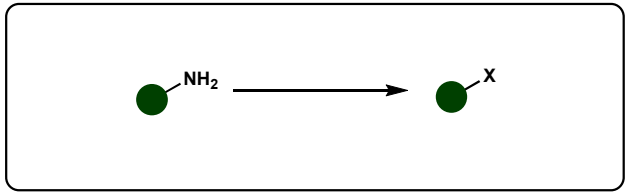
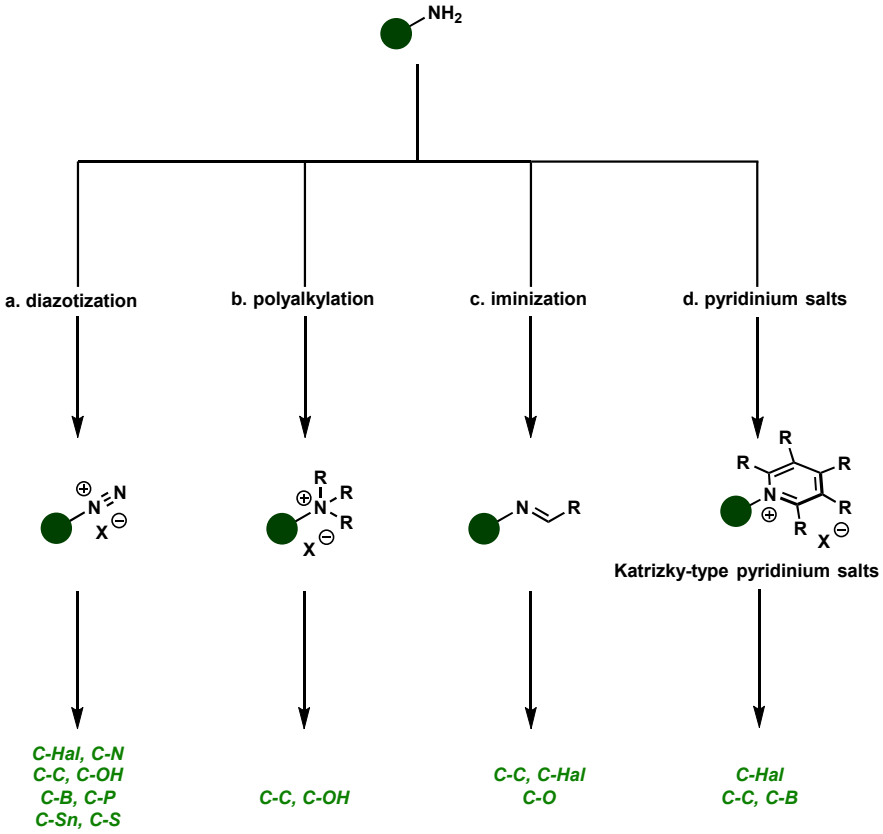


Leaving Group Ability

Leaving Group	pK_b	Comment
I^-	-10	Excellent to good leaving groups
N_2	<-10	
TfO^-	<-10	
Br^-	-9	
$ArSO_3^-$	-7	
Cl^-	-7	
$CF_3CO_2^-$	0.2	
$H_2PO_4^-$	2.2	
F^-	3.2	Fair to poor leaving groups
$CH_3CO_2^-$	4.8	
CN^-	9.1	
NH_3	9.2	
RNH_2, R_2NH, R_3N	10	
$CH_3CH_2S^-$	10.6	
CH_3O^-	15.5	
HO^-	15.7	
$CH_3CH_2O^-$	15.9	
$(CH_3)_3CO^-$	18	
H_2N^-	36	Not leaving groups
CH_3^-	49	

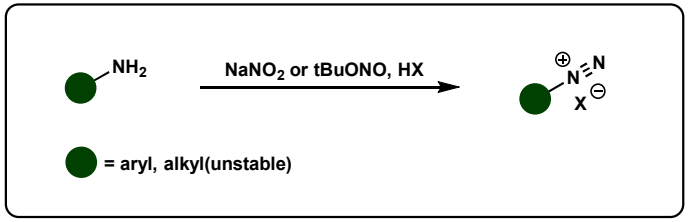
Leaving group ability is related with it's pK_b.
The less basic the leaving group is, the easier it is to dissociate.

Amines activation strategies

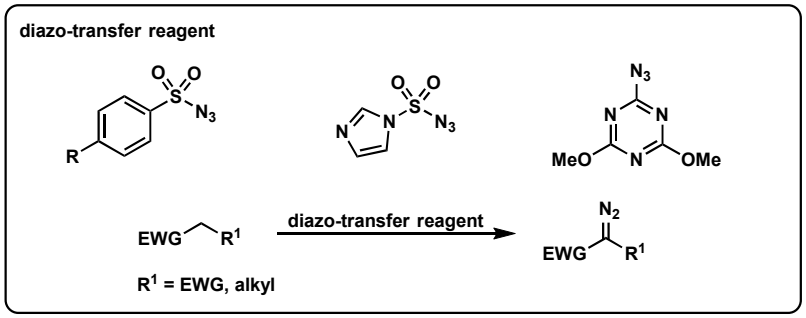


Synthesis of diazo compounds

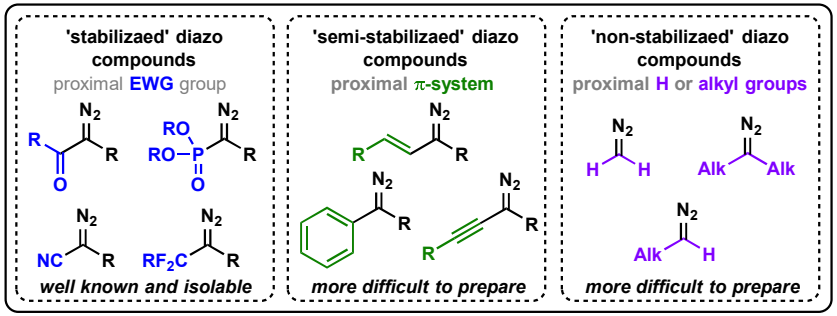
Diazotization of amine



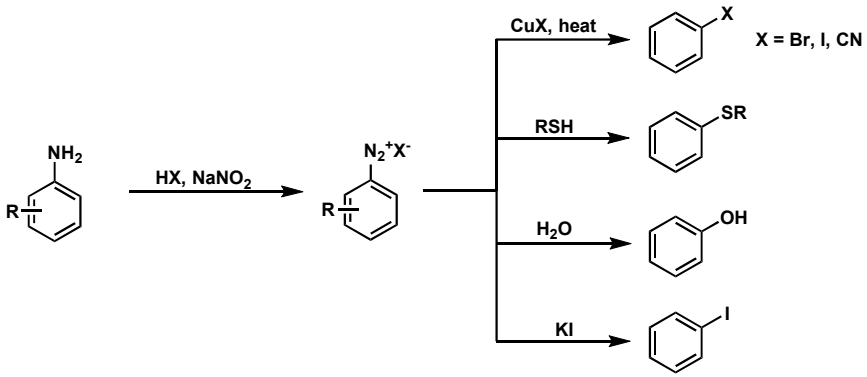
Prepare diazo compounds from diazo-transfer reagent



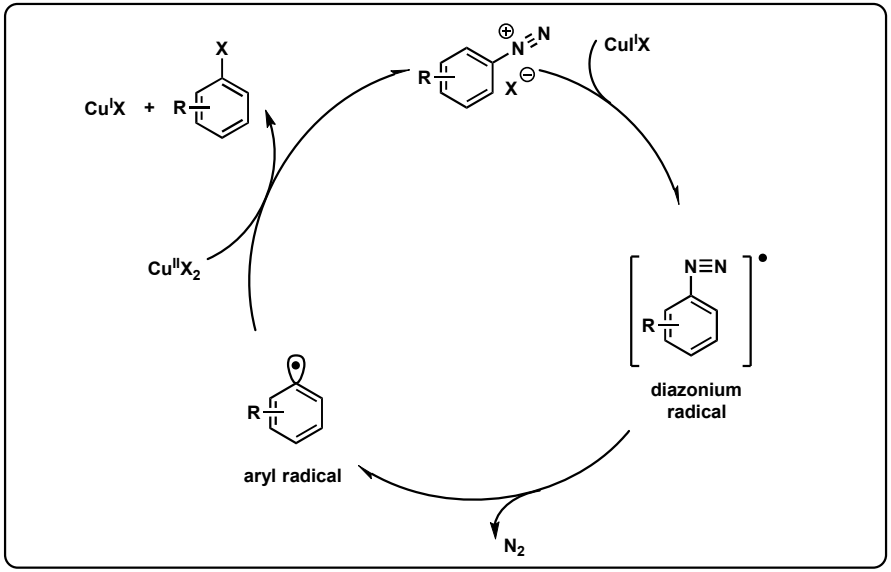
Stability of diazo compounds



Sandmeyer reaction(1884)

