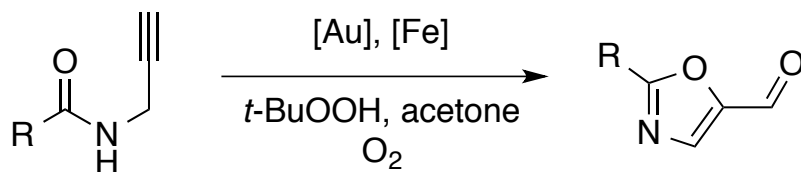
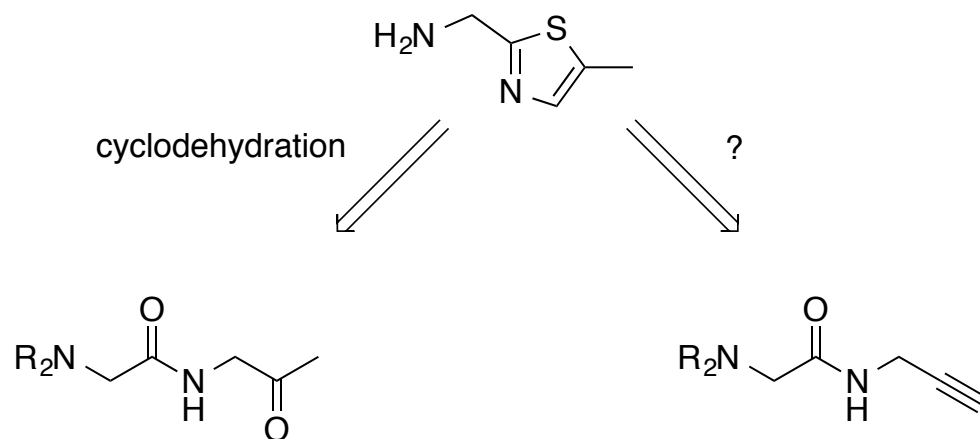


Synergistic Gold and Iron Dual Catalysis: Preferred Radical Addition Toward Vinyl-Gold Intermediate Over Alkene

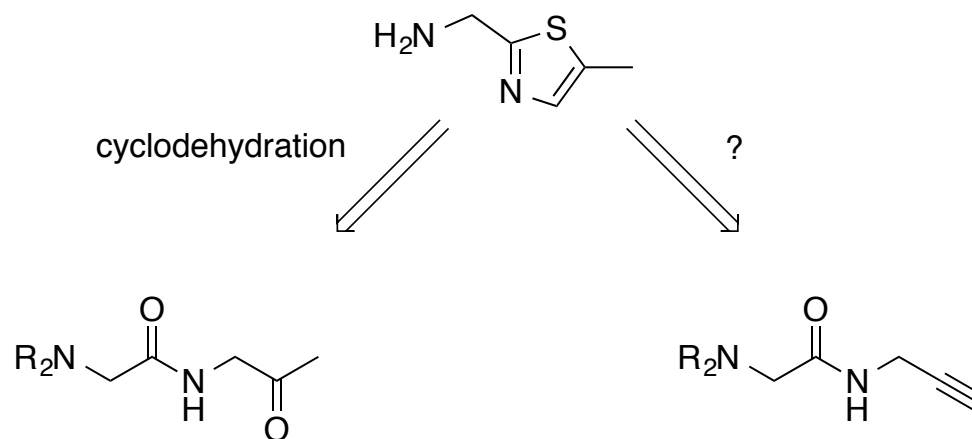
Haihui Peng, Novruz G. Akhmedov, Yu-Feng
Liang, Ning Jiao, and Xiaodong Shi
J. Am. Chem. Soc. **2015**, *137*, 8912-8915.



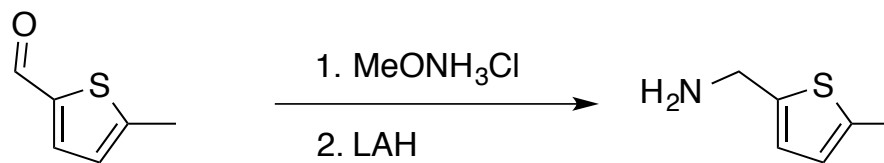
Why This Paper?



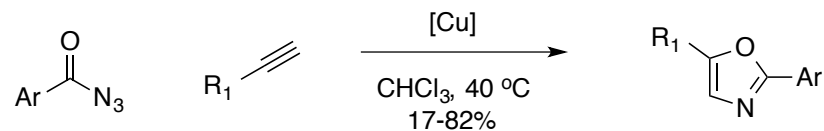
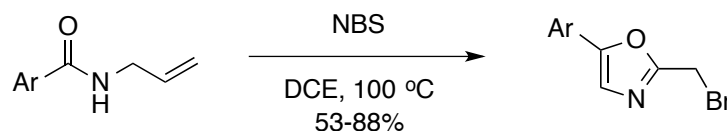
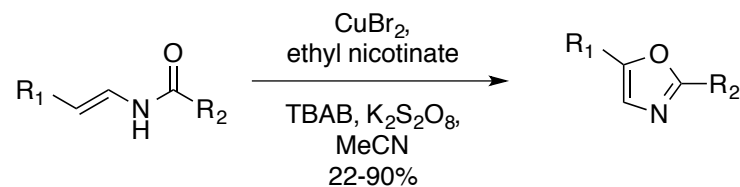
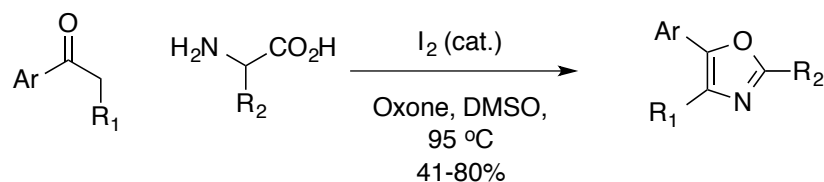
Why This Paper?



