Coinage Metal Catalyzed New Reactions

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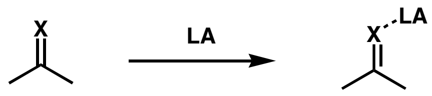
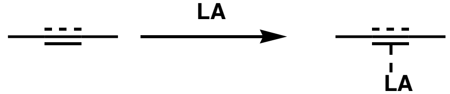
2008, 9, 30 IASOC, Ischia, Italy

σ-Electrophilic Lewis Acids



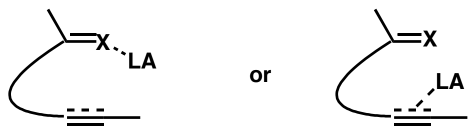
σ-binding
LA = BCl_3, $AlCl_3$, etc.
X = O, N

π-Electrophilic Lewis Acids



π-binding
LA = AuCl, $PtCl_2$, etc.

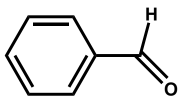
If there are two functional groups (C=X and ≡) in a molecule,



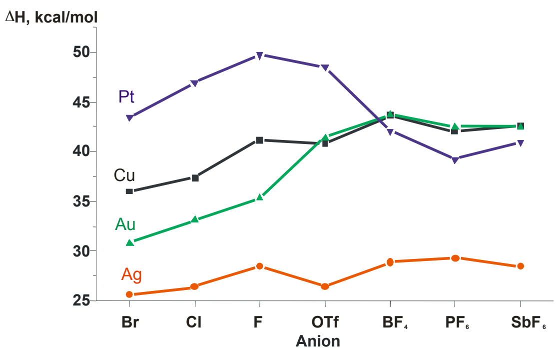
$$LA + S \xrightarrow{\Delta H} LA\text{--}S$$

S = Benzaldehyde

LA	BCl_3	$MgCl_2$	CuCl	$CuCl_2$	AuCl	$AuCl_3$	$PtCl_2$
−ΔH	18.9	34.5	37.4	25.4	33.1	35.9	46.9



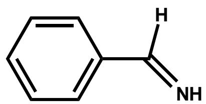
1



$$LA + S \xrightarrow{\Delta H} LA\text{--}S$$

S = Benzimine

LA	BCl_3	$MgCl_2$	CuCl	$CuCl_2$	AuCl	$AuCl_3$	$PtCl_2$
−ΔH	42.1	44.2	51.8	41.2	53.6	60.3	71.5



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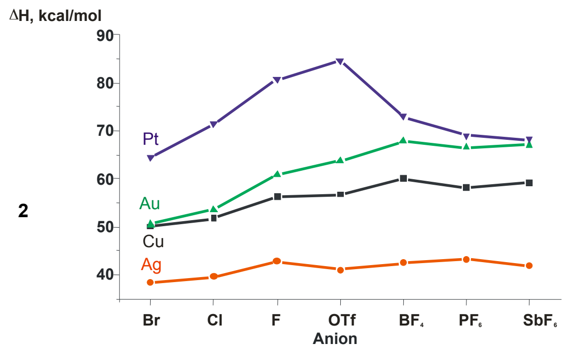
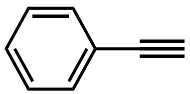


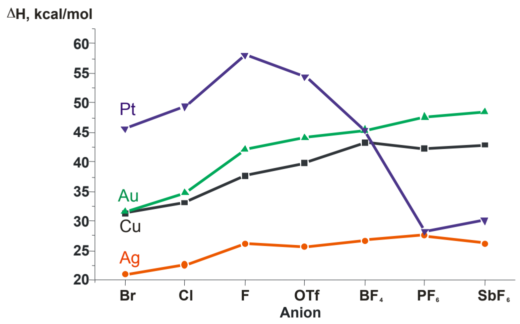
$$LA + S \xrightarrow{\Delta H} LA\text{- -}S$$

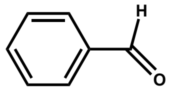
S = Phenylacetylene

LA	BCl_3	$MgCl_2$	CuCl	$CuCl_2$	AuCl	$AuCl_3$	$PtCl_2$
−ΔH	0.9	15.2	33.1	14.3	34.7	32.5	49.4

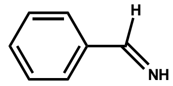


3





1



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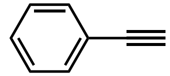
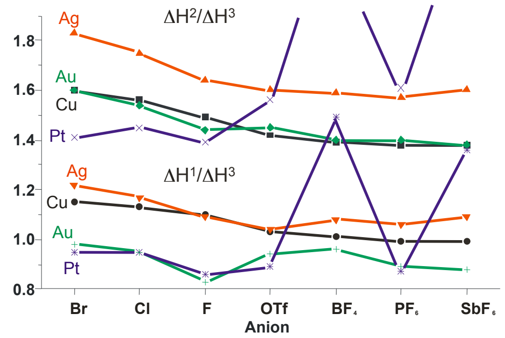


3

LA	BCl_3	$MgCl_2$	CuCl	$CuCl_2$	AuCl	$AuCl_3$	$PtCl_2$
$\Delta H^1/\Delta H^3$	21.0	2.3	1.1	1.8	1.0	1.1	1.0
$\Delta H^2/\Delta H^3$	46.7	2.9	1.6	2.9	1.5	1.9	1.4



Conclusions

(1) **CuCl and AuCl are comparable in strength of binding and preference for π-binding to $PtCl_2$, but are much more soluble.**

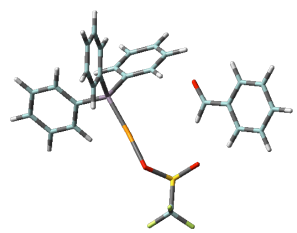
(2) **Relative ability to bind PhC≡CH increases with decreasing nucleophilicity (Br<Cl<F).**

(3) **Metals in higher oxidation state ($CuCl_2$, $AuCl_3$) decrease relative ability for carbon-carbon multiple bonds activation.**

(3) **The least nucleopholic anions (PF_6, SbF_6) increase the relative affinity to the carbon-carbon multiple bonds.**

(4) **$(Ph_3P)AuCl$; ΔH_3 and ΔH_4 are endothermic, 4.9 & 5.5 Kcal. $(Ph_3P)AuOTf$; slightly exothermic, - 0.5 & - 3.3 Kcal.**

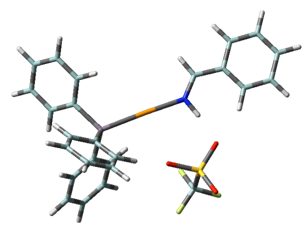
Influence of triphenylphosphine ligation



$(Ph_3P)AuOTf$ + benzaldehyde

ΔH = - 9.5 kcal/mol

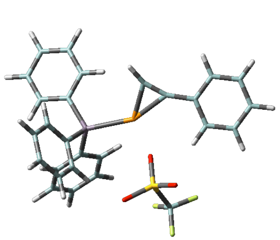
(no activation of aldehyde)

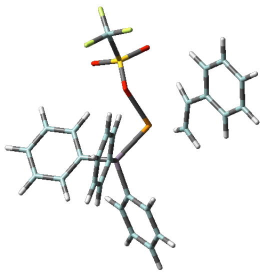


$(Ph_3P)AuOTf$ + benzimine

ΔH = - 28.8 kcal/mol

Influence of triphenylphosphine ligation





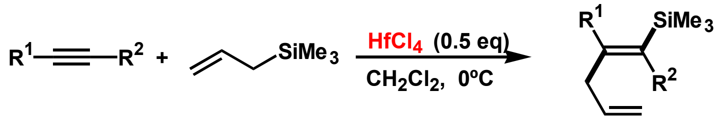
(Ph$_3$P)AuOTf + phenylacetylene

ΔH = - 0.5 kcal/mol

(Ph$_3$P)AuOTf + styrene

ΔH = - 3.3 kcal/mol

Heats of formation of the complexes of (Ph$_3$P)AuOTf with carbon-carbon multiple bonds are quite low, but the configuration of the complexes corresponds to proper activation of the substrates



