The 3rd South Lake Innovation Forum for International Young Talents

Transition-Metallocarbene Mediated Tandem Cyclization Reactions and Polynuclear Gold Clusters Synthesis

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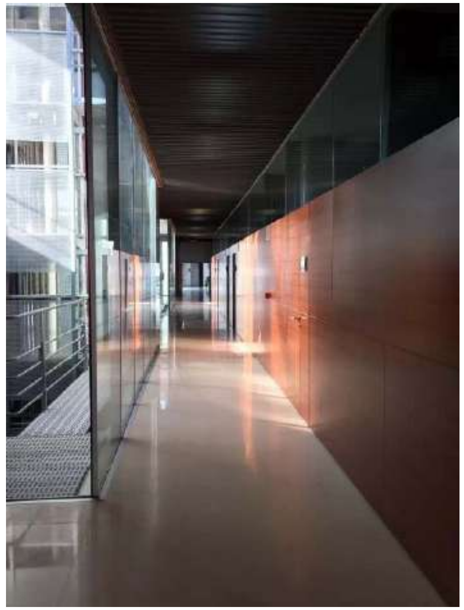
博后合作导师: Antonio M Echavarren (ICIQ)

05-12-2018

ICIQ

MARIE CURIE ACTIONS

Institute of Chemical Research of Catalonia (ICIQ)



Institute of Chemical Research of Catalonia (ICIQ)

Institute of Chemical Research of Catalonia (ICIQ)

Computational Chemistry

CO_2 recycling

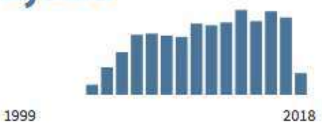
Renewable Fuels

Catalysis

Artificial Photosynthesis

Total Publications

2,018



h-index

125

Average citations per item

39.62

Sum of Times Cited

79,952

Without self citations

72,331

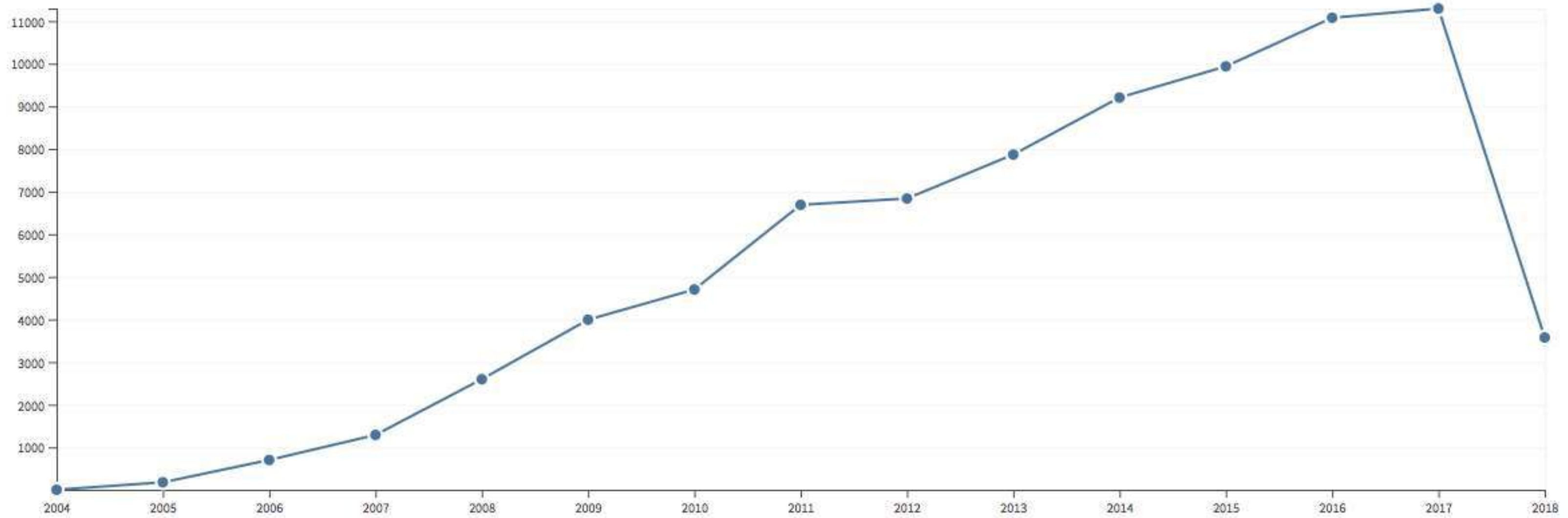
Citing articles

45,730

Without self citations

44,262

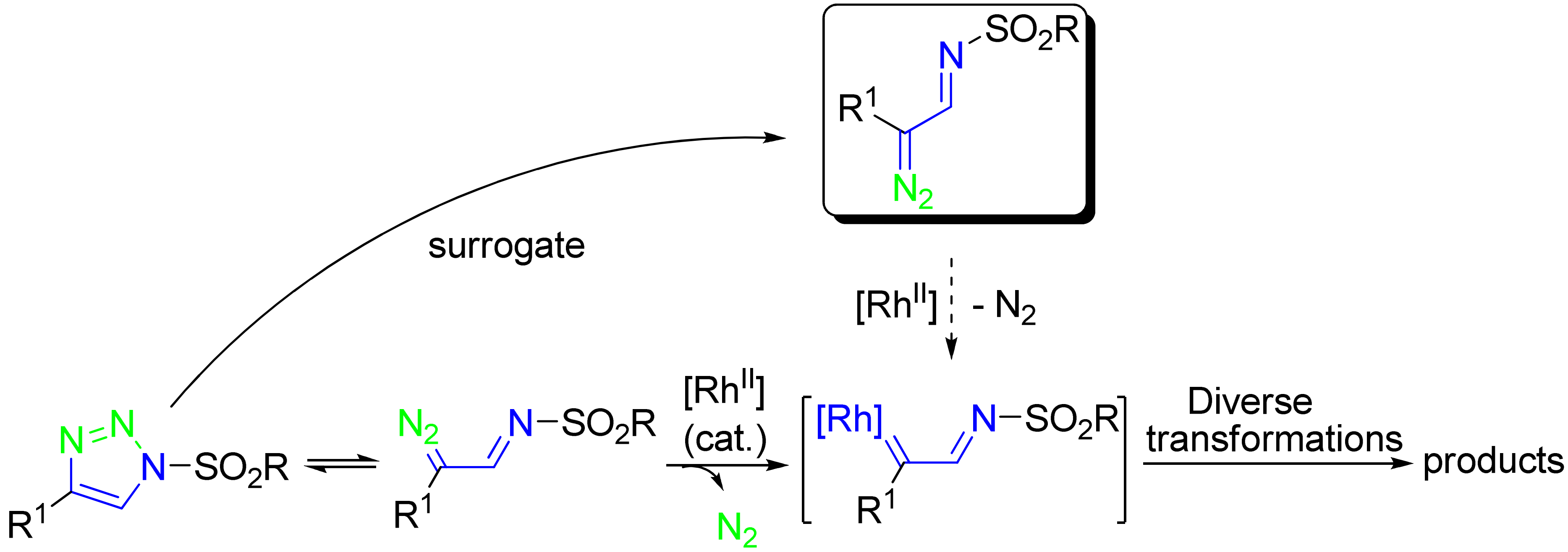
Sum of Times Cited per Year



Outline

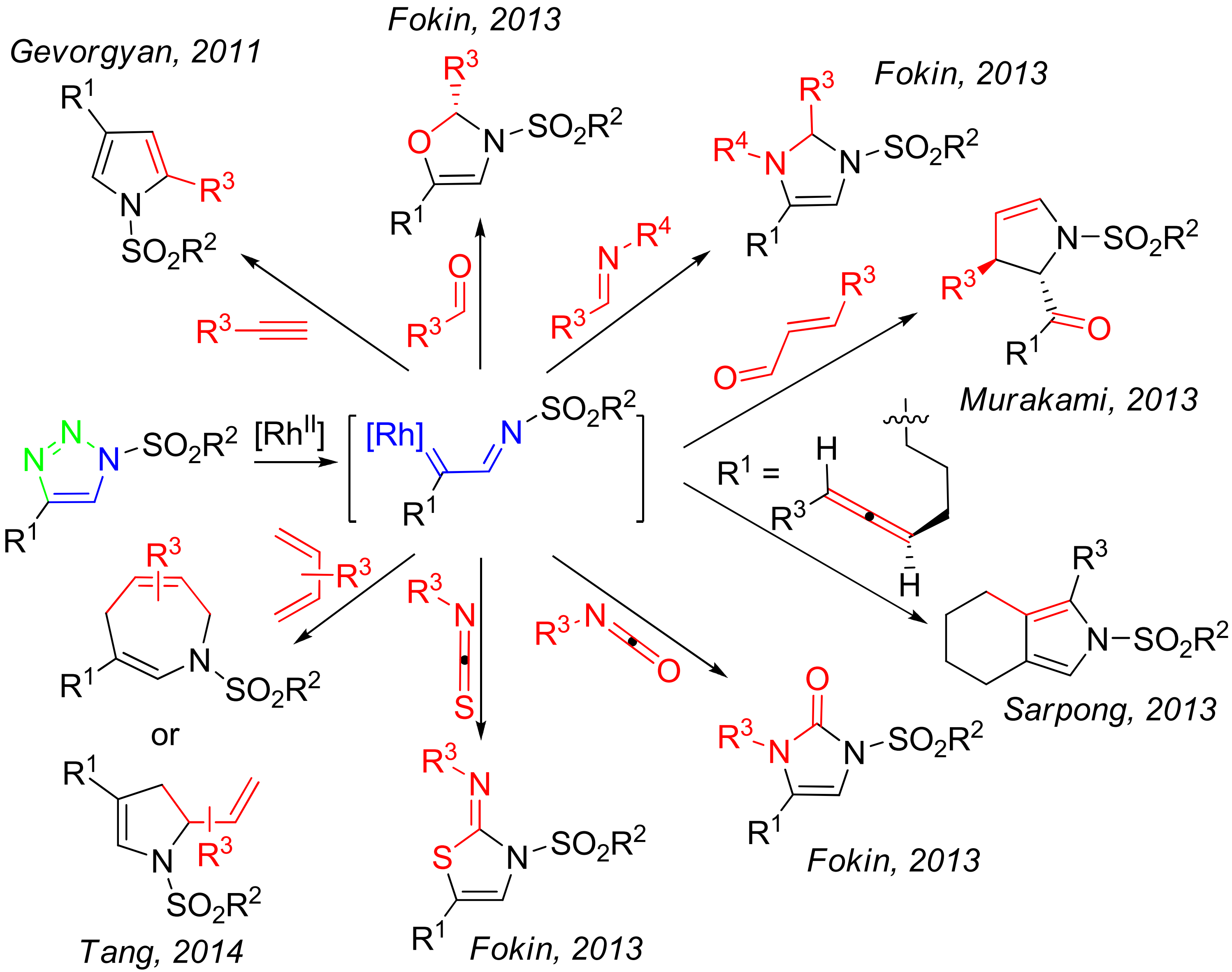
- **Background**
- **1) Rhodium-carbene Mediated Heterocycles Synthesis**
  - **Rhodium(II)-catalyzed intramolecular annulation of 1-sulfonyl-1,2,3-triazoles with pyrrole and indole rings**
- **2) Gold-carbene Mediated Tandem Cyclization Reactions**
  - **Gold(I)-Catalyzed Highly Stereoselective Synthesis of Polycyclic Indolines**
  - **Gold(I)-catalyzed intramolecular cycloisomerization of propargylic esters with furan rings**
- **3) Polynuclear Gold Clusters Synthesis**
- **Research Summary**
- **Acknowledgements**

Triazoles



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

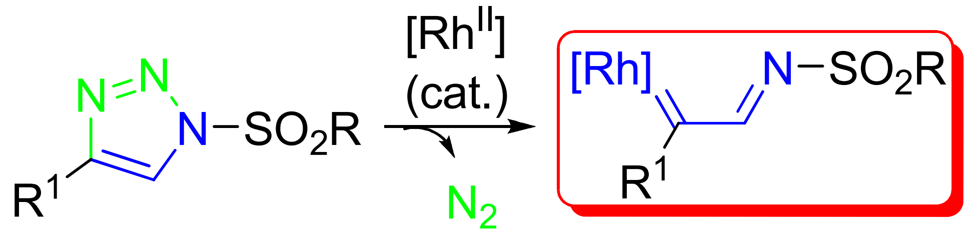
Transformations of Triazoles

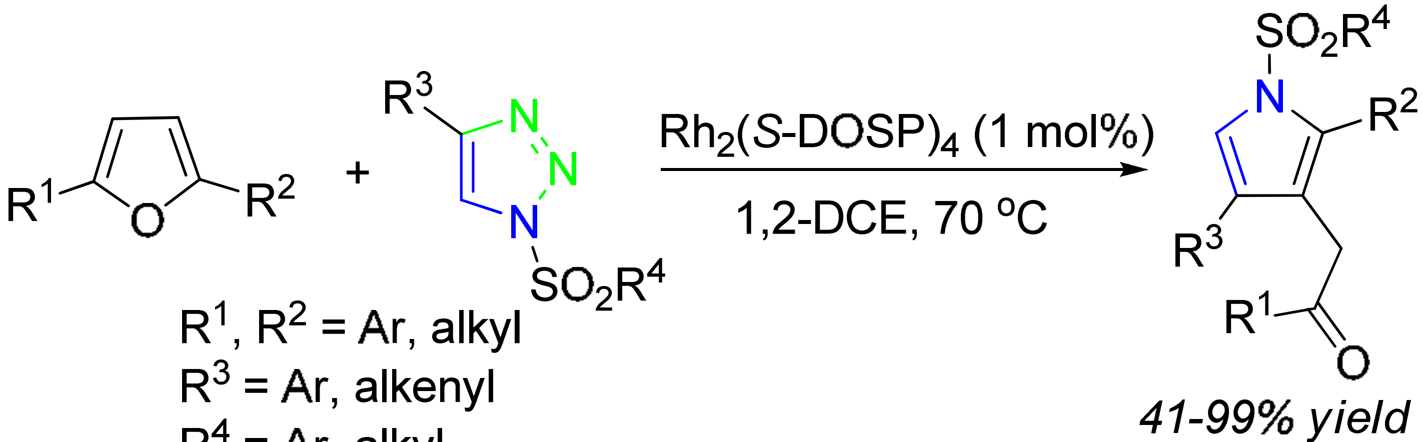


(a) Gulevich, A. V.; Gevorgyan, V. *Angew. Chem. Int. Ed.* **2013**, *52*, 1371-1373. (b) Davies, H. M. L.; Alford, J. S. *Chem. Soc. Rev.* **2014**, *43*, 5151-5162.

1) Rhodium-carbene Mediated Heterocycles Synthesis

Rh is one of the most popular catalysts for cycloaddidtion, Pauson-Khand reaction and C–H activation



