Merging Homogeneous Gold Catalysis with Light

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College of Chemistry and Molecular Engineering, PKU
Sept. 26th 2020

Outline

- History of Homogenous Gold Catalysis
- Atomic and Optical Properties of Gold
- Combining Gold Catalysis and Light
  - Gold complex as transition-metal catalyst
  - Gold complex as photosensitizer
- A Brief Conclusion
- Applications in Synthesis

Outline

- History of Homogenous Gold Catalysis
- Atomic and Optical Properties of Gold
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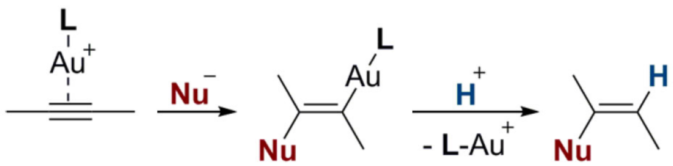
History and Development of Gold Catalysis

1986

Early application of homogenous gold(I) catalysis in asymmetric aldol reaction.

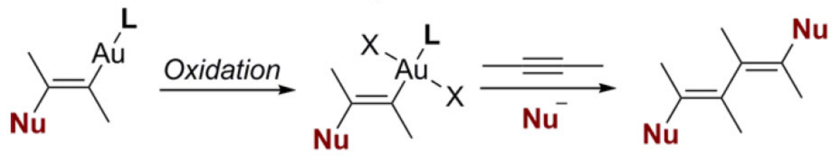
Around 2000

Application of homogenous gold(I) in **alkyne activation** by Hashmi et al.



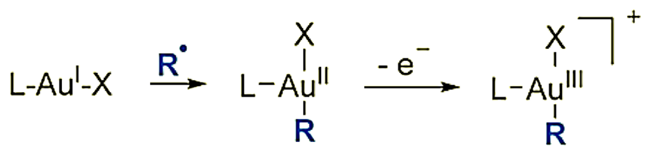
Around 2008

Oxidative coupling using gold complex and external stoichiometric oxidants.



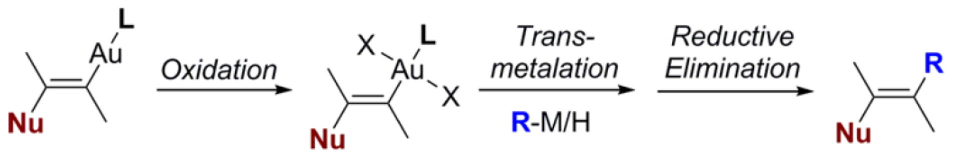
Around 2013

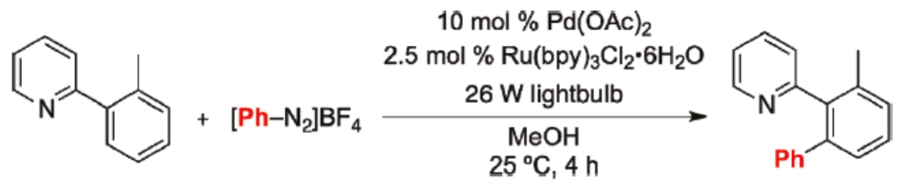
Pioneer works in merger of gold and photoredox catalysis by Toste and Glorius.



Hopkinson, M. N.; Tlahuext-Aca, A.; Glorius, F., *Acc. Chem. Res.* **2016,** *49* (10), 2261-2272.

History and Development of Gold Catalysis



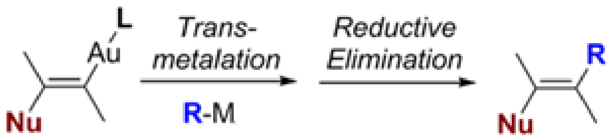


Around 2008

Oxidative coupling using gold complex and external stoichiometric oxidants.

2009

Using Stoichiometric gold with other transition metals (Pd) .

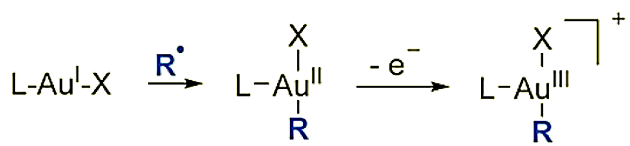


2011

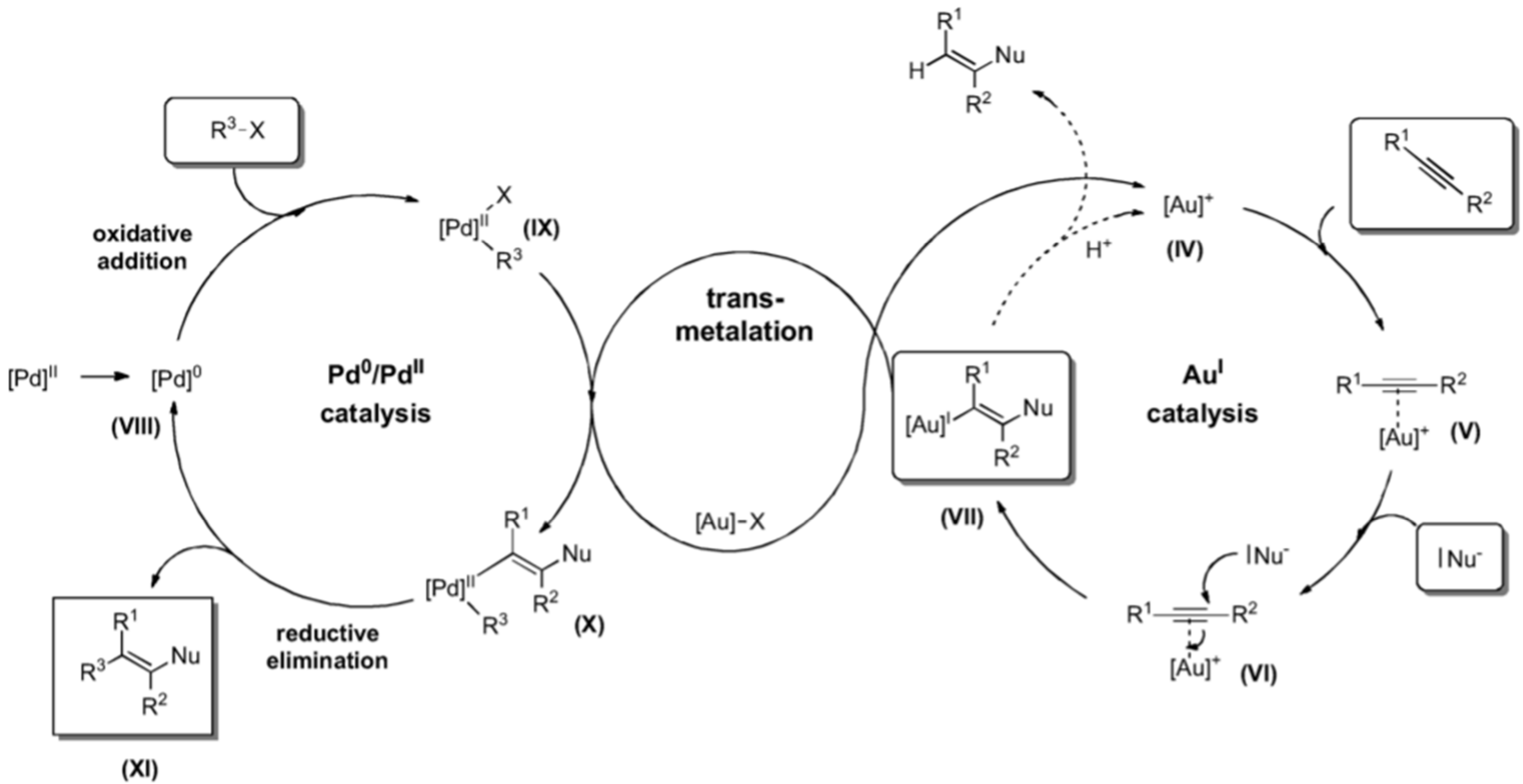
Merging transition metal catalysis with photoredox catalysis.

Around 2013

Pioneer works in merger of gold and photoredox catalysis by Toste and Glorius.



Kalyani, D.; McMurtrey, K. B.; Neufeldt, S. R.; Sanford, M. S., *J. Am. Chem. Soc.* **2011,** *133* (46), 18566-9.
Hopkinson, M. N.; Tlahuext-Aca, A.; Glorius, F., *Acc. Chem. Res.* **2016,** *49* (10), 2261-2272.



Hansmann M M, Pernpointner M, Döpp R, *et al*. *Chemistry–A European Journal*, **2013**, *19*(45): 15290-15303.

北京大學
PEKING UNIVERSITY

【Special Organic Chemistry Lecture】

Gold Catalysis and Light

报告人：Prof. A. Stephen. K. Hashmi
University of Heidelberg

时　间：10月10日 周四 下午3:00-4:30
地　点：化学院 A717

欢迎参加！

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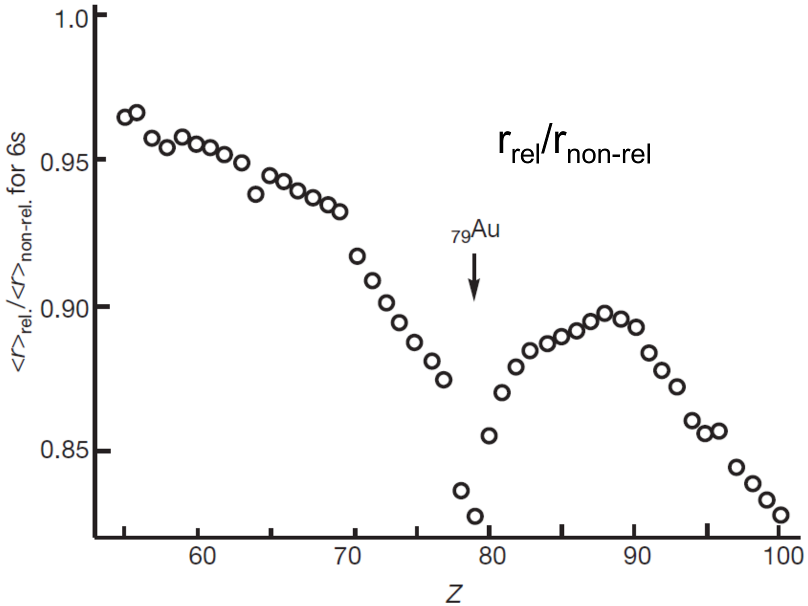
Atomic and Optical Properties of Gold

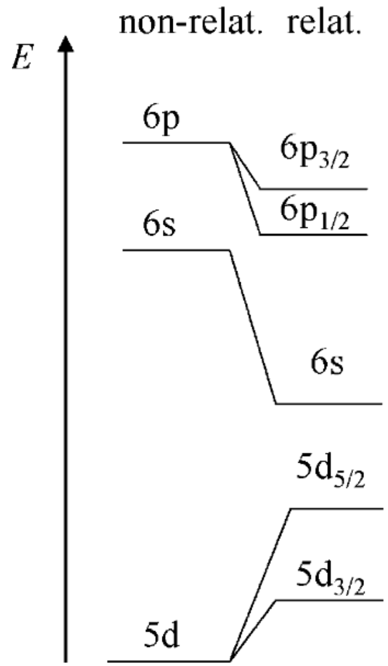
☐ Relativistic effects

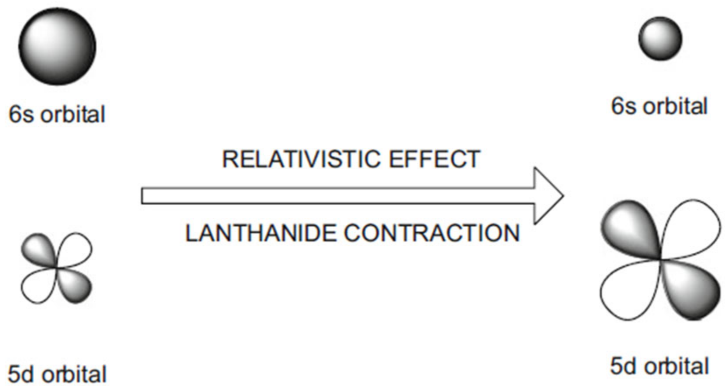
$$m = m_0\sqrt{(1-(v/c)^2}, \quad \langle v_r \rangle = Z$$

when $v \to c$: relativistic effect



Calculated relativistic contraction of the 6s orbital.





☐ Lanthanoid contraction

Weber, D.; Gagne, M. R., *Top. Curr. Chem.* **2015,** *357*, 167-211.

Gorin, D. J.; Toste, F. D., *Nature* **2007,** *446* (7134), 395-403.

Leyva-Perez, A.; Corma, A., *Angew. Chem. Int. Edit.* **2012,** *51* (3), 614-635.

Atomic and Optical Properties of Gold

Relativistic effects
Lanthanoid contraction

Enhanced Spin-orbit coupling

Expansion of 5d & 4f, Higher HOMO

Contraction of 6s & 6p, Lower LUMO

- Less important π back-bonding, more electron-deficient ligand
- Carbene character of Au(I)
- Aurophilicity
- Linear Au(I) complexes
- Hard to undergo oxidative addition

- Strong soft Lewis acid even in the presence of strongly donating ligands
- Stronger Au-L bond
- High electronegativity, pseudohalogen
- High oxidative potential for Au(III)
- Au(I) is air and moisture stable

Pyykko, P., *Angew. Chem. Int. Edit.* **2004,** *43* (34), 4412-4456.

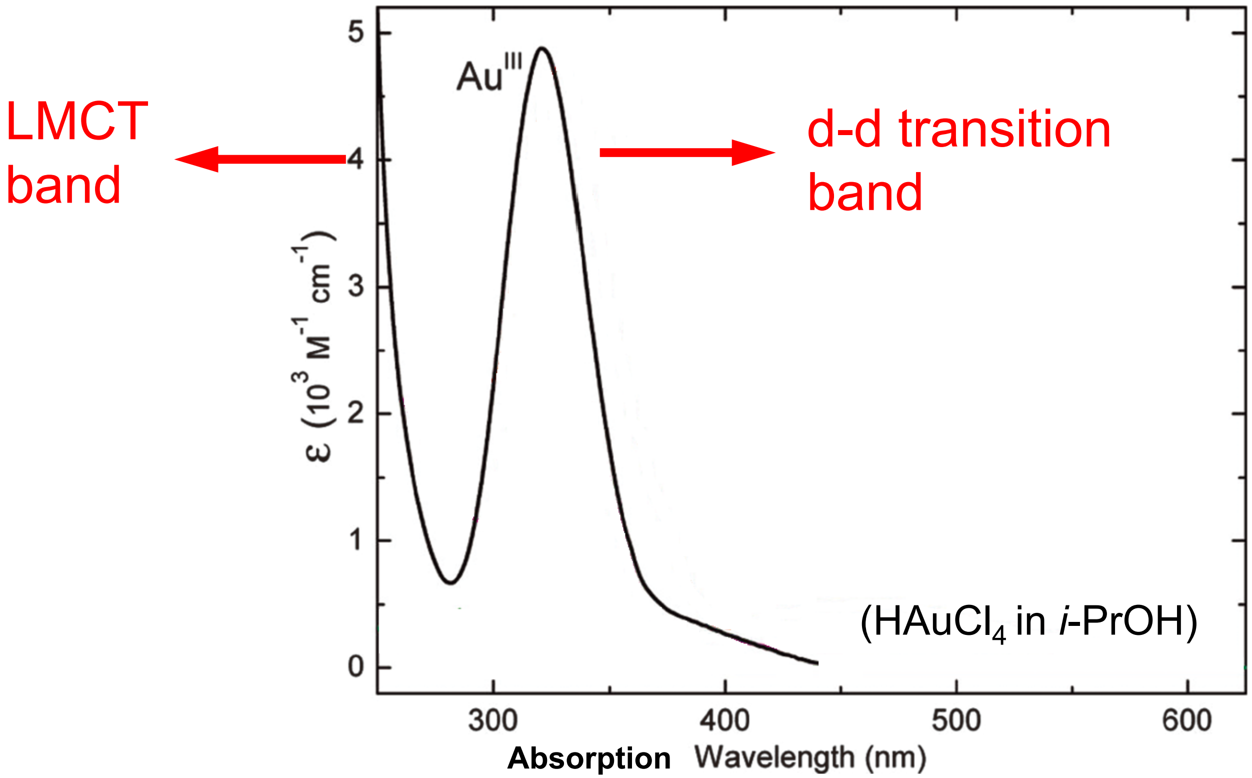
Gorin, D. J.; Toste, F. D., *Nature* **2007,** *446* (7134), 395-403.

Leyva-Perez, A.; Corma, A., *Angew. Chem. Int. Edit.* **2012,** *51* (3), 614-635.

Atomic and Optical Properties of Gold

☐ Au(III) species

- d^8 configuration → important non-emissive d-d transition.
- High electronegativity→ hardly observable MLCT, low energy LMCT.

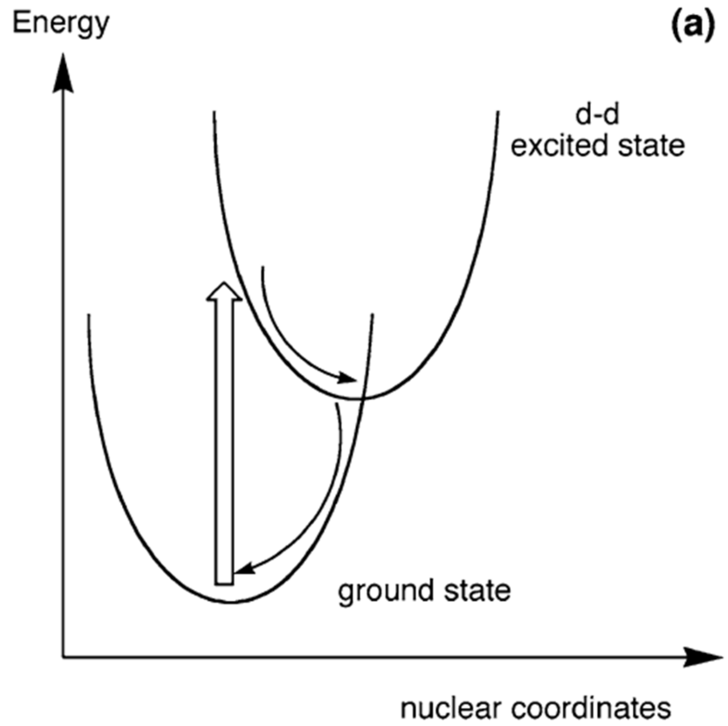


Vogler, A.; Kunkely, H., *Coordin. Chem. Rev.* **2001,** *219*, 489-507.
Cao, Z.; Bassani, D. M.; Bibal, B., Light activation of gold complexes. In *Photochemistry*, **2019**; pp 421-456.

Atomic and Optical Properties of Gold

□ Au(III) species

- d^8 configuration → important non-emissive d-d transition.
- High oxidizing state → dominant LMCT, with hardly observed MLCT.

