

Electron-Hole-Catalysis — An Approach towards non-acidic C(sp³)–H Functionalization

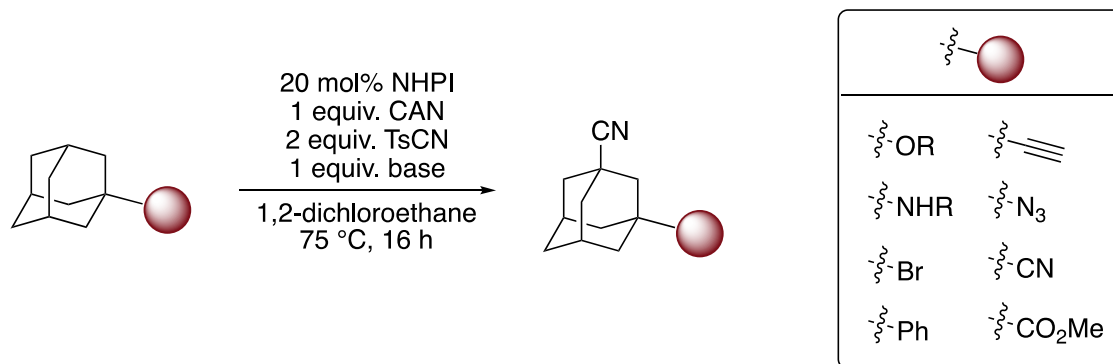
Group Seminar

Frederik R. Erb

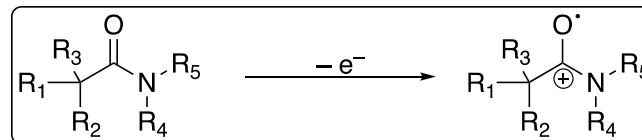
09.08.2019

Institute of Organic Chemistry, Justus Liebig University Giessen





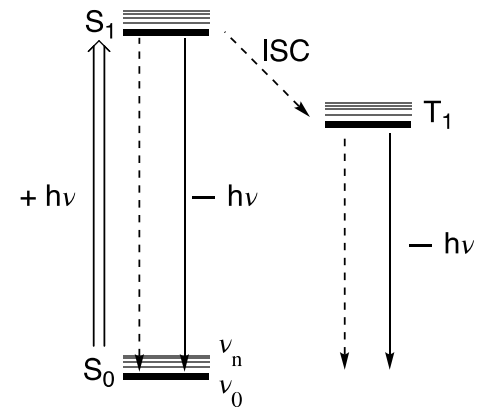
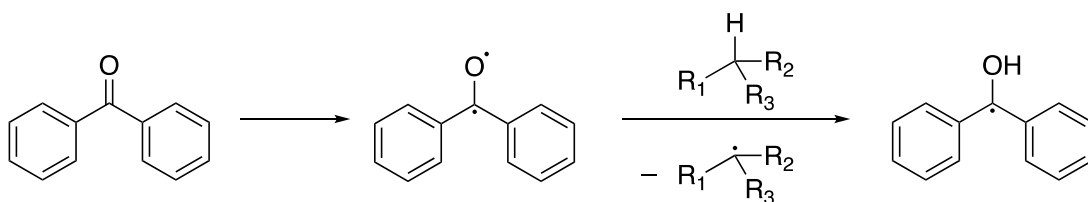
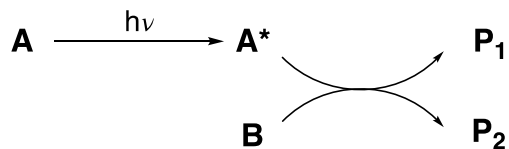
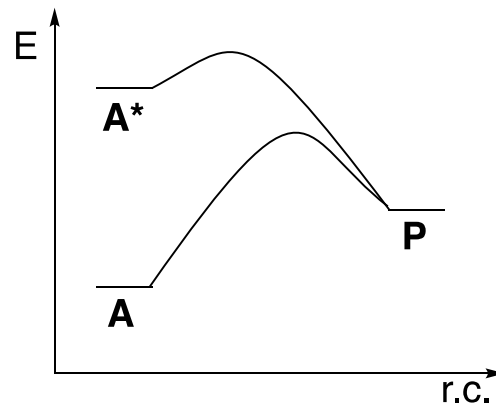
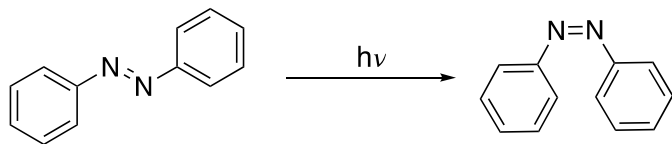
- Exchange radical precursor
 - Electrophilic character
 - Tunable
 - BDE > 95 kcal/mol
- Substitute oxidizing agent
 - Photoredox-Catalysis
 - Electrochemistry

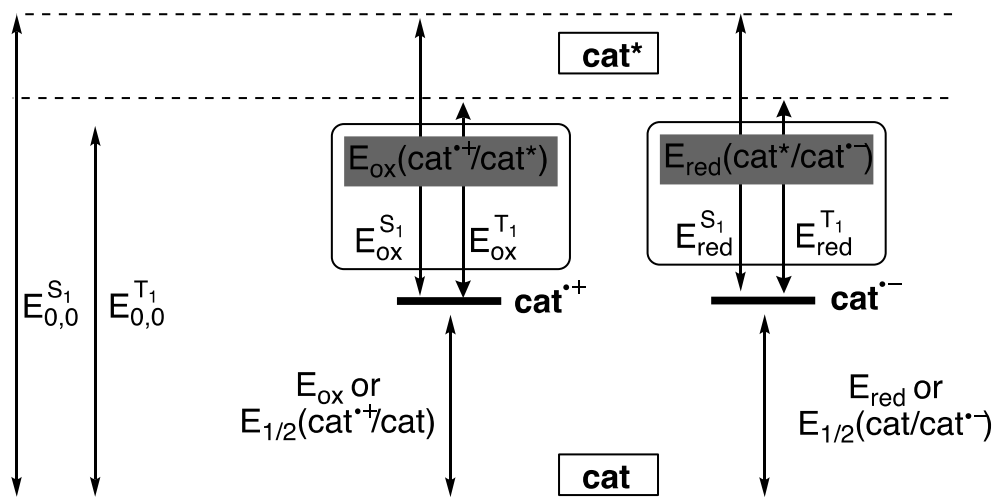
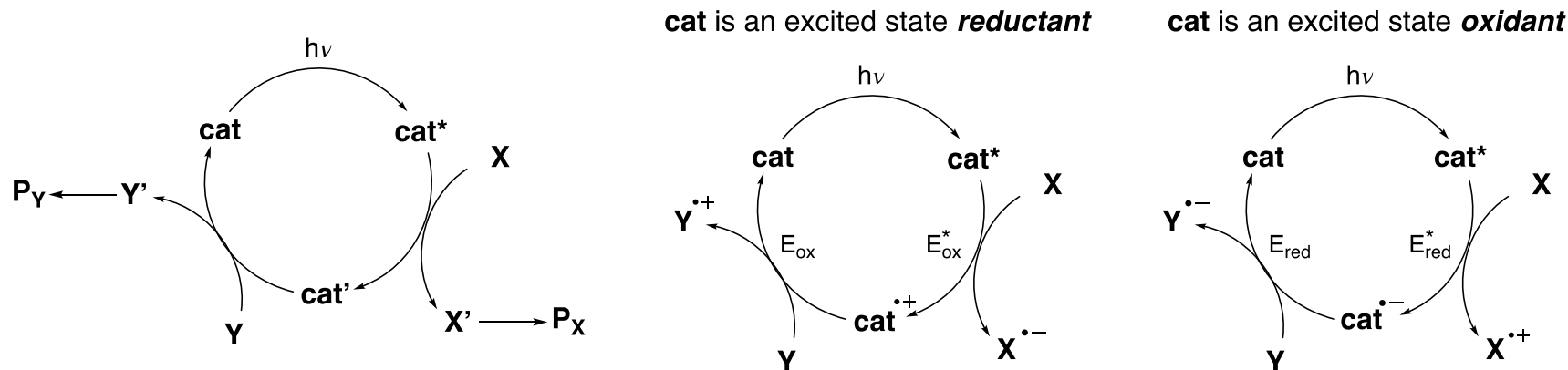




