福州大学第二届国际青年学者论坛

过渡金属卡宾参与的串联环化反应及多金簇合物的合成

杨金明 博士
jyang@iciq.es

博士导师: 施敏 研究员 (SIOC)
博后合作导师: Antonio M Echavarren (ICIQ)

2017-12-24

Institute of Chemical Research of Catalonia (ICIQ)

Institute of Chemical Research of Catalonia (ICIQ)

主要内容

- 背景介绍
- 正文部分

一、铑卡宾参与的杂环合成

- 铑催化的1-磺酰基-1,2,3-三氮唑的分子内环化反应

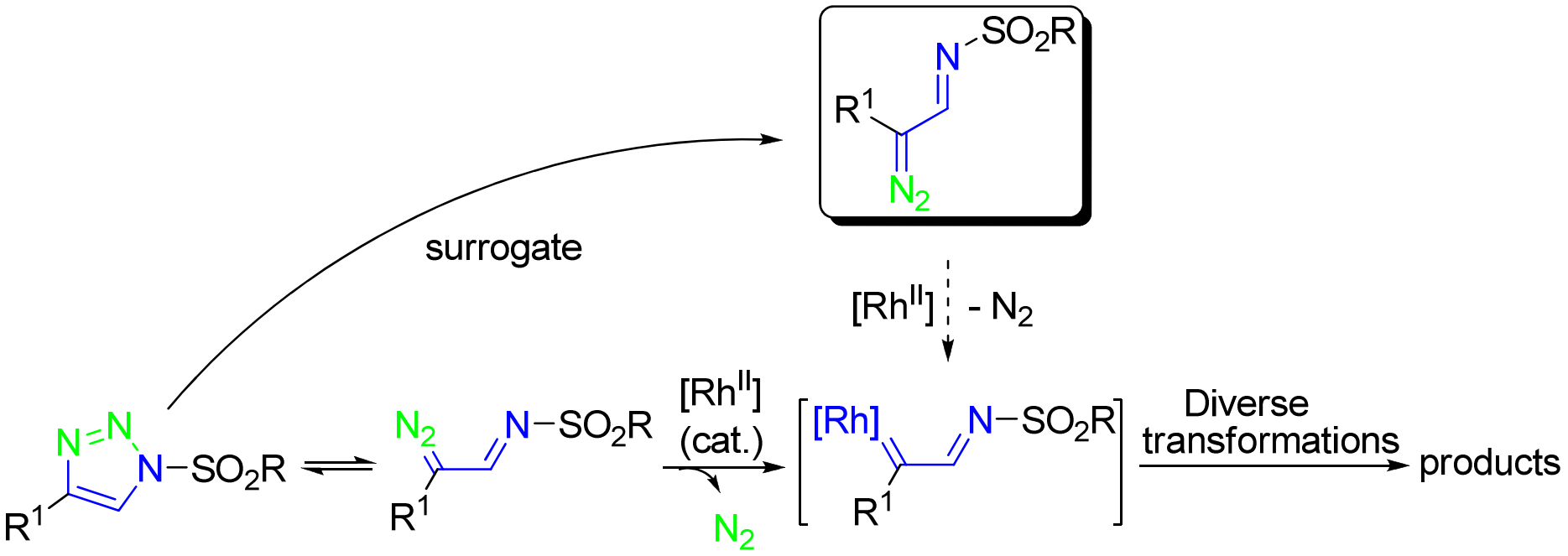
二、金卡宾参与的串联环化反应

- 金催化炔丙醇羧酸酯和呋喃分子内的环异构化反应
- 金催化炔丙醇羧酸酯和吲哚分子内的环化反应

三、多金簇合物的合成、表征以及催化活性研究

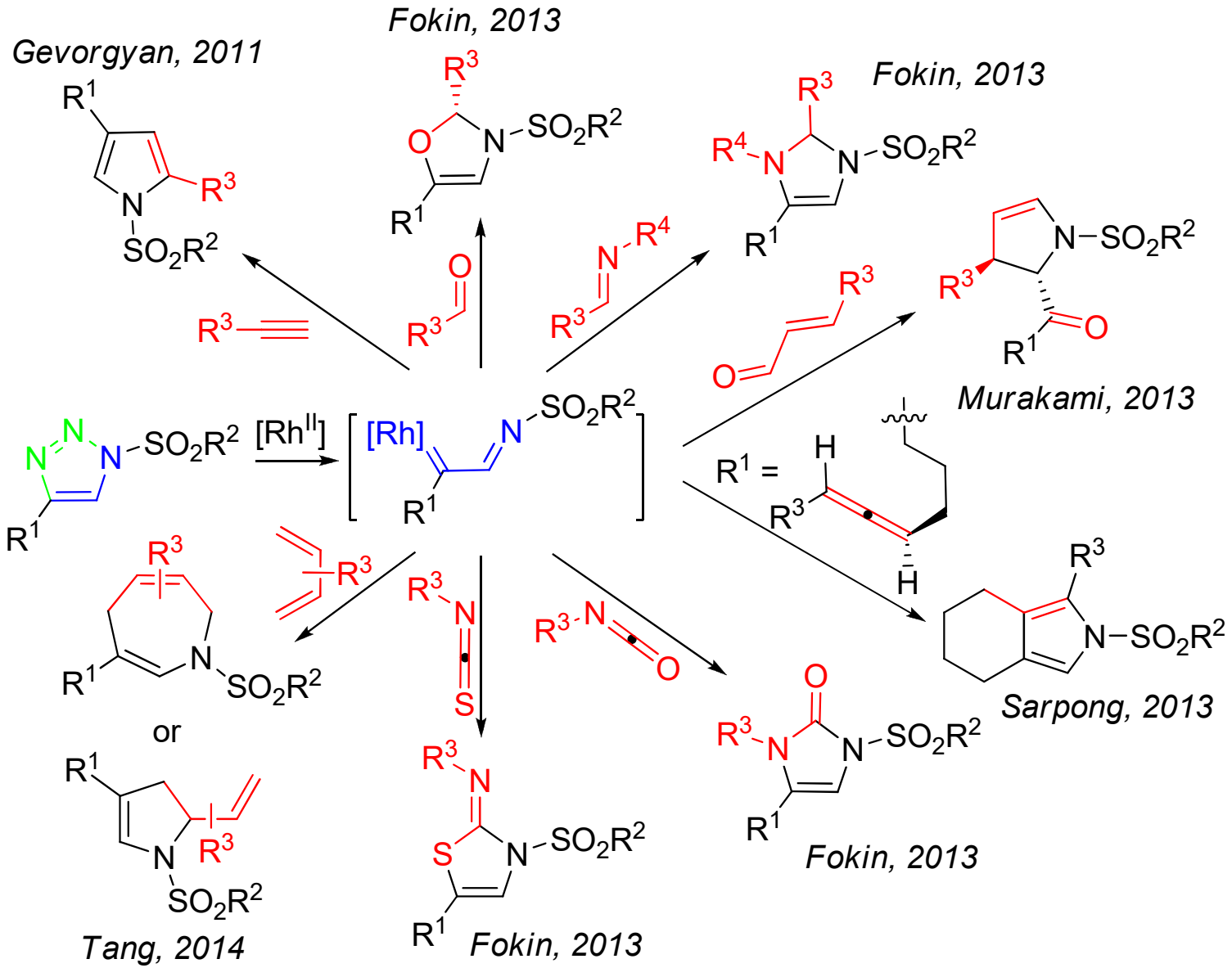
- 研究总结
- 致谢

三氮唑



Gulevich, A. V.; Gevorgyan, V. *Angew. Chem. Int. Ed.* **2013**, *52*, 1371-1373.

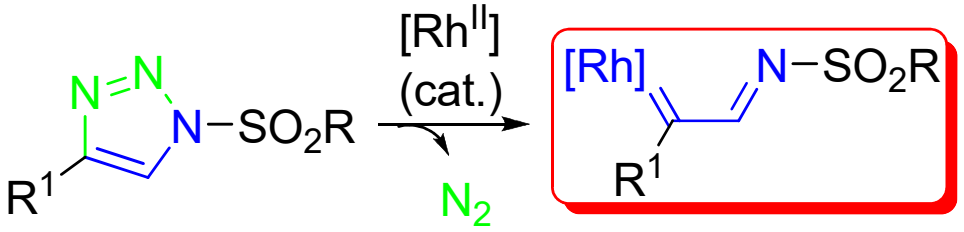
三氮唑产生铑卡宾后的转化

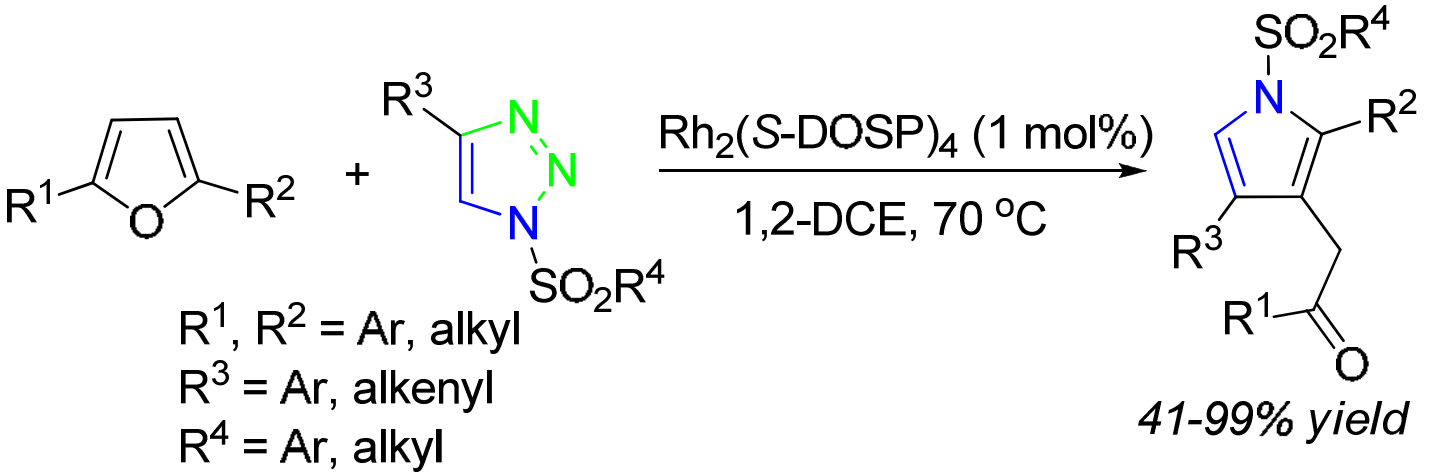


(a) Gulevich, A. V.; Gevorgyan, V. *Angew. Chem. Int. Ed.* **2013**, *52*, 1371-1373. (b) Davies, H. M. L.; Alford, J. S. *Chem. Soc. Rev.* **2014**, *43*, 5151-5162.

一、铑卡宾参与的杂环合成

铑是应用最多、最广泛的催化剂之一
环加成反应、PK反应、C–H键活化



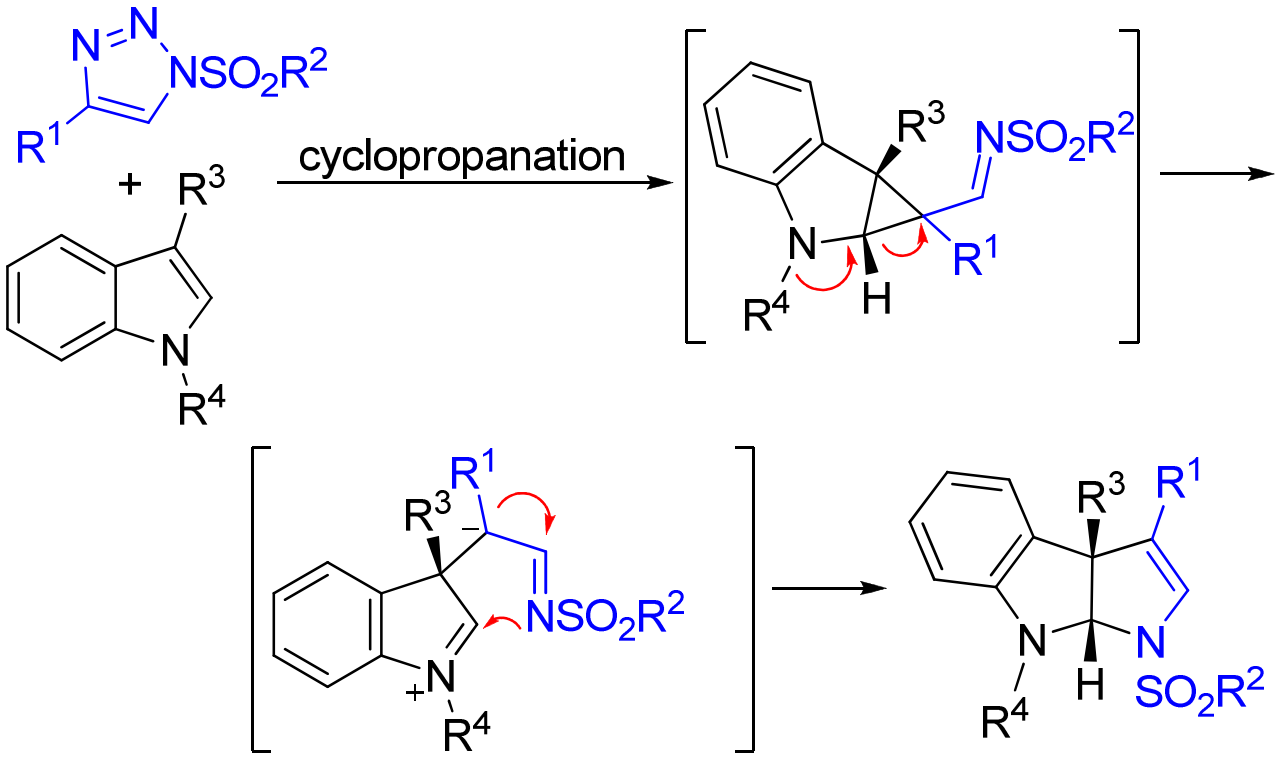


R^1, R^2 = Ar, alkyl
R^3 = Ar, alkenyl
R^4 = Ar, alkyl

Parr, B. T.; Green, S. A.; Davies, H. M. L. *J. Am. Chem. Soc.* **2013**, *135*, 4716-4718.

铑卡宾参与的杂环合成

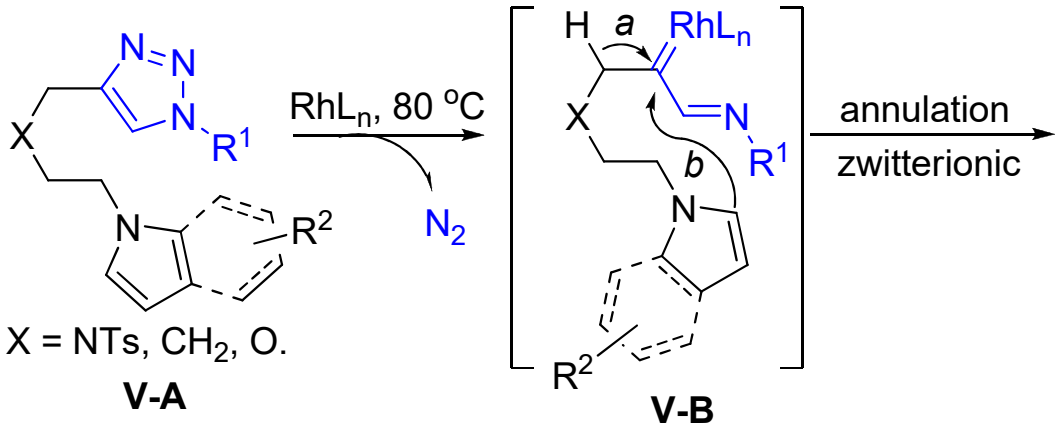
Intermolecular annulation of indoles (Davies's work)

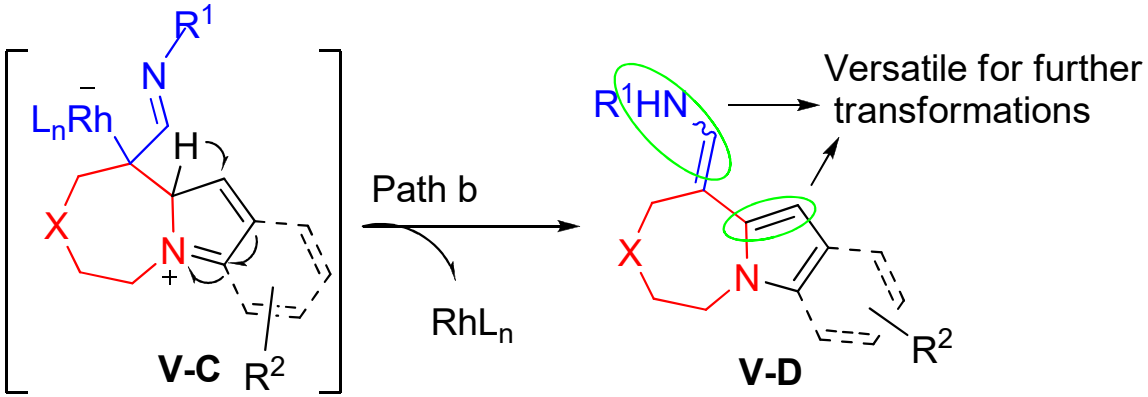


Spangler, J. E.; Davies, H. M. L. *J. Am. Chem. Soc.* **2013**, *135*, 6802-6805.

铑卡宾参与的杂环合成

Intramolecular annulation of pyrroles and indoles (This work)

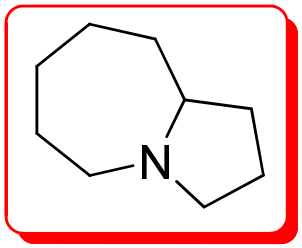


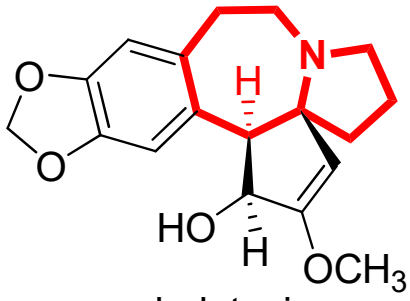


High chemoselectivity (path b only)!
Easy-to-handle functional groups!
Wide azepine ring flexibility (N, O, C)!

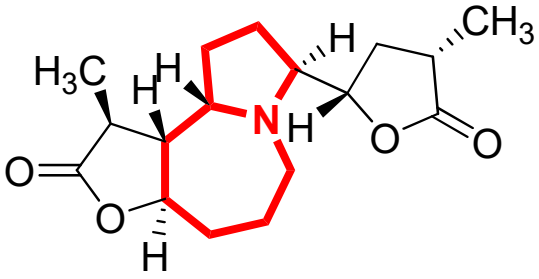
Yang, J.-M.; Zhu, C.-Z.; Tang, X.-Y.*; Shi, M.* *Angew. Chem. Int. Ed.* **2014**, *53*, 5142-5146.

铑卡宾参与的杂环合成

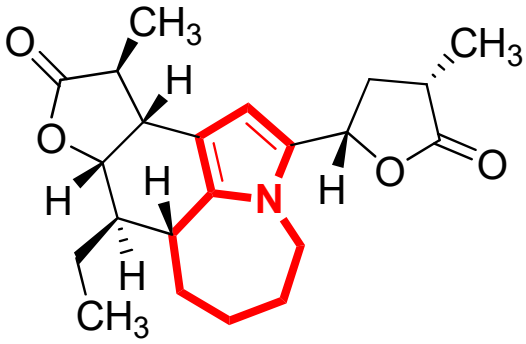




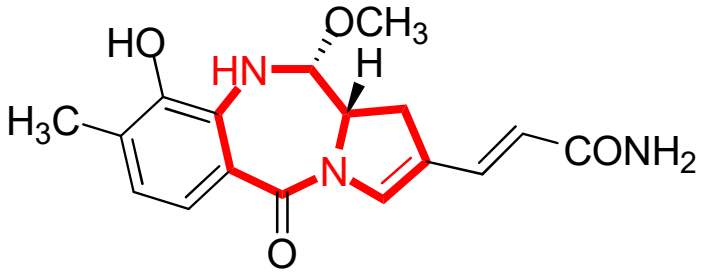
cephalotaxine



stemonine



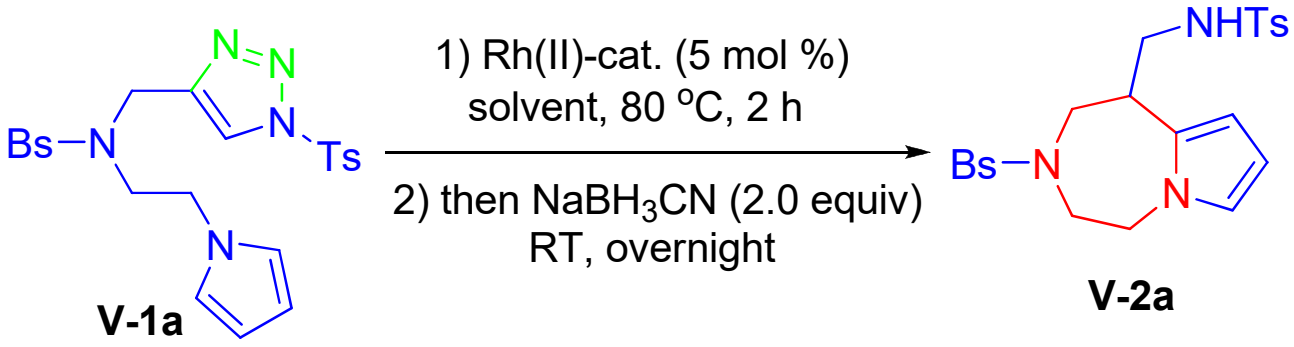
bisdehydrotuberostemonine
bisdehydroneotuberostemonine (H-11α, H-12α)
bisdehydrotuberostemonine B (H-10β)
bisdehydrotuberostemonine C (H-9α, H-10β)

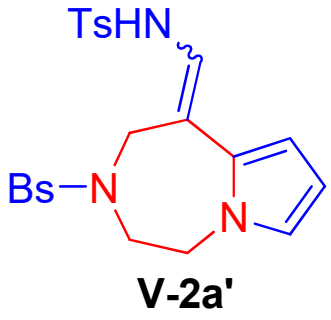


anthramycin

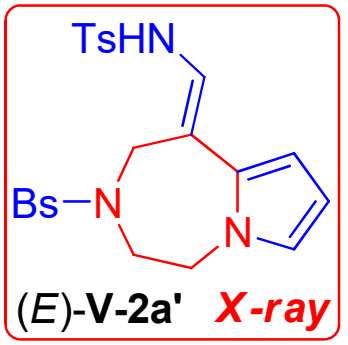
Yang, J.-M.; Zhu, C.-Z.; Tang, X.-Y.*; Shi, M.* *Angew. Chem. Int. Ed.* **2014**, *53*, 5142-5146.

