Evaluating Sunscreen Actives and Their Derivatives as Potential Sensitizers in DSSC

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Abstract

This project investigated the viability of utilizing species other than traditionally employed anthocyanin- rich fruit juices as the organic component of hybrid dye-sensitized solar cells. Two organic compounds approved by the Australian Therapeutic Goods Administration as UV-light absorbing active ingredients in sunscreens were tested as sensitizers. Both candidate compounds were used as starting materials in separate synthetic functionalizations whose products were also tested as potential sensitizers. Characterization methods included UV, IR, and NMR. The resulting voltages and currents generated by these cells were found to be comparable with baseline testing of previously tested sunscreen actives. The power output of cells constructed with the synthetic products was similar over time to those constructed with their respective starting materials; though cells made with Product C did not necessarily follow a consistent downward trend in power output over time. Also tested was the effect of addition of more sensitizer to cells on power output both immediately and over a one week period, although results were majorly inconclusive. Topics of future research include more thorough exploration of additional sensitizer deposits as well as investigating substitution of other electrolyte solutions, particularly in those cells assembled with product C as sensitizer.

1.0 Introduction

As the world population continues to grow, science is presented with new challenges to accommodate sustaining this rapid growth. An important example of one such challenge involves energy consumption, and the places from which the world's energy are sourced. Traditionally, oil, natural gas, and coal, all of which are categorized as non-renewable resources, have been utilized as the most cost effective and most popular energy sources worldwide. However, their nature as non-renewables that are not quickly replenished post-consumption and environmental concerns related to resultant carbon dioxide emissions have driven price up and decreased popularity of these materials in favor of renewable energy sources in recent years.

This project investigates perhaps the most promising renewable energy source as of present day; solar power. The cost of solar power per unit has fallen 60% in ten years, making it more appealing an option than ever for many consumers. Drawbacks include a large upfront investment and lengthy waiting period before being able to reap solar's full cost-saving benefits in addition to aesthetics and practicality in some locations; still, solar power seems to be a valid alternative for widespread energy sourcing over traditional methods.

One branch of solar power involves a series of photoelectrochemical reactions that mirror the process of photosynthesis by converting light into energy which take place within what is known as a dye-sensitized solar cell. A basic dye-sensitized solar cell (DSSC) has five major components: mechanical support with conductive oxide coating, semiconductor film (most often titanium dioxide), sensitizer dye adsorbed onto the semiconductor, an electrolyte, and counter electrode. While all of the components of a DSSC play an important role in its functionality, perhaps most important is the organic sensitizer layer which is responsible for light absorption and thus determines to what degree the reactions taking place within the cell will generate power.

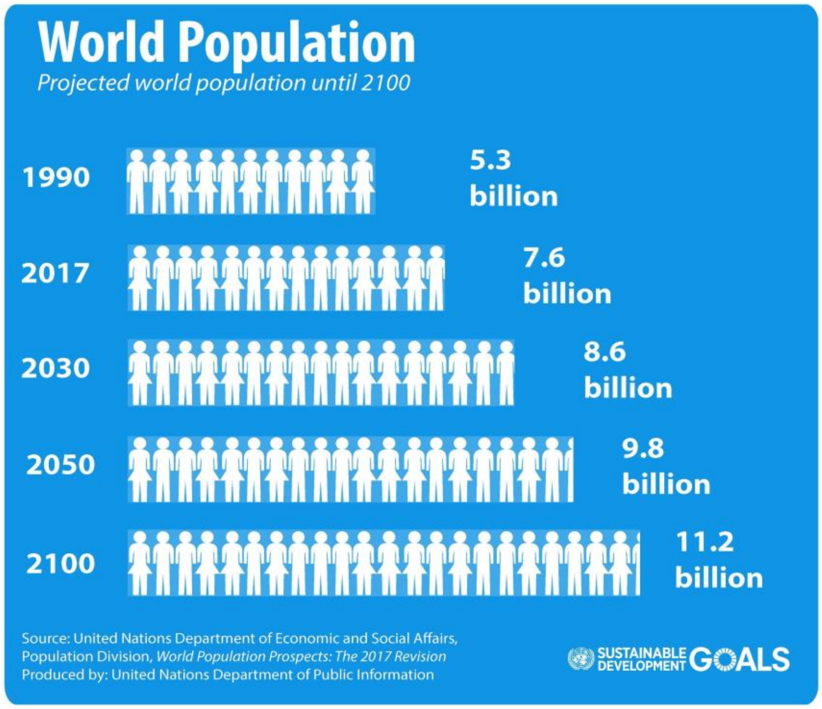
A previous MQP explored assembling solar cells with UV light-absorbing compounds used in sunscreen as the organic sensitizer component. These compounds were selected from a list of fourteen which are approved for use in sunscreen by the USFDA. The Australian Therapeutic Goods Administration approves these ingredients plus sixteen more for use in sunscreens, of which two were chosen for investigation in this project; sulisobenzone and 4-methylbenzylidene camphor.

Numerous cells were assembled using these two compounds as sensitizers, and the resultant voltage and current were measured both immediately following cell assembly and in intervals over a subsequent two-week period. The chosen compounds were also used as starting materials in synthetic functionalization reactions whose products were tested as sensitizers as well. The cells made with the products performed similarly to those made with their respective starting material, although one showed notably more consistent power output over time. Additionally, cells were prepared with successive deposits of sensitizer to investigate the effect of this on immediate and long-term power output, though results were mostly inconclusive.

2.0 Background

2.1 World Energy Crisis

As humankind continues to traverse the rapidly changing landscape that is the 21st century in which we live, there are concerns which come about as consequences of this rapid development. The world population has continued to increase dramatically over time; for example, this figure did not reach one billion until the onset of the 19th century. Given that this takes into account the centuries since the beginning of man, it is alarming to note that the subsequent doubling of that figure (population of 2 billion) was achieved only 130 years later. By the turn of the millennium, the population had reached six billion, with today's total tallying 7.7 billion (Current 2018).



Source: United Nations Department of Economic and Social Affairs, Population Division, *World Population Prospects: The 2017 Revision*
Produced by: United Nations Department of Public Information

Figure 1: Infographic from the UN showing a visual representation of world population growth (United Nations, 2017)

It only follows that an increased population leads to increased demand for resources vital to sustain humans and their activity, such as food, water, housing, and perhaps most urgently, energy. Less important are the actual quantities of energy consumed, but relative consumption from year to year is necessary to consider when the needs of the world are changing in accordance with the population growth detailed above. For example, the world saw an increase in overall energy consumption of 2.3% in 2017 versus a 1.1% increase in 2016. This increased consumption can be attributed in large part to the augmented quantities of oil, natural gas, and coal sources exhausted in 2017 relative to earlier years. These resources are all categorized as “non-renewable” because at any given time, they are available in finite quantities and are not quickly replenished post-consumption. Naturally, these characteristics lead to increased price points as these non-renewable resources are consistently depleted each year (World 2018). The US Energy Information Administration (EIA) projects that world energy consumption will have increased 28% since 2015 by the year 2040 as detailed in Figure 2: (EIA 2017).

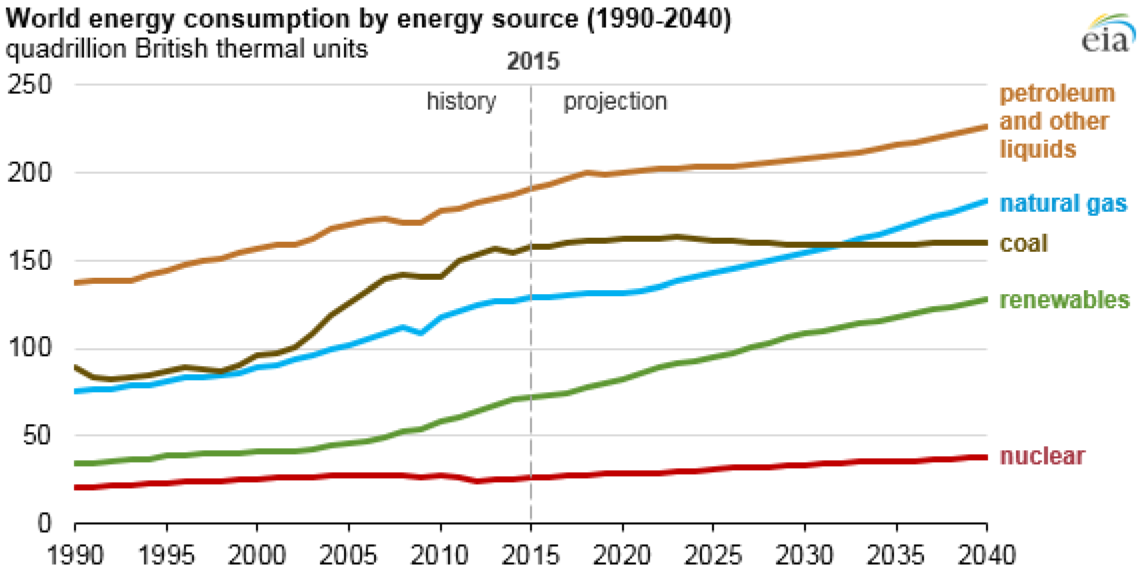


Figure 2: Past and predicted world energy consumption, 1990-2040 (EIA, 2017)

Another consequence of consumption of these resources is the emission of carbon dioxide gas into the atmosphere, which has detrimental effects on both human health and the environment. Like overall energy consumption, there was an increase in

CO_2 emissions in 2017 (2.1%); however, this figure had remained fairly constant in recent years prior (World 2018). Therefore, this change is of particular concern. Given this data, it becomes clear that the continued consumption of non-renewable resources will not sustain the growing needs of the planet as well as it once did. Renewable resources, including wind, hydropower, and most importantly for this project, solar energy are replenished relatively quickly in nature and are being adopted as alternatives to traditional energy sources at an increasing rate, as shown in Figure 2.

2.2 Solar Power as a Solution

Solar energy has become an increasingly popular alternative to fossil fuels in the US; for example, in 2016, of all of the new jobs generated nationwide, careers in the solar industry accounted for a whopping 2% of these. It is only natural that, with a market developing at this rate, solar energy is now considered one of the three main power sources along with natural gas and wind. In 2017, 53 billion kWh of solar power accounted for 1.3% of the total energy generated nationally that year (Solar Energy Jobs).

Although solar cells were first investigated in the 1800s, it wasn’t until 1954 that Bell Labs constructed a silicon solar cell with an efficiency of about 6% which was considered a bona fide advancement in the renewable energy industry. Nowadays, the efficiency figure for commercially available solar panels nears 30%. In fact, scientists have achieved as high an efficiency as 46% in laboratory settings; however, this design has not been popularized as an energy solution to consumers because of its lack of cost effectiveness (Matasci).

The cost of solar energy has, though, fallen notably in recent times. In 2008, the average cost of solar energy was $8.82/watt, which has now been reduced over 60% to

$3.14/watt in just ten years. With this being said, cost is still an issue because the initial costs are a considerable investment which the consumer does not see returned until an average of seven and a half years after installation despite the cost effectiveness of the energy being generated per watt (Matasci).

Although cost is a primary concern, there are other considerations which discredit some of the merit of modern solar energy. For example, solar panel assemblies mounted on the roofs of homes and other buildings or installed in nature are oftentimes seen as aesthetically unattractive and cumbersome, perhaps compromising a given area's status as historic. Furthermore, the large and complex installments could endanger the wellbeing of nearby biological ecosystems that are especially susceptible to negative impact due to changes in their surroundings. There is also a risk of environmental pollution (especially of local water sources) if there were to be an accidental release of chemicals used within the panels as coolant, which are in some cases carcinogenic (Tsoutsos, et al).

2.3 Dye-Sensitized Solar Cells

When considering the factors discussed above in relation to solar energy as it exists in the US today, some of the "problems" with modern solar power are less important or scientifically significant to go about trying to improve or solve. However, research can certainly be done to continue trying to improve cell efficiency without compromising cost effectiveness. One specialized area of solar energy which holds much promise involves the construction and characterization of nanocrystalline dye-sensitized solar cells.

Unlike traditional solar cells, DSSCs are photoelectrochemical cells that mirror the process of photosynthesis in nature. A basic dye-sensitized solar cell (DSSC) has five major components: mechanical support with conductive oxide coating, semiconductor film (most often titanium dioxide), sensitizer dye adsorbed onto the semiconductor, an electrolyte, and counter electrode (Nazeeruddin et al., 2011). The basic structure of the cell is as follows: a silicon dioxide glass slide with a thin tin dioxide layer is coated in a suspension of “nanometer size” (hence the terminology “nanocrystalline”) particles of titanium dioxide. The dye component, which is the light-absorbing component of the cell, which must have energy levels that allow for electron injection and sensitization, attaches to the titanium dioxide membrane. A liquid electrolyte (most commonly an iodine solution) to replenish electrons lost by the dye during light absorption and a conductive glass counter electrode round out the cell. The voltage produced by the cell is a product of the difference in energy between the titanium dioxide layer and iodide mediator ion, while the current generated depends solely on the intensity of light exposure.

