



六、周环反应

(三) 1,3-偶极环加成反应

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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

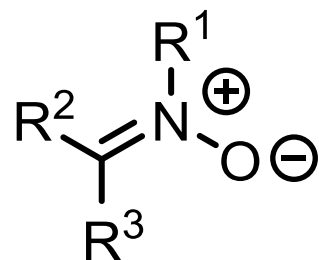
sigmatropic重排

七、阳离子参与的C-C键形成反应

常用的1,3-偶极化合物



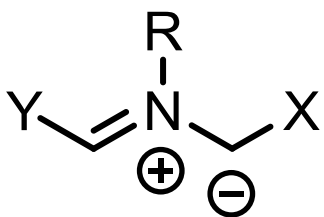
nitrile oxides



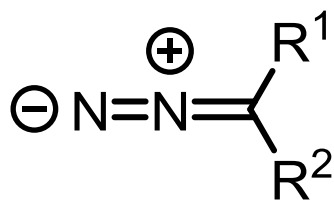
nitrones



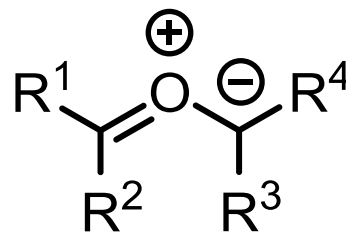
azides



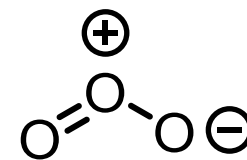
azomethine ylides



diazoalkanes

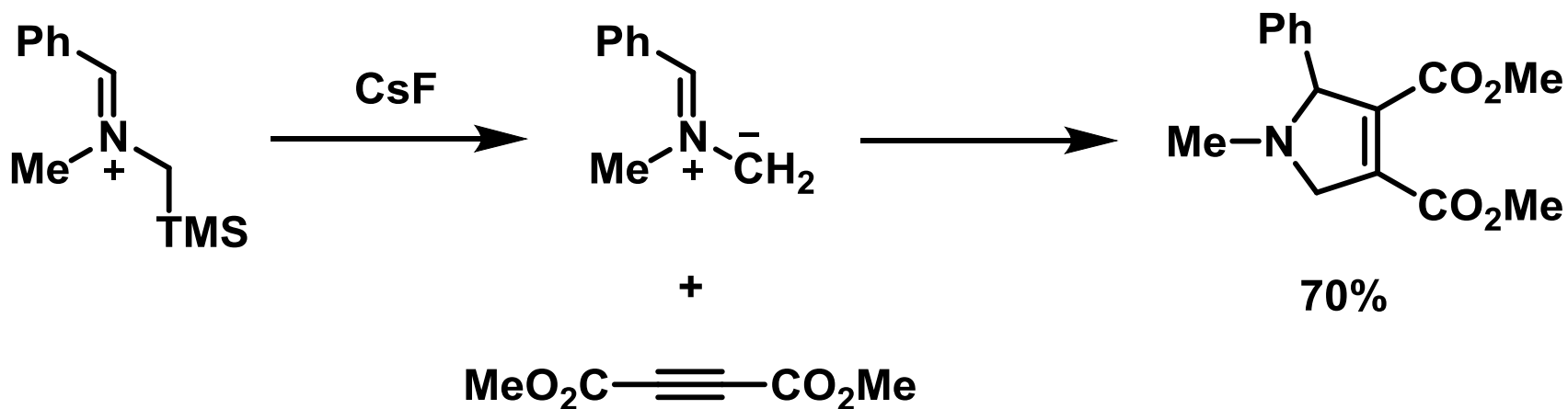


carbonyl ylides

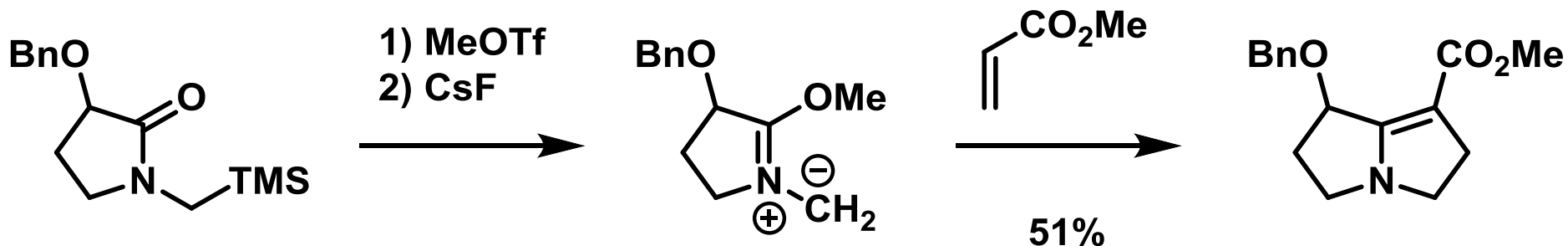


