Total Synthesis of (-)-Mitrephorone A

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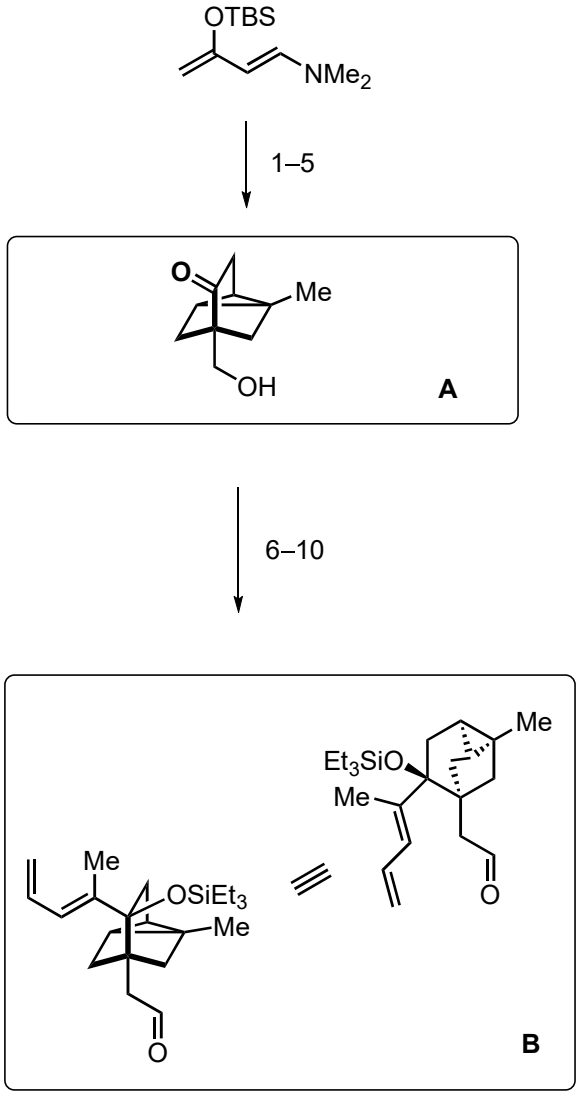
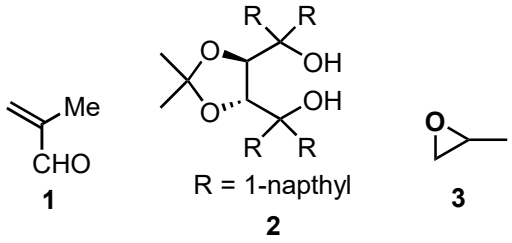
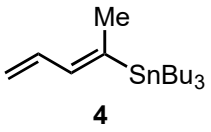


1) **1**, (S,S)-1-Np-TADDOL **2** (20 mmol%), -80 °C, PhMe, then $Ph_3P=CH_2$, PhMe, then aq HCl (1M)
2) LDA, THF, -78 °C, then HMPA, MeO_2CCN
3) LiHMDS, t-$BuMe_2SiOTf$, THF, -78 °C
4) propylene oxide **3**, PhMe, 190°C
5) DIBAL-H, -78 °C, then 1 M aq HCl, -78 °C to RT

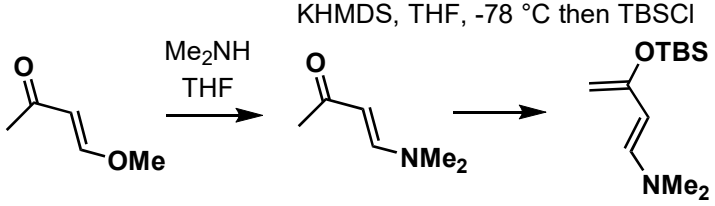


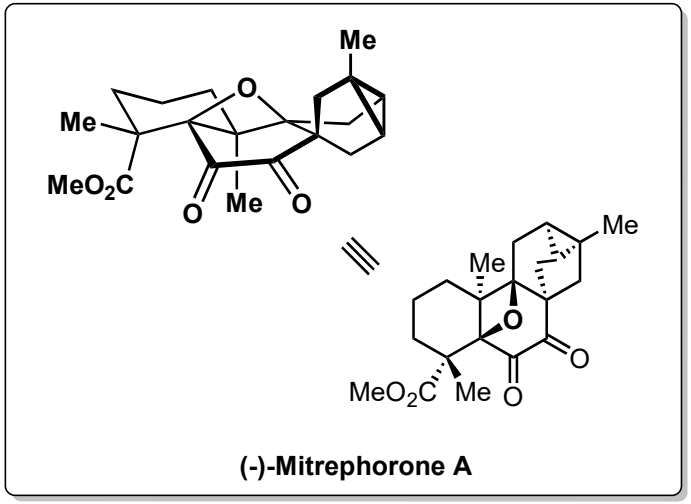


6) MsCl, Et_3N, CH_2Cl_2, 0 °C
7) KCN, DMSO, 80 °C
8) (E)-tributyl(penta-2,4-dien-2-yl)stannane **4**, n-BuLi , THF, -78 °C, $LaCl_3 \cdot 2LiCl$, THF, -78 °C
9) Et_3SiCl, imidazole, DMF, 80 °C
10) DIBAL-H, PhMe, -78 to 0 °C

