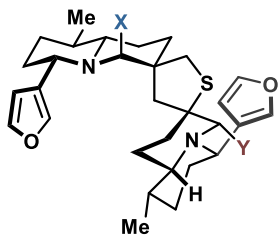
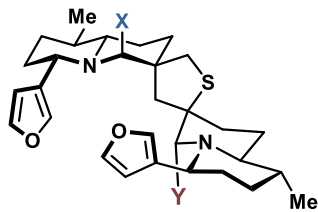


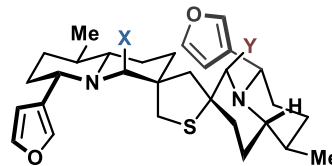
The stereoisomeric nuphar thiaspirane alkaloids:



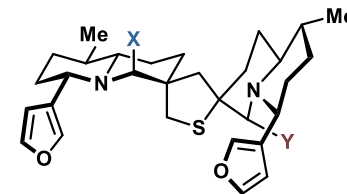
thibinupharidine series



thinuplutine series

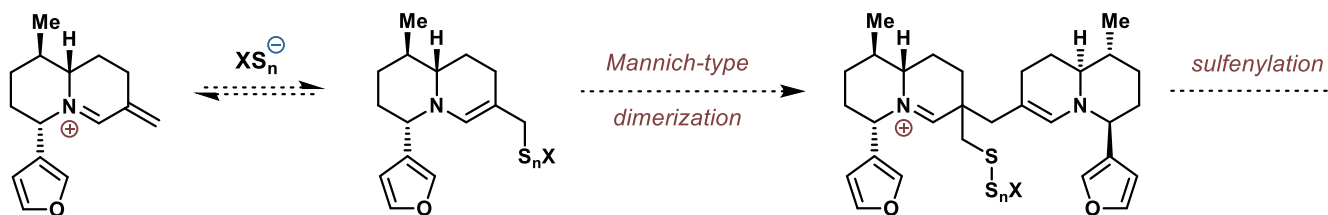


neothiobinupharidine series

neothionuplutine series  
(not isolated)

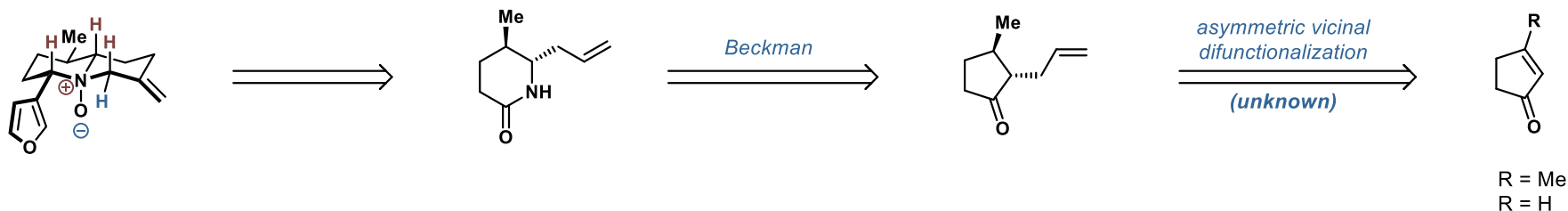
X,Y = OH; X,Y = H; X = H, Y = OH; X = OH, Y = H

LaLonde Hypothesis: a stereochemical mystery:

**distribution in *N. pumilim*:**

thibinupharidine:	87%
thinuplutine:	8%
neothiobinupharidine:	5%
neothionuplutine:	0%

retrosynthesis:



J. Am. Chem. Soc. 2013, 135, 1209.

## synthesis of (-)-neothiobinupharidine:

