



六、周环反应

(三) 1,3-偶极环加成反应

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生命有机化学国家重点实验室

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一、概论

二、基础知识

构象分析

有机反应的热力学和动力学

构象对反应活性的影响

立体电子效应

三、氧化态的调整

烯烃、醇和其他化合物的氧化

烯烃、羰基化合物和其他化合物的还原

四、C-X键形成反应

五、一些形成C-C键的基本反应

烯醇和烯醇负离子化学

有机锂、镁和铜试剂的制备和反应

自由基反应

烯基化反应

六、周环反应

非直观Diels-Alder反应

1,3-偶极环加成反应

电环化反应

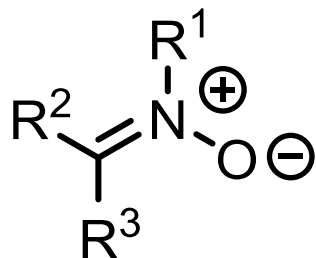
sigmatropic重排

七、阳离子参与的C-C键形成反应

部分1,3-偶极化合物



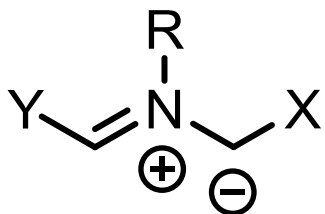
nitrile oxides



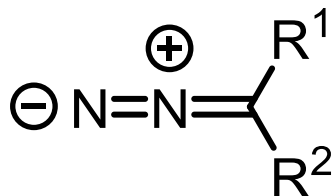
nitrones



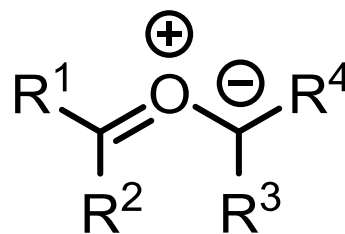
azides



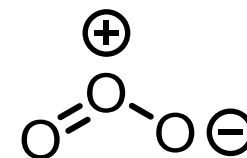
azomethine ylides



diazoalkanes



carbonyl ylides

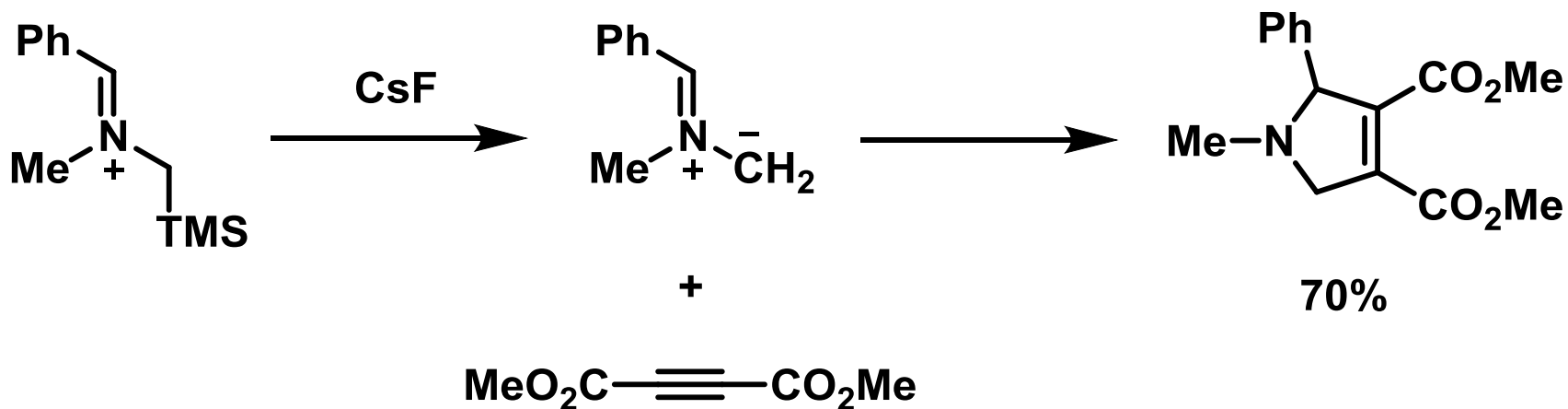


ozone

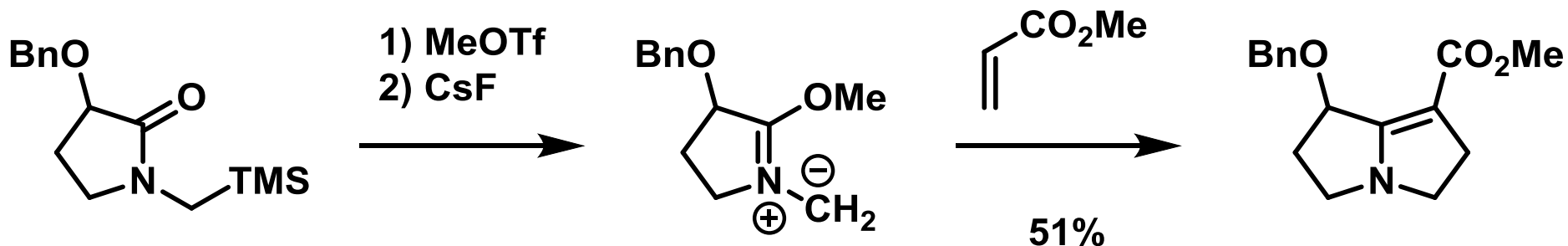
Huisgen, 1,3-Dipolar Cycloadditions. Past and Future. *Angew. Chem. Int. Ed.* **1963**, 2, 565.

