Acid-Catalyzed Small Ring Alcohols and Alkenes: An Artistic Approach to Visualizing Relationships Between Features Produced by UV-Visible Spectra

Madeleine Ware

Mitch Menzmer, Ph.D., Marc Boyson, MFA

Department of Chemistry

Southern Adventist University

Abstract

Southern Adventist University students completing physical-organic research projects supervised by Dr. Mitch Menzmer have performed numerous acid-catalyzed reactions involving groups of cyclopentanols, cyclohexanols, cyclopentenes, and cyclohexenes. In these reactions, a small ring alcohol or alkene, methylated or unmethylated, is protonated to form a cycloalkane and an allylic carbocation.[1] Dr. Menzmer utilizes UV-visible spectrophotometry to study the kinetics surrounding the formation of these allylic carbocations. In this particular work, we develop artistic analysis methods by which to search for uncharacterized relationships between the initial structures of the analyzed molecules and the wavelengths of maximum absorbance for features observed within a given spectrum, namely lambda max. Secondly, we use these methods to determine how changes in temperature, percent sulfuric acid (acidity), and position at which a ring is alkylated might influence the wavelength where lambda max absorbance occurs. Most lambda max peaks for acid-catalyzed formation of allylic carbocations via cyclohexanols, cyclopentanols, cyclohexenes, and cyclopentenes were located at wavelengths between 280 and 320 nanometers. Lambda max wavelengths seemed to undergo a bathochromic shift as temperature rose in 2-methylcyclopentanol, cyclohexene, and 4-methylcyclohexene. In experiments with cyclohexanol, 3-methylcyclohexanol, and 4-methylcyclohexanol lambda max appeared to undergo a hypsochromic shift as acidity increased. Cyclohexene, cyclopentene, and cyclohexanol all showed a significant increase the wavelength position of lambda max as the methyl group was added and moved further from the original position of proton attack (the hydroxyl group or double bond). Ring size did not seem to play a large part in the positioning of lambda max as both five and six membered rings showed peaks within +/- 5 of 300 nanometers on average.

Introduction

Over the last decade, Southern Adventist University students completing research projects supervised by Dr. Mitch Menzmer have observed numerous acid-catalyzed reactions involving groups of cyclopentanols, cyclohexanols, cyclopentene, and cyclohexene using UV-visible spectrophotometry. In the simplest, most representative reaction, a small ring alcohol or alkene, methylated or unmethylated, is protonated to form an alkane and an allylic carbocation.[1] A cycloalkene is protonated forming a second-degree carbocation in the first step (Figure 1a). This step is expected to be rate determining since an unstable, second-degree carbocation is formed. In the second step, a hydride is abstracted from the alpha position of the alkene and transferred to the carbocation, forming both an allylic carbocation and a cycloalkane (Figure 1b).[2,3] Due to their conjugated nature as well as the sulfuric acid matrix in which the reaction takes place, allylic carbocations are more stable than other carbocations, allowing them to have an extended half-life of days rather than hours.[3] When analyzed using a UV-visible spectrophotometer, most of the molecules had a single, mostly symmetrical, maximum absorbance peak between 275 and 307 nanometers.[1] The molar absorptivity for these allylic ring cations is approximately 10,000, causing them to produce very large absorbance signals.[3] Extended time in sulfuric acid, resonance, a strong absorbance signal, and lambda max within the wavelength range of commercially available UV-visible spectrophotometers, allow the allylic carbocations to be readily analyzed.

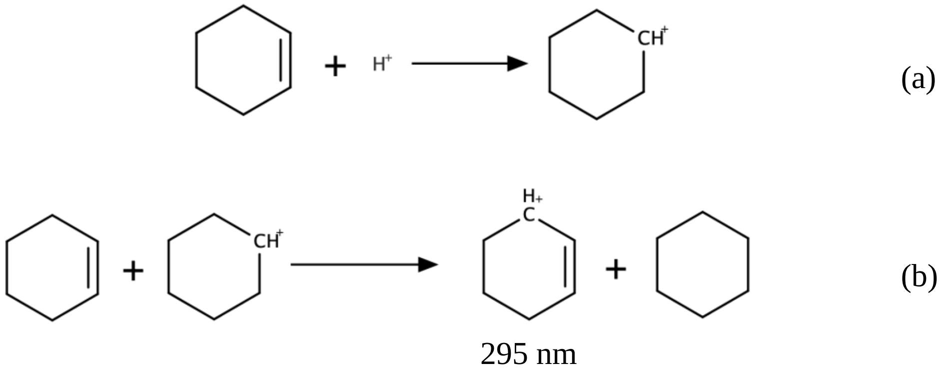


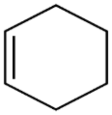
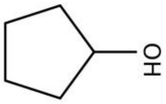
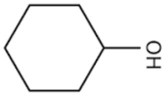
Figure 1. *Acid -catalyzed formation of an allylic carbocation via cyclohexene*

The relationship between the wavelength of maximum absorbance for allylic carbocations (lambda max) observed within a given spectrum, and the initial structures of molecules analyzed have not yet been characterized. In this work, we probe for bathochromic or hypsochromic shifts in the position of lambda max due to variation in the molecule's alkylation position. Additionally, we investigate how the temperature and acidity of a particular reaction may influence lambda max positioning. Although this particular physical-organic work is used primarily to help chemists better understand the kinetics of acid-catalyzed reactions, the findings from this research may be useful as a point of reference in predicting the structures of unknown molecules from their spectral features. Moreover this project seeks to involve an interdisciplinary approach by discussing how artistic analysis might be used to inform data interpretation techniques. Lastly, conclusions from the work may be used suggest future projects for students participating in chemistry research at Southern.

Determination of Wavelength Ranges for Spectral Features

We sought to determine the range of wavelengths over which lambda max appears for reactions with various molecules. Reaction spectra were sorted into four groups based on starting material: cyclohexanols, cyclopentanols, cyclohexenes, and cyclopentenes (Table 1).

Table 1. Basic reaction starting materials

Molecule	**Name**
	Cyclopentene
	Cyclohexene
	Cyclopentanol
	Cyclohexanol

For each spectrum analyzed, several notable components and their affiliated wavelengths were recorded, lambda max, minor peaks, and shoulders (Figure 2). The temperature and acidity were also recorded for each reaction.

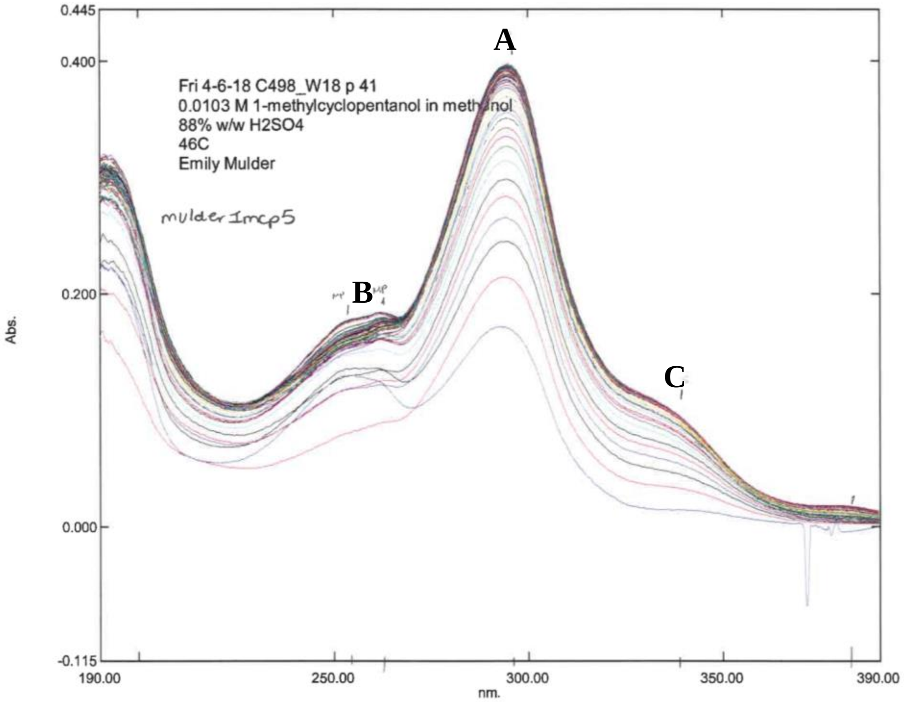
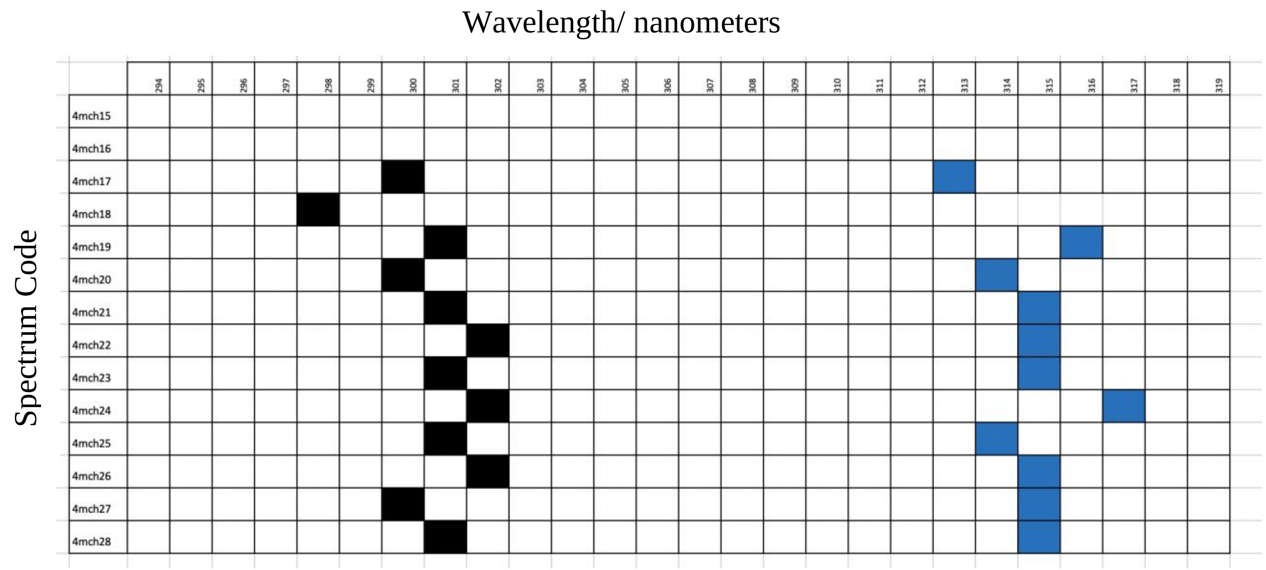


