January 24th, 2014

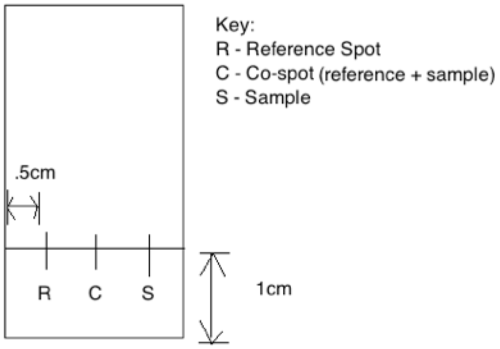
Experiment #1 - Extraction and Thin Layer Chromatography

Procedure & Observations:

Note: The lab was preformed in the order of part B, C, D, A.

- Part B:

Figure.1



1. 10.0 mL of a 2:8 mixture of ethyl acetate (EtOAc) and hexanes were added to a developing jar, a lid was then placed on the jar.
2. Two TLC plates were prepared, see figure 1.
3. In a small test tube, 10.0mg of unknown sample #69 were dissolved in 2.0mL of dichloromethane.
4. Using a capillary tube, a small amount of this sample was spotted to the co-spot and sample lanes of both TLC plates.
5. 2.0mL of a reference solution, benzophenone, was placed in a test tube. A small amount of the solution was spotted onto the reference, and then the co-spot lanes of one of the TLC plates.
6. 2.0mL of a reference solution, biphenyl, was placed in a test tube. A small amount of the solution was spotted onto the reference, and then the co-spot lanes the second TLC plate.
7. Both TLC plates were placed in a developing jar so that the silva gel layer was faced towards the center, but neither plate was in contact with the other. The cover was placed on the developing jar, the TLC plates were left in the jar until the solvent front was approximately 1cm from the top of the TLC plate.
8. The TLC plates were removed from the developing jar and a pencil mark was made at the solvent finish line. The plates were allowed to sit for approximately 1 minute.
9. Both TLC plates were placed underneath UV light. Any visible spots were lightly circled in pencil.

- Part C:

1. 10.0mL of ethyl acetate were placed into a clean developing jar. The lid was placed on the jar.
2. Steps 2-9 from part B were repeated.
3. 10.0mL of hexanes were added to a clean developing jar. The lid was placed on the jar.
4. steps 2-9 from part B were repeated.

- Part D:

1. 100.0mg of a mixture containing benzophenone and benzoic acid were placed in a 50ml Erlenmeyer flask. 10.0ml of dichloromethane were added to the same flask and the flask was swirled.
2. The solution prepared in step one was added to a secretory funnel. The Erlenmeyer flask was rinsed with approximately 5mL of dichloromethane. The risings were transferred to the secretory funnel.

3. 10.0mL of a 2M solution of NaOH were added to the secretory funnel. A stopper was placed on the secretory funnel, it was then inverted and shaken for approximately 30 seconds.
4. The secretory funnel was placed on a wooden rack and the aqueous and organic layers were allowed to separate. The lower phase (organic) was allowed to drain into a 50mL Erlenmeyer flask
5. The upper phase (aqueous) was allowed to drain into a 125mL Erlenmeyer flask.
6. The solution within the 50mL Erlenmeyer flask was re-added to the secretory funnel, steps 3-5 were repeated twice more.
7. Two TLC plates were prepared (see figure 1.) The solution prepared in step 1 part D was used to spot the reference and co-spot lanes on both TLC plates.
8. The organic layer was used to spot the sample and co-spot lanes on one TLC plate, and the aqueous layer was used to spot that of the other TLC plate.

