

Carbon–Carbon Bond Forming Reactions via Photogenerated Intermediates

Reporter: Rongyi Zhang

November 28 2016

Maurizio Fagnoni *et al.* *Chem. Rev.* **2016**, *116*, 9850–9913

DOI: [10.1021/acs.chemrev.5b00662](https://doi.org/10.1021/acs.chemrev.5b00662)

Content

Photogeneration of Reactive Intermediates

Radicals

Radical Pairs/Biradicals

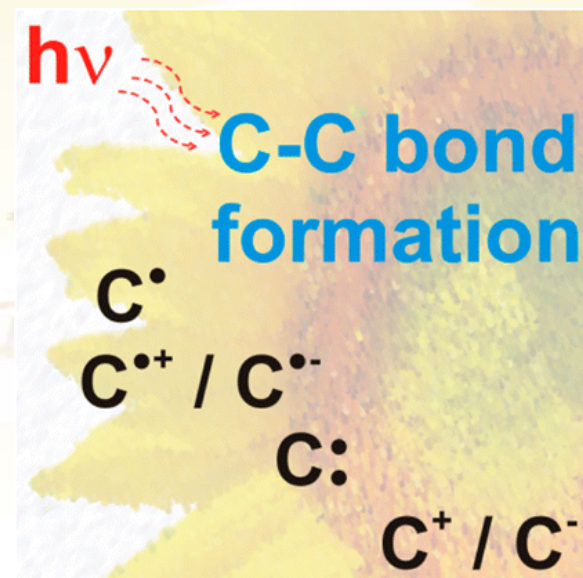
Radical Ions

Carbocations /Carbanions

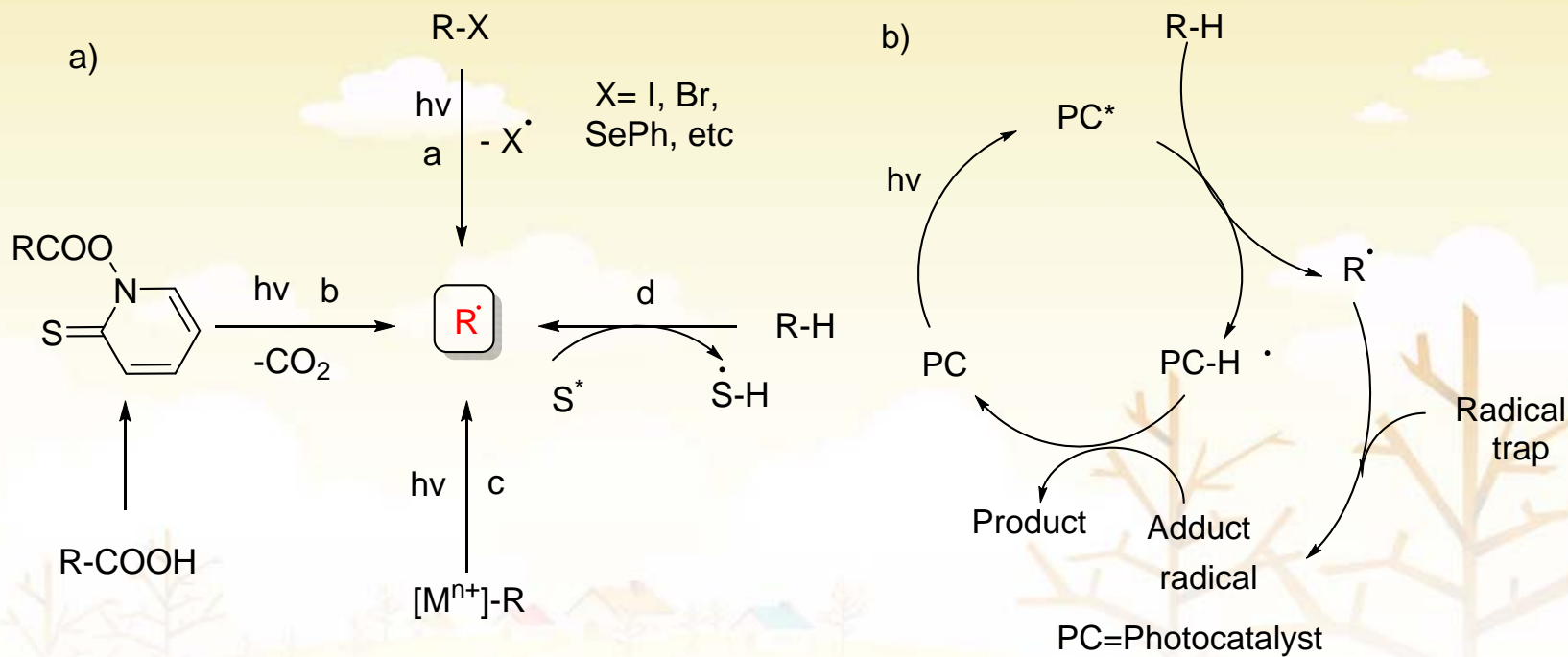
Carbenes

