

Jennifer M. Schomaker Group' s Research

Metal Catalyzed Nitrene Transfer Reaction

Reporter Zhang Jun-Chun

Date 2026.9.11

1

Professor Introduction

2

Earlier Nitrene Transfer Reaction

3

Ag Catalyzed Nitrene Transfer Reaction

4

Ag Catalyzed Nitrene Transfer Asymmetric Reaction

5

Conclusion and Proposal



Professional experience



Jennifer M. Schomaker

2009 - present Professor, University of Wisconsin–Madison (威斯康星大学麦迪逊分校).

2007 - 2009 Postdoctoral Fellow, University of California, Berkeley; Advisor: Prof. Robert G. Bergman and F. Dean Toste (金催化, 手性抗衡阴离子).

2001 - 2006 Ph.D., Michigan State University (密歇根州立大学); Advisor: Prof. Babak Borhan (生物有机化学、合成化学和有机光谱学).

1994 - 1998 M.S., Central Michigan University (中央密歇根大学); Advisor: Prof. Thomas J. Delia (杂环化学);

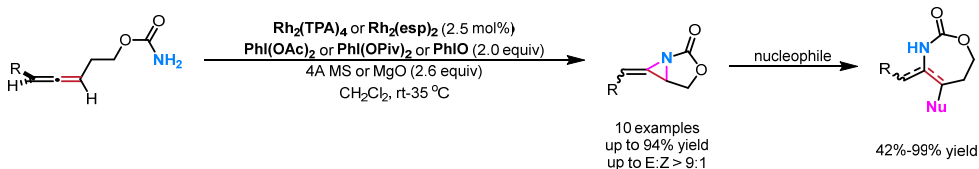
1990 - 1994 B.S., Saginaw Valley State University (塞基诺州立大学);

Research

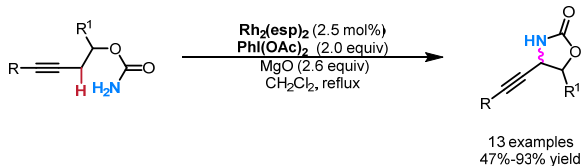
- (1) Total synthesis of natural and unnatural products with intriguing biological activities;
- (2) C-H functionalization reactions;
- (3) Unified strategies for the syntheses of N-heterocycles via aziridinium ylides.

2 Earlier Nitrene Transfer Reaction

(a) 2011, 1



(b) 2011, 11



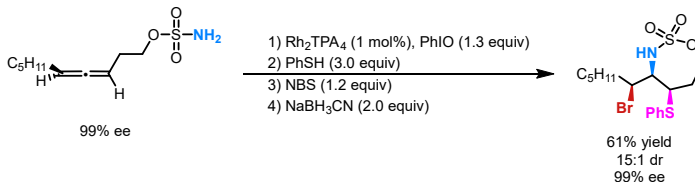
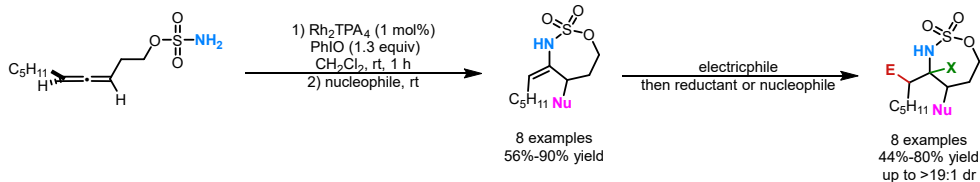
(a) *Org. Lett.* **2011**, 13, 1924. (b) *Org. Lett.* **2012**, 14, 280.

2 Earlier Nitrene Transfer Reaction



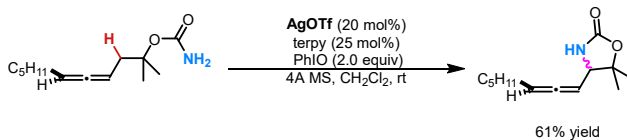
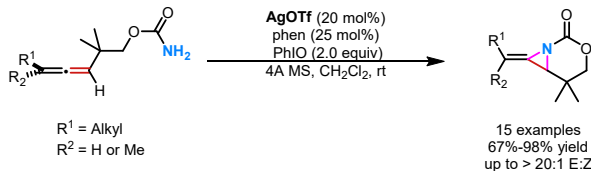
The Yang Research Group
Precise Synthesis Lab at Tongji University

(a) 2012, 6

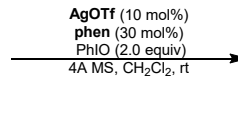
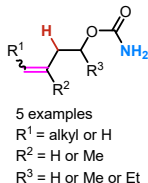
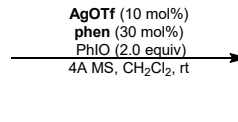
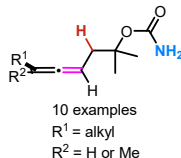
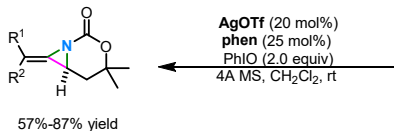


(a) *J. Am. Chem. Soc.* **2012**, *134*, 10807.

(a) 2012, 11

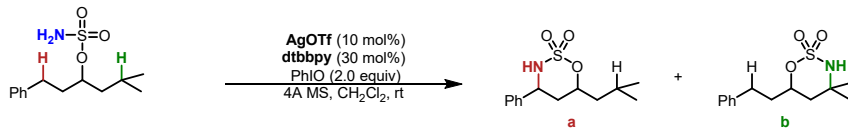
(a) *Org. Lett.* **2013**, *15*, 290.

(a) 2013, 11

(a) *J. Am. Chem. Soc.* **2013**, 135, 17238.

(a) 2014, 11

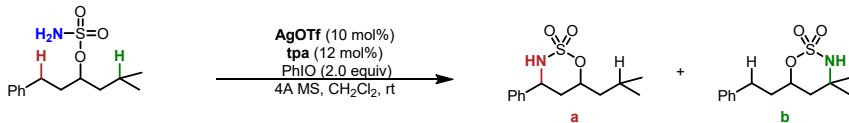
Condition A



1: 2.8

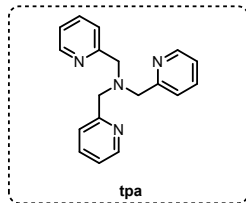
76% yield

Condition B

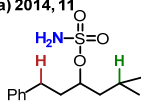


2.4: 1

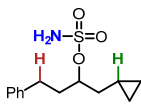
84% yield

(a) *J. Am. Chem. Soc.* **2014**, *136*, 16720.