-Part A

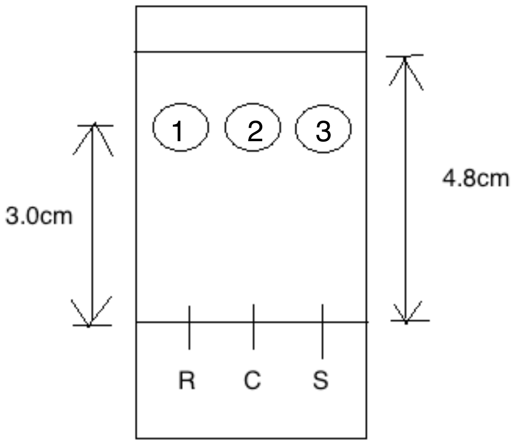
1. 1.0mL of ether, 1.0mL of distilled water, and 2 drops of a 0.006M methylene blue solution were placed in a test tube. A cap was placed on the test tube and it was shaken for roughly 15 seconds.
2. 1.0mL of ether, 1.0mL of distilled water, and 2 drops of a 0.006M methylene blue solution were placed in a test tube. A cap was placed on the test tube and it was shaken was roughly 15 seconds.
3. The contents of the test tubes from steps 1 & 2 were mixed. A cap was placed on the test tube and the tube and it was shaken for roughly 15 seconds
4. 5.0mL of distilled water, 1 drop of 0.003M aqueous crystal violet and 0.5mL of 1-butanol were placed into two different test tubes. A cap was placed on both test tubes and they were shaken for roughly 5 seconds.
5. Sold NaCl was added to one of the test tubes until a small amount precipitated. This test tube was then shaken again until the salt dissolved.

Observations:

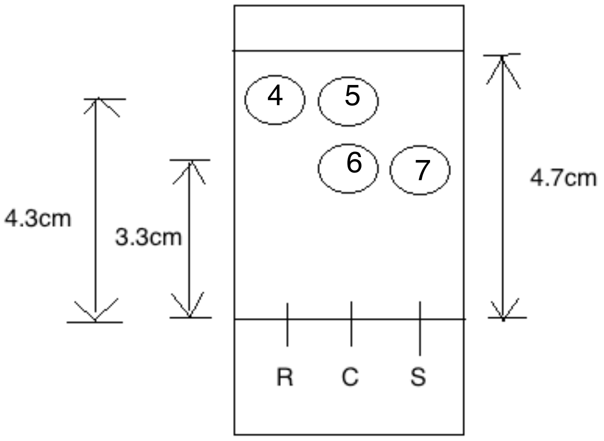
- Part B:

Sketches of TLC plates:

TCL Plate #1
(EtAOc:Hexanes 2:8)



TCL Plate #2
(EtAOc:Hexanes 2:8)



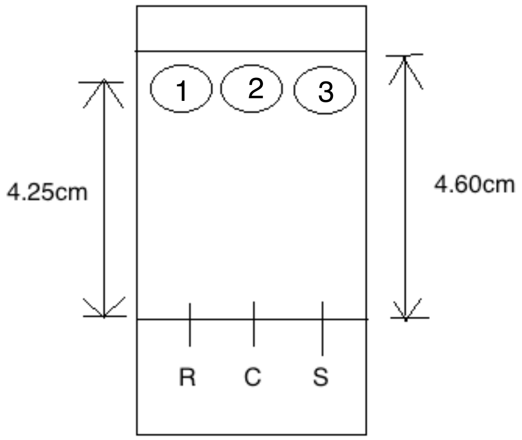
Spot(s)	Compound(s)	Solvent of TLC	Height raised(cm)	Rf Value TLC #1
1	Benzophenone	EtAOc:Hexanes 2:8	3.0	0.62
2	Benzophenone, unknown sample #69 + dichloromethane	EtAOc:Hexanes 2:8	3.0	0.62
3	Unknown sample #69 + diochlormethane	EtAOc:Hexanes 2:8	3.0	0.62
4,5	Biphenyl	EtAOc:Hexanes 2:8	4.3	0.91
6,7	Unknown sample #69 + dichloromethane	EtAOc:Hexanes 2:8	3.3	0.70

We notice that on both TLC Plate #1 and #2, the unknown sample 69 had the exact same Rf value as benzophenone. Therefore we can conclude confidently that the unknown solution has a polarity extremely similar to that of benzophenone. We note that the relative polarity of benzophenone is very low.

