Literature Report

Visible-Light-Mediated Organic Photoredox Catalysis in Functionlization of Alkenes

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Prof. Huang Group Meeting

August 22th 2016

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Organo-photocatalyst : Photophysical Processes

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III: Summary

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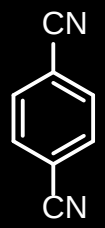
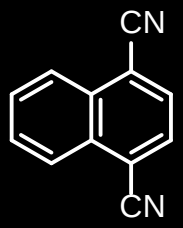
Organo-photocatalyst : What is?

Cyanoarenes



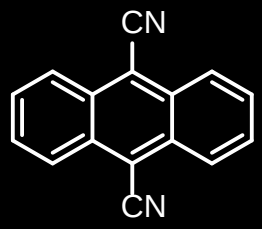
DCB

λ_{max}^{abs} = 291 nm



DCN

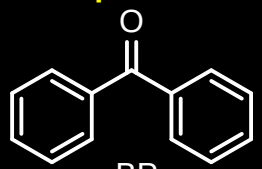
λ_{max}^{abs} = 325 nm



DCA

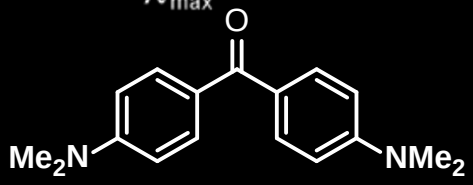
λ_{max}^{abs} = 422 nm

Benzophenones



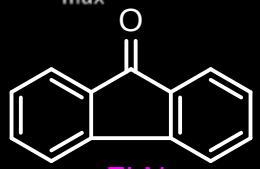
BP

λ_{max}^{abs} = 335 nm



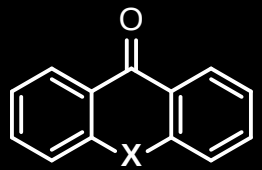
MK

λ_{max}^{abs} = 365 nm



FLN

λ_{max}^{abs} = 377 nm



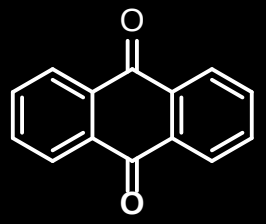
XO: X=O

λ_{max}^{abs} = 340 nm

TXO: X=S

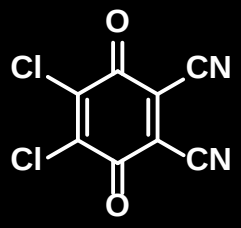
λ_{max}^{abs} = 360 nm

Quinones



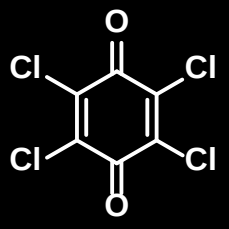
AQ

λ_{max}^{abs} = 326 nm



DDQ

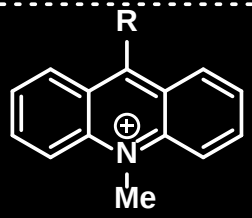
λ_{max}^{abs} ~377 nm



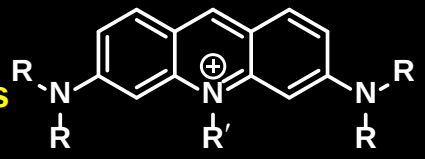
TCBQ

λ_{max}^{abs} = 450nm

Organo-photocatalyst : What is?



Acridiniums



Acr-Me$^+$

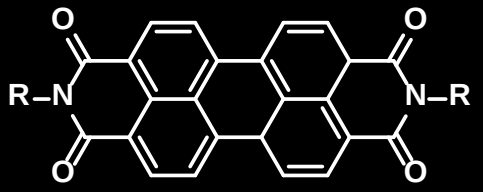
Ph-Acr-Me$^+$: λ_{max}^{abs} = 424nm

Mes-Acr-Me$^+$: λ_{max}^{abs} = 425nm

AOH$^+$: λ_{max}^{abs} = 495nm R= Me, R'=H

AcrF$^+$: λ_{max}^{abs} = 470nm R= H, R'=Me

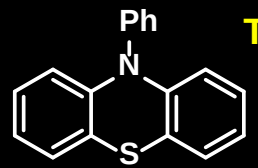
PFH$^+$: λ_{max}^{abs} = 470nm R= H, R'=H



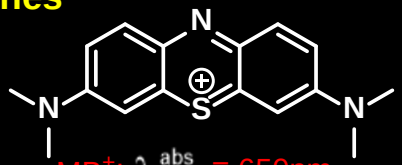
PDI: R=H

PDI-a: R=2,6-diisopropylphenyl

PDI-b: R=2,5-di-*tert*-butylphenyl

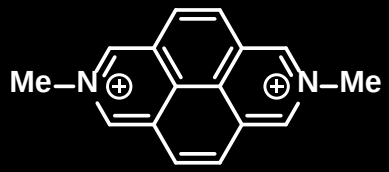


Thiazines

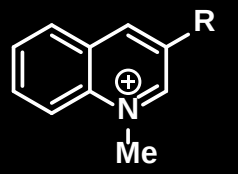


PTh: λ_{max}^{abs} < 300 nm

MB$^+$: λ_{max}^{abs} = 650nm



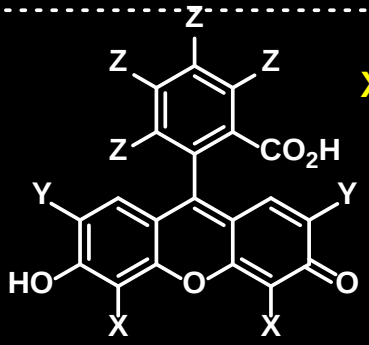
DAP^{2+}



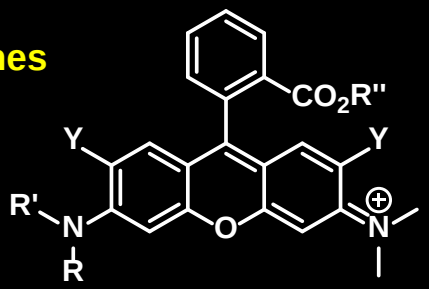
Quinoloniums

NMQ$^+$: λ_{max}^{abs} = 315 nm

QuCN$^+$: λ_{max}^{abs} = 329 nm



Xanthenes



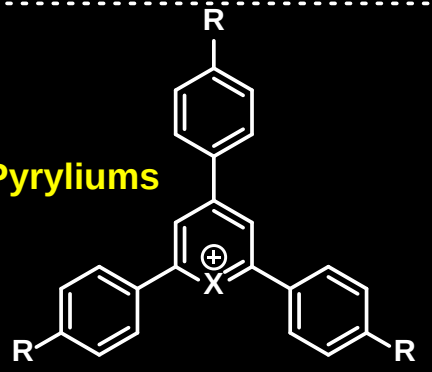
Fluorescein: λ_{max}^{abs} = 491nm X,Y,Z=H

Eosin Y: λ_{max}^{abs} = 533nm X,Y=Br, Z=H

Rose Bengal: λ_{max}^{abs} = 549nm X,Y=I, Z=Cl

Rhodamine B: λ_{max}^{abs} = 550nm R'',Y=I, R,R'=Et

Rhodomine 6G: λ_{max}^{abs} = 550nm R'=H,Y=Me, R,R''=Et



Pyryliums

X=O or S, R=H or OMe

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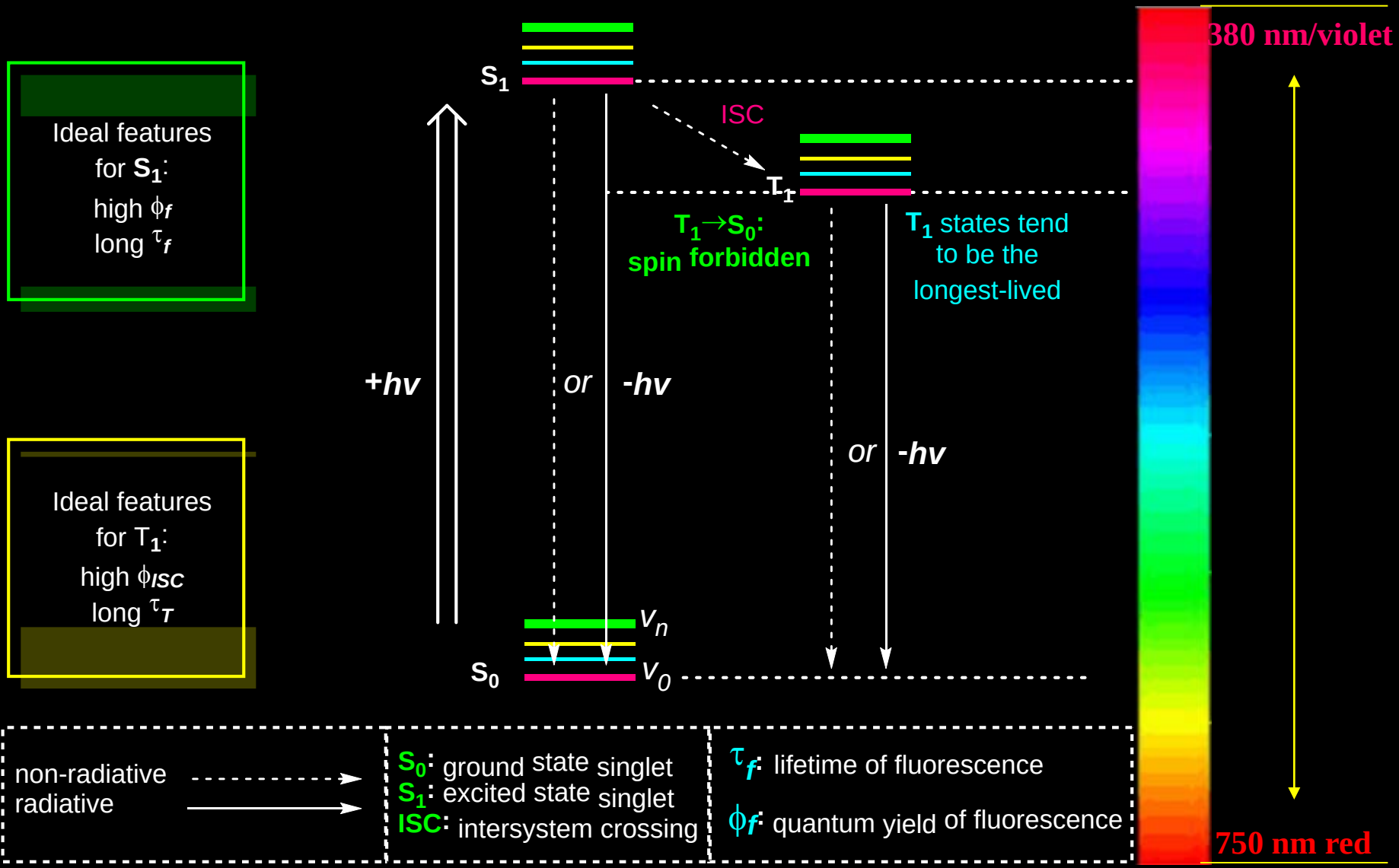
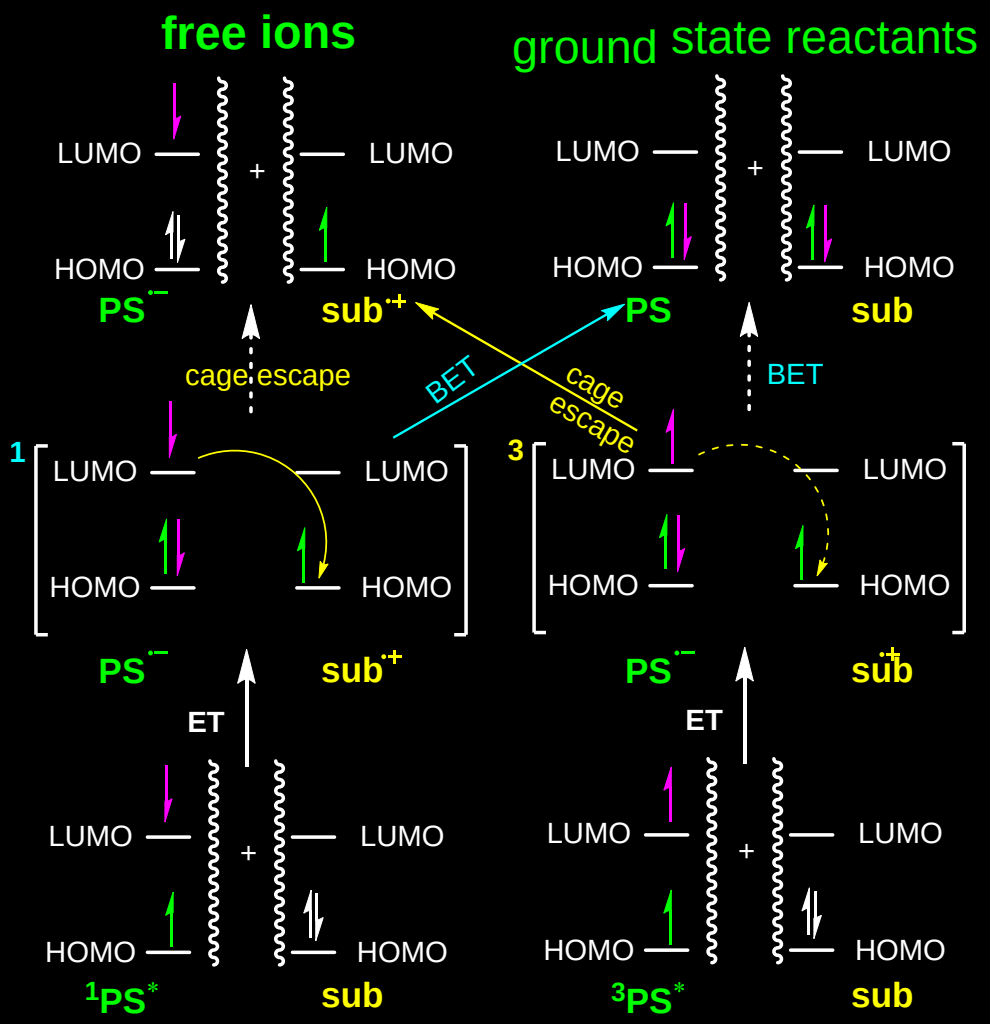
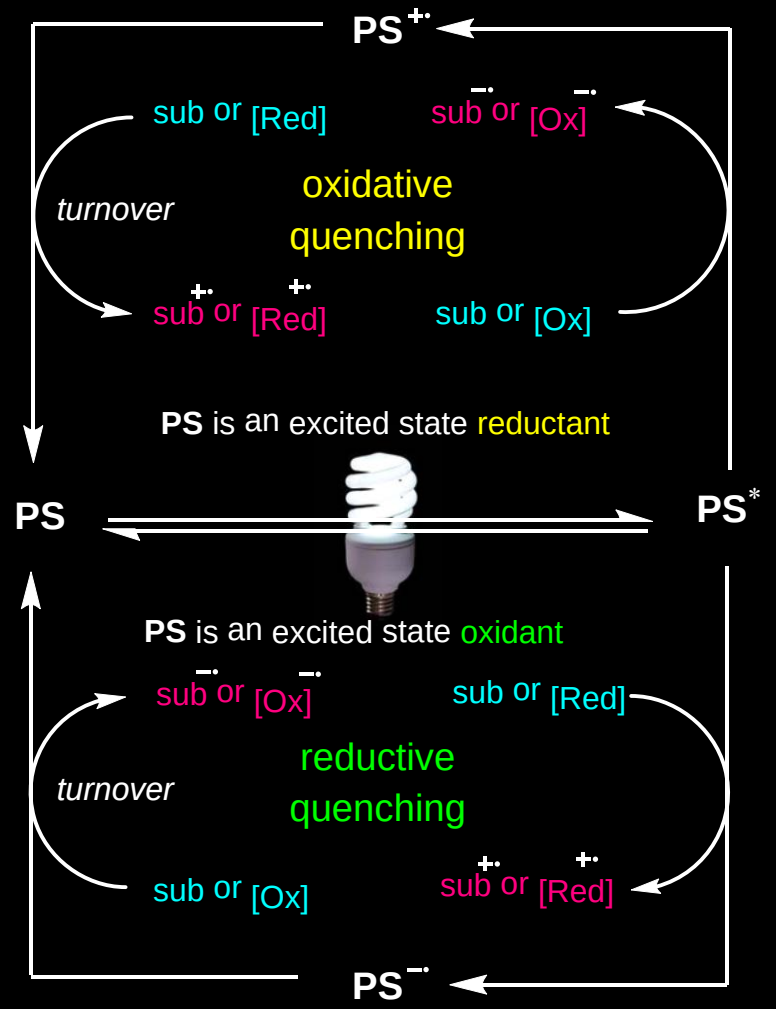
Photophysical Processes