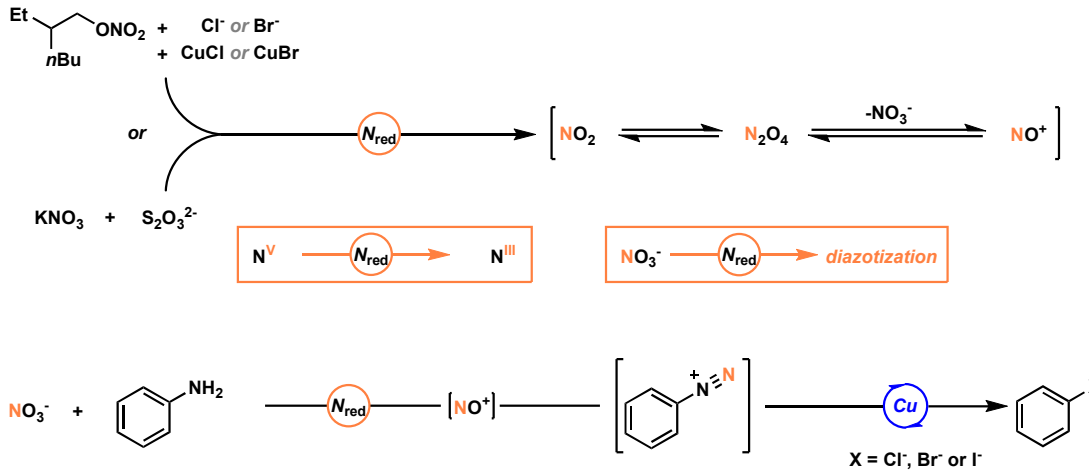


Mechanism:

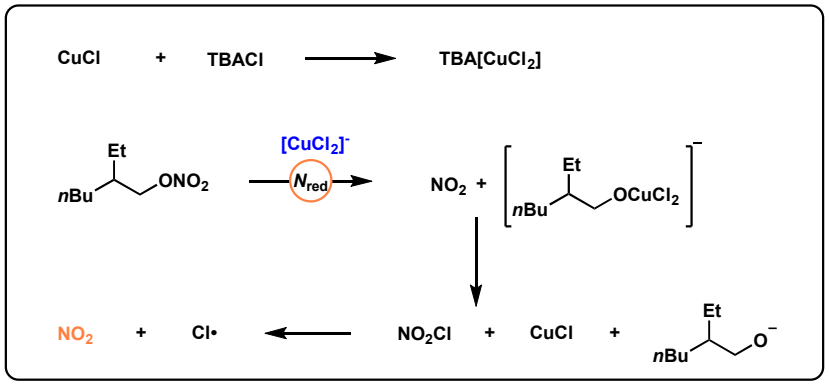


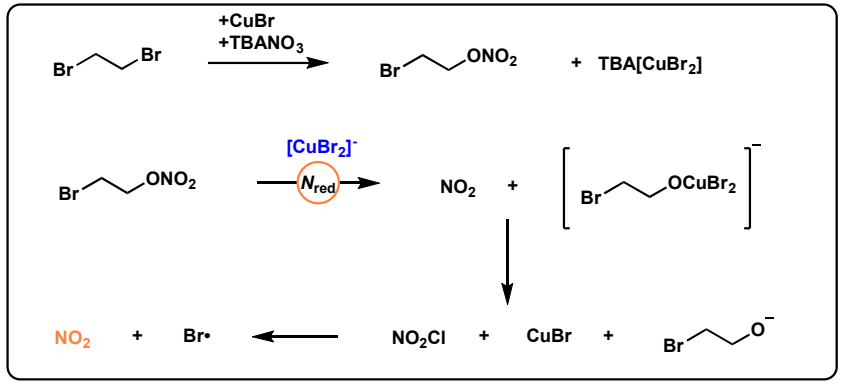
The mechanism of the Sandmeyer reaction is not completely understood.

Safer Sandmeyer Reaction



Mechanism:

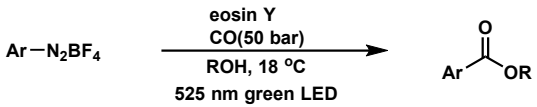




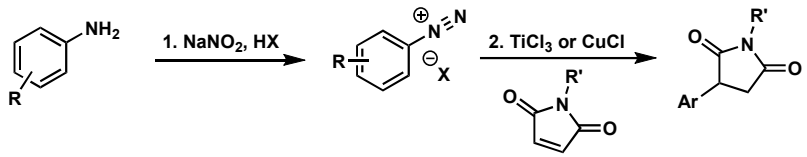
Ritter *et al.*, *Science* 2024, *384*, 446

C−C Bond Formations

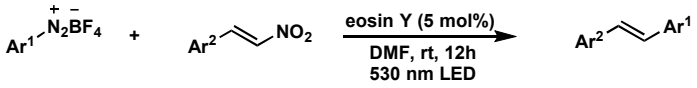
1. ArylRadical Intermediates



Wangelin et al., *Angew. Chem., Int. Ed.* 2015, *54*, 2270

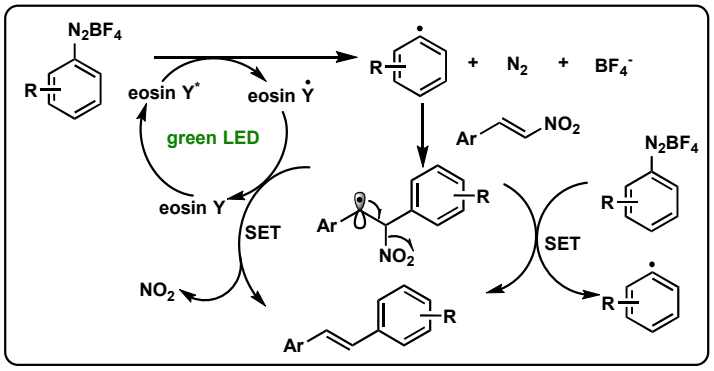


Zhao et al., *RSC Adv.* 2016, *6*, 23438

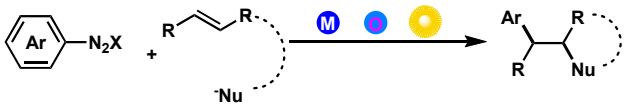


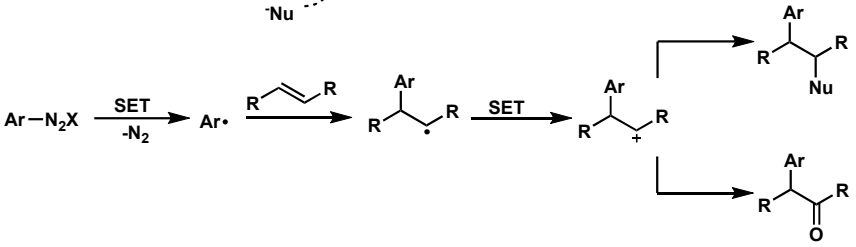
Wang et al., *Chem. Commun.* 2016, *52*, 14234

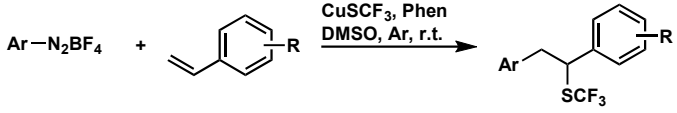
mechanism:



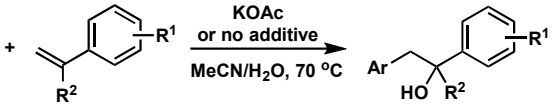
Difunctionalization



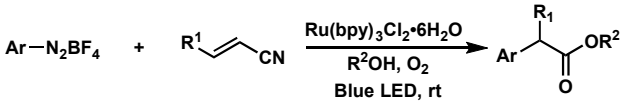




Chen et al., *J. Org. Chem.* 2018, *83*, 5836

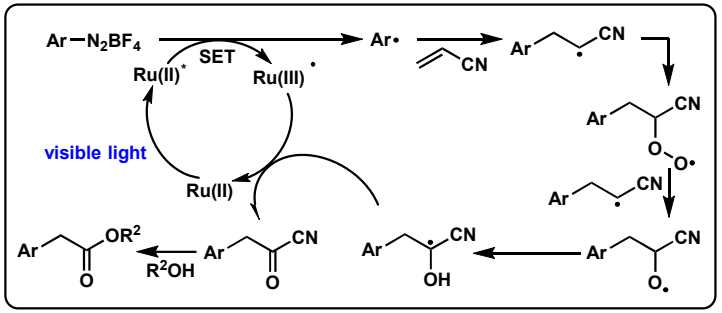


Heinrich et al., *Angew.Chem., Int. Ed. 2016, 55, 8744*



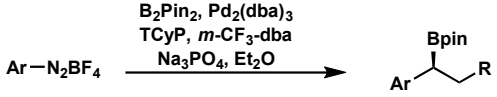
Jiang et al.,*Eur. J. Org. Chem.* 2015, *2015*, 5775

mechanism:

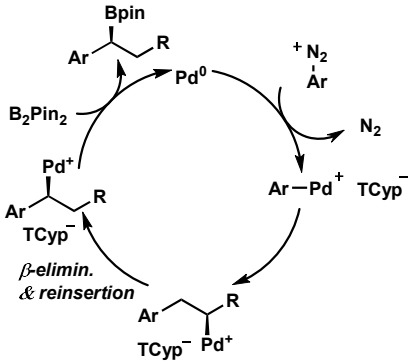


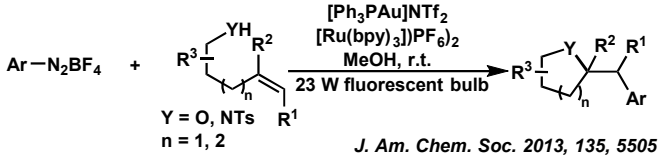
C−C Bond Formations

2. Transition-Metal-Catalyzed

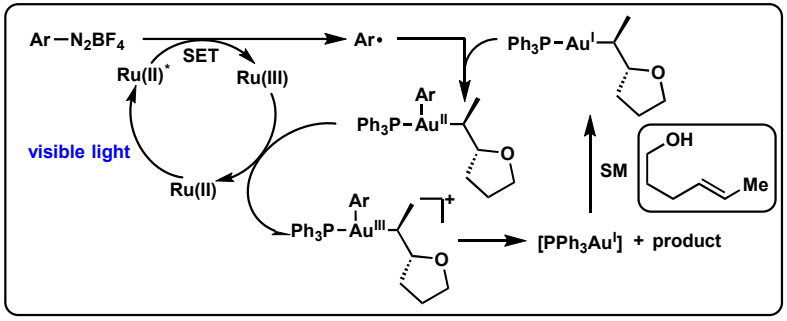


J. Am. Chem. Soc. 2015, *137*, 3213



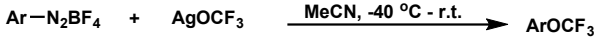


J. Am. Chem. Soc. 2013, 135, 5505

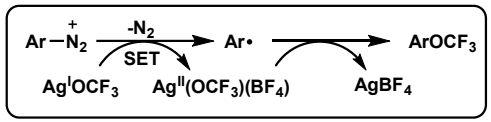


C−X Bond Formations

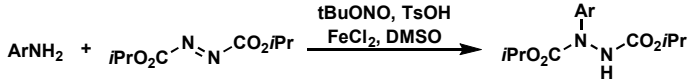
1). C-O Formations



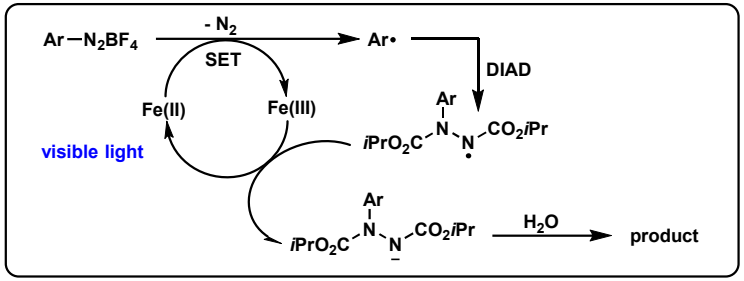
Org. Lett. 2019, 21, 8003



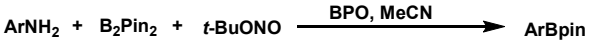
2). C-N Formations

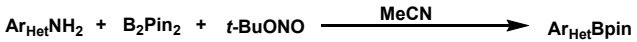


RSC Adv. 2015, *5*, 80698



3). C-B Formations

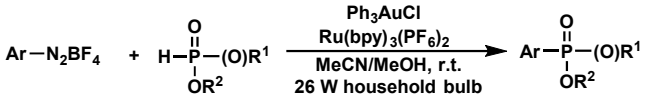




Angew. Chem., Int. Ed. 2010, 49, 1846

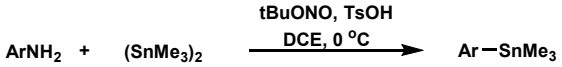
C−X Bond Formations

4). C-P Bond Formations



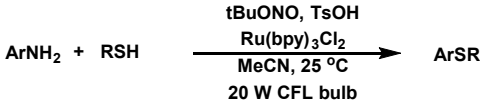
Chem. Sci. 2015, *6*, 1194

5). C-Sn Bond Formations

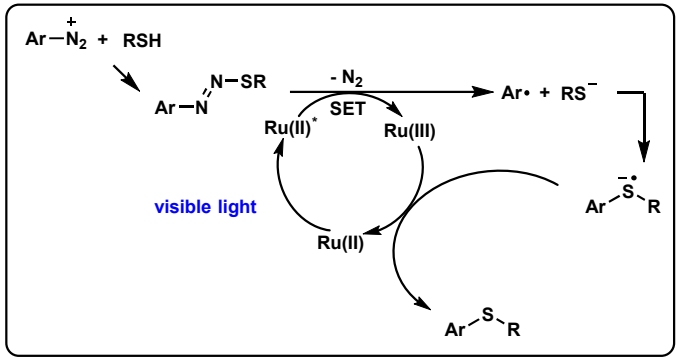


Angew.Chem., Int. Ed. 2013, *52*, 11581

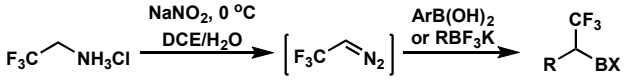
6). C-S Bond Formations



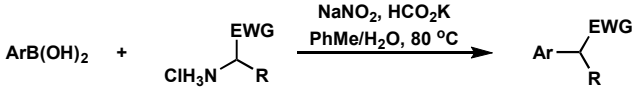
Angew. Chem., Int. Ed. 2013, *52*, 7860



Alkyl diazo compounds



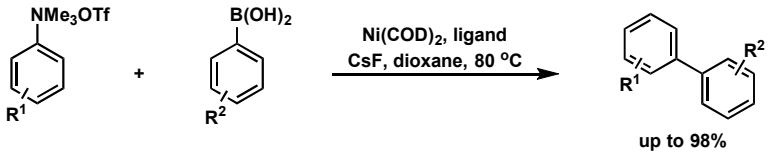
Angew. Chem. Int. Ed. 2013, *52*, 13656.

