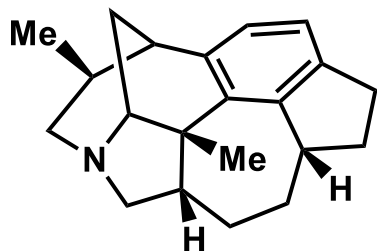
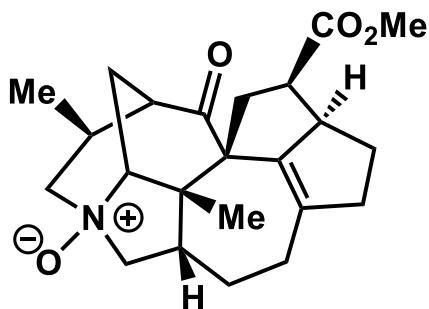


Navigating Excess Complexity: Total Synthesis of Daphenylline

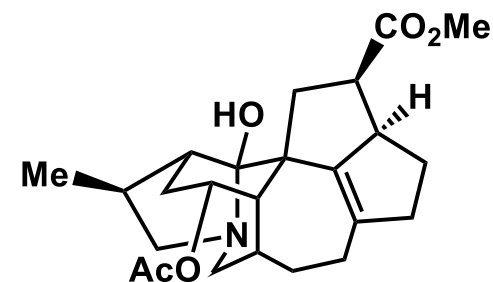
Brandon A. Wright, Alessio Regni, Nattawadee Chaisan, and Richmond Sarpong*



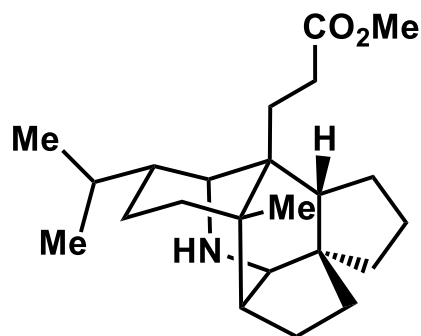
daphenylline (1)



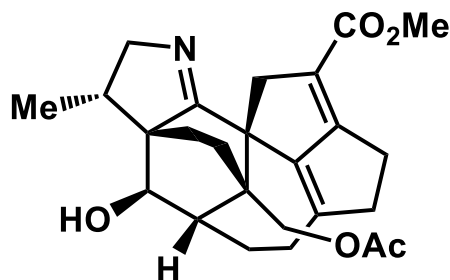
calyciphylline A (2)



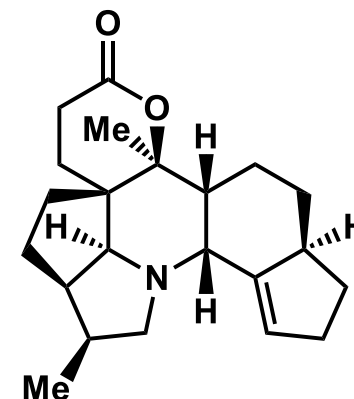
yuzurimine A (3)



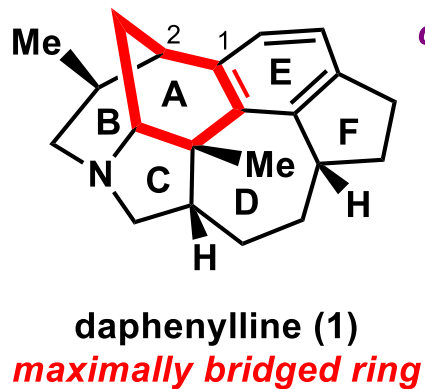
methyl homoseco-
daphniphyllate (4)



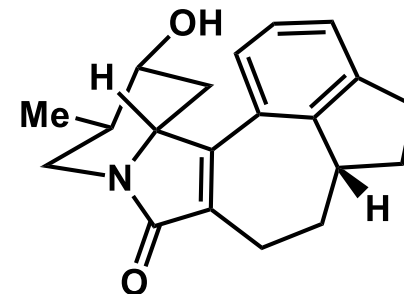
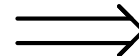
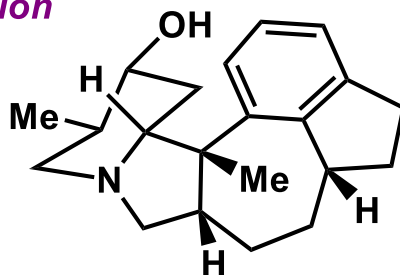
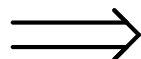
daphmanidin E (5)



daphongamine H (6)



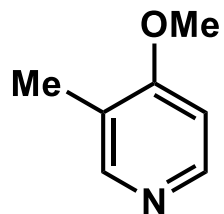
conjugate addition



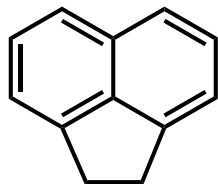
8



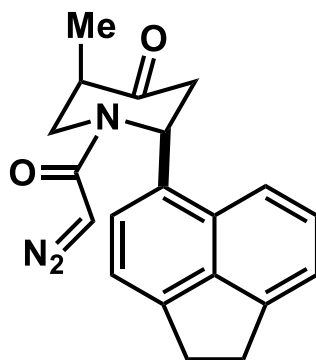
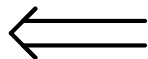
6π electrocyclic ring opening



