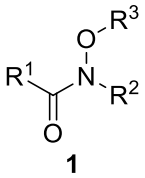
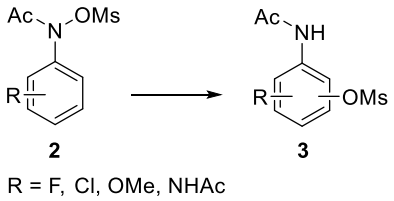
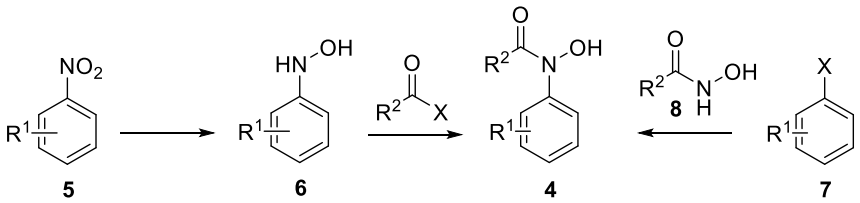


1

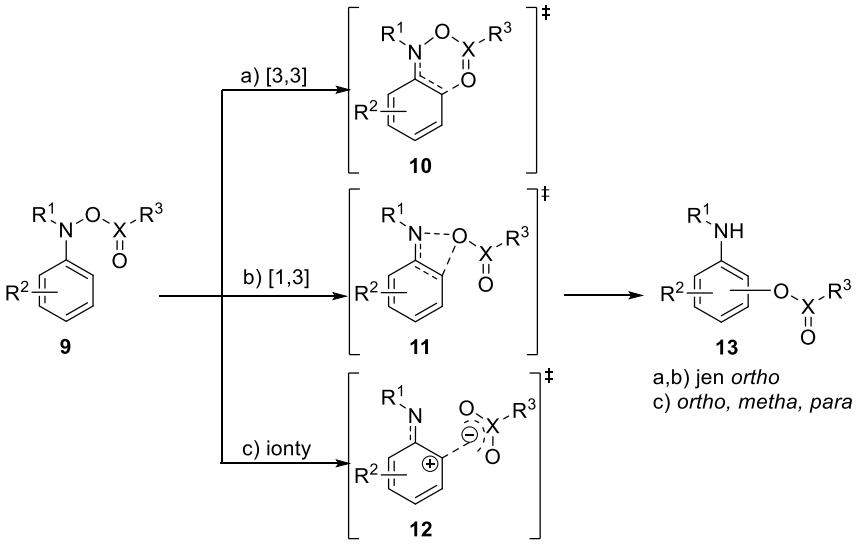
Figure 1: General structure of *O*-substituted hydroxamic acids



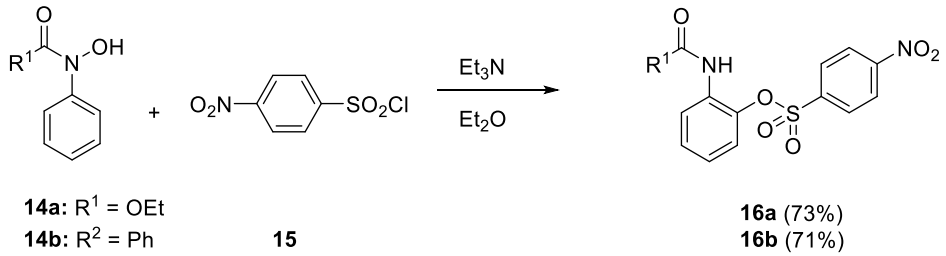
Scheme 1: Rearrangement of N-aryl-OMs hydroxamic acids **2**



Scheme 2: Synthesis of N-arylhydroxamic acids **4**



Scheme 3: Three basic mechanisms of rearrangement of *O*-substituted hydroxamic acids **9**

