The Yang Research Group
Precise Synthesis Lab at Tongji University

Alkene Functionalization by Metal-Nitrene

Reporter: Junchun Zhang

2025.3.14

Contents

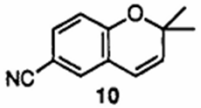
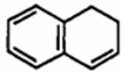
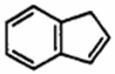
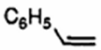
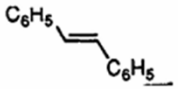
Cu Nitrene

Table I. Asymmetric Aziridination of 6-Cyano-2,2-dimethylchromene Catalyzed by CuOTf in the Presence of Ligands 3–9[a]

	ligand						
	3	4	5	6	7	8	9
ee (%)[b]	50	64	72	81	42	>98	92
total catalysts turnovers[c]	10	3.6	3.6	8.2	3.6	16	6.1

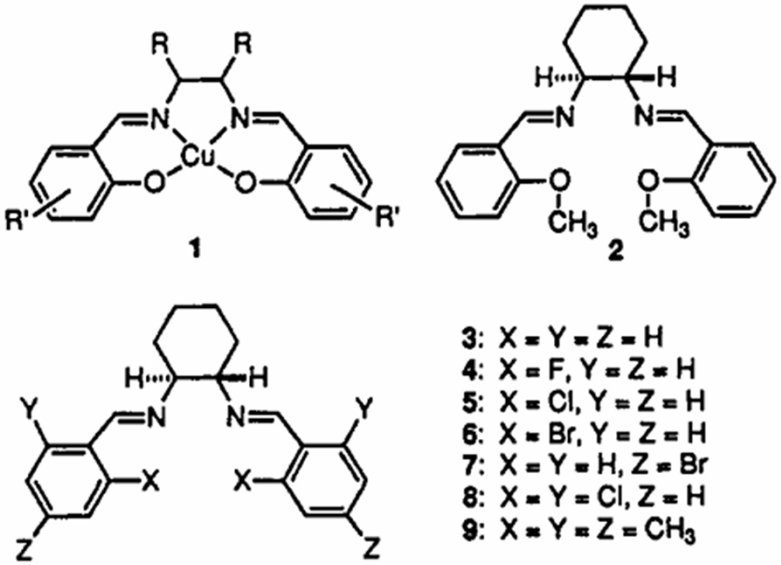
[a] Reactions were carried out at −78 °C with 5 mol % catalyst following the procedure described in note 14. [b] Determined by HPLC analysis of crude reaction mixtures using a commercial Whelk-O column (Regis). [c] Determined by HPLC analysis of crude reaction mixtures after reaction progress had ceased. In all cases, no significant products other than aziridine were detected.

Table II. Asymmetric Aziridination of Alkenes Catalyzed by (*S*,*S*)-8/CuOTf

substrate	aziridine yield (%)[a]	ee (%)[b]	aziridine config[c]
 10	75	>98	(3*R*,4*R*)-(+)
	70	87	(1*R*,2*S*)-(+)
	50	58	(1*R*,2*S*)-(−)
	79	67 (cis)	(1*R*,2*S*)-(−)
	(cis = trans, 3:1) 79	81 (trans) 66	(1*S*,2*S*)-(−) (*R*)-(−)[d]
	nd[e]	30	nd[e]

Aziridination by PhINTs

Chart I



Eric N. Jacobsen, *J. Am. Chem. Soc.* **1993**

Cu Nitrene

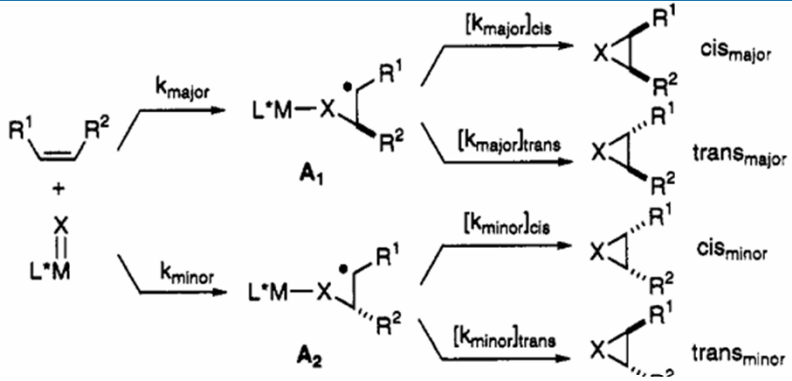
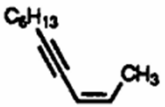
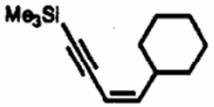
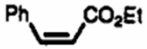
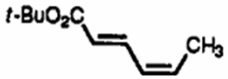
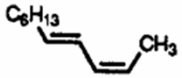
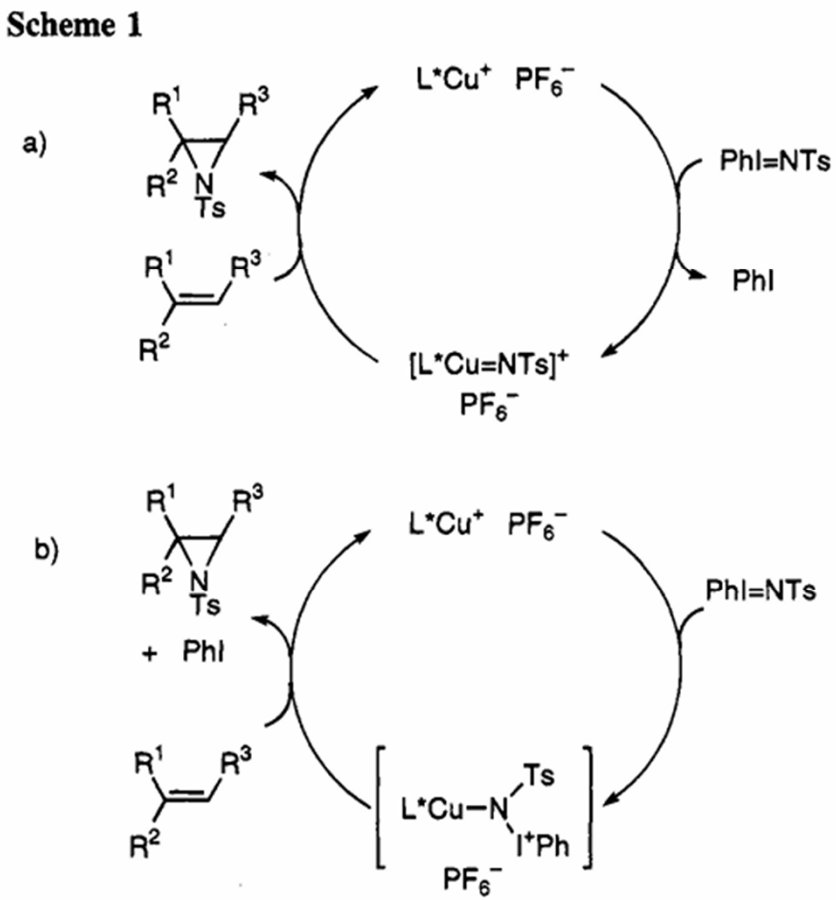


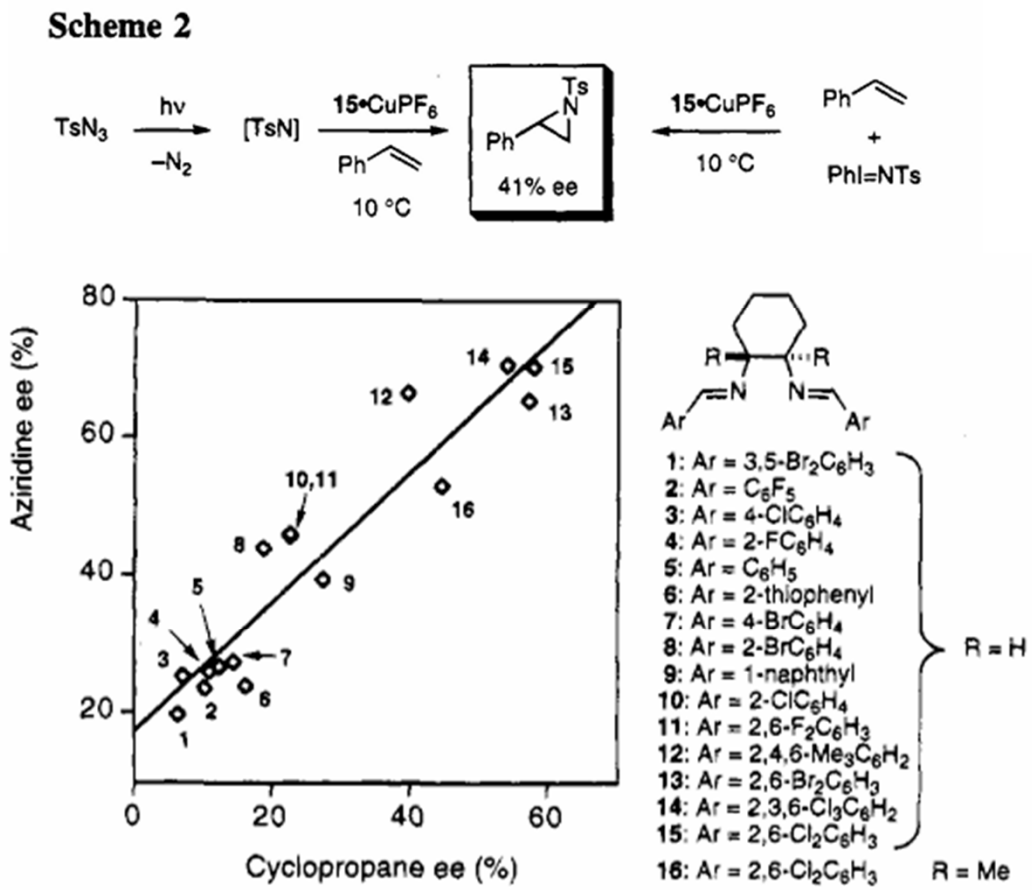
Table 1. Nonstereospecific, Enantioselective Oxidation of Cis Disubstituted Alkenes

entry	substrate	reaction[a]	ee_{cis} (%): ee_{trans} (%)	% cis/% trans	ee_{facial}[b]	$[cis/trans]_{major}/[cis/trans]_{minor}$[c]
1		E[d]	88:71	4.9	85	2.6
2		E[e]	43:90	0.62	72	0.13 (1:7.6)
3		E[e]	64:98	0.19	93	0.047 (1:21)
4		E[f]	92:64	4.0	86	5.3
5		E[e]	14:66	0.14	60	0.27 (1:3.7)
6		E[g]	55:92	0.91	74	0.14 (1:7.0)
7		A[h]	67:81	3.0	70	0.52 (1:1.9)

Eric N. Jacobsen, *J. Am. Chem. Soc.* **1994**

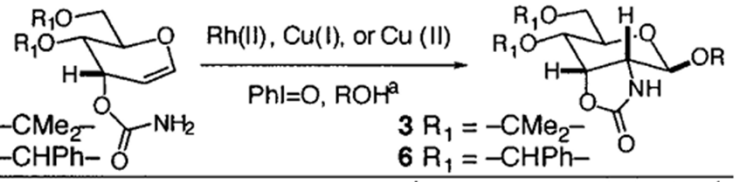
Cu Nitrene

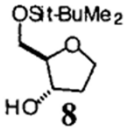
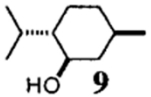




Eric N. Jacobsen, *J. Am. Chem. Soc.* **1995**

Cu Nitrene

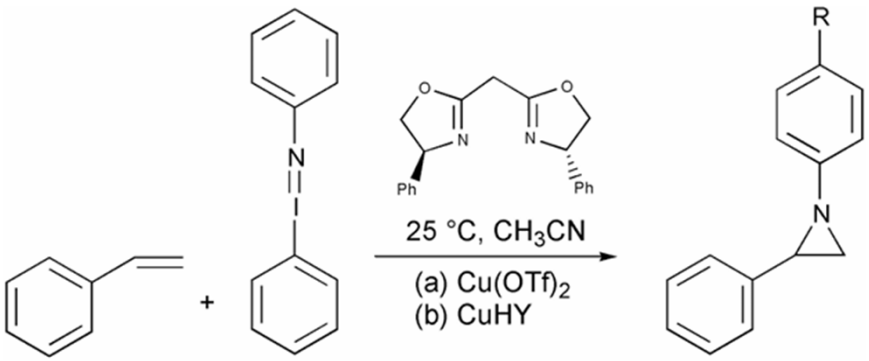


Entry	Allal	ROH	Catalyst[b] (equiv)	Product (% Yield[c])	β:α[d]
1	**2**	*i*-PrOH	A (0.1)	**3b** (75)	β only
2	**2**	**7**	A (0.1)	**3a** (58)	>20:1
3	**2**	 **8**	A (0.1)	**3e** (47[e])	>10:1
4	**2**	 **9**	A (0.1)	**3f** (65[f], 71[g])	>35:1
5	**5**	**9**	A (0.1)	**6a** (63[h])	>50:1
6[i]	**2**	*i*-PrOH	B (0.2)	**3b** (47)	β only
7[i]	**5**	*i*-PrOH	B (0.2)	**6b** (38)	β only
8	**2**	**9**	C (0.2)	**3f** (49[j])	>20:1

[a] Typical reaction conditions: ROH (5 equiv), PhI=O (1.8–2.0 equiv), 4 Å molecular sieves, CH_2Cl_2, 23 °C, 18–25 h. [b] Catalysts: A, $Rh_2(OAc)_4$; B, $Cu(MeCN)_4PF_6$; C, $Cu(acac)_2$. [c] Isolated yield after silica gel chroma-

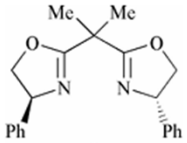
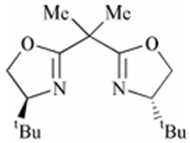
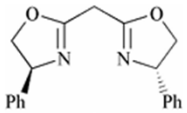
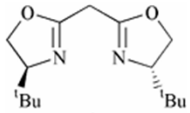
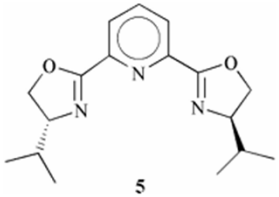
Christian M. Rojas, *Org. Lett.* **2002**.

Cu Nitrene



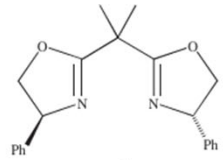
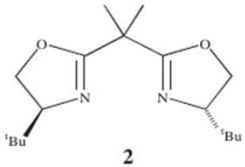
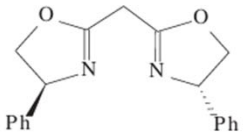
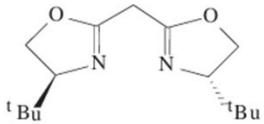
Graham J. Hutchings, *J. Chem. Soc., Perkin Trans.* **2001**

Table 6 Effect of bis(oxazoline) on the aziridination of styrene[a]

Bis(oxazoline)	PhI=NTs Yield (%)	PhI=NTs Ee (%)	PhI=NNs Yield (%)	PhI=NNs Ee (%)
 1	78 (91)	76 (73)	78 (96)	85 (81)
 2	58 (78)	24 (35)	68 (79)	82 (43)
 3	70 (74)	77 (28)	80 (85)	82 (54)
 4	80 (85)	28 (8)	72 (42)	77 (31)
 5	55 (70)	5 (11)	29 (42)	6 (15)

Cu Nitrene

Effect of bis(oxazoline) on the aziridination of styrene[a]

Bis(oxazoline)	PhI=NTs		PhI=NNs	
	Yield (%)	ee (%)	Yield (%)	ee (%)
 **1**	78(91)	76(73)	78(96)	85(81)
 **2**	58(78)	24(13)	68(79)	83(43)
 **3**	70(14)	77(28)	80(85)	82(54)
 **4**	80(85)	28(8)	72(42)	77(31)

Note: Figures in parenthesis are for $Cu(OTf)_2$ under identical conditions. All reactions followed by dissolution of the nitrene donor. Reaction times similar for all oxazolines: $Cu(OTf)_2$, 1 and 1.5 h for PhI=NTs and PhI=NNs and for CuHY, 3 and 5 h for PhI=NTs and PhI=NNs.

[a]25 °C, acetonitrile, nitrene donor: styrene = 1.5 : 1 mol ratio, CuHY.

Graham J. Hutchings, *Topics in Catalysis* **2003**.

Cu Nitrene

Table 1 Aziridination of styrene derivatives[a]

Substituent[b]	Cu–HY		
	Yield (%)	Ee (%)	Substituted benzaldehydes (%)
None	78	85	16
2-Cl	83	88	22
3-Cl	82	95	19
4-Cl	85	94	19
2-F	82	72	13
3-F	75	58	16
4-F	83	53	18
2-Br	60	85	15
3-Br	59	64	13
4-Br	90	74	17
2-CH_3	60	79	3
3-CH_3	75	48	3
4-CH_3	83	67	15
α-CH_3	57	34	12
trans-β-CH_3	42	24	10
4-OCH_3	71	64	20
3-NO_2	63	65	18

Graham J. Hutchings, *Org. Biomol . Chem.,* **2004**.

Cu Nitrene

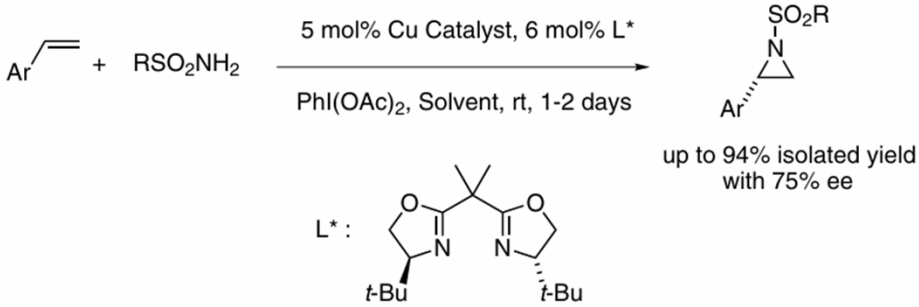
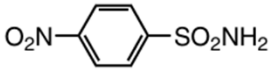
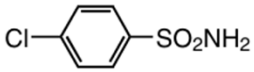
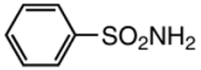
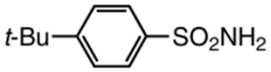
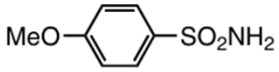
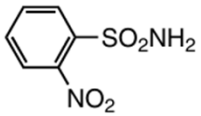
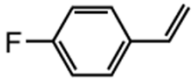
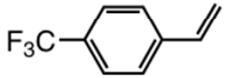
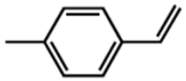
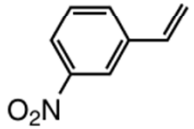
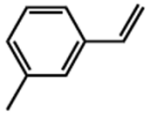


Table 2. Effects of sulfonamides[a]

Entry	Sulfonamide	% Yield[b]	% Ee[c]
1		94 (91)[d]	75 (66)[d]
2		90	52
3		82	50
4		75	44
5		55 (73)[d]	33 (78)[d]
6		66	22
7	$CH_3SO_2NH_2$	86	36

Chi-Ming Che, *Tetrahedron Letters,* **2004**.

Cu Nitrene

Entry	Substrate	Aziridine	% Yield[b]	% Ee[c]
1		**1a**: R = 4-NO_2–Ph **1b**: R = 4-Cl–Ph **1c**: R = 4-Me–Ph	95 95 84	72 51 40
2		**2a**: R = 4-NO_2–Ph **2b**: R = 4-Cl–Ph **2c**: R = 4-Me–Ph	64 68 43	51 43 38
3		**3a**: R = 4-NO_2–Ph **3b**: R = 4-Cl–Ph **3c**: R = 4-Me–Ph	78 80 61	45 43 32
4		**4a**: R = 4-NO_2–Ph **4b**: R = 4-Cl–Ph **4c**: R = 4-Me–Ph	82 89 77	52 48 45
5		**5a**: R = 4-NO_2–Ph **5b**: R = 4-Cl–Ph **5c**: R = 4-Me–Ph	68 78 76	57 42 37

Chi-Ming Che, *Tetrahedron Letters,* **2004**.

Cu Nitrene

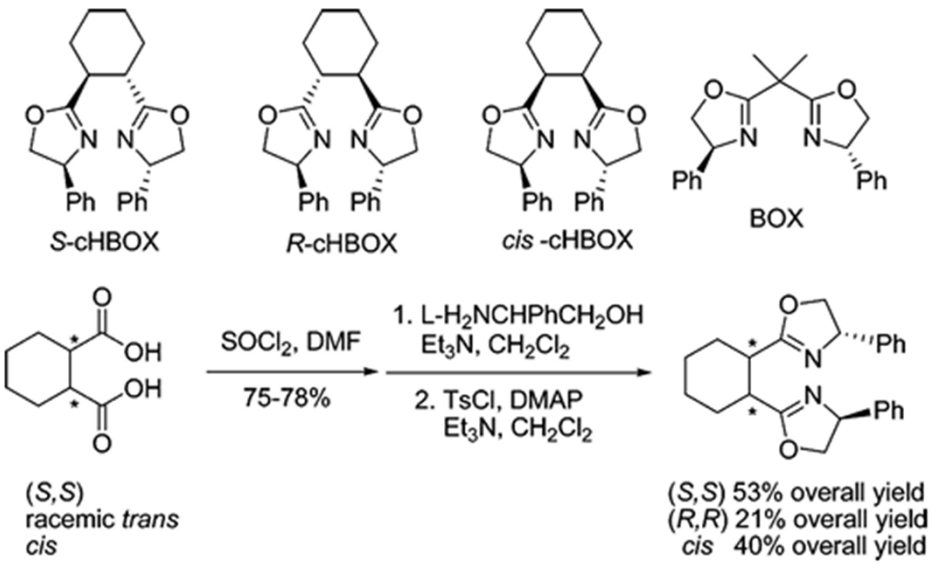
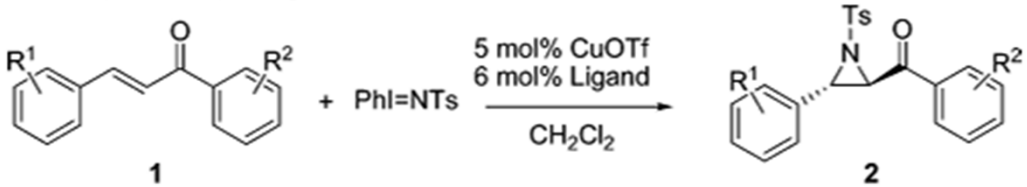


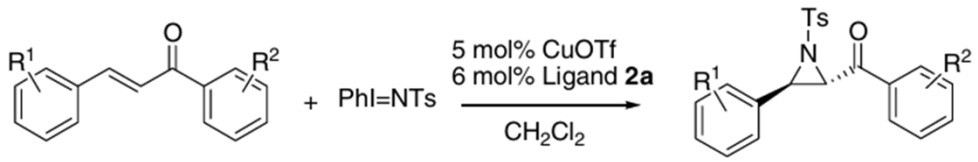
TABLE 1. Asymmetric Aziridination of Chalcones Catalyzed by Ligand and CuOTf



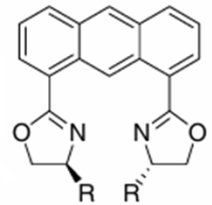
entry	ligand	product	R^1	R^2	yield[a] (%)	ee[b] (%)
1	(*R*)-cHBOX	**2a**	H	H	47	86
2	(*S*)-cHBOX	**2a**	H	H	56	91
3	*cis*-cHBOX	**2a**	H	H	45	80
4	BOX	**2a**	H	H	38	86
5	(*S*)-cHBOX	**2b**	*p*-Me	H	62	94
6	(*S*)-cHBOX	**2c**	*p*-F	H	62	90
7	(*S*)-cHBOX	**2d**	*p*-Cl	H	80	95
8	(*S*)-cHBOX	**2e**	*p*-Me	*p*-Me	50	>99
9	(*S*)-cHBOX	**2f**	H	*p*-Me	71	>99
10	(*S*)-cHBOX	**2g**	H	*p*-MeO	73	97
11	(*S*)-cHBOX	**2h**	*p*-Cl	*p*-Cl	80	95
12	(*S*)-cHBOX	**2i**	*p*-Cl	*p*-Me	72	85
13	(*S*)-cHBOX	**2j**	H	*p*-Br	63	86
14	(*S*)-cHBOX	**2k**	*m*-F	H	64	92
15	(*S*)-cHBOX	**2l**	*p*-CF_3	H	51	80

Jiaxi Xu, *J. Org. Chem.* **2005**.

Cu Nitrene



6 **7**

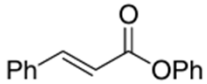
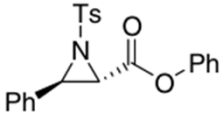
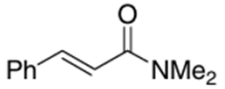
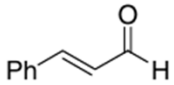
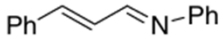
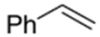
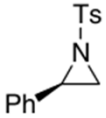
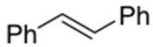
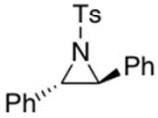
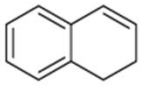
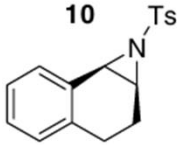


2a: R = $CHMe_2$, 80%
2b: R = CHMeEt, 54%
2c: R = CMe_3, overall yield 56%
2d: R = Bn, 52%
2e: R = Ph, 72%

Entry	Product	R^1	R^2	Yield[a] (%)	ee[b] (%)
1	**7a**	H	H	80	96
2	**7b**	*p*-Me	H	86	98
3	**7c**	*p*-Ph	H	35	87
4	**7d**	*p*-F	H	72	62
5	**7e**	*p*-Cl	H	70	76
6	**7f**	*p*-Br	H	58	52
7	**7g**	*p*-MeO	H	61	37
8	**7h**	*o*-MeO	H	21	27
9	**7i**	*p*-MeS	H	NR	—
10	**7j**	*p*-Me	*p*-Me	59	>99
11	**7k**	H	*p*-Me	92	>99
12	**7l**	H	*p*-F	72	54
13	**7m**	H	*p*-Cl	74	58
14	**7n**	H	*p*-Br	64	50
15	**7o**	H	*p*-NO_2	61	ND
16	**7p**	H	*p*-MeO	74	62
17	**7q**	*p*-Cl	*p*-Cl	68	43
18	**7r**	*p*-Cl	*p*-Me	66	39
19	**7s**	*p*-Me	*p*-Cl	51	68
20	**7t**	*o*-Cl	H	91	79
21	**7u**	*m*-Cl	H	76	84
22	**7v**	*m*-F	H	85	71
23	**7w**	*p*-CF_3	H	69	67

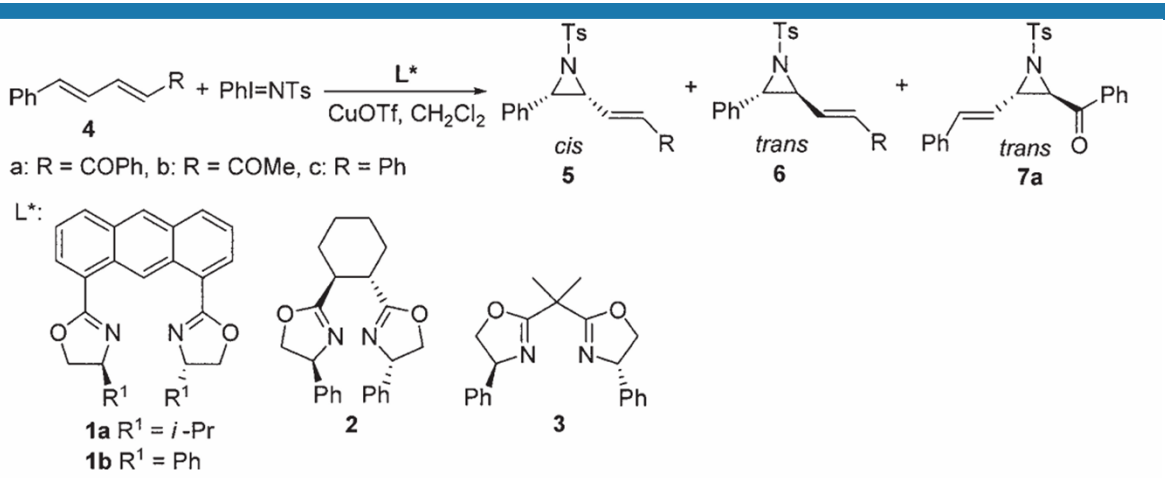
Jiaxi Xu, *Tetrahedron:Asymmetry* **2005**.

Cu Nitrene

Entry	Substrate	Product	Yield (%)[a]	ee (%)	Configuration[e]
1		 **8**	61	44[b]	(2*S*,3*R*)[24]
2			NR		
3			NR		
4			NR		
5		 **9**	92	7[c]	(*R*)[14a]
6		 **10**	71	13[d]	(*S*,*S*)[28]
7		 **11**	63	5[d]	(1*R*,2*S*)[14a]

Jiaxi Xu, *Tetrahedron:Asymmetry* **2005**.

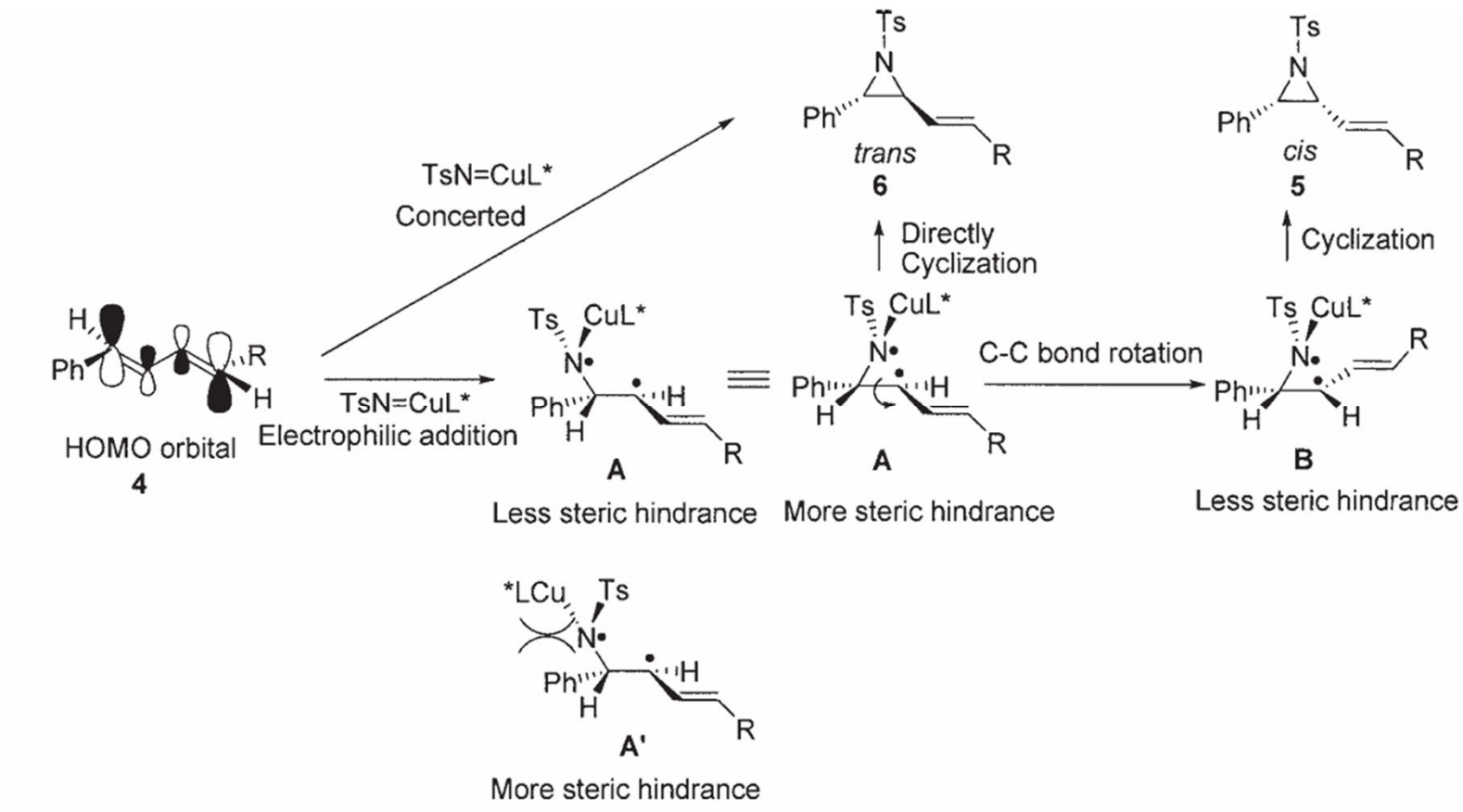
Cu Nitrene



Entry	Diene	Ligand	Yield[a] (%)	Ratio (**5**:**6**:**7**)	Ee%[b] and configuration		
					5	**6**	**7**
1	**4a**	**1a**	64	26:3:71	36 (*E*,2*S*,3*R*)		13 (*E*,2*S*,3*R*)
2	**4a**	**1b**	59	87:13:0	13 (*E*,2*S*,3*R*)		
3	**4a**	**2**	73	99:0:1	−72[c] (*E*,2*R*,3*S*)		−80[c] (*E*,2*R*,3*S*)
4	**4a**	**3**	28	100:0:0	−80[c] (*E*,2*R*,3*S*)		
5	**4b**	**1a**	51	100:0:0	−6[c] (*E*,2*R*,3*S*)		
6	**4b**	**2**	25	100:0:0	−19[c] (*E*,2*R*,3*S*)		
7	**4c**	**1a**	68	26:74	12 (*E*,2*S*,3*R*)	14 (*E*,*S*,*S*)	
8	**4c**	**1b**	32	61:39	22 (*E*,2*S*,3*R*)	24 (*E*,*S*,*S*)	
9	**4c**	**2**	21	68:32	−60[c] (*E*,2*R*,3*S*)	−48[c] (*E*,*R*,*R*)	
10	**4c**	**3**	22	18:82	−21[c] (*E*,2*R*,3*S*)	−34[c] (*E*,*R*,*R*)	

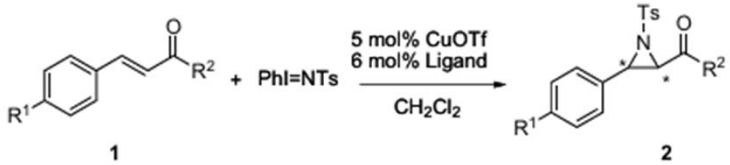
Jiaxi Xu, *Chirality* **2006**.

Cu Nitrene

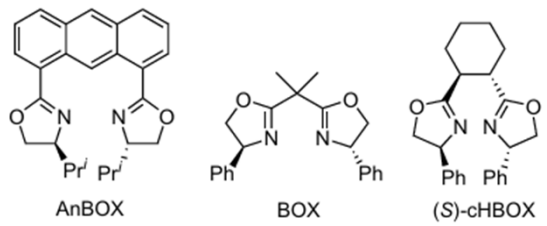


Jiaxi Xu, *Chirality* **2006**.

Cu Nitrene

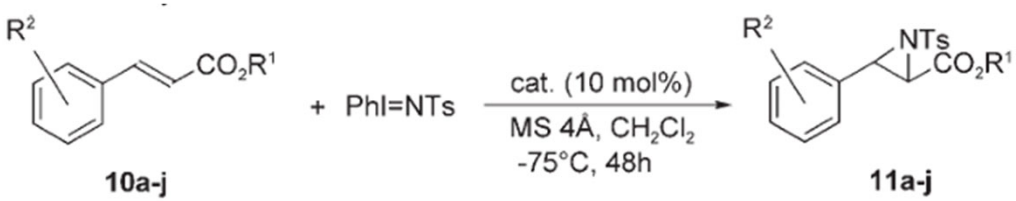


Entry	Ligand	Product	R^1	R^2	Yield[a] (%)	ee[b] (%)	Configuration[c]
1	AnBOX	**2a**	H	4-MeC_6H_4	92	>99	(2*S*,3*R*)
2	AnBOX	**2b**	H	Ph	80	96	(2*S*,3*R*)
3	AnBOX	**2c**	H	4-FC_6H_4	72	54	(2*S*,3*R*)
4	AnBOX	**2d**	H	4-ClC_6H_4	74	58	(2*S*,3*R*)
5	AnBOX	**2e**	H	4-BrC_6H_4	64	50	(2*S*,3*R*)
6	AnBOX	**2f**	H	4-$CF_3C_6H_4$	70	44	(2*S*,3*R*)[d]
7	*S*-cBOX	*ent*-**2f**	H	4-$CF_3C_6H_4$	56	85	(2*R*,3*S*)[d]
8	BOX	*ent*-**2a**	H	4-MeC_6H_4	24	85	(2*R*,3*S*)
9	BOX	*ent*-**2b**	H	Ph	38	86	(2*R*,3*S*)
10	BOX	*ent*-**2c**	H	4-FC_6H_4	10	86	(2*R*,3*S*)
11	BOX	*ent*-**2d**	H	4-ClC_6H_4	10	81	(2*R*,3*S*)
12	BOX	*ent*-**2e**	H	4-BrC_6H_4	12	84	(2*R*,3*S*)
13	BOX	*ent*-**2f**	H	4-$CF_3C_6H_4$	4	65	(2*R*,3*S*)
14	AnBOX	**2g**	H	4-$^iPrC_6H_4$	72	66	(2*S*,3*R*)[d]
15	BOX	*ent*-**2g**	H	4-$^iPrC_6H_4$	6	76	(2*R*,3*S*)[d]
16	*S*-*c*HBOX	*ent*-**2g**	H	4-$^iPrC_6H_4$	24	85	(2*R*,3*S*)[d]
17	AnBOX	**2h**	H	4-$^tBuC_6H_4$	79	70	(2*S*,3*R*)[d]
18	BOX	*ent*-**2h**	H	4-$^tBuC_6H_4$	10	87	(2*R*,3*S*)[d]
19	*S*-*c*HBOX	*ent*-**2h**	H	4-$^tBuC_6H_4$	43	98	(2*R*,3*S*)[d]
20	AnBOX	**2i**	Me	4-$^tBuC_6H_4$	86	71	(2*S*,3*R*)[d]
21	BOX	*ent*-**2i**	Me	4-$^tBuC_6H_4$	7	81	(2*R*,3*S*)[d]
22	*S*-*c*HBOX	*ent*-**2i**	Me	4-$^tBuC_6H_4$	53	89	(2*R*,3*S*)[d]
23	AnBOX	**2j**	H	*trans*-4-Pr-cC_6H_{10}	54	20	(2*S*,3*R*)[d]
24	BOX	*ent*-**2j**	H	*trans*-4-Pr-cC_6H_{10}	9	30	(2*R*,3*S*)[d]
25	*S*-*c*HBOX	**2j**	H	*trans*-4-Pr-cC_6H_{10}	9	48	(2*S*,3*R*)[d]
26	AnBOX	**2k**	H	Me	65	50[c]	(2*S*,3*R*)
27	BOX	*ent*-**2k**	H	Me	15	85	(2*R*,3*S*)
28	*S*-*c*HBOX	*rac*-**2k**	H	Me	37	0	



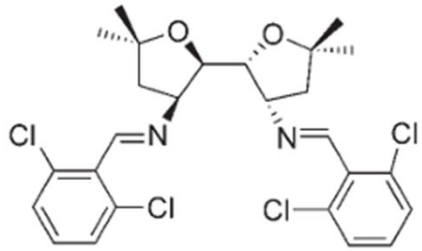
Jiaxi Xu, *Tetrahedron: Asymmetry* **2007**.

