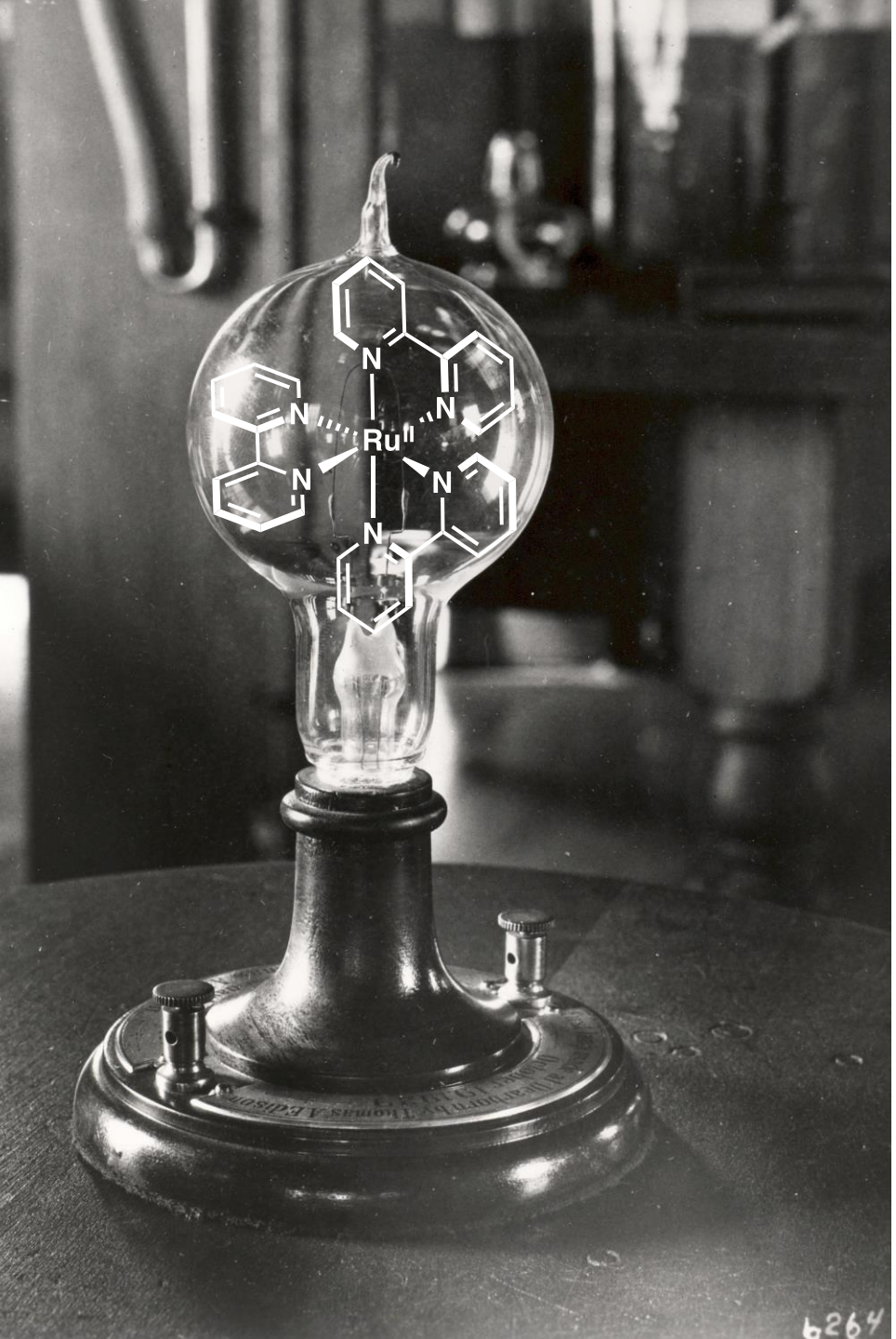
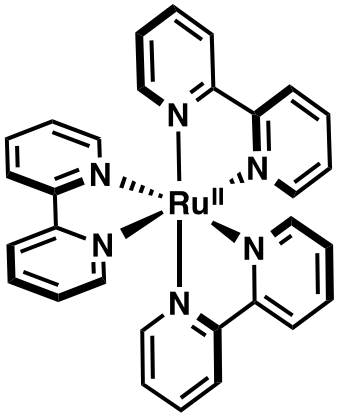


Visible Light Photoredox Catalysis

Literature Meeting
Christopher K. Haley
March 7, 2014
Noyes 147



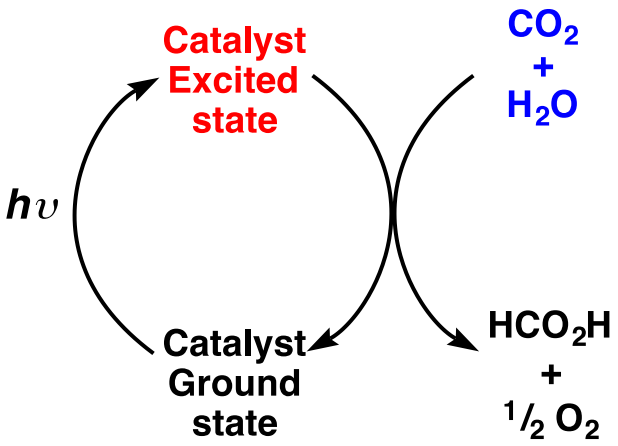
$Ru(bpy)_3^{2+}$

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

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

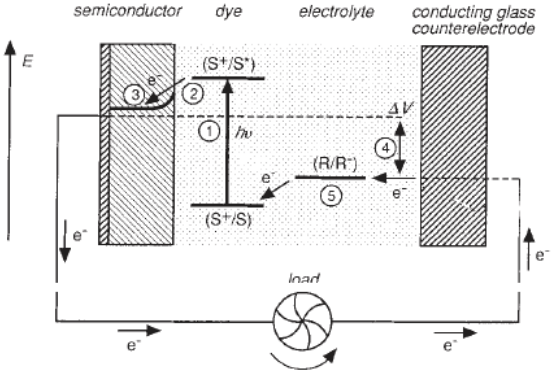
Applications of Visible Light Metal Complexes

Water Splitting



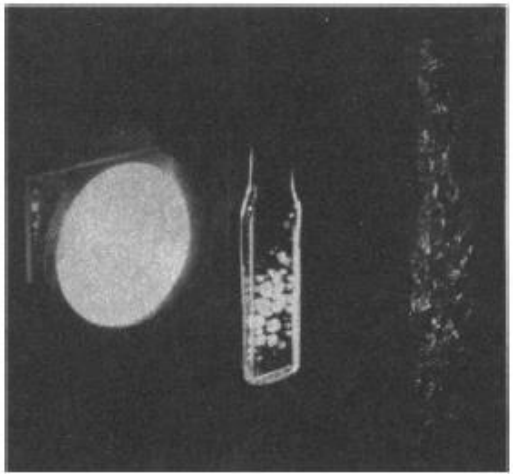
Meyer, T. J. *Acc. Chem. Res.* 1989, ***22***, 163.
Fox, M. A. *Acc. Chem. Res.* 1995, ***28***, 141.

Photovoltaic Cells



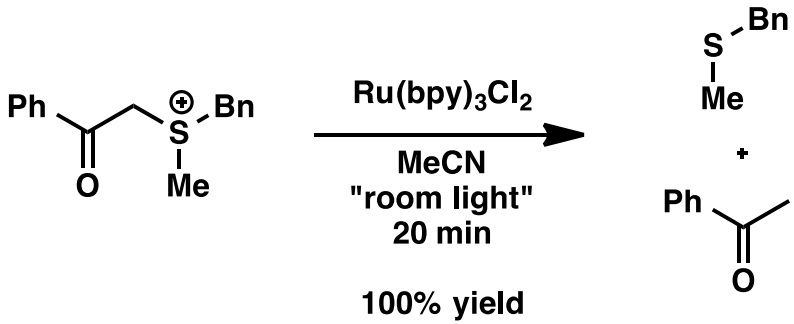
Gratäzel,M. *Nature* 1991, ***353***, 737.

Energy Storage

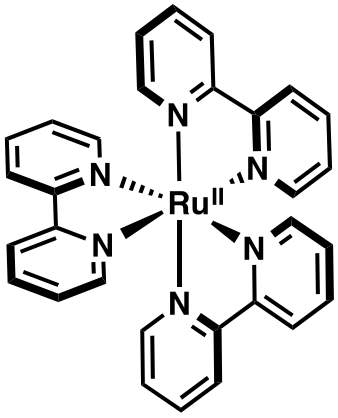


Gray, H. B. *Science* 1981, ***214***, 1201.

Photoredox Catalysis in Organic Synthesis



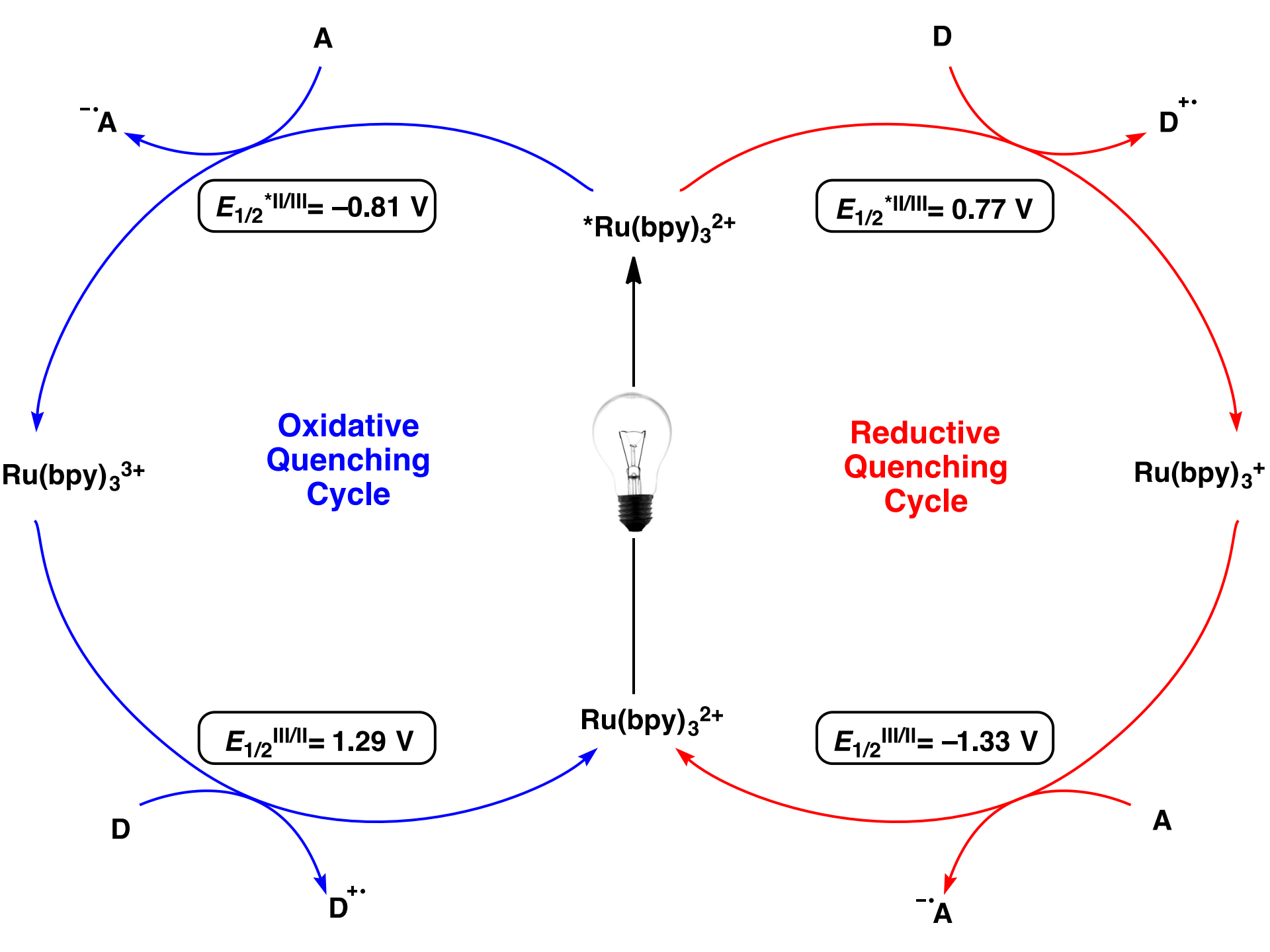
Kellogg, R. M. *Tetrahedron Lett.* 1978, ***19***, 1255.
Stephenson, C. R. J. Org. Chem. 2012, ***77***, 1617.
MacMillan, D. W. C. *Chem. Rev.* 2013, ***113***, 5322.
Yoon, T. P. *Science* 2013, ***343***, 985.



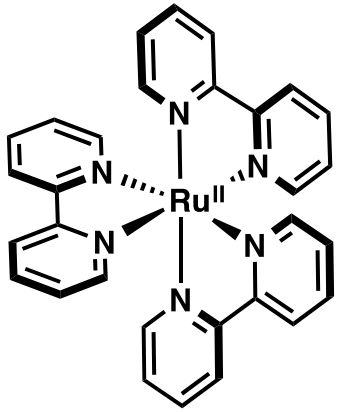
$Ru(bpy)_3^{2+}$

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

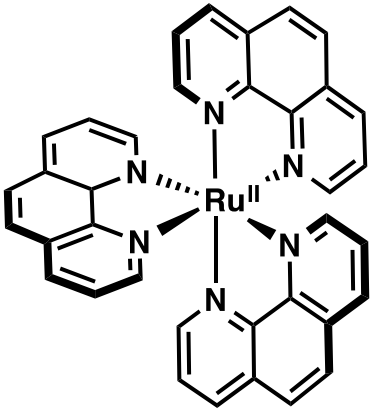
$Ru(bpy)_3^{2+}$


A
$^{-\bullet}$A
$E_{1/2}^{*II/III}$= –0.81 V
*Ru(bpy)$_3^{2+}$
D
D$^{+\bullet}$
$E_{1/2}^{*II/III}$= 0.77 V
Oxidative Quenching Cycle
Reductive Quenching Cycle
Ru(bpy)$_3^{3+}$
Ru(bpy)$_3^{+}$
Ru(bpy)$_3^{2+}$
$E_{1/2}^{III/II}$= 1.29 V
$E_{1/2}^{III/II}$= –1.33 V
D
D$^{+\bullet}$
A
$^{-\bullet}$A

