Triplet-Triplet Energy Transfer (TTEnT) on sp^2-C

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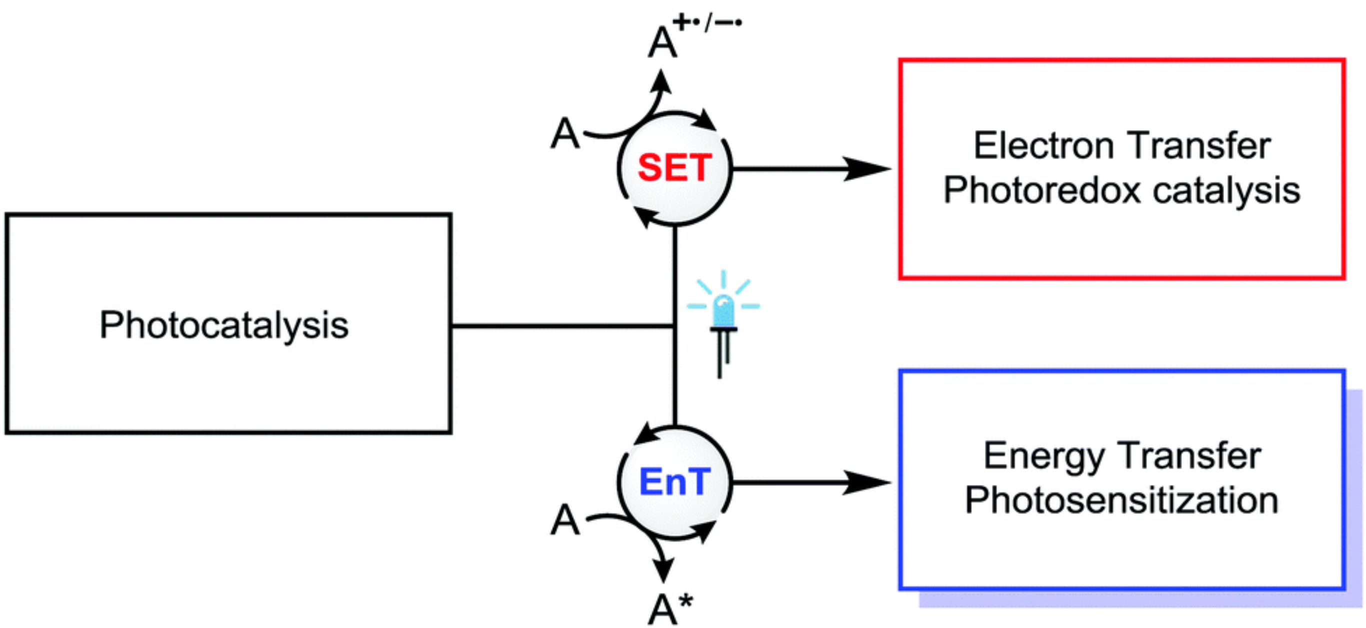
Outline

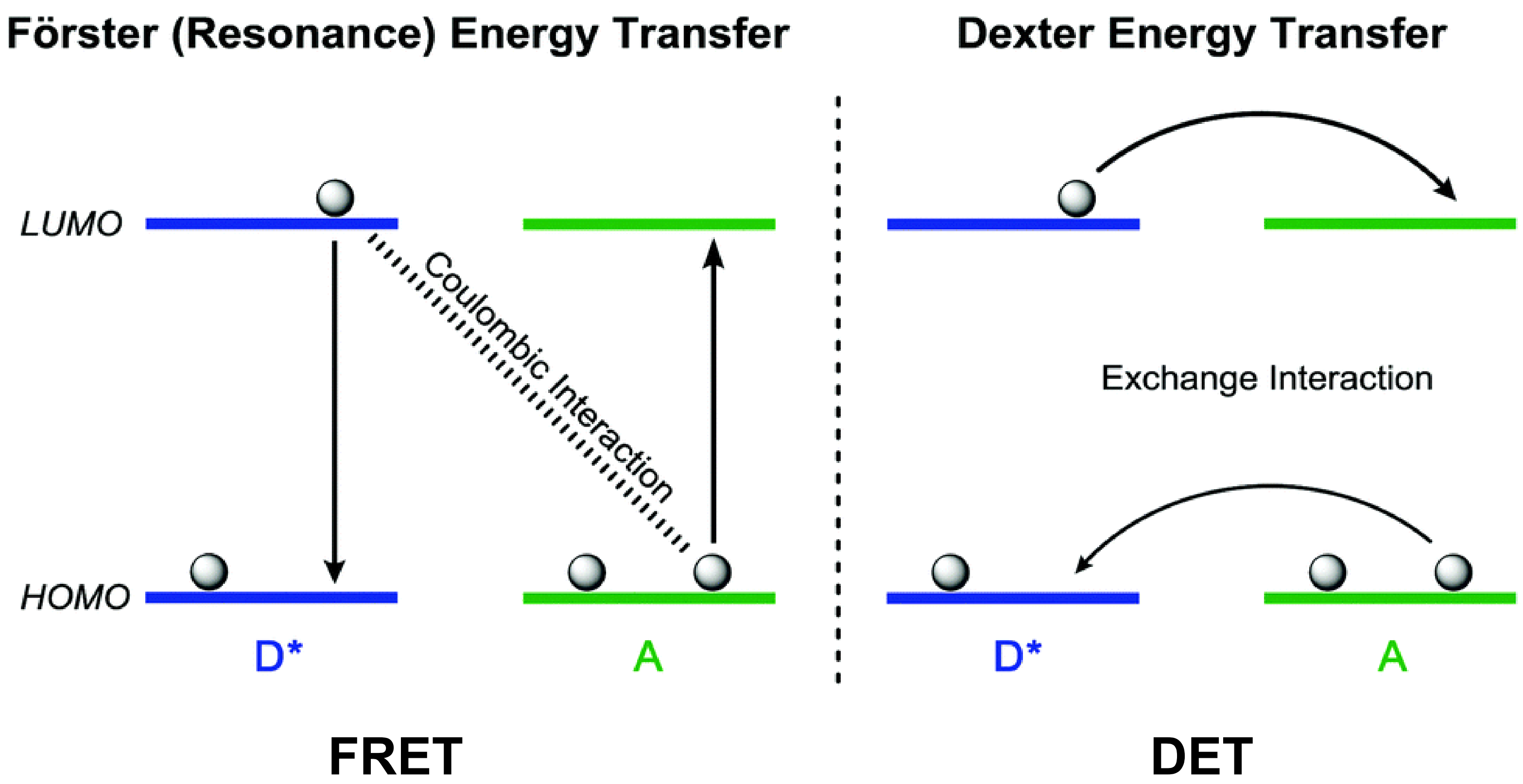
- Introduction
- E_T-based Selectivity: Stereo- or Chemoselectivity
- Merger of ET and EnT Catalysis
- Summary

Photocatalyst: ET and EnT



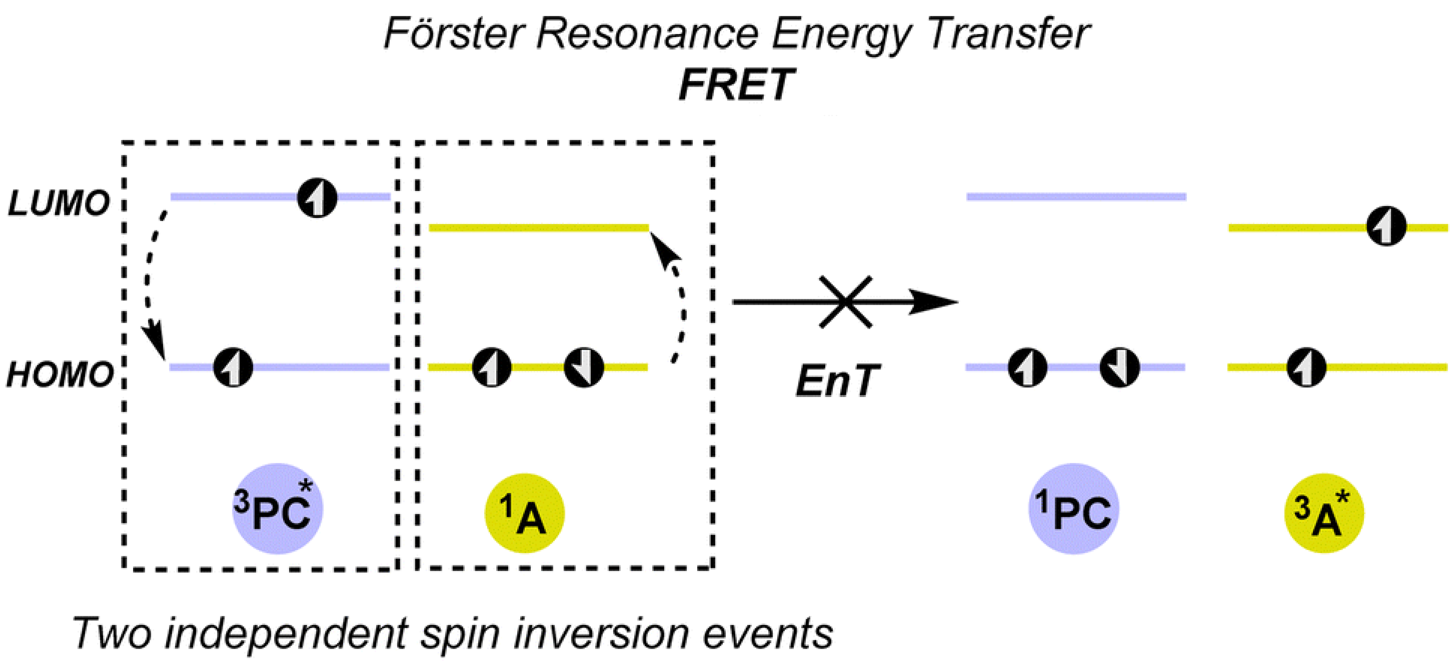
Strieth-Kalthoff, F. *et. al*. *Chem. Soc. Rev.* **2018**, *47*, 7190.

Energy Transfer Mechanisms



Strieth-Kalthoff, F. *et. al*. *Chem. Soc. Rev.* **2018**, *47*, 7190.

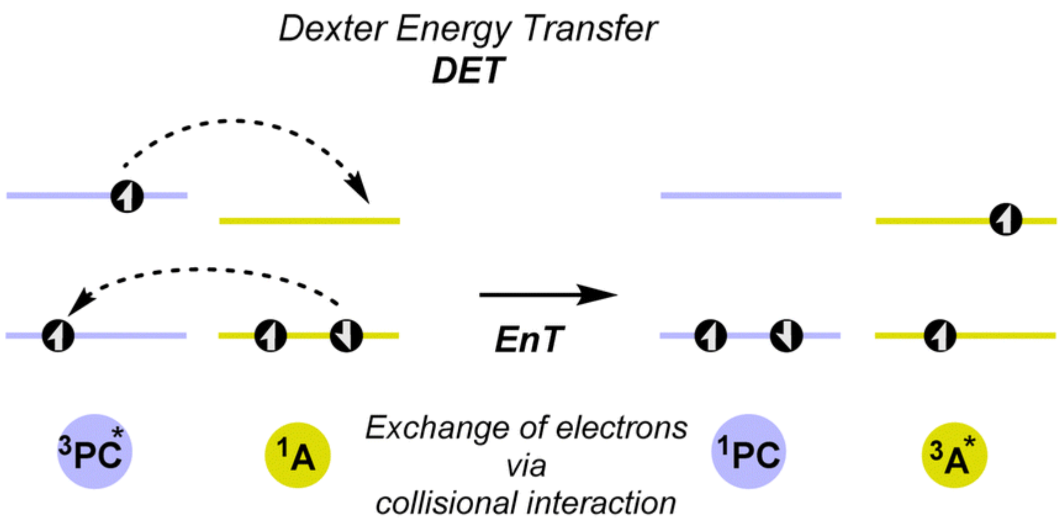
FRET for TTEnT: Forbidden

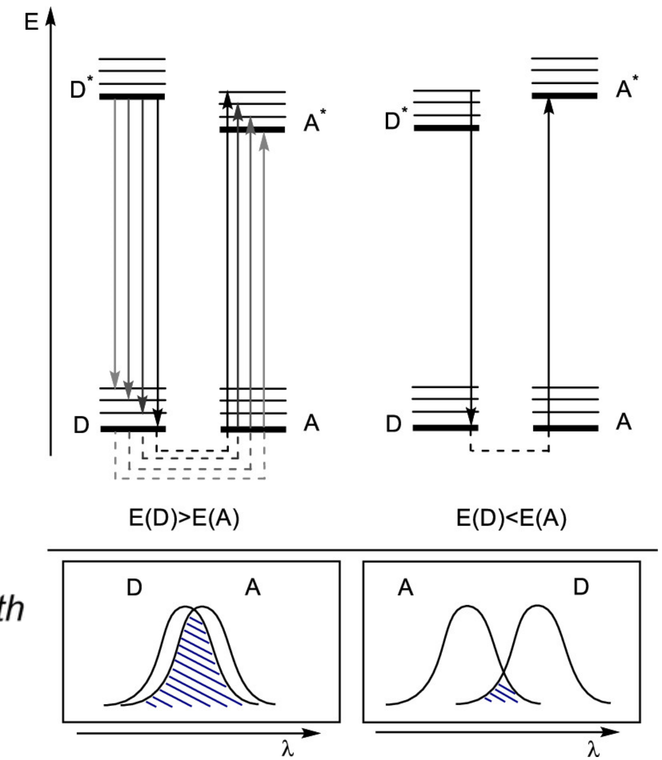


Irrelevent in TTEnT Catalysis

Dutta, S. *et. al*. *Chem. Soc. Rev.* **2024**, *53*, 1068.

