Reagent of the Month: $Ru(bpy)_3^{2+}$ in Photocatalysis

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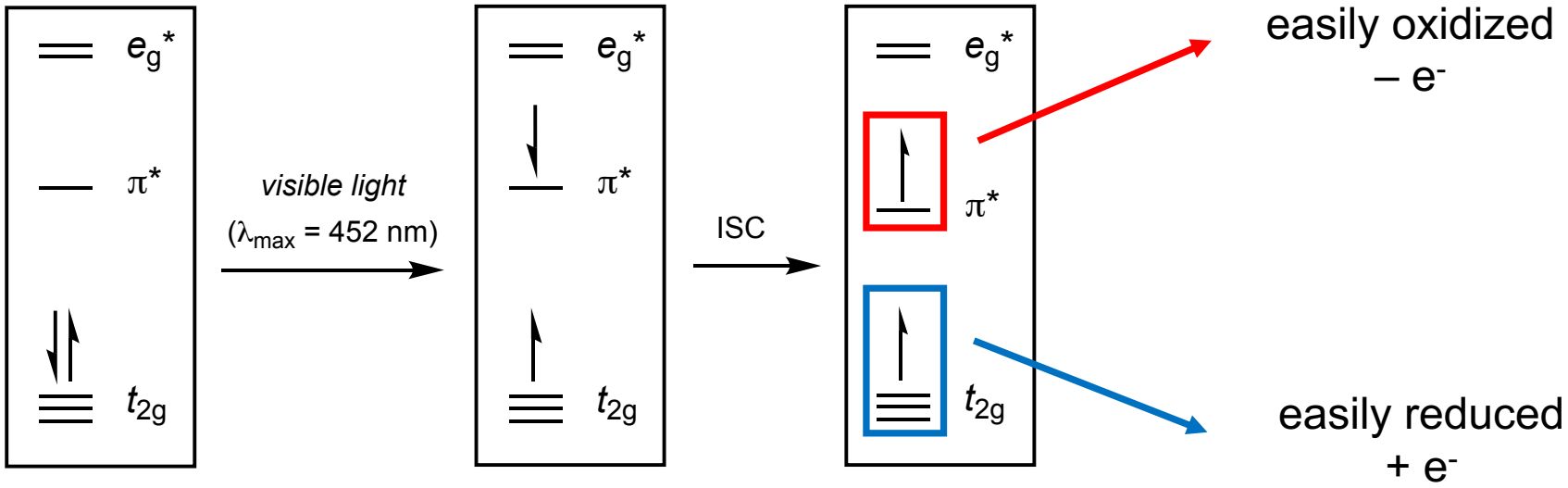
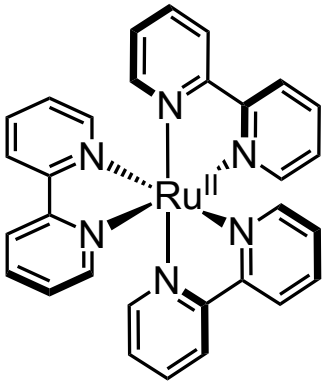
Synthesis Club

October 30th, 2018

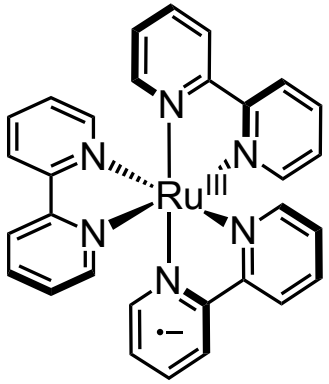
$Ru(bpy)_3^{2+}$ as a Photocatalyst

- Excited state complex better oxidant and reductant than ground state:





$Ru(bpy)_3^{2+}$



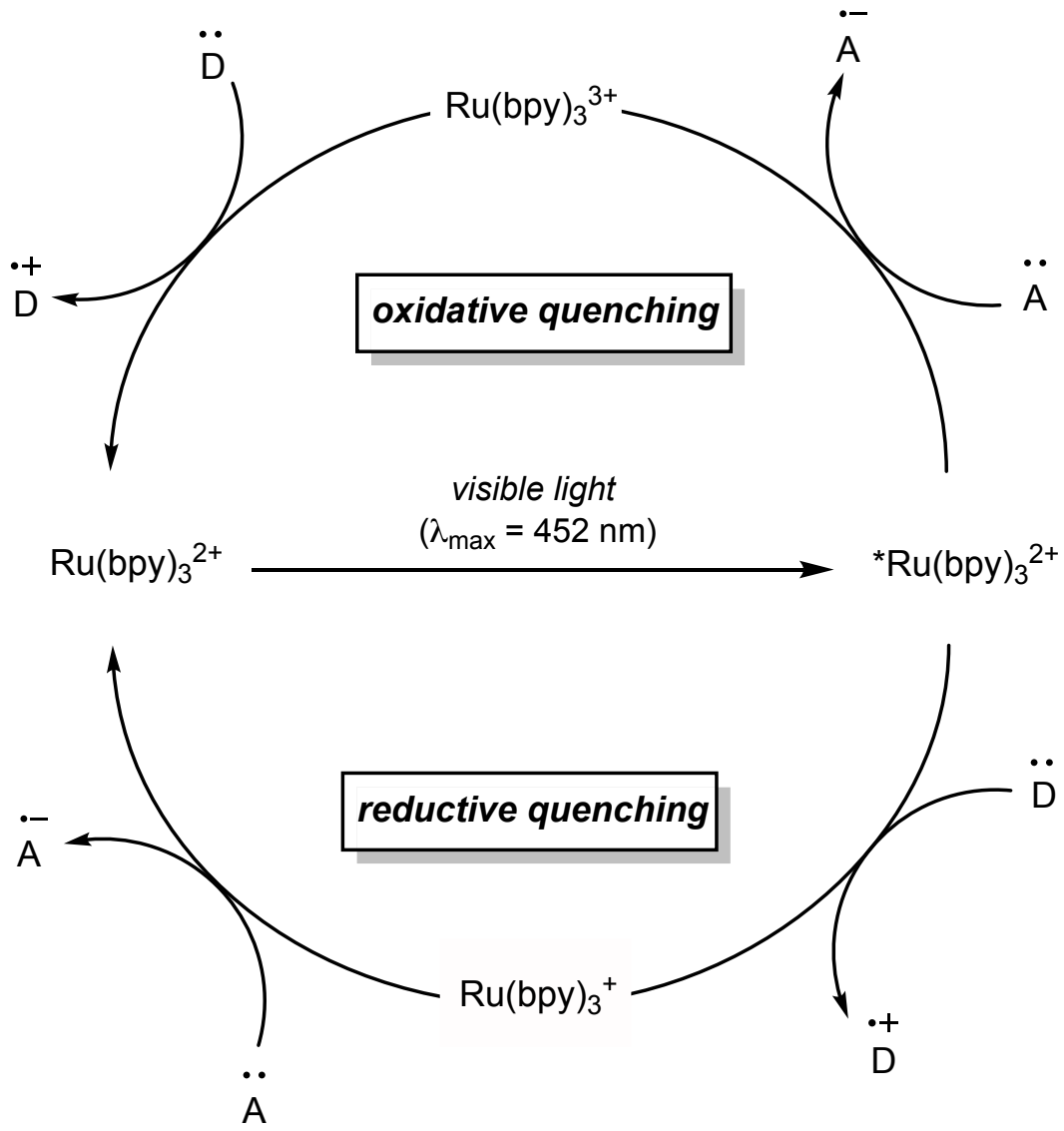
*$Ru(bpy)_3^{2+}$

- Excited state lasts 1100 ns, long enough for ET

MacMillan et al. *Chem. Rev.* **2013**, *113*, 5322; Tucker and Stephenson. *J. Org. Chem.* **2012**, *77*, 1617.