ozone

非稳定的Azomethine叶立德



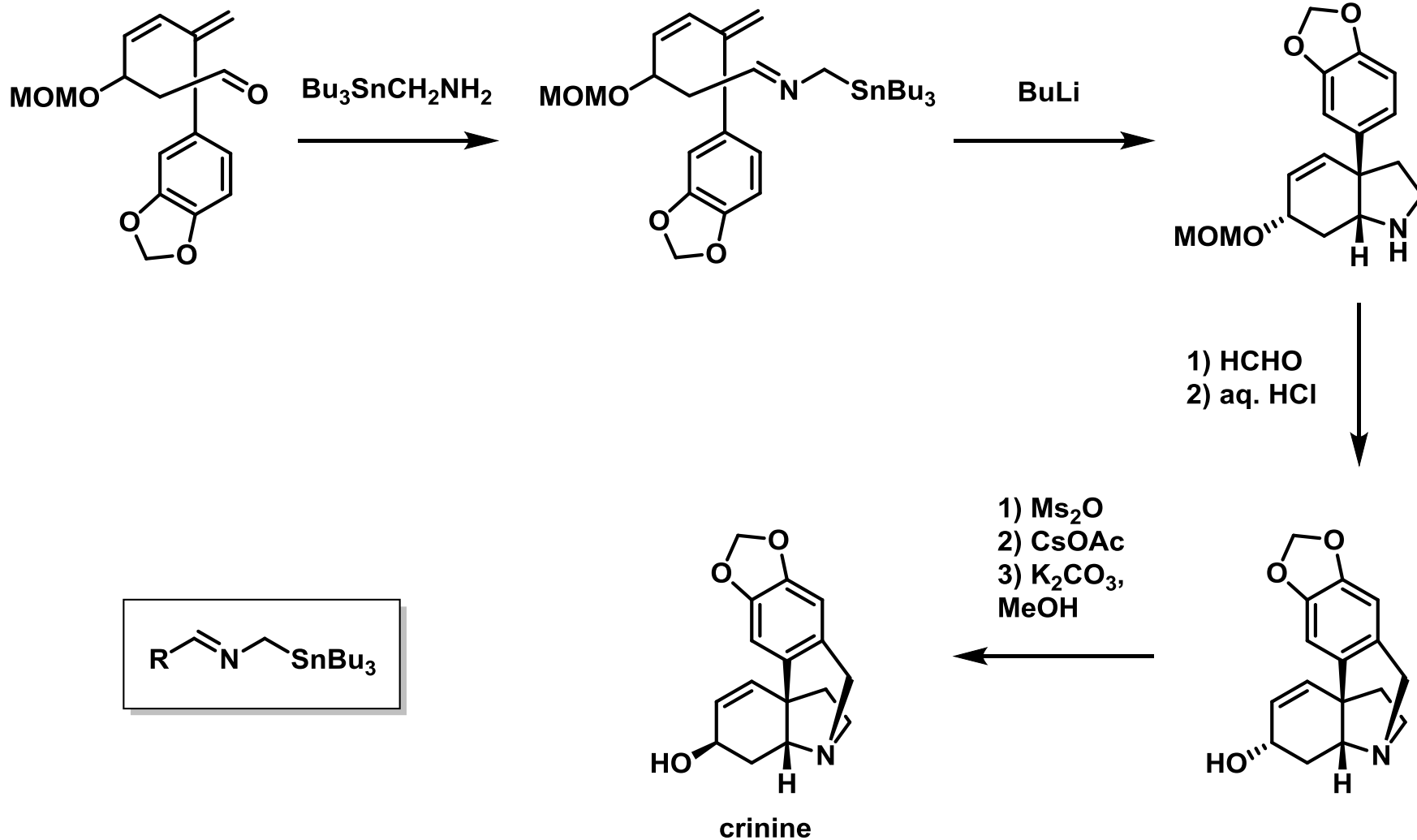
E. Vedejs, et al. *J. Am. Chem. Soc.* **1979**, 101, 6452.



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

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

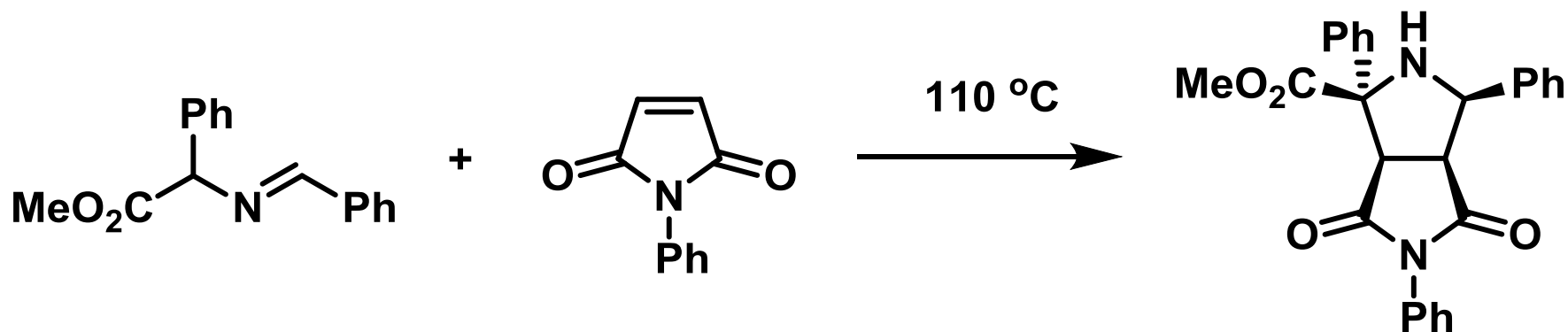
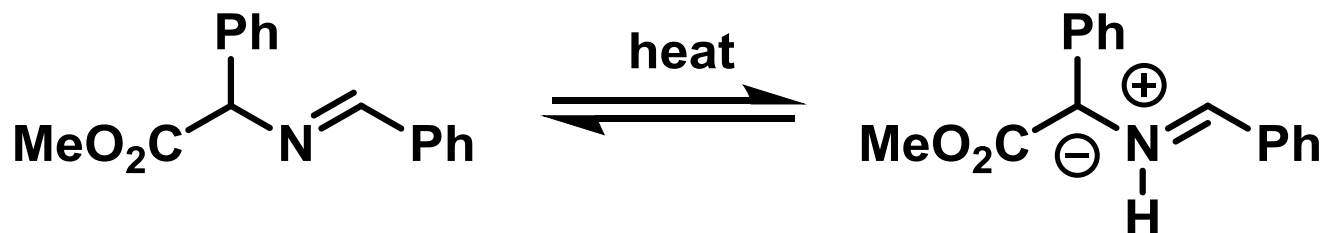
2-Azaallyl Anion



W. H. Pearson, et al. *J. Am. Chem. Soc.* **1992**, *114*, 1329.

W. H. Pearson, et al. *J. Org. Chem.* **1998**, *63*, 3607.

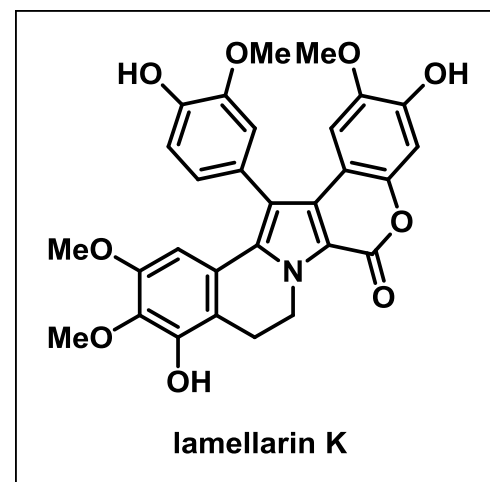
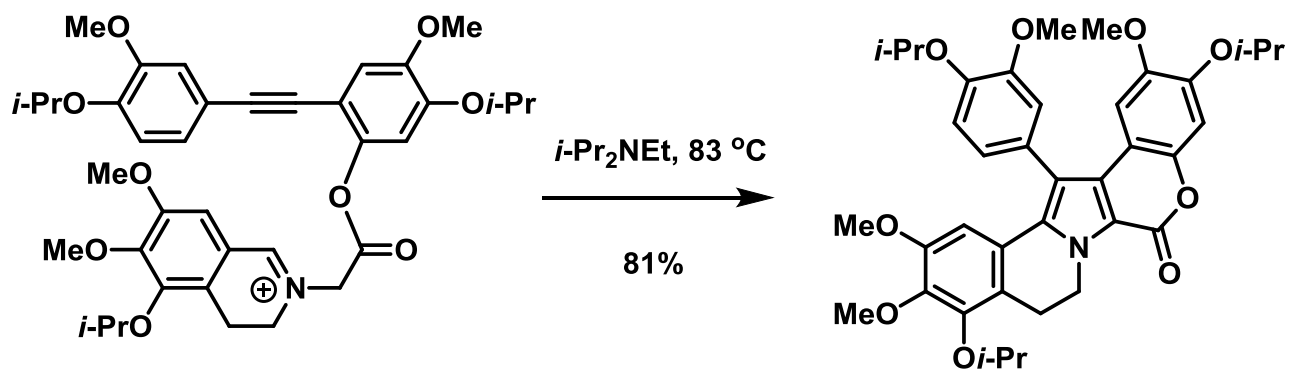
稳定的Azomethine叶立德



