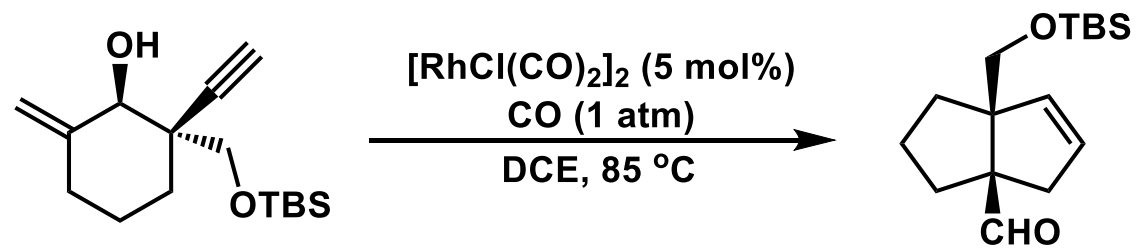
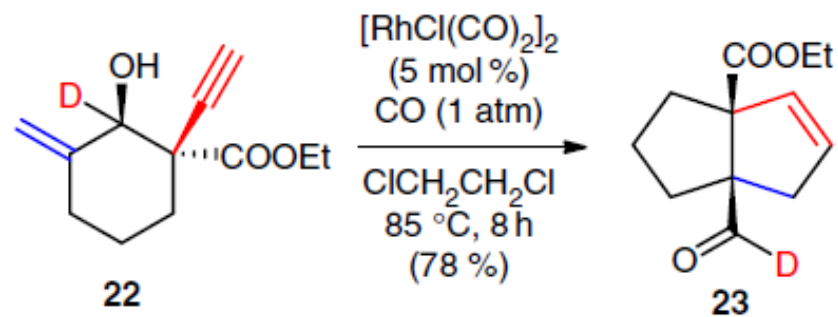


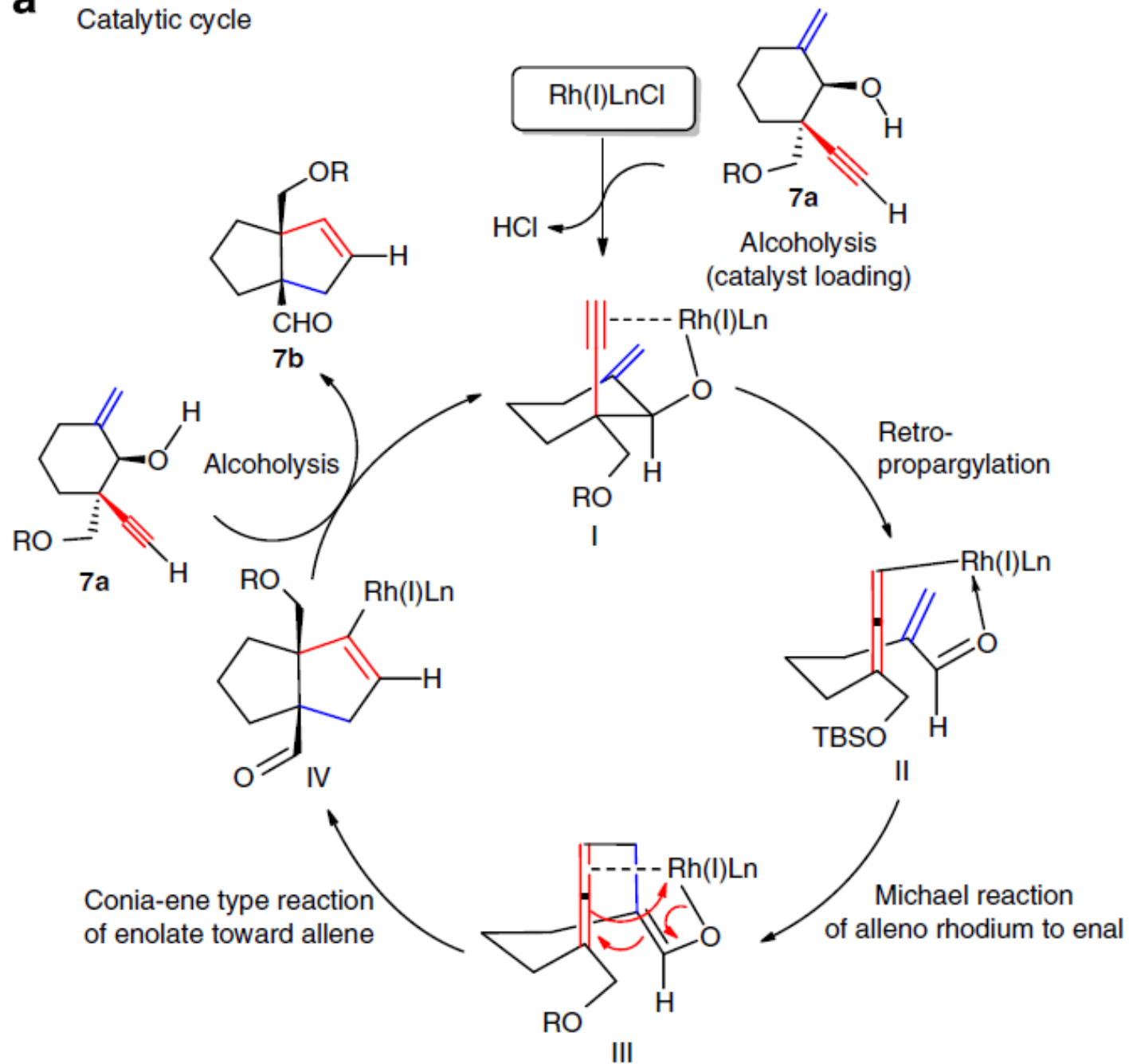
1.



