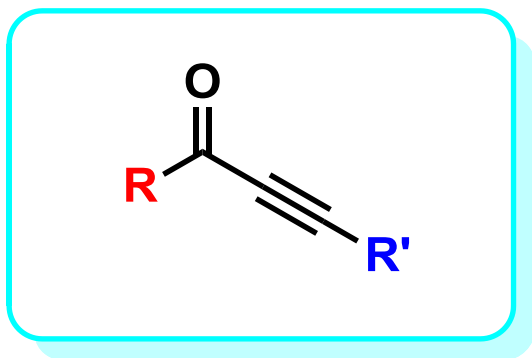


Recent Developments in Ynone Synthesis



Reporter: Zhao-feng Wang

Supervisor: Yong Huang

2014-02-17

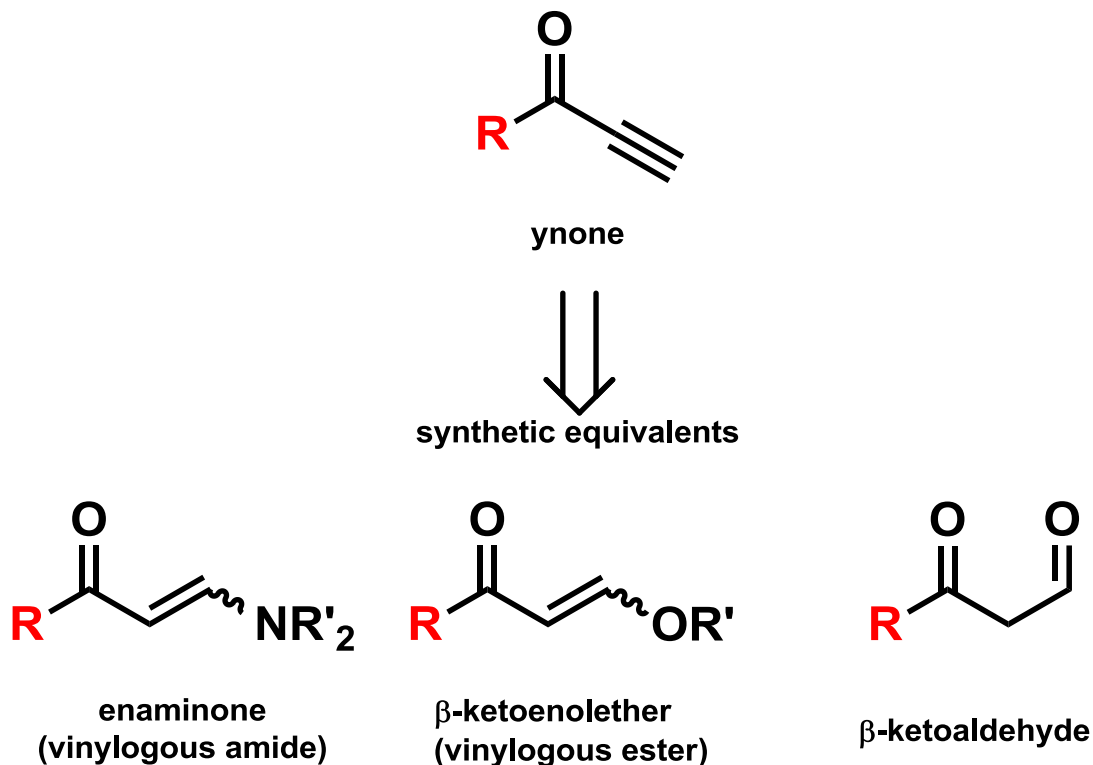


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- 2. Synthetic Method 1: Nucleophilic addition***
- 3. Synthetic Method 2: Coupling***
- 4. Synthetic Method 3: Rearrangement***
- 5. Summary and outlook***
- 6. Acknowledgement***