Figure 2. *UV-visible spectrum for 1-methylcyclopentanol.*
A: lambda max B: minor peak C: shoulder

Wavelengths at which spectral features occurred were entered into Microsoft Excel and tagged with colors according to feature type (Figure 3, Table 2). Figure 3 provides an example of the data input method used for each reaction analyzed. Each row in the sheet represents a multiple time series absorbance spectrum produced from one reaction and columns are wavelengths in nanometers (Figure 3, Table 3).



	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319
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Figure 3. *Spectral feature between 294 and 319 nanometers given by 4-methylcyclohexanol reactions. Black: Lambda max Blue: Shoulder*

Table 2. Spectral features by color.

Feature	**Color**
Major Peak	Black
Minor Peak	Red
Shoulder	Blue
*Other**	Green, Orange, Purple

* “Other” peak types were not used to inform conclusions

Unique codes were assigned to each type of reaction spectra (Table 3). A total of 175 spectra collected from reactions with cyclopentenes, cyclohexenes, cyclopentanols, and cyclohexanols were sorted analyzed using this method (Appendices A, B).

Table 3. Spectrum Codes

Starting Material	Code
cyclohexanol	chx
2-methylcyclohexanol	2mchx
3-methylcyclohexanol	3mchx
4-methylcyclohexanol	4mchx
cyclopentanol	cpx
1-methylcyclopentanol	1mcpx
2-methylcyclopentanol	2mcpx
3-methylcyclopentanol	3mcpx
Cyclohexene	chex
3-methylcyclohexene	3mchex
4-methylcyclohexene	4mchex
Cyclopentene	cpex

*x = spectrum 1, 2, 3, 4, 5 …. ect.

Generally, individual spectral features produced by each molecule type were clustered within a certain range of wavelengths. An average wavelength range was estimated for each spectral feature by starting material (Table 4, Appendices A, B)

Table 4. Average wavelength ranges for lambda max, shoulders, and minor peaks by starting material. Estimated from figures in Appendices A and B.

Starting Material	Lambda Max/nm	Shoulder/nm	Minor/nm
Cyclohexanol	282-313	311-338	333-436
Cyclohexene	290-317	N/A	N/A
Cyclopentanol	289-335	311-340	348-426
Cyclopentene	290-300	309-315	N/A

*****N/A indicates a small sample size and/or a lack of significant trends

In congruence with previous findings, lambda max (allylic carbocation) ranges were clustered around 300nm regardless of starting material.[1] The majority of minor peaks appeared in ranges that were distinct from those produced by major peaks. Cyclopentanol wavelength ranges for lambda max appear to be wider and shifted toward higher wavelengths than any other starting material. The experiments performed on cyclopentene contain less variety in methylation position than any other starting material analyzed, which may have led to the narrower wavelength ranges observed in major peaks and shoulders. Cyclohexene and cyclohexanol showed relatively similar lambda max positioning. The majority of cyclopentenes show shoulders while most cyclohexenes do not. This may be due in part to the fact that students performing experiments with cyclohexene in the Fall of 2019 did not scan wavelengths as high as in previously completed projects. A portion of the experiments from reactions with cyclohexene and cyclopentene did not include UV-Visible spectrophotometry scans to 500nm but instead only showed peaks to 320nm. Therefore, expected minor peaks beyond 320nm did not appear (Appendix B). The preliminary findings in Table 4 provided us with a basis to further examine the variation in lambda max positioning by starting material as well as other experimental parameters such as temperature and acidity.

Effects of Temperature, Acidity, and Methylation

We aimed to determine whether reaction temperature, reaction acidity, or location of proton attack on the starting material might have an effect on the wavelength of maximum absorbance for lambda max. Information from each starting material was sorted by prioritizing the desired conditions in two separate queries (Table 5).

Table 5. Sorting priorities for queries with starting material methylation, reaction acidity, and reaction temperature.

Query	1st Priority	2nd Priority
1	Methylation	Acidity (%H_2SO_4)
	0-4	Lowest to Highest
2	Methylation	Temperature (°C)
	0-4	Lowest to Highest

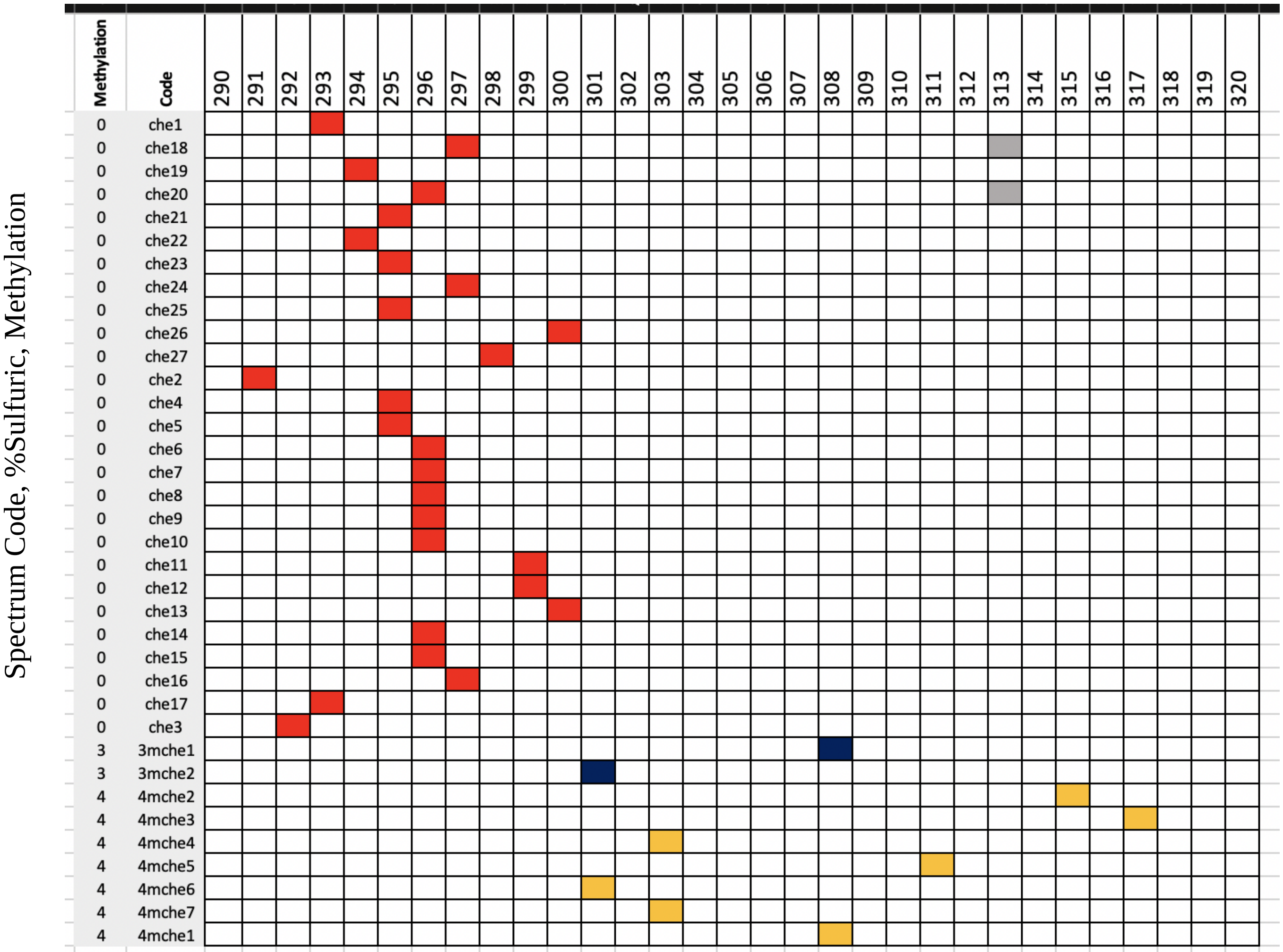
Following each query, data sets were cropped to show only wavelength ranges that included lambda max. In order to probe for general differences in lambda max positioning among homologous groups, colors were assigned to lambda max peaks according to methylation position (Table 6).