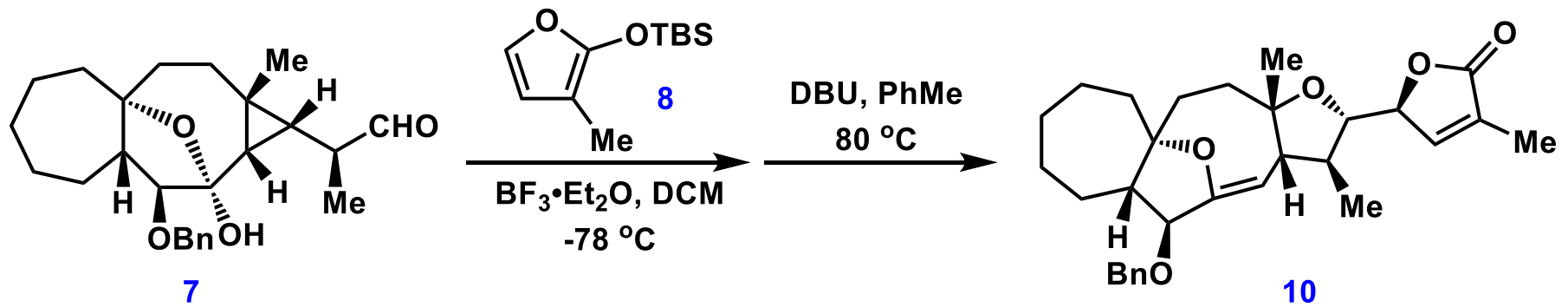
*Nat. Commun.* **2014**, 5, 5707.



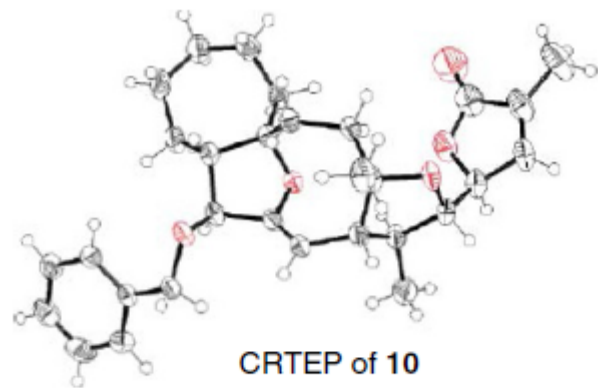
**a** Catalytic cycle



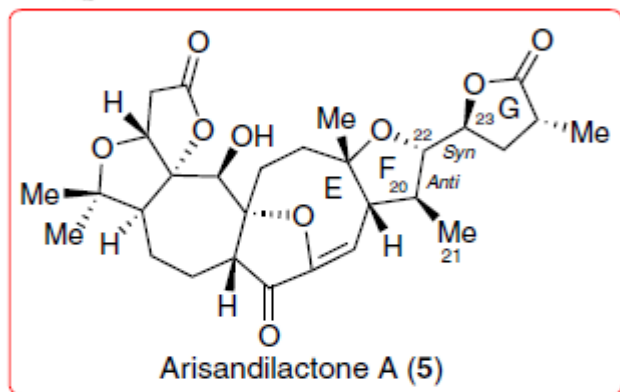
2.



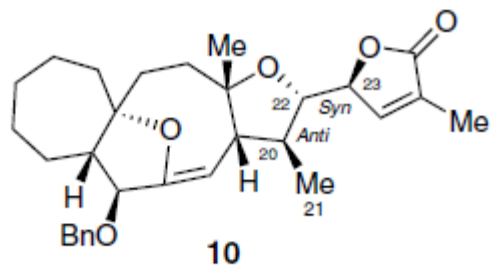
*Nat. Commun.* **2017**, *8*, 14233.



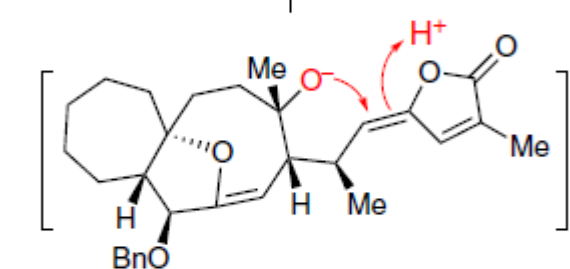
ORTEP of 10



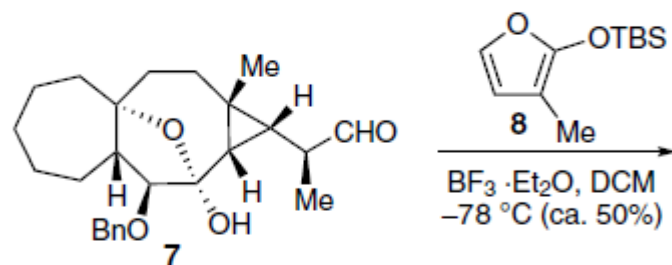
Arisandilactone A (5)