Recent Developments in Ynone Synthesis



Important and well-established three-carbon building blocks



Recent Developments in Ynone Synthesis

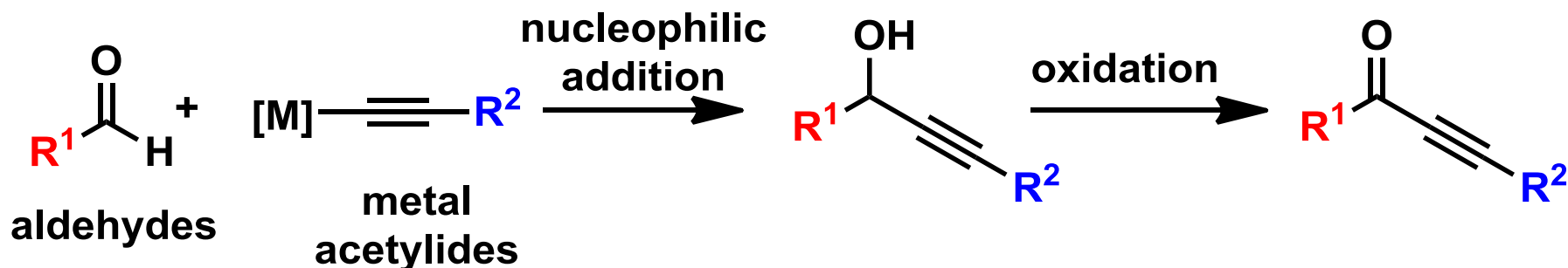
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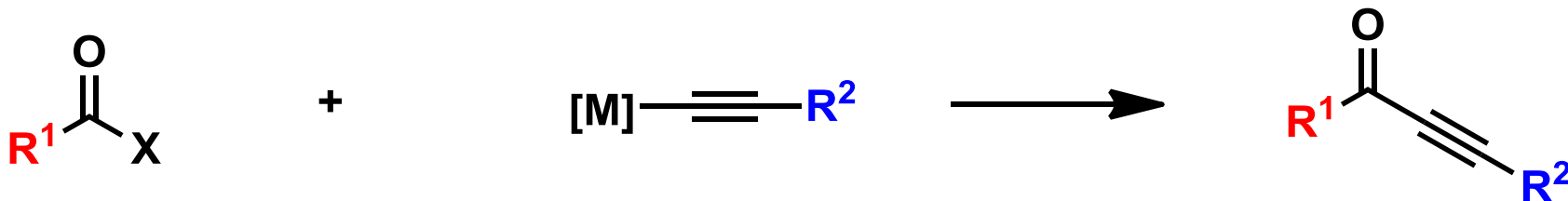
Recent Developments in Ynone Synthesis

Synthetic Method 1: Nucleophilic addition

Two-step strategy:



Carboxylic acid derivatives as substartes:



$X = Cl, OCOR', OR'', CN$ $M = Li, Mg, Cu, Cd, Si, Ag, Sn, Ti$

Maeda, Y.; Kakiuchi, N.; Matsumura, S.; Nishimura, T.; Kawamura, T.; Uemura, S. *J. Org. Chem.* **2002**, 67, 6718-6724

Brown, H. C.; Racherla, U. S.; Singh, S. M. *Tetrahedron Lett.* **1984**, 25, 2411-2414.

Kroeger, J. W.; Nieuwland, J. A. *J. Am. Chem. Soc.* **1936**, 58, 1861-1863.