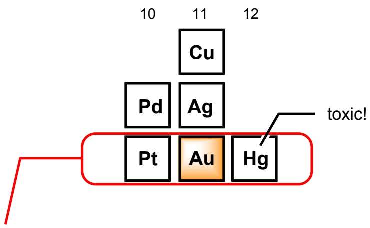
***trans* - addition**

R^1	R^2	yield (%)
Ph	H	95
nHex	H	87
Ph	Me	90
H	TMS	65

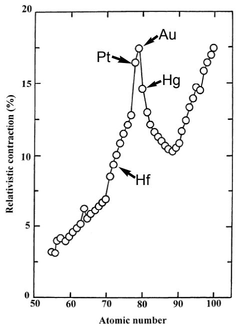
Yoshikawa, E.; Gevorgyan, V.; Asao, N.; Yamamoto, Y. *J. Am. Chem. Soc.* 1997, *119*, 6781.

Au 197 79

Gold
～A Special Transition Metal～



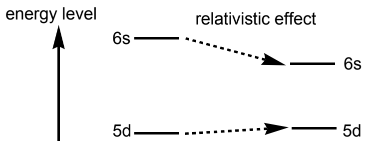
Relativistic Effect (shrink of 6s orbital)
This shrink becomes largest at Au.



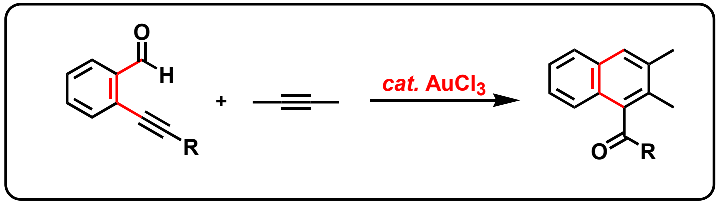
G. C. Bond *Catal. Today*, **2002**, *72*, 5.

Properties of Au

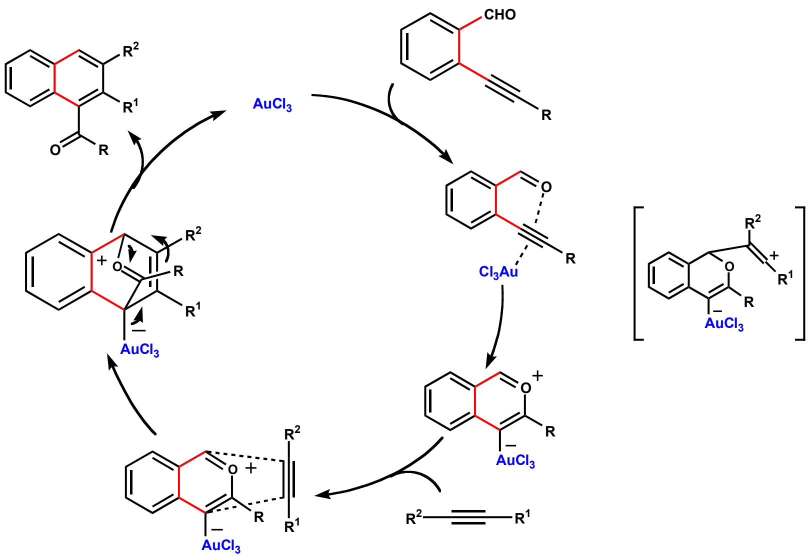
(1) Large relativistic effect
(2) By this effect, 6s orbital is stabilized.
(3) Small energy gap between 6s and 5d orbitals.
 (i) Very soft Lewis acid
 (ii) Both 6s and 5d orbitals can participate bond formation.



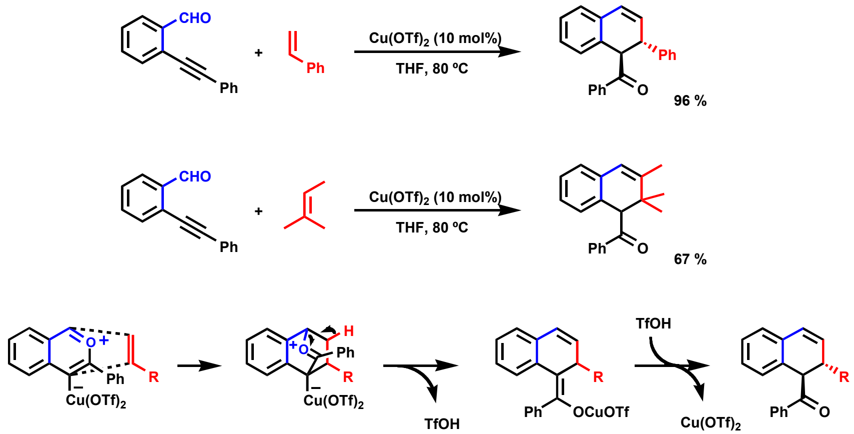
AuCl$_3$-Catalyzed Benzannulation: Synthesis of Functionalized Naphthyl Derivatives from *o*-Alkynylbenzaldehydes with Alkynes



Asao, N.; Takahashi, K.; Lee, S.; Kasahara, T.; Yamamoto, Y. *J. Am. Chem. Soc.* 2002, *124*, 12650-12651.

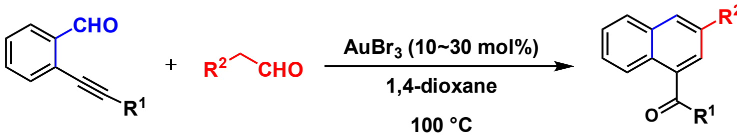


Functionalized 1,2-Dihydronaphthalenes with Cu(OTf)$_2$ Catalyst

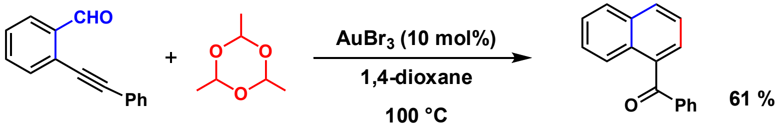


Asao, N.; Kasahara, T.; Yamamoto, Y. *Angew. Chem. Int. Ed.* 2003, *42*, 3504-3506.

