Au-Pd Bimetallic Catalysis: The Importance of Anionic Ligands in Catalyst Speciation

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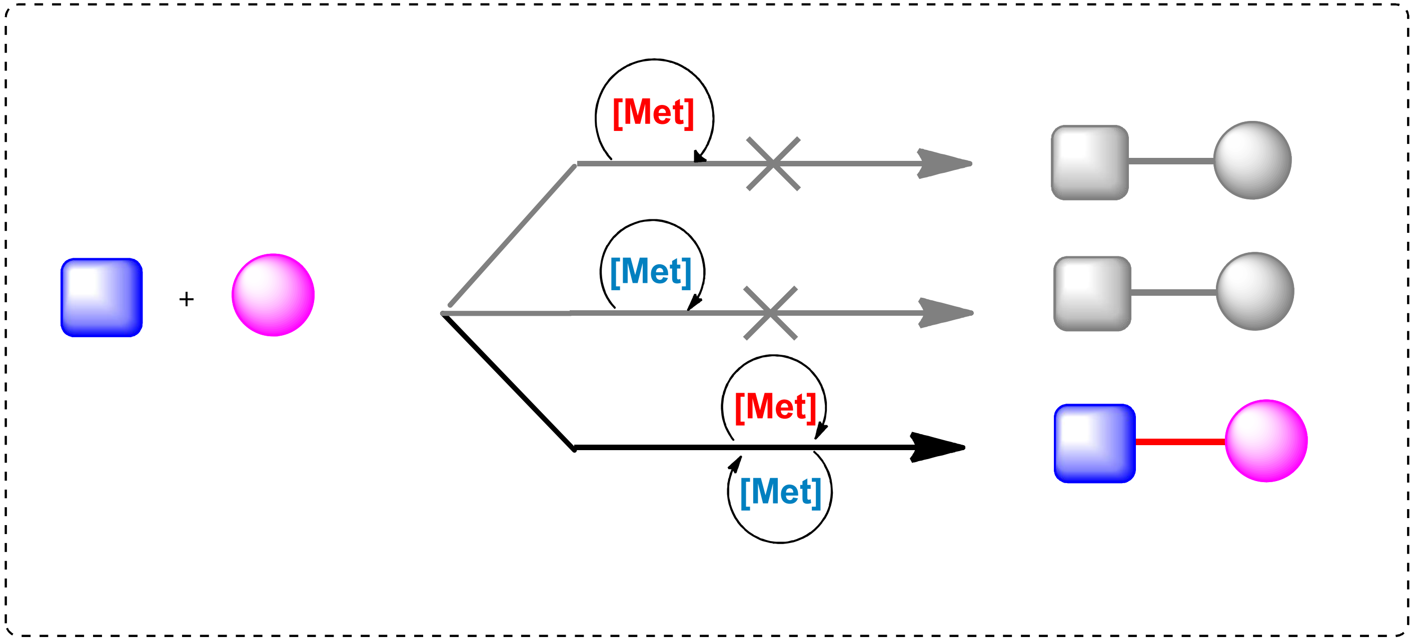
Ophélie Quinonero
31/03/2016

Generalities

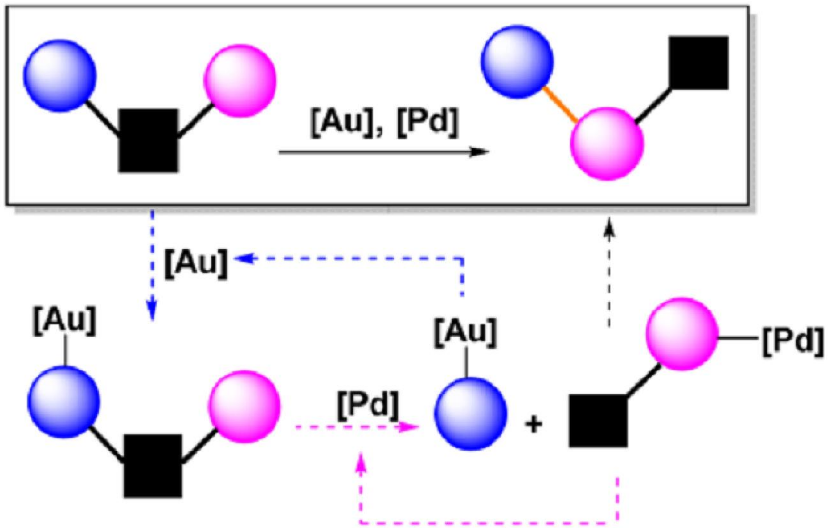
on Synergistic Bimetallic Catalysis



For example: Pd/Au, Fe/Pd, Rh/Pd, Au/Fe…

Literature precedents

Au-Pd « catalyzed catalysis »