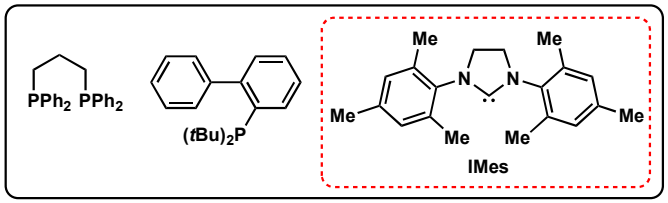


R = alkyl, EWG = CO_2R', CN

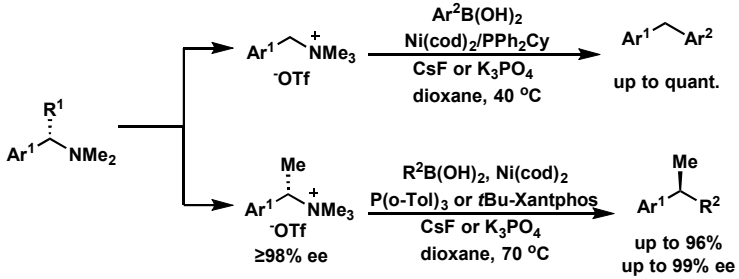
Angew. Chem. Int. Ed. 2014, *53*, 10510.