Common Photoredox Catalysts

Potential of molecules and photocatalysts

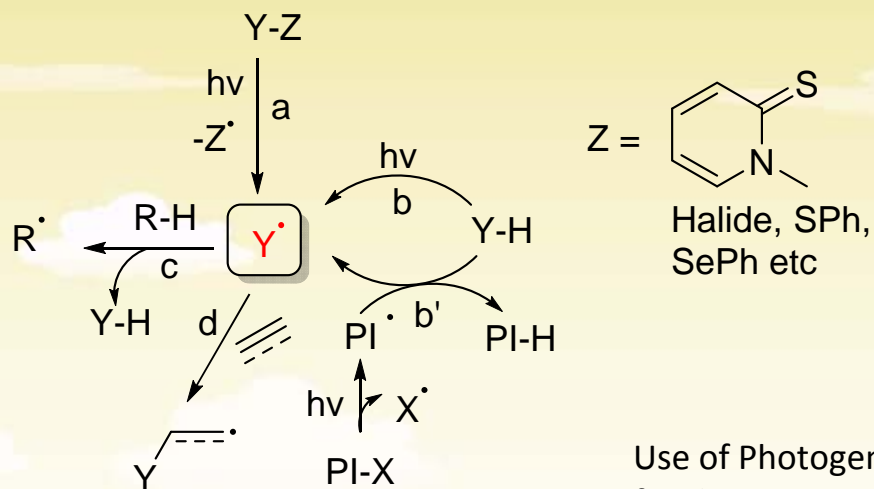


Radicals

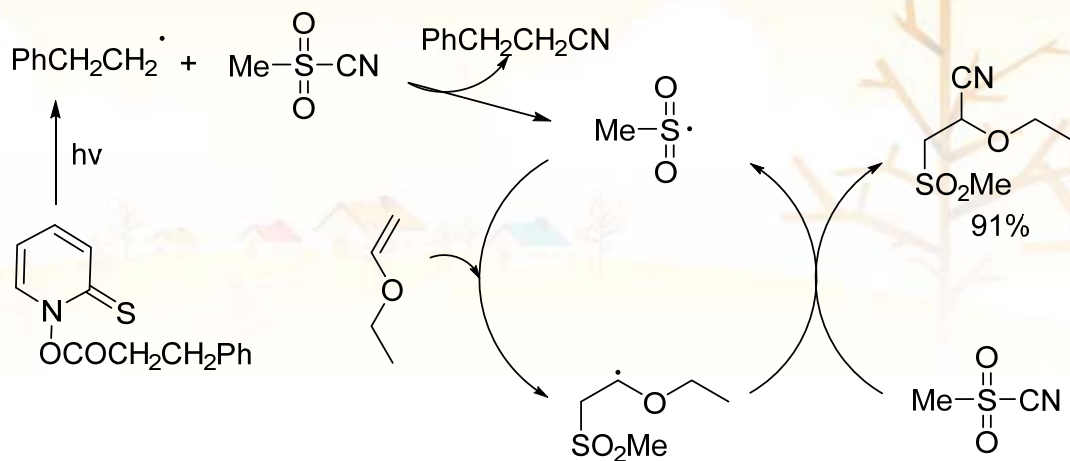


(a) Modes of Photogeneration of Radicals; (b) General Scheme of a Photocatalyzed Hydrogen Atom Transfer (HAT) Reaction

Radicals

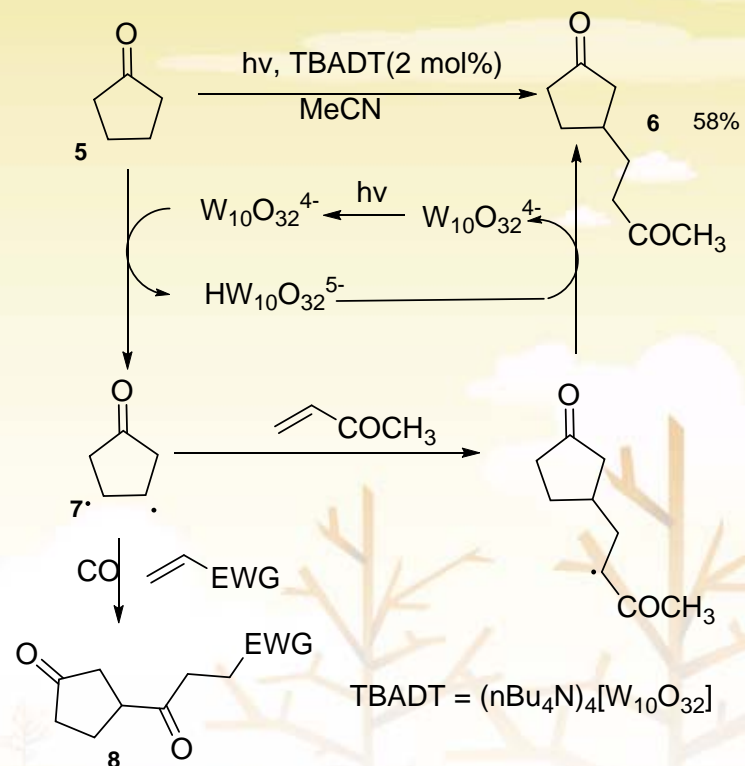
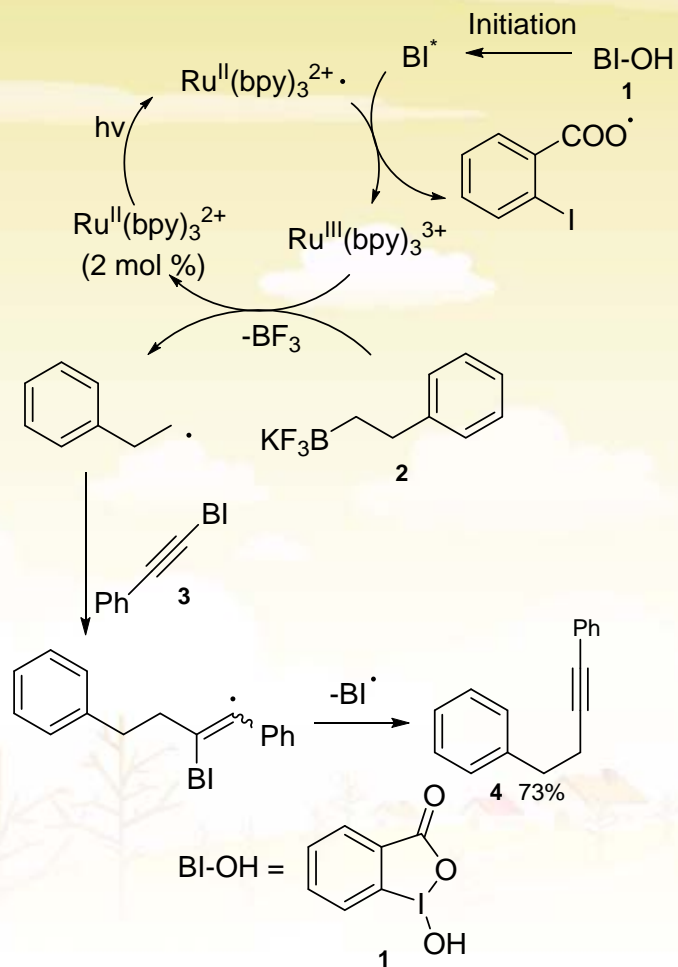


Use of Photogenerated Heteroatom Based Radicals for the Formation of Carbon Centered Radicals