反应条件优化



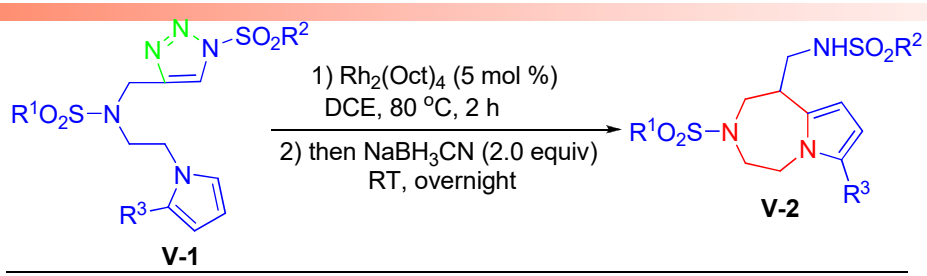


entry[a]	Rh(II)-cat.	solvent	yield (%)[b]
1	***$Rh_2(Oct)_4$***	***DCE***	***86***
2	$Rh_2(Piv)_4$	DCE	80
3	$Rh_2(esp)_2$	DCE	77
4	$Rh_2(OAc)_4$	DCE	78
5	$Rh_2(Adc)_4$	DCE	80
6	$Rh_2(tfa)_4$	DCE	0
7	Rh_2(S-NTTL)$_4$	DCE	70
8	$Rh_2(Oct)_4$	toluene	78
9	$Rh_2(Oct)_4$	cyclohexane	-[c]
10	$Rh_2(Oct)_4$	$CHCl_3$	-[c]

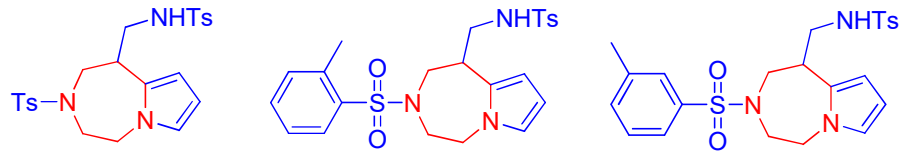


[a] Reaction conditions: 0.1 mmol of **V-1a**; 5 mol% of cat.; 1.0 mL of dry solvent. [b] Isolated yields. [c] undetermined. DCE =1,2-dichloroethane.

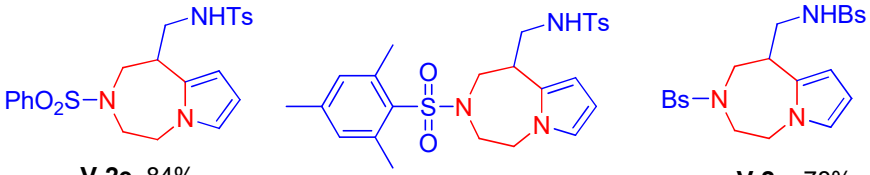
普适性考查



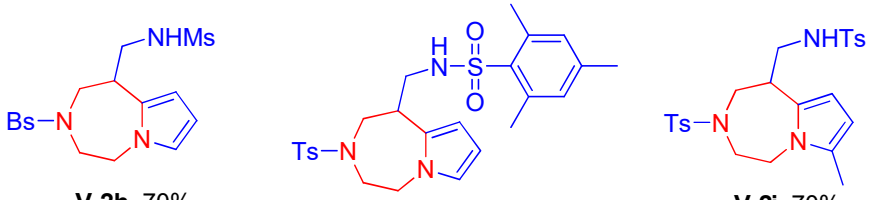
V-1 **V-2**



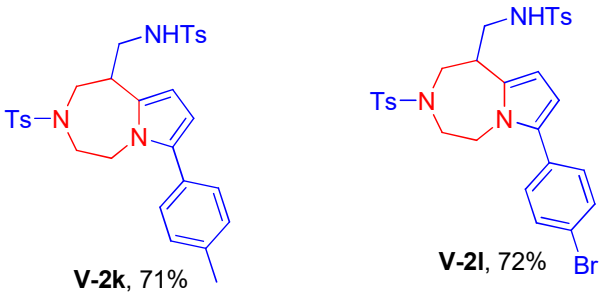
V-2b, 78% **V-2c**, 78% **V-2d**, 83%



V-2e, 84% **V-2f**, 80% **V-2g**, 78%



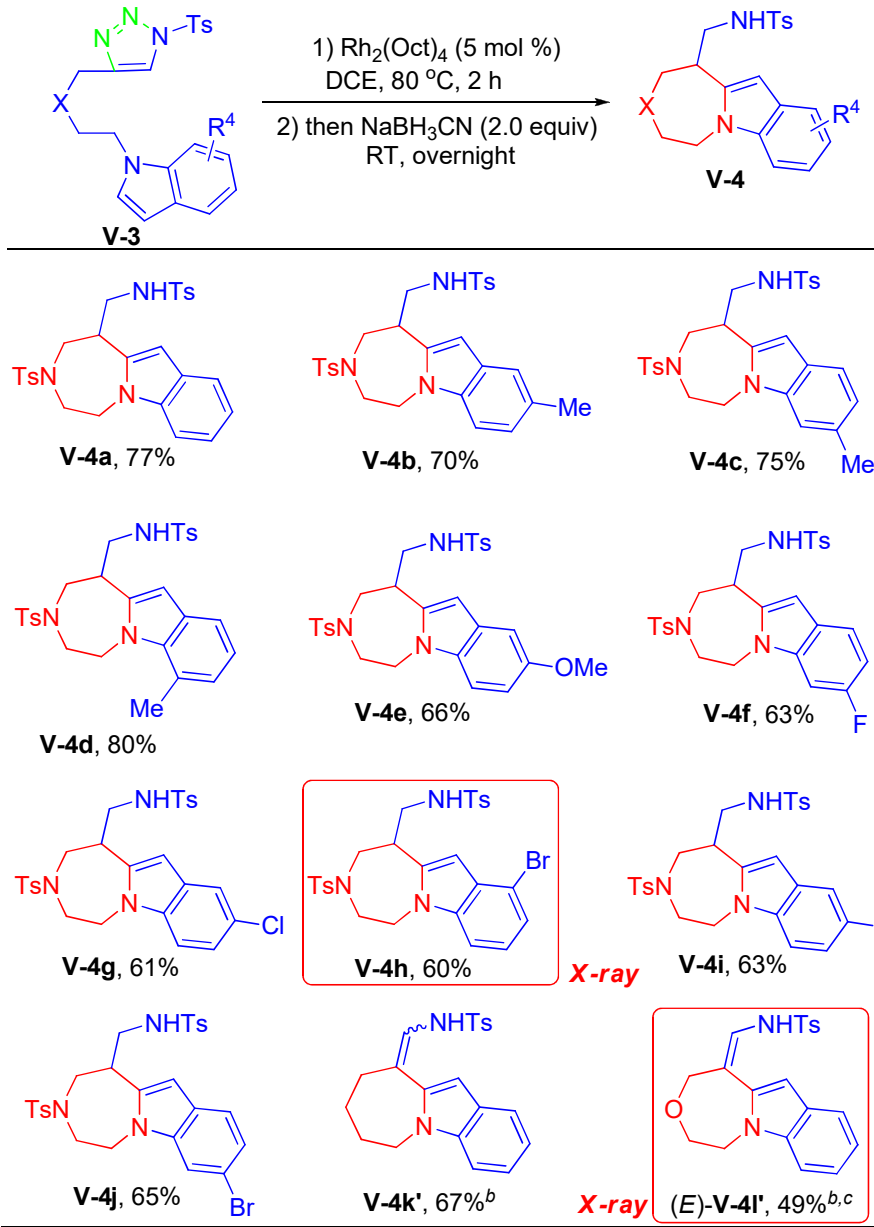
V-2h, 70% **V-2i**, 80% **V-2j**, 70%

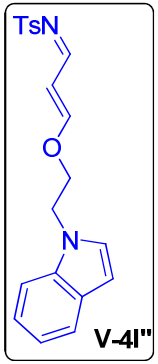


V-2k, 71% **V-2l**, 72%

Reaction conditions: 0.1 mmol of **V-1**; 5 mol % of $Rh_2(Oct)_4$; 1.0 mL anhydrous DCE. Isolated yields.

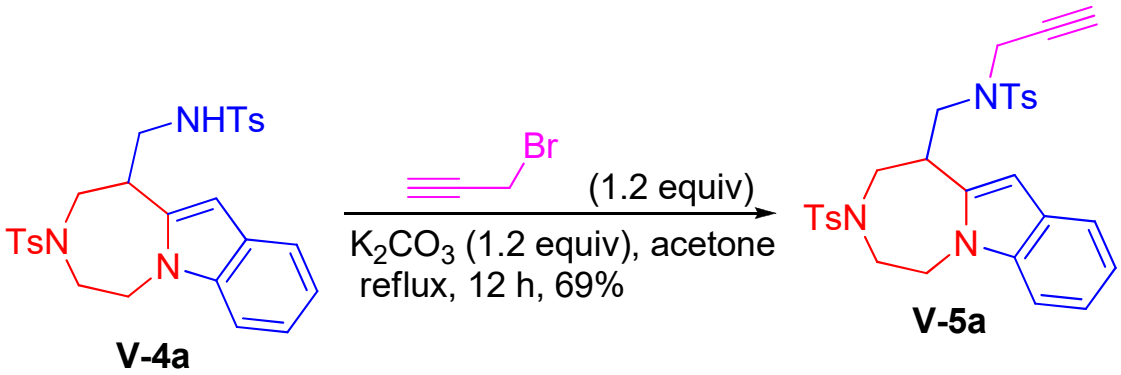
普适性考查

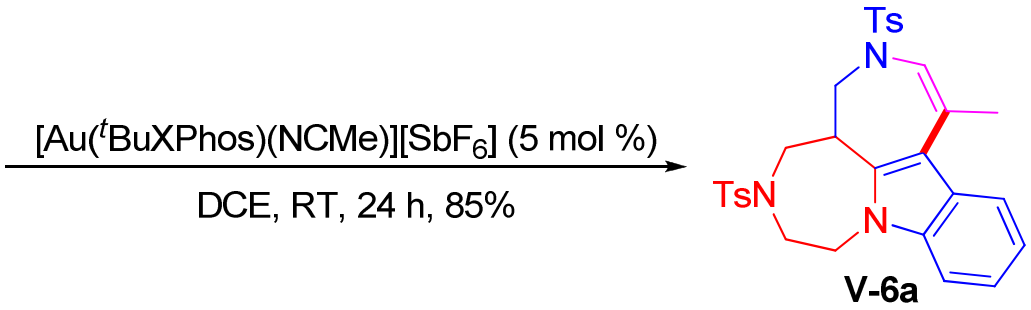


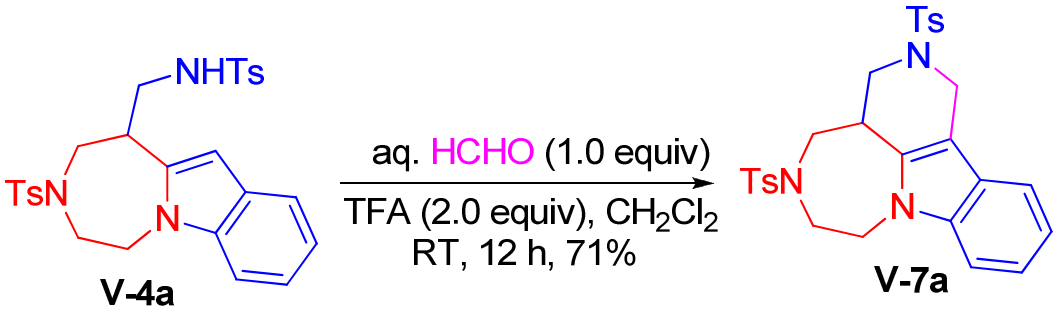


[a] Reaction conditions: 0.1 mmol of **V-3**; 5 mol % of $Rh_2(Oct)_4$; 1.0 mL anhydrous DCE. Isolated yields. [b] Substrates were performed only in the first step, and the two isomers were not reduced. [c] **V-4l''** was obtained in 43% yield.

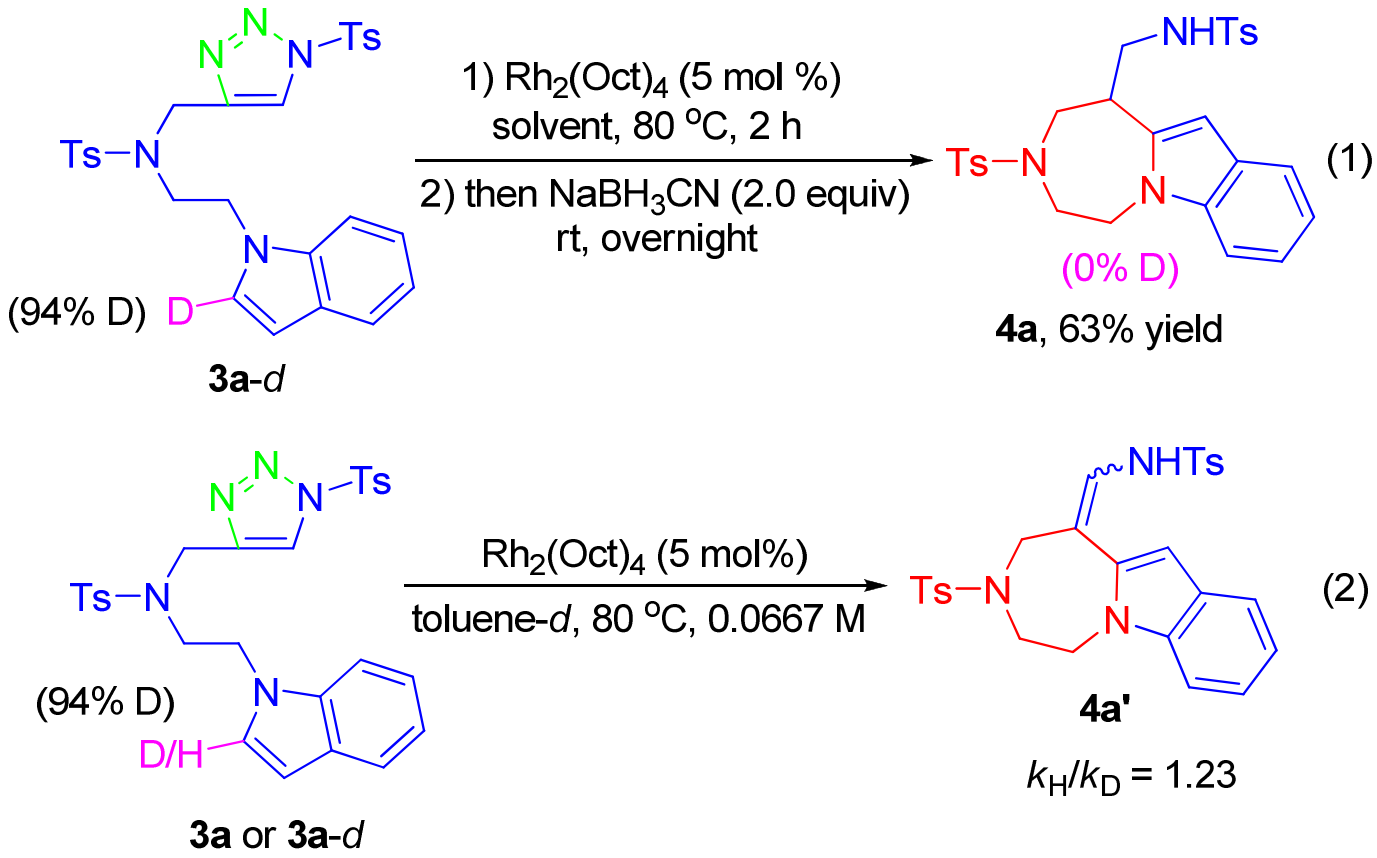
产物转化


NHTs
TsN
N
V-4a
Br
(1.2 equiv)
K2CO3 (1.2 equiv), acetone
reflux, 12 h, 69%
NTs
TsN
N
V-5a

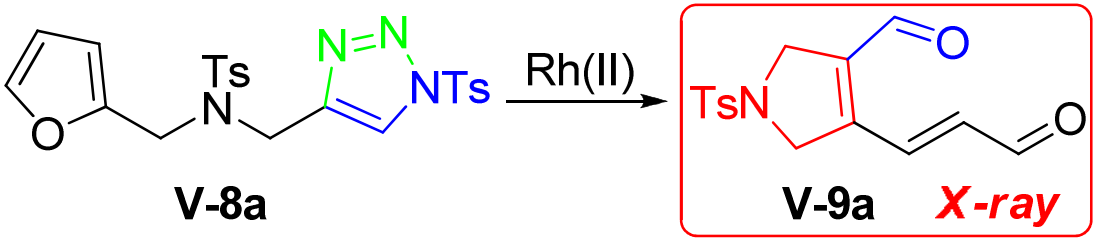

[Au(tBuXPhos)(NCMe)][SbF6] (5 mol %)
DCE, RT, 24 h, 85%
Ts
N
TsN
N
V-6a

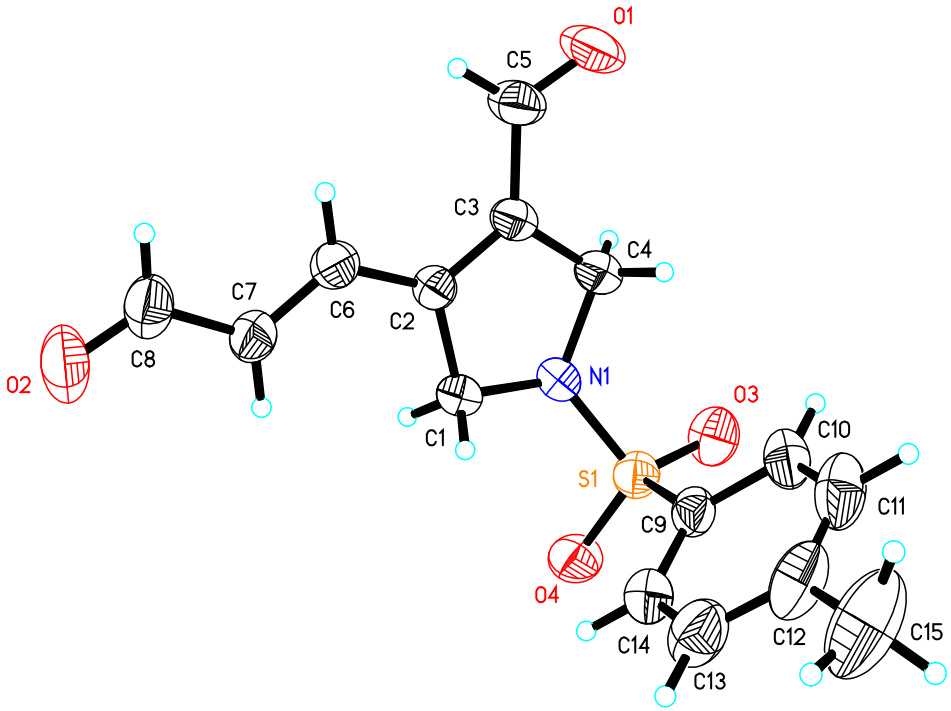

NHTs
TsN
N
V-4a
aq. HCHO (1.0 equiv)
TFA (2.0 equiv), CH2Cl2
RT, 12 h, 71%
Ts
N
TsN
N
V-7a

