An Introverted bis-Au Cavitand and its Catalytic Dimerization of Terminal Alkynes

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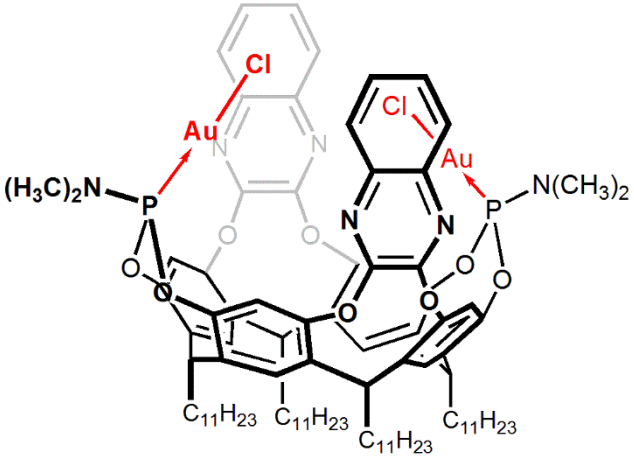
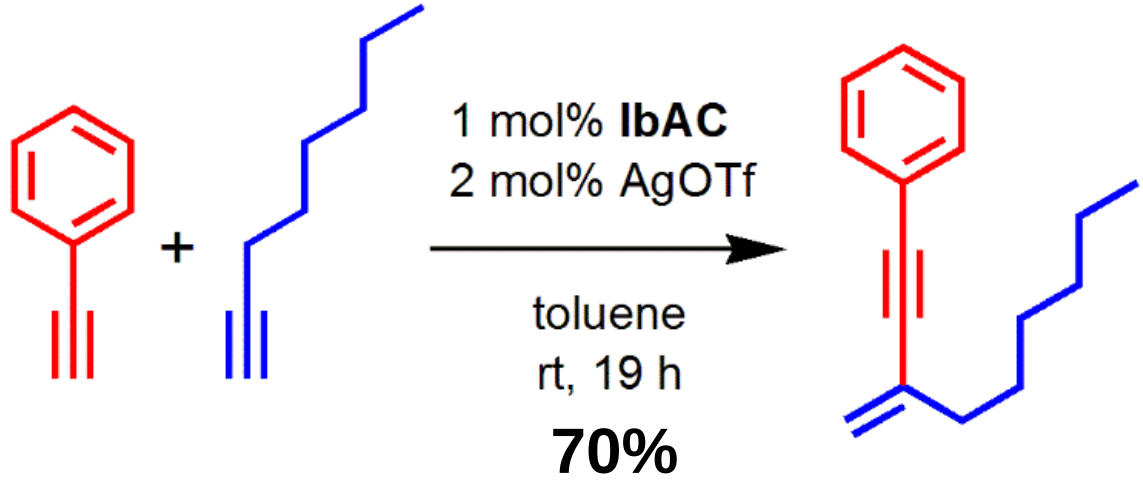
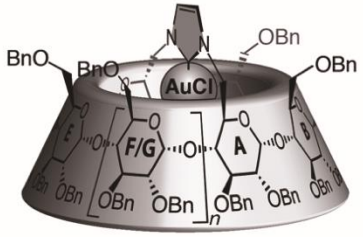


≡ **Introverted bis-Au Cavitand**

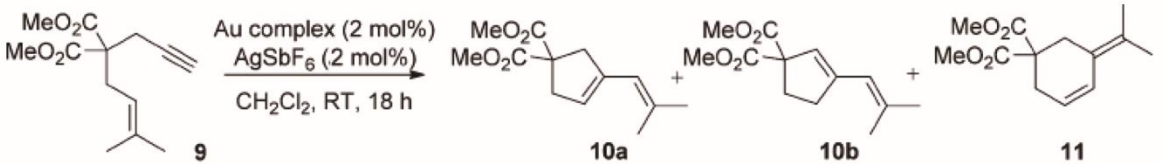
IbAC



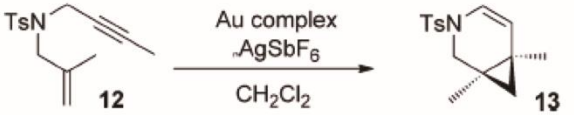
Background



7α•AuCl
7β•AuCl

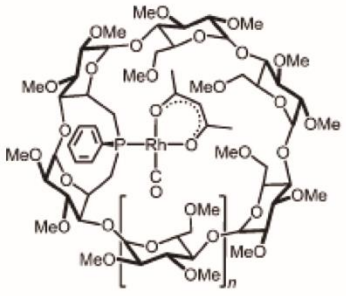


Au complex	Conversion	Yield	Selectivity (**10a/10b/11**)
IPr·AuCl	100%	88%	1 : 0.65 : 0
7α·AuCl	100%	52%	1 : 0.65 : 0
7β·AuCl	100%	63%	1 : 0 : 3.3

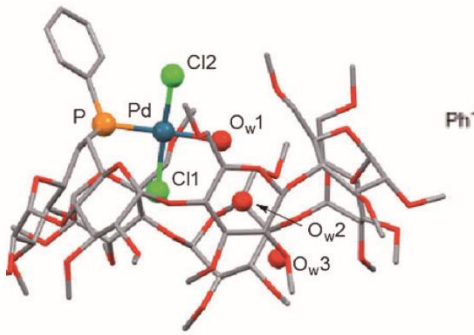


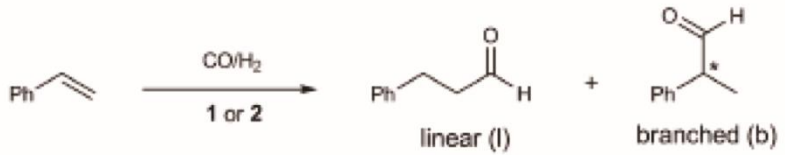
IPr·AuCl (2 mol%), RT, 3 h, 80%, 0% *ee*
7α·AuCl (5 mol%), 40°C, 18 h, 83%, 43% *ee*
7β·AuCl (2 mol%), 40°C, 15 h, 77%, 59% *ee*

"NHC-Capped Cyclodextrins: Insulated Metal Complexes, Commutable Multicoordination Sphere, and Cavity-Dependent Catalysis"
M. Sollogoub, *et al.*, *Angew. Chem. Int. Ed.* **2013**, *52*, 7213-7218.