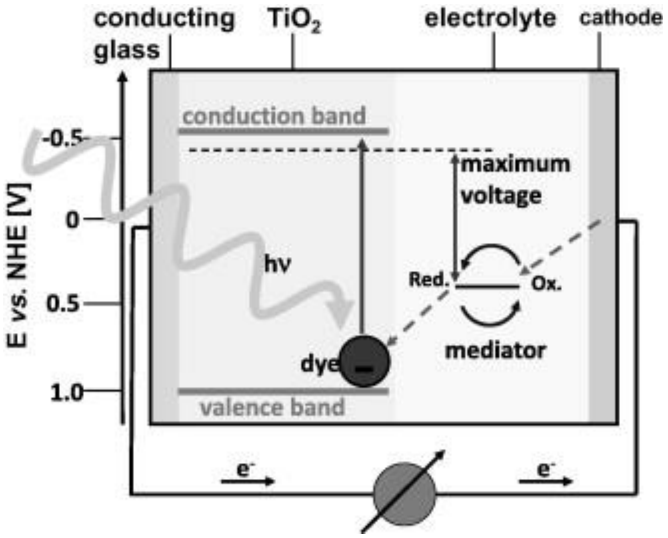


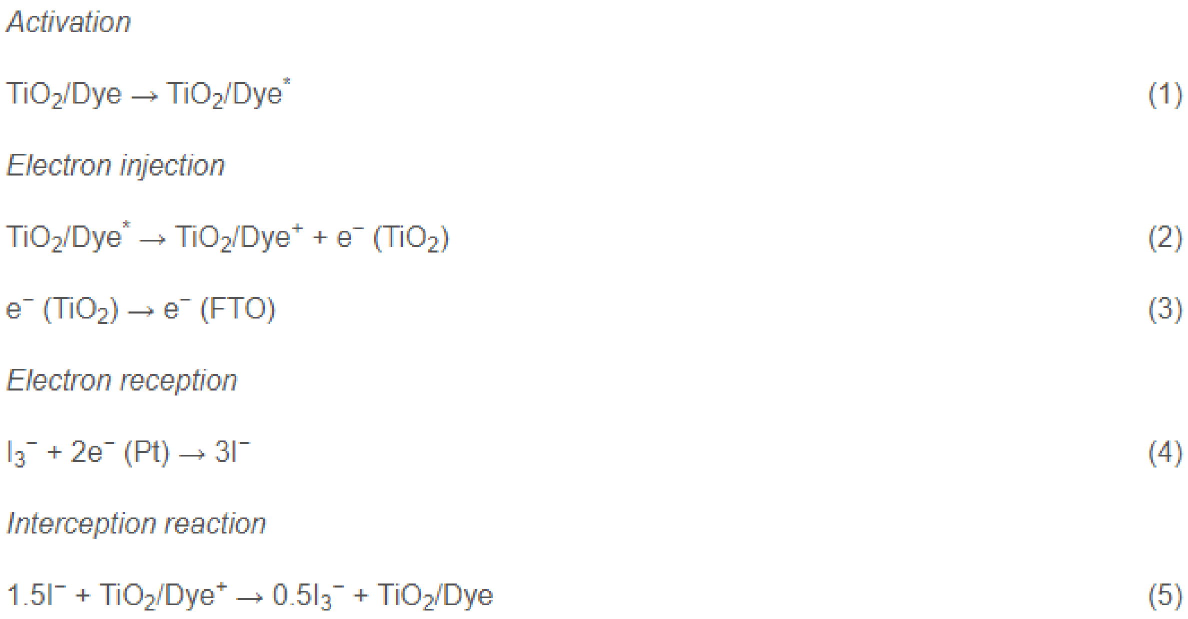
Figure 3: "Operating principles and energy level diagram of dye-sensitized solar cell" (Nazeeruddin et al., 2011)

2.4 Organic Sensitizers in DSSC

There are two major groups of dye sensitizers: metal-free organic dyes and metal-complex dyes. For DSSC applications, metal-free organic dyes are preferential due to their simple and adjustable synthesis and design, and high molar extinction coefficients (Lee et al., 2017). Additionally, metal-free dyes are more environmentally sustainable than their metal-complex alternatives. Different areas of non-metallic sensitizers for solar cells have been investigated in recent years.

Research has looked at using natural dyes from plants as sensitizers (Bayron Cerda et al., 2016), such as chlorophylls and carotenoids, due to their availability and simple extraction. Other research has looked at the functionalization of organic dyes. As of 2016, "most of the report on DSSCs focused on mechanisms of electron injection, modification of functional group (such as electron-donating group, π-conjugated linker, anchoring and acceptor groups)," (Obotowo et al., 2016).

"The organic dyes with near-infrared light absorption are designed to improve the solar-to-electricity conversion efficiency by extending the absorption threshold of the organic dyes to the near-infrared regions," (Lee et al., 2017). Fig. 4 shows the basic interactions of the components of a DSSC in action. The dye is activated by the light source, which excites the electrons. The excited electrons are then able to move across the cell, creating a potential difference. The electrolyte replenishes the electrons as the dye continues to be activated. A good dye should be relatively stable under light such that it doesn't degrade easily, but can still be activated by the light source.



Activation

$$TiO_2/Dye \rightarrow TiO_2/Dye^* \quad (1)$$

Electron injection

$$TiO_2/Dye^* \rightarrow TiO_2/Dye^+ + e^- \ (TiO_2) \quad (2)$$

$$e^- \ (TiO_2) \rightarrow e^- \ (FTO) \quad (3)$$

Electron reception

$$I_3^- + 2e^- \ (Pt) \rightarrow 3I^- \quad (4)$$

Interception reaction

$$1.5I^- + TiO_2/Dye^+ \rightarrow 0.5I_3^- + TiO_2/Dye \quad (5)$$

Figure 4: Sequence of events in a DSSC (Lee et al., 2017)

2.4.1 Characteristics of Good Sensitizers

As aforementioned, a major component of DSSCs is the sensitizer dye. Organic sensitizer dyes must have some sort of conjugated pi system in its structure to absorb energy from light (Fig. 5).

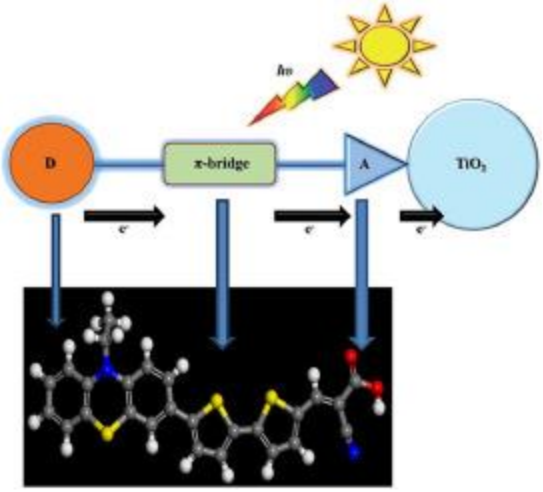


Figure 5: Diagram showing the flow of electrons from donor to acceptor through a pi bond system (Obotowo et al., 2016)

Good sensitizers should have a highest occupied molecular orbital (HOMO) that is localized by the electron donating group with an energy level that can be regenerated by the redox couple and a lowest unoccupied molecular orbital (LUMO) that is localized around the electron acceptor group with an energy level that facilitates electron flow to the semiconductor (Obotowo et al., 2016).

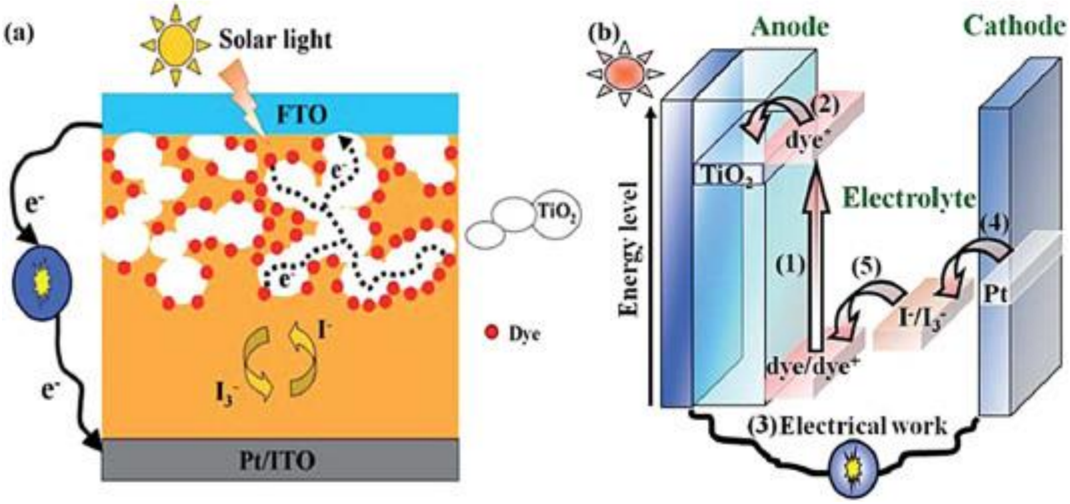


Figure 6: Diagram showing electrical work in a DSSC (Obotowo et al., 2016).

A 2006 study on functionalizing organic dyes for efficient molecular photovoltaics found that “alkyl chains are markedly effective in increasing the electron lifetimes. The longer electron lifetime may be realized by two possible mechanisms: one is that the alkyl chains block the I_3^- or cations approaching the TiO_2 surface, decreasing the I_3^- concentrations at the vicinity of the TiO_2, and the other is that the alkyl chains reduce the reorganization energy of the dyes, increasing the rate of dye-cation reduction,” (Koumura et al., 2006). Functionalizing the sunscreen actives with alkyl chains would theoretically allow the dyes to remain more stable over time.

2.5 Previous MQP Research on DSSC

The most recent Major Qualifying Project (MQP) based on a similar scope, completed during the 2014-2015 academic year, tested five active sunscreen ingredients as dye components of DSSCs. Ultimately, one species was functionalized to produce three different compounds which were tested to examine long term effects on cell performance as a result of the functionalizations (Mateo et al., 2015). At the time, little research had been done investigating other sunscreen active ingredients, and this category of chemicals has not been shopped as an option for DSSC sensitizer molecules since. The 2015 project concluded that the five ingredients tested do have potential as light absorbing components, and suggested that synthetic functional changes and solvent optimization could improve cell potential and long-term stability (Mateo et al., 2015). For the context of this project, the focus will be on synthetic functional changes on other sunscreen active ingredients and testing their feasibility as light absorbing components in a DSSC.

2.5.1 Additional Sunscreen Actives & Feasibility

In the United States, there are currently sixteen Food and Drug Administration (FDA) approved sunscreen active ingredients (FDA, 2018). However, this list has not been updated since 2001. In Australia, the average UV index during the year is much higher than the average UV index in the United states (World Health Organization, 2019) due to the hole in the ozone layer of the Earth’s atmosphere being physically closer to the Australian landmass. Australia’s equivalent of the American FDA, the Therapeutic Goods Administration (TGA) has approved a list of thirty sunscreen active ingredients (TGA, 2016). The 16 active ingredients that are approved in the United States all appear on the list of Australian-approved ingredients. The additional ingredients which are approved for use in sunscreens in Australia provide new resources to look into as options following the encouraging results obtained testing US-approved ingredients as sensitizers. Being an approved sunscreen ingredient in any region of the world bodes well for these experimental purposes, because (in some cases more than others) this designation acts as an indicator of somewhat wide availability, relative non-toxicity, and reasonable price point. These are the factors that were taken into account, along with ability to be functionalized to form new sensitizer molecules, when selecting materials to begin testing with. We decided on 4-methylbenzylidene camphor and sulisobenzone (pictured below).

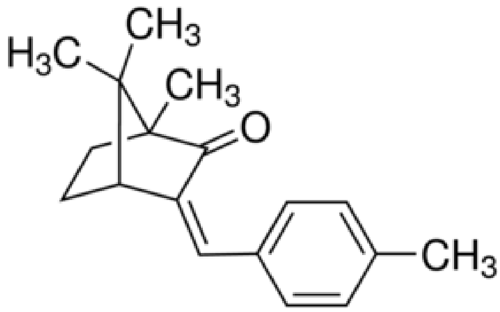


Figure 7: Molecular structure of 4-methylbenzylidene camphor

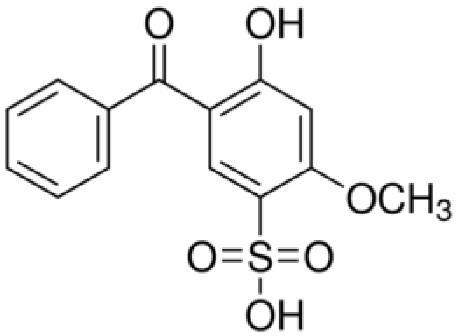


Figure 8: Molecular structure of sulisobenzone

3.0 Methodology

3.1 Procedure for cell preparation

A suspension was prepared by combining 6 g of TiO_2 nanoparticles (type P25, made by Degussa) with 7 mL of acetic acid (pH 3). The acetic acid was added 1 mL at a time to the solid and the mixture was combined with a mortar and pestle until a smooth but viscous consistency was achieved. A trivial amount of clear dish detergent was added to and stirred into the resulting mixture each time as a surfactant.

The glass slides used as either side of the solar cell assembly were rinsed with ethanol prior to testing to ensure dryness. The conductive sides of the glass slides were determined by measuring resistance in ohms through a handheld multimeter. One slide’s conductive side was coated in a layer of graphite using an art pencil while the other received an application of the previously prepared TiO_2 suspension. The suspension was applied to the slide while it was taped down to the lab bench on three sides so as to contain the coated area to within +/- 1 cm of the edges of the slide (see Fig. 9).

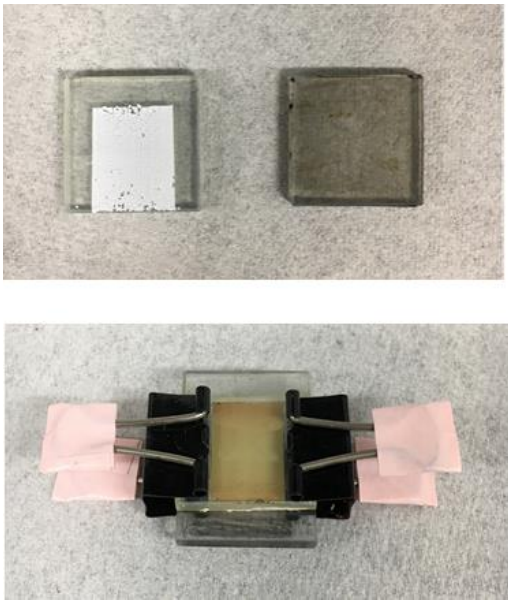


Figure 9: Slide preparation

The suspension was applied in repeated, unidirectional movements with a small glass stirring rod, and when an even layer (consistent in thickness and color to the naked eye) was achieved, the coated slides were immediately placed on a preheated hot plate at its maximum temperature setting. As the layer of suspension annealed to the slide, it was observed to turn dark brown and finally back to white. Once cooled, 0.05M solutions of sensitizer solutions were prepared as follows:

Sensitizer	**Solvent**
Octisalate	t-butyl alcohol
Octisalate	ethanol
Octisalate	Acetonitrile
Avobenzone	t-butyl alcohol
Avobenzone	ethanol
Oxybenzone	acetonitrile
Sulisobenzone (Compound B)	t-butyl alcohol
Sulisobenzone (Compound B)	ethanol
4-methylbenzylidene camphor (Compound A)	ethanol
4-methylbenzylidene camphor (Compound A)	acetonitrile
4-methylbenzylidene camphor (Compound A)	t-butyl alcohol

Table 1: Sensitizers and solvents used for baseline testing

200μL of a given sensitizer solution was deposited onto a TiO_2 coated slide with a micropipettor and set aside for the solvent to evaporate.