氘代及动力学同位素效应实验

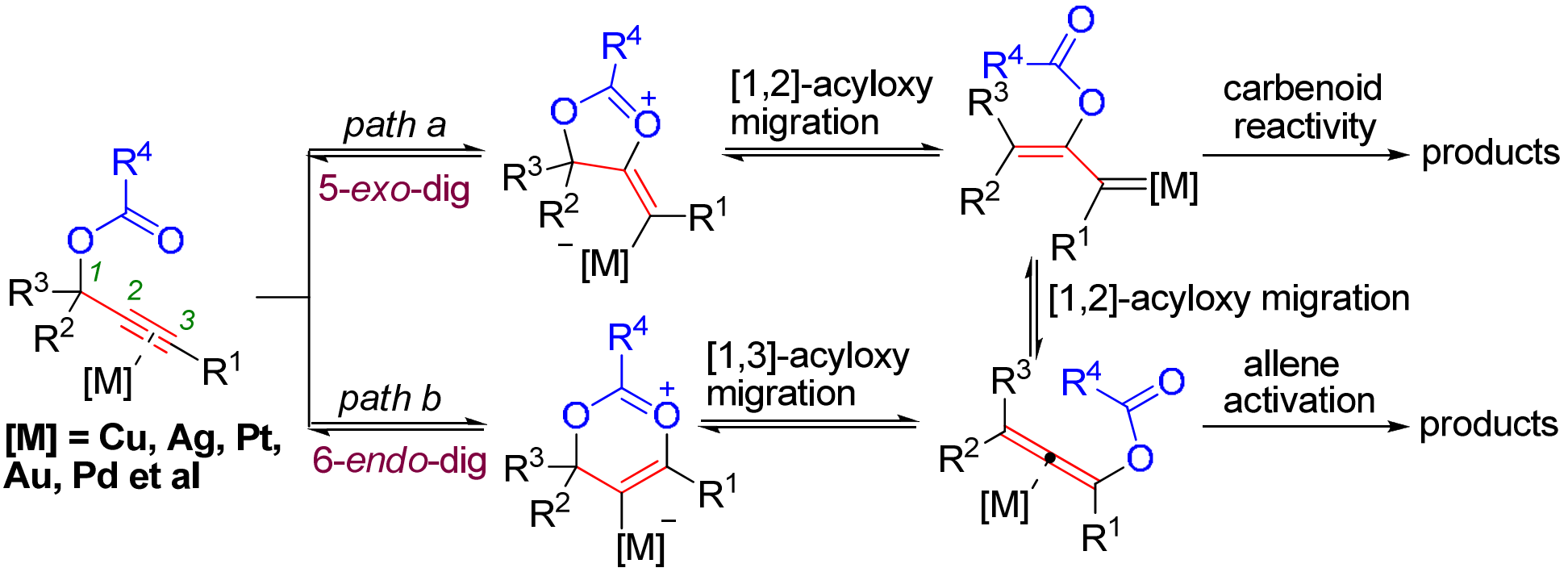


底物拓展


Ts
N
O
N=N
NTs
Rh(II)
TsN
O
O
V-8a
V-9a
X-ray

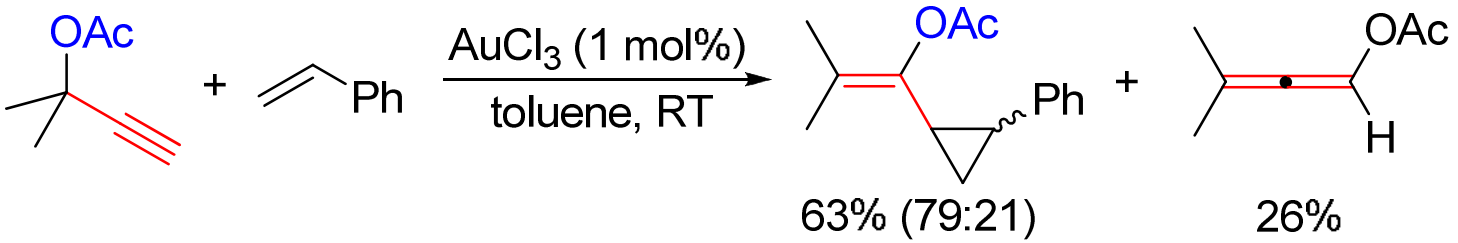

O1
C5
C3
C4
C7
C6
C2
O2
C8
N1
O3
C1
C10
S1
C11
C9
O4
C14
C12
C15
C13

炔丙醇羧酸酯

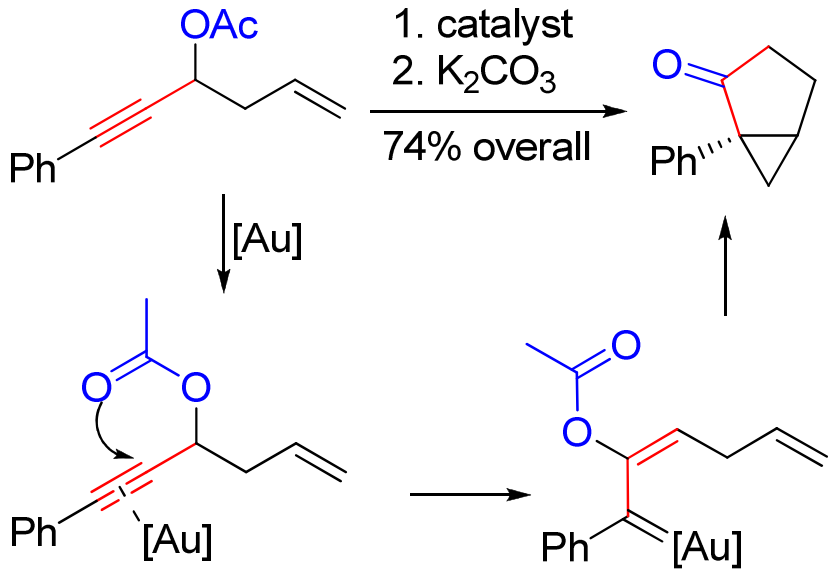


Wang, S.; Zhang, G.; Zhang, L. *Synlett* **2010**, 692-706.

炔丙醇羧酸酯[1,2]-迁移

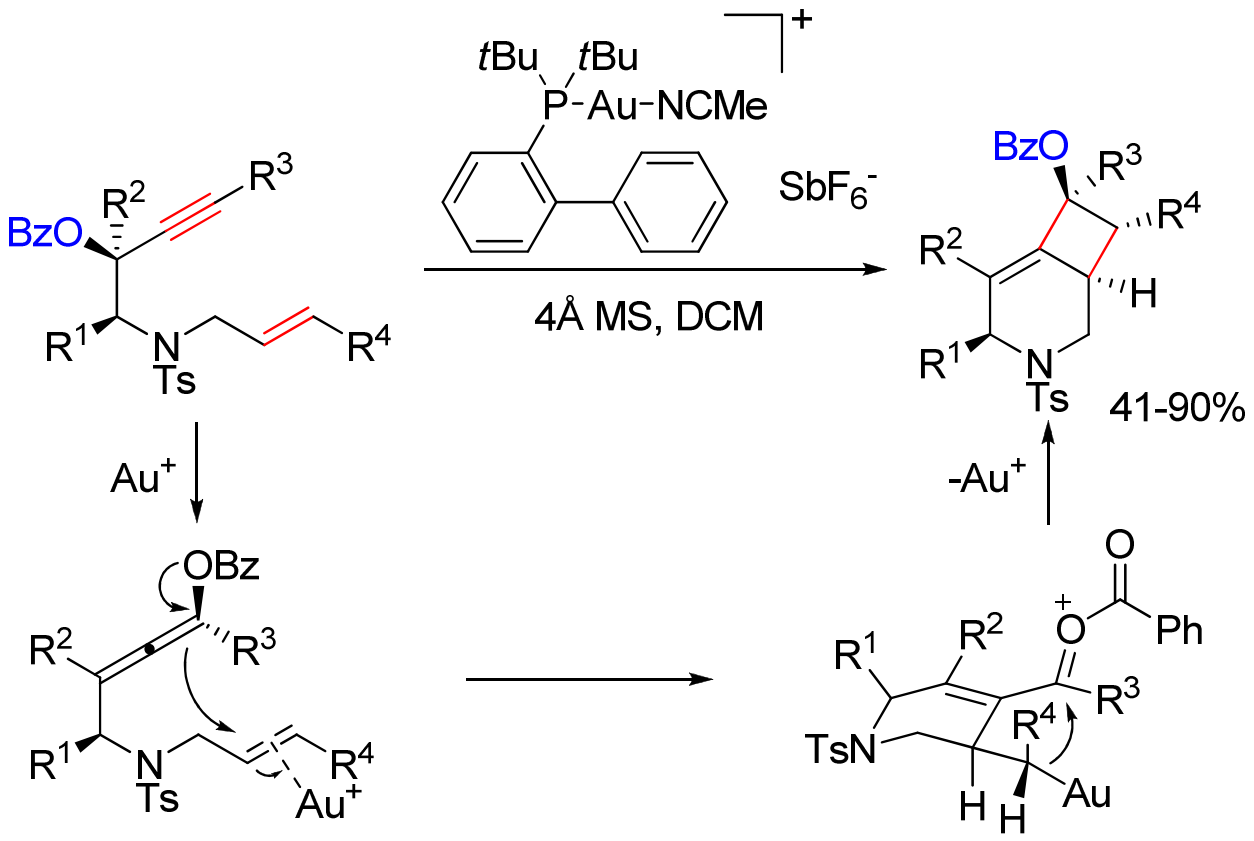


(a) Miki, K.; Ohe, K.; Uemura, S. *Tetrahedron Lett.* **2003**, *44*, 2019-2022. (b) Miki, K.; Ohe, K.; Uemura, S. *J. Org. Chem.* **2003**, *68*, 8505-8513.



Mamane, V.; Gress, T.; Krause, H.; Fürstner, *J. Am. Chem. Soc.* **2004**, *126*, 8654-8655.

炔丙醇羧酸酯[1,3]-迁移



Rao, W.; Susanti, D.; Chan, P. W. H. *J. Am. Chem. Soc.* **2011**, *133*, 15248-15251.

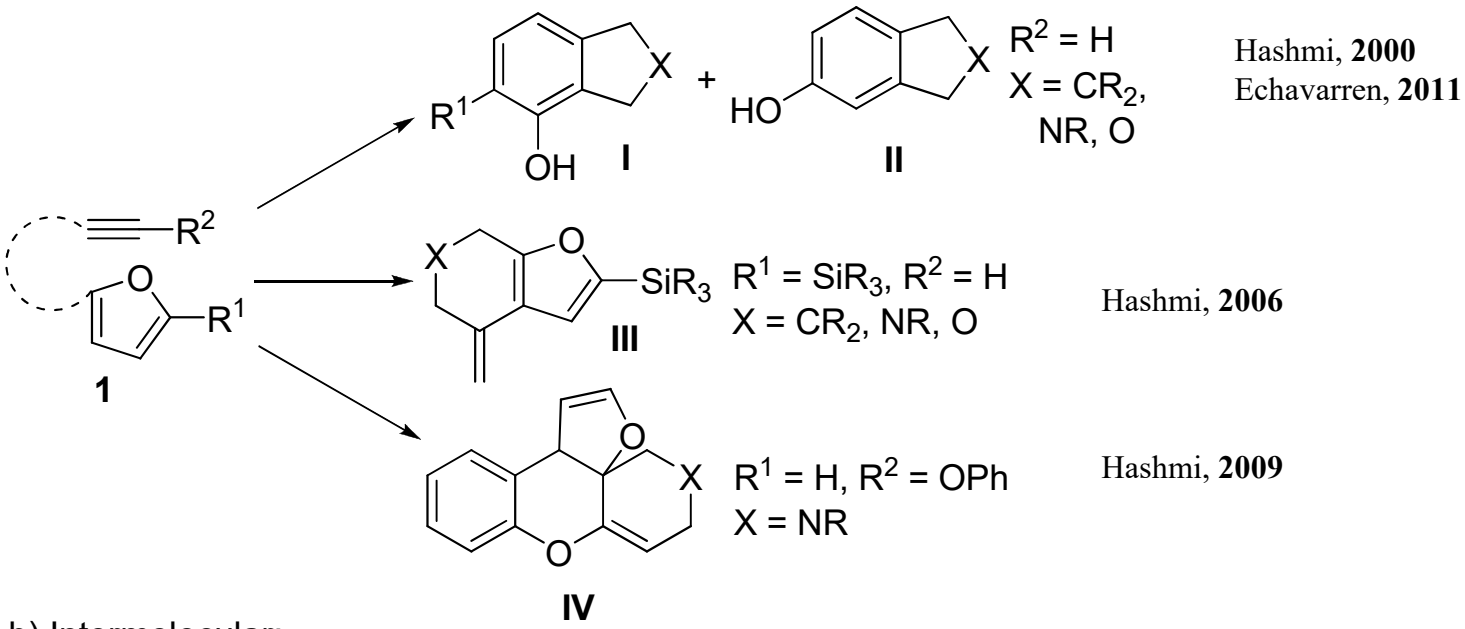
二、金卡宾参与串联环化反应

Gold catalysis

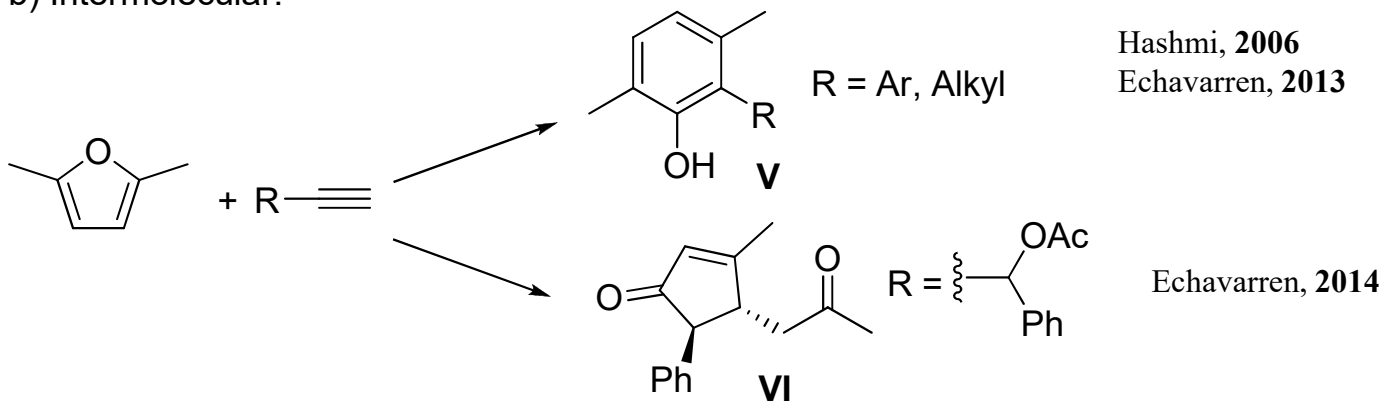
反应条件温和
操作简单
反应时间短
选择性高

Previous work

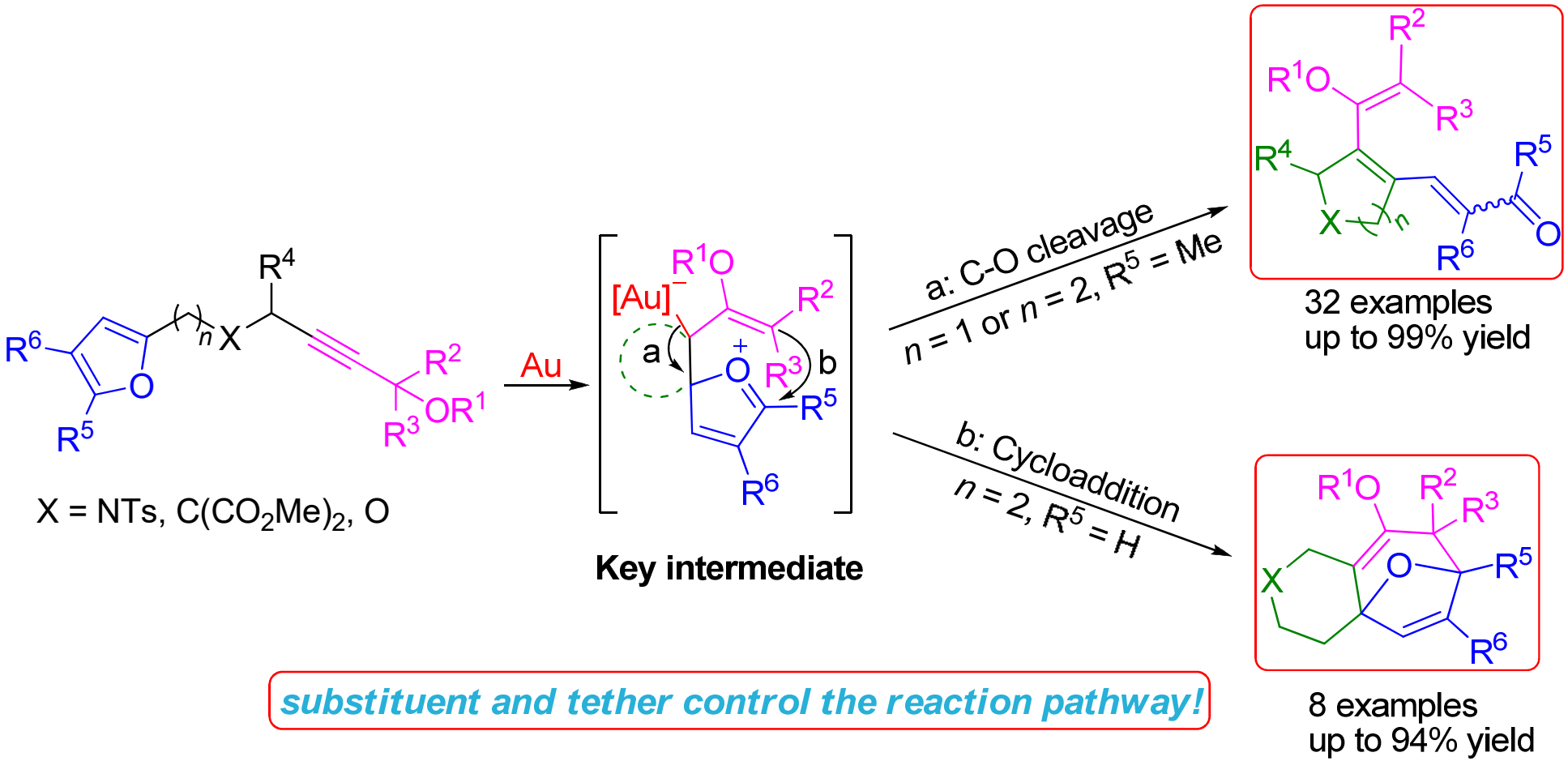
a) intramolecular:



b) Intermolecular:



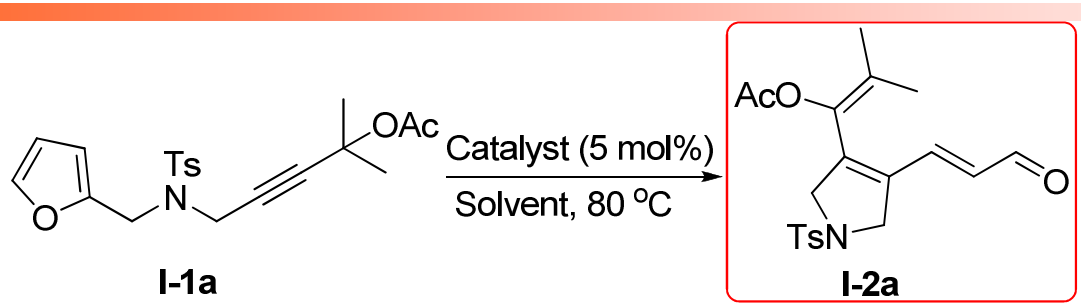
金催化炔丙醇羧酸酯和呋喃分子内的环异构化反应



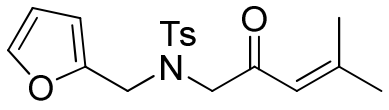
substituent and tether control the reaction pathway!

Yang, J.-M.; Tang, X.-Y.*; Shi, M.* *Chem. –Eur. J.* **2015**, *21*, 4534-4540.

