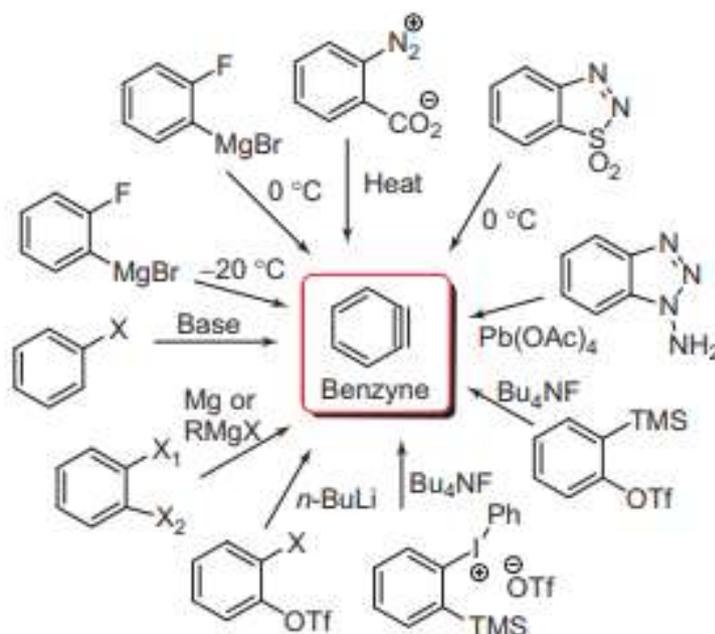
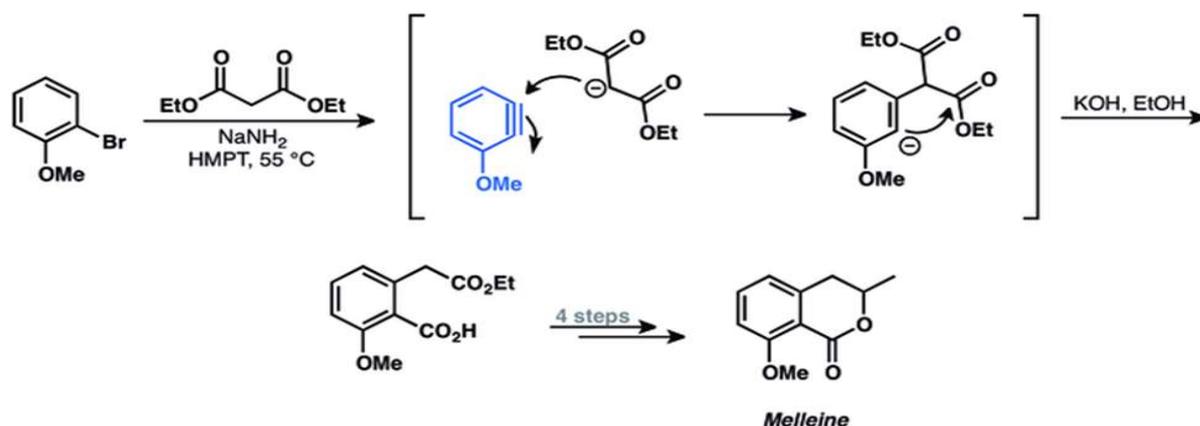


Generation of Benzyne:**Benzyne reactivity:**

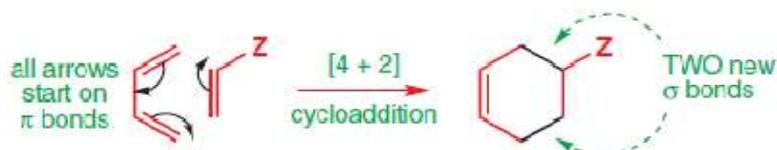
1- **Benzyne reacted** with any **carbanion**:

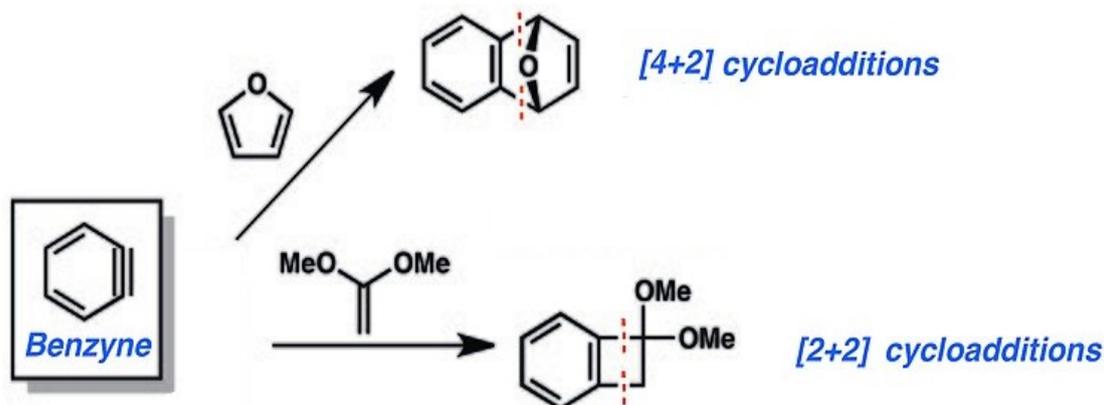
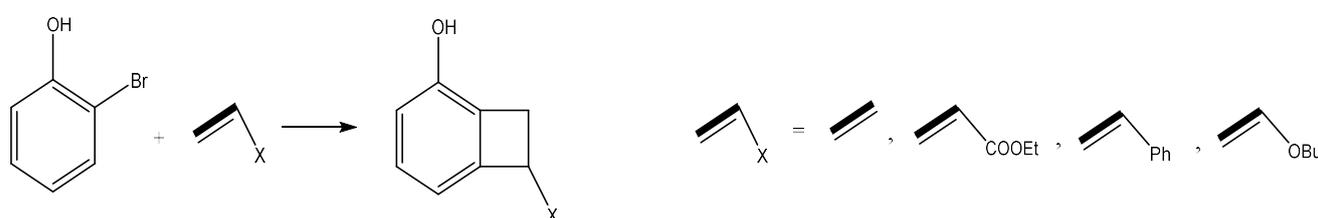
Example: *o*-bromoanisole reacts with ethylmalonate



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, NR₃, etc.**). Are also common leaving groups in **aromatic nucleophilic substitutions**, but the groups **NO, OR, OAr, SO₂R, and SR**, which are not generally lost in aliphatic systems, are leaving groups when attached to aromatic rings. Surprisingly **NO₂** is a particularly **good leaving** group. Here is an approximate order of leaving-group ability **F > NO₂ > OTs > SOPh > Cl, Br, I > N₃ > NR₃ > OAr, OR, SR, NH.**

Among the **halogens, fluoro** is generally a much **better leaving** group than the other **halogens**, which have reactivities 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 **NH₂ > PH₃C- > PhNH- (aryne mechanism) > ArS- > RO- > R₂NH > ArO > OH- > ArNH₂ > NH₃ > I- > Br- > Cl- > H₂O > ROH.**