

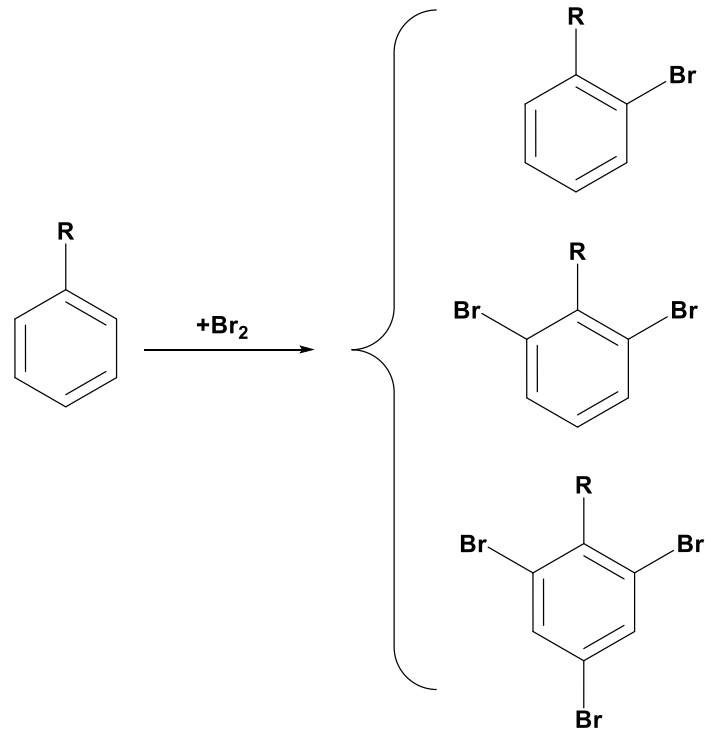
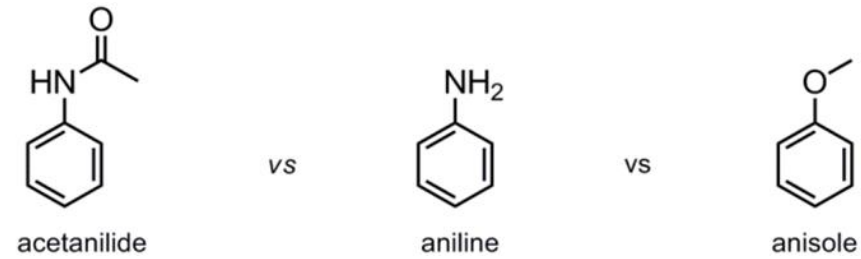


# Lab 4: Relative Reactivities of Aromatic Compounds

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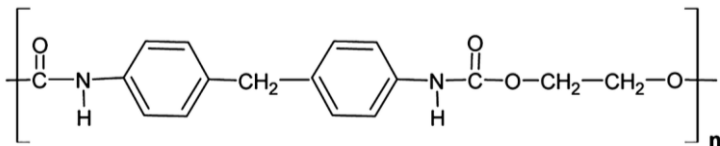
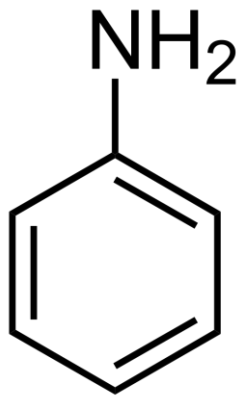
# Purpose:

Compare reactivity of three aromatic compounds

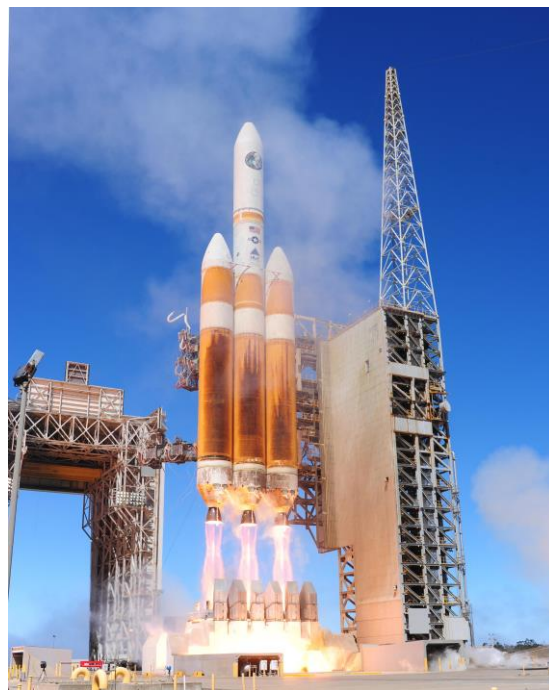




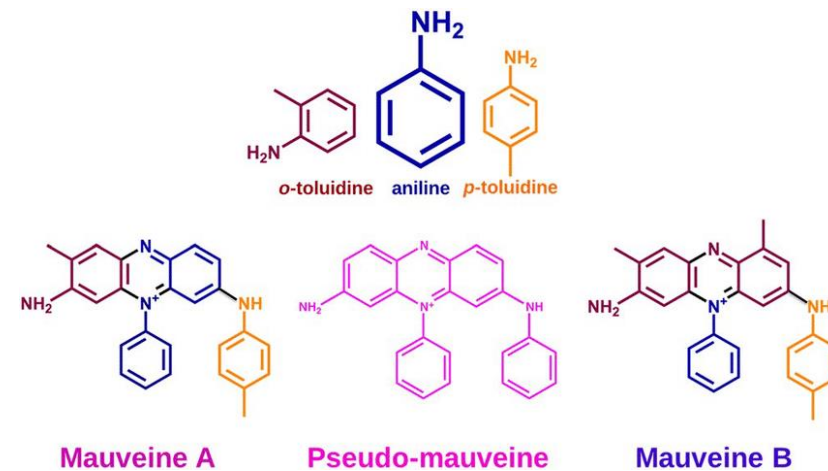
# Aniline



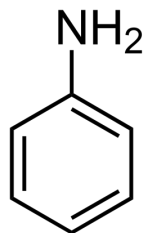
Polyurethane



Aniline + nitric acid



# Aniline

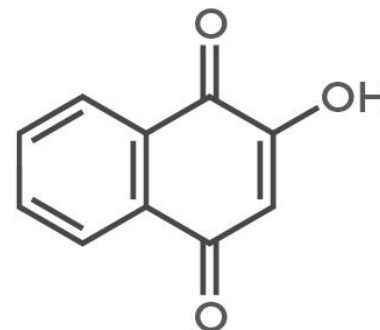


## THE CHEMISTRY OF HENNA

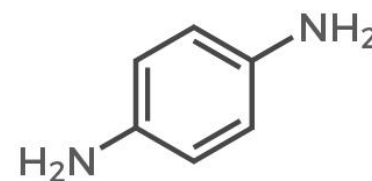
The red-orange dye from the leaves of the henna plant contains lawsone. Lawsone reacts chemically with keratin in the skin, leaving a stain that lasts for 2-6 weeks.



Black henna is red henna which has had the dye paraphenylenediamine (PPD) added to it. PPD can cause allergic skin reactions, and its use in black henna is discouraged.



**LAWSONE**



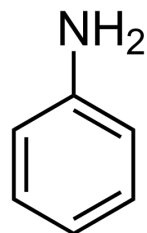
**PPD**



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This graphic is shared under a Creative Commons Attribution-NonCommercial-NoDerivatives licence.



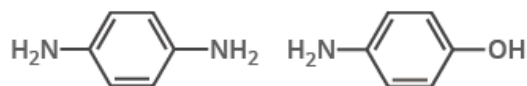
# Aniline



## THE CHEMISTRY OF PERMANENT HAIR DYES

There are a number of different types of hair dyes, but the most commonly used are permanent (oxidative) dyes. These dyes have a range of different components that react with each other to produce the desired end colour. In this graphic, we examine some of these chemicals, and how they form dyes.

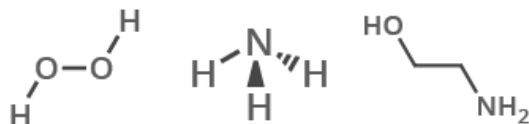
### 1 PRIMARY INTERMEDIATES



PARAPHENYLENEDIAMINE (PPD) & PARA-AMINOPHENOL

All permanent hair dyes contain a 'primary intermediate'; these are often p-diamines or p-aminophenols. They are oxidised by hydrogen peroxide to give reactive species which then go on to react with couplers to produce dyes. The exact structure of the reactive species produced by oxidation is still the subject of some debate.