Y. Shi, K.E. Roth, S.D. Ramgren, S.A. Blum, *J. Am. Chem. Soc.* **2009**, *131*, 18022
M. Al-Amin, K.E. Roth, S.A. Blum, *ACS Catal*. **2014**, *4*, 622
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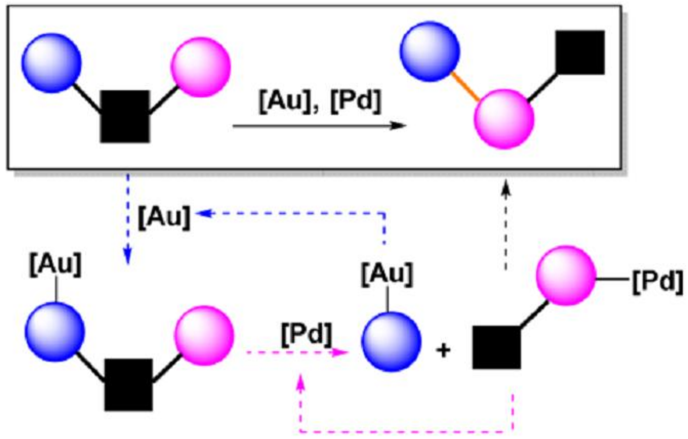

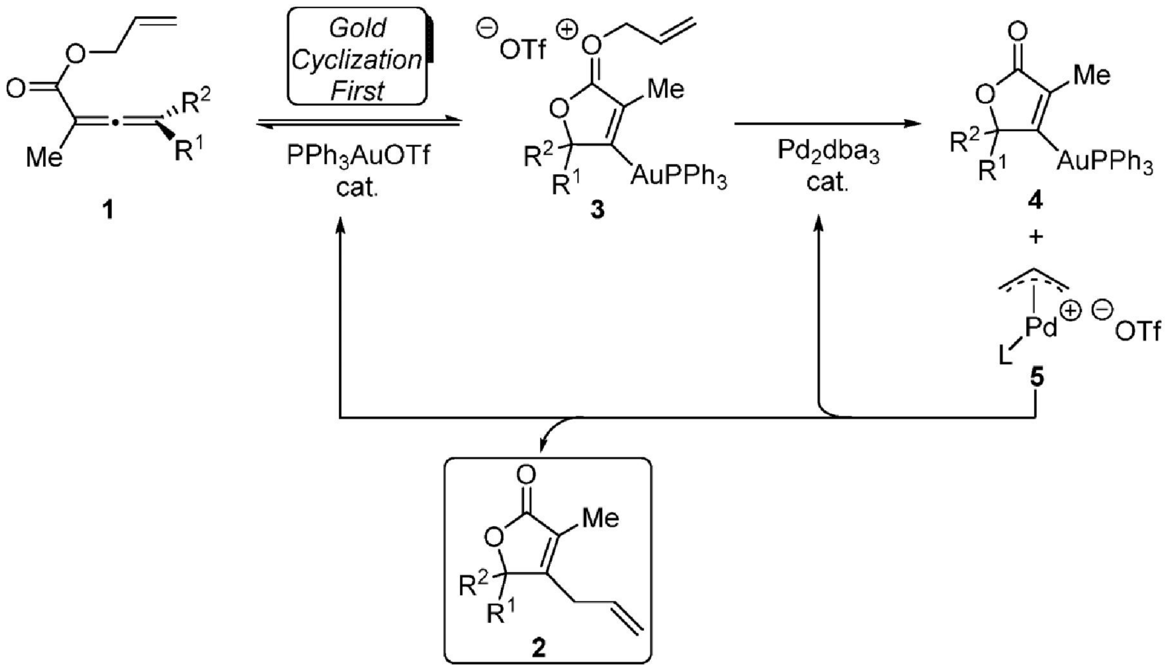

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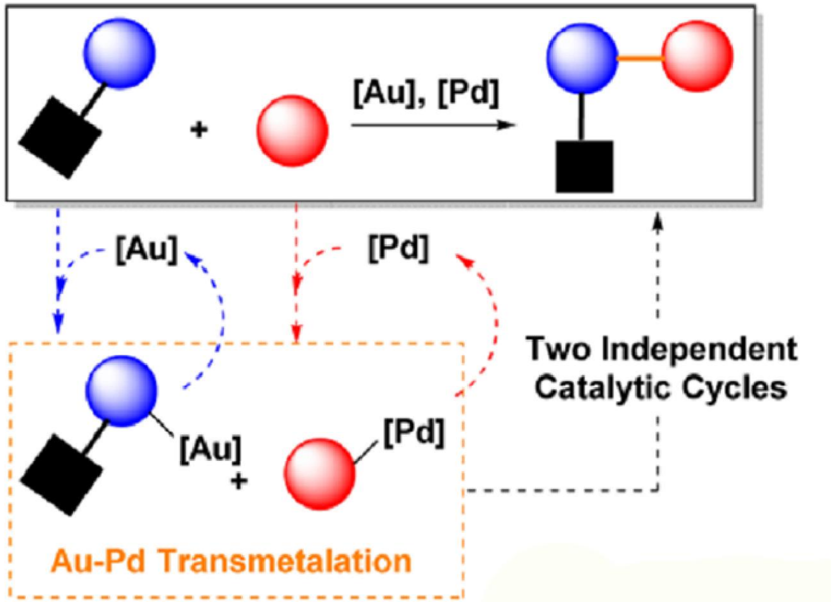
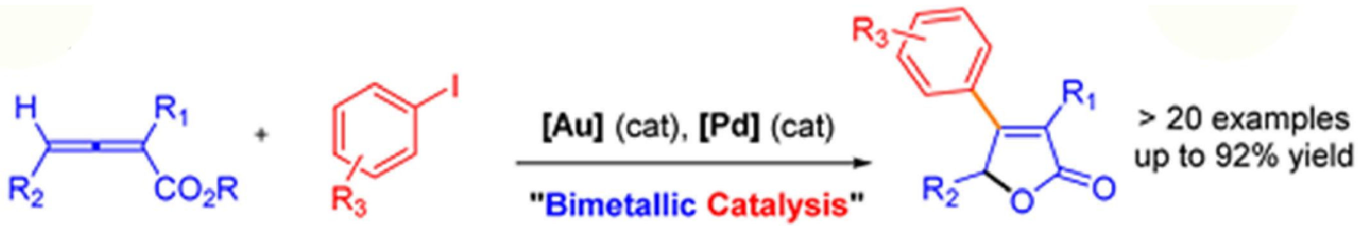
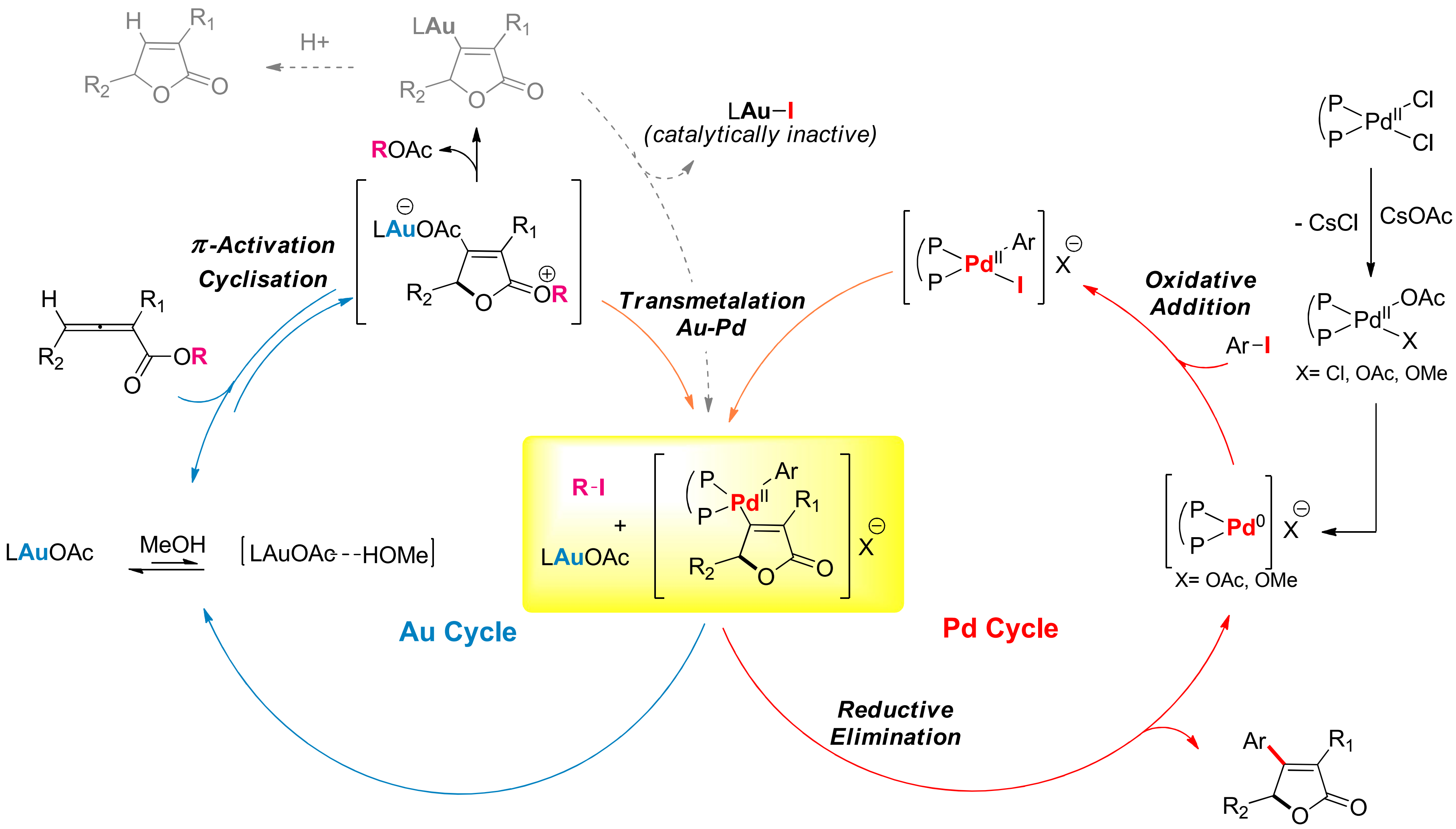
This work

