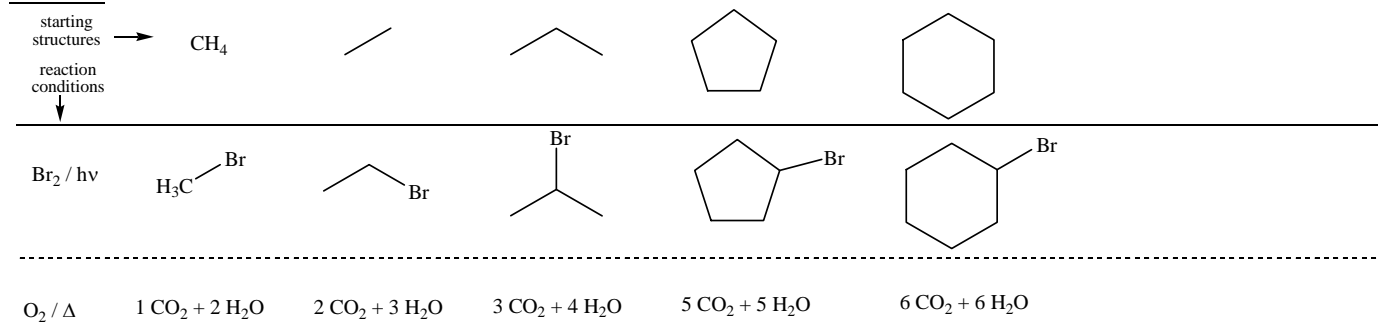
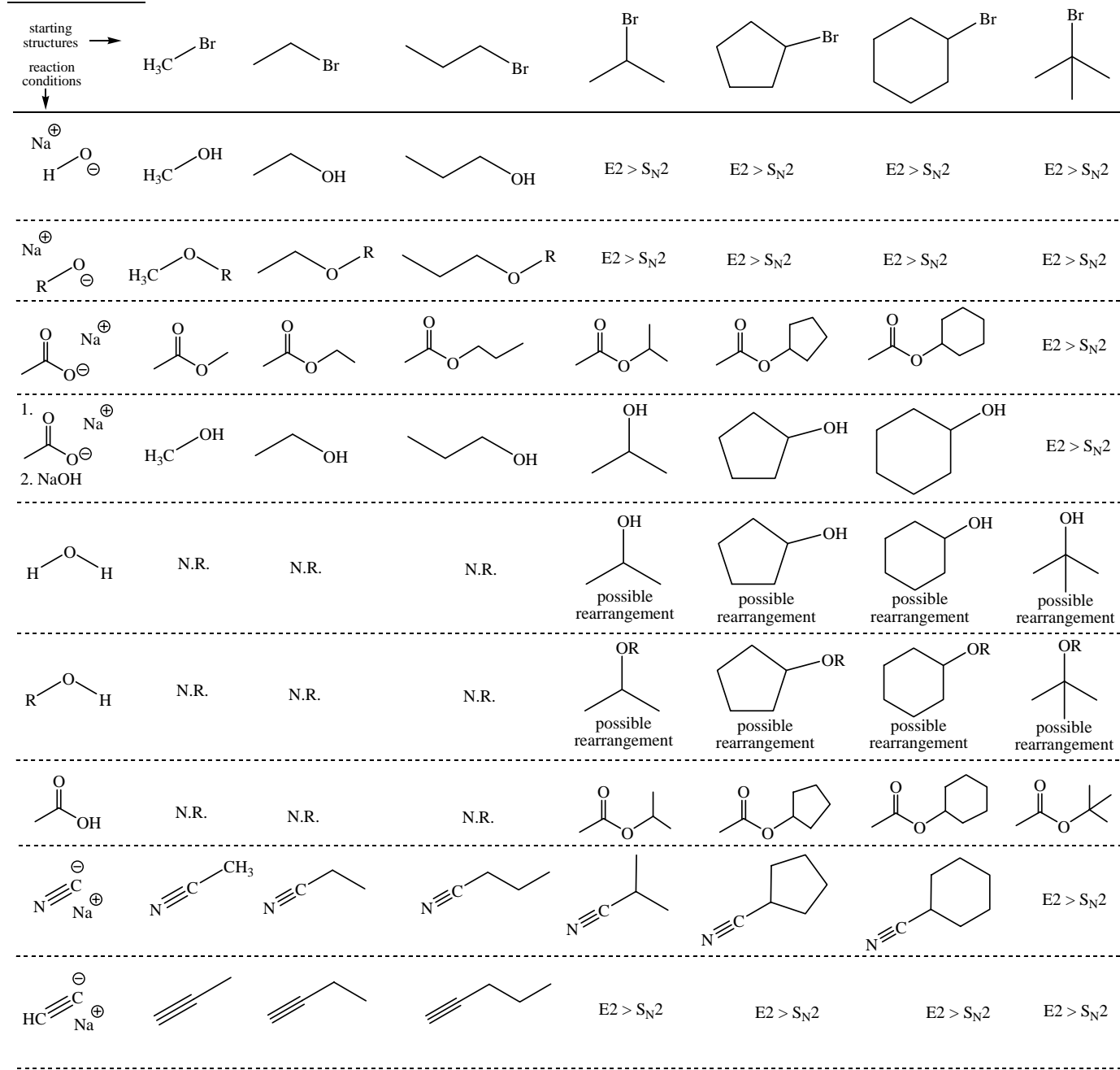
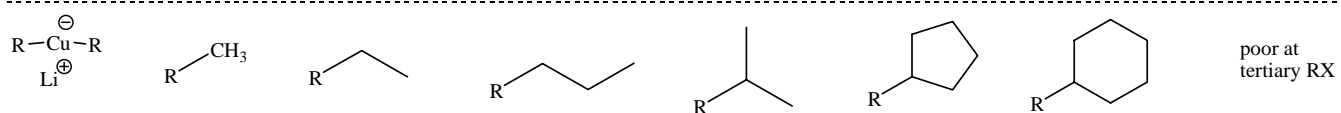
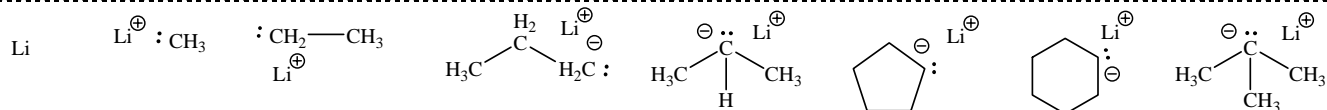
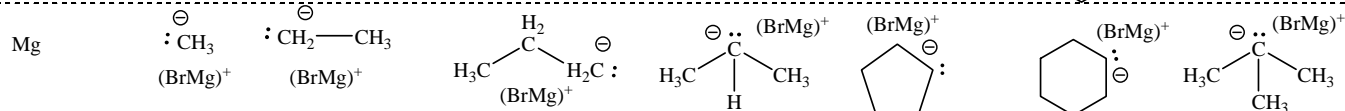
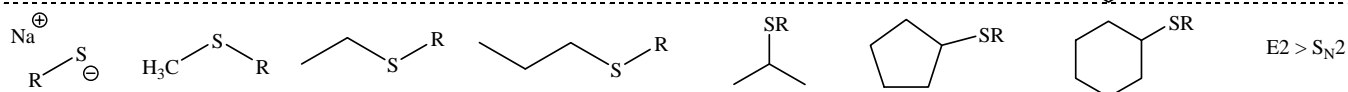
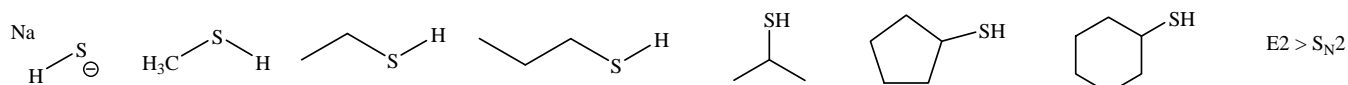
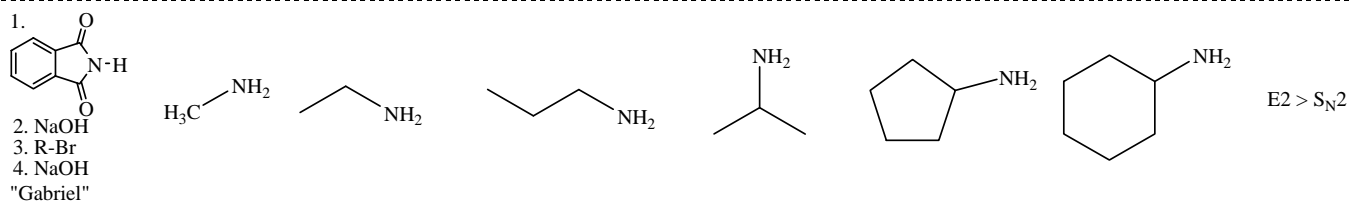
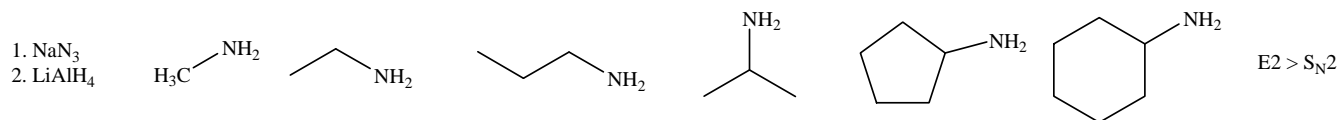
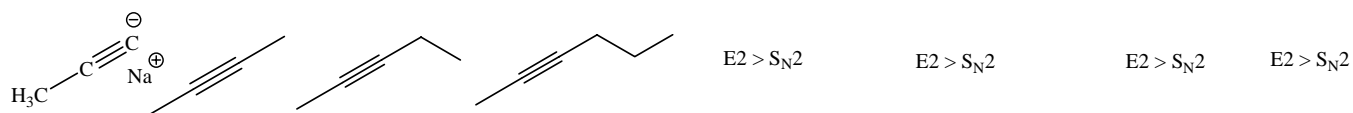
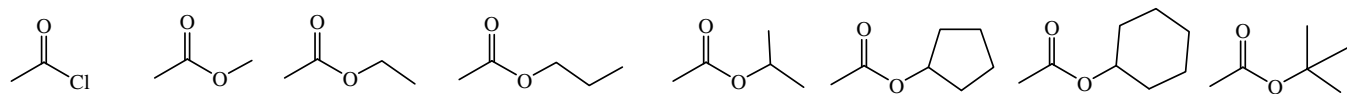
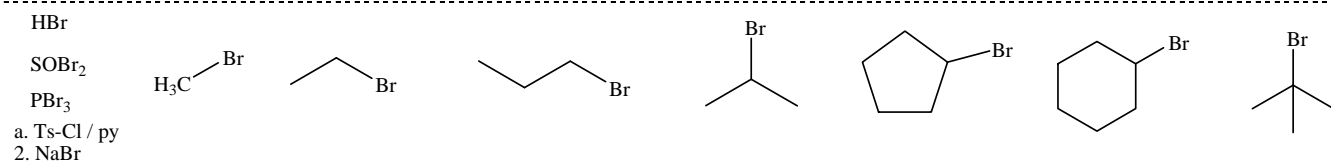
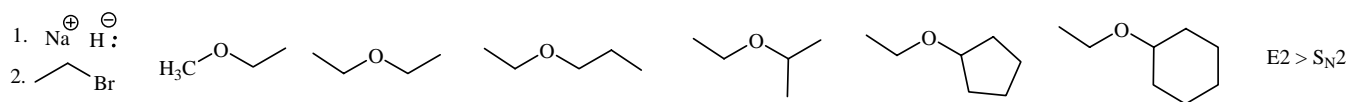
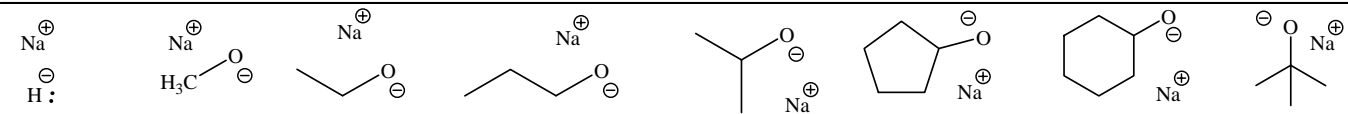
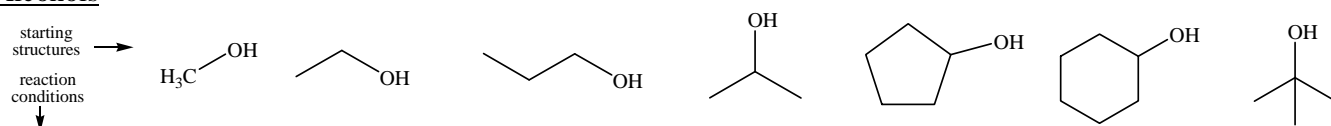
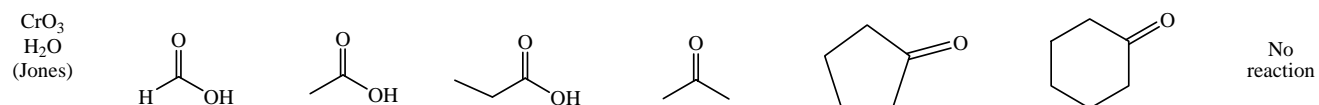
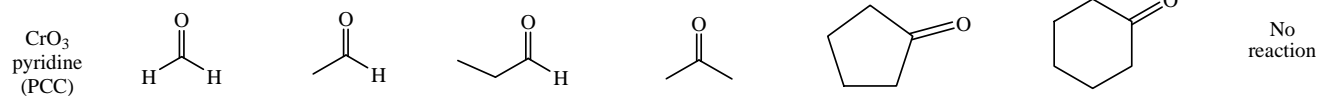
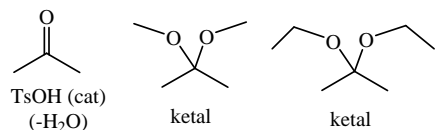
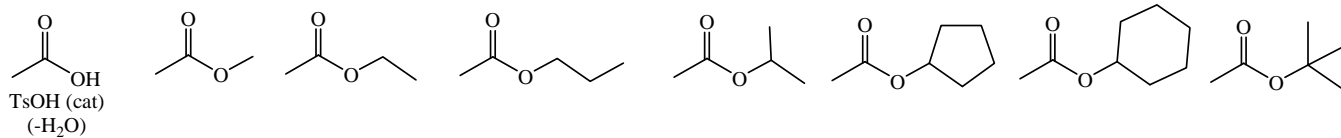
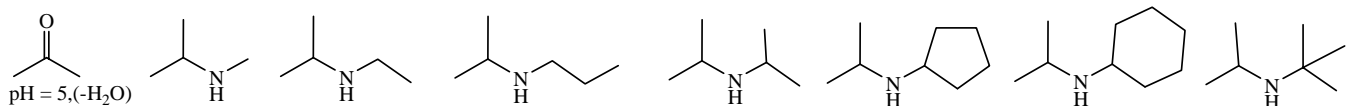
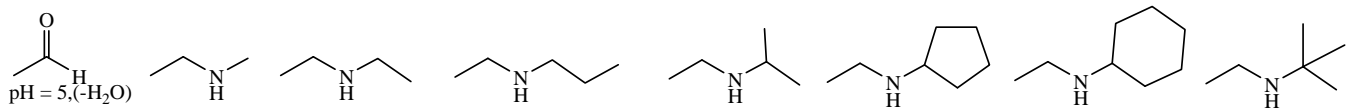
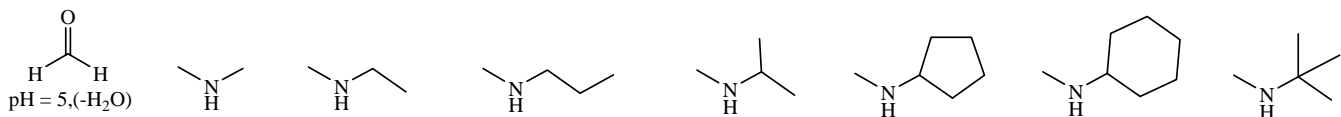
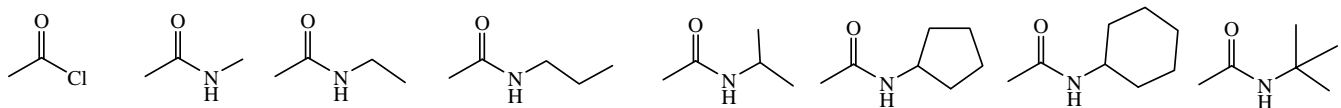
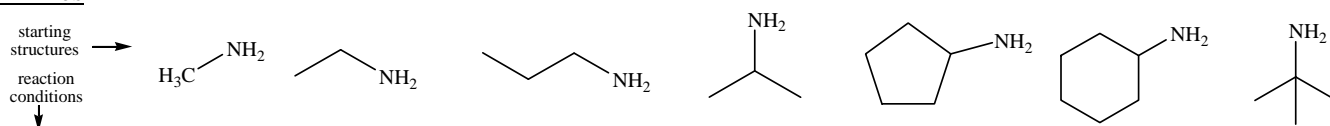
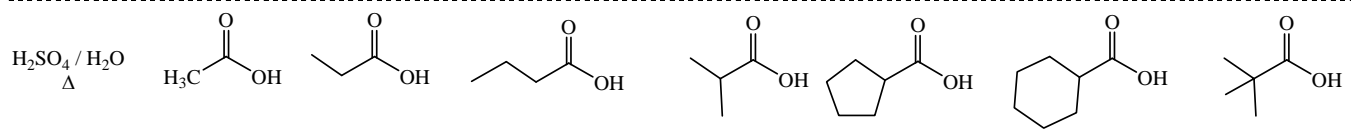
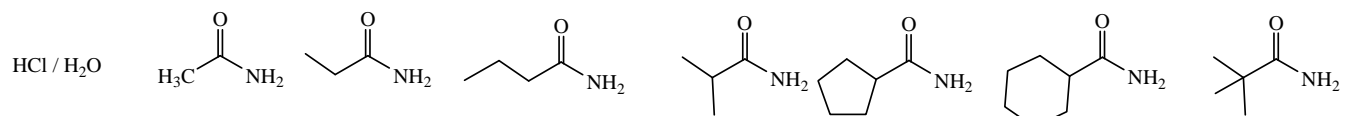
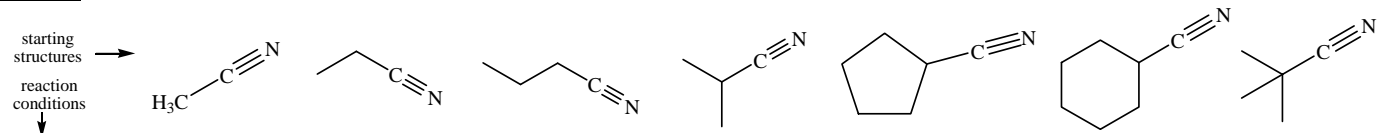
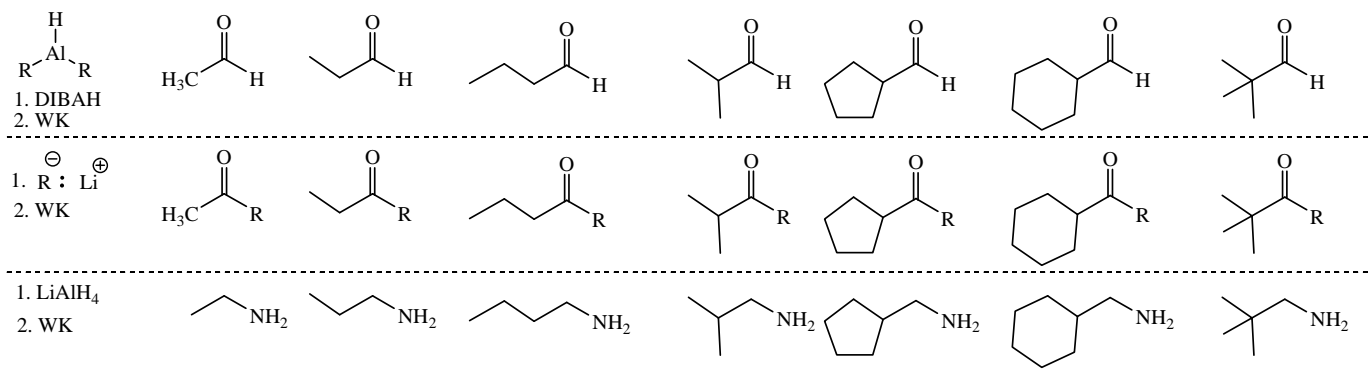


