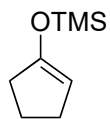


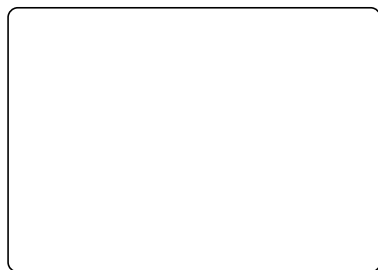
Total Synthesis of (±)-Cristaxenicin A

Wataru Kiuchi, Yuko Tsunoda, Kentaro Ishikura, Kosuke Kato, Junya Takino, Takahiro Suzuki, and Keiji Tanino*

Angew. Chem. Int. Ed. **2026**, *65*, e2485

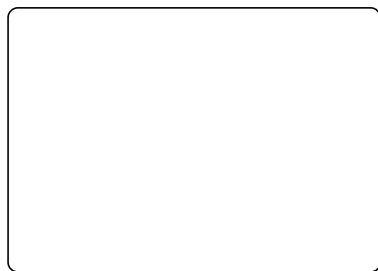


1–8



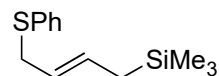
A

9–16

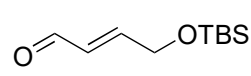


B

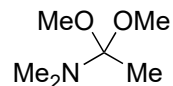
- 1) $\text{CH}_2(\text{OBn})_2$, TMSOTf, 2,6-DTBP, MeCN
- 2) **1**, Cp_2TiCl_2 , *n*-BuLi, THF, 0 °C
- 3) MsOH, CH_2Cl_2 , 0 °C
- 4) Li, $\text{NH}_3(\text{liq.})$, THF, -78 °C
- 5) ABNO, CH_2Cl_2 , 23 °C
- 6) $\text{H}_2\text{NOSO}_3\text{H}$, AcOH, H_2O , 50 °C
- 7) LiNEt_2 , **2**, HMPA, -30 °C
- 8) **3**, PhMe, 160 °C



1

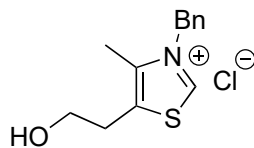


2

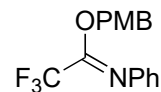


3

- 9) Cp_2ZrCl_2 , $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$, 0 °C
- 10) **4**, NEt_3 , EtOH, 50 °C
- 11) MeReO_3 , pyridine, H_2O_2 , CH_2Cl_2 , 0 °C
- 12) O_3 , MeOH, CH_2Cl_2 , -78 °C then Me_2S
- 13) Zn, AcOH, THF, 23 °C
- 14) **5**, $\text{Bi}(\text{OTf})_3$, PhMe, 23 °C
- 15) LHMDS, Tf_2O , Et_2O , -78 °C
- 16) $\text{Pd}(\text{PPh}_3)_4$, HCO_2NH_4 , DMF, 50 °C



4



5

2) Hint: SPh is not present in the product; branched product.

3) Hint: Strong acid, vinyl shifts

6) Hint: Does not stop at imine formation.

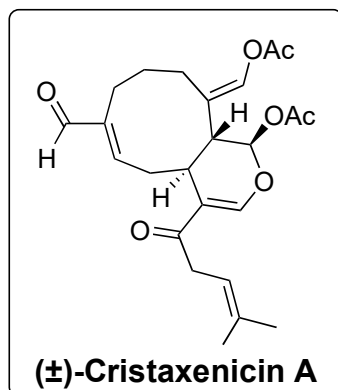
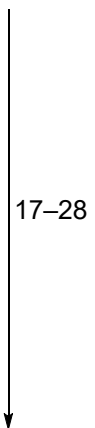
8) Draw the mechanism and name the reactions.
Hint: Two transformations.

10) Draw the mechanism, name reaction

11) Hint: Epoxidation of a diene; the double bond inside the ring gets oxidized.

13) Hint: An allylic alcohol is formed.

B



- 17) DIBAL-H, PhMe, 0 °C
- 18) *t*-BuOK, Ac₂O, THF, -78 °C
- 19) TBAF, AcOH, THF 50 °C
- 20) OsO₄ TMEDA, CH₂Cl₂, -78 °C
- 21) PhB(OH)₂, THF, -78 °C
- 22) DMP, pyridine, CH₂Cl₂, 23 °C
- 23) **6**, PhMe, 50 °C
- 24) DMP, pyridine, CH₂Cl₂, 23 °C
- 25) pinacol, AcOH, 23 °C
- 26) NaIO₄/SiO₂, CH₂Cl₂, 23 °C
- 27) AcOH, EDCI•HCl, DMAP, DCE, 35 °C
- 28) DDQ, buffer pH = 7, CH₂Cl₂ 23 °C