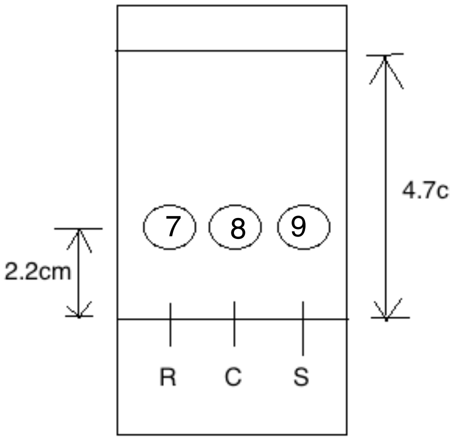
- Part C:

Sketches of TLC plates:

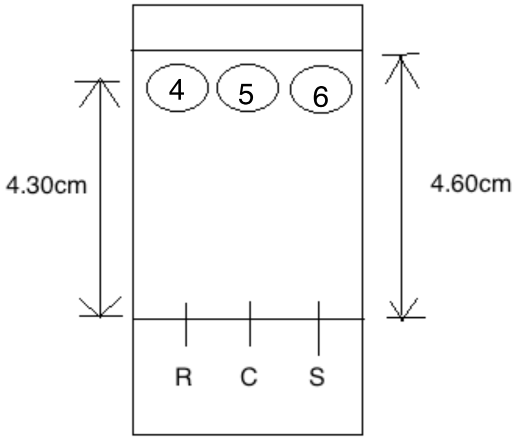
TLC Plate #1
(EtOAc)



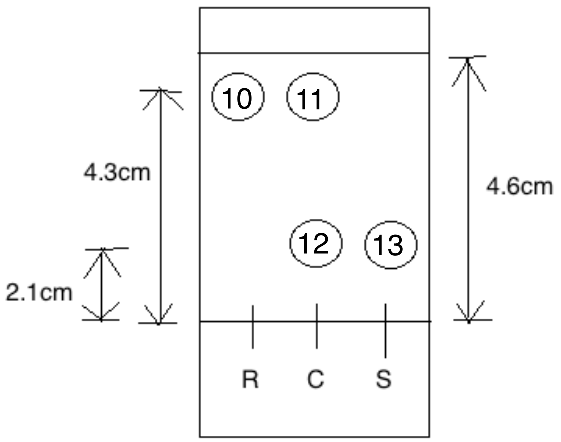
TLC Plate #3
(Hexanes)



TLC Plate #2
(EtOAc)



TLC Plate #4
(Hexanes)



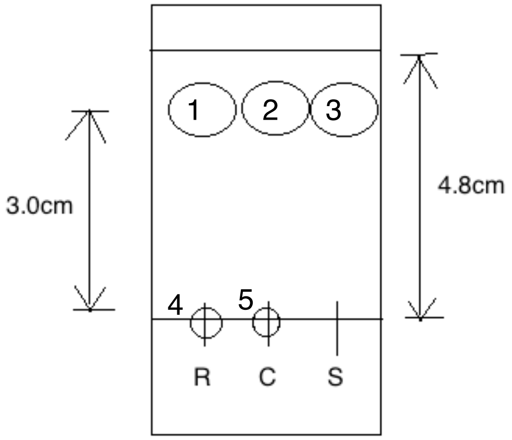
Spot(s)	Compound(s)	Solvant of TLC	Height raised (cm)	Rf Value
1	Benzophenone	EtOAc	4.25	0.92
2	Benzophenone, Dichloromethane and Unknown compound #69 solution	EtOAc	4.25	0.92
3	Dichloromethane and Unknown compound #69 solution	EtOAc	4.25	0.92
4	Biphenyl	EtOAc	4.30	0.93
5	Biphenyl, Dichloromethane and Unknown compound #69 solution	EtOAc	4.30	0.93
6	Dichloromethane and Unknown compound #69 solution	EtOAc	4.30	0.93
7	Benzophenone	Hexanes	2.2	0.47
8	Benzophenone, Dichloromethane and Unknown compound #69 solution	Hexanes	2.2	0.47
9	Dichloromethane and Unknown compound #69 solution	Hexanes	2.2	0.47
10,11	Biphenyl	Hexanes	4.3	0.93
12,13	Dichloromethane and Unknown compound #69 solution	Hexanes	2.1	0.46

By changing the solvent from one that is considerable polar to one that is non polar, namely from ethyl acetate to hexane, we reduce the attraction any polar compounds will have to the solvent, and therefore their attraction to the silica gel increases. More precisely, the slightly polar benzophenone and compound #69 (determined to have a very similar polarity to benzophenone in part B) are *more* attracted to the silica gel than the hexane, and therefore have a small Rf value. When pure Ethyl Acetate is used as the solvent, benzophenone and compound #69 are *more* attracted to the solvent than the silica gel, and therefore have a larger Rf value as they are drawn up the plate.

