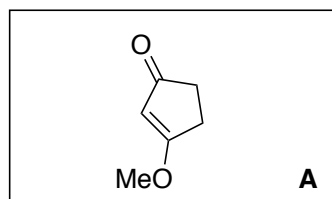


## Quaternary-Center-Guided Synthesis of Complex Polycyclic Terpenes

Hu, P.; Chi, H.; DeBacker, K. C.; Gong, X.; Keim, J. H.; Hsu, I. T.; Snyder, S. A.  
*Nature*, **2019**, *569*, 703.



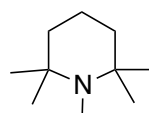
1-5



6-9

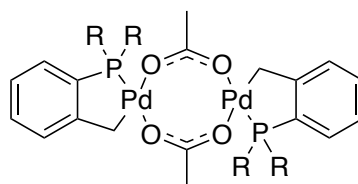


- 1) 4-bromo-2-methyl-1-butene, Mg, THF *then* 1N HCl
- 2) Cu(OTf)<sub>2</sub> (7.5 mol%), Hoveyda's NHC•Ag (3.75 mol%), AlMe<sub>3</sub>, -78 °C, THF
- 3) TMSOTf, PMP, CH<sub>2</sub>Cl<sub>2</sub>, -78 °C
- 4) IBX•MPO, DMSO, rt
- 5) Fe(acac)<sub>3</sub> (30 mol%), Ph<sub>3</sub>SiH, EtOH, (CH<sub>2</sub>OH)<sub>2</sub>



1,2,2,6,6-pentamethylpiperidine (PMP)

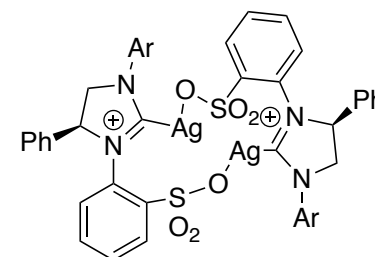
- 6) NH<sub>2</sub>NMe<sub>2</sub> (3 equiv.)
- 7) LDA, HMPA, 4-iodo-2-methyl-1-butene *then* 1N HCl
- 8) KHMDS, Comins' reagent, THF, -78 to 0 °C
- 9) Pd(OAc)<sub>2</sub> (10 mol%), t-BuMephos (15 mol%), n-Bu<sub>4</sub>NOAc (3 equiv.), toluene, 100 °C *then* K<sub>2</sub>CO<sub>3</sub>, MeOH



R = 2-MeC<sub>6</sub>H<sub>4</sub>  
 Herrmann's Catalyst

Step 4: What is the structure of IBX•MPO?  
 Propose a mechanism.

Step 5: Who first reported these conditions?



Ar = 2,6-(Et)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>  
 Hoveyda's NHC•Ag

Step 6: Who first reported these conditions?

Step 8: What is the structure of Comins' reagent?

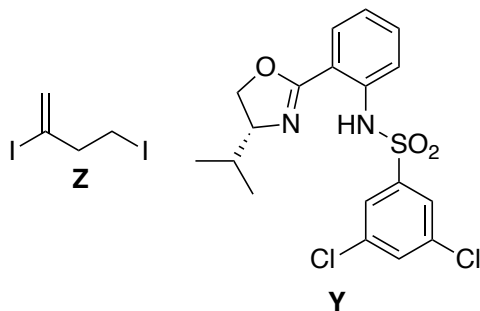
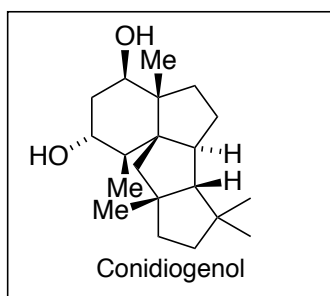
Step 9: Propose a mechanism



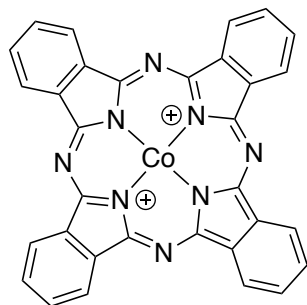
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10-12



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13-16



- 10) DMP, NaHCO<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C
- 11) CrCl<sub>2</sub>, **Y**, **Z**, CoPc, Mn, LiCl, TMSCl
- 12) Herrmann's Catalyst, HCO<sub>2</sub>Na, TBAB, DMF *then* TBAF, THF



Cobalt(II) Phthalocyanine (CoPc)

- 13) Pd/C (10 mol%), H<sub>2</sub>, EtOAc, *then* IBX, DMSO 80 °C
- 14) Triton B, t-BuOOH, THF
- 15) PhSeSePh (4.0 equiv.), NaBH<sub>4</sub> (8.0 equiv.), EtOH
- 16) L-Selectride, THF, -50 °C

Step 11: What is the name of this type of reaction?

Step 14: What is the structure of Triton B?