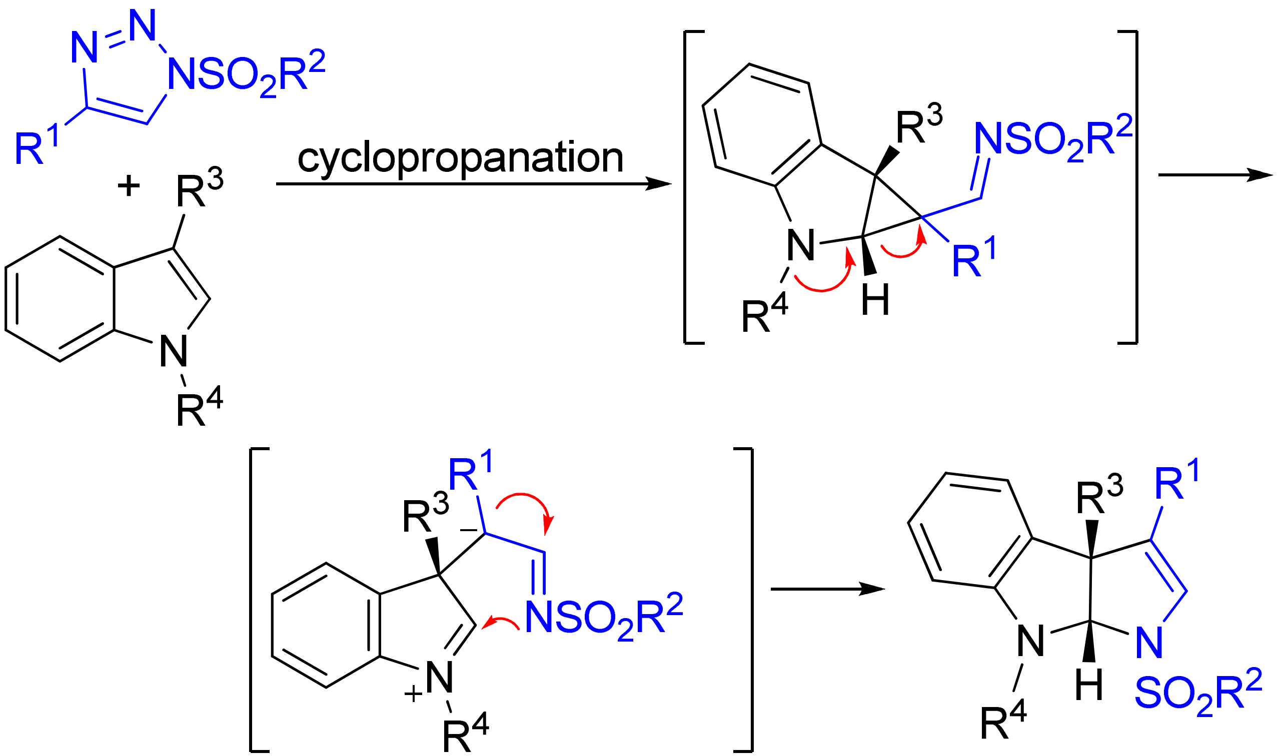


R^1, R^2 = Ar, alkyl
R^3 = Ar, alkenyl
R^4 = Ar, alkyl

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

1) Rhodium-carbene Mediated Heterocycles Synthesis

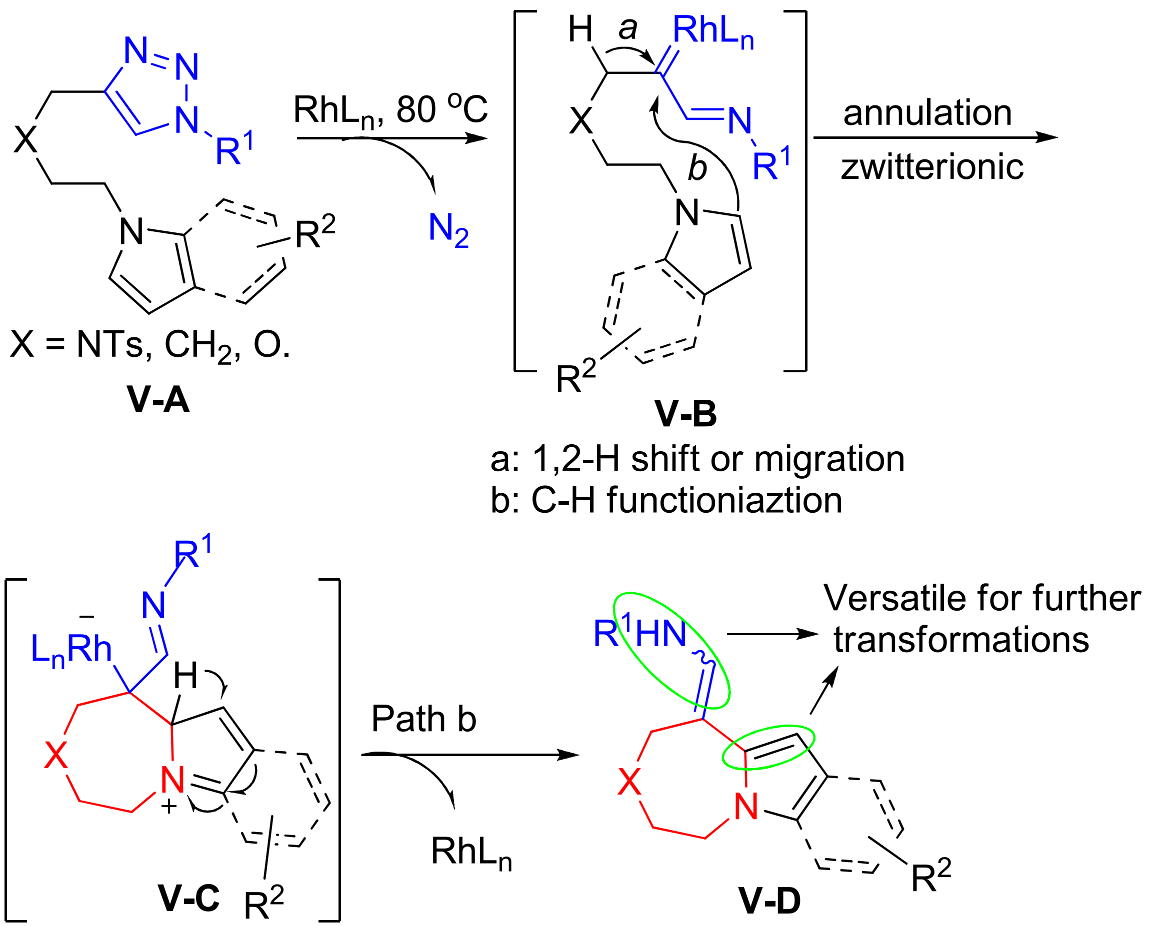
Intermolecular annulation of indoles (Davies's work)



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

1) Rhodium-carbene Mediated Heterocycles Synthesis

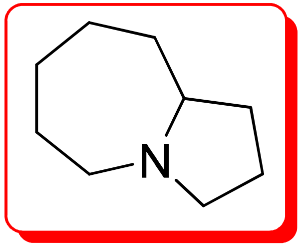
Intramolecular annulation of pyrroles and indoles (This work)

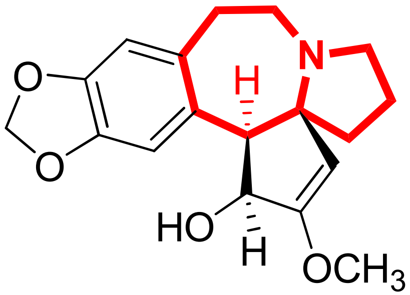


High chemoselectivity (path b only)!
Easy-to-handle functional groups!
Wide azepine ring flexibility (N, O, C)!

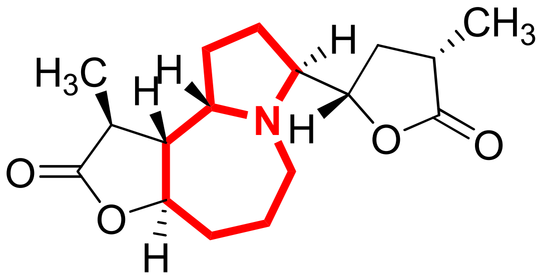
Yang, J.-M.; Zhu, C.-Z.; Tang, X.-Y.*; Shi, M.* *Angew. Chem. Int. Ed.* **2014**, *53*, 5142-5146.

1) Rhodium-carbene Mediated Heterocycles Synthesis

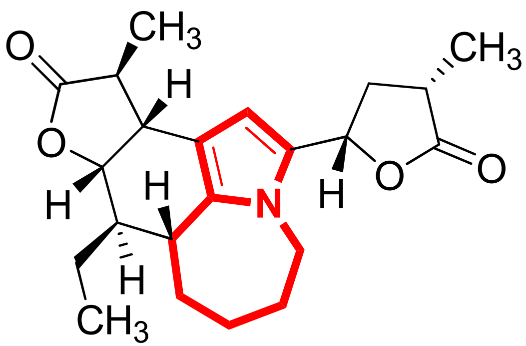




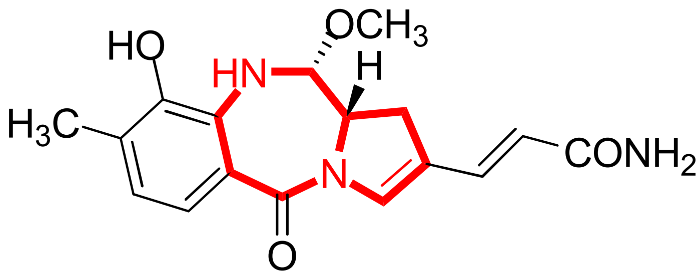
cephalotaxine



stemonine



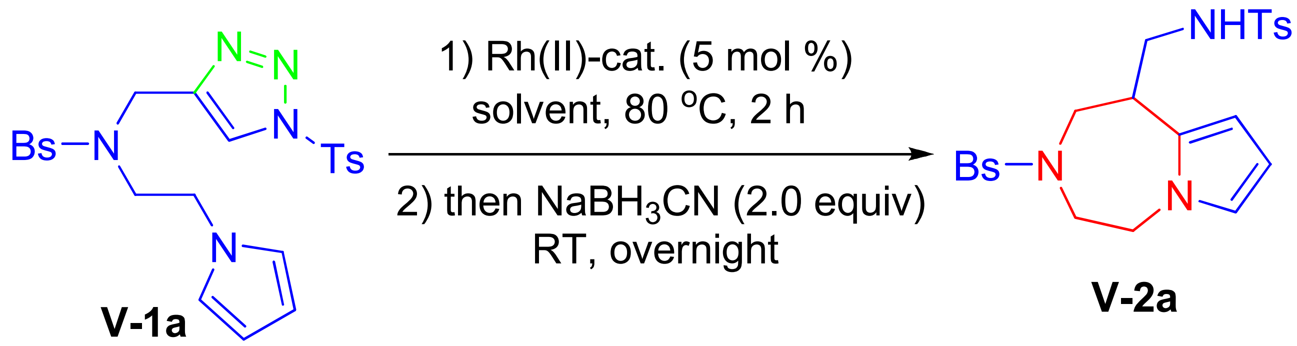
bisdehydrotuberostemonine
bisdehydroneotuberostemonine (H-11α, H-12α)
bisdehydrotuberostemonine B (H-10β)
bisdehydrotuberostemonine C (H-9α, H-10β)

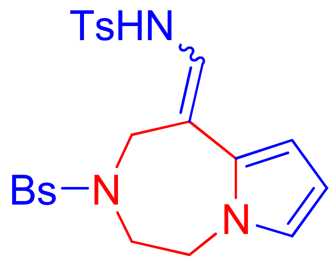


anthramycin

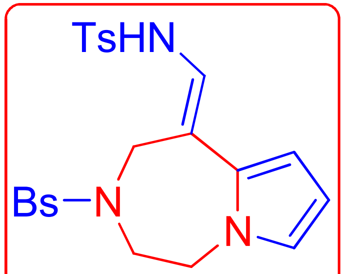
Yang, J.-M.; Zhu, C.-Z.; Tang, X.-Y.*; Shi, M.* *Angew. Chem. Int. Ed.* **2014**, *53*, 5142-5146.

Optimization of the reaction conditions





V-2a'

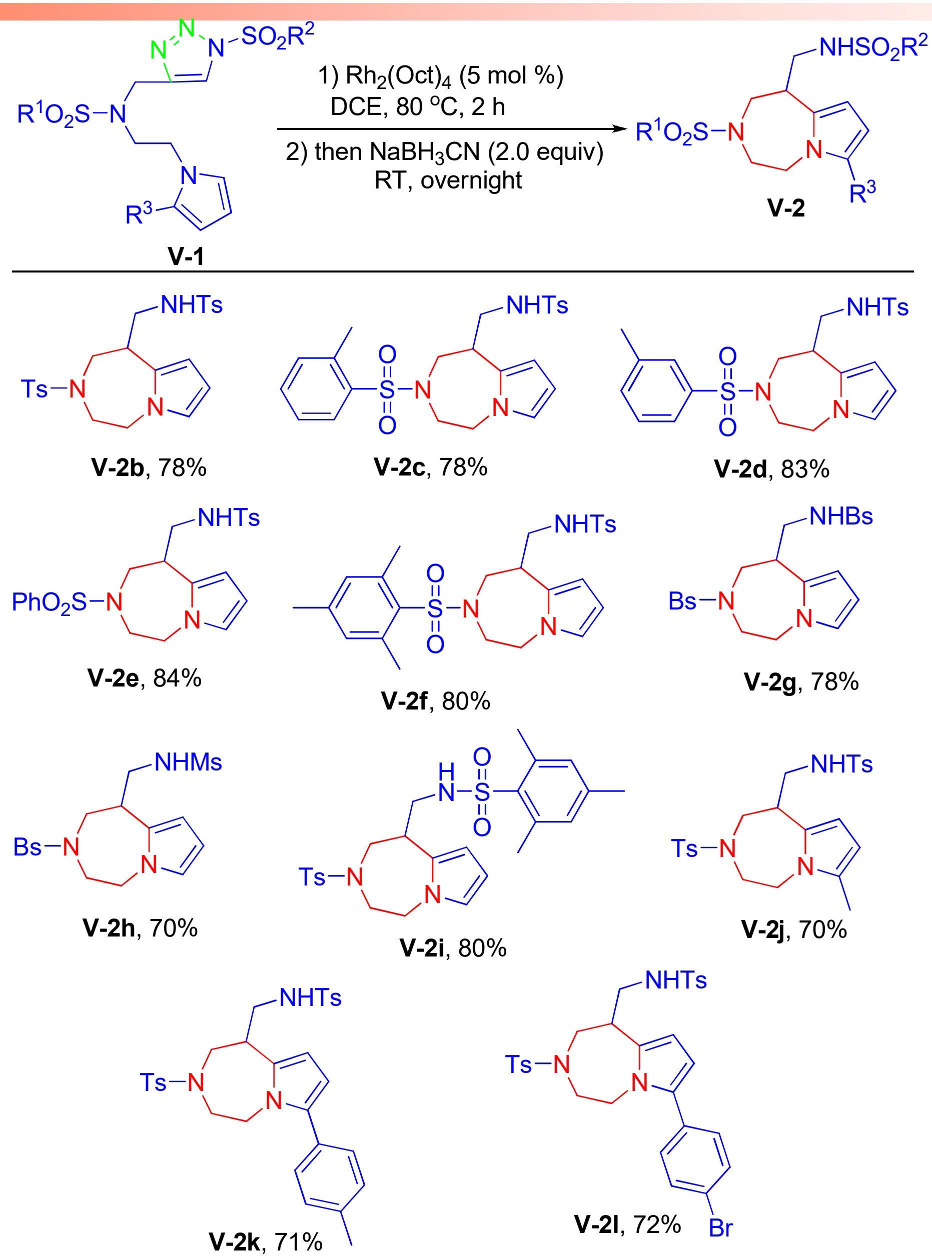


(*E*)-**V-2a'** ***X-ray***

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	$Rh_2(S\text{-}NTTL)_4$	DCE	70
8	$Rh_2(Oct)_4$	toluene	78
9	$Rh_2(Oct)_4$	cyclohexane	-[c]
10	$Rh_2(Oct)_4$	$CHCl_3$	-[c]

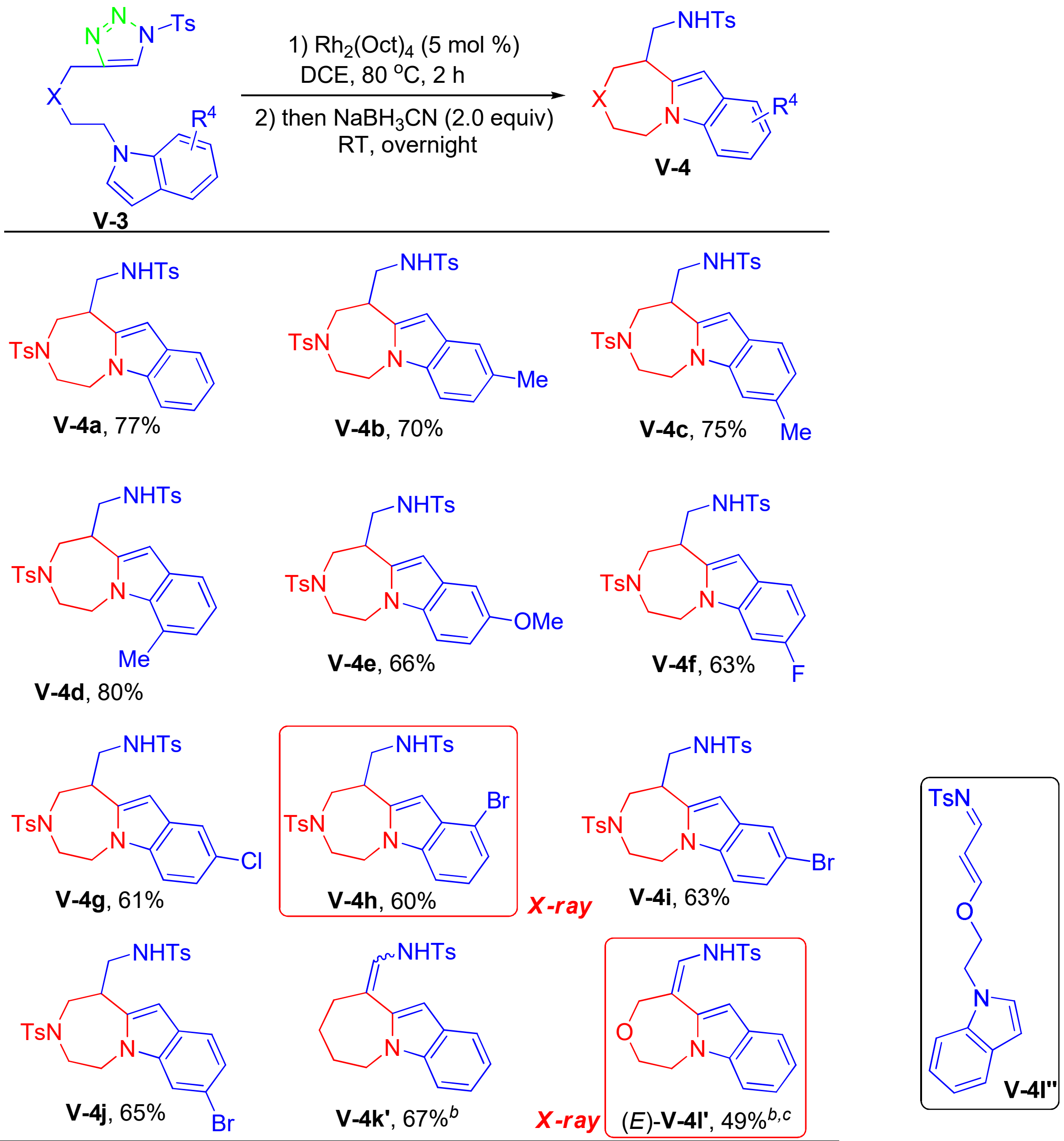
[a] Reaction conditions: 0.1 mmol of **V-1a**; 5 mol% of cat.; 1.0 mL of dry solvent. [b] Isolated yields. [c] undetermined. DCE =1,2-dichloroethane.

Substrate scope



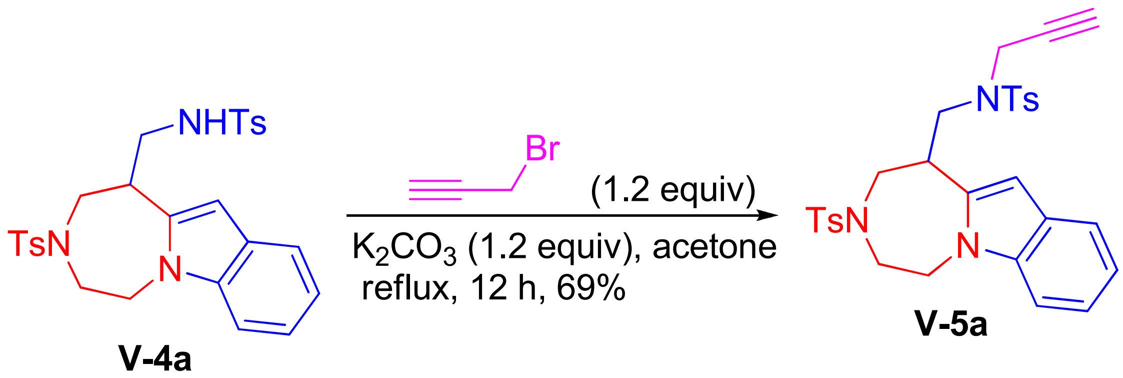
Reaction conditions: 0.1 mmol of **V-1**; 5 mol % of $Rh_2(Oct)_4$; 1.0 mL anhydrous DCE. Isolated yields.