http://www.scripps.edu/baran/images/grpmtgpdf/Hafensteiner_Oct_04.pdf

非稳定的Azomethine叶立德



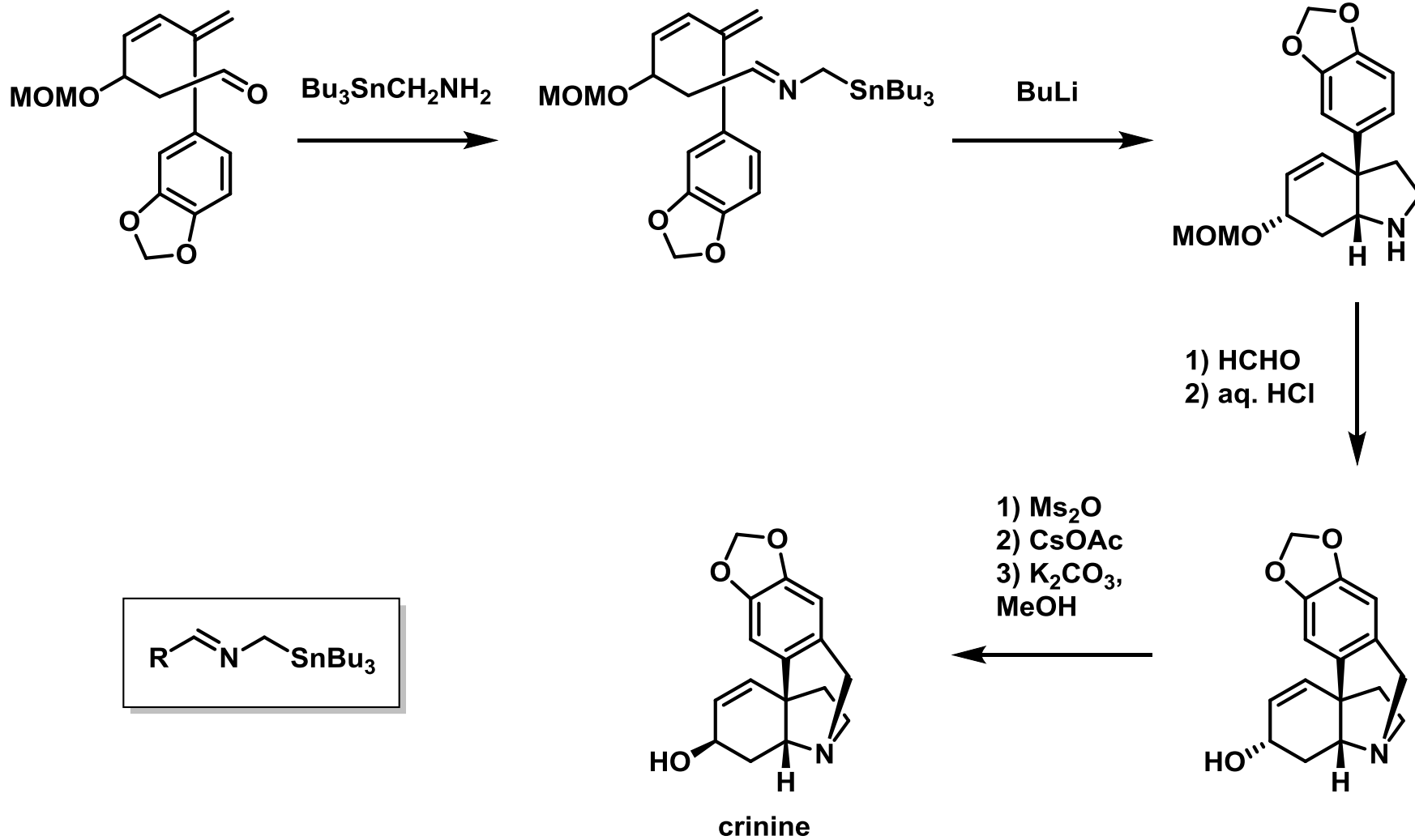
Vedejs, et al. *J. Am. Chem. Soc.* **1979**, *101*, 6452.



Vedejs, et al. *J. Am. Chem. Soc.* **1980**, *102*, 7993.

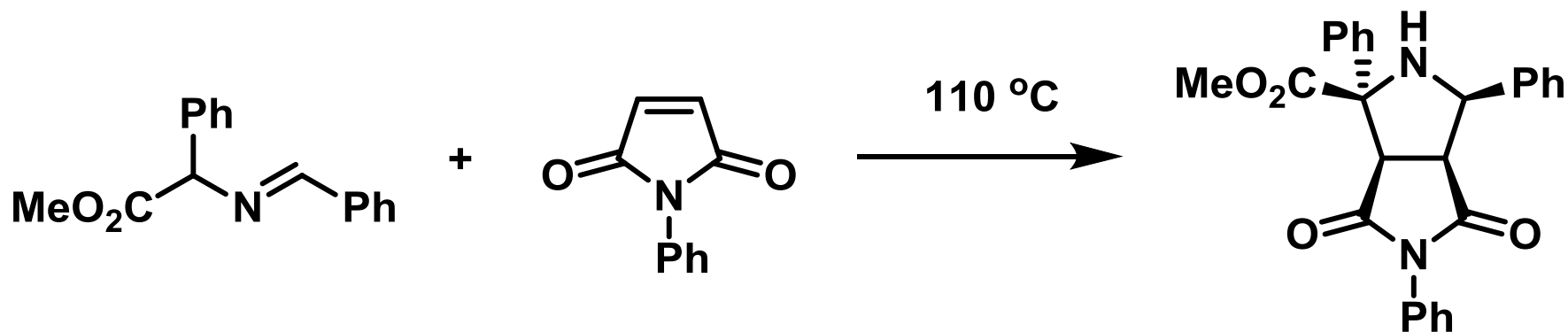
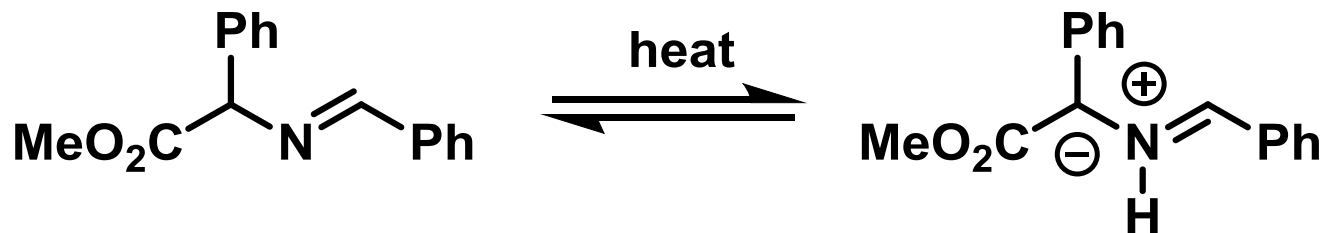
Vedejs, *J. Org. Chem.* **2004**, *69*, 5159.

2-Azaallyl Anion



Pearson, et al. *J. Am. Chem. Soc.* **1992**, *114*, 1329; *J. Org. Chem.* **1998**, *63*, 3607.

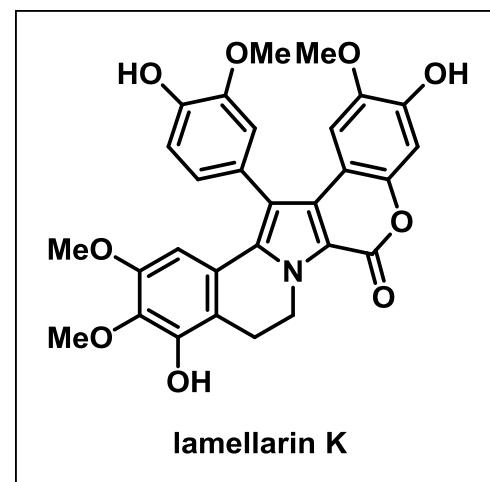
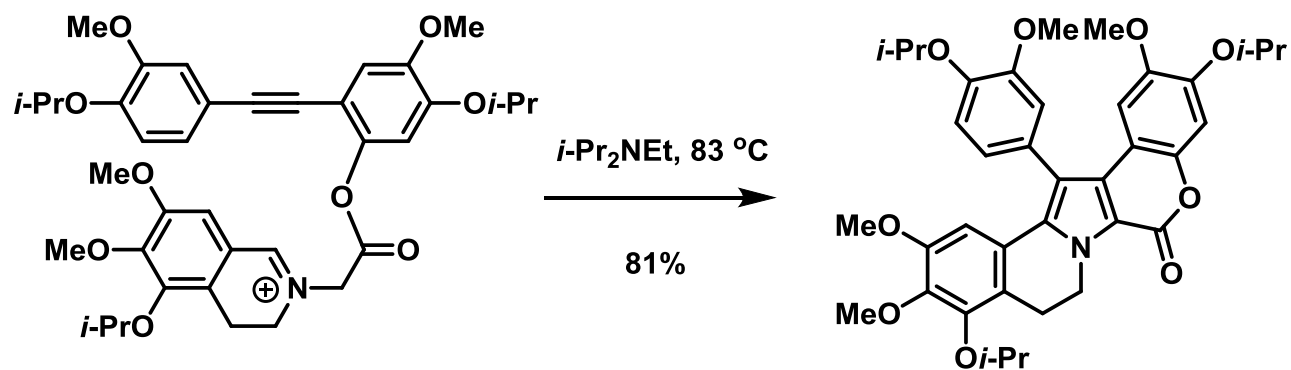
稳定的Azomethine叶立德



Grigg, et al. *J. Chem. Soc., Chem. Commun.* **1978**, 101.

