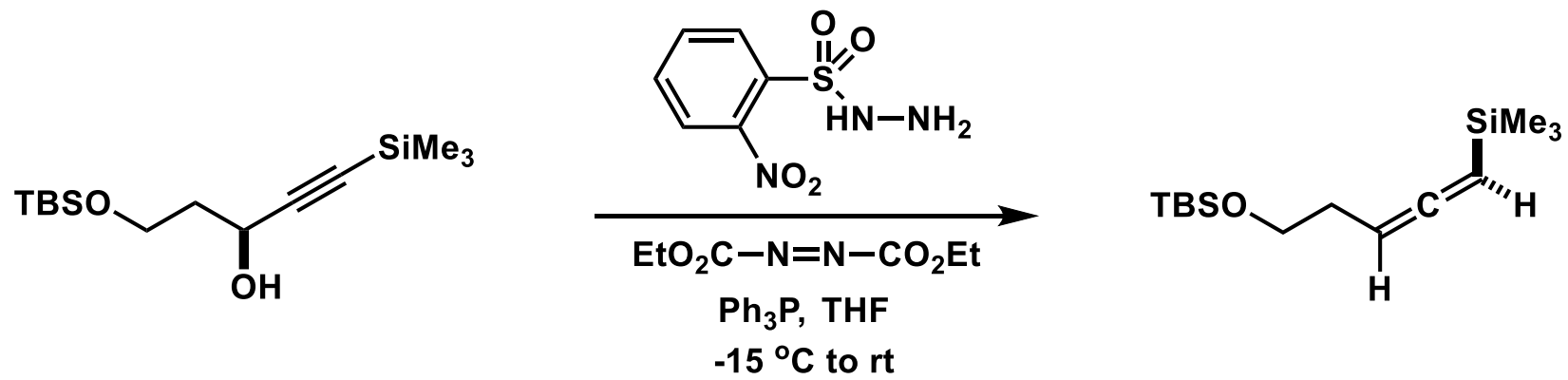
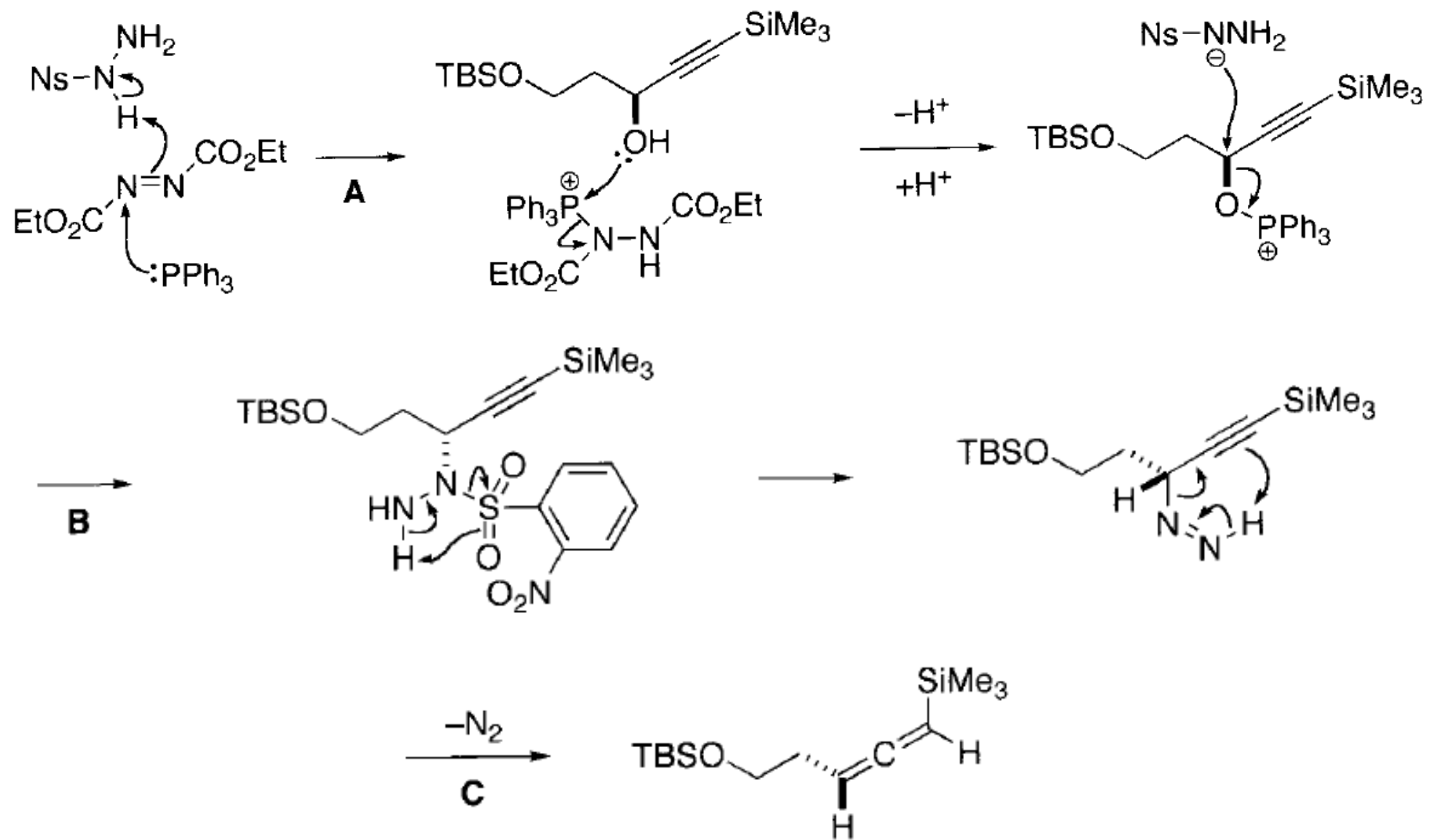


