Total Synthesis of (+)-Cyclobutastellettolide B

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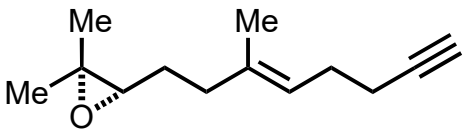
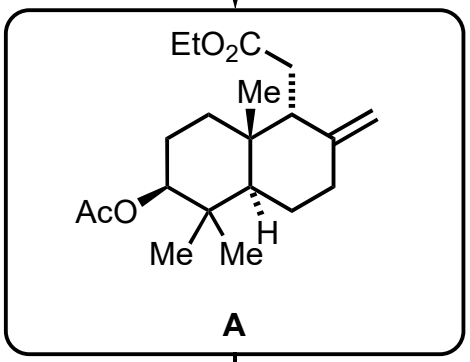
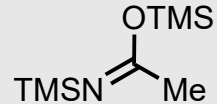


1–4

1) $TiCl_4$, CH_2Br_2
2) *t*BuLi, DMF
3) $NaBH_4$
4) Pivalic acid (cat.), $MeC(OEt)_3$, neat, reflux; *then* AcOH, Ac_2O; *then* Et_3N, 4-DMAP



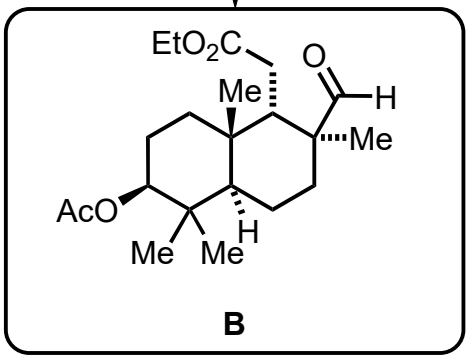
A



BSA

5–9

5) *m*CPBA
6) $B(C_6F_5)_3$
7) **BSA**, DBU
8) TFA, Et_2Zn,CH_2I_2
9) conc. HCl, acetone, reflux



B

Propose a route to the starting material.
see below

1) *Hint:* Product data:
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 120.9, 78.9, 49.1, 38.72, 38.70, 37.2, 36.9, 28.0, 27.7, 21.2, 20.9, 15.4 ppm.

2) Name of the reaction?
Bouveault aldehyde synthesis

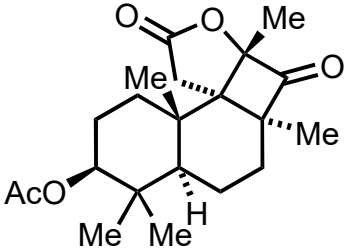
4) Name the reaction.
Johnson–Claisen rearrangement

Hint: All functional groups competent of reacting with the ortho ester under these reaction conditions reacted. The telescoped steps constitute a protecting group manipulation.

6) Name the reaction.
Meinwald rearrangement

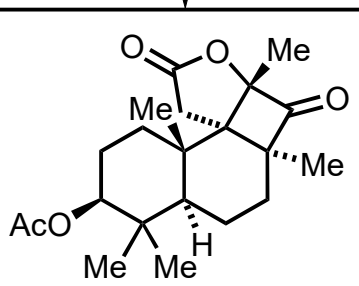
8) Name the reaction.
Simmons–Smith cyclopropanation

9) *Hint:* The structural motif generated in step 8 is known to shapeshift to a different constitutional isomer. Think Kulinkovich reaction.