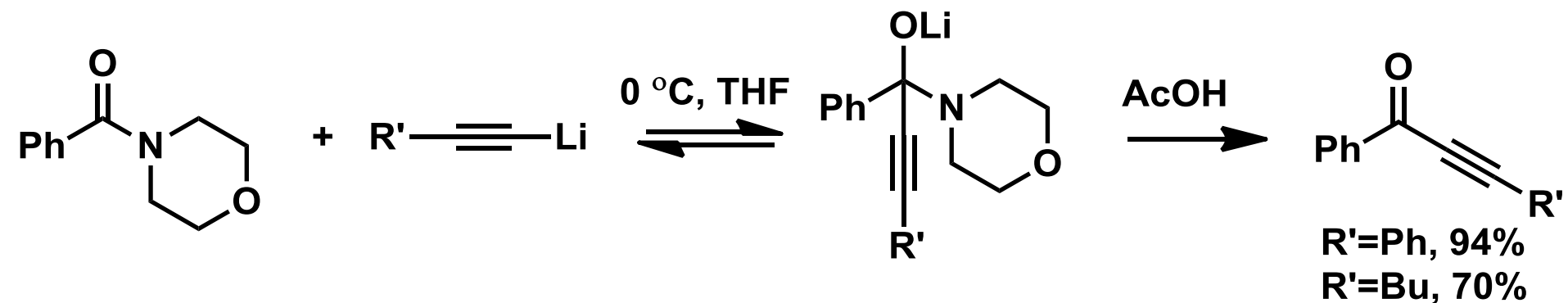
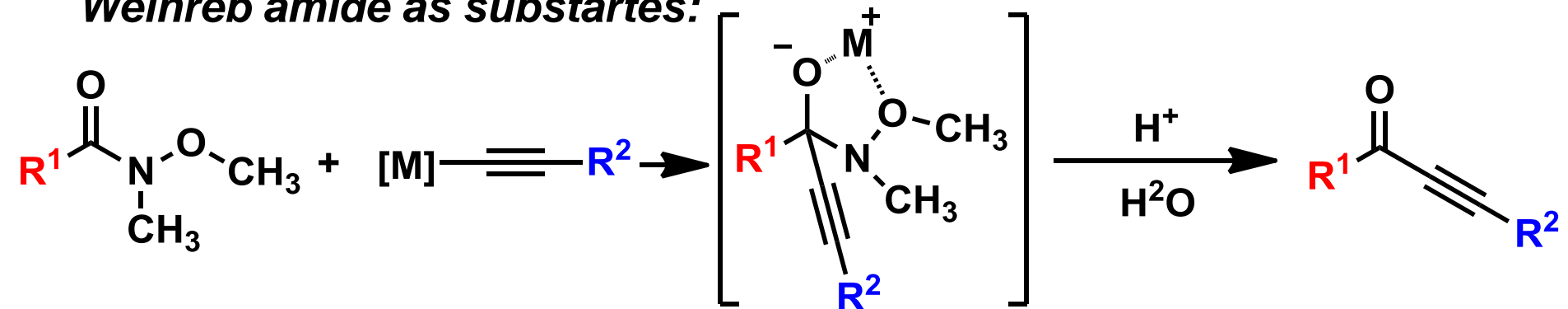
Normant, J. F. *Synthesis* **1972**, 63-90.

Utimoto, K.; Tanaka, M.; Kitai, M.; Nozaki, H. *Tetrahedron Lett.* **1978**, 19, 2301-2304.

Recent Developments in Ynone Synthesis

Synthetic Method 1: Nucleophilic addition

Weinreb amide as substartes:



Dixon, D. J.; Ley, S. V.; Tate, E. W. *Synlett* **1998**, 1093.

Molander, G. A.; McWilliams, J. C.; Noll, B. C. *J. Am. Chem. Soc.* **1997**, 119, 1265.

Trost, B. M.; Schmidt, T. *J. Am. Chem. Soc.* **1988**, 110, 2301.

Nahm, S.; Weinreb, S. M. *Tetrahedron Lett.* **1981**, 22, 3815.



