手性氮杂芳烃合成新策略

——江智勇课题组相关工作介绍

刘灿祥
化学科学与工程学院

同舟共济

人物介绍

同济大学 TONGJI UNIVERSITY

江智勇教授
国家杰青 河南师范大学副校长

- 教育及工作经历

1992.09-1996.06	浙江大学 理学学士
1999.09-2004.01	浙江大学 理学博士
2004.02—2005.04	香港浸会大学 博士后 导师：Wing-Hong Chan教授
2005.08—2009.08	新加坡国立大学 博士后 导师：Choon-Hong Tan教授
2009.08—2018.08	河南大学河南省天然药物与免疫工程重点实验室
2013.04—2013.10	新加坡南洋理工大学 高级研究员
2018.08—至今	河南师范大学化学化工学院教授
2021.09—至今	河南师范大学，学术副校长

研究领域：可见光不对称有机催化；不对称自由基化学；手性杂环化学

同舟共济

手性磷酸

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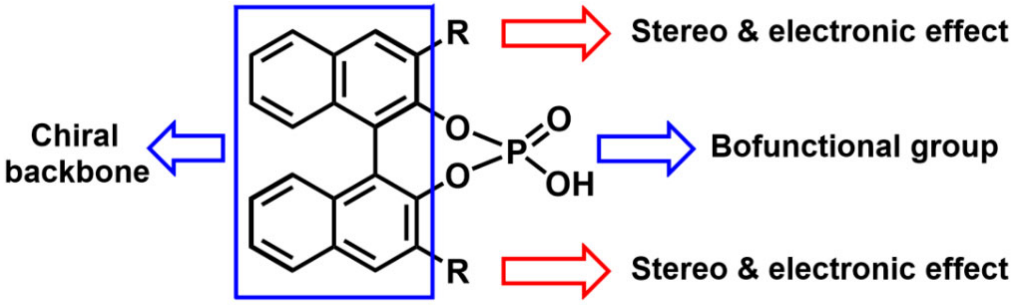
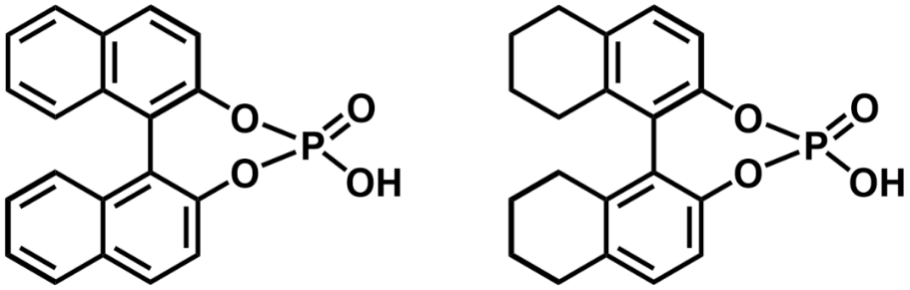
手性磷酸的结构特点



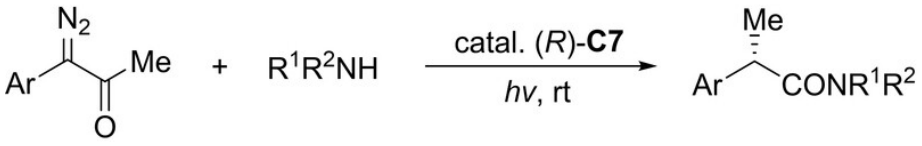
基于BINOL & 8H-BINOL骨架的手性磷酸



Angew. Chem. Int. Ed., **2016**, *55*, 1299; *Chem. Sci*. **2016**, *7*, 6060

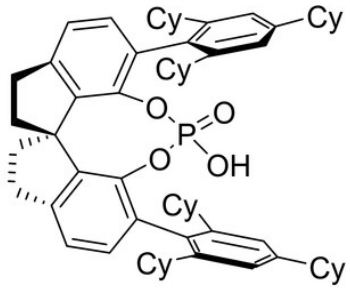
手性磷酸催化的不对称反应

Wolff重排反应



- *Asymmetric Wolff rearrangement*
- *Bifunctional phosphoric acid catalyzed*

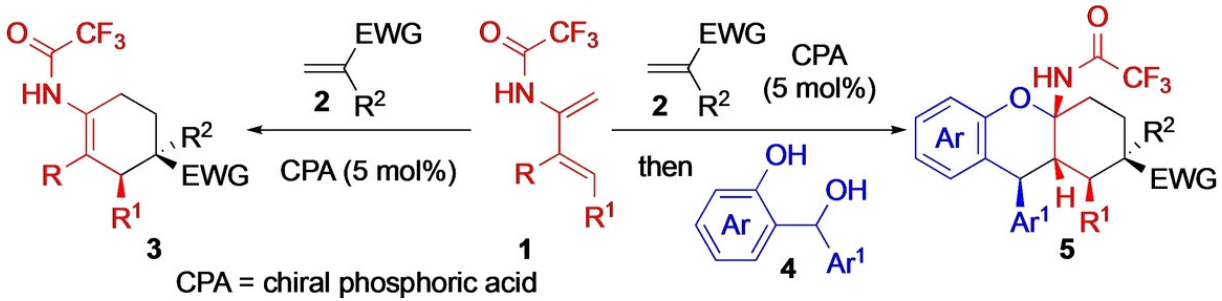
38 examples
up to 98% yield
up to 97% ee



(*R*)-**C7**

Zhou, Q.-L. et al., *Angew. Chem.Int. Ed.* **2023**, *62*, e2023081

Diels-Alder反应

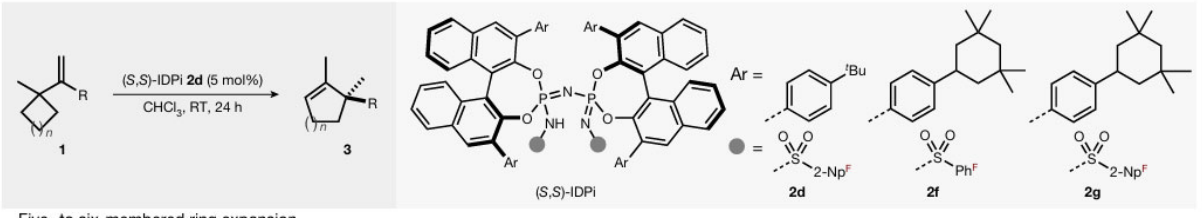


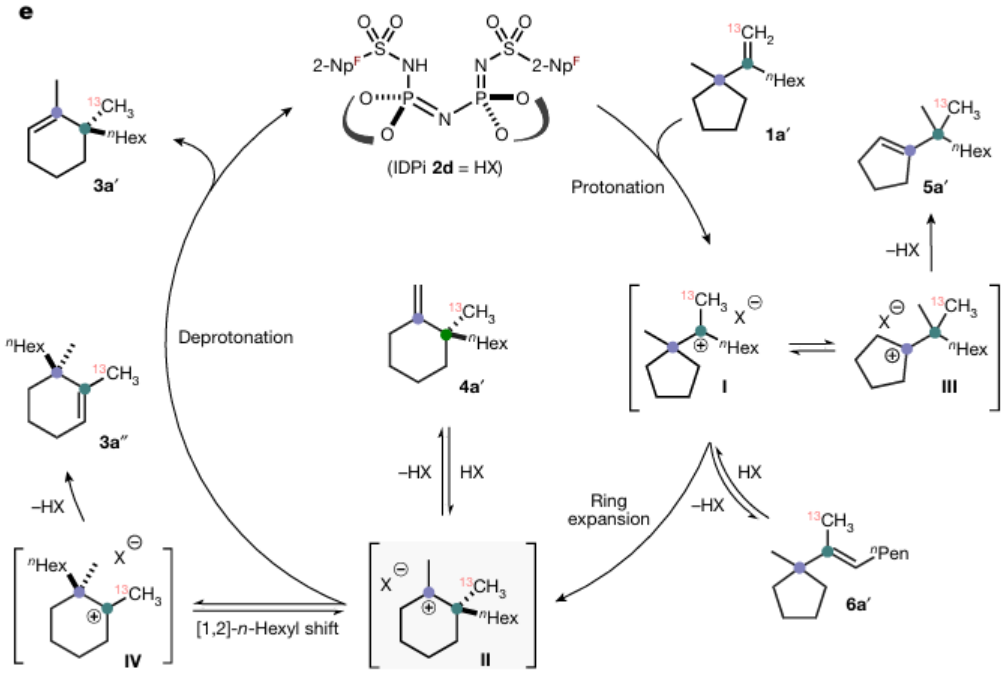
CPA = chiral phosphoric acid

Zhu, J.-P. et al., *Angew. Chem. Int. Ed*. **2023**,*62*, e2022149

手性磷酸催化的不对称反应

Wagner–Meerwein重排





含有全氟萘磺酰基片段的IDPi催化剂，具有优异的区域和对映选择性。具体表现为：1）IDPi的强酸性使烯烃能够高效质子化，而质子化是反应的决速步骤。2）IDPi形成的封闭手性空腔环境有助于控制重排的立体化学，而且能够稳定重排过程中形成的碳正离子中间体，以避免烯烃异构化或烷基迁移副反应的发生。

List, B., et al., *Nature*, **2024**, *625*, 287

手性磷酸催化的不对称反应

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Friedel–Crafts反应： Org. Lett. 2018, 20, 590−593; Org. Lett. 2018, 20, 2689−2692

Mannich反应: Tetrahedron, 2016, 72, 3687-3700; Adv. Synth.Catal. 2008, 350, 399

Biginelli反应: J. Org. Chem. 2008, 73, 7651; Synthesis 2018, 50, 2394–2406

不对称氢转移反应: J. Org. Chem. 2018, 83, 2779−2787; Angew. Chem. Int. Ed. 2006, 45, 4193

不对称Pictet-Spengler反应: Org. Lett., 2011，13, 5636–5639

不对称Robinson关环反应: Eur. J. Org. Chem. 2012, 4508–4514

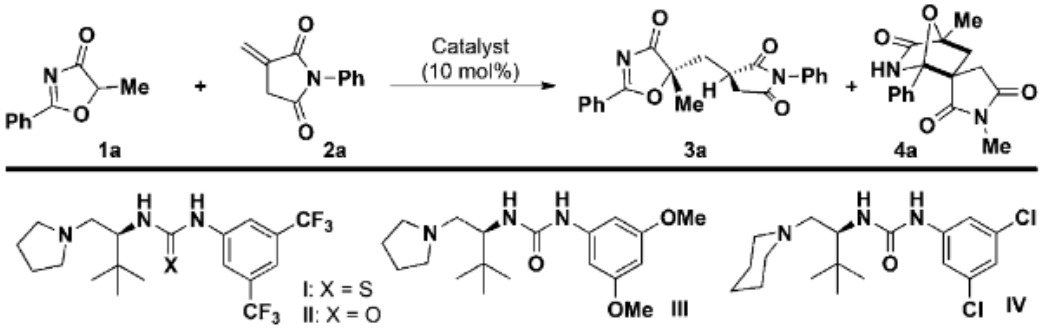
氮杂-Pinacol重排反应: Angew. Chem. Int. Ed. 2017, 56, 9217 –9221

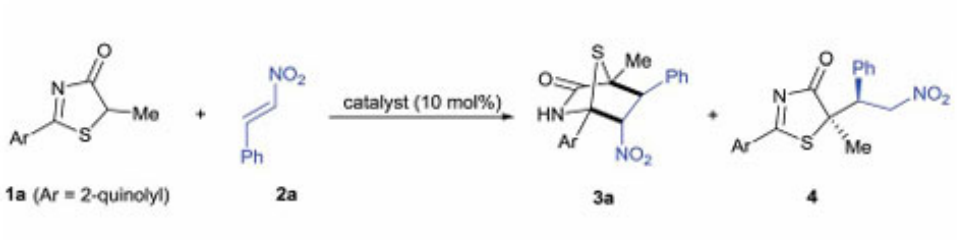
氮杂-Wacker氧化反应: Angew. Chem. Int. Ed. 2018, 57, 1995 –1999

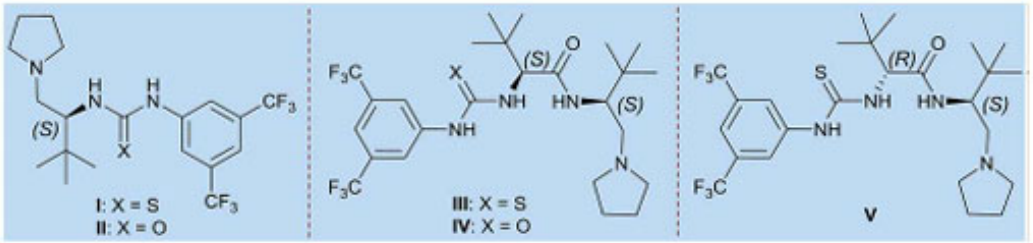
Heck反应: Angew. Chem. Int. Ed. 2017, 56, 5806 –5811 ……

背景介绍

离子型不对称共轭加成-质子化反应



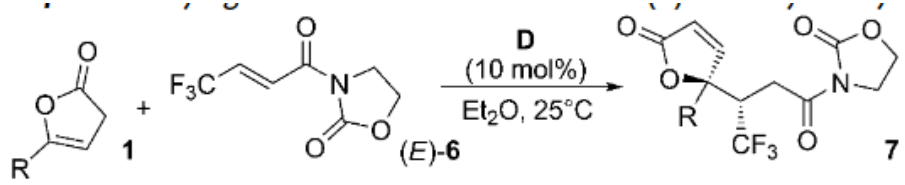




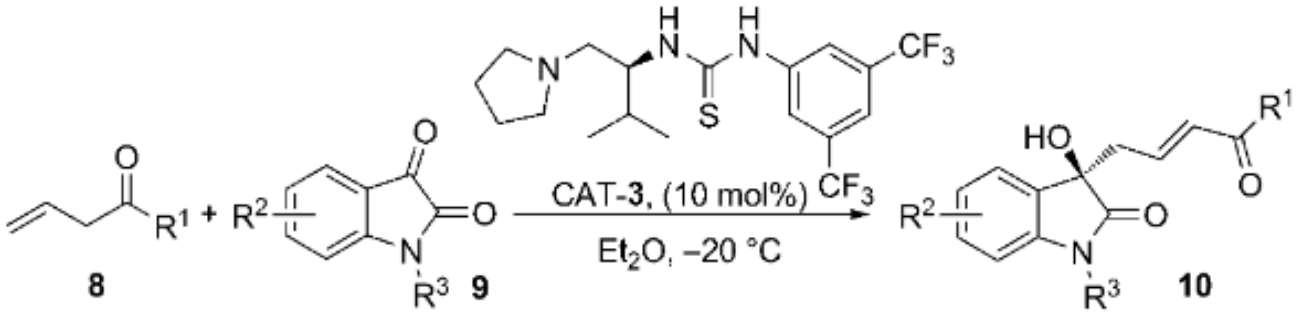
Angew. Chem. Int. Ed., **2016**, *55*, 1299; *Chem. Sci.* **2016**, *7*, 6060

背景介绍

不对称插烯反应

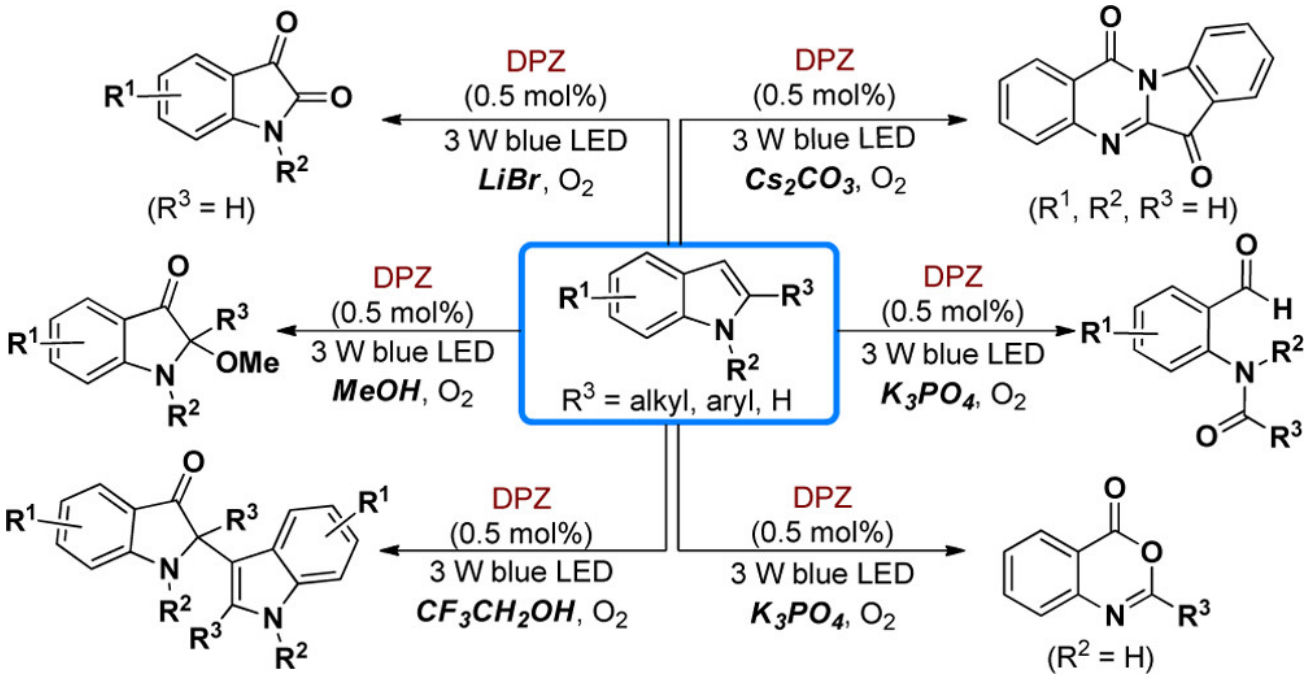


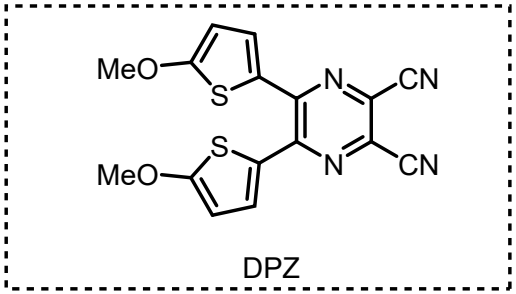
Entry	R (7)	*t* [h]	Yield [%][b]	*ee* [%][c]	d.r.[d]
1	C_6H_5 (**7a**)	24	82	98	>99:1
2	4-FC_6H_4 (**7b**)	24	78	97	>99:1
3	4-ClC_6H_4 (**7c**)	24	83	97	>99:1
4	4-BrC_6H_4 (**7d**)	24	86	98	>99:1
5	4-$CH_3C_6H_4$ (**7e**)	24	88	98	>99:1
6	CH_3 (**7f**)	72	77	98	>99:1



Angew. Chem. Int. Ed. 2012, 51, 10069; Angew. Chem. Int. Ed. 2013, 52, 6666.

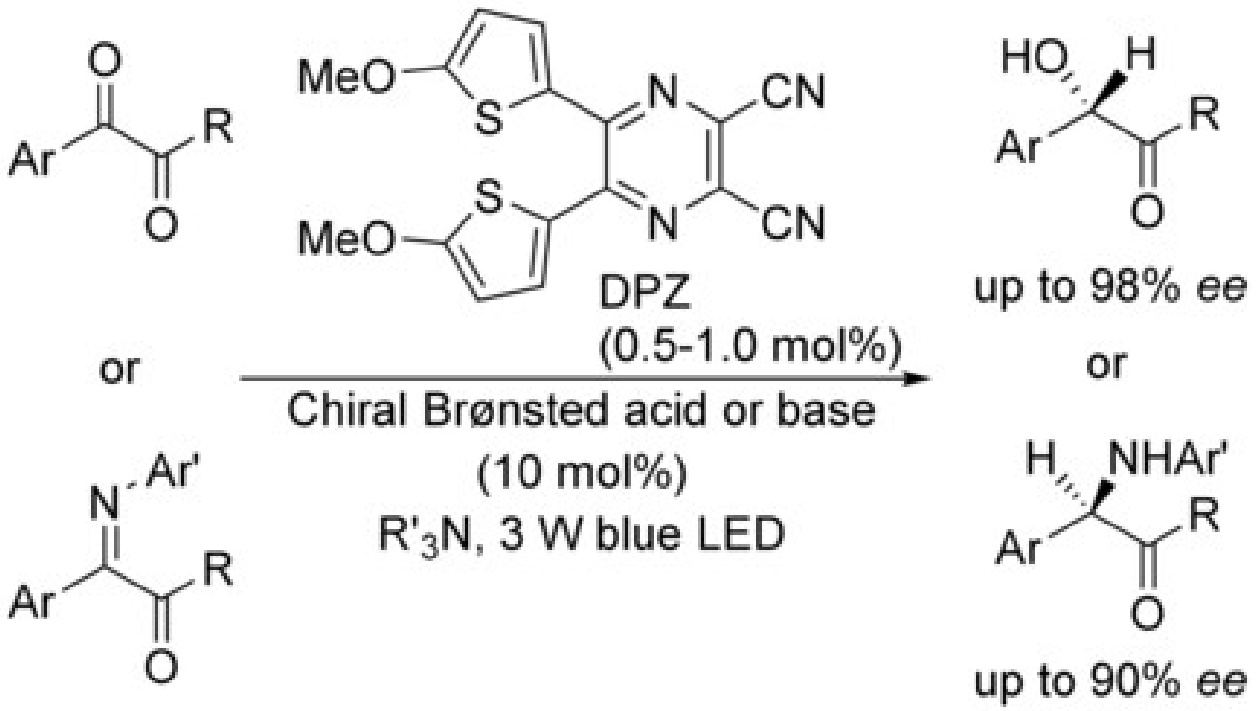
DPZ有机可见光催化剂





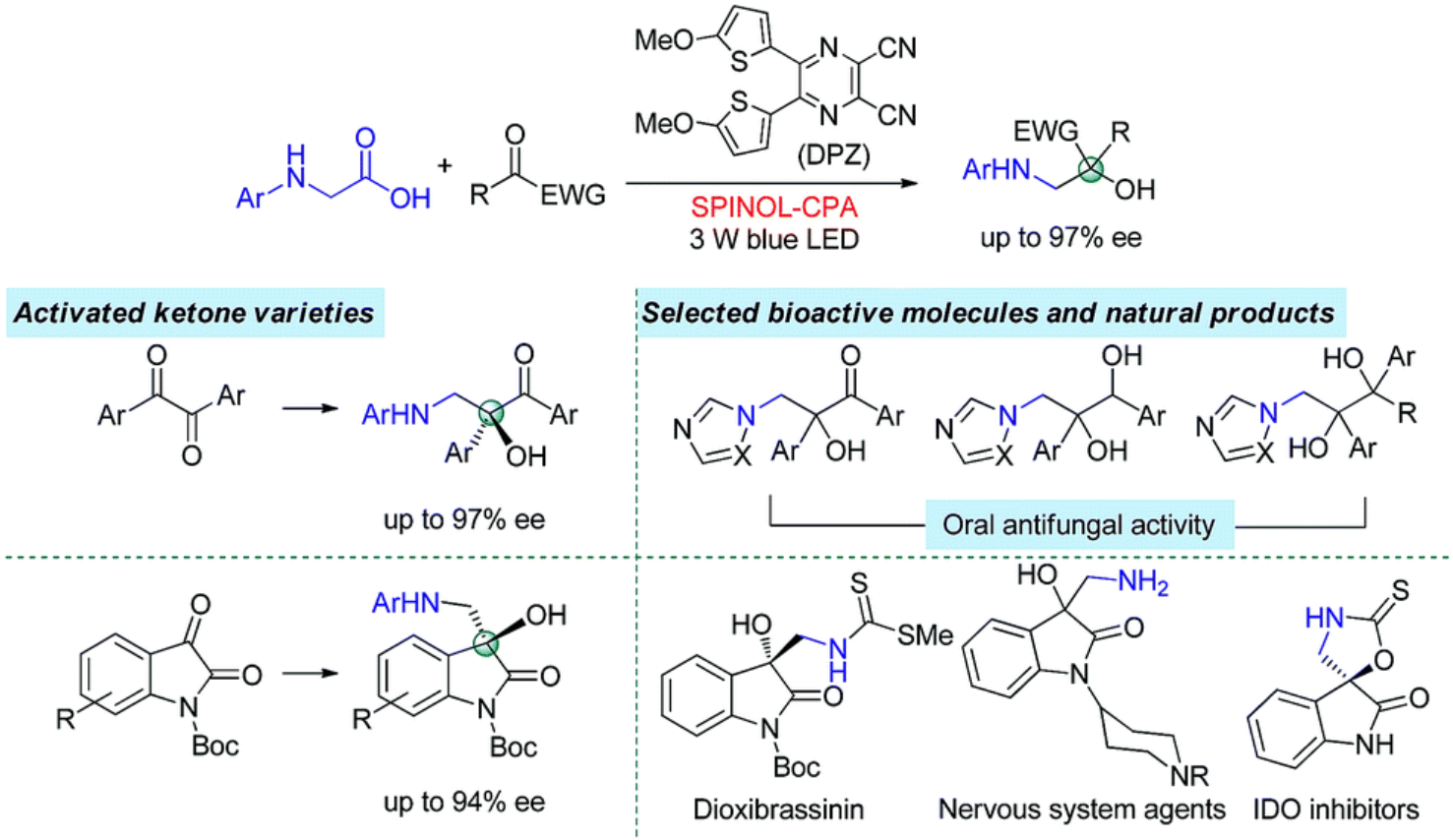
ACS Catal., **2016**, *6*, 6853

DPZ与手性氢键协同的光氧化还原不对称有机催化



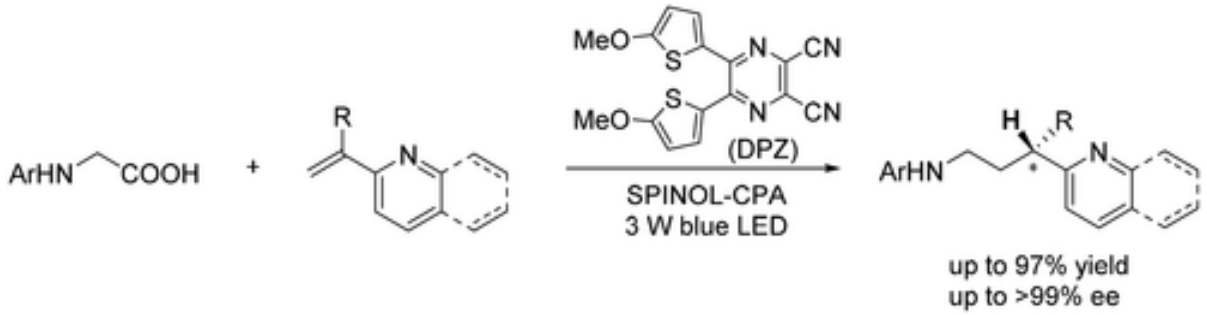
Angew. Chem. Int. Ed. **2017**, *56*, 13842

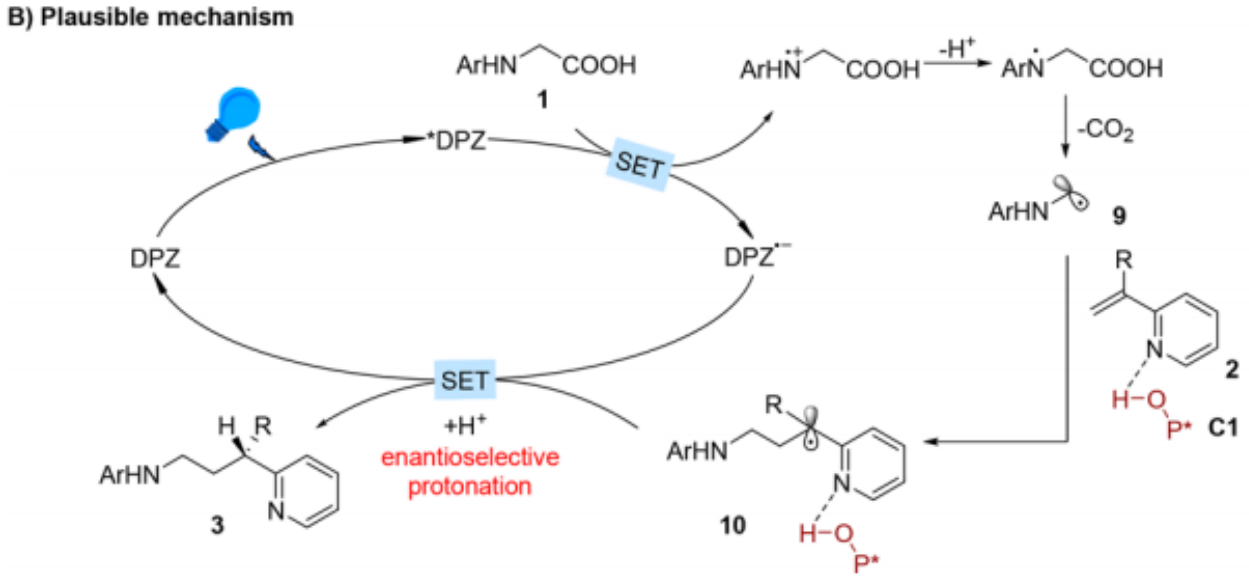
自由基的不对称偶联



Chem. Sci., **2018**, *9*, 8094

氮杂芳烃α位构建手性中心

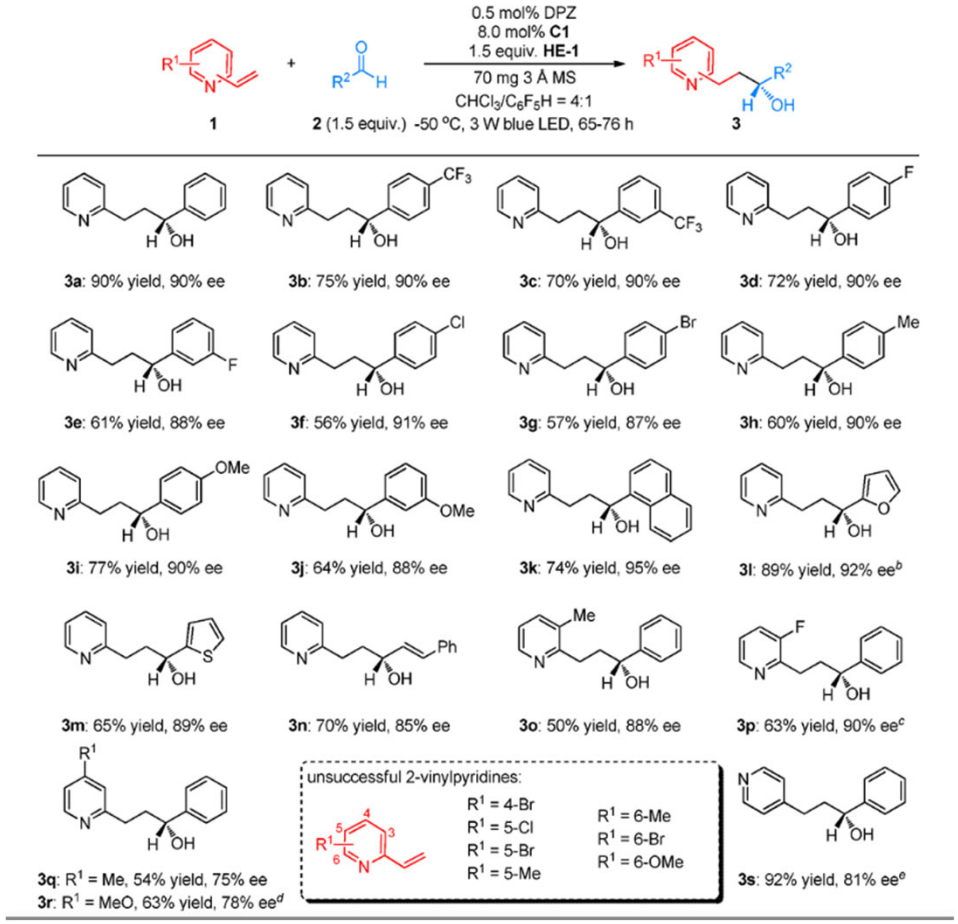


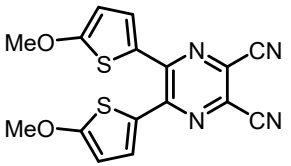


首例通过可见光不对称催化实现含氮芳香杂环化合物高立体选择性合成。建立了DPZ与手性膦酸协同不对称催化体系，发展了自由基型共轭加成-质子化途径，通过手性膦酸与氮杂芳烃碱性氮原子的氢键相互作用，实现了在氮杂芳烃α位构建手性中心，高反应活性与立体选择性充分体现了该催化体系对于构筑氮杂芳烃手性化合物的高效性。

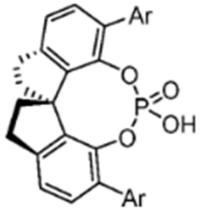
J. Am. Chem. Soc., **2018**, *140*, 6083

吡啶γ-位手性中心的构建

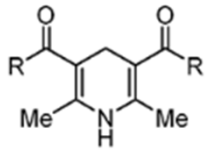




DPZ



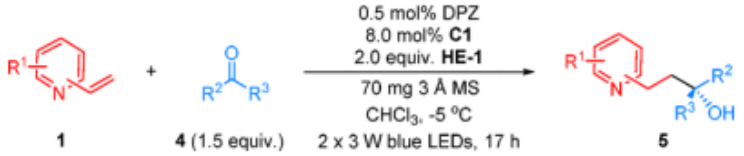
C1: Ar = 2,4,6-*i*Pr$_3$C$_6$H$_2$
C2: Ar = 3,5-Ph$_2$C$_6$H$_3$
C3: Ar = 9-anthryl



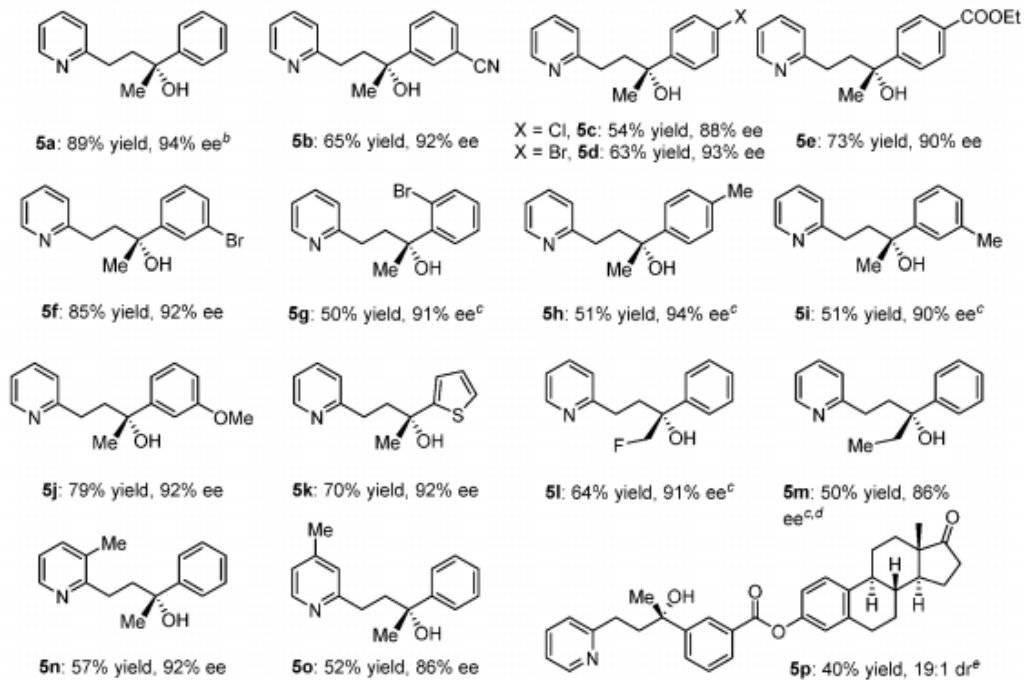
HE-1: R = *t*BuO
HE-2: R = EtO
HE-3: R = Me

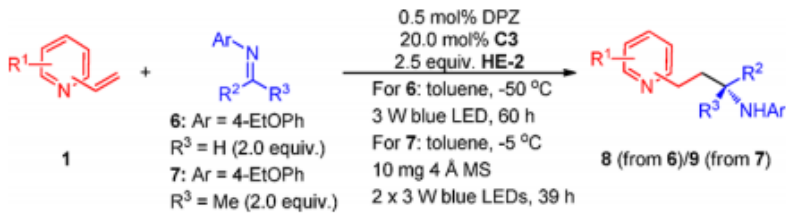
J. Am. Chem. Soc., **2019**, *141*, 5437.

