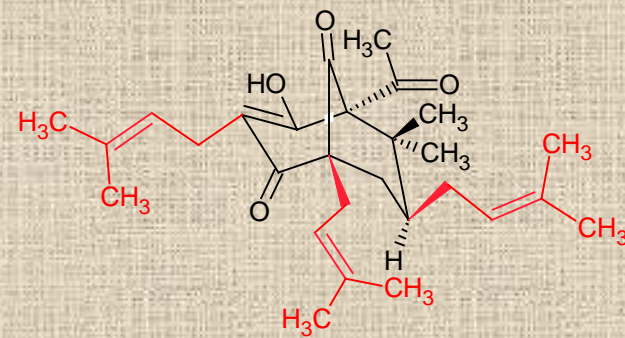
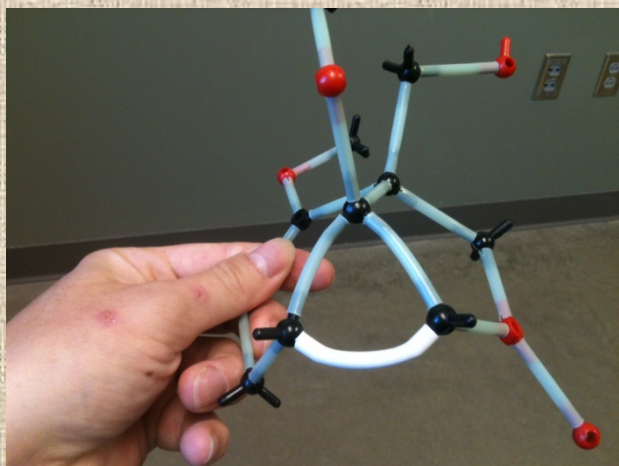


'Stereoselective Total Synthesis of Nemorosone'

Uwamori, M.; Saito, A.; Nakada, M. *J. Org. Chem.* **77** (2012) 5098-5107

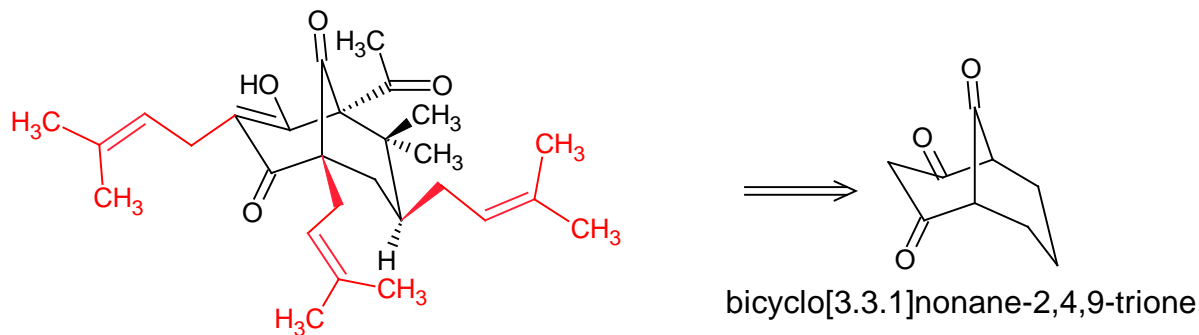


Nemorosone - a polycyclic
polyprenylated acylphloroglucinol

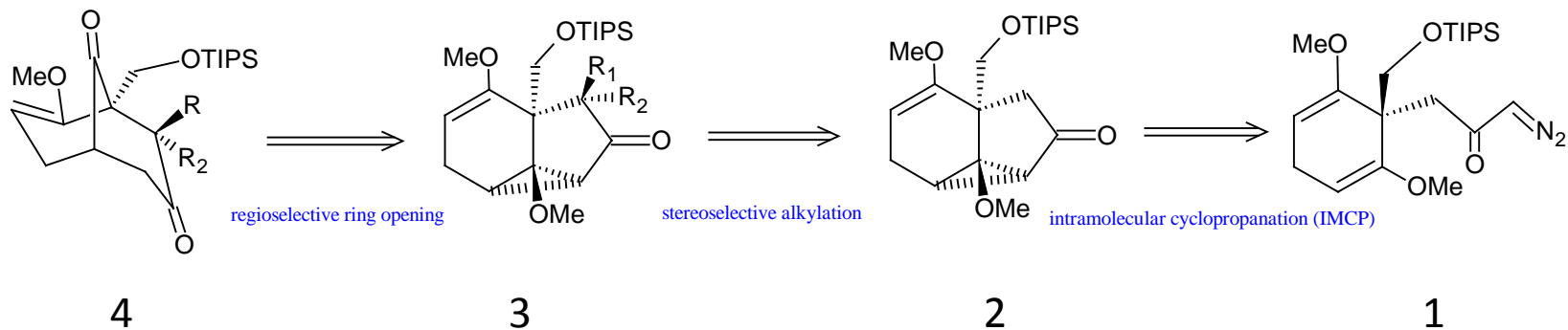
Selected items from the Chemical Literature