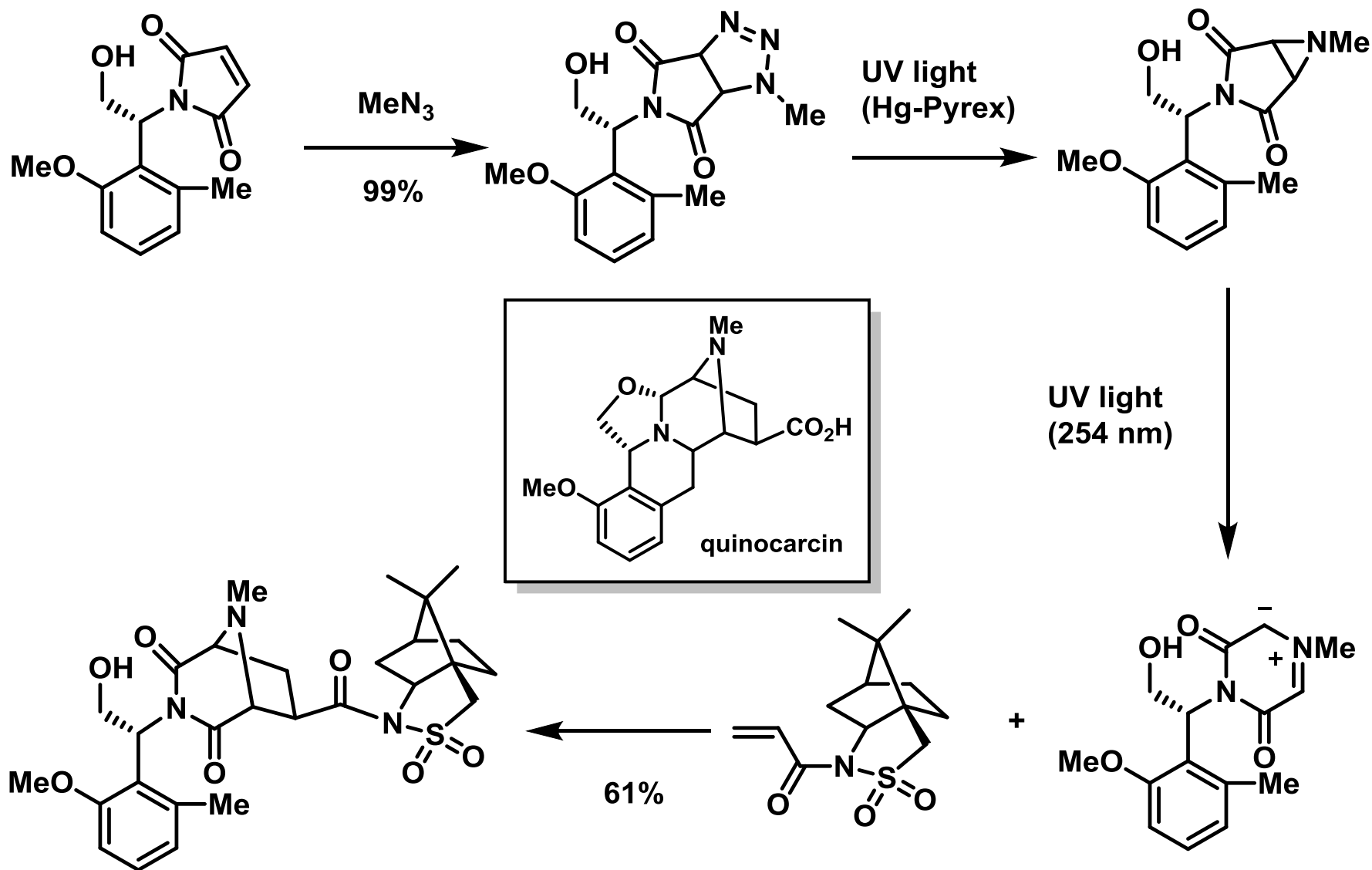
Grigg, et al. *J. Chem. Soc., Chem. Commun.* **1982**, 384.

稳定的Azomethine叶立德

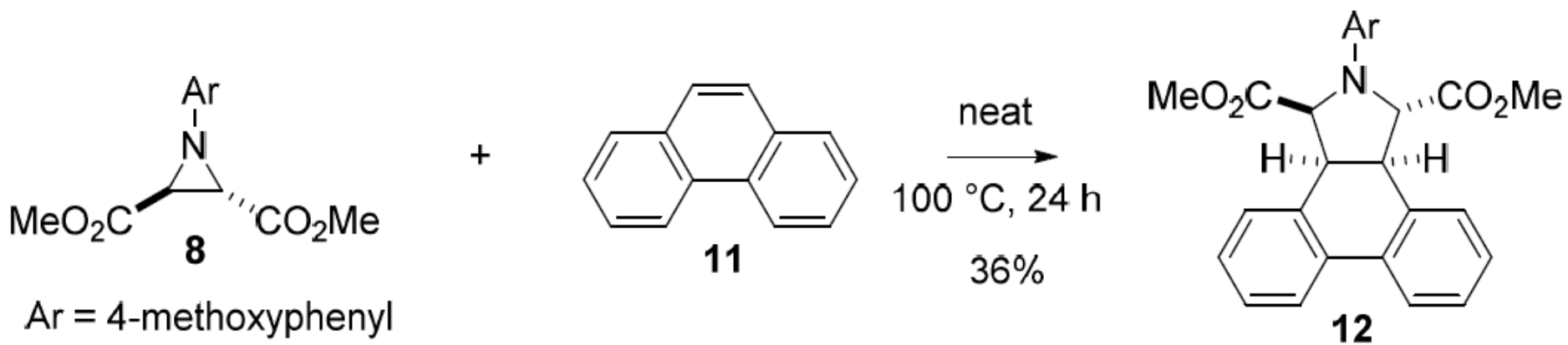


Banwell, et al. *Chem. Commun.* **1997**, 2259.

