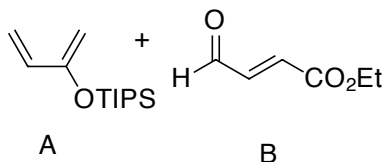
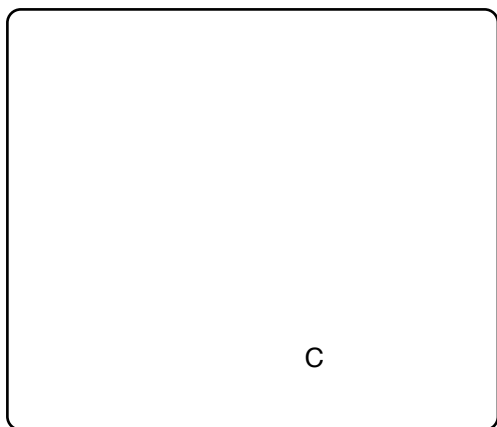


Synthesis Challenge # 39

AG Wegner
27.08.2015



↓ 1-7

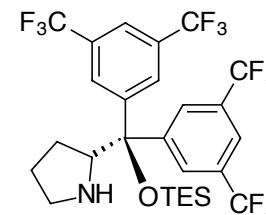


↓ 8-11



- 1) I (0.1 equiv), TFA (20 mol%), toluene, $-10\text{ }^{\circ}\text{C}$
- 2) AlMe_3 (2.3 equiv), MeMgBr (1.5 equiv), CH_2Cl_2 , $-78\text{ }^{\circ}\text{C}$
- 3) DMP (1.1 equiv), NaHCO_3 (8.0 equiv), CH_2Cl_2 , rt
- 4) MeMgCl , THF, -78 to $-25\text{ }^{\circ}\text{C}$
- 5) KHMDS (2.0 equiv), THF, -78 to $0\text{ }^{\circ}\text{C}$ followed by addition of $\text{P}(\text{OMe})_3$ (2.0 equiv), O_2 , $0\text{ }^{\circ}\text{C}$, 1 h, then TESCl (1.2 equiv)
- 6) KOtBu (10.0 equiv), CHBr_3 (7.5 equiv)
- 7) $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ (2.5 equiv), acetone, rt

- 8) ethynyltrimethylsilane (1.25 equiv), DIPA (3.0 equiv), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.06 equiv), CuI (20 mol%), THF,
- 9) (3-methylbut-3-en-1-yl)magnesium bromide CeCl_3 (3.0 equiv), THF, $0\text{ }^{\circ}\text{C}$
- 10) $\text{Co}_2(\text{CO})_8$ (0.5 equiv), Celite (10 wt), toluene, reflux
- 11) AgF (10.0 equiv), THF, MeOH , H_2O , $80\text{ }^{\circ}\text{C}$

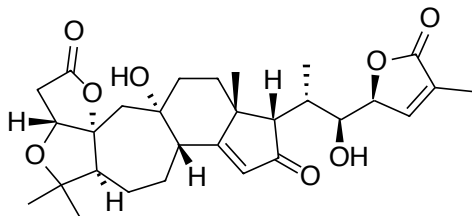


Please, provide a detailed mechanism for step 10).

12-17



18-19



- 12) Pd(OH)₂/C (0.7 wt), CH₂Cl₂, rt
- 13) *m*-CPBA (2.5 equiv), CH₂Cl₂, rt,
- 14) Ac₂O (3.0 equiv), Et₃N (10.0 equiv), CH₂Cl₂, 0 °C
- 15) LiHMDS (2.5 equiv), THF, -78 to -40 °C
- 16) Martin's sulfuran (1.8 equiv), CH₂Cl₂, rt
- 17) Pd₂dba₃·CHCl₃ (0.1 equiv), *n*Bu₃P (0.2 equiv), HCOOH (5.0 equiv), DIPEA (2.0 equiv), dioxane, 45 °C

- 18) TIPOTf (1.5 equiv), Et₃N (2.0 equiv) then enolsilane **II**, CAN (4.5 equiv), DTBP (10 equiv), CH₃CN, -50 to -30 °C
- 19) 18-crown-6 (15.0 equiv), KHMDS (5.0 equiv), **III** (5.0 equiv)
- 20) OsO₄ (0.07 equiv), NMO (2.0 equiv), THF/H₂O (1:1), 4 °C, 72 h

What is Martin's Sulfuran and how does it work?

Step 18 furnishes a mixture of isomers. Which ones and why?