吡啶γ-位手性中心的构建

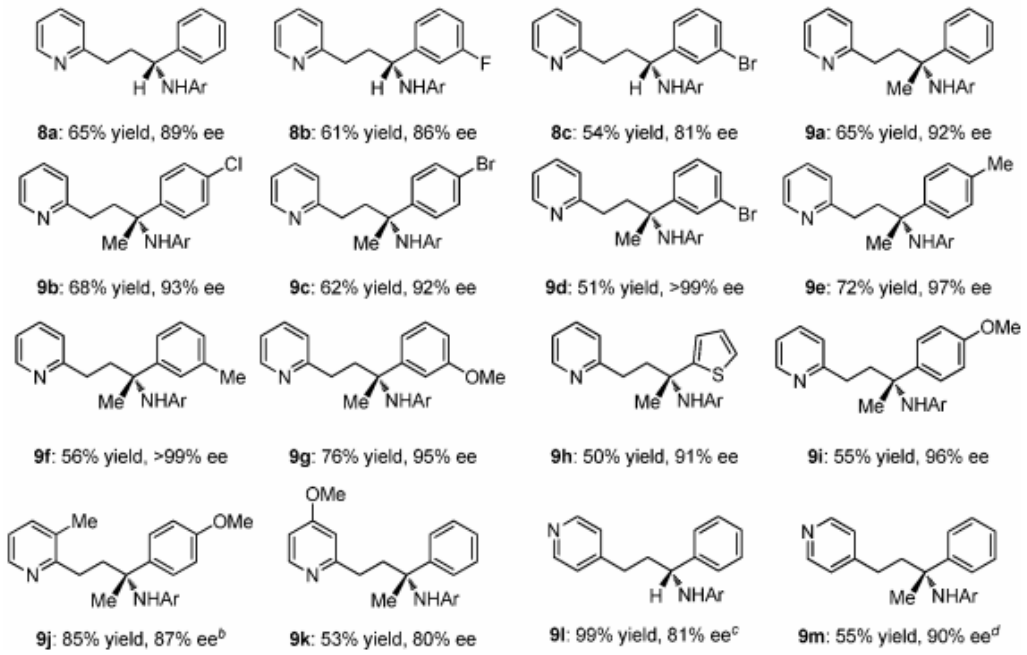


1 + 4 (1.5 equiv.) → 5





1 + 6/7 → 8/9



J. Am. Chem. Soc., **2019**, *141*, 5437.

吡啶γ-位手性中心的构建

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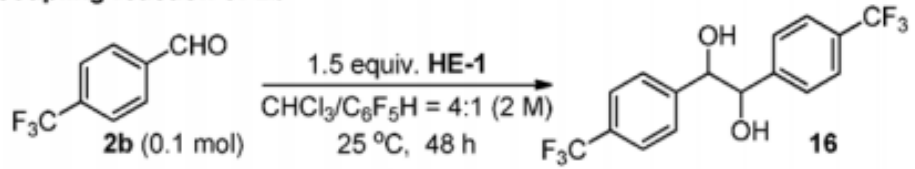
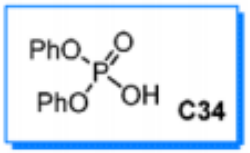
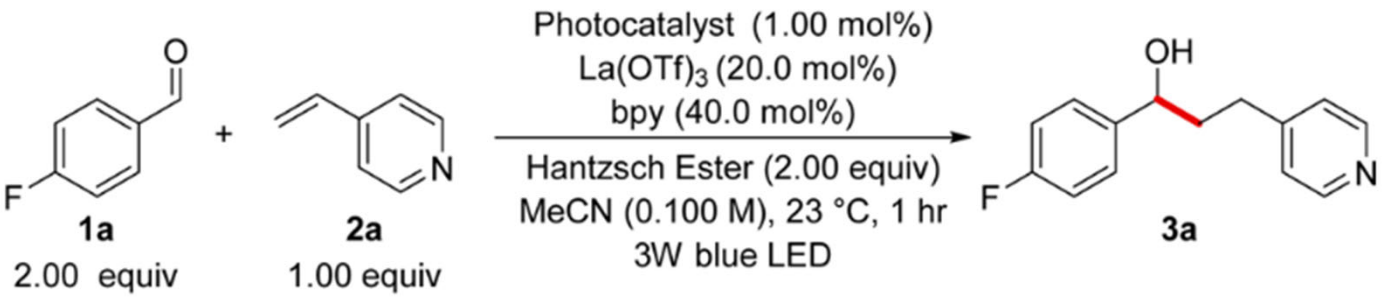
A) Pinacol coupling reaction of 2b





entry	wavelength of 3 W blue LED	0.5 mol% DPZ	10 mol% **C34**	yield of **16**
1	410-510 nm	no	no	15%
2	410-510 nm	with	no	55%
3	410-510 nm	no	with	37%
4	410-510 nm	with	with	70%
5	474-505 nm	with	with	0% (no reaction)



J. Am. Chem. Soc. **2017**, *139*, 5003.

吡啶γ-位手性中心的构建

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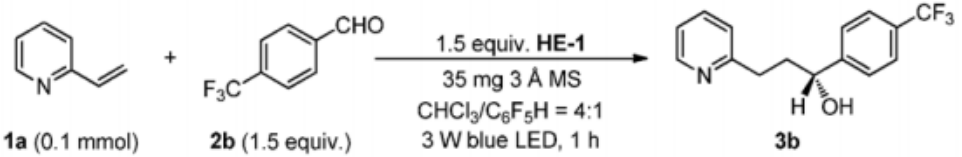
B) Transformation of 1a with 2b



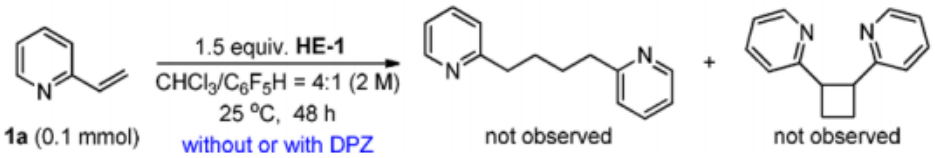
1a (0.1 mmol) **2b** (1.5 equiv.) **3b**

entry	0.5 mol% DPZ	8.0 mol% **C1**	temperature (°C)	yield of **3b**	ee of **3b**
1	no	no	25 °C	5% (48 h)	N.A.
2	with	no	25 °C	60% (18 h)	N.A.
3	with	with	25 °C	86%	76%
4	no	with	25 °C	84%	77%
5	no	with	-50 °C	0% (no reaction, 70 h)	N.A.
6	with	no	-50 °C	0% (no reaction, 70 h)	N.A.
7	with	with	-50 °C	75% (70 h)	90%
8[a]	no	with	-50 °C	0% (no reaction, 70 h)	N.A.
9[b]	with	with	-50 °C	0% (no reaction, 70 h)	N.A.

[a]**HE-3** instead of **HE-1** was used. [b]The emission wavelengths are from 474 to 505 nm

Note: Product **16** was not detected in any of the reactions. The results in entry 7 can also be found in Table 2.

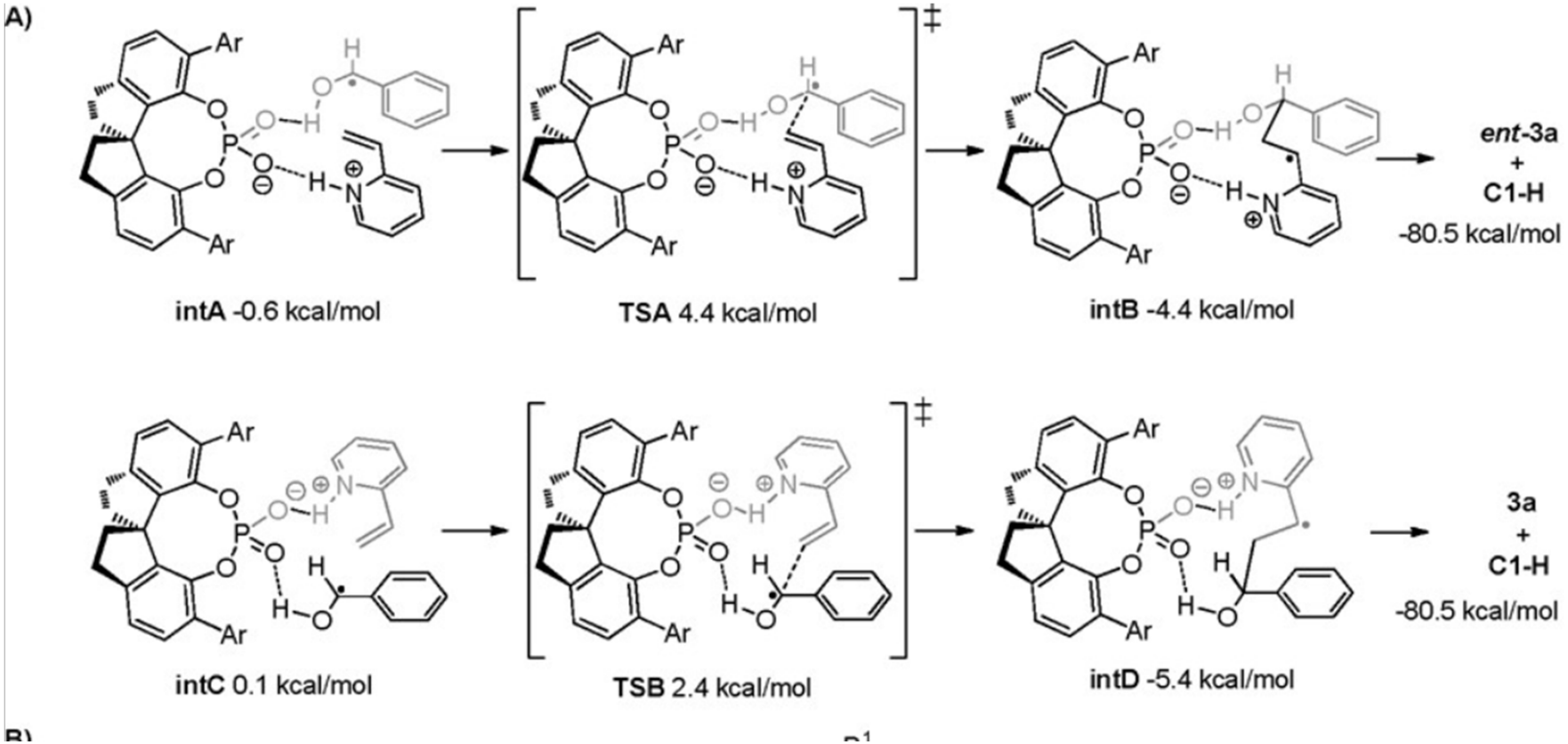
C) Transformation of 1a with HE-1



1a (0.1 mmol)

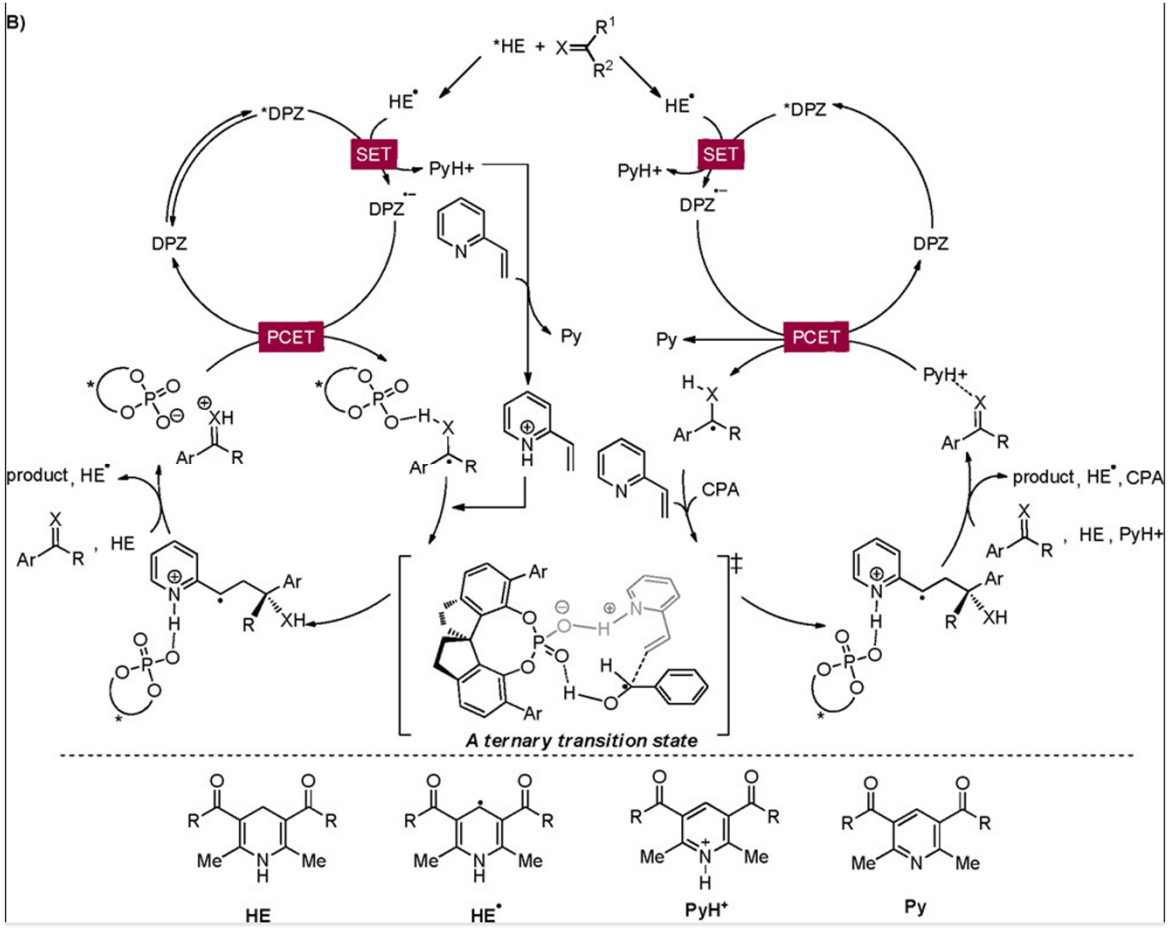
J. Am. Chem. Soc., **2019**, *141*, 5437.

吡啶γ-位手性中心的构建



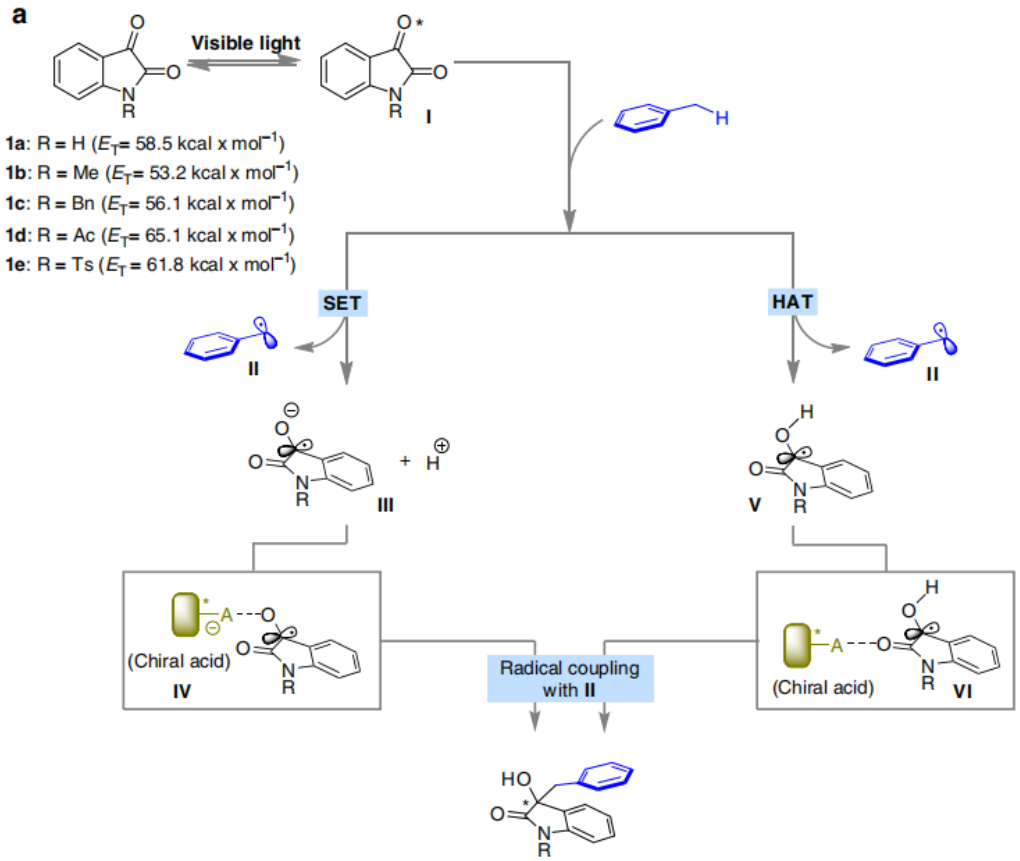
J. Am. Chem. Soc., **2019**, *141*, 5437.

吡啶γ-位手性中心的构建



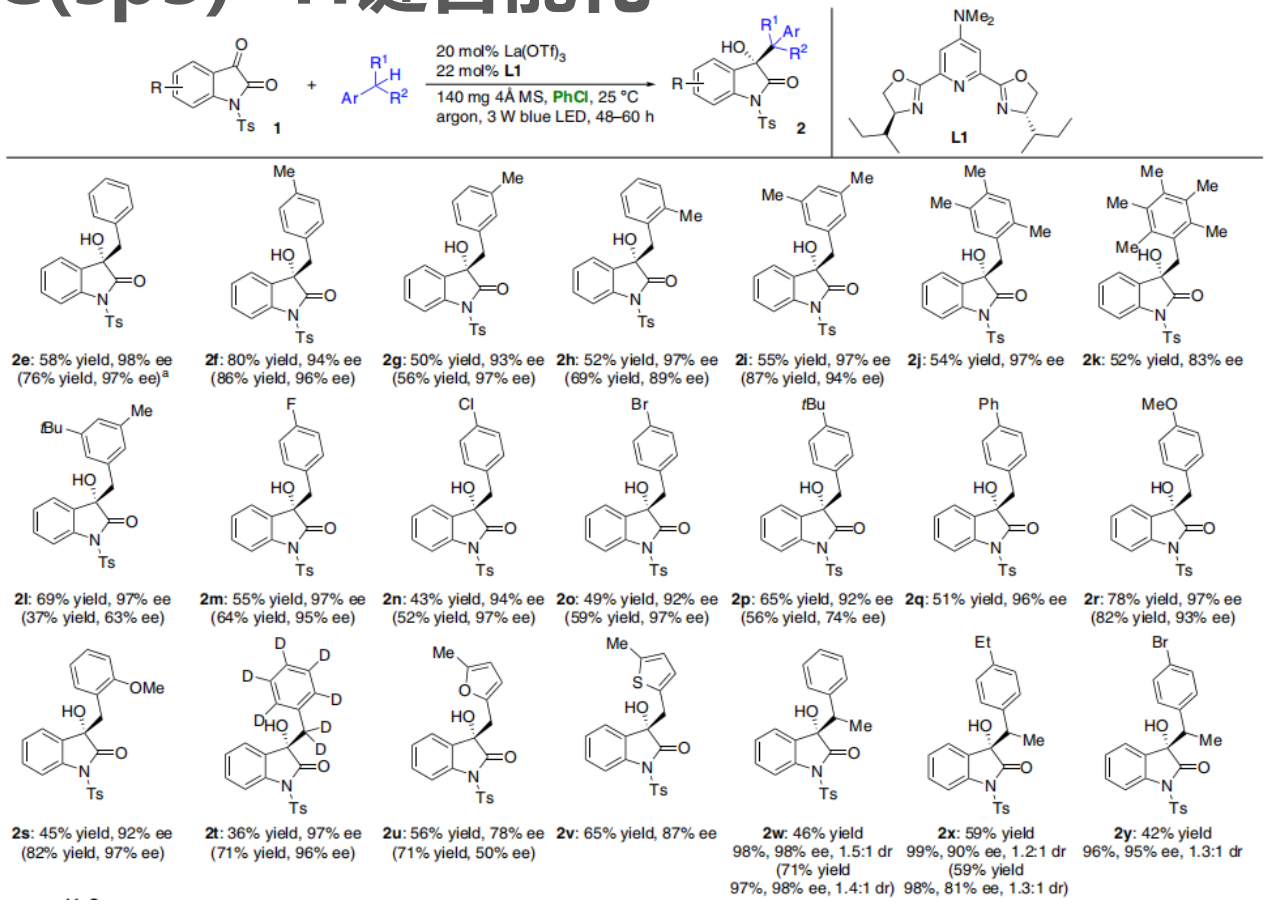
J. Am. Chem. Soc., **2019**, *141*, 5437.

可见光驱动手性酸催化甲苯及其衍生物的不对称C(sp3)–H键官能化



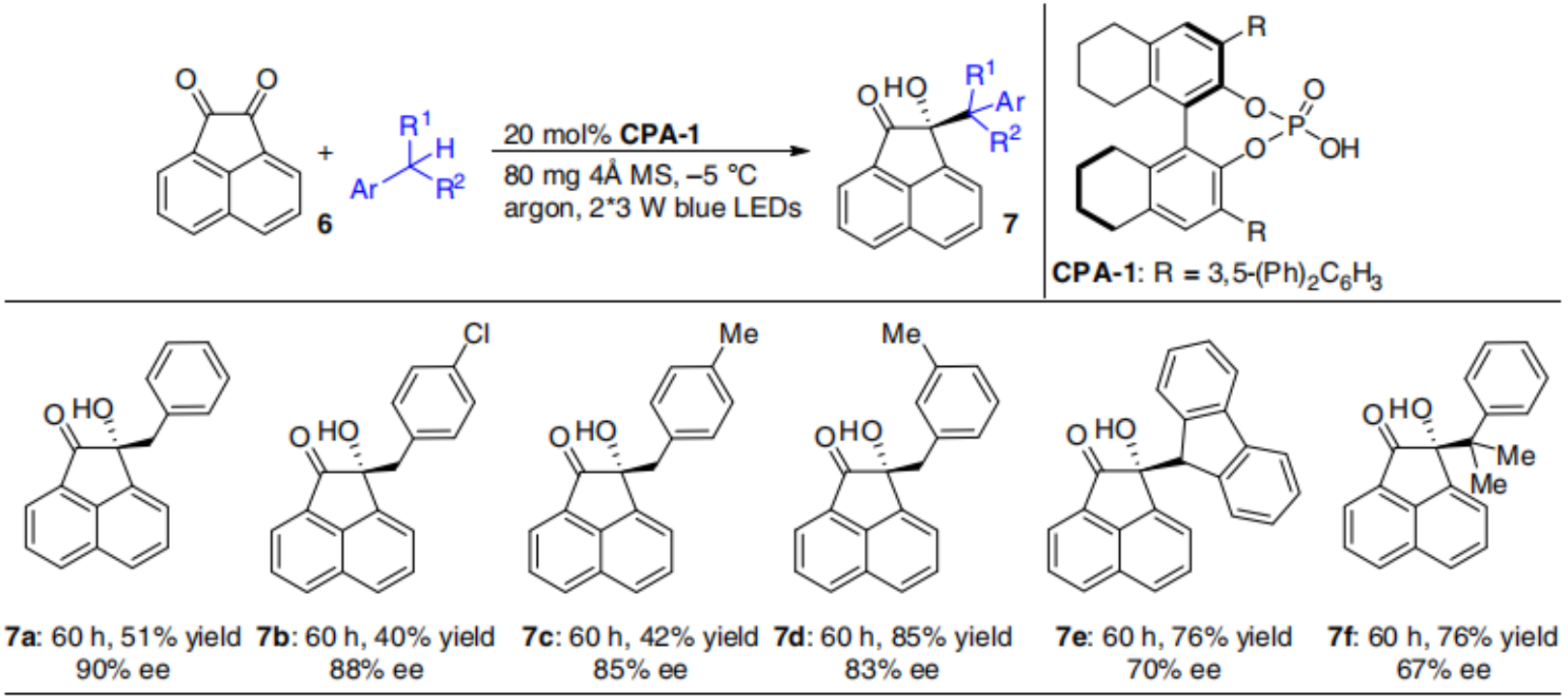
Nat. Commun., **2019**, *10*, 1774.

可见光驱动手性酸催化甲苯及其衍生物的不对称C(sp3)–H键官能化



Nat. Commun., **2019**, *10*, 1774.

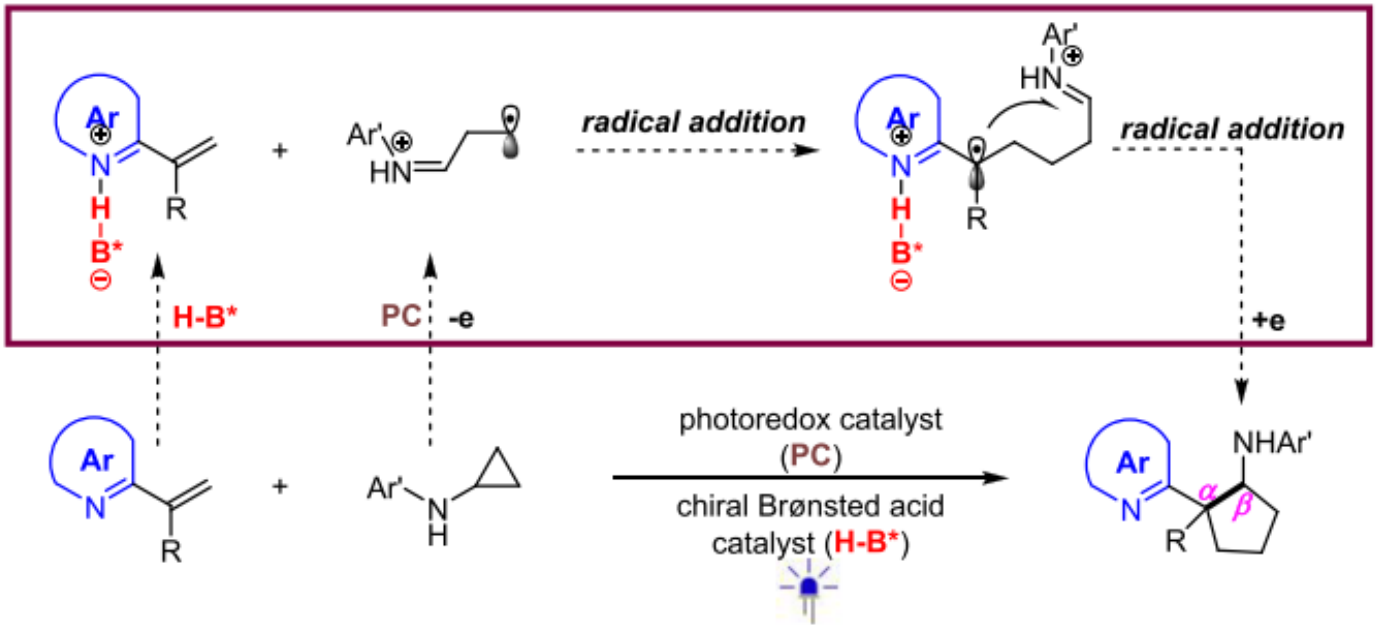
可见光驱动手性酸催化甲苯及其衍生物的不对称C(sp3)–H键官能化



Nat. Commun., **2019**, *10*, 1774.

含季碳手性中心的氮杂芳烃的构建

b) Design plan: Radical-based olefin difunctionalization

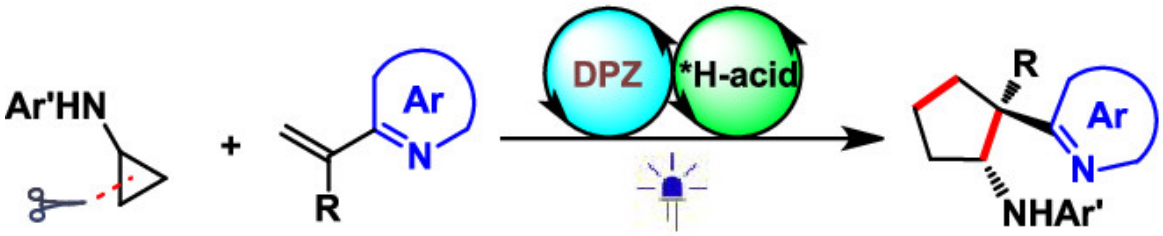


挑战：化学选择性，α-氮杂芳烃自由基具有氧化剂的作用

构型，氢键作用 VS 自由基加成

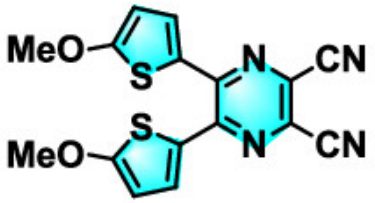
J. Am. Chem. Soc. **2020**, *142*, 19451.

