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# Solvent Free Vanadium Mediated Organic Transformations

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# **Solvent Free Vanadium Mediated Organic Transformations**

A Thesis

Presented to the Department of Chemistry

College of Liberal Arts and Sciences

And

The Honors Program

of

Butler University

In Partial Fulfillment

of the Requirements for Graduation Honors

Garrett Oberst

April 18, 2016

## **Abstract**

A mixture of vanadium(V) oxide and copper sulfate was used to catalyze oxidative transformations in a variety of organic compounds. Multiple functionalities were tested, including thiols, amines and alcohols. Various transformations were observed resulting in various oxidized products, including coupling reactions. Reactions were performed in a solvent-free environment due to the insoluble nature of vanadium(V) oxide in common organic solvents. Results were analyzed using HNMR and GCMS.

## **Acknowledgements**

The author would like to thank Dr. John Esteb for providing the opportunity to research in his lab, and for guidance and support throughout this project. A special thanks to the Butler Summer Institute for providing funding for this project.

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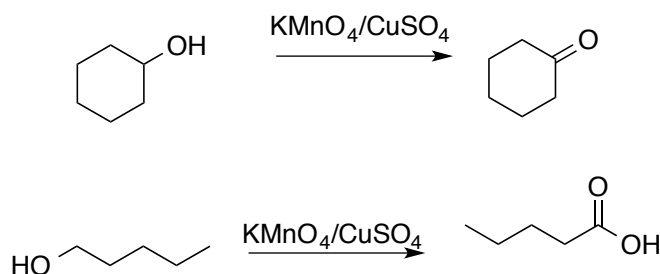
## **Introduction**

### **Oxidation Reactions**

An oxidation occurs anytime a chemical compound or element gives up electrons that are used to reduce another compound or element. An obvious example of an oxidation is the transformation of iron into rust upon interaction with environmental oxygen.<sup>1</sup> Whether it is apparent or not, oxidation reactions are important in the everyday lives of humans. For example, oxidation reactions occur in the environment when atmospheric ozone and hydrogen peroxide are able to oxidize sulfur dioxide in clouds and rainwater.<sup>2</sup> The oxidation of sulfur dioxide, a pollutant released from the burning of coal, is beneficial for the environment and decreases the amount of pollution in the air. Oxidation reactions are also important physiologically with glucose oxidation often decreased in diabetes patients.<sup>3</sup> In addition to these natural occurrences, oxidation reactions are useful industrially in the synthesis of any number of compounds in an efficient manner.

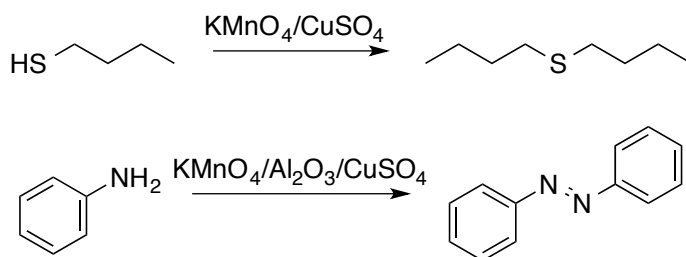
In order for an oxidation reaction to occur, an oxidizing agent must be present. The oxidizing agent is responsible for accepting the electrons that the element being oxidized is losing and is said to undergo a reduction. An ideal species to serve as an oxidizing agent has a high oxidation state. A higher oxidation state implies that the compound has a greater likelihood of accepting electrons, undergoing reduction. For example, a common oxidizing agent that is often used in an undergraduate organic laboratory is a  $\text{KMnO}_4$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  mixture. In this compound, the manganese has an oxidation number of +7, the maximum oxidation state for manganese. This  $\text{KMnO}_4$  when coupled with  $\text{CuSO}_4$  is able to oxidize

alcohols to ketones, aldehydes, and carboxylic acids (Figure 1).<sup>4</sup> The reduced manganese often forms a manganese oxide with a lower oxidation state.



**Figure 1.** Oxidations of alcohols into ketones and carboxylic acids.

The oxidative reactions extend beyond primary and secondary alcohols. Shaabani and Lee showed interesting transformations of thiols and amines could be achieved using the same  $\text{KMnO}_4$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  mixture (Figure 2).<sup>5</sup> These transformations included the creation of disulfides from thiols, coupling of aromatic amines, and the creation of sulfones from sulfides. A wide variety of oxidative transformations have been studied and the list of these continues to grow as new conditions, oxidizing agents, and substrates are employed.



**Figure 2.** Coupling of thiols and amines.

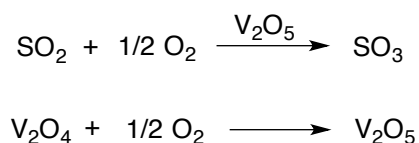
## Vanadium Chemistry

Vanadium is a trace metal that is naturally found in the environment in soil and water.<sup>6</sup> Vanadium compounds typically make good oxidizing agents due to the multiple stable oxidation states of vanadium. While many elements have multiple



oxidation states, vanadium is fairly unique for a transition metal in that it has four stable oxidation state, +2, +3, +4, and +5. Vanadium(V) oxide is important in the industrial world in the production of ferrovanadium, a frequent substitute for steel.<sup>7</sup> Ferrovanadium is formed by heating the vanadium(V) oxide with scrap iron, ferrosilicon and lime.<sup>8</sup>

Vanadium's main use in chemistry is as a catalyst. It used industrially to catalyze one of the steps in the production of sulfuric acid. During this step, sulfur dioxide and oxygen are passed over a vanadium(V) oxide catalyst, forming sulfur trioxide while vanadium(V) oxide is reduced to vanadium(IV) oxide. The vanadium(IV) oxide is then reoxidized by oxygen into vanadium(V) oxide and the process is repeated (Figure 3).<sup>9</sup>



**Figure 3.** Catalytic cycle of  $\text{V}_2\text{O}_5$  in the production of sulfuric acid.

Specific applications of vanadium chemistry have shown it to be valuable, but its lack of solubility in both water and other commonly used organic solvents has limited its ability to be studied.<sup>10</sup> The physiological effects of vanadium have also hindered its ability to be studied in the laboratory. While vanadium is not carcinogenic, it is classified as toxic, which presents certain challenges when handling. Exposure to vanadium can cause irritation of the skin and gastrointestinal tract. Additionally, vanadium can cause symptoms of bronchitis and other respiratory issues.<sup>10</sup> This is a result of the similarity in size and charge of vanadium(V) and phosphorous(V). Because phosphorous is an important cofactor

for many biological process, vanadium is often able to mimic phosphorous in biological systems and has been found to cause problems with ATPases, protein kinases, ribonucleases, and phosphatases.<sup>11</sup>

## **Project Background**

The goal of this project was to use the oxidative properties of vanadium(V) oxide in order to oxidize compounds in a solvent-free similar manner to the  $\text{KMnO}_4/\text{CuSO}_4$  reaction. Utilizing a solvent free reaction condition could circumvent the vanadium solubility issues. By using a vanadium(V) oxide and copper sulfate pentahydrate mixture, new transformations of thiols, amines, and alcohols were attempted. Because of the similarities in oxidation states between the vanadium of vanadium(V) oxide and the manganese of the potassium permanganate, it was theorized that similar and possibly new transformations could occur.

The reactions performed in this study were modeled after the reaction reported by Esteb et. al., but on a smaller scale. By discovering new transformations, these reactions could be optimized to develop potentially faster and easier ways to synthesize certain functionalities. While the reactions performed in this study were not necessarily optimized, this study lays the groundwork for further research into the oxidative properties of vanadium(V) oxide mixtures under solvent free conditions.

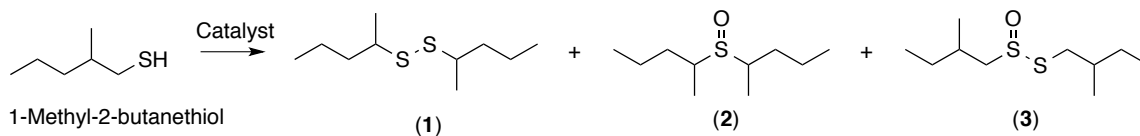
## **Results and Discussion**

The reactions reported were performed on a small scale using the method reported by Esteb, et. al. The identity of products of these reactions was determined by HNMR and GCMS.

### **Thiol Reactions**

Unfortunately, only a small number of thiol reactions could be performed due to ventilation difficulties in the laboratory. The most common result of the experimental reaction of the thiol compounds tested was the formation of a disulfide from the original starting reagents. The coupling product was seen in higher yield in the catalyzed reaction versus the catalyst free control reactions.

*Reactions 1-8: 2-methyl-1-butanethiol*



**Figure 4.** Reaction scheme of 1-methyl-2-butanethiol reaction.

Rxn #	Catalyst	Rxn Time	% 1	% 2	% 3
1	None	15 min	80	6	0
2	V2O5	15 min	83	0	0
3	CuSO4	15 min	93.5	0	0
4	V2O5 and CuSO4	15 min	92	0	0
5	None	1.5 hrs	36	0	36
6	V2O5	1.5 hrs	92	0	2
7	CuSO4	1.5 hrs	50	0	0
8	V2O5 and CuSO4	1.5 hrs	88	0	0

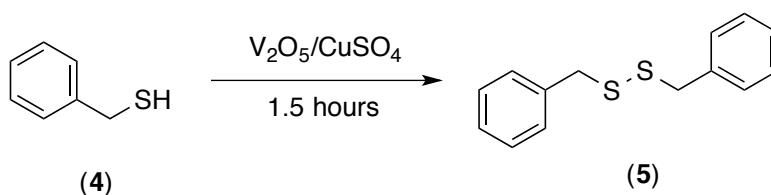
**Table 1.** Results of GCMS analysis of reactions using 1-methyl-2-butanethiol as a starting material.

Because the reactions of 2-methyl-1-butanethiol (Figure 4) were run at both 15 minutes and 1.5 hours, it is best to view these as two separate reactions for comparison. All 15 minute reactions gave yield of the disulfide (**1**) greater than 80% (Table 1). While the yield of product one for the reaction with  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  was higher than the reaction with both  $\text{V}_2\text{O}_5$  and  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ , both yields were very high (93.5% vs. 92%) (Table 1). The 15 minute catalyst free control reaction produced product 3 with 6% yield.

The 1.5 hour reactions showed varied results. While the reactions run without the catalyst showed product one yields of 50% or less, the yields of both reactions including the catalyst showed product one yield of greater than 85%. It is

important to note that in the 1.5 hour reaction without a catalyst, product three was formed with the same yield as product 1. This indicates that the vanadium/copper sulfate mixture may have inhibited the formation of product three while increasing the formation of product one. Side products were observed in some of these reactions as well.

*Reaction 9: Benzyl Mercaptan*



**Figure 5.** Benzyl mercaptan reaction scheme.

The benzyl mercaptan (4) reaction yielded benzyl disulfide (5) (Figure 5) with 98% relative yield and no apparent side products. Uncatalyzed control reactions of benzyl mercaptan were not run because of the ventilation problems.

## Amine Reactions

### Reactions 10-13: Benzhydryl Amine

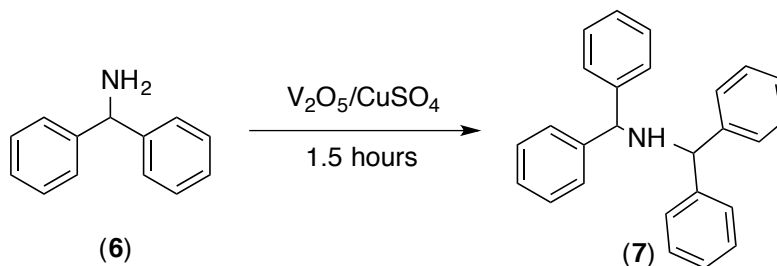
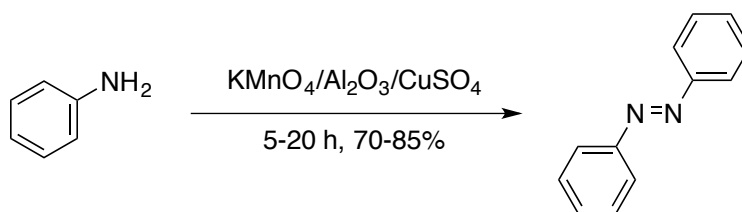


Figure 6. Benzhydryl amine reaction scheme.

Rxn #	Catalyst	% 6	% 7
10	None	17	83
11	$CuSO_4$	60	40
12	V2O5	45	55
13	V2O5 and $CuSO_4$	77	33

Table 2. Yield of N-diphenylmethylenediphenylamine for reactions of benzhydryl amine with both  $V_2O_5$  and  $CuSO_4 \cdot H_2O$ . All reactions were run for 1.5 hours at  $100^\circ C$ .

Benzhydryl amine (6) was also reaction with and without catalyst, but all reactions were run for 1.5 hours (Table 2). Catalyzed benzhydryl amine reactions (Figure 6) yielded a higher amount of N-diphenylmethylenediphenylamine (7) than did any of the uncatalyzed reactions (Table 2). This indicated that the vanadium/copper sulfate mixture might have poisoned the reaction instead of acting as a catalyst. This was surprising given the examples of aromatic amine coupling found by Shabbani and Lee. The product of this reaction was different than the diazo compounds observed by Shabbani and Lee (Figure 7).

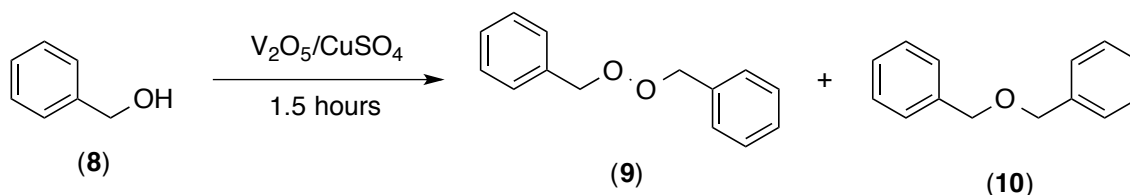


**Figure 7.** Shabbani and Lee reaction using aniline as a starting material.

## Alcohol Reactions

### *Reaction 14: Benzyl Alcohol*

Benzyl alcohol (**8**) was utilized as a representative alcohol and reaction under similar conditions (Table 3).