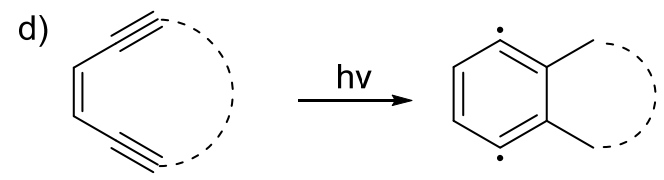
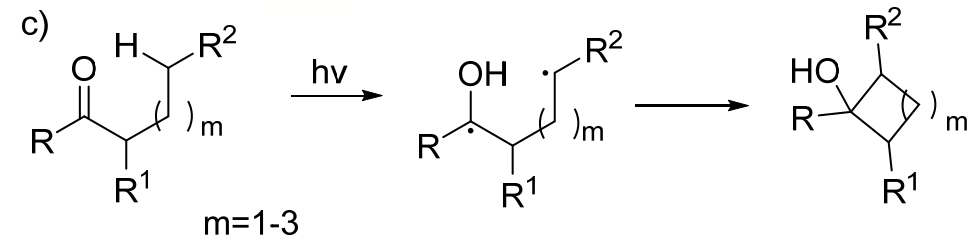
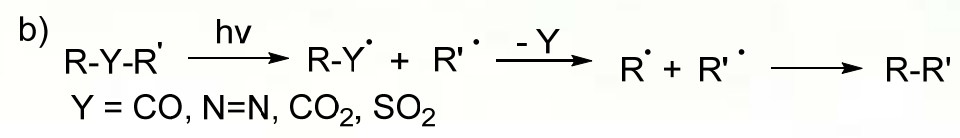
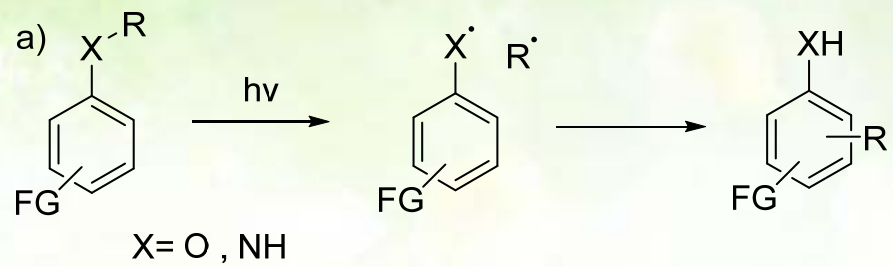


Barton, D. H. R et al. *Tetrahedron* **1992**, *48*, 2613–2626.

Radicals

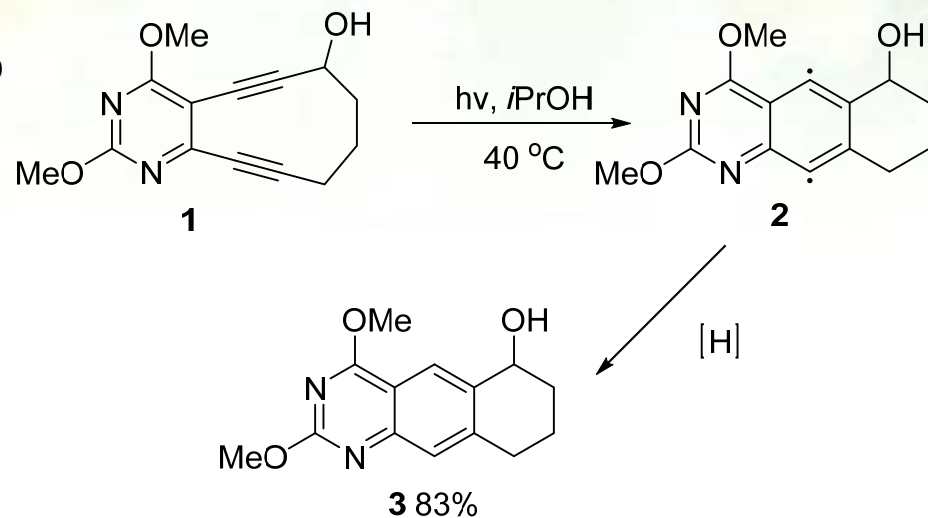
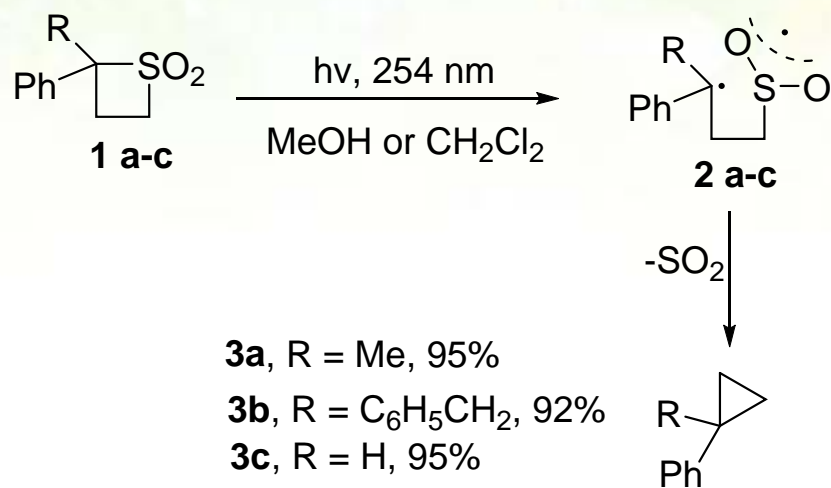


Radical Pairs/Biradicals



Modes of Photogeneration of (a and b) Radical Pairs and (c and d) Biradicals

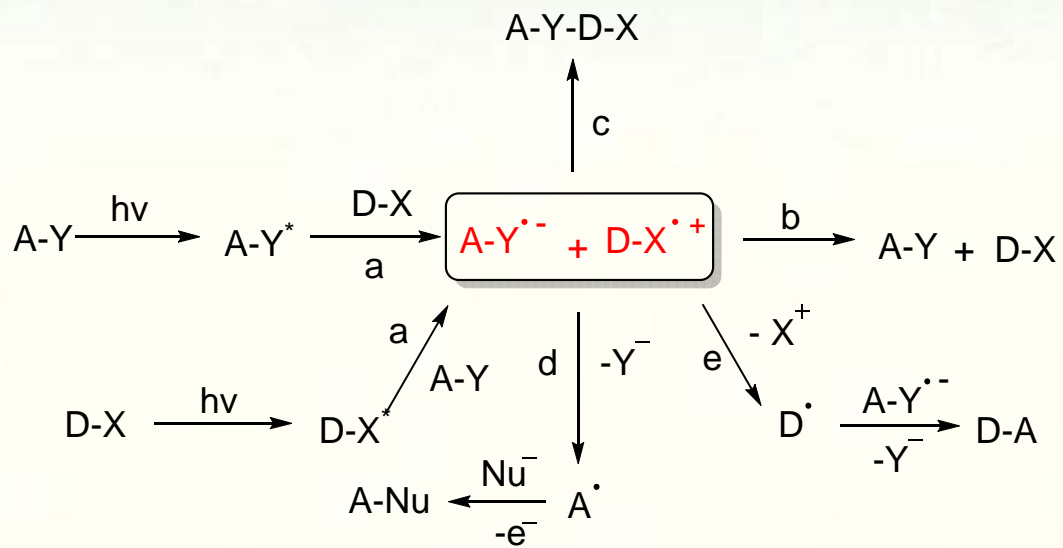
Radical Pairs/Biradicals



Smith, D. J. H. D et ac *Synthesis* **1978**, 1978, 579–580.