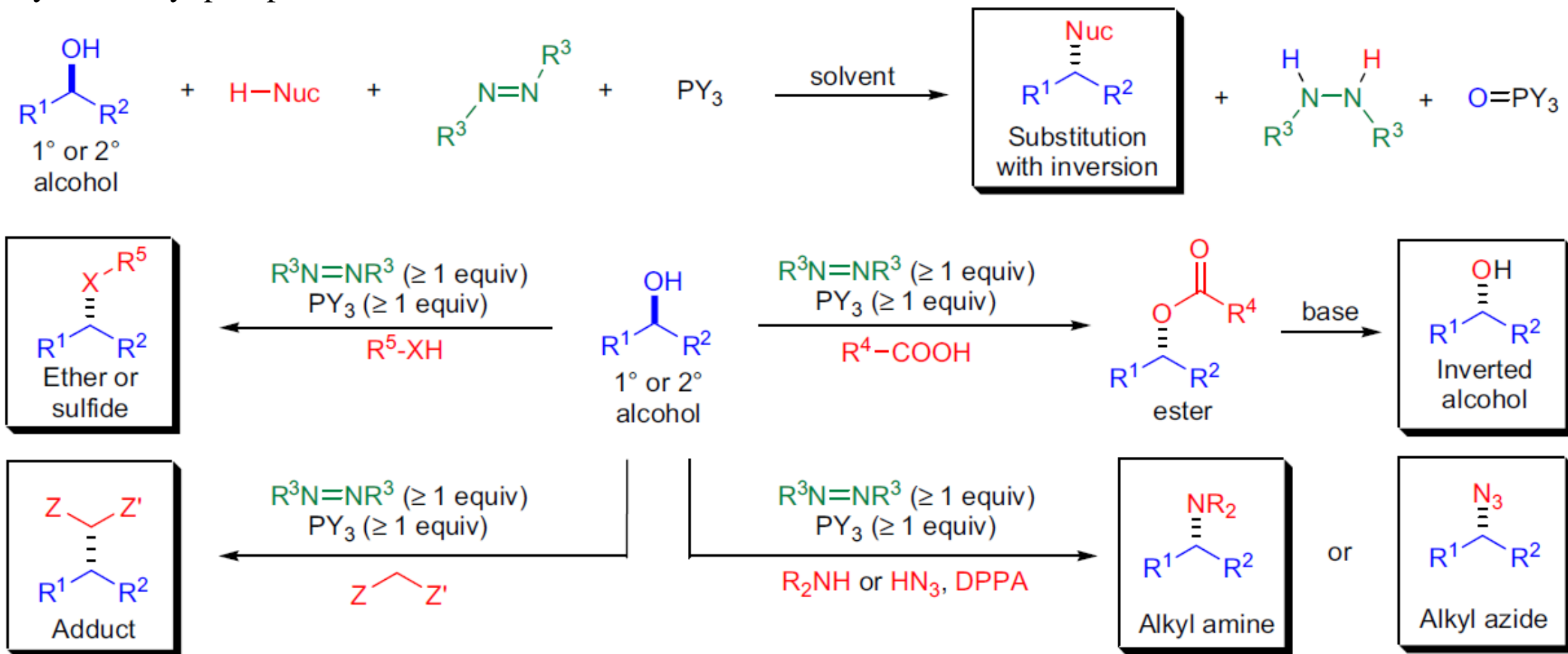
1.





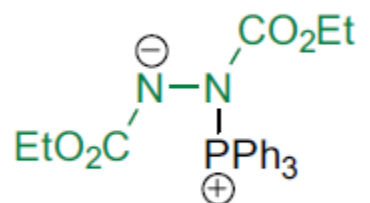
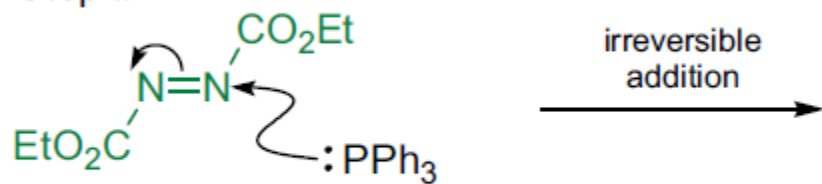
Mitsunobu reaction (光延反应)

The substitution of primary and secondary alcohols with nucleophiles in the presence of a dialkyl azodicarboxylate and a trialkyl- or triaryl phosphine is known as *the Mitsunobu reaction*.

