



The Yang Research Group
Precise Synthesis Lab at Tongji University



Group Topic

黄焕明课题组工作简介

Reporter: Canxiang Liu

Date: 2026.6.11

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黄焕明

个人简历

2021.06-至今 上海科技大学 助理教授、研究员

2018-2021, 德国明斯特大学, 洪堡学者 (Mentor: Prof. Frank Glorius)

2017-2018, 英国曼彻斯特大学, 博士后 (Mentor: Prof. David J. Procter)

2014-2017, 英国曼彻斯特大学, 博士 (Supervisor: Prof. David J. Procter)

Research

Photochemical Rearrangement

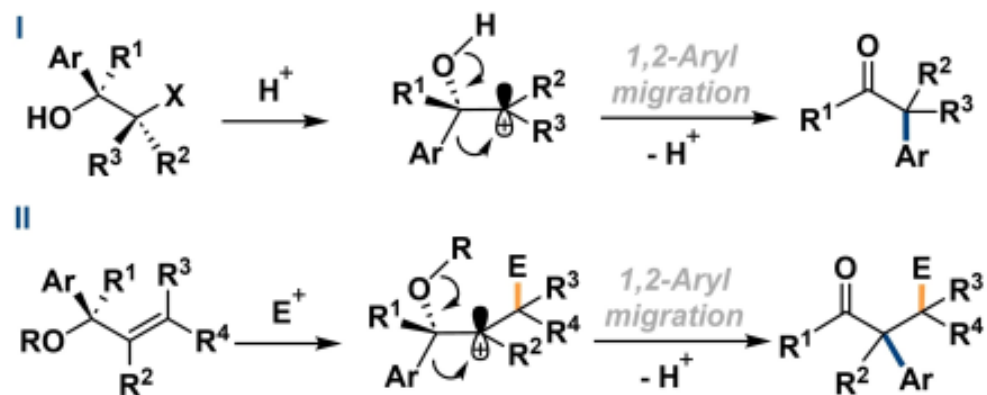
Photocatalytic Approaches to Access Bioisosteres

Photoexcited Transition Metal Catalysis

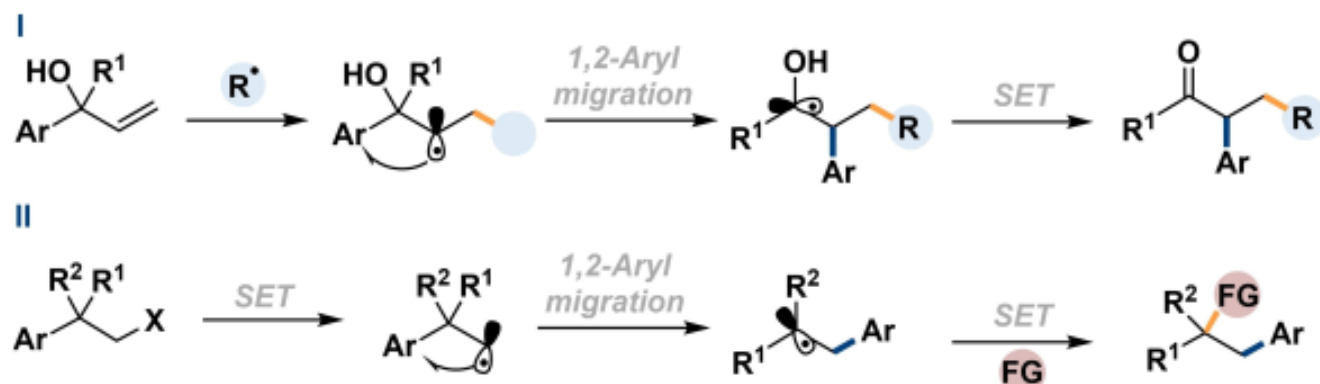


能量转移促进的1,4-芳基迁移

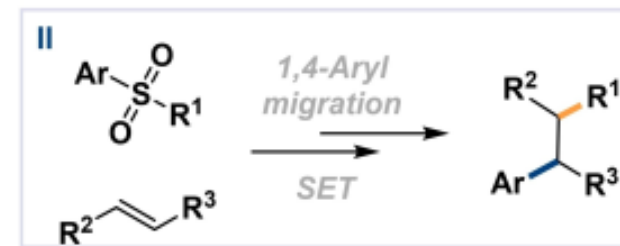
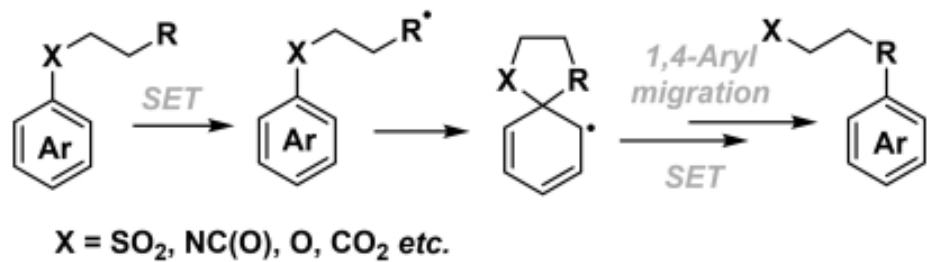
A. Polar 1,2-Aryl Migration (Semipinacol Rearrangement)



B. Radical 1,2-Aryl Migration (Neophyl-type Rearrangement)

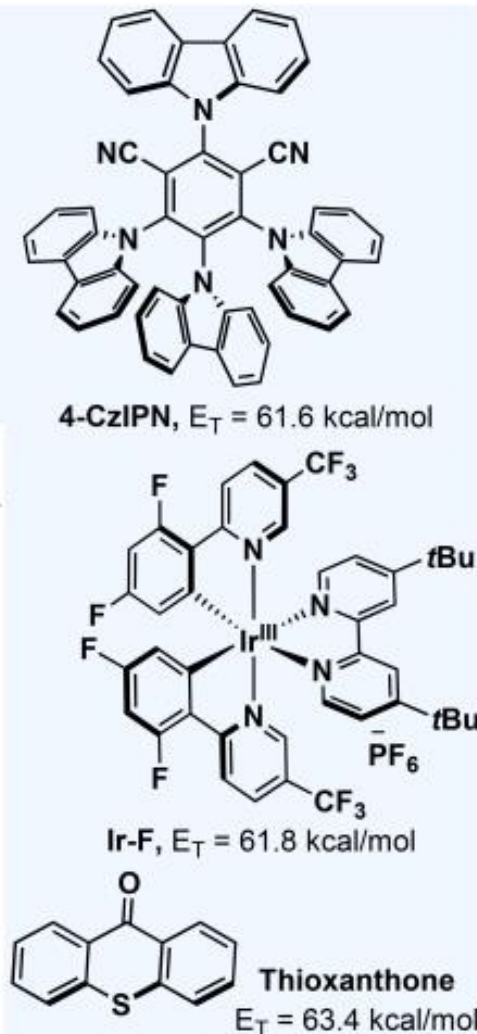
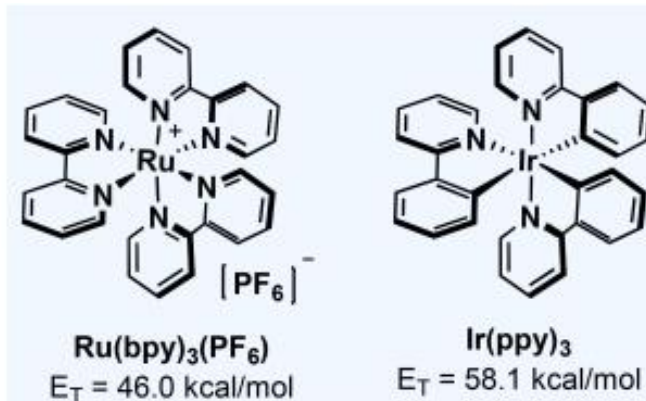
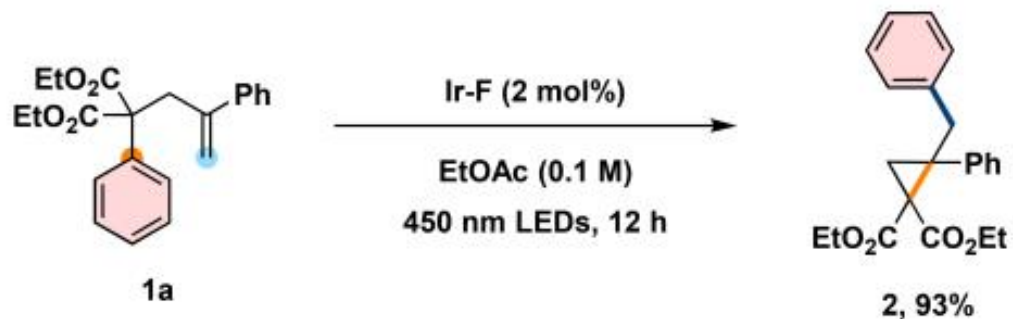


C. Radical 1,4-Aryl Migration (Single-Electron Smiles Rearrangement)





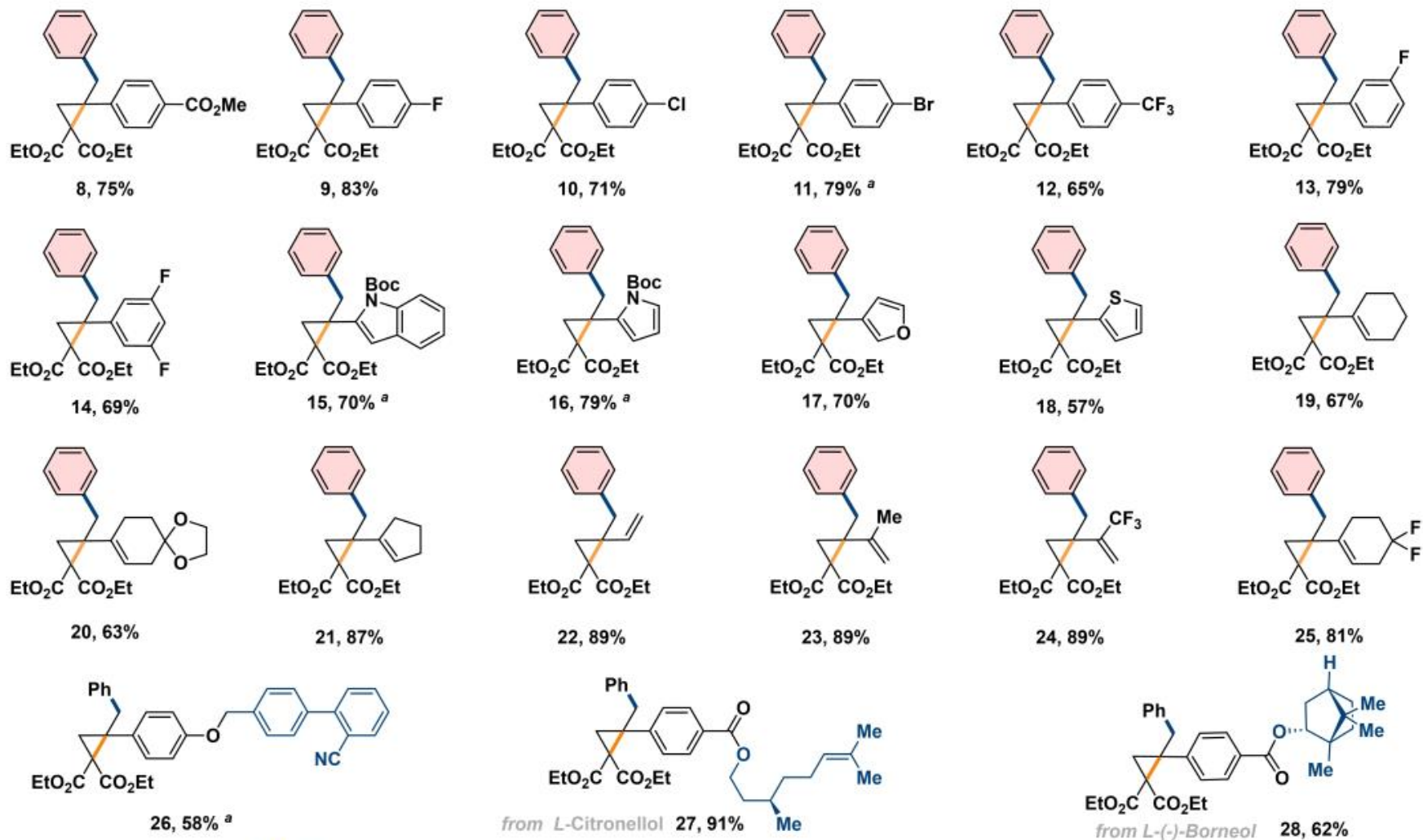
能量转移促进的1,4-芳基迁移



Entry	Variations from standard conditions	Yield (%)	Entry	Variations from standard conditions	Yield (%)
1	none	98(93) ^a	7	Ru(ppy) ₃ (PF ₆) ₂ instead of Ir-F	N.D.
2	MeCN or DCM instead of EtOAc	97, 96	8	Ir(ppy) ₃ instead of Ir-F	N.D.
3	DMA instead of EtOAc	trace	9	No PC under 450 nm	N.D.
4 ^b	Thioxanthone instead of Ir-F	97	10	No PC under 365 nm	N.D.
5 ^b	2-Chlorothioxanthone instead of Ir-F	98	11	40 °C instead of light	N.D.
6	4-CzIPN instead of Ir-F	60	12	No light	N.D.

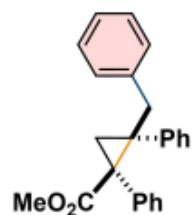
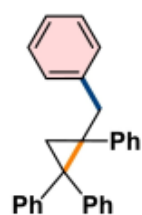
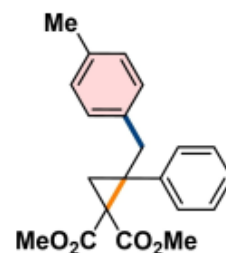


能量转移促进的1,4-芳基迁移

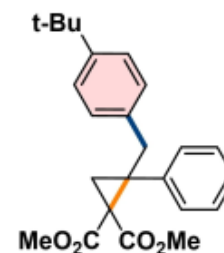




能量转移促进的1,4-芳基迁移

32, 83%, dr = 2:1^a33, 90%, dr = 3:2^a
CCDC 234644734, 75%^a

35, 89%



36, 74%



37, 96%



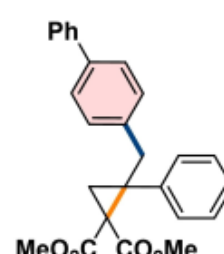
38, 73%



39, 72%



40, 82%



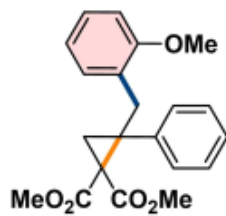
41, 73%



42, 82%



43, 81%



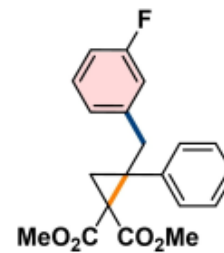
44, 65%



45, 67%



46, 79%



47, 75%



48, 79%

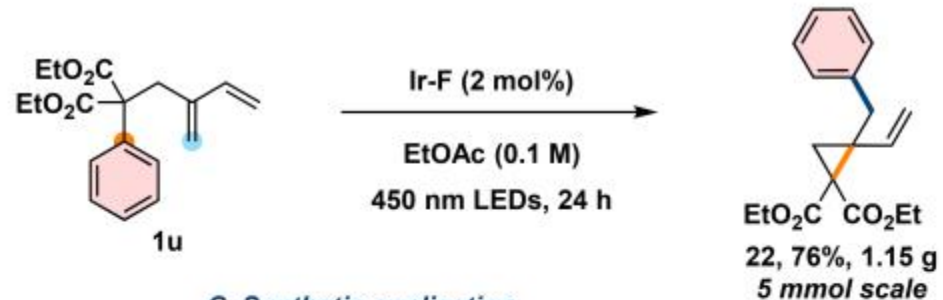
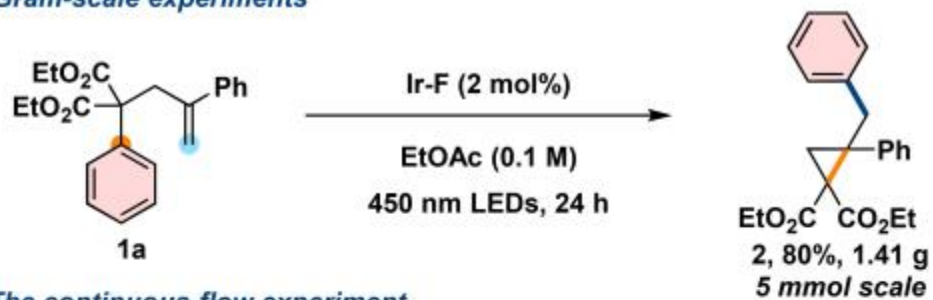


49, 73%



能量转移促进的1,4-芳基迁移

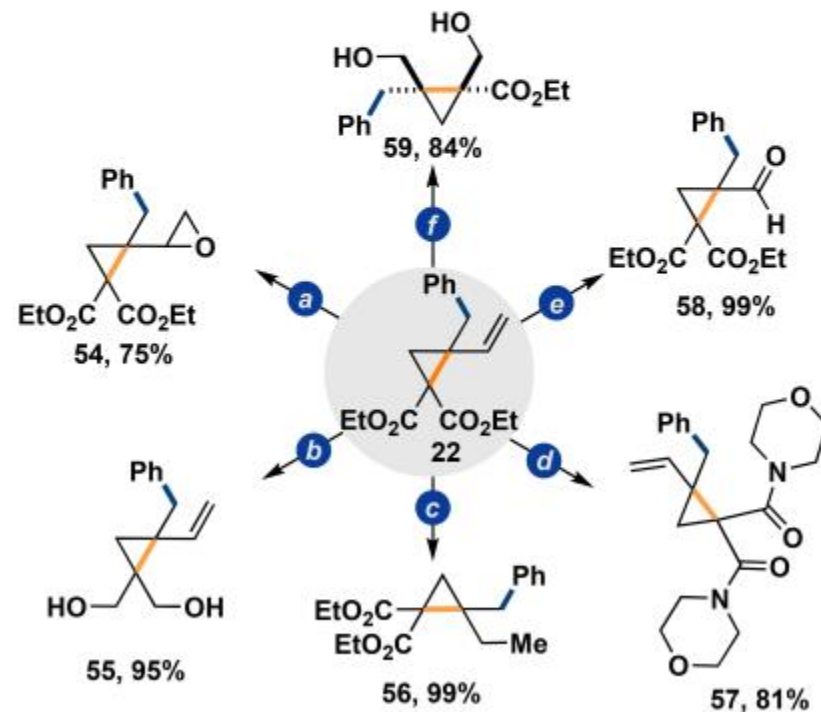
A. Gram-scale experiments



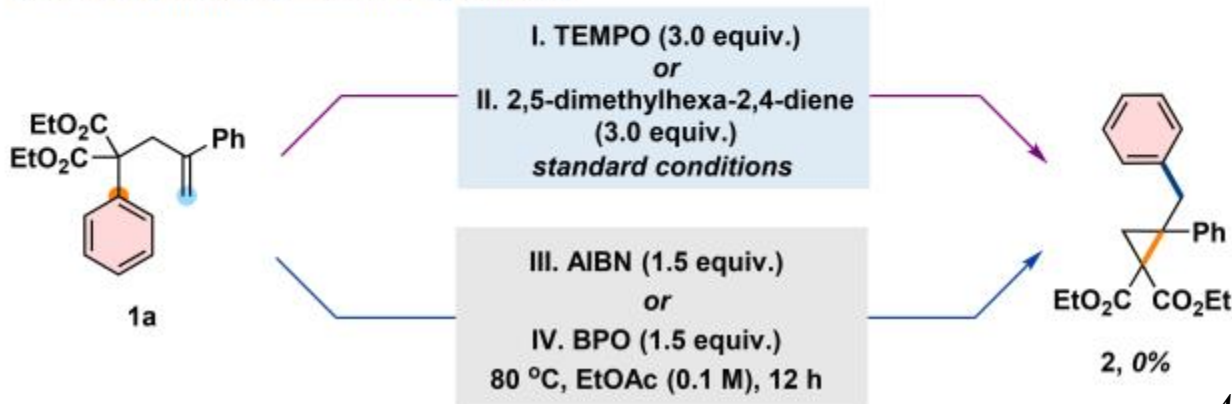
B. The continuous-flow experiment



C. Synthetic application



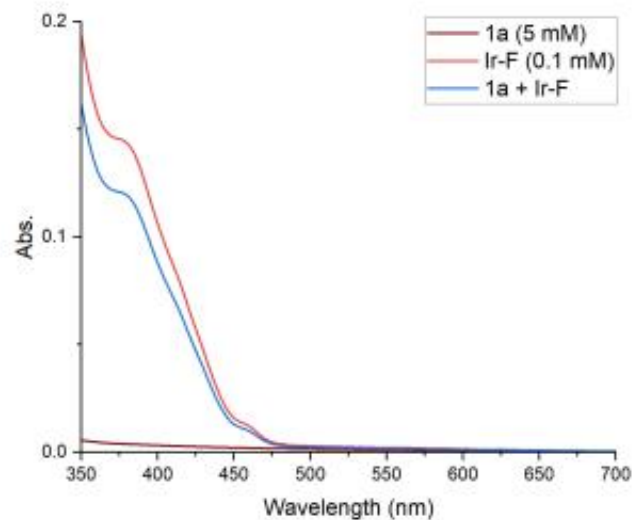
D. Radical inhibitor & initiation experiments



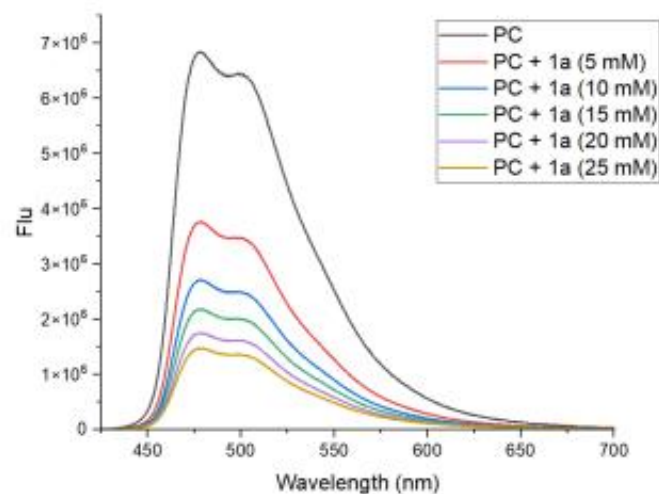


能量转移促进的1, 4-芳基迁移

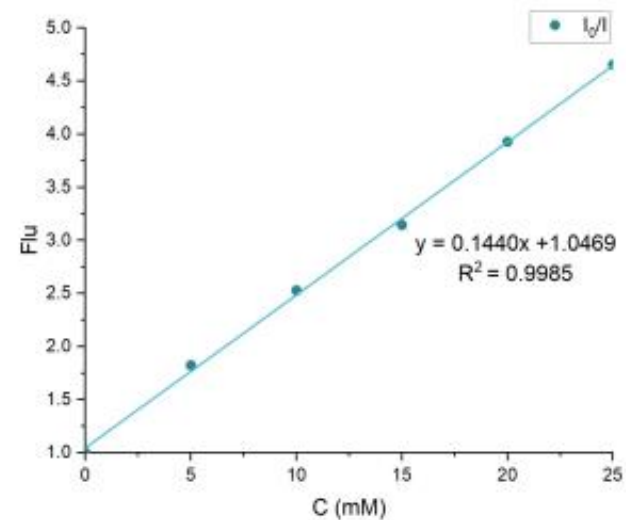
E. UV-vis experiment



F. Fluorescence study



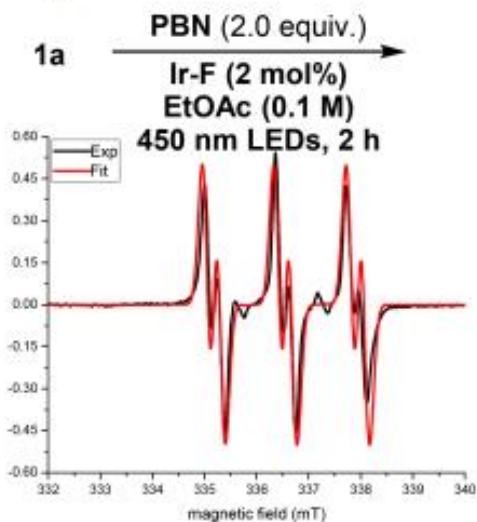
G. Stern-Volmer quenching experiment





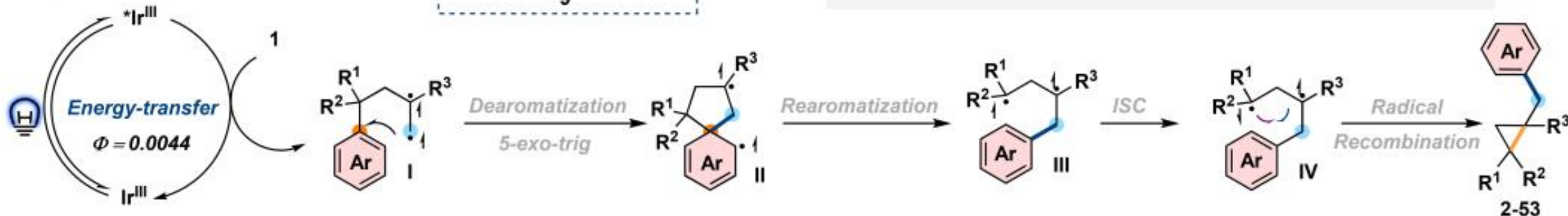
能量转移促进的1,4-芳基迁移

H. EPR experiment of substrate 1a

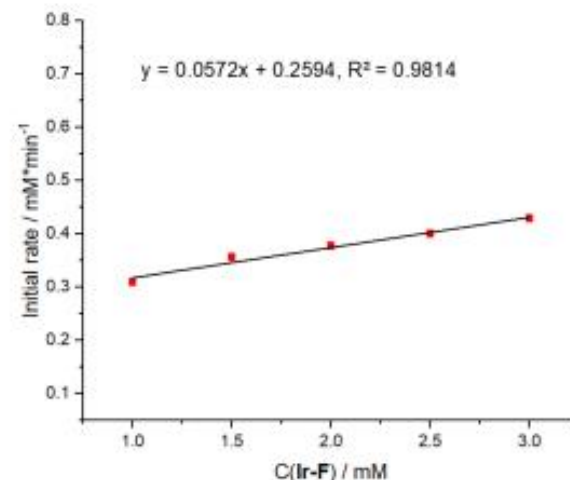
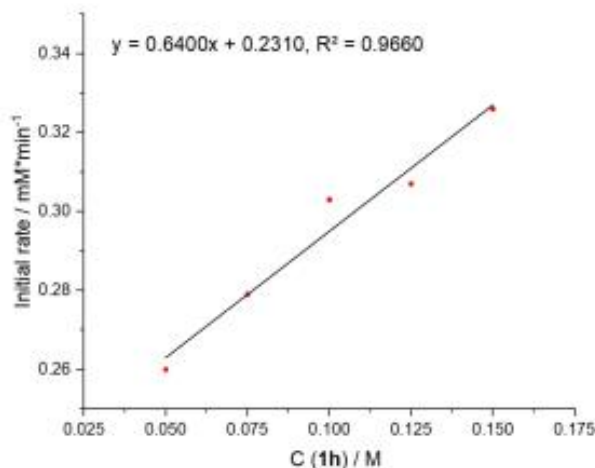
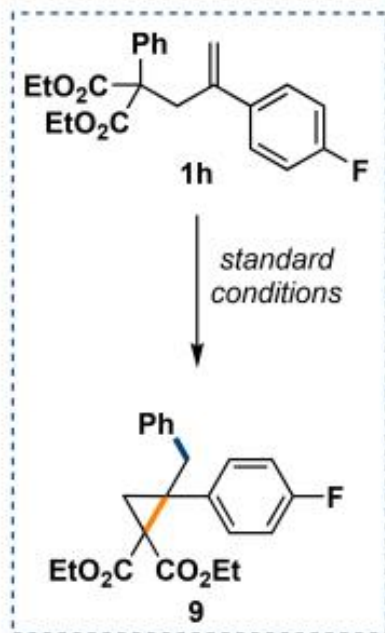


$A_N = 1.38 \text{ mT}$, $A_H = 0.25 \text{ mT}$

J. Proposed mechanism



I. Reaction kinetics for energy-transfer enabled 1,4-aryl migration and summary of rate law

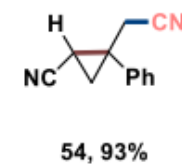
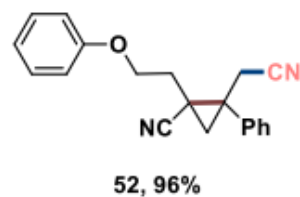
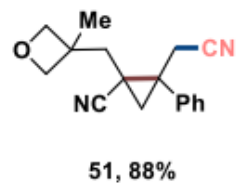
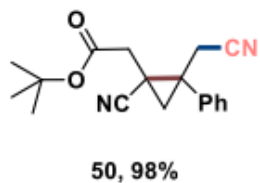
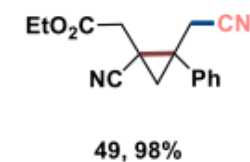
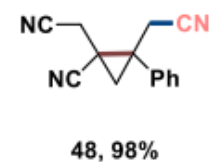
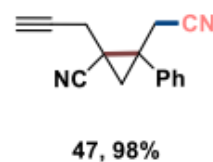
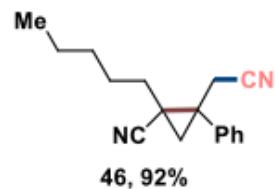
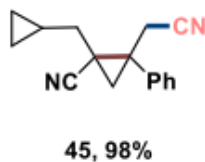
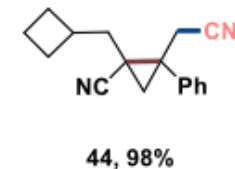
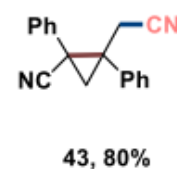
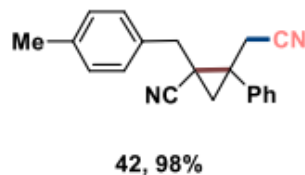
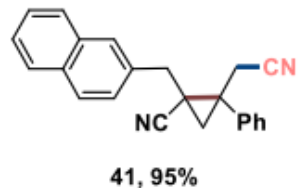
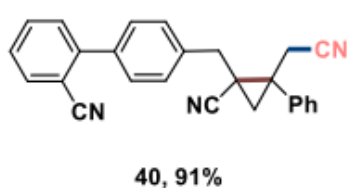
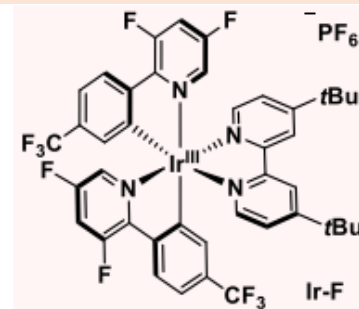
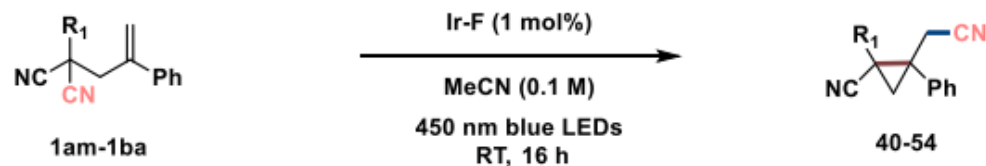


Rate law: $\text{rate} = k[1][\text{Ir-F}]$

$k = 0.45 \text{ M}^{-1}\text{min}^{-1}$



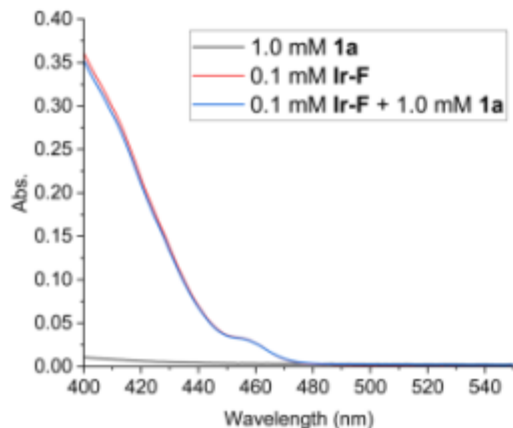
能量转移促进的1,4-氰基迁移



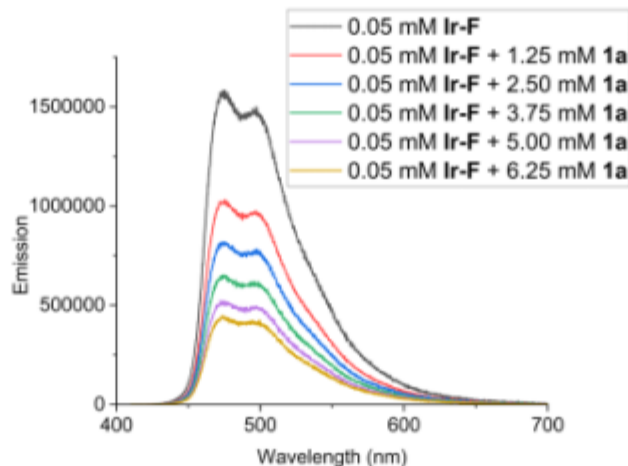


能量转移促进的1,4-氰基迁移

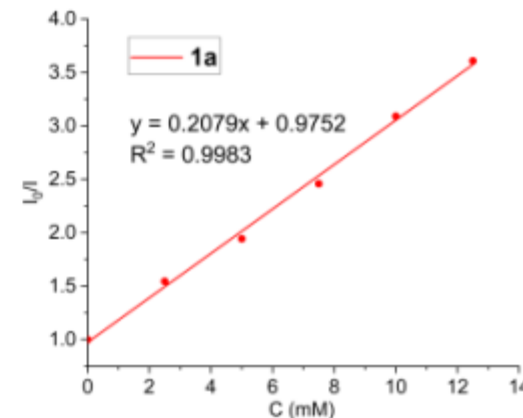
D. UV-Vis experiment



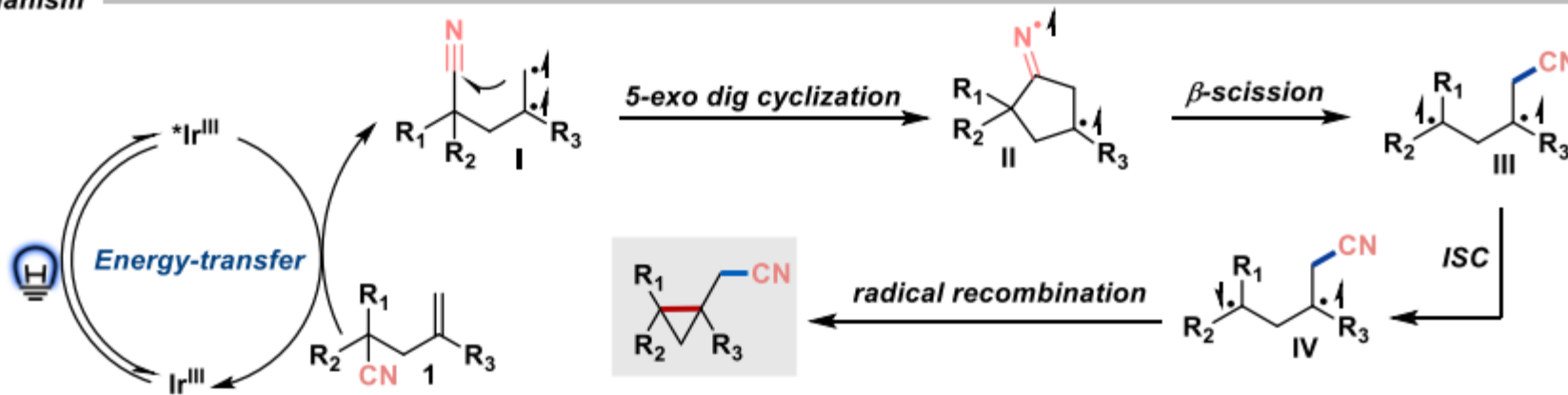
E. Fluorescence study



F. Stern-Volmer quenching experiment

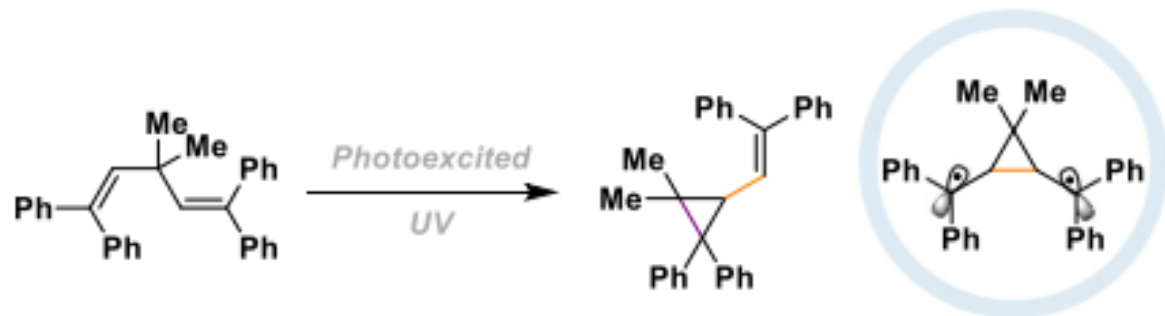


G. Proposed mechanism



通过能量转移催化的异腈光化学重排

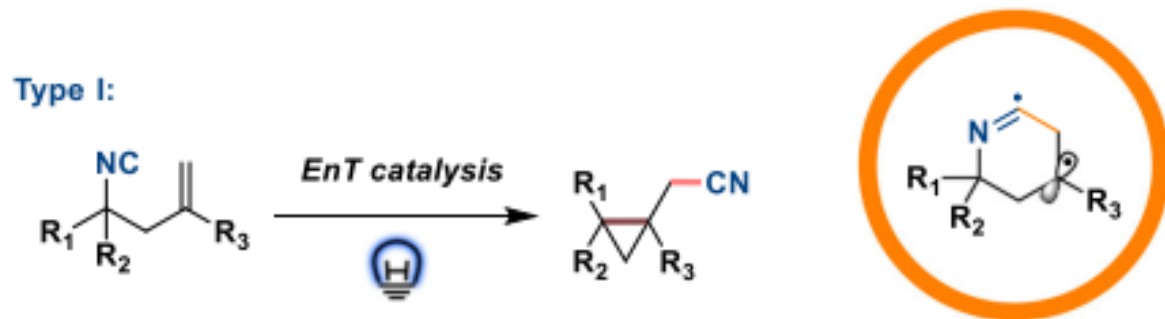
A: Seminal work: photochemical di- π -methane rearrangement



