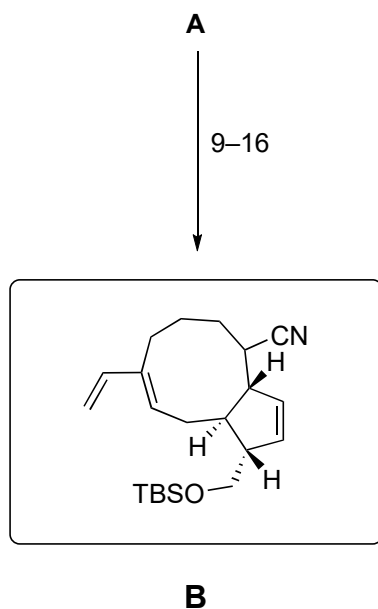
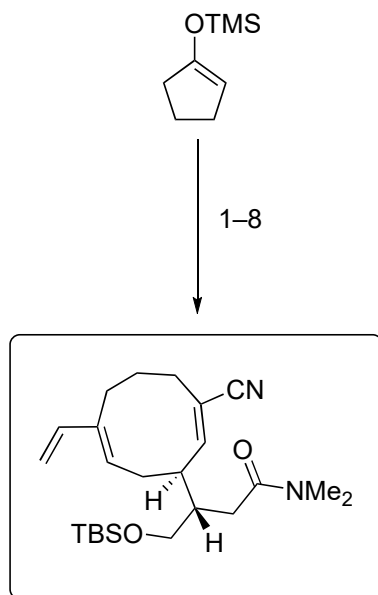


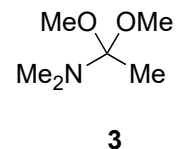
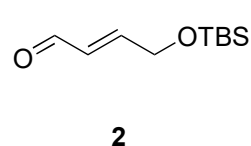
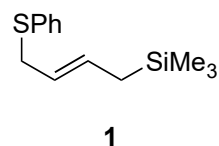
## Total Synthesis of (±)-Cristaxenicin A

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

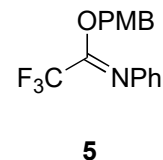
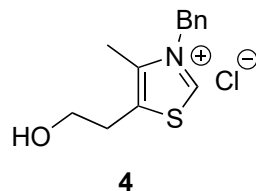
*Angew. Chem. Int. Ed.* **2026**, *65*, e2485



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



- 9)  $\text{Cp}_2\text{ZrCl}_2$ ,  $\text{LiAl}(\text{O}-t\text{-Bu})_3\text{H}$ , 0 °C
- 10) **4**,  $\text{NEt}_3$ , EtOH, 50 °C
- 11)  $\text{MeReO}_3$ , pyridine,  $\text{H}_2\text{O}_2$ ,  $\text{CH}_2\text{Cl}_2$ , 0 °C
- 12)  $\text{O}_3$ , MeOH,  $\text{CH}_2\text{Cl}_2$ , -78 °C then  $\text{Me}_2\text{S}$
- 13) Zn, AcOH, THF, 23 °C
- 14) **5**,  $\text{Bi}(\text{OTf})_3$ , PhMe, 23 °C
- 15) LHMDS,  $\text{Tf}_2\text{O}$ ,  $\text{Et}_2\text{O}$ , -78 °C
- 16)  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{HCO}_2\text{NH}_4$ , DMF, 50 °C



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.

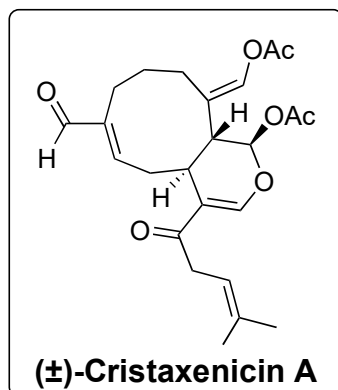
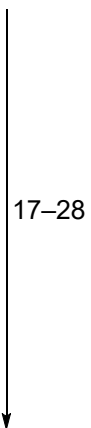
see, below [Eschenmoser-Claisen Rearrangement](#)  
[Cope Rearrangement](#)

10) Draw the mechanism, name reaction  
see below, [Stetter](#)

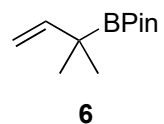
11) Hint: Epoxidation of a diene; the double bond inside the ring gets oxidized.

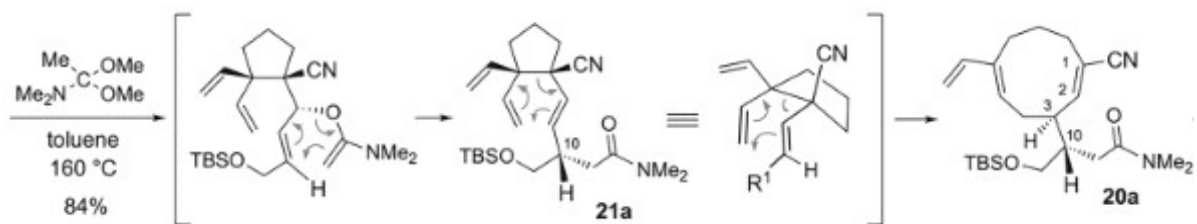
13) Hint: An allylic alcohol is formed.

**B**



- 17) DIBAL-H, PhMe, 0 °C
- 18) *t*-BuOK, Ac<sub>2</sub>O, THF, -78 °C
- 19) TBAF, AcOH, THF 50 °C
- 20) OsO<sub>4</sub> TMEDA, CH<sub>2</sub>Cl<sub>2</sub>, -78 °C
- 21) PhB(OH)<sub>2</sub>, THF, -78 °C
- 22) DMP, pyridine, CH<sub>2</sub>Cl<sub>2</sub>, 23 °C
- 23) **6**, PhMe, 50 °C
- 24) DMP, pyridine, CH<sub>2</sub>Cl<sub>2</sub>, 23 °C
- 25) pinacol, AcOH, 23 °C
- 26) NaIO<sub>4</sub>/SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 23 °C
- 27) AcOH, EDCI•HCl, DMAP, DCE, 35 °C
- 28) DDQ, buffer pH = 7, CH<sub>2</sub>Cl<sub>2</sub> 23 °C





## Stetter Catalytic Cycle

