

# Organic Chemistry Experiment 1: Thin Layer Chromatography

Jin Bai, 8541241

Lab Partners: Tom Podolsky, 3004280  
Jeremy Howard 4663199

Demonstrator: Yousef Risha

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University of Ottawa

## Procedure

- Same as described in the lab manual (CHM 1321 Organic Chemistry Laboratory Manual 2018, Dr. Tony Durst, Dr. Tito Scaiano, Dr. William Ogilvie, Dr. Alison Flynn, Exp. 1, p. 17 to 19), except for the following modifications:

**Part A: 1.** Add approximately 11 mL of a 2:8 mixture of ethyl acetate (EtOAc) and hexanes to your developing jar and place the lid on the jar.

**Part A: 9.** Remove the plates from the jar with tongs and mark the solvent finish line with a pencil...

**Part C: 1.** Your demonstrator will assign you unknown ZZ, which contains a mixture of compounds. Using a clean 50 mL beaker, obtain 2 mL of the unknown ZZ from the appropriate burette in the small fumehood.

**Part A: 9. and Part B. 3. and 6.** The  $R_f$ s are not calculated because our group only measured the displacement of the compounds and neglected to measure the displacement of the solvent front.

## Observations

### Part A:

- 2:8 mixture of ethyl acetate and hexanes are colourless, transparent liquids.
- Unknown compound #35 is a white crystalline powder.
- Dichloromethane is a colourless, transparent liquid.
- Benzophenone and biphenyl are both colourless, transparent liquids.

### Part B:

- Pure ethyl acetate is a colourless, transparent liquid.
- Pure hexanes are a colourless, transparent liquid.

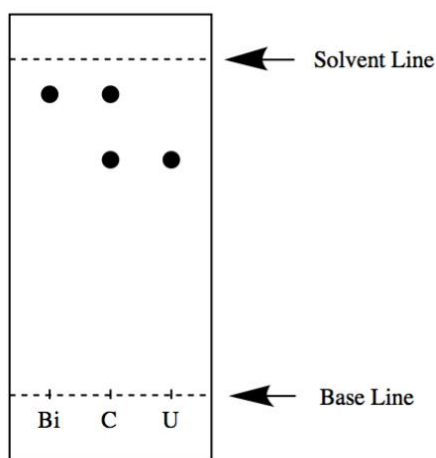
### Part C:

- Solution A (ortho-bromonitrobenzene) is a yellow, transparent liquid.
- Solution B (meta-bromonitrobenzene) is a colourless, transparent liquid.
- Solution C (para-bromonitrobenzene) is a colourless, transparent liquid.

## TLC Plates and Table of R<sub>f</sub>s

My lab partners and I were assigned unknown #35.

**Figure 1.** TLC 1: Biphenyl (edit: R<sub>f</sub> of Reference = 0.484, R<sub>f</sub> of Sample #35 = 0.899)



Solvent System: 2:8 Ethyl Acetate:Hexanes

Legend:

Bi: Biphenyl

C: Co-spot

U: Dichloromethane and Unknown Sample #35

Displacement of Compounds:

Reference Biphenyl: 3.92 cm

Co-spot (Top): 3.92 cm

Co-spot (Bottom): 3.11 cm

Sample: 3.11 cm

Displacement of Solvent: \*\* 4.36 cm \*\*

R<sub>f</sub> of Reference Biphenyl: 0.900

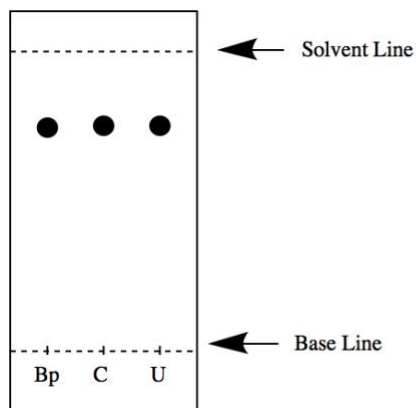
R<sub>f</sub> of Co-spot (Top): 0.900

R<sub>f</sub> of Co-spot (Bottom): 0.700

R<sub>f</sub> of Sample: 0.700

\*\* Calculated due to human error (neglected to measure displacement of solvent front)