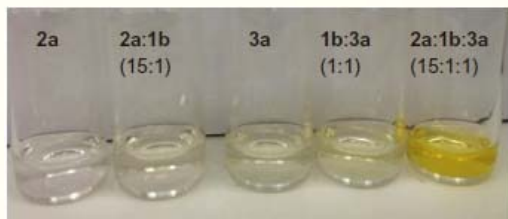
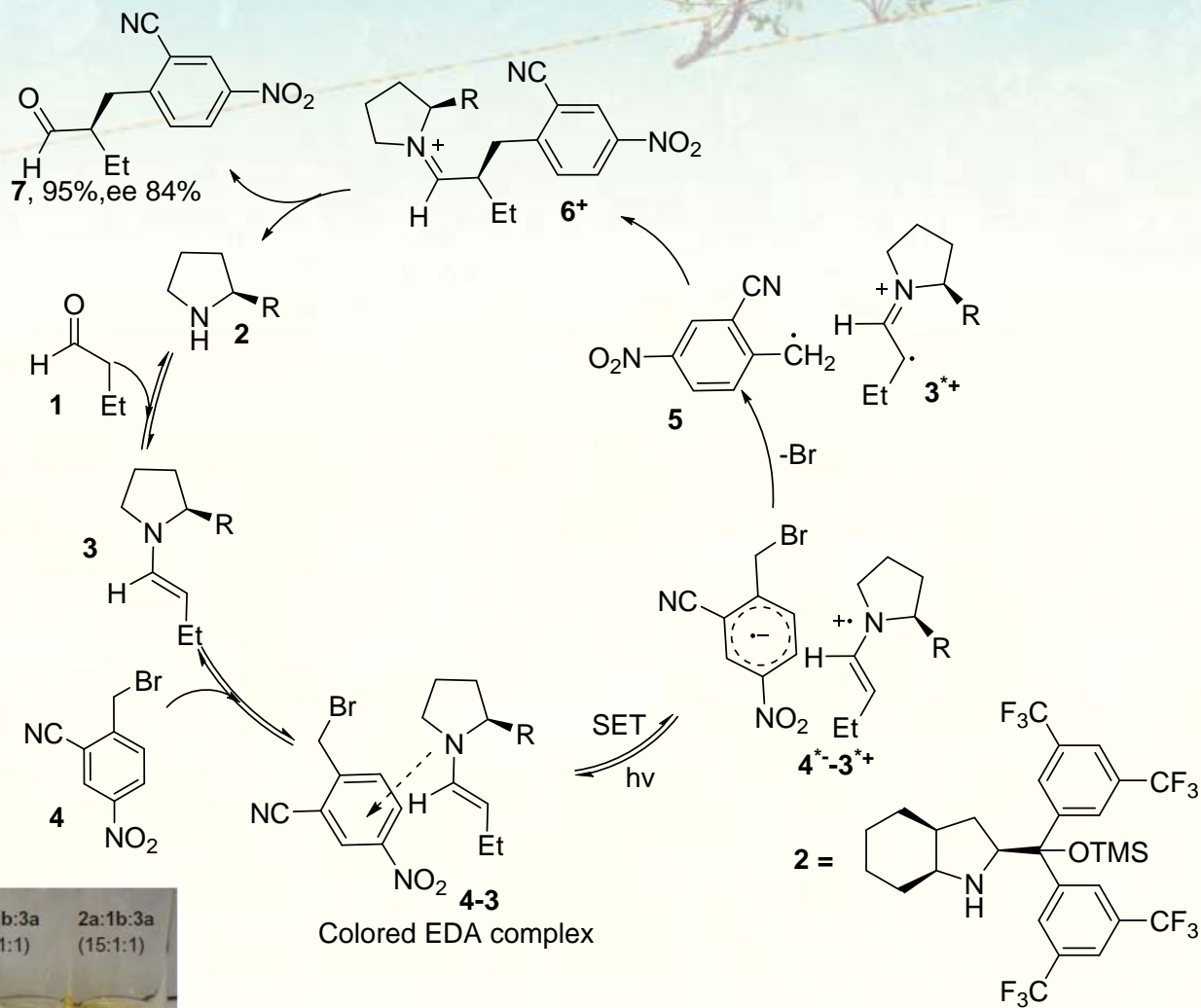
Russell, K. C. et ac *Org. Lett.* **2000**, 2, 3761–3764.

Radical Ions



Photogeneration and Fate of Radical Ions from Organic Molecules (A-Y, D-X)

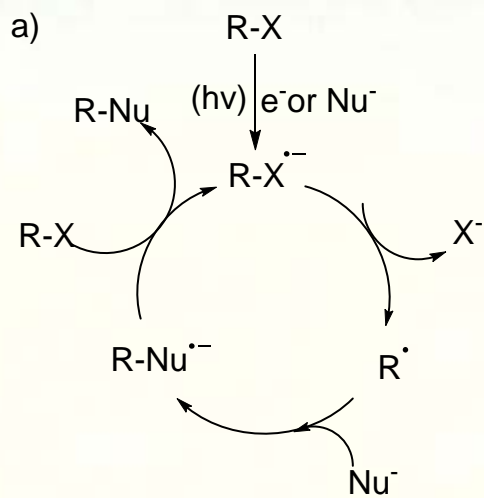
Radical Ions



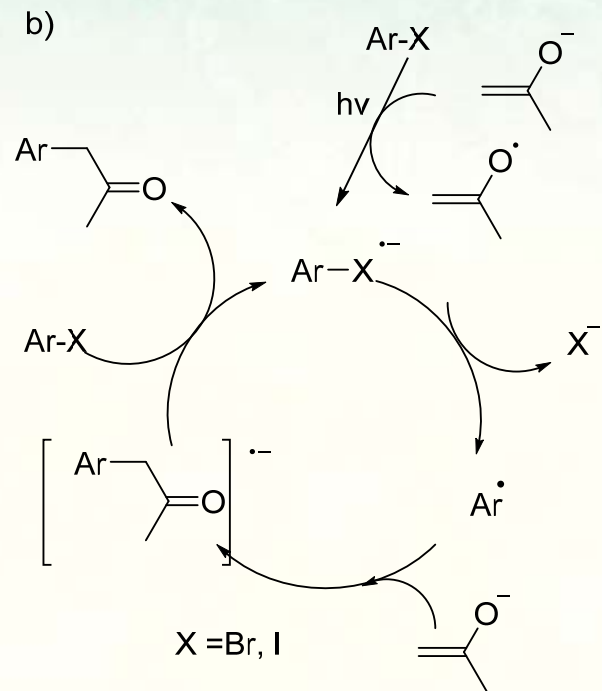
Melchiorre, P. et al *Nat. Chem.* **2013**, *5*, 750–756.

