EDA复合物在电子转移过程中的应用

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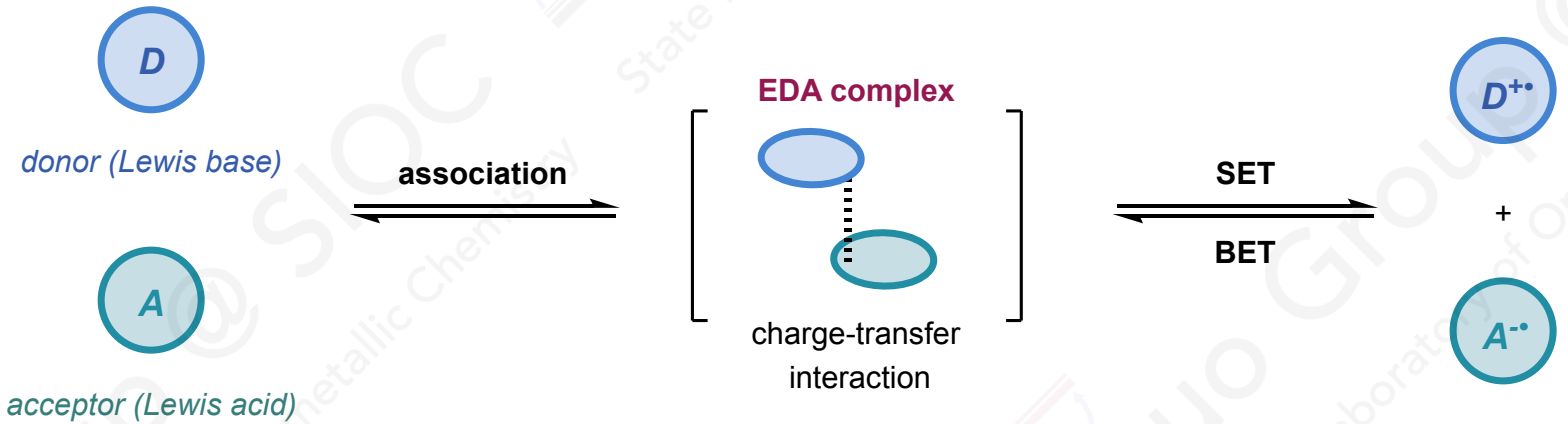
导师：左智伟 研究员

2023.12.1

Electron donor acceptor complex (EDA complex)

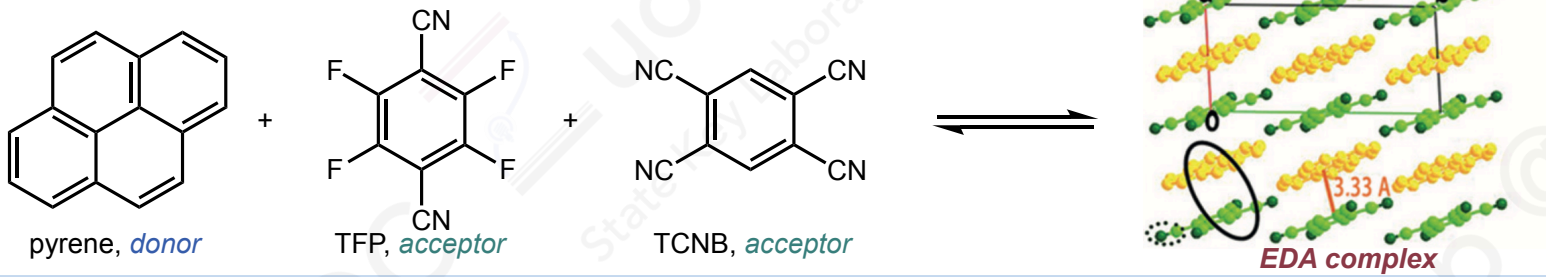
The association of an electron-rich substrate with an electron-accepting molecule can generate a new molecular aggregate in the ground state.

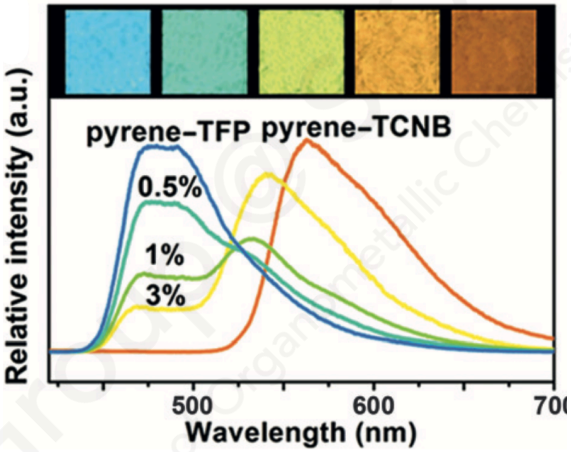


- firstly proposed by Mulliken in 1952
- typically formed between oxidants and reductants (Lewis acid and base)
- No covalent bonding occurs during complex formation, only attraction through intermolecular forces and orbital overlap

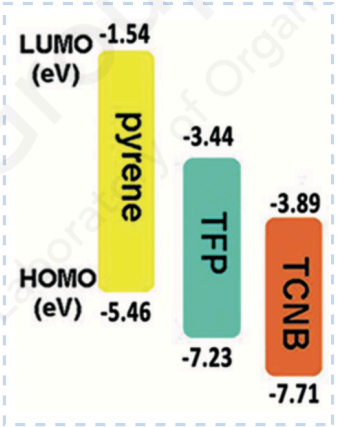
EDA复合物电子转移过程在材料中的应用

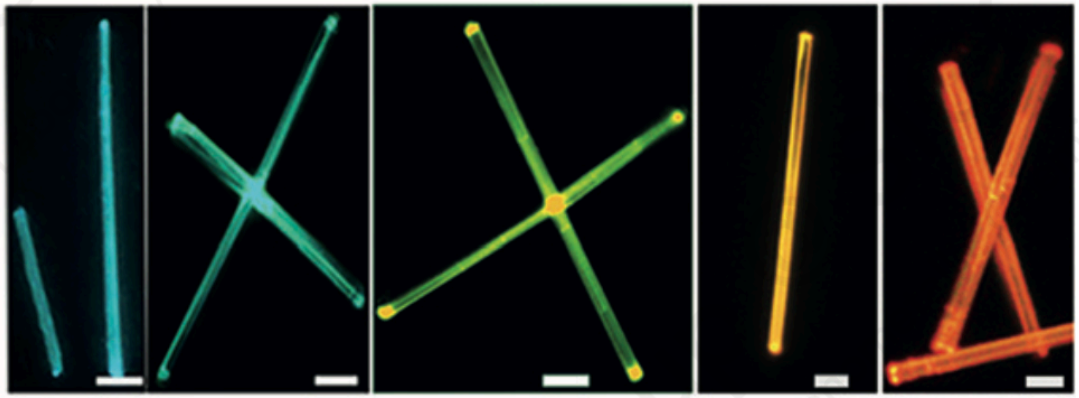
Charge-Transfer Interactions in Organic Light-Harvesting Systems





- 通过共结晶方式得到掺杂不同比例TCNB的EDA复合物
- 掺杂不同比例TCNB的EDA复合物产生不同EDA band





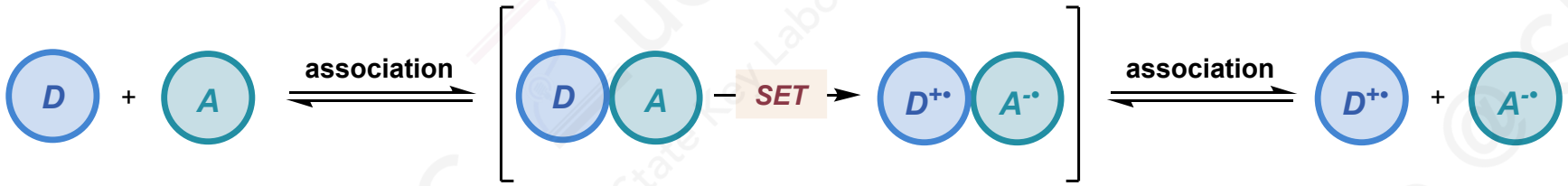
光致发光材料

- 荧光发射光谱取决于TCNB掺杂比例

Hu, W. et al. *Angew. Chem. Int. Ed.* **2017**, *56*, 10352 –10356.

电子转移过程的分类

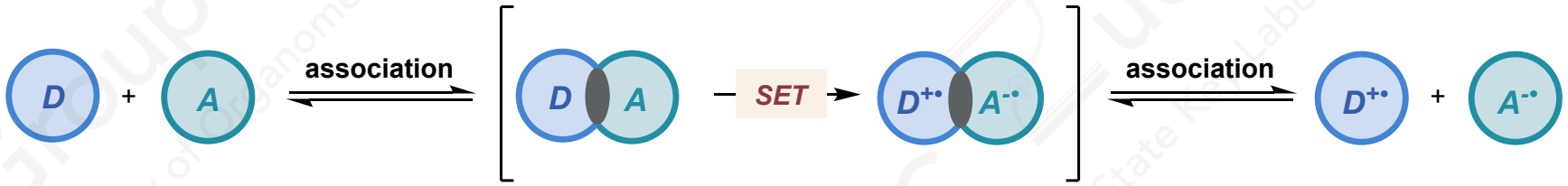
❑ Outer Sphere Electron Transfer



$r_{DA} = 5.0 - 6.0$ Å

- 电子转移步为决速步
- 非绝热过程

❑ Inner Sphere Electron Transfer



$r_{DA} = 3.0 - 3.3$ Å

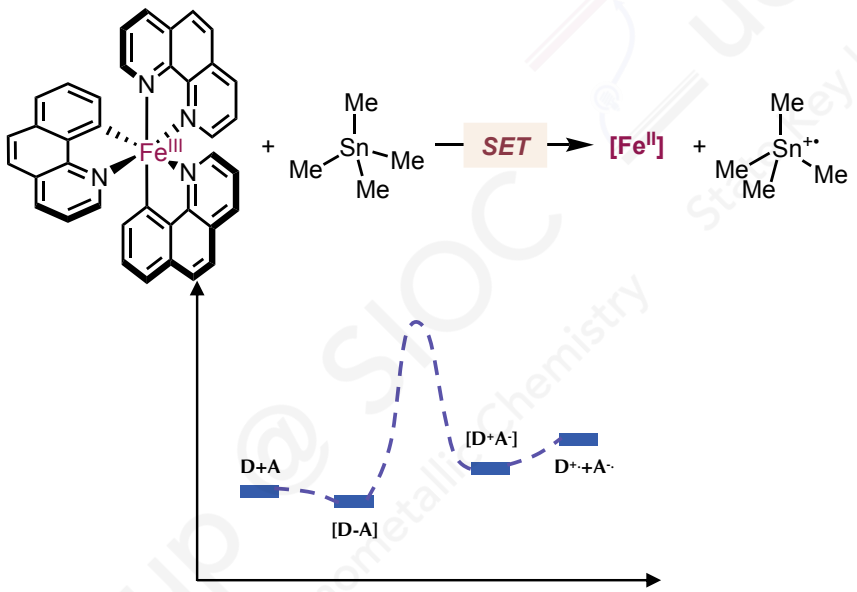
- 电子转移步可能不是决速步
- 绝热过程

Paixaõ, M.W. et al. *ACS catal.* **2016**, *6*, 1389–1407.

❑ EDA复合物通常发生内球电子转移反应

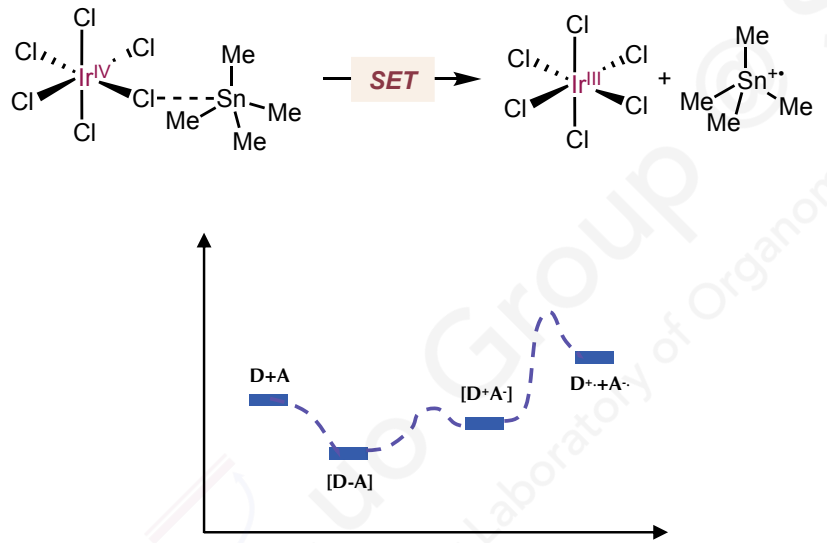
电子转移过程的分类

Outer Sphere Electron Transfer



外球机制只需距离靠近

Inner Sphere Electron Transfer



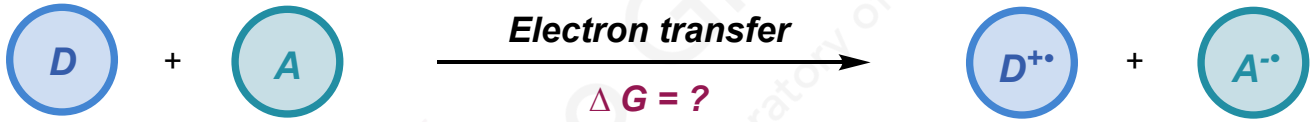
内球机制需要形成桥键等弱相互作用

形成EDA复合物后其偶极矩、溶解度、电导率和晶体结构等变化都可能影响电子转移

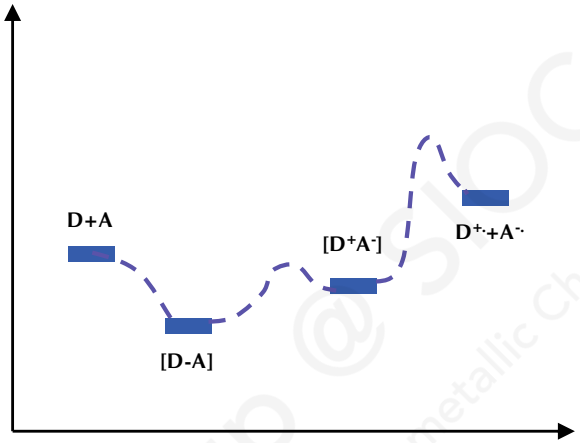
评估EDA复合物性质：X射线晶体衍射

- ❑ 评估D和A的哪些轨道用于CT稳定
- ❑ 提供了D–A距离，与范德华半径和共价键距离进行比较
- ❑ 评估D和A内部结构的变化

EDA复合物电子转移过程中的热力学研究



❑ 根据能斯特方程计算反应自由能

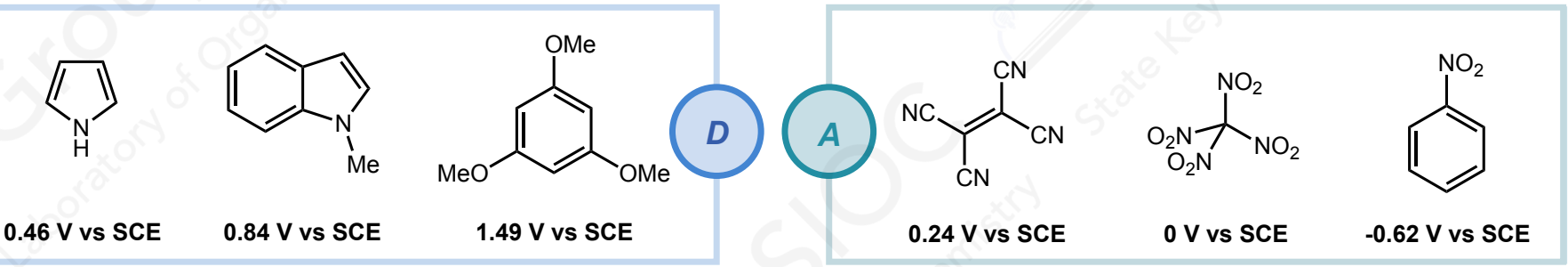


$$\Delta_{et}G^{\circ} = N_A[e(E^0(D^{+\bullet}/D) - E^0(A/A^{-\bullet})) + w(D^{+\bullet}, A^{-\bullet}) - w(D, A)] - \Delta E_{0,0}$$

$E^0(D^{+\bullet}/D) - E^0(A/A^{-\bullet})$ ： $E^0_{red}(A) - E^0_{red}(D)$

$w(D^{+\bullet}, A^{-\bullet})$ $w(D, A)]$ ：电荷分离功

$\Delta E_{0,0}$ ：EDA复合物基态到激发态能量

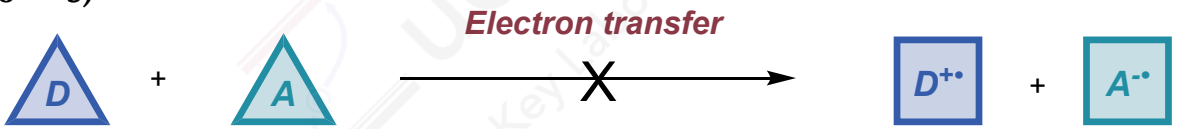


Kochi, J. K. et al. *J. Am. Chem. Soc.* **1997**, *119*, 9393–9404.

EDA复合物电子转移反应是否发生？什么条件能够激发电子转移反应？

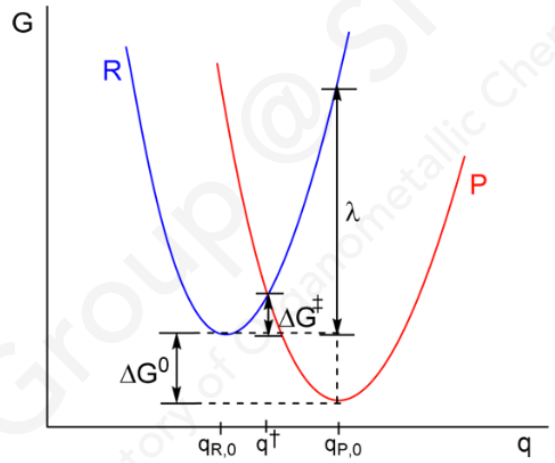
电子转移过程中的动力学研究

- **Franck-Condon principle : Electronic transitions (~10^{-16} s) are much faster than nuclear vibrations (~10^{-13} s)**



Eyring transition state theory 预测势能面和结构的关系在电子转移反应中不适用

Outer Sphere Electron Transfer



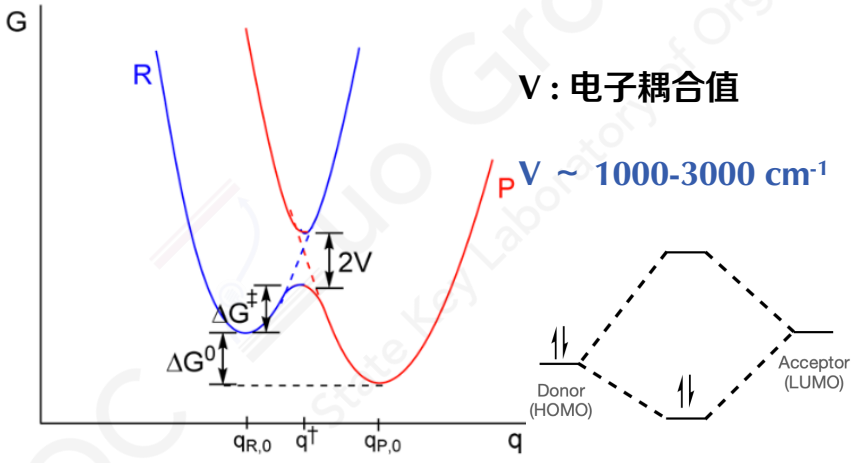
电子转移:
势能面发生切换

λ : 垂直跃迁能量

V ~ 100-300 cm^{-1}

$\Delta G^{\ddagger} = \lambda/4$

Inner Sphere Electron Transfer



V : 电子耦合值

V ~ 1000-3000 cm^{-1}

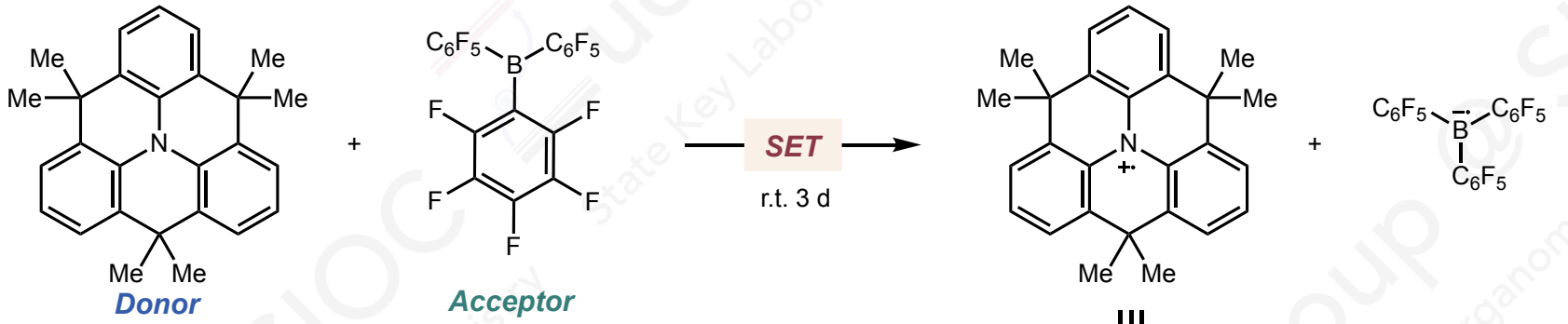
$\Delta G^{\ddagger} = (\lambda - 2V)^2/(4\lambda)$

Kochi, J. K. et al. *Acc. Chem. Res.* **2008**, *41*, 641–653.