**Figure 2.** TLC 2: Benzophenone



Solvent System: 2:8 Ethyl Acetate:Hexanes

Legend:

Bp: Benzophenone

C: Co-spot

U: Dichloromethane and Unknown Sample #35

Displacement of Compounds:

Reference Benzophenone: 3.43 cm

Co-spot: 3.43 cm

Sample: 3.43 cm

Displacement of Solvent: \*\* 4.57 cm \*\*

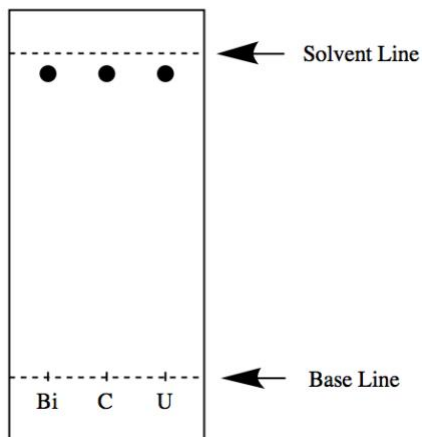
R<sub>f</sub> of Reference Benzophenone: 0.75

R<sub>f</sub> of Co-spot: 0.75

R<sub>f</sub> of Sample: 0.75

\*\* Calculated due to human error (neglected to measure displacement of solvent front)

**Figure 3.** TLC 3: Biphenyl



Solvent System: Ethyl Acetate

Legend:

Bi: Biphenyl

C: Co-spot

U: Dichloromethane and Unknown Sample #35

Displacement of Compounds:

Reference Biphenyl: 4.52 cm

Co-spot: 4.52 cm

Sample: 4.52 cm

Displacement of Solvent: \*\* 4.81 cm \*\*

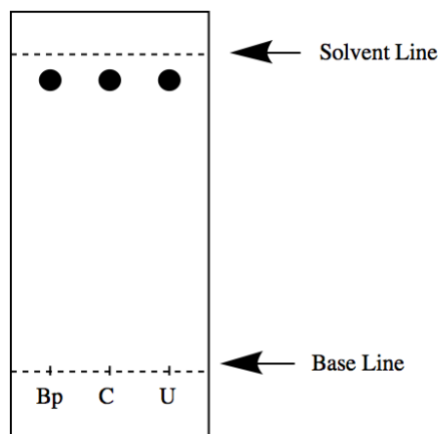
R<sub>f</sub> of Reference Biphenyl: 0.94

R<sub>f</sub> of Co-spot: 0.94

R<sub>f</sub> of Sample: 0.94

\*\* Calculated due to human error (neglected to measure displacement of solvent front)

**Figure 4. TLC 4: Benzophenone**



Solvent System: Ethyl Acetate

Legend:

Bp: Benzophenone

C: Co-spot

U: Dichloromethane and Unknown Sample #35

Displacement of Compounds:

Reference Benzophenone: 4.41 cm

Co-spot: 4.41 cm

Sample: 4.41 cm

Displacement of Solvent: \*\* 4.79 cm \*\*

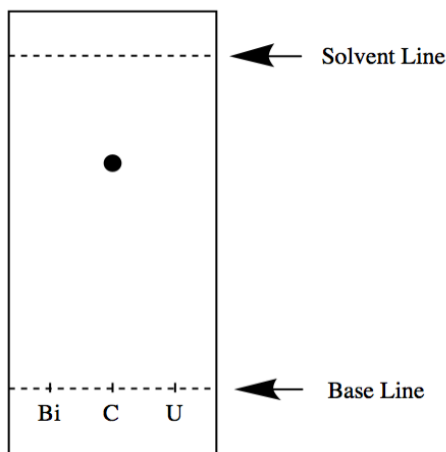
Rf of Reference Benzophenone: 0.92

Rf of Co-spot: 0.92

Rf of Sample: 0.92

\*\* Calculated due to human error (neglected to measure displacement of solvent front)

**Figure 5. TLC 5: Biphenyl**



Solvent System: Hexanes

Legend:

Bi: Biphenyl

C: Co-spot

U: Dichloromethane and Unknown Sample #35

Displacement of Compounds:

Reference Biphenyl: N/A

Co-spot: 3.32 cm

Sample: N/A

Displacement of Solvent: \*\* 4.88 cm \*\*

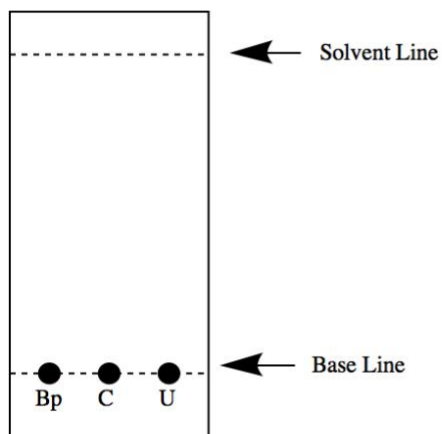
Rf of Reference Biphenyl: N/A

Rf of Co-spot: 0.68

Rf of Sample: N/A

\*\* Calculated due to human error (neglected to measure displacement of solvent front)

**Figure 6. TLC 6: Benzophenone**



Solvent System: Hexanes

Legend:

Bp: Benzophenone

C: Co-spot

U: Dichloromethane and Unknown Sample #35

Displacement of Compounds:

Reference Benzophenone: 0 cm

Co-spot: 0 cm

Sample: 0 cm

Displacement of Solvent: \*\* MISSING \*\*

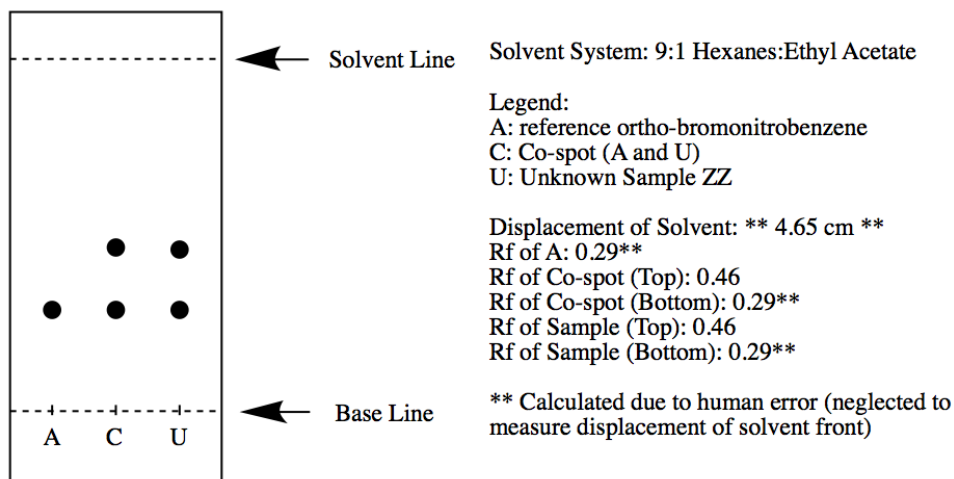
Rf of Reference Benzophenone: 0

Rf of Co-spot: 0

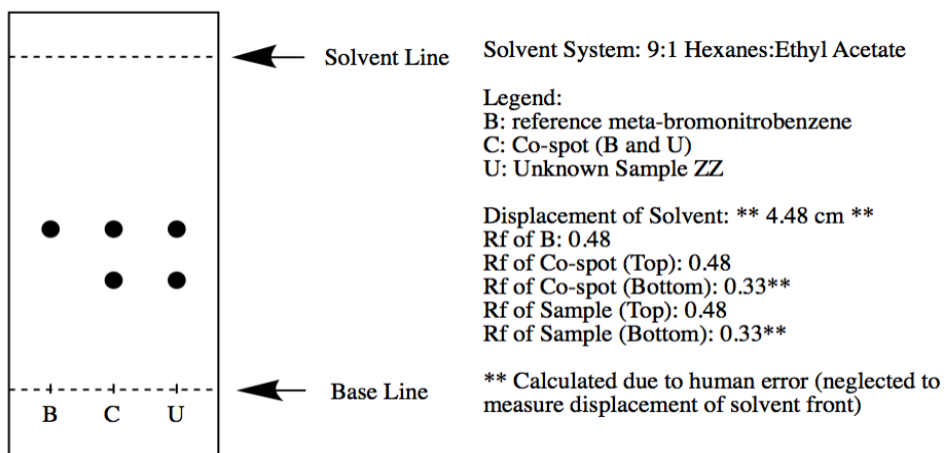
Rf of Sample: 0

\*\* due to human error, our group neglected to measure displacement of solvent front, but displacement of solvent does not matter if solvent does not move.