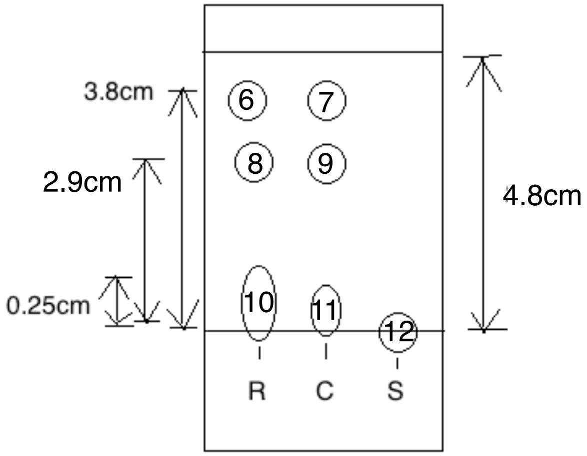
- Part D:

Sketches of TLC plates:

TLC Plate #1
(EtAOc:Hexanes 2:8)



TLC Plate #2
(EtAOc:Hexanes 2:8)



Spot(s)	Compound(s)	Solvent of TLC	Height raised(cm)	Rf Value TLC #1
1	Benzophenone, dichloromethane	EtAOc:Hexanes 2:8	3.0	0.62
2	Dichloromethane, Benzophenone	EtAOc:Hexanes 2:8	3.0	0.62
3	Organic phase	EtAOc:Hexanes 2:8	3.0	0.62
4	benzoic acid, dichloromethane	EtAOc:Hexanes 2:8	4.3	0.91
5	dichloromethane, benzoic acid	EtAOc:Hexanes 2:8	3.3	0.70
6,7	Suspected Impurity	EtAOc:Hexanes 2:8	3.8	0.79
8,9	benzophenone, dichloromethane	EtAOc:Hexanes 2:8	2.9	0.60
10,11	benzoic acid	EtAOc:Hexanes 2:8	0.75	0.16
12	Aqeuos layer	EtAOc:Hexanes 2:8	0	0

By examining TLC plate #1, and the table containing the Rf values, we see that the organic phase has the exact same Rf as benzophenone. Since benzophenone was intact the organic material we tried to isolate via reactive extraction, we can conclude that with respect to benzophenone, the extraction was successful. Furthermore, we again notice that the Rf values of both the aqueous layer and benzoic acid are identical. As benzoic acid was the polar compound we tired to isolate we can conclude that our reactive separation was also successful in isolating benzoic acid.

- Part A:

Observations Table 1: Part A

Appearance of layers with methylene blue added	- Clear, transparent top layer - Blue, translucent bottom layer
Appearance of layers with methyl red added	- Clear, translucent top layer - light reddish-orange translucent bottom layer
Appearance of layers with methylene blue and methyl red solutions	- clear, translucent blue bottom layer - clear, translucent red top layer
Appearance of tube without salt	- uniform dark, translucent purple.
Appearance of tube with salt	- cloudy white translucent bottom layer - dark purple, translucent top layer

Observations Table 2: Part A

Compound	Mixture	Soluble- in	Polarity
Test tube 1: methylene blue	ether, methylene blue, water	water	polar
Test tube 2: methyl red	ether, methyl red, water	ether	non-polar
Crystal violet	1-butanol, water, crystal violet	both	slightly polar
NaCl	1-butanol, water, NaCL	water	polar

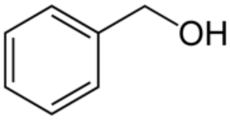
We note that methylene blue is polar, and methyl red is non-polar. Therefore and extraction using ether as the organic phase and water as the aqueous phase would in fact be a good way to separate a mixture of these two compounds. This was proved by mixing the contents of test tubes 1 and 2, and noticing the methylene remanned in the water layer while methyl red remained in the organic ether layer and moreover the water and ether existed as separated phases in the same test tube.

Adding NaCl to a test tube containing water, 1-butanol and crystal violet decreased the amount of dye in the aqueous layer. This is likely because the NaCl dissociated to form Na+ and Cl- ions that are attracted more strongly to the polar dipoles of the water molecules than the crystal blue. This effectively tied up more of the dipoles of the water molecules decreasing the number of bonds that could be made to the crystal violet dye, and so its concentration in the aqueous layer decreased.