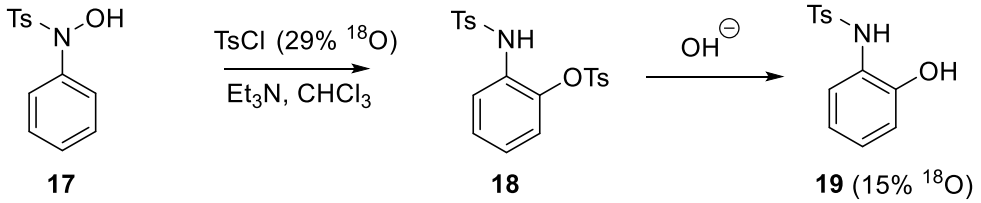


14a: R^1 = OEt
14b: R^2 = Ph

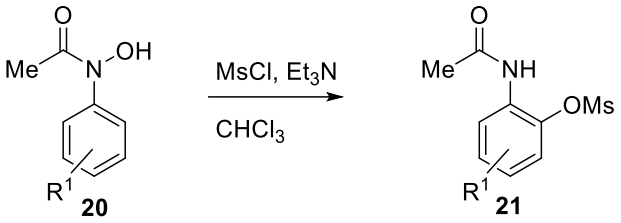
15

16a (73%)
16b (71%)

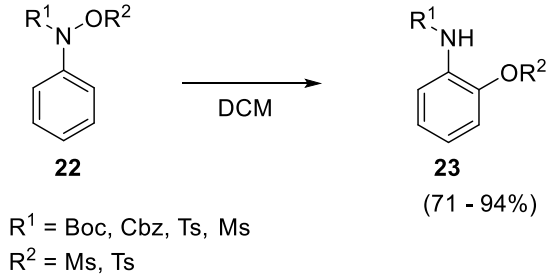
Scheme 4: Preparation of esters **16**



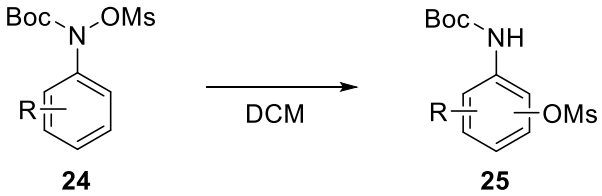
Scheme 5: Tosylation, rearrangement and hydrolysis with isotopically labelled oxygen



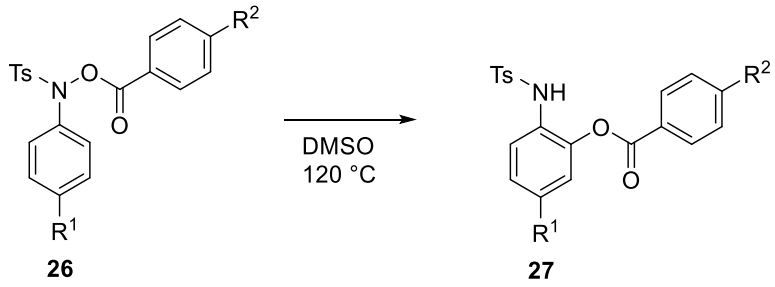
Scheme 6: Influence of R^1 substituent on rearrangement rate