11

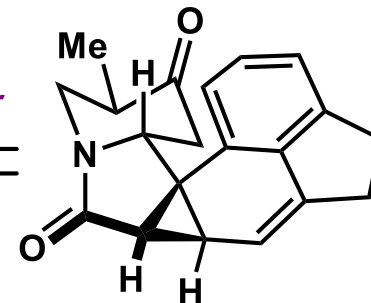
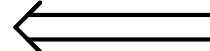


12

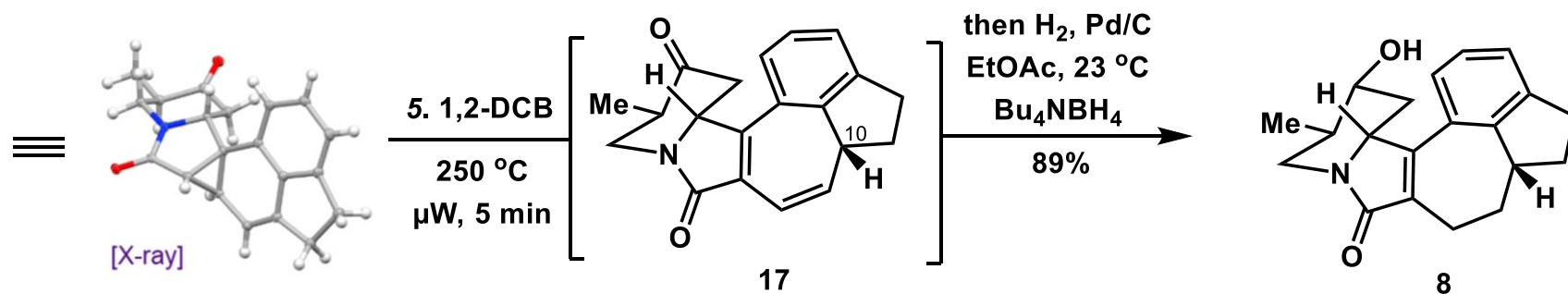
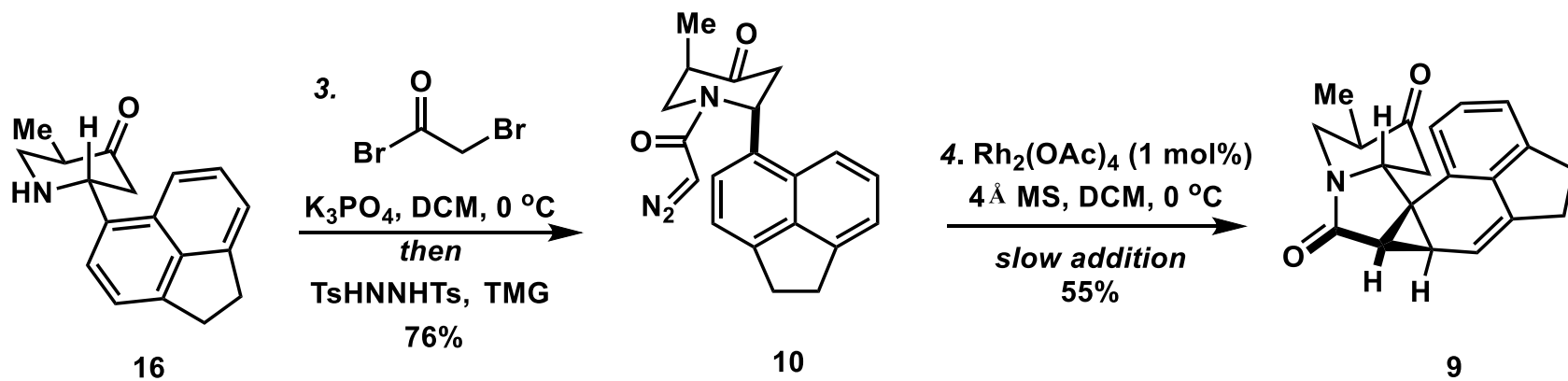
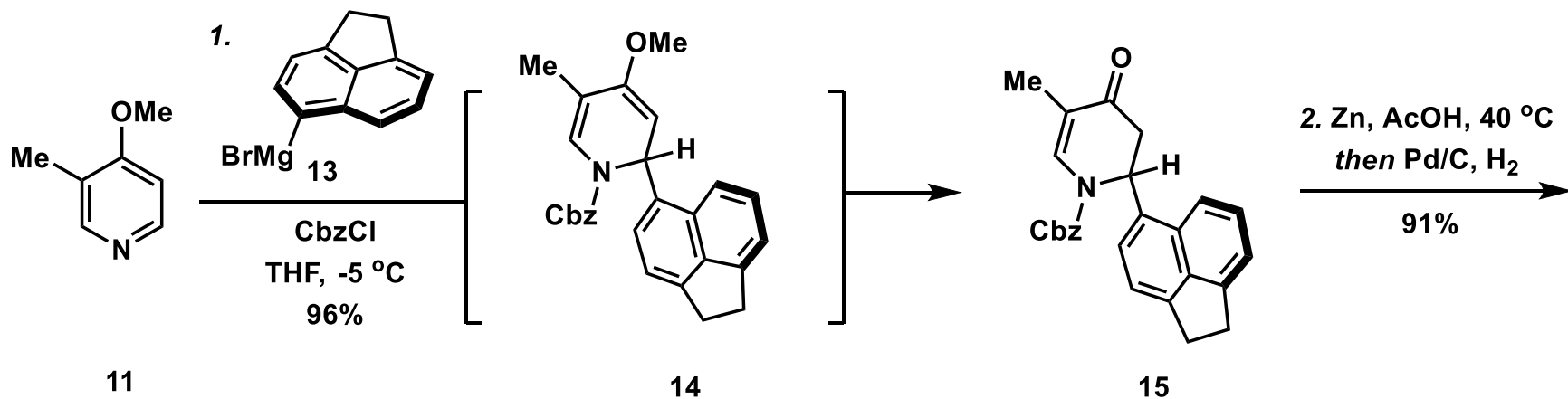