“When oil will have been all burned in our prodigal industries, it may become necessary, even on social grounds, to come to exploit solar energy.”

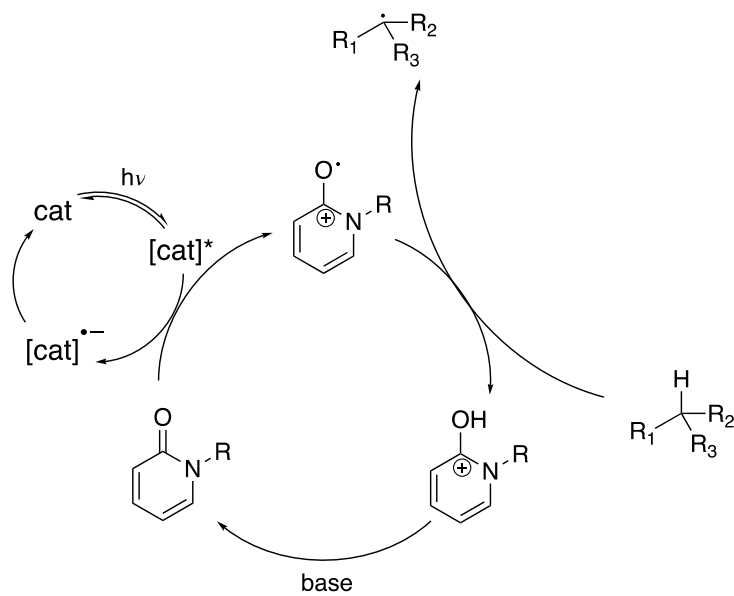
Giacomo Ciamician – **1908**

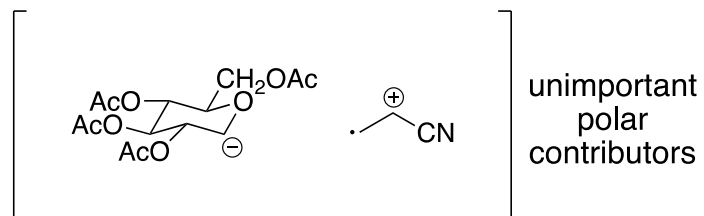
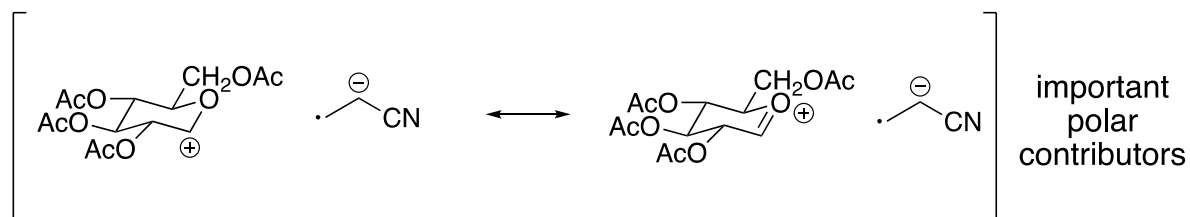
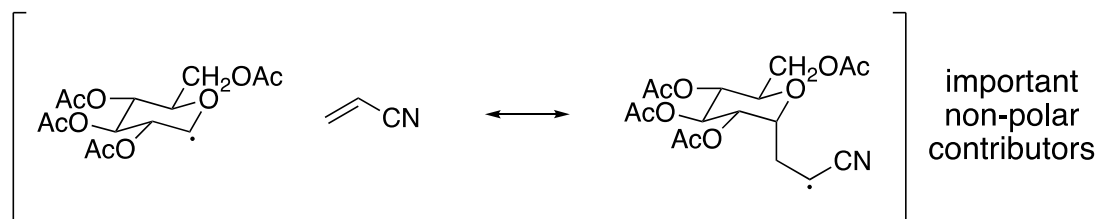
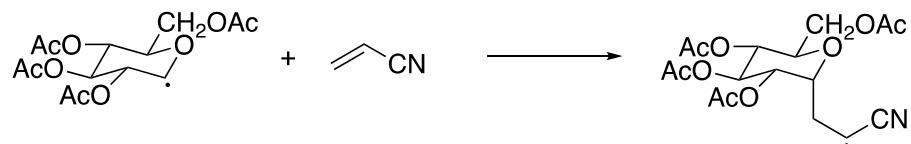




