Literature Report

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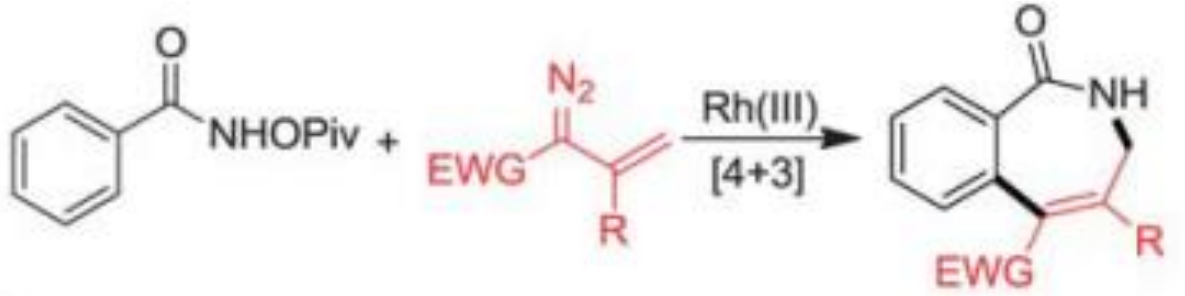
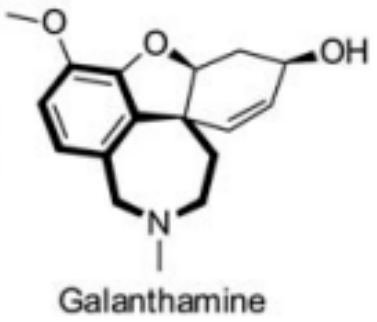
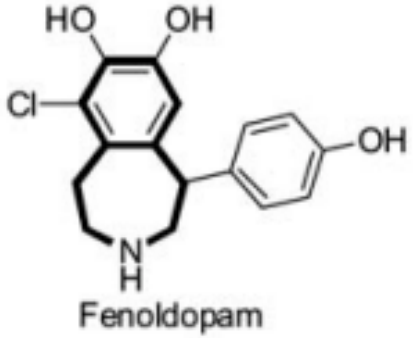
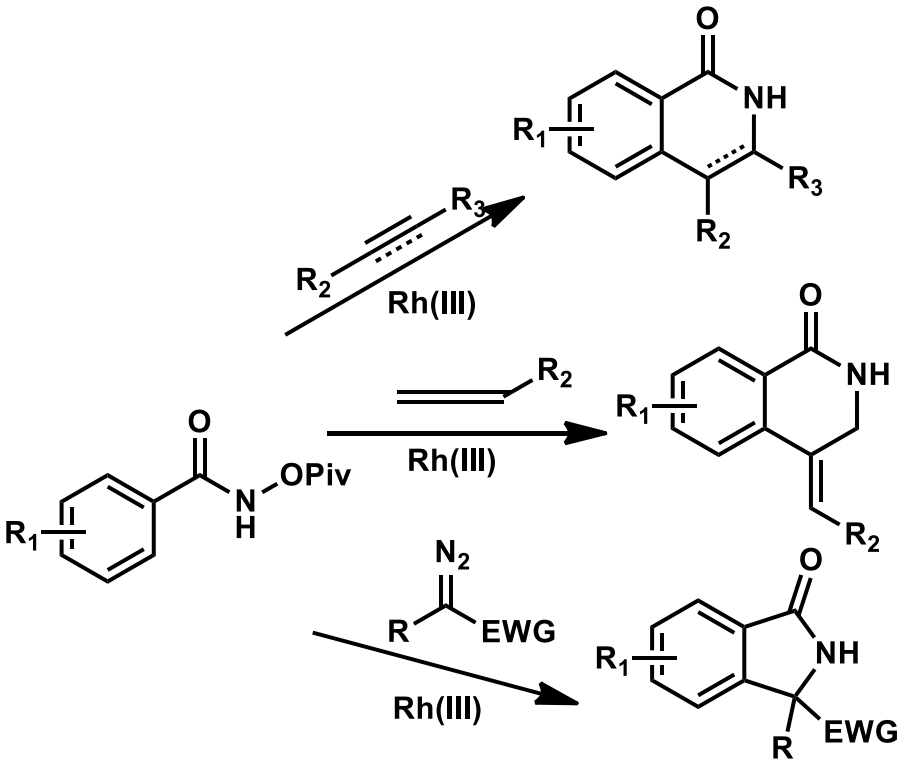
Supervisor: Prof. Zhao Jing