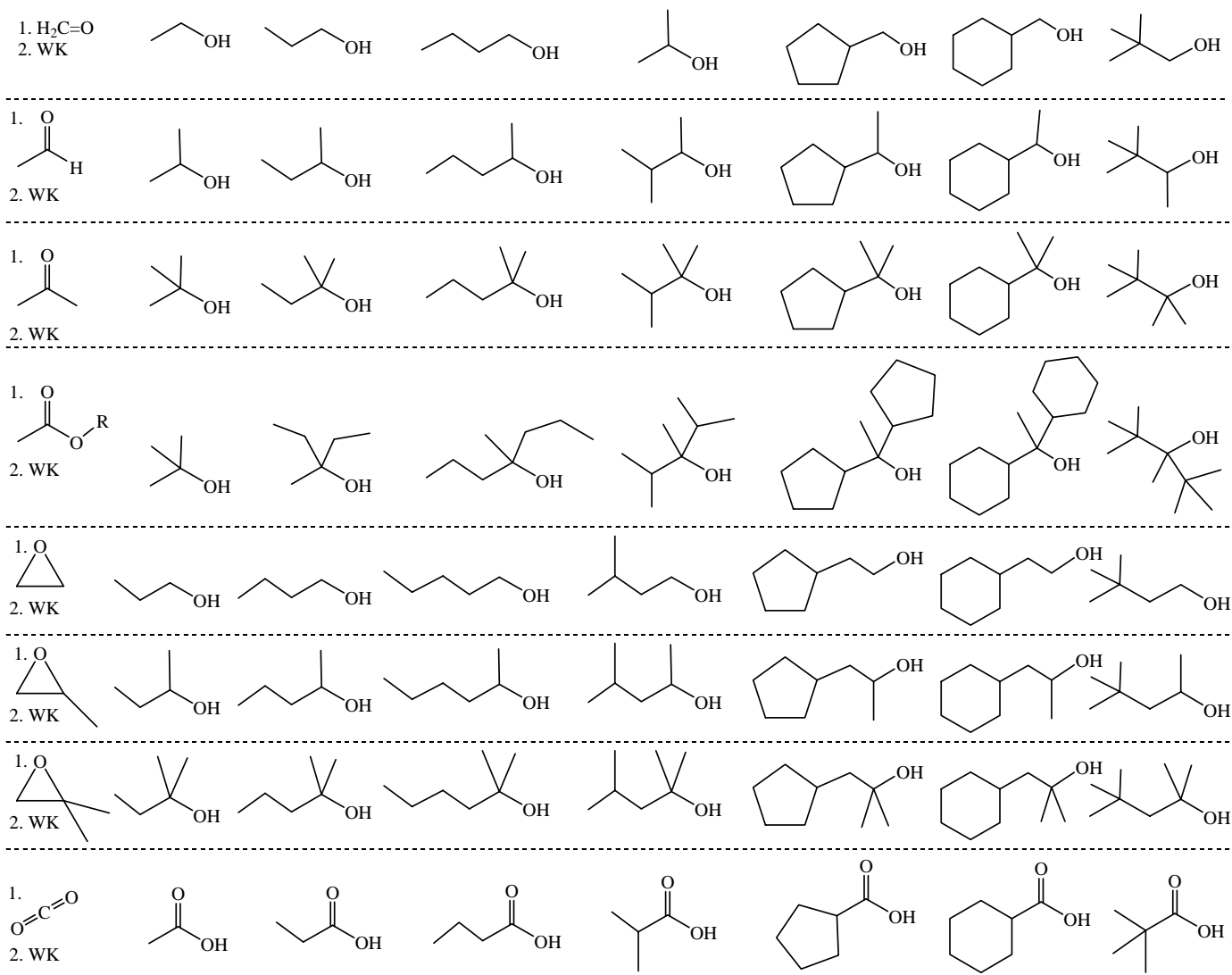
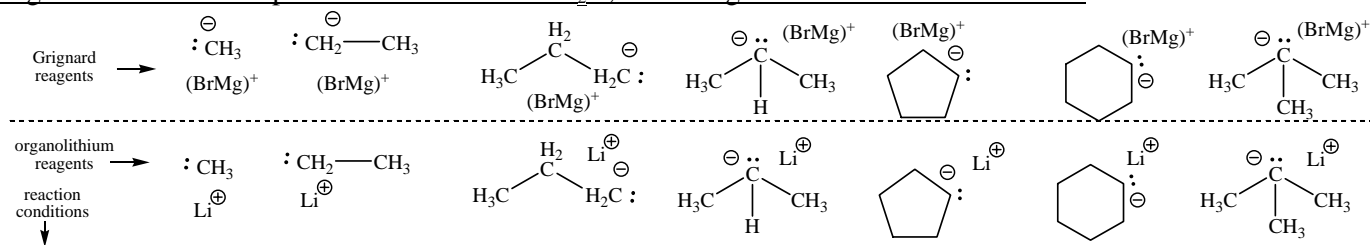
AlkanesBromoalkanes