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

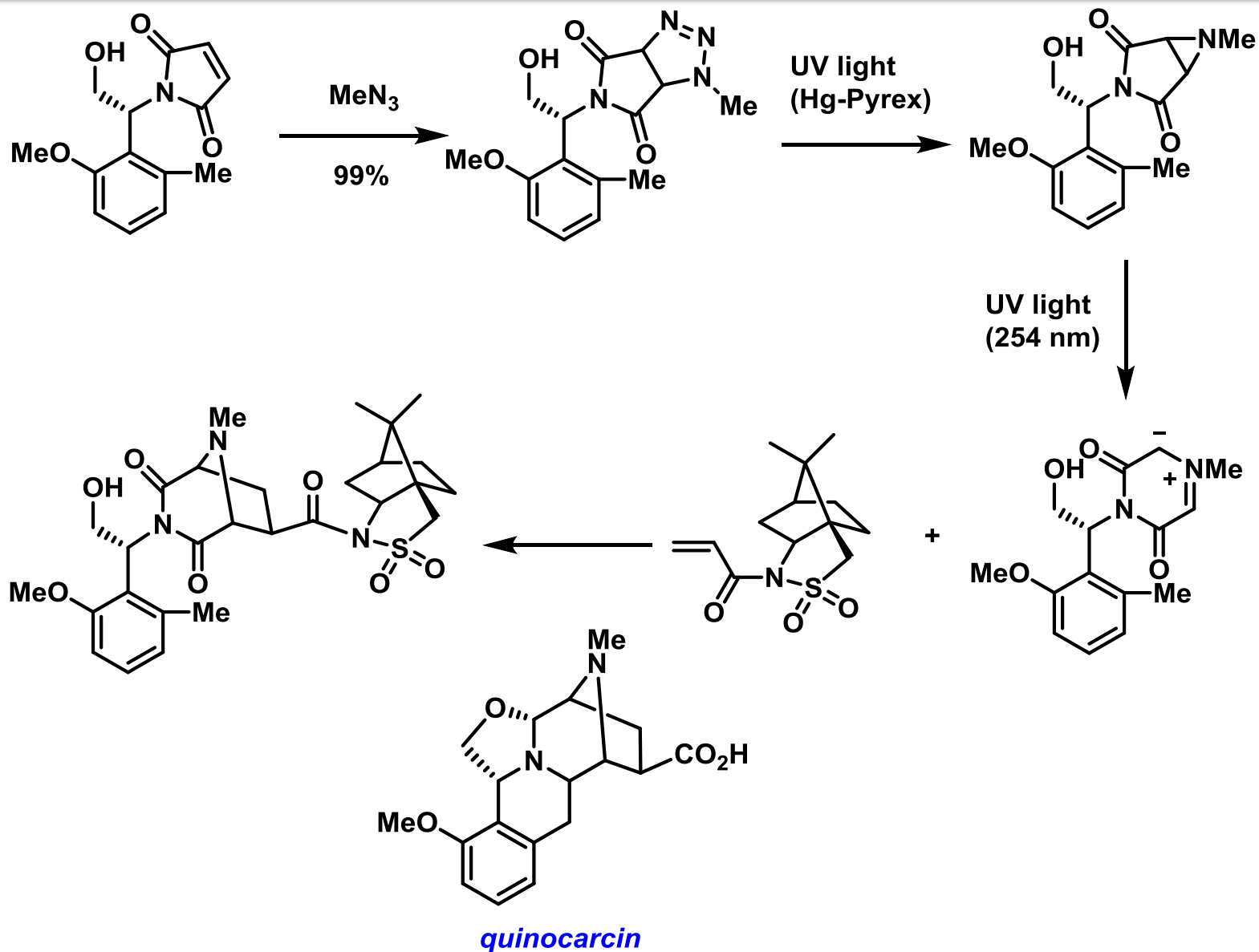
R. Grigg, et al. *J. Chem. Soc., Chem. Commun.* **1982**, 384.

稳定的Azomethine叶立德



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

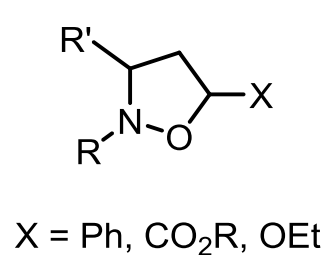
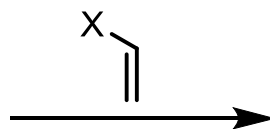
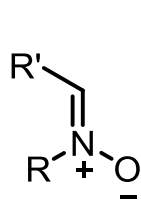
稳定的Azomethine叶立德：氮杂环丙烷开环



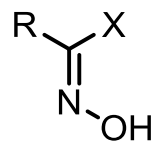
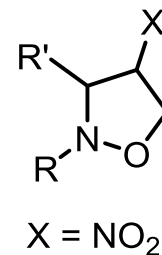
Nitrile-oxide/Nitrone



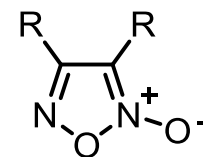
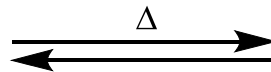
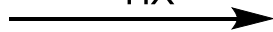
+



