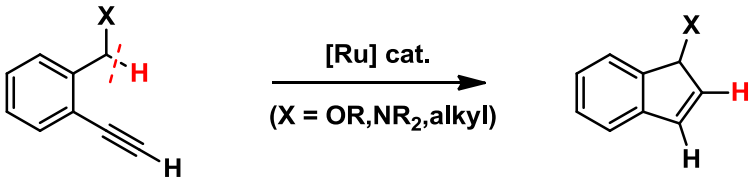
Intramolecular C-H Activation through Gold(I)-Catalyzed Reaction of Iodoalkynes

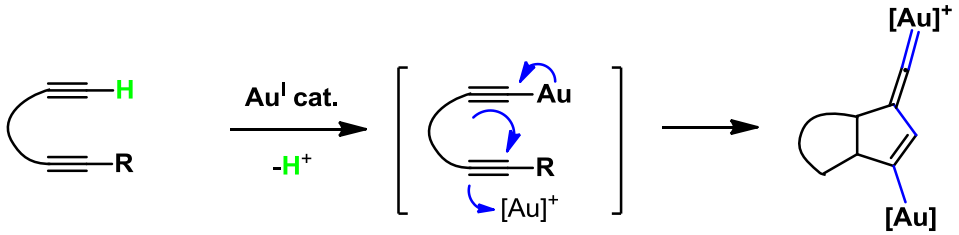
P. M. Poladura, E. Rubio, José M. Gonzalez. ***Angew. Chem. Int. Ed.*** **2015,** ***54*****, 1**

STEREO SEMINAR 05/02/2015 - Yajun REN

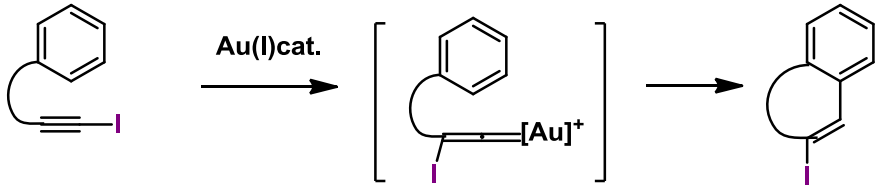
Ruthenium-catalysed terminal alkyne activation: stepwise 1,5-hydride shift

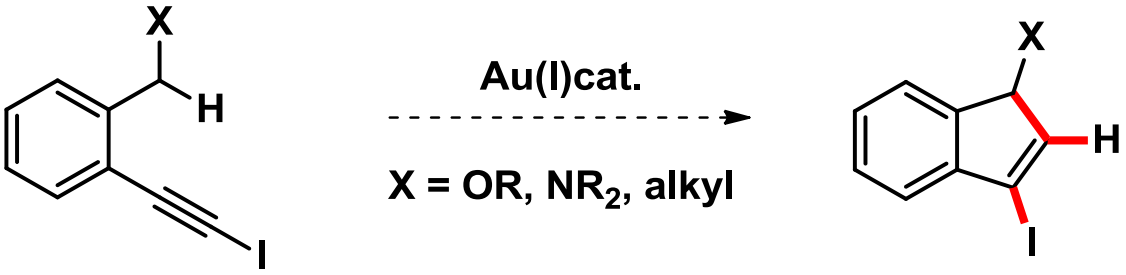


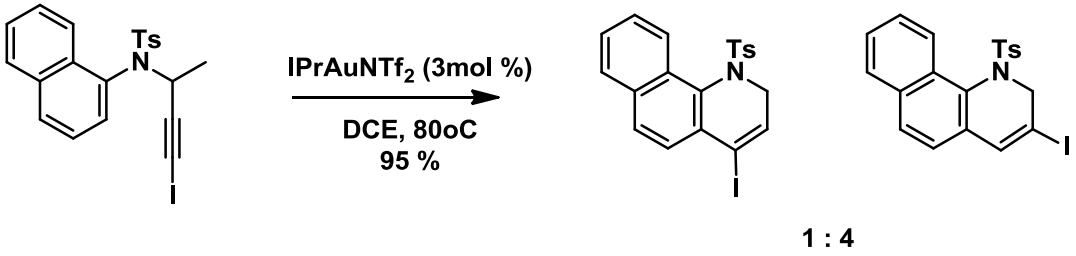
Gold vinylidenes from gold-catalysed dual activation