含季碳手性中心的氮杂芳烃的构建

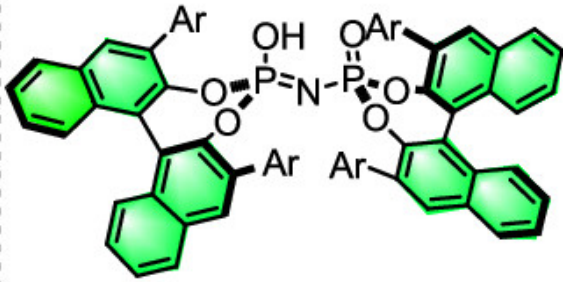


- All-Carbon quaternary stereocenter
- Azaarene-substituted cyclopentanes
- Radical-based olefin difunctionalization
- Straightforward
- Redox neutral
- Broad substrate scope

46 examples
up to >99% yield
up to 96% ee
up to >19:1 dr



DPZ



*H-acid

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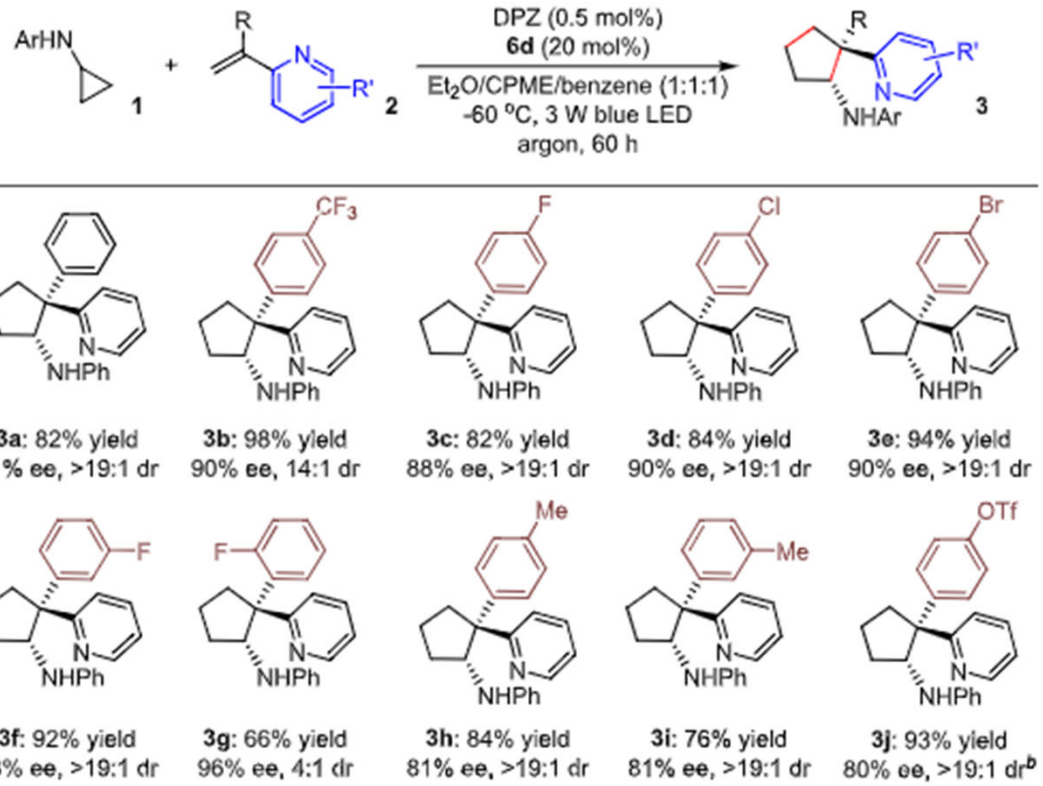

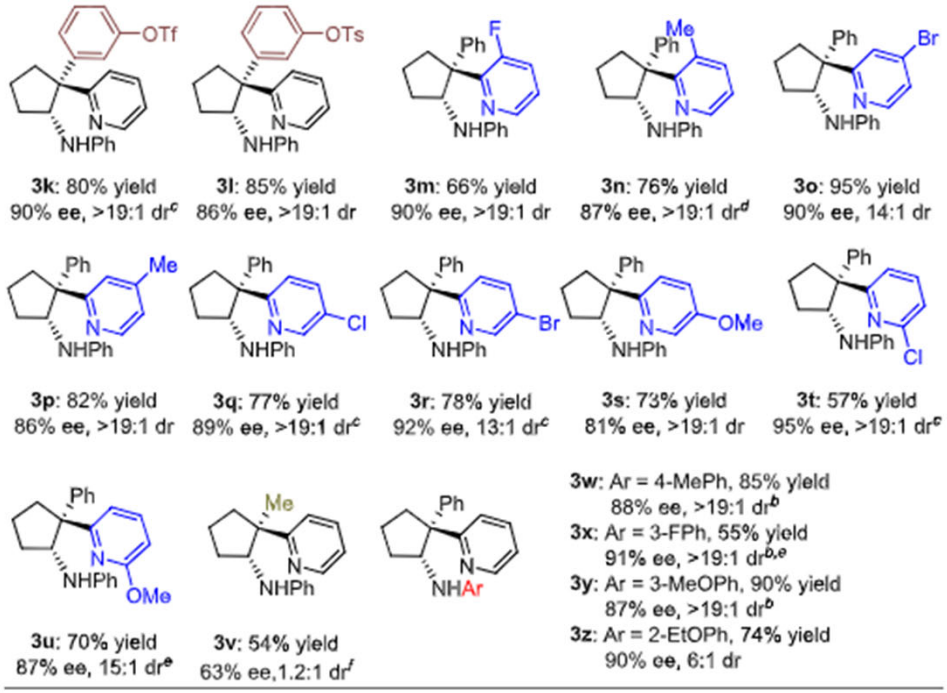

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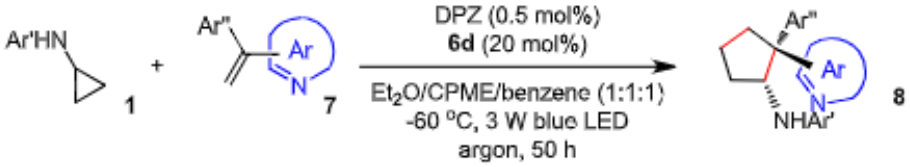
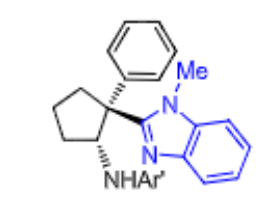


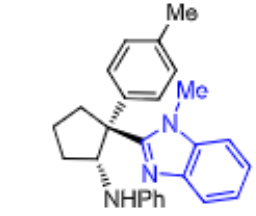


8a: Ar' = Ph, 87% yield
93% ee, >19:1 dr[b]
8b: Ar' = 3-MeOPh, >99% yield, 91% ee, >19:1 dr

8c: X = Cl, >99% yield
91% ee, >19:1 dr
8d: X = Br, 82% yield
90% ee, >19:1 dr

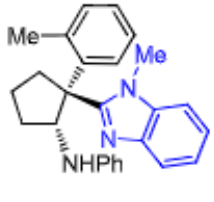
8e: X = F, 92% yield
92% ee, >19:1 dr
8f: X = Cl, >99% yield
91% ee, >19:1 dr

8g: 70% yield
96% ee, >19:1 dr

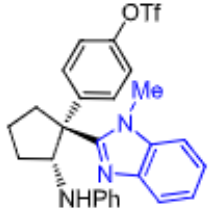


8h: 95% yield
82% ee, >19:1 dr

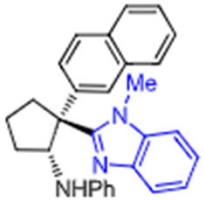
8i: 95% yield
88% ee, >19:1 dr[c]



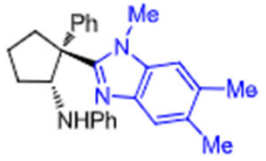
8j: 86% yield
91% ee, >19:1 dr[d]



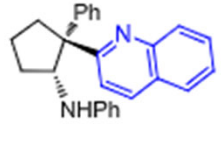
8k: 62% yield
81% ee, >19:1 dr[e]



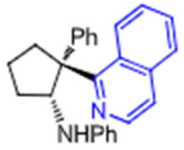
8l: 80% yield
77% ee, >19:1 dr



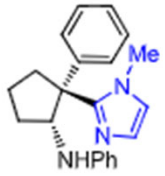
8m: 90% yield
93% ee, >19:1 dr



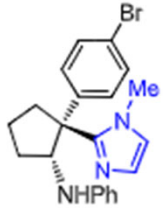
8n: 77% yield
87% ee, >19:1 dr



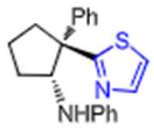
8o: 81% yield
80% ee, >19:1 dr[f]



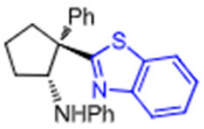
8p: 80% yield
91% ee, >19:1 dr[d]



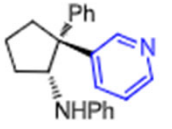
8q: 82% yield
90% ee, >19:1 dr[d]



8r: 70% yield
92% ee, >19:1 dr[g]



8s: 82% yield
94% ee, >19:1 dr[g]



8t: 83% yield
91% and 92% ee
1.5:1 dr[h]

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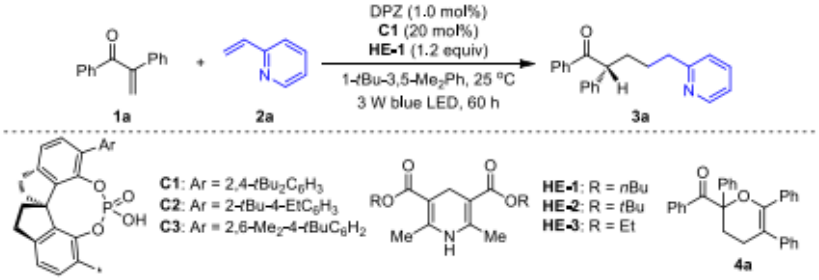
烯烃还原交叉偶联引发的对映选择性质子化反应



entry	variation from the standard conditions	yield[b] (%)	ee[c] (%)
1	none	73	90
2	**C2** instead of **C1**	51	52
3	**C3** instead of **C1**	trace	N.A.[d]
4	**HE-2** instead of **HE-1**	63	86
5	**HE-3** instead of **HE-1**	60	88
6	iPr$_2$NEt instead of **HE-1**	N.R.[e]	N.A.
7	[Ir(ppy)$_2$(dtbbpy)]PF$_6$ instead of DPZ	41	57
8	eosin Y instead of DPZ	29	88
9	no **C1**	N.R.	N.A.
10	no DPZ	0[f]	N.A.
11	no light	N.R.	N.A.
12	air	0[f]	N.A.

J. Am. Chem. Soc. **2021**, *143*, 4024.

烯烃还原交叉偶联引发的对映选择性质子化反应

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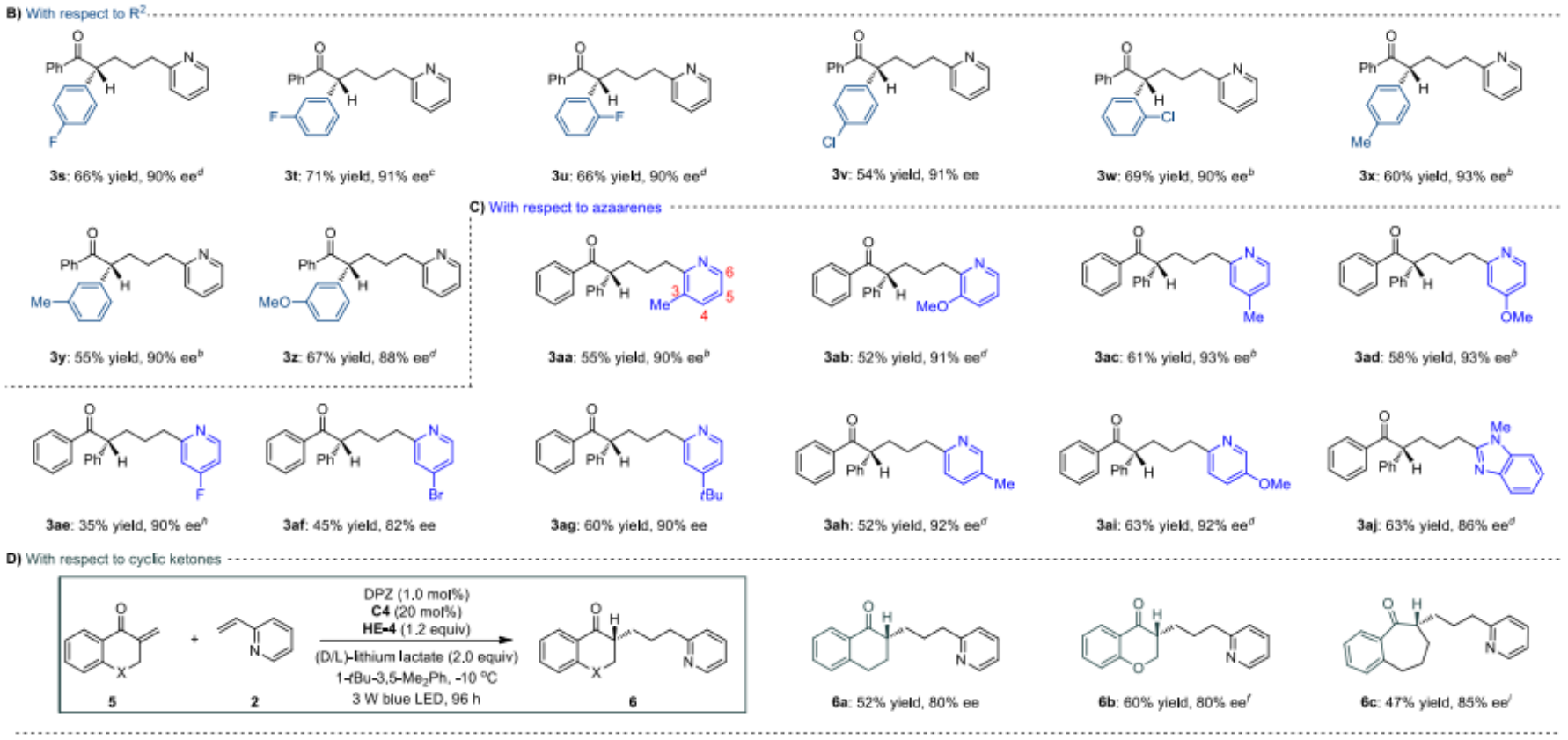

J. Am. Chem. Soc. **2021**, *143*, 4024.

烯烃还原交叉偶联引发的对映选择性质子化反应

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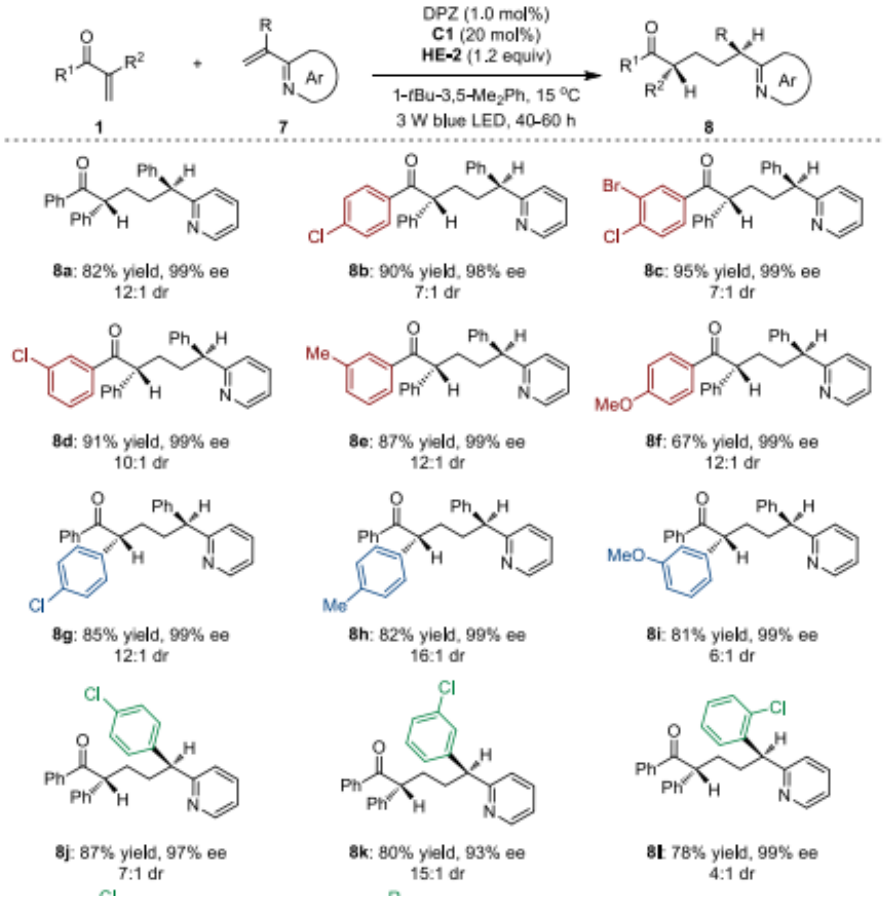

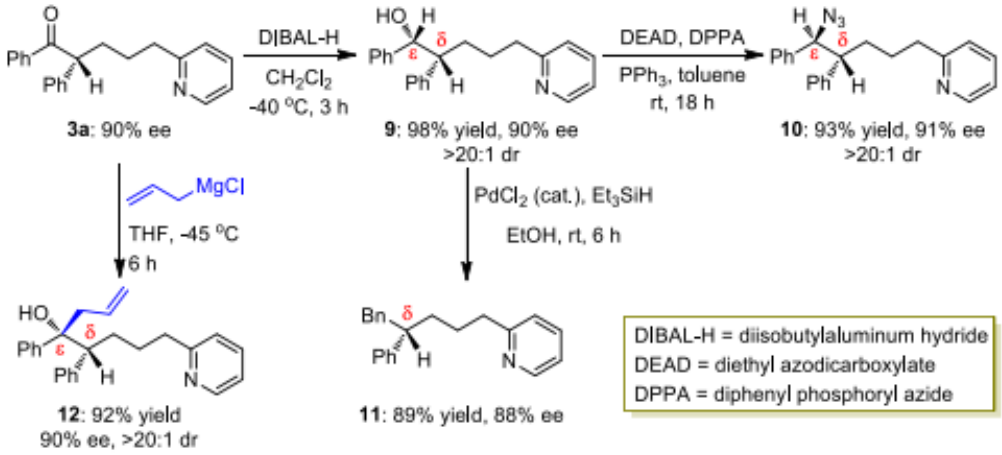

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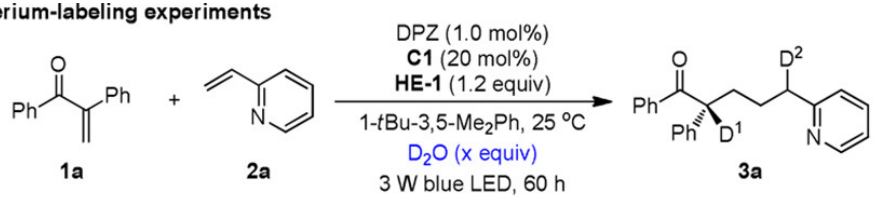
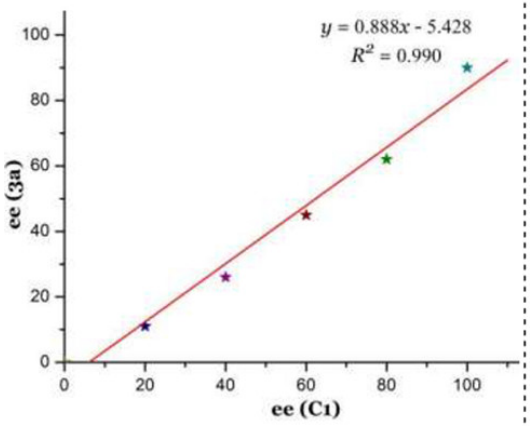
A) Deuterium-labeling experiments

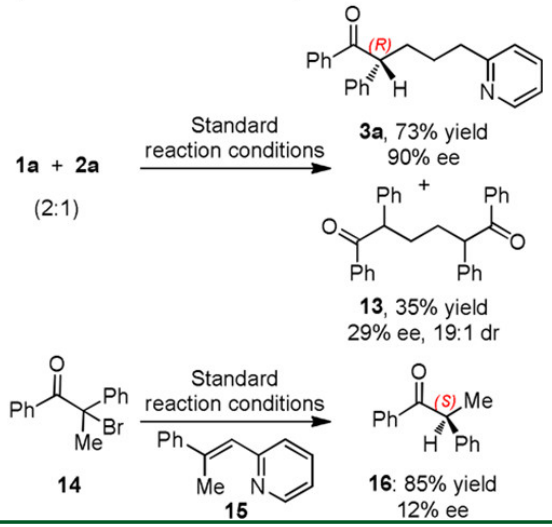


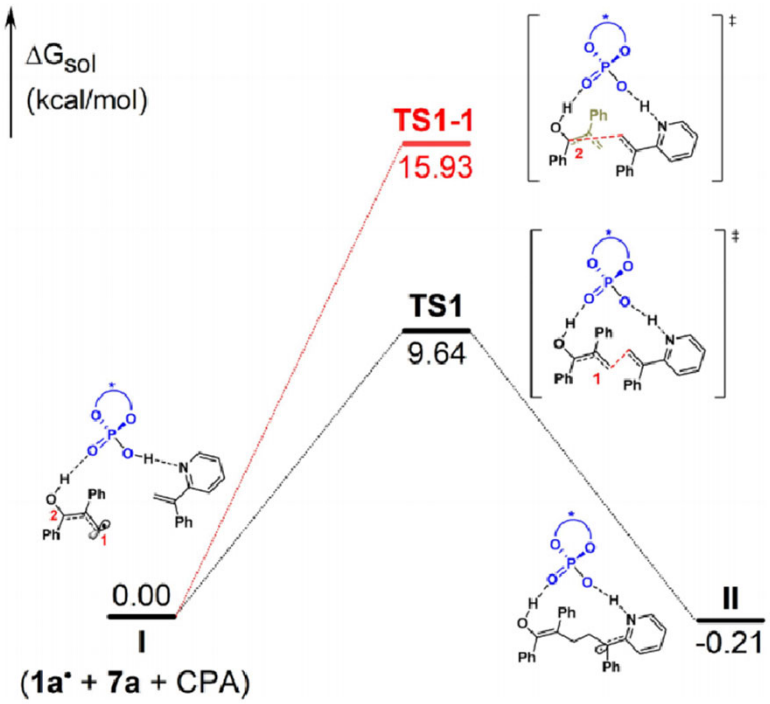
reductant	equiv of D_2O	yield of **3a** (%)	ee of **3a** (%)	D^1 (%)	D^2 (%)
HE-1	25	36	76	51	0
HE-1	250	29	70	88	0
4,4-D_2-**HE-1**	0	70	90	0	95

B) Relationship between ee values of C1 and 3a



C) Reductive debrominative protonation





自由基加成过程的吉布斯自由能谱

J. Am. Chem. Soc. **2021**, *143*, 4024.

烯烃还原交叉偶联引发的对映选择性质子化反应

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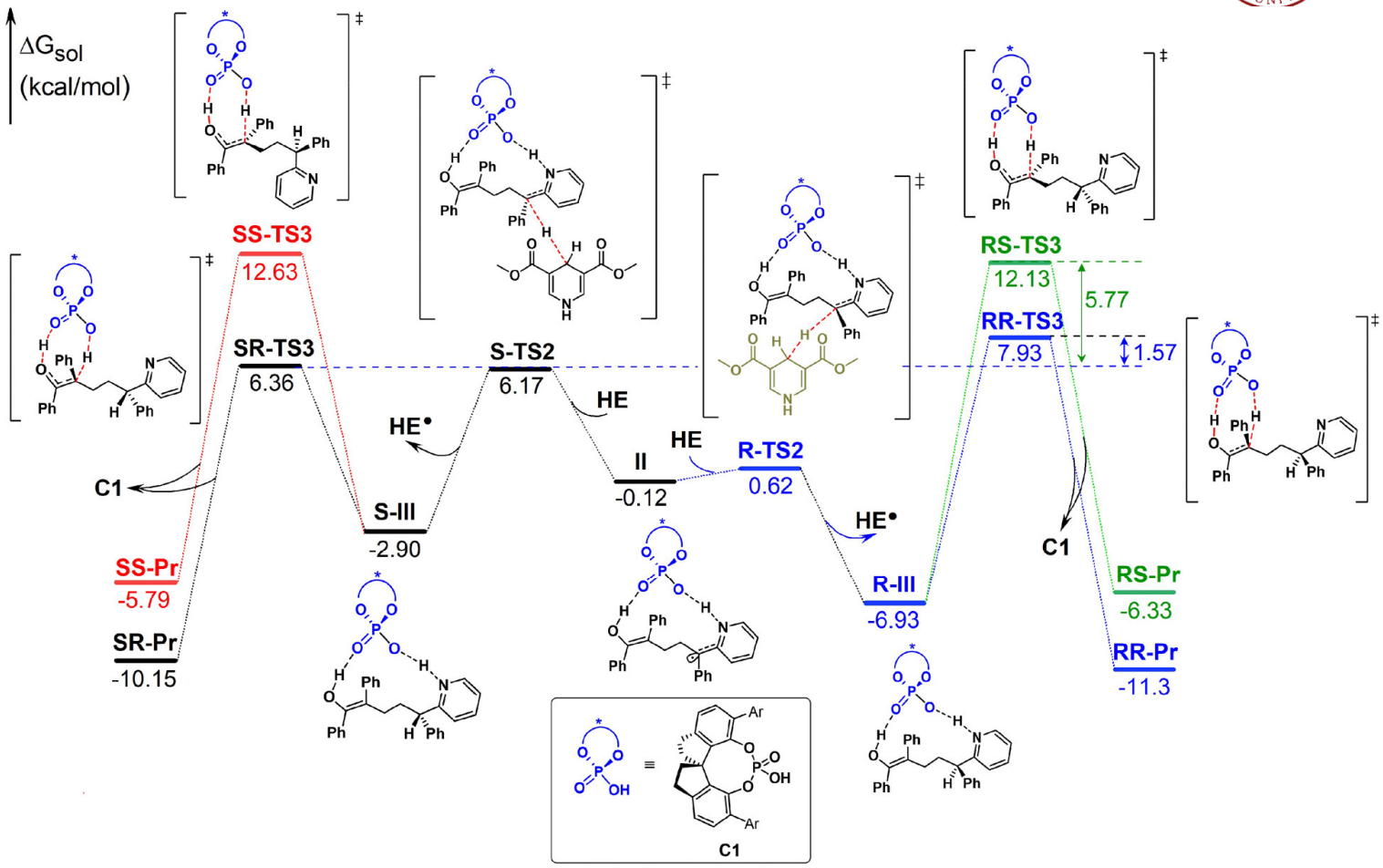

J. Am. Chem. Soc. **2021**, *143*, 4024.

烯烃还原交叉偶联引发的对映选择性质子化反应

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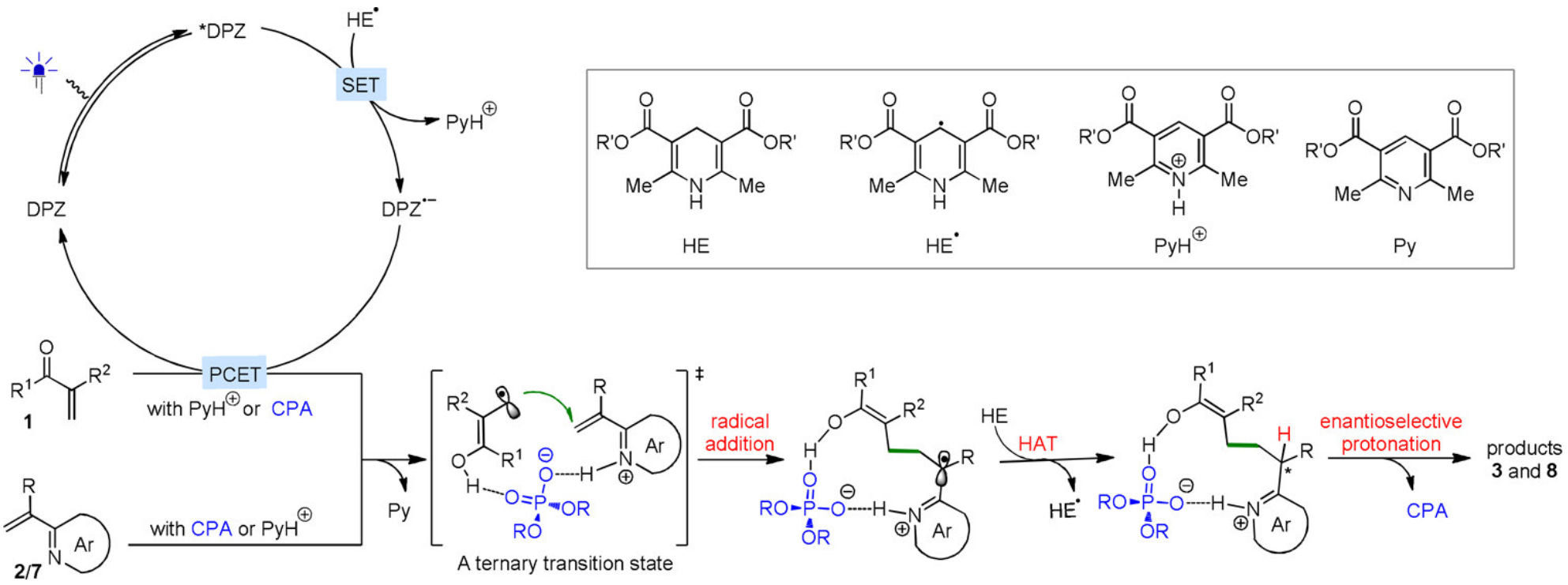
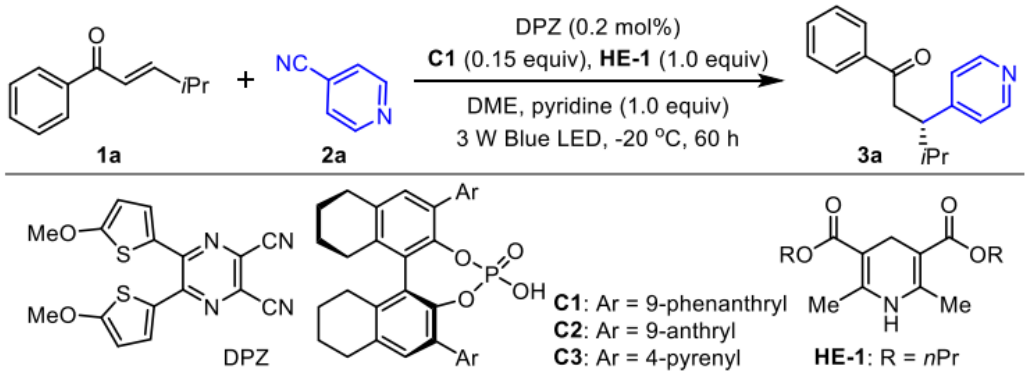


J. Am. Chem. Soc. **2021**, *143*, 4024.

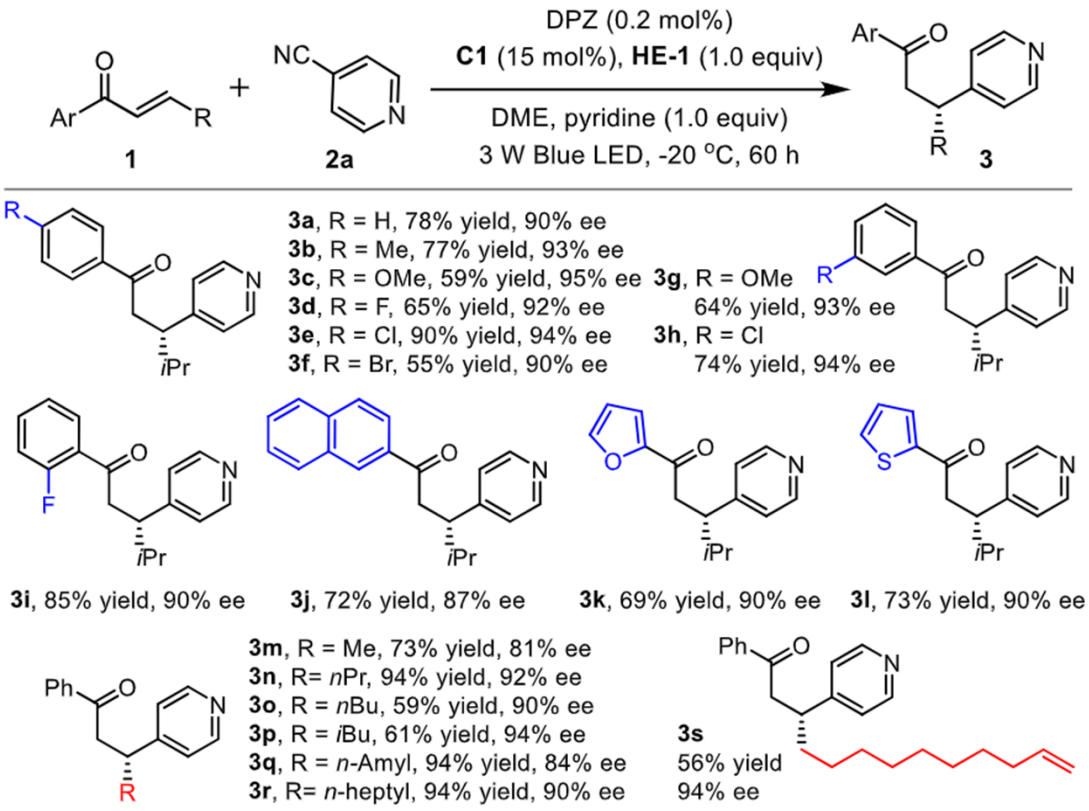
烯烃不对称还原氮芳基化反应

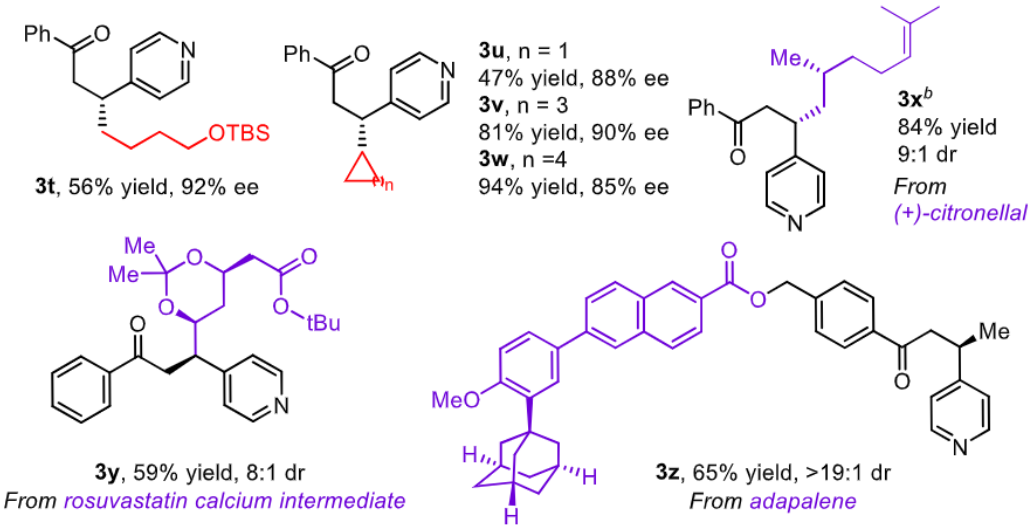


entry	alteration to conditions	yield (%)[b]	ee (%)[c]
1	None	78	90
2	**C2** instead of **C1**	52	43
3	**C3** instead of **C1**	57	63
4	Et_3N instead of **HE-1**	42	0
5	$[Ru(bpy)_3]Cl_2$ instead of DPZ	38	73
6	Ir^{III} instead of DPZ	93	9
7	3DPAFIPN instead of DPZ	84	2
8	no DPZ	13	91
9	no pyridine	28	91
10	no **C1**	91	N.A.
11	no **HE-1**	N.R.	N.A.
12	no light	N.R.	N.A.
13	under air	N.R.	N.A.