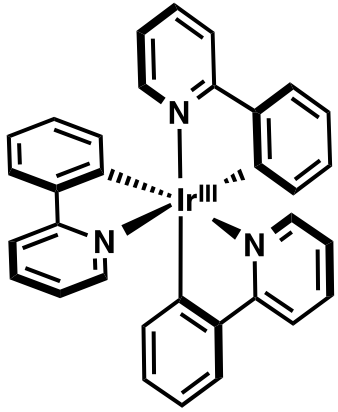
Examples of Photocatalysts



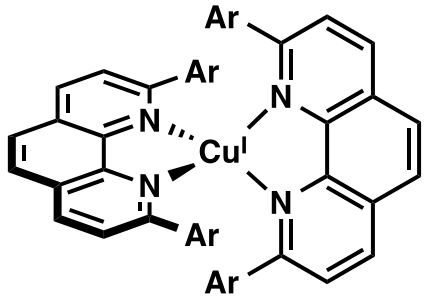
$Ru(bpy)_3^{2+}$



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

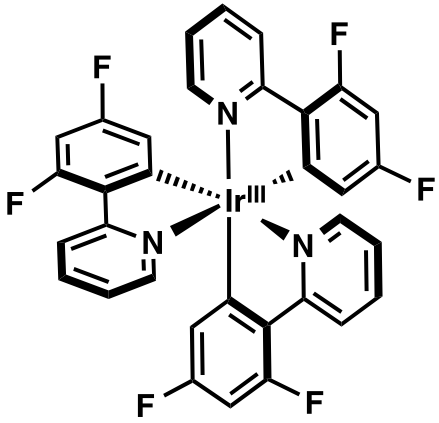


fac-$Ir(ppy)_3^{3+}$

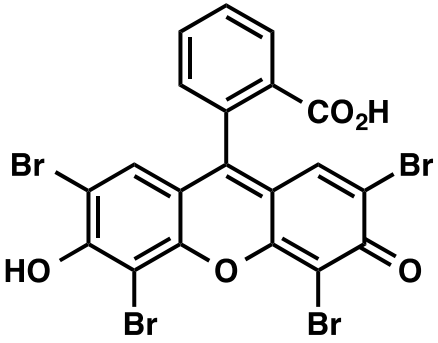


Ar = 4-OMe-Ph

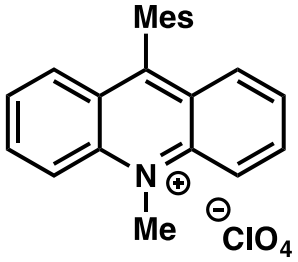
$Cu(dap)_2^{+}$

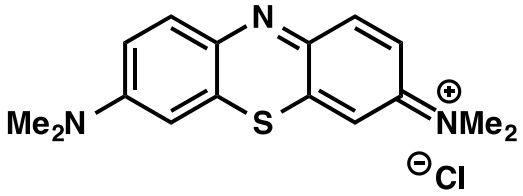


fac-$Ir(Fppy)_3^{3+}$



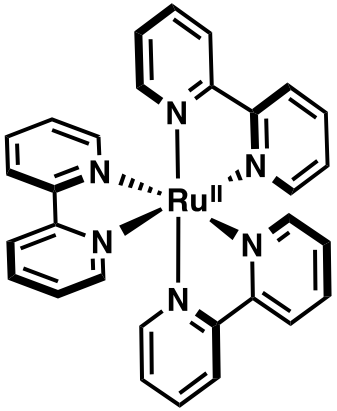
Eosin Y





Methylene Blue

Photophysics of $Ru(bpy)_3Cl_2$



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

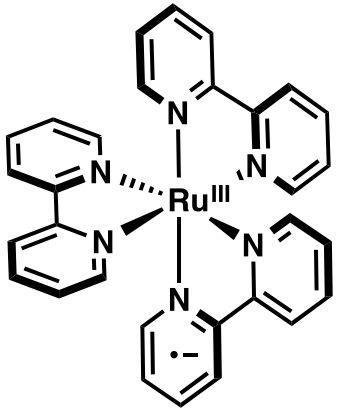
$h\upsilon$

λ_{max} = 452 nm

metal-to-ligand charge-transfer

(MLCT)

visible light = ~390 – 700 nm

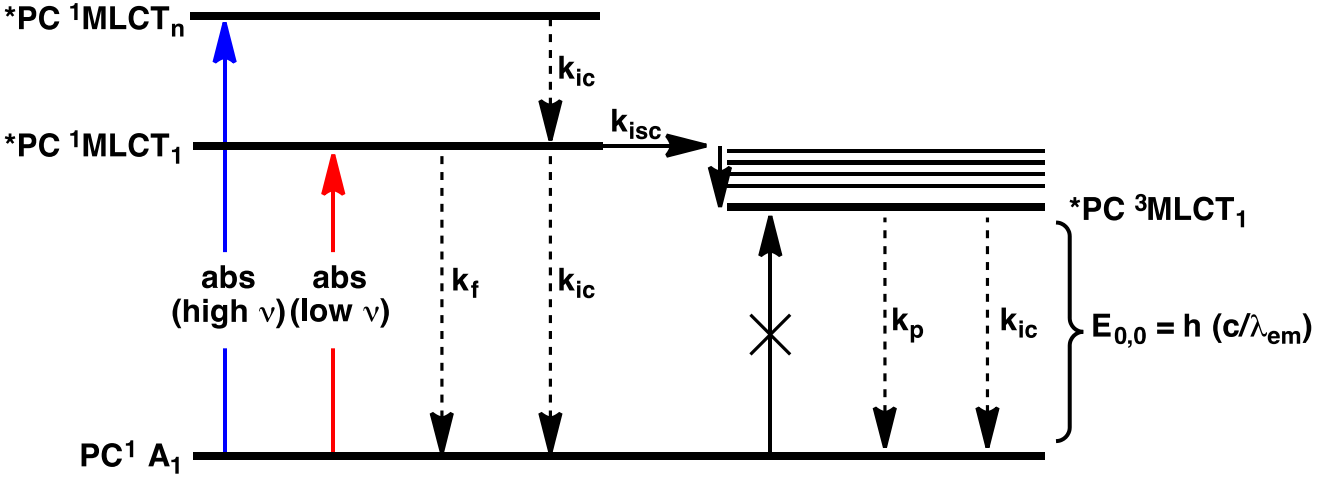


$Ru(bpy)_3^{2+}$

-Absorbtion 452 nm

-Stable long-lived excited state (τ = 1100 ns)

-Single electron transfer catalyst

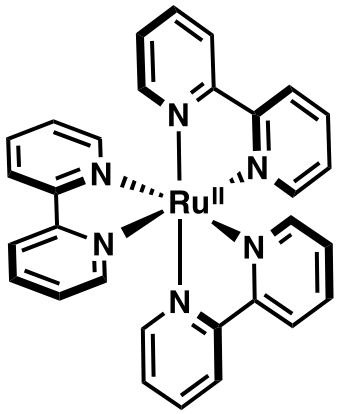


- $E_{0,0}$ can be calculated from emission

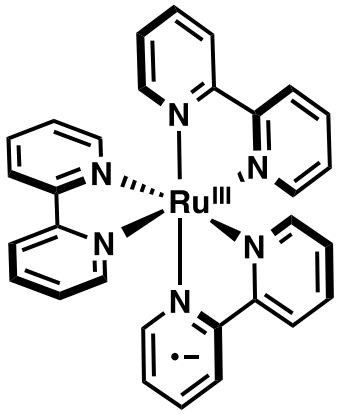
-λ_{em} = 615 nm at 23 °C in MeCN

-2.02 eV

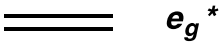
Photochemistry of $Ru(bpy)_3Cl_2$

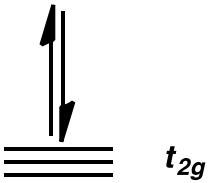


$Ru(bpy)_3^{2+}$



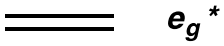
$Ru(bpy)_3^{2+}$

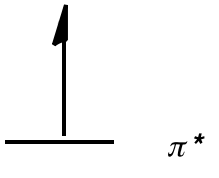


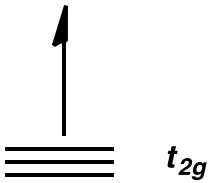


$Ru(bpy)_3^{2+}$

$h\upsilon$



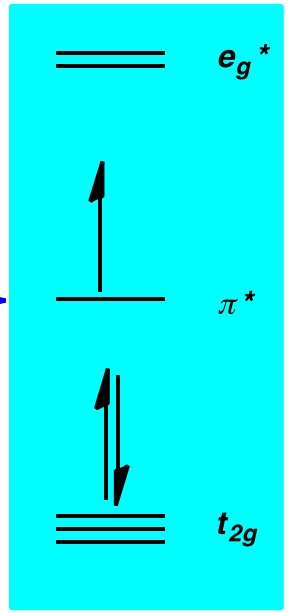


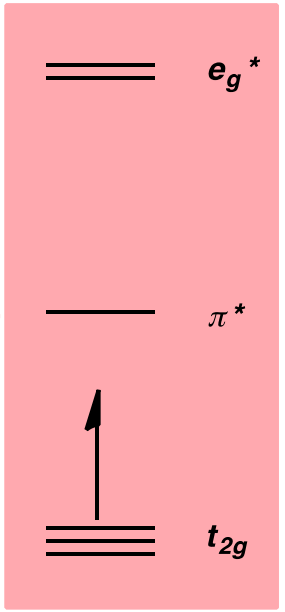


*$Ru(bpy)_3^{2+}$

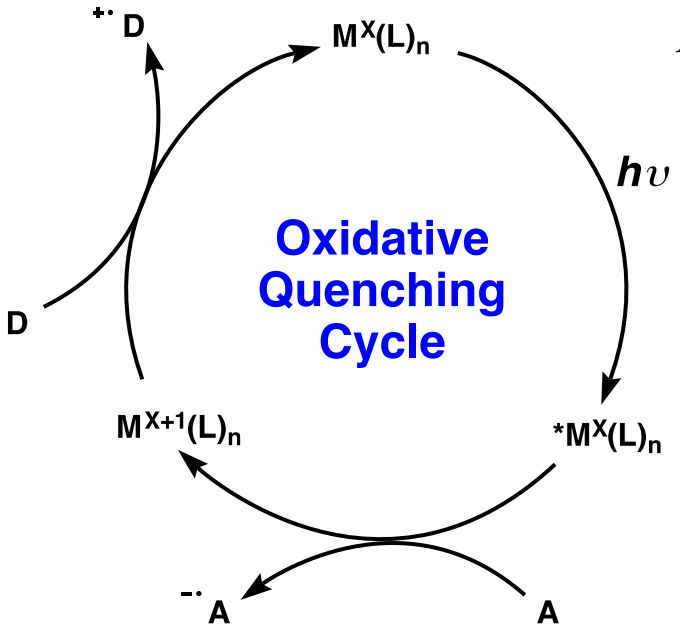
oxidant

reductant



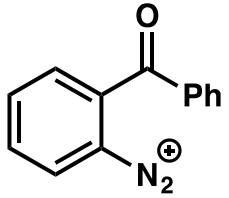


Redox Properties of Catalysts

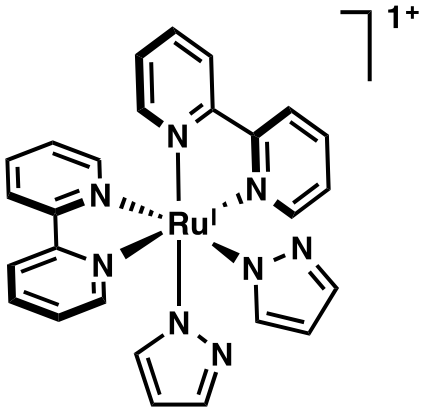


Some common oxidants

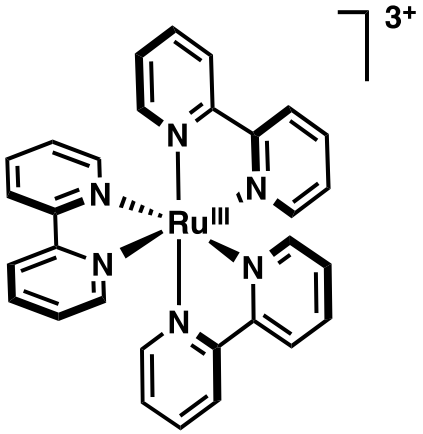
- O_2
- $Co(acac)_3$
- $BrCCl_3$
- $S_2O_8^{2-}$
- *m*-dinitrobenzene
- aryldiazoniums



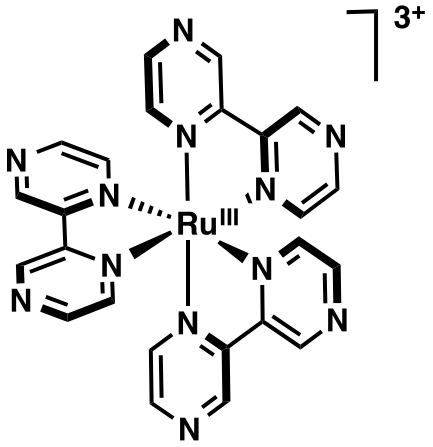
Oxidized complexes (metal-centered oxidation)



$Ru(bpy)_2(pz)_2$
E_{red} = 0.30 V



$Ru(bpy)_3$
E_{red} = 1.26 V

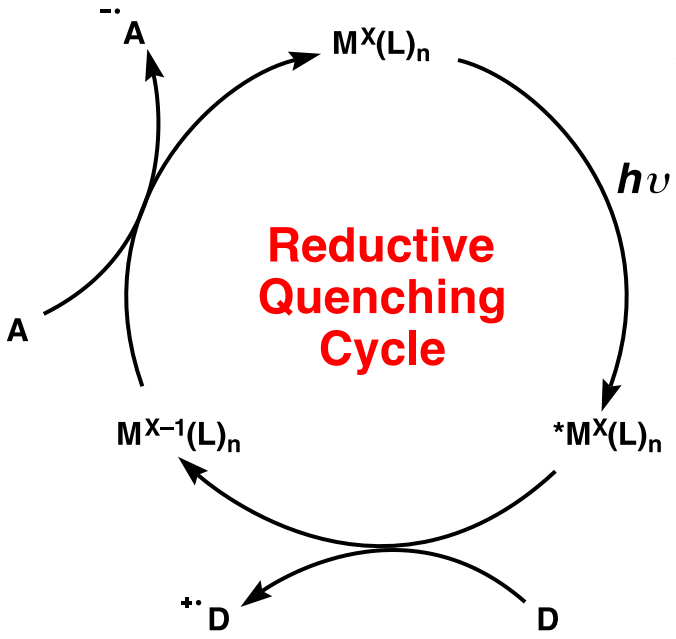


$Ru(bpz)_3$
E_{red} = 1.86 V

electron density of metal center

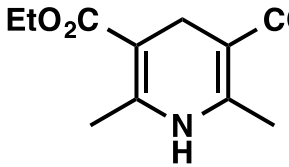
oxidative power of complex

Redox Properties of Catalysts



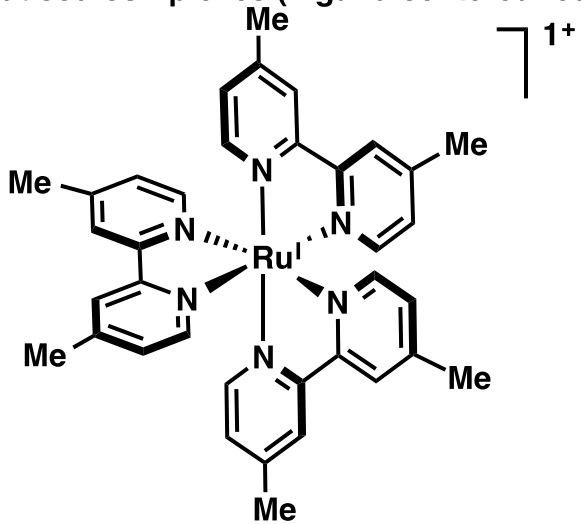
Some common reductants

- Hantzsch Ester
- hydrazine
- R_3N
- ascorbic acid
- NADH
- BNAH

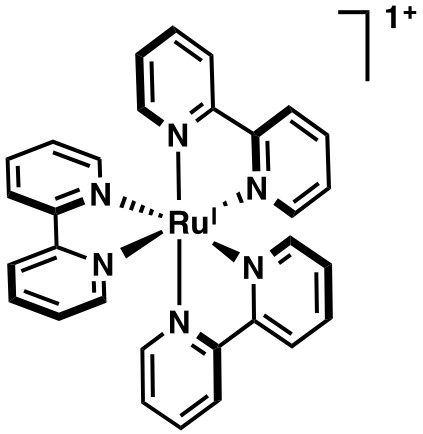


Hantzsch Ester

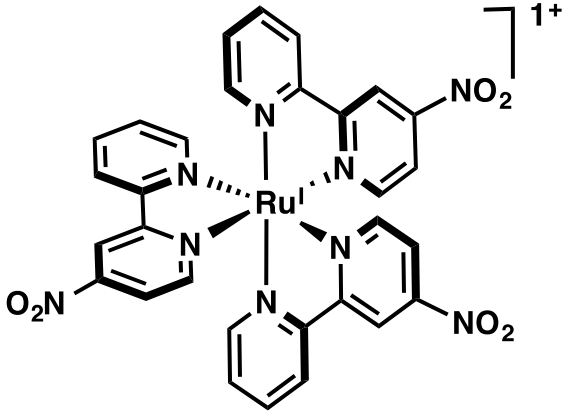
Reduced complexes (Ligand centered reduction)