Oxidative and Reductive Quenching Cycles

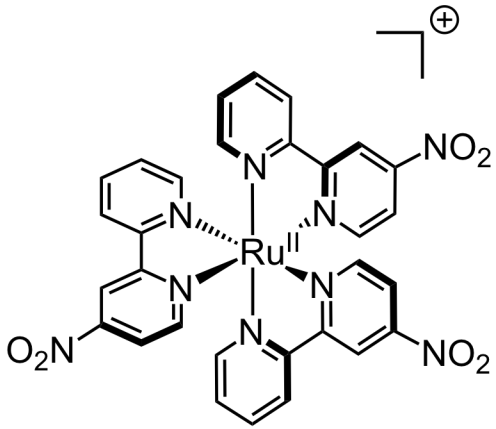
- *$Ru(bpy)_3^{2+}$ can participate in oxidative and reductive pathways:



MacMillan et al. *Chem. Rev.* **2013**, *113*, 5322; Tucker and Stephenson. *J. Org. Chem.* **2012**, *77*, 1617.

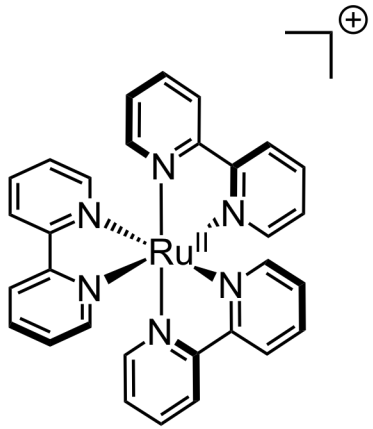
Tunable Redox Potentials

- Can vary the ligands and/or metal to tune redox potential:



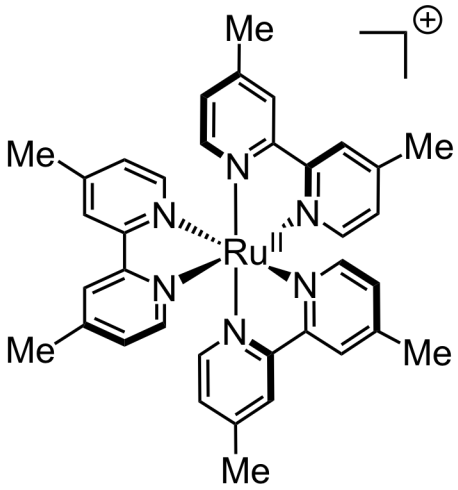
mer-Ru(4-O_2N-bpy)$_3^+$

E_{red} = –0.63V



Ru(bpy)$_3^+$

E_{red} = –1.35V



Ru(dmb)$_3^+$

E_{red} = –1.45V

More electron density

More powerful reductant

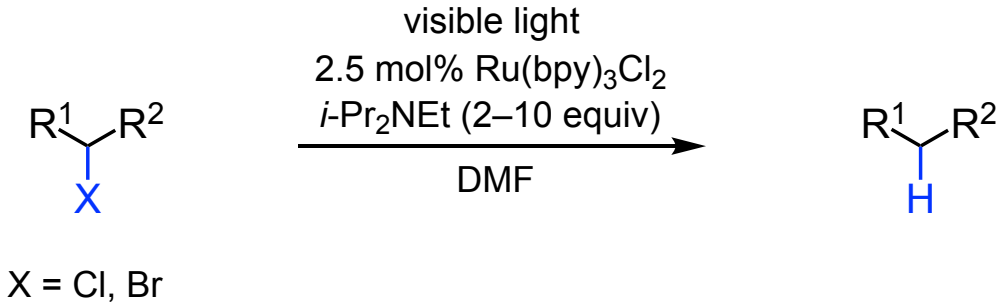
MacMillan et al. *Chem. Rev.* **2013**, *113*, 5322; Tucker and Stephenson. *J. Org. Chem.* **2012**, *77*, 1617.