**Figure 8.** Benzyl alcohol reaction scheme.

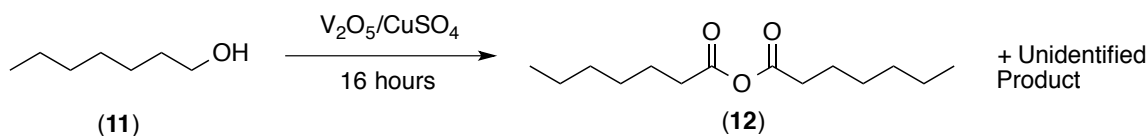
The reaction of benzyl alcohol (Figure 8) yielded two significant products. A product with the retention time of 11.109 and a fragment peak of 107 was identified as benzyl peroxide (**9**). The oxygen-oxygen bond of the product nine would be cleaved under GCMS conditions. Therefore, this identification can be made based upon the likely structures that would be present after cleavage of the oxygen-oxygen bond of product nine. The main product of this reaction was identified to be dibenzyl ether (**10**). Specific GCMS peaks and the products that each corresponds to are shown in Table 3.

Retention Time	M+	Probable ID	% of product
6.611	108	Benzyl Alcohol (8)	60
11.109	107	Benzyl Peroxide (9)	8
14.712	198	Dibenzyl Ether (10)	32

**Table 3.** GCMS results for reaction of benzyl alcohol with both  $V_2O_5$  and  $CuSO_4 \cdot H_2O$ . Reaction was run for 1.5 hours at  $100^\circ C$ .

### Reaction 15: 1-Heptanol

An alkyl alcohol, 1-heptanol (**11**), was also explored (Figure 9).



**Figure 9.** 1-Heptanol reaction scheme.

The reaction of 1-heptanol (Figure 9) produced two products. One product was identified as heptanoic anhydride (**12**) and the other could not be identified. It appears as though the vanadium/copper mixture acted as an oxidizing agent in this case as product twelve was formed along with another transformation. It is also noteworthy that the procedure was modified in order to produce a reaction with higher yield. This reaction was run for 16 hours. Specific GCMS peaks and the products that each corresponds to are shown in Table 4.

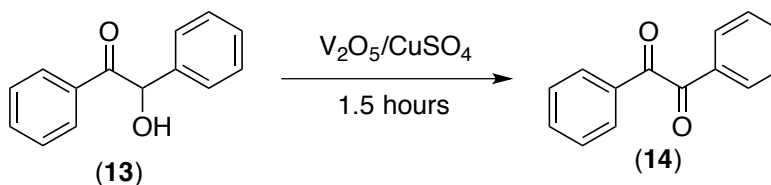


Retention Time	M+	Probable ID	% of product
5.972	98	Heptanol	42
9.862	215	Unknown	4
12.192-13.091	242	Heptanoic Anhydride	54

**Table 4.** GCMS results for reaction of 1-heptanol with both  $V_2O_5$  and  $CuSO_4 \cdot H_2O$ . Reaction was run for 16 hours at  $100^\circ C$ .

### Reactions 16-19: Benzoin

A final alcohol, benzoin (**13**), was also explored under both catalyzed and uncatalyzed conditions. (Figure 10) (Table 5). The products of these reactions were observed using HNMR due to similarities in polarity and molecular weight of the benzoin and the predicted product, benzil (**14**). The disappearance of peaks near in the range of four to six indicated the transformation of benzoin to product 14. Integration allowed the determination of relative amounts of each.



**Figure 10.** Benzoin reaction scheme.

Reaction #	Catalyst	% Benzil	% Benzoin
16	None	0%	100%
17	$V_2O_5$	96%	4%
18	$CuSO_4$	17%	83%
19	$V_2O_5$ and $CuSO_4$	95%	5%

**Table 5.** HNMR results for reaction of benzoin with various catalysts. Reactions were run for 1.5 hours at  $100^\circ C$ .

Reactions of benzoin formed product 14 at yields greater than 90% with the vanadium(V) oxide. In the absence of the vanadium catalyst, yields lower than 20%

were observed. This suggests that the vanadium specifically played a role in catalyzing the transformation of benzoin to product fourteen.  $\text{CuSO}_4$  exhibited a degree of catalytic activity as well since the yield in the presence of  $\text{CuSO}_4$  is greater than the reaction with no catalyst.

## **Conclusions and Future Work**

A variety of transformations were catalyzed by the vanadium(V) oxide and copper sulfate pentahydrate mixture. While the alcohol reactions resulted in a lower conversion of starting material to product, the amine and thiol reactions resulted in quite high percentage conversions to products. Because only a primary thiol was studied, it is difficult to draw a conclusion that can be applied to other thiols. Future work could be done in testing different types of thiols and attempting to identify consistencies and trends. The same can be said for amines.

The other aspect of the experimental procedure that can be altered is the reaction time. It is possible that some of the products observed in this project could be intermediates in forming further oxidized products. It is also possible that intermediates could have been formed during these reactions that were not observed during this project. Future work could be performed by intermittently monitoring the products of the reaction in order to identify which intermediates are present and when they are present. This would allow the reaction to be tailored in order to isolate certain products.

## **Experimental**

### **General Procedures and Chemical Information**

All chemicals were purchased from Sigma Aldrich and used without further purification. GCMS samples were prepared using ethyl acetate as a solvent. HNMR samples were run on a Broker Avance 250 MHz NMR Spectrometer using d-chloroform as a solvent. The GCMS samples were run on a Varian 450-GC Gas Chromatograph and a Varian 220-MS IT Mass Spectrometer. The GCMS samples were run on a nonpolar column.

### **Thiol Reactions**

#### *GCMS Analysis of Thiol Starting Materials*

GCMS was performed on starting materials to determine retention times and M+ peaks.

GCMS: 2-methyl-1-butanethiol (starting reagent):

2-methyl-1-butanethiol (4.342 min; M+=104; 93%)

Autoxidized product (**1**) (9.544 min; M+=206; 7%)

GCMS: benzyl mercaptan (starting reagent)

Benzyl mercaptan (**4**) (7.032 min; M+=124; 94%)

Benzyl disulfide (**5**) (13.284 min; M+=246; 6%)

#### *General Procedure for Thiol Reactions*

A mixture of V<sub>2</sub>O<sub>5</sub> and/or CuSO<sub>4</sub>•H<sub>2</sub>O was ground together using mortar and pestle and then transferred to a 50 mL round bottom flask. Thiol starting reagent was added to the round bottom flask, a condenser was immediately attached, and the

flask was placed in a boiling water bath. After the specified reaction time, the flask was removed from the water bath and the reaction was allowed to cool. After cooling, the condenser was removed and the product was extracted with three 5 mL aliquots of ethyl acetate. The mixture was then gravity filtered to remove any solid that may have been present. After gravity filtration, the mixture was washed with three 5 mL aliquots of water. The organic layer was kept, dried with  $\text{MgSO}_4$ , and gravity filtered. After gravity filtration, rotary evaporation was used in order to remove solvent. A sample of the product was then transferred to a GCMS vial, diluted with ethyl acetate and analyzed to determine reaction products.

*Reaction 1: 2-Methyl-1-butanethiol (no catalyst) – 15 minutes*

Starting Material: 0.47 mL 2-methyl-1-butanethiol ( $3.8 \times 10^{-3}$  mol)

Catalyst: None

Percent Conversion to Product: 86%

GCMS Analysis of Products: Product **1** (9.539 min;  $M^+=206$ ), Product **2** (11.14 min;  $M^+=221$ )

Product 1:2 ratio - 93:7

*Reaction 2: 2-Methyl-1-butanethiol and  $\text{V}_2\text{O}_5$  – 15 minutes*

Starting Material: 0.44 mL 2-methyl-1-butanethiol ( $3.5 \times 10^{-3}$  mol)

Catalyst: 1.89 g of  $\text{V}_2\text{O}_5$  ( $1.0 \times 10^{-2}$  mol)

Percent Conversion to Product: 83%

GCMS Analysis of products: Product **1** (9.535 min;  $M^+=206$ )

*Reaction 3: 2-Methyl-1-butanethiol and  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  – 15 minutes*

Starting Material: 0.55 mL 2-methyl-1-butanethiol ( $4.3 \times 10^{-3}$  mol)

Catalyst: 2.47 g ( $1.5 \times 10^{-2}$  mol)  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$

Percent Conversion to Product: 93.5%

GCMS Analysis of products: Product **1** (9.541 min;  $M^+=206$ )

*Reaction 4: 2-Methyl-1-butanethiol with  $\text{V}_2\text{O}_5$  and  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  – 15 minutes*

Starting Material: 0.58 mL 2-methyl-1-butanethiol ( $4.3 \times 10^{-3}$  mol)

Catalyst: mixture of 1.74 g of  $\text{V}_2\text{O}_5$  ( $9.5 \times 10^{-2}$  mol) and 2.42 g ( $1.5 \times 10^{-2}$  mol)

$\text{CuSO}_4 \cdot \text{H}_2\text{O}$

Percent Conversion to Product: 93.5%

GCMS Analysis of products: Product **1** (9.548 min;  $M^+=206$ )

*Reaction 5: 2-Methyl-1-butanethiol (no catalyst) – 1.5 hours*

Starting Material: 0.54 mL 2-methyl-1-butanethiol ( $4.3 \times 10^{-3}$  mol)

Catalyst: None

Percent Conversion to Product: 83%

GCMS Analysis of products: Product **1** (9.544 min;  $M^+=206$ ; 36% yield), Product **3** (13.159 min;  $M^+=193$ ; 2% yield), Unidentified product (6.60 min;  $M^+=108$ ; 26% yield)

*Reaction 6: 2-Methyl-1-butanethiol and  $\text{V}_2\text{O}_5$  – 1.5 hours*

Starting Material: 0.46 mL 2-methyl-1-butanethiol ( $3.7 \times 10^{-3}$  mol)

Catalyst: 1.83 g of  $\text{V}_2\text{O}_5$  ( $1.0 \times 10^{-2}$  mol)

Percent Conversion to Product: 94%

GCMS Analysis of products: Product **1** (9.544 min; M+=206), Product **3** (13.159 min; M+=193)

Product 1:3 ratio – 49:1

*Reaction 7: 2-Methyl-1-butanethiol with V<sub>2</sub>O<sub>5</sub> and CuSO<sub>4</sub>•H<sub>2</sub>O – 1.5 hours*

Starting Material: 0.49 mL 2-methyl-1-butanethiol (3.9x10<sup>-3</sup> mol)

Catalyst: Mixture of 1.81 g (9.95x10<sup>-3</sup> mol) of V<sub>2</sub>O<sub>5</sub> and 2.50 g (1.5x10<sup>-2</sup> mol) of CuSO<sub>4</sub>•H<sub>2</sub>O

Percent Conversion to Products: 88%

GCMS Analysis of products: Product **1** (9.545 min; M+=206)

*Reaction 8: 2-Methyl-1-butanethiol and CuSO<sub>4</sub>•H<sub>2</sub>O – 1.5 hours*

Starting Material: 0.56 mL 2-methyl-1-butanethiol (4.5x10<sup>-3</sup> mol)

Catalyst: 2.62 g (1.64x10<sup>-2</sup> mol) of CuSO<sub>4</sub>•H<sub>2</sub>O

Percent Conversion to Products: 50%

GCMS Analysis of products: Product **1** (9.544 min; M+=206; 50%)

*Reaction 9: Benzyl mercaptan with V<sub>2</sub>O<sub>5</sub> and CuSO<sub>4</sub>•H<sub>2</sub>O – 1.5 hours*

Starting Material: 0.122 g benzyl mercaptan (**4**) (9.8x10<sup>-4</sup> mol)

Catalyst: Mixture of 0.395 g of V<sub>2</sub>O<sub>5</sub> (2.1x10<sup>-3</sup> mol) and 0.625 g (3.9x10<sup>-3</sup> mol) CuSO<sub>4</sub>•H<sub>2</sub>O

Percent Conversion to Products: 98%

GCMS Analysis of products: Benzyl disulfide (**5**) (13.296 min; M+=246)

## Amine Reactions

### General Amine Reaction Procedure

A mixture of  $V_2O_5$  and/or  $CuSO_4 \cdot H_2O$  was ground together using mortar and pestle and then transferred to a 50 mL round bottom flask. The amine starting reagent was added to the round bottom flask, a condenser was immediately attached, and the flask was placed in a boiling water bath. After a the specified reaction time, the flask was removed from the water bath and the reaction was allowed to cool. After cooling, the condenser was removed and the product was extracted with three 5mL aliquots of ethyl acetate. The mixture was then gravity filtered to remove any solid that may have been present. After gravity filtration, the mixture was washed with three 5 mL aliquots of water. The organic layer was kept, dried with  $MgSO_4$ , and gravity filtered. After gravity filtration, rotary evaporation was used in order to solvent. A sample of the product was then transferred to a GCMS vial, diluted with ethyl acetate and analyzed to determine reaction products.

### *GCMS Analysis of Amine Starting Materials*

GCMS: Benzhydryl amine (starting material):

Benzhydryl amine (**6**) (10.89 min;  $M^+=183$ ; 90% yield).

Autoxidized product (**7**) (16.773 min;  $M^+=347$ ; 10% yield).