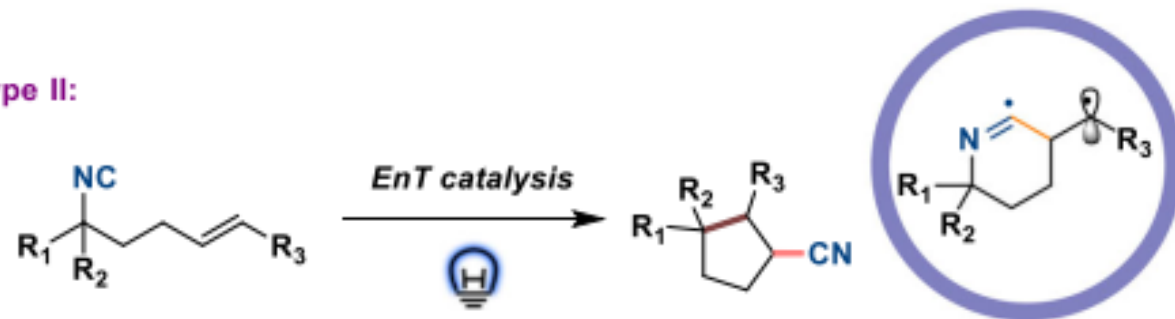
B: Previous work: di- π -ethane rearrangement via EnT catalysis

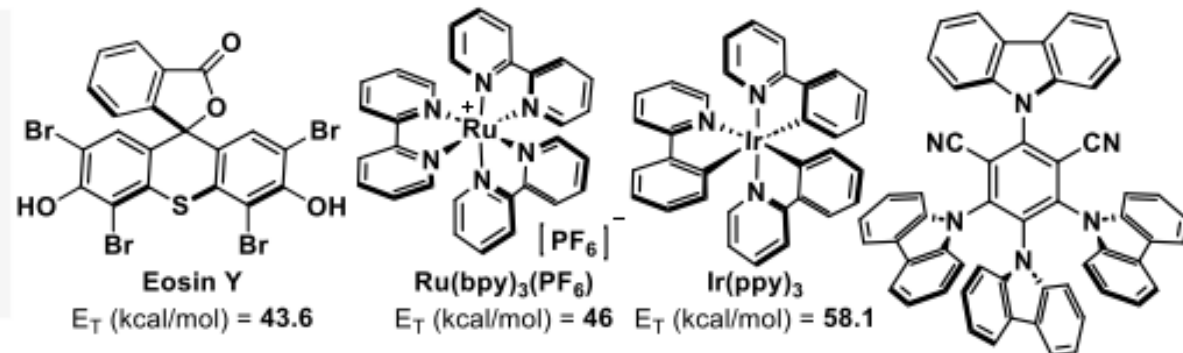
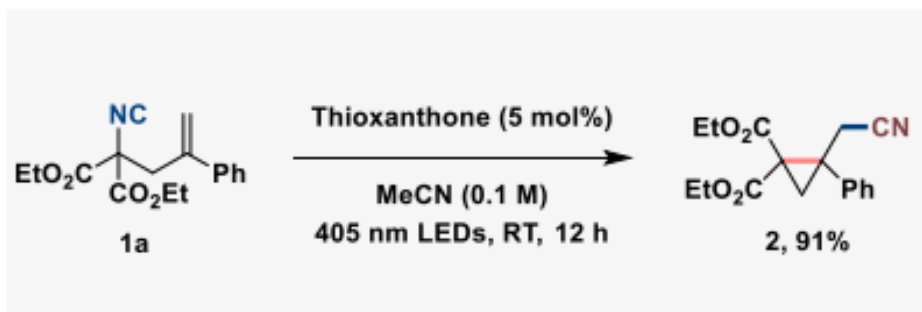


C: This work: photochemical rearrangement of isonitriles via EnT catalysis



Type II:




 通过能量转移催化的异腈光化学重排


Entry	Photocatalysis	Yield(%) ^a	Entry	Variations from standard conditions	Yield(%) ^a
1 ^b	Eosin Y (2 mol%)	0	7	PhCF ₃ /EtOAc/DCE	93/90/90
2 ^b	Ru(bpy) ₃ PF ₆ (1 mol%)	0	8	DMF/DMSO/THF	68/88/27
3 ^b	Ir(ppy) ₃ (1 mol%)	29	9 ^c	0.1 mol%/1 mol%/2 mol% of Thioxanthone	67/92/92
4 ^b	4CzIPN (2 mol%)	10	10 ^{c,d}	reaction time 1 h/6 h/9 h	27/89/92
5 ^b	Ir-F (1 mol%)	82	11	no PC	0
6	Thioxanthone (5 mol%)	91	12	no light	0

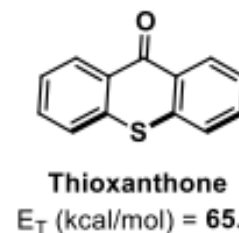
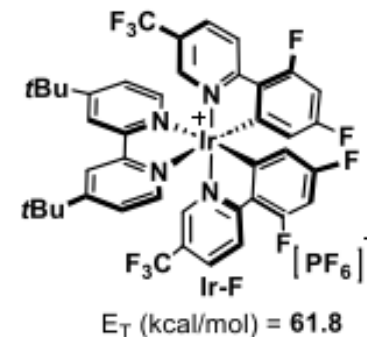
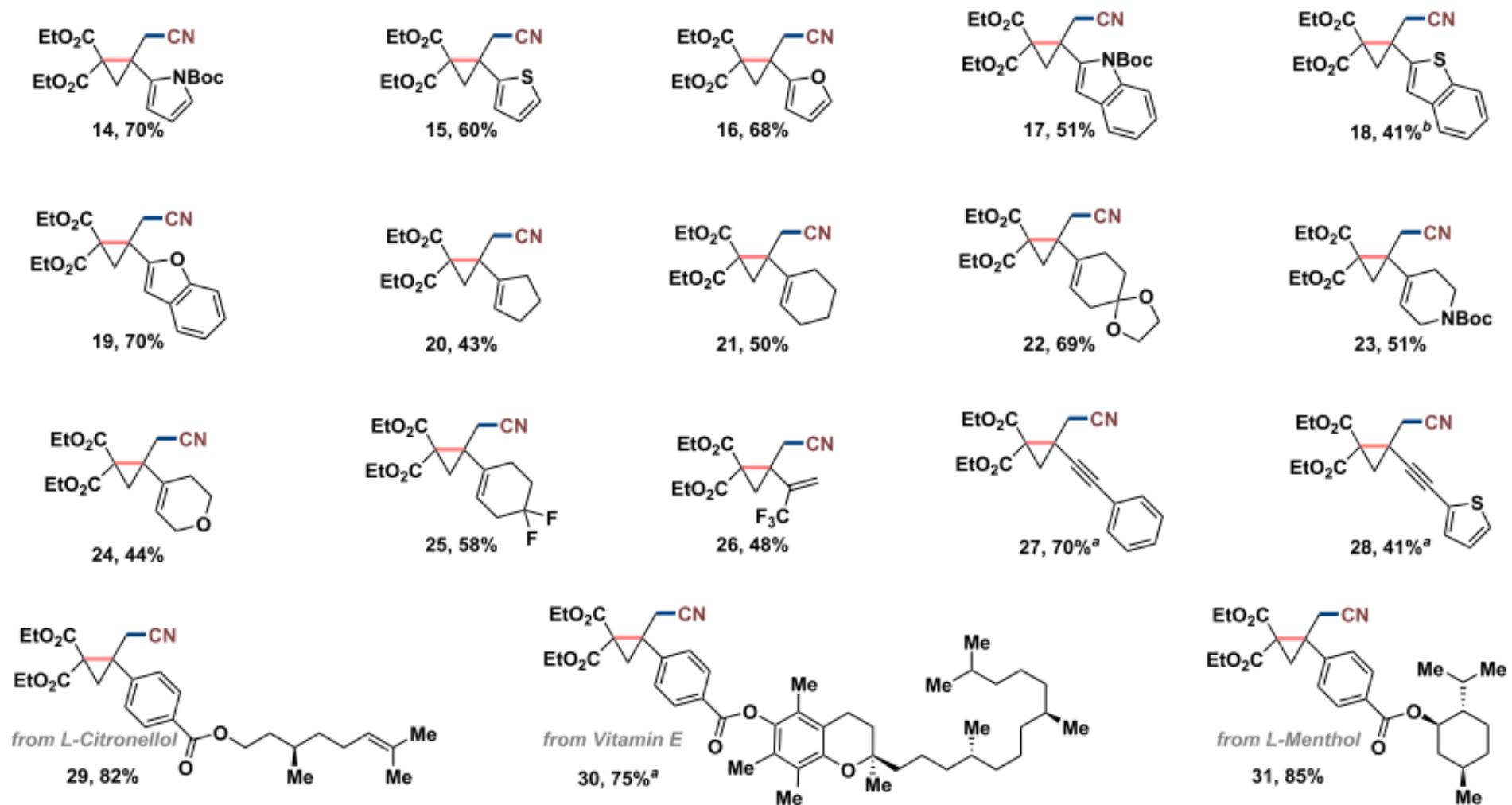


Fig. 2 | Rational design and optimization. Reaction condition. 1a (0.2 mmol), Thioxanthone (TXT, 5 mol %), and MeCN (2 mL, 0.1 M) at room temperature under 30 W 405 nm LEDs with a cooling fan for 12 h under N₂. ^a Isolated yield. ^b 450 nm

LEDs are used instead of 405 nm LEDs. ^c PhCF₃ as solvent. ^d Thioxanthone (TXT, 1 mol%) was used as photocatalyst.

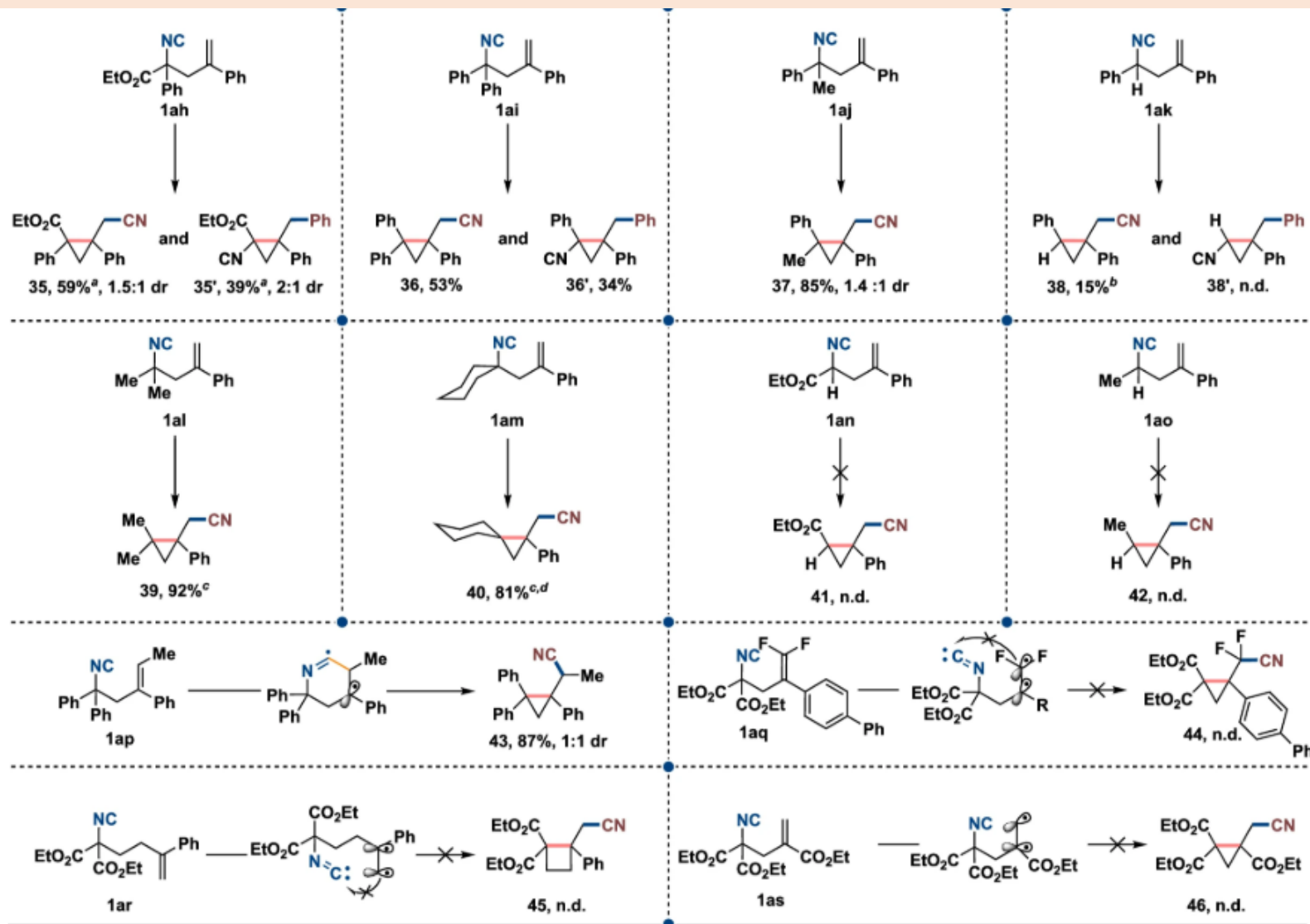


通过能量转移催化的异腈光化学重排

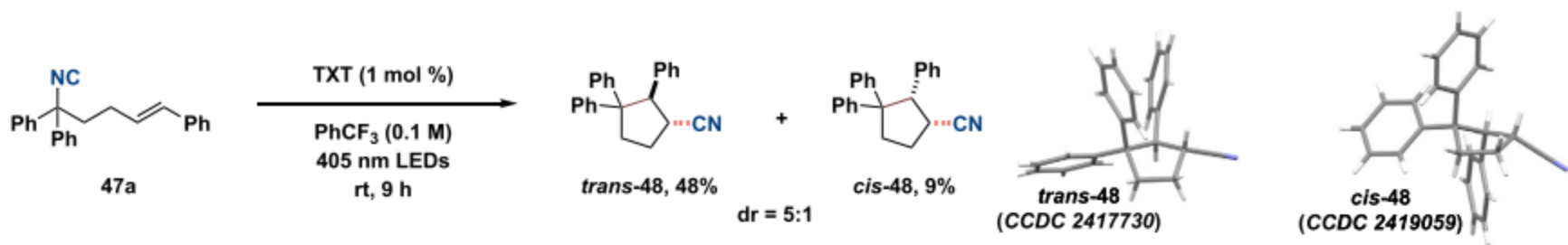




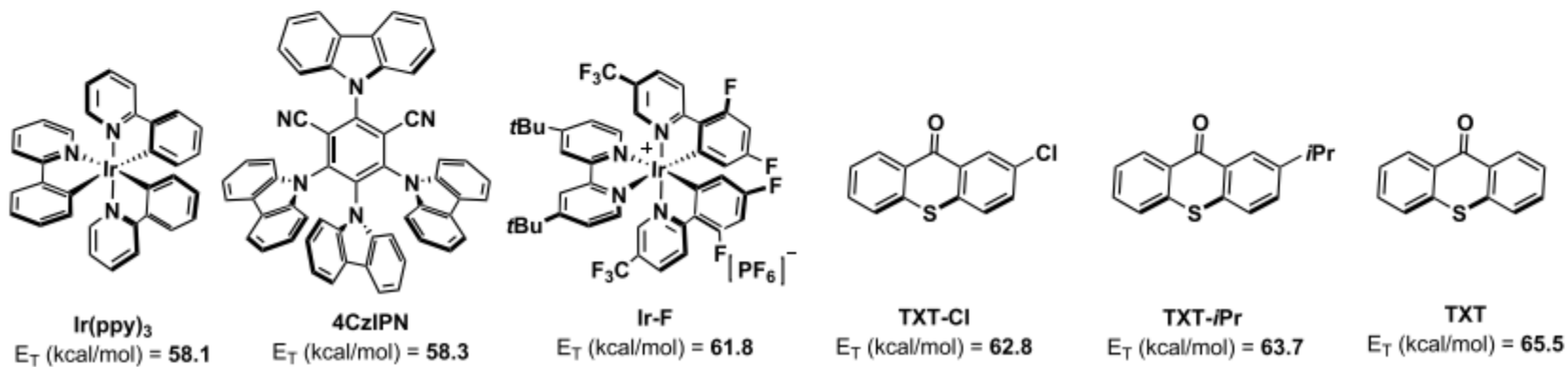
通过能量转移催化的异腈光化学重排



通过能量转移催化的异腈光化学重排



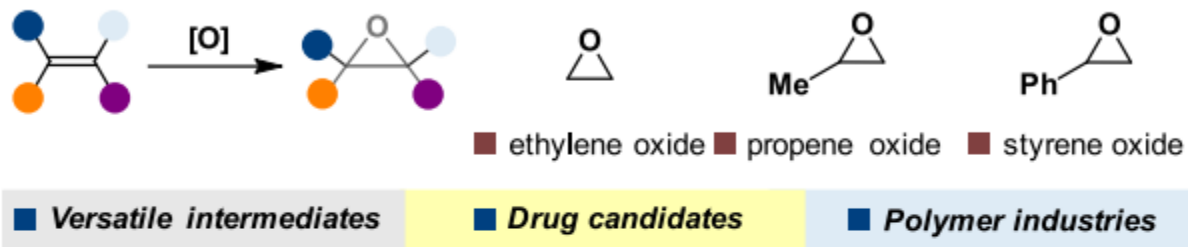
Entry	Variations from standard conditions	Yield(%) ^a	dr	Entry	Variations from standard conditions	Yield(%) ^a	dr
1	1 mol%/2 mol%/5 mol% of TXT	57/60/60	5:1	7 ^c	MeCN	71	6:1
2 ^{b,c}	Ir(ppy) ₃	13	5:1	8 ^c	EtOAc	53	4:1
3 ^{b,c}	4CzIPN	22	5:1	9 ^c	DCE	54	5:1
4 ^{b,c}	Ir-F	56	5:1	10 ^c	DMF	10	4:1
5 ^c	TXT-Cl	57	5:1	11 ^c	DMSO	51	5:1
6 ^c	TXT- <i>i</i> Pr	60	5:1	12 ^c	Acetone	58	7:1



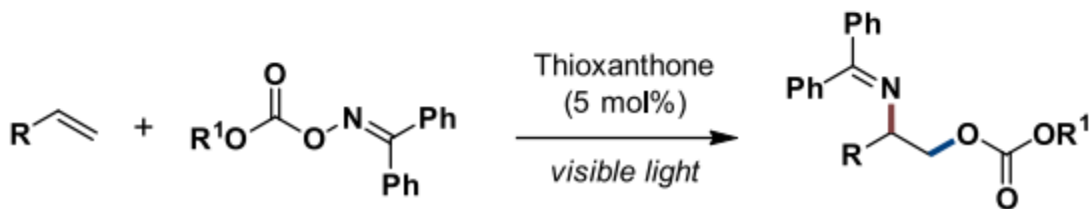


能量转移催化氧杂- π , σ -甲烷重排合成环氧化合物

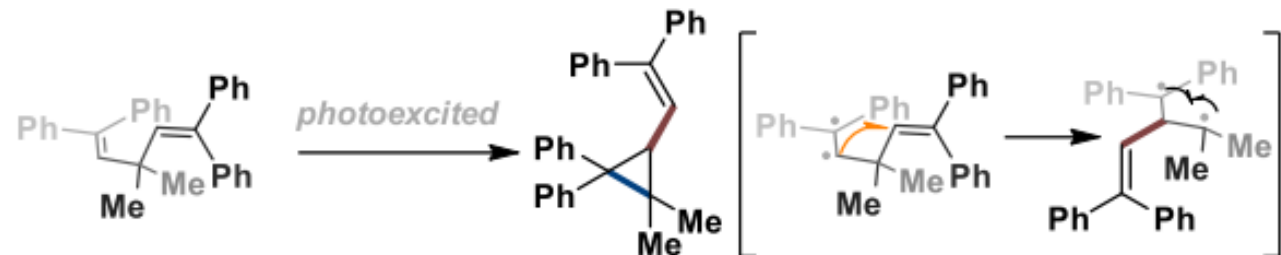
A. Epoxides are important chemicals and used in multiple fields



B. Difunctionalization of unactivated alkenes enabled by EnT Catalysis - *Glorius*

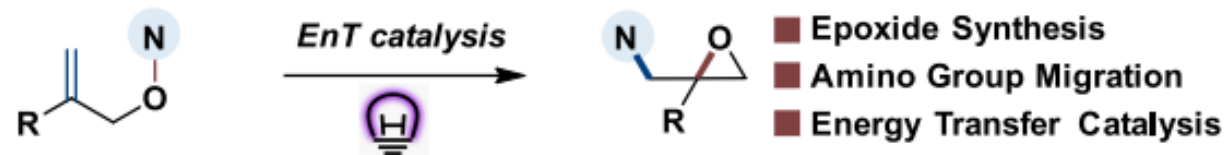


C. Di- π -methane rearrangement (Zimmerman et al. rearrangement) - *well established*



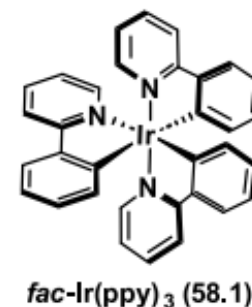
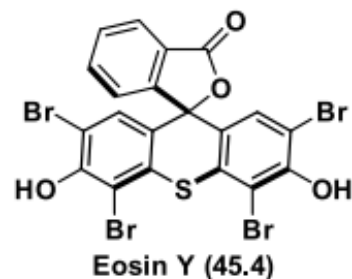
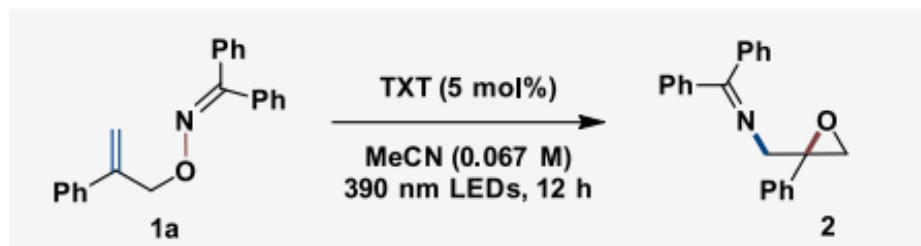
D. *This work*: a photochemical rearrangement approach for epoxide synthesis

Oxa- π , σ -Methane Rearrangement

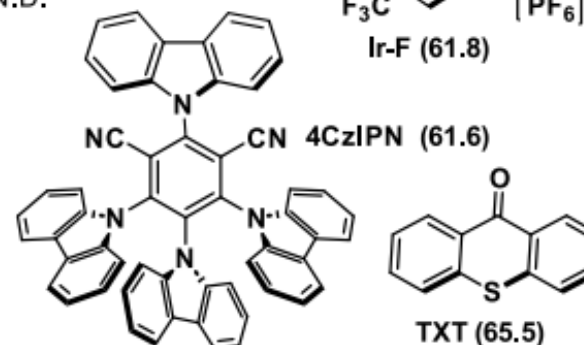
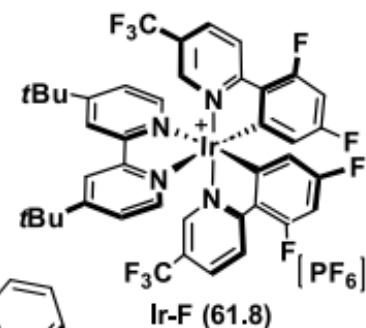




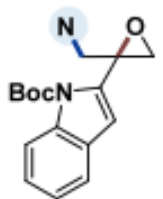
能量转移催化氧杂- π , σ -甲烷重排合成环氧化合物



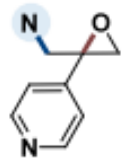
Entry	Photocatalyst	E _T (kcal/mol)	E _{1/2} ^{[M*]/[M⁺]} (V)	E _{1/2} ^{[M⁻]/[M^{•-}]} (V)	Yield(%)	Entry	Variations from standard condition	Yield(%)
1	Eosin Y	45.4	+1.18	-1.60	N.D.	7	EtOAc / PhCF ₃ / DMSO	78 / 66 / 60
2 ^a	Ru(bpy) ₃ (PF ₆) ₂	46.0	+0.77	-0.81	N.D.	8	MeOH / THF / DCM	60 / 46 / N.D.
3 ^a	fac-Ir(ppy) ₃	58.1	+0.31	-1.73	44	9	Toluene	Trace
4	4CzIPN	61.6	+1.43	-1.18	15	10	DMF	Trace
5 ^a	Ir-F	61.8	+1.21	-0.89	70 / 90 ^b	11	without TXT	N.D.
6	TXT	65.5	+1.18	-1.11	99 (84) ^c	12	without light	N.D.



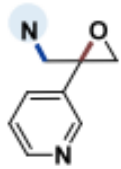
Reaction conditions: **1a** (0.2 mmol), photocatalyst (5 mol %), and MeCN (3.0 mL, 0.067 M) at room temperature under 10 W 390 nm LEDs with a cooling system for 12 h under N₂. ^a2 mol % PC was used. ^b450 nm LEDs were used instead of 390 nm LEDs. ^cIsolated yield.

能量转移催化氧杂- π , σ -甲烷重排合成环氧化合物

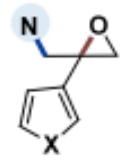
30, 76%



31, 55%

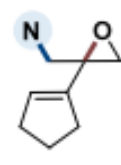


32, 94%

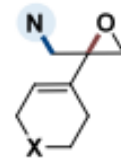


33, X = S, 41%

34, X = O, 45%

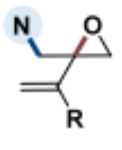


35, 60%

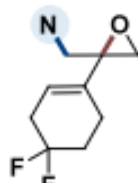


36, X = O, 74%

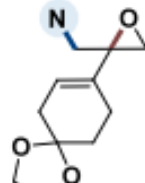
37, X = NBoc, 68%

38, R = CF₃, 75%

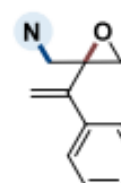
39, R = Me, 51%



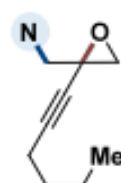
40, 58%



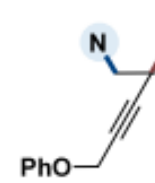
41, 85%



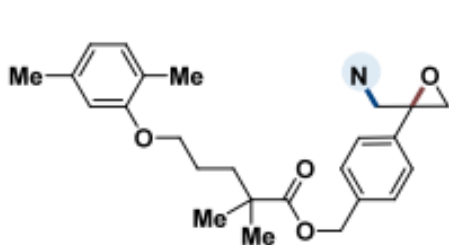
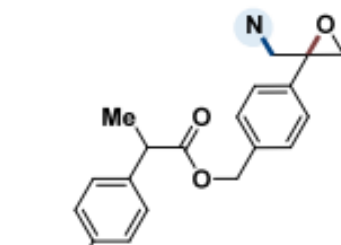
42, 49%



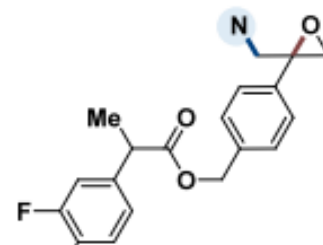
43, 41%



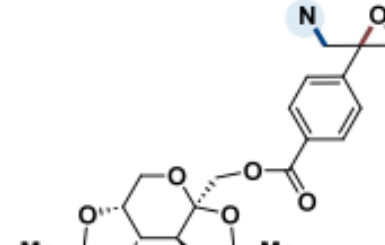
44, 44%

45, 48%^a

46, 75%



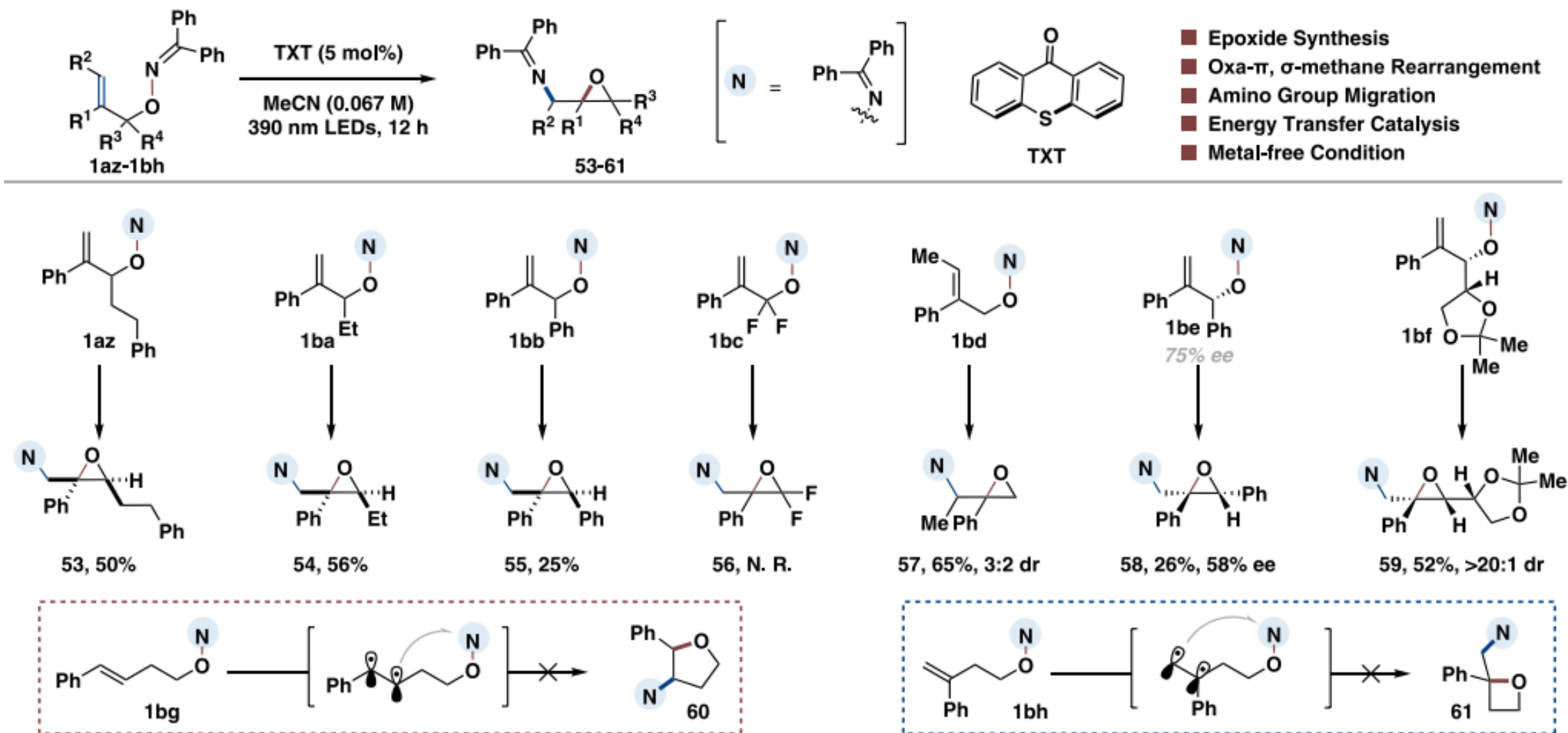
47, 57%



48, 74%



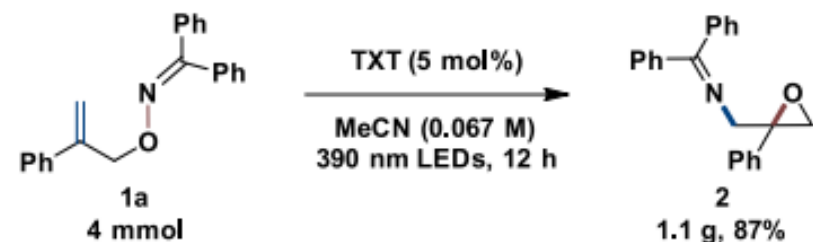
能量转移催化氧杂- π , σ -甲烷重排合成环氧化合物



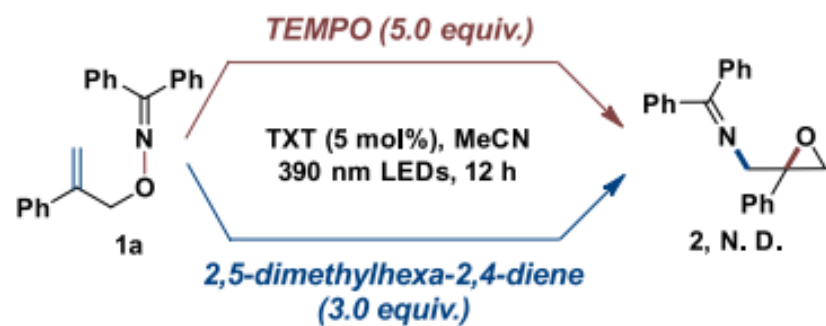


能量转移催化氧杂- π , σ -甲烷重排合成环氧化合物

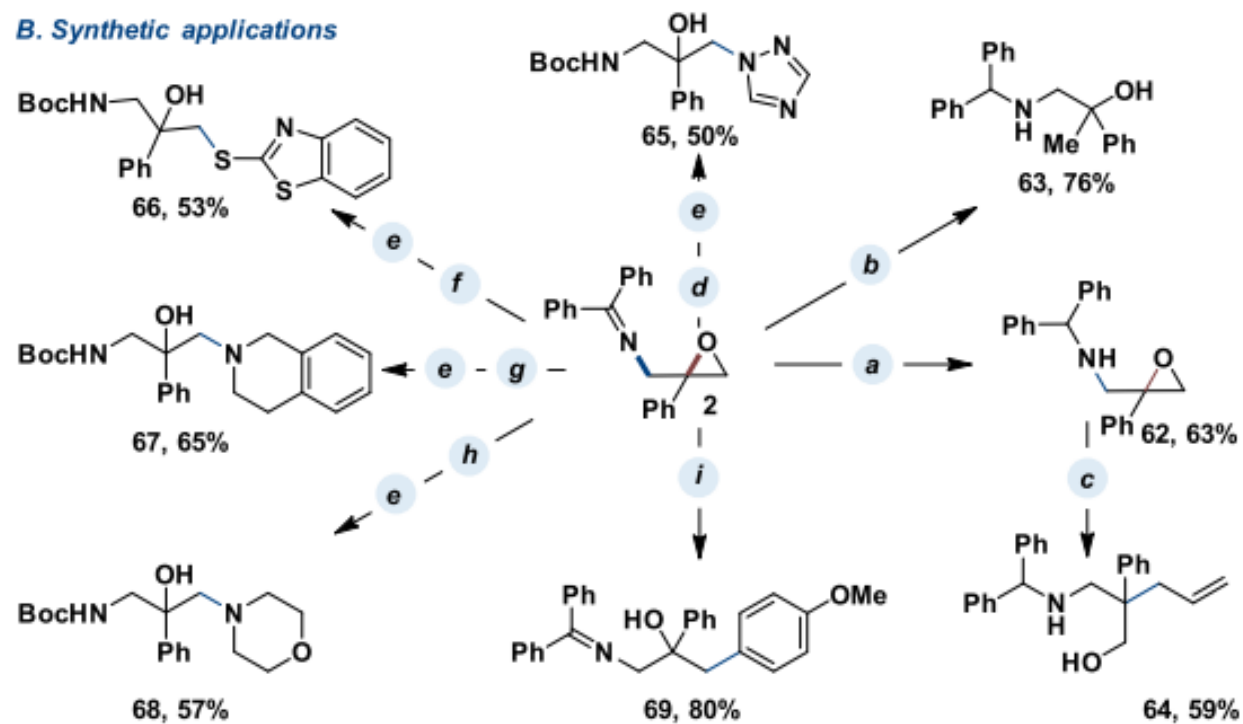
A. Gram-scale experiments



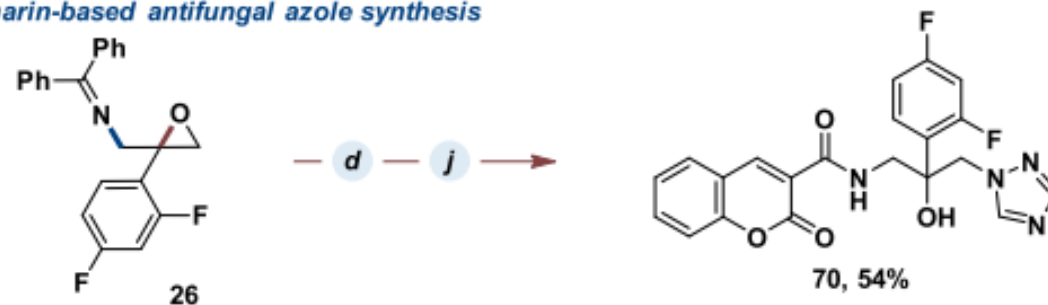
D. Radical inhibitor & triplet energy quenching experiments



B. Synthetic applications



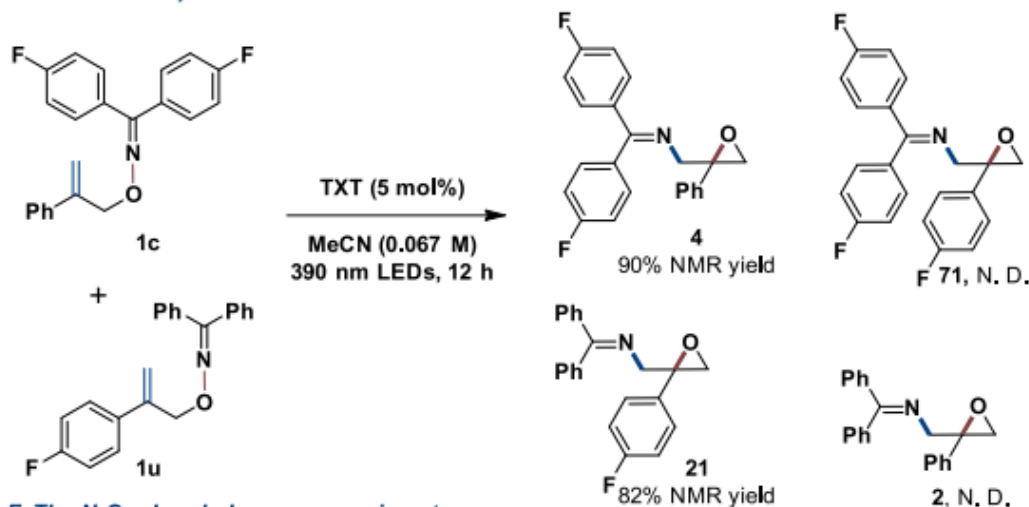
C. Coumarin-based antifungal azole synthesis



