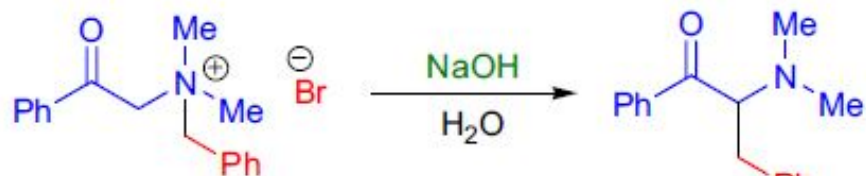


Stevens Rearrangement

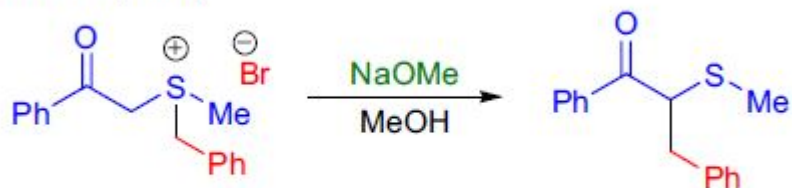
Stevens (1928):



phenacylbenzyltrimethyl
ammonium bromide

1-benzoyl-2-benzyl
dimethylamine

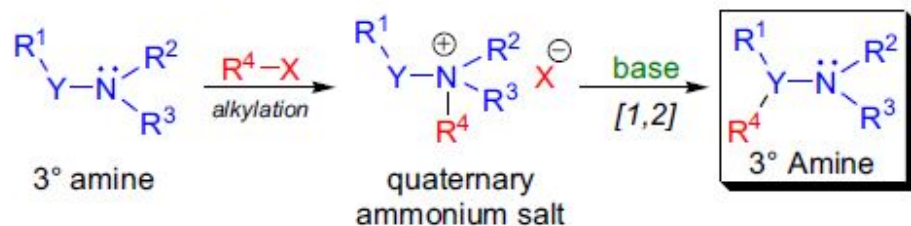
Stevens (1932):



phenacylbenzylmethyl
sulfonium bromide

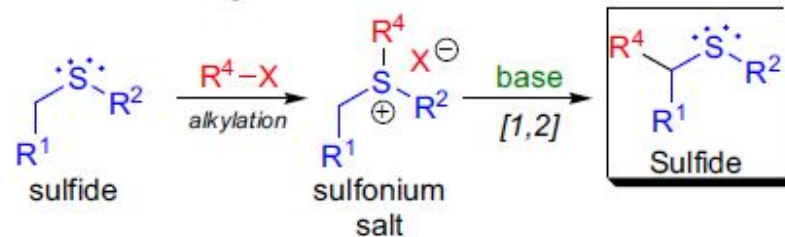
2-methylsulfanyl-1,3-
diphenylpropan-1-one

Stevens rearrangement of quaternary ammonium salts:



R^1 = EWG = Ar, heteroaryl, COR, COOR, CN; Y = CH_2 , CHR, NH; R^{2-3} = alkyl with no β -hydrogen, aryl; R^4 = CH_3 , alkyl, allyl, benzyl, CH_2COAr ; X = Cl, Br, I, OTs, OMs; base: NaH, KH, RLi, ArLi, RONA, ROK

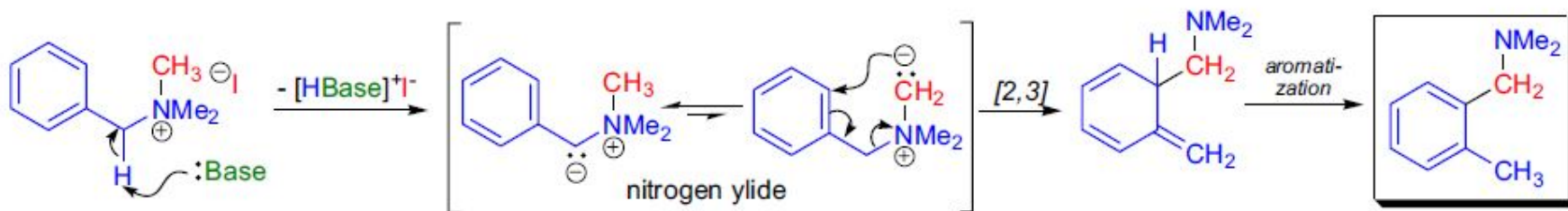
Stevens rearrangement of sulfonium salts:



Reaction features

1. the quaternary ammonium salts are readily available by the alkylation of the corresponding tertiary amines
2. The sulfonium salts are usually prepared by the direct alkylation of the corresponding sulfides.
3. The key intermediate of the rearrangement is the nitrogen or sulfur ylide.
4. the R^1 group has to be able to stabilize carbanions, so it is often an electron-withdrawing group.
5. Depending on the nature of R^1 , the acidity of the adjacent C-H bond varies so the type of base used for the deprotonation must be chosen accordingly.

6. When R1=aryl or heteroaryl, the *Sommelet-Hauser rearrangement* becomes competitive.



7. R2 and R3 groups of ammonium salts cannot contain a hydrogen at their β -position, since the *Hofmann elimination* may compete.

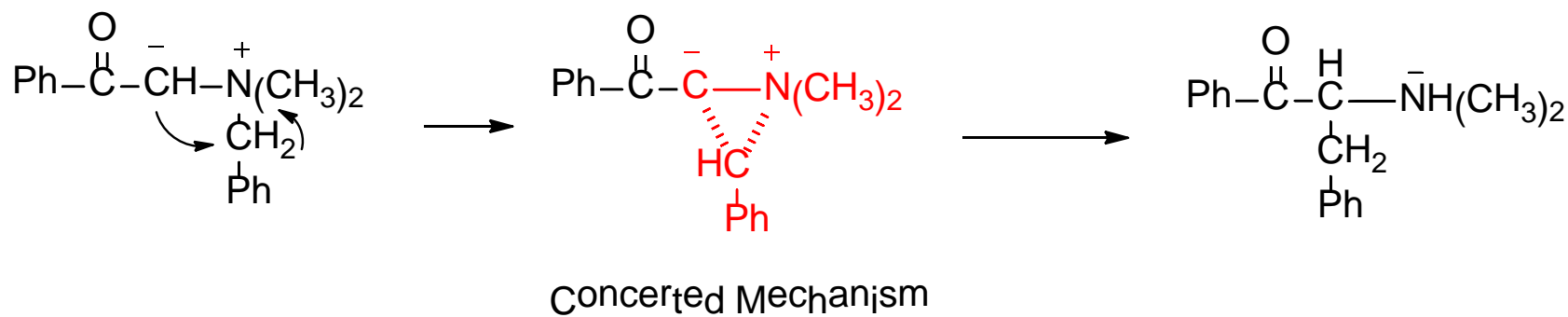
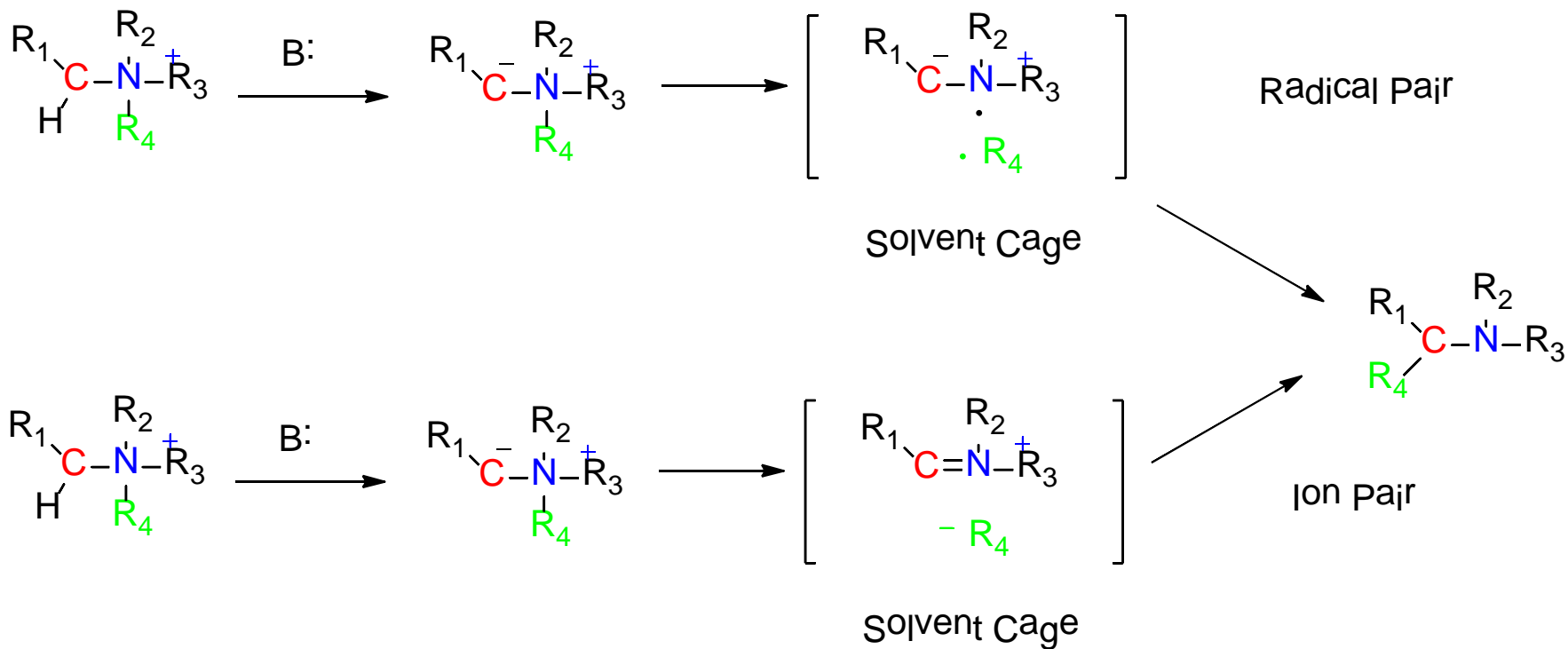
8. The migrating group (R4) is usually capable of stabilizing a carbon-centered radical.