10

Buchner

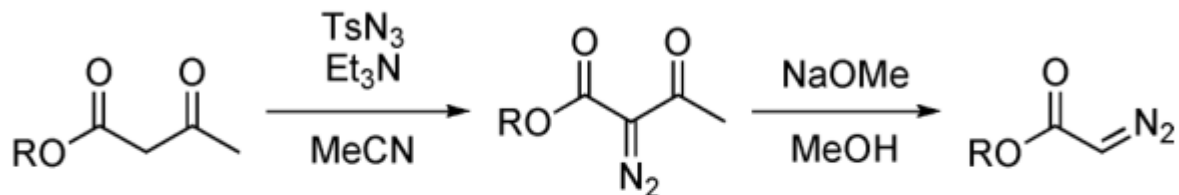


9

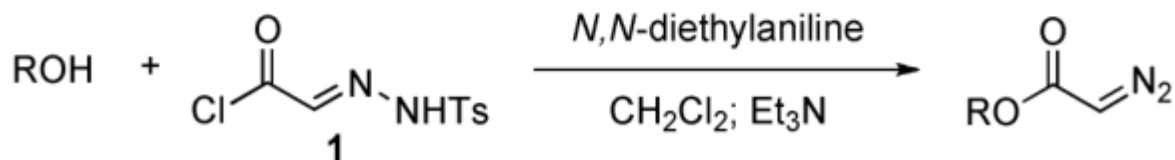


Scheme 1

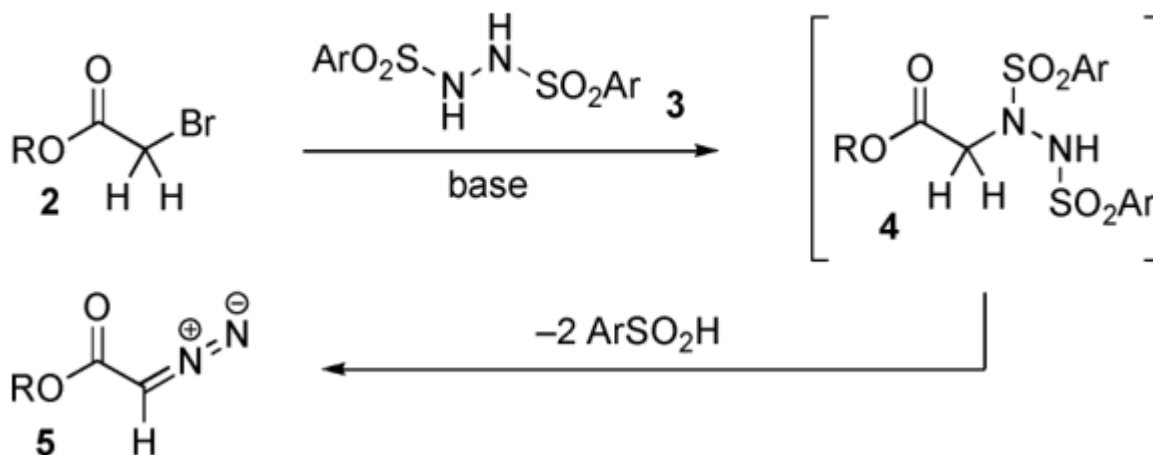
M. Regitz's procedure⁶

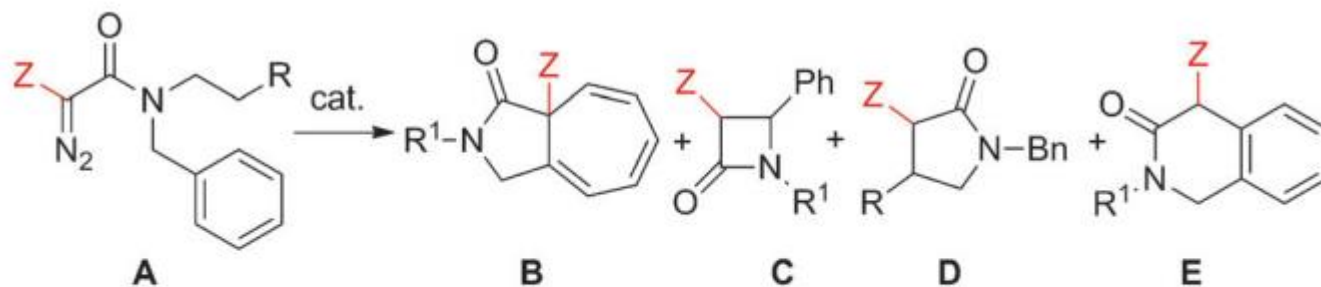


