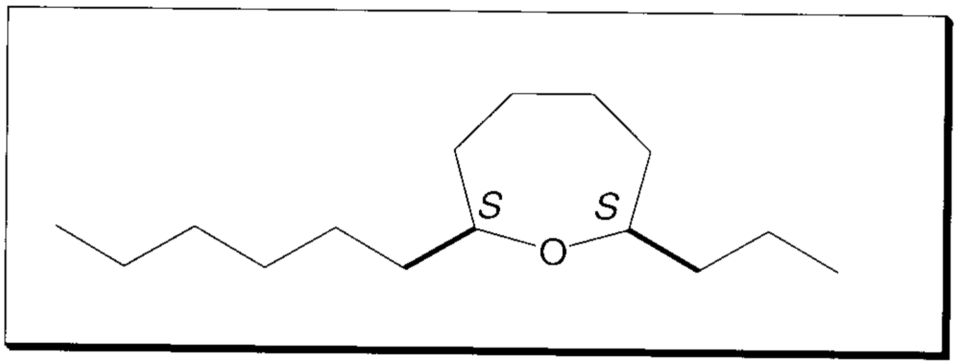
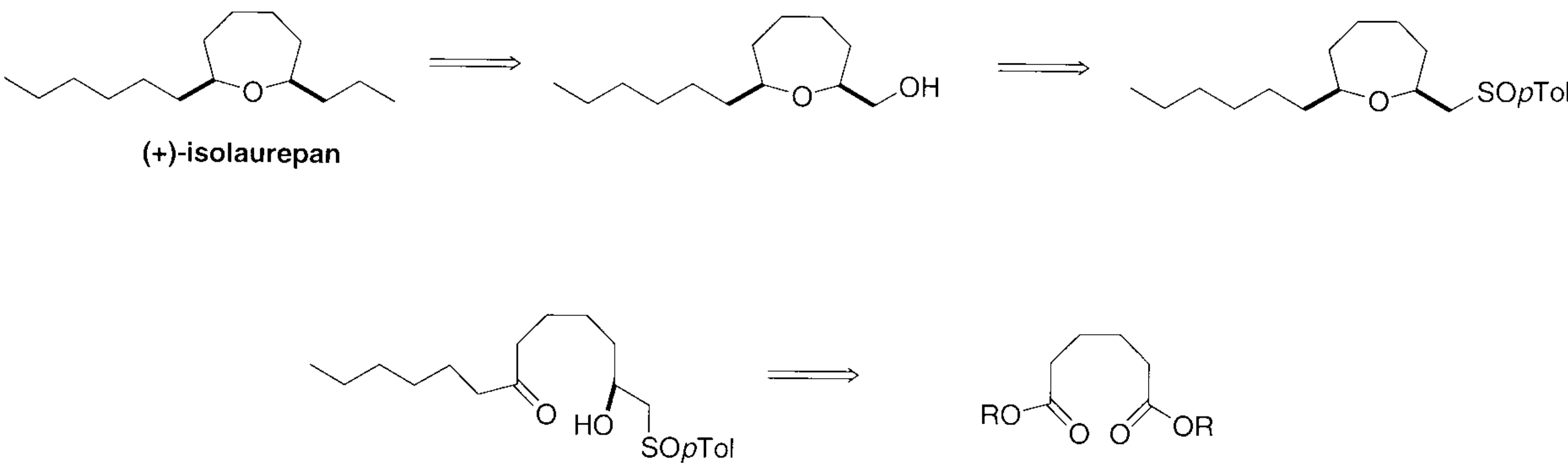
T. Hopkins
1/10/04

Enantioselective Access to 2,7-Cis-Disubstituted Oxepanes: Formal Synthesis of (+)-Isolaurepan



Carreno, M. C.; Des Mazery, R.; Urbano, A.; Colobert, F.;Solladie, G. *Org. Lett.* **ASAP**

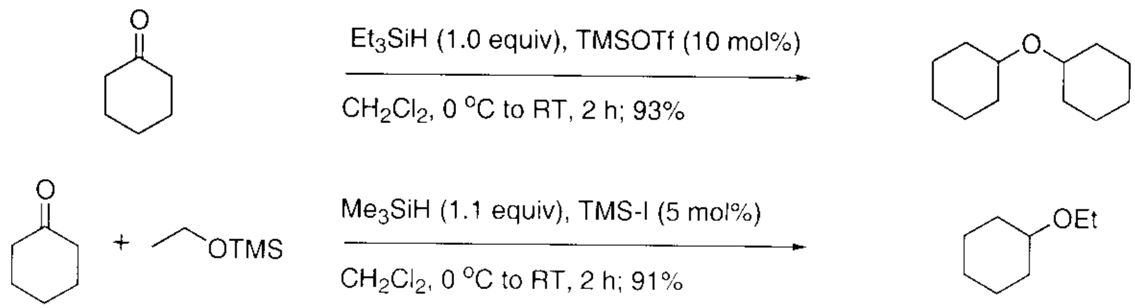
Retrosynthetic Analysis of (+)-Isolaurepan



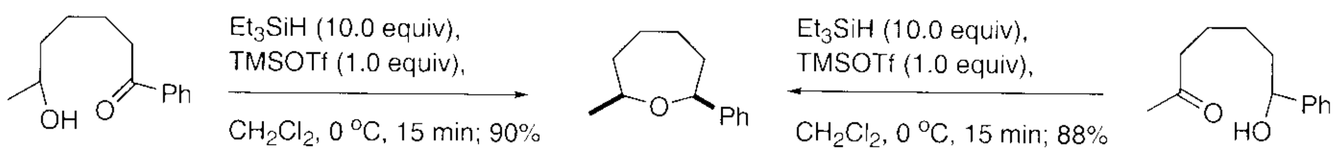
(+)-isolaurepan

Carreno, M. C.; Des Mazery, R.; Urbano, A.; Colobert, F.;Solladie, G. *Org. Lett.* **ASAP**

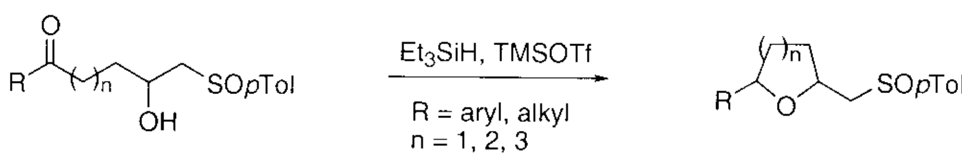
Reductive Etherification of Carbonyl Compounds



Sassaman, M. B.; Kotian, K. D.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.* **1987**, *52*, 4314.