1 *n* = 1
2 *n* = 2

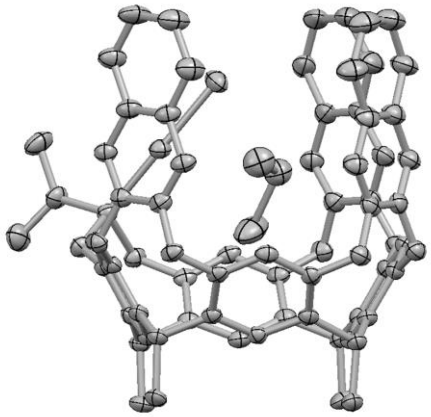


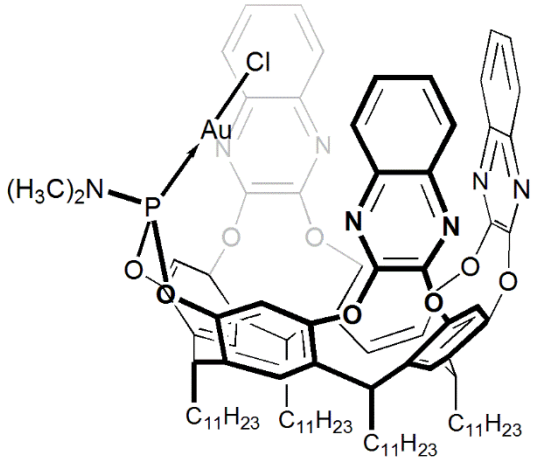


b/l: up to 100
ee: up to 95

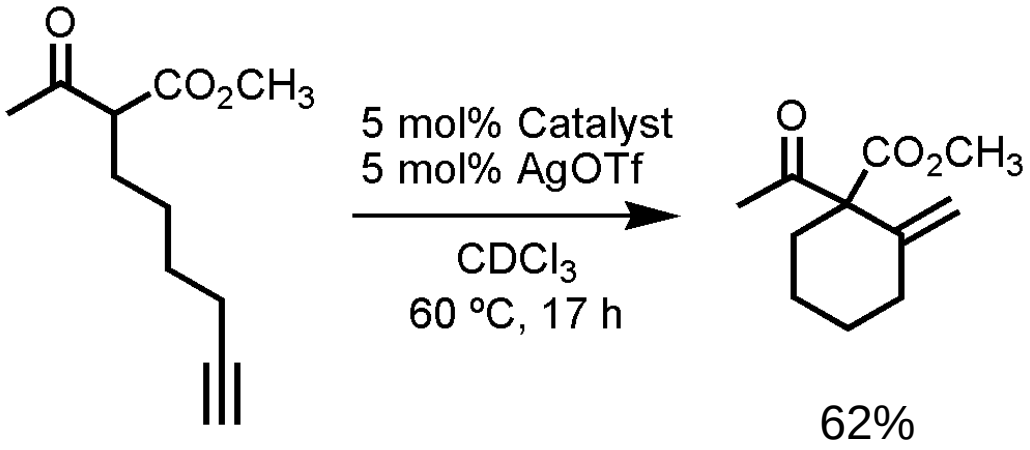
"Confining Phosphanes Derived from Cyclodextrins for Efficient Regio- and Enantioselective Hydroformylation"
D. Matt. *et al.*, *Angew. Chem. Int. Ed.* **2014**, *53*, 3937-3940.