Currently:



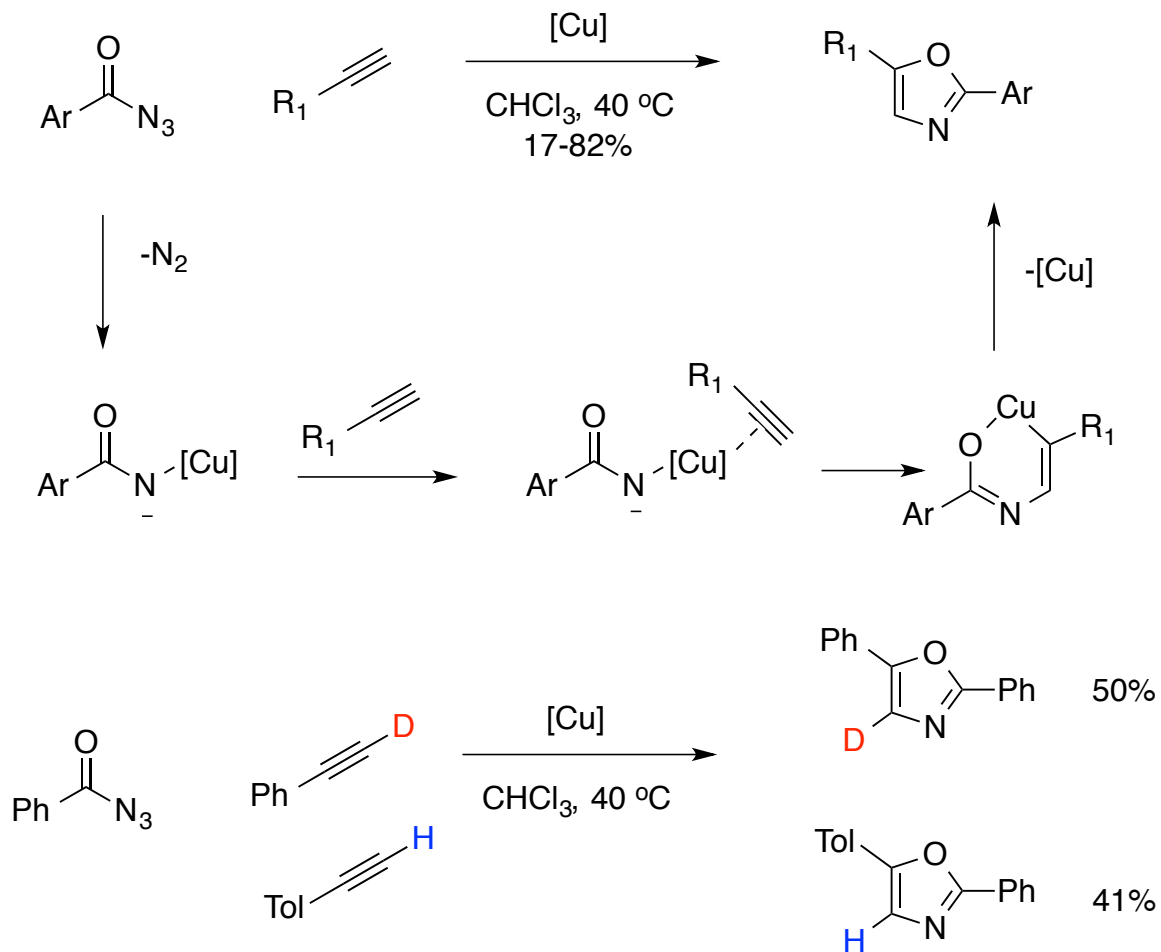
Selected Syntheses of 2-5-Disubstituted Oxazoles