反应条件优化



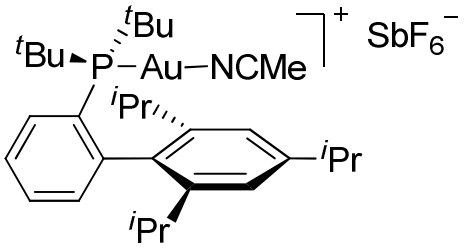
I-1a **I-2a**



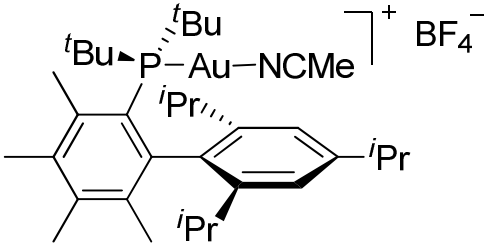
I-3a

X-ray

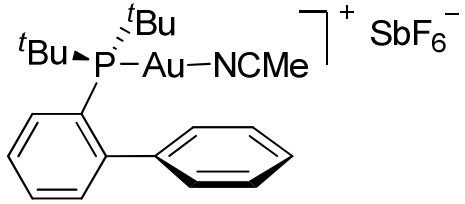
Entry[a]	Catalyst (5 mol%)	Time (h)	Solvent	Yield (%)[b]
1	$[Ph_3PAuCl]/AgSbF_6$	6	DCE	26
2	[IPrAuCl][c]/$AgNTf_2$	4	DCE	81
3	$[Au_2(CH_3CN)_2(dppm)][SbF_6]_2$	4	DCE	50[d]
4	**A**	18	DCE	48
5	**B**	23	DCE	38
6	**C**	5.5	DCE	74
7	$[Au(CH_3CN)(Ph_3P)][SbF_6]$	6	DCE	88
8	[(IPr)Au][OTf]	4	DCE	76
9	$[(IPr)Au(CH_3CN)][SbF_6]$	4	DCE	88
10	$[(IPr)Au(CH_3CN)][SbF_6]$	6	toluene	72
11	$[(IPr)Au(CH_3CN)][SbF_6]$	6	CH_3CN	77
12	$[(IPr)Au(CH_3CN)][SbF_6]$	4	1,4-dioxane	46
13[e]	$[(IPr)Au(CH_3CN)][SbF_6]$	4	DCE	85[f]
14[g]	$[(IPr)Au(CH_3CN)][SbF_6]$	4	DCE	84



Cat. **A**



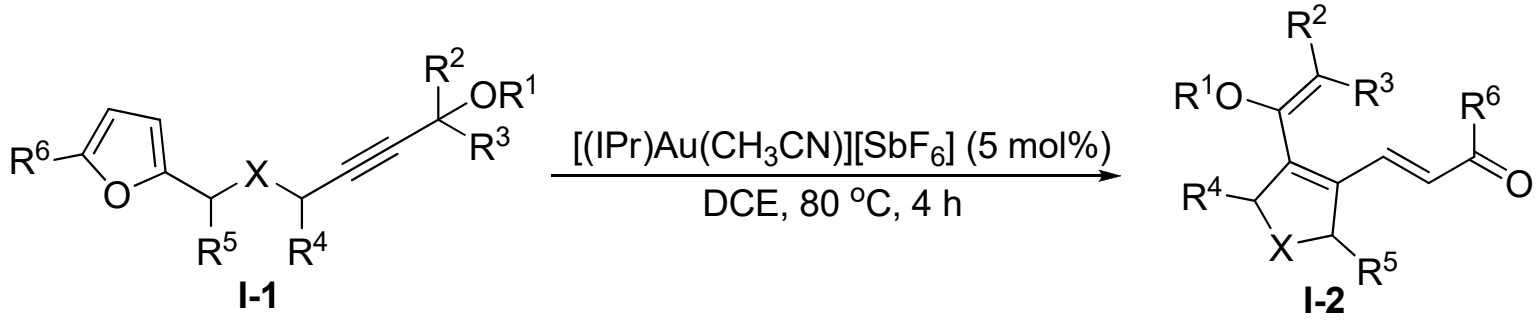
Cat. **B**



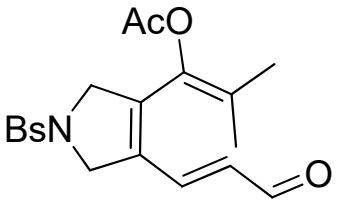
Cat. **C**

[a] Reaction conditions: **I-1a** (0.2 mmol); Au-cat. (5 mol%); dry solvent (1.0 mL). [b] Yield of isolated products. [c] IPr=[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]. [d] **I-3a** was obtained in 44% yield. [e] Reaction performed at room temperature. [f] Z/E=1.5/1, determined by ^1H NMR. [g] 10 mol% of catalyst. DCE = 1,2-dichloroethane.

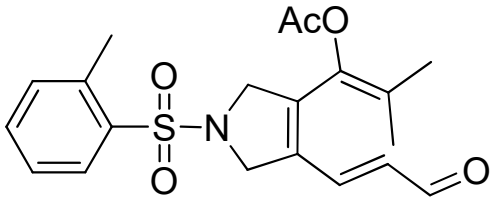
普适性考查



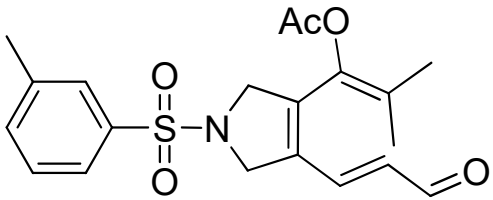
I-1 **I-2**



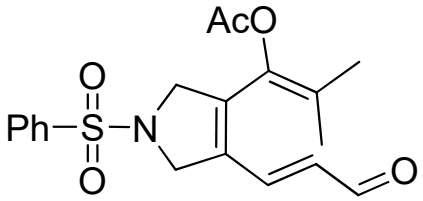
I-2b, 3 h, 93%



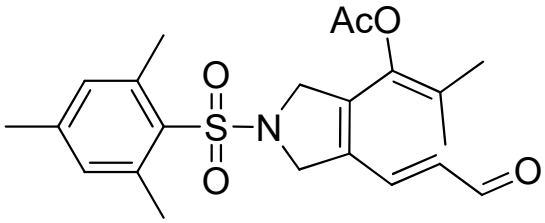
I-2c, 99%



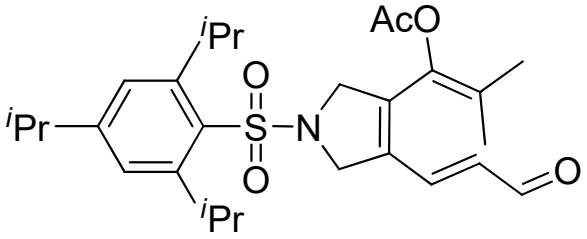
I-2d, 89%



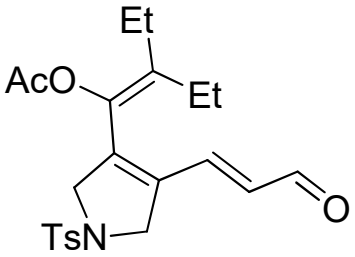
I-2e, 91%



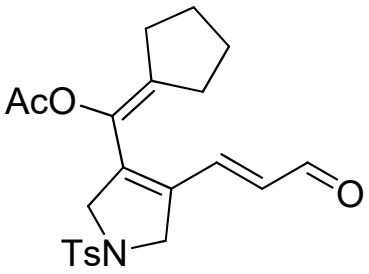
I-2f, 97%



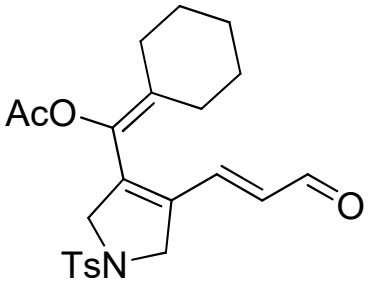
I-2g, 95%



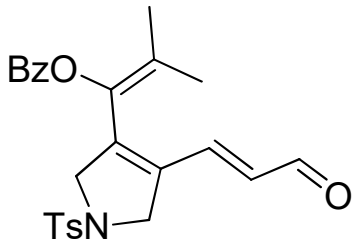
I-2h, 6 h, 43%



I-2i, 90%

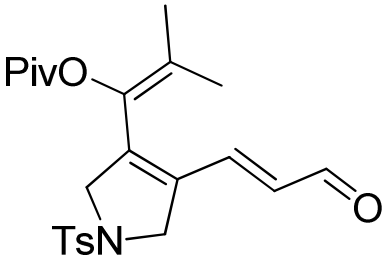


I-2j, 85%

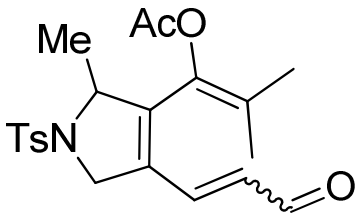


I-2k, 80%

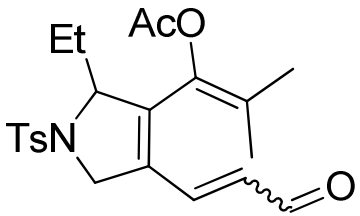
普适性考查



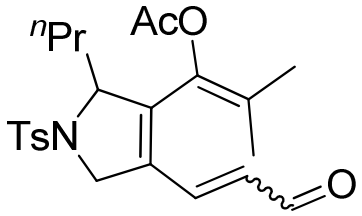
I-2l, 99%



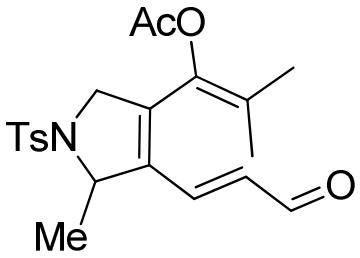
I-2m, 7 h,
99% (Z/E=1/6)



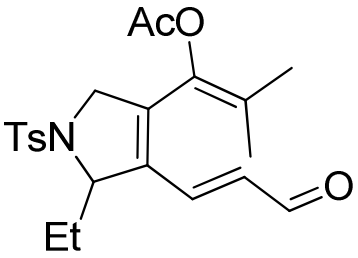
I-2n, 7 h,
90% (Z/E=1/6)



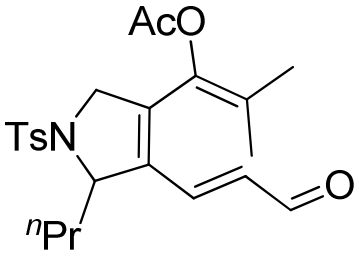
I-2o, 7 h,
85% (Z/E=1/9)



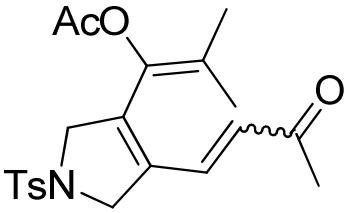
I-2p, 86%



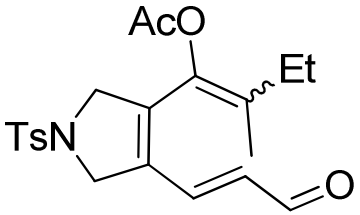
I-2q, 73%



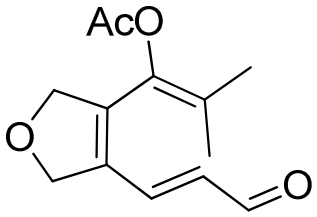
I-2r, 73%



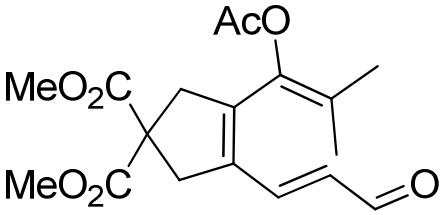
I-2s, 4.5 h,
92% (Z/E=1/10.5)



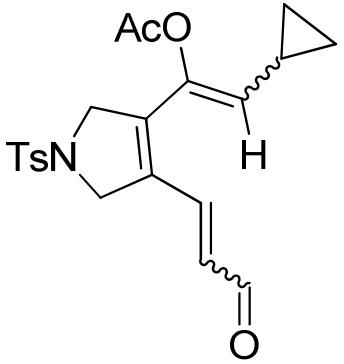
I-2t, 84%[b] (4:1)



I-2u, 4.5 h, 65%



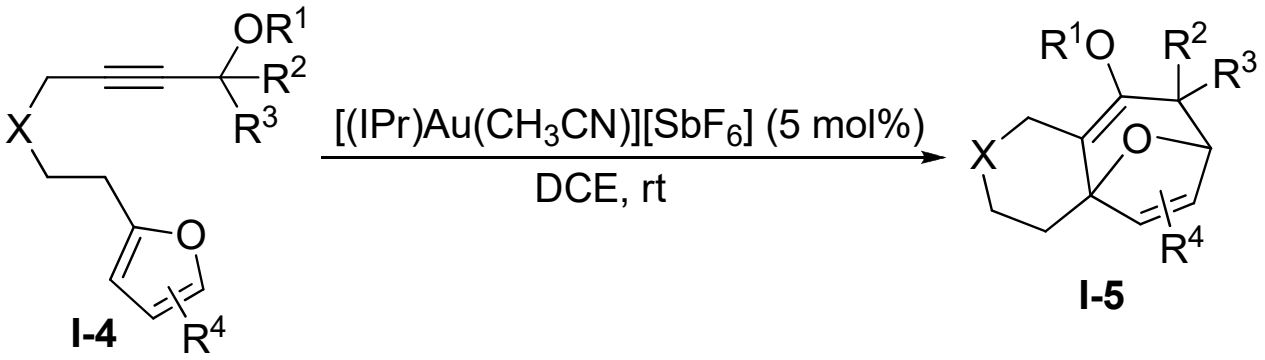
I-2v, 96%

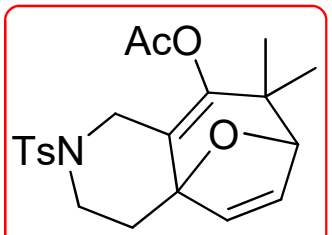


I-2w, 6.5 h, 60%[b] (1:0.72)

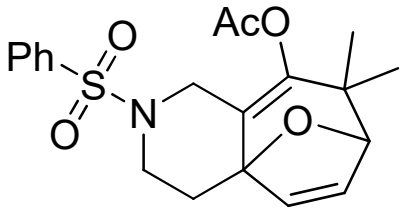
[a] Reaction conditions: **I-1** (0.2 mmol); [(IPr)Au(CH_3CN)][SbF_6] (5 mol%); anhydrous DCE (1.0 mL). Yields are those of the isolated products. [b] Mixture of Z/E isomers.

普适性考查

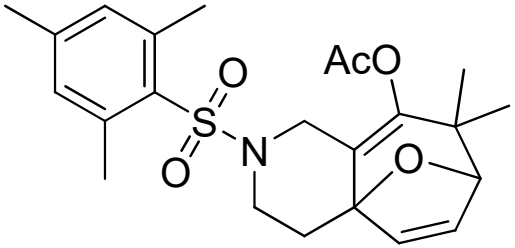




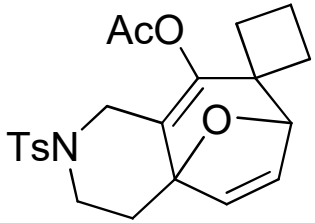
I-5a, 4 h, 69%



I-5b, 24 h, 68%

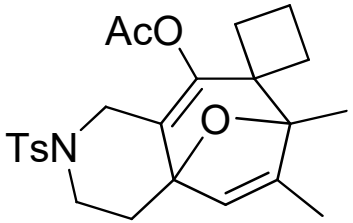


I-5c, 24 h, 54%

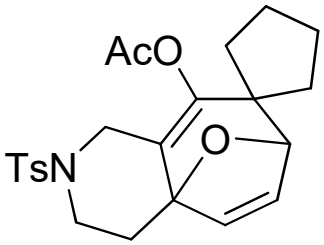


I-5d, 15 min, 94%

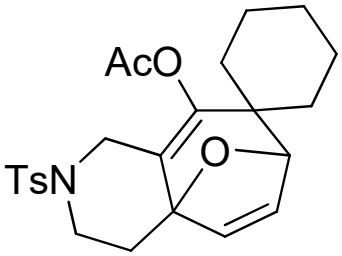
X-ray



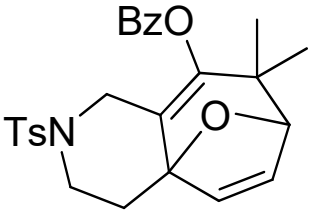
I-5e, 0.5 h, 65%



I-5f, 1 h, 43%[b]



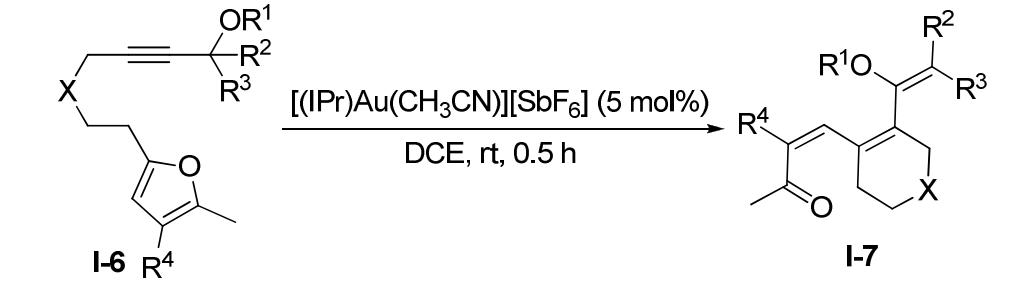
I-5g, 0.5 h, 38%



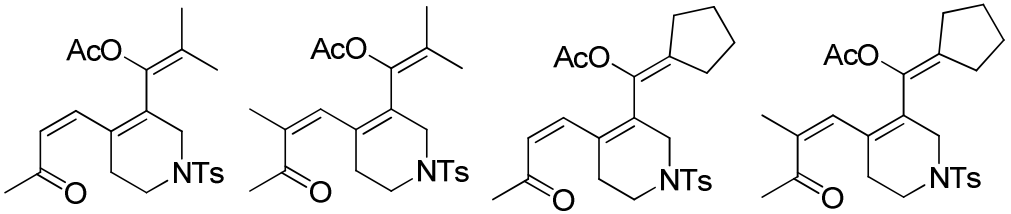
I-5h, 1 h, 42%

[a] Reaction conditions: **I-4** (0.1-0.2 mmol); [(IPr)Au(CH_3CN)][SbF_6] (5 mol%); anhydrous DCE (1.0 mL). Yields are those of the isolated products. [b] Reaction performed at 80 °C.

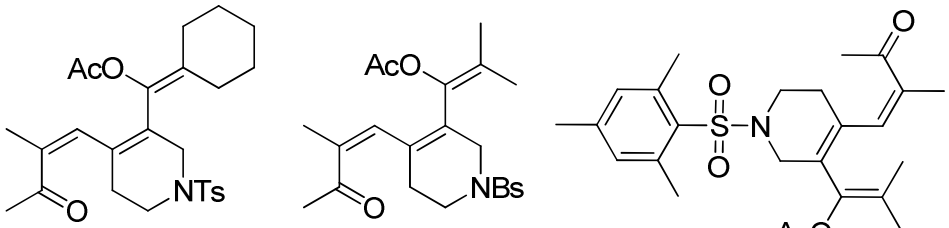
普适性考查



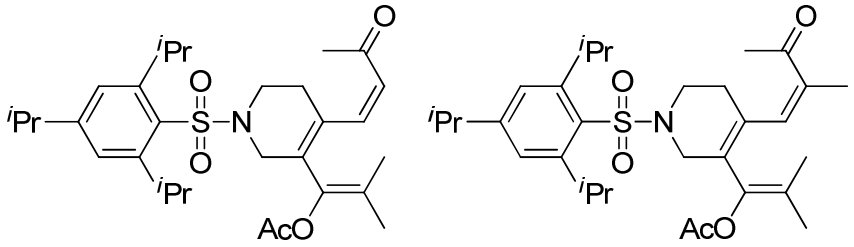
I-6 **I-7**



I-7a, 68% **I-7b**, 80% **I-7c**, 54% **I-7d**, 72%[b]



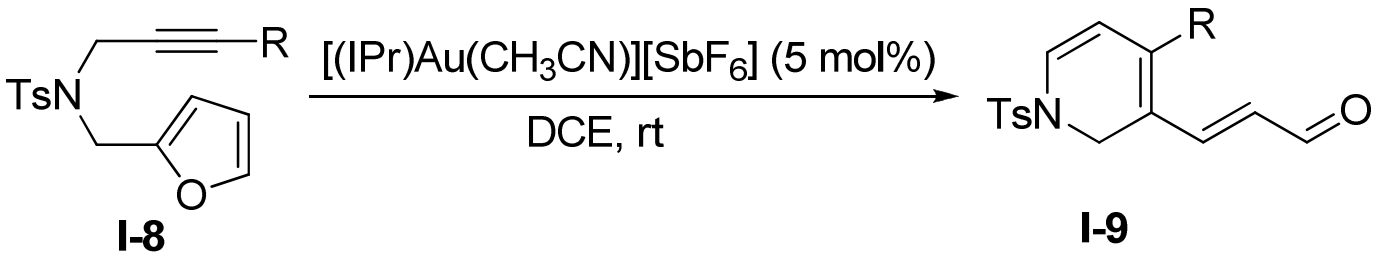
I-7e, 67%[c] **I-7f**, 86% **I-7g**, 57%



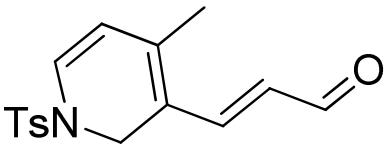
I-7h, 40%[b] **I-7i**, 72%

[a] Reaction conditions: **I-6** (0.1-0.2 mmol); [(IPr)Au(CH$_3$CN)][SbF$_6$] (5 mol%); anhydrous DCE (1.0 mL). Yields are those of the isolated products. [b] Reaction time: 1 h. [c] Reaction time: 2 h.