Reviewed by the Gaylord Chemical Literature Club

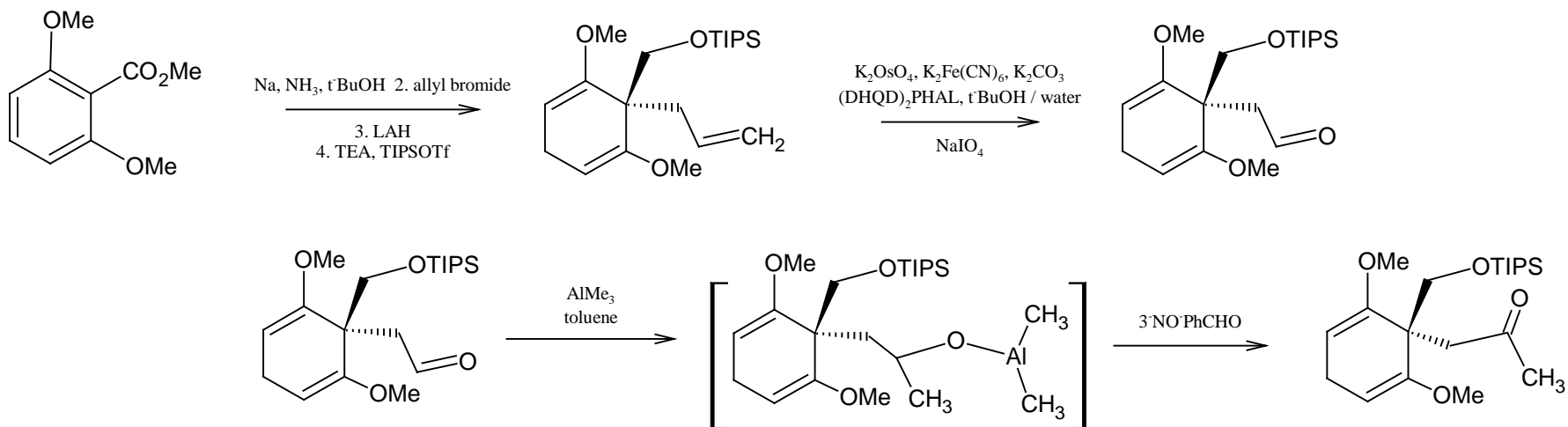
Nemorosone Retrosynthetic logic



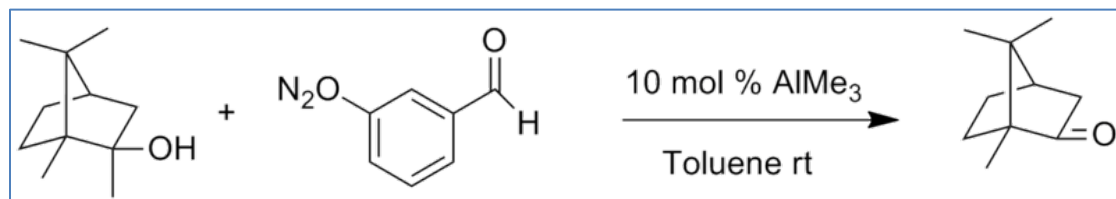
Nemorosone - a polycyclic
polyprenylated acylphloroglucinol



