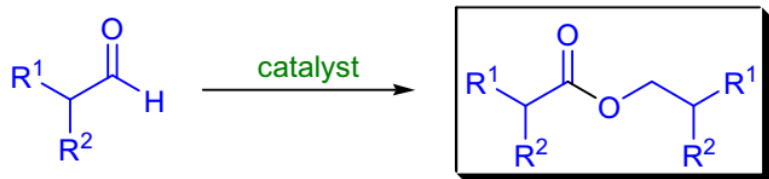
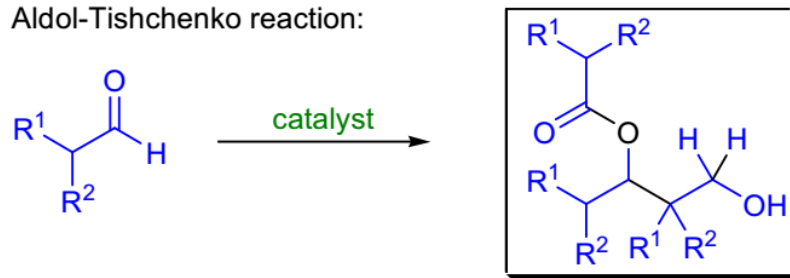


Tishchenko Reaction

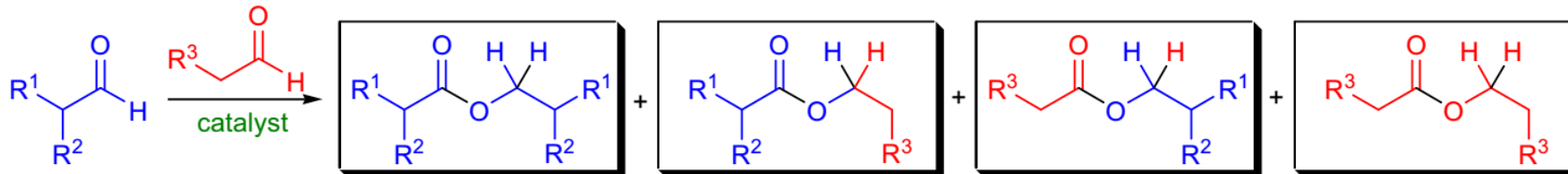
Traditional Tishchenko reaction:



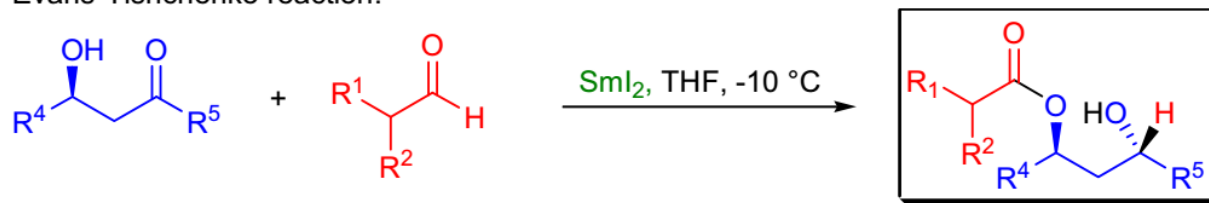
Aldol-Tishchenko reaction:



Crossed- (mixed-) Tishchenko reaction:



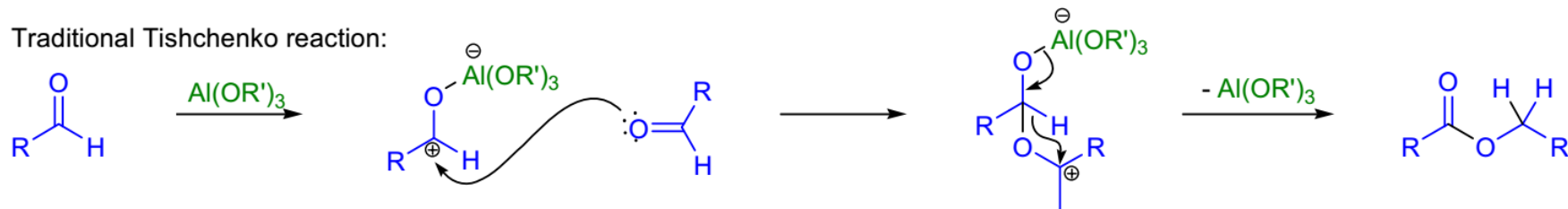
Evans-Tishchenko reaction:



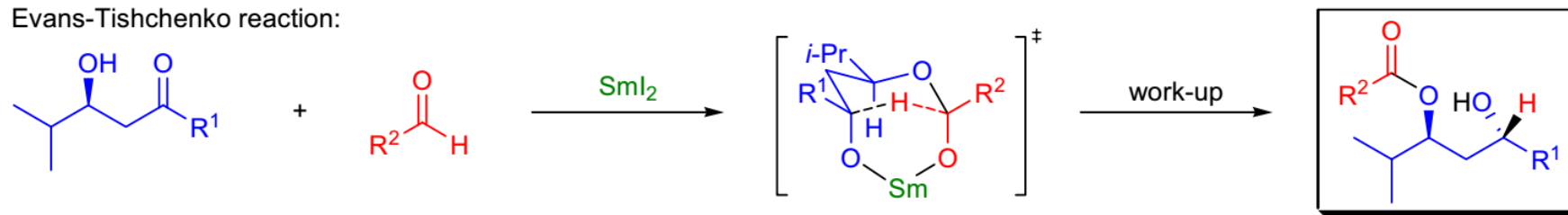
$R^1, R^2, R^3 = \text{H, alkyl, aryl}$; $R^4, R^5 = \text{alkyl, aryl}$; **catalyst**: $AlOR_3$; $NaOR$; MO , $M = \text{Ba, Sr, Mg}$; $RuH_2(PPh_3)_4$; $[\eta^4-C_4Ph_4-CO)Ru(CO)_3]_2$; $CpMH_2$, $M = \text{Hf, Zr}$; $Na_2Fe(CO)_4$; $ROIr(CO)(PPh_3)_2$; $Ln[N(SiMe_2)_3]$, $Ln = \text{La, Sm, Y}$; $EtLnI$, $Ln = \text{Pr, Nd, Sm}$; Sml_2

Mechanism

Traditional Tishchenko reaction:

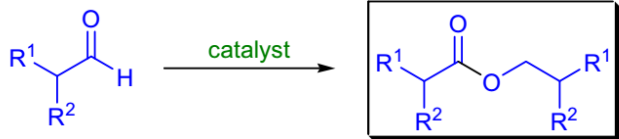


Evans-Tishchenko reaction:



Features

Traditional Tishchenko reaction:



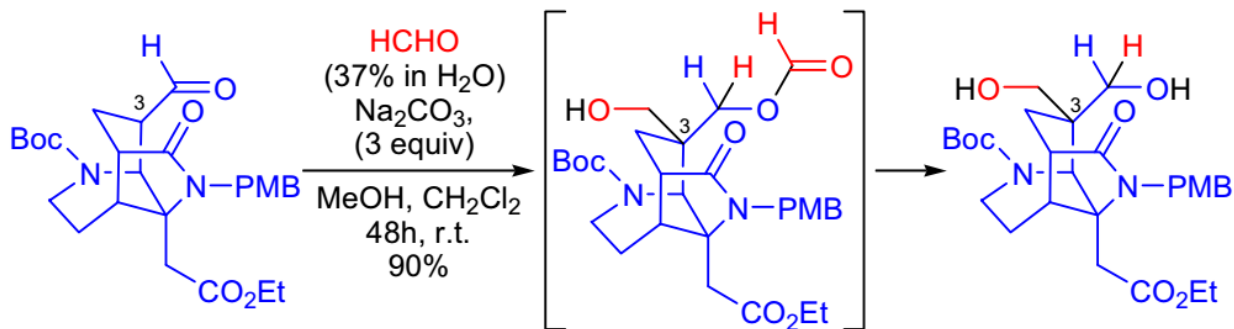
Crossed- (mixed-) Tishchenko reaction:

Aldol-Tishchenko reaction:

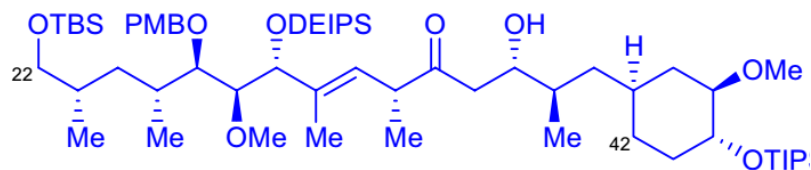
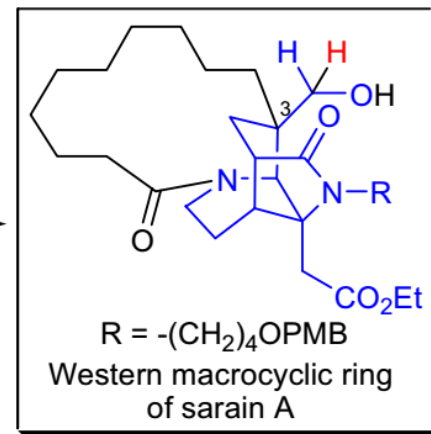


- 1) the reaction can take place between the same or different aldehydes;
- 2) the reaction can take place in an intramolecular fashion, yielding the corresponding lactone;
- 3) The most general catalysts in the traditional Tishchenko reaction are aluminum alkoxides, but a wide-variety of catalysts can be used: 1) alkali- and alkali earth metal oxides and alkoxides; 2) transition metal-based catalysts such as ruthenium complexes ($\text{RuH}_2(\text{PPh}_3)_4$, certain rhodium-, iridium-, and iron complexes, and metallocenes of group IV metals (Cp_2MH_2 , $\text{M} = \text{Hf}, \text{Zr}$); 3) lanthanide based catalyst such as lanthanide amides ($\text{Ln}[\text{NSiMe}_2)_3]$, $\text{Ln} = \text{La}, \text{Sm}, \text{Y}$), organolanthanoid halides (EtLnX , $\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}$, $\text{X} = \text{I}$) and SmI_2 .
- 4) A modification of the Tishchenko reaction is the aldol-Tishchenko reaction where the aldehyde first undergoes an aldol reaction followed by the Tishchenko reaction to form monoesters of 1,3-diols.
- 5) The most widely used modification of the Tishchenko reaction is the Evans Tishchenko reaction. In this transformation, a chiral β -hydroxy ketone reacts with an aldehyde in the presence of catalytic SmI_2 to provide the anti 1,3-diol monoester product with excellent diastereoselectivity.

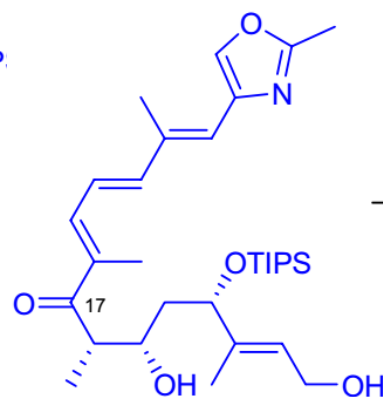
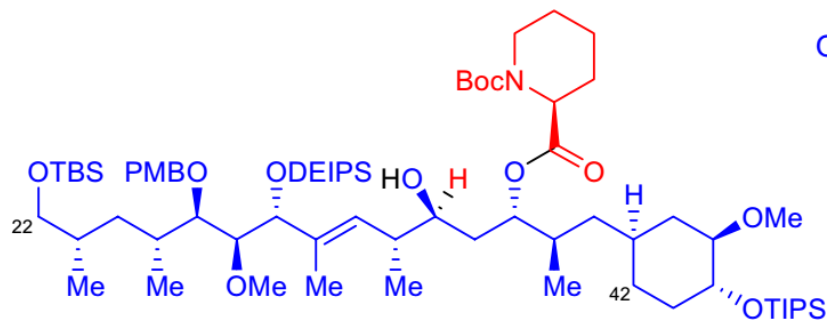
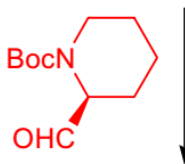
Applications



