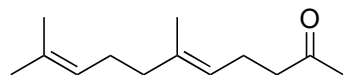
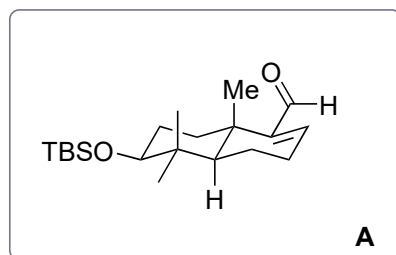


Synthetic Studies on Selective, Proapoptotic Isomalabaricane Triterpenoids Aided by Computational Techniques

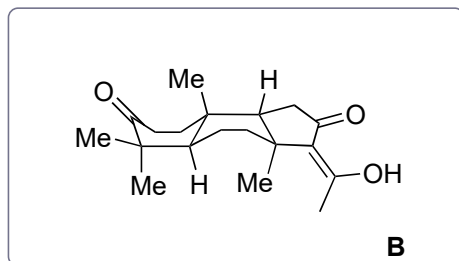
Y. D. Boyko, C. J. Huck, S. Ning, A. S. Shved, C. Yang, T. Chu, E. J. Tonogai, P. J. Hergenrother, D. Sarlah, *J. Am. Chem. Soc.* **2021**, *143*, 2138–2155.



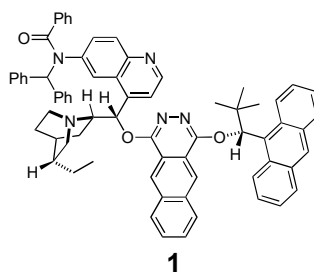
1 – 6



7 – 12



- 1, $K_2OsO_4 \cdot 2H_2O$, K_2CO_3 , $K_3[Fe(CN)_6]$, $CH_3SO_2NH_2$
- MsCl, py, then K_2CO_3 , MeOH
- TosMIC, *t*-BuOK, EtOH
- Cp_2TiCl_2 , Zn
- TBSOTf, 2,6-lutidine
- LDA, THF/ CH_2Cl_2 , $-100\text{ }^\circ\text{C} \rightarrow 60\text{ }^\circ\text{C}$, then $LiClO_4$, $CaCO_3$, DMPU, $140\text{ }^\circ\text{C}$

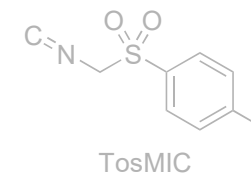


- C_2H_2 , *n*-BuLi, then PivCl
- $Au(PPh_3)Cl$, AgOTf, selectfluor, then NH_2NHTs
- NEt_3 , $CHCl_3/MeOH$, then catecholborane, AcOH, then NaOAc, Δ
- Cp_2ZrCl_2 (1.3 equiv), *n*-BuLi (2.4 equiv), then CuOAc, AcCl
- $BH_3 \cdot SMe_2$, then HF, then H_2O_2 , NaOH
- IBX (10 equiv)

- Name of the starting material? geranylacetone
- Structure of TosMIC? Name of the reaction? van Leusen reductive cyanation

What happens with aldehydes under the same conditions? What change in the experimental procedure needs to be made to get the same product as with ketones? Aldehydes typically form oxazoles with TosMIC (van Leusen oxazole synthesis). Later addition of alcohol (protic reagents) enables reductive cyanation for aldehydes (A. M. van Leusen, P. G. Oomkes, *Synth. Commun.* **1980**, *10*, 399–403).

- Propose a mechanism. see below; Name of the reaction? Nozaki–Yamamoto homologation



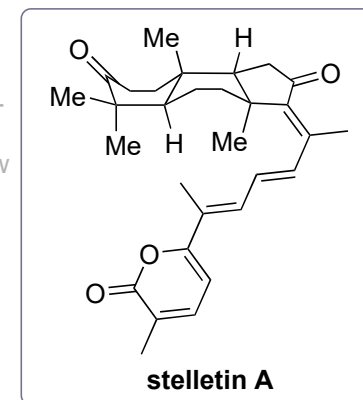
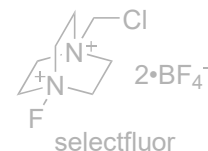
- Propose a mechanism. see below; Name of the first reaction?

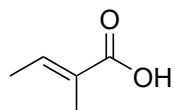
Rautenstrauch cycloisomerization
Structure of selectfluor?