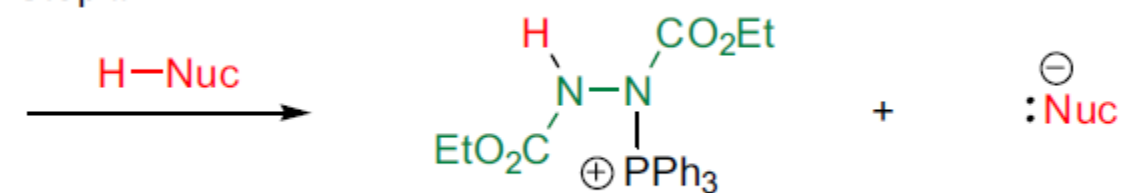


R¹⁻² = alkyl, aryl, heteroaryl, alkenyl; H-Nuc: O-, S-, N- and C-nucleophiles; R³ = CO₂Et (DEAD), CO₂*i*-Pr (DIAD), CON(CH₂)₅ (ADDP), CONMe₂ (TMAD); Y = alkyl, aryl, heteroaryl, O-alkyl; solvent: THF, dioxane, DCM, CHCl₃, DMF, toluene, benzene, HMPA; R⁴ = H, CH₃, Ph, 4-NO₂C₆H₄, 3,5-(NO₂)₂C₆H₃, alkyl, aryl; R⁵ = alkyl, aryl, heteroaryl; X = O, S; Z & Z' = CO-alkyl, CO-aryl, CO₂-alkyl, CO₂-aryl, CN

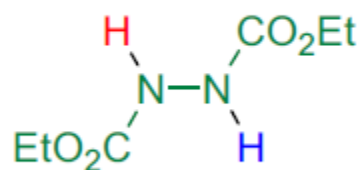
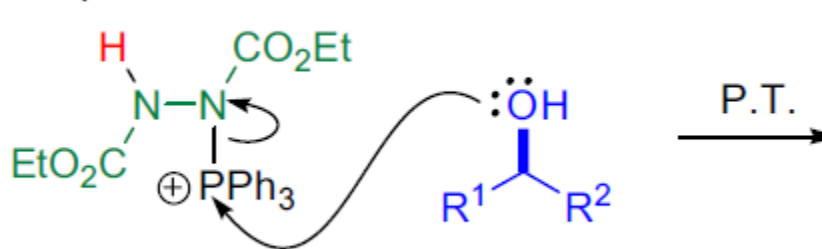
Step #1:



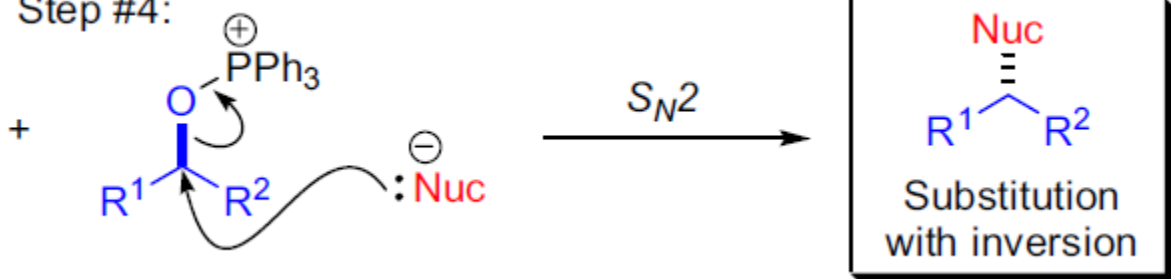
Step #2:



Step #3:



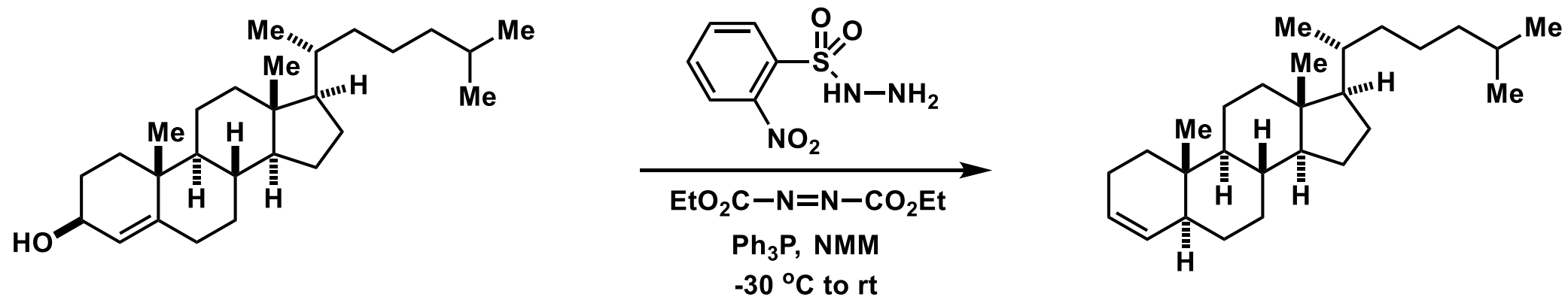
Step #4:

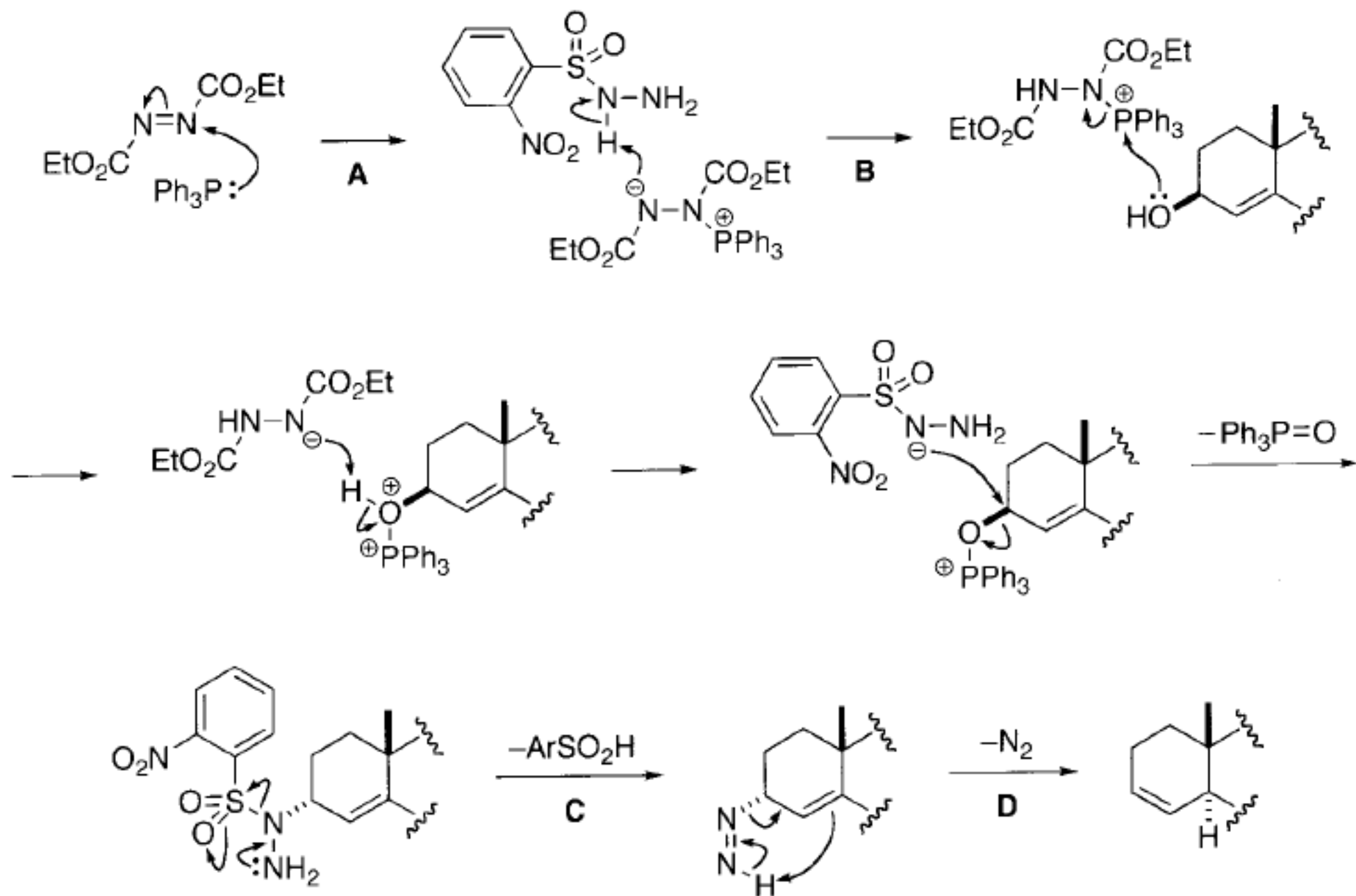


反应特点:

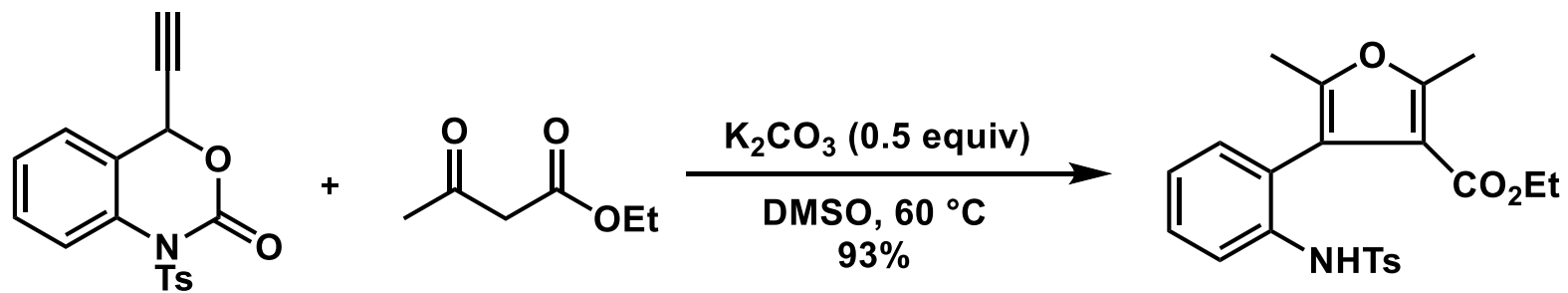
- 伯醇和仲醇可以进行Mitsunobu反应，仲醇手性翻转；
- 亲核试剂需具有一定酸性；
- 低极性的溶剂有利于反应，通常用THF，Et₂O，CH₂Cl₂和PhMe作为溶剂；
- PPh₃和 P(*n*-Bu)₃是最常用的磷配体，常用的偶氮二羧酸酯是DEAD 和 DIAD；
- 反应温度通常在0℃到25℃之间，底物的位阻较大的反应温度也要提高；
- 加料顺序：
 - 1) 底物+亲核试剂+磷+溶剂；然后DEAD (或DIAD)滴加
 - 2) 磷+ DEAD (或DIAD) +溶剂；然后底物+亲核试剂

2.