Melchiorre, P. et al *Chem. Sci.* **2014**, *5*, 2438–2442.

S_{RN}1 Reaction

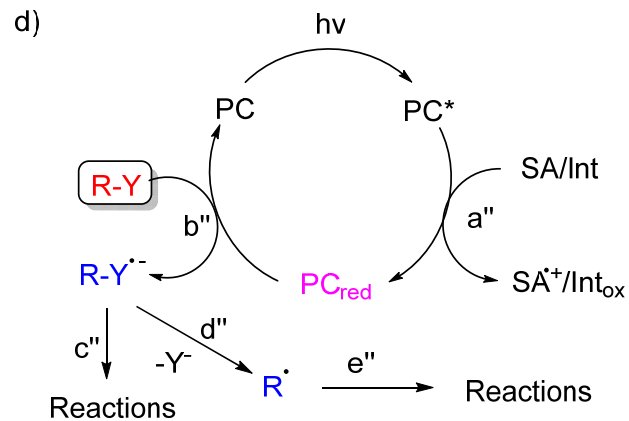
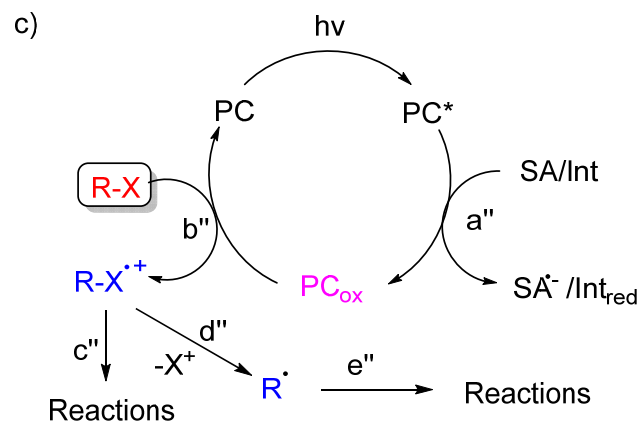
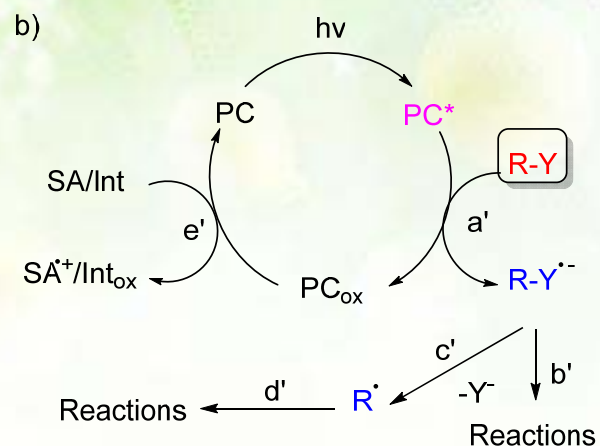
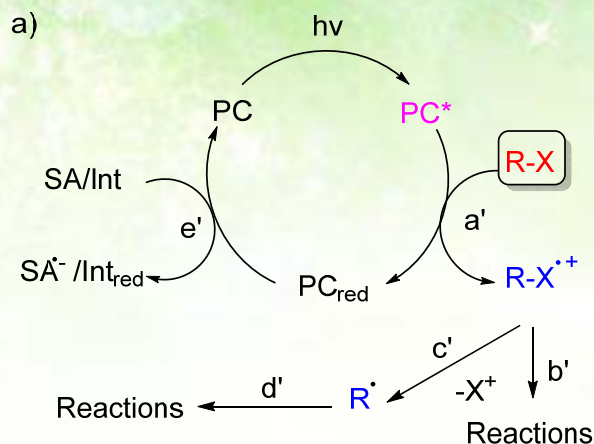


General Scheme of an S_{RN}1 Reaction



Example of an S_{RN}1 Reaction

General Scheme of Photoredox Catalysis



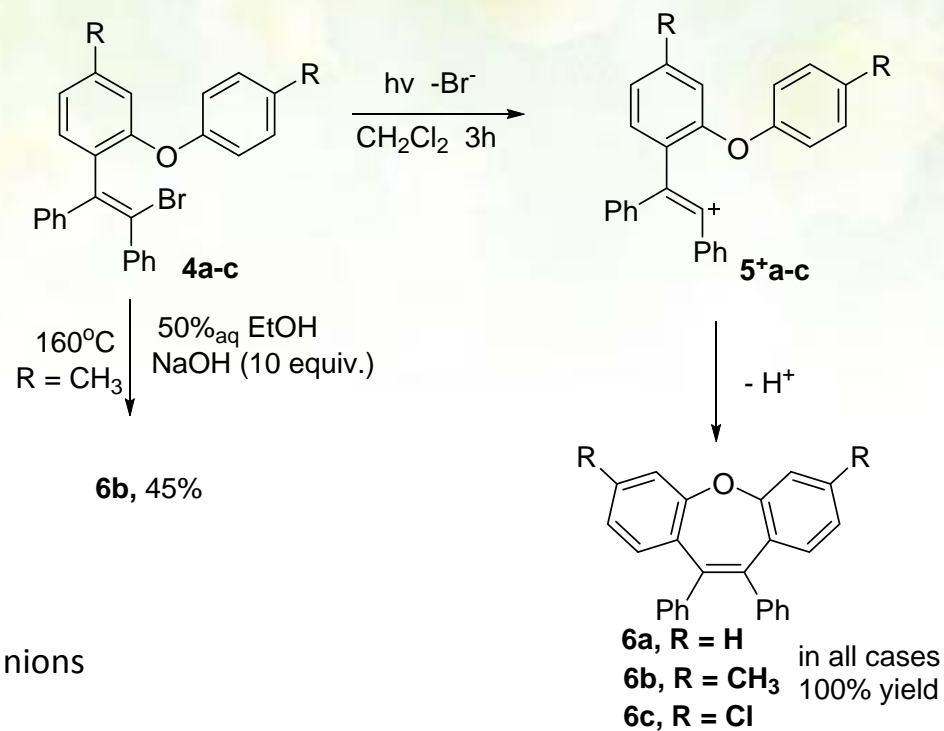
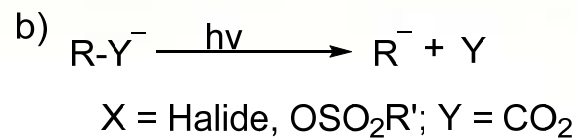
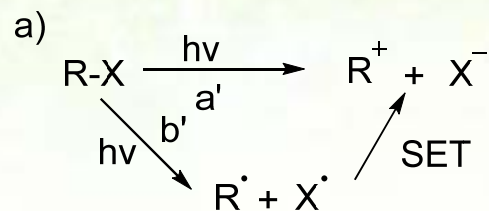
R-X = Reagent to be oxidized; R-Y = Reagent to be reduced

SD = Sacrificial electron donor; SA = Sacrificial electron acceptor

Int = Intermediate involved in the process

In purple the species generating the synthetic intermediates (a radical ion or a radical from it, in blue).