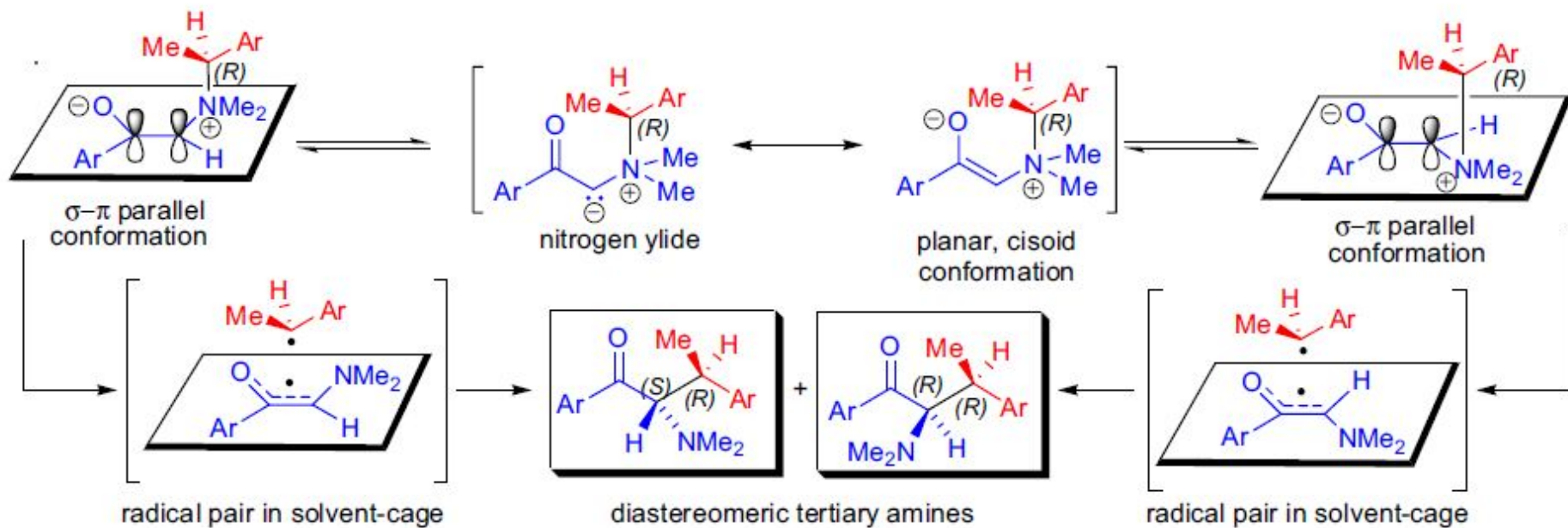
9. The migratory aptitude of benzyl groups depends on the substituents on the phenyl ring and decrease in the following order: $p\text{-NO}_2 > p\text{-halogen} > p\text{-Me} > p\text{-OMe}$.