- Hint: No fluorine is left in the molecule after NEt_3 , $CHCl_3/MeOH$. Who developed this reduction?

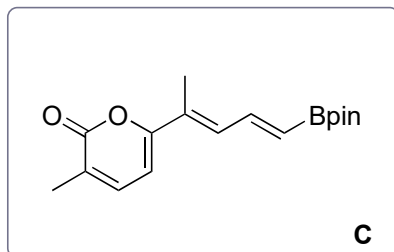
Kabalka; Classify the reaction. Retro-rene reaction

- Propose a mechanism. see below



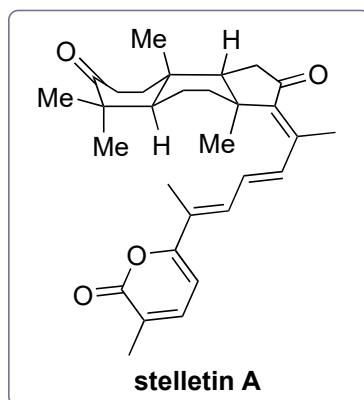


13 – 16

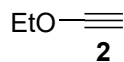


B

17 – 18



- 13) $(\text{COCl})_2$, DMF, *then* NEt_3
14) OsO_4 , NMO, *then* $\text{PhI}(\text{OAc})_2$
15) $\text{BH}_3 \cdot \text{SMe}_2$, **2**, Et_2Zn , *then* substrate, *then* aq. HCl
16) LiTMP, $\text{CH}_2(\text{Bpin})_2$

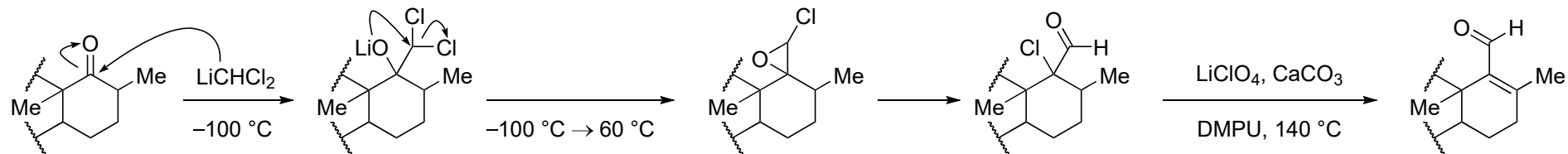


- 17) $(\text{COBr})_2$, DMF
18) $\text{Pd}(\text{OAc})_2$, PPh_3 , TMSOK, **C**

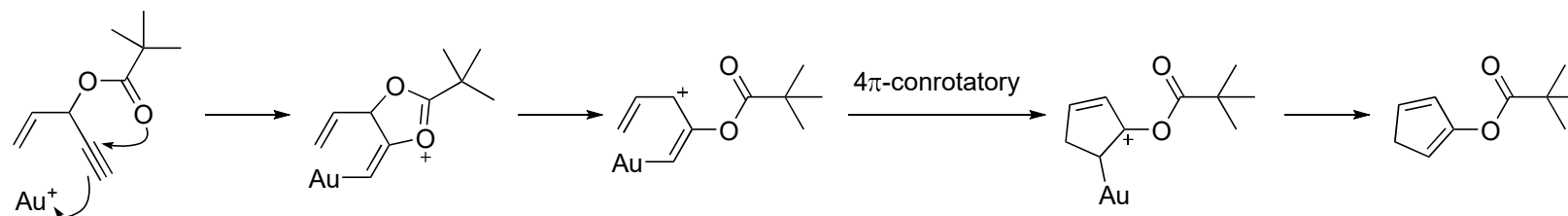
- 13) Hint: Dimerization
14) Name of the reaction? Lemieux–Johnson oxidation
16) Name of the reaction? Boron–Wittig reaction

- 18) Name of the reaction? Suzuki–Miyaura coupling

ad 6) proposed mechanism (H. Taguchi, S. Tanaka, H. Yamamoto, H. Nozaki, *Tetrahedron Lett.* **1973**, *14*, 2465–2468.)



ad 8) proposed mechanism



ad 10) proposed mechanism (H. Ito, T. Taguchi, Y. Hanzawa, *Tetrahedron Lett.* **1992**, *33*, 1295–1298.)