H. O. House's procedure (Corey and Myers' modification)⁸



Scheme 2



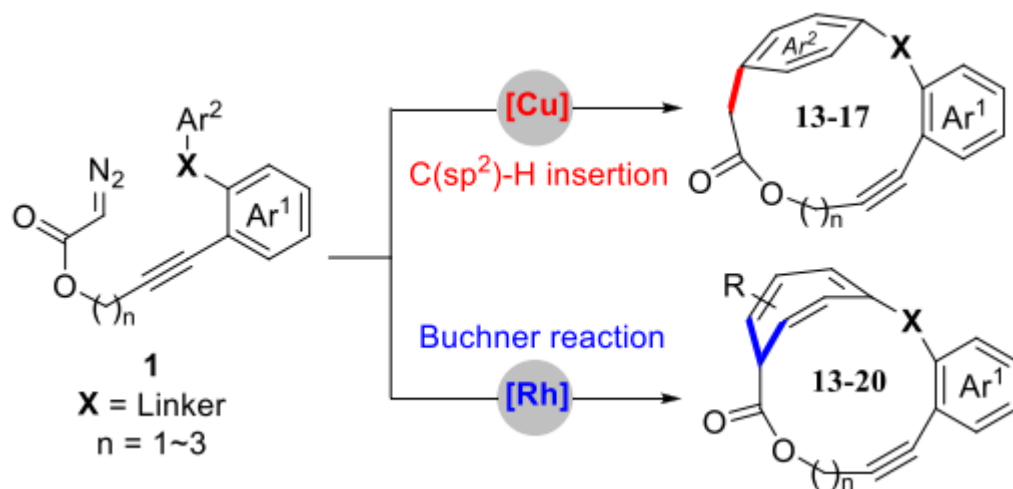


R = Ph, OTBS, alkyl R¹ = -CH₂CH₂R

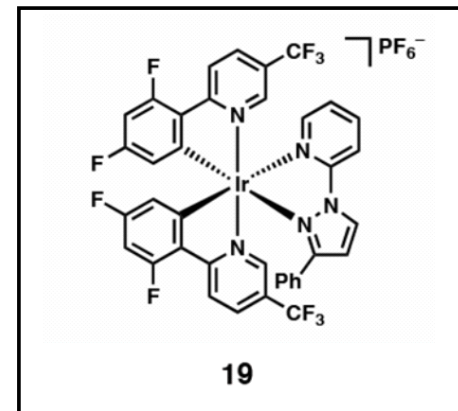
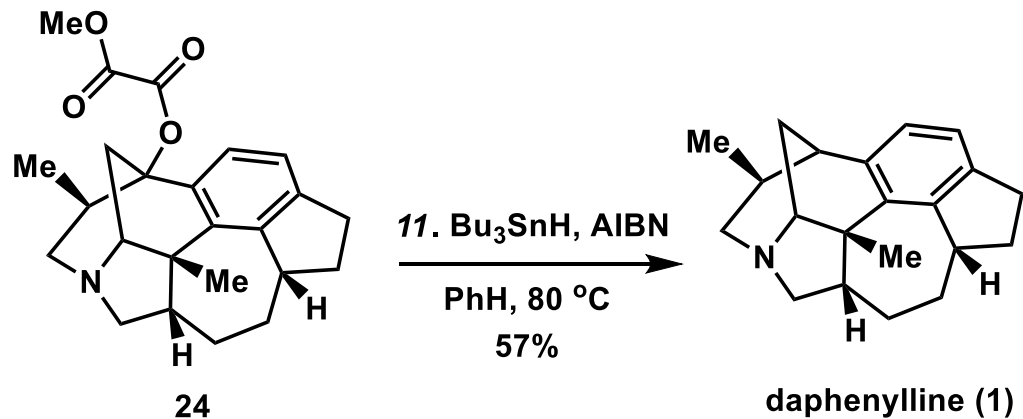