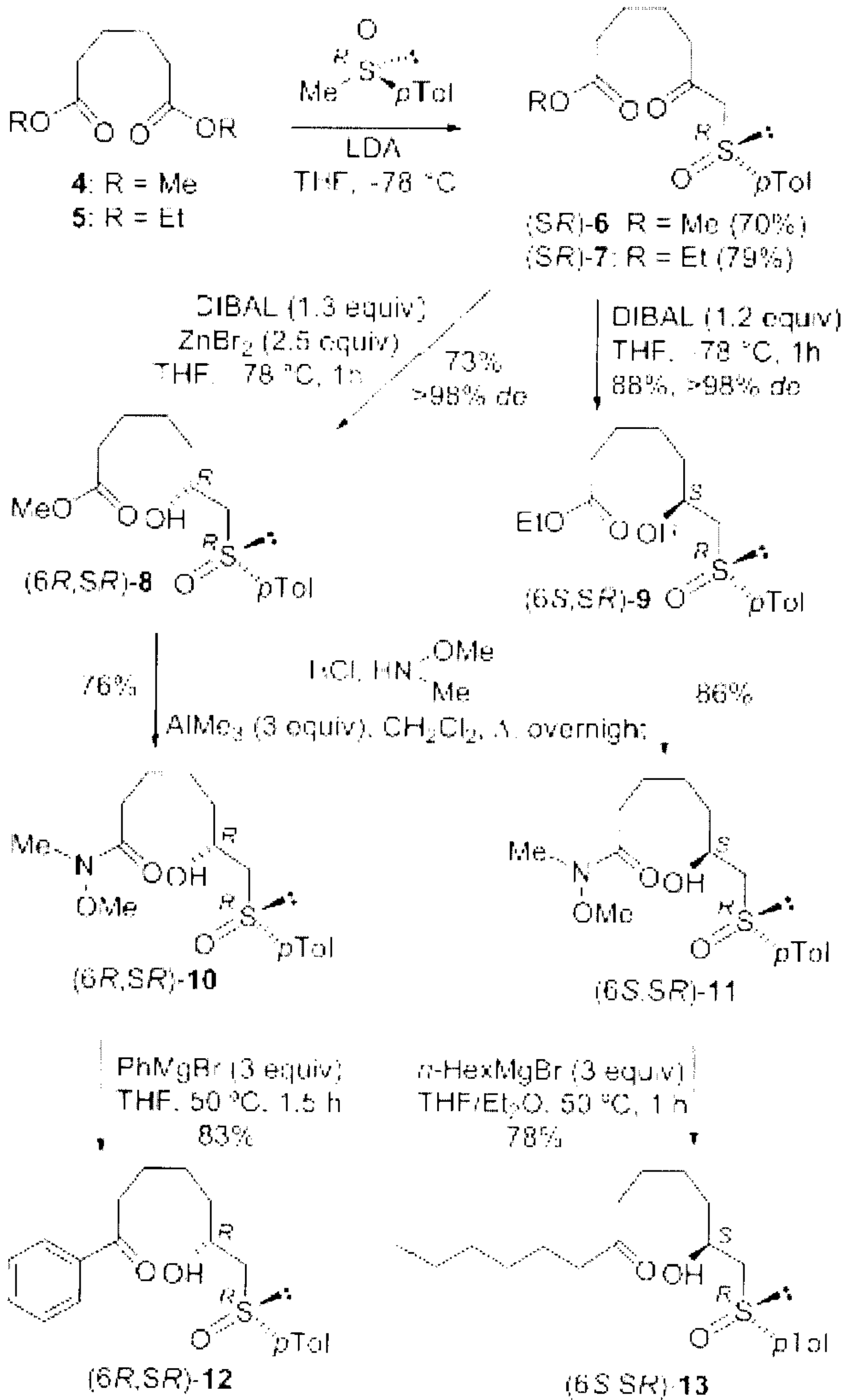


Nicolaou, K. C.; Hwang, C.-K.; Nugiel, D. A. *J. Am.Chem. Soc.* **1989**, *111*, 4136.
Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E.; Nugiel, D. A.; Abe, Y.; Bal Reddy, K.; DeFrees, S. A.; Reddy, D. R.; Awartani, R. A.; Conley, S. R.; Rutjes, F. P. J. T.; Theodorakis, E. A. *J. Am. Chem. Soc.* **1995**, *117*, 10227. (Brevetoxin B)



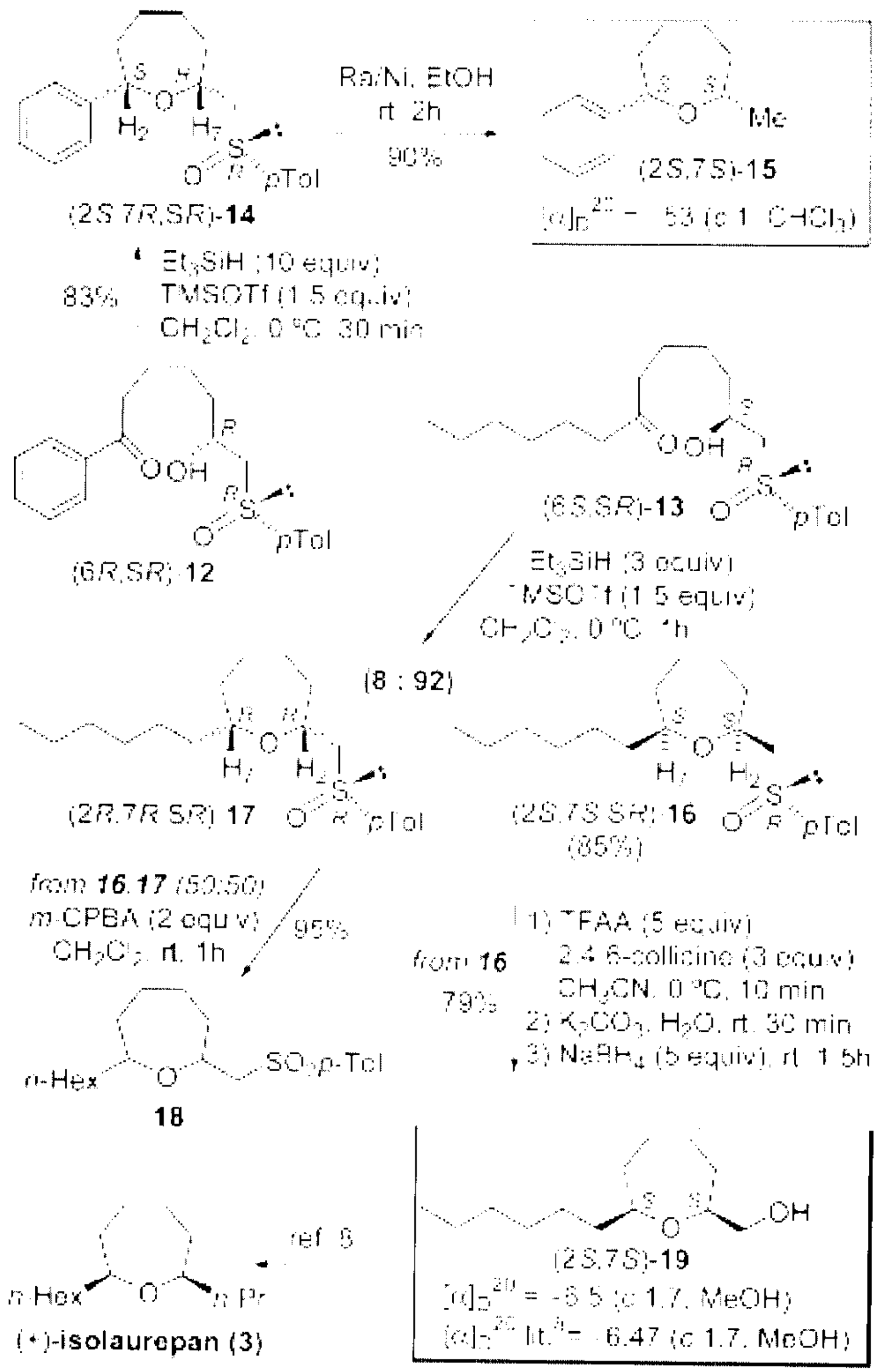
Carreno, M. C.; Des Mazery, R.; Urbano, A.; Colobert, F.; Solladie, G. *J. Org. Chem.* **2003**, *68*, 7779.