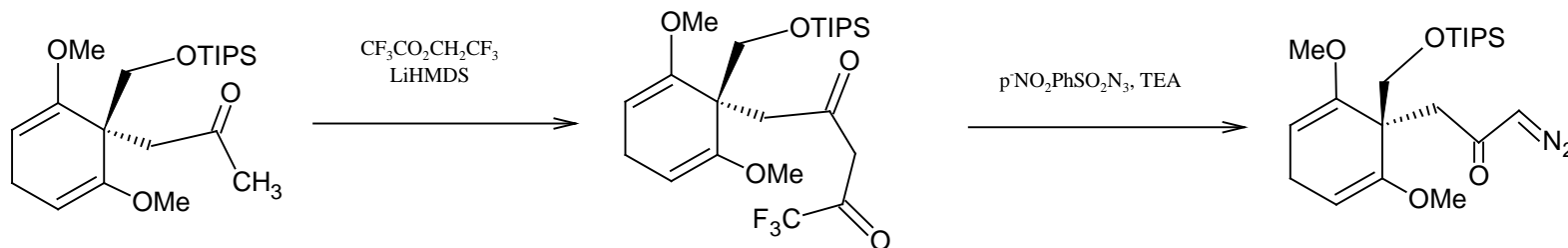
Synthesis of diazoketone 1



A modified Oppenauer Oxidation!



Christopher R. Graves, Bi-Shun Zeng, and SonBinh T. Nguyen [J. Am. Chem. Soc.](#); 2006

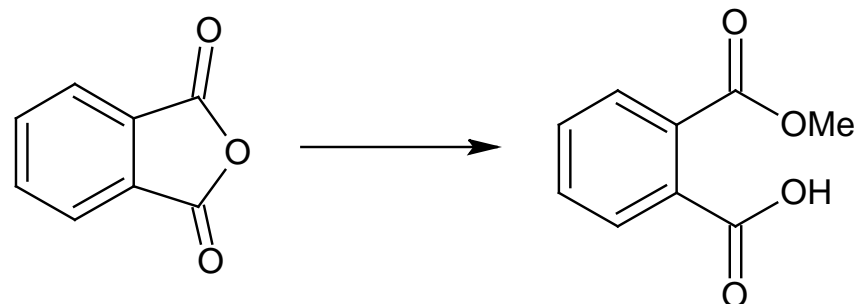


A Word about desymmetrization

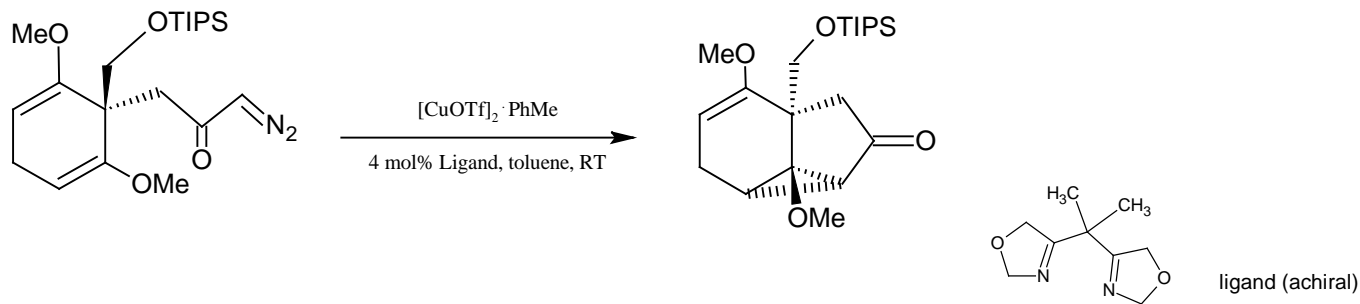


Wikipedia says:

Desymmetrization in [stereochemistry](#) is the modification of a [molecule](#) that results in the loss of one or more symmetry elements. An important application involves the introduction of [chirality](#). Formally, such conversion require the loss of an improper axis of rotation (mirror plane, center of inversion, rotation-reflection axis). In other words, desymmetrizations convert [prochiral](#) precursors into a [chiral](#) products.^[1]