Cu Nitrene



Entry	Substrate	R^1	R^2	Yield [%][b]	*ee* [%][c]	Config.[d]
1	**10a**	Me	H	97	87.6	2*S*,3*R* (−)
2	**10b**	Ph	H	96	87.1	2*S*,3*R* (−)
3	**10c**	*t*Bu	H	99	>99	2*S*,3*R* (−)
4	**10d**	*t*Bu	4-F	99	97.8	(−)
5	**10e**	*t*Bu	4-Cl	97	98.1	(−)
6	**10f**	*t*Bu	4-Br	97	98.3	2*S*,3*R* (−)
7	**10g**	*t*Bu	4-Me	86	94.4	(−)
8	**10h**	*t*Bu	4-MeO	95	80.1	(+)
9	**10i**	*t*Bu	2-NO_2	63	98.6	(+)
10	**10j**	*t*Bu	2,3-MeO	67	97.0	(+)

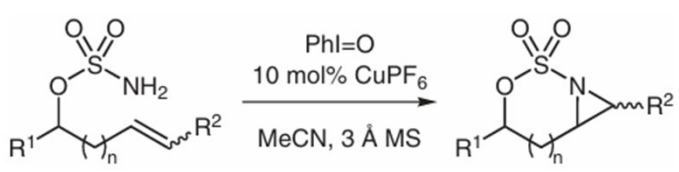
[a] The reactions were carried out with the ratio of **10**/PhI=NTs/**3a**/Cu 5:1:0.11:0.1 in a 0.125 mmol scale of PhI=NTs (0.042 M) in the presence of 100 mg of MS 4 Å. [b] The yield of isolated product. [c] The enantiomeric excess was determined by HPLC on Chiralcel columns. [d] The absolute configurations of **11a–c** and **11k–l** were determined by comparison of their optical rotations with those of literature data.[4b] The absolute configuration of (−)-**11f** was determined to be (2*S*,3*R*) by the Bijvoet method based on the anomalous dispersion of Br heavy atom.[10]

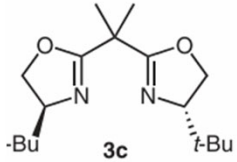


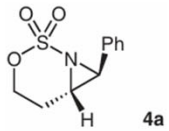
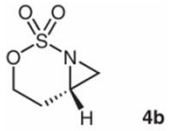
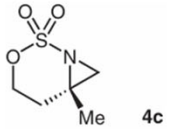
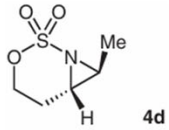
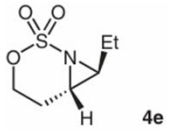
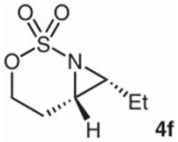
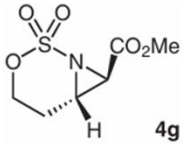
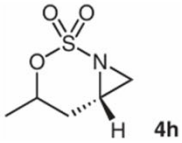
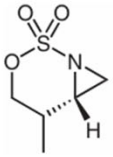
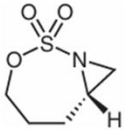
3a

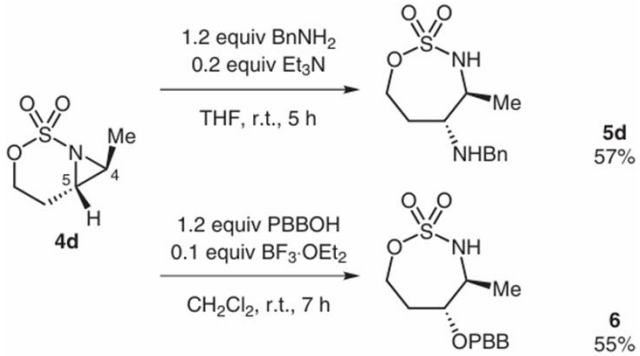
Kuiling Ding, *Chem. Eur. J.* **2006**.

Cu Nitrene



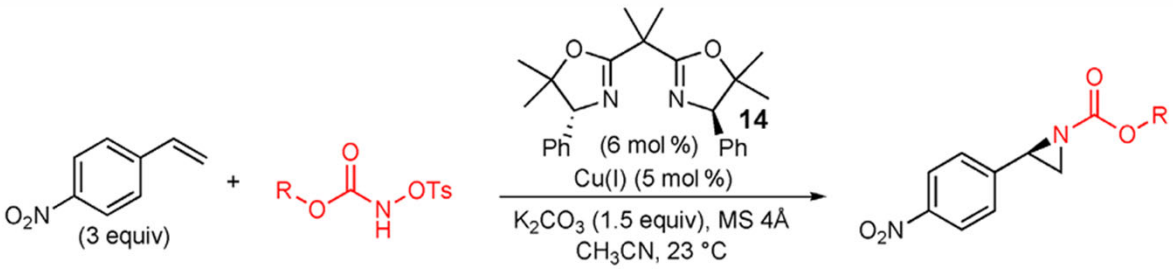


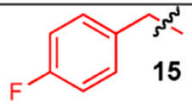
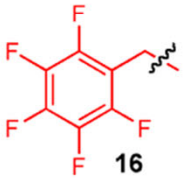
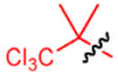
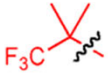
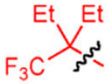
Entry	Product	Yield[b] (%)	ee[c] (%)
1	 **4a**	86	84
2	 **4b**	81	52
3	 **4c**	24	36
4	 **4d**	80	80
5	 **4e**	83	80
6[d]	 **4f**	86	72
7	 **4g**	79	62
8	 **4h**	82 (30:70)[e]	78, 24[f]
9	 **4i**	85 (45:55)[e]	68, 28[f]
10	 **4j**	72	47



Philippe Dauban, *Synthesis* **2007**.

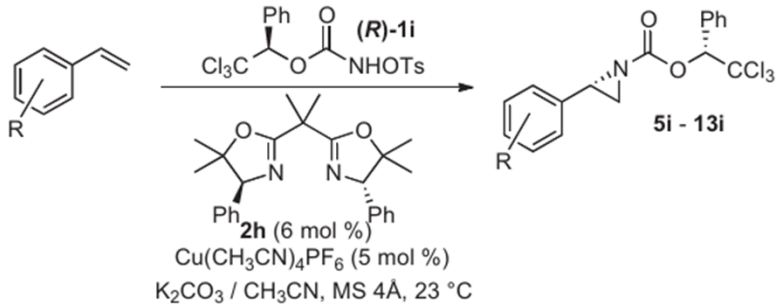
Cu Nitrene

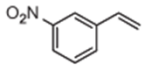
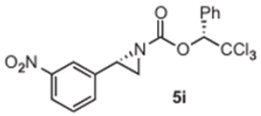
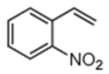
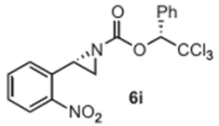
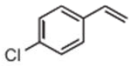
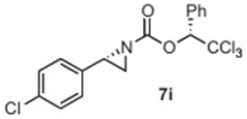
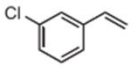
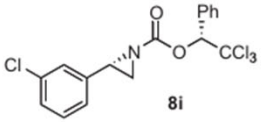
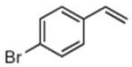
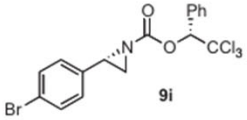
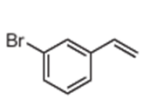
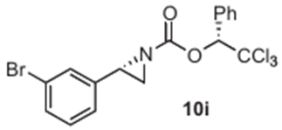
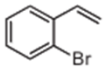
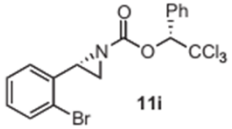
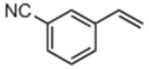
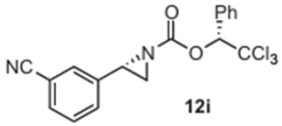


Entry	R	ee[a]	Yields[b]
1	 **15**	13 %	17 %
2	 **16**	20 %	46 %
3	 **17**	85 %	52 %
4		71 %	82 %
5	 **18**	82 %[c]	44 %[c]
6	 **19**	---	decomp

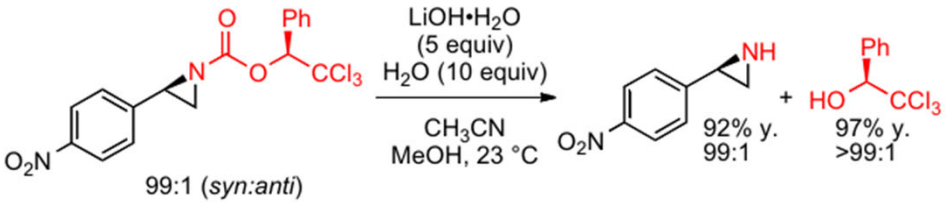
Helene Lebel, *Pure Appl. Chem* **2010**.

Cu Nitrene



Entry	Styrene	Aziridine	Yield[b] (%)	Diastereomeric ratio[c]
1		 **5i**	84	89:11
2		 **6i**	50	93:7
3		 **7i**	70	81:19
4		 **8i**	47	84:16
5		 **9i**	80	81:19
6		 **10i**	71	81:19
7		 **11i**	73	89:11
8		 **12i**	44	82:18

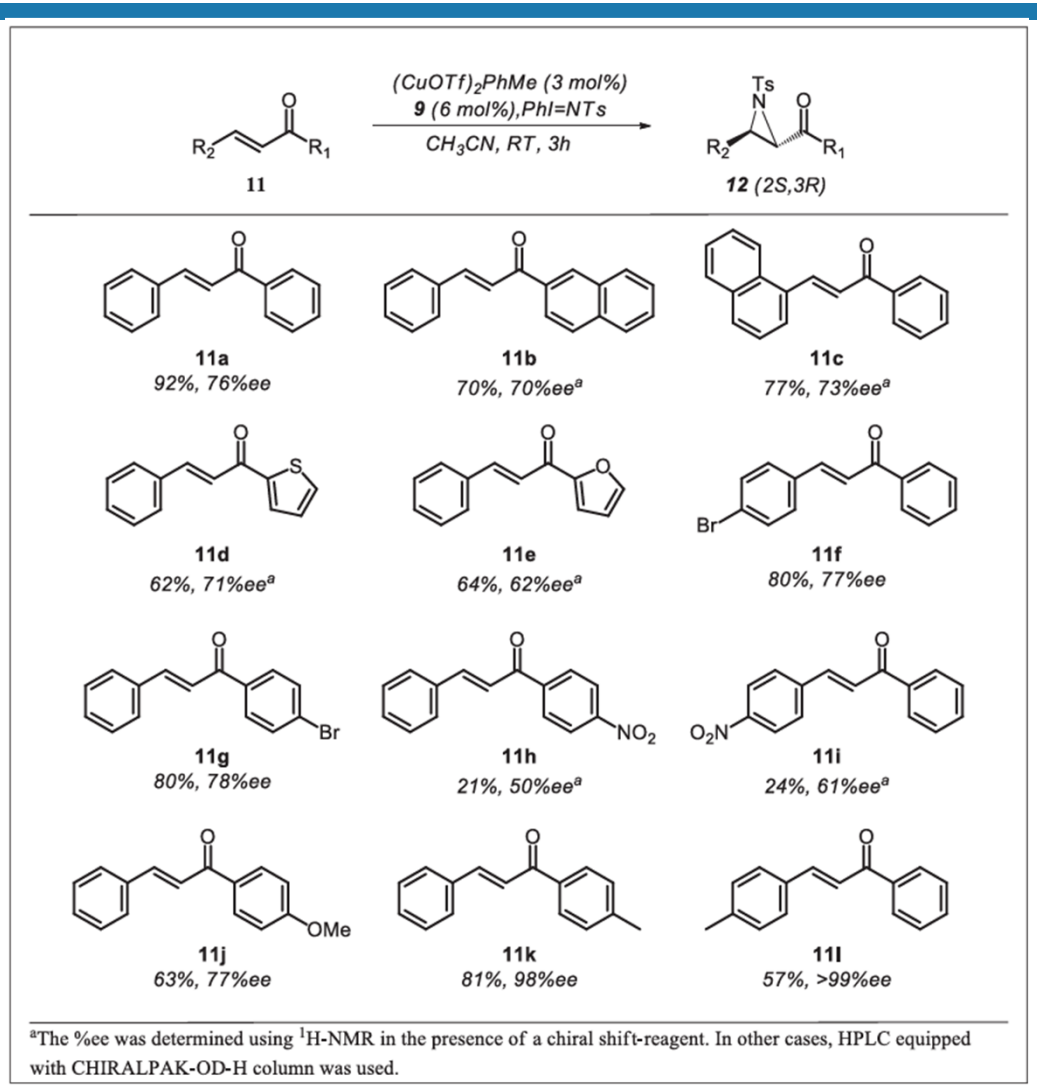
[a] Styrene (3 equiv); K_2CO_3 (1.5 equiv).
[b] Isolated yield.
[c] Ratio *SR*:*RR* (*syn*:*anti*), determined by ^{1}H NMR on the crude mixture.



Scheme 4. Cleavage of the protecting group and recovery of the chiral alcohol.

Helene Lebel, *Tetrahedron* **2012**.

Cu Nitrene



[a]The %ee was determined using ^{1}H-NMR in the presence of a chiral shift-reagent. In other cases, HPLC equipped with CHIRALPAK-OD-H column was used.

Dmitri Gelman, *Journal of Organometallic Chemistry* **2021**.

Rh Nitrene

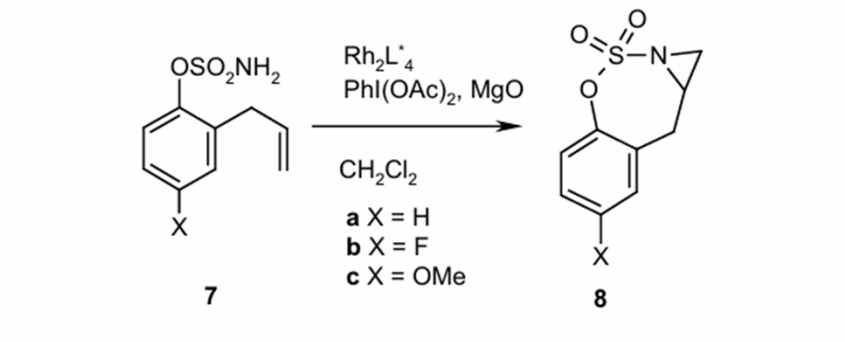


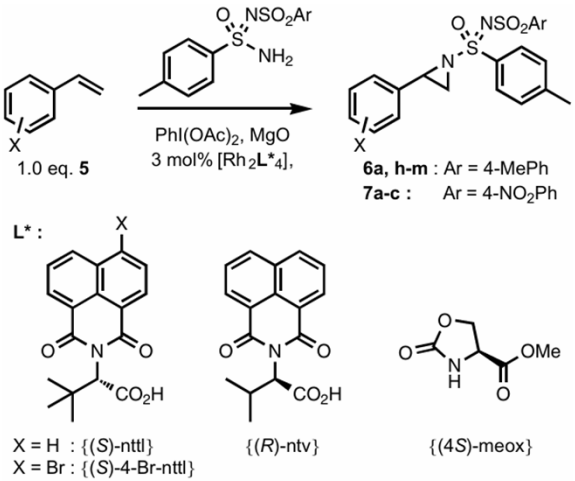
Table 3. Enantioselective intramolecular aziridination by dirhodium(II) complexes[a]

Compound	Catalyst	t (h)	Yield (%)	Ee (%)
7a	$[Rh_2(OAc)_4]$[b]	1.5	62	—
7b	$[Rh_2(OAc)_4]$[b]	2	60	—
7c	$[Rh_2(OAc)_4]$[b]	3	58	—
7a	$[Rh_2\{(5S)\text{-mepy}\}_4]$	5.5	32	50
7a	$[Rh_2\{(5S)\text{-mepy}\}_4]$[c]	9.5	10	52
7b	$[Rh_2\{(5S)\text{-mepy}\}_4]$	4	63	17
7c	$[Rh_2\{(5S)\text{-mepy}\}_4]$	7	18	39
7a	$[Rh_2\{(4S)\text{-meox}\}_4]$	5.5	55	18
7b	$[Rh_2\{(4S)\text{-meox}\}_4]$	4	51	21
7c	$[Rh_2\{(4S)\text{-meox}\}_4]$	7	23	24
7a	$[Rh_2\{(S)\text{-ptpa}\}_4]$	2	79	30
7b	$[Rh_2\{(S)\text{-ptpa}\}_4]$	1.5	70	19
7c	$[Rh_2\{(S)\text{-ptpa}\}_4]$	3	53	27
7a	$[Rh_2\{(S)\text{-nttl}\}_4]$	1.5	68	19
7b	$[Rh_2\{(S)\text{-nttl}\}_4]$	1.5	72	15
7c	$[Rh_2\{(S)\text{-nttl}\}_4]$	3	36	22
7a	$[Rh_2\{(R)\text{-ntv}\}_4]$	2	63	15
7b	$[Rh_2\{(R)\text{-ntv}\}_4]$	1.5	75	7
7c	$[Rh_2\{(R)\text{-ntv}\}_4]$	3	64	15
7b	$[Rh_2\{(S)\text{-dosp}\}_4]$	1.5	80	<5

[a] Reactions carried out in CH_2Cl_2 with 3.5 mol% of catalyst (see Experimental part).
[b] 5% of catalyst.
[c] −20 °C.

Paul Muller, *Tetrahedron:Asymmetry* **2004**.

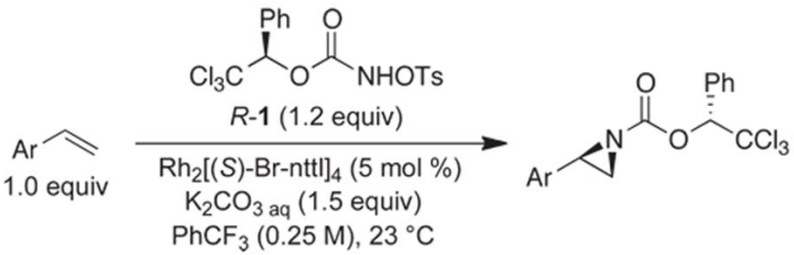
Rh Nitrene

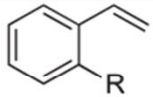
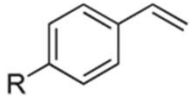
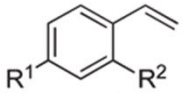
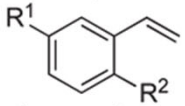
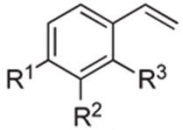


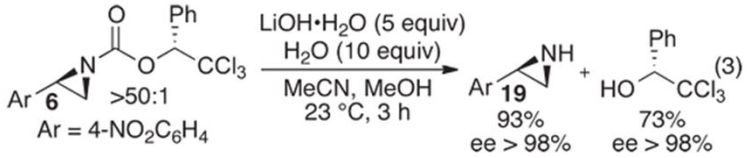
Entry	Sulfonimidamide	Chiral rhodium catalyst $[Rh_2L*_4]$	X	Aziridine	Yield (%)[a]	de (%)[b]
1	(*S*)-**1a**	$[Rh_2\{(S)\text{-nttl}\}_4]$	H	**6a**	63	80
2	(*S*)-**1a**	$[Rh_2\{(S)\text{-4-Br-nttl}\}_4]$[c]	H	**6a**	66	43
3	(*S*)-**1a**	$[Rh_2\{(R)\text{-ntv}\}_4]$	H	**6a**	54	20
4	(*R*)-**1a**	$[Rh_2\{(R)\text{-ntv}\}_4]$	H	**6a**	55	74
5	(*S*)-**1a**	$[Rh_2\{(S)\text{-meox}\}_4]$	H	**6a**	42	20
6	(*S*)-**1b**	$[Rh_2\{(S)\text{-nttl}\}_4]$	H	**7a**	29	61
7	(S)-**1a**	$[Rh_2\{(S)\text{-nttl}\}_4]$	4-Br	**6h**	59	82
8	(*S*)-**1b**	$[Rh_2\{(S)\text{-nttl}\}_4]$	4-Br	**7b**	30	54
9	(*R*)-**1a**	$[Rh_2\{(R)\text{-ntv}\}_4]$	4-Cl	**6i**	52	70
10	(*S*)-**1b**	$[Rh_2\{(S)\text{-nttl}\}_4]$	4-Cl	**7c**	25	54
11	(*S*)-**1a**	$[Rh_2\{(S)\text{-nttl}\}_4]$	4-CF_3	**6j**	55	60
12	(*S*)-**1a**	$[Rh_2\{(S)\text{-nttl}\}_4]$	4-OMe	**6k**	17	49
13	(*R*)-**1a**	$[Rh_2\{(R)\text{-ntv}\}_4]$	4-Me	**6l**	33	36
14	(*R*)-**1a**	$[Rh_2\{(R)\text{-ntv}\}_4]$	3-NO_2	**6m**	18	55

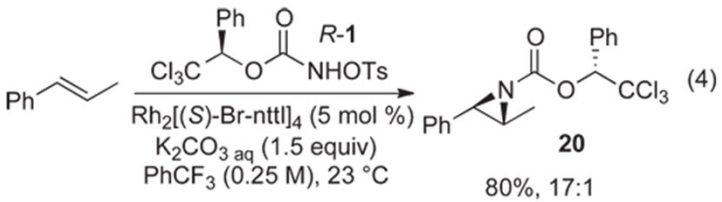
Philippe Dauban, *Tetrahedron:Asymmetry* **2005**.

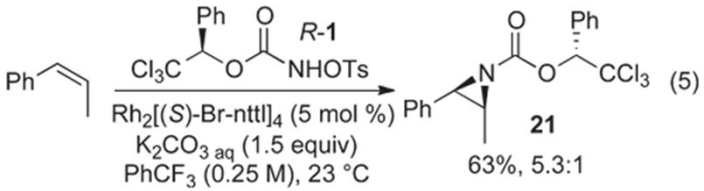
Rh Nitrene



entry	alkene	yield (%)[a]	dr[b]
			
1	R = Cl	(**2**) 84	30:1
2	R = Br	(**3**) 78	33:1
3	R = I	(**4**) 77	>50:1
4	R = Me	(**5**) 72	5.5:1
			
5	R = NO_2	(**6**) 75	8.5:1
6	R = NO_2	(**6**) 63[c]	>50:1[c]
7	R = Cl	(**7**) 76	8.0:1
8	R = Br	(**8**) 77	12:1
9	R = CF_3	(**9**) 74	8.0:1
			
10	R^1 = Cl, R^2 = Cl	(**10**) 85	25:1
11	R^1 = F, R^2 = Me	(**11**) 72	8.5:1
12	R^1 = Me, R^2 = Br	(**12**) 79	25:1
			
13	R^1 = Cl, R^2 = Cl	(**13**) 52	14:1
14	R^1 = Cl, R^2 = NO_2	(**14**) 51[d]	30:1[d]
			
15	R^1 = H, R^2 = Cl, R^3 = Cl	(**15**) 77	14:1
16	R^1 = Cl, R^2 = Cl, R^3 = H	(**16**) 82	7.0:1
17	R^1 = Br, R^2 = NO_2, R^3 = H	(**17**) 63[d]	9.0:1[d]
18	R^1 = H, R^2 = Br, R^3 = H	(**18**) 66[d]	2.8:1[e]

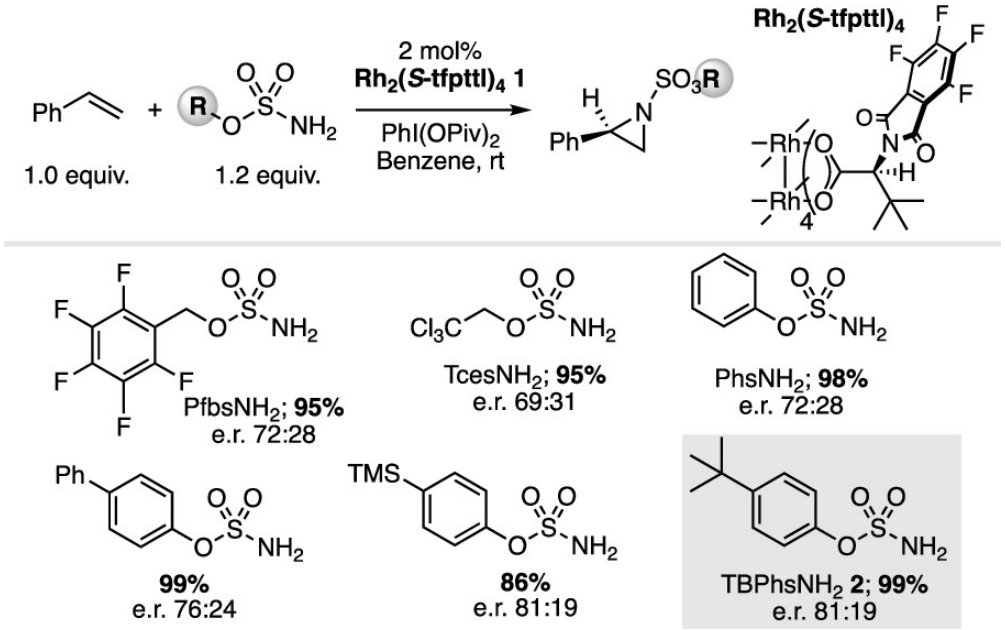


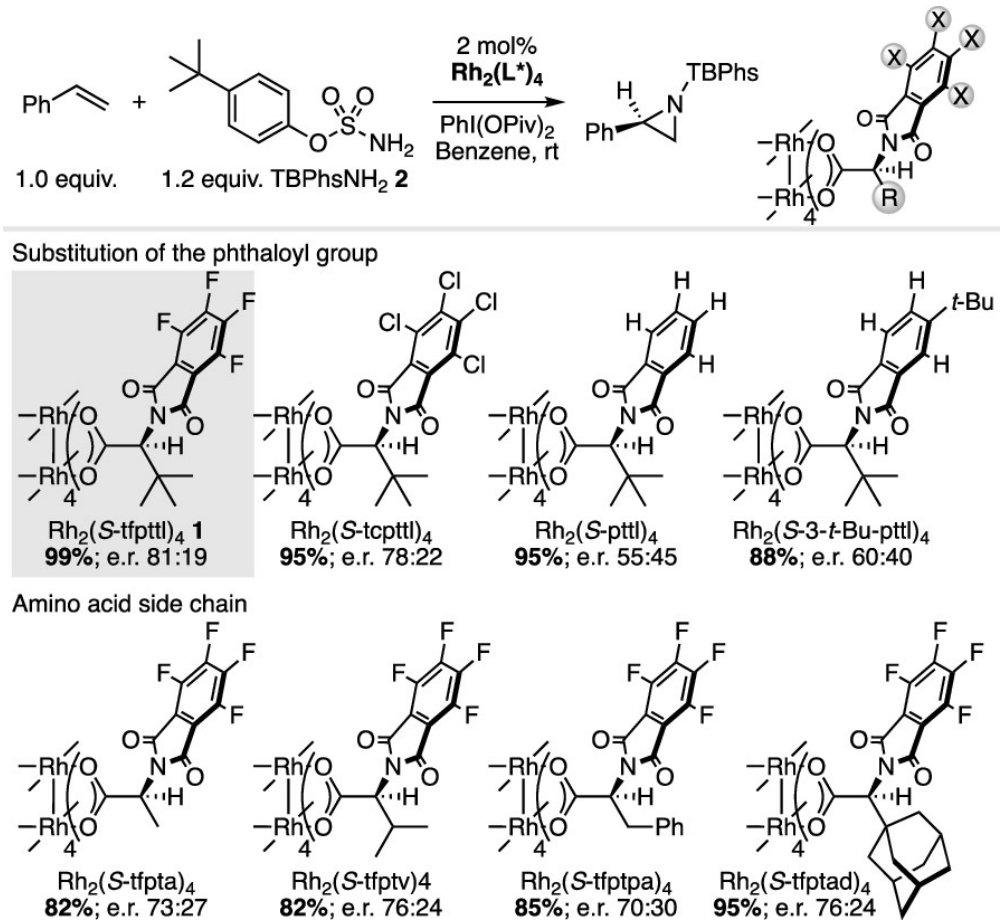




Helene Lebel, *Org. Lett.* **2011**.

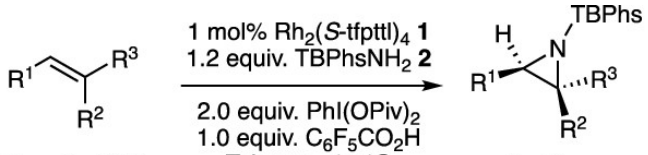
Rh Nitrene

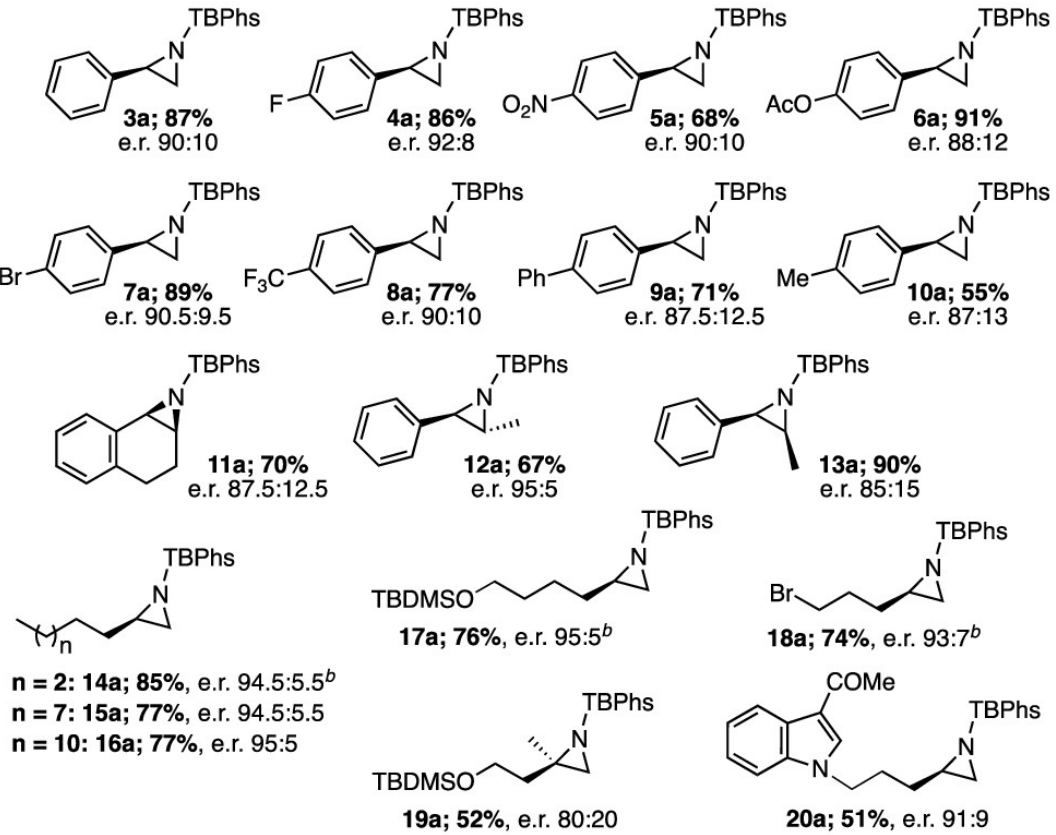


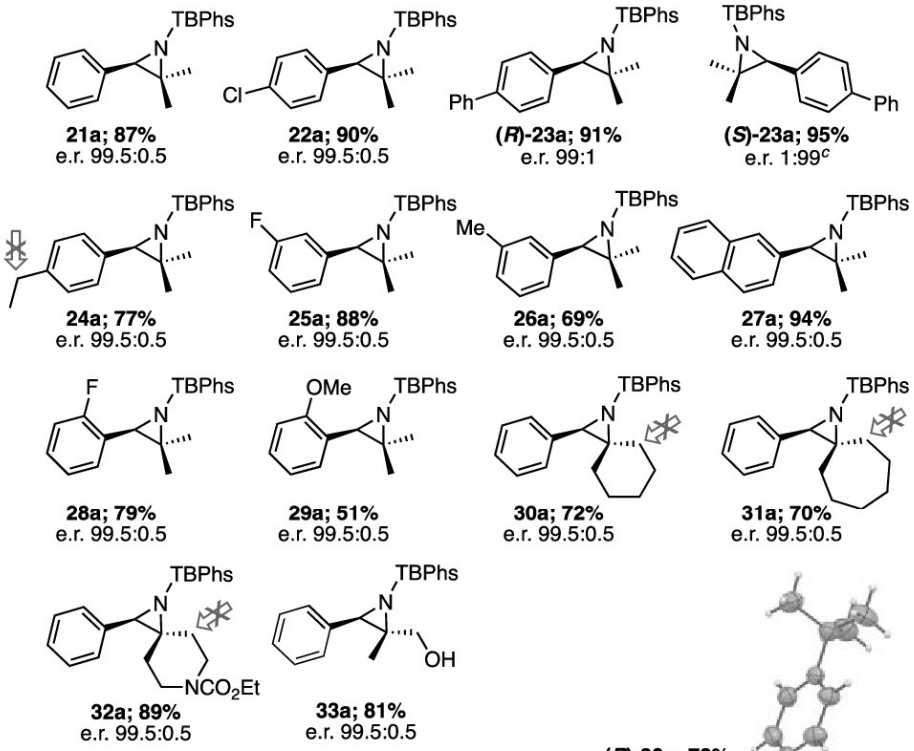


Philippe Dauban, *J. Am. Chem. Soc.* **2022**.

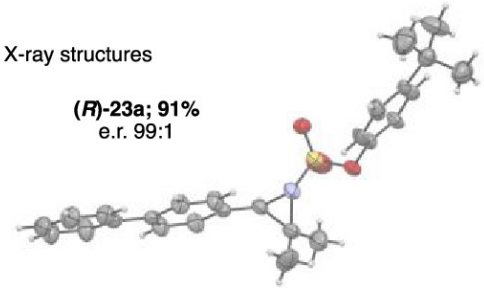
Rh Nitrene



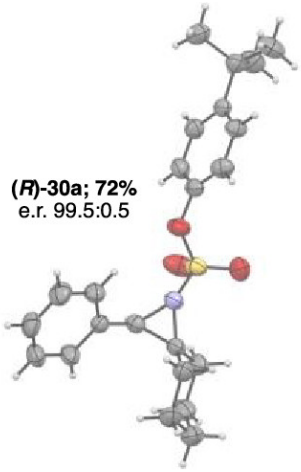




X-ray structures



(R)-23a; 91%
e.r. 99:1

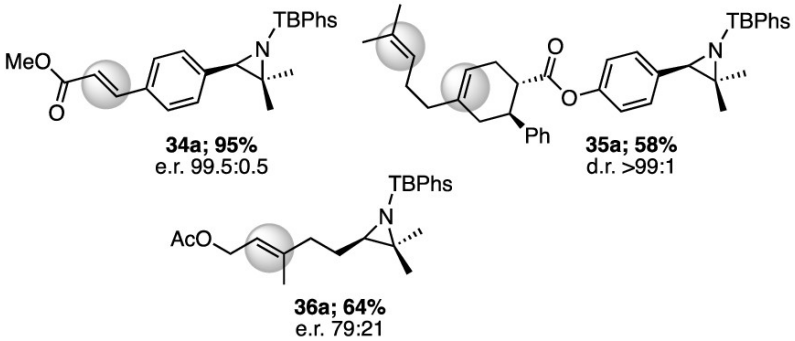


(R)-30a; 72%
e.r. 99.5:0.5

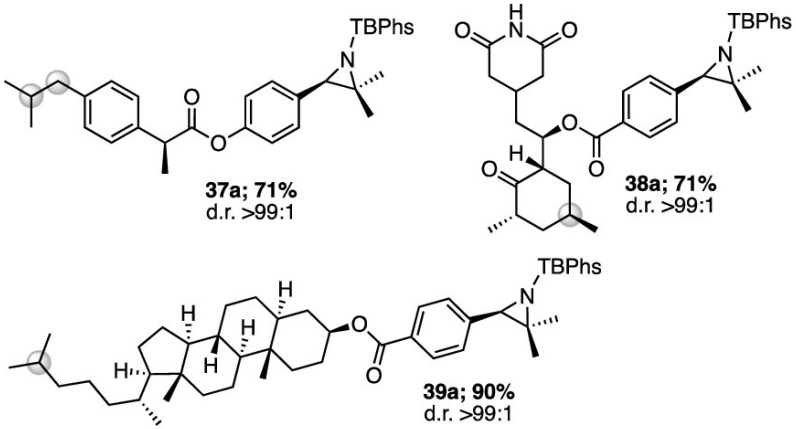
Philippe Dauban, *J. Am. Chem. Soc.* **2022**.