稳定的Azomethine叶立德



稳定的Azomethine叶立德



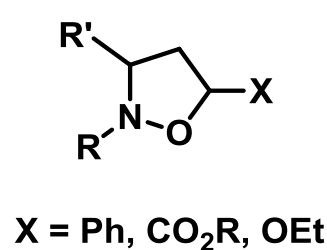
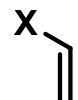
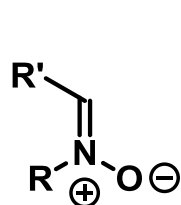
Huisgen and Scheer, *Tetrahedron Lett.* **1971**, 12, 481.

Nitrone/Nitrile Oxide

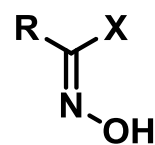
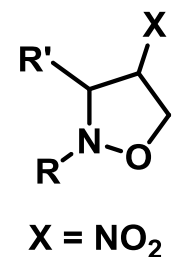
R'CHO

+

RNHOH



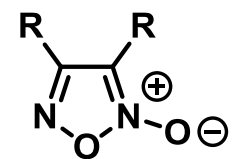
+



-HX

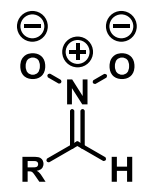


heat

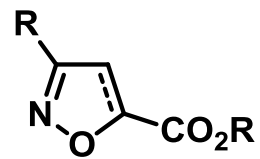
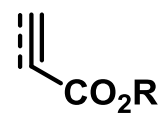
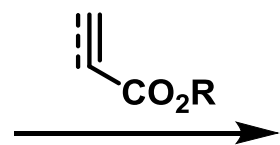


X = H
X = Cl, Br, I

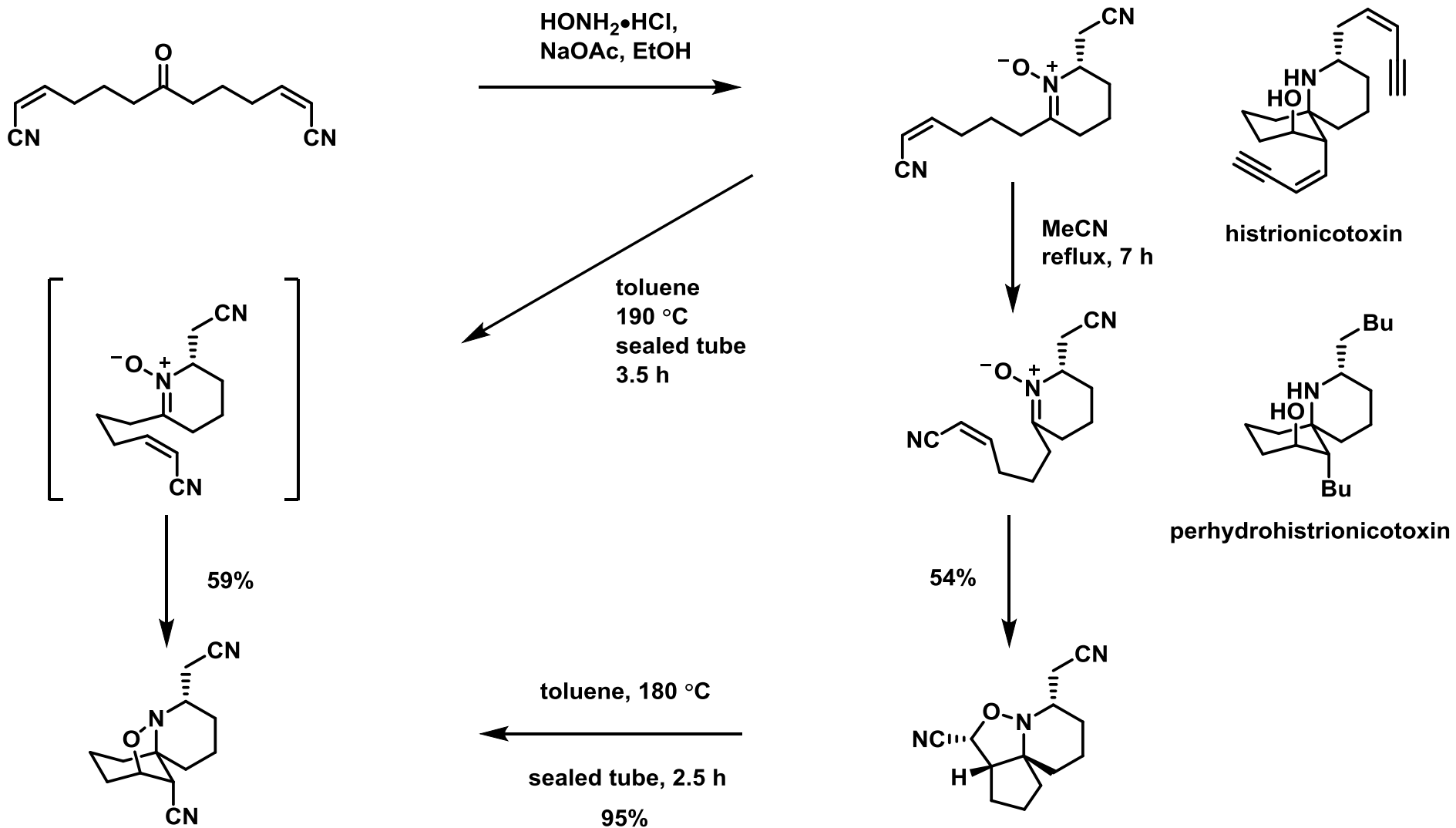
RCH₂NO₂



R-N=C=O

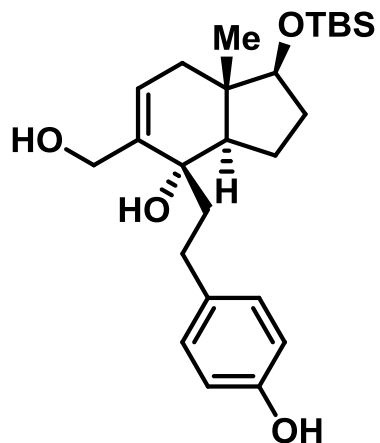


Nitrone



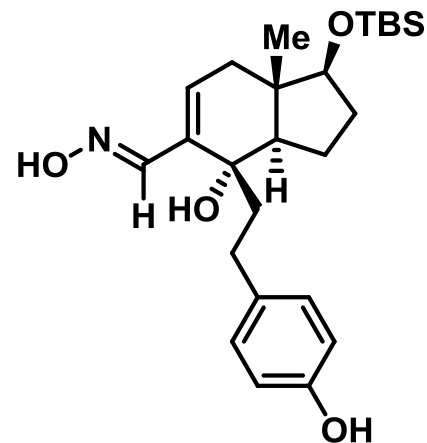
Stockman, et al. *J. Org. Chem.* **2004**, 69, 1598.