10. When the migrating group has a stereocenter, it is transferred with retention of configuration at the migrating terminus.

11. The degree of the retention of configuration is influenced by the nature of substituents present on the migrating group.

13. In addition to nitrogen to carbon migrations, there are nitrogen to heteroatom migrations as well (when Y=NH).





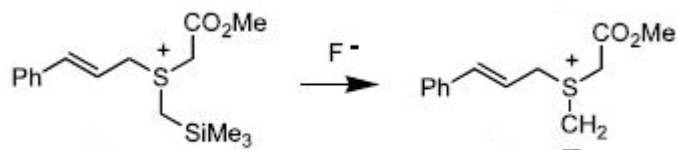
If the *Stevens rearrangement* is a concerted reaction, it is a symmetry-forbidden process based on the *Woodward-Hoffmann rules*.

Indeed, it was shown to occur *via* an intramolecular *homolytic cleavage-radical pair recombination* process, which explains the lack of crossover products and the observed retention of configuration at the migrating terminus.

The radicals are held in a solvent-cage in which there is a lack of rotation, and they recombine quickly.

Methods to generate ylide

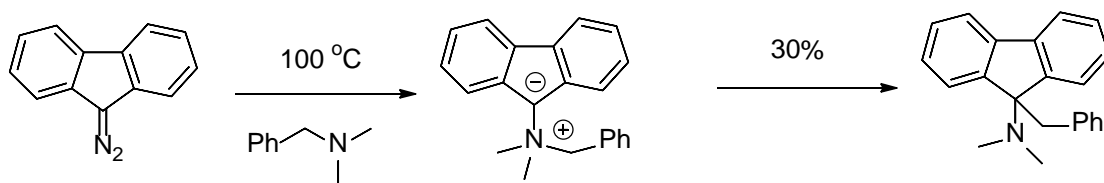
Fluoride-mediated desilylation to generate ylide



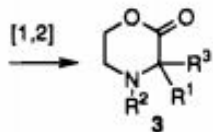
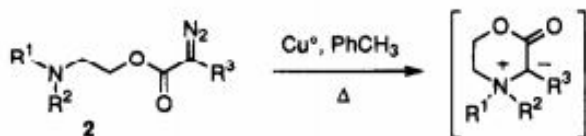
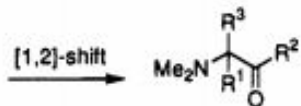
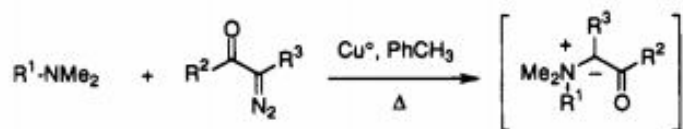
J. Am. Chem. Soc. 2001, 66, 2414-2421

J. Org. Chem. 1980, 45, 613-617

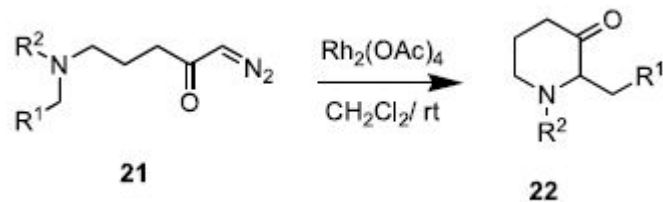
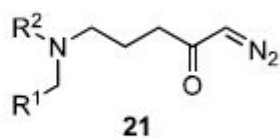
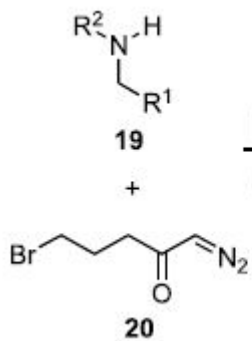
Ylide generation via carbenes