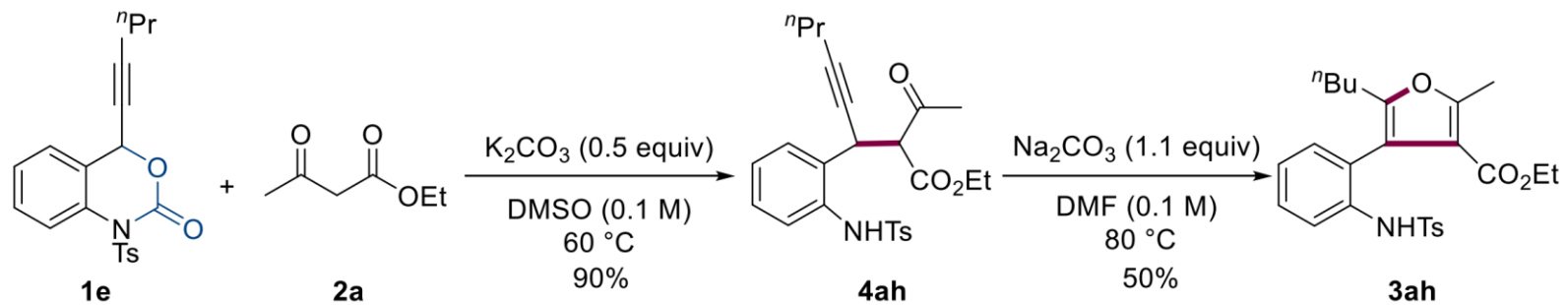
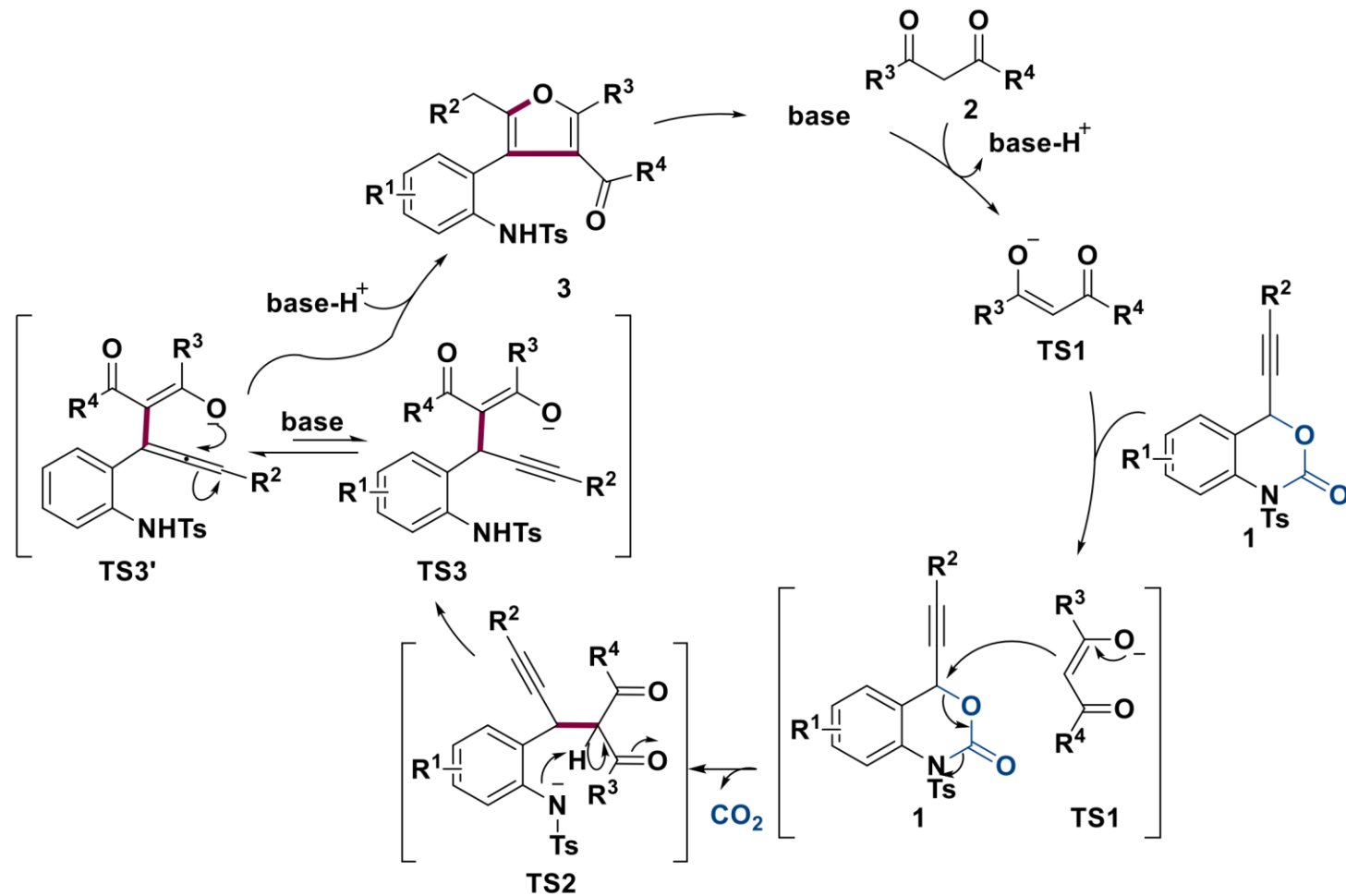