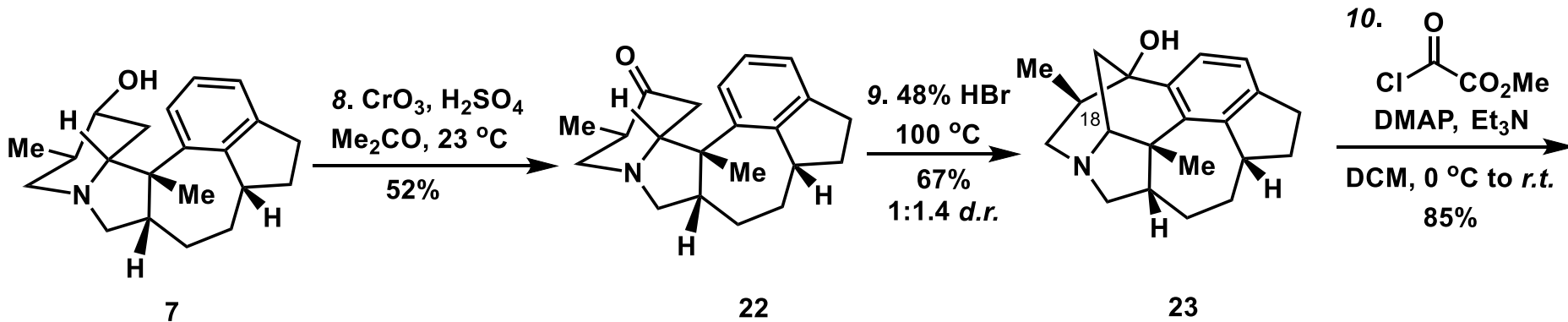
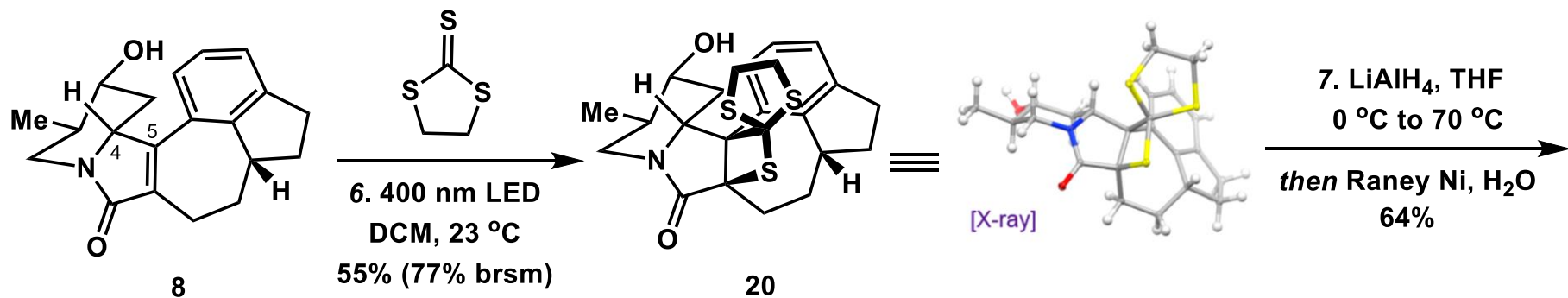
If Z = Ac, -CO₂R, H, Ar: mixed products

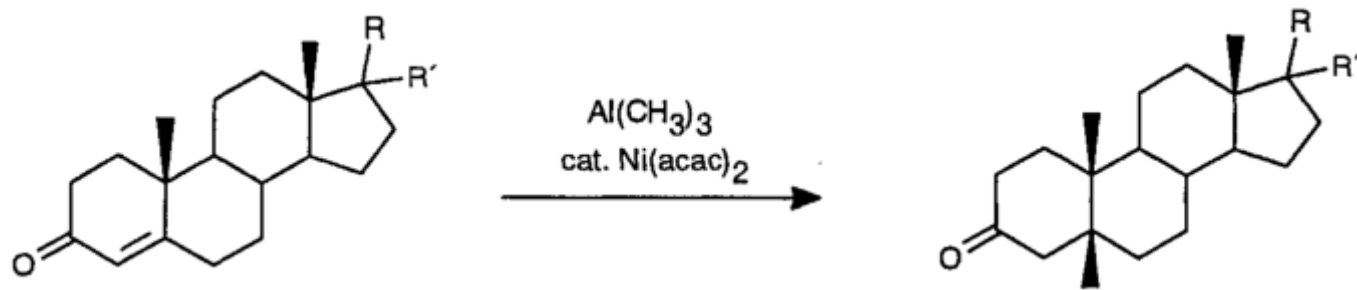
This work, Z = CN: product **B** only

Chemcatchem, **2014**, 6, 1679.