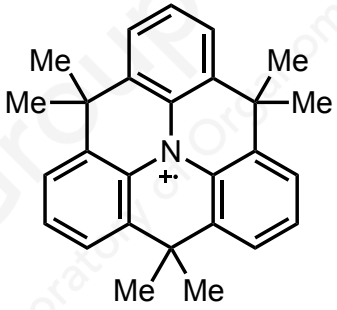
❑ EDA复合物电子转移动力学还与D、A本身性质，π体系大小，溶剂化等因素有关

EDA复合物的激发模式

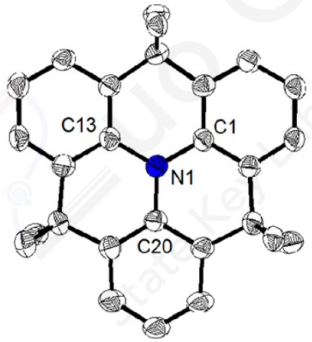
❑ 加热条件激发EDA复合物电子转移



EPR specture of N radical



a^N 9.40 G
a^H = 3.04 G, 0.71 G



首个EDA复合物发生单电子转移的直接实验证据

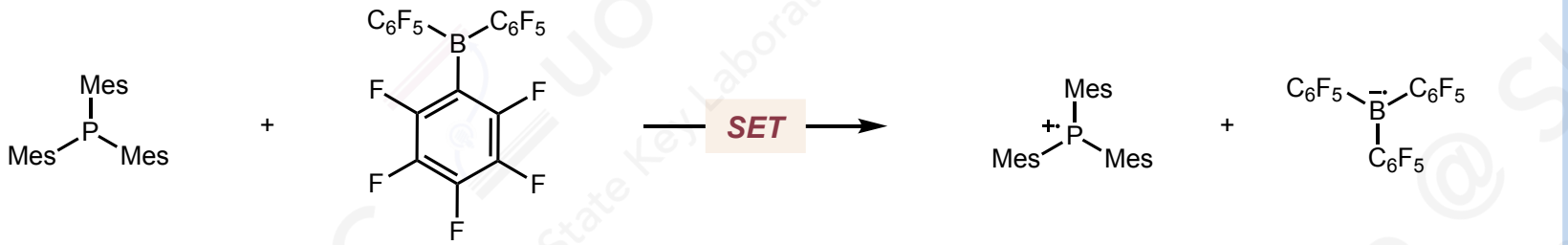
electron affinity of $B(C_6F_5)_3$: 3.03 eV

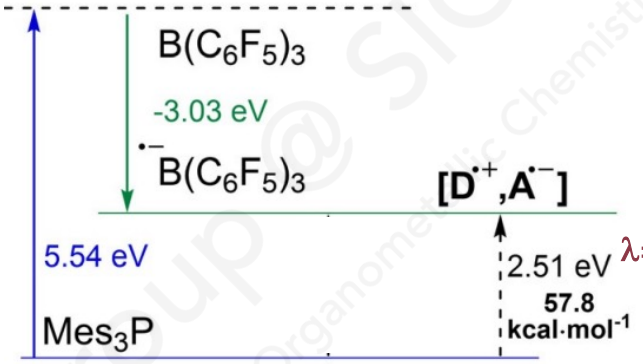
ionization energy of donor : 3.30 eV

Wang, X. et al. *J. Am. Chem. Soc.* **2013**, *135*, 14912–14915.

EDA复合物的激发模式

❑ 光照条件激发EDA复合物电子转移





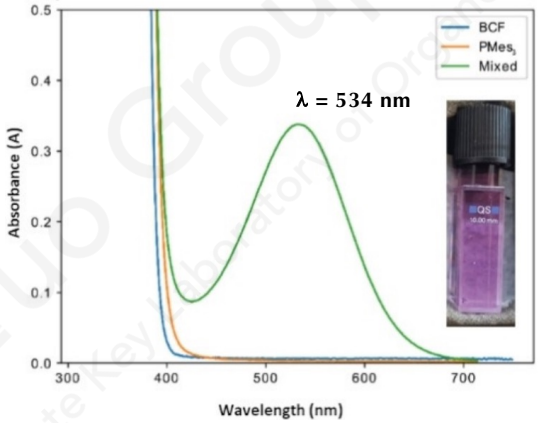
electron affinity of $B(C_6F_5)_3$: 3.03 eV

ionization energy of $P(Mes)_3$: 5.54 eV

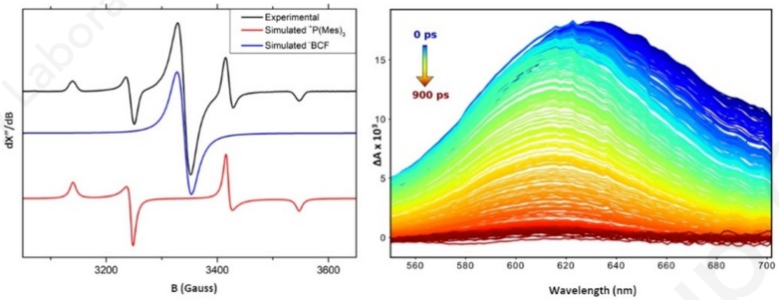
加热条件无法完成激发

λ= 400-800 nm, ΔE = 71.4-35.7 kcal/mol

可见光区域能量较匹配



EPR and TA specture



EPR : 颜色变化来自EDA复合物的形成而不是产生自由基

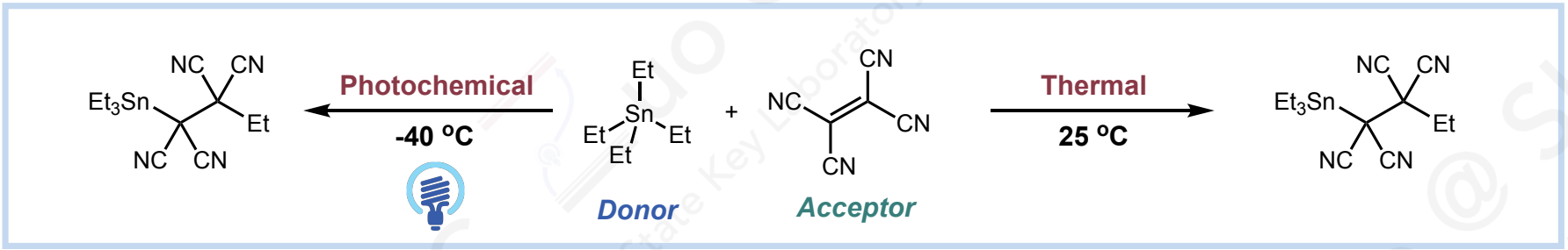
TA : lifetime of the radical ion $PMes_3/B(C_6F_5)_3$: 6 ps

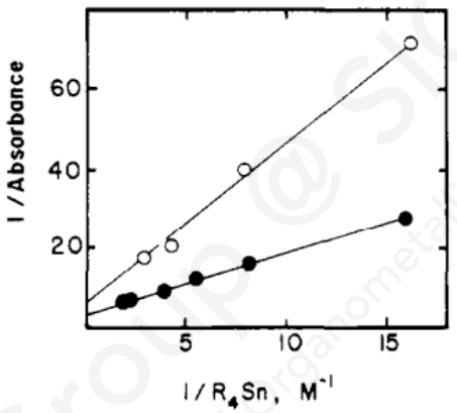
SET之后发生快速的BET， 绝大多数平衡于EDA复合物一侧

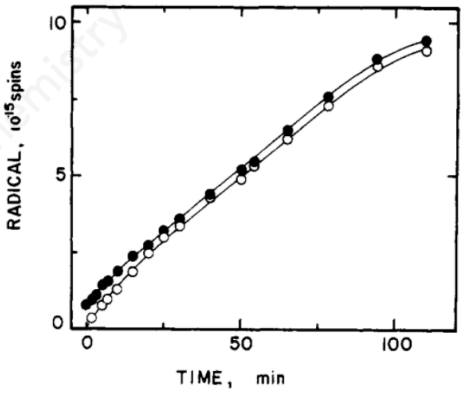
Slootweg, J. C. et al. *Chem. Eur. J.* **2020**, *26*, 9005–9011.

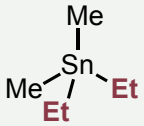
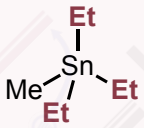
EDA复合物的激发模式

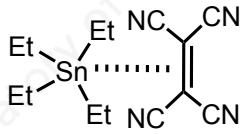
❑ 光照与加热条件激发过程比较



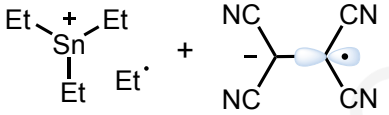




Organotin	Method	Product Ratio (Et:Me)
	Thermal	7:1
	Photo.	7:1
	Thermal	11:1
	Photo.	11:1



➢ UV-vis光谱证明EDA复合物加和比例为1:1



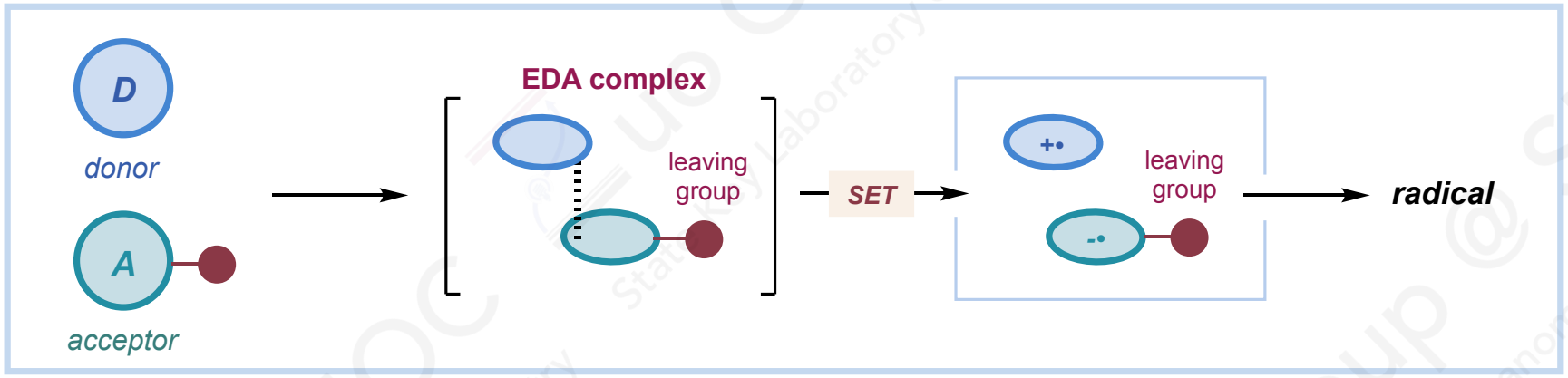
➢ 低温EPR实验证明两种自由基以相同的速率生成

➢ 使用不同有机锡试剂时，不同激发模式得到相同选择性产物

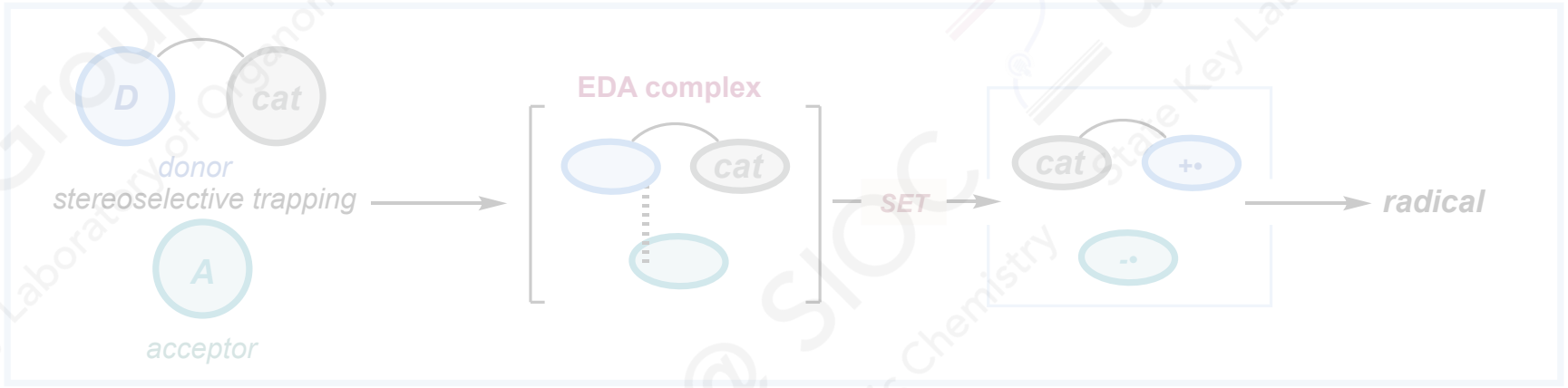
Kochi, J. K. et al. *J. Am. Chem. Soc.* **1979**, *101*, 5961-5972.

❑ EDA复合物热激发和光激发电子转移经历相同机理

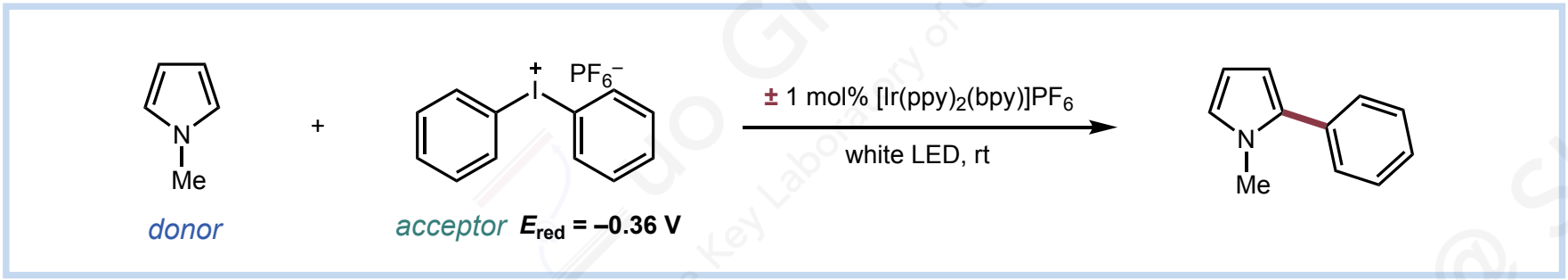
一、化学计量EDA电子转移反应



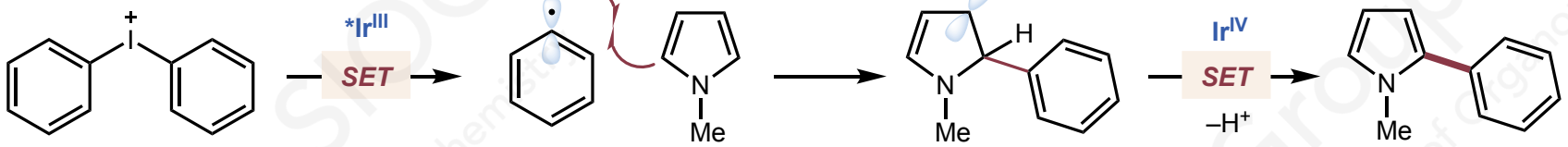
二、催化EDA电子转移反应



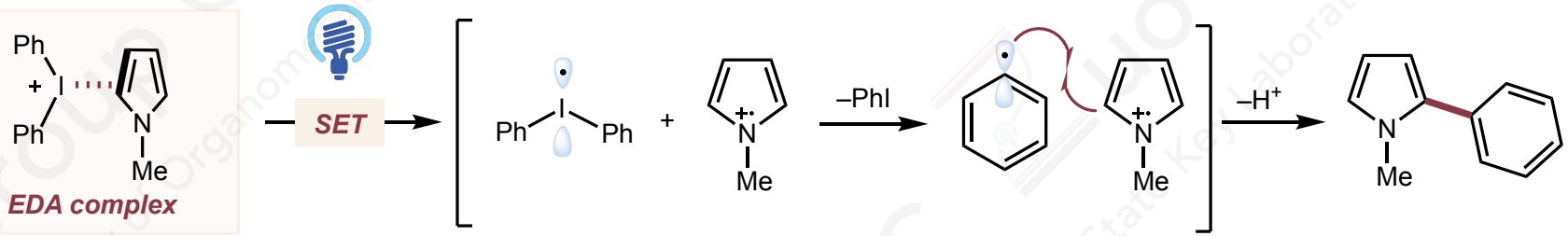
Stoichiometric EDA complex: C–C Bond formation

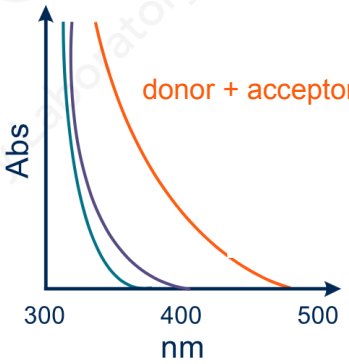


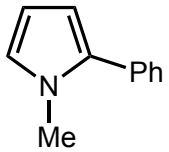
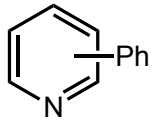
Photocatalytic Mechanism



EDA Mechanism



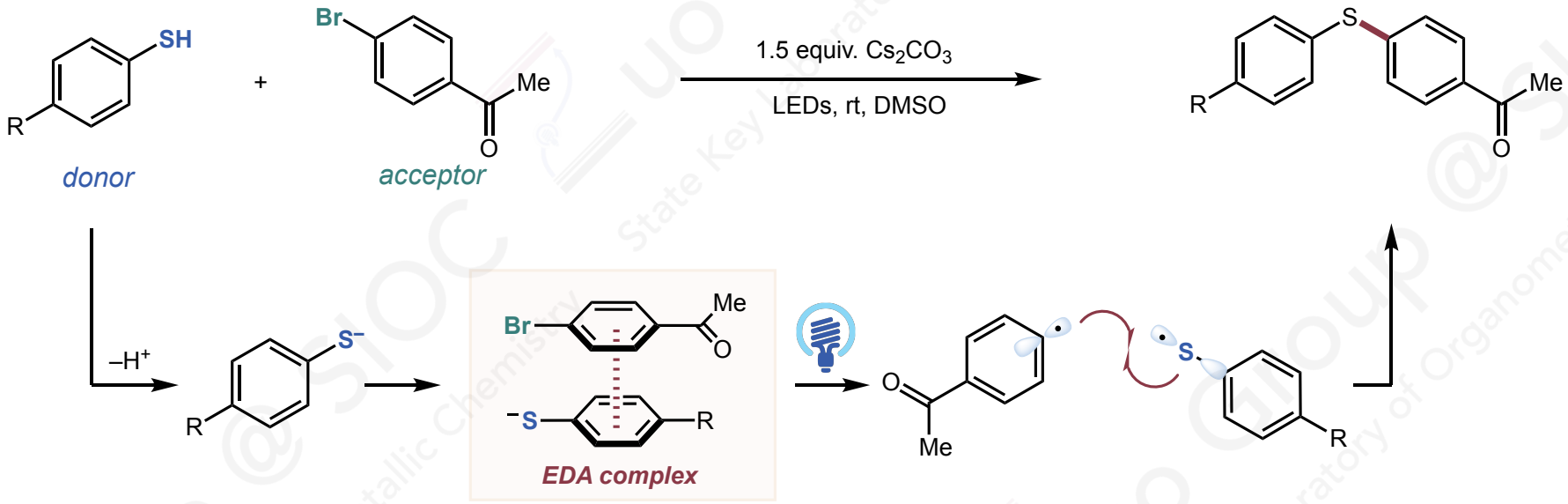


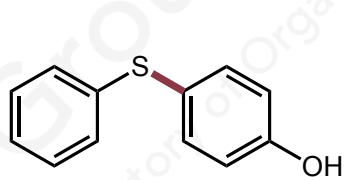
		with $[Ir(ppy)_2(bpy)]PF_6$	without $[Ir(ppy)_2(bpy)]PF_6$
	E_{ox} = 1.2 V	88% yield	54% yield
	E_{ox} = 1.8 V	57% yield (54:30:16)	9% yield (56:44:0)

Chatani, N. et al. *Chem. Lett.* **2013,** *42*, 1203-1205.