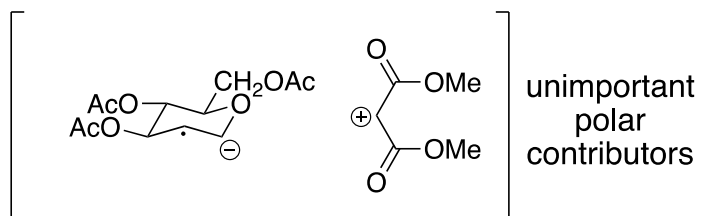
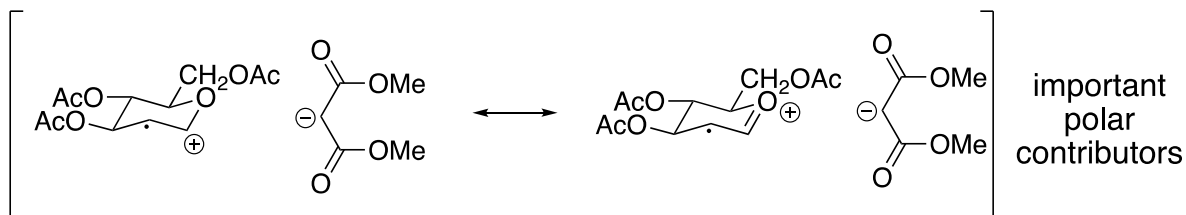
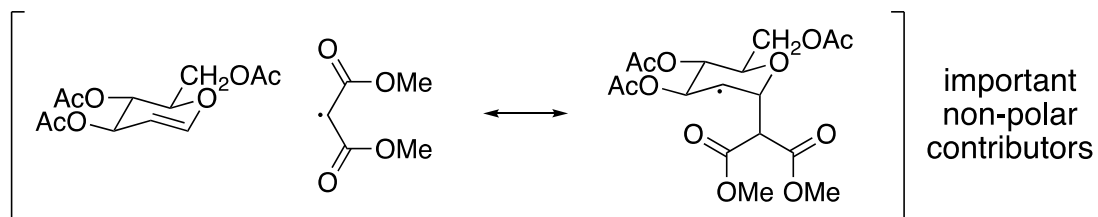
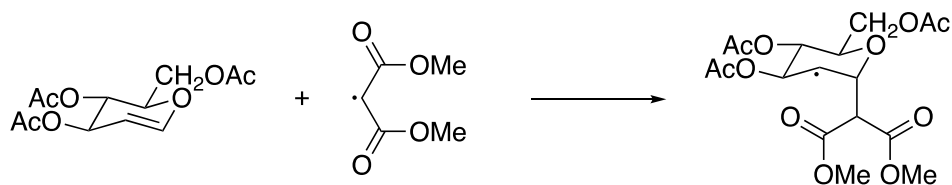
$$E^*_{red}(\mathbf{C}^*/\mathbf{C}^{\bullet-}) = E_{red}(\mathbf{C}/\mathbf{C}^{\bullet-}) + E_{0,0}$$

$$E^*_{ox}(\mathbf{C}^{\bullet+}/\mathbf{C}^*) = E_{ox}(\mathbf{C}^{\bullet+}/\mathbf{C}) - E_{0,0}$$

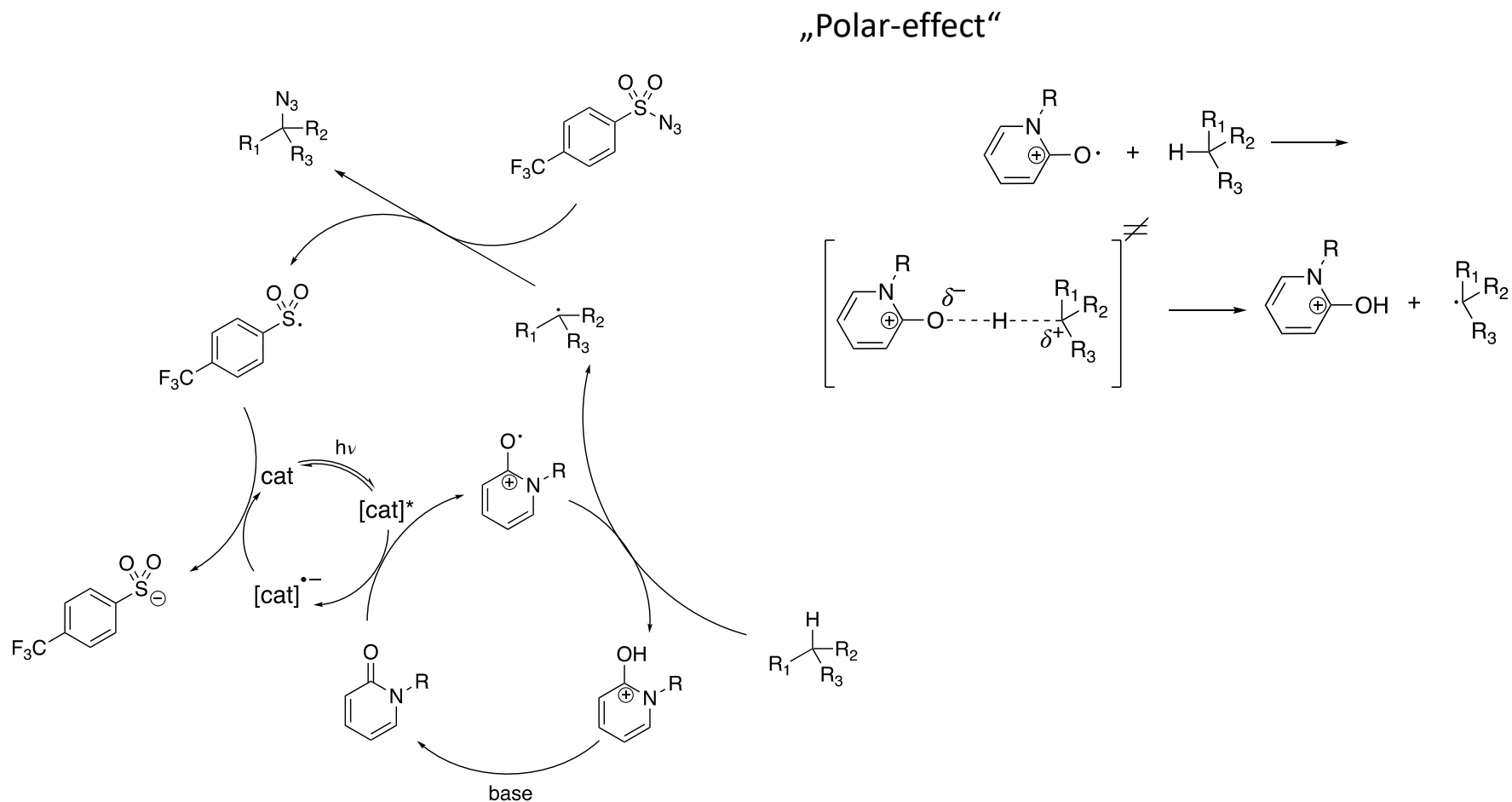


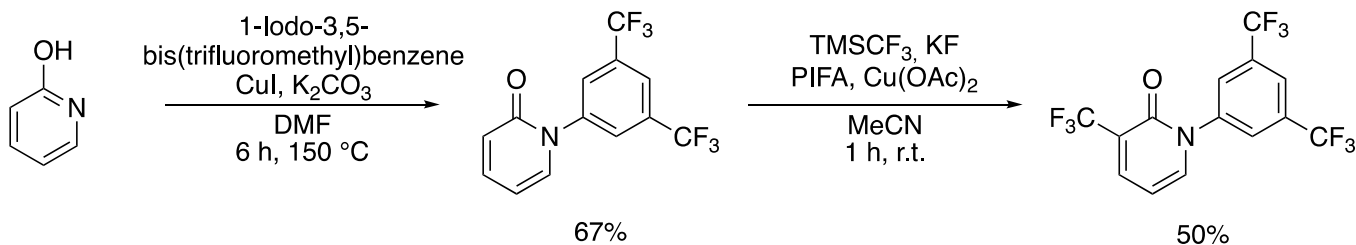
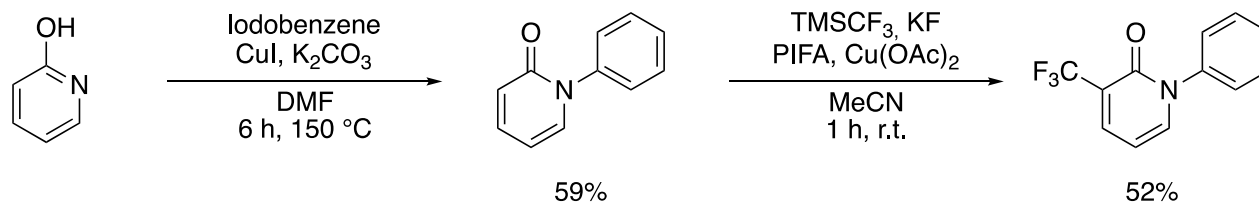