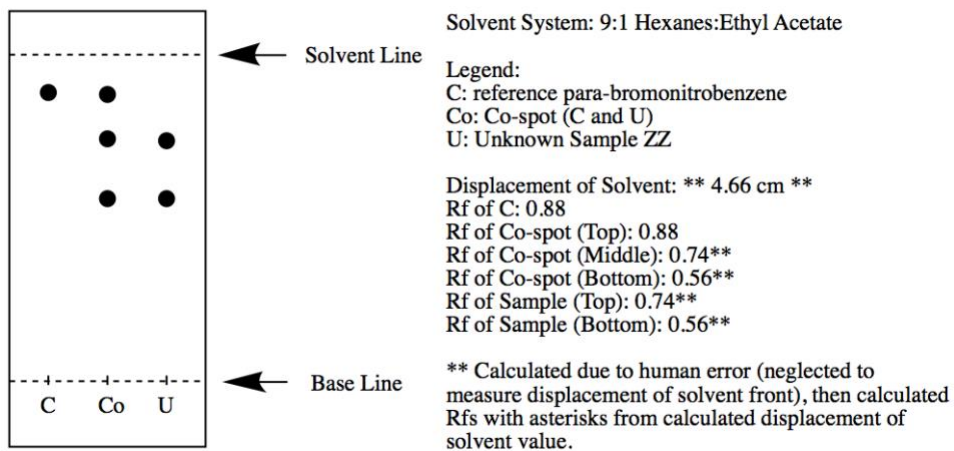
**Figure 7. TLC 7: ortho-bromonitrobenzene**



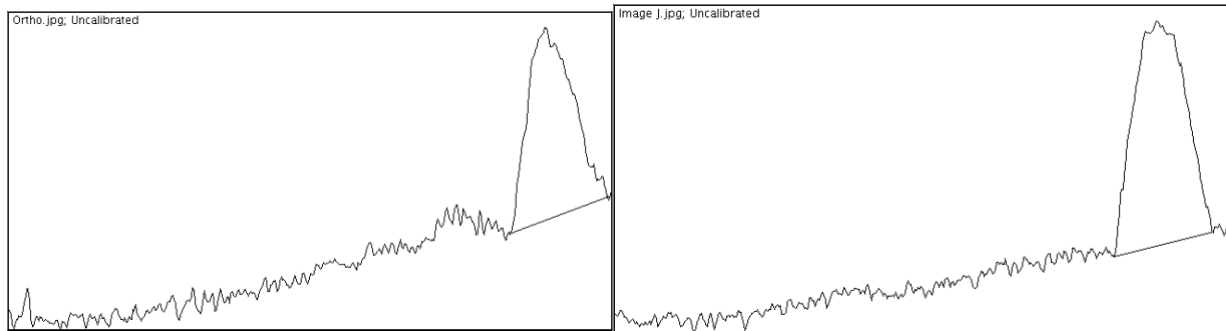
**Figure 8. TLC 8: meta-bromonitrobenzene**