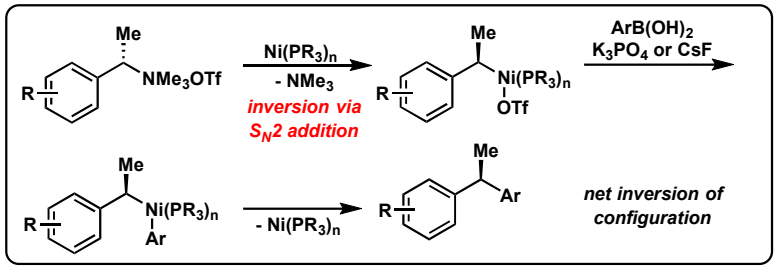
Quaternary Ammonium Salt



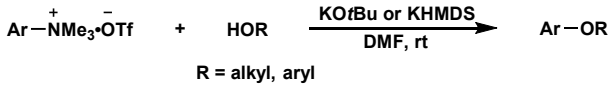


J. Am. Chem. Soc. 2003, *125*, 6046



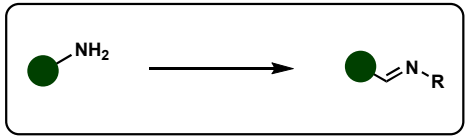


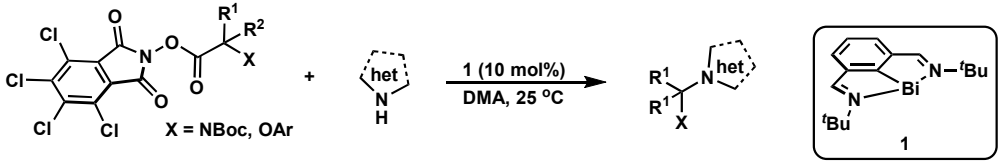
J. Am. Chem. Soc. 2013, *135*, 280

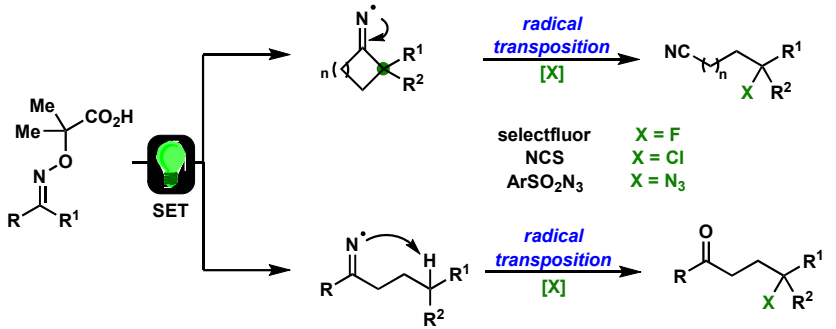


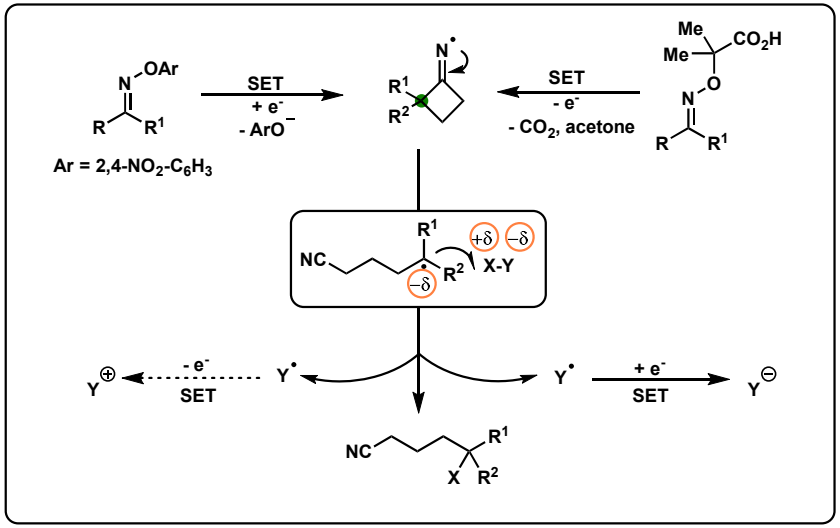
Angew.Chem. Int.Ed. 2018, *57*, 3641

Imine Derivatives

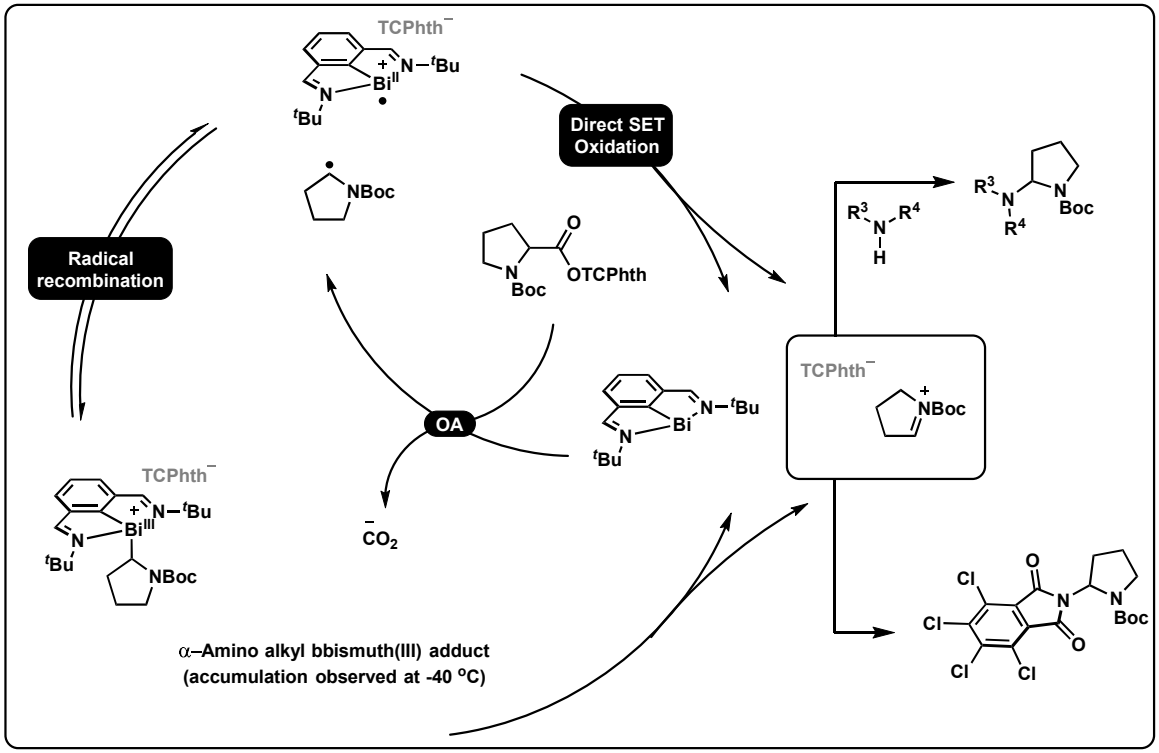






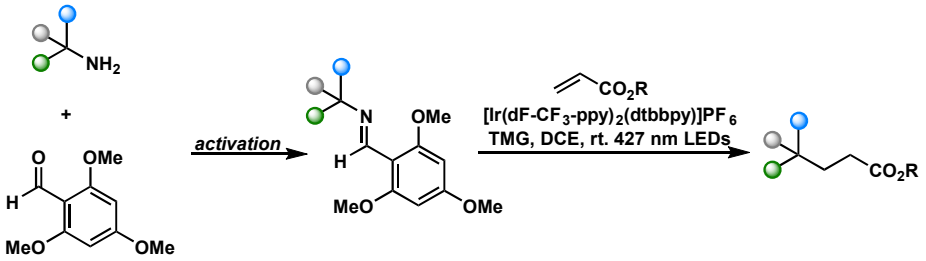


Angew.Chem. Int. Ed. 2018, *57*, 744

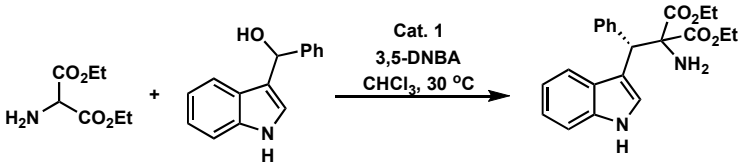


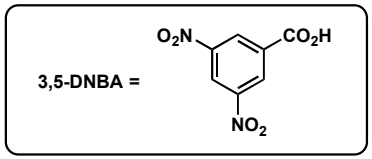