Table 6. Peak color by position of methyl group in relation to original position of attack from the proton

Methylation	Peak Color
0	Red
1	Green
2	Purple
3	Dark Blue
4	Yellow Orange

We discovered that cyclohexene and cyclohexanol all showed an increase the wavelength position of lambda max as the methyl group was added and moved further from the original position of proton attack (the hydroxyl group or double bond). Figure 4 shows cyclohexene query 1. Data was sorted by methylation then acidity, where columns are wavelengths (nm) and rows are each time series spectra's reaction acidity and starting material's methylation position (Figure 4, see Appendix C for cyclohexanol). Although there are fewer reactions with 4-methylcyclohexene as the starting material than there are reactions starting with cyclohexene, a clear shift is observed. Neither cyclopentene nor cyclopentanol showed clear trends associated with methyl group position.

Wavelength/ nanometers (280 – 320)



Spectrum Code, %Sulfuric, Methylation

Methylation	Code	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320
0	che1				🟥																											
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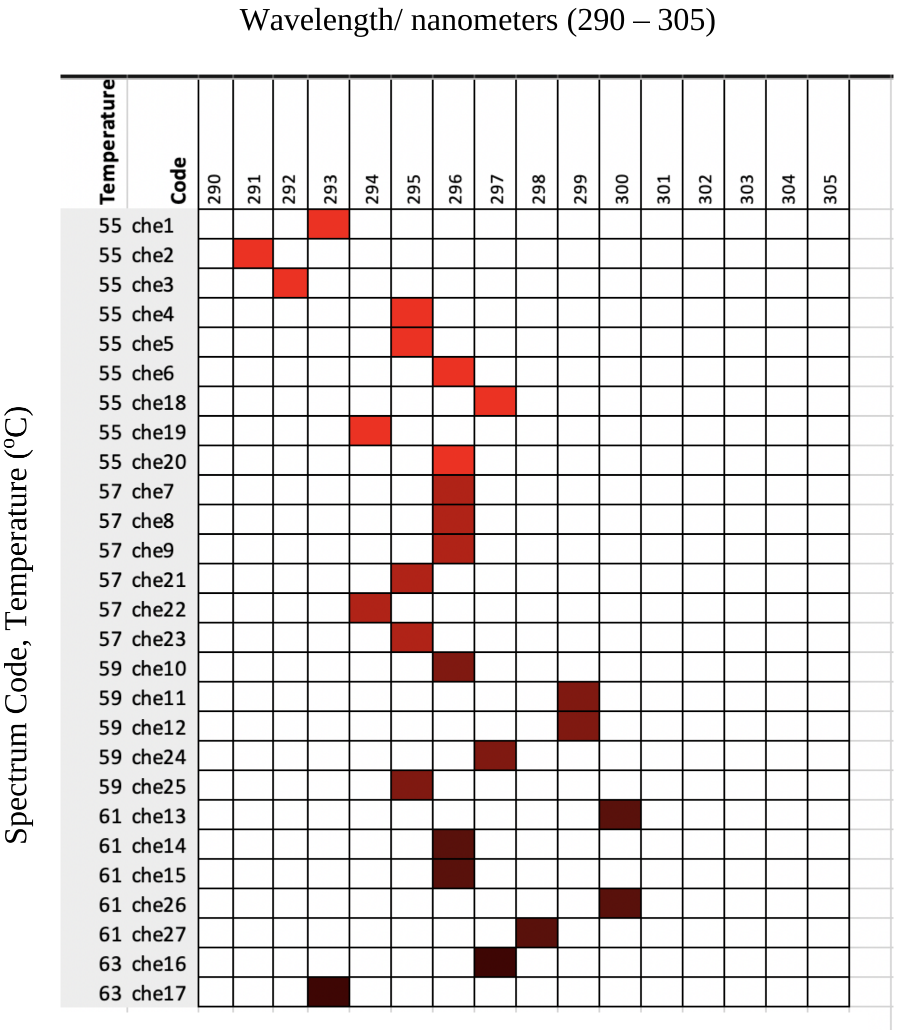
Figure 4. *Cyclohexene reactions sorted by methylation and then acidity. Lambda max peaks are marked by a color under the wavelength at which they appear.*
Red: cyclohexene Dark Blue: 3-methylcyclohexene Yellow: 4-methylcyclohexene

We explored the possibility that temperature might play a role in the wavelength position of lambda max. Using query 2, we were able to more closely observe the effects of temperature on reactions with an identical starting material (Table 5). We found that in reactions with 2-methylcyclopentanol, cyclohexene, and 4-methylcyclohexene, lambda max positioning appeared to undergo a slight bathochromic shift as temperature rose. Figure 5 shows cyclohexene query 2. Data was divided into groups by methylation then sorted by temperature, where columns are wavelengths (nm) and rows are each time series spectra's reaction temperature and starting material (Figure 5, see Appendix D, E for 2-methylcyclopentanol and 4-methylcyclohexene). The +3nm shift in lambda max for cyclohexene is visible in reactions carried out between 59°C and 61°C. No other permutations prioritizing temperature appeared to change the positioning of lambda max in a significant way.



Temperature	Code	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305
55	che1				🟥												
55	che2		🟥														
55	che3			🟥													
55	che4						🟥										
55	che5						🟥										
55	che6							🟥									
55	che18								🟥								
55	che19					🟥											
55	che20							🟥									
57	che7							🟥									
57	che8							🟥									
57	che9							🟥									
57	che21						🟥										
57	che22					🟥											
57	che23						🟥										
59	che10							🟥									
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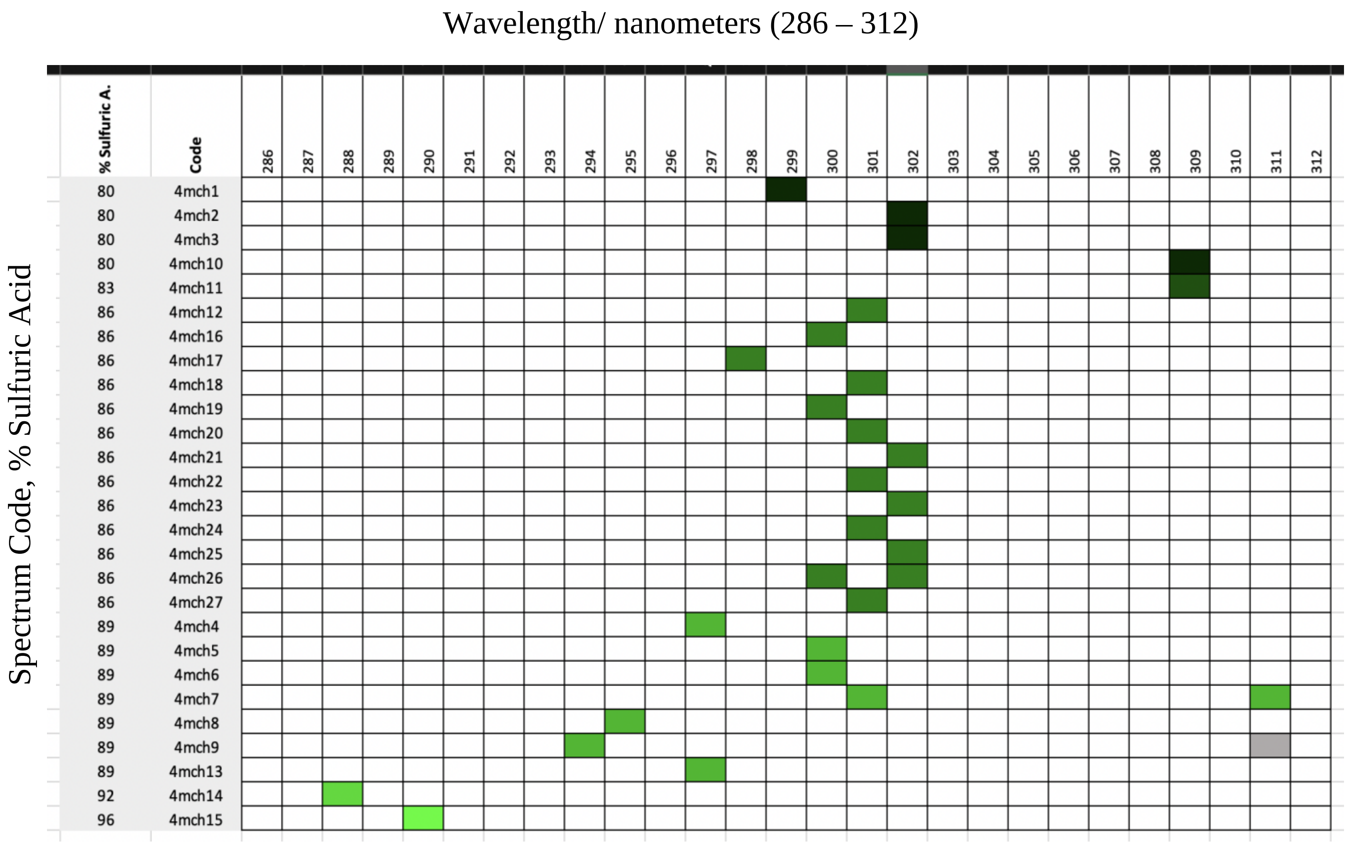
61	che15							🟥									
61	che26											🟥					
61	che27									🟥							
63	che16								🟥								
63	che17				🟥												