J. Org. Chem. **2013**, *78*, 6065-6074
Org. Lett. **2012**, *14*, 4766-4769

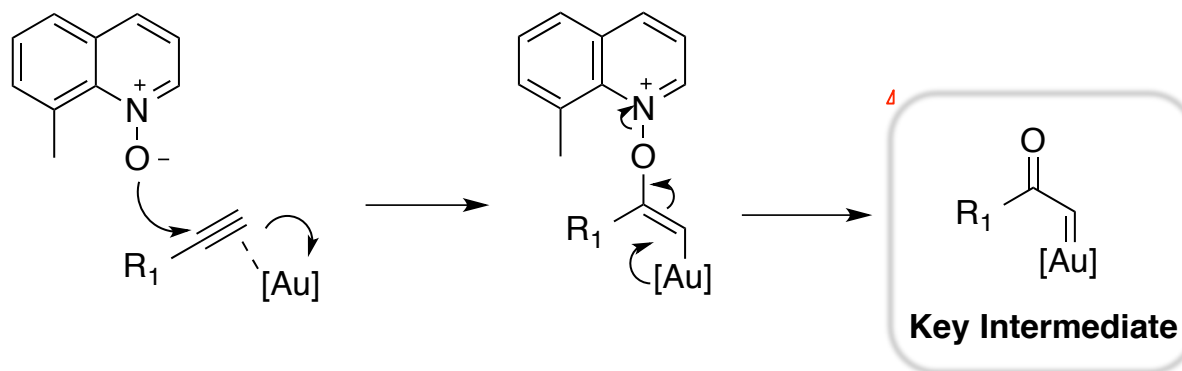
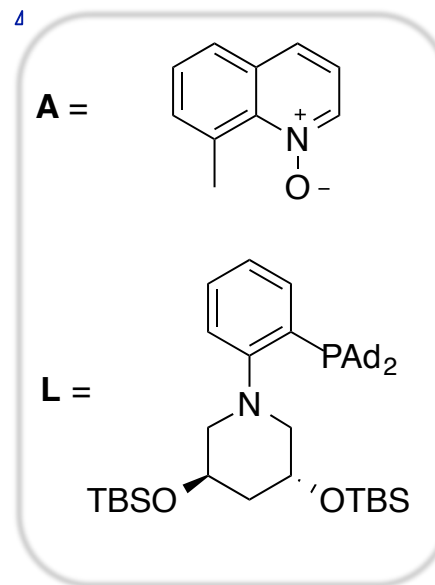
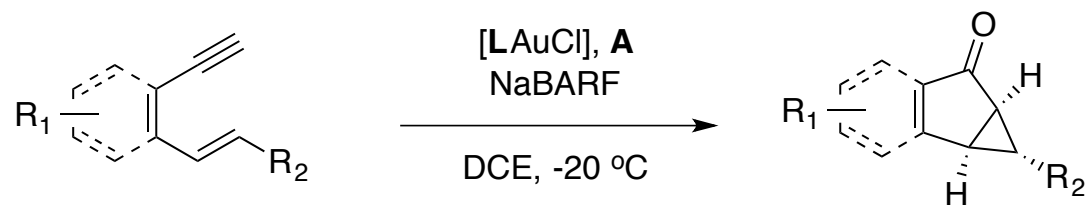
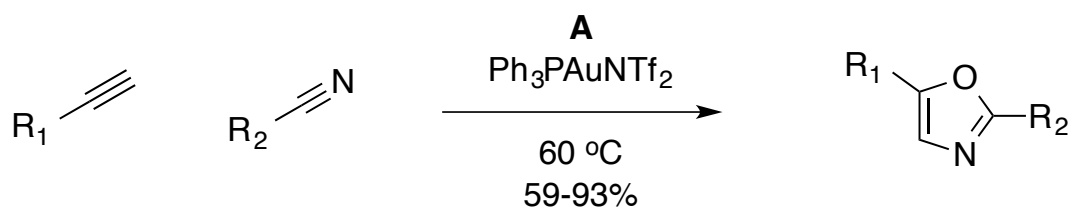
J. Org. Chem. **2012**, *77*, 7526-7537
J. Am. Chem. Soc. **2011**, *133*, 191-193

Mechanism of Cu Catalyzed Oxazole Formation



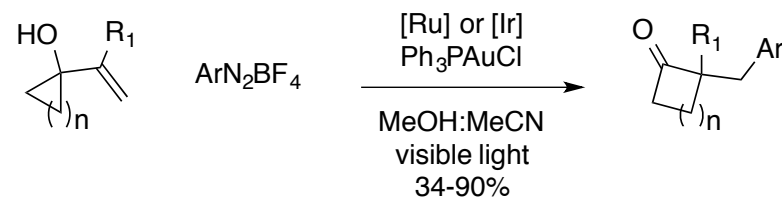
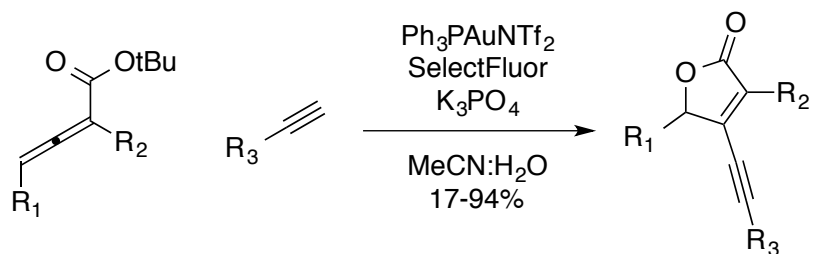
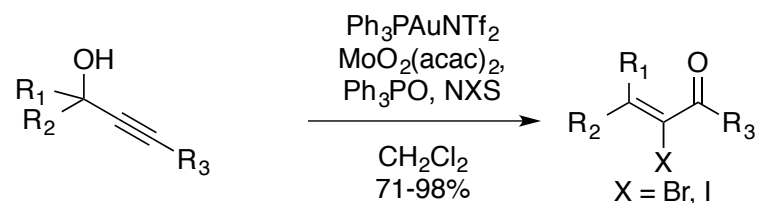
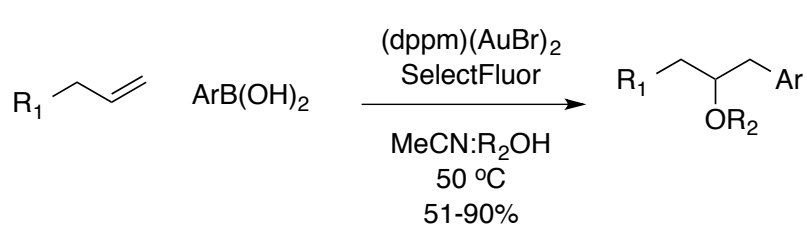
Chem. Eur. J. **2014**, *20*, 3463-3474
J. Am. Chem. Soc. **2011**, *133*, 191-193