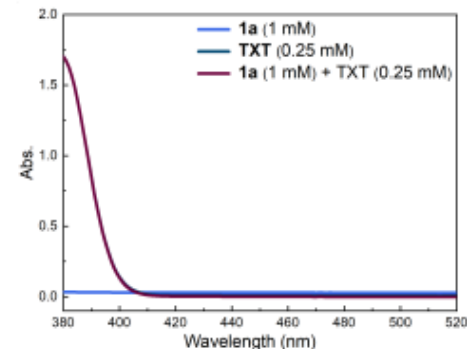


能量转移催化氧杂- π , σ -甲烷重排合成环氧化合物

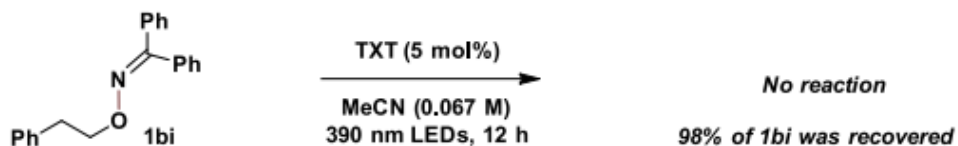
E. Crossover experiments



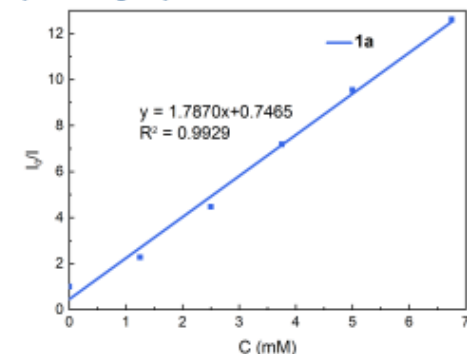
G. UV-vis experiment



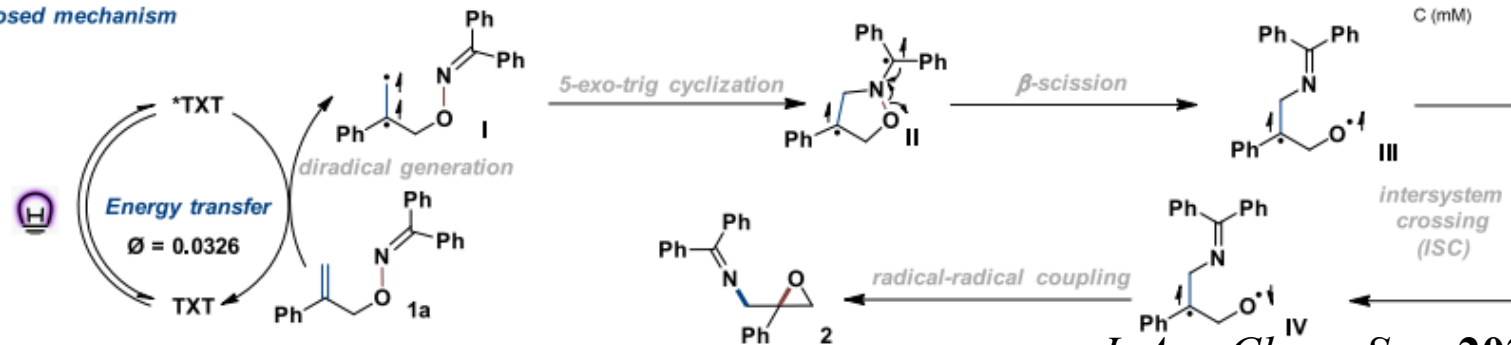
F. The N-O σ -bond cleavage experiment



H. Stern-Volmer quenching experiment



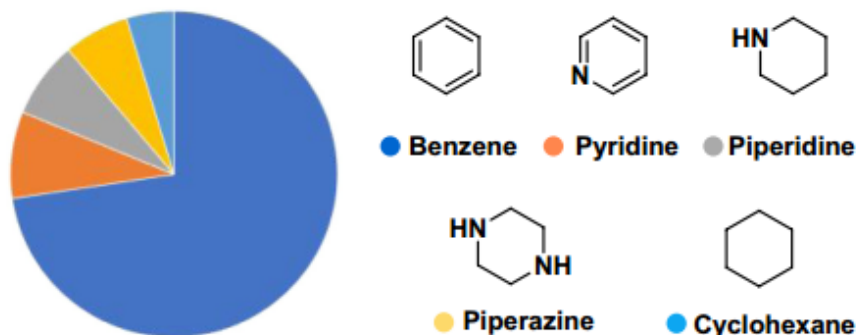
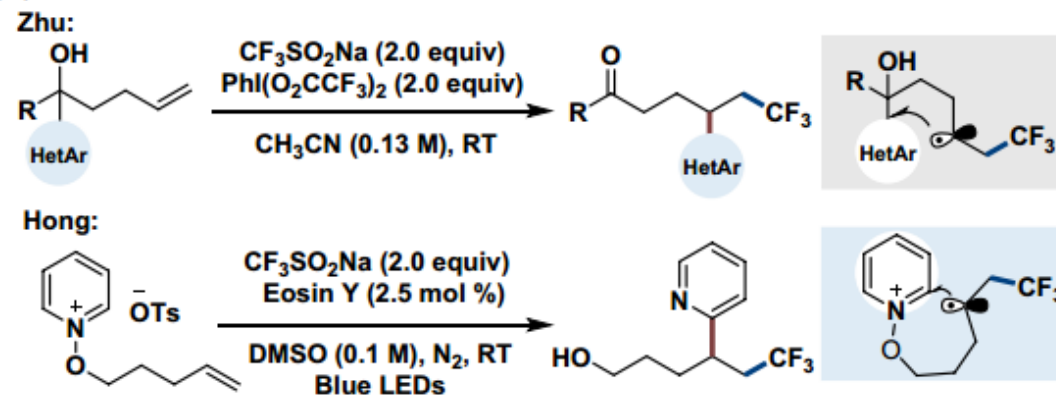
I. Proposed mechanism



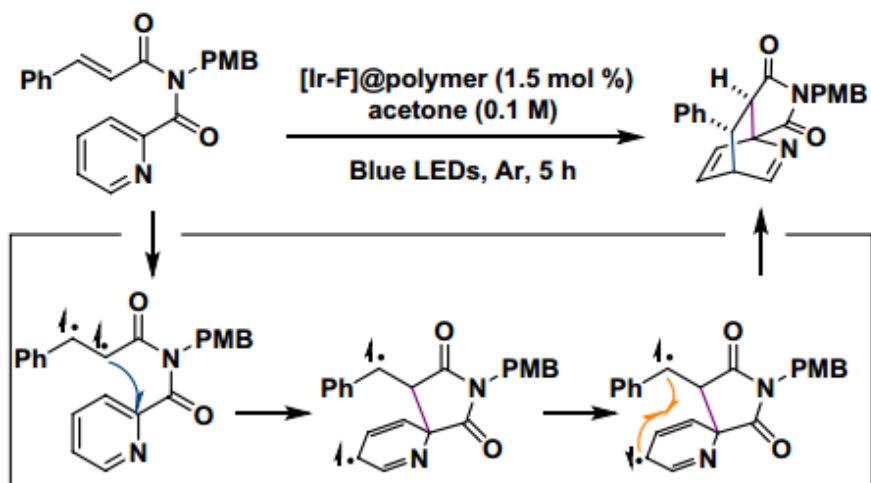
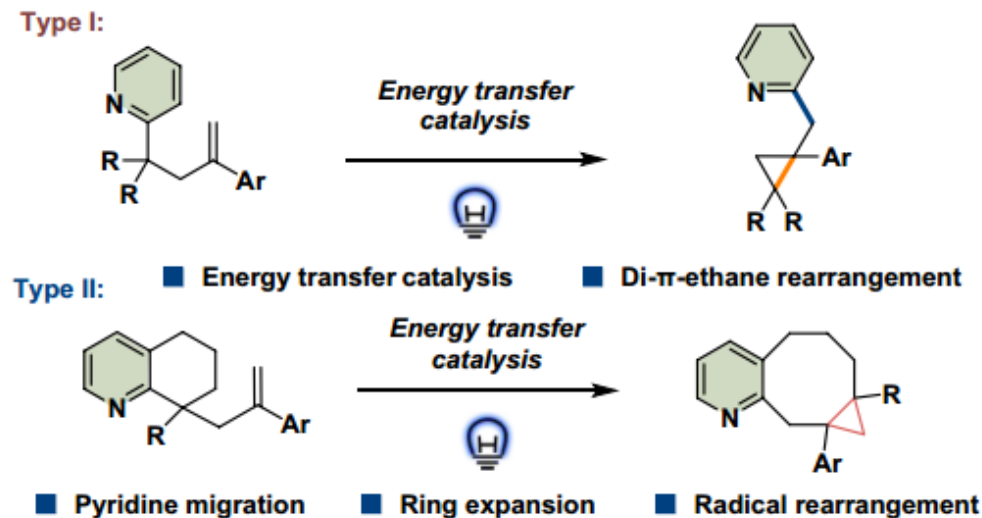


吡啶的能量转移重排反应

(a) Top 5 most frequently used rings from small molecule drugs

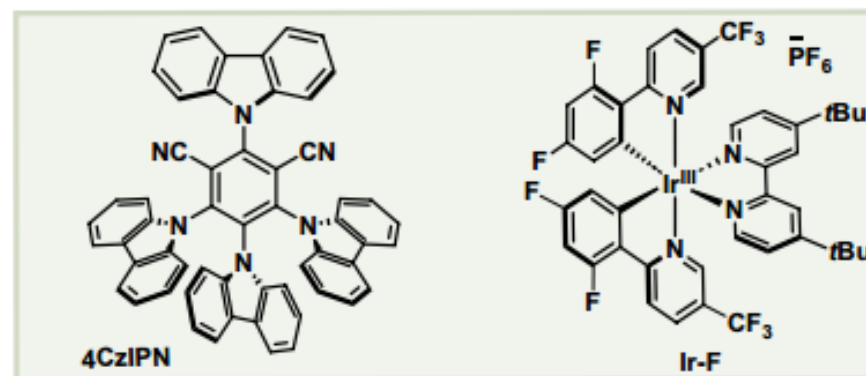
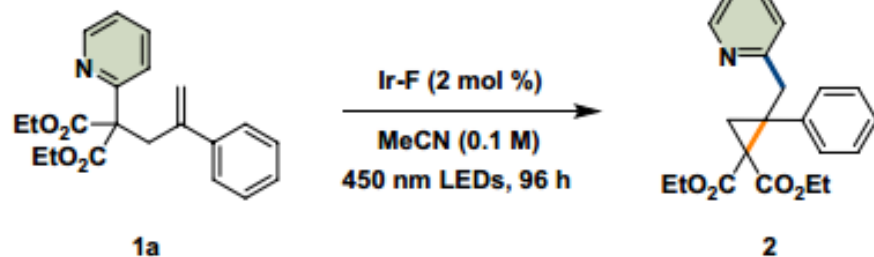
(b) Radical migration of pyridines enabled by *electron transfer*

(c) Radical cycloaddition with pyridines enabled by energy transfer

(d) *This work*: energy transfer enabled rearrangement involving pyridine motifs



吡啶的能量转移重排反应



Entry	Variations from Standard Conditions	Yield (%)	Entry	Variations from Standard Conditions	Yield (%)
1	None	87 (80) ^a	7	24 h, 48 h, 72 h instead of 96 h	38, 56, 71
2	No photocatalysis or no light	N.D.	8	DCE instead of MeCN	80
3	40 °C instead of light	N.D.	9	EtOAc instead of MeCN	68
4	4CzIPN (10 mol %) instead of Ir-F	N.D.	10	0.1 equiv TFA was added	Trace
5 ^b	Thioxanthone (10 mol %) instead of Ir-F	Trace	11	2 equiv Gd(OTf) ₃ was added	N.D.
6 ^c	Benzophenone (10 mol %) instead of Ir-F	Trace	12	2 equiv TFA was added	N.D.

Reaction conditions: **1a** (0.2 mmol), Ir-F (2 mol %), and MeCN (2 mL, 0.1 M) at room temperature under 30 W 450 nm LEDs with a cooling fan for 96 h under N₂.

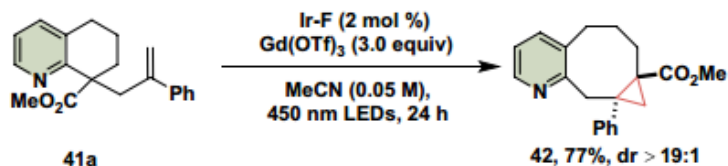
^a Isolated yield.

^b 390 nm instead of 450 nm.

^c 365 nm instead of 450 nm.

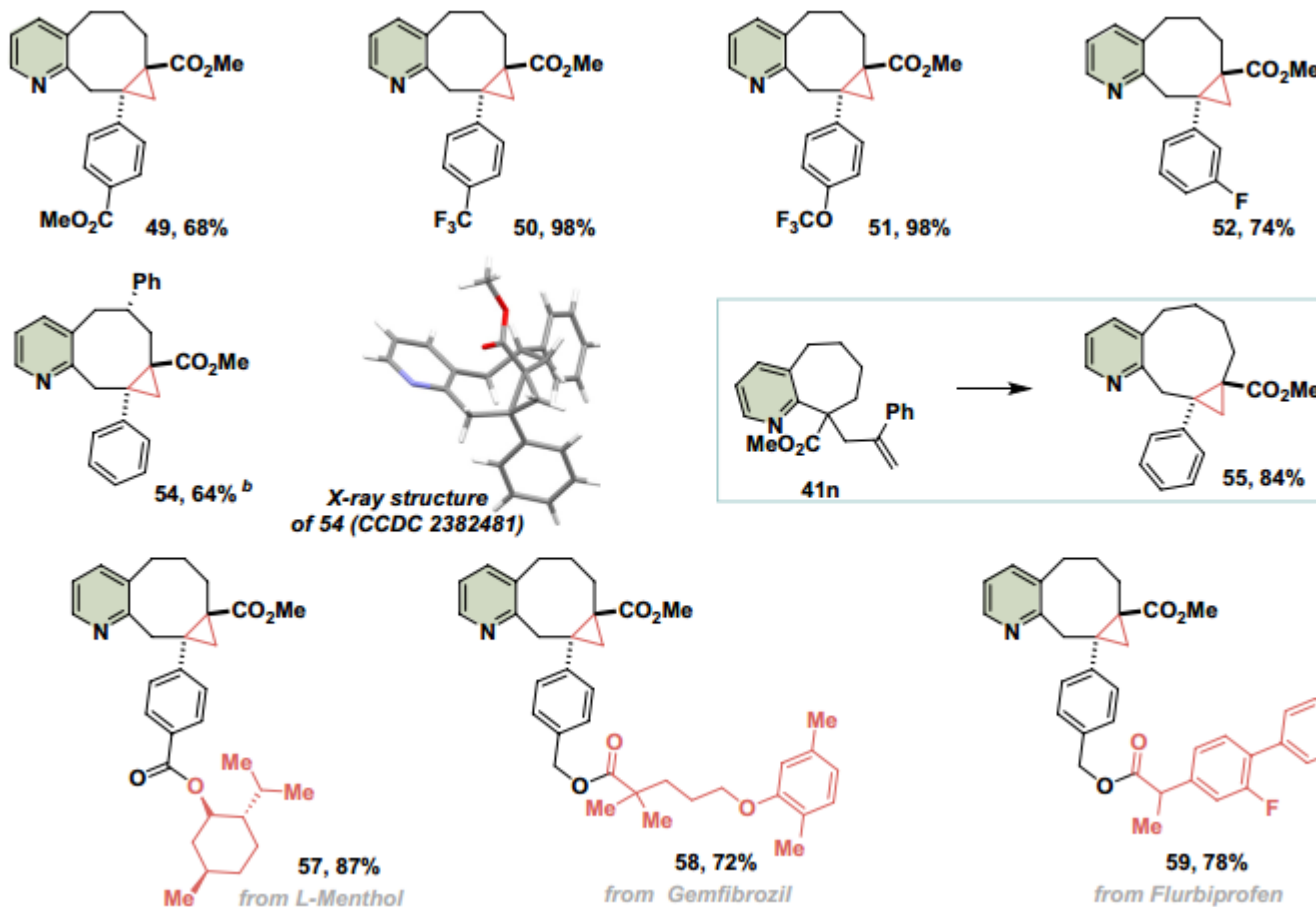
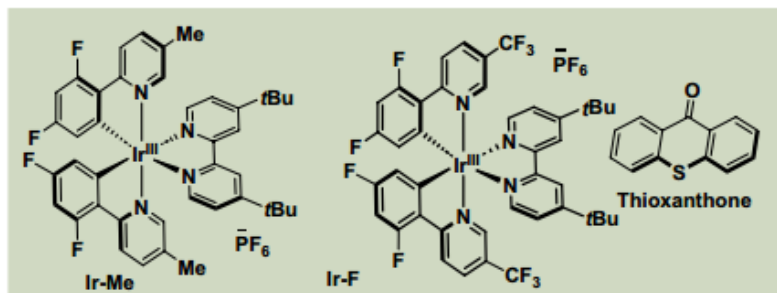


吡啶的能量转移重排反应



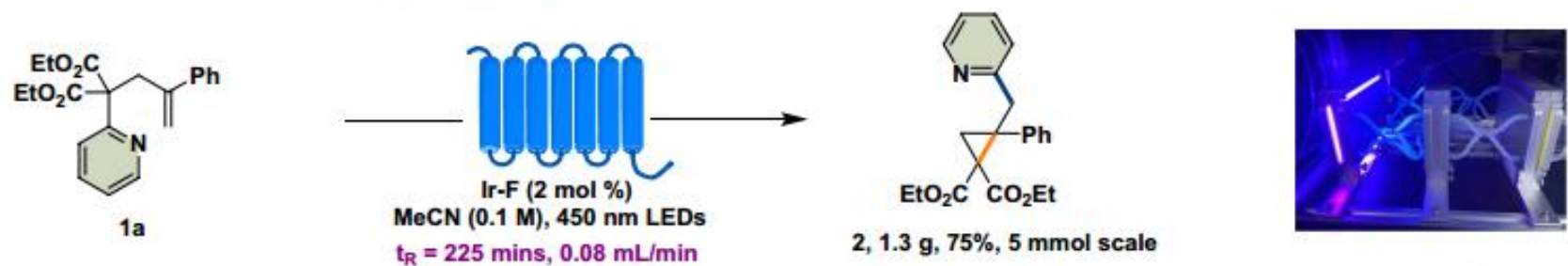
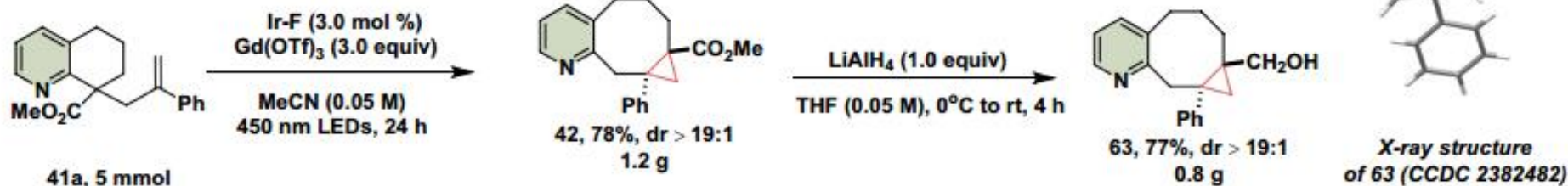
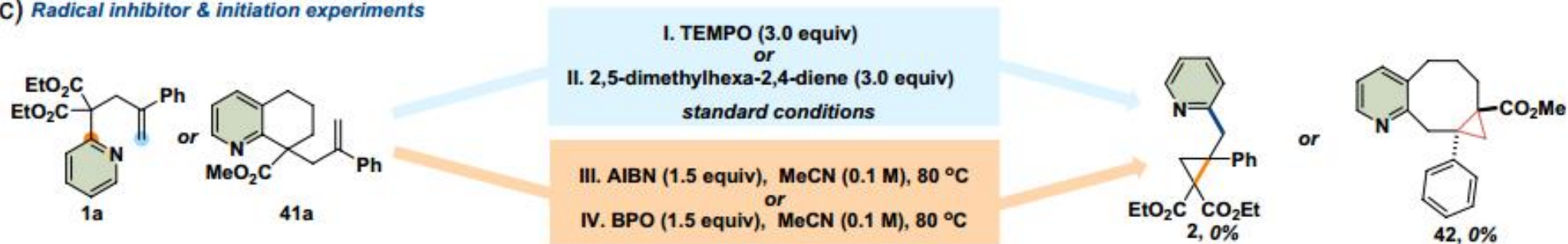
Entry Variations from Standard Conditions Yield (%)

1	Without Gd(OTf) ₃	N.D.
2	TFA, Zn(OTf) ₂ or Lu(OTf) ₃ instead of Gd(OTf) ₃	45, 46, 54
3	Using 0.2 equiv Gd(OTf) ₃	Trace
4	Using 2.0 equiv or 4.0 equiv Gd(OTf) ₃	45, 55
5	Using 0.1 M MeCN	63
6	Ir-Me (2 mol %) instead of Ir-F	60
7 ^a	Thioxanthone (5 mol %) instead of Ir-F	Trace
8	3 mol % Ir-F	81
9	No photocatalyst under 450 nm or 365 nm	N.D.
10	40 °C instead of light	N.D.





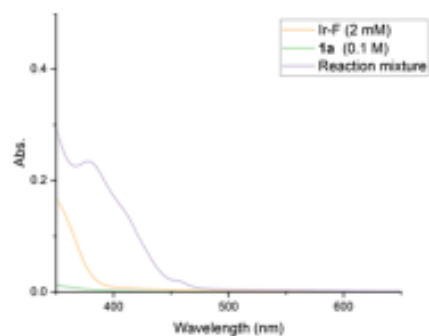
吡啶的能量转移重排反应

(a) *The continuous-flow experiment & gram-scale experiment*(b) *Gram-scale experiment and synthetic application*(c) *Radical inhibitor & initiation experiments*

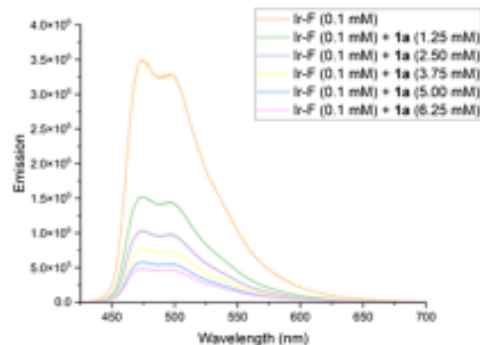


吡啶的能量转移重排反应

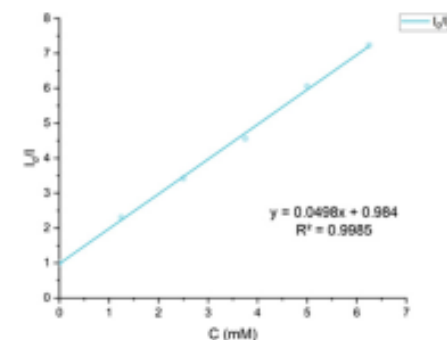
(d) UV-vis experiment



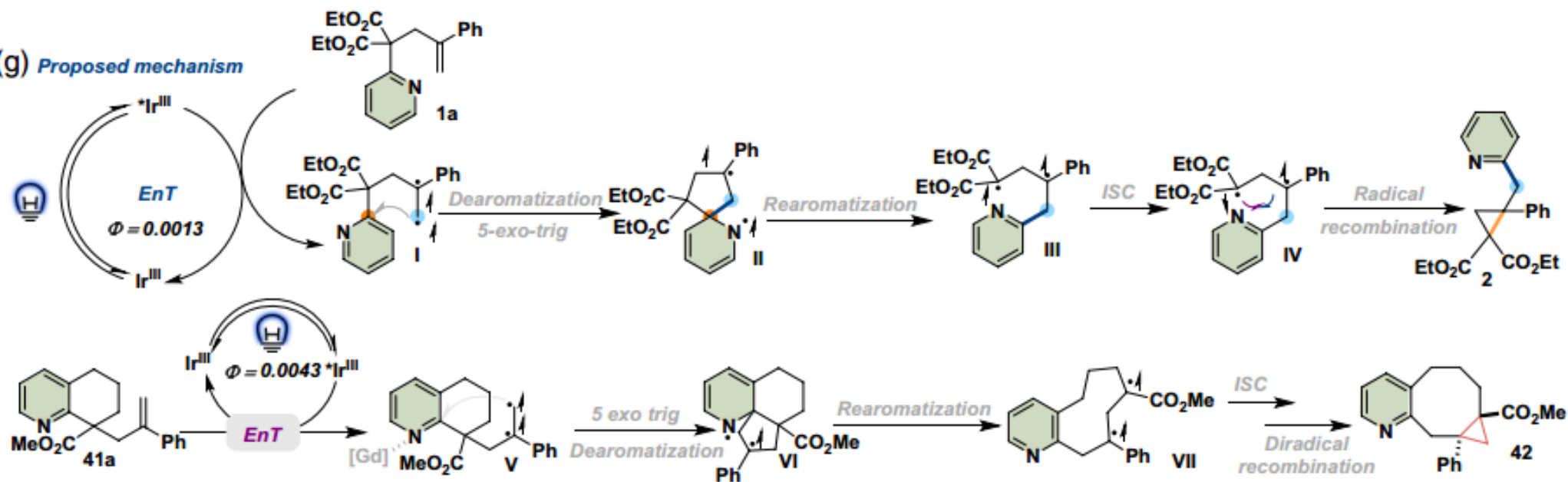
(e) Fluorescence study



(f) Stern-Volmer quenching experiment



(g) Proposed mechanism

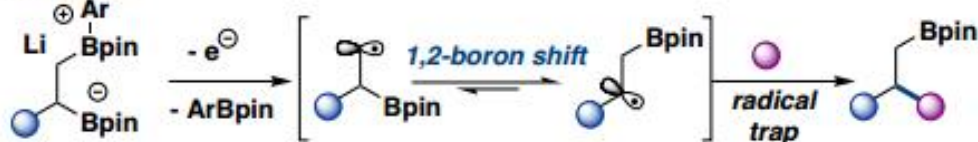




通过能量传递催化的光重排反应合成硼化碳环化合物

A. Radical migration involving 1,2-boron shift via SET

Aggarwal:

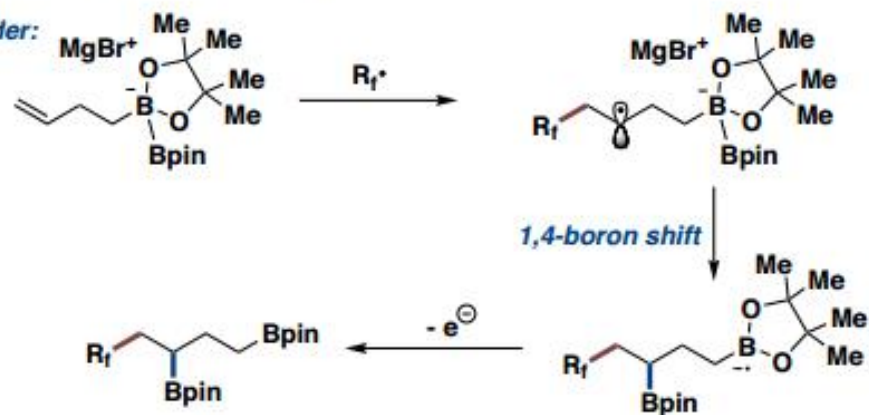


Studer:



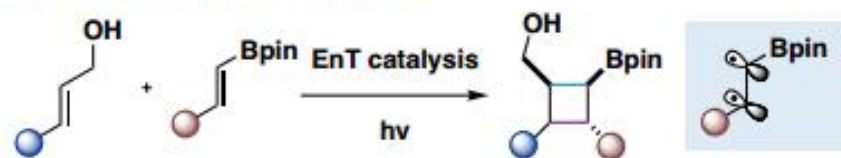
B. Radical migration involving 1,4-boron shift via SET

Studer:

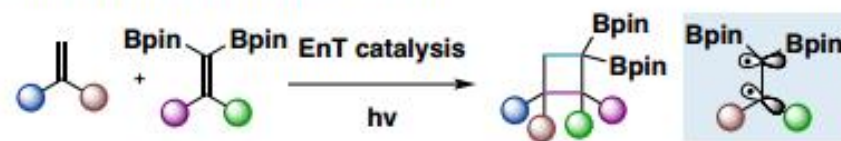


C. Boronic Ester Enabled [2 + 2]-Cycloadditions

Monoborylated alkenes (Brown):

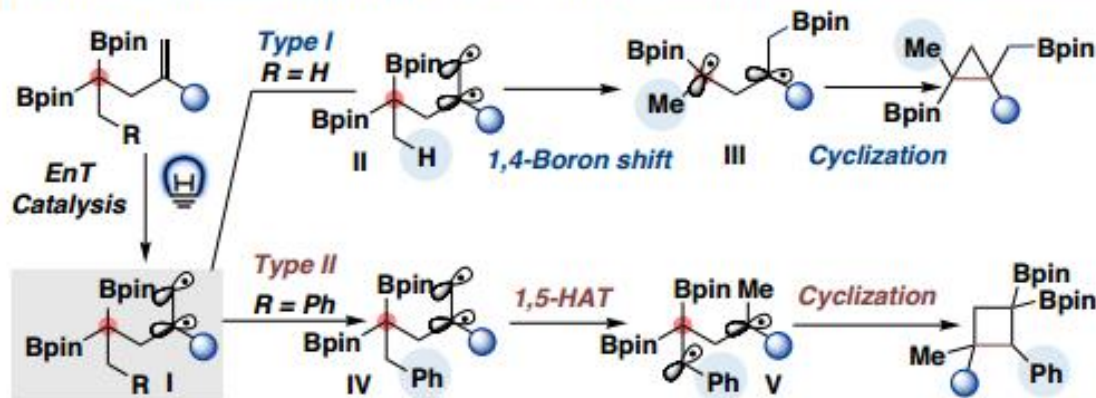


Polyborylated alkenes (Masarwa):



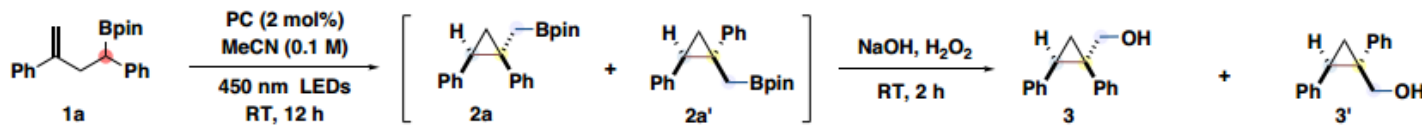
D. Our design - Borylated Carbocycles Synthesis Enabled by Energy Transfer Catalysis

Type I: *p, s*-Methane rearrangement Type II: Hydrogen Atom Transfer (HAT)/Cyclization

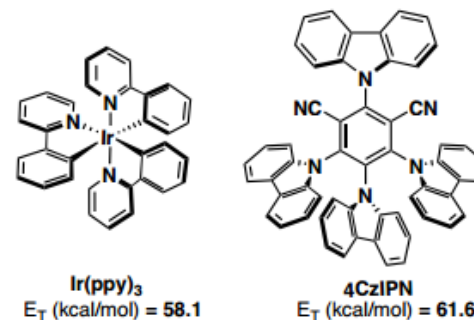




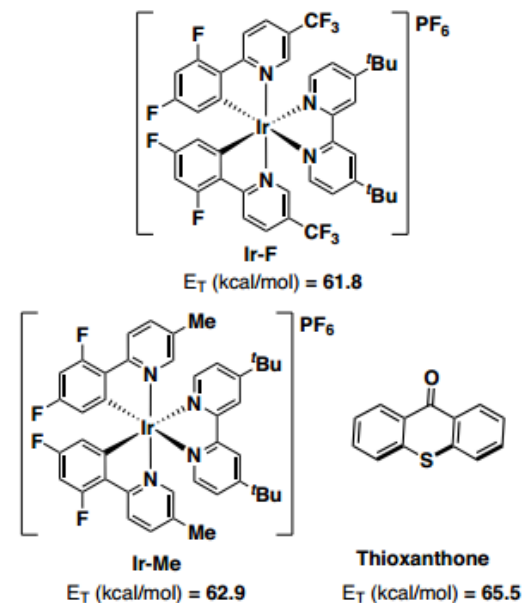
通过能量传递催化的光重排反应合成硼化碳环化合物



Entry	Photocatalyst	E _T (kcal/mol)	E _{1/2} ^{[M⁺]/[M⁺]} (V)	E _{1/2} ^{[M⁻]/[M]} (V)	Solvent	Yield (%)	dr (3:3')
1	Ir(ppy) ₃	58.1	+0.31	-1.73	MeCN	0	0
2 ^a	4CzIPN	61.6	+1.43	-1.18	MeCN	0	0
3	Ir-F	61.8	+1.21	-0.89	MeCN	87	1.8:1
4	Ir-Me	62.9	+0.97	-0.92	MeCN	86	1.8:1
5 ^b	Thioxanthone	65.5	+1.18	-1.11	MeCN	73	1.8:1

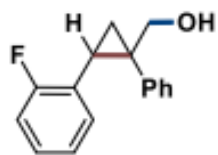


Entry	Variations from Entry 3	Yield (%)	dr (3:3')
6	without PC, under 365 nm or 385 nm or 450 nm	0	0
7	without light	0	0
8	EA instead of MeCN	77	1.2:1
9	DCM instead of MeCN	76	2.1:1
10	THF instead of MeCN	55	0.9:1
11	PhCF ₃ instead of MeCN	90 (86) ^c	3.2:1 (2.9:1)
12	PhMe instead of MeCN	71	1.2:1
13	DMF instead of MeCN	71	1.1:1
14	DMSO instead of MeCN	87	3.4:1
15	MeOH instead of MeCN	77	2.1:1

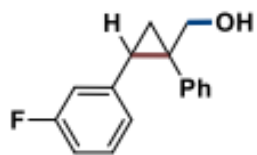




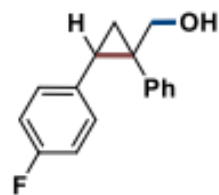
通过能量传递催化的光重排反应合成硼化碳环化合物



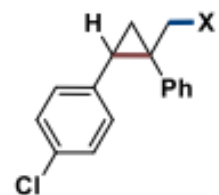
22^a, 46%, 1.4:1 dr



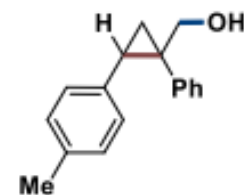
23, 78%, 1.2:1 dr



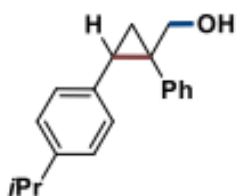
24^b, 71%, 1.5:1 dr



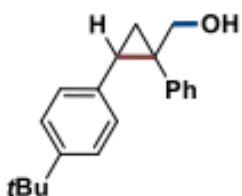
2w, X = Bpin, 77%, 1.8:1 dr
25, X = OH, 90%, 2.2:1 dr



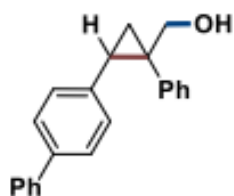
26^b, 61%, 2.1:1 dr



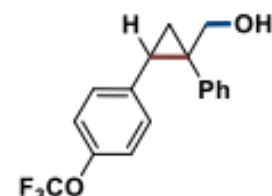
27^a, 66%, 2.0:1 dr



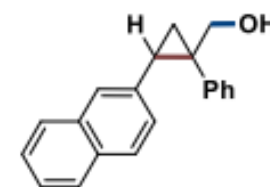
28^a, 60%, 1.9:1 dr



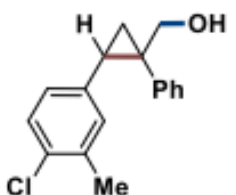
29^a, 44%, 1:1 dr



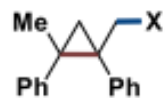
30, 83%, 1.8:1 dr



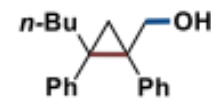
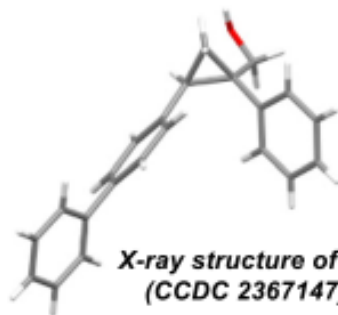
31, 60%, 1.2:1 dr



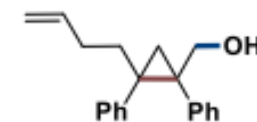
32^a, 86%, 2.1:1 dr



2ae, X = Bpin, 87%, 1:4.4 dr
33, X = OH, 89%, 1:3.4 dr



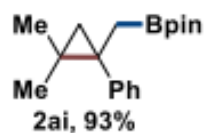
34, 68%, 1:3.4 dr



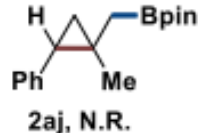
35^c, 50%, 1:2.3 dr



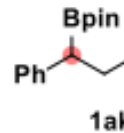
2ah, N.R.



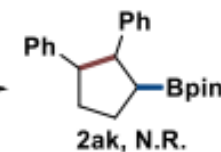
2ai, 93%



2aj, N.R.



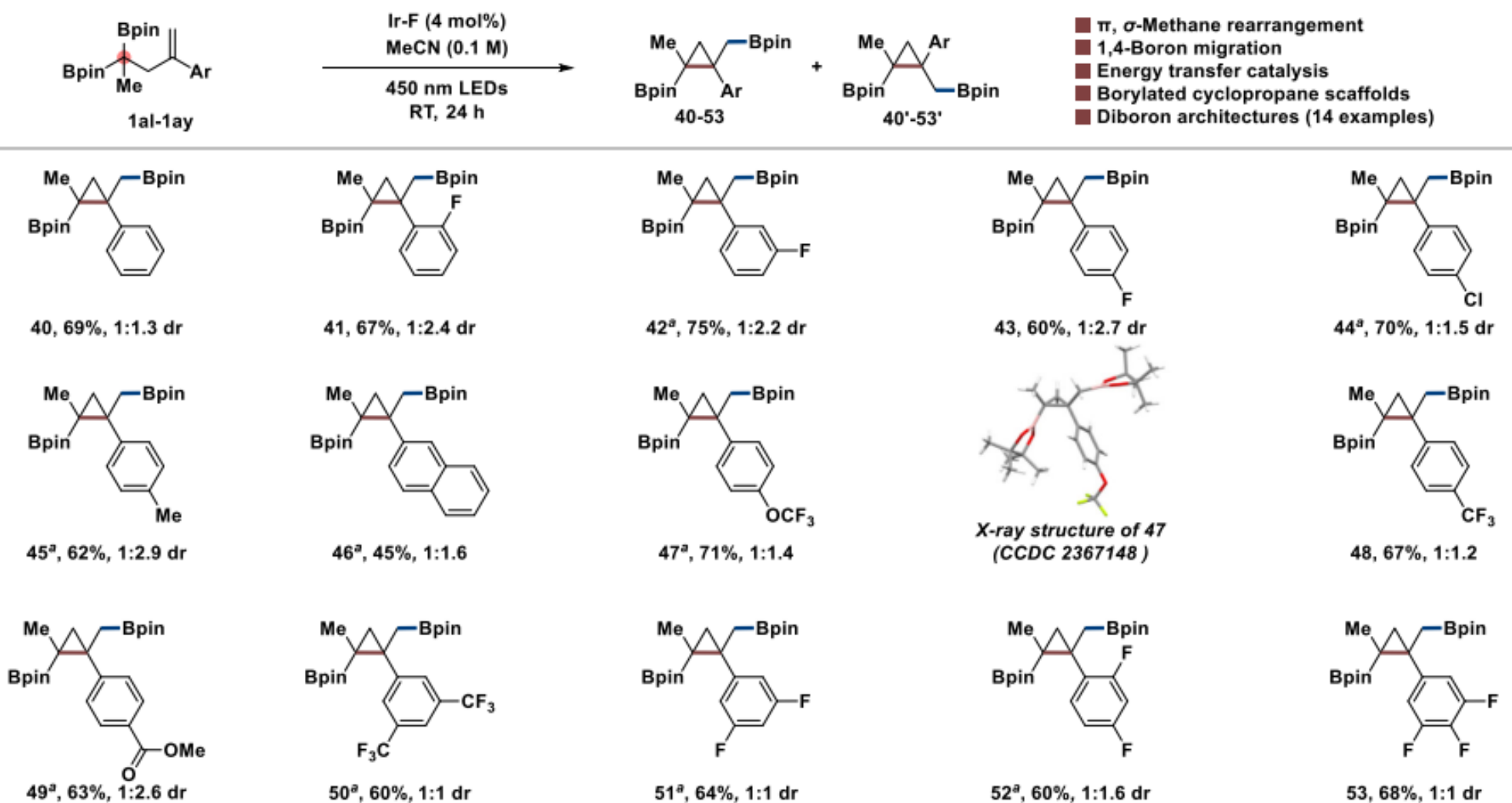
1ak



2ak, N.R.

