PROTECTING-GROUP-FREE ENANTIOSELECTIVE SYNTHESIS OF (-)-PALLAVICININ AND (+)-NEOPALLAVICININ

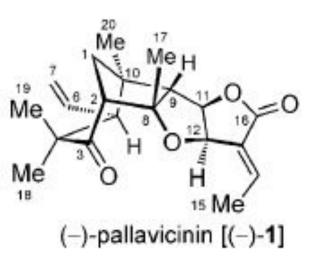
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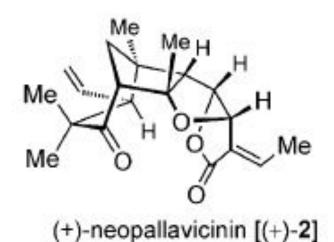
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Target substances





- □ Novel [6-5-5-5] tetracyclic skeleton
- □ Bicyclo[3.2.1] moiety
- ☐ 7 contiguous stereocenters
- 1 chiral all-carbon quaternary center

Retrosynthetic analysis of (-)-1 and

(S)-tBu-PHOX

Me Me H H

21 (15%)

- 1. LDA, CH₃CHO THF, -78 °C
- MsCl, Et₃N DMAP, CH₂Cl₂
- 1: 55% (2 steps)
- 2: 12% (2 steps)

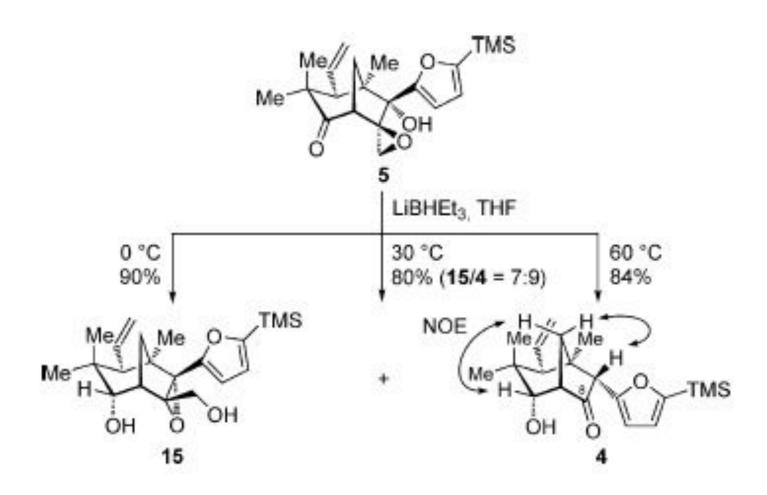
(-)-pallavicinin [(-)-1]

(+)-neopallavicinin [(+)-1]

absolute configuration of (-)-1

Completing the total synthesis of (-)-1 and (+)-2

LiBHEt3-induced fragmentation of 5



Proposed mechanism for reaction of 5 with LiBHEt3