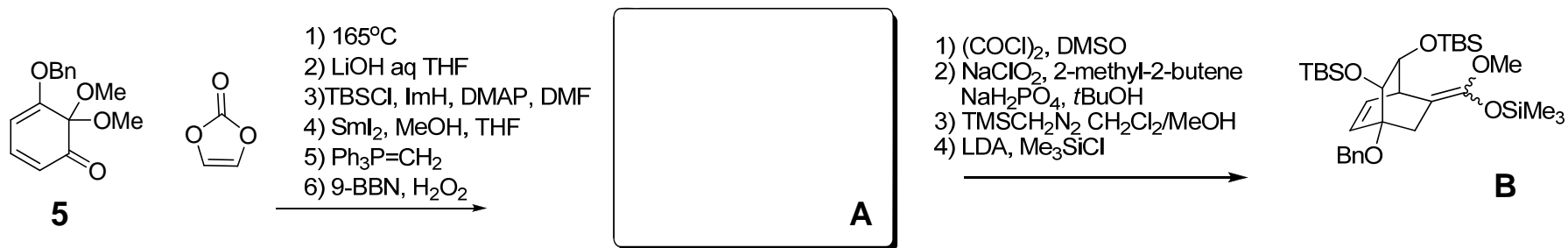
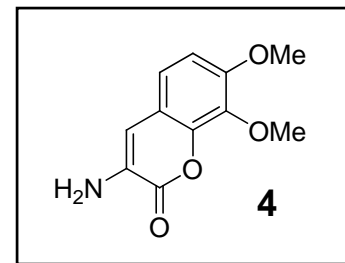


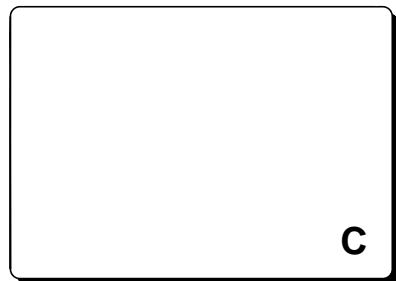
# Total Synthesis of (±)-Trichodermamide B and of a Putative Biosynthetic Precursor to Aspergillazine A Using an Oxaza-Cope Rearrangement

Chong-Dao Lu and Armen Zakarian

Angew. Chem. Int. Ed. **2008**, 47, 6829–6831



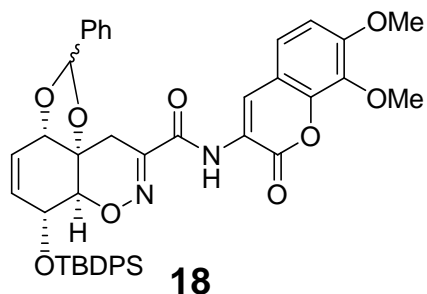
1)  $i\text{C}_5\text{H}_{11}\text{ONO}$  2.1eq  
 $\text{TiCl}_4$ ,  $\text{CH}_2\text{Cl}_2$



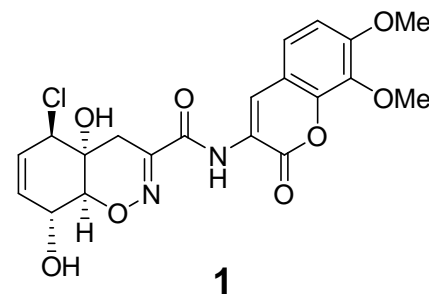
- 1) aq HF, MeCN
- 2) DDQ, MS 3A,  $\text{CH}_2\text{Cl}_2$
- 3) *o*- $\text{O}_2\text{NPhSeCN}$ , *n*Bu<sub>3</sub>P, THF
- 4)  $\text{H}_2\text{O}_2$ , Py, THF



- 1) TBDPSOTf, Py
- 2) LiOH, MeOH
- 3) **4**, EDC, DMAP,  $\text{CH}_2\text{Cl}_2$