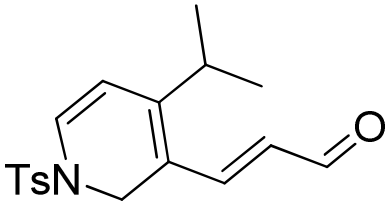
普适性考查



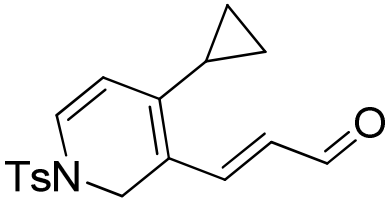
I-8 **I-9**



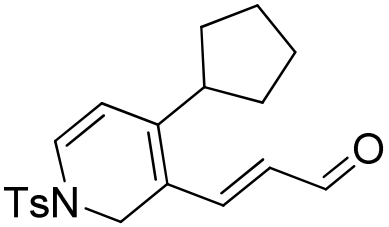
I-9a, 4 h, 62%[b]



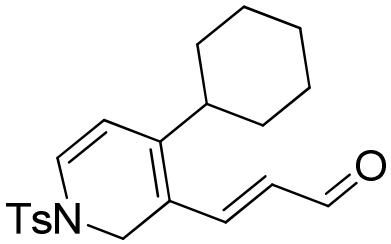
I-9b, 4 h, 52%



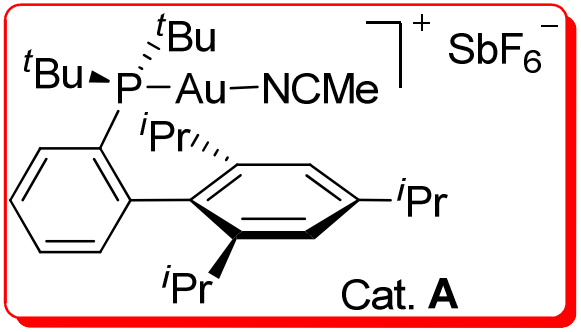
I-9c, 15 min, 55%



I-9d, 16 h, 54%[c]

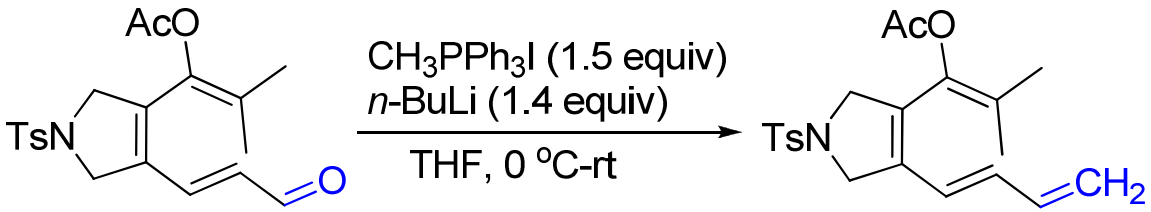


I-9e, 20 h, 68%[c]

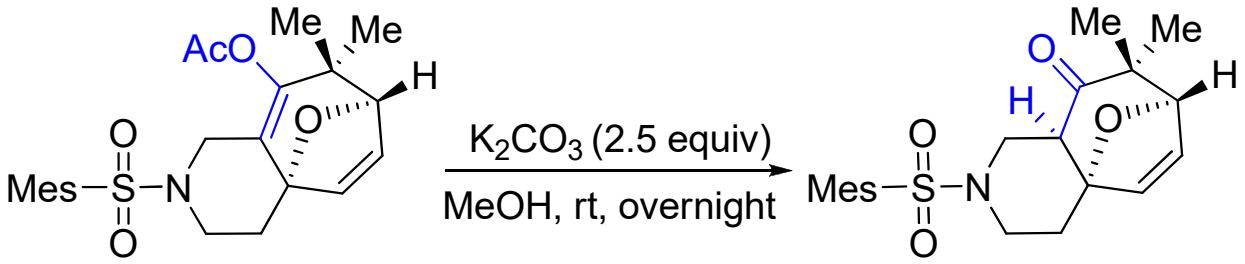


[a] Reaction conditions: **I-8** (0.1 mmol); [(IPr)Au(CH$_3$CN)][SbF$_6$] (5 mol%); anhydrous DCE (1.0 mL). Yields are those of the isolated products. [b] Reaction performed at 80 ^{o}C. [c] Cat. **A** was used.

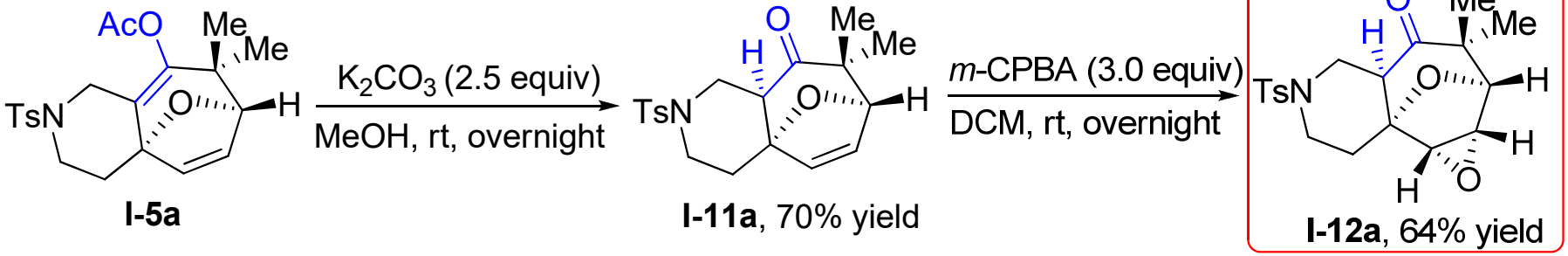
产物转化



I-2a **I-10a**, 54% yield



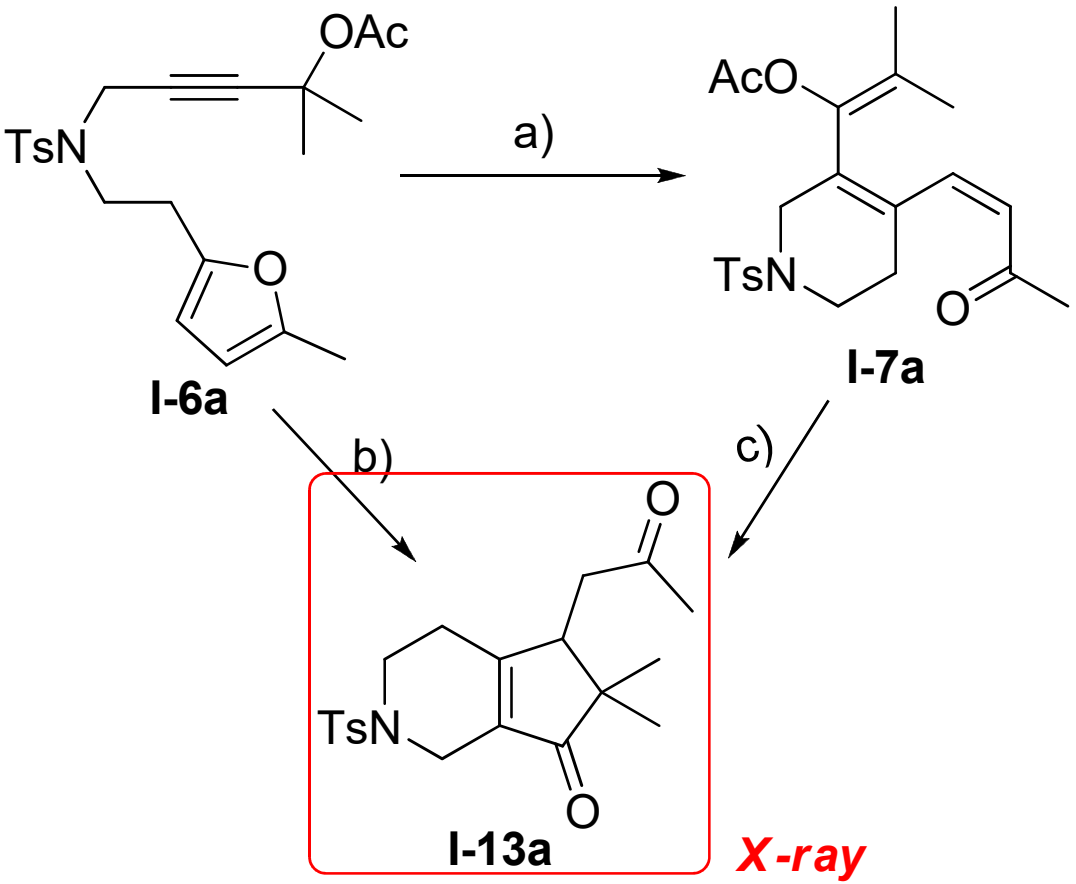
I-5c **I-11c**, 72% yield



I-5a **I-11a**, 70% yield **I-12a**, 64% yield

X-ray

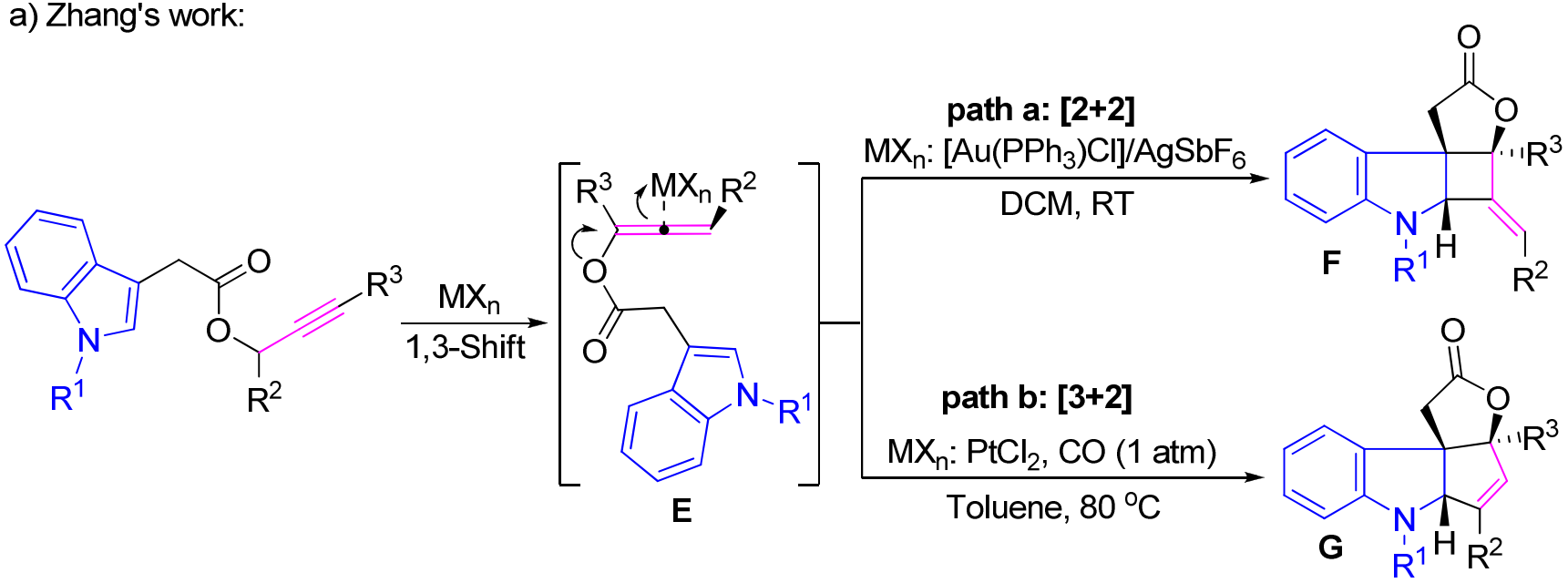
产物转化



a) $[(IPr)Au(CH_3CN)][SbF_6]$ (5 mol%), DCE, rt, 0.5 h, 68%;
b) $[(IPr)Au(CH_3CN)][SbF_6]$ (5 mol%), DCE, rt, 0.5 h;
then HOTf (1.0 equiv), rt, 2 h, 80 %;
c) HOTf (1.0 equiv), DCM, rt, 2 h, 91%.

金催化炔丙醇羧酸酯和吲哚分子内的环化反应

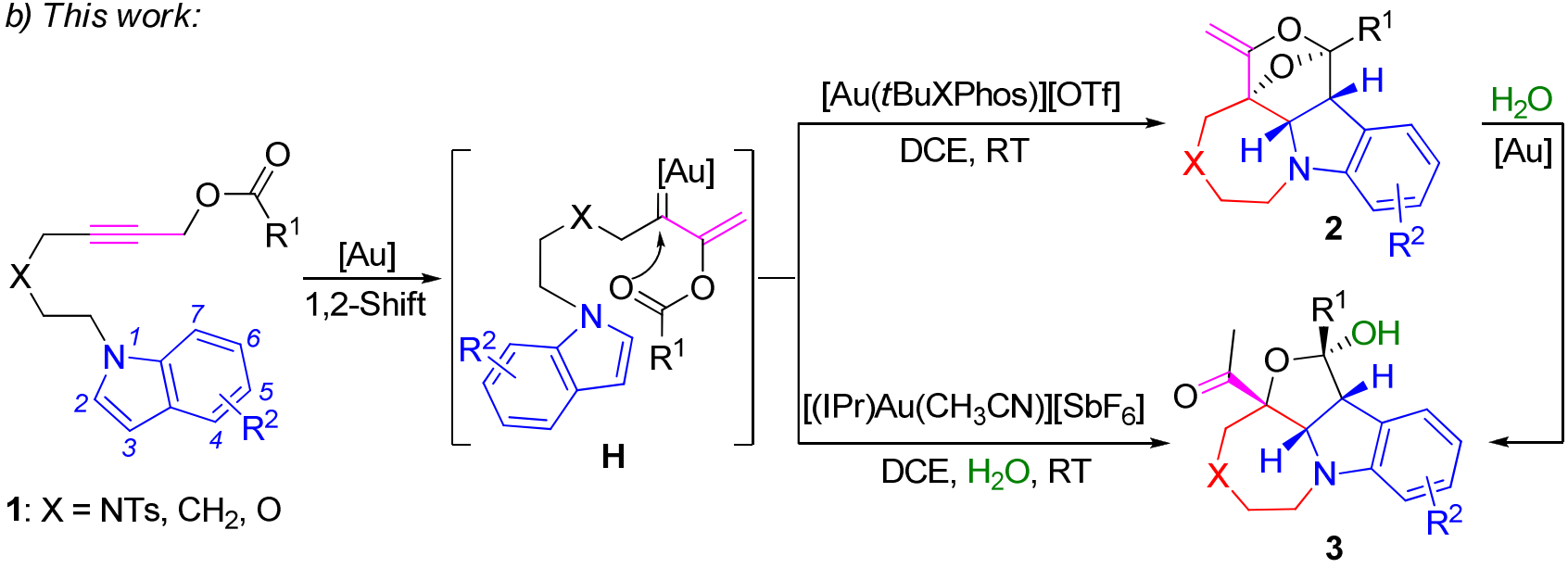
a) Zhang's work:



(a) Zhang, L. *J. Am. Chem. Soc.* **2005**, *127*, 16804-16805. (b) Zhang, G.; Catalano, V. J.; Zhang, L. *J. Am. Chem. Soc.* **2007**, *129*, 11358-11359.

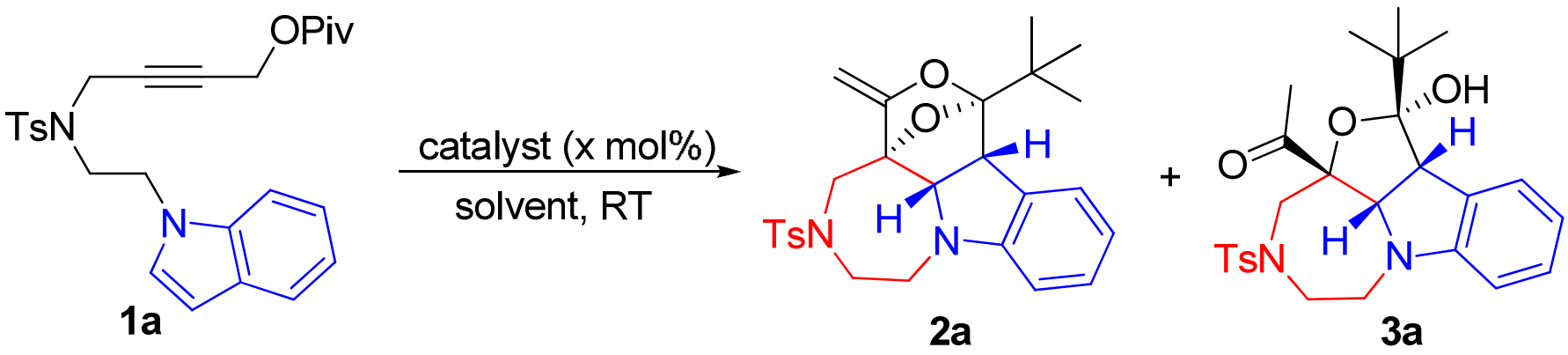
金催化炔丙醇羧酸酯和吲哚分子内的环化反应

b) This work:



Yang, J.-M.; Li, P.-H.; Wei, Y.; Tang, X.-Y.*; Shi, M.* *Chem. Commun.* **2016**, *52*, 346-349.

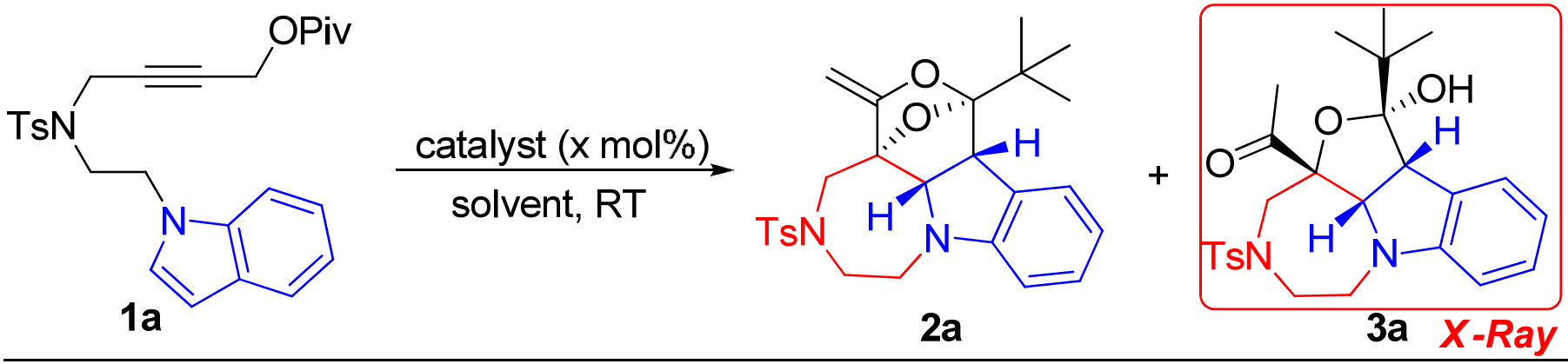
反应条件优化



entry[a]	catalyst (x mol%)	solvent	H_2O (y eq.)	time	yield (%)[b]	
					2a	**3a**
1	***[Au(tBuXPhos)][OTf] (5)***	***DCE***	-	***2 h***	***95***	***0***
2	[Au(Me_4*t*BuXPhos)(CH_3CN)][SbF_6] (5)	DCE	-	6 h	0	0
3	[(IPr)Au(CH_3CN)][SbF_6] (5)	DCE	-	2 h	0	70
4	[Au(*n*BuPAd_2)(CH_3CN)][SbF_6] (5)	DCE	-	4 h	0	89
5	[$(ArO)_3$PAu][NTf_2] (5)	DCE	-	4 h	0	70
6	[(IPr)Au(CH_3CN)][SbF_6] (5)	DCE	1.0	2 h	0	85
7	[Ph_3PAuCl] (5)/$AgNTf_2$ (5)	DCE	1.0	1 h	0	74
8	***[(IPr)Au(CH_3CN)][SbF_6] (2.5)***	***DCE***	***1.0***	***5 h***	***0***	***86***

[a] All reactions were carried out using **1a** (0.1 mmol) in the presence of catalyst (x mol%) in DCE (1.0 mL) unless otherwise specified. [b] Isolated yields. Ar = 2,4-di-tert-butylphenyl. DCE = 1,2-dichloroethane.

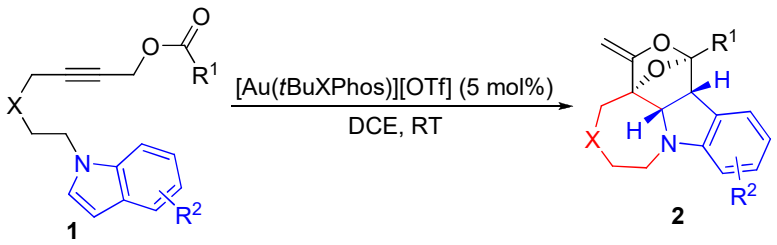
反应条件优化

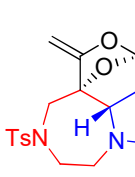


entry[a]	catalyst (x mol%)	solvent	H_2O (y eq.)	time	yield (%)[b]	
					2a	**3a**
1	***[Au(tBuXPhos)][OTf] (5)***	***DCE***	-	***2 h***	***95***	***0***
2	[Au(Me_4*t*BuXPhos)(CH_3CN)][SbF_6] (5)	DCE	-	6 h	0	0
3	[(IPr)Au(CH_3CN)][SbF_6] (5)	DCE	-	2 h	0	70
4	[Au(*n*BuPAd_2)(CH_3CN)][SbF_6] (5)	DCE	-	4 h	0	89
5	[$(ArO)_3$PAu][NTf_2] (5)	DCE	-	4 h	0	70
6	[(IPr)Au(CH_3CN)][SbF_6] (5)	DCE	1.0	2 h	0	85
7	[Ph_3PAuCl] (5)/$AgNTf_2$ (5)	DCE	1.0	1 h	0	74
8	***[(IPr)Au(CH_3CN)][SbF_6] (2.5)***	***DCE***	***1.0***	***5 h***	***0***	***86***

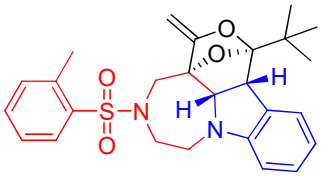
[a] All reactions were carried out using **1a** (0.1 mmol) in the presence of catalyst (x mol%) in DCE (1.0 mL) unless otherwise specified. [b] Isolated yields. Ar = 2,4-di-tert-butylphenyl. DCE = 1,2-dichloroethane.