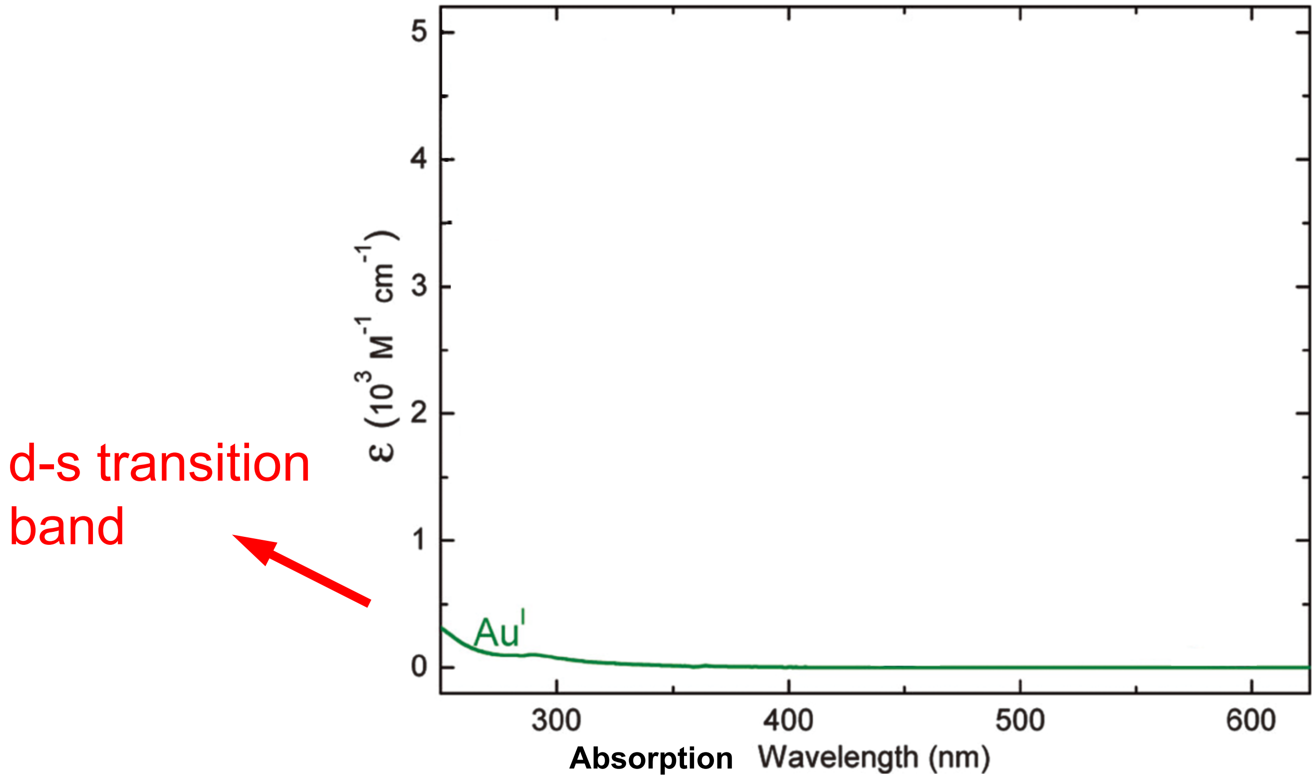


J. A. G. Williams, *Top. Curr. Chem*. **2007**, *281*, 205.

Atomic and Optical Properties of Gold

☐ Au(I) species

- d^{10} configuration → accessible d-s/d-p transition only.
- LMCT and MLCT could occur at reasonable energies.

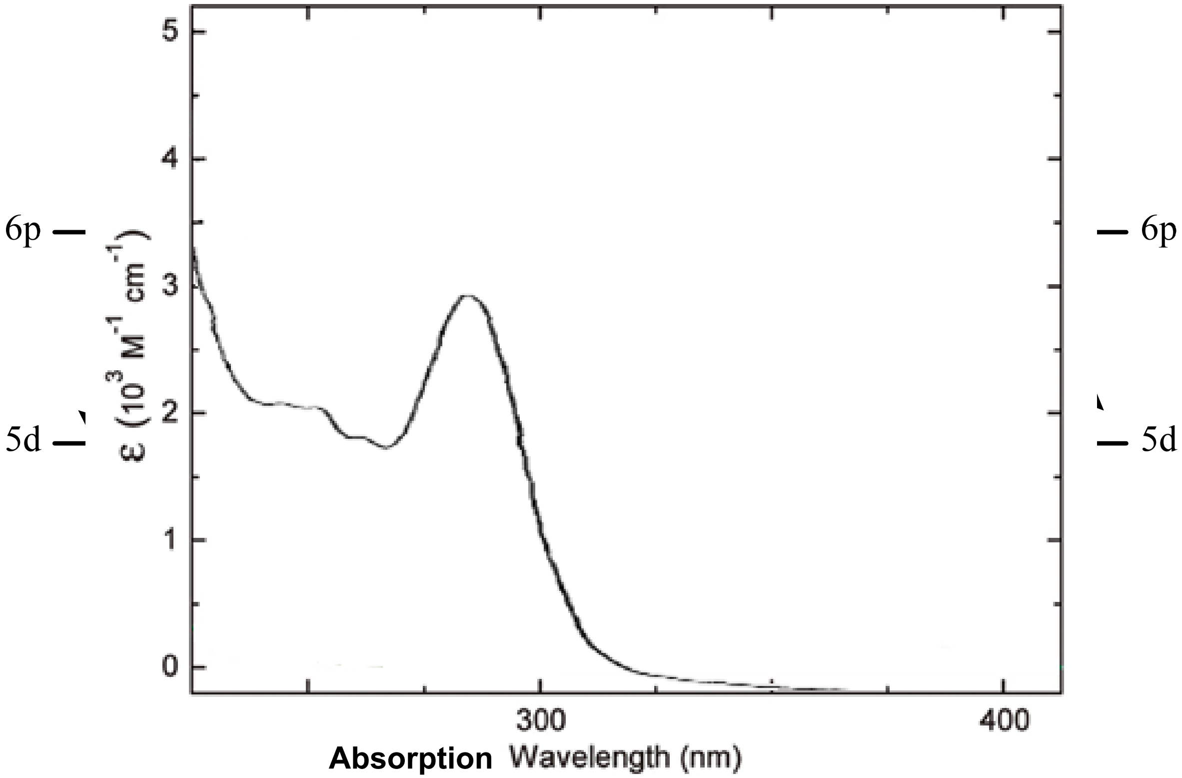


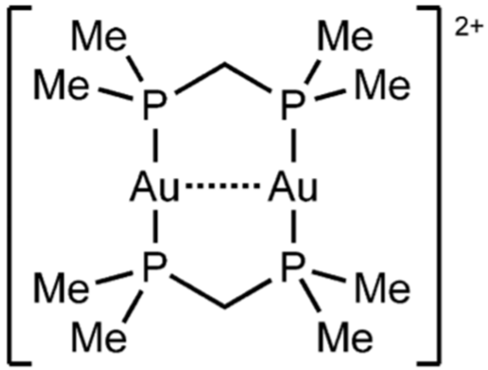
Vogler, A.; Kunkely, H., *Coordin. Chem. Rev.* **2001,** *219*, 489-507.
Cao, Z.; Bassani, D. M.; Bibal, B., Light activation of gold complexes. In *Photochemistry*, **2019**; pp 421-456.

Atomic and Optical Properties of Gold

☐ Dimeric Au(I) species

- The Au-Au interaction leads to a σ overlap of 5d and 6p orbitals.
- $(\sigma_{\mathrm{d}})^2(\sigma_{\mathrm{d}}^*)^2 \rightarrow (\sigma_{\mathrm{d}})^2(\sigma_{\mathrm{d}}^*)^1(\sigma_{\mathrm{p}})^1$ transition, with an Au-Au bond forming.





$[Au_2(dppm)_2]^{2+}$

λ_{max}=292 nm

Vogler, A.; Kunkely, H., *Coordin. Chem. Rev.* **2001,** *219*, 489-507.
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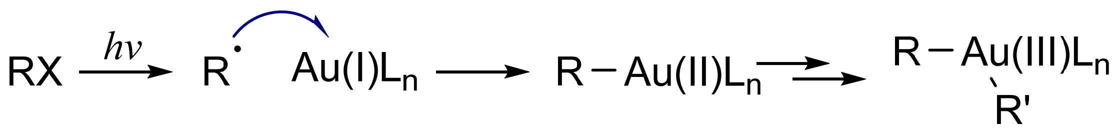
Gold complex as transition-metal catalyst

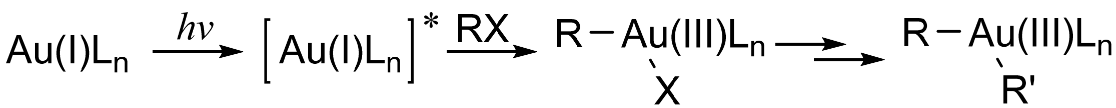
- Gold complex as transition-metal catalyst
  - The vital question: How to perform oxidative addition?
  - What can light do to facilitate oxidative addition?

Direct Oxidation Addition: Possible but Hard (Ligand design, directing group…)

Radical Addition

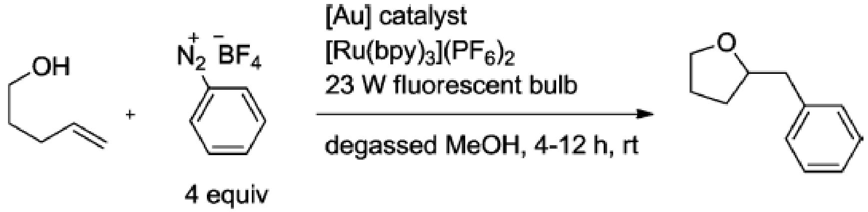


Light promoted
Oxidation Addition

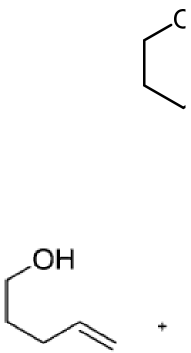


Gold complex as transition-metal catalyst

- Gold-photoredox catalysis involving radical addition



Zhang 2010



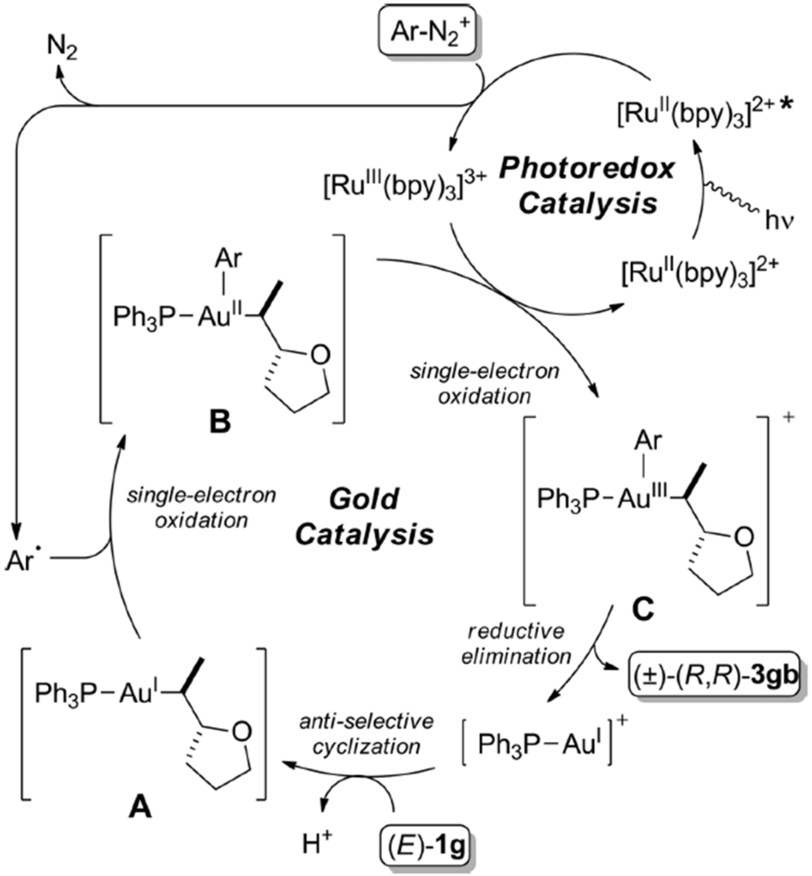
us 2013

entry[a]	[Au] catalyst	[Au]/[Ru] (mol%)	yield (%)[b]
1	Ph_3PAuCl	10/5	51
2	$[dppm(AuCl)_2]$	10/5	22
3	$AuCl_3$	10/5	trace
4	$(pic)AuCl_2$	10/5	trace
5	IPrAuCl	10/5	trace
6	$[Ph_3PAu]NTf_2$	10/5	84
7	$[Ph_3PAu]NTf_2$	10/2.5	88 (79)
8	$[Ph_3PAu]NTf_2$	10/1	61
9	$[Ph_3PAu]NTf_2$	5/2.5	50
10	$[Ph_3PAu]NTf_2$	1/2.5	22
11[c]	$[Ph_3PAu]NTf_2$	10/2.5	6
12	$[Ph_3PAu]NTf_2$	10/—	4
13	—	—/2.5	0

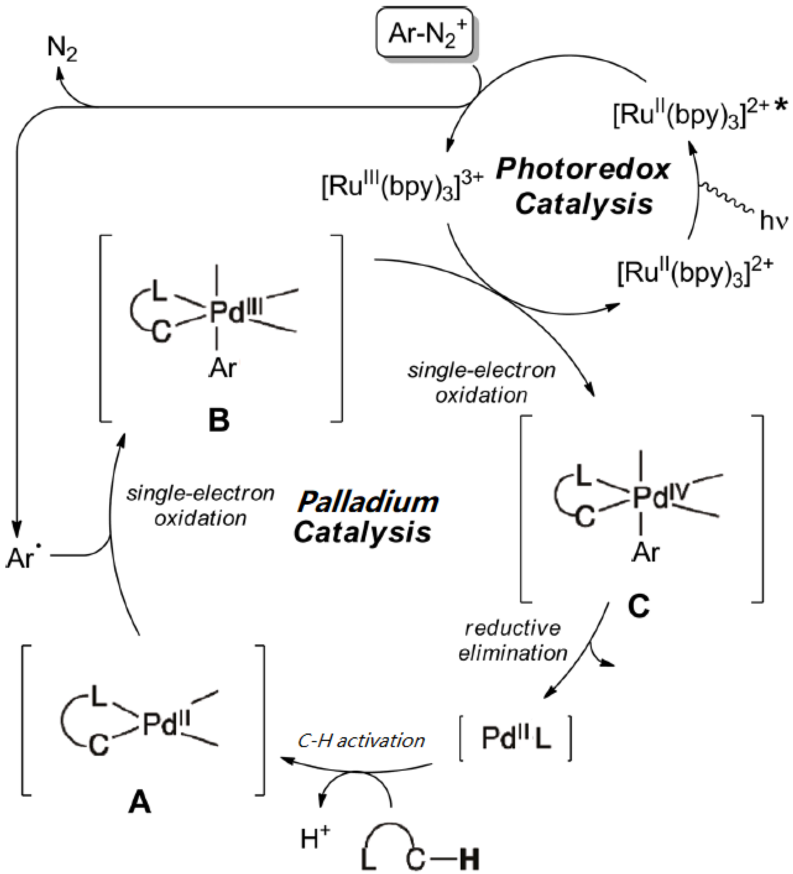
Zhang, G. Z.; Cui, L.; Wang, Y. Z.; Zhang, L. M., *J. Am. Chem. Soc.* **2010,** *132* (5), 1474-+.
Sahoo, B.; Hopkinson, M. N.; Glorius, F., *J. Am. Chem. Soc.* **2013,** *135* (15), 5505-5508.

Gold complex as transition-metal catalyst

- Gold-photoredox catalysis involving radical addition



Glorius 2013



Sanford 2011

Kalyani, D.; McMurtrey, K. B.; Neufeldt, S. R.; Sanford, M. S., *J. Am. Chem. Soc.* **2011,** *133* (46), 18566-9.

Sahoo, B.; Hopkinson, M. N.; Glorius, F., *J. Am. Chem. Soc.* **2013,** *135* (15), 5505-5508.

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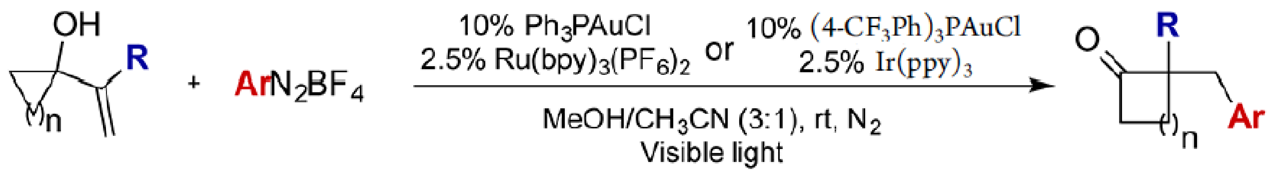
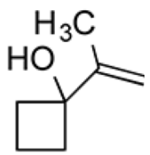




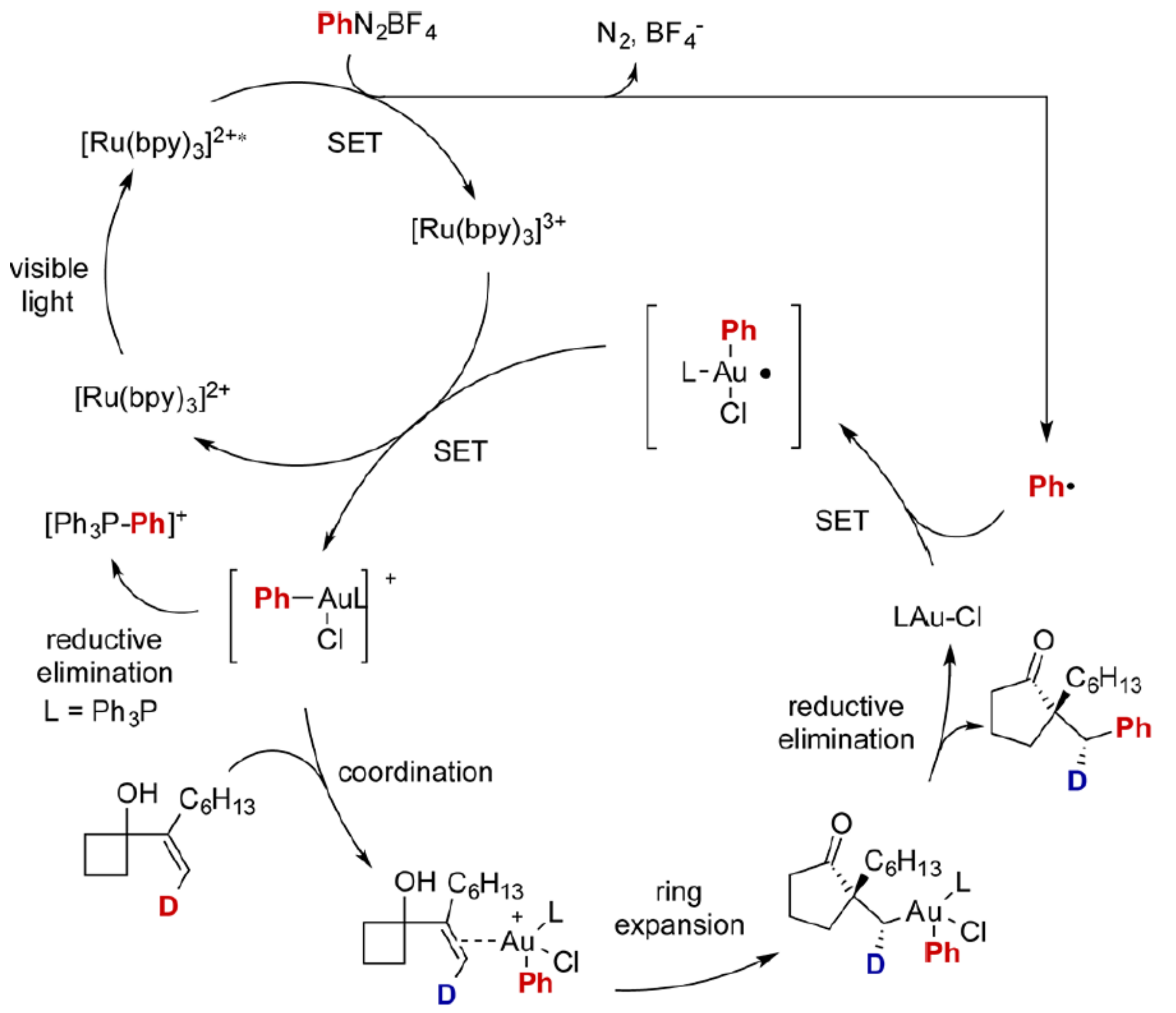
entry	*n*	R	Ar	time (h)	**3** (% yield)
1	2	*n*-hexyl	Ph	6	(90)
2	2	isopropyl	Ph	6	(81)
3	2	Bn	Ph	6	(83)
4	2	PhthN(CH$_2$)$_3$	Ph	4	(80)
5	2	Ph	Ph	24	(34)
6[b]	2	Ph	4-FPh	24	(71)
7[b]	2	4-ClPh	4-FPh	24	(67)
8[b]	2	4-MePh	4-FPh	6	(80)
9[b]	2	2-MePh	4-FPh	24	(32)
10	1	Ph	Ph	15	(67)
11	1	Bn	Ph	6	(51)

ste 2014

Walkinshaw, A. J.; Xu, W.; Suero, M. G.; Gaunt, M. J., *J. Am. Chem. Soc.* **2013,** *135* (34), 12532-5.
Shu, X. Z.; Zhang, M.; He, Y.; Frei, H.; Toste, F. D., *J. Am. Chem. Soc.* **2014,** *136* (16), 5844-5847.