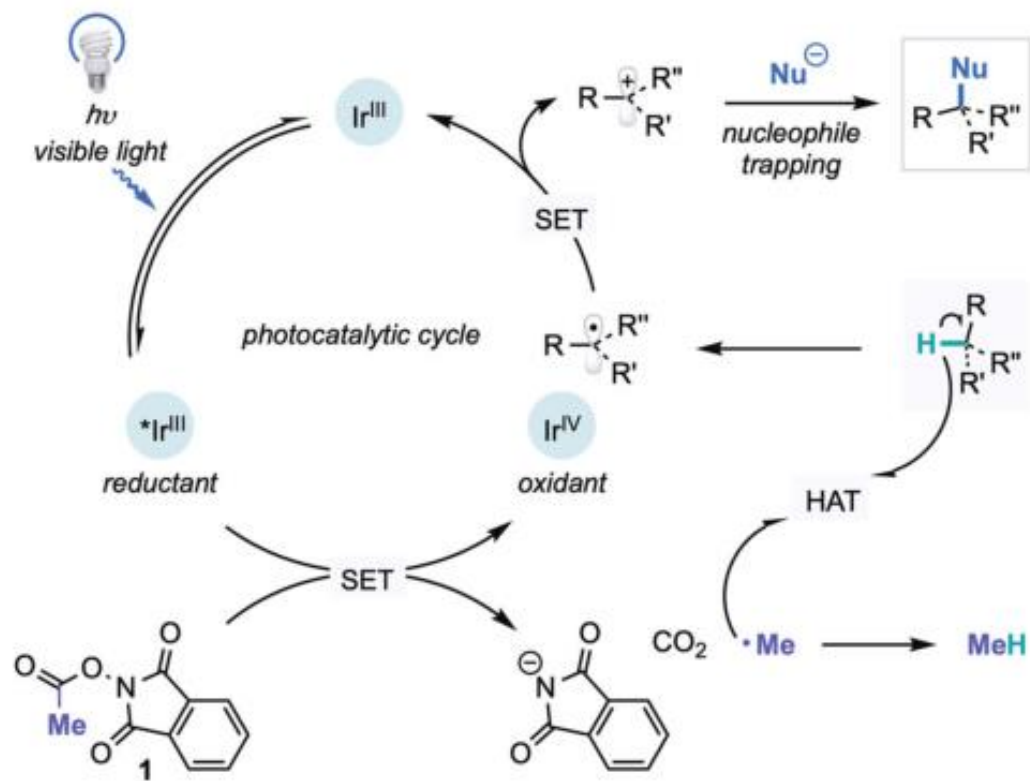
ACS Catal., **2019**, 9, 10773.





Synthesis, **1995**, *16*, 317.

A. Catalytic Cycle

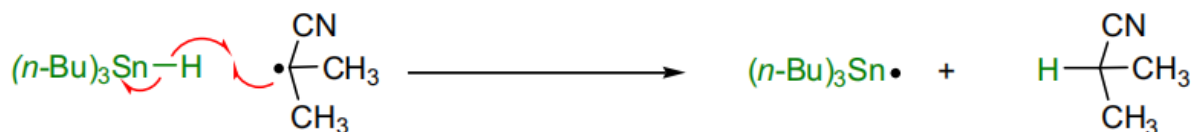
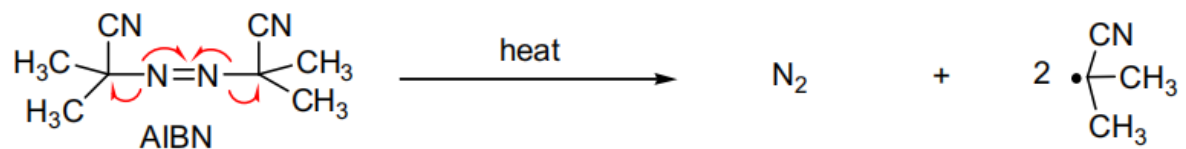


Nat. Commun., **2021**, *12*, 6950.

