

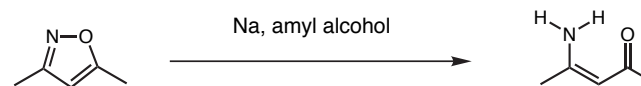
The Use of Isoxazoles as 1,3 Dicarbonyl Equivalents in Organic Synthesis

David H. Brown Ripin
1997

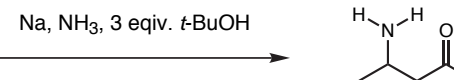
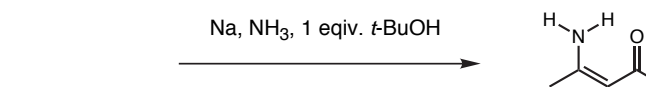
Leading reference:

Baraldi, P.G.; Barco, A.; Benetti, S.; Pollini, G.P.; Simoni, D. *Synthesis* **1987**, 857.

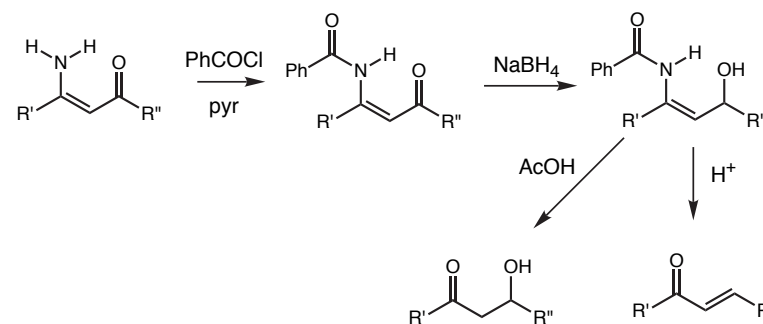
N-O Bond Cleavage of Isoxazoles



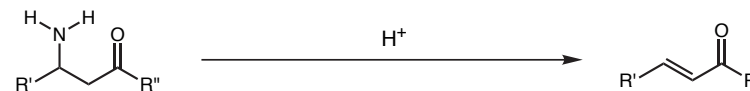
Claisen, L. *Ber. Dtsch. Chem. Ges.* **1891**, 24, 3900



Buchi, G.; Vederas, J. C. *JACS* **1972**, 94, 9128.

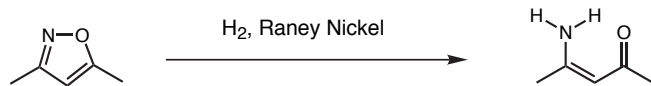


Kashima, C.; Yamamoto, Y.; Tsuda, Y. *JOC* **1975**, 40, 526.
Barco, A.; Benetti, S.; Baraldi, P.G.; Guarneri, M.; Pollini, G.P.; Simoni, D. *JCSCC* **1981**, 599.



Buchi, G.; Vederas, J. C. *JACS* **1972**, 94, 9128.

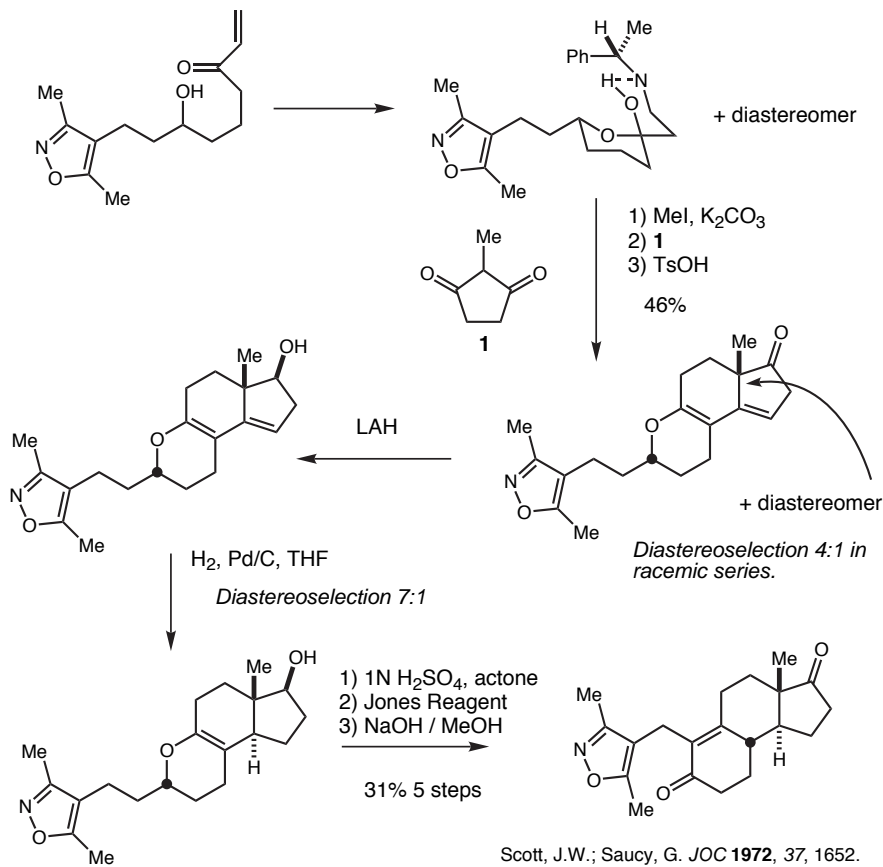
N-O Bond Cleavage of Isoxazoles



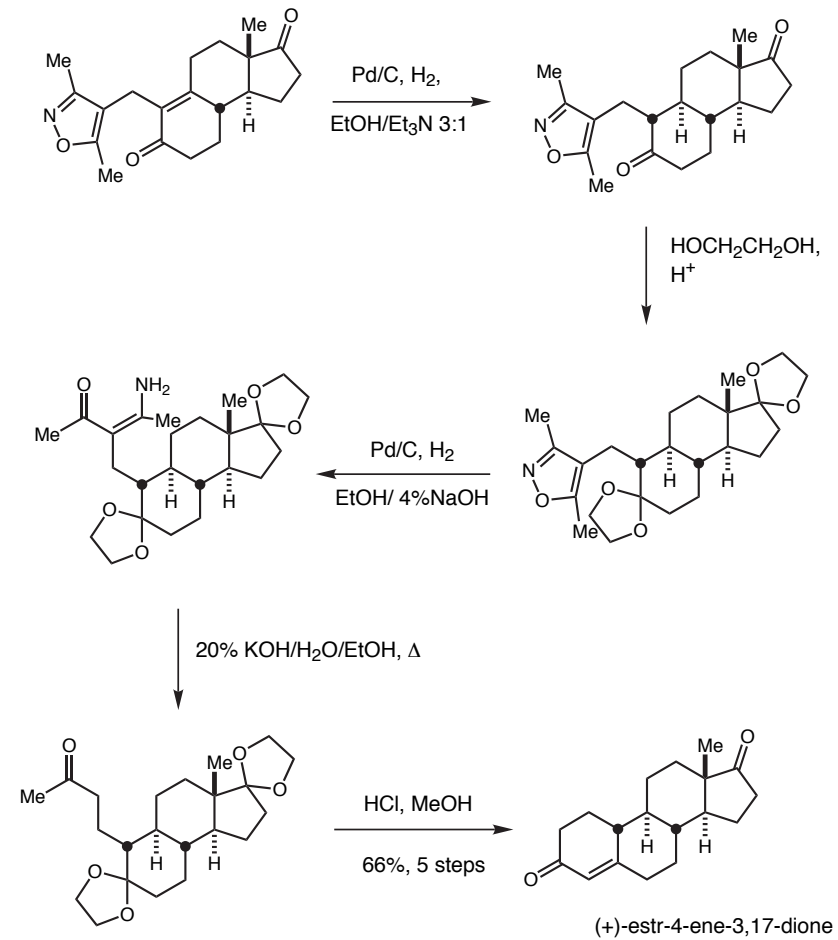
Stagno D'Alcontres, G. *Gazz. Chim. Ital.* **1950**, *80*, 441.

