

Experiment 1  
Thin Layer Chromatography  
January 16, 2018  
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## Protocol

See laboratory manual page 14 to 19.

Minor adjustments were made to the protocol.

- Instead of using 10 mg of the unknown sample substance, we used 0.05 g or 50 mg of the substance 22.
- Rather than dissolving the substance in 2 ml of dichloromethane, it was dissolved in 2.10 ml.

## Observations

### Part A

Reference, Solvent, and Sample	Observations
Reference: Benzophenone Solvent System: 2:8 Ethyl Acetate:Hexanes Sample: Unknown Substance 22	<ul style="list-style-type: none"><li>- 6 dots formed</li><li>- 1 dot on sample lane moved way up the TLC plate</li><li>- 3 dots at different displacements on co-spot</li><li>- 2 spots at different displacements on reference lane</li></ul> <b>Refer to figure 1</b>
Reference: Biphenyl Solvent System: 2:8 Ethyl Acetate:Hexanes Sample: Unknown Substance 22	<ul style="list-style-type: none"><li>- 5 spots formed</li><li>- 1 dot moved way up TLC plate on sample lane</li><li>- 2 spots at different displacements on co-spot</li><li>- 2 spots at different displacements on reference lane</li></ul> <b>Refer to figure 2</b>

### Part B

Reference, Solvent, and Sample	Observations
Reference: Benzophenone Solvent System: Pure Ethyl Acetate Sample: Unknown Substance 22	<ul style="list-style-type: none"><li>- Three dots formed; moved almost all the way up the TLC plate</li><li>- All dots were aligned in the same place; same Rf values</li><li>- This suggests that the sample compound and the reference compound are of the same polarity</li></ul> <b>Refer to figure 3</b>
Reference: Biphenyl Solvent System: Pure Ethyl Acetate Sample: Unknown Substance 22	<ul style="list-style-type: none"><li>- Three dots formed: moved almost all the way up the TLC plate</li><li>- All dots were aligned in the same place; same Rf values</li></ul>

	<ul style="list-style-type: none"> <li>- This suggests that the sample compound and the reference compound are of the same polarity</li> </ul> <p><b>Refer to figure 4</b></p>
Reference: Benzophenone Solvent System: Pure Hexanes Sample: Unknown Substance 22	<ul style="list-style-type: none"> <li>- 4 dots formed</li> <li>- 1 dot formed on sample lane; moved halfway up the TLC plate</li> <li>- 1 dot formed on reference lane; dot remained at tic mark, no displacement</li> <li>- 2 dots at different displacements on co-spot lane</li> </ul> <p><b>Refer to figure 5</b></p>
Reference: Biphenyl Solvent System: Pure Hexanes Sample: Unknown Substance 22	<ul style="list-style-type: none"> <li>- 3 dots formed; moved halfway up the TLC plate</li> <li>- All dots were aligned in the same place; same Rf values</li> <li>- This suggests that the sample compound and the reference compound are of the same polarity</li> </ul> <p><b>Refer to figure 6</b></p>

### Part C

Reference, Solvent, and Sample	Observations
Reference: <i>o</i> -bromonitrobenzene Solvent System: 9:1 Hexanes:Ethyl Acetate Sample: Unknown Sample YY	<ul style="list-style-type: none"> <li>- 6 dots formed; moved halfway up the TLC plate</li> <li>- 2 spots on sample lane at different displacements</li> <li>- 2 spots on reference lane at different displacements</li> <li>- 2 spots on co-spot lane at different displacements</li> <li>- Indicates <i>o</i>-bromonitrobenzene is not in the sample</li> </ul> <p><b>Refer to figure 7</b></p>
Reference: <i>m</i> -bromonitrobenzene Solvent System: 9:1 Hexanes:Ethyl Acetate Sample: Unknown Sample YY	<ul style="list-style-type: none"> <li>- 5 dots formed: moved halfway up TLC plate</li> <li>- 2 spots on sample lane at different displacements</li> <li>- 1 spots on reference lane at different displacements</li> <li>- 2 spots on co-spot lane at different displacements</li> <li>- 3 dots are aligned at same displacement; indicates <i>m</i>-bromonitrobenzene is found in the sample</li> </ul> <p><b>Refer to figure 8</b></p>
Reference: <i>p</i> -bromonitrobenzene Solvent System: 9:1 Hexanes:Ethyl Acetate Sample: Unknown Sample YY	<ul style="list-style-type: none"> <li>- 5 dots formed; moved halfway up the TLC plate</li> <li>- 2 spots on sample lane at different displacements</li> <li>- 1 spots on reference lane at different displacements</li> </ul>

