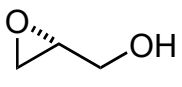
A biomimetic total synthesis of (+)-intricarene

Tang, B.; Bray, C. D.; Pattenden G.

Tetrahedron Lett. **2006**, *47*, 6401–6404.



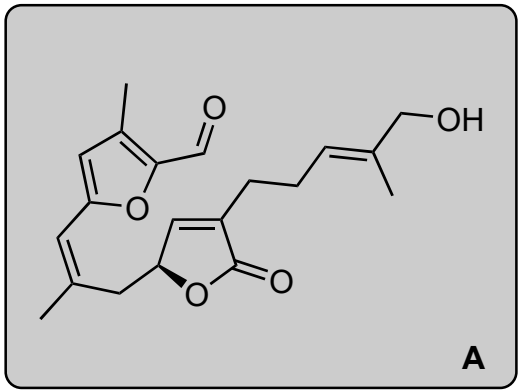
1-10

1) TMS-acetylene, *n*-BuLi, BF_3•OEt_2, -78°C to -30°C
2) K_2CO_3
3) Cp_2ZrCl_2, $AlMe_3$, r.t., *then* reflux *then* I_2, -30°C
4) TsCl, pyridine
5) K_2CO_3
6) **1**, NaHMDS, -78°C *then* substrate, BF_3•OEt_2, 0°C
7) *p*-TSA
8) H_2O_2, 0°C
9) PPTS (cat.)
10) **2**, $Pd(PPh_3)_4$, CuI, CsF

1) Please name the starting material.
(+)-glycidol

3) Hint: Isomerization occurs upon reflux.

10) Please name the reaction.
Stille coupling



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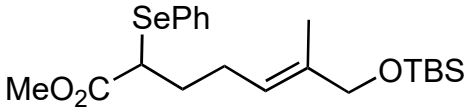

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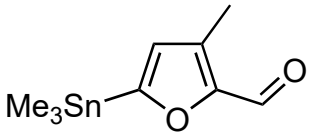

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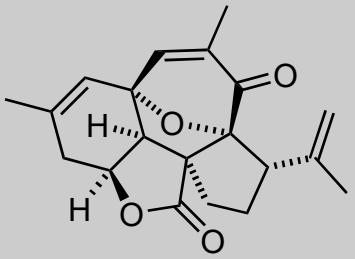


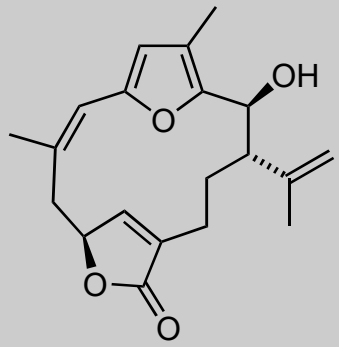
(+)-intricarene

11-12

11) Ph_3P, NBS
12) $CrCl_2$

12) These conditions were a precursor to a named coupling reaction. Name this reaction and identify the missing co-catalyst.
Nozaki–Hiyama–Kishi reaction. $NiCl_2$ is the co-catalyst needed for NHK conditions

J. Am. Chem. Soc. **1986**, *108(19)*, 6048–6050.

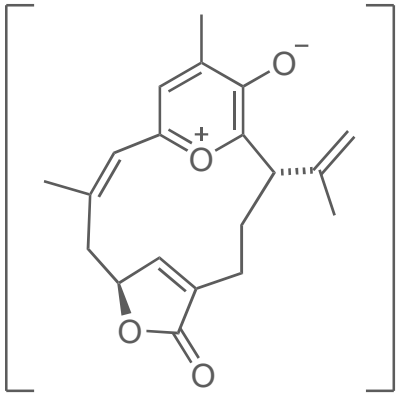


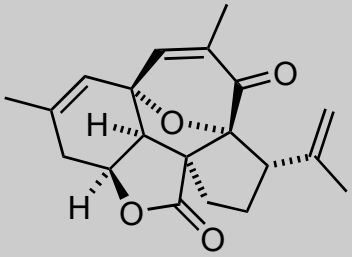
(–)-Bipinnatin J

13-15

13) $VO(acac)_2$, *t*-BuOOH, -20°C
14) Ac_2O, Et_3N, DMAP (cat.)
15) DBU, reflux

15) Please classify the reaction and classify and draw its key intermediate. *Hint*: an ylide is formed.
Oxidopyrylium [5+2] cycloaddition





(+)-Intricarene