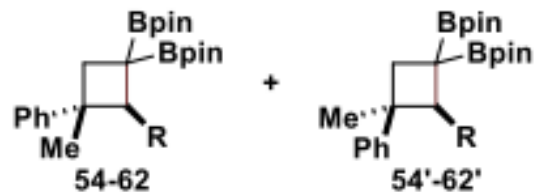
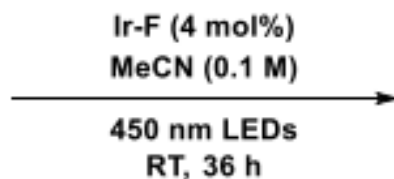
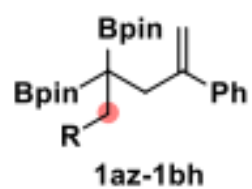


通过能量传递催化的光重排反应合成硼化碳环化合物

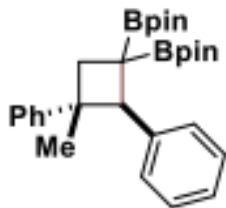




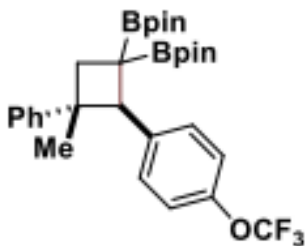
通过能量传递催化的光重排反应合成硼化碳环化合物



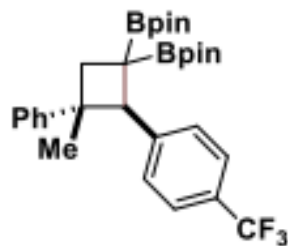
- Boron mediated HAT/cyclization
- Energy transfer catalysis
- Borylated cyclobutane frameworks
- Diboron architectures (9 examples)



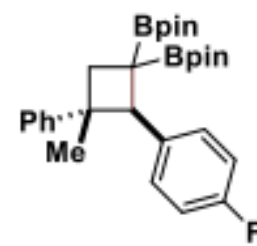
54, 48%, 1:1.1 dr



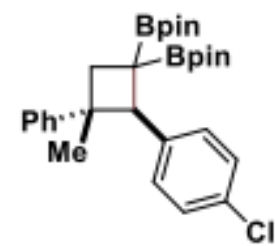
55, 53%, 1:1.2 dr



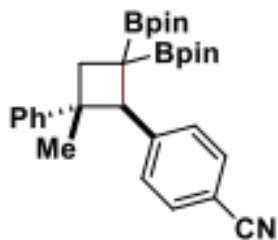
56, 64%, 1:1 dr



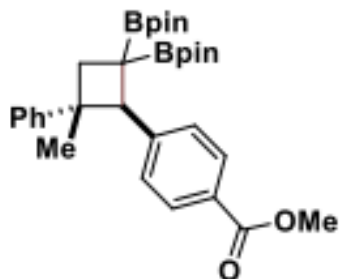
57, 68%, 1:1.7 dr



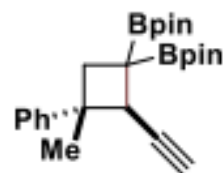
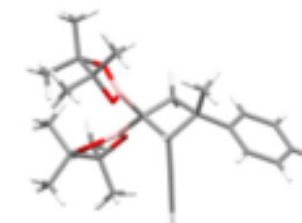
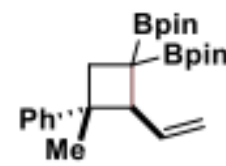
58, 65%, 1:1.4 dr



59, 65%, 1:1.7 dr



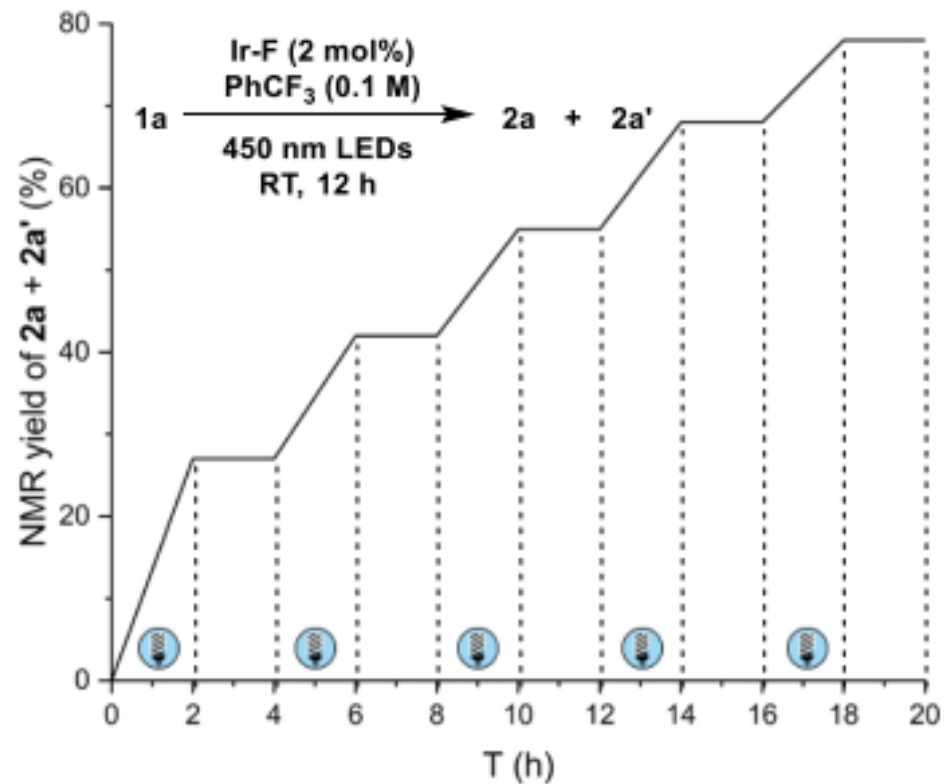
60, 51%, 2.2:1 dr

61^b, 47%, 1:7.7 drX-ray structure of 61^a
(CCDC 2367149)62^c, 55%, 1:2 dr

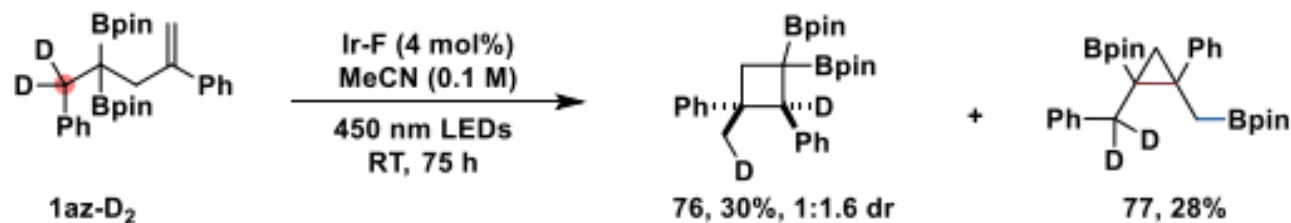


通过能量传递催化的光重排反应合成硼化碳环化合物

E. Light on-off experiments



F. Deuterium Labeling Experiment

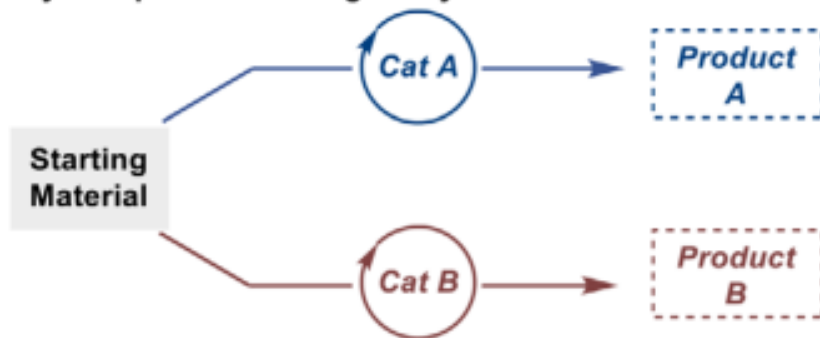


G. UV-Vis experiment

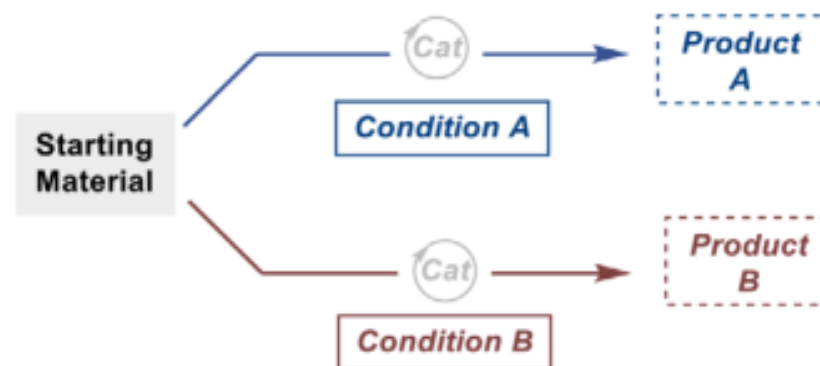
H. Stern-Volmer quenching experiment

光化学重排反应实现时间依赖性发散合成

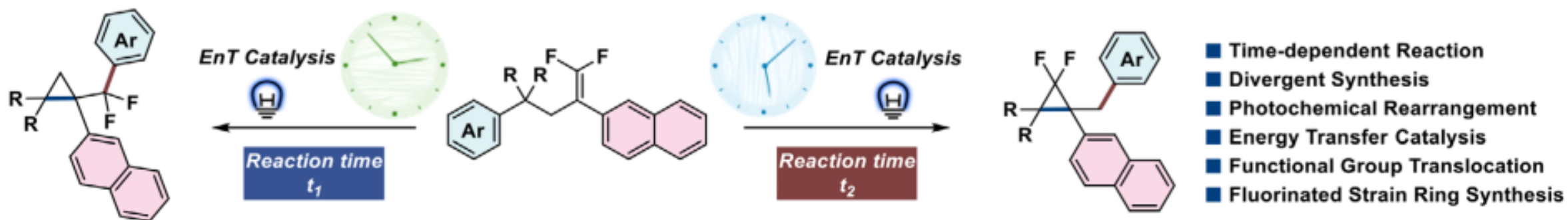
a) Catalyst-dependent Divergent Synthesis

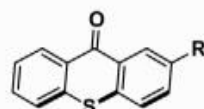
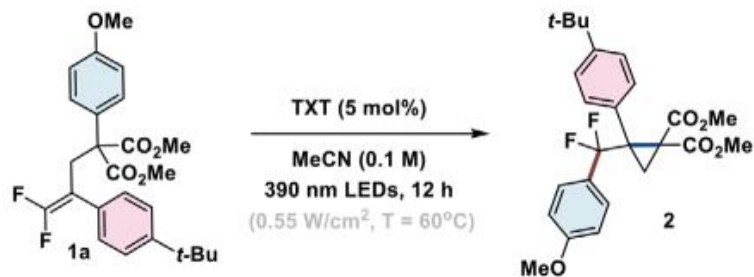


b) Reaction Conditions-dependent Divergent Synthesis



c) This Work: Time-dependent Photochemical Rearrangement

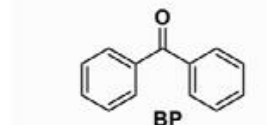



 光化学重排反应实现时间依赖性发散合成


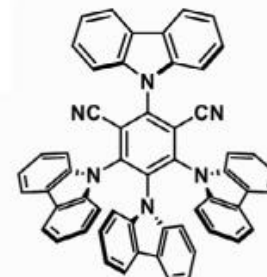
TXT, R = H
 2-CF₃-TXT, R = CF₃
 2-Cl-TXT, R = Cl
 2-*i*Pr-TXT, R = *i*Pr

Entry	Variations from standard conditions	¹ H NMR Yield	Entry	Variations from standard conditions	¹ H NMR Yield
1	none	99% (90%) ^{a)}	7	2-CF ₃ -TXT (5 mol%) instead of TXT	76%
2	no photocatalyst under 365 nm or 390 nm	N.D. ^{b)}	8	2-Cl-TXT (5 mol%) instead of TXT	88%
3	80 °C instead of light	N.D. ^{b)}	9	2- <i>i</i> Pr-TXT (5 mol%) instead of TXT	91%
4	4CzIPN ^{c)} (5 mol%) instead of TXT	N.D. ^{b)}	10	385 nm ^{e)} instead of 390 nm	trace
5	Ir - F ^{c)} (2 mol%) instead of TXT	trace	11	385 nm ^{f)} instead of 390 nm	97%
6	BP ^{d)} (10 mol%) instead of TXT	trace	12	405 nm ^{g)} instead of 390 nm	trace

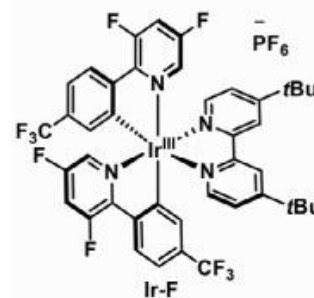
Standard conditions: **1a** (0.2 mmol, 1 equiv.), TXT (5 mol%), MeCN (0.1 M), 390 nm LEDs (0.55 W cm⁻², T = 60 °C), 12 h. ^{a)} Isolate yield. ^{b)} N. d. = not detected. ^{c)} 450 nm (0.15 W cm⁻², T = 40 °C) instead of 390 nm (0.55 W cm⁻², T = 60 °C). ^{d)} 365 nm (0.12 W cm⁻², T = 40 °C) instead of 390 nm (0.55 W cm⁻², T = 60 °C). ^{e)} 385 nm LEDs (0.11 W cm⁻², T = 40 °C). ^{f)} 385 nm LEDs (0.54 W cm⁻², T = 60 °C). ^{g)} 405 nm (0.15 W cm⁻², T = 40 °C) instead of 390 nm (0.55 W cm⁻², T = 60 °C).



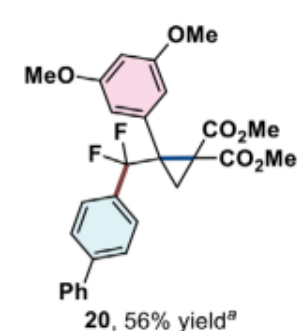
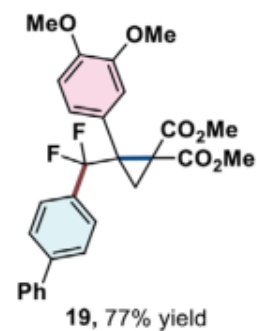
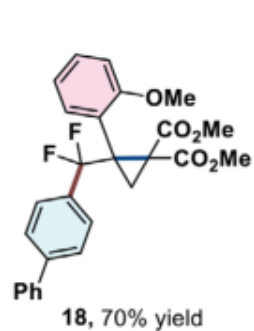
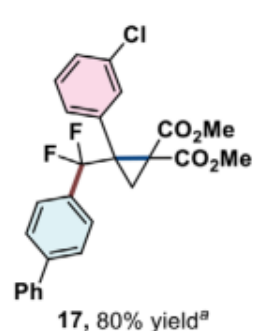
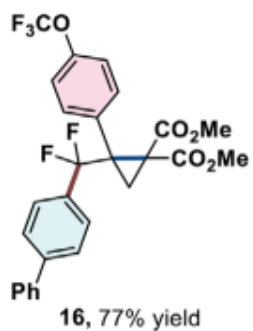
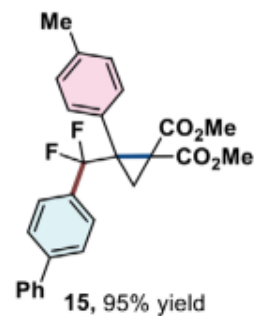
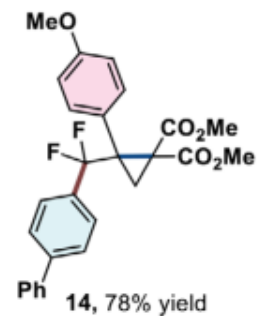
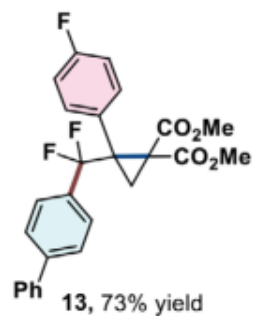
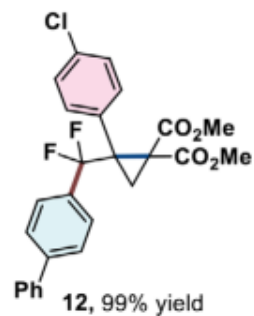
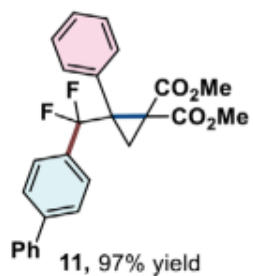
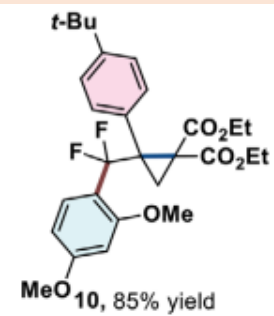
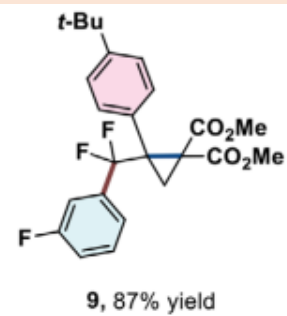
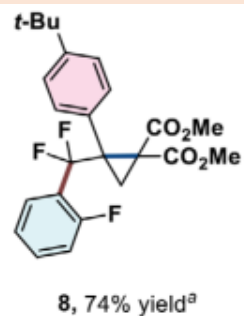
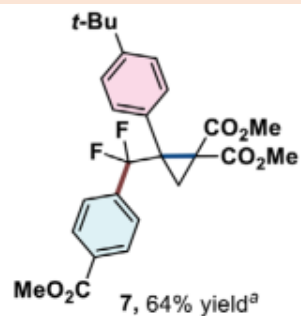
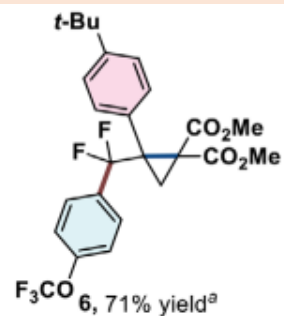
BP

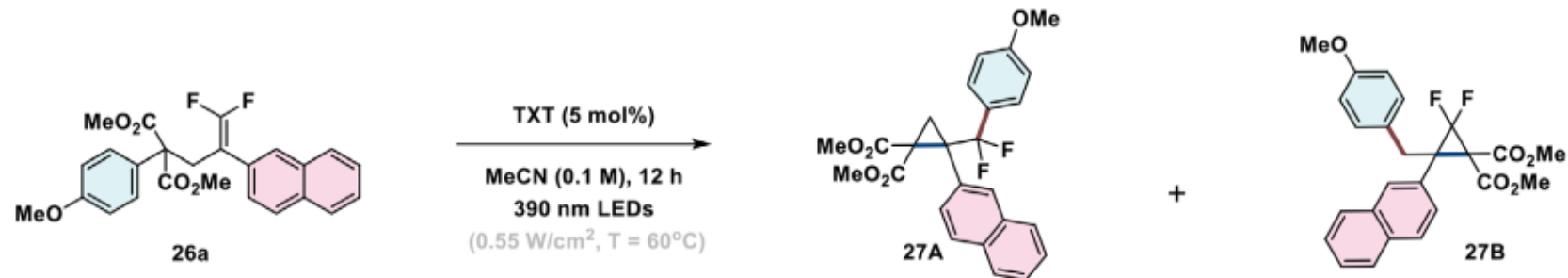


4CzIPN

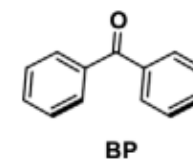
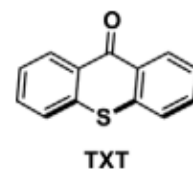
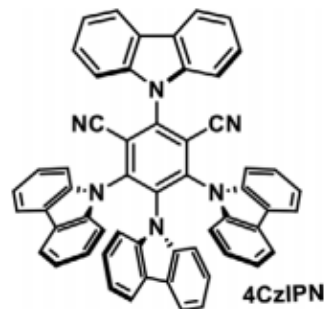
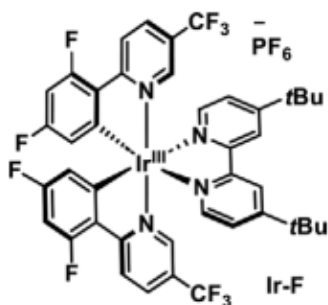


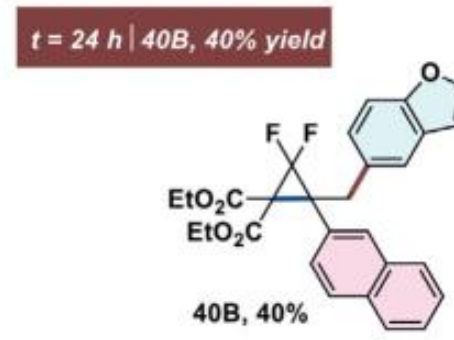
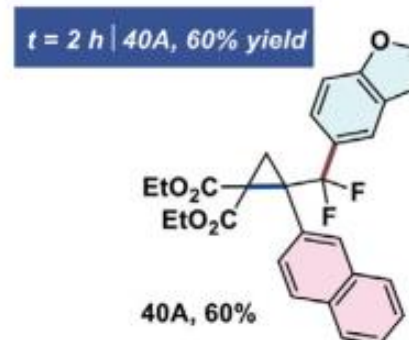
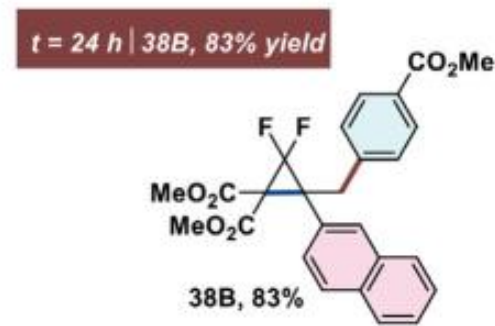
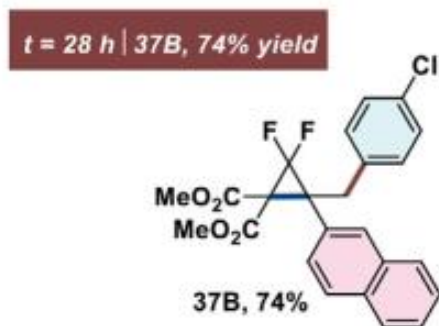
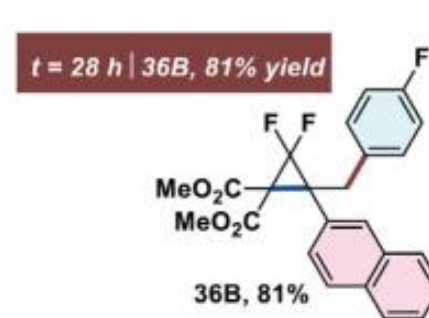
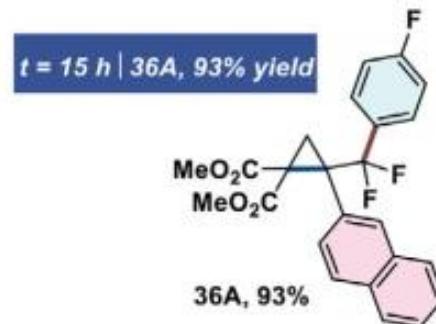
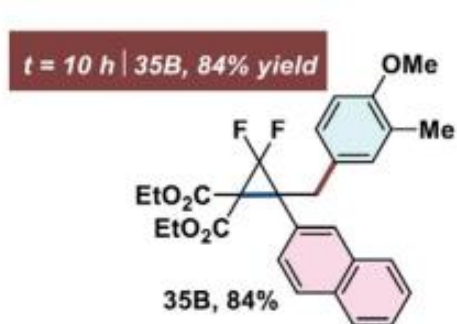
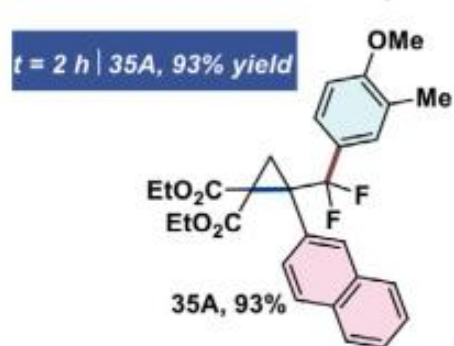
Ir-F

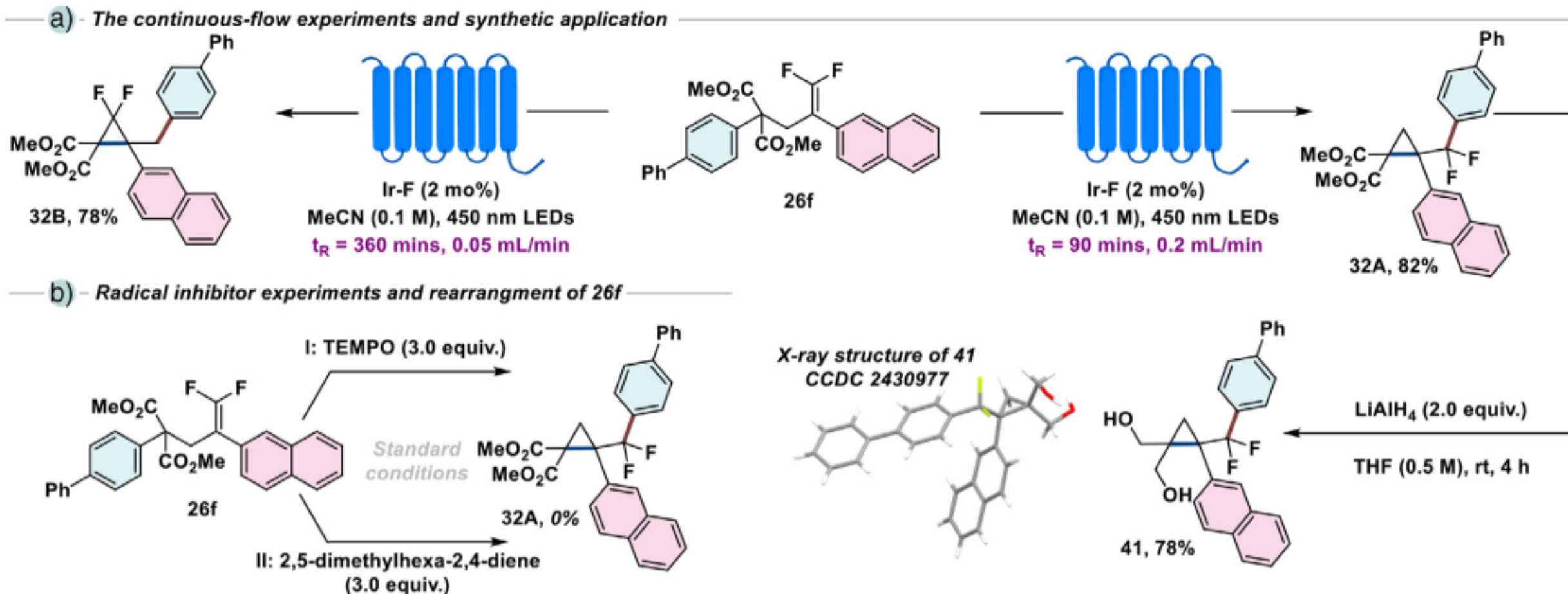
 光化学重排反应实现时间依赖性发散合成


 光化学重排反应实现时间依赖性发散合成


Entry	Variations from standard conditions	¹ H NMR Yield (27A:27B)	Entry	Variations from standard conditions	¹ H NMR Yield (27A:27B)
1	none	10%: 62%	7	no photocatalysis under 365 nm	N.d. ^{d)}
2	4CzIPN ^{a)} (5 mol%) instead of TXT	5%: 38%	8	80 °C instead of light	N.d. ^{d)}
3	BP ^{b)} (5 mol%) instead of TXT	trace	9 ^{e)}	EA instead of MeCN	0%: 84%(80%) ^{c)}
4	Ir-F ^{a)} (2 mol%) instead of TXT	0%: 90%(88%) ^{c)}	10 ^{e)}	THF instead of MeCN	0%: 69%
5	no light	N.d. ^{d)}	11 ^{f)}	6 h instead of 12 h	0%: 88% ^{c)}
6	no photocatalysis under 450 nm	N.d. ^{d)}	12 ^{f)}	1 h instead of 12 h	81% ^{c)} : 0%

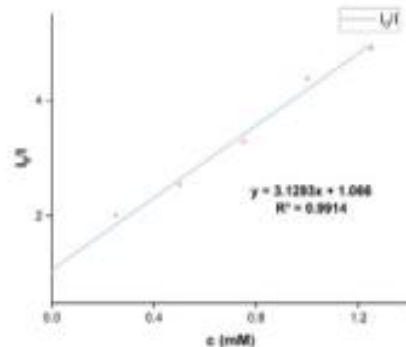
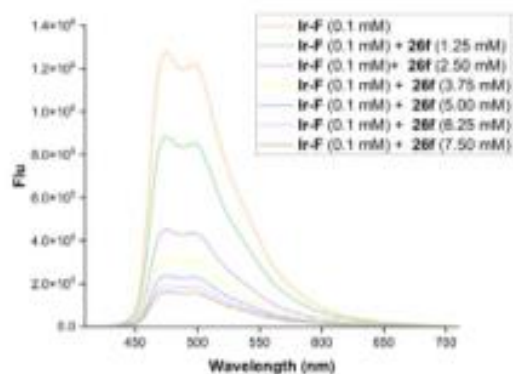


 光化学重排反应实现时间依赖性发散合成

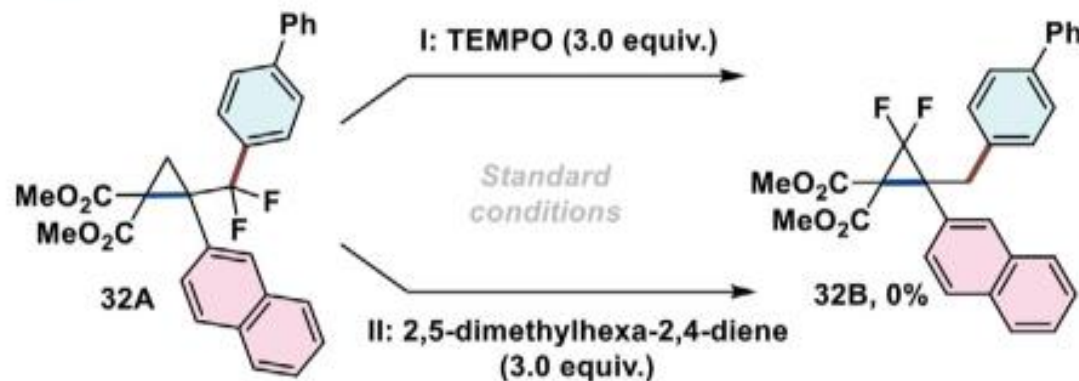

 光化学重排反应实现时间依赖性发散合成


光化学重排反应实现时间依赖性发散合成

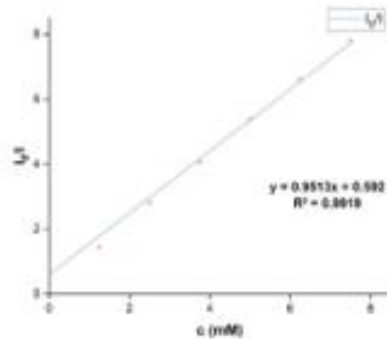
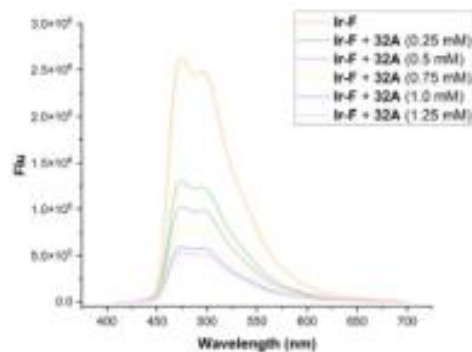
c) Stern-Volmer quenching experiment of 26f



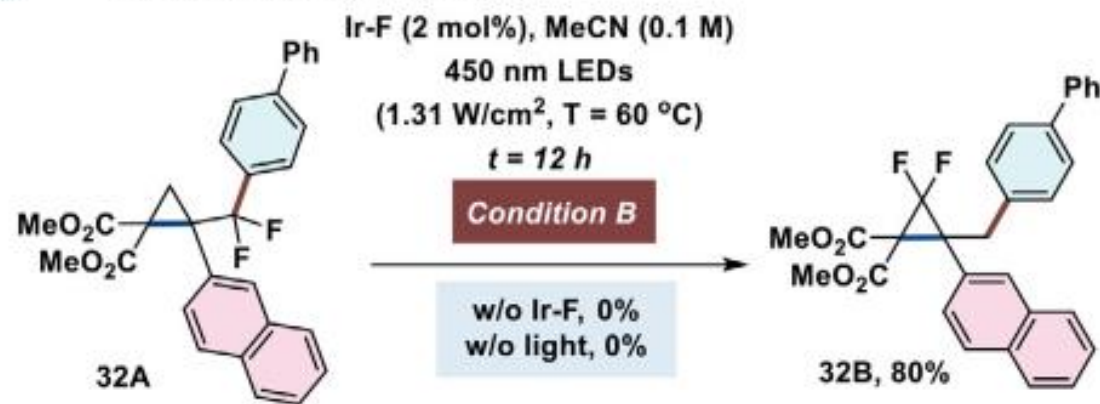
d) Radical inhibitor experiments of 32A



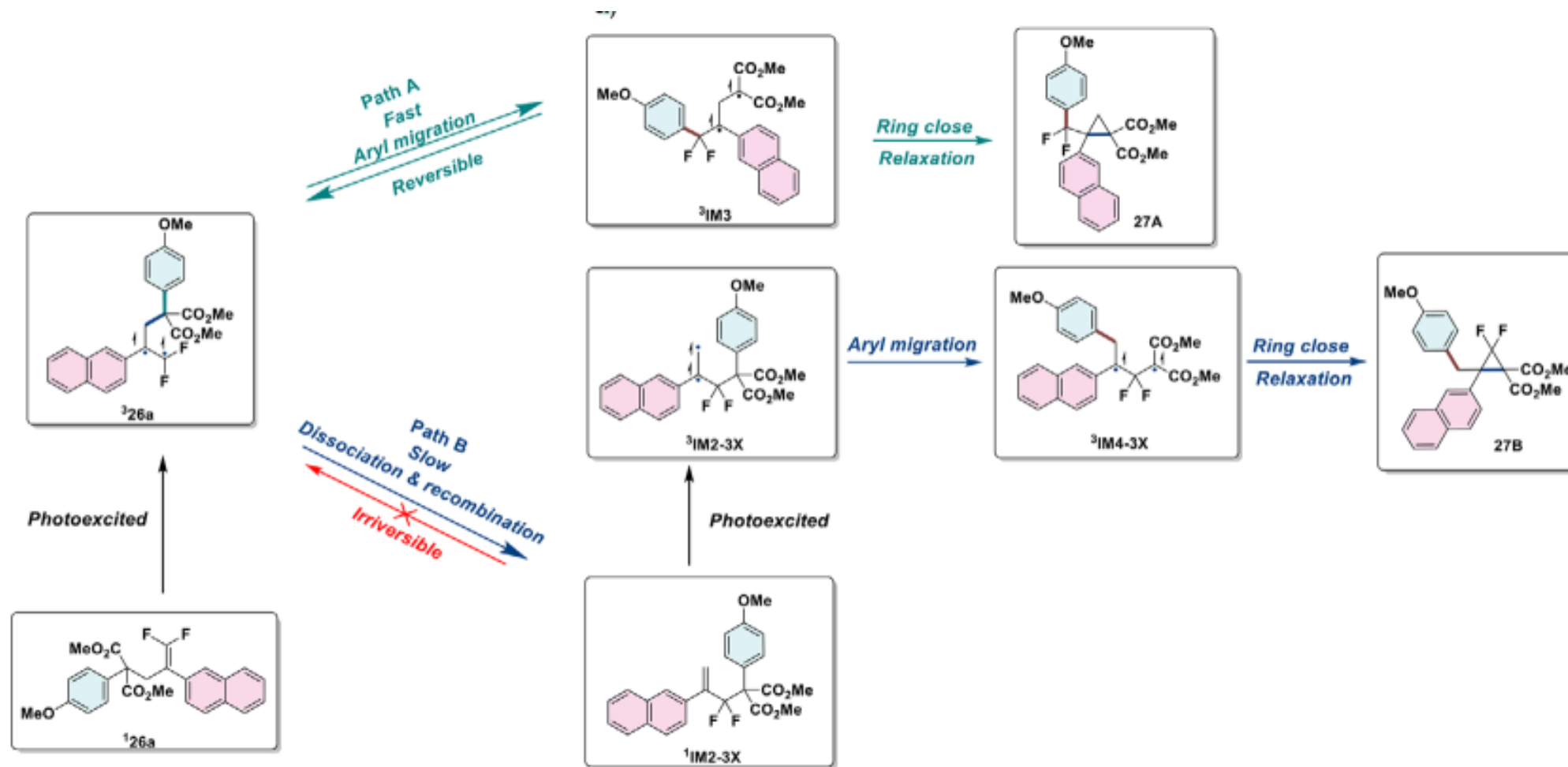
e) Stern-Volmer quenching experiment of 32A