The TiO_2 + sensitizer slide (anode) and a graphite-coated slide (cathode) were clamped together with binder clips in an off-set manner such that there would be some overhang of the glass on either side to connect the electrodes to. KI/I^- electrolyte solution in ethylene glycol was applied using a dropper bottle to along the seam of the slides and allowed to diffuse and cover the inner surface. Alligator clipped electrodes were clamped to the glass (negative to TiO_2, positive to graphite). The slide was then placed TIO_2 slide up under a UV lamp (366 nm, Model UVL-21) parallel to the lamp with incident light exposure normal to the surface. Readings were taken with a DT830B digital multimeter for voltage and current. For previously explored sensitizer compounds, readings were taken immediately after cell assembly to establish a baseline for the chosen “new compounds” (HMBS and camphor), which were tested at time intervals of 0, 1, 8, 16, 24, 48, 120, 168, 240, and 336 hours. The same time intervals were used for cells made with products C & D as sensitizers, which were synthesized via functionalization of Compound A and Compound B, respectively, as follows:

3.2 Functionalization of Compound A

Compound A (2.290 g) was dissolved in ethanol (125 mL) and refluxed for ~3 hours with ethanolamine (0.54 mL). The resulting solution was dried down via rotary evaporation to obtain solid product (1.3421 g, 49.5% yield).

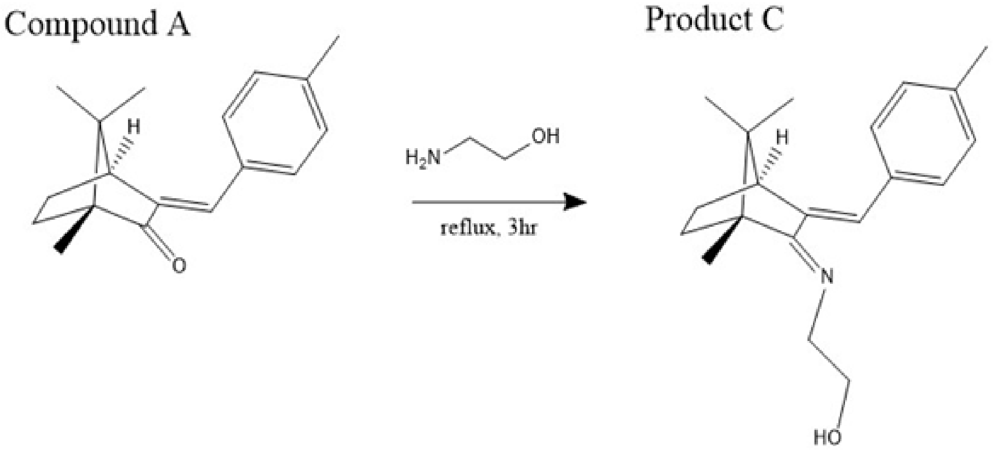


Figure 10: Reaction scheme for synthesis of Product C

3.3 Functionalization of Compound B

Compound B (0.9183 g) was added to ethyl acetate (100 mL) with stirring and heat until dissolved. n-Chlorobutane (1.00 mL) was added to the mixture with continued stirring. The reaction mixture was cooled with an ice bath for the addition of aluminum chloride (0.05 g) in three equal portions. Between each addition of $AlCl_3$, the reaction mixture was allowed to rest for an interval of five minutes. The resulting solution was dried down via rotary evaporation to obtain solid product (0.6683 g, 62.3% yield).

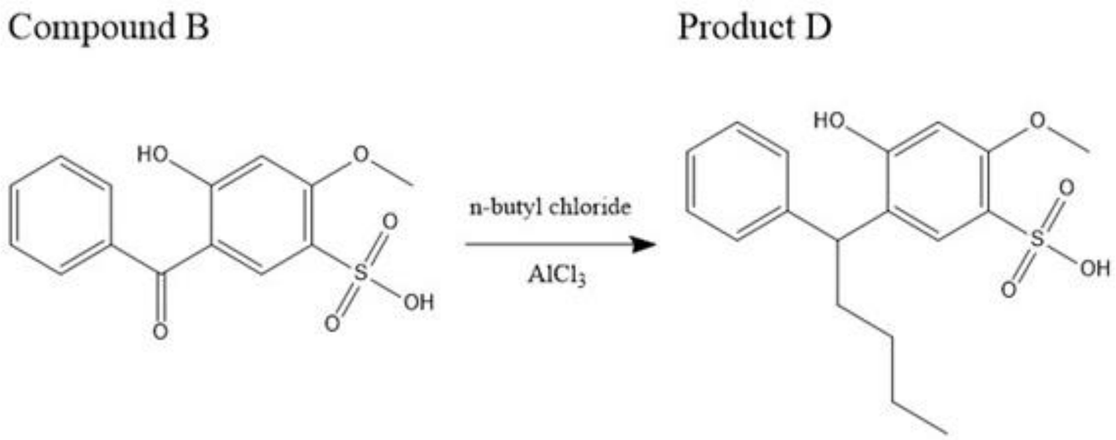


Figure 11:Reaction scheme for synthesis of Product D

3.4 Applications of Additional Sensitizer

As an additional experiment to testing the functionalized compounds, the effect of multiple applications of sensitizer solution to a single cell was investigated. The same 0.05 M solutions of both Compounds A and B in ethanol were deposited onto six slides; three of each compound. One of each received one 200μL application of sensitizer solution (as before, as a control), one of each received three 200μL applications, and one of each received five 200μL applications. The current and voltage readings of these cells were recorded at intervals of 0, 1, 8, 16, 24, 48, 120, 168 hours.

4.0 Results and Discussion

4.1 Baseline Establishment

In order to build on the work of the 2015 MQP that was similar in function and scope to our project, we found it fit to reproduce the group's results on our own. The exact batches of sensitizer chemicals tested during that project were readily available in the lab space and were used to prepare 0.05 M solutions of the top two performing sensitizers (in terms of highest voltage/current) in each of three solvents (ethanol, acetonitrile, and t-butyl alcohol). Multiple cells were assembled with each of the six combinations and their instantaneous power output was measured in order to establish a baseline for comparison for the selected "new" sensitizer compounds (HMBS and camphor). To maintain consistency, these same three solvents were the ones used for preparing solutions of the new sensitizers to be tested.

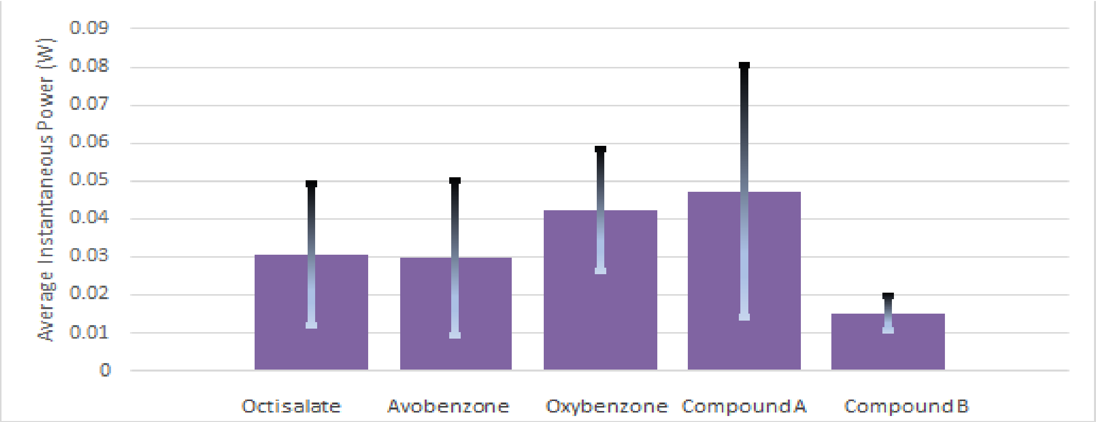


Figure 12: Summary graph of baseline testing. Octisalate, avobenzone, and oxybenzone were compounds tested in the 2015 MQP, and compounds A and B are the test compounds for this MQP. Compound A was found to perform as good or better than baseline sensitizers. B performed poorly in this capacity but showed promise in other areas.

4.2 Long-Term Testing

Voltage and current readings were taken at the following intervals: 0, 1, 8, 16, 24, 48, 120, 168, 240, and 336 hours. Comparisons between synthetic products and starting materials showed that functionalized compounds performed similarly to their respective starting materials. The cells made with Product D as sensitizer performed more consistently (not necessarily higher power output, but following a more likely downward trend over time) than product C. When cells were assembled using product C as a sensitizer, the electrolyte solution was observed to gravitate outward toward the edges of the cell as opposed to seeping downward to coat the entire inner surface as was observed in other cells. This observation led us to believe there may have been interactions between the synthesized sensitizer compound and the electrolyte solution that hindered cell performance and made power output readings erratic over time. For example, it was difficult to obtain a “correct” reading many times for these cells, as the current or voltage displayed on the multimeter would start in a range of the original/expected value and then either quickly rise or fall to rest at a figure several orders of magnitude larger or smaller.

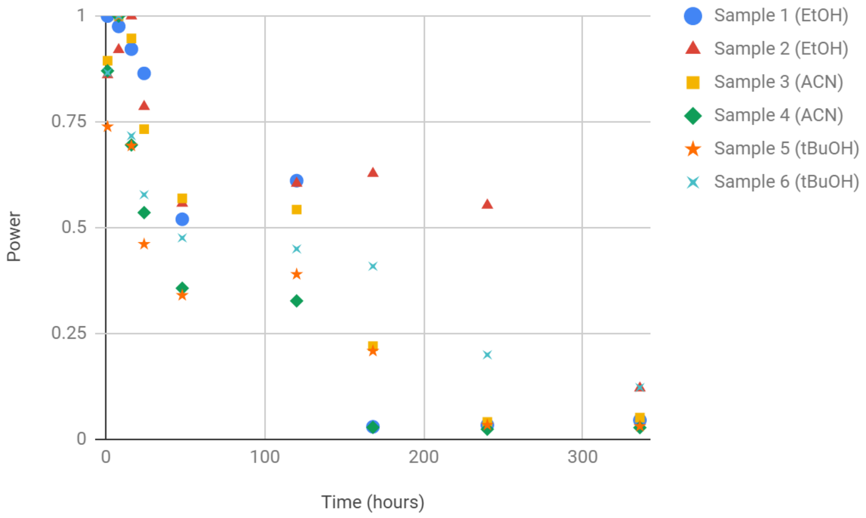


Figure 13: Long-term testing of Compound A

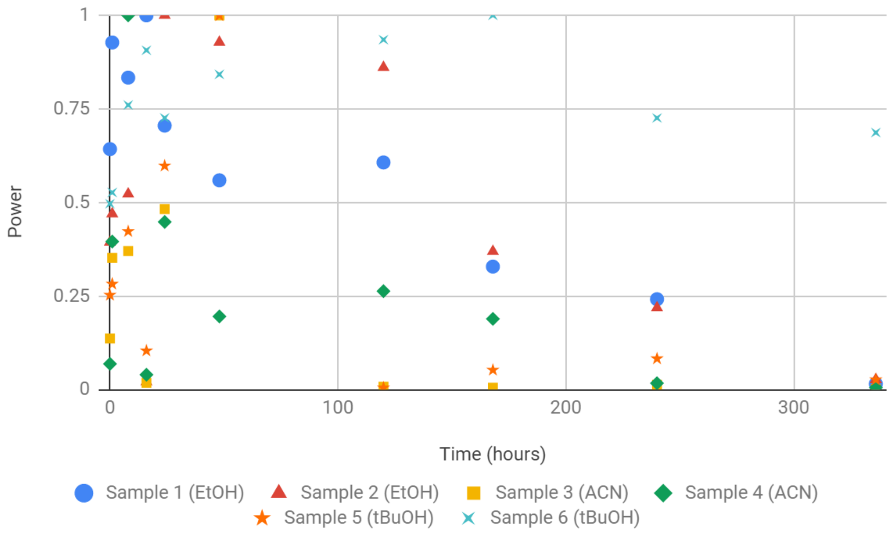


Figure 14: Long-term testing of Product C. Readings were inconsistent and showed little pattern due to the interaction of the electrolyte solution with the sensitizer.

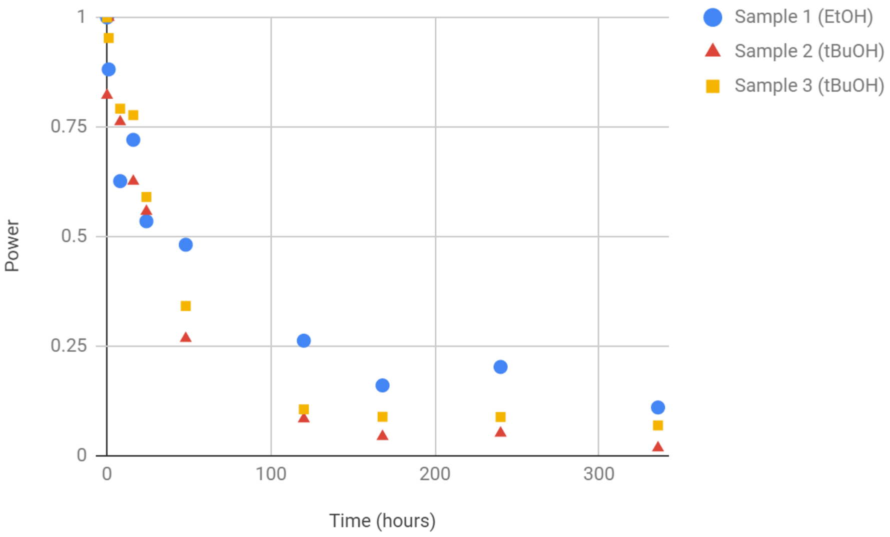


Figure 15: Long-term testing of Compound B. Showed an expected downward trend of power output over time.

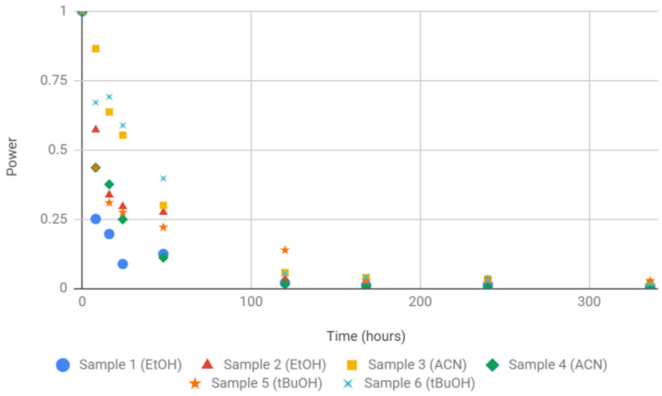


Figure 16: Long-term testing of Product D. Showed a similar expected downward trend of power output over time.

4.3 Importance of TiO_2 Layer

The integrity of the TiO_2 layer is crucial. The slides that showed patchiness in the layer had consistently lower voltage and current readings than the slides that were more uniform. The quality of the TiO_2 layer seemed to depend on how rapidly the coating was applied before being placed on the hot plate and how thickly it was applied; layers that were either too thin, too dry, or too thick often crumbled either upon being placed on the hot plate or somewhere along the removal and cooling process.