Figure 5. *Cyclohexene reactions sorted by temperature. Lambda max peaks are marked by a color under the wavelength at which they appear. Lighter reds indicate lower temperature while darker reds indicate higher temperature.*

Finally, we considered the possibility that % sulfuric acid could play a role in the wavelength position of lambda max. Using query 1, we were able to more closely observe the effects of acidity on reactions with an identical starting material (Table 5). The results suggested that in experiments with cyclohexanol, 3-methylcyclohexanol, and 4-methylcyclohexanol, lambda max underwent a hypsochromic shift as acidity increased (Figure 6, see Appendices F, G for cyclohexanol and 3-methylcyclohexanol). Figure 6 depicts 4-methlcyclohexanol reactions sorted by acidity, where columns are wavelengths (nm) and rows are each time series spectra's reaction acidity and starting material. The shift toward lower wavelengths in lambda max for 4-methylcyclohexanol is most visible beginning at 89% sulfuric acid (Figure 6). No other permutations prioritizing acidity appeared to change the positioning of lambda max in a significant way.



% Sulfuric A.	Code	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312
80	4mch1														🟩													
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80	4mch10																								🟩			
83	4mch11																								🟩			
86	4mch12																🟩											
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86	4mch27																🟩											
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92	4mch14			🟩																								
96	4mch15					🟩																						

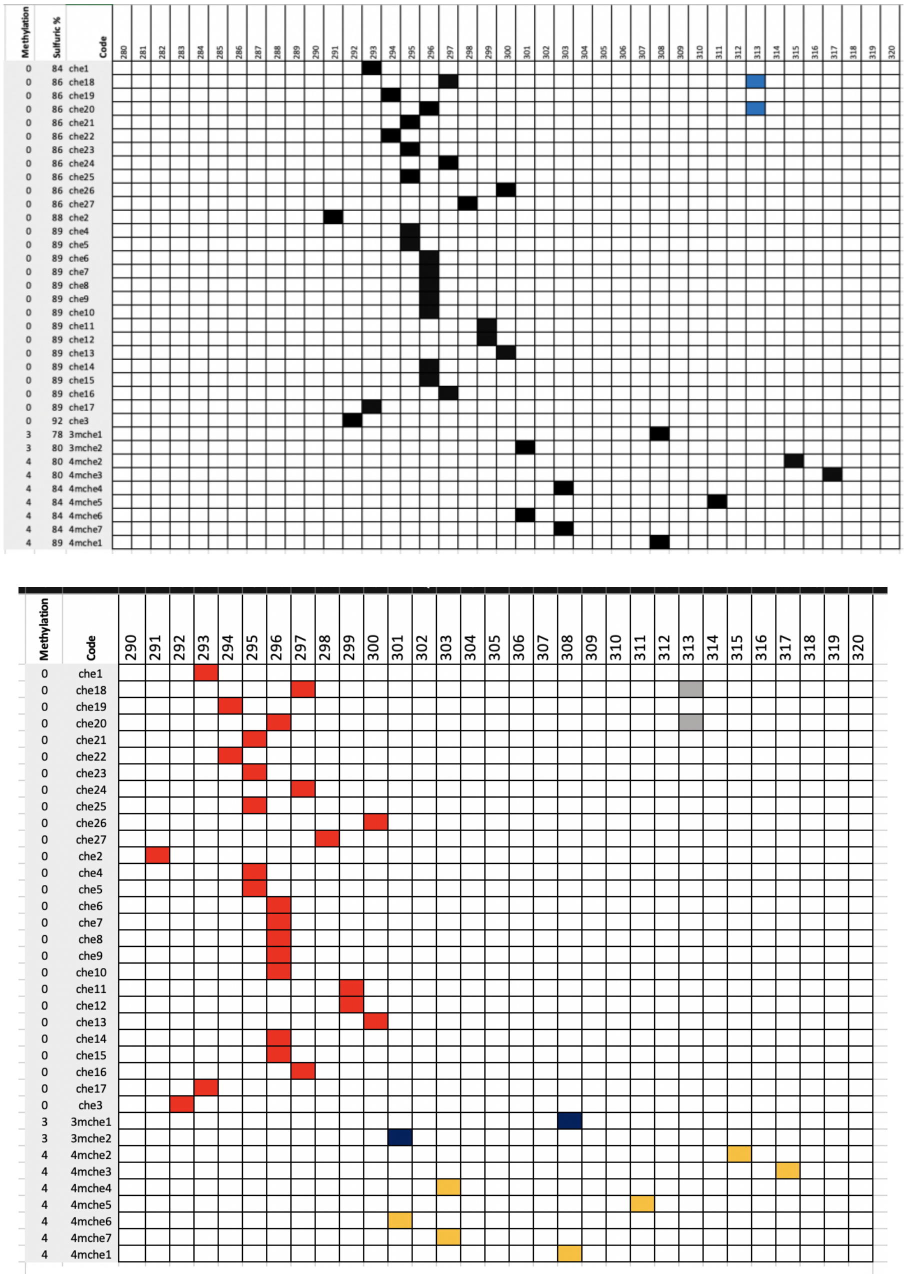
Figure 6. *4-methylcyclohexanol reactions sorted by acidity. Lambda max peaks are marked by a color under the wavelength at which they appear. Lighter greens indicate higher acidity while darker greens indicate lower acidity.*

Artistic Analysis

In the physical sciences, we use our own unique language to communicate complex ideas. Often times, understanding published works in the areas of physics and chemistry requires at least a foundational knowledge of the concepts presented in undergraduate scientific coursework. A lack of similar educational background and stark differences in communication style have contributed to a divide between the arts and sciences. This is an unfortunate obstacle that more physical scientists should attempt to overcome. It is crucial that chemists be able to effectively communicate their findings to audiences outside of the discipline, not just to obtain funding- but also to generate stronger interest in the implications of their work on society.

My particular research project faces intense communication challenges not only because it implements concepts from both organic and physical chemistry, but also due to the fact that it is largely a meta-analysis. Art can be used as tool for communicating complex concepts in a manner that provides more universal appeal than a sheet of numbers. In my work, I decided to implement artistic techniques as a way to more clearly communicate overarching themes in the project. In addition to learning about the way artists might perceive my research, throughout this process I also began to understand how artistic techniques could be used to inform the way I approached analyzing data.

Marc Boyson specializes in creating memory art from large masses of geographic data and was able to see artistic potential in my large masses of data. Boyson taught me the importance of color in directing the attention of viewers to meaningful details in a complicated picture. In analyzing artwork, Boyson usually processes colors first, then texture, and finally the relationship between texture and subject matter. As I began to sort by alkylation position, he suggested that I use bold colors to create distinctions between peaks from molecules within each homologous group. Additionally, he emphasized the concept that colors do not inherently clash. Using this information, I created several graphs with bright distinct colors to differentiate between starting material and found an immediate enhancement in my ability to interpret the information (Figure 7).