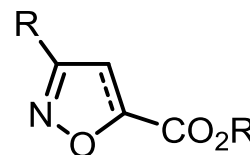
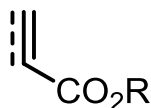
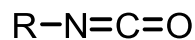
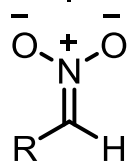
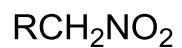
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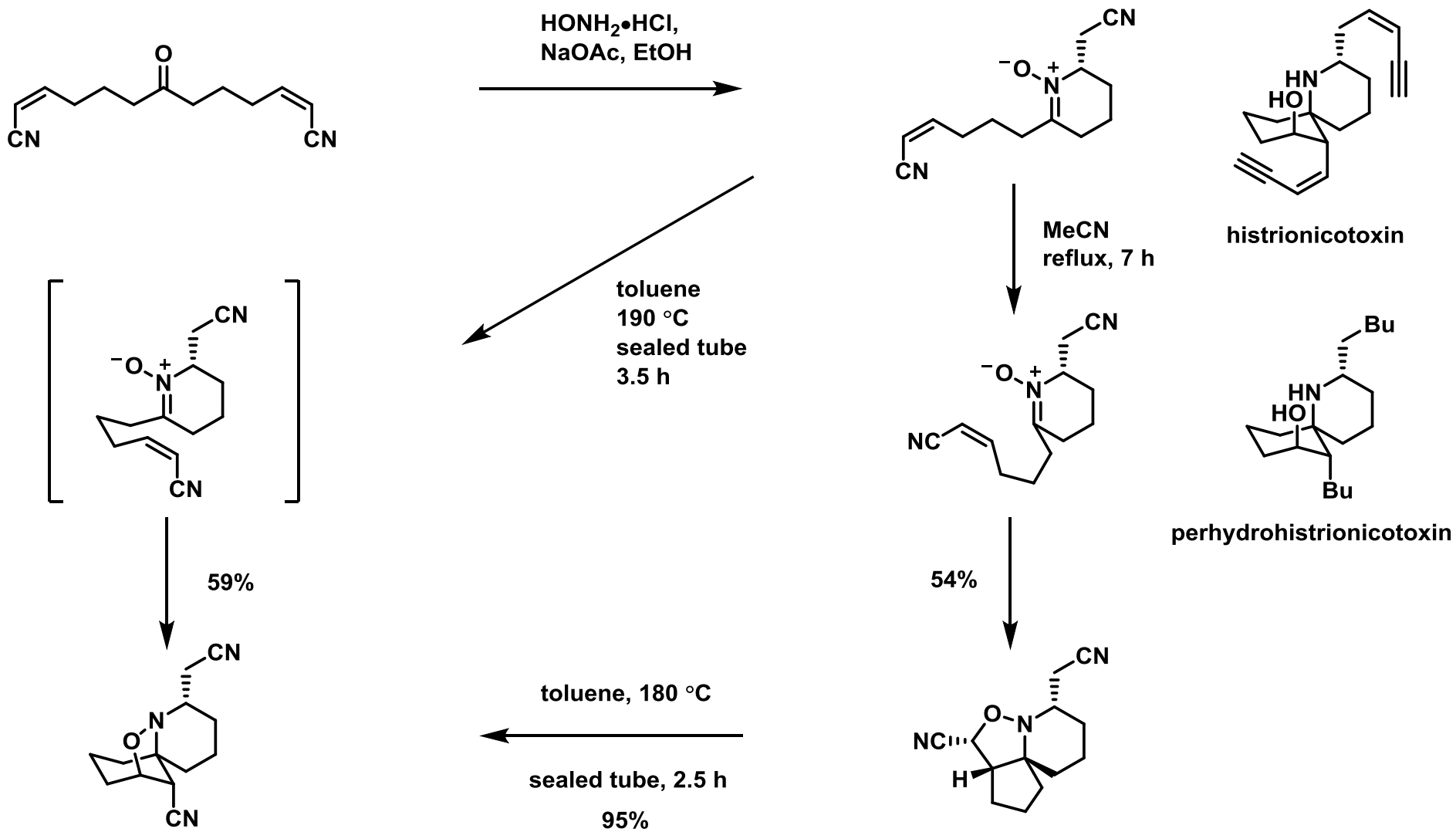
-HX



X = H
X = Cl, Br, I

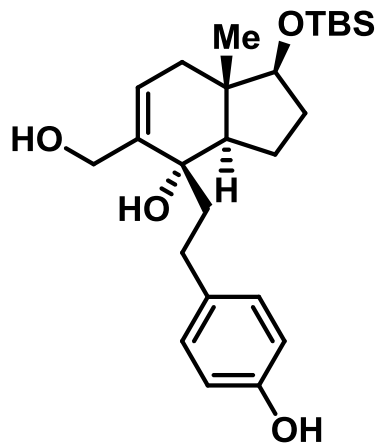


Nitrone: Histrionicotoxin Synthesis



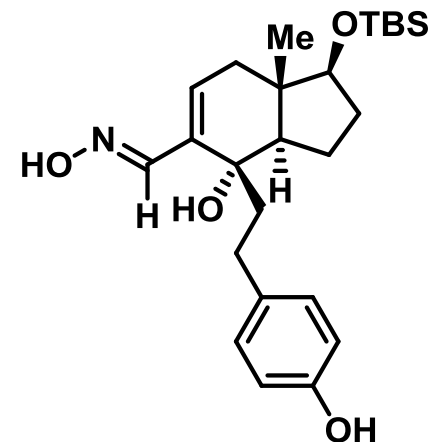
R. A. Stockman, et al. *J. Org. Chem.* **2004**, 69, 1598.

Nitrile Oxide: Cortistatin A Core Synthesis

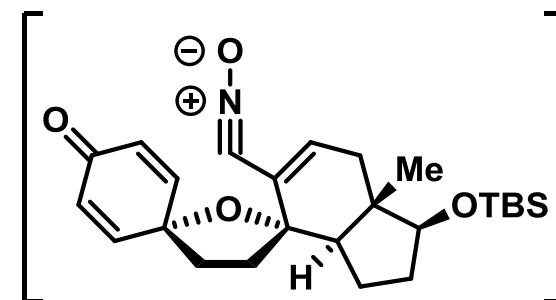
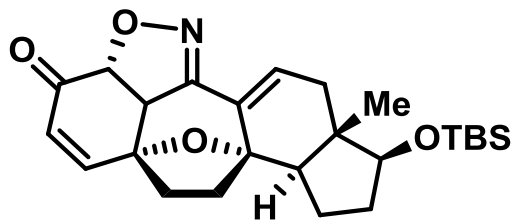
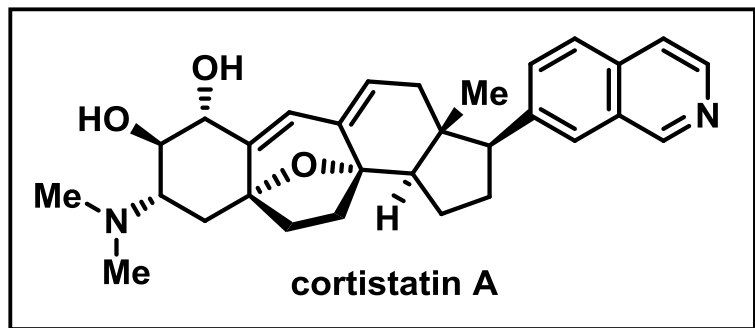