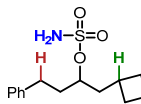
(a) 2014, 11



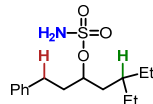
A 19% 56%
B 60% 24%
> 19:1 dr, *syn* main



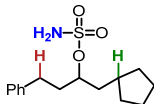
A 28% 0%
B 63% 0%
> 19:1 dr, *syn* main



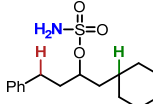
A 27% 30%
B 64% 21%
> 19:1 dr, *syn* main



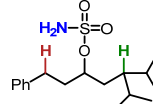
A 13% 68%
B 65% 22%
> 19:1 dr, *syn* main



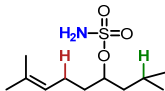
A 14% 67%
B 54% 38%
> 19:1 dr, *syn* main



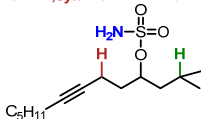
A 9% 72%
B 73% 20%
> 19:1 dr, *syn* main



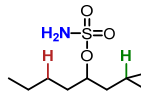
A 21% 54%
B 63% 0%
> 19:1 dr, *syn* main



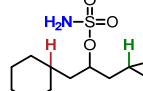
A 28% (3.7:1 *syn:anti*) 30%
10% aziridination product
B 60% (12:1 *syn:anti*) 24%



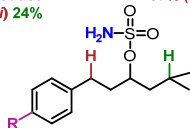
A 21% (1.2:1 *syn:anti*) 51%
B 37% (2.2:1 *syn:anti*) 26%



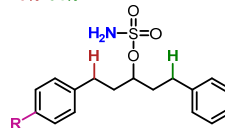
A 0% 64%
B 0% 94%



A 74% 21%
B 36% 50%

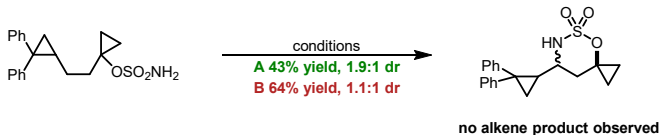
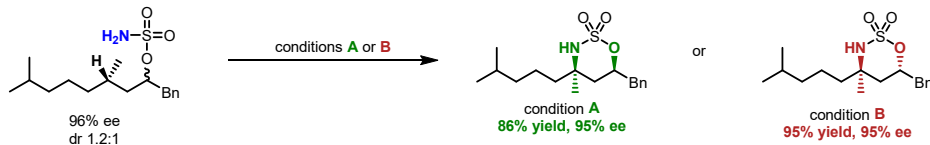
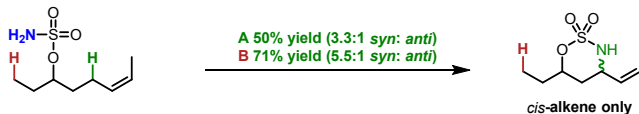


OMe	Me	Br	CF ₃
A 31% 38%	A 25% 52%	A 16% 44%	A 11% 69%
B 70% 15%	B 66% 15%	B 55% 33%	B 42% 54%

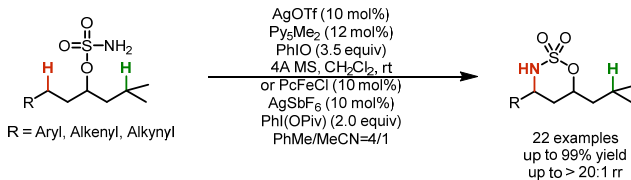
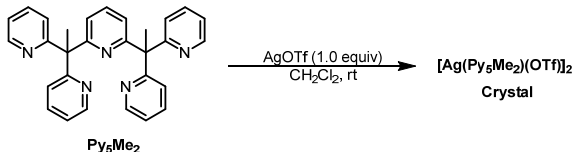


OMe	Me	Br	CF ₃
A 44% 23%	A 39% 28%	A 34% 37%	A 21% 53%
B 51% 23%	B 45% 31%	B 33% 58%	B 19% 61%

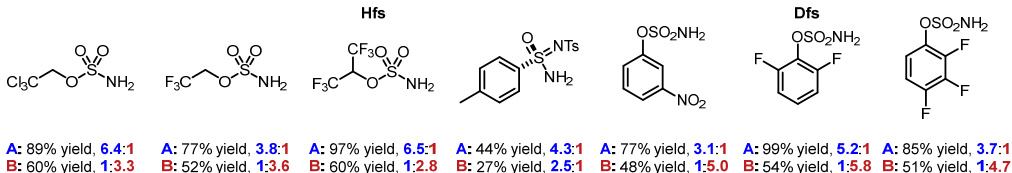
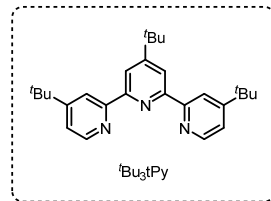
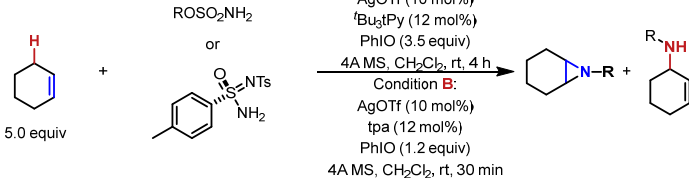
(a) 2014, 11



(a) 2016, 5



(a) 2016, 10

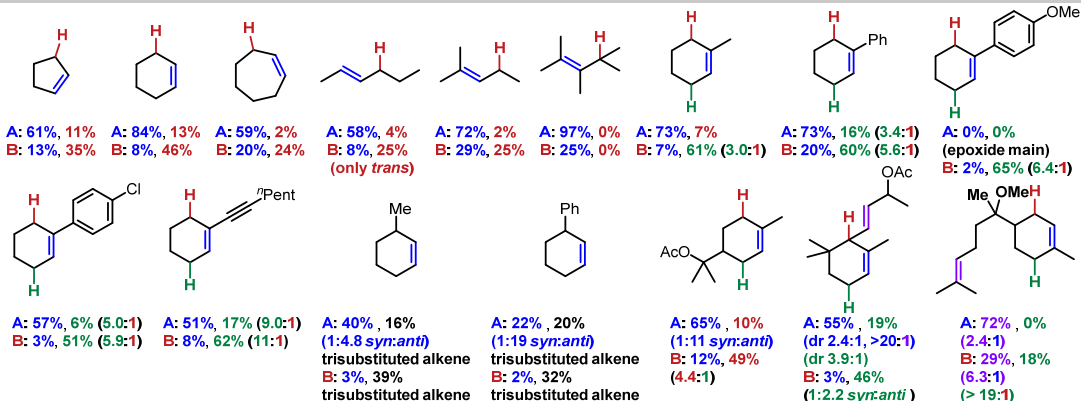
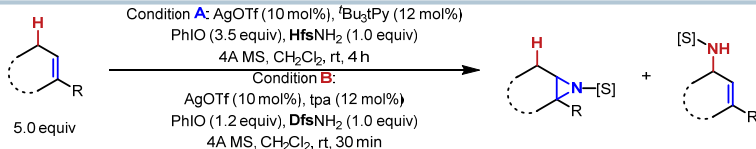