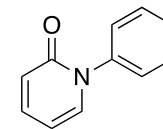
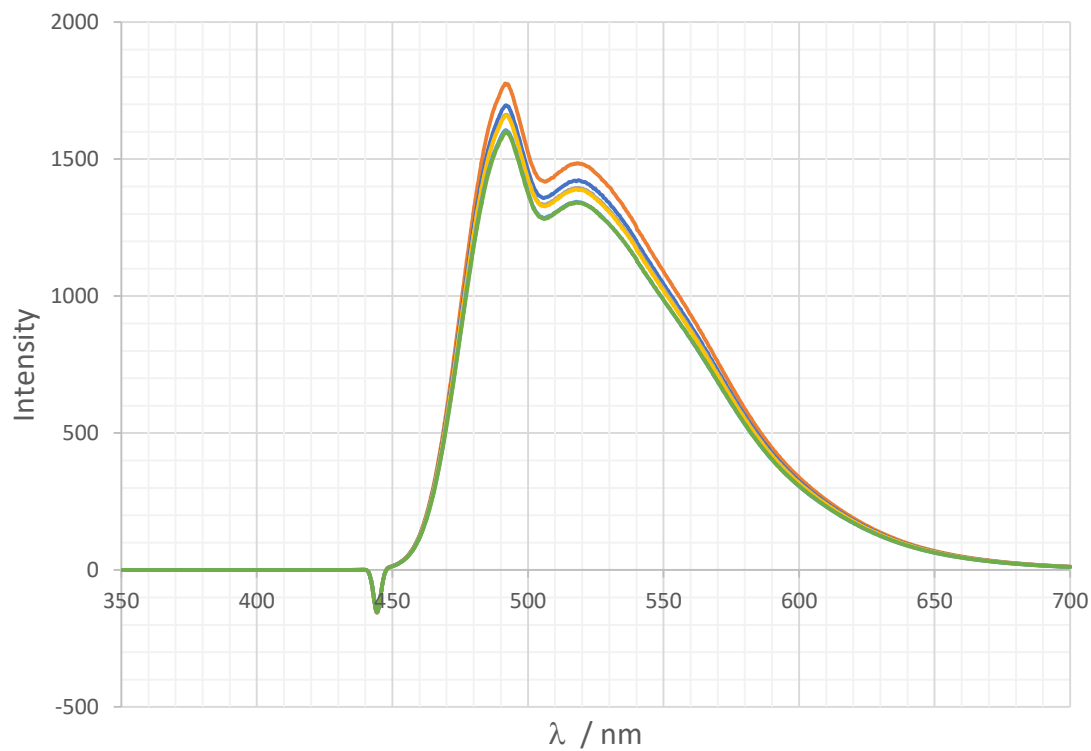
Nucleophilic radicals act as net electron-donors at the TS



Electrophilic radicals act as net electron-acceptors at the TS



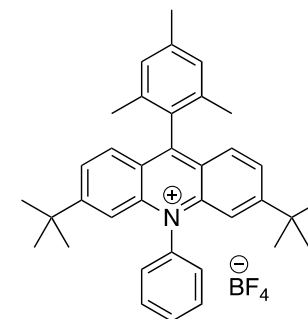




BDE = 104.0 kcal/mol

$E_{Ox} = 1.65$ V vs. SCE

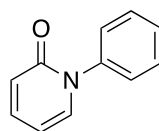
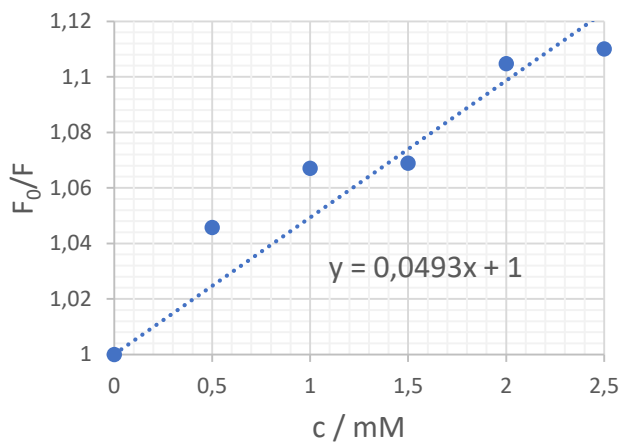
$\lambda_{max} = 311$ nm



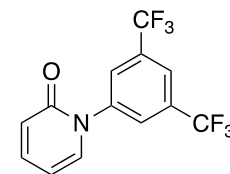
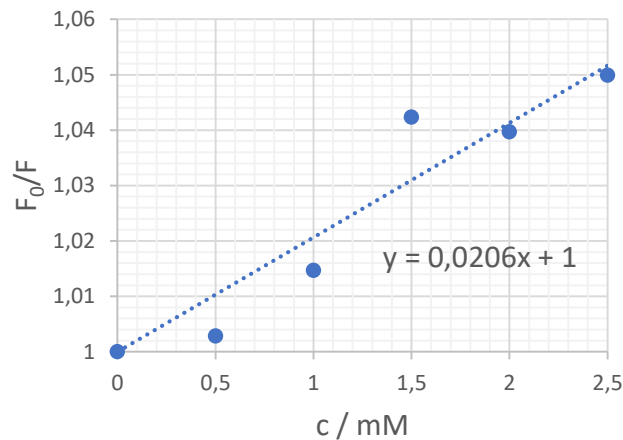
$E_{1/2}(Acr^+/Acr^{\bullet}) = + 2.08$ V vs SCE