4.4 Addition of More Sensitizer

Testing was done with one application, three applications, and five applications of sensitizer on the slides. Solutions were prepared to 0.05M in ethanol with 200μL applications each time. Upon successive additions of Compound A, it initially showed a maximum power output at 3 applications. Compound B increased power output with more applications. Over time, the power output of Compound A was better for the slides with more sensitizer applications, and the opposite was observed for Compound B. The same samples used for instantaneous readings were also used for testing over time. More sensitizer does not necessarily indicate that the cells will perform better either instantaneously or over time.

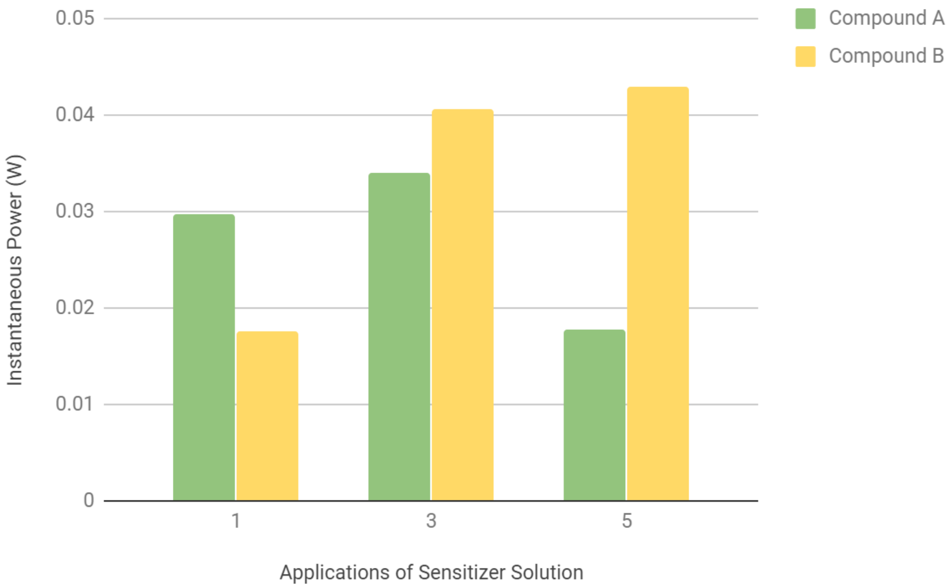


Figure 17: Instantaneous power output of additional applications of Compounds A and B.

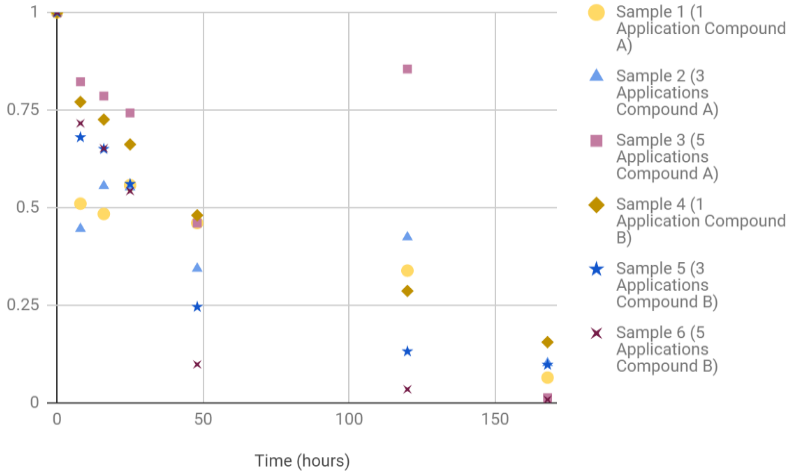


Figure 18: Long-term power output for additional applications of Compounds A and B in ethanol

5.0 Conclusions and Recommendations

Compounds A and B were selected based on their approval as active ingredients in sunscreens in Australia, molecular structure, and relative availability. They proved to be comparable as sensitizers with the active ingredients that are approved in the United States used for baseline testing. Baseline testing provided a comparison of known sensitizers to the Compounds A and B that were selected as potential to determine whether moving forward with long term testing would be viable for the starting materials and for the functionalizations.

Compound B performed about as well as its derivative, Product D. There was not a significant difference in the power outputs over time of Compound B and Product D. Compound A performed much better than its derivative, Product C. The power outputs over time of Product C were inconsistent due to the electrolyte solution used. As aforementioned, the ethylene glycol solution that was used did not coat the product C sensitizer cells in the same fashion as it did for Compounds A and B and Product D, which is believed to be the reason for their poor performance. Based on this observation, a future area of study could be looking at different electrolyte solutions, changing either the solvent or redox couple that may interact with the sensitizer compounds in different ways.

Other testing included the addition of more sensitizer solution onto the slides before constructing the cell. Based on the results that were obtained, a future area of research that would be viable would be to do extended long-term testing, and to widen the range of sensitizer additions. The effects would be expected to be different for different sensitizers based on the initial data obtained in this study. Long-term testing of additional sensitizers would provide more definitive data.

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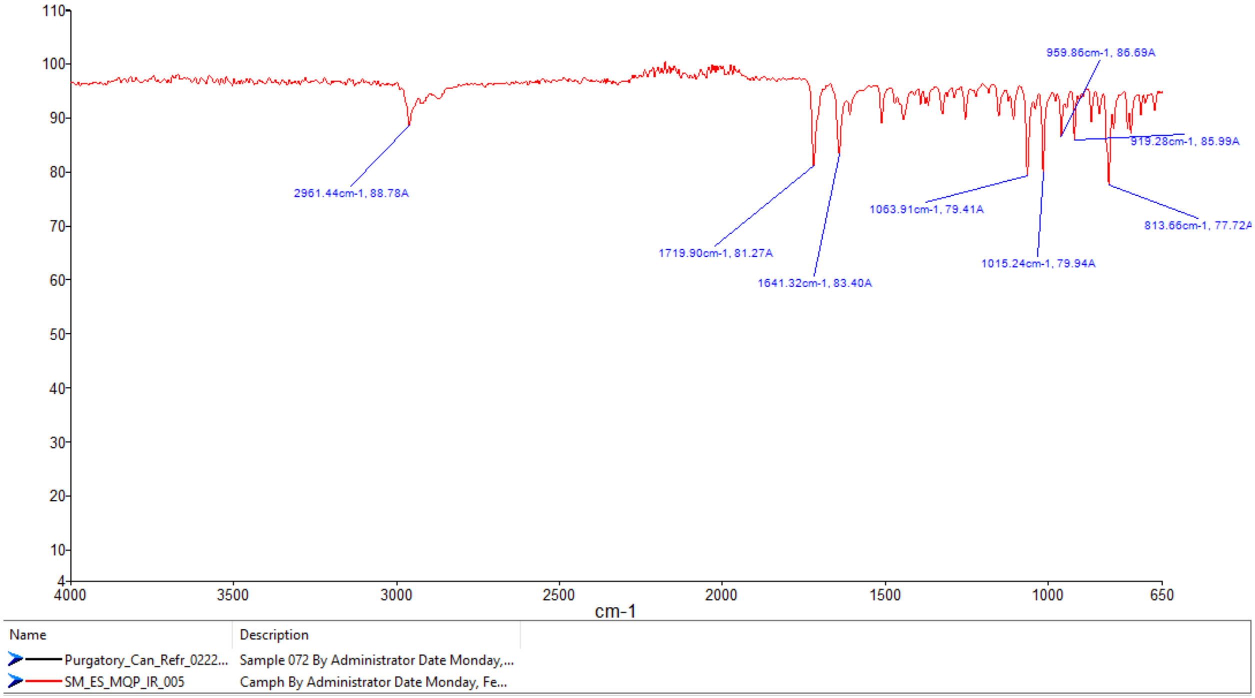
Appendices

Appendix 1: IR



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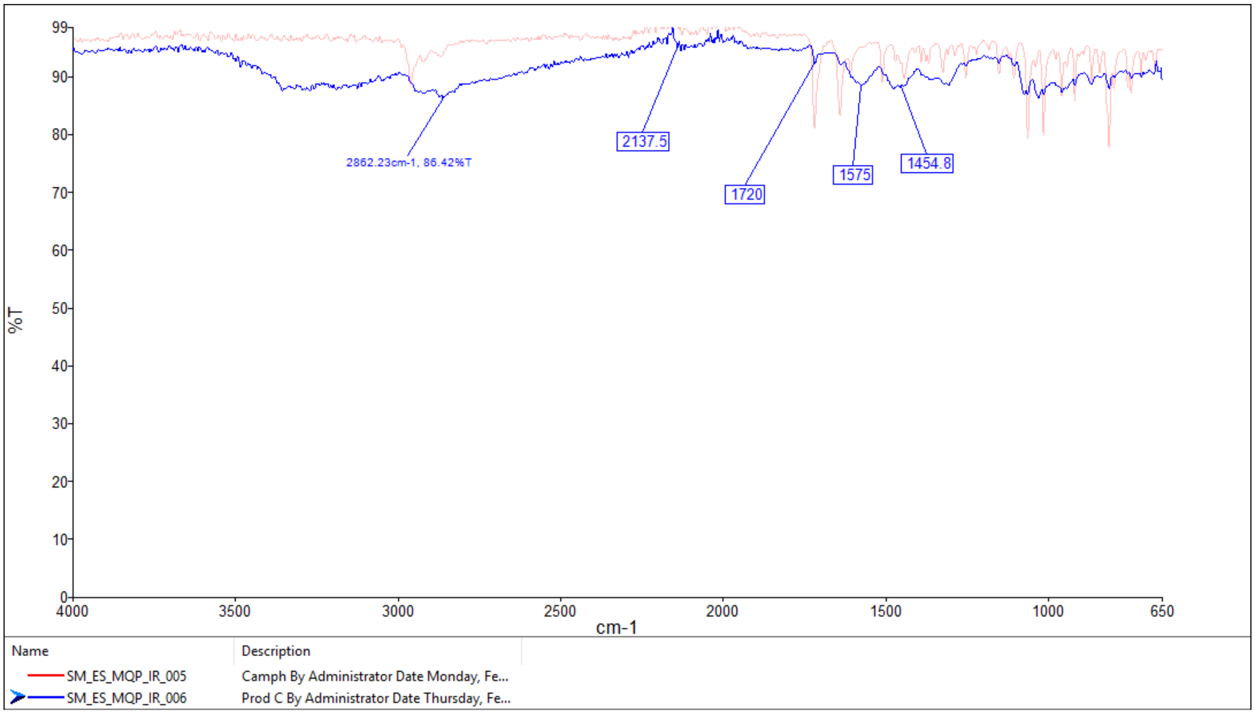
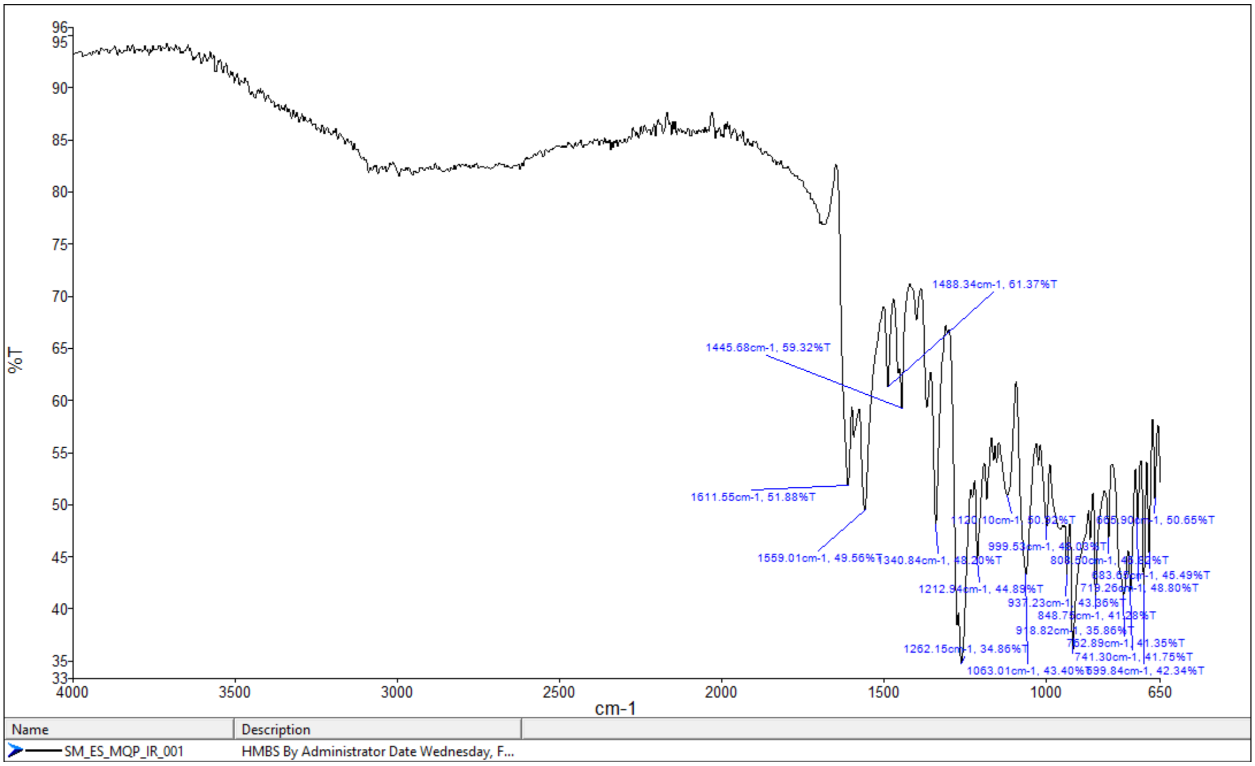
SM_ES_MQP_IR_005	Camph By Administrator Date Monday, Fe...