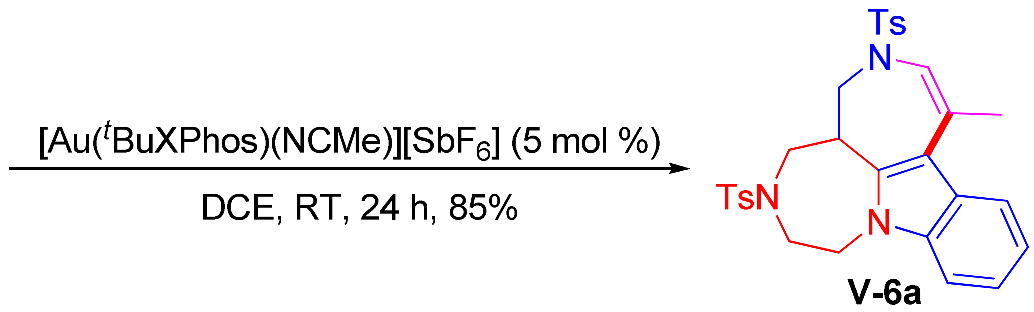
Substrate scope

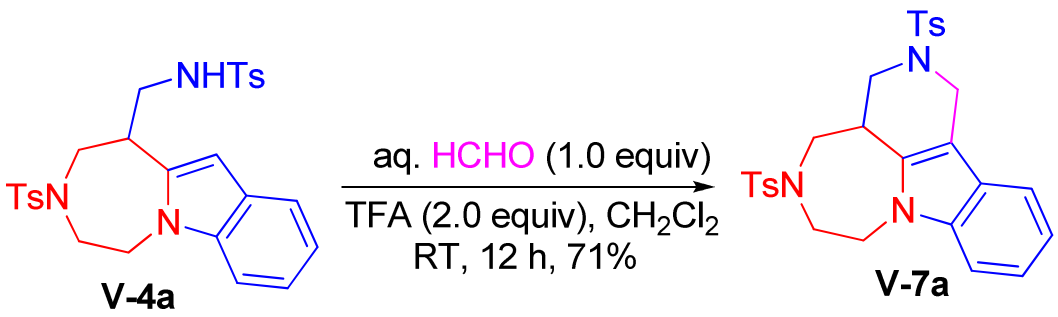


[a] Reaction conditions: 0.1 mmol of **V-3**; 5 mol % of $Rh_2(Oct)_4$; 1.0 mL anhydrous DCE. Isolated yields. [b] Substrates were performed only in the first step, and the two isomers were not reduced. [c] **V-4l''** was obtained in 43% yield.

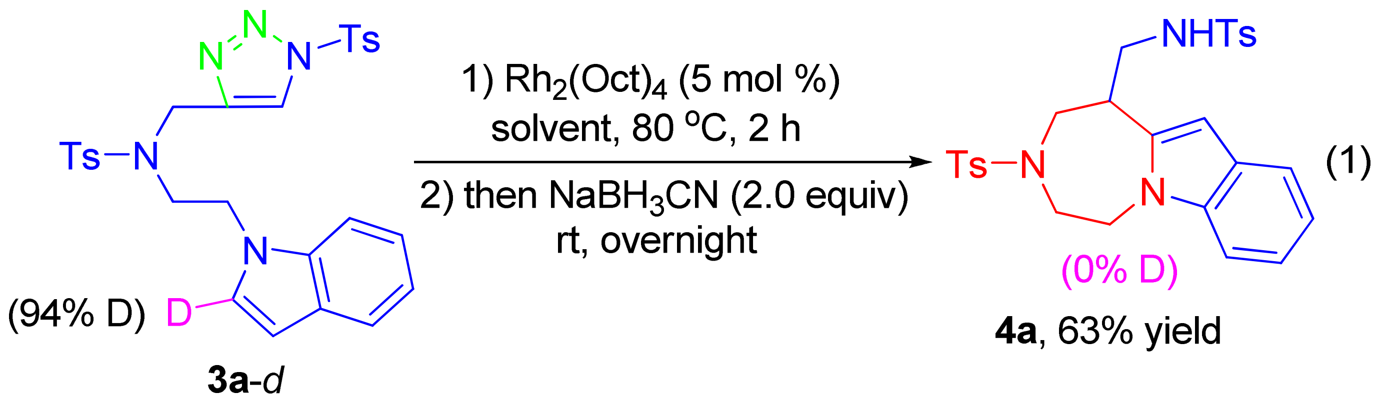
Further transformations of the products

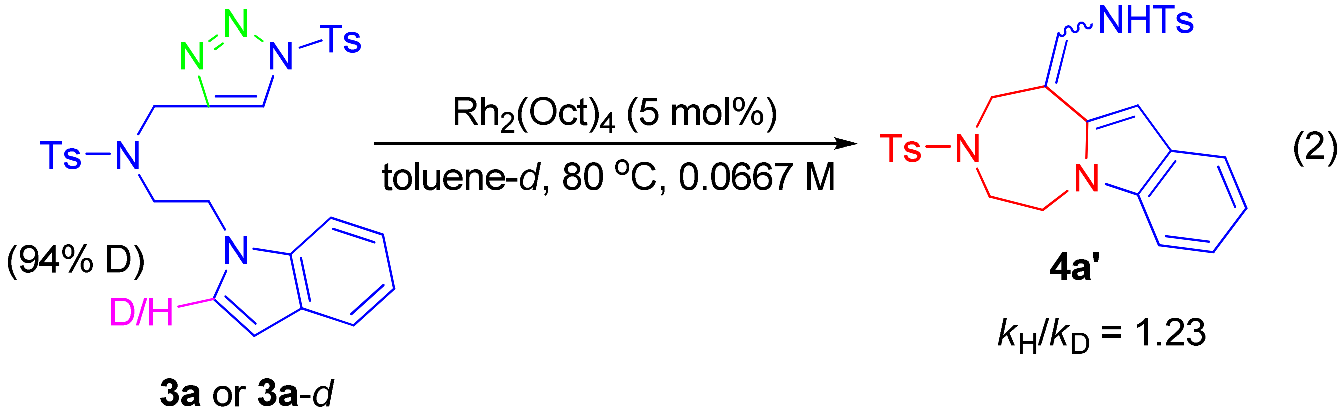




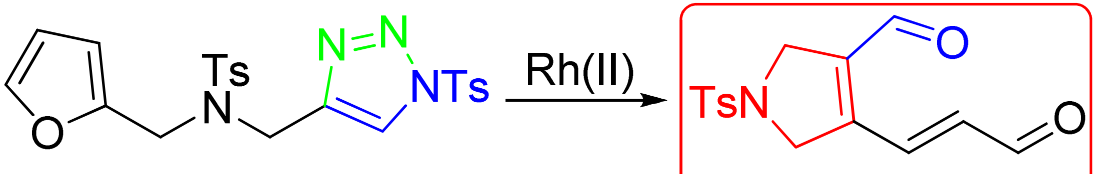


Kinetic isotope effect study



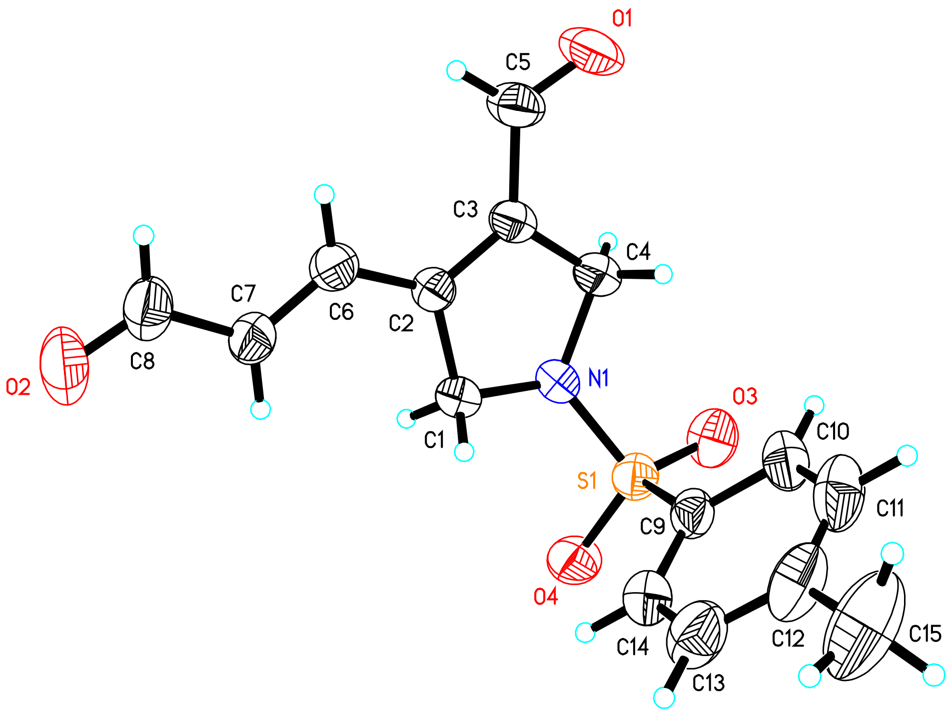


Substrate scope

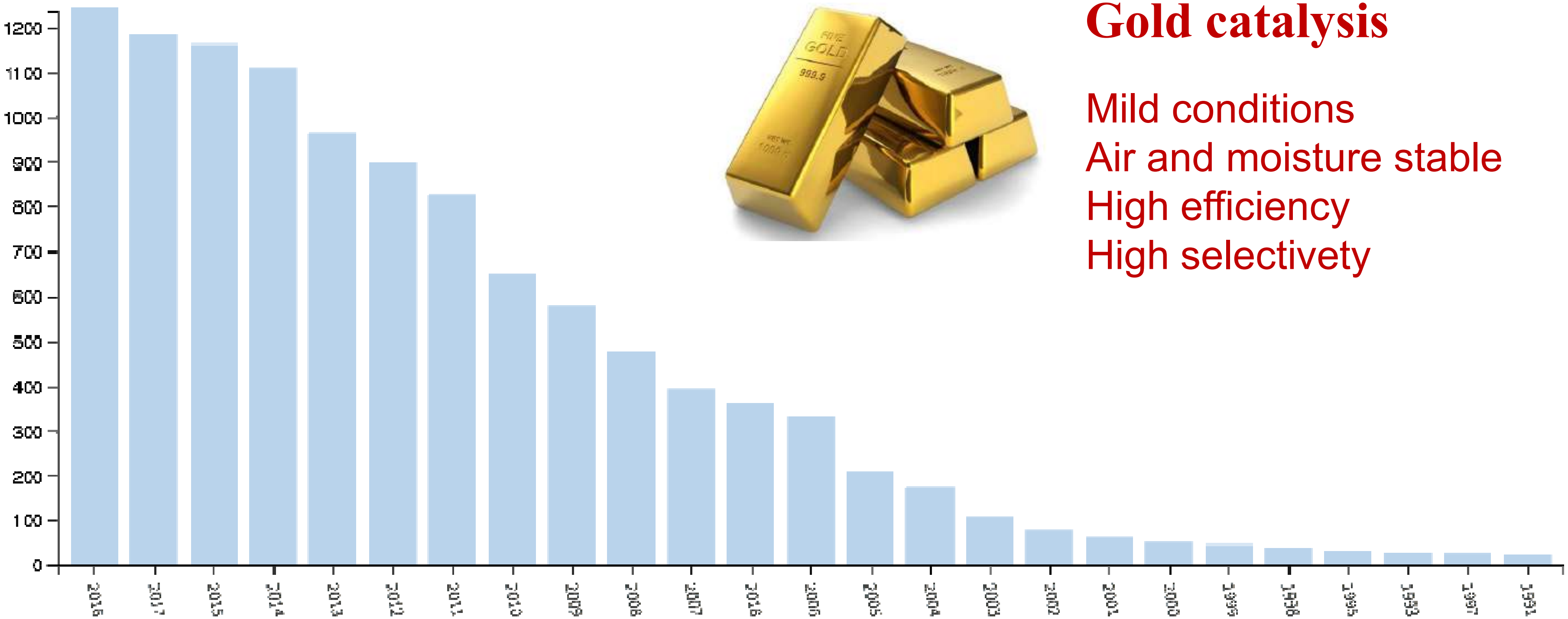


V-8a

V-9a ***X-ray***



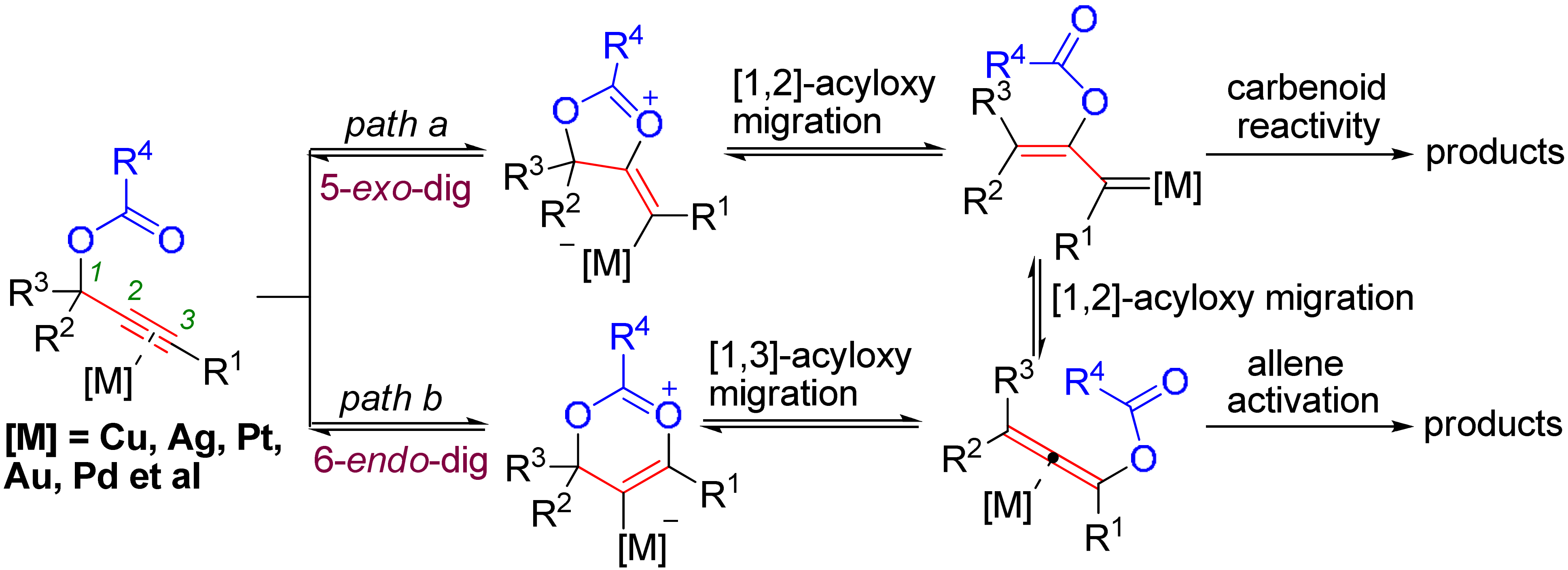
Gold catalysis



Gold catalysis

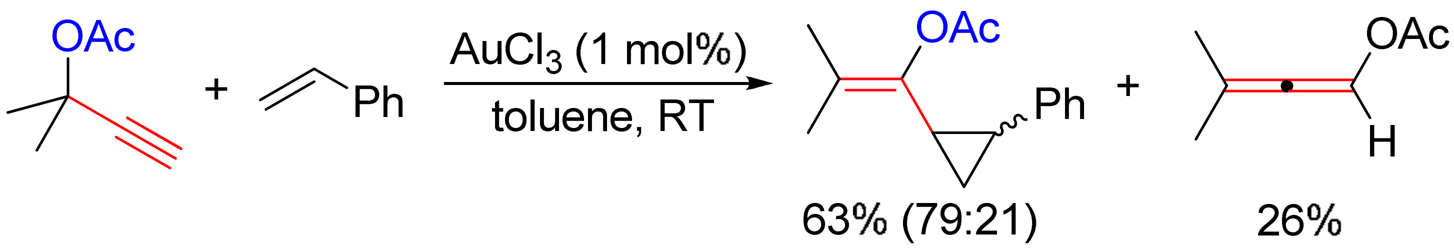
Mild conditions
Air and moisture stable
High efficiency
High selectivety

Propargylic Esters

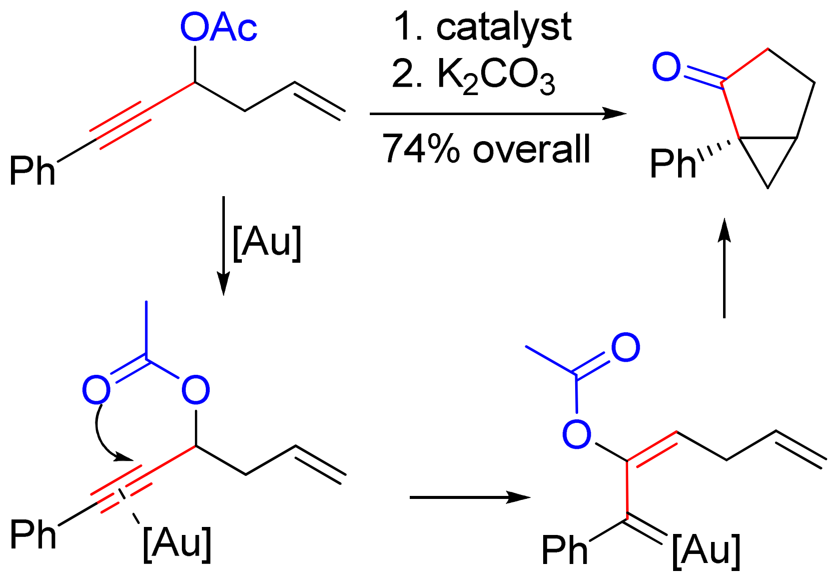


Wang, S.; Zhang, G.; Zhang, L. *Synlett* **2010**, 692-706.