- 2 spots on co-spot lane at different displacements
- 3 dots are aligned at same displacement; indicates *p*-bromonitrobenzene is found in the sample

Refer to figure 9

## Thin Line Chromatography

### Part A:

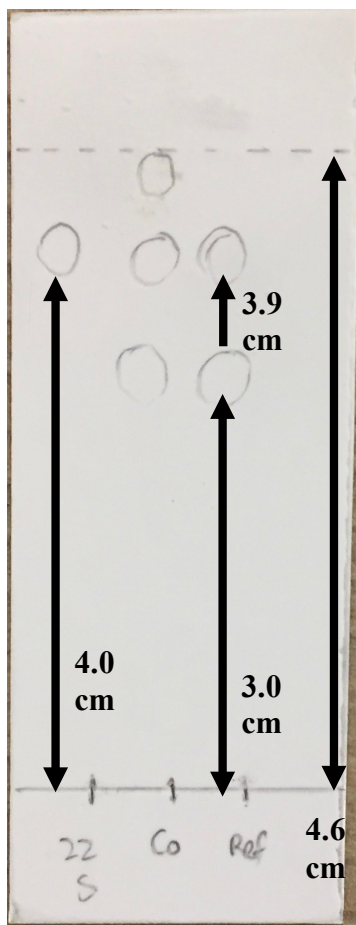


Figure 1:  
Unknown substance 22  
in solution of  
dichloromethane with  
reference solution  
benzophenone in  
solvent system of 2:8  
ethyl acetate:hexanes

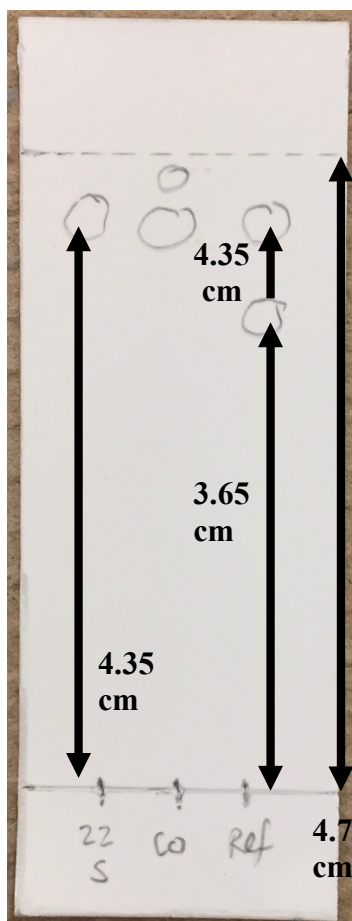


Figure 2:  
Unknown substance 22  
in solution of  
dichloromethane with  
reference solution  
biphenyl in solvent  
system of 2:8 ethyl  
acetate:hexanes

#### Legend:

22 S – unknown  
sample substance #22

CO – cospot

Reference – reference  
solution of either  
benzophenone or  
biphenyl

### R<sub>f</sub> Values

R <sub>f</sub> (sample) of Figure 1	R <sub>f</sub> = d <sub>1</sub> (displacement of compound)/d <sub>s</sub> (displacement of solvent) = 4.0/4.6 = 0.86
R <sub>f</sub> (reference) of Figure 1	R <sub>f</sub> = 3.0/4.6 = 0.65 R <sub>f</sub> = 3.9/4.6 = 0.84
R <sub>f</sub> (sample) of Figure 2	R <sub>f</sub> = 4.35/4.7 = 0.92
R <sub>f</sub> (reference) of Figure 2	R <sub>f</sub> = 3.65/4.7 = 0.77 R <sub>f</sub> = 4.35/4.7 = 0.92