$E_{1/2}(Acr^{\bullet}/Acr^{\bullet-}) = - 0.57$ V vs SCE

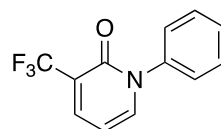
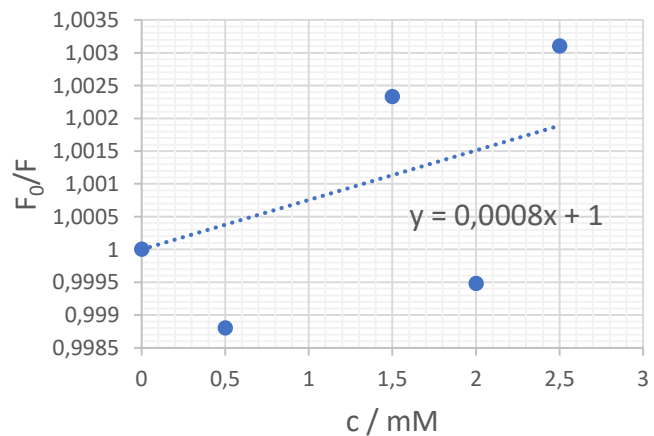
Stern-Volmer Kinetics



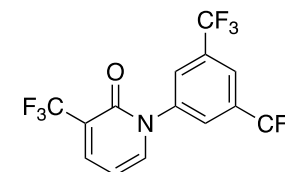
BDE = 104.0 kcal/mol
 E_{Ox} = 1.65 V vs. SCE
 λ_{max} = 311 nm



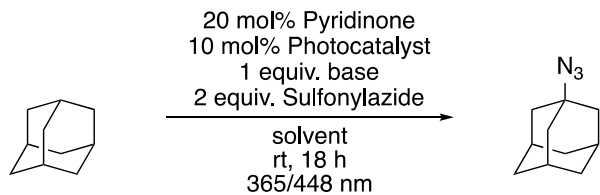
BDE = 105.0 kcal/mol
 E_{Ox} = 1.75 V vs. SCE
 λ_{max} = 321 nm



BDE = 107.1 kcal/mol
 E_{Ox} = 2.05 V vs. SCE
 λ_{max} = 320 nm

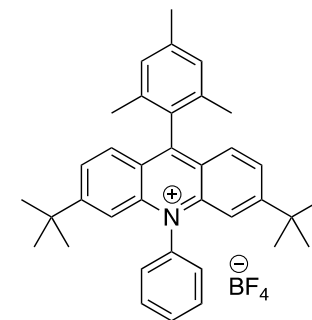
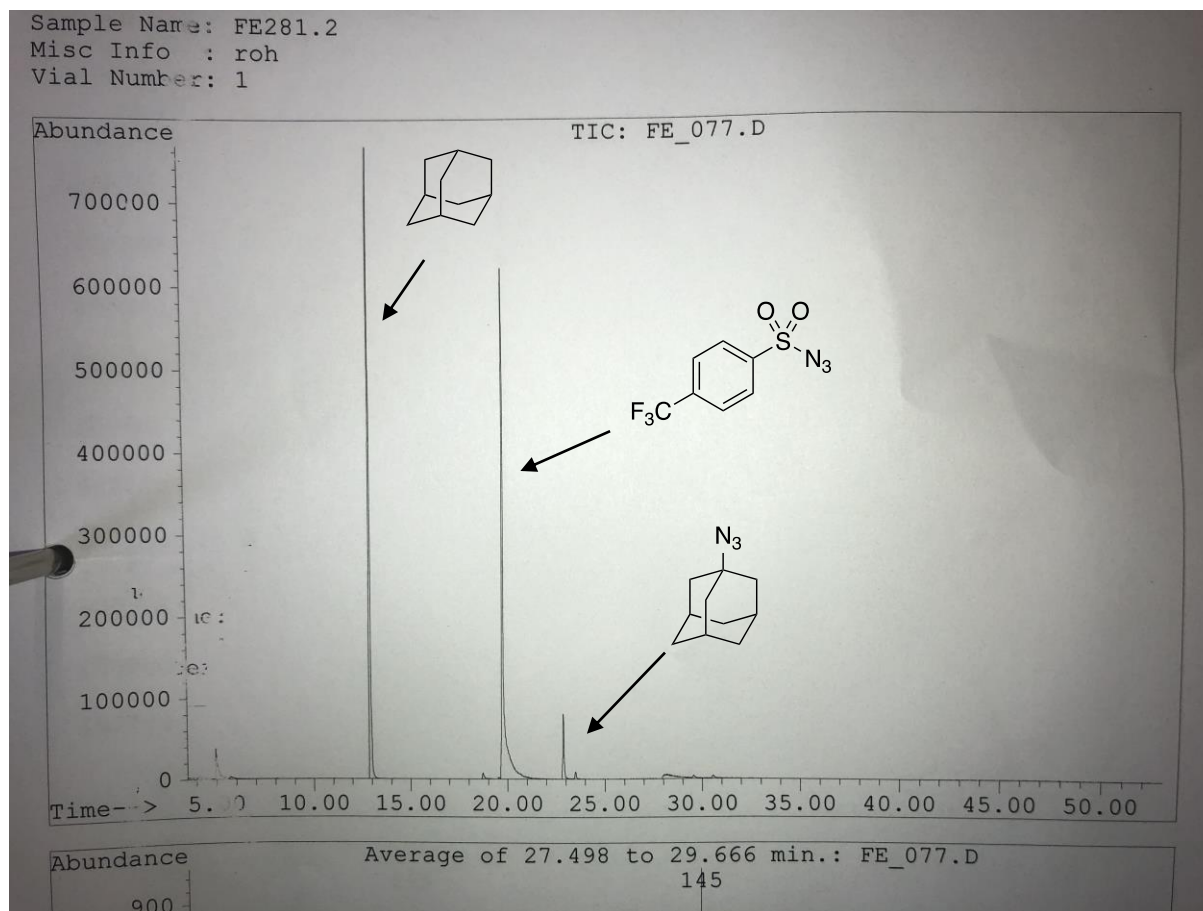


BDE = 108.0 kcal/mol
 E_{Ox} = 2.19 V vs. SCE
 λ_{max} = 314 nm



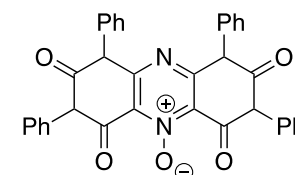
Base: Li_2CO_3 , 2,6-^tButylpyridine, Imidazole