Gold vinylidenes from activation of iodoalkynes

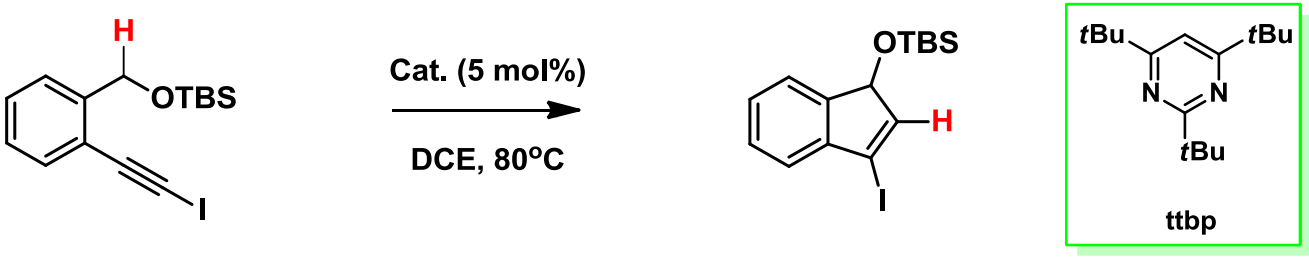



X
H
I
Au(I)cat.
X = OR, NR2, alkyl
X
H
I


Ts
N
I
IPrAuNTf2 (3mol %)
DCE, 80oC
95 %
Ts
N
I
Ts
N
I

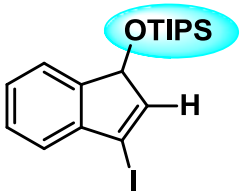
1 : 4

Optimization of cycloisomerization conditions



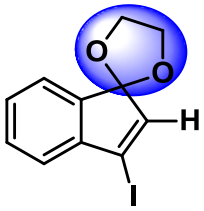
Entry	Catalyst	Additive (equiv)	t [h]	Conv. [%]	Yield [%]
1	$IPrAuNTf_2$	-	1	100	decomposition
2	$JohnPhosAuNTf_2$	-	24	10	0
3	$(RO)_3PAuNTf_2$	-	24		0
4	$Ph_3PAuNTf_2$	-	24	14	0
5	$IPrAuNTf_2$	ttbp (0.25)	2.5	100	60
6	$IPrAuNTf_2$	dtmp(0.25)	24	65	24
7	$IPrAuNTf_2$	lut (0.25)	24	24	0
8	$IPrAuNTf_2$	tBuOK(0.25)	24	65	20
9	$IPrAuNTf_2$	nor(0.25)	18	100	6
10	$IPrAuNTf_2$	ttbp (0.1)	1	100	61