2013-08-12

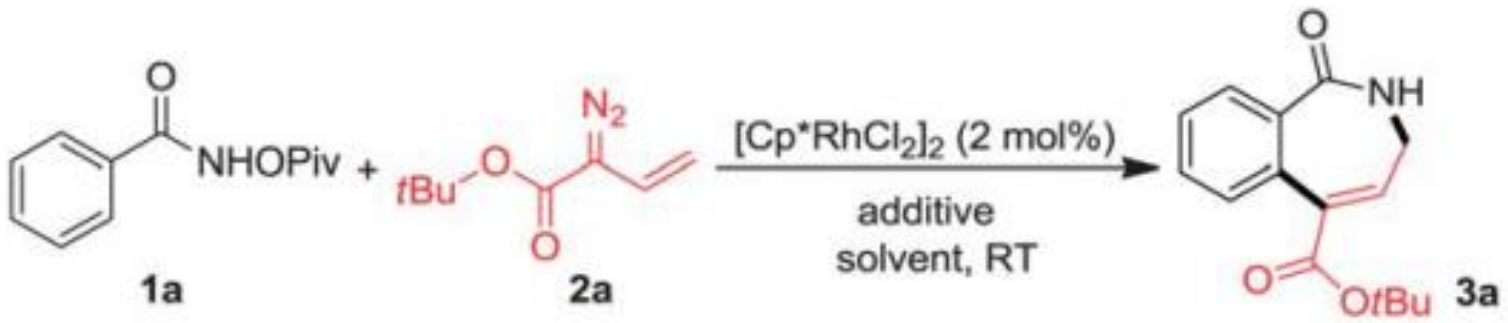








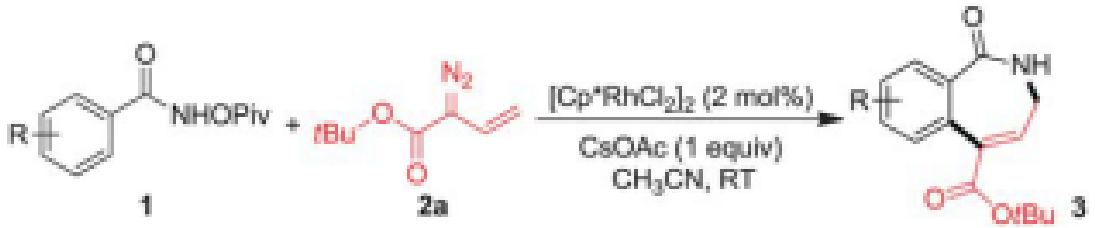
Chem. Sci. DOI: 10.1039/c3sc51777b

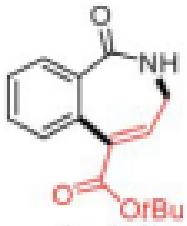


1a 2a 3a

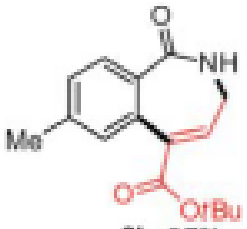
Entry	Additive	Solvent	Yield[b] [%]
1	CsOAc (1 equiv.)	MeOH	10
2	CsOAc (1 equiv.)	TFE	Trace
3	CsOAc (1 equiv.)	CH_3CN	95
4	CsOAc (0.5 equiv.)	CH_3CN	81
5	—	CH_3CN	0
6	NaOAc (1 equiv.)	CH_3CN	35

[a] *Reaction conditions*: **1a** (0.2 mmol), **2a** (0.3 mmol), $[Cp^*RhCl_2]_2$ (2 mol %), additive, solvent (1.5 mL). [b] Yields of isolated products.

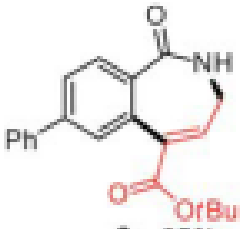




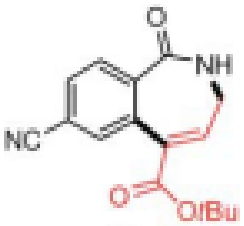
3a, 95%



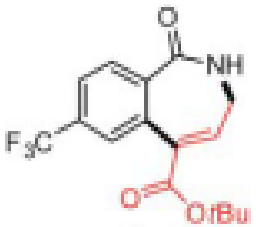
3b, 97%



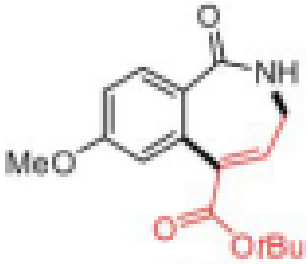
3c, 95%



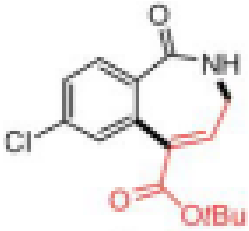
3d, 62%



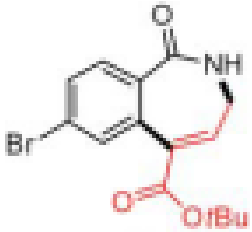
3e, 95%



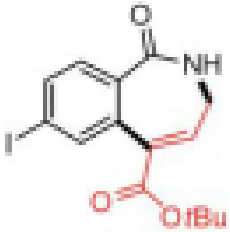
3f, 93%



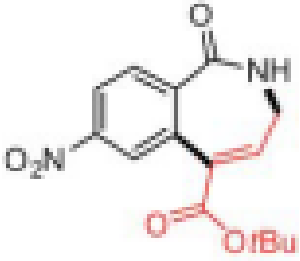
3g, 93%



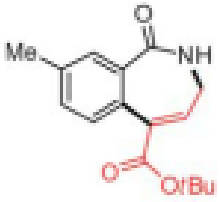
3h, 74%



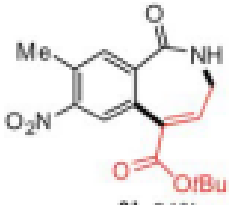
3i, 91%



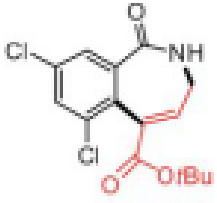
3j, 76%[b]