Reactions with Various Aldehydes and Ketones

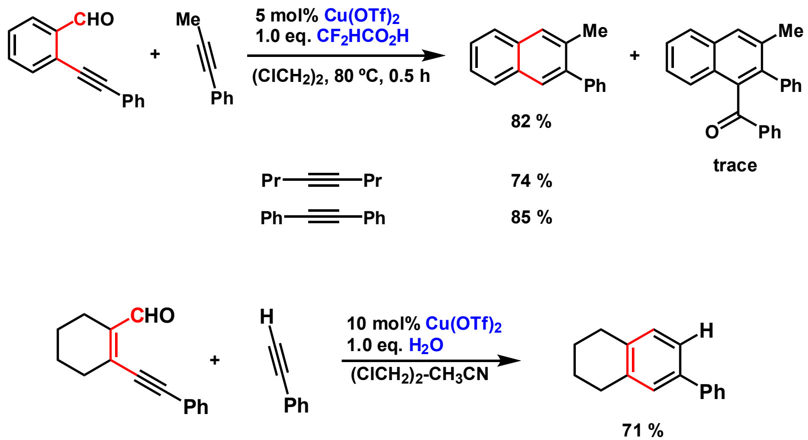


R^1 =	R^2 =	
Bu	Me	71 %
Ph	^{i}Pr	65 %
Ph	C_5H_{11}	81 %
Ph	Ph	78 %
Ph	OBn	45 %



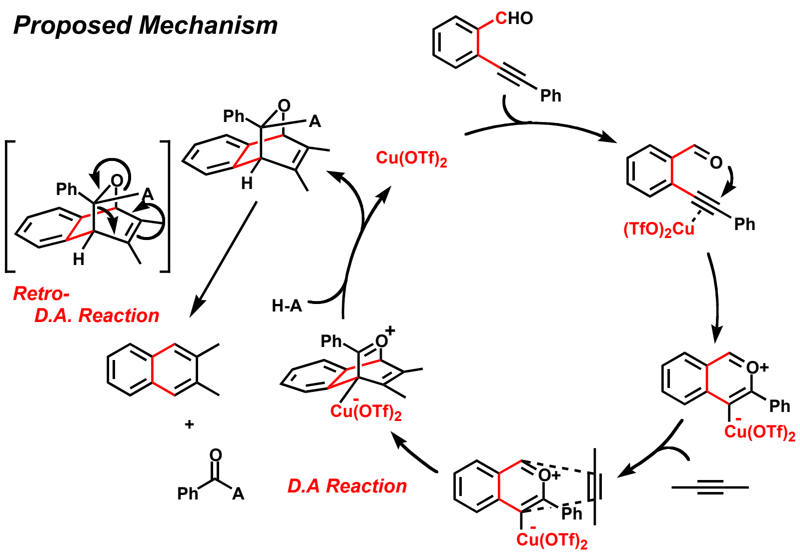
Asao, N.; Aikawa, H.; Yamamoto, Y. *J. Am. Chem. Soc.* 2004, *126*, 7458-7459.

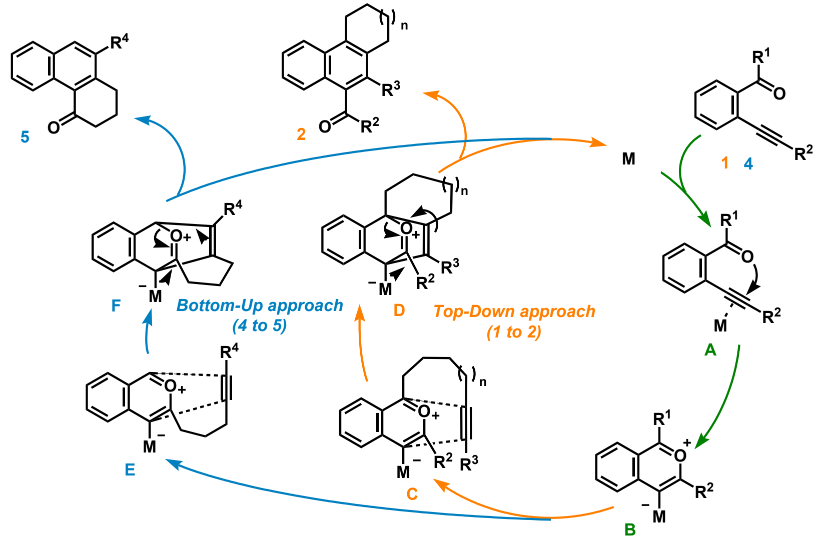
Dephenacylative Benzannulation with Cu(OTf)$_2$-HA System



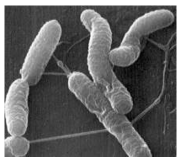
Asao, N.; Nogami, T.; Lee, S.; Yamamoto, Y. *J. Am. Chem. Soc.* 2003, *125*, 10921-10925.

Proposed Mechanism





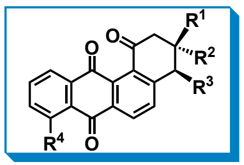
Total Synthesis of (+)-Ochromycinone via Gold-Catalyzed Intramolecular [4 + 2] Benzannulation



Helicobacter pylori

H. Pylori is infested in half man's stomach of about all population and is considered as a leading cause of gastric ulcer and cancer.

B. J. Marshall and *J. B. Warren* won *Nobel prize* in 2005 by distinguished achievement that had discovered *H. Pylori*.



Angucyclinone Group [1)]

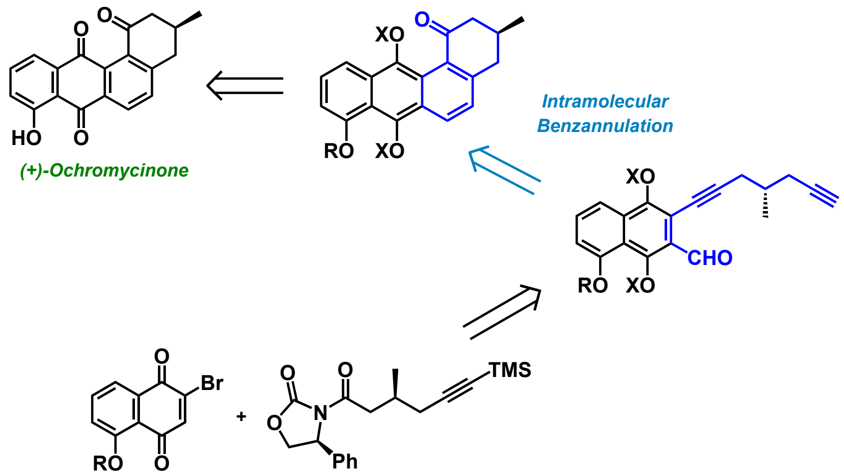
R^1 = Me, R^2 = R^3 = H, R^4 = OH

(+)-Ochromycinone

Selective activity against *H. pylori* [2)]

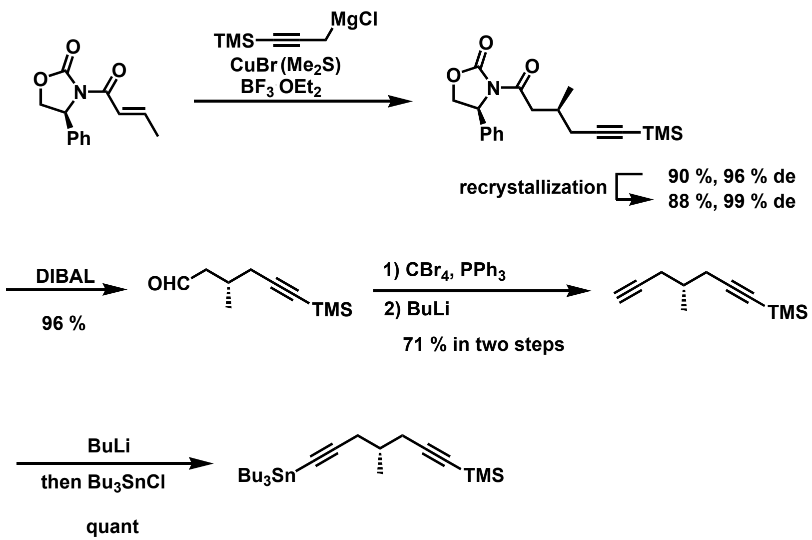
1) Carreño, M. C.; Urbano, A. *Synlett* 2005, *1*, 1-25.
2) Taniguchi, M.; Nagai, K., Watanabe, M.; Niimura, N.; Suzuki, K.; Tanaka, A. *J. Antibiot.* 2002, *55*, 30-35.