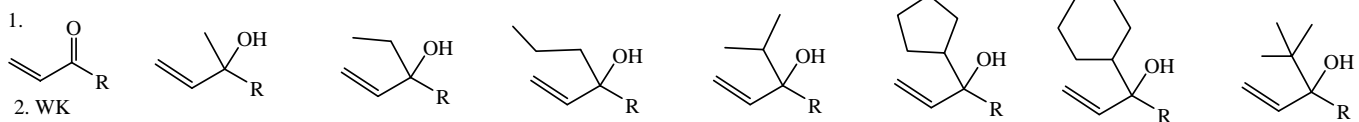
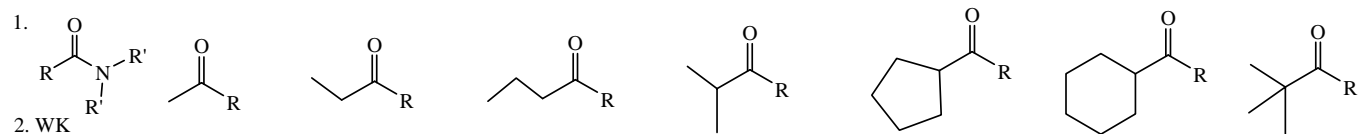
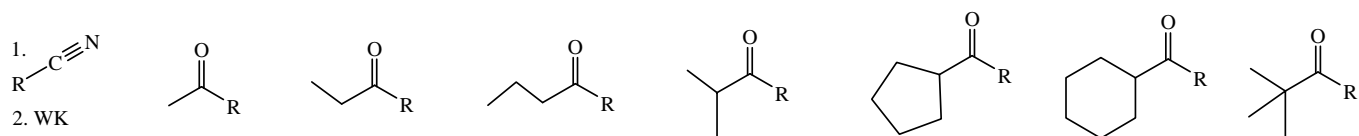
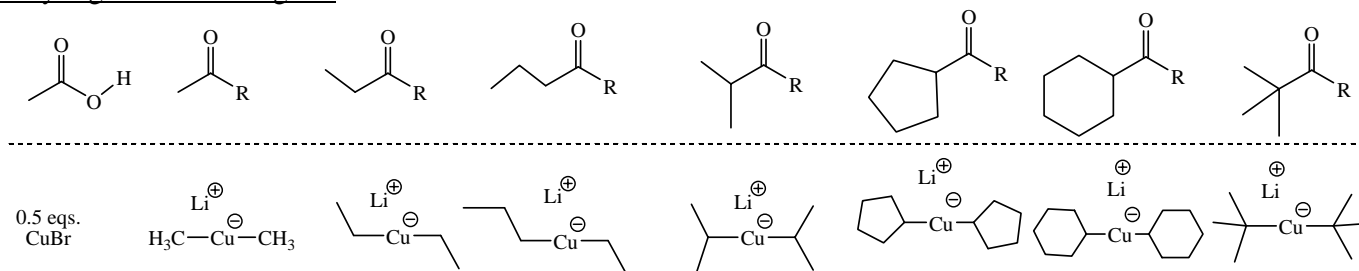
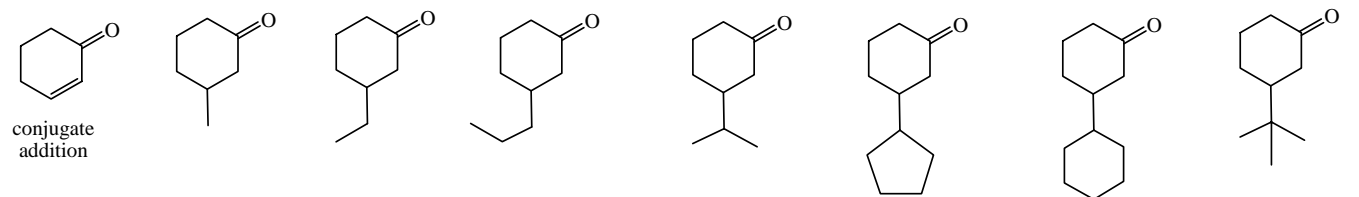
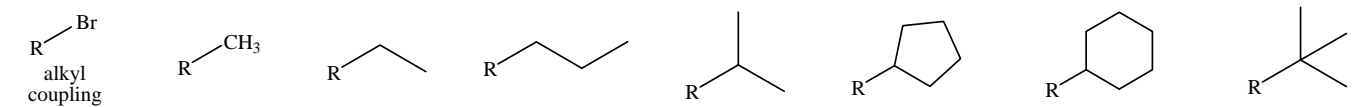
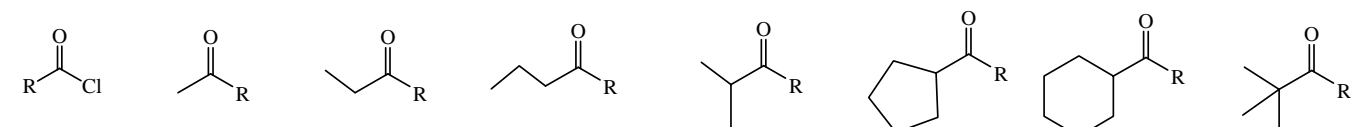
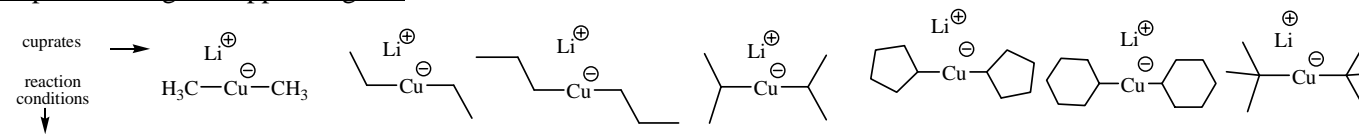
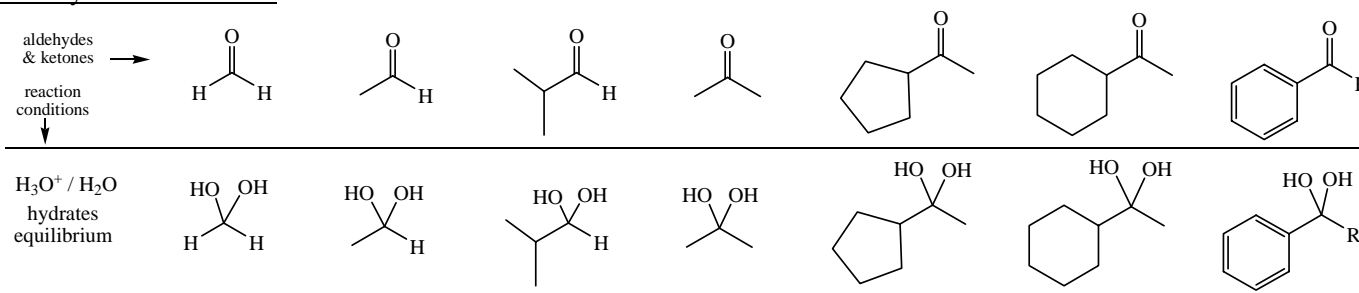
**Alcohols**

