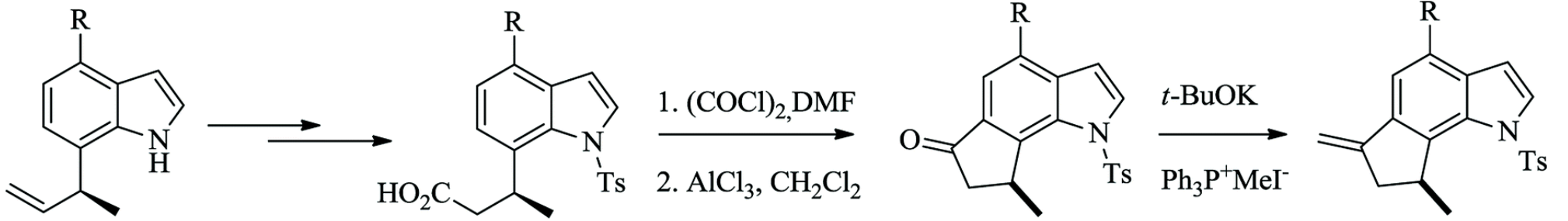
Friedel-Crafts Acylation & Column Chromatography

CHEM 241

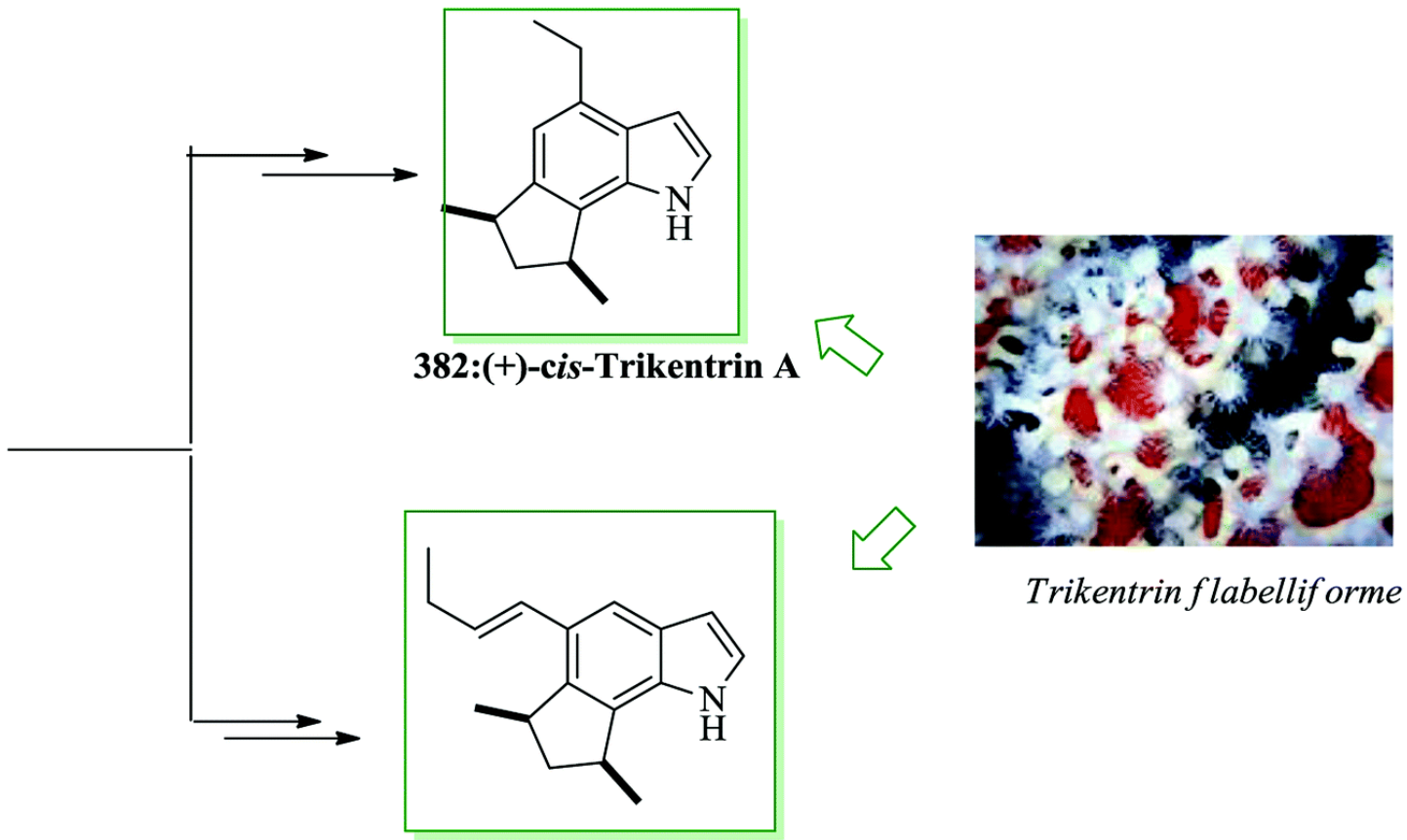


384a R=Et 53%
384b R=H 83%

385a R=Et 85%
385b R=H 88%

386a R=Et 74%
386b R=H 68%

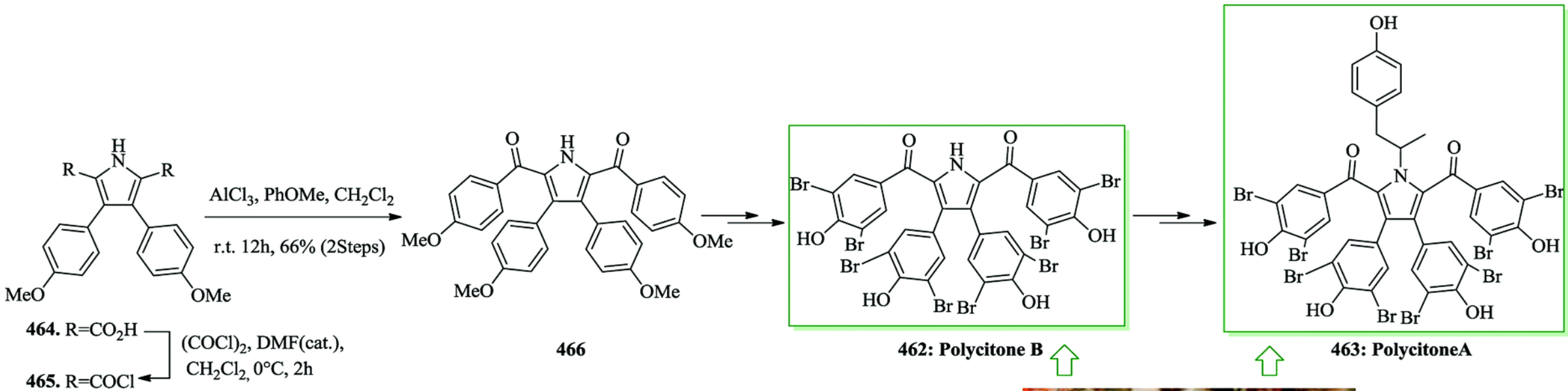
387a R=Et 94%
387b R=H 95%

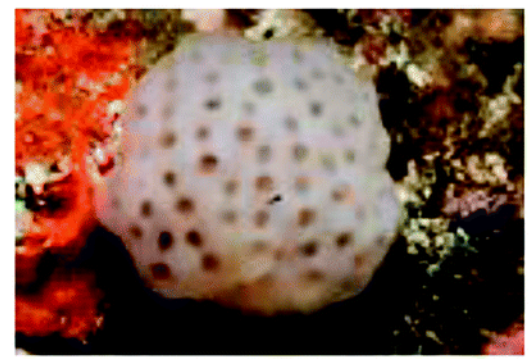