Scheme 7: Effect od N-substituent R^1 on rearrangement rate

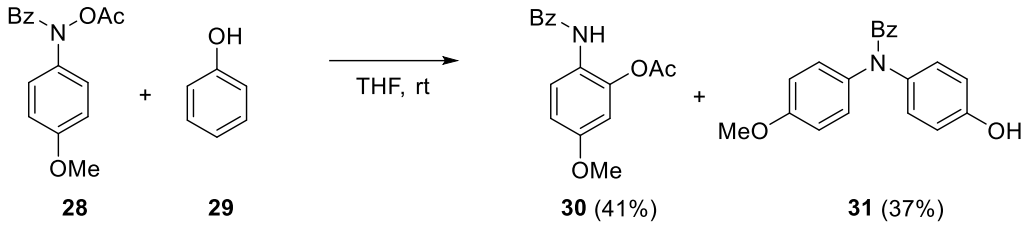


Scheme 8: Effect of substituent R on rearrangement rate and regio-selectivity

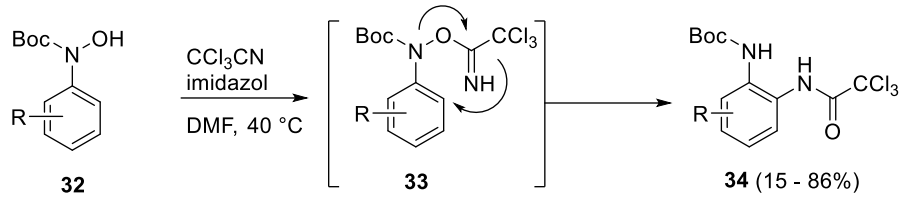


rychlost (R^1): Me > Cl > H
rychlost (R^2): NO_2 > Cl > H > Me

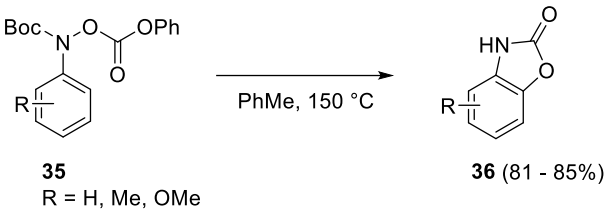
Scheme 9: Effect of substituent R^1 and R^2 on rearrangement rate of *O*-acyl hydroxamic acids **26**



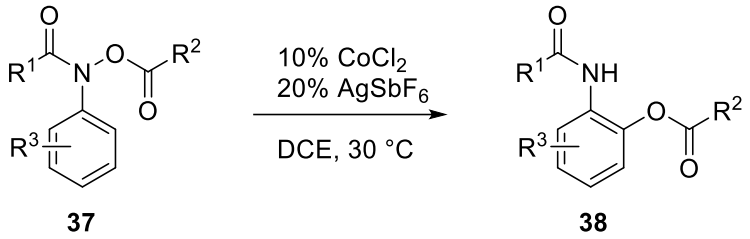
Scheme 10: Rearrangement of *O*-Ac hydroxamic acid **28** in presence of phenol **29**



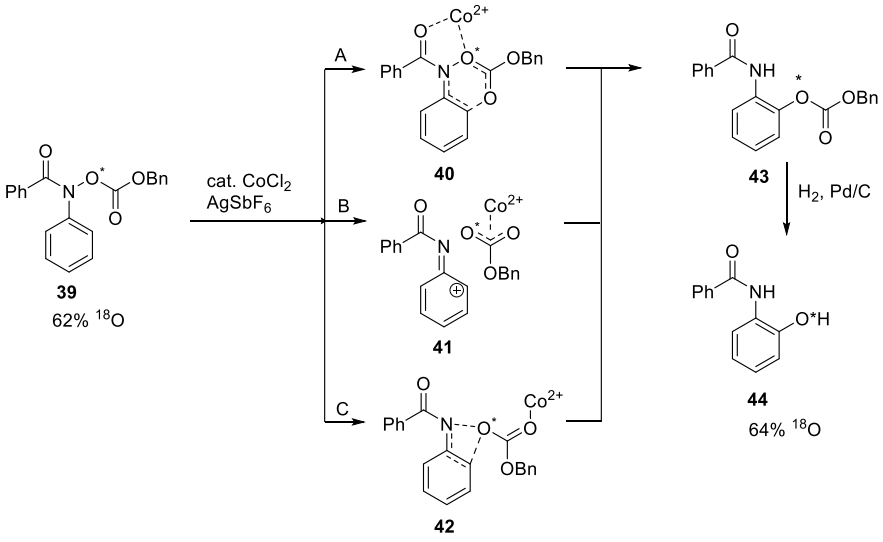
Scheme 11: Preparation of *ortho*-phenylendiamine **34**



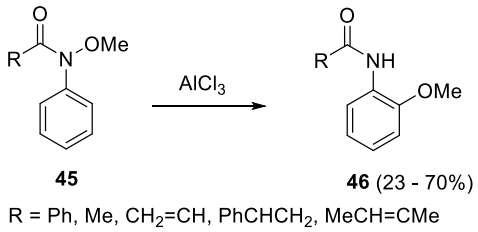
Scheme 12: Preparation of benzoxazole **36**