### Part B:

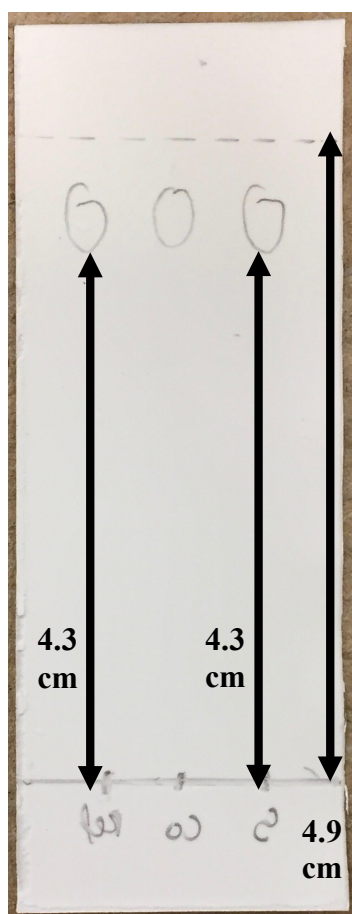


Figure 3:  
TLC of unknown substance 22 in solution of dichloromethane with reference solution benzophenone in solvent system of pure ethyl acetate.

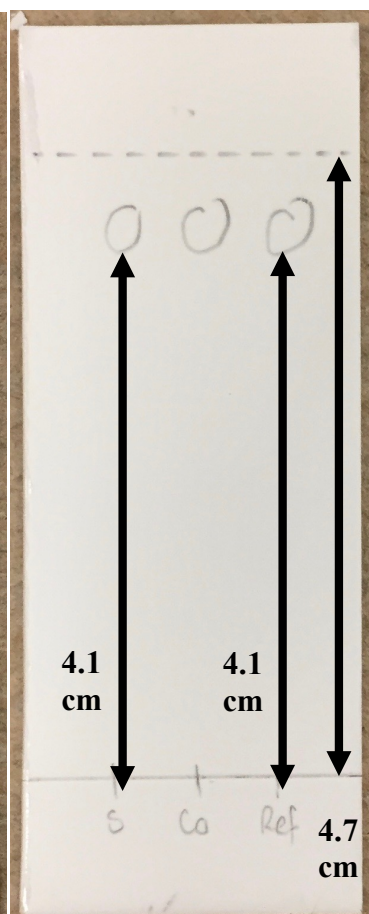


Figure 4:  
TLC of unknown substance 22 in solution of dichloromethane with reference solution biphenyl in solvent system of pure ethyl acetate.

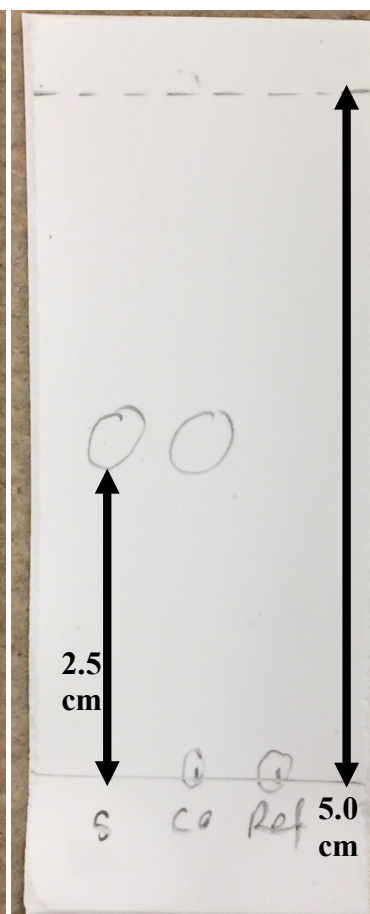


Figure 5:  
TLC of unknown substance 22 in solution of dichloromethane with reference solution benzophenone in solvent system of pure hexanes.