1) SO₃•pyr, Et₃N,
DMSO, 57%

2) HONH₂•HCl, NaOAc,
60 °C, ca. 100%

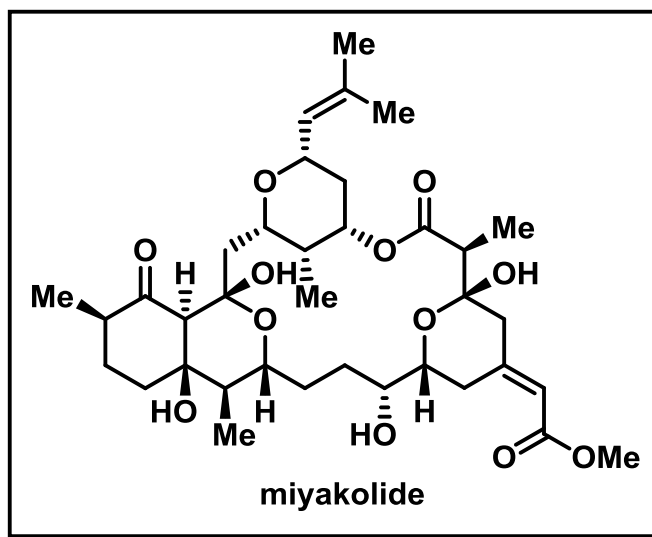
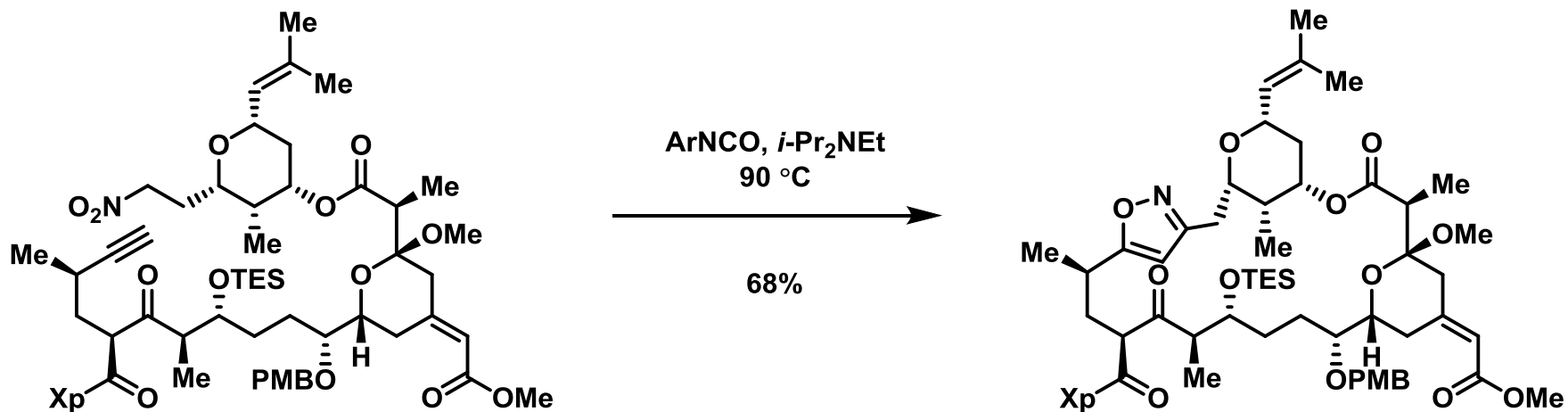


PhI(OAc)₂, TFA;
then 50 °C, 80%



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

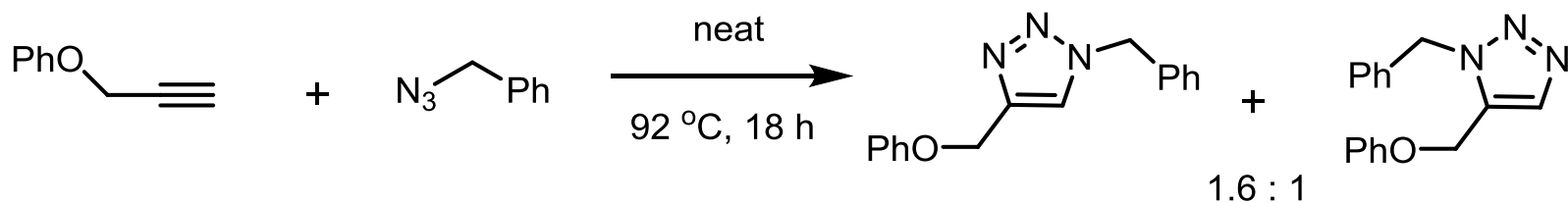
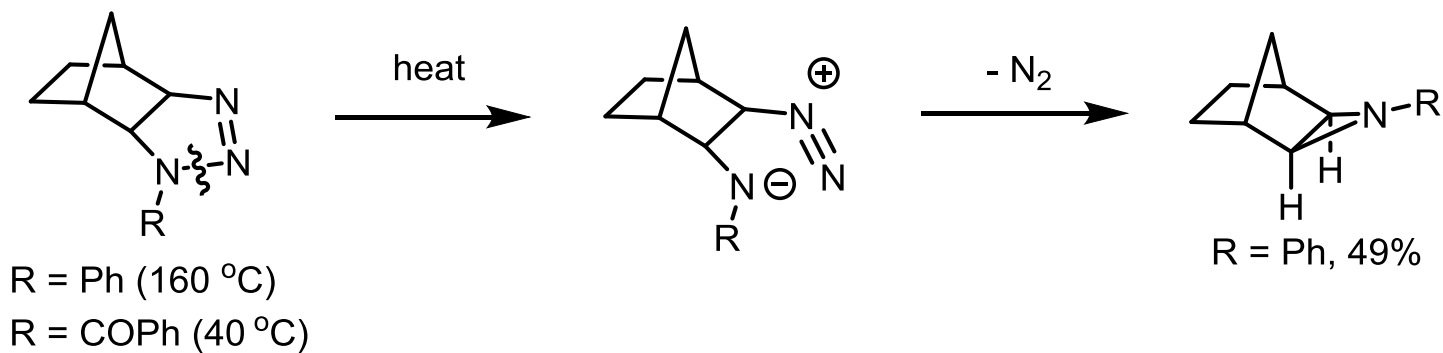
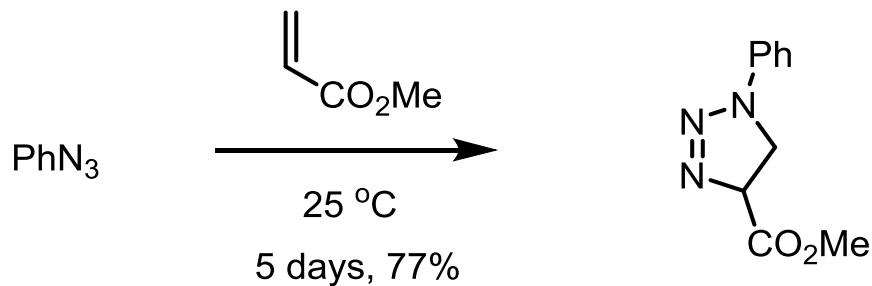
Nitrile Oxide: Miyakolide Synthesis