Other Catalysts employed include Pt and Pd, although these reactions are highly sensitive to reaction conditions. (*vide infra*)

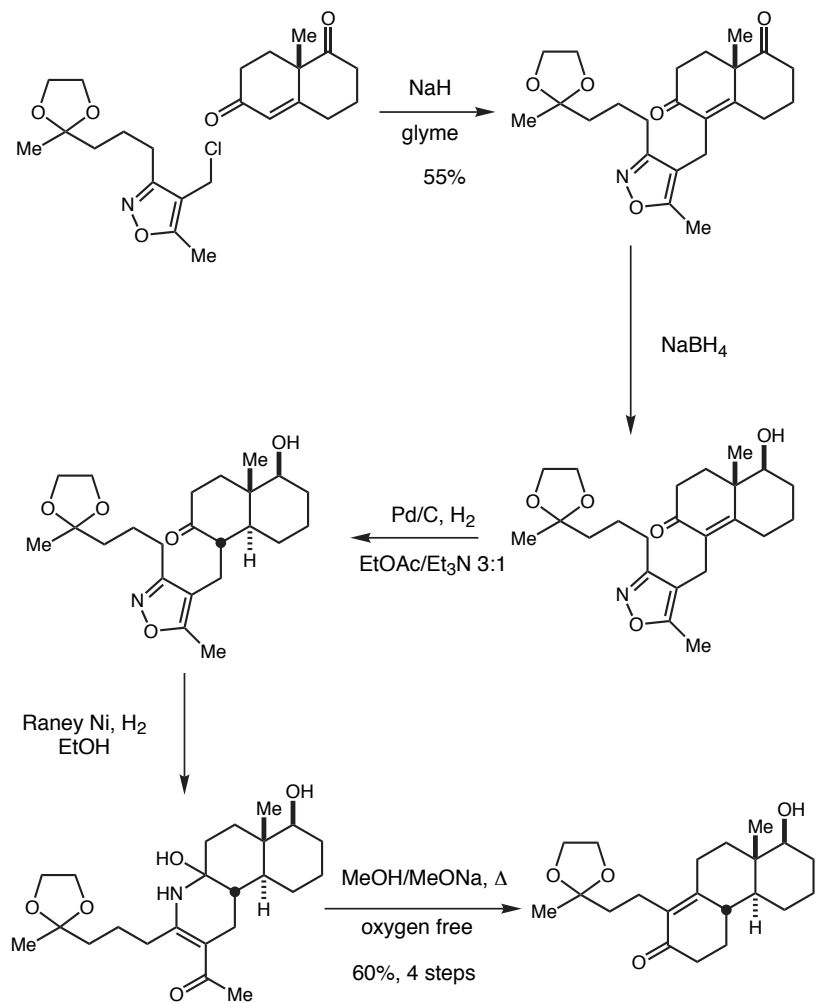
Estrone derivative synthesis: a case study in selective hydrogenations.



Estrone derivative synthesis continued

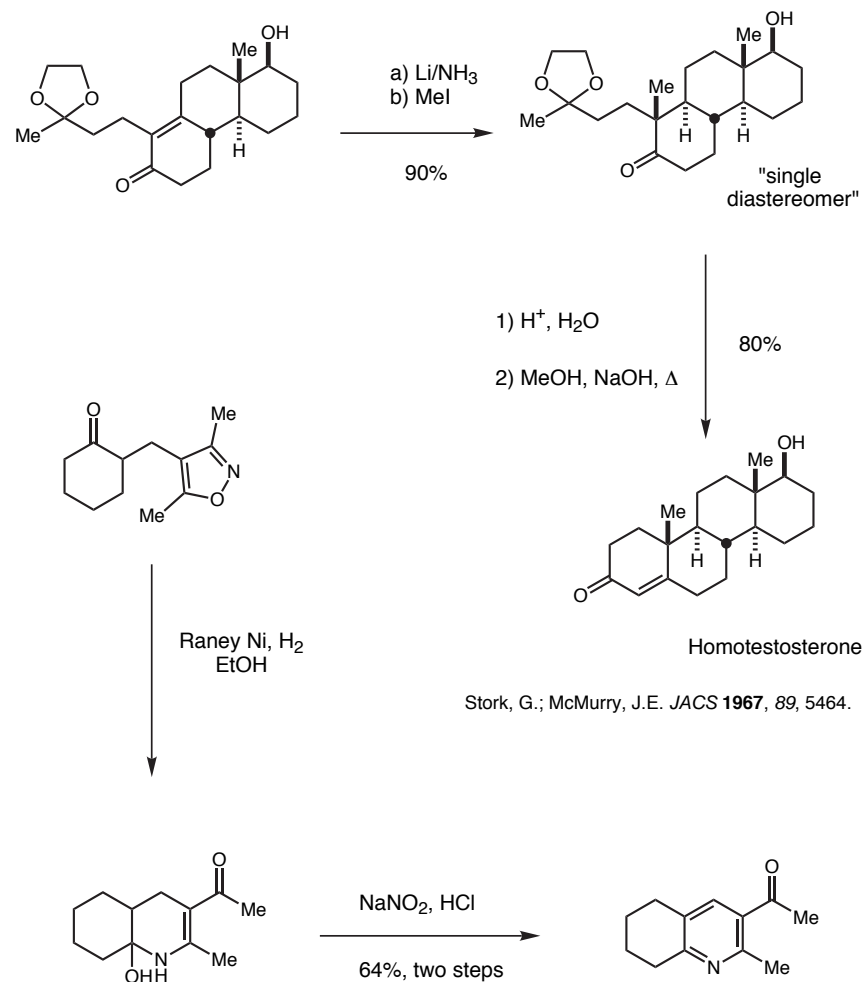


Homotestosterone synthesis



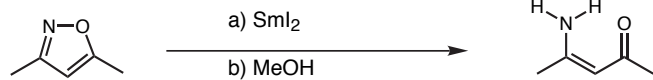
Stork, G.; McMurry, J.E. *JACS* **1967**, *89*, 5464. See also the preceding three papers.

Homotestosterone synthesis continued

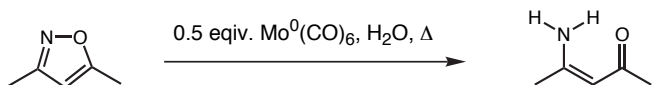


Ohashi, M.; Kamachi, H.; Kakisawa, H.; Stork, G. *JACS* **1967**, *89*, 5464.

N-O Bond Cleavage of Isoxazoles



Natale, N.R. *TL* **1982**, 5009.

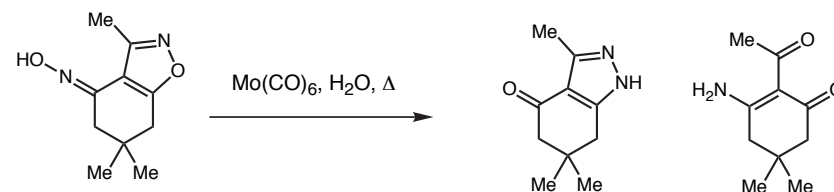


Nitta, M.; Kobayashi, T. *JCSCC* **1982**, 877.

$\text{M}^0(\text{CO})_n = \text{Fe}^0(\text{CO})_5, \text{Fe}_2^0(\text{CO})_9$

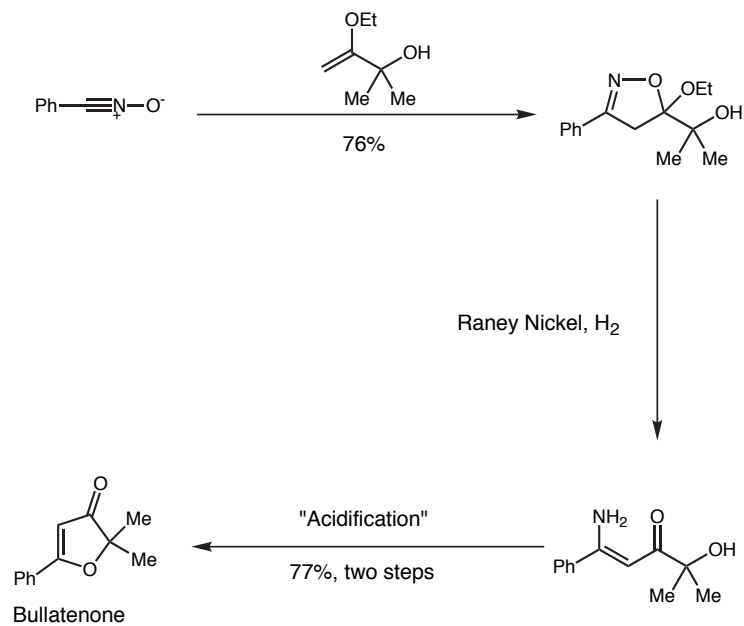
Nitta, M.; Kobayashi, T. *TL* **1982**, 3925.
Kijima, M. Nambu, Y.; Endo, T. *JOC* **1985**, 50, 1140.