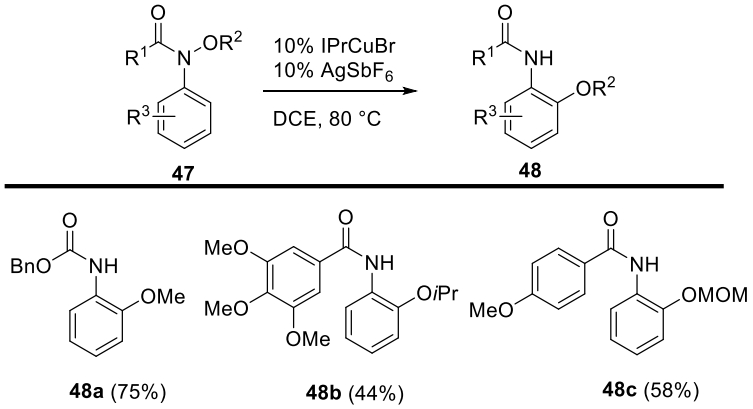
Scheme 13: $CoCl_2/AgSbF_6$ catalysed rearrangement *O*-acyl hydroxamic acid **37**



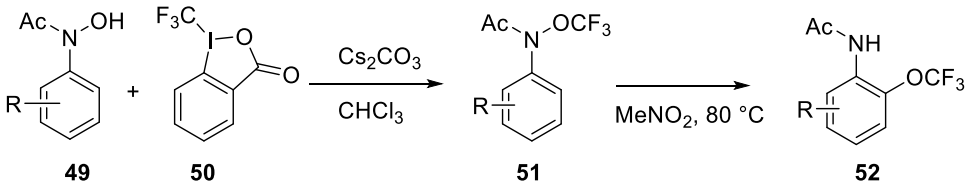
Scheme 14: Isotope labelling clarifying mechanism of $CoCl_2/AgSbF_6$ catalysed rearrangement



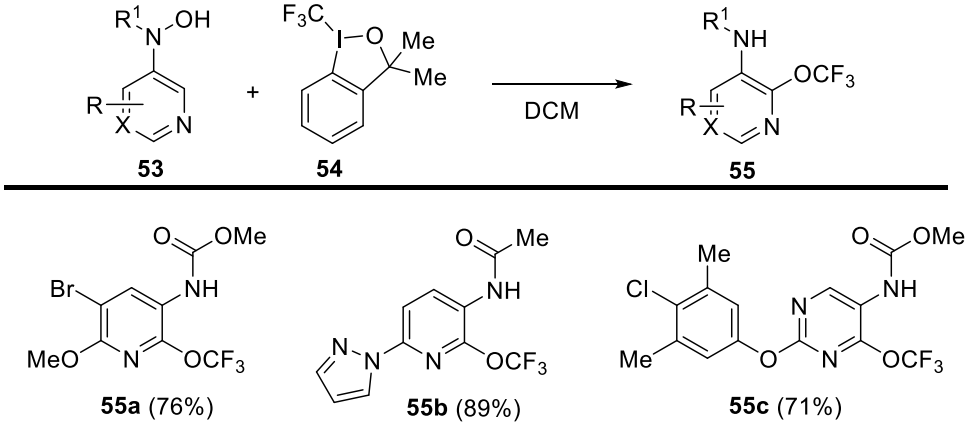
Scheme 15: Rearrangement of *O*-alkyl hydroxamic acid **45** catalysed by aluminium chloride