J. Am. Chem. Soc. **2022**, *144*, 7805.

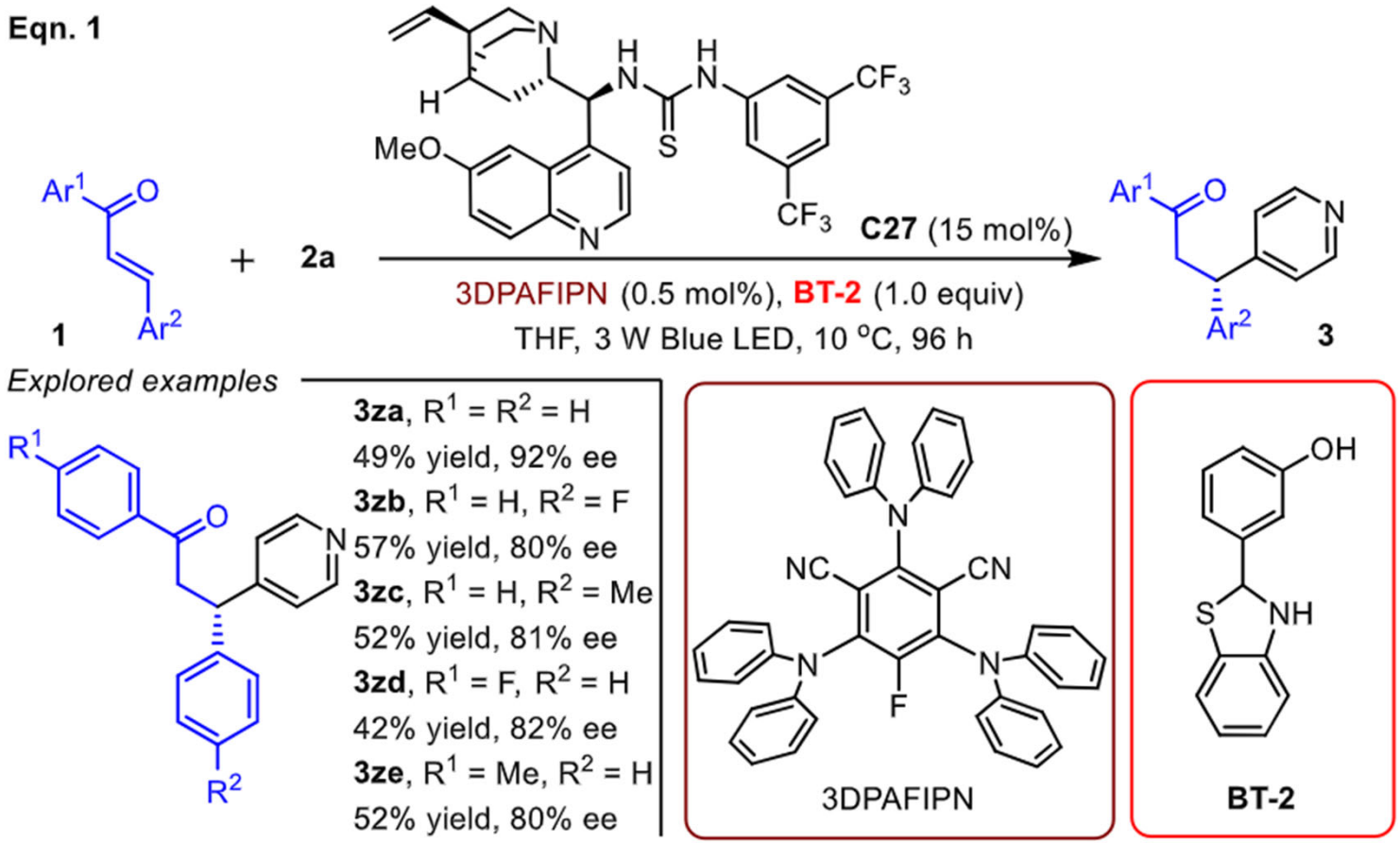
烯烃不对称还原氮芳基化反应





J. Am. Chem. Soc. **2022**, *144*, 7805.

烯烃不对称还原氮芳基化反应



J. Am. Chem. Soc. **2022**, *144*, 7805.

烯烃不对称还原氮芳基化反应

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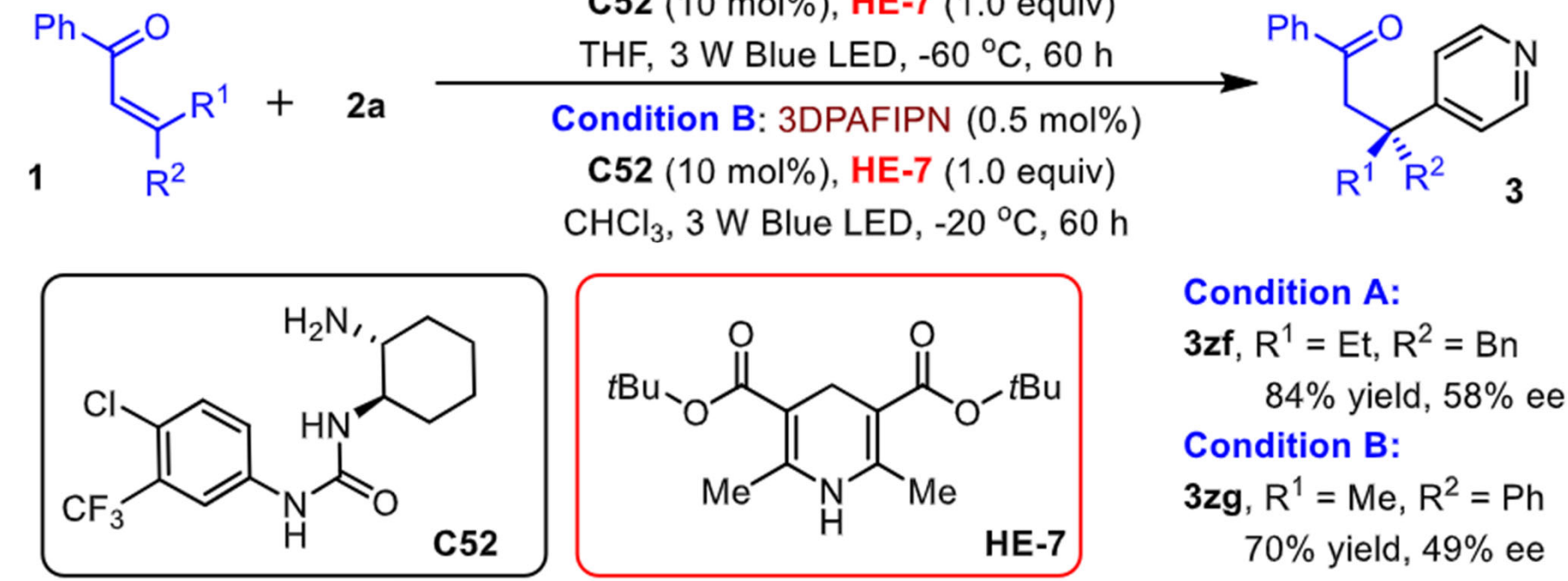
Eqn. 2



Condition A:

3zf, R^1 = Et, R^2 = Bn

84% yield, 58% ee

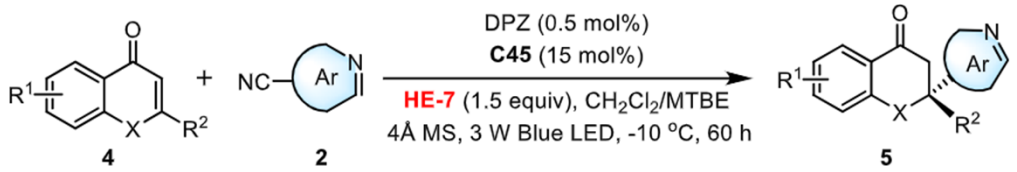
Condition B:

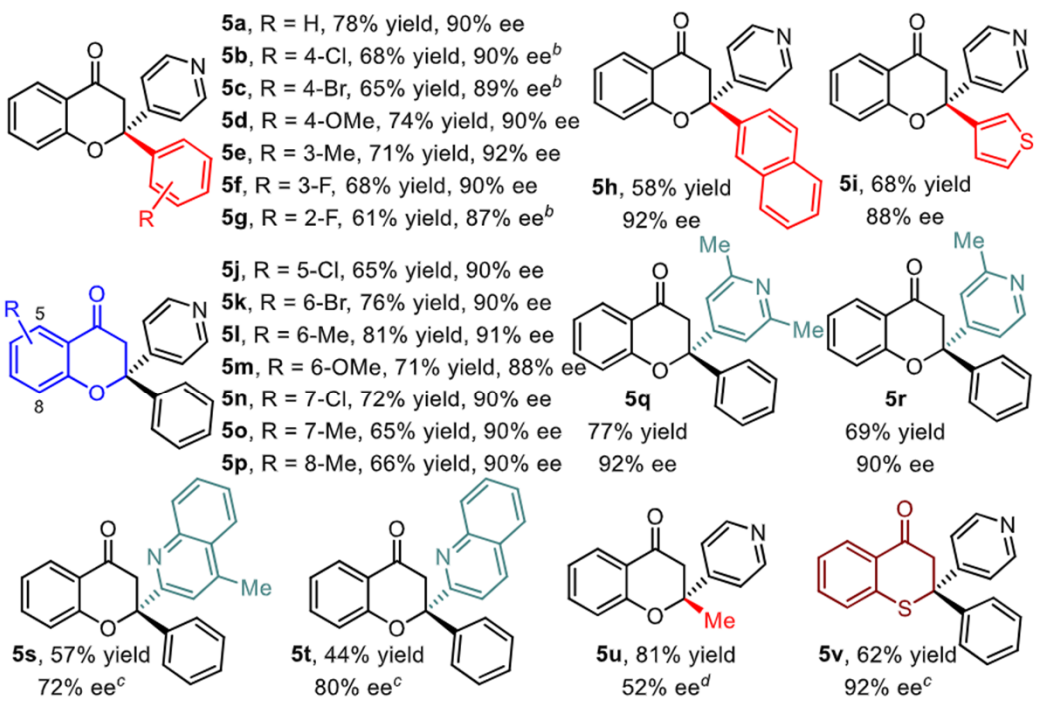
3zg, R^1 = Me, R^2 = Ph

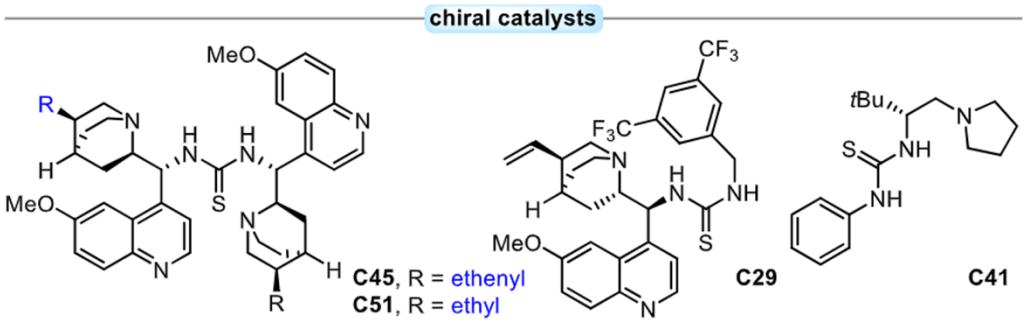
70% yield, 49% ee

J. Am. Chem. Soc. **2022**, *144*, 7805.

烯烃不对称还原氮芳基化反应



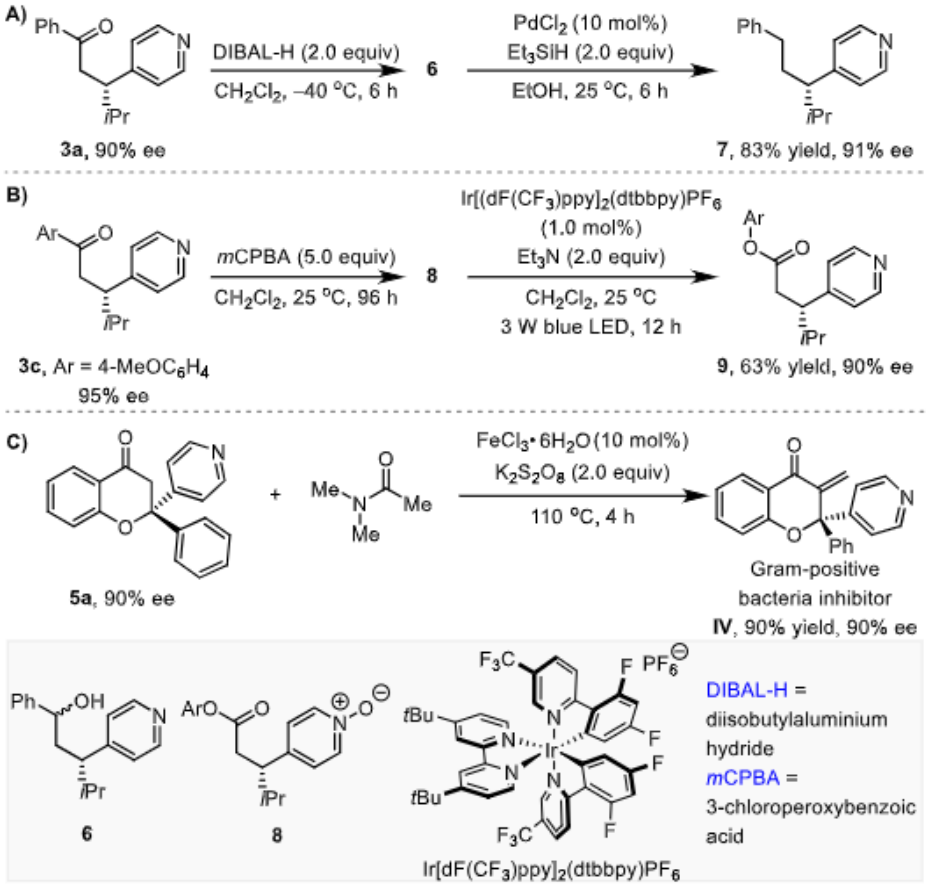




[a]The reaction was performed on a 0.10 mmol scale. See the Supporting Information for the detailed reaction conditions. [b]C51 instead of C45 wasused. [c]C29 instead of C45 was used. [d]C41 instead of C45 was used

J. Am. Chem. Soc. **2022**, *144*, 7805.

烯烃不对称还原氮芳基化反应



J. Am. Chem. Soc. **2022**, *144*, 7805.

烯烃不对称还原氮芳基化反应

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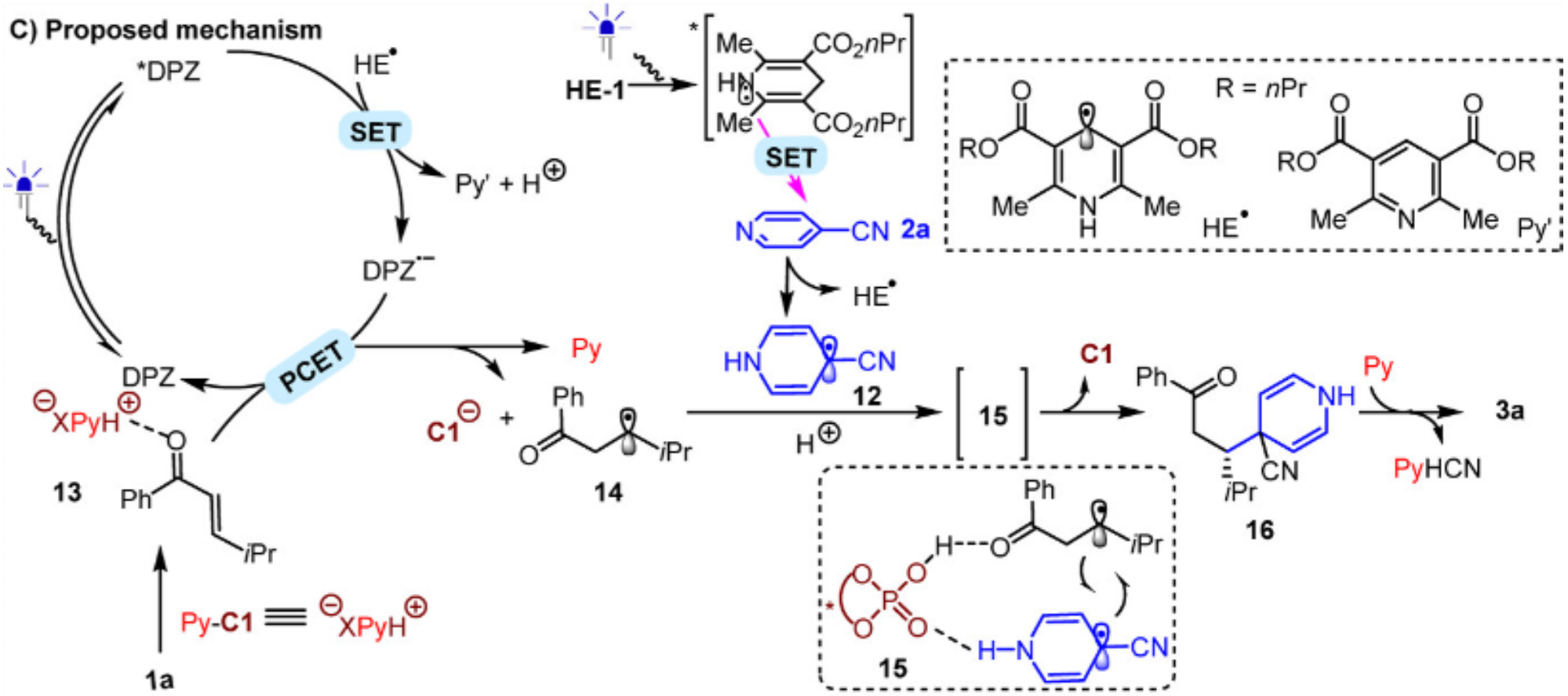
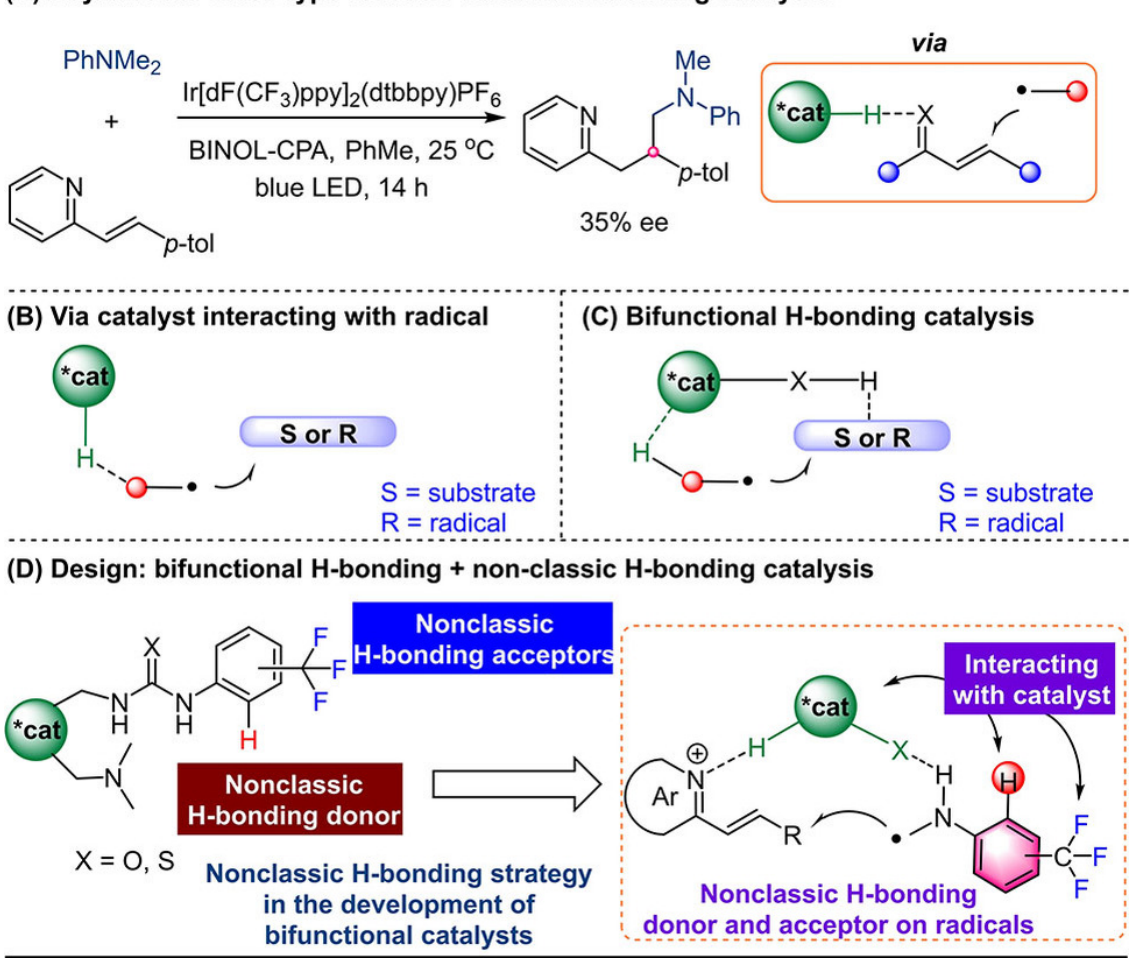


同舟共济

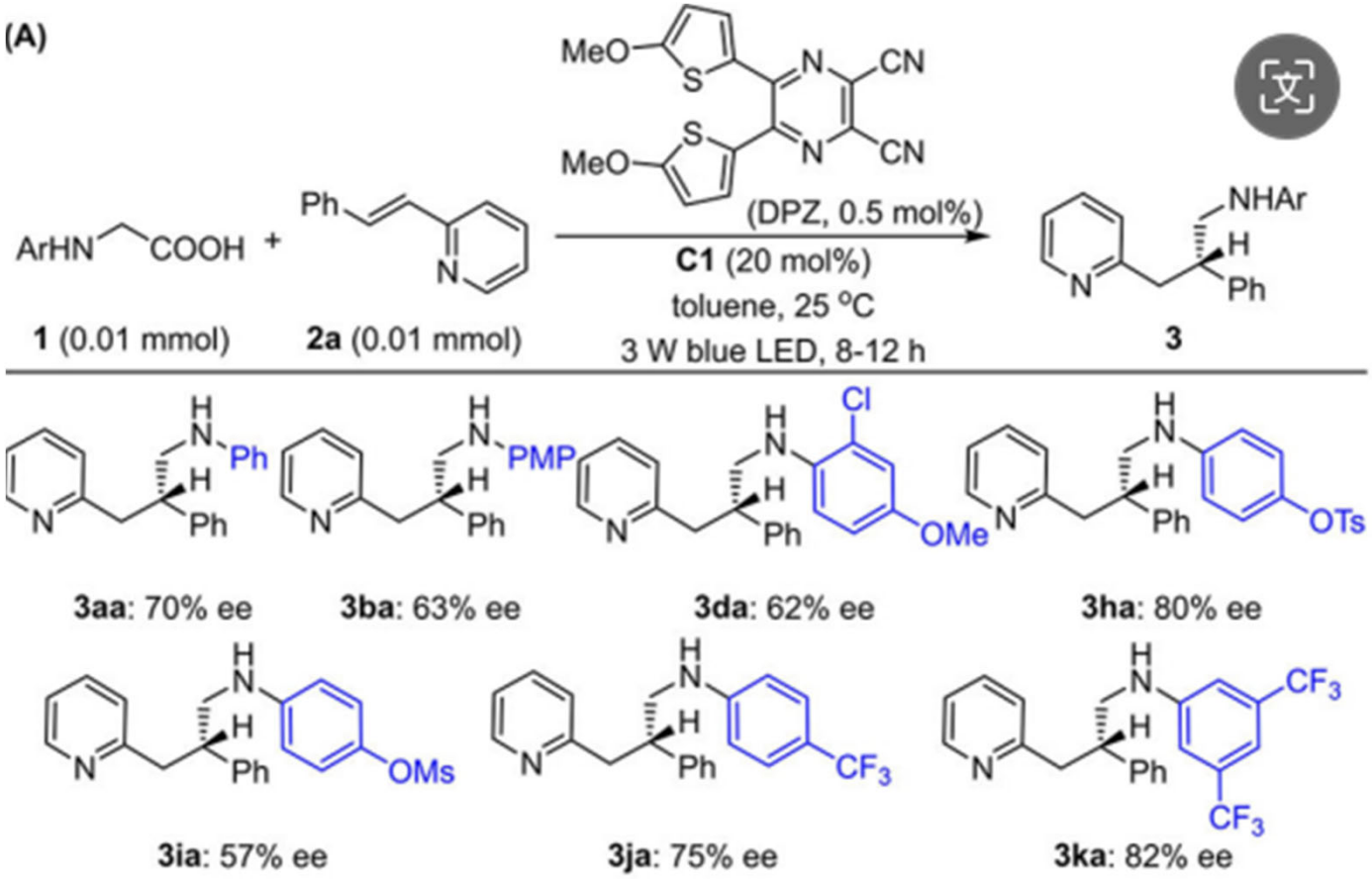
J. Am. Chem. Soc. **2022**, *144*, 7805.

烯基氮杂芳烃的不对称氢氨基烷基化反应



Chem. Commun. **2016**, *52*,3520; , *J. Am. Chem. Soc.* **2013**, *135*, 17735.

烯基氮杂芳烃的不对称氢氨基烷基化反应



Angew. Chem. Int. Ed. **2022**, *61*, e202115110

烯基氮杂芳烃的不对称氢氨基烷基化反应

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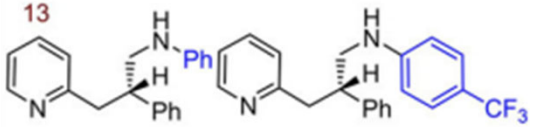
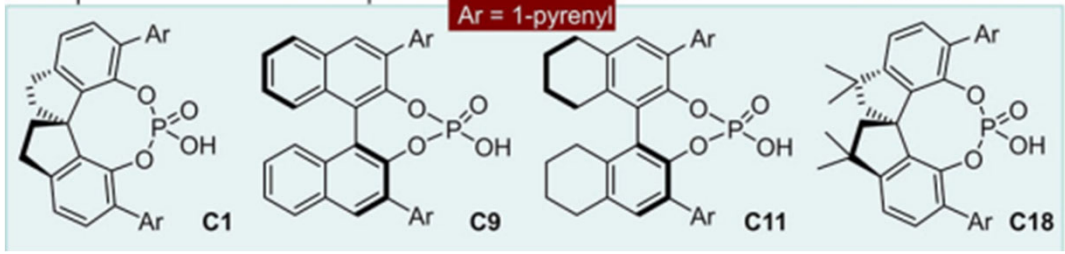
(B)

Entry	Variation from the standard conditions	Yield [%]	Ee [%]	Entry	Variation from the standard conditions	Yield [%]	Ee [%]
1	none	71	93	9	no DPZ	55	93
2	**C9** instead of **C1**	54	-25	10	no DPZ and **C1**	trace	--
3	**C11** instead of **C1**	51	-29	11	no light	N.R.	--
4	**C18** instead of **C1**	28	50	12	under air	trace	--
5	$Ir(bpy)_3$ instead of DPZ	60	87	13			
6	$Ru(bpy)_3$ instead of DPZ	41	90				
7	no anthracene	64	83				
8	no **C1**	74	--				

3aa: 19% yield
70% ee

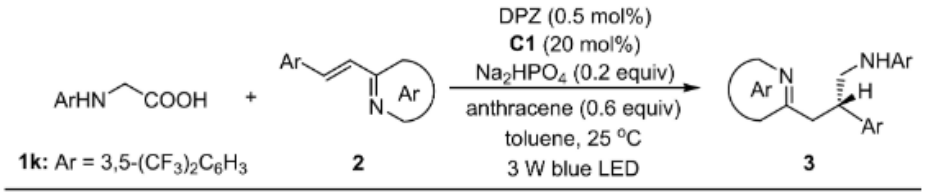
3ja: 87% yield
75% ee

Ar = 1-pyrenyl

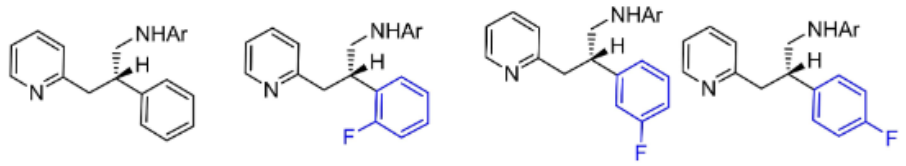


Angew. Chem. Int. Ed. **2022**, *61*, e202115110

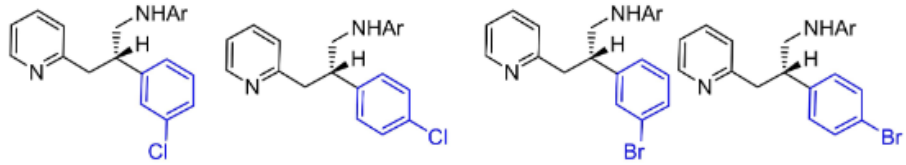
烯基氮杂芳烃的不对称氢氨基烷基化反应



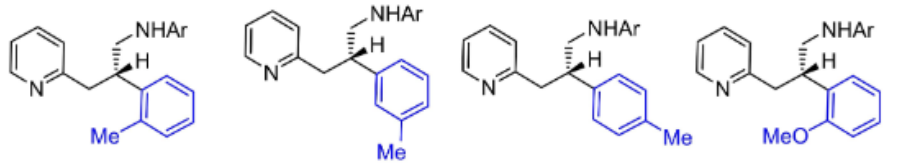
1k: Ar = 3,5-$(CF_3)_2C_6H_3$ **2** **3**



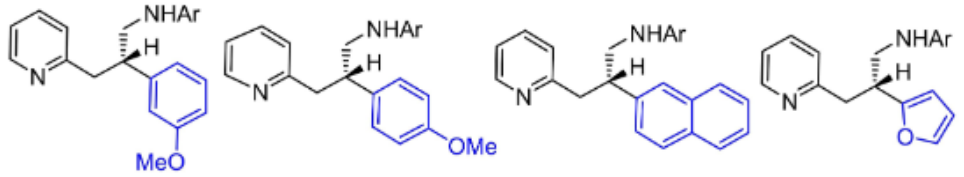
3ka: 48 h, 68% yield, 93% ee[b] **3kb**: 60 h, 59% yield, 92% ee **3kc**: 60 h, 50% yield, 91% ee **3kd**: 60 h, 77% yield, 94% ee



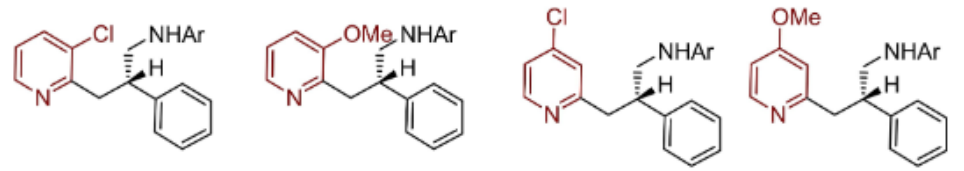
3ke: 60 h, 60% yield, 94% ee **3kf**: 60 h, 81% yield, 90% ee **3kg**: 60 h, 57% yield, 94% ee **3kh**: 60 h, 73% yield, 94% ee



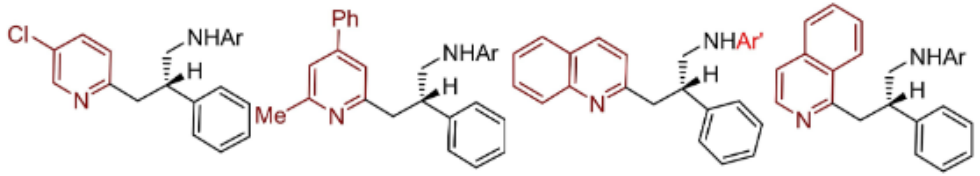
3ki: 23 h, 72% yield, 90% ee **3kj**: 23 h, 57% yield, 90% ee **3kk**: 60 h, 57% yield, 90% ee **3kl**: 23 h, 65% yield, 90% ee



3km: 23 h, 53% yield, 91% ee **3kn**: 60 h, 53% yield, 98% ee **3ko**: 60 h, 50% yield, 90% ee **3kp**: 60 h, 52% yield, 98% ee



3kq: 60 h, 61% yield, 92% ee **3kr**: 60 h, 67% yield, 86% ee **3ks**: 60 h, 52% yield, 95% ee **3kt**: 60 h, 50% yield, >99% ee