Solvents: MeCN, Dichloroethane, HFIP, Trifluorotoluene, Chlorobenzene



$$E_{1/2}(\text{Acr}^+/\text{Acr}^\bullet) = +2.08 \text{ V vs SCE}$$

$$E_{1/2}(\text{Acr}^+/\text{Acr}^-) = -0.57 \text{ V vs SCE}$$

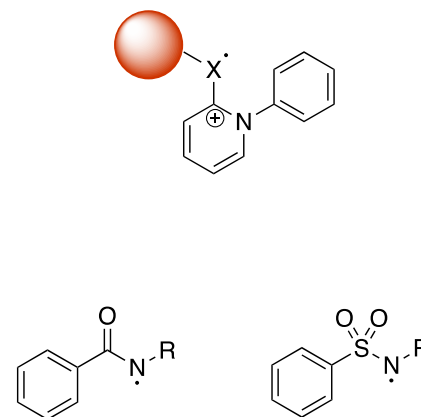
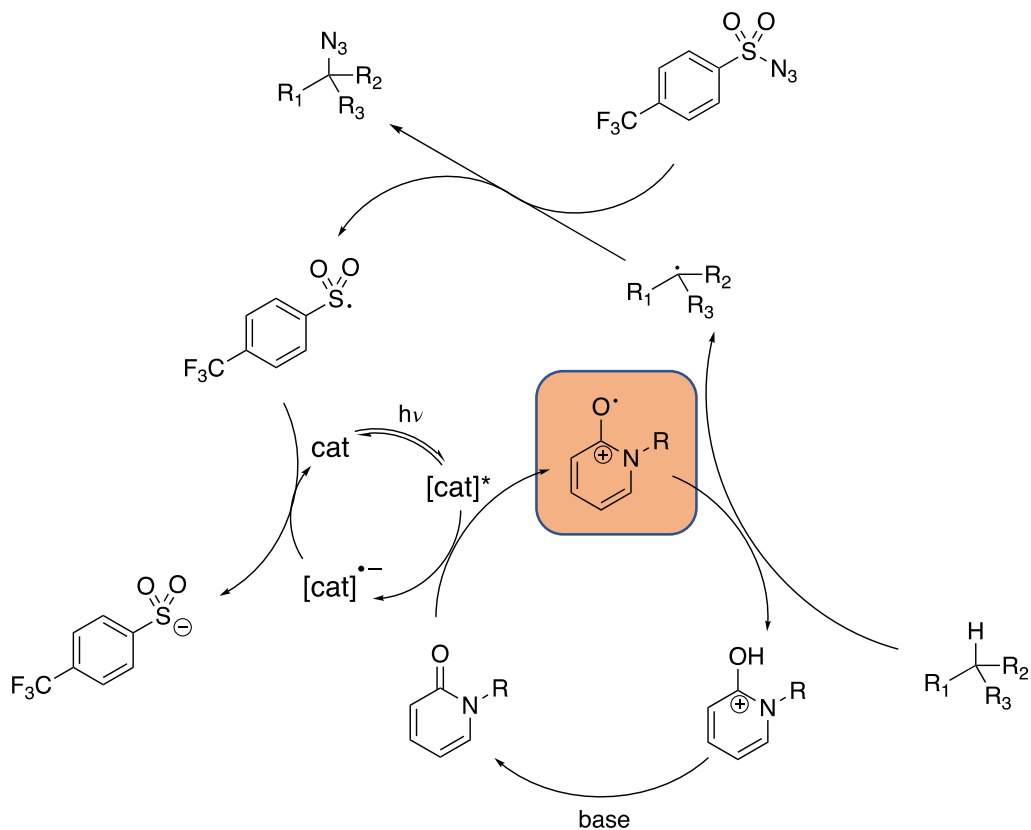


$$E_{1/2}(\text{PPTNO}^+/\text{PPTNO}^\bullet) = +2.32 \text{ V vs SCE}$$

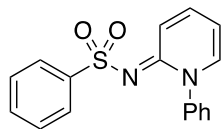
$$E_{1/2}(\text{PPTNO}^+/\text{PPTNO}^-) = -0.92 \text{ V vs SCE}$$



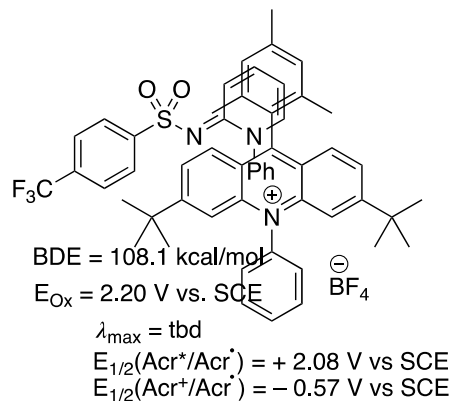
Increase lifetime of radical cation



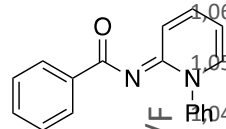
Sulfonylimines



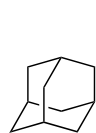
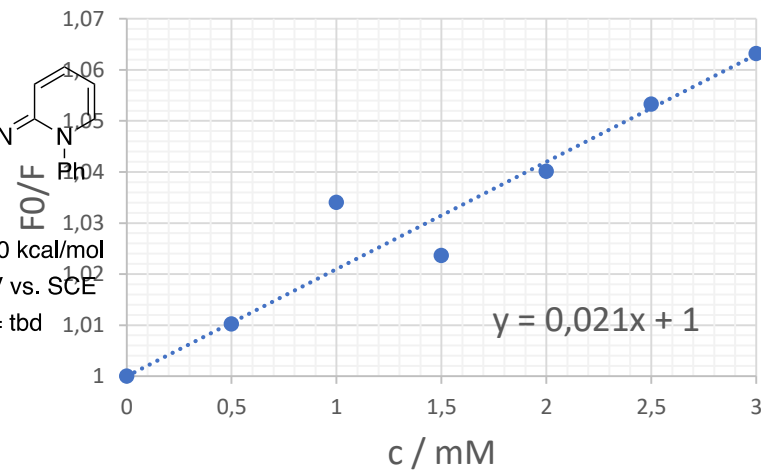
BDE = 108.6 kcal/mol
 $E_{Ox} = 1.80$ V vs. SCE
 $\lambda_{max} = 356$ nm



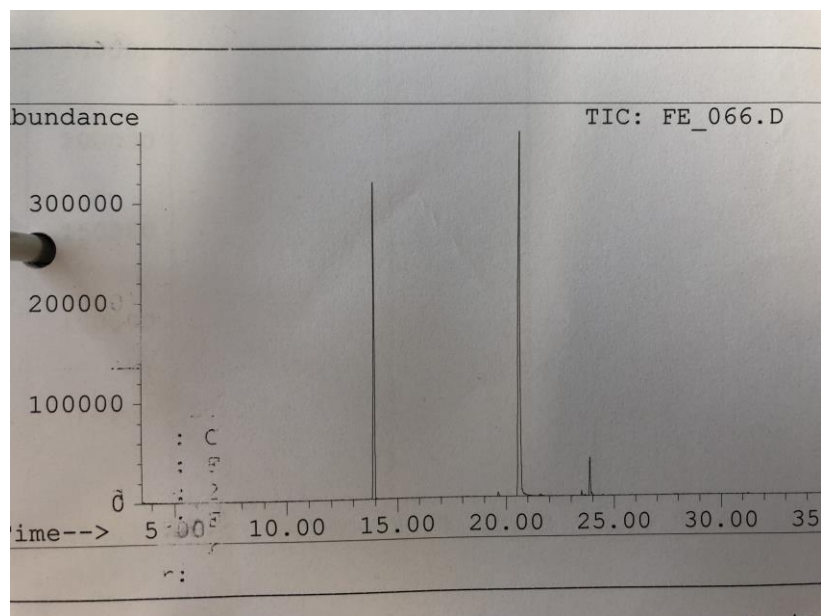
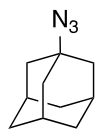
BDE = 108.1 kcal/mol
 $E_{Ox} = 2.20$ V vs. SCE
 $\lambda_{max} = \text{tbd}$
 $E_{1/2}(Acr^+/Acr^*) = +2.08$ V vs SCE
 $E_{1/2}(Acr^+/Acr^*) = -0.57$ V vs SCE