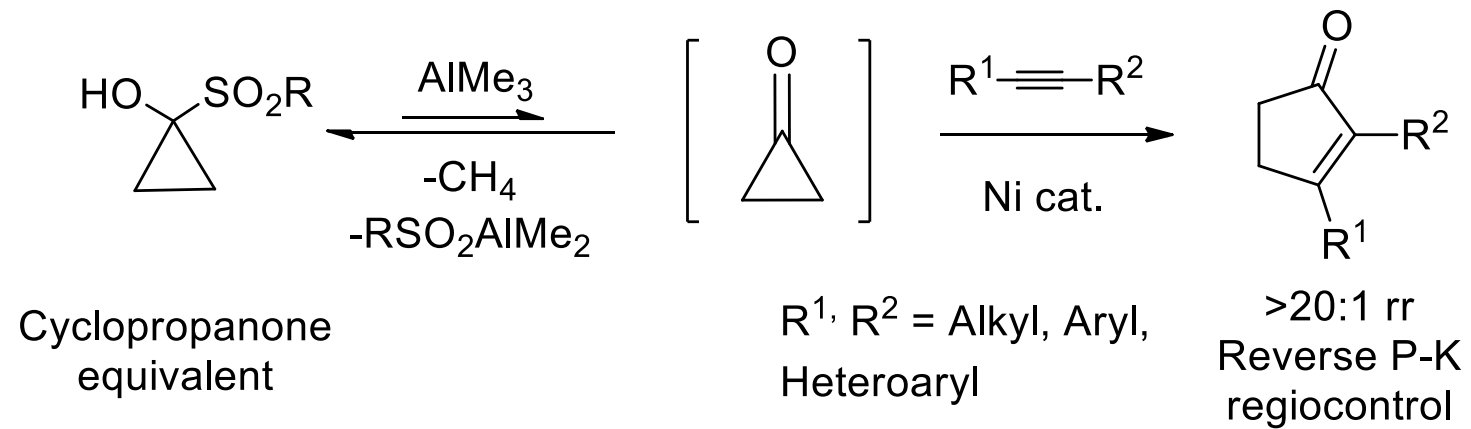
3.



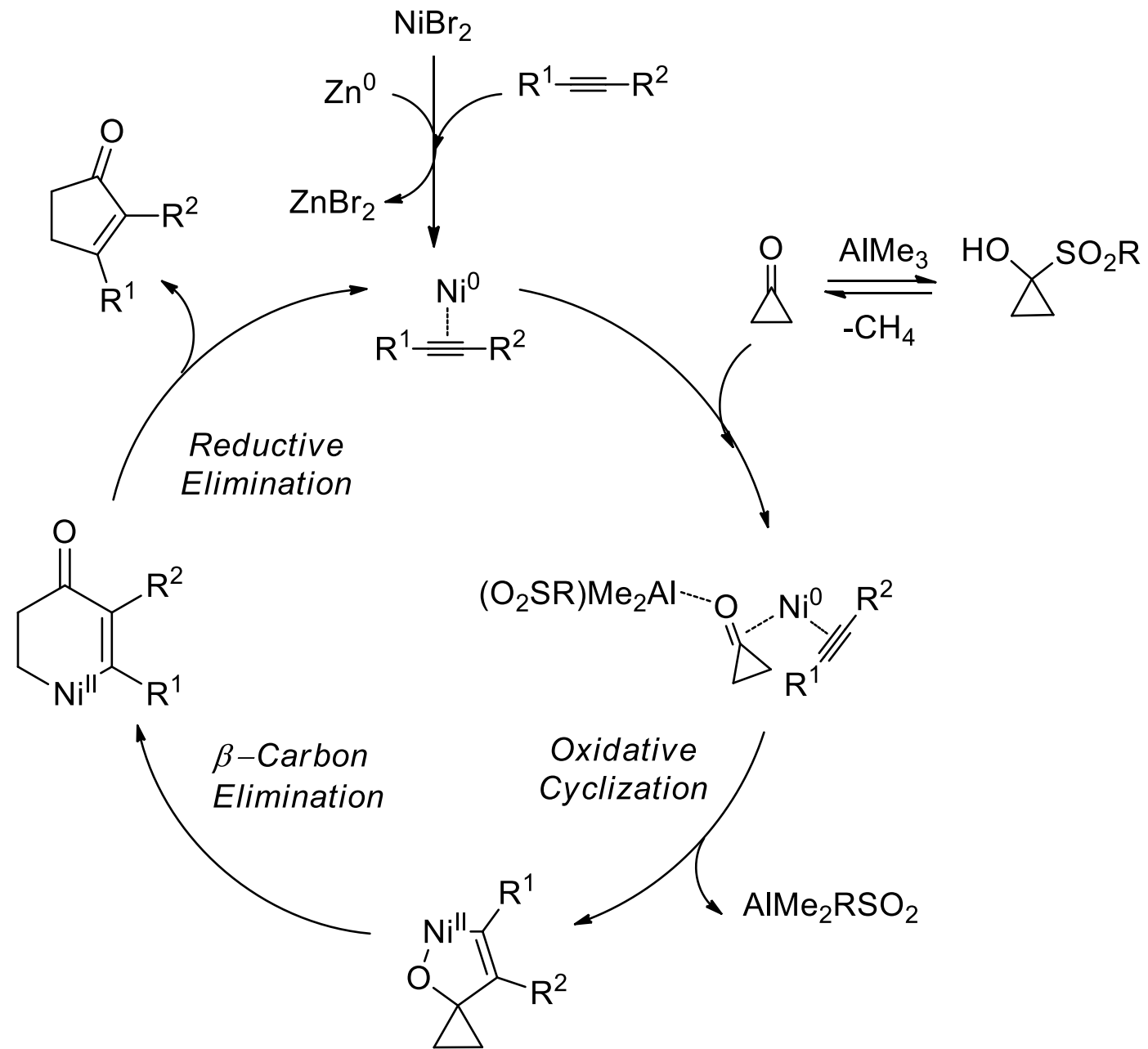
Org. Lett. **2020**, *22*, 8752.