Methylation	Sulfuric %	Code	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320
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Methylation	Code	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320
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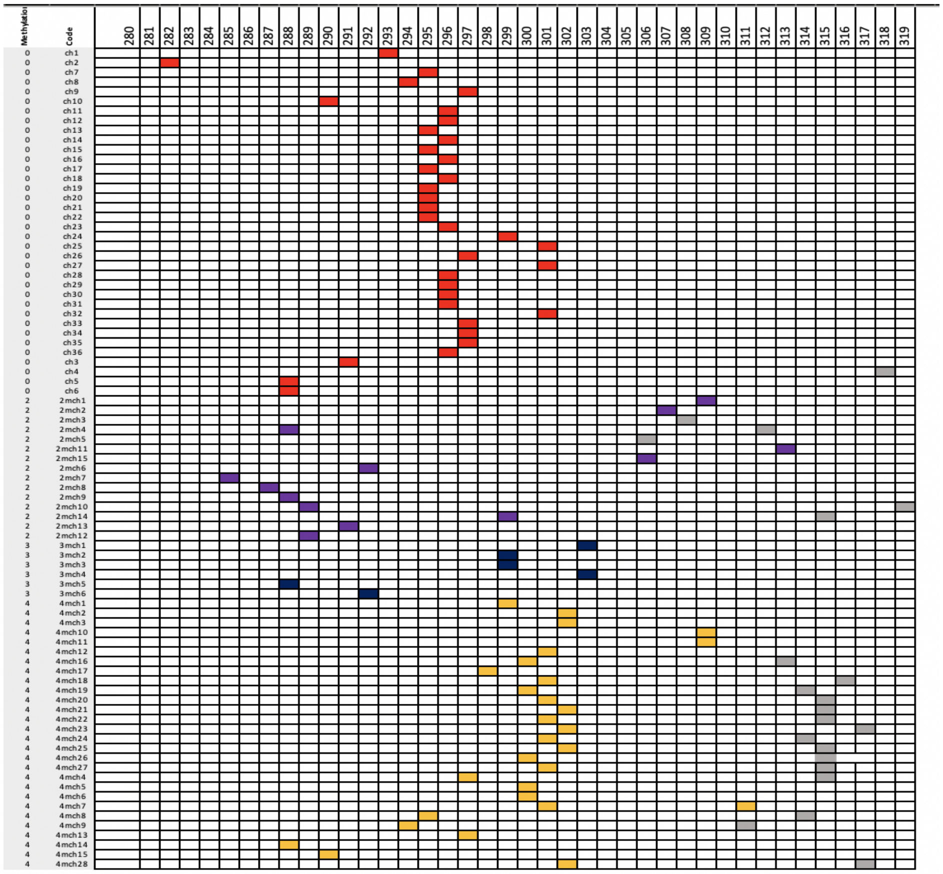
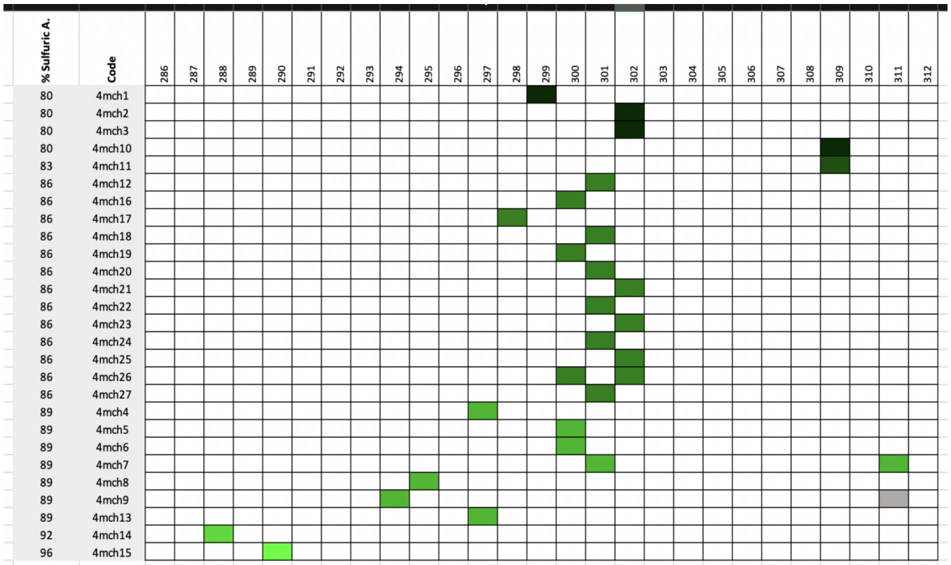
Figure 7. *Top: cyclohexene group lambda max positioning Bottom: cyclohexene group lambda max positioning after addition of color to distinguish between starting materials*

Boyson also recommended that only the most important features be represented in order to draw audience attention toward important results- like lambda max. I reduced distractions by both cropping the wavelength ranges on my data sets and by using neutral colors like gray to divert attention away from minor peaks when presenting more detailed queries (Figure 7). When I began to sort for changes in the lambda max wavelengths due to temperature and acidity, I was attempting to analyze and writeup results using overwhelming images. Boyson suggested that I create more focused charts not only for my own benefit but for audience's (Figure 8).





% Sulfuric A.	Code	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312
80	4mch1															🟩													
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83	4mch11																									🟩			
86	4mch12																	🟩											
86	4mch16																🟩												
86	4mch17														🟩														
86	4mch18																	🟩											
86	4mch19																🟩												
86	4mch20																	🟩											
86	4mch21																		🟩										
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89	4mch13													🟩															
92	4mch14				🟩																								
96	4mch15						🟩																						

Figure 8. *Top: All lambda max peaks given by cyclohexanols*
Bottom: lambda max peaks given by 4-methylcyclohexanol sorted by acidity (given in yellow on top chart)

Instead of trying to come to conclusions in the face of such a large picture of information, I used gradients created with dominant colors like red and green to better visualize patterns. Sometimes snapshots of information can more effectively communicate purpose than large albeit more complete datasets (Figure 8).

I believe that art and visual design should actually play a large role in shaping the way scientists choose to present results to any audience. Moreover, implementation of color theory throughout my analysis allowed me to interpret results more effectively. Lastly, using data snapshots not enabled me to come to more succinct conclusions in my analysis but also impacted the way I will present my work audiences in the future.

Conclusions and Future Work

In alignment with prior work, most lambda max peaks for acid-catalyzed formation of allylic carbocations via cyclohexanols, cyclopentanols, cyclohexenes, and cyclopentenes were located at wavelengths between 280 and 320 nanometers. Lambda max wavelengths seemed to undergo a bathochromic shift as temperature rose in 2-methylcyclopentanol, cyclohexene, and 4-methylcyclohexene. In experiments with cyclohexanol, 3-methylcyclohexanol, and 4-methylcyclohexanol lambda max appeared to undergo a hypsochromic shift as acidity increased. Cyclohexene, cyclopentene, and cyclohexanol all showed a significant increase the wavelength position of lambda max as the methyl group was added and moved further from the original position of proton attack (the hydroxyl group or double bond).

The findings from this work prompt me to suggest three future research projects. Our results show that only six membered rings produced a bathochromic shift in the location of lambda max associated with the methylation position moving further from the origin of proton attack. However, I believe this may be due to lack of adequate variety and sample size for experiments with five membered rings. It would be worthwhile to conduct a more focused study on a sufficient variety cyclopentenes or cyclopentanols.

Secondly, cyclohexenes showed the most variability on lambda max positioning associated with temperature increase. Future researchers should carry out a number of reactions on each type of cyclohexene (1-methyl, 2-methyl, 3-methyl, ect.) at both 55ºC and 65ºC to probe for stark differences in lambda max positioning due to temperature.

Lastly, all lambda max shifts associated with acidity were observed in cyclohexanols. Future projects might seek to increase the data pool for cyclohexanol reactions at varying acidities in order to solidify the preliminary finding of a hypsochromic shift associated with higher acidities and improve consistency.

Many trends are present in data sets from spectra produced from reactions with six membered rings. However, there was a large pool of spectra for reactions with six membered rings – a good indicator that similar trends for five membered rings may exist but are not presenting themselves due to inadequate sample size.

Acknowledgements

I would like to extend my sincere thanks to Dr. Mitch Menzmer for helping me to construct and carry out my experiment and for providing invaluable mentorship throughout the research process.

Thank you to Mark Boyson for helping me to evaluate my research from an alternative perspective and for assisting me in devising new ways to present my research to a variety of audiences.

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Lastly, I would like to thank the entire Chemistry Department at Southern Adventist University for inspiring me to put forth my best effort and for reminding me to always continue pursuing my goals.