TTEnT: Only for DET



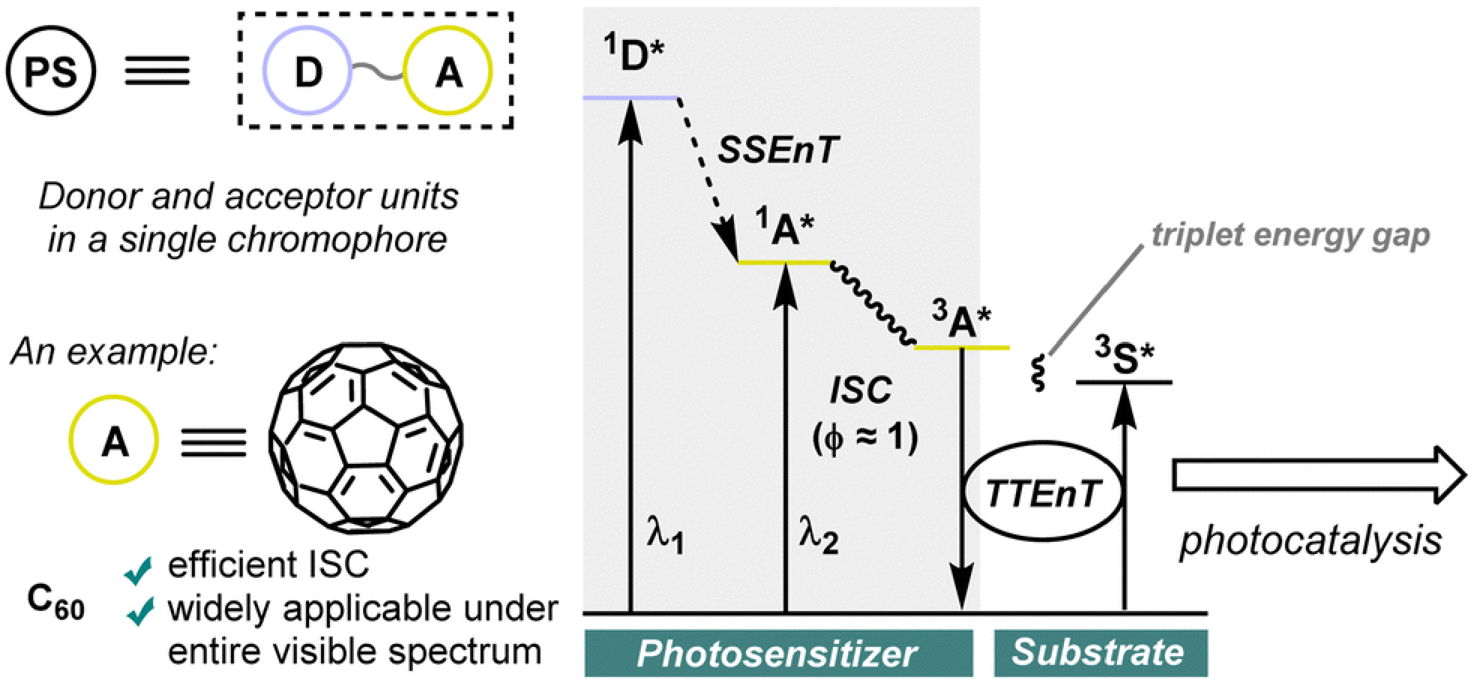


$$k_{DET} = k_{exp} \cdot J \cdot e^{\frac{-2R_{DA}}{L_{DA}}}$$

- *wavefunction/orbital overlap*
- *independent of oscillator strength*
- *r ~ 10 Å*

Dutta, S. *et. al*. *Chem. Soc. Rev.* **2024**, *53*, 1068.
Nevesely, T. *et. al*. *Chem. Rev.* **2022**, *122*, 2650.

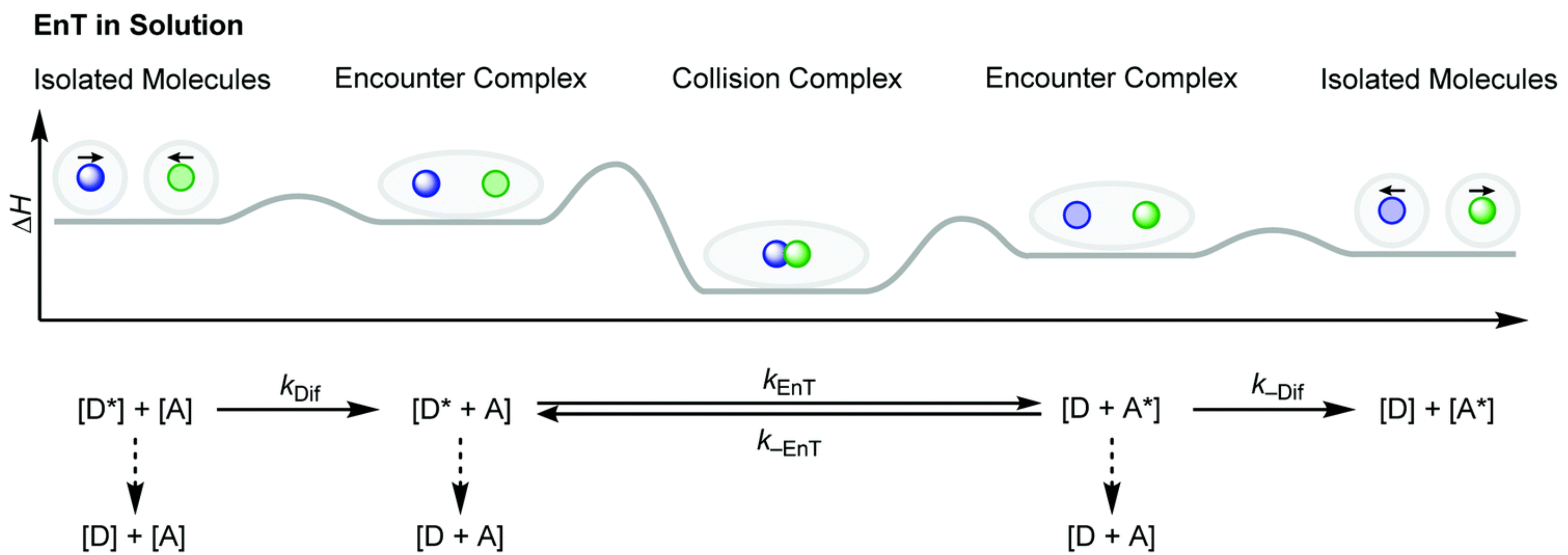
C_{60}: Spin Converter



Dutta, S. *et. al*. *Chem. Soc. Rev.* **2024**, *53*, 1068.

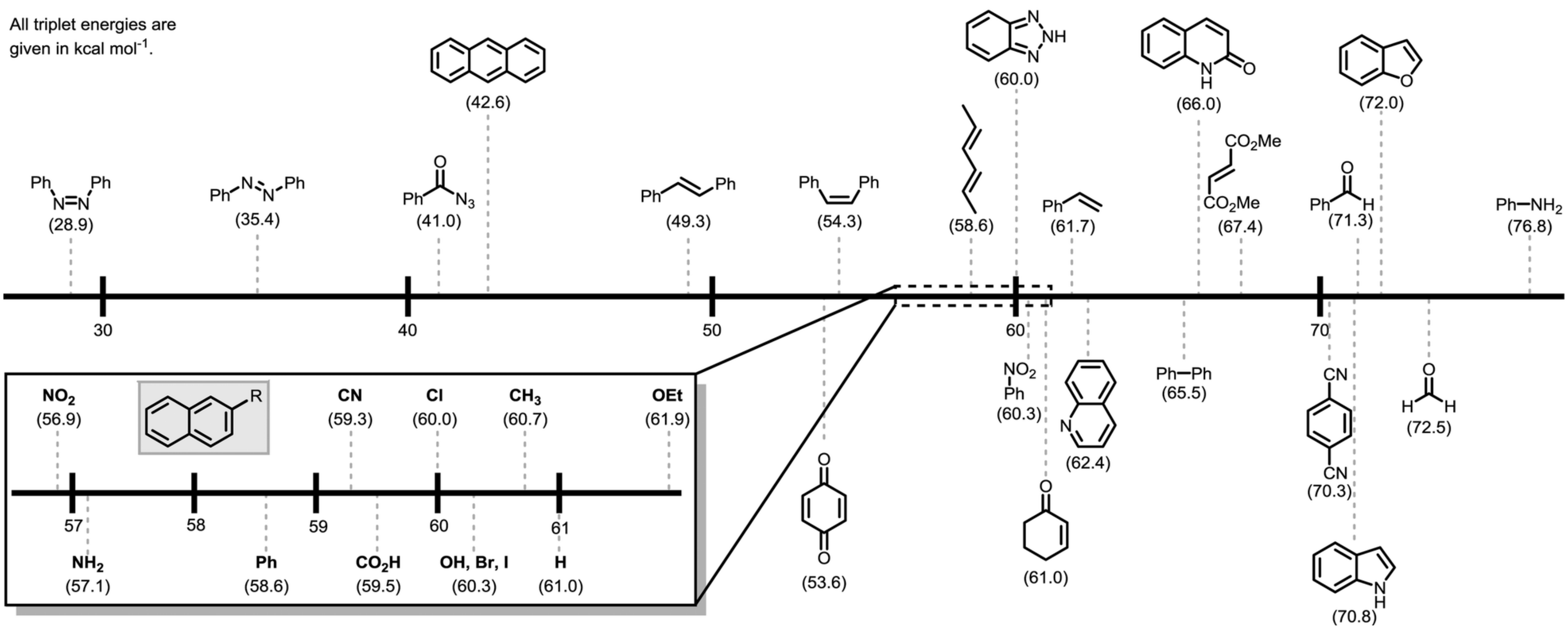
Simplified Overview of TTEnT in Solution

For exergonic EnT: close to diffusion limit



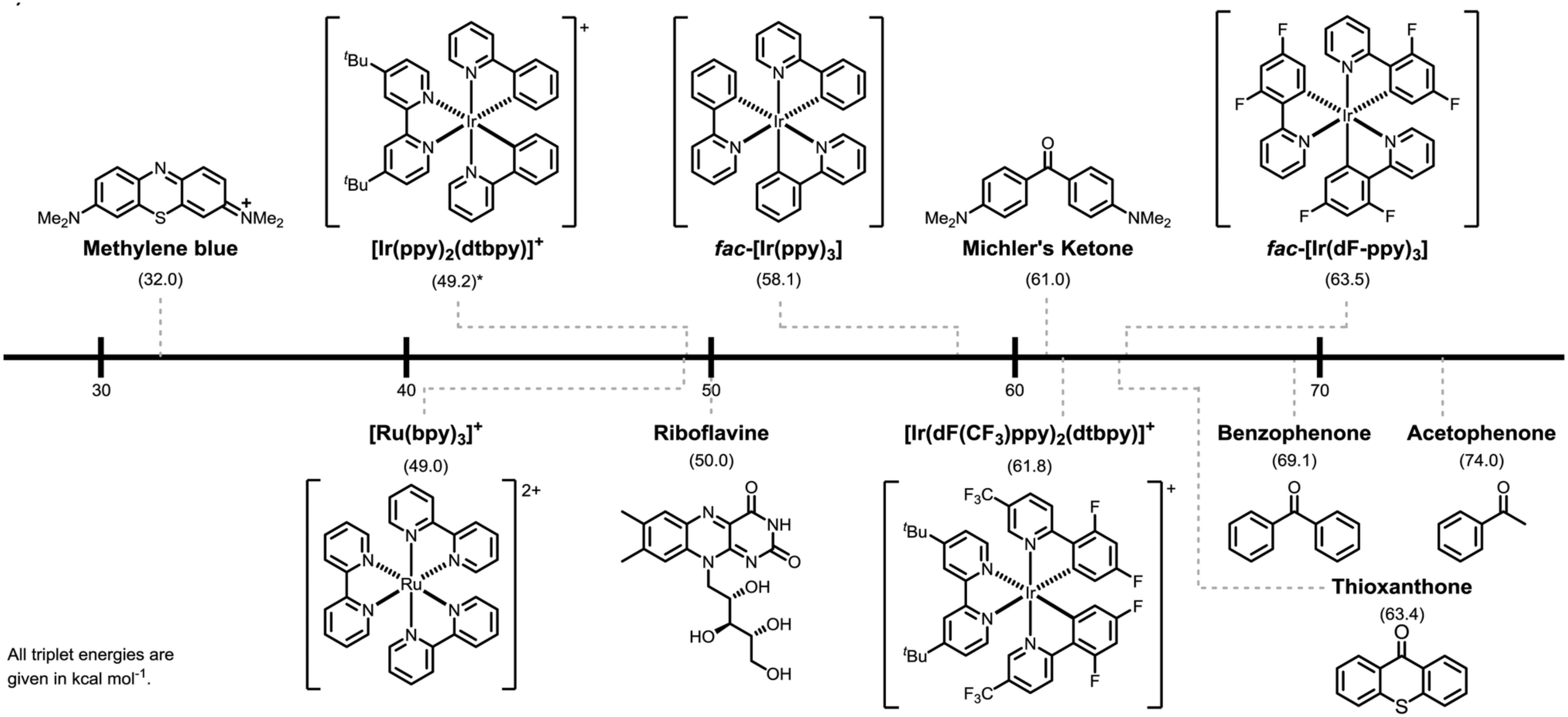
Strieth-Kalthoff, F. *et. al*. *Chem. Soc. Rev.* **2018**, *47*, 7190.