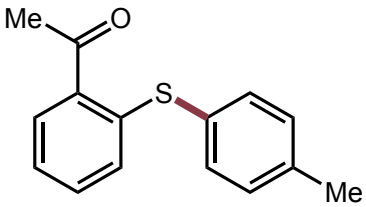
Stoichiometric EDA complex: C–S Bond formation

Visible-Light-Promoted C–S Cross-Coupling via Intermolecular Charge Transfer

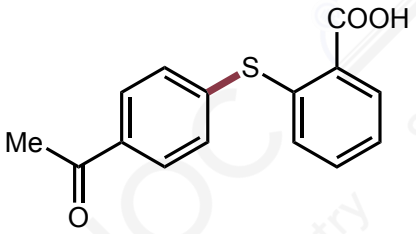




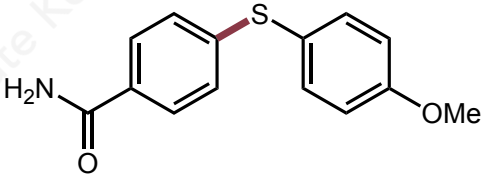
25% yield



X = I, 76% yield, 1 h
X = Cl, 82% yield, 12 h



64% yield

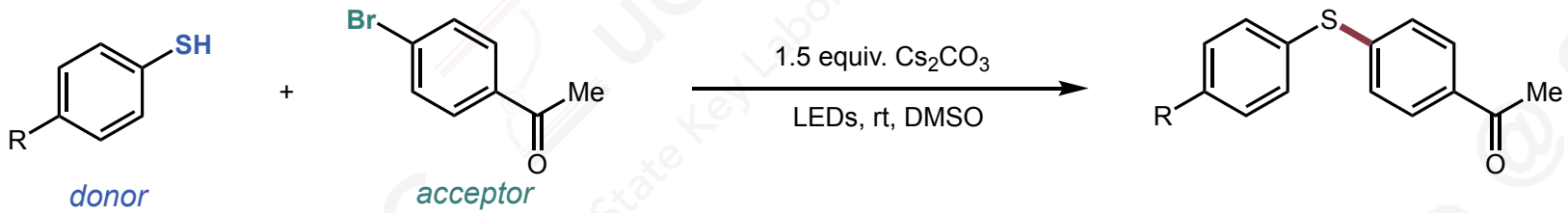


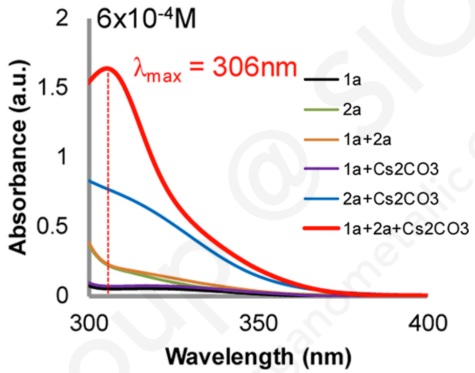
80% yield

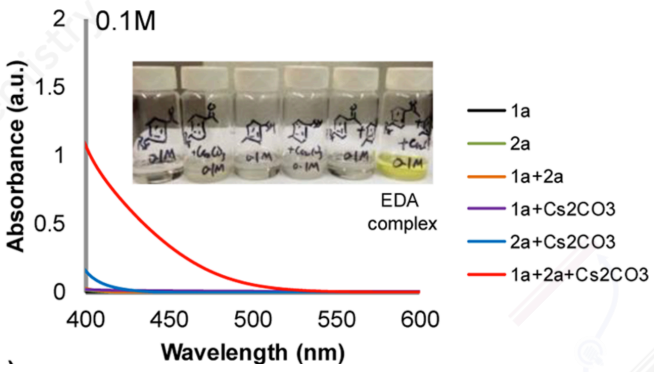
Miyake, G. M. et al. *J. Am. Chem. Soc.* **2017**, *137*, 13616-13619.

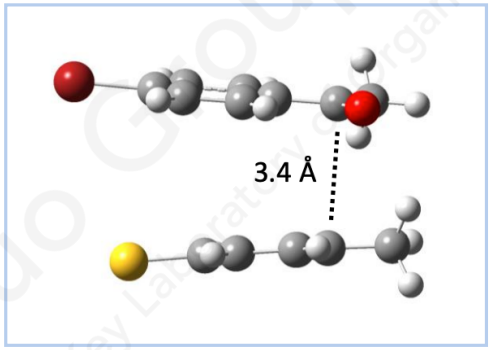
Stoichiometric EDA complex: C–S Bond formation

Visible-Light-Promoted C–S Cross-Coupling via Intermolecular Charge Transfer









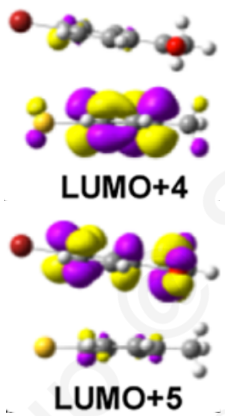
λ = 282 nm

35 % π HOMO-π LUMO+4

硫醇负离子自身跃迁

32 % π HOMO-π LUMO+5

EDA复合物跃迁

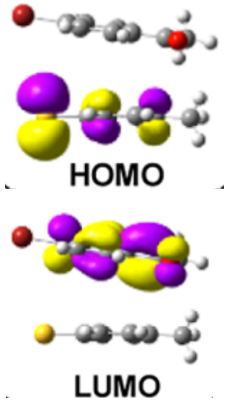


λ = 383 nm

98 % π HOMO-π LUMO

EDA复合物跃迁

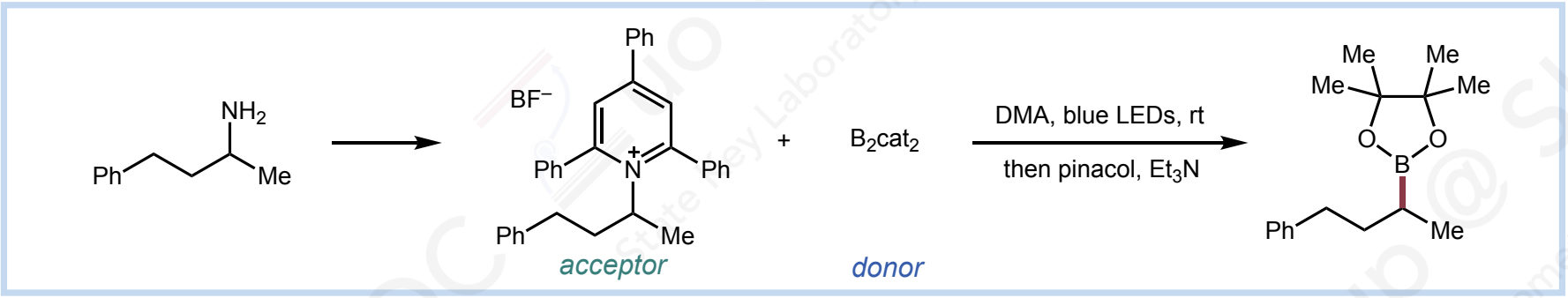
产生可见光区吸收主要原因

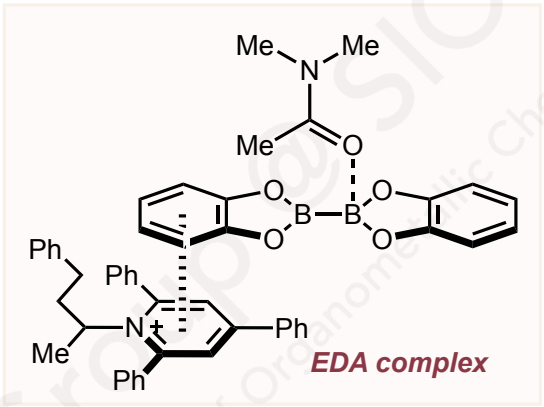


Miyake, G. M. et al. *J. Am. Chem. Soc.* **2017**, *137*, 13616-13619.

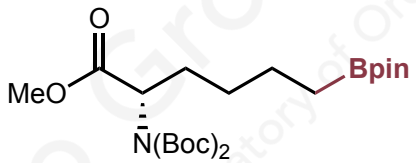
Stoichiometric EDA complex: C–B Bond formation

■ *Photoinduced Deaminative Borylation of Alkylamines*

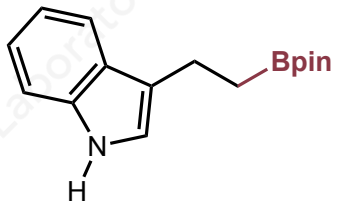




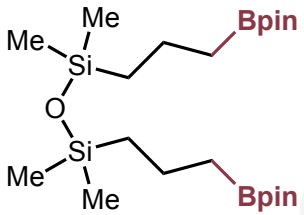
modifications	yield
none	89 %
no light	35 %
no light, 65 °C	72 %



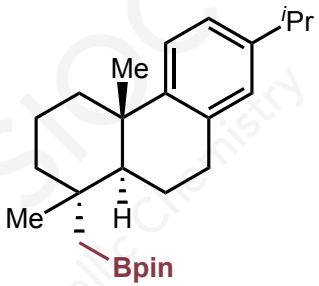
58% yield, 98% ee
from lysine



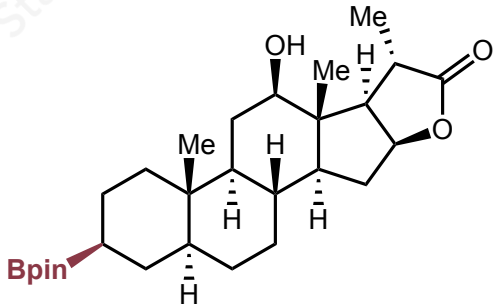
52% yield



64% yield



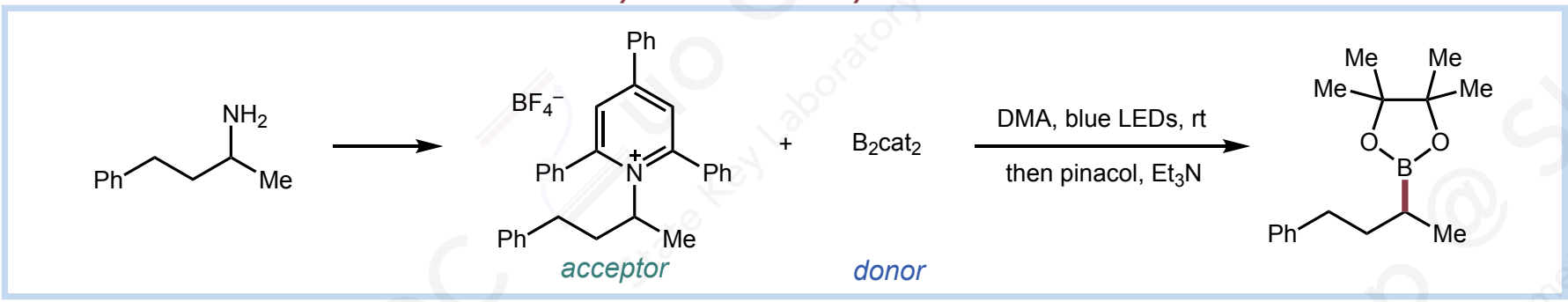
55% yield
from leelamine

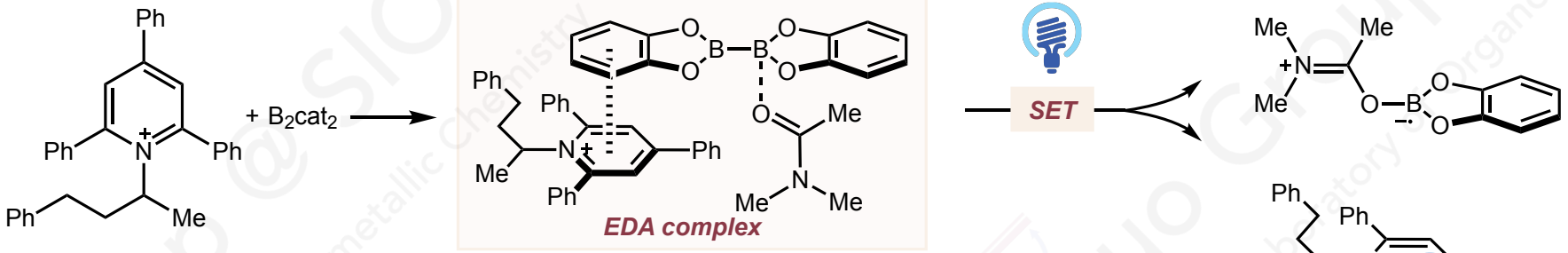


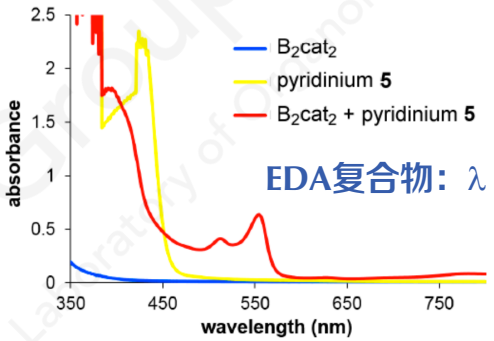
76% yield, 95:5 d.r.
from hecogenin

Stoichiometric EDA complex: C–B Bond formation

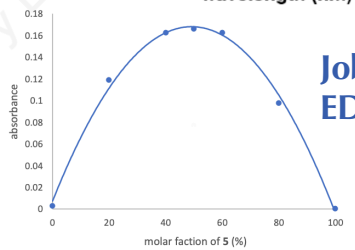
■ *Photoinduced Deaminative Borylation of Alkylamines*



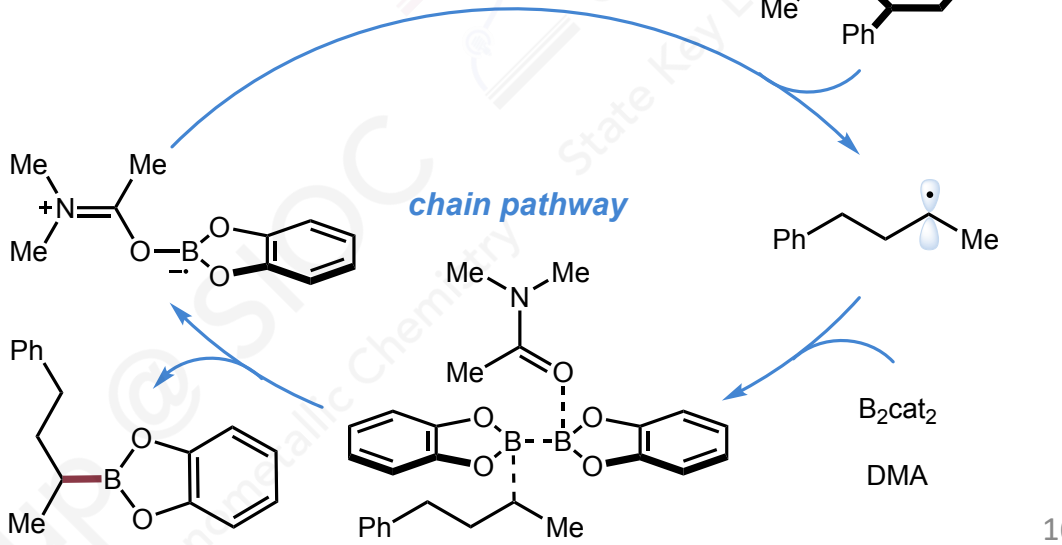




EDA复合物：λ = 550 nm

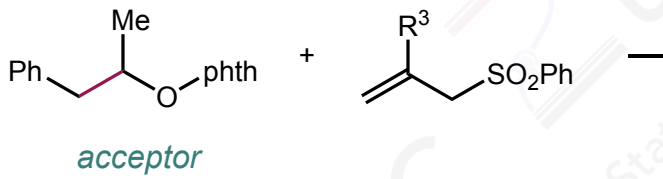


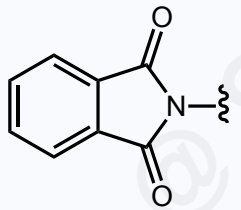
Job's plot:
EDA复合物比例为1:1



Stoichiometric EDA complex: C–C Bond formation

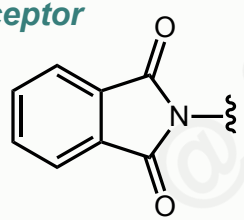
EDA Complex Enables Alkoxyl Radical Generation for C(sp^3)–C(sp^3) Cleavage





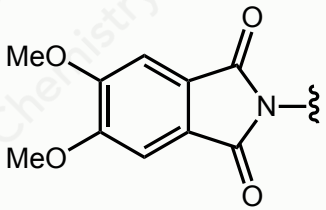
phth

acceptor



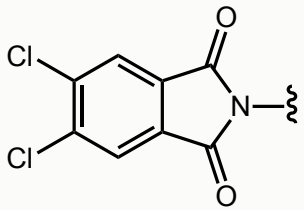
E_{red} = –1.40 V (SCE)

72% yield, >95% conversion



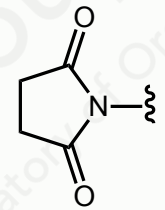
E_{red} = –1.50 V (SCE)

64% yield, 70% conversion



E_{red} = –1.19 V (SCE)

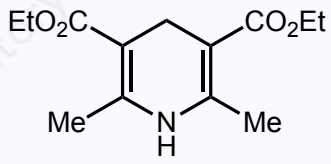
66% yield, >95% conversion



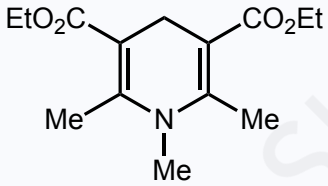
E_{red} = –0.98 V (SCE)

<5% yield, <5% conversion

donor



67% yield, 79% conversion



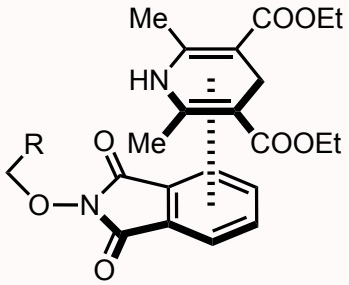
<5% yield, <5% conversion

no light: <5% yield

no light, 50 °C: 28% yield

450 nm LED: 70% yield

475 nm LED: 37% yield

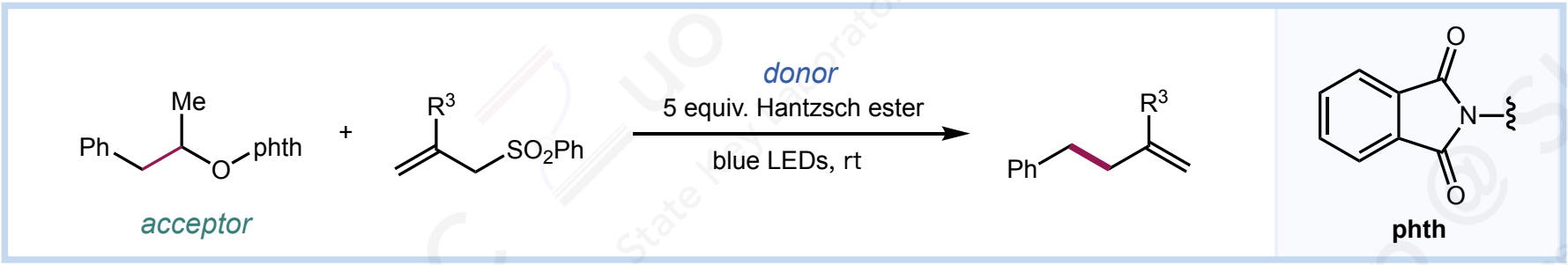


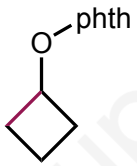
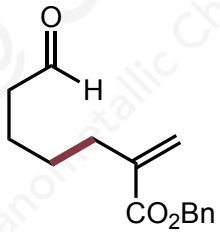
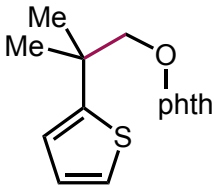
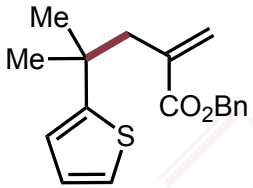
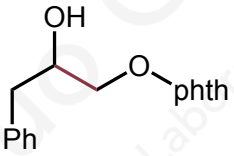
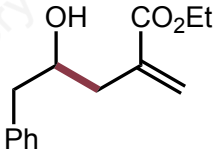
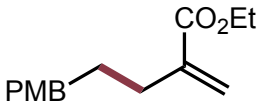
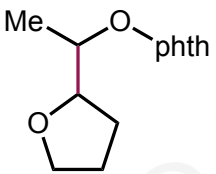
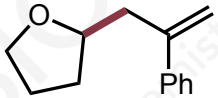
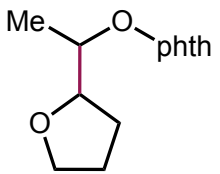
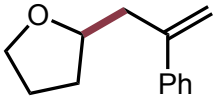
EDA complex

Chen, Y. et al. *Angew. Chem. Int. Ed.* **2017**, *56*, 12619 –12623.