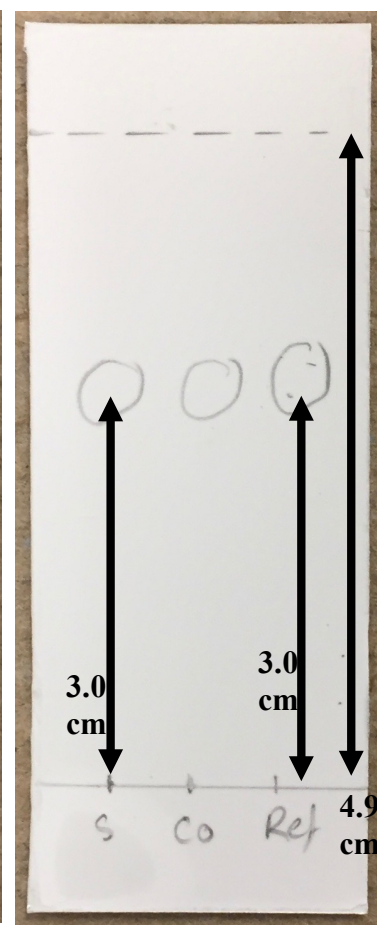


Figure 6:  
TLC of unknown substance 22 in solution of dichloromethane with reference solution biphenyl in solvent system of pure hexanes.

### R<sub>f</sub> Values

R <sub>f</sub> (sample) of Figure 3	R <sub>f</sub> = 4.3/4.9 = 0.87
R <sub>f</sub> (reference) of Figure 3	R <sub>f</sub> = 0.87
R <sub>f</sub> (sample) of Figure 4	R <sub>f</sub> = 4.1/4.7 = 0.7
R <sub>f</sub> (reference) of Figure 4	R <sub>f</sub> = 0.7
R <sub>f</sub> (sample) of Figure 5	R <sub>f</sub> = 2.5/5.0 = 0.5

$R_f$ (reference) of Figure 5	$R_f = 0$
$R_f$ (sample) of Figure 6	$R_f = 3.0/4.0 = 0.61$
$R_f$ (reference) of Figure 6	$R_f = 0.61$

**Part C:**

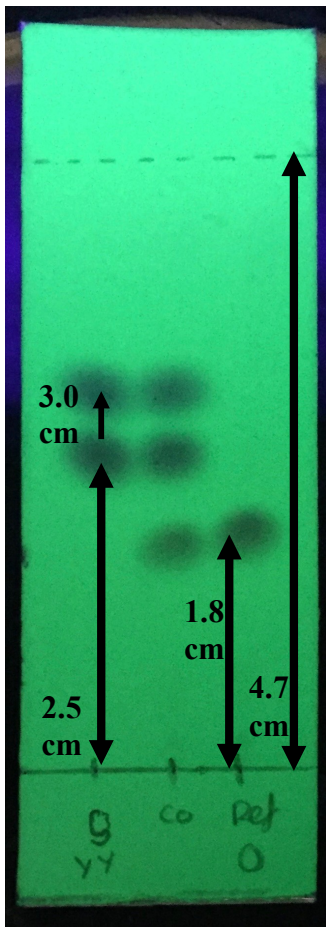


Figure 7:  
TLC of unknown substance YY with reference solution *o*-bromonitrobenzene in solvent system of 9:1 Hexanes:Ethyl Acetate.

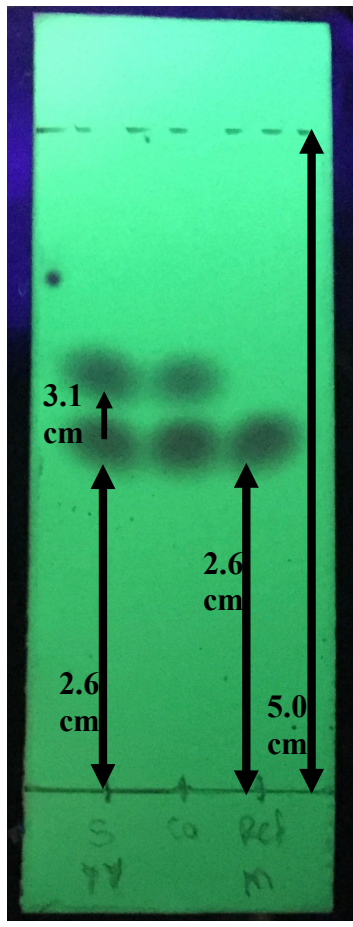


Figure 8:  
TLC of unknown substance YY with reference solution *m*-bromonitrobenzene in solvent system of 9:1 Hexanes:Ethyl Acetate.

