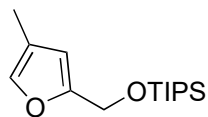
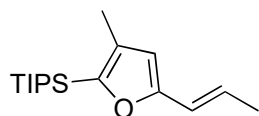


Total Synthesis of (±)-Rubriflorldilactone A

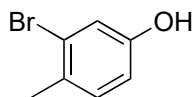
Xudong Zheng, Xinlong Guo, Hongyu Wang, Pan-Pan Zhou, and Xiaoming Chen, *J. Am. Chem. Soc.* 2024, 146, 7198–7203



1-4

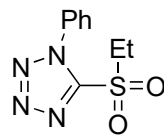


A

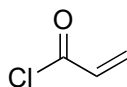


1-13

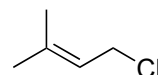
- 1) *n*-BuLi, TIPSCl
- 2) TBAF
- 3) IBX
- 4) KHMDS, **1**



1

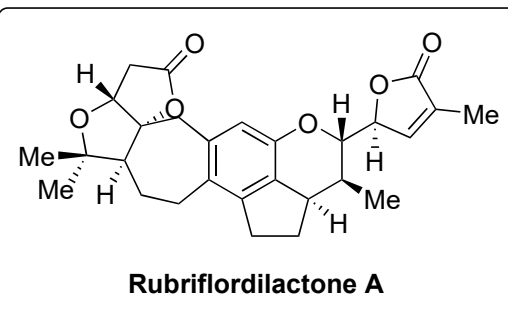


2



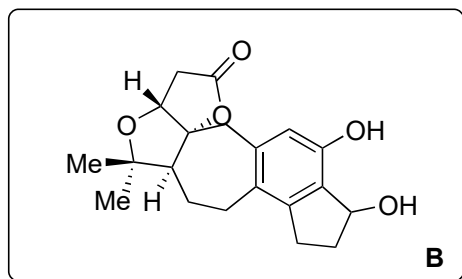
3

- 1) AlCl₃, **2**, 0 °C, then AlCl₃, 180 °C
- 2) CuCN, 150 °C, then MOMCl, DIPEA
- 3) DIBAL-H, then TBSOTf, DMAP
- 4) *n*-BuLi, TMEDA, **3**, then NaBH₄
- 5) NBS, Me₂S
- 6) *n*-BuLi, furan
- 7) *hν*, MB, ¹O₂, MeOH, then Ac₂O, pyr.
- 8) TBAF
- 9) IBX
- 10) BF₃·OEt₂, 2-methyl-2-butene, 4Å MS, DCE, reflux

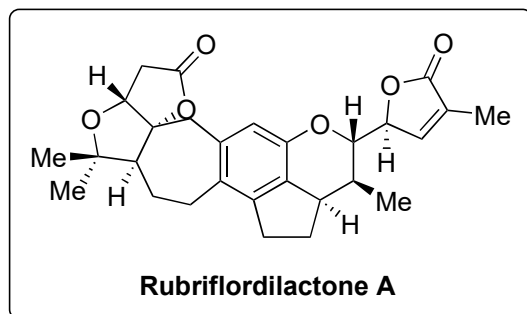


1) Name both reactions
Fries rearrangement + Nazarov cyclization

7) Propose a mechanism for this transformation
Prins reaction, may proceed by a carbocation intermediate



14-15



- 11) DIPEA, MOMCl
- 12) Fe(acac)₃, NaHCO₃, *p*-NO₂PhSO₃Me, PhSiH₃, *then* TFA
- 13) NaBH₄

- 14) Sc(OTf)₃, **A**, 4Å MS, DCM, r.t.
- 15) *hν*, MB, ¹O₂, DCM, *then* NaBH₄, *then* silica gel

- 12) Name the iron-catalyzed step
What is the purpose of TFA?
It is a Mukaiyama-type hydration
TFA promotes oxa-Michael reaction

- 14) How would you call this step?
Propose a mechanism
Authors call it intermolecular ortho-quinone methide type [4+2]-cycloaddition

- 15) What is the purpose of NaBH₄ and silica gel?
Dehydration of the intermediate formed in singlet-oxygen reaction