Singlet or Triplet Excited States: Does It Matter?



Oxidative and Reductive Quenching Cycles of a Photoredox Catalyst



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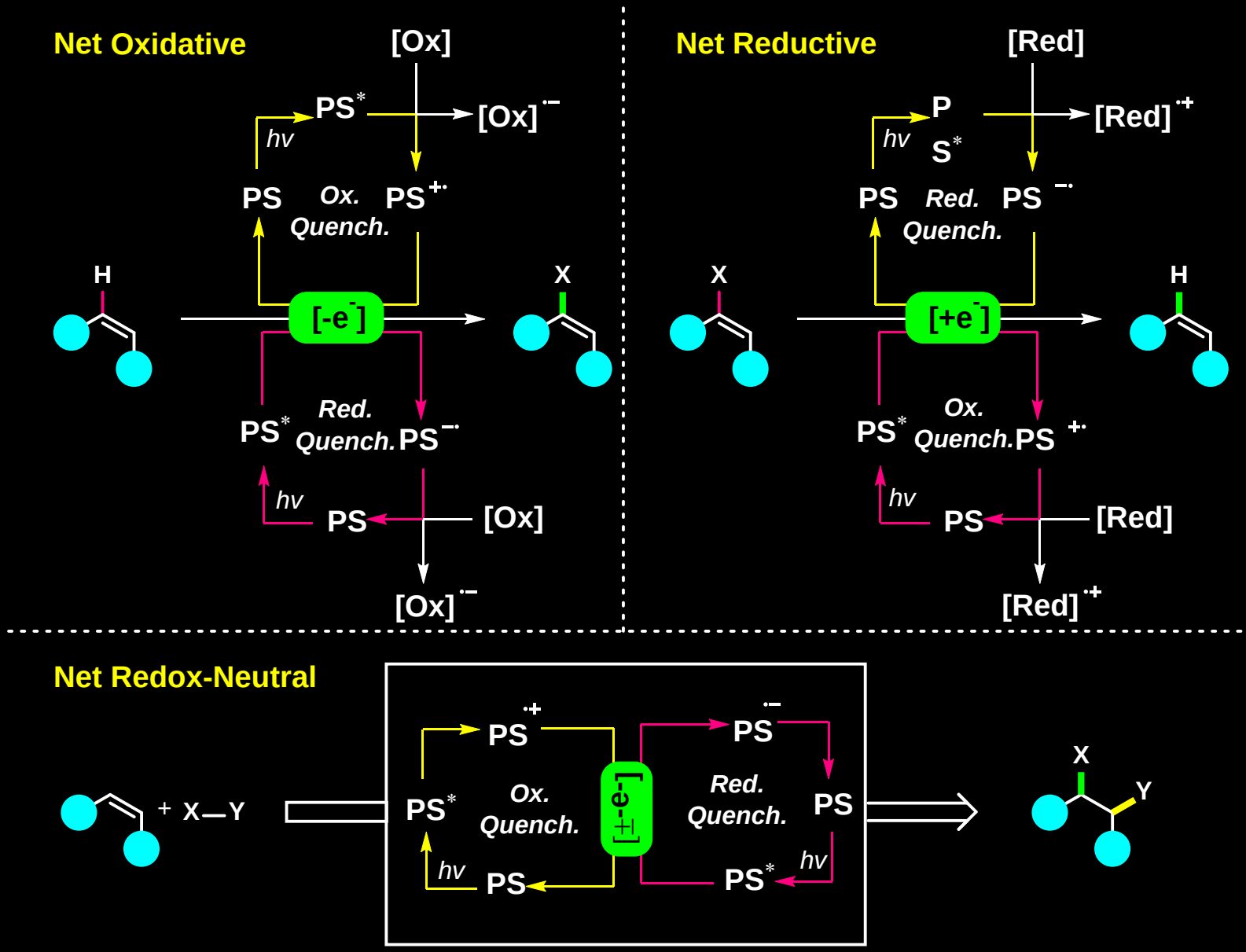
Net Redox Outcomes for Photoredox Transformations



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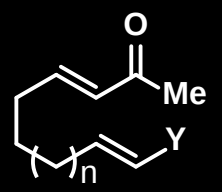
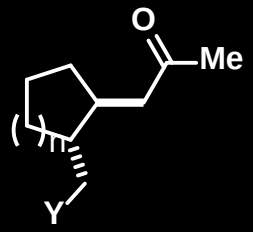
Reductive Cyclizations of Unsaturated Enones

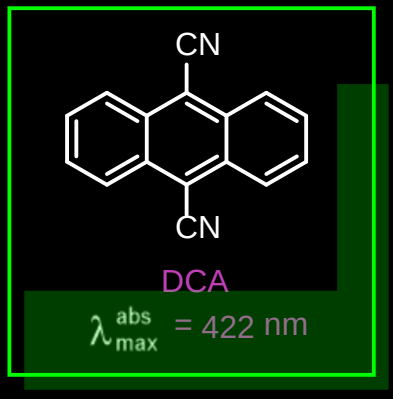
A:



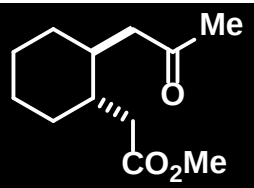
DCA (20 mol %)
λ = 405 nm

PPh_3(0.6 eq.)
DMF/*i*-PrOH/H_2O





Selected Products



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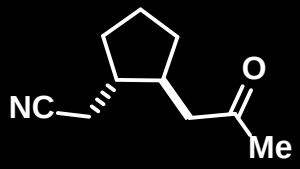

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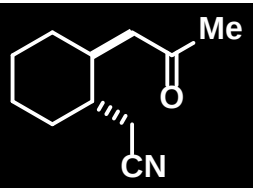

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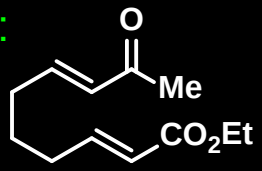
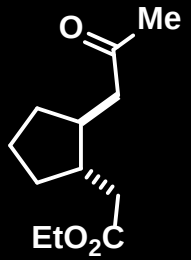
B:



DCA (20 mol %)
λ = 405 nm

condition



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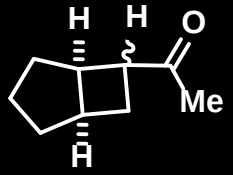


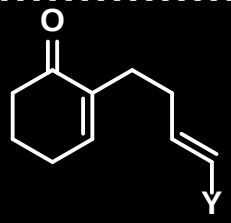
condition A: PPh_3(0.6 eq.), DMF/*i*-PrOH/H_2O
condition B: 1,5-dimethoxynaphatene(15 mol%), ascorbic acid(2.6 equiv), DMF/*i*-PrOH/H_2O

76%

<20%

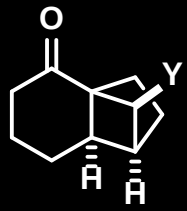
14%
1.6:1 cis:trans
70%
1.6:1 cis:trans

C:



DCA (20 mol %)
λ = 405 nm

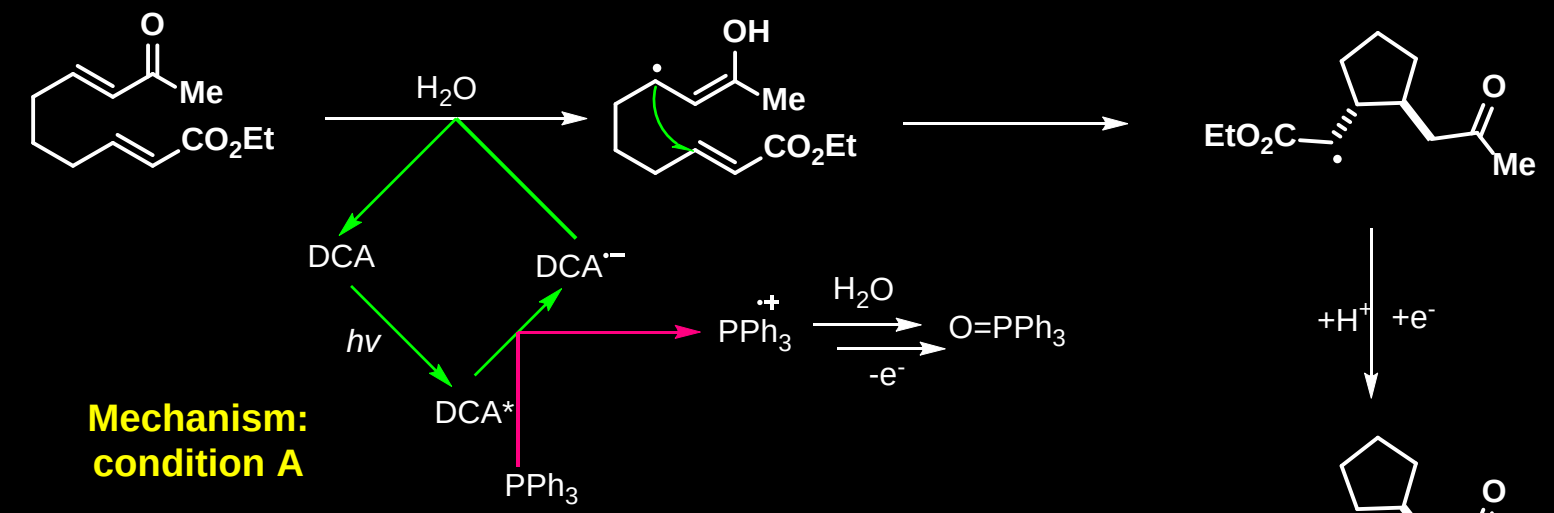
PPh_3(0.6 eq.)
DMF/*i*-PrOH/H_2O

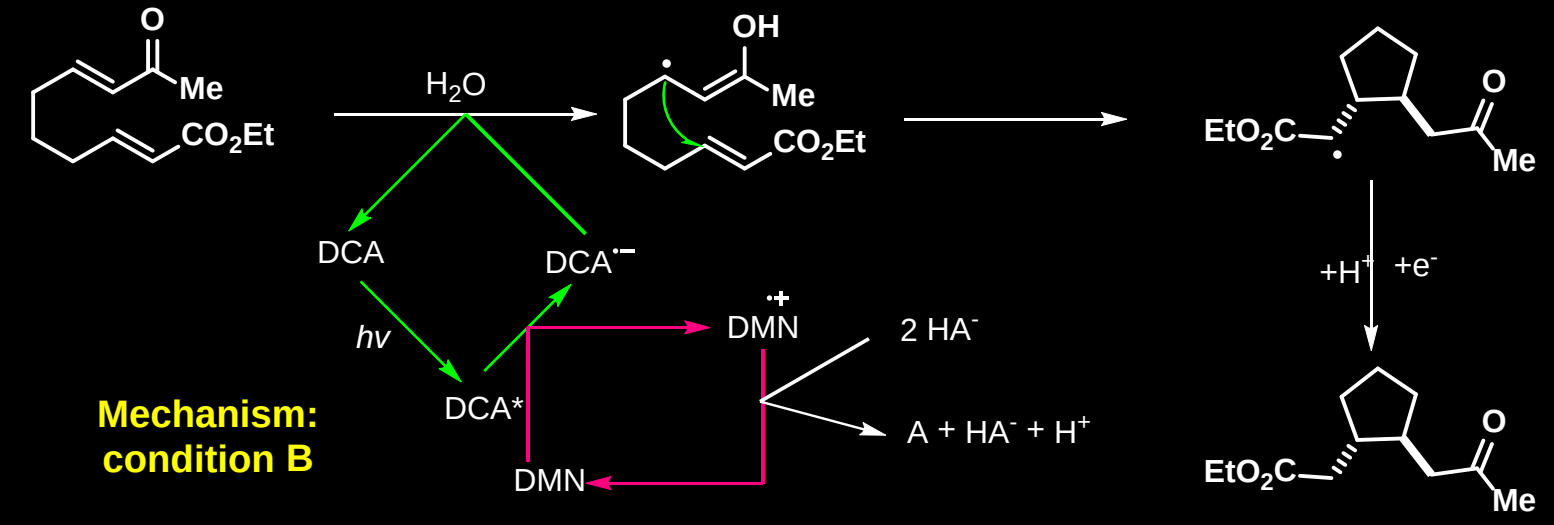


Y = CO_2Et: 84%
Y = CN: 72%

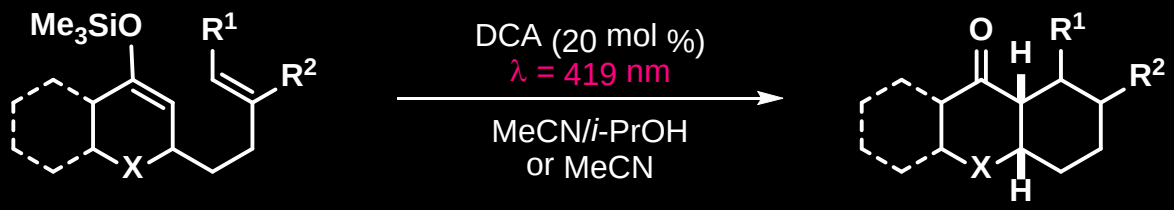
Ghorai, M. :
Tetrahedron Lett.
1994, *35*, 7837