382:(+)-c*is*-Trikentrin A

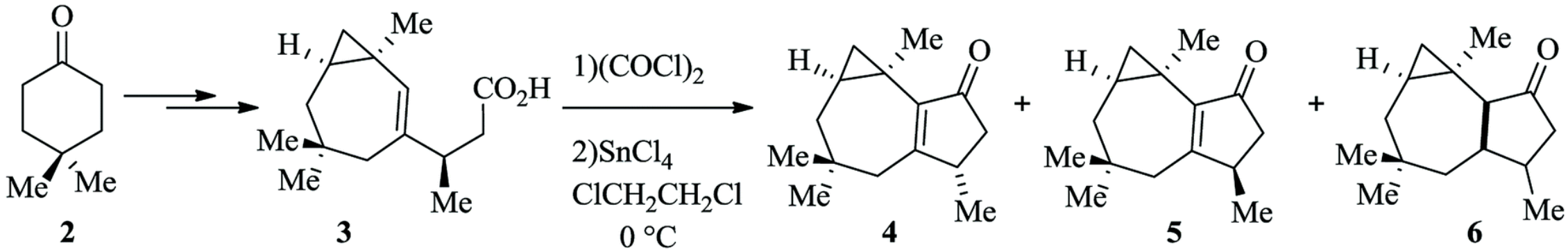
Trikentrin f labellif orme

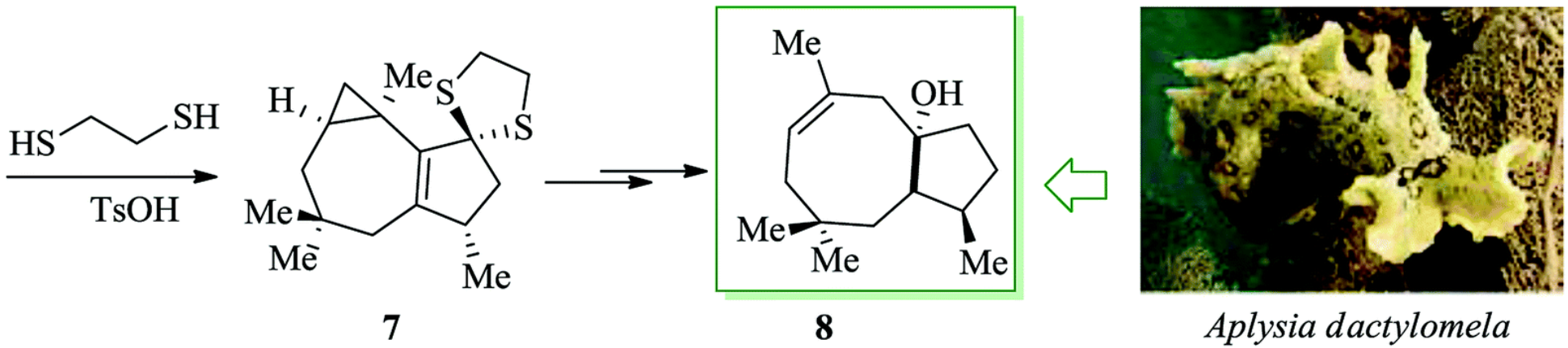
383:(+)-c*is*-Trikentrin B


AlCl3, PhOMe, CH2Cl2
r.t. 12h, 66% (2Steps)
464. R=CO2H
465. R=COCl
(COCl)2, DMF(cat.),
CH2Cl2, 0°C, 2h
466
462: Polycitone B
463: PolycitoneA