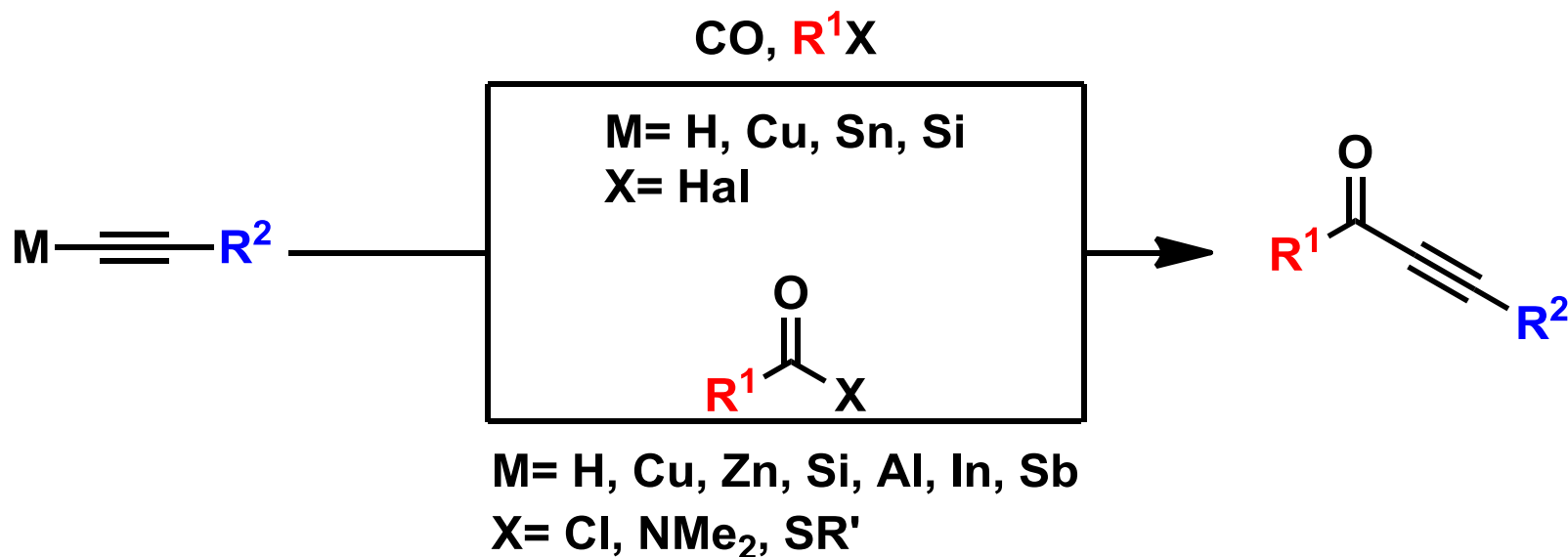
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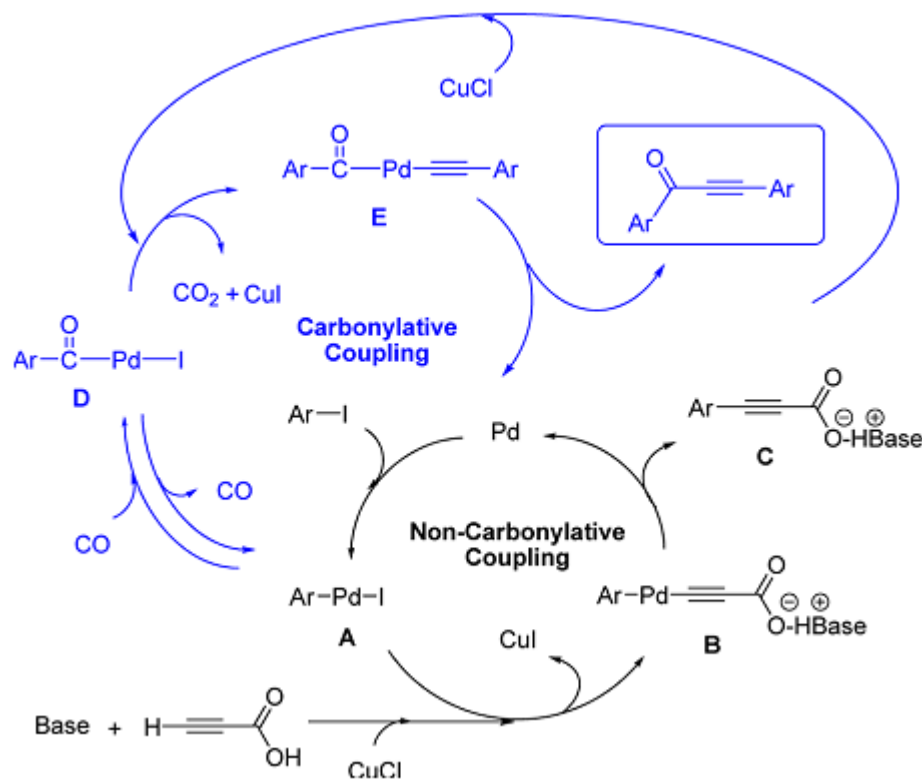
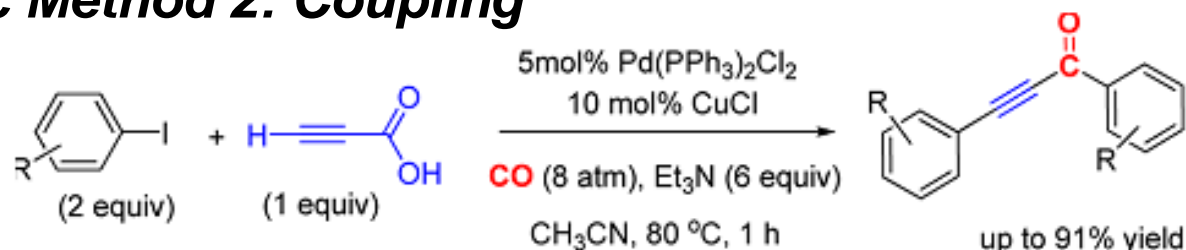
Recent Developments in Ynone Synthesis

Synthetic Method 2: Coupling



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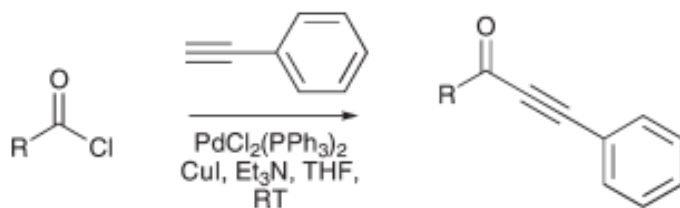
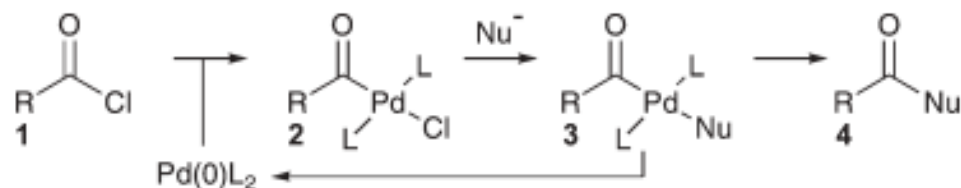
Synthetic Method 2: Coupling



Recent Developments in Ynone Synthesis

Synthetic Method 2: Coupling

Sonogashira type reaction



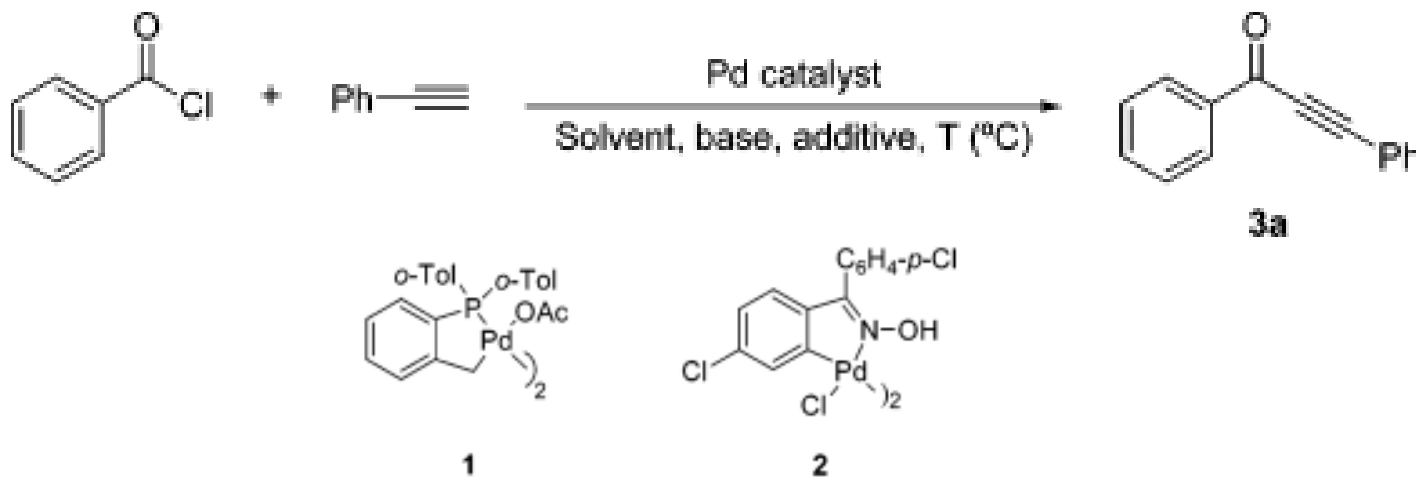
$\text{PdCl}_2(\text{PPh}_3)_2$ (0.9 mol%) and CuI (3.0 mol%) in dry THF at RT, the reaction was completed within 10 minutes

Entry	R	Product	Yield (%) ^a
1	<i>p</i> MeOC ₆ H ₄	13	98
2	<i>p</i> O ₂ NC ₆ H ₄	14	50 ^b
3	<i>p</i> BrC ₆ H ₄	15	89
4	<i>p</i> IC ₆ H ₄	16	66 ^c
5	^t Bu ^c	17	86
6	C ₆ H ₁₁	18	96
7	(CH ₃) ₂ CH	19	97
8	CH ₃ (CH ₂) ₂	21/22	43 ^d