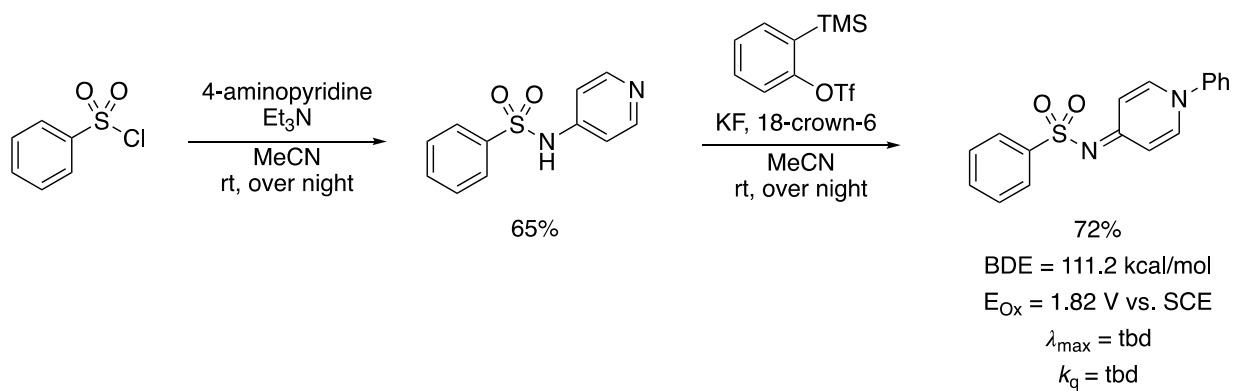
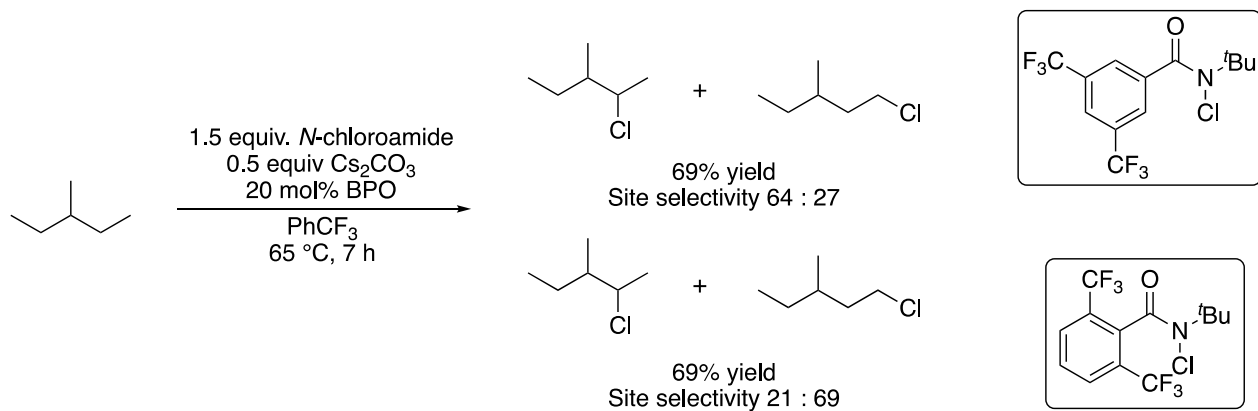


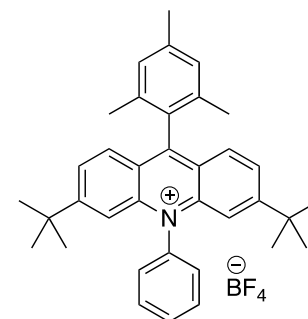
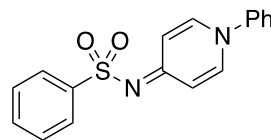
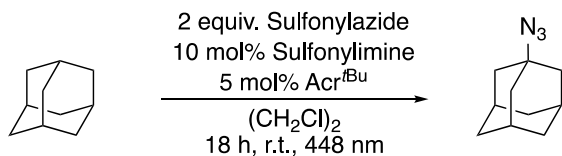
BDE = 106.0 kcal/mol
 $E_{Ox} > 2.5$ V vs. SCE
 $\lambda_{max} = \text{tbd}$



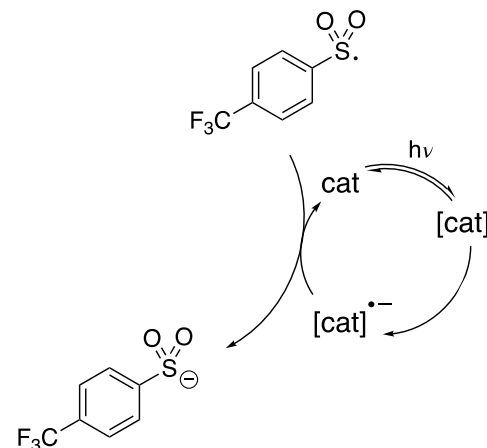
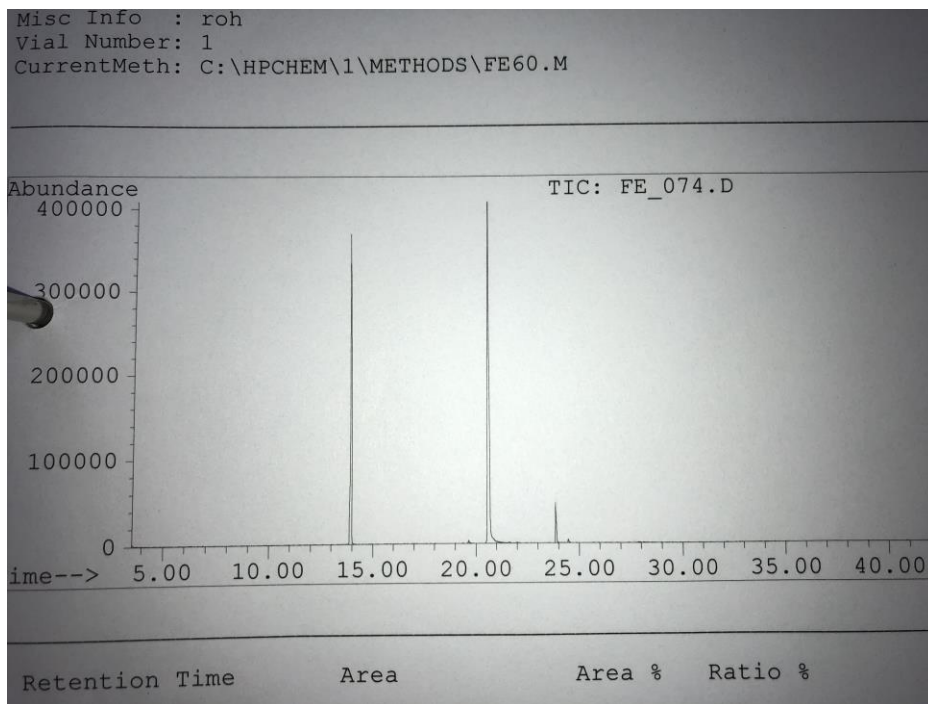
2 equiv. Sulfonylazide
 10 mol% Sulfonylimine
 5 mol% Acr^{tBu}
 $PhCF_3$
 18 h, r.t., 448 nm