Bimetallic Catalysis

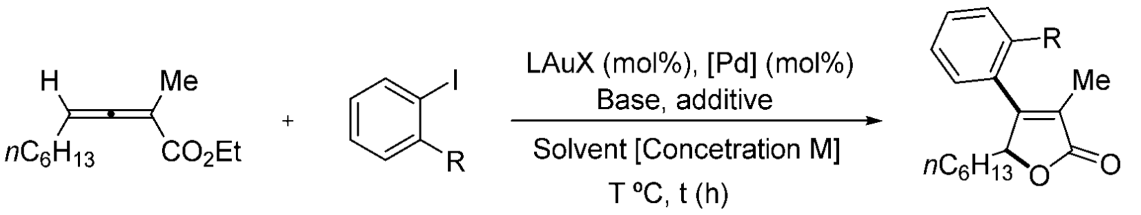




Mechanistic Proposal



Optimization of the Reactions Conditions



1 (Y equiv.)

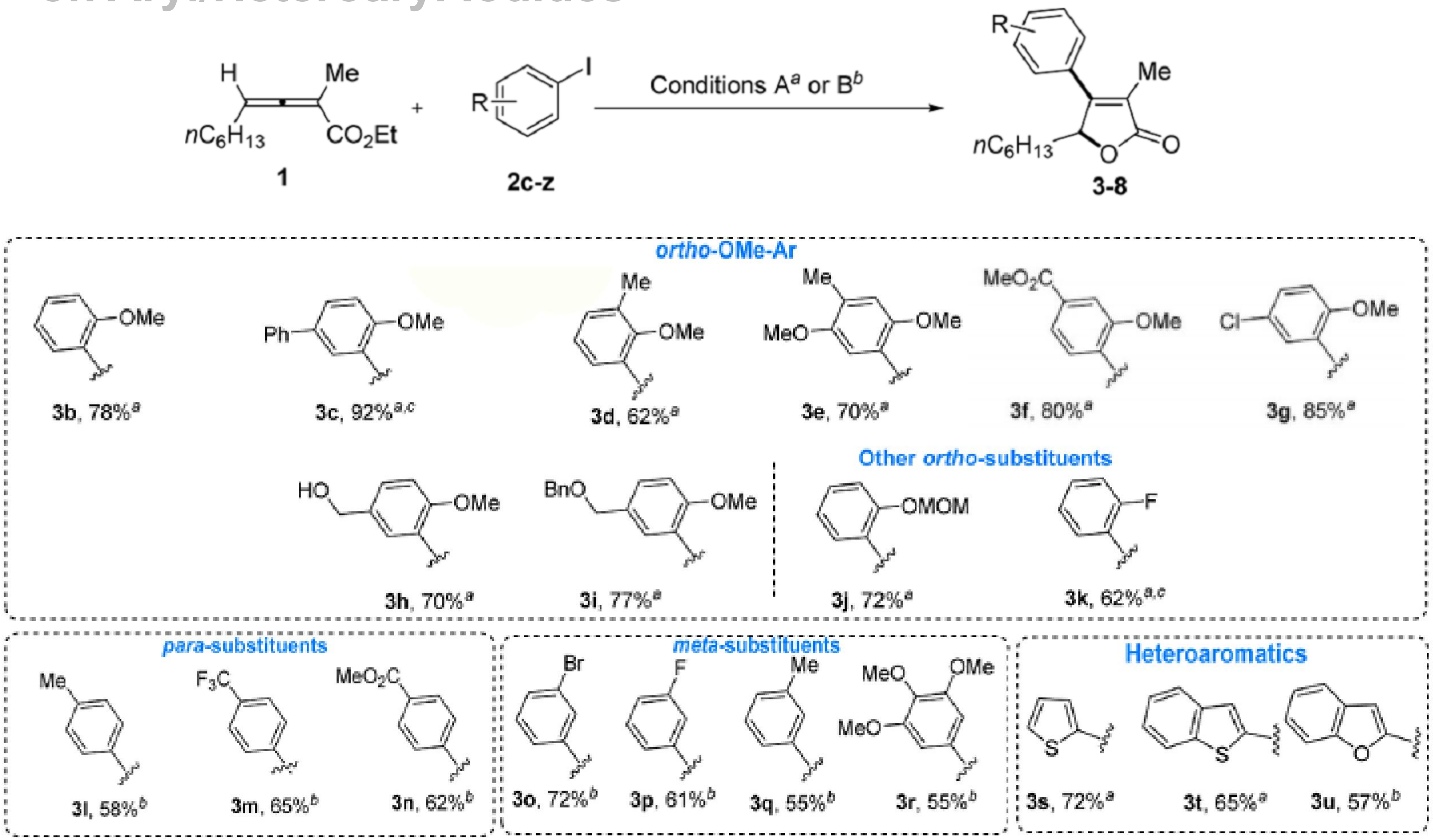
2a: R = H
2b: R = OMe
(Z equiv.)

3a: R = H
3b: R = OMe

Entry	Reaction Conditions	Product Yield (%)[a]
1	**Ph_3PAuCl (20 mol%)**, $[PdCl_2(dppf)]$ (5 mol%), NaOAc (200 mol%), DCE/MeOH (1:1) [0.3M], 70 °C, 21h; Y = 1 equiv; **2a**, Z = 1.5 equiv.	**3a**, 5 [b,c]
2	**Ph_3AuOAc (5 mol%)**, $[PdCl_2(dppf)]$ (5 mol%), CsOAc (200 mol%), DCE/MeOH (1:1) [1.2 M], 80 °C, 21 h; Y = 2 equiv; 2a, Z =1 equiv.	**3a**, 17 (24[b])
3	**$(p\text{-}CF_3Ph)_3PAuCl$ (5 mol%)**, $[PdCl_2(dppf)]$ (5 mol%), CsOAc (10 mol%), toluene/MeOH (1:1) [1.2 M], 80 °C, 21 h; Y = 2 equiv; 2a, Z =1 equiv.	**3a**, 46
4	**$(p\text{-}CF_3Ph)_3PAuOAc$ (5 mol%)**, $[PdCl_2(dppf)]$ (5 mol%), CsOAc (10 mol%), toluene/MeOH (1:1) [1.2 M], 80 °C, 21 h; Y = 2 equiv; 2a, Z =1 equiv.	**3b**, 78[d] *(conditions A)*
5	as entry 4, but with $[PdCl_2(dppf)]$ (2.5 mol%)	**3b**, 67[d]
6	as entry 4, but with $(p\text{-}CF_3Ph)_3PAuOAc$ (2.5 mol%)	**3b**, 46[d]
7	as entry 4, but with $[PdCl_2(DPEPhos)]$ (5 mol%), 100 °C	**3b**, 78[d] *(conditions B)*