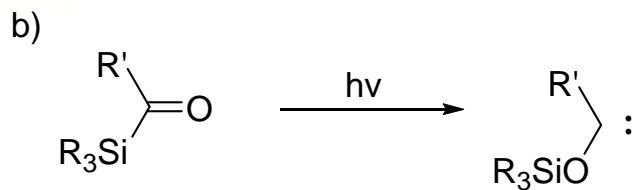
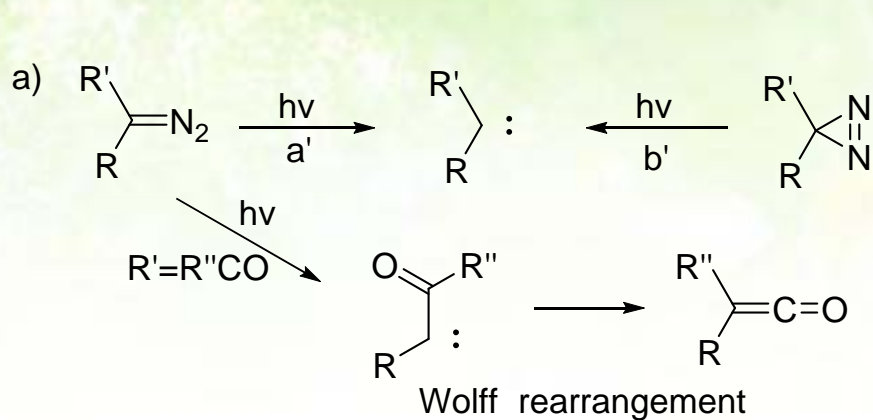
Carbocations /Carbanions



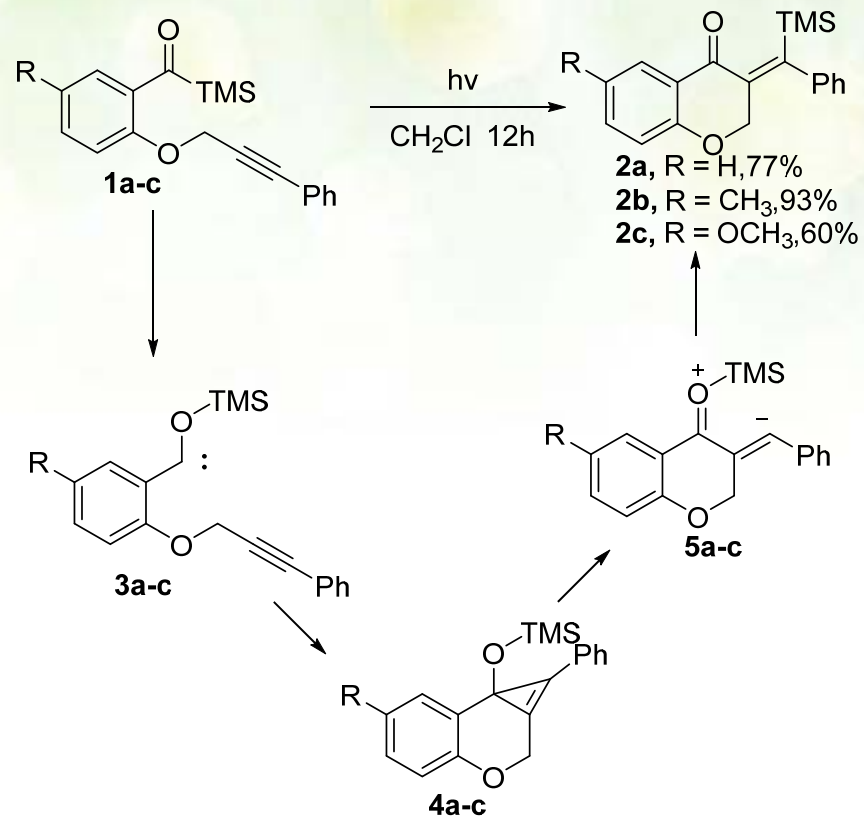
Modes of Photogeneration of Carbocations and Carbanions

Taniguchi, H. et al *Chem. Soc.* **1991**, *113*, 6240–6245.

