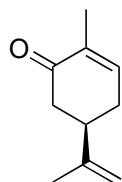


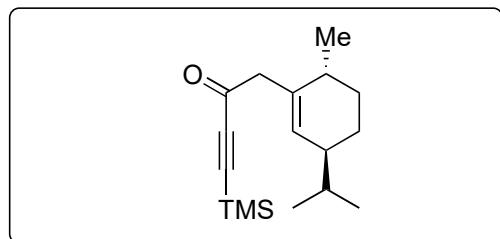
Platinum- and Gold-Catalyzed Rearrangement Reactions of Propargyl Acetates: Total Syntheses of (-)- α -Cubebene, (-)-Cubebol, Sesquicarene and Related Terpenes.

Alois Fürstner and Peter Hannen.

Chem. - Eur. J. **2006**, *12*, 3006–3019.

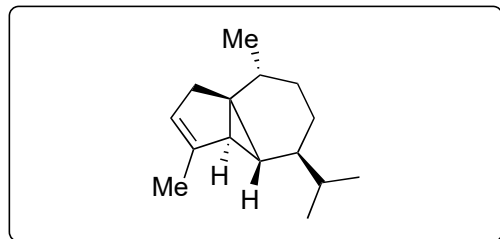


1 - 9



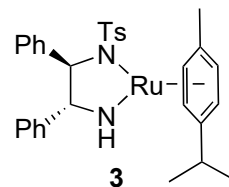
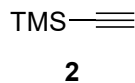
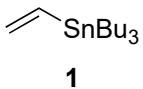
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10 - 16



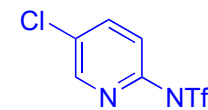
(-)- α -Cubebene

- 1) cat. [(PPh₃)₃RhCl], H₂, benzene
- 2) Pd/C, H₂, MeOH
- 3) NaOMe, MeOH
- 4) LiTMP, comins reagent, THF, -78 \rightarrow 0 $^{\circ}$ C
- 5) **1**, cat. [Pd(PPh₃)₄], LiCl, THF, reflux
- 6) 9-BBN, THF, then H₂O₂, aq. NaOH
- 7) DMP, CH₂Cl₂
- 8) **2**, *n*-BuLi, THF, then CeCl₃, -78 $^{\circ}$ C
- 9) DMP, CH₂Cl₂



- 10) cat. **3**, *i*-PrOH
- 11) TBAF, THF
- 12) Ac₂O, NEt₃, cat. DMAP, CH₂Cl₂
- 13) cat. PtCl₂, toluene, 80 $^{\circ}$ C
- 14) K₂CO₃, MeOH
- 15) LDA, comins reagent, THF, -78 \rightarrow 22 $^{\circ}$ C
- 16) cat. [Fe(acac)₃], MeMgBr, THF, NMP, -30 $^{\circ}$ C

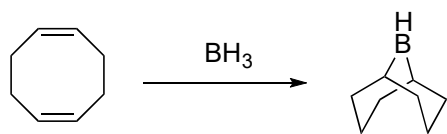
- 1) Name of starting material and catalyst?
(-)-carvon, wilkinson catalyst
- 4) Structure of comins reagent?



- 5) Name of reaction?
Stille coupling
- 6) Structure and preparation of 9-BBN?
see below
- 8) pK_a of terminal alkynes?
around 25

- 10) Name of reaction?
Noyori asymmetric hydrogenation
- 13) Propose mechanism
see below

Preparation and structure of 9-BBN



Proposed mechanism