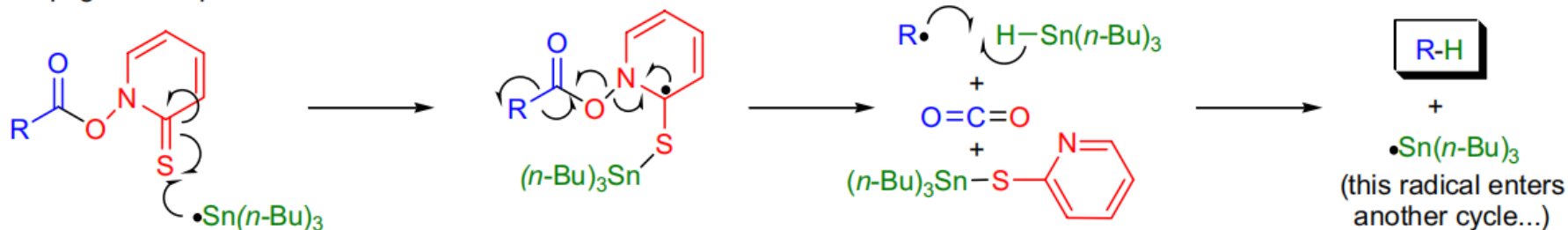
BARTON RADICAL DECARBOXYLATION REACTION

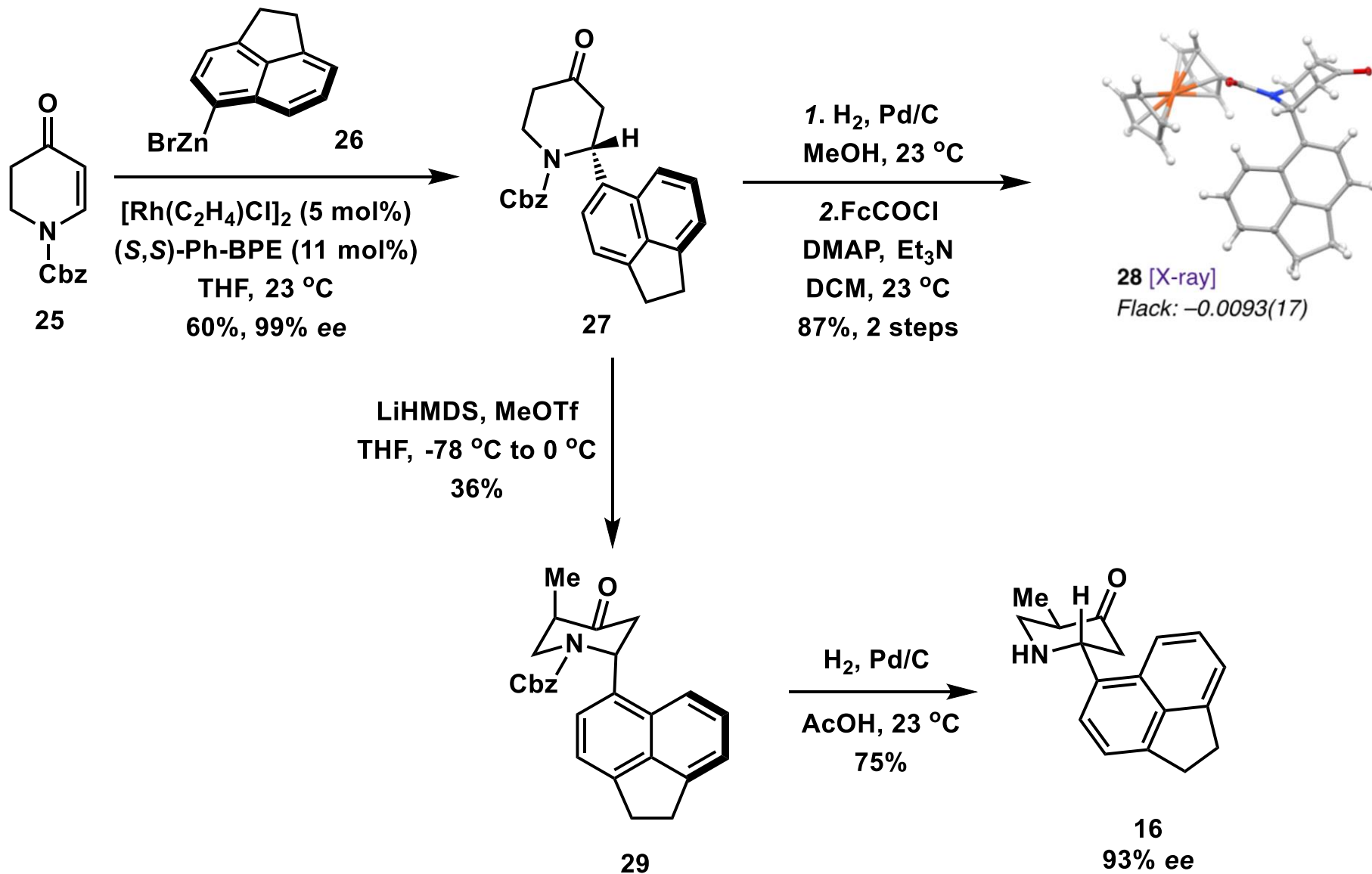
(References are on page 546)

Initiation step:

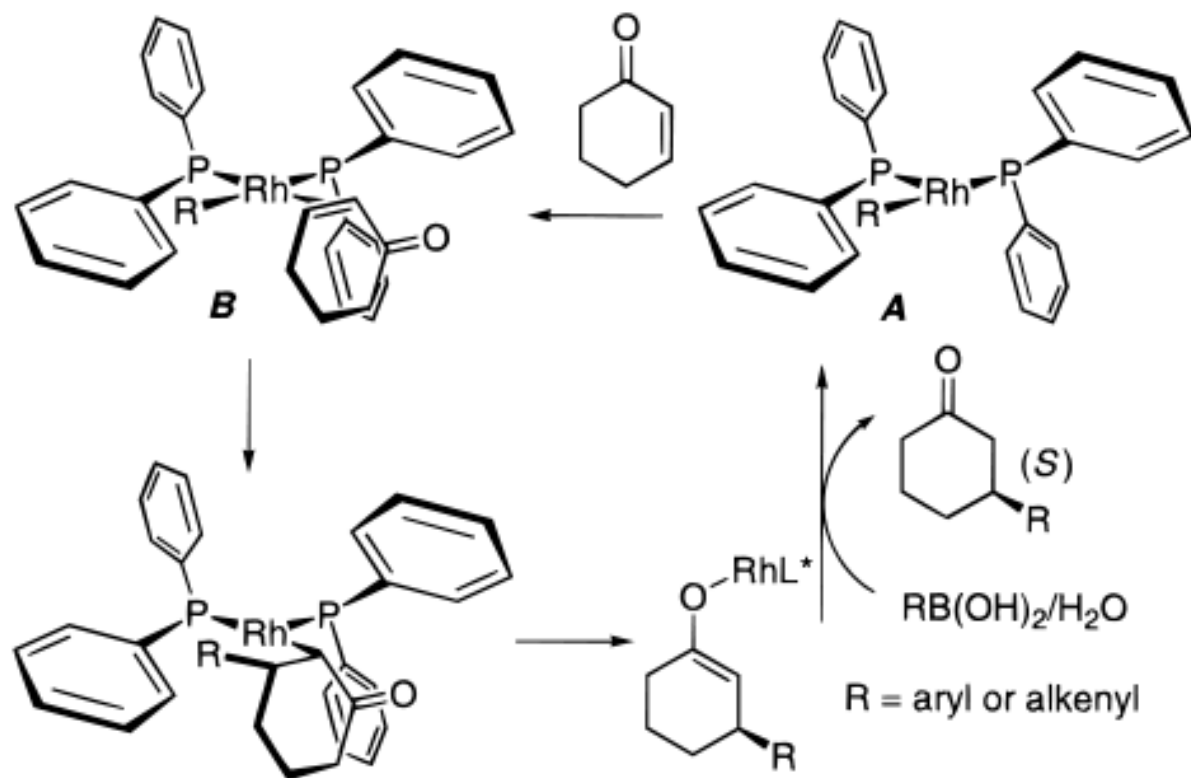


Propagation step:



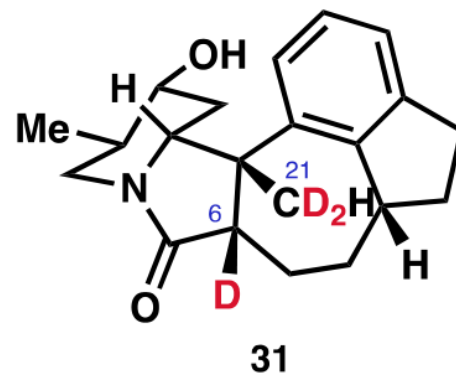
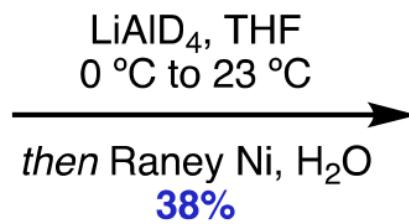
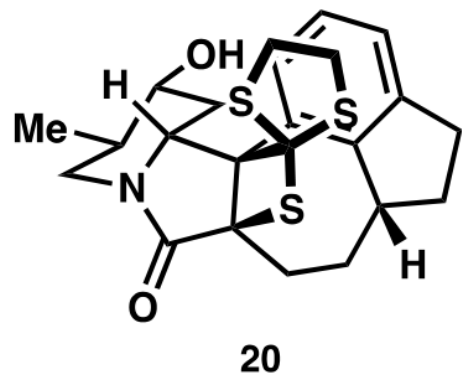
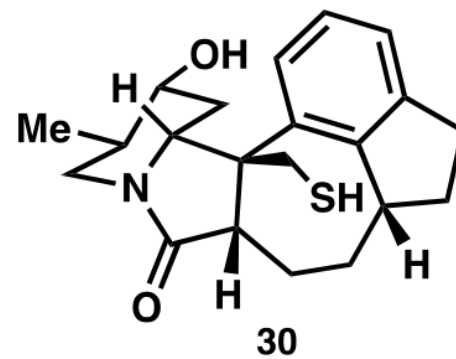
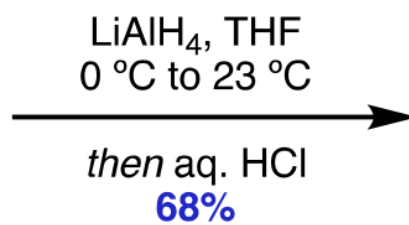
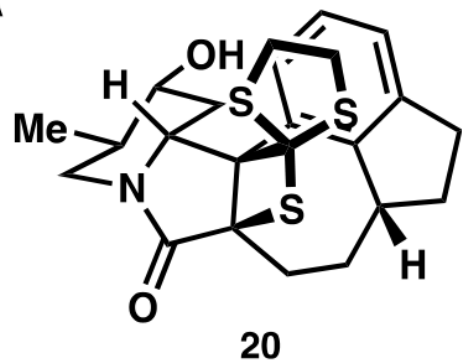


Scheme 2^a



^a The binaphthylene moiety in (*S*)-binap is omitted for clarity.

J. Am. Chem. Soc., **1998**, *120*, 5579.

A

B