$Ru(dmb)_3$
E_{red} = –1.45 V



$Ru(bpy)_3$
E_{red} = –1.35 V

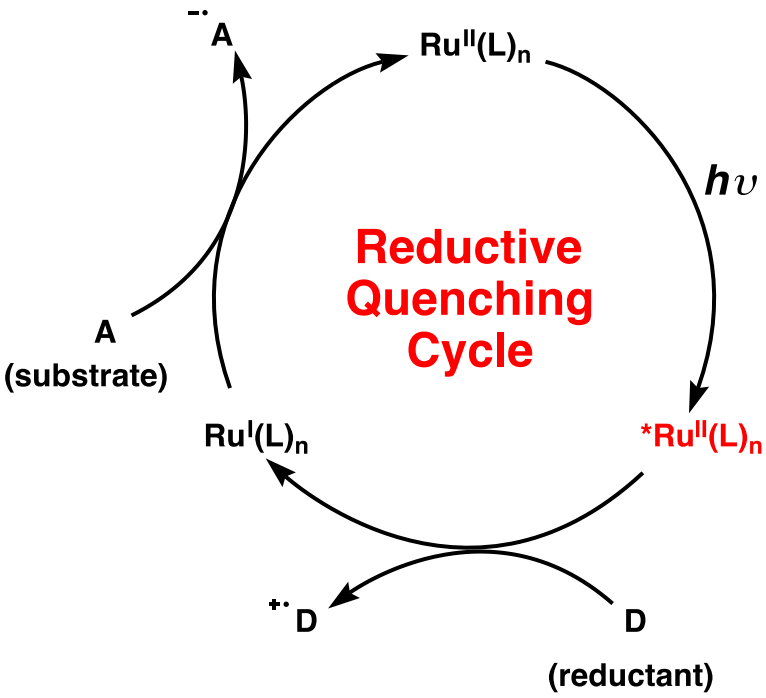


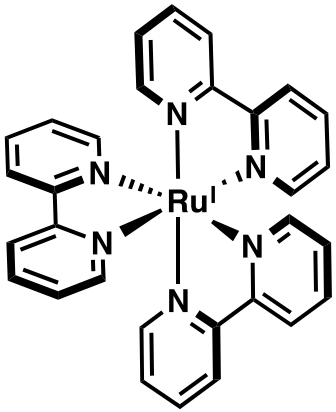
mer-$Ru(4\text{-}O_2N\text{-}bpy)_3$
E_{red} = –0.63 V

electron density of ligand

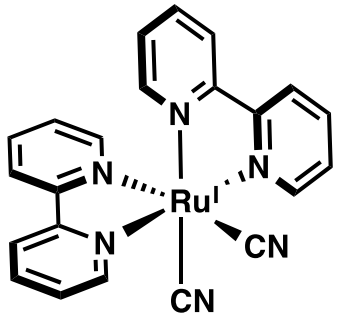
reductive power of complex

The Importance of Redox Properties of Catalysts



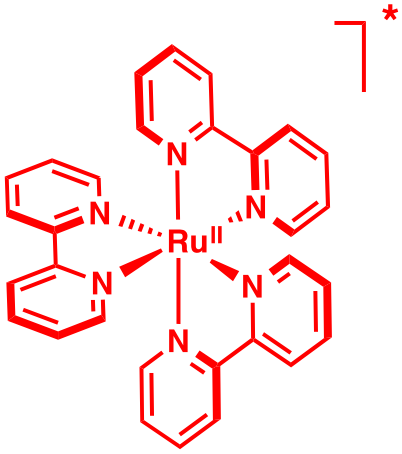


$Ru(bpy)_3$
E_{red} = –1.35 V

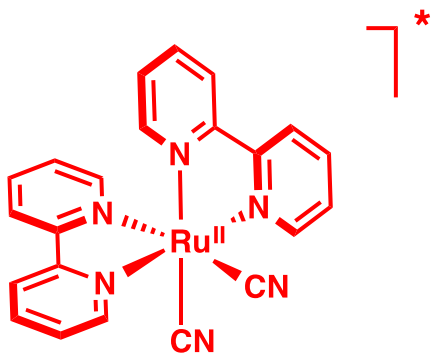


$Ru(bpy)_2(CN)_2$
E_{red} = –1.67 V

Stronger reductant



$Ru(bpy)_3$
E_{red} = 0.78 V

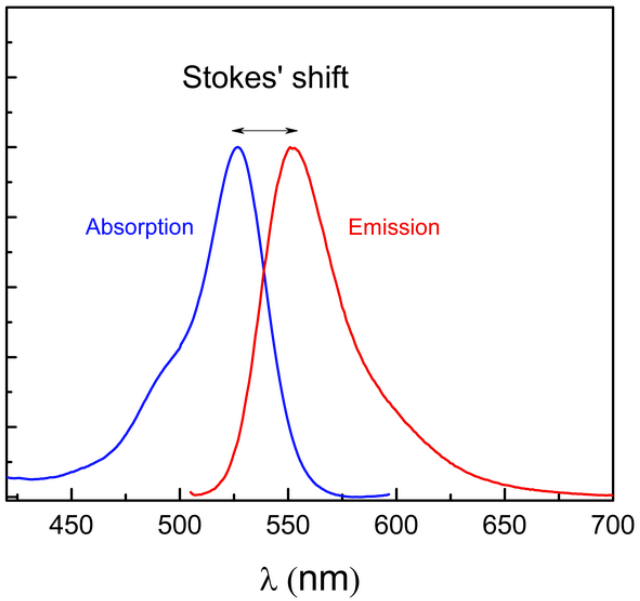


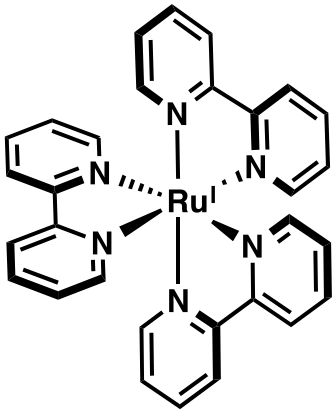
$Ru(bpy)_2(CN)_2$
E_{red} = 0.37 V

More easily quenched

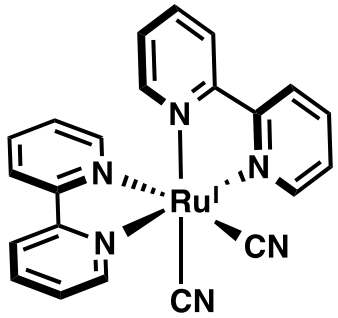
Bignozzi, C. A. ***Inorg. Chem.*** 1984, ***23***, **1540.**

The Importance of Redox Properties of Catalysts





$Ru(bpy)_3$
E_{red} = –1.35 V

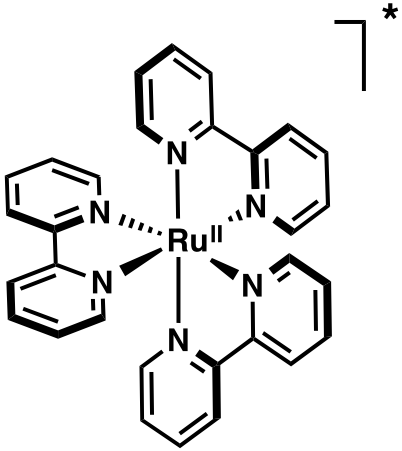


$Ru(bpy)_2(CN)_2$
E_{red} = –1.67 V

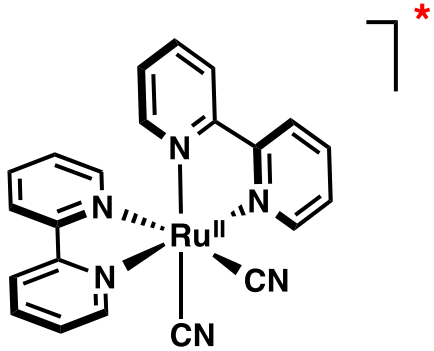
Stronger reductant

These differences can be attributed to the large Stokes shift Ru complexes experience.

i.e. The lower $E_{0,0}$ makes the excited state both a weaker oxidant and weaker reductant



$Ru(bpy)_3$
E_{red} = 0.78 V

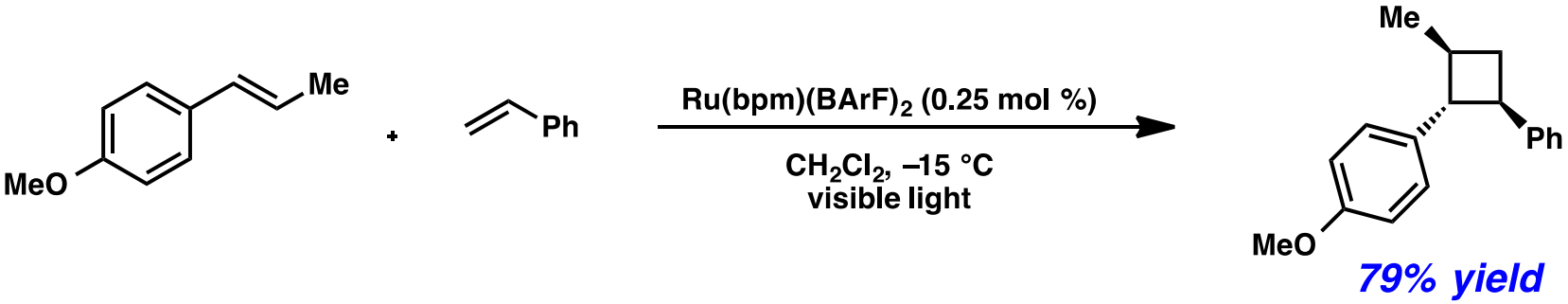


$Ru(bpy)_2(CN)_2$
E_{red} = 0.37 V

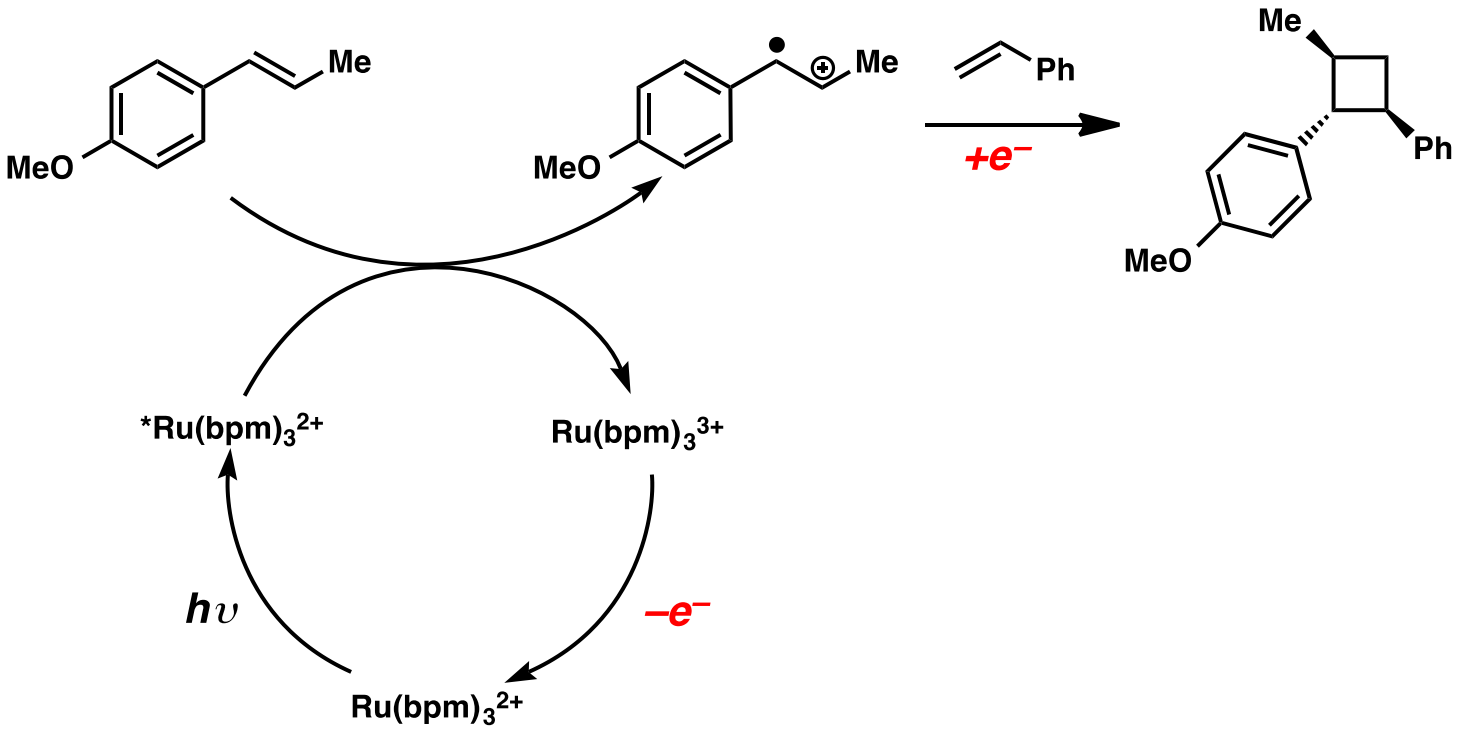
More easily quenched

Bignozzi, C. A. ***Inorg. Chem.*** 1984, ***23***, **1540.**

[2+2] Cycloadditions

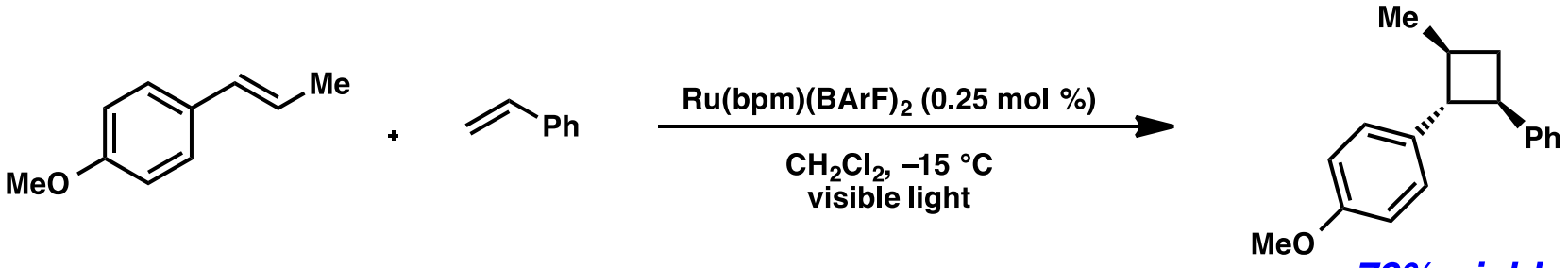


79% yield

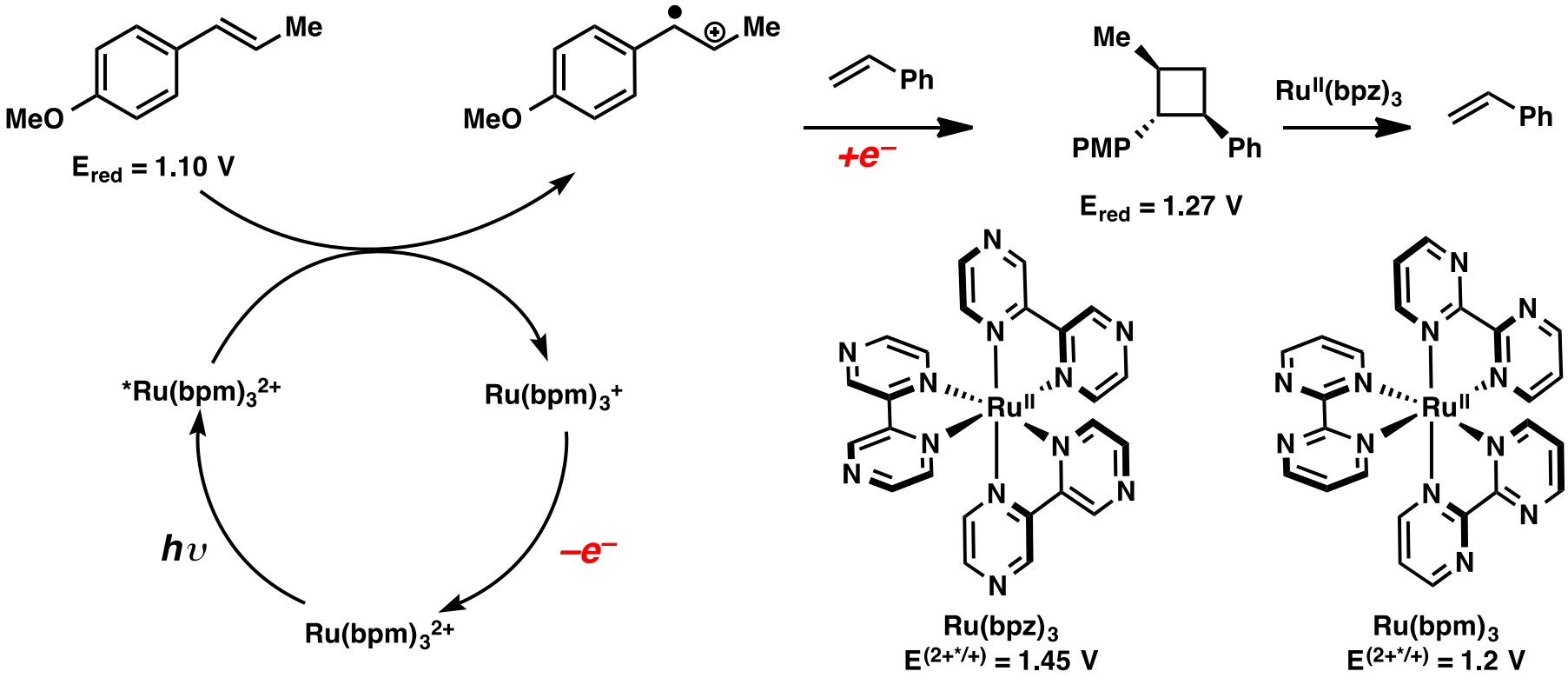


Yoon, T. P. *Chem. Sci.* 2012, *3,* 2811.