[1,2]-Migration

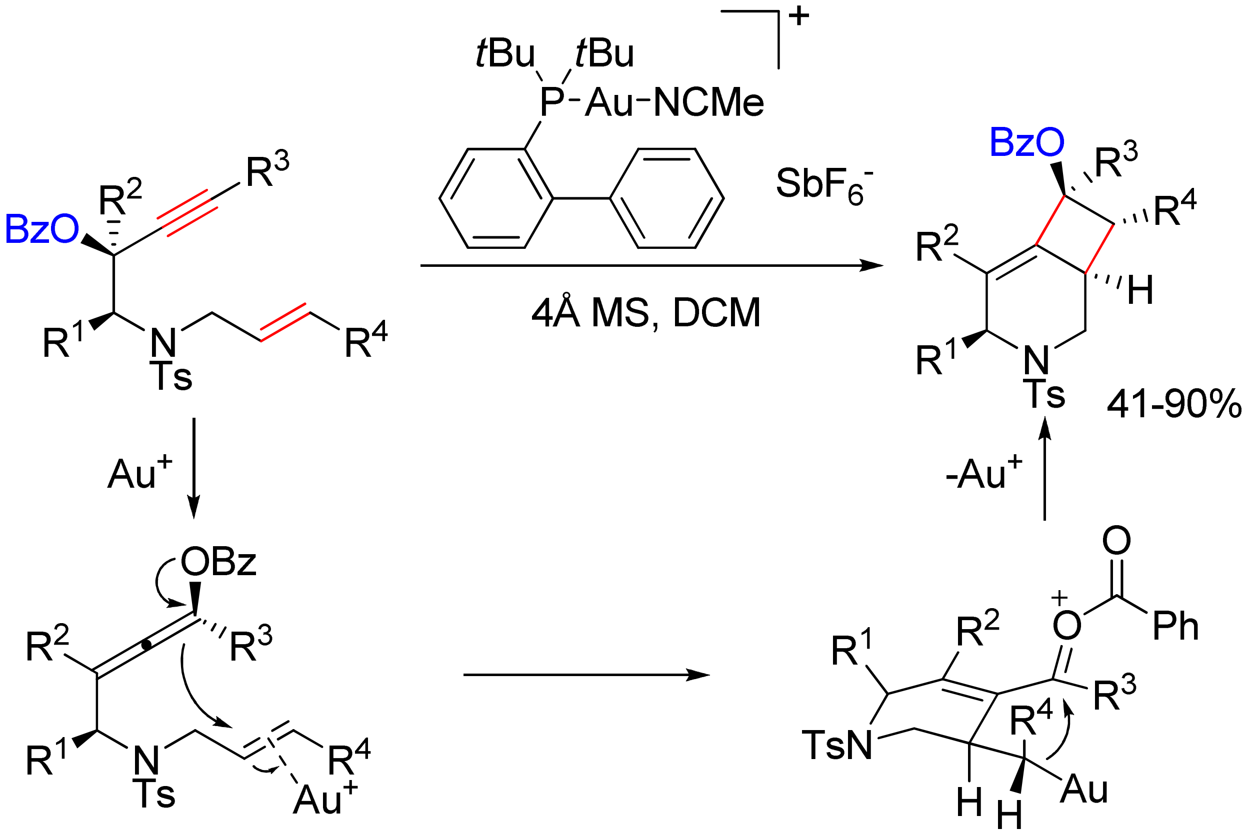


(a) Miki, K.; Ohe, K.; Uemura, S. *Tetrahedron Lett.* **2003**, *44*, 2019-2022. (b) Miki, K.; Ohe, K.; Uemura, S. *J. Org. Chem.* **2003**, *68*, 8505-8513.



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

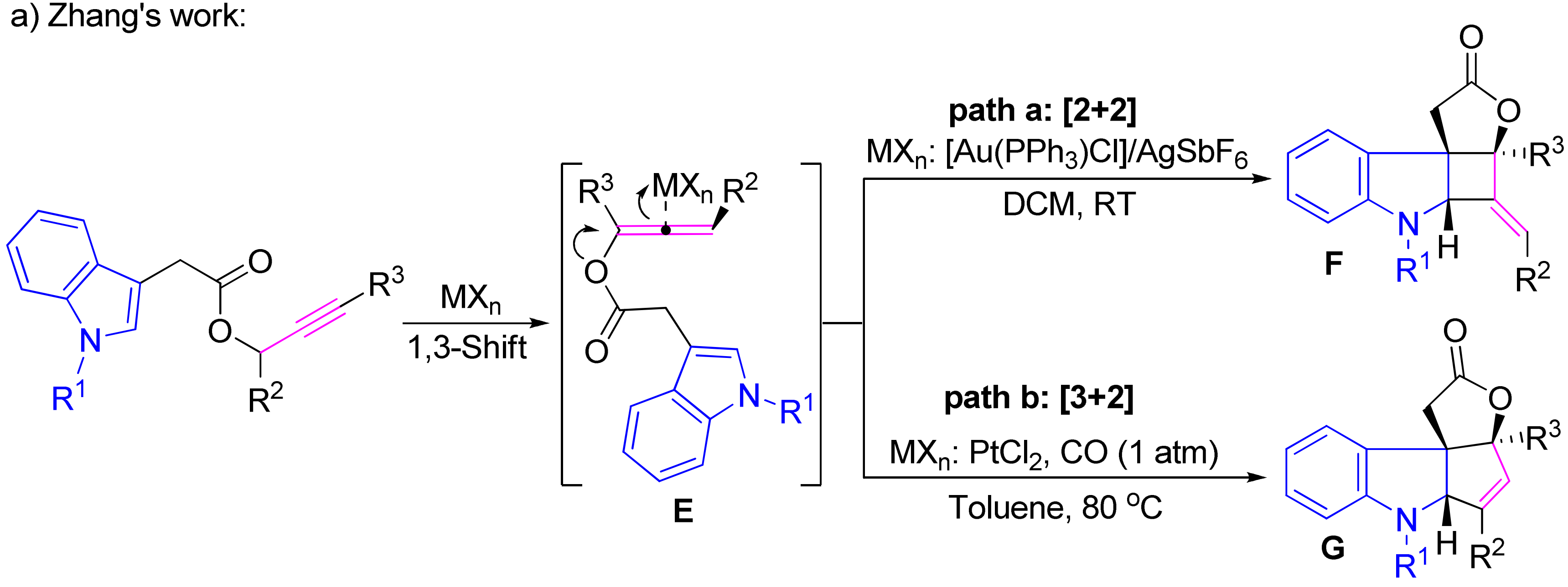
[1,3]-Migration



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

Gold(I)-Catalyzed Highly Stereoselective Synthesis of Polycyclic Indolines

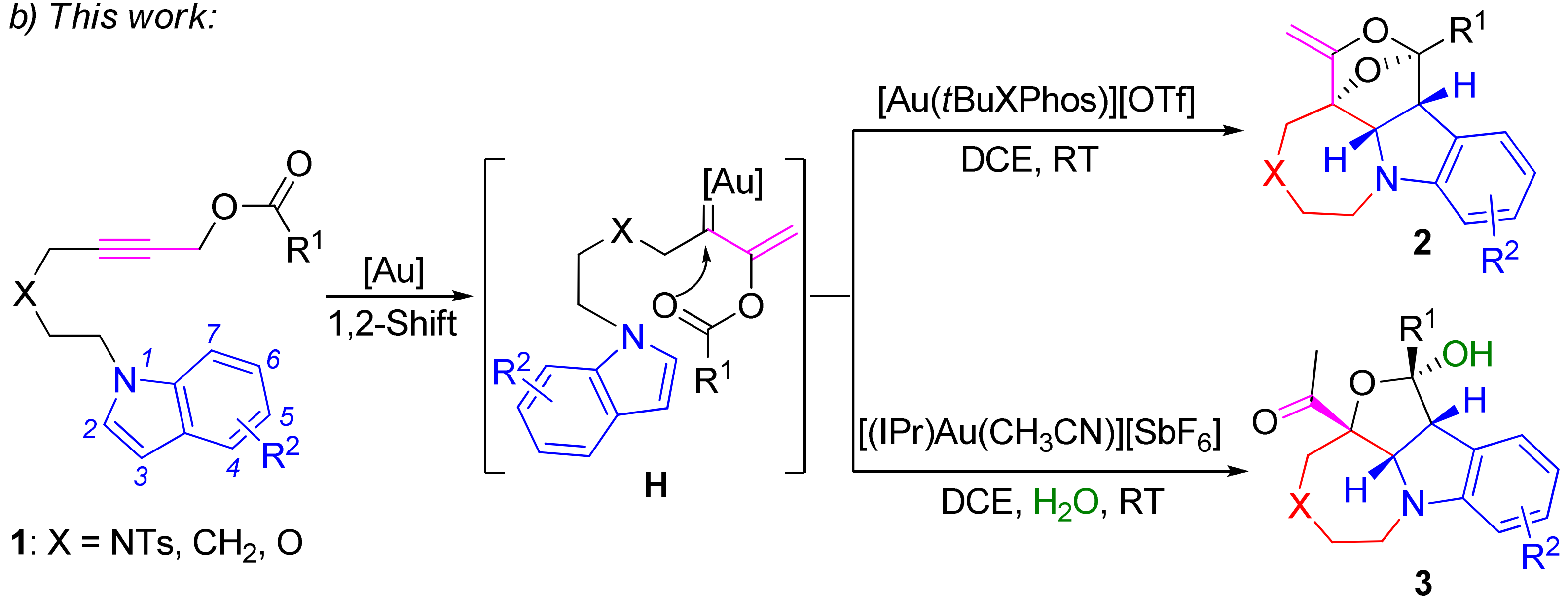
a) Zhang's work:



(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.

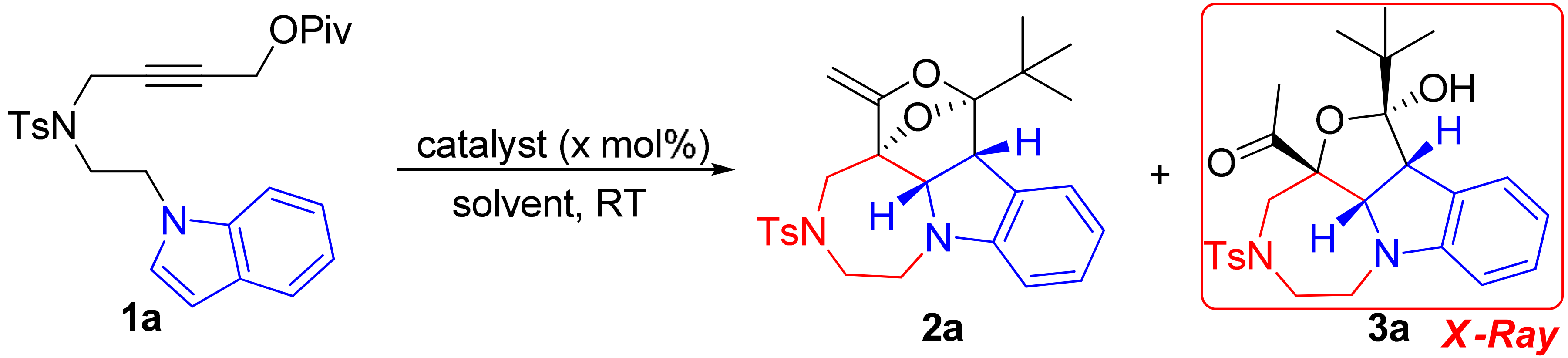
Gold(I)-Catalyzed Highly Stereoselective Synthesis of Polycyclic Indolines

b) This work:



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

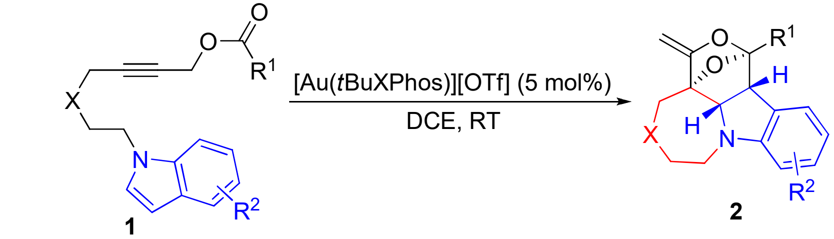
Optimization of the reaction conditions

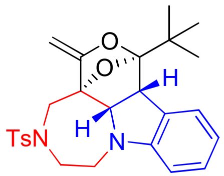


entry[a]	catalyst (x mol%)	solvent	H_2O (y eq.)	time	yield (%)[b] 2a	yield (%)[b] 3a
1	***[Au(tBuXPhos)][OTf] (5)***	***DCE***	-	***2 h***	***95***	***0***
2	[Au(Me_4*t*BuXPhos)(CH_3CN)][SbF_6] (5)	DCE	-	6 h	0	0
3	[(IPr)Au(CH_3CN)][SbF_6] (5)	DCE	-	2 h	0	70
4	[Au(*n*BuPAd_2)(CH_3CN)][SbF_6] (5)	DCE	-	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***

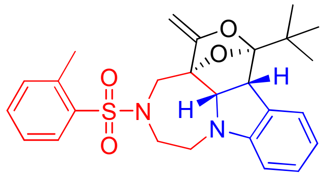
[a] All reactions were carried out using **1a** (0.1 mmol) in the presence of catalyst (x mol%) in DCE (1.0 mL) unless otherwise specified. [b] Isolated yields. Ar = 2,4-di-tert-butylphenyl. DCE = 1,2-dichloroethane.

Substrate scope

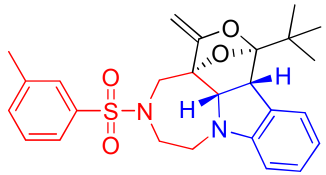




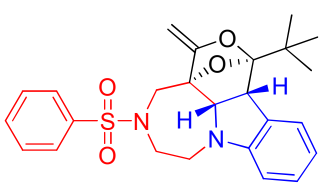
2a, 2 h, 95% yield



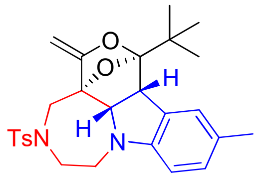
2b, 4 h, 80% yield



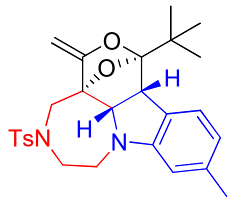
2c, 3.5 h, 96% yield



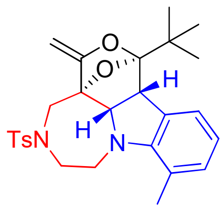
2d, 3.5 h, 85% yield



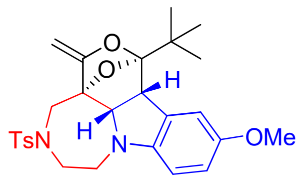
2h,4 h, 88% yield



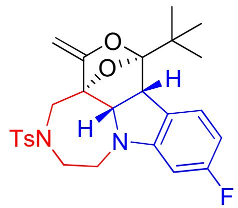
2i, 4 h, 83% yield



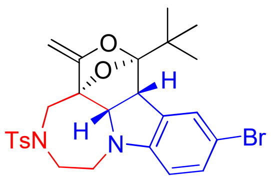
2j, 3 h, 73% yield



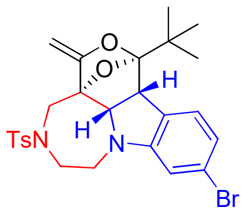
2k, 5 h, 78% yield



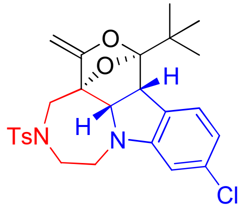
2l, 4 h, 76% yield



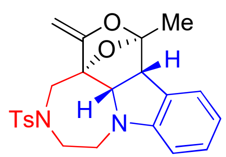
2m, 4 h, 72% yield



2n, 4 h, 70% yield



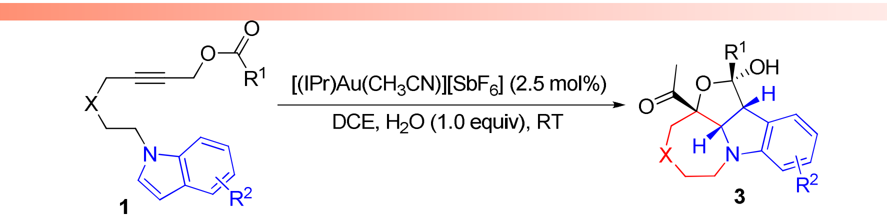
2o, 4 h, 74% yield

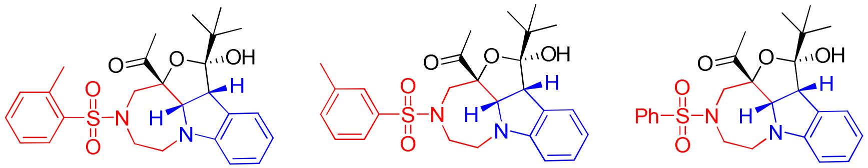


2r, 2 h, 79% yield[b]

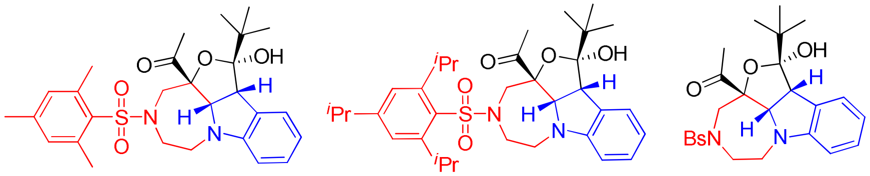
[a] Reaction conditions: **1** (0.1 mmol); [Au(*t*BuXPhos)][OTf] (5 mol%); anhydrous DCE (1.0 mL). Yields are those of the isolated yields. [b] 2.5 mol% of [(IPr)Au(CH_3CN)][SbF_6] was used as the catalyst.

Substrate scope

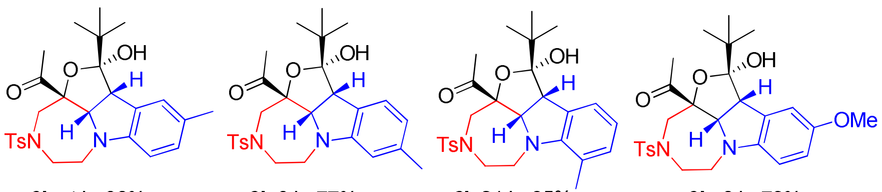




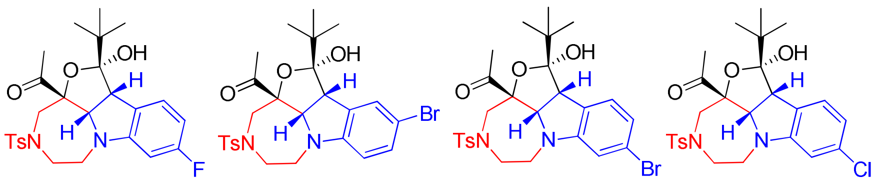
3b, 4 h, 82% | **3c**, 3 h, 87% | **3d**, 6 h, 71%



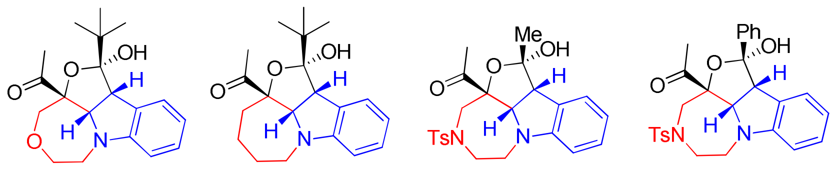
3e, 4 h, 89% | **3f**, 5 h, 76% | **3g**, 5 h, 86%



3h, 4 h, 66% | **3i**, 6 h, 77% | **3j**, 21 h, 85% | **3k**, 6 h, 79%



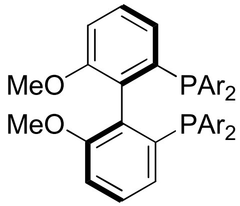
3l, 4 h, 77% | **3m**, 4 h, 72% | **3n**, 4 h, 64% | **3o**, 5 h, 83%



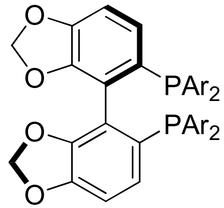
3p, 4 h, 86% | **3q**, 16 h, 46% | **3r**, 16 h, 94% | **3s**, 16 h, 70%

Reaction conditions: **1** (0.1 mmol); $[(IPr)Au(CH_3CN)][SbF_6]$ (2.5 mol%); H_2O (1.0 equiv); anhydrous DCE (1.0 mL). Yields are those of the isolated yields. DCE = 1,2-dichloroethane.