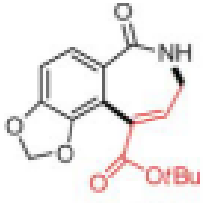
3k, 55%



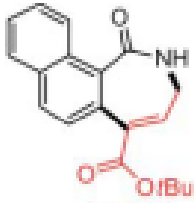
3l, 91%



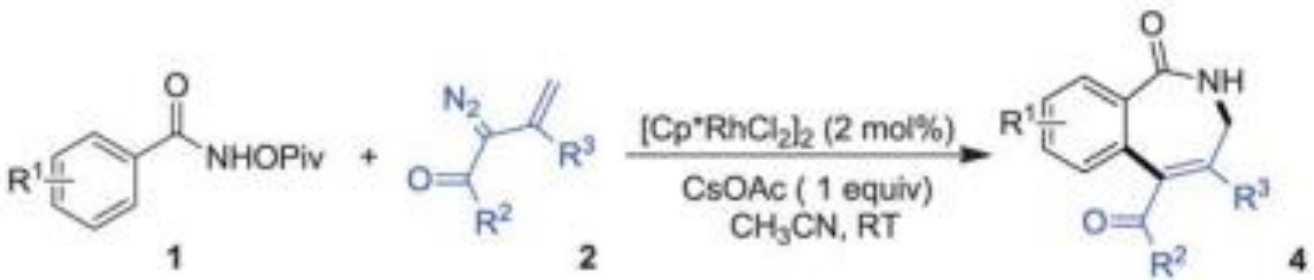
3m, 97%[c]

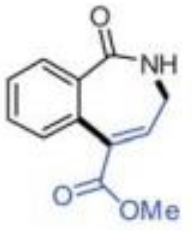


3n, 90%

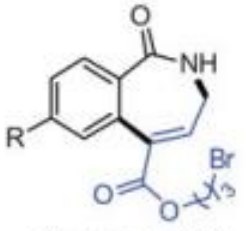


3o, 75%

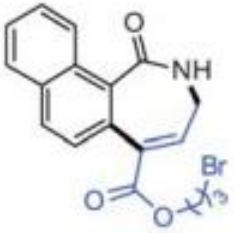




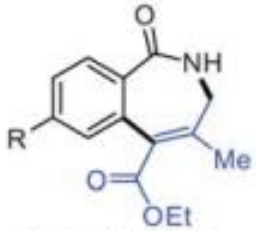
4a, 95%



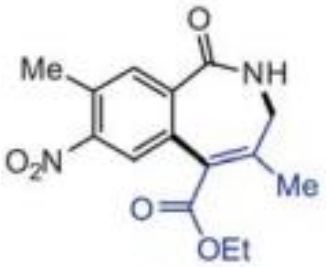
4b, R = H, 83%
4c, R = Ph, 77%



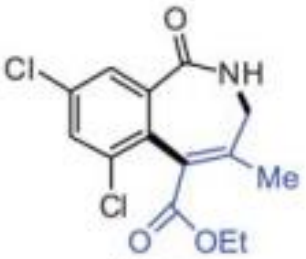
4d, 57%



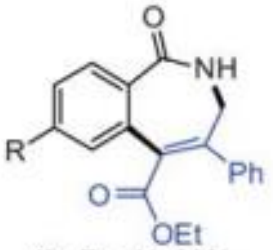
4e, R = H, 83%
4f, R = CF_3, 78%
4g, R = OMe, 70%
4h, R = I, 82%



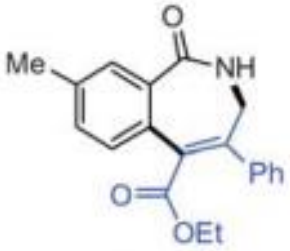
4i, 80%



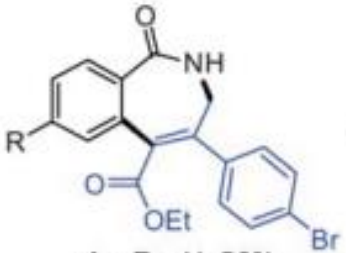
4j, 83%



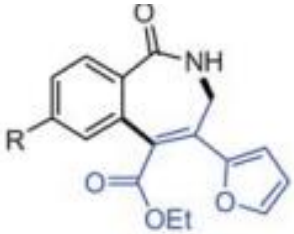
4k, R = H, 90%
4l, R = Me, 83%
4m, R = CN, 76%
4n, R = OMe, 79%
4o, R = Cl, 83%