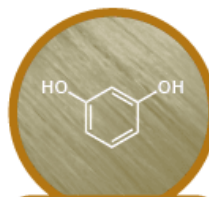
### 2 OTHER COMPOUNDS



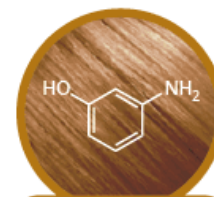
HYDROGEN PEROXIDE, AMMONIA, & ETHANOLAMINE

Hydrogen peroxide is the agent responsible for oxidation of primary intermediates, and also lightens the natural pigments present in the hair, the melanins eumelanin and pheomelanin. The dye-forming reactions are carried out at an alkaline pH, which is why ammonia is also required in the dye mixture. This raised pH causes the hair cuticle to swell, which in turn allows hydrogen peroxide and dye molecules to pass into the cortex. Ethanolamine can be used as an alternative, milder alkaline agent.

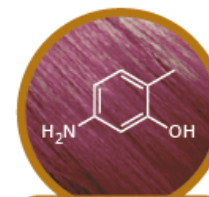
### 3 COUPLING AGENTS



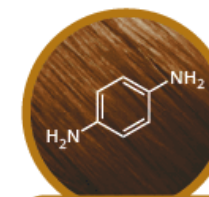
RESORCINOL  
GREENISH YELLOW



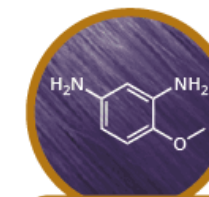
m-AMINOPHENOL  
LIGHT BROWN



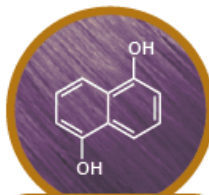
2-METHYL-5-AMINOPHENOL  
MAGENTA



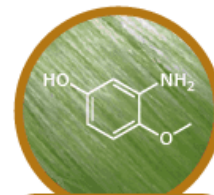
p-PHENYLENEDIAMINE  
DARK BROWN



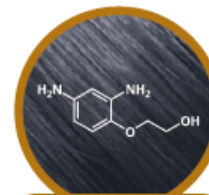
2,4-DIAMINOANISOLE  
PURPLE-BLUE



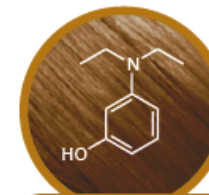
1,5-DIHYDROXYNAPHTHALENE  
BLUE-VIOLET



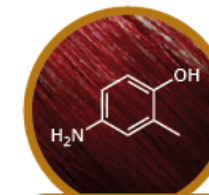
4-METHOXY-3-AMINOPHENOL  
GREEN



2,4-DIAMINOPHENOXYETHANOL  
DARK BLUE

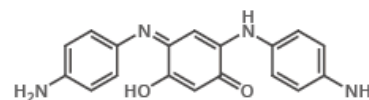


m-DIETHYLAMINOPHENOL  
OLIVE BROWN

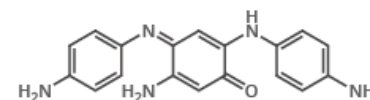


p-AMINO-o-CRESOL  
DARK RED

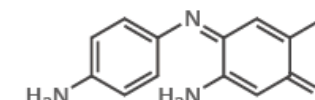
Coupling agents, also referred to as colour couplers, are the other component in the dye mixture. Independently, they contribute little in the way of colour, but they can react with primary intermediates in the presence of an oxidising agent to produce dye molecules, some examples of which are shown below. Most dyes will contain a mix of different coupling agents, rather than just one. Primary intermediates can, in some cases, couple to themselves to produce colouration. In the end, multiple different dye products are formed from a single formulation of hair dye.



GREEN INDO DYE  
FROM PPD & RESORCINOL



BROWN INDO DYE  
FROM PPD & m-AMINOPHENOL

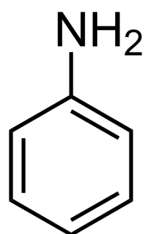


MAGENTA INDO DYE  
FROM PPD & 2-METHYL-5-AMINOPHENOL





# Aniline

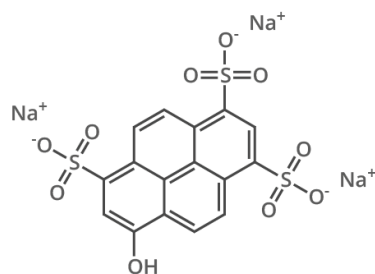


# THE CHEMISTRY OF HIGHLIGHTER COLOURS

HIGHLIGHTERS COME IN A RANGE OF COLOURS. THIS GRAPHIC SHOWS A SELECTION OF COMPOUNDS THAT CAN BE USED TO IMPART THESE COLOURS TO THE INK.