Synthetic Plan

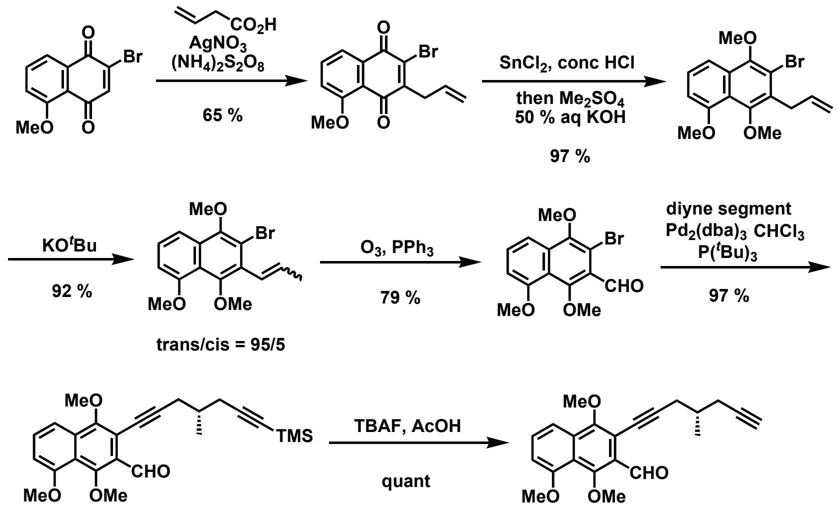


Sato, K.; Asao, N.; Yamamoto,Y. *J. Org. Chem.* 2005, *70*, 8977-8981.

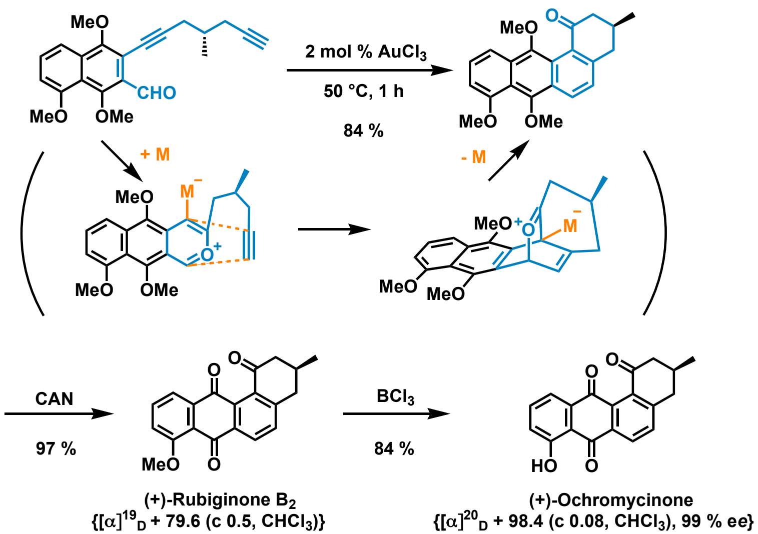
Synthesis of Diyne Segment

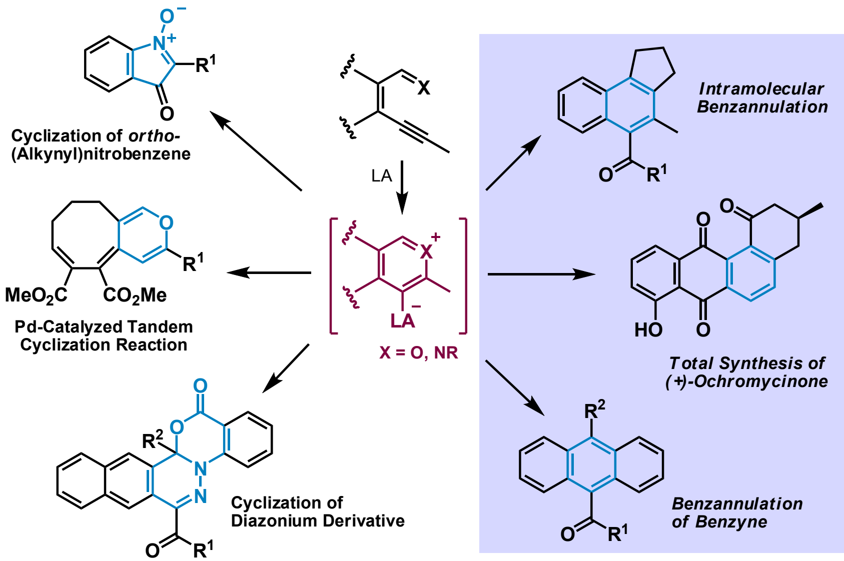


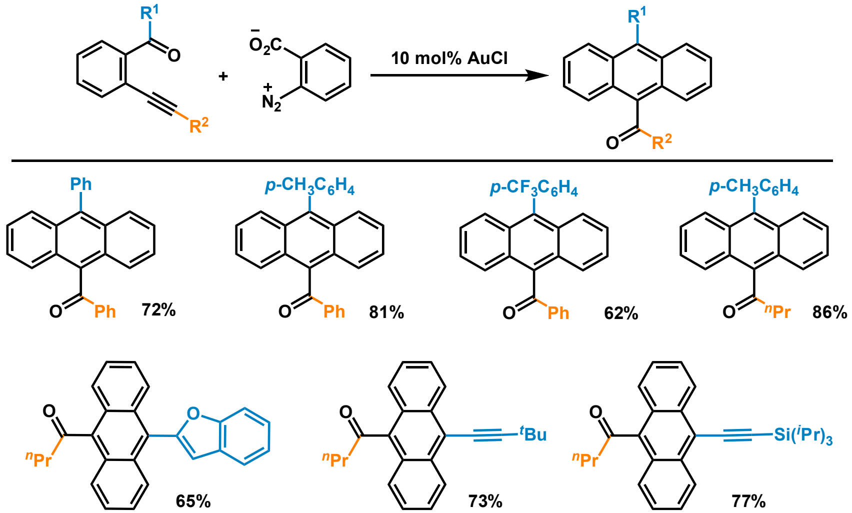
Synthesis of Intramolecular Benzannulation Precursor



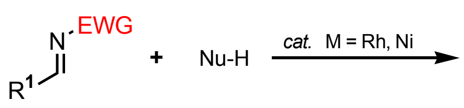
Total Synthesis of (+)-Ochromycinone







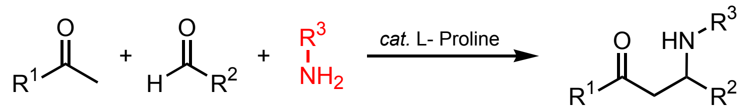
Transition metal-Catalyzed Direct Addition of Pronucleophiles to Imines



Nu-H : $CH_2(CN)_2$, $CH_2(CO_2Me)_2$, $(CH_3)_2CO$, ...

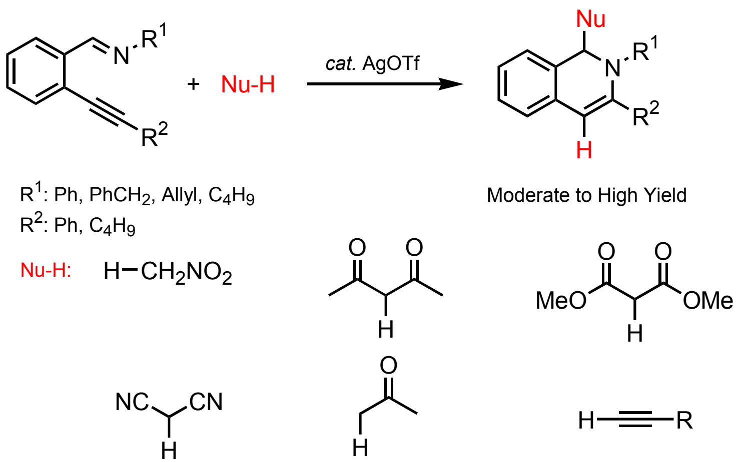
Yamamoto, Y.; Kubota, Y.; Honda, Y.; Fukui,H.; Asao, N.; Nemoto, H. *J. Am.Chem. Soc.* **1994**, *116*, 3161.
Shida, N.; Kubota, Y.; Fukui, H.; Asao, N.; Kadota, I.; Yamamoto, Y. *Tetrahedron Lett.***1995**, *36*, 5023.