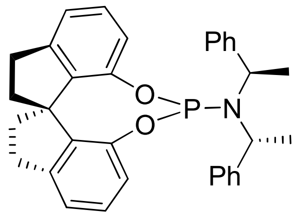
Ligands for asymmetric synthesis



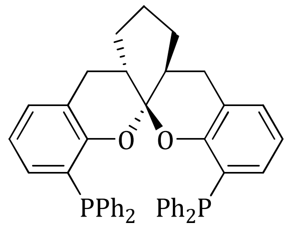
Ar = 3,5-(tBu)$_2$-4-MeOC$_6$H$_2$;
(*R*)-MeO-DTBM-BIPHEP (**L1**)



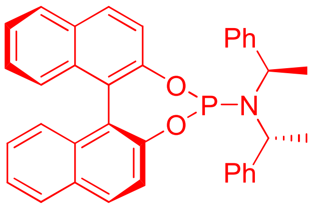
Ar = 3,5-(Me)$_2$C$_6$H$_3$;
(*R*)-DM-SEGPHOS (**L2**)



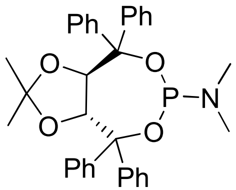
L3



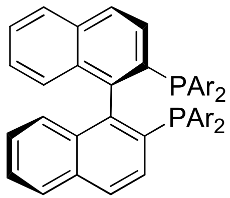
L4



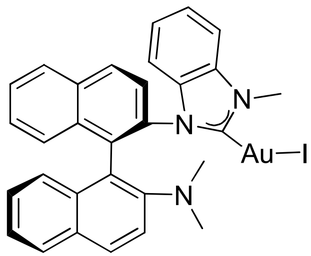
L5



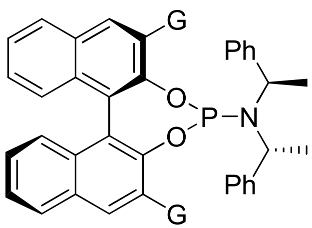
L6

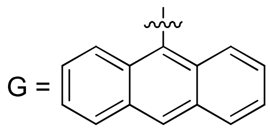


Ar = 3,5-(Me)$_2$C$_6$H$_3$;
(*R*)-Xylyl-BINAP (**L7**)

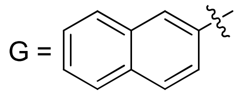


(a*R*)-**8**

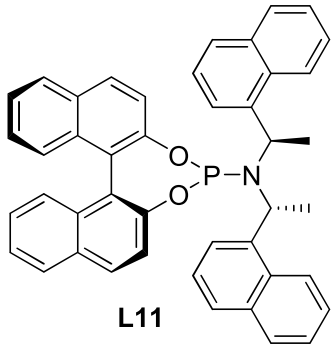




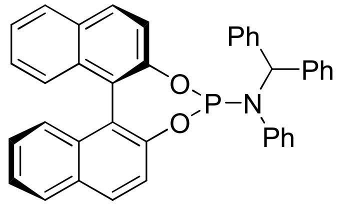
L9



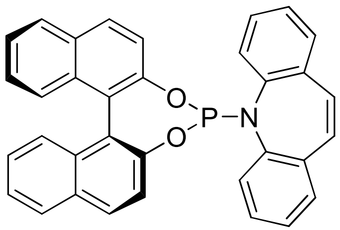
L10



L11

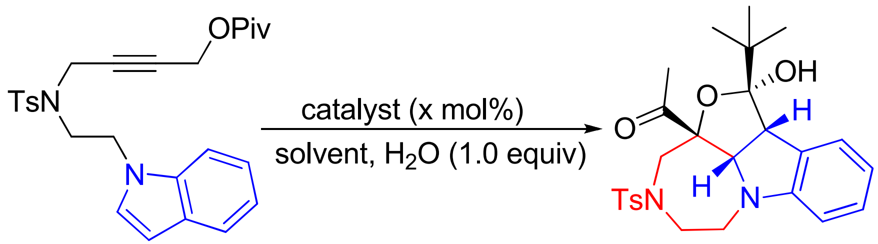


L12



L13

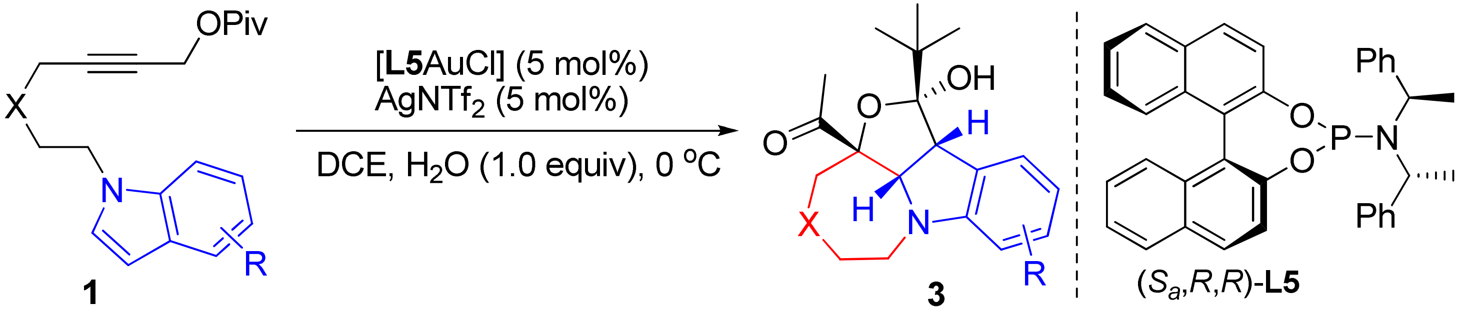
Optimization of the reaction conditions



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

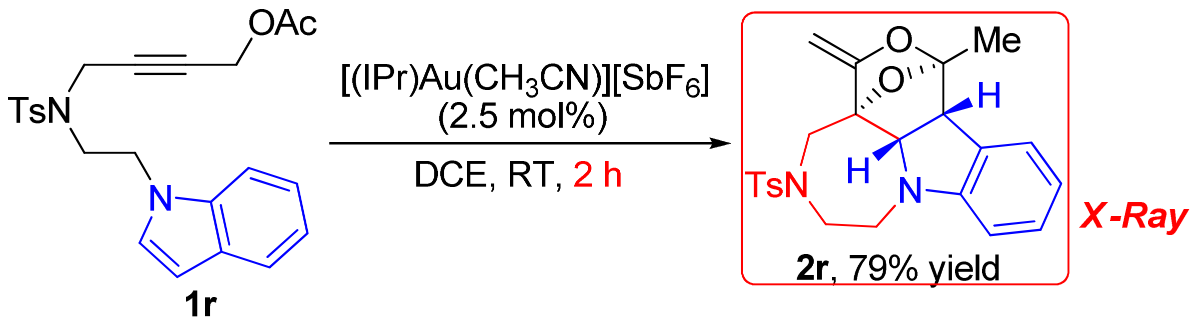
Substrate scope

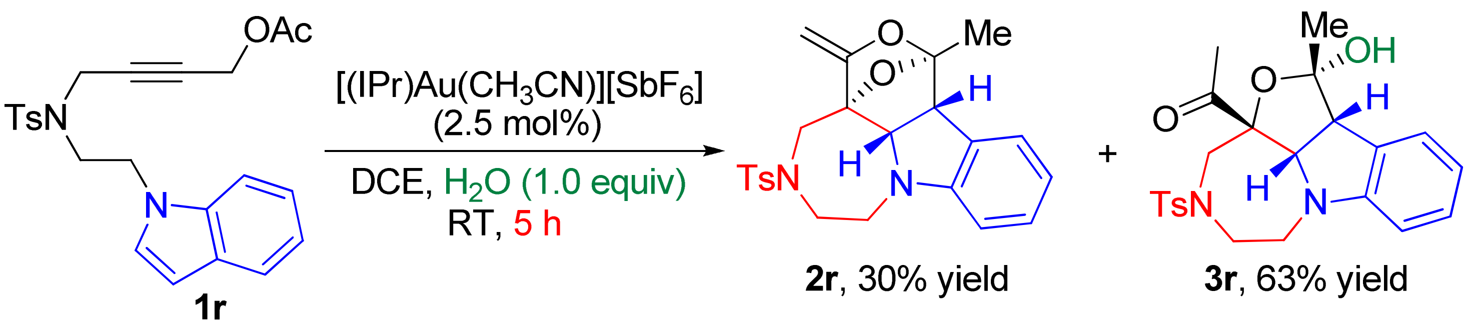


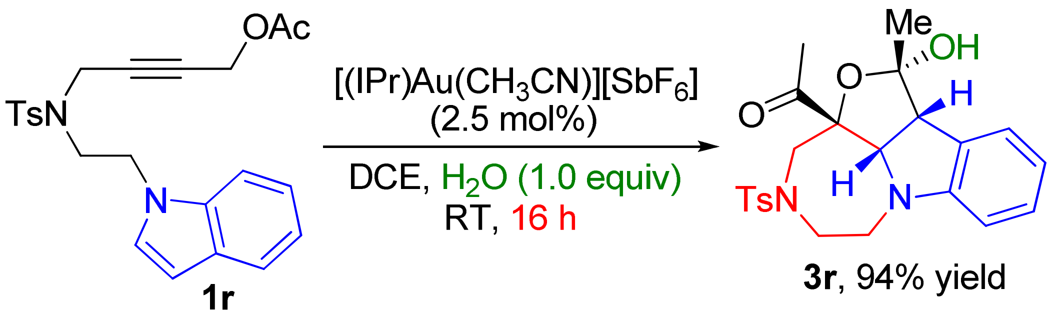
entry[a]	1	X	R	time [days]	3	yield [%][b]	ee [%][c]
1	**1b**	2-$MeC_6H_4SO_2N$	H	3	**3b**	30	74
2	**1c**	3-$MeC_6H_4SO_2N$	H	2	**3c**	60	80
3	**1d**	$PhSO_2N$	H	2	**3d**	43	90
4	**1e**	$MesSO_2N$	H	2	**3e**	51	83
5	**1f**	2,4,6-$^iPr_3C_6H_2SO_2N$	H	2	**3f**	40	91
6	**1h**	TsN	5-Me	2	**3h**	50	74
7	**1i**	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.