Stoichiometric EDA complex: C–C Bond formation

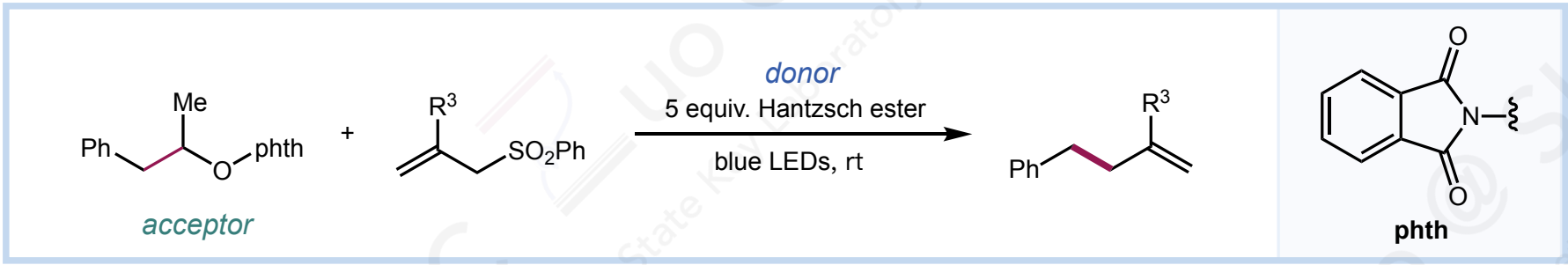
EDA Complex Enables Alkoxyl Radical Generation for C(sp^3)–C(sp^3) Cleavage



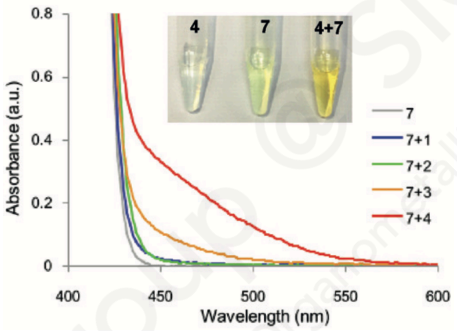
Starting material	Product	Starting material	Product	Starting material	Product
					
61% yield		53% yield		64% yield	
					
71% yield		88% yield		88% yield	

Stoichiometric EDA complex: C–C Bond formation

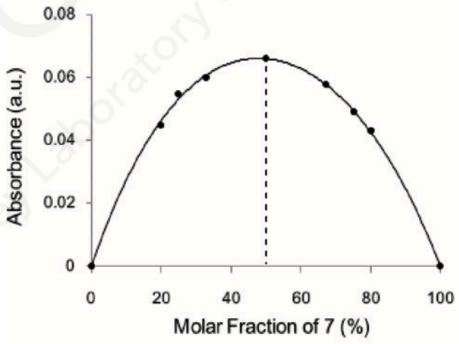
EDA Complex Enables Alkoxyl Radical Generation for C(sp^3)–C(sp^3) Cleavage



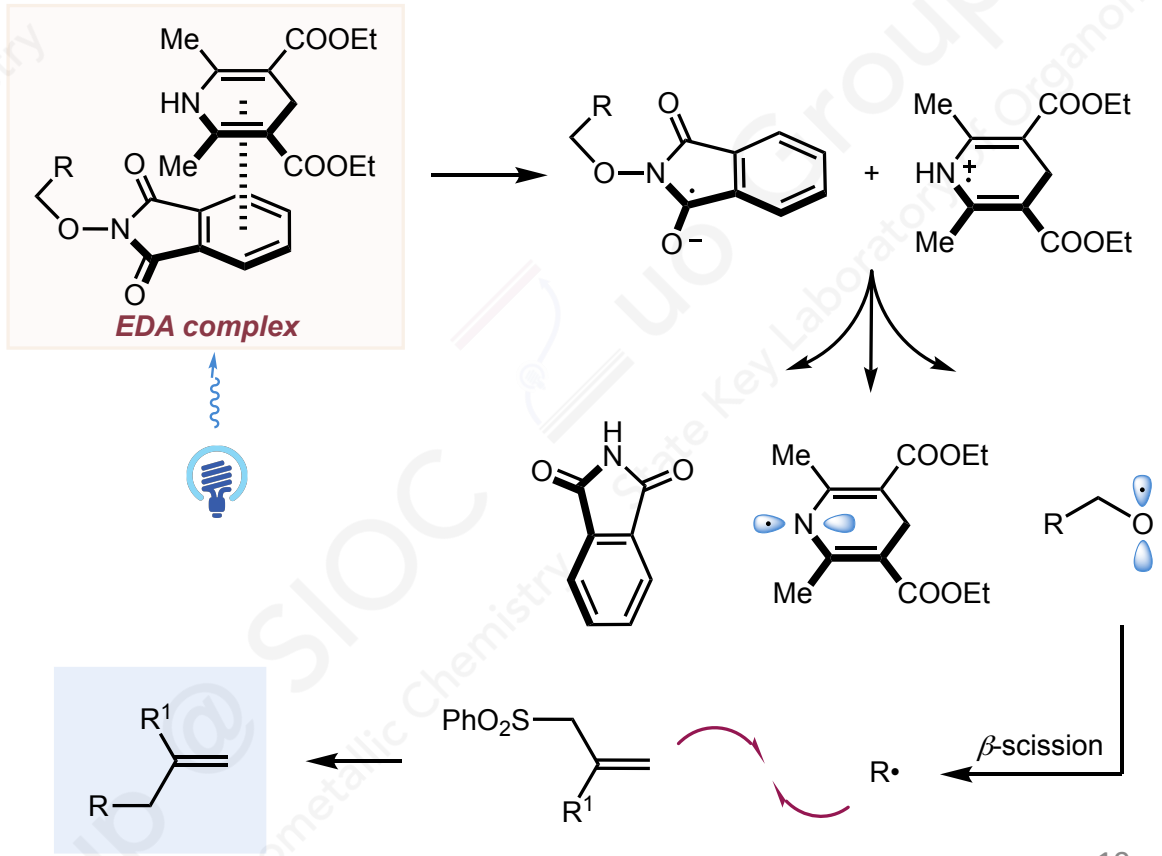
proposed mechanism



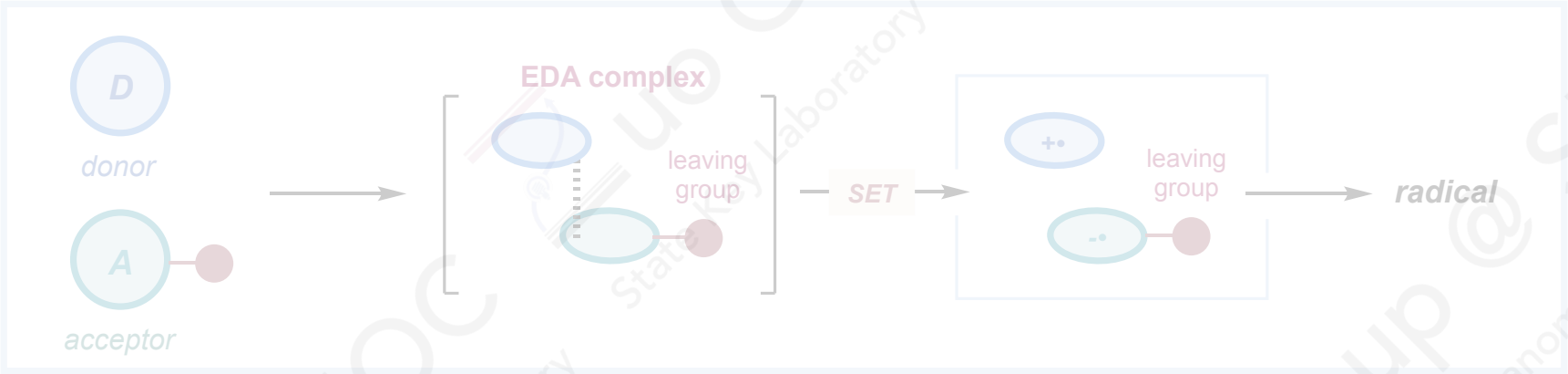
EDA band: λ = 450 nm



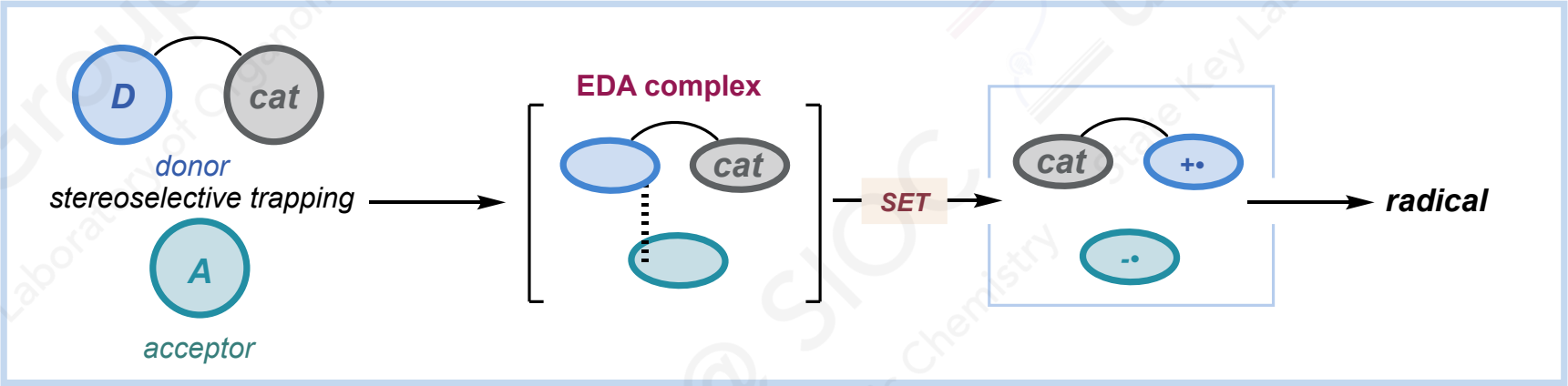
EDA ratio: 1:1



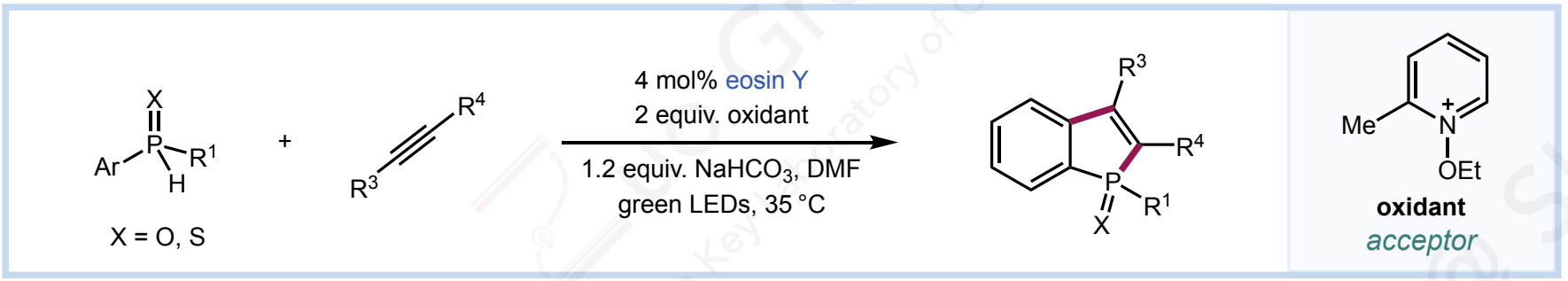
一、化学计量EDA电子转移反应

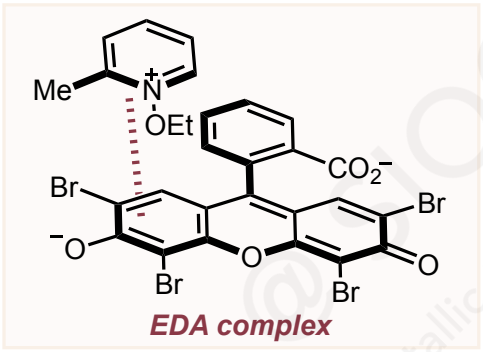


二、催化EDA电子转移反应

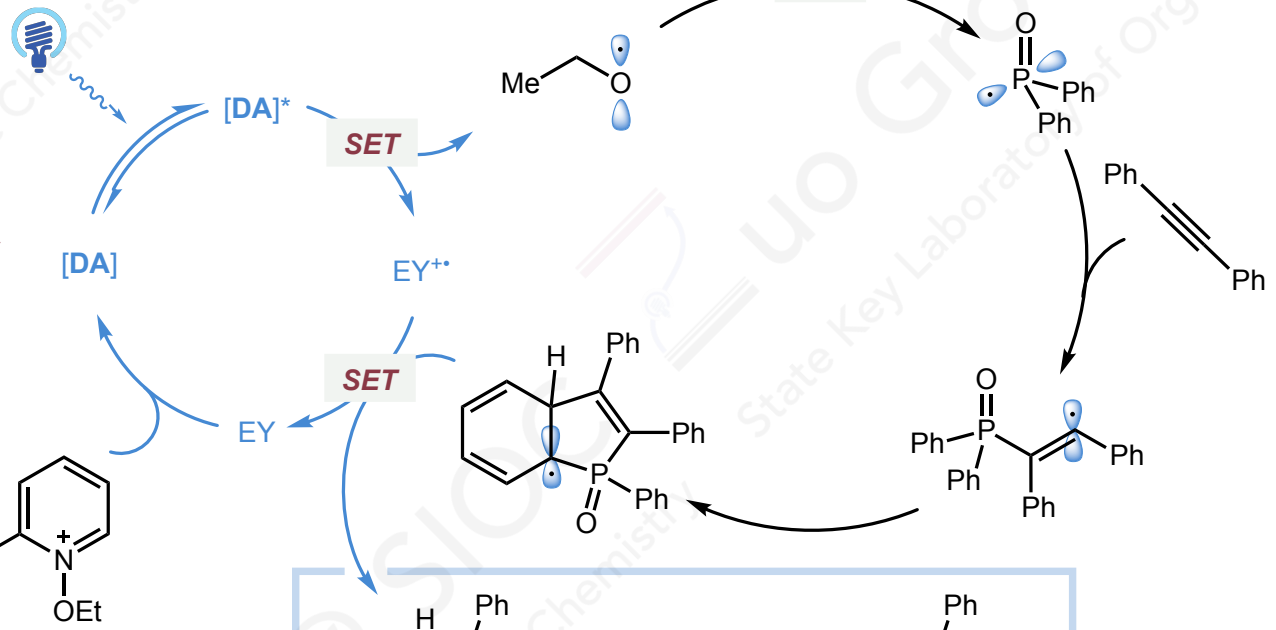


Catalytic EDA complex: Cyclization reaction





characterized by XRD, NMR



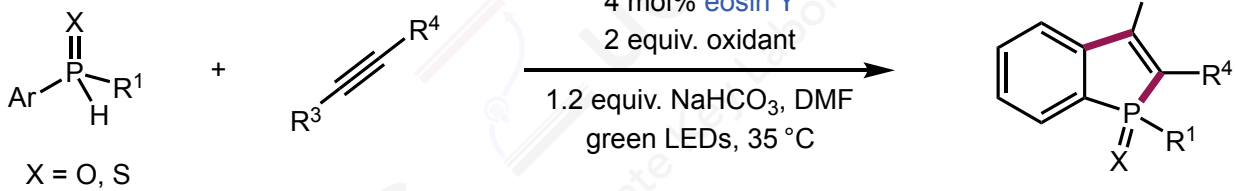
E_{red} (EY) = –1.11 V (SCE)

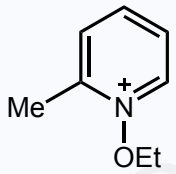
E_{red} (oxidant) = –0.60 V (SCE)

Lakhdar, S. et al. *J. Am. Chem. Soc.* **2016**, *138*, 7436–7441.