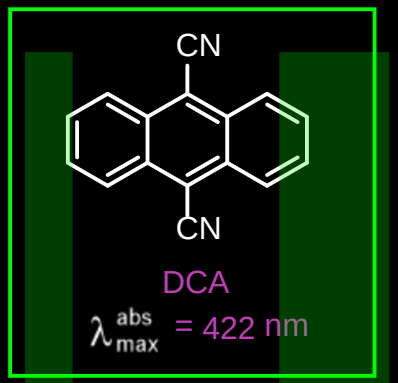
Reductive Cyclizations of Unsaturated Enones



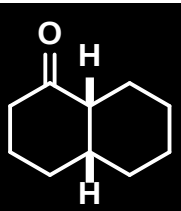


Oxidative Cyclization of Unsaturated Silyl Enol Ethers





selected products:



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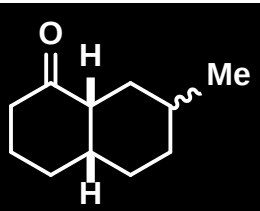

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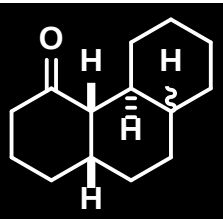
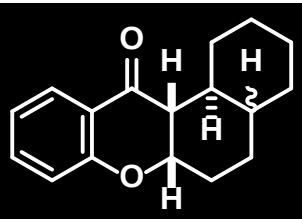
1:1 dr



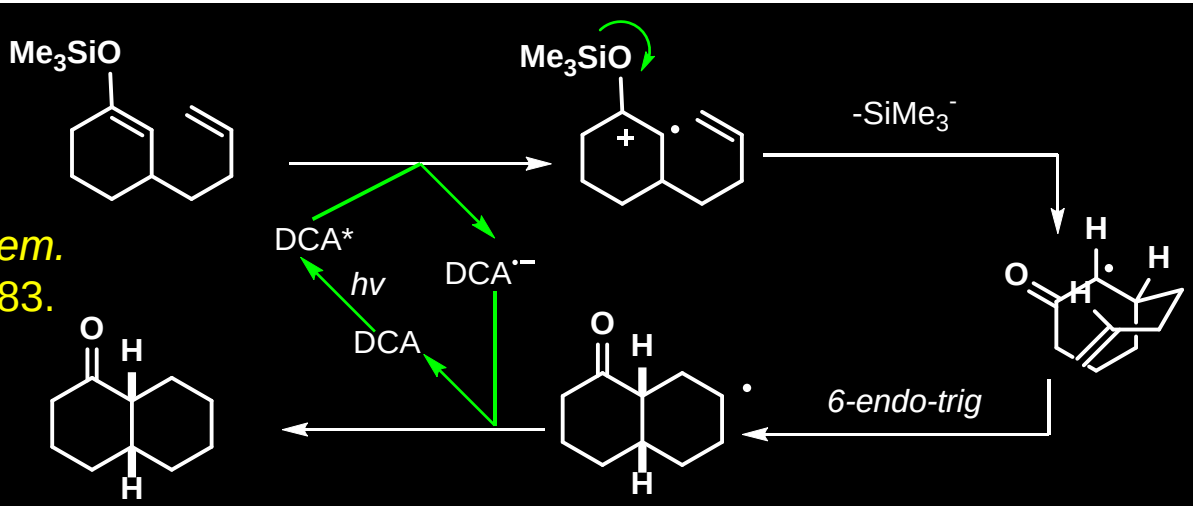
51%
1.1:1 dr



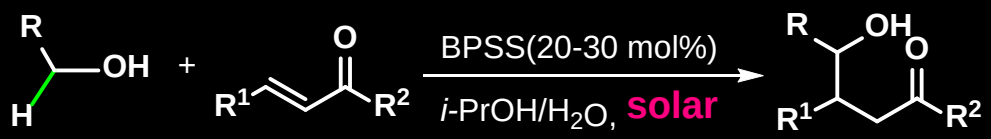
20%
2.3:1 dr

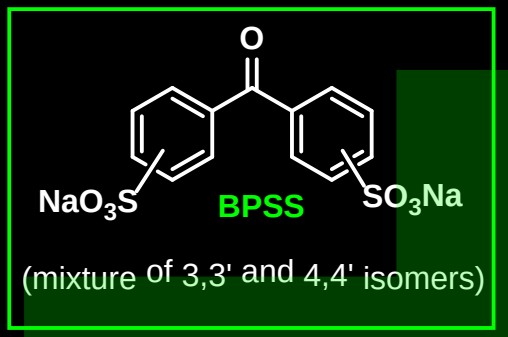
Mechanism

Fu, W.-F.:
Eur. J. Org. Chem.
1998, *1998*, 1583.

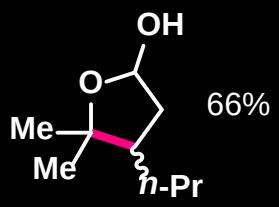


Radical Conjugate Addition Reactions in Flowwith Solar Irradiation





Selected Products



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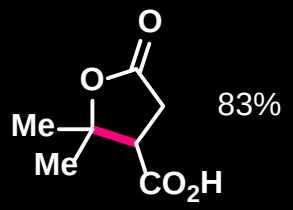

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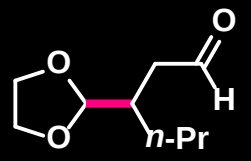
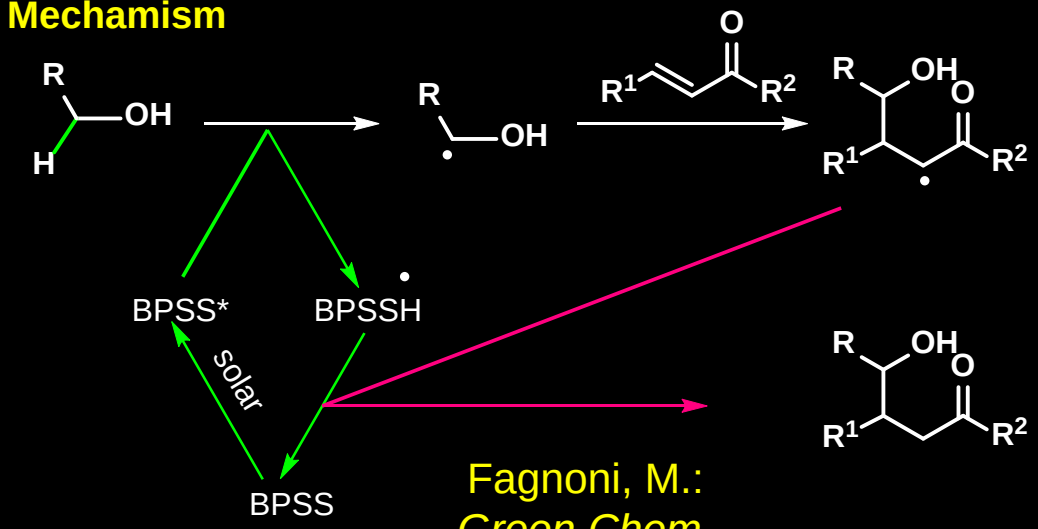


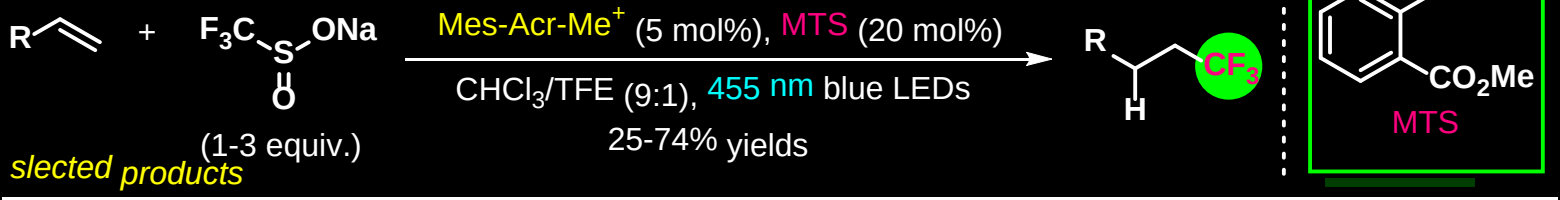
40%

Mechamism

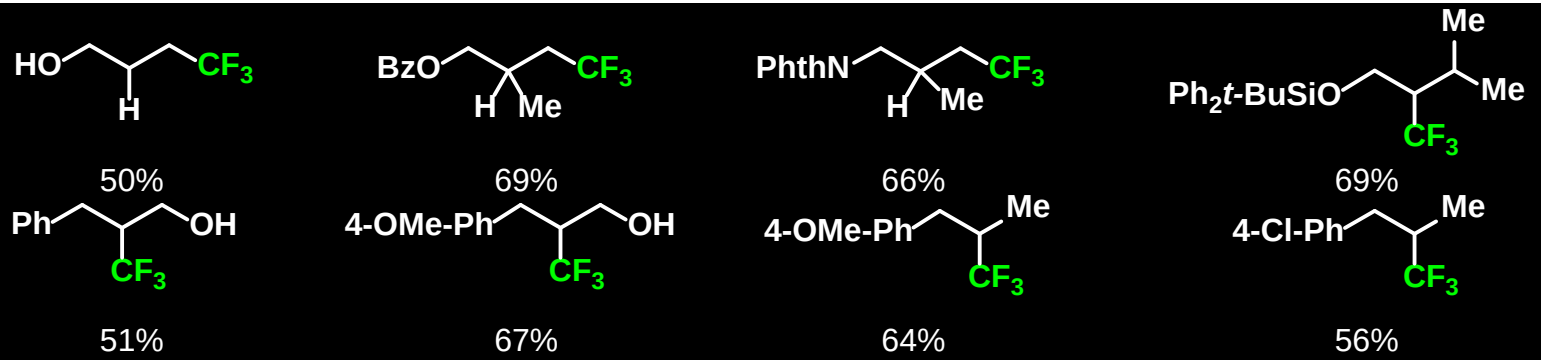


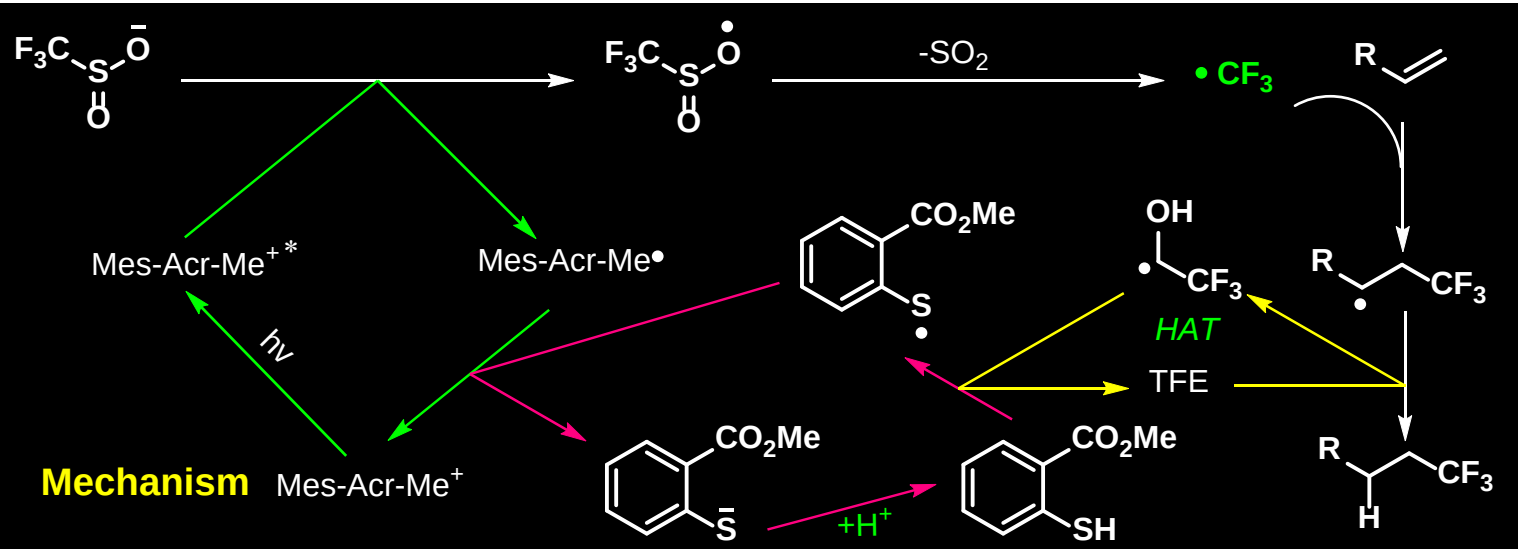
Fagnoni, M.:
Green Chem.
2009, *11*, 1653