3 Ag Catalyzed Nitrene Transfer Reaction



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(a) 2016, 10

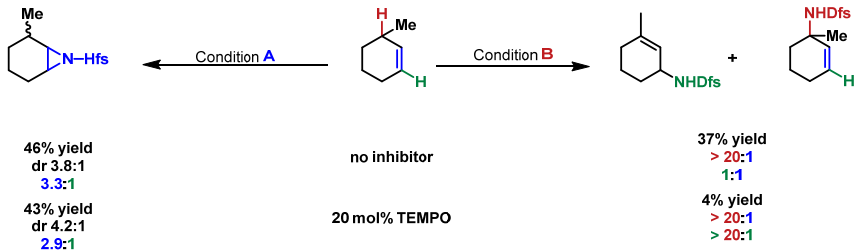
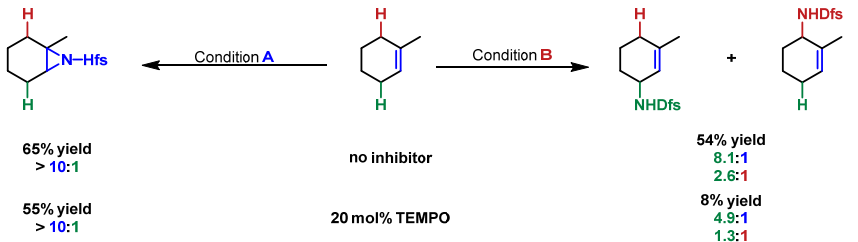


3 Ag Catalyzed Nitrene Transfer Reaction



The Yang Research Group
Precise Synthesis Lab at Tongji University

(a) 2016, 10

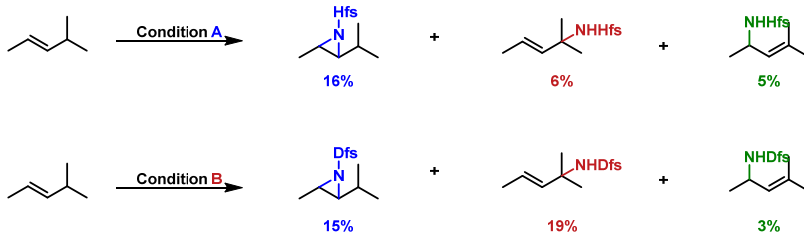
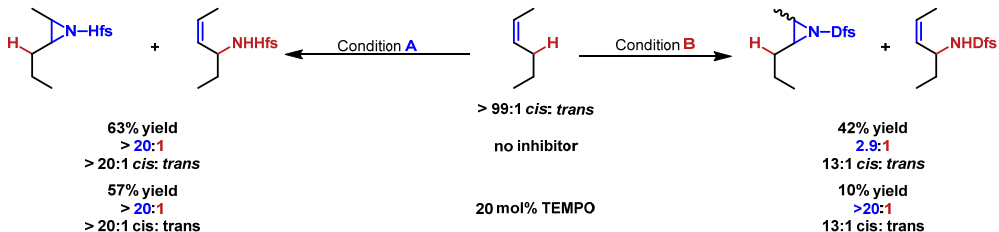


3 Ag Catalyzed Nitrene Transfer Reaction

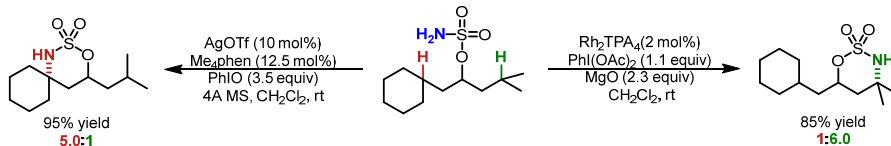


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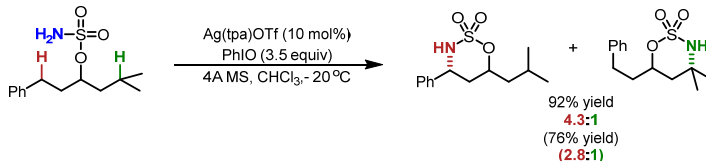
(a) 2016, 10



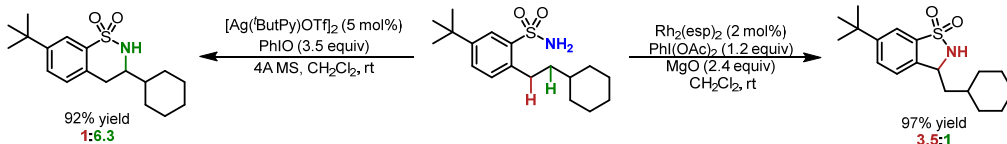
(a) 2017, 5



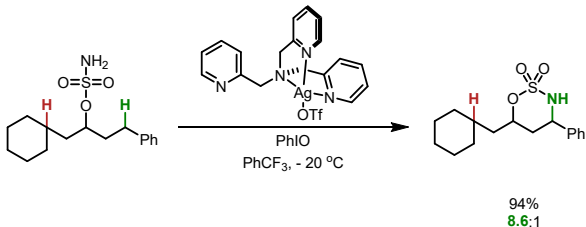
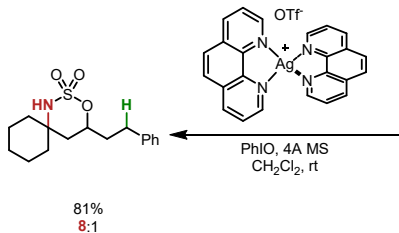
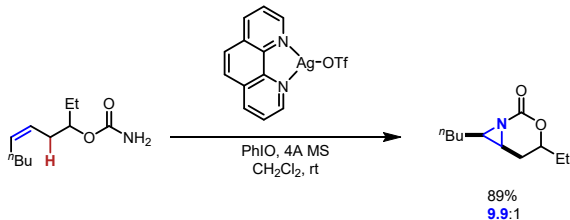
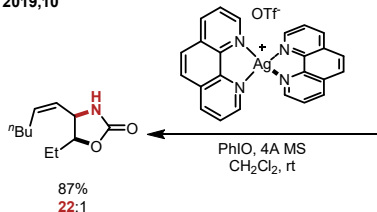
(b) 2017, 11