Nitrile Oxide

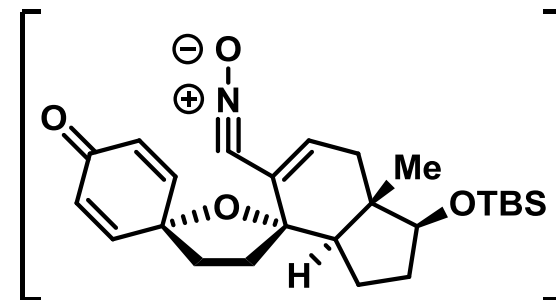
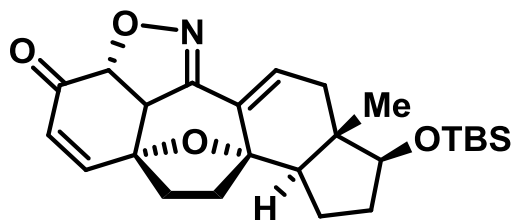
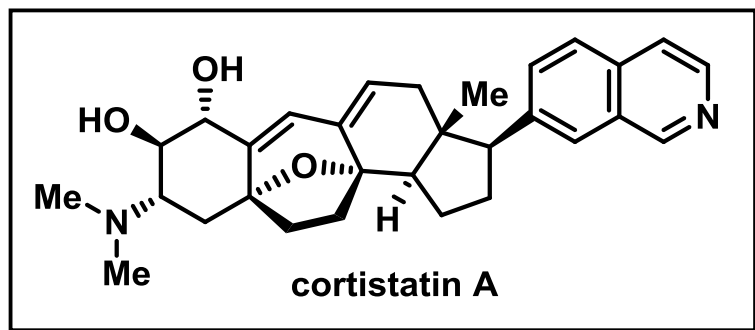


1) $\text{SO}_3 \cdot \text{pyr}$, Et_3N ,
DMSO, 57%

2) $\text{HONH}_2 \cdot \text{HCl}$, NaOAc ,
 60°C , ca. 100%

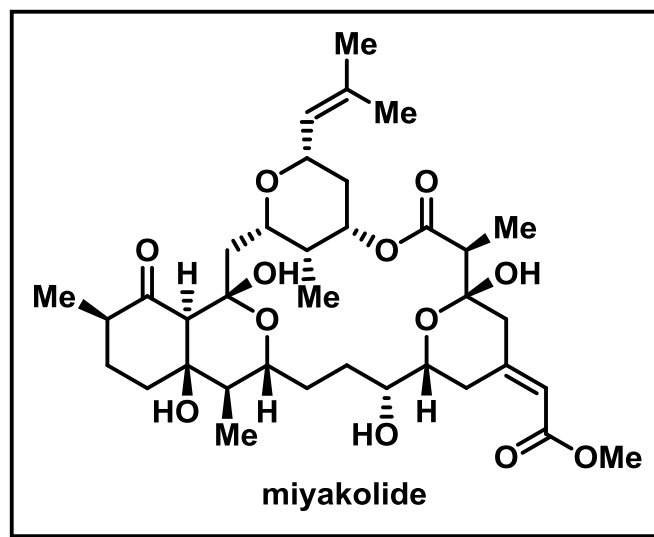
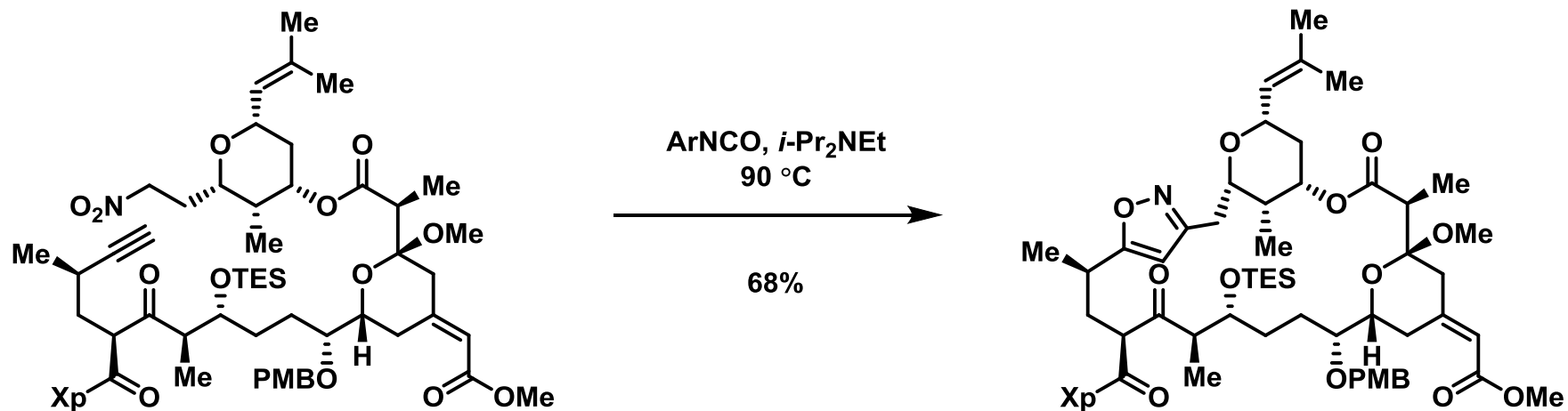


$\text{PhI}(\text{OAc})_2$, TFA;
then 50°C , 80%



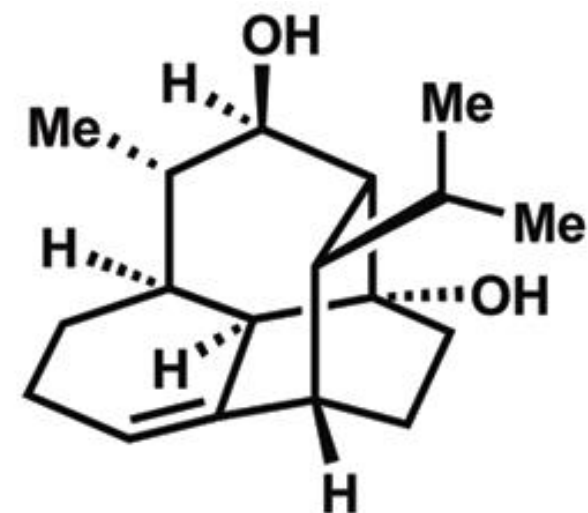
Sorensen, et al. *Org. Lett.* **2009**, *11*, 5394.

Nitrile Oxide



Evans, et al. *J. Am. Chem. Soc.* **1999**, 121, 6816.

Nitrile Oxide

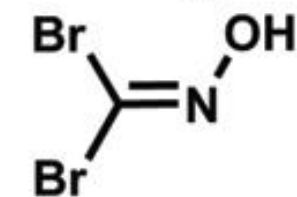


[single diastereomer]

d. MsCl, pyr.