Catalytic EDA complex: Cyclization reaction

Visible Light-Photocatalyzed Synthesis of Benzo[b]phosphole Oxides

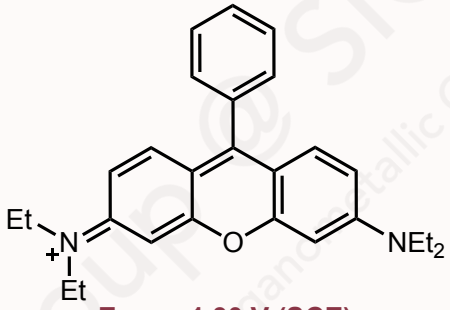




oxidant

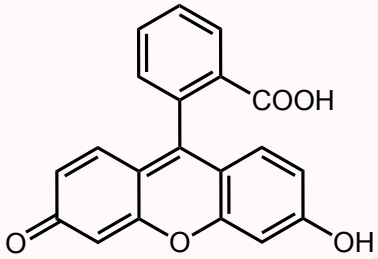
acceptor

氧化电势对EDA复合物SET速率的影响



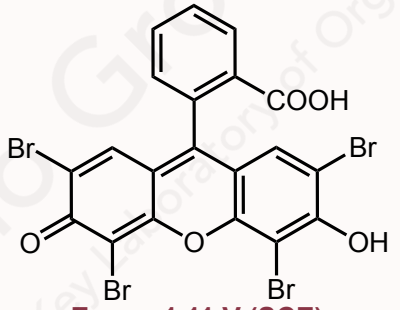
E_{red} = -1.30 V (SCE)

25% yield, 25% conversion



E_{red} = -1.26 V (SCE)

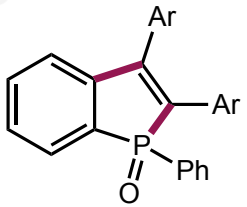
37% yield, 43% conversion



E_{red} = -1.11 V (SCE)

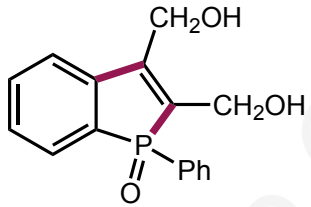
75% yield, 95% conversion

Scope of substrates

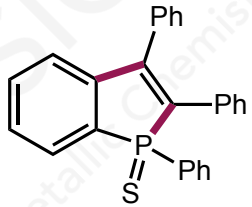


Ar = *p*-OMe, 88% yield

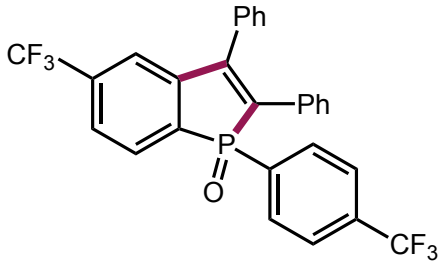
Ar = *p*-CF_3, 64% yield



53% yield



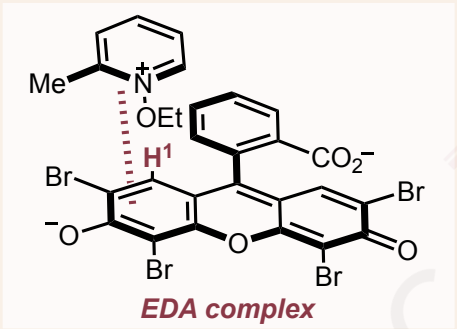
74% yield



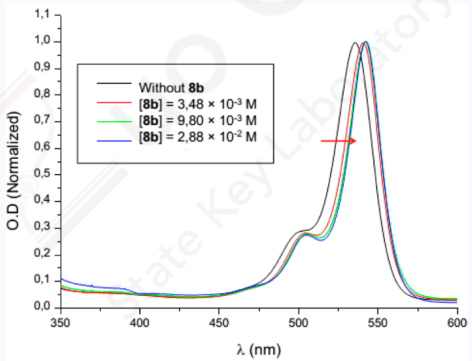
69% yield

Catalytic EDA complex: Cyclization reaction

Mechanistic investigations of Electron transfer with EDA complex

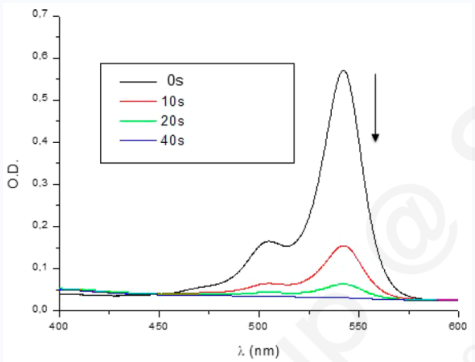


EDA complex

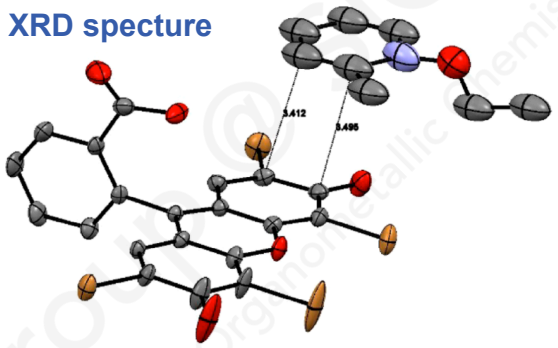


λ = 530 nm

UV-vis

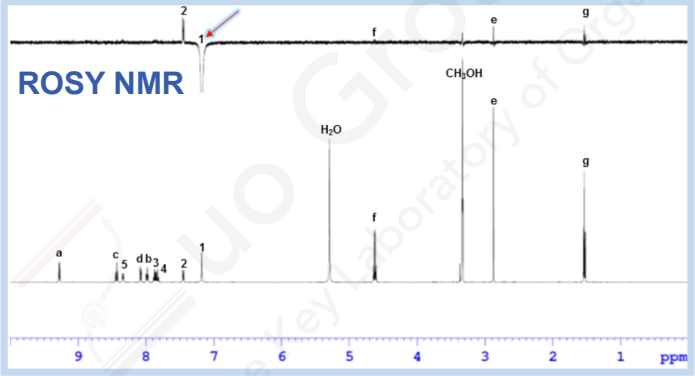


XRD specture

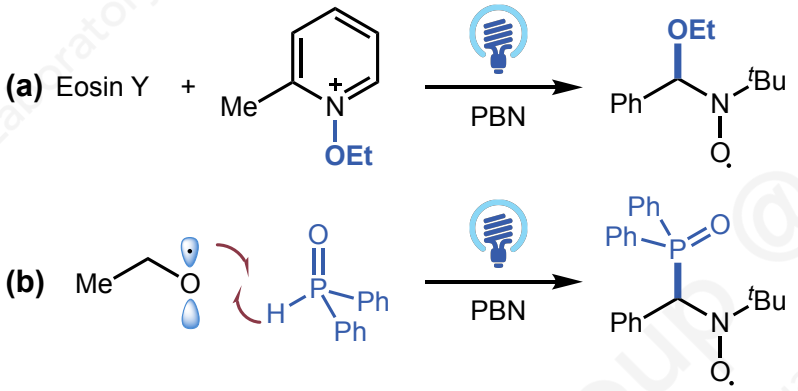


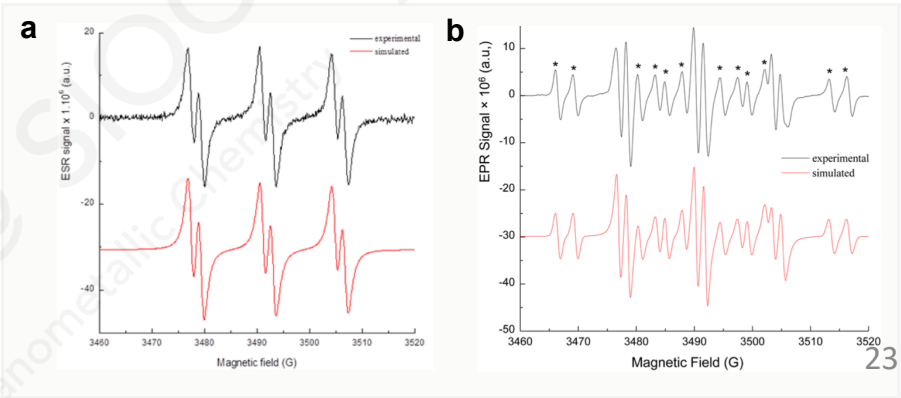
- EDA complex 吸收峰红移
- *XRD: C1–C2 = 3.412 Å*
- *ROSY:* H¹与OEt上H距离接近

ROSY NMR



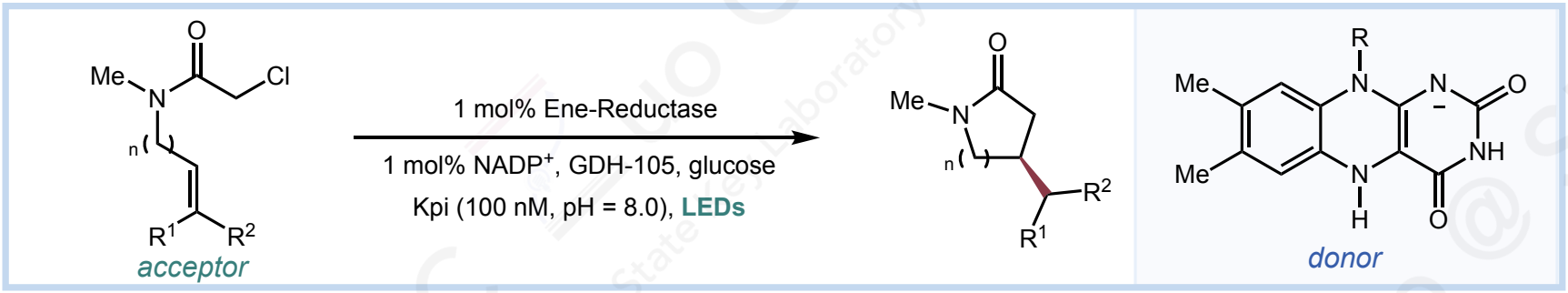
EPR specture

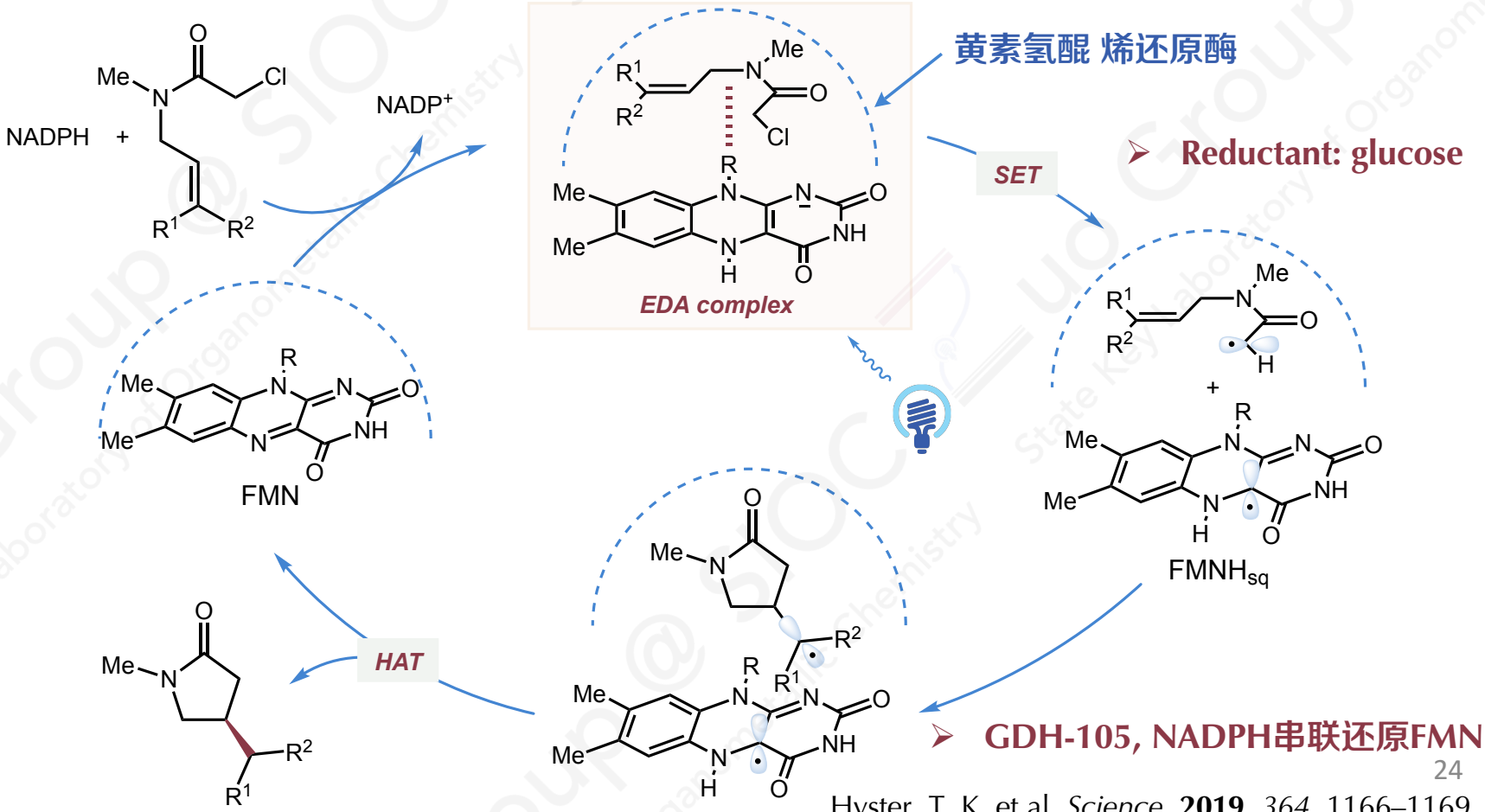




Catalytic EDA complex: Cyclization reaction

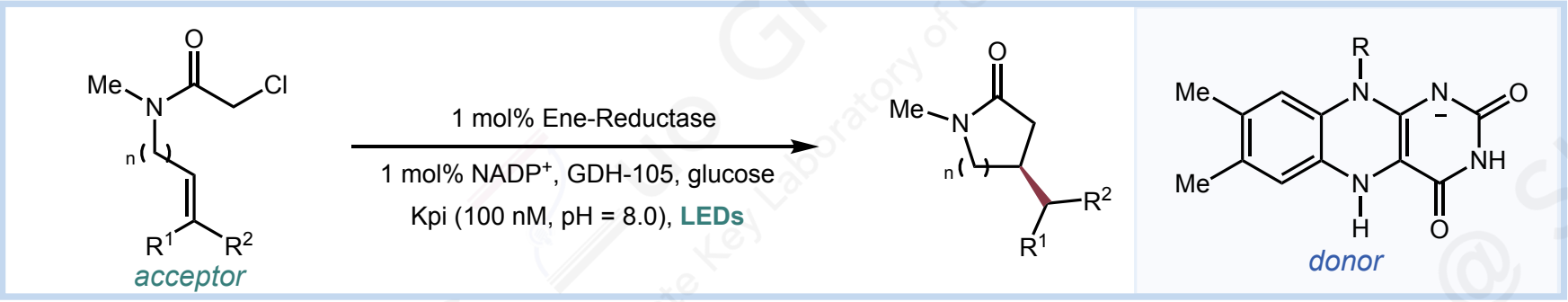
■ *Photoexcitation of flavoenzymes enables a stereoselective radical cyclization*



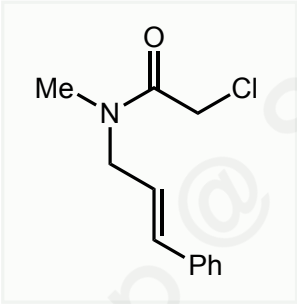


Hyster, T. K. et al. *Science*. **2019**, *364*, 1166–1169.

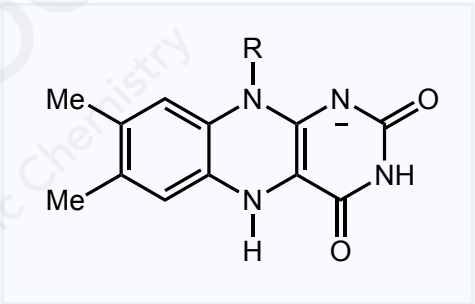
Catalytic EDA complex: Cyclization reaction



■ *Thermodynamics*

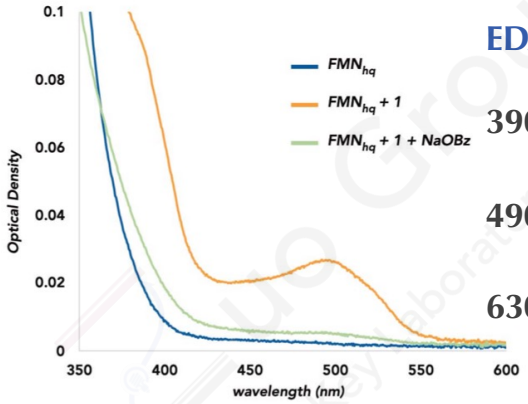


E_{red} (acceptor) = –1.65 V (SCE)



E_{red} (FMN_{hq}) = -0.45 V (SCE)

E_{red} (*FMN_{hq}) = -2.26 V (SCE)



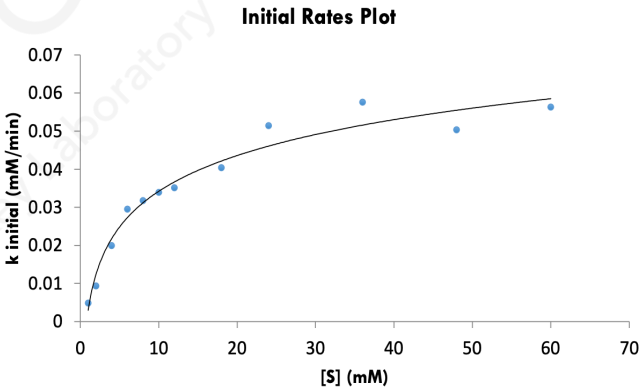
EDA band: 500 nm

390 nm: 42% yield

490 nm: 68% yield

630 nm: 2% yield

■ *Kinetics*



Michaelis-Menten kinetics: K_m = 9.69 mM

$$K_M = \frac{k_{cat} + k_{-1}}{k_1}$$ EDA复合物平衡常数

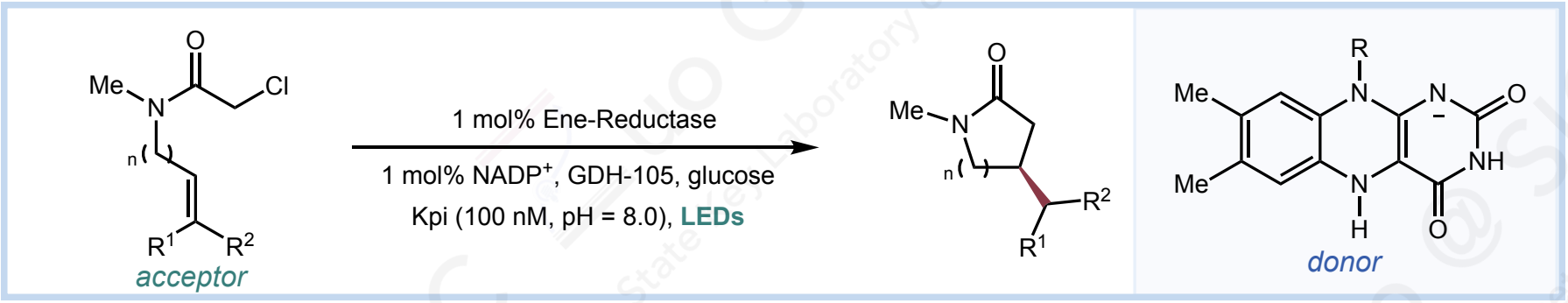
$$D + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [D\text{–}A] \xrightarrow{k_{cat}} [D^{+\bullet}\ A^{-\bullet}]$$

k_{cat}: EDA生成产物的表观一级速率常数

$$\frac{Flux_1}{Flux_2} \cong \frac{k_{cat\,1}}{k_{cat\,2}}$$ 决速步具有光依赖性

Hyster, T. K. et al. *Science*. **2019**, *364*, 1166–1169.