### *Reaction 10: Benzhydryl amine (no catalyst)- 1.5 hours*

Starting Material: 0.45 mL benzhydryl amine (**6**) ( $2.6 \times 10^{-3}$  mol)

Catalyst: None

Percent Conversion to Products: 13%



GCMS Analysis of products: Product 7 (16.788 min; M+=347)

*Reaction 11: Benzhydryl amine and CuSO<sub>4</sub>•H<sub>2</sub>O – 1.5 hours*

Starting Material: 0.42 mL benzhydryl amine (6) (2.4x10<sup>-3</sup> mol)

Catalyst: 1.28 g (8.0x10<sup>-3</sup> mol) of CuSO<sub>4</sub>•H<sub>2</sub>O

Percent Conversion to Products: 54%

GCMS Analysis of products: Product 7 (16.786 min; M+=347)

*Reaction 12: Benzhydryl amine and V<sub>2</sub>O<sub>5</sub>– 1.5 hours*

Starting Material: 0.39 mL benzhydryl amine (6) (2.2x10<sup>-3</sup> mol)

Catalyst: 0.791 g of V<sub>2</sub>O<sub>5</sub> (4.3x10<sup>-3</sup> mol)

Percent Conversion to Products: 19%

GCMS Analysis of products: Product 7 (16.788 min; M+=347)

*Reaction 13: Benzhydryl amine with V<sub>2</sub>O<sub>5</sub> and CuSO<sub>4</sub>•H<sub>2</sub>O – 1.5 hours*

Starting Material: 0.37 mL benzhydryl amine (6) (2.1x10<sup>-3</sup> mol)

Catalyst: Mixture of 0.801 g V<sub>2</sub>O<sub>5</sub> (4.4x10<sup>-3</sup> mol) and 1.37 g (8.5x10<sup>-3</sup> mol)

CuSO<sub>4</sub>•H<sub>2</sub>O

Percent Conversion to Products: 66%

GCMS Analysis of products: Product 7 (16.787 min; M+=347)

## Alcohol Reactions

### General Alcohol Reaction Procedure

A mixture of  $V_2O_5$  and/or  $CuSO_4 \cdot H_2O$  was ground together using mortar and pestle and then transferred to a 50 mL round bottom flask. The alcohol starting reagent was added to the round bottom flask, a condenser was immediately attached, and the flask was placed in a boiling water bath. After the specified reaction time, the flask was removed from the water bath and the reaction was allowed to cool. After cooling, the condenser was removed and the product was extracted with three 5 mL aliquots of ethyl acetate. The mixture was then gravity filtered to remove any solid that may have been present. After gravity filtration, the mixture was washed with three 5 mL aliquots of water. The organic layer was kept, dried with  $MgSO_4$ , and gravity filtered. After gravity filtration, rotary evaporation was used in order to remove any solvent. If analyzed by GCMS analysis, a small sample of the product was then transferred to a GCMS vial, diluted with ethyl acetate and analyzed to determine reaction products. If analyzed via HNMR, a small sample of the product was transferred to an NMR tube, diluted with d-chloroform and analyzed to determine reaction products.

### *GCMS Analysis of Alcohol Starting Materials and Predicted Products*

GCMS: Benzyl alcohol (starting material):

Benzyl alcohol (**8**) (6.634 min;  $M^+=108$ ; 97%)

Dibenzyl ether (**10**) (14.712 min;  $M^+=197$ ; 3%)

GCMS: 1-heptanol (starting material):

1-heptanol (**11**) (5.967 min;  $M^+=115$ ; 100%)

*Reaction 14: Benzyl Alcohol with V<sub>2</sub>O<sub>5</sub> and CuSO<sub>4</sub>•H<sub>2</sub>O – 1.5 hours*

Starting Material: 0.24 mL of benzyl alcohol (**8**) ( $2.2 \times 10^{-3}$  mol)

Catalyst: Mixture of 0.822 g ( $4.5 \times 10^{-3}$  mol) of V<sub>2</sub>O<sub>5</sub> and 1.41 g ( $8.8 \times 10^{-3}$  mol) of CuSO<sub>4</sub>•H<sub>2</sub>O

Percentage Conversion to Products: 40%

GCMS Analysis of products: Benzyl peroxide (**9**) (16.788 min; M+=347), dibenzyl ether (**10**) (14.712 min; M+=197)

Ratio of benzyl peroxide:dibenzyl ether – 1:4

*Reaction 15: 1-Heptanol with V<sub>2</sub>O<sub>5</sub> and CuSO<sub>4</sub>•H<sub>2</sub>O – 16 hours*

Starting Material: 0.28 mL of 1-heptanol (**11**) ( $1.9 \times 10^{-3}$  mol)

Catalyst: Mixture of 0.789 g of V<sub>2</sub>O<sub>5</sub> ( $4.3 \times 10^{-3}$  mol) and 1.24 g ( $7.7 \times 10^{-2}$  mol) of CuSO<sub>4</sub>•H<sub>2</sub>O

Percentage Conversion to Products: 58%

Ratio of Unidentified product:heptanoic anhydride – 2:27

GCMS Analysis of products: Unidentified product (9.862 min; M+=215), heptanoic anhydride (**12**) (12.192-13.091 min; M+=242).

*Reaction 16: Benzoin (no catalyst) – 1.5 hours*

Starting Material: 0.029 g of benzoin (**13**) ( $1.3 \times 10^{-4}$  mol)

Catalyst: None

HNMR Analysis: 100% benzoin (**13**), 0% benzil (**14**)

*Reaction 17: Benzoin and V<sub>2</sub>O<sub>5</sub> – 1.5 hours*

Starting Material: 0.022 g of benzoin (**13**) ( $1.0 \times 10^{-4}$  mol)

Catalyst: 0.788 g ( $4.3 \times 10^{-3}$  mol) of  $V_2O_5$

HNMR analysis: 4% benzoin (**13**), 96% benzil, (**14**)

*Reaction 18: Benzoin and  $CuSO_4 \cdot H_2O$  – 1.5 hours*

Starting Material: 0.025 g of benzoin (**13**) ( $1.1 \times 10^{-4}$  mol)

Catalyst: 1.39 g ( $8.6 \times 10^{-3}$  mol)  $CuSO_4 \cdot H_2O$

HNMR: 83% benzoin (**13**), 17% benzil (**14**)

**Reaction 19: Benzoin with  $V_2O_5$  and  $CuSO_4 \cdot H_2O$  – 1.5 hours**

Starting Material: 0.021 g of benzoin (**13**) ( $9.8 \times 10^{-5}$  mol)

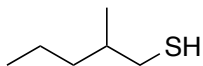
Catalyst: Mixture of 0.795 g ( $4.3 \times 10^{-3}$  mol) of  $V_2O_5$  and 1.22 g ( $7.6 \times 10^{-3}$  mol) of  $CuSO_4 \cdot H_2O$

HNMR: 5% benzoin (**13**), 95% benzil. (**14**)

## References

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# Appendix I: Spectra of Starting Materials and Predicted Products



1-Methyl-2-butanethiol

## MS Data Review Active Chromatogram Plot - 4/20/2016 11:33 AM

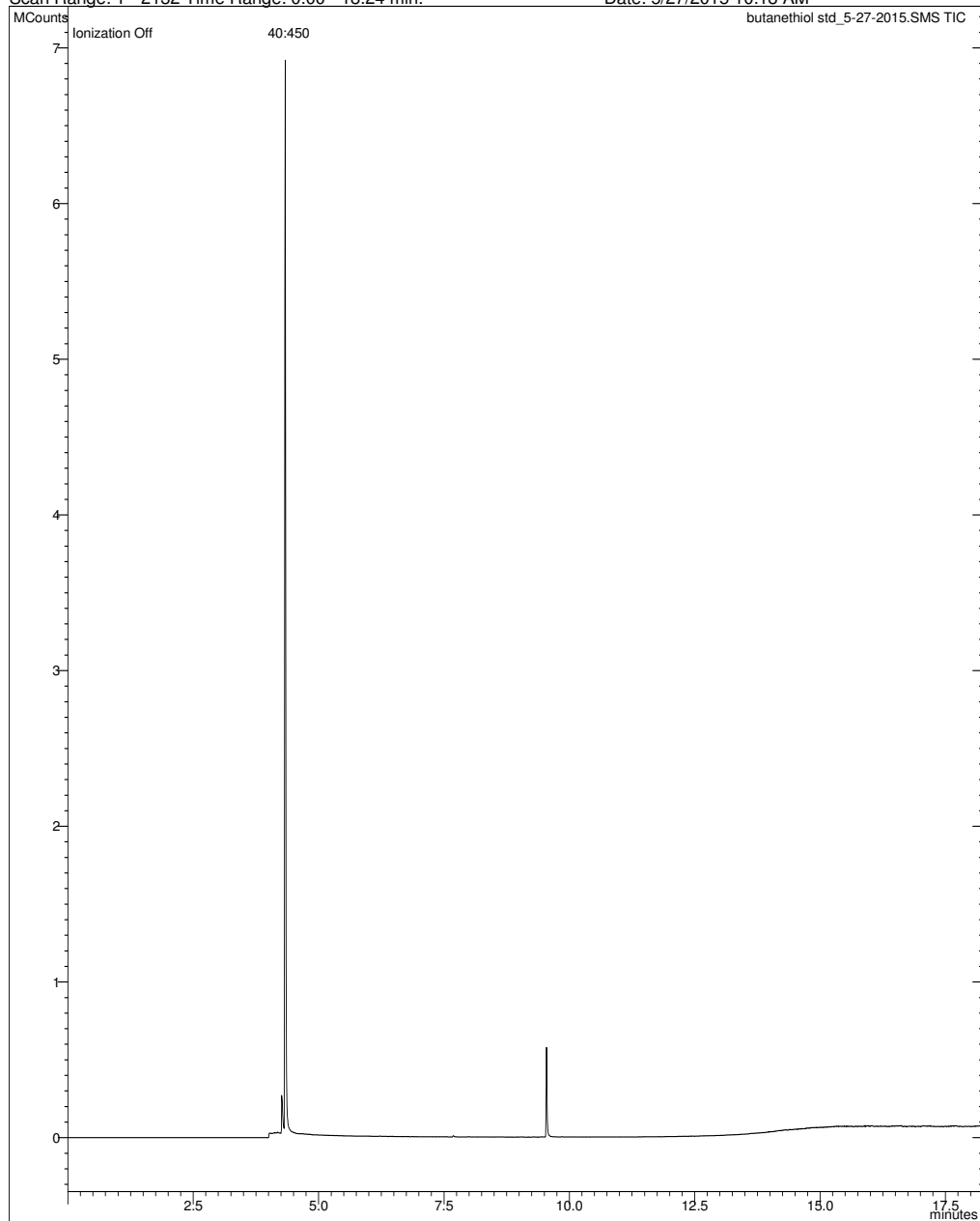
File: ...b\oberst research\vanadium oxide rxns\butanethiol std\_5-27-2015.sms

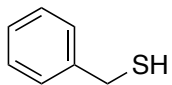
Sample: butanethiol std

Operator: jab

Scan Range: 1 - 2132 Time Range: 0.00 - 18.24 min.

Date: 5/27/2015 10:18 AM





(4)

### MS Data Review Active Chromatogram Plot - 4/20/2016 11:32 AM

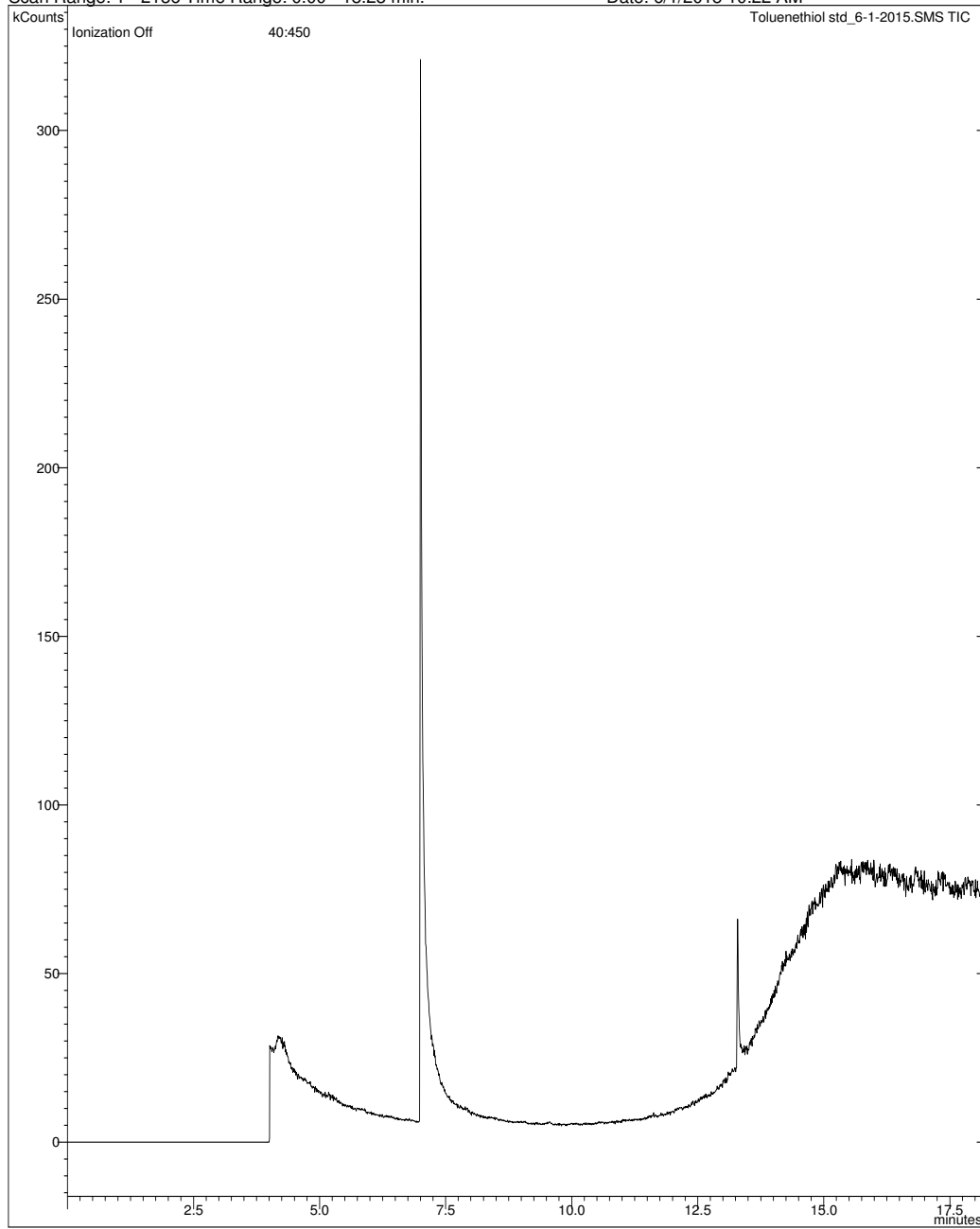
File: ...b\oberst research\vanadium oxide rxns\toluenethiol std\_6-1-2015.sms

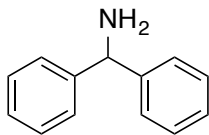
Sample: Tolueneithiol std

Operator: jab

Scan Range: 1 - 2136 Time Range: 0.00 - 18.23 min.