E_T of Selected Substrates



Strieth-Kalthoff, F. *et. al*. *Chem. Soc. Rev.* **2018**, *47*, 7190.

E_T of Common Photosensitizers



Strieth-Kalthoff, F. *et. al*. *Chem. Soc. Rev.* **2018**, *47*, 7190.

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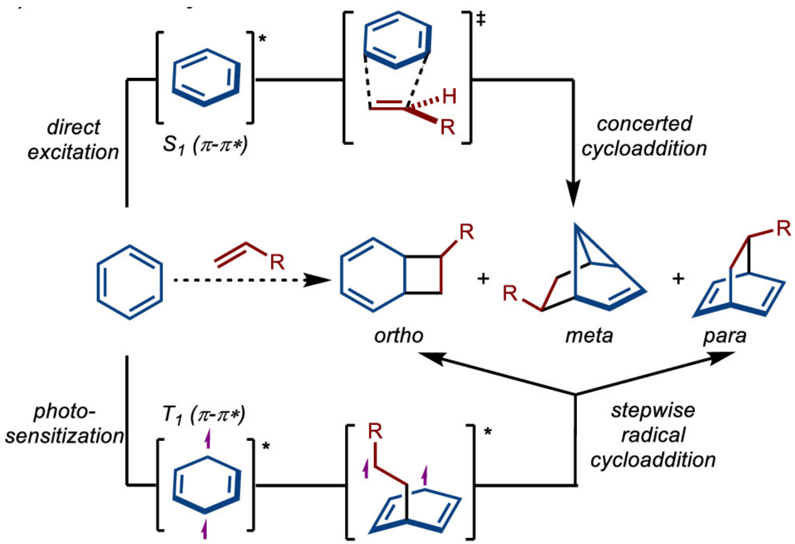
Dearomative Cycloaddition (DAC)

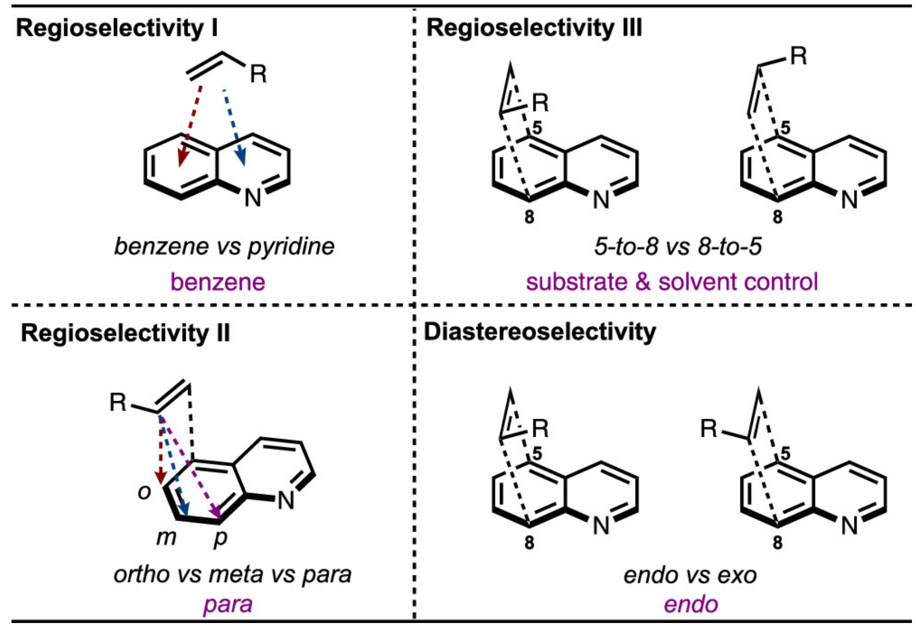


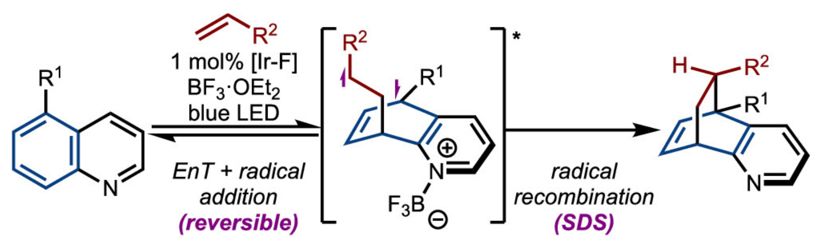
Direct excitation

- High energy gap from S_0 to S_1
- meta is symmetry allowed from S_1
- Slow ISC (El-Sayed forbbidden) to T_1
- Competitive reactions of S_1 and T_1

Photosensitization

- Longer wavelength for sensitizer
- Radical chemistry enables ortho & para
- Efficient Dexter energy transfer to T_1
- No S_1 reactivity

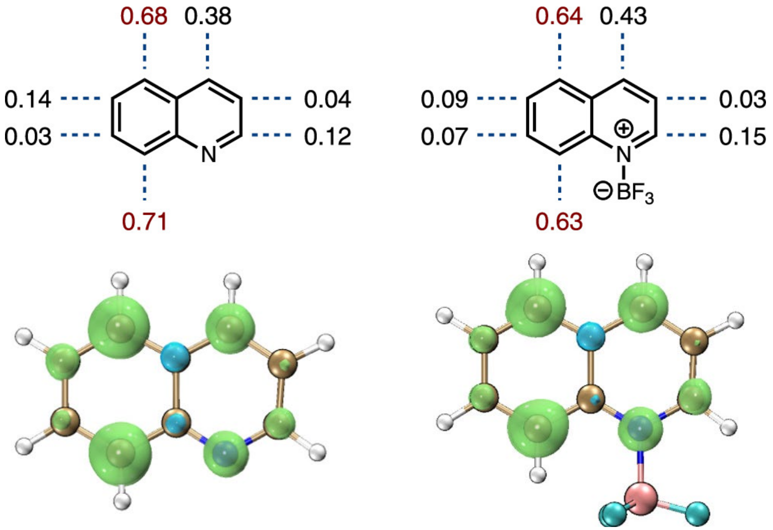




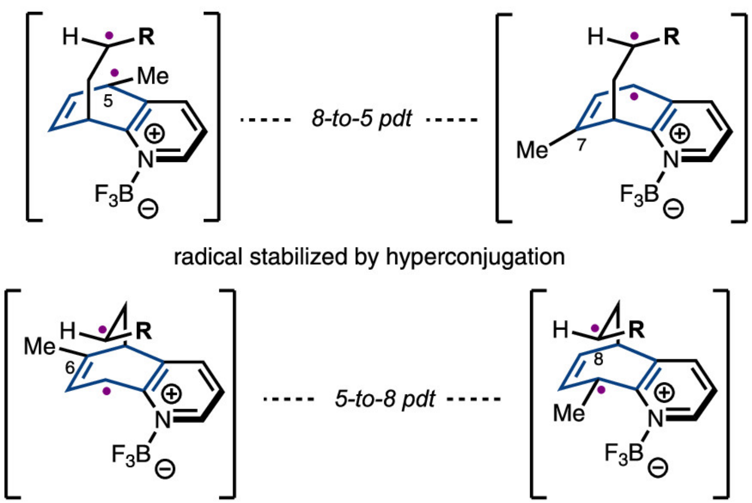
■ Broad Scope ■ Mechanism Studies

Ma, J. *et al. Science* **2021**, *371*, 1338.
Guo, R. *et al. J. Am. Chem. Soc.* **2022**, *144*, 17680.

Regioselectivity in EnT-enabled DAC

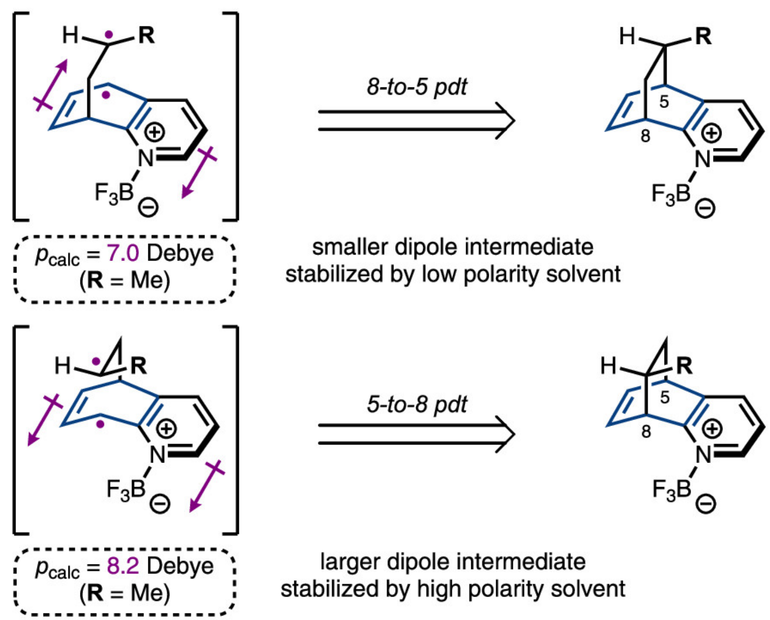


Substitution-controlled



5-8 selectivity: spin density, substitution and solvent

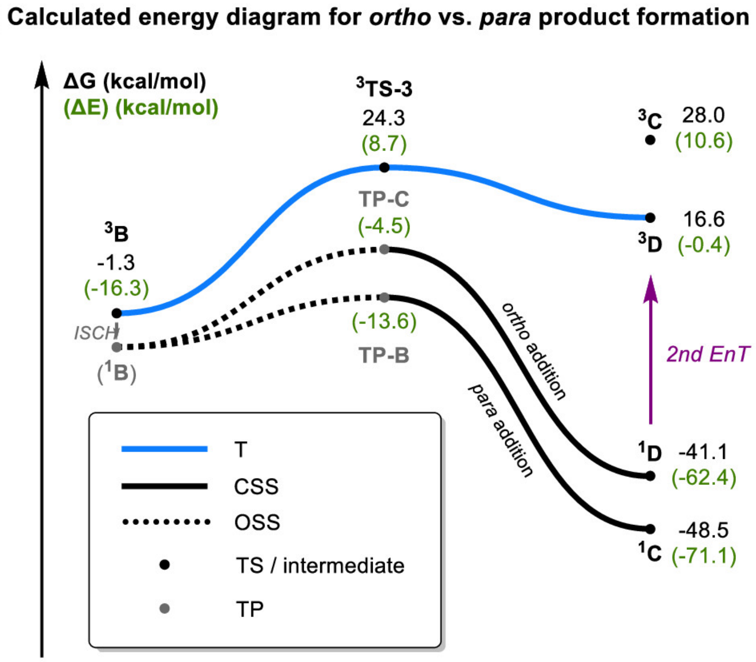
Solvent-controlled

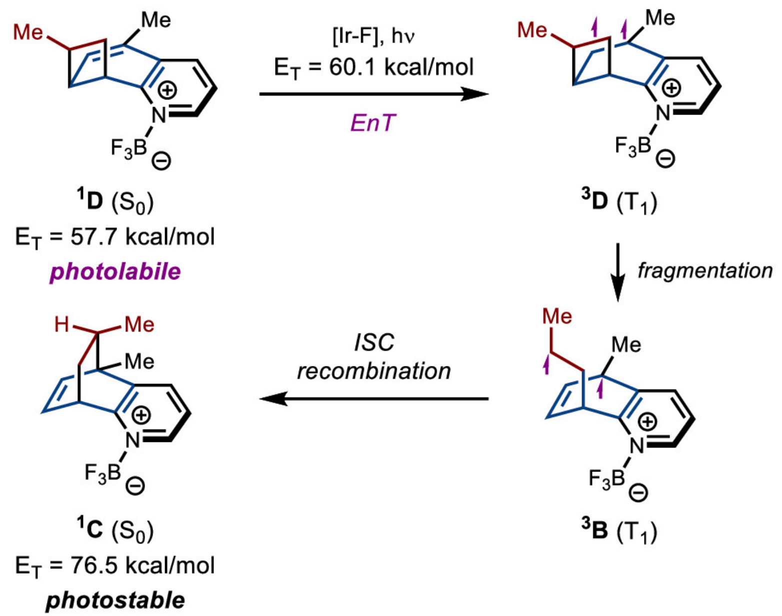


Guo, R. *et al. J. Am. Chem. Soc.* **2022**, *144* (38), 17680.