Recent Developments in Ynone Synthesis

Synthetic Method 2: Coupling

Sonogashira type reaction

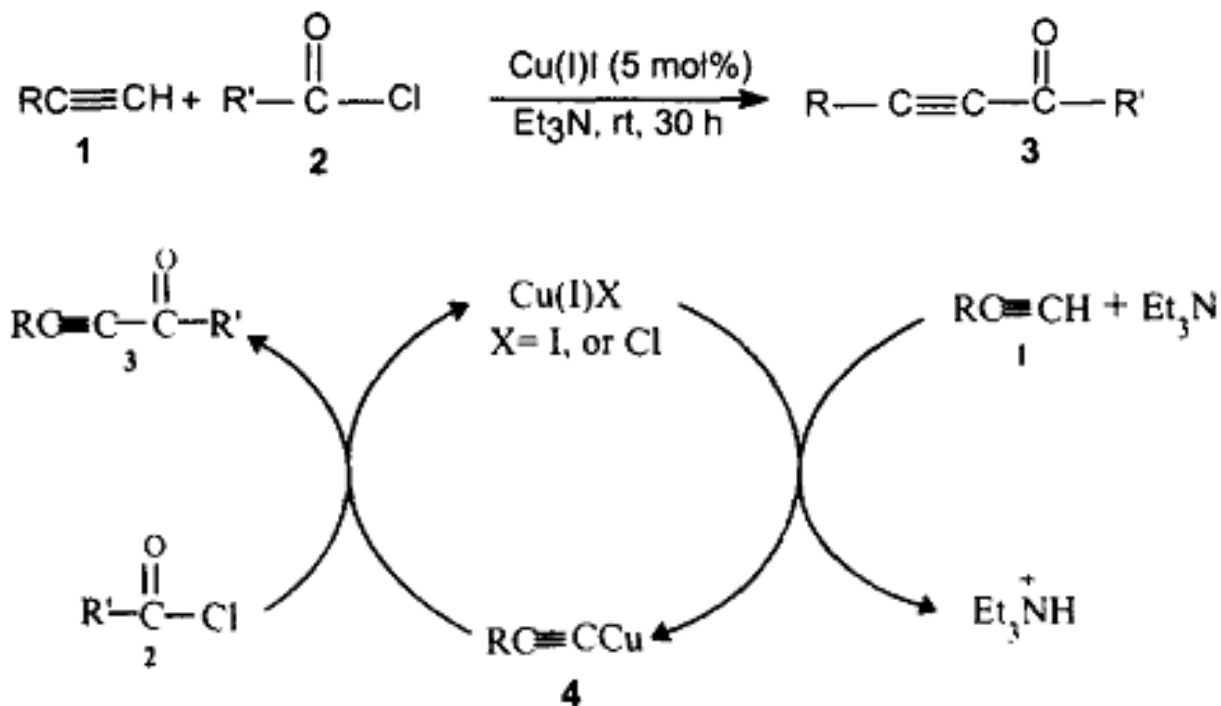


Oxime derived palladacycle as the catalyst alone instead of Pd/Cu
Phosphine and copper free conditions at high temperature