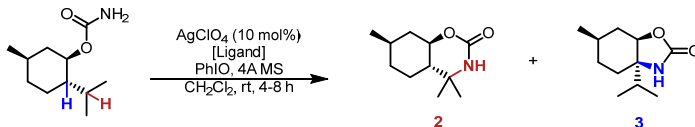
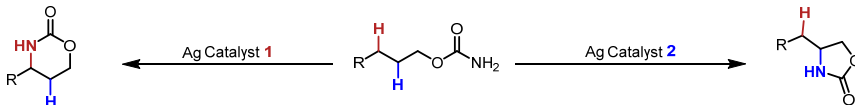
(c) 2019, 5

(a) *Chem. Commun.* **2017**, 53, 4346. (b) *J. Am. Chem. Soc.* **2017**, 139, 17376. (c) *Chem. Commun.* **2019**, 55, 7362.

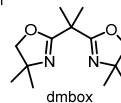
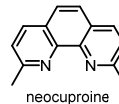
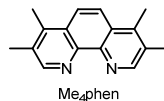
(a) 2019,10

(a) *Nat. Catal.* **2019**, 2, 899.

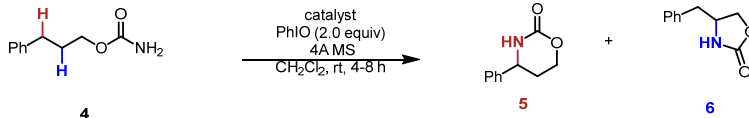
(a) 2019,10



entry	Ligand (mol%)	2 yield	3 yield
1	tpa (10)	18%	73%
2	^t Bu ₃ Py (10)	17%	71%
3	Me ₄ phen (10)	73%	19%
4	Me ₄ phen (30)	4%	89%
5	neocuproine (10)	70%	30%
6	dmbox (10)	84%	15%
7	dmbox (30)	84%	16%
8	Py₅Me₂ (10)	n.d.	84%

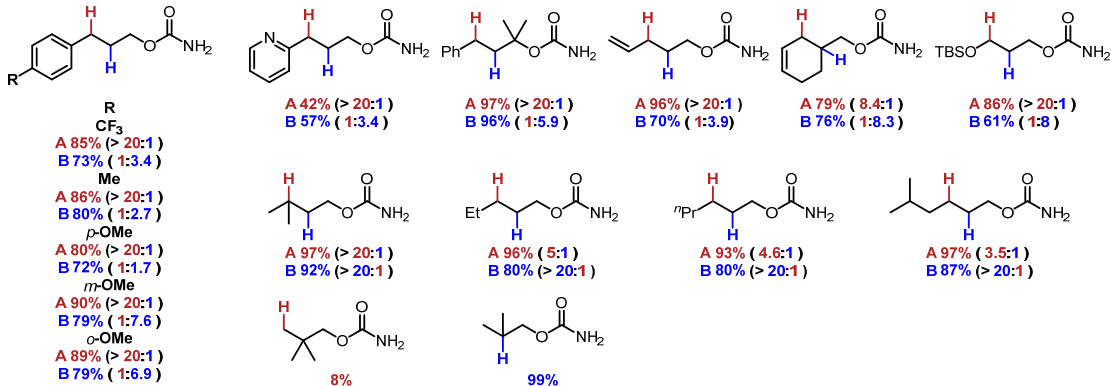
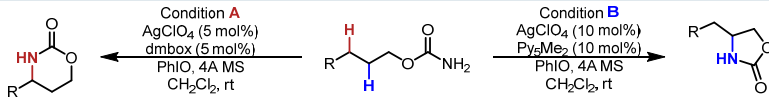


(a) 2019,10



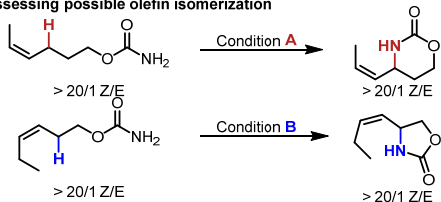
entry	catalyst (mol%)	5:6	total yield	4
1	AgClO ₄ /dmbox (5)	5 only	95%	n.d.
2	AgClO ₄ /Py ₅ Me ₂ (10)	1:3.3	85%	n.d.
3	Rh ₂ (esp) ₂ (5)	1:1.1	39%	30%
4	Rh ₂ (tpa) ₄ (5)	1:1.4	41%	43%
5	Rh ₂ (OAc) ₄ (5)	1:2.8	15%	56%
6	[FePc]SbF ₆ (10)	1:1.8	11%	62%
7	[Mn(^t BuPc)]SbF ₆ (10)	1:2.5	7%	72%
8	Ru ₂ (hp) ₂ Cl (2.5)	n/a	<4%	74%
9	Cu(CH ₃ CN) ₄ PF ₆ (10) bisimine ligand	5 only	54%	43%

