CHEM95002: Orbitals in Organic Chemistry - Pericyclics

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1. Draw the approach trajectory, the transition state and the Diels-Alder product for the following two diene/dienophile combinations (assume they obey the *endo* rule). *NB*. The second reaction is the first step in an Overman synthesis of racemic pumiliotoxin C.

a)
$$CO_2H$$
 O $NHCO_2Bn$ O H H H H (\pm) -pumiliotoxin C

2. The molecule below was synthesized from a heterocycle, a diene and a disubstituted alkyne in three steps including a selective reduction. Perform a retrosynthetic analysis on the target molecule and hence deduce the synthetic route used:

3. Predict the products of the following reactions:

$$\begin{array}{c|c} CO_2Me & \Delta \\ \hline & CO_2Me \\ \hline & NaN_3 \\ \hline & NH_4CI, LiCI \\ DMF \\ 100 \ ^{\circ}C \\ \hline \\ O & \hline & CO_2Me \\ \hline & 1. \ Et_3N, Me_3SiCI, ZnCI_2 \\ \hline & \Delta \\ \hline & 2. \ H_2O \ work-up \\ \hline \end{array}$$