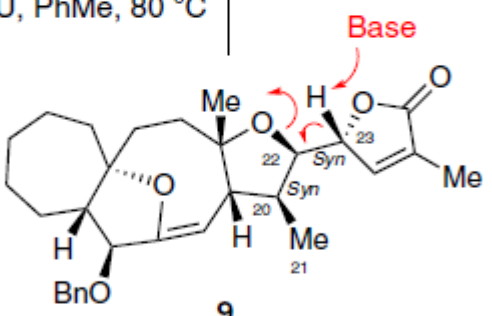
10



DBU, PhMe, 80 °C

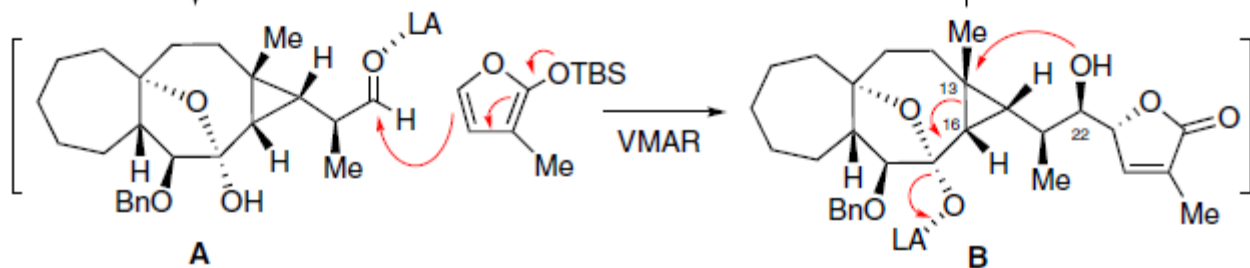


7



9

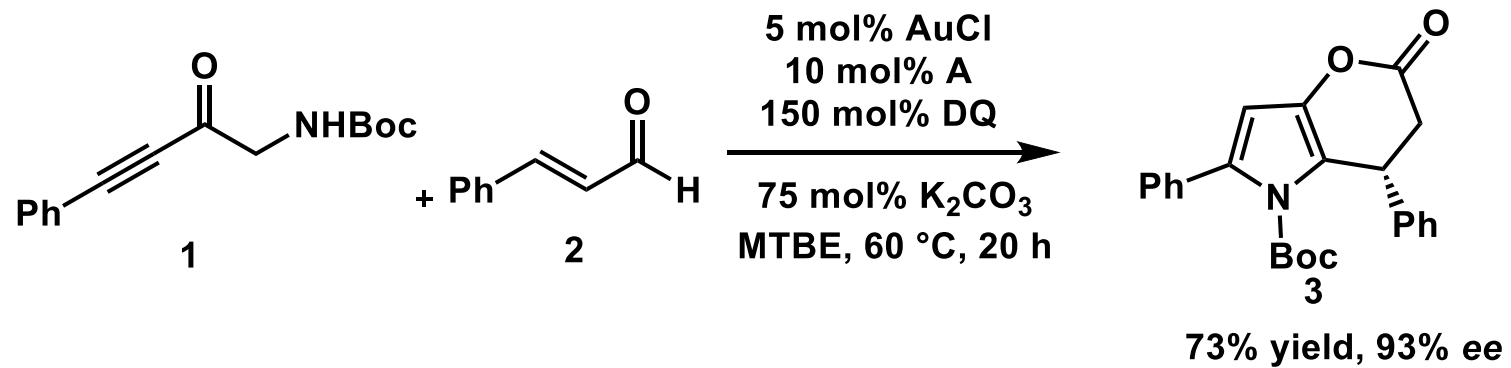
Homo-Michael reaction