## Yellow

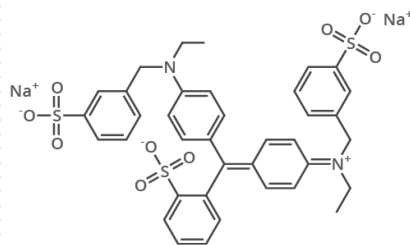


PYRANINE - SOLVENT GREEN 7  
(Pyrene dye)

Pyranine, a pyrene dye, is the dye commonly used in yellow highlighters. Another compound that can be utilised is fluorescein. By mixing a pyrene dye with a triphenylmethane dye, a green ink can also be obtained.



## Blue

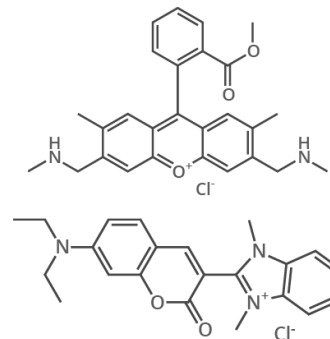


ACID BLUE 9  
(Triphenylmethane dye)

A triphenylmethane dye such as Acid Blue 9 is commonly used to achieve a blue ink colour; it is used in combination with a colour-brightening compound, for example an anionic stilbene derivative.



## Orange

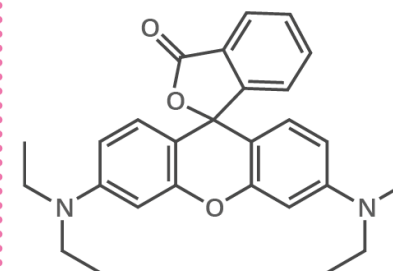


BASONYL RED 485 (TOP) & BASIC YELLOW 40  
(Xanthene dye and Coumarin dye)

A mix of a xanthene dye and a coumarin dye is required to achieve an orange colour.



## Pink

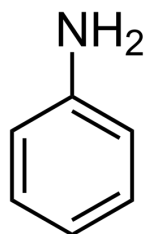


SOLVENT RED 49  
(Rhodamine dye)

A rhodamine dye can be used to impart a pink colour to the highlighter ink. A rhodamine dye can also be combined with a triphenylmethane dye in order to produce a purple-coloured highlighter.



# Aniline



PICTURE OF  
SOURCE (natural  
compounds only)  
OR CHEMICAL  
STRUCTURE

Colour guide →

**E-number**

**Chemical name**

Description and quick facts



**E100**

**Curcumin**

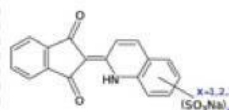
Found in turmeric roots. Buddhist monks have used E100 to dye their robes for centuries. Stains clothes well.



**E101**

**Riboflavin**

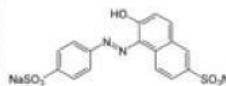
Vitamin B2. Adults require at least 1.2mg daily. Deficiency can cause mouth ulcers and a sore throat. Produced by microbes, animals and plants.



**E104**

**Quinoline yellow**

Synthetic. Also under scrutiny by the Food Standards Agency for the same reasons as E102.



**E110**

**Sunset Yellow FCF**

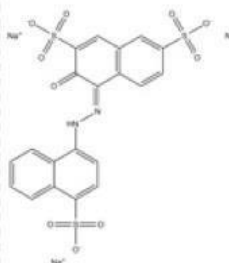
Synthetic azo dye. The FSA is considering banning E110 because it sometimes contains traces of a carcinogen called Sudan I.



**E120**

**Cochineal**

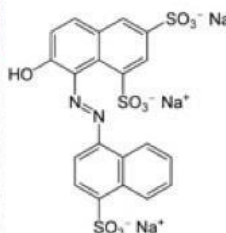
Crushed female cochineal insects mixed with alum to produce a crimson-coloured aluminium salt.



**E123**

**Amaranth**

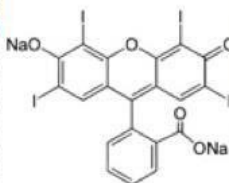
Synthetic azo dye. Allergenic and thus not recommended for children. Named after a similar-coloured plant with the same name. Banned in USA.