Formal Synthesis of (+)-Isolaurepan



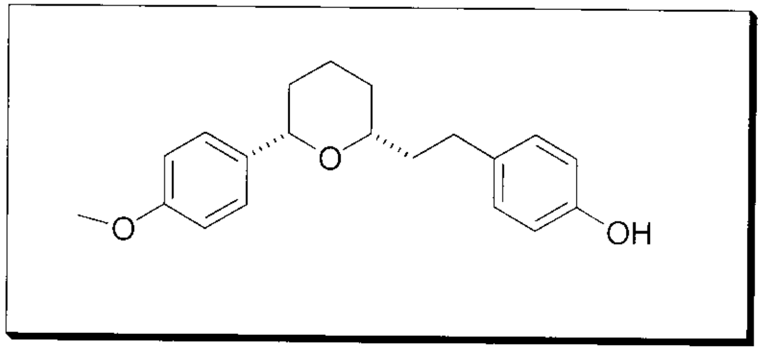
Carreno, M. C.; Des Mazery, R.; Urbano, A.; Colobert, F.;Solladie, G. *Org. Lett.* **ASAP**

Formal Synthesis of (+)-Isolaurepan



Carreno, M. C.; Des Mazery, R.; Urbano, A.; Colobert, F.;Solladie, G. *Org. Lett.* **ASAP**

(-)-Centrolobine



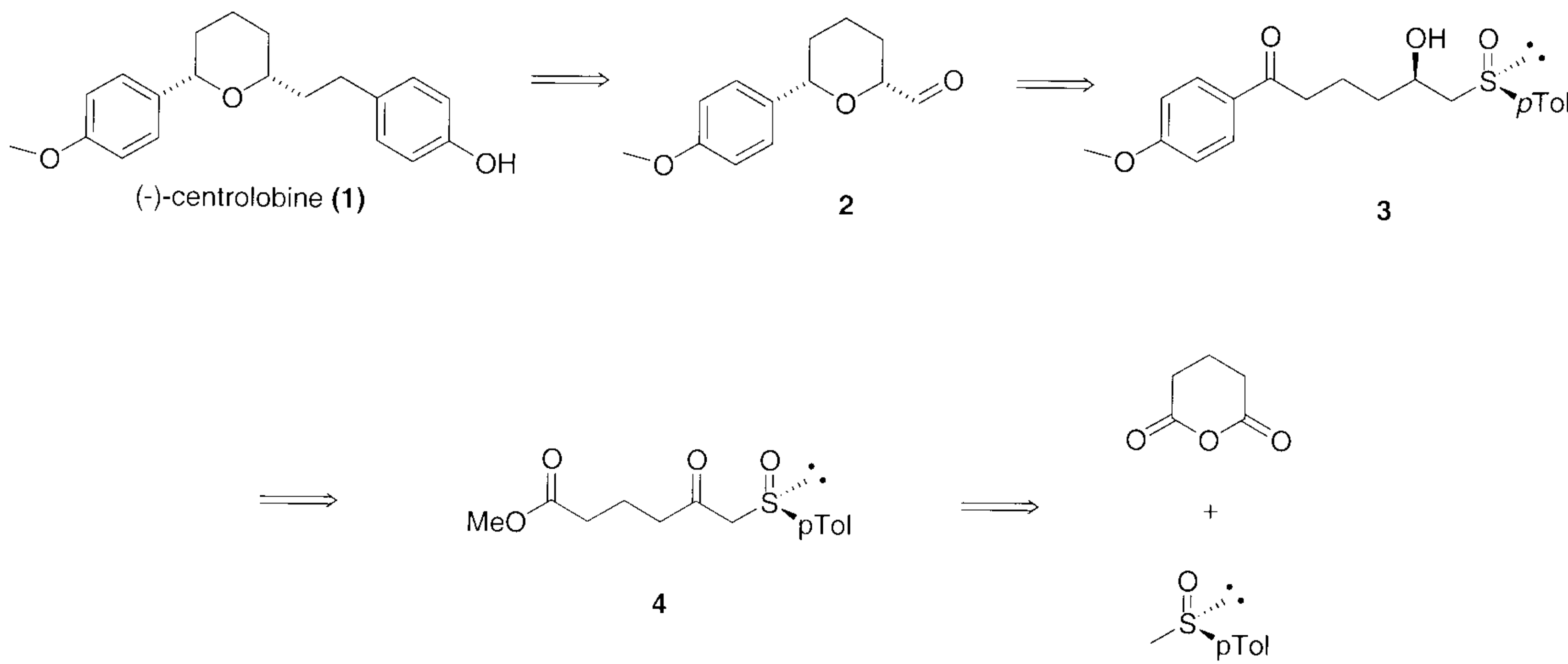
*isolated from the heartwood of *Centrolobium robustum* and from the stem of *Brosinum potabile*