Recent Developments in Ynone Synthesis

Synthetic Method 2: Coupling

Sonogashira type reaction

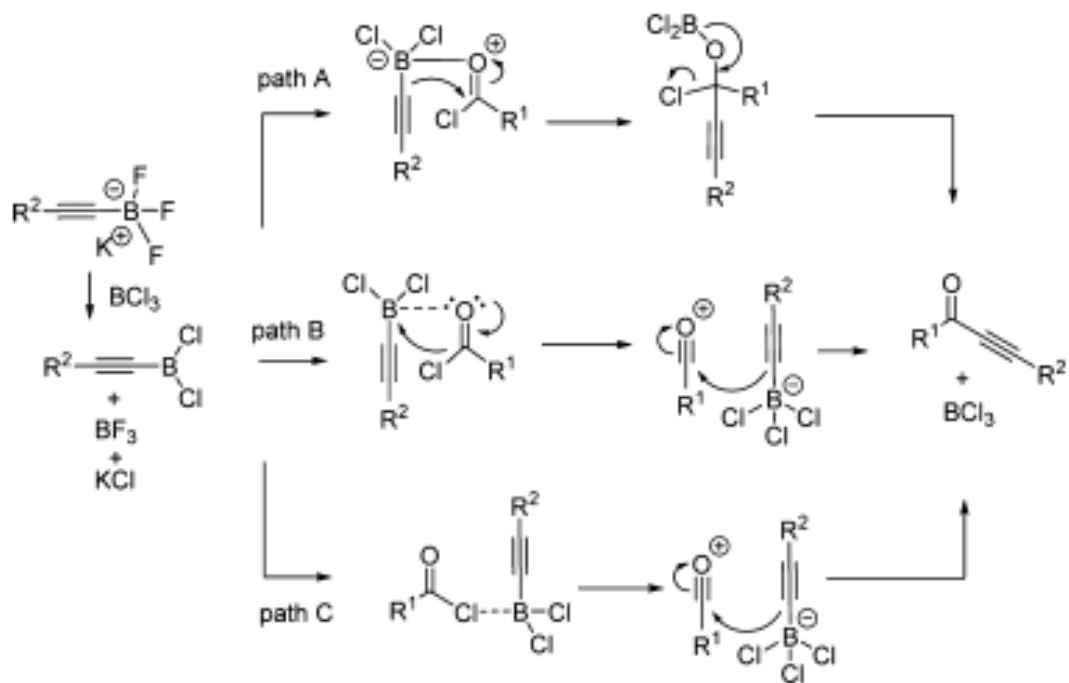
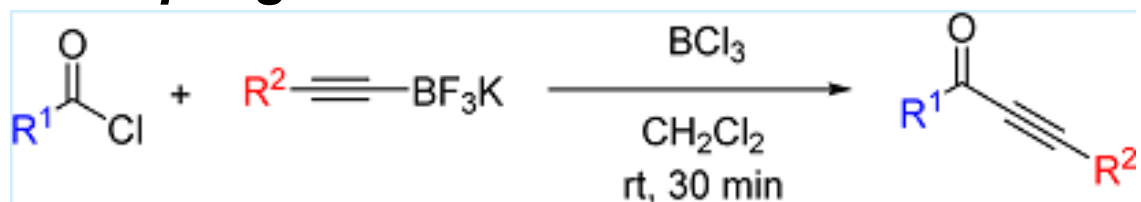


Palladium-free catalytic reaction

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Synthetic Method 2: Coupling