Background





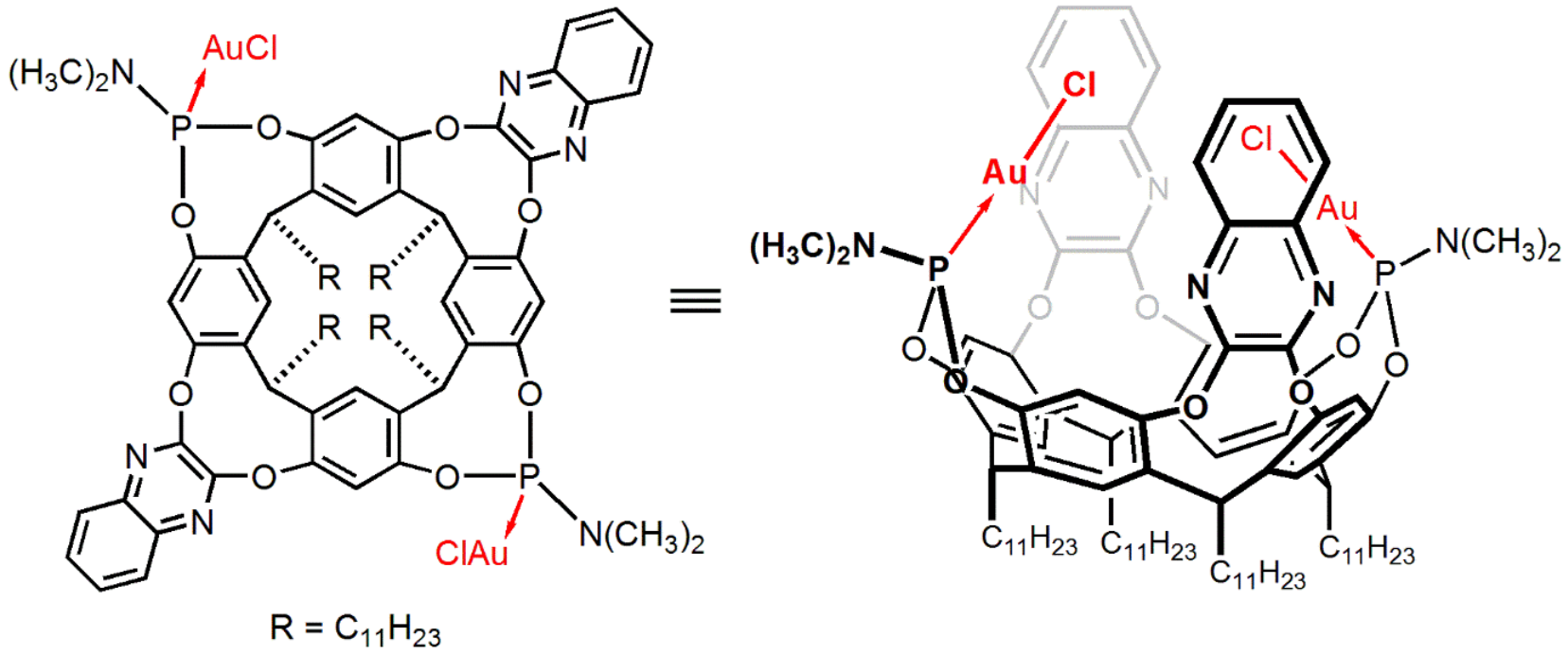
Conia-Ene reaction



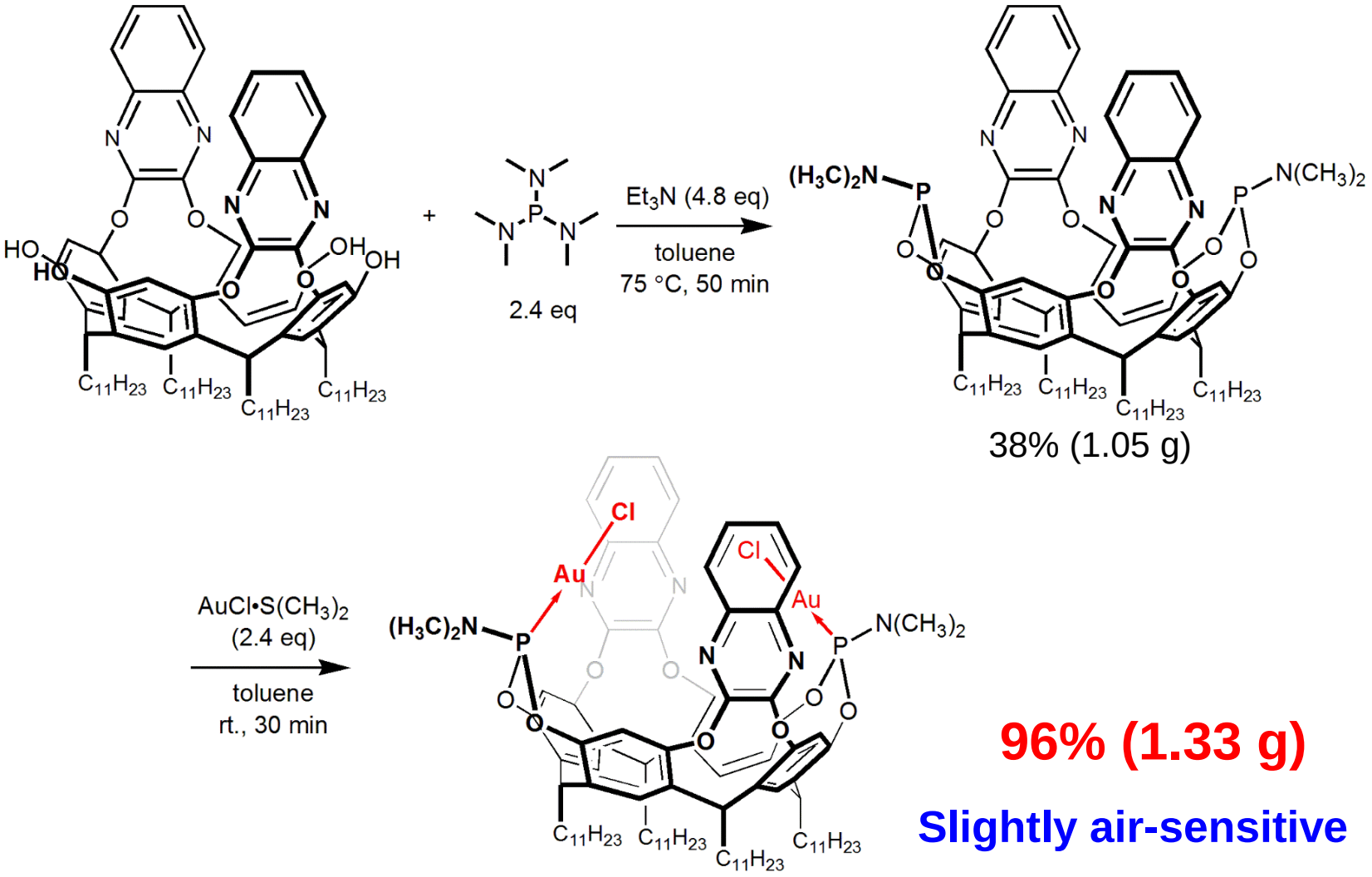
62%

Schramm, M. P.; Kanaura, M.; Ito, K.; Ide, M.; Iwasawa, T. *Eur. J. Org. Chem*. **2016**, 813-820.

Approach


(H3C)2N
AuCl
P
O
N
R
R
R
R
ClAu
N(CH3)2
R = C11H23
Cl
Au
Cl
Au
(H3C)2N
P
N(CH3)2
C11H23
C11H23
C11H23
C11H23

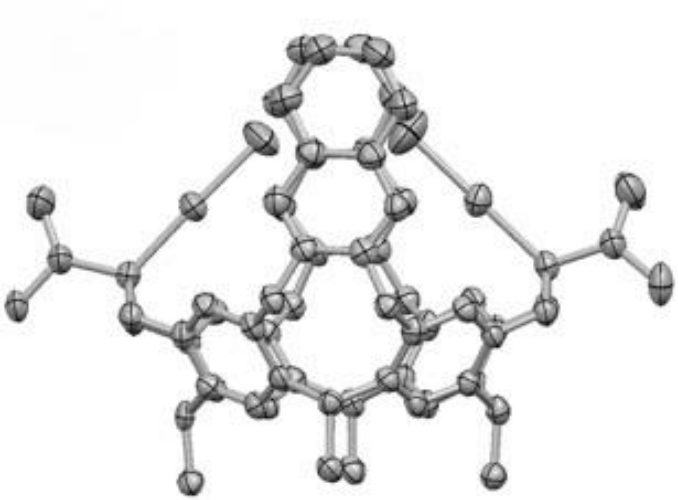
Scalable synthesis of the bis-Au cavitand

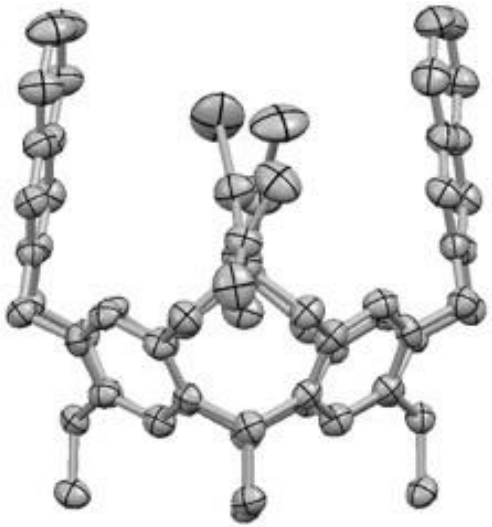


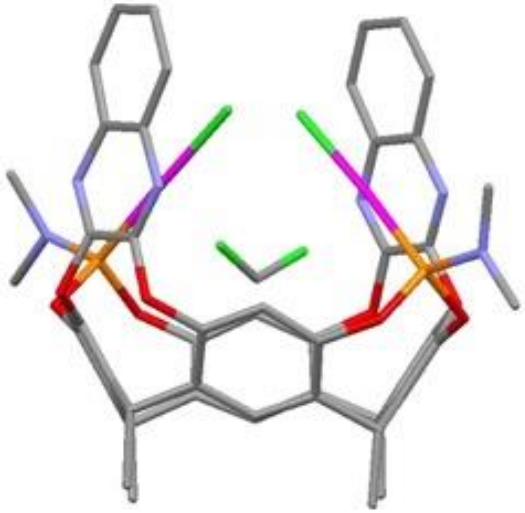
96% (1.33 g)