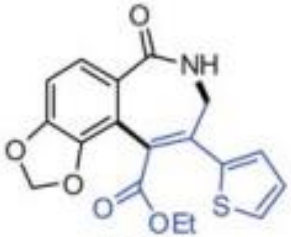
4p, 50%



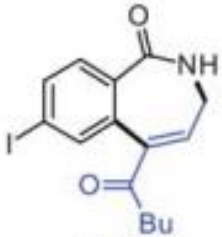
4q, R = H, 58%
4r, R = Cl, 55%



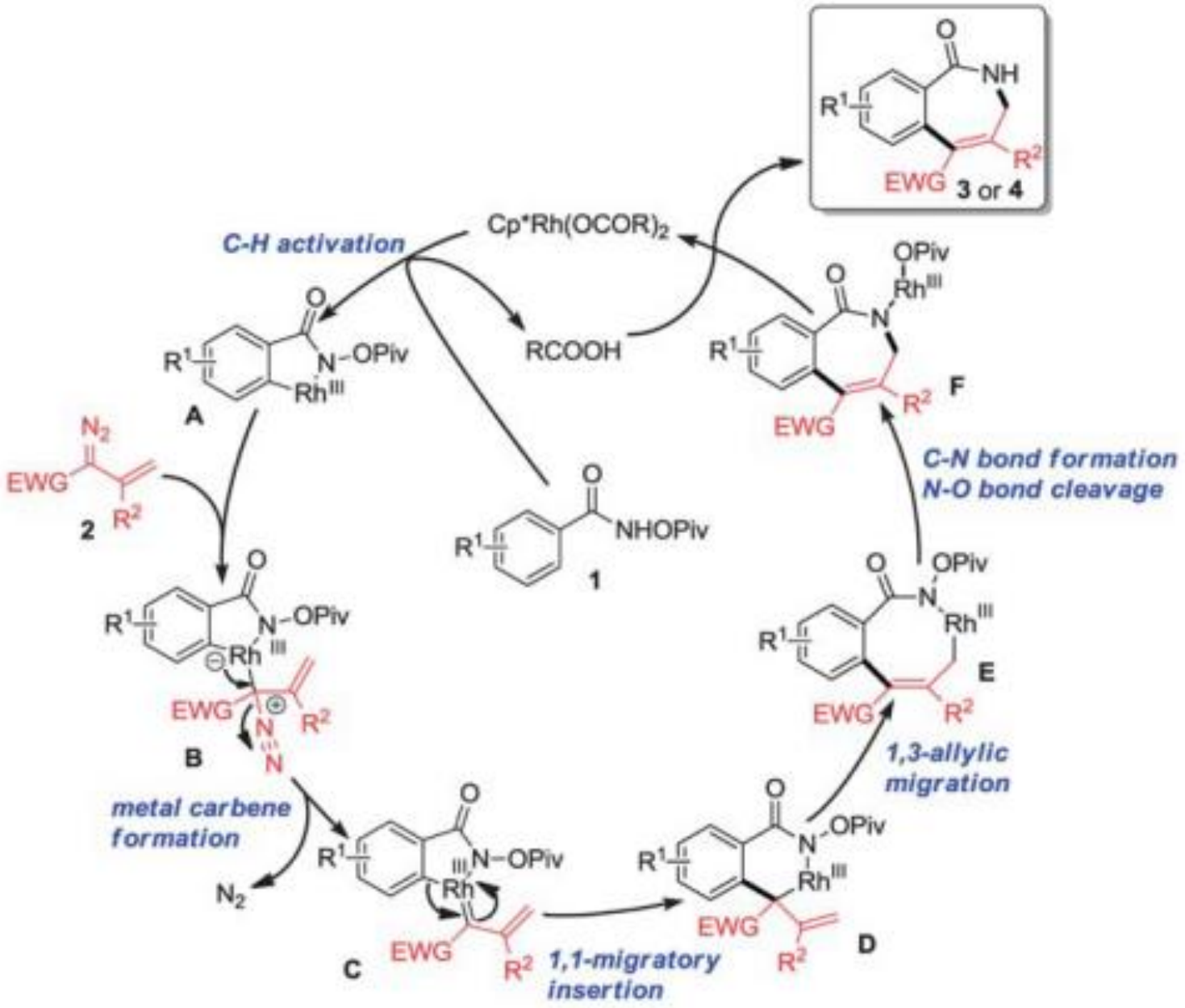
4s, R = H, 60%
4t, R = Me, 58%
4u, R = I, 60%

