Massachusetts Institute of Technology
Organic Chemistry 5.511

November 30, 2007
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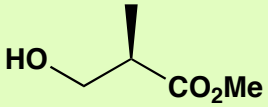
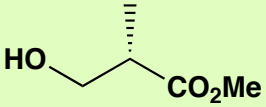
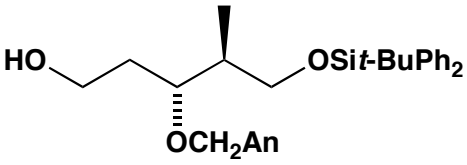
Problem Set 9
Stereocontrolled Addition of Allylmetal Compounds

This problem set focuses on Unit 5 (addition of allylmetal compounds to carbonyl groups) but also employs chemistry introduced in earlier units. In each case, design a highly stereoselective synthesis of the target molecule beginning with commercially available materials. Be sure to explicitly identify all reagents necessary for each transformation. Enantiomerically enriched reagents may be used if they are commercially available; however, with the exception of the two compounds shown below, each stereogenic center in the target molecule must be generated in your synthetic route. In other words, the stereogenic carbons in the chiral reagents you employ cannot be directly incorporated in the final product. The exceptions are (S) and (R) methyl 3-hydroxy-2-methylpropionate, which are commercially available and have been widely employed in total synthesis. A stereoselective synthesis of each of many of these target molecules has been reported in the literature and a reference for each synthesis will be provided with the solutions posted on the 5.511 website.





(1)



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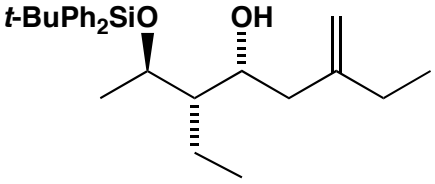

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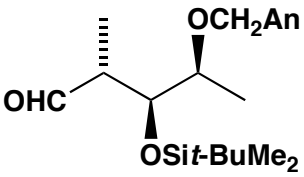
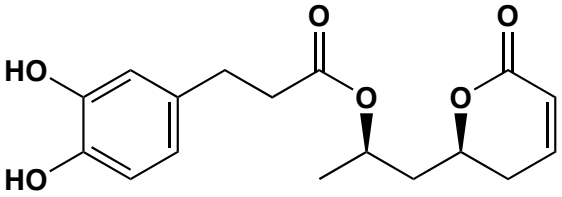
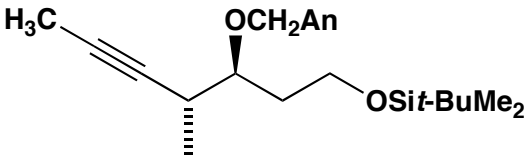


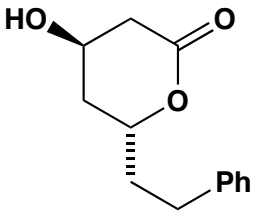
(4)


HO
HO
O
O
O
O

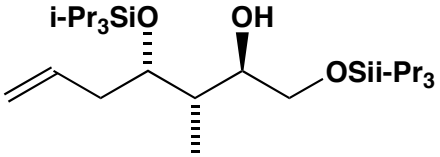
(5)


H3C
OCH2An
OSit-BuMe2

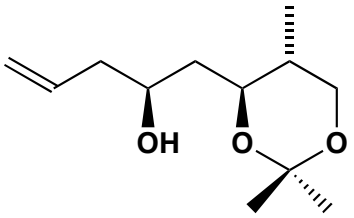
(6)


HO
O
O
Ph

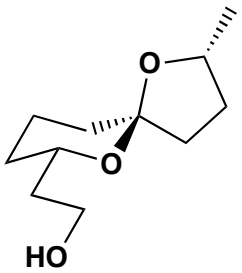
(7)


i-Pr3SiO
OH
OSii-Pr3

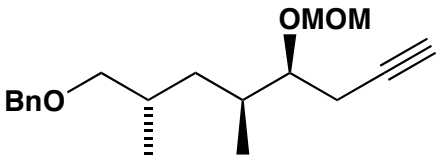
(8)


OH
O
O

(9)


O
O
HO

(10)


OMOM
BnO