J. Chem. Soc. 1952, 4675-4678

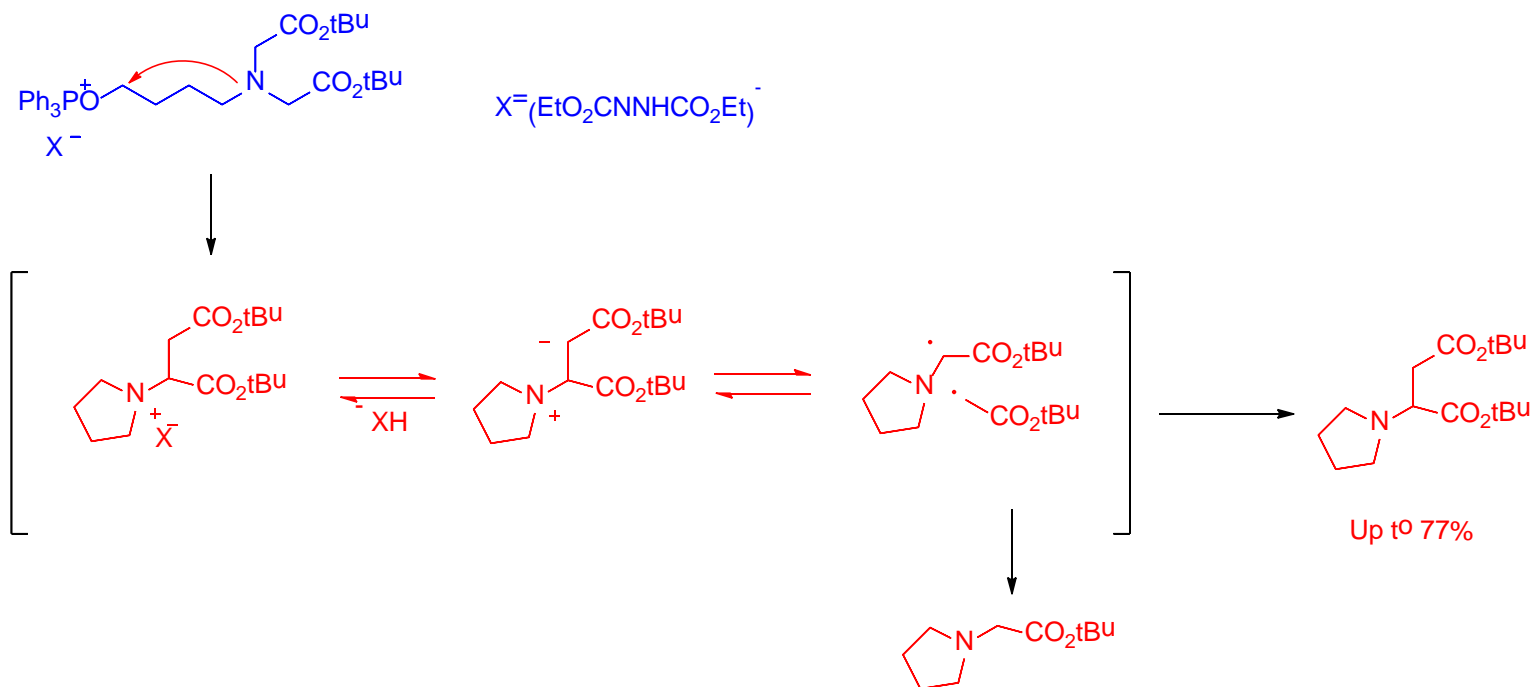
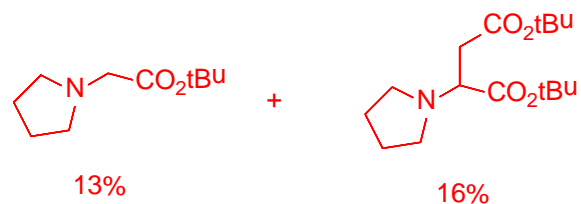
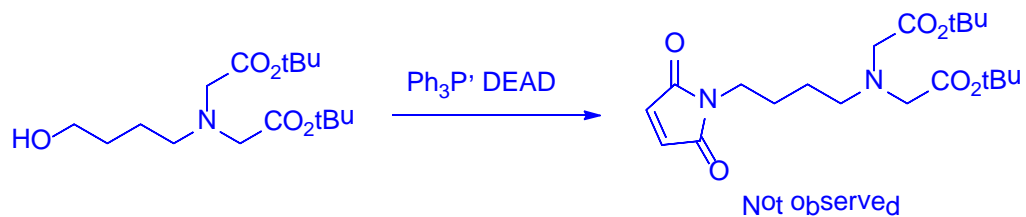