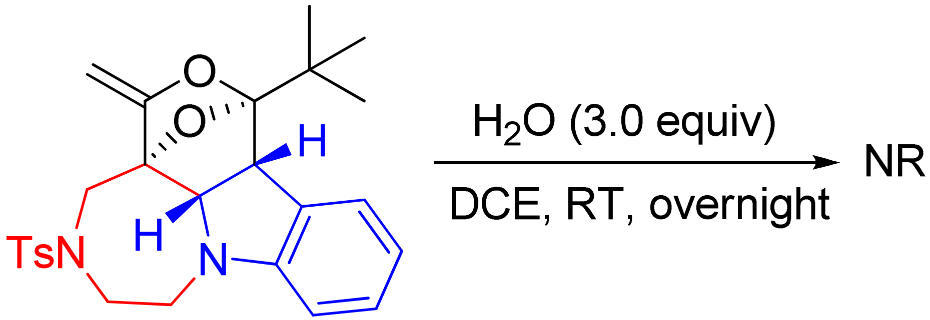
The control experiments



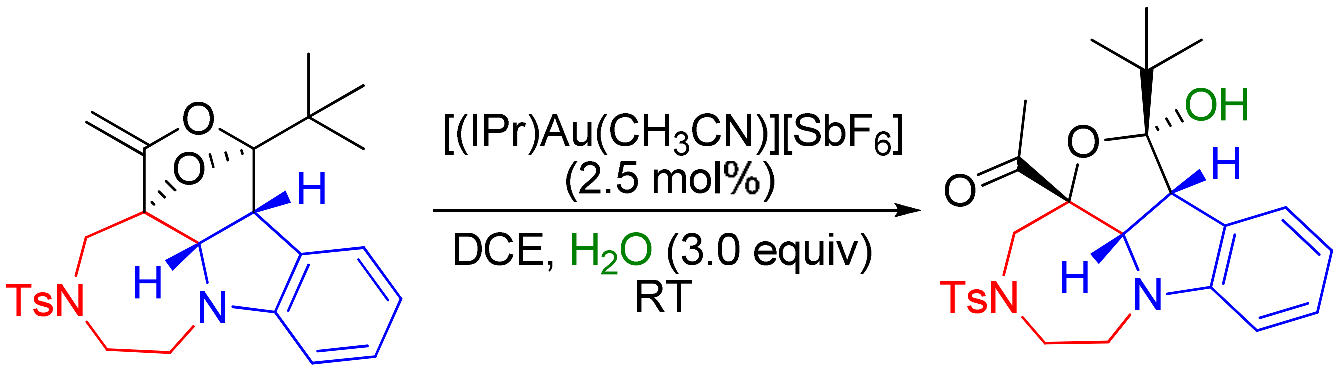




The control experiments

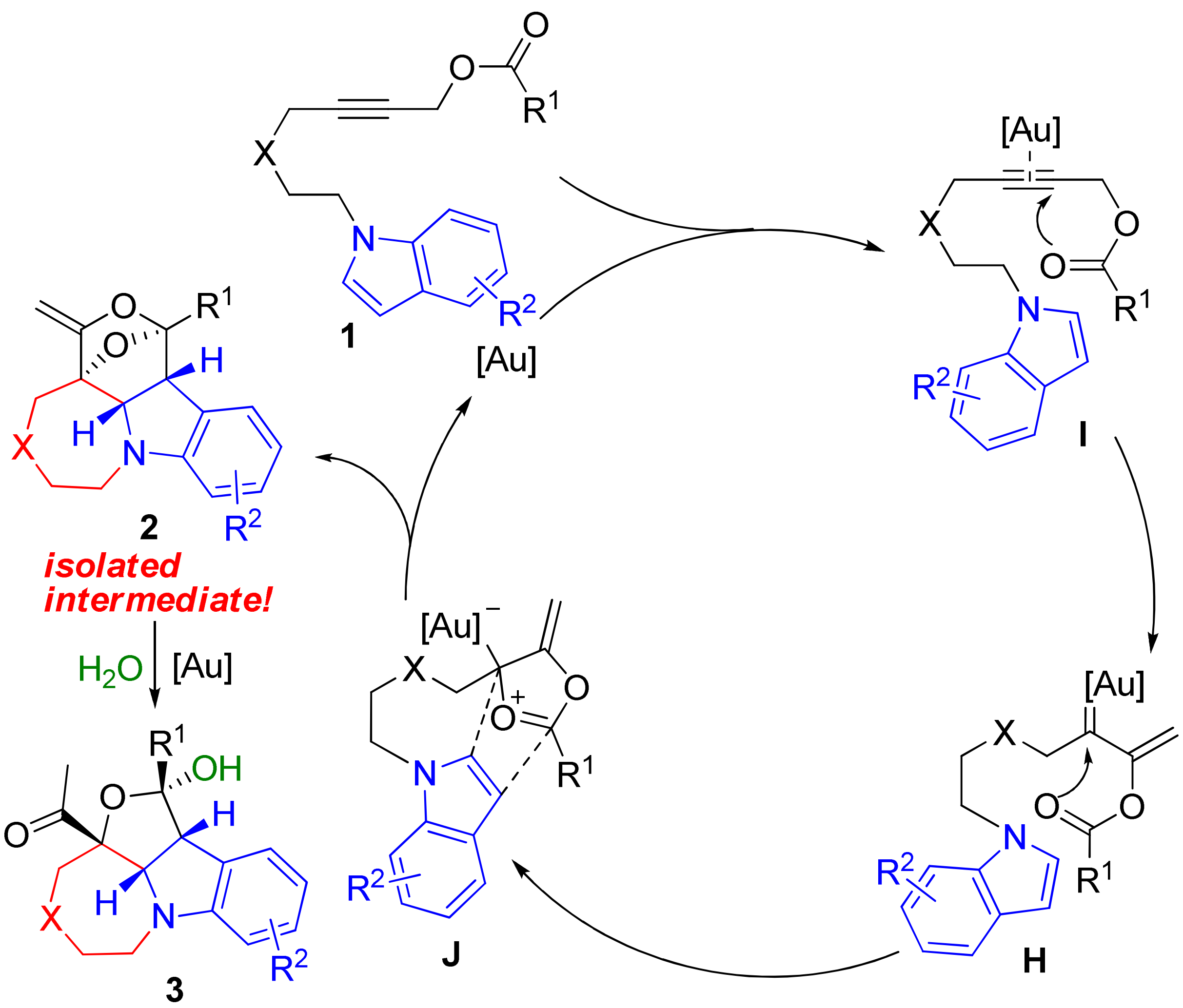


2a

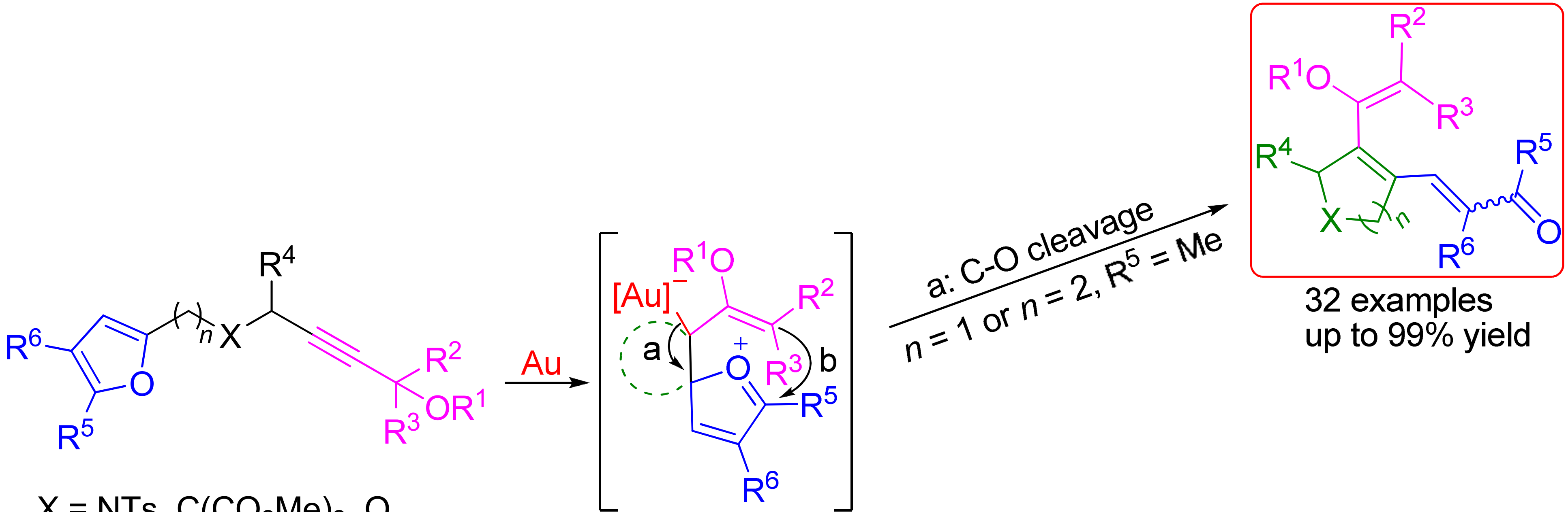


2a **3a**, 86% yield

A plausible mechanism



Gold(I)-catalyzed intramolecular cycloisomerization of α–yne furans



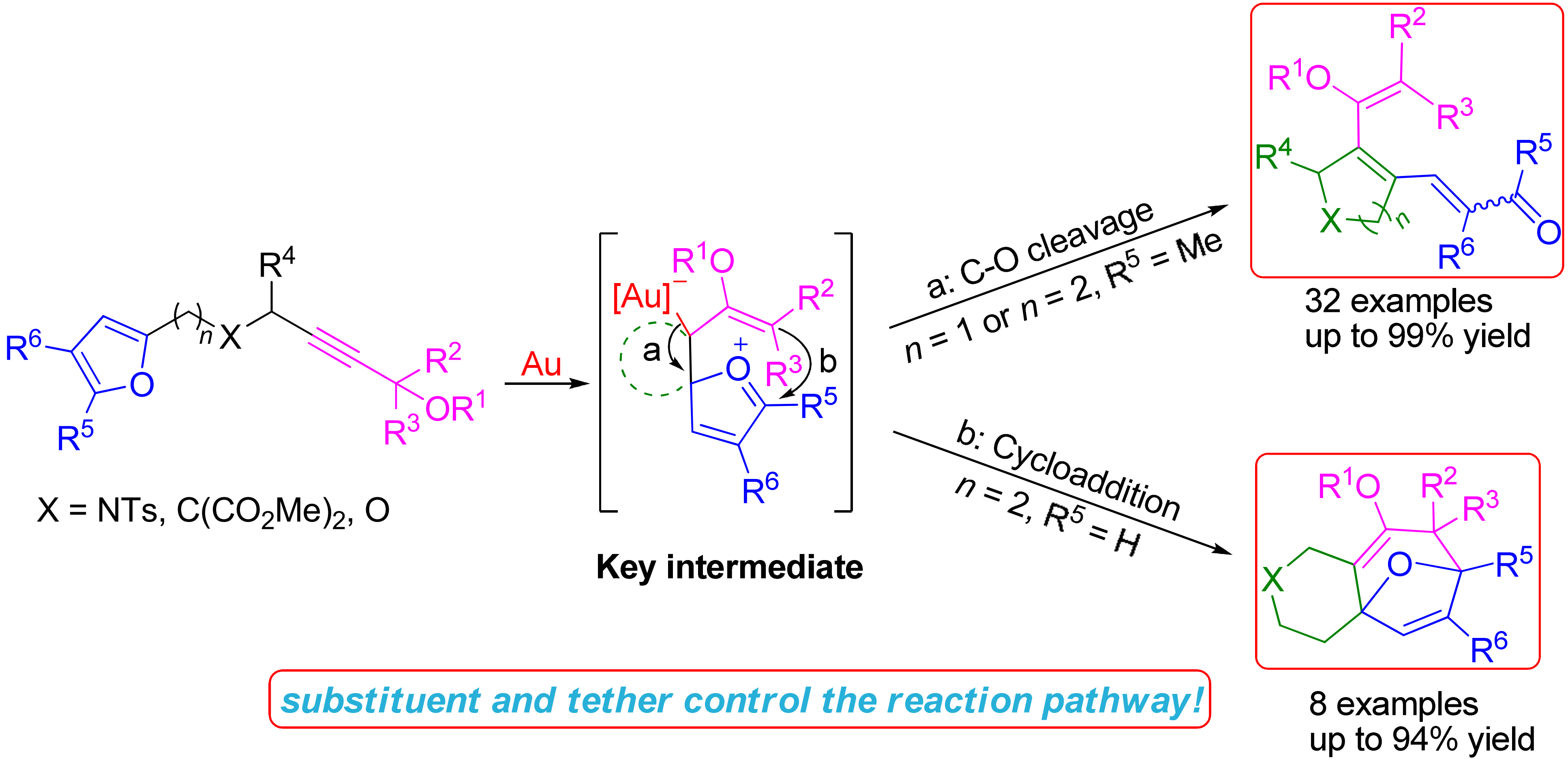
X = NTs, $C(CO_2Me)_2$, O

Key intermediate

32 examples
up to 99% yield

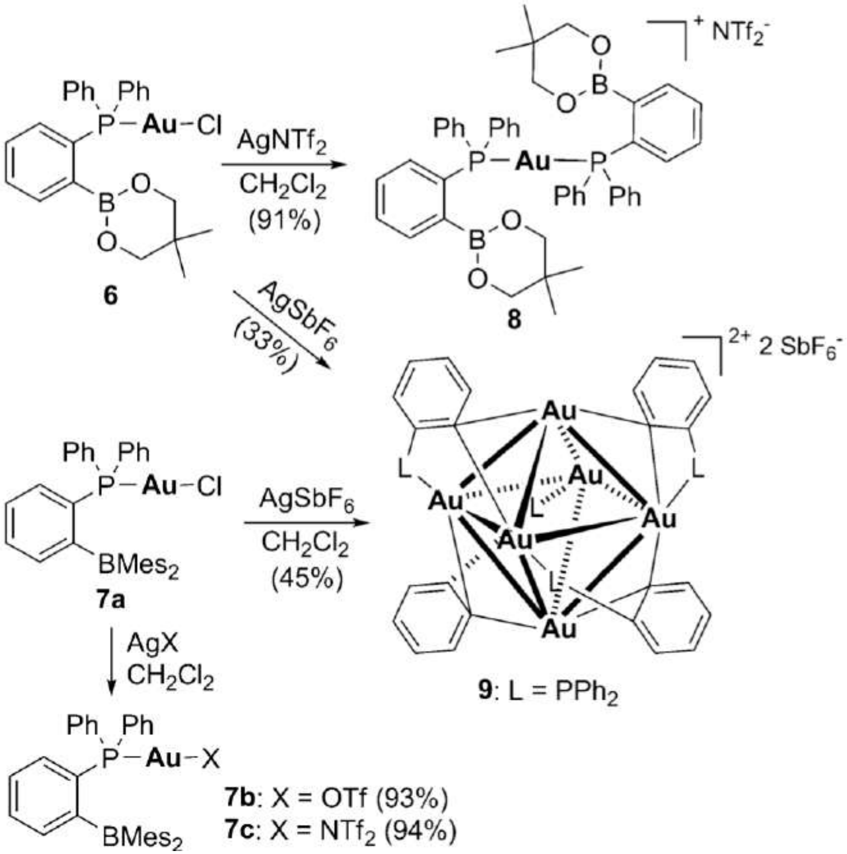
substituent and tether control the reaction pathway!

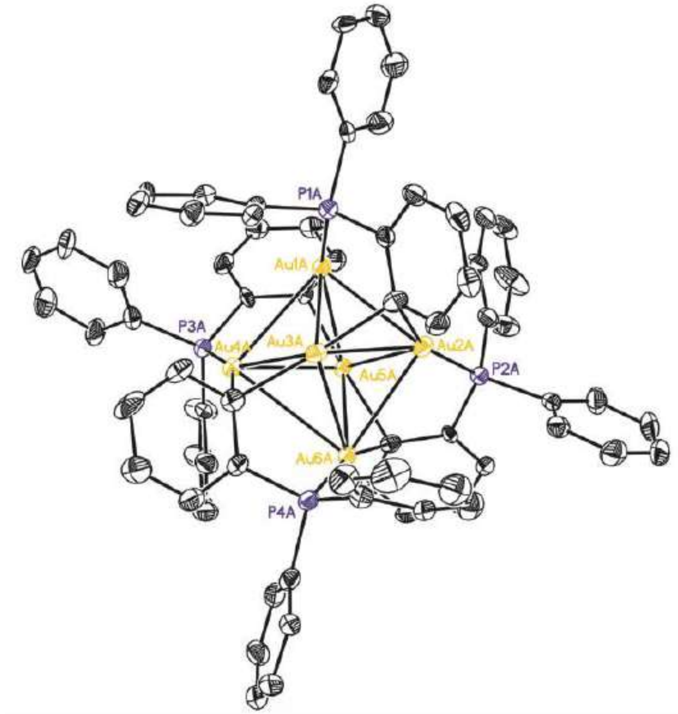
Gold(I)-catalyzed intramolecular cycloisomerization of α–yne furans

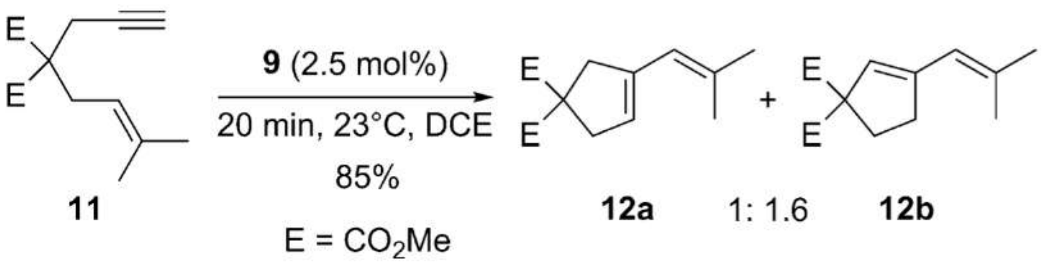


Yang, J.-M.; Tang, X.-Y.*; Shi, M.* *Chem. – Eur. J.* **2015**, *21*, 4534-4540.

Polynuclear Gold Clusters Synthesis

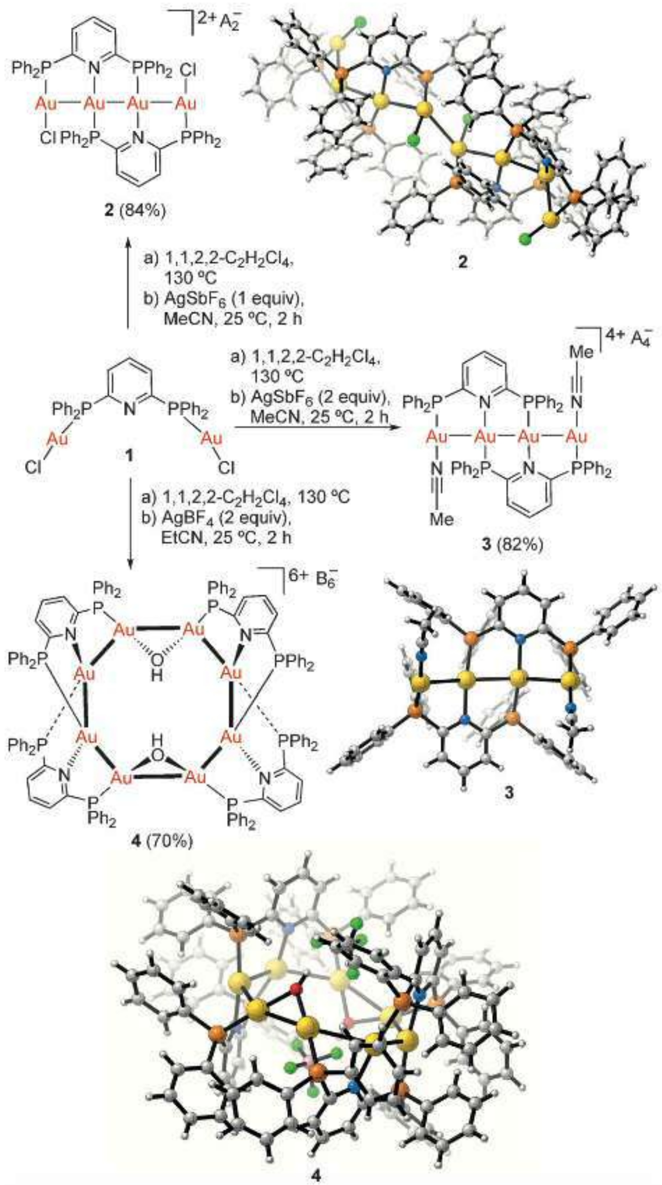


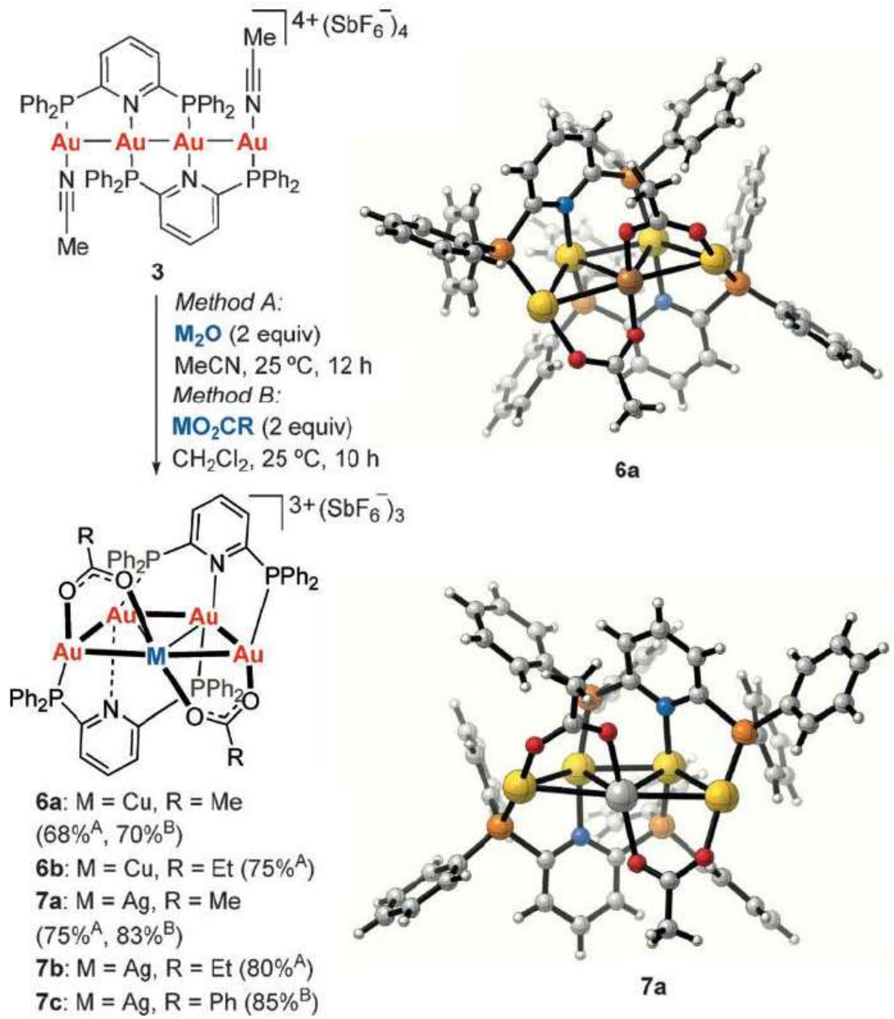




Smirnova, E. S.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2013**, *52*, 9023.

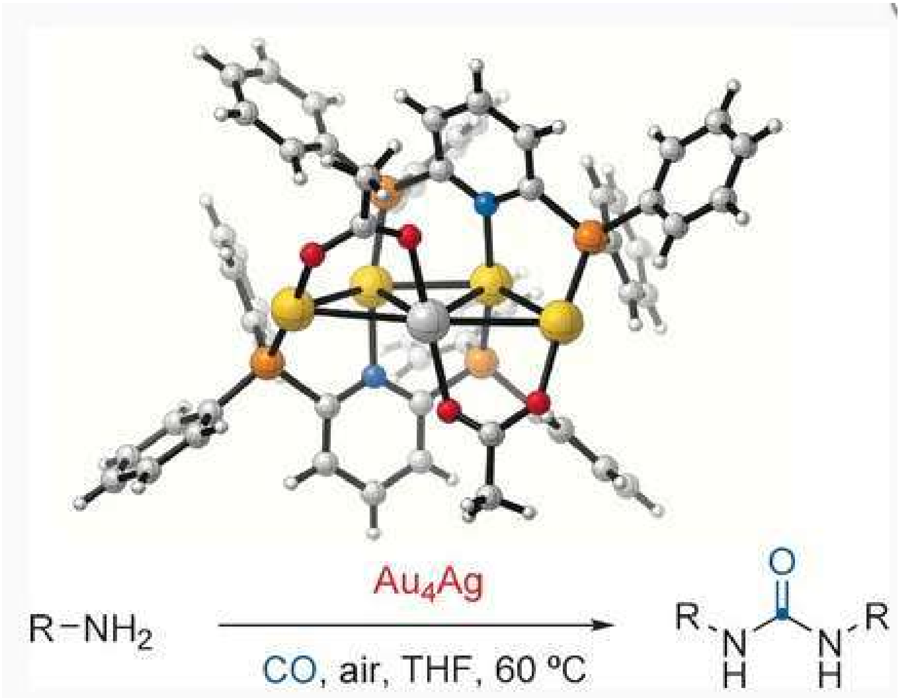
Polynuclear Gold Clusters Synthesis





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.