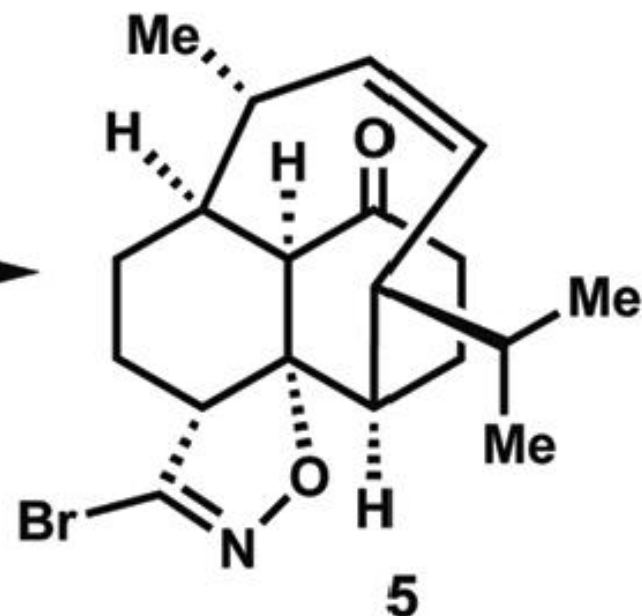
e. KHMDS

f. KHCO₃,



(75% overall)

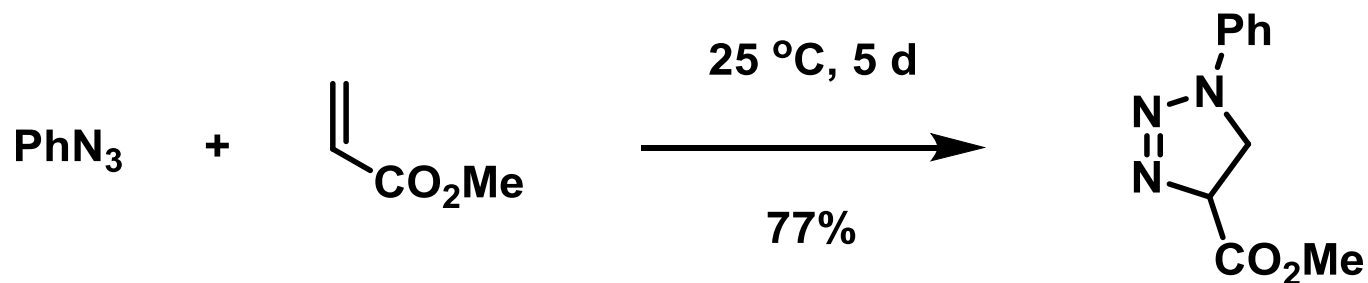
[gram-scale]



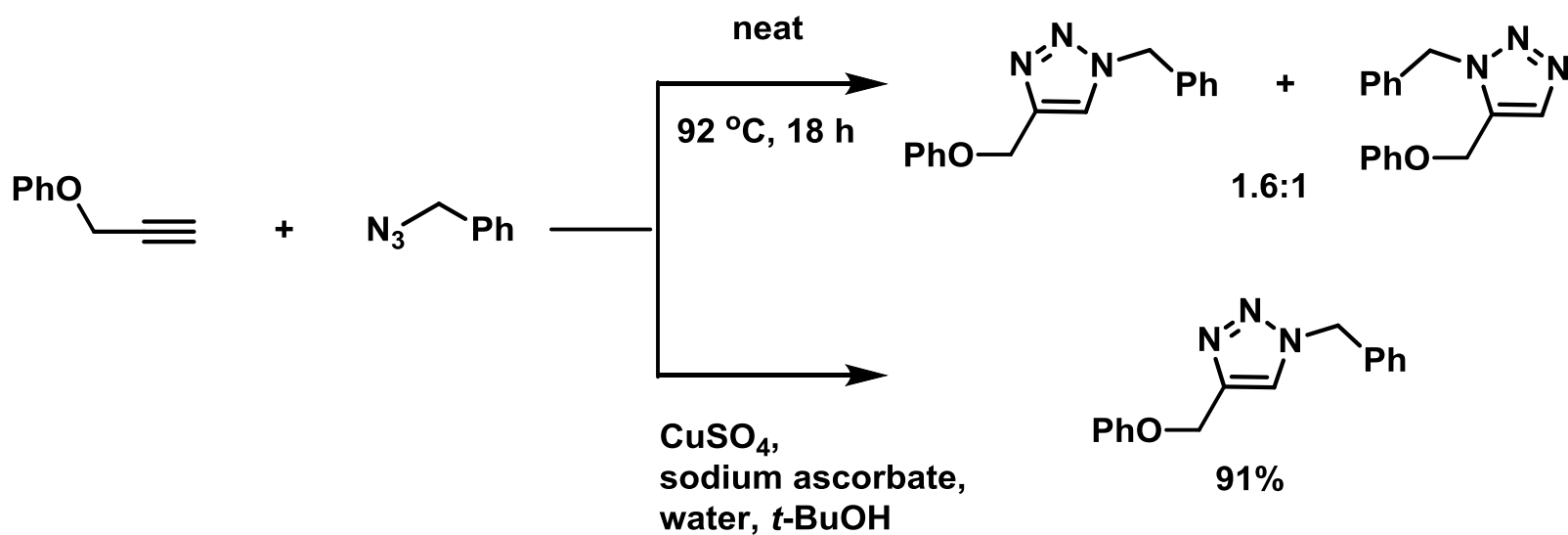
[single diastereomer]
[single regioisomer]
[single positional isomer]

Baran, et al. *J. Am. Chem. Soc.* **2009**, 131, 17066.