[2+2] Cycloadditions

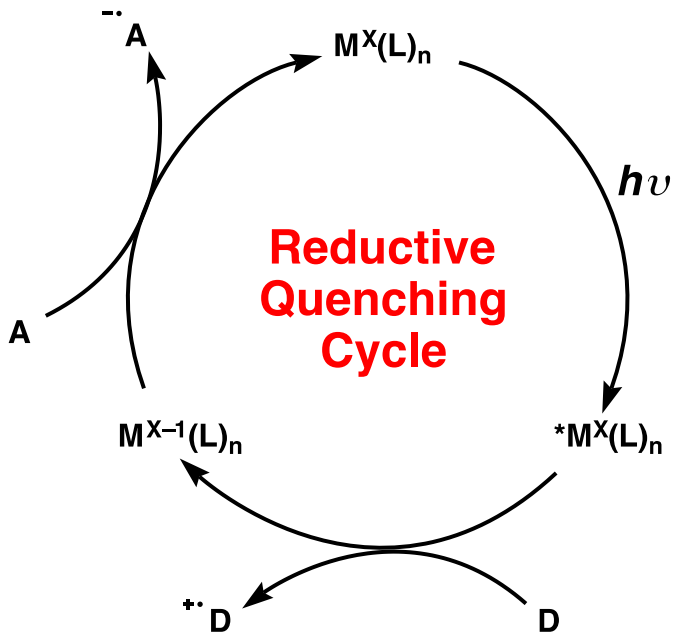


79% yield

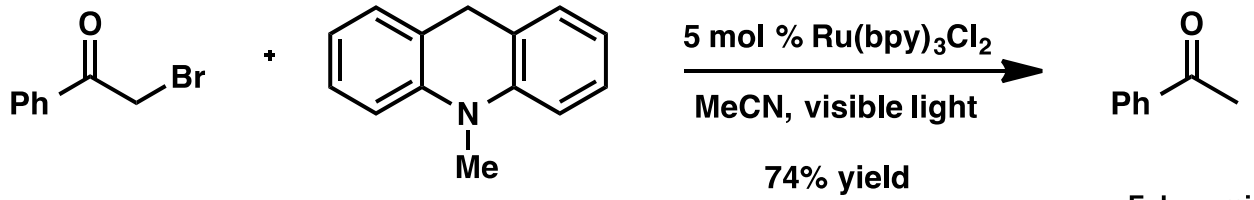


Yoon, T. P. *Chem. Sci.* 2012, *3,* 2811.

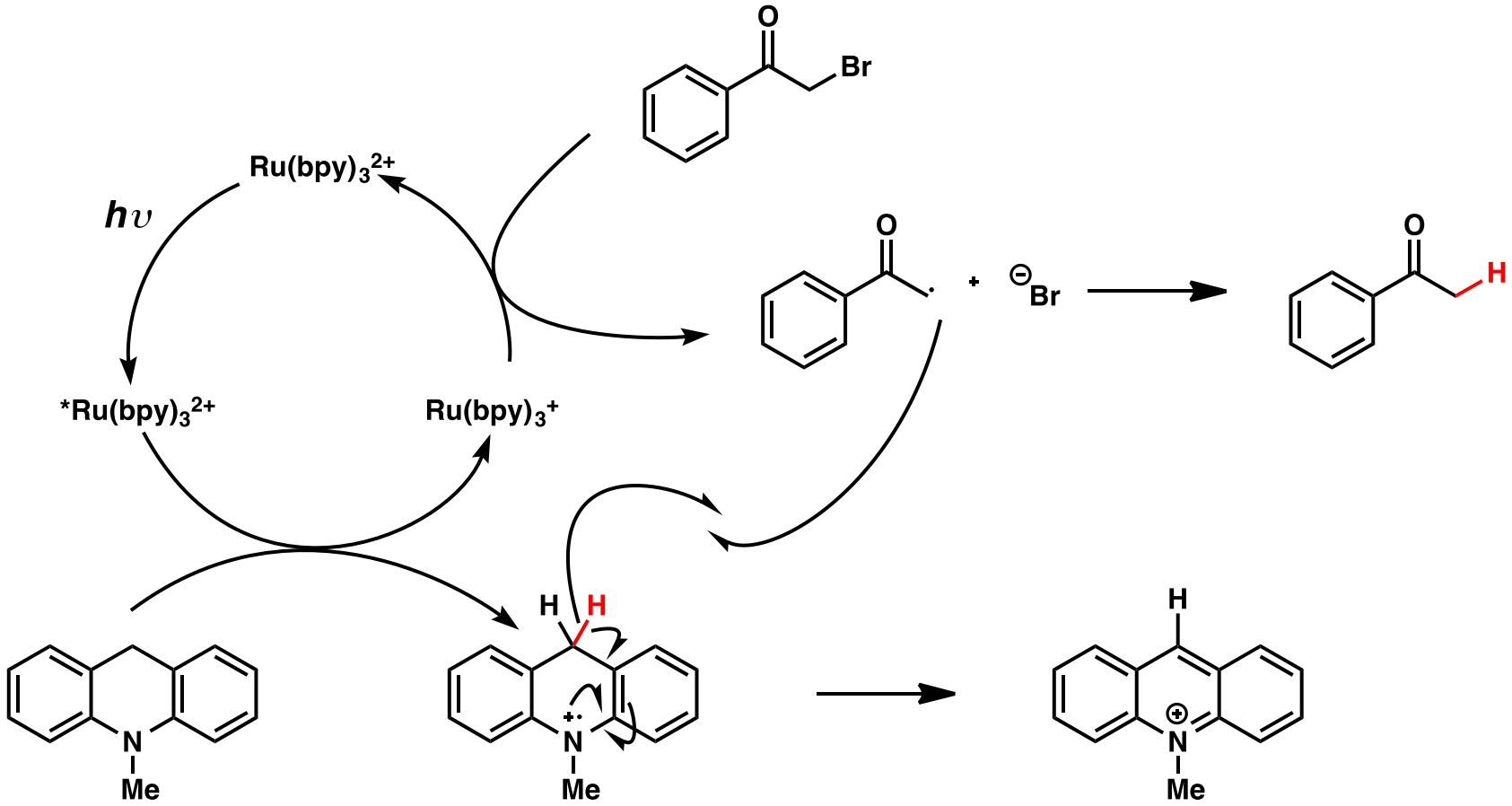
The Reductive Quenching Cycle



Photocatalyzed Dehalogenation

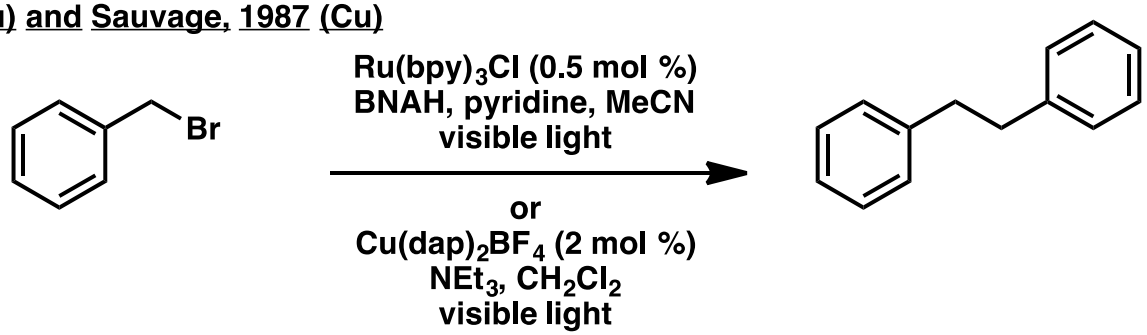


Fukuzumi, S. *J. Phys. Chem.* 1990, ***94***, 722

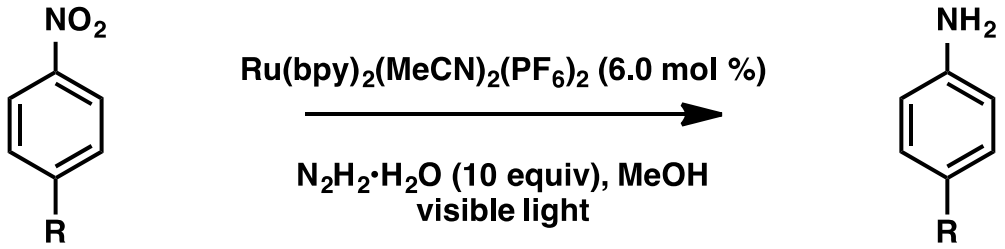


Other Reductive Reactions

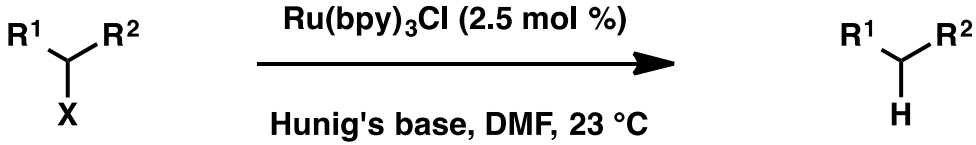
Tanaka, 1984 (Ru) and Sauvage, 1987 (Cu)



Hirao, 2004

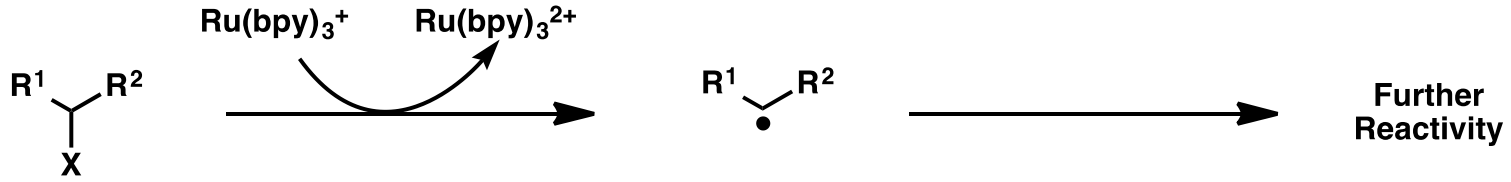


Stephenson, 2009

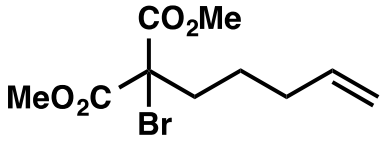


Tanaka, T. *J. Chem Soc., Perkin Trans. 2* 1984, **1705.**
Sauvage, J.-P. *J. Chem. Soc., Chem. Commun* 1987, **546.**
Hirao, T. *Bull Chem. Soc. Jpn.* 2004, ***77***, **1763.**
Stephenson, C. R. *J. Am. Chem. Soc.* 2009, ***131***, **8756.**

Utilizing the Radical Intermediate

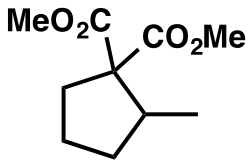


Stephenson, 2010



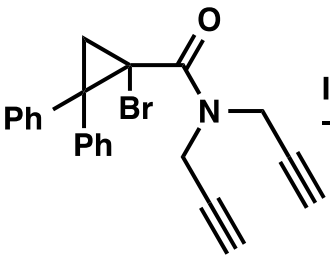
$Ru(bpy)_3Cl$ (2.5 mol %)
or
$Ir(ppy)_2(dtbbpy)PF_6$

NEt_3, DMF
visible light



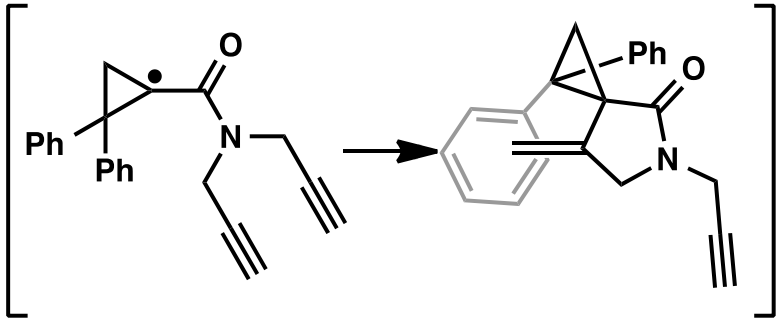
77% yield

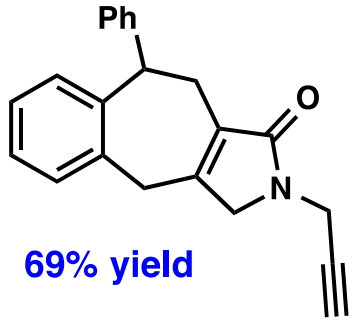
Stephenson, 2011



$Ir(ppy)_2(dtbbpy)PF_6$

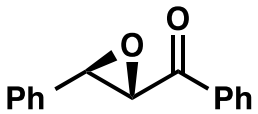
NEt_3, DMF
visible light





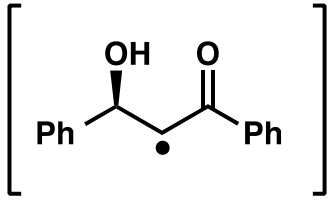
69% yield

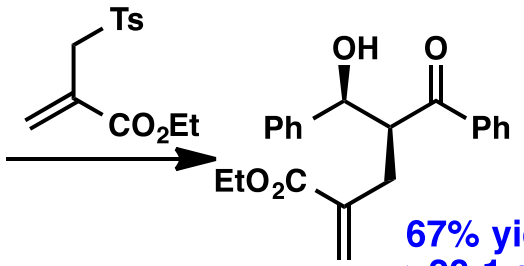
Ollivier, 2011



$Ir(ppy)_2(dtbbpy)PF_6$ (5.0 mol %)
4-Me-Hantzsch ester

allylsulfone
visible light

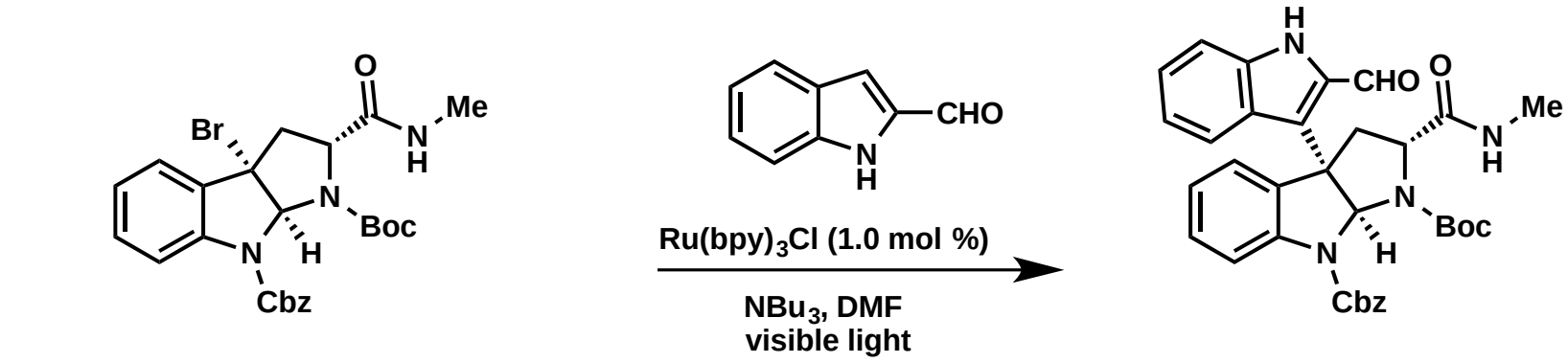


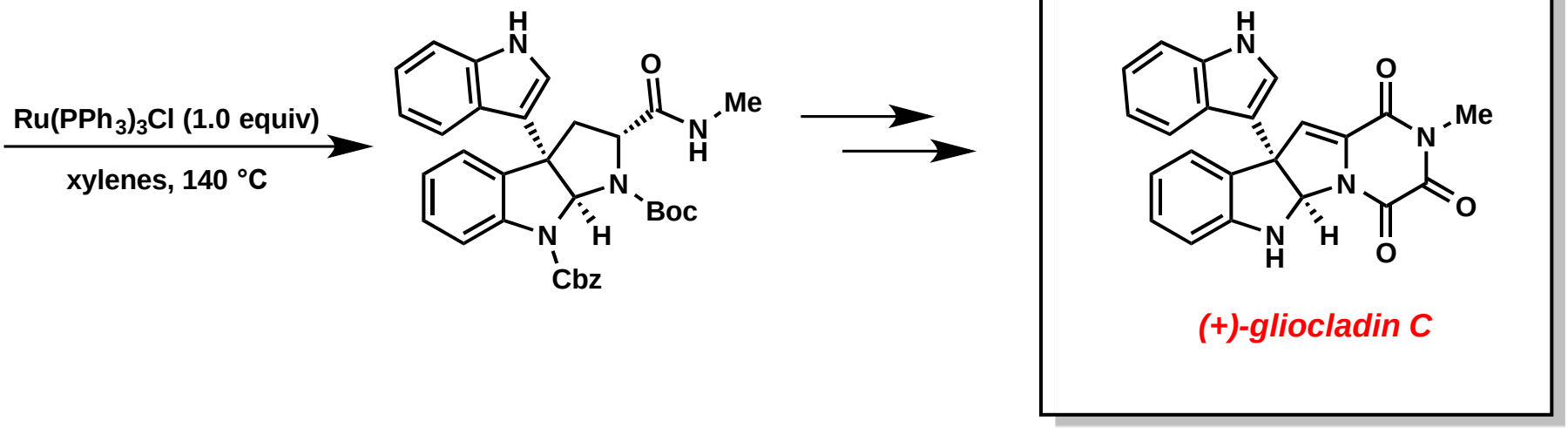


67% yield
>20:1 d.r.