Polynuclear Gold Clusters Synthesis



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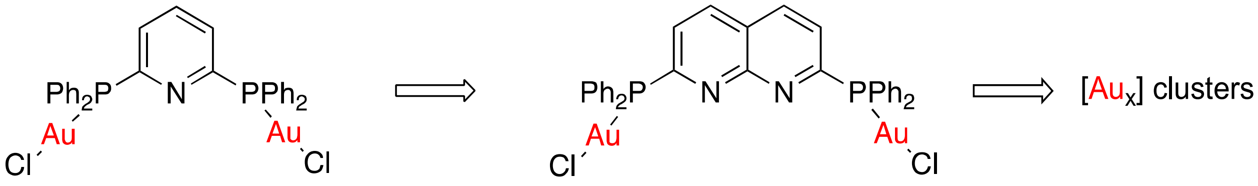
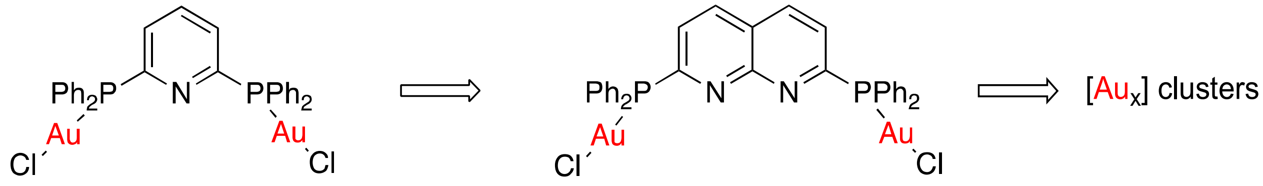
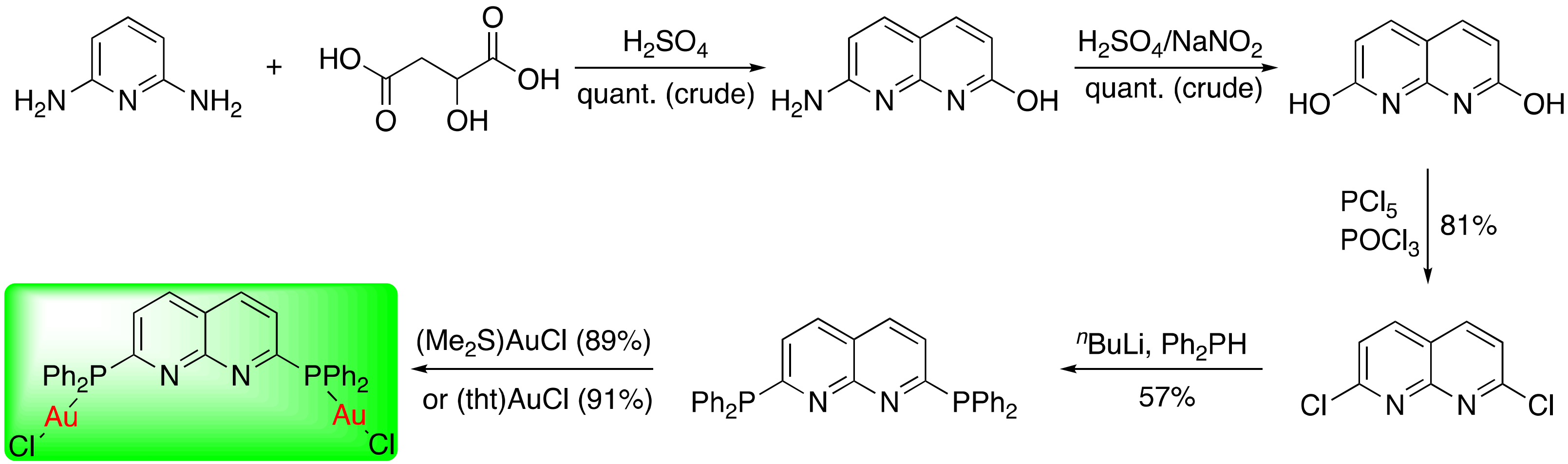
Ligand synthesis



Ligand synthesis

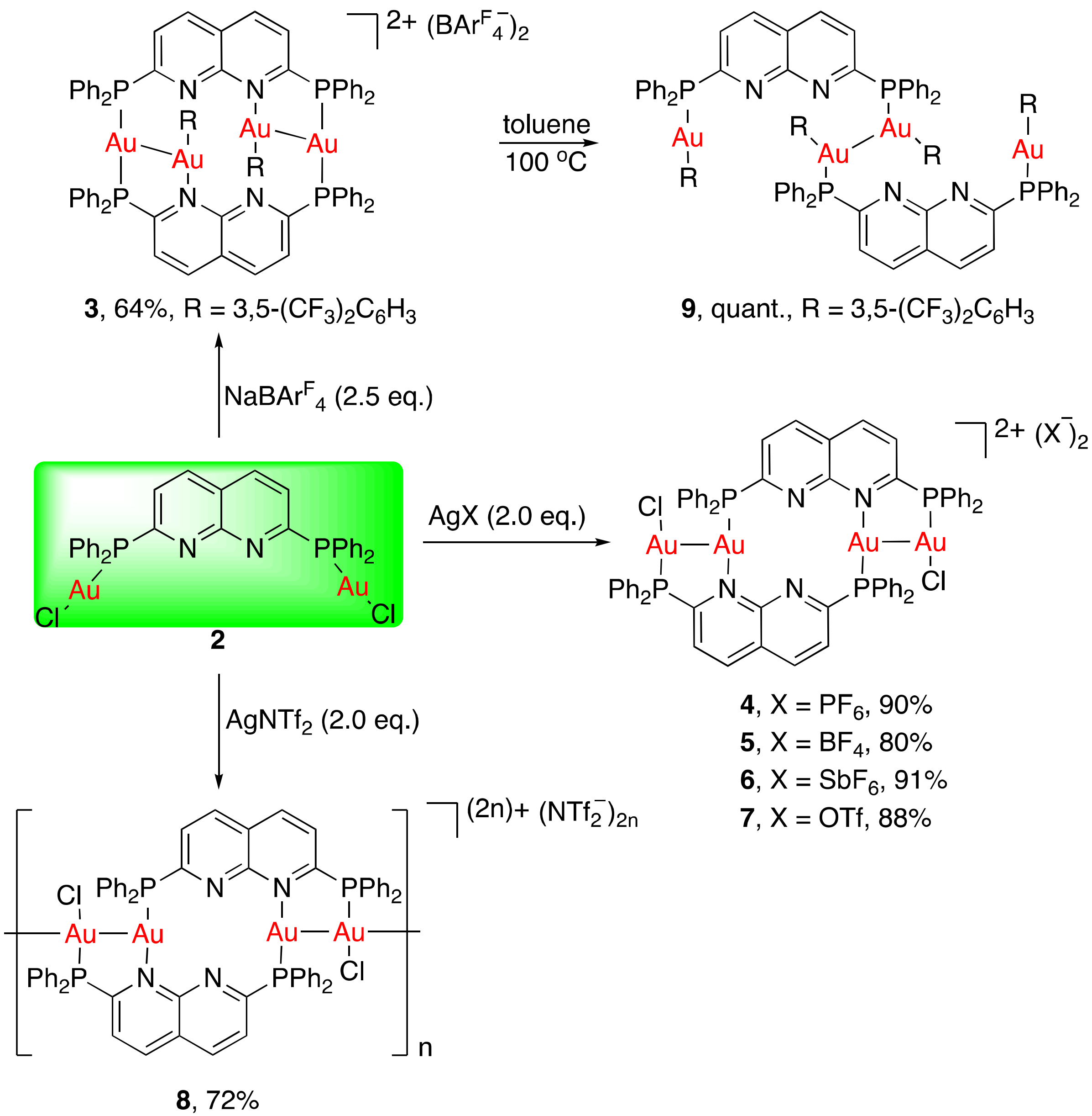




2 **1**

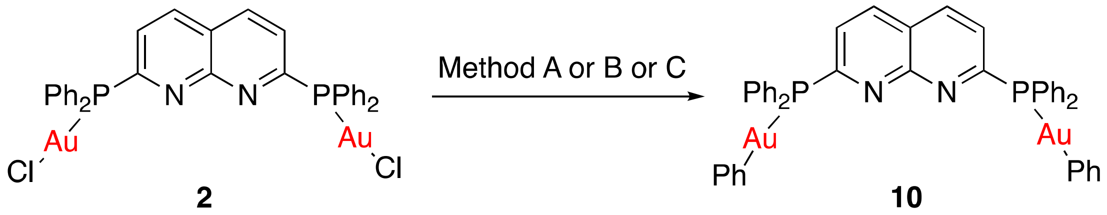
(a) Ziessel, R. *Tetrahedron Lett.* **1989**, *30*, 463-466. (b) Catalano, V. J.; Kar, H. M.; Bennett, B. L. *Inorg. Chem.* **2000**, *39*, 121-127.

Polynucler gold clusters synthesis

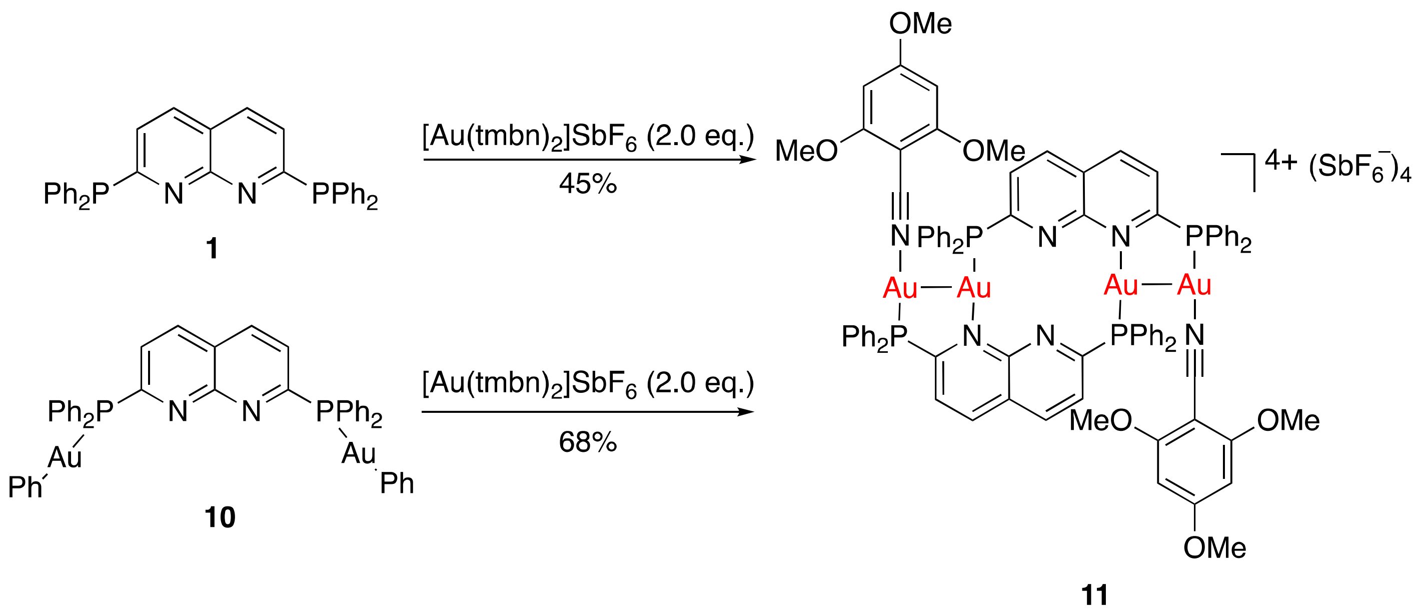


Yang, J.-M.; Echavarren, A. M.* **2018**, *To be submitted*.

Polynucler gold clusters synthesis

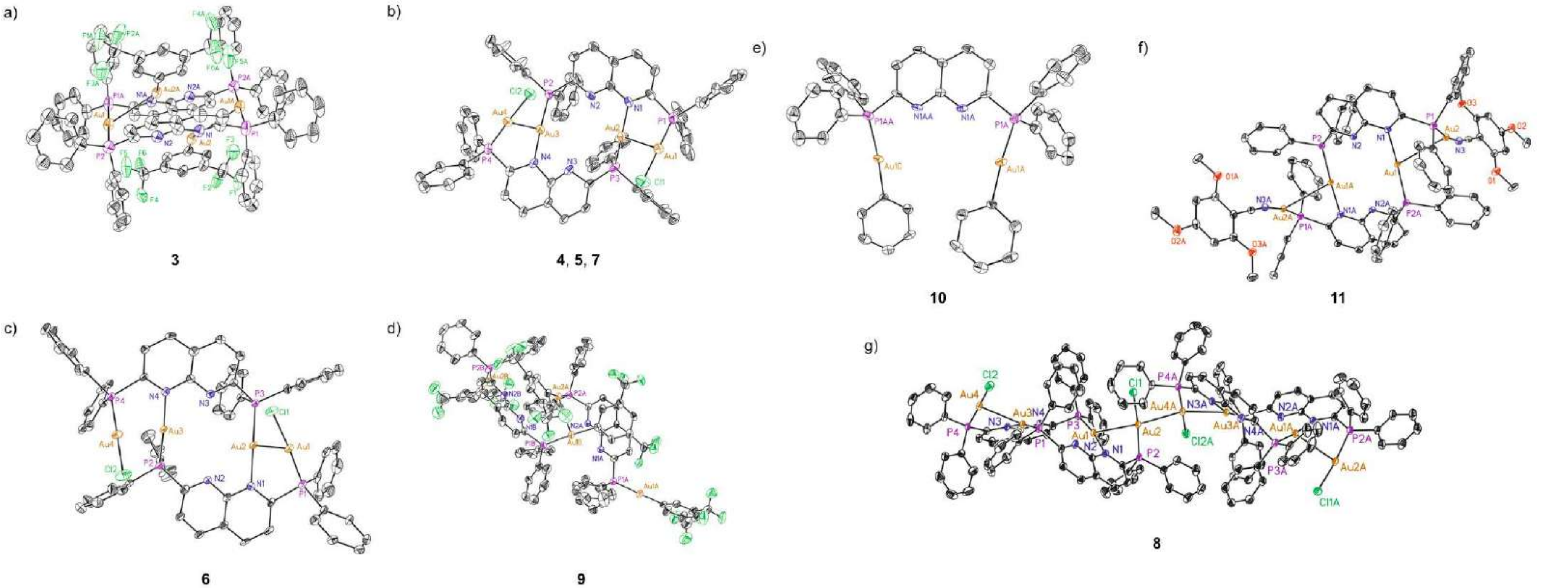


A: $NaBPh_4$ (2.5 eq.) rt, 98%; B: $PhB(OH)_2$ (2.5 eq.), Cs_2CO_3 (2.0 eq.), rt, 98%;
C: Me_3SnPh (4.0 eq.), Cs_2CO_3 (2.0 eq.), 50 ^oC, 83%



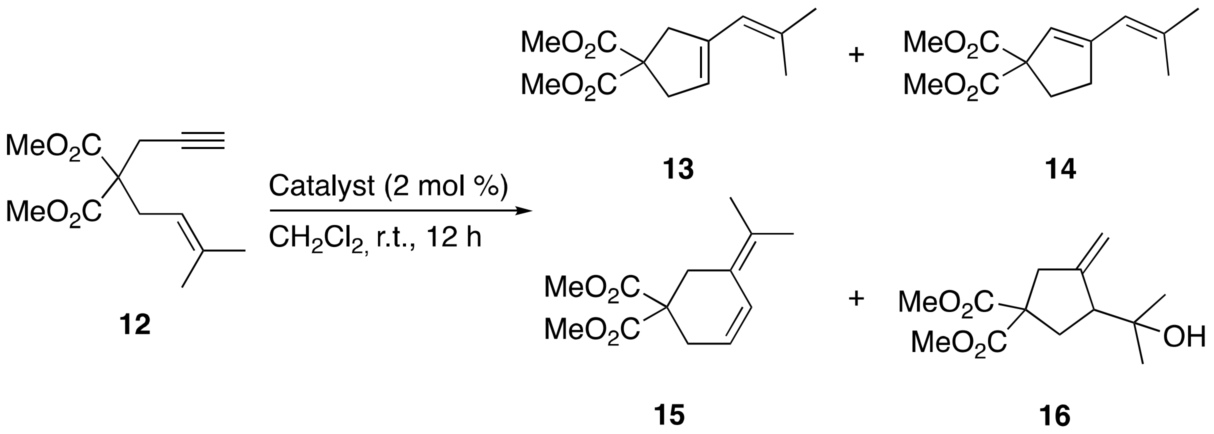
Yang, J.-M.; Echavarren, A. M.* **2018**, *To be submitted.*

Polynucler gold clusters synthesis



Yang, J.-M.; Echavarren, A. M.* **2018**, *To be submitted*.

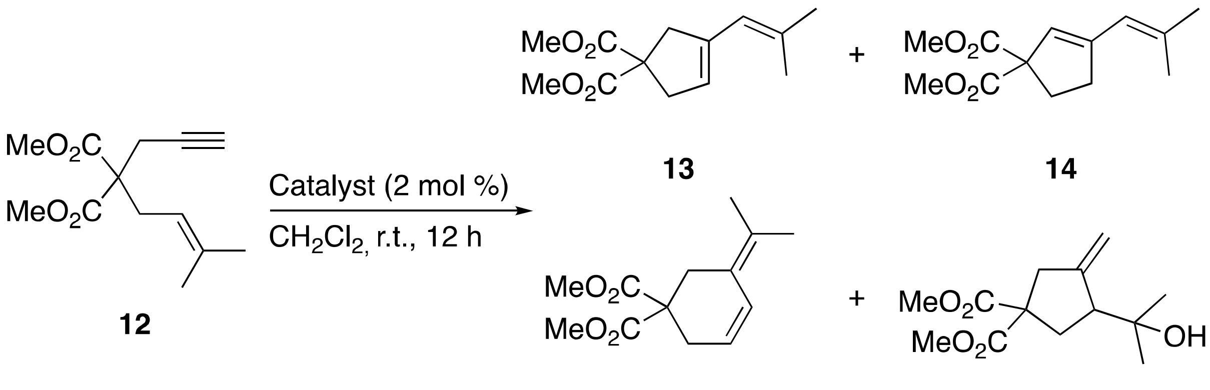
Catalytic studies



Entry[a]	Catalyst	Conv. [%][b]	Yield [%][b]			
			13	**14**	**15**	**16**
1	**3**, $\mathbf{L_2Au_4R_2(BAr^F{}_4)_2}$	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
8	**10**, $\mathbf{LAu_2Ph_2}$	0	0	0	0	0
9	**11**, $\mathbf{L_2Au_4(tmbn)_2(SbF_6)_4}$	100	63	0	35	0
10[d]	**11**, $\mathbf{L_2Au_4(tmbn)_2(SbF_6)_4}$	90	54	0	20	2

[a] Reaction conditions : **12** (0.1 mmol), cat. (2 mol %), CH_2Cl_2 (1.0 mL). [b] Conversions 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. [d] 0.5 mol % of **11**. L = 2,9-bis(diphenylphosphino)-1,8-naphthyridine (dppn). R = 3,5-$(CF_3)_2C_6H_3$. tmbn = 2,4,6-trimethoxybenzonitrile.