Nat. Chem. 2023, *15*, 1138

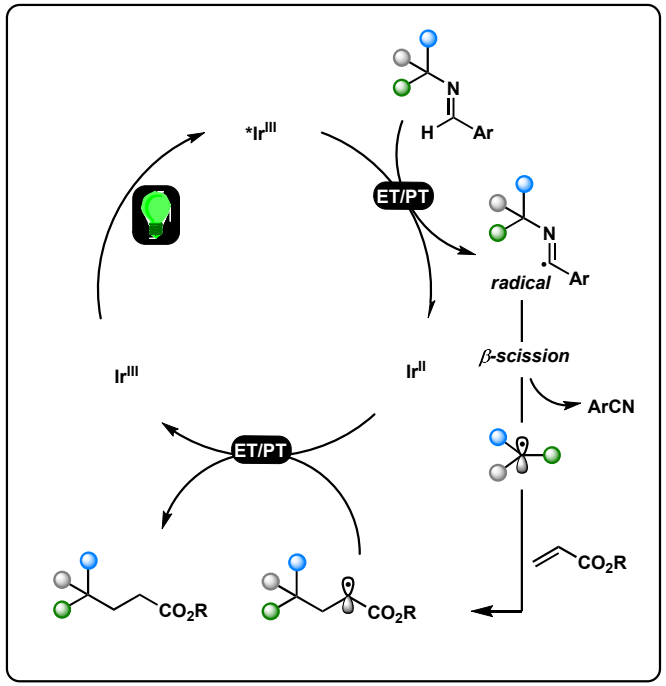
Imine Derivatives



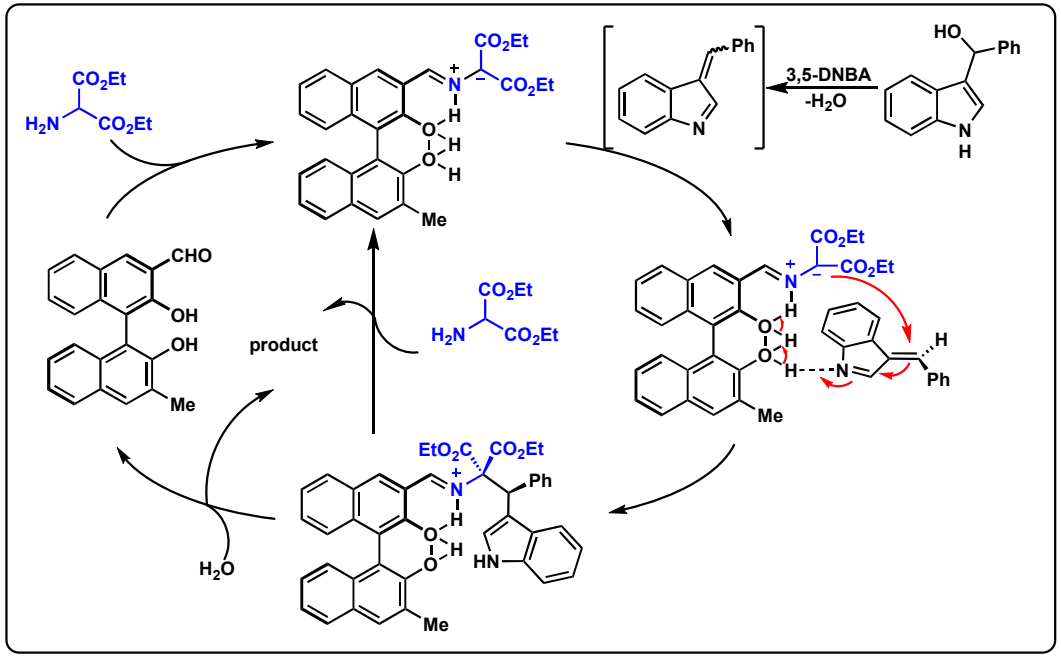
J. Am. Chem. Soc. 2020, *142*, 18310



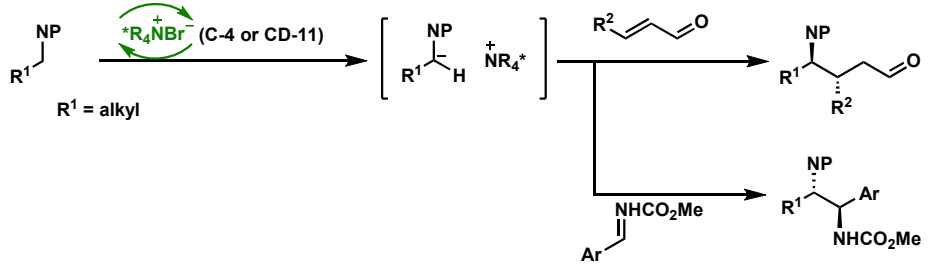


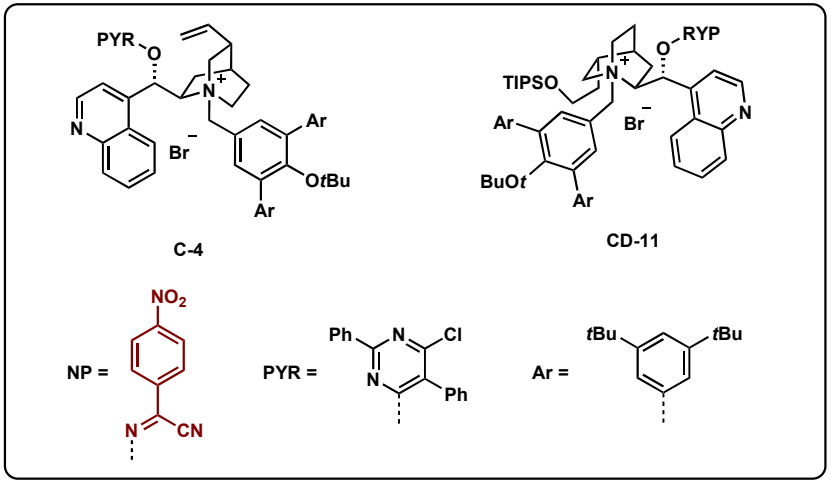


Chem. Sci. 2014, *5*, 1988

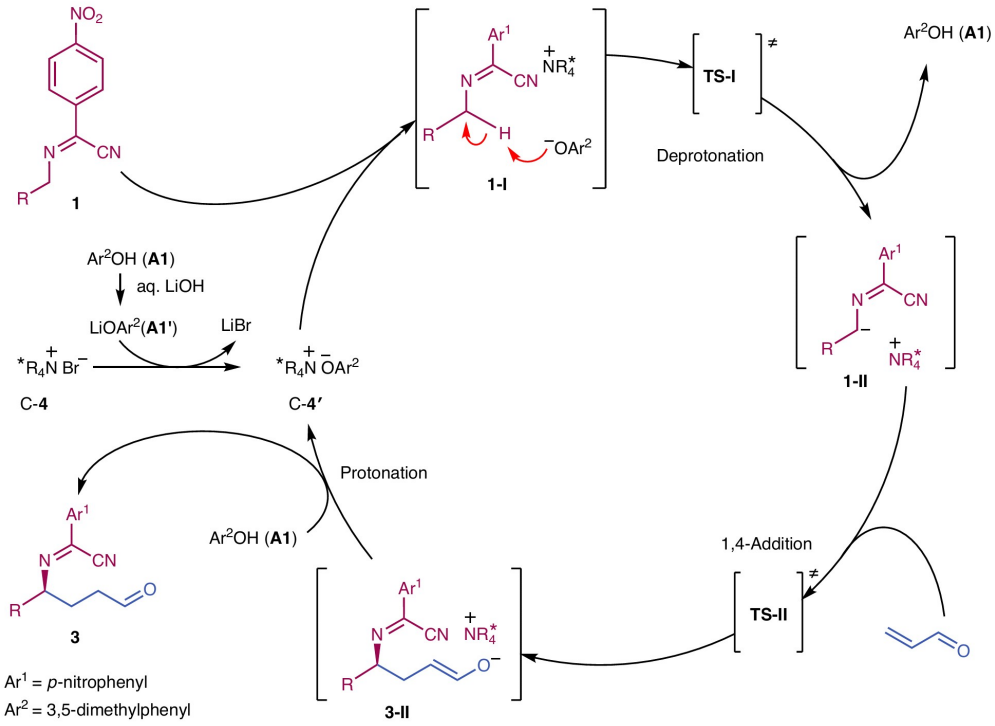


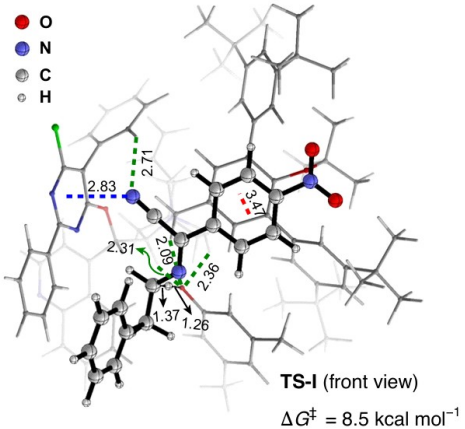
Imine Derivatives





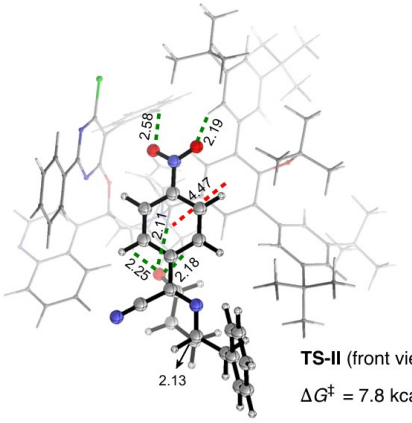
Nat. Catal., 2024, *7*, 1076





TS-I (front view)

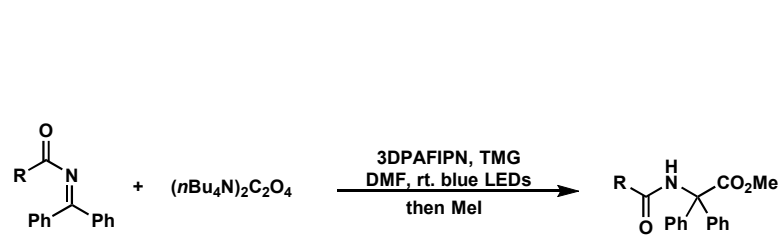
$\Delta G^{\ddagger}$ = 8.5 kcal mol^{-1}

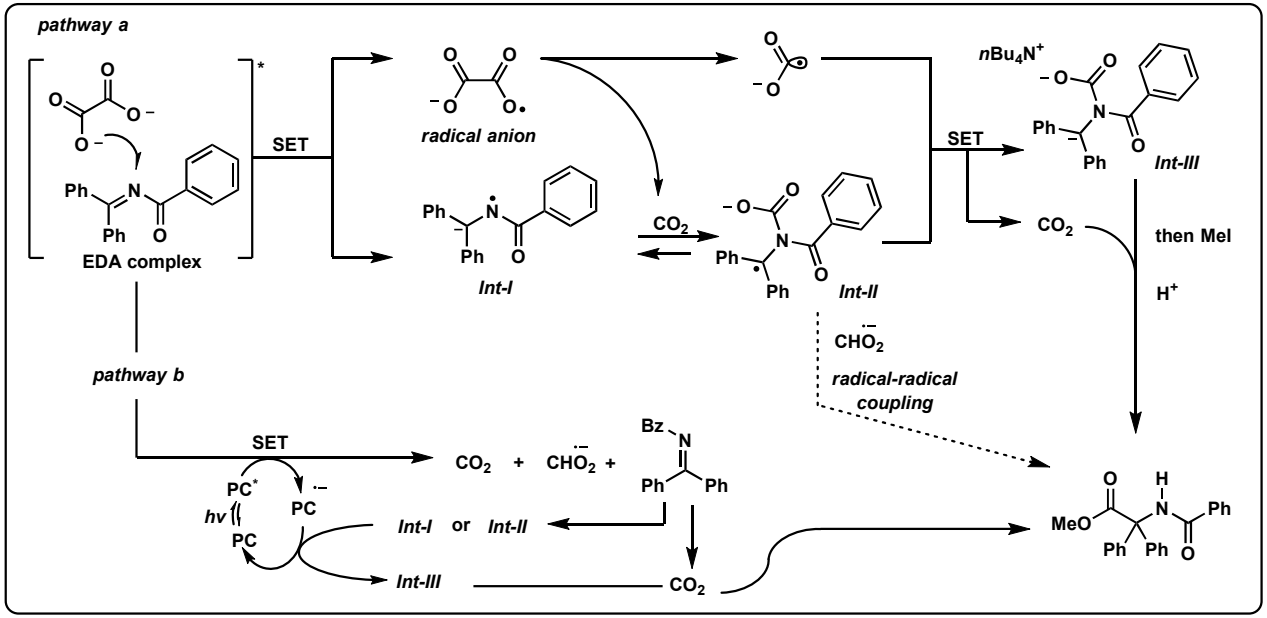


TS-II (front view)

