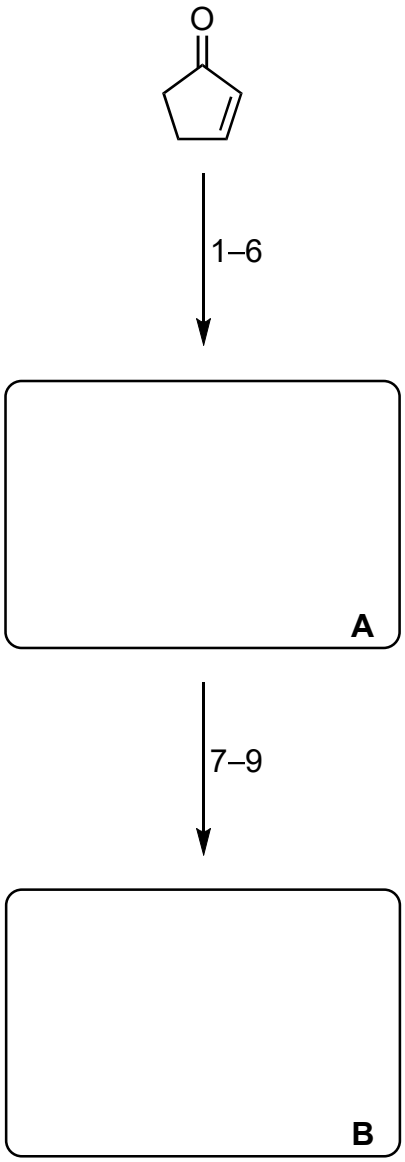
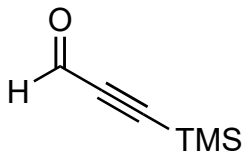
Total Synthesis of Chalcitrin

M. Yang, F. Yin, H. Fujino, S. A. Synder, *J. Am. Chem. Soc.* **2019**, *141*, 4515–4520.



1) $PhMe_2SiLi$, MeLi, CuCN, *then* **1**
2) MOMBr, DIPEA
3) $AgNO_3$, NIS
4) KHMDS, TIPSCl
5) **2**, AgOTf
6) allylTMS, $SnCl_4$



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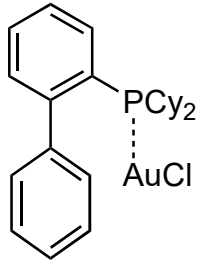

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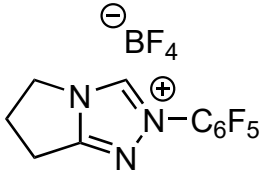
7) $(Sia)_2BH$, *then* $NaBO_3 \cdot H_2O$
8) DMP
9) **3**, NEt_3



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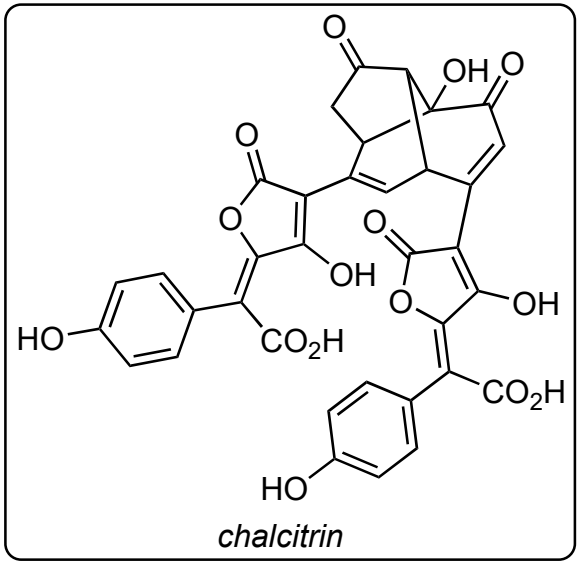
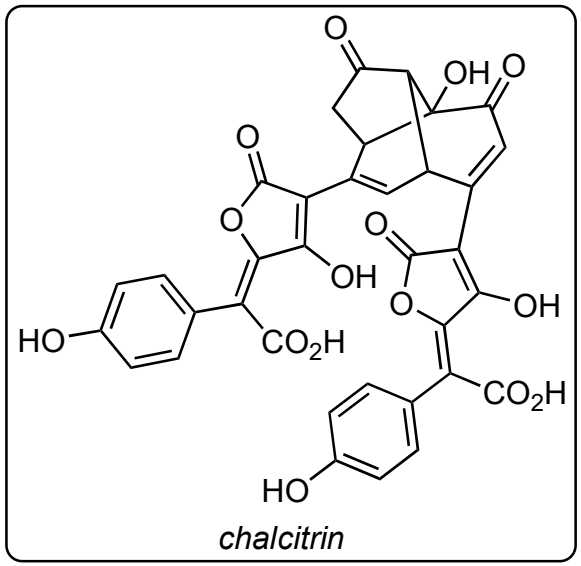
1) Hint: No methyl addition.
5) Name of the reaction?
6) Who developed this? The reaction is more known with carbonyls instead of allylic halides, ethers, and acetates.
7) Who developed this chemistry (nobel prize 1979)? Structure of $NaBO_3 \cdot H_2O$?
9) Mechanism? Name of the reaction?



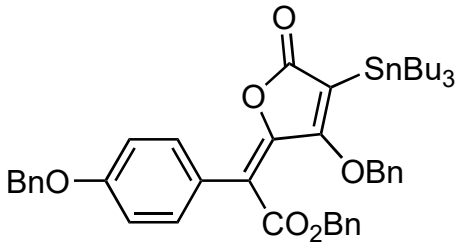
chalcitrin

10–17



chalcitrin

10) BF_3, AcOH
11) CSA, $CH(OMe)_3$, MeOH, *then* H_2O_2, KF, $NaHCO_3$
12) DMP
13) *t*-BuOOH, PIDA, Cs_2CO_3
14) LiOH
15) $(COBr)_2$, DMF
16) $Pd(PPh_3)_4$, CuTC, **4**
17) BBr_3



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10–11) Name of the reaction?
11) Hint: An enol ether is formed in the first part of reaction 11.
13) Mechanism?
16) Name of the reaction?
Structure of CuTC? What is the role of copper(I) here?

NMR hint for compounds with readily protonated/deprotonated species: Only when synthetic chalcitrin was titrated in DMSO-d_6 with NaDMSO-d_5 did its NMR data match that of the natural.