Stephenson, C. R. *Chem. Commun.* 2010, ***46***, **4985.**
Stephenson, C. R. *Org. Lett.* 2011, ***13***, **5468.**
Ollivier, C. *Angew. Chem., Int. Ed.* 2011, ***50, 4463.***

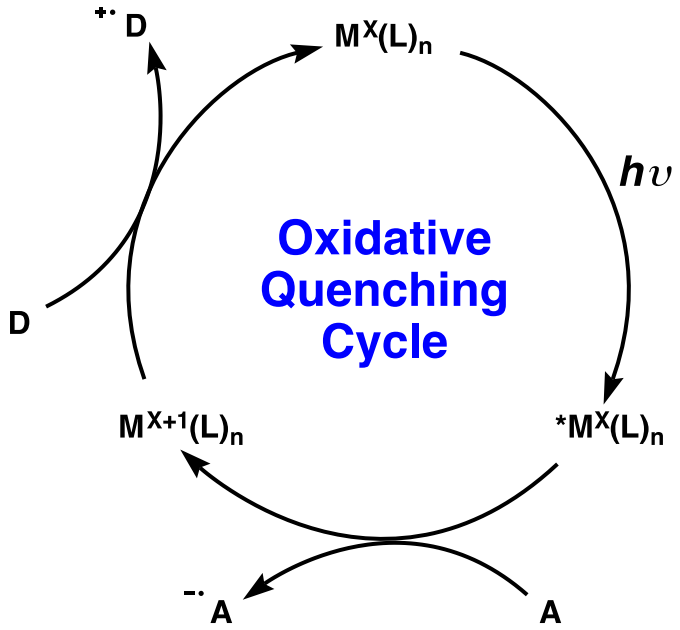
Utilizing the Radical Intermediate
Total Synthesis of (+)-Gliocladin C



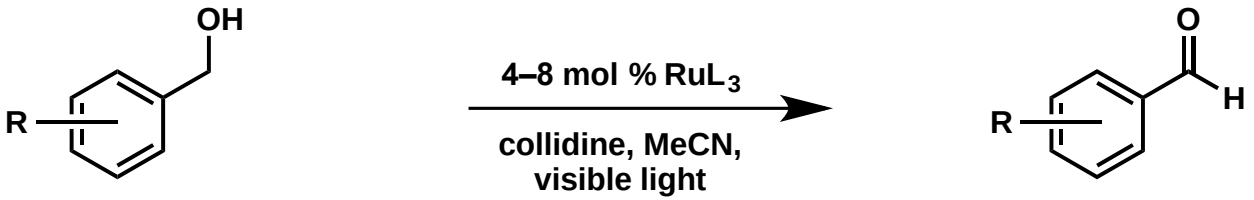


Stephenson, C. R. ***Angew. Chem., Int. Ed.*** 2011**, *50, 9655.***

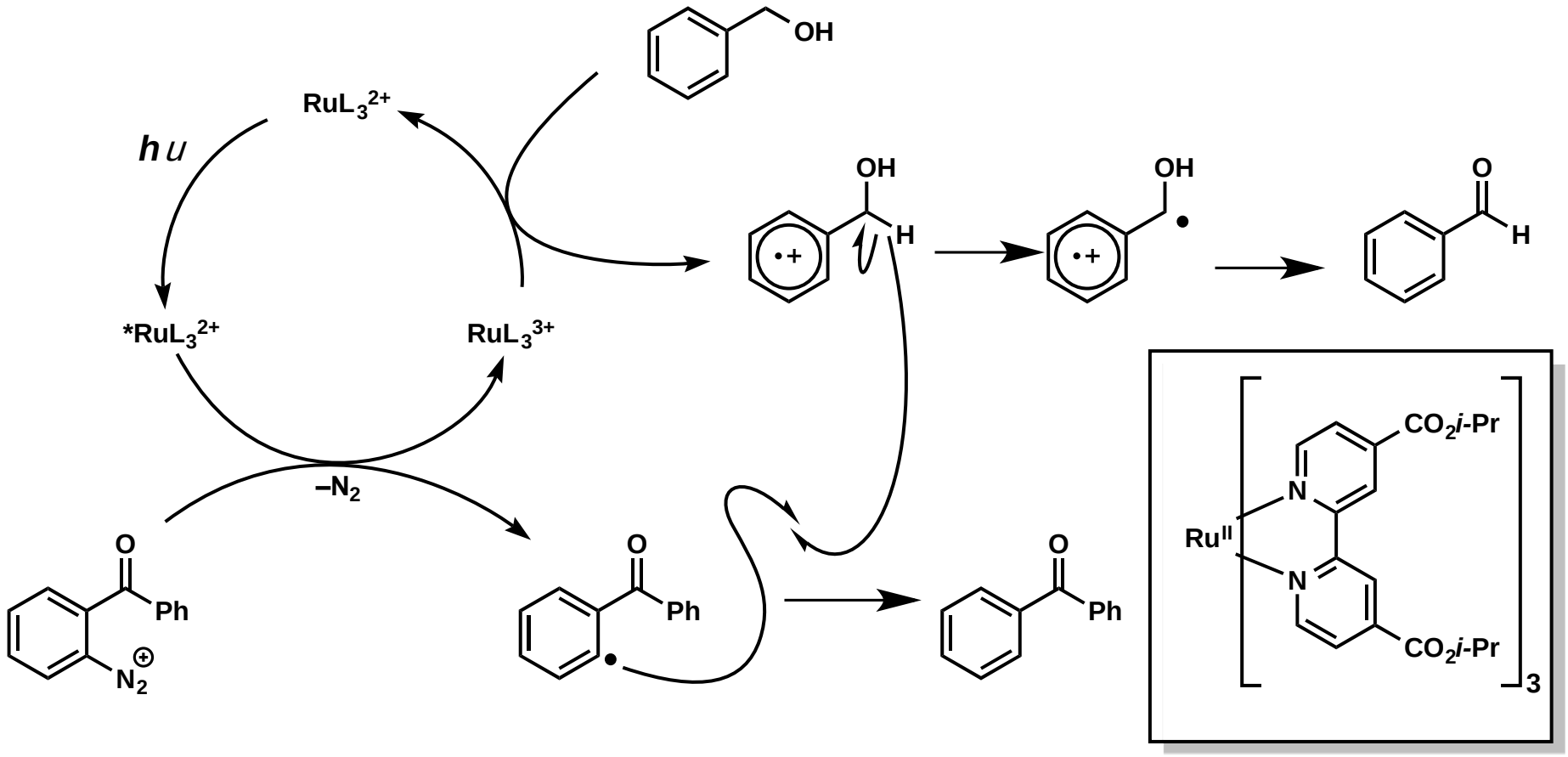
The Oxidative Quenching Cycle



Photocatalyzed Oxidation

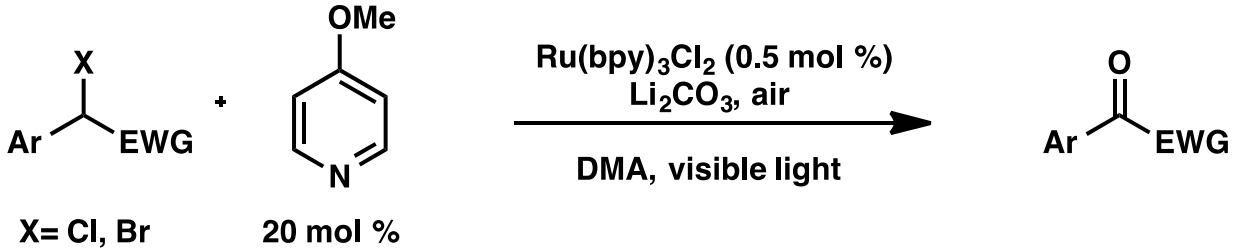


Cano-Yelo, H. *Tetrahedron Lett.* 1984, ***25***, **5517**



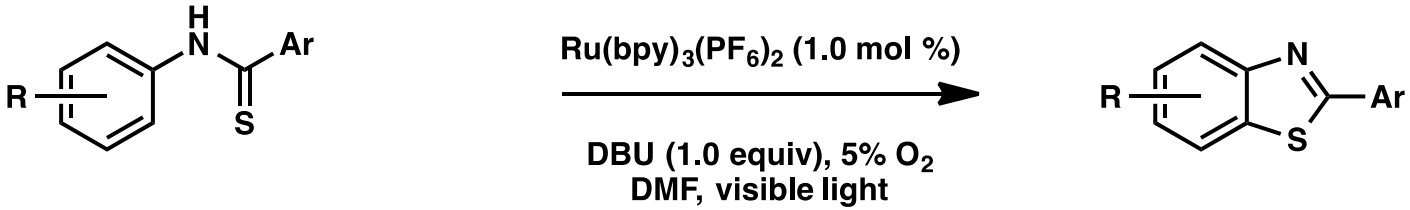
Other Oxidative Reactions

Jiao, 2011

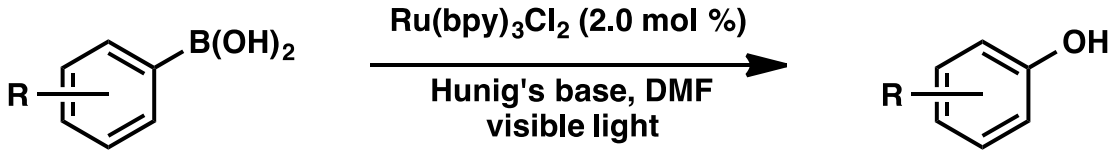


X= Cl, Br 20 mol %

Li, 2012

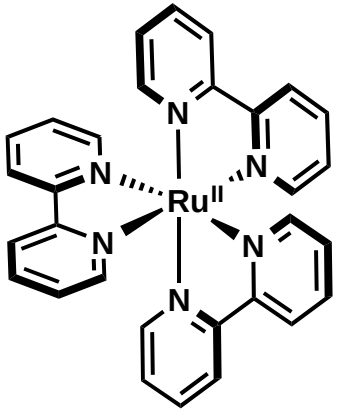


K. A. Jørgensen/Xiao, 2012

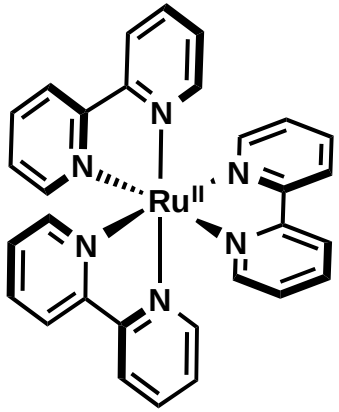


Jiao, N. *Org. Lett.* 2011, ***13, 2168.***
Li, P. *Org. Lett.* 2012, ***14***, **98.**
Xiao, W.-J. *Angew. Chem., Int. Ed.* 2012, ***51***, **784.**

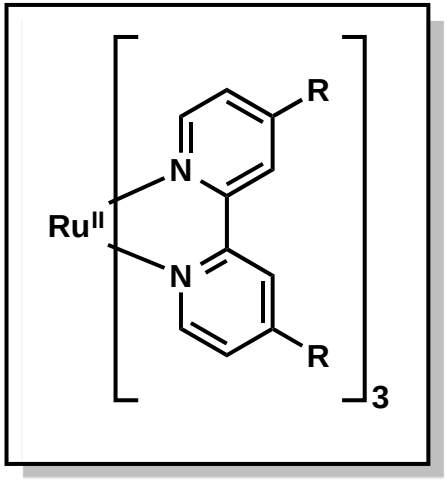
Enantiomeric Ru(bpy)$^{2+}$



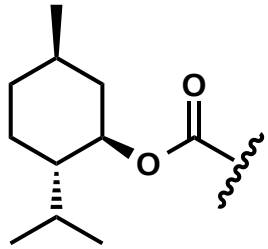
Ru(bpy)$_3^{2+}$
D

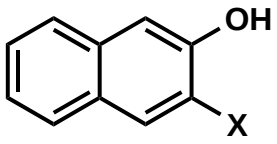


Ru(bpy)$_3^{2+}$
L



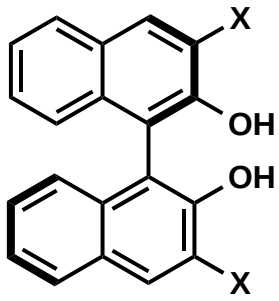
R=





D-Ru(menbpy)$_3^{2+}$

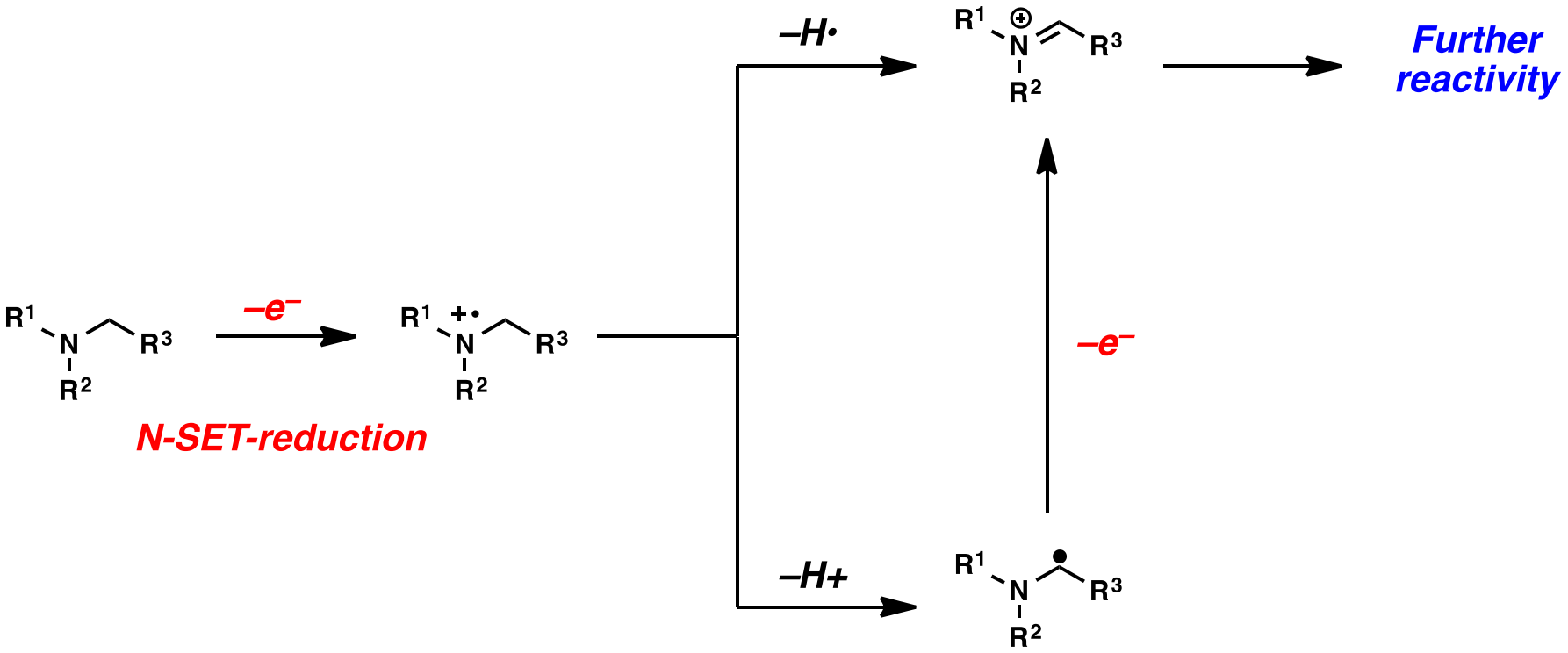
Co(acac)$_3$ (1.2 equiv)
MeCN, visible light