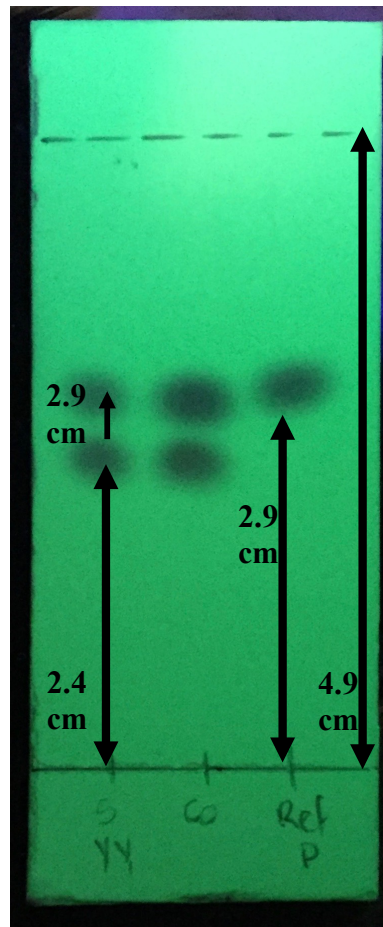


Figure 9:  
TLC of unknown substance YY with reference solution *p*-bromonitrobenzene in solvent system of 9:1 Hexanes:Ethyl Acetate.

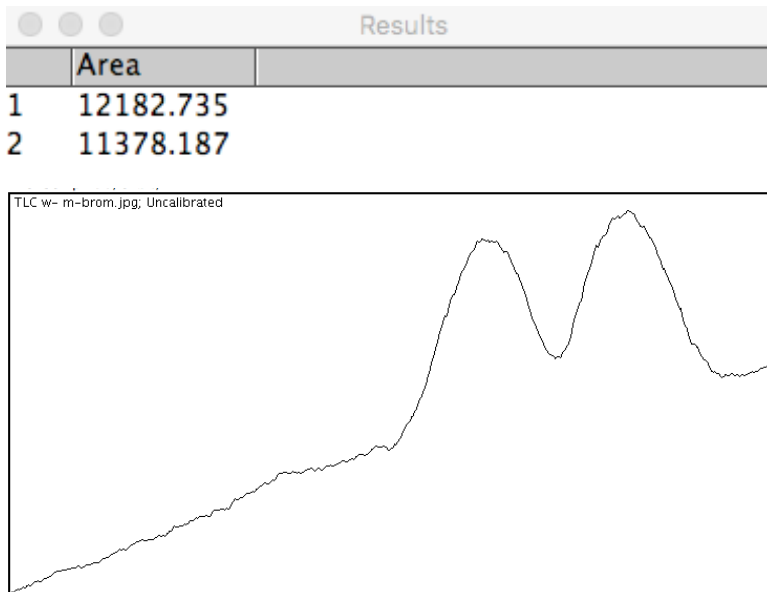
Legend:
SYY – Unknown substance YY
CO – co-output
RefO – <i>o</i> -bromonitrobenzene
RefM – <i>m</i> -bromonitrobenzene
RefP – <i>p</i> -bromonitrobenzene

**$R_f$  Values**

$R_f$ (sample) of Figure 7	$R_f = 2.5/4.7 = 0.53$
	$R_f = 3.0/4.7 = 0.63$
$R_f$ (reference) of Figure 7	$R_f = 1.8/4.7 = 0.38$

R <sub>f</sub> (sample) of Figure 8	R <sub>f</sub> = 2.6/5.0 = 0.52 R <sub>f</sub> = 3.1/5.0 = 0.62
R <sub>f</sub> (reference) of Figure 8	R <sub>f</sub> = 2.6/5.0 = 0.52
R <sub>f</sub> (sample) of Figure 9	R <sub>f</sub> = 2.4/4.9 = 0.48 R <sub>f</sub> = 2.9/4.9 = 0.59
R <sub>f</sub> (reference) of Figure 9	R <sub>f</sub> = 2.9/4.9 = 0.59