Gold complex as transition-metal catalyst

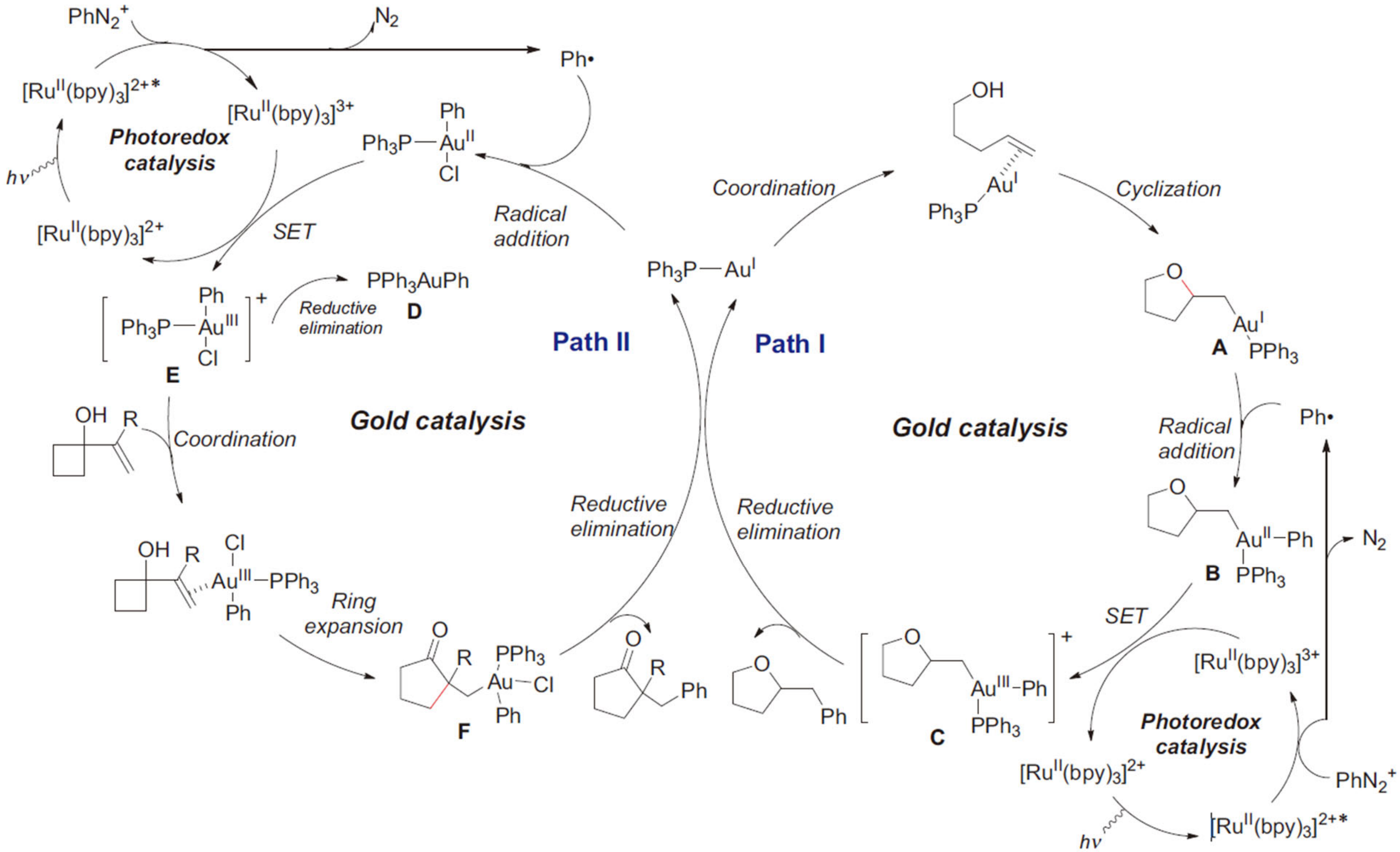
- Gold-photoredox catalysis involving radical addition



Cao, Z.; Bassani, D. M.; Bibal, B., Light activation of gold complexes. In *Photochemistry*, **2019**; pp 421-456.

Gold complex as transition-metal catalyst

- Two proposed mechanism

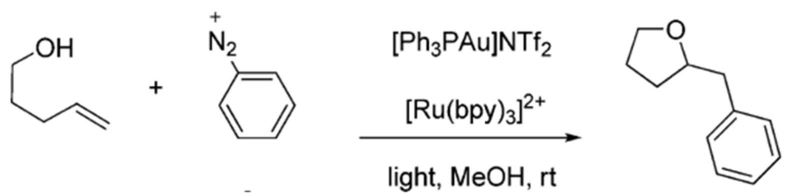


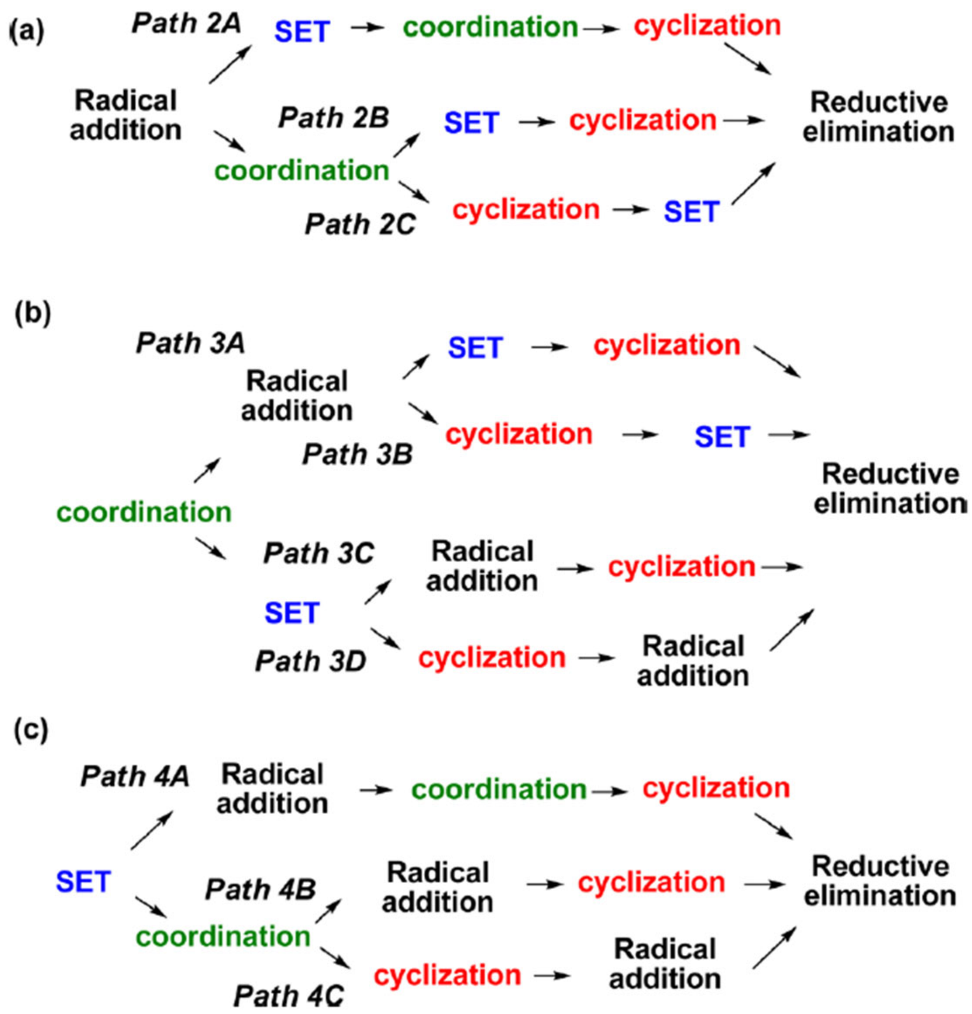
Cao, Z.; Bassani, D. M.; Bibal, B., Light activation of gold complexes. In *Photochemistry*, **2019**; pp 421-456.

Gold complex as transition-metal catalyst

■ Computational studies

- Reductive or oxidative quenching?
- Sequences of the steps?
- Chain process or not?

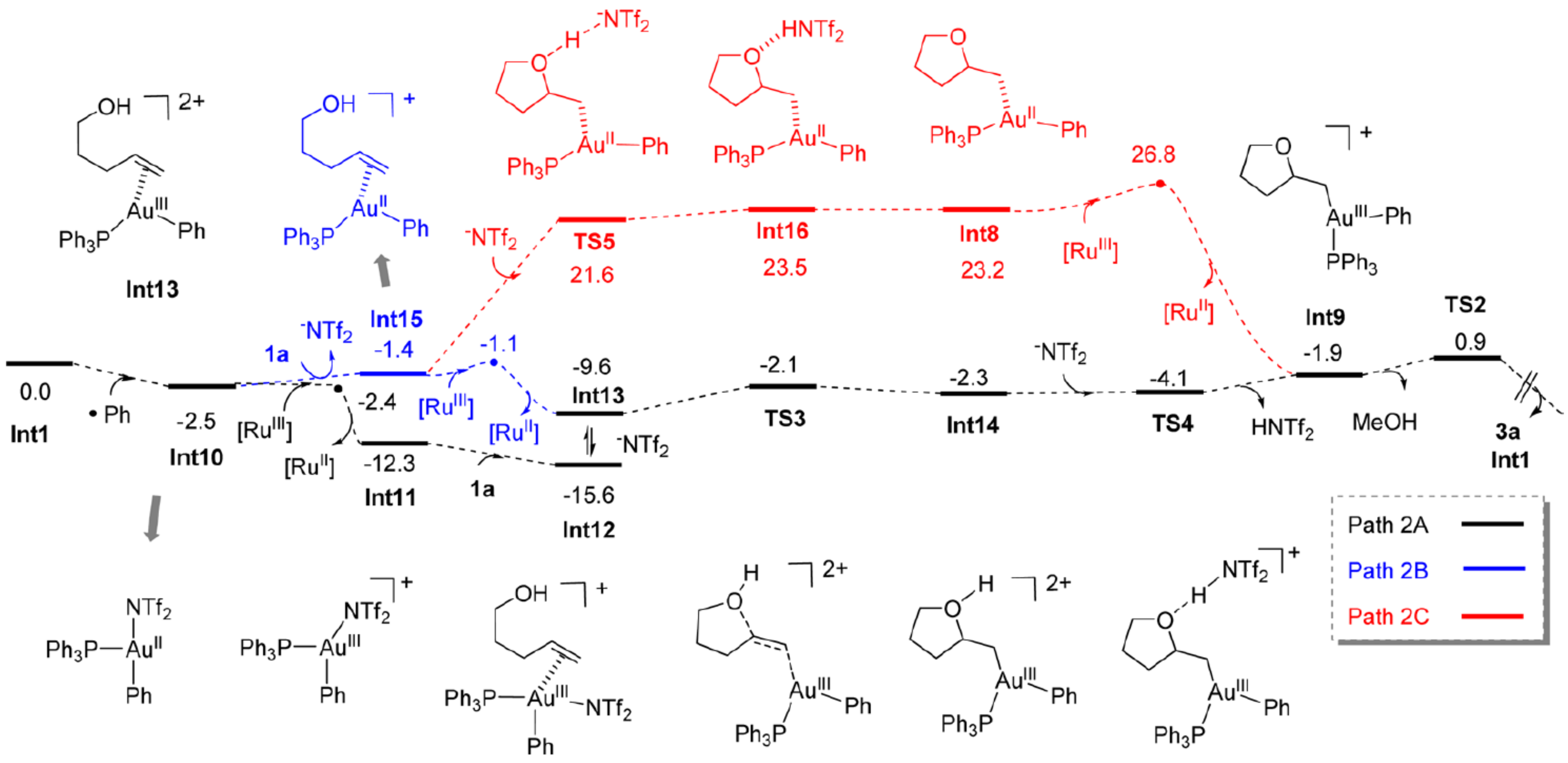




Zhang, Q.; Zhang, Z. Q.; Fu, Y.; Yu, H. Z., *Acs. Catal.* **2016,** *6* (2), 798-808.

Gold complex as transition-metal catalyst

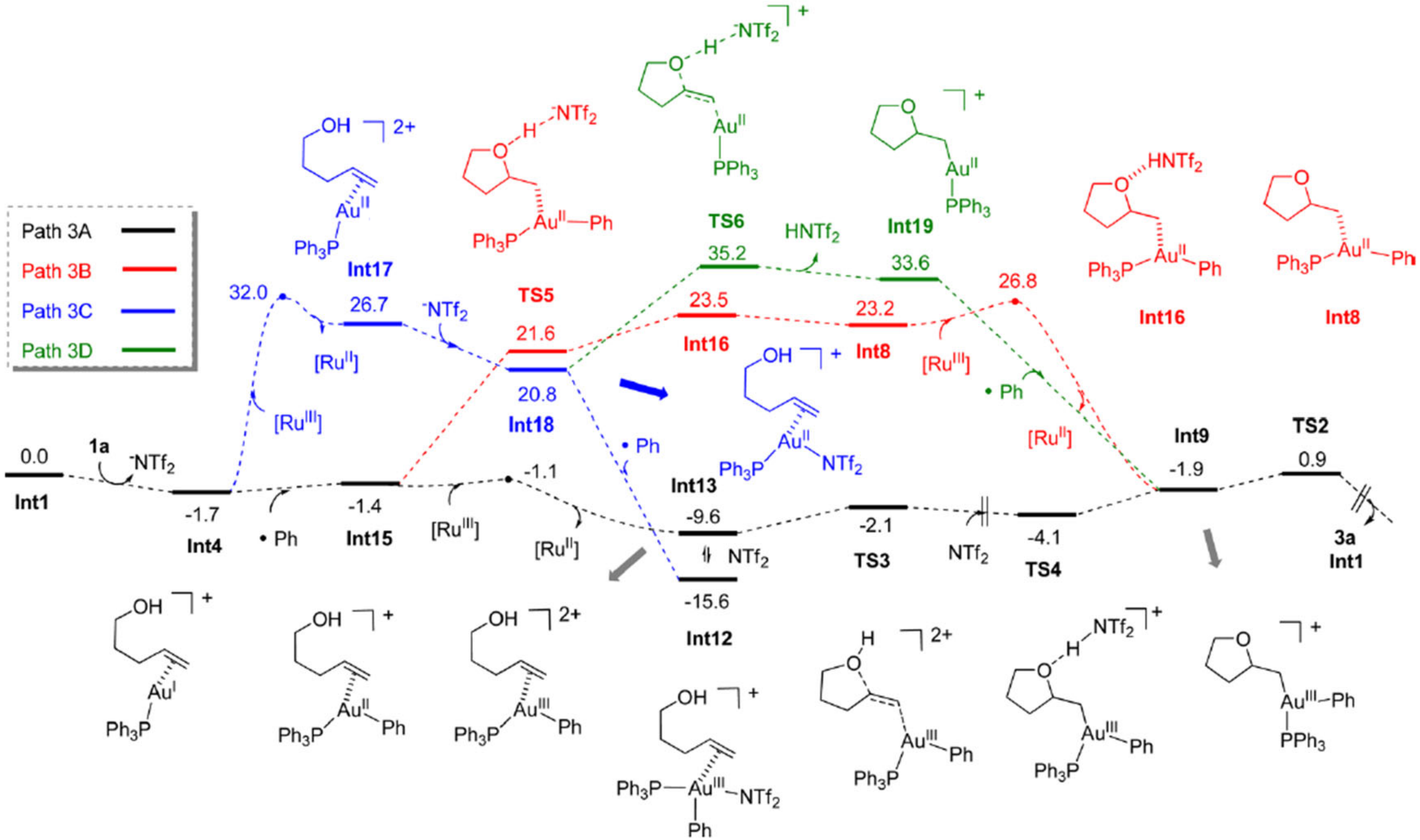
- Computational studies: radical-addition-first



Zhang, Q.; Zhang, Z. Q.; Fu, Y.; Yu, H. Z., *Acs. Catal.* **2016,** *6* (2), 798-808.

Gold complex as transition-metal catalyst

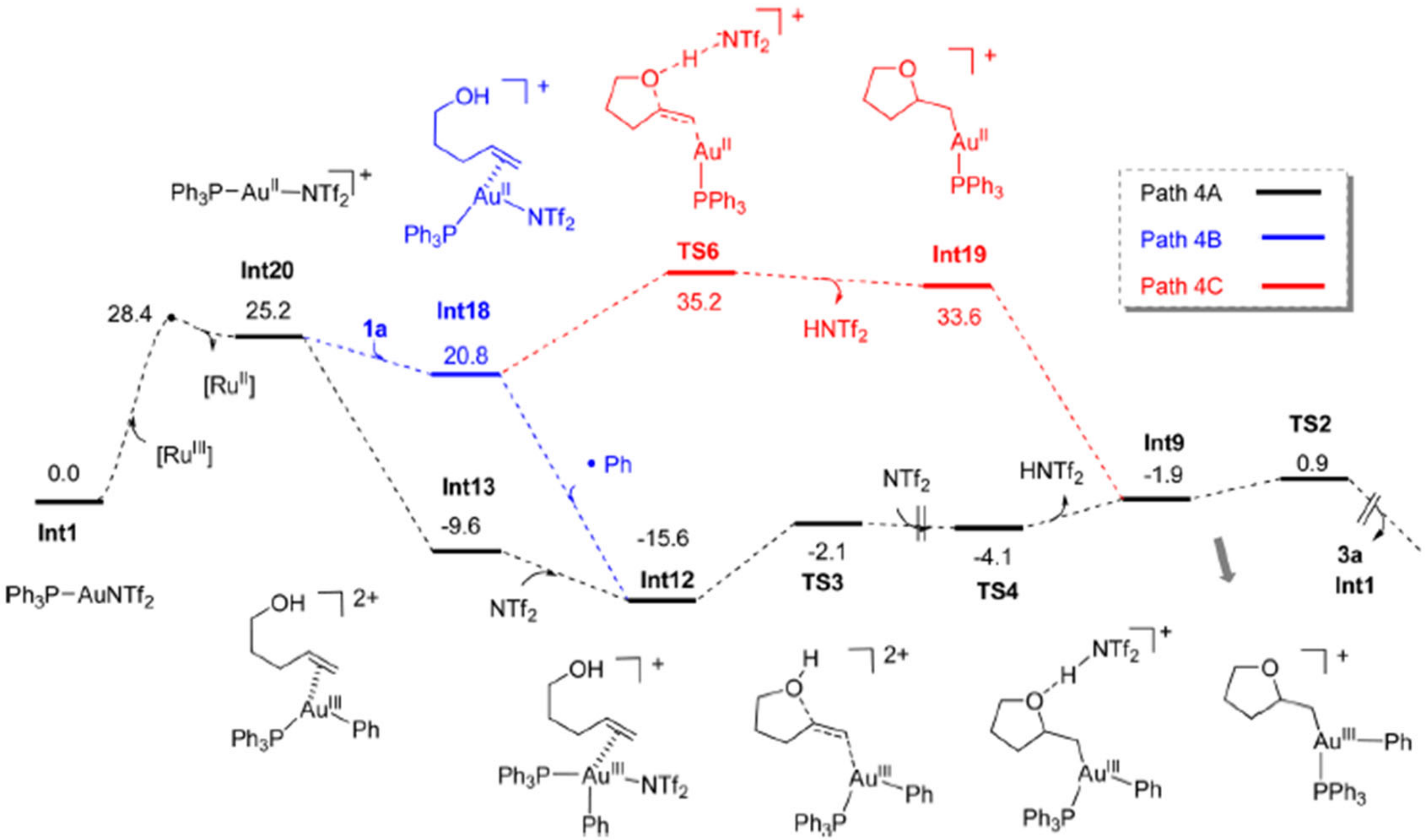
- Computational studies: alkene-coordination-first



Zhang, Q.; Zhang, Z. Q.; Fu, Y.; Yu, H. Z., *Acs. Catal.* **2016,** *6* (2), 798-808.