"Unexpected Pyrazole Formation"



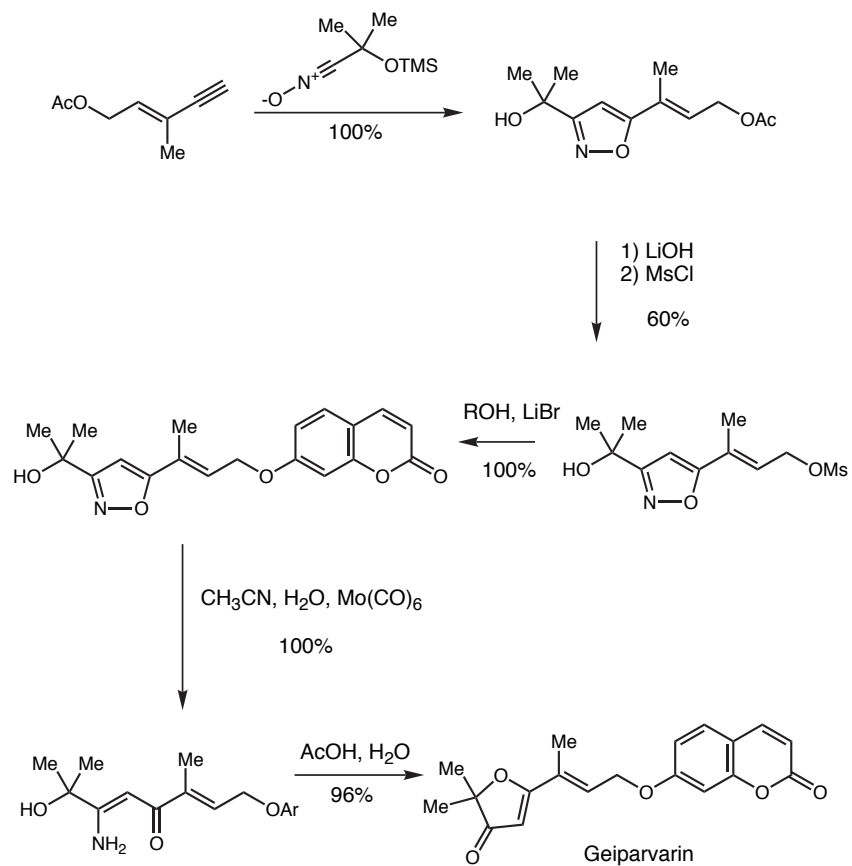
Anderson-McKay, J.; Savage G.P.; Simpson G.W. *Aust. J. Chem.* **1996**, 49, 163.

Synthesis of 3(2H)-furanones



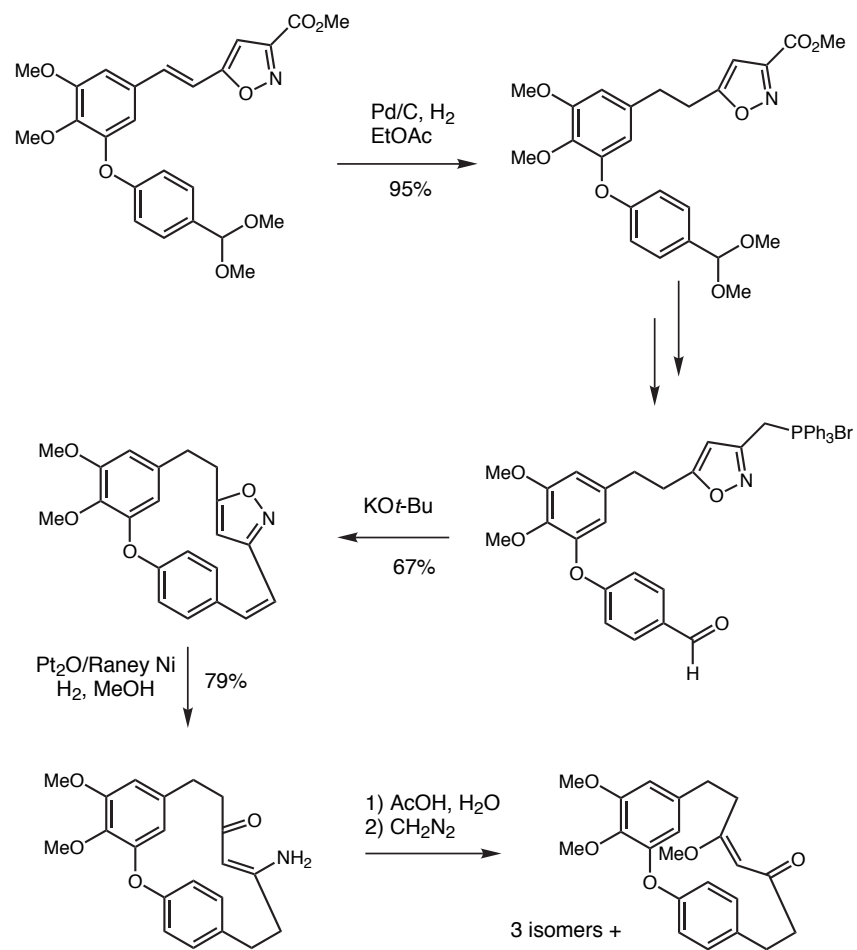
Curran, D.P.; Singleton, D.H. *TL* **1983**, 24, 2079.

Synthesis of 3(2H)-furanones



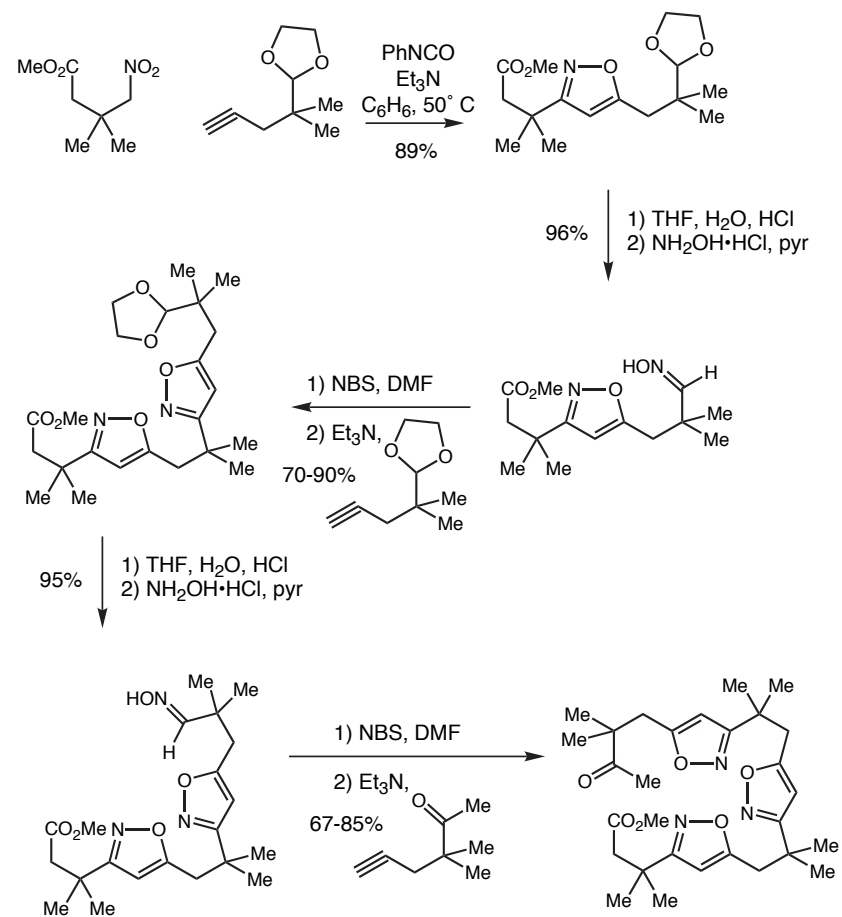
Baraldi, P.G.; Barco, A.; Benetti, S.; Guarneri, M. *TL* **1985** 26, 5319.

Synthesis of Garugambin 3



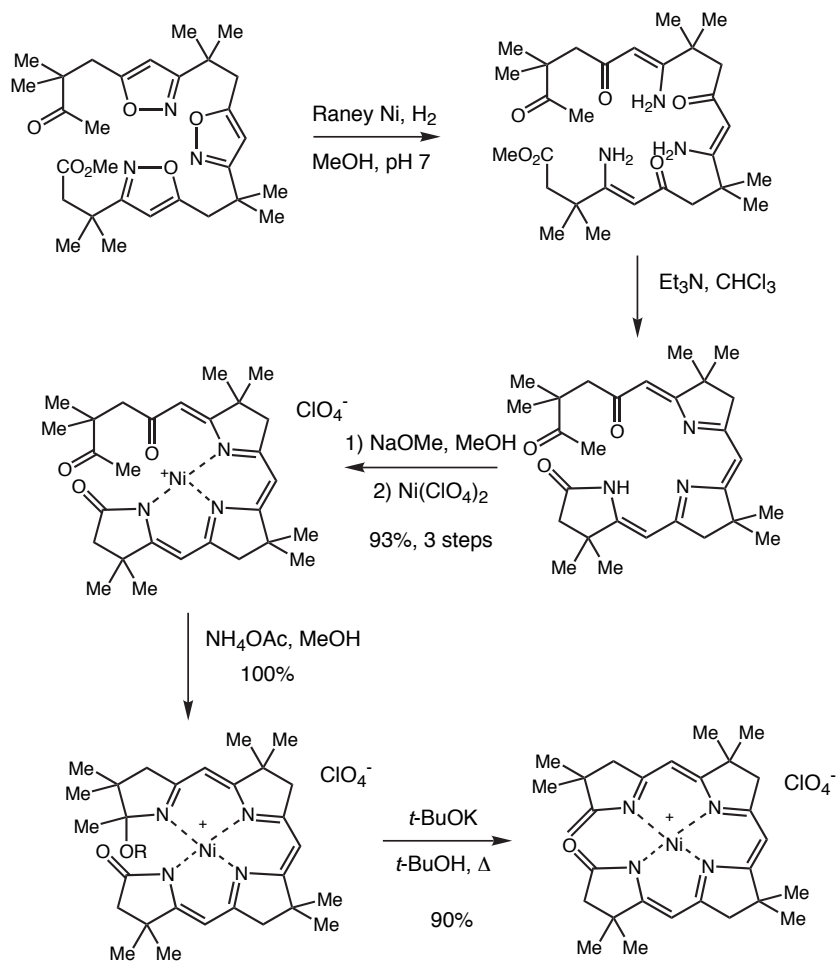
Keseru, G.M.; Dienes, Z; Nogradi, M. *JOC* **1993**, *58*, 6725.