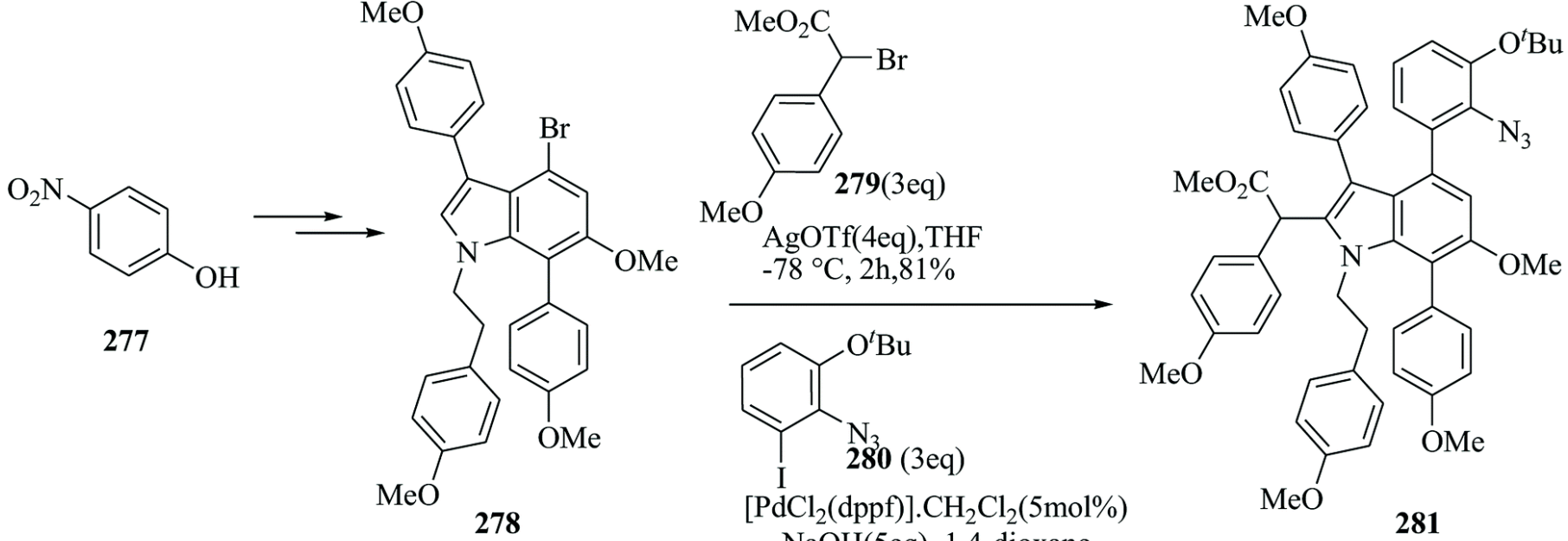


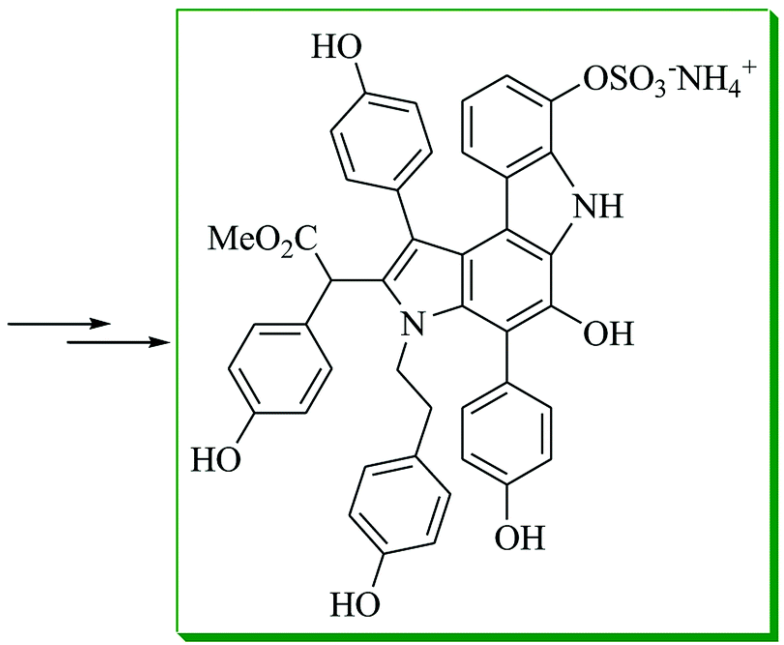
Polycitor



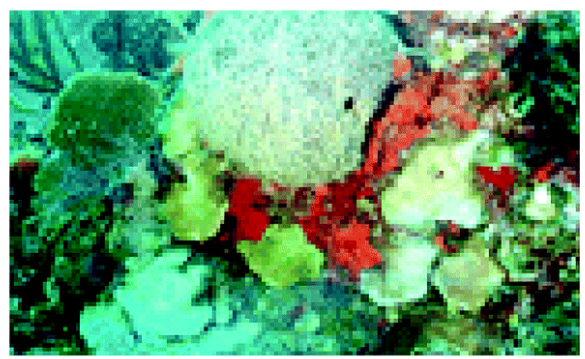


Aplysia dactylomela



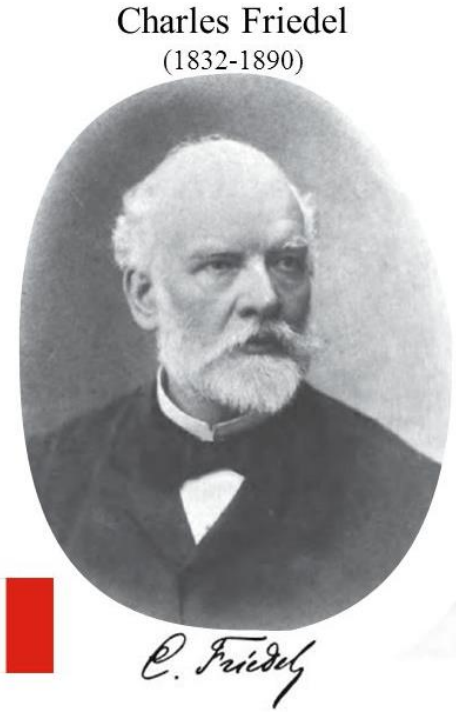