Gold complex as transition-metal catalyst

- Computational studies: SET-first



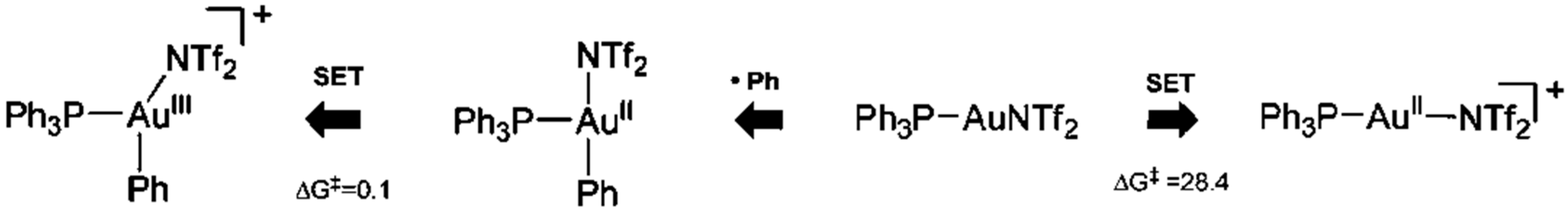
Zhang, Q.; Zhang, Z. Q.; Fu, Y.; Yu, H. Z., *Acs. Catal.* **2016,** *6* (2), 798-808.

Gold complex as transition-metal catalyst

- Mechanistic rationale

  - Higher electrophilic Au(III) center results in lower alkene LUMO energy, thus favoring the cyclization.

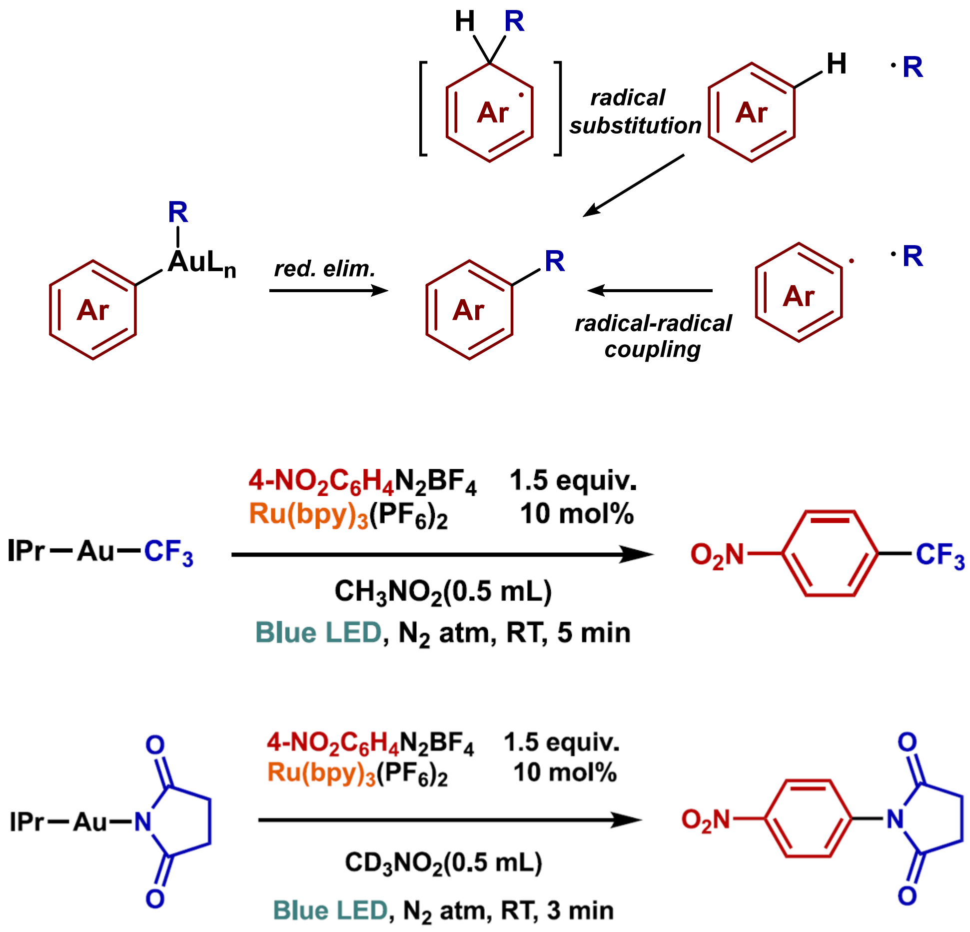
  - Radical addition occurs preferentially before the SET step.



Zhang, Q.; Zhang, Z. Q.; Fu, Y.; Yu, H. Z., *Acs. Catal.* **2016,** *6* (2), 798-808.

Gold complex as transition-metal catalyst

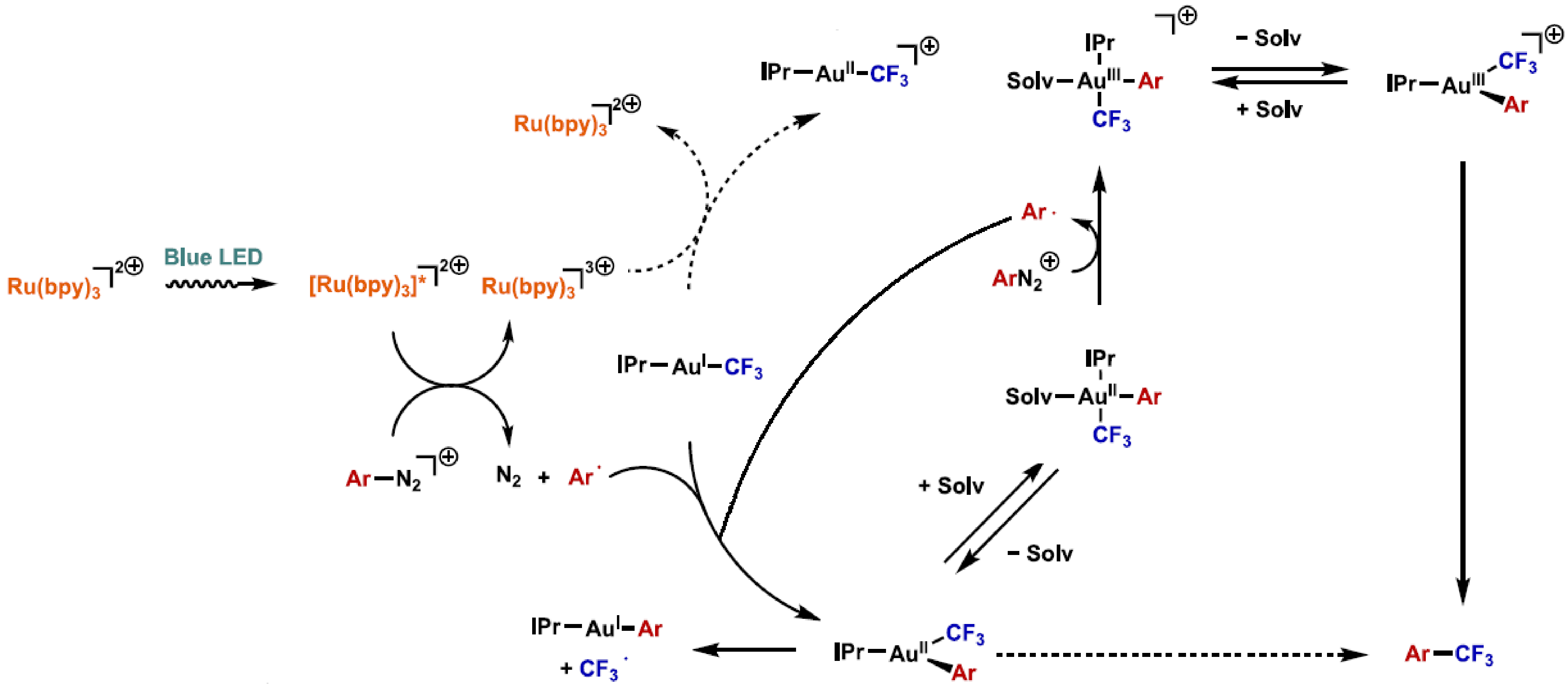
- Elucidating the bond-forming step



Kim, S.; Toste, F. D., *J. Am. Chem. Soc.* **2019,** *141* (10), 4308-4315.

Gold complex as transition-metal catalyst

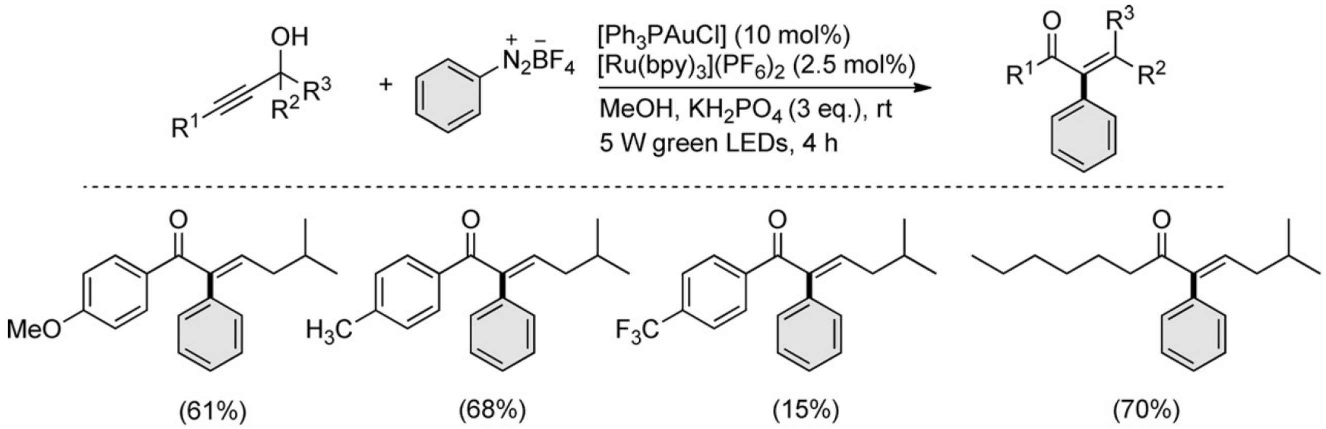
- Elucidating the bond-forming step



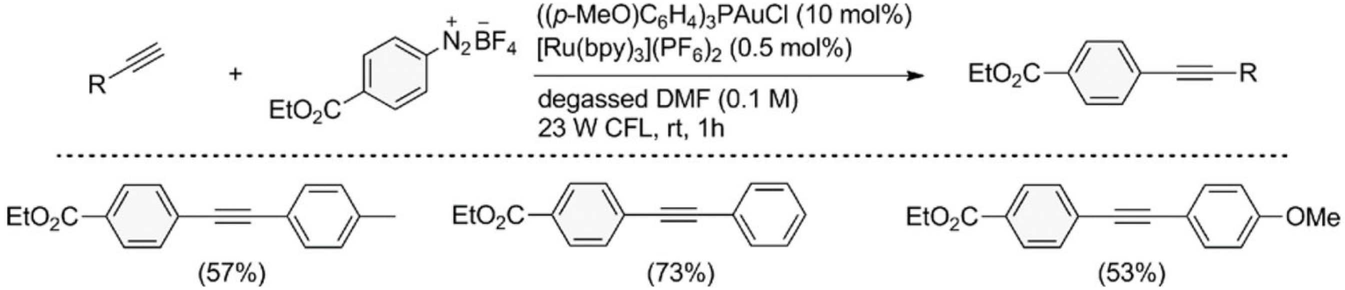
Kim, S.; Toste, F. D., *J. Am. Chem. Soc.* **2019,** *141* (10), 4308-4315.

Gold complex as transition-metal catalyst

- Scope



Meyer–Schuster rearrangement

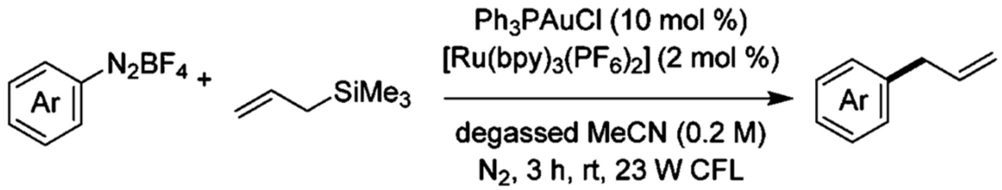


Terminal alkynes C-H (or C-Si) arylation

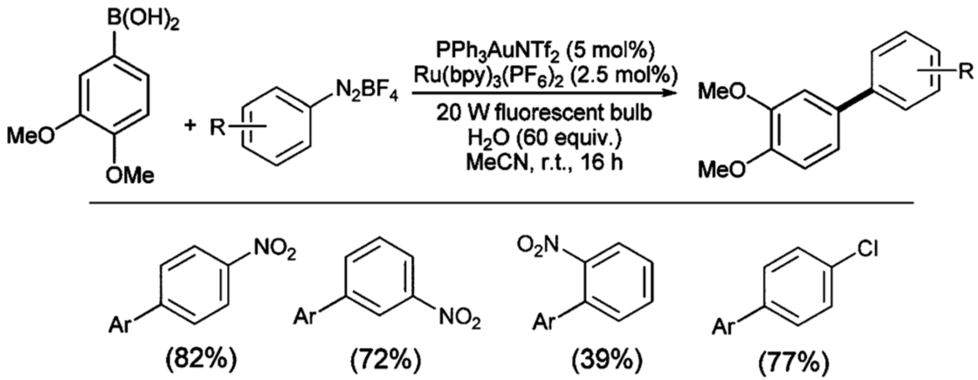
Tlahuext-Aca, A.; Hopkinson, M. N.; Garza-Sanchez, R. A.; Glorius, F., *Chemistry* **2016,** *22* (17), 5909-13.
Tlahuext-Aca, A.; Hopkinson, M. N.; Sahoo, B.; Glorius, F., *Chem. Sci.* **2016,** *7* (1), 89-93.

Gold complex as transition-metal catalyst

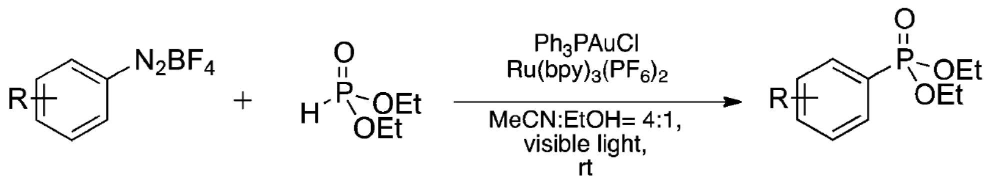
- Scope



Cross-coupling



Cross-coupling



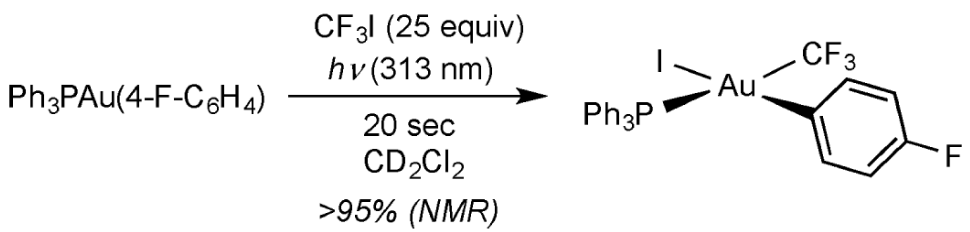
C-P Cross-coupling

Akram, M. O.; Mali, P. S.; Patil, N. T., *Org. Lett.* **2017,** *19* (12), 3075-3078.
Gauchot, V.; Lee, A. L., *Chem Commun (Camb)* **2016,** *52* (66), 10163-6.
He, Y.; Wu, H.; Toste, F. D., *Chem Sci* **2015,** *6* (2), 1194-1198.

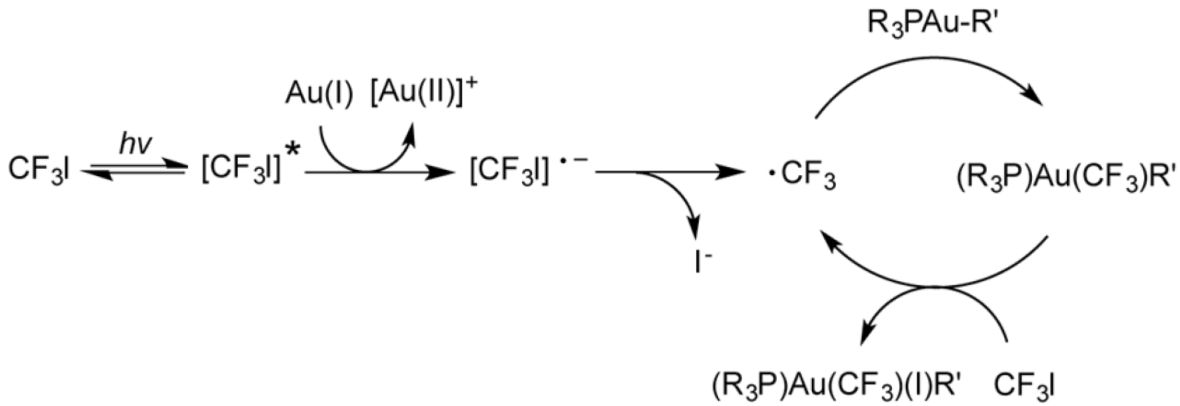
Gold complex as transition-metal catalyst

- Energy-transfer promoted oxidation addition

  - Early report of light facilitated oxidative addition to Au(I)



Toste 2014



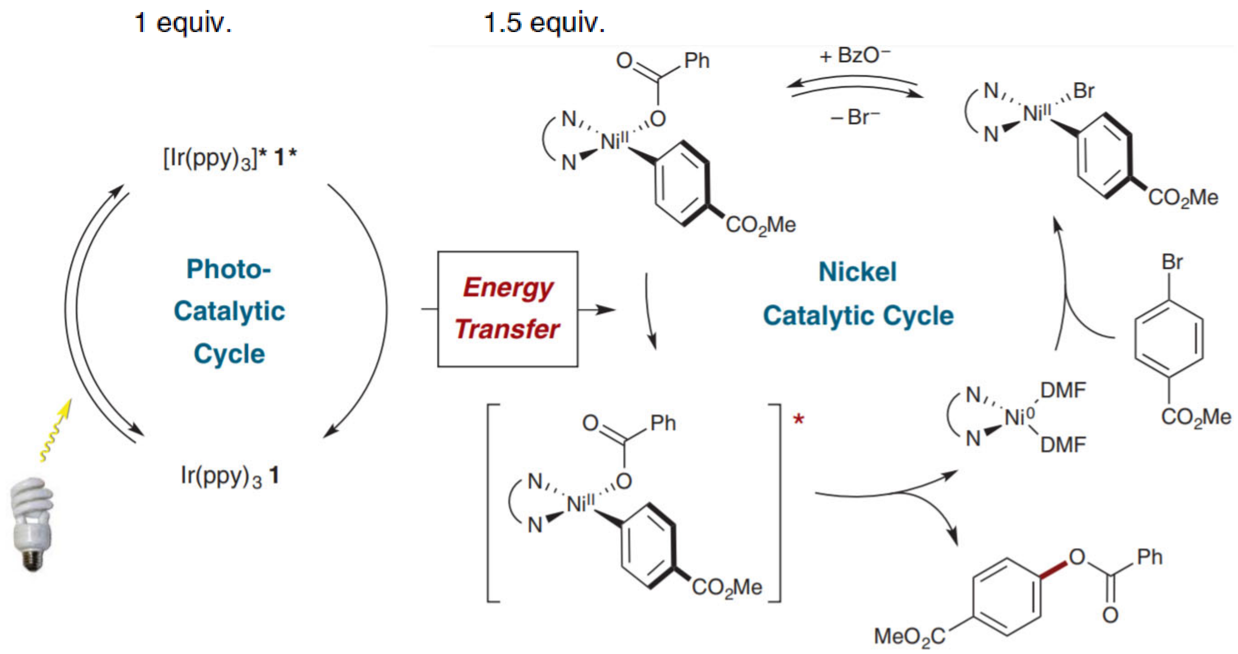
Winston M S, Wolf W J, Toste F D. *J. Am. Chem. Soc.*, **2014**, *136*(21), 7777-7782.