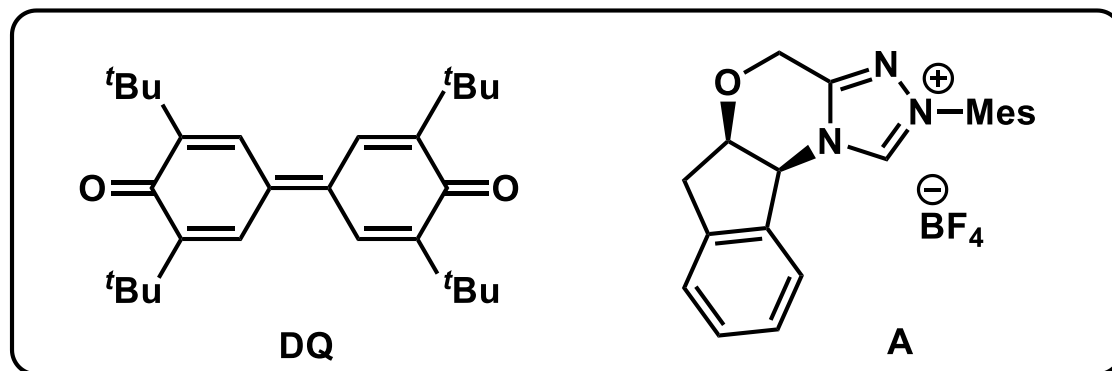
A

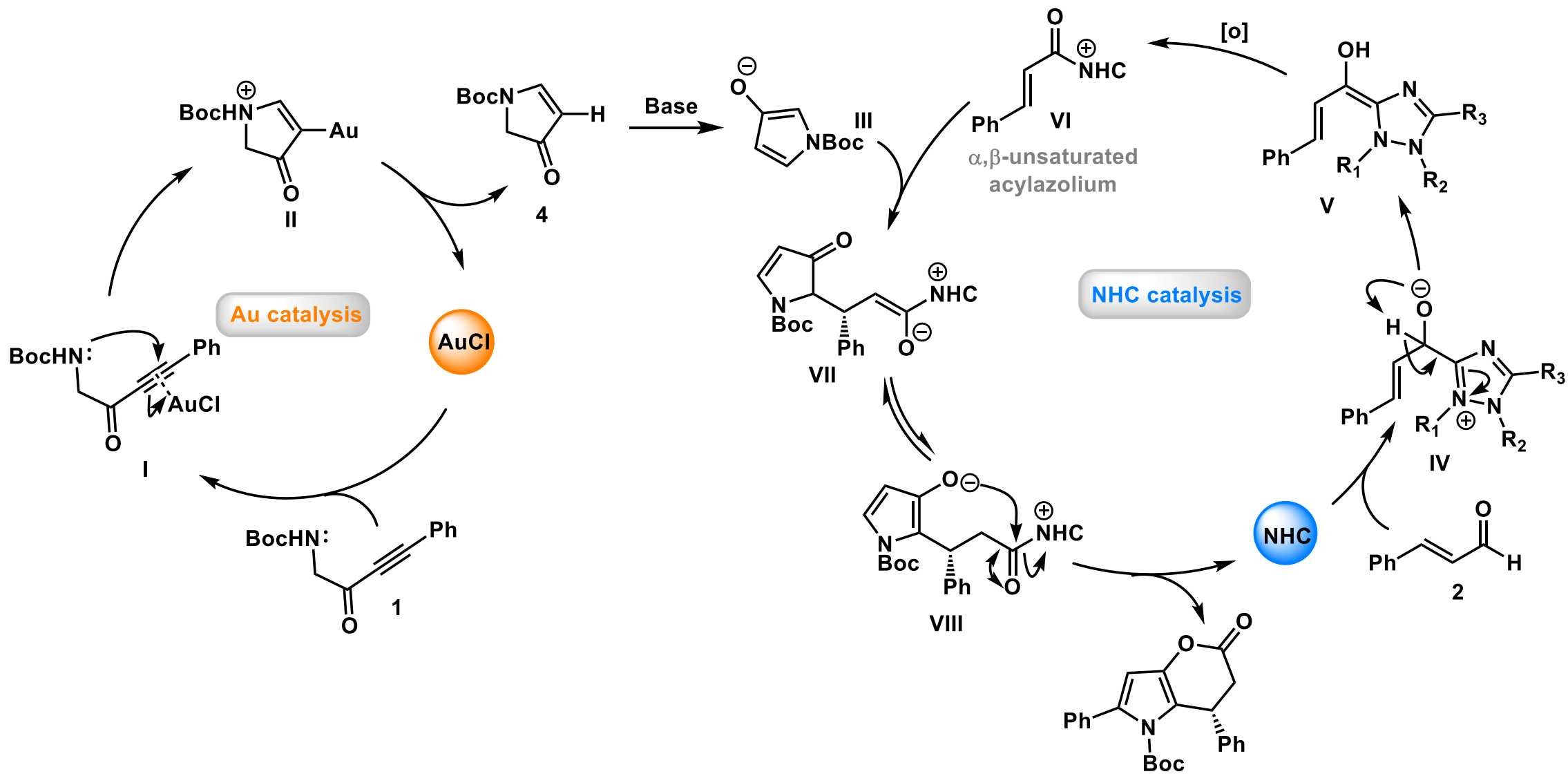
B

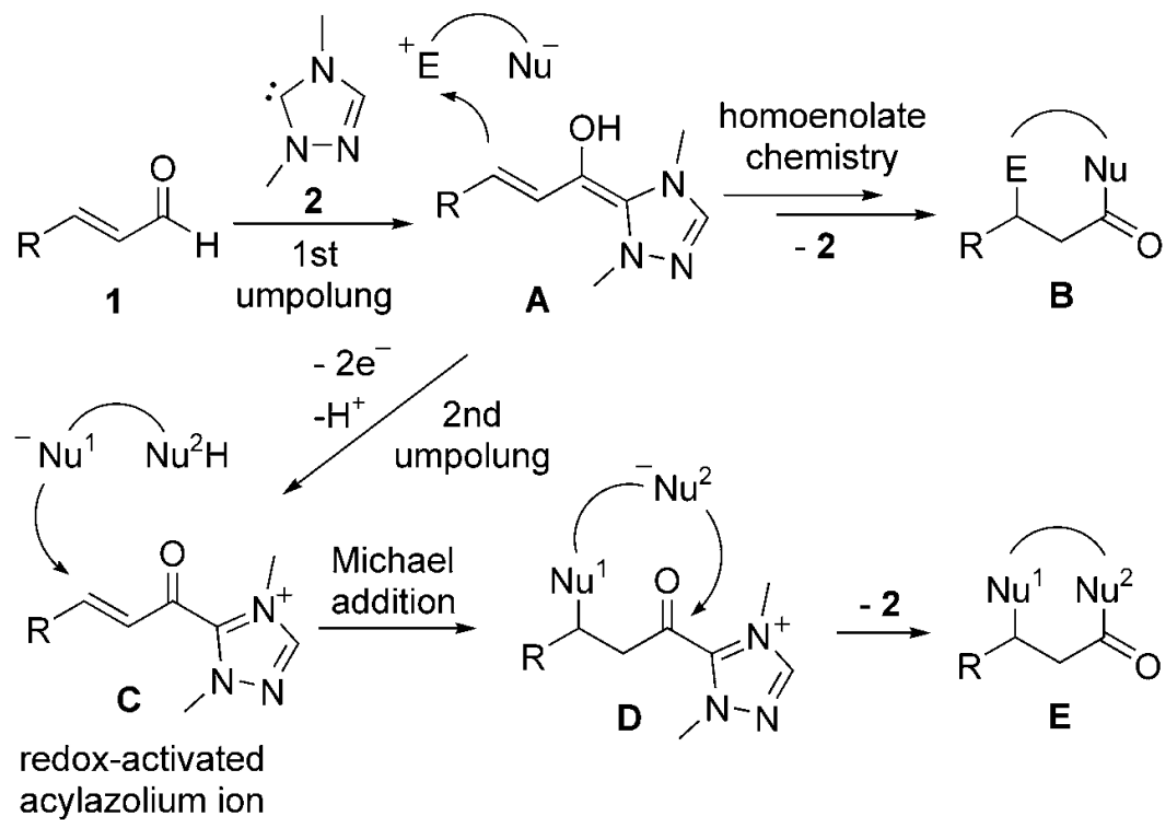
3.



DOI: 10.1002/anie.202115464.