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

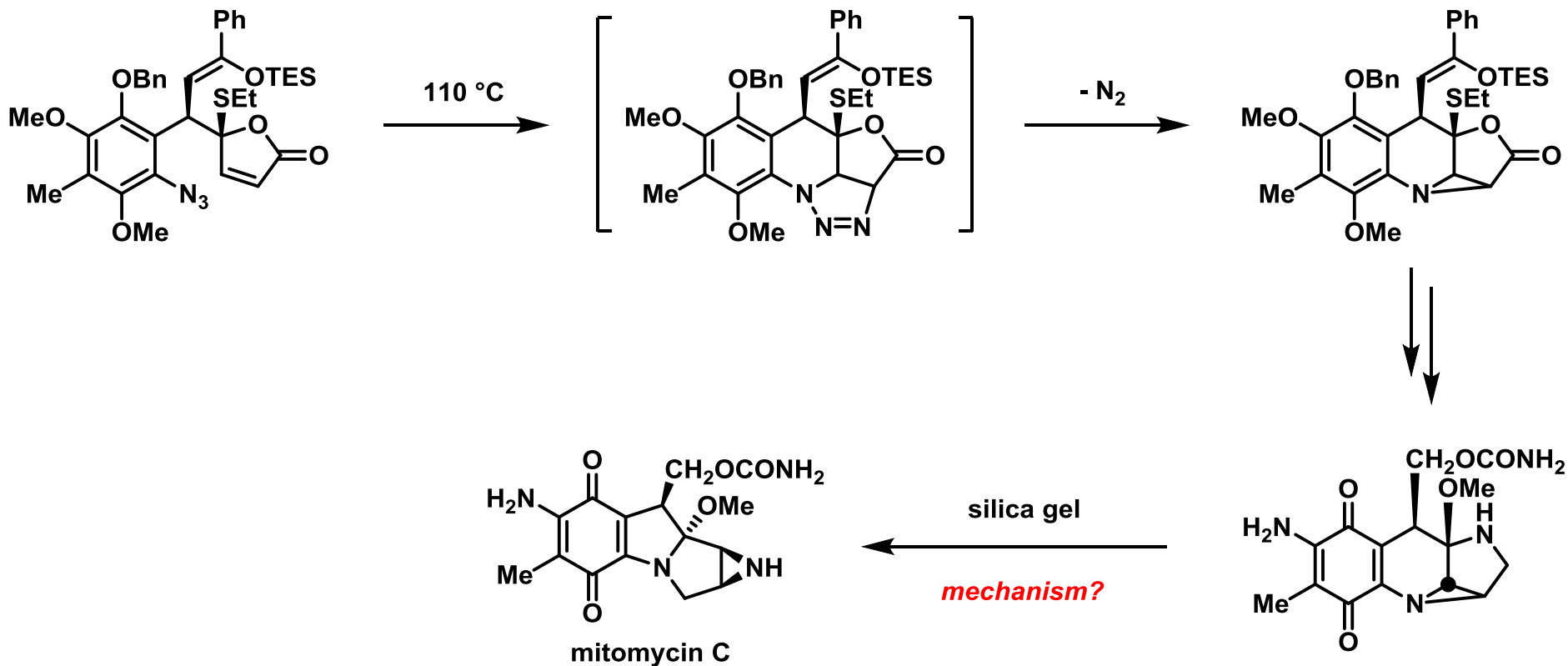
Azide

Huisgen Cycloaddition



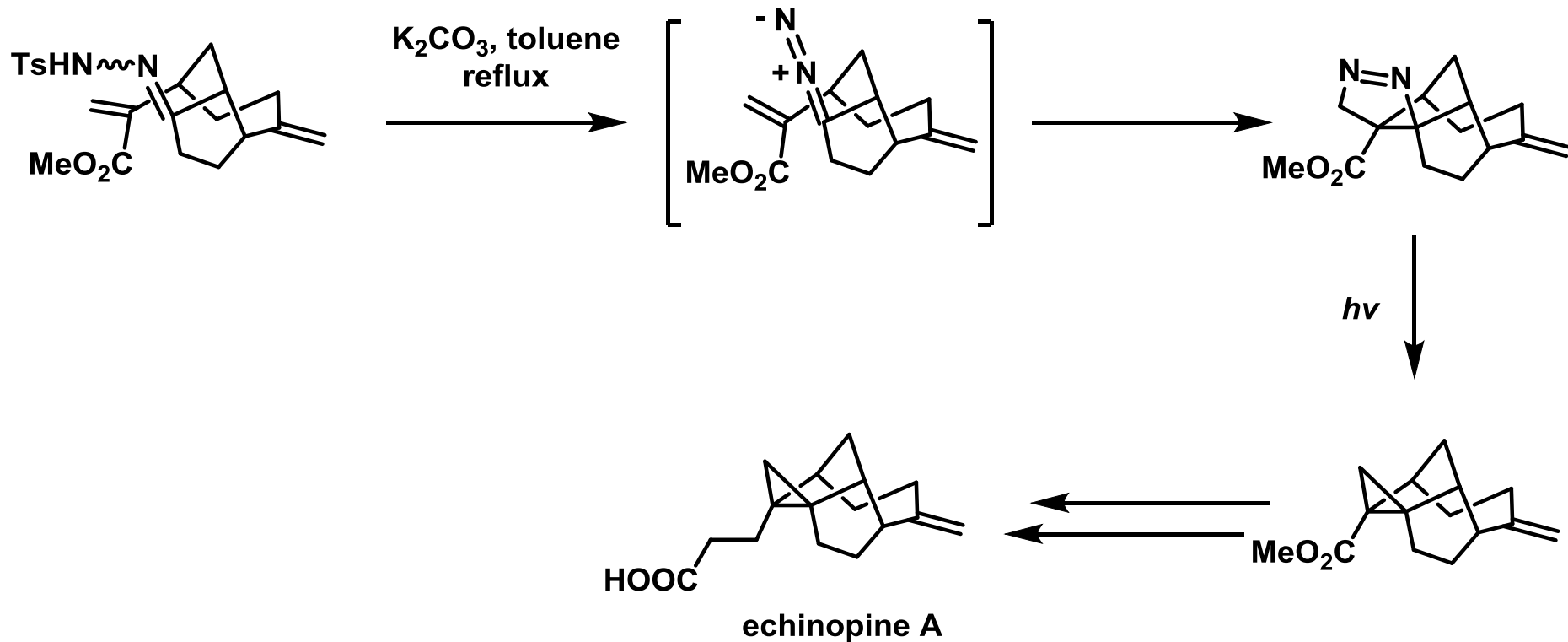
V. V. Fokin, K. B. Sharpless, et al. *Angew. Chem. Int. Ed.*, **2002**, 41, 2596.