Catalytic studies



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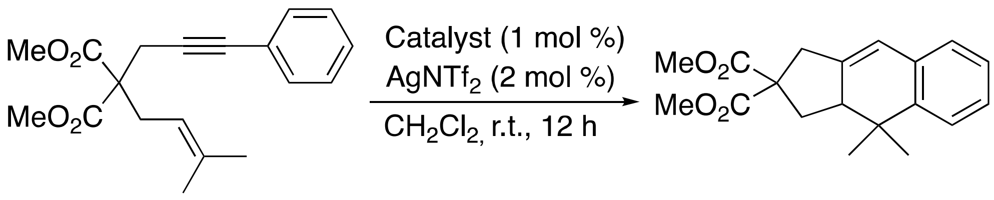
4	**5**, $\mathbf{L_2Au_4Cl_2(BF_4)_2}$	42	28	0	3	9
5	**6**, $\mathbf{L_2Au_4Cl_2(SbF_6)_2}$	100	74	0	17	4
6	**7**, $\mathbf{L_2Au_4Cl_2(OTf)_2}$	100	22	0	23	0
7	**8**, $\mathbf{[L_2Au_4Cl_2(NTf_2)_2]_n}$	100	14	27	29	0
8	**10**, $\mathbf{LAu_2Ph_2}$	0	0	0	0	0
9	**11**, $\mathbf{L_2Au_4(tmbn)_2(SbF_6)_4}$	100	63	0	35	0
10[d]	**11**, $\mathbf{L_2Au_4(tmbn)_2(SbF_6)_4}$	90	54	0	20	2

[a] Reaction conditions : **12** (0.1 mmol), cat. (2 mol %), CH_2Cl_2 (1.0 mL). [b] Conversions 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. [d] 0.5 mol % of **11**. L = 2,9-bis(diphenylphosphino)-1,8-naphthyridine (dppn). R = 3,5-$(CF_3)_2C_6H_3$. tmbn = 2,4,6-trimethoxybenzonitrile.

Catalytic studies

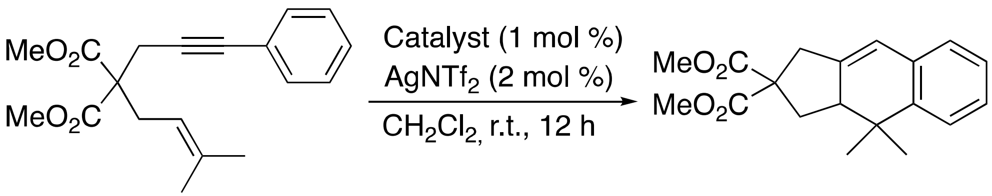


17 **18**

Entry[a]	Catalyst	Conv. [%][b]	Yield [%][b]
1	**3**, $L_2Au_4R_2(BAr^F{}_4)_2$	35	23
2[c]	**3**, $L_2Au_4R_2(BAr^F{}_4)_2$	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	**10**, LAu_2Ph_2	28	25
10[d]	**11**, $L_2Au_4(tmbn)_2(SbF_6)_4$	79	59
11	**11**, $L_2Au_4(tmbn)_2(SbF_6)_4$	100	60
12	-	39[e]	0

[a] Reaction conditions : **17** (0.1 mmol), cat. (1 mol %), AgNTf$_2$ (2 mol %), CH$_2$Cl$_2$ (1.0 mL). [b] Conversions and yields were determined by ^{1}H 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 **17**. L = 2,9-bis(diphenylphosphino)-1,8-naphthyridine (dppn). R = 3,5-(CF$_3$)$_2$C$_6$H$_3$. tmbn = 2,4,6-trimethoxybenzonitrile.

Catalytic studies



17 **18**

Entry[a]	Catalyst	Conv. [%][b]	Yield [%][b]
1	**3**, $L_2Au_4R_2(BAr^F{}_4)_2$	35	23
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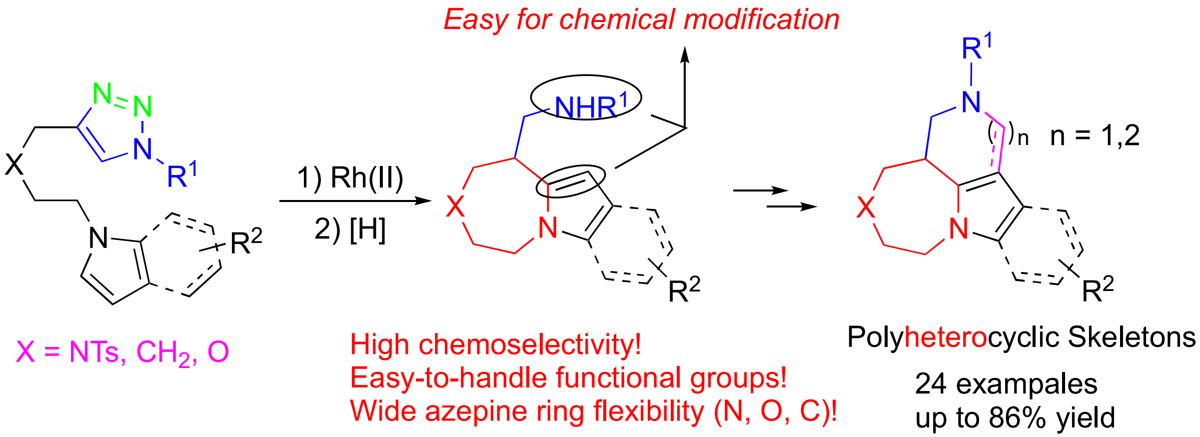
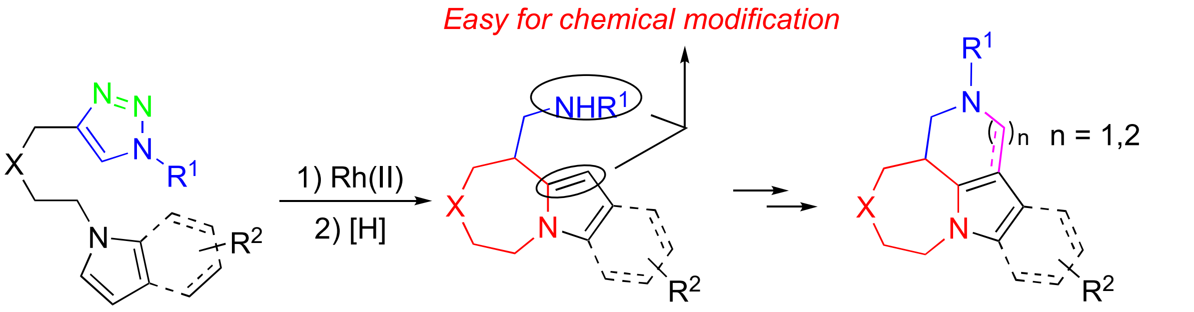
[a] Reaction conditions : **17** (0.1 mmol), cat. (1 mol %), $AgNTf_2$ (2 mol %), CH_2Cl_2 (1.0 mL). [b] Conversions and yields were determined by ^1H NMR spectroscopy using 1,4-diacetylbenzene as internal standard. Value within parentheses is that of the yield of the isolated product after column chromatography. [c] $NaBAr^F{}_4$ (2 mol %) was added instead of $AgNTf_2$. [d] Absence of $AgNTf_2$. [e] Partial decomposition of **17**. L = 2,9-bis(diphenylphosphino)-1,8-naphthyridine (dppn). R = 3,5-$(CF_3)_2C_6H_3$. tmbn = 2,4,6-trimethoxybenzonitrile.

Research Summary

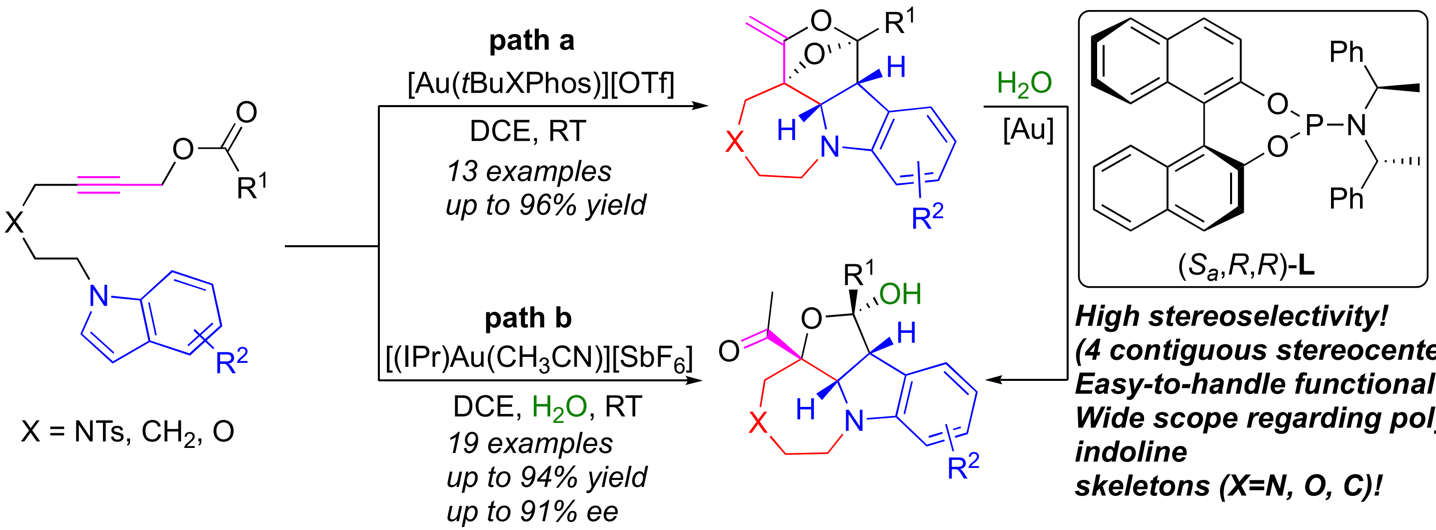


Research Summary



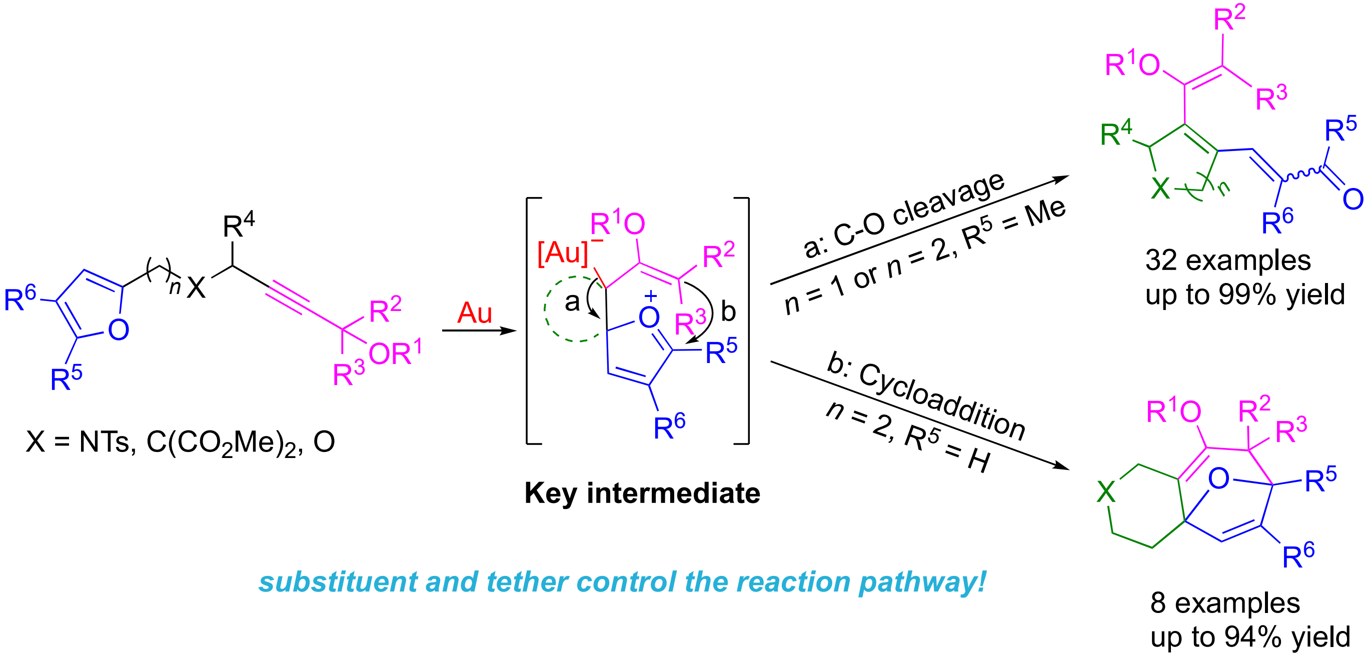
High chemoselectivity!
Easy-to-handle functional groups!
Wide azepine ring flexibility (N, O, C)!

Polyheterocyclic Skeletons
24 exampales
up to 86% yield



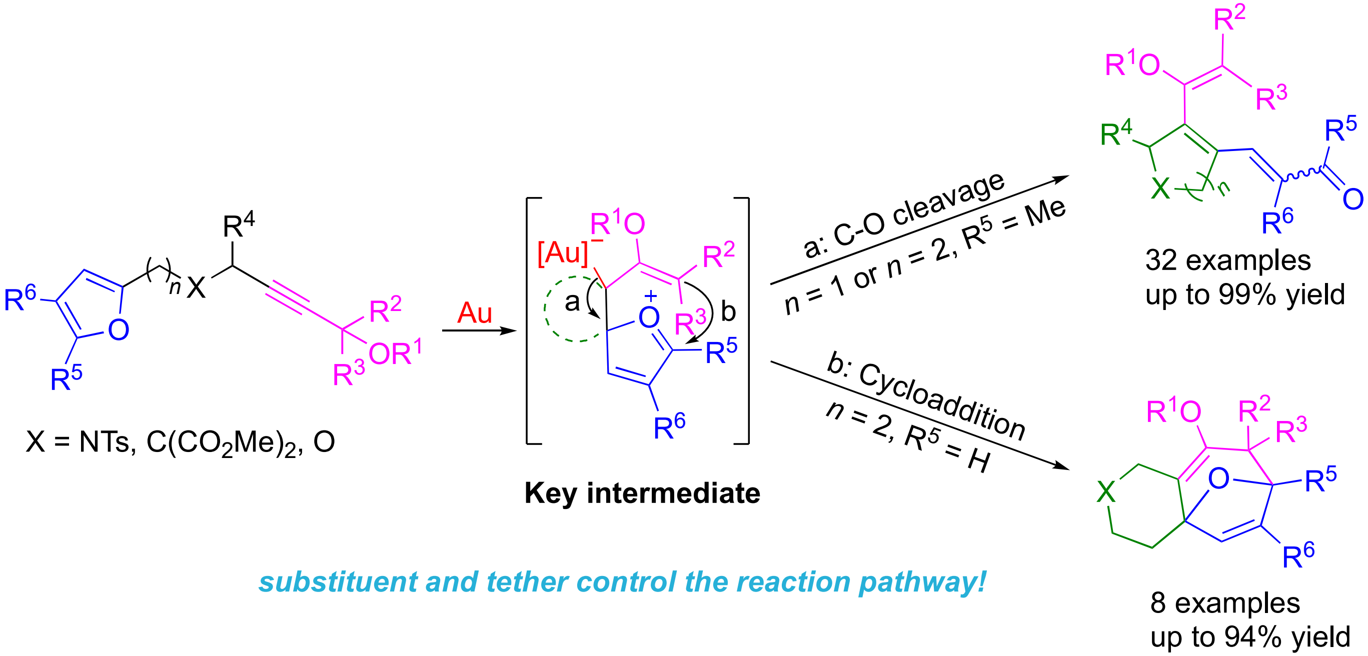
High stereoselectivity!
(4 contiguous stereocenters)!
Easy-to-handle functional groups!
Wide scope regarding polycyclic indoline skeletons (X=N, O, C)!

Research Summary

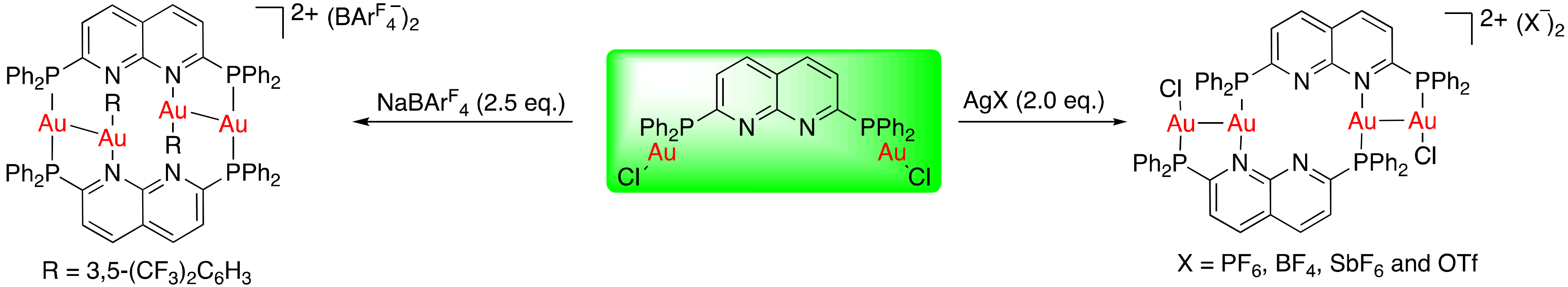


substituent and tether control the reaction pathway!

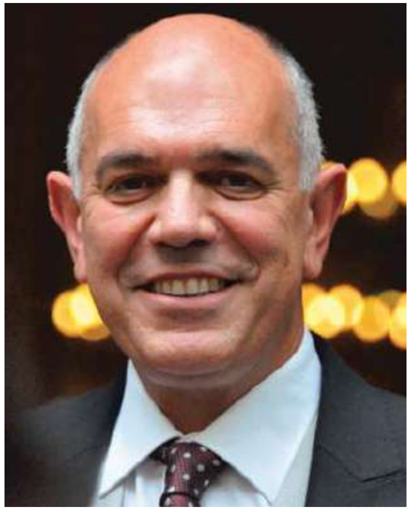
Research Summary



substituent and tether control the reaction pathway!



Acknowledgements



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

THE FRAMEWORK PROGRAMME FOR RESEARCH AND INNOVATION
HORIZON 2020

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Thank you for your attention !