Azide

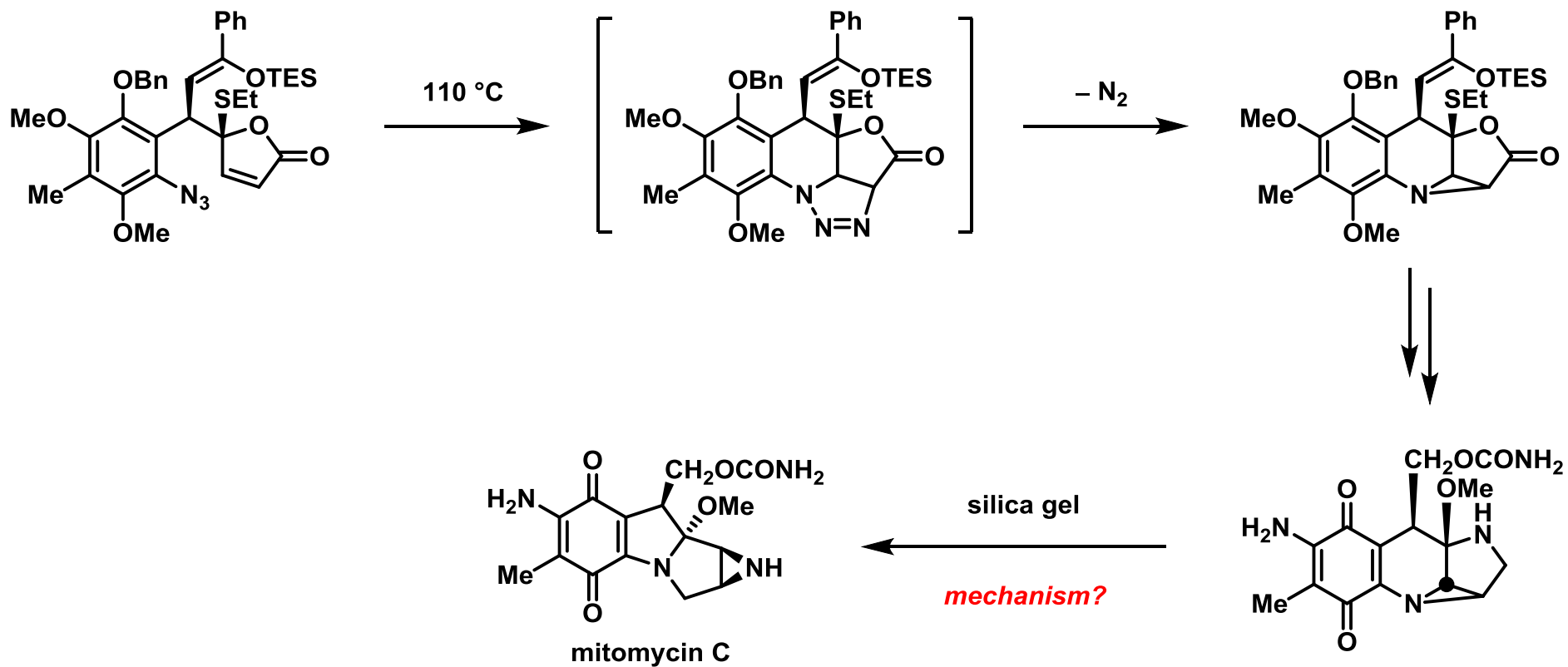


Huisgen, et al. *Chem. Ber.* **1966**, *99*, 475.



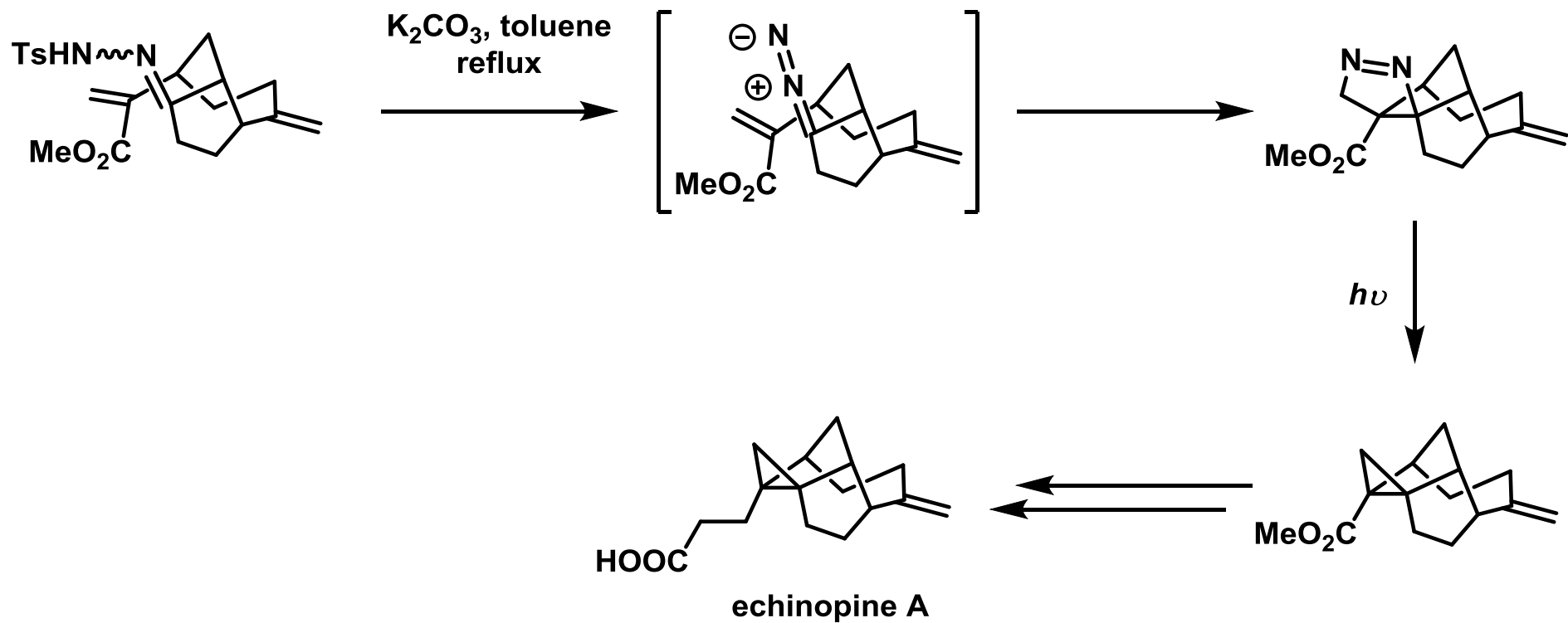
Fokin, Sharpless, et al. *Angew. Chem. Int. Ed.*, **2002**, *41*, 2596.

Azide



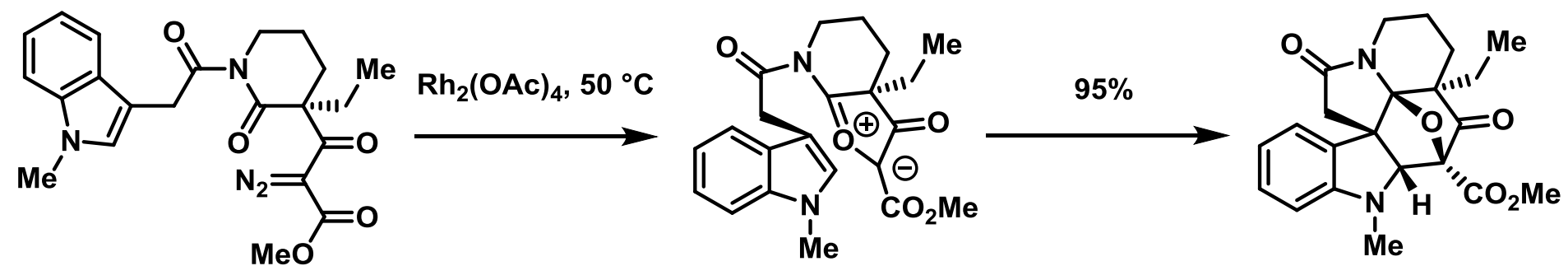
Fukuyama, et al. *J. Am. Chem. Soc.* **1989**, *111*, 8303.