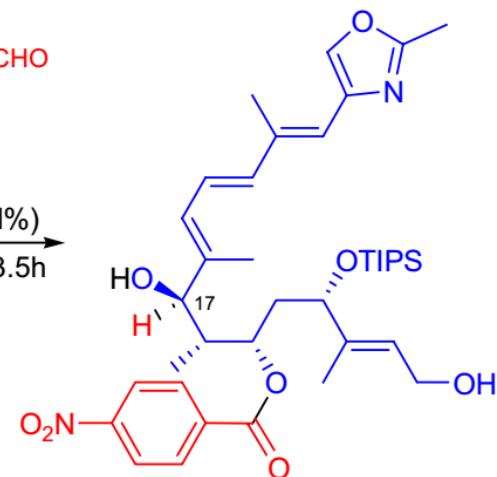
steps



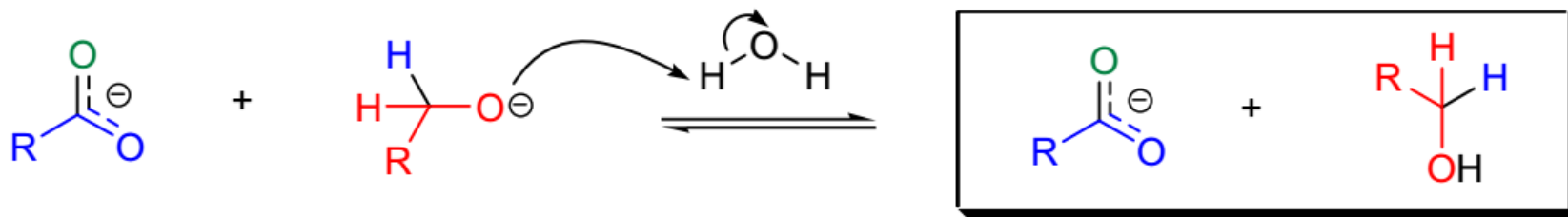
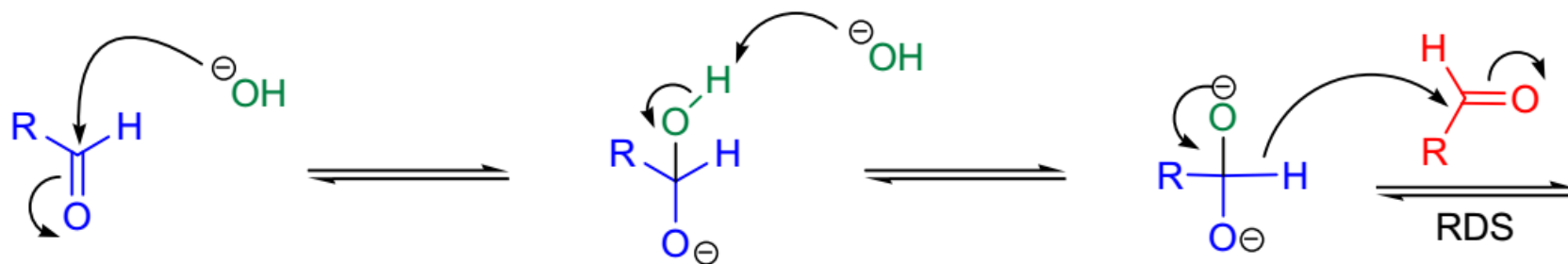
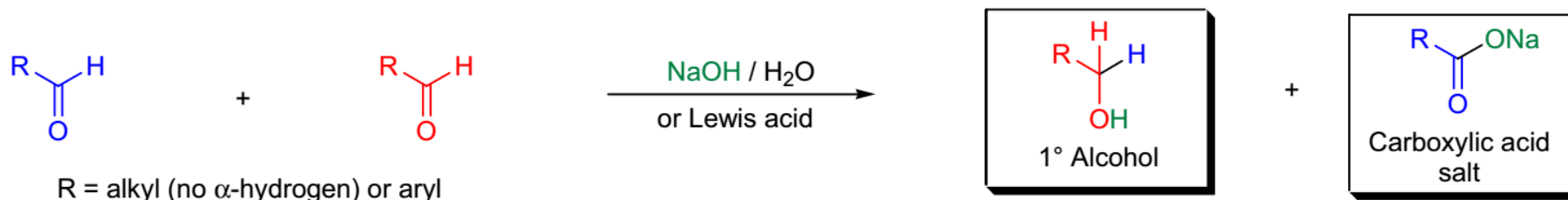
$\text{Sml}_2\text{-PhCHO}$
 $\text{THF}, -10^\circ\text{C}$
 $> 20:1, 95\%$