∴ the mixture of unknown substance YY is of meta and para



Absorbency Percentage:

Absorbency of meta = 12183

Absorbency of para = 11378

$$\% \text{ absorbency of meta} = \frac{12183}{(11378+12183)} \cdot 100 = 51.7\%$$

$$\% \text{ absorbency of para} = 100 - 51.7 = 48.3\%$$

Mole Percentage:

$$y = 51.7\%$$

$$y = 0.976x + 0.804$$

$$51.7 = 0.976x + 0.804$$

$$51.7 - 0.804 = 0.976x$$

$$50.896/0.976 = 0.976x/0.976$$

$$x = 52.1\%$$

$$y = 48.3\%$$

$$y = 0.976x + 0.804$$

$$x = 48.6\%$$

## Questions

1. How does increasing the polarity of the solvent system affect the results of a TLC? (3 points)

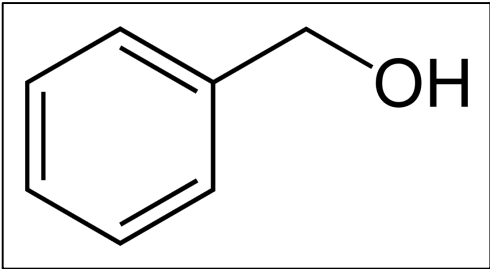
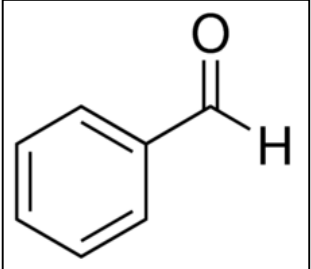
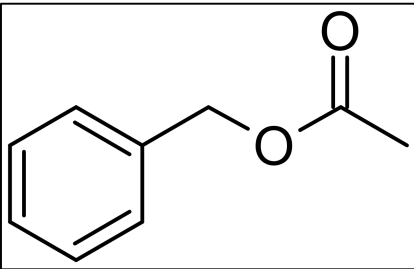
- Increasing the polarity of the solvent system does affect the results of the TLC.
- For example, if you choose a more polar solvent system, there is stronger attraction between the silica and the solvent and thus the movement up the TLC plate is less quick and the distance travelled is less far.
- Whereas, less polar compounds are not as strongly attracted to the silica and therefore, movement up the TLC plate is quicker.
- However, the distance travelled by both polar and non-polar compounds can be increased with and increasing polarity of the solvent system. The more polar the solvent is, the more the intermolecular forces between the silica and the compound are disrupted, thus making the compound move further along the TLC plate.
- For example, when working with pure hexanes, a less polar solvent, dots were formed only halfway up the TLC plate, compared to when working pure ethyl acetate, a more polar solvent, dots were formed almost further up the TLC plate. This would affect the displacement of the compound and thus the results of the  $R_f$  values.

2. In the following sets of compounds, which would have the smallest  $R_F$  on silica gel? Use a sentence to explain your reasoning. Draw line structures of each compound

\* **From most to least polar**

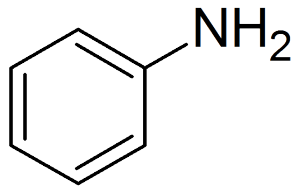
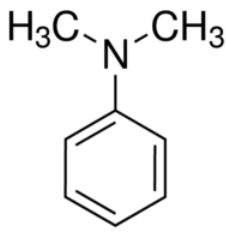
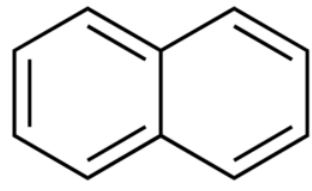
- a. Benzyl alcohol, benzaldehyde, benzyl acetate