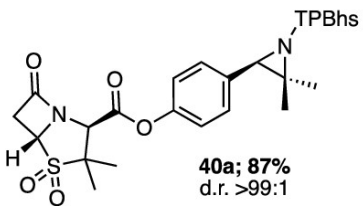
Rh Nitrene

Chemoselective aziridination of poly-olefinic substrates

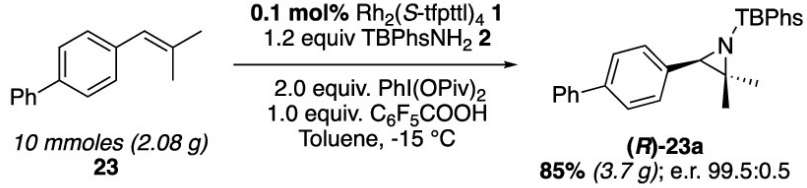


Chemoselective aziridination *vs.* catalytic C(sp^3)–H amination

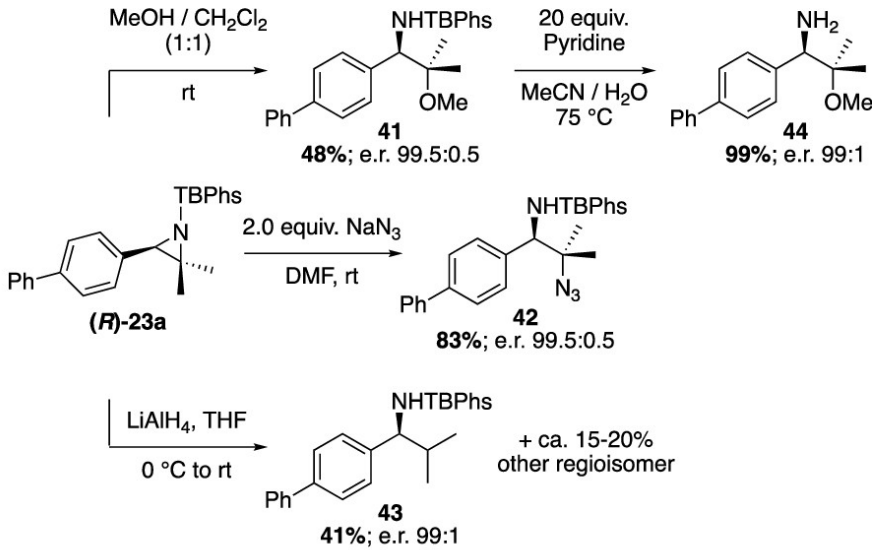




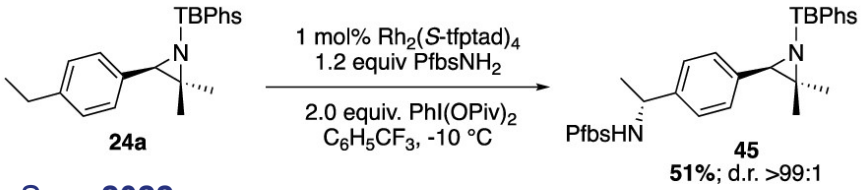
Gram-scale reaction



Aziridine ring-opening

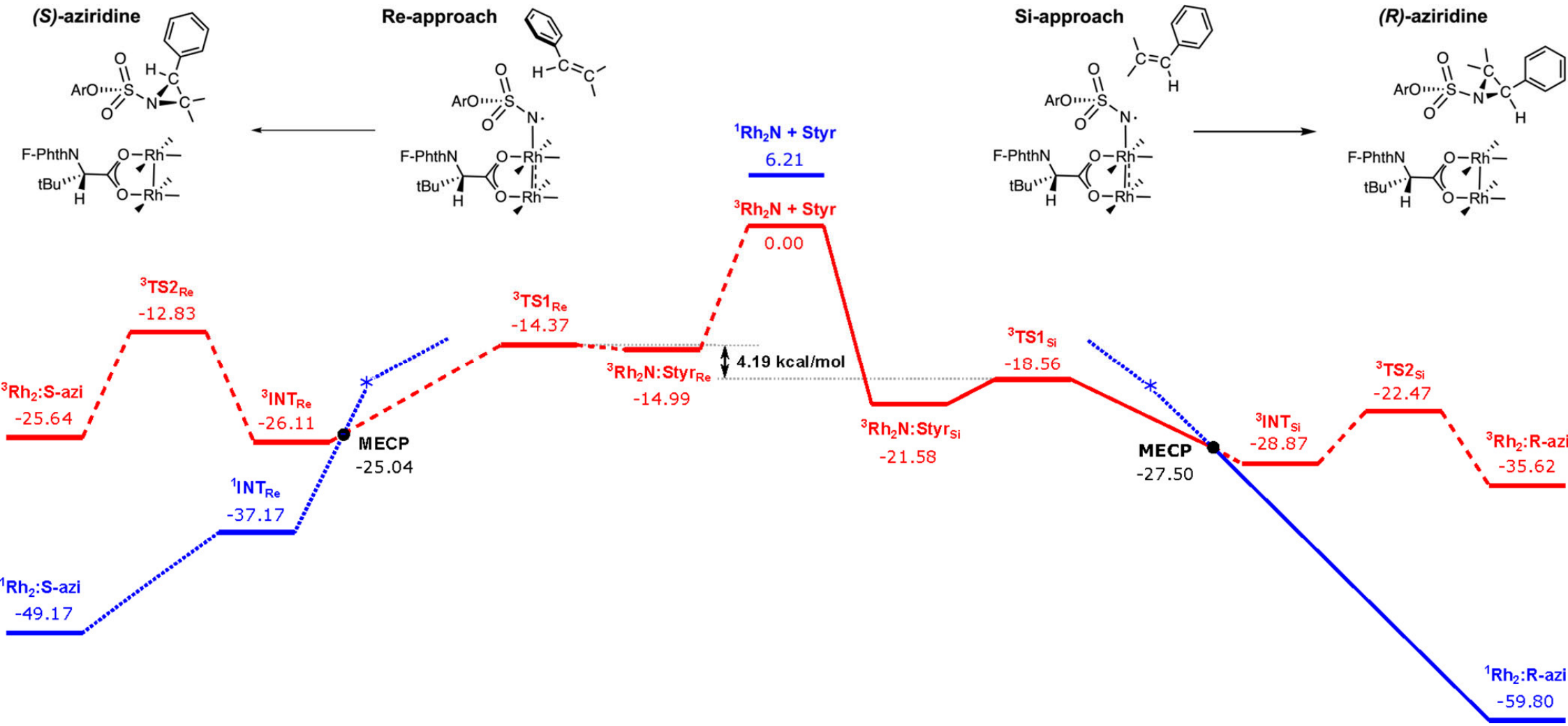


Combination of alkene aziridination with C(sp^3)–H amination



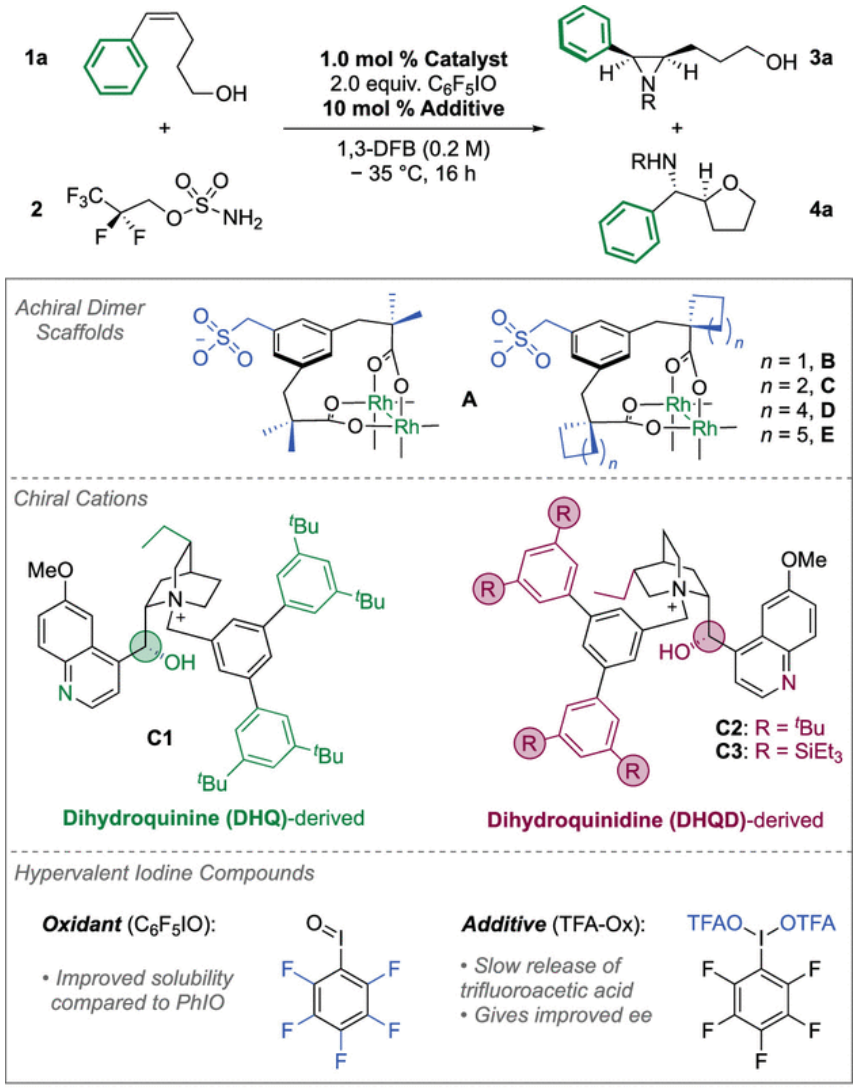
Philippe Dauban, *J. Am. Chem. Soc.* **2022**.

Rh Nitrene



Philippe Dauban, *J. Am. Chem. Soc.* **2022**.

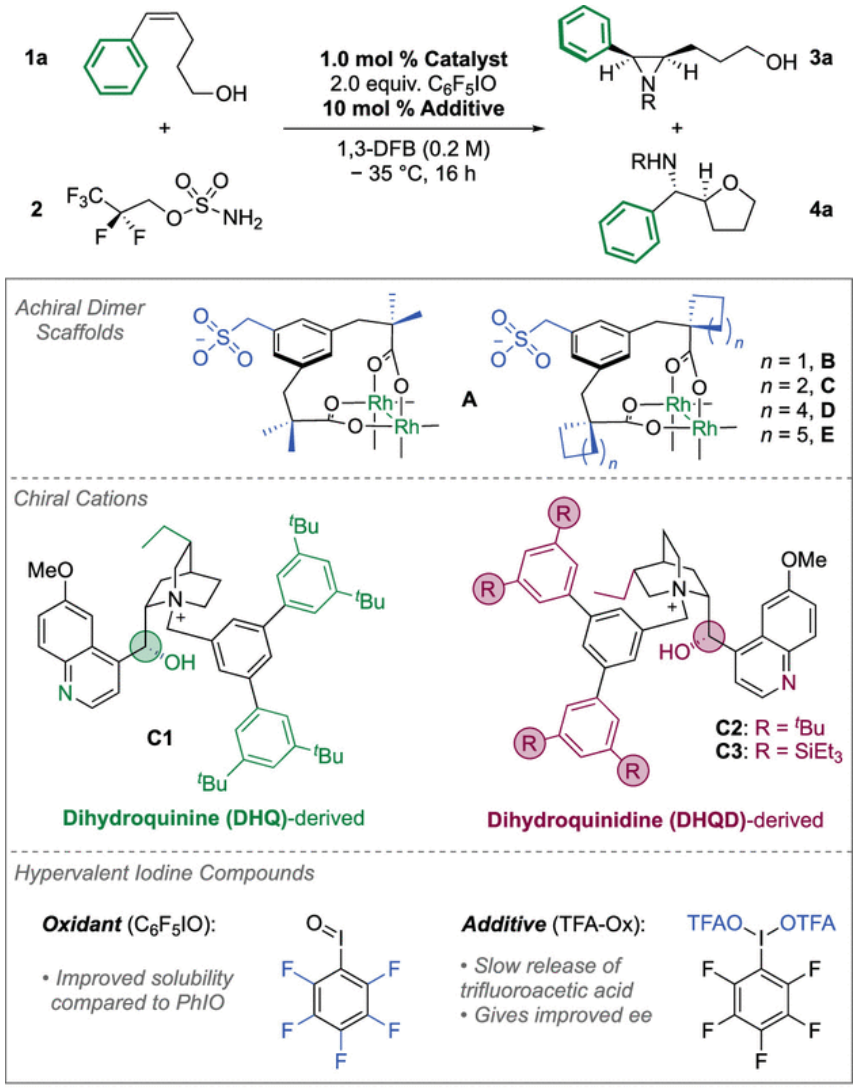
Rh Nitrene



entry	catalyst	yield (3a + 4a)/%[a]	*ee*/%[b]	*additive*
1	$Rh_2(\mathbf{A})_2\bullet(\mathbf{C1})_2$	70	− 57	×
2	$Rh_2(\mathbf{A})_2\bullet(\mathbf{C2})_2$	73	+ 68	×
3	$Rh_2(\mathbf{A})_2\bullet(\mathbf{C2})_2\bullet(Pyr)_2$	57	+ 76	×
4	$Rh_2(\mathbf{A})_2\bullet(\mathbf{C2})_2$	78	+ 80	✓
5	$Rh_2(\mathbf{A})_2\bullet(\mathbf{C2})_2\bullet(Pyr)_2$	82	+ 90	✓
6	$Rh_2(\mathbf{B})_2\bullet(\mathbf{C2})_2\bullet(Pyr)_2$	77	+ 91	✓
7	$Rh_2(\mathbf{C})_2\bullet(\mathbf{C2})_2\bullet(Pyr)_2$	76	+ 90	✓
8	$Rh_2(\mathbf{D})_2\bullet(\mathbf{C2})_2\bullet(Pyr)_2$	75	+ 87	✓
9	$Rh_2(\mathbf{E})_2\bullet(\mathbf{C2})_2\bullet(Pyr)_2$	78	+ 82	✓
10	$Rh_2(\mathbf{A})_2\bullet(\mathbf{C3})_2\bullet(Pyr)_2$	76	+ 89	✓
11[c]	$Rh_2(\mathbf{B})_2\bullet(\mathbf{C3})_2\bullet(Pyr)_2$	76 (58)	+ 93 (+ 92)	✓
12	$Rh_2(\mathbf{C})_2\bullet(\mathbf{C3})_2\bullet(Pyr)_2$	62	+ 90	✓

Philippe Dauban, *J. Am. Chem. Soc.* **2022**.

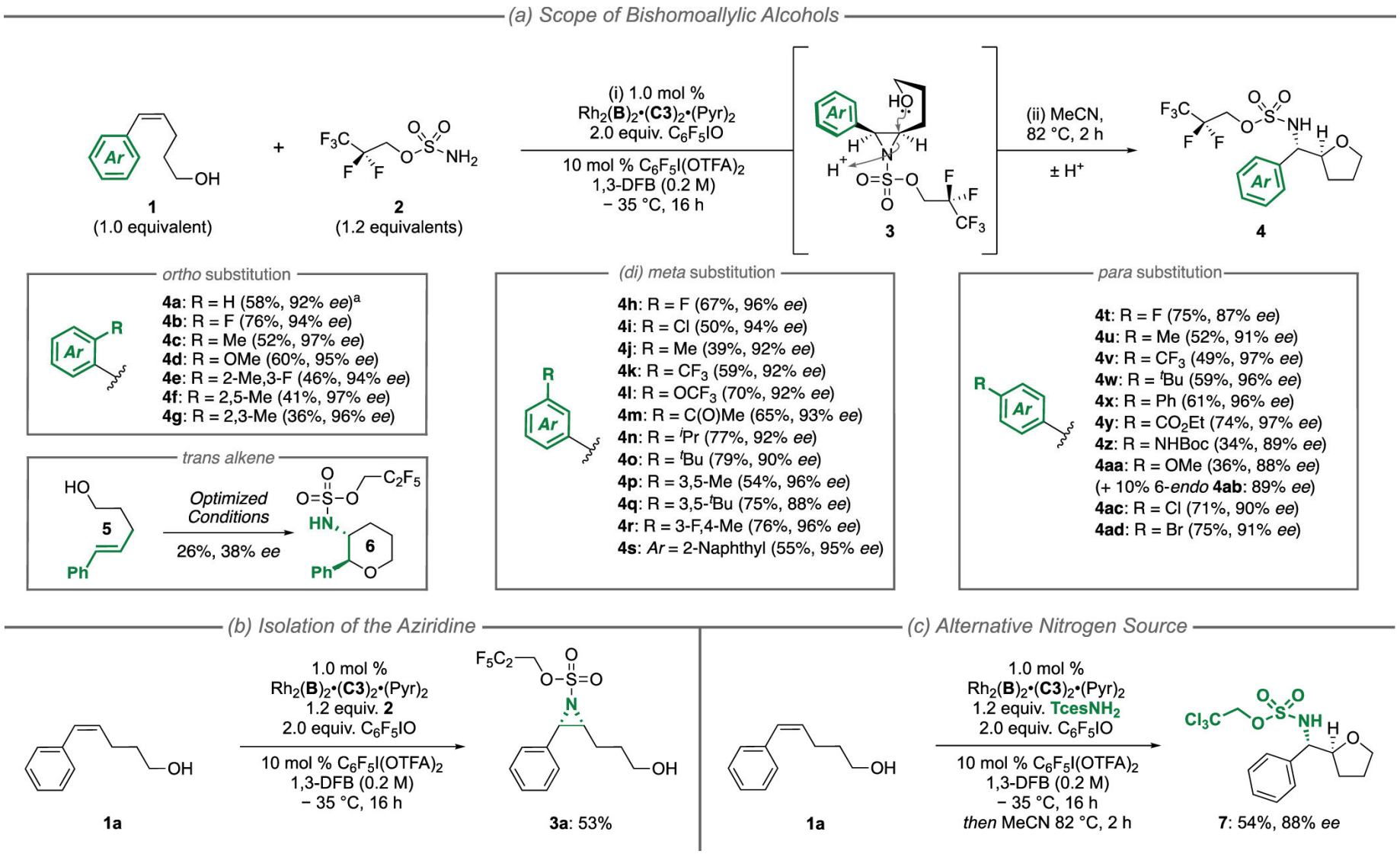
Rh Nitrene



entry	catalyst	yield (3a + 4a)/%[a]	*ee*/%[b]	*additive*
1	$Rh_2(\mathbf{A})_2\bullet(\mathbf{C1})_2$	70	− 57	×
2	$Rh_2(\mathbf{A})_2\bullet(\mathbf{C2})_2$	73	+ 68	×
3	$Rh_2(\mathbf{A})_2\bullet(\mathbf{C2})_2\bullet(Pyr)_2$	57	+ 76	×
4	$Rh_2(\mathbf{A})_2\bullet(\mathbf{C2})_2$	78	+ 80	✓
5	$Rh_2(\mathbf{A})_2\bullet(\mathbf{C2})_2\bullet(Pyr)_2$	82	+ 90	✓
6	$Rh_2(\mathbf{B})_2\bullet(\mathbf{C2})_2\bullet(Pyr)_2$	77	+ 91	✓
7	$Rh_2(\mathbf{C})_2\bullet(\mathbf{C2})_2\bullet(Pyr)_2$	76	+ 90	✓
8	$Rh_2(\mathbf{D})_2\bullet(\mathbf{C2})_2\bullet(Pyr)_2$	75	+ 87	✓
9	$Rh_2(\mathbf{E})_2\bullet(\mathbf{C2})_2\bullet(Pyr)_2$	78	+ 82	✓
10	$Rh_2(\mathbf{A})_2\bullet(\mathbf{C3})_2\bullet(Pyr)_2$	76	+ 89	✓
11[c]	$Rh_2(\mathbf{B})_2\bullet(\mathbf{C3})_2\bullet(Pyr)_2$	76 (58)	+ 93 (+ 92)	✓
12	$Rh_2(\mathbf{C})_2\bullet(\mathbf{C3})_2\bullet(Pyr)_2$	62	+ 90	✓

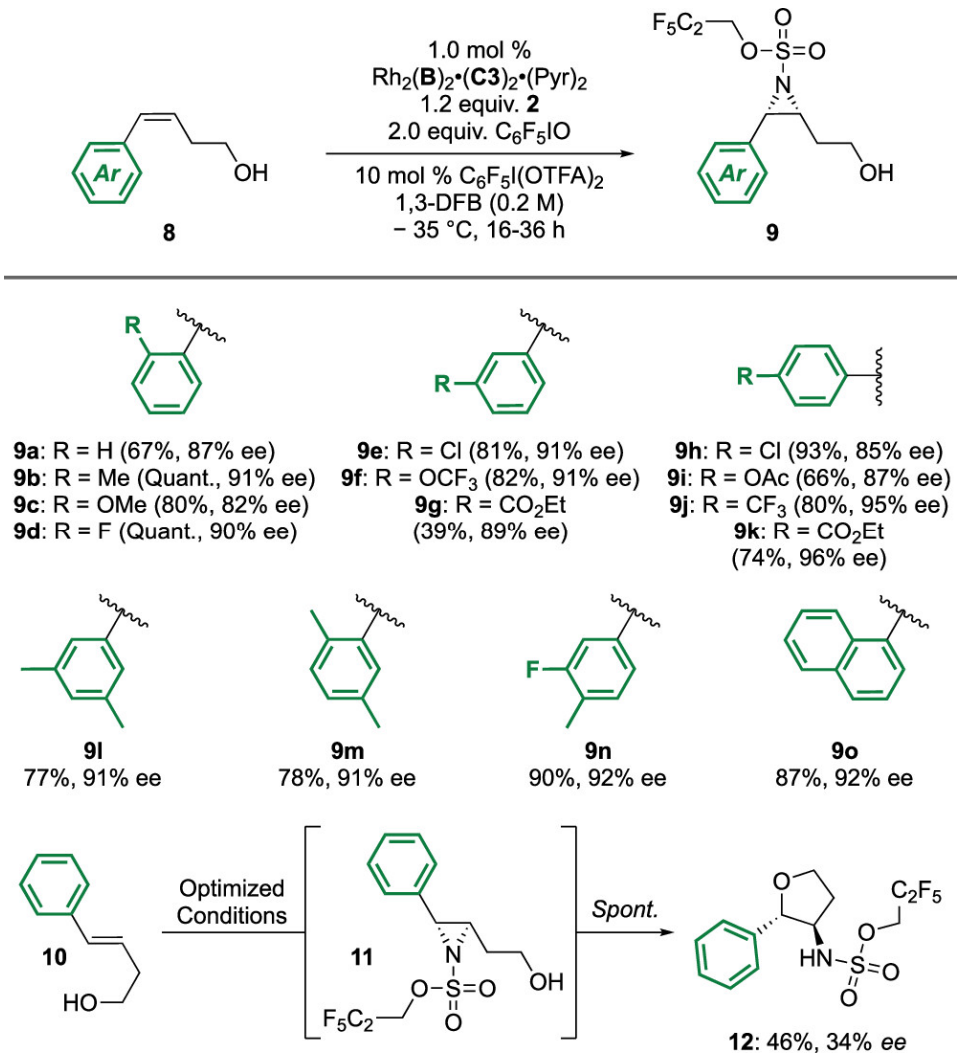
Robert J. Phipps, *J. Am. Chem. Soc.* **2023**.

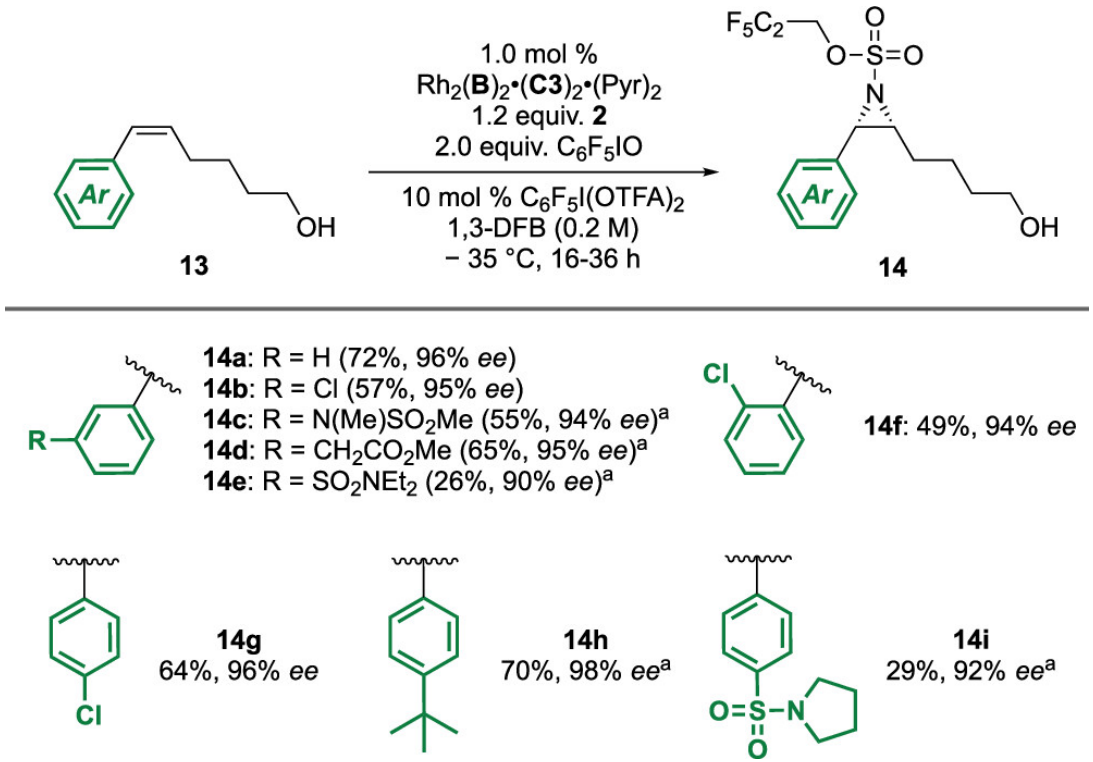
Rh Nitrene



Robert J. Phipps, *J. Am. Chem. Soc.* **2023**.

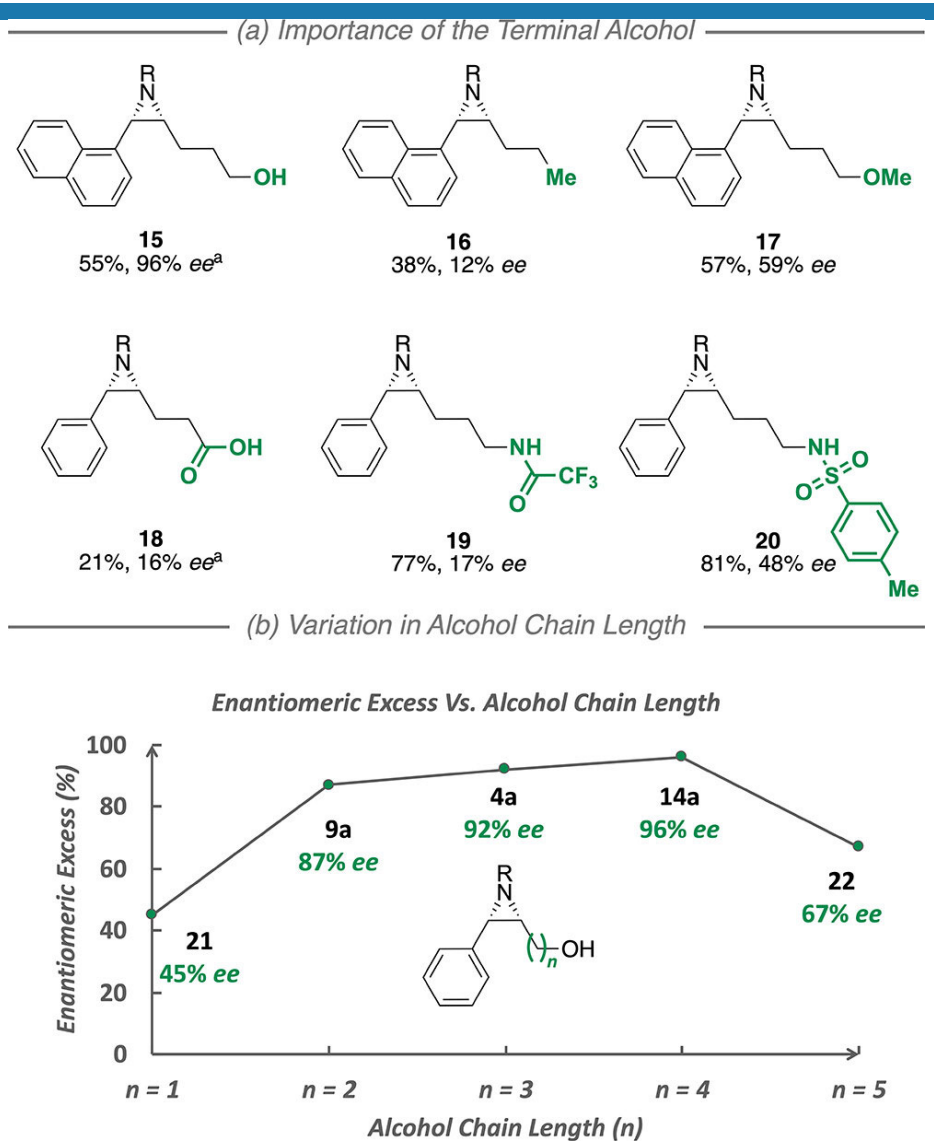
Rh Nitrene





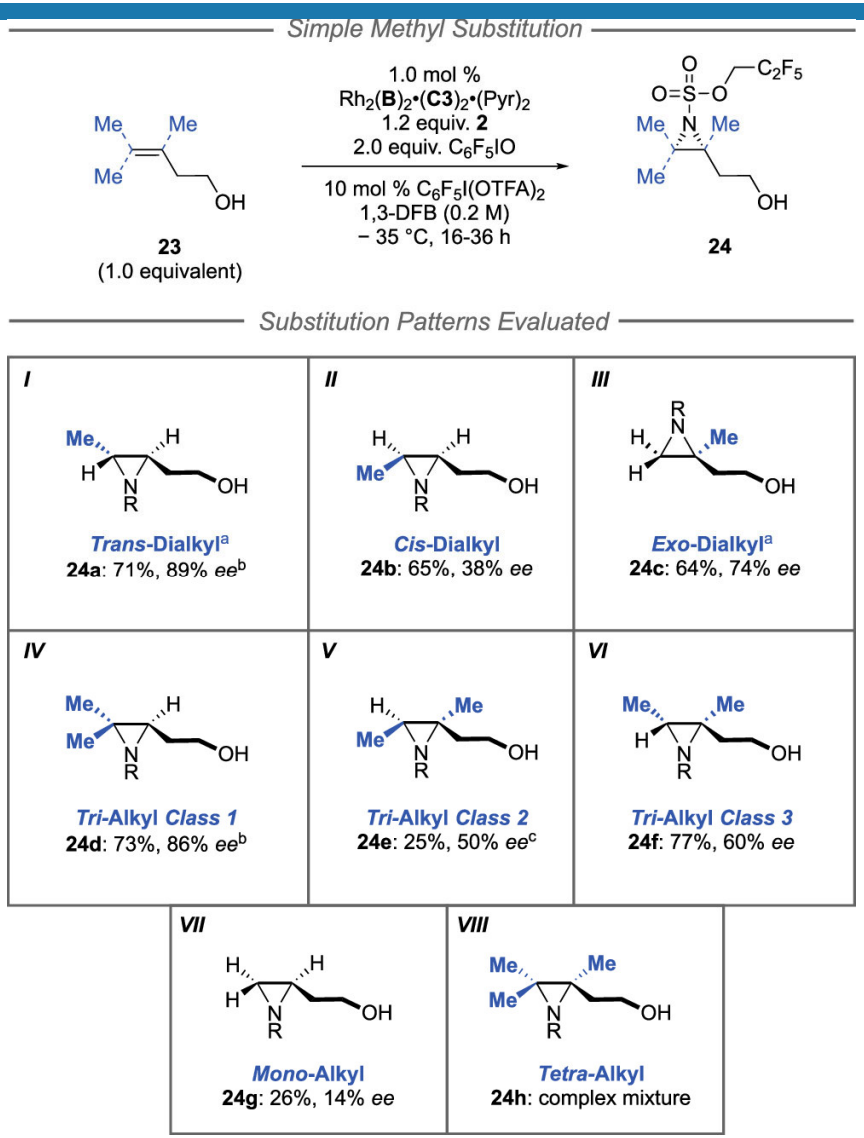
Robert J. Phipps, *J. Am. Chem. Soc.* **2023**.

Rh Nitrene



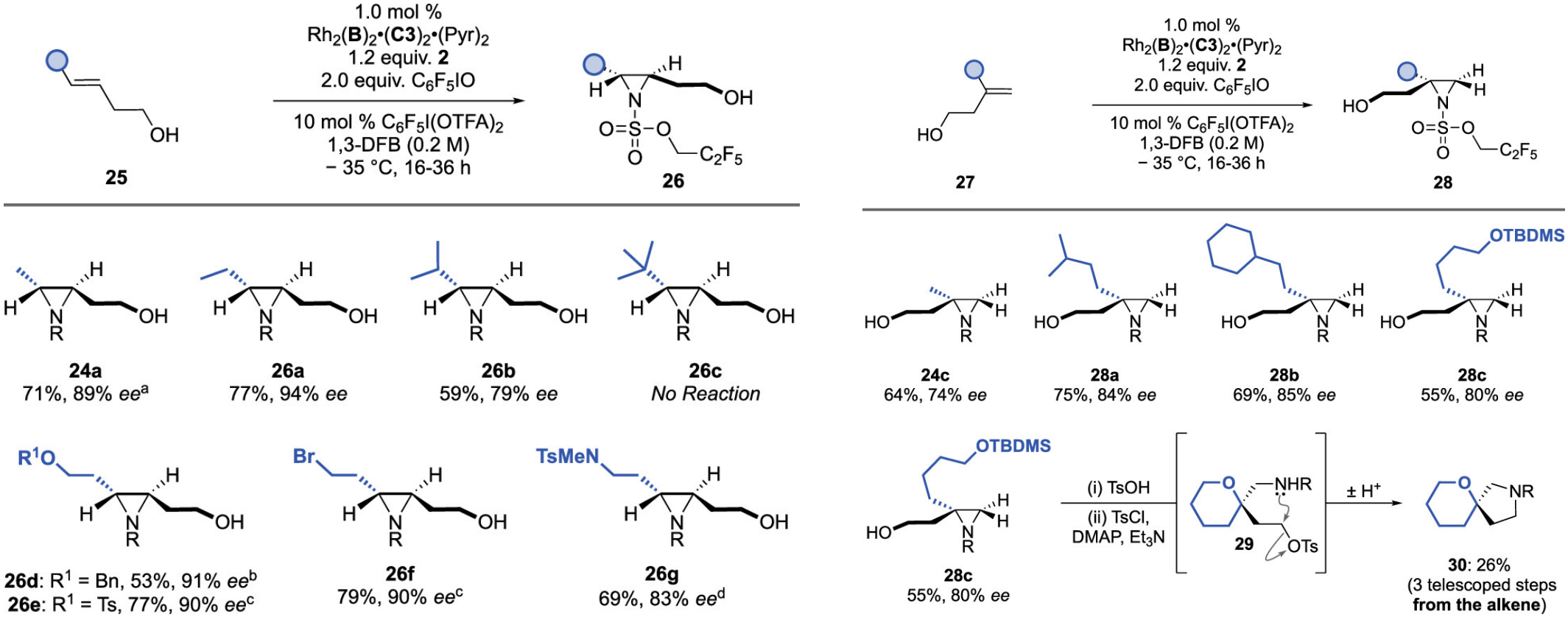
Robert J. Phipps, *J. Am. Chem. Soc.* **2023**.