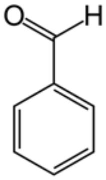
Questions:

1. The greater the polarity of a compound, the more attraction it will have to the silva gel, and the smaller its Rf value will be. By increasing the polarity of the solvent, you effectively increase the attraction between polar compounds and the solvent, increasing their Rf values. Note that the reverse is true, namely to decrease the polarity of the solvent will decrease the attraction between polar compounds and the solvent decreasing their Rf values.
2. a)

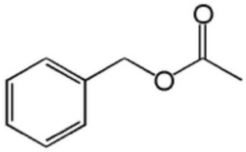
- Benzyl alcohol



- benzaldehyde



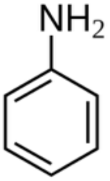
- benzyl acetate



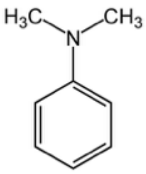
Since benzyl alcohol is the most polar of these three compounds, it would be the most attracted to the silva gel layer and therefore it would move the shortest distance up the plate. This would give it the lowest Rf value of the listed compounds, since Rf = (distance travelled up the plate/distance the solvent front travels up the plate).

b)

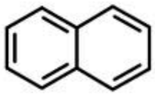
- Aniline



- N, N-dimethylaniline



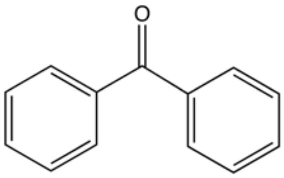
- naphthalene



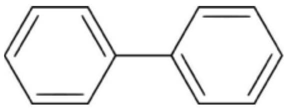
c)

Since aniline is the most polar of these three compounds, it would be the most attracted to the silva gel layer and therefore it would move the shortest distance up the plate. This would give it the lowest Rf value of the listed compounds, since Rf = (distance travelled up the plate/distance the solvent front travels up the plate).

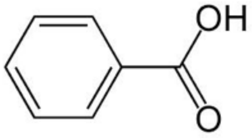
- Benzophenone



- Biphenyl



- Benzoic acid



Since benzoic acid is the most polar of these three compounds, it would be the most attracted to the silva gel layer and therefore it would move the shortest distance up the plate. This would give it the lowest Rf value of the listed compounds, since Rf = (distance travelled up the plate/distance the solvent front travels up the plate).

3. Ethanol and water are both very polar compounds, and so they would both mix with polar compounds, yielding an aqueous layer containing both ethanol, water and any polar compounds used in the extraction. This would make the extraction difficult because the aqueous layer would consist of both eluting solvents and any polar compounds you wished to extract.

4. Adding NaCl to a test tube containing water, ether and methylene blue would decrease the amount of dye in the aqueous layer. This is because the NaCl would dissociate to form Na+ and Cl- ions that would be attracted more strongly to the polar dipoles of the water molecules than the methylene blue. This would effectively tie up more of the dipoles of the water molecules decreasing the number of bonds that could be made to the methylene dye, and so its concentration in the aqueous layer would decrease.

5.

$KD = [A]_{\text{solvent 1}}/[A]_{\text{solvent 2}}$

$KD = (W1/V1)/(W2/V2)$

$$KD = [A]_{\text{solvent 1}}/[A]_{\text{solvent 2}}$$
$$= (2.0g/100mL)/(20.0g/100mL)$$
$$0.10$$

$$KD = (W1/V1)/(W2/V2)$$
$$0.10 = (1.8g-W2/100mL)/(W2/100mL)$$
$$W2 = 1.8g/1.1$$
$$= 1.6g$$

Therefore the mass of compound y removed from the water solution by extraction with ether is 1.6g

6.

Extraction 1

$$KD = (W1/V1)/(W2/V2)$$
$$0.10 = (1.8g-W2/100mL)/(W2/50mL)$$
$$W2 = 1.8g/1.2$$
$$= 1.5g$$

So! 1.8g - 1.5g = 0.3g remains.

Extraction 2

$$KD = (W1/V1)/(W2/V2)$$
$$0.10 = (0.3g-W2/100mL)/(W2/50mL)$$
$$W2 = 0.3g/1.2$$
$$= 0.2g$$

total mass removed = 1.5g + 0.2g = 1.7g

Therefore the mass of compound y removed from the water solution by two extractions with ether is 1.7g

7. By adding a drop of water to the solution and carefully noting which layer the water droplet associates itself with, the student could confidently determine the aqueous layer as the layer in which the water droplet was drawn.