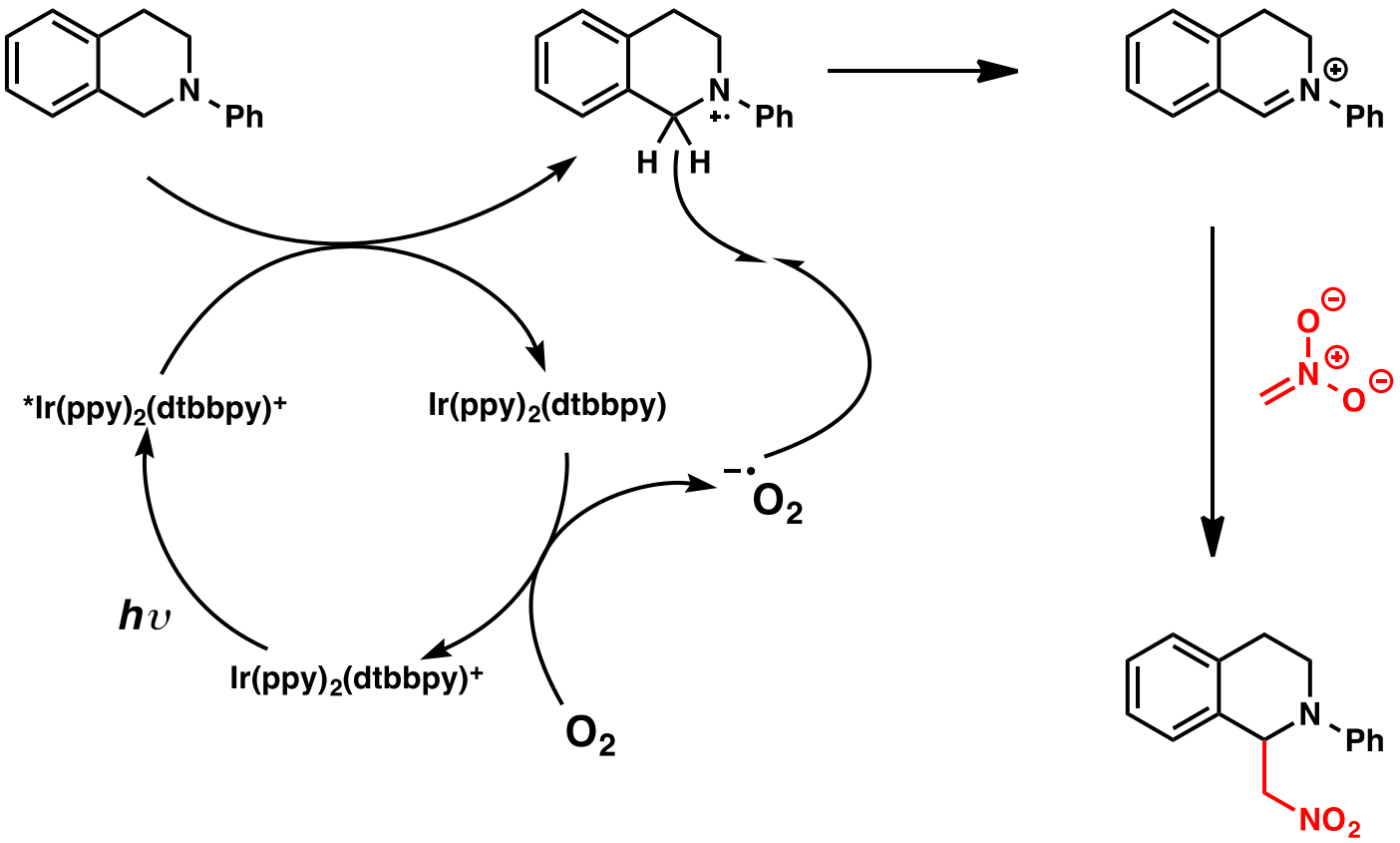
X= H, 16% ee **X= OMe, 4% ee**

Ohkudo, K. ***J. Chem. Soc., Chem Commun.*** 1993**, 909.**

Amine Oxidation

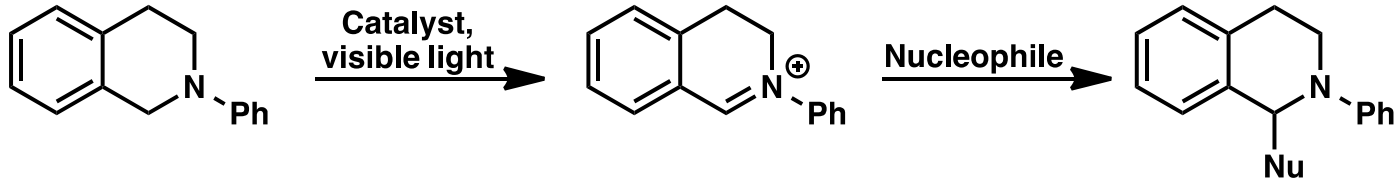


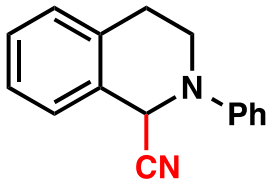
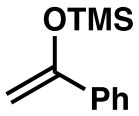
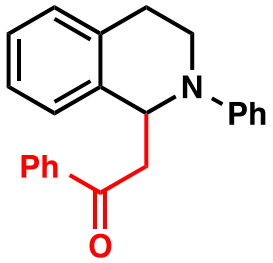
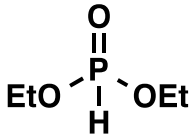
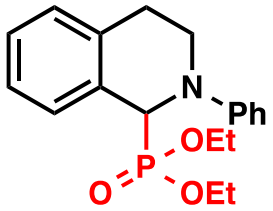
Amine Oxidation
Iminium Ions

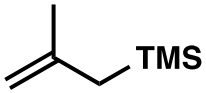
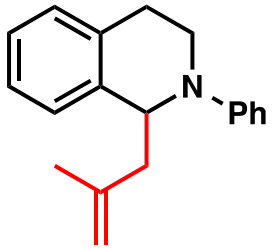
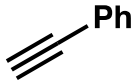
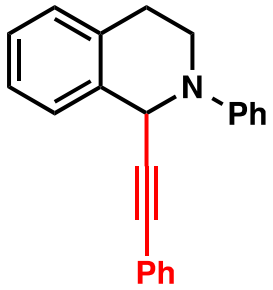
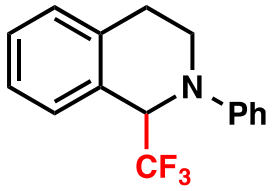


Stephenson, C. R. *Angew. Chem., Int. Ed.* 2011, ***50***, 9655

Amine Oxidation
Iminium Ions



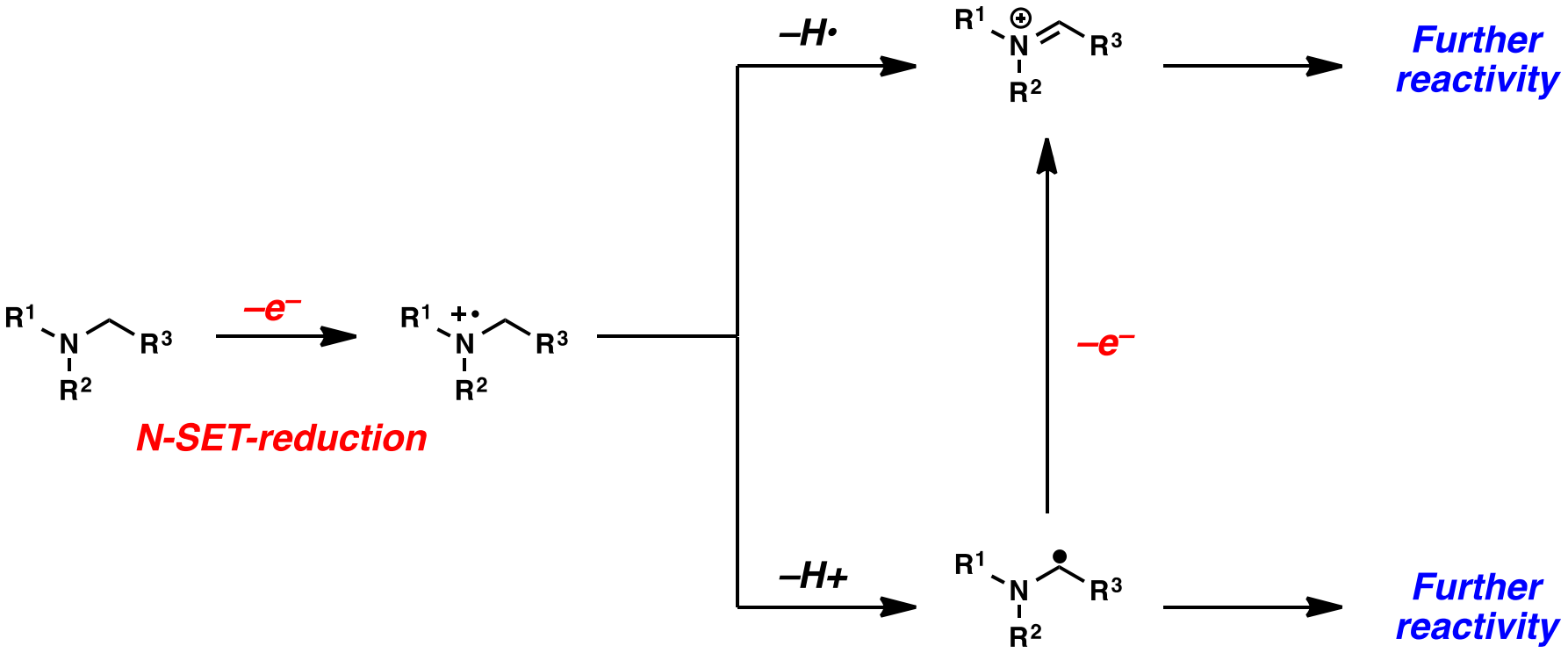
Nucleophile	Catalyst	Product	% Yield
KCN	$Ir(ppy)_2(bpy)PF_6$		*94*
	$Ru(bpy)_3Cl_2$		*96*
	$Ir(ppy)_2(bpy)PF_6$		*89*

Nucleophile	Catalyst	Product	% Yield
	$Ru(bpy)_3Cl_2$		*85*
	$Ru(bpy)_2(dtbbpy)Cl_2$		*88*
$TMSCF_3$	rose bengal		*75*

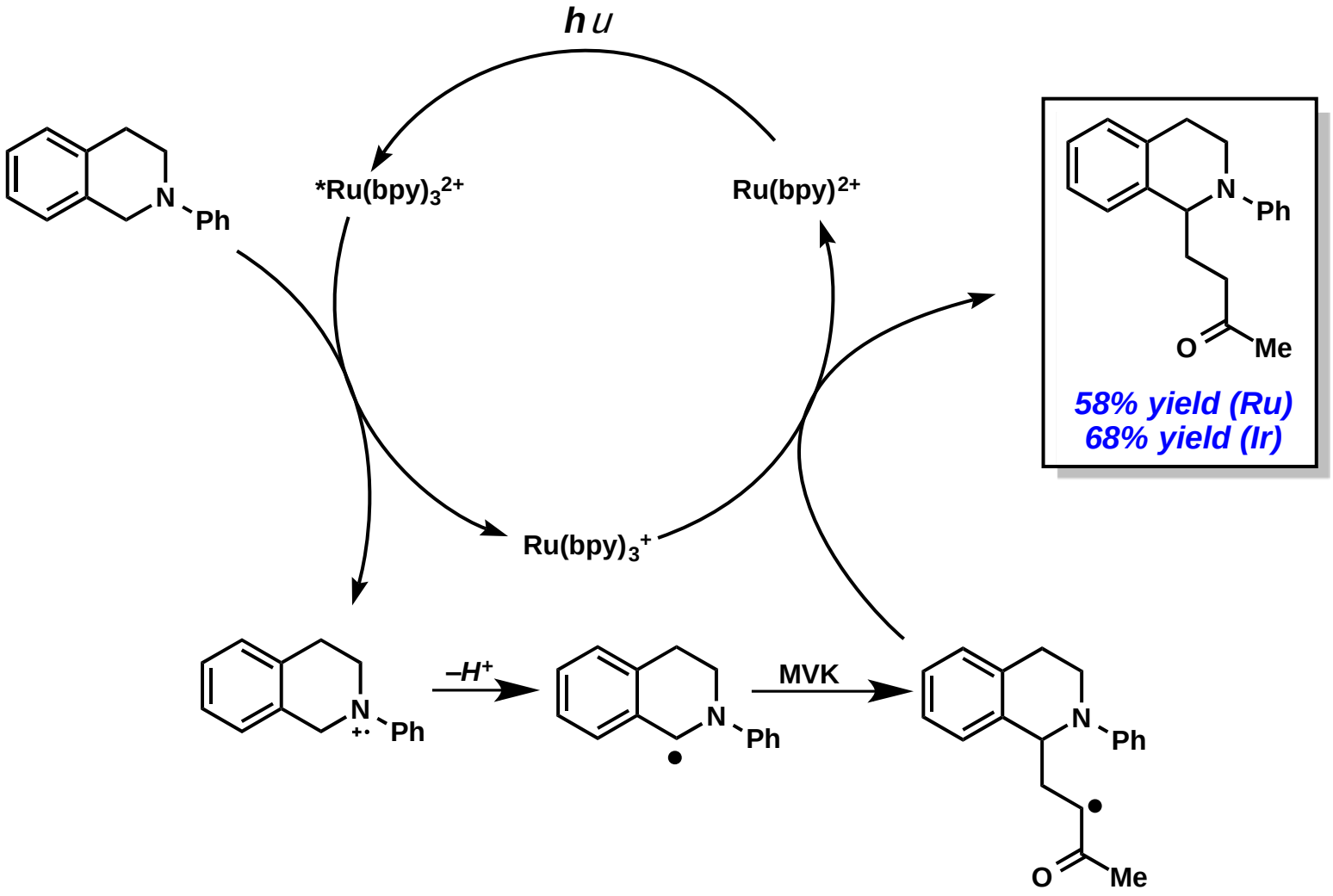
Koenigs, R. M. *Chem. Commun.* 2011, ***47***, **12709.**
Xia, W. *Chem. Commun.* 2012, ***48***, **2337.**
Koenigs, R. M. *Chem. Commun.* 2011, ***47***, **8679.**

Stephenson, C. R. *Org. Lett.* 2012, ***14***, **94.**
Vila, C. *Chem.-Eur. J.* 2012, ***18***, **5170.**
Xu, C. *Green Chem.* 2012, ***140***, **88.**