α -Oxo Gold Transformations



J. Am. Chem. Soc. **2011**, *133*, 8482-8485
Angew. Chem. Int. Ed. **2015**, *54*, 1245-1249

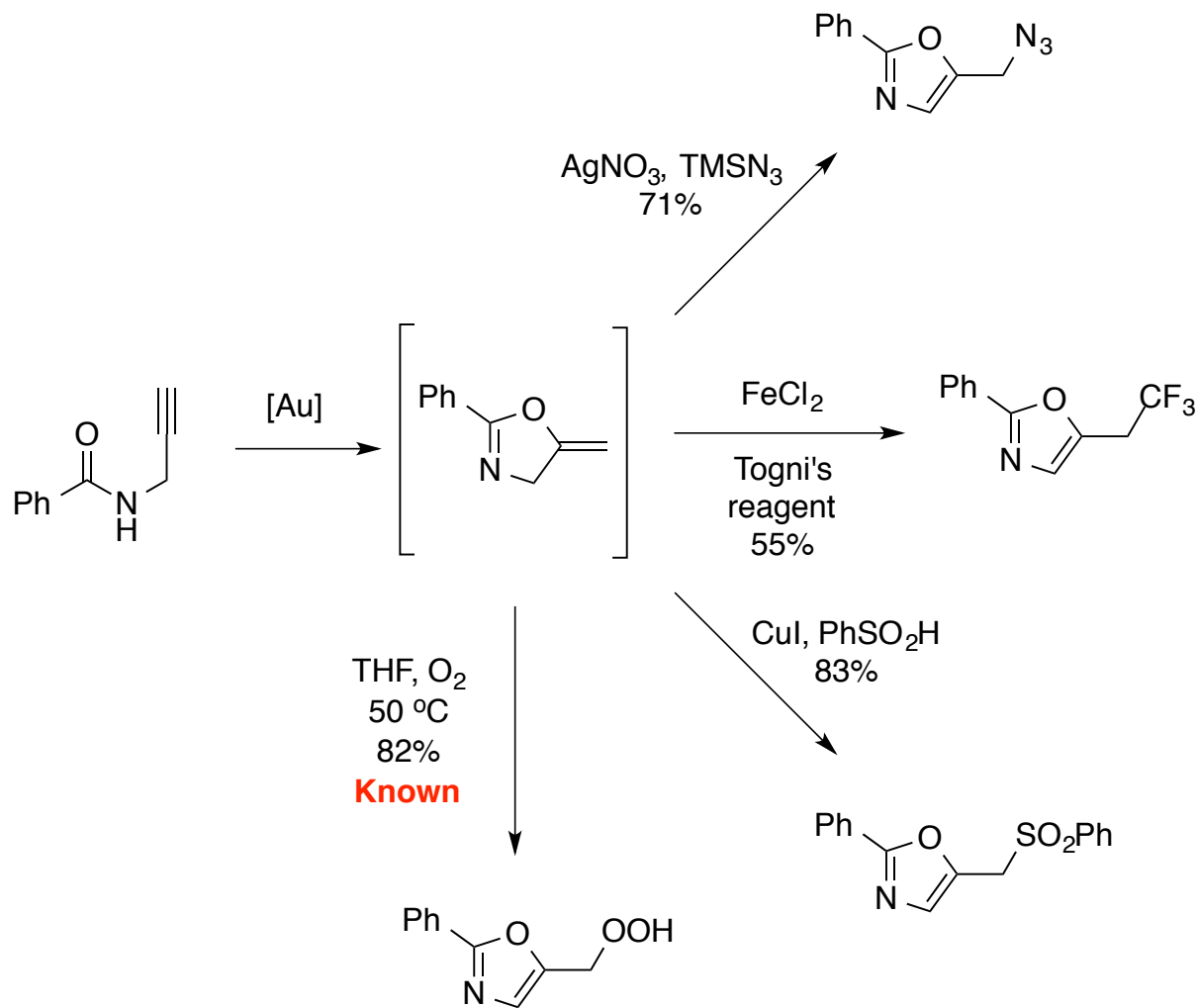
Tandem Gold Catalyzed Reactions



J. Am. Chem. Soc. **2010**, *132*, 8885-8887
Org. Lett. **2010**, *12*, 4904-4907

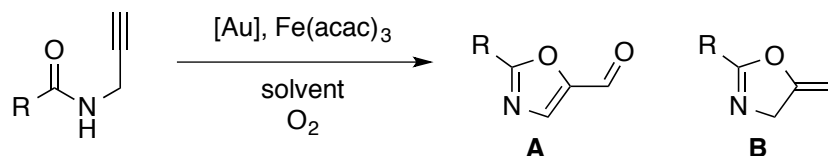
Org. Lett. **2009**, *11*, 3646-3649
J. Am. Chem. Soc. **2014**, *136*, 5844-5847

Title Paper: Three Preliminary Transformations



J. Am. Chem. Soc. **2015**, *137*, 8912-8915

Title Paper: Screening of Conditions

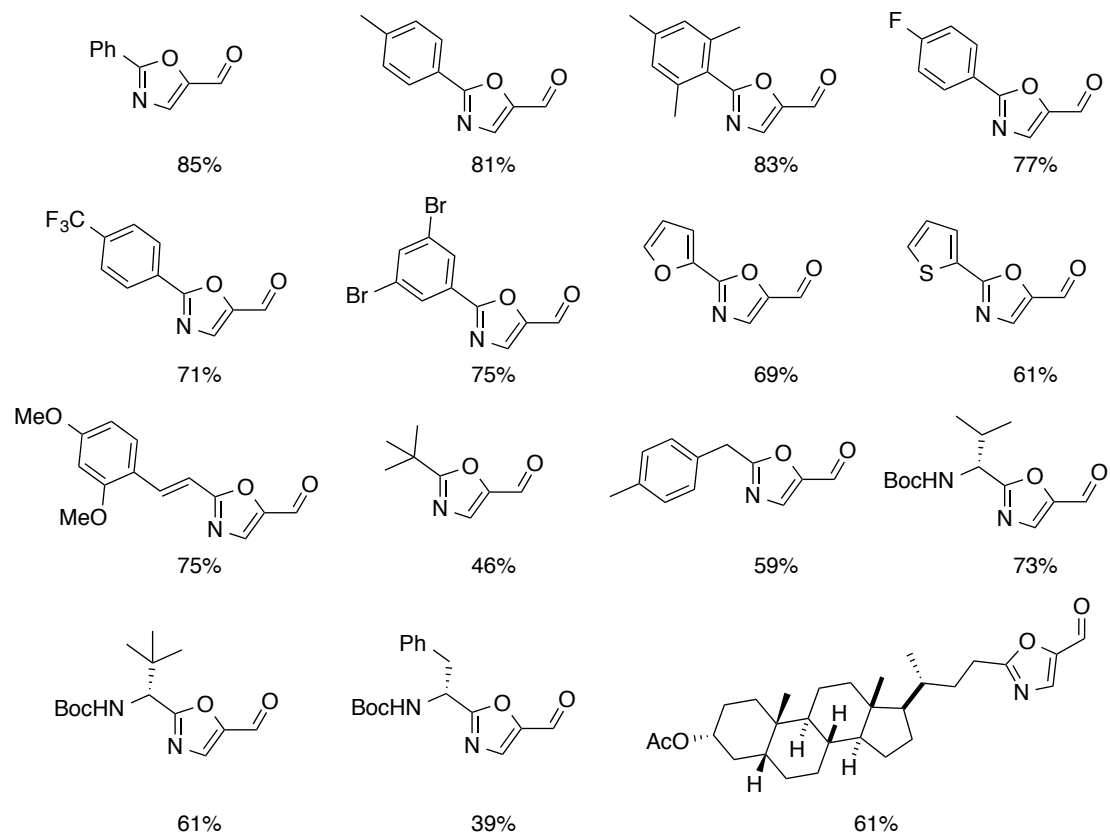
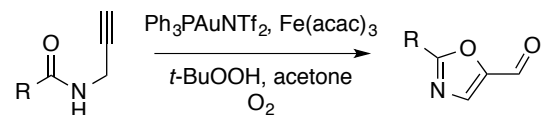


