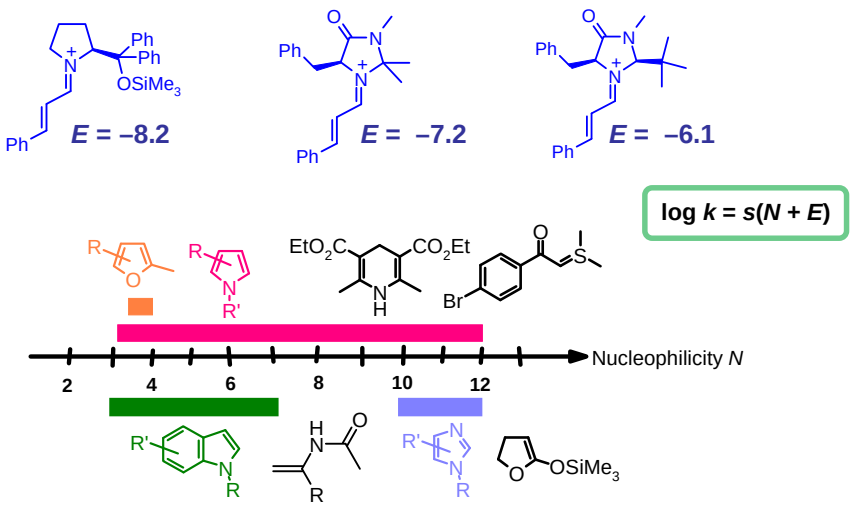
G. **Nucleophilic Organocatalysis** (Review #334)

The key-steps in many organocatalytic cycles are electrophile-nucleophile combinations as investigated in part F. Benzhydrylium ions and structurally related quinone methides have been employed to compare nucleophilicities (*k*) and Lewis basicities of tertiary amines (# 239, 275, 287), pyridines (# 235, 302), amidines (# 255), guanidines (#328), isothiourea derivatives (# 309, 320), and phosphines (# 214), i. e., nucleophilic organocatalysts. We have also determined reactivity parameters of intermediates, e. g. iminium ions (# 260, 310, 349, 361) or enamines (# 195, 295, 325, 326), as well as of potential substrates of iminium and enamine activated reactions (# 270, 284, 295, 315, 321, 324, 356, 366). Since nucleophilic substrates suitable for iminium activated reactions must react fast with iminium ions, but not with the precursor carbonyl compounds, nucleophiles with $3 < N < 12$ appear to be the most suitable substrates (# 290, 334). Particular attention has been paid to the unique reactivities of N-heterocyclic carbenes (# 308) and the resulting intermediates (# 329, 333, 353)



Nucleophiles must be strong enough to react with iminium ions and weak enough not to react with the precursor carbonyl compounds.

Figure 3. Nucleophiles suitable for iminium activated reactions