Hydrotrifluoromethylation of Alkenes Using the Langlois Reagent



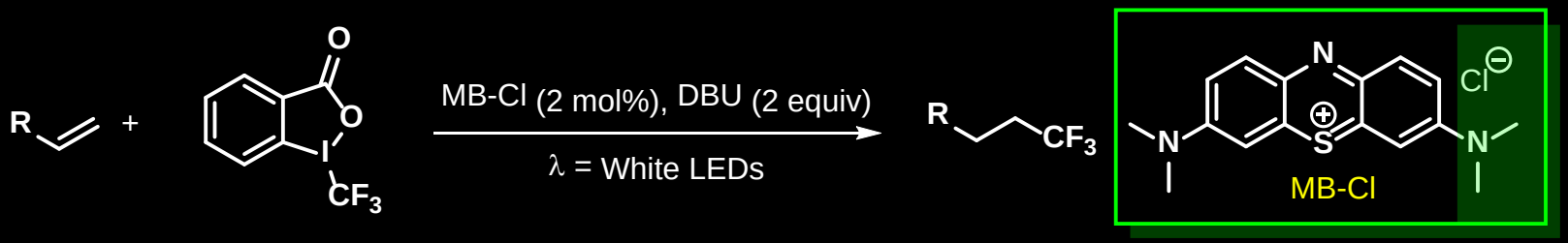
slected products





Nicewicz:
Chem. Sci. **2013**, *4*, 3160

Olefin Hydrotrifluoromethylation



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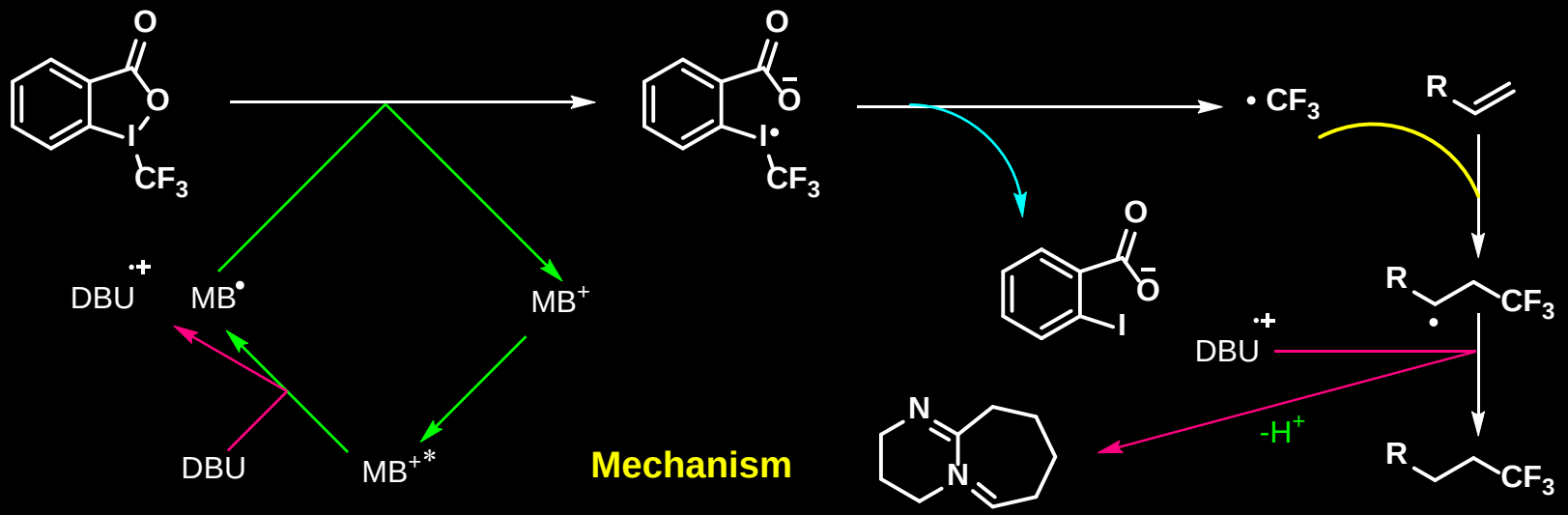
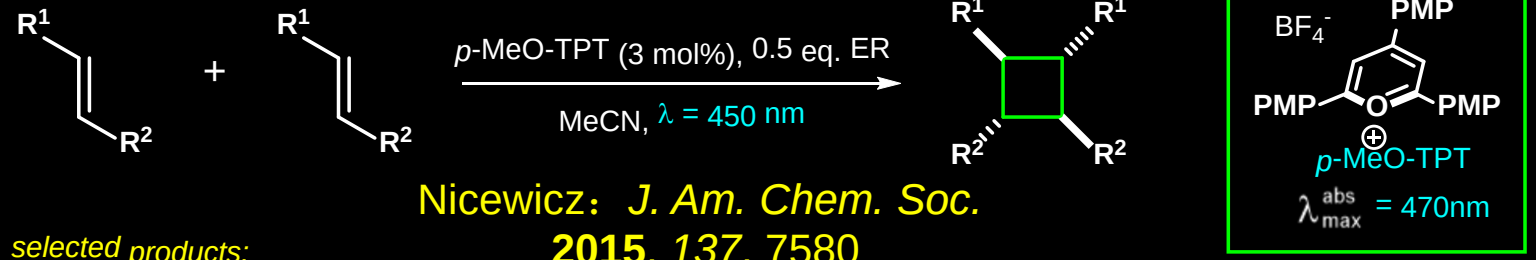


Scaiano, J. C: *ACS Catal.* **2014**, *4*, 2530

Styrene Cyclodimerization



Nicewicz：*J. Am. Chem. Soc.* **2015**, *137*, 7580

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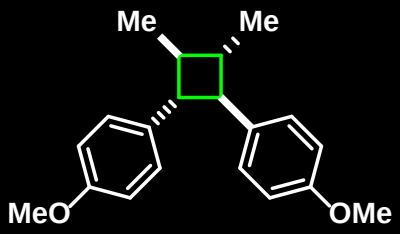

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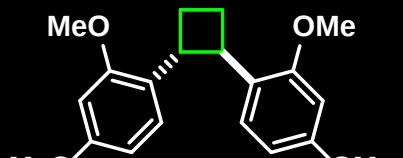

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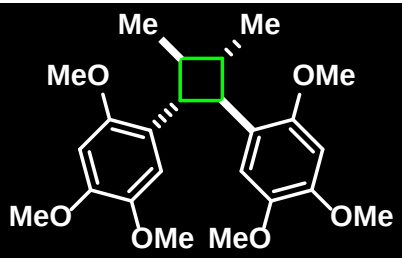
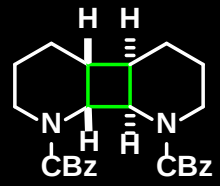


50%

(±)-*magnosalin*



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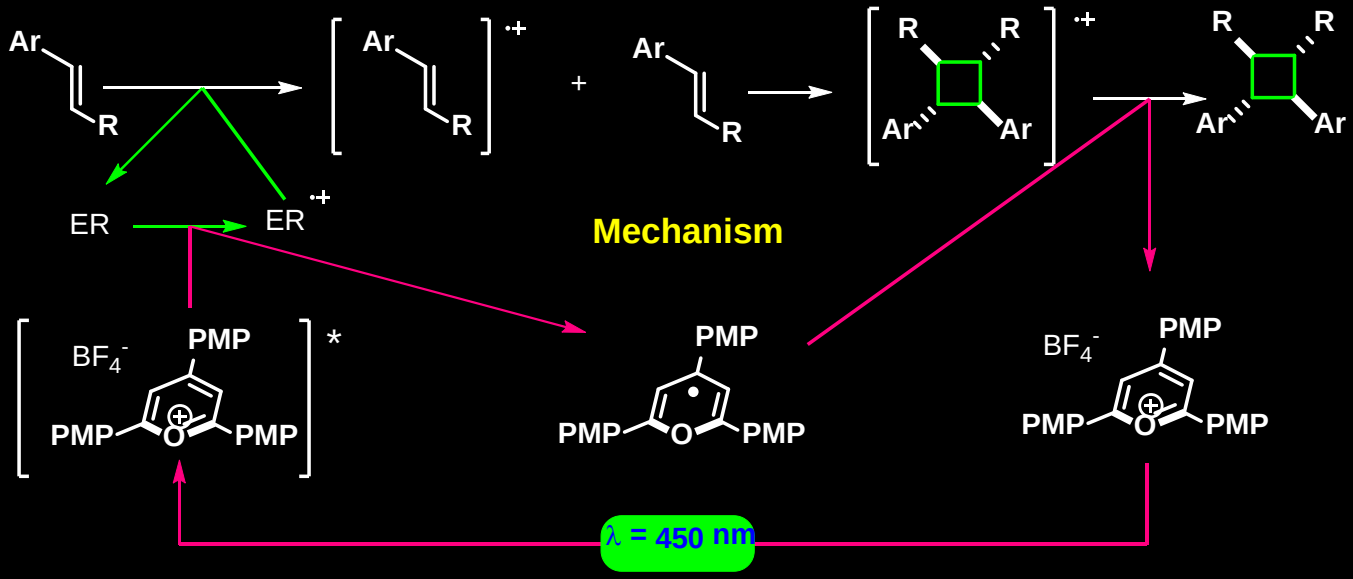
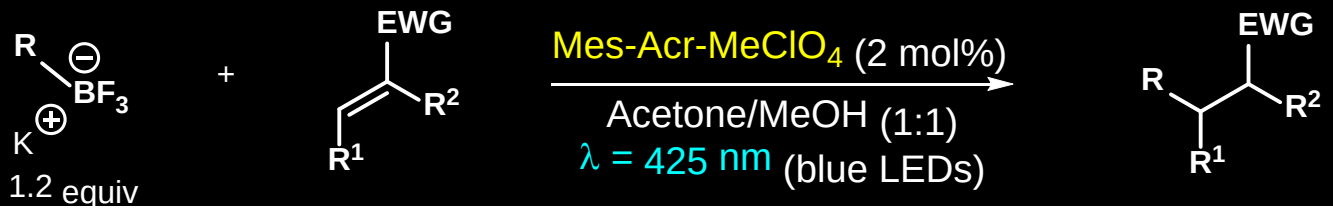
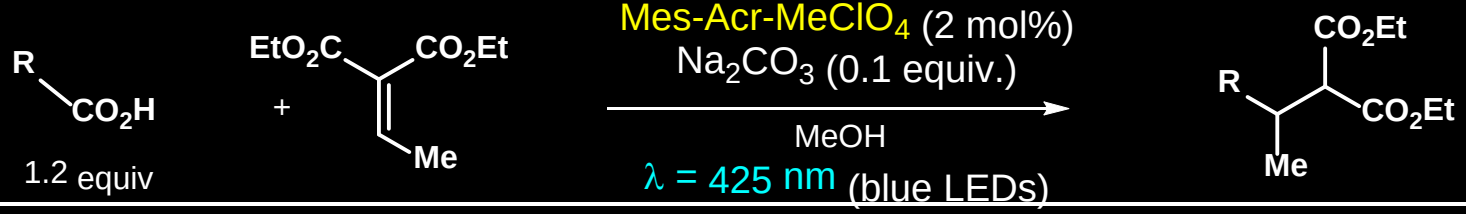


Deborylative and Decarboxylative Radical Conjugate Addition Reactions



Selected Products:

Akita, M.: *RSC Adv.* **2015**, *5*, 21297



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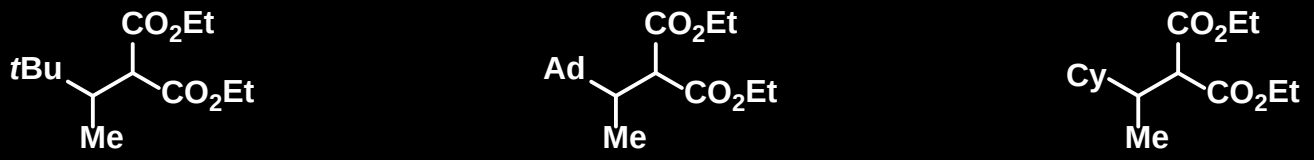

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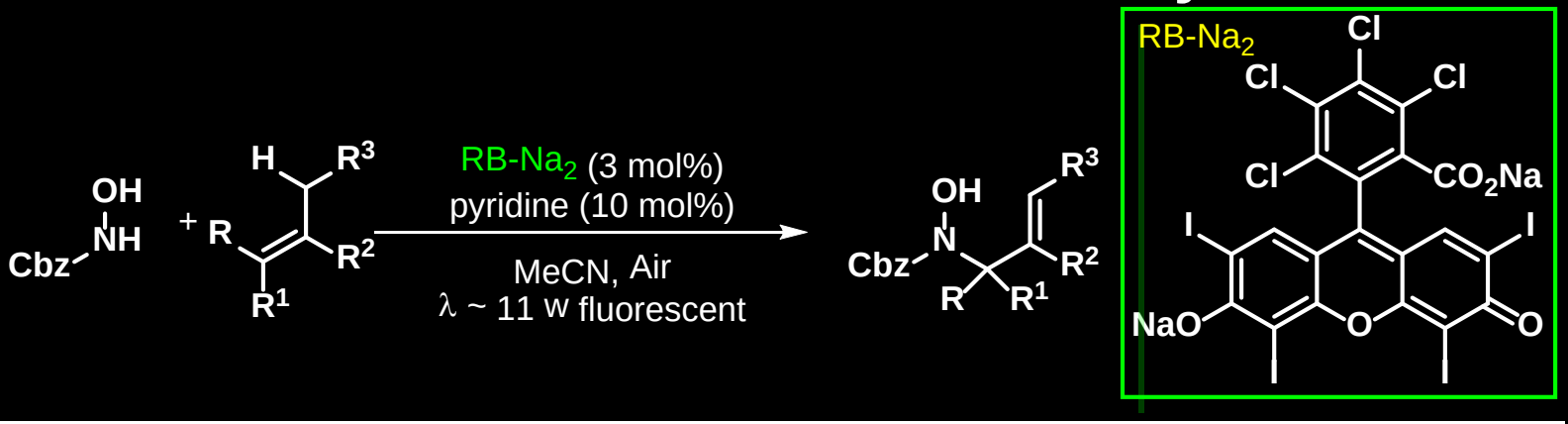
Nitroso-Ene Reaction Enabled by PET