<u>Entry</u>	<u>[Au]</u>	<u>Solvent</u>	<u>Time (h)</u>	<u>Conv. (%)</u>	<u>Yield (%A:%B)</u>
1	Ph ₃ PAuNTf ₂	MeCN	12	<10	0:0
2	iPrAuNTf ₂	MeCN	8	100	<10:85
3	di <i>t</i> BuXPhos AuNTf ₂	MeCN	8	100	17:65
4	di <i>t</i> BuXPhos Au(MeCN)SbF ₆	MeCN	8	100	33:45
5	(ArO) ₃ PAuNTf ₂	MeCN	8	100	11:58
6	JackiePhosAuNTf ₂	MeCN	8	100	15:71
7	Ph ₃ PAuNTf ₂	acetone	8	100	43:38
8	Ph ₃ PAuNTf ₂	CH ₂ Cl ₂	8	100	25:65
9	Ph ₃ PAuNTf ₂	PhMe	8	100	29:69
10	Ph ₃ PAuNTf ₂	Dioxane	8	100	45:38
11*	Ph ₃ PAuNTf ₂	acetone	2	100	83:--

* 50% *t*-BuOOH

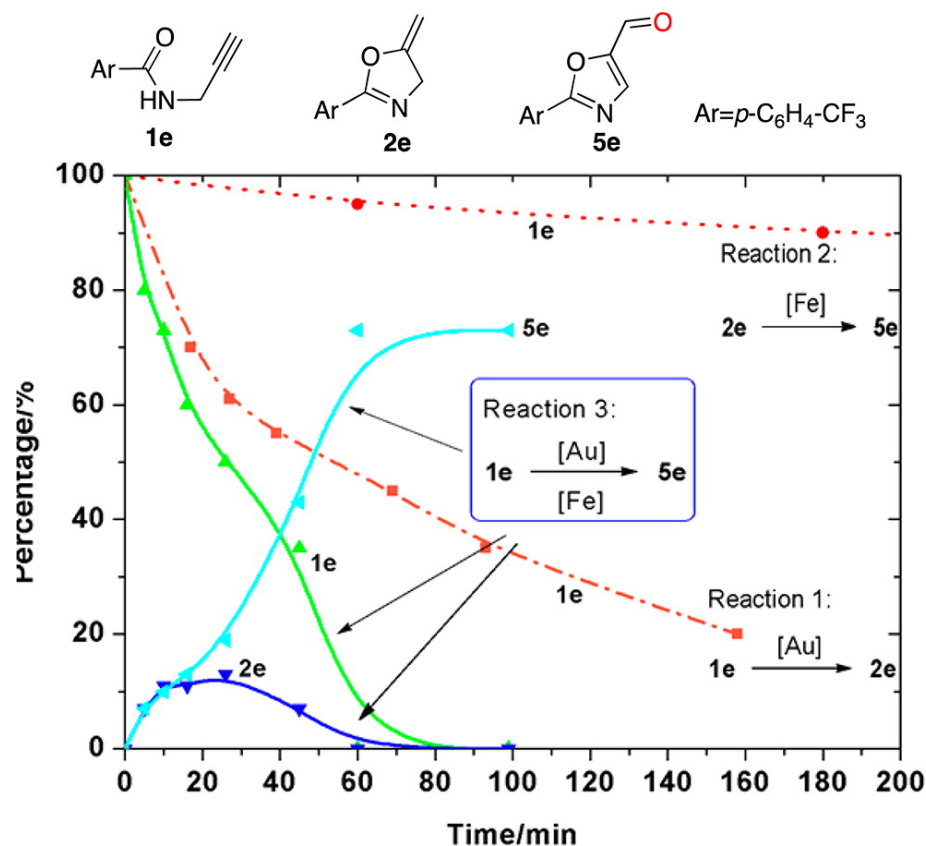
J. Am. Chem. Soc. **2015**, *137*, 8912-8915