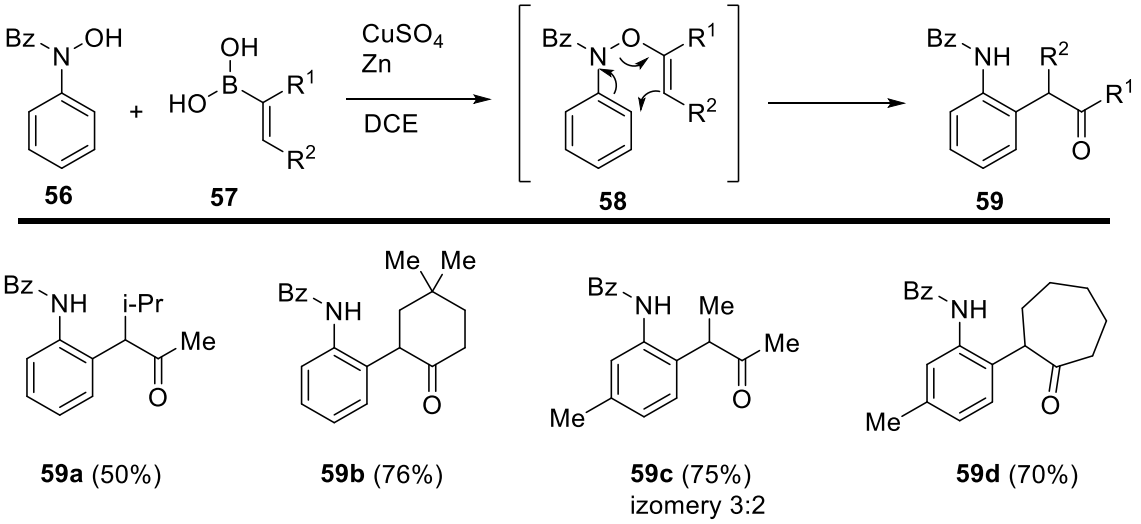
Scheme 16: NHC-Cu catalysed rearrangement of *O*-alkyl hydroxamic acids **47**