**Figure 9. TLC 9: para-bromonitrobenzene**



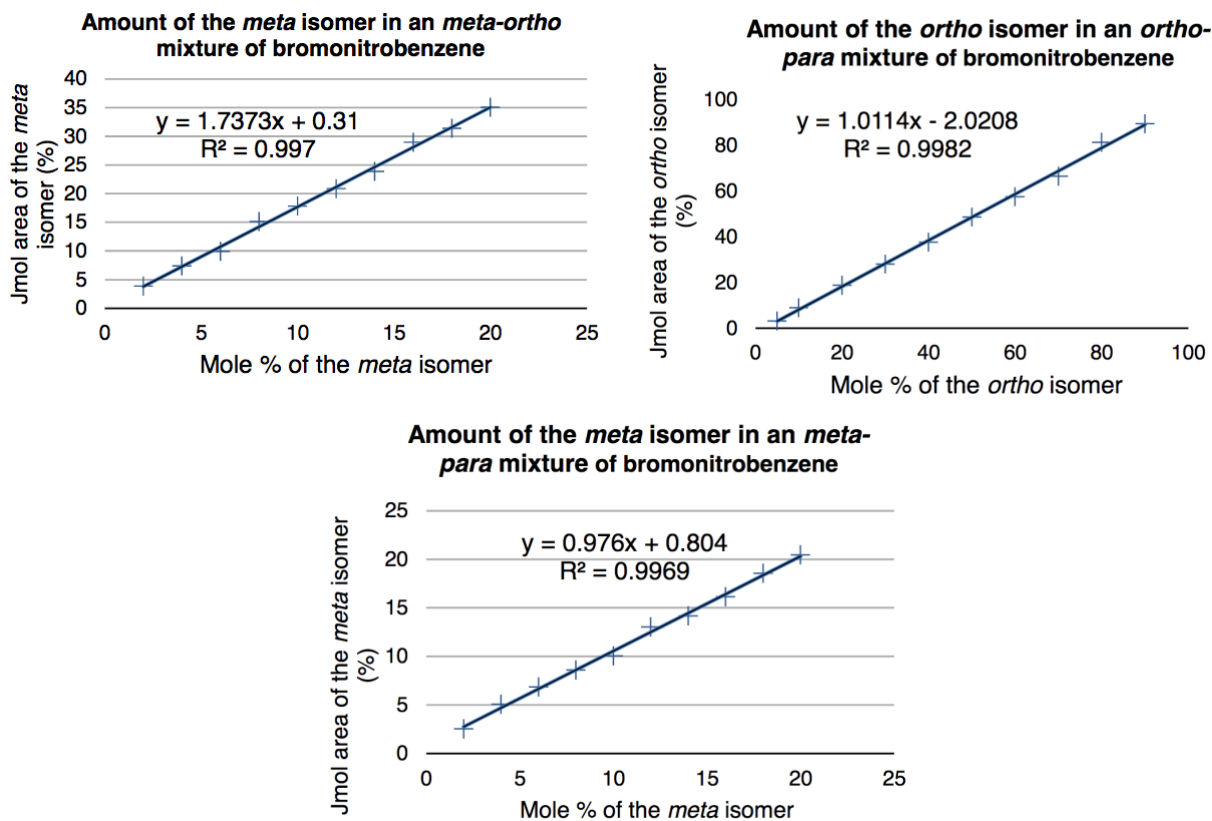
**Figure 10.** Lane Plots for ortho- and meta-bromonitrobenzene TLC plates, respectively



**Areas Between Curves and Drawn Lines:**

	Area
1	14906.681
2	11670.874

**Figure 11.** Calibration curves for calculating mole percentage



## Calculations

Example of an  $R_f$  Calculation (Figure 1):

$R_f = \text{displacement of compound} / \text{displacement of solvent} = d_1 / d_s$

Displacement of compound (dichloromethane and sample #35): 3.92 cm

Displacement of reference (biphenyl): 2.11 cm

Displacement of solvent: 4.36 cm\*\*

$R_f$  of Reference =  $2.11 \text{ cm} / 4.36 \text{ cm} = 0.484$

$R_f$  of Sample #35 =  $3.92 \text{ cm} / 4.36 \text{ cm} = 0.899$

\*\*Neglected to measure displacement of solvent (human error). This value has been calculated according to the displacement of the compound and the appearance of the TLC plate.