Rh Nitrene



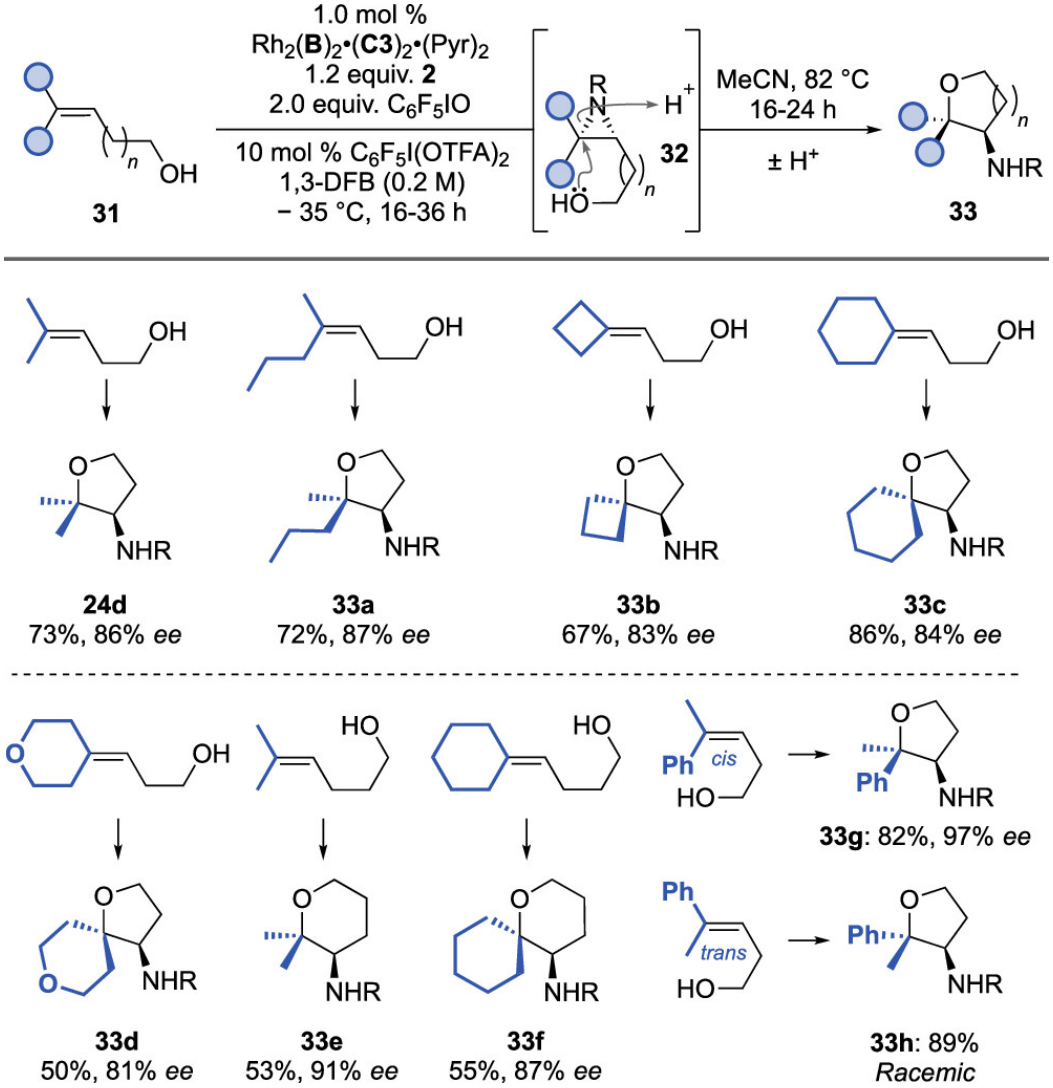
Robert J. Phipps, *J. Am. Chem. Soc.* **2023**.

Rh Nitrene



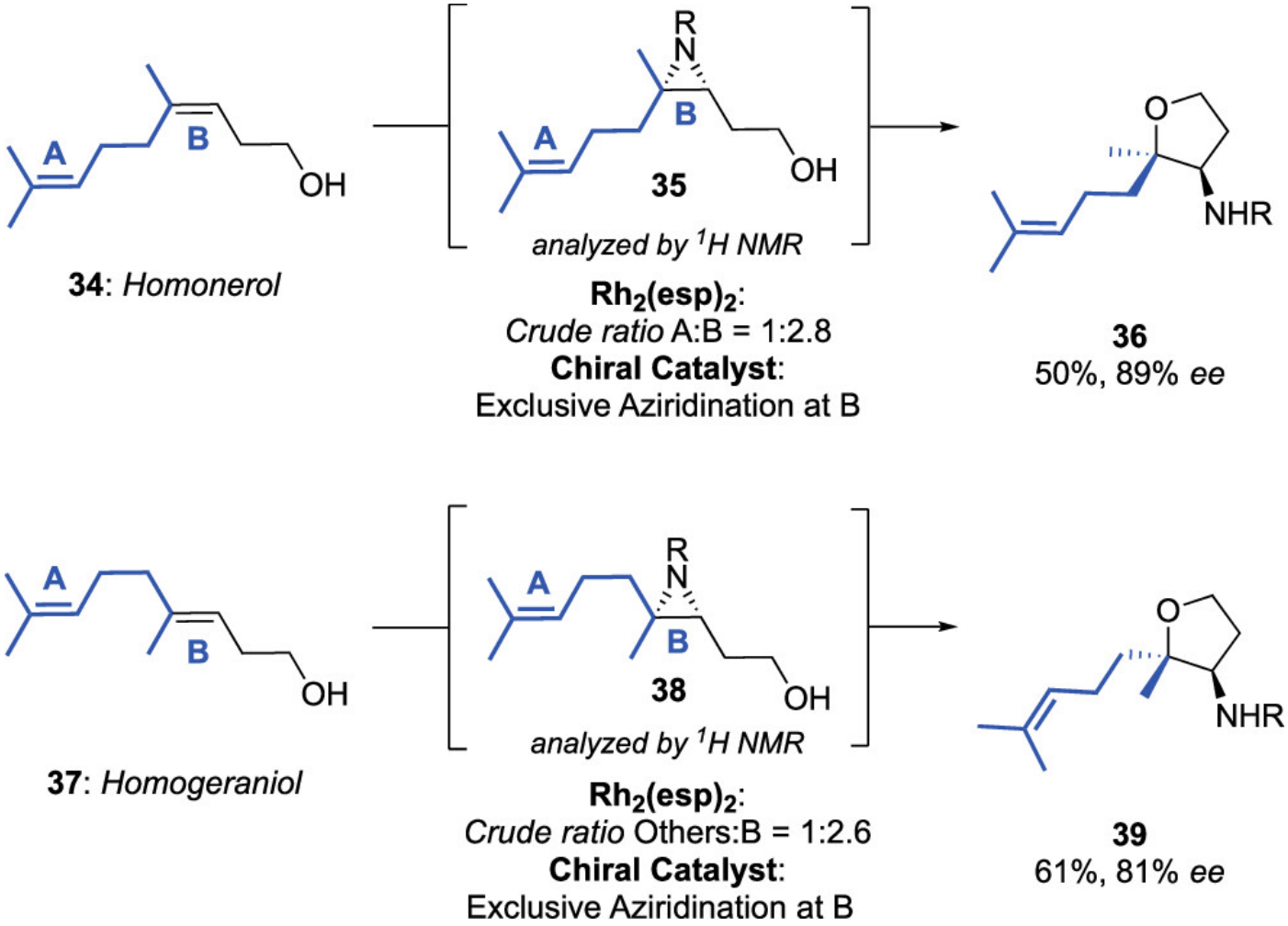
Robert J. Phipps, *J. Am. Chem. Soc.* **2023**.

Rh Nitrene



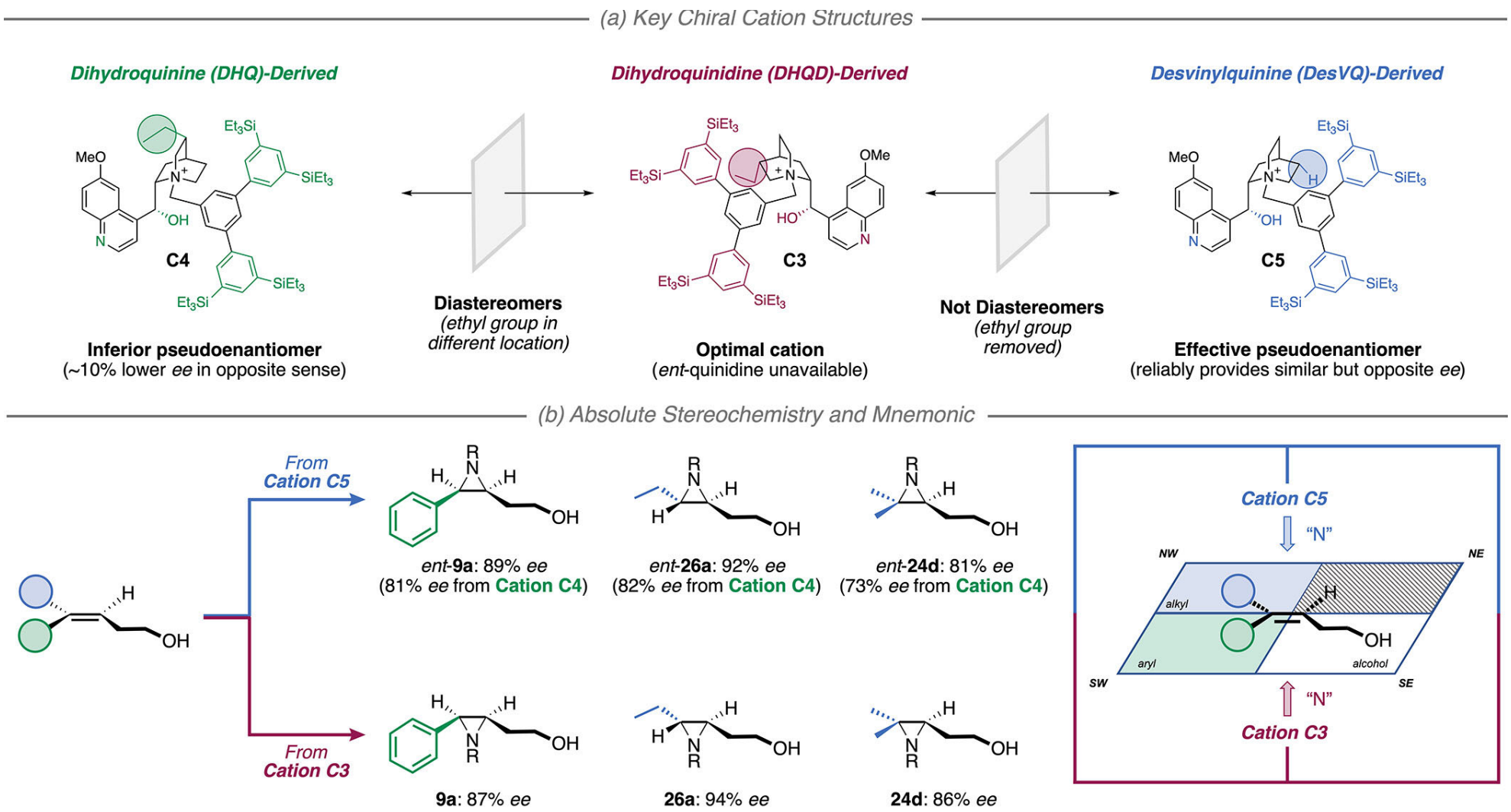
Robert J. Phipps, *J. Am. Chem. Soc.* **2023**.

Rh Nitrene



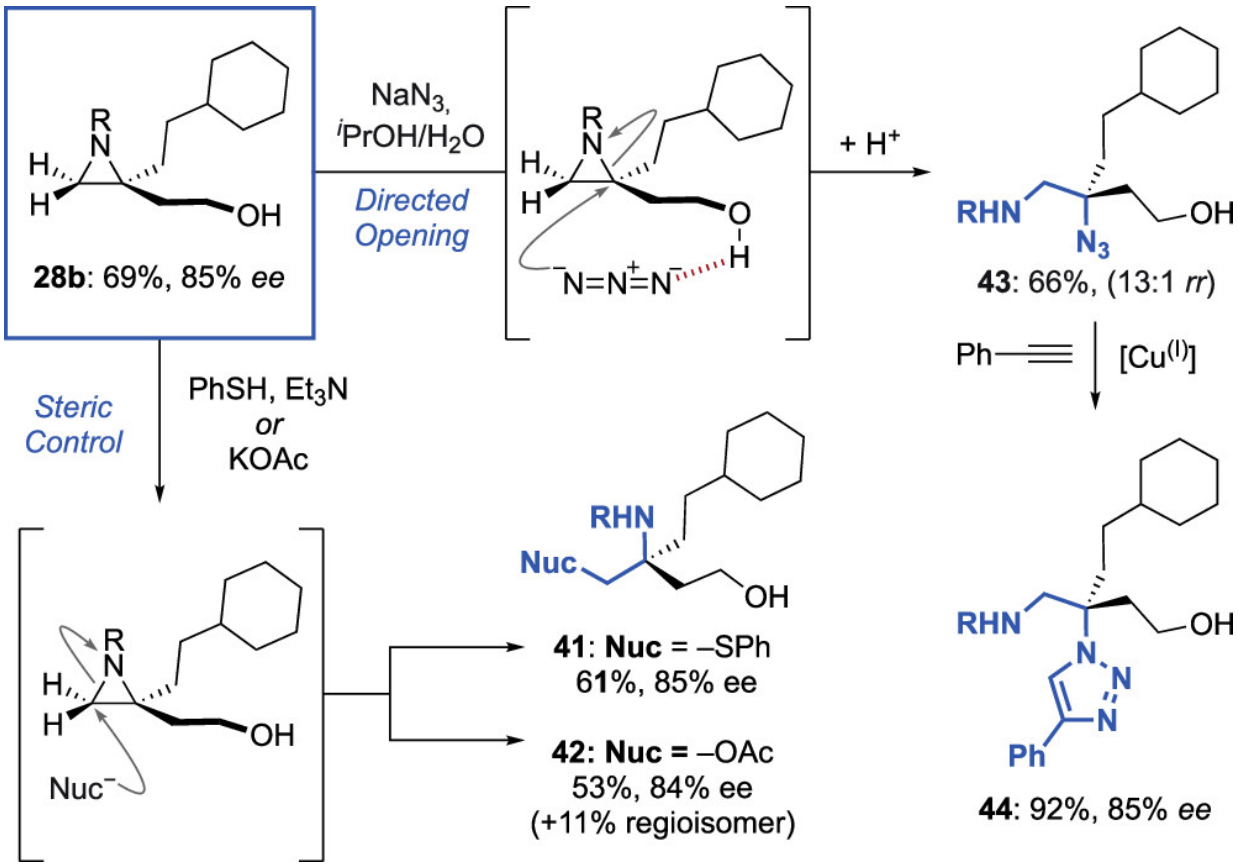
Robert J. Phipps, *J. Am. Chem. Soc.* **2023**.

Rh Nitrene



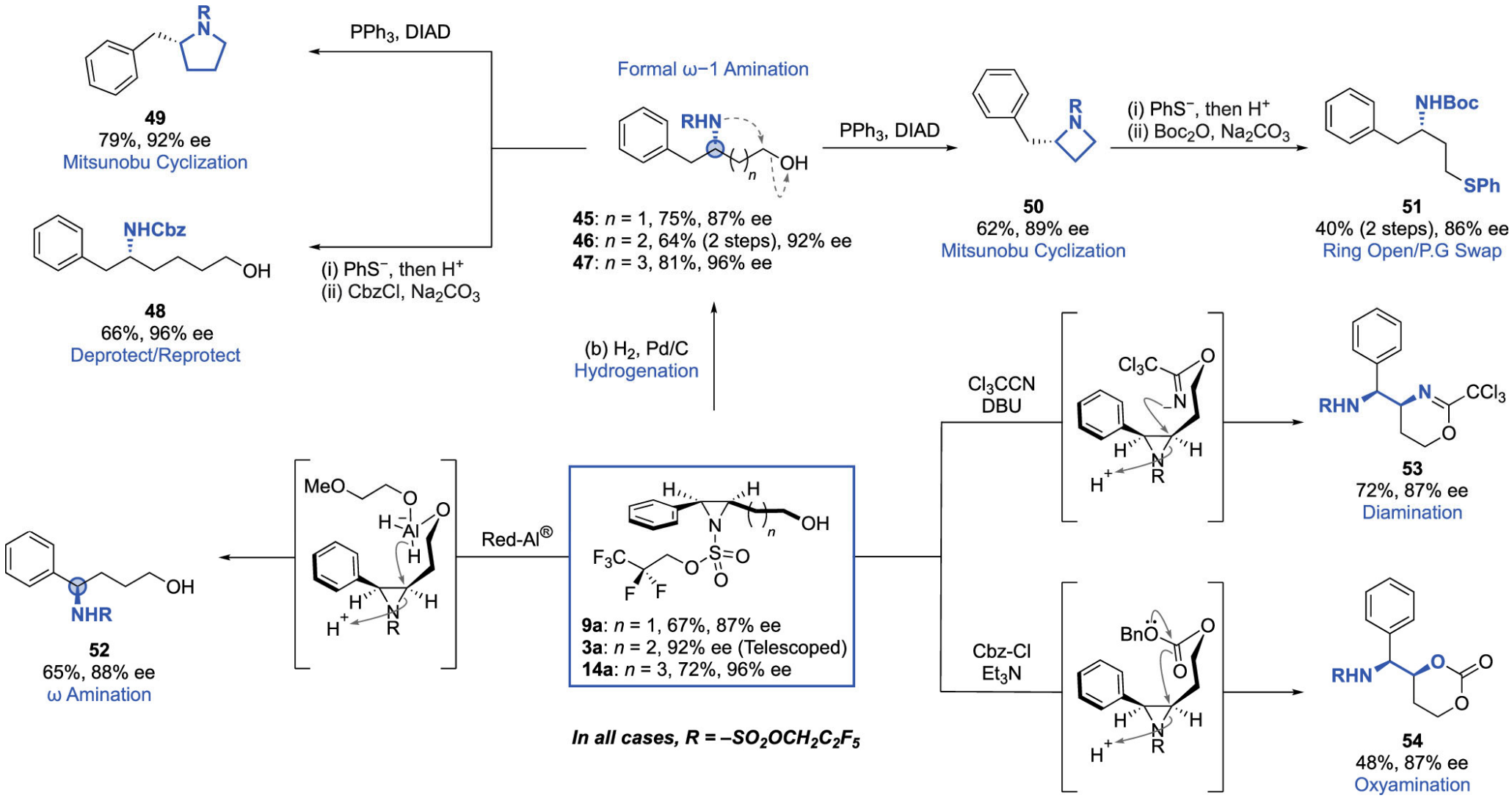
Robert J. Phipps, *J. Am. Chem. Soc.* **2023**.

Rh Nitrene



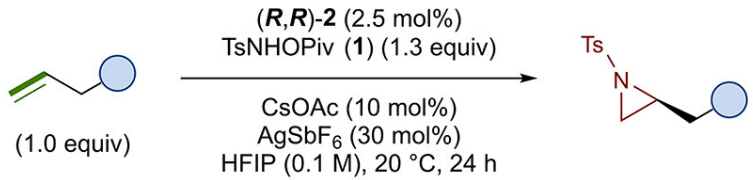
Robert J. Phipps, *J. Am. Chem. Soc.* **2023**.

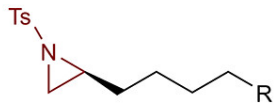
Rh Nitrene



Robert J. Phipps, *J. Am. Chem. Soc.* **2023**.

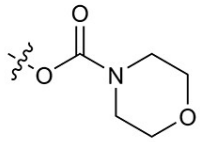
Rh Nitrene





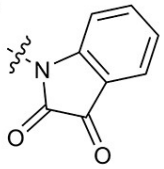
11, R = OAc	77%, 95:5 e.r.
12, R = OBz	60%, 95:5 e.r.
13, R = OTBS	47%, 95:5 e.r.
14, R = OTs	21%, 95:5 e.r.
15, R = OH	49%, 95:5 e.r.
16, R = NPhth	52%, 94:6 e.r.
17, R = NHAc	71%, 94:6 e.r.
18, R = NO_2	88%, 94:6 e.r.
19, R = Br	56%, 96:4 e.r.
20, R = Bpin	57%, 96:4 e.r.
21, R = $PO(OEt)_2$	67%, 95:5 e.r.

R =



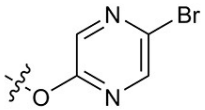
22, 62%
94:6 e.r.

R =



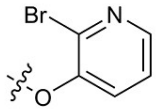
23, 78%
93:7 e.r.

R =



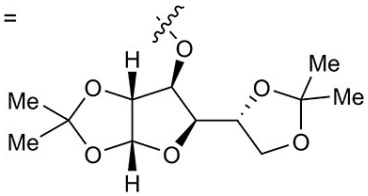
24, 67%
95:5 e.r.

R =



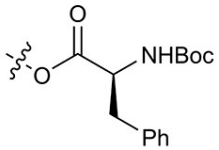
25, 28%
96:4 e.r.

R =

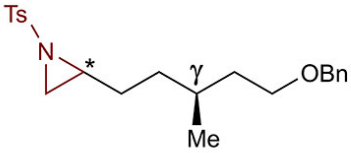


26, 69%
95:5 d.r.[a]

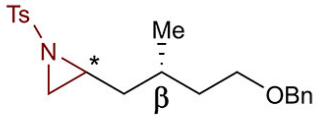
R =



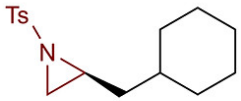
27, 82%
94:6 d.r.[a]



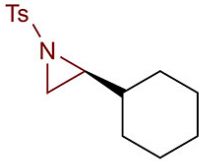
(***S***,***S***)-**28**, 77%, 97:3 d.r.[a]
(***R***,***S***)-**28**, 72%, 7:93 d.r.[a,b]



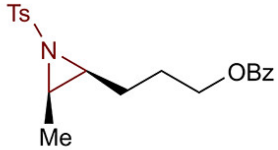
(***S***,***S***)-**29**, 24%, 91:9 d.r.[a]
(***R***,***S***)-**29**, 30%, 3:97 d.r.[a,b]



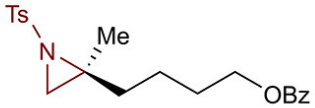
30, 83%
96:4 e.r.



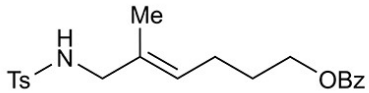
31, 14%
91:9 e.r.



32, 61%
86:14 e.r., >20:1 d.r.[c]



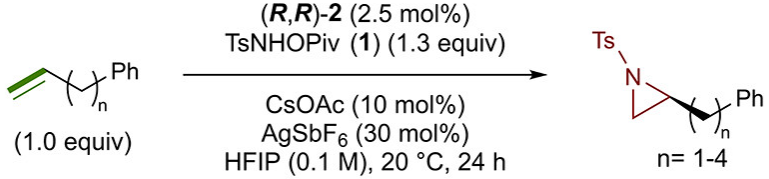
33, 0%

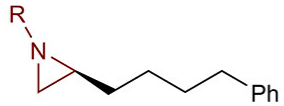


34, 56%
3:1 d.r.[c]

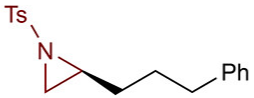
Simon B. Blakey*, *J. Am. Chem. Soc.* **2024**.

Rh Nitrene



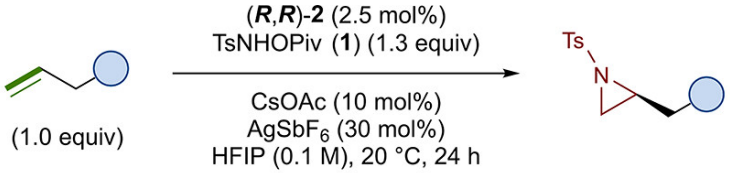


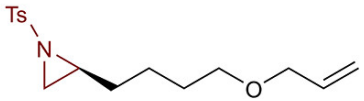
35, R = Ts, 82%, 95:5 e.r.
38, R = Ns, 16%, 94:6 e.r.[a]
39, R = Ms, 26%, 87:13 e.r.[b]



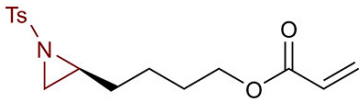
36
54%, 95:5 e.r.

37
18%, 95:5 e.r.
32%, 95:5 e.r.[c]
23%, 93:7 e.r.[c,d]

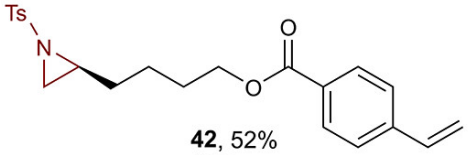




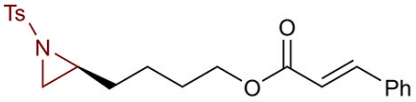
40, 69%
95:5 e.r.



41, 49%
95:5 e.r.



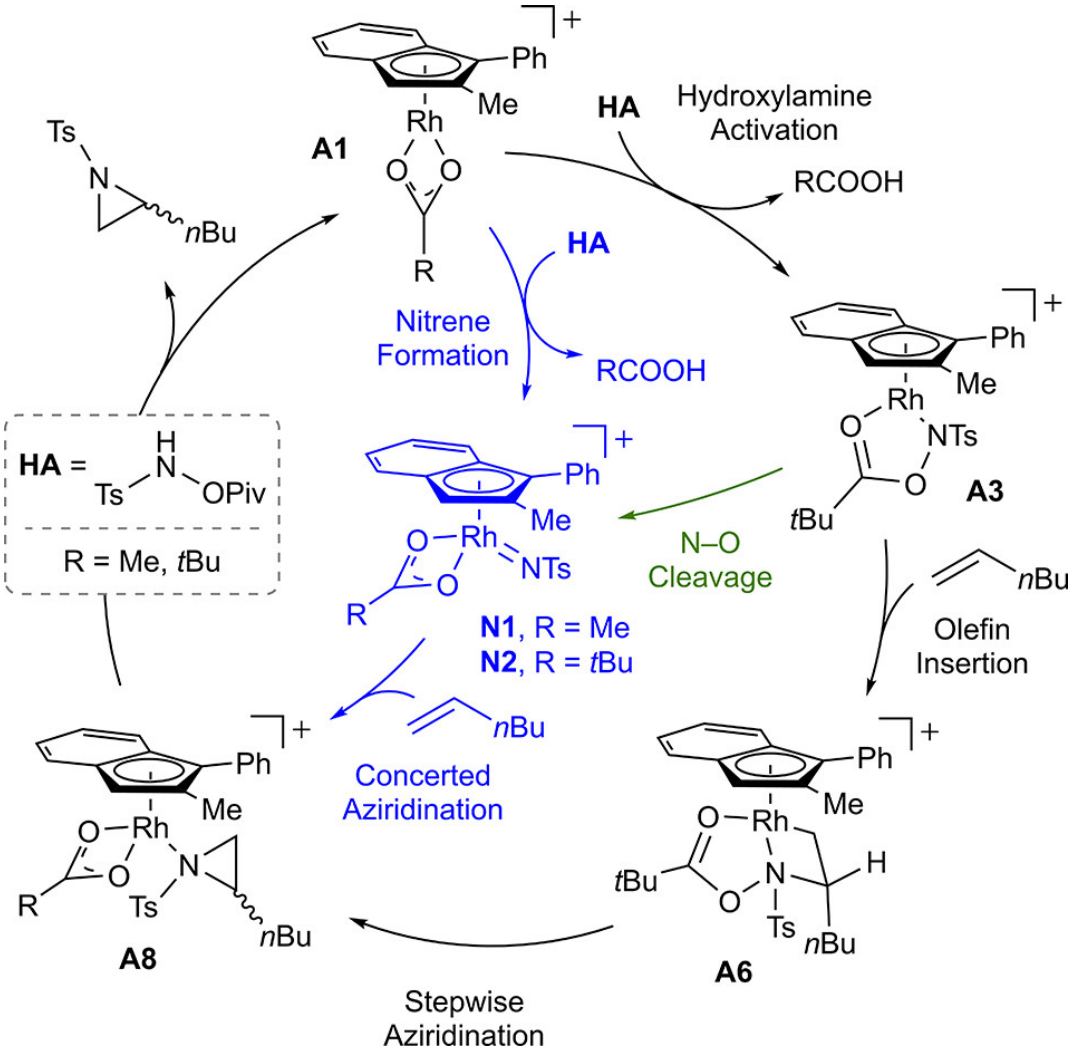
42, 52%
95:5 e.r.



43, 68%
95:5 e.r.

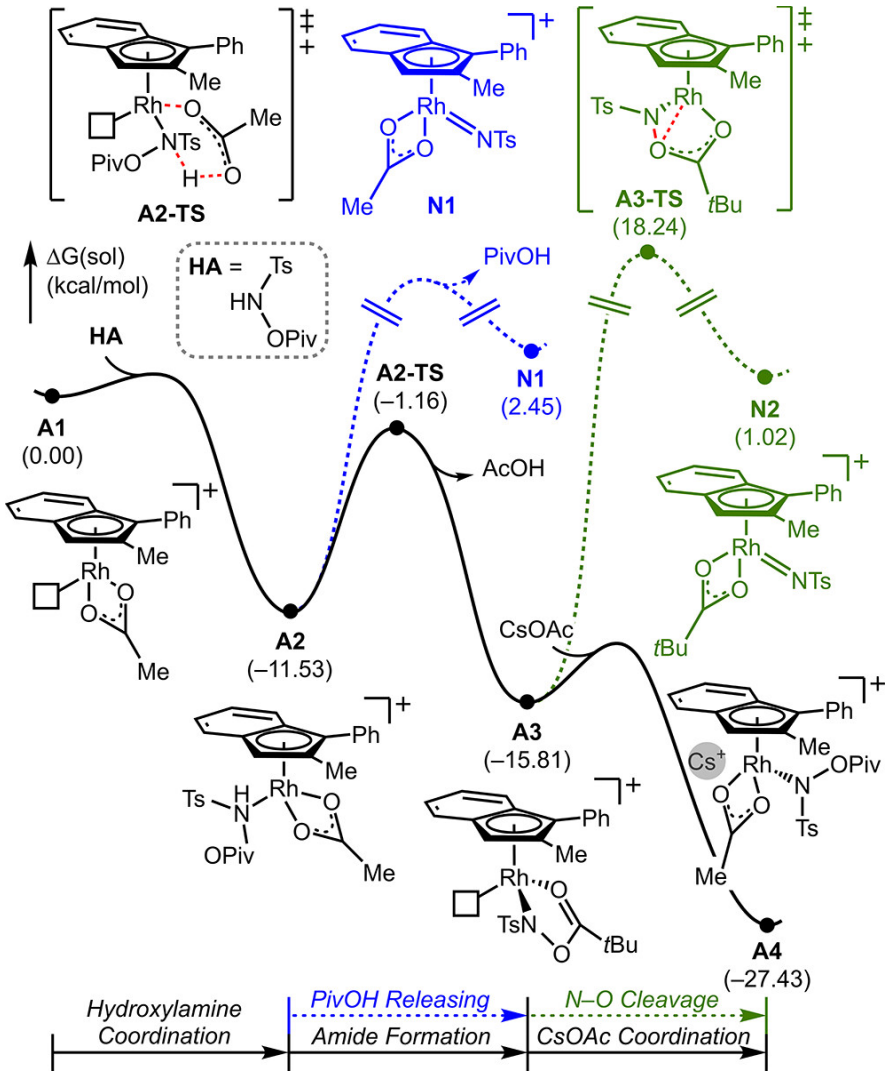
Simon B. Blakey*, *J. Am. Chem. Soc.* **2024**.

Rh Nitrene



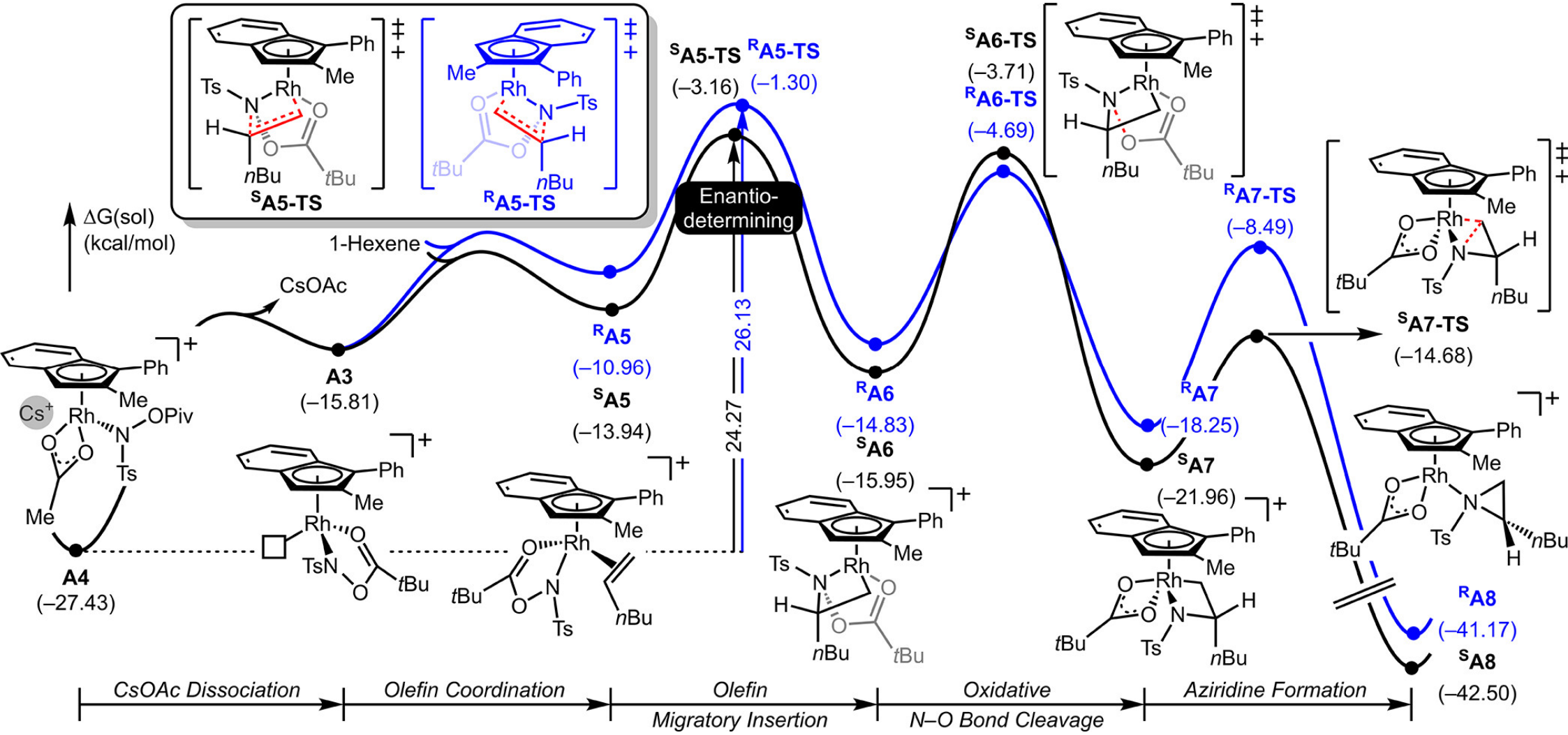
Simon B. Blakey*, *J. Am. Chem. Soc.* **2024**.

Rh Nitrene



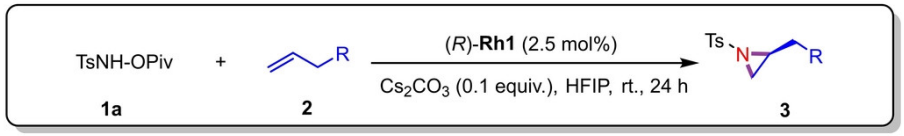
Simon B. Blakey*, *J. Am. Chem. Soc.* **2024**.

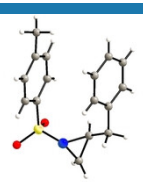
Rh Nitrene



Simon B. Blakey*, *J. Am. Chem. Soc.* **2024**.