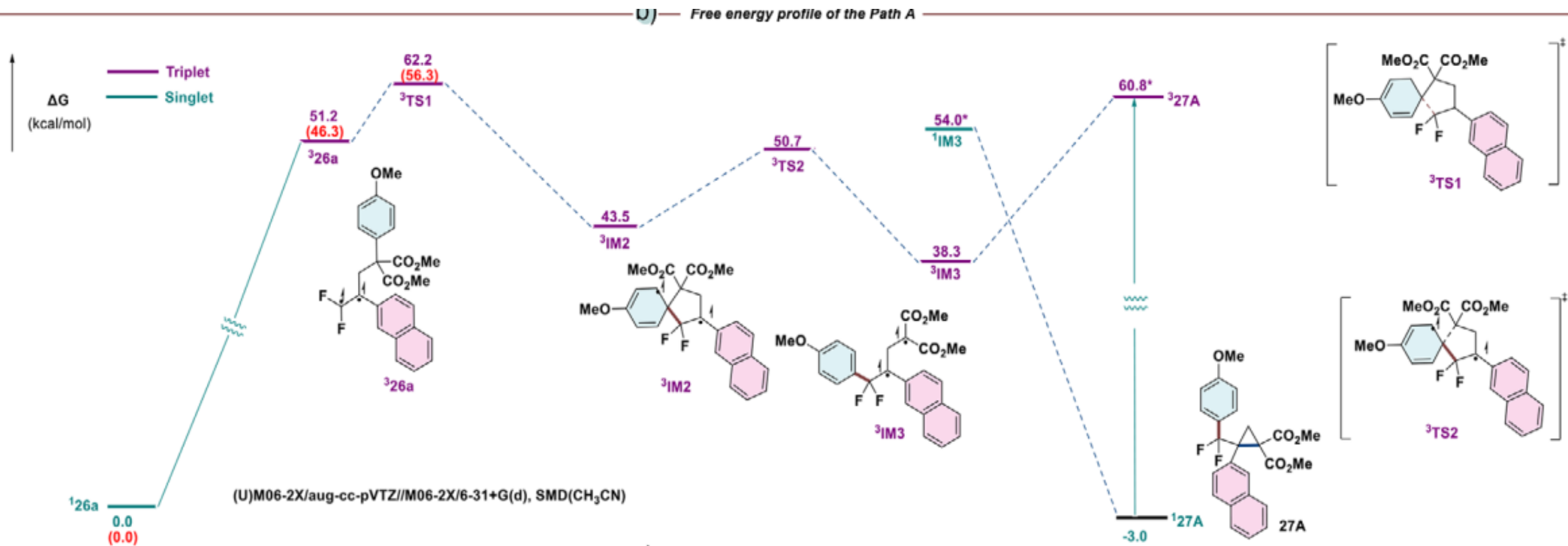


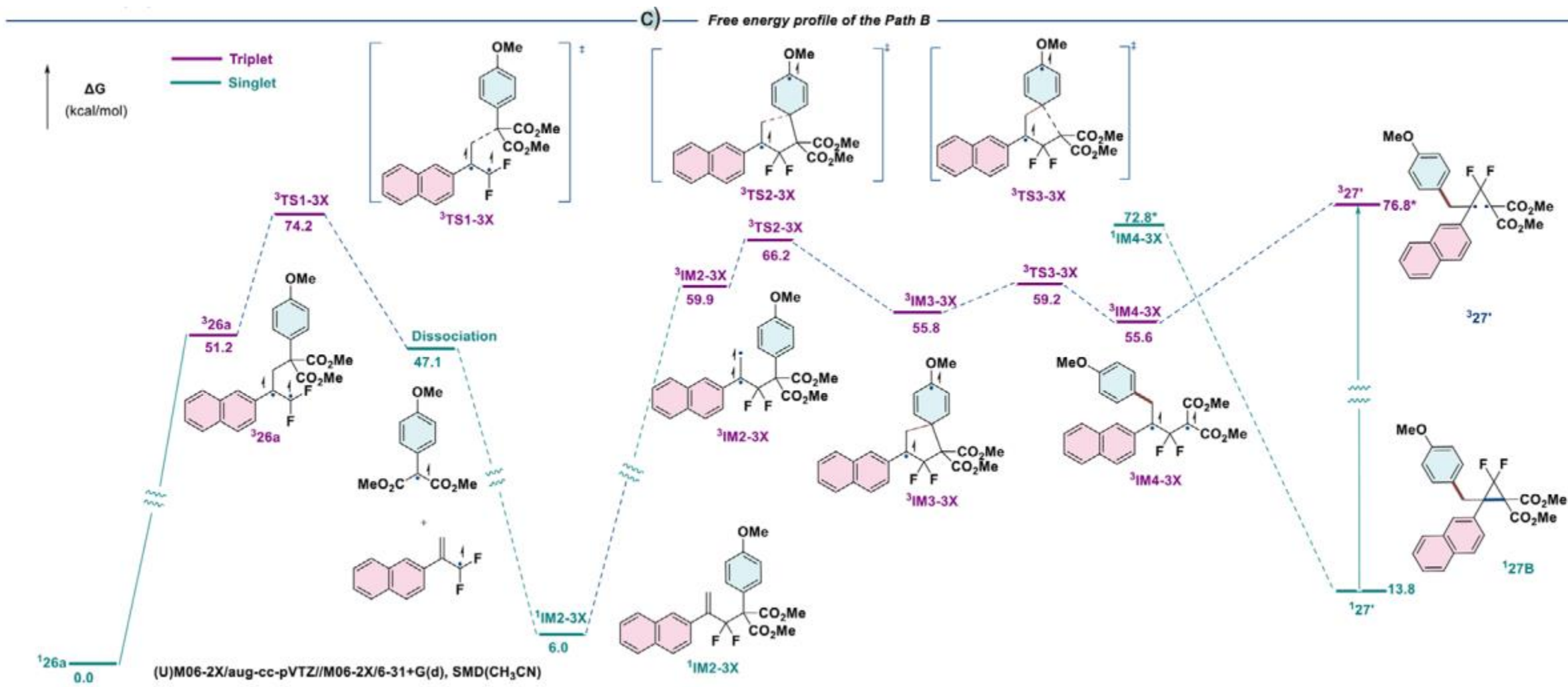
f) The formation of 32B from 32A



光化学重排反应实现时间依赖性发散合成



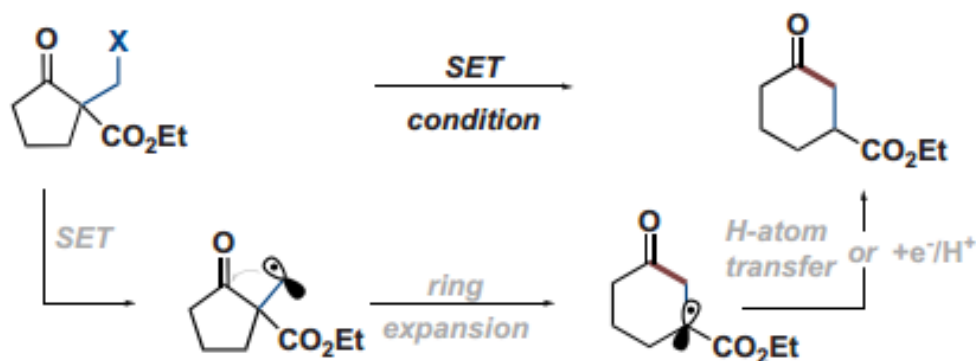
 光化学重排反应实现时间依赖性发散合成


 光化学重排反应实现时间依赖性发散合成


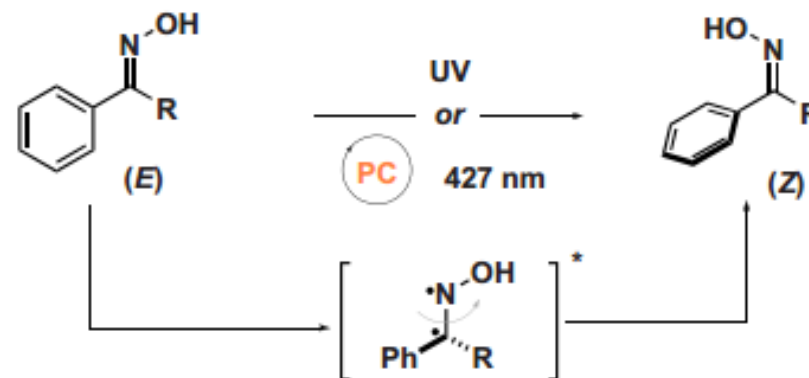


脞类化合物通过光化学氮杂-二- π -甲烷重排实现环扩张反应

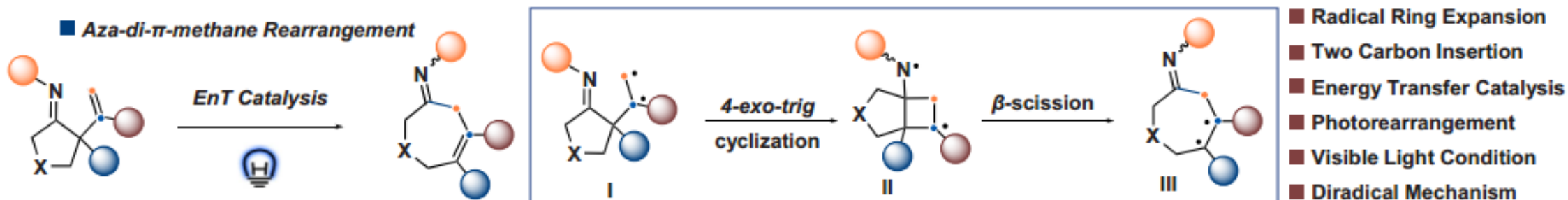
a) The Dowd-Beckwith reaction enabled by single-electron-transfer (SET) mechanism



b) Photoisomerization of acetophenone oxime derivatives

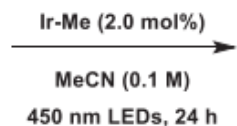
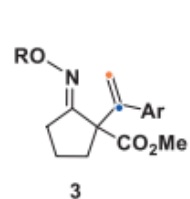


c) This work: Oximes skeletal editing via photochemical rearrangement enabled by energy transfer catalysis

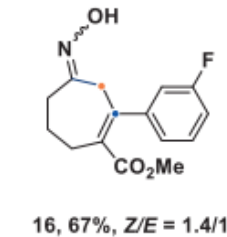
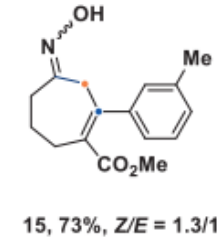
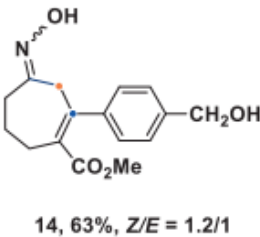
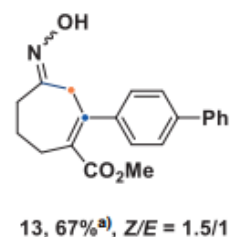
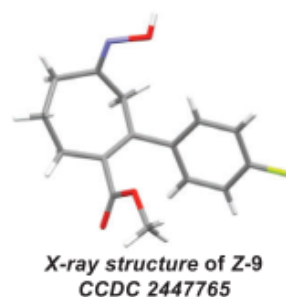
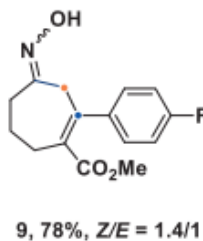
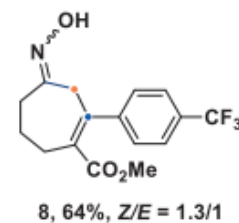
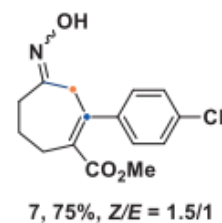
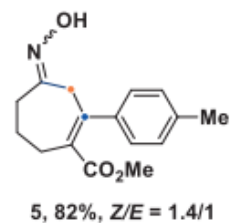
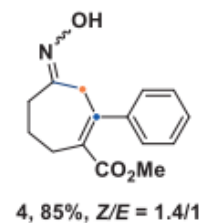
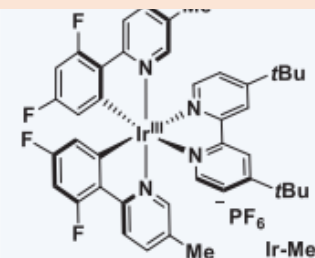




脞类化合物通过光化学氮杂-二-π-甲烷重排实现环扩张反应

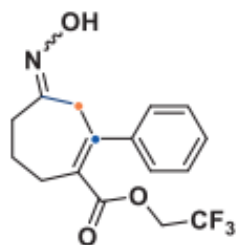


- Radical Ring Expansion
- Aza-di-π-methane Rearrangement
- Two Carbon Atom Insertion
- Energy Transfer Catalysis
- Photochemical Rearrangement
- Visible Light Condition

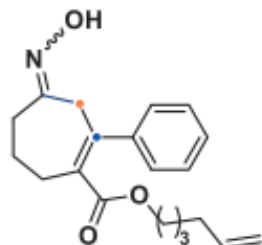




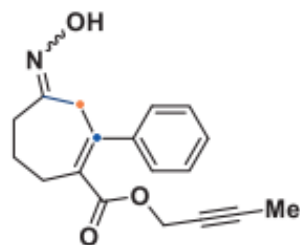
脞类化合物通过光化学氮杂-二-π-甲烷重排实现环扩张反应



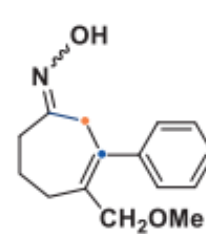
42, 71%, Z/E = 1.3/1



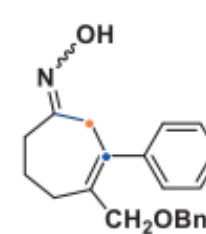
43, 64%, Z/E = 1.3/1



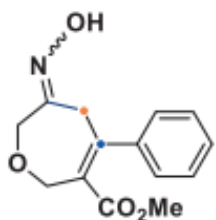
44, 80%, Z/E = 1.5/1



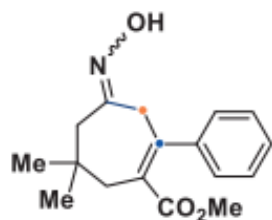
45, 56%^{b), c)}, Z/E = 3.5/1



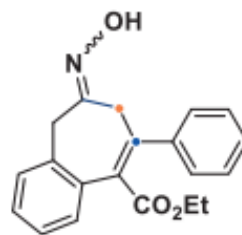
46, 55%^{b), c)}, Z/E = 3.5/1



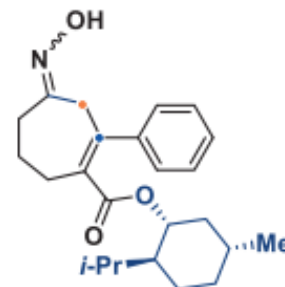
47, 76%, Z/E = 1.4/1



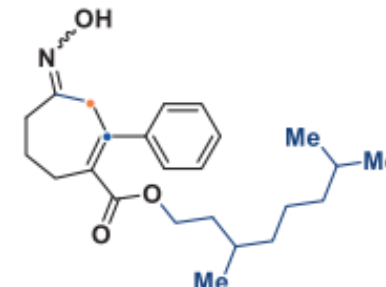
48, 63%^{c)}, Z/E = 2.0/1



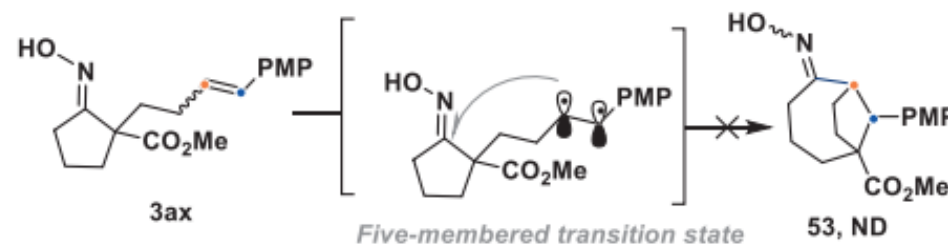
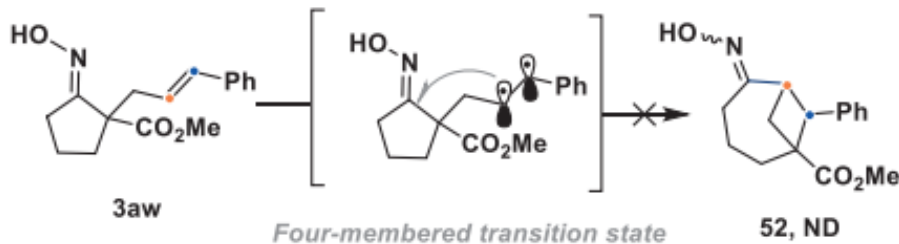
49, 43%^{d)}, Z/E = 1/1.2


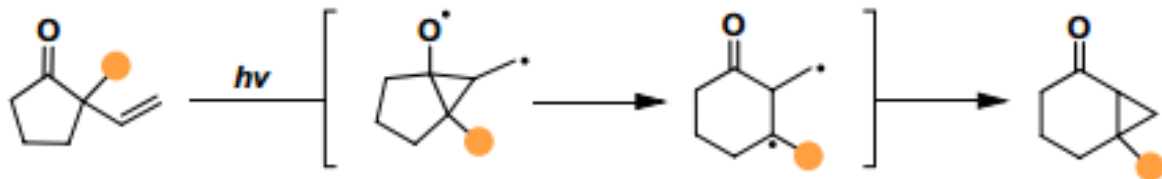
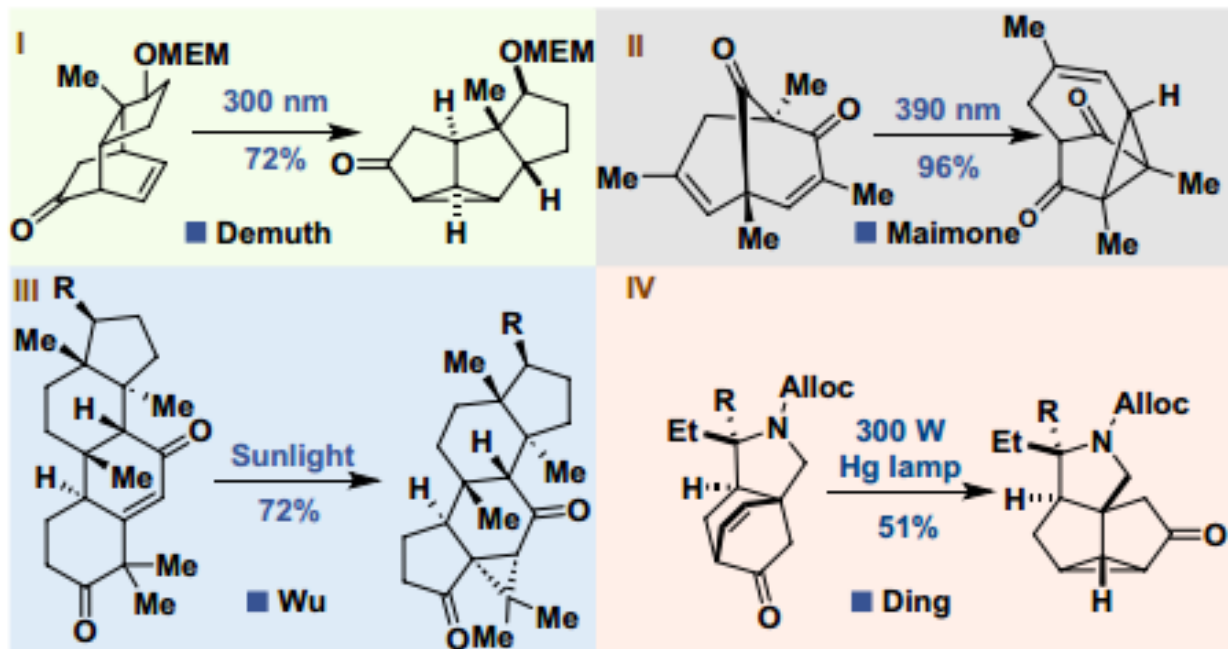


50, 60%^{d)}, Z/E = 1.4/1
from L-Menthol

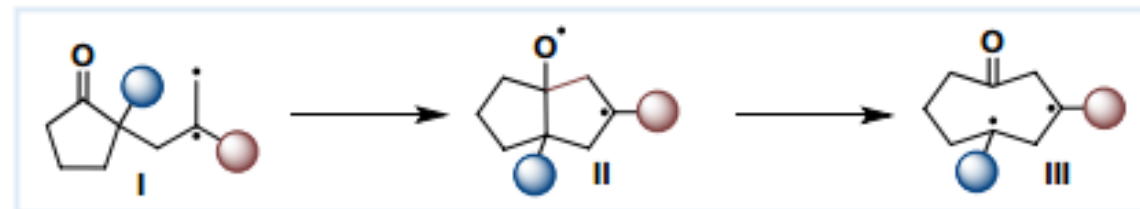
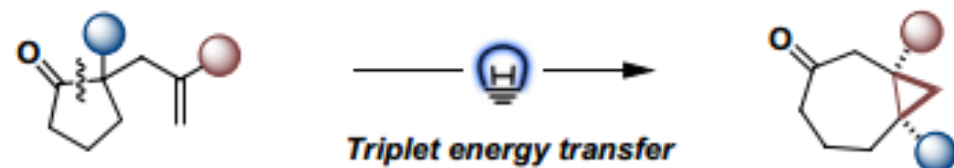


51, 63%^{d)}, Z/E = 1.3/1
from Tetrahydrogeraniol

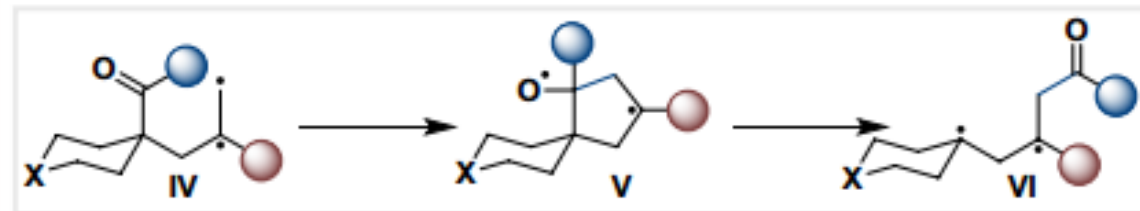
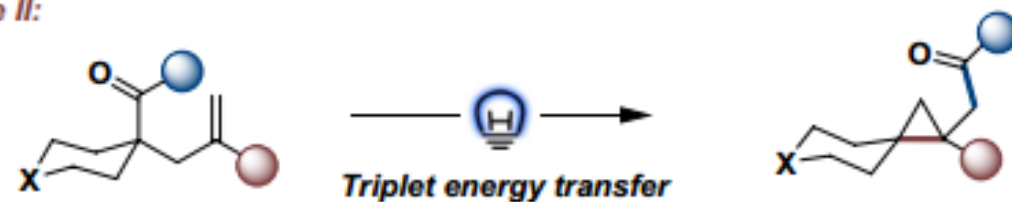



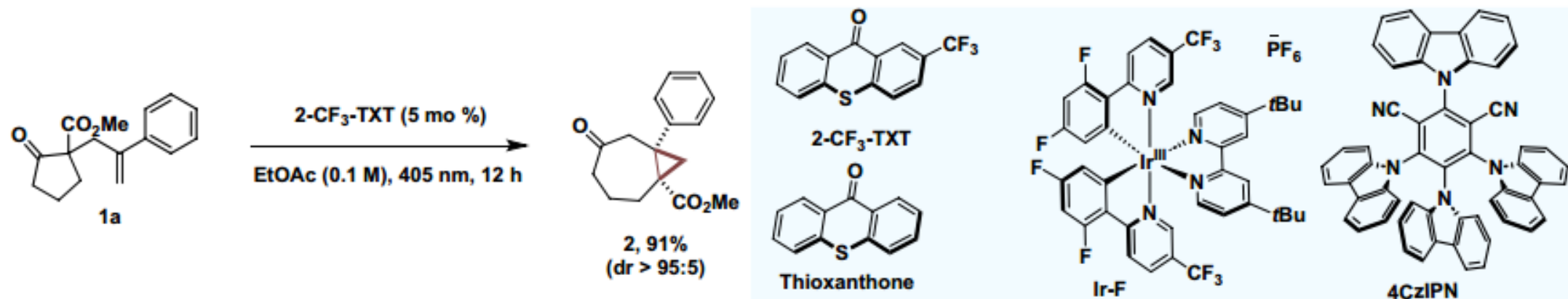

 可见光驱动氧杂-双-π-乙烷重排反应
(a) Oxa-di- π -methane (ODPM) rearrangement - well established(b) Oxa-di- π -methane (ODPM) rearrangements in synthesis(c) This work: Oxa-di- π -ethane (ODPE) reactions enabled by triplet EnT

Type I:



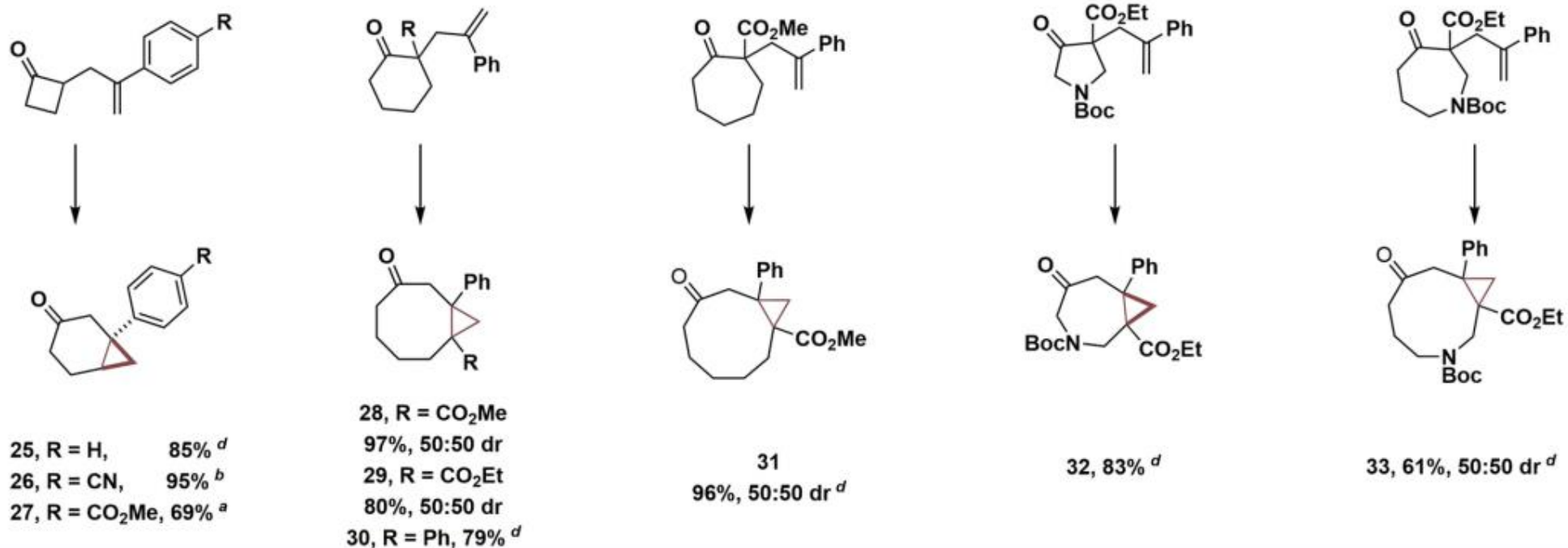
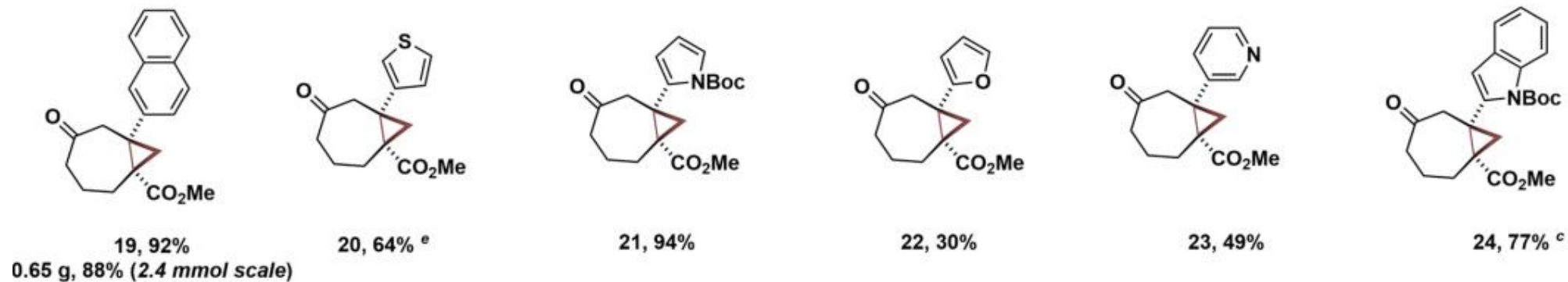
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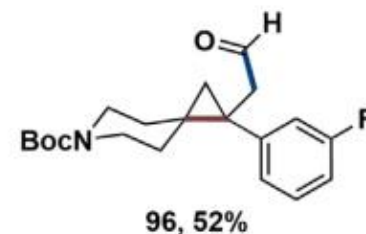
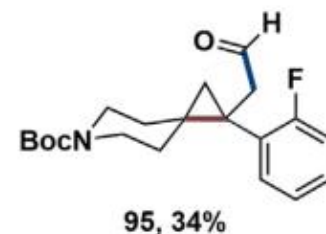
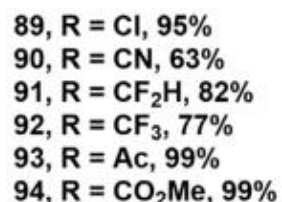
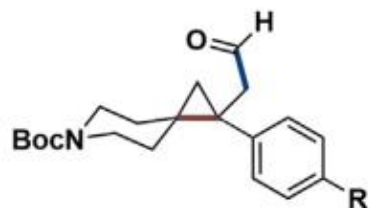
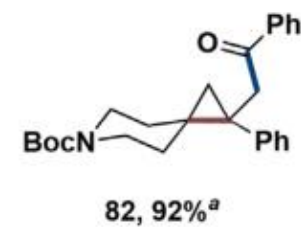
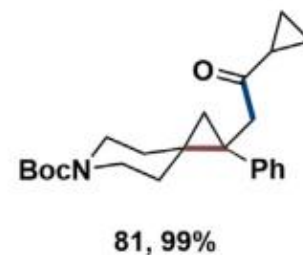
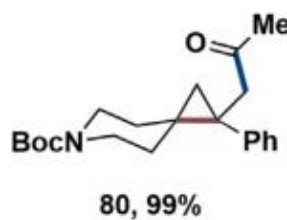
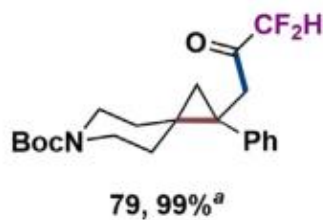
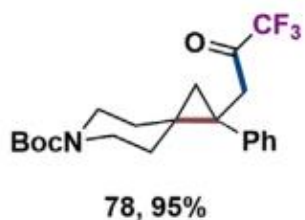
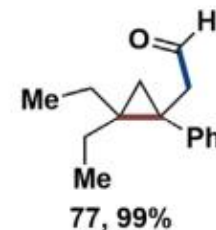
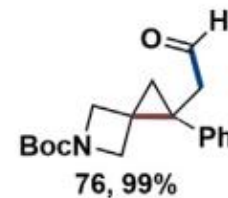
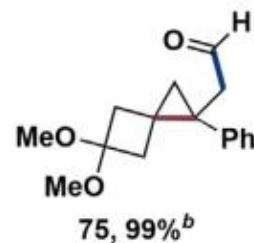
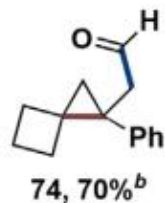
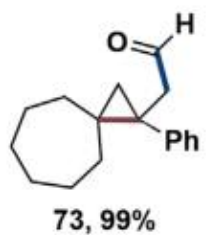
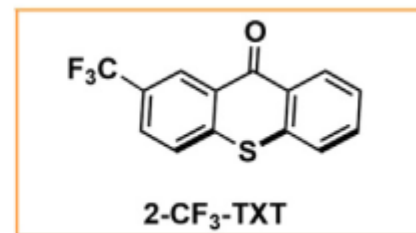
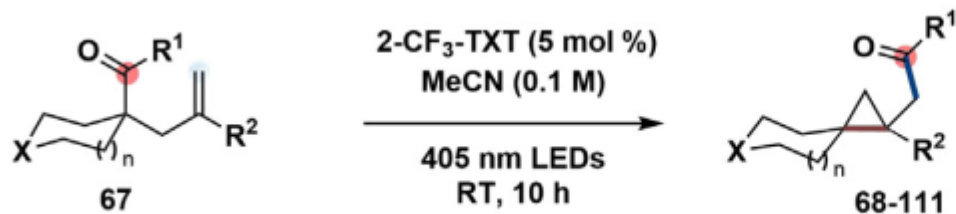



 可见光驱动氧杂-双-π-乙烷重排反应


Entry	Photocatalyst	E _T (kcal/mol)	Yield (%)	Entry	Variations from Standard Conditions	Yield (%)
1	Ru(bpy) ₃ (PF ₆) ₂	46.5	<5	7	MeCN instead of EtOAc	94
2	fac-[Ir(ppy) ₃]	57.8	23	8	THF instead of EtOAc	94
3	4CzIPN	58.3	51	9	No PC under 405 nm	n.d. ^[d]
4	Ir-F	60.8	98 (92) ^[a, b]	10	No PC under 365 nm	n.d. ^[d]
5	Thioxanthone	63.4	89 (82) ^[a, c]	11	40 °C instead of light	n.d. ^[d]
6	2-CF ₃ -TXT	69.3	98 (91) ^[a]	12	No light	n.d. ^[d]

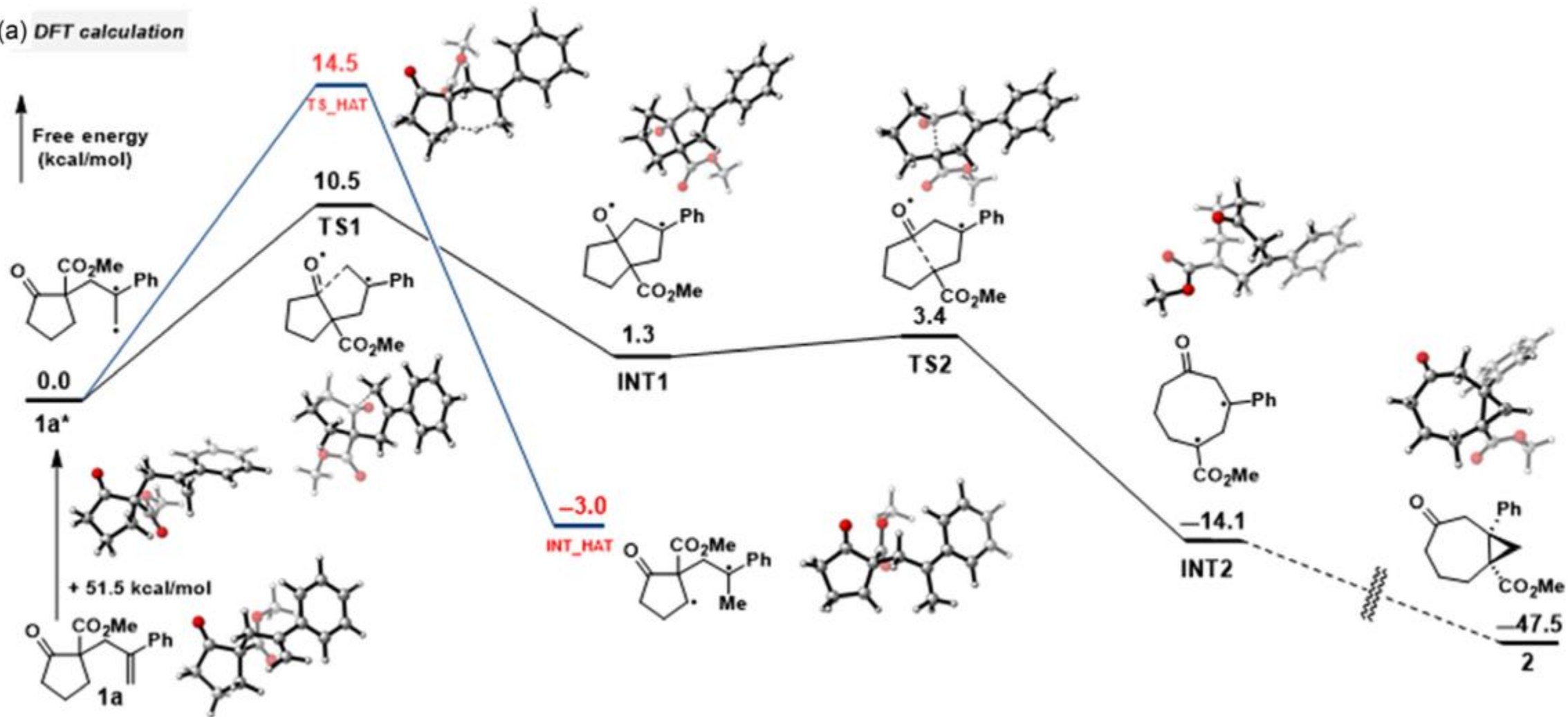
可见光驱动氧杂-双- π -乙烷重排反应


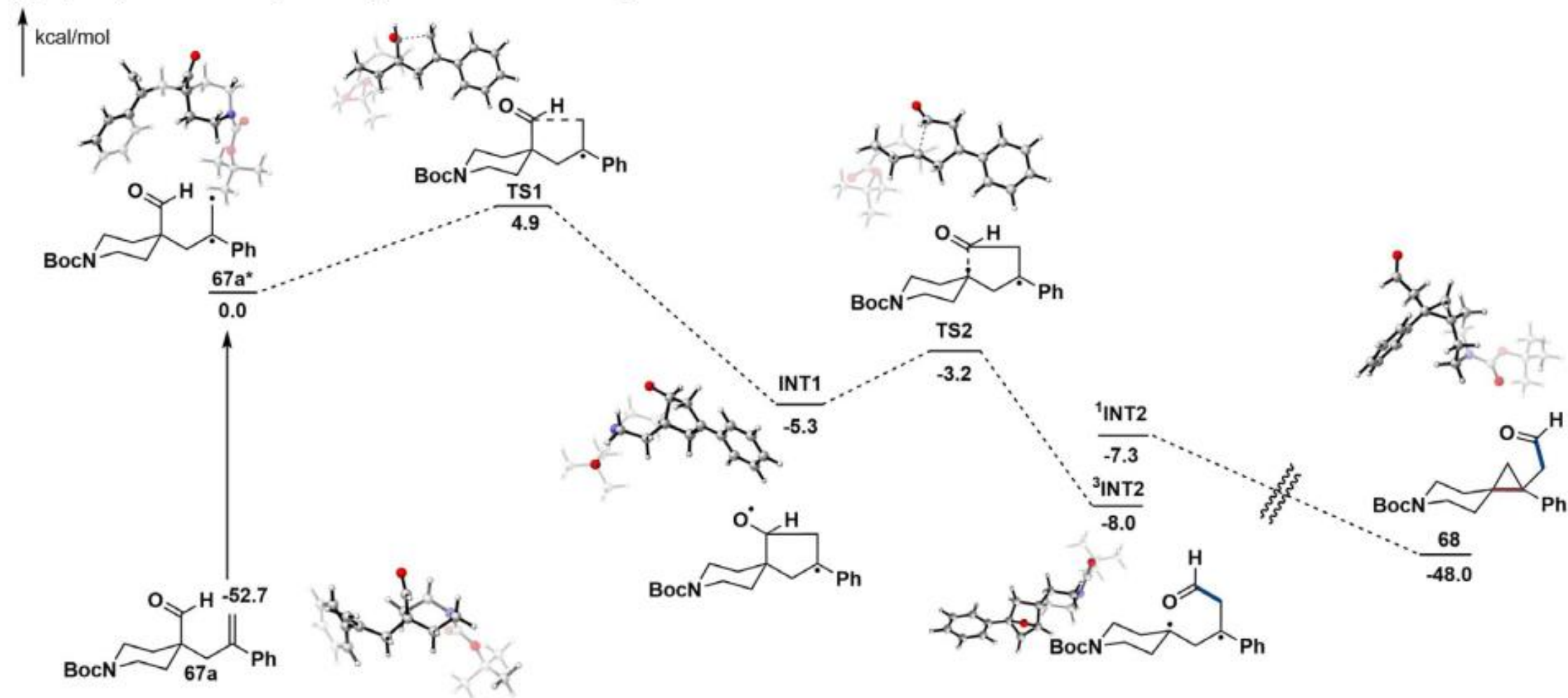



 可见光驱动氧杂-双- π -乙烷重排反应


 可见光驱动氧杂-双- π -乙烷重排反应

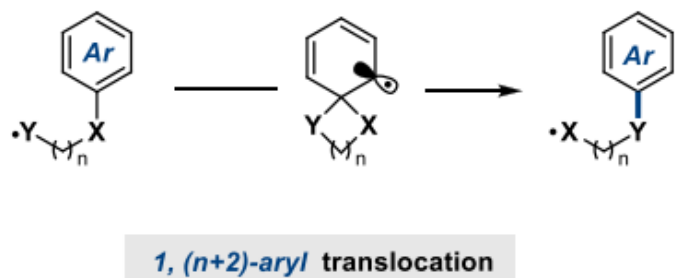
(a) DFT calculation



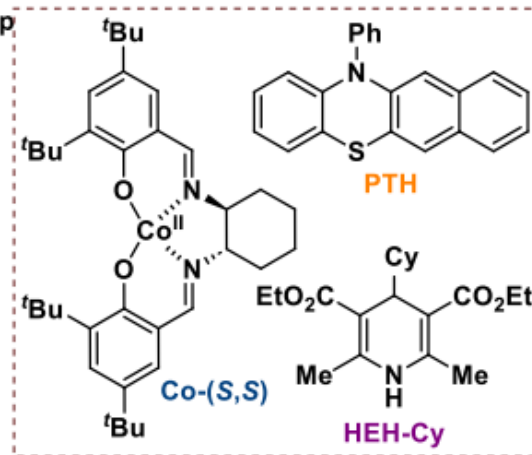
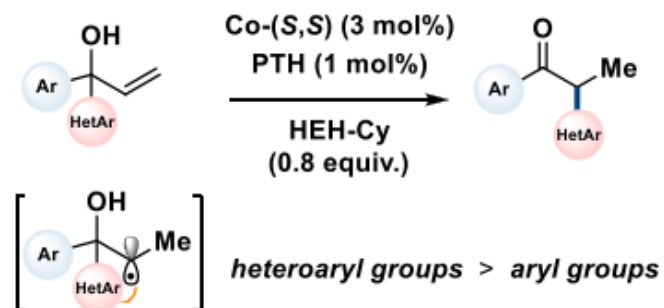
 可见光驱动氧杂-双- π -乙烷重排反应(a) Spirocyclic scaffolds synthesis by oxa-di- π -ethane rearrangement