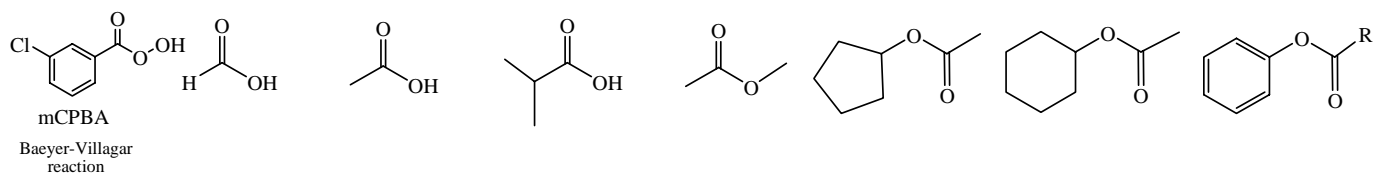
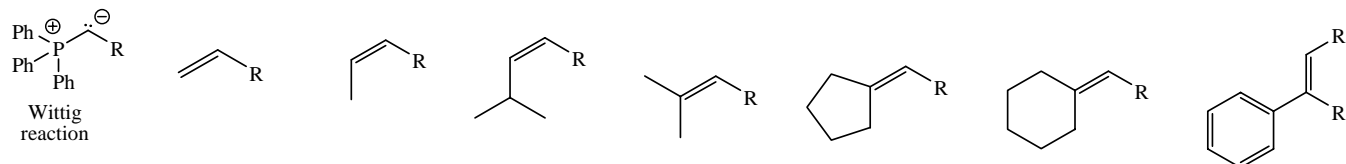
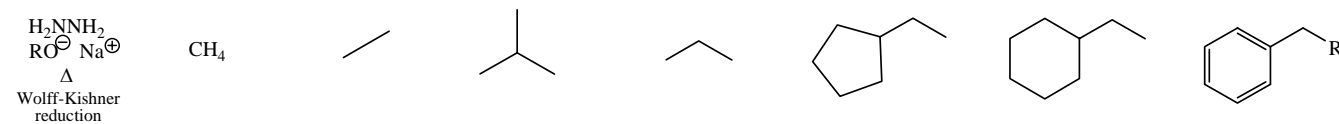
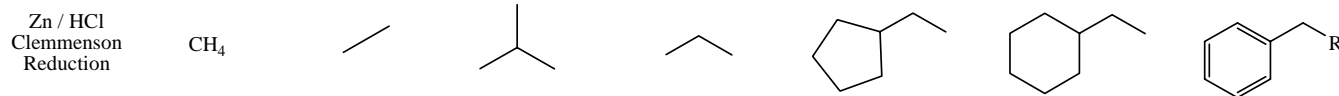
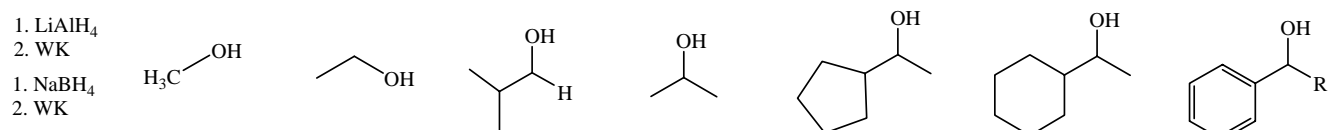
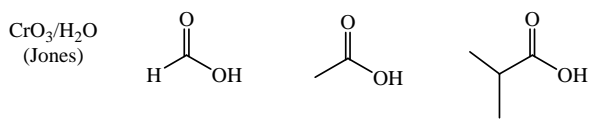
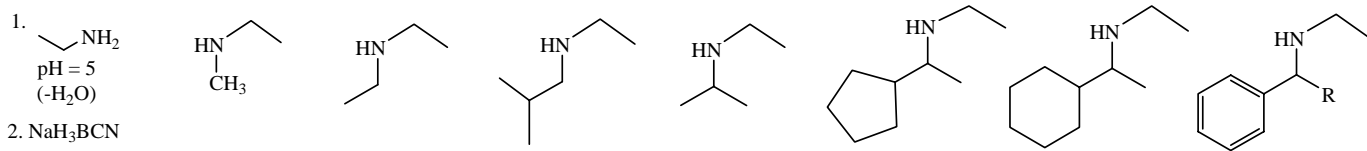
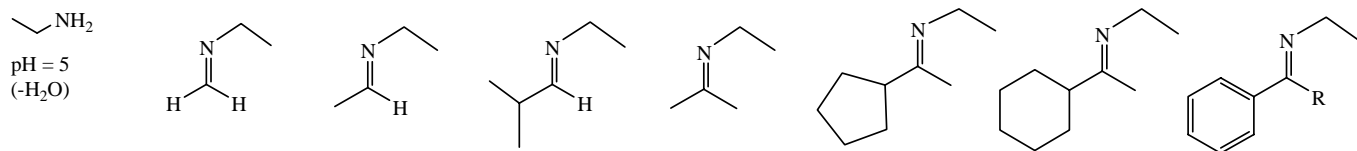
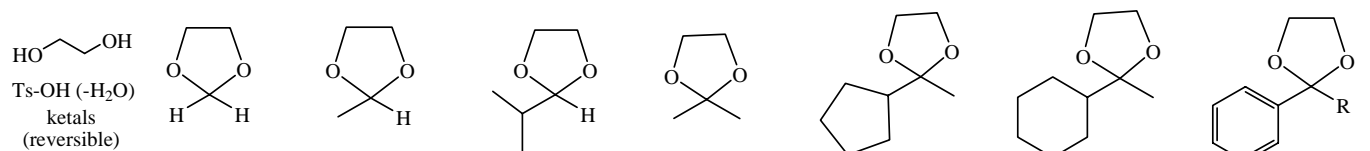
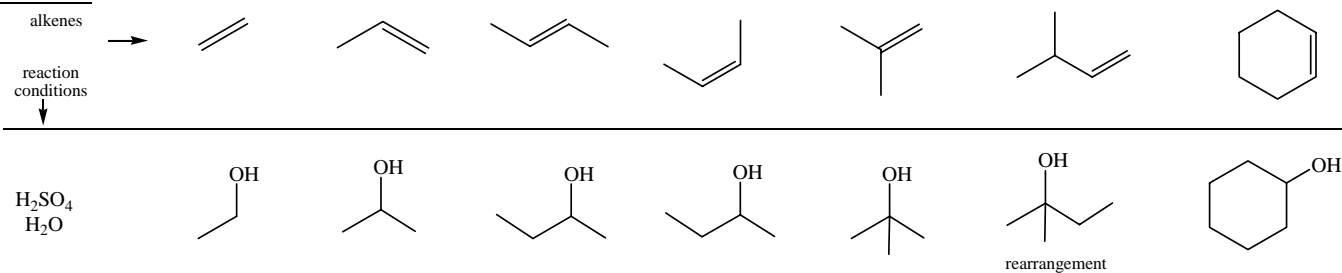
**Amines****Nitriles**