**E124**

**Ponceau 4R**

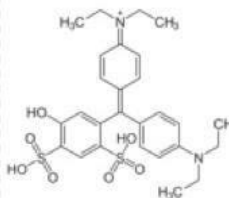
Synthetic azo dye. Can intensify asthma and elicit intolerance in people allergic to aspirin. Banned in many countries including the USA.



**E127**

**Erythrosine**

Synthetic. Breaks down above 200°C and releases iodine, which can interfere with thyroid function. Banned in the USA.



**E131**

**Patent Blue V**

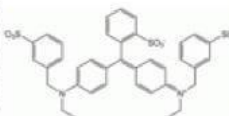
Synthetic dye also used in dental tablets to help people brush their teeth. Banned in Australia and in the USA as a food additive.



**E132**

**Indigo dye**

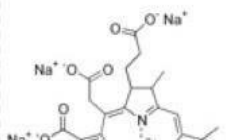
Has been used to dye jeans blue for centuries. Originally obtained naturally from rare indigo plants, E132 is now produced cheaply in the lab.



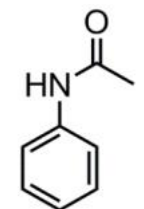
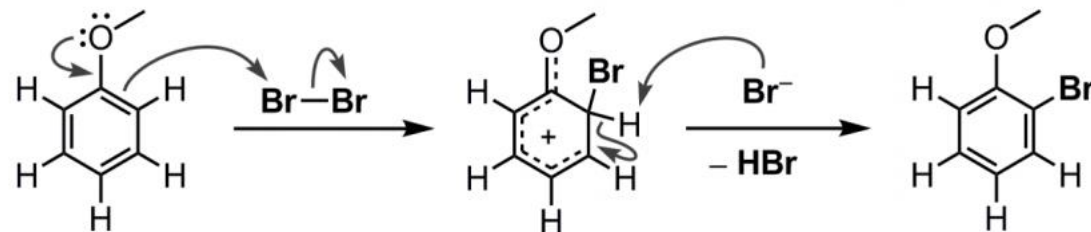
**E133**

**Brilliant Blue FCF**

Synthetic. Usually mixed with E102 to make green, which is used in processed peas, Listerine mouthwash and Blue Curacao liqueur.

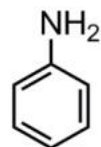


# Reaction



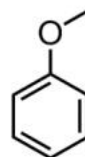
acetanilide

vs



aniline

vs



anisole

## Possible Brominated Products

Compound	mp (°C)	Compound	mp (°C)	Compound	mp (°C)
 <i>o</i> -Bromoacetanilide	99	 <i>o</i> -Bromoaniline	32	 <i>o</i> -Bromoanisole	3
 <i>p</i> -Bromoacetanilide	168	 <i>p</i> -Bromoaniline	66	 <i>p</i> -Bromoanisole	13
 2,4-Dibromoacetanilide	145	 2,4-Dibromoaniline	80	 2,4-Dibromoanisole	60
 2,6-Dibromoacetanilide	208	 2,6-Dibromoaniline	87	 2,6-Dibromoanisole	13
 2,4,6-Tribromoacetanilide	232	 2,4,6-Tribromoaniline	122	 2,4,6-Tribromoanisole	87



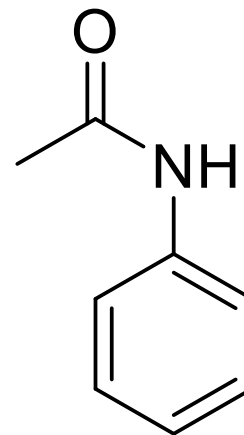
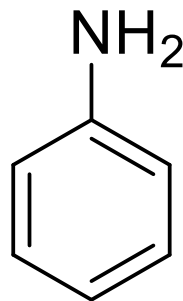
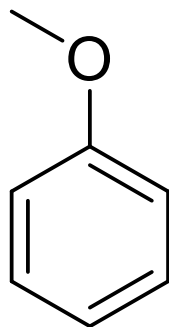
# Glassware/instruments/chemicals



Chemicals	Appearance	MW (g/mol)	Equivalent	Amount	Note
Aniline	Clear solution			0.060 g	
Anisole	Clear solution			0.075 g	
Acetanilide	Clear solution			0.090 g	
Br <sub>2</sub> /HBr	Orange solution			1.0 mL	
Acetic acid	Clear solution			0.5 mL	Strong smell

