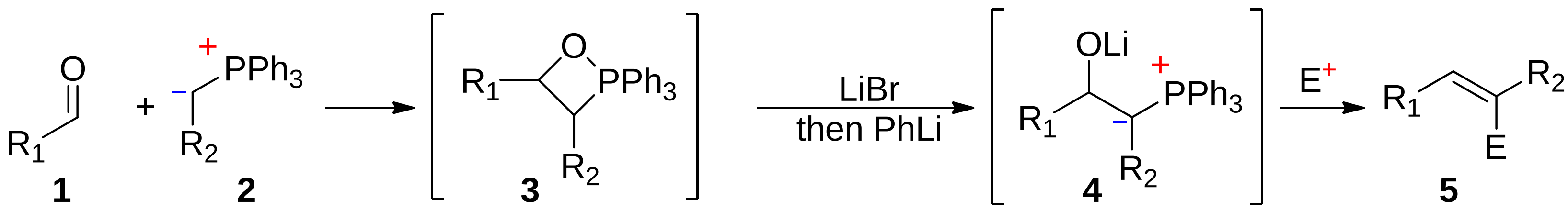
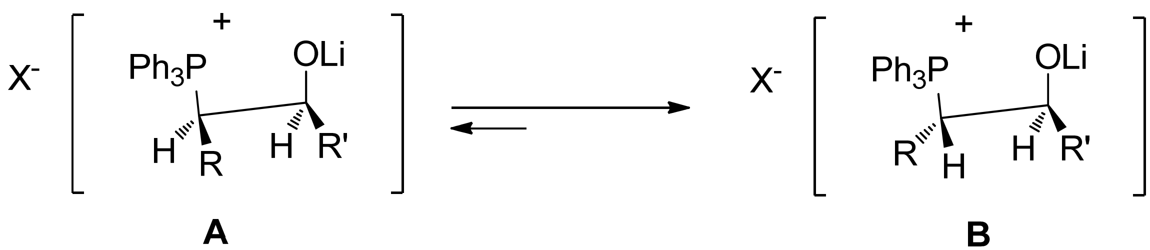
Convergent Synthesis of Trisubstituted Z-Allylic Esters by Wittig-Schlosser Reaction

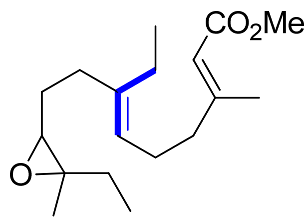
Hodgson, D.M.; Arif, T. *Org. Lett.* **2010**, 12, 4202
University of Oxford

Wittig-Schlosser Reaction

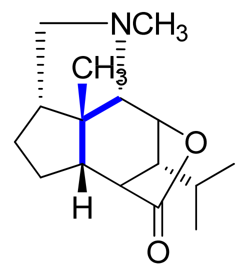




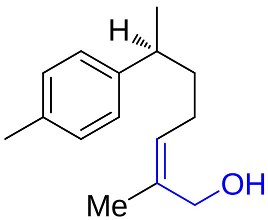
Natural Products through Wittig-Schlosser Reaction



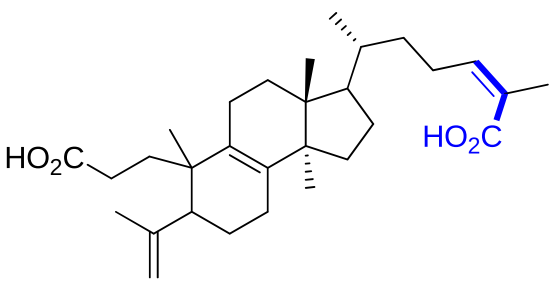
Cecropia juvenile hormone
46% yield
Corey, E.J., Yamamoto, H.
JACS, **1970**, *92*, 6637