J. Org. Chem. 2001, 66, 2414-2421

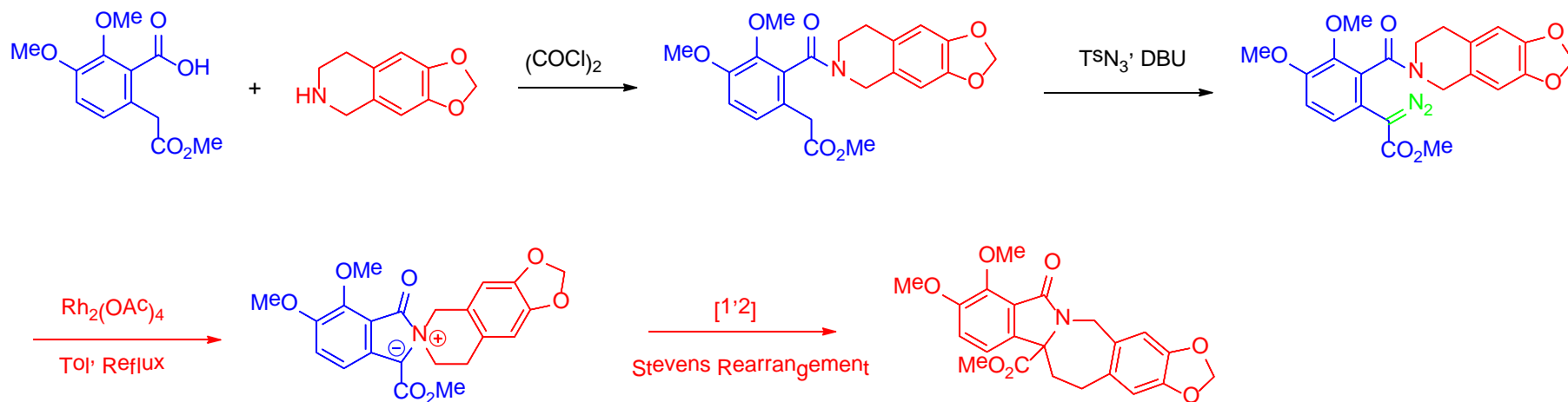


Prog. Inorg. Chem. 1982, 29, 73-154

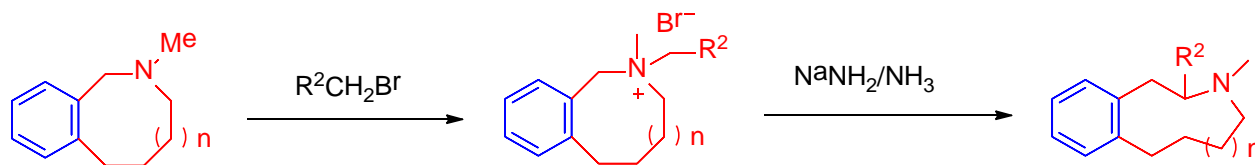
Ylide formation via Mitsunobu reaction