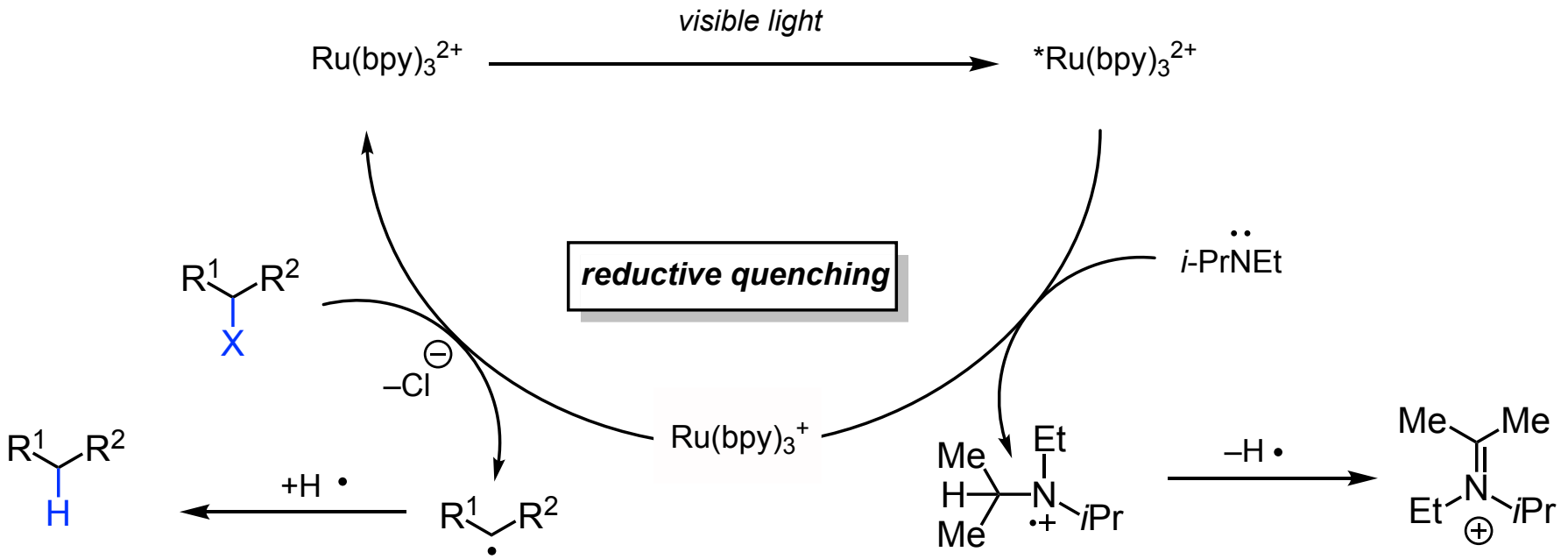
Scope of Reactions Capable

- $Ru(bpy)_3^{2+}$ and related photocatalysts can facilitate a wide variety of transformations:
  - Cycloaddition reactions
  - α-Amino C–H functionalization
  - C–X bond formation (X= C, O, N, S, Br, F, B, etc.)
  - Arene functionalization
  - Alkene difunctionalization
  - Polymerization reactions

Stephenson, Yoon, and MacMillan. *Visible Light Photocatalysis in Organic Chemistry* (Wiley-VCH, Weinheim, Germany, 2018).