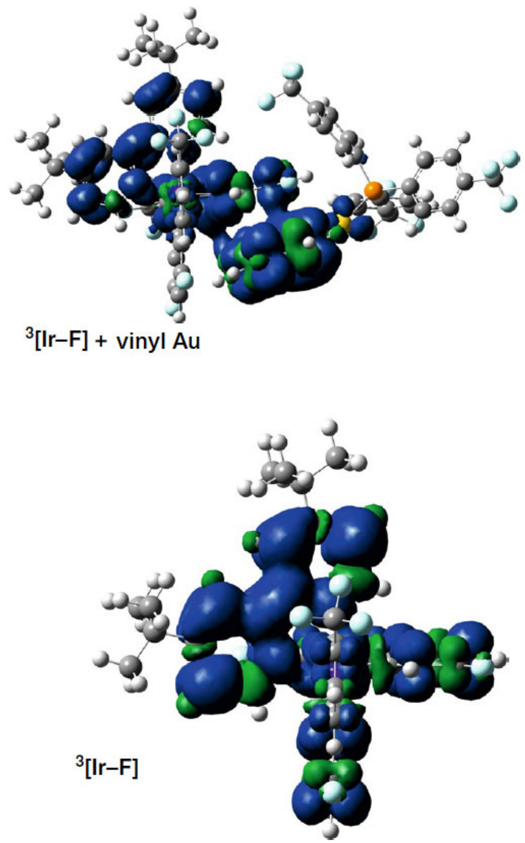
For photoinduced reductive elimination, see: Cao, Z.; Bassani, D. M.; Bibal, B., In *Photochemistry*, **2020,** *47,* pp 423-456.

Gold complex as transition-metal catalyst

Energy-transfer promoted oxidation addition

- No conversion in the absence of irradiation, low conversion in the absence of [IrF]
- No florescence quenching of $[IrF]^*$ by RI or $[AuCF_3]$ is observed.
- Vinyl-Au intermediate is formed and isolated.
- Quenching of $[IrF]^*$ by vinyl-Au intermediate is confirmed.



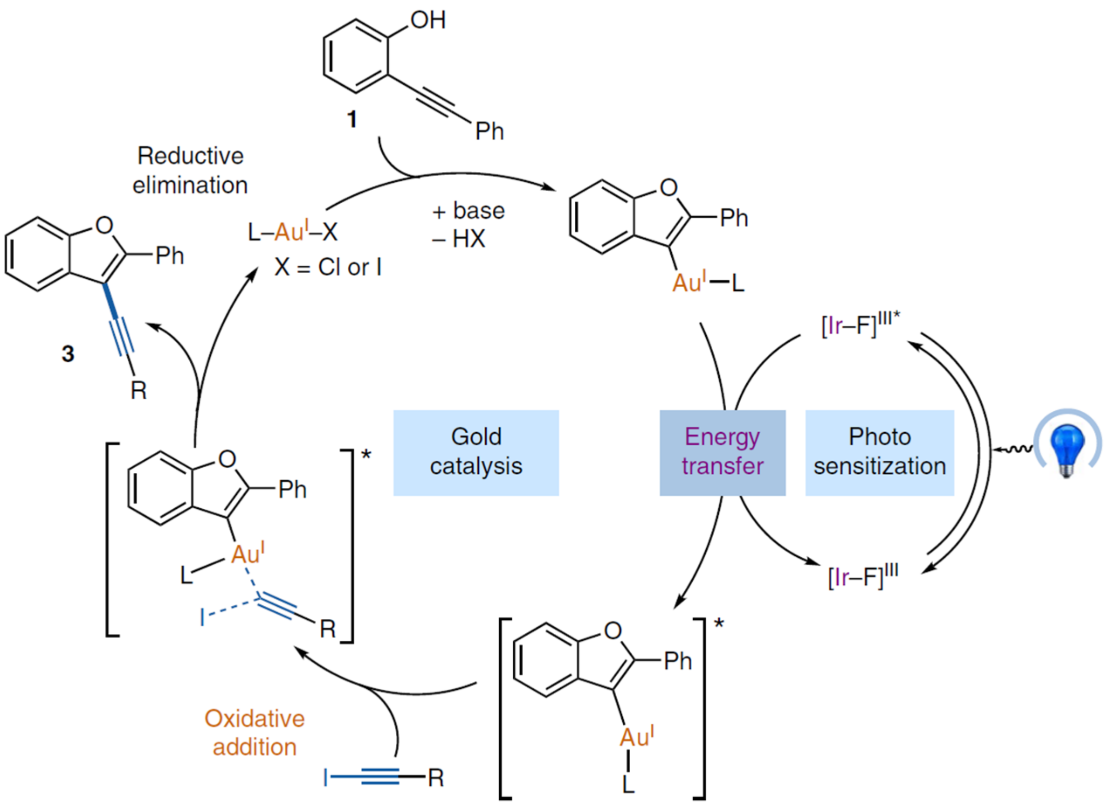


Welin, E. R.; Le, C.; Arias-Rotondo, D. M.; McCusker, J. K.; *Science* **2017,** *355* (6323), 380-385.
Xia, Z.; Corcé, V.; Zhao, F.; L. Fensterbank, *et al.*, *Nat. chem.* **2019,** *11* (9), 797-805.

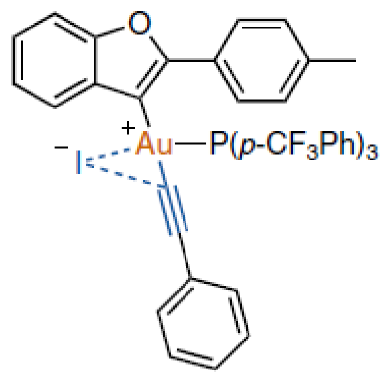
Gold complex as transition-metal catalyst

Energy-transfer promoted oxidation addition

- The reaction proceeds on the triplet potential energy surface.
- Catalytic cycle:



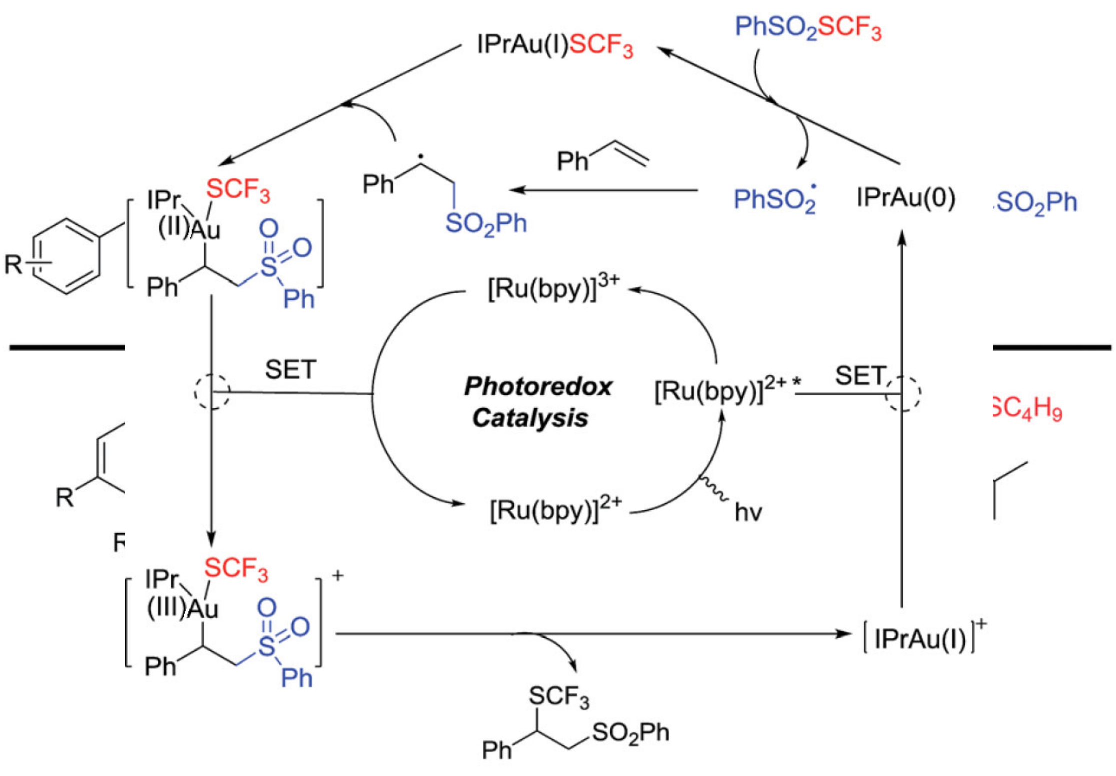
via



Xia, Z.; Corcé, V.; Zhao, F.; L. Fensterbank, *et al.*, *Nat. chem.* **2019,** *11* (9), 797-805.

Gold complex as transition-metal catalyst

- Scope

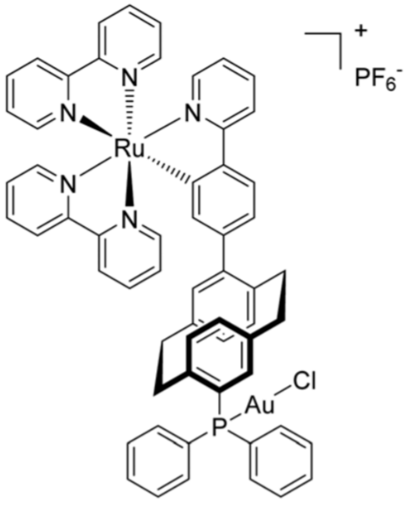


Atom transfer radical addition (ATRA)

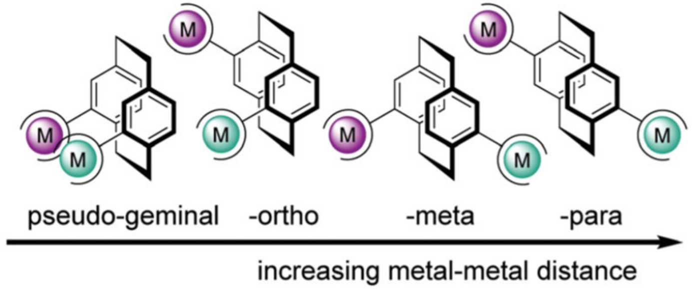
Li, H.; Shan, C.; Tung, C. H.; Xu, Z., *Chem. Sci.* **2017,** *8* (4), 2610-2615.

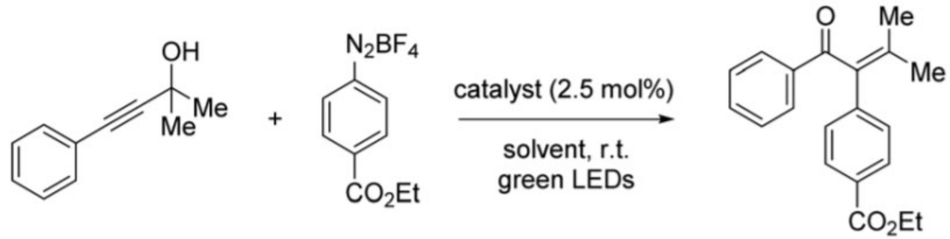
Gold complex as transition-metal catalyst

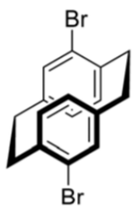
- Designing a tethered dual catalyst



pAuRu





5 steps, 25% from 

Entry	Catalyst	Solvent	Yield [%]
1	PPh_3AuCl, $Ru(bpy)_3Cl_2$	MeOH	76
2	PPh_3AuCl, $Ru(bpy)_3Cl_2$	MeCN/MeOH 3 : 1	73
3	PPh_3AuCl, $Ru(bpy)_2(ppy)PF_6$	MeCN/MeOH 3 : 1	73
4	**PCP-Au, PCP-Ru**	MeCN/MeOH 3 : 1	70
5	**pAuRu**	MeCN/MeOH 3 : 1	63

Knoll, D. M.; Zippel, C.; Hassan, Z.; Nieger, M.; Weis, P.; Bräse, S., *Dalton Trans.* **2019,** *48* (48), 17704-17708.

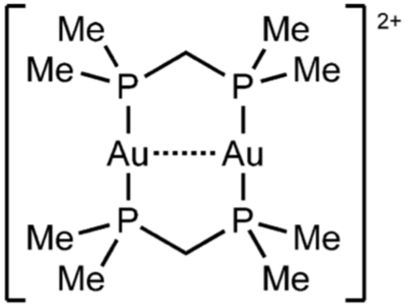
Outline

- History of Homogenous Gold Catalysis
- Atomic and Optical Properties of Gold
- Combining Gold Catalysis and Light
  - Gold complex as a transition-metal catalyst
  - Gold complex as photosensitizer
- A Brief Conclusion
- Application in Synthesis

Gold complex as photosensitizer

■ Properties of dimeric gold complex

- The dimeric gold(I) complex $[Au_2(\mu\text{-dppm})_2]^{2+}$



$[Au_2(dppm)_2]^{2+}$

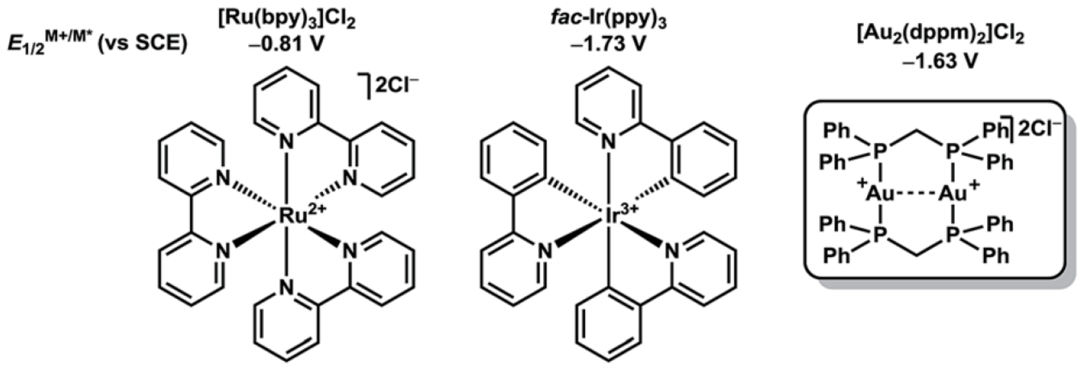
Quencher	k_q (M^{-1} s^{-1})[a]
Tetrabromomethane	8.90×10^9
Bromoform	8.70×10^9
Tetrachloromethane	3.37×10^9
Ethyl iodide	1.73×10^9
Methyl iodide	1.00×10^9
Allyl bromide	7.58×10^8
Chloroform	4.59×10^7
n-Butyl bromide	2.85×10^6
Benzyl chloride	1.85×10^6

Obtained from Stern–Volmer analysis where $\tau_o/\tau = 1 + k_q\tau_o[Q]$

McTiernan, C. D.; Morin, M.; McCallum, T.; Scaiano, J. C.; Barriault, L., *Catal. Sci. Technol.* **2016,** *6* (1), 201-207.
Che, C.-M.; Kwong, H.-L.; Poon, C.-K.; Yam, V. W.-W., *J. Chem. Soc., Dalton Trans.* **1990,** (11), 3215-3219.
Che, C.-M.; Kwong, H.-L.; Yam, V. W.-W.; Cho, K.-C., *J. Chem. Soc, Chem. Comm.* **1989,** (13), 885-886.

Gold complex as photosensitizer

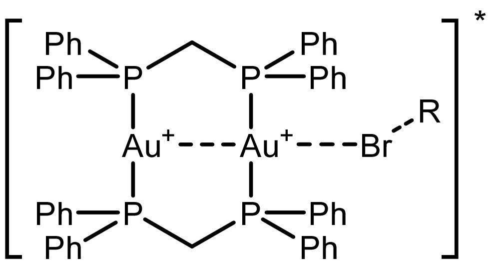
- Inner-sphere electron transfer

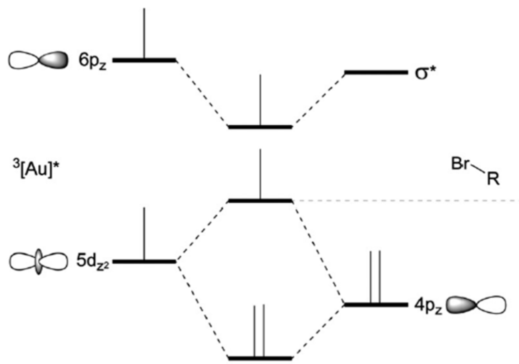


-1.9 ~ -2.5 V

Outer-Sphere MLCT Inner-Sphere PeT

- Upon excitation, an exciplex forms which facilitates the PeT.

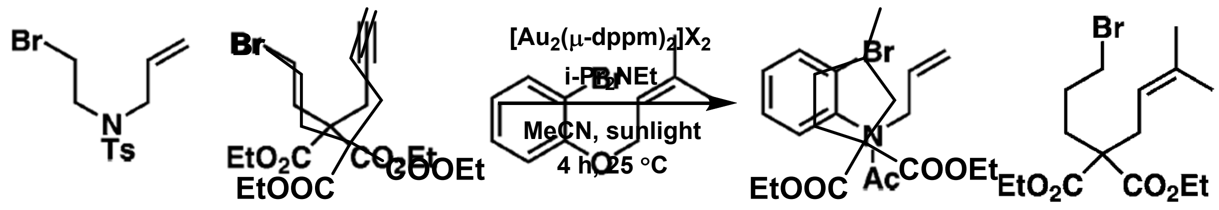




Zidan, M.; Rohe, S.; McCallum, T.; Barriault, L., *Catal. Sci. Technol.* **2018**, *8* (23), 6019-6028.
McCallum, T.; Rohe, S.; Barriault, L., *Synlett.* **2017**, *28* (03), 289-305.

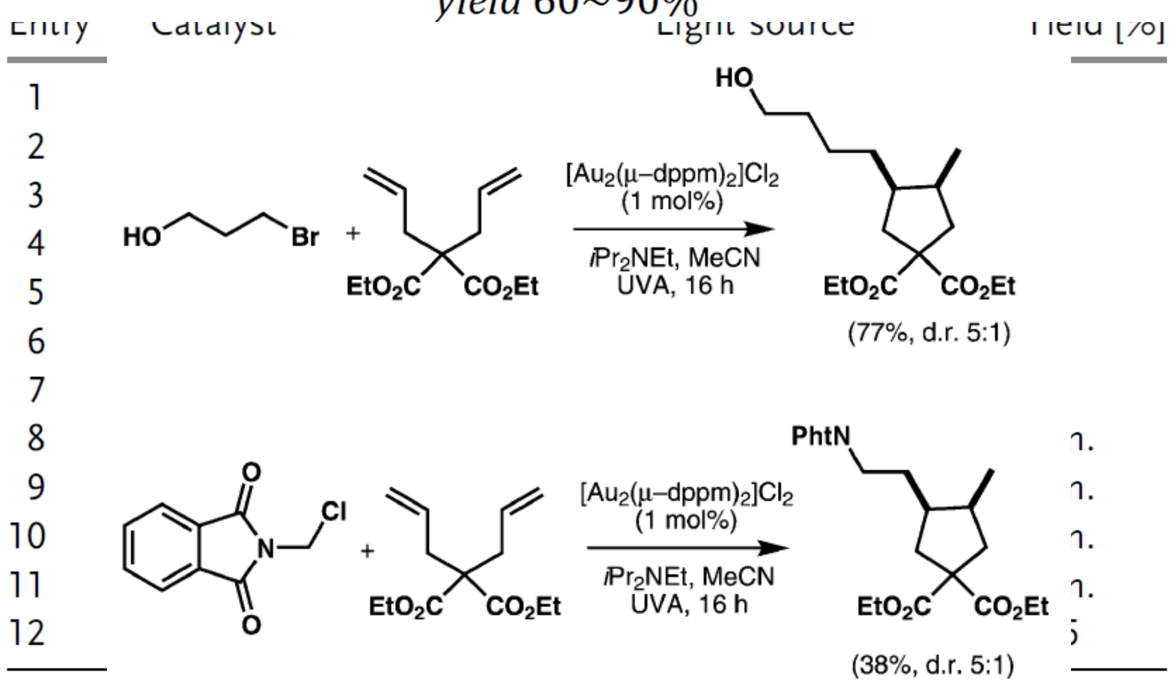
Gold complex as photosensitizer

- Reductive debromination radical cyclization



Barriault 2013

yield 60~90%



Revol, G.; McCallum, T.; Morin, M.; Gagosz, F.; Barriault, L., *Angew. Chem. Int. Ed.* **2013,** *52* (50), 13342-13345.