$\Delta G^{\ddagger}$ = 7.8 kcal mol^{-1}

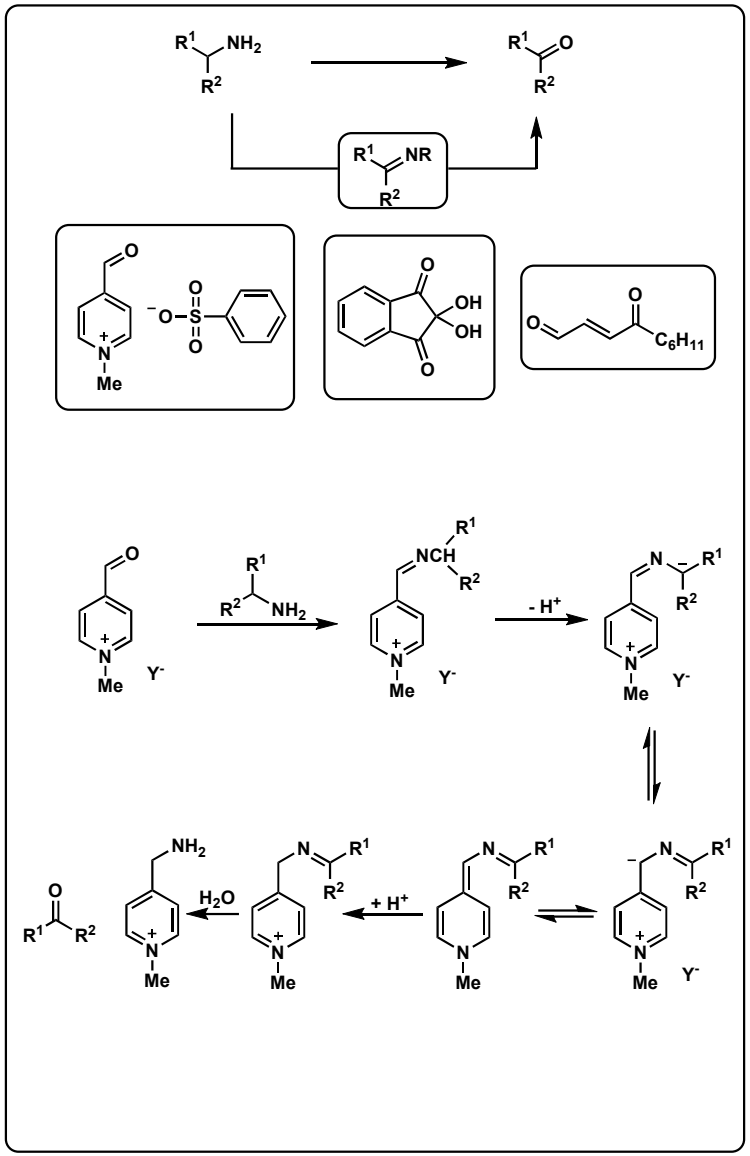
Imine Derivatives



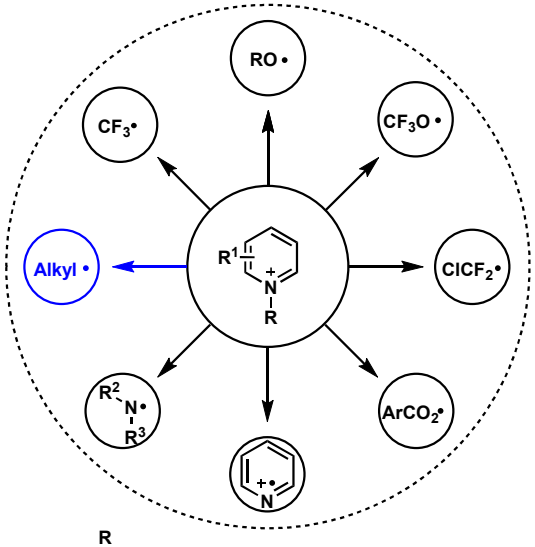


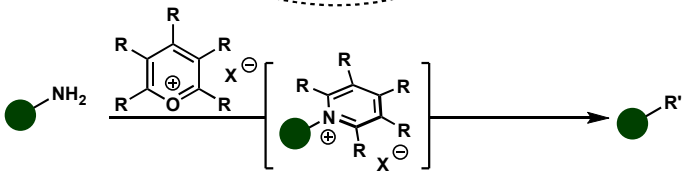
ACS Catal. 2024, *14*, 10053

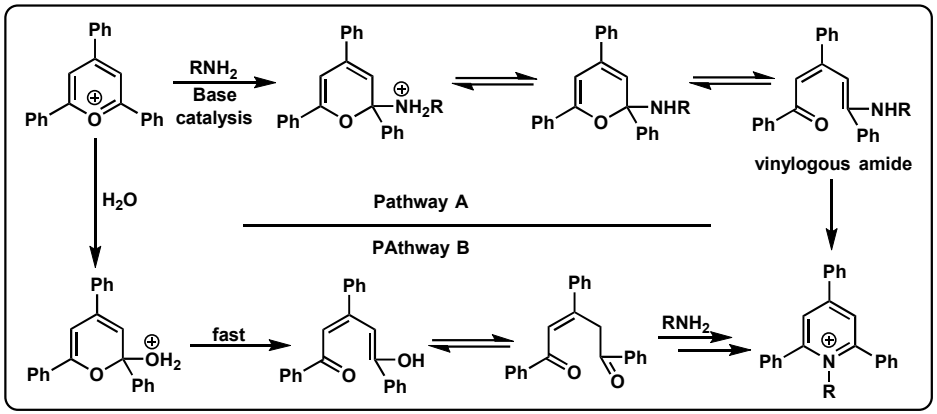
Transfer to Ketone(Aldehyde)