(a) 2019,10

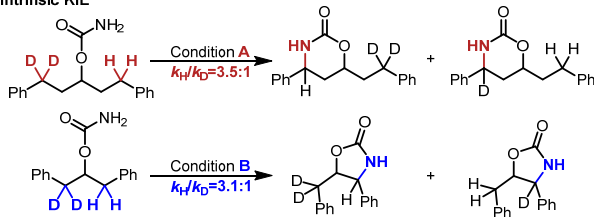


(a) 2019,10

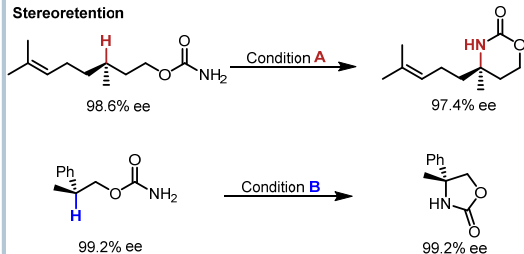
Assessing possible olefin isomerization



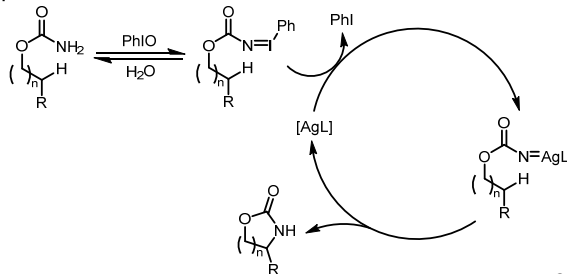
Intrinsic KIE



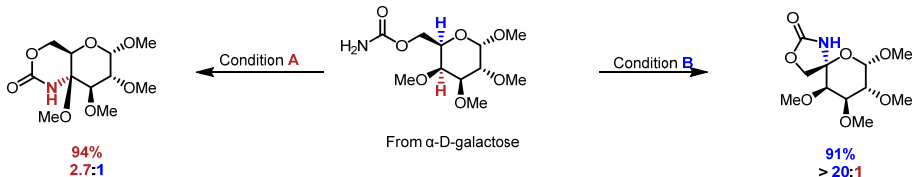
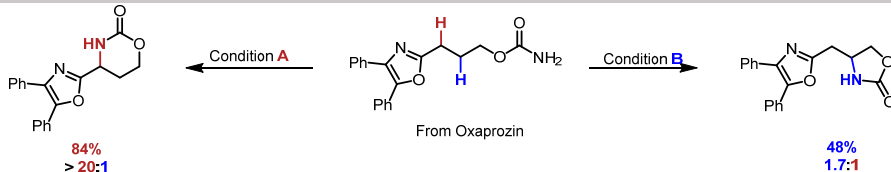
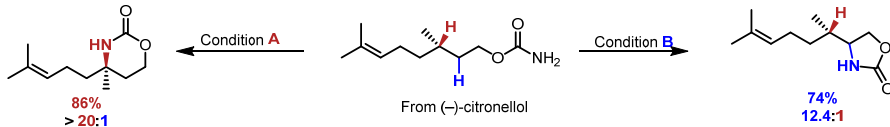
Stereoretention



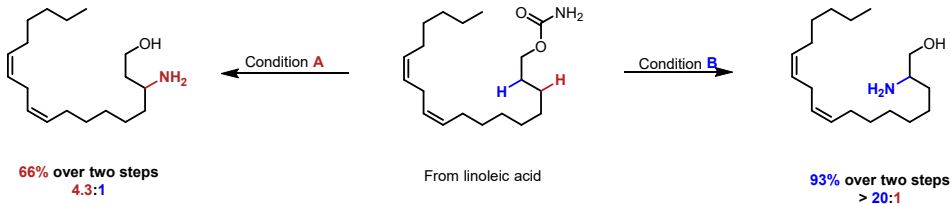
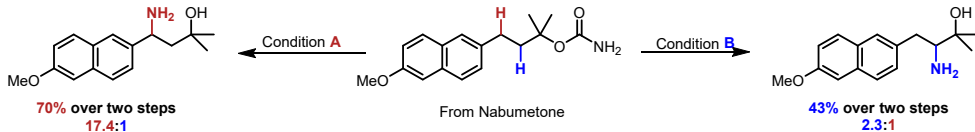
Proposed Mechanism



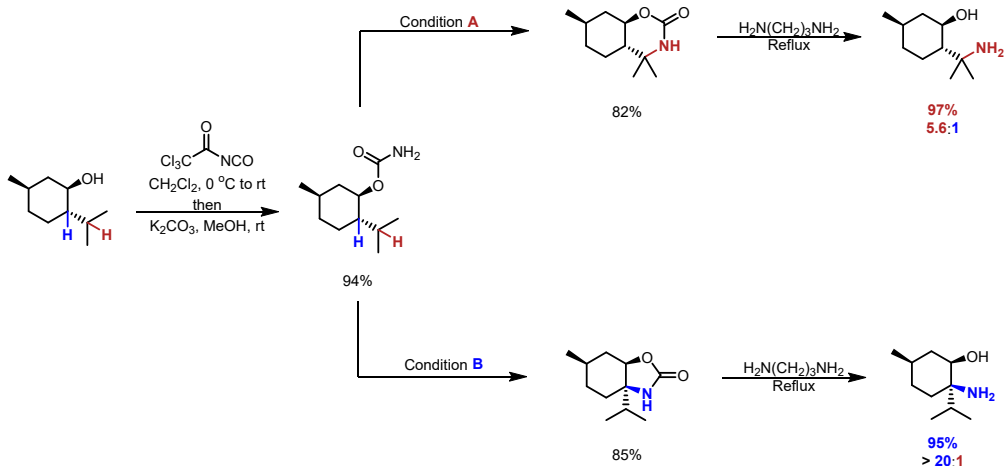
(a) 2019,10



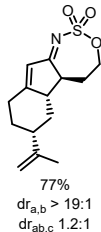
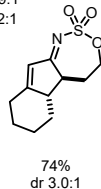
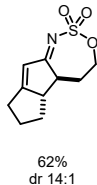
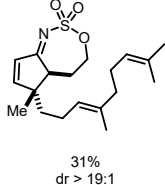
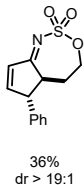
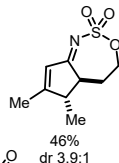
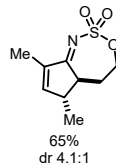
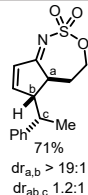
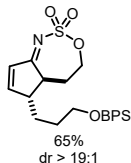
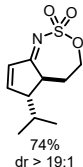
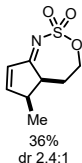
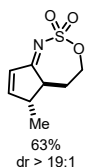
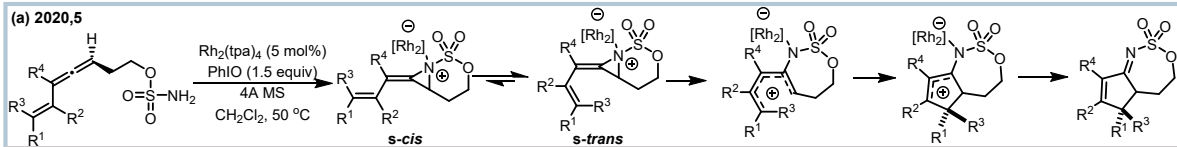
(a) 2019,10



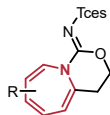
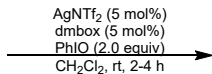
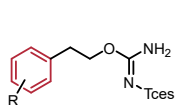
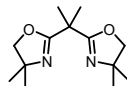
(a) 2019,10



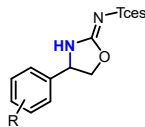
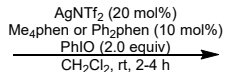
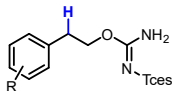
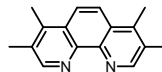
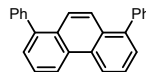
(a) 2020,5