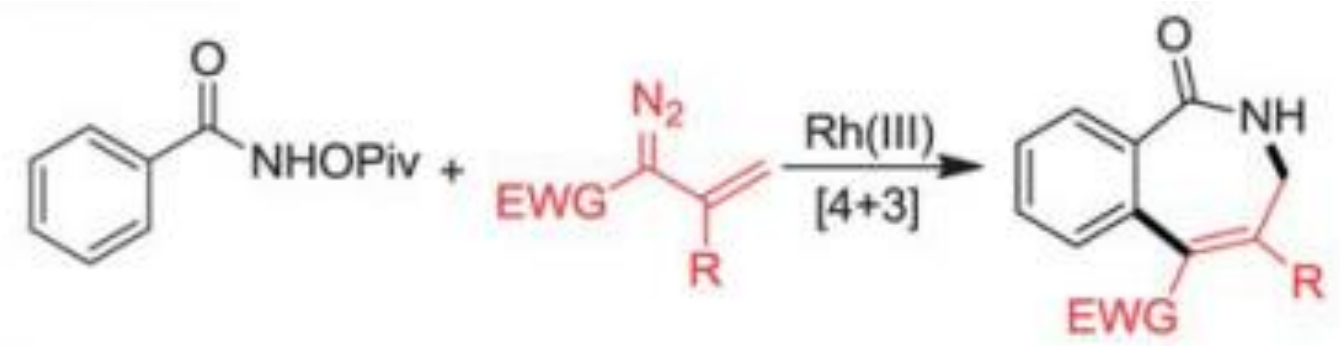


4v, 64%

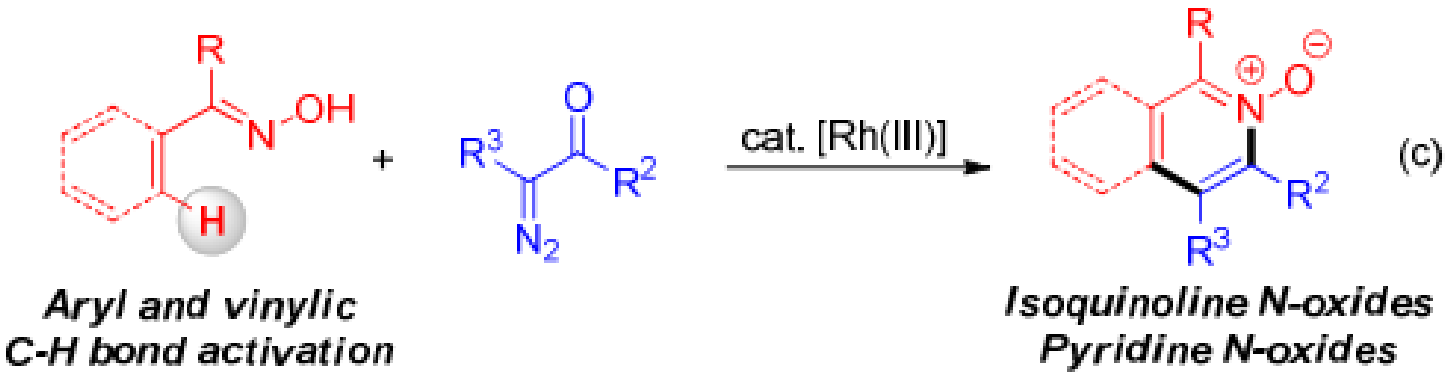


4w, 43%

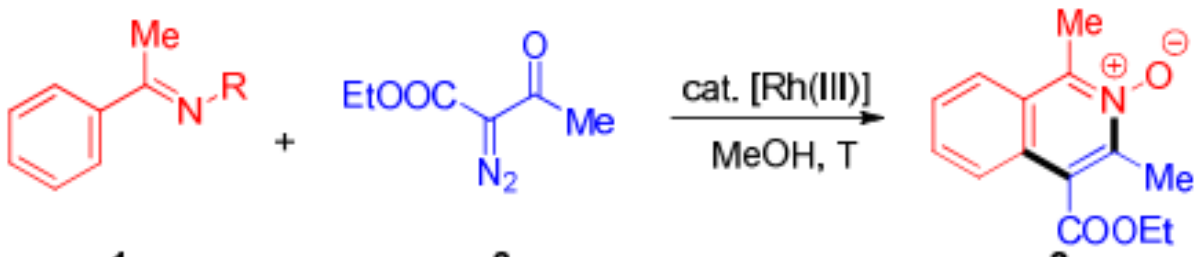

3 or 4
Cp*Rh(OCOR)2
C-H activation
RCOOH
A
F
2
1
C-N bond formation
N-O bond cleavage
B
E
1,3-allylic
migration
metal carbene
formation
C
D
1,1-migratory
insertion



Simple starting materials；
mild reaction conditions；
broad substrate scope；
high efficiency.



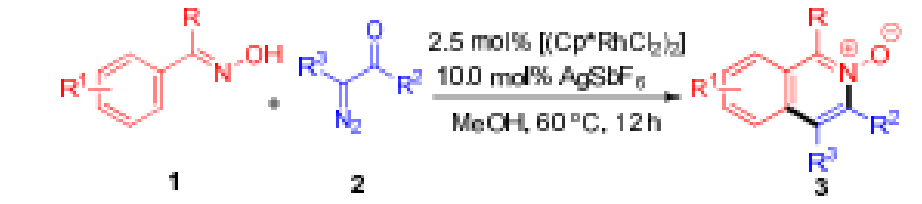
J. Am. Chem. Soc. DOI: 10.1021/ja406338r



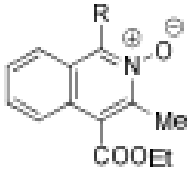
1 **2a** **3aa**

entry	R	catalyst system (mol%)	T (°C)	Yield (%)[b]
1	OBoc	$[(Cp^*RhCl_2)_2]$ (2.5) + AgOAc (15.0)	60	19
2	OPiv	$[(Cp^*RhCl_2)_2]$ (2.5) + AgOAc (15.0)	60	34
3	OPiv	$[(Cp^*RhCl_2)_2]$ (2.5) + $AgSbF_6$ (10.0)	60	76
4	OAc	$[(Cp^*RhCl_2)_2]$ (2.5) + $AgSbF_6$ (10.0)	60	99
5	**OH (1a)**	**$[(Cp^*RhCl_2)_2]$ (2.5) + $AgSbF_6$ (10.0)**	**60**	**99**
6	OH (**1a**)	$[(Cp^*RhCl_2)_2]$ (1.0) + $AgSbF_6$ (4.0)	60	92
7	OH (**1a**)	$[(Cp^*RhCl_2)_2]$ (2.5) + $AgSbF_6$ (10.0)	rt	69
8	OH (**1a**)	$AgSbF_6$ (10.0)	60	0

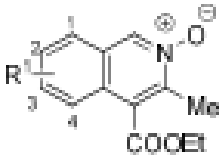
[a] Conditions: **1** (0.20 mmol), **2a** (0.24 mmol), 2.5 mol% $[(Cp^*RhCl_2)_2]$, 10 mol% $AgSbF_6$, MeOH(1.0 mL), 12 h, under Ar. [b] Isolated yield.