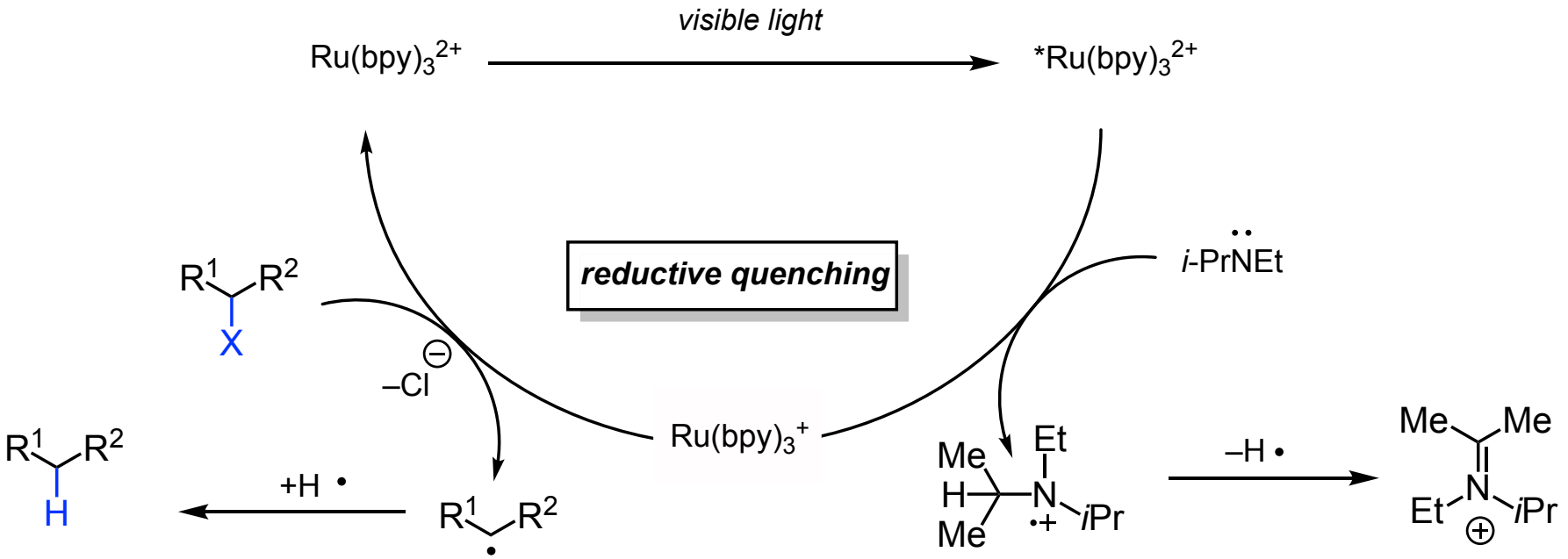
Dehalogenation Reaction: Reductive Quenching

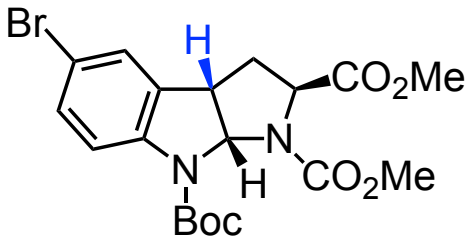




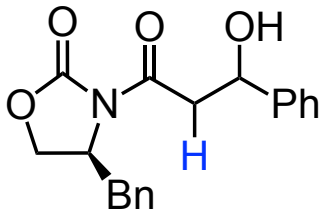
Stephenson et al. *J. Am. Chem. Soc.* **2009**, *131*, 8756.