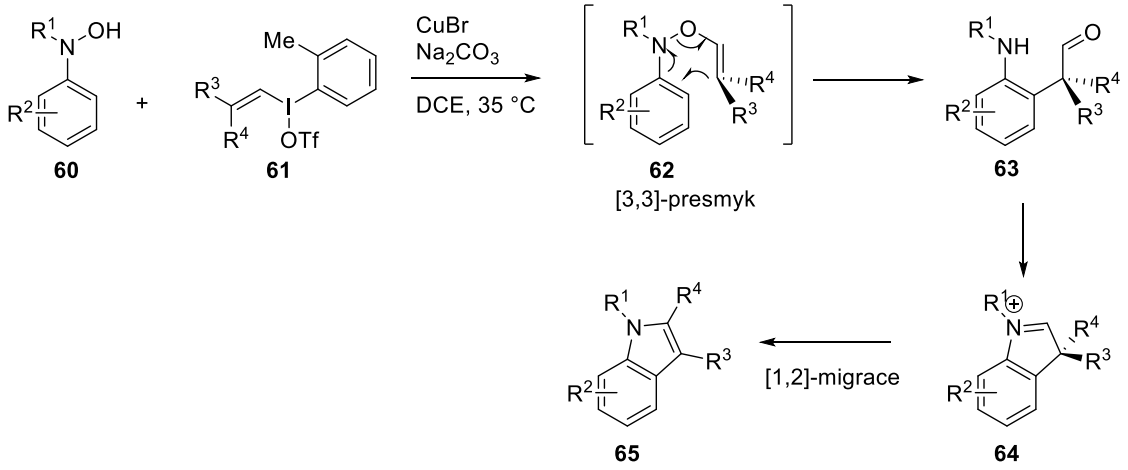
Scheme 17: Rearrangement of OCF_3 group



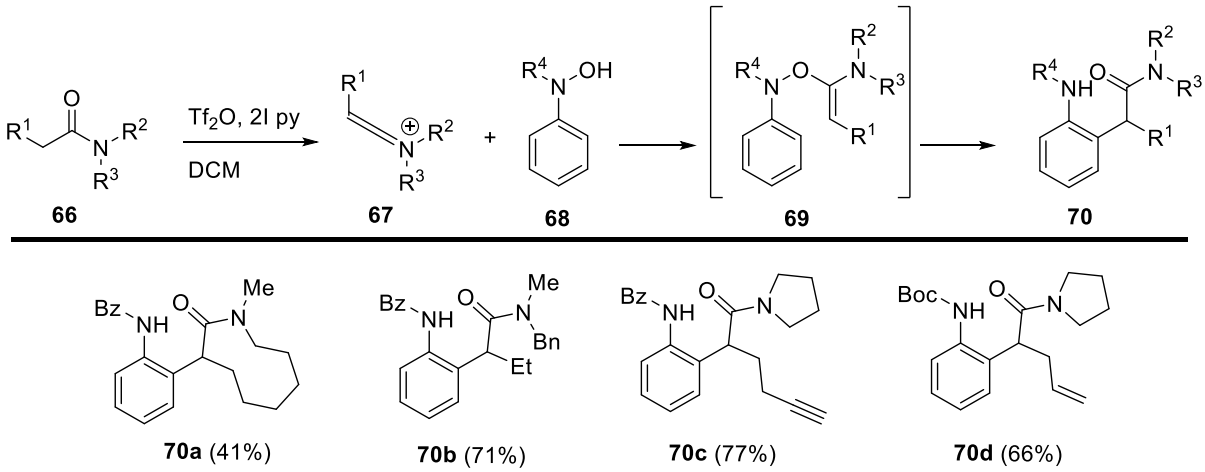
Scheme 18: Rearrangement of OCF_3 group at heterocyclic compounds



Scheme 19: Synthesis of α-arylketones **59** by rearrangement reaction

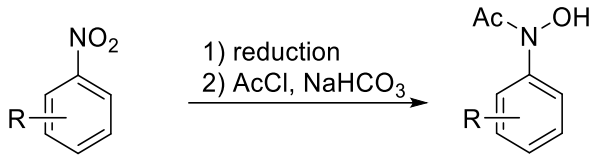


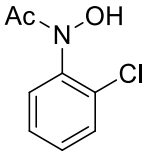
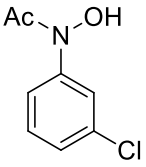
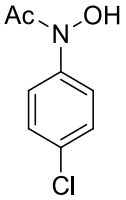
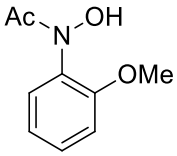
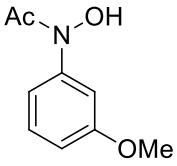
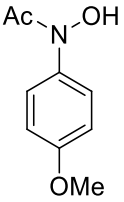
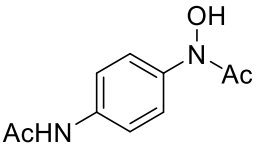
Scheme 20: Preparation of indoles **65** by cascade reaction



Scheme 21: Preparation of α-arylamides **70** by rearrangement reaction

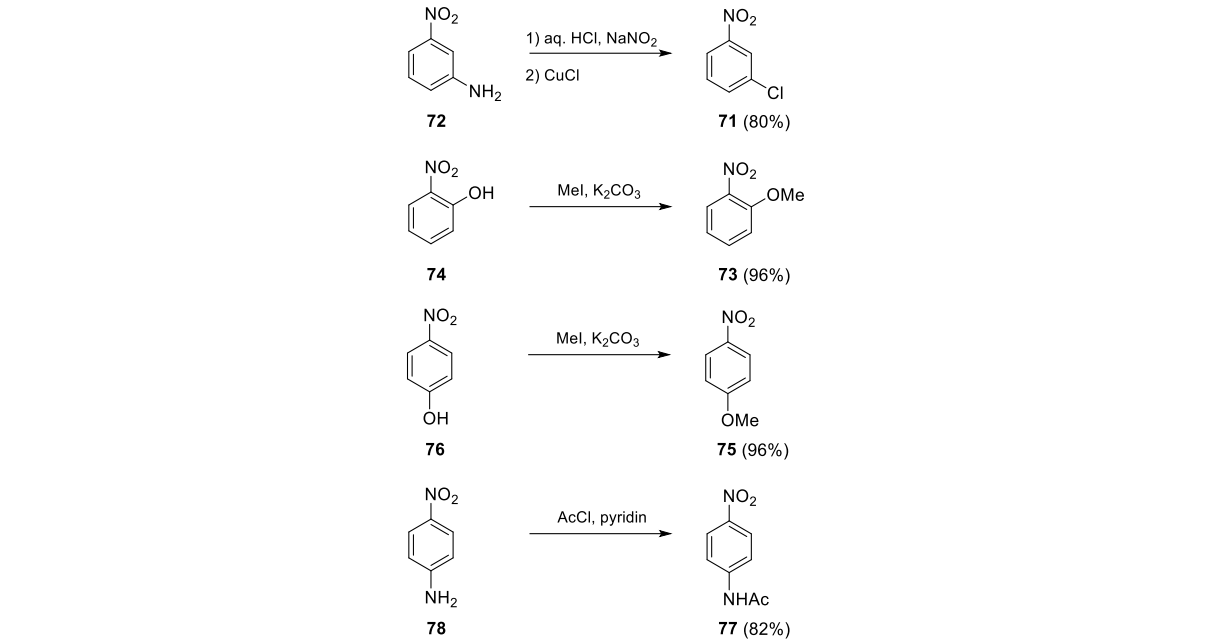
Table 1: Synthesis of N-arylhydroxamic acids