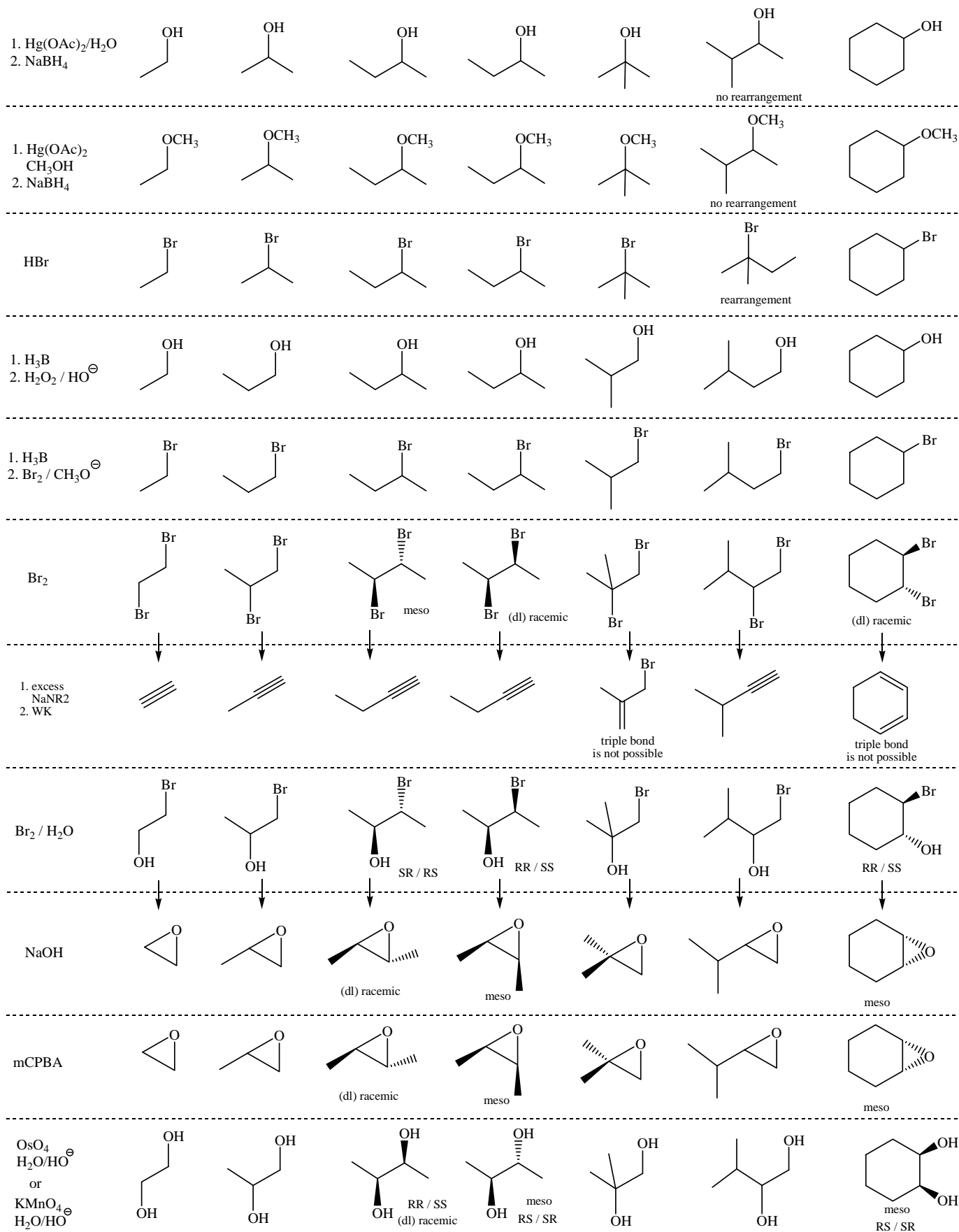


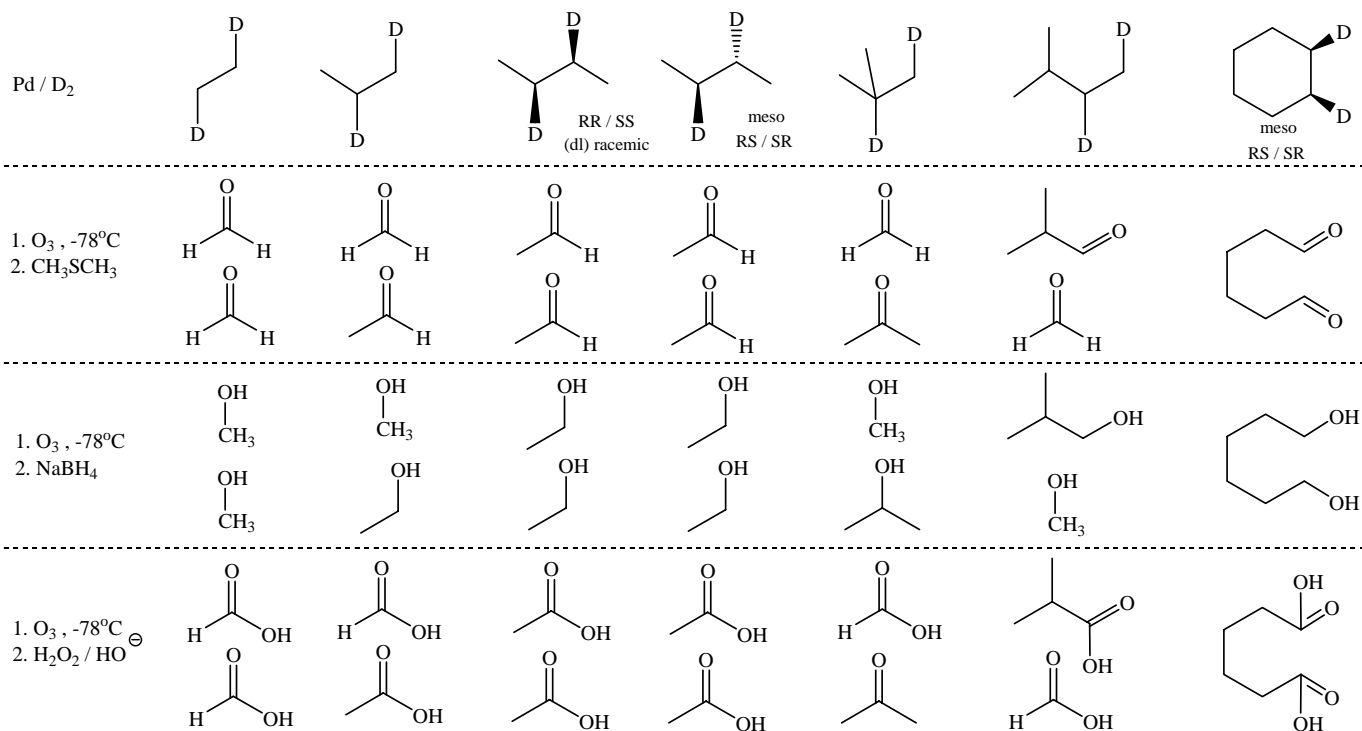
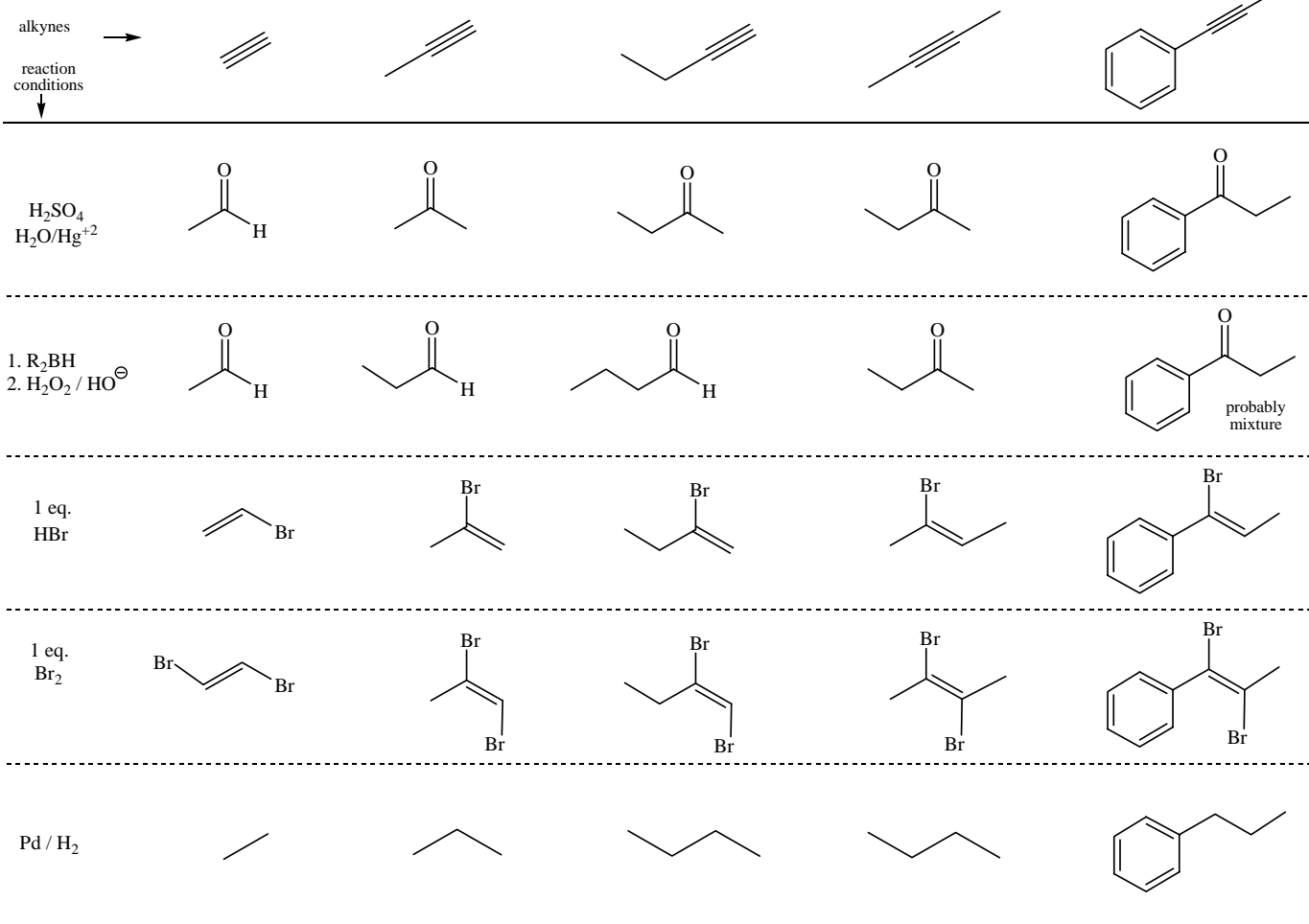
Organometallics – except for reactions with RCO₂H, these reagents react in a similar manner



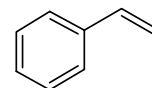
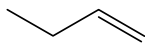
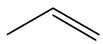
Only organolithium reagentsCuprates – Organocopper reagentsAldehydes and Ketones

**Alkenes**



Alkynes

Pd / D₂
quinoline
(Lindlar's cat.)