Regioselectivity in EnT-enabled DAC

Ortho-para selectivity: Transition point(TP) energy, photostability

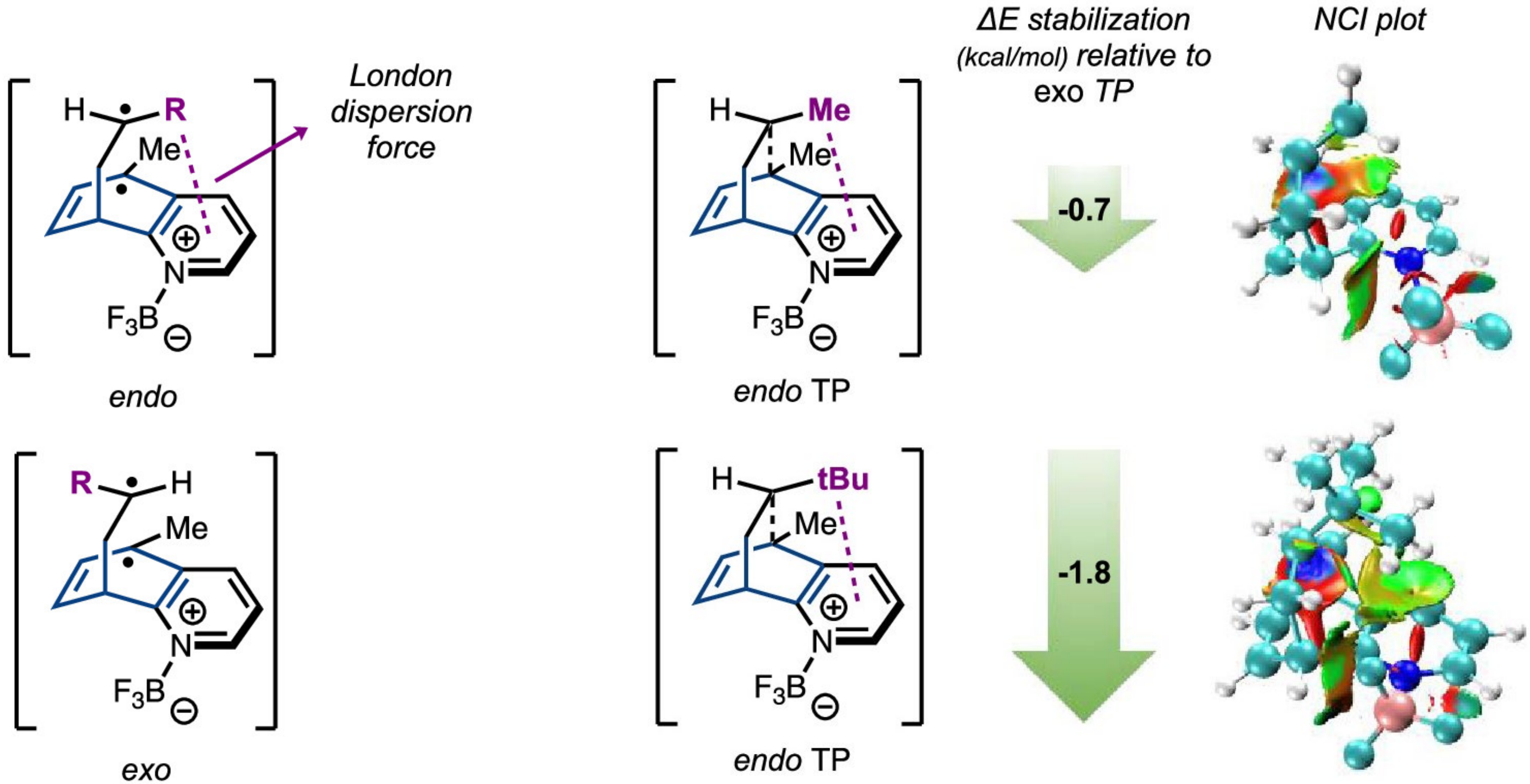




Guo, R. *et al. J. Am. Chem. Soc.* **2022**, *144* (38), 17680.

Stereoselectivity in EnT-enabled DAC

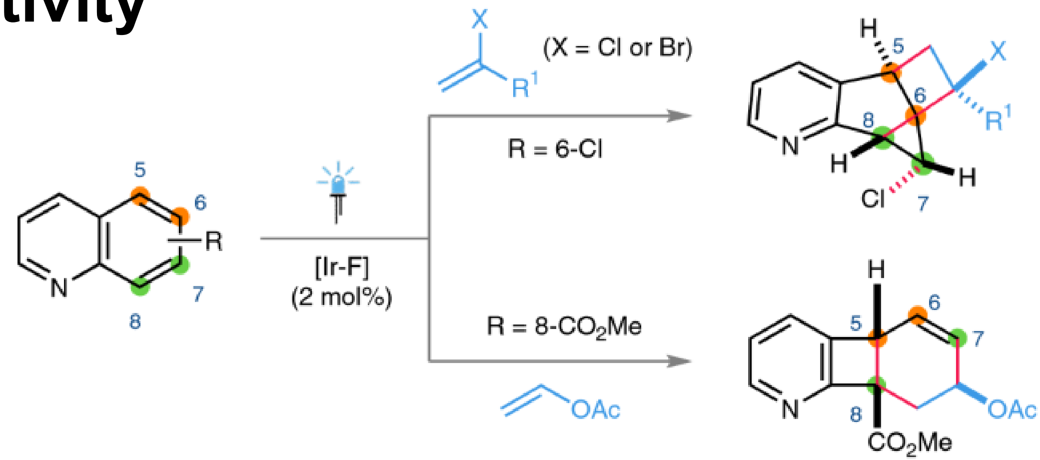
endo- selectivity: dispersion attraction



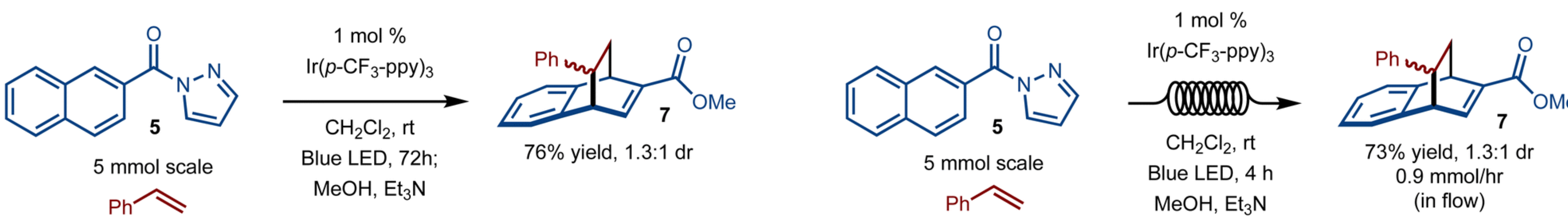
Guo, R. *et al. J. Am. Chem. Soc.* **2022**, *144* (38), 17680.

Substrate Modification

Ortho- selectivity

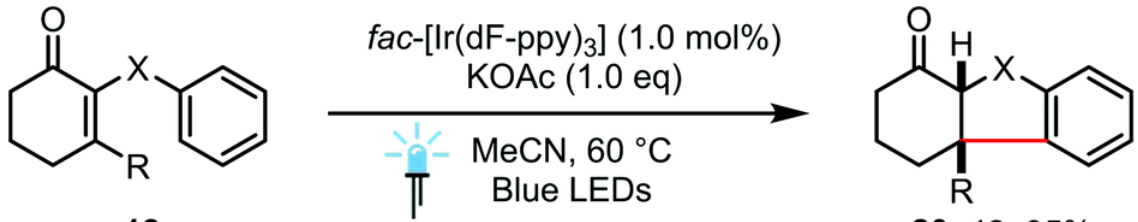


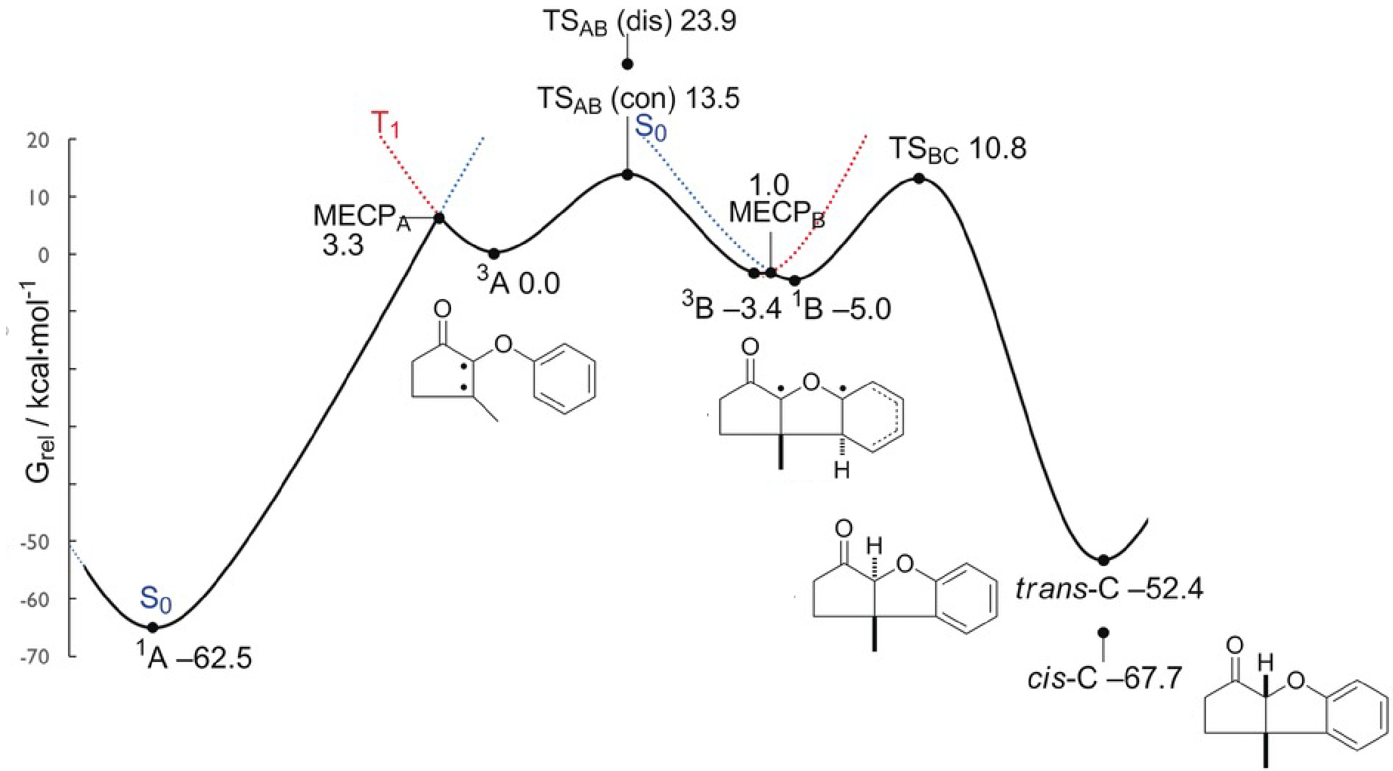
DAC for naphthalene derivative



Ma, J. *et al. Nat. Catal.* **2022**, *5*, 405.
Wang, W. *et al. Chem. Sci.* **2022**, *13*, 13582.