Indene derivatives through C-H bond activation



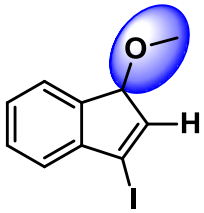
15 min, 26%

1h, 91%



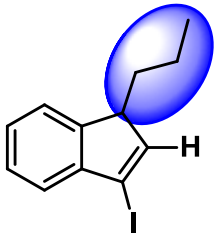
1h, 79%

1h, 91%



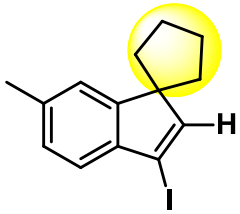
10 min, 45%

1.5 h, 87%



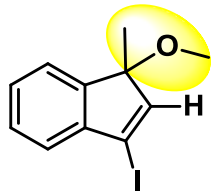
15 min, 90%

1h, 97%



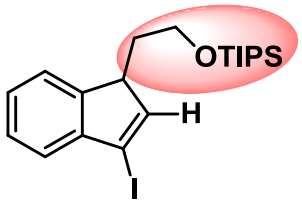
1.5h, 89%

2.25h, 93%



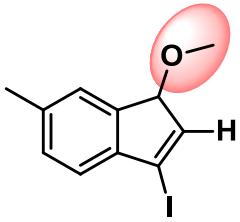
decomposition

1.5h, 84%



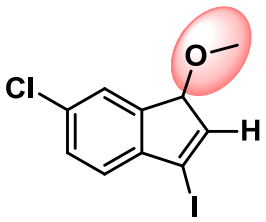
4h, 28%

18h, 84%



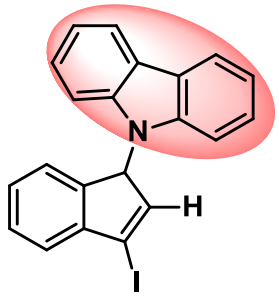
decomposition

40 min, 78%