Date: 6/1/2015 10:22 AM





(6)

MS Data Review Active Chromatogram Plot - 4/20/2016 11:36 AM

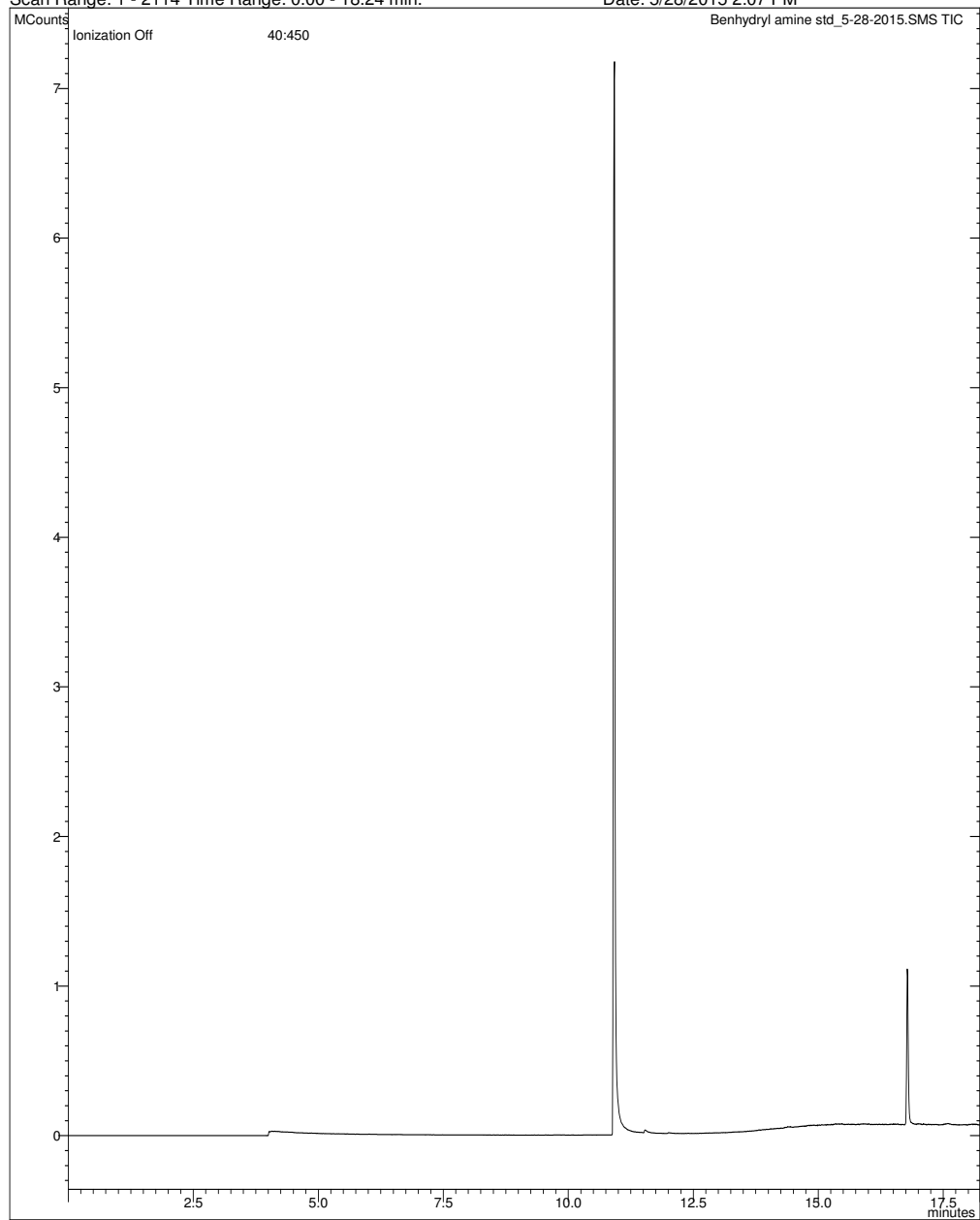
File: ...erst research\vanadium oxide rxns\benhydrl amine std\_5-28-2015.sms

Sample: Benhydrl amine std

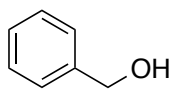
Operator: jab

Scan Range: 1 - 2114 Time Range: 0.00 - 18.24 min.

Date: 5/28/2015 2:07 PM







(8)

### MS Data Review Active Chromatogram Plot - 4/20/2016 11:39 AM

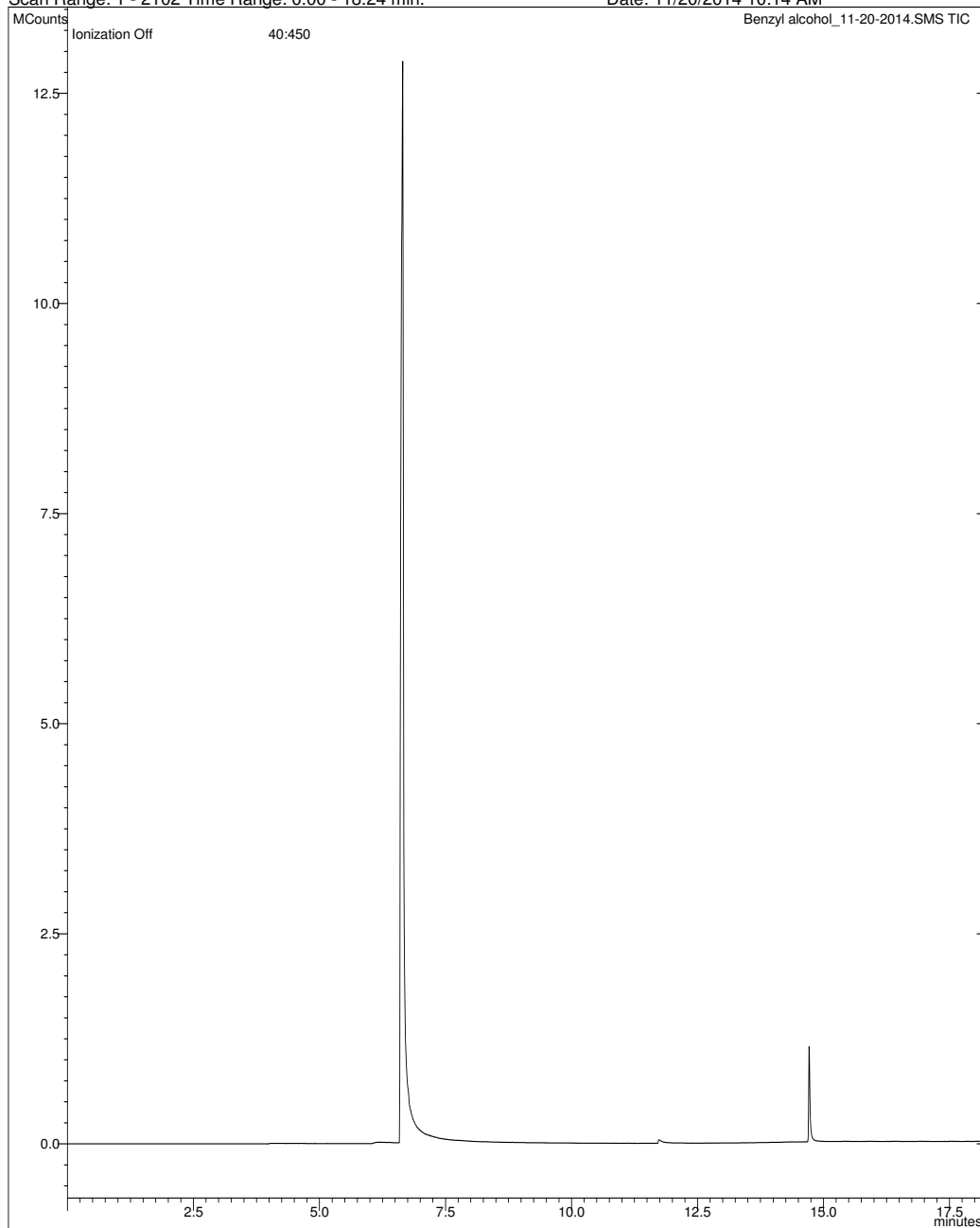
File: ...b\oberst research\vanadium oxide rxns\benzyl alcohol\_11-20-2014.sms

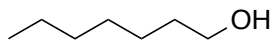
Sample: Benzyl alcohol

Operator: jab

Scan Range: 1 - 2102 Time Range: 0.00 - 18.24 min.

Date: 11/20/2014 10:14 AM





(11)

### MS Data Review Active Chromatogram Plot - 4/20/2016 11:40 AM

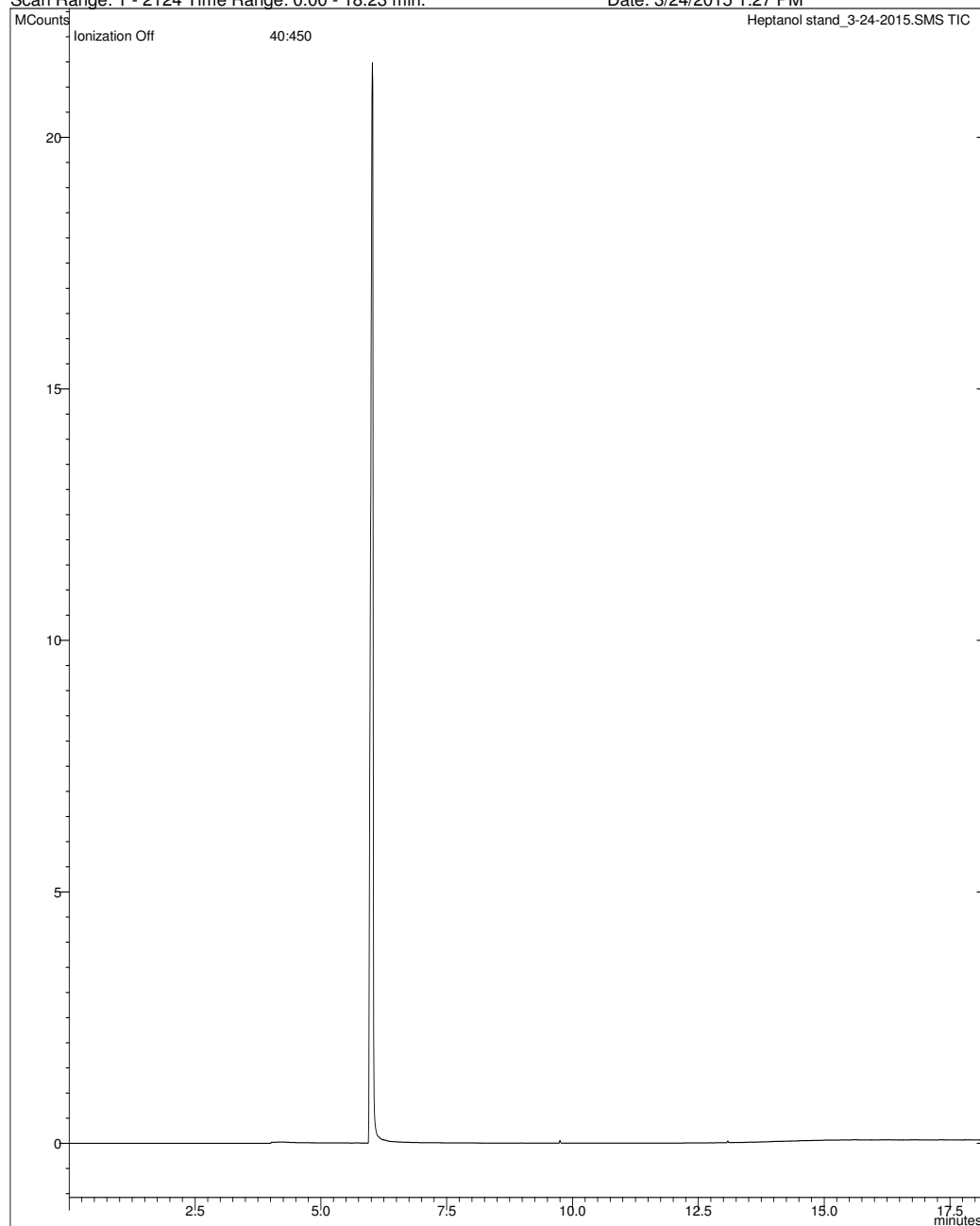
File: ...eb\oberst research\vanadium oxide rxns\heptanol stand\_3-24-2015.sms