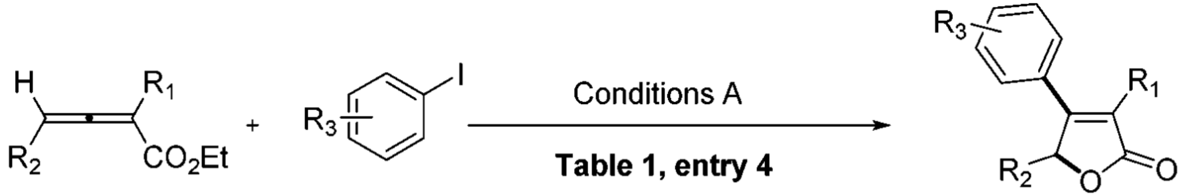
[a] Isolated yield after column chromatography in silica gel. [b] Yields determined by GC-MS using dodecane as internal standard. [c] In the initial screening, reactions were carried out in parallels reactor vessels. All others were performed in Schlenk. [d] Reaction scale : 0.48 mmol (limiting reagent) Reaction scale in all the other entries: 0.14 or 0.24 mmol. [PdCl2(DPEPhos)] = dichloro[bis(2-(diphenylphosphino)phenyl)-ether]Pd(II)

Scope of the reaction
on Aryl/Heteroaryl Iodides

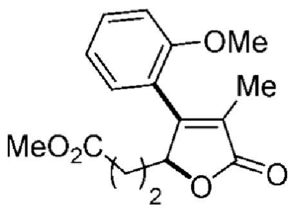


[a] ***Conditions A**:* (p-CF_3Ph)$_3$PAuOAc (5 mol%), [$PdCl_2$(dppf)] (5 mol%), CsOAc (10 mol%), toluene/MeOH (1:1) [1.2M], 80°C, 21 h, **1** = 2 equiv; **2** = 1 equiv. [b] ***Conditions B**:* Same as conditions A but with [PdCl2(DPEPhos)] (5 mol%), 100°C. [c] Average of two independants runs

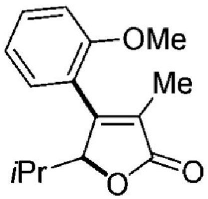
Scope of the reaction
on Allenoates



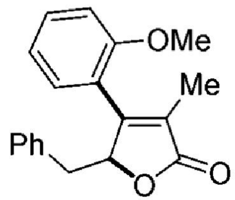
2b **4b-8b**



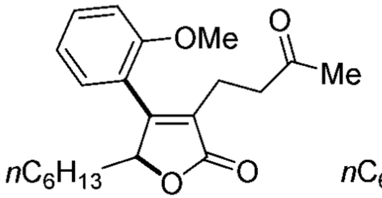
4b, 70%



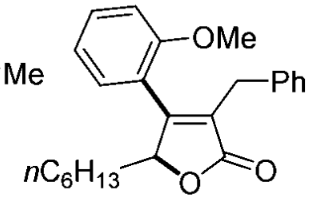
5b, 68%



6b, 47%



7b, 77%



8b, 17%

[a] ***Conditions A**:* (p-CF_3Ph)$_3$PAuOAc (5 mol%), [PdCl$_2$(dppf)] (5 mol%), CsOAc (10 mol%), toluene/MeOH (1:1) [1.2M], 80°C, 21 h, **1** = 2 equiv; **2** = 1 equiv.