Synthesis of Corphins



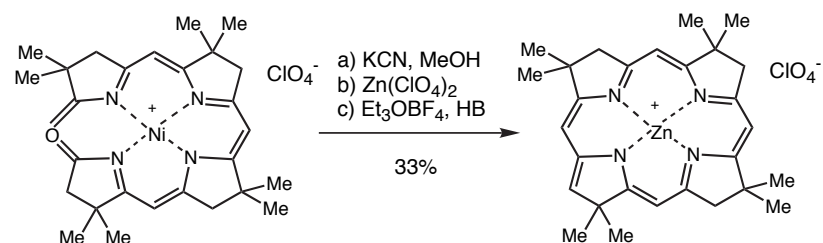
Stevens, R.V.; Christensen, C.G.; Cory, R.M.; Thorsett, E. *JACS* **1975**, *97*, 5940.

Synthesis of Corphins



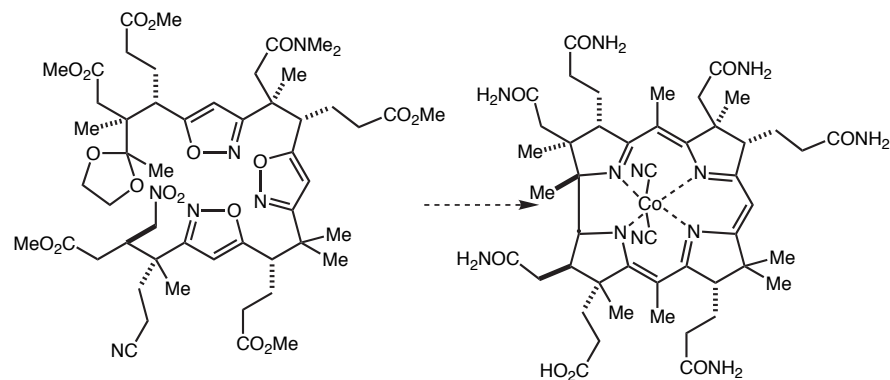
Stevens, R.V.; Christensen, C.G.; Cory, R.M.; Thorsett, E. *JACS* **1975**, *97*, 5940.

Synthesis of Corphins



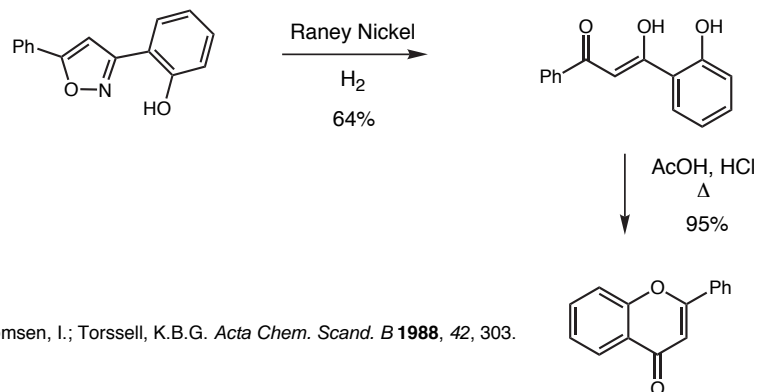
Muller, P.; Farooq, S.; Hardegger, B.; Salmund, W.S.; Eschenmoser, A *ACIEE* **1973**, *12*, 914.

State of the Vitamin B₁₂ Synthesis when Stevens died:

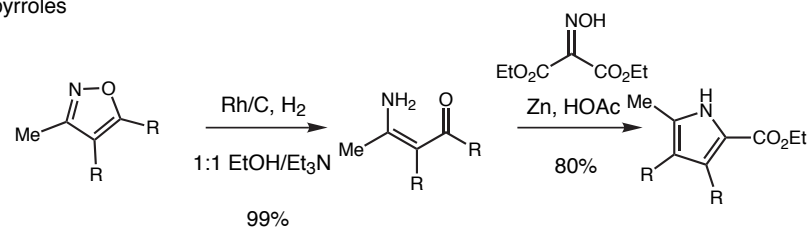


Stevens, R.V.; Beaulieu, N.; Chan, W.H.; Daniewski, A.R; Takeda, T. Waldner, A.; Williard, P.G.; Zutter, U. *JACS* **1986**, *108*, 1039.