4.

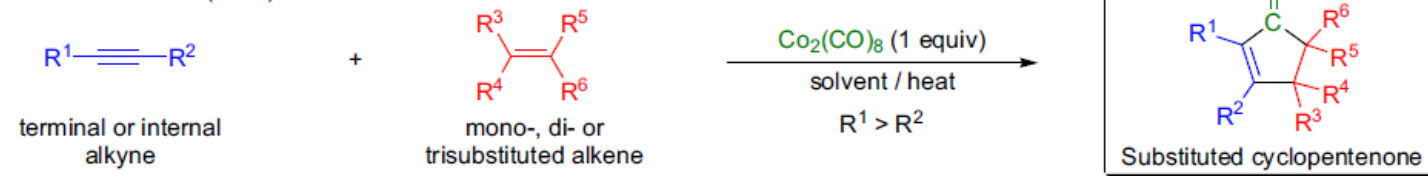


Org. Lett. **2020**, *22*, 8872.

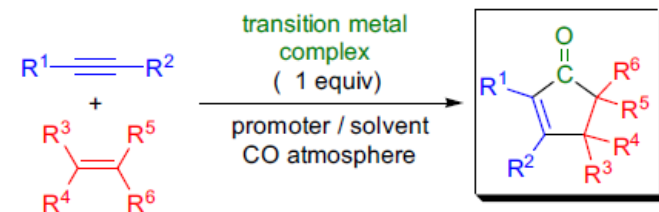


PAUSON-KHAND REACTION

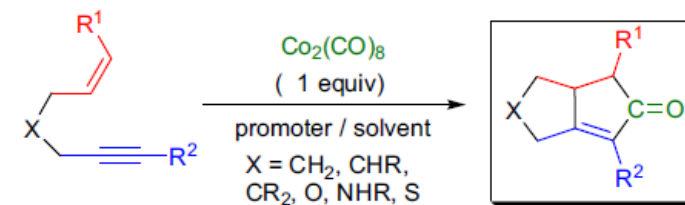
Pauson & Khand (1973):



Modified P-K reaction:

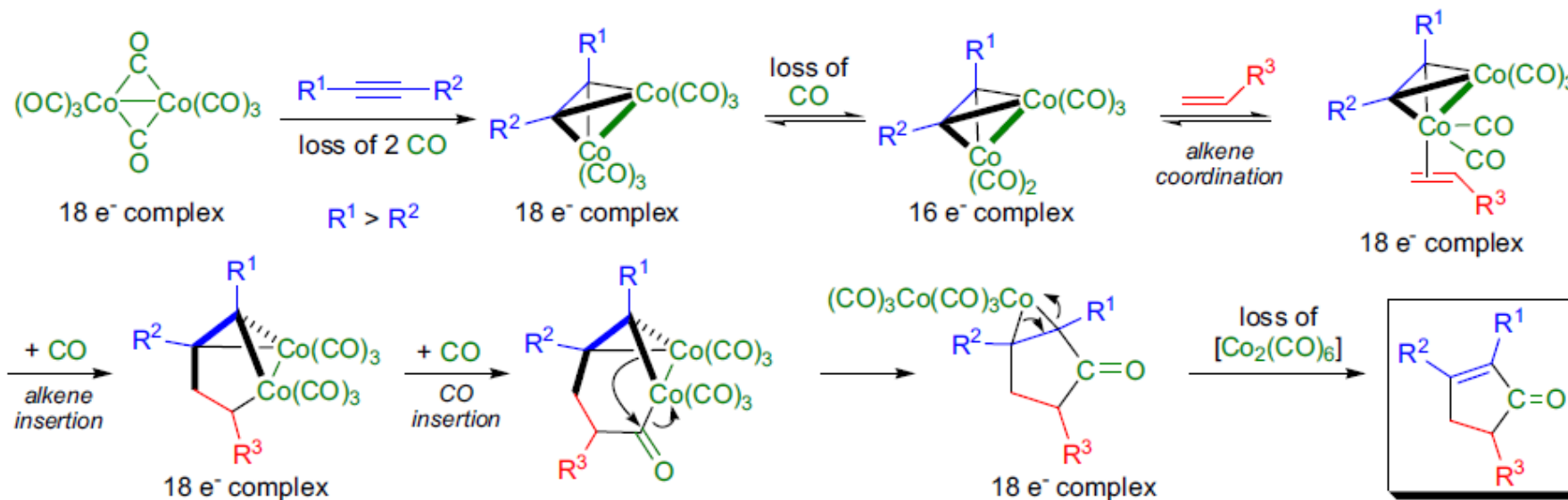


Intramolecular variant:



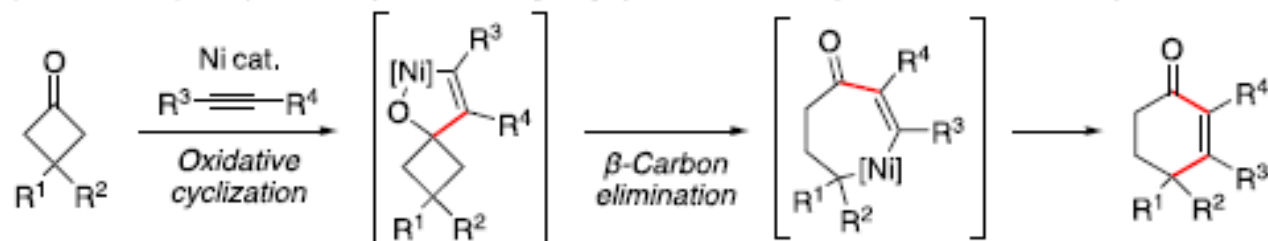
R^{1-6} = H, alkyl, aryl, substituted alkyl and aryl; transition metal complex: $Co_2(CO)_8$, $Fe(CO)_5$, $Ru_2(CO)_{12}$, Cp_2TiR_2 , $Ni(COD)_2$, $W(CO)_6$, $Mo(CO)_6$, $[RhCl(CO)_2]_2$; promoter: NMO, TMAO, $RSCH_3$, high-intensity light/photolysis, "hard" Lewis base

The mechanism of the Pauson-Khand reaction has not been fully elucidated.

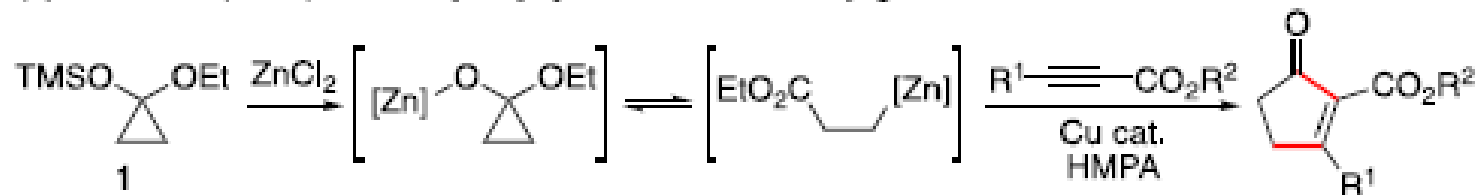




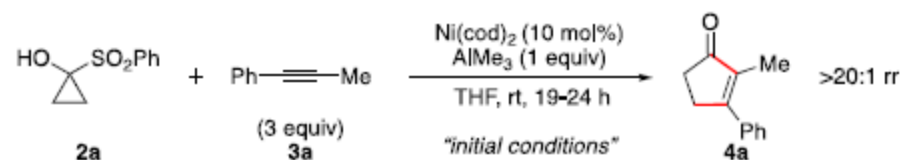
(a) Murakami (2005): Ni-catalyzed formal [4+2] cycloaddition of cyclobutanone and alkynes



(c) Crimmins (1990): Formal [3+2] cycloaddition via conjugate addition of zinc homoenolates



cyclopropanone equivalents are more commonly known to competitively equilibrate to β -nucleophilic esters in basic conditions, thus often reacting more like cyclopropanols rather than cyclopropanones.



entry	deviation from initial conditions	yield (%) ^a
1	none	21
2	Ni(cod)(DQ) instead of Ni(cod) ₂	23
3	AlMe ₂ Cl instead of AlMe ₃	<5
4	without AlMe ₃	<5
5	without Ni(cod) ₂	<5
6 ^b	NiBr ₂ /Zn ⁰ (10 mol % each) instead of Ni(cod) ₂	35
7 ^b	NiBr ₂ /Zn ⁰ (20 mol % each) instead of Ni(cod) ₂	40
8 ^{b,c}	NiBr ₂ /Zn ⁰ (20 mol % each) instead of Ni(cod) ₂	42
9 ^{b,c}	NiBr ₂ /Zn ⁰ (30 mol % each) instead of Ni(cod) ₂	46 ^d
10 ^{c,e}	NiBr ₂ /Zn ⁰ (30 mol % each) instead of Ni(cod) ₂	29
11 ^{e,f}	NiBr ₂ /Zn ⁰ (30 mol % each), CuBr ₂ (3 mol %)	48 ^{d,g}
12 ^{e,f,h}	NiBr ₂ /Zn ⁰ (30 mol % each), CuBr ₂ (3 mol %)	15
13 ^f	Ni(cod) ₂ (30 mol %), CuBr ₂ (3 mol %)	6
14 ^c	no Ni cat, CuBr ₂ (5 mol %), Zn ⁰ (30 mol %)	<5

^aYield determined by ¹H NMR using 1,3,5-trimethoxybenzene as standard unless otherwise noted. ^bNiBr₂ (98% pure) was used. ^cThe reaction was run for 5 h. ^dDisplayed yields are the average of three runs. ^eNiBr₂ (99.9% pure) was used. ^fThe reaction was run for 7 h. ^gIsolated yield = 43%. ^hAlkyne 3a was used as limiting reagent with 2 equiv of 2a.