Control Experiments

Entry	Conditions	Isolated Yield (%)[a]
1	**Conditions A[a]**	**78**
2	Conditions A **without [Au]**	**9[b]**
3	Conditions A **without [Pd]**	**0**
4	Conditions A **without Cs**	**37**

- background reaction in the absence of [Au]
- no reaction without [Pd]
- poor conversion without Cs

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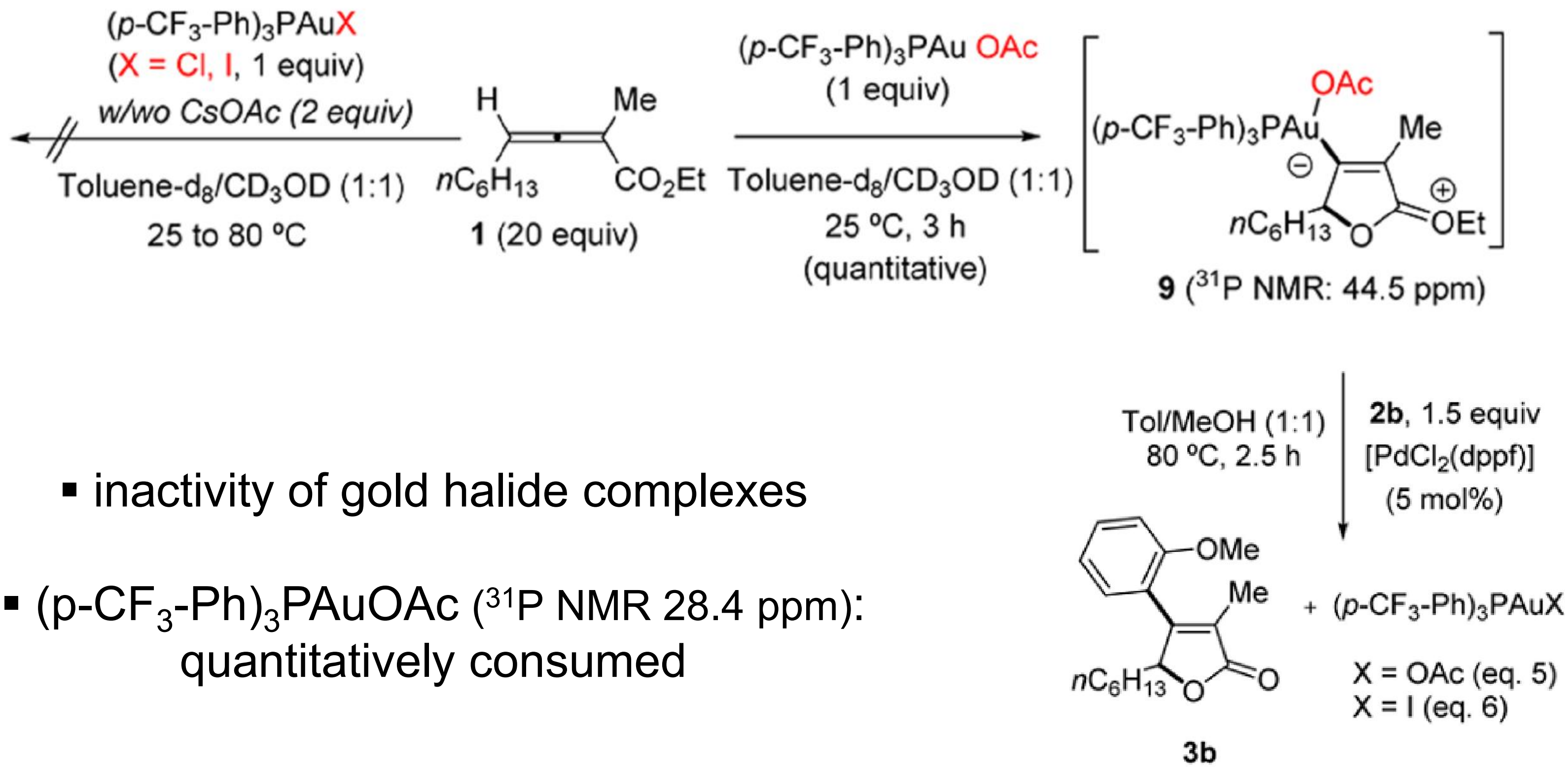

- inactivity of gold halide complexes

- $(p\text{-}CF_3\text{-}Ph)_3PAuOAc$ (^{31}P NMR 28.4 ppm): quantitatively consumed

Conclusion

- ❑ Efficient Au-Pd bimetallic catalysis using allenoate and Ar-I
- ❑ 2 co-existing independant catalytic cycles
- ❑ Key Pd/Au transmetalation step
- ❑ Importance of CsOAc (chloride abstraction)

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Thank you for your attention