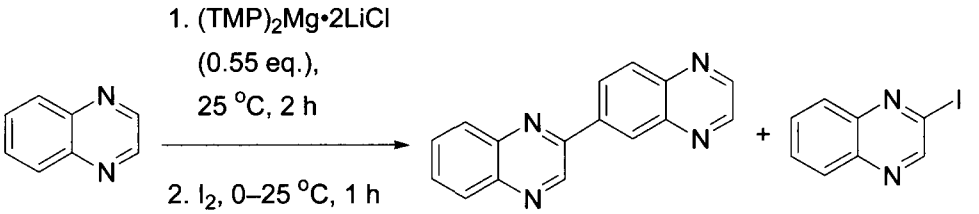
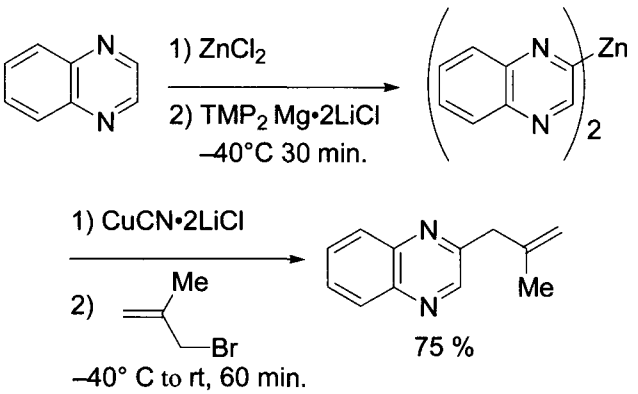
It has been demonstrated that the metallation of diazines can be challenging due to the facile competitive nucleophilic addition reaction to provide the dimer above.[43,47] Dong and co-workers speculated that the less reactive organozinc intermediate might not dimerize.[48] Upon deprotonation of the diazine ring using magnesium bases, poor yields of the desired halogenated product were isolated due to the high reactivity of the magnesium species. Dong and co-workers recently determined that stabilization of the reactive intermediate with the inclusion of zinc chloride provided the aryl iodide in excellent yields. This metallation procedure provides a pathway to form many aromatic and heterocyclic organometallic reagents at room temperature.



without $ZnCl_2$	34 %	Trace
with $ZnCl_2$ (0.5 eq.)	Trace	94 %

Continuing to examine the scope of the zincation of pyrazine rings, Dong[49] used $TMP_2Mg{\cdot}2LiCl$ (TMP = 2,2,6,6-tetramethyl-piperamidyl) to deprotonate pyrazine in the presence zinc chloride to provide the zincated aryl ring. Addition of copper cyanide followed by the allylic bromide provided the coupled product in moderate yield. This metallation of the quinoxaline ring provides the *ortho*-metallated intermediate with high selectivity.



When inductively electron-withdrawing groups are located on the carbocycle of a quinoxaline, the metallation occurs selectively at the *ortho*-