Enone Sensitization: Milder Condition



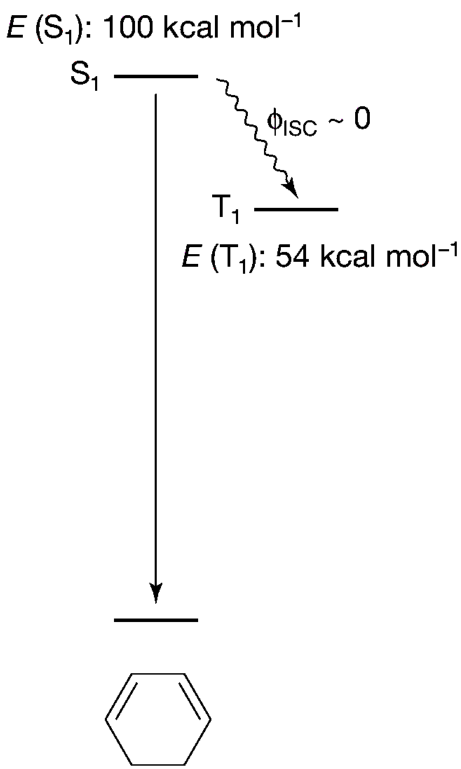


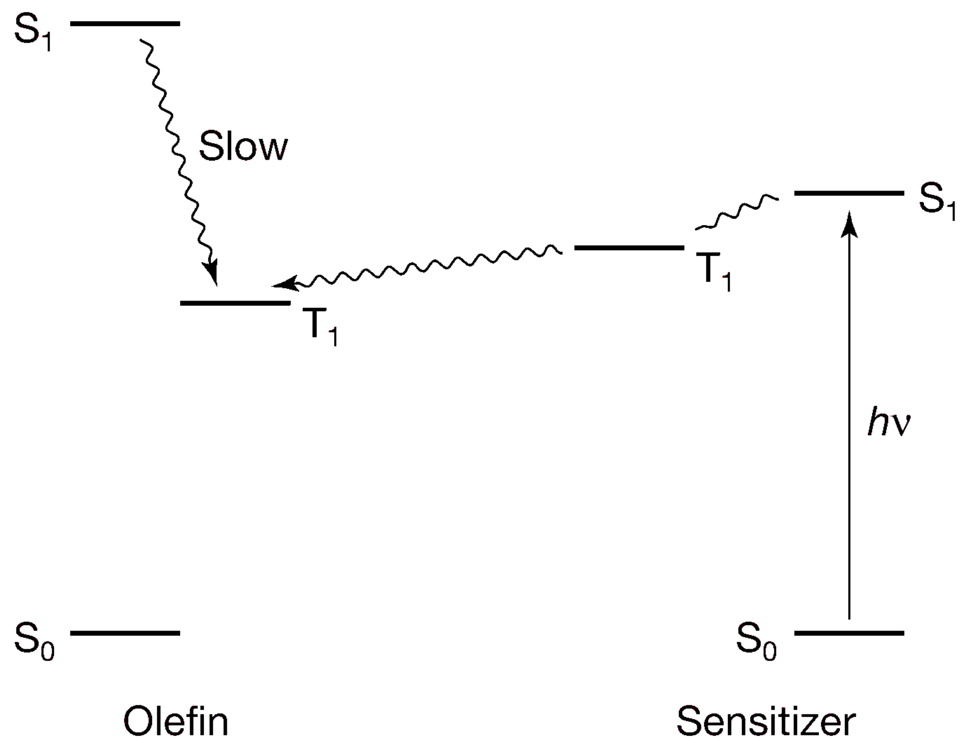
Münster, N. *et al. Angew. Chem., Int. Ed.* **2017**, *56*, 9468.

Alkene Sensitization: Fundamental Logic

Very large energy gap **(typically > 40 kcal mol^{-1}) between S_1 and T_1**

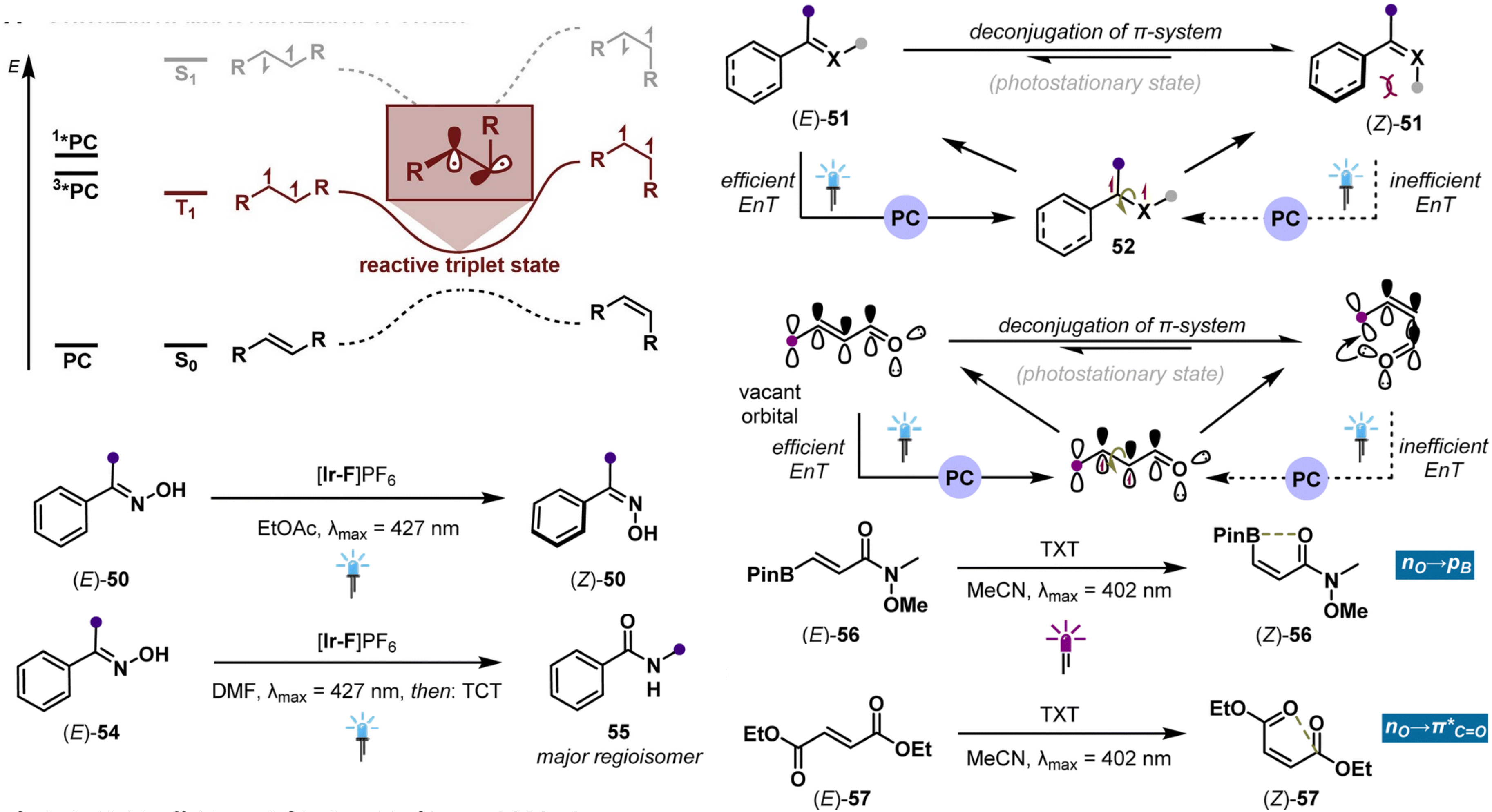
Low ISC yield **from S_1 to T_1 (ϕ_{ISC} for alkyl alkene/polyenes ~ 0)**





Turro, N. J. *et. al*. Modern Molecular Photochemistry of Organic Molecules, pp 710-713.

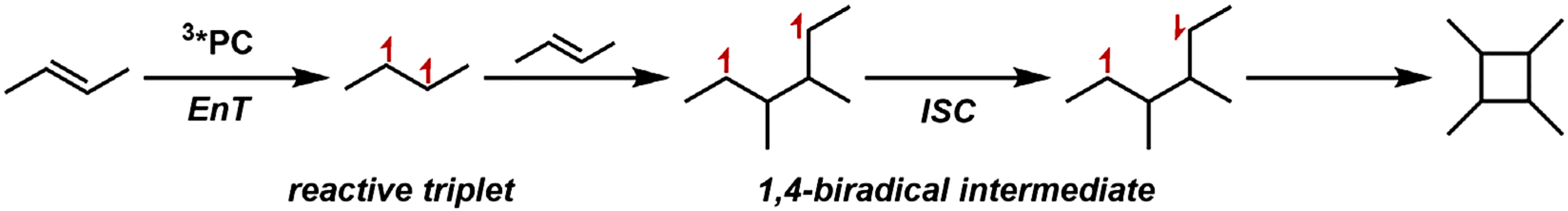
$E \rightarrow Z$ Isomerization: 2D Stereoselective



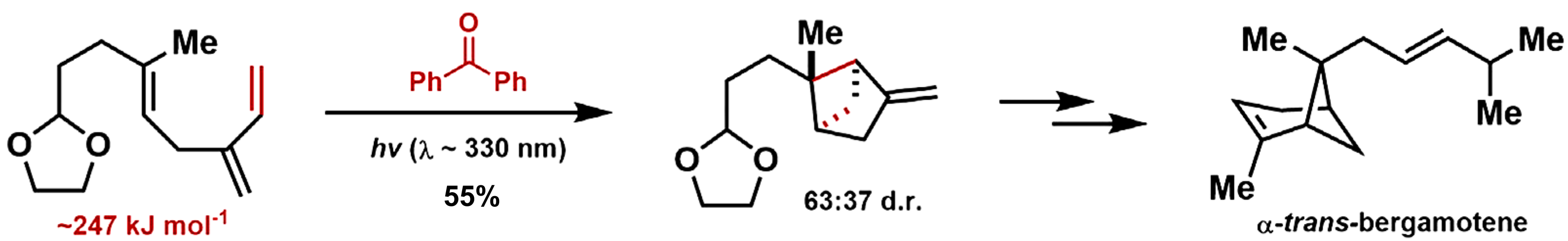
Strieth-Kalthoff, F. and Glorius, F. *Chem.* **2020**, *6*, 1888.
Dutta, S. *et. al. Chem. Soc. Rev.* **2024**, *53*, 1068.
Zhang, X. *et. al. J. Am. Chem. Soc.* **2021**, *143*, 21211.
Molloy. J. *et al. Science* **2020**, *369*, 302.
Neveselý. T. *et al. Angew. Chem. Int. Ed.* **2022**, *61*, e202113600.

Triplet [2+2]: Broadening Substrate Scope

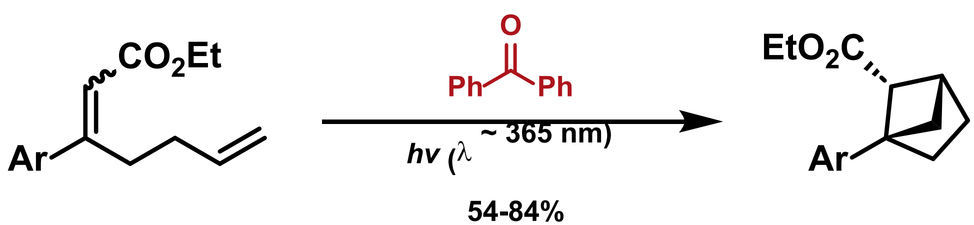
Stepwise Mechanism:



Corey (1971) – Application to Total Synthesis

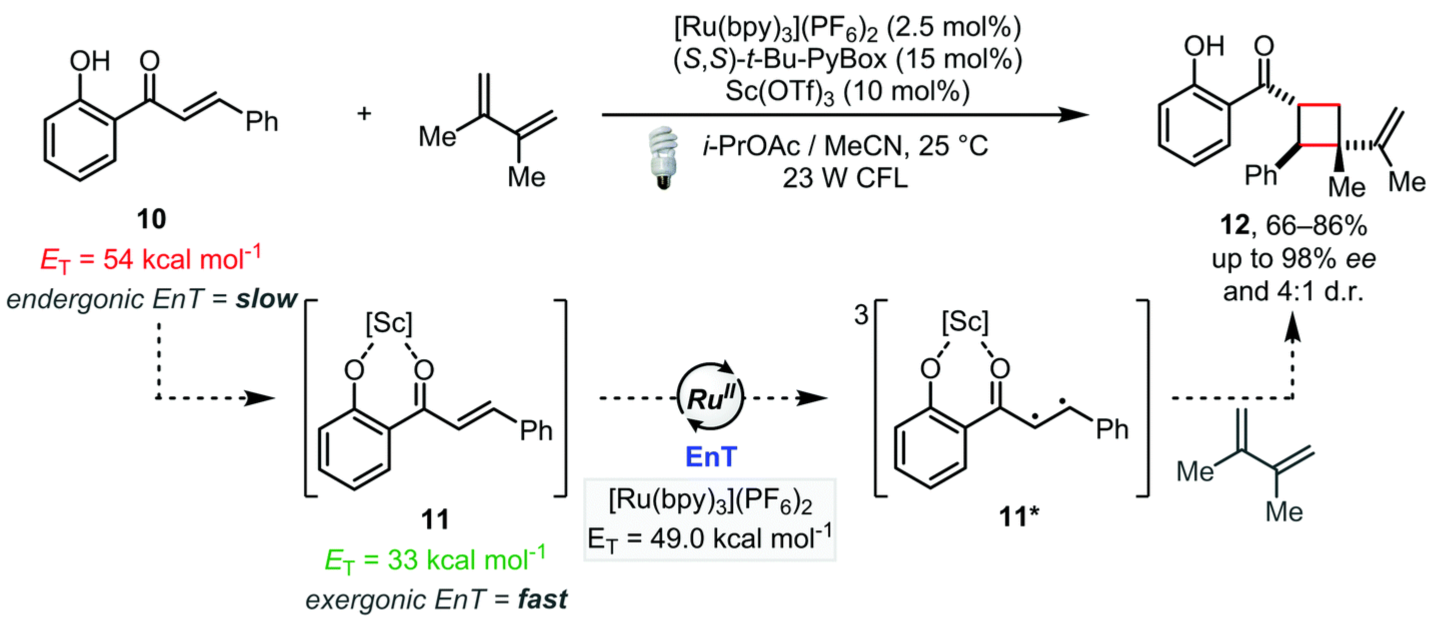


Mykhaliliuk (2020) - Appliction to Bioisosteres Synthesis



Strieth-Kalthoff, F. and Glorius, F. *Chem.* **2020**, *6*, 1888.
Corey, E. J. *et. al*. *J. Am. Chem. Soc.* **1971**, *93*, 7016.
Denisenko, A. *et. al*. *Angew. Chem., Int. Ed.* **2020**, *59*, 20515.

