Problem Sheet

1) Give a mechanism for the intramolecular Heck reaction C to D shown below, explaining carefully the reasons for the position of the alkene double bond in the product D.

\[
\text{C} \xrightarrow{\text{Pd(CF}_3\text{CO}_2)_2(\text{PPh}_3)_2, \text{base, toluene, heat}} \text{D}
\]

2) Devise a synthesis of the compounds shown below. Each starting material should have 5 carbons or fewer. Show clearly your retrosynthetic analysis and synthetic equivalents where appropriate. Optimally, no more than 3 steps are required. Propose reagents for your forward synthesis.

a)

\[
\text{O} \begin{array}{c}
\text{O}
\end{array} \quad \text{O}
\]

(racemic) (racemic)

b)

\[
\begin{array}{c}
\text{CH}_3
\end{array} \quad \text{N}
\]

\[
\begin{array}{c}
\text{CH}
\end{array} \quad \text{CH}_3
\]

3) a) Suggest a radical-based method for carrying out the following transformations (how is it called?), giving reagents and a mechanism.

\[
\text{OTBDMS} \quad \xrightarrow{\text{}} \quad \text{OTBDMS}
\]
b) Provide a detailed, annotated mechanism for the transformation shown below commenting on all aspects of selectivity.

![Mechanism Diagram]

4)

The synthesis of rosemic tetramethylmediterraneol B was reported by workers in Japan (*J. Org. Chem. 1985, 60, 3318-33*). The pivotal step was the rearrangement of compound 1 into the [1.2.1] bicycle 2, as found in the natural product. Provide a mechanism for the formation of 2 and 3.

![Rearrangement Diagram]

5) Name the following transformations and provide complete curved-arrow mechanisms, and fill in the structures of the products in each case.

a)

![Transformation a Diagram]

b)

![Transformation b Diagram]
6)

Give structures for the products formed in the following reactions and identify all unknown compounds. Explain any issues of selectivity.

a) D-glucose $\xrightarrow{2 \times \text{Me}_2\text{CO}, \text{ZnCl}_2} \text{F} \xrightarrow{\text{NaH, CS}_2, \text{MeI}} \text{G} \xrightarrow{\text{Bu}_3\text{SnH, AIBN, PhH, reflux}} \text{H}$

b) D-mannitol

$\xrightarrow{2 \times \text{Me}_2\text{CO, ZnCl}_2} \text{I} \xrightarrow{\text{Pb(OAc)}_4} \text{J}$

c) D-galactose

$\xrightarrow{2 \times \text{Me}_2\text{CO, ZnCl}_2} \text{K} \xrightarrow{\text{PhCH}_2\text{Br, NaH, THF}} \text{L}$