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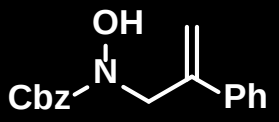

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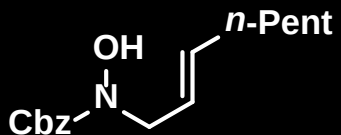

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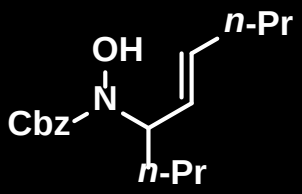

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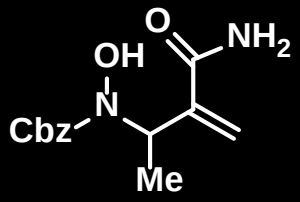

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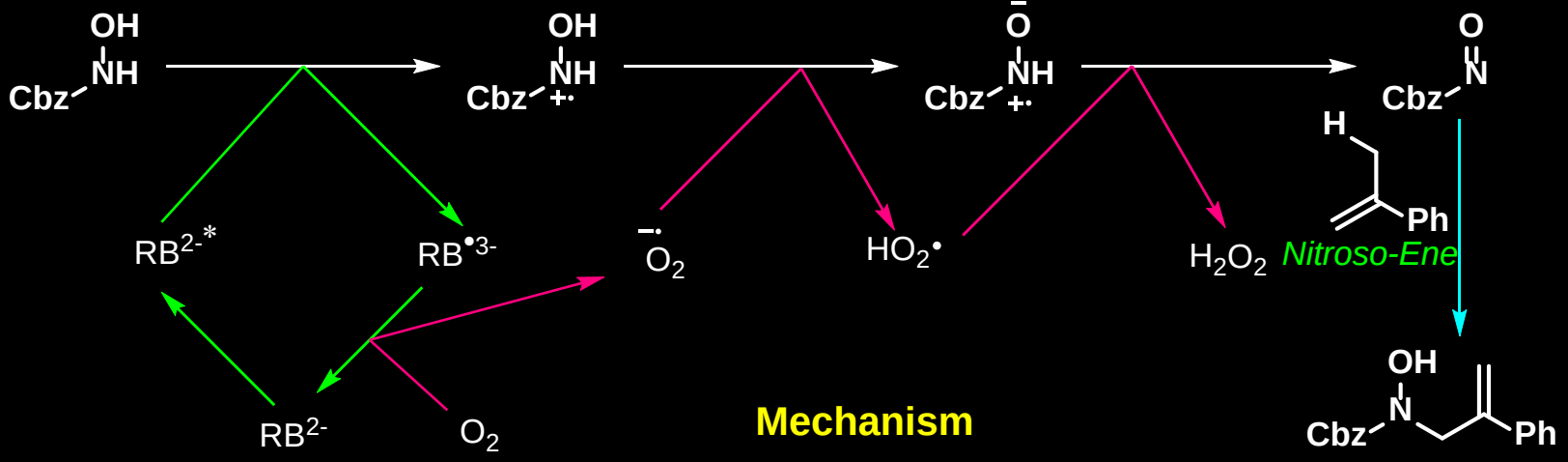
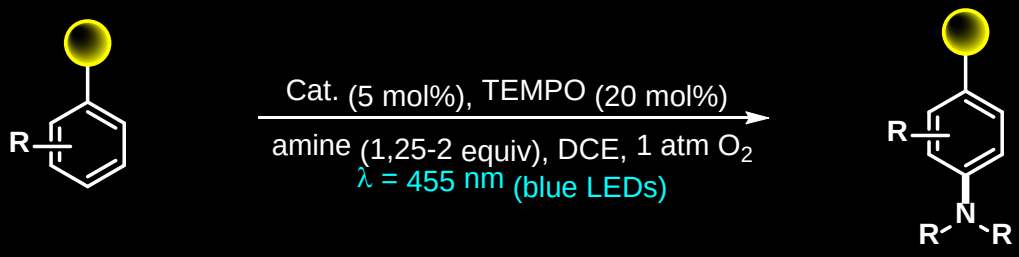
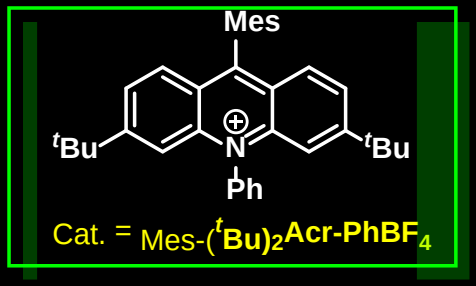


Mechanism

Tan C.H.: *ChemCatChem* **2013**, *5*, 235

Aryl C–H Amination





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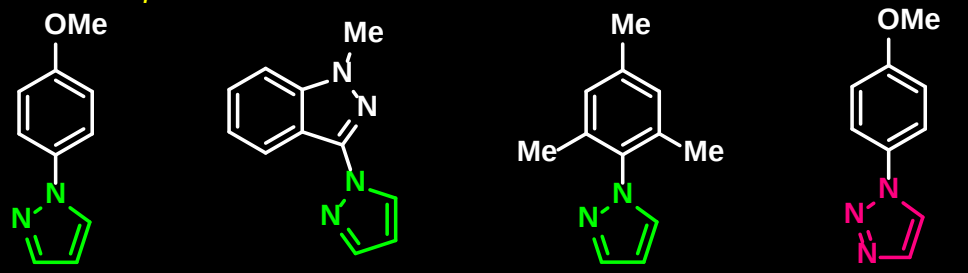
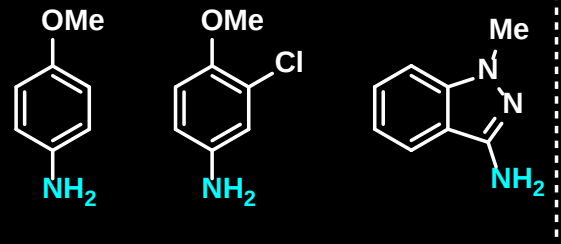
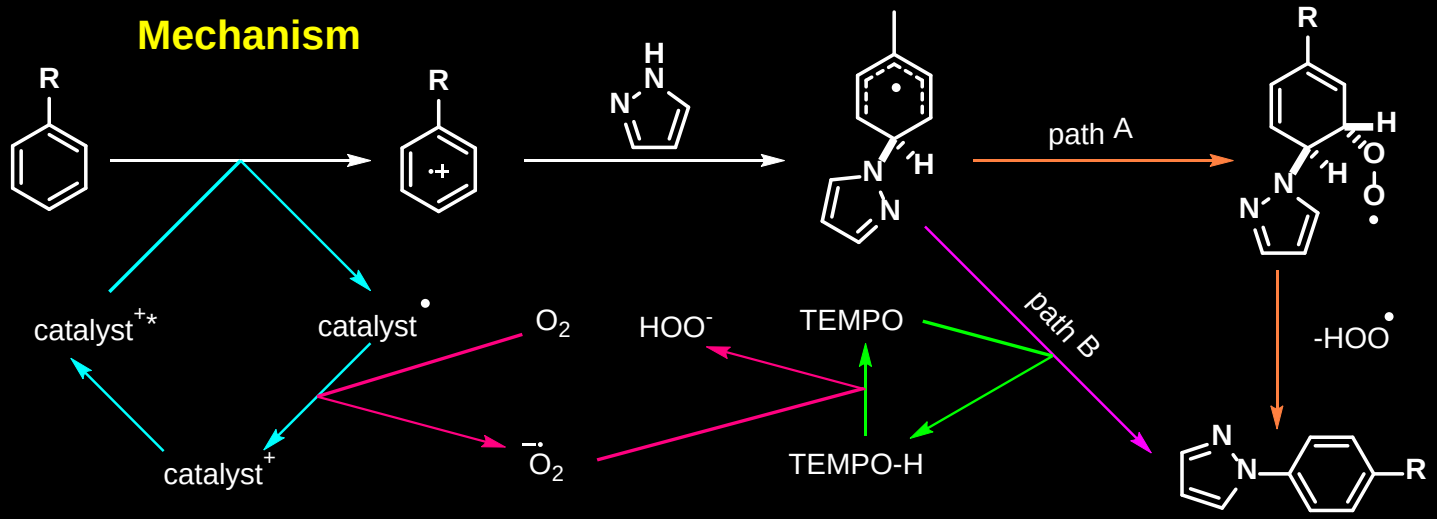


using 4 equiv. amine = $NH_2CO_2NH_4$



Mechanism



Nicewicz: *Science* **2015**, *349*, 1326

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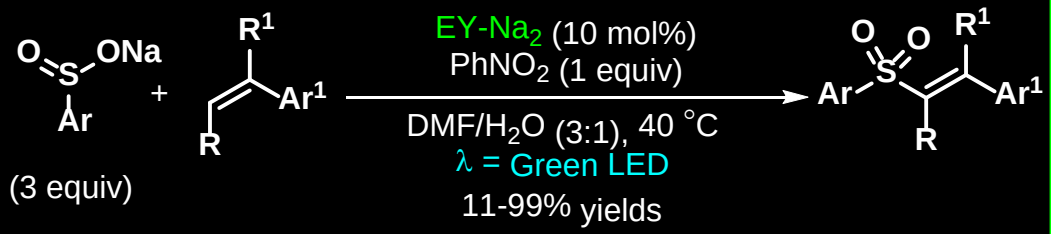
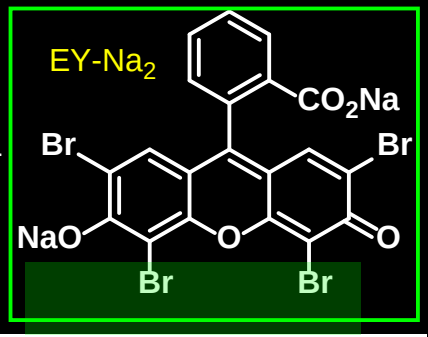
Vinyl C–H Sulfonylation via PET-Generated Sulfinyl Radicals





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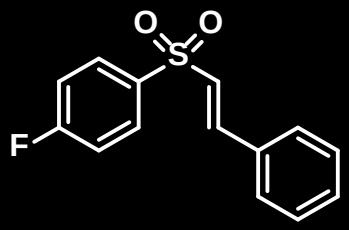

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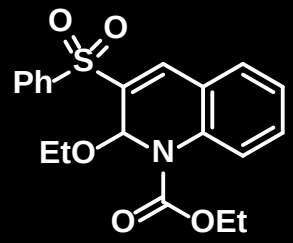

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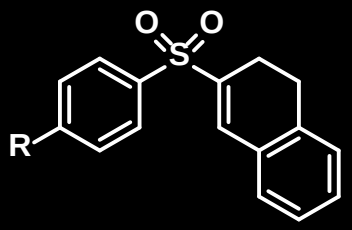
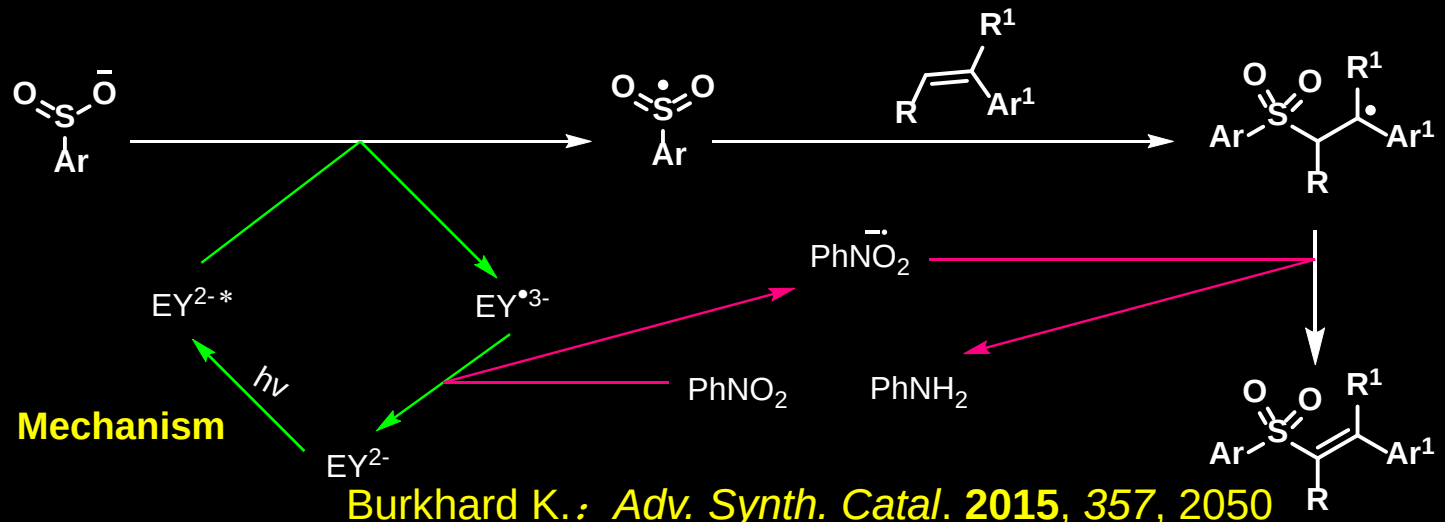