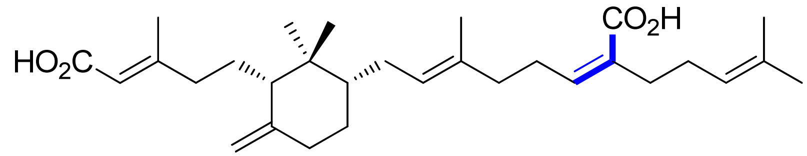
Dendrobine
40% yield
Borch, R.F.; et al
JACS, **1977**, *99*, 1612



(+)-Nuciferol
42% yield
Takano, S. et al
Tetrahedron Lett. **1982**, *23*, 5567



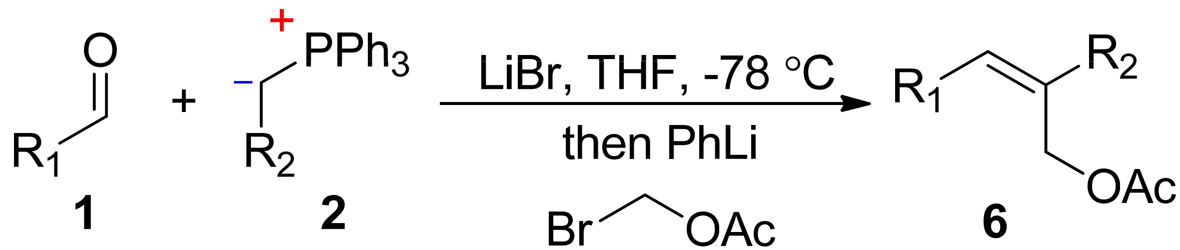
manwuweizic acid
54% yield
Liu, J.-S.; Tao, Y.
Tetrahedron **1992**, *48*, 6793



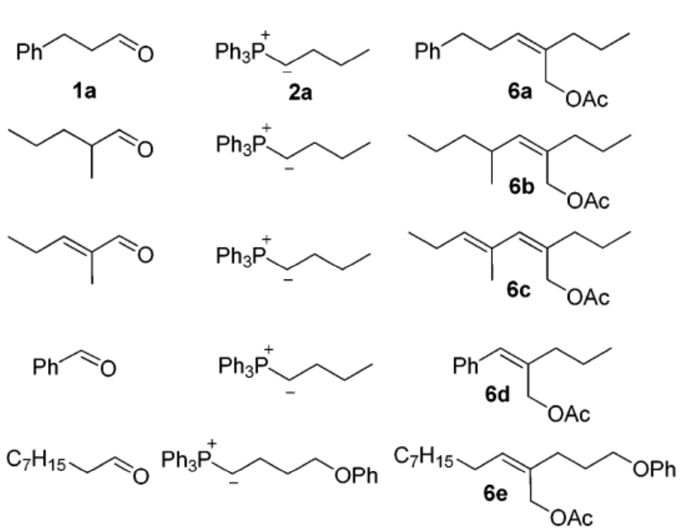
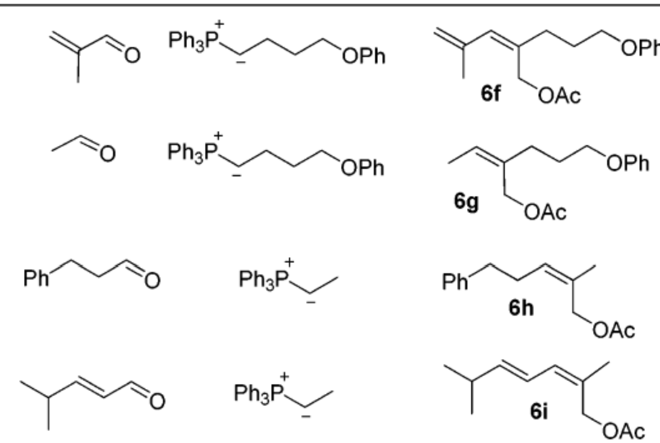
Mispyric acid
22% yield
Takikawa, H, et al
Org. Biomol. Chem. **2004**, *2*, 2236