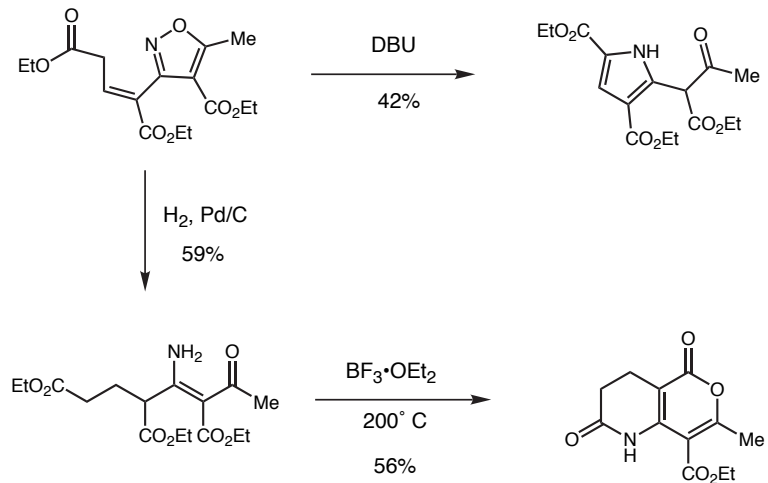
synthesis of flavones



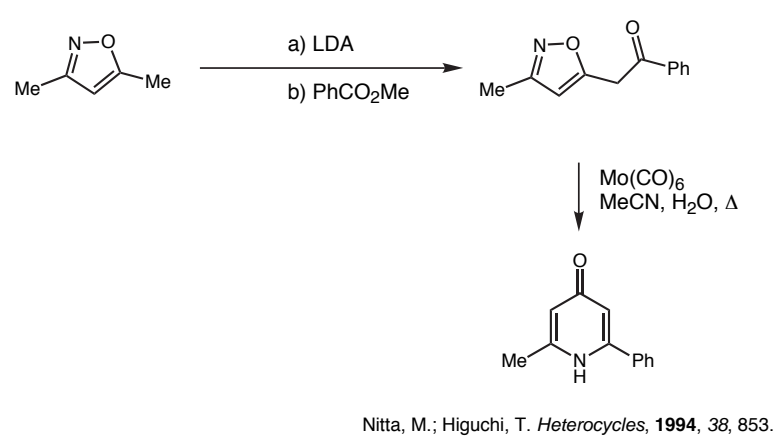
pyrroles



pyrroles and bicyclic lactams

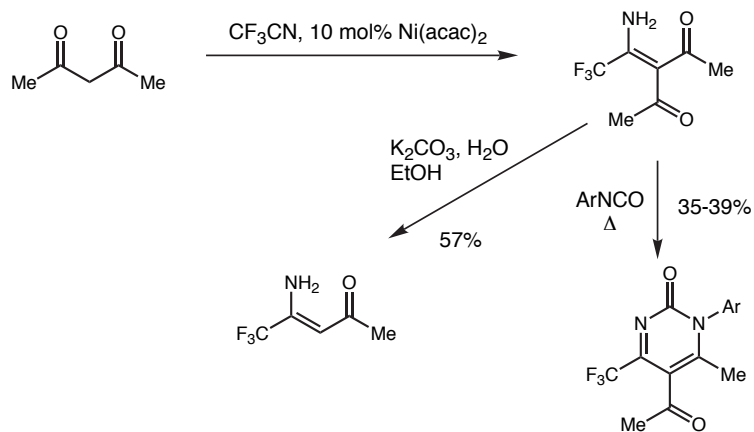


pyridones



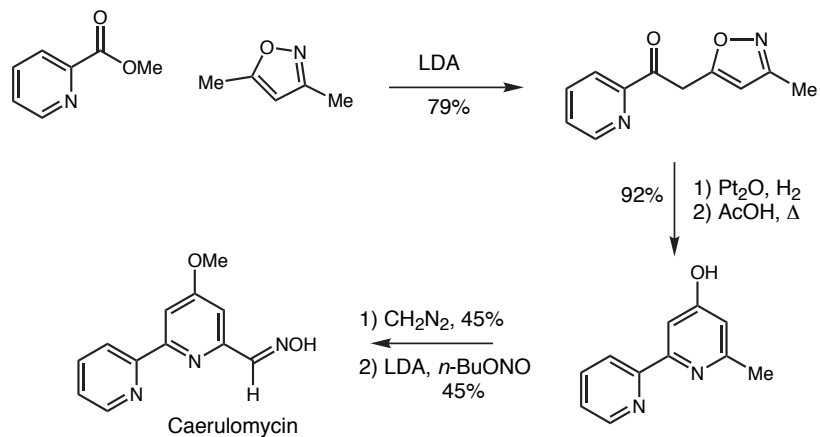
Synthesis of heterocycles

pyrimidinones



Dorokhov, V.A.; Vomkov, A.V.; Vasil'ev, L.S.; Azarevich, O.G.; Gordeev, M.F. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1991**, *11*, 2639.

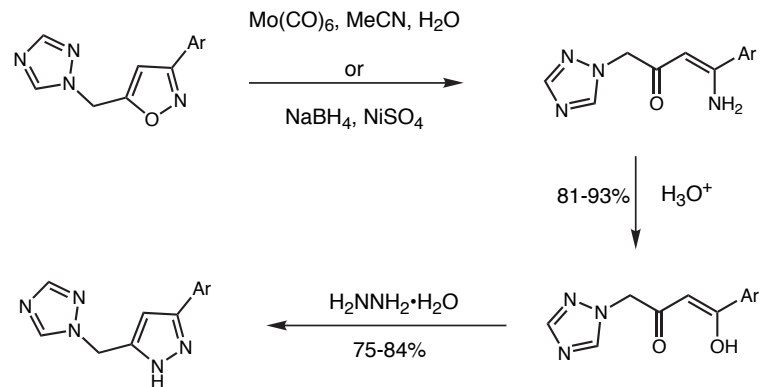
pyridones



Alreja, B.D.; Kattige, L.S.; Lal, B.; deSouza, N.J. *Heterocycles* **1986**, *24*, 1637.

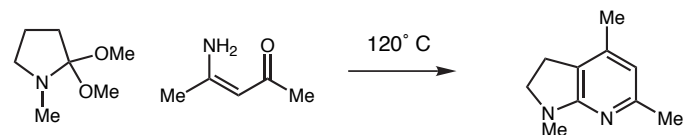
Synthesis of heterocycles

pyrazoles



Skacani, I.; Fiserá, L.; Bartovicová, M.; Varkonda, S.; Hyblova, O.; *Collect. Czech. Chem. Comm.* **1991**, *56*, 1926.

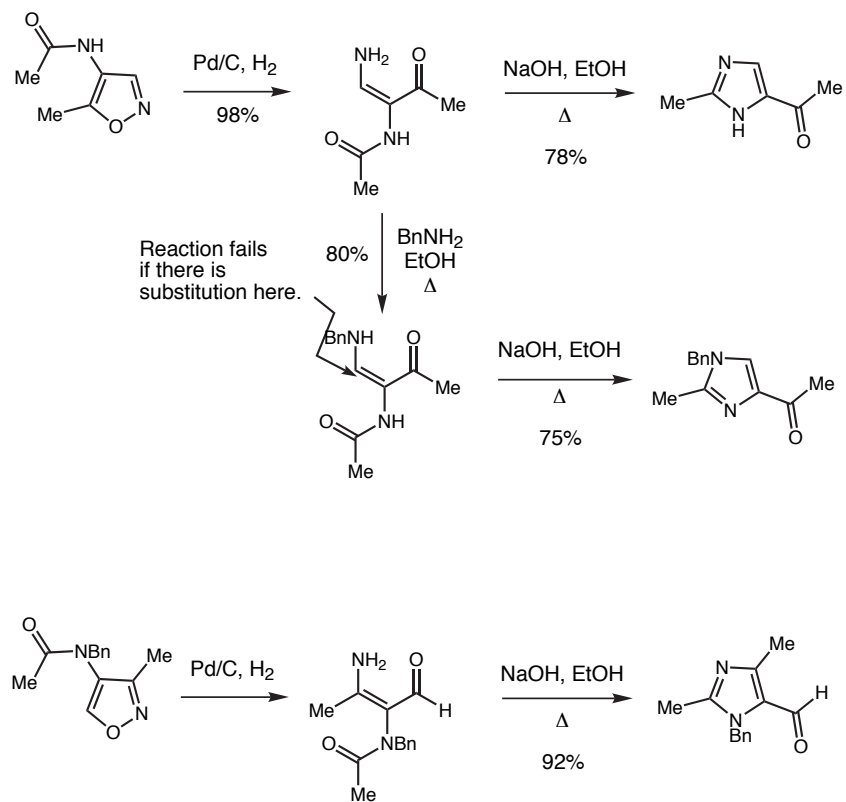
dihydropyrrolopyridines



Jotwani, P.; Singh, J.; Anand, N. *Ind. J. Chem.* **1988**, *27B*, 166.

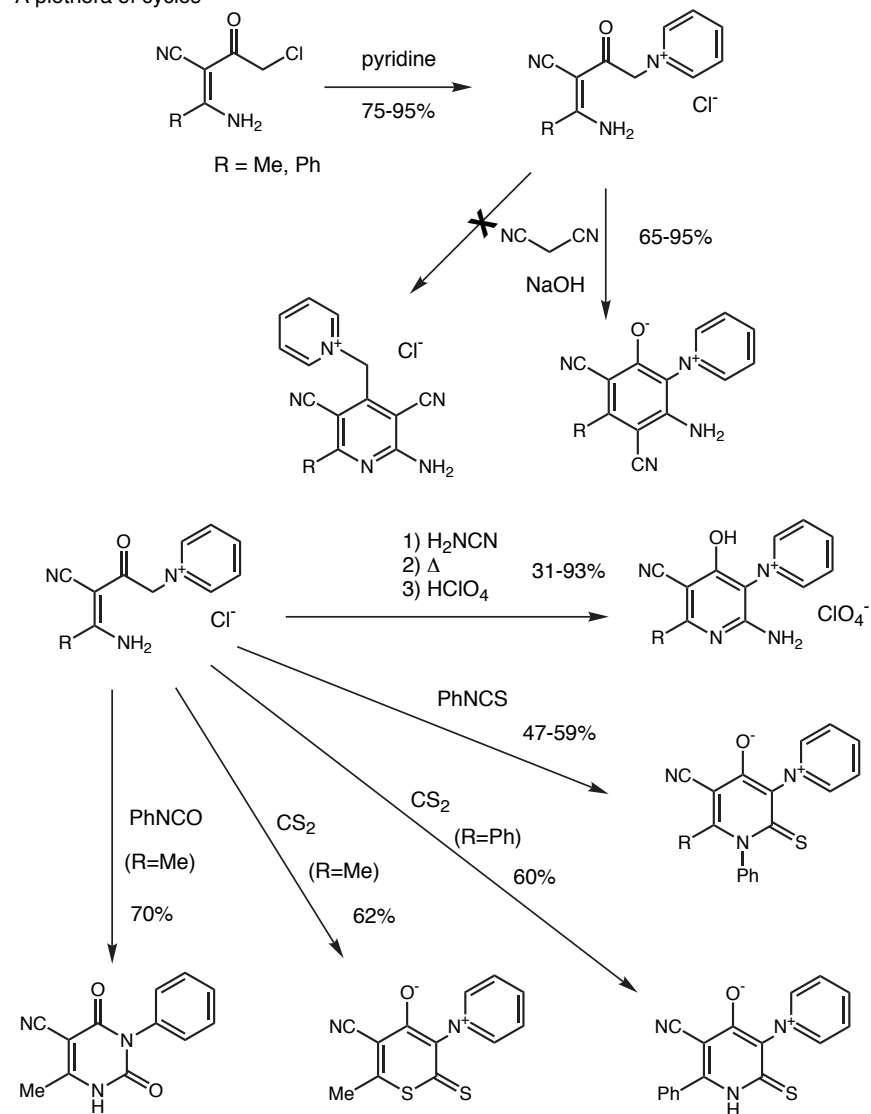
Synthesis of heterocycles

Acyl substituted imidazoles



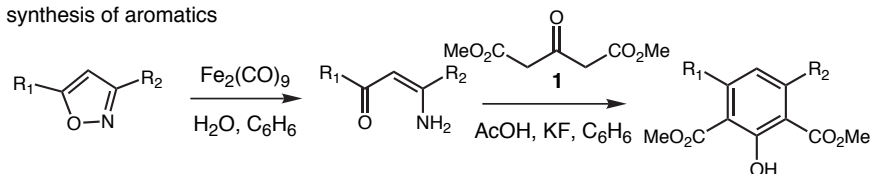
Reiter, L.A. *JOC* **1987**, 52, 2714.