光敏化重塑自由基芳基迁移的选择性

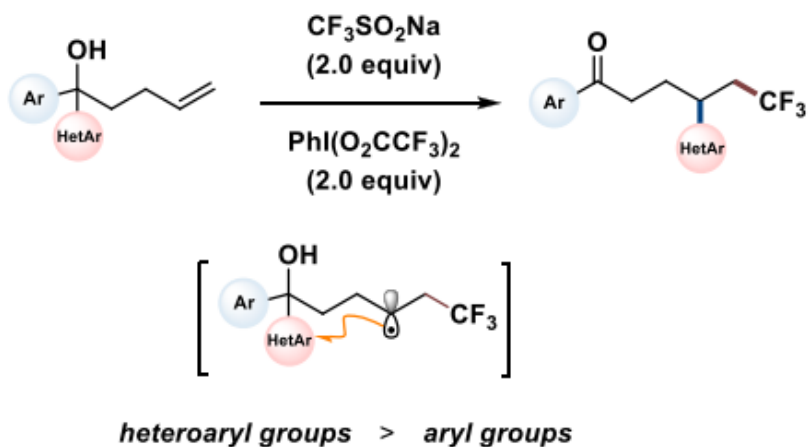
A. Radical aryl translocation in synthetic chemistry



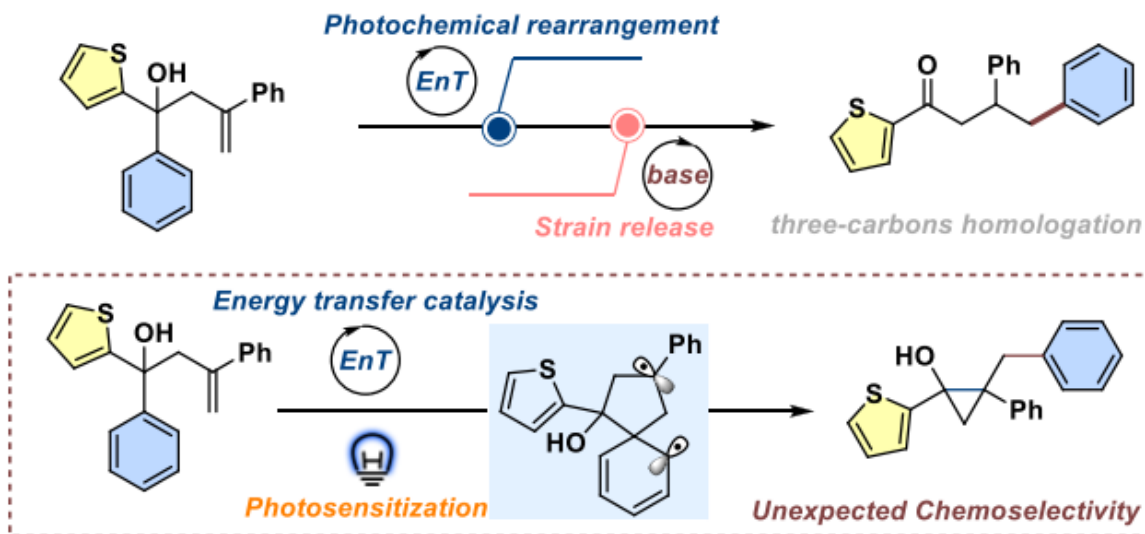
B. Chemoselectivity in 1,2- translocation of an aryl group


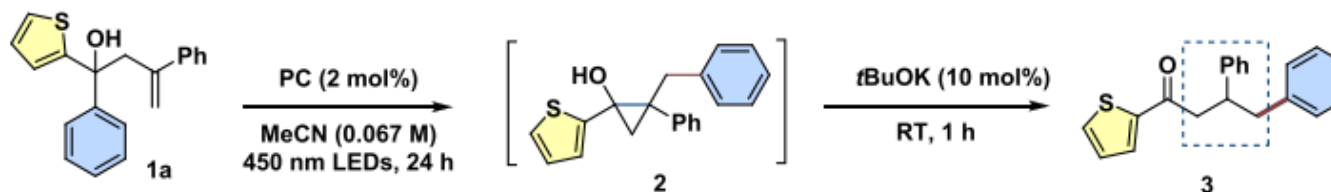


C. Chemoselectivity in 1,4- translocation of an aryl group

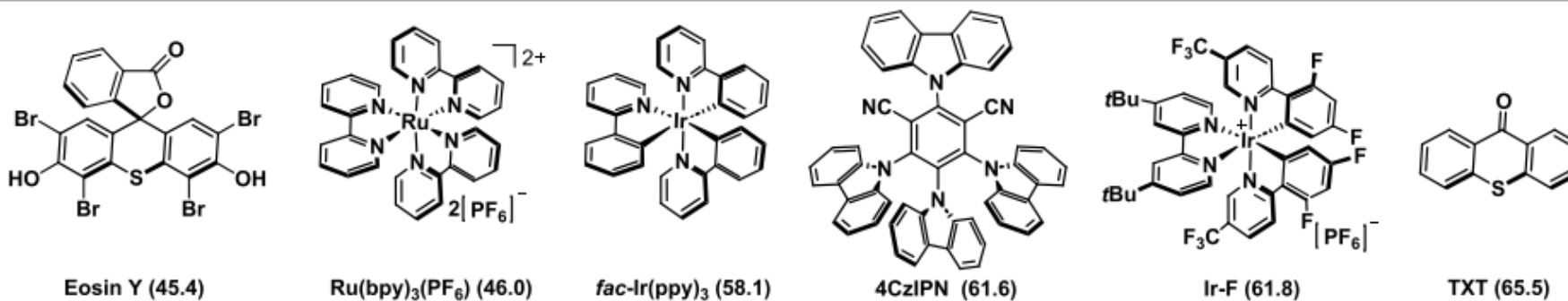


D. This work: Unexpected chemoselectivity in radical aryl translocation via photosensitization



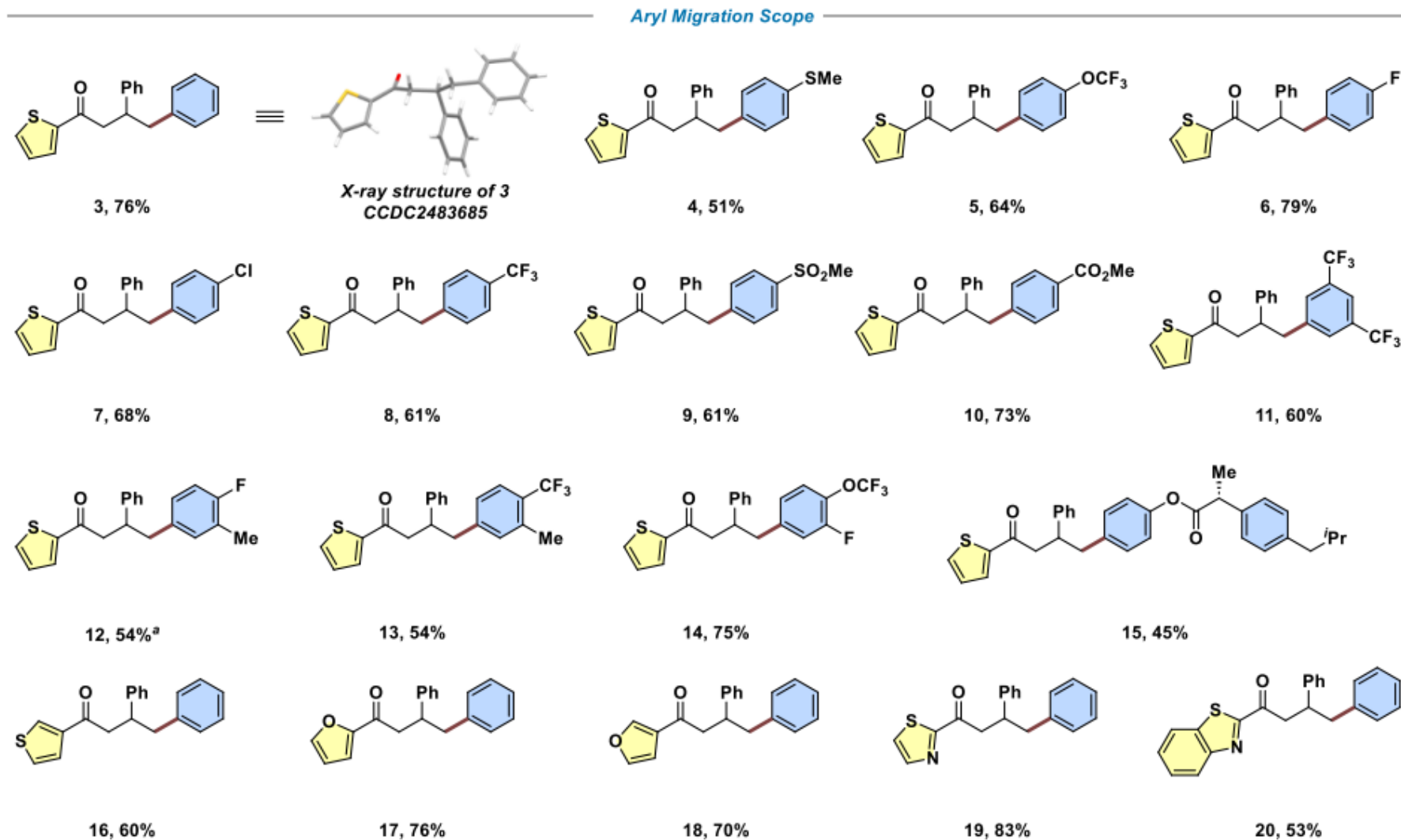

 光敏化重塑自由基芳基迁移的选择性


Entry	Photocatalyst	E_T (kcal/mol)	$E_{1/2}^{[M^+]/[M^*]}$ (V)	$E_{1/2}^{[M^-]/[M^*]}$ (V)	Yield(%) ^a	Entry	Variations from standard condition	Yield(%) ^a
1	Eosin Y	45.4	+1.18	-1.60	N.D.	7	EtOAc / DMF / THF	58 / 70 / 45
2	Ru(bpy) ₃ (PF ₆) ₂	46.0	+0.77	-0.81	10	8	tBuOH / PhCF ₃ / DCM / MeOH	10 / 9 / 10 / N.D.
3	fac-Ir(ppy) ₃	58.1	+0.31	-1.73	23	9 ^c	MeCN	74
4	4CzIPN	61.6	+1.35	-1.21	Trace	10 ^d	MeCN	77(76 ^a)
5	Ir-F	61.8	+1.43	-1.18	73 ^a	11	without Ir-F	N.D.
6 ^b	TXT	65.5	+1.43	-1.18	15	12	without light	N.D.

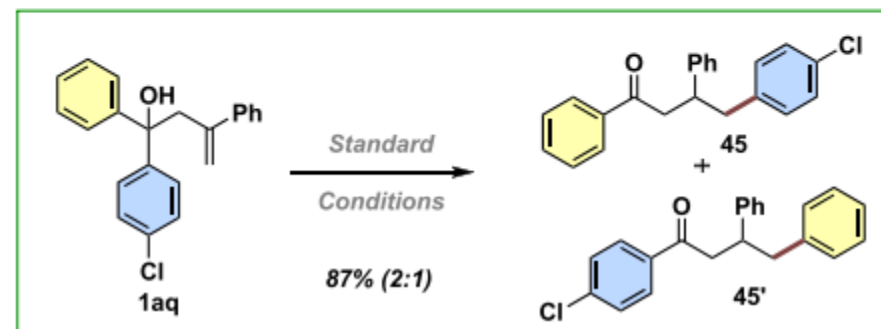
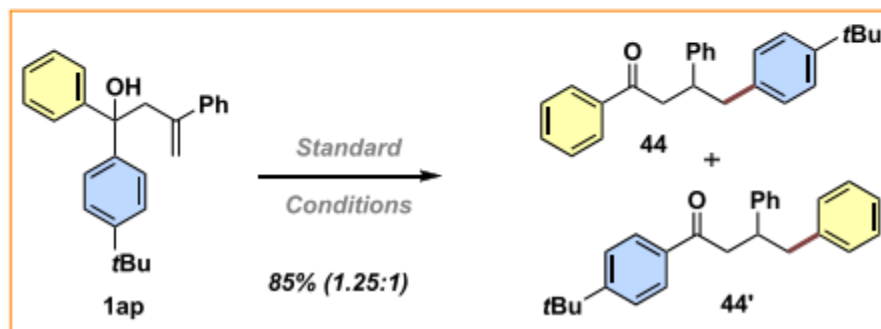
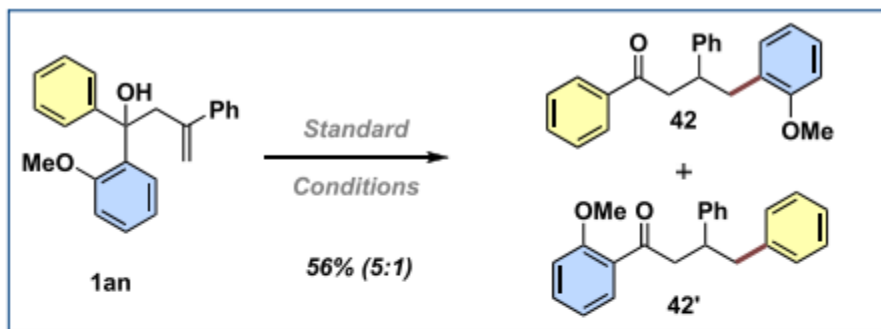
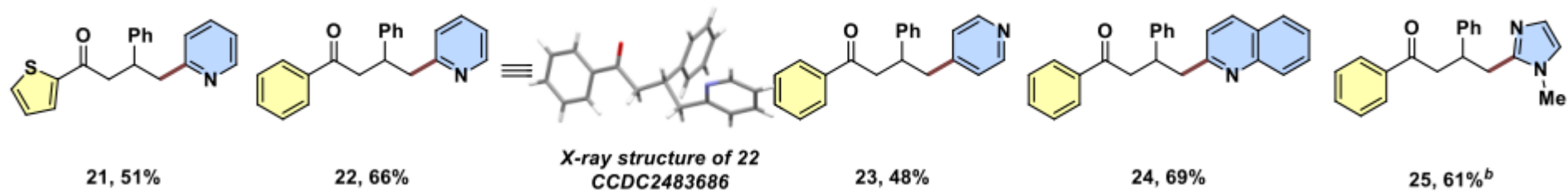




光敏化重塑自由基芳基迁移的选择性



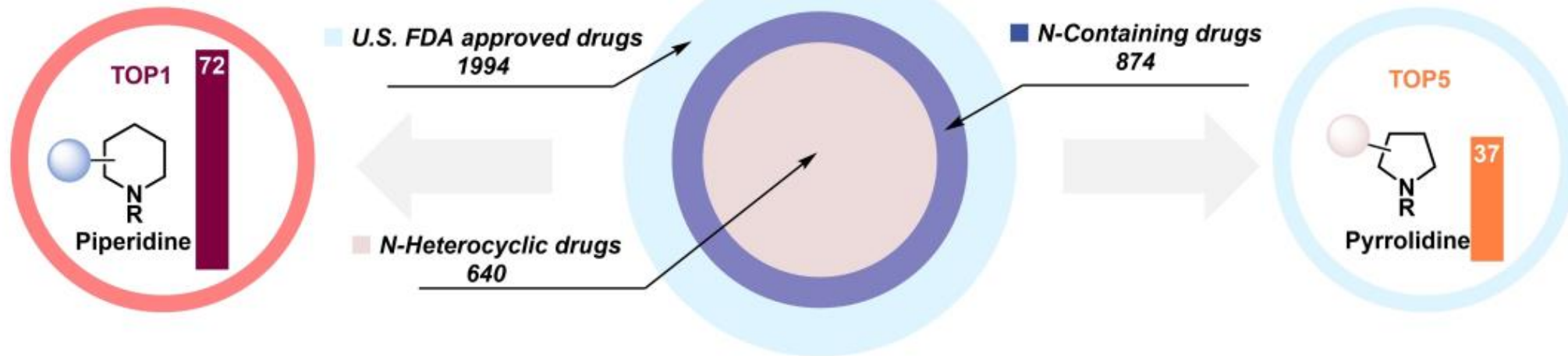
光敏化重塑自由基芳基迁移的选择性



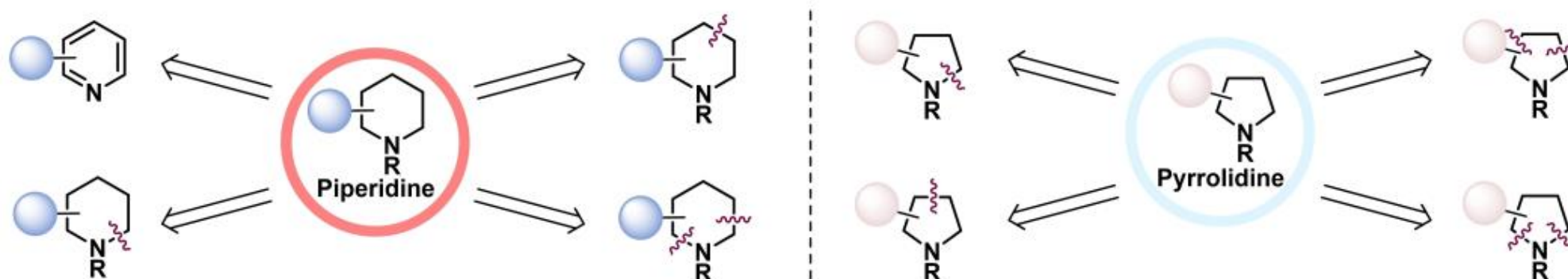


自由基-极性交叉环加成反应合成环胺

A. Breakdown of U.S. FDA approved drugs

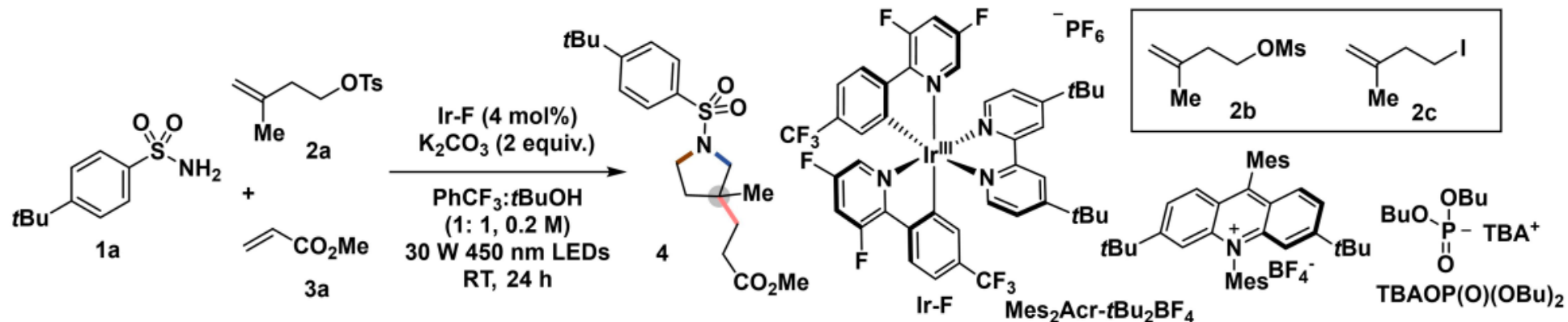


B. Traditional synthetic transformations to construct piperidine and pyrrolidine derivatives

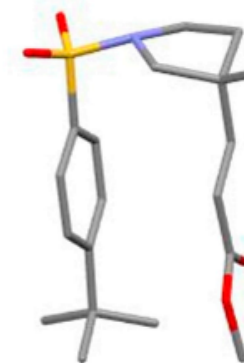




自由基-极性交叉环加成反应合成环胺



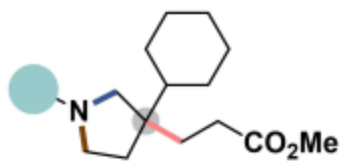
Entry	Alteration to conditions	yield% ^b	Entry	Alteration to conditions	yield% ^b
1	none	80	12	PhCF ₃ : tBuOH = 2: 3 as solvent	67
2	12 h	67	13	2b instead of 2a	71
3	36 h	64	14	2c instead of 2a	11
4	PhCN as solvent	53	15	K ₃ PO ₄ as base	79
5	MeCN as solvent	63	16	Na ₂ CO ₃ as base	27
6	PhCF ₃ as solvent	78	17	TBAOP(O)(OBu) ₂ as base	0
7	DCM as solvent	3	18	2,4,6-collidine as base	0
8	EA as solvent	24	19	fac-Ir(ppy) ₃ as PC	0
9	PhMe as solvent	19	20	Ru(bpy) ₃ as PC	0
10	tBuOH as solvent	44	21	Mes ₂ Acr-tBu ₂ BF ₄ as PC	0
11	PhCF ₃ : tBuOH = 3: 2 as solvent	74	22	No base/No PC/No light/No light and heated to 50°C	0/0/0/0



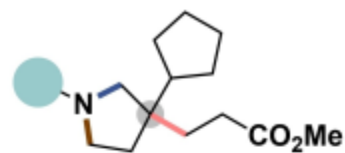
X-ray crystal structure of 4



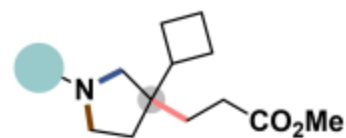
自由基-极性交叉环加成反应合成环胺



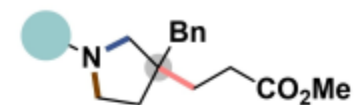
23, 60%



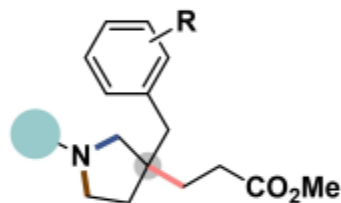
24, 65%



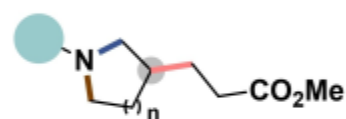
25, 59%



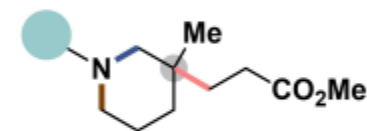
26, 52%



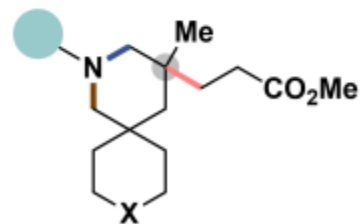
27, R = 4-Ph, 67%
28, R = 4-F, 30%
29, R = 4-Cl, 41%
30, R = 4-Me, 70%
31, R = 3-Me, 69%
32, R = 2-Me, 69%



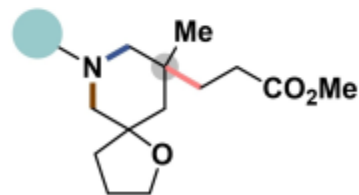
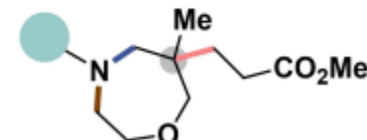
33, n = 1, 49%
34, n = 2, 46%



35, 67%

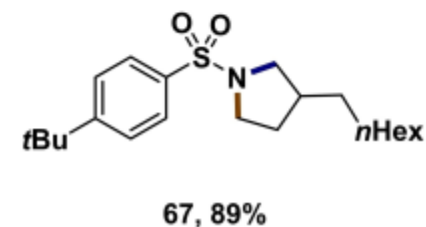
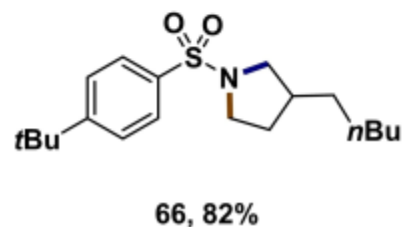
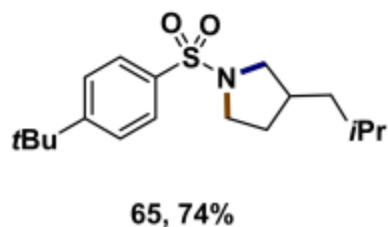
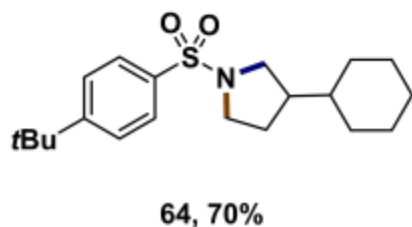
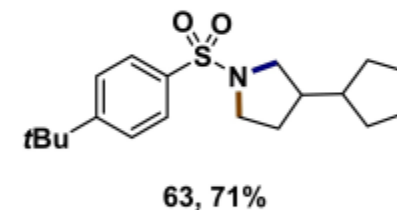
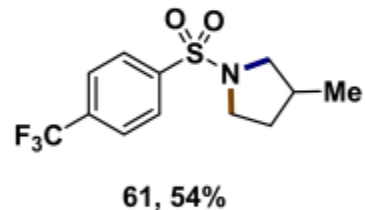
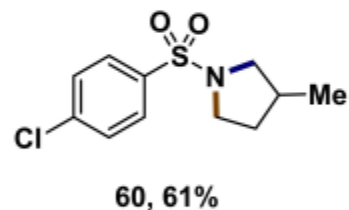
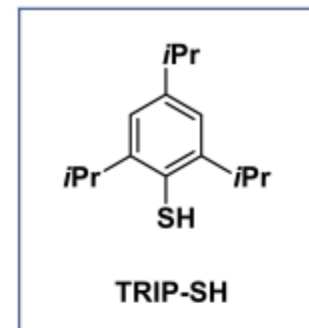
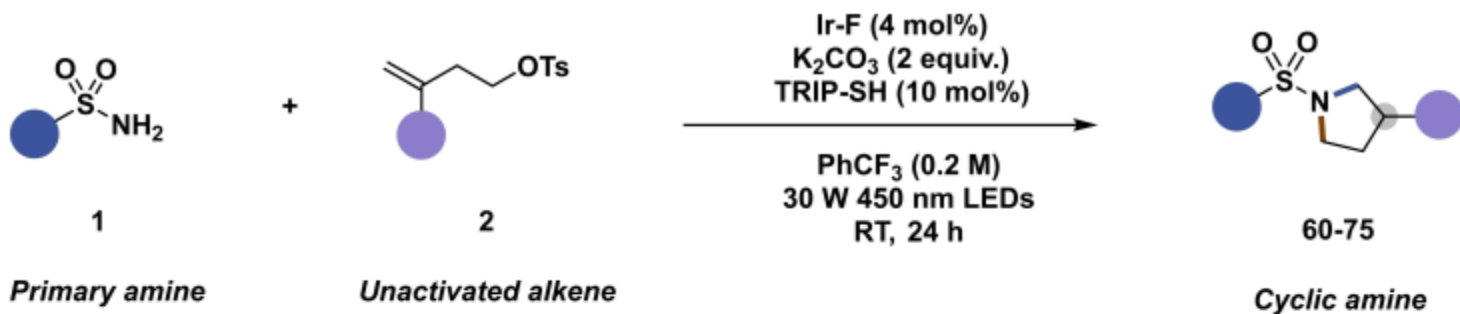


36, X = CH₂, 70%
37, X = O, 74%

38, 42%
dr = 1.5:139, 83%^a40, 36%^a



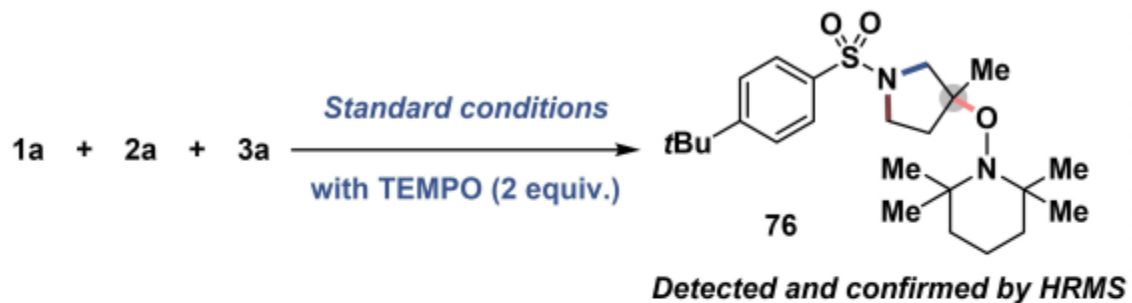
自由基-极性交叉环加成反应合成环胺



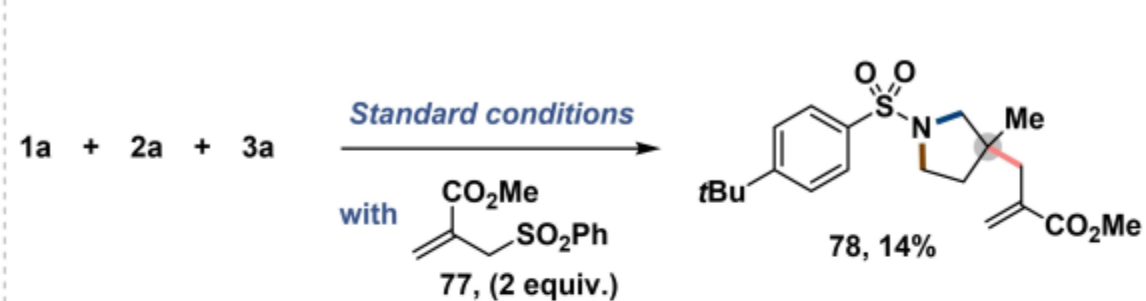


自由基-极性交叉环加成反应合成环胺

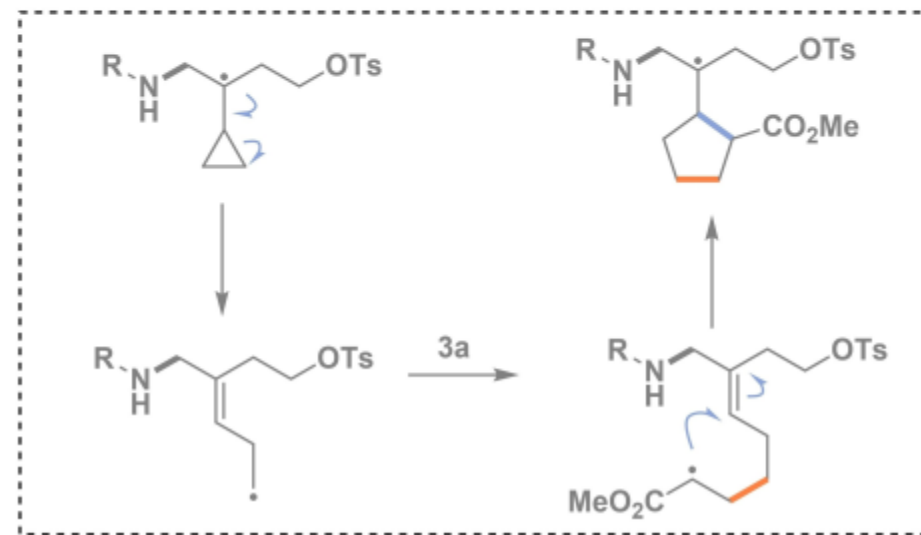
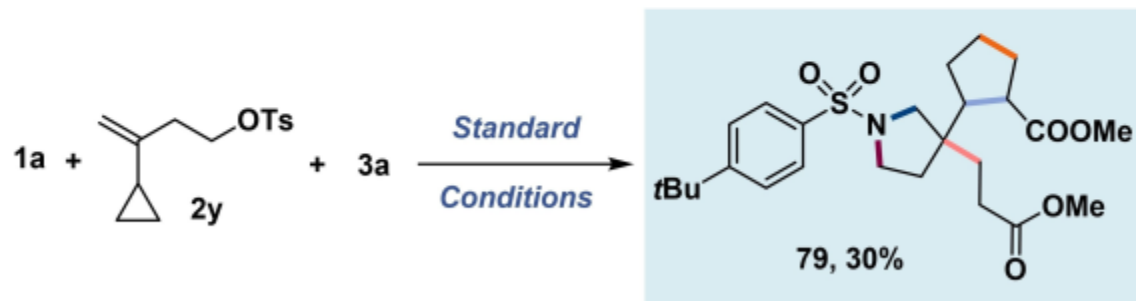
B. Radical inhibitor experiment



C. Radical probing experiment I

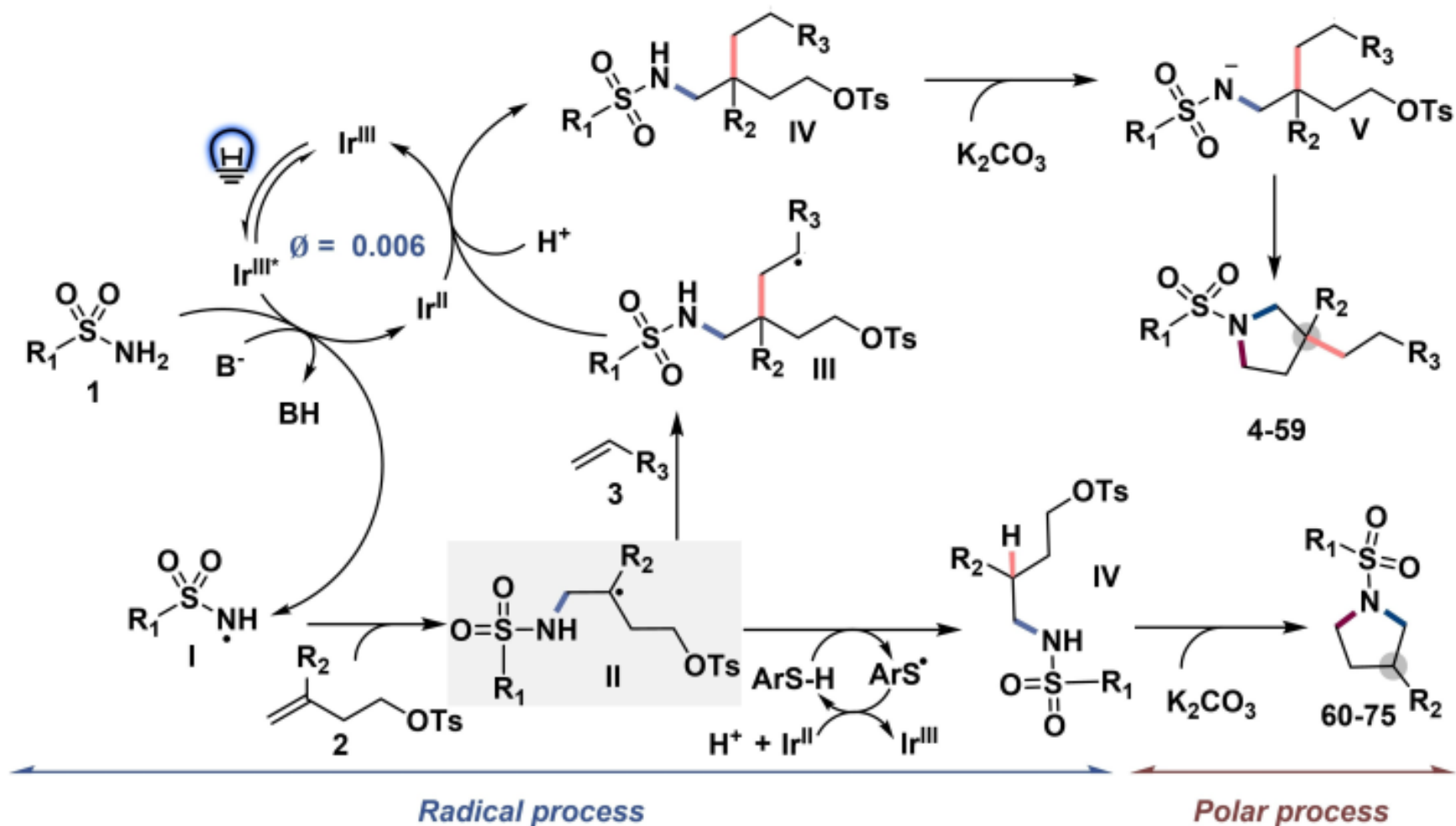


D. Radical probing experiment II





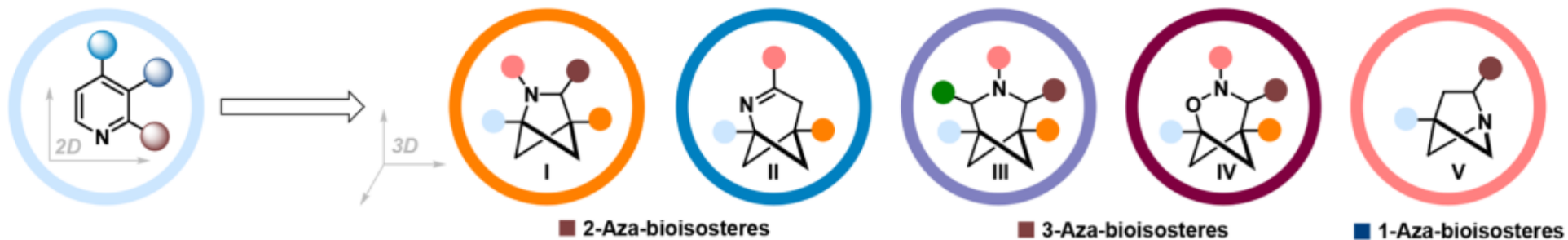
自由基-极性交叉环加成反应合成环胺





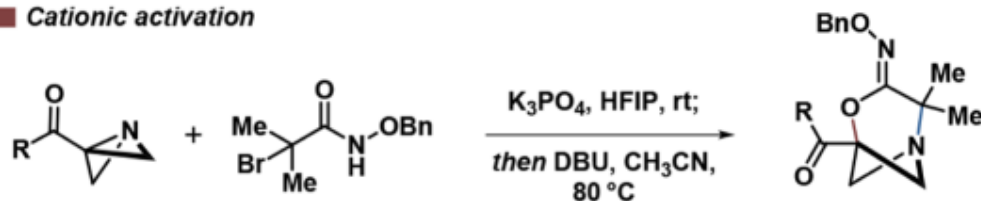
光钯催化实现1-氮杂双环[n. 1. 1]烷烃的自由基区域选择性合成

A. Aza-bioisosteres of pyridine derivatives



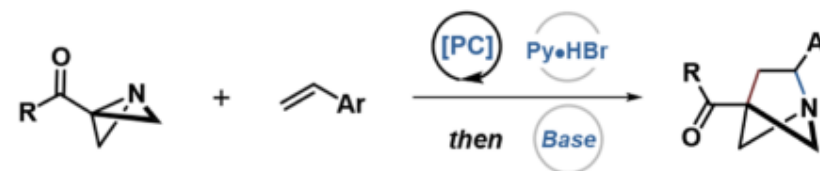
B. Formal [3+2] annulation between (aza)oxyallyl cations and azabicyclo[1.1.0]butanes

■ Cationic activation



C. Radical coupling between azabicyclo[1.1.0]butanes and styrenes

■ Photoredox catalysis



D. *This work*: switchable 1-aza-bioisosteres synthesis via photoinduced palladium catalysis

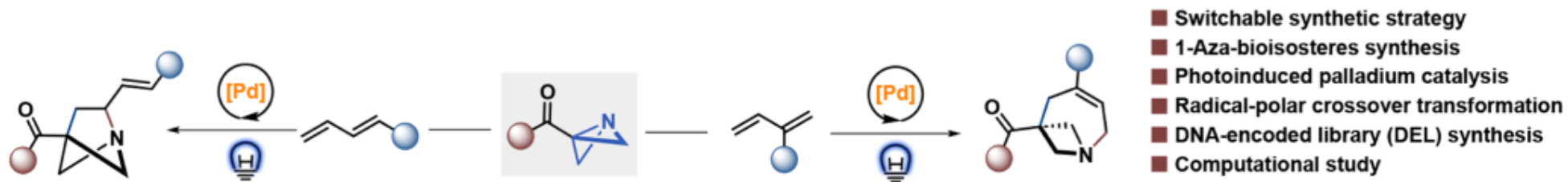
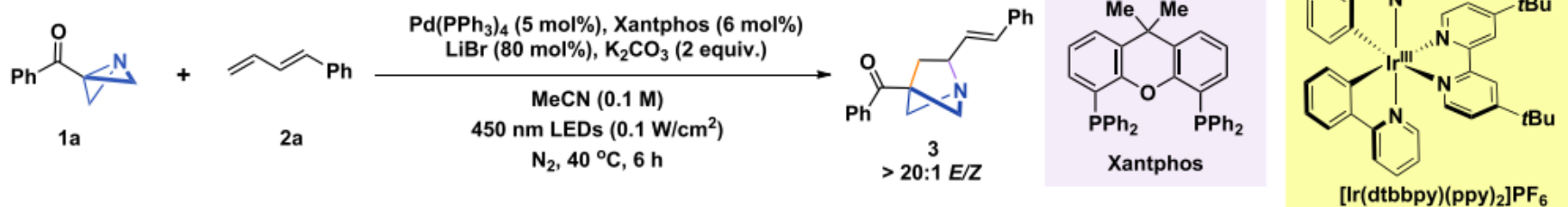


Figure 1. Background and reaction design.