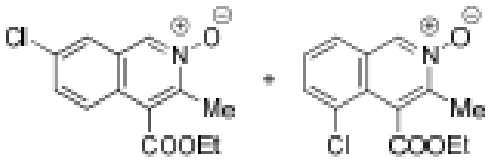
1 2 3



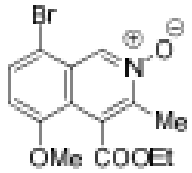
3aa, R = Me, 99%
3ba, R = ^{i}Pr, 85%
3ca, R = Ph, 70%
3da, R = H, 62%



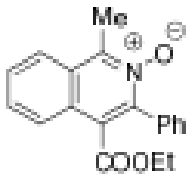
3ea, R^1 = 3-Me, 58%
3fa, R^1 = 1-OMe, 78%
3ga, R^1 = 1-F, 58%
3ha, R^1 = 3-COOMe, 45%[b]



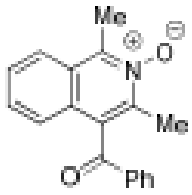
3ia + 3ia' (1.8 :1), 63%



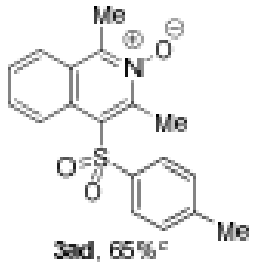
3ja, 87%



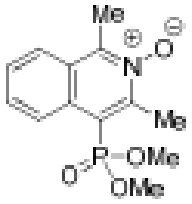
3ab, 68%



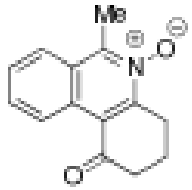
3ac, 99%



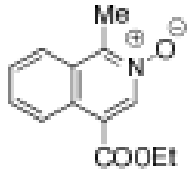
3ad, 65%[c]