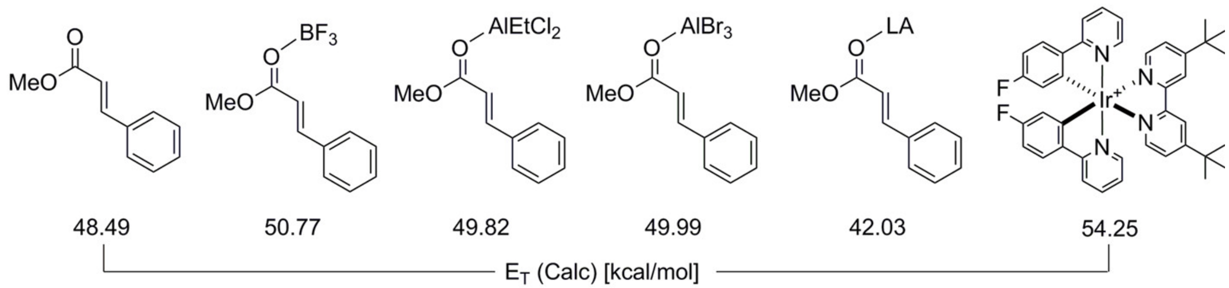
Stereoselective [2+2]: Chiral E_T Lowering Reagent



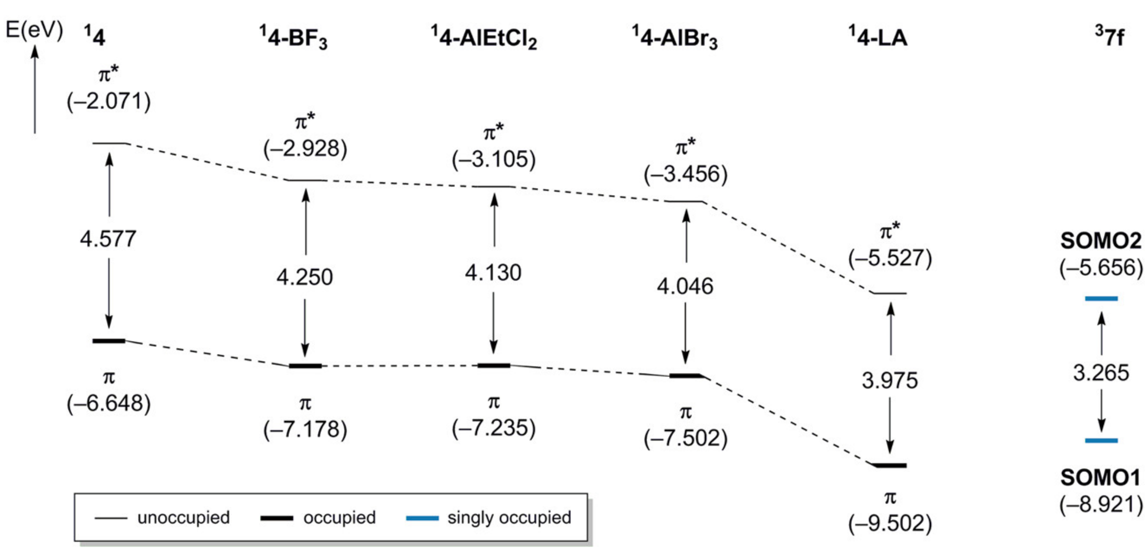
Blum, T. R. *et. al*. *Science* **2016**, *354*, 1391.

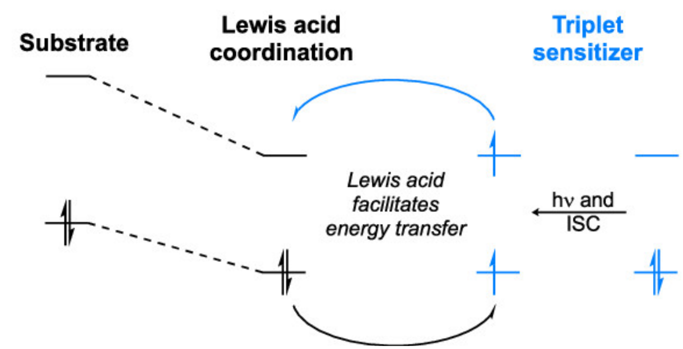
LA Coordination: More than E_T Lowering

(b) Triplet energies of ¹**4**, Lewis acid bound adducts and ¹**7f**



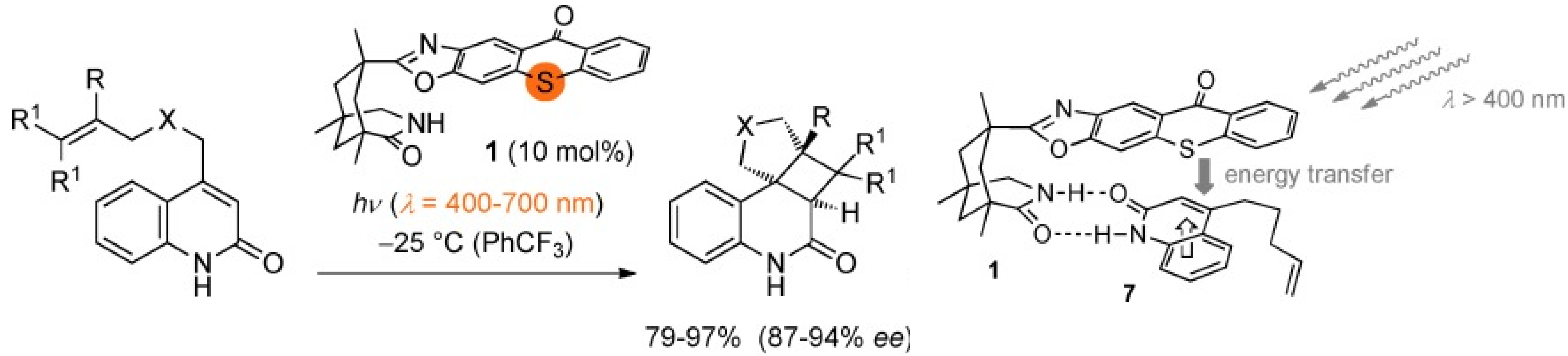
(c) Frontier orbital energies of ¹**4**, Lewis acid bound adducts and ³**7f**

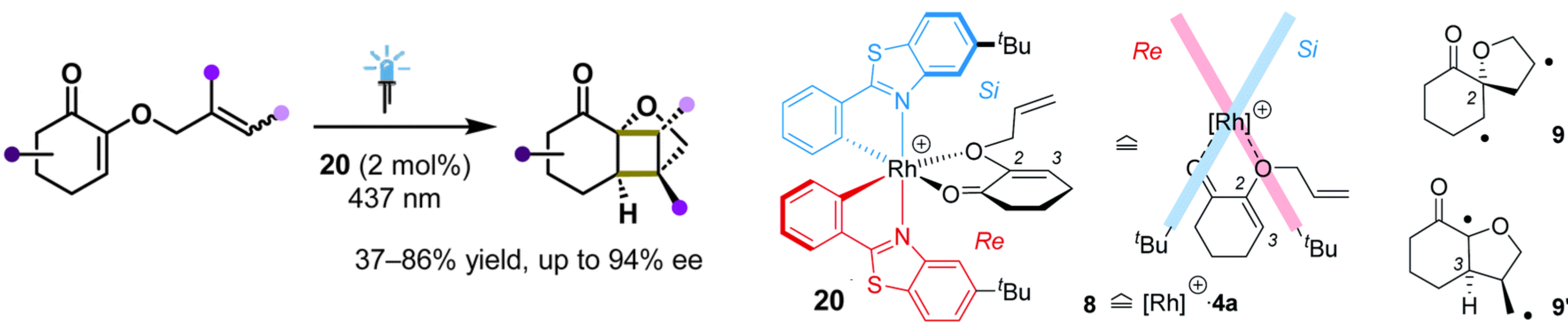




Daub, M. E. *et. al*. *J. Am. Chem. Soc.* **2019**, *141*, 9543.

Stereoselective [2+2]: Chiral PC

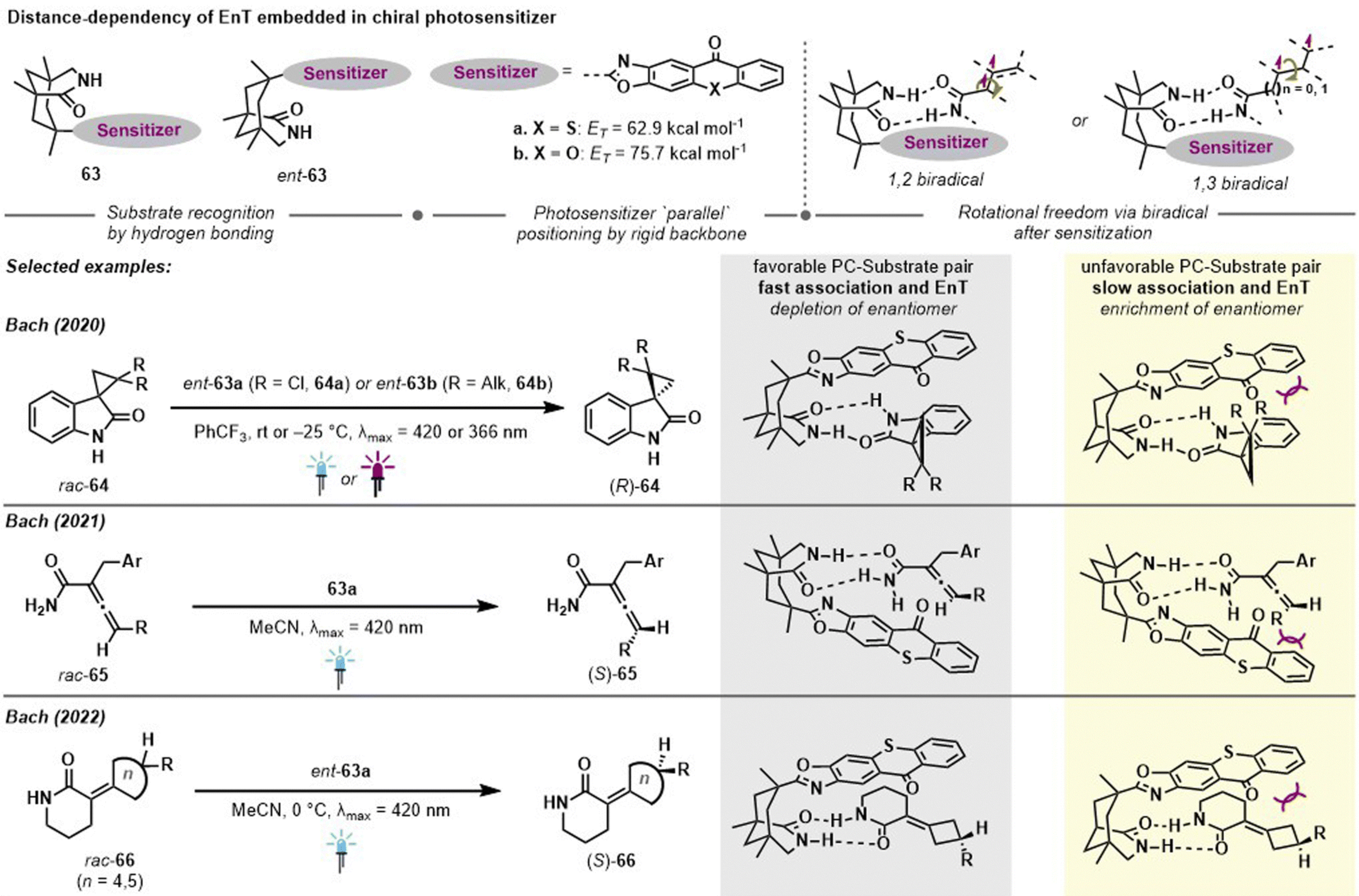




Alonso, R.; Bach, T. *Angew. Chem., Int. Ed*. **2014**, *53*, 4368.

Thomas, R. *et. al. Chem. Sci.* **2022**, *13*, 2378.