A plethora of cycles

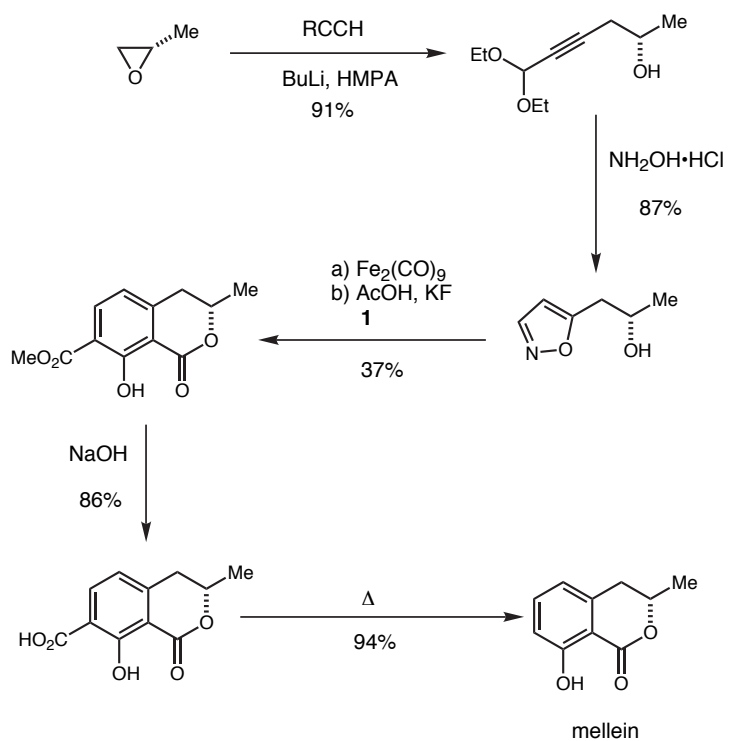


Gewald, K.; Rehwald, M.; Eckert, K.; Schafer, H.; Gruner, M. *Monatsh. Chem.* **1995**, 126, 711.

synthesis of aromatics

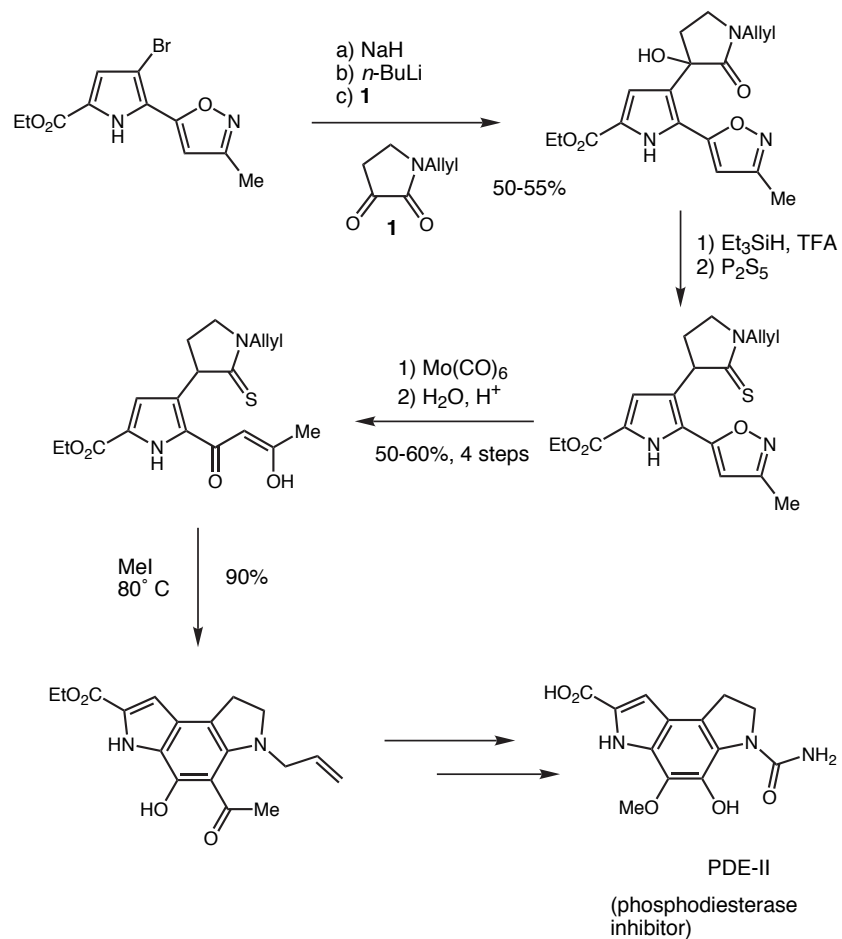


21-51% yields for two steps.



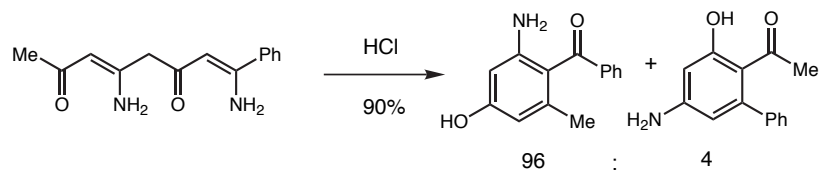
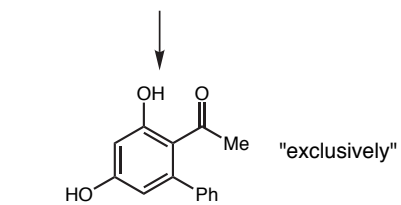
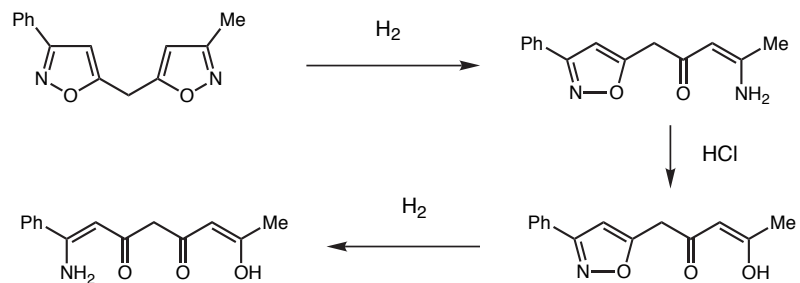
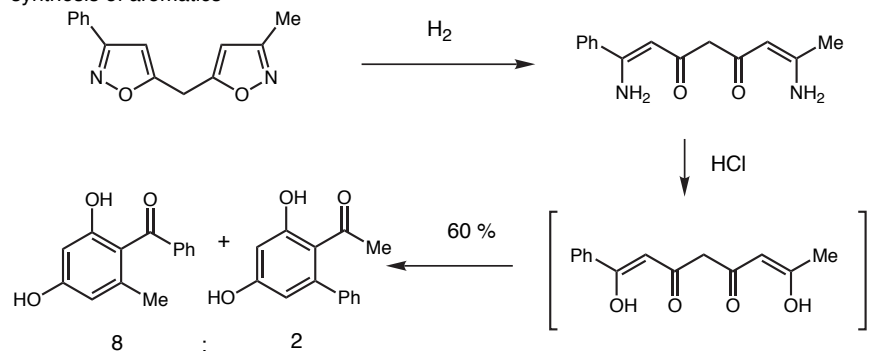
Takeuchi, N.; Goto, K.; Sasaki, Y.; Fujita, T.; Okazake, K.; Kamata, K.; Tobinaga, S. *Heterocycles* **1992**, *33*, 357.