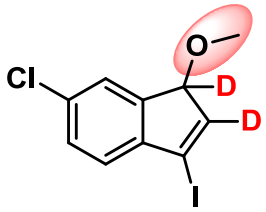
35min, 89%

1h, 96%



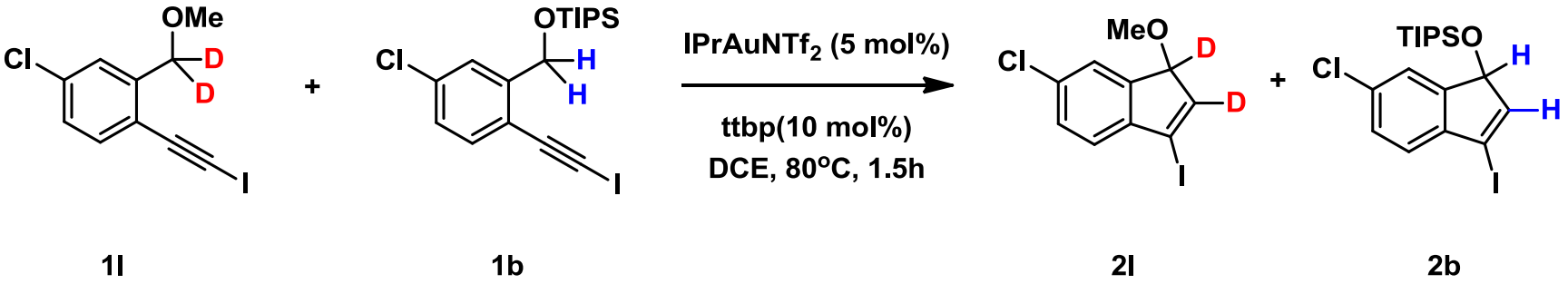
24h, 32%

1.5h, 78%

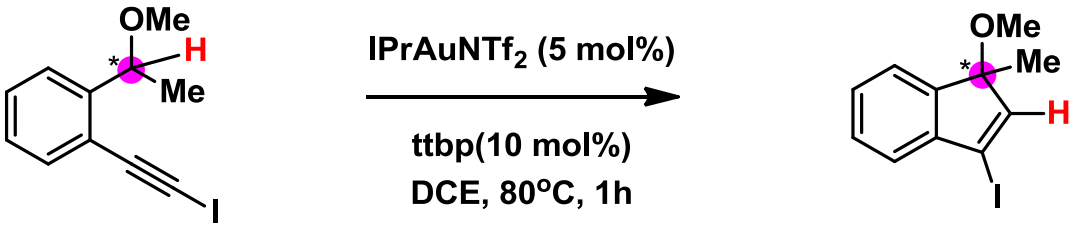


4h, 72%

Mechanism insights



1l 1b 2l 2b

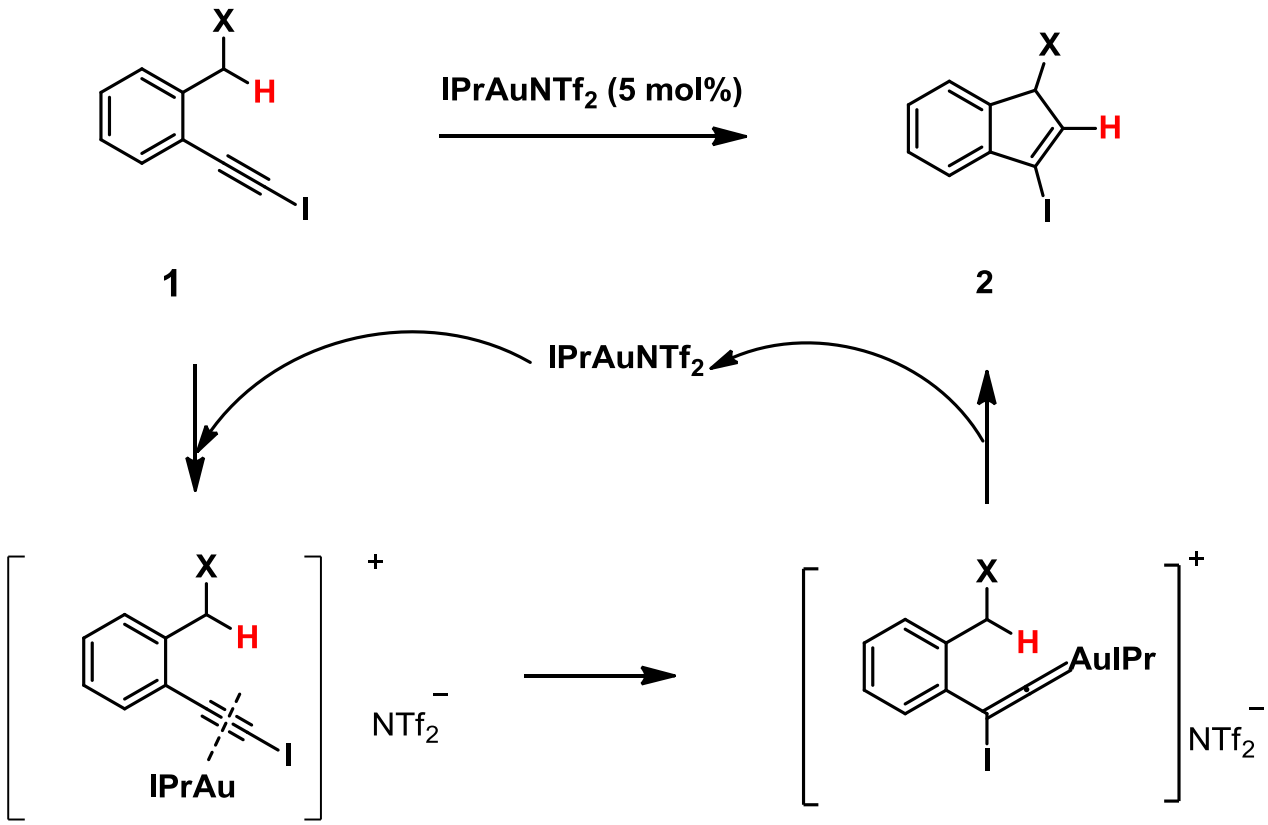


e.r. 86:14

74%

e.r. 82:18

Proposed mechanism



Conclusion

- A new catalytic transformation of iodoalkynes is presented
- A wide range of iodine-substituted indenes are obtained
- This study reveals a distinct reaction path for C-H insertion reactions involving metal vinylidenes
- The function of additive is still not clear

Thank you for your attention