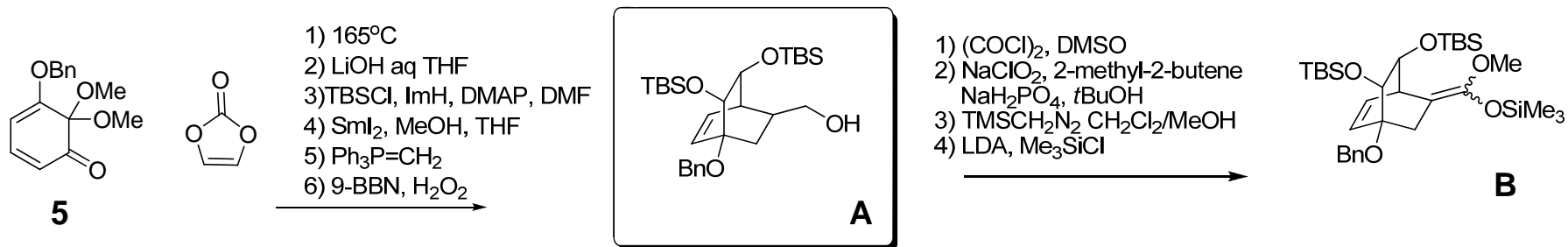
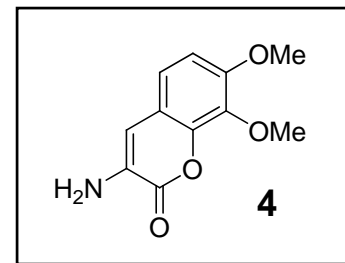
- 1)  $\text{Zn}(\text{OTf})_2$ , EtSH,  $\text{NaHCO}_3$ ,  $\text{CH}_2\text{Cl}_2$
- 2)  $\text{CH}_3\text{SO}_2\text{Cl}$ , Py,  $\text{CH}_2\text{Cl}_2$
- 3) LiCl, DMF
- 4) aq. HF, THF



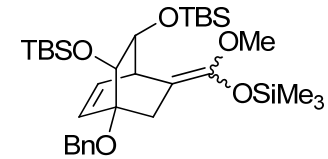
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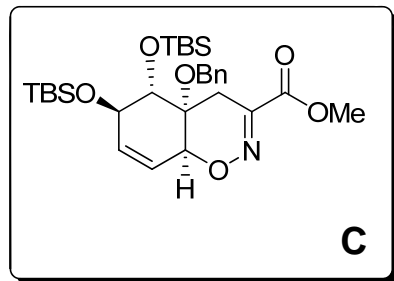
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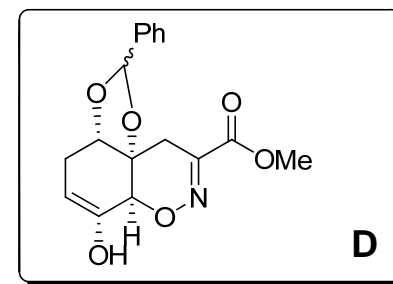
- 1) (COCl)<sub>2</sub>, DMSO  
2) NaClO<sub>2</sub>, 2-methyl-2-butene, NaH<sub>2</sub>PO<sub>4</sub>, *t*BuOH  
3) TMSCH<sub>2</sub>N<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH  
4) LDA, Me<sub>3</sub>SiCl



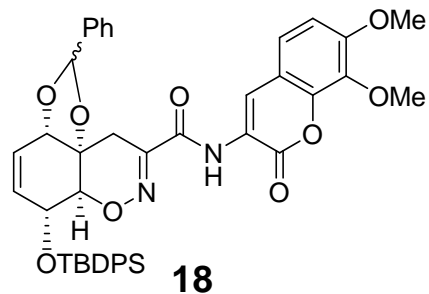
- 1) *i*C<sub>5</sub>H<sub>11</sub>ONO 2.1eq  
TiCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>



- 1) aq HF, MeCN  
2) DDQ, MS 3A, CH<sub>2</sub>Cl<sub>2</sub>  
3) *o*-O<sub>2</sub>NPhSeCN, *n*Bu<sub>3</sub>P, THF  
4) H<sub>2</sub>O<sub>2</sub>, Py, THF



- 1) TBDPSOTf, Py  
2) LiOH, MeOH  
3) **4**, EDC, DMAP, CH<sub>2</sub>Cl<sub>2</sub>



- 1) Zn(OTf)<sub>2</sub>, EtSH, NaHCO<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>  
2) CH<sub>3</sub>SO<sub>2</sub>Cl, Py, CH<sub>2</sub>Cl<sub>2</sub>  
3) LiCl, DMF  
4) aq. HF, THF

