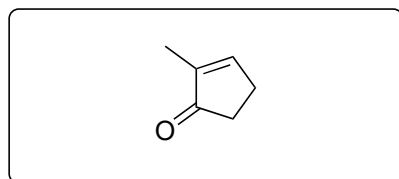


# Catalysis-Enabled 13-Step Total Synthesis of (-)-Peyssonoside A

Bo Xu, Chang Liu, Mingji Dai

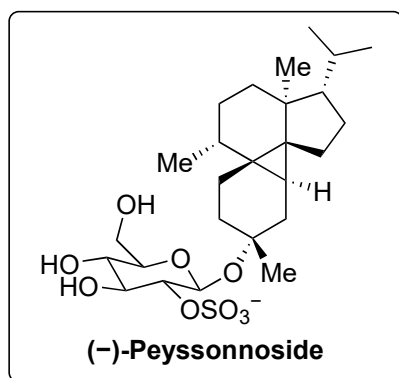
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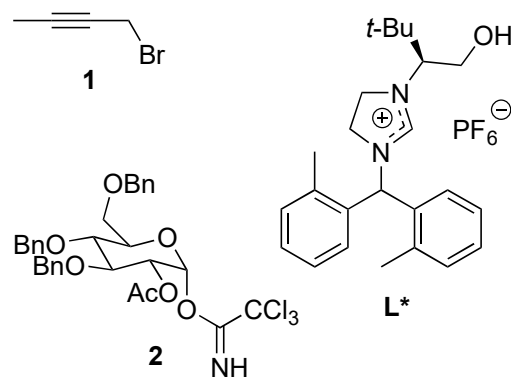
1–6



7–12



- 1)  $\text{Cu}(\text{OTf})_2$ , *i*-PrMgBr, **L\***; HMPA, **1**
- 2)  $\text{Pd}(\text{OAc})_2$ , *p*-MeOC<sub>6</sub>H<sub>4</sub>B(OH)<sub>2</sub>, PCy<sub>3</sub>•HBF<sub>4</sub>, KOAc
- 3) (*S,S*)-[(COD)Ir(Cy<sub>2</sub>PThrePHOX)][BAR<sup>F</sup><sub>4</sub>], H<sub>2</sub>
- 4) KHMDS, PhNTf<sub>2</sub>
- 5) BBr<sub>3</sub>
- 6) [Pd(cinnamyl)Cl]<sub>2</sub>, RuPhos, K<sub>2</sub>CO<sub>3</sub>



- 7)  $\text{Fe}(\text{acac})_3$ , Ph(*i*-PrO)SiH<sub>2</sub>, *i*-PrOH/DCM
- 8) Pd/C, H<sub>2</sub>
- 9) (PPh<sub>3</sub>)<sub>3</sub>RhCl, TMSCHN<sub>2</sub>, PPh<sub>3</sub>, *i*-PrOH
- 10)  $\text{Fe}(\text{acac})_3$ , PhSiH<sub>3</sub>, *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Me
- 11) **2**, AgOTf
- 12) KOH, MeOH; py•SO<sub>3</sub>, py; NaHCO<sub>3</sub>, Amberlite
- 13) Pd(OH)<sub>2</sub>/C, H<sub>2</sub>

6) Give the structure of RuPhos.

9) Name the reaction.

10) Name the reaction.

10') What is special about Studer's conditions?

11) Name the reaction.

13) Name the catalyst.