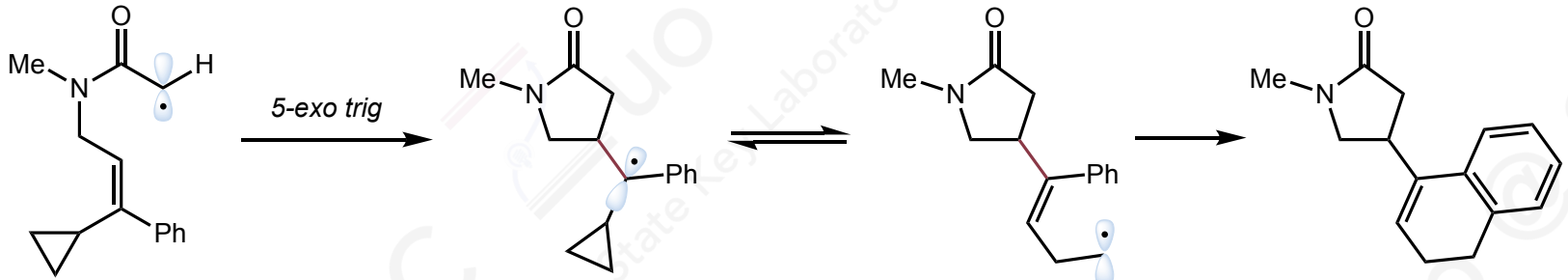
Catalytic EDA complex: Cyclization reaction



Starting material	Product	Starting material	Product	Starting material	Product
6-*exo*	44% yield 86:14 er	5-*endo*	51% yield 93:7 er		67% yield 95:5 er, 87:13 dr
7-*exo*	87% yield 90:10 er	8-*endo*	67% yield 83:17 er		84% yield 99:1 er, 79:21 dr

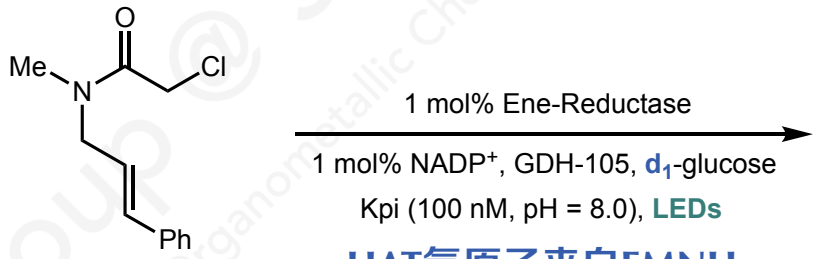
Catalytic EDA complex: Cyclization reaction

■ *Radical clock*

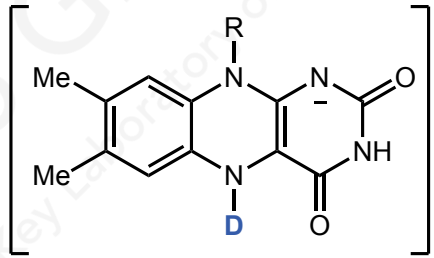


EDA复合物SET过程顺利发生

■ *Isotope labeling*

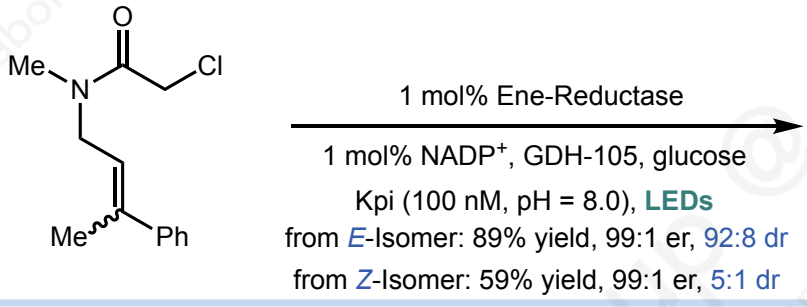


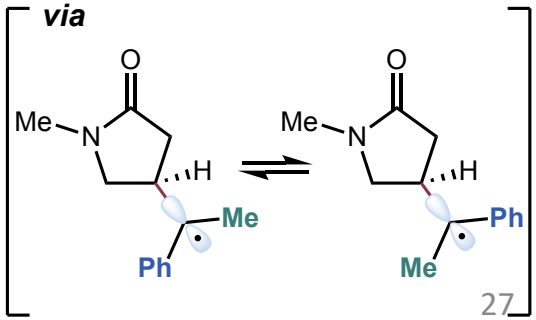
HAT氢原子来自FMNH



formed in situ

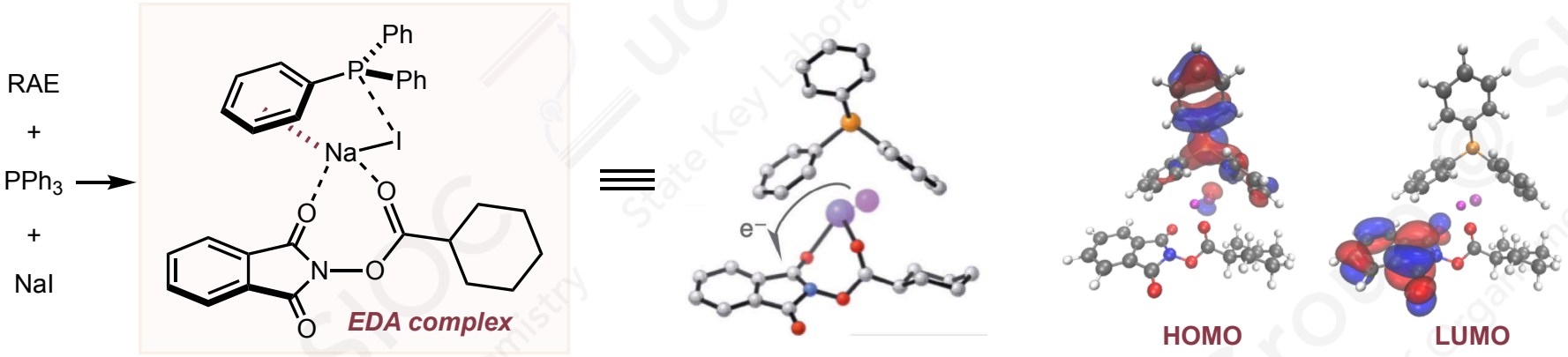
■ *Conformation-selective HAT*





Catalytic EDA complex: C–C Bond formation

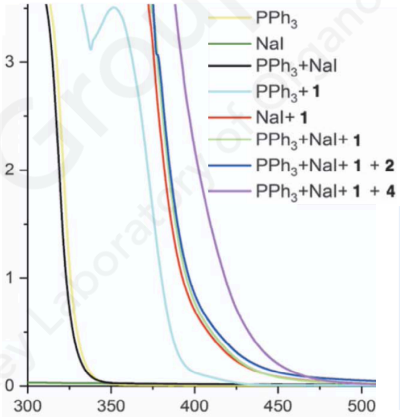
■ *Decarboxylative alkylations mediated by triphenylphosphine and sodium iodide*

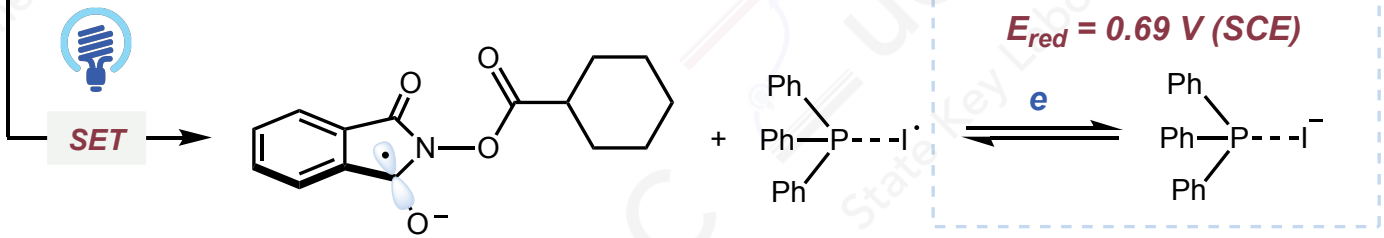


ΔG = -3.8 kcal/mol

Excitation energy = 2.85 eV (436 nm light)

UV-vis specture





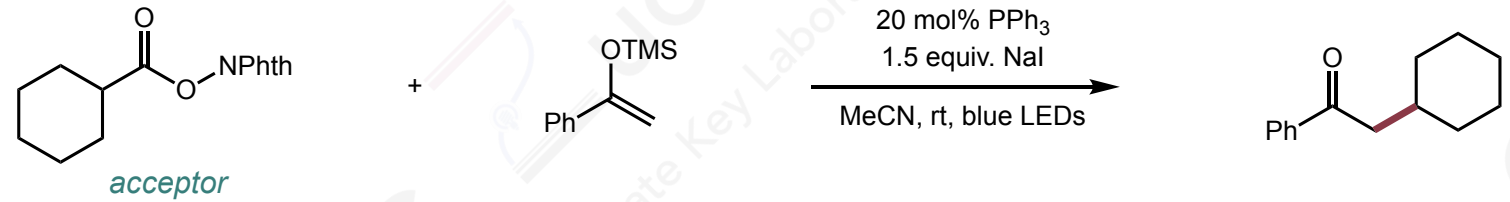
w/o PPh_3	ΔG = 56.2 kcal/mol
with PPh_3	ΔG = 44.3 kcal/mol

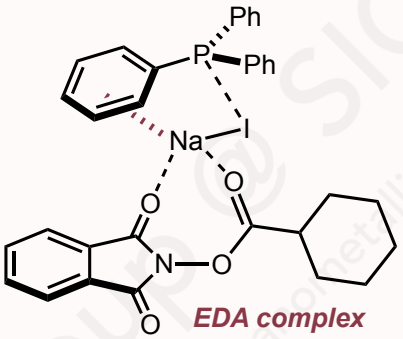
w/o PPh_3	$\Delta G^{\ddagger}$ = 86.5 kcal/mol
with PPh_3	$\Delta G^{\ddagger}$ = 61.2 kcal/mol

Fu, Y. et al. *Science*. **2019**, *363*, 1429–1434.

Catalytic EDA complex: C–C Bond formation

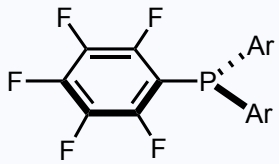
Decarboxylative alkylations mediated by triphenylphosphine and sodium iodide



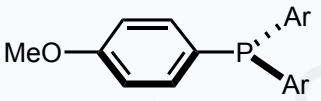


氧化电势对EDA复合物电子转移速率的影响

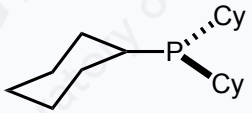
donor



<5% yield



85% yield



32% yield

EDA band

λ = 520 nm	<5% yield
λ = 440 nm	81% yield
λ = 365 nm	36% yield

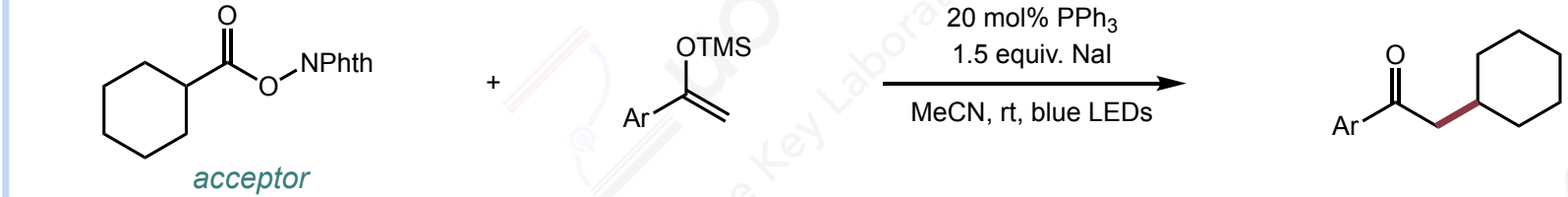
EDA复合物稳定性对反应的影响

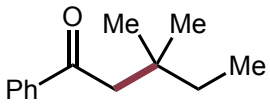
NaI	LiI	KI	*n*-Bu_4NI
82% yield	74% yield	50% yield	<1% yield
ΔG = -3.8 kcal/mol	ΔG = -1.1 kcal/mol	ΔG = -2.9 kcal/mol	

Fu, Y. et al. *Science*. **2019**, *363*, 1429–1434.

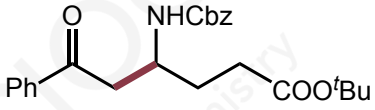
Catalytic EDA complex: C–C Bond formation