The Direct Organocatalytic Mannich Reaction



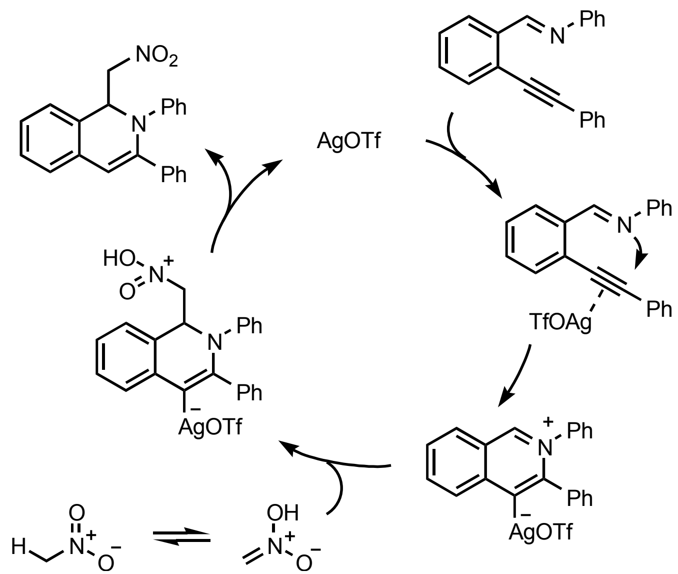
List, B. *J. Am. Chem. Soc.* **2000,** *122*, 9336.

AgOTf-Catalyzed Direct Mannich and Nitro-Mannich Reactions with Non-Activated Imines

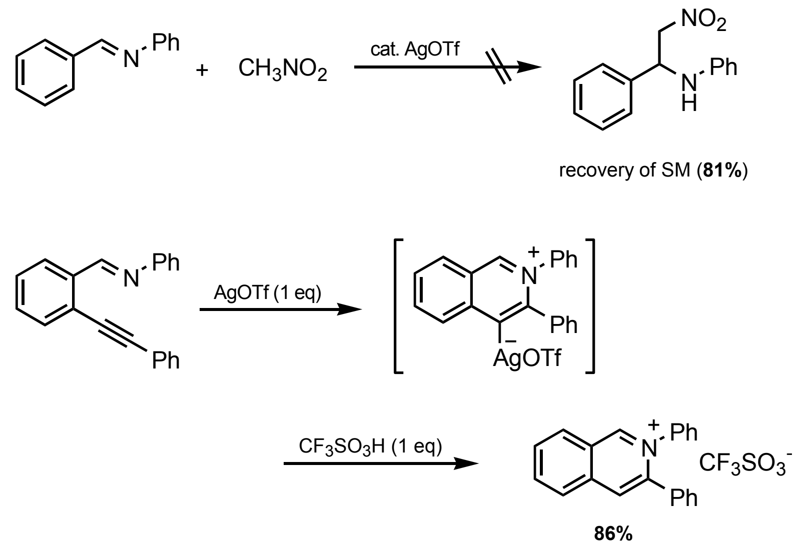


Asao, N.; Yudha S. S.; Nogami, T.; Yamamoto, Y. *Angew. Chem. Int. Ed.* 2005, *44*, 5526-5528.

Proposed Mechanism



Mechanistic Study



Coinage Metals in Organic Synthesis

Chemical Reviews Volume 108, Issue 8

Guest Editors:

Yoshinori Yamamoto,

Tohoku University

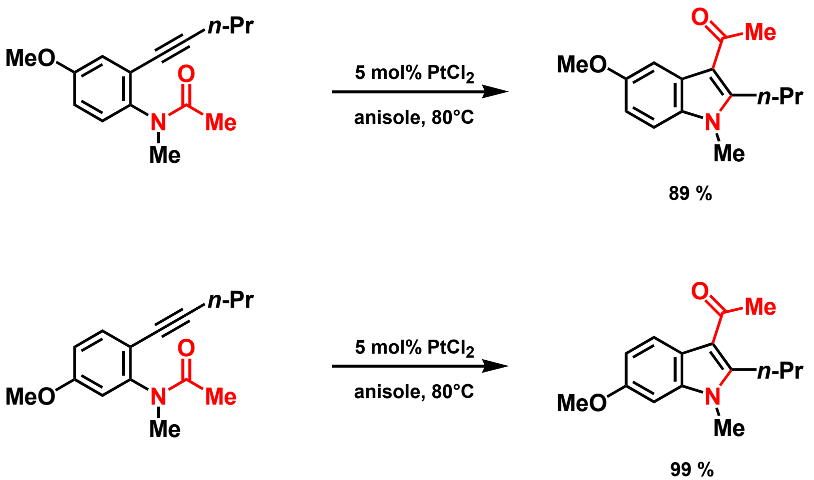
Bruce H. Lipshutz,

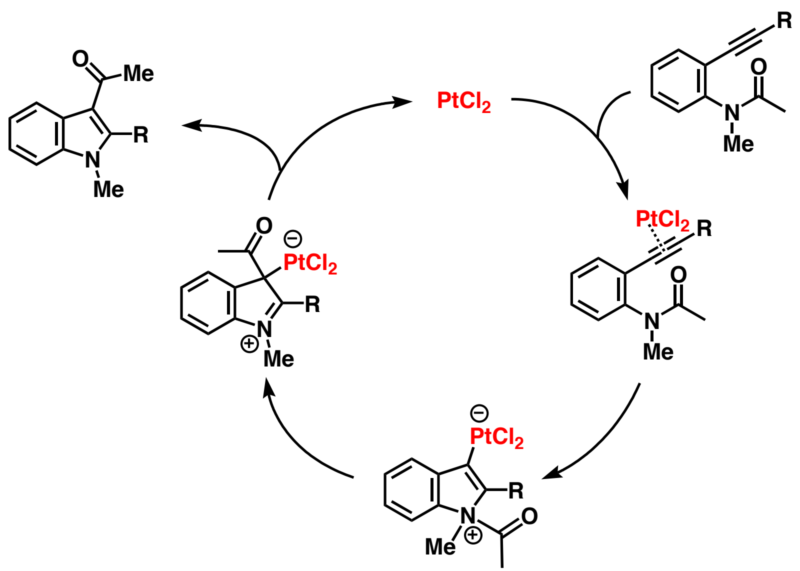
University of California, Santa Barbara

This thematic issue contains a series of reviews covering the latest developments in synthesis using coinage metals. These papers have been written by an international group of authors with a wide range of experience in the field, and who have devoted years to research involving the chemistry of copper, silver, and gold. In line with the times, there is a heavy accent on catalytic processes, in both racemic and non-racemic manifolds. Please sign up to receive ***Chemical Reviews*** TOC Alerts at **http://pubs.acs.org/CR** to receive a complete table of contents of the upcoming issue and every issue on the day it is posted to the web. For a complete listing of all Chemical Reviews thematic issues, go to ***http://pubs.acs.org/CR***