Azide: Mitomycin C Synthesis



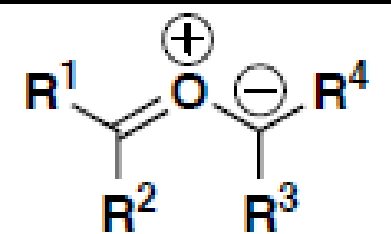
T. Fukuyama, et al. *J. Am. Chem. Soc.* **1989**, *111*, 8303.

Diazoalkane: Echinopine A Synthesis



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

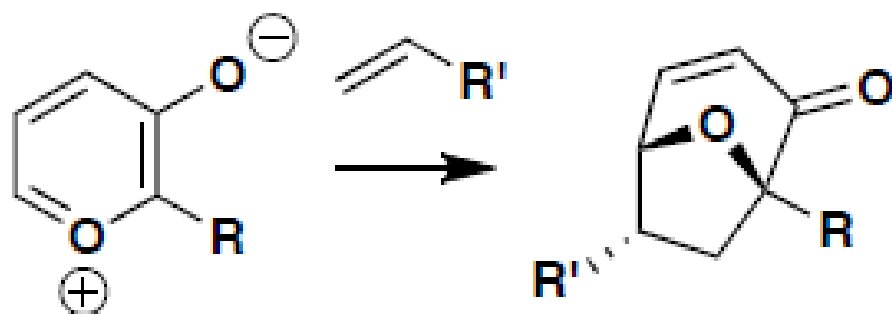
Carbonyl Ylide



carbonyl ylides

- bent, allyl type
- usually used in intramolecular cases, *exo* or *endo* product observed
- in intermolecular cases, symmetrical dipolariphiles usually employed

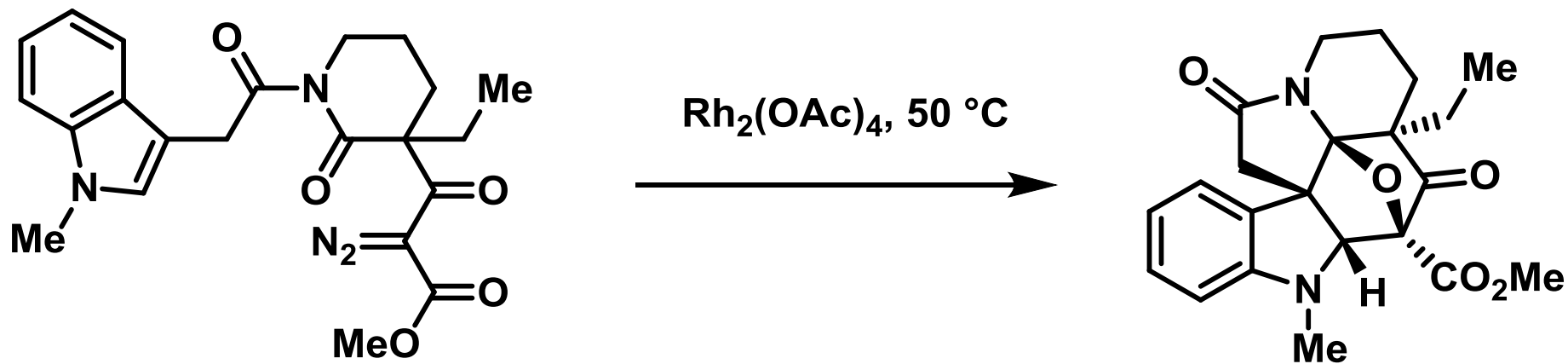
important subset:



3-oxidopyrylium

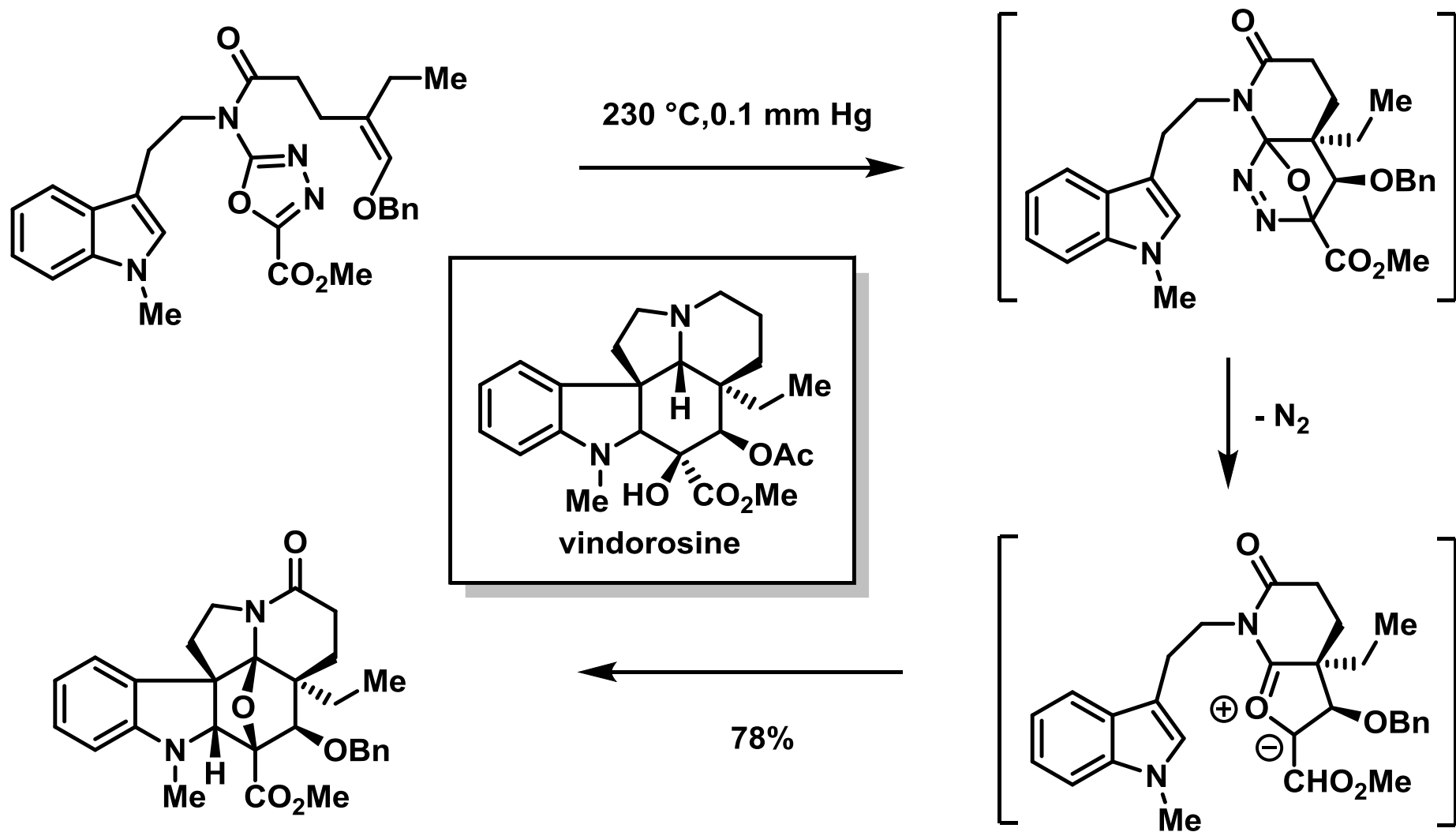
- R' = e⁻ rich or poor = 1 regioisomer shown
- intermolecular proceeds *endo*
- intramolecular proceeds *exo*

Carbonyl Ylide



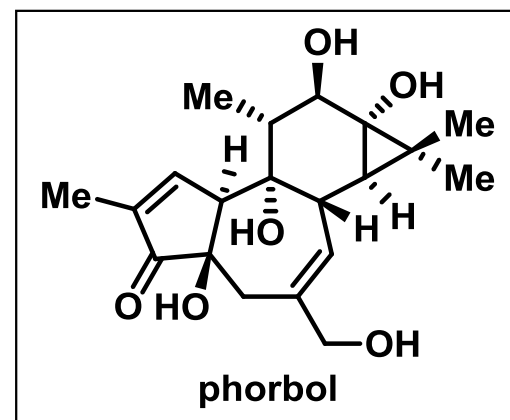
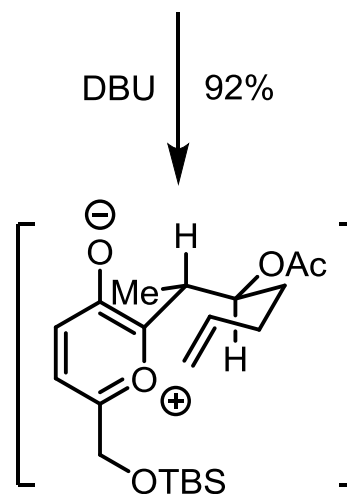
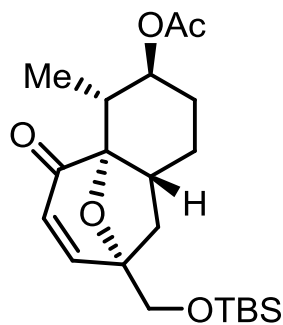
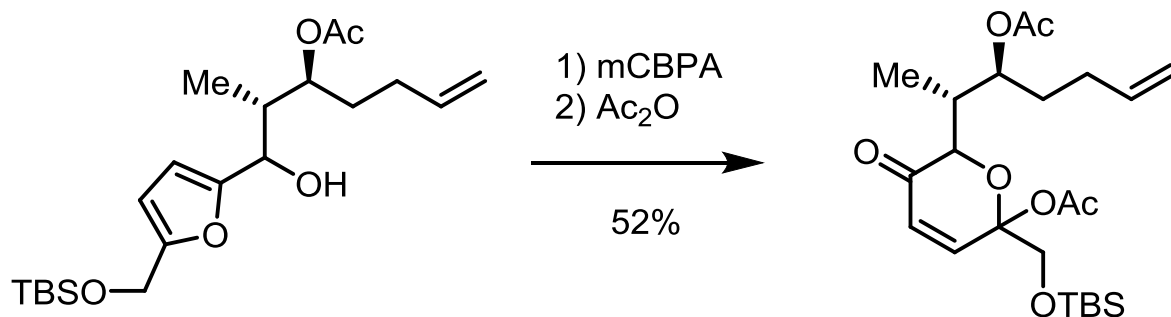
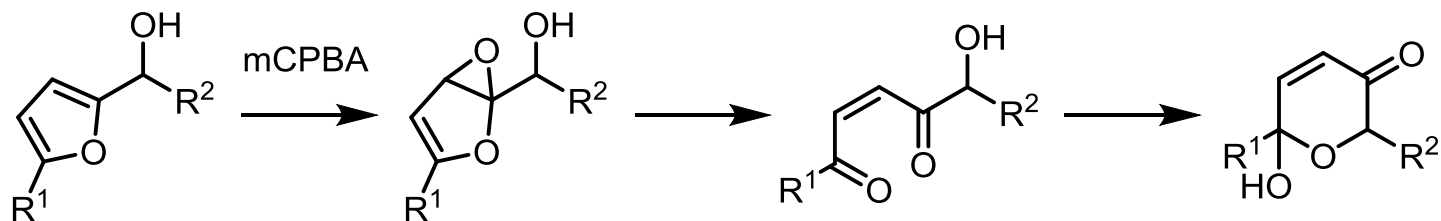
A, Padwa, et al. *Org. Lett.* **2006**, *8*, 3275.

Carbonyl Ylide



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

Oxidopyrylium [5 + 2]



Oxidopyridinium [5 + 2]