Rh Nitrene





3l: CCDC: 2309810

3a, 90% yield, 91% ee

3b, 99% yield, 88% ee

3c, 65% yield, 90% ee

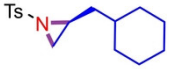
3d, 82% yield, 89% ee

3e, 98% yield, 88% ee

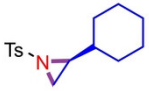
3f, 76% yield, 91% ee

3g, 75% yield, 93% ee

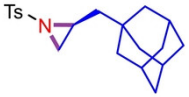
3h, 90% yield, 92% ee



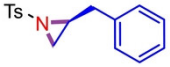
3i, 83% yield, 91% ee



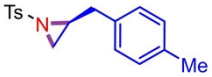
3j, 56% yield, 86% ee



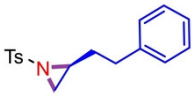
3k,72% yield, 92% ee



3l, 48% yield, 90% ee



3m, 40% yield, 90% ee

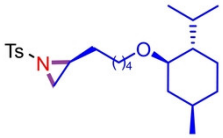


3n, 93% yield, 92% ee

3o, 96% yield, 89% ee

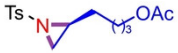
3p, 90% yield, 88% ee

3q, 75% yield, 85% ee

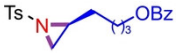


3r, 97% yield, 93.5:6.5 de

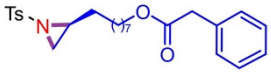
3s, 71% yield, 91% ee



3t, 85% yield, 86% ee

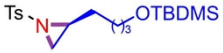


3u, 59% yield, 87% ee

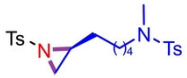


3v, 79% yield, 89% ee

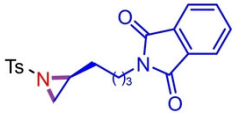
3w, 88% yield, 88% ee



3x, 92% yield, 88% ee

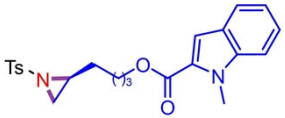


3y, 90% yield, 88% ee

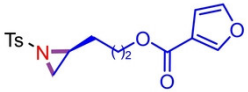


3z, 82% yield, 83% ee

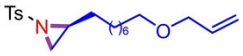
3aa, 99% yield, 92% ee



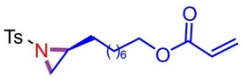
3ab, 61% yield, 85% ee



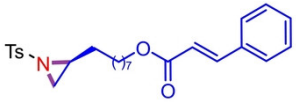
3ac, 77% yield, 83% ee



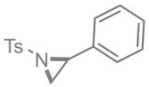
3ad, 87% yield, 90% ee



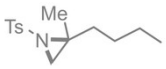
3ae, 96% yield, 90% ee



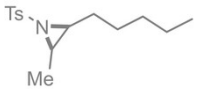
3af, 92% yield, 89% ee



3ag, not formed



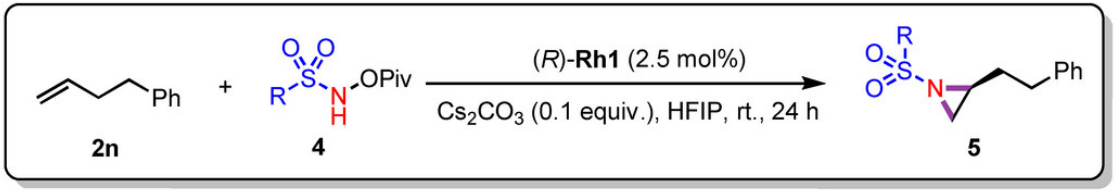
3ah, not formed

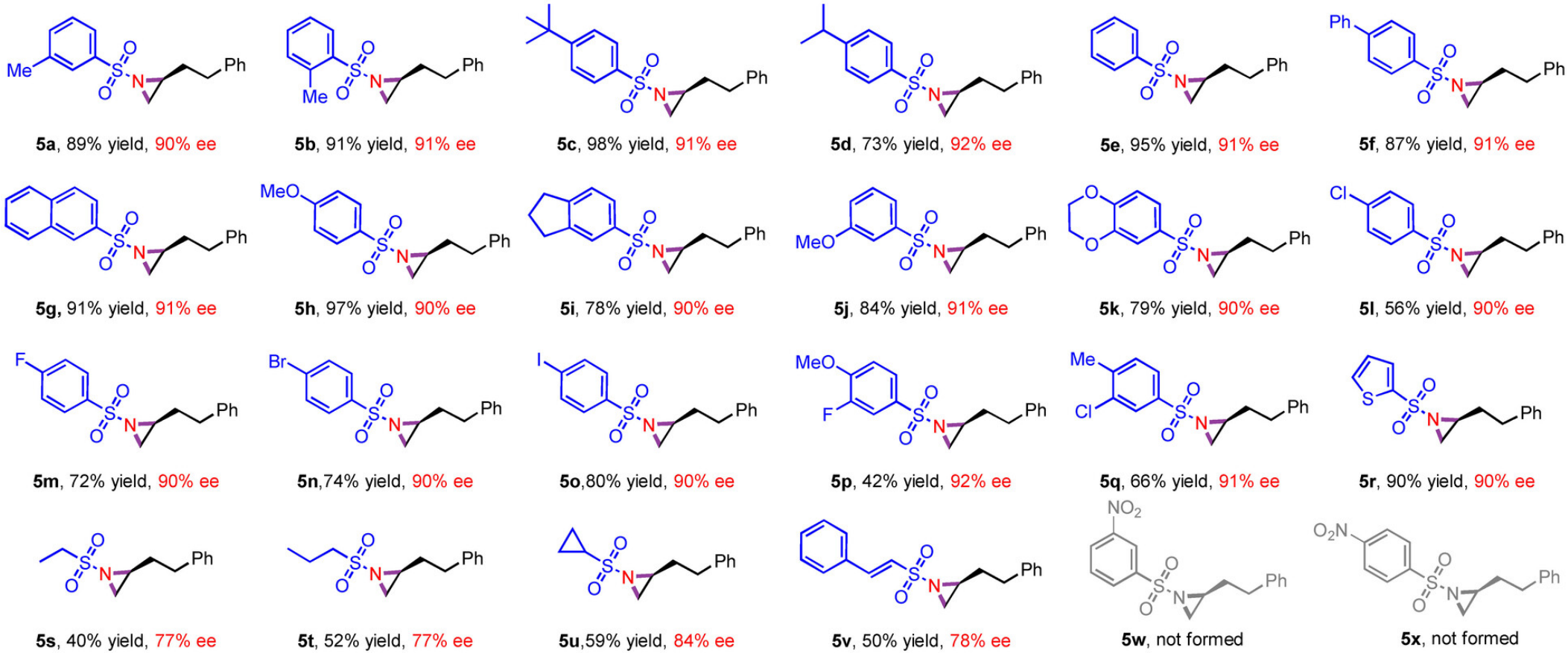


3ai, not formed

Shou-Guo Wang, *Angew.Chem. Int.Ed.* **2024**.

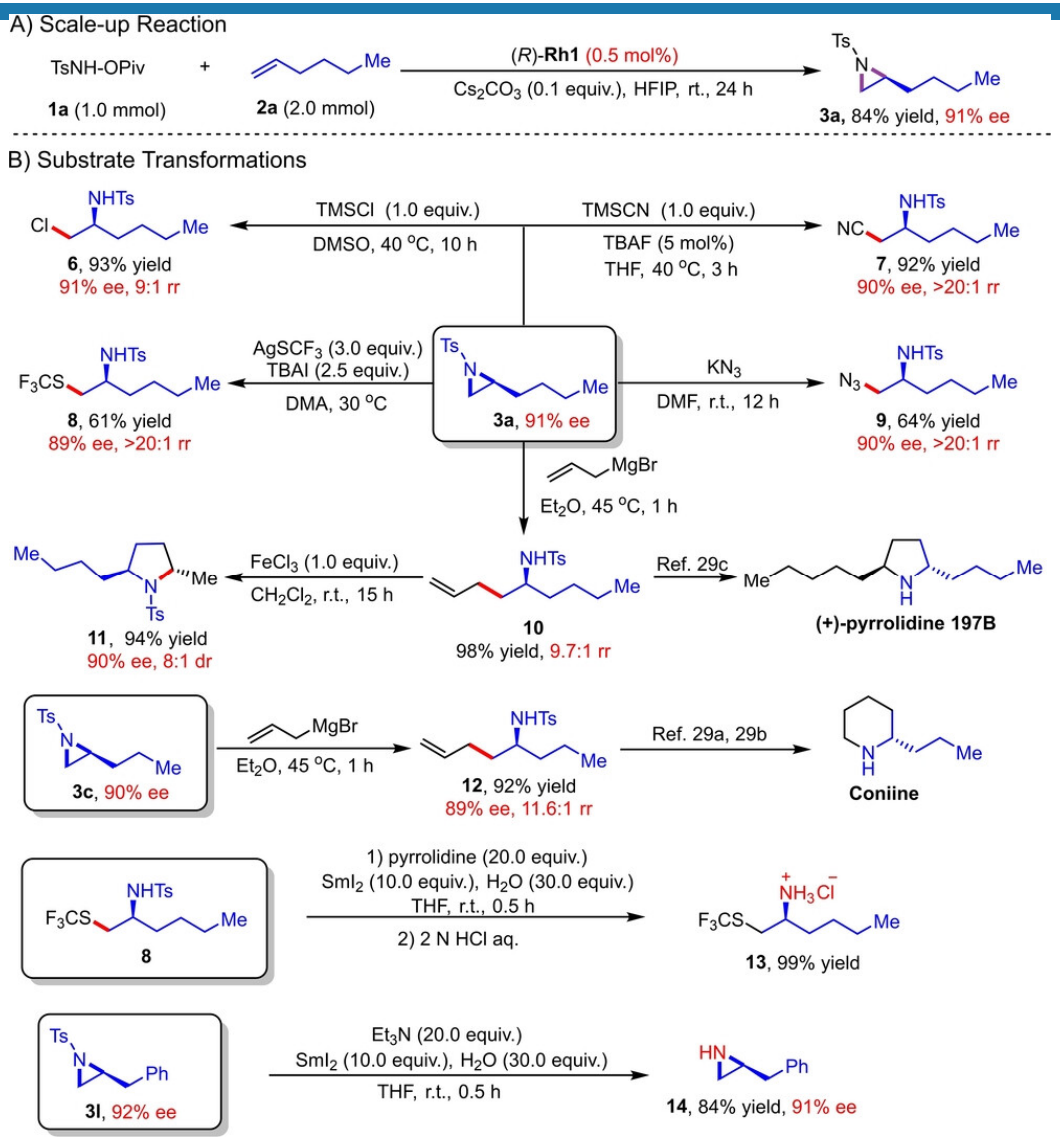
Rh Nitrene





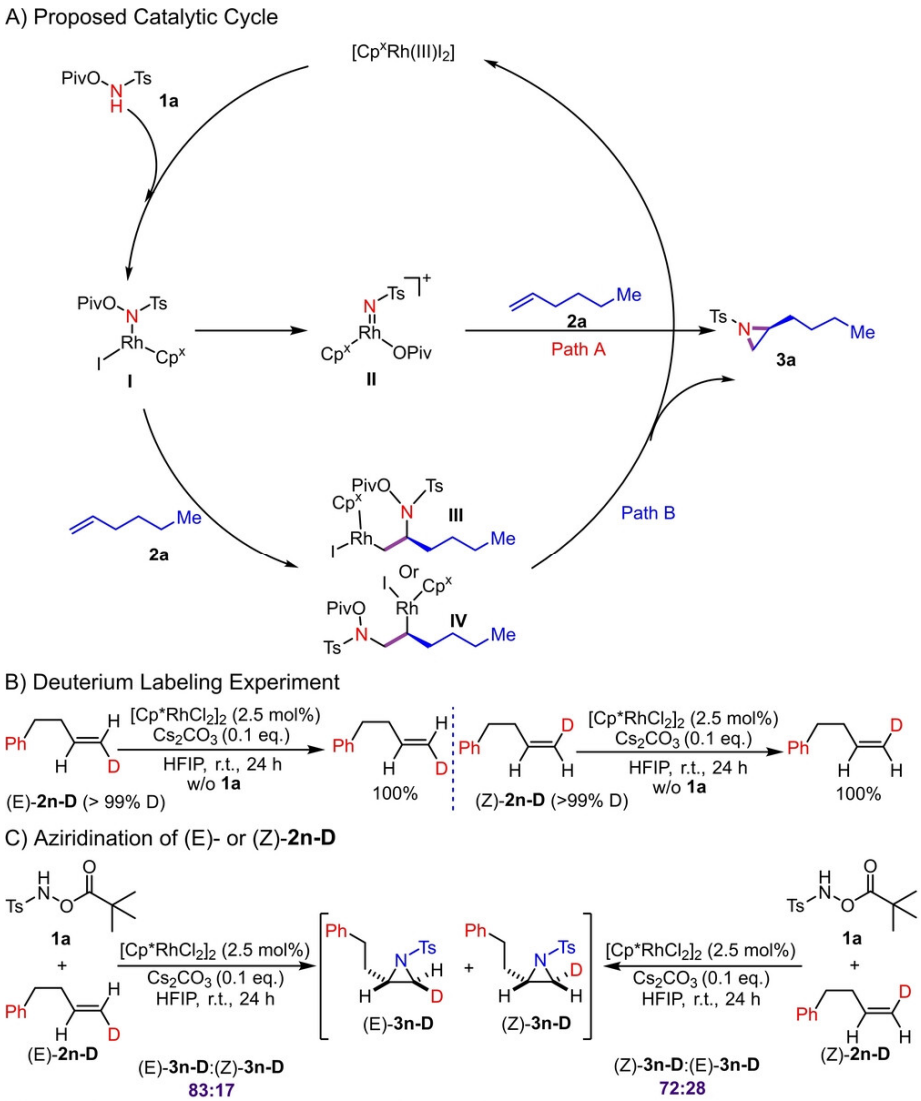
Shou-Guo Wang, *Angew.Chem. Int.Ed.* **2024**.

Rh Nitrene



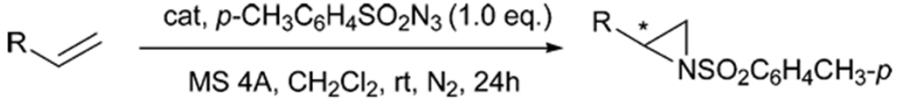
Shou-Guo Wang, *Angew.Chem. Int.Ed.* **2024**.

Rh Nitrene



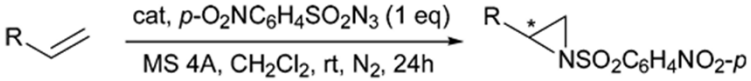
Shou-Guo Wang, *Angew.Chem. Int.Ed.* **2024**.

Ru Nitrene



Entry	Catalyst	R or substrate	Yield (%)	ee (%)	TON
1[b]	**3** (2)	Ph	100	87	—
2[b]	**3** (0.1)	Ph	41	87	410
3[b]	**1** (2)	Ph	71	87	36
4[b]	**4** (0.1)	Ph	23	87	230
5[b]	**5** (0.09)	Ph	78	85	867
6	**3** (0.1)	p-BrC_6H_4	33	90	330
7	**5** (0.09)	p-BrC_6H_4	79	90	878
8	**5** (0.09)	p-$O_2NC_6H_4$	34	87	378
9	**5** (0.09)	2-$C_{10}H_7$	65	87	722
10	**5** (0.09)	PhC≡C	61	96	678
11	**5** (2)	n-C_6H_{13}	20	86	10
12	**3** (2)	n-C_6H_{13}	30	86	15
13[c]	**5** (2)	Indene	36	>99	18

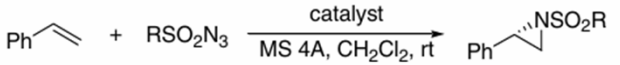
[a] See ESI for the typical experimental procedures and the determination of ee. [b] Absolute configuration of the product is *S*. [c] Absolute configuration of the product is 1*S*,2*R*.



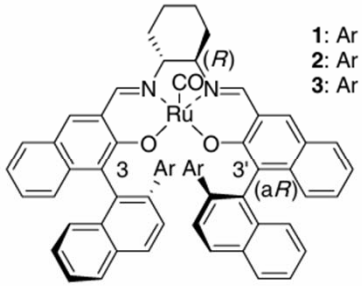
R= Ph: **1** (4 mol%): 82% ee, 22%, (*S*), TON= 5
R= Ph: **5** (1 mol%): 84% ee, 34%, (*S*), TON= 34
R= Ph: **5** (4 mol%): 84% ee, 100%, (*S*)
R= PhC≡C: **5** (4 mol%): 90% ee, 100%
R= p-BrC_6H_4: **5** (4 mol%): 81% ee, 66%

Tsutomu Katsuki, *Chem. Commun.* **2004**.

Ru Nitrene



1 (2 mol%), R = *p*-$CH_3C_6H_4$: 87% ee, 71% (TON = 36)
2 (0.09 mol%), R = *p*-$CH_3C_6H_4$: 85% ee, 78% (TON = 867)
2 (1 mol%), R = *p*-$O_2NC_6H_4$: 84% ee, 34% (TON = 34)
3 (0.1 mol%), R = *p*-$CH_3C_6H_4$: 86% ee, 93% (TON = 982)

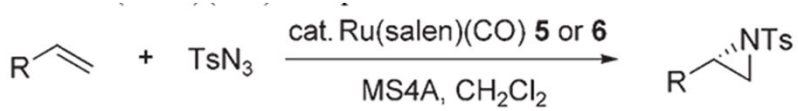


1: Ar = Ph
2: Ar = 3,5-F_2-4-$CH_3C_6H_2$
3: Ar = 3,5-Cl_2-4-$(CH_3)_3SiC_6H_2$

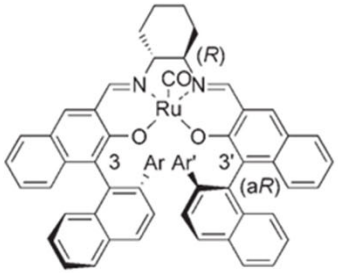
Entry	Azide	Catalyst/mol %	R or substrate	Temp/°C	Time/h	Yield/%[a]	% ee[b]	TON[c]
1	*p*-NsN_3	0.1	Ph	rt	38	70	81	746
2	*p*-NsN_3	1	Ph	0	12	90	87	97
3	*p*-NsN_3	1	4-BrC_6H_4	0	12	93	83	94
4	*p*-NsN_3	1	PhC≡C—	0	12	98	98	99
5	*p*-NsN_3	2	1-Octene	Reflux	38	32[c]	56	16
6	*o*-NsN_3	0.1	Ph	rt	12	62	73	660
7	*o*-NsN_3	1	Ph	0	12	60	81	68
8	*o*-NsN_3	1	PhC≡C—	rt	12	58	87	59
9	$SESN_3$	0.1	Ph	rt	12	26	91	260
10	$SESN_3$	1	Ph	rt	12	100	90	—
11	$SESN_3$	1	Ph	0	12	99	92	99
12	$SESN_3$	1	4-BrC_6H_4	0	12	76	92	98
13	$SESN_3$	1	PhC≡C—	0	12	50	>99	51
14	$SESN_3$	5	1-Octene	Reflux	38	28[c]	77[d]	6
15	$SESN_3$	5	Indene	Reflux	38	47	98	26

Tsutomu Katsuki, *Tetrahedron Letters.* **2006**.

Ru Nitrene



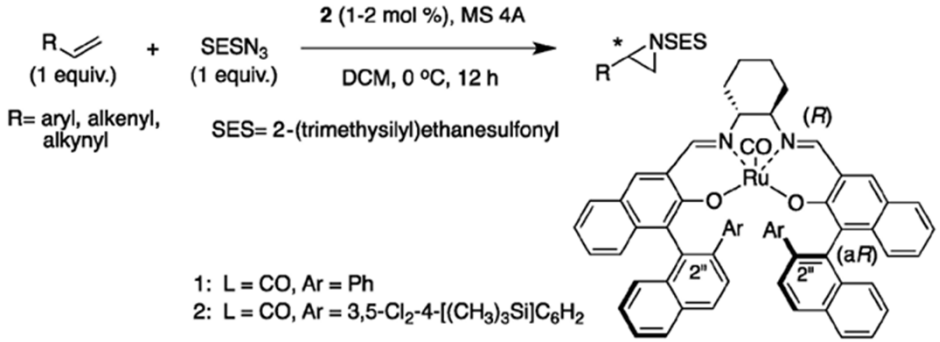
Entry	Azide	Catalyst [mol %]	Substrate	T [°C]	t [h]	Yield[a] [%]	ee[b] [%]	TON[c]
1	*p*-NsN_3	**1** (4.0)	styrene	RT	24	22	84	5
2	*p*-NsN_3	**5** (1.0)	styrene	RT	24	34	84	34
3	*p*-NsN_3	**6** (0.1)	styrene	RT	38	70	81	746
4	*o*-NsN_3	**6** (0.1)	styrene	RT	12	62	73	660
5	$SESN_3$	**5** (1.0)	styrene	RT	12	67	88 (*S*)	67
6	$SESN_3$	**6** (0.1)	styrene	RT	12	26	91 (*S*)	260
7	$SESN_3$	**6** (1.0)	styrene	0	12	99	92 (*S*)	99
8	$SESN_3$	**6** (1.0)	4-BrC_6H_4-CH=CH_2	0	12	76	92	98
9	$SESN_3$	**6** (1.0)	PhC≡C-CH=CH_2	0	12	50	>99	51
10	$SESN_3$	**6** (5.0)	1-octene	reflux	38	28[c]	77[d]	6
11	$SESN_3$	**6** (5.0)	indene	reflux	38	65	98	13
12	$SESN_3$	**6** (2.0)	CH_2=$CHCO_2Bn$	RT	24	81	>99 (*R*)	41
13	$SESN_3$	**6** (2.0)	CH_2=CHCON(OMe)Bn	RT	24	85	>99	43

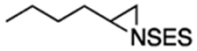
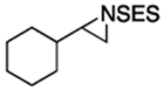
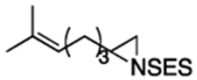
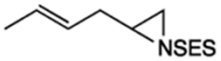
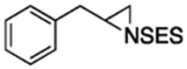
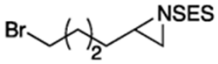
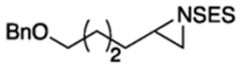


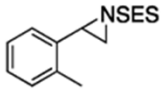
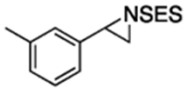
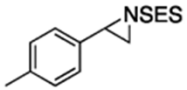
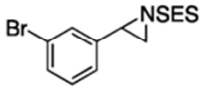
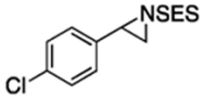
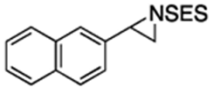
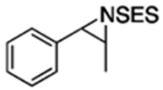
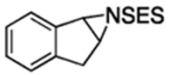
1: Ar = Ar' = Ph
2: Ar = Ph, Ar' = $Cl_3CCMe_2OCONHC_6H_4$
3: Ar = Ar' = 4-*t*$BuMe_2SiC_6H_4$
4: Ar = Ar' = 4-*t*$BuPh_2SiC_6H_4$
5: Ar = Ar' = 3,5-F_2-4-MeC_6H_2
6: Ar = Ar' = 3,5-Cl_2-4-$Me_3SiC_6H_2$

Tsutomu Katsuki, *Chem. Asian J.* **2007**.

Ru Nitrene

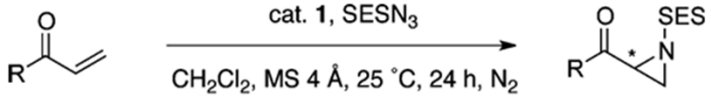


Entrty	Substrate	mol (%)	Temp (°C)	Time (h)	Yield[b] (%)	ee[c] (%)
1		3	25	24	74	99
2		3	25	24	45	99
3[d]		3	0	24	54	89
4[e]		3	25	24	58	91
5[f]		3	40	24	91	90
6		3	0	24	95	91
7		3	0	24	65	87

Entry	Substrate	mol (%)	Temp (°C)	Time (h)	Yield[b] (%)	ee[c] (%)
1		0.5	25	6	95	97
2		0.5	25	6	98	90
3		0.5	25	6	95	89
4		1	25	6	95	90
5		1	25	6	96	90
6		0.5	25	6	99	91
7		1	25	12	72	99
8		1	25	12	66	97

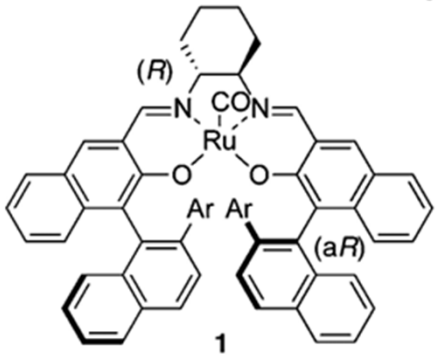
Tsutomu Katsuki, *Chem. Commun.* **2012**.

Ru Nitrene



3 4

entry	vinyl ketone (R)	cat. (mol %)	yield (%)[b]	% ee[c]
1	Ph (**3a**)	2.0	99	>99
2	Ph (**3a**)	1.0	99	>99
3	Ph (**3a**)	0.5	99	>99
4	p-ClC_6H_4 (**3b**)	0.5	96	>99
5	m-ClC_6H_4 (**3c**)	0.5	96	>99
6	o-ClC_6H_4 (**3d**)	0.5	98	>99
7	p-$MeOC_6H_4$ (**3e**)	0.5	92	>99
8	m-$MeOC_6H_4$ (**3f**)	0.5	99	>99
9	$PhCH_2CH_2$ (**3g**)	1.0	99 (64)[d]	>99
10	1-cyclohexenyl (**3h**)	1.0	92 (67)[d]	>99 (R)[e]
11	(E)-PhCH=CH (**3i**)	0.5	95	>99

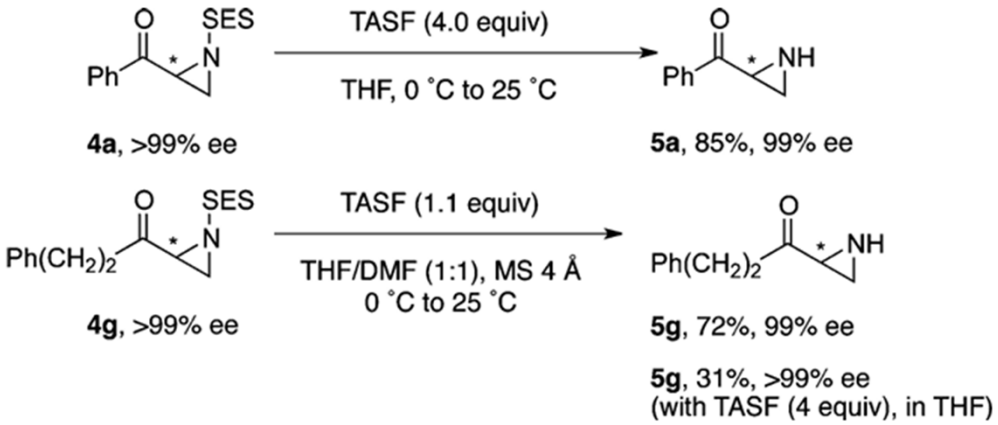


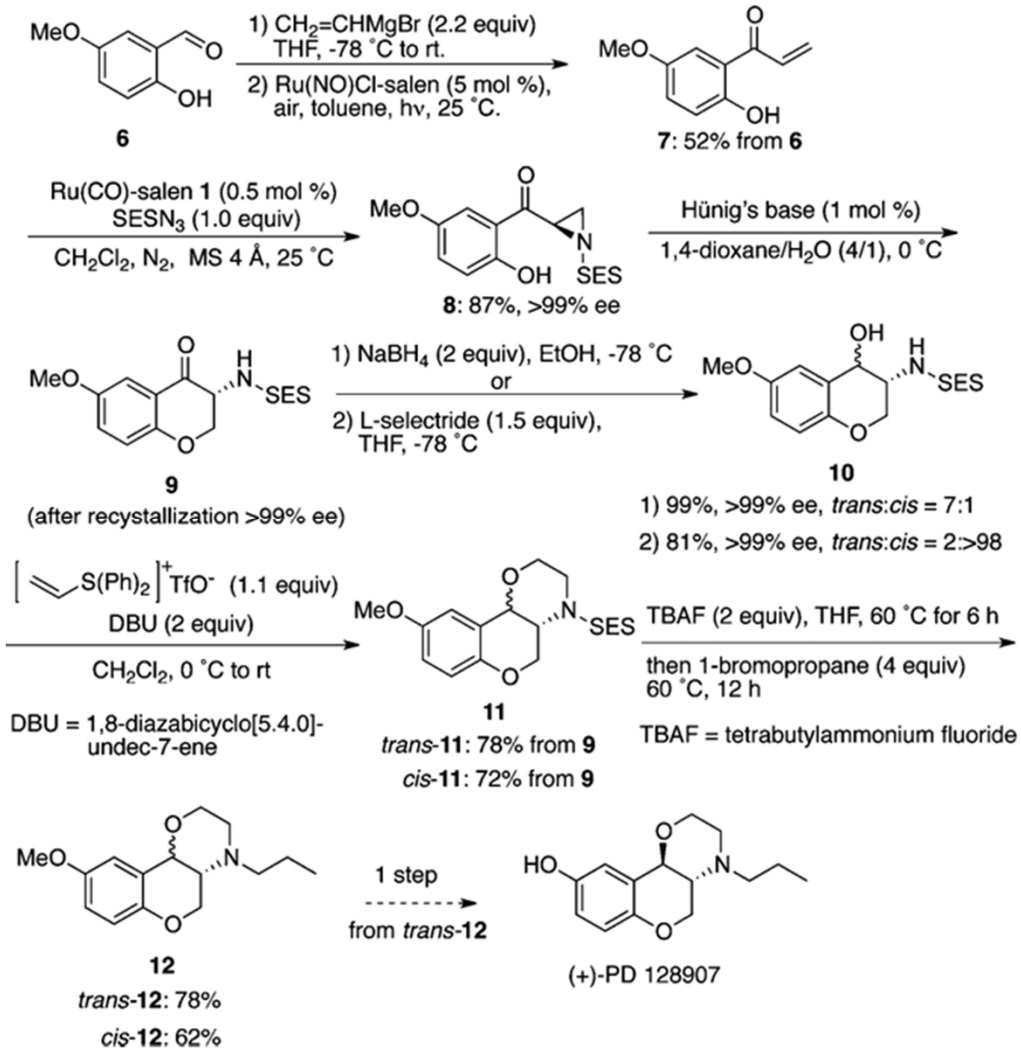
1

Ar = 3,5-Cl_2-4-$(CH_3)_3Si$-C_6H_2

Tsutomu Katsuki, *Org. Lett.* **2012**.

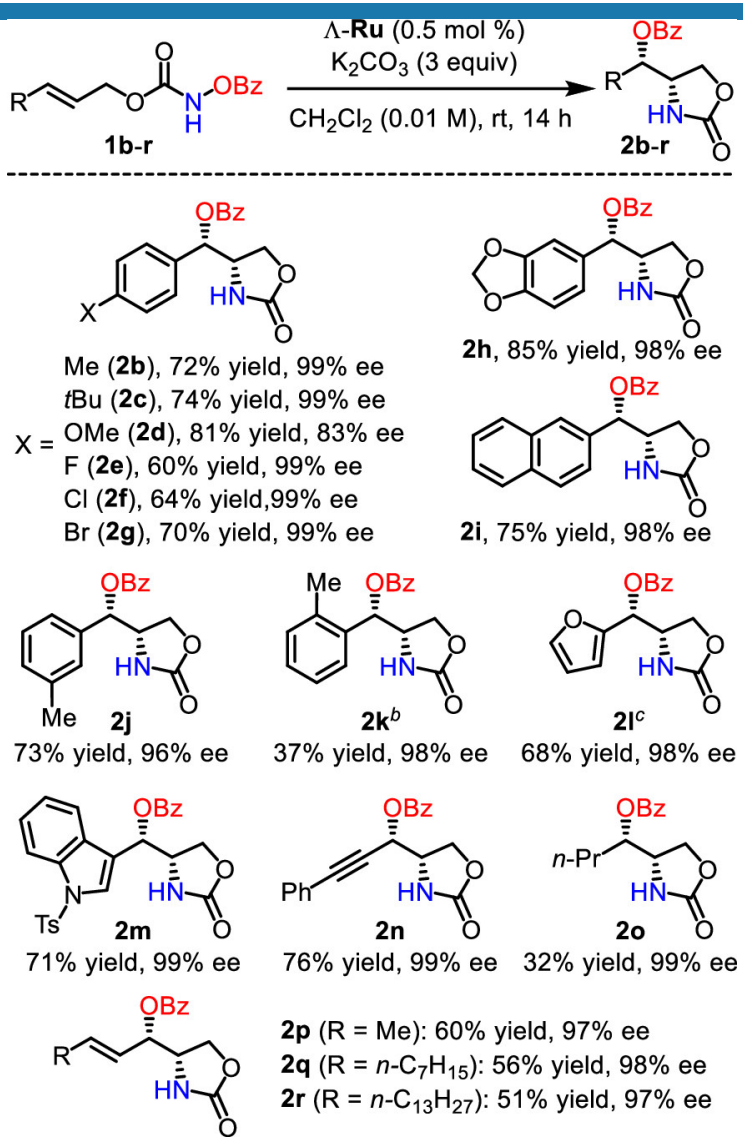
Ru Nitrene

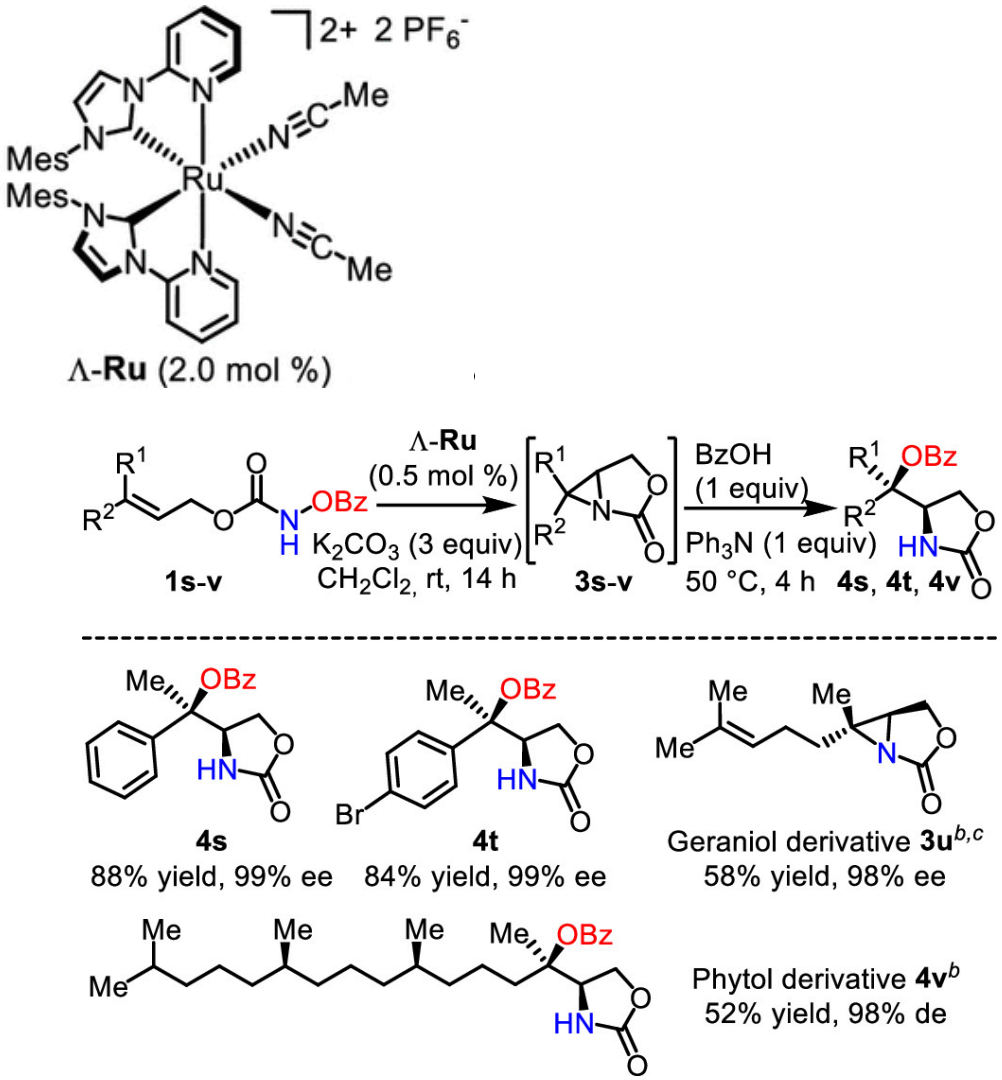




Tsutomu Katsuki, *Org. Lett.* **2012**.

Ru Nitrene

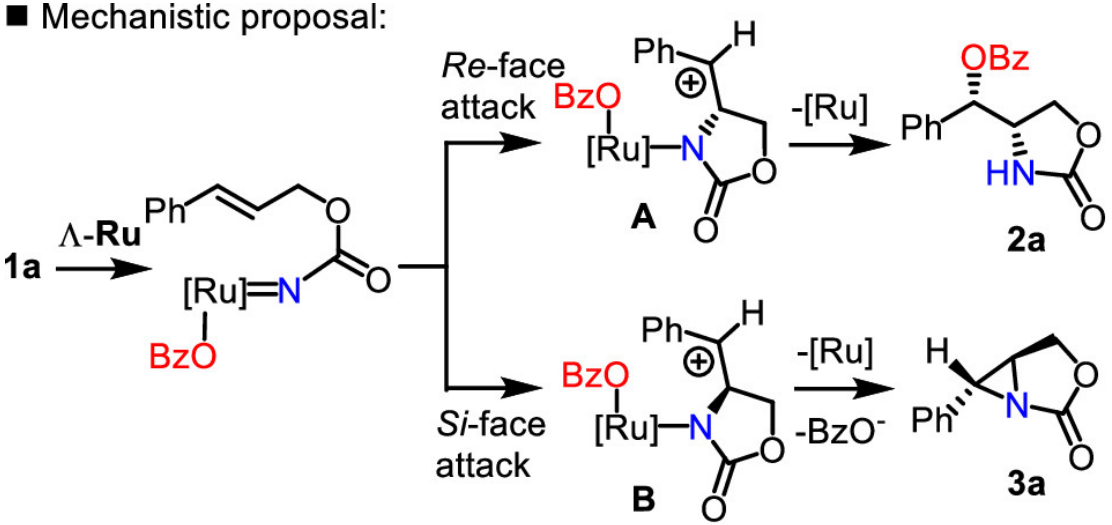




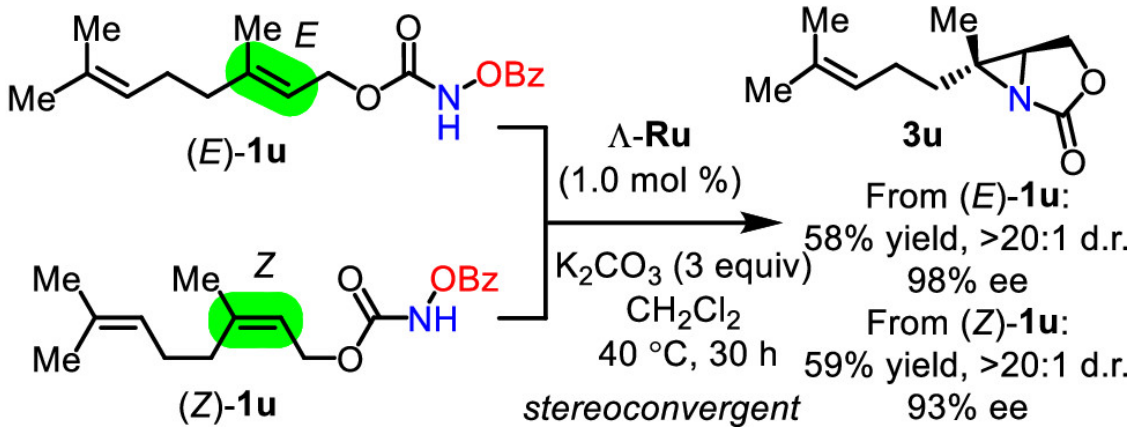
Eric Meggers, *Org. Lett.* **2020**.