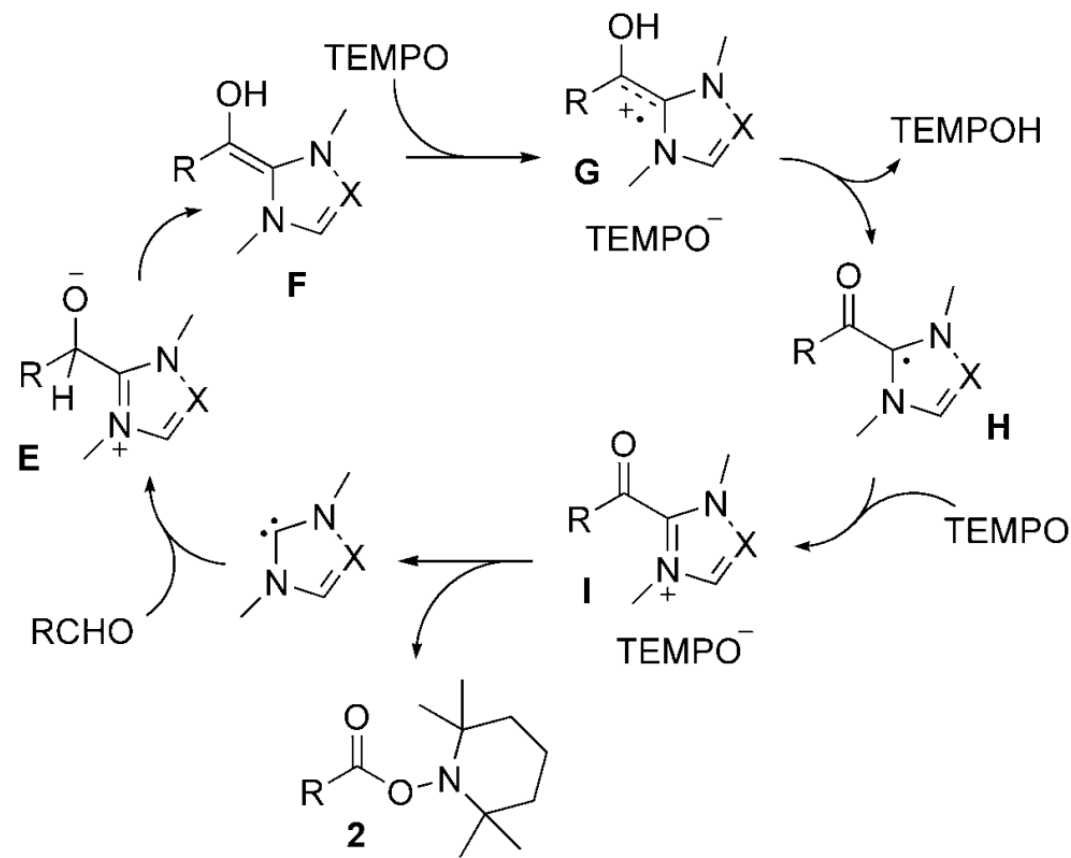






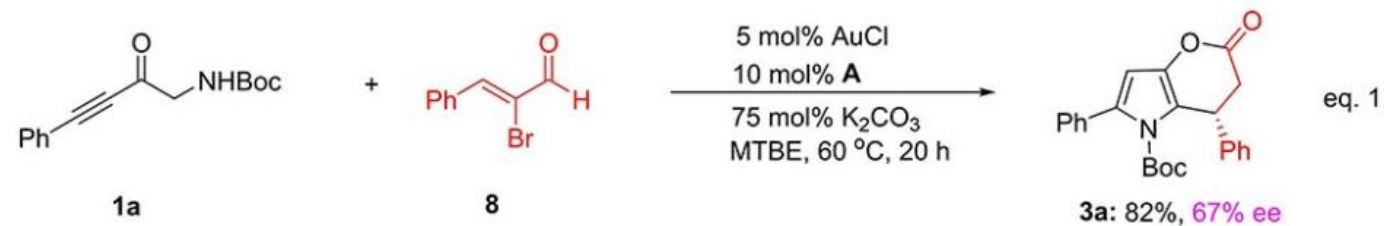
**Scheme 1.** Redox activation of  $\alpha,\beta$ -unsaturated aldehydes and subsequent 1,4-addition.