普适性考查

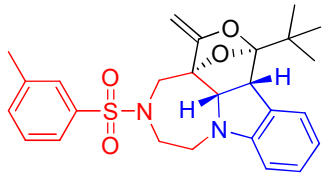




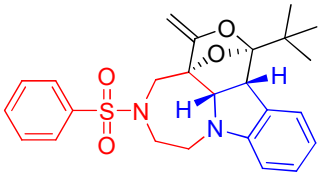
2a, 2 h, 95% yield



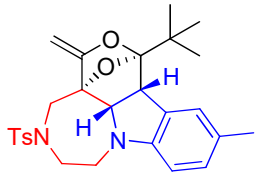
2b, 4 h, 80% yield



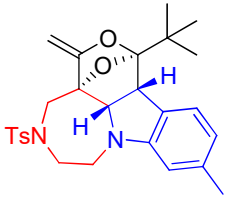
2c, 3.5 h, 96% yield



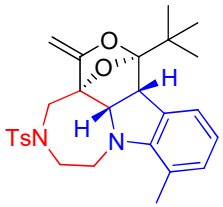
2d, 3.5 h, 85% yield



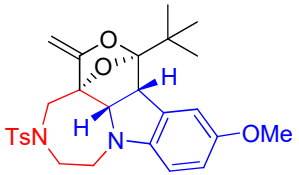
2h,4 h, 88% yield



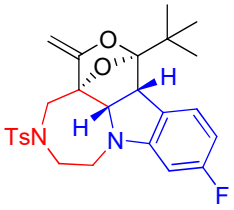
2i, 4 h, 83% yield



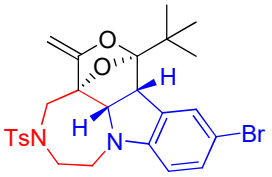
2j, 3 h, 73% yield



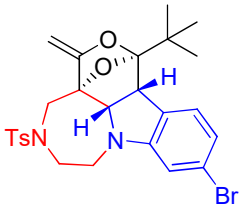
2k, 5 h, 78% yield



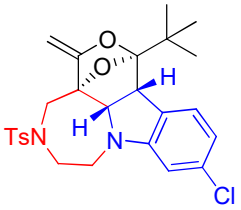
2l, 4 h, 76% yield



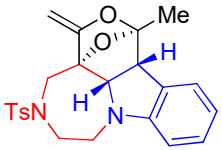
2m, 4 h, 72% yield



2n, 4 h, 70% yield



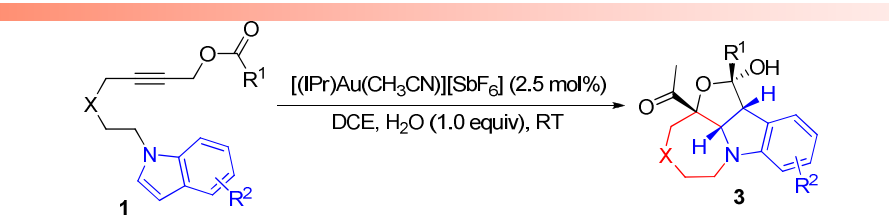
2o, 4 h, 74% yield

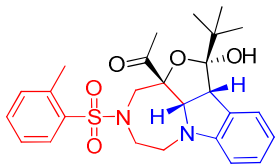


2r, 2 h, 79% yield[b]

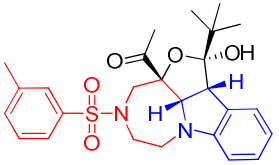
[a] Reaction conditions: **1** (0.1 mmol); [Au(*t*BuXPhos)][OTf] (5 mol%); anhydrous DCE (1.0 mL). Yields are those of the isolated yields. [b] 2.5 mol% of [(IPr)Au(CH_3CN)][SbF_6] was used as the catalyst.

普适性考查

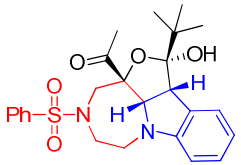




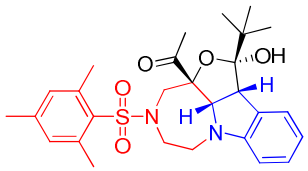
3b, 4 h, 82%



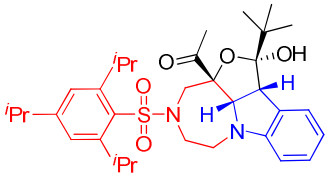
3c, 3 h, 87%



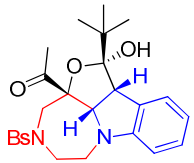
3d, 6 h, 71%



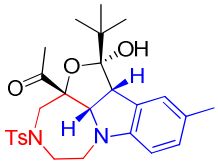
3e, 4 h, 89%



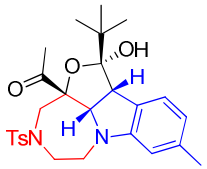
3f, 5 h, 76%



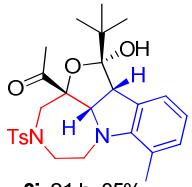
3g, 5 h, 86%



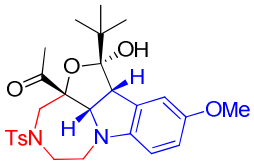
3h, 4 h, 66%



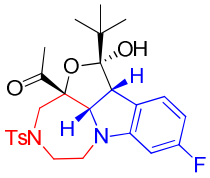
3i, 6 h, 77%



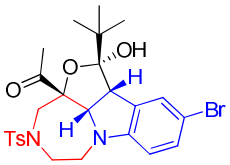
3j, 21 h, 85%



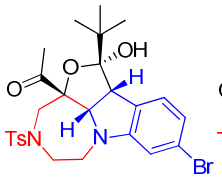
3k, 6 h, 79%



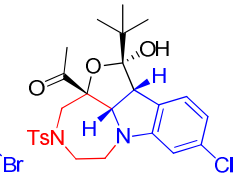
3l, 4 h, 77%



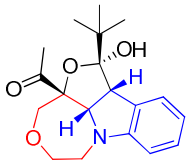
3m, 4 h, 72%



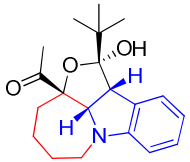
3n, 4 h, 64%



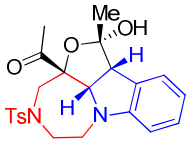
3o, 5 h, 83%



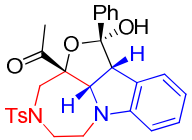
3p, 4 h, 86%



3q, 16 h, 46%



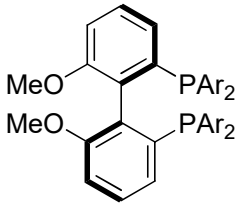
3r, 16 h, 94%



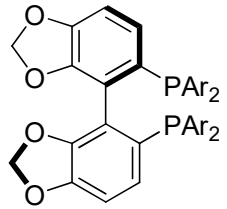
3s, 16 h, 70%

Reaction conditions: **1** (0.1 mmol); [(IPr)Au(CH$_3$CN)][SbF$_6$] (2.5 mol%); H$_2$O (1.0 equiv); anhydrous DCE (1.0 mL). Yields are those of the isolated yields. DCE = 1,2-dichloroethane.

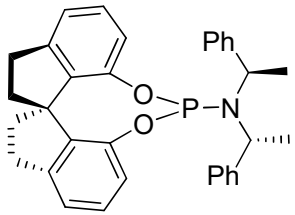
不对称优化条件使用的配体



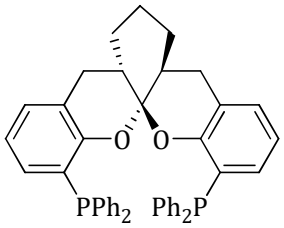
Ar = 3,5-$(tBu)_2$-4-$MeOC_6H_2$;
(*R*)-MeO-DTBM-BIPHEP (**L1**)



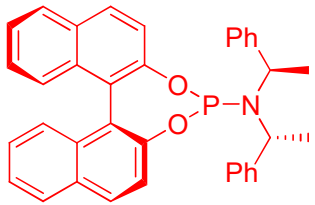
Ar = 3,5-$(Me)_2C_6H_3$;
(*R*)-DM-SEGPHOS (**L2**)



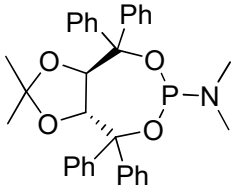
L3



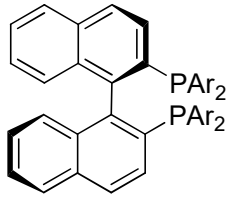
L4



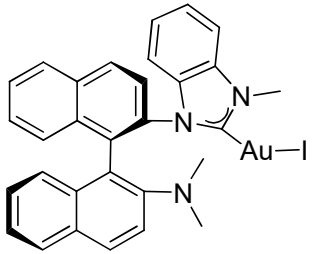
L5



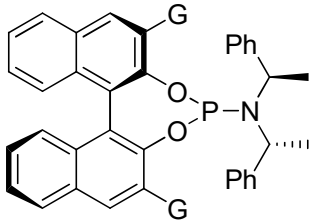
L6

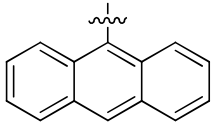


Ar = 3,5-$(Me)_2C_6H_3$;
(*R*)-Xylyl-BINAP (**L7**)

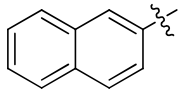


(a*R*)-**8**

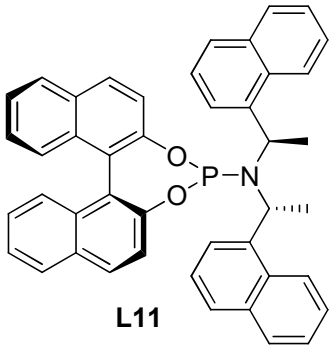


G = 

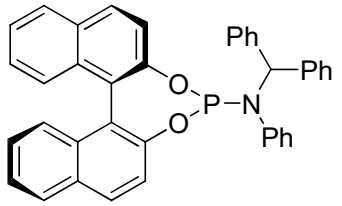
L9

G = 

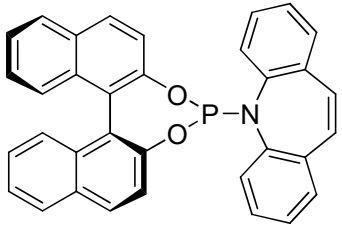
L10



L11

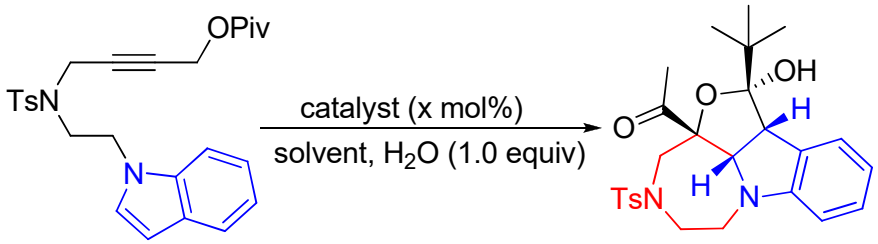


L12



L13

反应条件优化

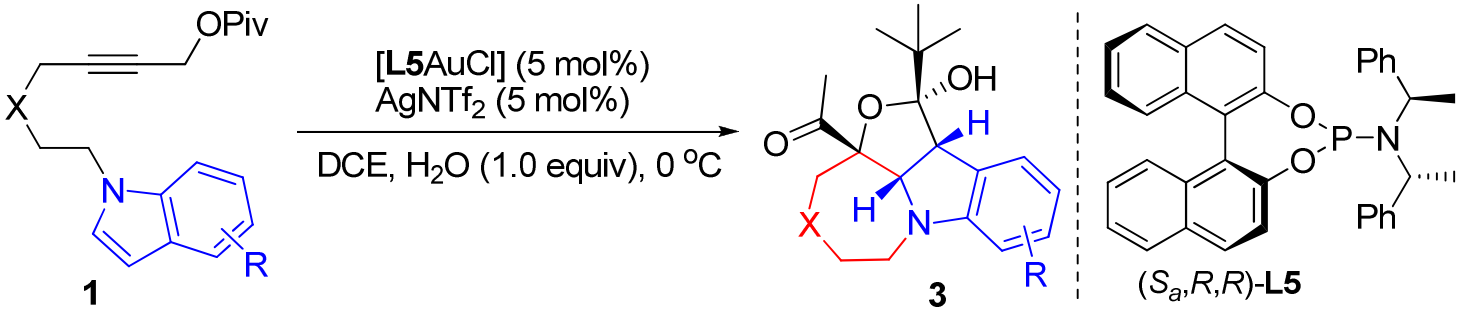


1a **3a**

entry[a]	catalyst (x mol%)	solvent	T (°C)	time	yield (%)[b]	ee (%)[c]
1	[**L1**AuCl] (5)/$AgSbF_6$ (5)	DCE	RT	1 h	74	0
2	[**L2**Au_2Cl_2] (5)/AgOPNB (5)	DCE	RT	2 d	trace	-[d]
3	[**L2**Au_2Cl_2] (5)/$AgSbF_6$ (5)	DCE	RT	2 h	72	0
4	[**L3**Au(CH_3CN)][SbF_6] (5)	DCE	RT	3 h	85	40
5	[**L4**$Au_2(CH_3CN)_2$][$(SbF_6)_2$] (5)	DCE	RT	3 d	67	15
6	[**L5**Au(CH_3CN)][SbF_6] (5)	DCE	RT	1 h	86	71
7	[**L5**AuCl] (5)/$AgNTf_2$ (5)	DCE	RT	3.5 h	79	71
8	[**L5**AuCl] (5)/$AgNTf_2$ (5)	Toluene	RT	4 h	23	47
9	[**L5**Au(CH_3CN)][SbF_6] (5)	DCM	RT	1 h	87	67
10	[**L5**Au(CH_3CN)][SbF_6] (5)	$CHCl_3$	RT	5 h	85	50
11	[**L5**AuCl] (5)/$AgBF_4$ (5)	DCE	RT	45 min	65	31
12	[**L5**AuCl] (5)/$AgSbF_6$ (5)	DCE	RT	4 h	77	14
13	[**L5**AuCl] (5)/AgOTf (5)	DCE	RT	4 h	trace	-[d]
14	[**L5**AuCl] (5)/AgOONB (5)	DCE	RT	4 d	trace	-[d]
15	[**L6**Au(CH_3CN)][SbF_6] (5)	DCE	RT	6 h	55	-7
16	[**L7**Au_2Cl_2] (5)/$AgSbF_6$ (10)	DCE	RT	5 h	67	2
17	(a*R*)-**8** (5)/$AgSbF_6$ (5)	DCE	RT	30 min	79	0
18	[**L9**AuCl] (5)/$AgNTf_2$ (5)	DCE	RT	4 h	78	-17
19	[**L10**AuCl] (5)/$AgNTf_2$ (5)	DCE	RT	22 h	77	43
20	[**L11**AuCl] (5)/$AgNTf_2$ (5)	DCE	RT	2 h	84	52
21	[**L12**AuCl] (5)/$AgNTf_2$ (5)	DCE	RT	18 h	69	-46
22	[**L13**AuCl] (5)/$AgNTf_2$ (5)	DCE	RT	1.5 h	72	27
23	**[L5AuCl] (5)/$AgNTf_2$ (5)**	**DCE**	**0**	**16 h**	**72**	**77**

[a] All reactions were carried out using **1a** (0.1 mmol) in the presence of catalyst (x mol%) in various solvents (1.0 mL) unless otherwise specified. [b] Yield of isolated product. [c] Determined by HPLC on a chiral stationary phase. [d] Not determined.
OPNB = *p*-nitrobenzoate, OONB = *o*-nitrobenzoate

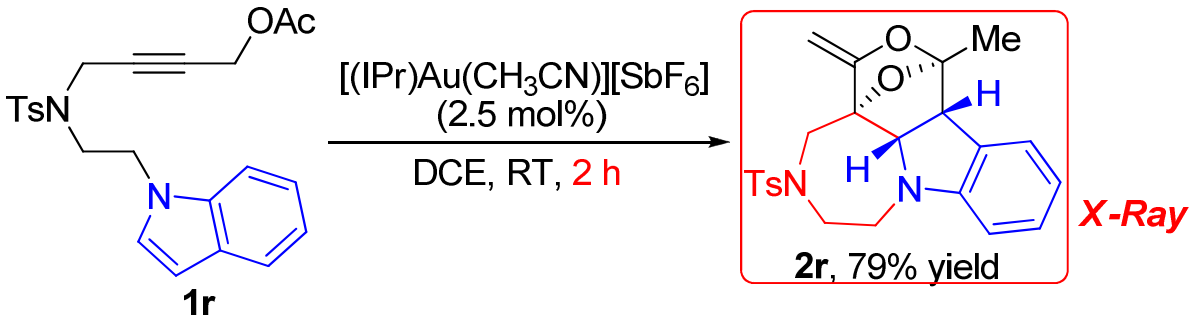
普适性考查

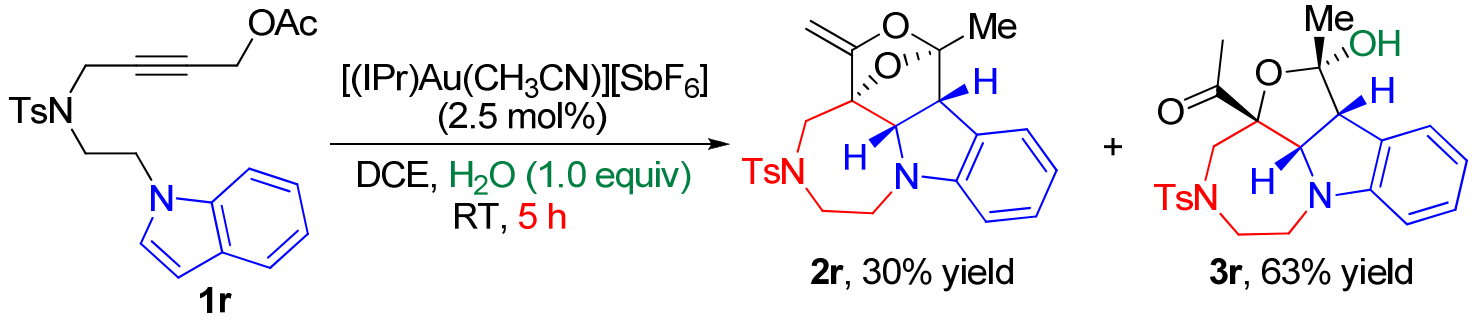


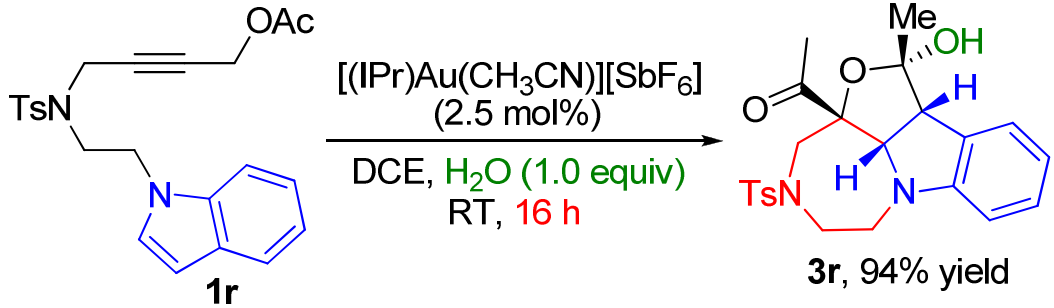
entry[a]	1	X	R	time [days]	3	yield [%][b]	ee [%][c]
1	**1b**	2-$MeC_6H_4SO_2N$	H	3	**3b**	30	74
2	**1c**	3-$MeC_6H_4SO_2N$	H	2	**3c**	60	80
3	**1d**	$PhSO_2N$	H	2	**3d**	43	90
4	**1e**	$MesSO_2N$	H	2	**3e**	51	83
5	**1f**	2,4,6-$^i Pr_3C_6H_2SO_2N$	H	2	**3f**	40	91
6	**1h**	TsN	5-Me	2	**3h**	50	74
7	**1i**	TsN	6-Me	0.5	**3i**	46	71
8	**1j**	TsN	7-Me	2	**3j**	88	81
9	**1k**	TsN	5-OMe	2	**3k**	62	82
10	**1l**	TsN	6-F	0.5	**3l**	72	82
11[d]	**1m**	TsN	5-Br	2	**3m**	66	62
12	**1n**	TsN	6-Br	1	**3n**	85	82
13	**1o**	TsN	6-Cl	3		_[e]	_[e]
14	**1p**	O	H	3	**3p**	30	72
15	**1q**	CH_2	H	3	**3q**	25	60

[a] Reaction conditions: **1** (0.1 mmol), [**L5**AuCl] (5 mol%), $AgNTf_2$ (5 mol%), H_2O (1.0 equiv), anhydrous DCE (1.0 mL). [b] Yields are those of the isolated yields. [c] Determined by HPLC on a chiral stationary phase. [d] Reaction performed at room temperature. [e] Complex mixtures, not determined. DCE=1,2-dichloroethane.