3ku: 23 h, 57% yield, 92% ee **3kv**: 60 h, 58% yield, 96% ee **3jb**: 60 h, 64% yield, 92% ee[c] **3kw**: 60 h, 56% yield, 92% ee[d]

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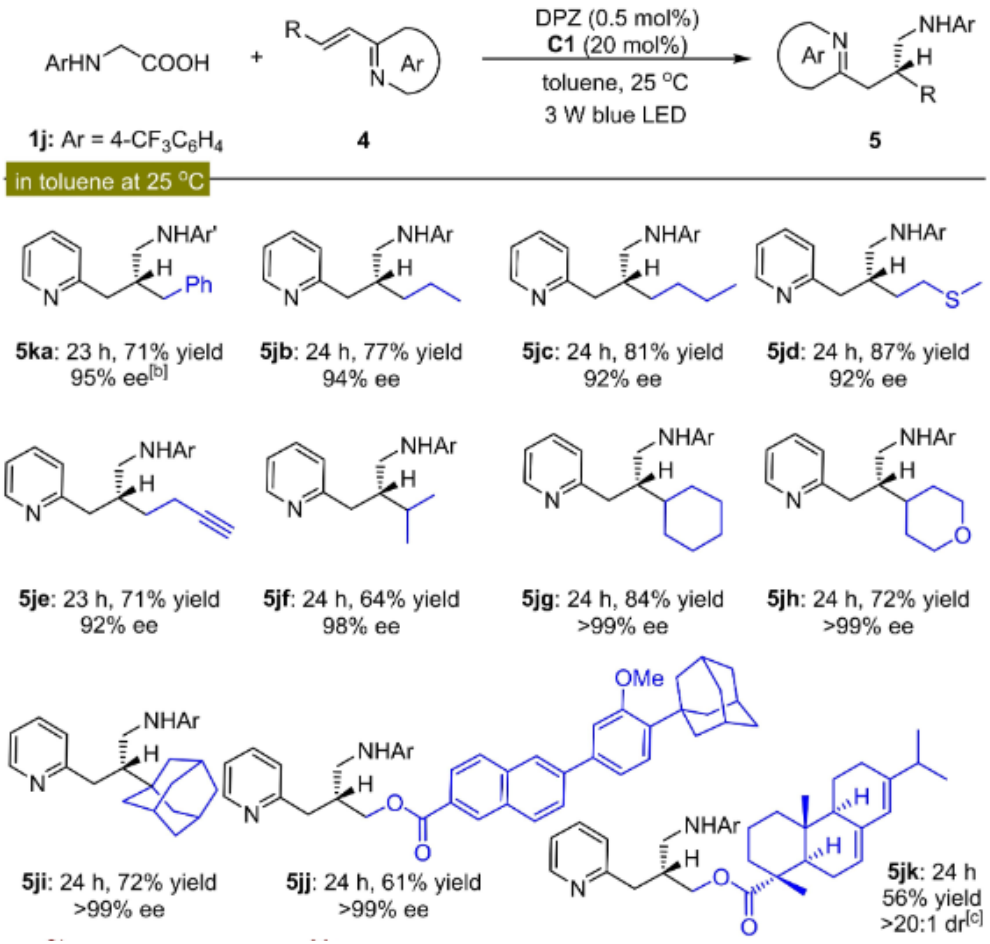
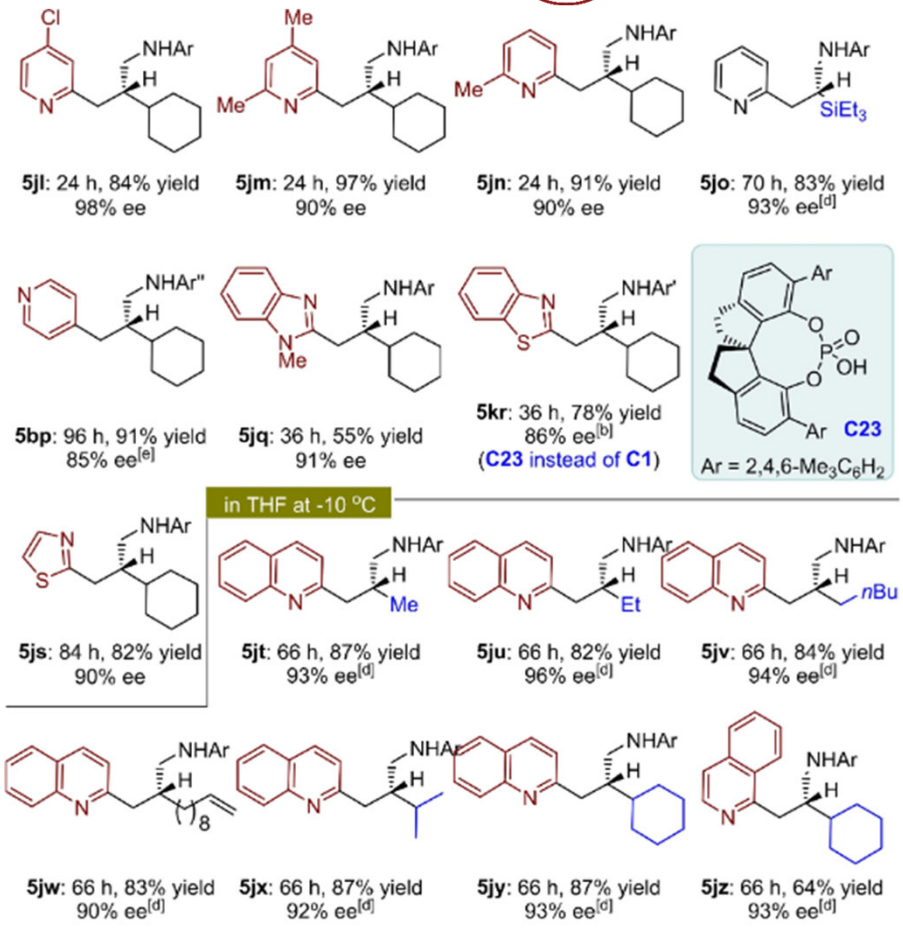
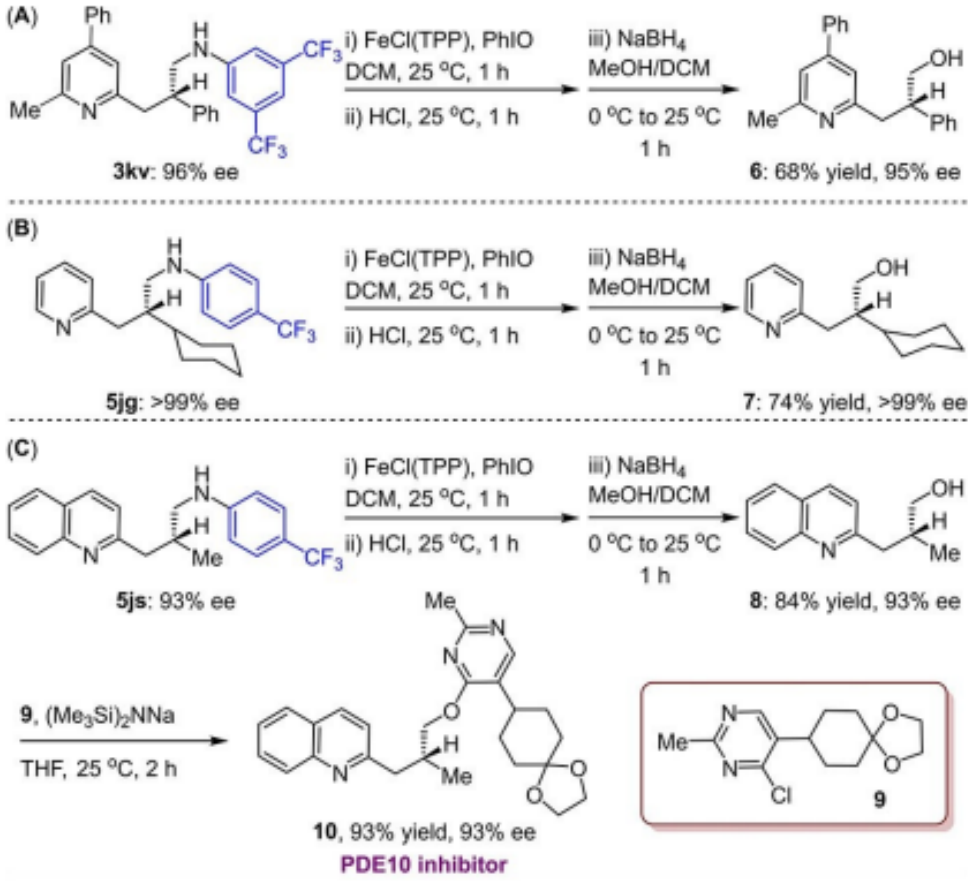
烯基氮杂芳烃的不对称氢氨基烷基化反应





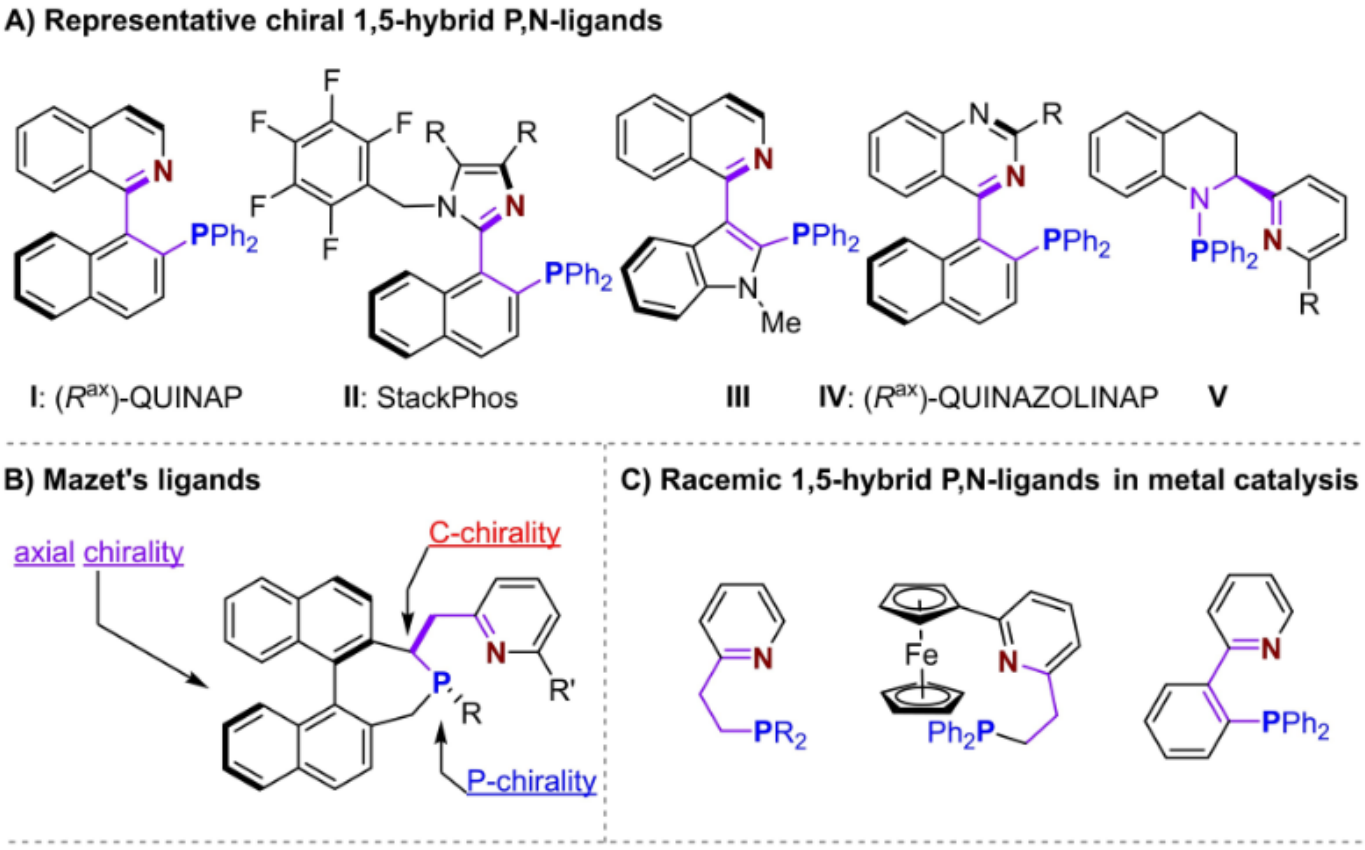
Angew. Chem. Int. Ed. **2022**, *61*, e202115110

烯基氮杂芳烃的不对称氢氨基烷基化反应



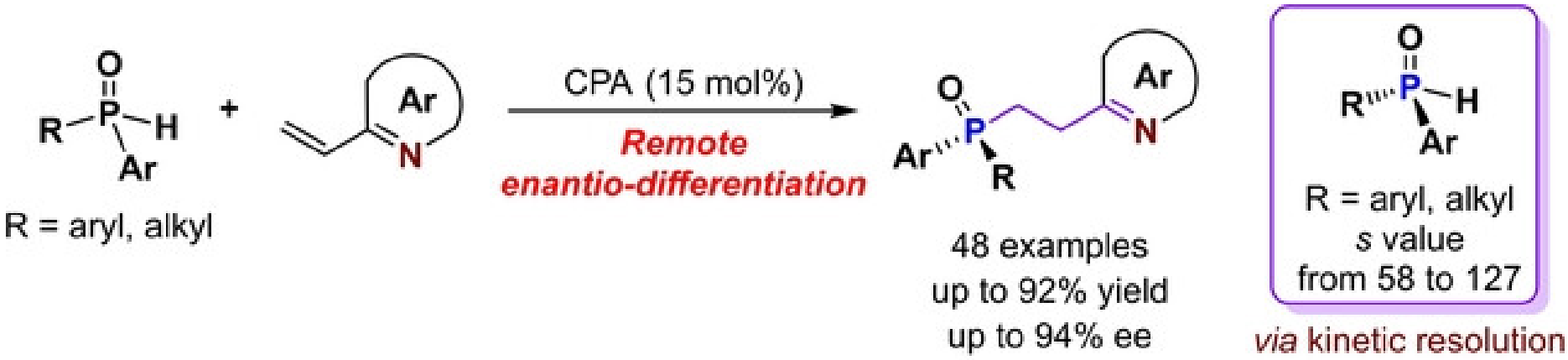
Angew. Chem. Int. Ed. **2022**, *61*, e202115110

不对称氢膦酰化反应



Angew. Chem. Int. Ed. **2023**, *62*, e202216605.

不对称氢膦酰化反应



- ***Readily accessible feedstocks • Easily modulating the types of phosphines and azaarenes***
- ***Demonstrated viability of products as chiral ligands • Metal Free • High yields and ees***
- ***A general kinetic resolution platform to access enantioenriched secondary phosphine oxides***

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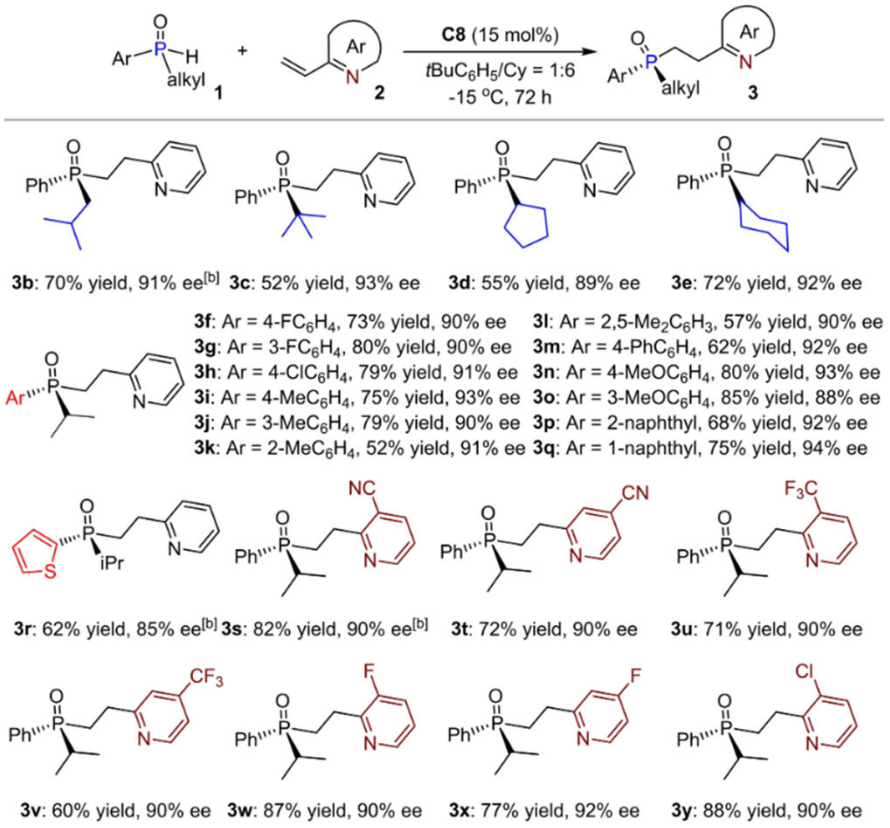
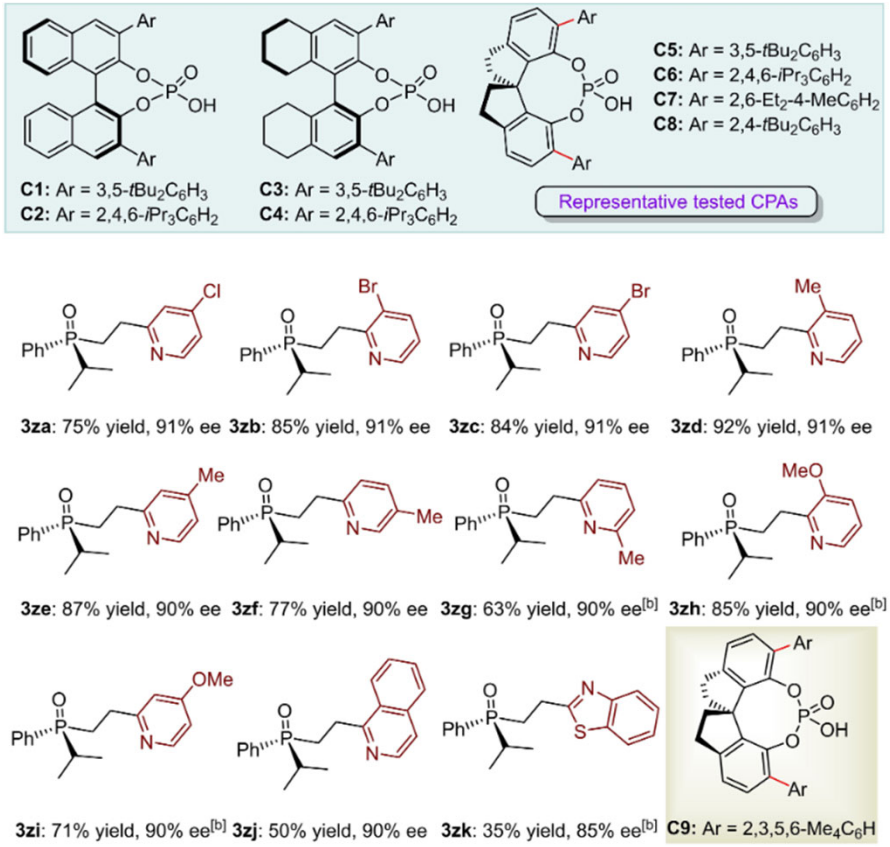
不对称氢膦酰化反应





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不对称氢膦酰化反应

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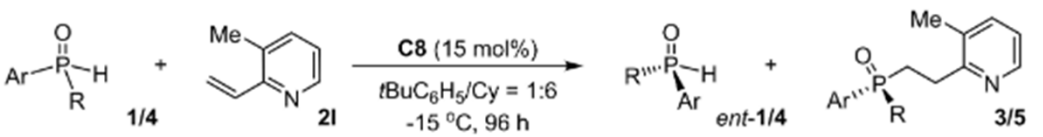
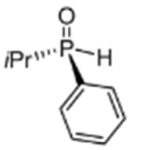
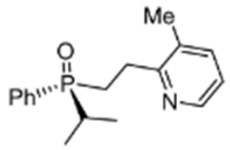
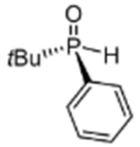




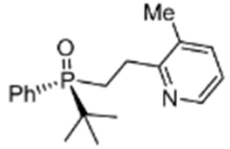
ent-**1a**: 53% yield
90% ee, *s* = 65[b]



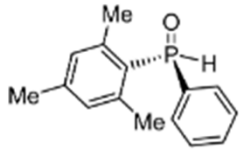
3zd: 41% yield, 90% ee



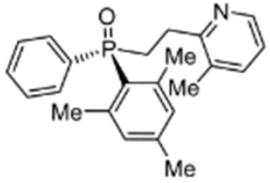
ent-**1c**: 58% yield
89% ee, *s* = 63



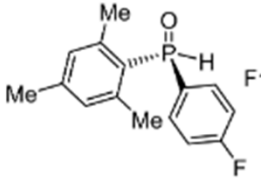
3zl: 35% yield, 91% ee



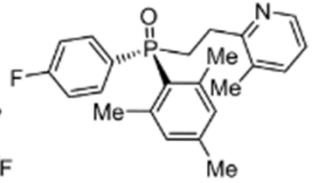
ent-**4a**: 53% yield
96% ee, *s* = 127



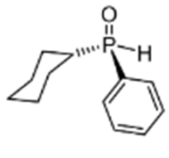
5m: 41% yield, 94% ee



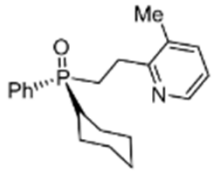
ent-**4b**: 53% yield
93% ee, *s* = 94



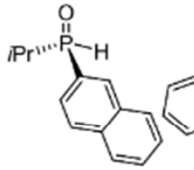
5n:43% yield, 93% ee



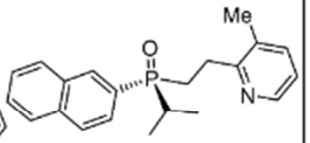
ent-**1e**: 51% yield
95% ee, *s* = 89



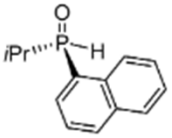
3zm: 45% yield, 92% ee



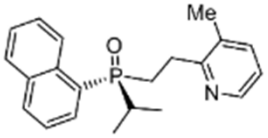
ent-**1p**: 51% yield
90% ee, *s* = 65



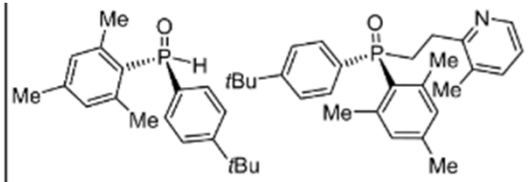
3zn: 43% yield, 91% ee



ent-**1q**: 49% yield
95% ee, *s* = 79

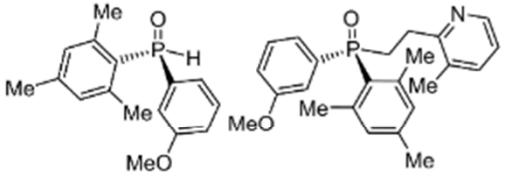


3zo: 46% yield, 91% ee



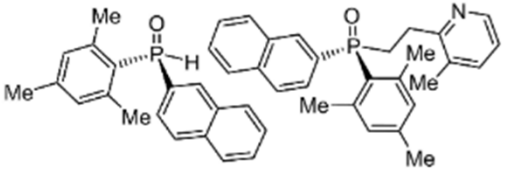
ent-**4g**: 53% yield
94% ee, *s* = 115

5o: 38% yield, 94% ee



ent-**4j**: 58% yield
92% ee, *s* = 79

5p: 35% yield, 92% ee



ent-**4m**: 56% yield
90% ee, *s* = 58

5q: 39% yield, 90% ee

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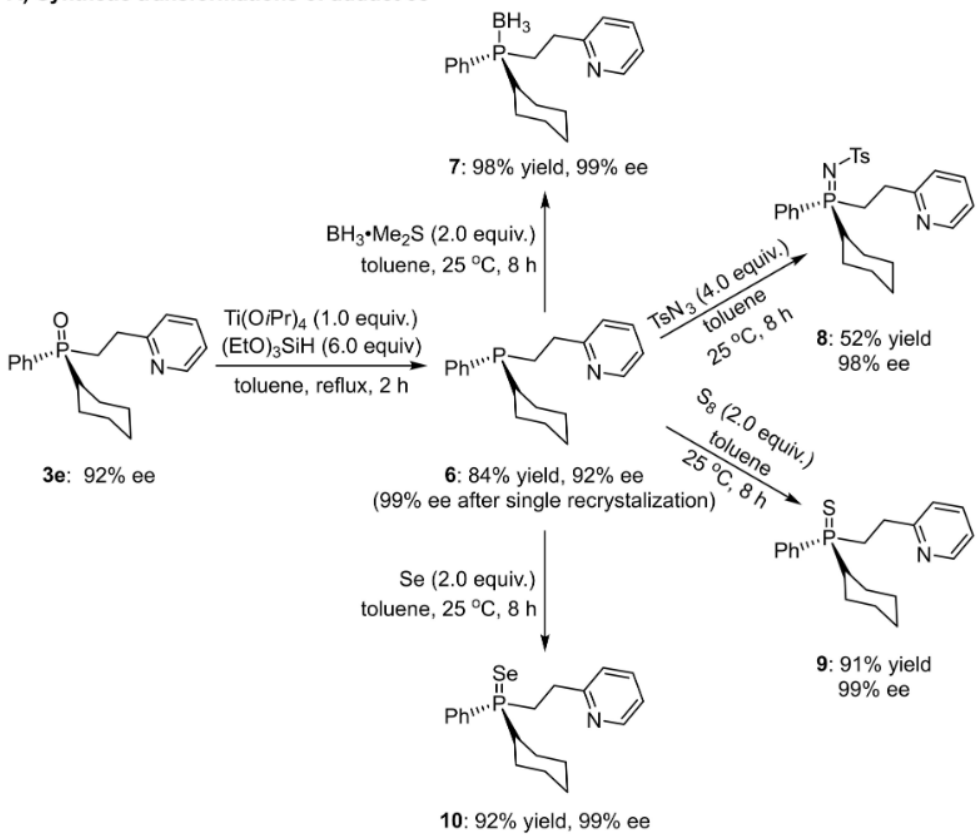
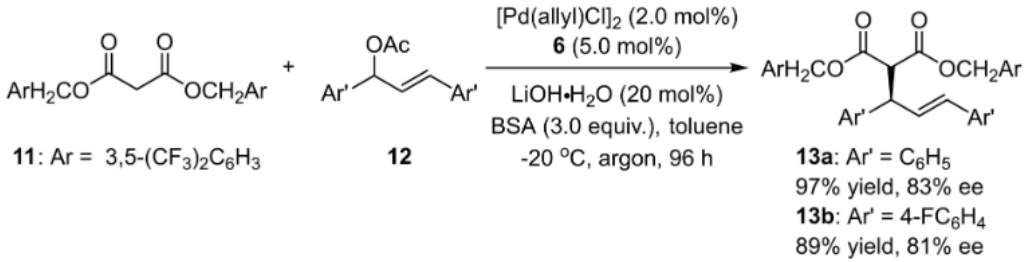
A) Synthetic transformations of adduct 3e



B) Preliminary study on the use of 6 as the chiral ligand



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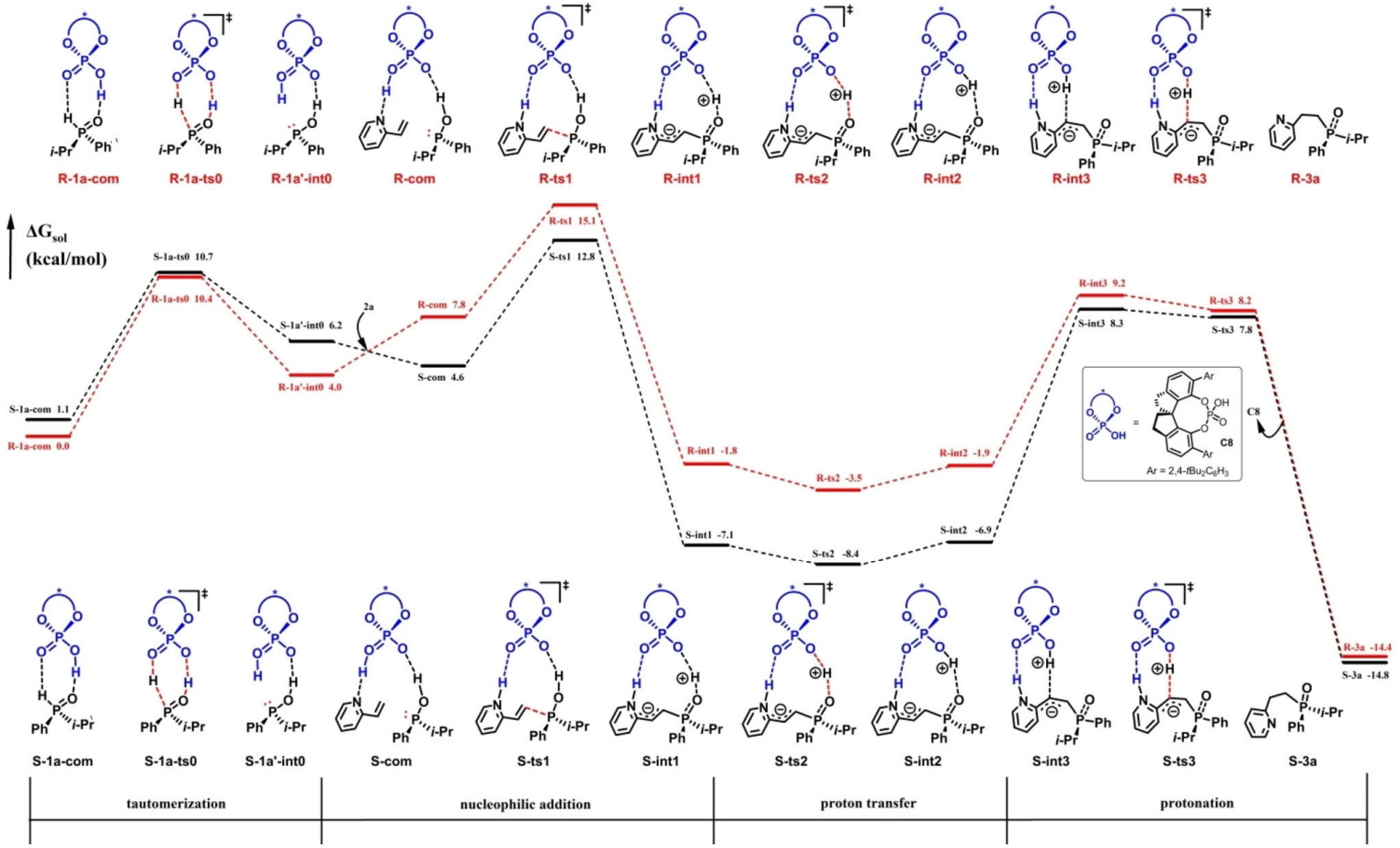