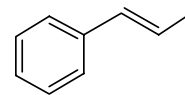
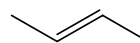


Na / NH₃
(Birch Reduction)

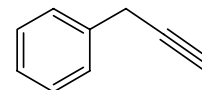
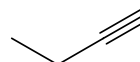
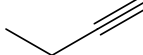
does not work
well on
terminal alkynes


does not work
well on
terminal alkynes

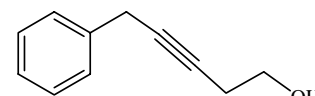
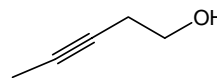
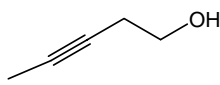
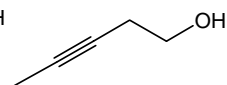
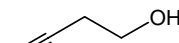
does not work
well on
terminal alkynes




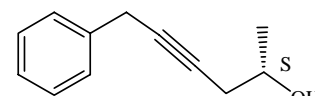
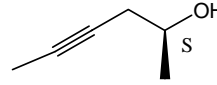
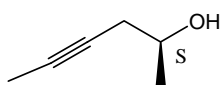
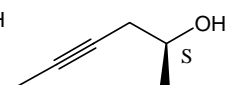
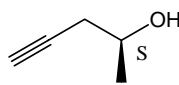
1. excess
NaNR₂
2. WK
(zipper rxn)




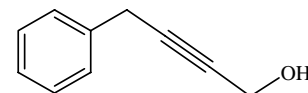
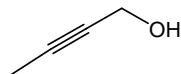
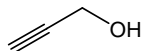
1. excess
NaNR₂
2. 
3. WK




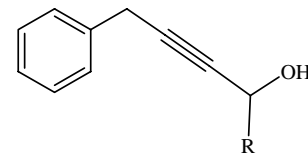
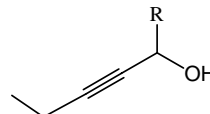
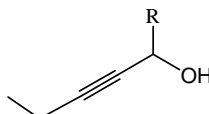
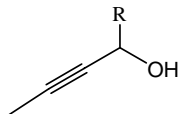
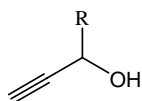
1. excess
NaNR₂
2. 
3. WK




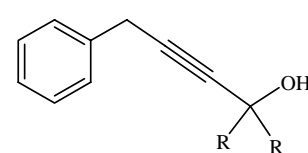
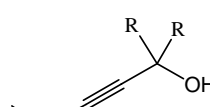
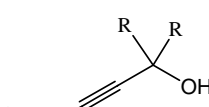
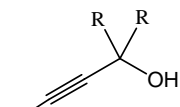
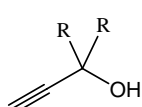
1. excess
NaNR₂
2. 
3. WK



1. excess
NaNR₂
2. 
3. WK



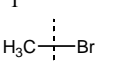
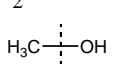
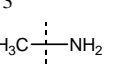
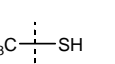
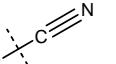


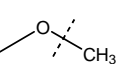
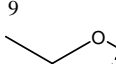
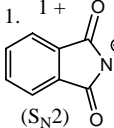
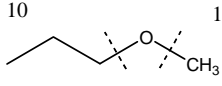
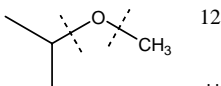
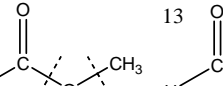
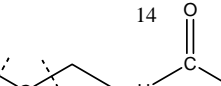
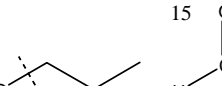
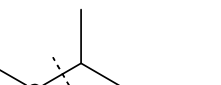
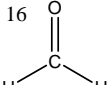
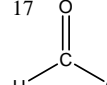
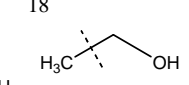
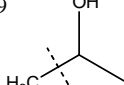
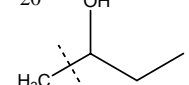
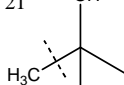
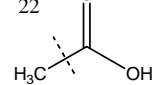
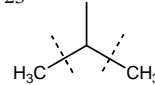
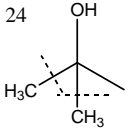
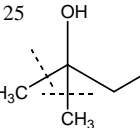
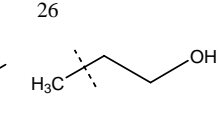
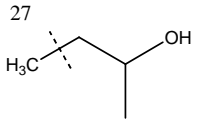
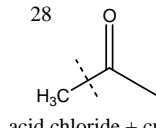
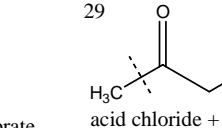
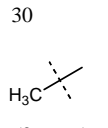
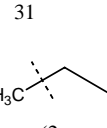
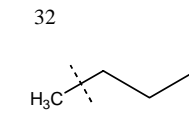
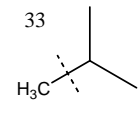
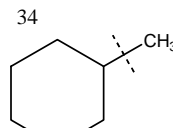
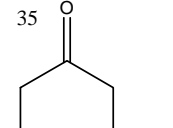
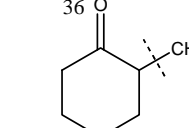
1. excess
NaNR₂
2. 
3. WK



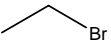
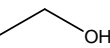
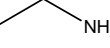
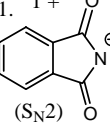
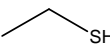
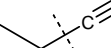
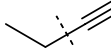
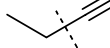
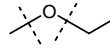
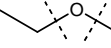
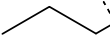
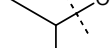
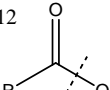
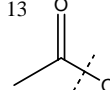
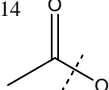
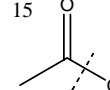
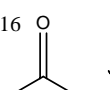
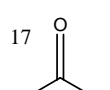
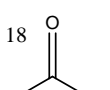
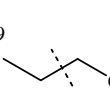
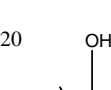
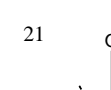
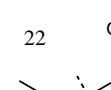
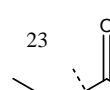
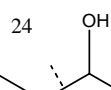
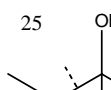
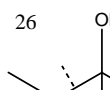
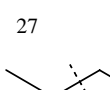
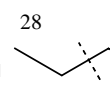
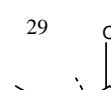
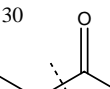
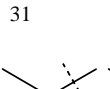
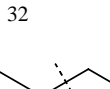
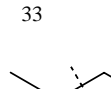
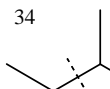
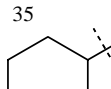
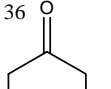
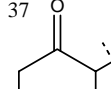

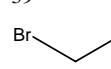

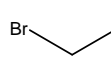

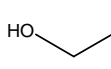
Propose synthetic reactions for the indicated target structures from the given starting materials. Show the starting material (methane, ethane and propane), a reaction arrow with the reagent and a product for each synthetic step of your synthesis. If a compound has been prepared earlier you do not need to remake it (just refer to the part where you made it). Common organic reagents may be used as needed. Additional "carbon" compounds available include bromobenzene, cyclohexane, carbon dioxide and sodium cyanide.

1. Given starting material = methane, (CH₄)

Target molecules (the part from methane has the "C" written out).

1 	2 	3 	4 	5 	6 	7 	8 	9 
methane + Br ₂ /hν 2 + HBr 2 + PBr ₃ 2 + SOBr ₂ 2 + a. TsCl/py b. NaBr	a. 1 + ester (S _N 2) b. ester + NaOH 31 + H ₃ O ⁺ , H ₂ O a. 31 + HgX ₂ /H ₂ O b. NaBH ₄ a. 13 + NaBH ₄ b. WK	1. 1 +  (S _N 2) 2. NaOH	1 + NaSH (S _N 2)	1 + NaCN (S _N 2)	a. 40 + NaNR ₂ b. bromomethane	a. propyne + NaNR ₂ b. bromomethane	(2 ways) RO [⊖] + RBr (S _N 2)	(2 ways)
10 	11 	12 	13 	14 	15 			
(2 ways) RO [⊖] + RBr (S _N 2)	(2 ways) RO + RBr (S _N 2) ROH + RBr (S _N 1)	(2 ways) RCO ₂ [⊖] + RBr (S _N 2) RCOCl + ROH (acyl substitution)	(2 ways) RCO ₂ [⊖] + RBr (S _N 2) RCOCl + ROH (acyl substitution)	(2 ways) RCO ₂ [⊖] + RBr (S _N 2) RCOCl + ROH (acyl substitution)	(2 ways) RCO ₂ [⊖] + RBr (S _N 2) RCOCl + ROH (acyl substitution)			
16 	17 	18 	19 	20 	21 	22 	23 	
2 + CrO ₃ /py (PCC)	2 + CrO ₃ /H ₂ O (Jones)	a. 1 + Mg (or Li) b. methanal c. WK	a. 1 + Mg (or Li) b. ethanal c. WK	a. 1 + Mg (or Li) b. propanal c. WK	a. 1 + Mg (or Li) b. propanone c. WK	a. 1 + Mg (or Li) b. CO ₂ c. WK	a. 1 + Mg (or Li) b. alkyl methanoate c. WK	
24 	25 	26 	27 	28 	29 			
a. 1 + Mg (or Li) b. alkyl ethanoate c. WK	a. 1 + Mg (or Li) b. alkyl propanoate c. WK	a. 1 + Mg (or Li) b. 2C epoxide c. WK	a. 1 + Mg (or Li) b. 3C epoxide c. WK	acid chloride + cuprate a. 1 + Mg (or Li) b. ethanenitrile ethanoic acid + 2 eqs methyl lithium	acid chloride + cuprate a. 1 + Mg (or Li) b. propanenitrile propanoic acid + 2 eqs methyl lithium			
30 	31 	32 	33 	34 	35 	36 		
(2 ways) cuprate + RBr	(2 ways) cuprate + RBr	(2 ways) cuprate + RBr	(2 ways) cuprate + RBr	(2 ways) cuprate + RBr	(2 ways) cuprate + enone (conjugate addition)	1. ketone + LDA 2. RBr (compound 1) a. enamine + 1 b. H ₂ O (hydrolysis)		

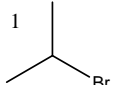
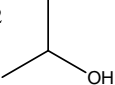
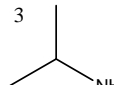
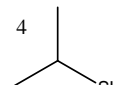
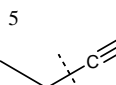
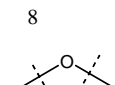
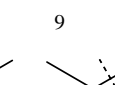
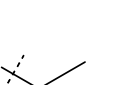
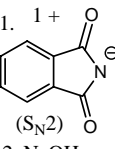
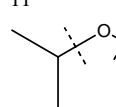
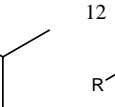
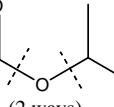
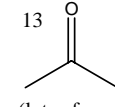
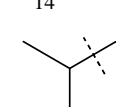
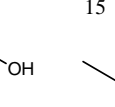
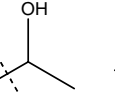
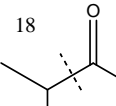
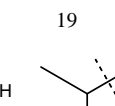
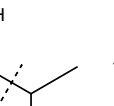
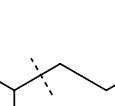
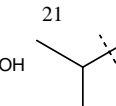
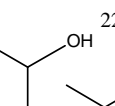
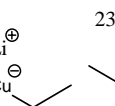
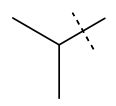
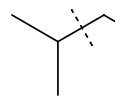
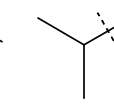
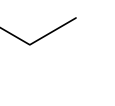
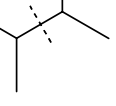
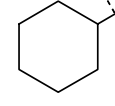
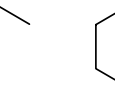
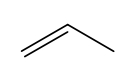
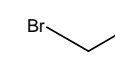
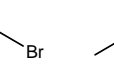
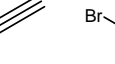
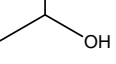
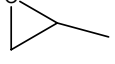
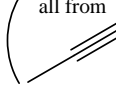
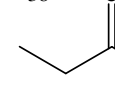
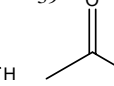
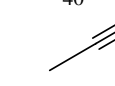
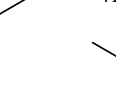
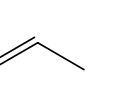
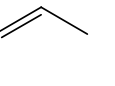
2. Given starting material = ethane, (CH₃CH₃)