Carbenes

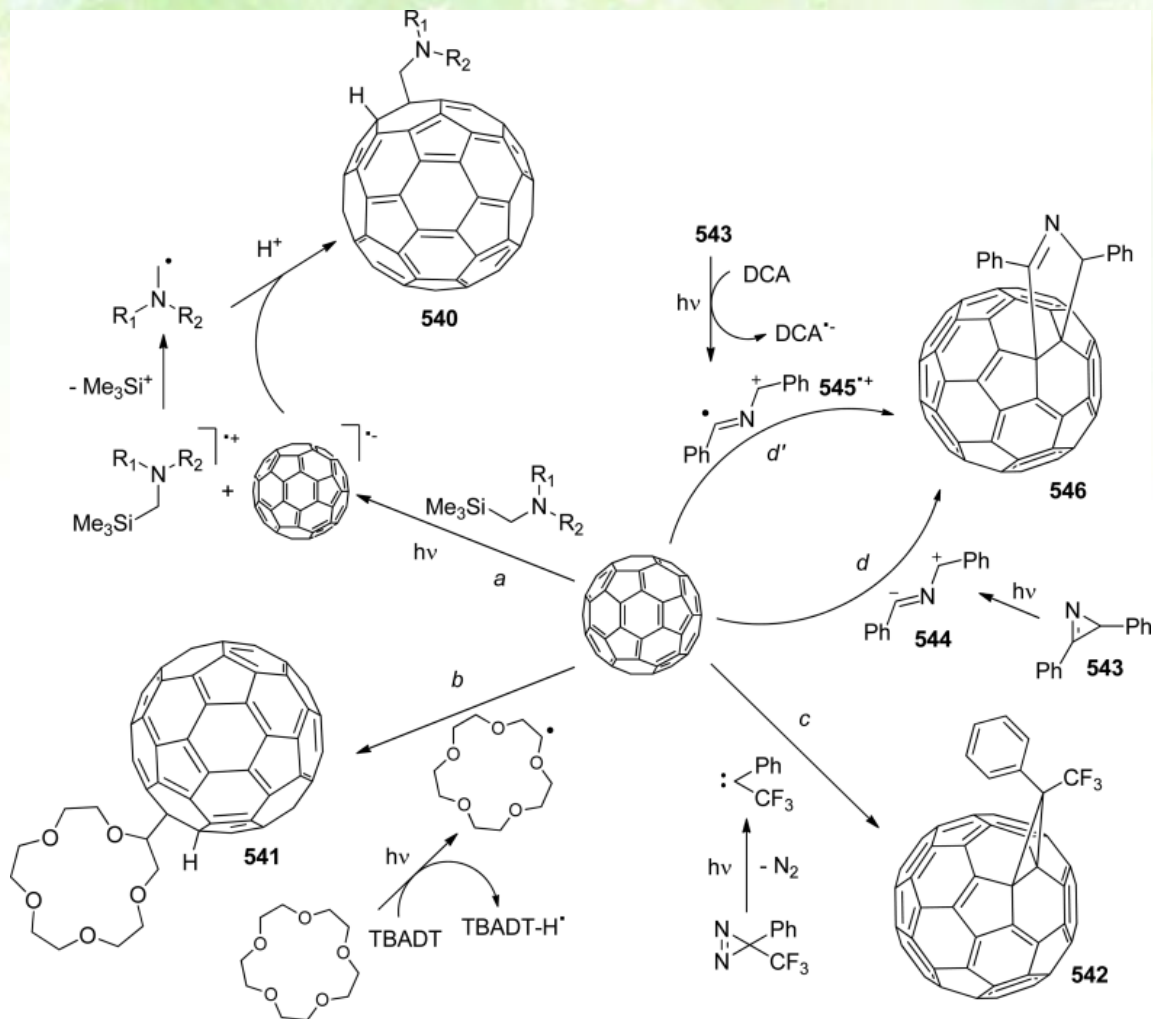


Modes of Photogeneration of Carbenes



Carsten Bolm. et al. *Synth. Catal.* **2012**, 354, 2157–2161.

Functionalization of Carbon Nanostructures



Suk Hyun Lim et al *J. Org. Chem.* **2014**, 79, 6946–6958.

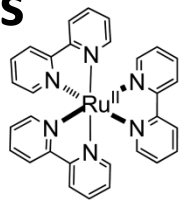
Michael Orfanopoulos et al *Angew. Chem., Int. Ed.* **2010**, 49, 5891–5893.

Liu, M. T. H et al *Tetrahedron Lett.* **2007**, 48, 6290–6293.

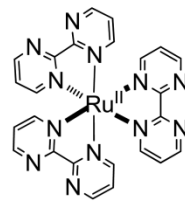
Jochen Mattay et al *Chem. Ber.* **1994**, 127, 787–789.

Photoredox Catalysts

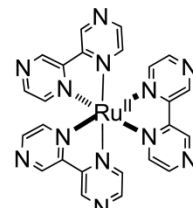
Metal



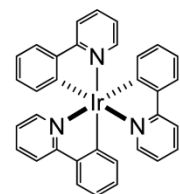
$\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$



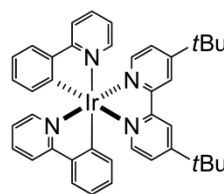
$\text{Ru}^{\text{II}}(\text{bpm})_3^{2+}$



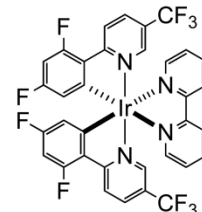
$\text{Ru}^{\text{II}}(\text{bpz})_3^{2+}$



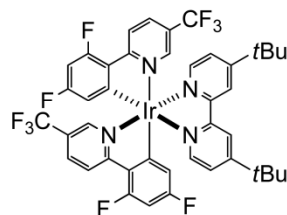
$\text{fac-Ir}^{\text{III}}(\text{ppy})_3$



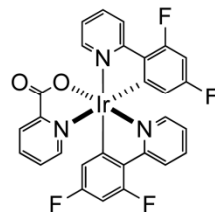
$\text{Ir}^{\text{III}}(\text{ppy})_2(\text{dtbbpy})^+$



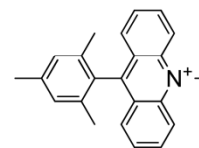
$\text{Ir}^{\text{III}}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{bpy})^+$



$\text{Ir}^{\text{III}}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})^+$