Slightly air-sensitive

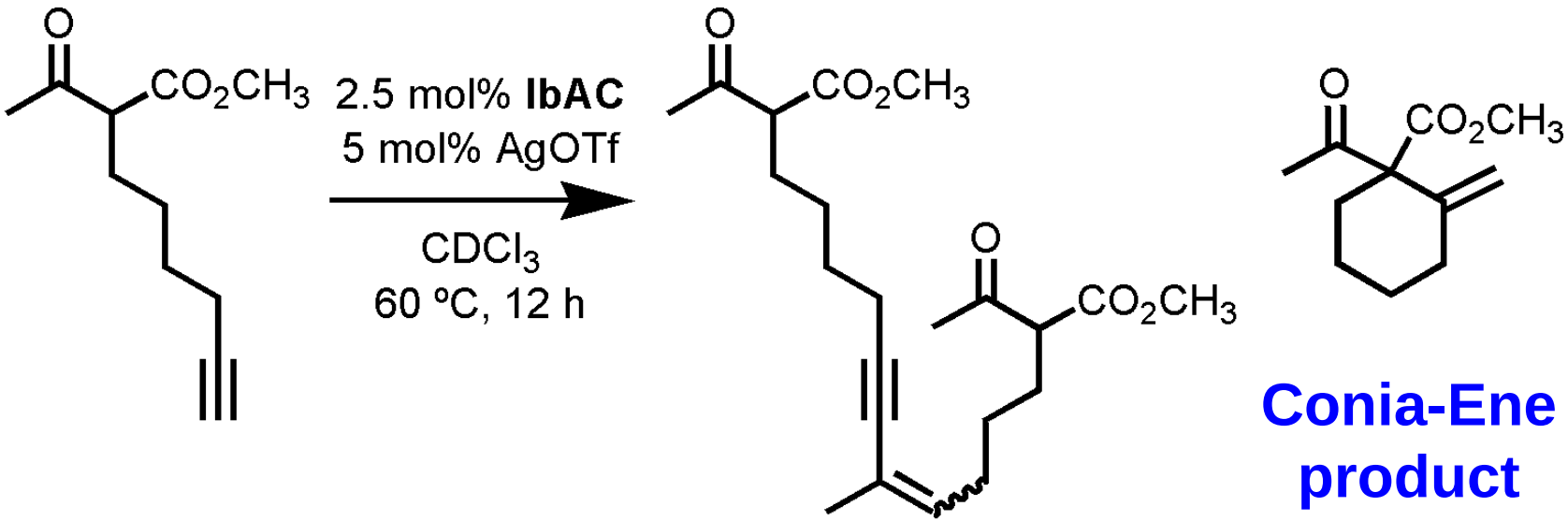
X-ray structure; result of inward orientation