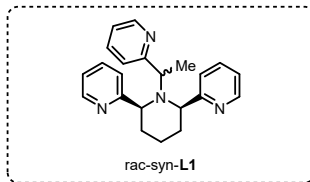
(a) 2024,7

24 examples
36%-98% yield

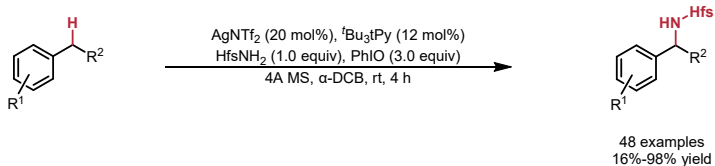
dmbox

23 examples
36%-90% yieldMe₄phenPh₂phen

(a) 2025,2



(b) 2026,3

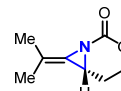
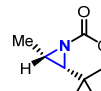
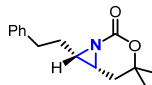
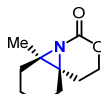
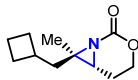
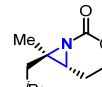
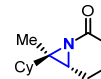
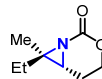
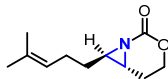
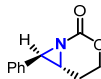
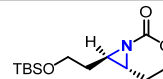
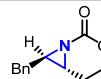
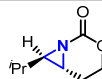
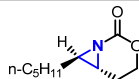
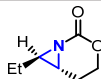
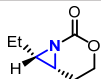
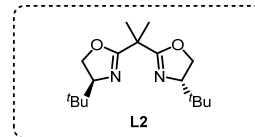
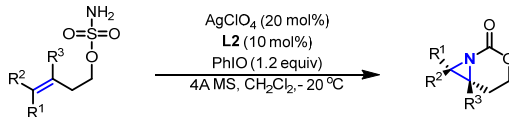


Ag Catalyzed Nitrene Transfer Asymmetric Reaction



The Yang Research Group
Precise Synthesis Lab at Tongji University

(a) 2017,6

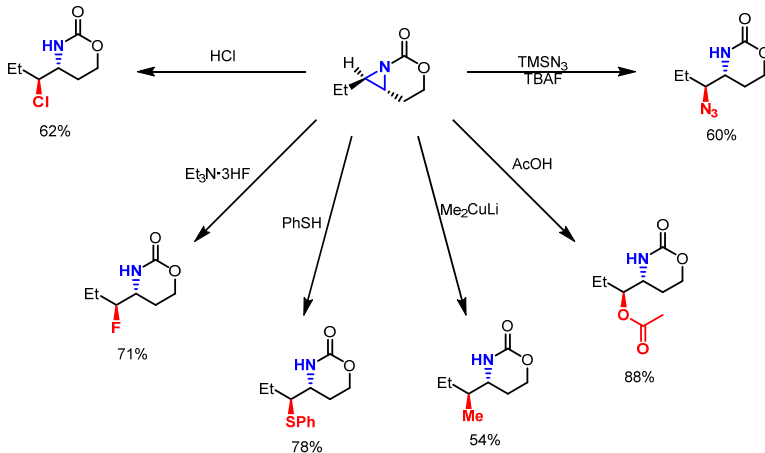


Ag Catalyzed Nitrene Transfer Asymmetric Reaction



The Yang Research Group
Precise Synthesis Lab at Tongji University

(a) 2017,6

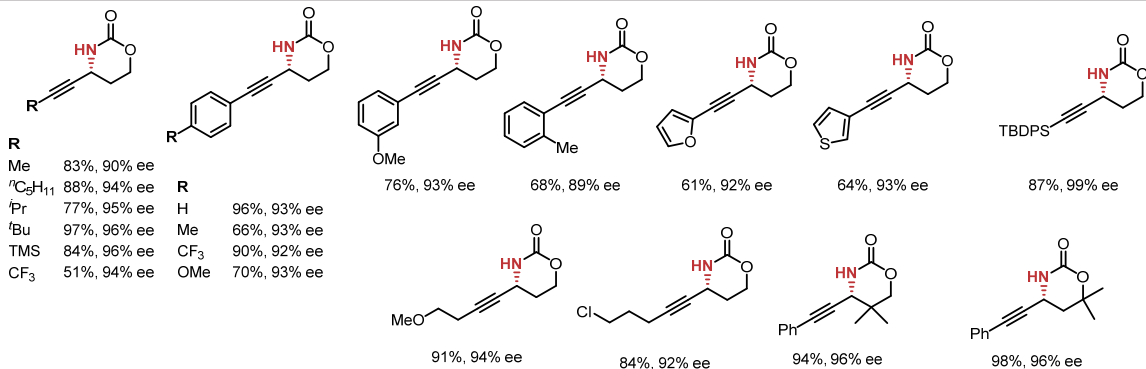
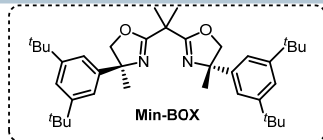
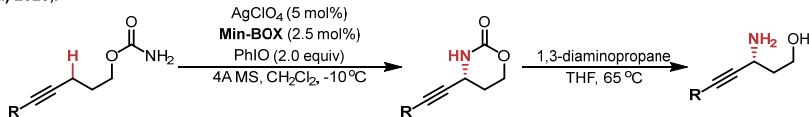


Ag Catalyzed Nitrene Transfer Asymmetric Reaction



The Yang Research Group
Precise Synthesis Lab at Tongji University

(a) 2020,7

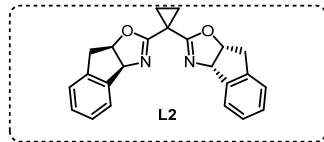
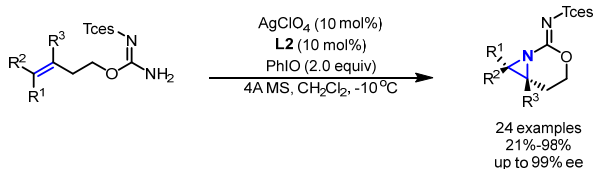


Ag Catalyzed Nitrene Transfer Asymmetric Reaction

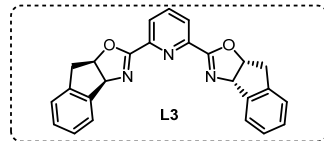
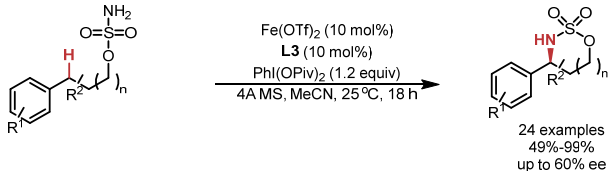