*Angew. Chem. Int. Ed.* **2010**, *49*, 9266.



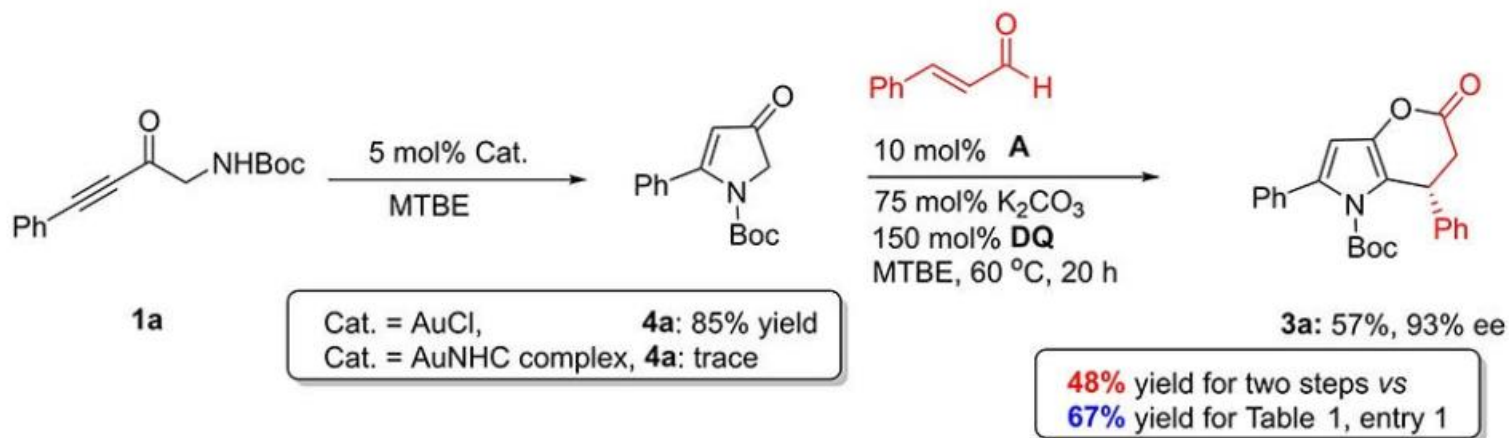
**Scheme 3.** Suggested mechanism (X=N, CH).

*Angew. Chem. Int. Ed.* **2008**, *47*, 8727.