275: Dictyodedrin

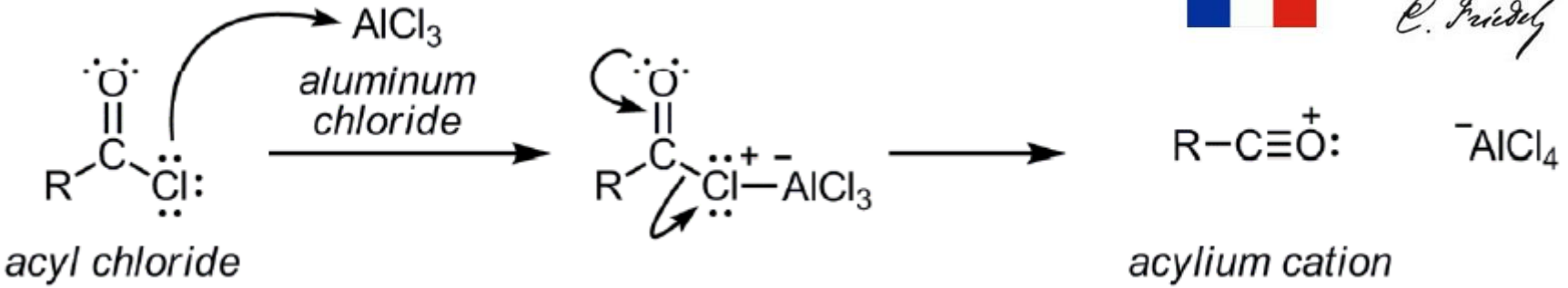


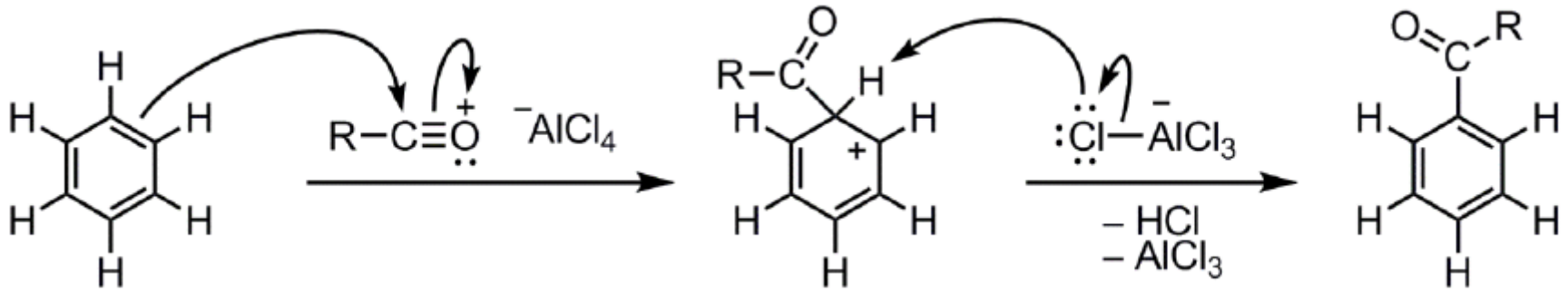
Dictyodedrilla

Theory

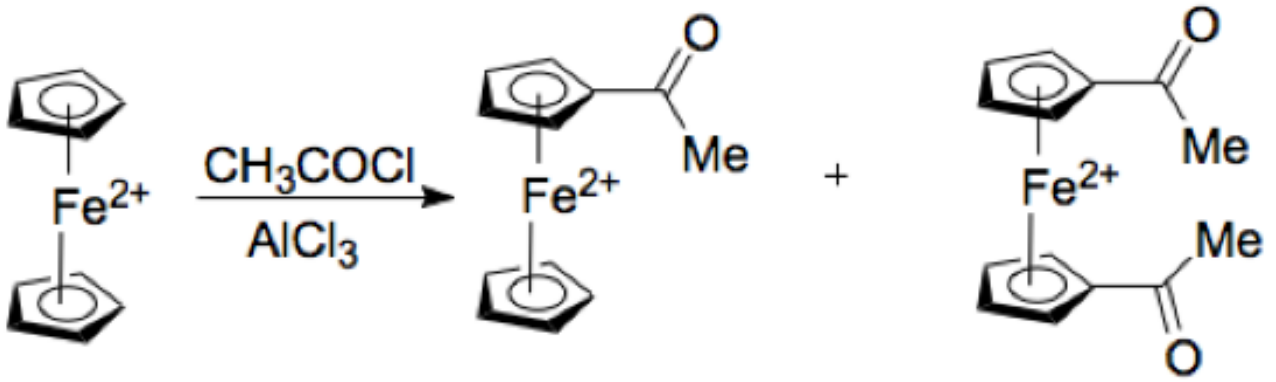

Charles Friedel
(1832-1890)