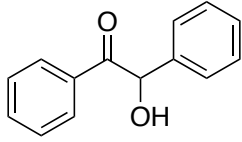
Sample: Heptanol stand

Operator: jab

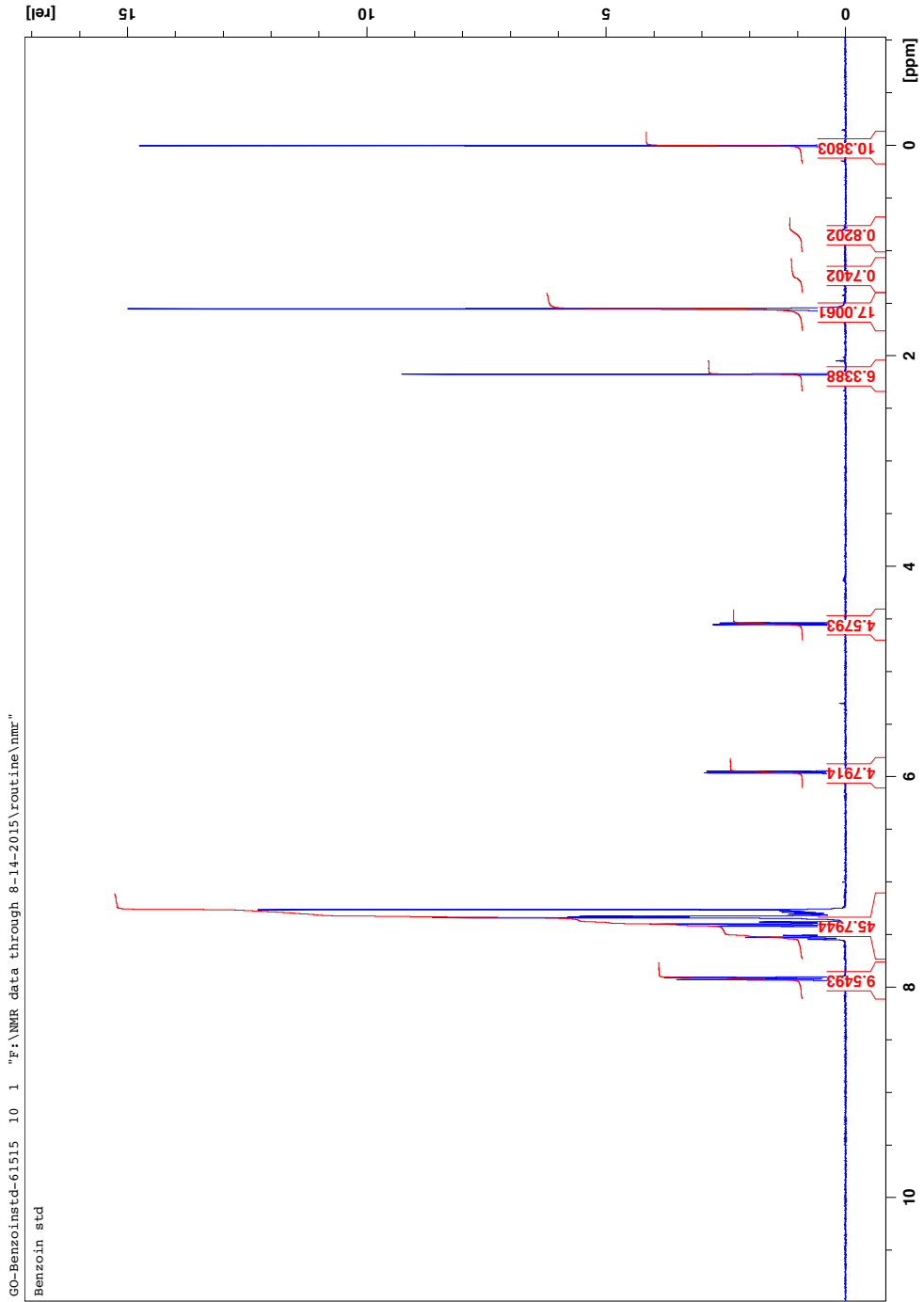
Scan Range: 1 - 2124 Time Range: 0.00 - 18.23 min.

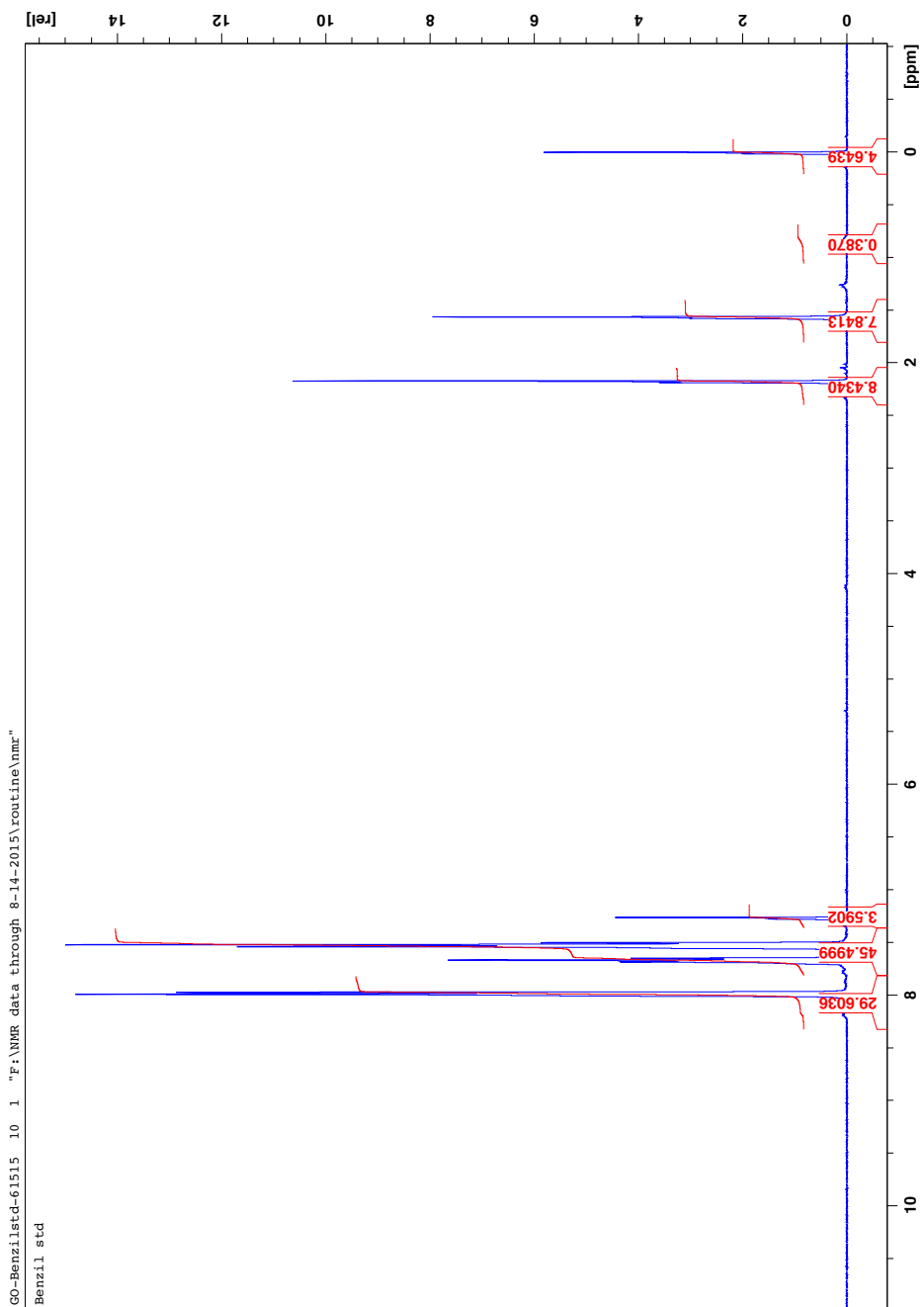
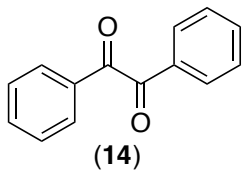
Date: 3/24/2015 1:27 PM





(13)





## **Appendix II: Spectra of Reaction Products**

*Reaction 1: 2-Methyl-1-butanethiol (no catalyst) – 15 minutes*

### **MS Data Review Active Chromatogram Plot - 4/20/2016 11:27 AM**

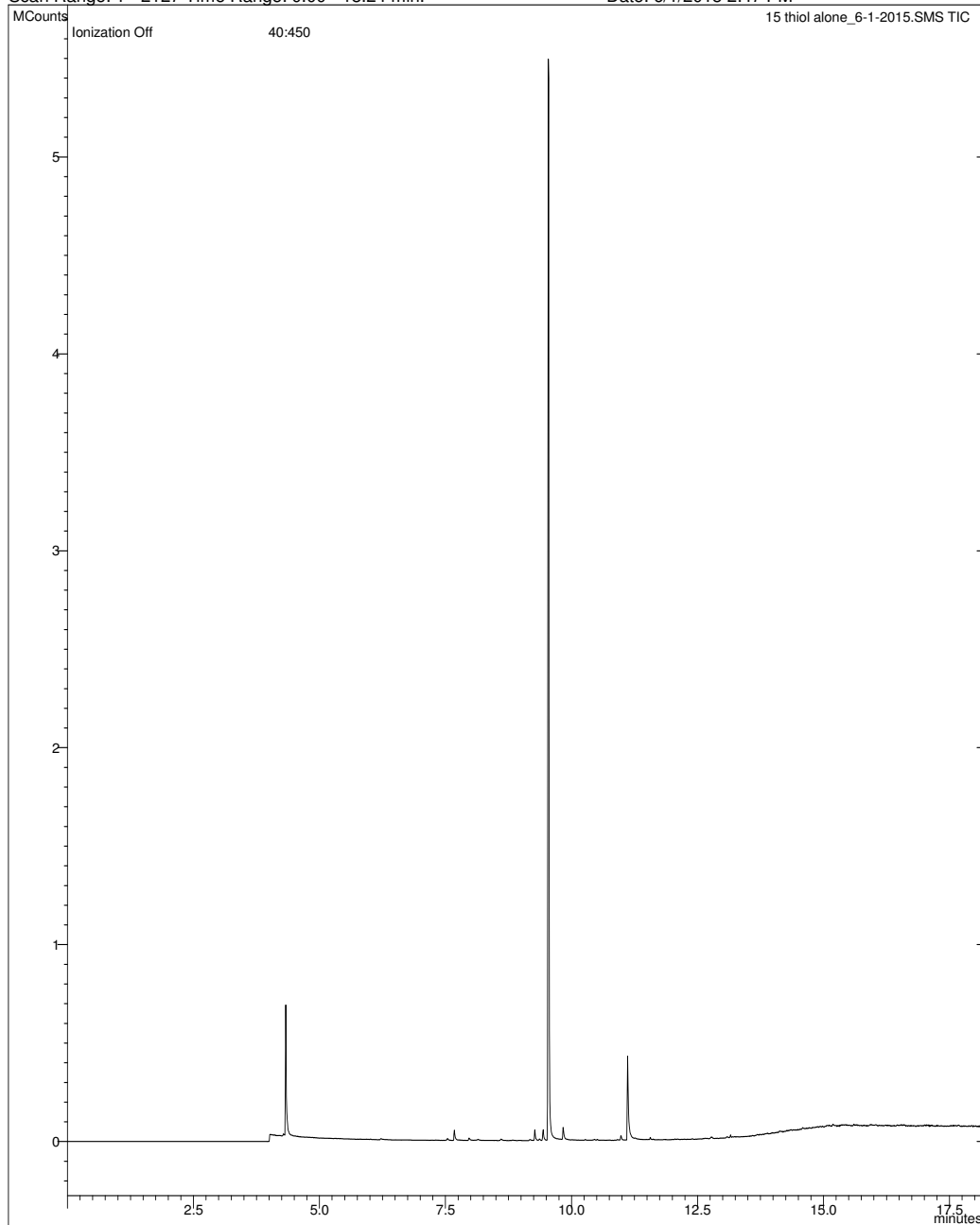
File: ...tebloberst research\vanadium oxide rxns\15 thiol alone\_6-1-2015.sms

Sample: 15 thiol alone

Operator: jab

Scan Range: 1 - 2127 Time Range: 0.00 - 18.24 min.