# Determining Products Using NMR

- For practice we can determine which NMR goes with which of the starting materials from Lab 4



- Quick Prediction:

Side chain:

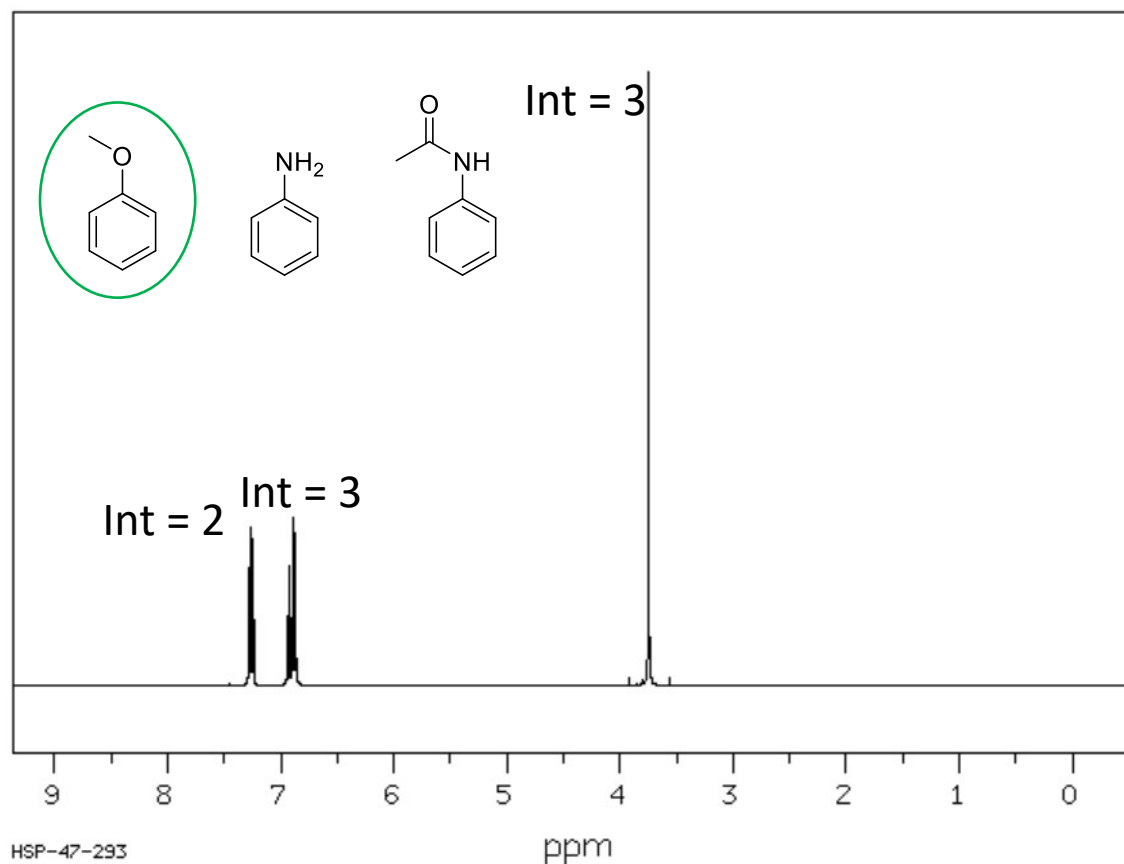
Aryl region:

Anisole	Aniline	Acetanilide
3H singlet ~3-4 ppm	2H broad singlet ~2-5 ppm	3H singlet ~2-3 ppm
2H doublet ~6.5-8 ppm	2H doublet ~6.5-8 ppm	2H doublet ~6.5-8 ppm
2H triplet ~6.5-8 ppm	2H triplet ~6.5-8 ppm	2H triplet ~6.5-8 ppm
1H triplet ~6.5-8 ppm	1H triplet ~6.5-8 ppm	1H triplet ~6.5-8 ppm
		1H broad singlet ~5-9 ppm



# Determining Products Using NMR

- Aryl region isn't helpful
- Peak at ~3.75 is worth 3H
  - Int = 3 rules out aniline
- Shift of 3.75 ppm can only be one of remaining two
  - Acyl protons are ~2-3 ppm
  - H-C-O are ~3-4
- What about the bromide products?
  - Will the aryl region help here?
  - Will the side chain tell us anything?