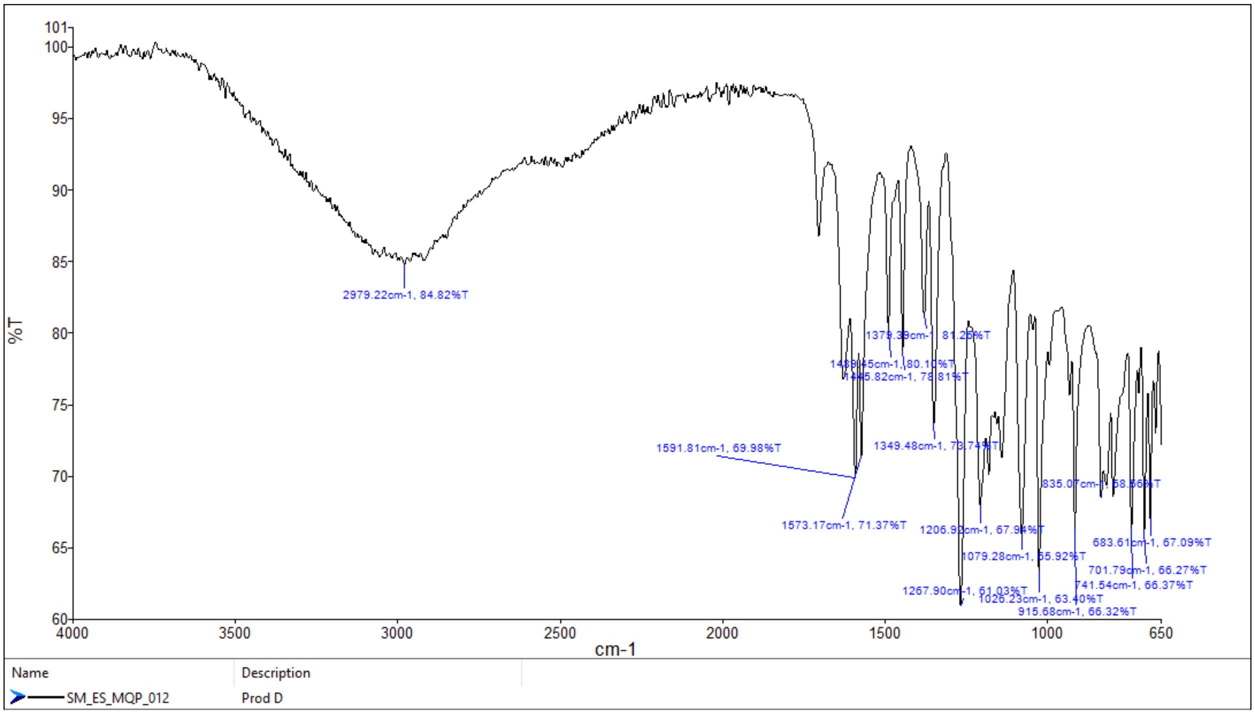
Camph IR



Product C IR

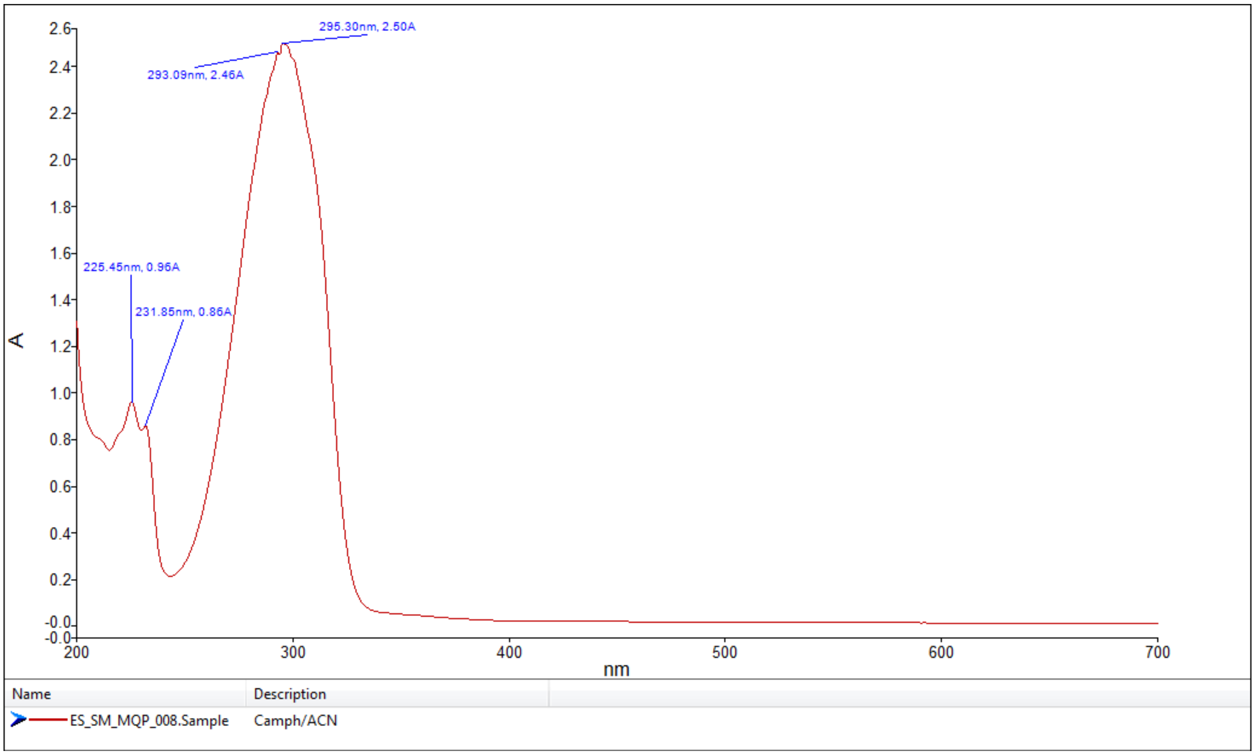


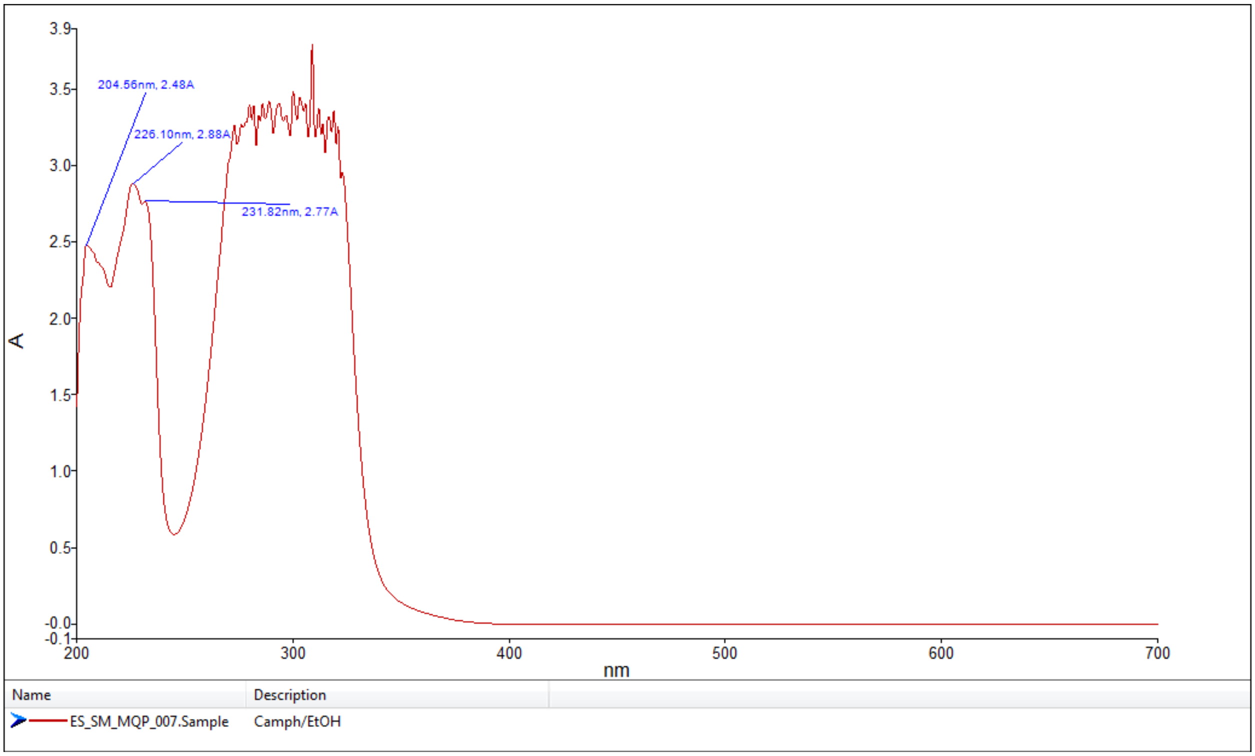
HMBS IR

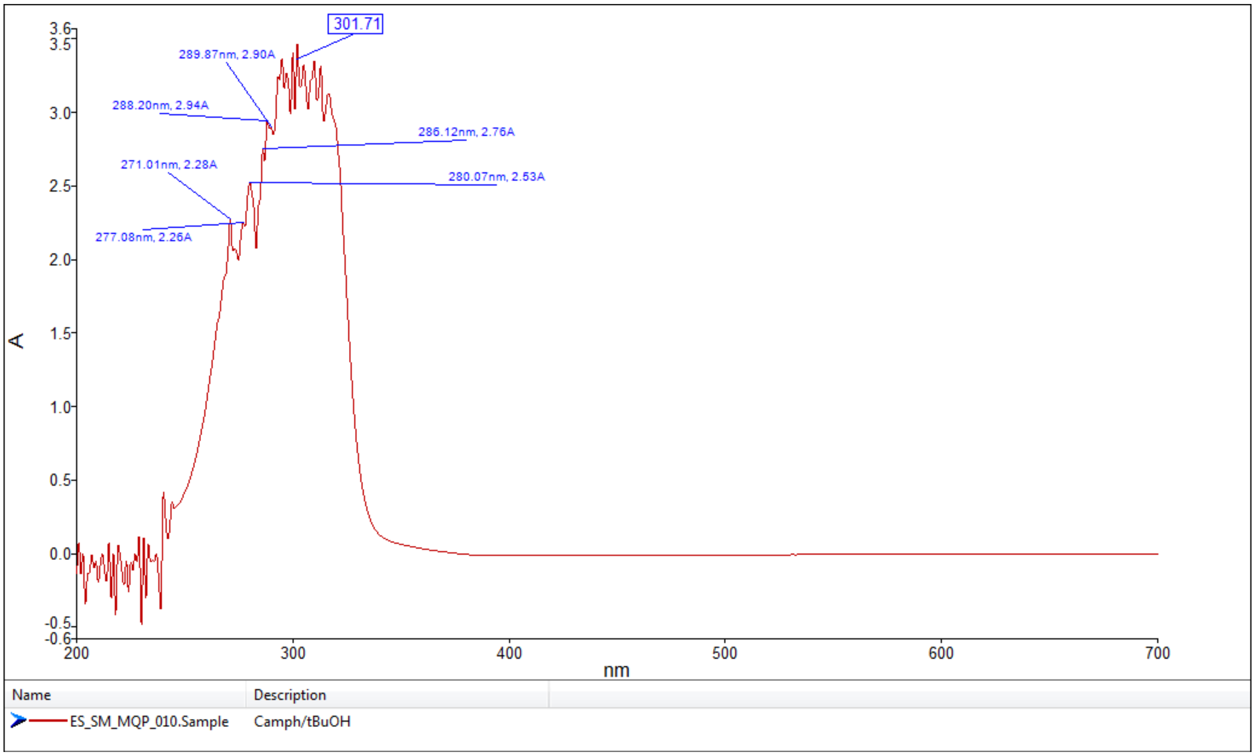

101
100
95
90
85
80
75
70
65
60
%T
4000
3500
3000
2500
2000
1500
1000
650
cm-1
2979.22cm-1, 84.82%T
1379.39cm-1, 81.26%T
1489.45cm-1, 80.10%T
1445.82cm-1, 78.81%T
1591.81cm-1, 69.98%T
1349.48cm-1, 73.74%T
1573.17cm-1, 71.37%T
835.07cm-1, 68.56%T
1206.92cm-1, 67.94%T
683.61cm-1, 67.09%T
1079.28cm-1, 65.92%T
701.79cm-1, 66.27%T
741.54cm-1, 66.37%T
1267.90cm-1, 61.03%T
1026.23cm-1, 63.40%T
915.68cm-1, 66.32%T
Name
Description
SM_ES_MQP_012
Prod D

Product D IR

Appendix 2: UV







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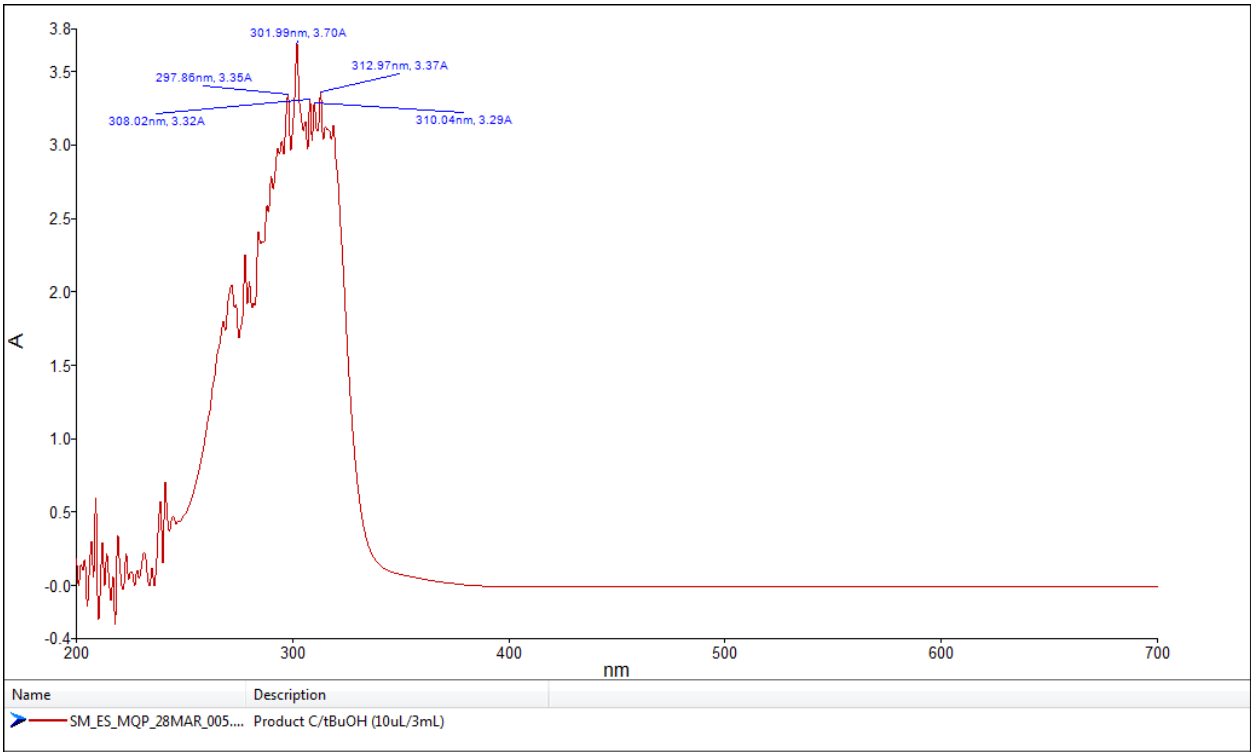