- Yields are indicated for Wittig-Schlosser reaction only

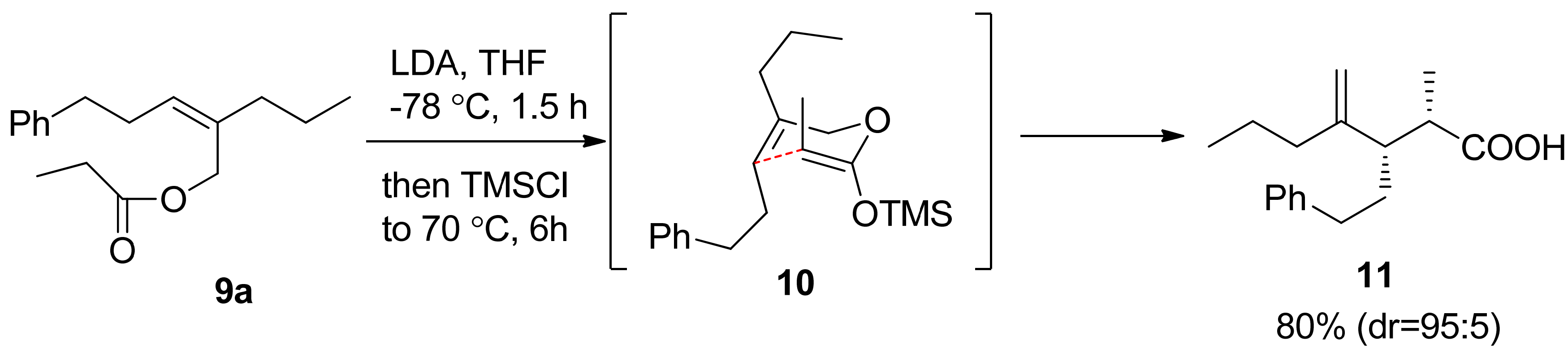
Z-Allylic Acetates from β-Lithiooxyphosphonium Ylides



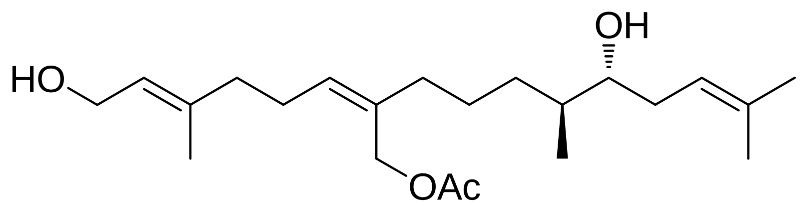
entry	aldehyde 1	phosphorane 2	allylic acetate 6	yield, Z/E[11]
1	1a	2a	6a	80%, >99%
2			6b	73%, >99%
3			6c	76%, >99%
4			6d	71%, 92:8
5			6e	68%, >99%
6			6f	69%, >99%
7			6g	64%, >99%
8			6h	78%, 87:13
9			6i	51%, >99%