**From most to least polar**

Benzyl Alcohol	Benzaldehyde	Benzyl Acetate
		

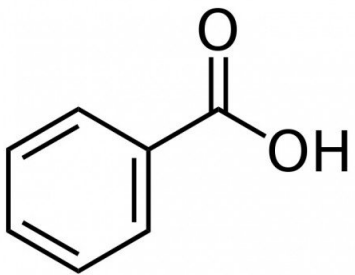
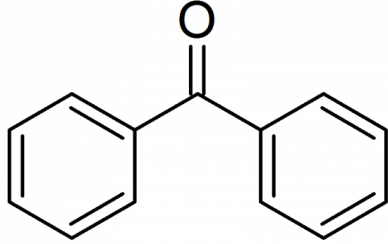
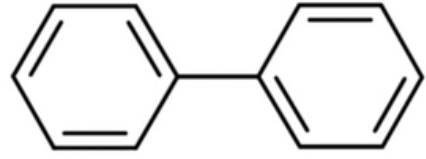
- Benzyl alcohol is the most polar compound because of its hydroxyl functional group
- Its polarity is a result of its hydrogen bonding capabilities because of the presence of the oxygen molecule
- Thus, this compound would have the smallest  $R_f$  value and move the least quickly and the least far up the silica gel TLC plate

b. Aniline, N,N-dimethylaniline, Naphthalene

Aniline	N, N-Dimethylaniline	Naphthalene
		

- The amine group on the carbon ring of aniline makes it the most polar compound.
- Therefore, aniline will be most attracted to the silica gel, and thus have a smaller  $R_f$  value.
- Naphthalene is a non-polar molecule because of its structural symmetry

c. Benzophenone, Biphenyl, Benzoic acid

Benzoic Acid	Benzophenone	Biphenyl
		

- Benzoic acid is the most polar compound and therefore, will have the smallest  $R_f$  value on silica gel due to its stronger attraction.
- Its polarity is the result of a hydroxyl and a carboxyl group attached to its carbon ring.

## Discussion

### Part A:

- With benzophenone as a reference, 6 spots formed. There were three spots that did not align indicating that the sample was not benzophenone. The  $R_f$  values of the sample and the reference differed,  $0.86 \neq 0.84$ .
- With biphenyl as a reference, 5 spots formed. There were three spots aligned indicating that the sample contained biphenyl. The  $R_f$  values of the sample and reference were the same at 0.92

- It should be considered that the biphenyl moved further up the TLC plate in comparison to the benzophenone. Biphenyl had an  $R_f$  value of 0.92 and benzophenone had an  $R_f$  value of 0.84.
- This shows that benzophenone is more polar than biphenyl because benzophenone contains the polar carbonyl group.
- This part of the experiment could be a source of error as how closely aligned the three dots were for both the benzophenone and biphenyl TLCs. One could assume that the sample 22 could have both benzophenone and biphenyl, but this would be incorrect. Perhaps if we had done the same experiment twice three times to compare results, it would have been more accurate.

#### Part B:

- When using a solvent system of ethyl acetate, both benzophenone and biphenyl moved further along the TLC plate.
- This is because ethyl acetate is a more polar solvent, causing the intermolecular forces between the compound and the silica gel to be disrupted.
- The  $R_f$  values for both benzophenone and biphenyl were rather large, 0.87 and 0.7 respectively
- When using a solvent system of hexanes, a non-polar solvent, the dots formed did not move far along the TLC plate; only about halfway. This resulted in smaller  $R_f$  values due to a shorter distance travelled.
- Part B demonstrates that the more polar the solvent system, the greater the  $R_f$  value.

#### Part C:

- In part C, 9:1 Hexanes:Ethyl Acetate was used as a solvent system. The TLC plates show that the dots only travelled about halfway along the plate.
- Hexanes are a less polar compound than ethyl acetate, but in this solution hexanes are in larger amount than EtOAc, making the solvent less polar and as seen in Part B, the less polar the solvent, the smaller the  $R_f$  value.
- The TLC plates show that *o*-bromonitrobenzene is more polar than *m*-bromonitrobenzene and *p*-bromonitrobenzene as it did not move as far along the plate.
- The mole percentage of meta- and para- were close in range, 51.7% and 48.6% respectively.
- It is evident that sample YY consisted of *m*-bromonitrobenzene and *p*-bromonitrobenzene.