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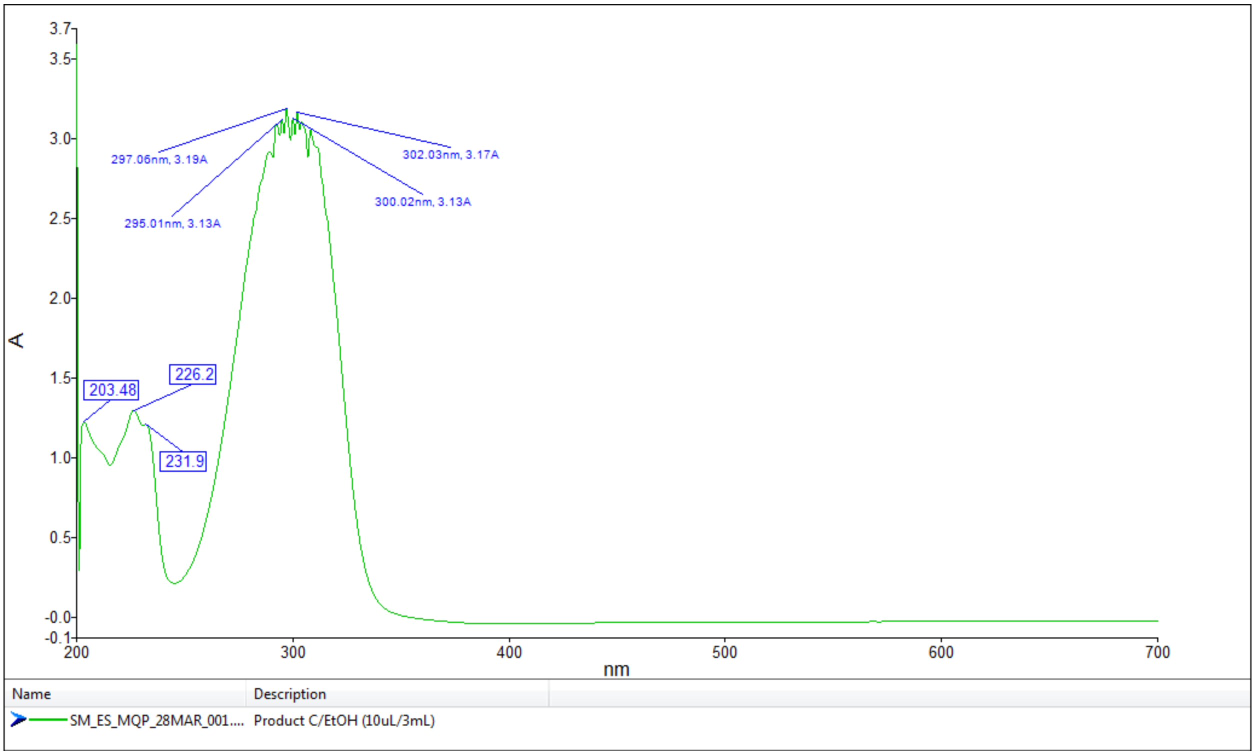

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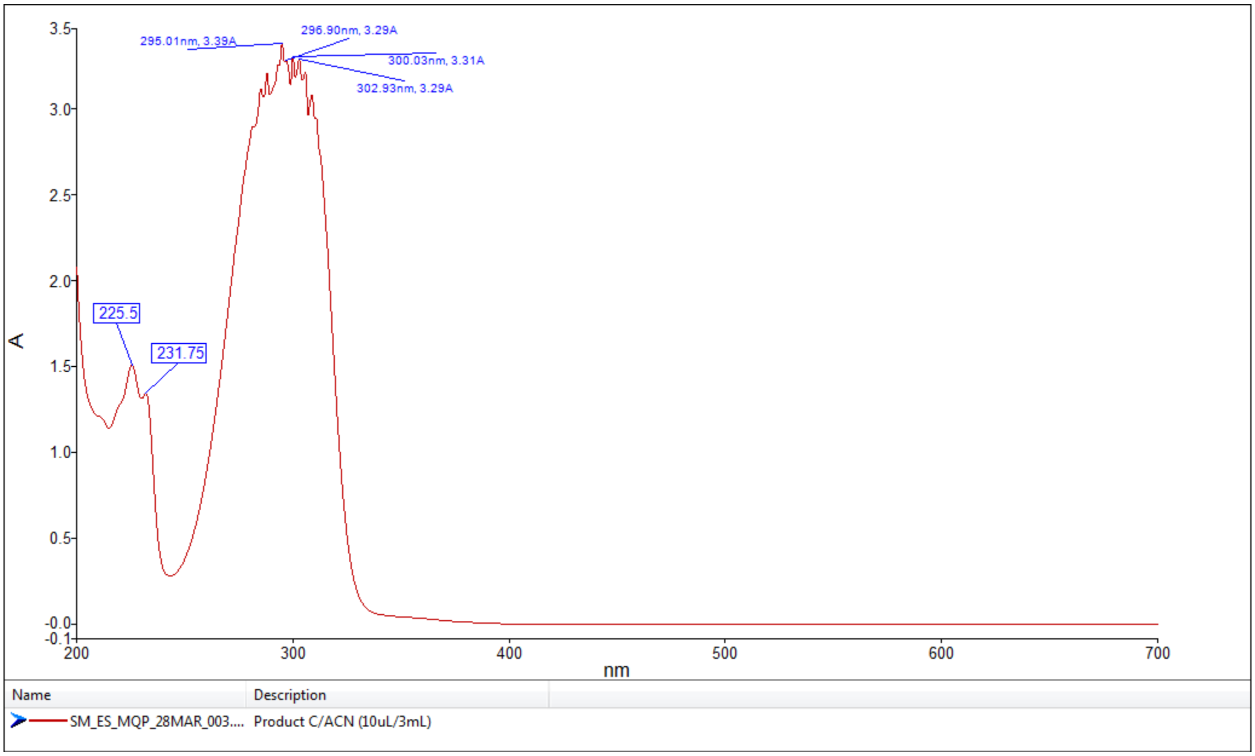

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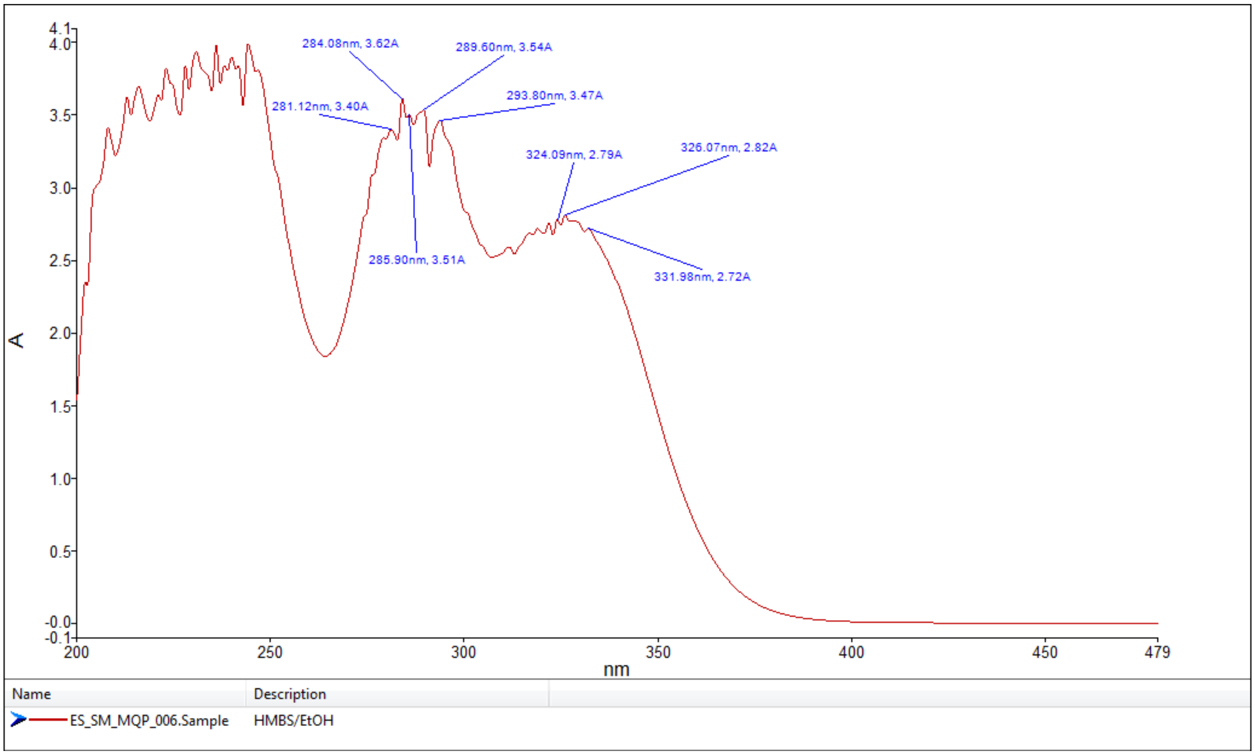

Name	Description
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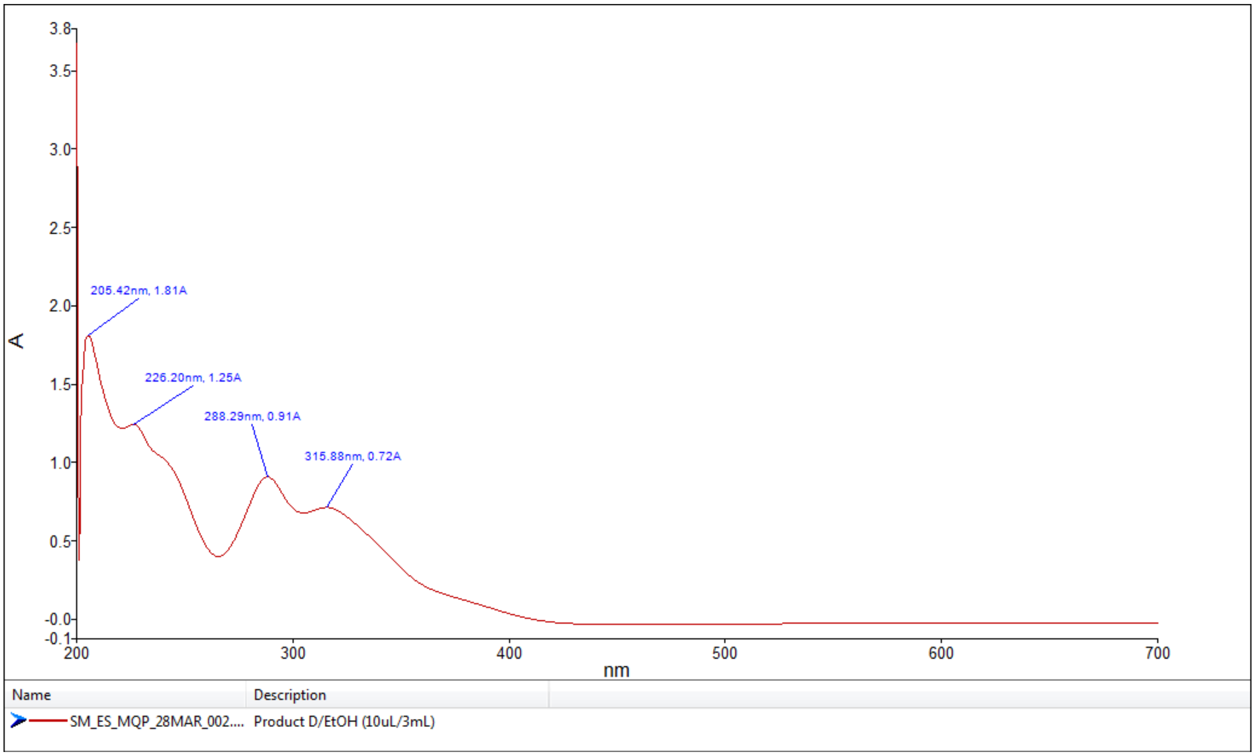

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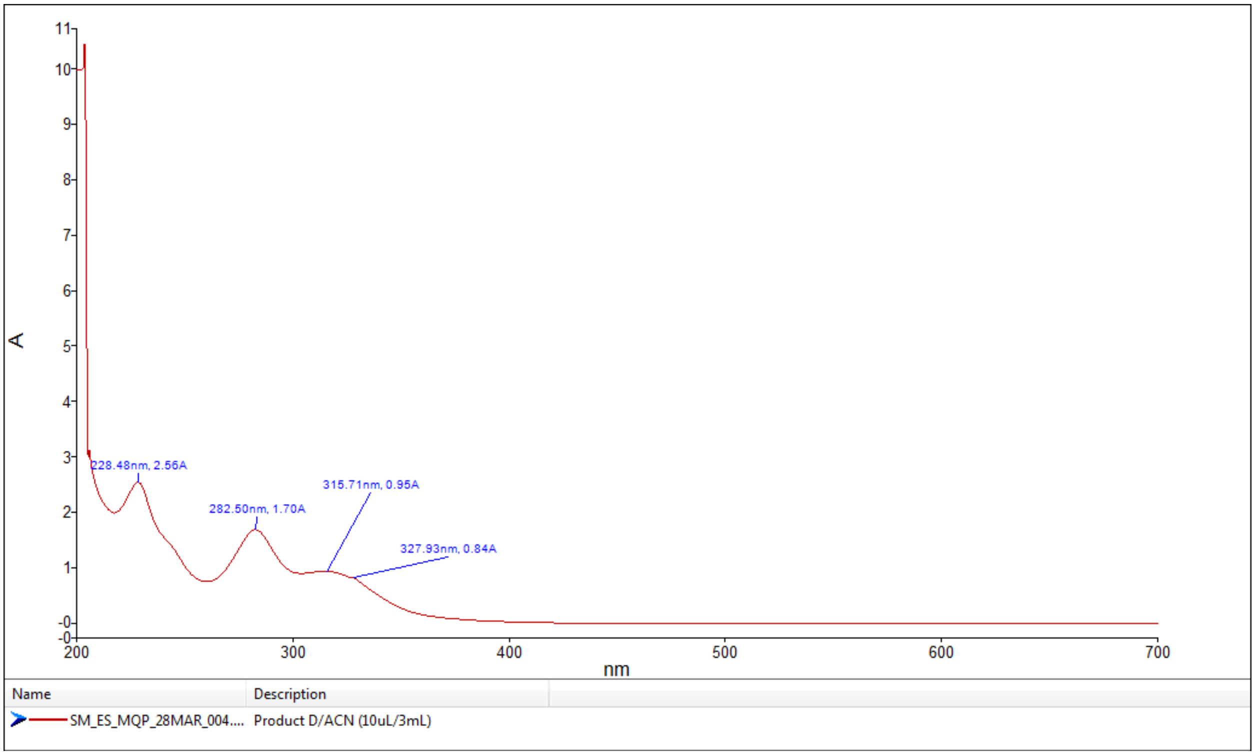