Amine Oxidation

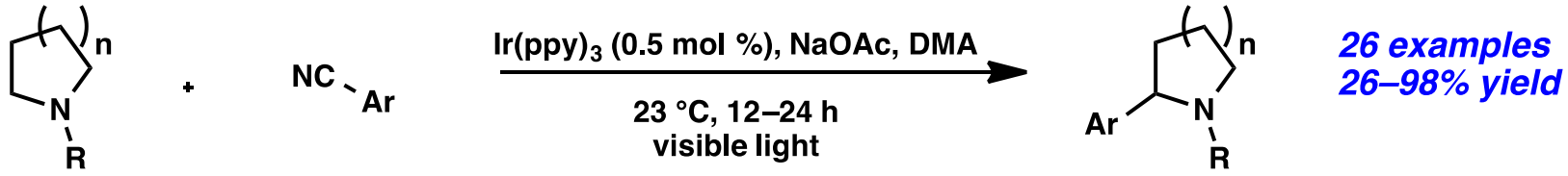


Amine Oxidation
a-Amino Radicals



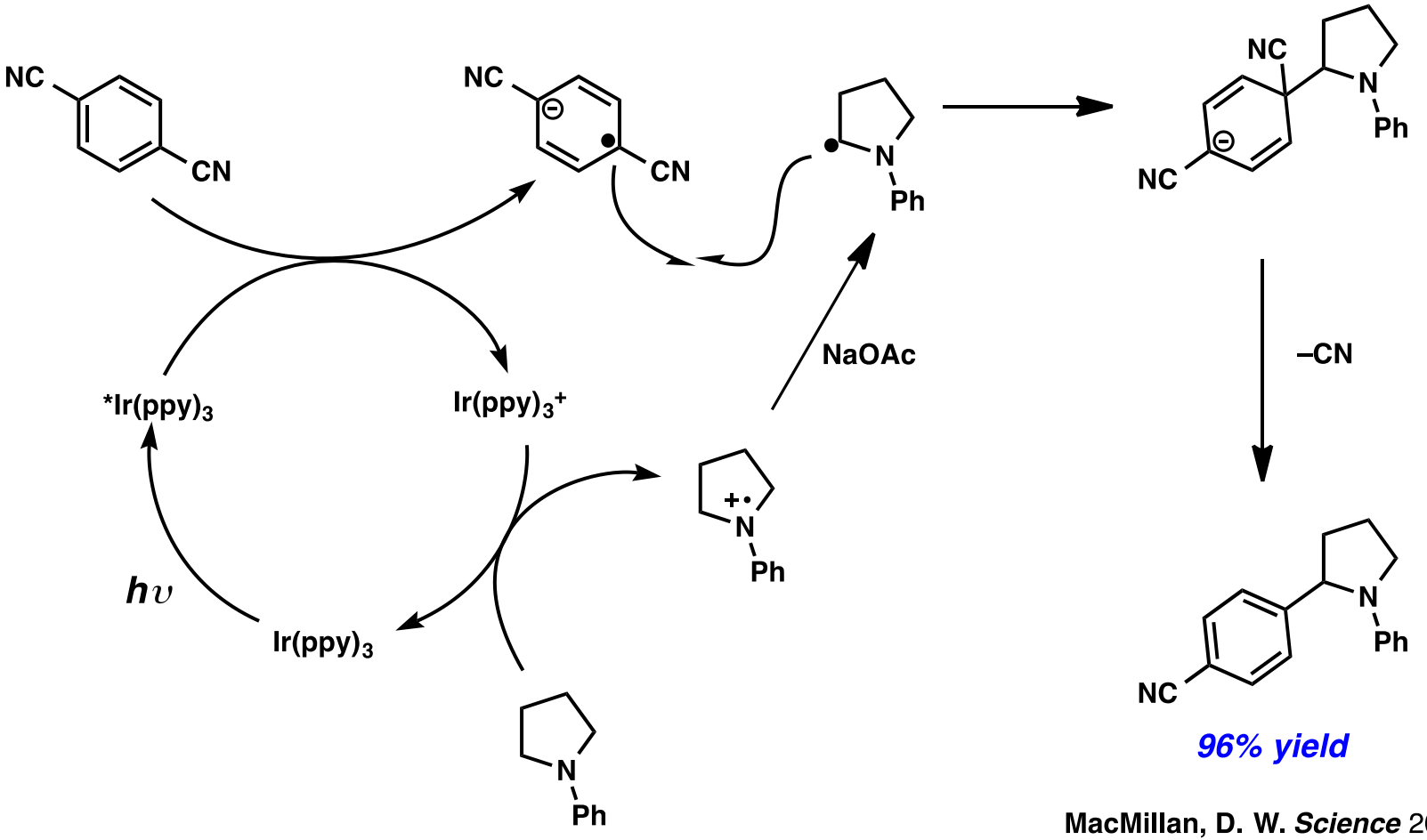
Reiser, O. *Org. Lett.* 2012, ***14***, **672**

Amine Oxidation
α-Amino Radicals



26 examples
26–98% yield

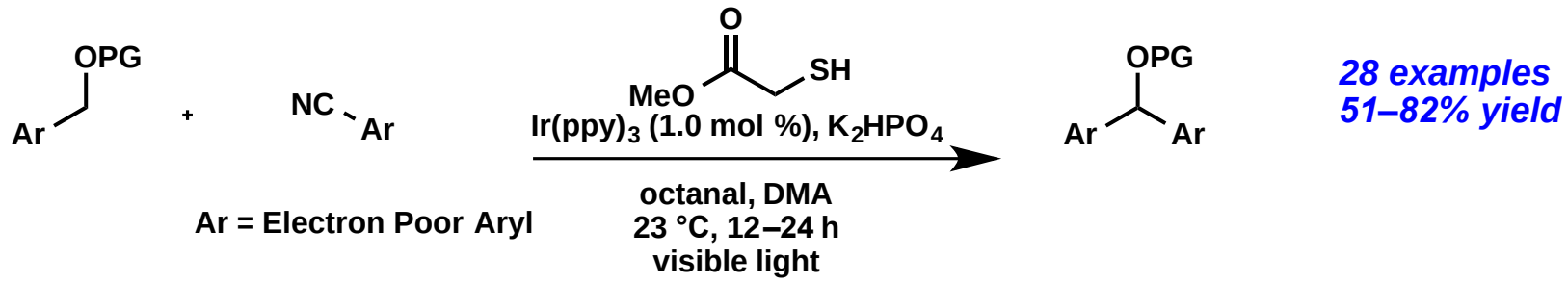
Ar = Electron Poor Aryl

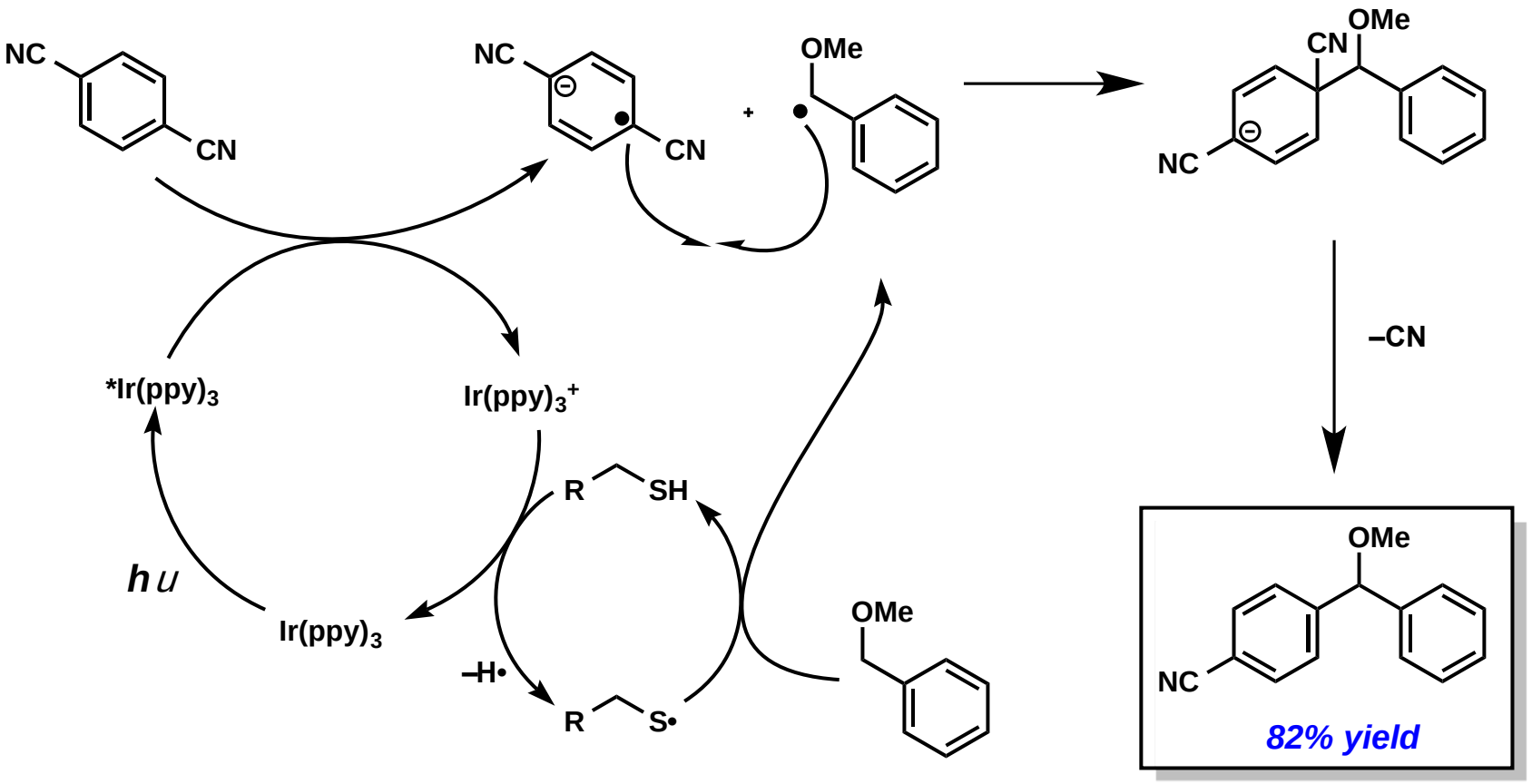


96% yield

MacMillan, D. W. *Science* 2011, *334*, 1114.

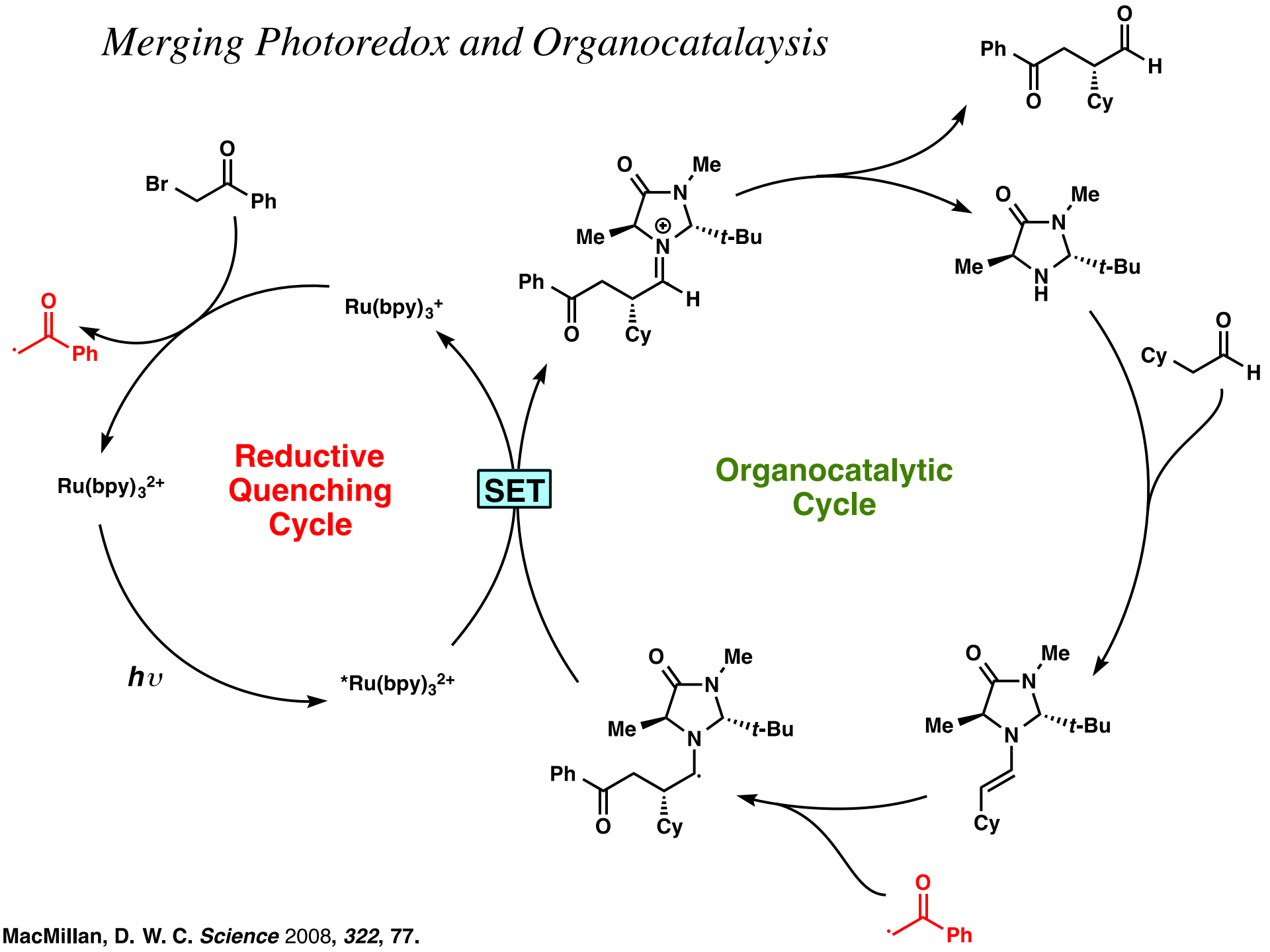
Amine Oxidation
a-Amino Radicals





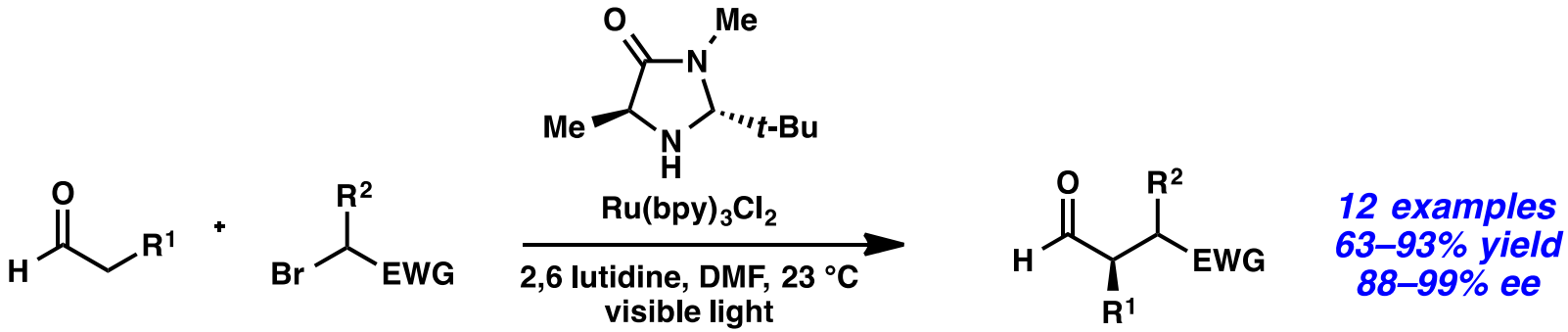
MacMillan, D. W. *J. Am. Chem. Soc.* 2014, ***136***, 626.

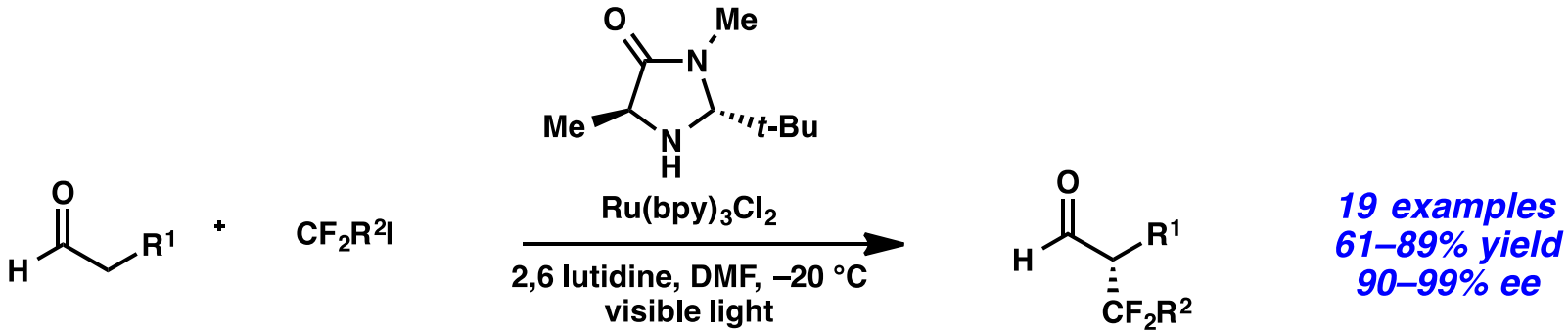
Merging Photoredox and Organocatalaysis



MacMillan, D. W. C. *Science* 2008, ***322***, 77.

