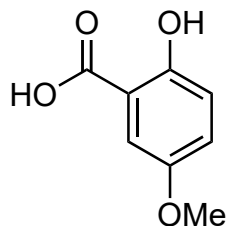


# Total Synthesis of Allocyclinone A via Late-Stage Halogen Swapping

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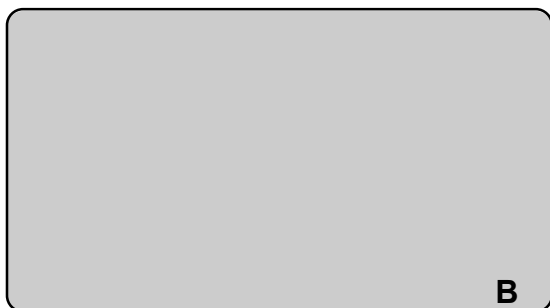
*Angew. Chem. Int. Ed.* **2026**, 65, e6162176. DOI: 10.1002/anie.6162176



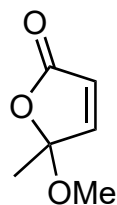
1-4



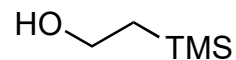
5-9



- 1) BnBr (3 equiv.), K<sub>2</sub>CO<sub>3</sub> *then* 40% NaOH (aq.)
- 2) Me<sub>2</sub>NH • HCl, Et<sub>3</sub>N, EDCI
- 3) *n*-BuLi, TMEDA *then* DMF
- 4) HCl, AcOH, workup *then* PhSH, PTSA



1

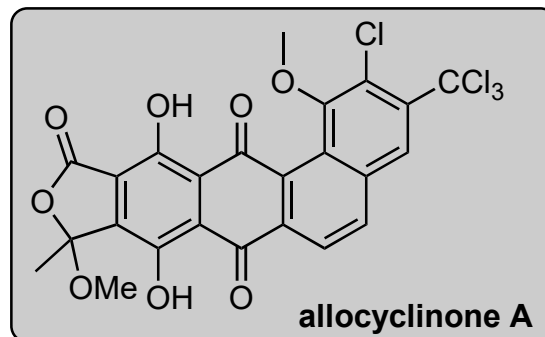


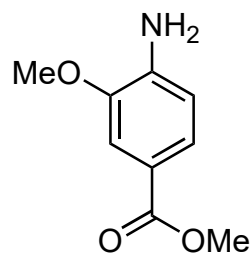
TMSEOH

- 5) LiHMDS *then* 1
- 6) TMSEOH (2.2 equiv.), PPh<sub>3</sub>, DIAD
- 7) H<sub>2</sub>, Pd
- 8) Py • HBr<sub>3</sub>, pyridine
- 9) TBAB (cat.), oxone

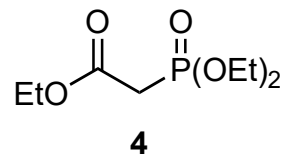
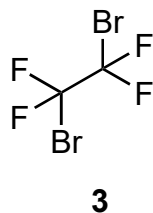
3) Which group is the strongest directing group?

5) New ring formed. Reaction name?





10-18



- 10) TBHP (7 equiv.), NaSO<sub>2</sub>CF<sub>3</sub>, Cu(OTf)<sub>2</sub>
- 11) NaNO<sub>2</sub>, CuCl, HCl (aq.)
- 12) LiAlH<sub>4</sub>
- 13) DMP
- 14) *n*-BuLi, MeNHCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> then *n*-BuLi, **3**
- 15) NaH, **4**
- 16) NH<sub>2</sub>NHTs, NaOAc
- 17) NaOH (aq.)
- 18) AgNO<sub>3</sub>, **B**, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

10) HINT: Generates •CF<sub>3</sub> equivalent.

14) HINT: **3** is a Br<sup>+</sup> equivalent.

16) Name of active reductant?

18) Ag<sup>+</sup> catalyzes decarboxylation.  
Reaction name?

**C**

19-21

- 19) Pd<sub>2</sub>dba<sub>3</sub>, P(o-toyl)<sub>3</sub>, CuTC, (*n*-Bu<sub>3</sub>Sn)<sub>2</sub>
- 20) TBAF
- 21) AlCl<sub>3</sub>

19) HINT: Stille-Kelly conditions  
20) HINT: Spontaneous aromatization occurs after TBAF step.