*structure elucidation by total synthesis of the racemic methyl ether-1964

*revision of absolute configuration-2002

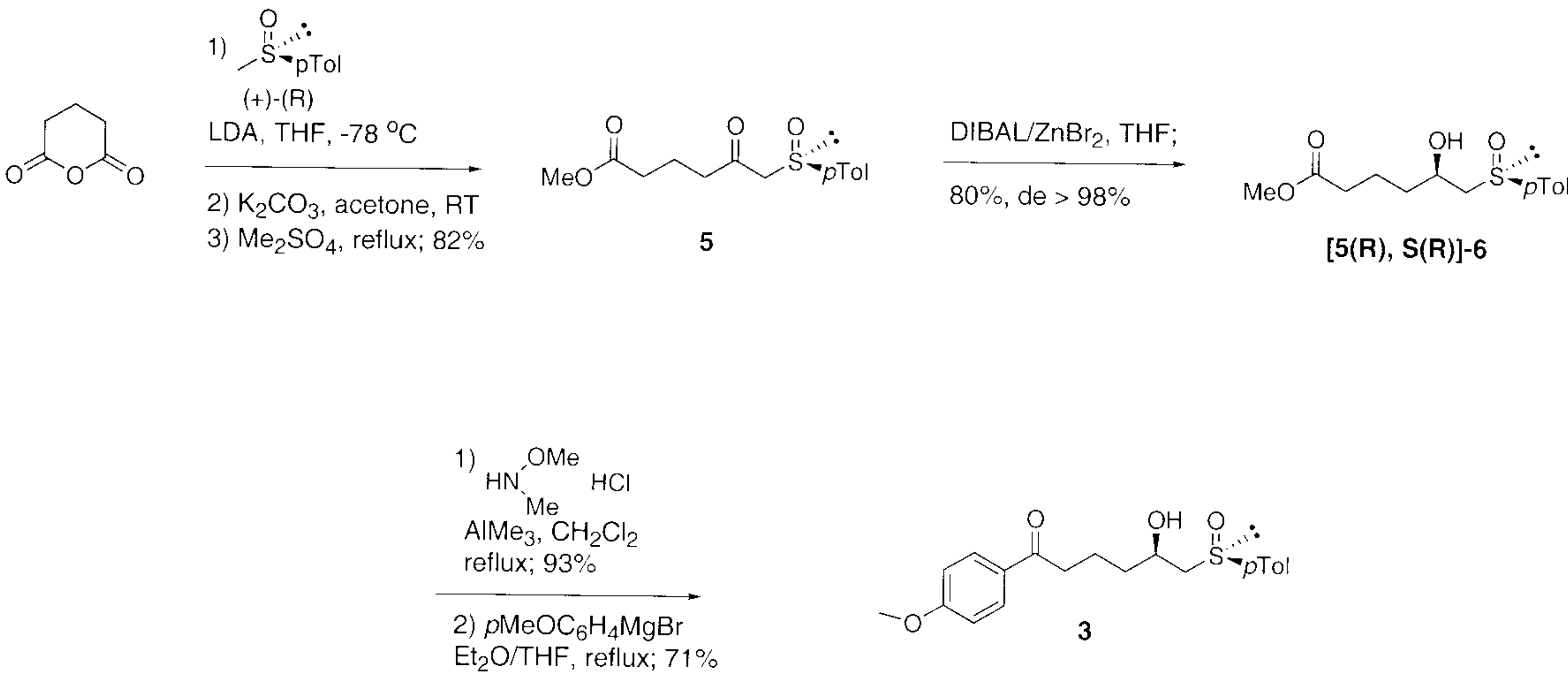
Isolation: De Albuquerque, I. L.; Galeffi, C.; Casinov, C. G.; Marini-Bettolo, G. B. *Gazz. Chim. Ital.* **1964**, 287.
Galeffi, C.; Casinovi, C. G.; Marini-Bettolo, G. B. *Gazz. Chim. Ital.* **1965**, 95.
Aragao Craveiro, A.; da Costa Prado, A.; Gottleib, O. R.; Welerson de Albuquerque, P. C. *Phytochemistry* **1970**, *9*, 1869.
Alcantara, A. F. de C.; Souza, M. R.; Pilo-Veloso, D. *Fitoterapia* **2000**, *71*, 613.

Retrosynthetic Analysis of (-)-Centrolobine



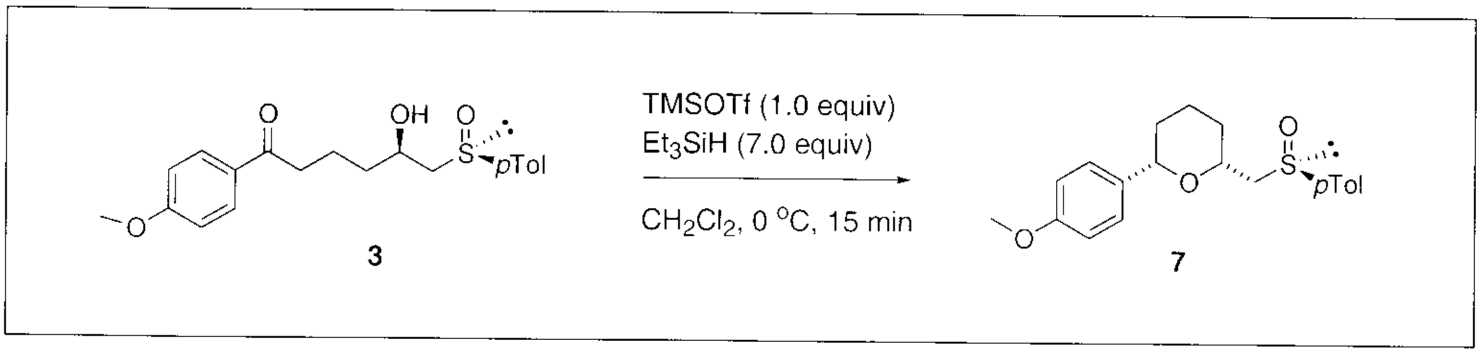
Colobert, F.; Des Mazery, R.; Solladie, G.; Carreno, M. C. *Org. Lett.* **2002**, *4*, 1723.

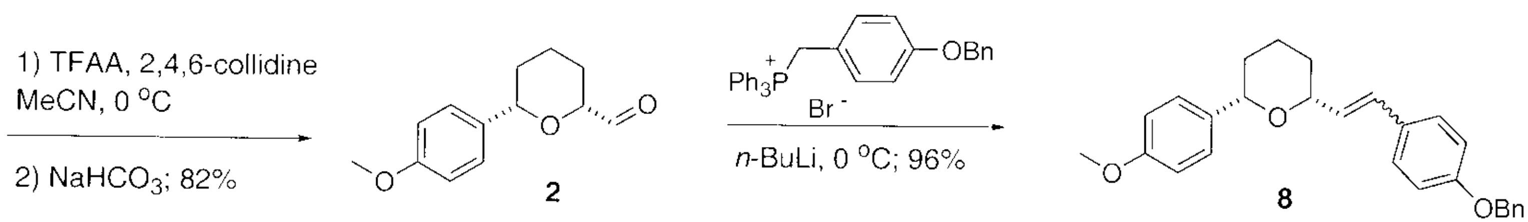
First Enantioselective Total Synthesis of (-)-Centrolobine

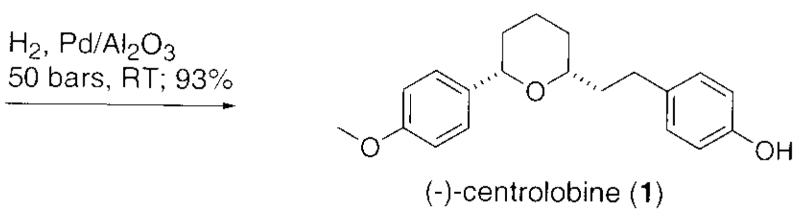


Colobert, F.; Des Mazery, R.; Solladie, G.; Carreno, M. C. *Org. Lett.* **2002**, *4*, 1723.