3ae, 99%

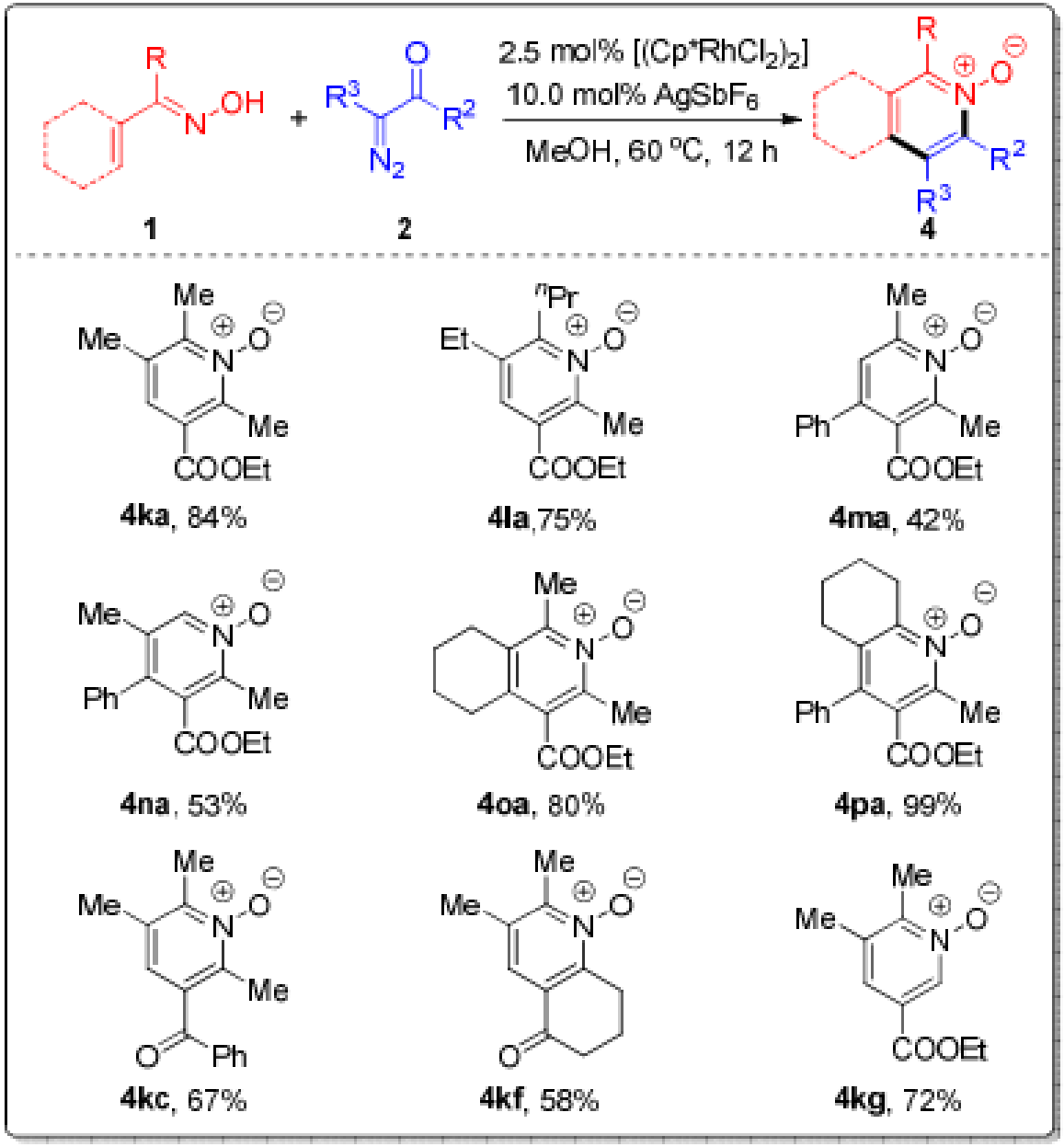


3af, 62%

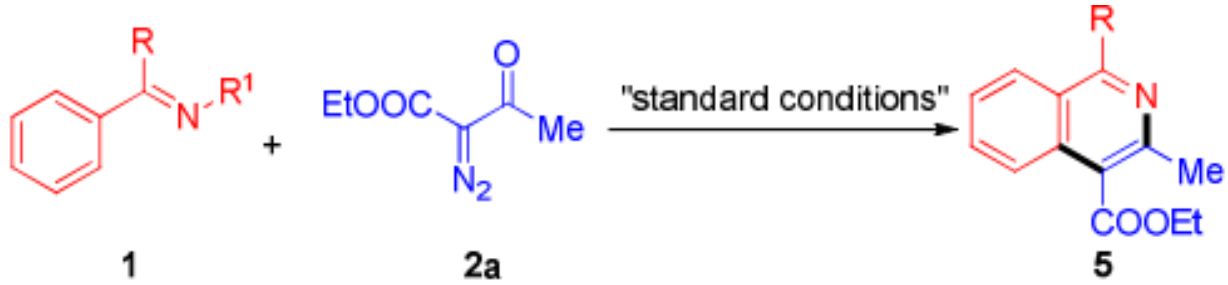


3ag, 58%

[a] Conditions: **1** (0.20 mmol), **2** (0.24 mmol), 2.5 mol% $[Cp^*RhCl_2]_2$, 10.0 mol% $AgSbF_6$ in MeOH (1.0 mL) at 60 °C 12 h, under Ar; isolated yield. [b] Using 5.0 mol% $[Cp^*RhCl_2]_2$ 20.0 mol% $AgSbF_6$, at 100 °C. [c] At 100 °C.



[a] Conditions: **1** (0.20 mmol), **2** (0.24 mmol), 2.5 mol% $[Cp^*RhCl_2]_2$, 10.0 mol% $AgSbF_6$ in MeOH (1.0 mL) at 60 °C, 12 h, under Ar; isolated yield.