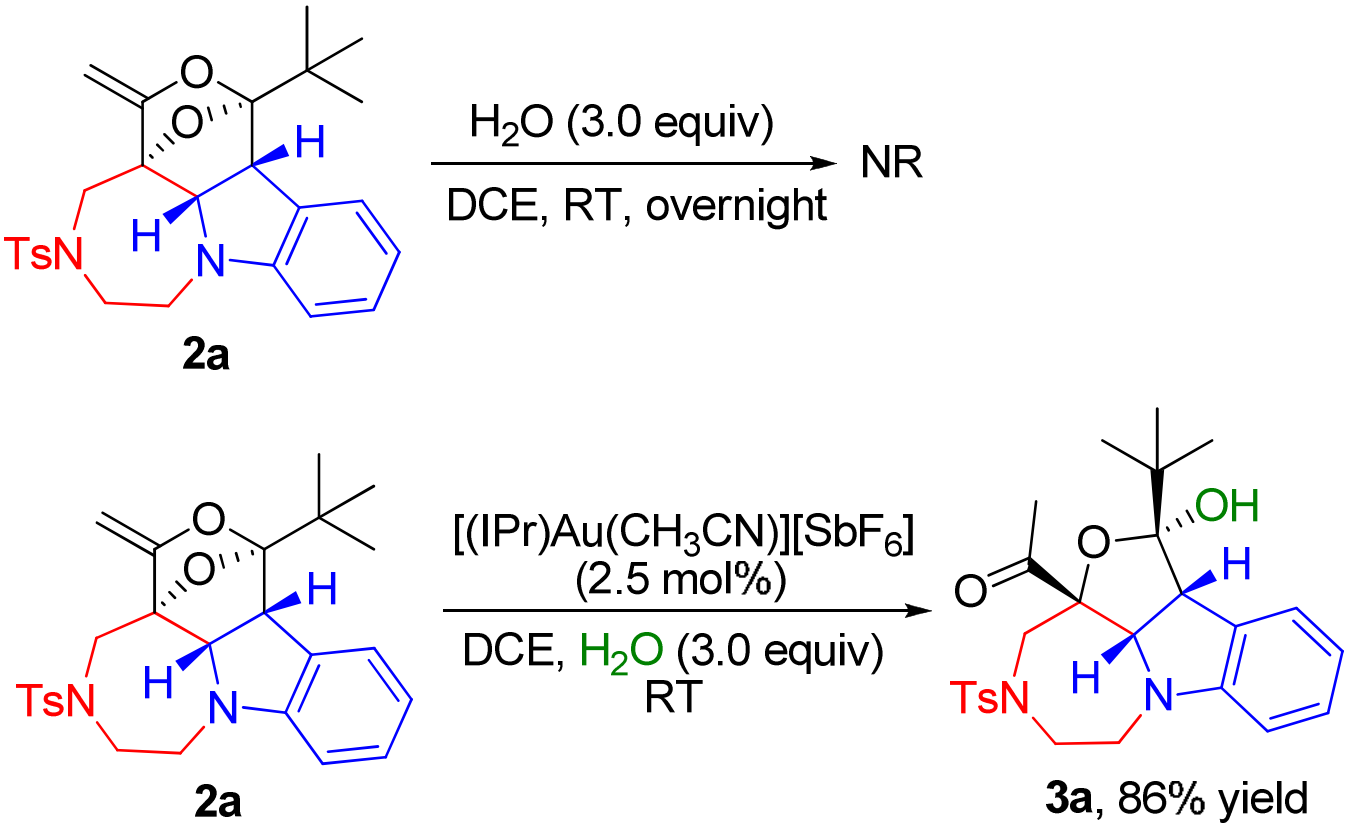
控制实验


OAc
TsN
N
1r
[(IPr)Au(CH3CN)][SbF6]
(2.5 mol%)
DCE, RT, 2 h
O
Me
O
H
TsN
H
N
2r, 79% yield
X-Ray

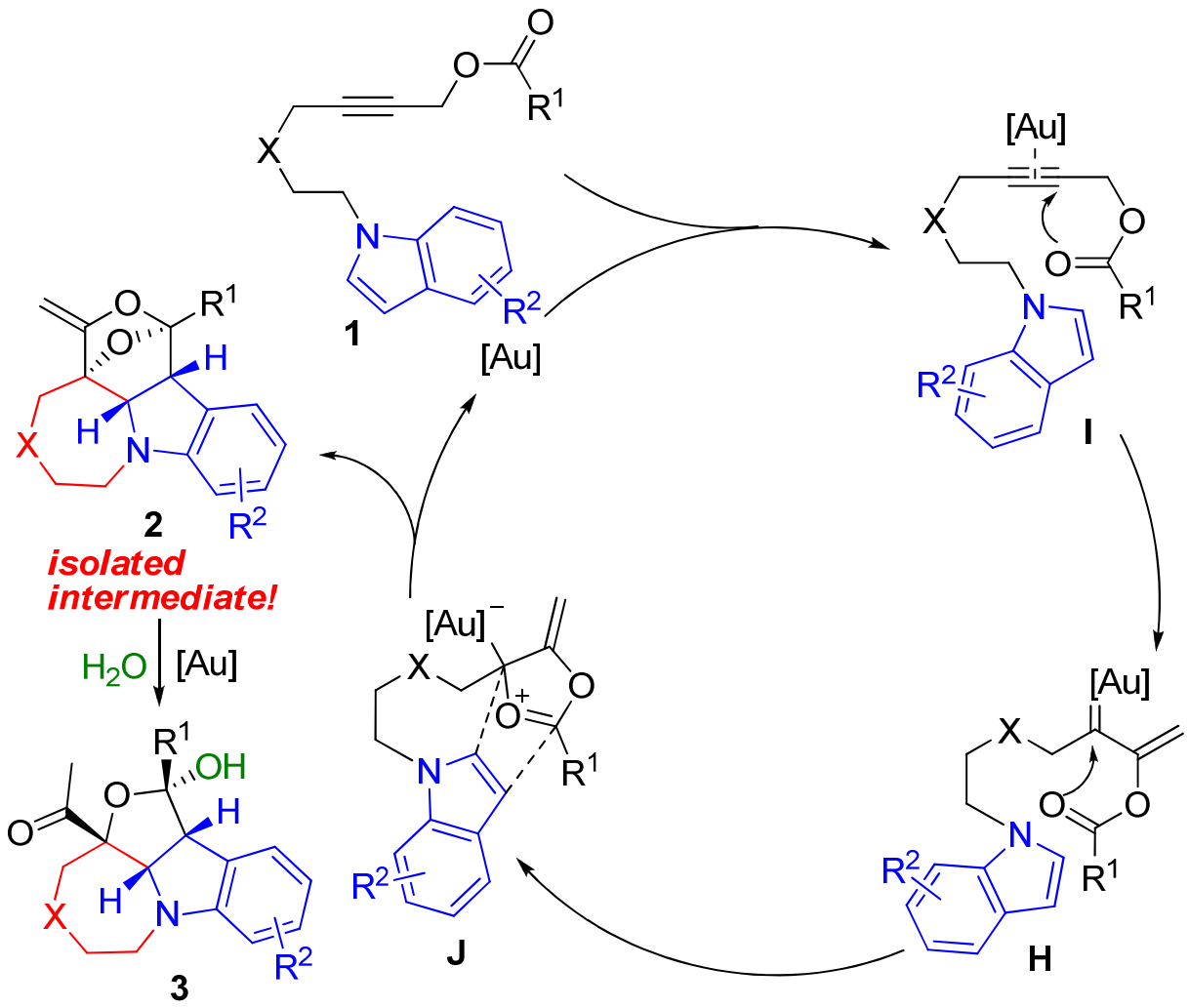

OAc
TsN
N
1r
[(IPr)Au(CH3CN)][SbF6]
(2.5 mol%)
DCE, H2O (1.0 equiv)
RT, 5 h
O
Me
O
H
TsN
H
N
2r, 30% yield
+
Me
OH
O
O
H
TsN
H
N
3r, 63% yield


OAc
TsN
N
1r
[(IPr)Au(CH3CN)][SbF6]
(2.5 mol%)
DCE, H2O (1.0 equiv)
RT, 16 h
Me
OH
O
O
H
TsN
H
N
3r, 94% yield

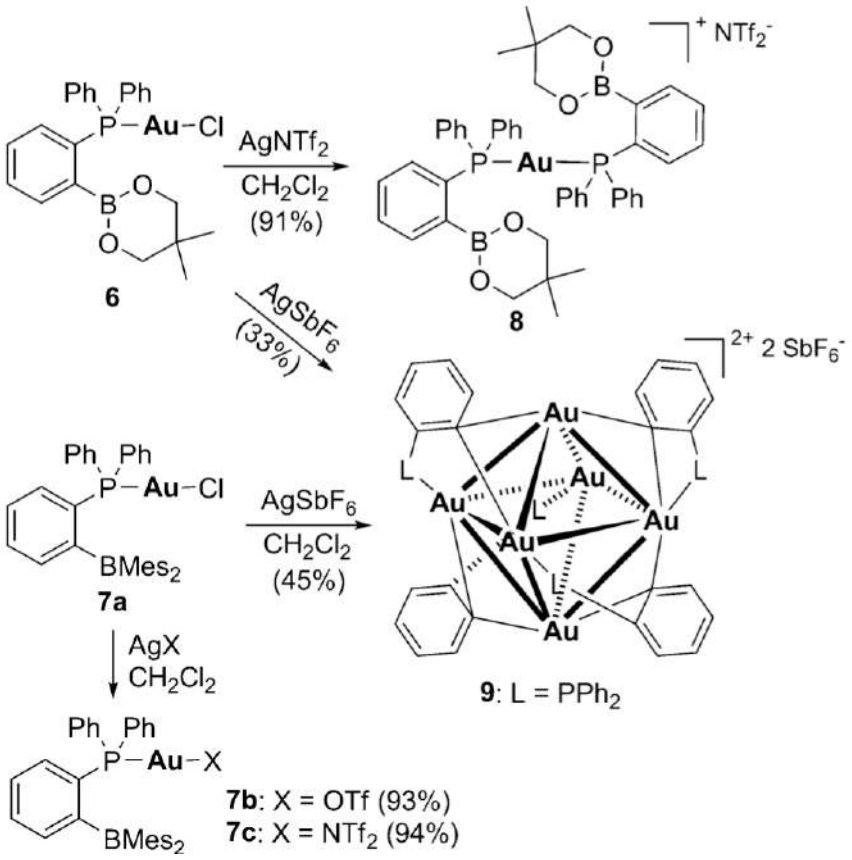
控制实验

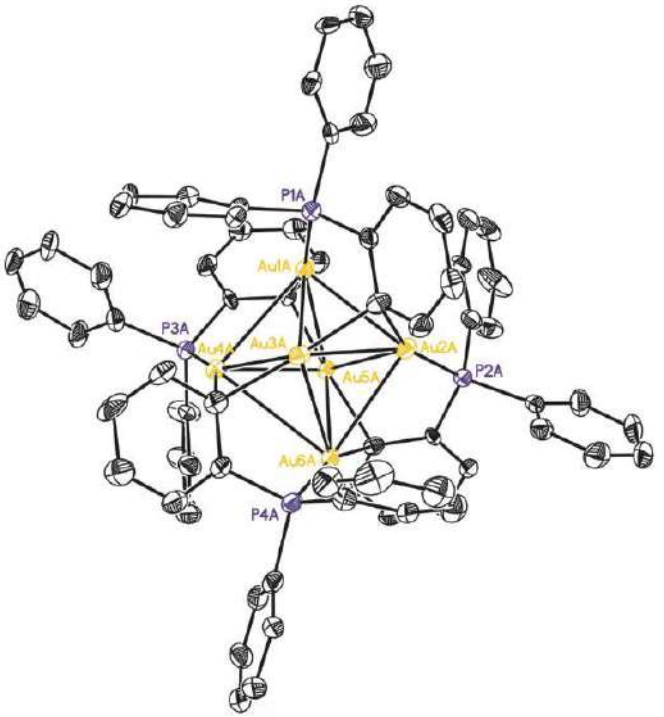

O
O
H
H
TsN
N
2a
H2O (3.0 equiv)
DCE, RT, overnight
NR
[(IPr)Au(CH3CN)][SbF6]
(2.5 mol%)
DCE, H2O (3.0 equiv)
RT
OH
3a, 86% yield

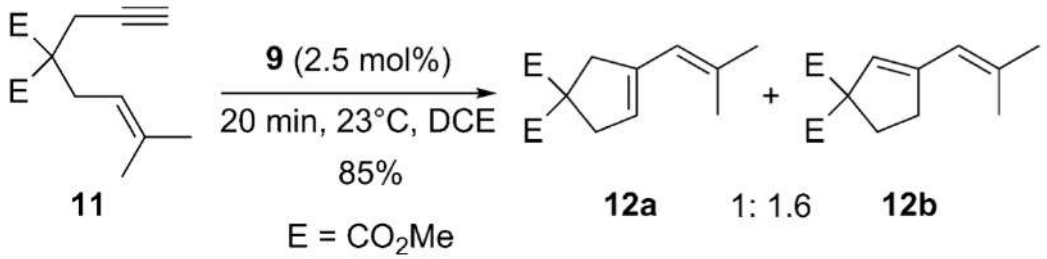
反应机理



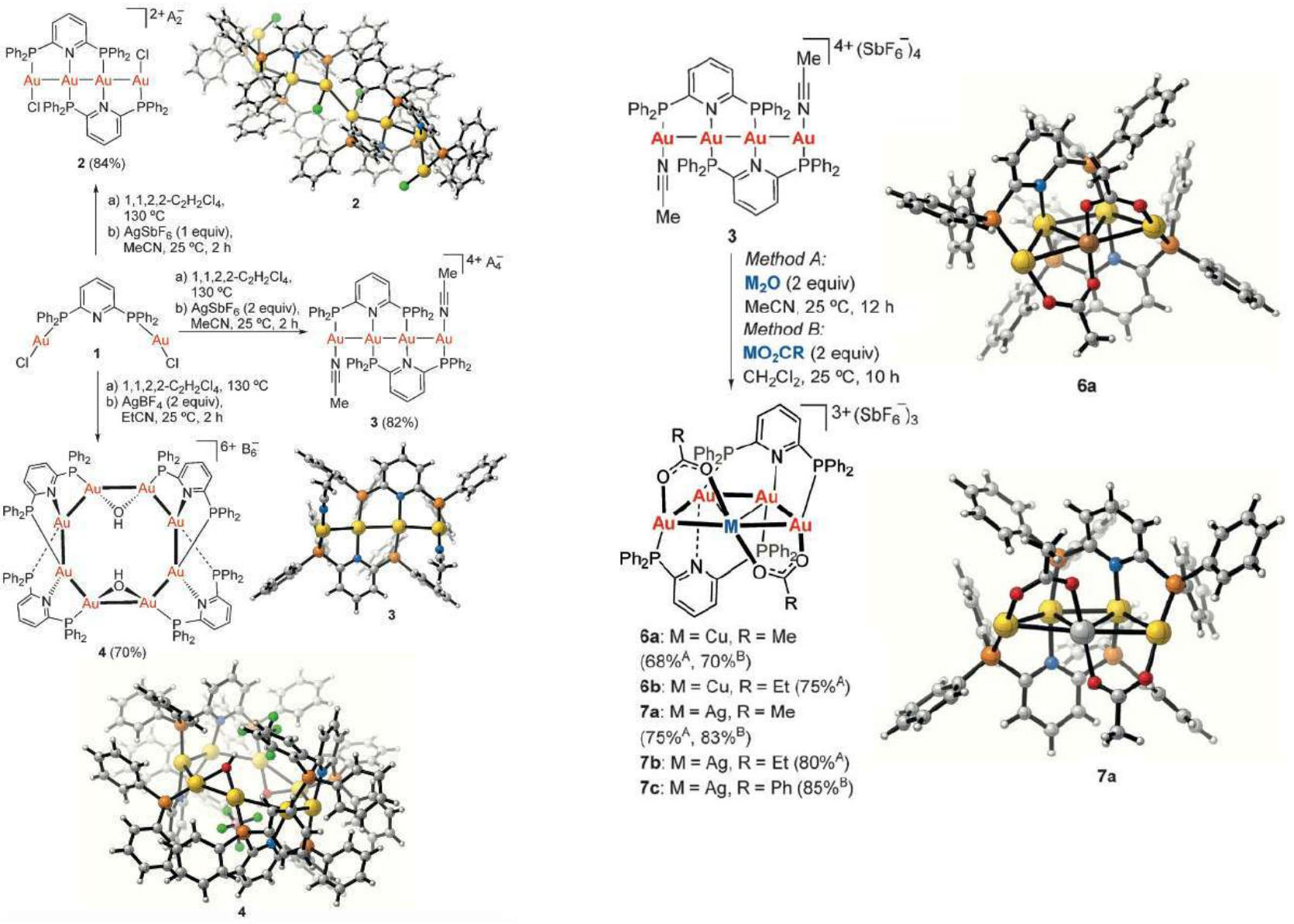
三、多金簇合物的合成、表征以及催化活性研究



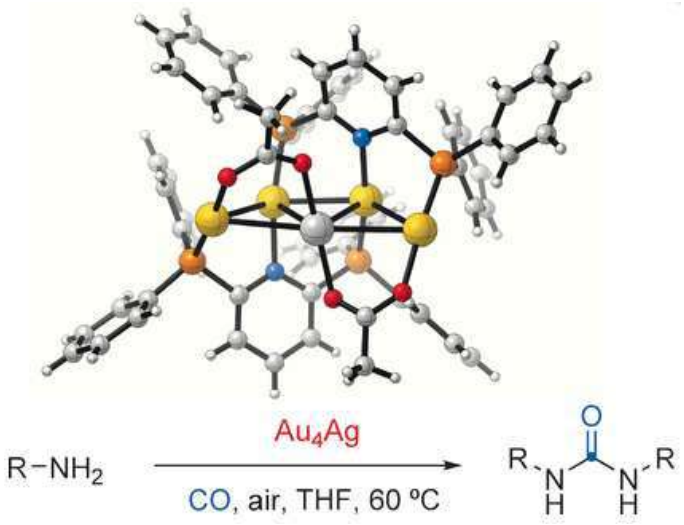




Smirnova, E. S.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2013**, *52*, 9023.



Smirnova, E. S.; Molina, J. M. M.; Johnson, A.; Bandeira, N. A. G.; Bo, C., Echavarren, A. M. *Angew. Chem. Int. Ed.* **2016**, *55*, 7487.



8b (93 %)[b]

8c (88 %)

8d: Ar = Ph (97 %)
8e: Ar = *p*-$MeOC_6H_4$ (55 %)
8f: Ar = *p*-$CF_3C_6H_4$ (61 %)
8g: Ar = *o*-$CF_3C_6H_4$ (98 %)
8h: Ar = *o*-FC_6H_4 (97 %)
8i: Ar = 2-Furyl (93 %)

8j: *n* = 1 (97 %)[c]
8k: *n* = 2 (75 %)[c]

8l: R = OPh (66 %)
8m: R = Ph (97 %)

8n (89%)

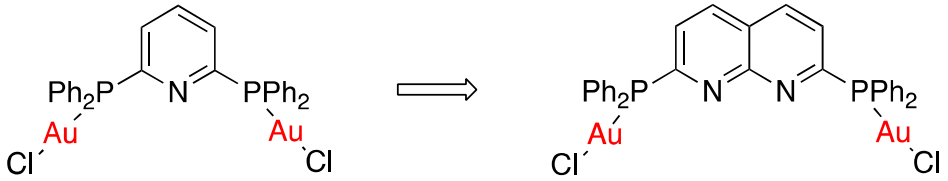
8o (92%)

8p (35 %)[d]

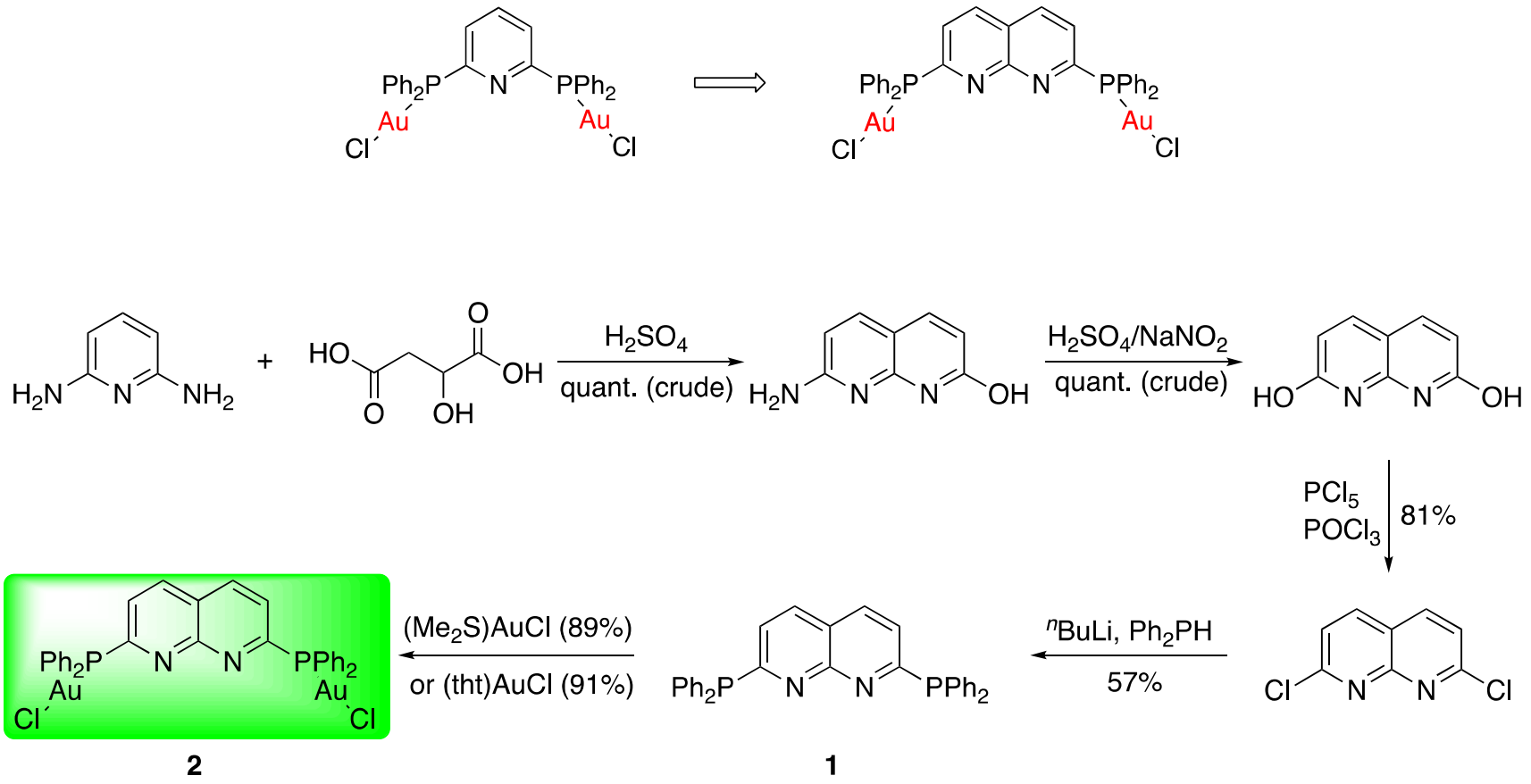
8q (16 %)[e]

Smirnova, E. S.; Molina, J. M. M.; Johnson, A.; Bandeira, N. A. G.; Bo, C., Echavarren, A. M. *Angew. Chem. Int. Ed.* **2016**, *55*, 7487.