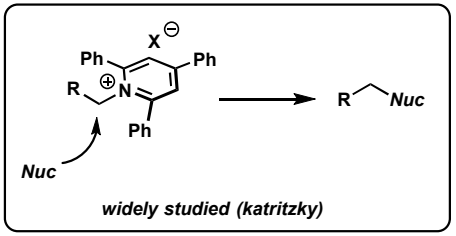
Pyridinium Salts

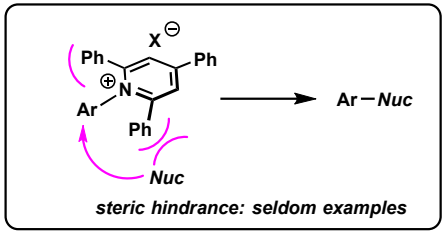


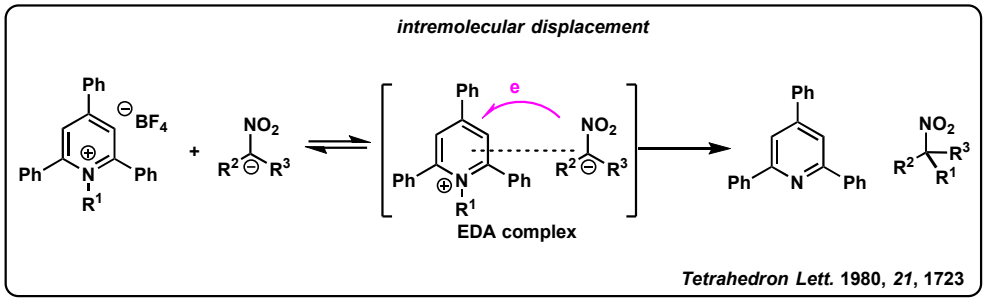


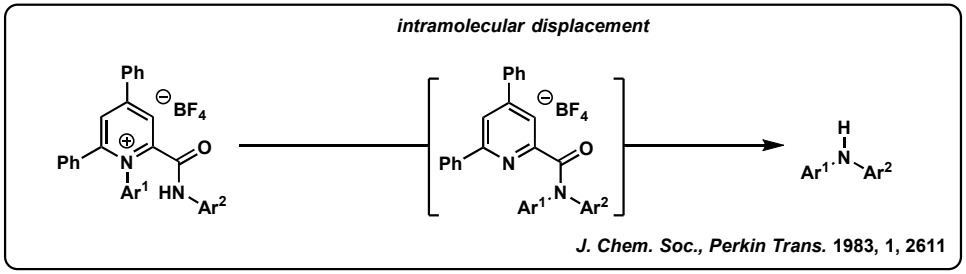


SN_2 or SN_1 Type

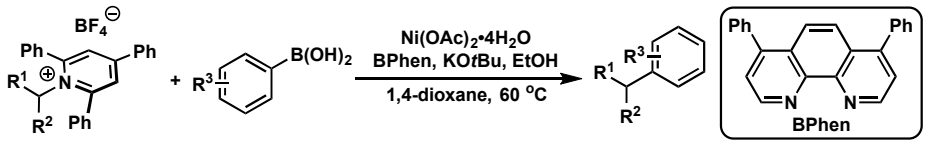




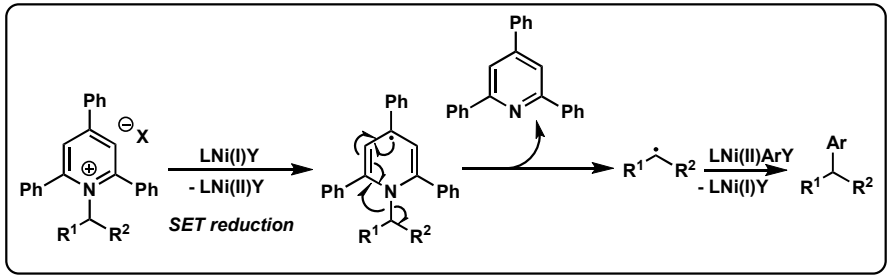


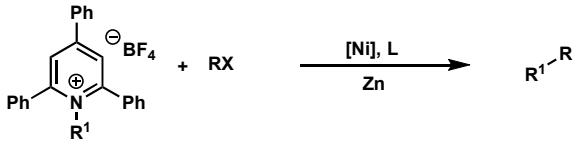


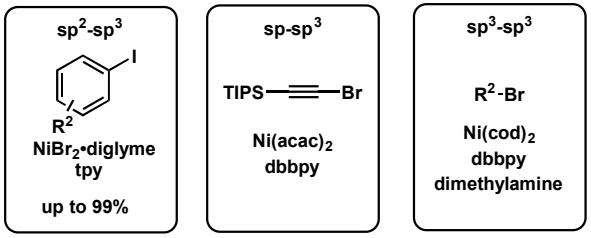
Metal-Catalyzed Cross-Couplings



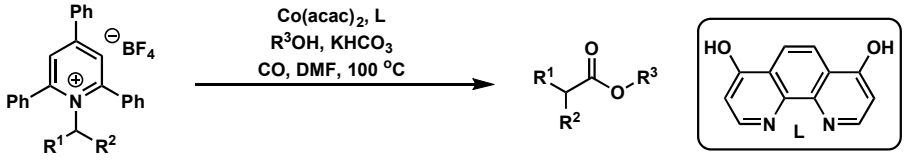
J. Am. Chem.Soc. 2017, *139*, 5313



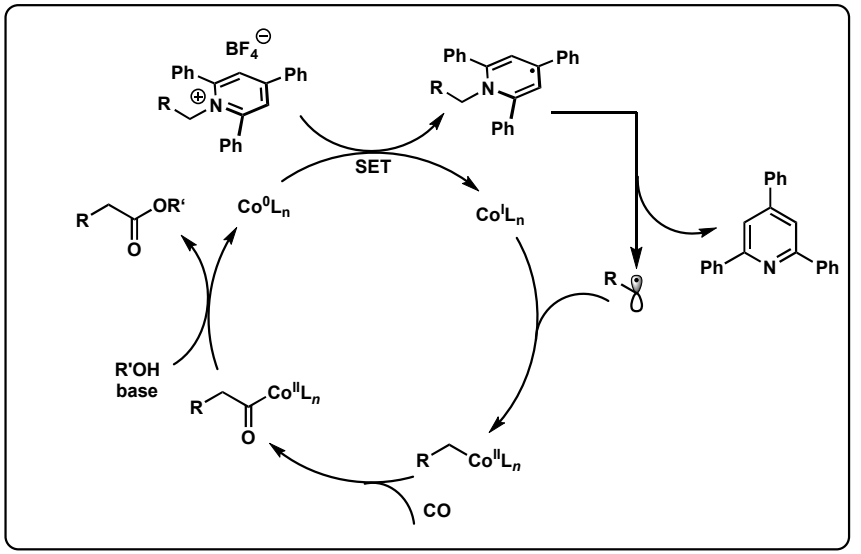




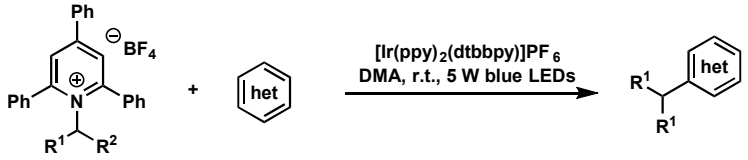
Sci.Adv. 2019, *5*, 9516.



Org. Lett. 2019, *21*, 6919

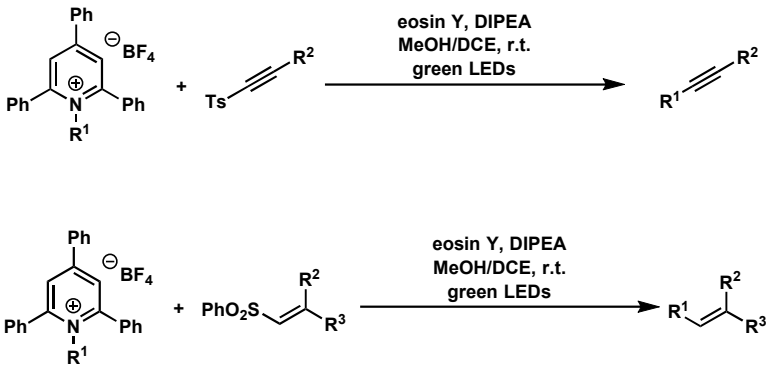


Photoinduced Reactions C–C Bond Constructions



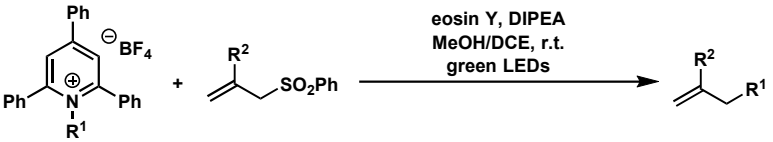
Angew. Chem. Int. Ed. 2017, *56*, 12336

Desulfonylative Alkynylation/Alkenylation



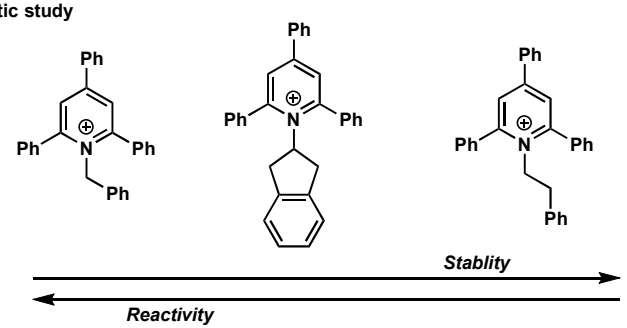
ACS Catal. 2018, *8*, 11362

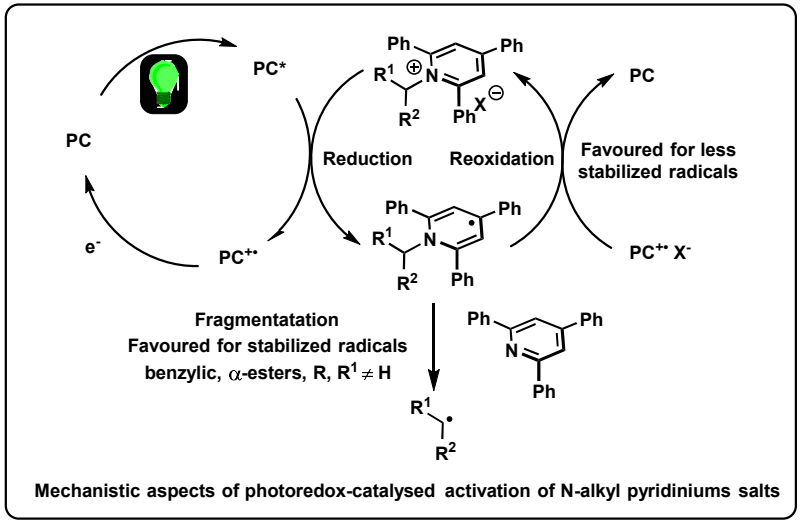
Desulfonylative Allylation



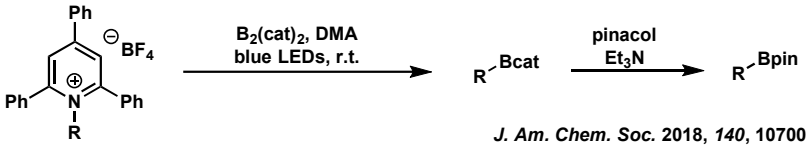
Angew. Chem. Int. Ed. 2019, *58,* 5697

Kinetic study





Mechanistic aspects of photoredox-catalysed activation of N-alkyl pyridiniums salts



J. Am. Chem. Soc. 2018, *140*, 10700