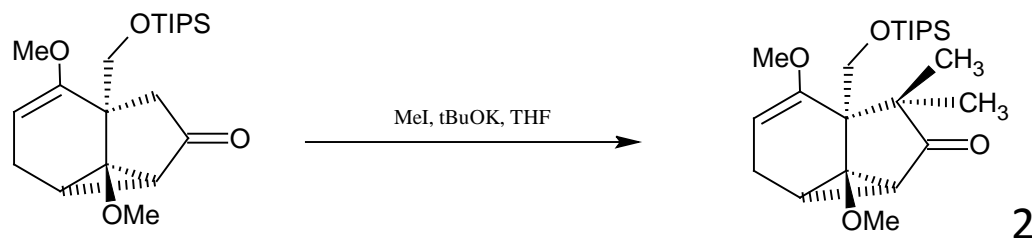
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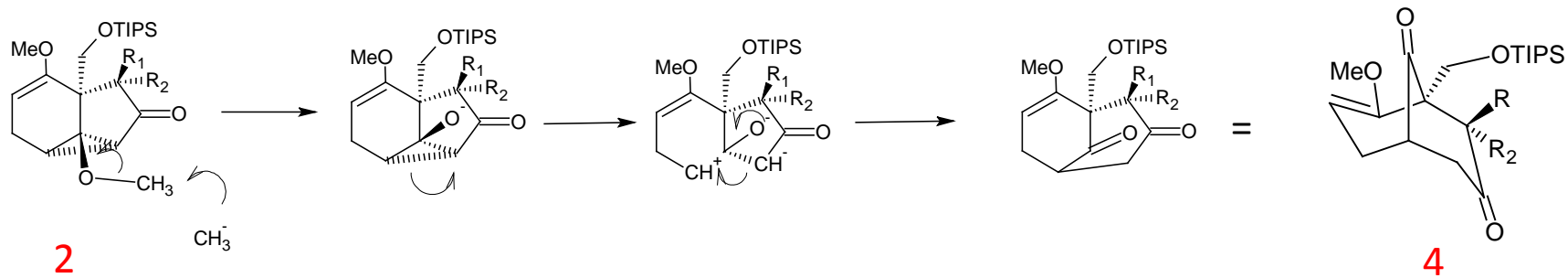
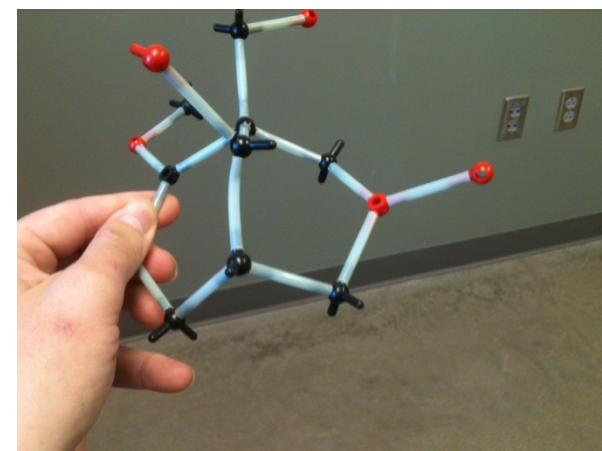
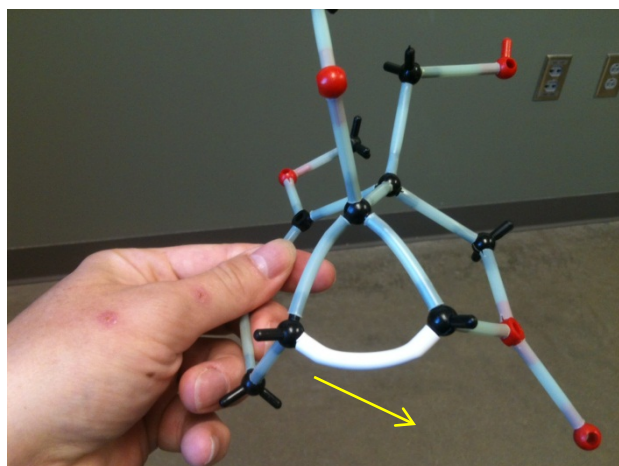
The authors used an achiral ligand to facilitate the cyclopropanation step

Further work is planned to develop/implement an asymmetric desymmetrization of the diazoketone.