光钯催化实现1-氮杂双环[n. 1. 1]烷烃的自由基区域选择性合成

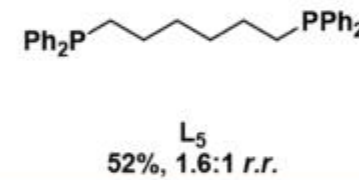
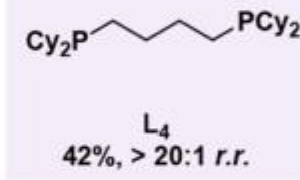
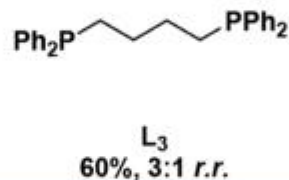
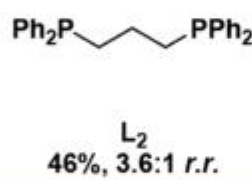
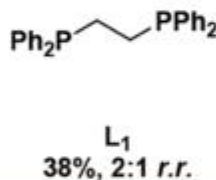
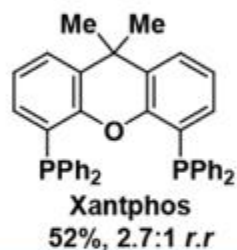
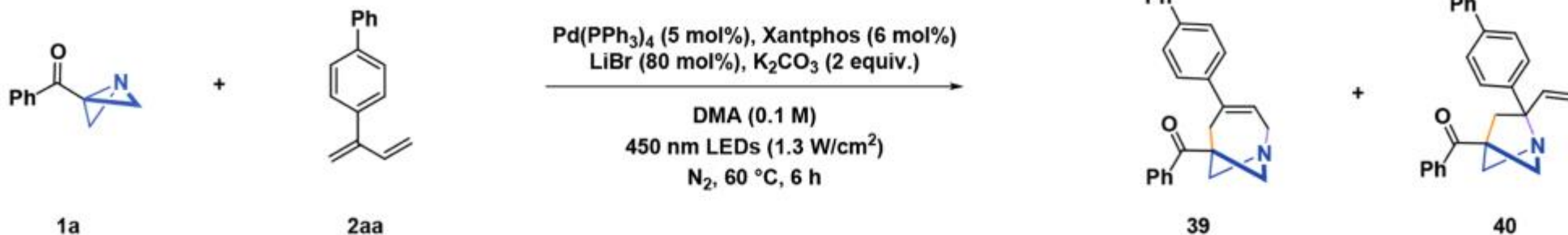


Entry	Alteration to conditions	yield% ^b	Entry	Alteration to Entry 6	yield% ^b
1	none	trace	13	Pd(PPh ₃) ₄ (2.0 mol%), Xantphos (2.4 mol%)	85
2	60 °C	26	14	Pd(PPh ₃) ₄ (10 mol%), Xantphos (12 mol%)	88
3	1.0 W/cm ² , 60 °C	47	15	[Ir(dtbbpy)(ppy) ₂] ⁺ PF ₆ ⁻ (1.5 mol%)	0
4	1.0 W/cm ² , 60 °C, LiBr (40 mol%)/(1.6 equiv.)	36/32	16	K ₂ CO ₃ (5 equiv.)/(60 mol%)	95/80
5	1.3 W/cm ² , 60 °C	71	17	K ₃ PO ₄ /Cs ₂ CO ₃ /Na ₂ CO ₃	89/82/95
6	DMA (0.1 M), 1.3 W/cm ² , 60 °C	95 (88 ^c)	18	LiBr (40 mol%)/(2 equiv.)	95/95
Entry	Alteration to Entry 6	yield% ^b	Entry	Alteration to Entry 6	yield% ^b
7	PdCl ₂ (5 mol%)	67	19	405 nm LEDs, 0.5 W/cm ²	60
8	Pd(OAc) ₂ (5 mol%)	68	20	THF/DME/1,4-dioxane/PhH	0/0/0/0
9	BINAP (6 mol%)	64	21	DMA (0.05 M)/(0.2 M)	95/84
10	1a:2a = 1.5:1/1:1/1:2	51/29/63	22	No Ligand	69
11	Py•HBr/NH ₄ Br/NaBr	88/88/95	23	No LiBr & base	64
12	2 h/4 h/8 h	62/93/95	24	No [Pd] & Ligand/No light and heated to 65°C	0/0

^aOptimized reaction conditions: **1a** (0.4 mmol, 2.0 equiv), **2a** (0.2 mmol, 1.0 equiv), Pd(PPh₃)₄ (5 mol %), Xantphos (6 mol %), LiBr (80 mol %), K₂CO₃ (2.0 equiv) in DMA (2.0 mL, 0.1 M) at 60 °C under irradiation of 450 nm LEDs (1.3 W/cm²) in a water-cooled aluminum heat block for 6 h. ^bYields determined by ¹H NMR with dibromomethane as the internal standard. ^cYields of the isolated product **3**.



光钯催化实现1-氮杂双环[n. 1. 1]烷烃的自由基区域选择性合成

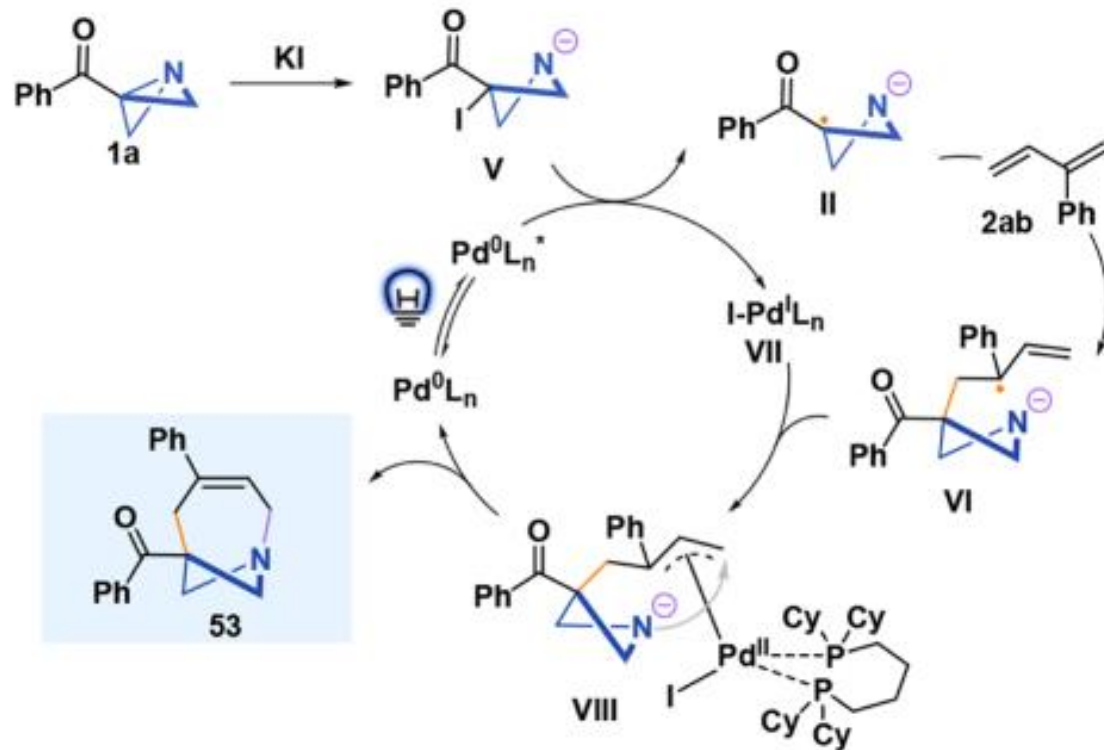
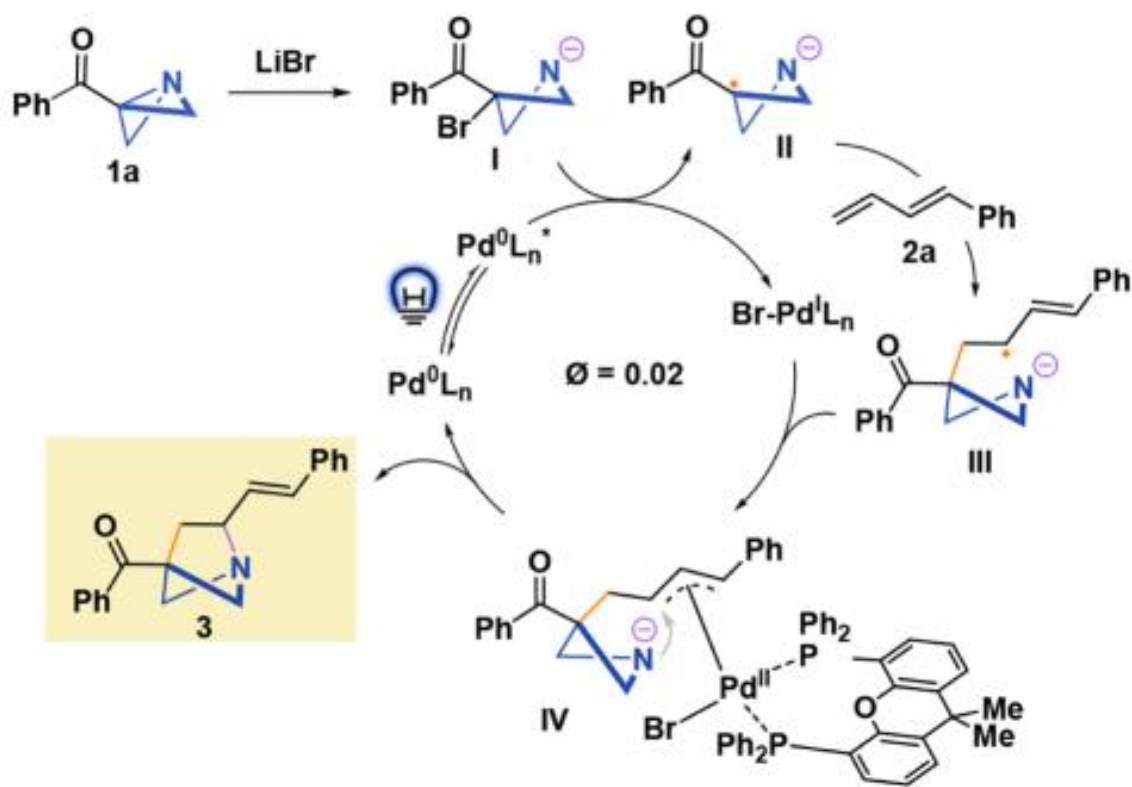


Entry	Alteration to conditions	yield% ^b	r.r. ^d	Entry	Alteration to entry 1	yield% ^b	r.r. ^d
1	L ₄ (6 mol%)	42	> 20:1	5	1.0 W/cm ² , 60 °C	40	> 20:1
2	Nal (80 mol%)	59	> 20:1	6	405 nm LEDs, 0.5 W/cm ²	33	> 20:1
3	KI (80 mol%)/(1.5 equiv.)	57/64	> 20:1	7	KI (1.5 equiv.), 15 h	75 (68 ^c)	> 20:1
4	Na ₂ CO ₃ /NaHCO ₃ /CS ₂ CO ₃ /Na ₃ PO ₄	56/54/28/33	> 20:1	8	KI (1.5 equiv.), 15 h Pd(PPh ₃) ₄ (10 mol%), L ₄ (12 mol%)	64	> 20:1



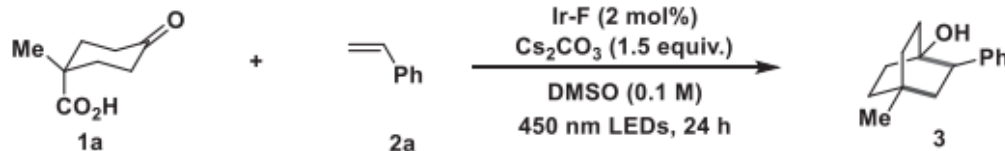
光钯催化实现1-氮杂双环[n. 1. 1]烷烃的自由基区域选择性合成

G. Proposed mechanism

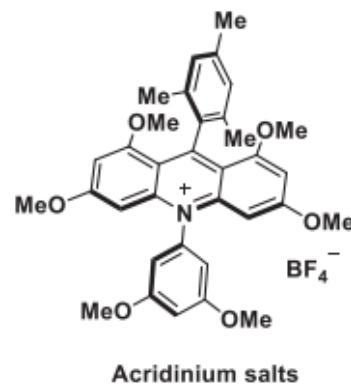
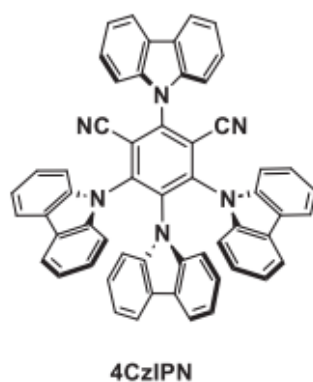
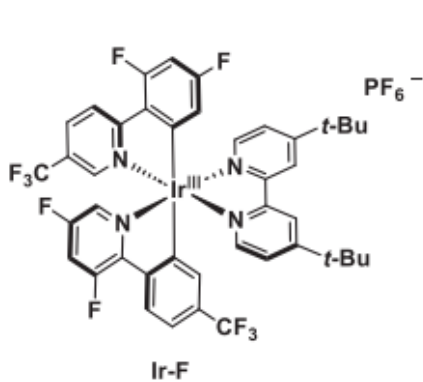




光催化自由基-极性交叉实现双环[2. m. n]烷醇生物电子等排体的模块化合成

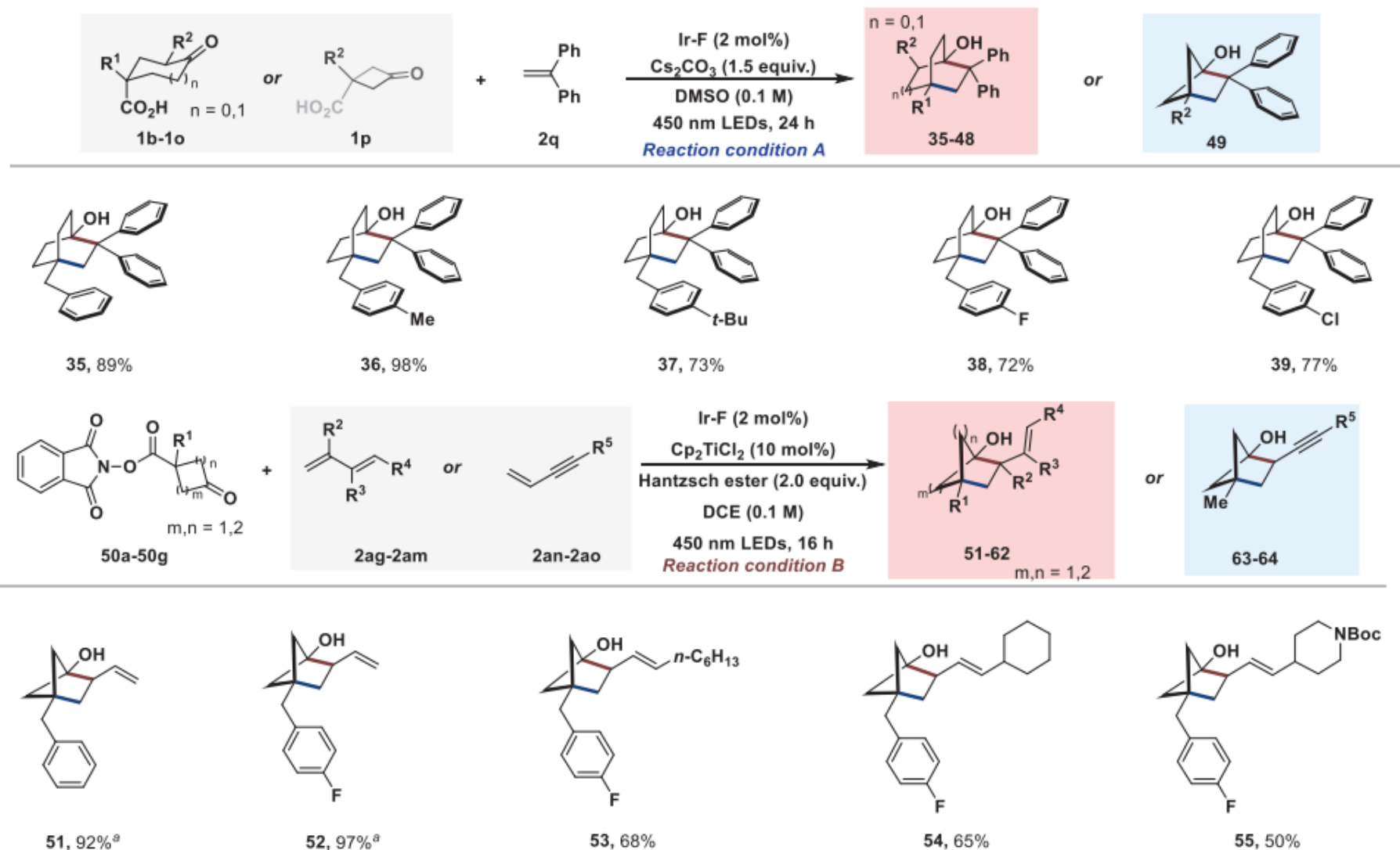


Entry	Variations from standard conditions	Yield(%)	Entry	Variations from standard conditions	Yield(%)
1	none	75 (73) ^a	8	THF instead of DMSO	N. R.
2	1.5 equiv. Na ₂ CO ₃ instead of Cs ₂ CO ₃	63	9	EA instead of DMSO	N. R.
3	1.5 equiv. K ₃ PO ₄ instead of Cs ₂ CO ₃	50	10	4CzIPN instead of Ir-F	48
4	1.5 equiv. K ₂ HPO ₄ instead of Cs ₂ CO ₃	39	11	5CzBN instead of Ir-F	48
5	1.5 equiv. DIPEA instead of Cs ₂ CO ₃	trace	12	Acridinium salts instead of Ir-F	N. R.
6	2.0 equiv. 2a instead of 3.0 equiv.	64	13	no photocatalysis or no light	N. R.
7	DMA, DMF instead of DMSO	50, 52	14	no base	N. R.





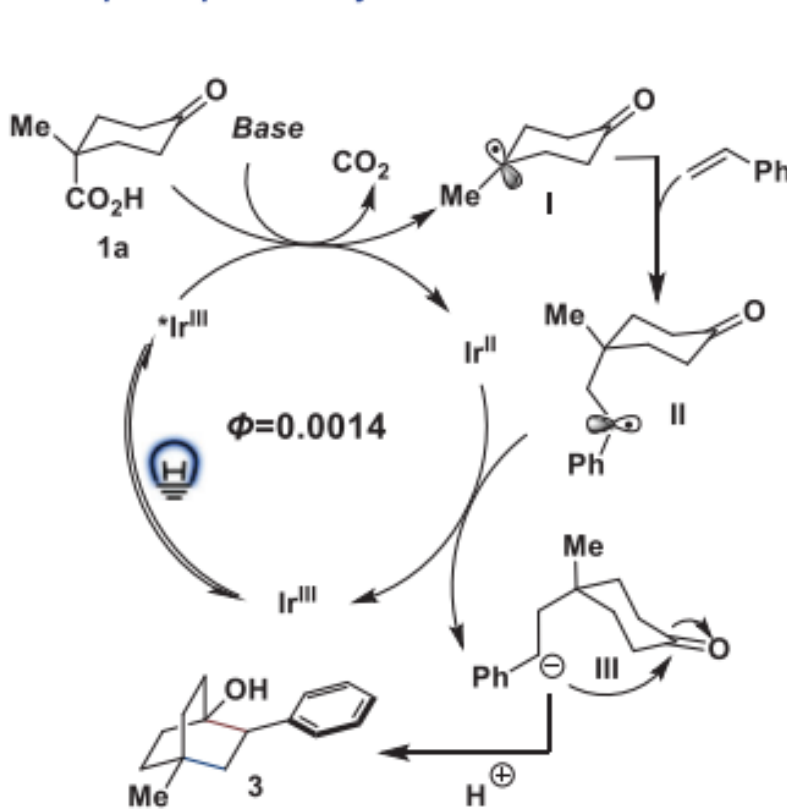
光催化自由基-极性交叉实现双环[2. m. n]烷醇生物电子等排体的模块化合成



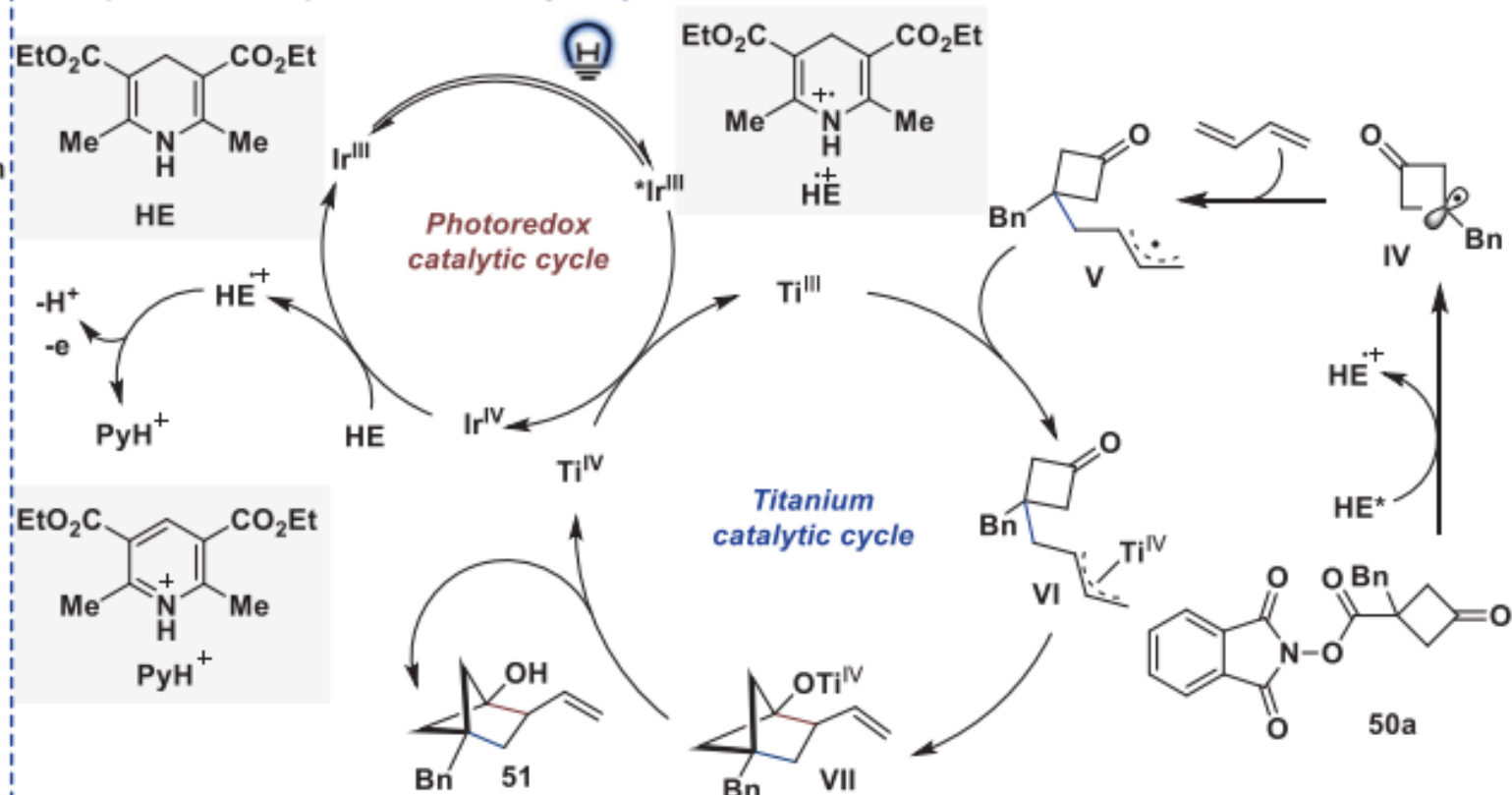


光催化自由基-极性交叉实现双环[2. m. n]烷醇生物电子等排体的模块化合成

H. Proposed photocatalytic mechanism

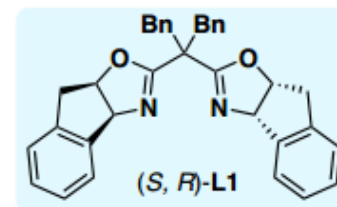
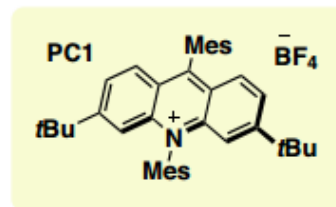
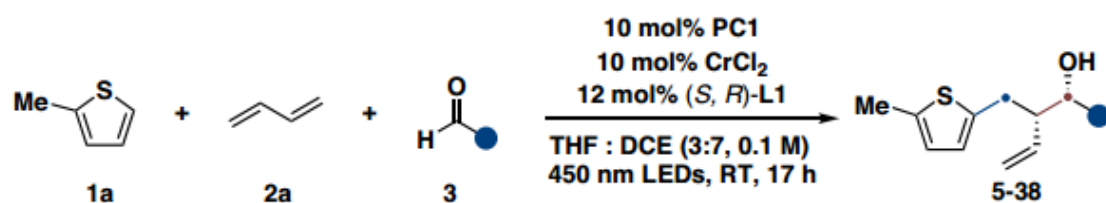


I. Proposed metallaphotoredox catalytic cycle

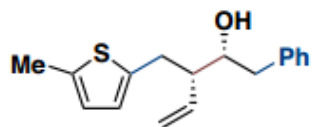




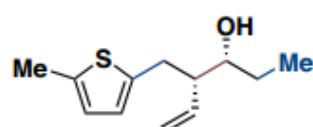
光/铬催化C-H官能化实现的对映选择性自由基-极性交叉转化



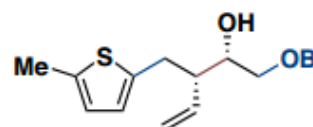
Aliphatic Aldehydes



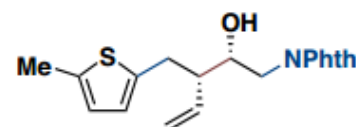
5, 70%
10:1 dr, 97% ee



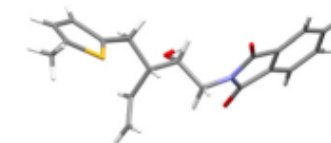
6, 86%
12:1 dr, 98% ee



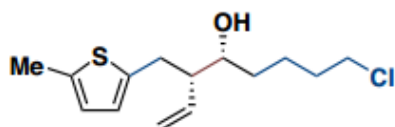
7, 58%
12:1 dr, 97% ee



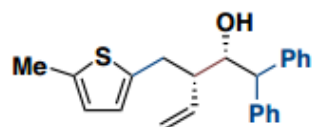
8, 85%
12:1 dr, 94% ee



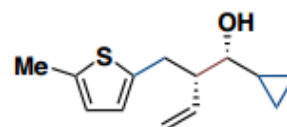
X-ray structure of 8
(CCDC 2344646)



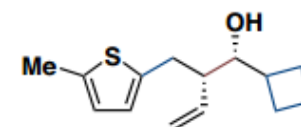
9, 81%
12:1 dr, >99% ee



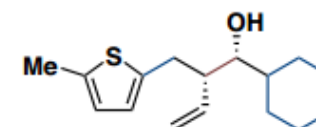
10, 91%
13:1 dr, 98% ee



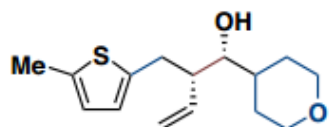
11, 86%
12:1 dr, 96% ee



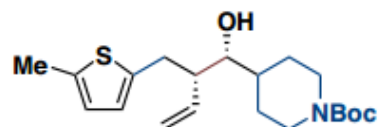
12, 68%
14:1 dr, 92% ee



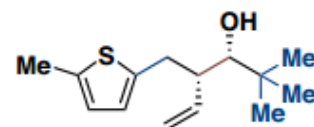
13, 80%
12:1 dr, 95% ee



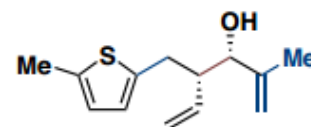
14, 62%
14:1 dr, 98% ee



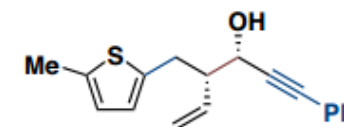
15, 73%
11:1 dr, 99% ee



16, 88%
16:1 dr, 92% ee



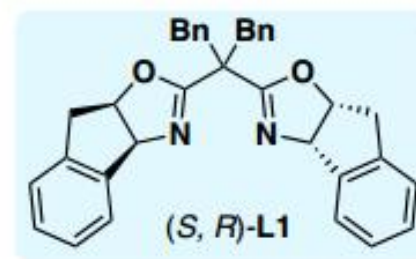
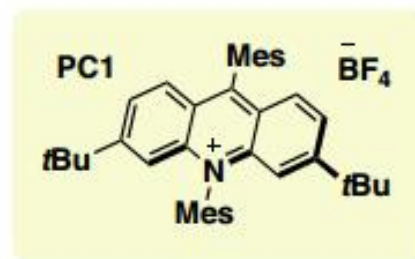
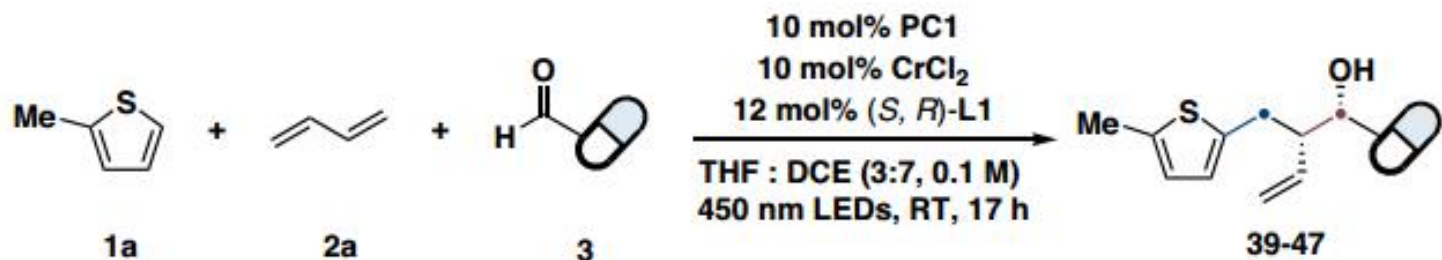
17, 77%
9:1 dr, 97% ee



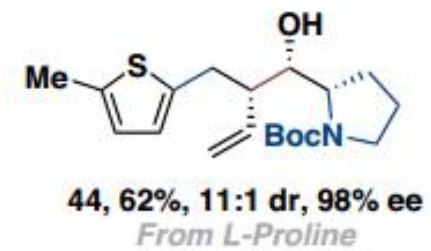
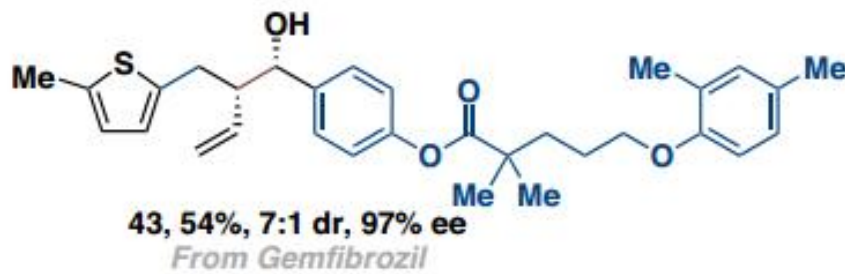
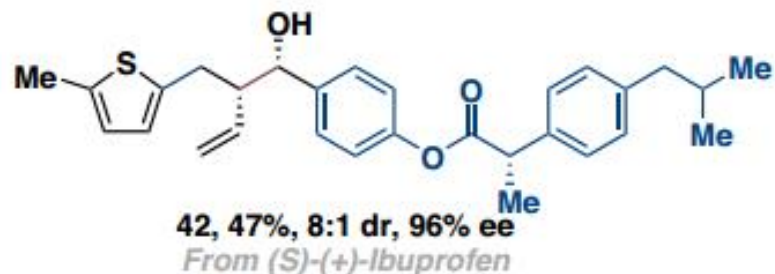
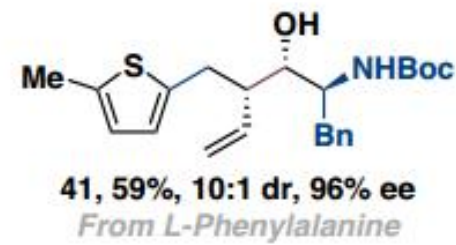
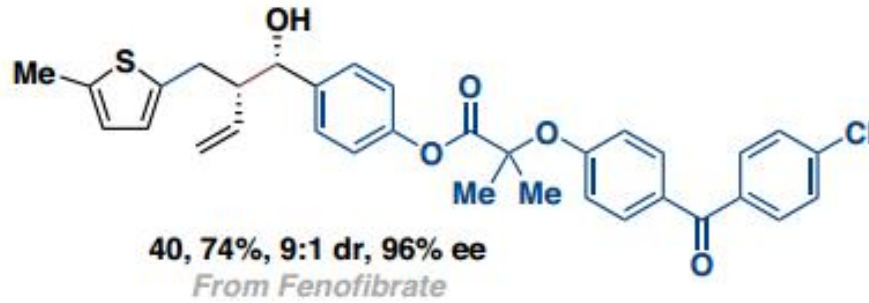
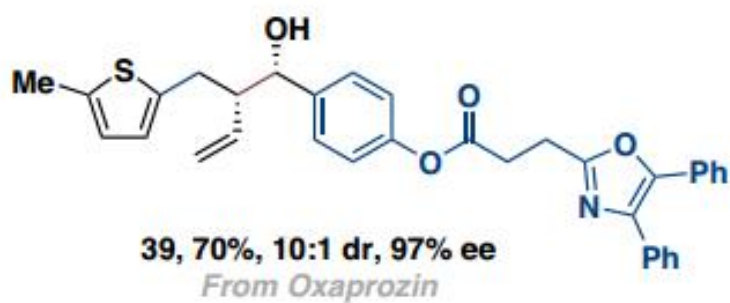
18, 61%
12:1 dr, 98% ee