Title Paper: Reaction Scope



J. Am. Chem. Soc. **2015**, *137*, 8912-8915

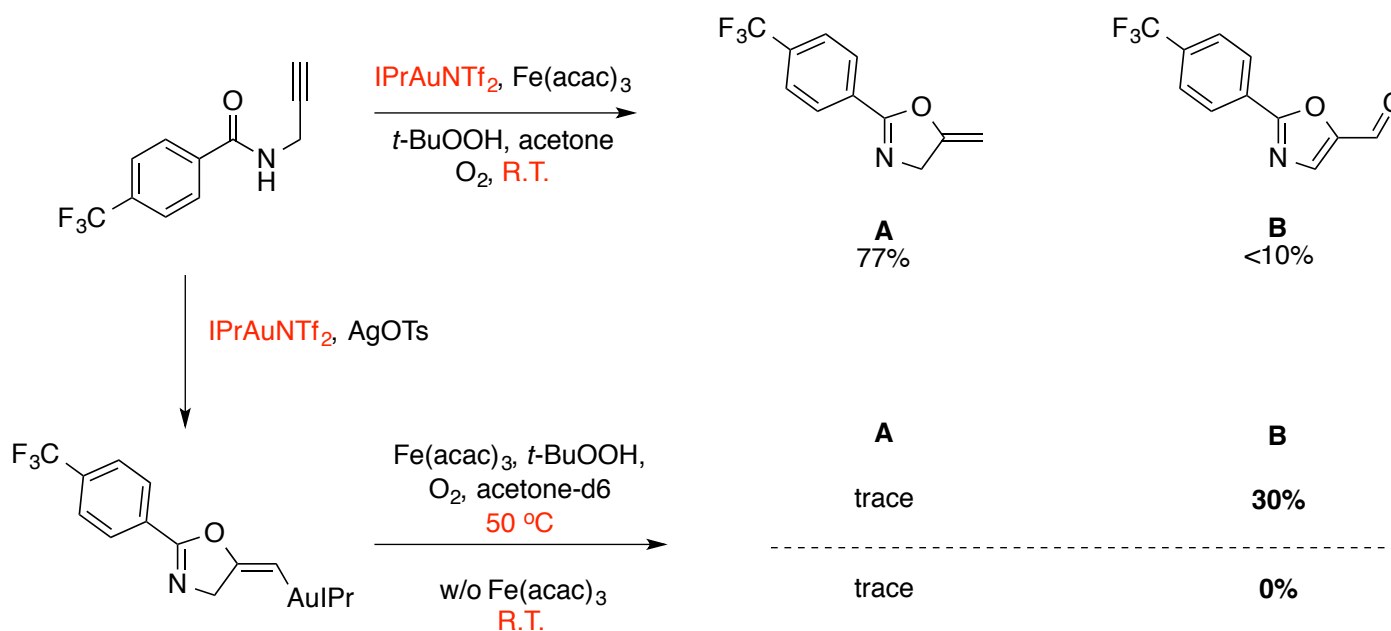
Synergistic or Sequential Catalysis?



- Slow conversion of **2e** to **5e** with $\text{Fe}(\text{acac})_3$
- Slow conversion of **1e** to **5e** with $\text{Ph}_3\text{PAuNTf}_2$
- **1e** to **5e** faster with $[\text{Au}]$ and $[\text{Fe}]$
- Suggests that $[\text{O}]$ occurs on vinyl Au, not alkene

J. Am. Chem. Soc. **2015**, *137*, 8912-8915

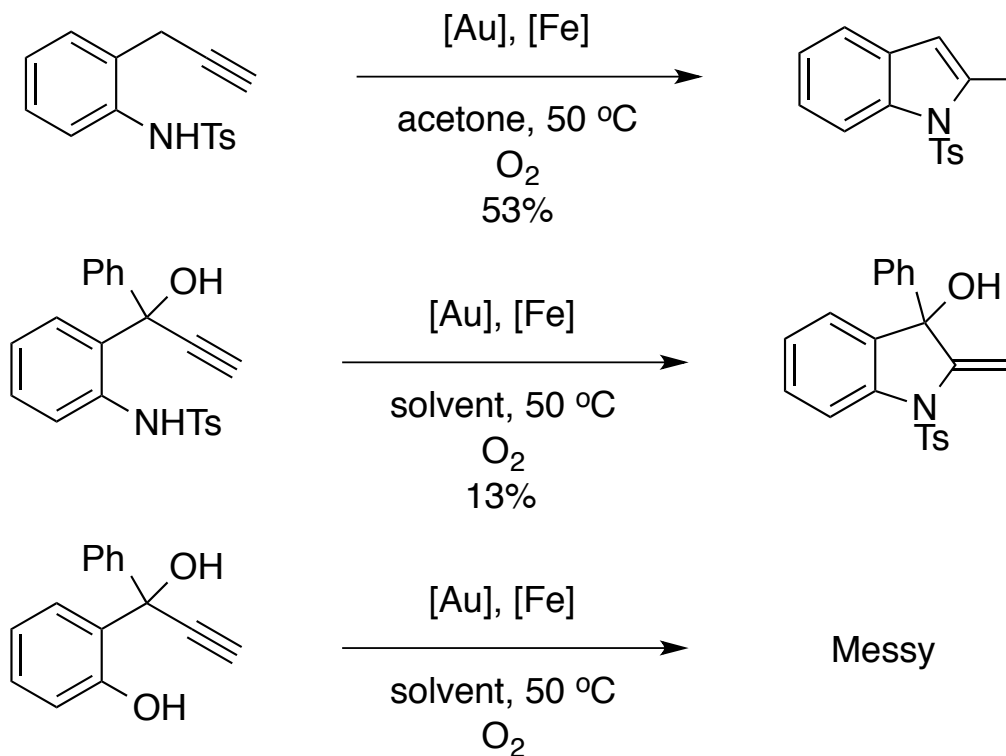
Competency of Vinyl Gold Intermediate



- $\text{Ph}_3\text{PAuNTf}_2$ analog not isolable
- 1 eq. TEMPO inhibits reaction
- Questionable reaction temperatures