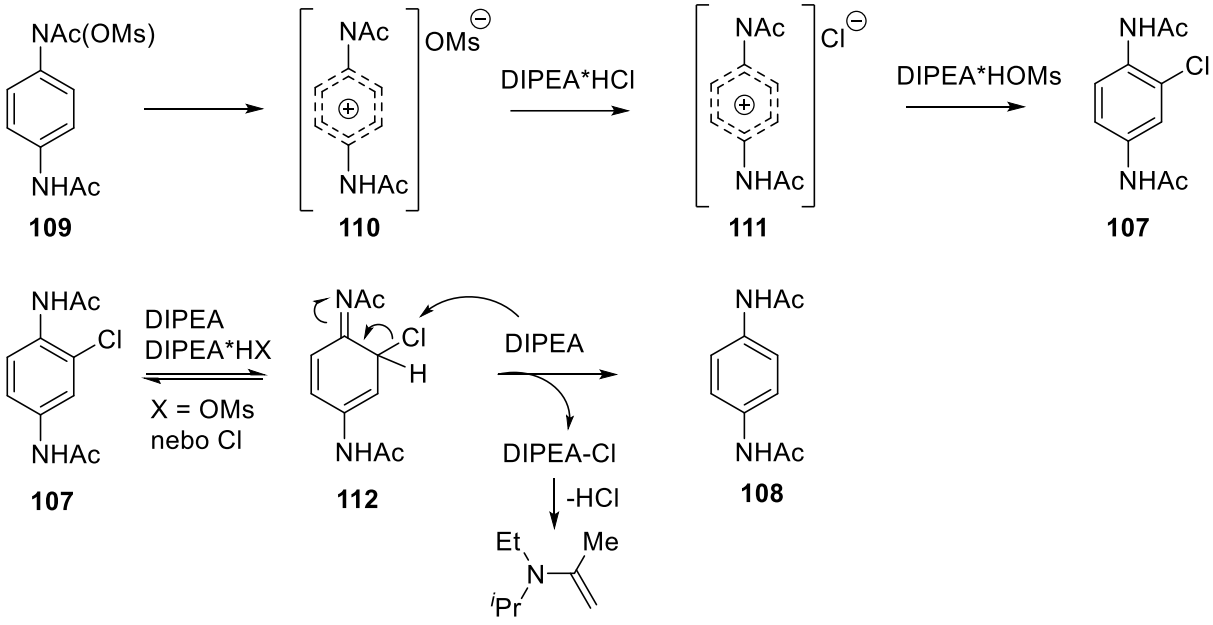
			
Method A	Method A	Method B	Method A
79 (50%)	81 (46%)	83 (12%)	84 (68%)
			
Method A	Method B	Method A	Method A
86 (51%)	87 (8%)	89 (79%)	90 (50%)

Method A: a) 5% Rh/C, N_2H_4, THF; b) $NaHCO_3$, AcCl.