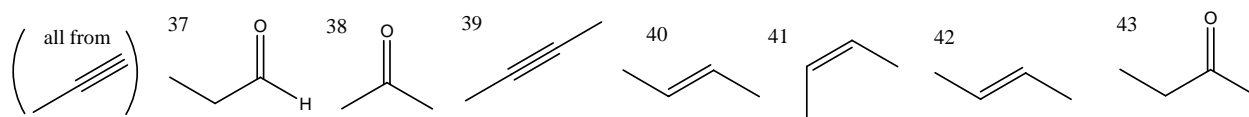
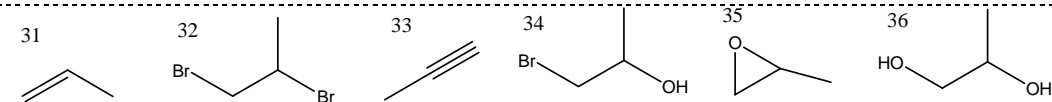
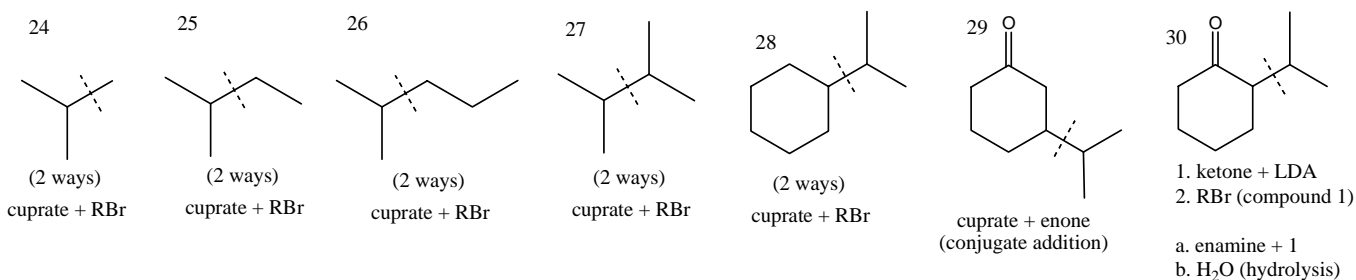
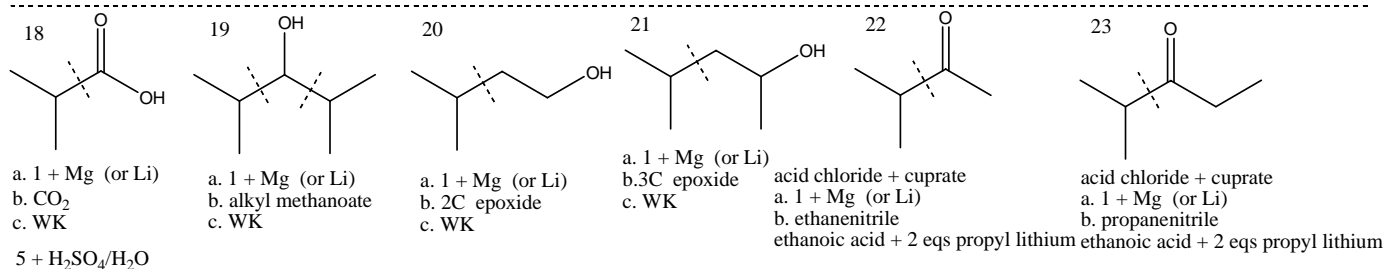
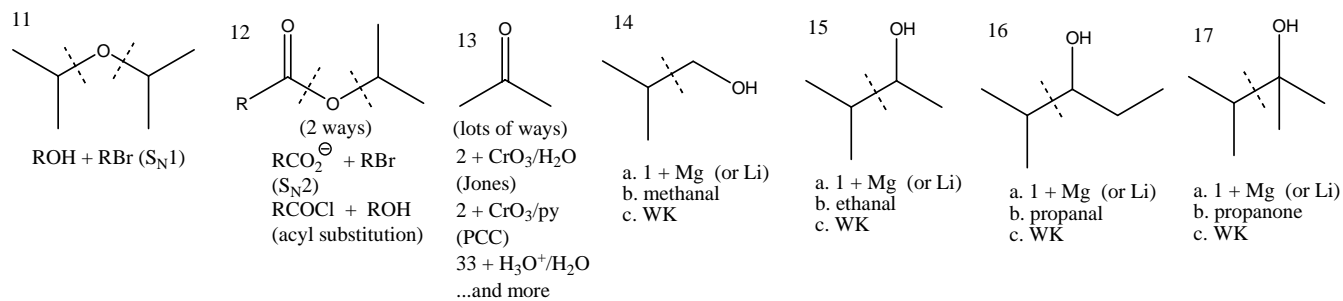
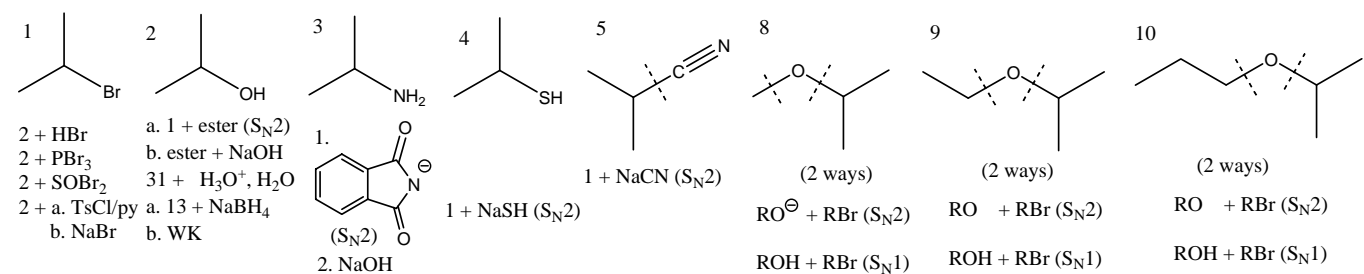
1  ethane + Br ₂ /hν 2 + HBr 2 + PBr ₃ 2 + SOBr ₂ 2 + a. TsCl/py b. NaBr	2  a. 1 + ester (S _N 2) b. ester + NaOH 31 + H ₃ O ⁺ , H ₂ O a. 31 + HgX ₂ /H ₂ O b. NaBH ₄ a. 13 + NaBH ₄ b. WK	3  1. 1 +  (S _N 2) 2. NaOH	4  1 + NaSH (S _N 2)	5  1 + NaCN (S _N 2)	6  a. 40 + NaNR ₂ b. bromoethane	7  a. propyne + NaNR ₂ b. bromoethane	8  (2 ways) RO [⊖] + RBr (S _N 2)	9  (2 ways) RO [⊖] + RBr (S _N 2)
10  (2 ways) RO [⊖] + RBr (S _N 2)	11  (2 ways) RO + RBr (S _N 2) ROH + RBr (S _N 1)	12  (2 ways) RCO ₂ [⊖] + RBr (S _N 2) RCOCl + ROH (acyl substitution)	13  (2 ways) RCO ₂ [⊖] + RBr (S _N 2) RCOCl + ROH (acyl substitution)	14  (2 ways) RCO ₂ [⊖] + RBr (S _N 2) RCOCl + ROH (acyl substitution)	15  (2 ways) RCO ₂ [⊖] + RBr (S _N 2) RCOCl + ROH (acyl substitution)			
16  (2 ways) RCO ₂ [⊖] + RBr (S _N 2) RCOCl + ROH (acyl substitution)	17  a. 40 + R ₂ BH b. H ₂ O ₂ / HO [⊖] 40 + H ₃ O ⁺ /H ₂ O 2 + CrO ₃ /py (PCC)	18  2 + CrO ₃ /H ₂ O (Jones) a. CH ₃ Br/Mg b. CO ₂ c. WK	19  a. 1 + Mg (or Li) b. methanal c. WK	20  a. 1 + Mg (or Li) b. ethanal c. WK	21  a. 1 + Mg (or Li) b. propanal c. WK	22  a. 1 + Mg (or Li) b. propanone c. WK	23  a. 1 + Mg (or Li) b. CO ₂ c. WK 5 + H ₂ SO ₄ /H ₂ O	
24  a. 1 + Mg (or Li) b. alkyl methanoate c. WK	25  a. 1 + Mg (or Li) b. alkyl ethanoate c. WK	26  a. 1 + Mg (or Li) b. alkyl propanoate c. WK	27  a. 1 + Mg (or Li) b. 2C epoxide c. WK	28  a. 1 + Mg (or Li) b. 3C epoxide c. WK	29  acid chloride + cuprate a. 1 + Mg (or Li) b. ethanenitrile ethanoic acid + 2 eqs ethyl lithium			
30  acid chloride + cuprate a. 1 + Mg (or Li) b. propanenitrile ethanoic acid + 2 eqs propyl lithium	31  (2 ways) cuprate + RBr	32  (2 ways) cuprate + RBr	33  (2 ways) cuprate + RBr	34  (2 ways) cuprate + RBr	35  (2 ways) cuprate + RBr	36  cuprate + enone (conjugate addition)	37  1. ketone + LDA 2. RBr (compound 1) a. enamine + 1 b. H ₂ O (hydrolysis)	
38  1 + K ⁺ t-butoxide 2 + H ₂ SO ₄ /Δ	39  Br ₂	40  a. 39 + NaNR ₂ b. WK	41  Br ₂ / H ₂ O	42  38 + mCPBA 41 + NaOH	43  38 + OsO ₄ (or KMnO ₄)			