Completion of the Total Synthesis of (-)-Centrolobine



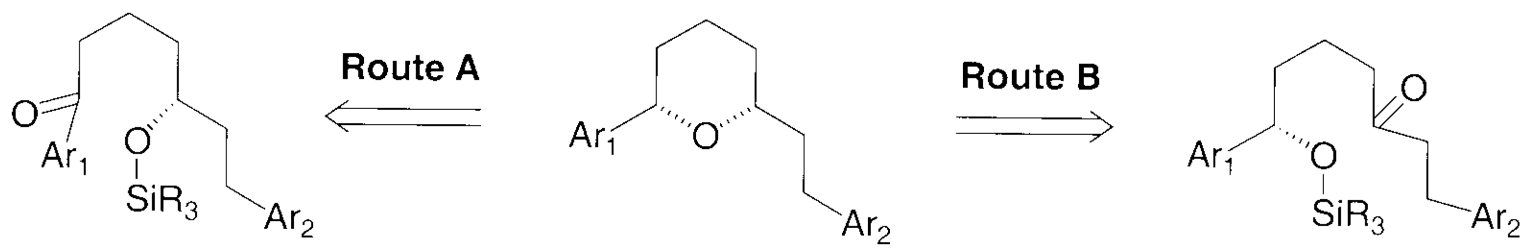




9 linear steps
26% overall yield from glutaric anhydride

Colobert, F.; Des Mazery, R.; Solladie, G.; Carreno, M. C. *Org. Lett.* **2002**, *4*, 1723.

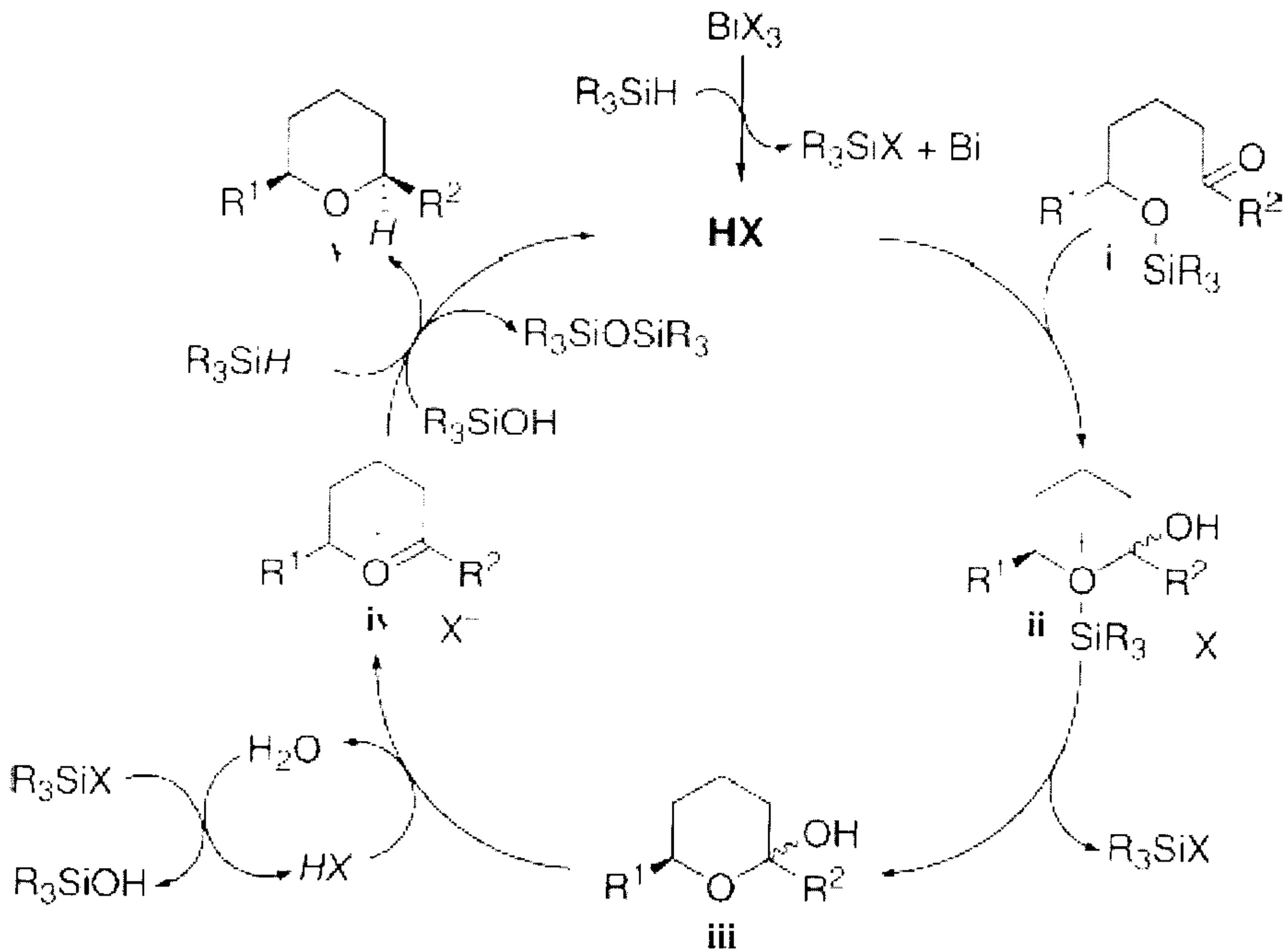
Retrosynthetic Analysis of (-)-Centrolobine: Potential Reductive Etherification Reactions



(-)-centrolobine (**1**)