Ru Nitrene

■ Mechanistic proposal:

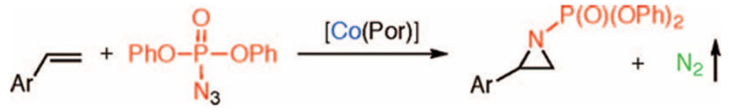


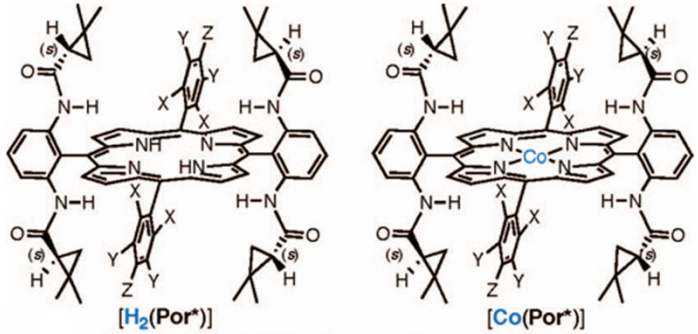
■ Support for carbenium ion intermediate:



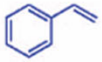
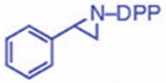
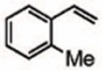
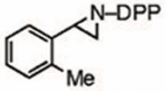
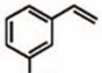
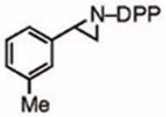
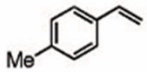
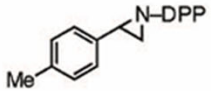
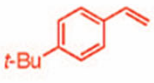
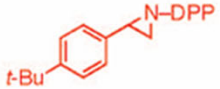
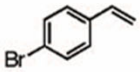
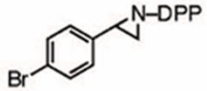
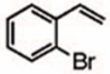
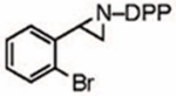
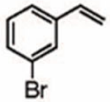
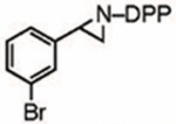
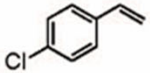
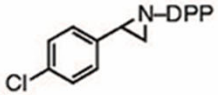
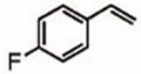
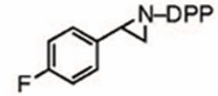
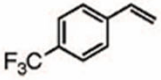
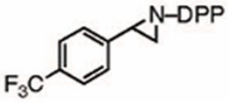
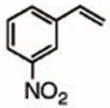
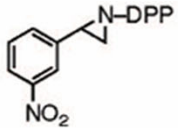
Eric Meggers, *Org. Lett.* **2020**.

Co Nitrene



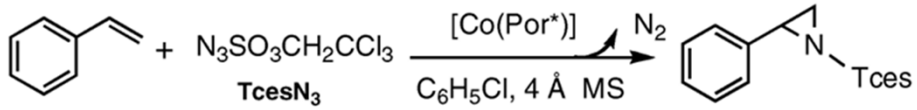


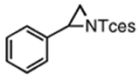
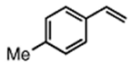
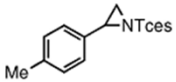
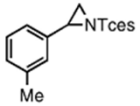
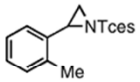
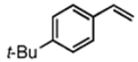
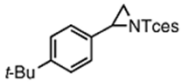
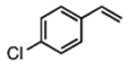
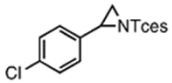
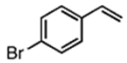
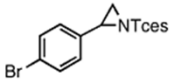
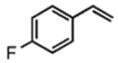
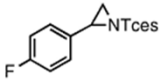
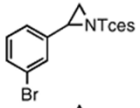
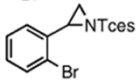
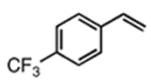
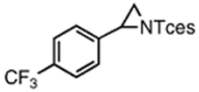
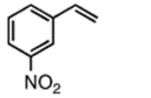
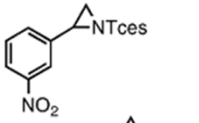
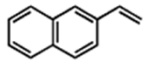
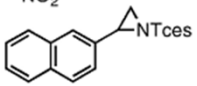
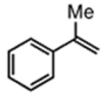
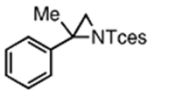
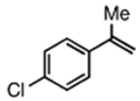
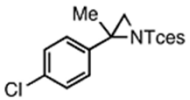
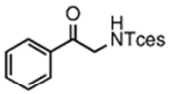
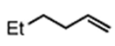
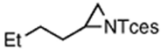
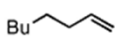
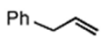
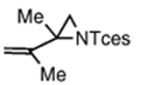
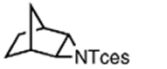
P1 (ChenPhyrin): X = Y = Z = H
P2 (2,6-DiMeO-ChenPhyrin): X = MeO; Y = Z = H
P3 (2,4,6-TriMe-ChenPhyrin): X = Z = Me; Y = H
P4 (3,5-DiMeO-ChenPhyrin): X = Z = H; Y = MeO
P5 (3,5-Di^{t}Bu-ChenPhyrin): X = Z = H; Y = *t*-Bu
P6 (4-^{t}Bu-ChenPhyrin): X = Y = H; Z = *t*-Bu

entry	olefin	aziridine	yield (%)[b]	ee (%)[c]
1			88	37
2			35 70[d]	46 33[d]
3			52 78[d]	44 32[d]
4			58 55[d]	37 21[d]
5			77	53
6			65	28
7			68	7
8			58	45
9			64	6
10			39 72[d]	10 17[d]
11			64	44
12			58	46

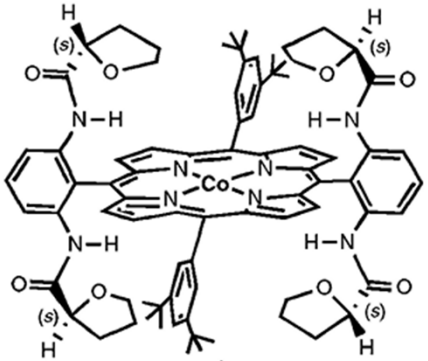
X. Peter Zhang, *J. Org. Chem.* **2008**.

Co Nitrene

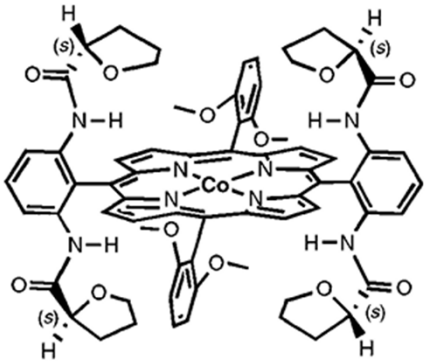


Entry	Olefin	Aziridine	Temp/°C	Yield[b] (%)	Ee[c] (%)	[α][d]
1			0	91	94	(−)
2			0	89	90	(−)
3[f]			RT	85	82	(−)
4[f]			RT	86	84	(−)
5			0	89	85	(−)
6			0	93	91	(−) (*R*)[e]
7			0	92	91	(−)
8			0	90	90	(−)
9			0	91	88	(−)
10			0	92	99	(−)
11			0	88	81	(−)
12			0	82	80	(−)
13			0	85	90	(−)
14[f]			RT	48	80	(−)
15[f]			RT	43	80	(−)
16[f]			40	87	—	—
17[g]			40	42	91	(+)
18[g]			40	30	90	(+)
19[f]			0	26	94	(+)
20[h]			RT	53	87	(−)
21[f]			40	85	—	—

[a] Performed in C_6H_5Cl using 5 mol% [Co(**P6**)] for 48 h under N_2 with 4 Å MS in the presence of 5 mol% $Pd(OAc)_2$; alkene : $TcesN_3$ = 5 : 1; [alkene] = 0.25 M. [b] Isolated yields. [c] Measured by chiral HPLC. [d] Sign of optical rotation. [e] Determined by X-ray crystal structural analysis. [f] 24 h without $Pd(OAc)_2$. [g] Using [Co(**P5**)] in CH_2Cl_2 for 48 h. [h] In $MeCO_2Et$.



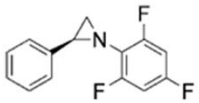
[Co(**P5**)] (3,5-Di^{t}Bu-ZhuPhyrin)



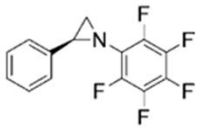
[Co(**P6**)] (2,6-DiMeO-ZhuPhyrin)

X. Peter Zhang. *Chem. Commun.* **2009**.

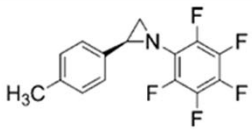
Co Nitrene



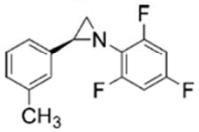
entry 1: **3 ab**;
99 % yield, 94 % *ee*



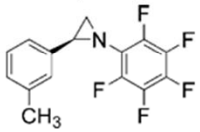
entry 2: **3 af**;
99 % yield, 92 % *ee*



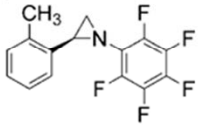
entry 3: **3 bf**;
99 % yield, 96 % *ee*



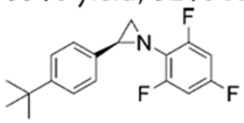
entry 4: **3 cb**;
99 % yield, 92 % *ee*



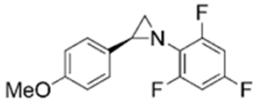
entry 5: **3 cf**;
95 % yield, 94 % *ee*



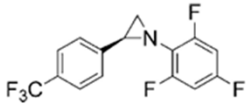
entry 6: **3 df**;
99 % yield, 87 % *ee*



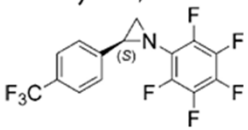
entry 7: **3 eb**;
85 % yield, 92 % *ee*



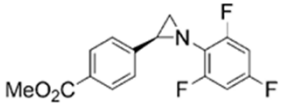
entry 8: **3 fb**;
99 % yield, 87 % *ee*



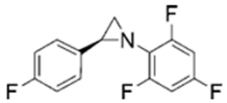
entry 9: **3 gb**;
77 % yield, 92 % *ee*



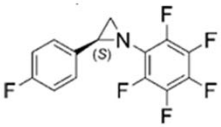
entry 10:[d] **3 gf**;
91 % yield, 85 % *ee*



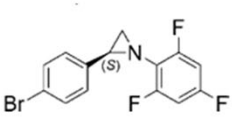
entry 11: **3 hb**;
80 % yield, 92 % *ee*



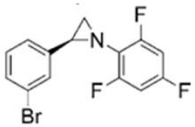
entry 12: **3 ib**;
93 % yield, 95 % *ee*



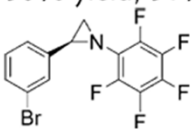
entry 13:[d] **3 if**;
90 % yield, 91 % *ee*



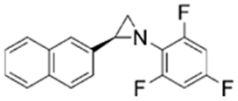
entry 14:[d] **3 jb**;
81 % yield, 92 % *ee*



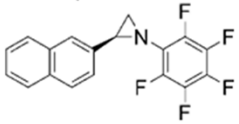
entry 15: **3 kb**;
82 % yield, 93 % *ee*



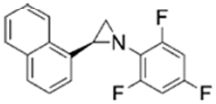
entry 16: **3 kf**; 95 %
yield, 89 % *ee*



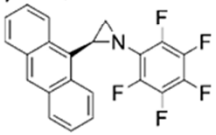
entry 17: **3 lb**; 80 %
yield, 90 % *ee*



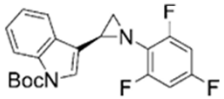
entry 18: **3 lf**; 73 %
yield, 98 % *ee*



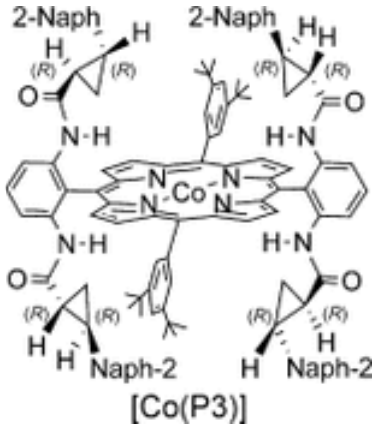
entry 19: **3 mb**; 74 %
yield, 86 % *ee*



entry 20: **3 nf**; 90 %
yield, 85 % *ee*

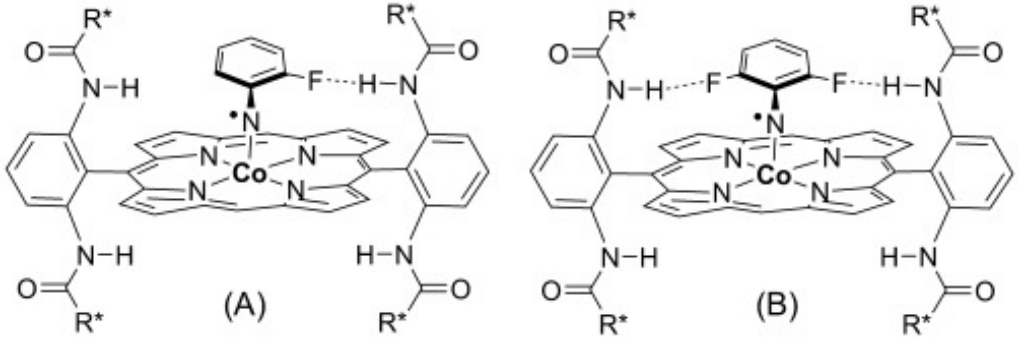


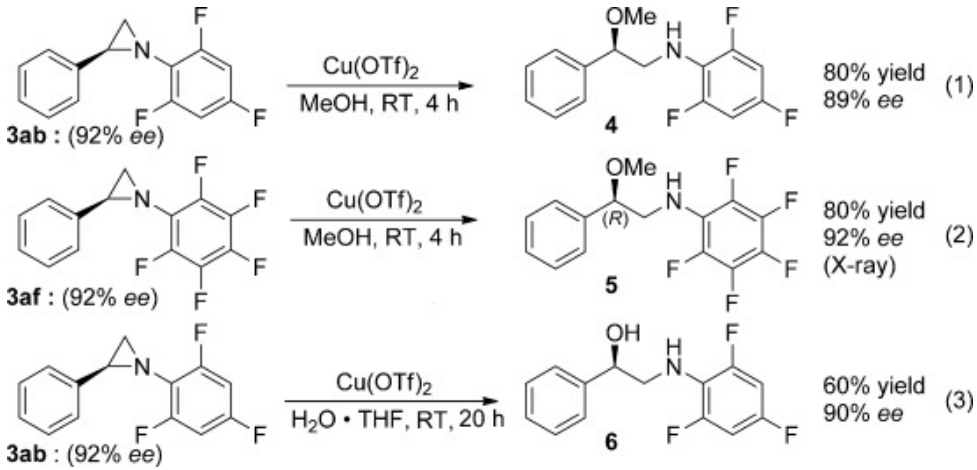
entry 21: **3 ob**; 80 %
yield, 96 % *ee*



X. Peter Zhang, *Angew. Chem. Int. Ed.* **2013**.

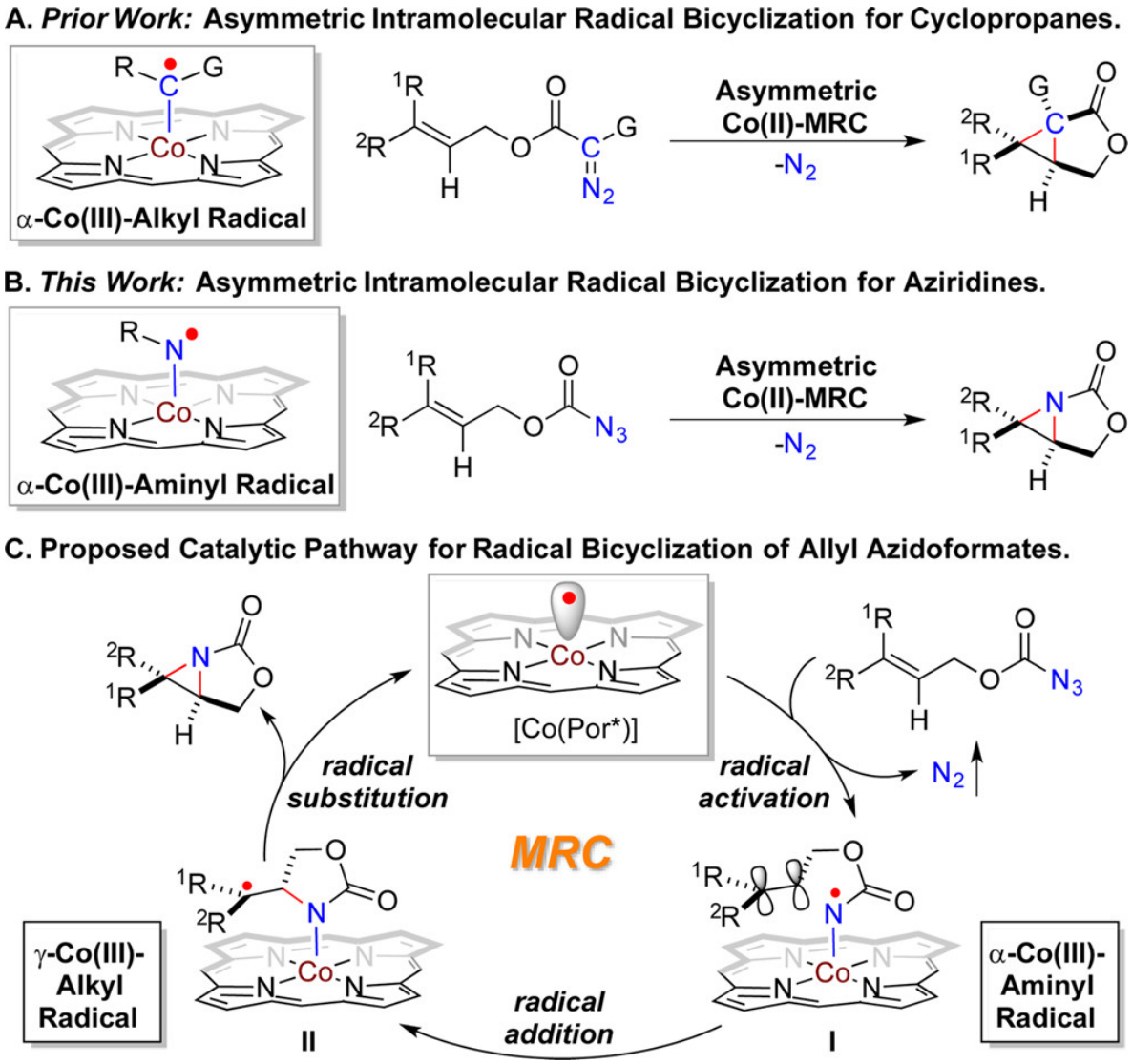
Co Nitrene





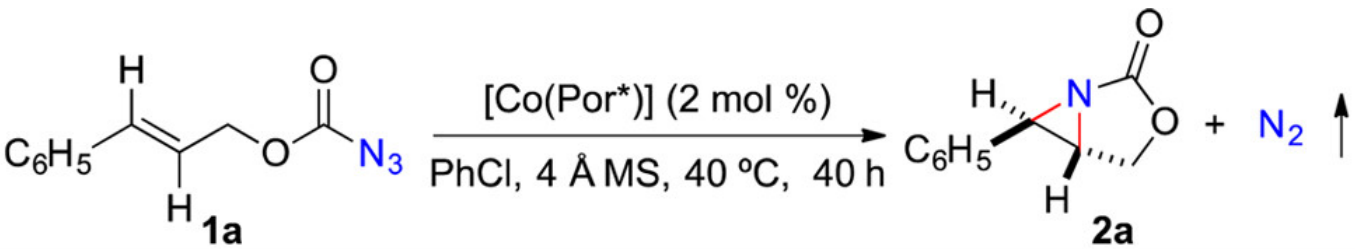
X. Peter Zhang, *Angew. Chem. Int. Ed.* **2013**.

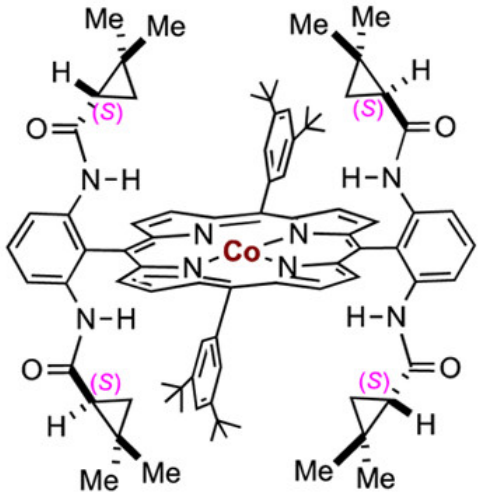
Co Nitrene



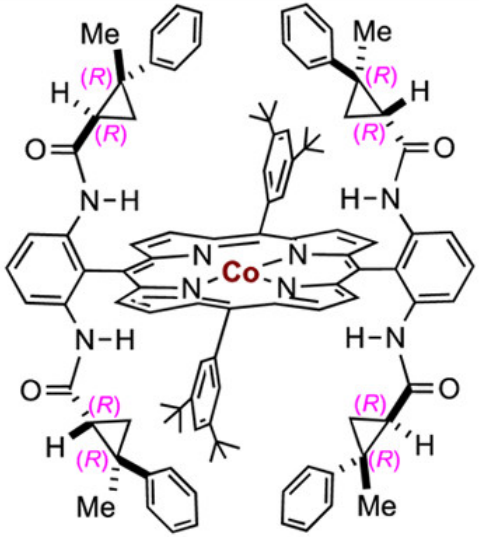
X. Peter Zhang, *J. Am. Chem. Soc.* **2017**.

Co Nitrene





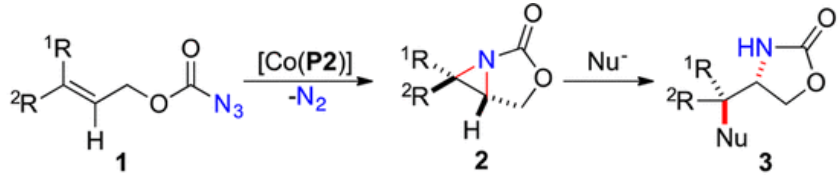
[Co(**P1**)] (**P1** = 3,5-Di^{t}Bu-ChenPhyrin)
yield^b: 99%, de: 99%, ee: 20%

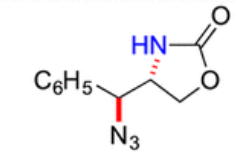


[Co(**P2**)] (**P2** = 3,5-Di^{t}Bu-QingPhyrin)
yield^b: 99%, de: 99%, ee: >99%

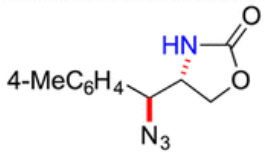
X. Peter Zhang, *J. Am. Chem. Soc.* **2017**.

Co Nitrene

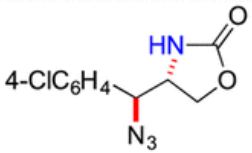




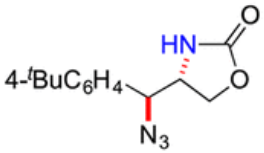
entry 1[b]: (**3a**); yield: 92%
de: 99%, ee: >99%



entry 2[b]: (**3b**); yield: 95%
de: 99%, ee: 97%



entry 3[b]: (**3c**); yield: 84%
de: 99%, ee: 95%

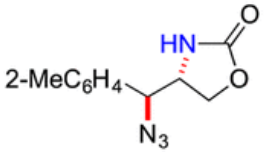


entry 4[b]: (**3d**); yield: 95%
de: 99%, ee: 93%

(X-ray)[d]

entry 5[c]: (**3e**); yield: 89%
de: 99%, ee: 91%

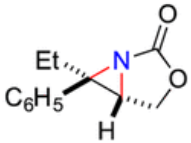
entry 6[b]: (**3f**); yield: 71%
de: 99%, ee: 95%



entry 7[b]: (**3g**); yield: 99%
de: 99%, ee: >99%

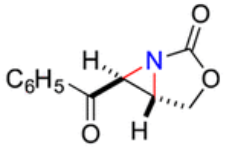
entry 8[c]: (**3h**); yield: 99%
de: 99%, ee: 94%

entry 9[b]: (**3i**); yield: 89%
de: 99%, ee: 94%



entry 10[e]: (**2j**); yield: 62%[f]
de: 99%, ee: >99%

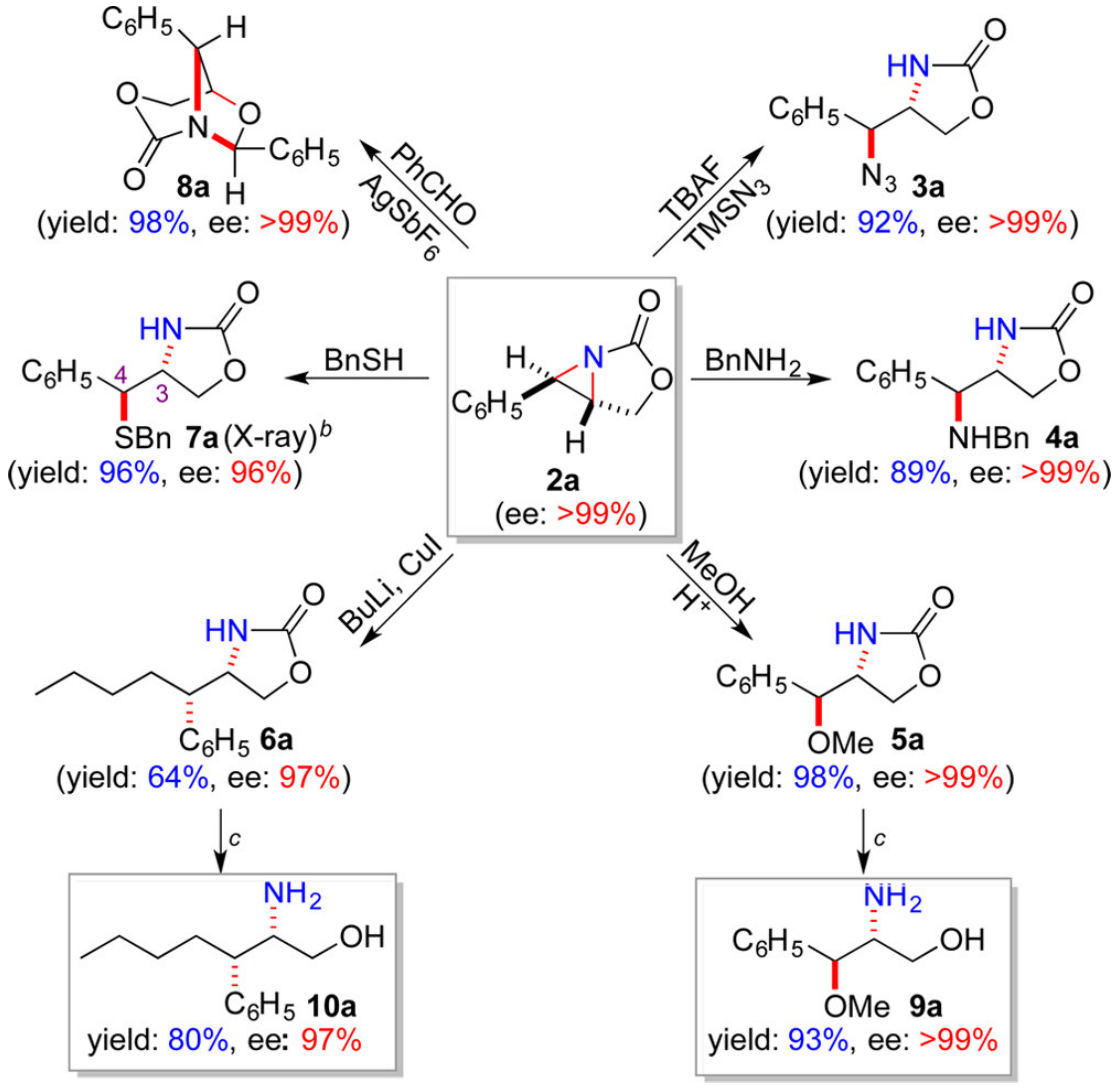
entry 11[c]: (**3k**); yield: 94%
de: 99%, ee: 93%



entry 12: (**2l**); yield: 95%
de: 99%, ee: 70%

X. Peter Zhang, *J. Am. Chem. Soc.* **2017**.

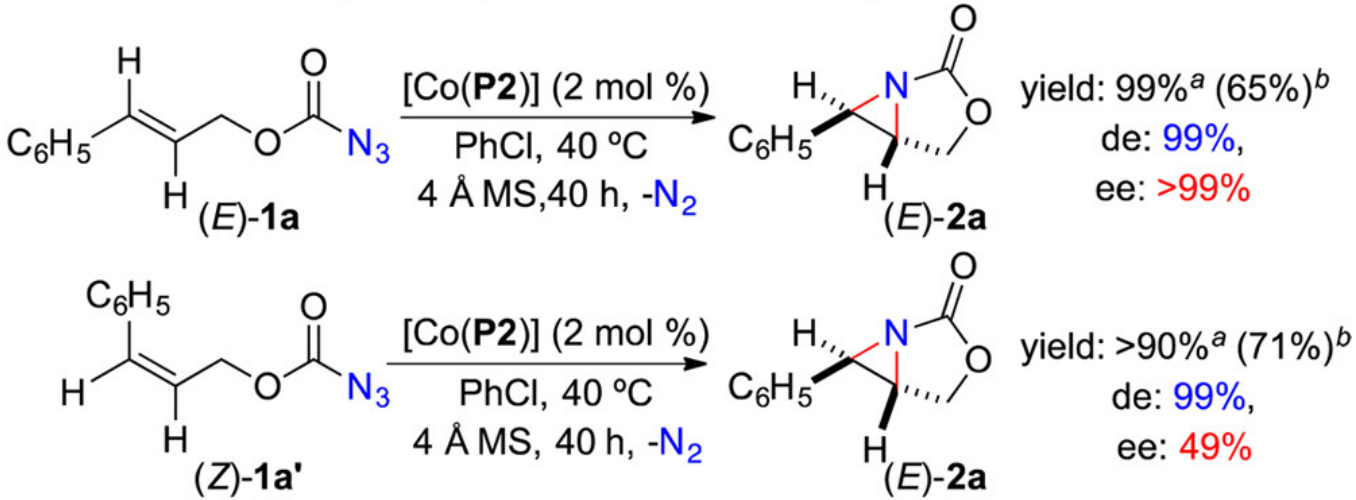
Co Nitrene



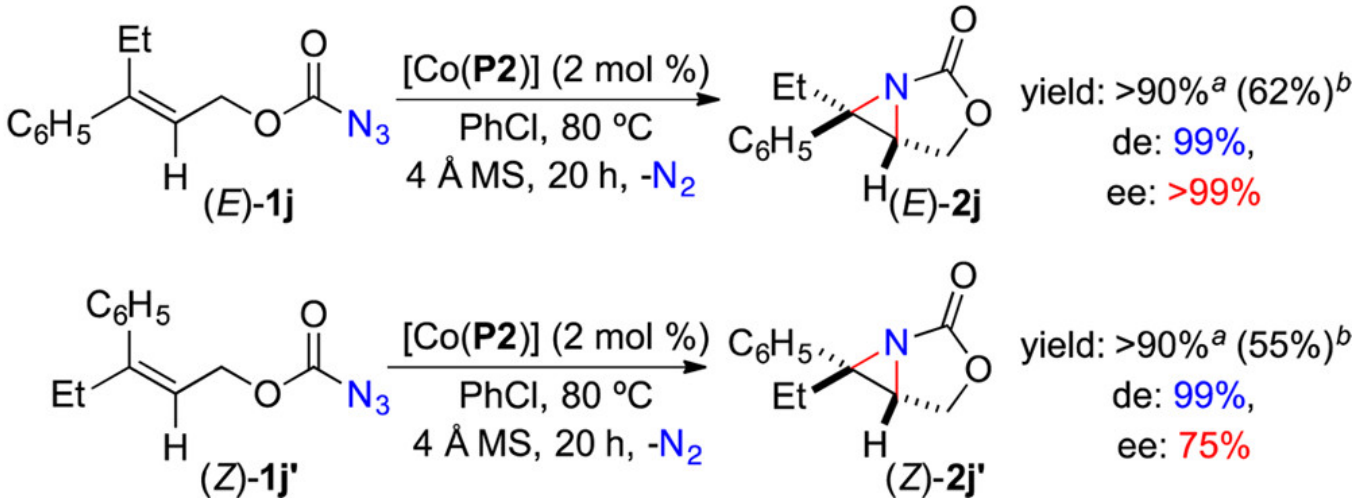
X. Peter Zhang, *J. Am. Chem. Soc.* **2017**.

