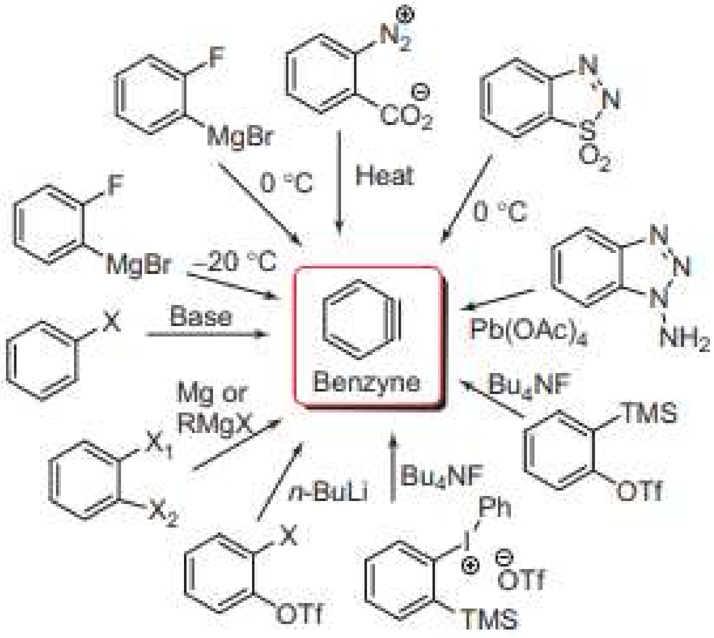
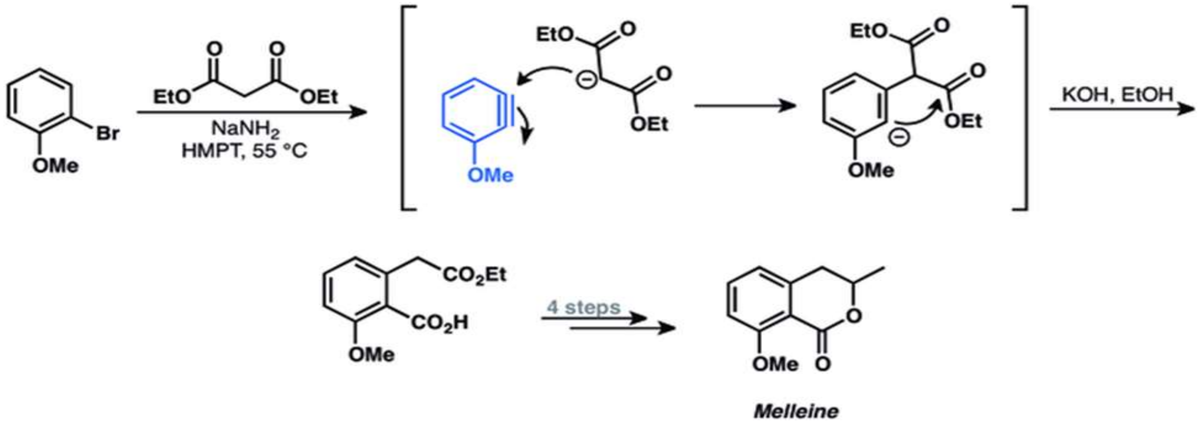
Generation of Benzyne:



Benzyne reactivity:

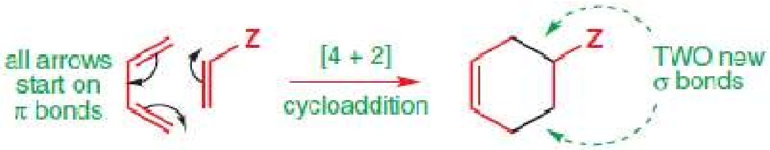
1- **Benzyne reacted** with any **carbaion**:

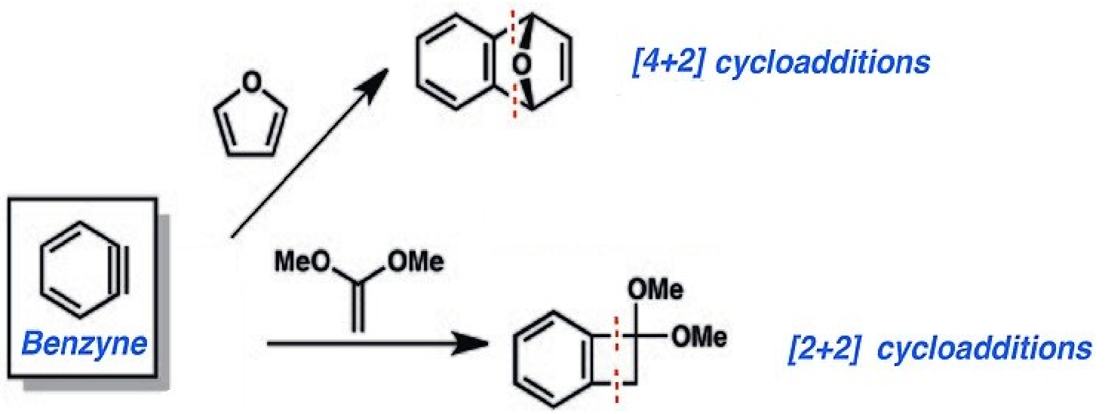
Example: *o*-bromoanisole reacts with ethylmalonate



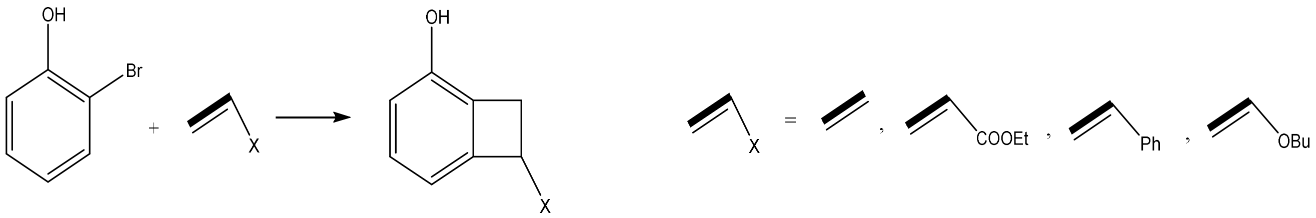
2- **Cycloadditions**: [**2+2**] , [**4+2**] of **Diels-Alder**:

Benzyne reacts with a **wide range** of **olefins** to **give** the **[2+2] cycloadducts** (**four-membered ring**), and **react** with **diene** to **give** the **[2+4] cycloadducts** (**six-membered ring**).





Example:



The Effect of the Leaving Group:

The common leaving groups in **aliphatic nucleophilic substitution** (**halide, sulfate, sulfonate, NR_3, etc.**). Are also common leaving groups in **aromatic nucleophilic substitutions,** but the groups **NO, OR, OAr, SO_2R, and SR**, which are not generally lost in aliphatic systems, are leaving groups when attached to aromatic rings. Surprisingly **NO_2** is a particularly **good leaving** group. fll' an approximate order of leaving-group ability **F > NO_2 > OTs > SOPh > Cl, Br, I > N_3 > NR_3 > OAr, OR, SR, NH**.

Among the **halogens, ftuoro** is generally a much **better leaving** group than the other **halogens**, which have reactivates fairly close together. The order is usually **Cl > Br > I** but not always.

The Effect of the Attacking Nucleophile:

It is not possible to construct an invariant nucleophilicity order because different substrates and different conditions lead to different orders of nucleophilicity, but an overall approximate order is **NH_2 > Ph_3C- > PhNH- (aryne mechanism) > Ars- > RO- > R_2NH- > ArO- > OH- > $ArNH_2$ > NH_3 > I- > Br- > Cl- > H_2O > ROH**.