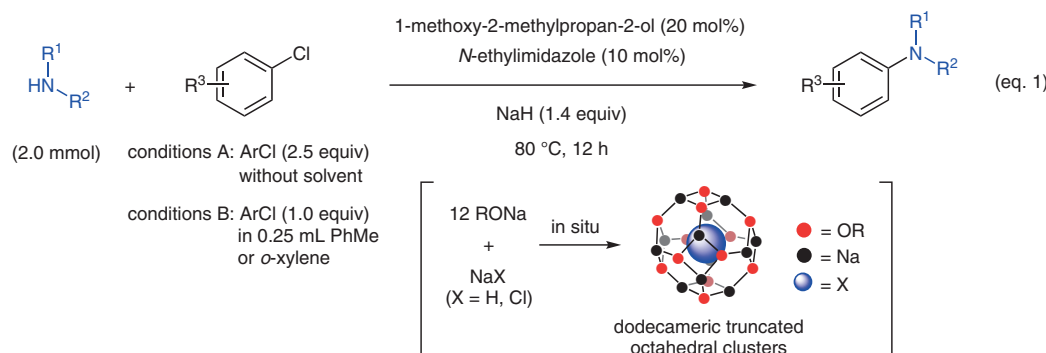
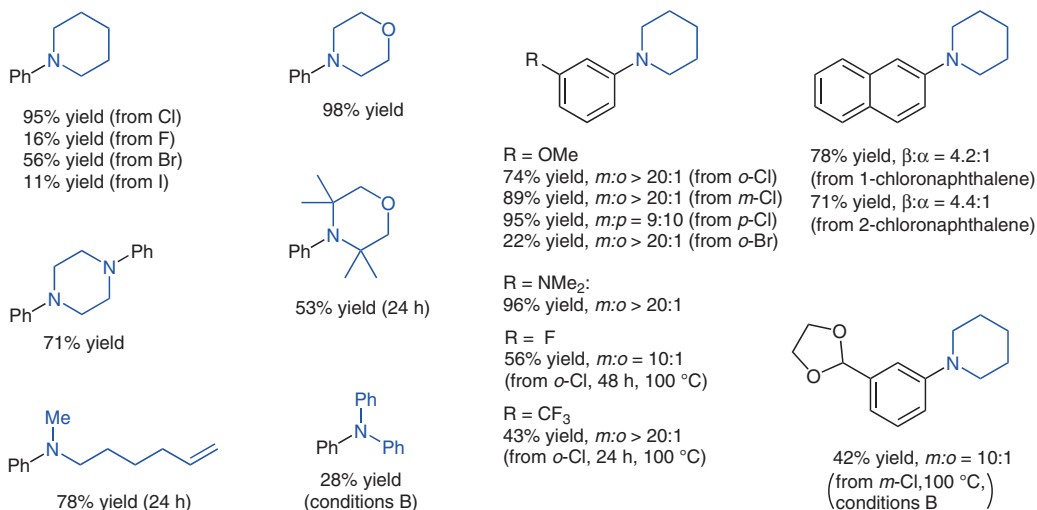


## Amination of Aryl Chlorides via Benzyne Catalyzed by Sodium Alkoxide Clusters



### Selected results (under conditions A unless otherwise noted):



**Significance:** Amination of aryl chlorides took place with NaH in the presence of catalytic 1-methoxy-2-methylpropan-2-ol and *N*-ethylimidazole at 80 °C to give aryl amines (60 examples) via the corresponding benzyne in up to 98% yield (eq. 1). A molar scale reaction of 4-methylpiperidine (0.5 mol) with PhCl was performed to afford 4-methyl-1-phenylpiperidine in 80% yield (86.5 g).

**Comment:** In this reaction, PhCl showed superior reactivity over PhF, PhBr, and PhI. ArCls with *ortho* or *meta* substituents provided *meta*-aminated products with high regioselectivity. The authors discovered that sodium tertiary alkoxides assemble to form dodecameric truncated octahedral clusters which dissolve NaH to promote the benzyne formation from aryl chlorides.