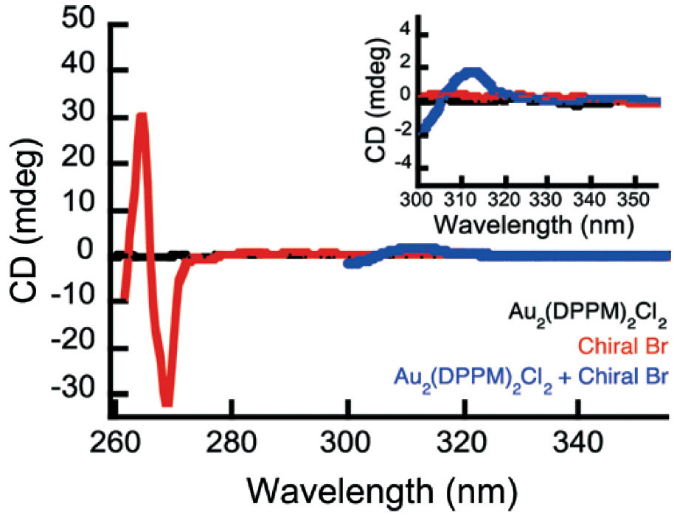
Gold complex as photosensitizer

- Mechanism studies

  - Reductive or oxidative quenching?

E^*_{ox} = −1.63 V *vs.* SCE and E^*_{red} = 0.70 V *vs.* SCE

E_{RX} = −1.90 V *vs.* SCE and E_{DIPEA} = 0.50 V *vs.* SCE



Quenching rate constant:

$Au_2(dppm)_2Cl_2$

Quencher	k_q (M^{-1} s^{-1})
ButylBr	2.9×10^6
RBr	3.1×10^7
DIPEA	2.7×10^7

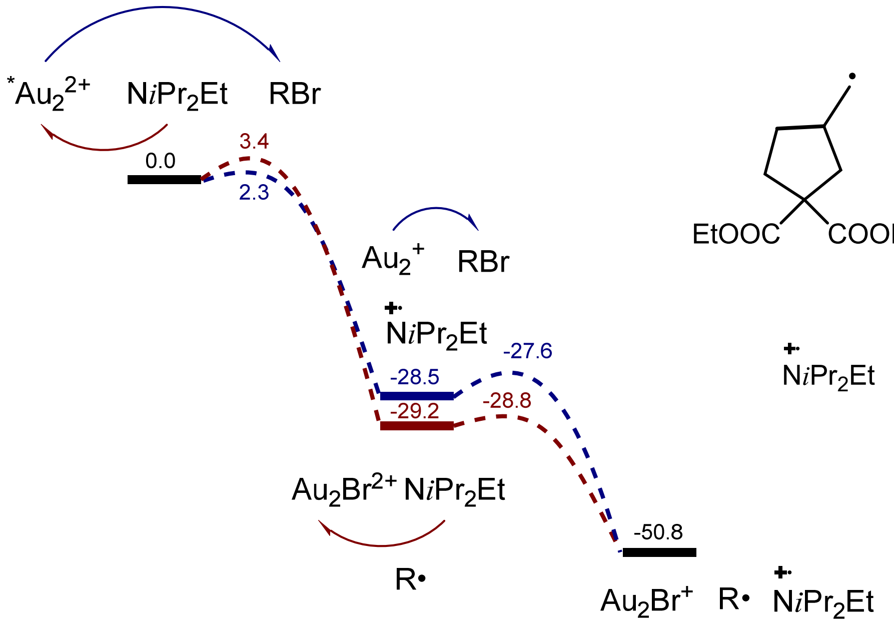
⇨ 18% quenched by RBr;
78% by DIPEA (excess).

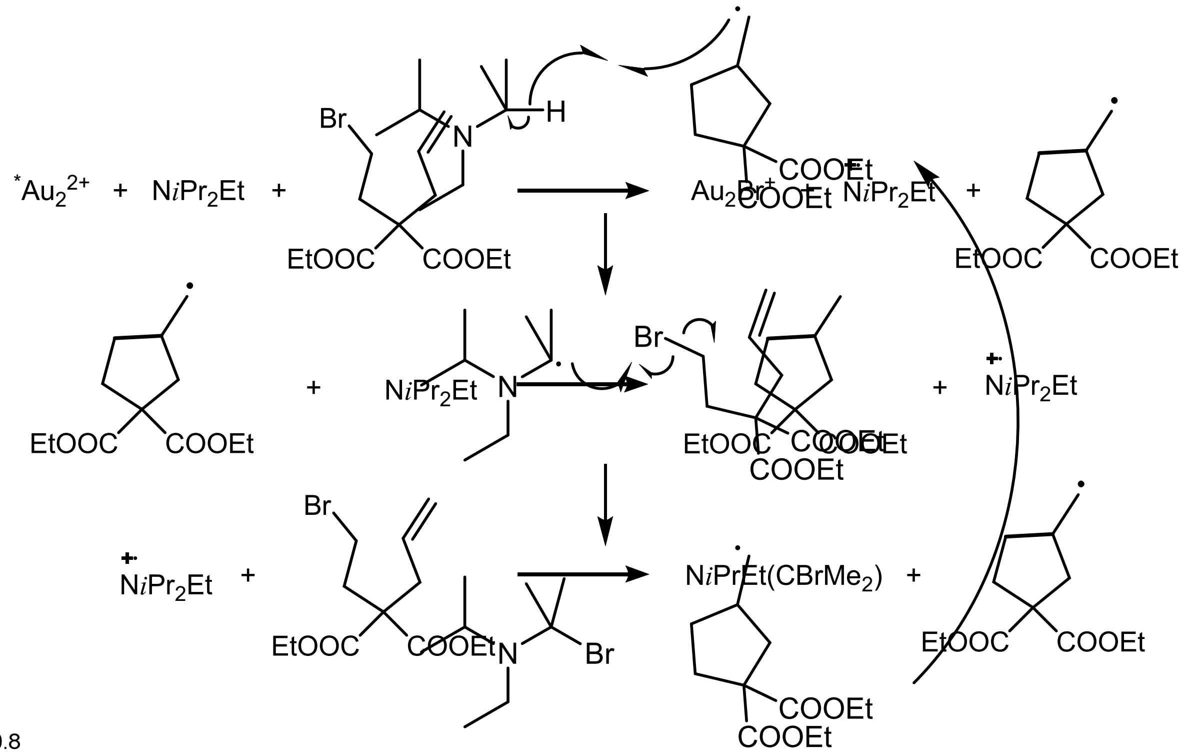
McTiernan, C. D.; Morin, M.; McCallum, T.; Scaiano, J. C.; Barriault, L., *Catal. Sci. Technol.* **2016,** *6* (1), 201-207.

Gold complex as photosensitizer

- Mechanism studies

  - Reductive or oxidative quenching?
  - Sequences of the steps?
  - Chain process or not?

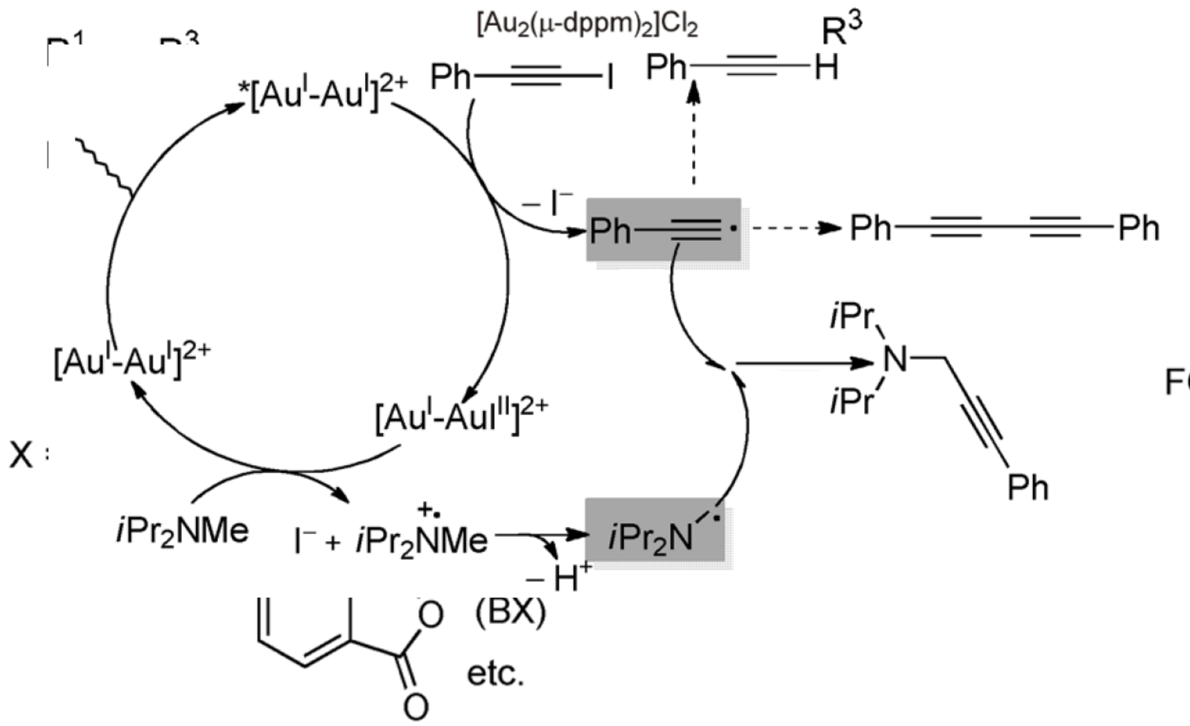




Yu, H.; Zhang, X.; Zhang, S., *Organomet.* **2018,** *37* (11), 1725-1733.

Gold complex as photosensitizer

- Scope



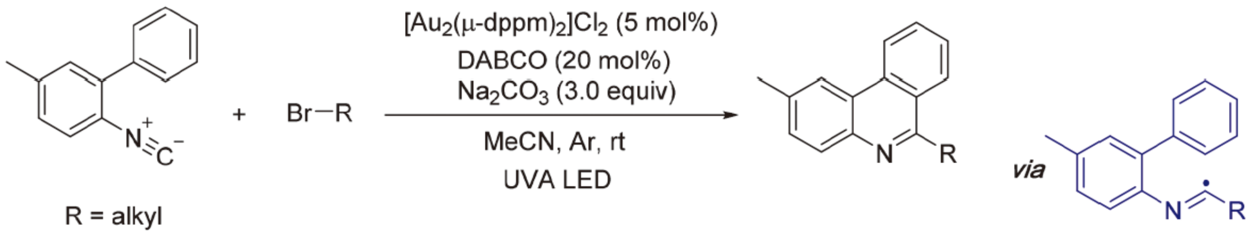
Hashmi 2014

FG

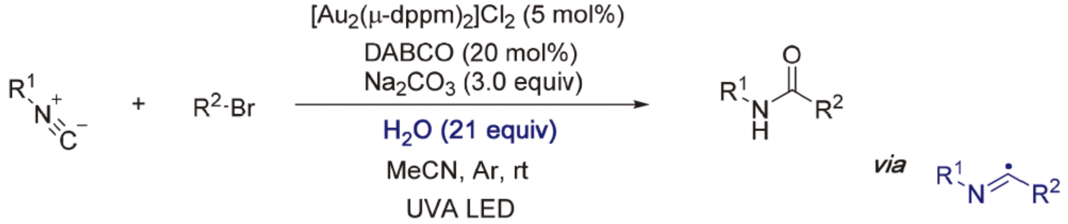
Xie, J.; Shi, S.; Zhang, T.; Mehrkens, N.; Rudolph, M.; Hashmi, A. S. K., *Angew. Chem. Int. Ed.* **2015,** *54* (20), 6046-6050.

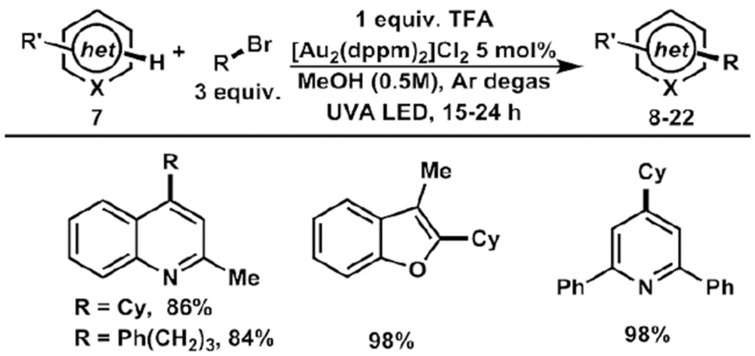
Gold complex as photosensitizer

- Scope



Addition to isonitriles



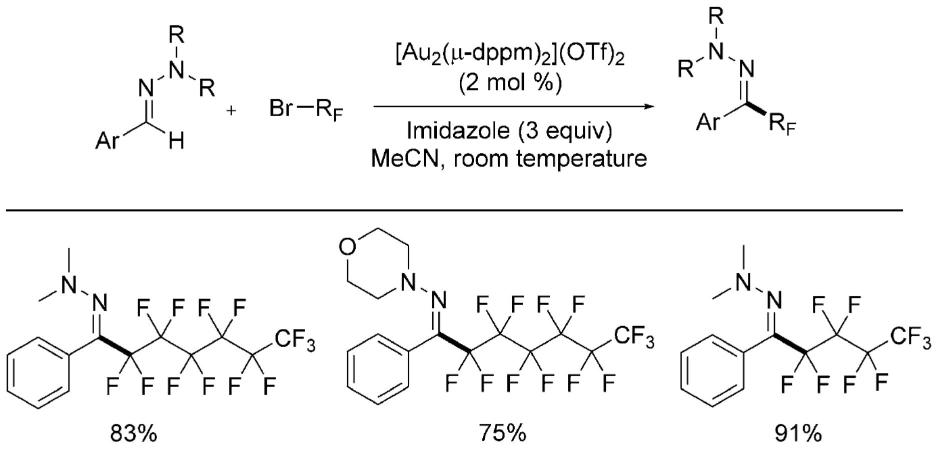


Addition to heteroarene

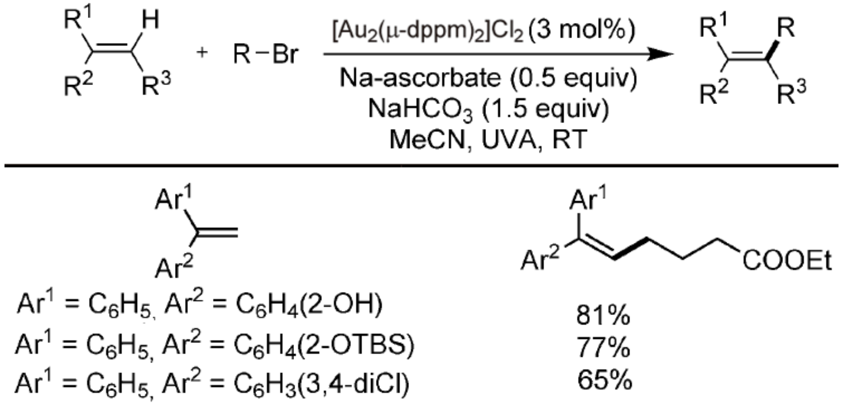
Rohe, S.; McCallum, T.; Morris, A. O.; Barriault, L., *J. org. chem.* **2018**, *83* (17), 10015-10024.
McCallum, T.; Barriault, L., *Chem. Sci.* **2016**, *7* (7), 4754-4758.

Gold complex as photosensitizer

- Scope



Addition to hydrazones

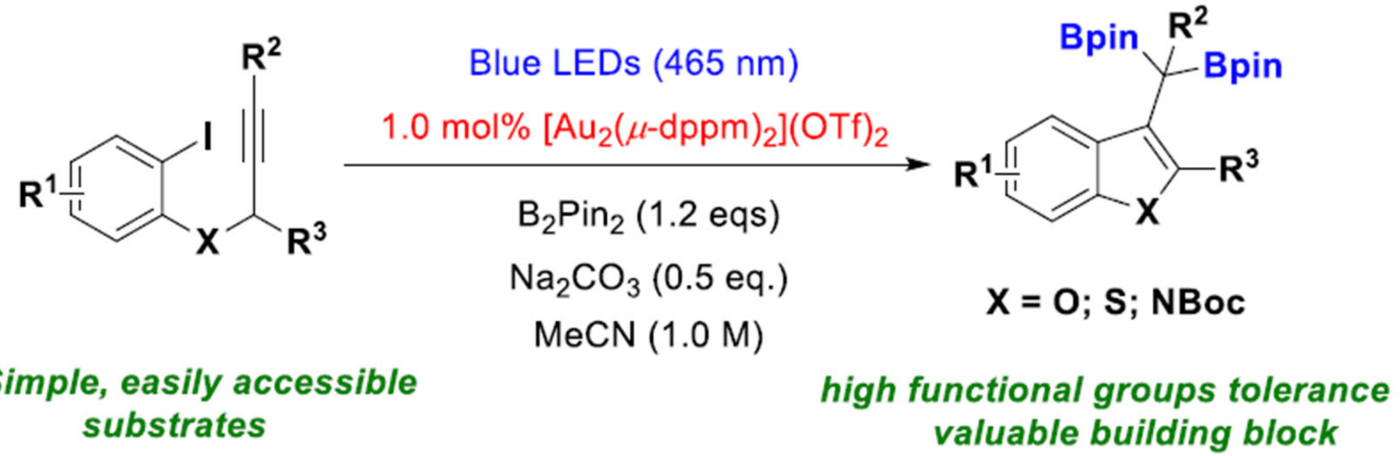


Addition to alkenes

Xie, J.; Li, J.; Weingand, V.; Rudolph, M.; Hashmi, A. S. K., *Chem.–Eur. J.* **2016,** *22* (36), 12646-12650.
Xie, J.; Zhang, T.; Chen, F.; Mehrkens, N.; Hashmi, A. S. K., *Angew. Chem. Int. Ed.* **2016,** *55* (8), 2934-2938.

Gold complex as photosensitizer

- Dimeric Au(I) photocatalysis via energy transfer

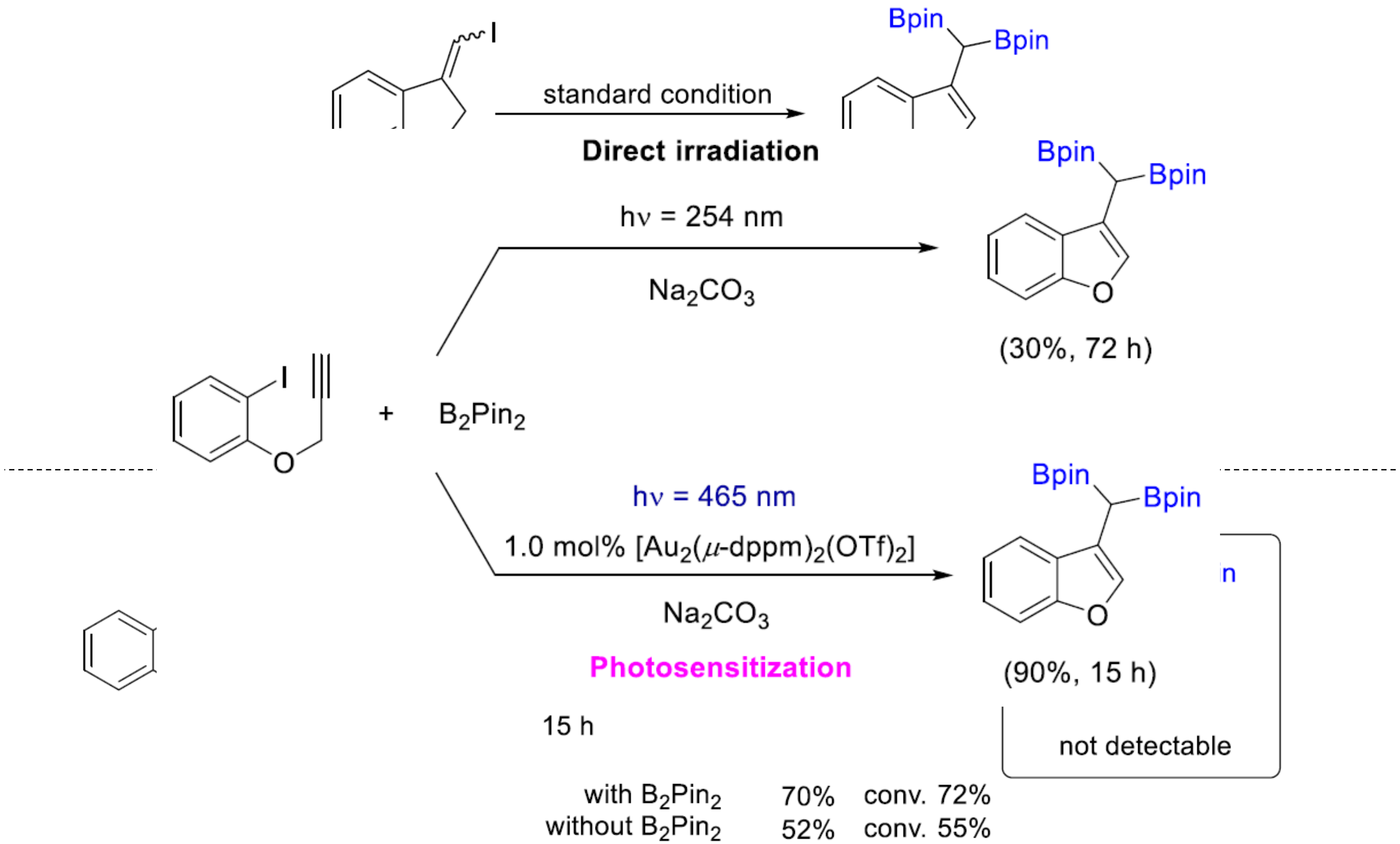


- New absorption peak arises in $[Au_2(\mu\text{-dppm})_2](OTf)_2$ + Na_2CO_3 solution;
- Aryl bromide resulted in no conversion;
- Quantum yield ~ 0.34

Zhang L, Si X, Rominger F, *et al.*, *J. Am. Chem. Soc.*, **2020**, *142*(23), 10485-10493.

