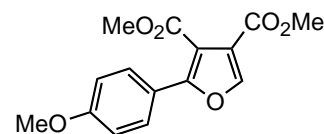


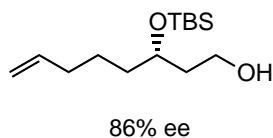
- 1) $(\text{COCl})_2$, $(\text{CH}_2\text{Cl})_2$, reflux, 24 h
- 2) evaporation


- 3) TMSCHN_2 (1.2 equiv), MeCN, 0 °C, 0.5h
- 4) DMAD (2.0 equiv), reflux, 11 h
(62 %, for 3 steps)

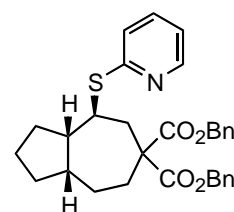


DMAD = dimethyl acetylenedicarboxylate

Hari, Y.; Iguchi, T.; Aoyama, T. *Synthesis* **2004**, 9, 1359-1362



1. I_2 , PPh_3 , imidazole, CH_2Cl_2 , 0 °C (94%)
2. NaH, allylmalonic acid dibenzyl ester, THF, 0 °C to rt (96%)
3. 20 mol% Grubbs' 2 nd-generation catalyst, 1mM CH_2Cl_2 , 40 °C, 16 hr (88%)
4. TBAF, THF, 0 °C to rt (95%)
5. (i) oxalyl chloride
(ii)  toluene, hv, -15 °C (51%)



68% ee

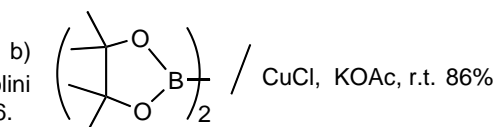
Dalgard J. E.; Rychnovsky, S. D.
Org. Lett. **2004**, 6, 2713

TS
9.04



- 1) $\text{PhI}(\text{OAc})_2$, $(\text{CF}_3)_2\text{CHOH}$, r.t.
- 2) TBDPSCl, imidazole, DMF, 82%
- 3) KHMDS, THF, -100 °C, 89%
- 4) PhSH , $\text{BF}_3\text{-OEt}_2$ (cat.), CH_2Cl_2 , 0 °C, 77%
- 5) Raney Ni, EtOH/THF, 77%
- 6) tBuLi , THF, -77 °C, (\pm) -1-octene oxide, $\text{BF}_3\text{-OEt}_2$
- 7) Dess-Martin periodinane, CH_2Cl_2 , 88%
- 8) a) DBU, DMF, then

S. Canesi, D. Bouchu, and M. A. Ciufolini
Angew. Chem. Int. Ed. **2004**, 43, 4336.



- 9) -1) a) NaBH_3CN , AcOH, MeOH, 0 °C, then
b) H_2O_2 , NaOH, 80%
- 9) -2) a) TBAF, 95%
b) $\text{NaBH}(\text{OAc})_3$, AcOH (cat.), CH_2Cl_2 , 73%
c) TBDPSCl, imidazole, DMF, 95%
d) H_2O_2 , NaOH, 97%

