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

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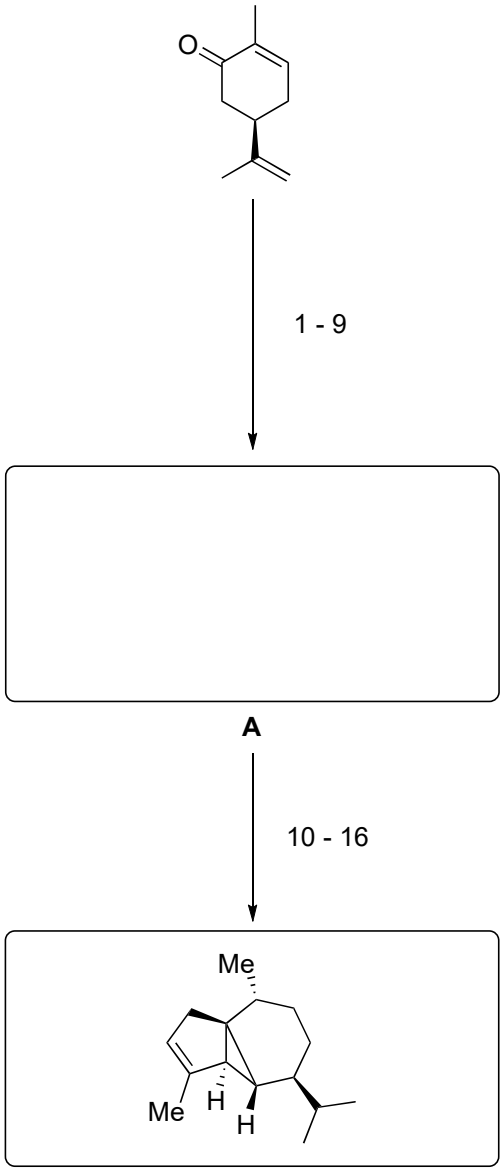

(–)-α-Cubebene

1) cat. $[(PPh_3)_3RhCl]$, H_2, benzene
2) Pd/C, H_2, MeOH
3) NaOMe, MeOH
4) LiTMP, comins reagent, THF, –78 → 0 °C
5) **1**, cat. $[Pd(PPh_3)_4]$, LiCl, THF, reflux
6) 9-BBN, THF, *then* H_2O_2, aq. NaOH
7) DMP, CH_2Cl_2
8) **2**, *n*-BuLi, THF, *then* $CeCl_3$, –78 °C
9) DMP, CH_2Cl_2

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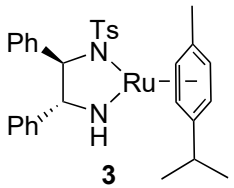

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10) cat. **3**, *i*-PrOH
11) TBAF, THF
12) Ac_2O, NEt_3, cat. DMAP, CH_2Cl_2
13) cat. $PtCl_2$, toluene, 80 °C
14) K_2CO_3, MeOH
15) LDA, comins reagent, THF, –78 → 22 °C
16) cat. $[Fe(acac)_3]$, MeMgBr, THF, NMP, –30 °C

1) Name of starting material and catalyst?

4) Structure of comins reagent?

5) Name of reaction?

6) Structure and preparation of 9-BBN?

8) pK_a of terminal alkynes?

10) Name of reaction?

13) Propose mechanism