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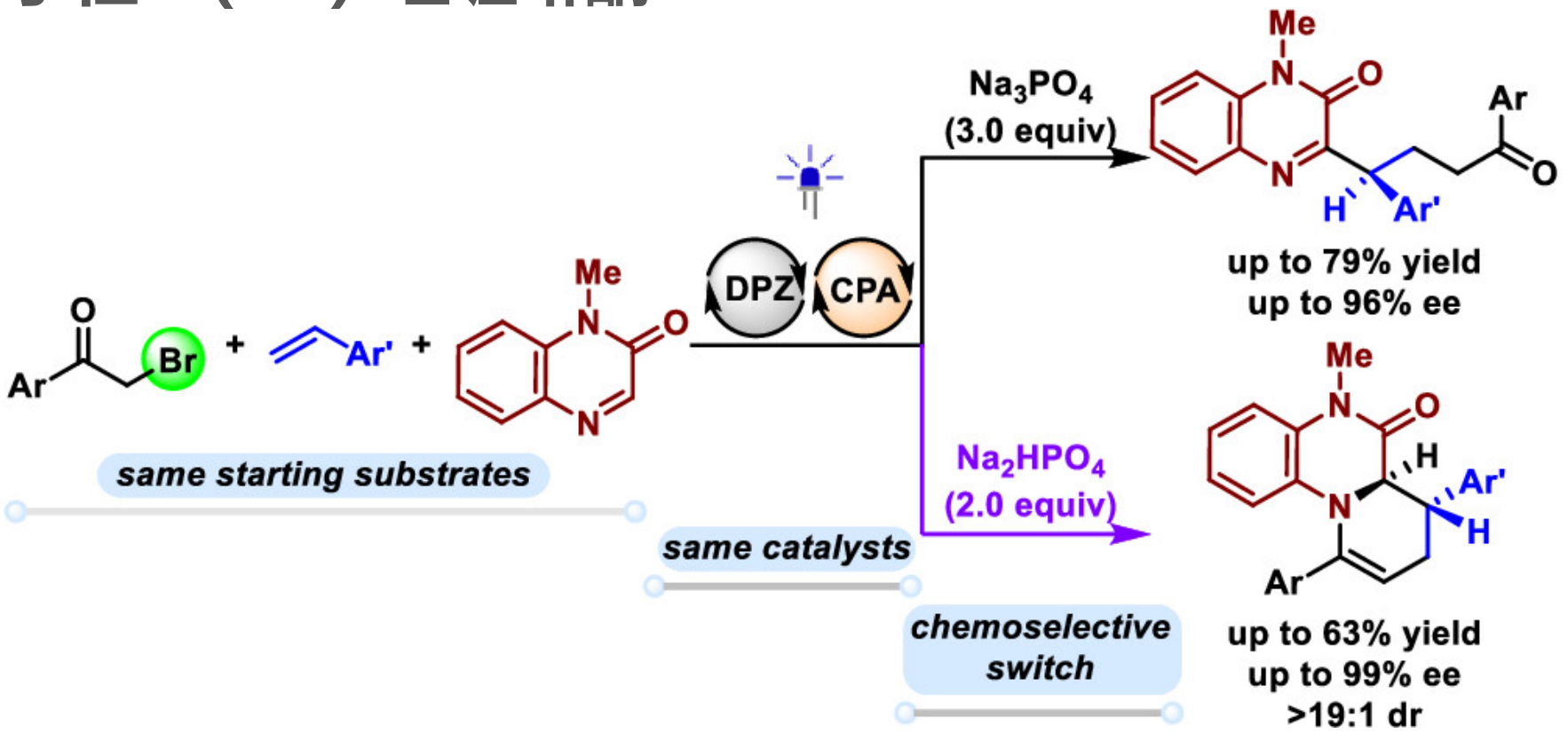
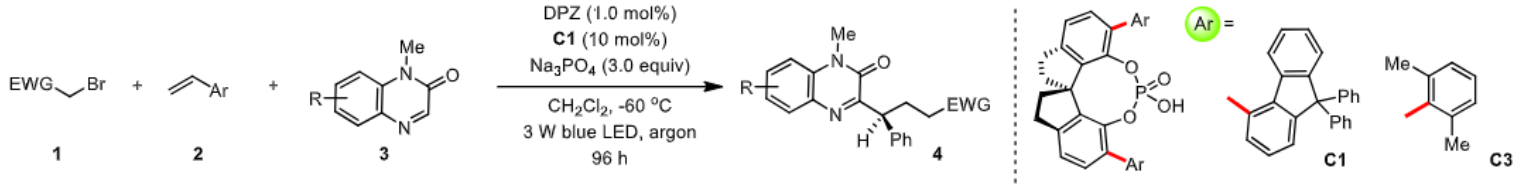
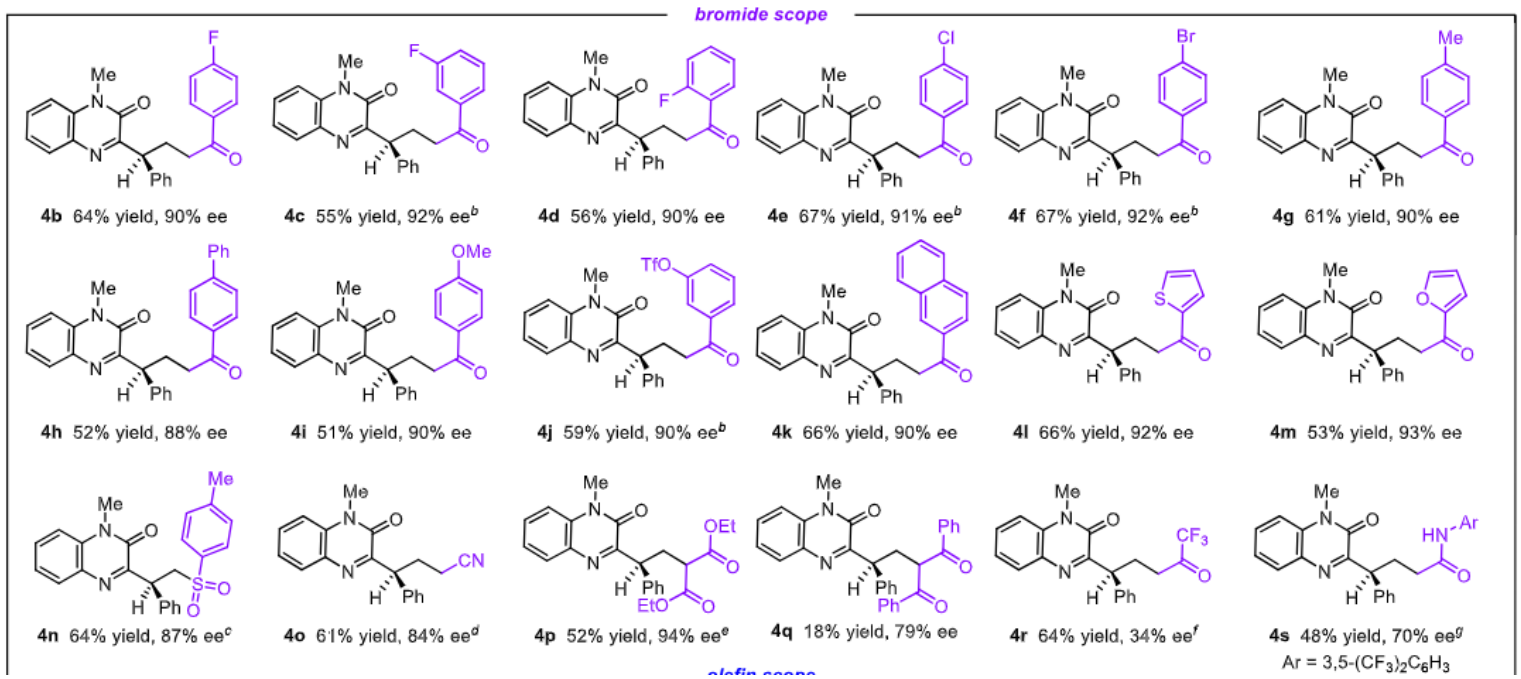
可见光不对称催化直接构建功能化手性2-(1H)-喹喔啉酮



J. Am. Chem. Soc. **2023**, *145*, 20141.

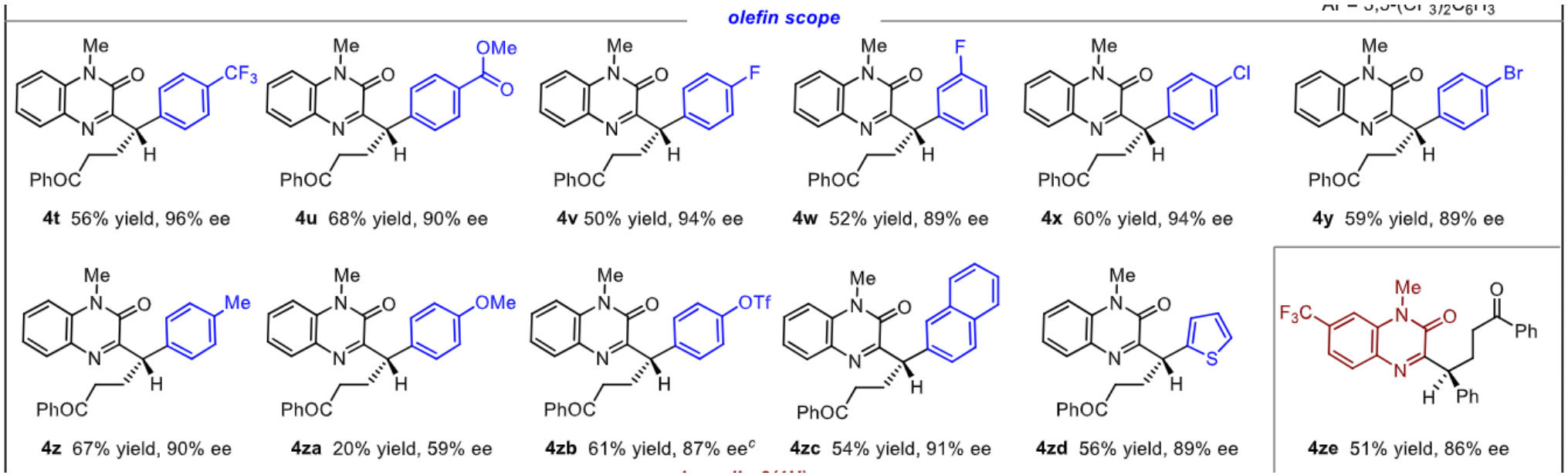
可见光不对称催化直接构建功能化手性2-(1H)-喹喔啉酮





J. Am. Chem. Soc. **2023**, *145*, 20141.

可见光不对称催化直接构建功能化手性2-(1H)-喹喔啉酮



J. Am. Chem. Soc. **2023**, *145*, 20141.

可见光不对称催化直接构建功能化手性2-(1H)-喹喔啉酮

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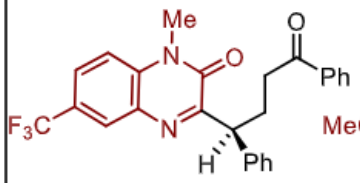
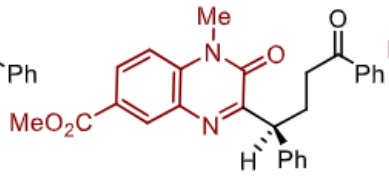
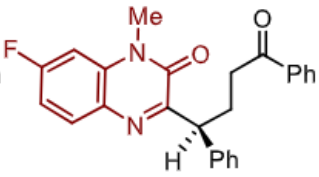
quinoxalin-2(1H)-one scope



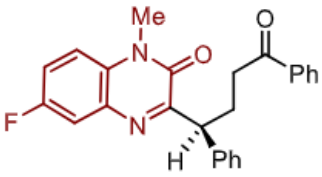
4zf 79% yield, 93% ee



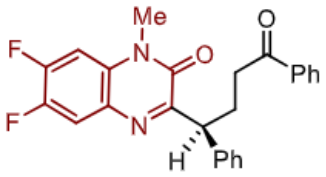
4zg 62% yield, 95% ee



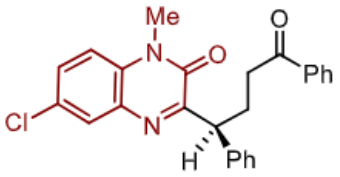
4zh 61% yield, 95% ee



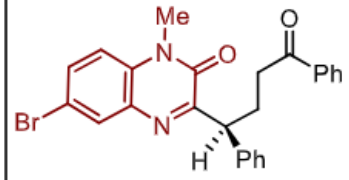
4zi 64% yield, 93% ee



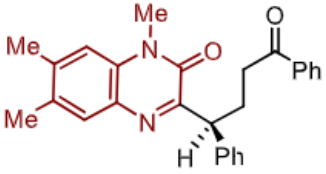
4zj 61% yield, 91% ee



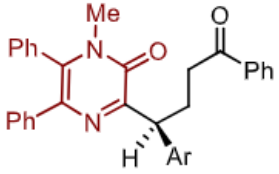
4zk 67% yield, 91% ee



4zl 70% yield, 94% ee



4zm 67% yield, 87% ee



4zn 52% yield, 86% ee[h]
Ar = 4-ClC_6H_4

[a]Reaction conditions: **1** (0.10 mmol), **2** (0.20 mmol), **3** (0.10 mmol), DPZ (1.0 mol%), **C1** (10 mol%), Na_3PO_4 (0.3 mmol), CH_2Cl_2 (3.0 mL), -60 °C, 3 W blue LED (2 cm), argon. [b]2 x 3 W blue LED (4 cm). [c]CH_2Cl_2:C_6H_5F = 1:1 (3.0 mL). [d]CH_2Cl_2:$C_6H_5CF_3$ = 1:1 (3.0 mL). [e]CH_2Cl_2:C_6H_5F = 1:1 (3.0 mL), K_2HPO_4 (2.0 equiv) instead of Na_3PO_4. [f]3DPAFIPN instead of DPZ, $NaHCO_3$ (2.0 equiv) instead of Na_3PO_4, 25 °C. [g]3DPAFIPN instead of DPZ, $NaHCO_3$ (2.0 equiv) instead of Na_3PO_4, -20 °C. [h]**C3** instead of **C1**, Na_2HPO_4 (3.0 equiv) instead of Na_3PO_4.

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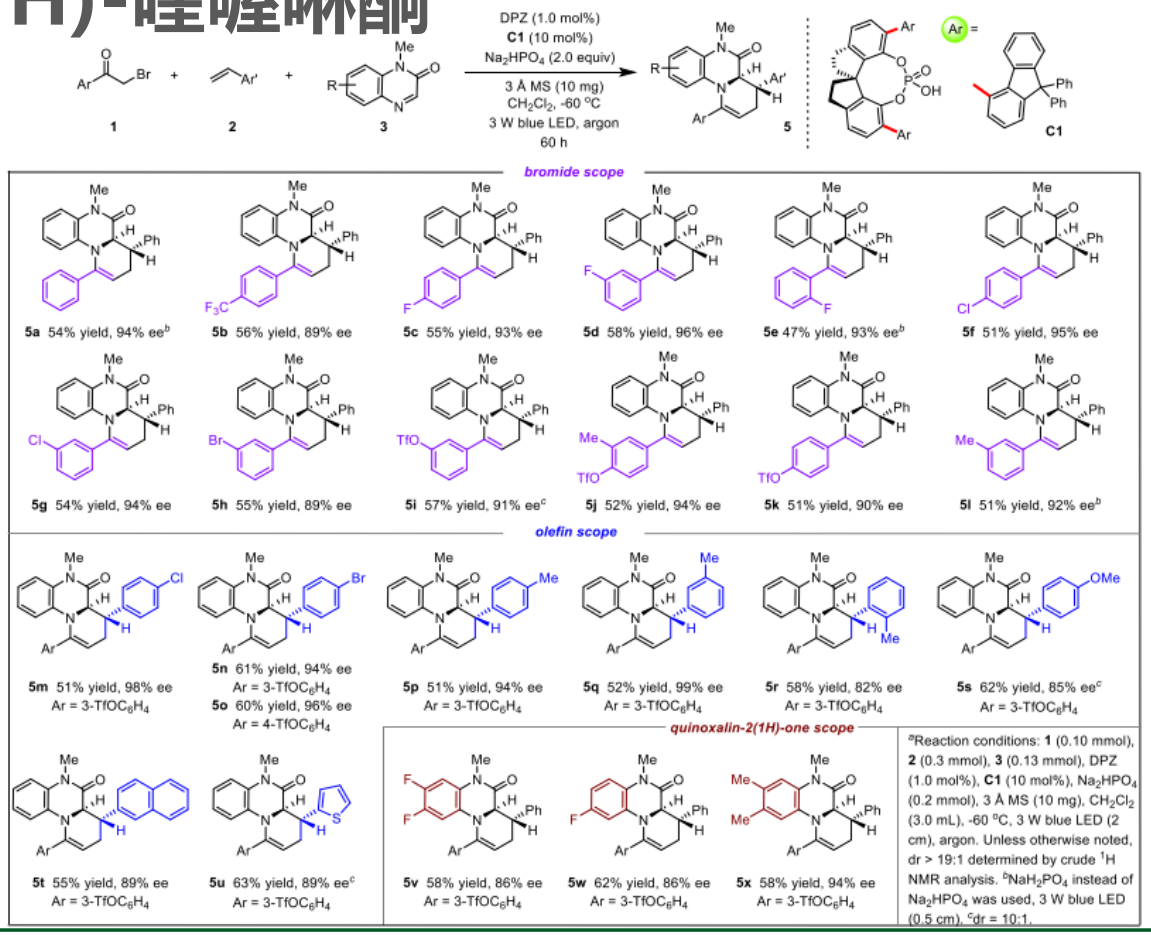
可见光不对称催化直接构建功能化手性2-(1H)-喹喔啉酮

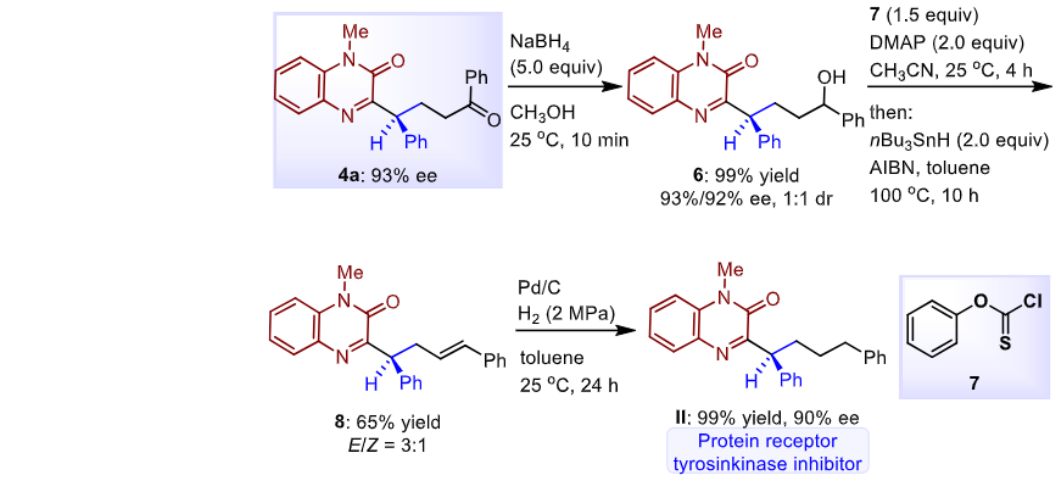


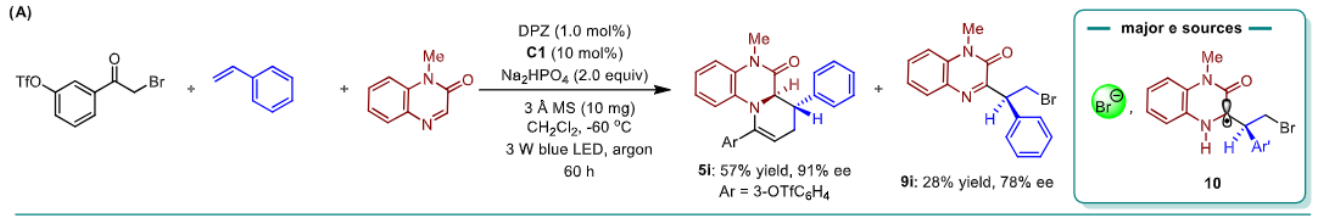
J. Am. Chem. Soc. **2023**, *145*, 20141.

可见光不对称催化直接构建功能化手性2-(1H)-喹喔啉酮

同济大学 TONGJI UNIVERSITY

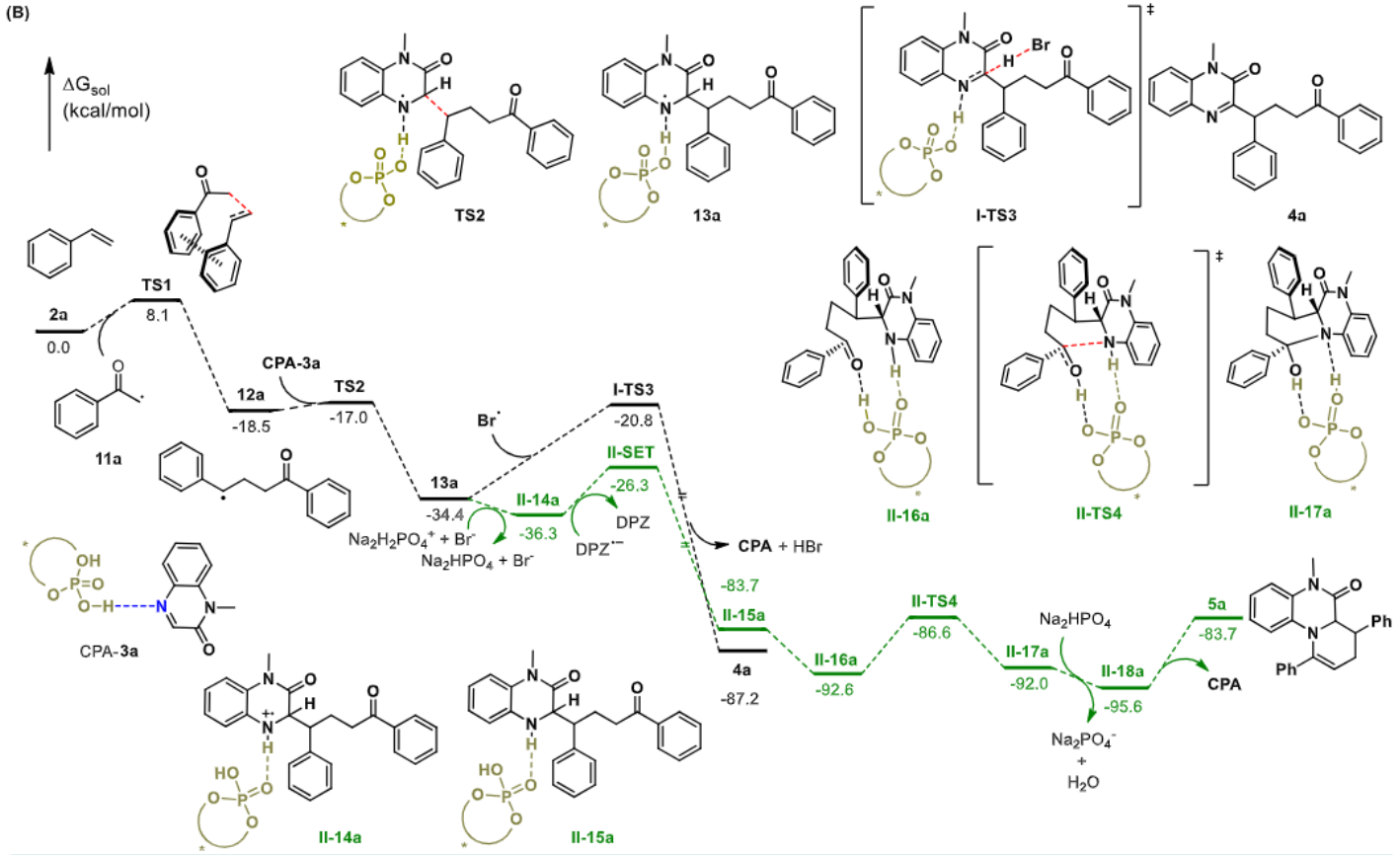
Scheme 2. Synthesis of Enantioenriched II





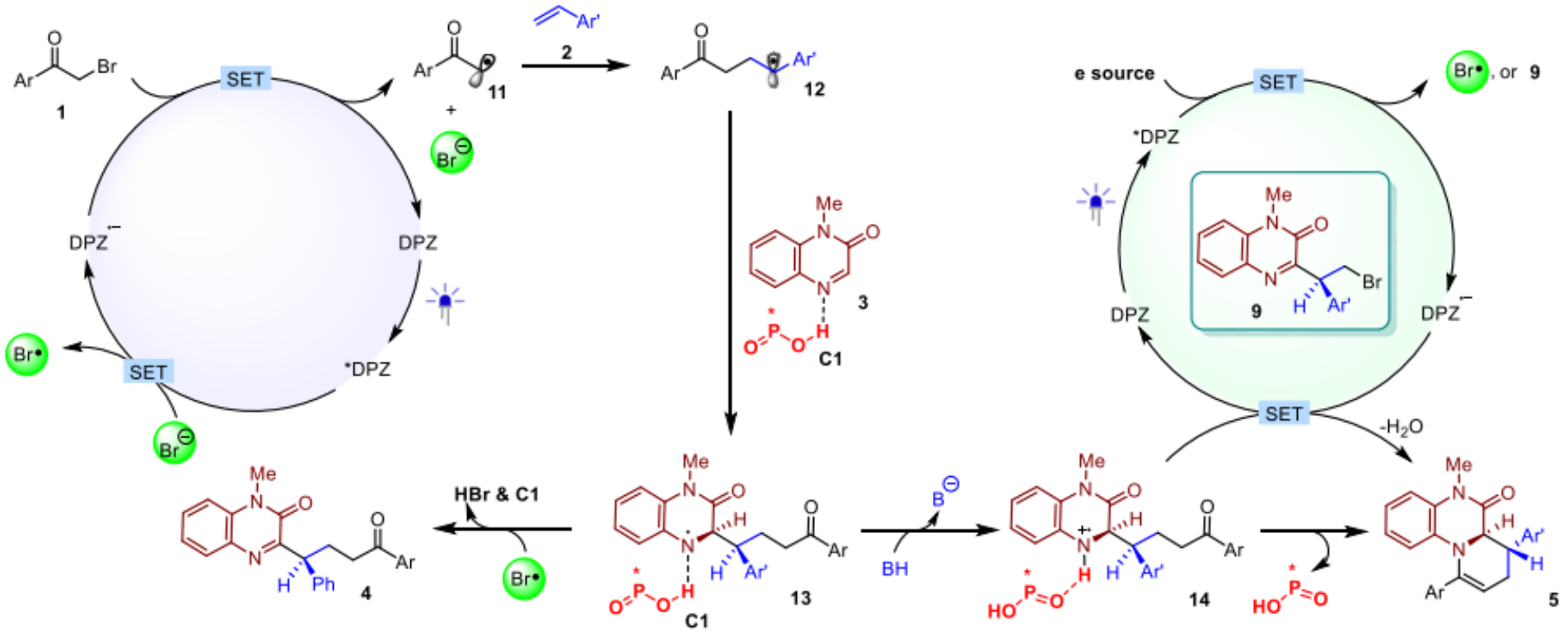
J. Am. Chem. Soc. **2023**, *145*, 20141.

可见光不对称催化直接构建功能化手性2-(1H)-喹喔啉酮



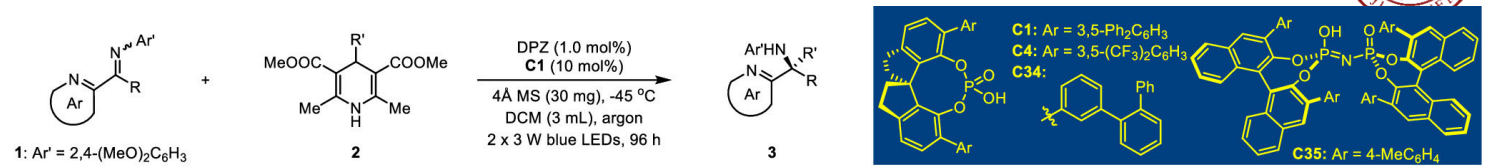
J. Am. Chem. Soc. **2023**, *145*, 20141.

可见光不对称催化直接构建功能化手性2-(1H)-喹喔啉酮



J. Am. Chem. Soc. **2023**, *145*, 20141.

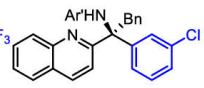
氮杂芳烃叔胺和α-氨基酸衍生物



3j: 51% yield, 92% ee

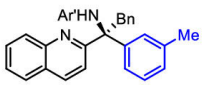
3k: 51% yield, 93% ee

3l: 56% yield, 94% ee

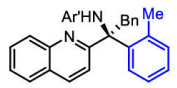


3m: 50% yield, 95% ee

3n: 53% yield, 91% ee



3o: 56% yield, 92% ee[a]

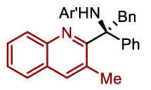


3p: 59% yield, 90% ee[b]

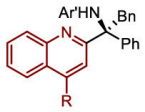
3q: R = 3-OMe, 55% yield, 93% ee
3r: R = 4-OMOM, 51% yield, 94% ee

3s: 54% yield, 94% ee

3t: 51% yield, 91% ee



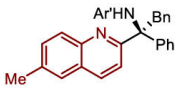
3u: 57% yield, 89% ee[c]



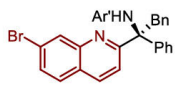
3v: R = Cl, 58% yield, 91% ee[d]
3w: R = COOEt, 56% yield, 96% ee[c]

3x: 48% yield, 91% ee

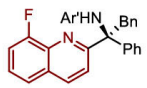
3y: 65% yield, 90% ee[e]



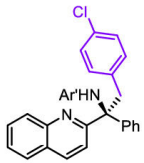
3za: 59% yield, 92% ee[d]



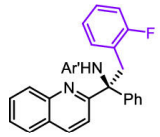
3zb: 65% yield, 93% ee[c]



3zc: 54% yield, 90% ee[f]

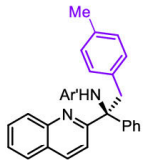


3zd: 51% yield, 94% ee

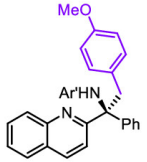


3ze: 61% yield, 93% ee

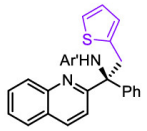
3zf: 56% yield, 94% ee



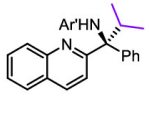
3zg: 55% yield, 92% ee



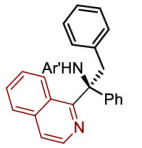
3zh: 67% yield, 92% ee



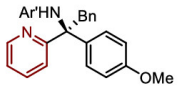
3zi: 67% yield, 91% ee



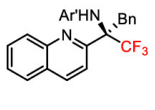
3zj: 43% yield, 91% ee[g]



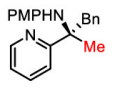
3zk: 50% yield, 82% ee[h]



3zl: 46% yield, 90% ee



3zm: 55% yield, 82% ee[i]

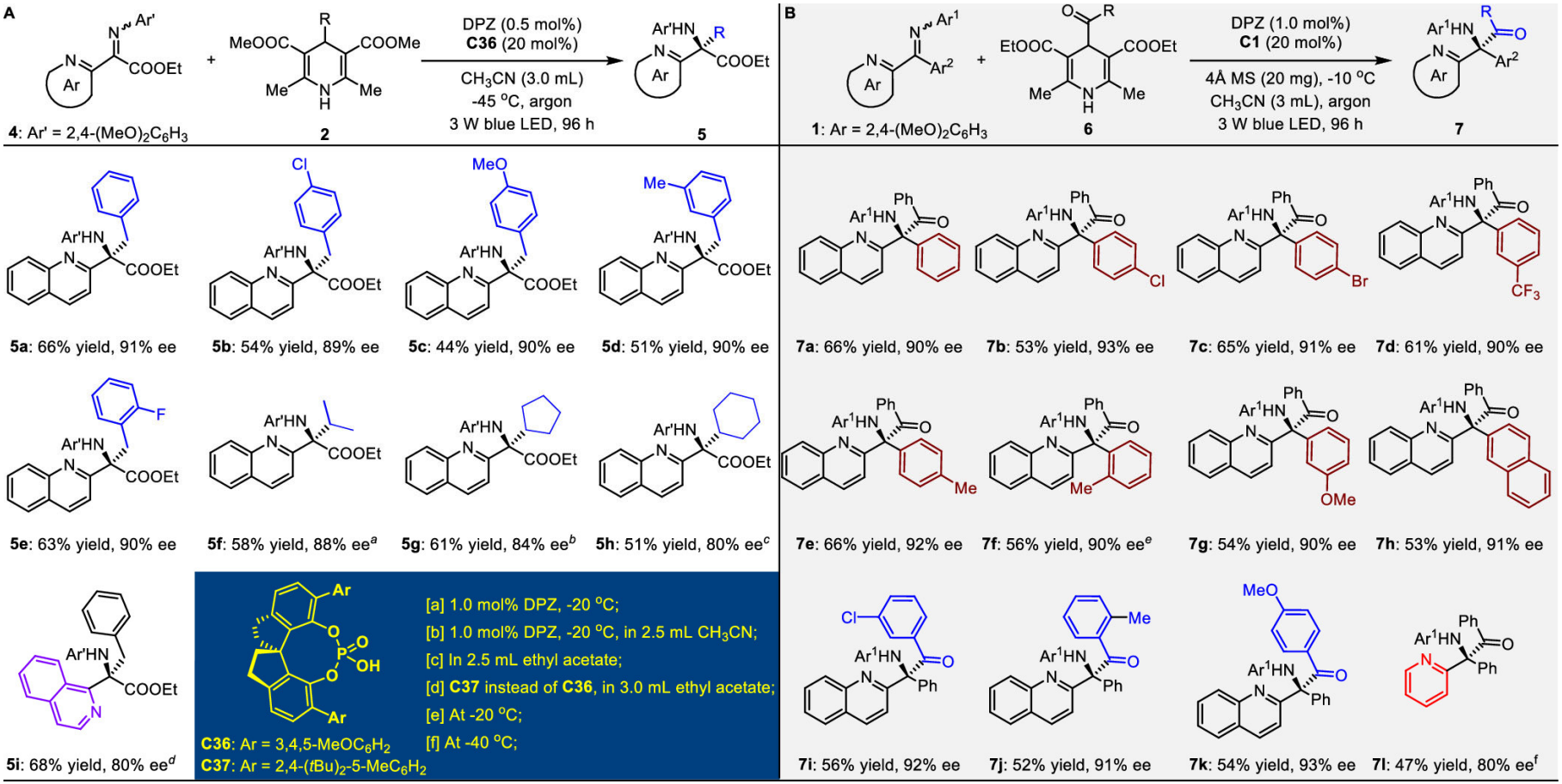


3zn: 60% yield, 80% ee[j]

[a]At -20 °C. [b]At -10 °C. [c]Using 20 mol% **C1** in 3.0 mL CH_3CN. [d]Using 20 mol% **C1**. [e]In 3.0 mL CH_3CN. [f]Using 10 mol% **C4**.
[g]At -10 °C, using 3.0 mL CH_3CN, 5 mol% **C1** and 3 W blue LEDs. [h]Using 10 mol% **C34**. [i]Using 20 mol% **C1**. [j]Using 10 mol% **C35** and 3 W blue LED. MOM = methyloxymethyl

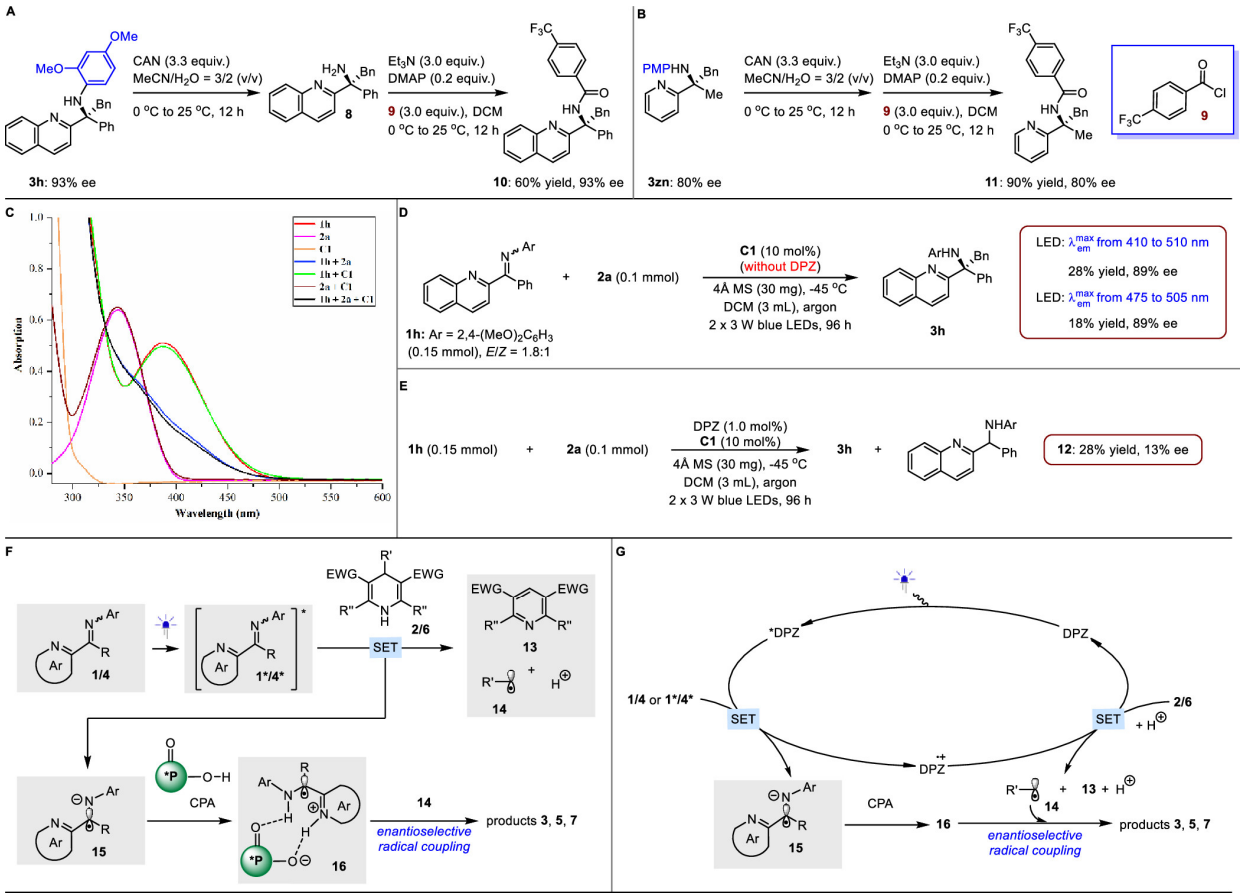
ACS Catal. **2023**, *13*, 6396.