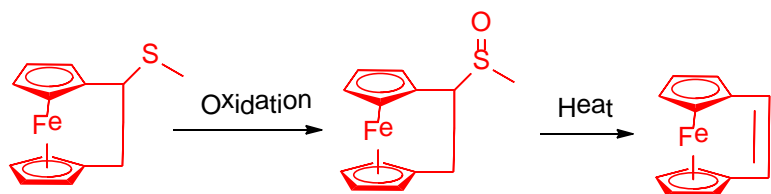
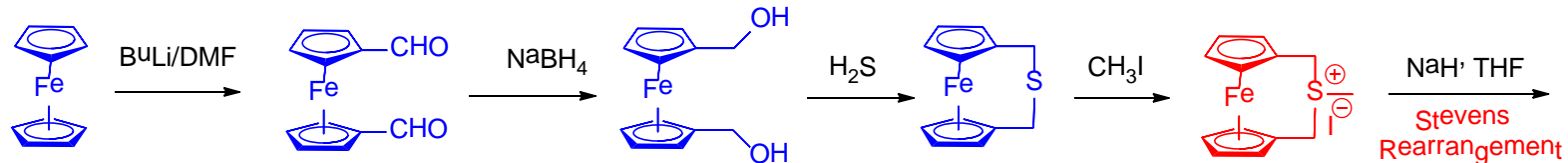
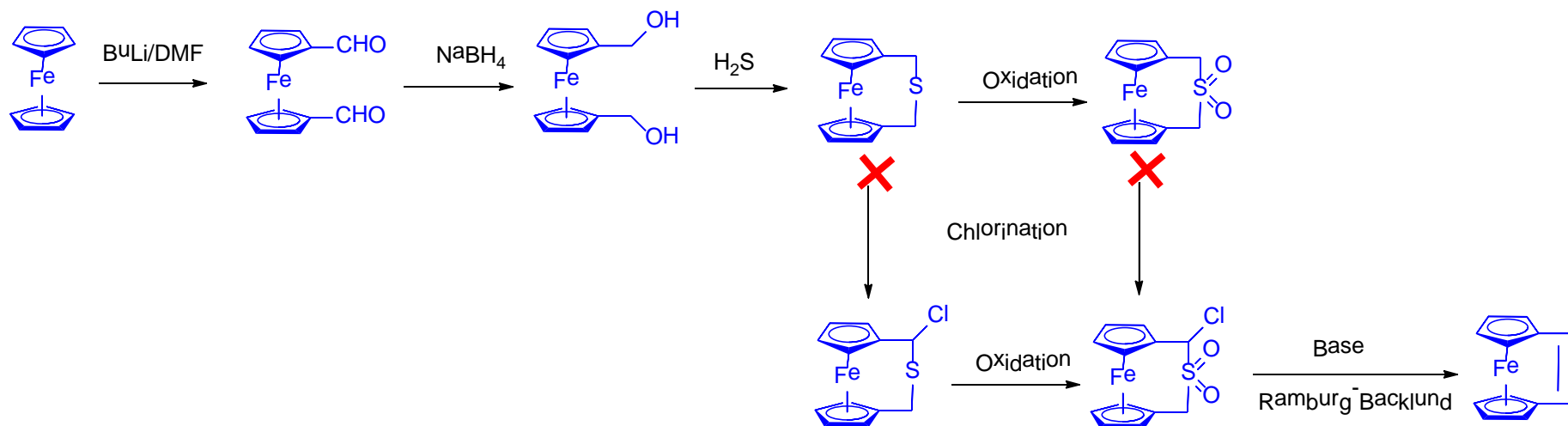
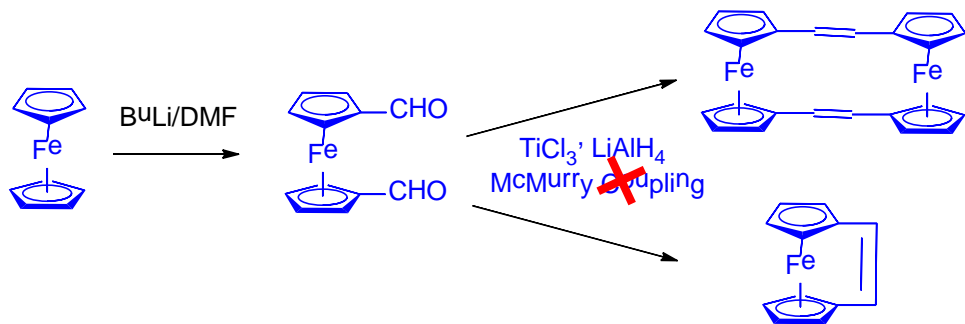
Applications in organic synthesis