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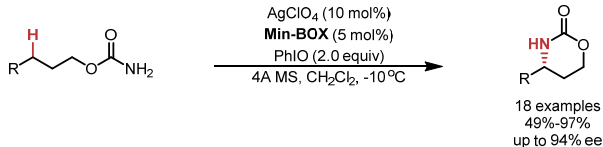
(a) 2023,11



(b) 2025,2



(c) 2025,8

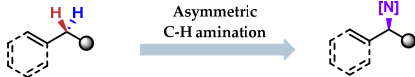


Ag Catalyzed Nitrene Transfer Asymmetric Reaction

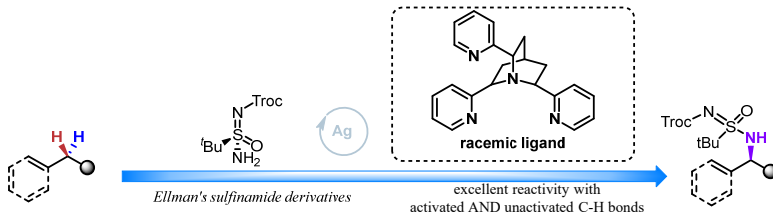


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Precise Synthesis Lab at Tongji University

(a) 2026,4



- substrate-specific tailored catalysts
- tedious purification for non-ideal enantioselectivity
- limited late-stage applicability
- harsh conditions
- low reactivity and selectivity
- neat or large excess of substrates

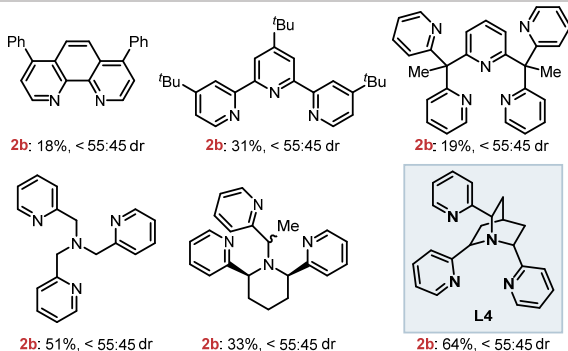
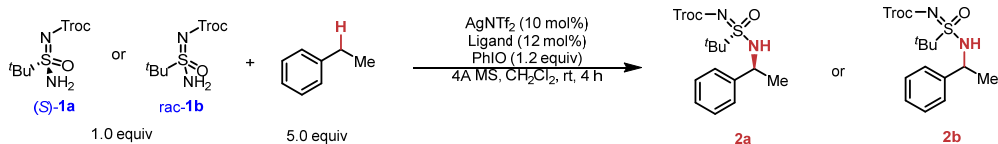


Ag Catalyzed Nitrene Transfer Asymmetric Reaction



The Yang Research Group
Precise Synthesis Lab at Tongji University

(a) 2026,4



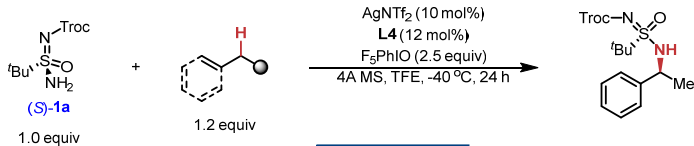
entry	variations	yield	dr
1	TFE	90%	55:45
2	(S)-1a, TFE	93%	73:27
3	(S)-1a, PhEt (1.2 equiv), TFE	47%	78:22
4	(S)-1a, PhEt (1.2 equiv), TFE, 0 °C	72%	77:23
5	(S)-1a, PhEt (1.2 equiv), F ₅ PhIO, TFE, 0 °C	86%	71:29
6	(S)-1a, PhEt (1.2 equiv), F ₅ PhIO, TFE, -40 °C, 24 h	86%	79:21

Ag Catalyzed Nitrene Transfer Asymmetric Reaction

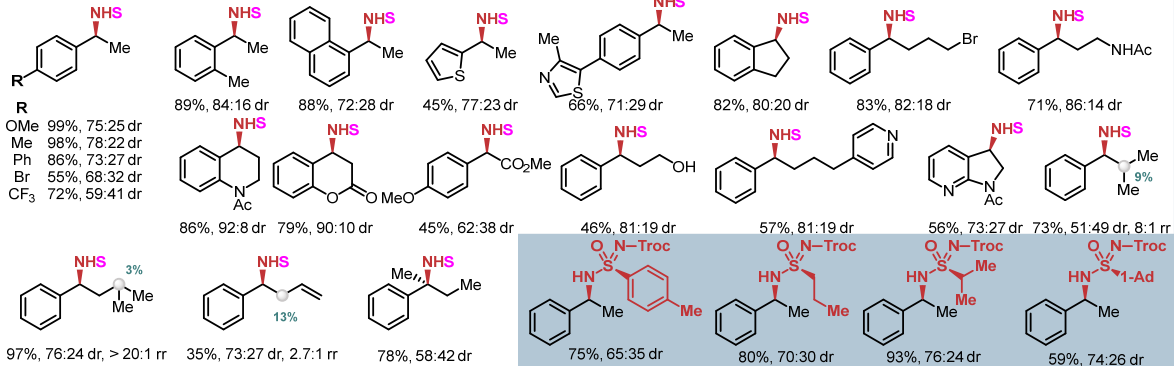


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(a) 2026,4



Benzylic C-H bonds



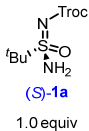
(a) *Science* **2026**, 392, 6796.

Ag Catalyzed Nitrene Transfer Asymmetric Reaction

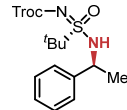
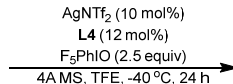
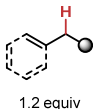