■ *Decarboxylative alkylation of silyl enol ether*

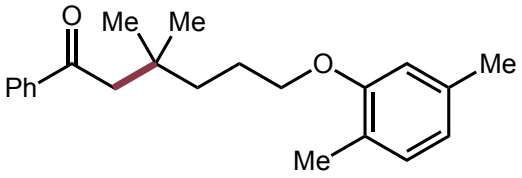




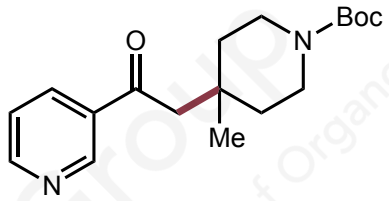
79% yield



88% yield

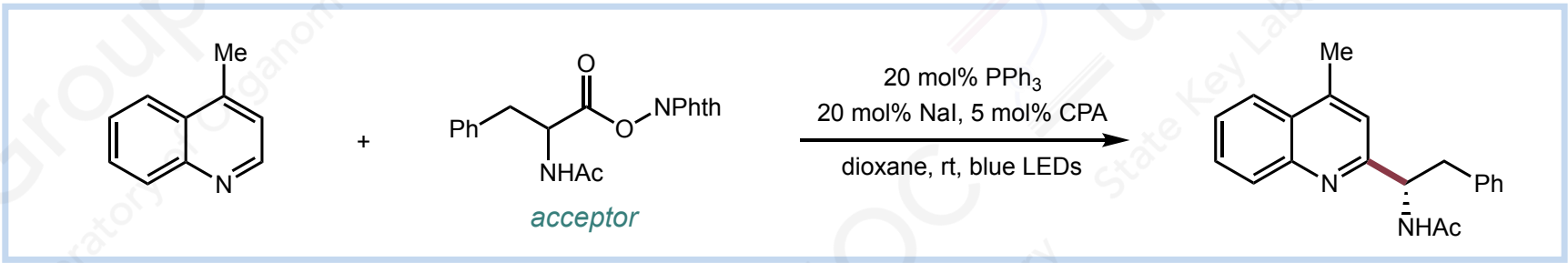


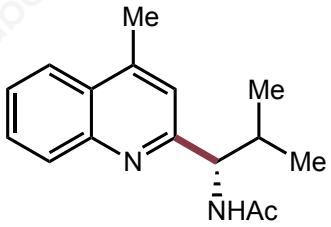
86% yield



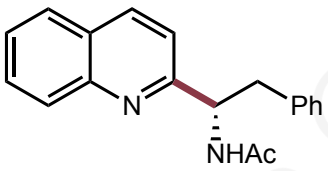
86% yield

■ *Minisci-type decarboxylative alkylation*

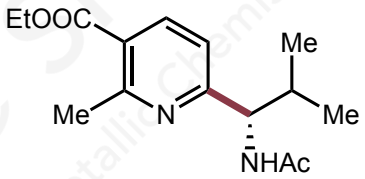




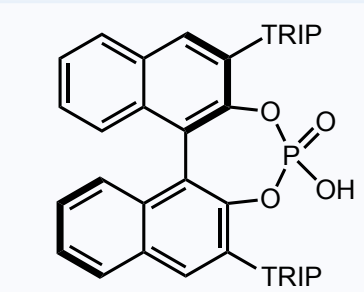
86% yield, 94% ee



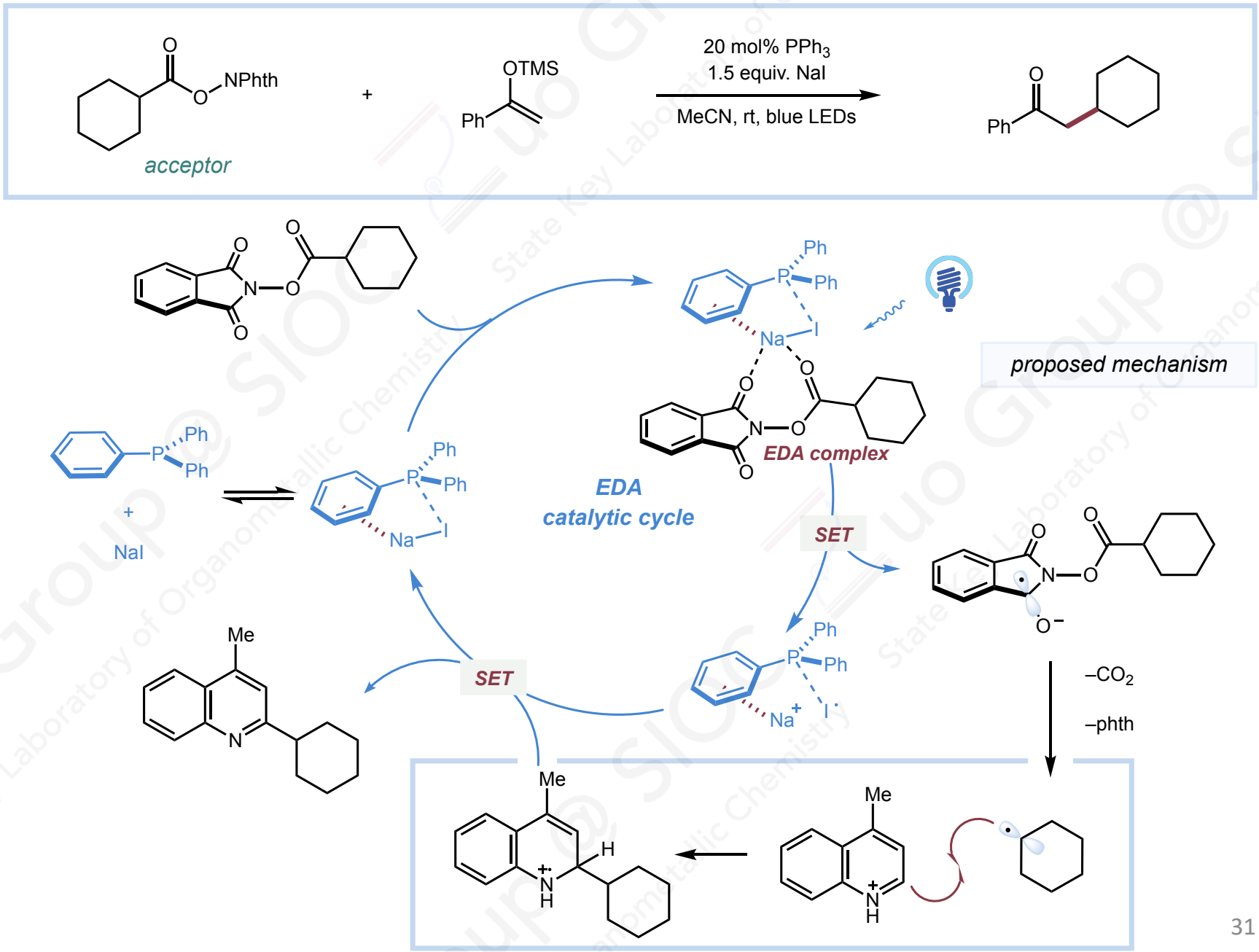
51% yield, 93% ee



87% yield, 96% ee

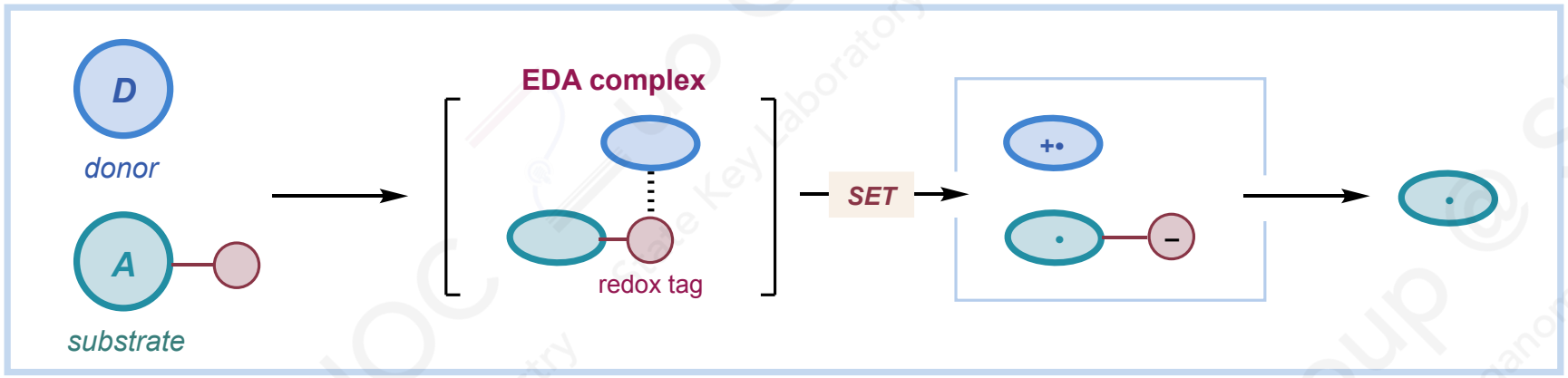


Catalytic EDA complex: C–C Bond formation



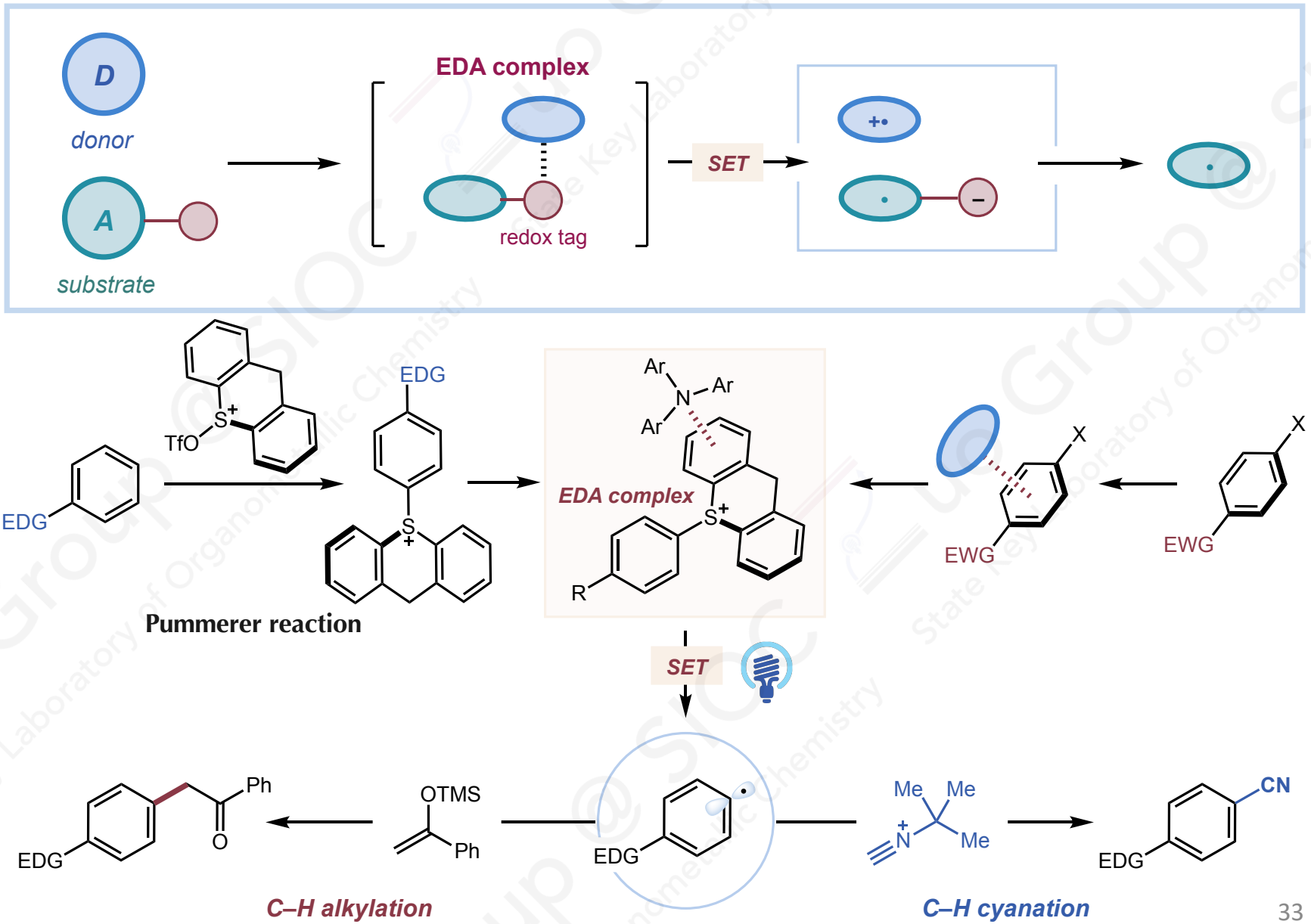
Catalytic EDA complex: C–C Bond formation

- *Arene C–H functionalization strategy via electron donor–acceptor complex*



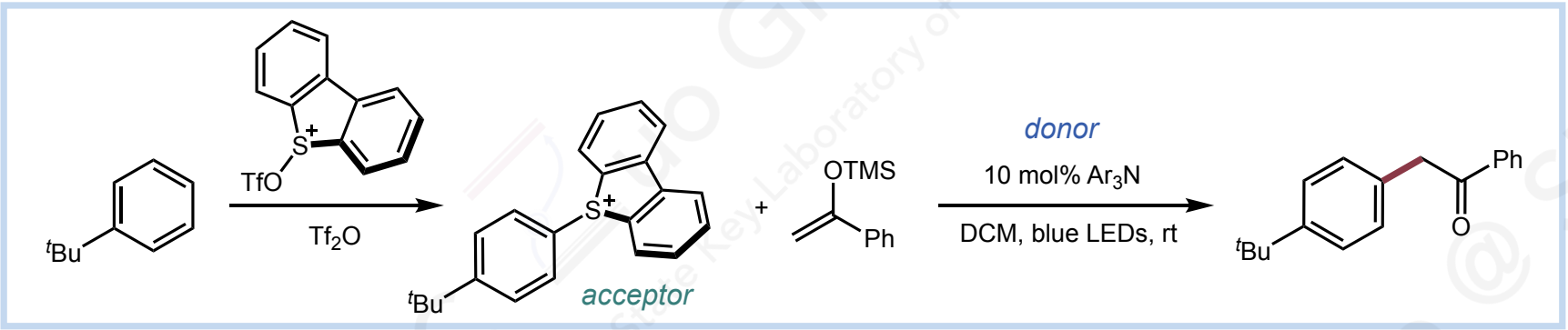
Catalytic EDA complex: C–C Bond formation

■ *Arene C–H functionalization strategy via electron donor–acceptor complex*

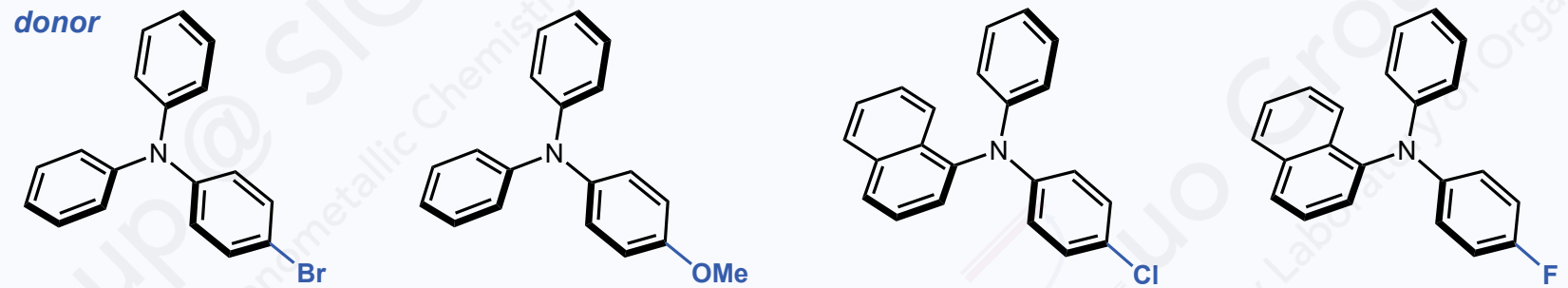


Procter, D. J. et al. *Nature Chem.* **2023**, *15*, 43 –52.

Catalytic EDA complex: C–C Bond formation

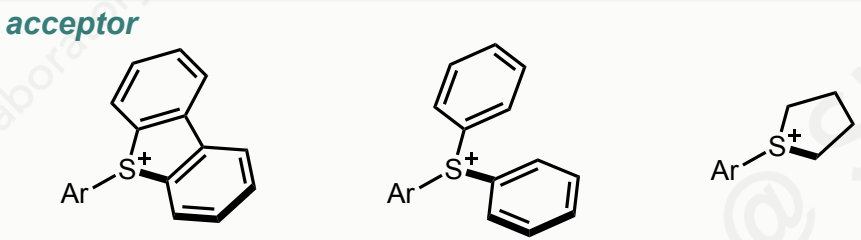


■ 供体还原电势对EDA电子转移的影响



12% yield | 46% yield | 61% yield | 51% yield

■ 受体共轭体系对EDA电子转移的影响



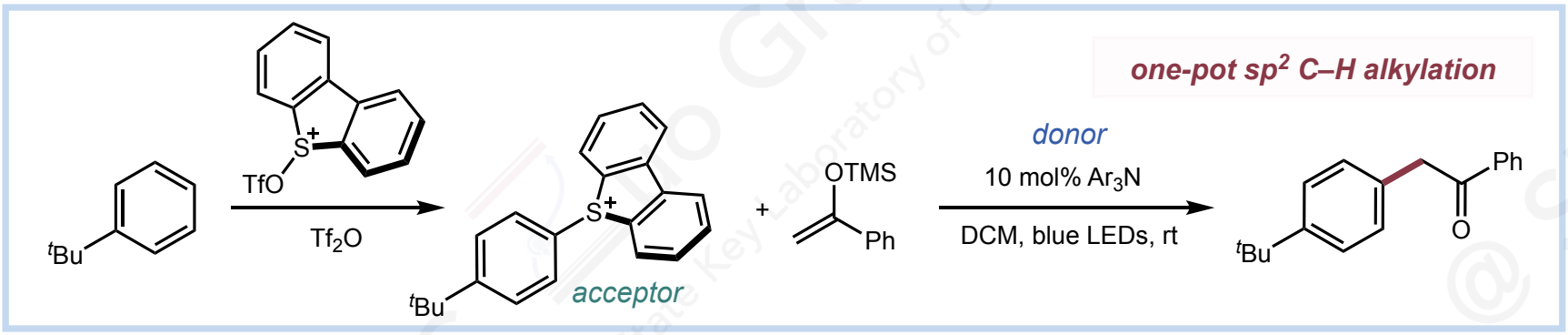
63% yield | 5% yield | trace

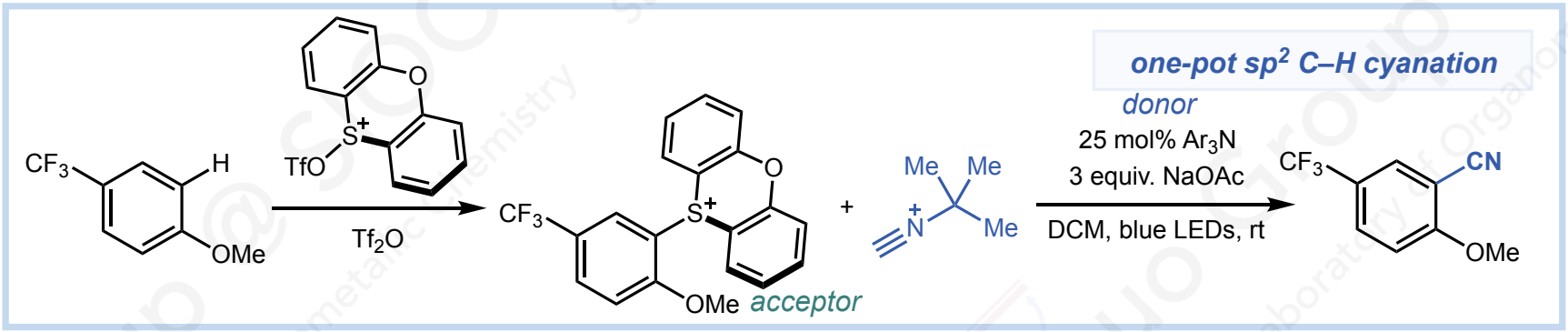
■ EDA band对电子转移的影响

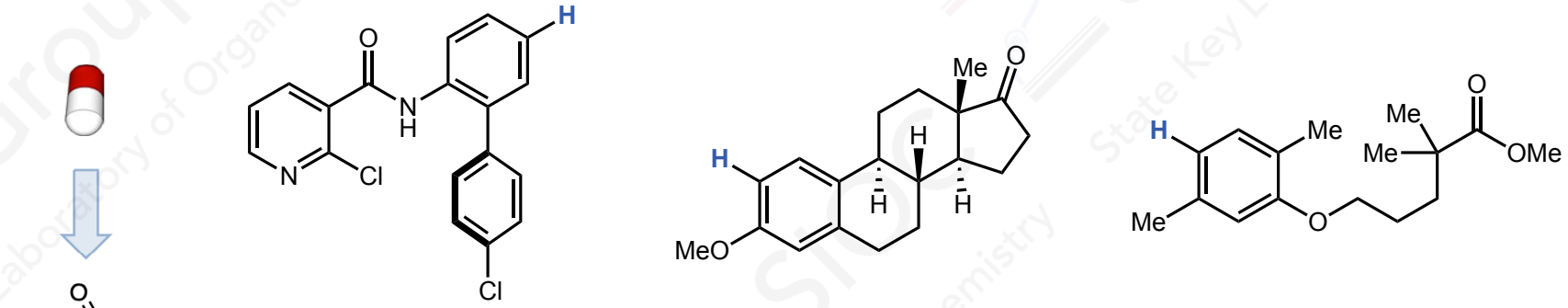
λ = 390 nm, **w/o** donor	40% yield
λ = 456 nm, **w/o** donor	34% yield
λ = 456 nm, with donor	63% yield
dark, 60 °C	0% yield

Procter, D. J. et al. *Nature Chem.* **2023**, *15*, 43 –52.

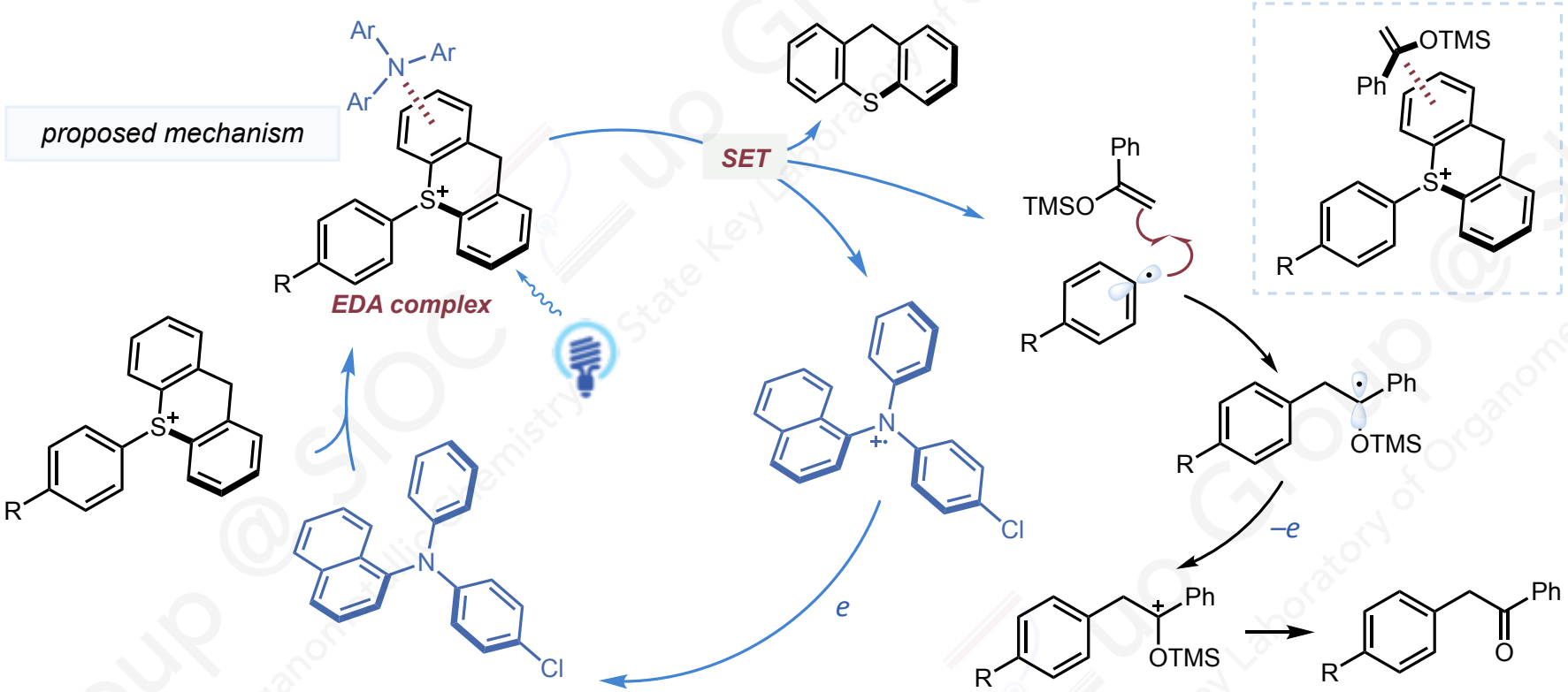
Catalytic EDA complex: C–C Bond formation



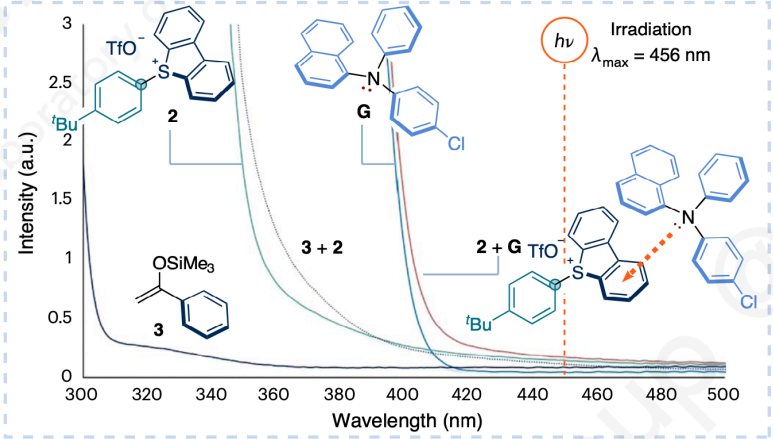




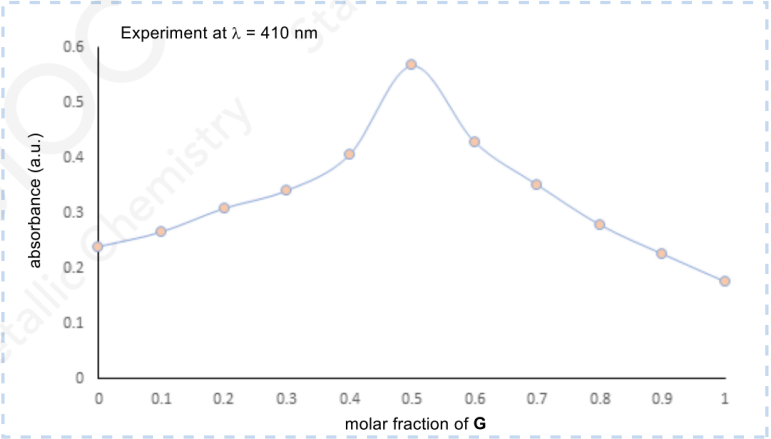
Catalytic EDA complex: C–C Bond formation



➢ EDA band: λ = 440 nm, 烯烃也可能作为电子供体

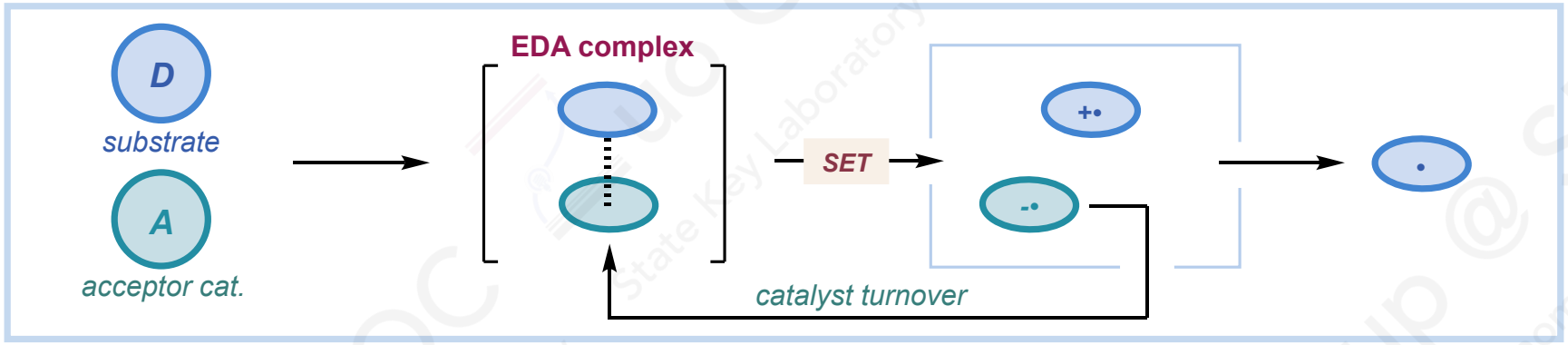


➢ Job's plot: EDA复合物比例为1:1



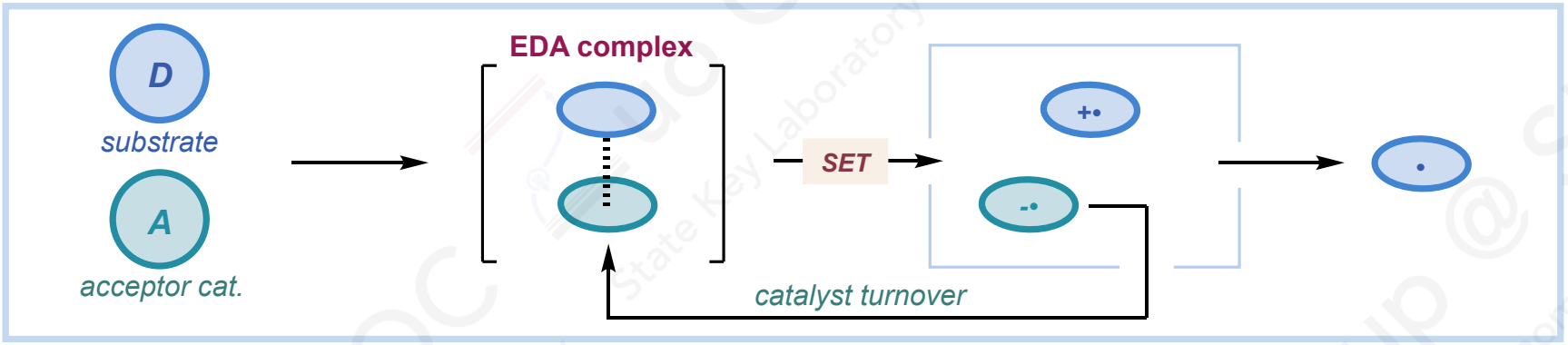
Catalytic EDA complex: C=C Bond formation