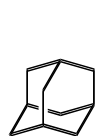




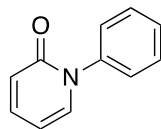
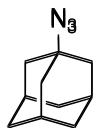
$E_{1/2}(\text{Acr}^*/\text{Acr}^+) = + 2.08 \text{ V vs SCE}$
 $E_{1/2}(\text{Acr}^+/\text{Acr}^{\cdot-}) = - 0.57 \text{ V vs SCE}$



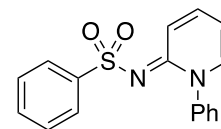
What is the outcome?



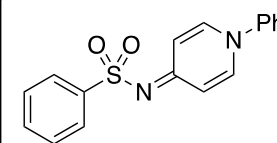
2 equiv. Sulfonylazide
10 mol% Sulfonylimine
5 mol% Acr^{IBu}
 $(\text{CH}_2\text{Cl})_2$
 50 °C, 18 h, 448 nm



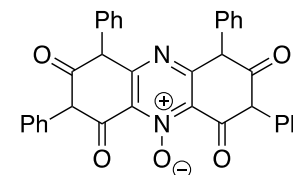
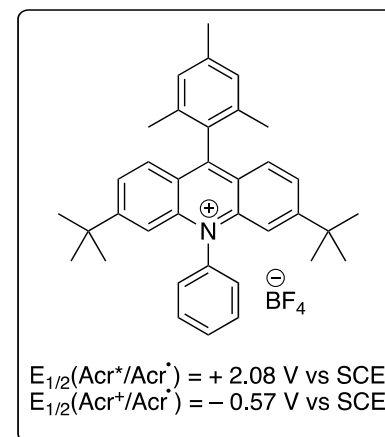
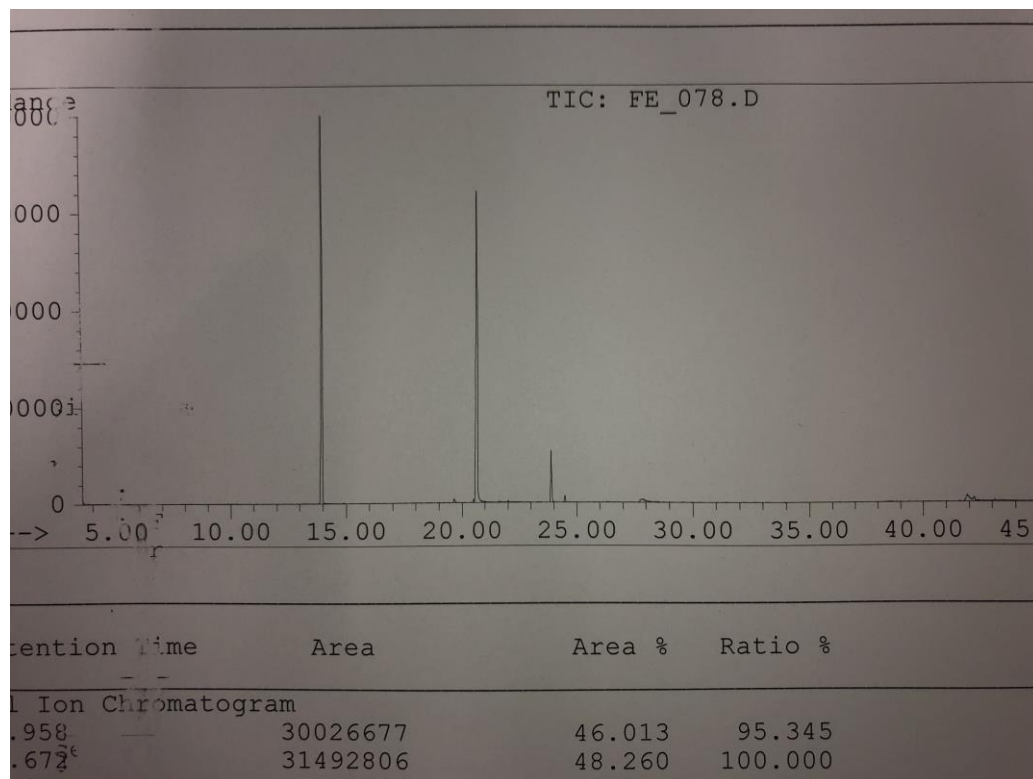
BDE = 104.0 kcal/mol
 $E_{\text{Ox}} = 1.65 \text{ V vs. SCE}$
 $\lambda_{\text{max}} = 311 \text{ nm}$



BDE = 108.6 kcal/mol
 $E_{\text{Ox}} = 1.80 \text{ V vs. SCE}$
 $\lambda_{\text{max}} = 356 \text{ nm}$



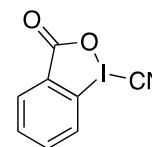
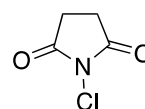
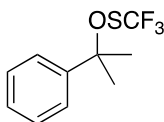
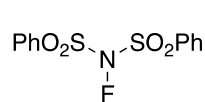
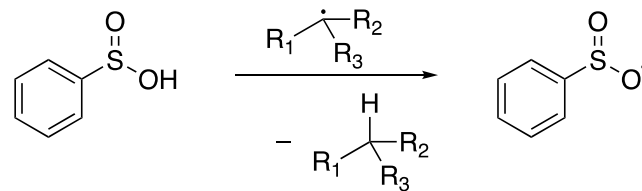
BDE = 111.2 kcal/mol
 $E_{\text{Ox}} = 1.82 \text{ V vs. SCE}$
 $\lambda_{\text{max}} = \text{tbd}$



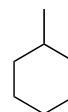
$E_{1/2}(\text{PPTNO}^+/\text{PPTNO}^\bullet) = + 2.32 \text{ V vs SCE}$
 $E_{1/2}(\text{PPTNO}^+/\text{PPTNO}^-) = - 0.92 \text{ V vs SCE}$



- Influence of sulfinic acid
- Electron vs energy transfer
- Conformational analysis of the transition state
- Computing activation barrier
- Reaction optimization
- Applying different trapping agents



- Screening of different substrates





Prof. Dr. Peter R. Schreiner

Marvin, Jonas, Lukas, JPB, Dominik,
Friedhelm, Tpsi, Alex, Markus,
Eschi, Jan, Kai, Keule

Quanzi, Dennis

PRS Group