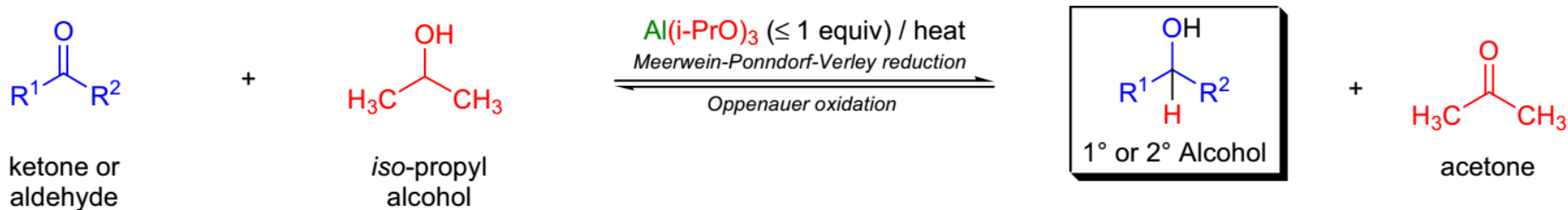
$\text{O}_2\text{N-CHO}$
 (5 equiv)
 Sml_2 (30 mol%)
 $\text{THF}, -10^\circ\text{C}, 3.5\text{h}$
 83%



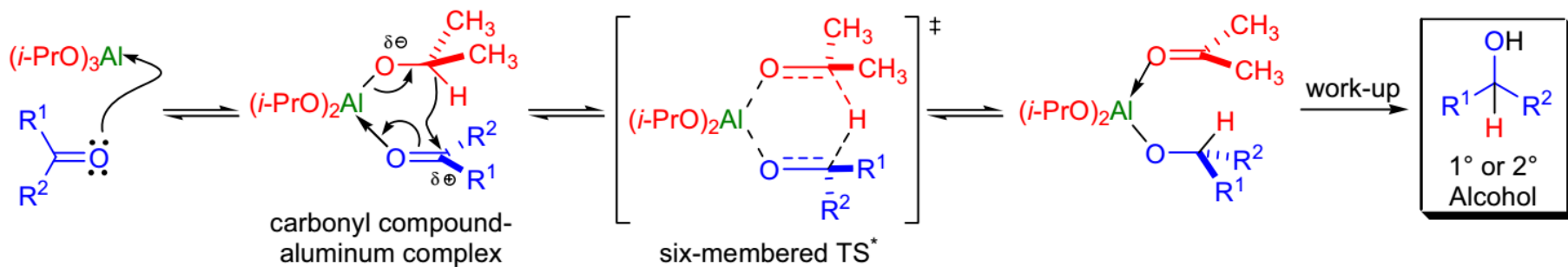
Cannizzaro Reaction



Meerwein-Ponndorf-Verley Reduction (MPV Reduction)



R^1 = alkyl, aryl, alkenyl; R^2 = H, alkyl, aryl, alkenyl



Oppenauer Oxidation