Ireland-Claisen Rearrangment

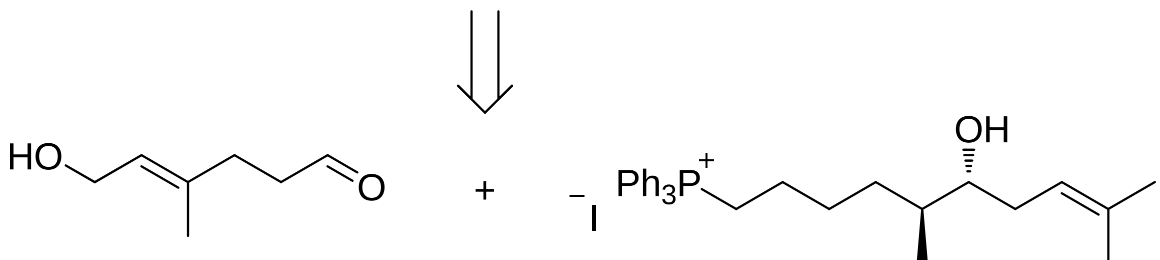


Diterpene 12 synthesis



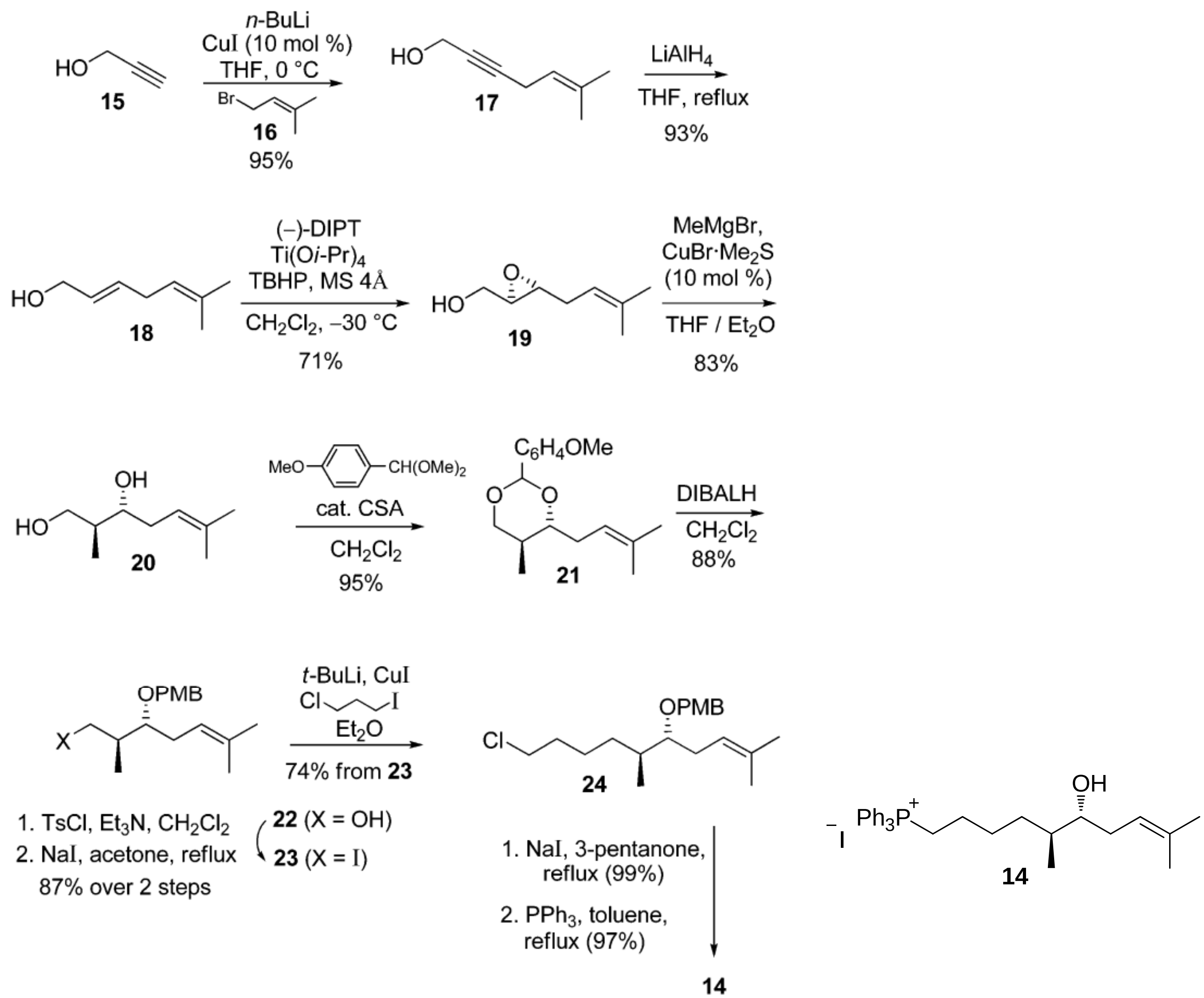
12

Geranyl-geraniol derived diteppene
isolated from the seeds of *Carpesium triste*
cytotoxic activity

