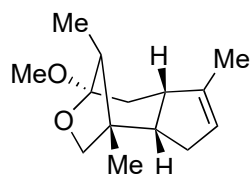
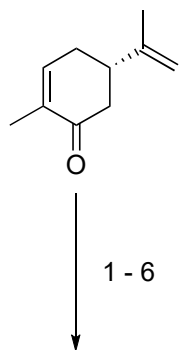


Total synthesis of (-)-Illisimonin A Enabled by pattern recognition and olefin transposition

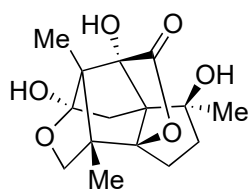
Bo Xu, Ziyao Zhang and Mingji Dai

J. Am. Chem. Soc. **2025**, *147*, 21, 17592–17597



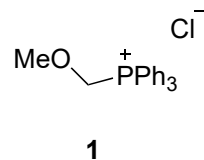
A

7 - 19



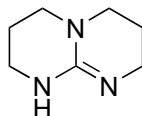
(-)-Illisimonin A

- 1) LDA, DMPU, allyl-Br
- 2) Grubbs II *then* DBU
- 3) H₂O₂, NaOH
- 4) **1**, t-BuOK
- 5) t-BuOK, MeI *then* NaBH₄
- 6) Crabtree catalyst



- 7) O₂, *hν* (427nm), TPP *then* PMe₃
- 8) Ac₂O, DMAP, Et₃N
- 9) KHMDS, TMSCl
- 10) Pd(OAc)₂, O₂, NaOAc
- 11) *hν* (370nm), Na₄W₁₀O₃₂, TripSH
- 12) Co(acac)₂, O₂, PhSiH₃
- 13) Toluene, 140°C
- 14) Ag₂O, TBAI, BnBr
- 15) LiHMDS, MoOPH
- 16) CrO₃, H₂SO₄
- 17) HCl, H₂O
- 18) TBD, THF
- 19) Pd/C, H₂

TBD:



Overall hint: look at the title

- 1) Name of SM ? **(S)-Carvone**
- 2) Structure of Grubbs II ?

6) *Hint*: isomerization, 1 ring is formed

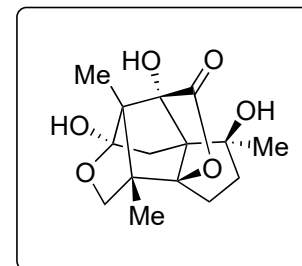
7) Name of the reaction ? **Schenck ene reaction**

9) Name of the reaction ? **Ireland-Claisen rearrangement**

11) isomerization

12) Name of the reaction ? **Mukaiyama hydration**

16) Name of the conditions ? **Jones**



(-)-Illisimonin A