8. In order to separate a mixture of benzyl amine and naphthalene a reactive extraction could be used. To preform this extraction, a strong acid such as HCL could be used in order to cause the organic base (benzyl amine) to become positively charged (forming a polyatomic ion while leaving the naphthalene unaffected. The positive charge would then cause the benzyl amine to be polar, and thus it would dissolve in a aqueous water layer. Carrying out the reaction in a seperatory funnel using water as the aqueous and ether as the organic solvent, you will end up with the charged benzyl amine in the aqueous layer and ether remaining in the organic phase. Next, introduce a strong base such as NaOH to the aqueous layer in order to deprotanate the benzyl amine and return its charge to zero. Use a secretory funnel with water as the aqueous phase and ether as the organic phase once again, this will effectively isolate the benzyl amine in the organic phase and the inorganic salts will remain in the aqueous phase. Finally, the benzyl amine can be dryer by using a drying agent such as MgSO4, or even boiling of the ether (ether has a very low boiling point, approximately 30 degrees celsius, so leaving it in a warm room would also dry the benzyl amine).

Discussion/ Conclusion:

In Part A of this lab, we placed two dies of varying polarity (methylene blue and methyl red) in different test tubes containing a solutions of ether and distilled water. By examining the layer that contained the die, we were able to comment on the relative polarity of the dyes. It was found that methylene blue was polar, while methyl right was non-polar. Next, the hypothesis was made that by using ether and water, a solution of methyl red and methylene blue could be successfully separated. This hypothesis was then tested by intact mixing the contents of the two aforementioned test tubes. It as observed that the methyl red remained in the ether, while the methylene blue remained in the water, and importantly the water and ether layer existed as separate phases, therefore our hypothesis was confirmed. Next, we prepared two test tubes that contained distilled water, aqueous crystal violet, and 1-butanol. We then added NaCl to one of the two test tubes, and noticed that most of the dye was forced out of the water layer. This can be explained by the simply fact that the water and 1-butanol was more attracted to the ion formed by placing NaCl in the test tube(namely Na+ and Cl-) and so less bonding opportunity was available for the crystal violet, which began to form its own layer int the tube .

In part B of this lab TLC was used to compare the Rf values of an unknown compound (#69) to reference solutions of benzophenone and biphenyl. The two TLC plates were developed in a 2:8 mixture of ethyl acetate. It was observed that the Rf value of the unknown compound #69 and benzophenone were identical, and so the postulate was made that the relative polarity of compound 69 must be extremely similar to benzophenone (which is notably, only very slightly polar).

In part C of this lab, TLC was carried out much the same way as in part B. This time four TLC plates were developed. Plates containing the unknown compound 69 and benzophenone as the reference solution were developed in ethyl acetate and then pure hexanes as the solvent. The same was done with two plates containing unknown 69 and biphenyl as the reference. Again, it was observed across all plates that the Rf values of benzophenone and unknown compound 69 were identical, offering further evidence for our postulate made in part B. More notably, it was observed that reducing the polarity of the solvent decreased the Rf values of the slight polar compounds (compound 69 and benzophenone) while have almost no affect on the non-polar compounds (biphenyl). And explanation for this is stated in question 2 of the questions section.

In Part D of this lab, an extraction was preformed to extract each of benzophenone and benzoic acid from a solution prepared containing both compounds. NaOH was used to reactively separate these two compounds. Once the organic phase was isolated from the aqueous phase, it was then run through the secretory funnel twice more with NaOH. On completion, the organic phase (presumably containing the benzophenone) was used to spot a TLC plate, while the original mixture of benzophenone and benzoic acid was used as the reference. A second TLC using the same reference was spotted using the aqueous phase separated during the first extraction. It was observed that benzophenone and the organic phase had identical Rf values, and that the same was true for benzoic acid and the aqueous phase. This allows us to conclude we that the extraction was successful. As noted in observations, spots 6 and 7 on TLC plate #2 in part D are believed to be impurities, likely of biphenyl. This was deduced by noticing that their Rf values correspond to that of biphenyl in part b, were it was used as a reference in the same solvent. The likely source of this impurity is from the capillary tube, as we did not use a fresh one each time, biphenyl residue may have existed on the tube we used to spot the plate containing the impurities in part D.