**Scheme 4.** Other methods for the generation of  $\alpha,\beta$ -unsaturated acylazoliums.

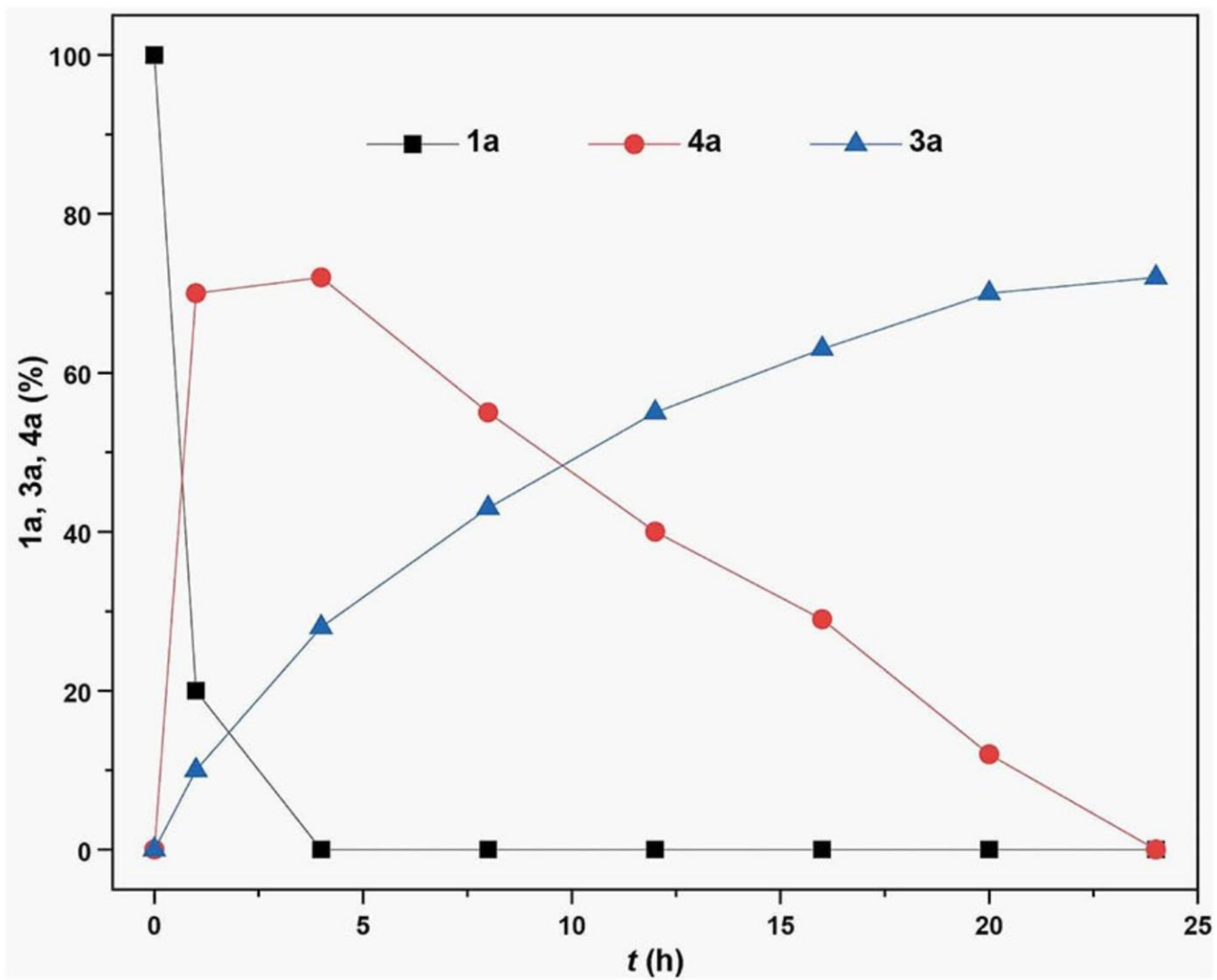
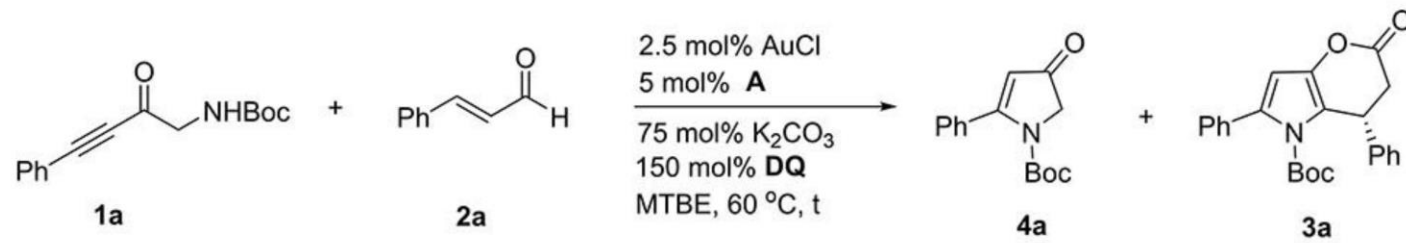
b) The reaction was performed in a stepwise manner



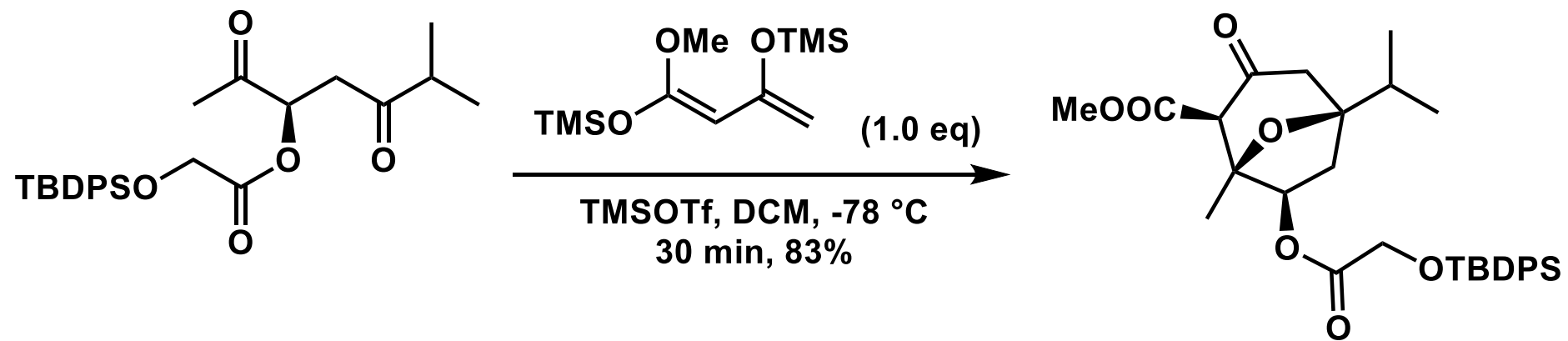
**Scheme 5.** Investigation of the relay catalysis and stepwise reactions.