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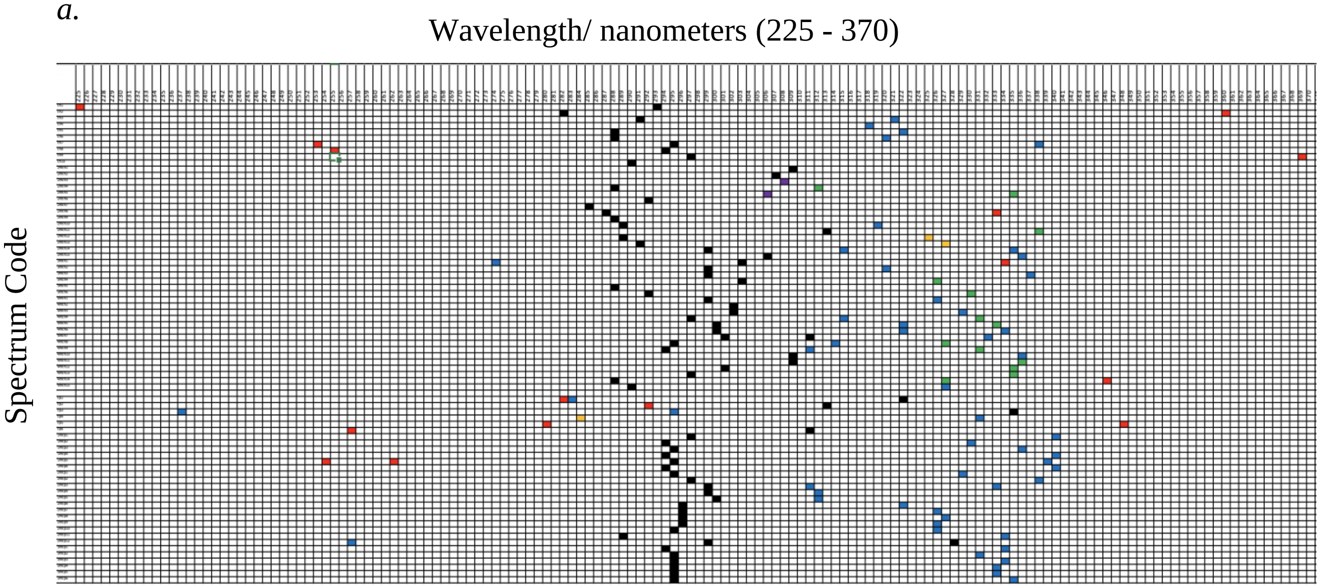
Appendices

Determination of Wavelength Ranges for Spectral Features

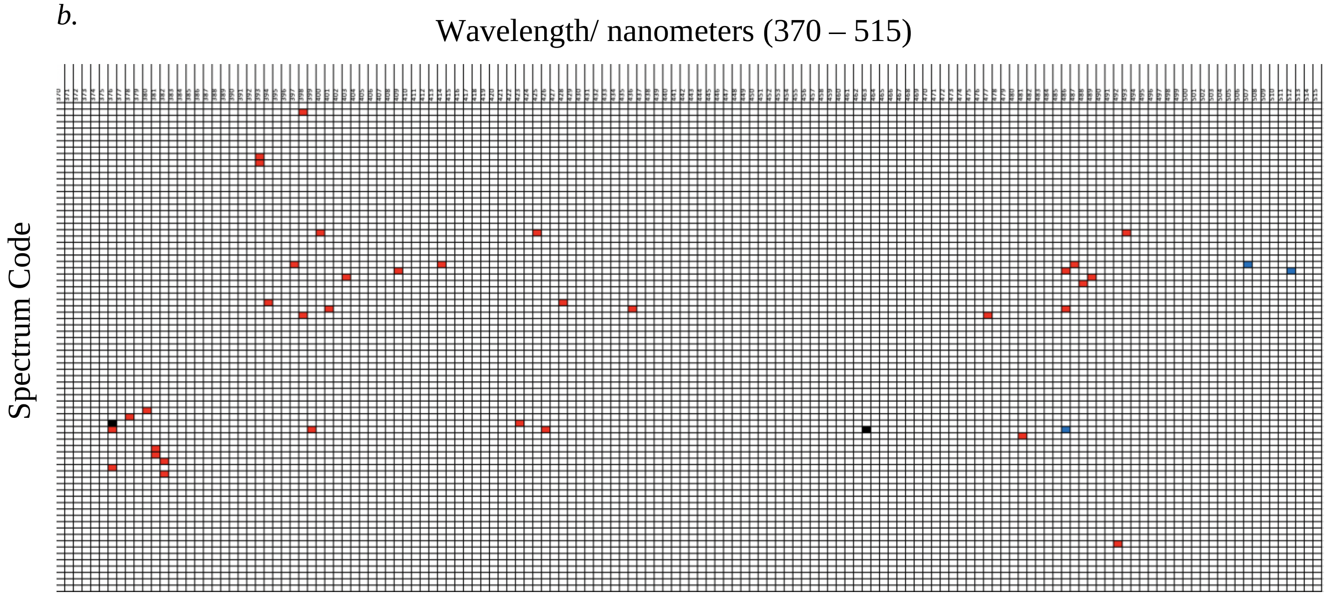
A. Cyclohexanol and Cyclopentanol

Peak absorbance wavelengths of major peaks, minor peaks, and shoulders for cyclohexanols and cyclopentanols. Part a shows peaks at wavelengths from 225 to 370 nanometers. Part b shows peaks at wavelengths from 370 to 515 nanometers. Table 2 gives the peak type associated with each cell color.

a.

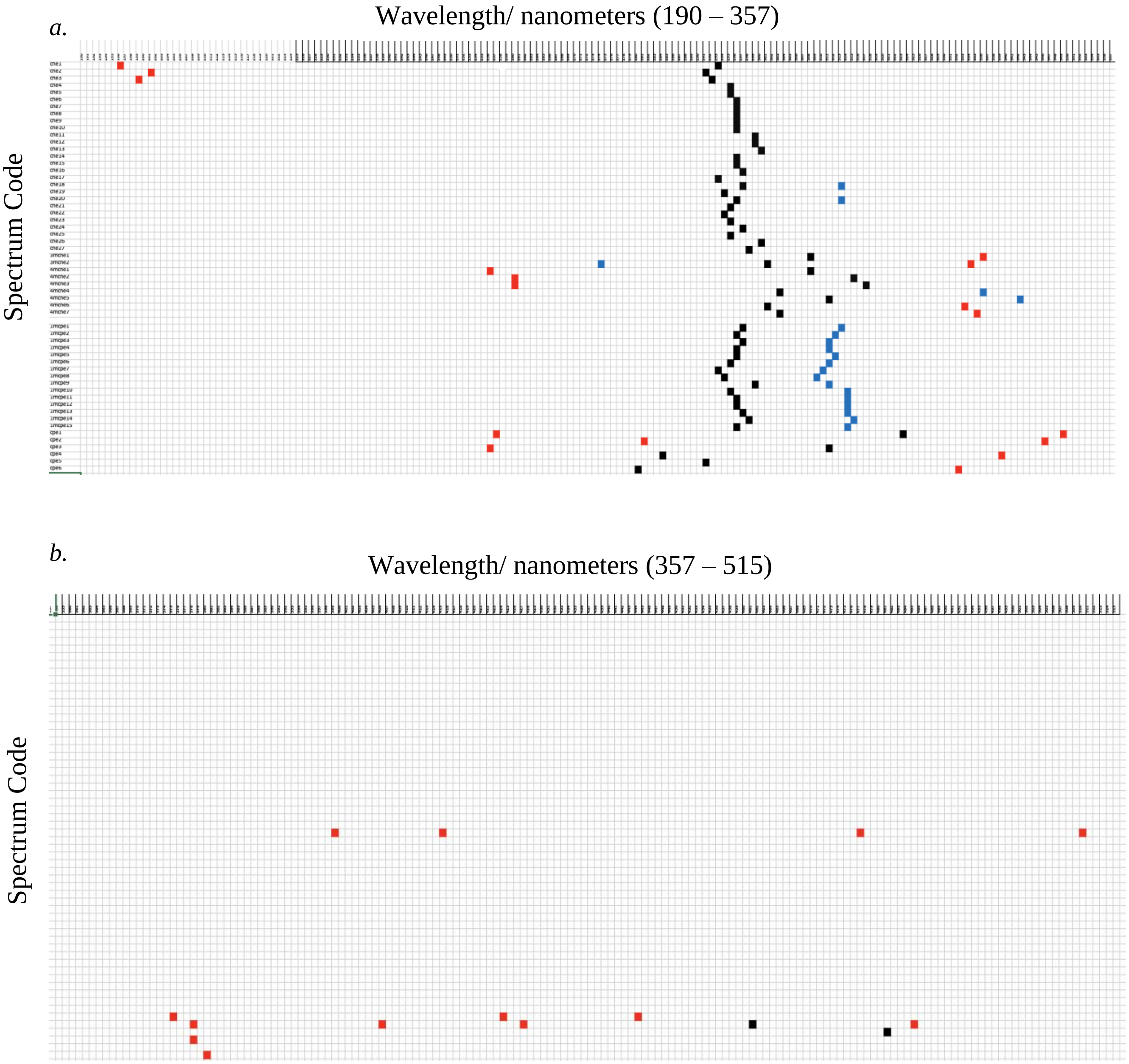


b.



B. Cyclohexene and Cyclopentene

Peak absorbance wavelengths of major peaks, minor peaks, and shoulders for cyclopentenes and cyclohexenes. Part a shows peaks at wavelengths from 190 to 357 nanometers. Part b shows peaks at wavelengths from 357 to 515 nanometers. Table 2 gives the peak type associated with each cell color.