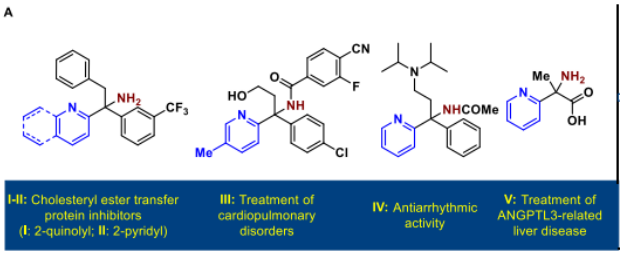
氮杂芳烃叔胺和α-氨基酸衍生物



ACS Catal. **2023**, *13*, 6396.

氮杂芳烃叔胺和α-氨基酸衍生物

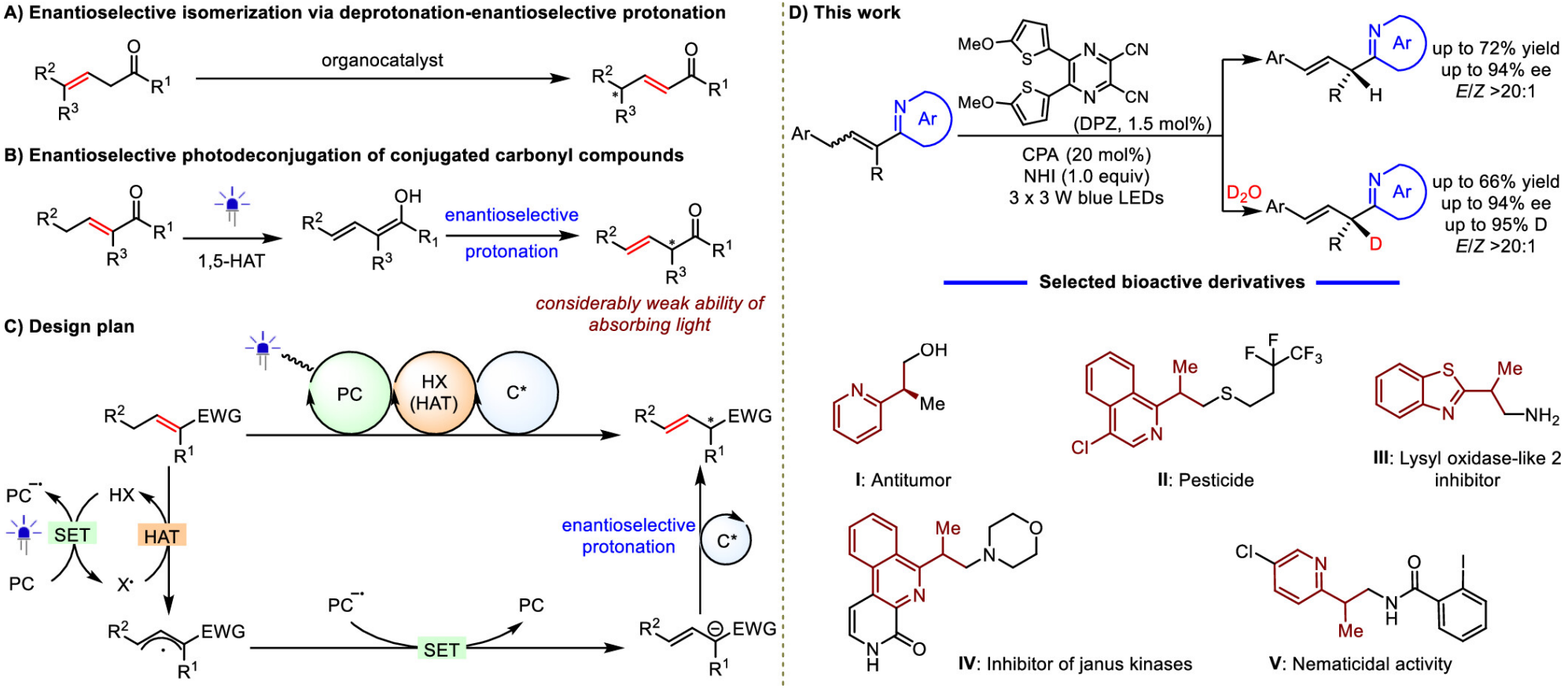




- 氧化还原中性自由基偶联
- E/Z亚胺做为底物
- 氮杂芳烃叔胺和α-氨基酸衍生物
- 广泛的底物适用性
- 高的产率和对映选择性

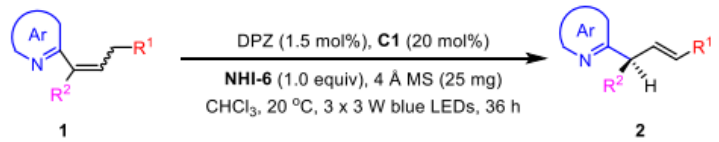
ACS Catal. **2023**, *13*, 6396.

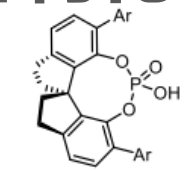
光氧化还原不对称催化烯烃异构化



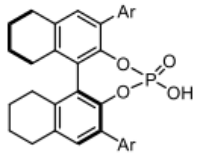
J. Am. Chem. Soc. **2023**, *145*, 18307.

光氧化还原不对称催化烯烃异构化

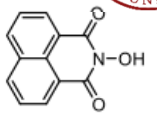




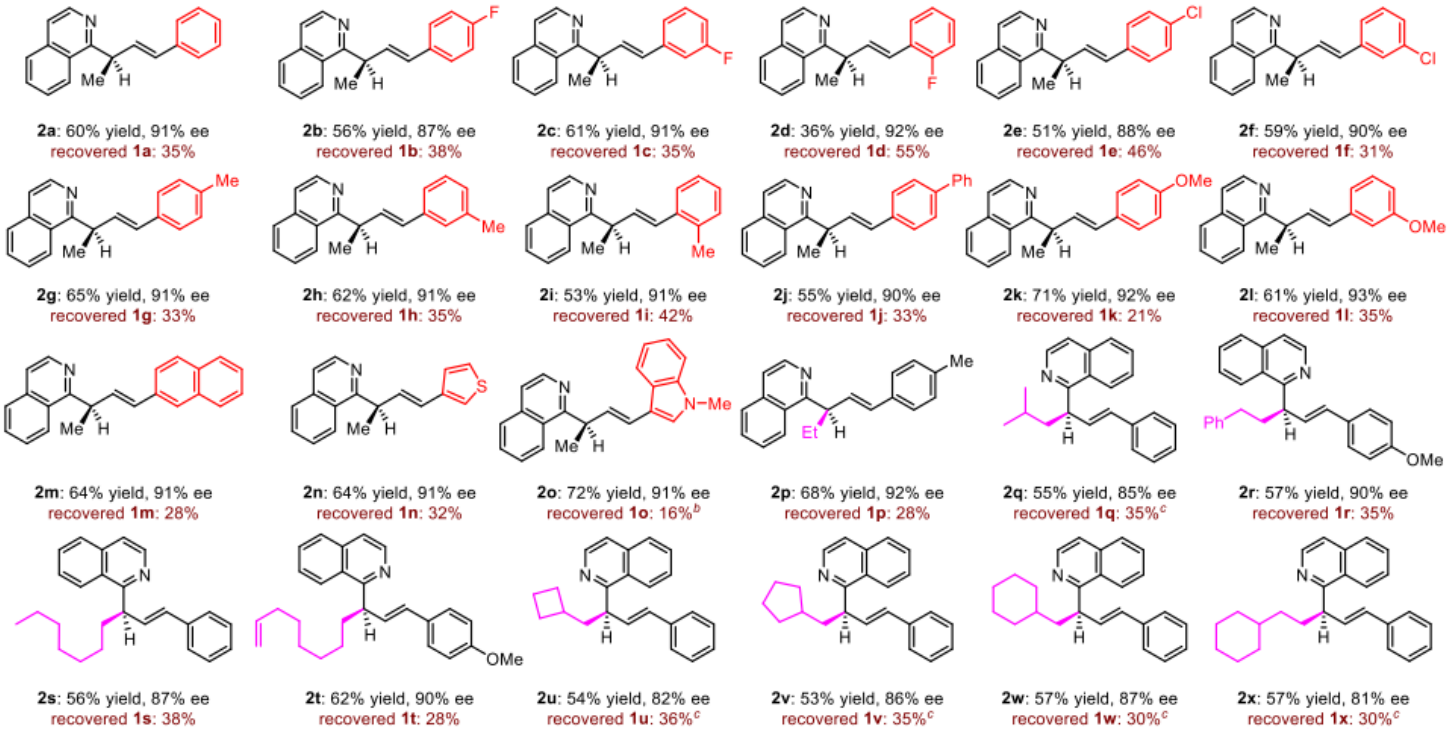
C1: Ar = 2,4,6-iPr$_3$C$_6$H$_2$
C2: Ar = 2,3,5,6-Me$_4$C$_6$H



C21: Ar = 2,4,-(MeO)$_2$C$_6$H$_3$



NHI-6



2a: 60% yield, 91% ee
recovered **1a**: 35%

2b: 56% yield, 87% ee
recovered **1b**: 38%

2c: 61% yield, 91% ee
recovered **1c**: 35%

2d: 36% yield, 92% ee
recovered **1d**: 55%

2e: 51% yield, 88% ee
recovered **1e**: 46%

2f: 59% yield, 90% ee
recovered **1f**: 31%

2g: 65% yield, 91% ee
recovered **1g**: 33%

2h: 62% yield, 91% ee
recovered **1h**: 35%

2i: 53% yield, 91% ee
recovered **1i**: 42%

2j: 55% yield, 90% ee
recovered **1j**: 33%

2k: 71% yield, 92% ee
recovered **1k**: 21%

2l: 61% yield, 93% ee
recovered **1l**: 35%

2m: 64% yield, 91% ee
recovered **1m**: 28%

2n: 64% yield, 91% ee
recovered **1n**: 32%

2o: 72% yield, 91% ee
recovered **1o**: 16%[b]

2p: 68% yield, 92% ee
recovered **1p**: 28%

2q: 55% yield, 85% ee
recovered **1q**: 35%[c]

2r: 57% yield, 90% ee
recovered **1r**: 35%

2s: 56% yield, 87% ee
recovered **1s**: 38%

2t: 62% yield, 90% ee
recovered **1t**: 28%

2u: 54% yield, 82% ee
recovered **1u**: 36%[c]

2v: 53% yield, 86% ee
recovered **1v**: 35%[c]

2w: 57% yield, 87% ee
recovered **1w**: 30%[c]

2x: 57% yield, 81% ee
recovered **1x**: 30%[c]

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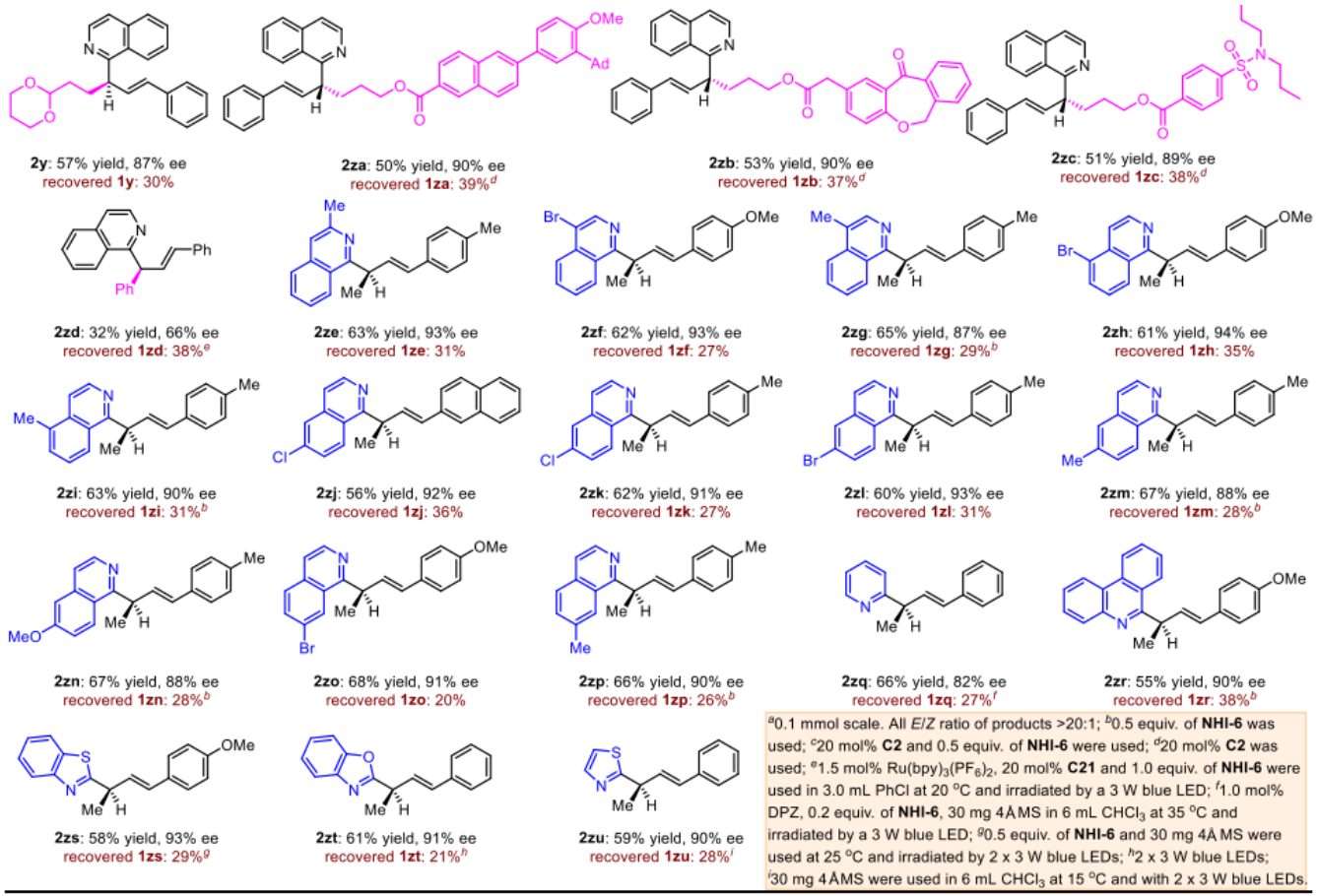
光氧化还原不对称催化烯烃异构化



[a]0.1 mmol scale. All *E*/*Z* ratio of products >20:1; [b]0.5 equiv. of **NHI-6** was used; [c]20 mol% **C2** and 0.5 equiv. of **NHI-6** were used; [d]20 mol% **C2** was used; [e]1.5 mol% $Ru(bpy)_3(PF_6)_2$, 20 mol% **C21** and 1.0 equiv. of **NHI-6** were used in 3.0 mL PhCl at 20 °C and irradiated by a 3 W blue LED; [f]1.0 mol% DPZ, 0.2 equiv. of **NHI-6**, 30 mg 4Å MS in 6 mL $CHCl_3$ at 35 °C and irradiated by a 3 W blue LED; [g]0.5 equiv. of **NHI-6** and 30 mg 4Å MS were used at 25 °C and irradiated by 2 x 3 W blue LEDs; [h]2 x 3 W blue LEDs; [i]30 mg 4Å MS were used in 6 mL $CHCl_3$ at 15 °C and with 2 x 3 W blue LEDs.

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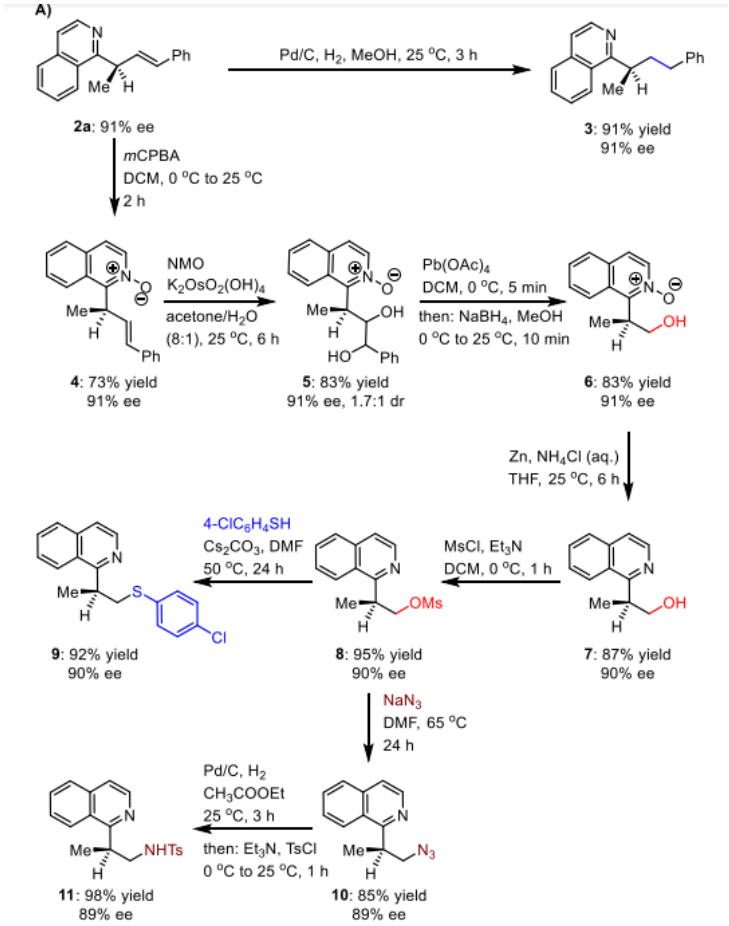
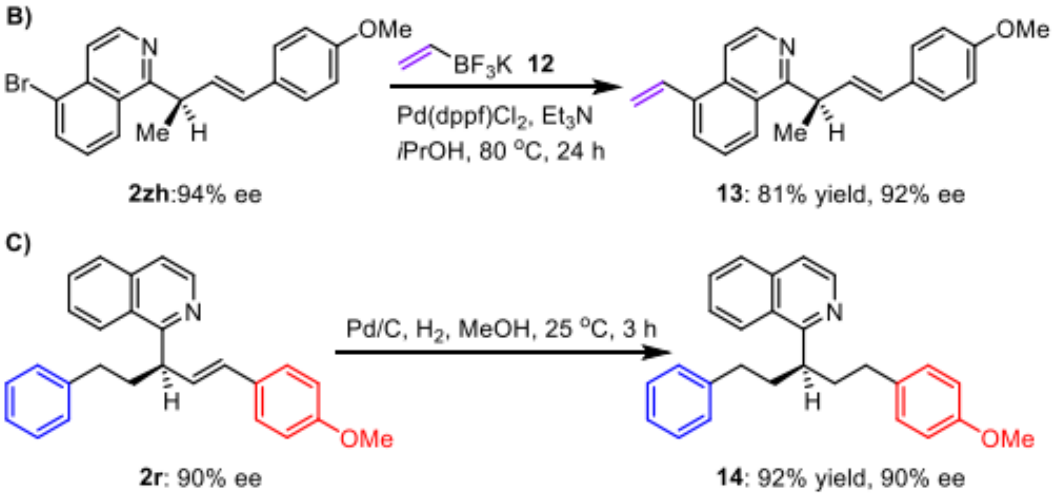
光氧化还原不对称催化烯烃异构化





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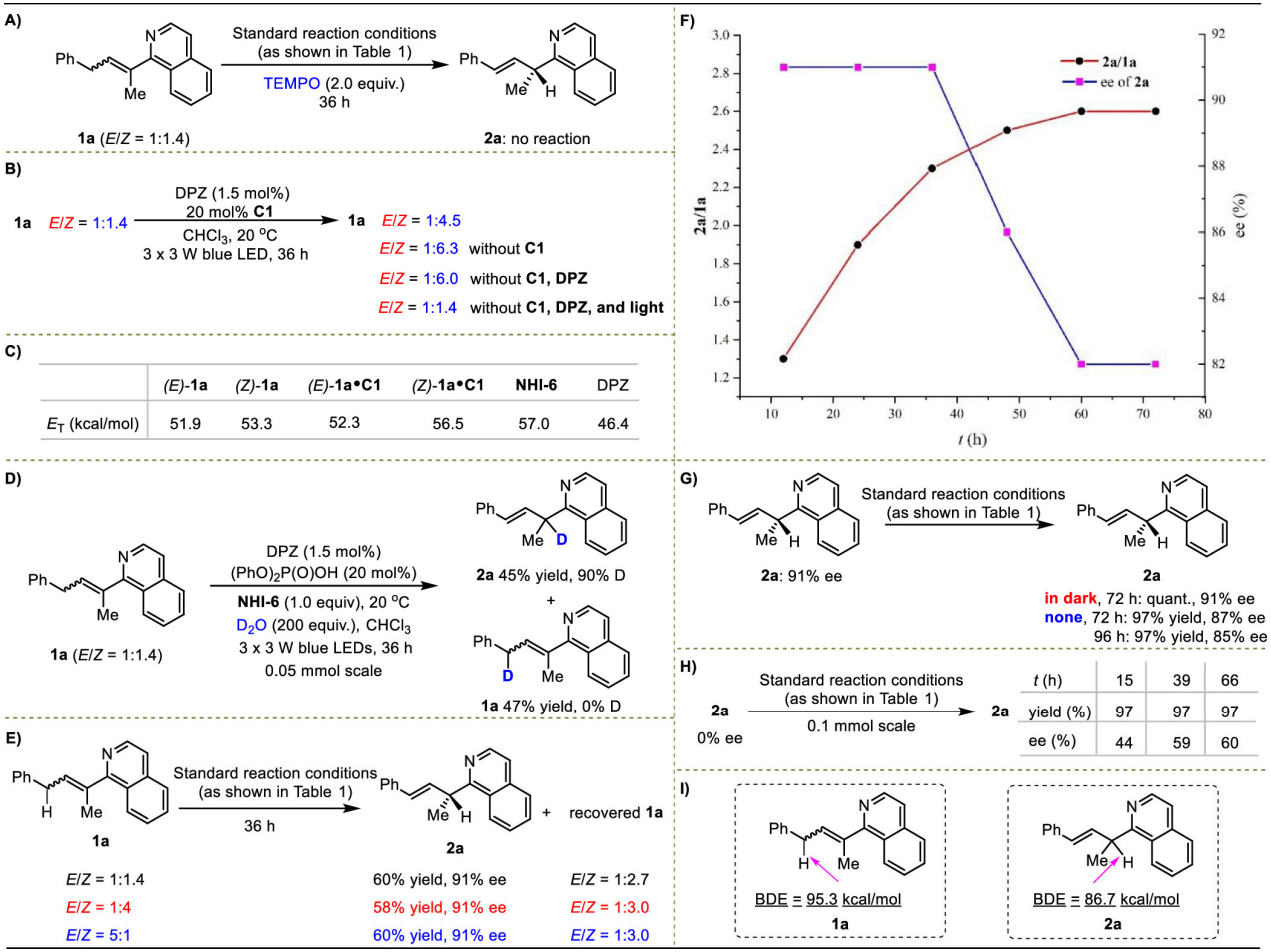
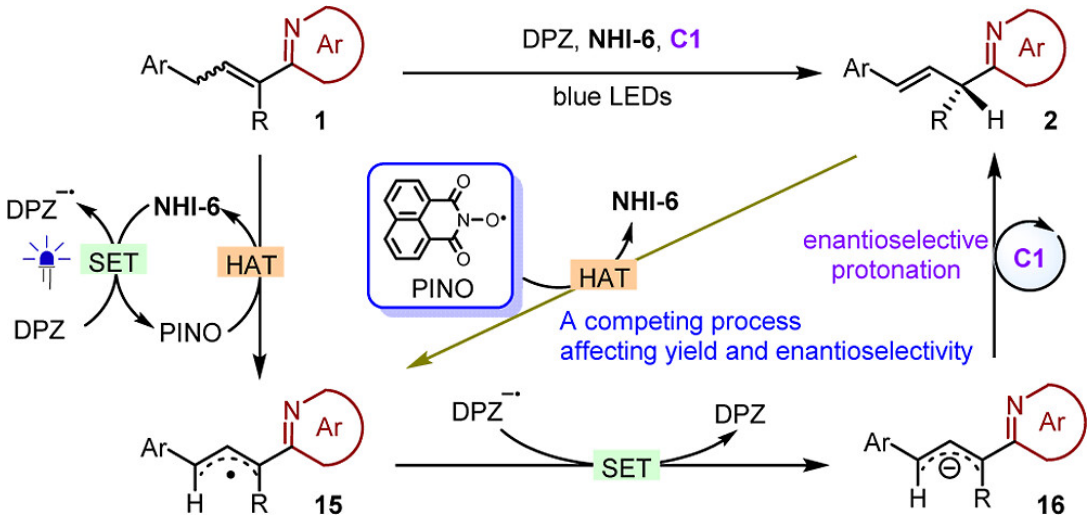
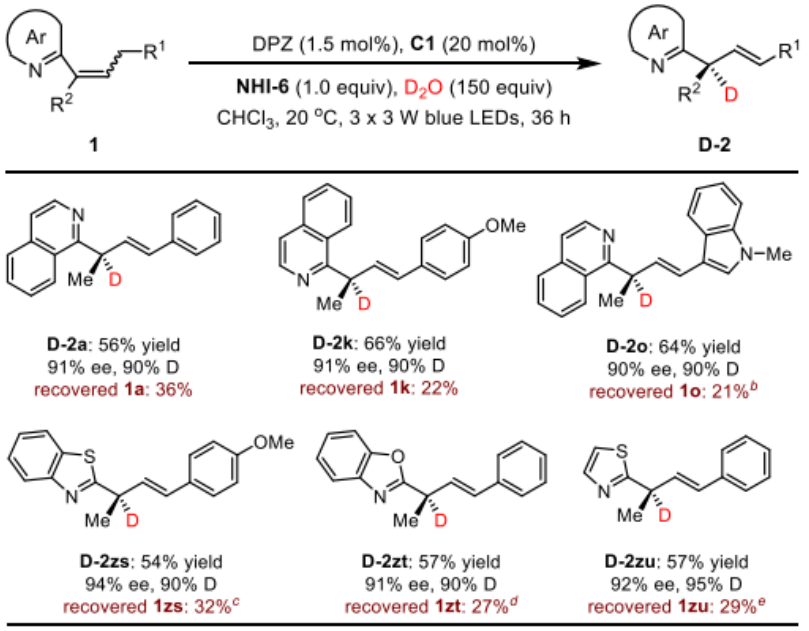
光氧化还原不对称催化烯烃异构化



J. Am. Chem. Soc. **2023**, *145*, 18307.

光氧化还原不对称催化烯烃异构化





[a]0.1 mmol scale. All the *E*/*Z* ratio of products >20:1. [b]**NHI-6** (0.5 equiv) was used. [c]**NHI-6** (0.5 equiv) was used at 25 °C and irradiated by 2 × 3 W blue LEDs. [d]Irradiated by 2 × 3 W blue LEDs. [e]$CHCl_3$ (6.0 mL) as the solvent at 15 °C and irradiated by 2 × 3 W blue LEDs.