Regioselective alkylation to 2



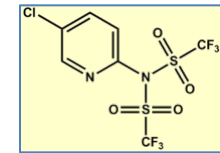
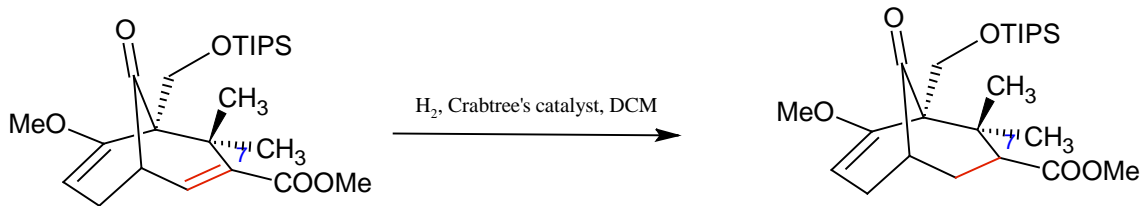
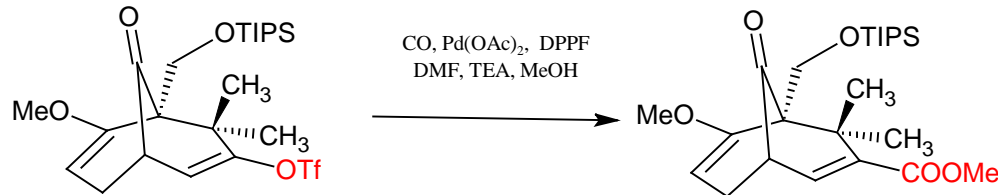
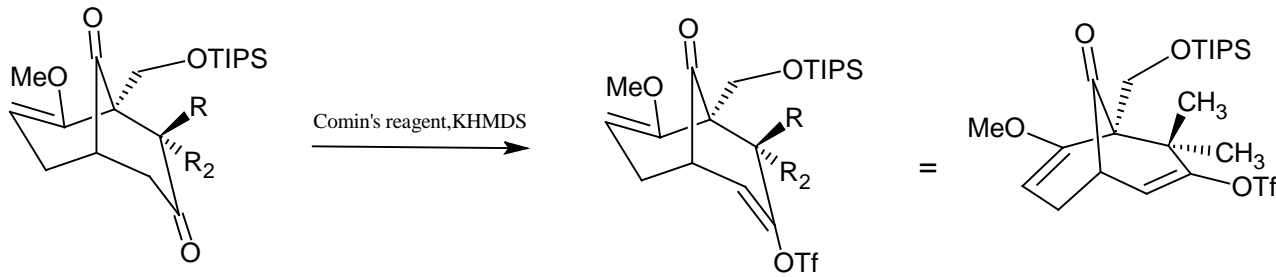
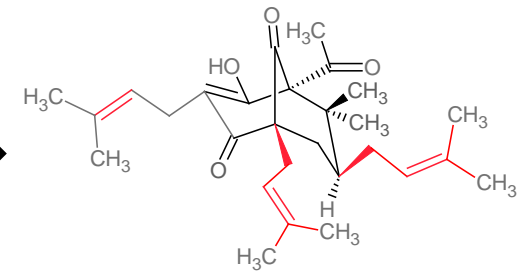
Regioselective Ring Opening to provide 3



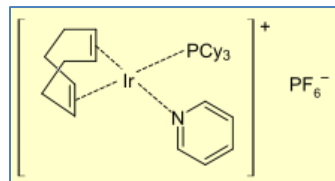
Functionalization of 4 → Nemorosone

- 4 → 14
- Crabtree hydrogenation and unusual result
- Triflate preparation
- Cuprate couplings
- Two more allyl groups
- Deprotect TIPS
- Grubbs CM prenylation to target.