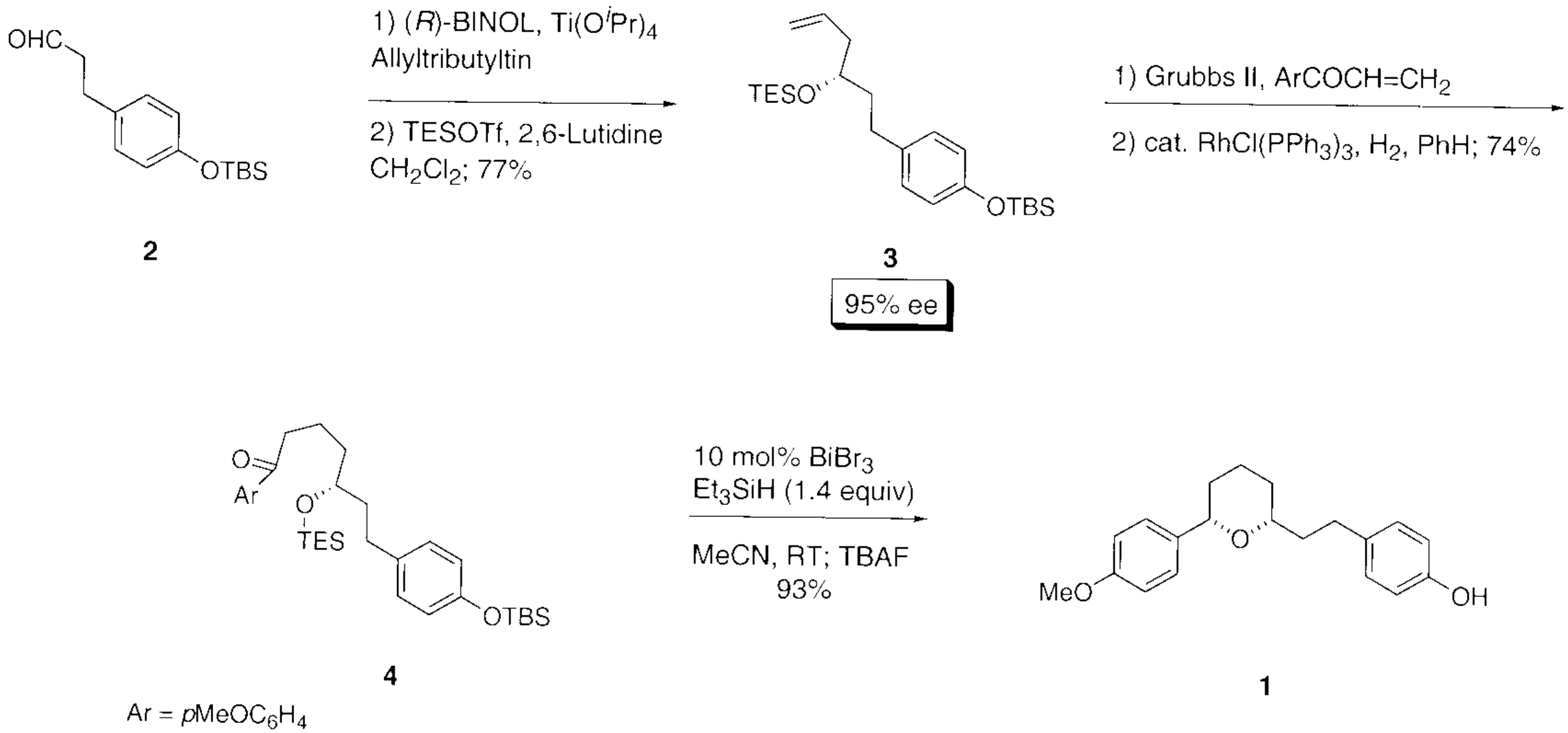
Evans, P. A.; Cui, J.; Gharpure, S. J. *Org. Lett.* **2003**, *5*, 3883.

Proposed Catalytic Cycle for the Reductive Etherification Process



Evans, P. A.; Cui, J.; Gharpure, S. J. *Org. Lett.* **2003**, *5*, 3883.

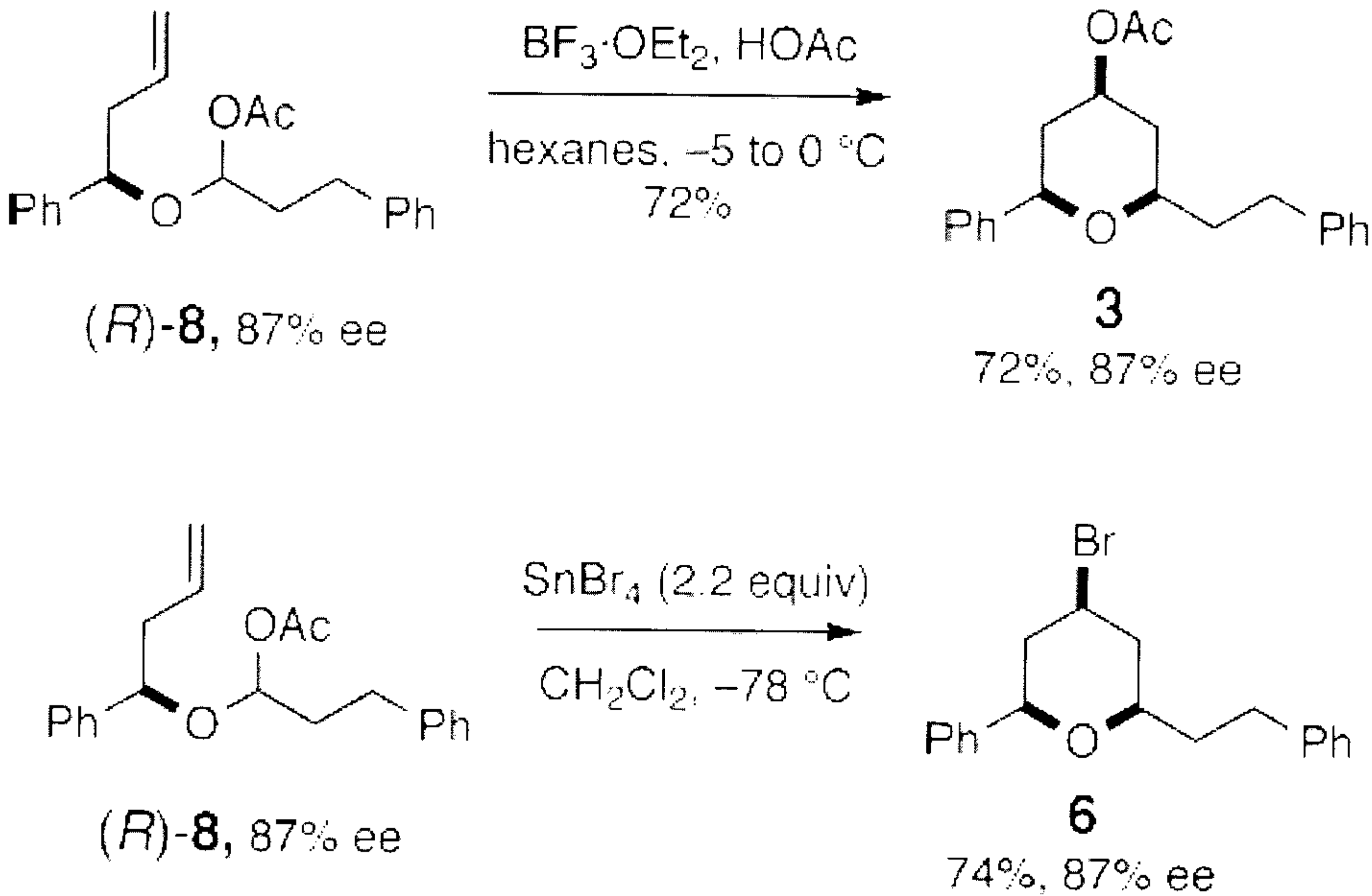
Stereoselective Synthesis of (-)-Centrolobine