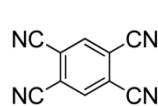


$\text{FIr}^{\text{III}}\text{pic}$

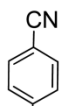


Mes-Acr^+

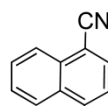
Metal-free



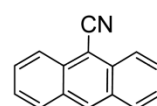
TCB



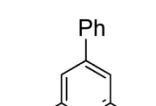
p-DCB



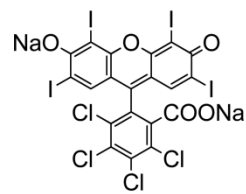
DCN



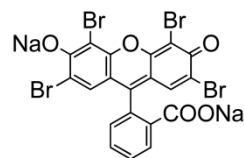
DCA



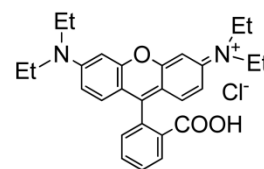
Pyrylium



Rose Bengal



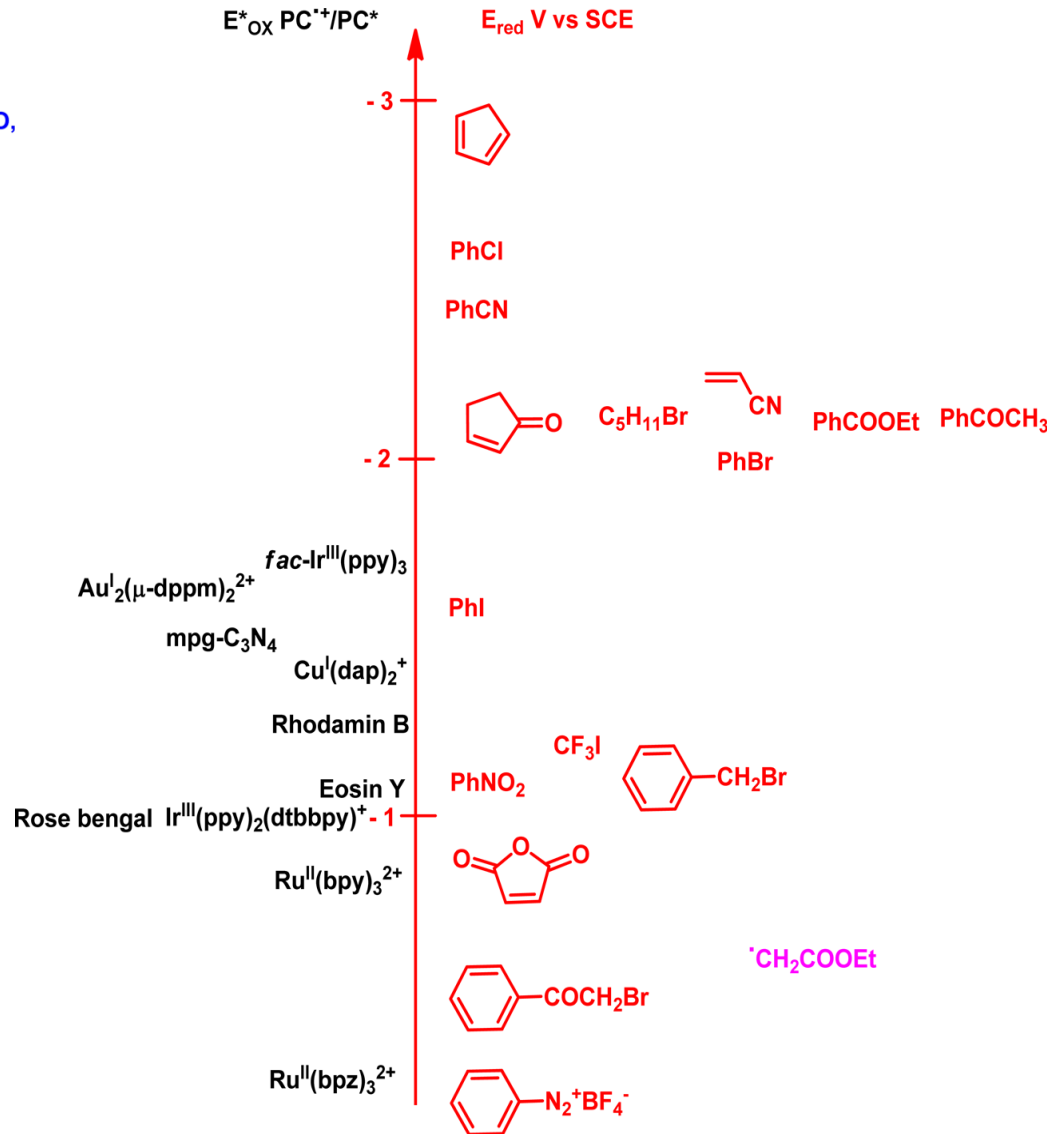
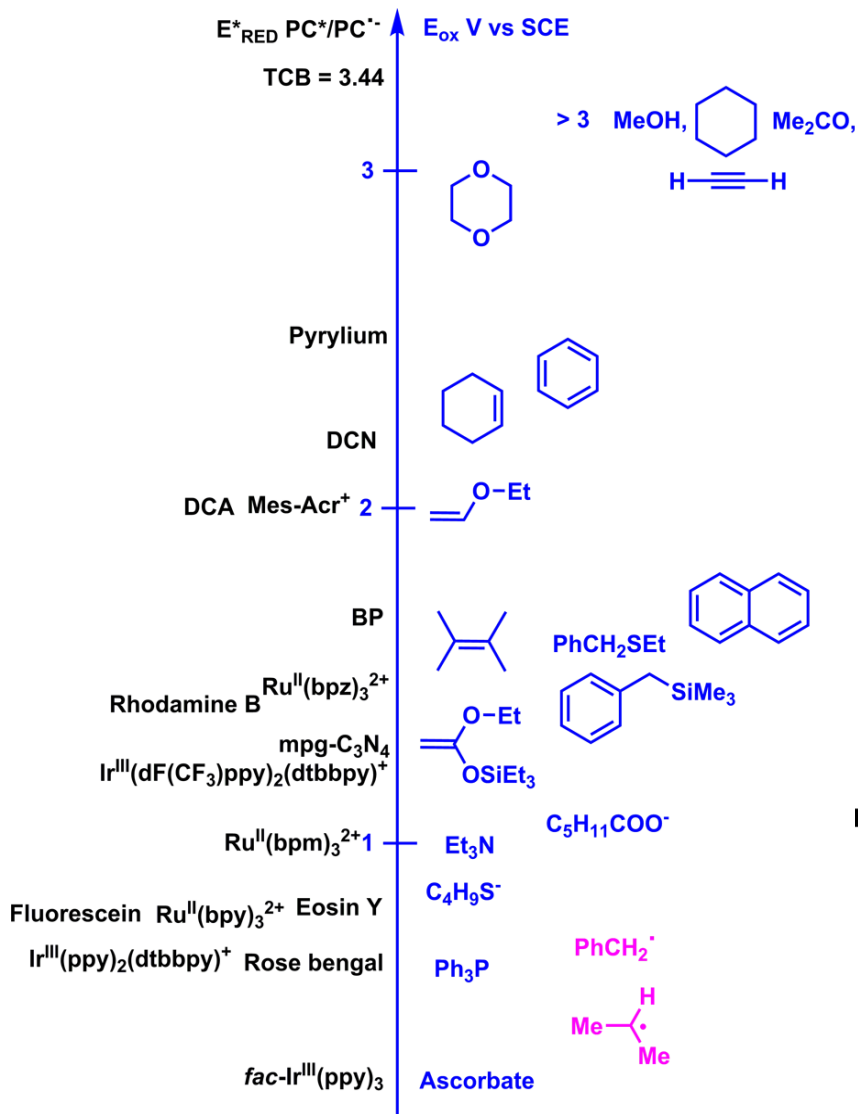
Eosin Y



Rhodamine B

Common Photoredox Catalysts Used for (Visible Light) C–C Bond Formation in Synthesis

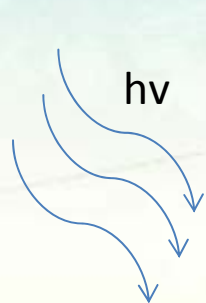
potential of molecules and photocatalysts



Oxidation potential of selected organic molecules (and radicals) in comparison with the reduction potential in the excited state of common photocatalysts

Reduction potential of selected organic molecules (and radicals) in comparison with the oxidation potential in the excited state of common photocatalysts.

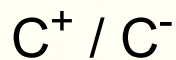
Summary



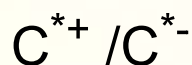
Norrish-Yang cyclizations
photo-Fries rearrangements



α -diazoketones or diazirines



aryl and vinyl halides
Few decarboxylation



photoinduced electron transfer (PET)



photocatalyzed hydrogen atom transfer

Ring Alkynes

Ar-C Bond

Addition onto C=X Bond

α / β -Substituted Carbonyl

Thanks for your attention

Spring