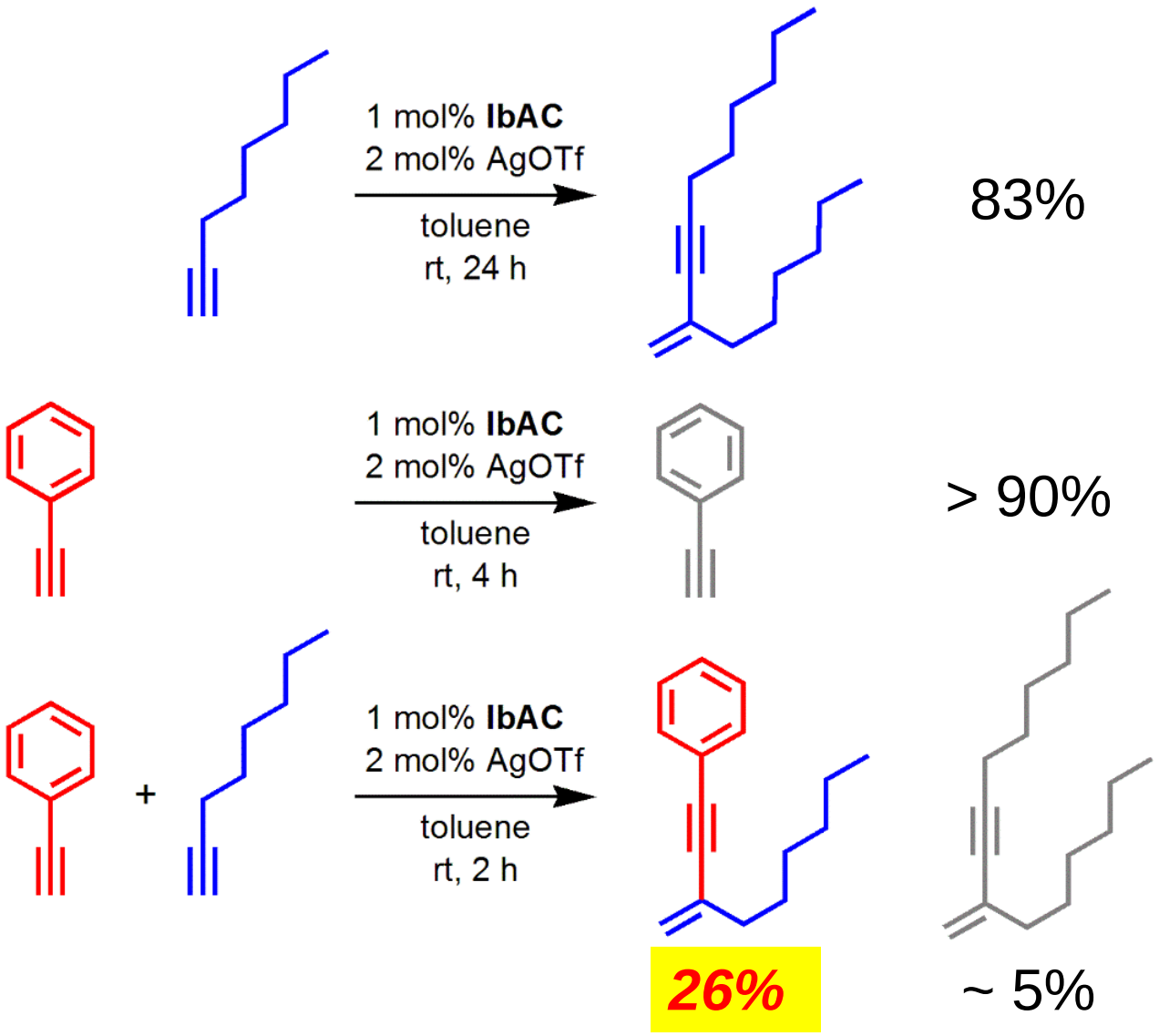
Preliminary research



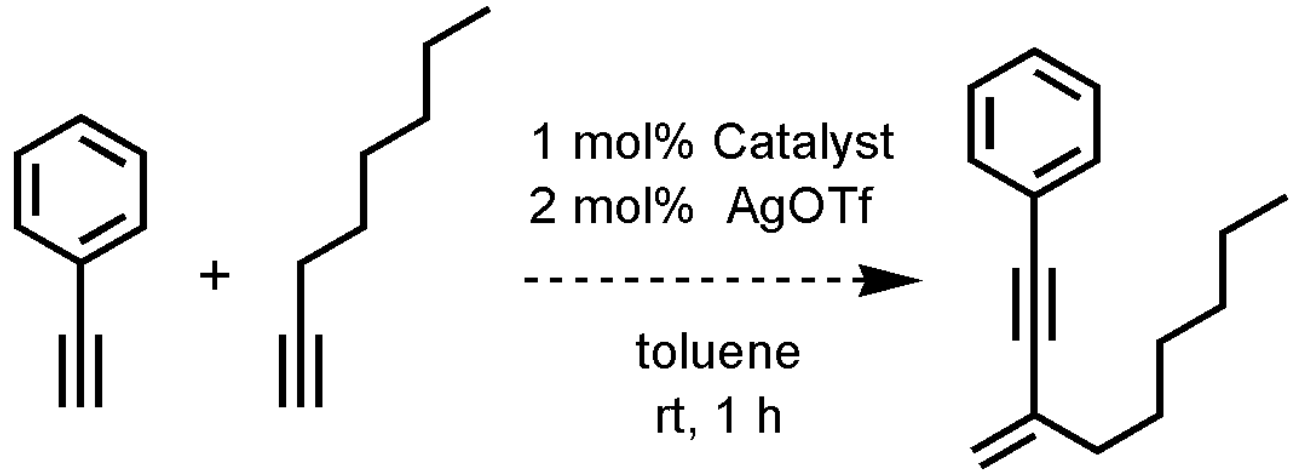
Isolated
45%

Conia-Ene product
0%

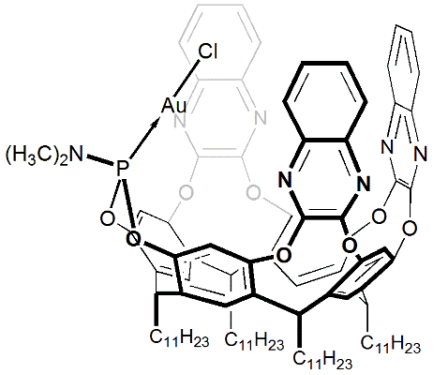
hetero-Dimerization



Control experiments



Catalyst



0%

$AuCl \cdot SMe_2$

0%

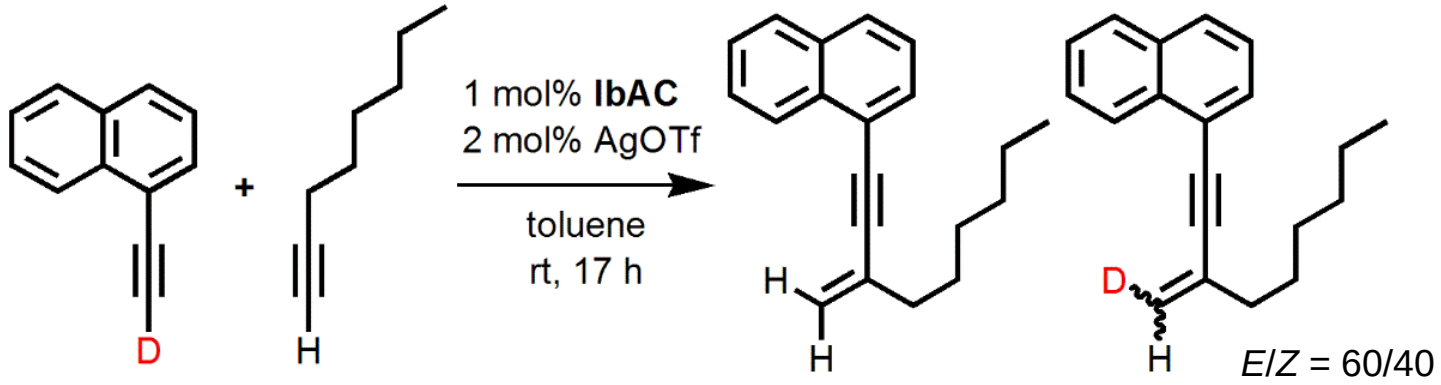
$AuCl \cdot PPh_3$

0%

without any catalyst

0%

Dimerization of deuterated terminal alkynes

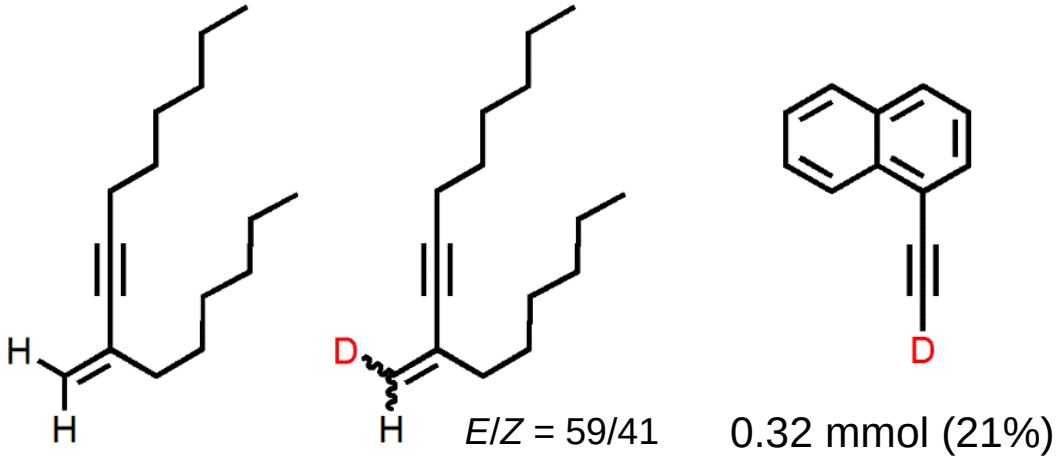


1.5 mmol
(94% D)

2.25 mmol
(1.5 eq)

0.77 mmol (49%)