5 linear steps
53% overall yield
from 2

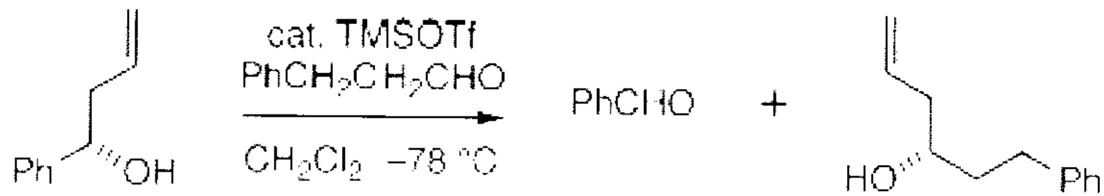
Evans, P. A.; Cui, J.; Gharpure, S. J. *Org. Lett.* **2003**, *5*, 3883.

Prins Cyclizations with Acetoxy Ethers



Marumoto, S.; Jaber, J. J.; Vitale, J. P.; Rychnovsky, S. D. *Org. Lett.* **2002**, *4*, 3919.

Partial Racemization in a 2-Oxonia Cope Allyl Transfer Reaction



(*S*)-**1**, 91% ee (*S*)-**2**

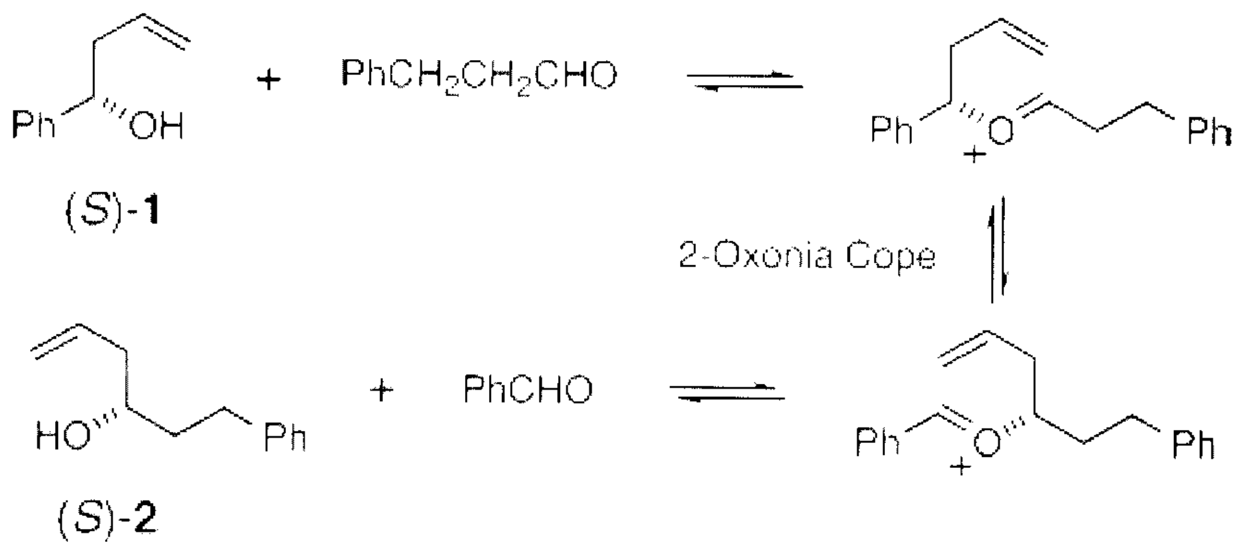
entry[a]	equiv of (*S*)-**1**	equiv of aldehyde	% ee of (*S*)-**2**[b]
1	1.0	0.9	20
2	1.5	1.0	63
3	1.5	1.0	60[c]
4	3.0	1.0	68[c]

[a] Yields were not determined. All of the aldehyde was consumed within minutes. [b] The ees were determined by GC analysis on a Chiraldex γ-TA column. [c] In these reactions, 1.5 equiv of TMSOTf was used.

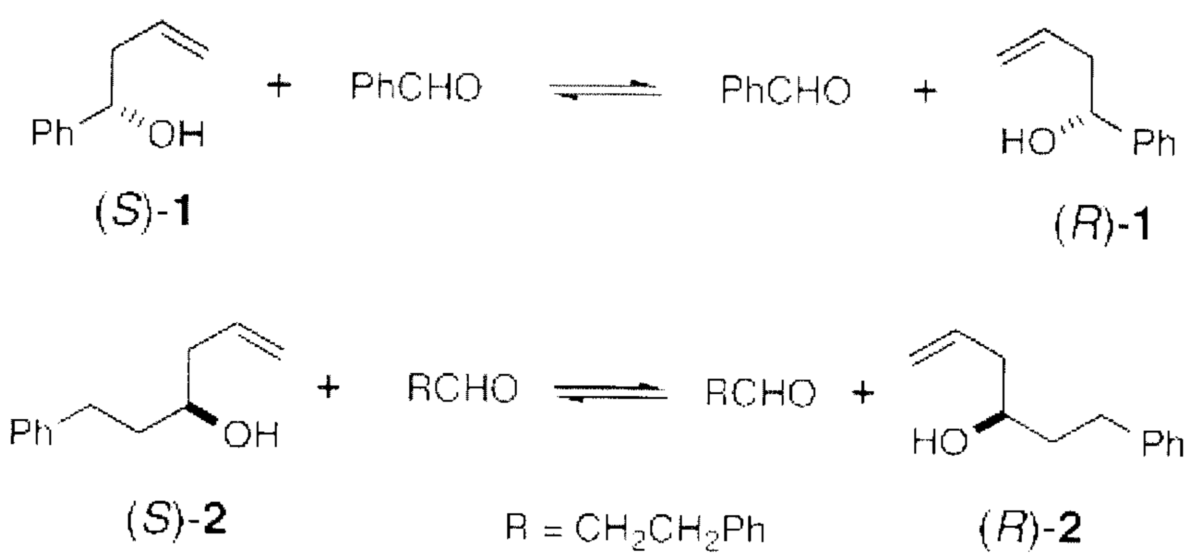
Marumoto, S.; Jaber, J. J.; Vitale, J. P.; Rychnovsky, S. D. *Org. Lett.* **2002**, *4*, 3919.