Date: 6/1/2015 2:47 PM



*Reaction 2: 2-Methyl-1-butanethiol and V<sub>2</sub>O<sub>5</sub> – 15 minutes*

**MS Data Review Active Chromatogram Plot - 4/20/2016 11:29 AM**

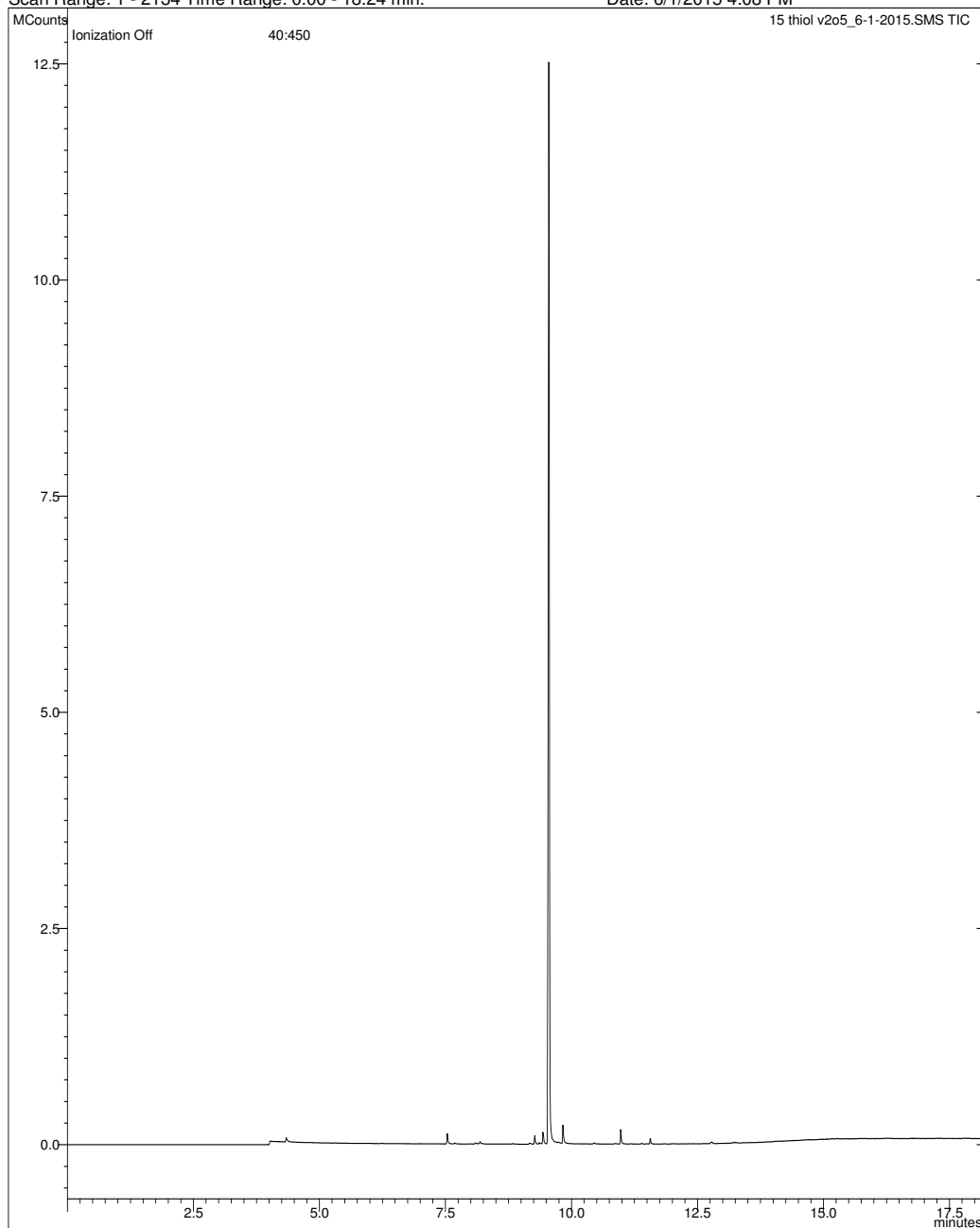
File: ...steb\oberst research\vanadium oxide rxns\15 thiol v2o5\_6-1-2015.sms

Sample: 15 thiol v2o5

Scan Range: 1 - 2134 Time Range: 0.00 - 18.24 min.

Operator: jab

Date: 6/1/2015 4:08 PM



*Reaction 3: 2-Methyl-1-butanethiol and CuSO<sub>4</sub>•H<sub>2</sub>O – 15 minutes*

**MS Data Review Active Chromatogram Plot - 4/20/2016 11:29 AM**

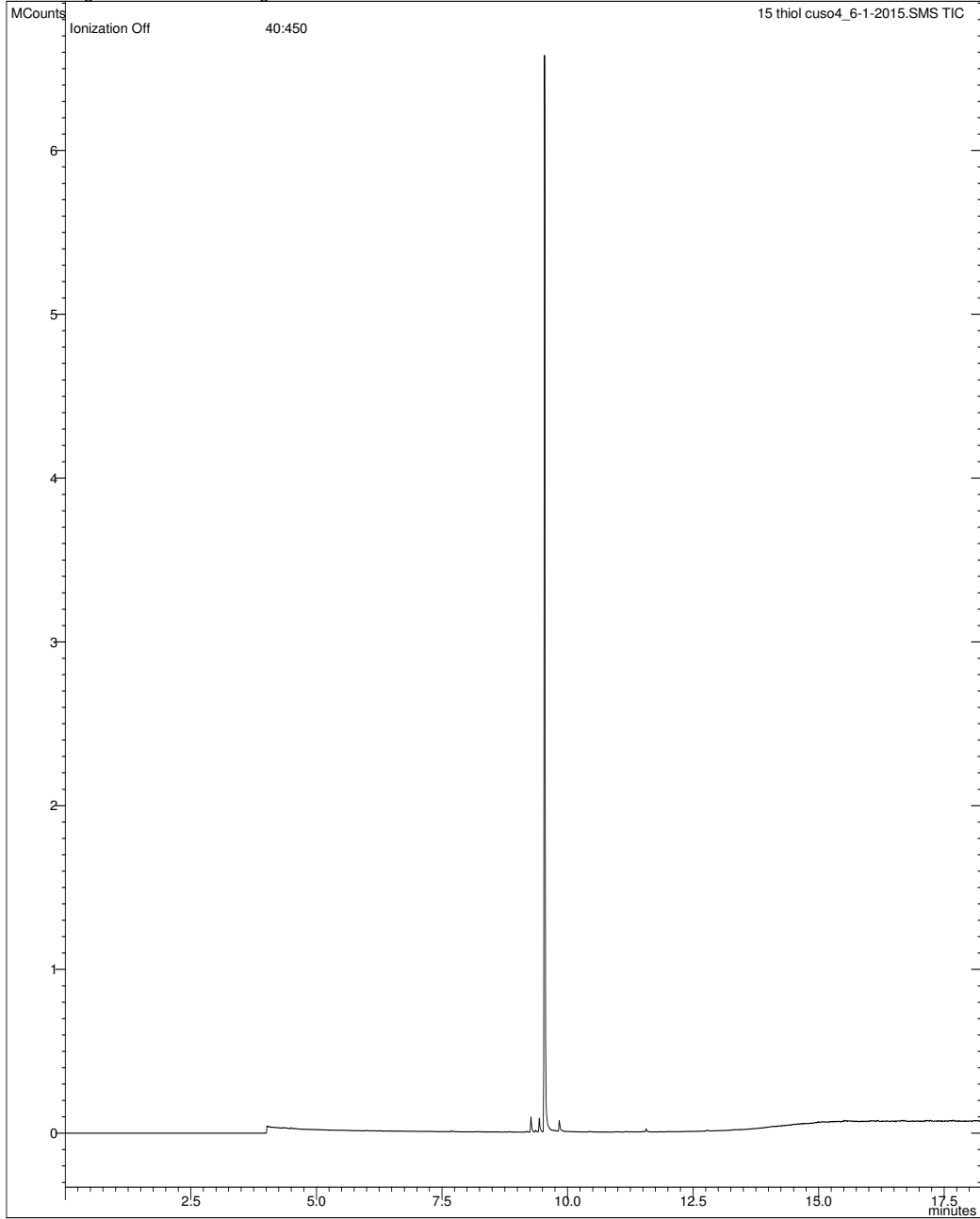
File: ...teb\oberst research\vanadium oxide rxns\15 thiol cuso4\_6-1-2015.sms

Sample: 15 thiol cuso4

Operator: jab

Scan Range: 1 - 2141 Time Range: 0.00 - 18.24 min.

Date: 6/1/2015 3:41 PM



*Reaction 4: 2-Methyl-1-butanethiol with V<sub>2</sub>O<sub>5</sub> and CuSO<sub>4</sub>•H<sub>2</sub>O – 15 minutes*

MS Data Review Active Chromatogram Plot - 4/20/2016 11:28 AM

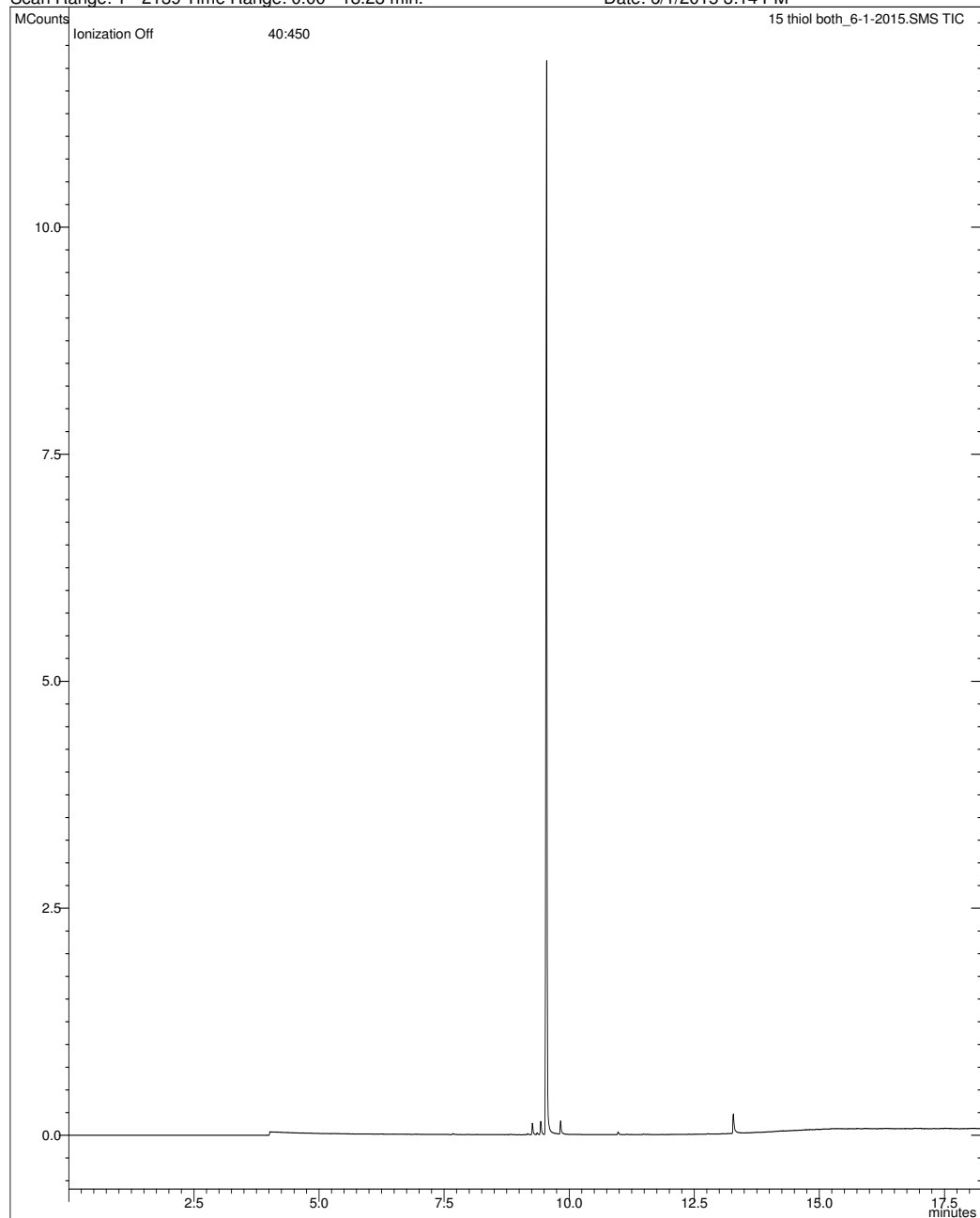
File: ...steb\oberst research\vanadium oxide rxns\15 thiol both\_6-1-2015.sms

Sample: 15 thiol both

Operator: jab

Scan Range: 1 - 2139 Time Range: 0.00 - 18.23 min.

Date: 6/1/2015 3:14 PM





*Reaction 5: 2-Methyl-1-butanethiol (no catalyst) – 1.5 hours*

**MS Data Review Active Chromatogram Plot - 4/20/2016 11:30 AM**

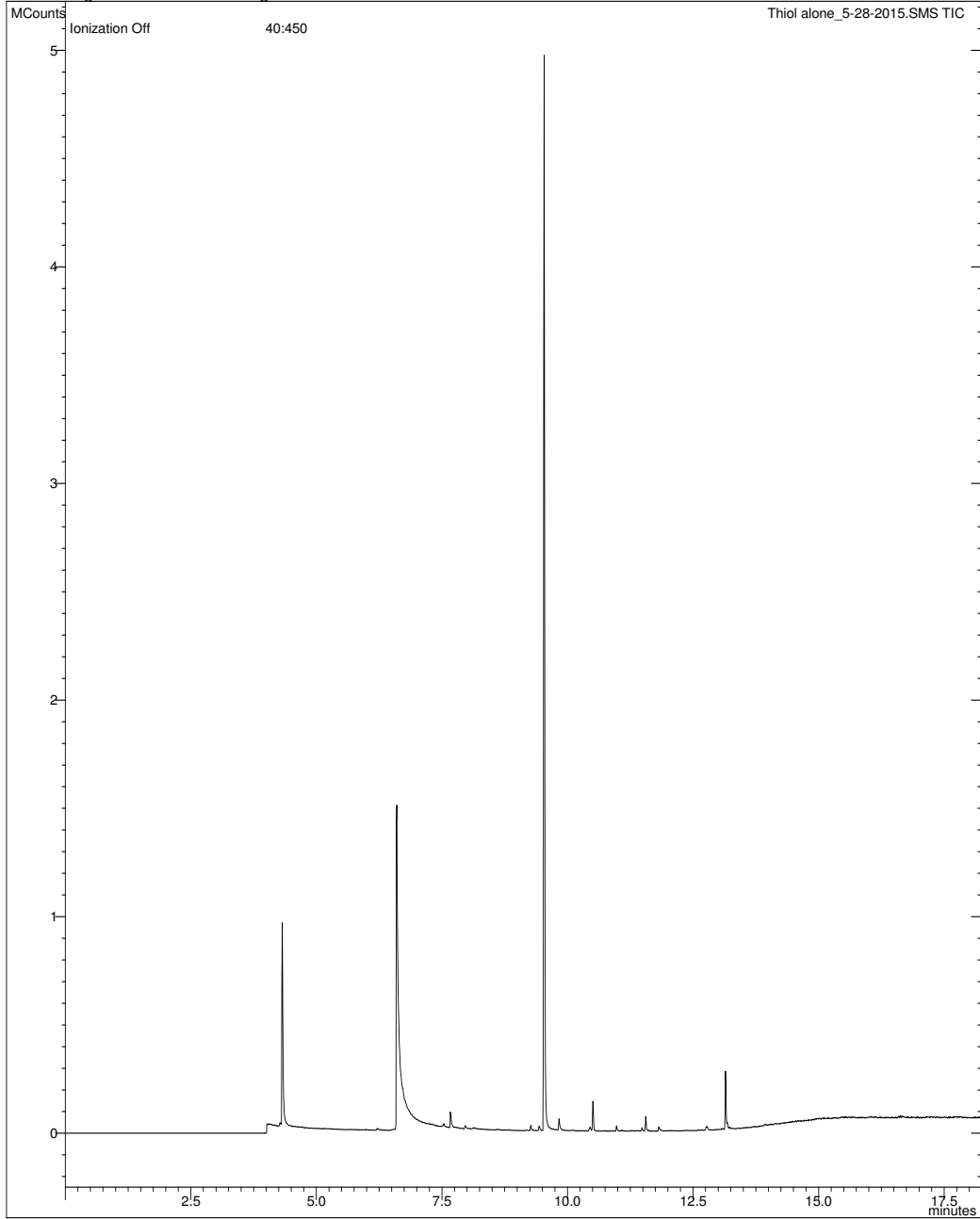
File: ...esteb\oberst research\vanadium oxide rxns\thiol alone\_5-28-2015.sms

Sample: Thiol alone

Operator: jab

Scan Range: 1 - 2105 Time Range: 0.00 - 18.24 min.