73 : 27

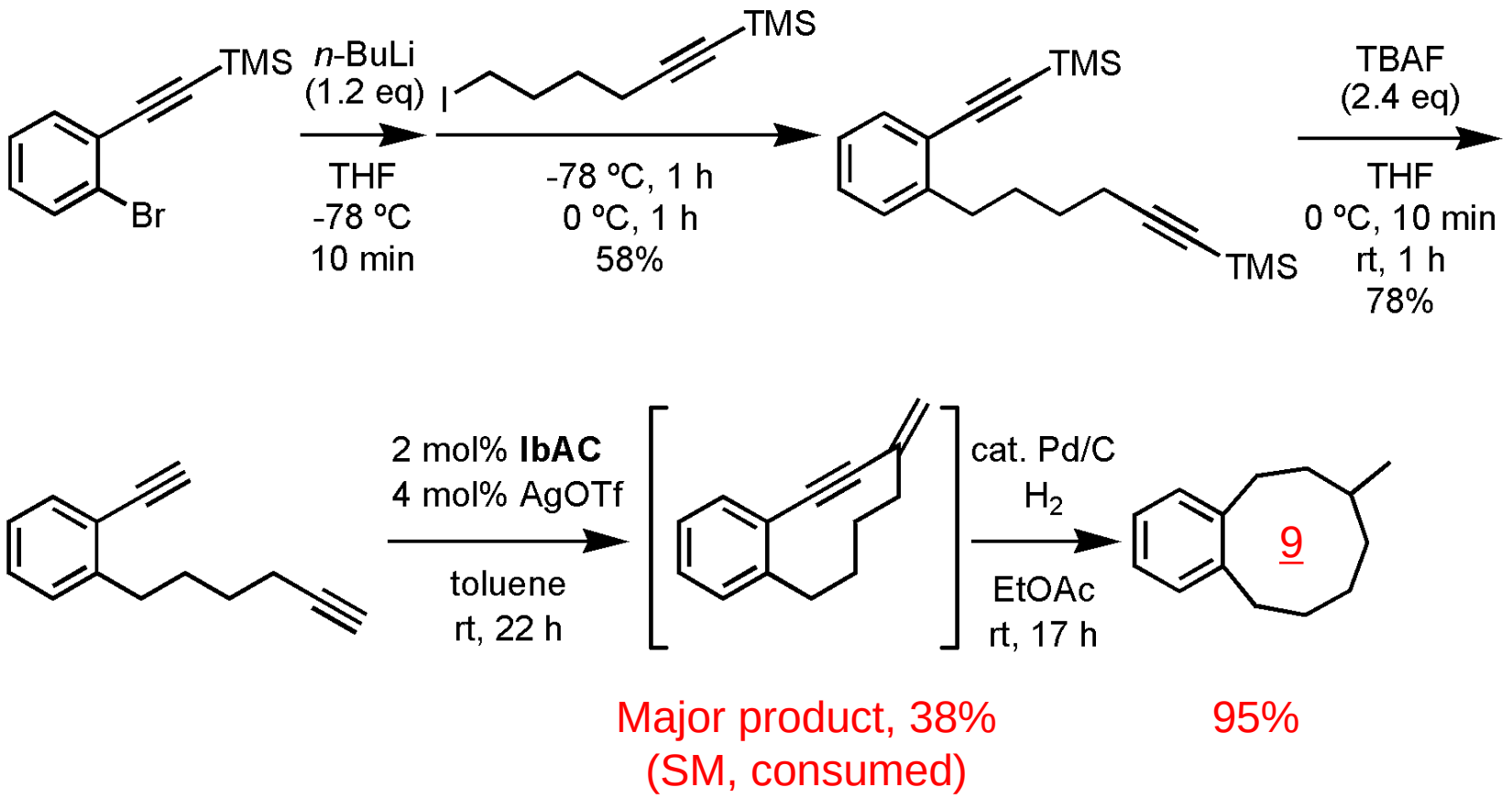


0.36 mmol

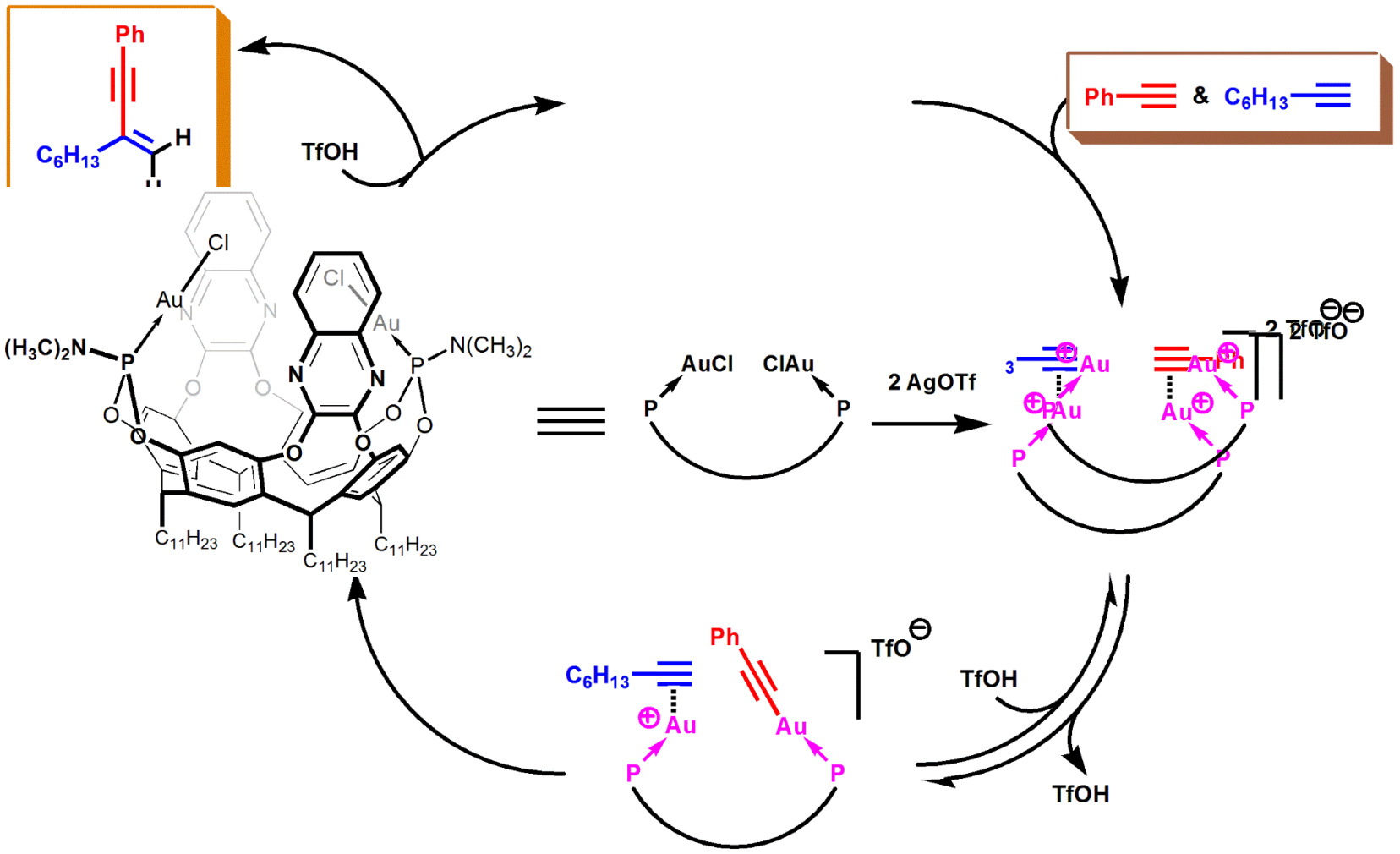
69 : 31

0.32 mmol (21%)
(30%D)

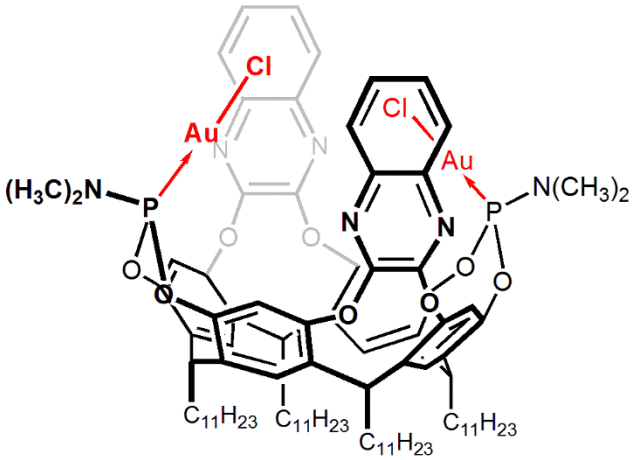
Intramolecular dimerization of terminal alkynes