Dehalogenation Reaction: Reductive Quenching

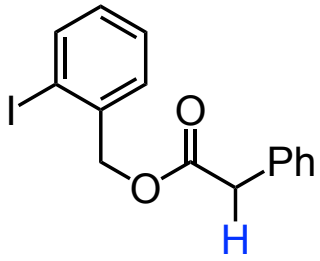




92%



99%

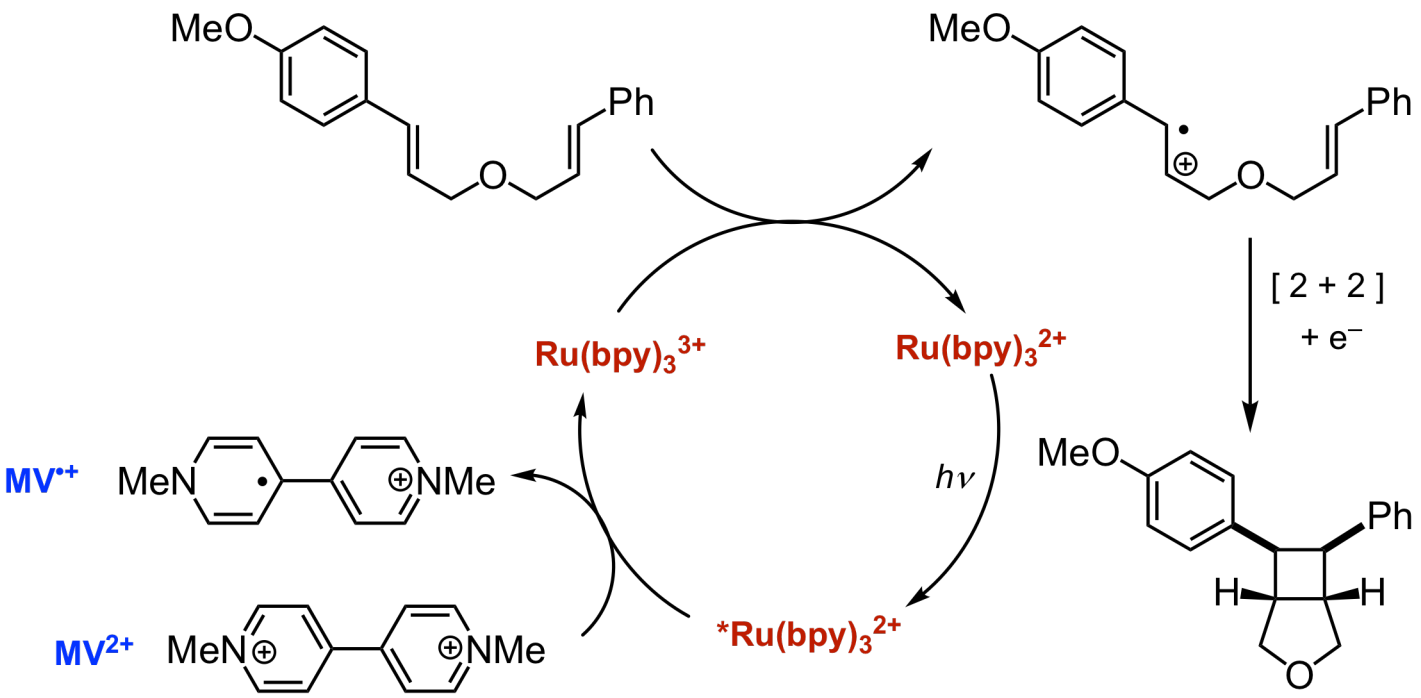


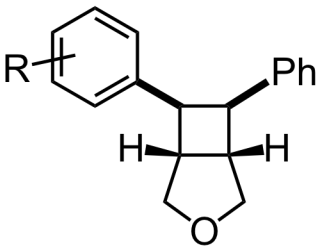
88%

Stephenson et al. *J. Am. Chem. Soc.* **2009**, *131*, 8756.

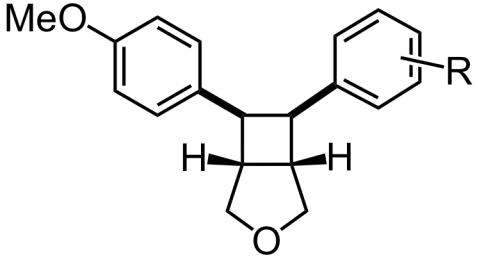
[2 + 2] Cycloaddition: Oxidative Quenching

Conditions: **1–5 mol% $Ru(bpy)_3(PF_6)_2$**, **15 mol% $MV(PF_6)_2$**, $MgSO_4$, $MeNO_2$, visible light