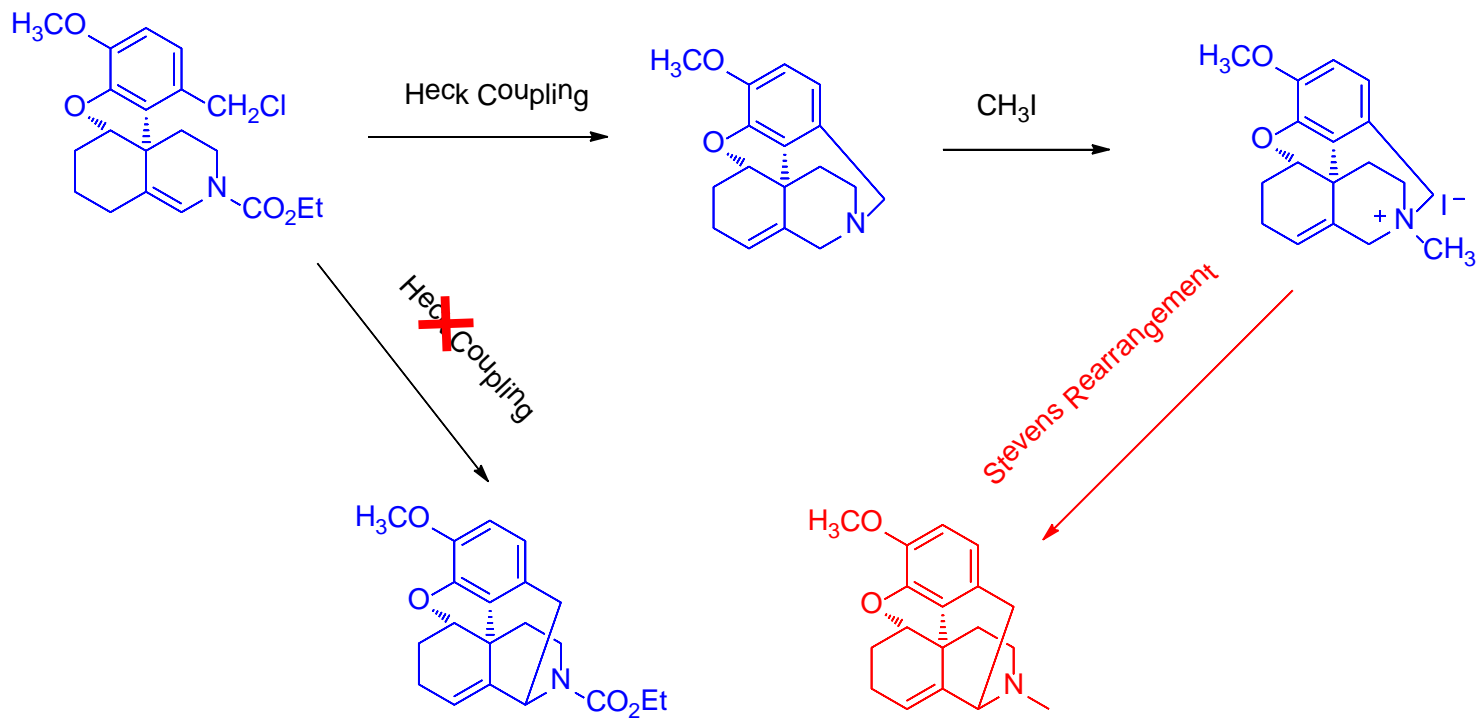


J. Org. Chem. 2001, 66, 2414-2421



Synthesis 1989, 327





Tetrahedron Letters, 2000, 41, 915-918

Thanks