James Mason Crafts
(1839-1917)

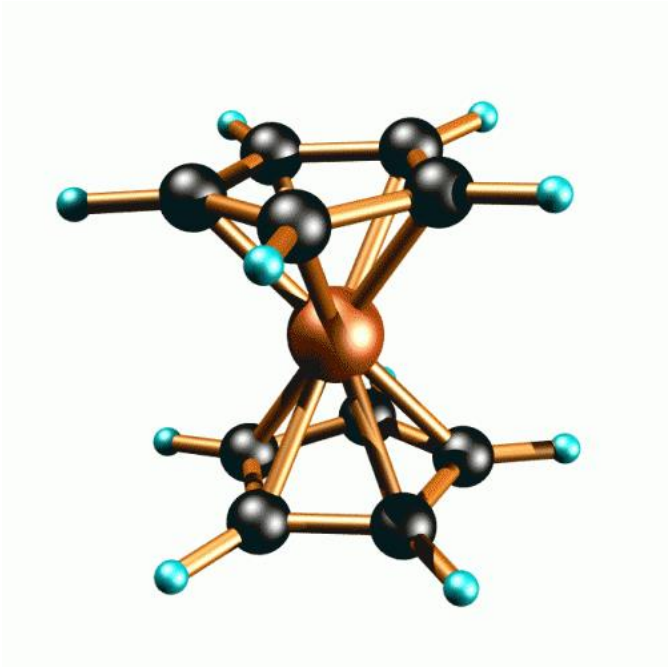

AlCl3
aluminum chloride
acyl chloride
R–C≡O:
−AlCl4
acylium cation

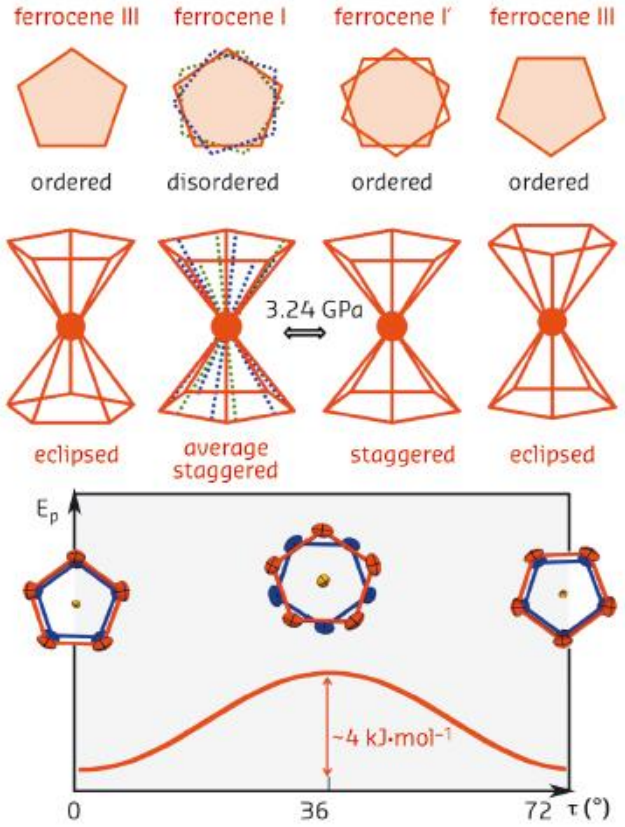

R–C≡O:
−AlCl4
:Cl–AlCl3
– HCl
– AlCl3

Reaction

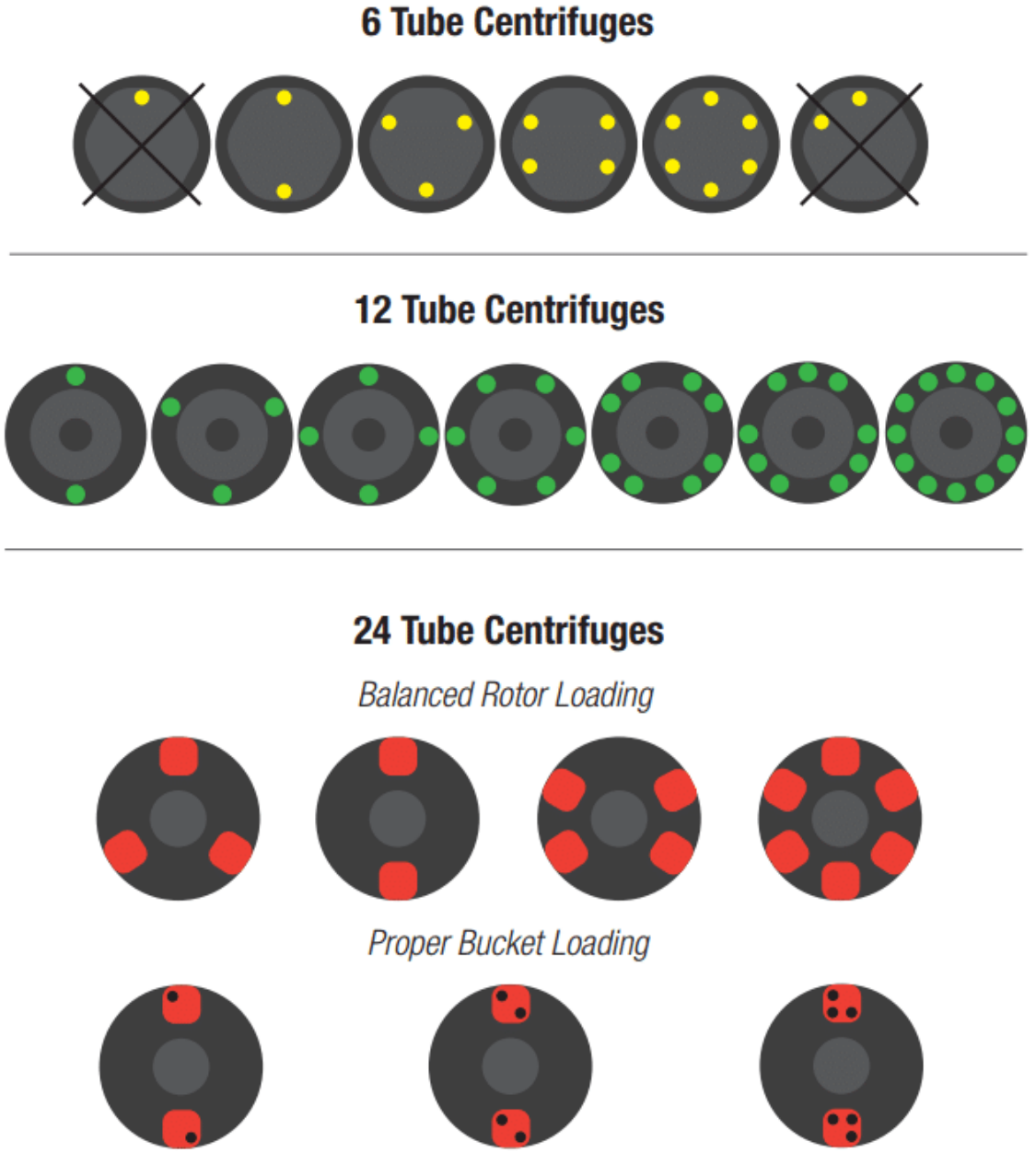


Ferrocene





Glassware/ instruments

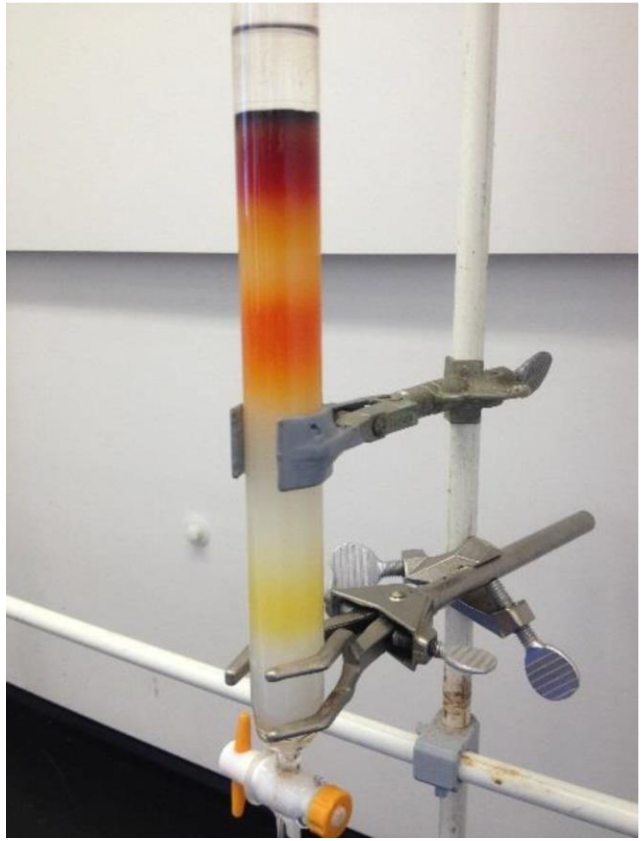


Chemicals

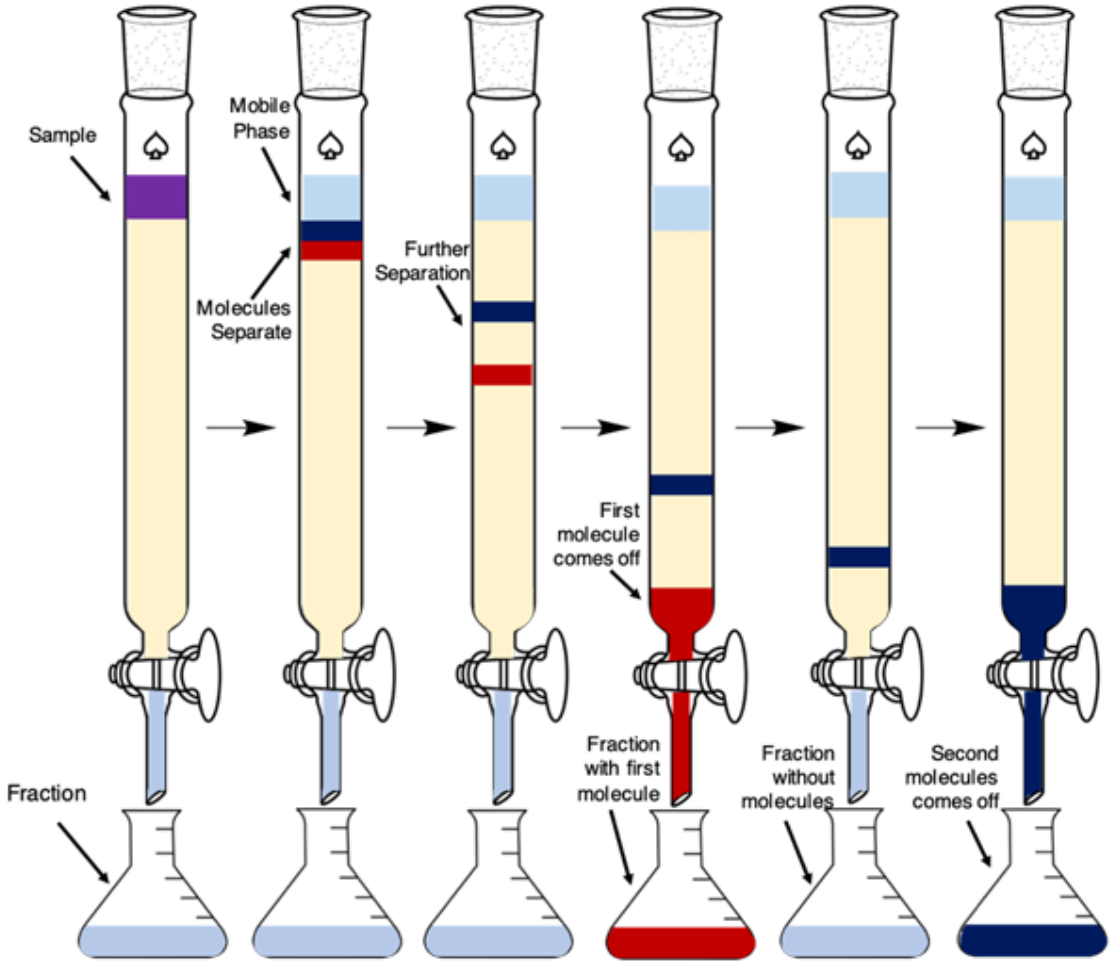
Chemicals	Appearance	MW (g/mol)	Equivalent	Amount	Note
ferrocene	Orange pwoder	186		0.1	
$AlCl_3$	yellow powder	133		0.15 g	
methylene chloride	Clear solution			solvent	Density?
Acetyl chloride	Clear solution			varied	Density?
NaOH				Neutralizer	
sodium sulfate				Drying reagent	
acetylferrocene		228			
diacetylferrocene		270			

Column Chromatography

- Separate a mixture of compounds based on polarity
- Compounds will pass through and stick to polar silica
- Mobile phases with increasing polarity will pull down every compound faster
- Each compound with a difference in polarity will reach the bottom of the column at a different time