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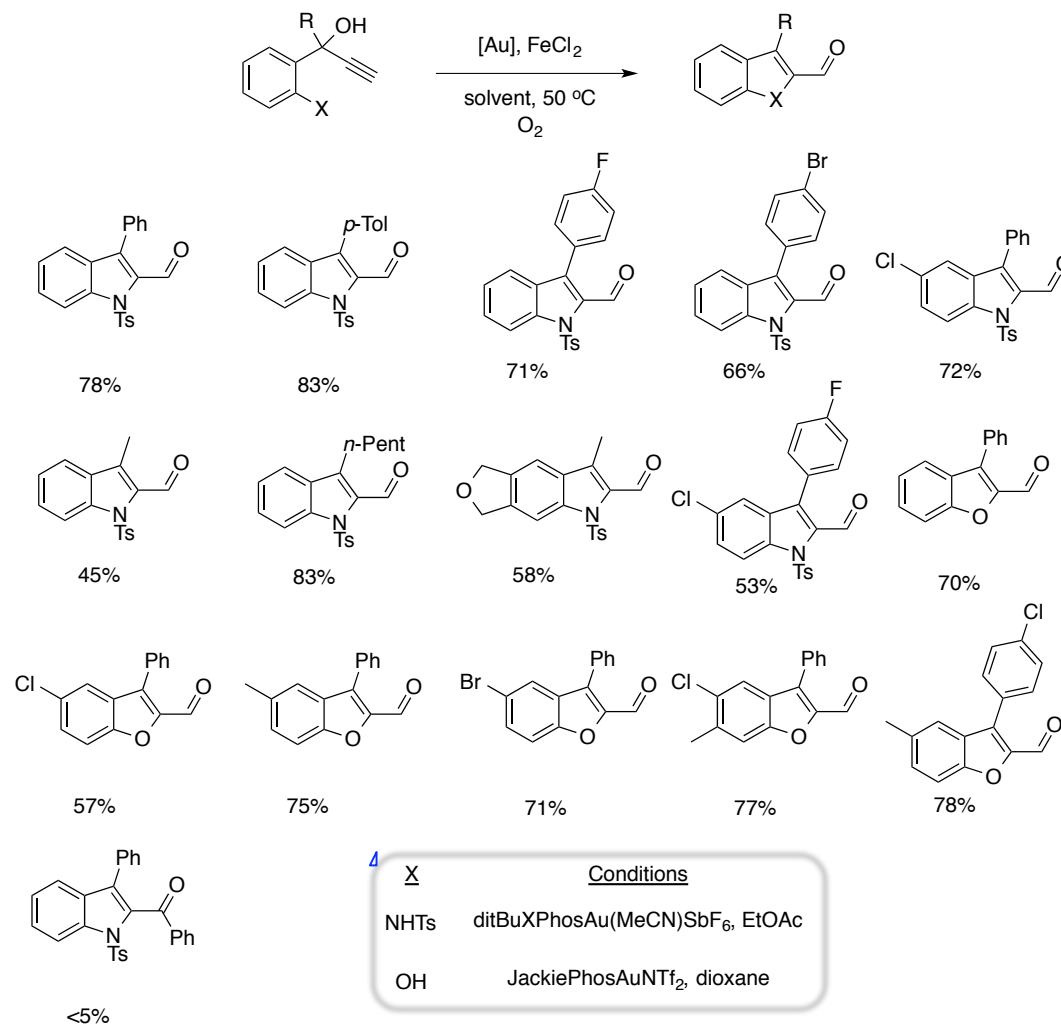
Slow Protodeauration?



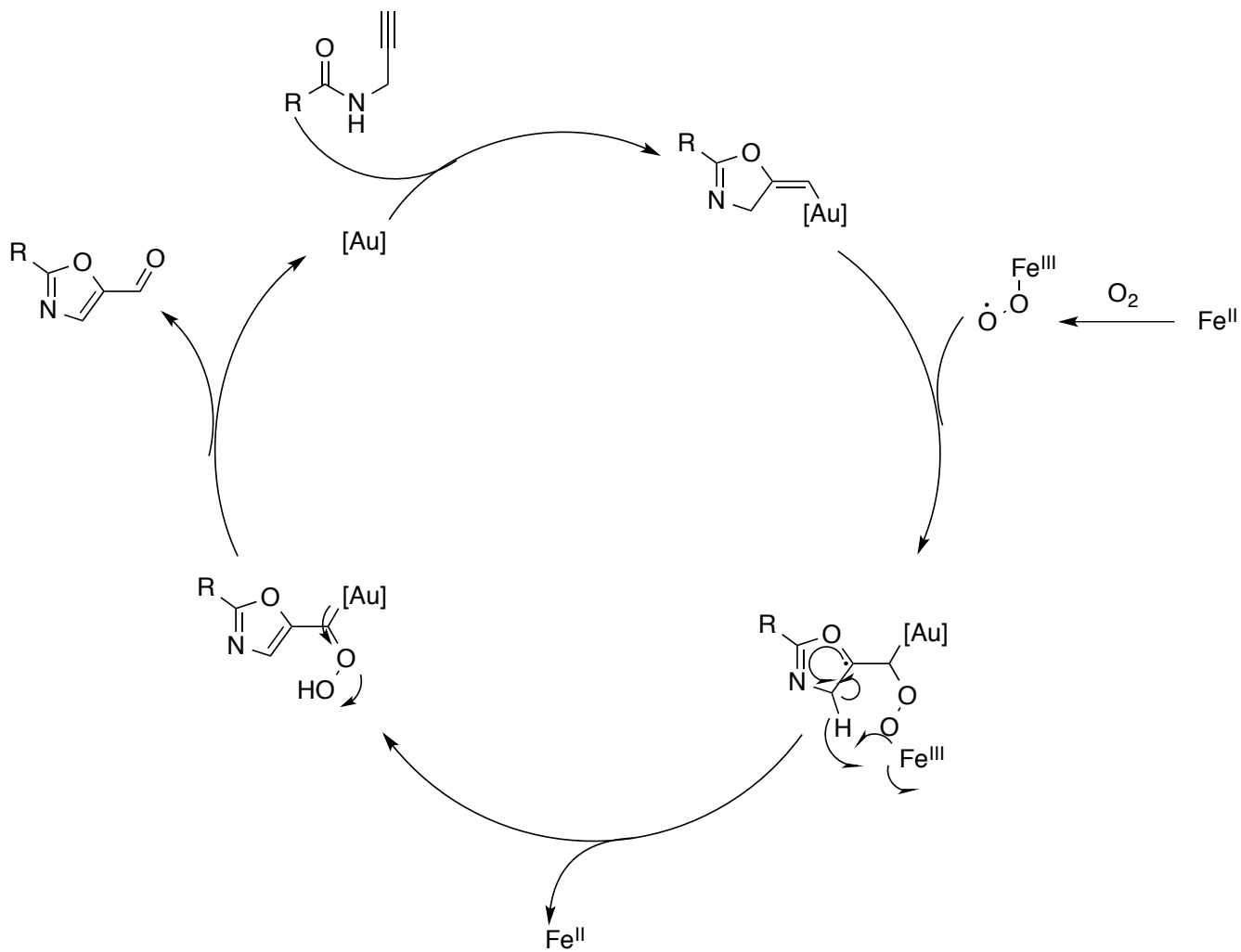
“The major challenge for this synthetic route was the slow protodeauration, which led to the poor yields of the cyclization products.”