Our Prediction

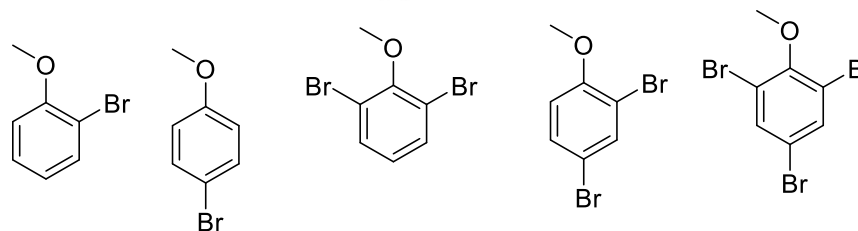
**Anisole**

3H singlet ~3-4 ppm

2H doublet ~6.5-8 ppm

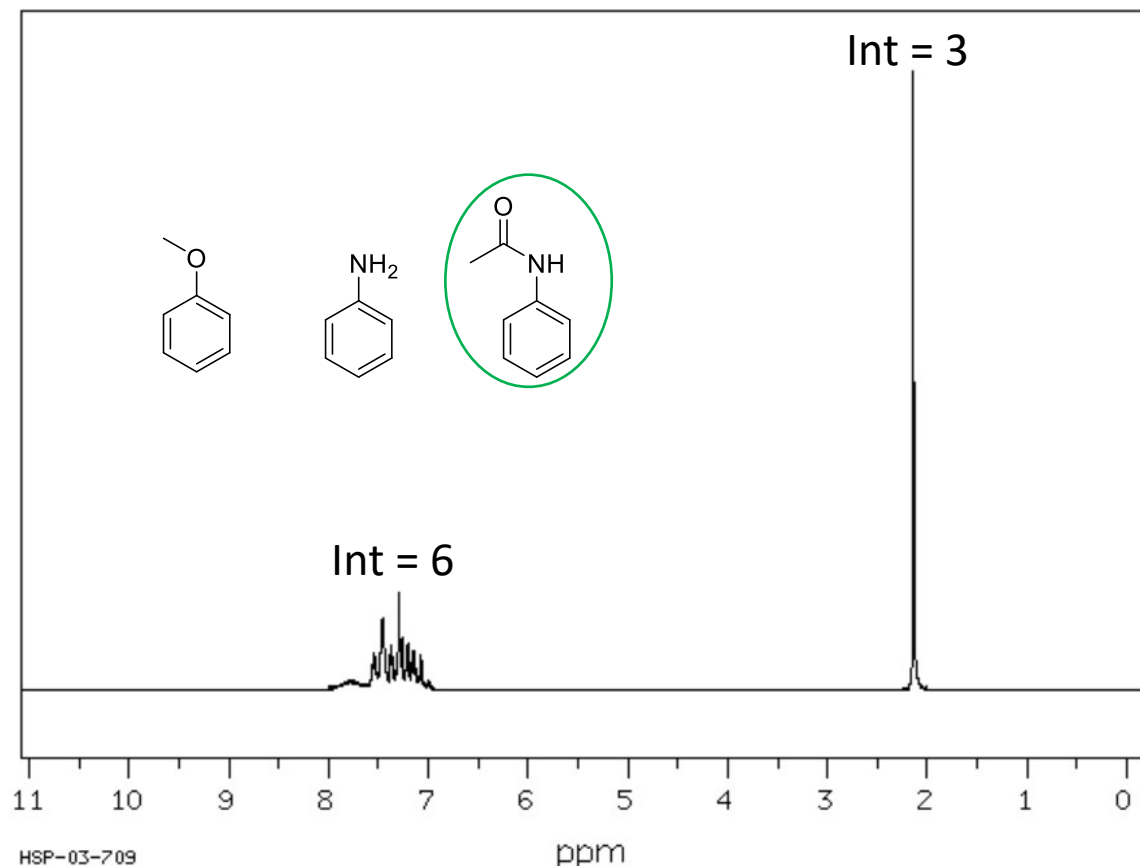
2H triplet ~6.5-8 ppm

1H triplet ~6.5-8 ppm



# Determining Products Using NMR

- Aryl region somewhat helpful – integration **6**
  - NH peak overlaps benzene
- Peak at ~2 is worth 3H
  - Int = 3 rules out aniline
- Shift of 2.1 ppm can only be one of remaining two
  - Acyl protons are ~2-3 ppm
  - H-C-O are ~3-4
- What about the bromide products?
  - Will the aryl region help here?
  - Will the side chain tell us anything?