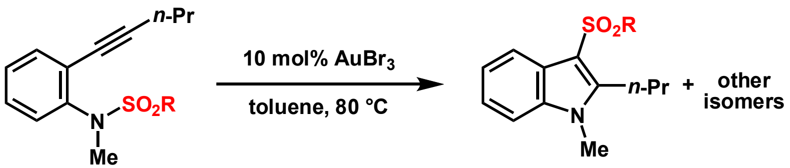
COMING IN AUGUST 2008

Thematic





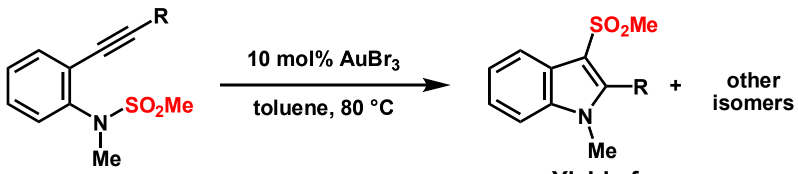
Gold-Catalyzed Aminosulfonylation; Synthesis of 3-Sulfonylindoles (a) Sulfonyl Moiety



R	Yield / %	Yield of other isomers / %
Me	95	-
CH_2CF_3	63	28
Ph	52	22
p-$MeOC_6H_4$	85	7
p-$O_2NC_6H_4$	79	11
p-AcC_6H_4	80	5

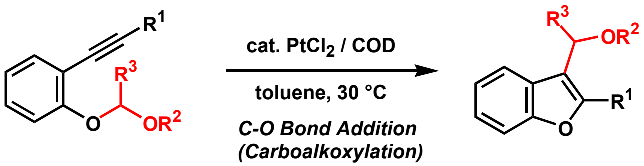
Angew. Chem. Int. Ed. 2007, *46*, 2284-2287.

Gold-Catalyzed Aminosulfonylation; Synthesis of 3-Sulfonylindoles (b) Alkynyl Moiety



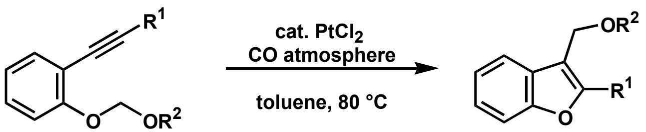
R	Yield / %	Yield of other isomers / %
n-Pr	95	-
t-Bu	38	10
H	71	-
Ph	92	2
p-MeC_6H_4	87	-
p-$MeOC_6H_4$	81	5
p-$F_3CC_6H_4$	51	20

Synthesis of 2,3-Disubstituted Benzofurans via Acetal C-O Bond Addition

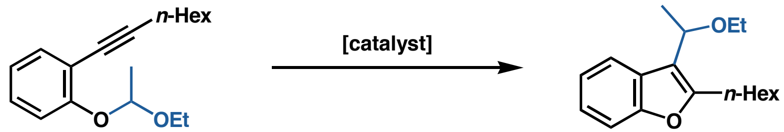


Nakamura, I.; Mizushima, Y.; Yamamoto, Y. *J. Am. Chem. Soc.* 2005, *127*, 15022.

Cf.

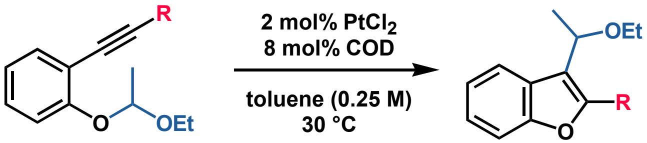


Fürstner, A.; Davies, P. W. *J. Am. Chem. Soc.* 2005, *127*, 15024.

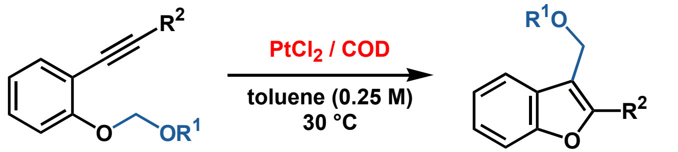


catalyst	additive	solvent	temp / °C	yield / %
10 mol% $PtCl_2$	40 mol% COD	CH_3CN	50	60
10 mol% $PtCl_2$	-	CH_3CN	50	6
10 mol% $PtCl_2$(cod)	-	CH_3CN	50	0
2 mol% $PtCl_2$	8 mol% COD	toluene	30	>99

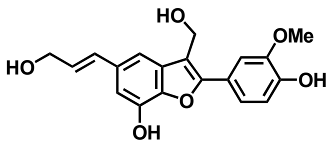
Scope and Limitation



R	time (h)	yield (%)
n-Hex	1	91
$(CH_2)_4Cl$	1	92
cyclohexyl	2.5	94
t-Bu	24	5
4-MeO-C_6H_4	24	90
Ph	3	88
4-CF_3-C_6H_4	5 d	60



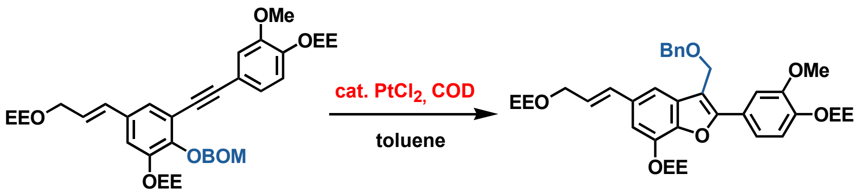
R^1	R^2	$PtCl_2$ (mol%)	COD (mol%)	time (h)	yield (%)
Me	*n*-Pr	20	80	22	92
Me	Ph	20	80	24	73
Bn	*n*-Pr	10	40	20	94
Bn	Ph	10	40	48	83
TBS	Ph	100	80	4 d	61



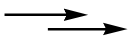
Vibsanol

Isolated from the wood of
Viburnum awabuki (Caprifoliaceae)
Inhibitor of lipid peroxidation

Fukuyama, Y. et al. *Chem. Pharm. Bull.* 1996, *44*, 1418.
Aoyama, T.; Shioiri, T. et al. *Tetrahedron Lett.* 1999, *40*, 4211.

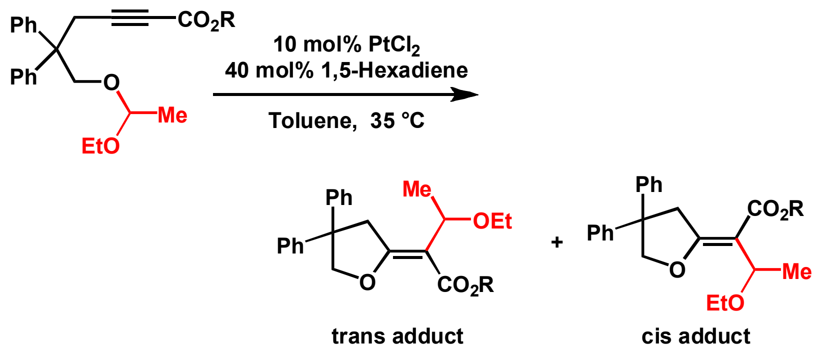


74%



Vibsanol

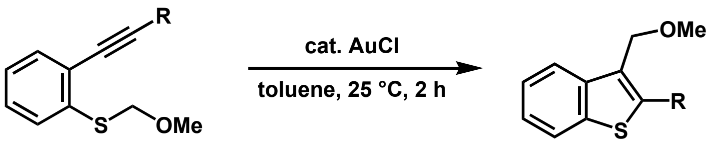
Platinum-Olefin-Catalyzed Carboalkoxylation of Acyclic Substrates



$CO_2CH_2CCl_3$	84% yield, trans:cis = 99:1
CO_2Ph	71% yield, trans:cis = 1:99

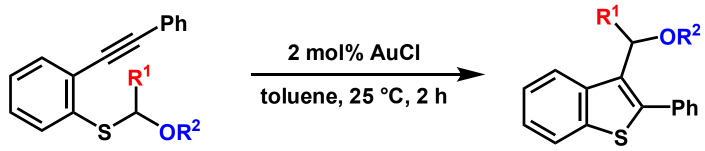
Org. Lett. 2008, *10*, 309.