Plausible catalytic cycle

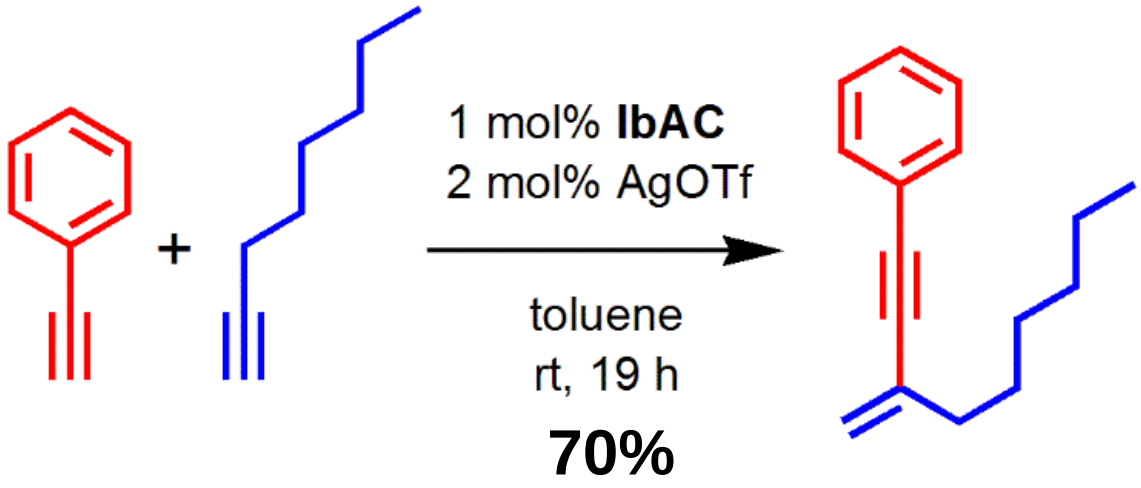


Summary



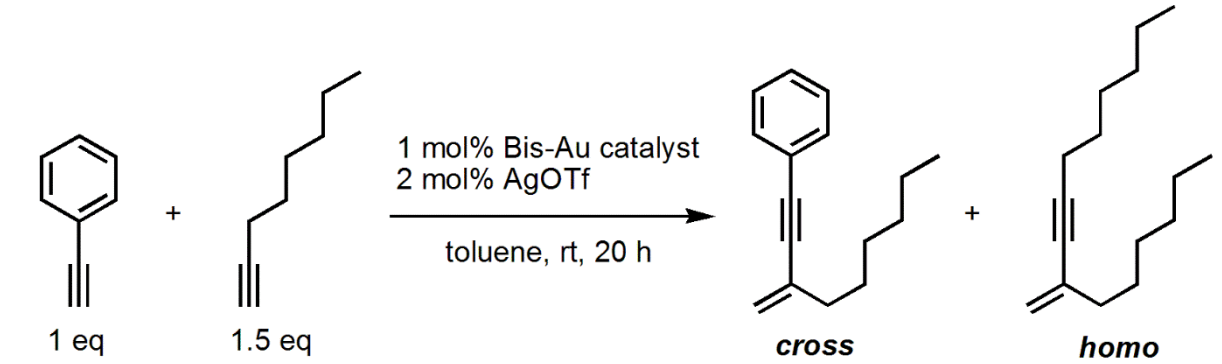
≡ **Introverted bis-Au Cavitand**

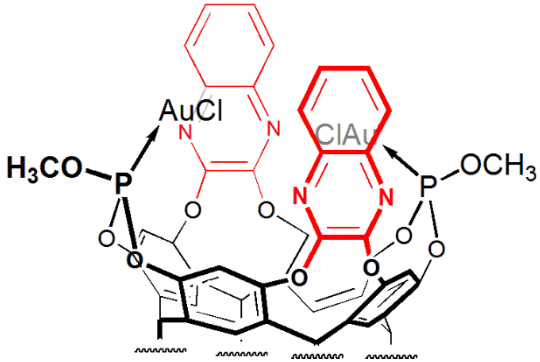
IbAC



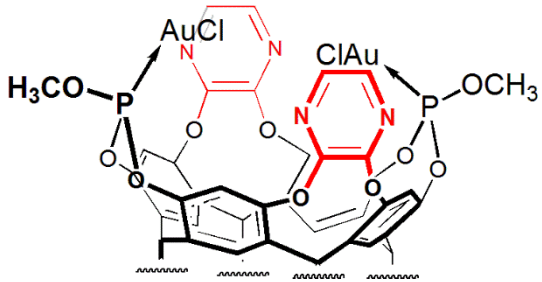
Endo, N.; Kanaura, M.; Schramm, M. P.; Iwasawa, T. *Eur. J. Org. Chem*. **2016**, 2514-2521.

Comparison with the models in the *cross*-dimerization between 1-octyne and ethynylbenzene