Our Prediction

**Acetanilide**

3H singlet ~2-3 ppm

2H doublet ~6.5-8 ppm

2H triplet ~6.5-8 ppm

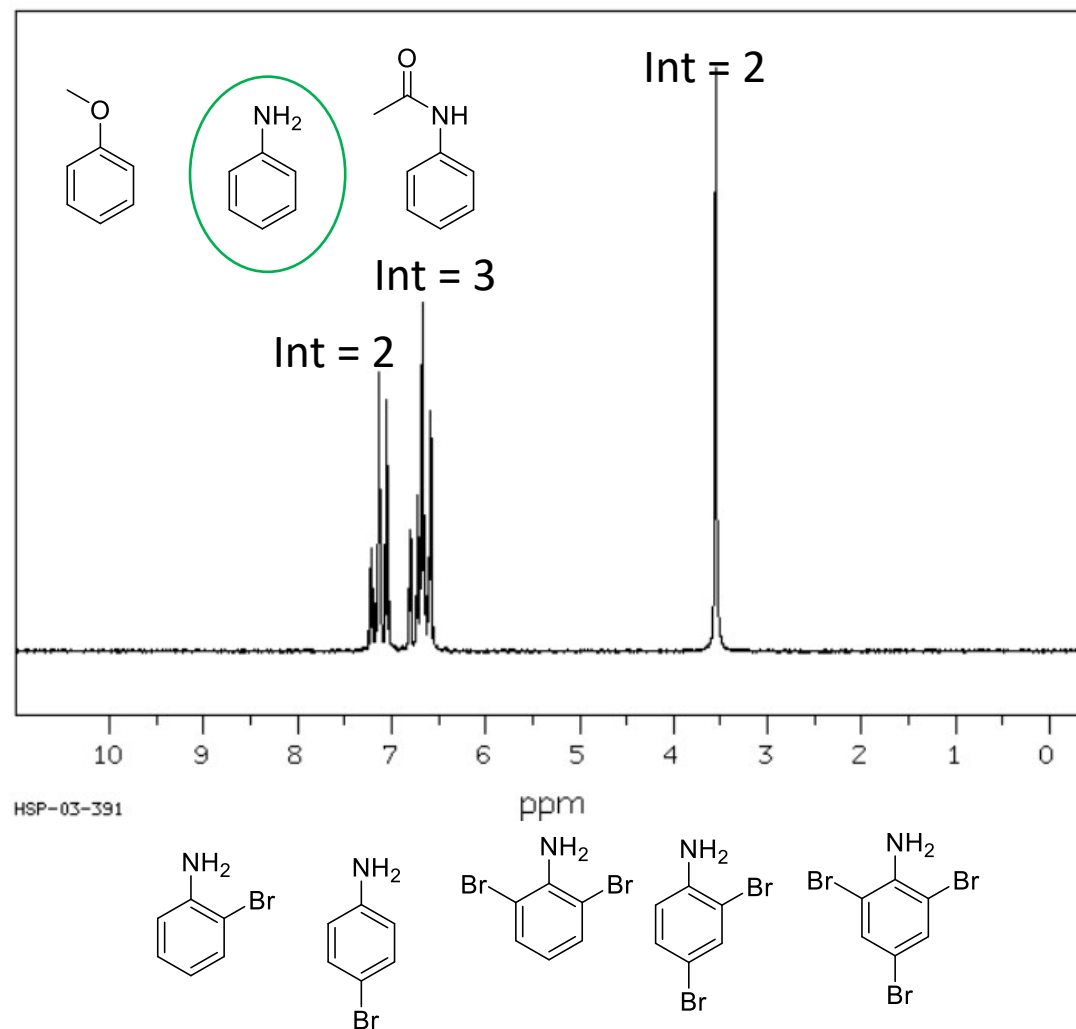
1H triplet ~6.5-8 ppm

1H broad singlet ~5-9 ppm



# Determining Products Using NMR

- Aryl region isn't helpful
- Peak at ~3.5 is worth 2H
  - Int = 2 rules out acetanilide and anisole
- Shift of 3.5 ppm makes sense for N-H
- What about the bromide products?
  - Will the aryl region help here?
  - Will the side chain tell us anything?



Our Prediction

## Aniline

2H broad singlet ~2-5 ppm

2H doublet ~6.5-8 ppm

2H triplet ~6.5-8 ppm

1H triplet ~6.5-8 ppm