Effects of Temperature, Acidity, and Methylation

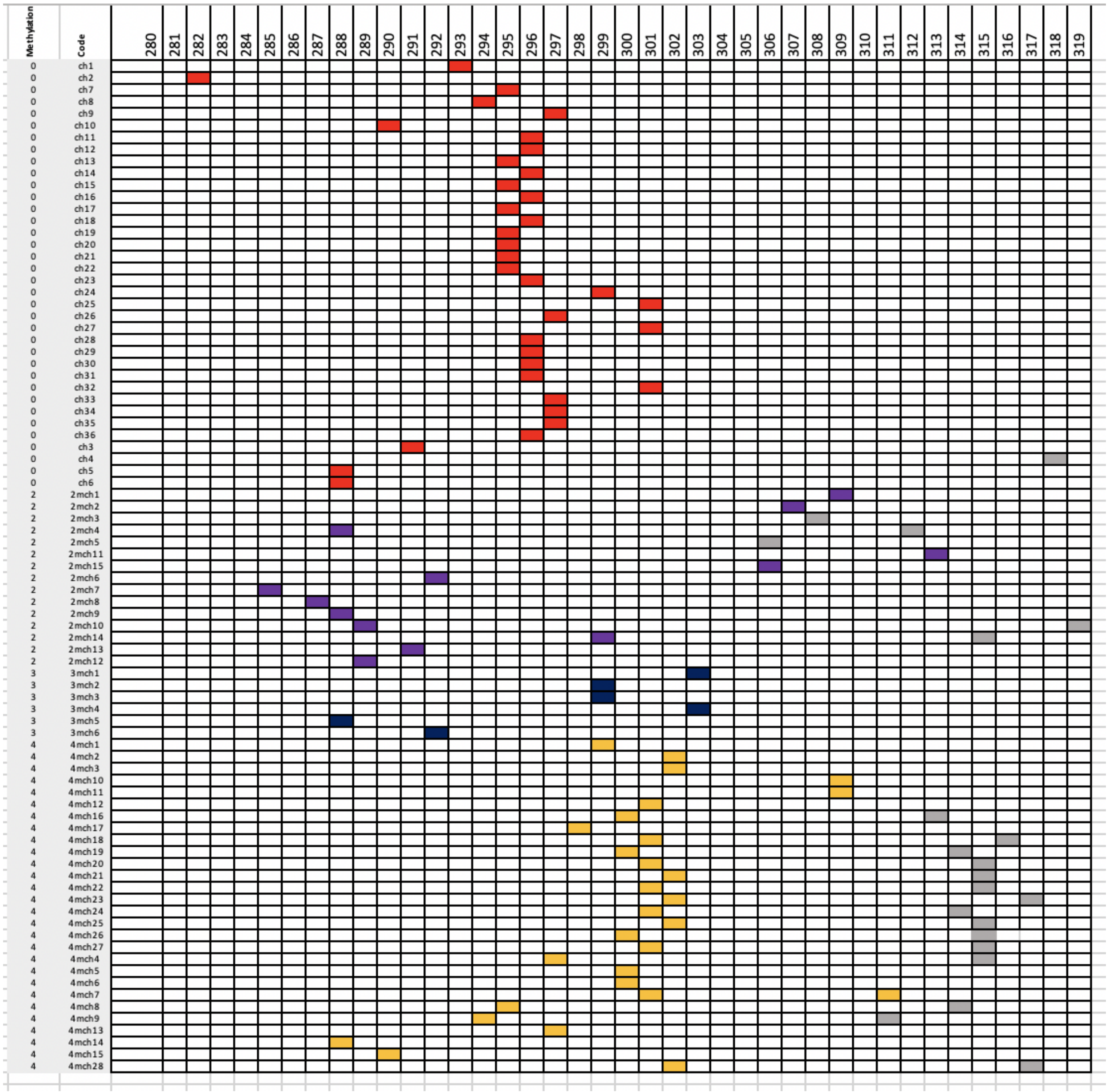
Methylation

C. Cyclohexanol

Cyclohexanol reactions sorted by methylation. Lambda max peaks are marked by a color under the wavelength at which they appear. Wavelengths between 280 and 319 nm are shown. An increase of around +5nm is observed from cyclohexene reactions to 4-methylcyclohexanol.
Red: cyclohexanol Purple: 2-methylcyclohexanol Dark Blue: 3-methylcyclohexanol
Yellow: 4-methylcyclohexanol

Wavelength/ nanometers (280 – 319)

Spectrum Code and Methylation



Methylation	Code	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319
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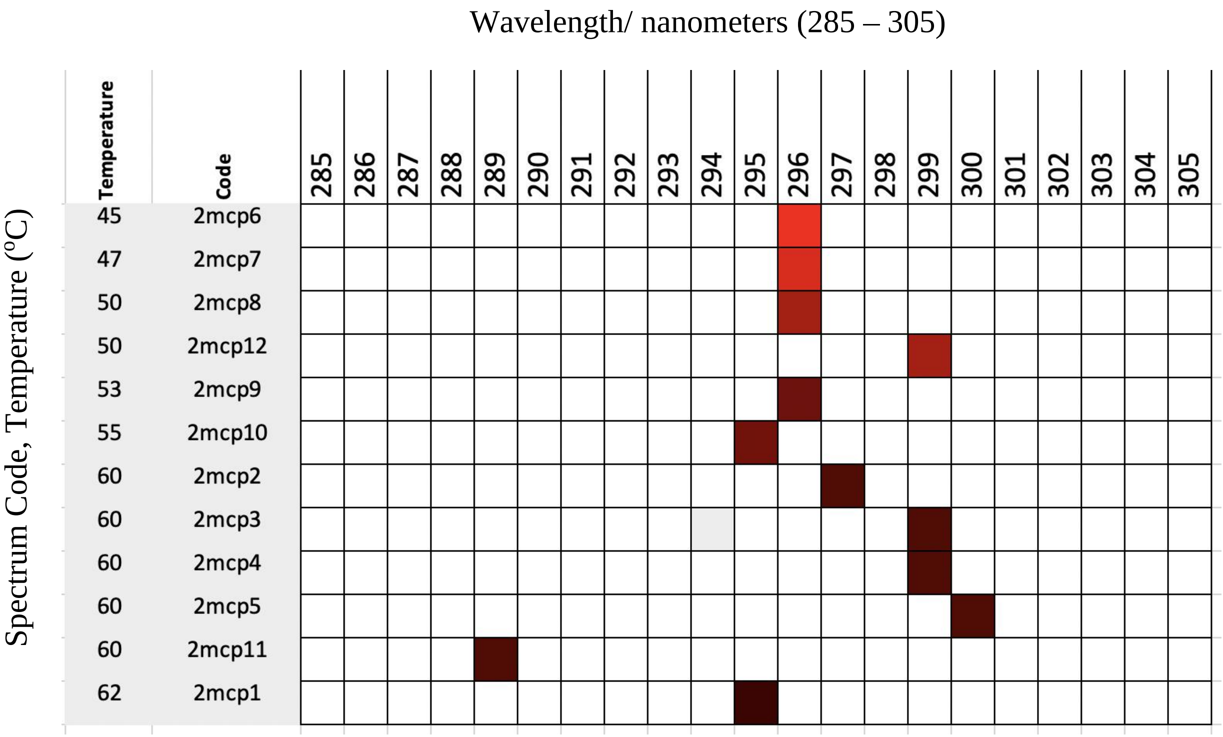
Temperature

D. 2-methylcyclopentanol

2-methylcyclopentanol reactions sorted by temperature. Lambda max peaks are marked by a color under the wavelength at which they appear. Lighter reds indicate lower temperature while darker reds indicate higher temperature. Wavelengths between 285 and 305 nm are shown. A bathochromic shift of around +3nm is observed in lambda max as temperature reaches 60°C.