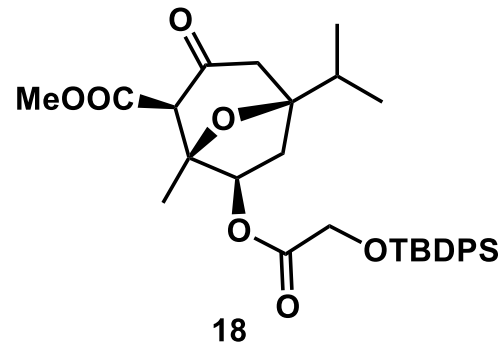
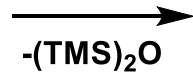
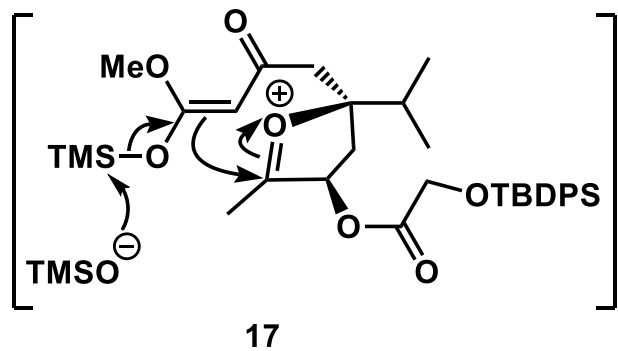
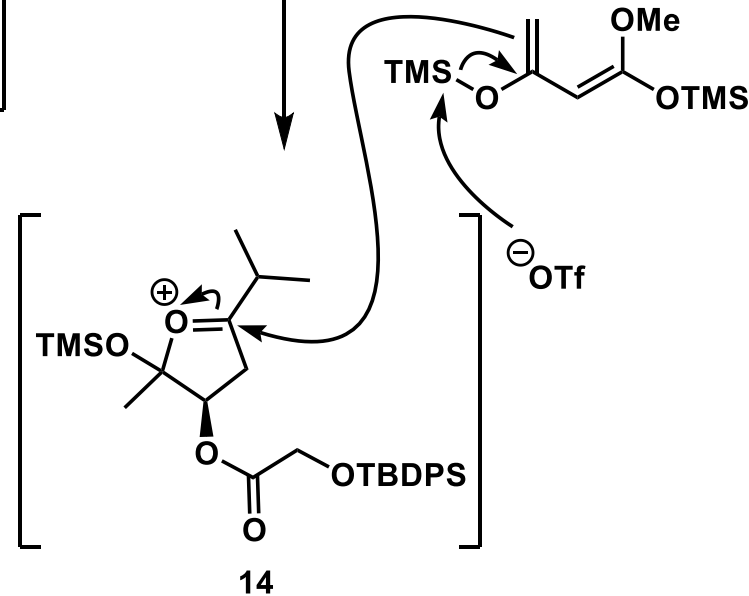
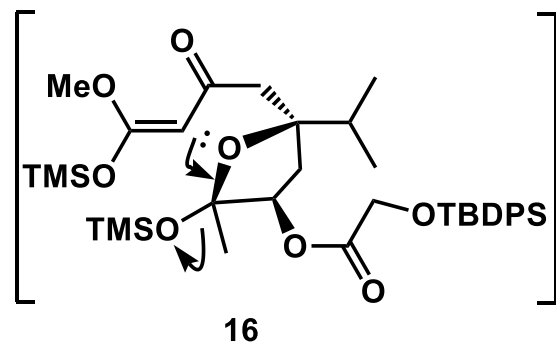
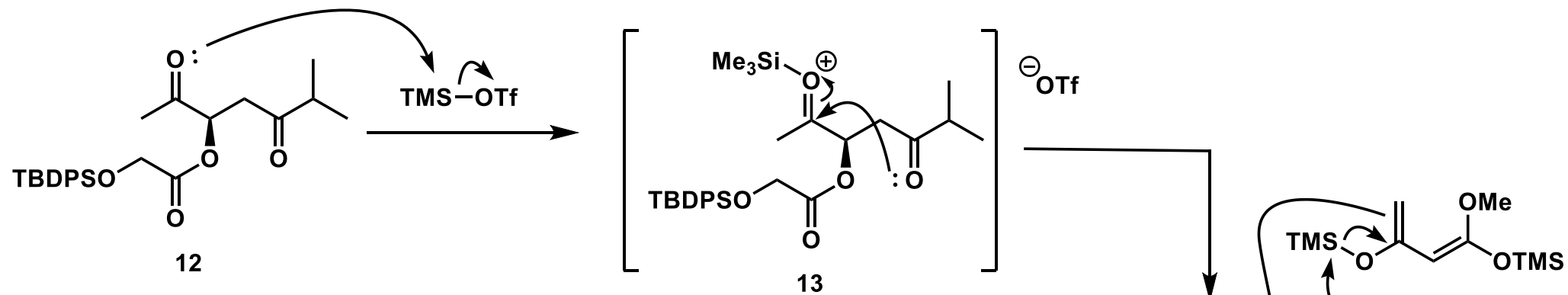
a) NMR studies revealed the two catalytic reactions



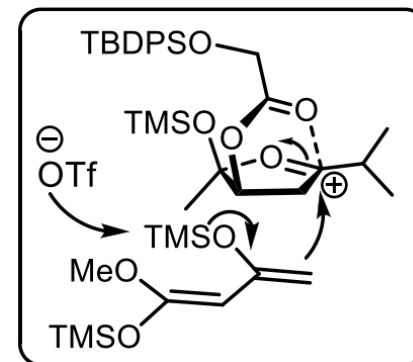
4.



DOI: 10.1002/anie.201900401.



*neighboring group controlled regioselectivity*



*rigid structure fully controlled diastereoselectivity*