Co Nitrene

A. Diastereoconvergent Asymmetric Radical Bicyclization of Azidoformates

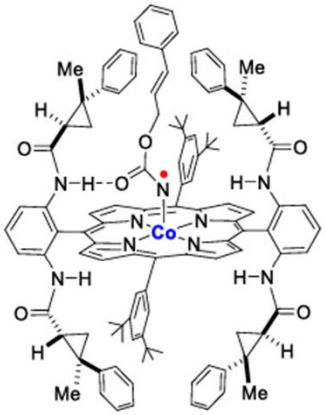


B. Diastereospecific Asymmetric Radical Bicyclization of Azidoformates



X. Peter Zhang, *J. Am. Chem. Soc.* **2017**.

Co Nitrene



α-Co(III)-aminyl radical I

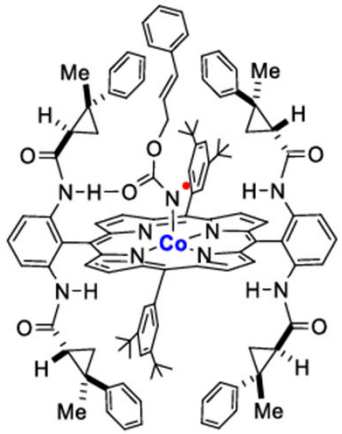
From simulation: g_{iso}: 2.00417;

$A_{(Co)}$: 6.05729 x 2.00417 x 1.399611451 = 16.99 MHz

$A_{(N)}$: 5.39222 x 2.00417 x 1.399611451 = 15.1 MHz

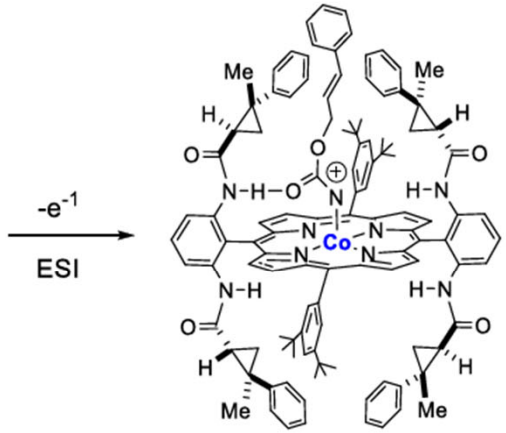
From experimental: g_{iso}: 2.00406

Figure S2. Experimental and Simulated X-Band EPR Spectra for α-Co(III)-Aminyl Radical **I** (when R^1=H, R^2=Ph) in Benzene at RT



[M]•

α-Co(III)-aminyl radical I



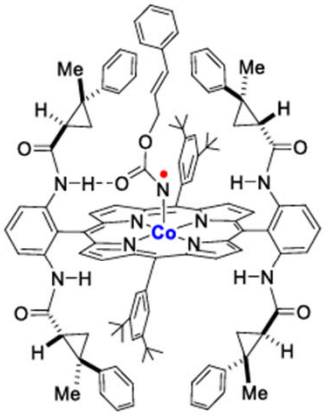
[M]+

Chemical Formula: $C_{114}H_{113}CoN_9O_6^+$

Calculated Exact Mass: 1762.8140

X. Peter Zhang, *J. Am. Chem. Soc.* **2017**.

Co Nitrene



α-Co(III)-aminyl radical I

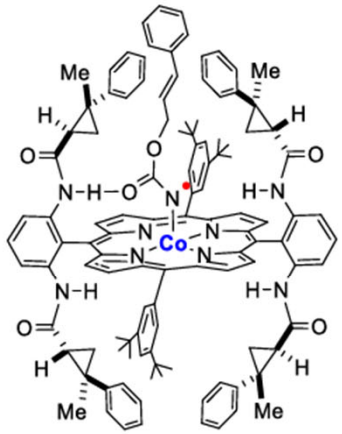
From simulation: g_{iso}: 2.00417;

$A_{(Co)}$: 6.05729 x 2.00417 x 1.399611451 = 16.99 MHz

$A_{(N)}$: 5.39222 x 2.00417 x 1.399611451 = 15.1 MHz

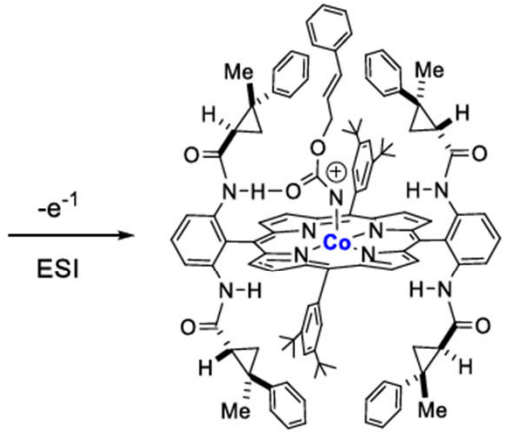
From experimental: g_{iso}: 2.00406

Figure S2. Experimental and Simulated X-Band EPR Spectra for α-Co(III)-Aminyl Radical **I** (when R^1=H, R^2=Ph) in Benzene at RT



[M]•

α-Co(III)-aminyl radical I



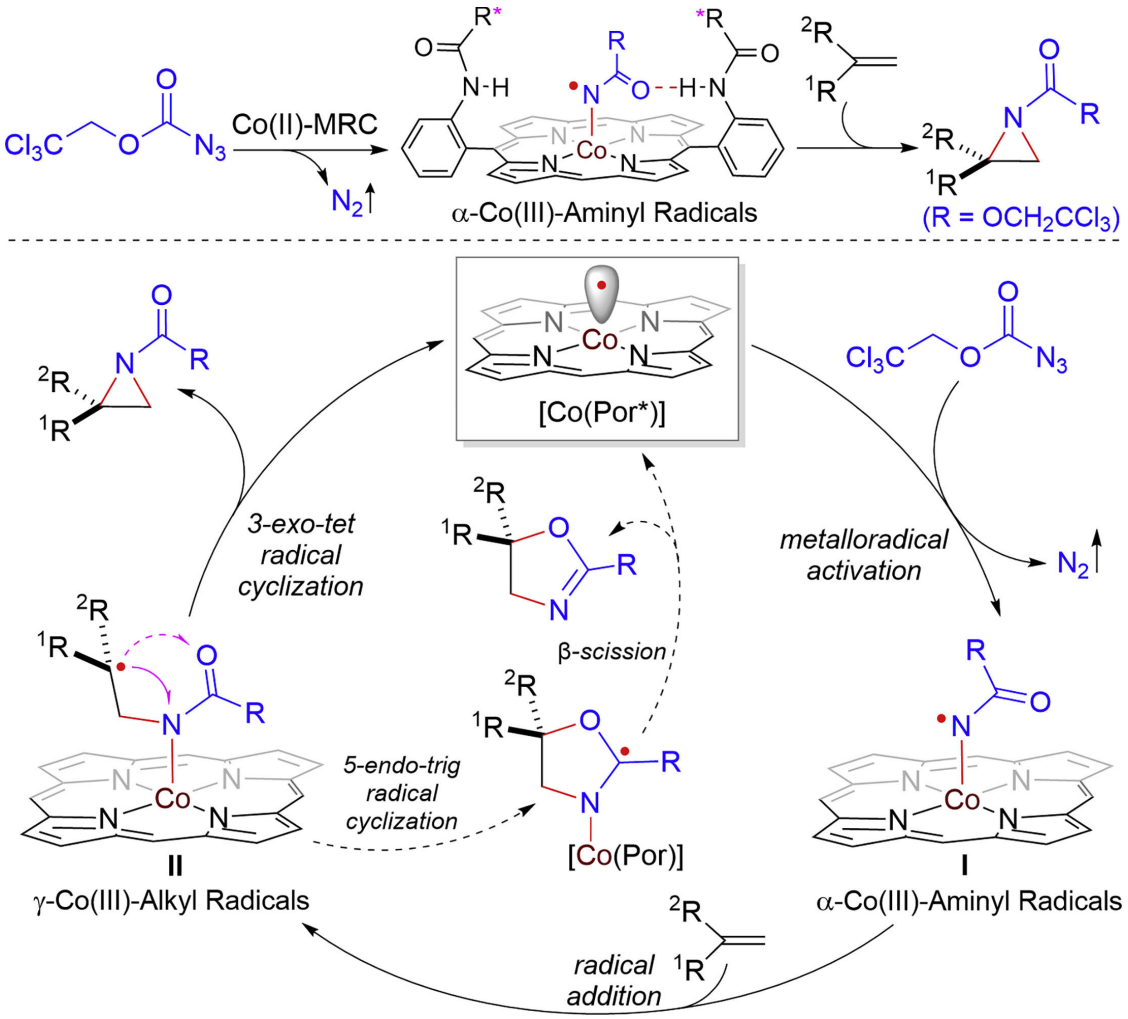
[M]+

Chemical Formula: $C_{114}H_{113}CoN_9O_6^+$

Calculated Exact Mass: 1762.8140

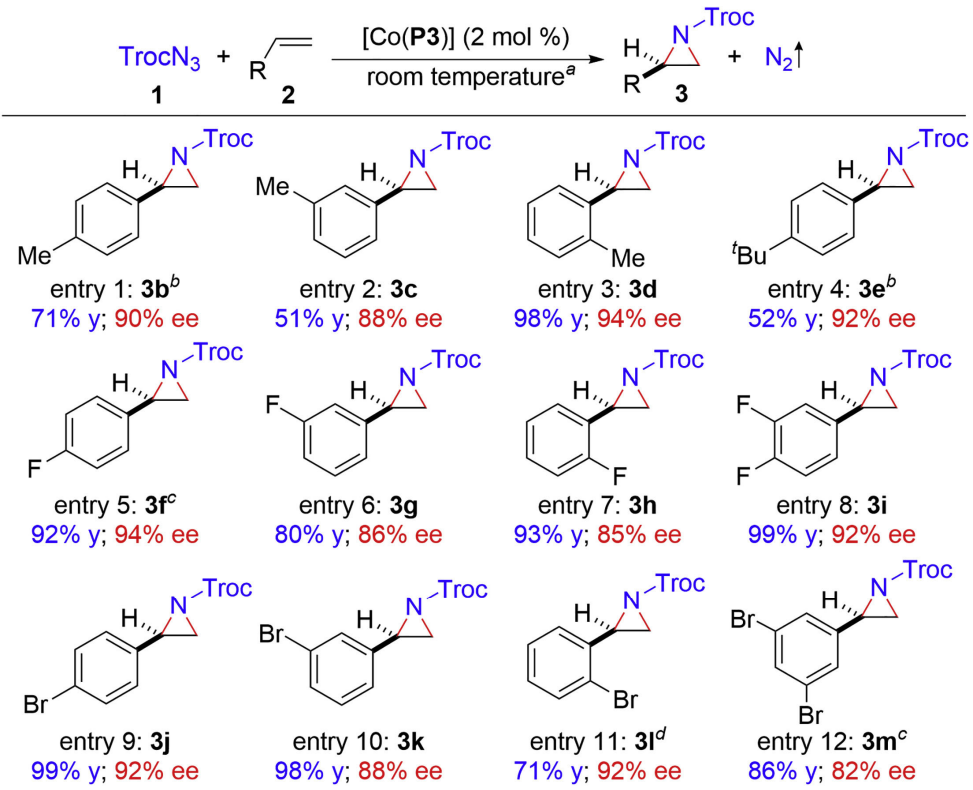
X. Peter Zhang, *J. Am. Chem. Soc.* **2017**.

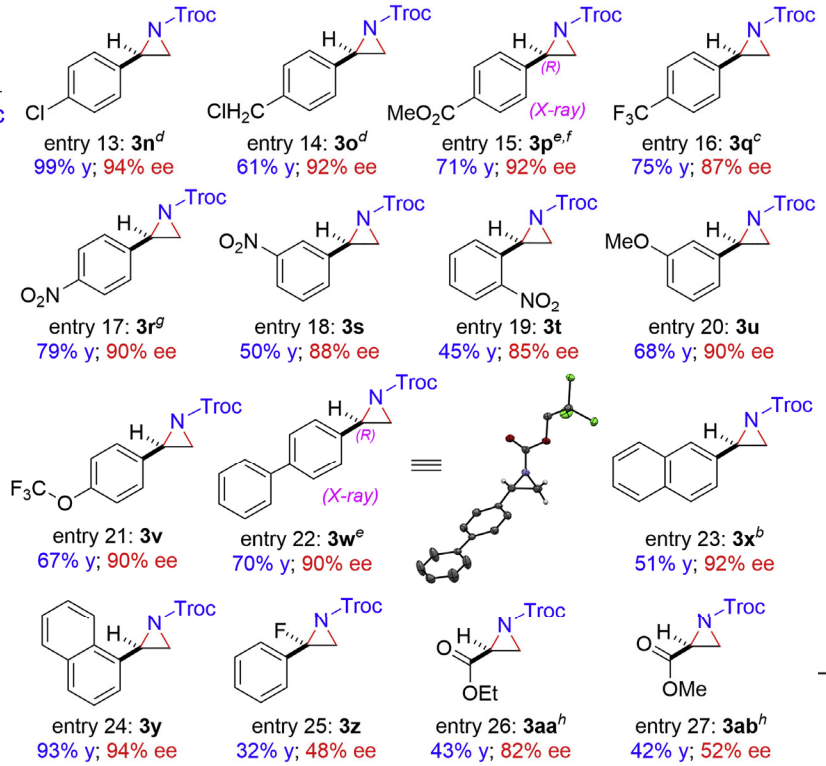
Co Nitrene

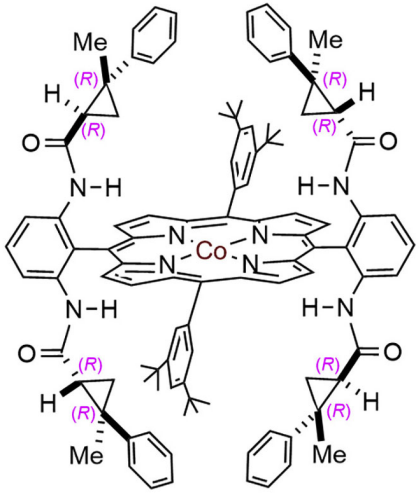


X. Peter Zhang, *Chem* **2021**.

Co Nitrene





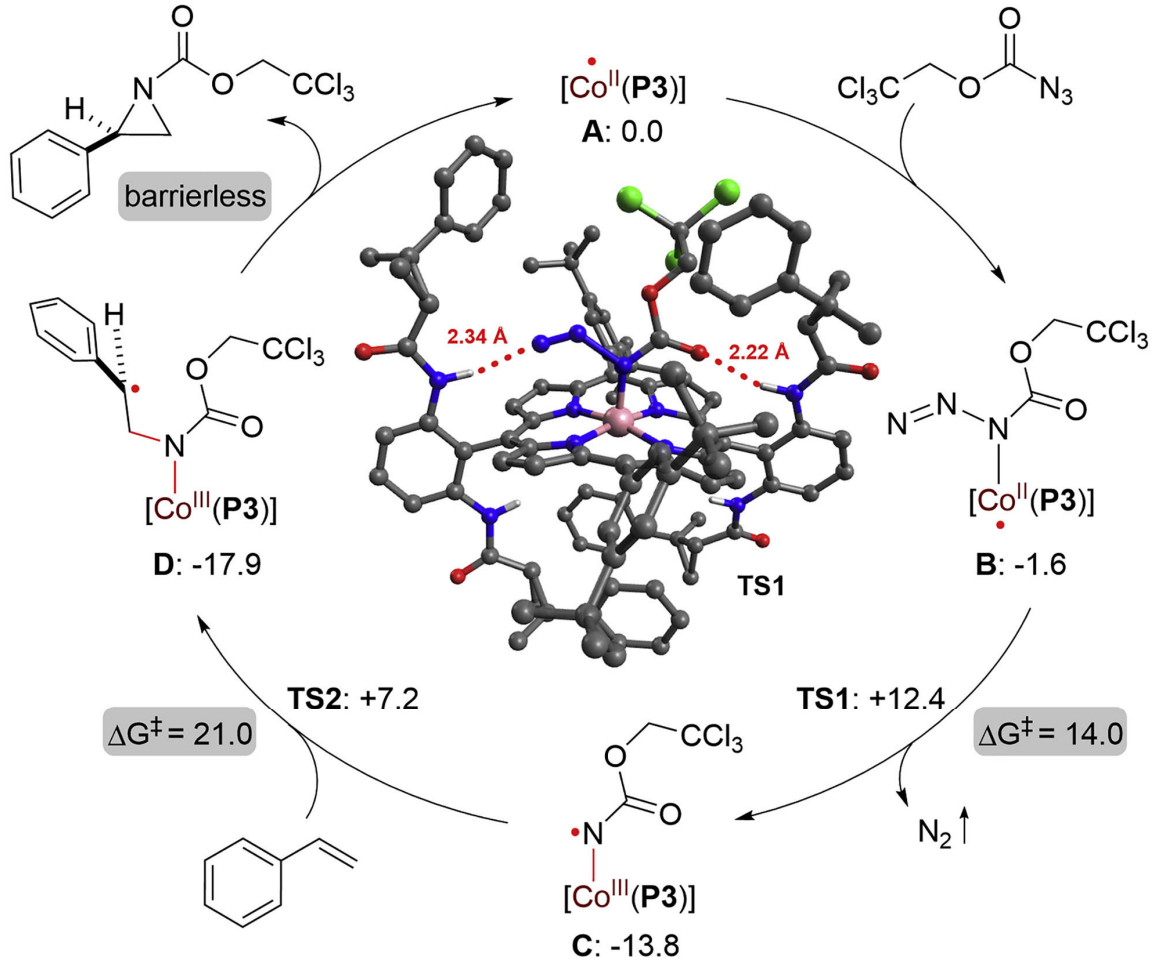


[Co(**P3**)]
(**P3** = 3,5-Di^{t}Bu-QingPhyrin)

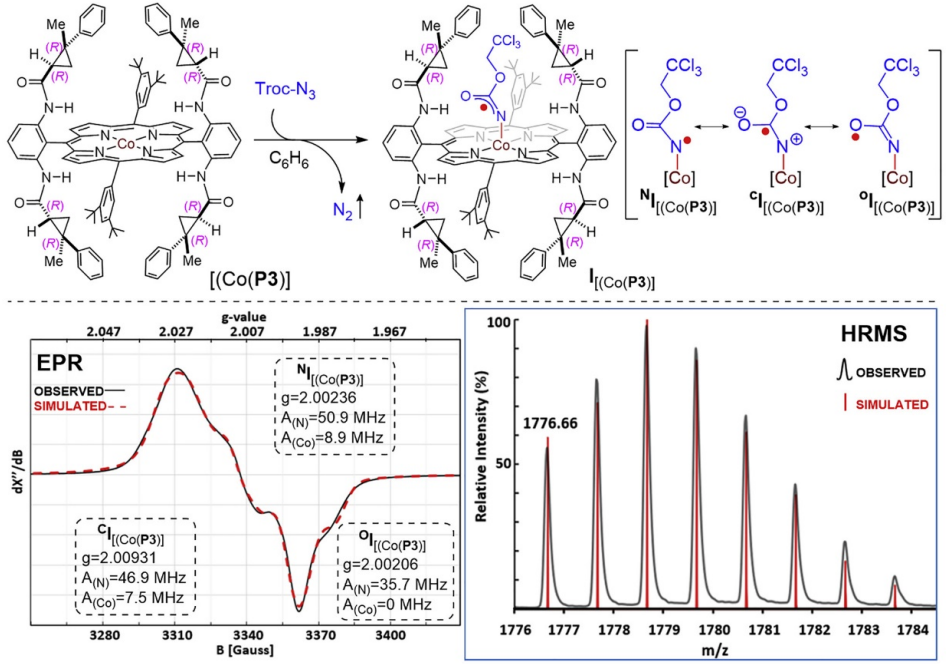
X. Peter Zhang, *Chem* **2021**.

Co Nitrene

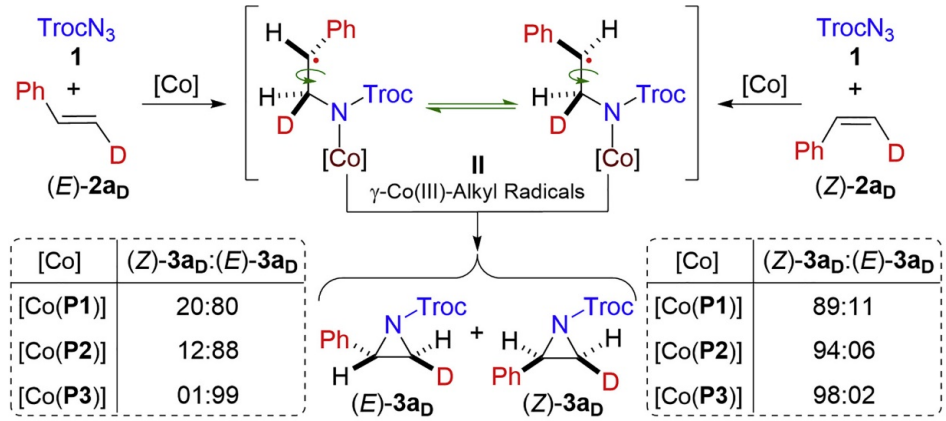
A DFT Study on Catalytic Pathway for Aziridination of Styrene with Troc-N_3 by [Co(P3)]^a



B Generation and Detection of α-Co(III)-Aminyl Radical Intermediate by EPR and HRMS



C Aziridination of *(E)*- or *(Z)*-β-Deuterostyrenes^b

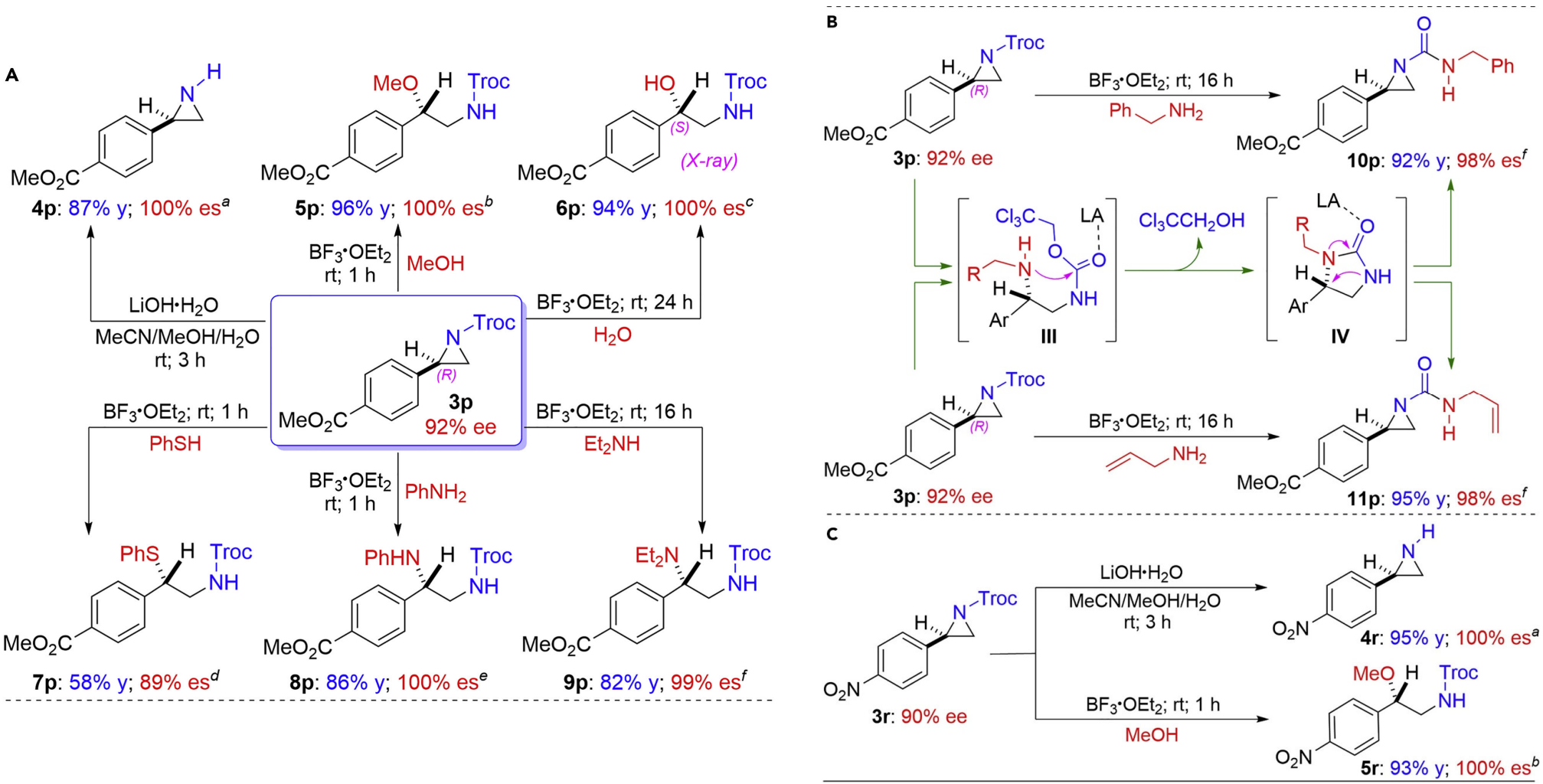


[Co]	(*Z*)-3a$_D$:(*E*)-3a$_D$
[Co(**P1**)]	20:80
[Co(**P2**)]	12:88
[Co(**P3**)]	01:99

[Co]	(*Z*)-3a$_D$:(*E*)-3a$_D$
[Co(**P1**)]	89:11
[Co(**P2**)]	94:06
[Co(**P3**)]	98:02

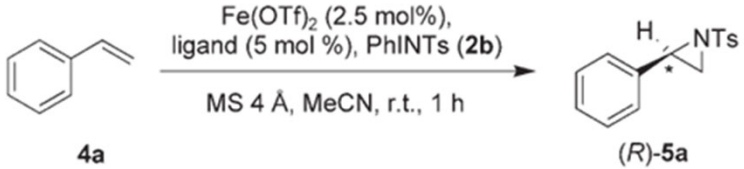
X. Peter Zhang, *Chem* **2021**.

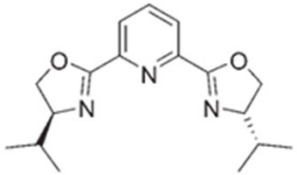
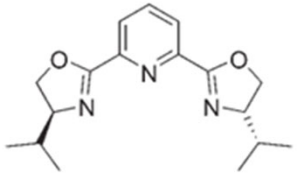
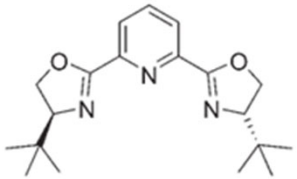
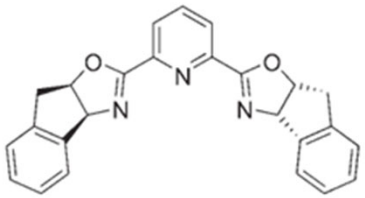
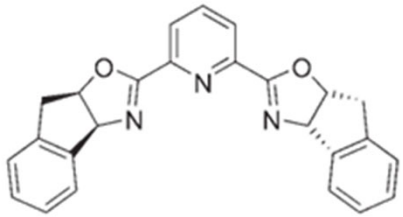
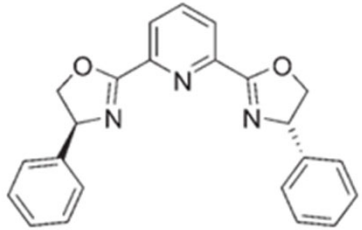
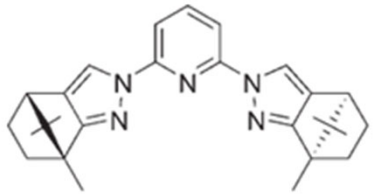
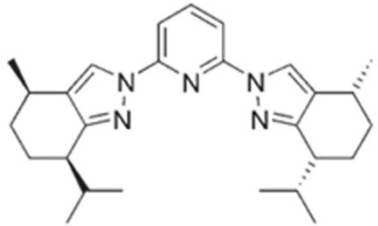
Co Nitrene



X. Peter Zhang, *Chem* **2021**.

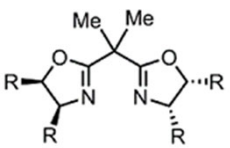
Fe Nitrene



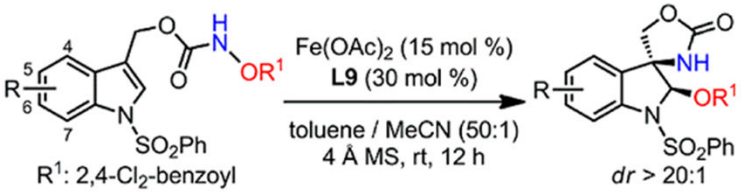
Entry	Ligand	Yield [%] of **5a**	*ee* [%] of **5a**
1	**7a** 	67	15
2[b]	**7a** 	72	40
3	**7b** 	67	15
4	**7c** 	75	10
4	**7c** 	75	10
5	**7d** 	51	25
6	**7e** 	60	20
7	**7f** 	40	6

Carsten Bolm, *Adv. Synth. Catal.* **2008**.

Fe Nitrene

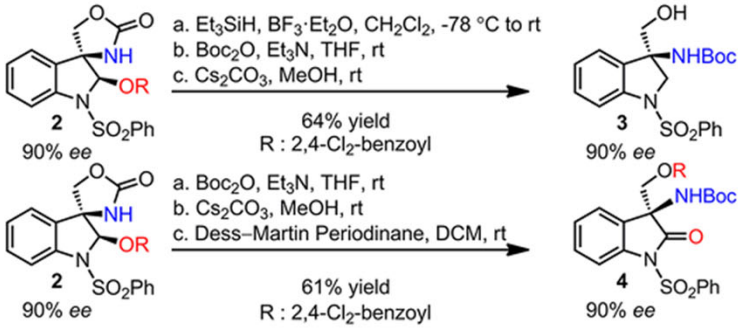


L9 : R = Ph
L10 : R = 1–Naph

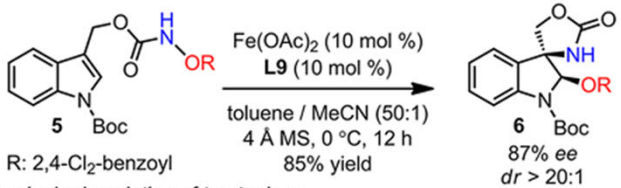


entry[a]	R	yield[b] (%)	ee[c] (%)
1	H	67	90
2[d]	5-Me	72	94
3[d,e]	5-OMe	75	93
4	6-Me	65	95
5	6-Br	64	91
6	6-Cl	70	99
7[e]	7-Ph	65	91
8[d]	7-Me	62	85
9	4-Br	67	74

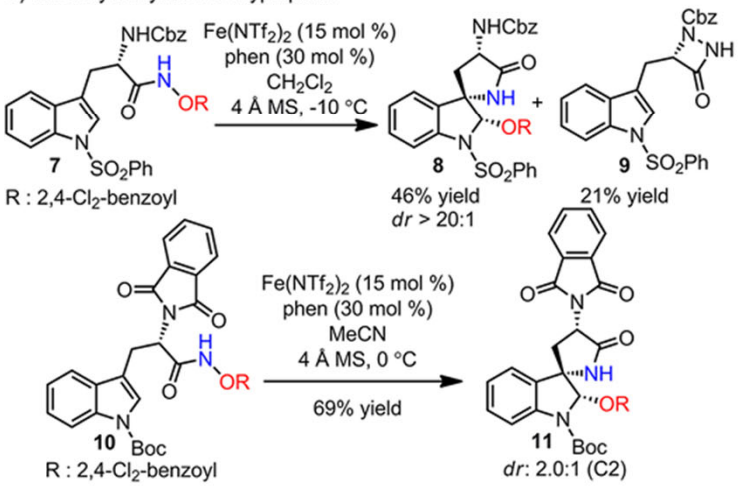
A) synthetic transformation of the product: an entry to amino indolanes and amino oxindoles



B) asymmetric aminohydroxylation of an *N*-Boc indole



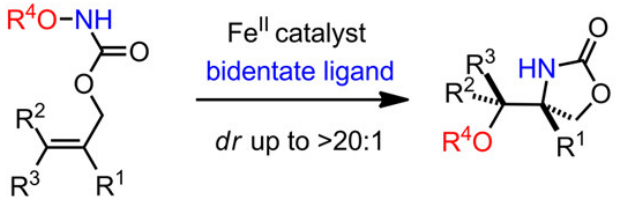
C) aminohydroxylation of tryptophan



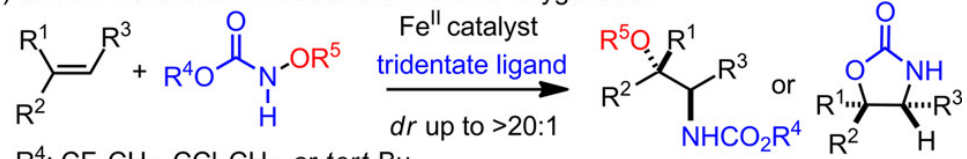
Hao Xu, *Org. Lett.* **2013**.

Fe Nitrene

A) previous work: intramolecular olefin amino-oxygenation

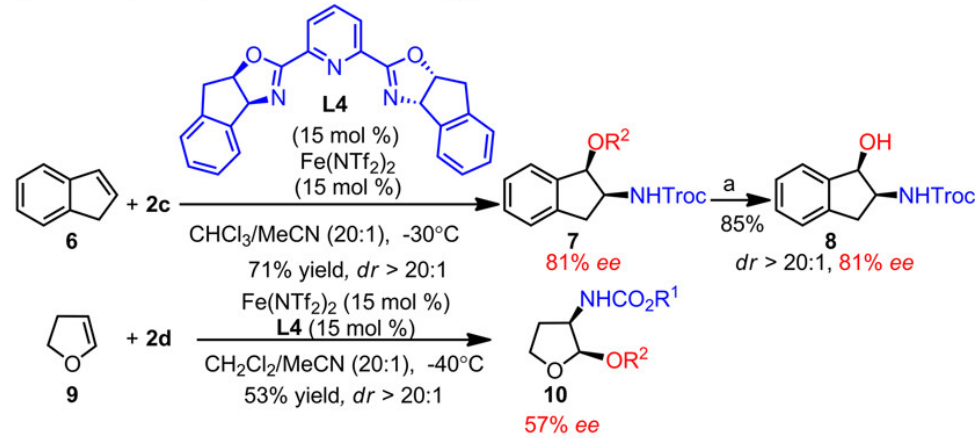


B) current work: intermolecular olefin amino-oxygenation

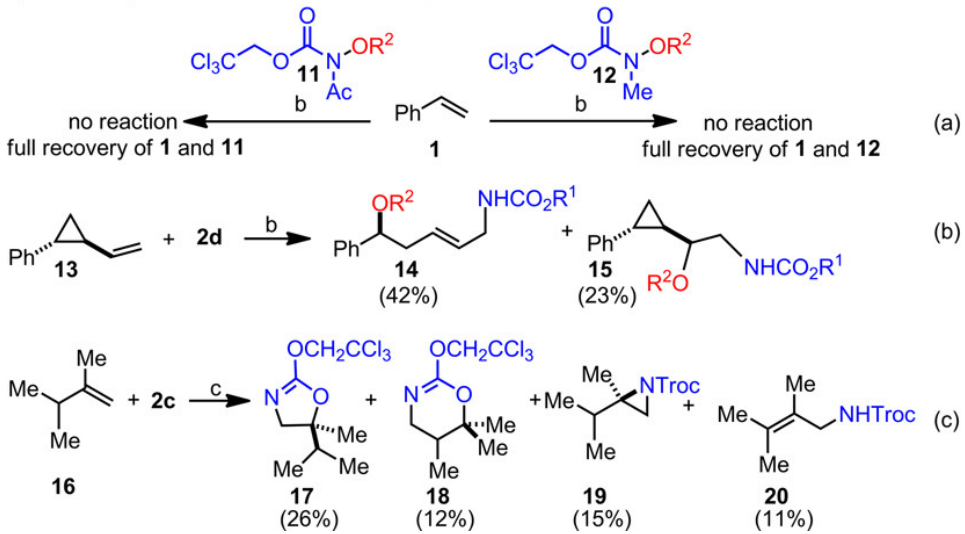


R^4: CF_3CH_2, CCl_3CH_2, or *tert*-Bu

A) iron-catalyzed asymmetric olefin amino-oxygenation

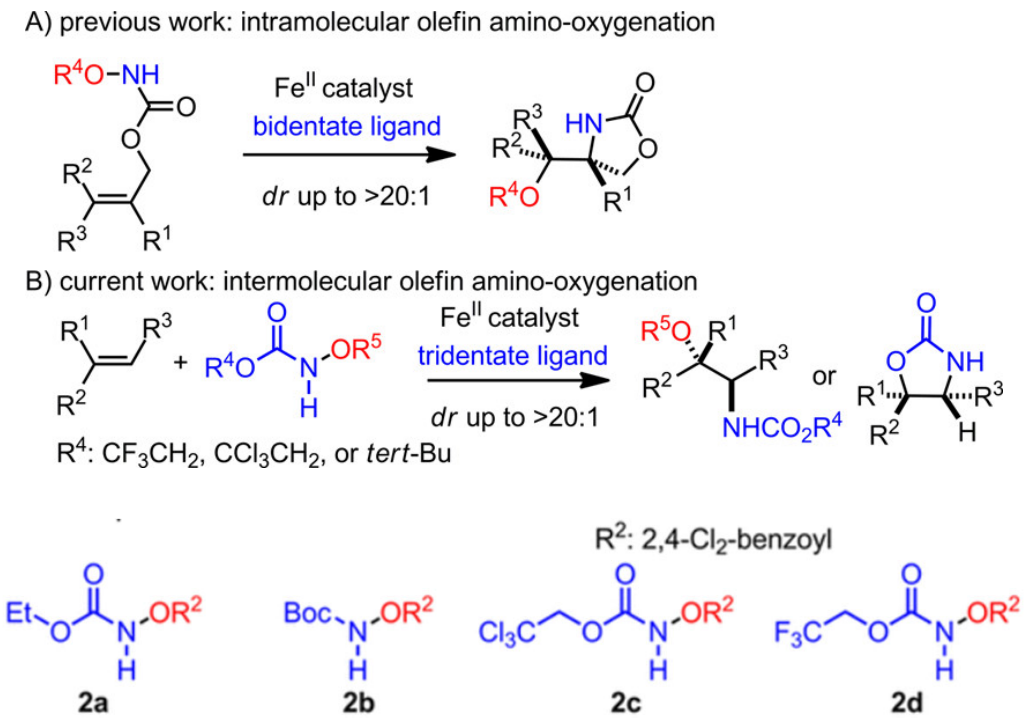


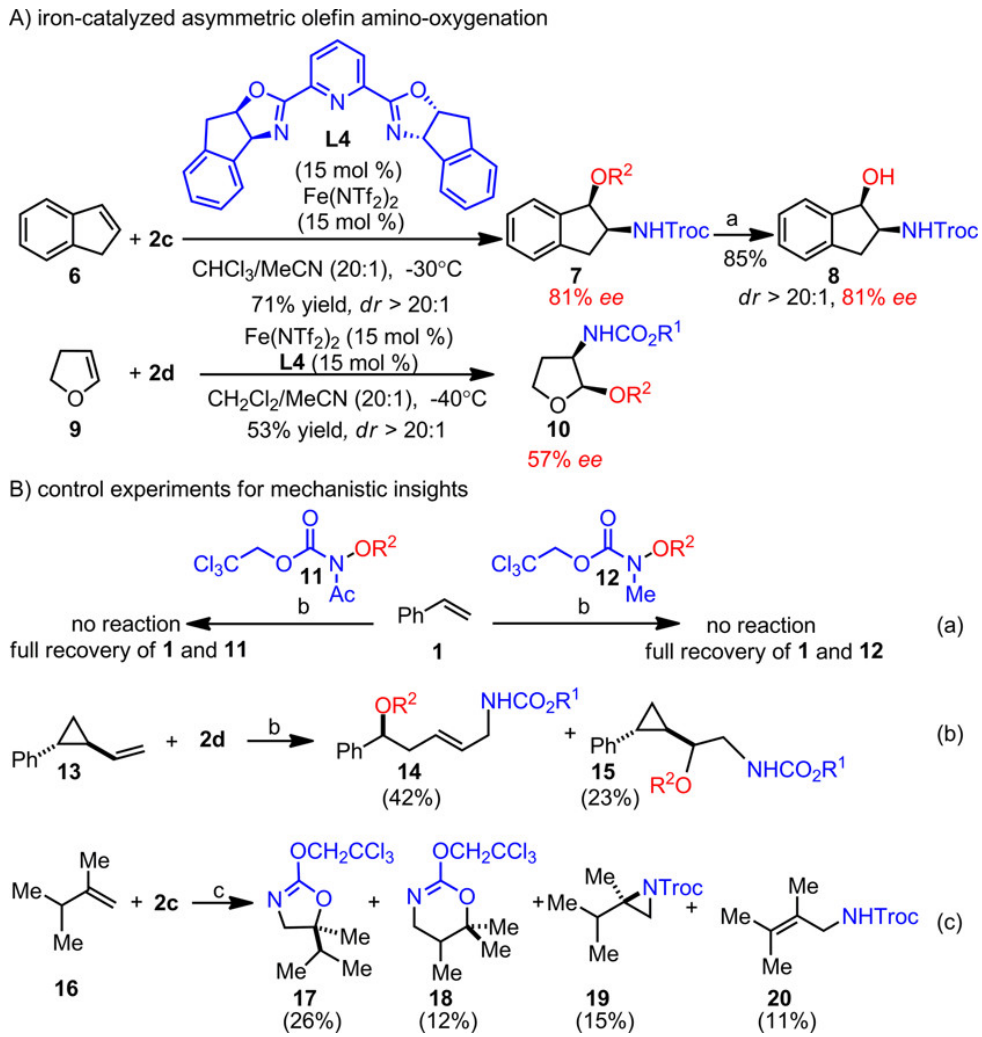
B) control experiments for mechanistic insights



Hao Xu, *J. Am. Chem. Soc.* **2014**.