Date: 5/28/2015 3:30 PM



Reaction 6: 2-Methyl-1-butanethiol and V<sub>2</sub>O<sub>5</sub> – 1.5 hours

MS Data Review Active Chromatogram Plot - 4/20/2016 11:31 AM

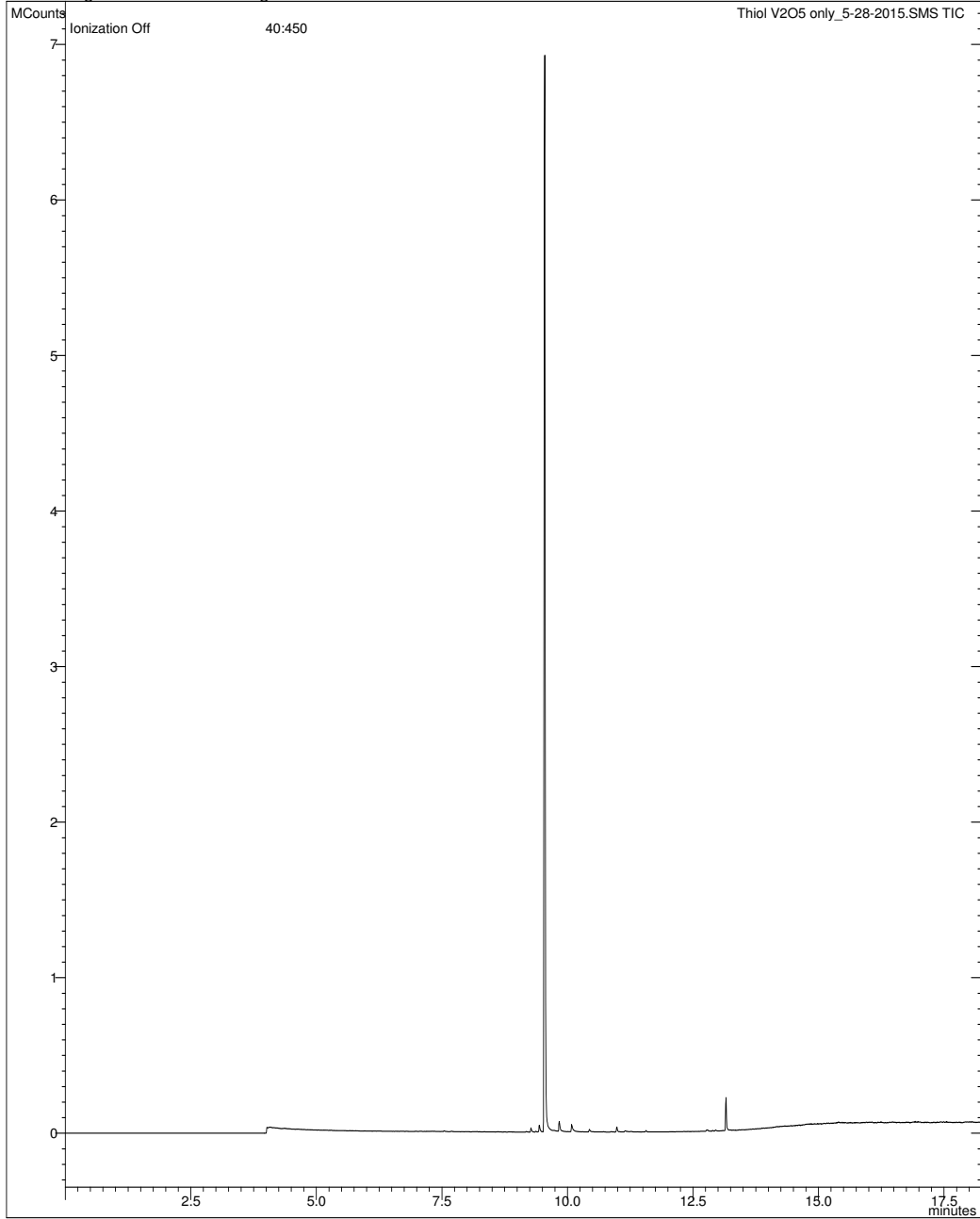
File: ...b\oberst research\vanadium oxide rxns\thiol v2o5 only\_5-28-2015.sms

Sample: Thiol V2O5 only

Operator: jab

Scan Range: 1 - 2142 Time Range: 0.00 - 18.24 min.

Date: 5/28/2015 3:02 PM



*Reaction 7: 2-Methyl-1-butanethiol with V<sub>2</sub>O<sub>5</sub> and CuSO<sub>4</sub>•H<sub>2</sub>O – 1.5 hours*

**MS Data Review Active Chromatogram Plot - 4/20/2016 11:33 AM**

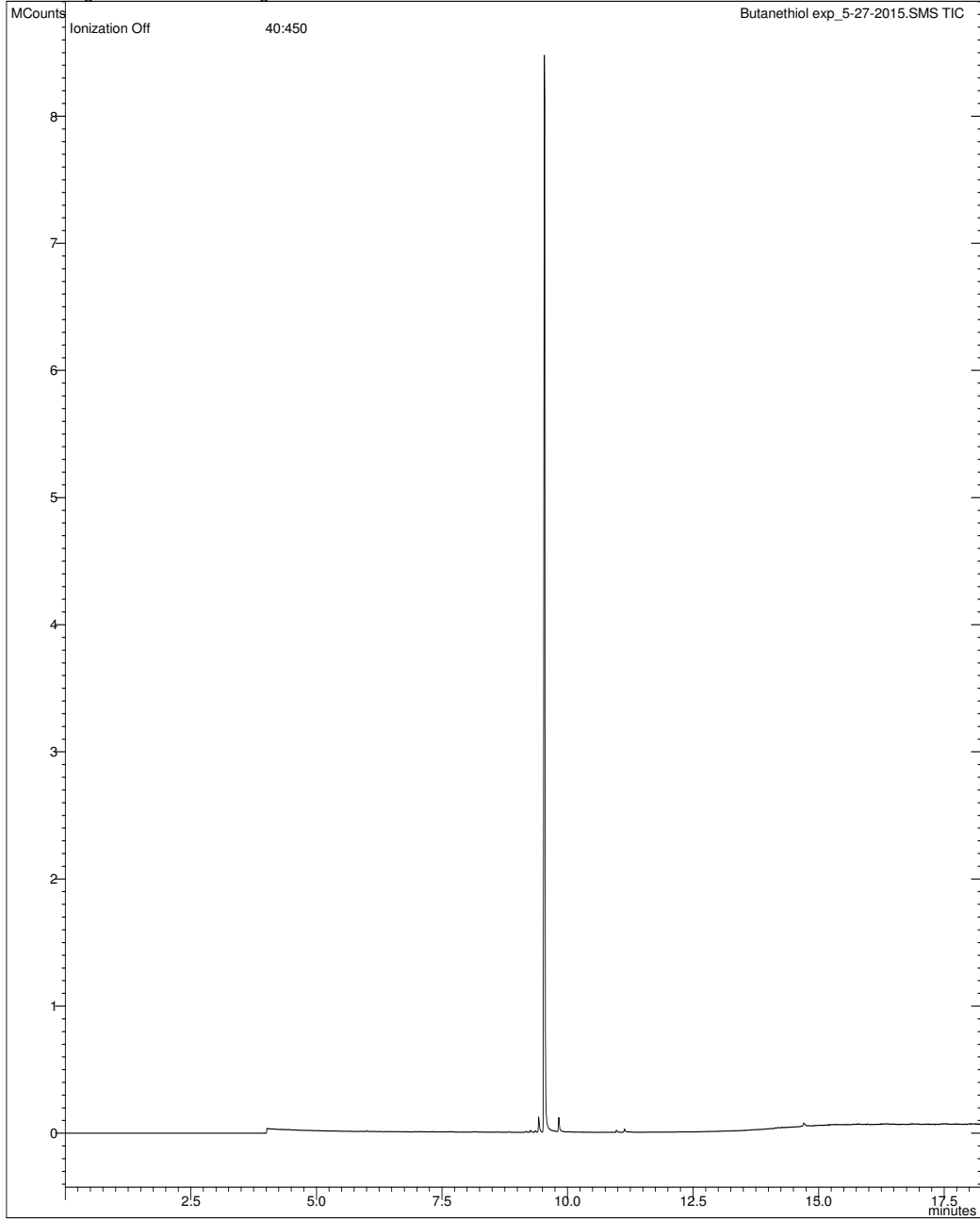
File: ...b\oberst research\vanadium oxide rxns\butanethiol exp\_5-27-2015.sms

Sample: Butanethiol exp

Operator: jab

Scan Range: 1 - 2143 Time Range: 0.00 - 18.24 min.

Date: 5/27/2015 11:13 AM



*Reaction 8: 2-Methyl-1-butanethiol and CuSO<sub>4</sub>•H<sub>2</sub>O – 1.5 hours*

**MS Data Review Active Chromatogram Plot - 4/20/2016 11:35 AM**

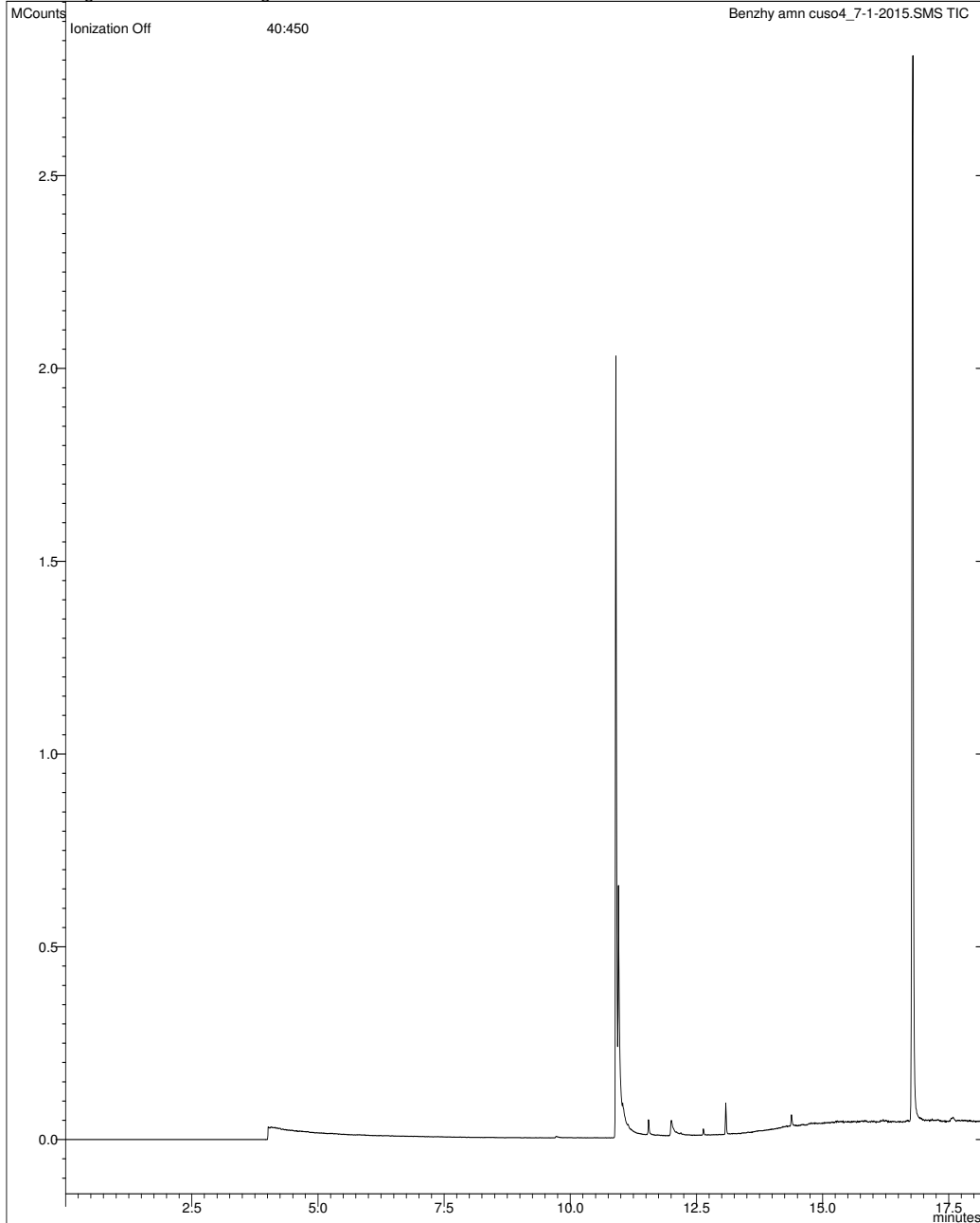
File: ...b\oberst research\vanadium oxide rxns\benzhy amn cuso4\_7-1-2015.sms

Sample: Benzhy amn cuso4

Operator: jab

Scan Range: 1 - 2134 Time Range: 0.00 - 18.24 min.