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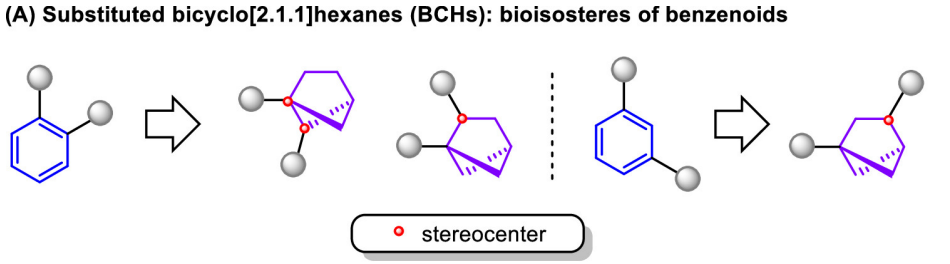
双环丁烷与乙烯基氮杂芳烃环加成反应



- 为足够的对映体控制提供相当的空间位阻
- 作为完成光氧化还原催化循环的敏化剂，从而有效地抑制显著的外消旋背景反应。

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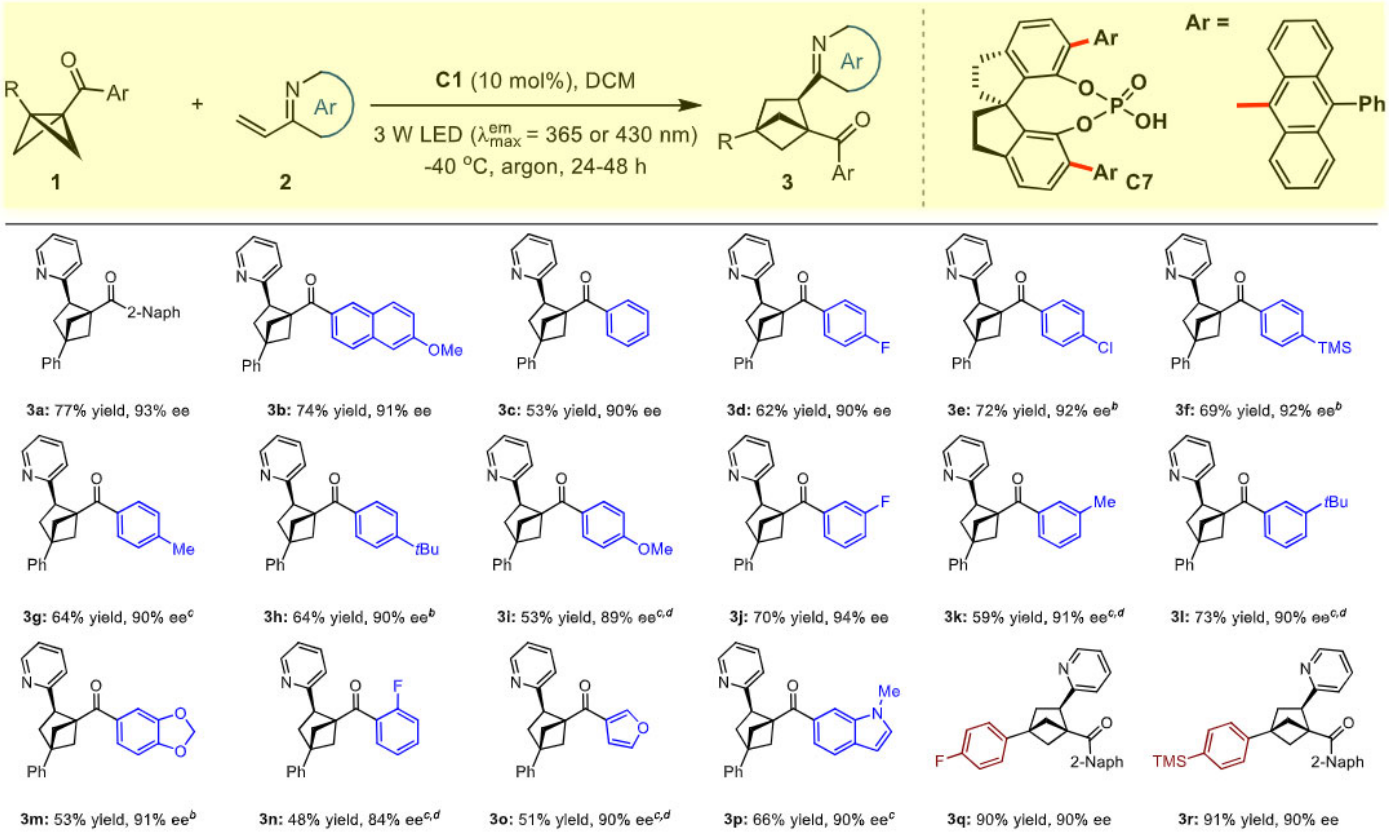
双环丁烷与乙烯基氮杂芳烃环加成反应



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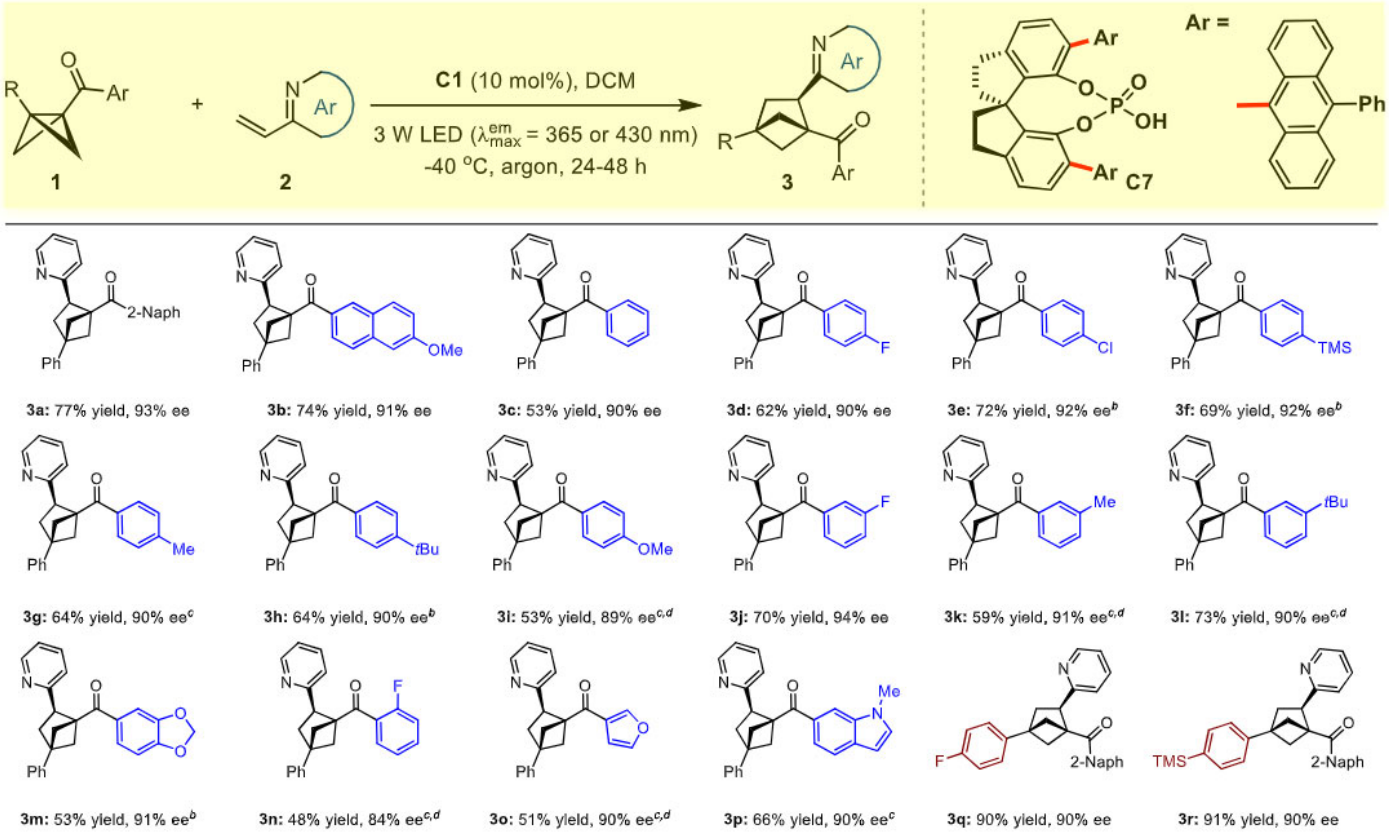

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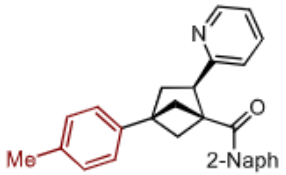
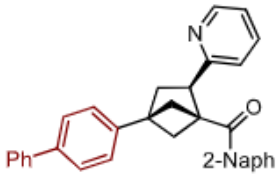
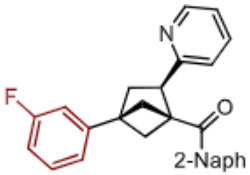


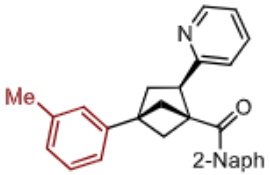
3s: 60% yield, 85% ee



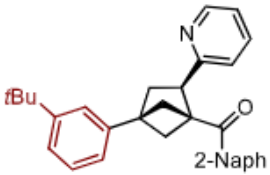
3t: 56% yield, 87% ee



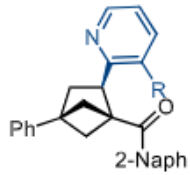
3u: 75% yield, 90% ee



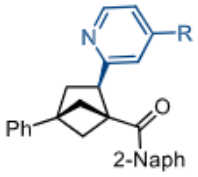
3v: 77% yield, 87% ee



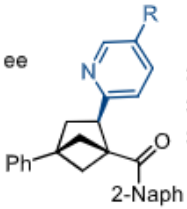
3w: 56% yield, 83% ee



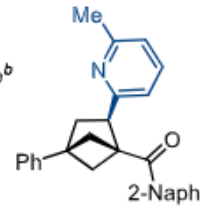
3x: R = F, 55% yield, 97% ee
3y: R = Cl, 71% yield, 93% ee
3za: R = Me, 99% yield, 98% ee



3zb: R = CN, 65% yield, 88% ee[b]
3zc: R = COOMe, 42% yield, 94% ee
3zd: R = CF_3, 60% yield, 99% ee
3ze: R = F, 50% yield, 93% ee
3zf: R = Me, 99% yield, 93% ee
3zg: R = OMe, 99% yield, 94% ee

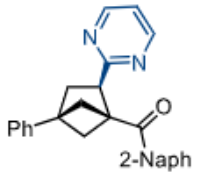


3zh: R = CF_3, 46% yield, 96% ee[b]
3zi: R = F, 59% yield, 90% ee
3zj: R = Me, 97% yield, 97% ee



3zk: 87% yield, 86% ee

3zl: 61% yield, 97% ee[b]



3zm: 24% yield, 99% ee

[a]The reaction was performed on a 0.10 mmol scale. If not otherwise noted, for yielding products **3a–p** and **3y–zl**, λ_{max}^{em} = 365 nm, **1:2** = 2.5:1, t = 24 h; for yielding products **3q–w**, λ_{max}^{em} = 430 nm, **1:2** = 1:2, t = 48 h. [b]t = 48 h. [c]t = 72 h. [d]−50 °C. 2-Naph = 2-naphthyl.

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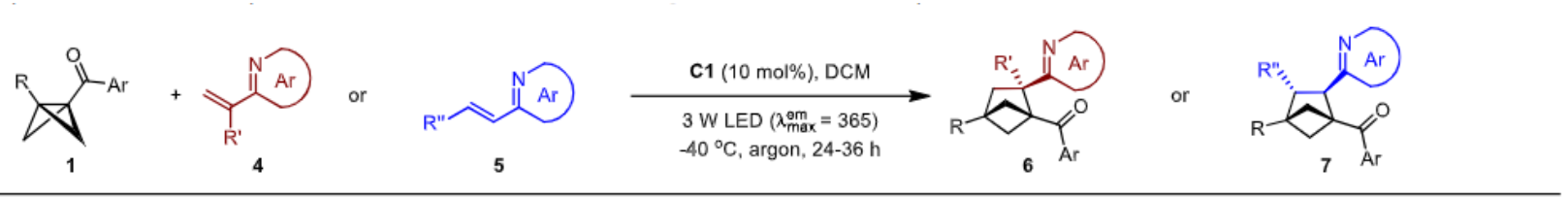

1 4 5 6 7

6a: 77% yield, 95% ee

6b: 48% yield, 93% ee
63% yield, 93% ee[b]

6c: 83% yield, 95% ee[c]

6d: 76% yield, 96% ee

6e: 70% yield, >99% ee

6f: 70% yield, >99% ee

6g: 62% yield, 85% ee[c]

6h: 79% yield, 96% ee[d]

6i: 97% yield, 90% ee

6j: 81% yield, 94% ee[c]

6k: 76% yield, 97% ee

6l: 63% yield, 98% ee

7a: 63% yield, 95% ee
d.r. > 19:1

7b: 46% yield, 91% ee
d.r. > 19:1[c]

[a]The reaction was performed on a 0.10 mmol scale. If not otherwise noted, for yielding products **6a–f** and **7a–b**, **1:4/1:5** = 2.5:1, t = 24 h; for yielding products **6g–l**, **1:4** = 2:1, t = 36 h. [b]3 W blue LED (λ_{max}^{em} = 445 nm), 10 mol % TXT, **1:4** = 1:2. [c]t = 48 h. [d]–20 °C, **1:4** = 1:2. TXT = thioxanthone.

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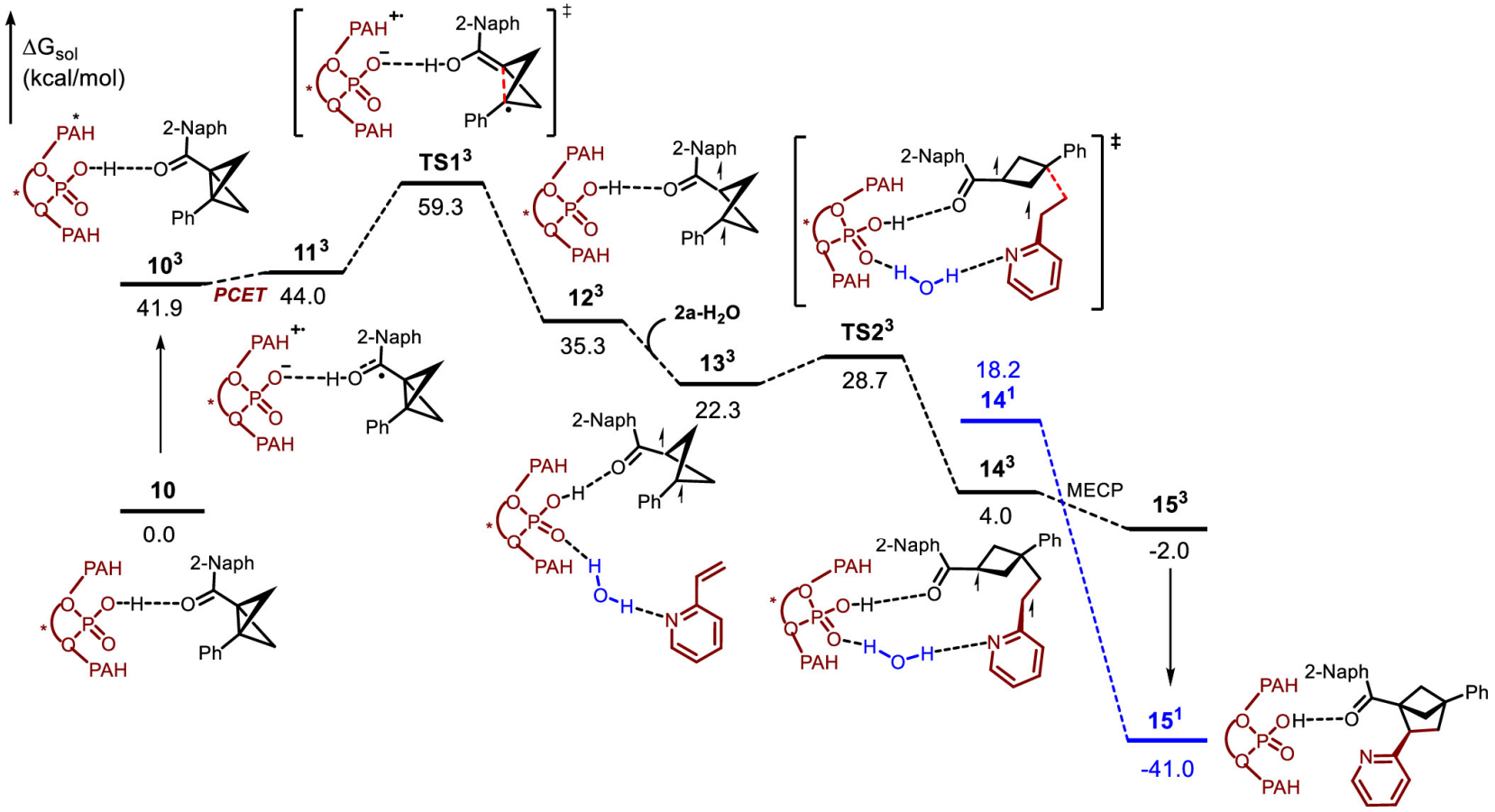

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光促[3+2]环加成反应

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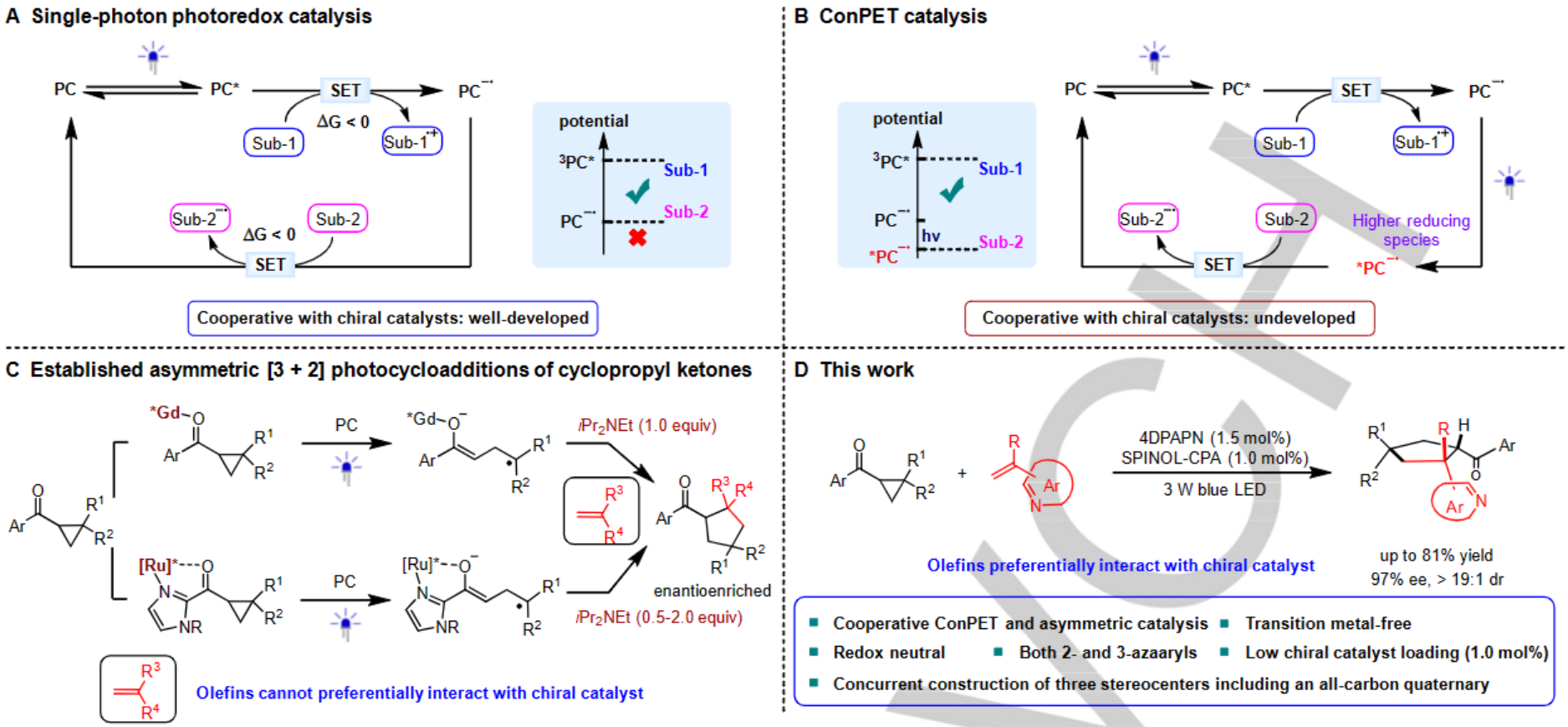
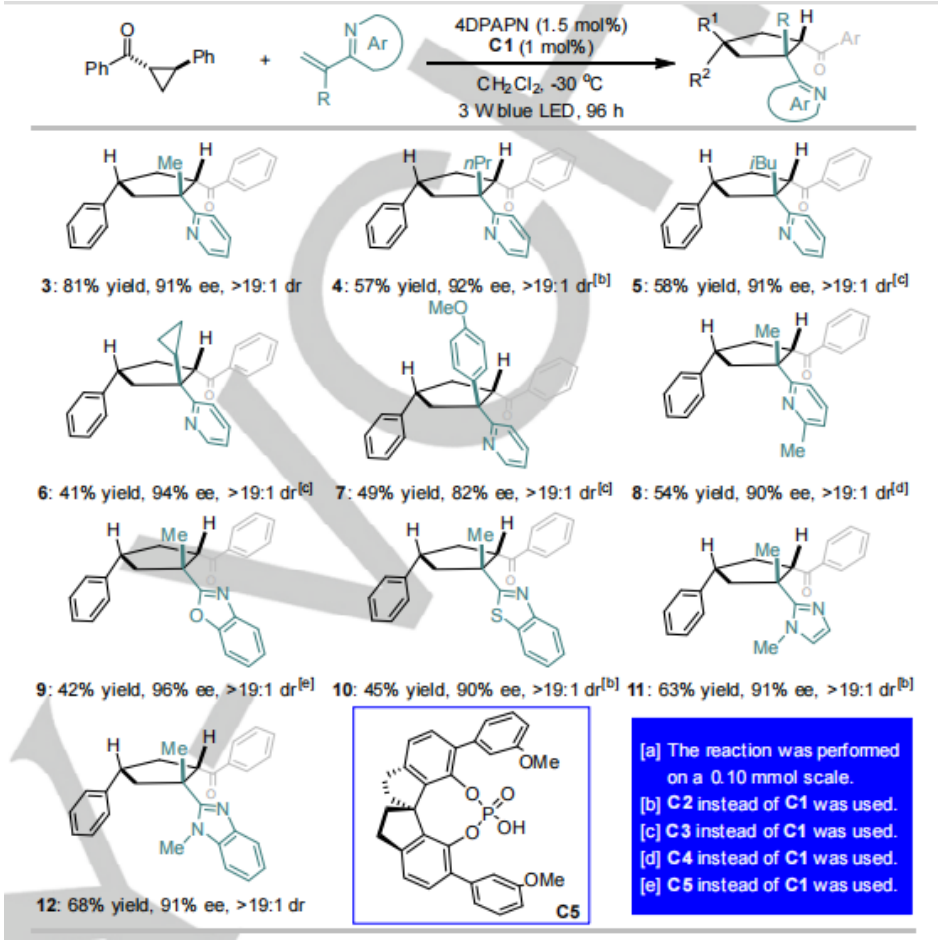
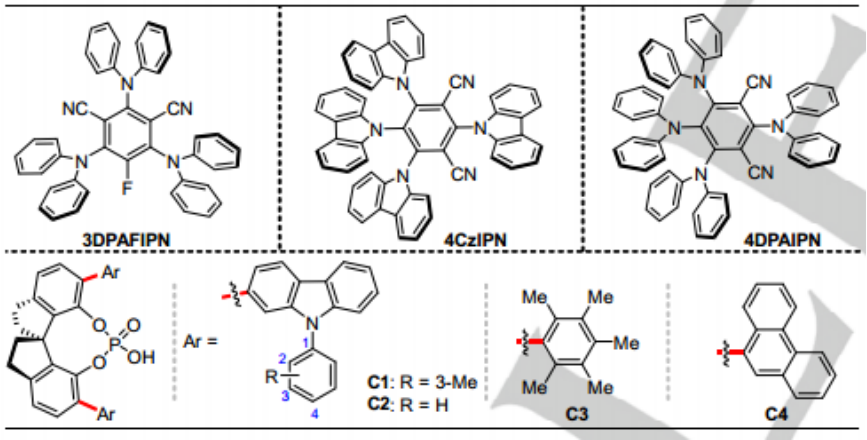


https://doi.org/10.1002/anie.202406845

光促[3+2]环加成反应





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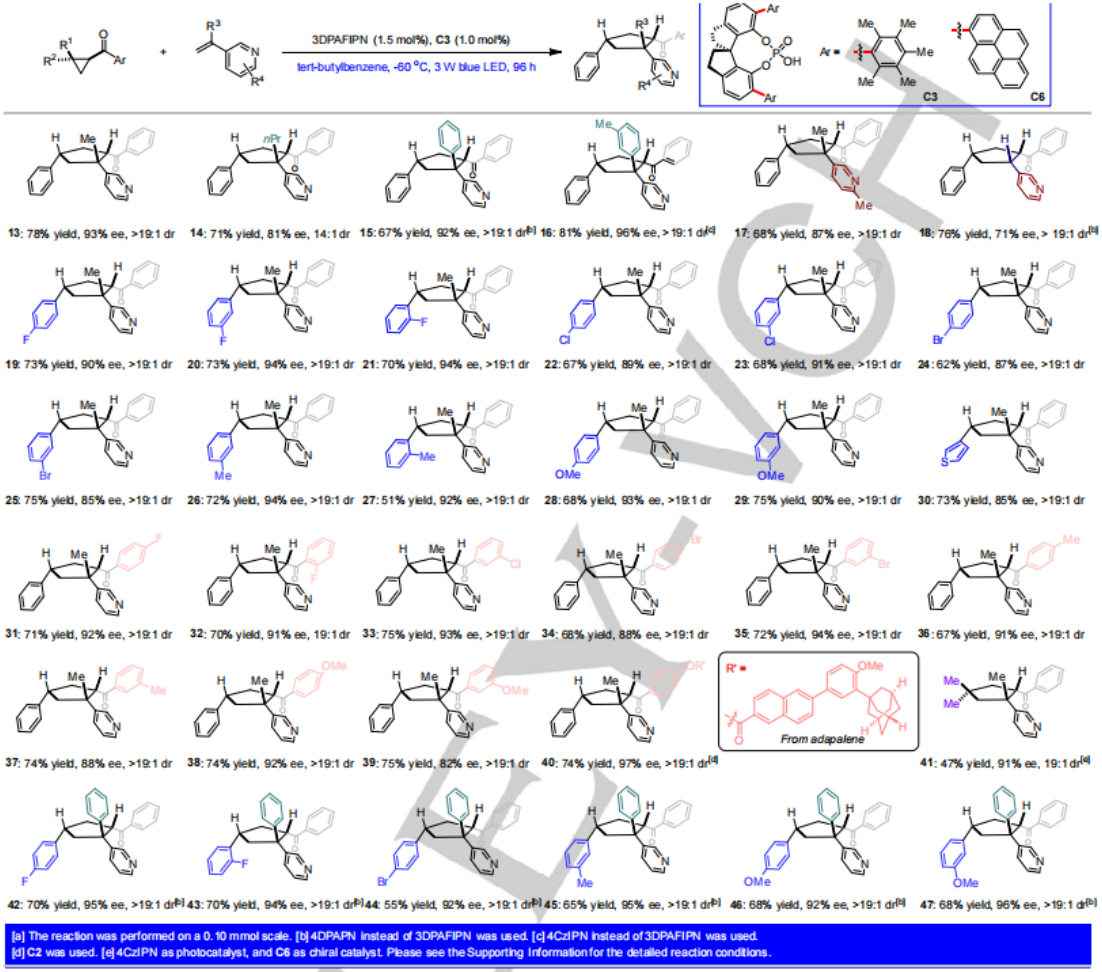
光促[3+2]环加成反应



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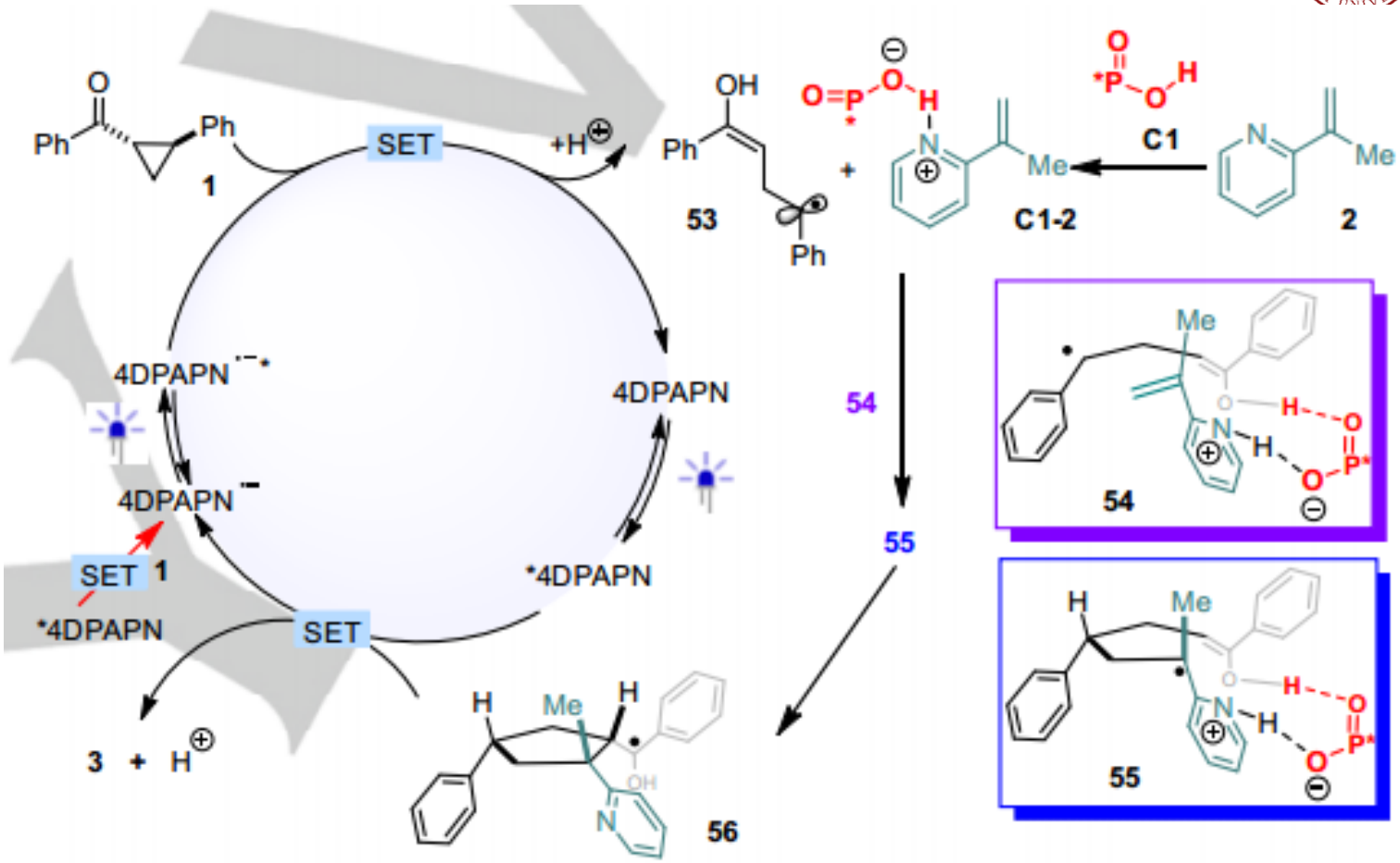
光促[3+2]环加成反应



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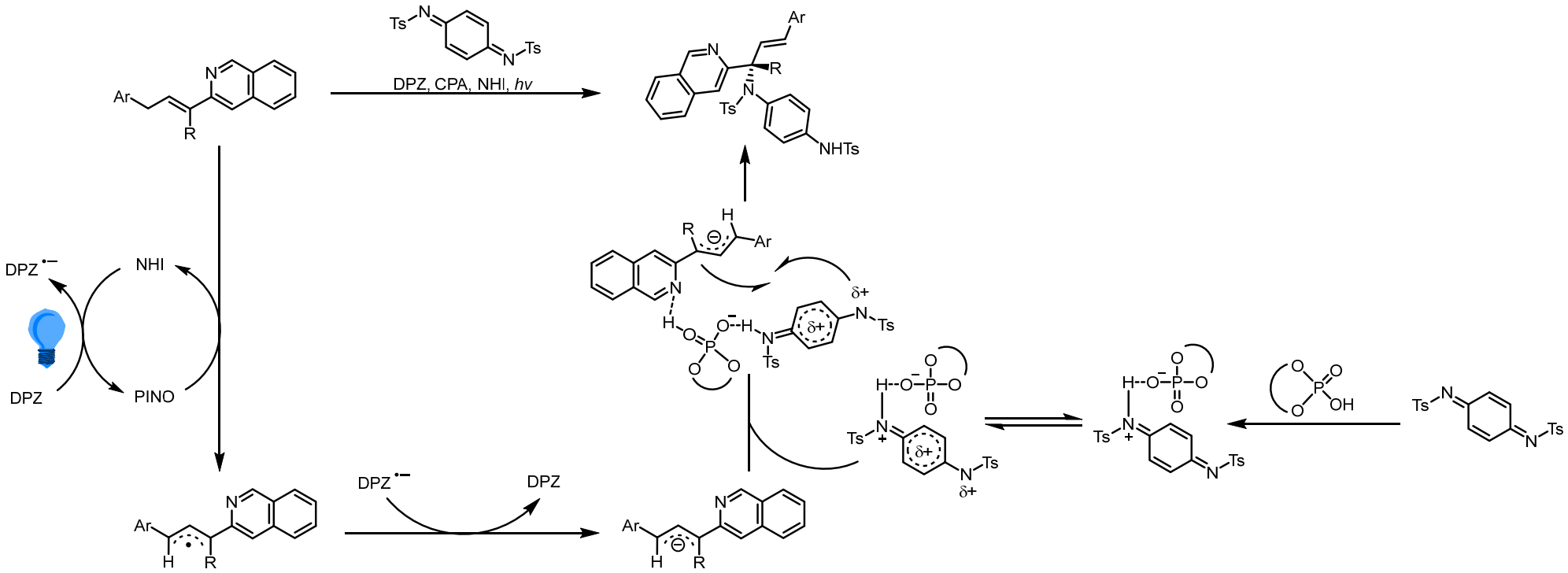
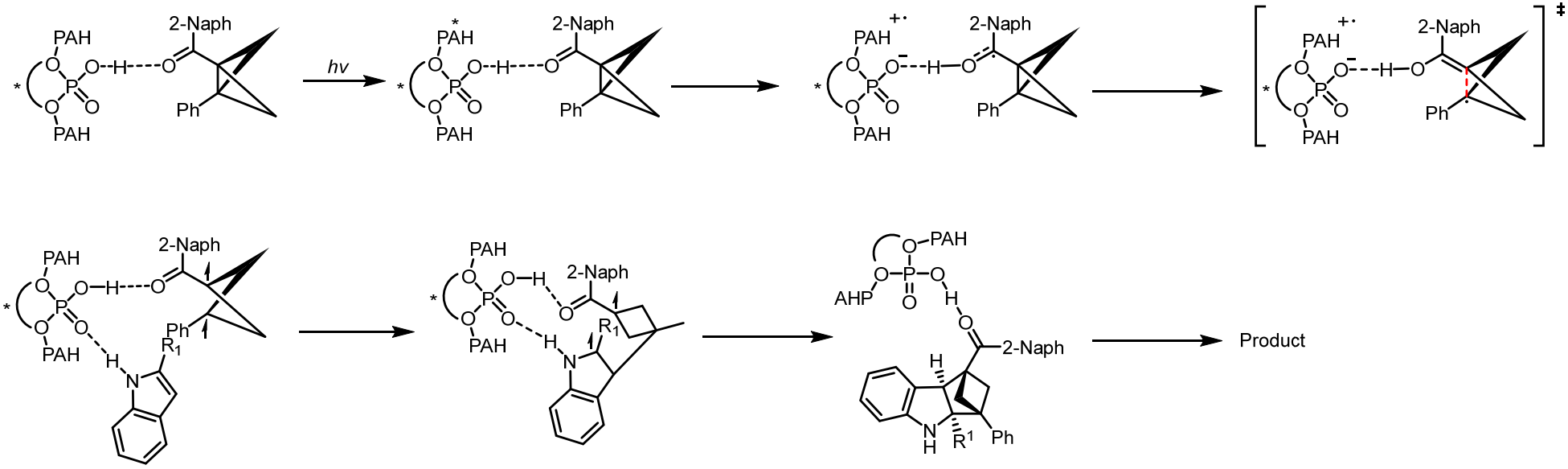
Proposal



Proposal



汇报结束 感谢聆听！

X L E R O W J S V] S Y V P M W X I R M R K %

同舟共济