光/铬催化C-H官能化实现的对映选择性自由基-极性交叉转化

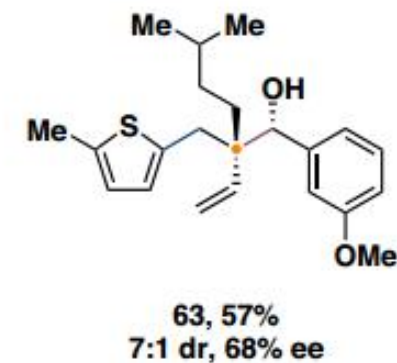
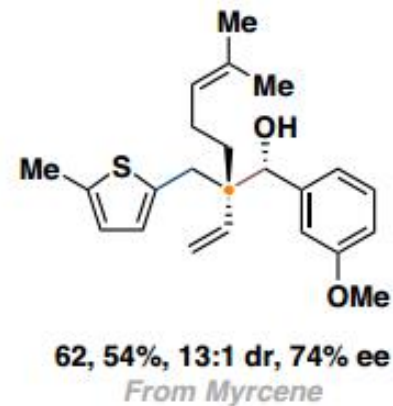
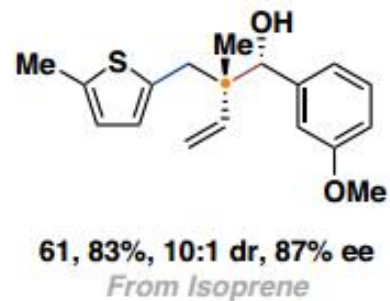
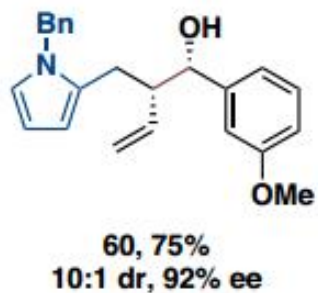
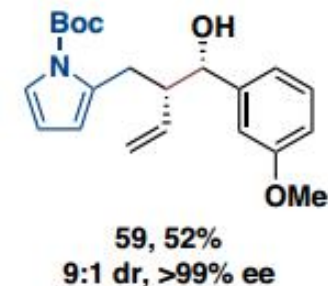
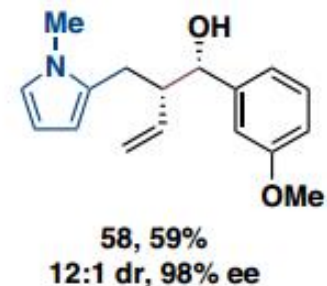
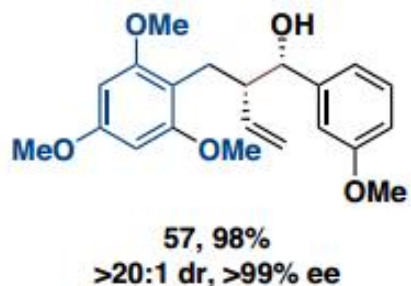
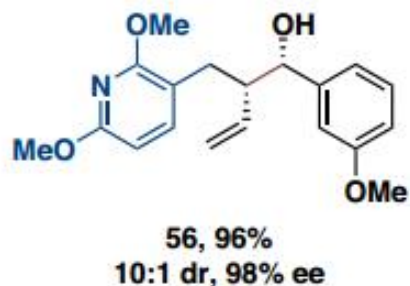
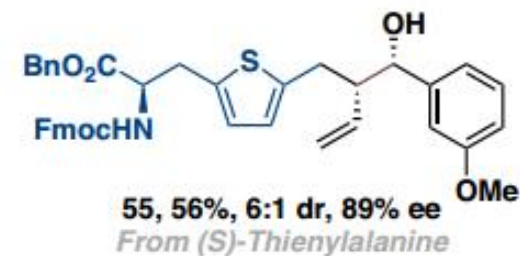
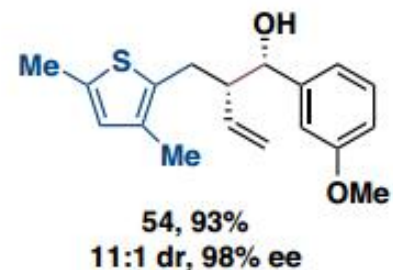
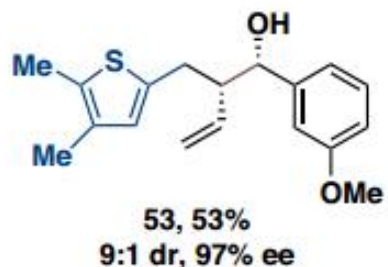
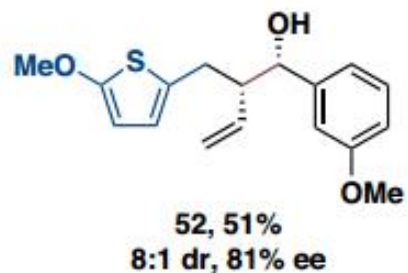


Natural Products and Drugs



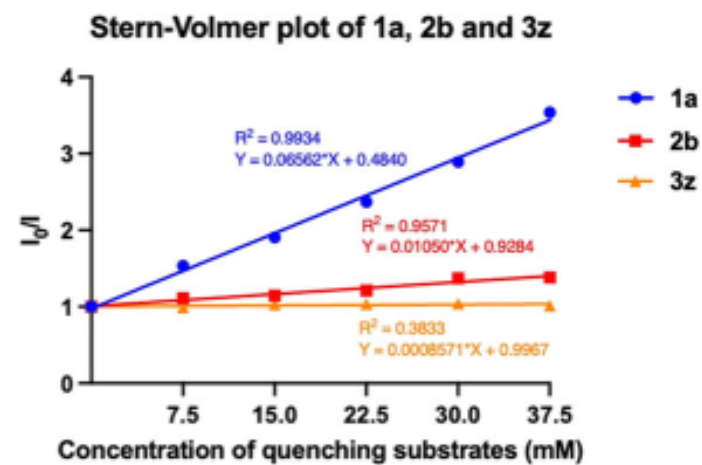
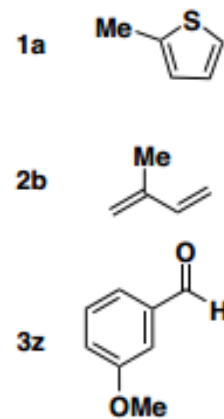
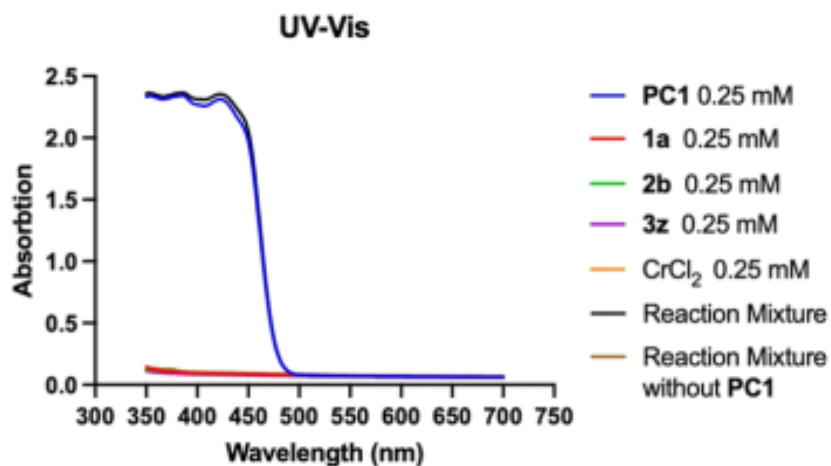
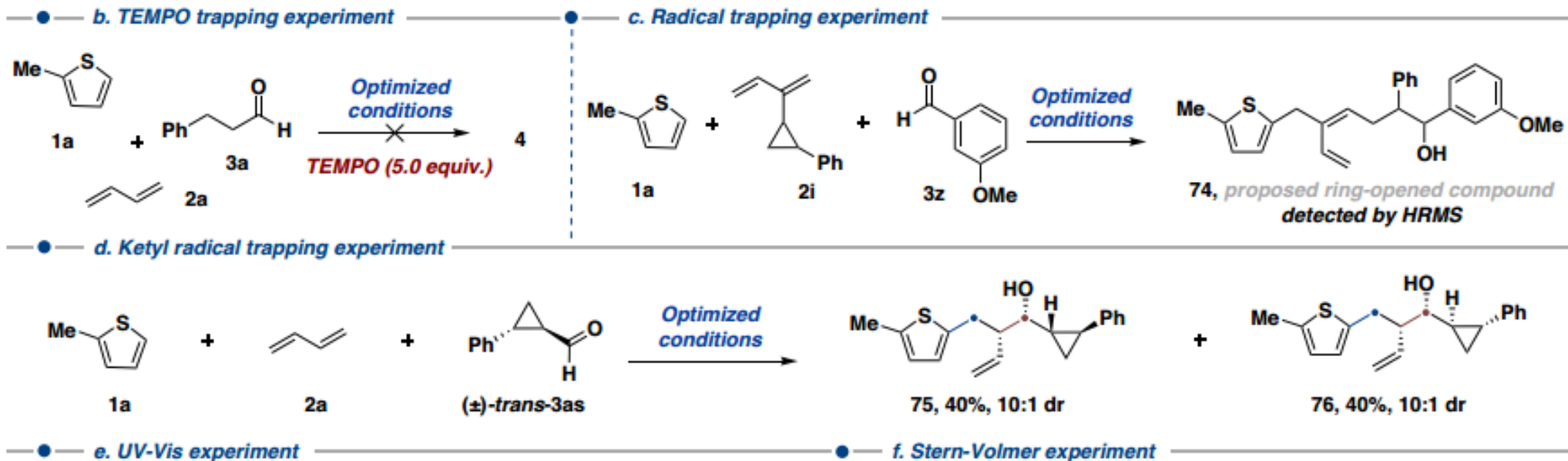


光/铬催化C-H官能化实现的对映选择性自由基-极性交叉转化





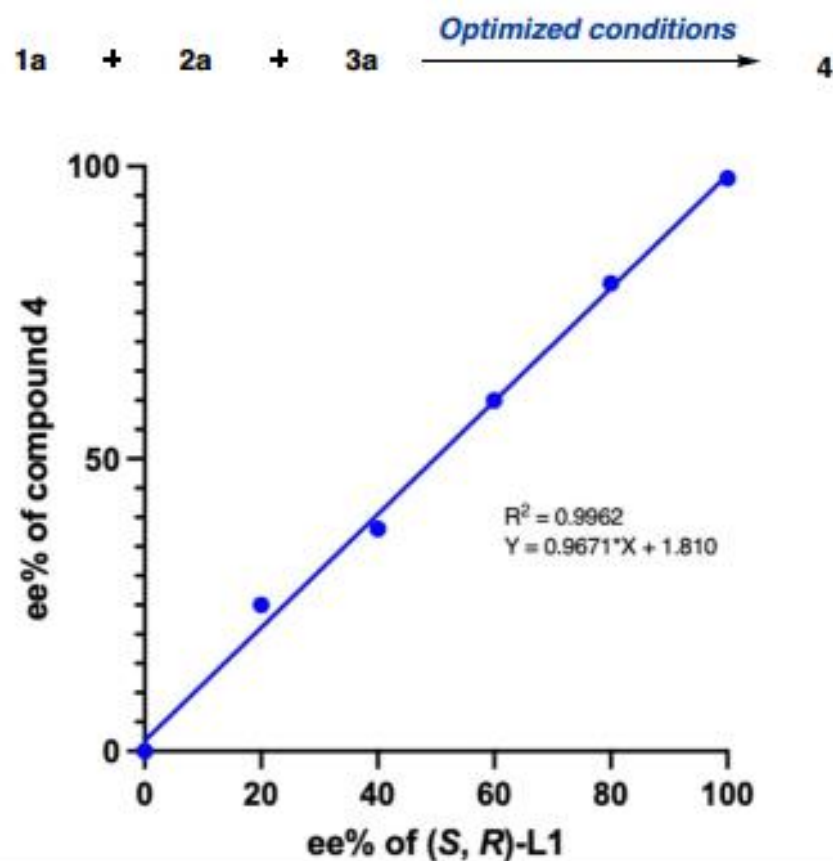
光/铬催化C-H官能化实现的对映选择性自由基-极性交叉转化



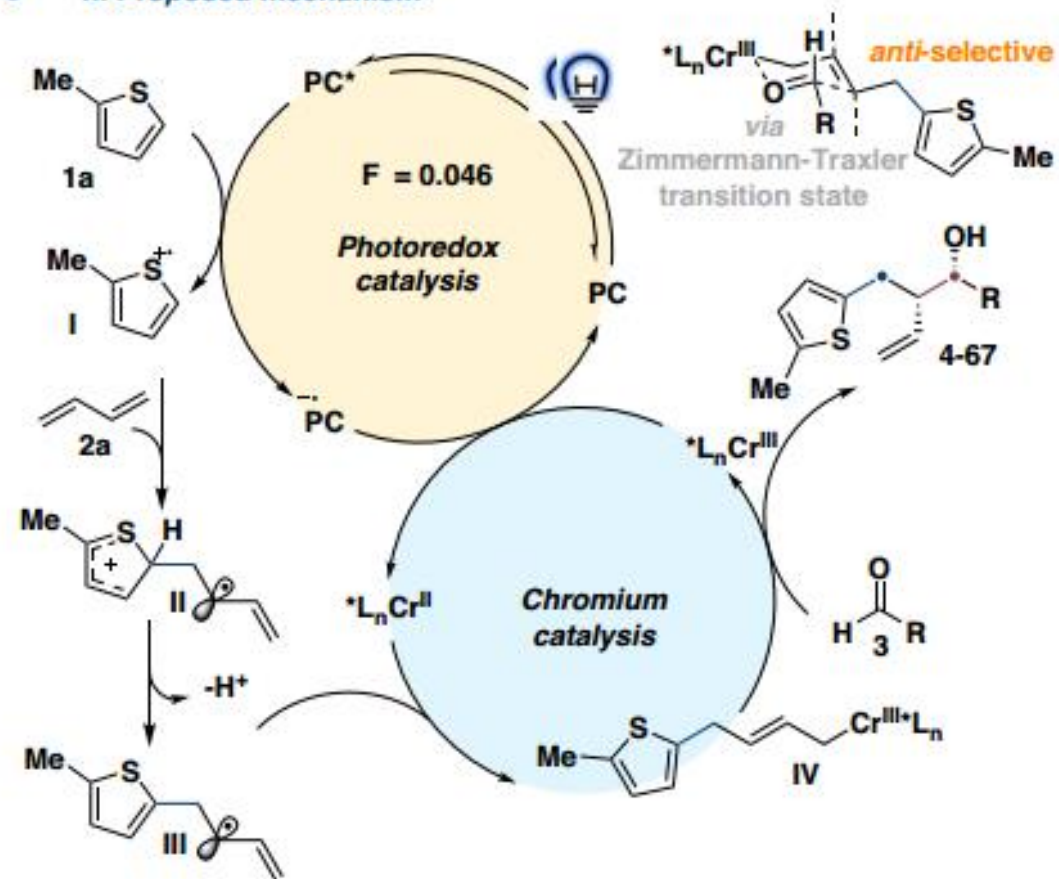


光/铬催化C-H官能化实现的对映选择性自由基-极性交叉转化

g. Non-linear effects study



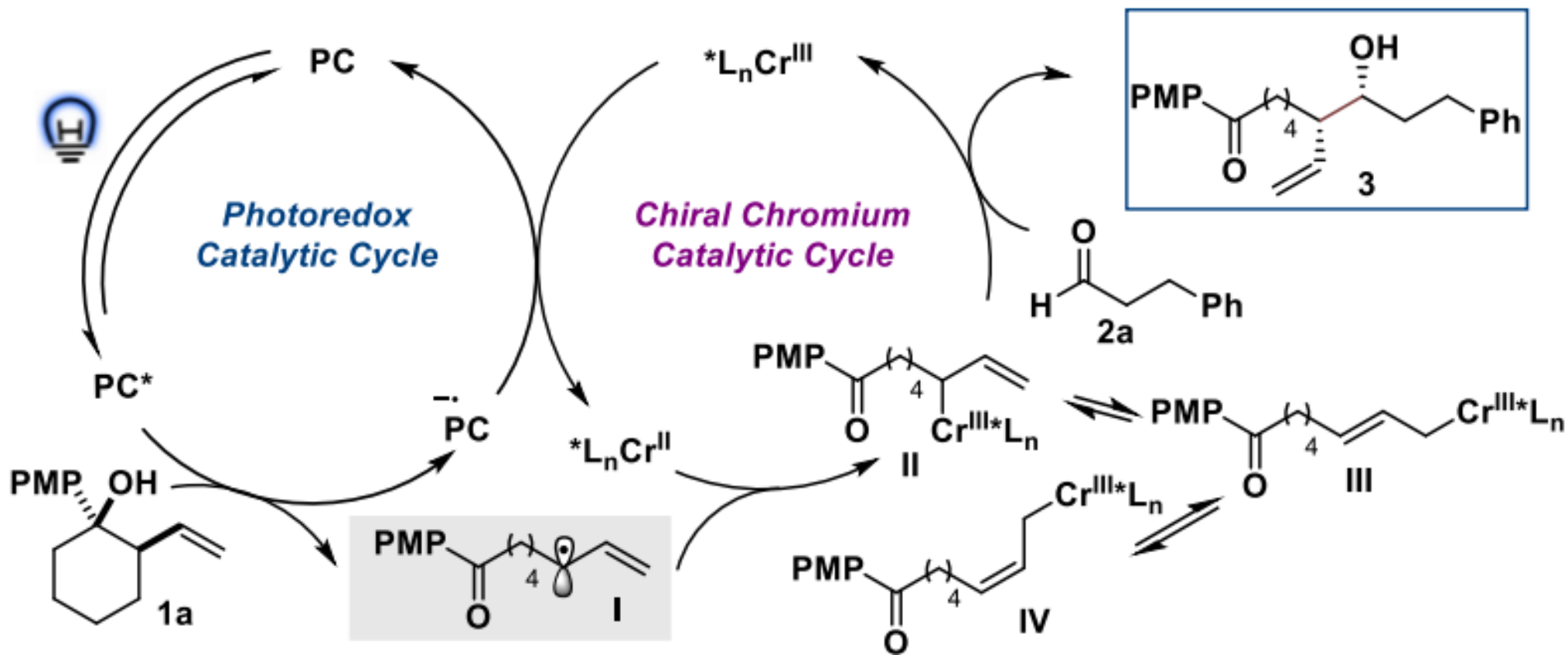
h. Proposed mechanism





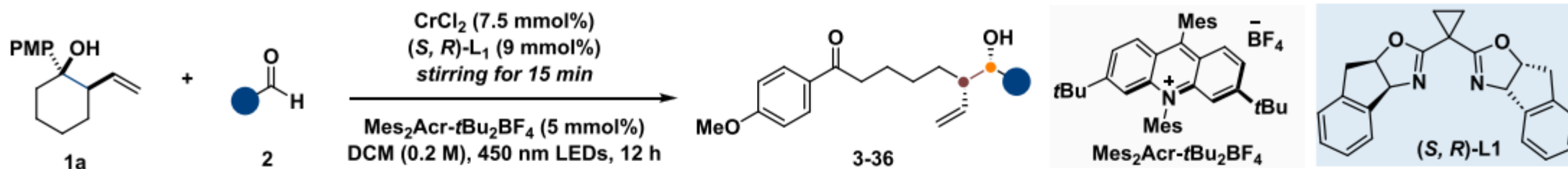
光氧化还原和手性铬双催化的对映选择性烯丙基烷基化反应

● H. Proposed mechanism

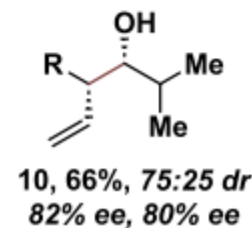
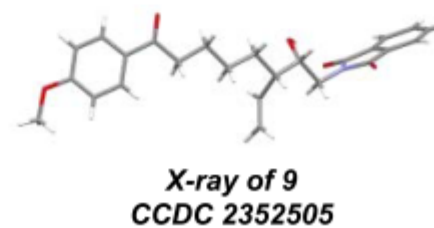
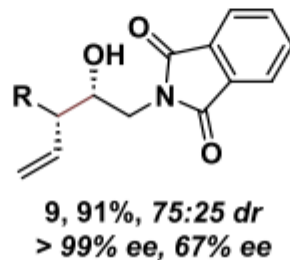
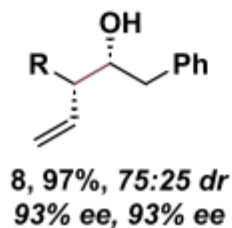
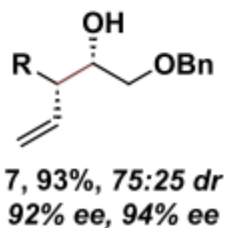
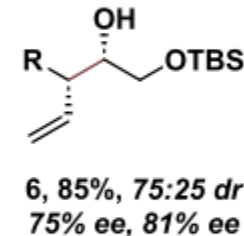
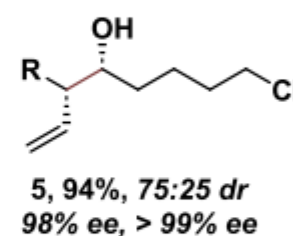
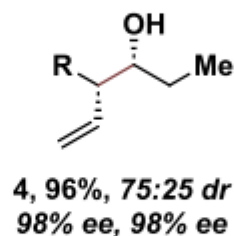
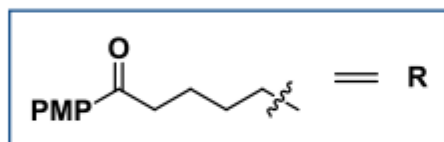
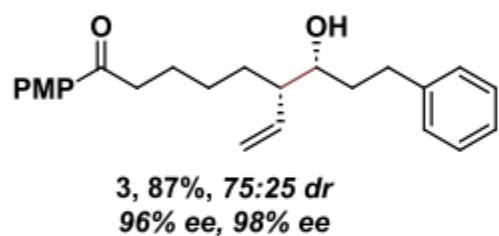




光氧化还原和手性铬双催化的对映选择性烯丙基烷基化反应



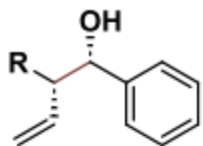
Aliphatic Aldehydes



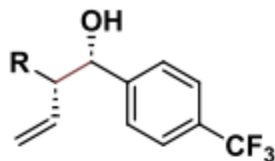


光氧化还原和手性铬双催化的对映选择性烯丙基烷基化反应

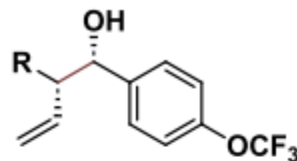
Aromatic Aldehydes



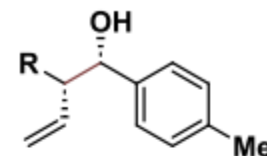
21, 72%, 70:30 dr
91% ee, 93% ee



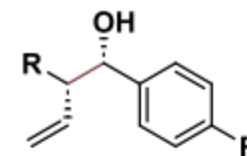
22, 84%, 70:30 dr
98% ee, 99% ee



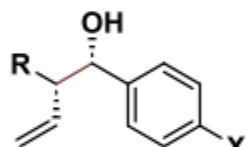
23, 94%, 70:30 dr
93% ee, 96% ee



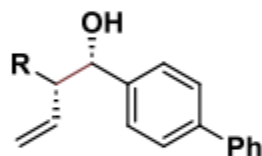
24, 81%, 75:25 dr
92% ee, 94% ee



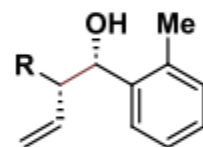
25, 45%, 75:25 dr
95% ee, 97% ee



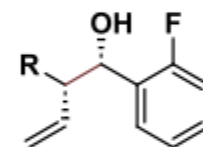
26, R¹ = Cl, 82%, 70:30 dr
98% ee, 99% ee



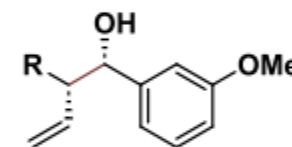
28, 68%, 75:25 dr
93% ee, 93% ee



29, 84%, 70:30 dr
91% ee, 90% ee

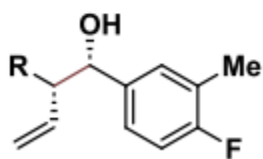


30, 87%, 70:30 dr
96% ee, 97% ee

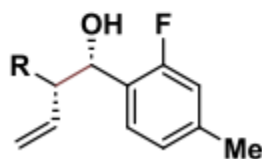


31, 90%, 75:25 dr
85% ee, 83% ee

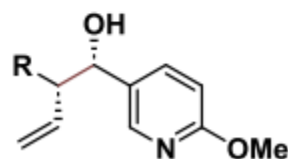
27, R¹ = Br, 70%, 75:25 dr
76% ee, 78% ee



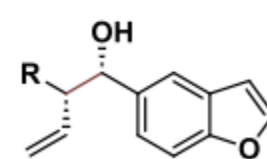
32, 59%, 70:30 dr
71% ee, 66% ee



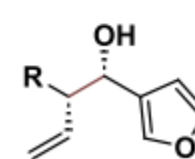
33, 86%, 75:25 dr
97% ee, 98% ee



34, 81%, 75:25 dr
97% ee, 97% ee



35, 65%, 75:25 dr
94% ee, 93% ee



36, 52%, 64:36 dr
87% ee, 88% ee

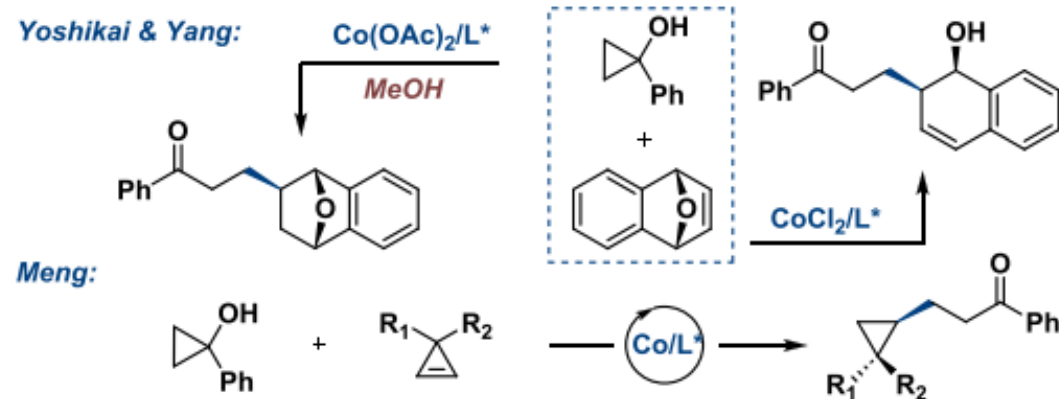


手性铬催化环丙醇的立体选择性自由基-极性交叉反应

A. Transition Metal Catalyzed C-C or C-X Bond Couplings Using Cyclopropanols

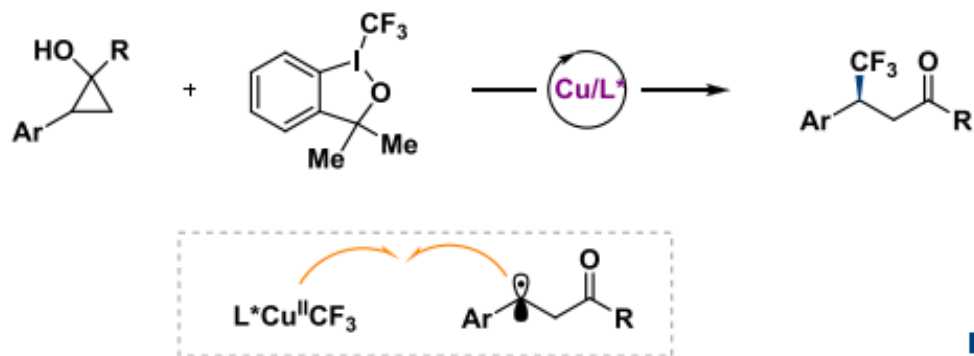


B. Co-Catalyzed Polar Two-Component Enantioselective of Cyclopropanols



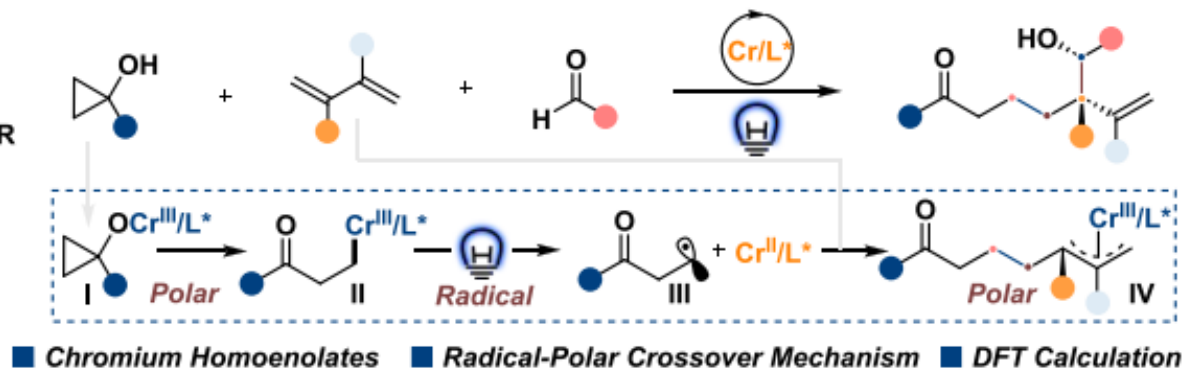
C. Cu-Catalyzed Radical Two-Component Enantioselective of Cyclopropanols

Liu:



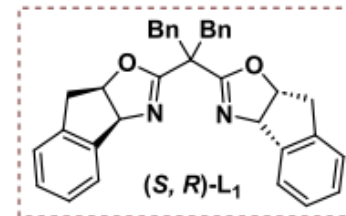
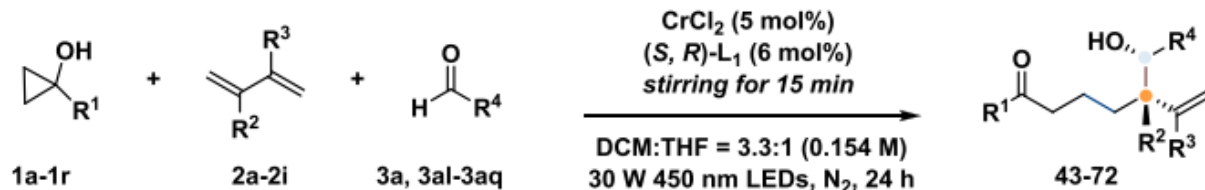
D. This Work: Cr-Catalyzed Enantioselective Radical Three-Component Reaction

■ Chiral Radical-Polar Crossover Chromium Catalysis

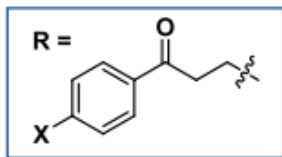
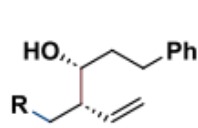




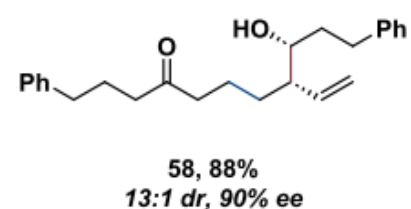
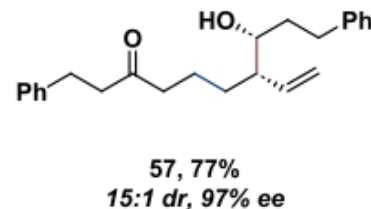
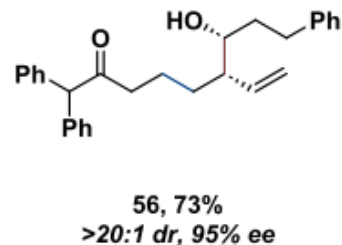
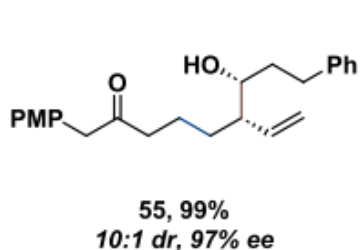
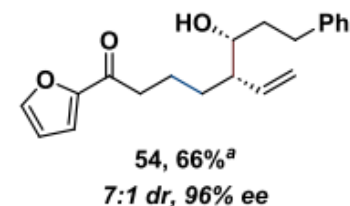
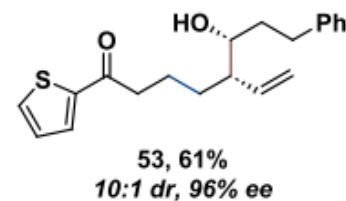
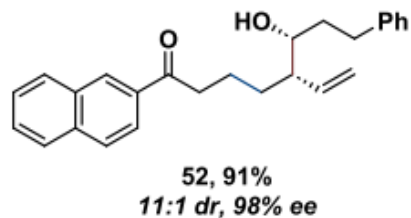
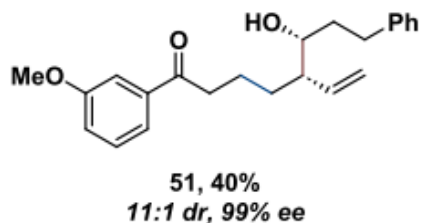
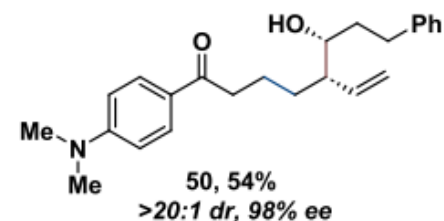
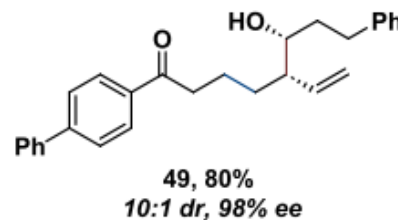
手性铬催化环丙醇的立体选择性自由基-极性交叉反应

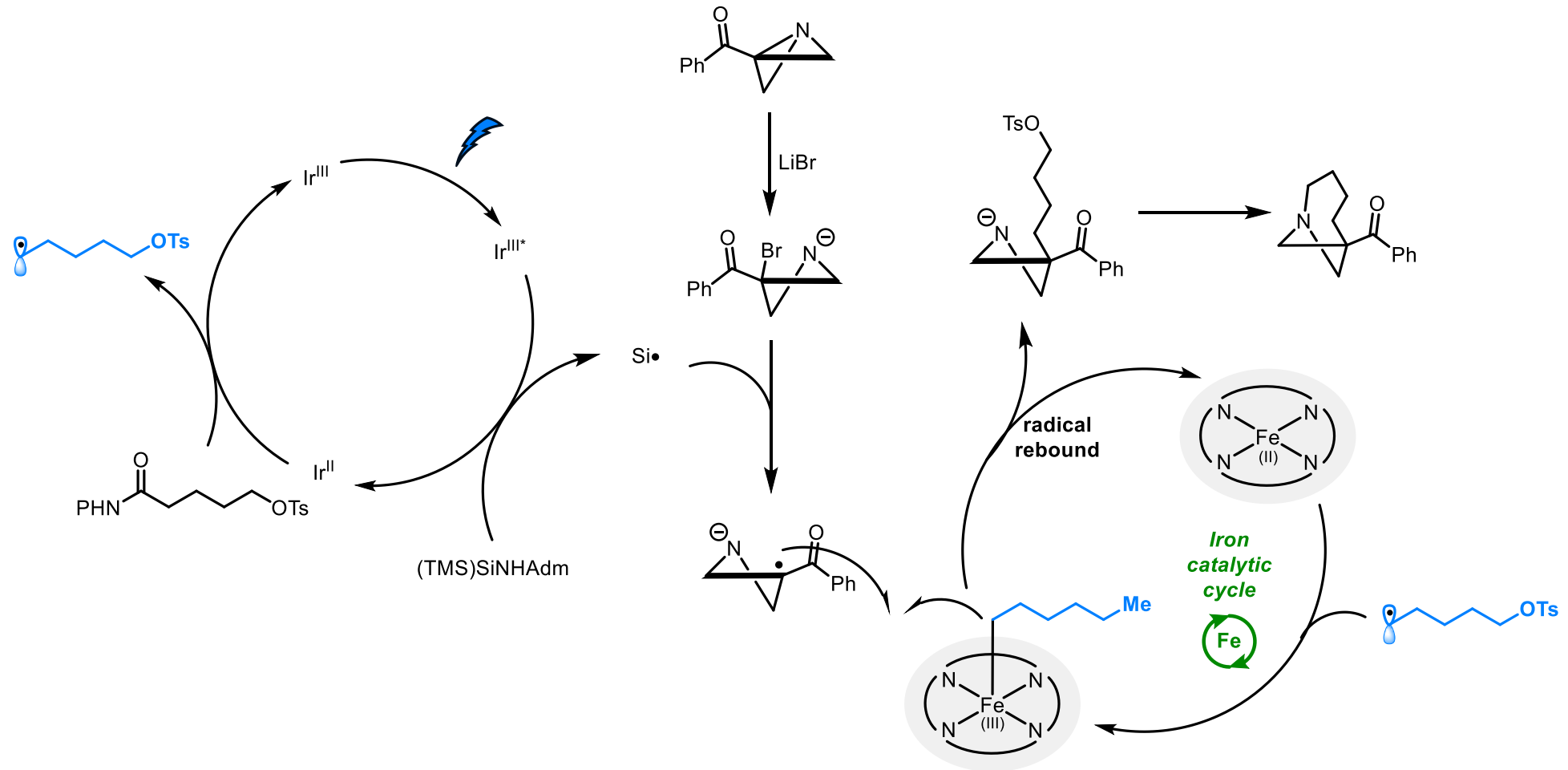


Different Cyclic Alcohols



- 43, X = H, 52%, 11:1 dr, 97% ee
- 44, X = F, 93%, 10:1 dr, 97% ee
- 45, X = Cl, 99%, 13:1 dr, 97% ee
- 46, X = Br, 70%, 15:1 dr, 90% ee
- 47, X = Me, 99%, >20:1 dr, 97% ee
- 48, X = CF₃, 64%, 7:1 dr, 96% ee





Thanks