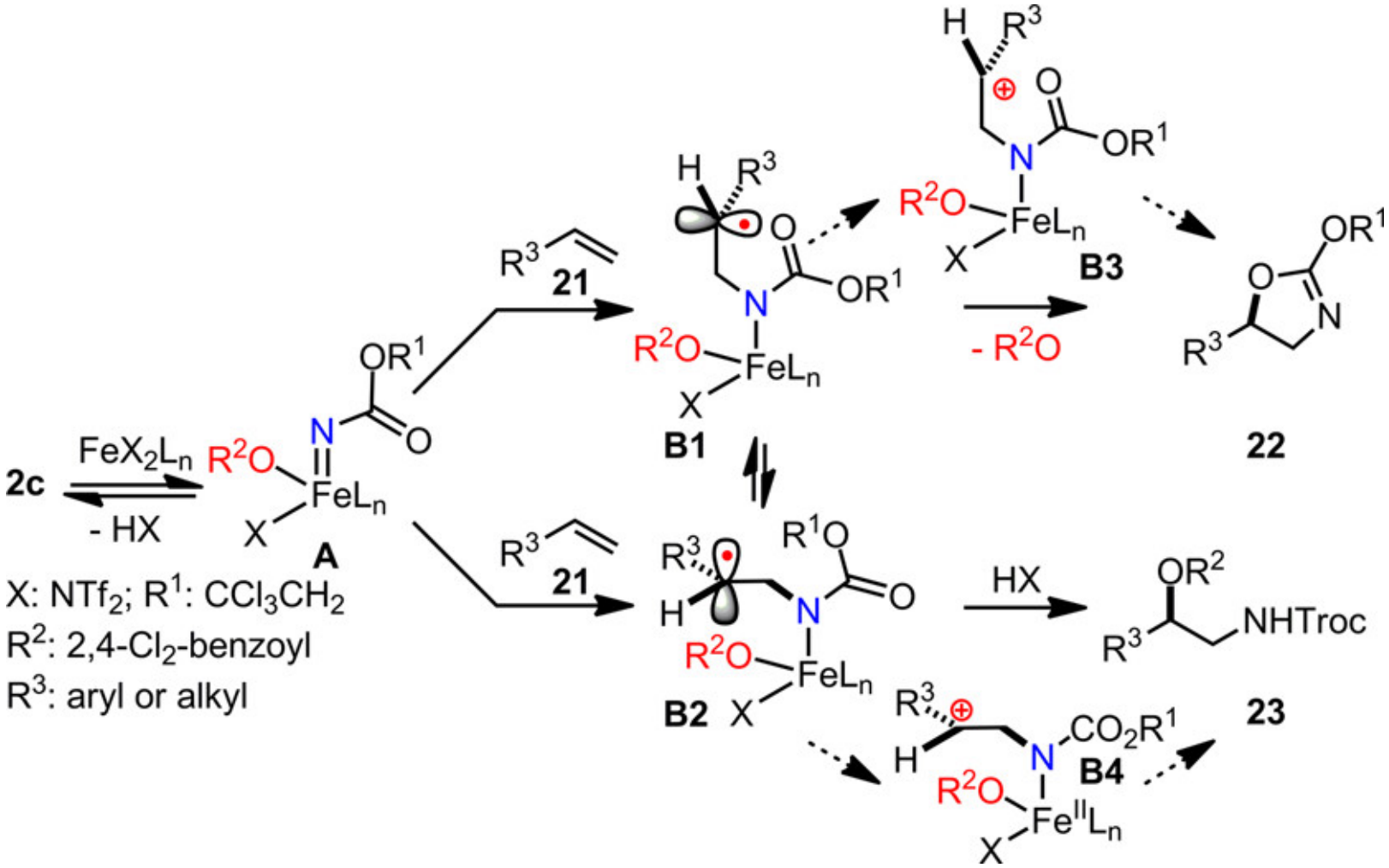
Fe Nitrene





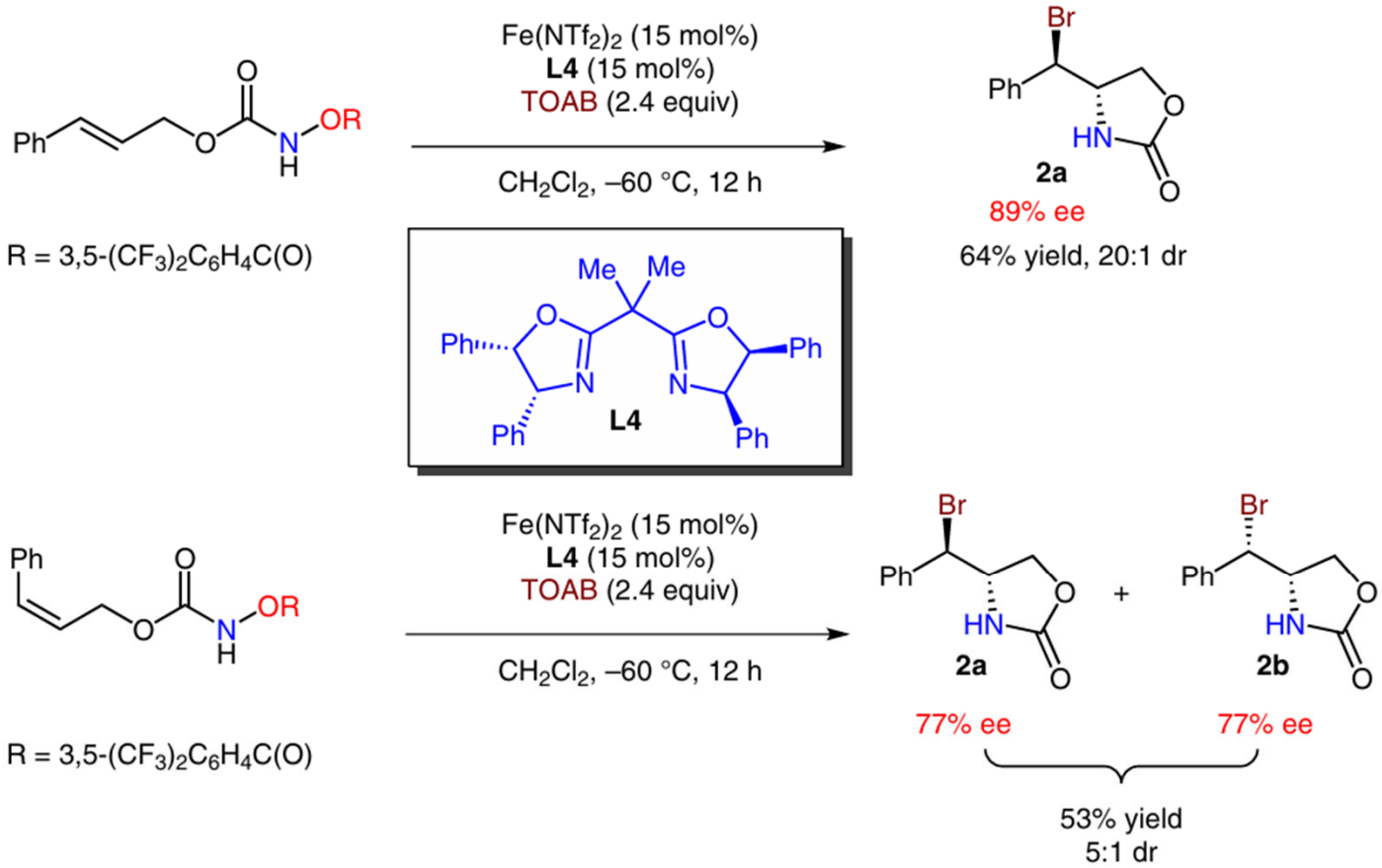
Hao Xu, *J. Am. Chem. Soc.* **2014**.

Fe Nitrene



Hao Xu, *J. Am. Chem. Soc.* **2014**.

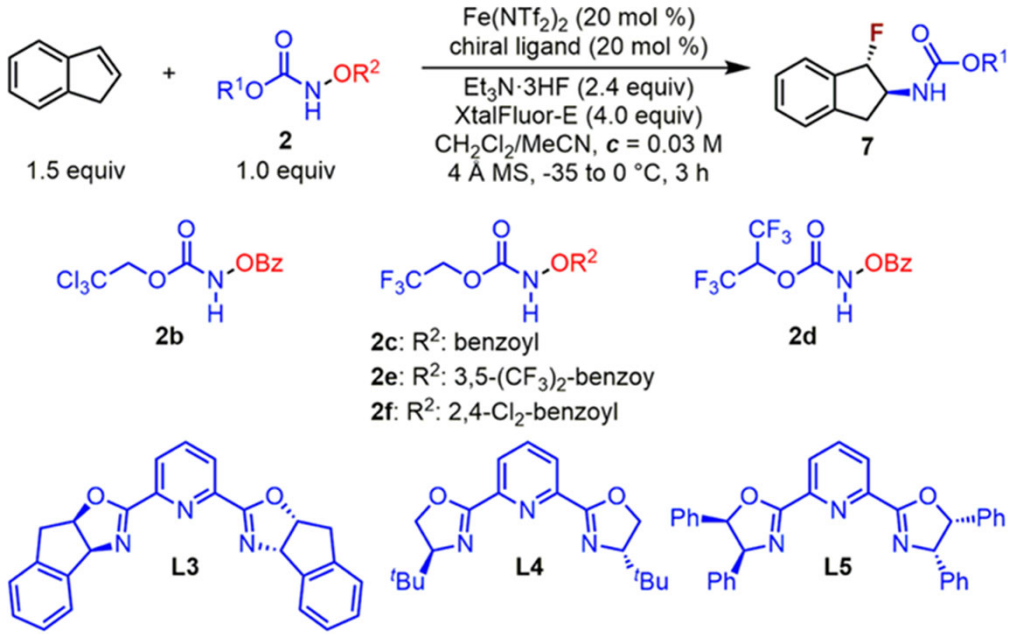
Fe Nitrene



TOAB: tetraoctylammonium bromide

Hao Xu, *Synthesis* **2015**.

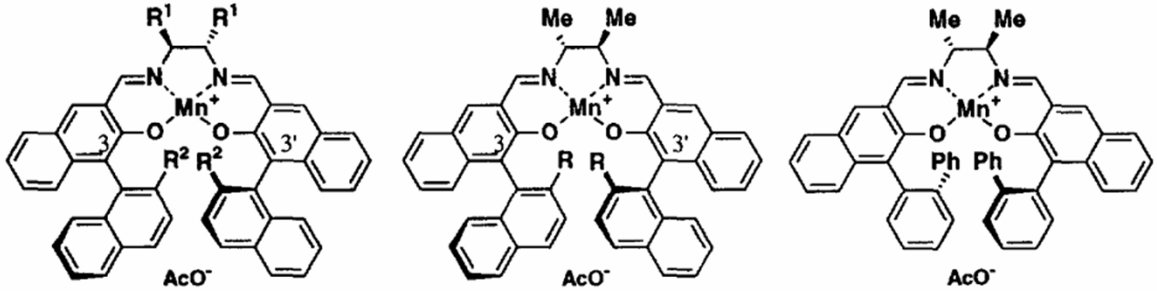
Fe Nitrene



entry[a]	2	ligand	yield[b]	dr[c]	ee (major/minor)[d]
1	**2d**	**L3**	48%	5.2:1	60%/60%
2	**2b**	**L3**	38%	2.5:1	78%/77%
3	**2c**	**L3**	35%	2.4:1	83%/82%
4	**2e**	**L3**	55%	2.2:1	55%/55%
5	**2f**	**L3**	59%	3.0:1	84%/84%
6	**2f**	**L4**	32%	1.8:1	36%/37%
7	**2f**	**L5**	39%	1.9:1	32%/30%

Hao Xu, *J. Am. Chem. Soc.* **2016**.

Other Nitrene: Mn



2: R^1= C_6H_3-3,5-Me_2, R^2= Ph
3: R^1= Me, R^2= Ph
4: R^1= Me, R^2= Me

5: R= Me
6: R= H

7

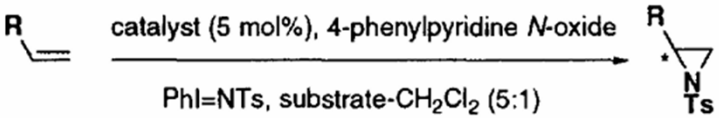
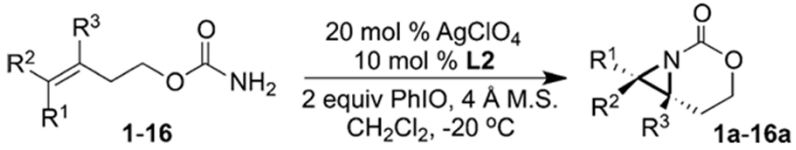


Table 1. Catalytic aziridination of styrene derivatives using (salen)manganese(III) complex as a catalyst.

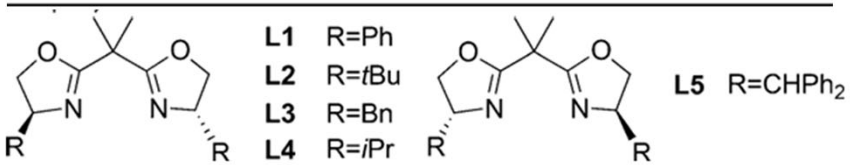
Entry	Substrate	Catalyst	Temp.	Yield (%)	%ee	Confign.[a)]
1	styrene	**7**	rt	76	94[b)]	*S*
2	*p*-chlorostyrene	**7**	rt	70	86[c)]	-
3	*p*-methylstyrene	**7**	rt	75	81[b)]	-
4	indene	**7**	rt	10	50[d)]	-
5	styrene	**8**	rt	25	13	*S*

Tsutomu Katsuki, *Tetrahedron Letters*, ***1996***.

Other Nitrene: Ag

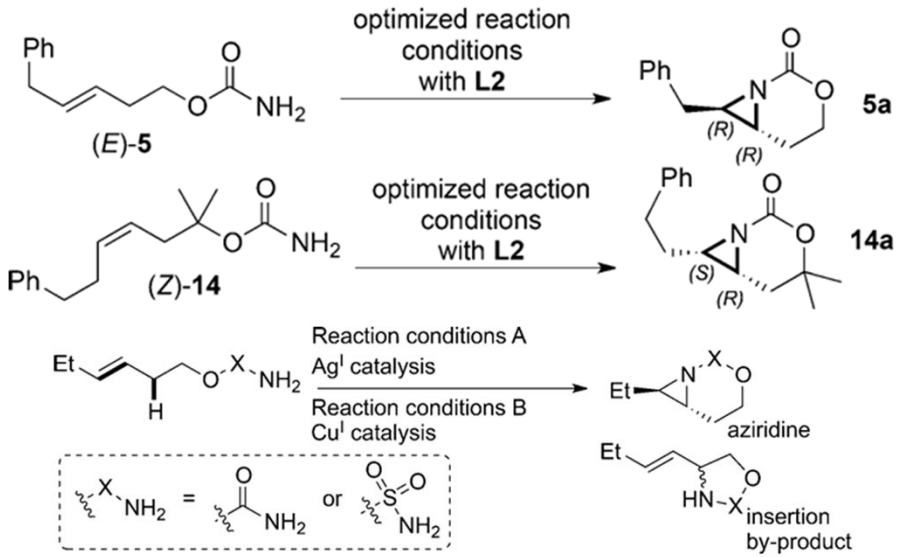


Entry	Substrate	Product	Entry	Substrate	Product
1	(*Z*)-**1**	83% **1a** 91% *ee*[a]	9	(*E*)-**9**	81% **9a** 92% *ee*[a]
2	(*E*)-**2**	87% **2a** 92% *ee*[a]	10	(*E*)-**10**	84% **10a** 90% *ee*
3	(*E*)-**3**	85% **3a** 91% *ee*[a]	11	(*E*)-**11**	81% **11a** 87% *ee*
4	(*E*)-**4**	63% **4a** 92% *ee*[a]	12	(*E*)-**12**	84% **12a** 89% *ee*
5	(*E*)-**5**	80% **5a** 91% *ee* >99% *ee*[b]	13	(*E*)-**13**	89% **13a** 22% *ee*[a]
6	(*E*)-**6**	87% **6a** 92% *ee*[a]	14	(*Z*)-**14**	55% **14a** 88% *ee*[b]
7[c]	(*E*)-**7**	52% **7a** 70% *ee*	15	(*Z*)-**15**	94% **15a** 48% *ee*[a]
8	(*E*)-**8**	84% **8a** 87% *ee*	16	**16** allene	57% **16a** 62% *ee*



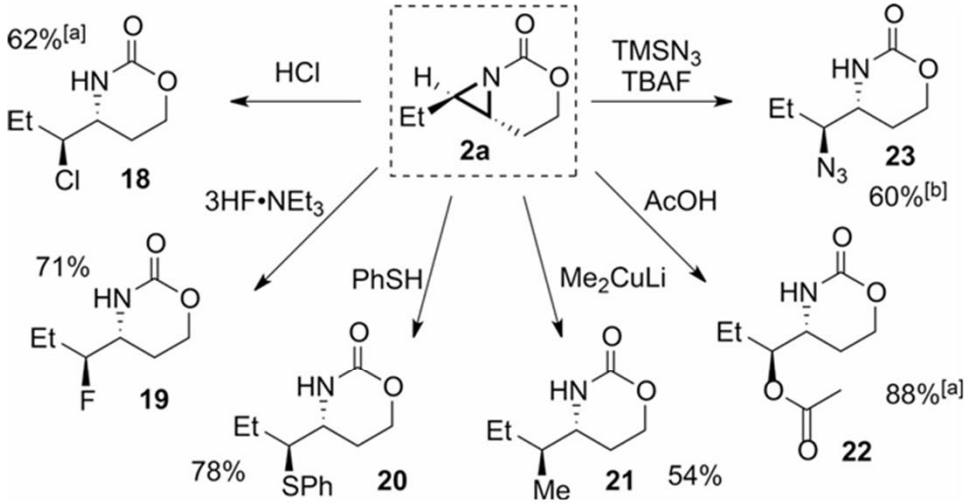
Jennifer M. Schomaker, *Angew. Chem. Int. Ed.* ***2017***.

Other Nitrene: Ag



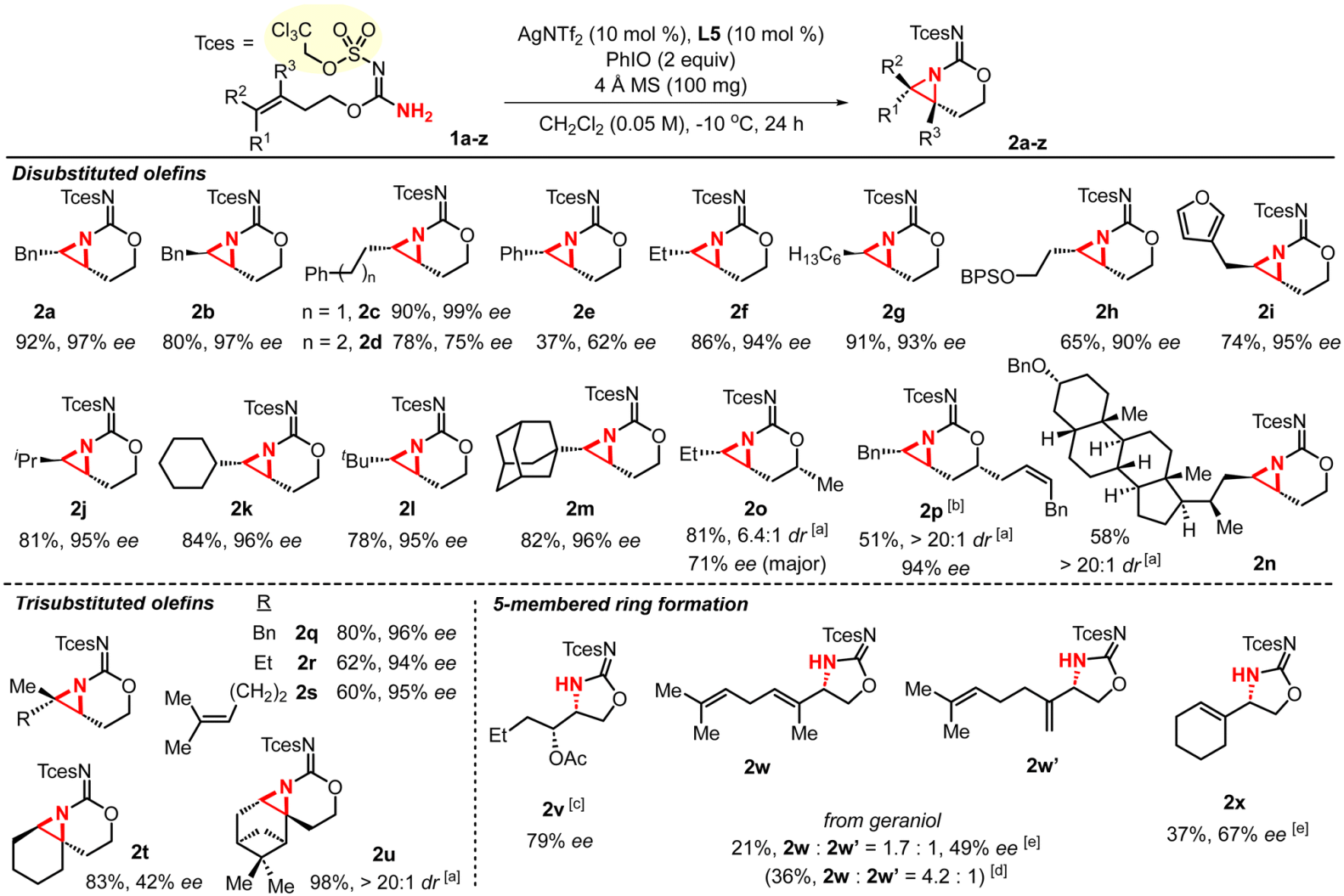
Entry	Substrate		Cond.	Yield [%] aziridine	Yield [%] insertion byproduct	Recovered substrate	*ee* [%] aziridine
1	X = CO	(*E*)-**2**	A	87	10[a]	n.d.	92
2	X = CO	(*E*)-**2**	B	15[a]	5[a]	44[a]	n.a.
3	X = SO_2	(*E*)-**17**	A	3[a]	n.d.	28[a]	n.a.
4	X = SO_2	(*E*)-**17**	B	83	n.a.	n.a.	80

Reaction conditions A: 20 mol% $AgClO_4$, 10 mol% **L2**, PhIO, 4 Å M.S., CH_2Cl_2, −20 °C. Reaction conditions B: 5 mol% $Cu(CH_3CN)_4PF_6$, 5.5 mol% **L2**, PhIO, 3 Å M.S., CH_3CN, −20 °C. [a] Yield determined by NMR spectroscopy using mesitylene as the internal standard. [b] See Ref. [10]. n.a. = not applicable, n.d. = not determined.



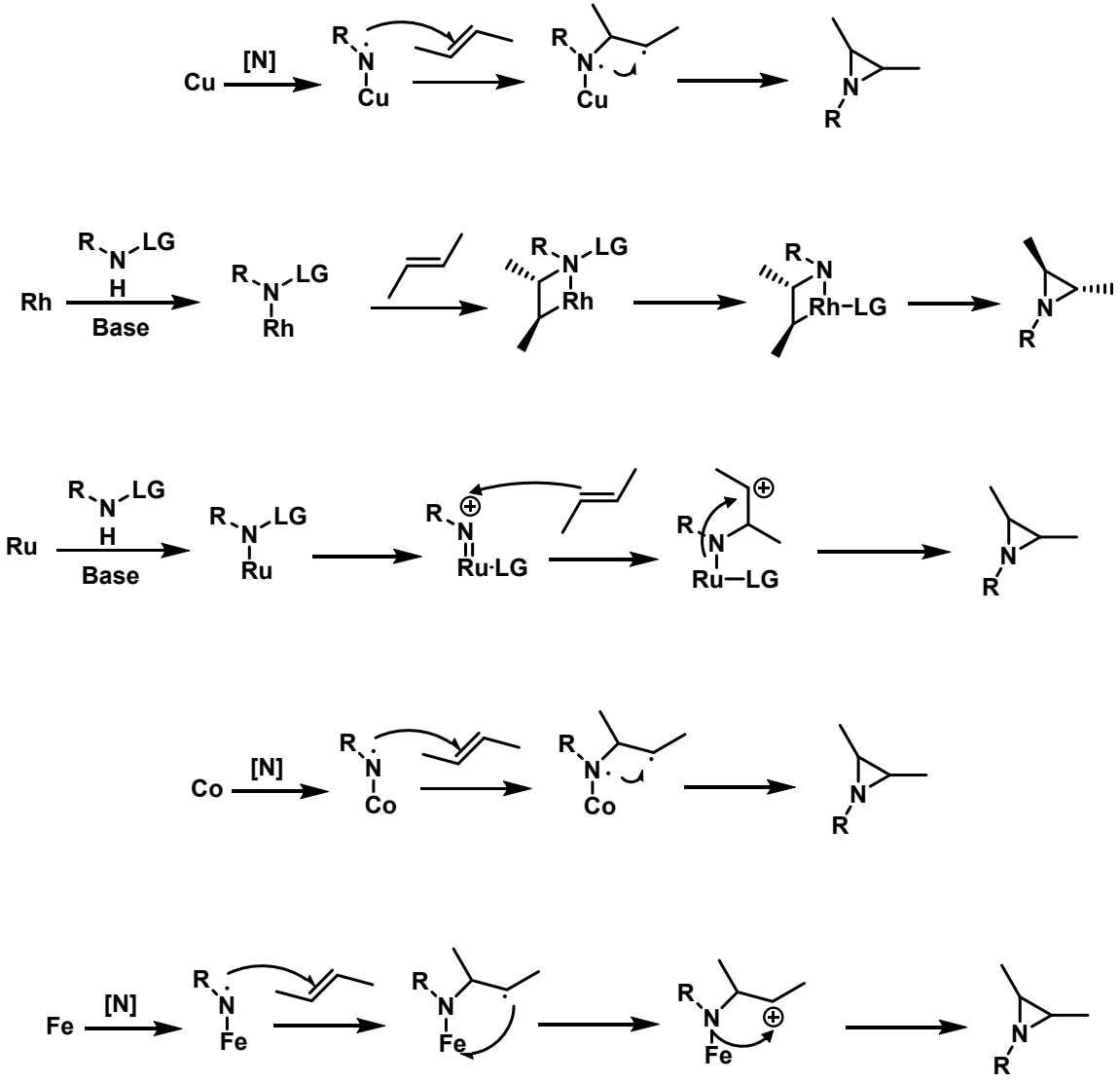
Jennifer M. Schomaker, *Angew. Chem. Int. Ed.* ***2017***.

Other Nitrene: Ag

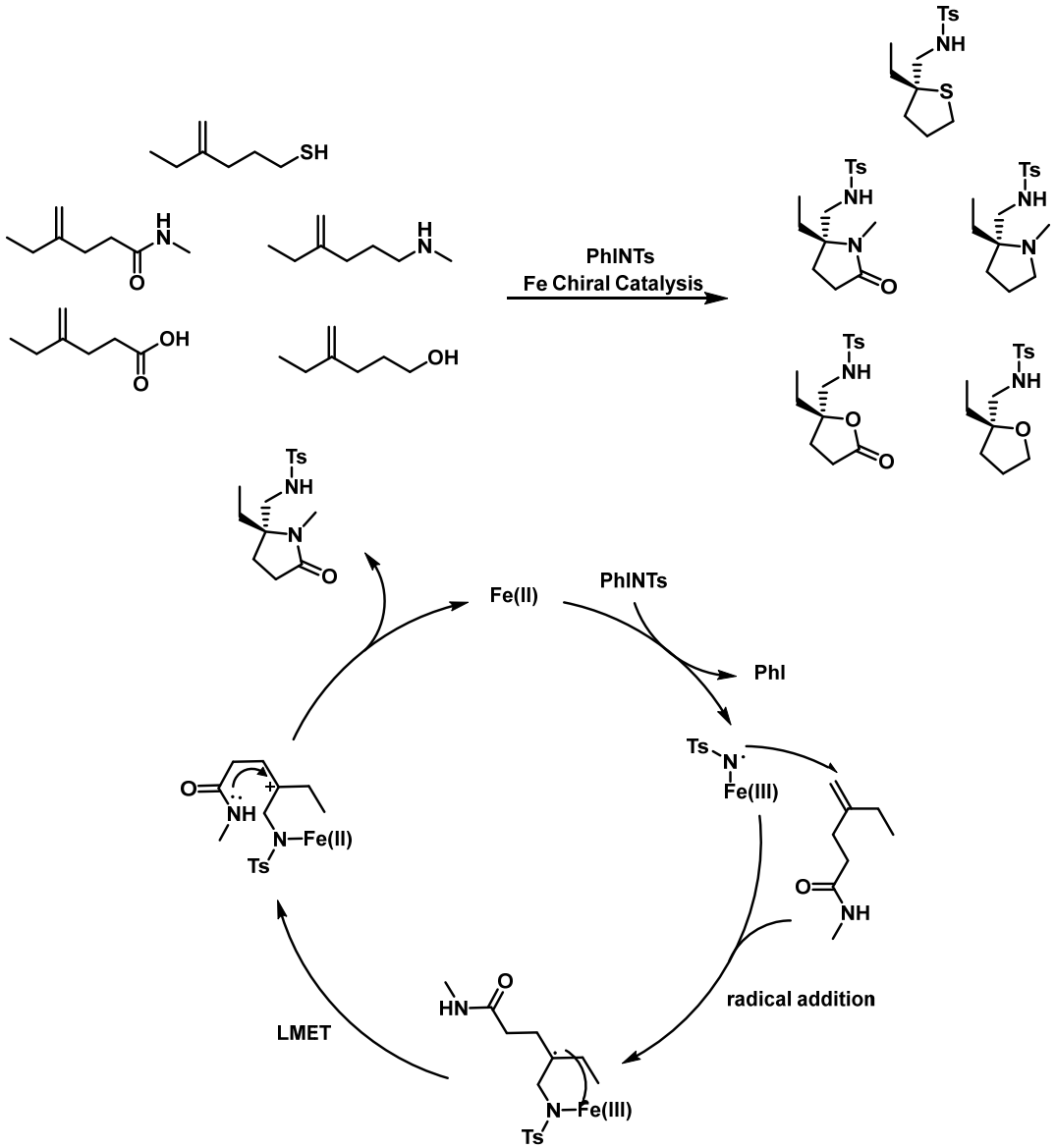


Jennifer M. Schomaker, *Chem. Commun.* ***2024***.

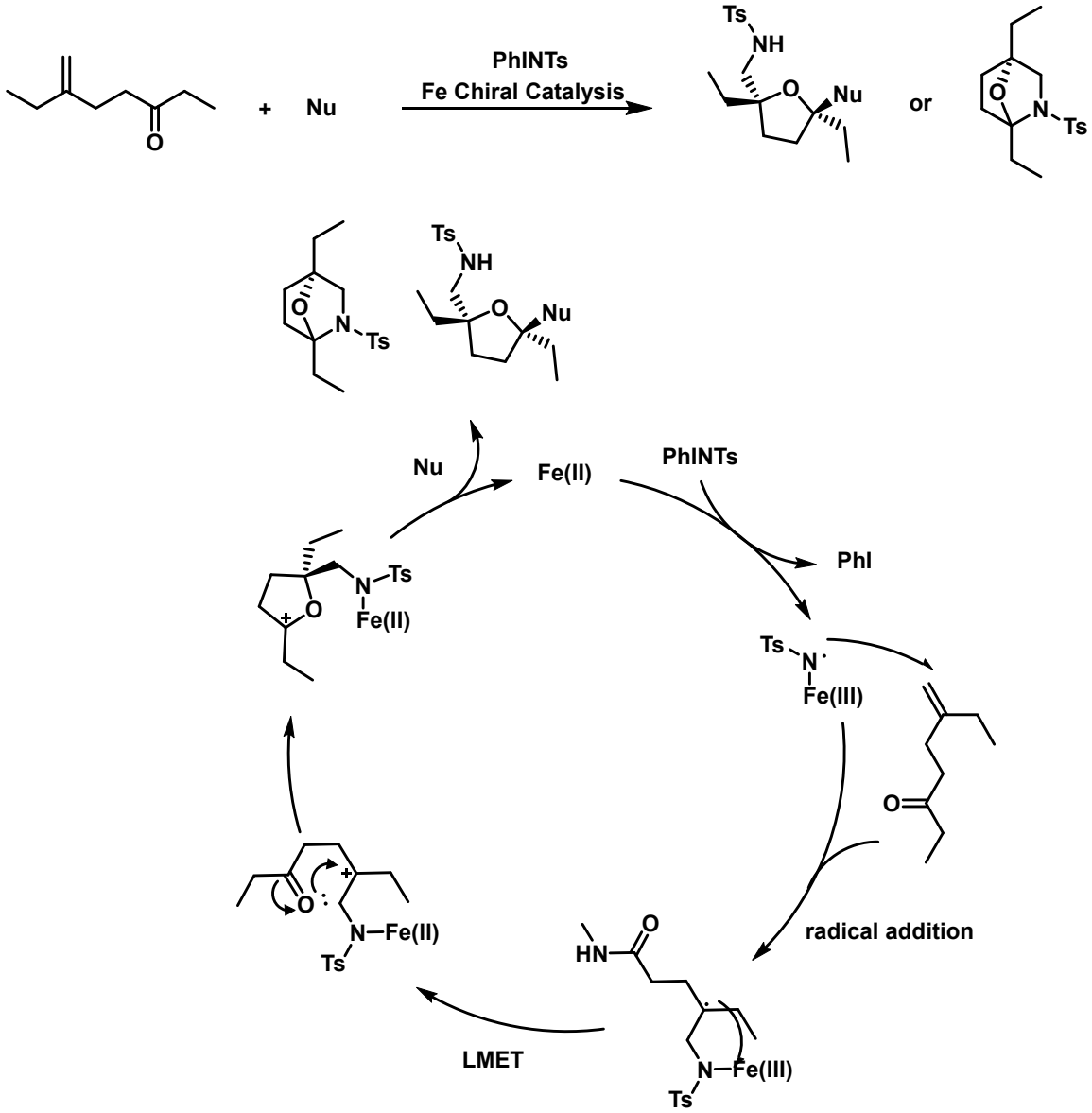
Mechanism Conclusion



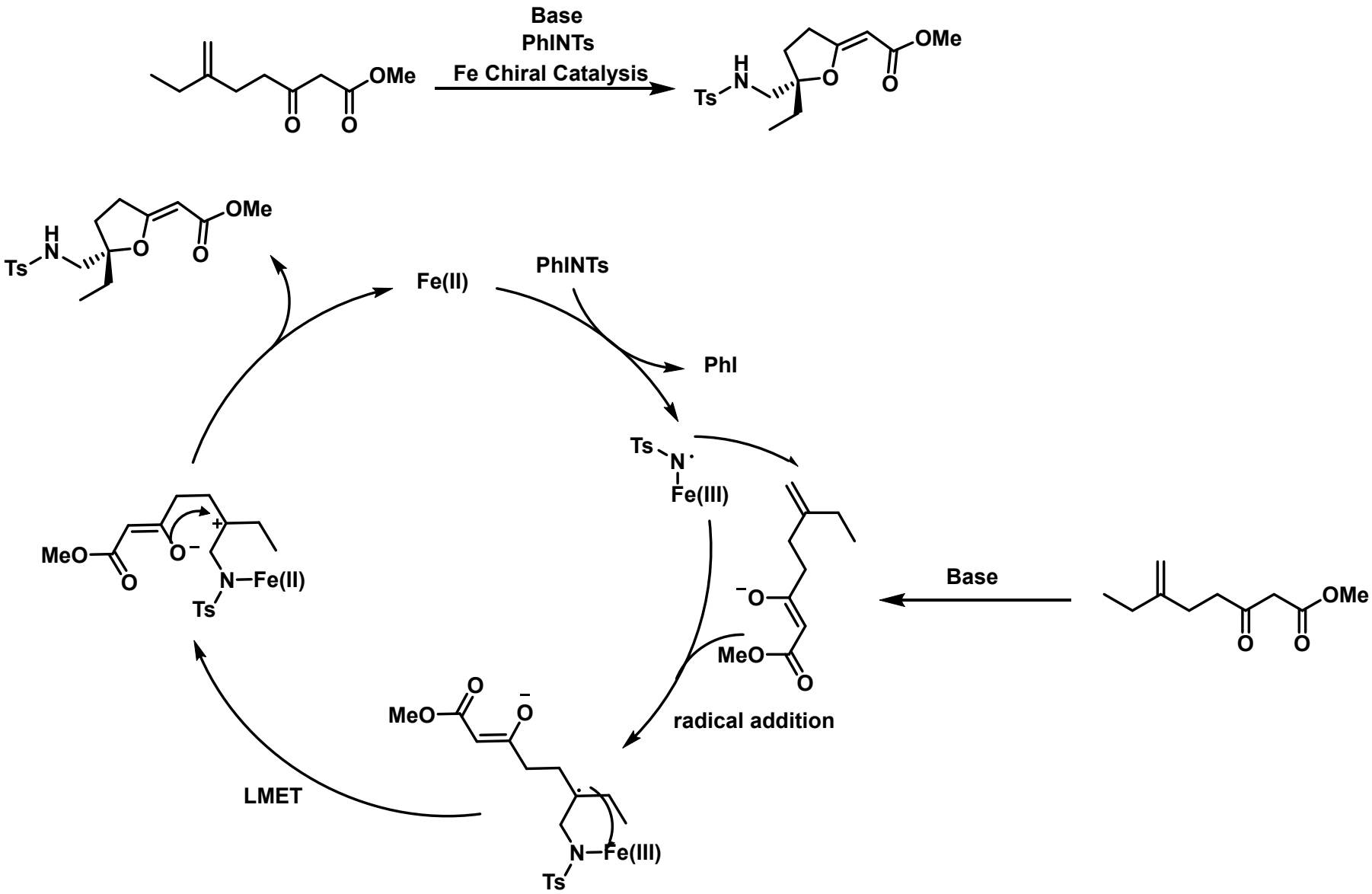
Proposal


PhINTs
Fe Chiral Catalysis
Fe(II)
PhINTs
PhI
radical addition
LMET

Proposal


PhINTs
Fe Chiral Catalysis
+ Nu
or
Ts
NH
O
Nu
N
Ts
Fe(II)
PhI
Fe(III)
radical addition
LMET
HN
N—Fe(II)
N—Fe(III)

Proposal


Base
PhINTs
Fe Chiral Catalysis
OMe
O
O
H
N
Ts
O
OMe
O
Fe(II)
PhINTs
PhI
Ts
N
Fe(III)
Base
OMe
O
O
O
MeO
O
radical addition
MeO
O
O
LMET
N—Fe(III)
Ts
MeO
O
O
N—Fe(II)
Ts
H
N
Ts
O
OMe
O

The Yang Research Group
Precise Synthesis Lab at Tongji University

Thanks!