### Calculate percentage of absorbance:

Absorbance of meta = 14 907

Absorbance of ortho = 11 671

%Absorbance (meta) =  $(14\ 907 / (14\ 907 + 11\ 671)) \times 100 = 56.1\%$

%Absorbance (ortho) =  $100 - 56.1 = 43.9\%$

### Calculate mole percentage:

$y = \text{\%Absorbance (meta)} = 56.1\%$

$y = 1.7373(x) + 0.31$ , where  $x = 32.1\%$  (see Figure 11 above for Calibration Curves)

**%mole (meta) = 32.1%**

**%mole (ortho) = 67.9%**

## Discussion

### Part A: comparing polarity of unknown sample #35 to biphenyl and benzophenone.

- Biphenyl = symmetrical, no polar functional groups. Benzophenone = polar.
- Spots on biphenyl plate are separated, so unknown sample has different polarity and adsorption than reference biphenyl.
- 2:8 ethyl acetate:hexanes solvent system works well in ensuring unknown sample and references travel up the silica gel (stationary adsorbent) TLC plate.
- Solvent climbing up adsorbent barely interacts with compound being carried by solvent.
- Retention factor ( $R_f$ ) for biphenyl = 0.9, which is different from  $R_f$  of the unknown sample's compound. Visually, the spot in the reference lane is not horizontally in line with the spot in the sample lane, meaning unknown is not biphenyl. Unknown's lower  $R_f$  shows stronger affinity for silica than biphenyl. Unknown travels less far than biphenyl because it is more polar than biphenyl.

- Unknown #35 is benzophenone because on TLC 2, the spots are all aligned with each other, meaning that the compound in the reference lane (benzophenone) exists in the previously unknown sample. Their  $R_f$  values are identical at 0.75
- Benzophenone is lower than biphenyl because it is more polar. Benzophenone has two free electron pairs that make the molecule polar. Benzophenone's polarity means a stronger affinity with the silica gel, which is the stationary phase. As the solvent elutes up the TLC plate, the benzophenone's attraction to the silica gel makes it resistant to the movement of the solvent. On the other hand, biphenyl has no free electron pairs and is symmetrical, making it non-polar. Its affinity with the silica gel is minimal. Thus, biphenyl is easily moved by the solvent up the TLC plate, leading to a higher  $R_f$  than the "sticky" benzophenone.

**Part B: comparing different solvent systems.**

- Ethyl acetate is highly polar compared to hexanes. It steals bonds so that the unknown compound will bond more with it, the solvent, than the silica plate. Whether the compound is polar or not does not matter as the compound will be dragged by ethyl acetate all the way up. The solvent is important to TLC.
- Distances travelled by reference and sample are dependent on their polarity and resulting affinities for the solvent versus the silica gel. Whichever of the two are more polar will have more affinity. Biphenyl is non-polar, meaning it has less affinity and will go up the TLC plate faster and farther, as it's not being dragged down by bonding with the silica.
- Hexanes are not good solvents because they are extremely non-polar, and won't have any affinity with the compound, making the compound bond with the silica.
- Reference of benzophenone for sample #35 is developed in both ethyl acetate and then hexane solvent systems, and the same is done with biphenyl. As ethyl acetate is more polar than hexanes, ethyl acetate's plates should show greater  $R_f$  values than those developed in hexanes because the solvent is weaker in affinity than ethyl acetate.
- $R_f$  values are only comparable in this section because solvent system is strongly polar. This effect is not caused by the sample having a compound similar in polarity to benzophenone; it is merely a poor choice of solvent as it does not clearly separate the spots for easy distinction.

**Part C: determining compounds in unknown sample ZZ.**

- 3 reference solutions are compared to the same sample ZZ to identify whether ZZ has ortho-, meta-, or para-bromonitrobenzene. The solvent used is 9:1 Hexanes:Ethyl Acetate, which is more non-polar due to its larger portion of non-polar hexanes.
- In Figure 7, the reference (ortho-bromonitrobenzene) spot is aligned with one of the unknown's spots, and the co-spot completes the image of a straight horizontal line of 3 spots. The  $R_f$  of the reference is 0.29, which is identical to the  $R_f$  of the sample's spot closer to the base line. This suggests that the unknown sample ZZ contains ortho-bromonitrobenzene.