Wittig =
methanal + ylid

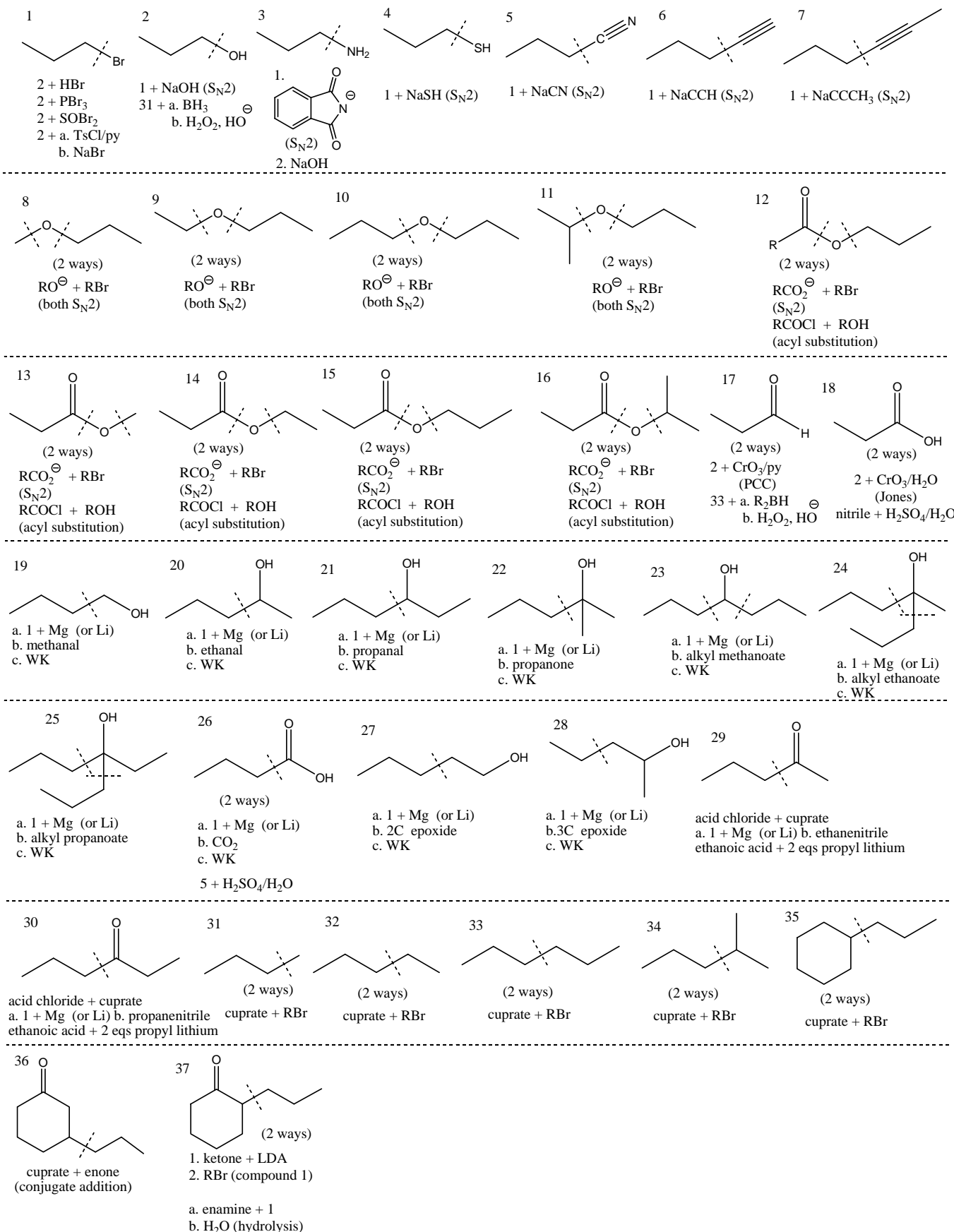
3. Given starting material = propane, (CH₃CH₂CH₃)

a.

1 	2 	3 	4 	5 	8 	9 	10 
propane + Br ₂ /hv 2 + HBr 2 + PBr ₃ 2 + SOBr ₂ 2 + a. TsCl/py b. NaBr	a. 1 + ester (S _N 2) b. ester + NaOH 31 + H ₃ O ⁺ , H ₂ O a. 31 + HgX ₂ /H ₂ O b. NaBH ₄ a. 13 + NaBH ₄ b. WK	1.  (S _N 2) 2. NaOH	1 + NaSH (S _N 2)	1 + NaCN (S _N 2)	(2 ways) RO [⊖] + RBr (S _N 2) ROH + RBr (S _N 1)	(2 ways) RO + RBr (S _N 2) ROH + RBr (S _N 1)	(2 ways) RO + RBr (S _N 2) ROH + RBr (S _N 1)
11 	12 	13 	14 	15 	16 	17 	
ROH + RBr (S _N 1)	(2 ways) RCO ₂ [⊖] + RBr (S _N 2) RCOCl + ROH (acyl substitution)	(lots of ways) 2 + CrO ₃ /H ₂ O (Jones) 2 + CrO ₃ /py (PCC) 33 + H ₃ O ⁺ /H ₂ O ...and more	a. 1 + Mg (or Li) b. methanal c. WK	a. 1 + Mg (or Li) b. ethanal c. WK	a. 1 + Mg (or Li) b. propanal c. WK	a. 1 + Mg (or Li) b. propanone c. WK	
18 	19 	20 	21 	22 	23 	24 	
a. 1 + Mg (or Li) b. CO ₂ c. WK 5 + H ₂ SO ₄ /H ₂ O	a. 1 + Mg (or Li) b. alkyl methanoate c. WK	a. 1 + Mg (or Li) b. 2C epoxide c. WK	a. 1 + Mg (or Li) b. 3C epoxide c. WK	cuprate 2RLi + CuBr	acid chloride + cuprate a. 1 + Mg (or Li) b. ethanenitrile ethanoic acid + 2 eqs propyl lithium	acid chloride + cuprate a. 1 + Mg (or Li) b. propanenitrile ethanoic acid + 2 eqs propyl lithium	
25 	26 	27 	28 	29 	30 	31 	
(2 ways) cuprate + RBr	(2 ways) cuprate + RBr	(2 ways) cuprate + RBr	(2 ways) cuprate + RBr	(2 ways) cuprate + RBr	(2 ways) cuprate + enone (conjugate addition)	1. ketone + LDA 2. RBr (compound 1) a. enamine + 1 b. H ₂ O (hydrolysis)	
32 	33 	34 	35 	36 	37 		
1 + K ⁺ t-butoxide	31 + Br ₂	a. 32 + NaNR ₂ b. WK	31 + Br ₂ /H ₂ O	31 + mCPBA 34 + NaOH	31 + H ₂ O ₂ / HO [⊖]		
(all from )	38 	39 	40 	41 	42 	43 	
	1. R ₂ BH b. H ₂ O ₂ / HO [⊖]	(lots of ways) 2 + CrO ₃ /H ₂ O (Jones) 2 + CrO ₃ /py (PCC) 33 + H ₃ O ⁺ /H ₂ O ...and more	a. NaNR ₂ b. CH ₃ -Br	39 + Na / NH ₃	39 + Pd / H ₂ quinoline	39 + Pd / H ₂	



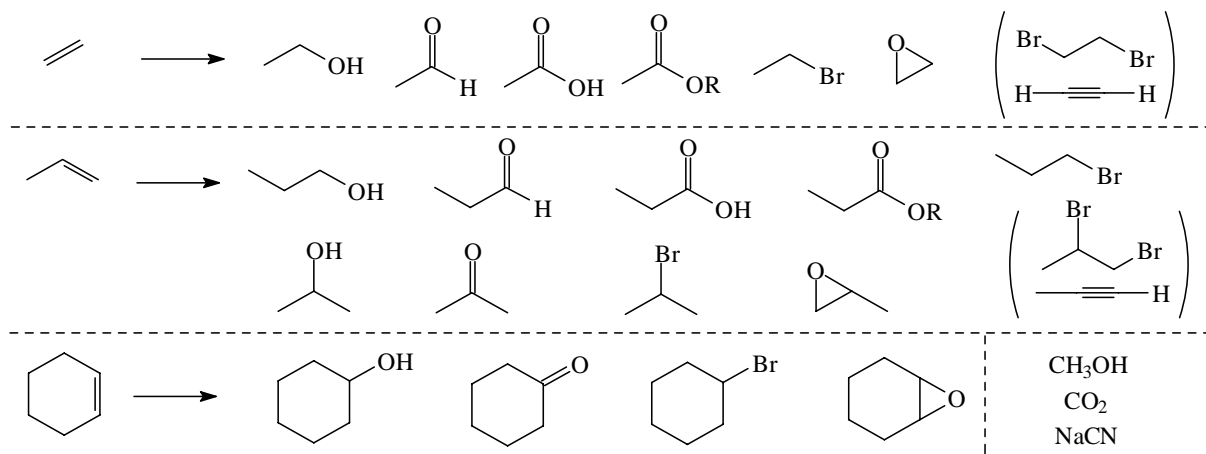
b.



Propose a synthesis for the following compounds using only *CH_3OH , Na^*CN , and *CO_2 as your source of radioactive ^{14}C isotope. Bromobenzene, methanol, ethene, propene and cyclohexene are also available. Work backwards from the target. The last step of the synthesis should be your first step. Show the reagents and reactant for each backwards step until you reach one of the ^{14}C compounds above and the other allowed starting structures. If a specific functional group or type of reaction is listed, you must use that group or reaction in your synthesis. For many of the target structures, there is more than one possible approach and for some there may be several possible approaches. Any approach is acceptable for this problem as long as the steps are reasonable and any necessary conditions are met. Do not show mechanisms.

Allowed ^{14}C precursors *CH_3OH *CO_2 Na^*CN Use any typical reagents from our course.

Other allowed starting structures and some possible structures that might be derived from them in a small number of steps.



Targets

- use an acid chloride
- use a nitrile
- use an ester
- use a carboxylic acid and a lithium reagent
- use a cuprate coupling reaction
- use any approach
- use the Wittig reaction
- use Gabriel amine synthesis and approach #1 use $NaCN$
 approach #2 use CO_2
 Can you make this into a secondary amine?
- use the zipper reaction
- use an alkyne
- use any approach
- use an enamine
- use an imine