(+)-Cyclobutastellettolide B

10–13



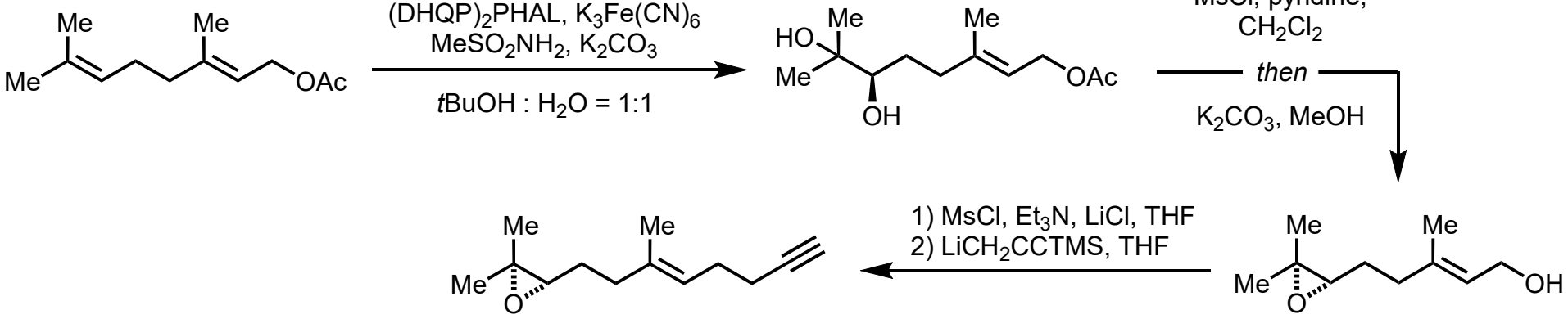
(+)-Cyclobutastellettolide B

10) $EtPPh_3Br$, *n*BuLi
11) K_2OsO_4, NMO
12) $(COCl)_2$, DMSO, Et_3N
13) Compact fluorescent lamp (CFL), $CHCl_3$

10–13) Name the reactions.
Wittig olefination, Upjohn dihydroxylation, Swern oxidation, Norrish–Yang cyclization.

For 13: Also consider writing the detailed reaction mechanism.
see below

Starting material synthesis



Tetrahedron Lett. **1993**, *34*, 5995–5998.
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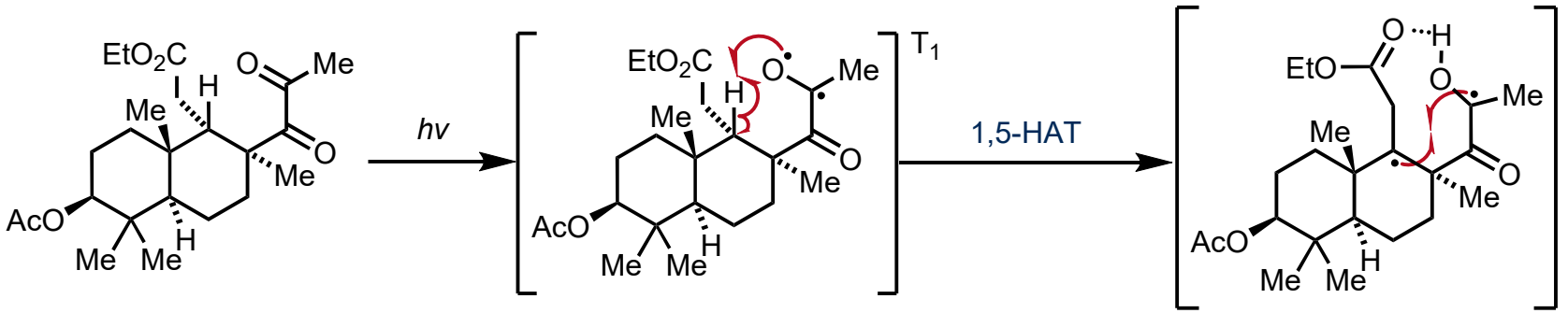
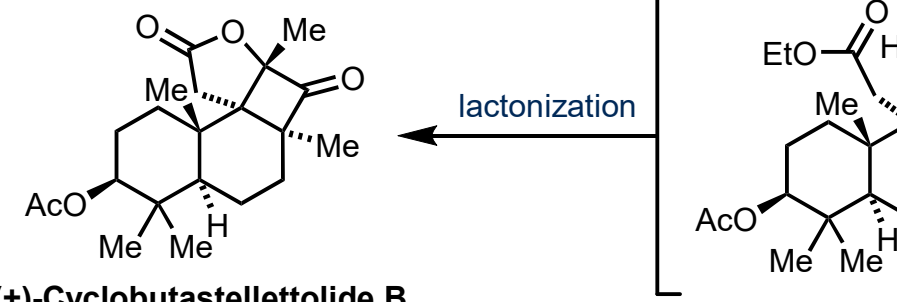
Proposed mechanism for the Norrish–Yang cyclization



hydrogen bonding as proposed stereocontrolling interaction



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