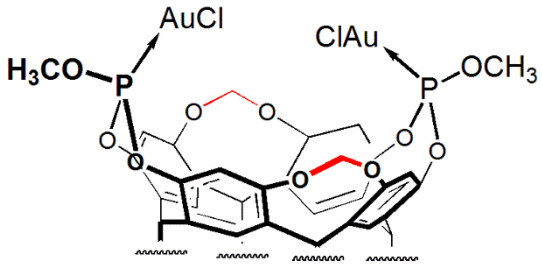




cross 58%
homo 19%

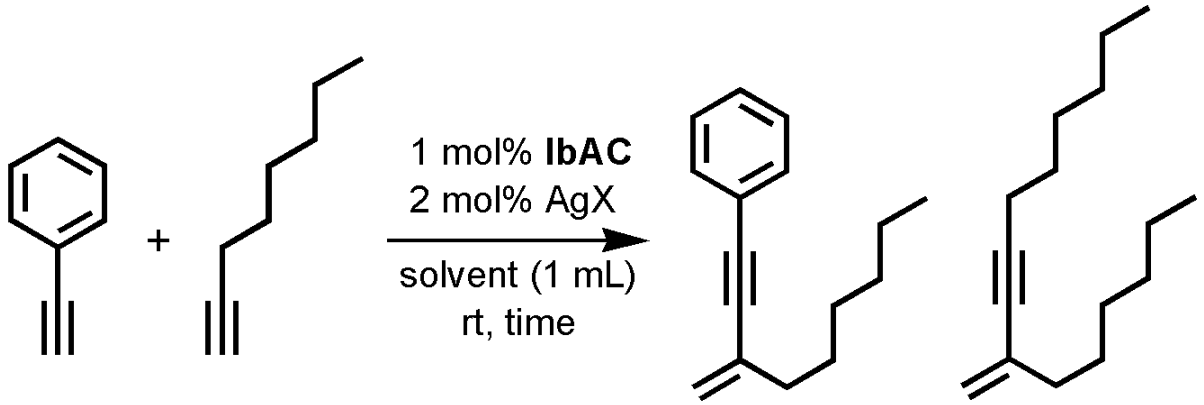


cross 6%
homo 1%



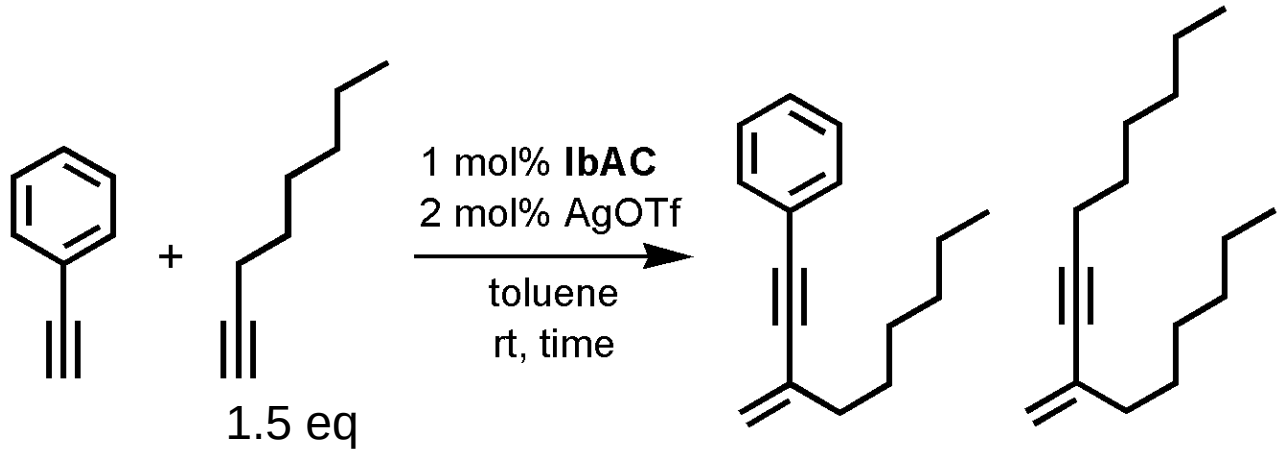
0%
-

Optimization of reaction conditions



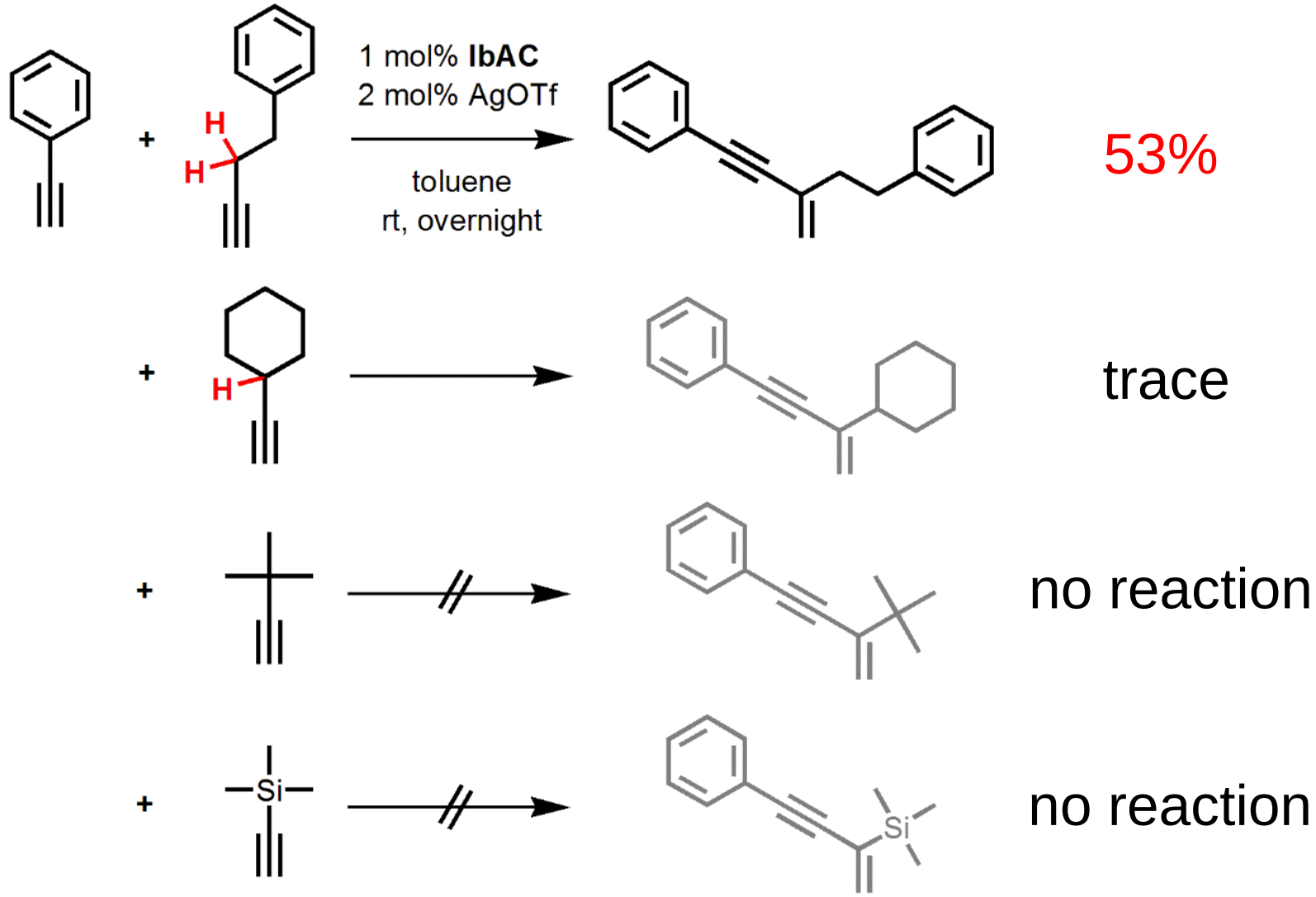
Octyne/eq	X for AgX	Solvent	Time/h	hetero/%Yield	Hetero to homo molar ratios
1.2	OTf	toluene	37	47	5.4/1
1.5	OTf	toluene	20	62	3.4/1
1.2	OTf	CH_2Cl_2	19	36	3.6/1
1.2	OTf	mesitylene	37	32	4.3/1
1.2	OTf	THF	19	~ 0	-
1.2	SbF_6	toluene	20	17	3.6/1
1.2	BF_4	toluene	20	49	3.3/1
1.5	NTf_2	toluene	18	51	3.1/1

Substrate concentrations



toluene/mL	Time/h	Hetero %yield	Hetero to homo molar ratio
1	2	47	2.8/1
	20	62	3.4/1
5	2	31	2.9/1
	20	**70**	**4.1/1**
10	2	25	3.4/1
	20	62	2.5/1

Substrate scope



Substrate scope