Diazoalkane



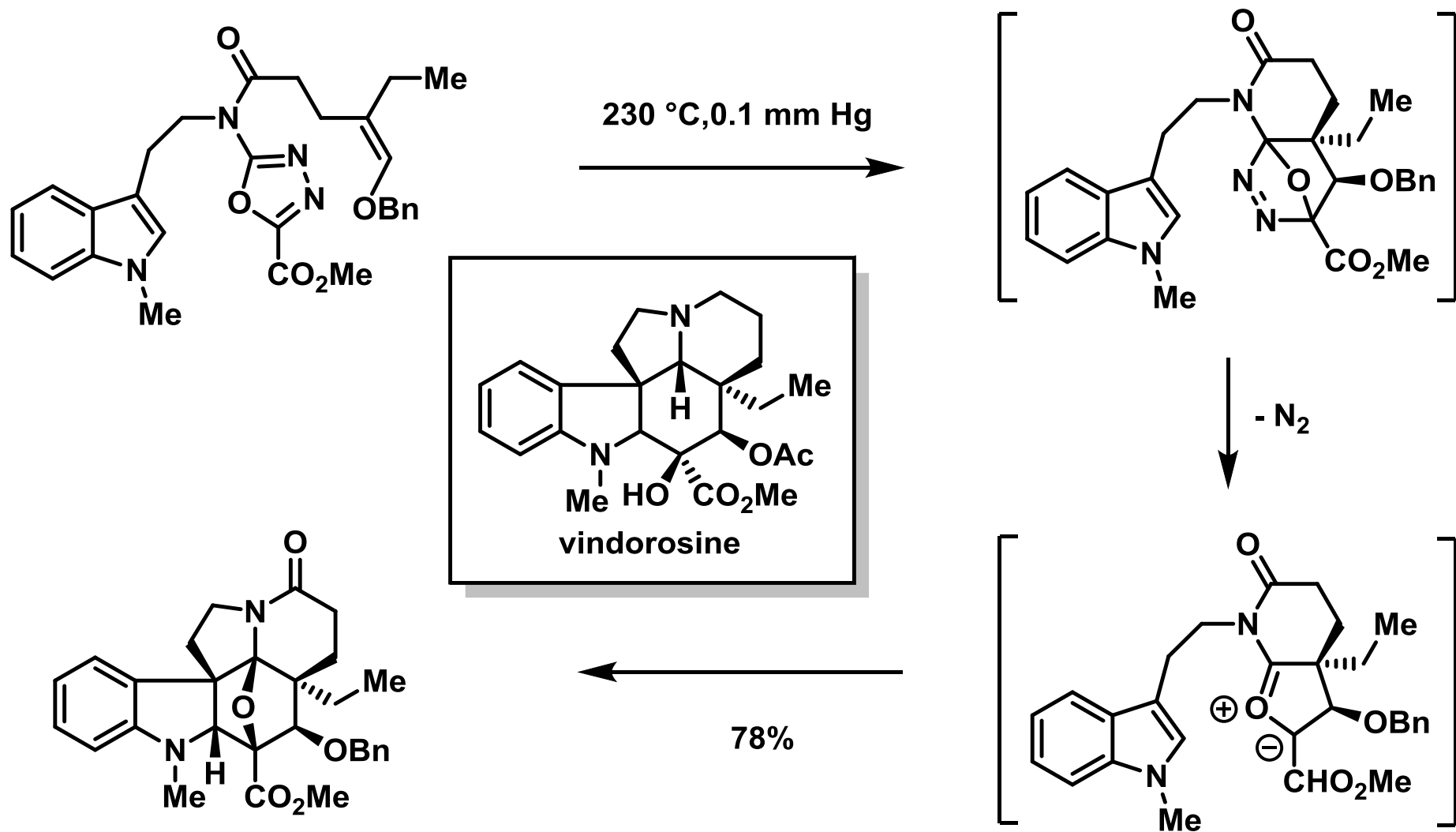
Liang, et al. *Org. Lett.* **2013**, *15*, 1978.

Carbonyl Ylide



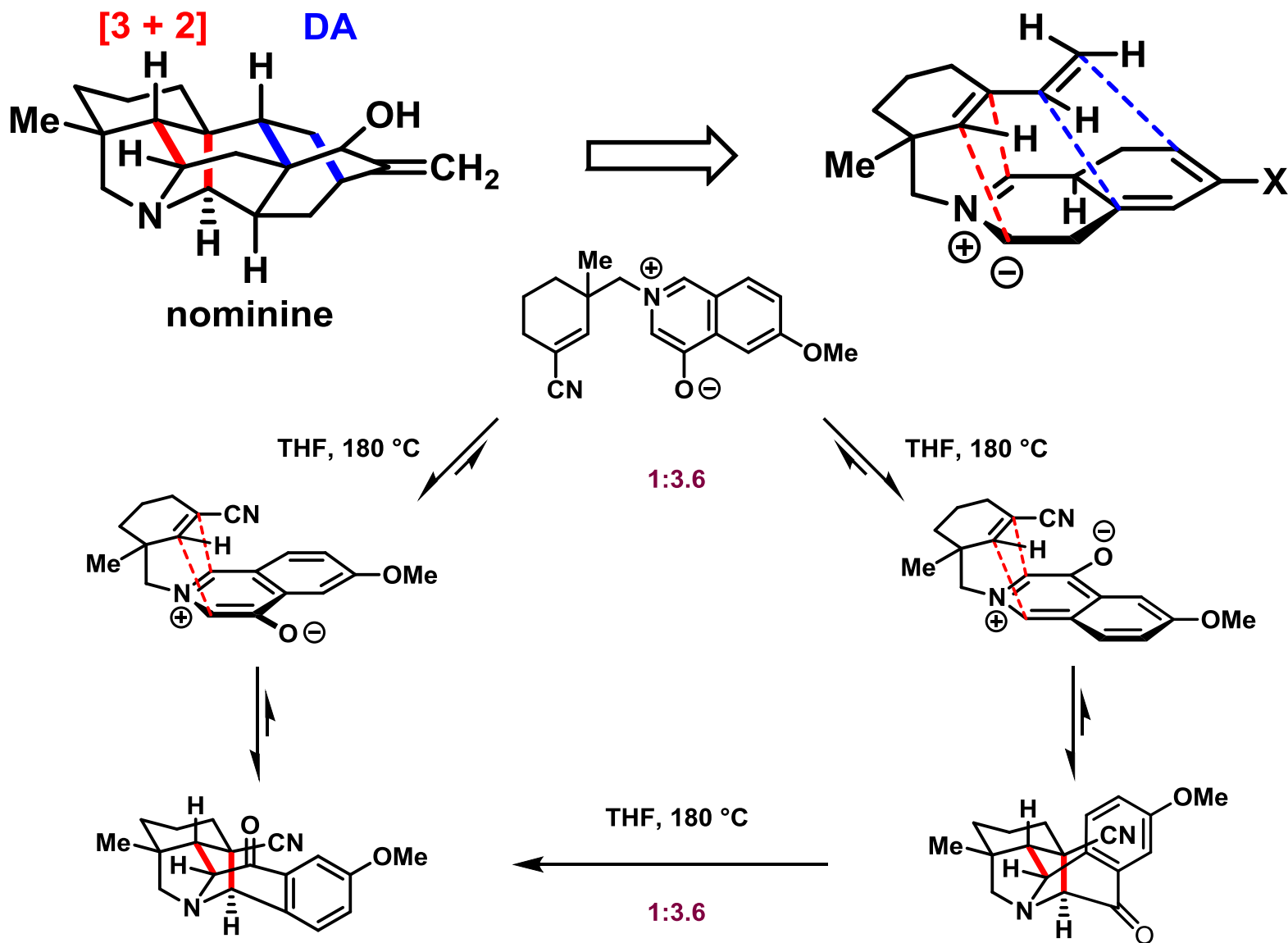
Padwa and Price, *J. Org. Chem.* **1995**, *60*, 6258; *J. Org. Chem.* **1998**, *63*, 556.

Carbonyl Ylide



Boger, et al. *Angew. Chem. Int. Ed.* **2006**, 45, 620.

Oxidopyridinium [5 + 2] cycloaddition





谢 谢!