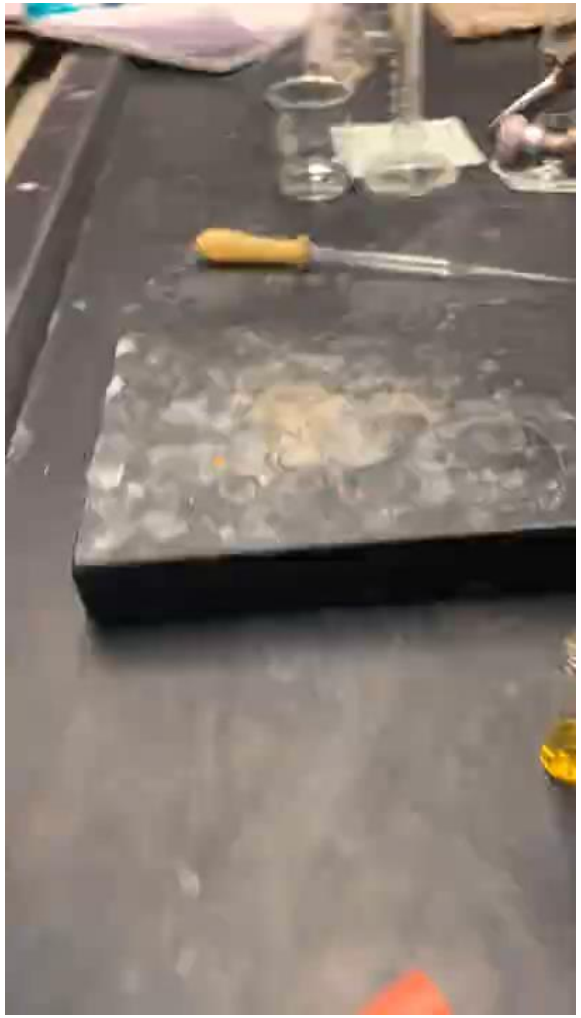


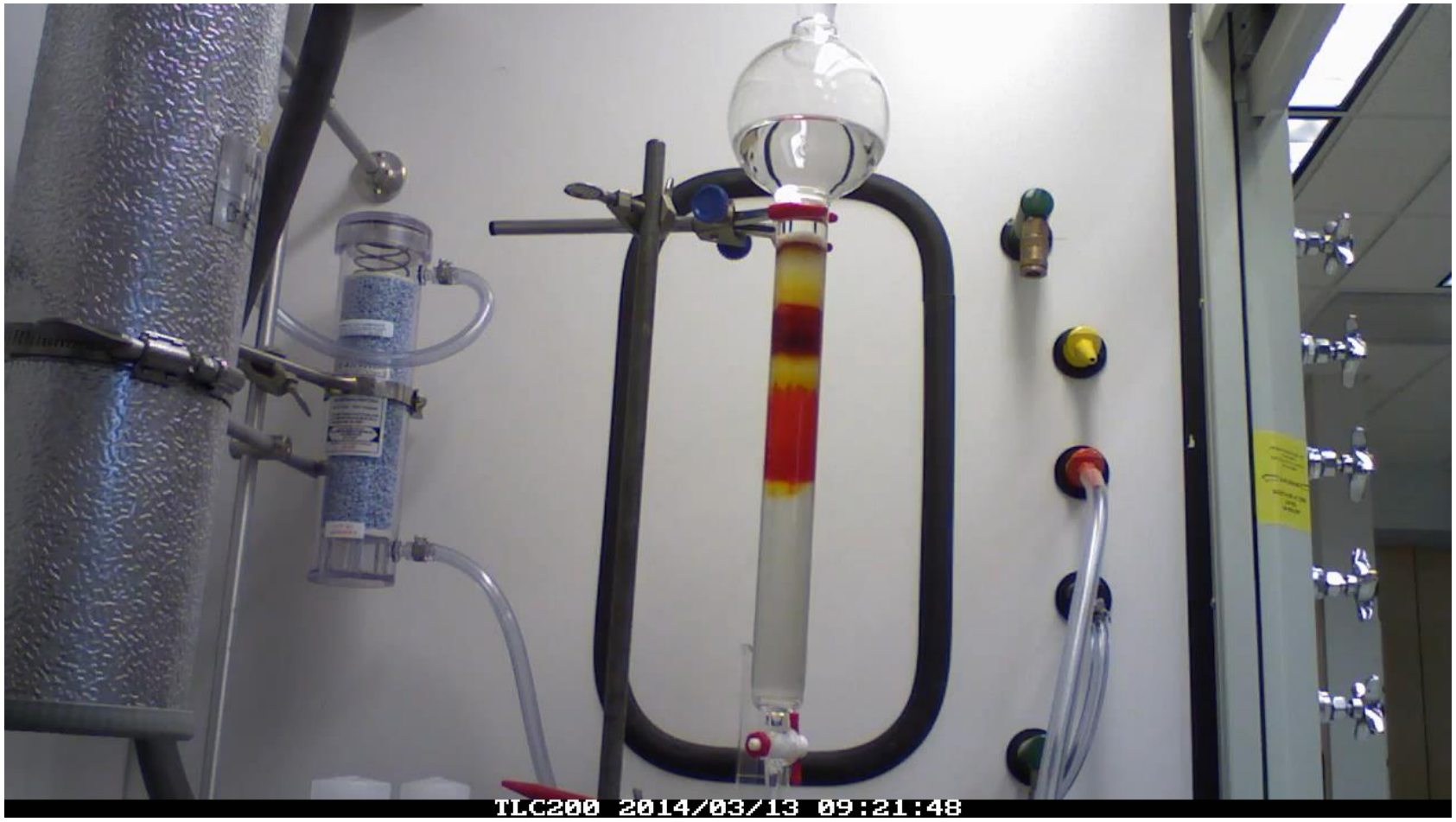
Column Chromatography



Column Chromatography

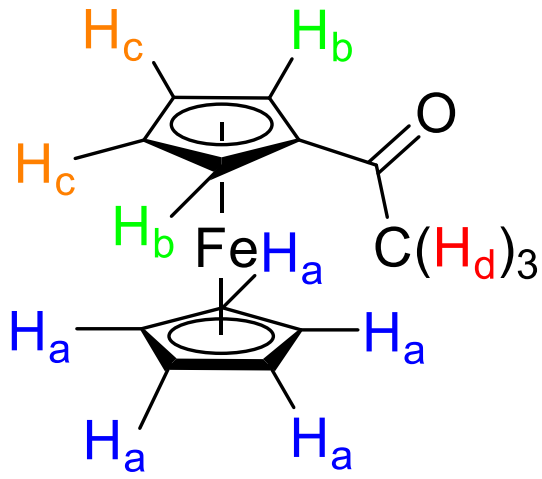
https://youtu.be/MM2F1gIzpVg?t=3





Identification of Products via Melting Point and NMR

- Experimental melting points (MPs) can be compared to literature MPs to determine identity
  - Experimental MP ranges will be lower and broader if they are impure
- Relative integration of aromatic and acetyl ^{1}H signals can be used to determine number of acetyl groups
- Presence of signal at the chemical shift corresponding to the acetyl CH_3 group indicates reaction success
- Online chemical databases and commercial sellers often have NMR spectra and MPs that can be used for comparison
- Important note – while ferrocene is aromatic, the Hs tend to be around 4-5ppm, not 7-8 ppm
- Pay attention to symmetry – when are 2 ferrocene ring Hs equivalent or not?



Report yields

0.538 mmol x 228 g/mol

0.02 mL
0.022 g
0.28 mmol

# drops of Acetyl chloride	Equivalents of acetyl chloride	Mass and % recovery of ferrocene	Mass and % yield of acetylferrocene	Mass and % yield of diacetylferrocene
2	(to 0.538 mmol Fc) 0.5 eq	(0.031 g x 100% / 0.1 g) 31%	(0.036 g x 100% / ?) 29%	(0.008 g x 100% / ?) ?%
4				
6				
8				
10				
12				