What is the name of the SM and how would you synthesize it?

Rawal's diene





(-)-Mitrephorone A

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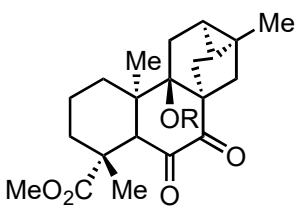

R = TES **C**

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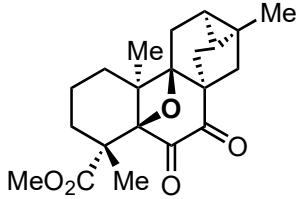

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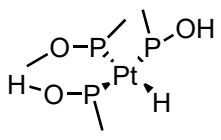

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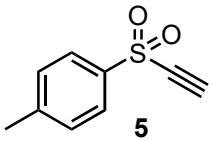

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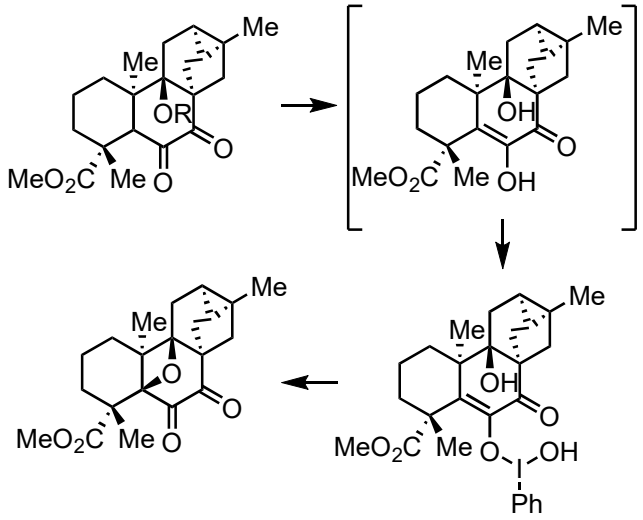
11) ethynyl p-tolyl sulfone **5**, LDA, THF, -78 °C, then **B**
12) DMP, t-BuOH, RT
13) Me_2CuLi, Et_2O, 0 °C
14) PtO_2 (10 mol %), H_2 (1 atm), EtOH, RT
15) Et_2AlCN, PhMe, 0 °C
16) Ghaffar-Parkins catalyst **6** (50 mol %), EtOH-H_2O (4:1), 80 °C, then KOH, 170 °C
17) $TMSCHN_2$, PhH-MeOH (4:1), 0 °C to RT
18) SeO_2, 1,4-dioxane, 100 °C

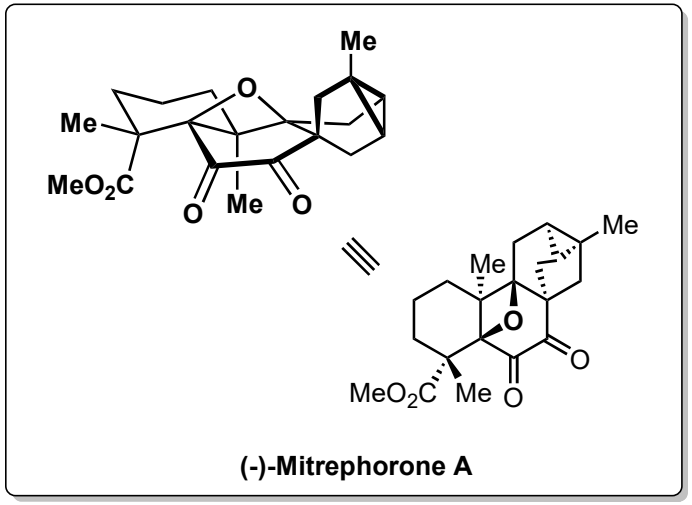
19) TASF, H_2O, DMF, 0 °C, then PhI(OH)OTs

Step 14: Name of catalyst **Adam's catalyst**

Step 18: Name of reaction **Riley oxidation**

Step 19: Mechanism of this step





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