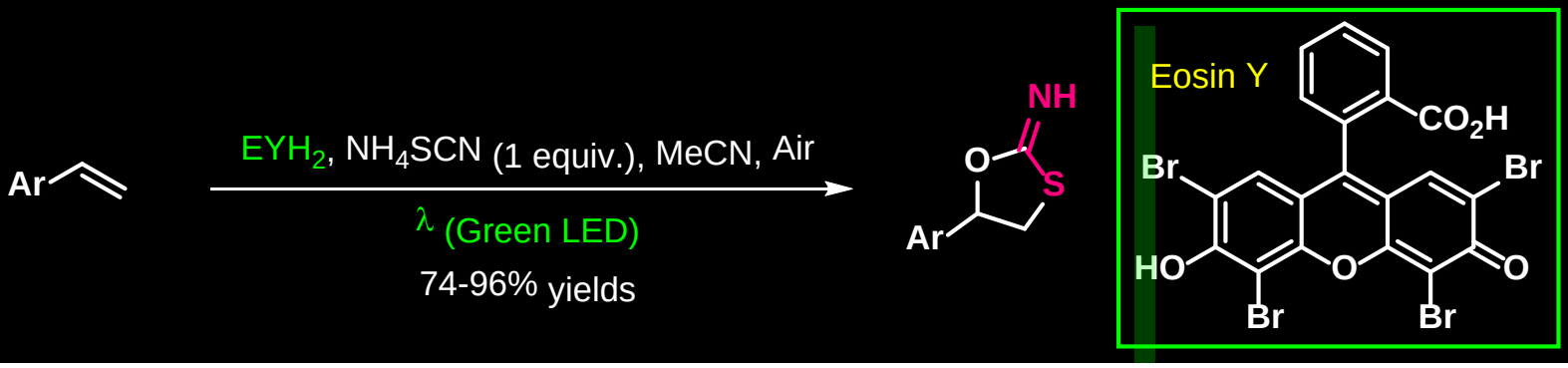
R = H, 99%, R = Me, 79%
R = OMe, 51%, R = F, 79%

Mechanism



Burkhard K.: *Adv. Synth. Catal*. **2015**, *357*, 2050

2-Imino-1,3-Oxathiolanes by Difunctionalization of Styrenes



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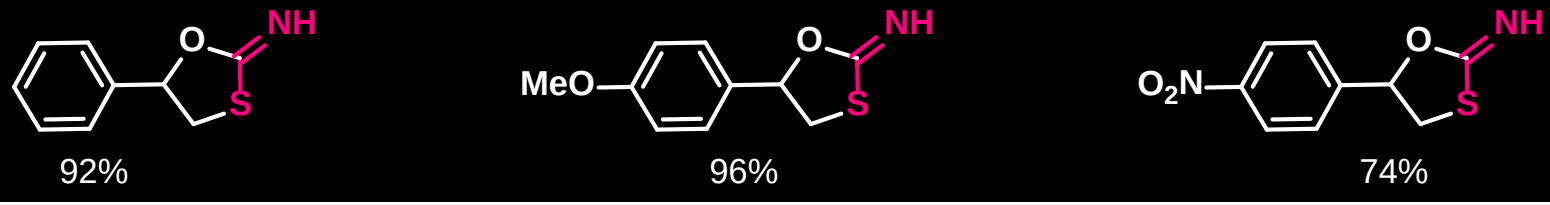

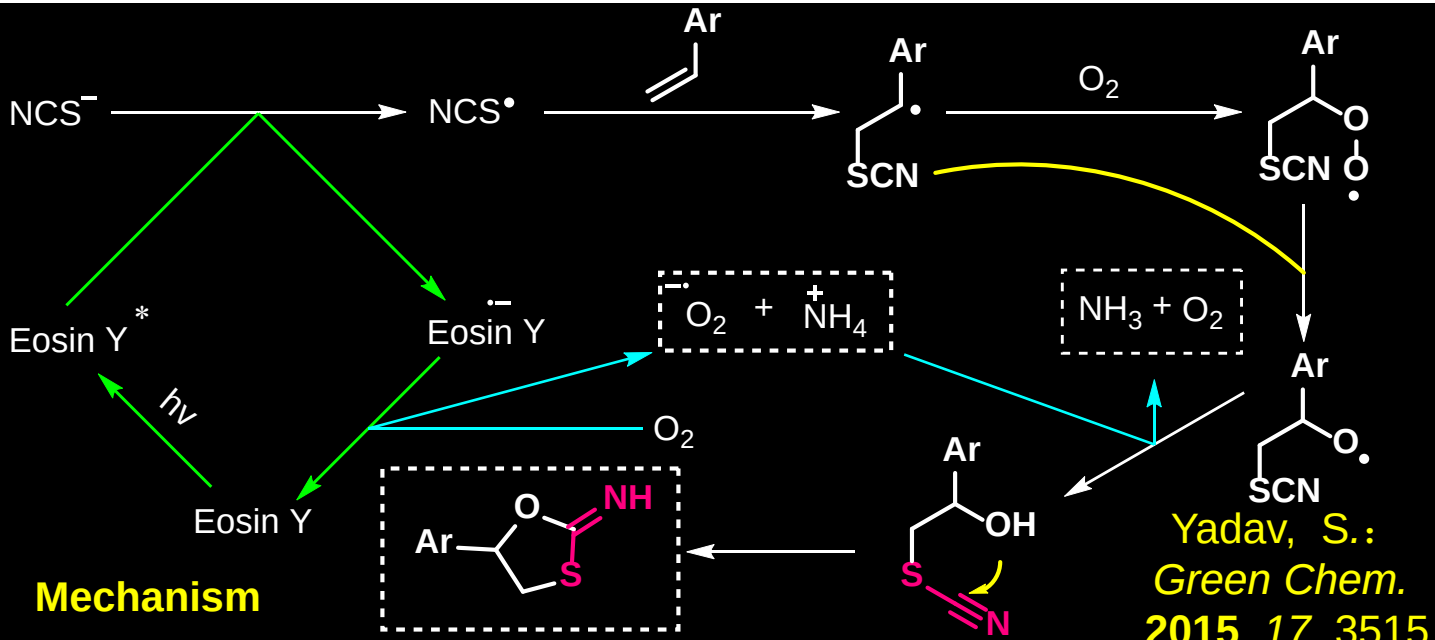

Yadav, S.: *Green Chem.* **2015**, *17*, 3515

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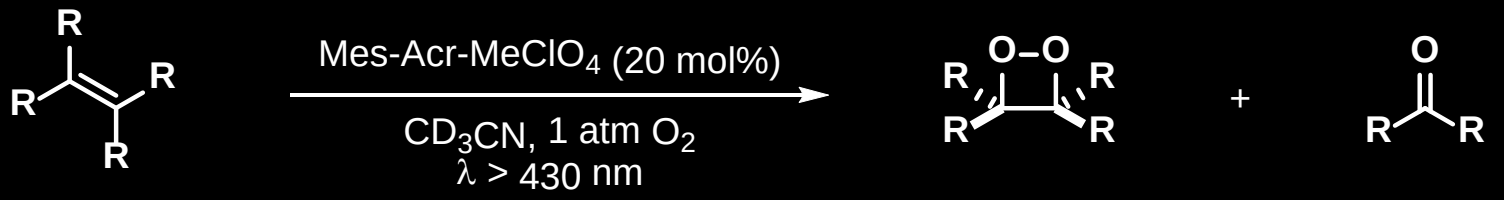
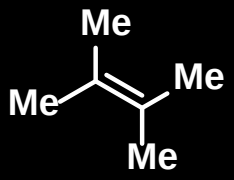
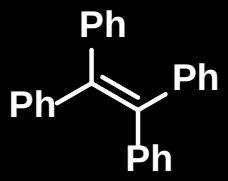
Tetrasubstituted Alkene Oxygenation

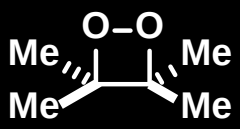


reactants





products



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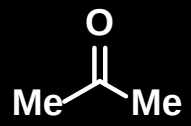

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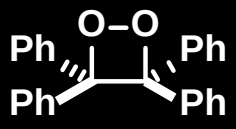

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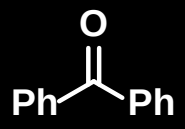

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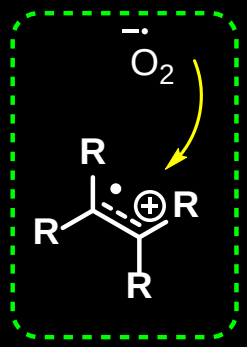
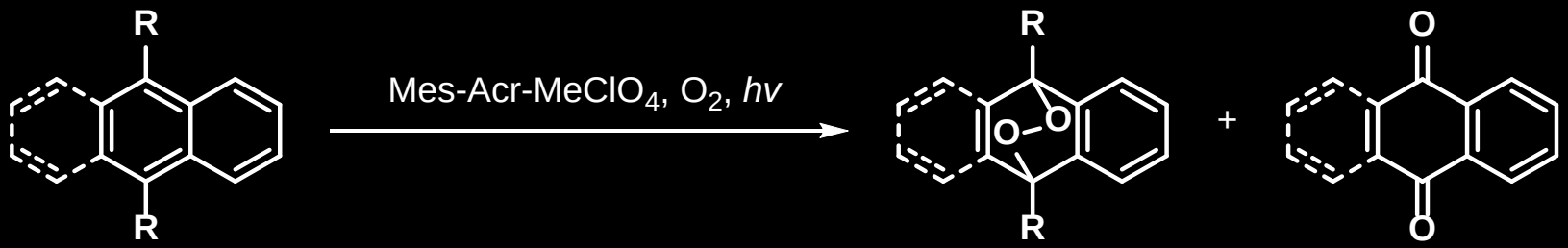
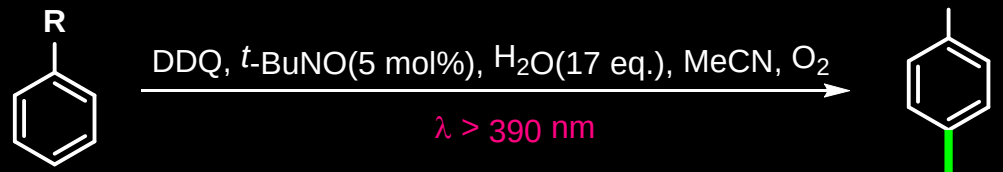
Proposed Key Step

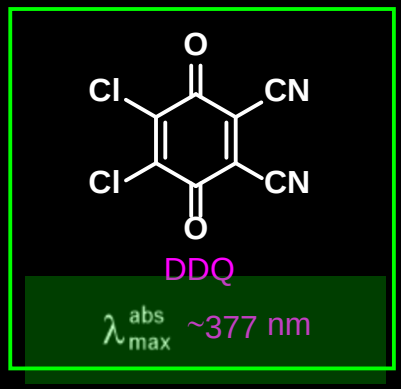




Fukuzumi, S：*J. Am. Chem. Soc.* **2004**, *126*, 15999

C–H Hydroxylation of Benzene and Halobenzenes





Fuzukimi, S:
J. Am. Chem. Soc.
2013, *135*, 5368.

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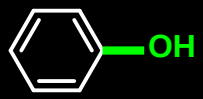

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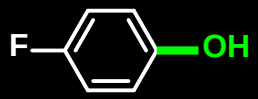

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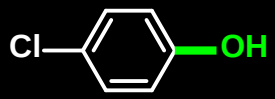

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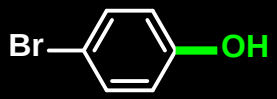

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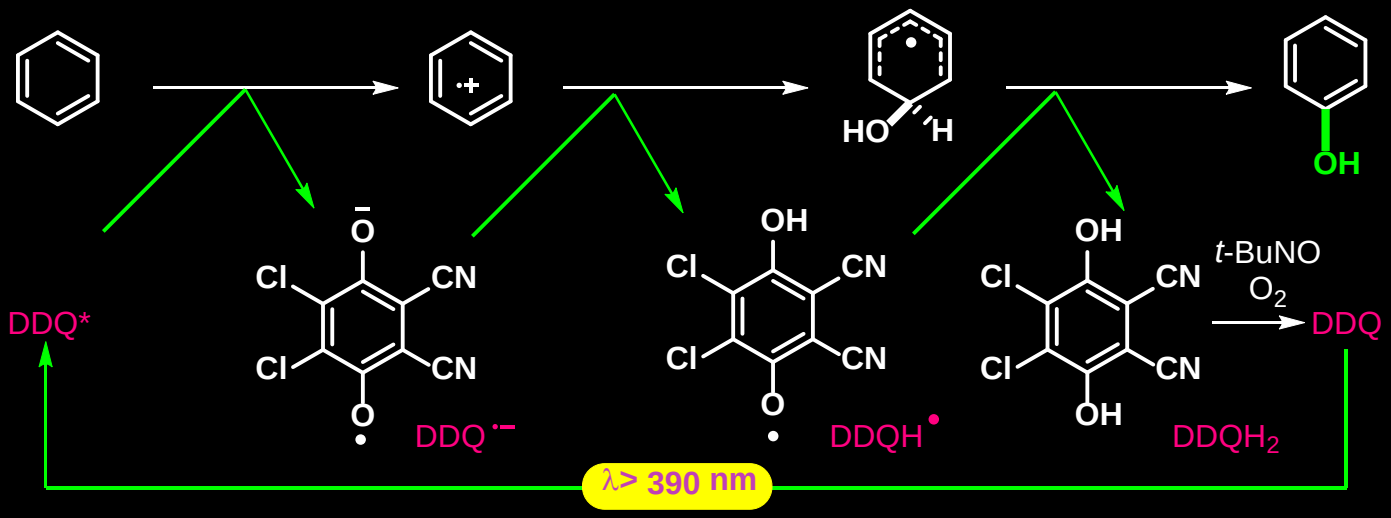
Mechanism



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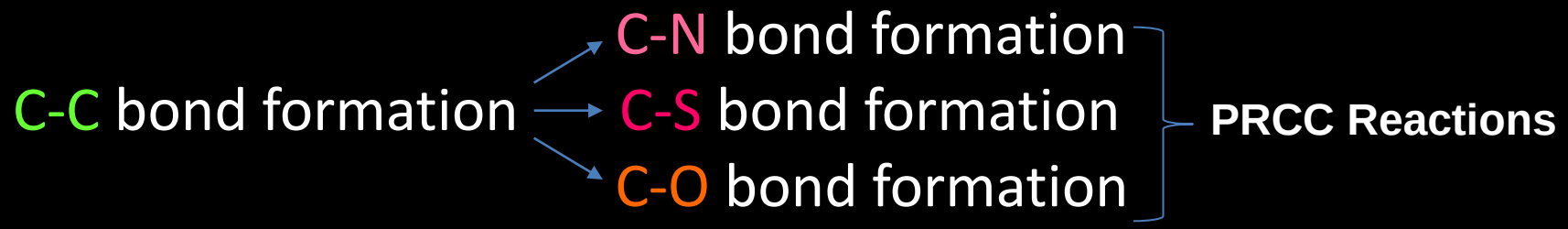
I: Background

Organo-photocatalyst : What is?