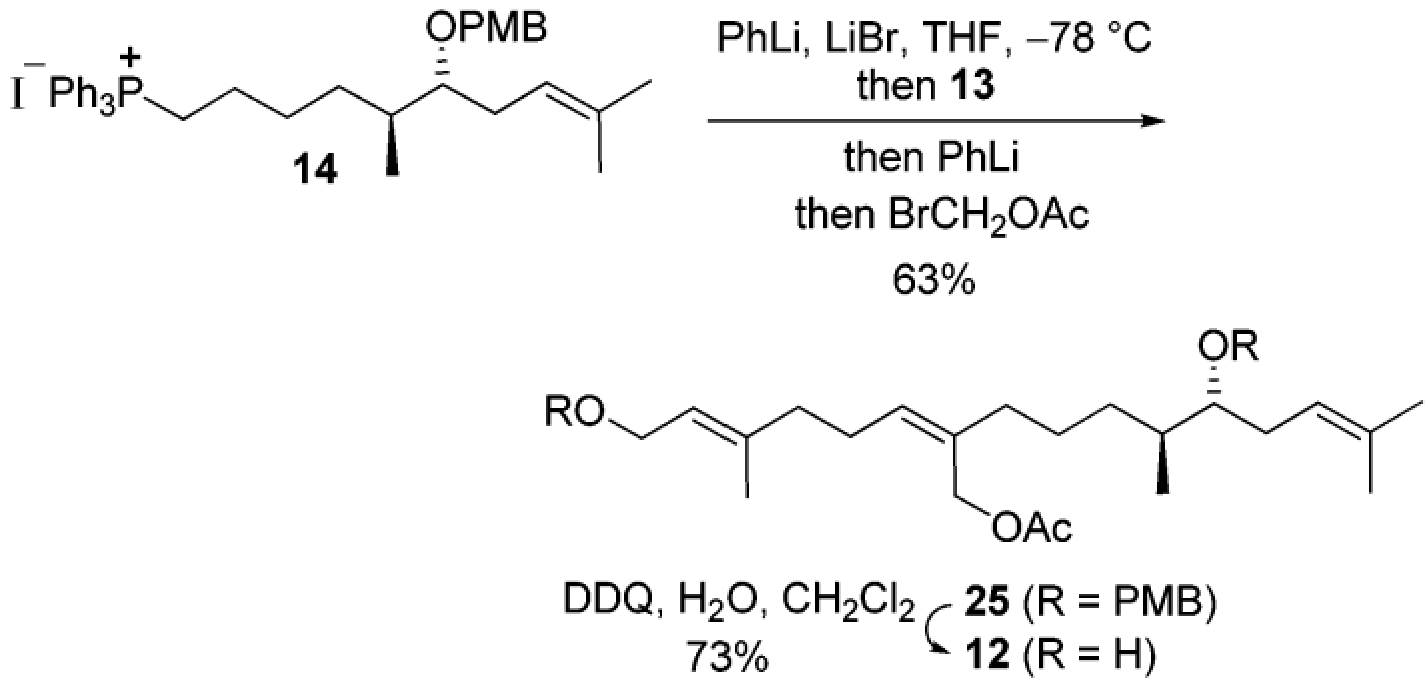


13 **14**

Synthesis of Phosponium Salt 14



Completion of the Synthesis of Diterpene 12



Conclusion

- Efficient Cascade process
- Highly stereoselective trisubstituted olefins
- Rapid increase of complexity
- Improved yields

Potential Project, One Pot Preparation of Target Molecule