Metal-Free Coupling





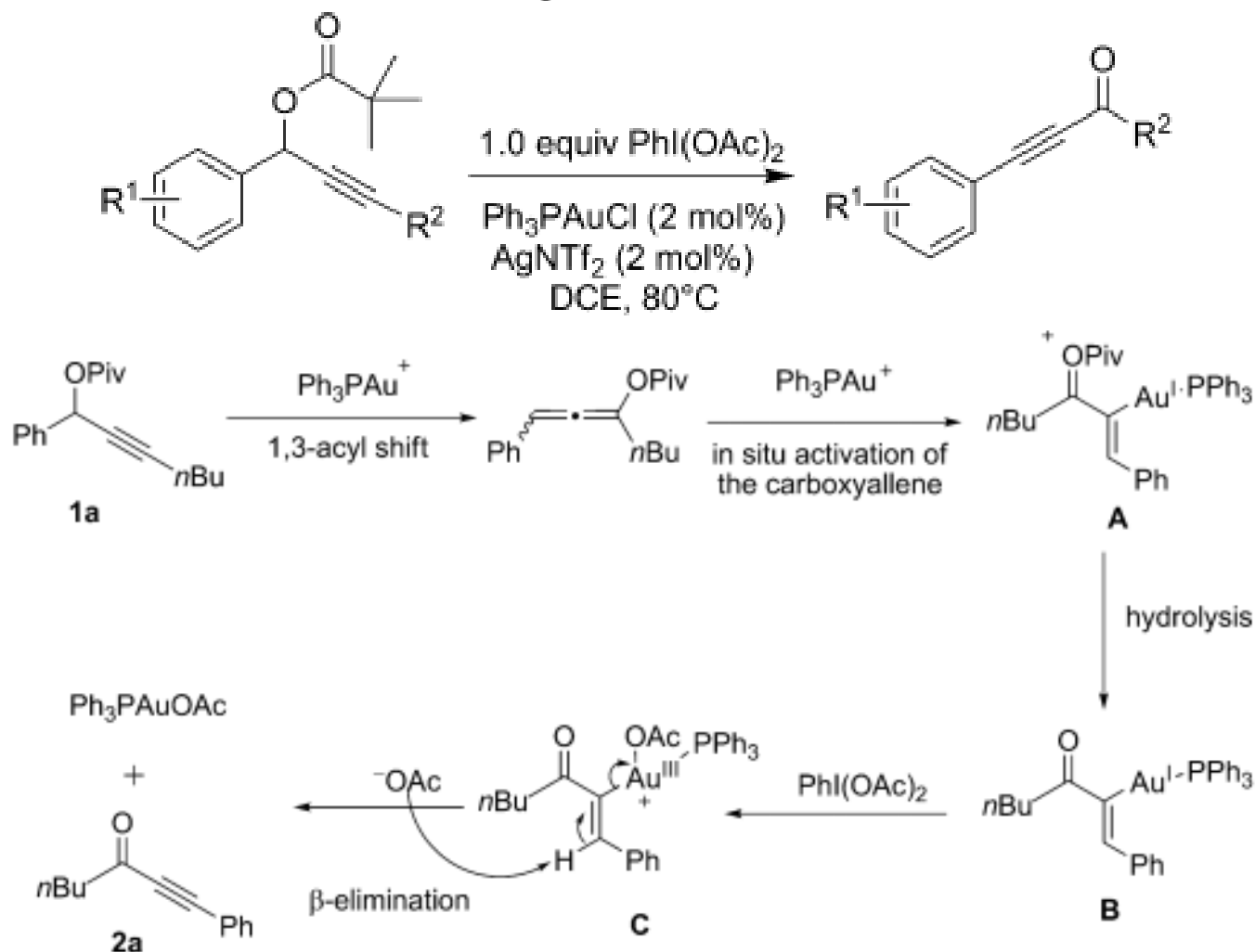
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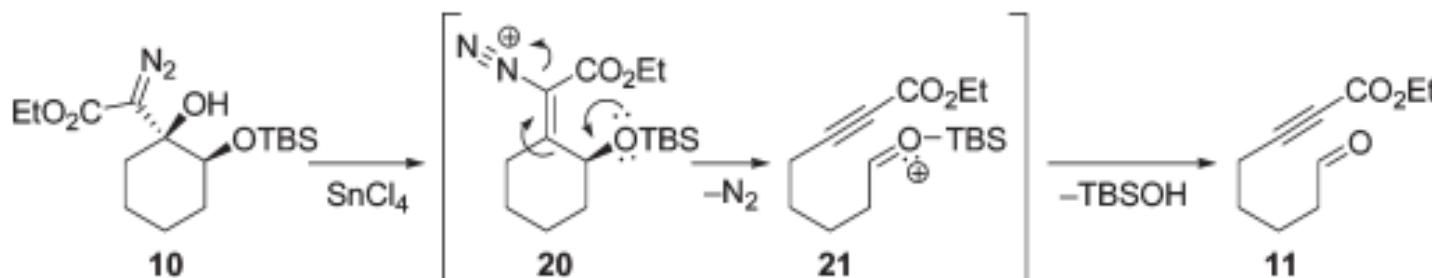
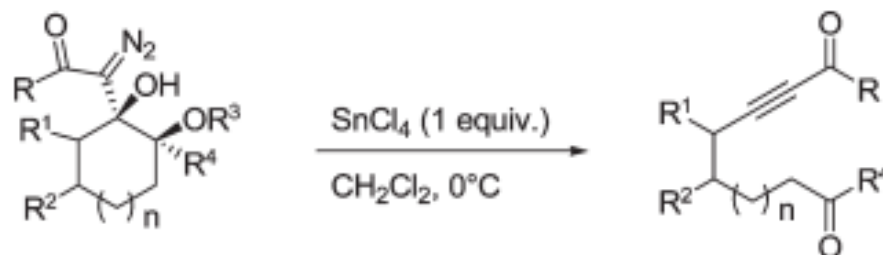
Recent Developments in Ynone Synthesis

Synthetic Method 3: Rearrangement



Recent Developments in Ynone Synthesis

Synthetic Method 3: Rearrangement





Recent Developments in Ynone Synthesis

Summary and outlook

Ynones are of great interest due to their extensive application in natural products and organic synthesis. Many synthetic strategies for ynones have been reported.

More economical methods with broader substrate scope need to be developed.



Recent Developments in Ynone Synthesis

Acknowledgement



Prof. Yong Huang



All my labmates in E201



All the members in SCBB



Thank you!