Scope and Limitaion (a) Alkyne Moiety



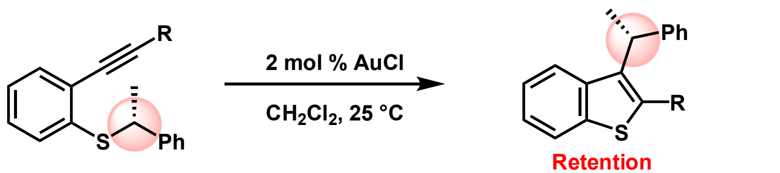
R	AuCl (mol%)	Yield (%)
n-Pr	2	98
Cy	10	92
t-Bu	10	96
p-$F_3CC_6H_4$	2	quant.
Ph	2	99
p-$MeOC_6H_4$	2	96
CO_2Et	5	85

Scope and Limitation: *O,S*-Acetal Moiety



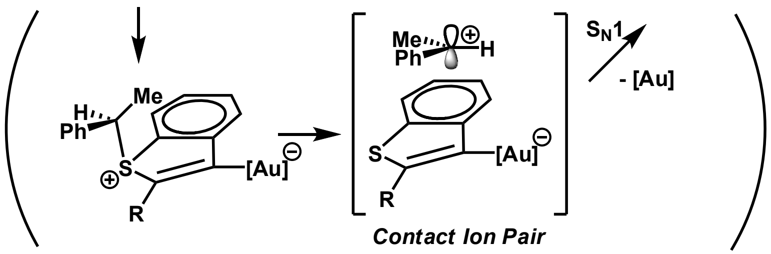
R^1	R^2	Yield (%)
Me	Et	98
-$(CH_2)_4$-		93
H	MPM	95
H	TMSE	92
H	TBS	97

Chirality Transfer in Gold-Catalyzed Carbothiolation



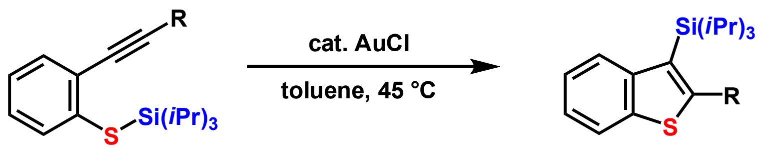
R = *p*-Anisyl 98% yield, 91% Chirality Transfer

R = Ph 99% yield, 79% Chirality Transfer



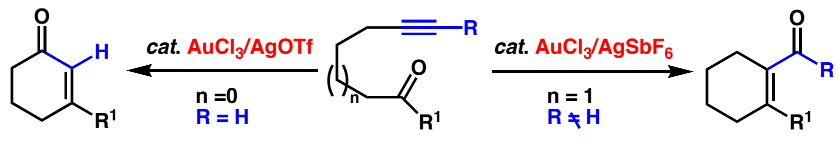
Org. Lett. 2008, ASAP.

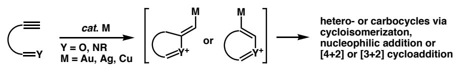
Gold-Catalyzed Thiosilylation



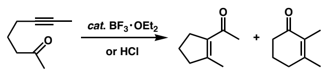
R	AuCl (mol%)	Time (h)	Yield (%)
n-Pr	2	5	98
Cy	25	21	44
p-$F_3CC_6H_4$	10	21	60
Ph	2	19	97
p-tolyl	10	24	96
p-$MeOC_6H_4$	2	8	99
2,4-$(MeO)_2C_6H_3$	5	5	quant.
p-(*i*-Pr)$_2NC_6H_4$	10	18	89
N-Me-pyrrol-2-yl	10	18	90

Org. Lett. 2007, *9*, 4081.

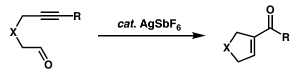




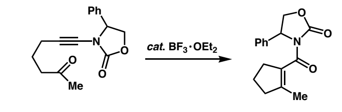
Yamamoto, Y. *J. Org. Chem.* 2007, *72*, ASAP.
Hashmi, A. S. K. *Chem. Rev.* 2007, *107*, 3180.



Harding, C. E.; King, S. L. *J. Org. Chem.* 1992, *57*, 883.

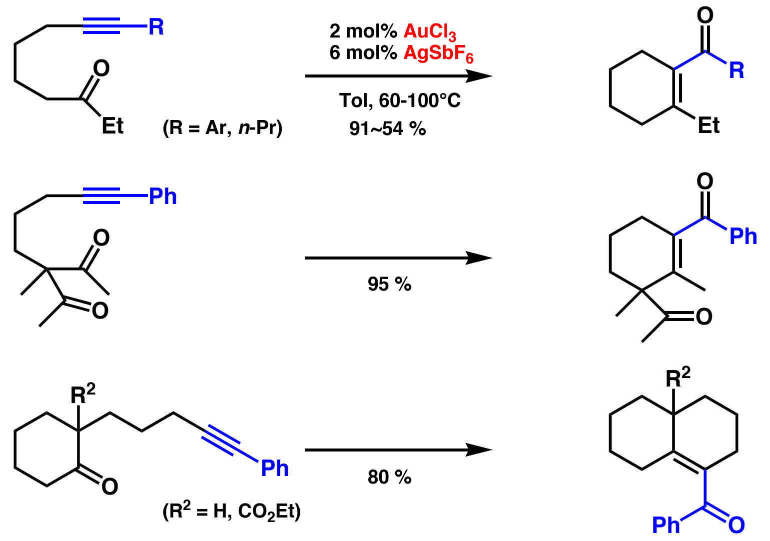


Rhee, J. U.; Krische, M. *Org. Lett.* 2005, *7*, 2493.

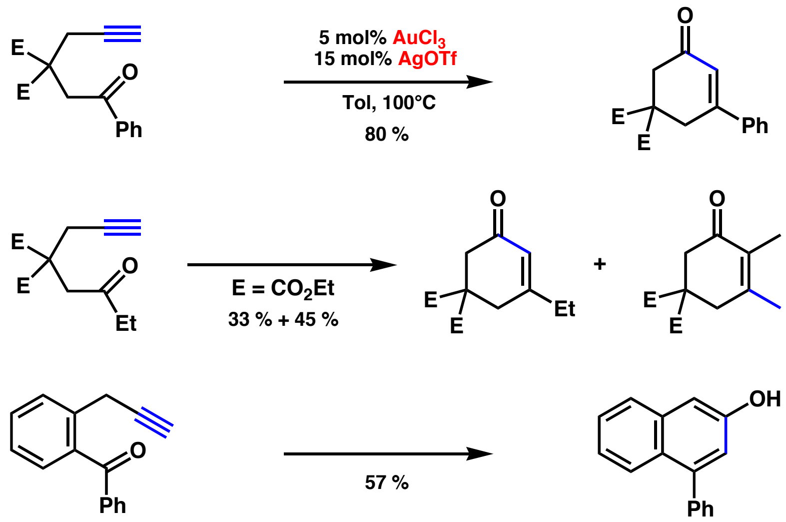


Kurtz, K. C. M.; Hsung, R. P.; Zhang, Y. *Org. Lett.* 2006, *8*, 231.