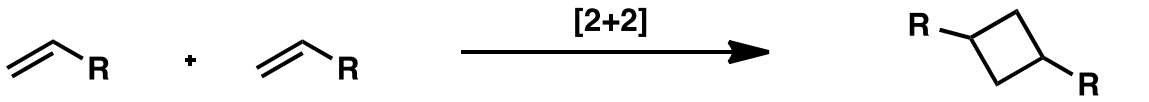
Merging Photoredox and Organocatalaysis

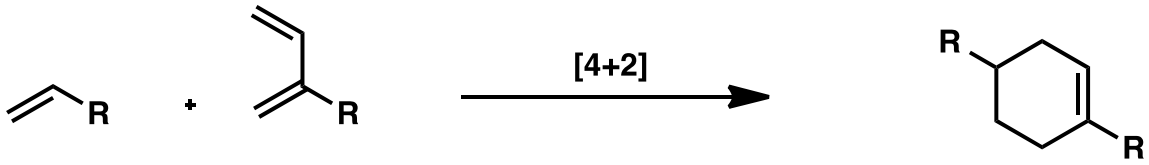




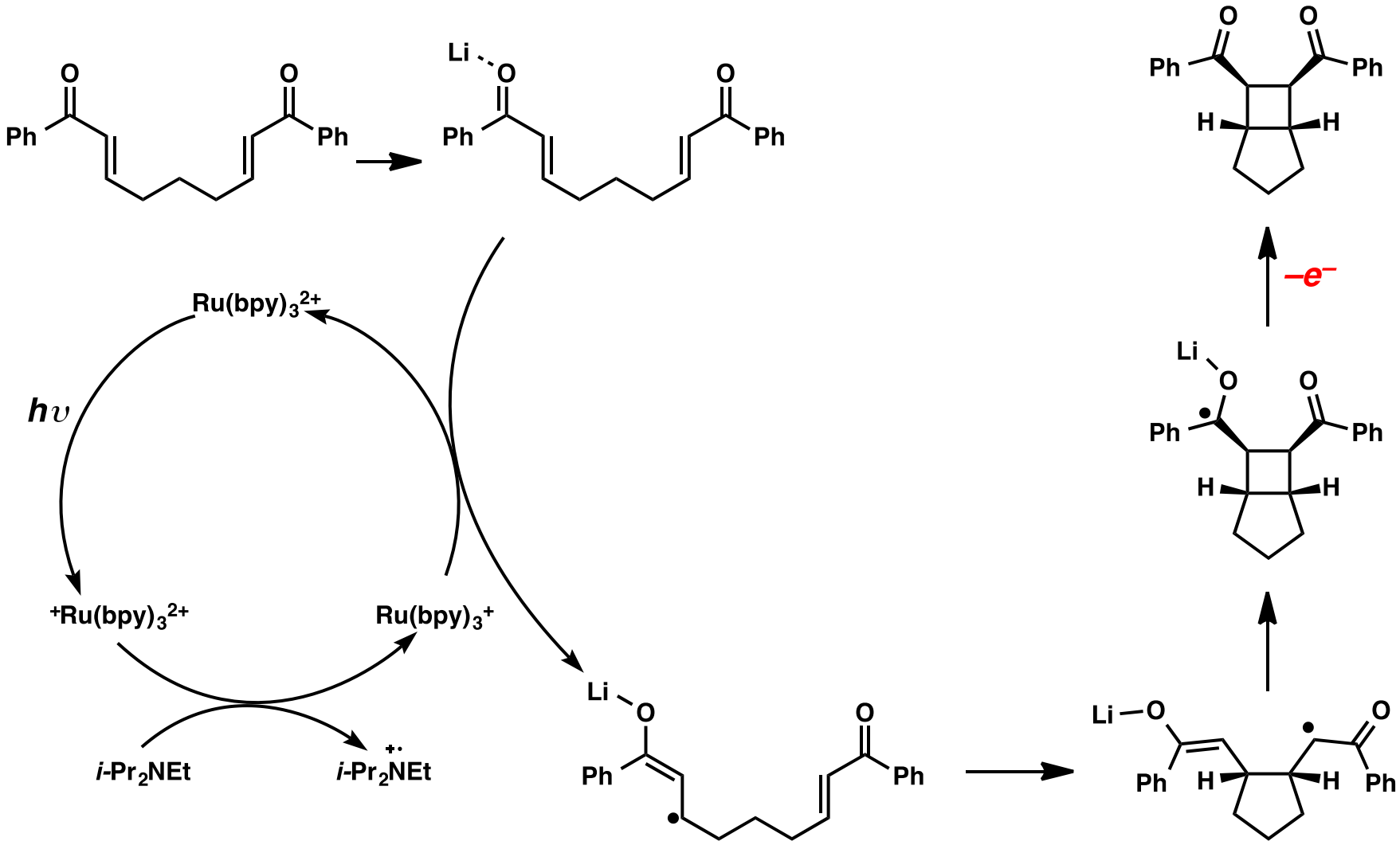
MacMillan, D. W. C. *Science* 2008, ***322***, 77.
MacMillan, D. W. C. *J. Am. Chem. Soc.* 2009, ***131***, 10875.

Cycloaddition Reactions



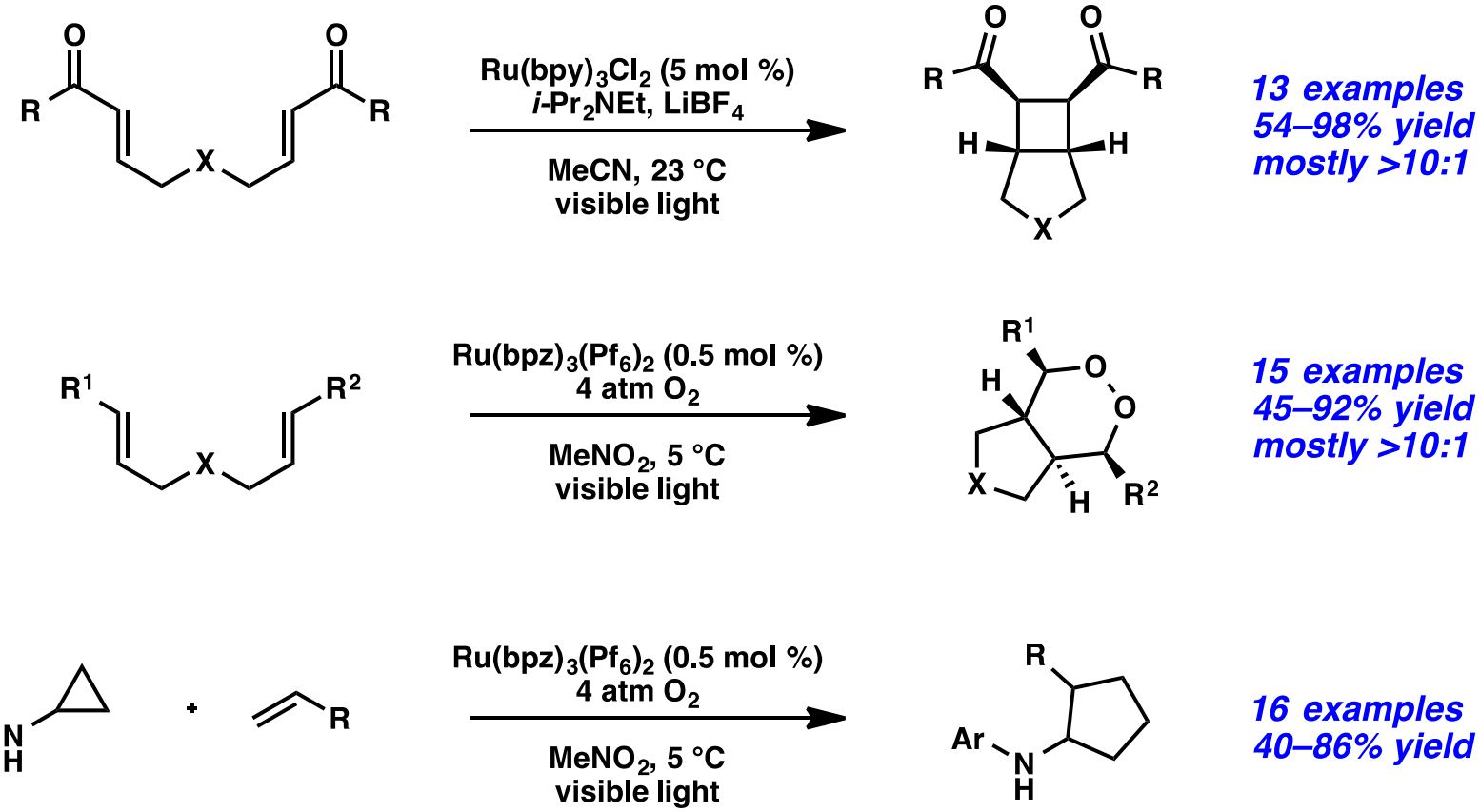


[2+2] Cycloadditions



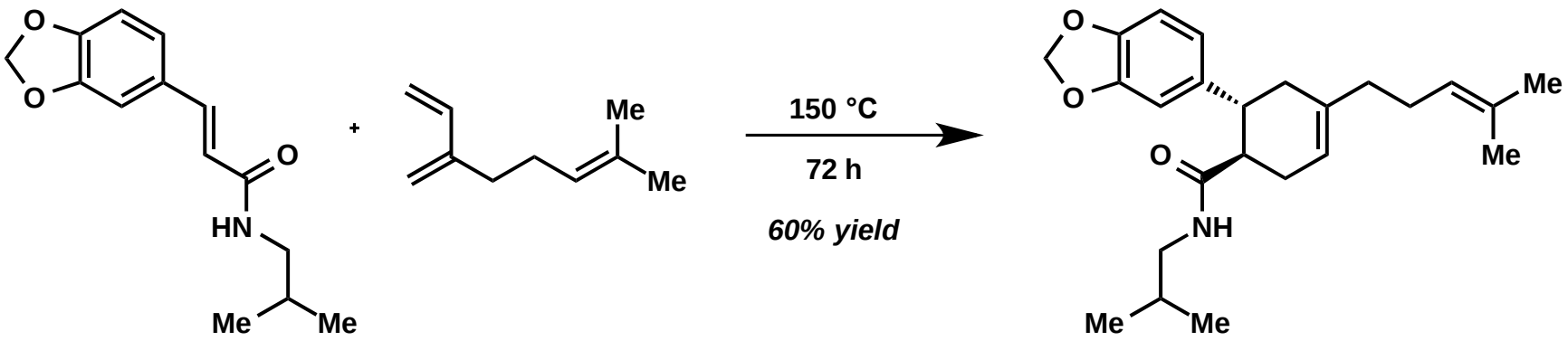
Yoon, T. P. ***J. Am. Chem. Soc*** 2008, ***130,*** **12886**

Cycloadditions

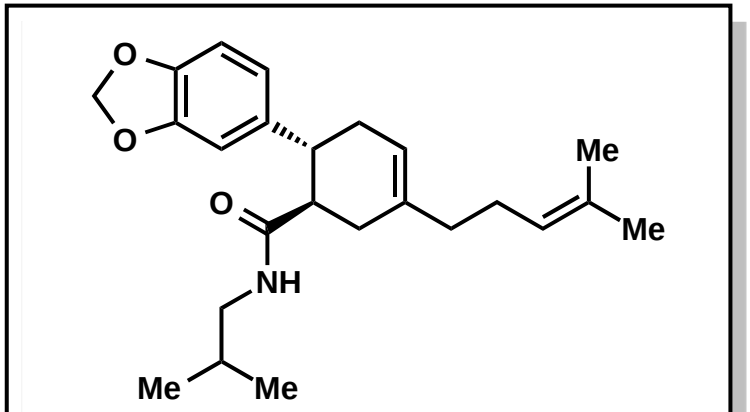


Yoon, T. P. *J. Am. Chem. Soc* 2008, ***130,*** 12886.
Yoon, T.P. *Org. Lett.* 2012, ***14***, 1640.
Zheng, N. *Angew. Chem., Int. Ed.* 2012, ***51***, 222.

Diels–Alder Cycloaddition



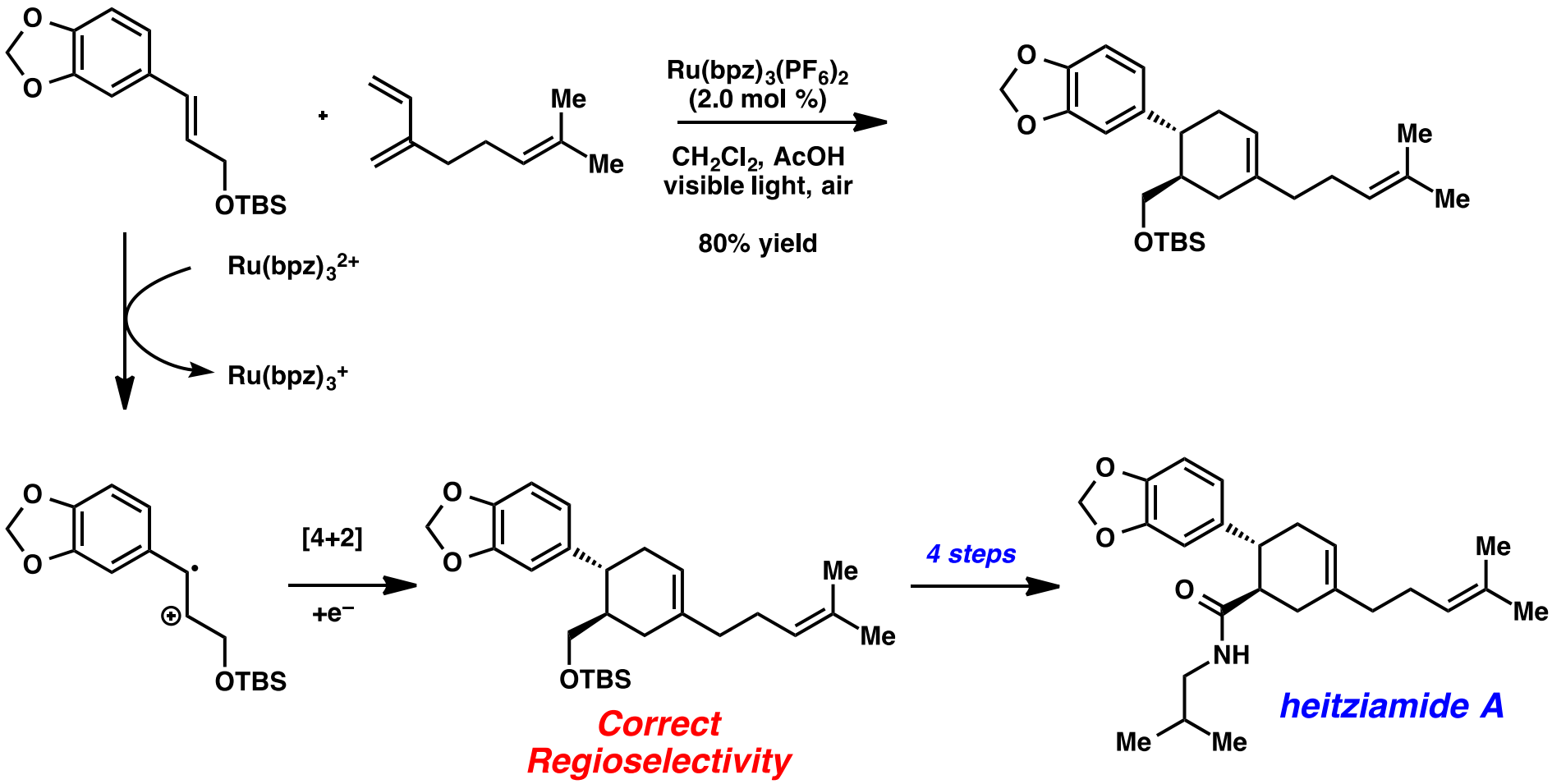
Incorrect Regioselectivity



heitziamide A

Yoon, T. P. ***J. Am. Chem. Soc*** 2011, ***133,*** **19350.**

Diels–Alder Cycloaddition



Yoon, T. P. *J. Am. Chem. Soc* 2011, ***133,*** **19350.**

Summary

-*Visible light photoredox catalysts can be easily tuned*

-Catalysts can act as either a reductant or oxidant, causing net oxidative, reductive or neutral reactions.

-Photoredox catalysis provides a mild way of affecting a wide variety of reacions.