Gold complex as photosensitizer

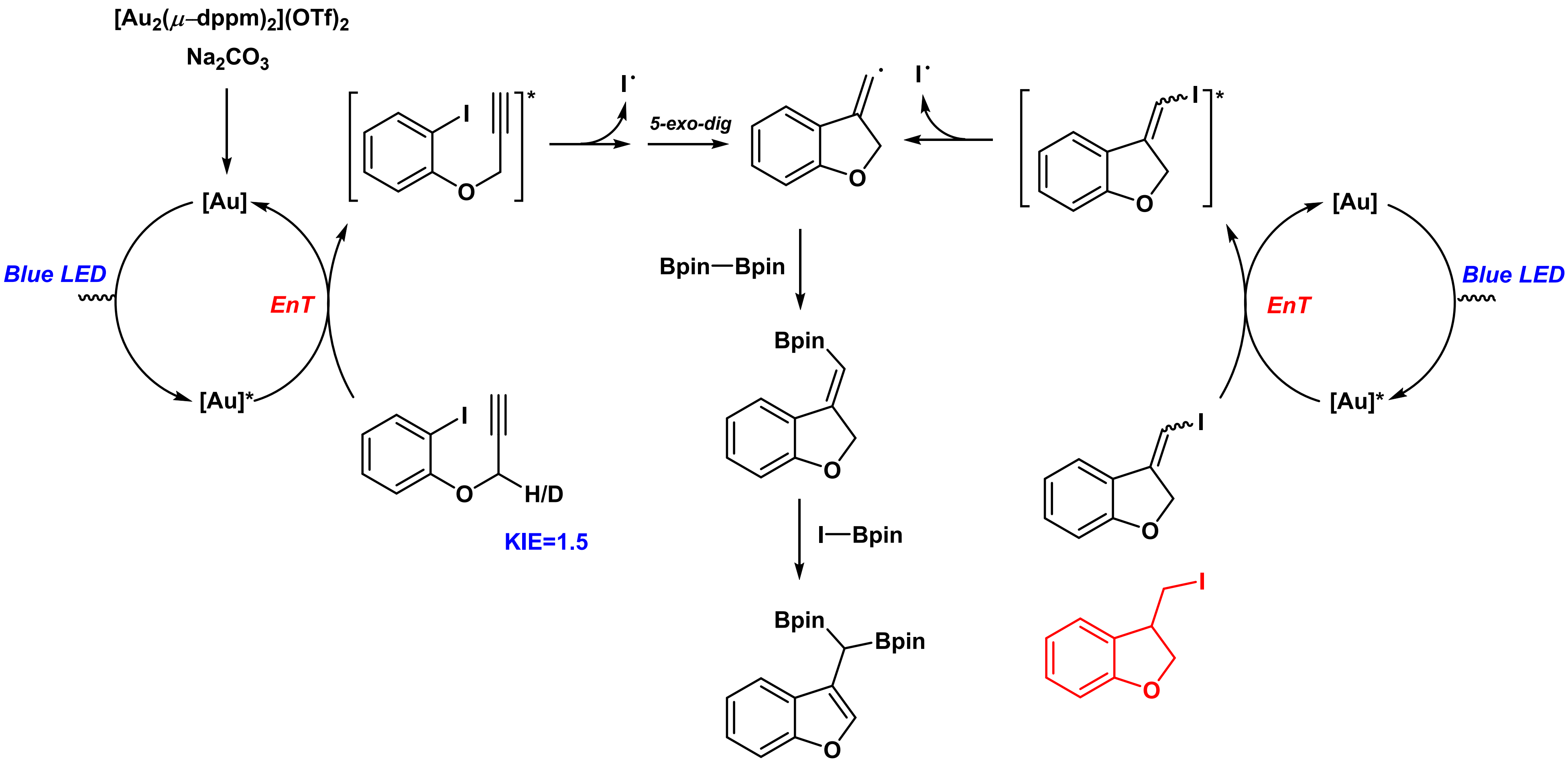
- Dimeric Au(I) catalysis via energy transfer



Zhang L, Si X, Rominger F, *et al.*, *J. Am. Chem. Soc.*, **2020**, *142*(23), 10485-10493.

Gold complex as photosensitizer

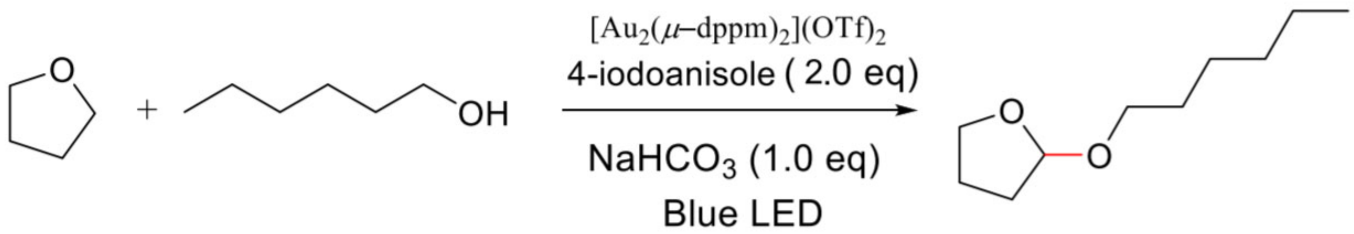
- Proposed mechanism

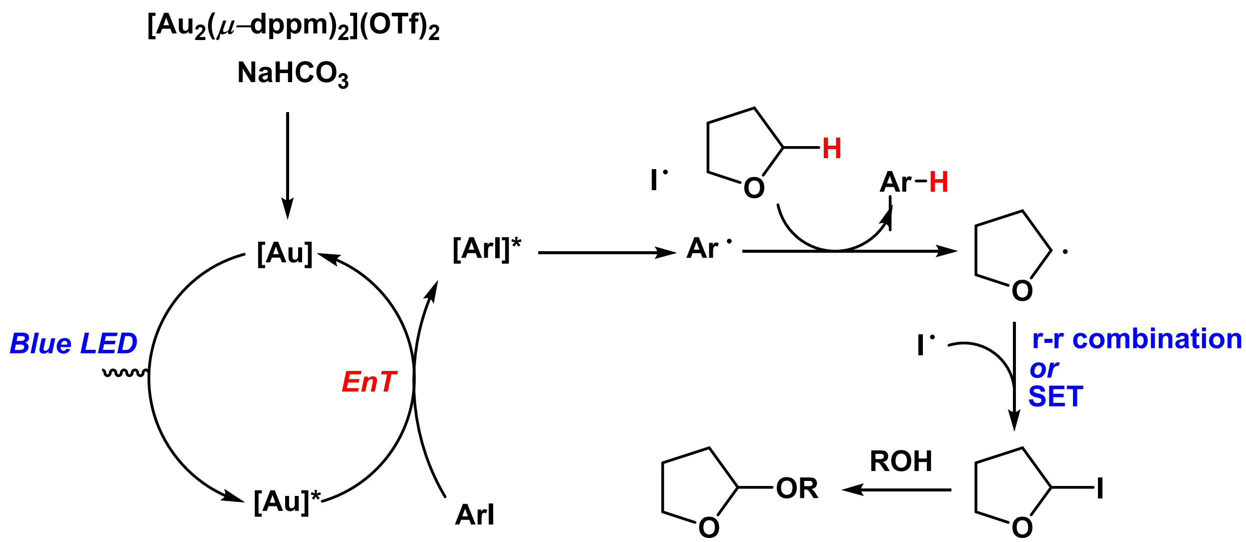


Zhang L, Si X, Rominger F, *et al.*, *J. Am. Chem. Soc.*, **2020**, *142*(23), 10485-10493.

Gold complex as photosensitizer

- Variation

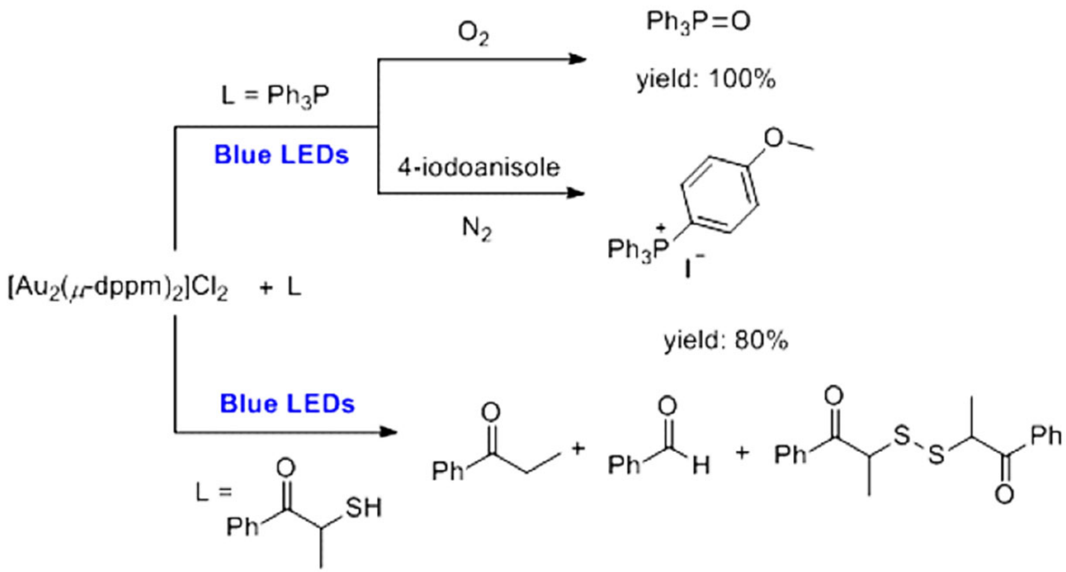


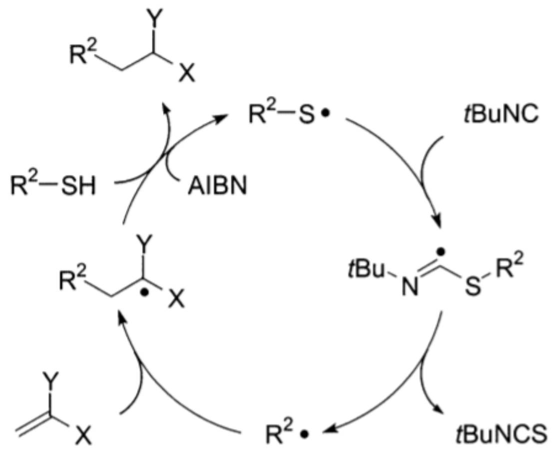


Si X, Zhang L, Wu Z, et al. *Org. Lett.*, **2020**, *22*(15), 5844-5849.

Gold complex as photosensitizer

- Reductive desulfurizing C-C coupling

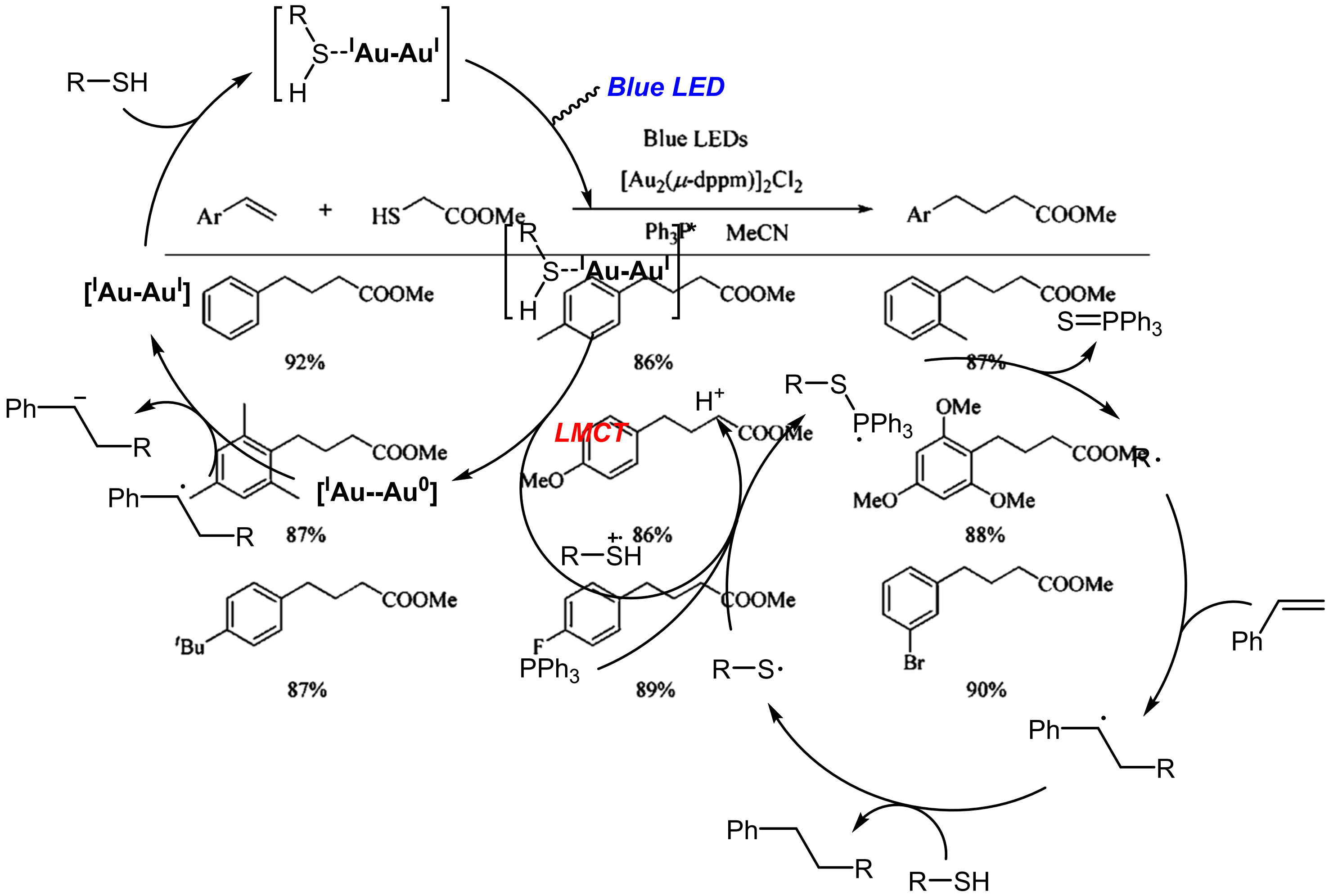




Benati L, Leardini R, Minozzi M, *et al., Angew. Chem. Int. Ed.*, **2004**, *43*(27), 3598-3601.
Zhang, L.; Si, X.; Yang, Y.; Witzel, S.; Sekine, K.; Rudolph, M.; Hashmi, A. S. K., *Acs. Catal.* **2019,** *9* (7), 6118-6123.

Gold complex as photosensitizer

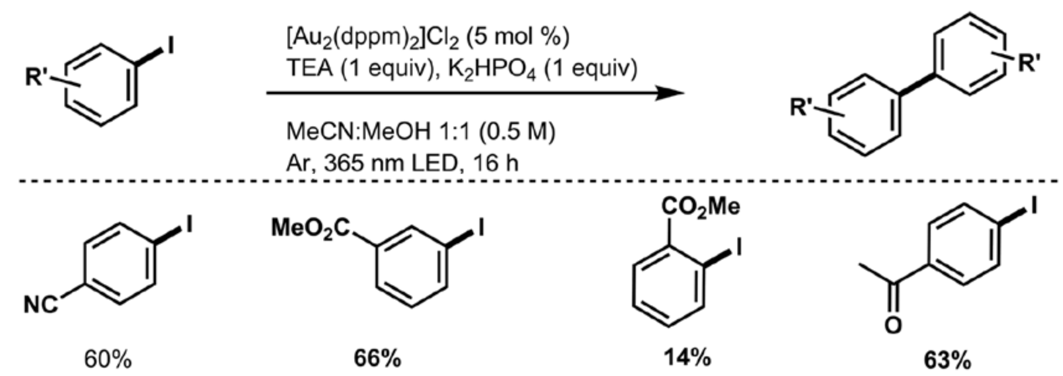
- Reductive desulfurizing C-C coupling

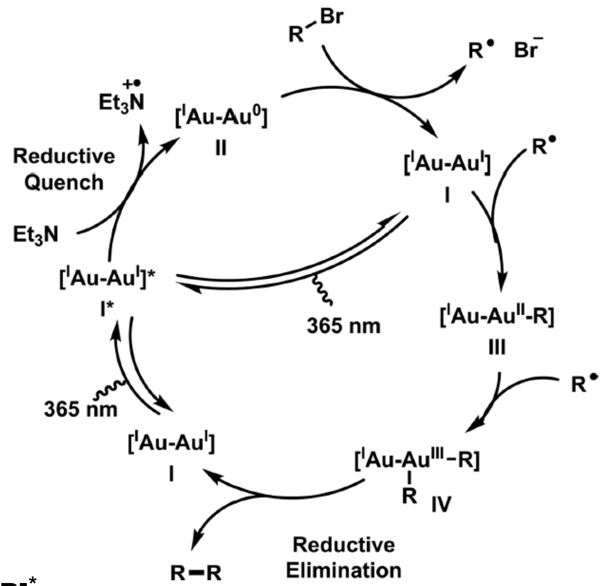


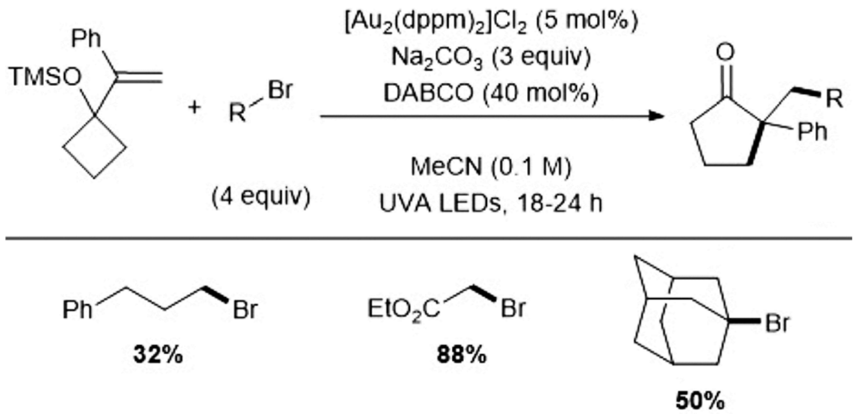
Zhang, L.; Si, X.; Yang, Y.; Witzel, S.; Sekine, K.; Rudolph, M.; Hashmi, A. S. K., *Acs. Catal.* **2019,** *9* (7), 6118-6123.