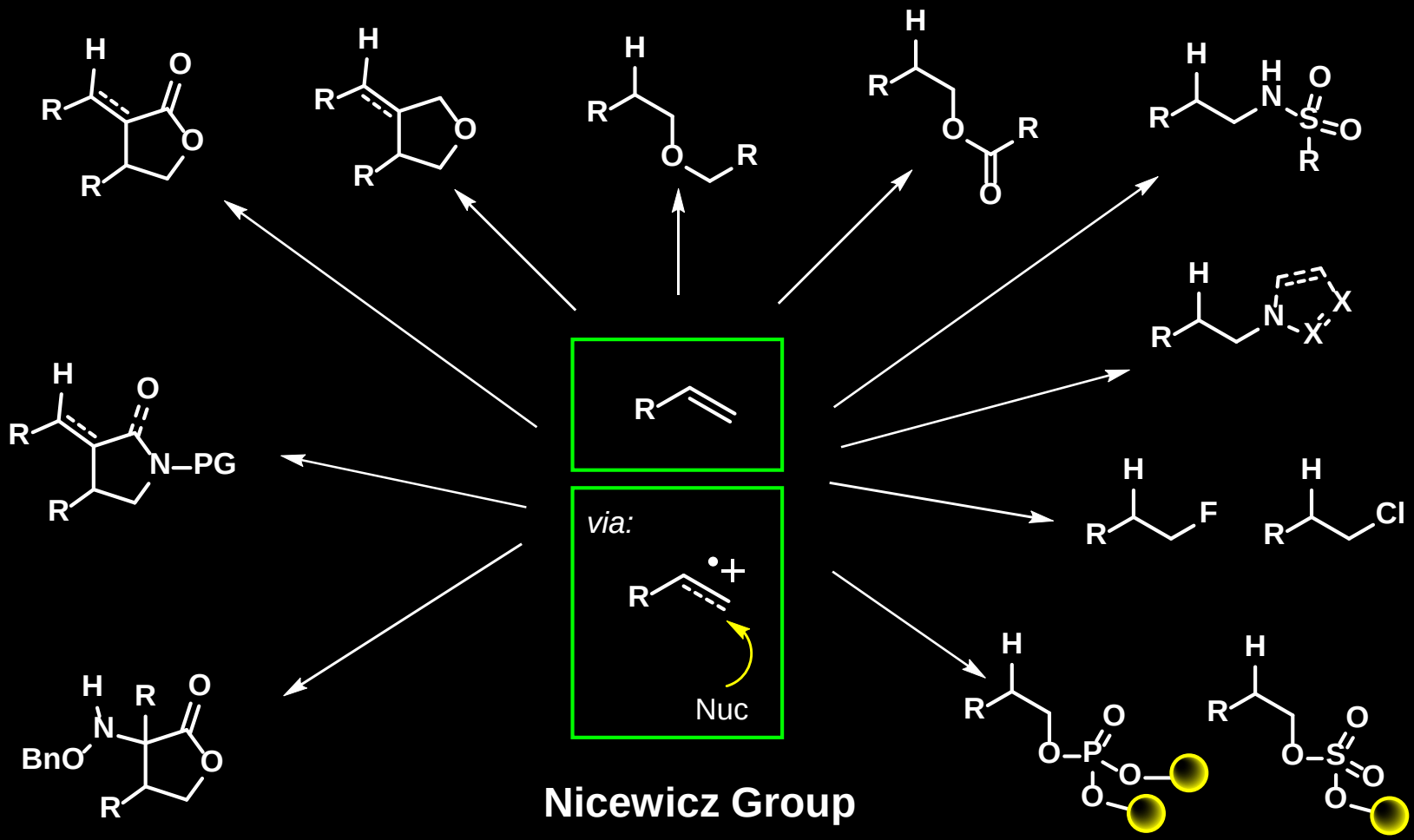
Organo-photocatalyst : Photophysical Processes

II: Visible-Light-Mediated Organic Photoredox Catalysis in Functionlization of alkenes



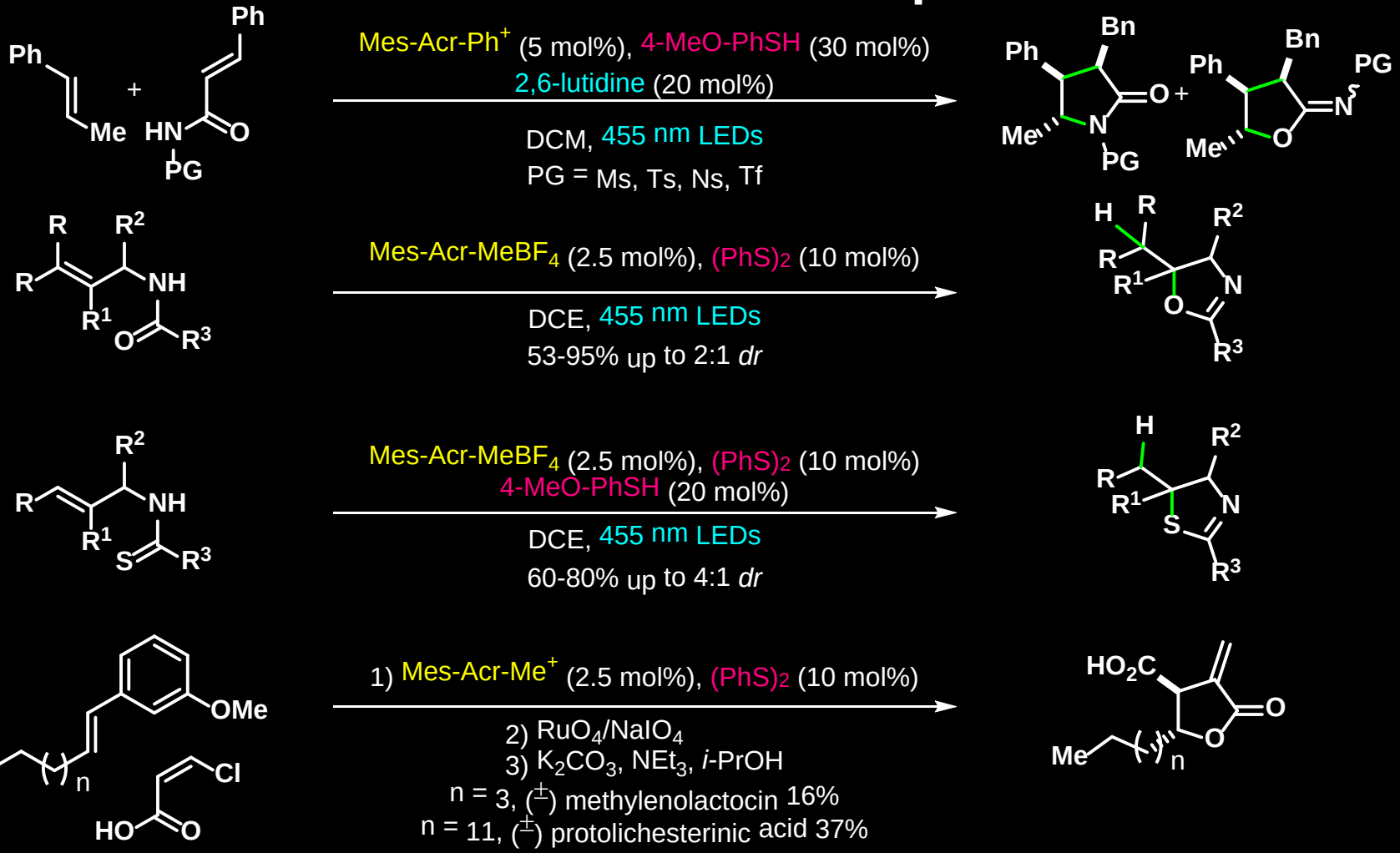
III: Summary

Anti-Markovnikov Alkene Hydrofunctionalization and PRCC Reactions



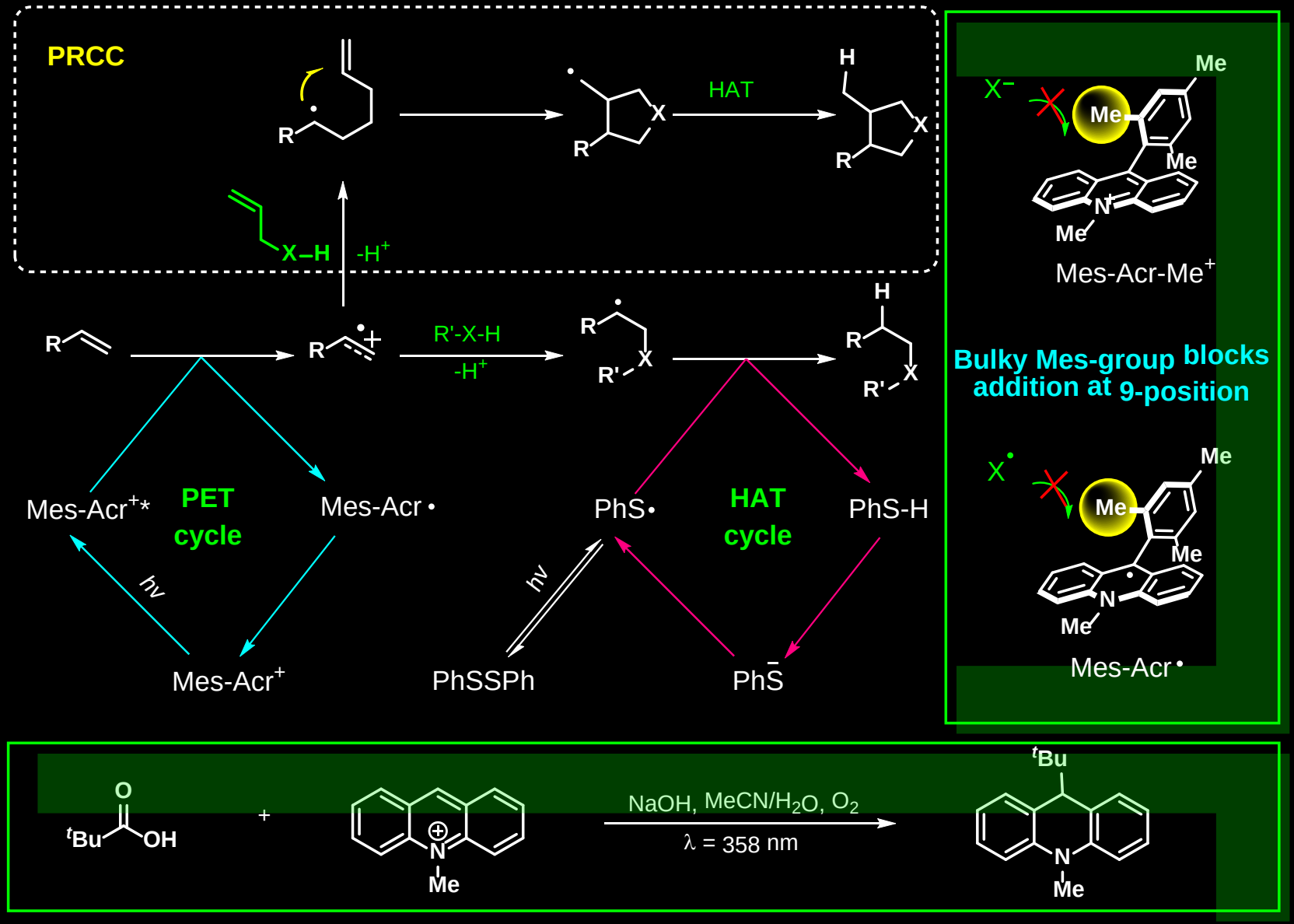
Nicewicz Group

Highlights of Anti-Markovnikov Alkene Hydrofunctionalization and PRCC Reactions from Nicewicz Group



Org. Lett. **2014**, *16*, 4810 *Chem. Sci.* **2015**, *6*, 270 *Org. Lett.* **2015**, *17*, 1316

Proposed Mechanism for Anti-Markovnikov Alkene Hydrofunctionalization and PRCC Reactions