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(a) 2026,4



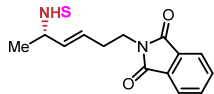
+



S =



Other Activated C-H bonds



50%, 70:30 dr, > 20:1 rr



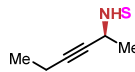
77%, 69:31 dr



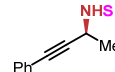
86%, 63:37 dr



50%, 74:26 dr, 2.2:1 rr



23%, 70:30 dr



30%, 73:27 dr

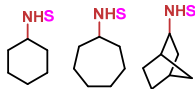


97%, 66:34 dr



98%, 67:33 dr

Unactivated C-H bonds



70%



79%



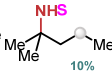
72%



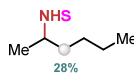
75%



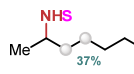
99%



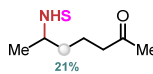
70%
7:1 rr



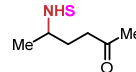
56%
57:43 dr
2:1 rr



45%
55:45 dr
1.2:1 rr



75%
53:47 dr
3.6:1 rr



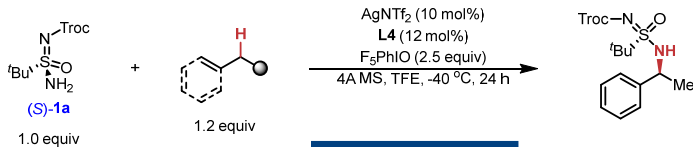
34%
53:47 dr
> 20:1 rr

Ag Catalyzed Nitrene Transfer Asymmetric Reaction

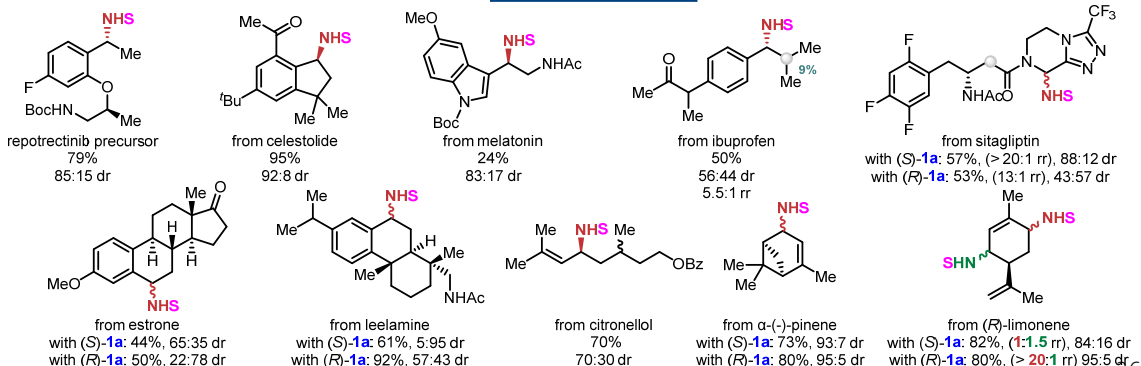


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Late-Stage C-H Amination

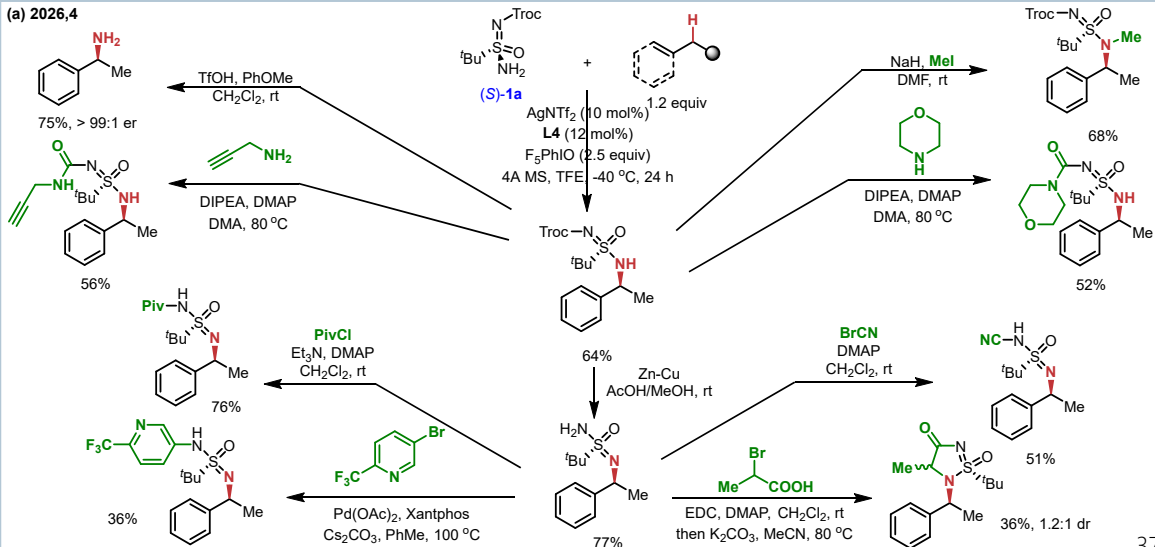


Ag Catalyzed Nitrene Transfer Asymmetric Reaction



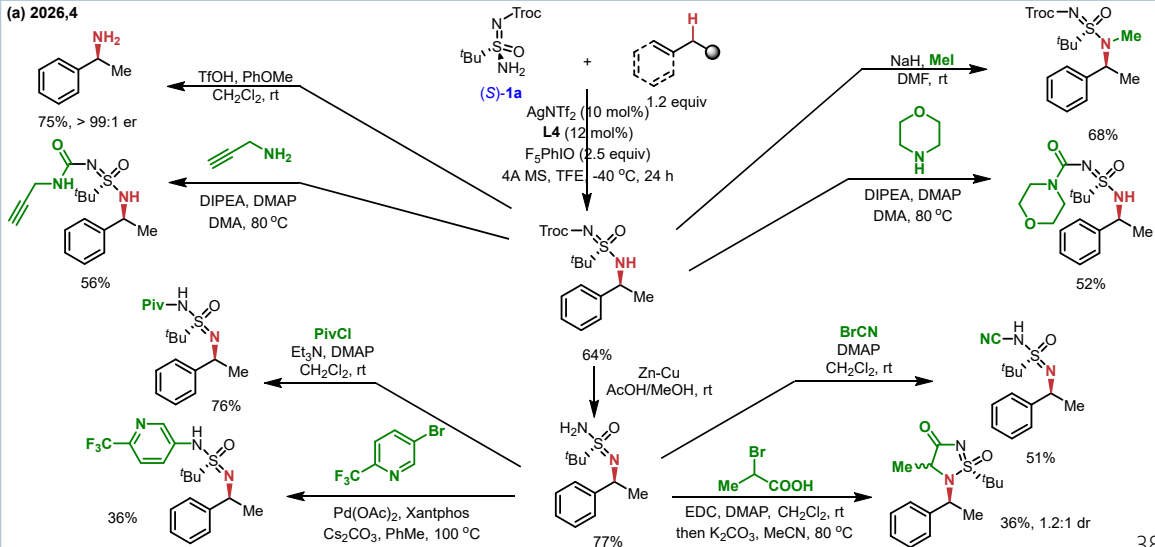
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(a) 2026,4



(a) *Science* **2026**, 392, 6796.

(a) 2026,4

(a) *Science* 2026, 392, 6796.