Mechanism of Allyl Transfer and Racemization

Mechanism of allyl transfer reaction:

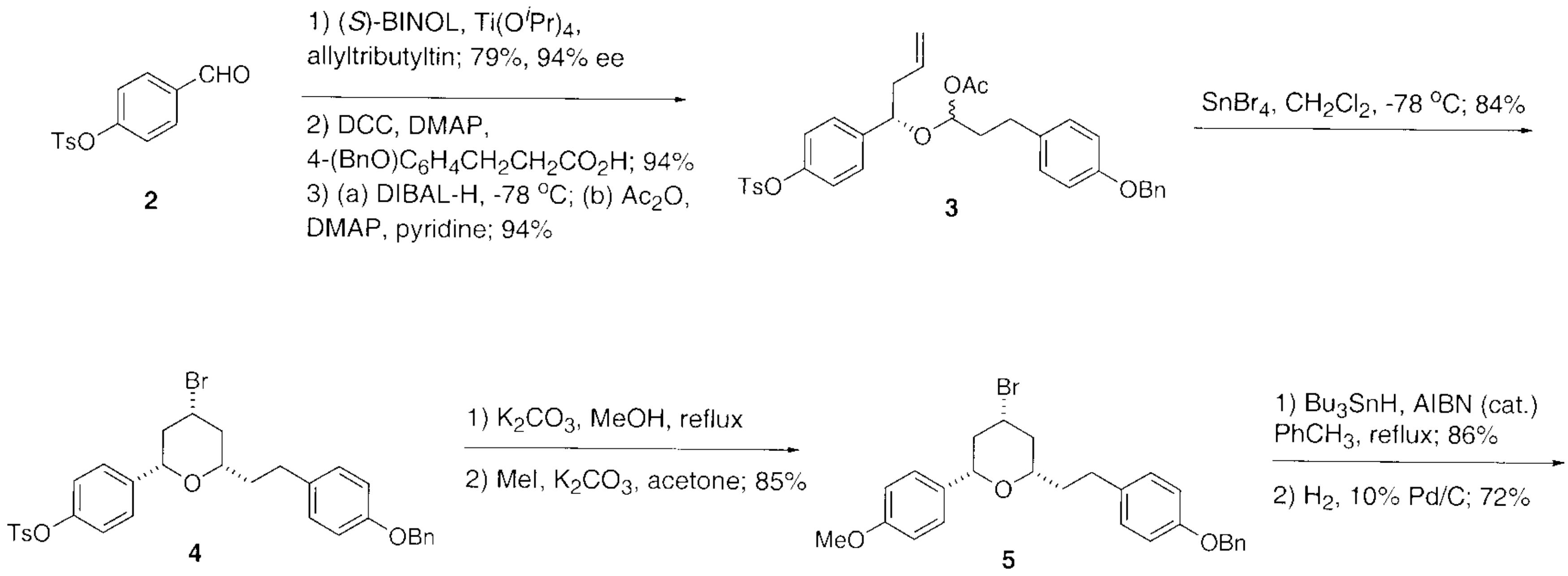


Racemization in *symmetric* 2-oxonia Cope rearrangements:



Marumoto, S.; Jaber, J. J.; Vitale, J. P.; Rychnovsky, S. D. *Org. Lett.* **2002**, *4*, 3919.

Synthesis of (-)-Centrolobine Via a Segment-Coupling Prins Cyclization Reaction

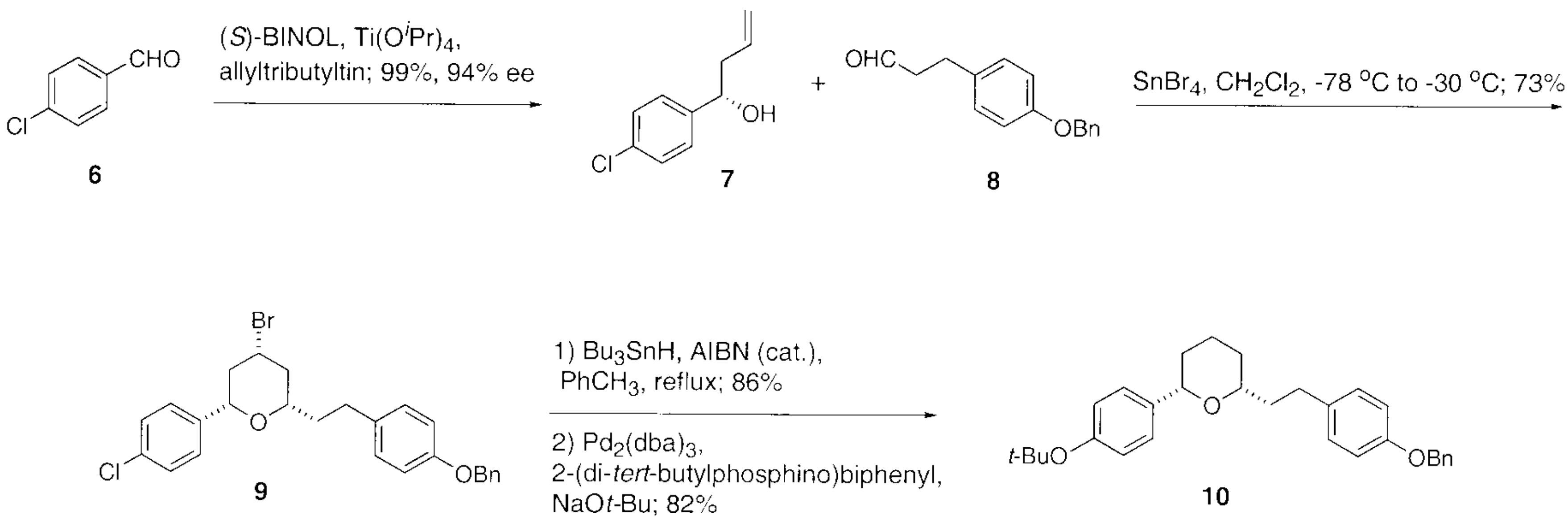


(-)-Centrolobine (**1**)

8 linear steps
30.5% overall
yield from 2

Marumoto, S.; Jaber, J. J.; Vitale, J. P.; Rychnovsky, S. D. *Org. Lett.* **2002**, *4*, 3919.

Synthesis of (-)-Centrolobine Via a Direct Alcohol-Aldehyde Prins Cyclization Reaction



1) TFA, CH_2Cl_2
2) MeI, K_2CO_3, acetone
3) H_2, 10% Pd/C; 57%

→ (-)-Centrolobine (**1**)

7 linear steps
30% overall
yield from 6

Marumoto, S.; Jaber, J. J.; Vitale, J. P.; Rychnovsky, S. D. *Org. Lett.* **2002**, *4*, 3919.