

1. Identify the intermediate in Taylor and co-workers' synthesis of the aglycon portion of neopeltolide (*Org. Lett.* **2008**, *10*, 5047–5050). Additionally, rationalize the observed diastereoselectivity. (Proton sponge, 1,8-bis(dimethylamino)naphthalene) [★]

2. Identify the intermediates of the following synthetic sequence and identify the type of transformation involved. [★★]

3. In 2020, Chen, Xie and co-workers (*Green Chem.* **2020**, *22*, 1542–1547) developed the polymer species in figure. Identify a possible synthesis (including conditions) of the monomer precursor. [★]

4. The team of Kirsch reported the synthesis of Cryptoconcatone C, a natural product polyketide (*J. Org. Chem.* **2022**, *87*, 14899–14908). Identify the missing intermediates and locate the fragment structure in the final molecule. [★]

5. Houk and McGlacken reported the following transformation, which proceeds with remarkable diastereoselectivity. Describe the possible steps of the transformation that can account for the stereochemical outcome and provide a rationalization of it (*Org. Lett.* **2021**, *23*, 6372−6376). [★★★]



6. Identify the starting material, intermediates, and reaction conditions of the following synthetic sequence (HMPA, hexamethylphosphoramide; LDA, lithium diisopropylamide; TBS, *tert*-butylphenylsilyl; TMS, trimethylsilyl). [★★]

7. Propose a synthetic strategy of the following molecule, starting from butanal and 2-pentanone, which involves the Evans-Tishchenko reaction. [★★]

8. Schneider and co-workers reported the following transformation. Explain the mechanism underlying the transformation (*Chem. Commun.* **2001**, 1218–1219). [★★]

9. In their seminal publication in 1990 (*J. Am. Chem. Soc.* **1990**, *112*, 6447-6449), Evans and Hoveyda observed the following: (a) Complete deuterium incorporation; (b) Absence of kinetic isotope effect when deuterated acetaldehyde was used. Explain the mechanistic conclusions that can be drawn. [★★]

$$Me \xrightarrow{OH} O \xrightarrow{Me} + D \xrightarrow{D} O \xrightarrow{Sml_2 (15 \text{ mol}\%)} D_3C \xrightarrow{OH} Me$$

$$Me \xrightarrow{Me} Me + H \xrightarrow{H} H \xrightarrow{1:1} D \xrightarrow{D} O \xrightarrow{Sml_2 (15 \text{ mol}\%)} D_3C \xrightarrow{OH} Me$$

$$Me \xrightarrow{Me} Me + H \xrightarrow{H} H \xrightarrow{I:1} D \xrightarrow{D} O \xrightarrow{Sml_2 (15 \text{ mol}\%)} Me$$

$$Me \xrightarrow{Me} Me \xrightarrow{Me} H \xrightarrow{I:1} D \xrightarrow{D} O \xrightarrow{Sml_2 (15 \text{ mol}\%)} O \xrightarrow{Me} Me$$

$$Me \xrightarrow{Me} Me \xrightarrow{Me} H \xrightarrow{I:1} D \xrightarrow{I$$

10. Upon subtle modification from the original Evans-Hoveyda conditions (*J. Org. Chem.* **1999**, *64*, 843-853), epimerization of the α-carbonyl position was observed. Rationalize this observation. [★★]



11. Rationalize the observed relative stereochemistry in the following reaction (J. Org. Chem. 1999, 64, 843-853). [★★★]

12. Hypothesize why the Tishchenko reaction was used to achieve the overall aldehyde oxidation (*J. Am. Chem. Soc.* **2003**, 125, 350-351). (DEIPS, diethylisopropylsilyl; PMB, para-methoxybenzyl; SEM, trimethylsilylethoxymethyl, TIPS, triisopropylsilyl) [★★]