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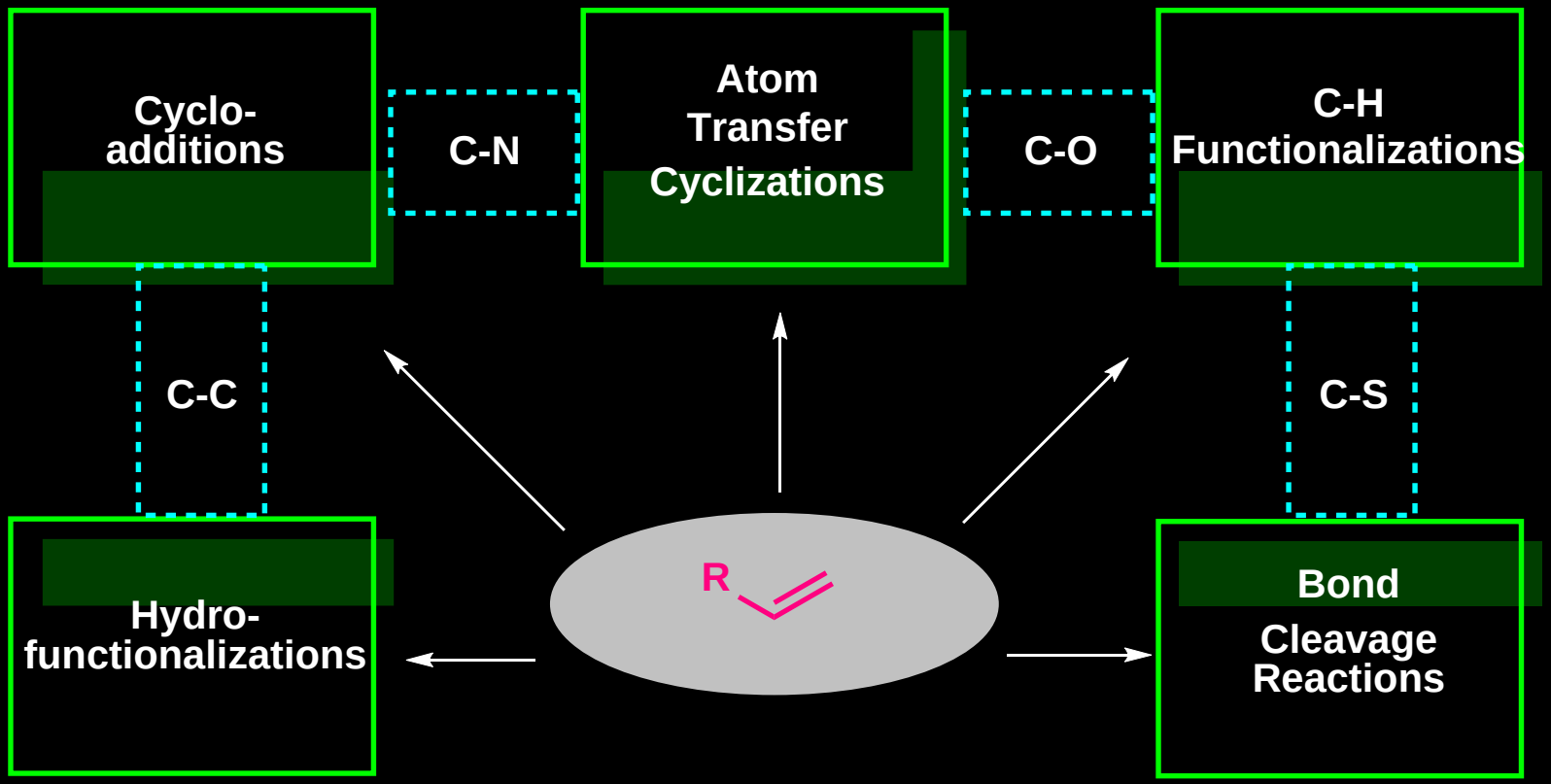
i) C-C bond formation ii) C-N bond formation

iii) C-S bond formation iv) C-O bond formation

III: Summary

Summary

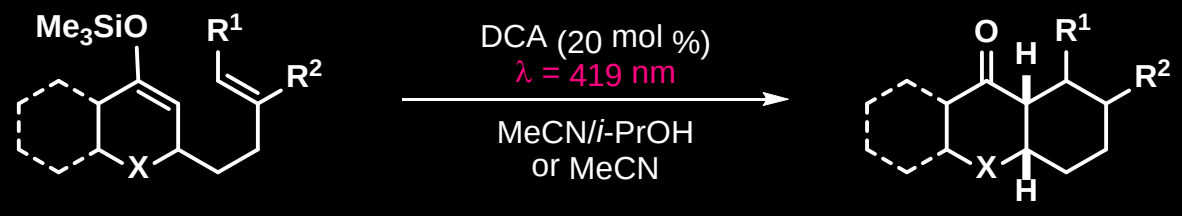


Challenges Remain:

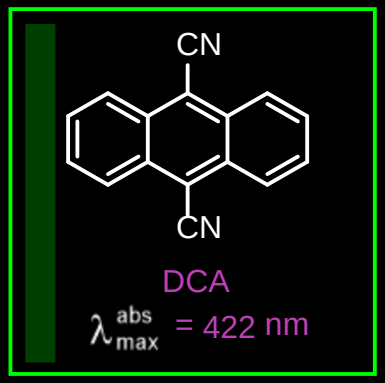
1) Site specificity and functionalization of stronger C–H bonds present new challenges
2) Methods for controlling enantioselectivity are scarce
3) Applications of organic photoredox catalysis to natural product synthesis are just starting to occur
4) Highly reducing catalysts and more robust chromophores are always in demand

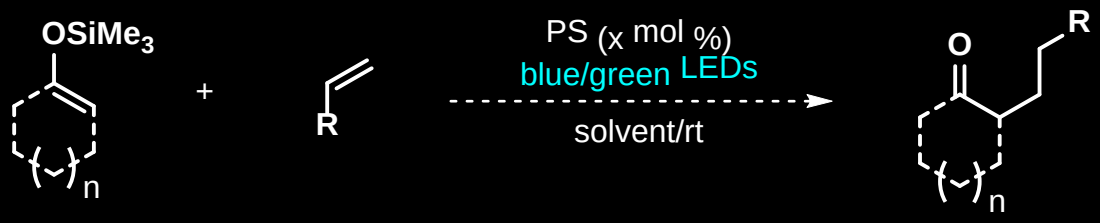
Thank You for Your Kind Attention!

What Can We Do



Intramolecular



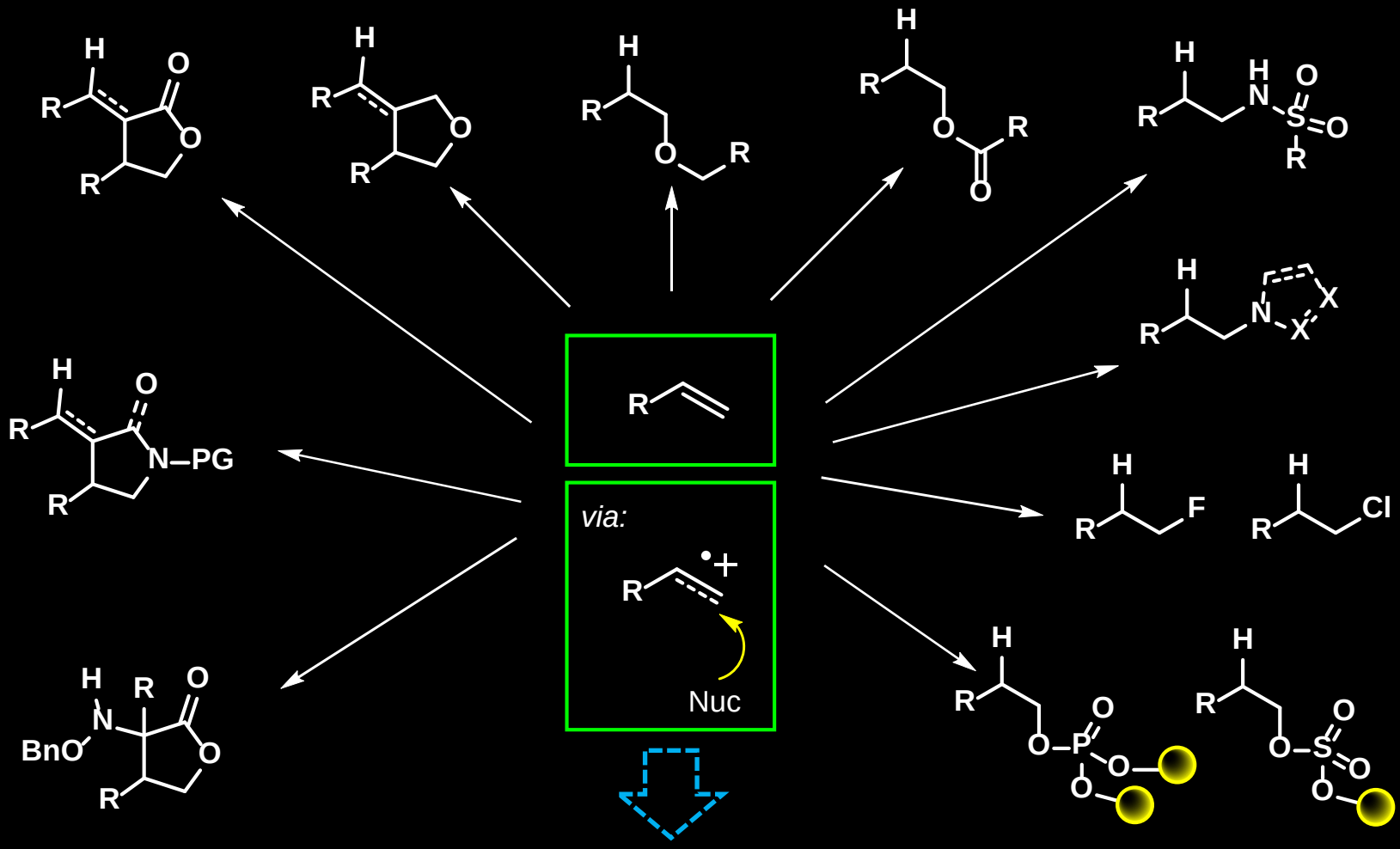


PS

λ_{max}^{abs} > 650 nm

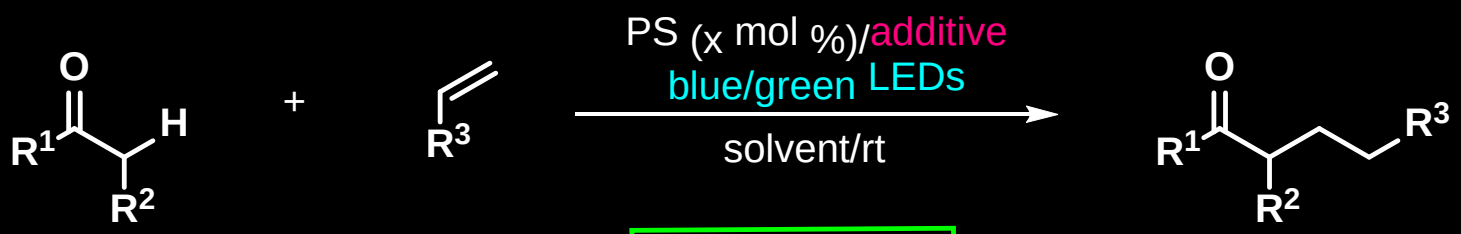
Intermolecular

Anti-Markovnikov Alkene Hydrofunctionalization and PRCC Reactions



Nuc = Carbon & Organic Photoredox Catalysis/Transition Metal Catalysis

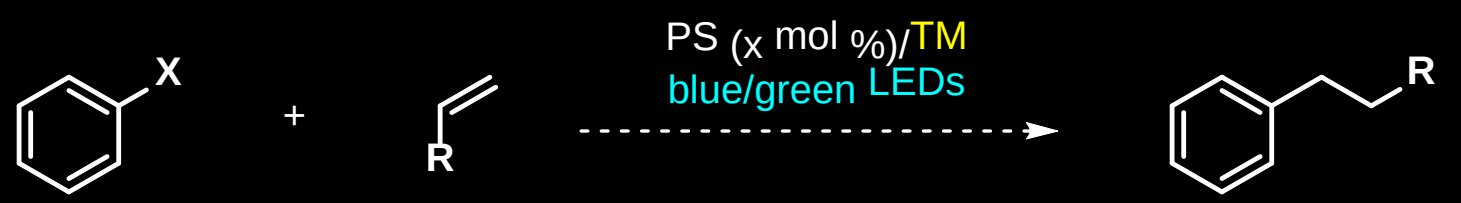
Anti-Markovnikov Alkene Hydrofunctionalization Reactions



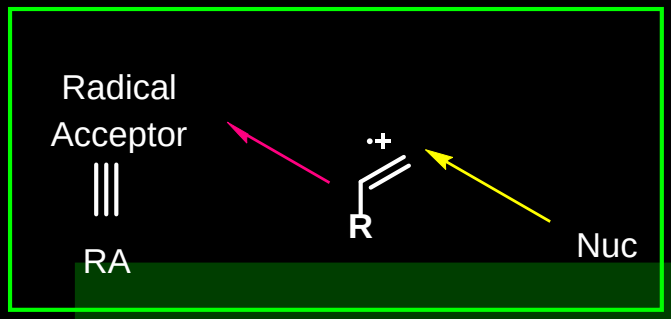
Nuc = Carbon

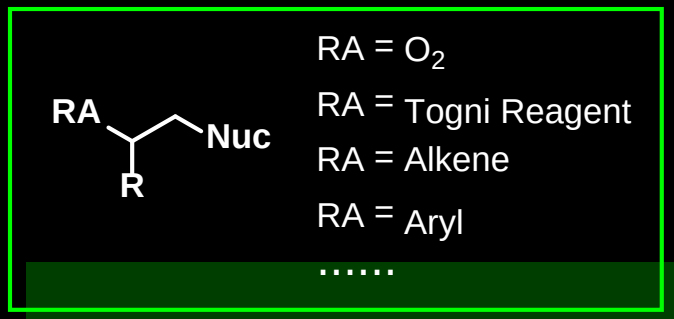
PS

λ_{max}^{abs} > 650 nm



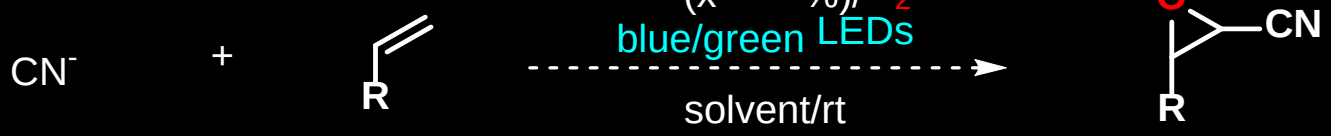
Difuctionalization of Alkenes





PS

λ_{max}^{abs} > 650 nm



Organic Photoredox Catalysis/Transition Metal Catalysis