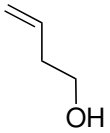
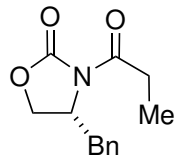


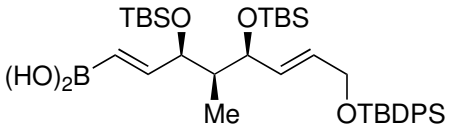
1. TBSCl, DMF, imid., (90%)
2. O_3/O_2 then PPh_3, (83%)
3. isopropenylmagnesium bromide, THF;
4. triethylorthoacetate, propionic acid, 150°C (75% over two steps): NAME REACTION, *provide a transition state drawing*
5. DIBAL, CH_2Cl_2, -78°C, (97%)

A



1. Bu_2BOTf, TEA, then **A** (88%), *provide a transition state drawing, indicate all forms of diastereoselection*
2. MeNHOMe-HCl, Me_3Al, THF (96%)
3. TBSCl, DMF, imid., (96%)
4. TSOH/ nBu_4NHSO_4 (1:4), MeOH, 0°C, (89%)
5. DMP, $NaHCO_3$, (94%)
6. CBr_4, PPh_3, CH_2Cl_2, $NaHCO_3$, (74%) NAME REACTION, *MECHANISM*

B +

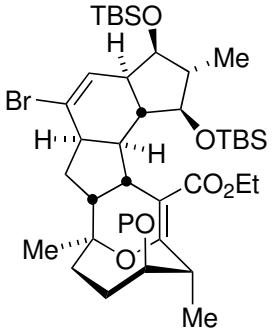


1. $Pd(PPh_3)_4$ (0.05 equiv.), Tl_2CO_3, H_2O-THF (1:3), (84%)
2. DIBAL, CH_2Cl_2, -78°C
3. ethyldiazoacetate, $SnCl_2$, (70% over two steps) NAME REACTION, *MECHANISM*
4. TBAF, AcOH, DMF, (92%)
5. I_2, PPh_3, CH_2Cl_2
6. Cs_2CO_3, THF (0.005 M), (77% over two steps)

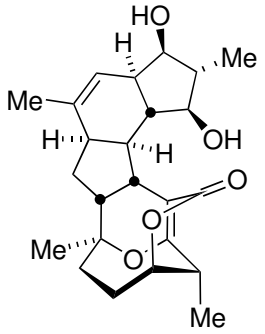
C

$Ph_2Se_2O_3$, SO_3-Pyr, TEA, THF then hexanes, 50°C

(63% over two steps)



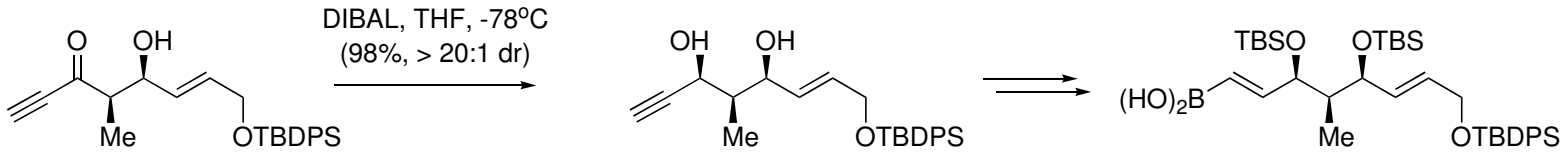
1. $Me_3B_3O_3$, $Pd(dppf)Cl$ (0.1 equiv), Cs_2CO_3, DMF-H_2O (2:1), 100°C, (71%)
2. TMSOK, THF
3. Mukaiyama's Reagent, $NaHCO_3$, CH_2Cl_2, (62%)



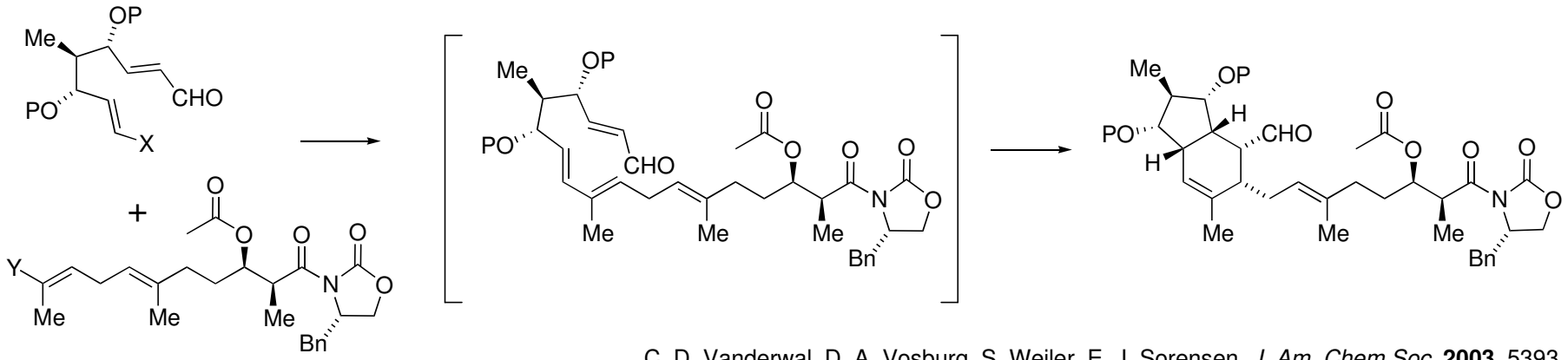
(-)-FR182877

Starr, J.; Evans, D. *JACS*, **2003**, 13537.

Kiyooka's Method for syn 1,3 reduction: provide a transition state drawing that predicts the correct diastereoselection in this reduction



FR 182877 was a molecule that recieved considerable interest from the chemical community during the late 90's until it's synthesis in 2003. While a similar biosynthetic proposal was put forth by Sorensen and co-workers their initial synthetic attempts involved a different appraoch:



C. D. Vanderwal, D. A. Vosburg, S. Weiler, E. J. Sorensen, *J. Am. Chem Soc.* **2003**, 5393.

What type of Diels-Alder is presented in Sorensen's work? While this reaction proceeded with a high degree of diastereoselection favoring the *endo* adduct, the product was dissapointingly issolated as a 1.6-1 mixture of diastereomers. What type of diastereoselection is lacking in the above Diels-Alder? Evans and Starr observed a similar phenomenon while performing mechanistic investigations on FR182877. Remarkably, the pentacyclic adduct shown above was isolated as a *single* diastereomer. Use this information to select the stereocenters present in **C** that impart this high diastereocontrol.