PNNP类型配体的合成

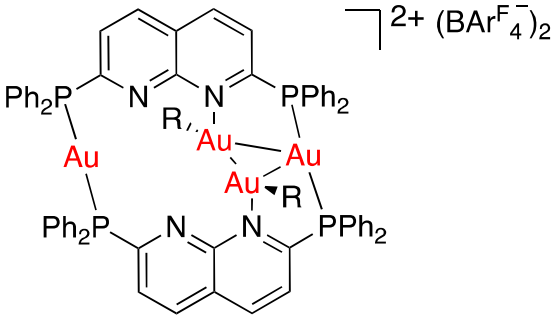


PNNP类型配体的合成

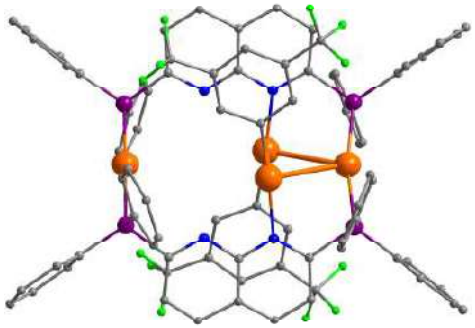


(a) Ziessel, R. *Tetrahedron Lett.* **1989**, *30*, 463-466. (b) Catalano, V. J.; Kar, H. M.; Bennett, B. L. *Inorg. Chem.* **2000**, *39*, 121-127.

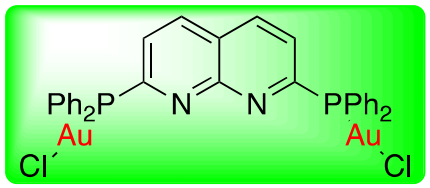
多金簇合物的合成与表征



3, 64%, R = 3,5-(CF$_3$)$_2$C$_6$H$_3$

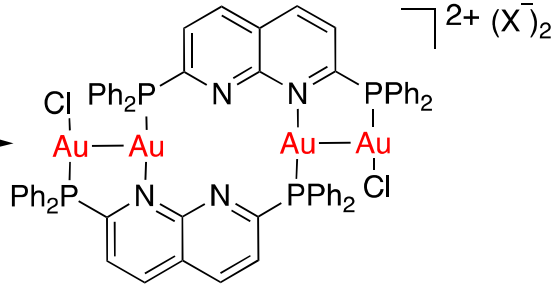


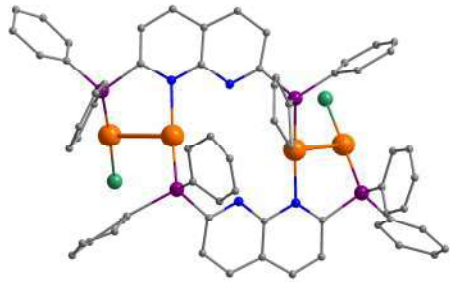
NaBAr$^F_4$ (2.5 eq.)



2

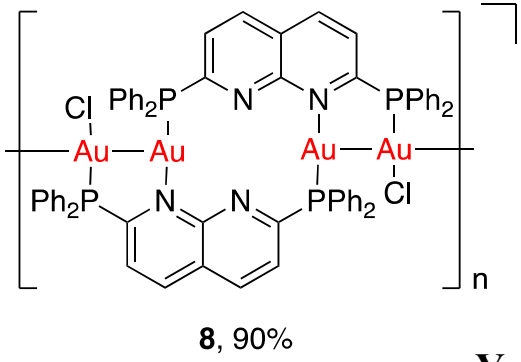
AgX (2.0 eq.)



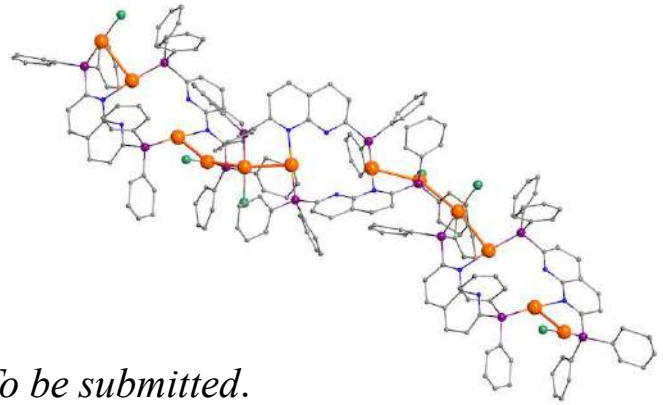


4, X = PF$_6$, 90%
5, X = BF$_4$, 80%
6, X = SbF$_6$, 91%
7, X = OTf, 88%

AgNTf$_2$ (2.0 eq.)

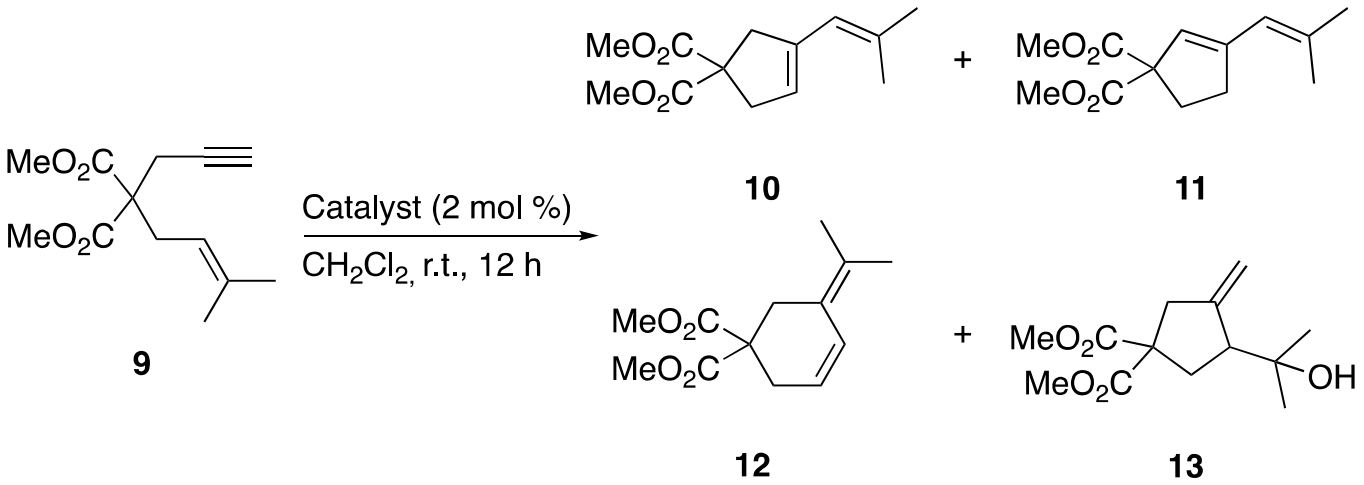


8, 90%



Yang, J.-M.; Echavarren, A. M.* **2017**, *To be submitted*.

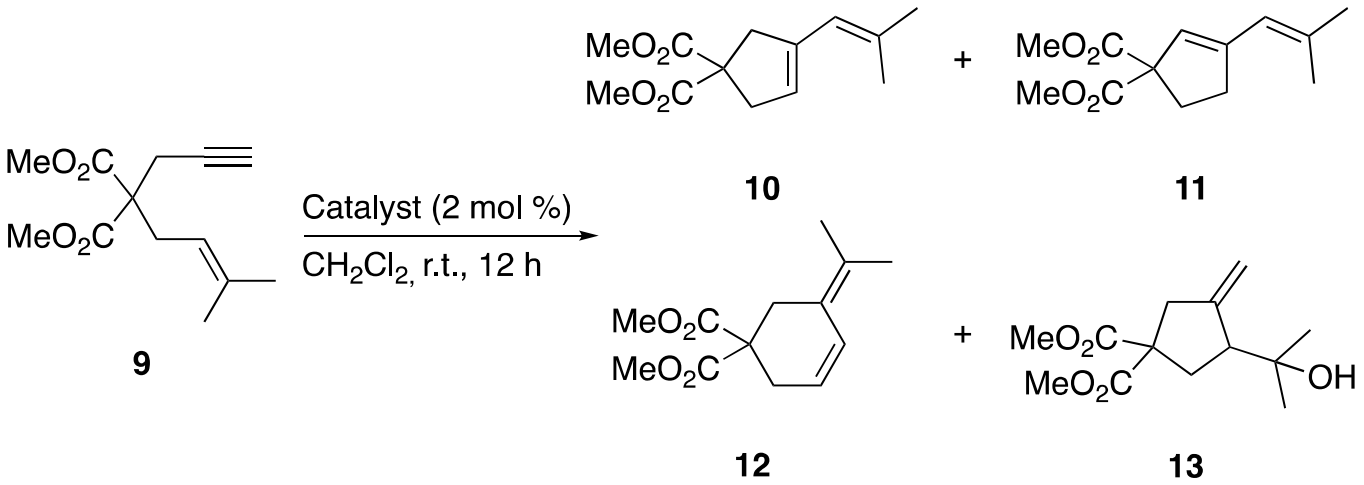
催化活性研究



Entry[a]	Catalyst	Conv. [%][b]	**10**	**11**	**12**	**13**
1	**3**, $\mathbf{L_2Au_4(BAr^F{}_4)_4}$	100	85 (83)	0	10	1
2[c]	**4**, $\mathbf{L_2Au_4Cl_2(PF_6)_2}$	35	21	0	5	1
3	**4**, $\mathbf{L_2Au_4Cl_2(PF_6)_2}$	100	58	0	18	0
4	**5**, $\mathbf{L_2Au_4Cl_2(BF_4)_2}$	42	28	0	3	9
5	**6**, $\mathbf{L_2Au_4Cl_2(SbF_6)_2}$	100	74	0	17	4
6	**7**, $\mathbf{L_2Au_4Cl_2(OTf)_2}$	100	22	0	23	0
7	**8**, $\mathbf{[L_2Au_4Cl_2(NTf_2)_2]_n}$	100	14	27	29	0

[a] Reaction conditions : **9** (0.1 mmol), cat. (2 mol %), CH_2Cl_2 (1.0 mL). [b] Conversion and yields were determined by ^1H NMR spectroscopy using 1,4-diacetylbenzene as internal standard. Value within parentheses is that of the yield of the isolated product after column chromatography. [c] 1 mol % of **4**, reaction time: 3 h. L = 2,9-bis(diphenylphosphino)-1,8-naphthyridine (dppn).

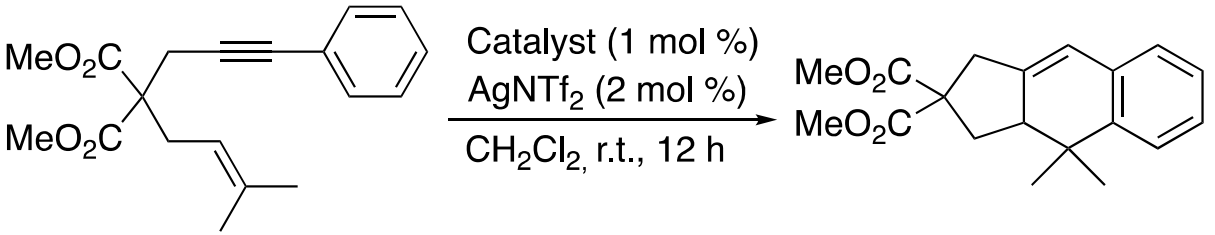
催化活性研究



Entry[a]	Catalyst	Conv. [%][b]	**10**	**11**	**12**	**13**
1	**3**, $L_2Au_4(BAr^F{}_4)_4$	100	85 (83)	0	10	1
2[c]	**4**, $L_2Au_4Cl_2(PF_6)_2$	35	21	0	5	1
3	**4**, $L_2Au_4Cl_2(PF_6)_2$	100	58	0	18	0
4	**5**, $L_2Au_4Cl_2(BF_4)_2$	42	28	0	3	9
5	**6**, $L_2Au_4Cl_2(SbF_6)_2$	100	74	0	17	4
6	**7**, $L_2Au_4Cl_2(OTf)_2$	100	22	0	23	0
7	**8**, $[L_2Au_4Cl_2(NTf_2)_2]_n$	100	14	27	29	0

[a] Reaction conditions : **9** (0.1 mmol), cat. (2 mol %), CH_2Cl_2 (1.0 mL). [b] Conversion and yields were determined by ^1H NMR spectroscopy using 1,4-diacetylbenzene as internal standard. Value within parentheses is that of the yield of the isolated product after column chromatography. [c] 1 mol % of **4**, reaction time: 3 h. L = 2,9-bis(diphenylphosphino)-1,8-naphthyridine (dppn).

催化活性研究

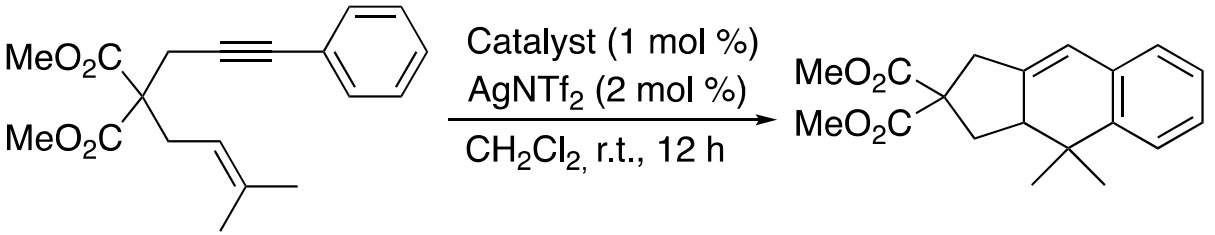


14 **15**

Entry[a]	Catalyst	Conv. [%][b]	**15**[b]
1	**3**, $L_2Au_4(BAr^F{}_4)_4$	35	23
2[c]	**3**, $L_2Au_4(BAr^F{}_4)_4$	0	0
3[d]	**4**, $L_2Au_4Cl_2(PF_6)_2$	0	0
4	**4**, $L_2Au_4Cl_2(PF_6)_2$	100	83 (77)
5	**5**, $L_2Au_4Cl_2(BF_4)_2$	100	81 (76)
6	**6**, $L_2Au_4Cl_2(SbF_6)_2$	100	75
7	**7**, $L_2Au_4Cl_2(OTf)_2$	100	81 (74)
8	**8**, $[L_2Au_4Cl_2(NTf_2)_2]_n$	100	68
9	-	39[e]	0

[a] Reaction conditions : **14** (0.1 mmol), cat. (1 mol %), $AgNTf_2$ (2 mol %), CH_2Cl_2 (1.0 mL). [b] Conversion and yields were determined by ^1H NMR spectroscopy using 1,4-diacetylbenzene as internal standard. Value within parentheses is that of the yield of the isolated product after column chromatography. [c] $NaBAr^F{}_4$ (2 mol %) was added instead of $AgNTf_2$. [d] Absence of $AgNTf_2$. [e] Partial decomposition of **14**. L = 2,9-bis(diphenylphosphino)-1,8-naphthyridine (dppn).

催化活性研究



14 **15**

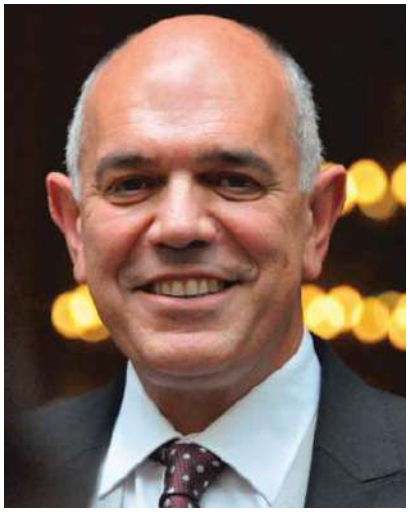
Entry[a]	Catalyst	Conv. [%][b]	**15**[b]
1	**3**, $L_2Au_4(BAr^F{}_4)_4$	35	23
2[c]	**3**, $L_2Au_4(BAr^F{}_4)_4$	0	0
3[d]	**4**, $L_2Au_4Cl_2(PF_6)_2$	0	0
4	**4**, $L_2Au_4Cl_2(PF_6)_2$	100	83 (77)
5	**5**, $L_2Au_4Cl_2(BF_4)_2$	100	81 (76)
6	**6**, $L_2Au_4Cl_2(SbF_6)_2$	100	75
7	**7**, $L_2Au_4Cl_2(OTf)_2$	100	81 (74)
8	**8**, $[L_2Au_4Cl_2(NTf_2)_2]_n$	100	68
9	-	39[e]	0

[a] Reaction conditions : **14** (0.1 mmol), cat. (1 mol %), $AgNTf_2$ (2 mol %), CH_2Cl_2 (1.0 mL). [b] Conversion and yields were determined by ^1H NMR spectroscopy using 1,4-diacetylbenzene as internal standard. Value within parentheses is that of the yield of the isolated product after column chromatography. [c] $NaBAr^F{}_4$ (2 mol %) was added instead of $AgNTf_2$. [d] Absence of $AgNTf_2$. [e] Partial decomposition of **14**. L = 2,9-bis(diphenylphosphino)-1,8-naphthyridine (dppn).

研究总结

- 发展了一系列过渡金属催化的串联环化反应合成方法学，构建了多种杂环和稠环化合物，并对反应机理进行了探讨，提出了合理的反应机理。
- 主要包括：1）铑催化的三氮唑与吡咯和吲哚的分子内C-H键官能团化反应（发表于*Angew. Chem. Int. Ed.*，高引用论文，Top 1%，截至2017年8月，106次引用）； 2）金或银催化的炔丙醇羧酸酯与呋喃、吲哚、氮杂环丙烷的分子内串联环化反应；3）以PNNP类型配体为原料，合成并表征了一系列多金簇合物，并对其催化活性进行了研究。
- 已发表SCI论文8篇，JCR化学大类一区3篇（*Angew. Chem. Int. Ed.*, *Chem. Commun.*, *Adv. Synth. Catal.* ），二区2篇（*Chem. Eur. J.*, *Organometallics*, ），三区3篇（*Tetrahedron Lett.*, *Tetrahedron Asymmetry*, *ChemistryOpen*）。其中第一作者6篇，第二作者2篇，论文总影响因子40.375，总引用次数216次，他引209次。

致谢



Prof. Dr. Min Shi
Prof. Dr. Antonio M Echavarren

THE FRAMEWORK PROGRAMME FOR RESEARCH AND INNOVATION
HORIZON 2020

MARIE CURIE ACTIONS

erc
European Research Council
Established by the European Commission

NSFC
国家自然科学基金委员会
National Natural Science Foundation of China

SIOC 1950

East China University of Science and Technology

ICIQ
Institut Català d'Investigació Química

973
National Basic Research Program of China

GOBIERNO DE ESPAÑA
MINISTERIO DE ECONOMÍA, INDUSTRIA Y COMPETITIVIDAD