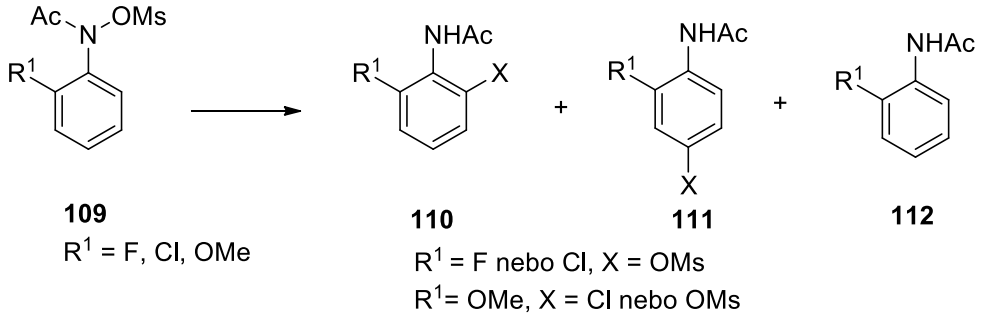
Method B: a) Zn, NH_4Cl; b) $NaHCO_3$, AcCl.



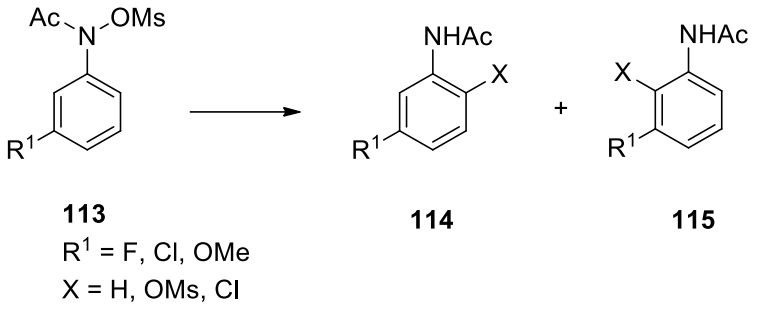
Scheme 22: Preparation of starting nitrocompounds



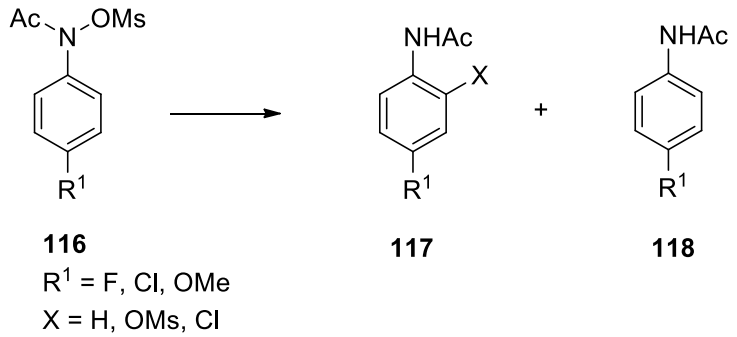
Scheme 23: Predicted mechanism of compound **107** and **108** formation



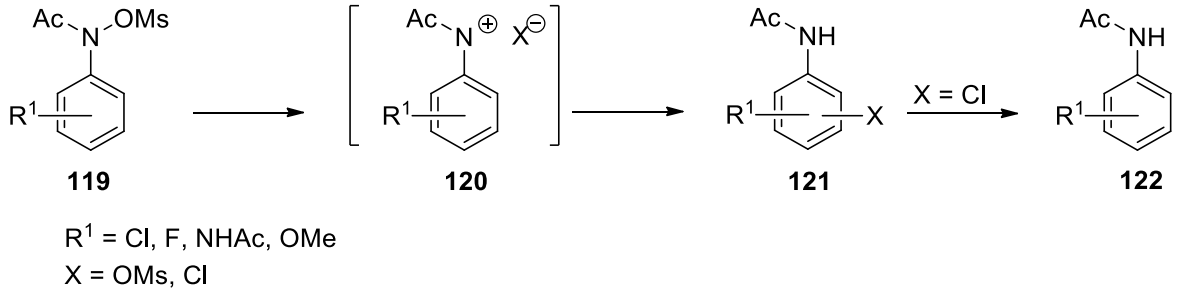
Scheme 34: Effect of *ortho* substituents on rearrangement



Scheme 35. Effect of *meta* substituents on rearrangement



Scheme 36: Effect of *para* substituents on rearrangement



Scheme 37: Proposed rearrangement mechanism