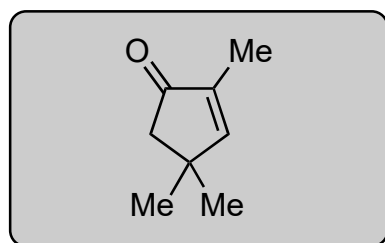
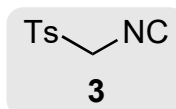
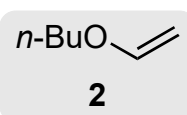
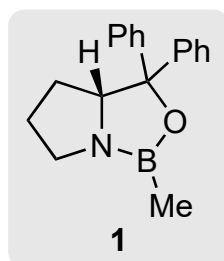
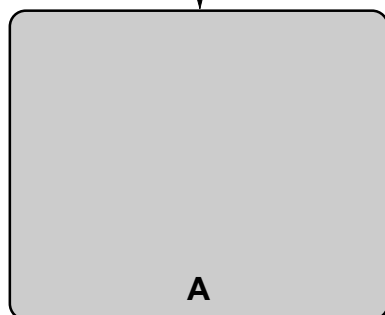


## Total Synthesis of (-)-Conidiogenone B

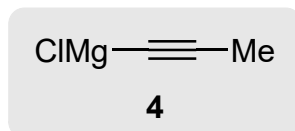
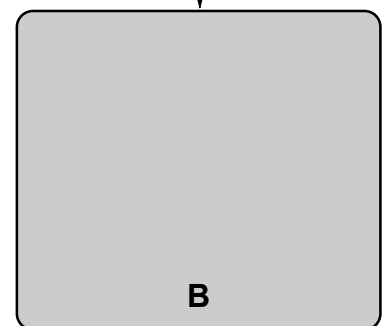
Bo Xu, Wen Xun, Shaobin Su, Hongbin Zhai  
*Angew. Chem. Int. Ed.* **2020**, 59, 16475–16479.



- 1) **1**, catecholborane, toluene/THF
- 2) **2**, Hg(OAc)<sub>2</sub>, Et<sub>3</sub>N
- 3) **3**, *t*-BuOK, THF
- 4) PhSiH<sub>3</sub>, Fe(acac)<sub>3</sub>, HFIP/EtOH



- 5) TMSOTf, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>; then MeReO<sub>3</sub>, pyridine, H<sub>2</sub>O<sub>2</sub>, HOAc/MeCN
- 6) **4**, THF
- 7) Pb(OAc)<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>; then CeCl<sub>3</sub>, NaBH<sub>4</sub>, MeOH
- 8) *n*-Bu<sub>3</sub>P, *o*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SeCN; then H<sub>2</sub>O<sub>2</sub>



1) Name of reaction?

*hint*: the new stereocenter is (*S*)-configured

2) Name of reaction?

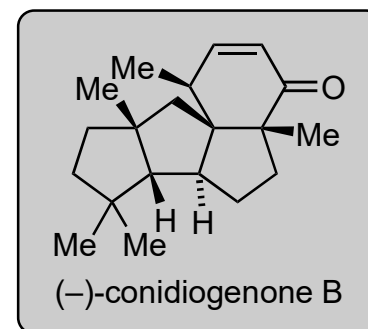
3) Name reagent and affiliated name reaction, and write out mechanism.

*hint*: Product exhibits a pronounced IR band at 2245 cm<sup>-1</sup> and features a total of three <sup>13</sup>C NMR signals between 150–110 ppm

5) Name of reaction?

*hint*: Very special oxidation conditions. Textbook conditions would have employed *m*-CPBA.

8) Name of reaction?

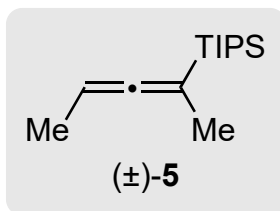


9)  $\text{Co}_2(\text{CO})_8$ ,  $\text{CH}_2\text{Cl}_2$ , TFA,  $\text{BH}_3 \cdot \text{SMe}_2$ ; then NMO

C

10) **5**,  $\text{TiCl}_4$ ,  $\text{CH}_2\text{Cl}_2$ ; then  $\text{BF}_3 \cdot (\text{HOAc})_2$

D

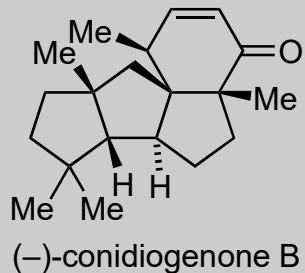


11)  $\text{NaBH}_4$ , MeOH

12)  $\text{NaH}$ ,  $\text{CS}_2$ , MeI, THF

13)  $n\text{-Bu}_3\text{SnH}$ , AIBN, toluene

14)  $\text{O}_3$ ,  $\text{CH}_2\text{Cl}_2$ ; then  $\text{Me}_2\text{S}$ ; then 3 M HCl, THF, reflux



9) *hint*: Two reactions are performed consecutively. Name both reactions.

Some data of the product:

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  211.2, 181.4, 130.8, 67.6, 52.8, 45.7, 42.9, 42.8, 40.9, 39.8, 39.6, 31.7, 29.3, 25.5, 8.2.

HRMS (ESI-TOF): calculated for  $\text{C}_{15}\text{H}_{23}\text{O}$   
[M+H]<sup>+</sup> 219.1743, found 219.1743

10) Name of reaction?

*hint*: (a)  $\text{BF}_3 \cdot (\text{HOAc})_2$  is used for a subsequent desilylation.

(b) The tertiary stereocenter that is formed features the opposite configuration compared to the corresponding position in the natural product. This will be corrected later.

13) Name of reaction?

14) *hint*: (a) Classic ring expansion move.

(b) The configuration of the tertiary stereocenter that was formed in step 10 is inverted in this step. Suggest how.