Deracemization through ‘Stereoselective EnT’

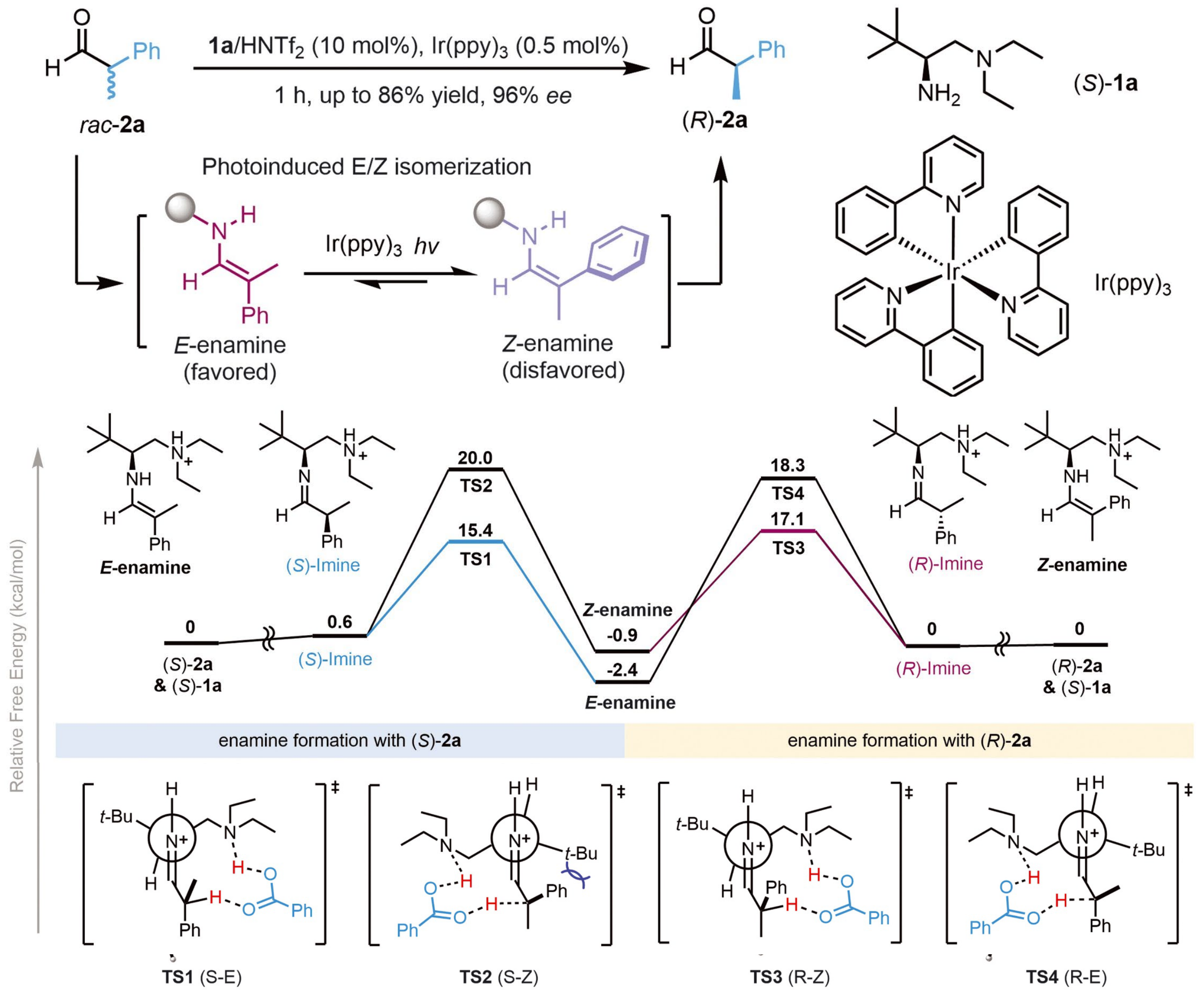


Li, X. *et al*. *Angew. Chem., Int. Ed.* **2020**, *59*, 21640.

Kratz, T. *et al*. *J. Am. Chem. Soc.* **2022**, *144*, 10133.

Hölzl-Hobmeier, A. *et al*. *Nature* **2018**, *564*, 240

'Chemoselective' EnT: Deracemization through Enamine

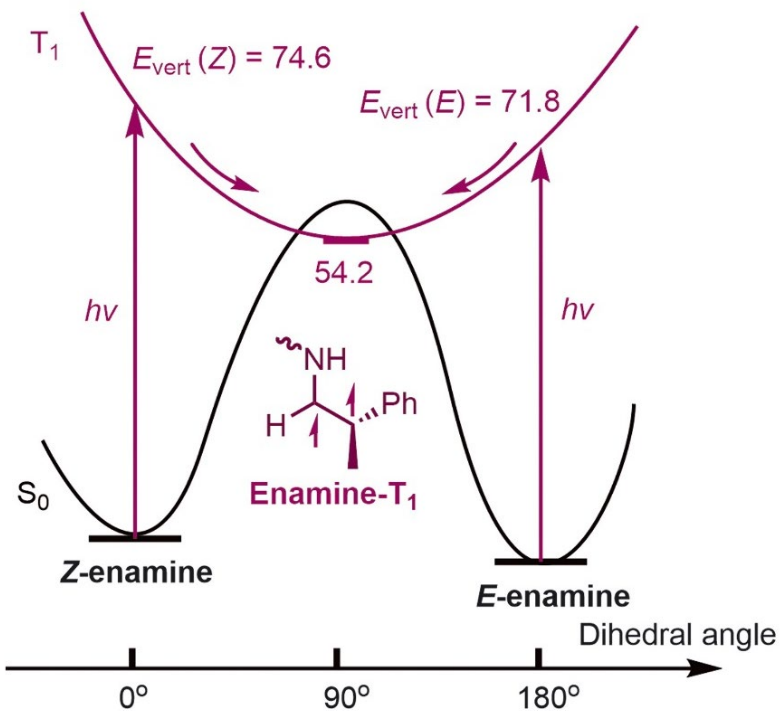


Huang. M. *et al. Science* **2022**, *375*, 869.

Vertical or Adiabatic?

Reactivity criteria: $E_{T(adiabatic)}$

Selectivity criteria: $E_{T(vertical)}$



Photocatalyst	E_T (kcal/mol)	$E_{1/2}^{PC+/PC*}$(V)	ee (%)
Thioxanthone	64.4	+1.18	64
$Ir(dFCF_3ppy)_2dtbbpyPF_6$	61.8	+1.21	73
$Ir(ppy)_3$	58.1	+0.31	94
$Ir(pCF_3\text{-}ppy)_3$	56.4	+0.59	93
2,4,6-triphenylpyrylium	53.0	+2.02	18
$Ru(bpy)_3Cl_2 \cdot 6H_2O$	46.5	+0.77	39
E-enamine	54.2	+0.73*	

Huang. M. *et al. Science* **2022**, *375*, 869.

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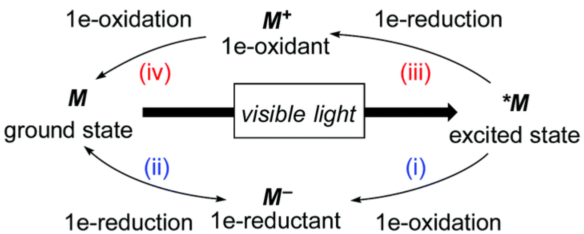
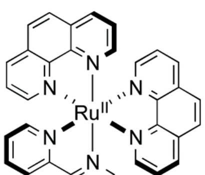
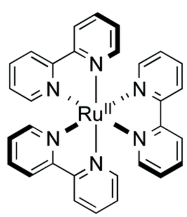
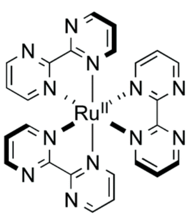
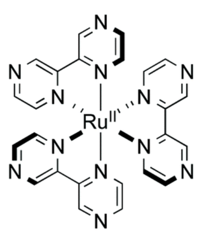
ET and/or EnT: Selected Redox Potential for PCs