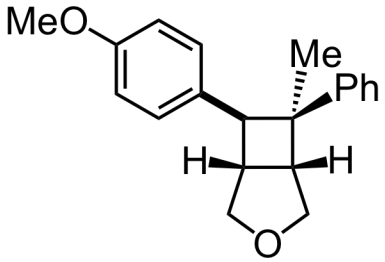




R = 4-OMe 89%, >10:1 dr
R = 2-OMe 73%, >10:1 dr
R = 4-OH 64%, >10:1 dr



R = 4-OMe 67%, >10:1 dr
R = 4-Cl 92%, >10:1 dr
R = 3-F 78%, >10:1 dr

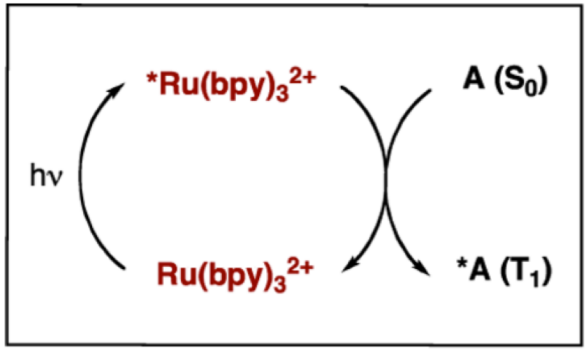


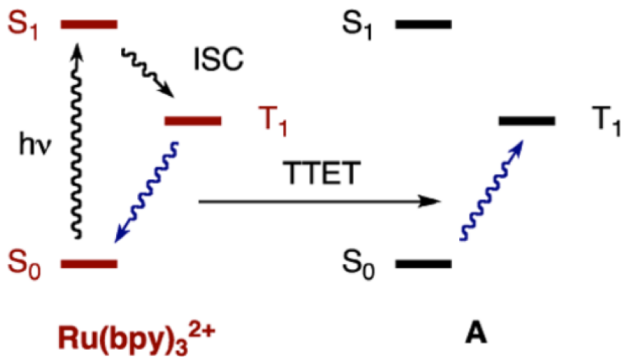
54%, >10:1 dr

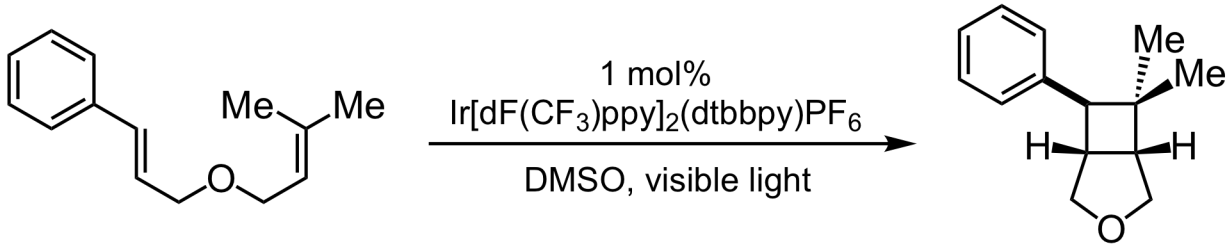
MacMillan et al. *Chem. Rev.* **2013**, *113*, 5322; Yoon et al. *J. Am. Chem. Soc.* **2010** *132*, 8572.

Triplet–Triplet Energy Transfer

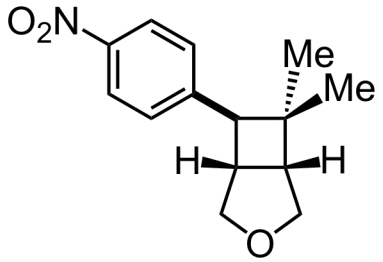
- Photocatalyst can also activate substrate through TTET, no ET:



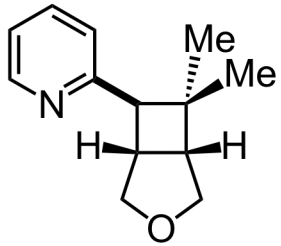




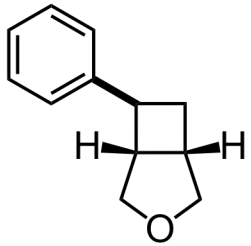
84%, >10:1 dr



71%, >10:1 dr



71%, >10:1 dr



80%, 7:1 dr

MacMillan et al. *Chem. Rev.* **2013**, *113*, 5322; Lu and Yoon. *Angew. Chem. Int. Ed.* **2012**, *51*, 10329.