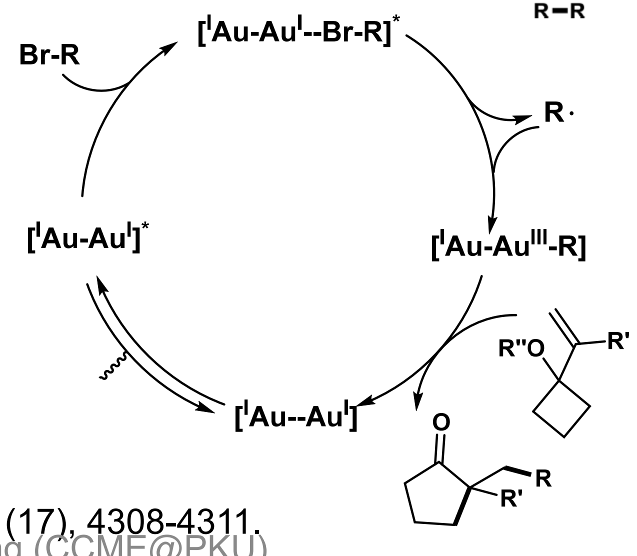
Gold complex as photosensitizer

- Multiple role of dimeric Au(I) catalyst





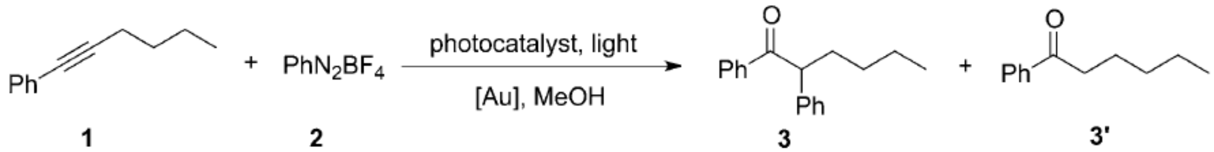




Tran, H.; McCallum, T.; Morin, M.; Barriault, L., *Org. let.* **2016,** *18* (17), 4308-4311.
Zidan, M.; McCallum, T.; Thai-Savard, L.; Barriault, L., *Org. Chem. Front.* **2017,** *4* (11), 2092-2096.

Gold complex as photosensitizer

- Mononuclear gold(I) complex as photosensitizer



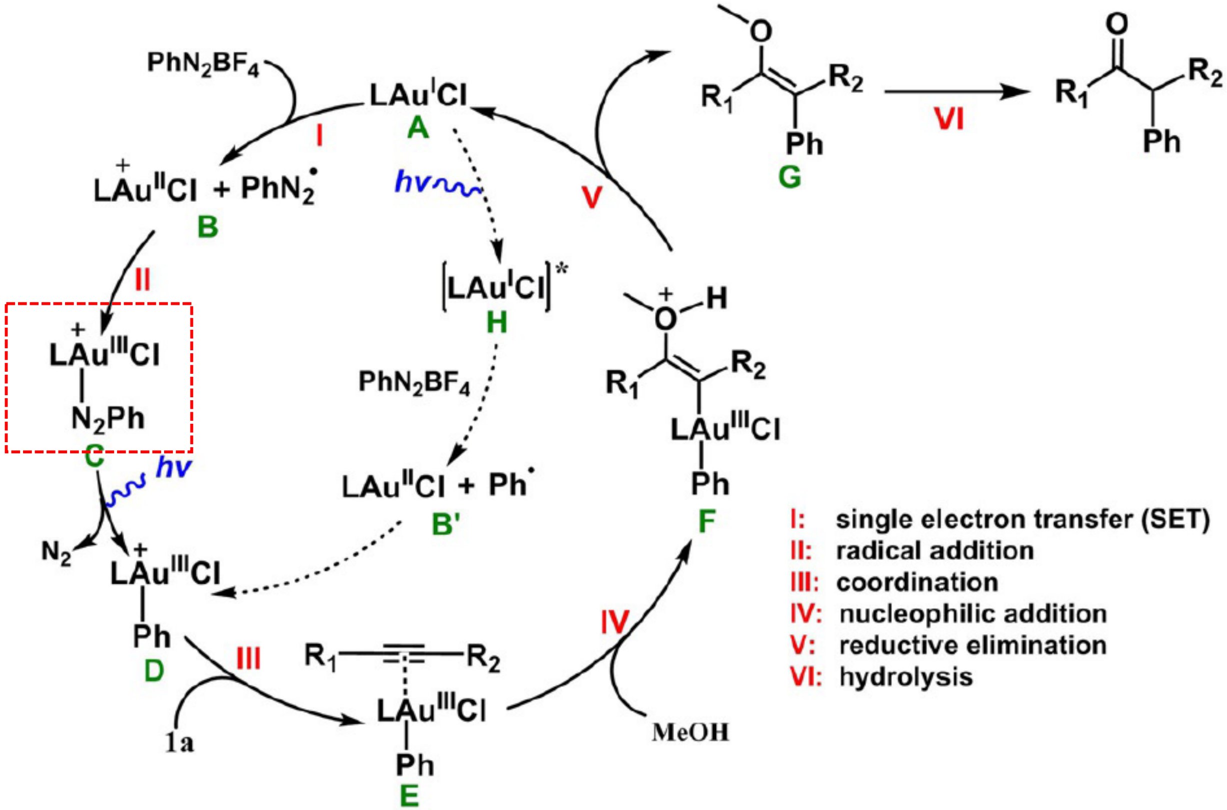
Photocatalyst (5 mol%)	Light source	Au (10 mol%)	Additive	Yield of **3**	Ratio **3/3'**
$[Ru(bpy)_3]Cl_2\cdot 6H_2O$	UVA	Ph_3PAuCl	–	27%	5:1
$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	UVA	Ph_3PAuCl	–	57%	9:1
$[Au_2(\mu\text{-dppm})_2](NTf_2)_2$	UVA	Ph_3PAuCl	–	65%	11:1
–	UVA	–	–	–	–
$[Au_2(\mu\text{-dppm})_2](NTf_2)_2$	UVA	–	–	trace	–
–	UVA	Ph_3PAuCl	–	76%	14:1
–	–	Ph_3PAuCl	–	–	–
–	20 W CFL	Ph_3PAuCl	–	9%	6:1
–	blue LEDs	Ph_3PAuCl	–	79%	>20:1
–	blue LEDs	$Pd(OAc)_2$	–	–	–
–	blue LEDs	$Cu(OAc)_2$	–	–	–
–	blue LEDs	$(4\text{-}CH_3C_6H_4)_3PAuCl$	–	71%	13:1
–	blue LEDs	$(4\text{-}CF_3C_6H_4)_3PAuCl$	–	87% (81%)	15:1
–	blue LEDs	AuCl	–	trace	–
Ph_2IOTf was used instead of **2**	blue LEDs	Ph_3PAuCl	–	–	–

Witzel, S.; Xie, J.; Rudolph, M.; Hashmi, A. S. K., *Adv. Synth. Cat.* **2017**, *359* (9), 1522-1528.
Huang, L.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K., *Angew. Chem. Int. Ed.* **2016,** *55* (15), 4808-4813.

Gold complex as photosensitizer

- Proposed mechanism

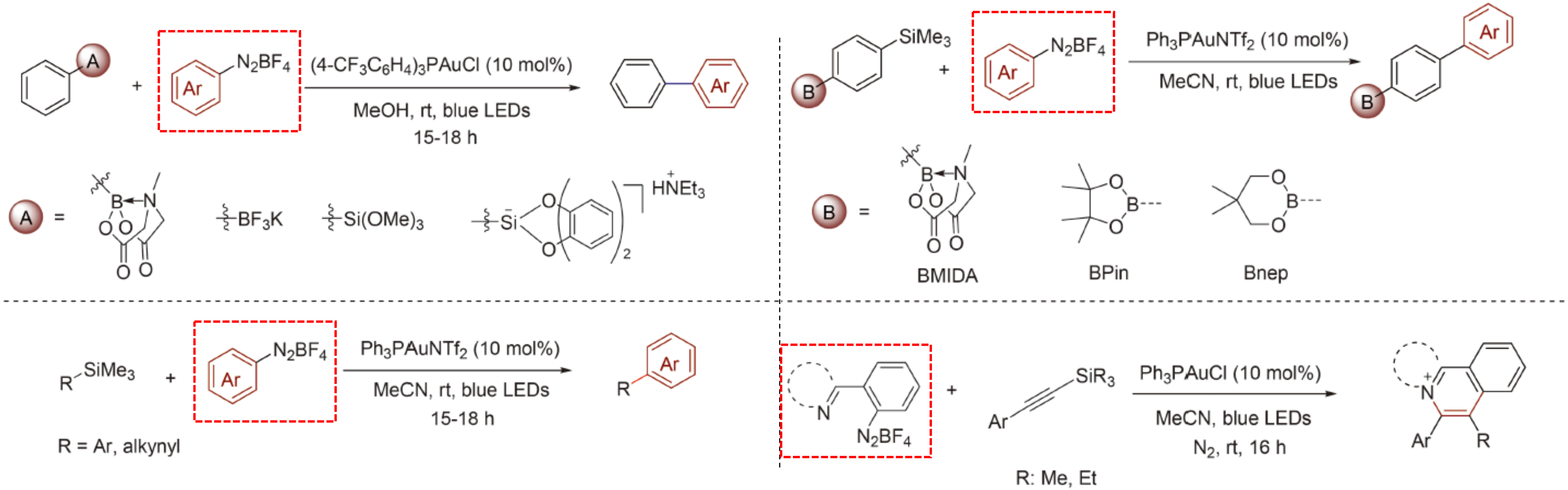
  - No absorption of Au(I) or PhN_2^+ in the region of 400-500 nm (blue LED).



Liu, Y.; Yang, Y.; Zhu, R.; Liu, C.; Zhang, D., *Chem. Eur. J.* **2018,** *24* (53), 14119-14126.

Gold complex as photosensitizer

- Other examples



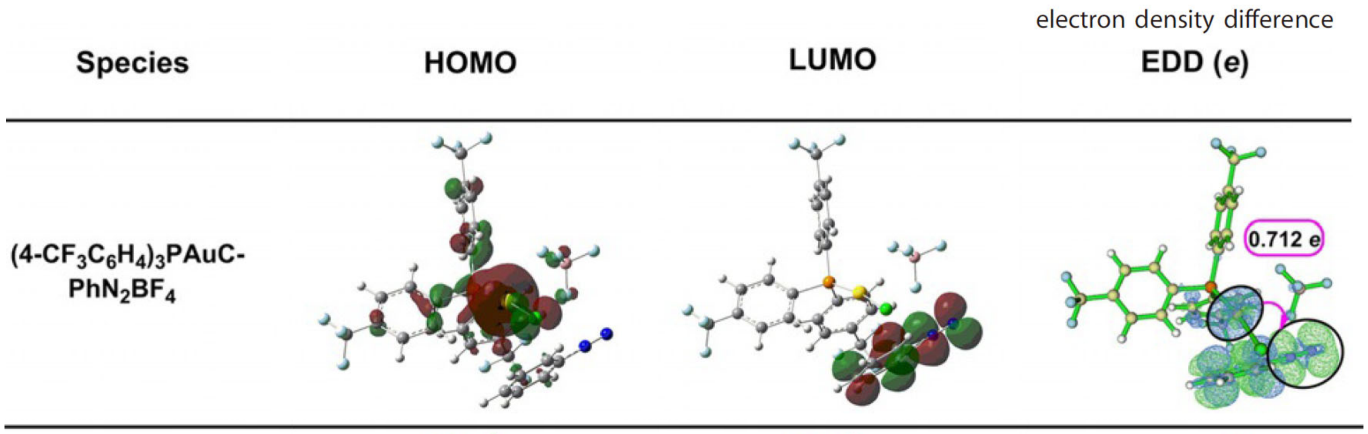
Cao, Z.; Bassani, D. M.; Bibal, B., In *Photochemistry*, **2020,** *47,* pp 423-456.

Gold complex as photosensitizer

Computational study

- Au(I) associates with PhN_2^+ to form a charge-transfer (CT) complex

Species	E_{ex}/eV	λ/nm	E_{HOMO}	E_{LUMO}	E_{gap}
$(4\text{-}CF_3C_6H_4)_3PAuCl$	4.86	255	−7.43	−1.56	5.87
PhN_2BF_4	4.00	310	−8.42	−3.41	5.01
$(4\text{-}CF_3C_6H_4)_3PAuCl\text{-}PhN_2BF_4$	2.83	439	−7.16	−3.56	3.60

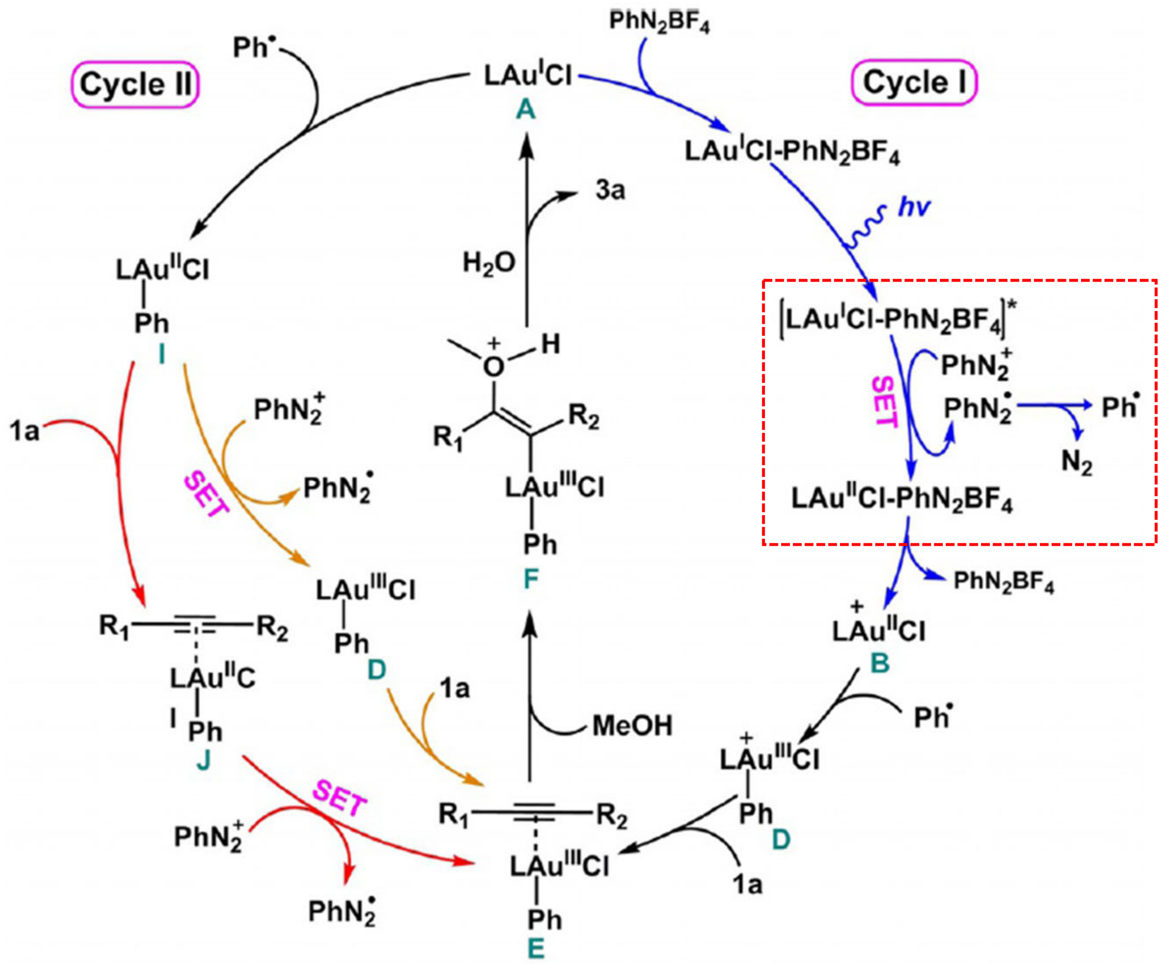


TD-M06/LANL2DZ(f)/6-31G(d,p) level

Liu, Y.; Yang, Y.; Zhu, R.; Liu, C.; Zhang, D., *Chem. Eur. J.* **2018,** *24* (53), 14119-14126.

Gold complex as photosensitizer

- Calculated mechanism



Liu, Y.; Yang, Y.; Zhu, R.; Liu, C.; Zhang, D., *Chem. Eur. J.* **2018,** *24* (53), 14119-14126.

A Brief Conclusion

- Characteristics

! Readily activation of unactivated alkenes and alkynes.

! Readily generation of C-centered radical from unactivated R-Br and R-I.

! Au(III) readily undergoes reductive elimination.

! Better stability (than Pd, etc) when exposed to moisture and oxygen.

! Circumventing β-H elimination to achieve difunctionalization.

! Multiple catalytic mechanism at multiple conditions.

! ……

A Brief Conclusion

- More to be developed…

… UVA is generally requisite for excitation of $[Au_2(dppm)_2]X_2$.

… Dual photoredox/Au catalysis mainly relies on diazonium salt as substrates.

… Some mechanisms remain elusive and unpredicable.

… Asymmetric transformations largely unexplored.

… Au photocatalyst limited to several compounds.

… Utilizing LMCT in Au(III) complexes?

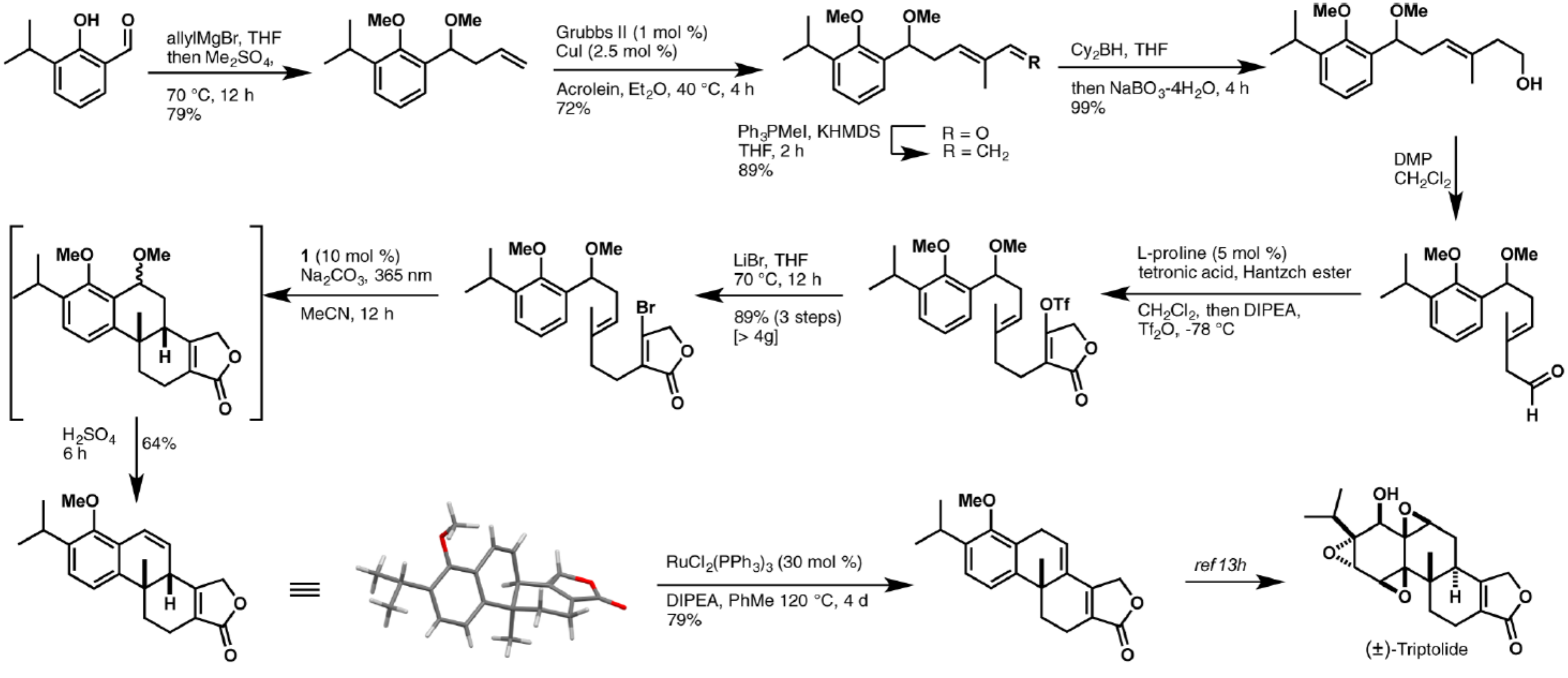
… ……

Outline

- Atomic and Optical Properties of Gold
- History of Homogenous Gold Catalysis
- Combining Gold Catalysis and Light
  - Gold complex as transition-metal catalyst
  - Gold complex as photosensitizer
- A Brief Conclusion
- Application in Synthesis

The Application in Synthesis

- Formal synthesis of (±)-Triptolide:



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