synthesis of PDE-II



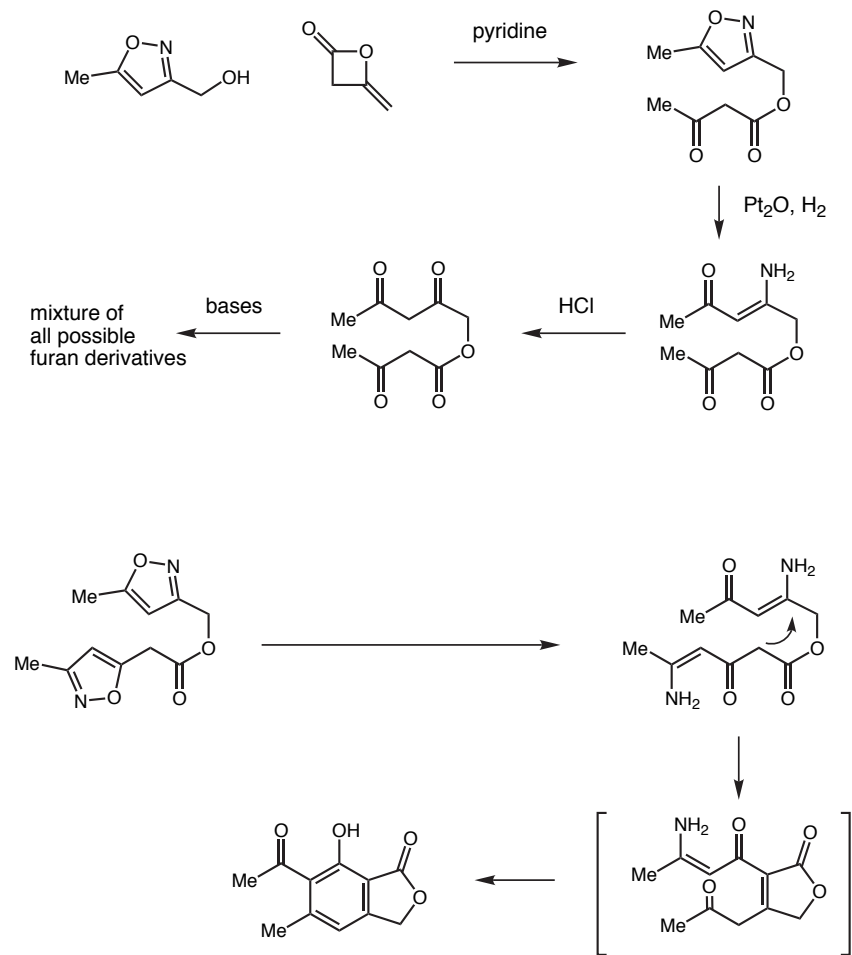
Sundberg, R.J.; Hamilton, G.S.; Laurino, J.P. *JOC* **1988**, *53*, 976.

synthesis of aromatics



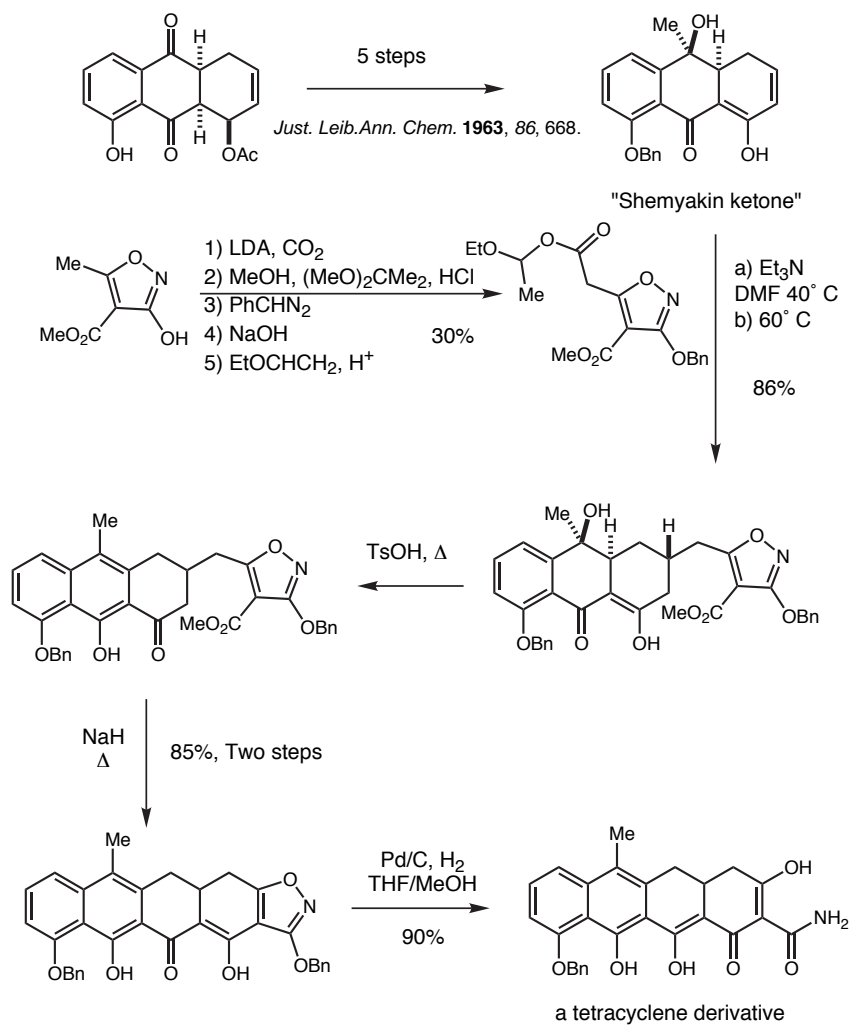
Arruchio, S.; Morrocchi, S.; Ricca, A. *TL* **1974**, 33, 2793.

synthesis of aromatics



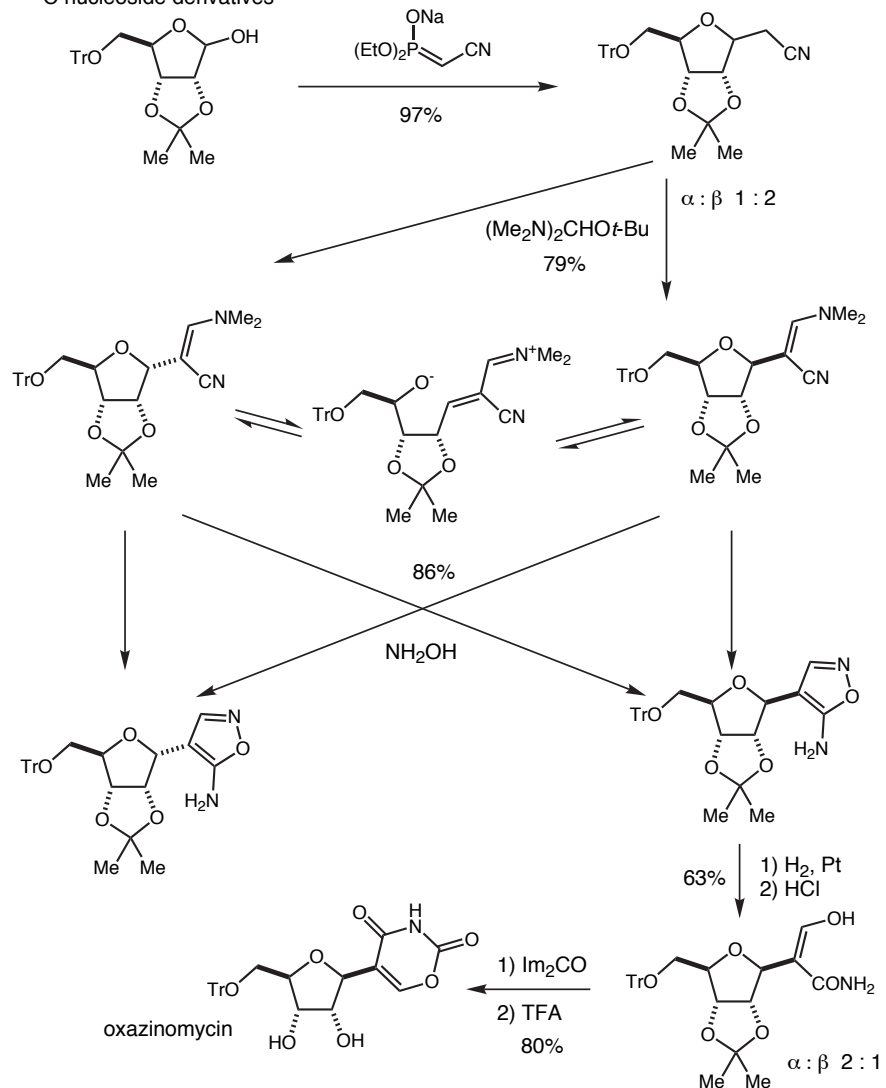
Auricchio, S.; Ricca, A.; Vajna dePava, O. *Gaz. Chim. Ital.* **1980**, 110, 567.