Wavelength/ nanometers (285 – 305)

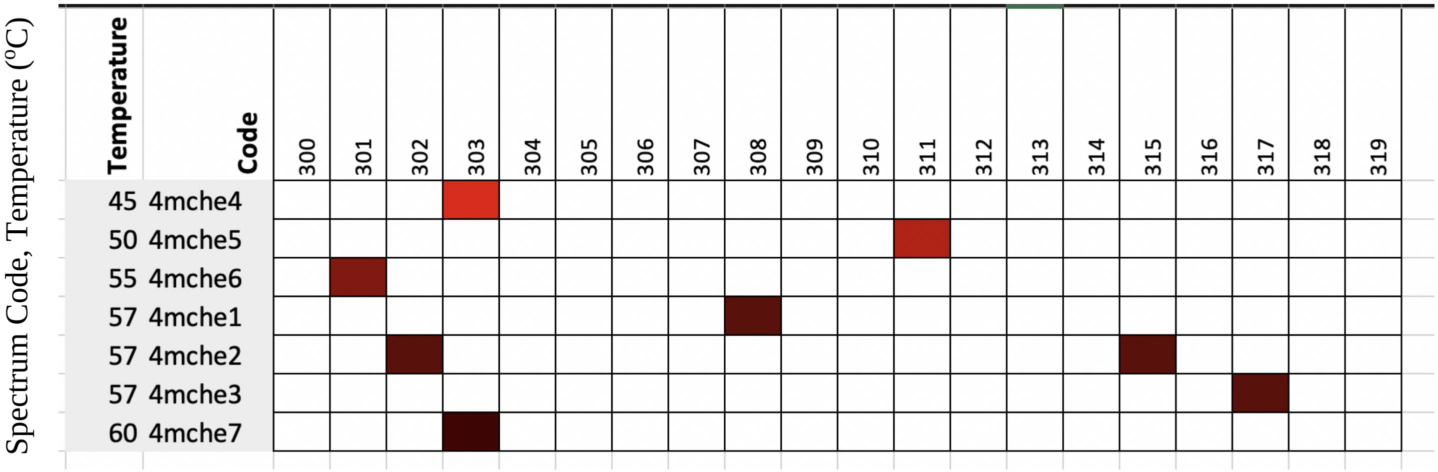
Spectrum Code, Temperature (°C)

Temperature	Code	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305
45	2mcp6												■									
47	2mcp7												■									
50	2mcp8												■									
50	2mcp12															■						
53	2mcp9												■									
55	2mcp10											■										
60	2mcp2													■								
60	2mcp3										░					■						
60	2mcp4															■						
60	2mcp5																■					
60	2mcp11					■																
62	2mcp1											■										

E. 4-methylcyclohexene

4-methylcyclohexene reactions sorted by temperature. Lambda max peaks are marked by a color under the wavelength at which they appear. Lighter reds indicate lower temperature while darker reds indicate higher temperature. Wavelengths between 300 and 319 nm are shown. Possible slight trend that requires further investigation via additional experimentation.

Wavelength/ nanometers (300 – 319)



Spectrum Code, Temperature (°C)

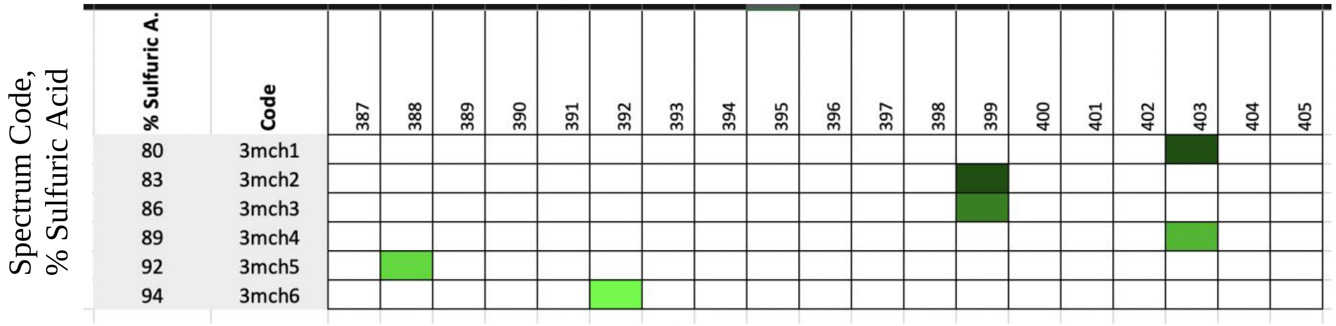
Temperature	Code	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319
45	4mche4				🟥																
50	4mche5												🟥								
55	4mche6		🟥																		
57	4mche1									🟥											
57	4mche2			🟥													🟥				
57	4mche3																		🟥		
60	4mche7				🟥																

Acidity

F. 3-methylcyclohexanol

3-methlcyclohexanol reactions sorted by acidity, where columns are wavelengths (nm) and rows are each time series spectra's reaction acidity and starting material. The shift toward lower wavelengths in lambda max for 3-methylcyclohexanol seems to begin above 90% sulfuric acid. Lambda max peaks are marked by a color under the wavelength at which they appear. Lighter greens indicate higher acidity while darker greens indicate lower acidity.

Wavelength/ nanometers (387 – 405)



Spectrum Code, % Sulfuric Acid

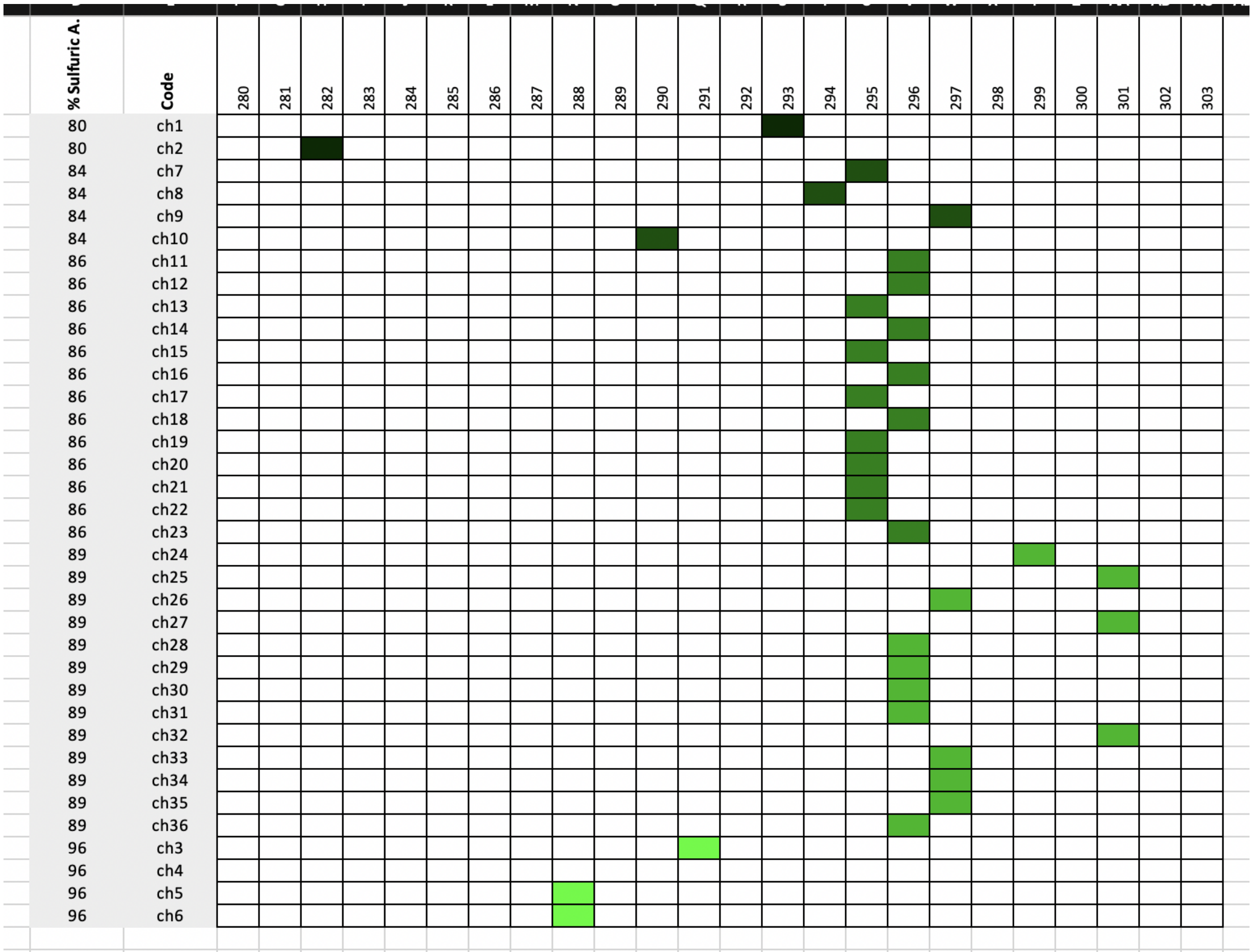
% Sulfuric A.	Code	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405
80	3mch1																	🟩		
83	3mch2													🟩						
86	3mch3													🟩						
89	3mch4																	🟩		
92	3mch5		🟩																	
94	3mch6						🟩													

G. Cyclohexanol

Cyclohexanol reactions sorted by acidity, where columns are wavelengths (nm) and rows are each time series spectra's reaction acidity and starting material. The shift toward lower wavelengths in lambda max cyclohexanol seems to begin above 90% sulfuric acid. Lambda max peaks are marked by a color under the wavelength at which they appear. Lighter greens indicate higher acidity while darker greens indicate lower acidity.

Wavelength/ nanometers (280 – 303)

Spectrum Code, % Sulfuric Acid



% Sulfuric A.	Code	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303
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80	ch2			🟩																					
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89	ch36																	🟩							
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96	ch4																								
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