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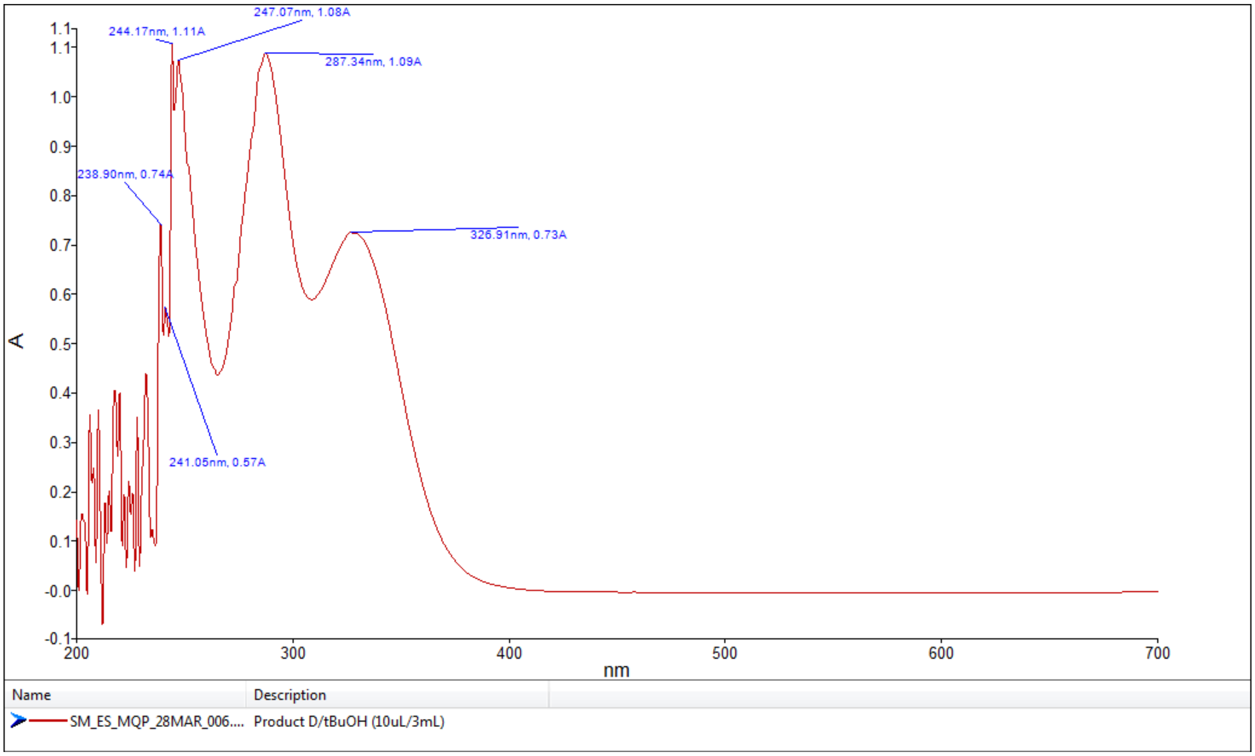

Name	Description
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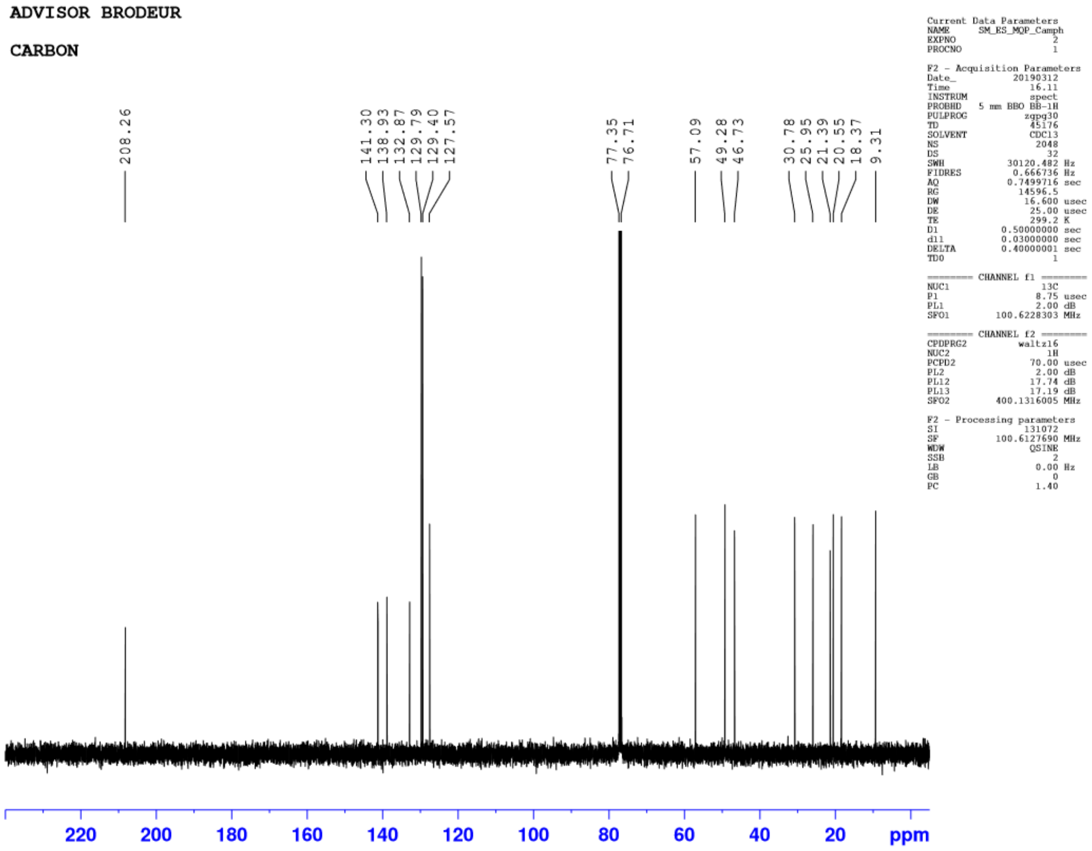
Appendix 3: NMR



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EXPNO                   2
PROCNO                  1

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Date_            20190312
Time                16.11
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PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 45176
SOLVENT            CDCl3
NS                  2048
DS                    32
SWH            30120.482 Hz
FIDRES          0.666736 Hz
AQ             0.7499716 sec
RG               14596.5
DW                16.600 usec
DE                 25.00 usec
TE                 299.2 K
D1            0.50000000 sec
d11           0.03000000 sec
DELTA         0.40000001 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.75 usec
PL1                 2.00 dB
SFO1         100.6228303 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PL2                 2.00 dB
PL12               17.74 dB
PL13               17.19 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
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SF           100.6127690 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
PC                  1.40
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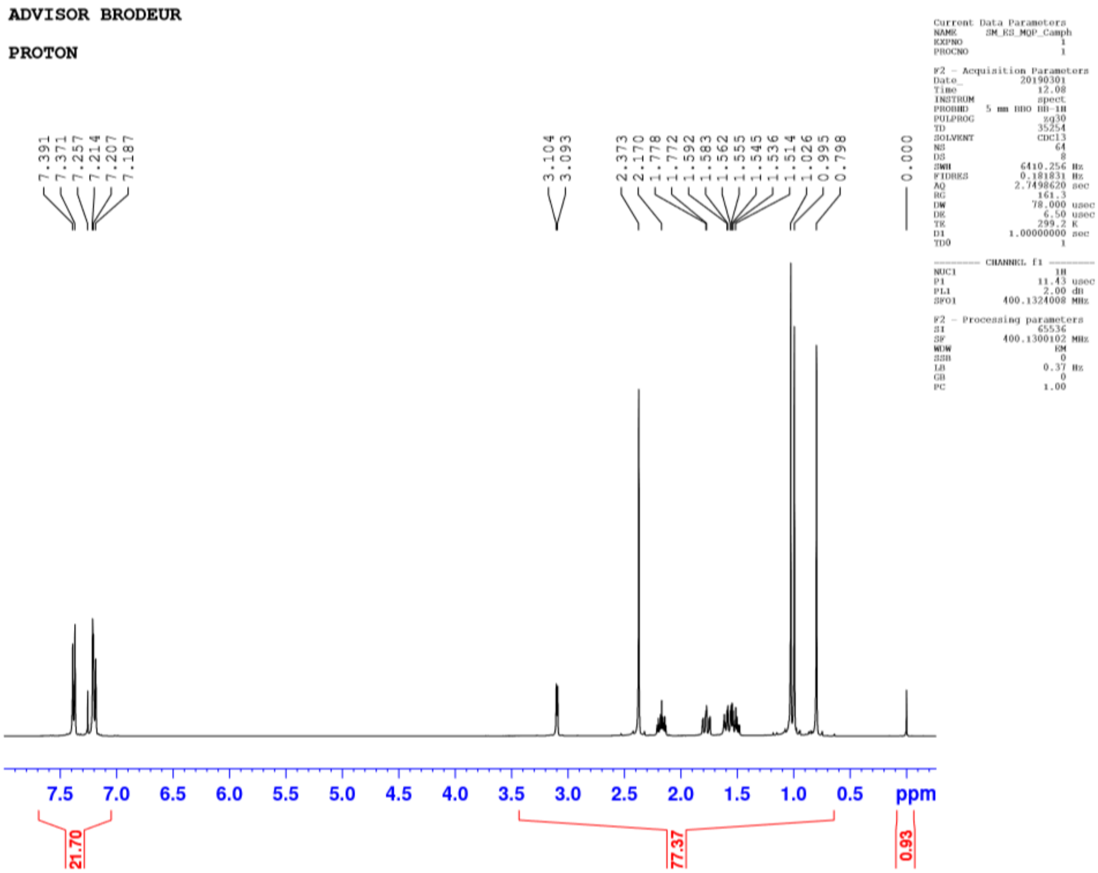
Compound A Carbon NMR



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SOLVENT             CDCl3
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DS                      8
SWH              6410.256 Hz
FIDRES           0.181831 Hz
AQ              2.7498620 sec
RG                  161.3
DW                 78.000 usec
DE                   6.50 usec
TE                  299.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.43 usec
PL1                  2.00 dB
SFO1          400.1324008 MHz

F2 - Processing parameters
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GB                      0
PC                   1.00
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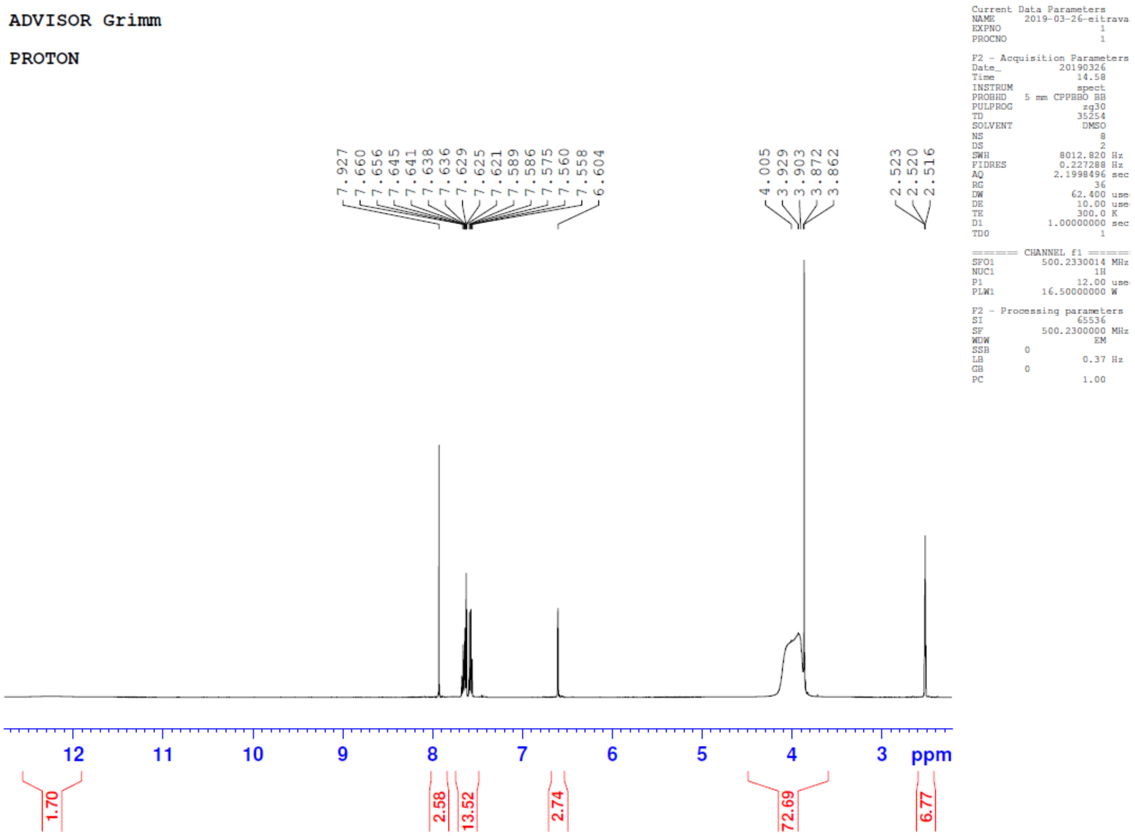
Compound A Proton NMR



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PULPROG               zg30
TD                   35254
SOLVENT               DMSO
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.227288 Hz
AQ               2.1998496 sec
RG                      36
DW                  62.400 use
DE                   10.00 use
TE                   300.0 K
D1              1.00000000 sec
TD0                      1

====== CHANNEL f1 ======
SFO1           500.2330014 MHz
NUC1                    1H
P1                   12.00 use
PLW1           16.50000000 W