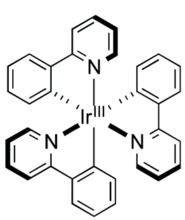


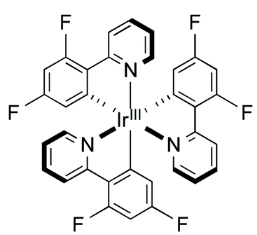

$[Ru(phen)_3]^{2+}$

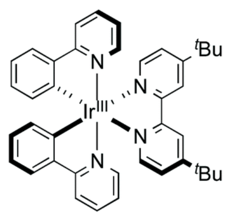

$[Ru(bpy)_3]^{2+}$

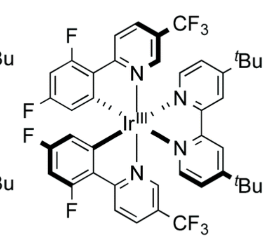

$[Ru(bpm)_3]^{2+}$

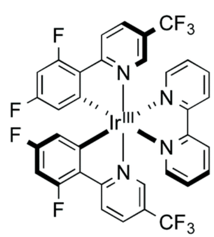

$[Ru(bpz)_3]^{2+}$

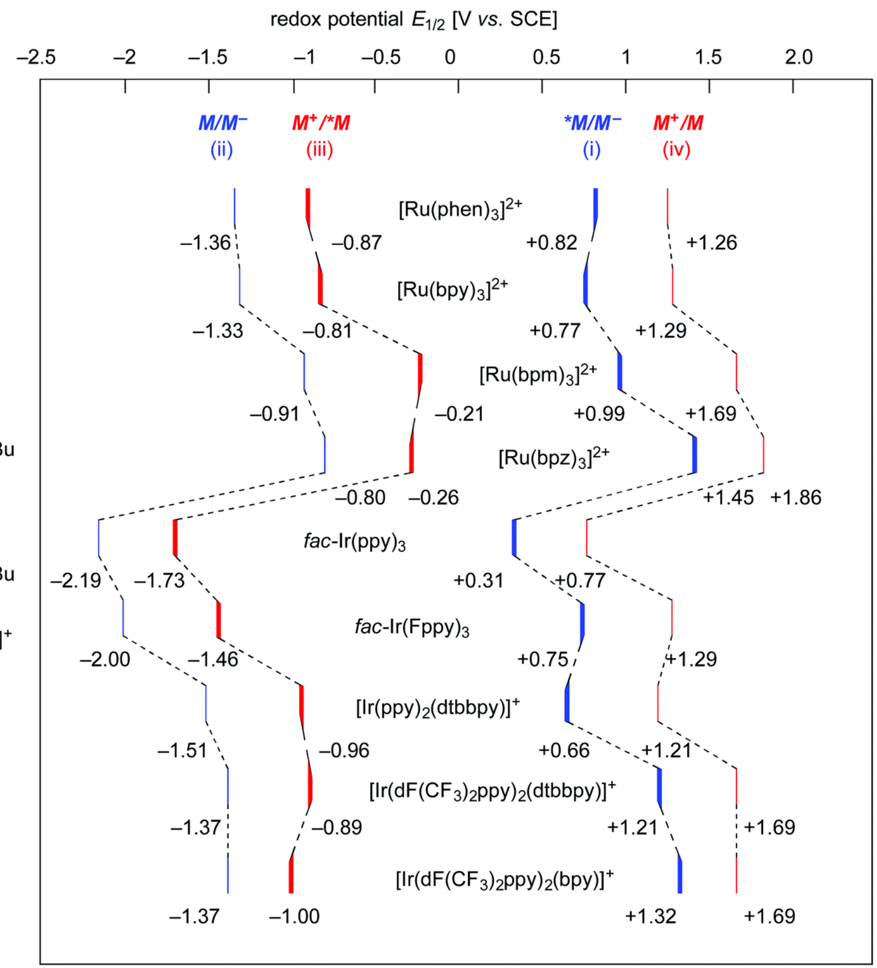

fac-Ir(ppy)$_3$


fac-Ir(Fppy)$_3$


$[Ir(ppy)_2(dtbbpy)]^+$

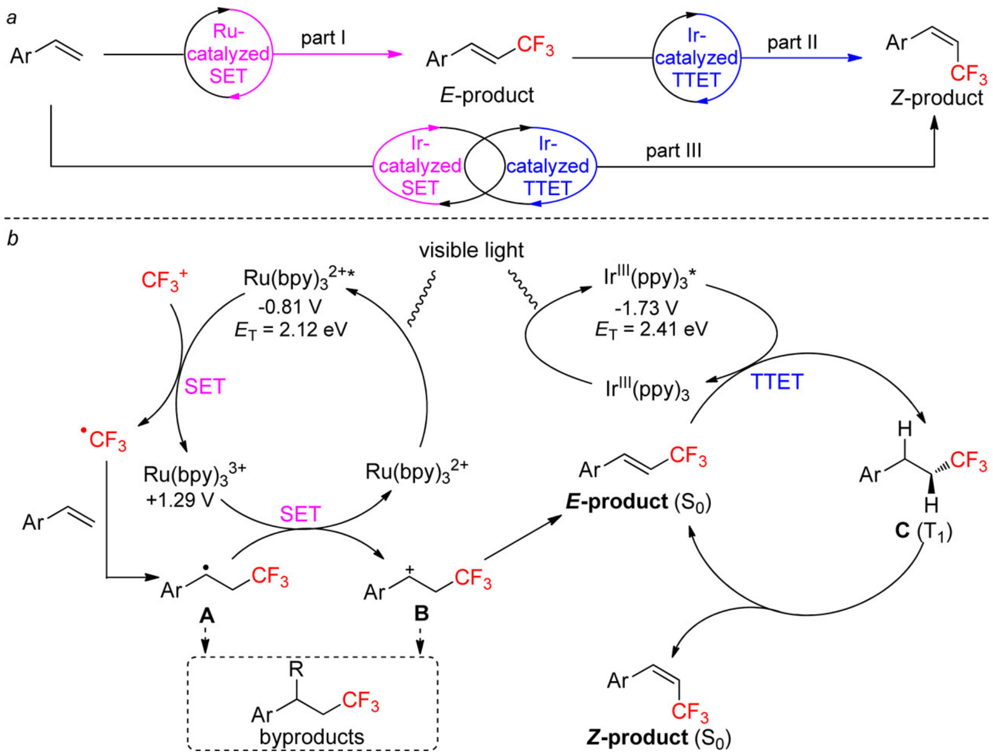

$[Ir(dF(CF_3)_2ppy)_2(dtbbpy)]^+$

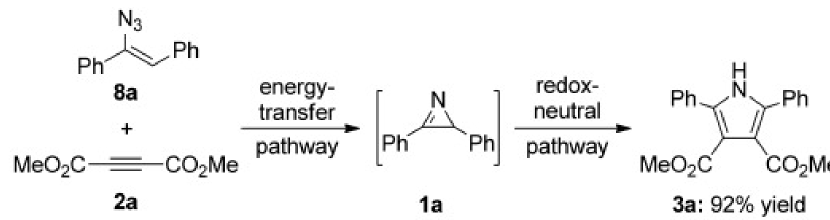

$[Ir(dF(CF_3)_2ppy)_2(bpy)]^+$



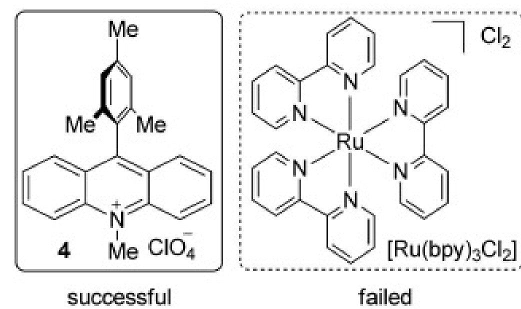
Takashi, K. *et. al*. *Inorg. Chem. Front*. **2014**, *1*, 562.

EnT and ET in Sequence





Reaction conditions:
0.3 mmol of **11a**,1.5 mmol of **2a** and 0.015 mmol of photocatalyst **4** or $[Ru(bpy)_3Cl_2]$ in 3 mL DCE for 16 h under the irradition of 450–460 nm blue LED.

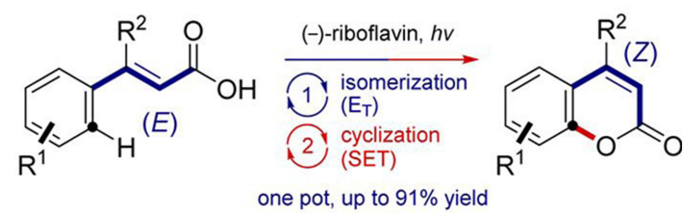


Control experiments for the reaction from **8a** to **1a**:

standard conditions (2.5 h): 95% yield

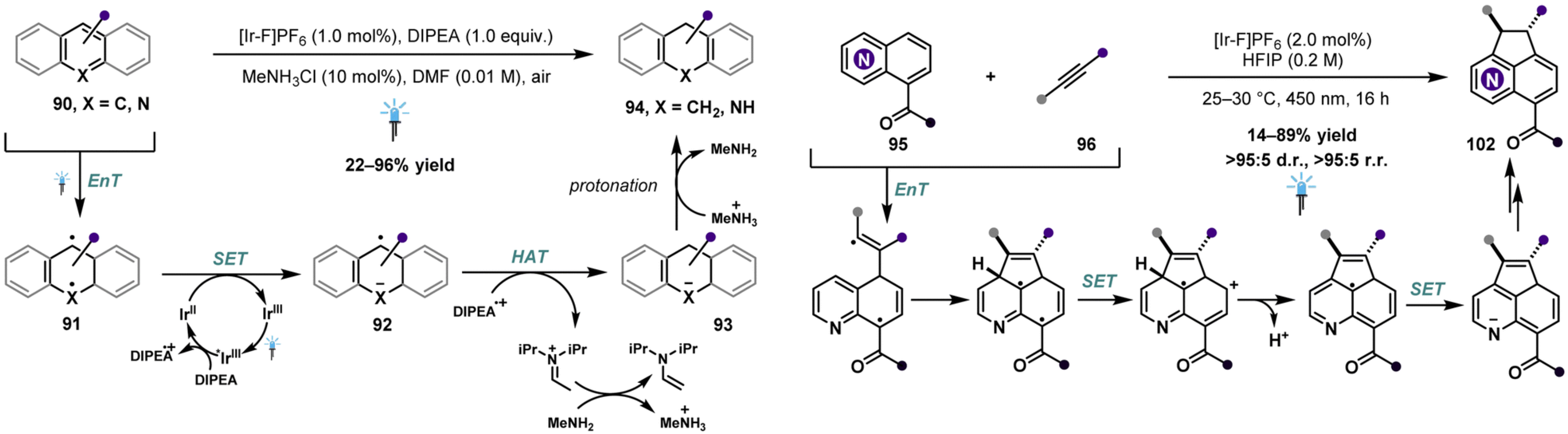
without visible light (2.5 h): 19% yield

without photocatalyst (2.5 h): 26% yield



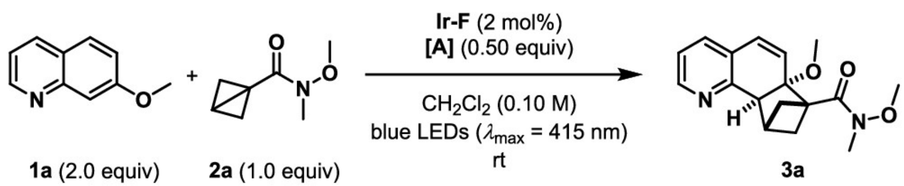
Xuan, J. *et al. Angew. Chem., Int. Ed.* **2014**, *53*, 5653.
Lin, Q. *et al. J. Org. Chem.* **2014**, *79*, 10434.
Metternich, J. B.; Gilmour, R. *J. Am. Chem. Soc.*, **2016**, *138* , 1040.

SET at Long-lived Triplet State

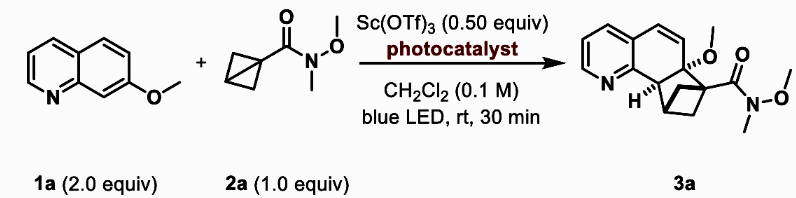


Chatterjee, A.; Konig, B. *Angew. Chem., Int. Ed.* **2019**, *58*, 14289.
Bellotti, P. *et al. J. Am. Chem. Soc.* **2022**, *144*, 15662.

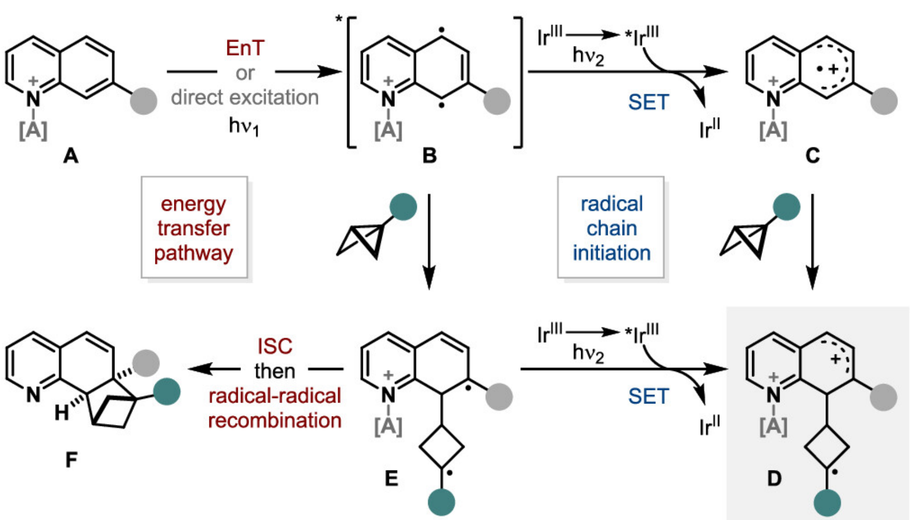
SET at Long-lived Triplet State: Chain Reaction

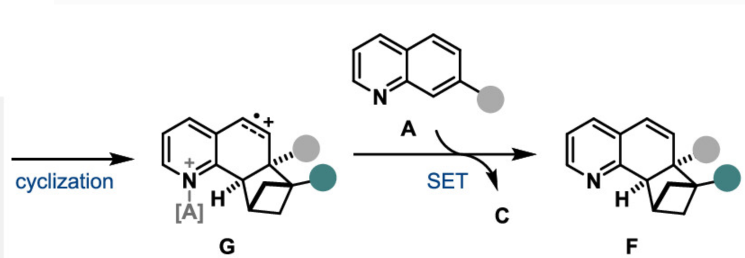


[A] = none, Φ = 0.20	**[A]** = $Sc(OTf)_3$, Φ = 8.8
[A] = *p*-TsOH·H_2O, Φ = 7.7	**[A]** = $Sc(OTf)_3$, no **Ir-F**, Φ = 0.48



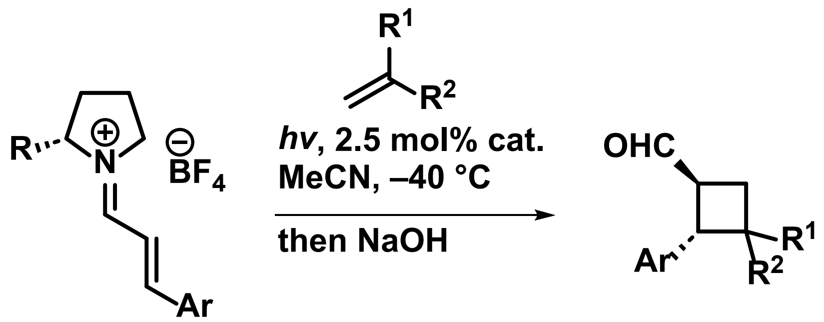
entry	PC (2 mol%)	$E_{1/2}$ ($M^*/M^{\bullet -}$) (V)	$E_{1/2}$ ($M^{\bullet +}/M^*$) (V)	E_T (kcal/mol)	**3a** yield (%)	**Chain?!**
1	$[Mes_2Acr(t\text{-}Bu)_2]ClO_4$	+2.00	---	---	1	x
2	$[Ru(bpy)_3](PF_6)_2$	+0.77	−0.81	46.5	<1	x
3	$[Ru(bpz)_3](PF_6)_2$	+1.45	−0.26	48.4	1	x
4	$[Ir(ppy)_2(dtbbpy)](PF_6)$	+0.66	−0.96	49.2	<1	x
5	*fac*-$[Ir(ppy)_3]$	+0.31	−1.73	58.1	<1	x
6	4CzIPN	+1.35	−1.04	~60	17	yes
7	**Ir-F**	+1.21	−0.89	61.8	32	yes
8	*fac*-$[Ir(dFppy)_3]$	+0.34	−1.44	63.5	2	x





Kleinmans, R. *et al*. *J. Am. Chem. Soc.* **2023**, *145*, 12324.

ET vs. EnT: Comparing ΔG?



cat.	$E_{1/2}(M^{n+1}/M^{n}*)$ (V vs. SCE.)	E_T(kcal/mol)	conversion(2 h)	
$Ru(bpz)_3(PF_6)_2$	–0.26	50	100%	EnT only
$Ru(bpy)_3(PF_6)_2$	–0.81	49	100%	EnT and SET
$Ir(ppy)_3$	–1.73	58	<10%	EnT and SET
sub.	–0.83	49		

Hörmann, F. M. *et al. Angew. Chem., Int. Ed.* **2020**, *59*, 9659.

Outline

- Introduction
- E_T-based Selectivity: Stereo- or Chemoselectivity
- Merger of ET and EnT Catalysis
- Summary

Summary and Outlook

- **Different reaction mode for relatively low ISC rate systems**

- **Alkene isomerization:**

$E_{T(adiabatic)}$ for reactivity

$E_{T(vertical)}$ for selectivity

- **ET and SET: compete, circumvent and merge**