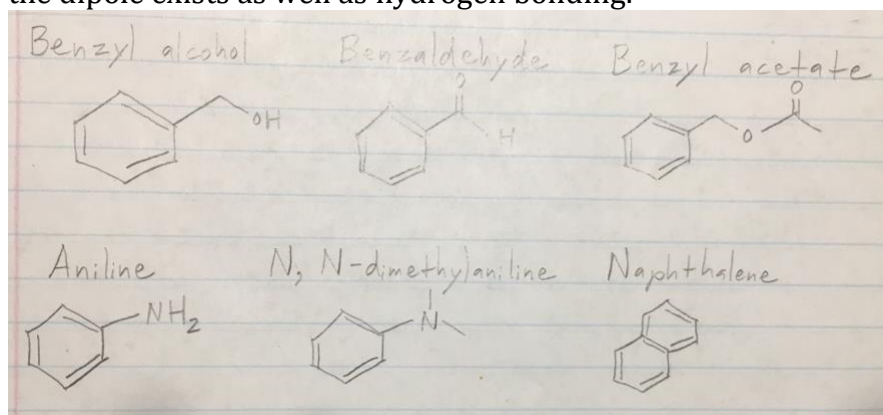
- In Figure 8, the reference (meta-bromonitrobenzene) spot is aligned with another one of the unknown's spots, and the co-spot again completes the image of a straight horizontal line of 3 spots. The  $R_f$  of the reference is 0.48, which is identical to the  $R_f$  of the sample's spot closer to the solvent front. This suggests that the unknown sample ZZ contains meta-bromonitrobenzene as well.
- However, Figure 9 shows no horizontal lines of 3 spots across. The reference (para-bromonitrobenzene) spot is not aligned with either of the two previously identified spots of ortho- and meta-bromonitrobenzene. With an  $R_f$  of 0.88, para-bromonitrobenzene is not present in the sample lane, which has 2 spots of  $R_f$  0.56 and 0.74 only, suggesting that the unknown sample ZZ cannot contain para-bromonitrobenzene.

### Sources of Error:

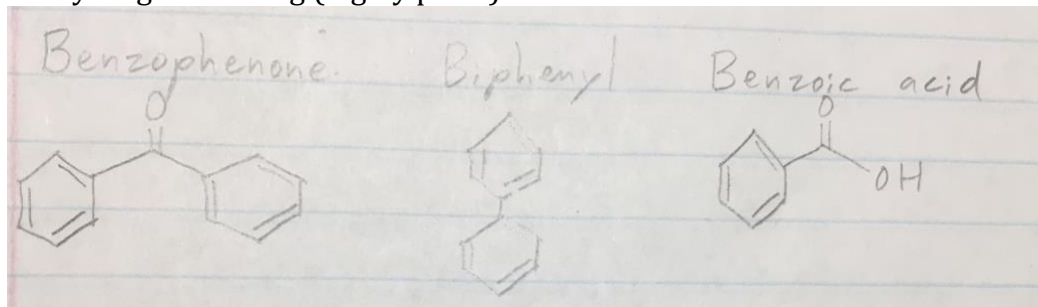
- Due to neglectful human error, the displacements of the solvent are often not measured, leading to incomplete data. Improvement would be to be more prepared for the experiment and to read the instructions more carefully.
- After TLC plate is taken out of developing jar, the solvent front should have been traced quicker for more accurate displacement of solvent.
- The measurements of displacement of the unknown compound are hastily made and might not reach the very middle of the spots. Even with a precise displacement of solvent value, the  $R_f$  would be flawed.

### Questions

1. Polarity of the solvent system affects distance that compound travels up TLC coated in silica gel. A more polar solvent system means compounds, regardless of their polarity, travel higher up the plate (higher  $R_f$ ), whereas a less polar solvent system means compounds stay low on the plate (lower  $R_f$ , ie. more hexanes mean less travel, if at all, up the TLC plate).
2. More polar a compound is, the more it performs hydrogen bonding with silica gel, the less it bonds with solvent, the less it displaces from the base line on the TLC plate. Thus, the most polar compound has the smallest  $R_f$  values.
  - a. Benzyl alcohol is the most polar compound due to its hydroxyl group, where the dipole exists as well as hydrogen bonding.



- b. Aniline would have the smallest  $R_f$  because of its polarity; it has two hydrogens that can participate in hydrogen bonding and a nitrogen with an electron pair for bonding.
- c. Benzoic acid has the lowest  $R_f$  because of its hydroxyl group ready for hydrogen bonding (highly polar).



## Raw Data