An approach to tetracyclenes



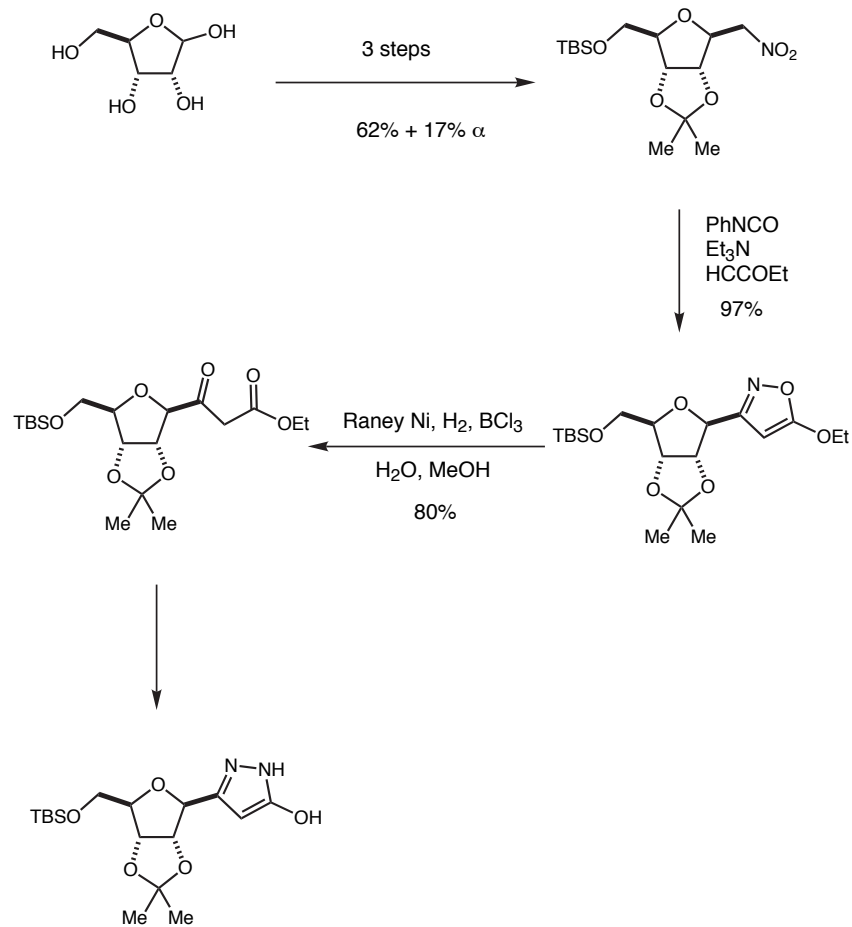
Stork, G.; Hagedorn, A.A. *JACS* **1978**, *100*, 3609.

C nucleoside derivatives



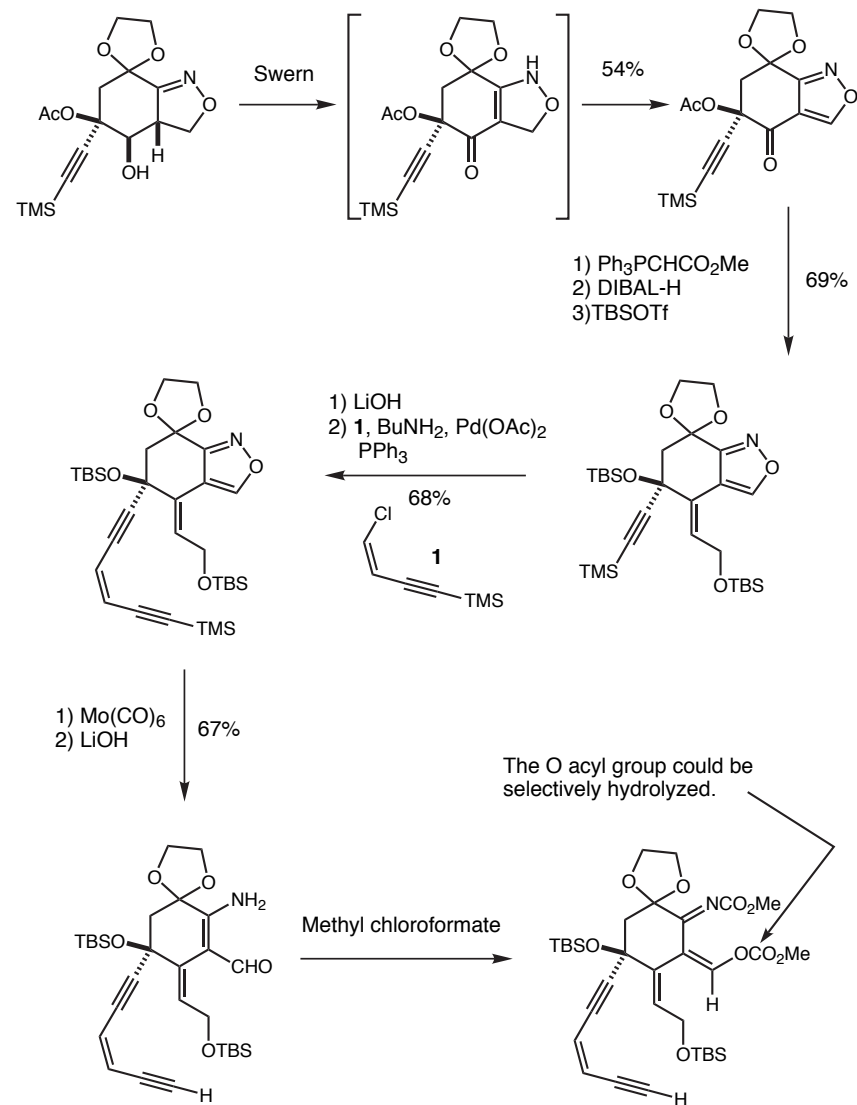
DeBernardo, S.; Weigle, M. *JOC* **1977**, *42*, 109.

C nucleoside derivatives



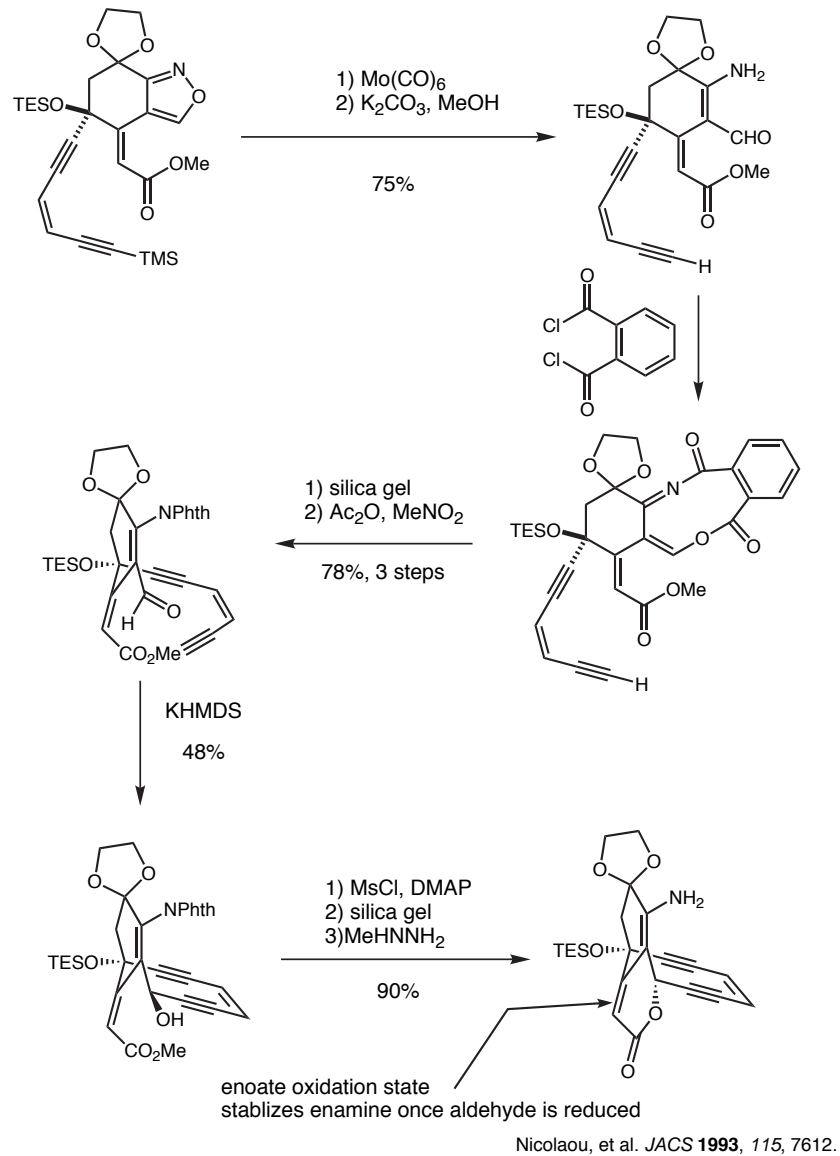
Kozikowski, A.P.; Goldstein, S. *JOC* **1983**, *48*, 1141.

Calicheamicinone



Nicolaou, et al. *JACS* **1993**, *115*, 7612.

Calicheamicinone



Calicheamicinone