Functionalization of 4 →



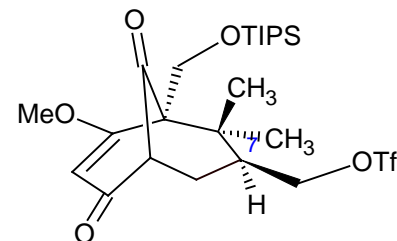
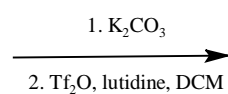
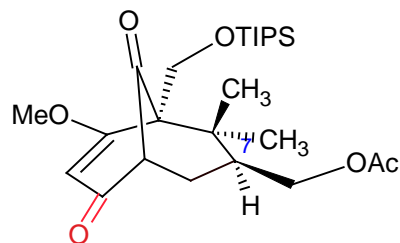
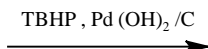
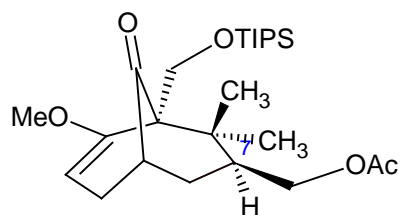
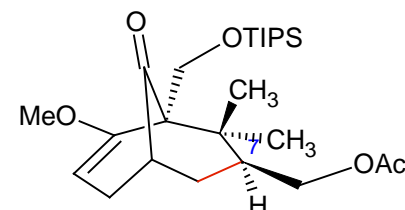
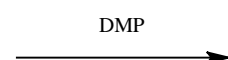
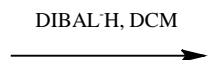
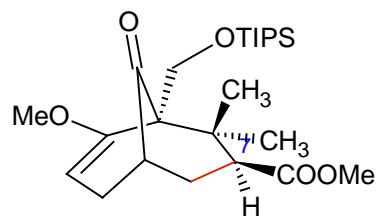
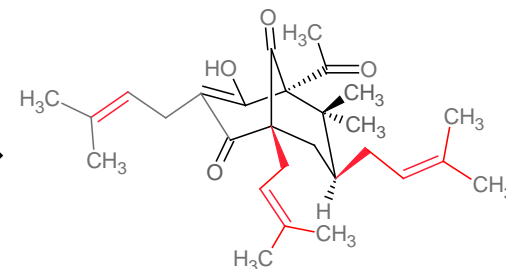
Comin's Reagent
(Wikipedia.org)



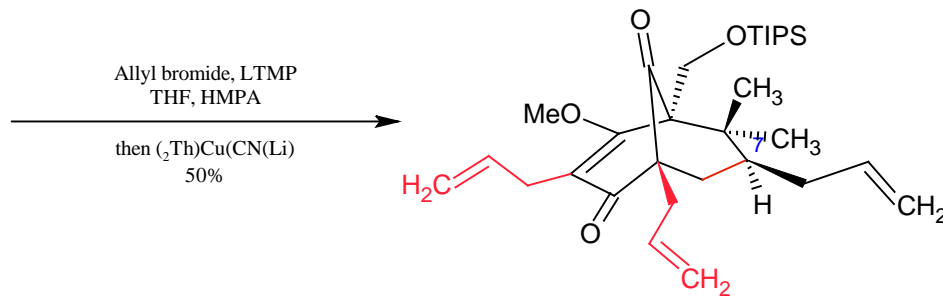
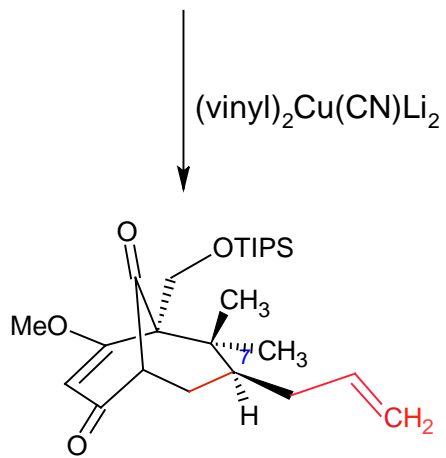
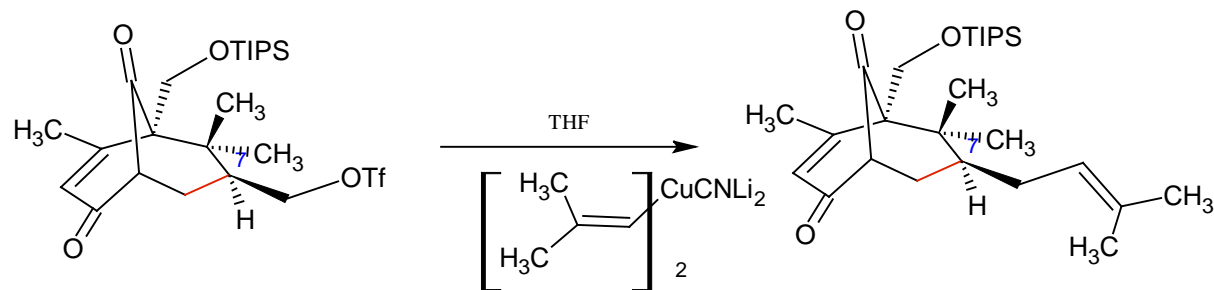
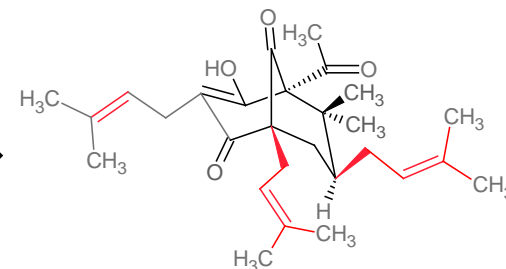
Crabtree's catalyst
(Wikipedia.org)