F2 - Processing parameters
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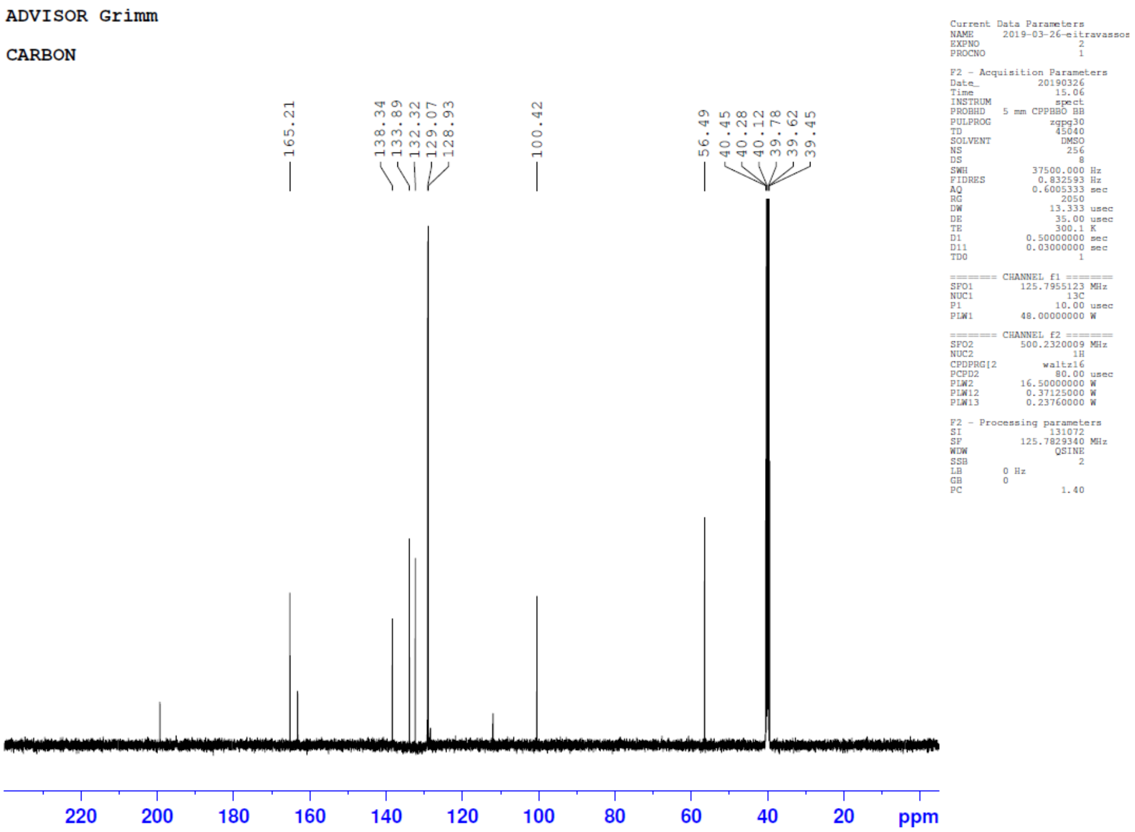
GB       0
PC                    1.00
```

Compound B proton NMR



ADVISOR Grimm

CARBON

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DS                        8
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FIDRES         0.832593 Hz
AQ            0.6005333 sec
RG                     2050
DW               13.333 usec
DE                35.00 usec
TE                300.1 K
D1           0.50000000 sec
D11          0.03000000 sec
TD0                       1

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NUC1                    13C
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PLW1        48.00000000 W

======= CHANNEL f2 =======
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NUC2                     1H
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PCPD2             80.00 usec
PLW2        16.50000000 W
PLW12        0.37125000 W
PLW13        0.23760000 W

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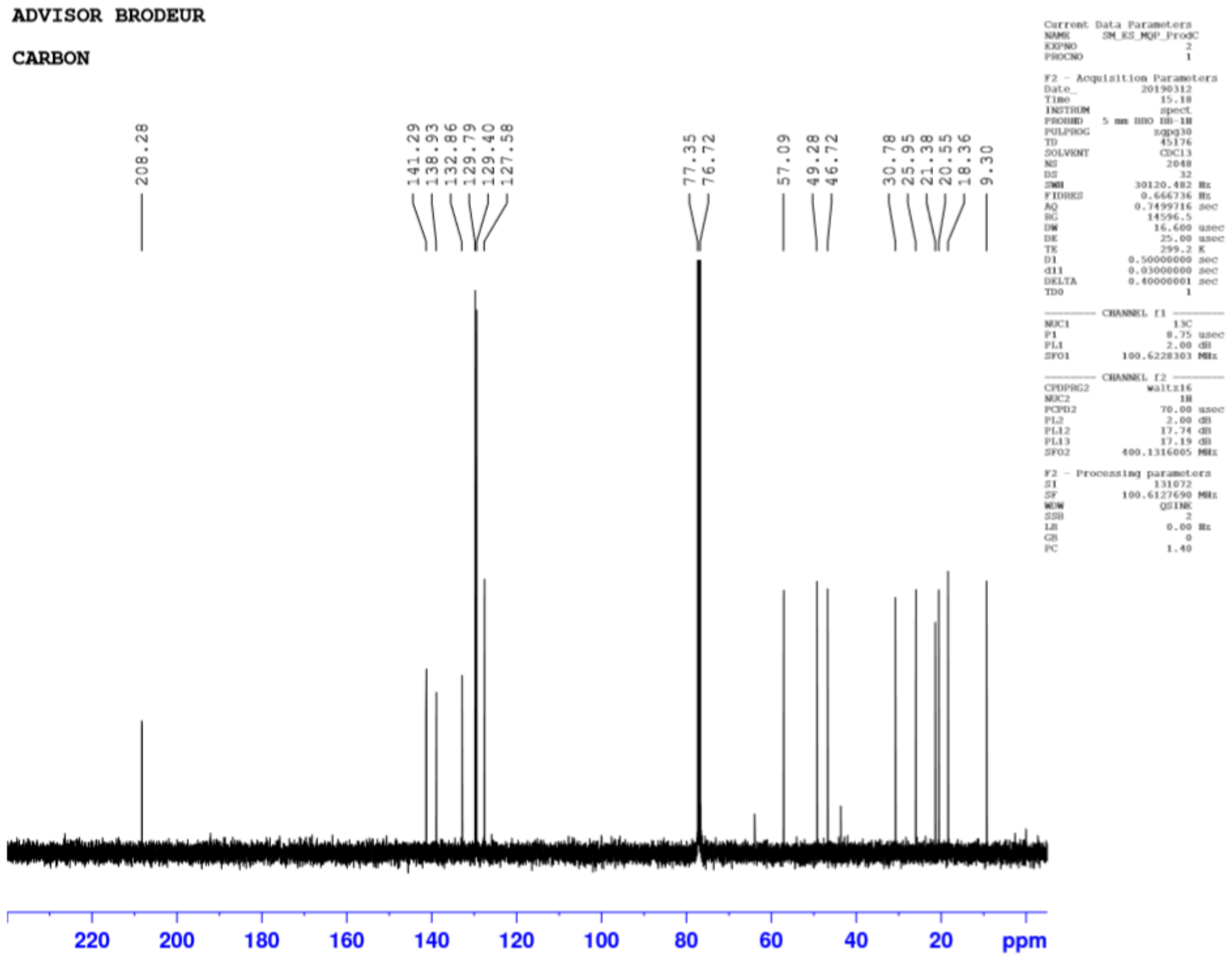
Compound B Carbon NMR



ADVISOR BRODEUR

CARBON

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PROCNO                 1

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FIDRES          0.666736 Hz
AQ             0.7499716 sec
RG               14596.5
DW                16.600 usec
DE                 25.00 usec
TE                 299.2 K
D1            0.50000000 sec
d11           0.03000000 sec
DELTA         0.40000001 sec
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======== CHANNEL f1 ========
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P1                  8.75 usec
PL1                 2.00 dB
SFO1         100.6228303 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PL2                 2.00 dB
PL12               17.74 dB
PL13               17.19 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
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GB                     0
PC                  1.40
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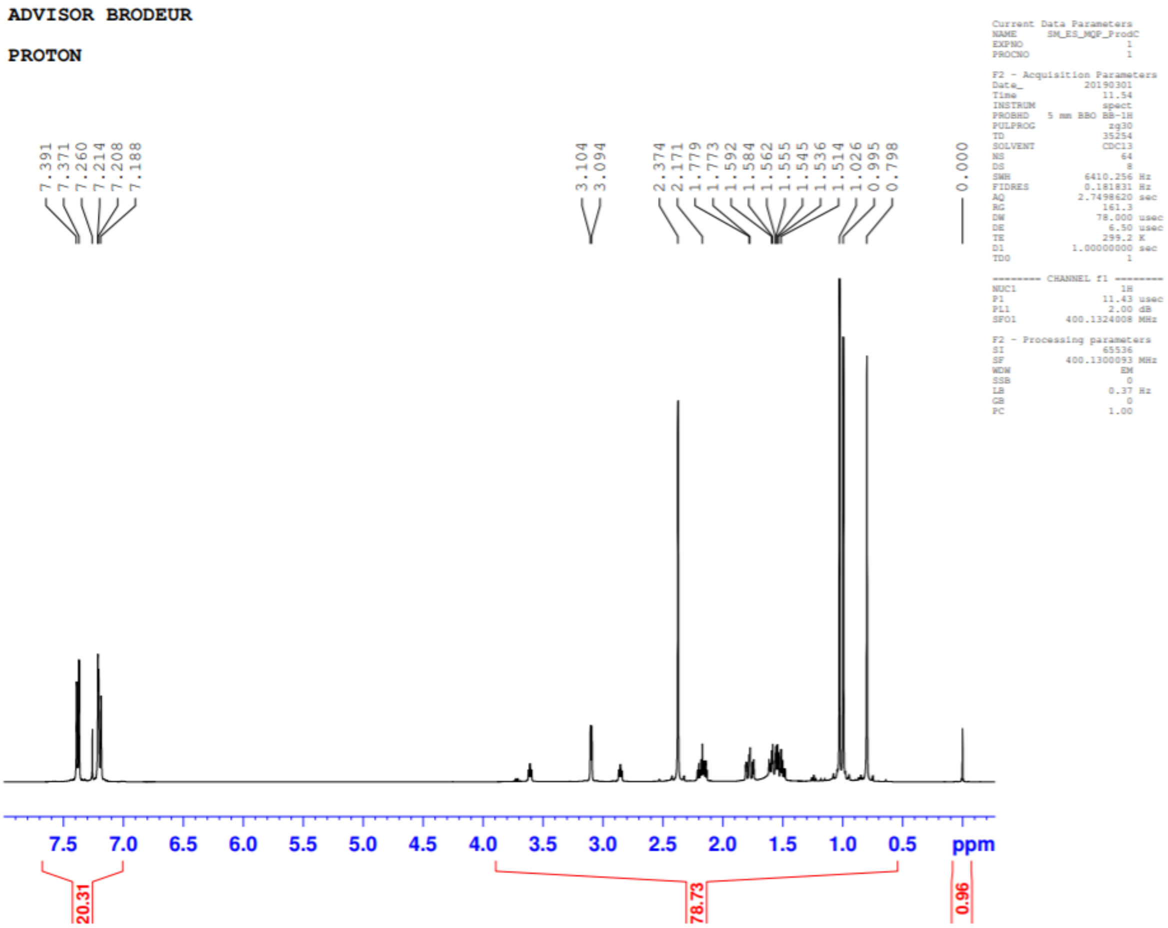
Prod C Carbon NMR



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PROCNO                  1

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FIDRES           0.181831 Hz
AQ              2.7498620 sec
RG                  161.3
DW                 78.000 usec
DE                   6.50 usec
TE                  299.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
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P1                  11.43 usec
PL1                  2.00 dB
SFO1          400.1324008 MHz

F2 - Processing parameters
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WDW                    EM
SSB                     0
LB                   0.37 Hz
GB                      0
PC                   1.00
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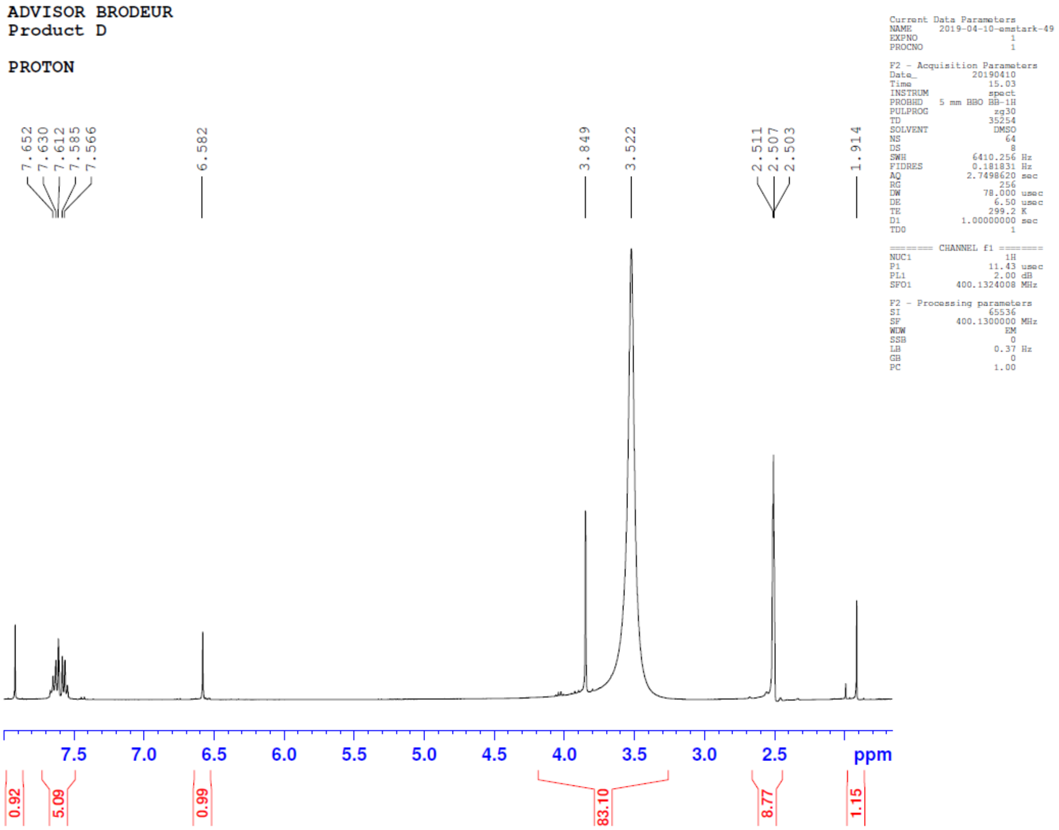
Prod C Proton NMR



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PROCNO                       1

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TD                   35254
SOLVENT               DMSO
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DS                       8
SWH               6410.256 Hz
FIDRES            0.181831 Hz
AQ               2.7498620 sec
RG                     256
DW                  78.000 usec
DE                    6.50 usec
TE                   299.2 K
D1              1.00000000 sec
TD0                      1

======= CHANNEL f1 =======
NUC1                    1H
P1                   11.43 usec
PL1                   2.00 dB
SFO1           400.1324008 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.37 Hz
GB                       0
PC                    1.00
```

Product D proton NMR