1 **2a** **5**

R = Me, R^1 = OMe, **1q**

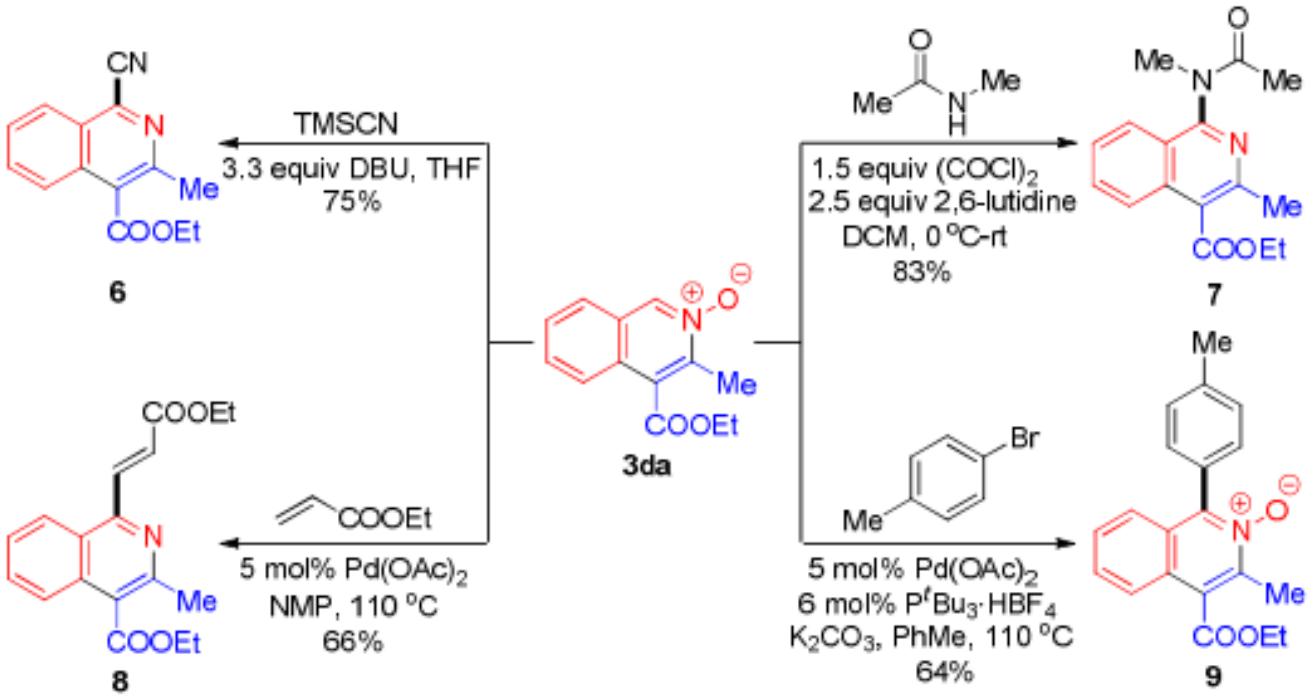
R = Ph, R^1 = H, **1r**

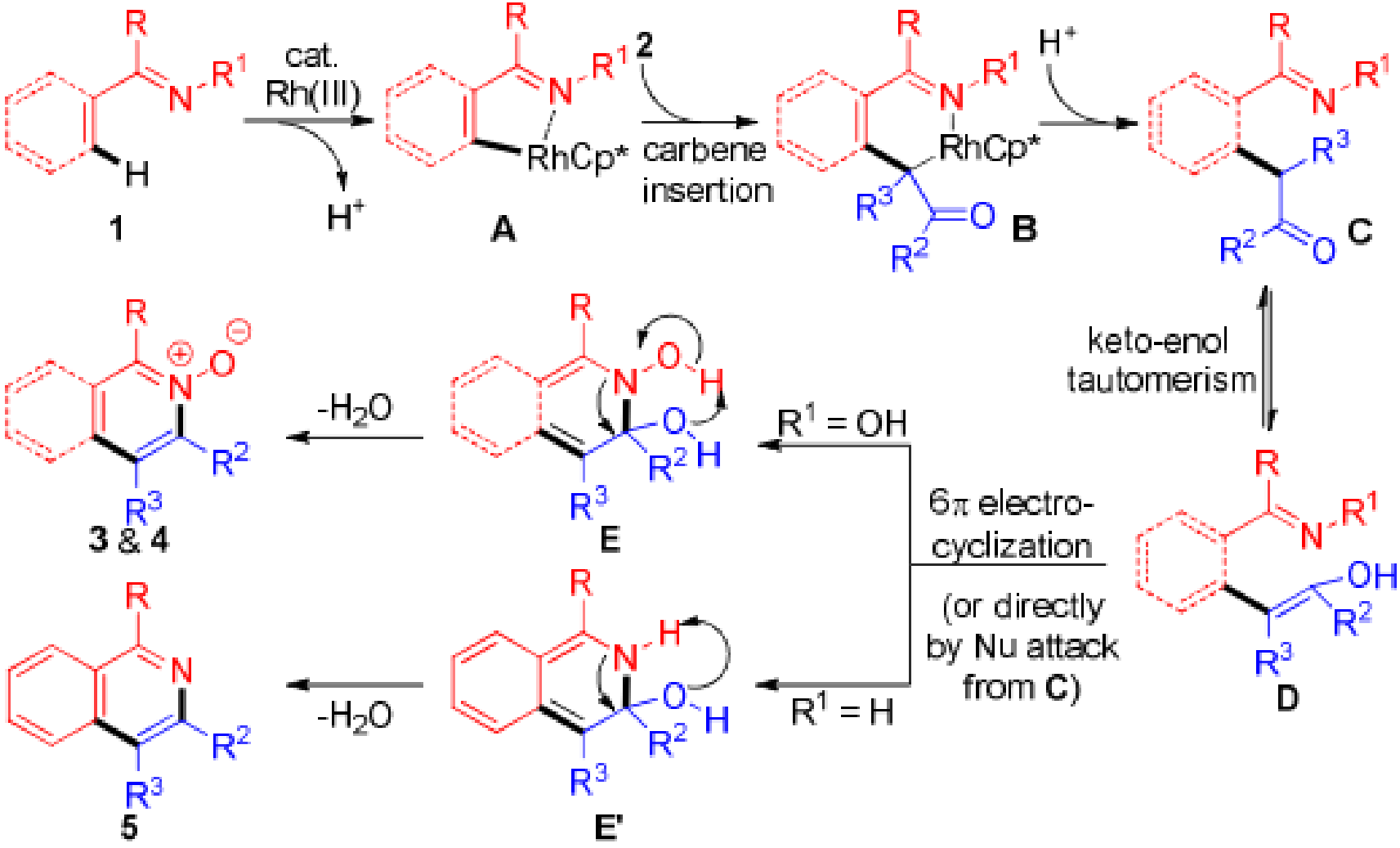
R = OEt, R^1 = H, **1s**

R = Me, **5qa**, 28%

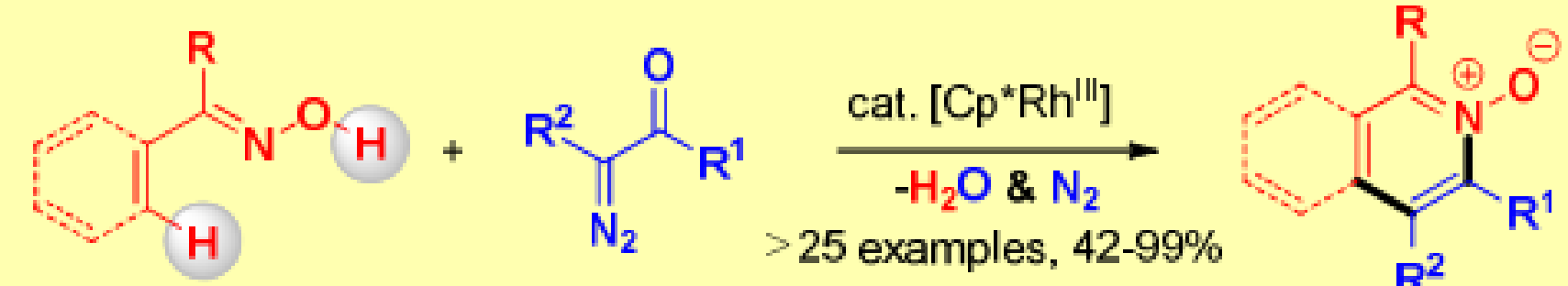
R = Ph, **5ra**, 88%

R = OEt, **5sa**, 95%




R
N
R1
H
1
cat.
Rh(III)
H+
RhCp*
A
2
carbene
insertion
B
H+
C
keto-enol
tautomerism
D
6π electro-
cyclization
(or directly
by Nu attack
from C)
R1 = OH
R1 = H
E
E'
-H2O
-H2O
3 & 4
5
R2
R3
O
OH

Isoquinoline and Pyridine N-Oxide Construction:



R = H, alkyl, aryl R^1 = H, alkyl, aryl; R^2 = EWG

Simple Substrates

Broad substrate scope

Mild conditions

Valuable products

Completely regioselective