Hydrogenation at more hindered face aided by the isolated double bond?

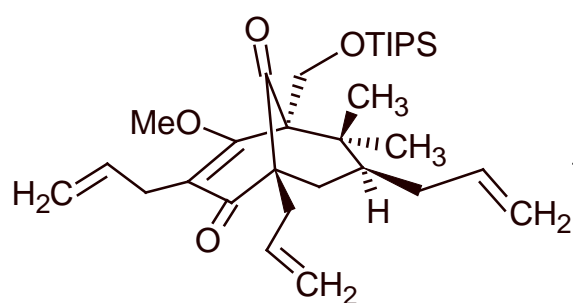
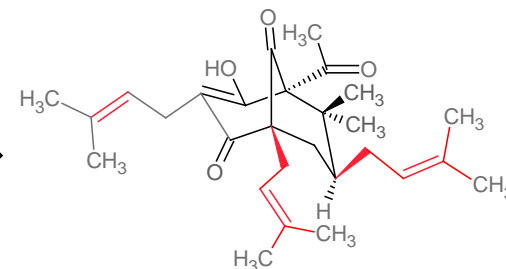
Functionalization of 4 →



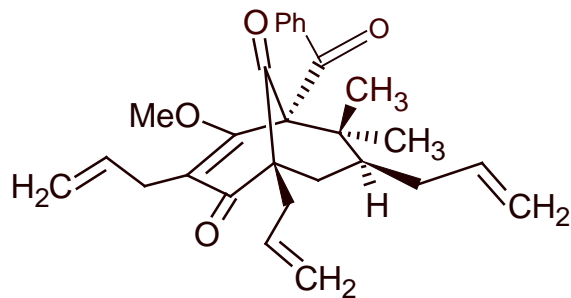
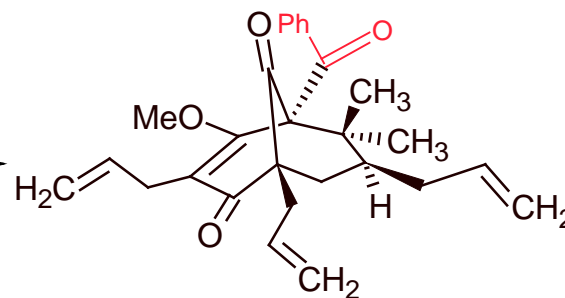
Functionalization of 4 →



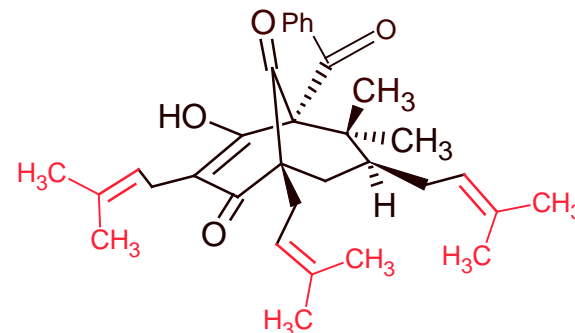
Functionalization of 4 →



1. TBAF
2. DMP
3. PhMgBr
4. DMP



1. 2-methylpropene, Grubbs II
2. LiCl, DMSO



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There are almost certainly errors contained in these slides which are the fault of the reviewer (A.S. McKim) and not the responsibility of the publishing scientists.

Miscellany

- HMBC / NOESY correlations used to establish the stereochemistry of key C, H atoms in bicyclic nucleosides

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