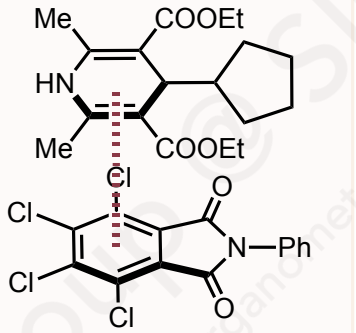
- *Tetrachlorophthalimides as Organocatalytic Acceptors for EDA complex Photoactivation*

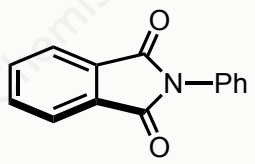


Catalytic EDA complex: C=C Bond formation

Tetrachlorophthalimides as Organocatalytic Acceptors for EDA complex Photoactivation

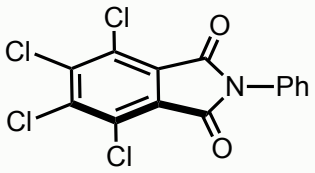






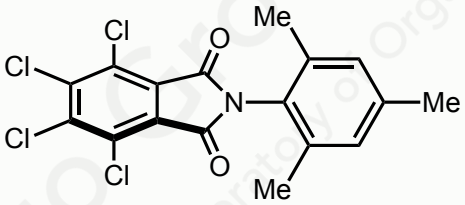
A. E_{red} = -1.78 V (SCE)

0% yield



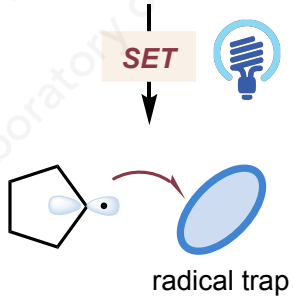
B. E_{red} = -0.84 V (SCE)

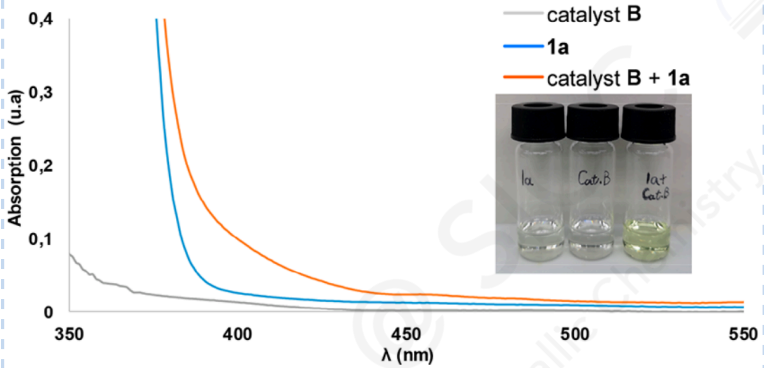
89% yield

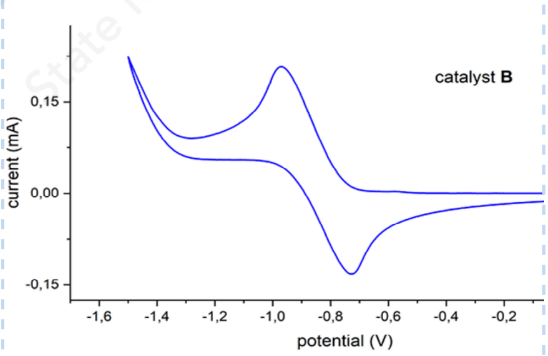


C. E_{red} = -0.86 V (SCE)

85% yield







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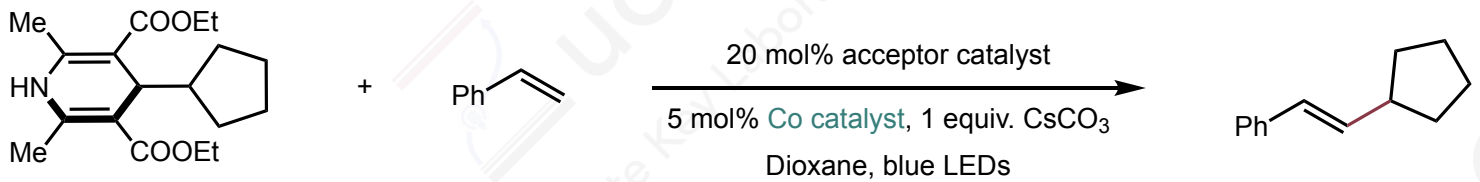
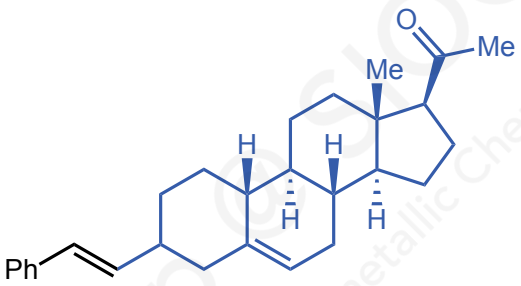
Catalytic EDA complex: C=C Bond formation

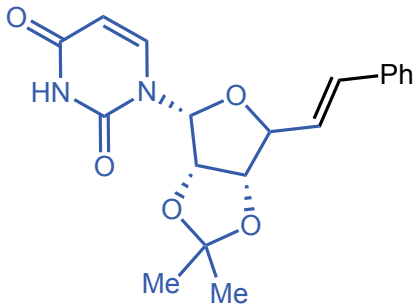
Tetrachlorophthalimides as Organocatalytic Acceptors for EDA complex Photoactivation





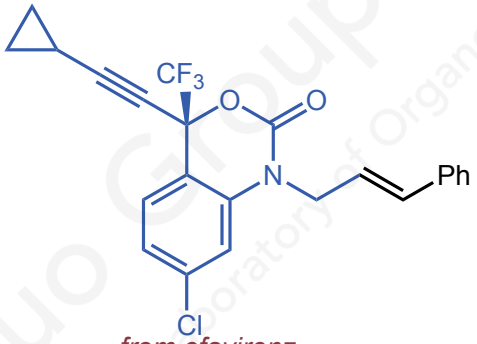
from pregnenolone

70% yield, E/Z = 8:1



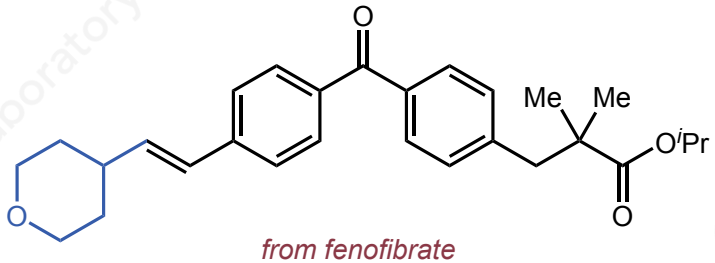
from pseudouridine

81% yield, E/Z = 7:1



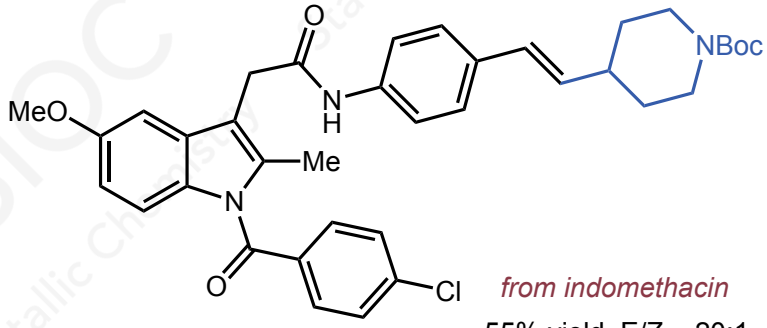
from efavirenz

63% yield, E/Z = 20:1



from fenofibrate

73% yield, E/Z = 15:1

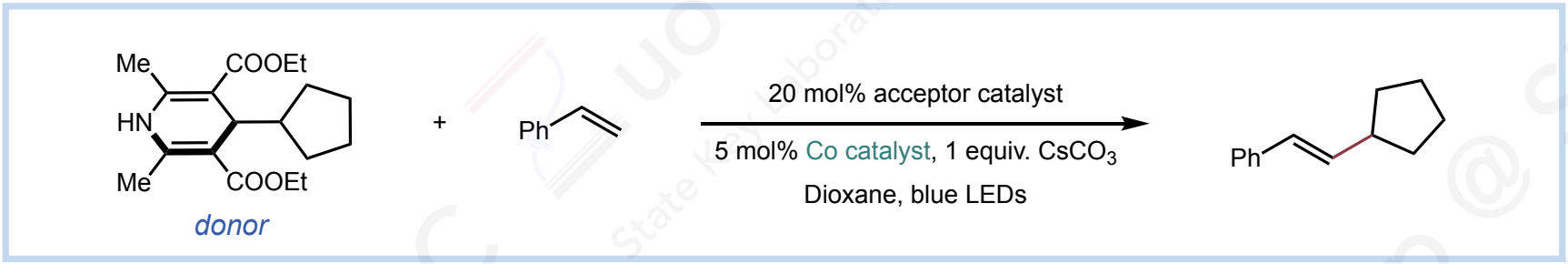


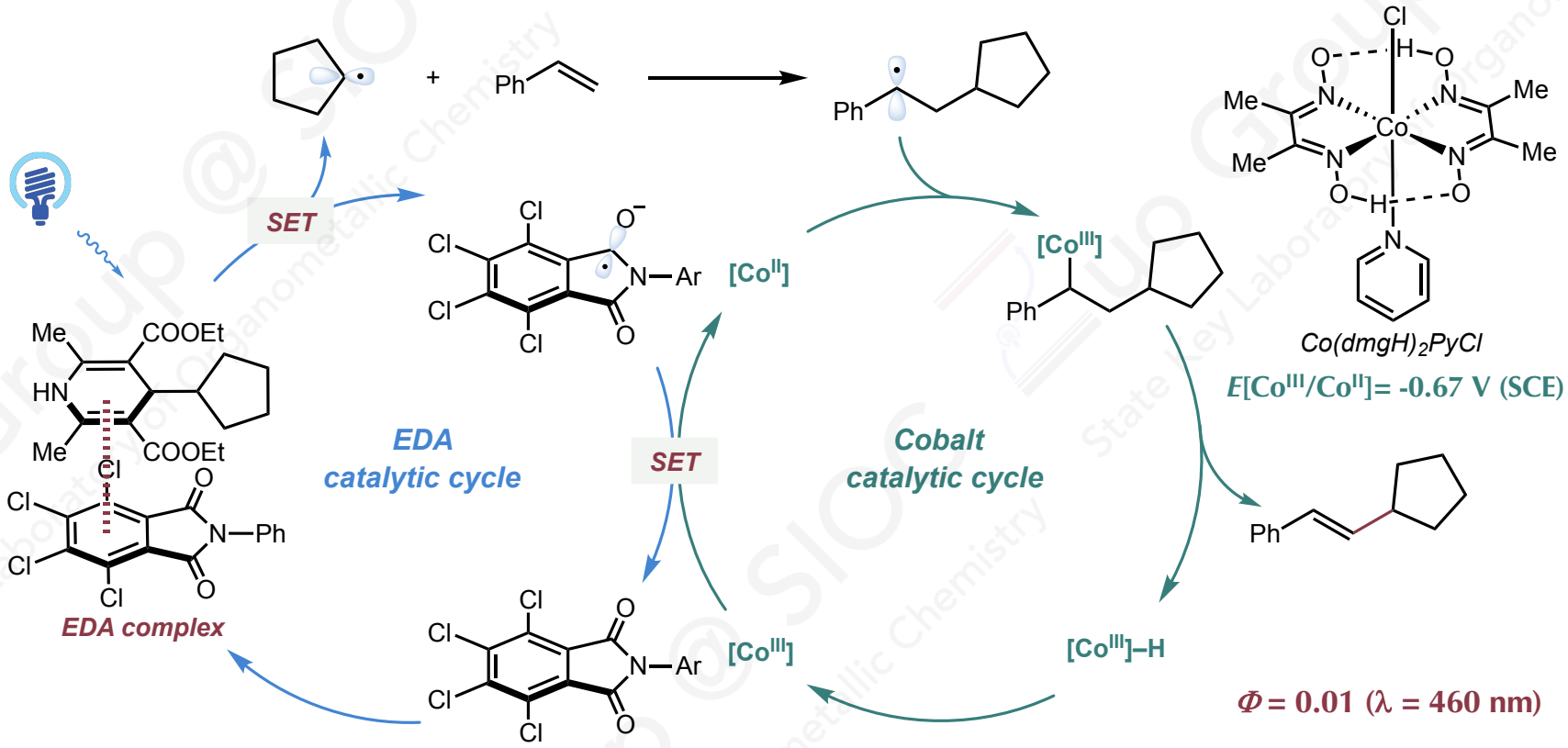
from indomethacin

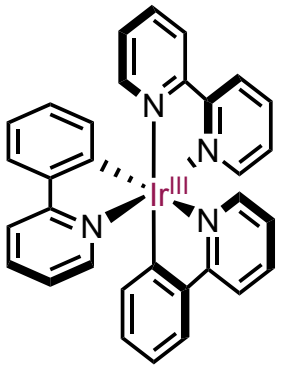
55% yield, E/Z = 20:1

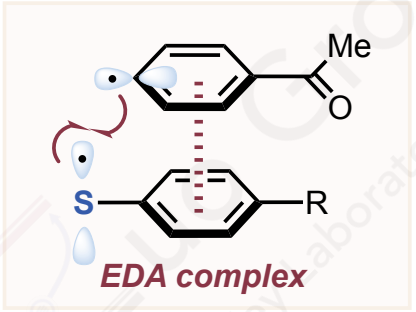
Catalytic EDA complex: C=C Bond formation

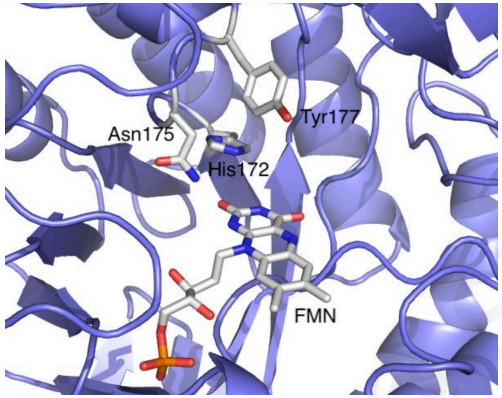
■ *Tetrachlorophthalimides as Organocatalytic Acceptors for EDA complex Photoactivation*

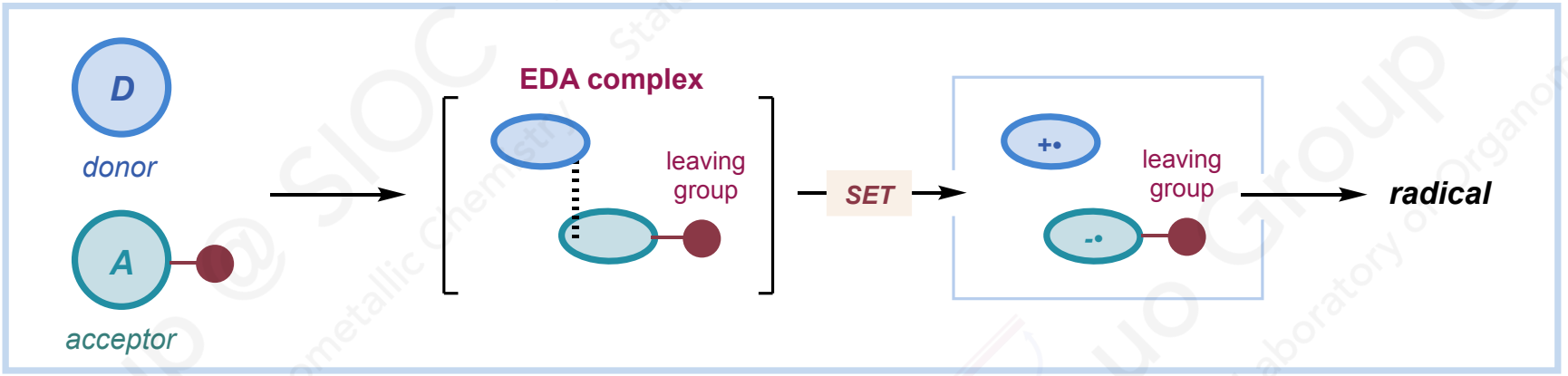


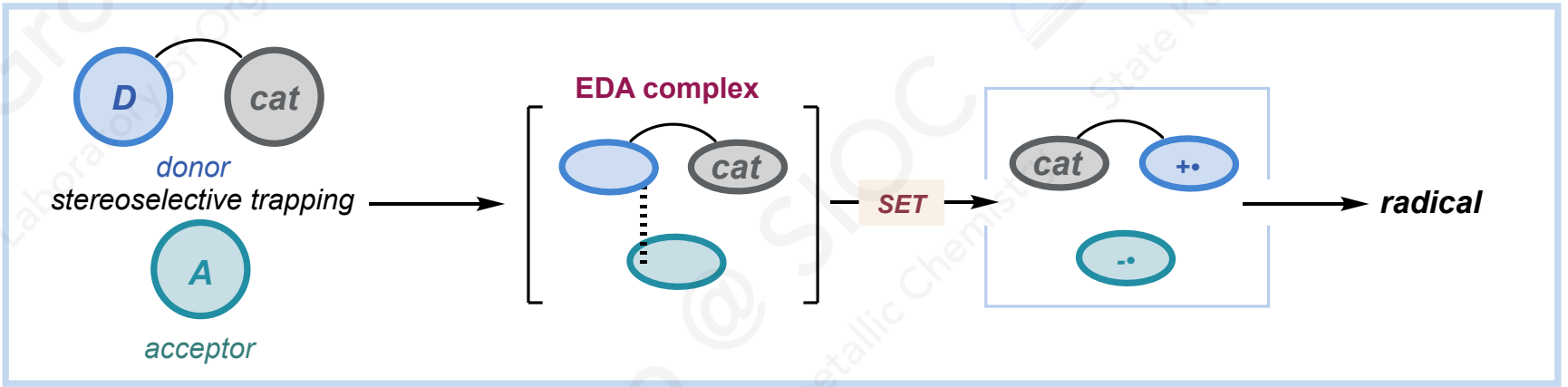



N
N
N
N
Ir^III


Me
O
S
R
EDA complex


Asn175
Tyr177
His172
FMN


D
donor
A
acceptor
EDA complex
leaving group
SET
+•
-•
leaving group
radical


D
cat
donor
stereoselective trapping
A
acceptor
EDA complex
cat
SET
cat
+•
-•
radical

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