J. Am. Chem. Soc. **2015**, *137*, 8912-8915

Indole and Benzofuran Scope

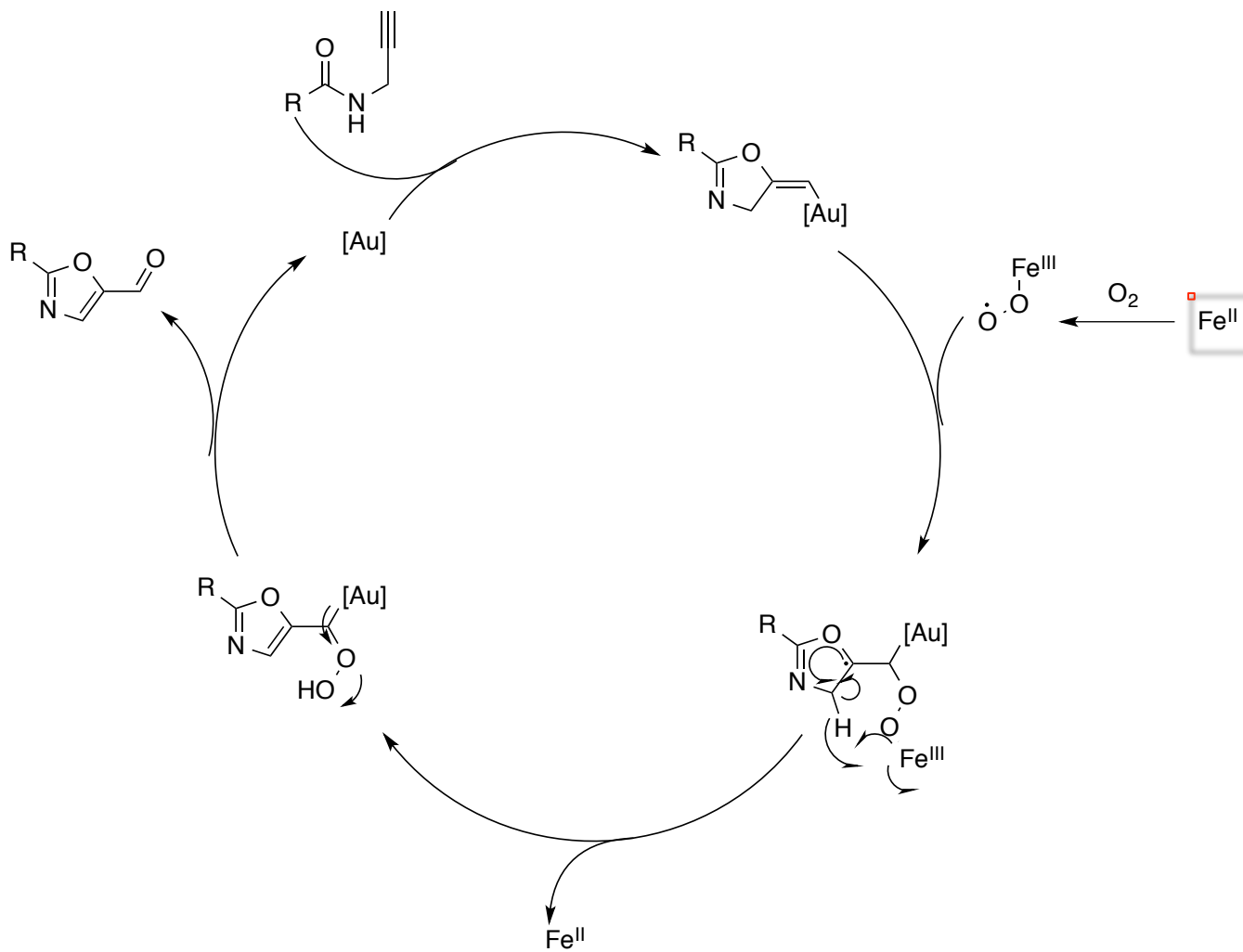


Proposed Mechanism



J. Am. Chem. Soc. **2015**, *137*, 8912-8915

Proposed Mechanism



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Conclusions

- Experiments suggest oxidation of a vinyl gold intermediate
- Sloppiness of the rest of the paper and supporting information raises questions about what was done and why