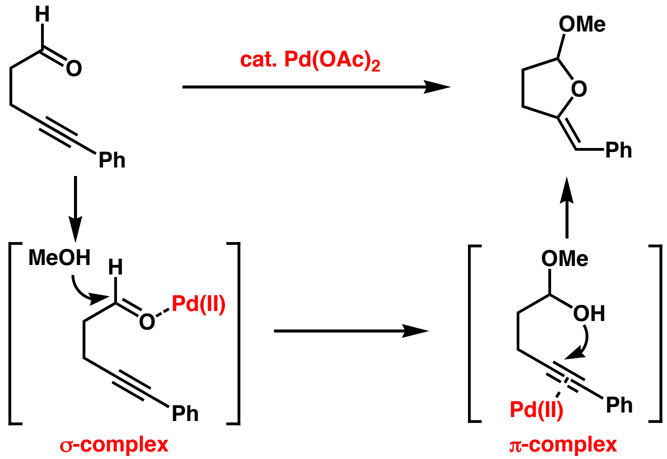
Internal Alkynes



Terminal Alkynes

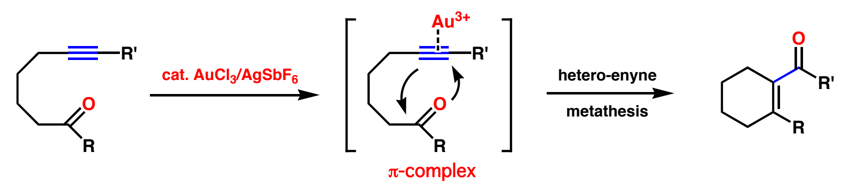


Dual Roles of Pd(II) Catalyst

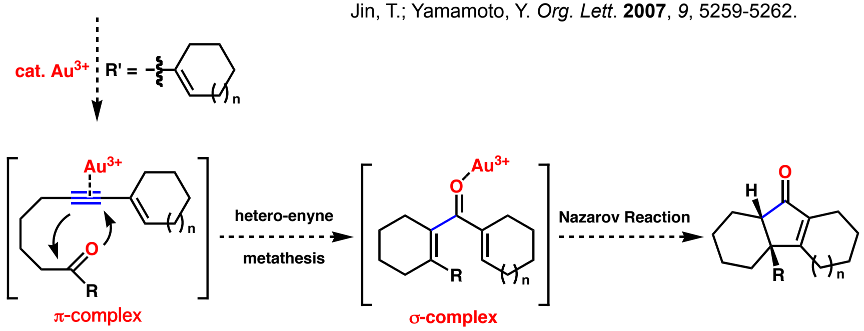


Asao, N.; Nogami, T.; Takahashi, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 764-765.

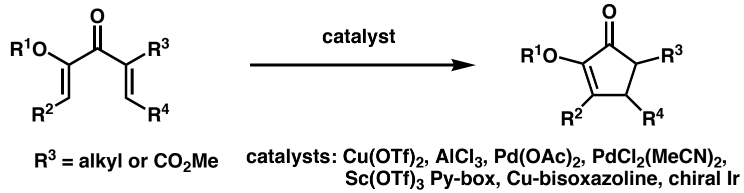
Dual Roles of Cationic Gold Catalyst



Jin, T.; Yamamoto, Y. *Org. Lett.* **2007**, *9*, 5259-5262.

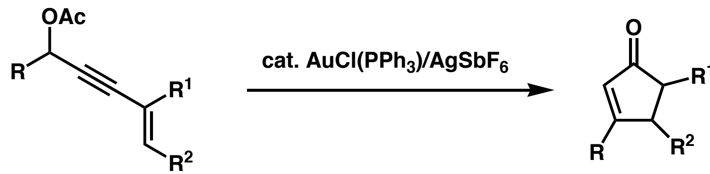


Catalytic Nazarov Cyclization of Divinyl Ketones



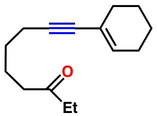
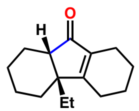
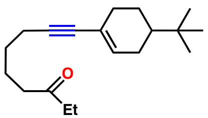
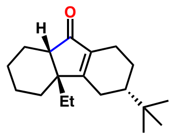
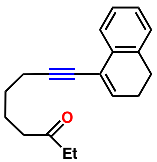
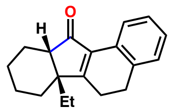
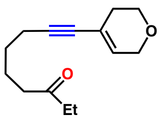
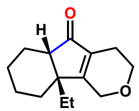
Frontier, A. J. et al, *Tetrahedron* **2005**, *61*, 7577-7606.
Pellissier, H. *Tetrahedron* **2005**, *61*, 6479-6517.
Tius. M. A. *Eur. J. Org. Chem.* **2005**, *11*, 2193-2206.

Tandem Au-Catalyzed 3,3-Rearrangement and Nazarov Reaction



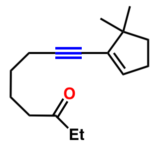
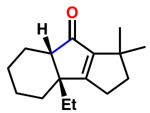
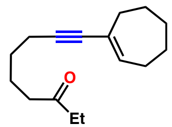
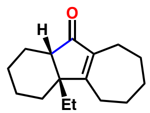
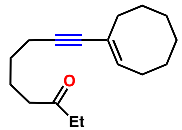
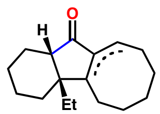
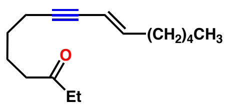
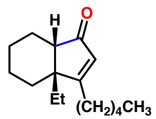
Zhang, L. et al, *J. Am. Chem. Soc.* **2006**, *128*, 1442-1443.

6-Membered Cyclic Enynyl Carbonyls

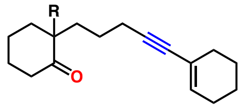
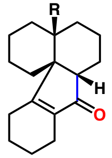
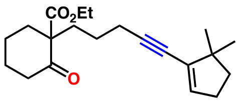
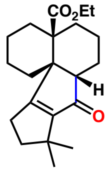
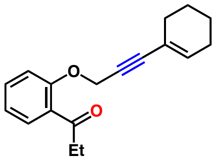
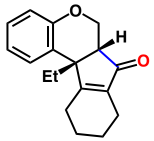
substrate 1		time (h)	temp. (°C)	product 2		yield (%)
	1a	1	50		2a	80
	1b	2	50		2b	85 dr = 5:1
	1c	2	100		2c	60
	1d	4	100		2d	40[a]

[a] 5 mol% $AuCl_3$/15 mol% $AgSbF_6$.

Various Enynyl Carbonyls

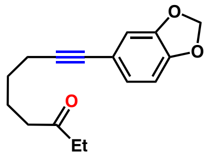
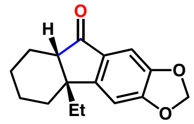
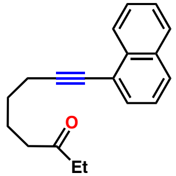
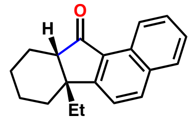
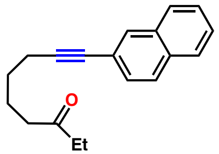
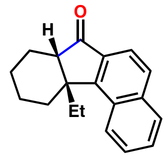
substrate 1		time (h)	temp. (°C)	product 2		yield (%)
	1e	4	50		2e	70
	1f	3	100		2f	72
	1g	3	100		2g : 2g'	52 : 33
	1h	4	100		2h	50

Construction of Tetracycles

substrate 1		time (h)	temp. (°C)	product 2		yield (%)
	1i R = CO_2Et	2	100		2i	61[a]
	1j R = H	3	100		2j	50
	1k	2	100		2k	75[a]
	1l	2	100		2l	40

[a] 5 mol% $AuCl_3$/15 mol% $AgSbF_6$.

Tandem Alkyne-Carbonyl / Aromatic Nazarov Cyclization

substrate 1		time (h)	temp. (°C)	product 2		yield (%)
	1m	4	100		2m	66
	1n	4	100		2n	92
	1o	4	100		2o	96

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\; MEXT (Ministry of Education, Science, Culture, Sports, Science and Technology)