Date: 7/1/2015 2:24 PM



*Reaction 9: Benzyl mercaptan with V<sub>2</sub>O<sub>5</sub> and CuSO<sub>4</sub>•H<sub>2</sub>O – 1.5 hours*

**MS Data Review Active Chromatogram Plot - 4/20/2016 11:32 AM**

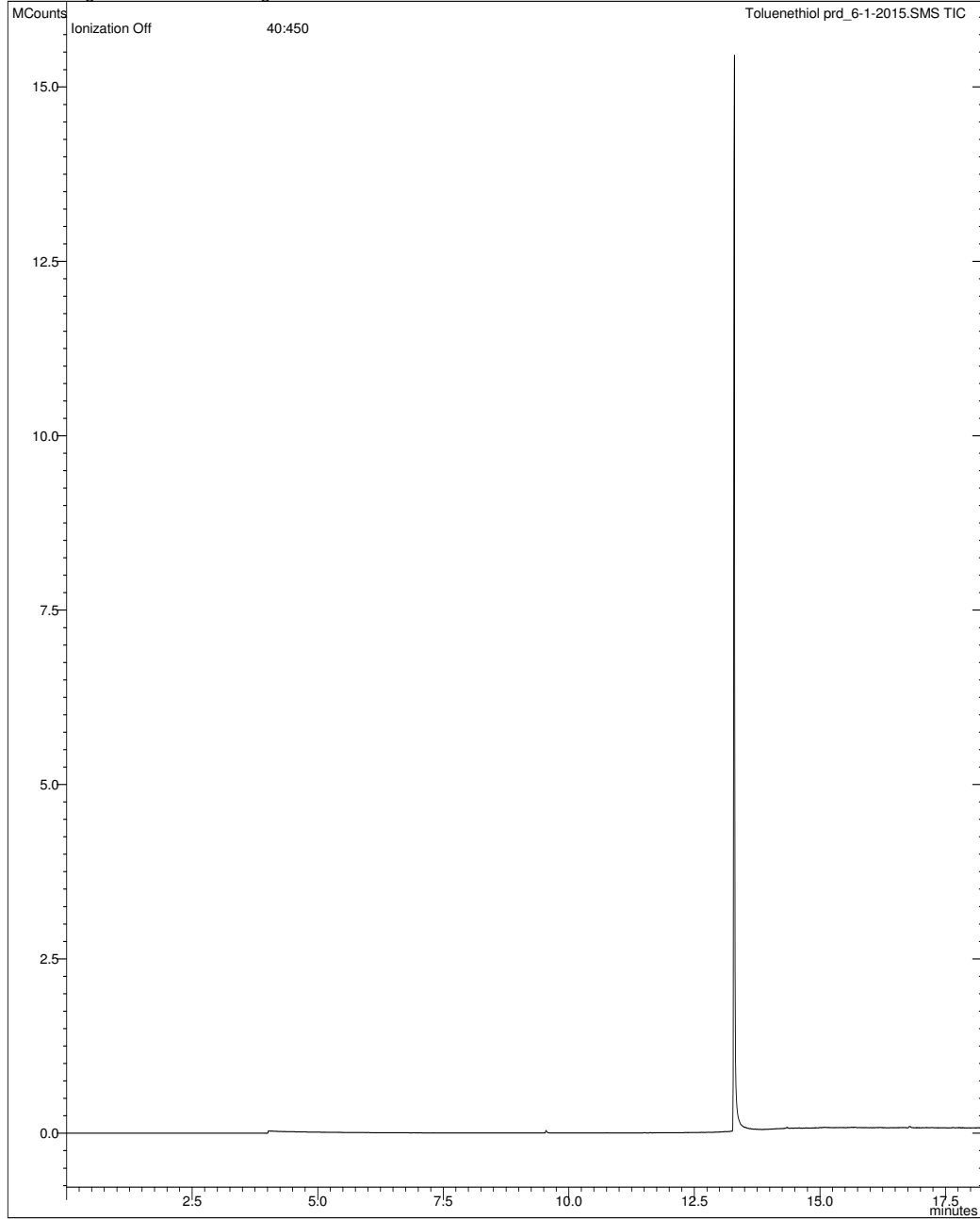
File: ...b\oberst research\vanadium oxide rxns\toluenethiol prd\_6-1-2015.sms

Sample: Tolueneithiol prd

Operator: jab

Scan Range: 1 - 2125 Time Range: 0.00 - 18.24 min.

Date: 6/1/2015 1:28 PM



*Reaction 10: Benzhydryl amine (no catalyst)– 1.5 hours*

**MS Data Review Active Chromatogram Plot - 4/20/2016 11:34 AM**

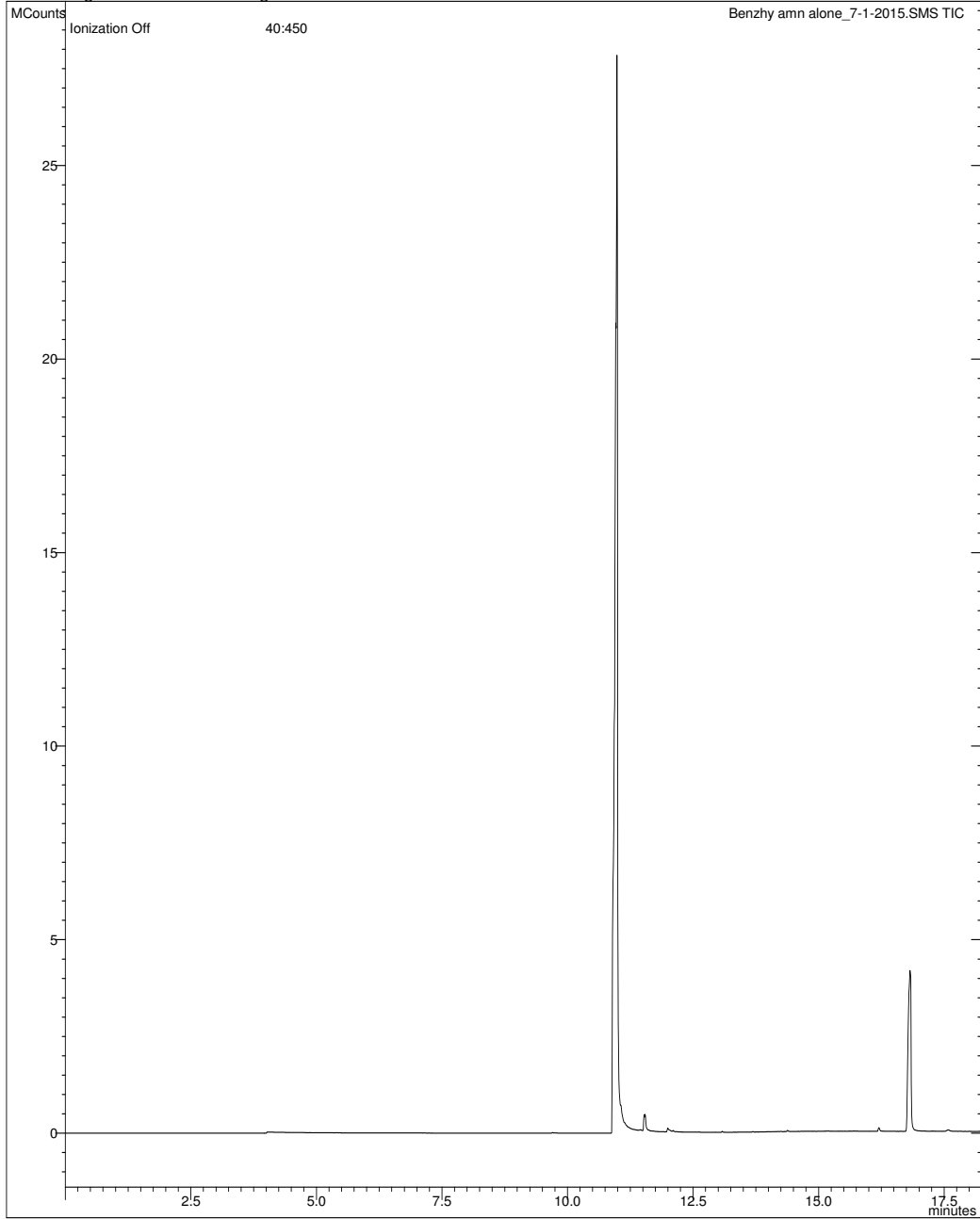
File: ...b\oberst research\vanadium oxide rxns\benzhy amn alone\_7-1-2015.sms

Sample: Benzhy amn alone

Operator: jab

Scan Range: 1 - 2132 Time Range: 0.00 - 18.24 min.

Date: 7/1/2015 1:56 PM



*Reaction 11: Benzhydryl amine and CuSO<sub>4</sub>•H<sub>2</sub>O – 1.5 hours*

**MS Data Review Active Chromatogram Plot - 4/20/2016 11:35 AM**

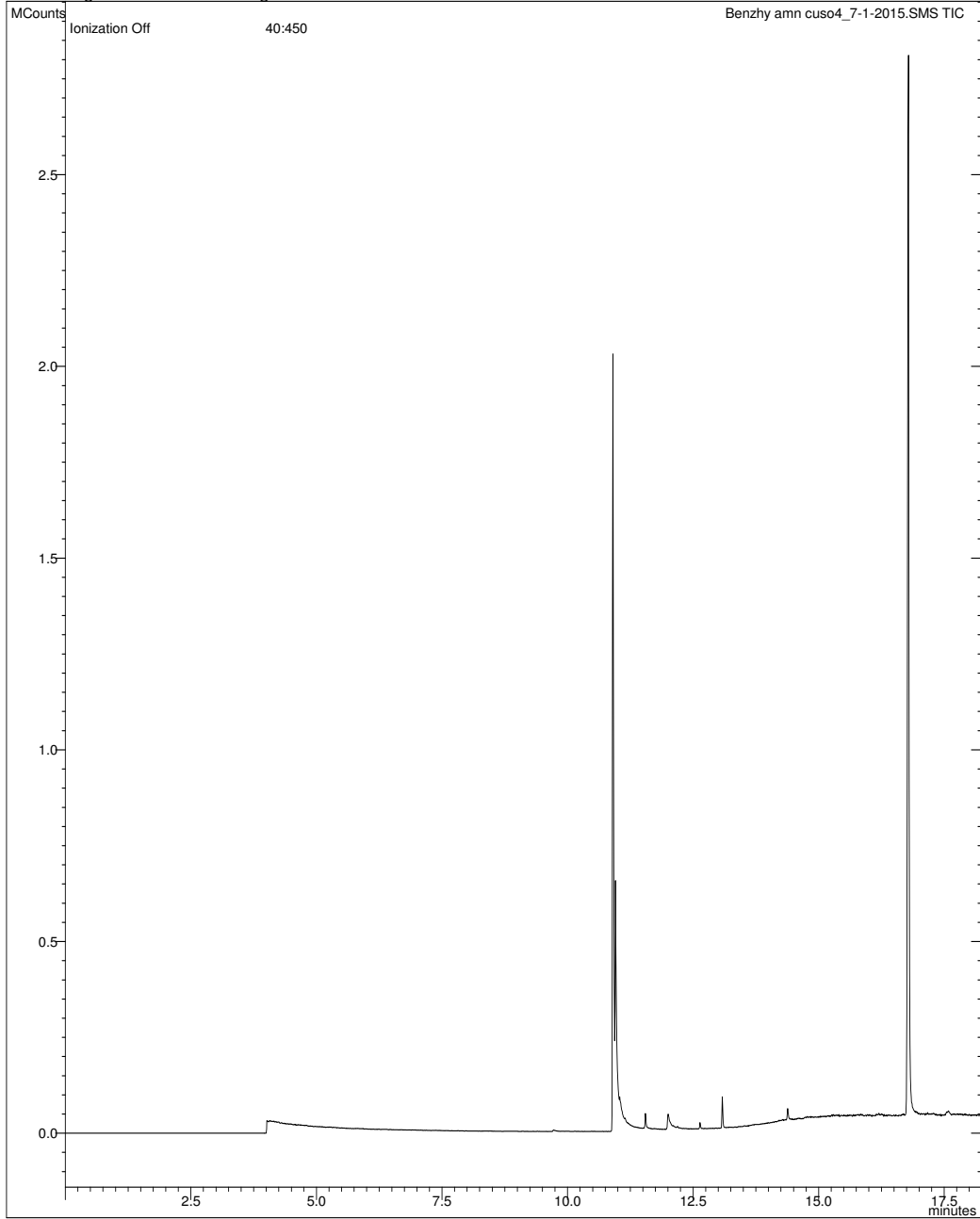
File: ...b\oberst research\vanadium oxide rxns\benzhy amn cuso4\_7-1-2015.sms

Sample: Benzhy amn cuso4

Operator: jab

Scan Range: 1 - 2134 Time Range: 0.00 - 18.24 min.

Date: 7/1/2015 2:24 PM



*Reaction 12: Benzhydryl amine and V<sub>2</sub>O<sub>5</sub>– 1.5 hours*

**MS Data Review Active Chromatogram Plot - 4/20/2016 11:35 AM**

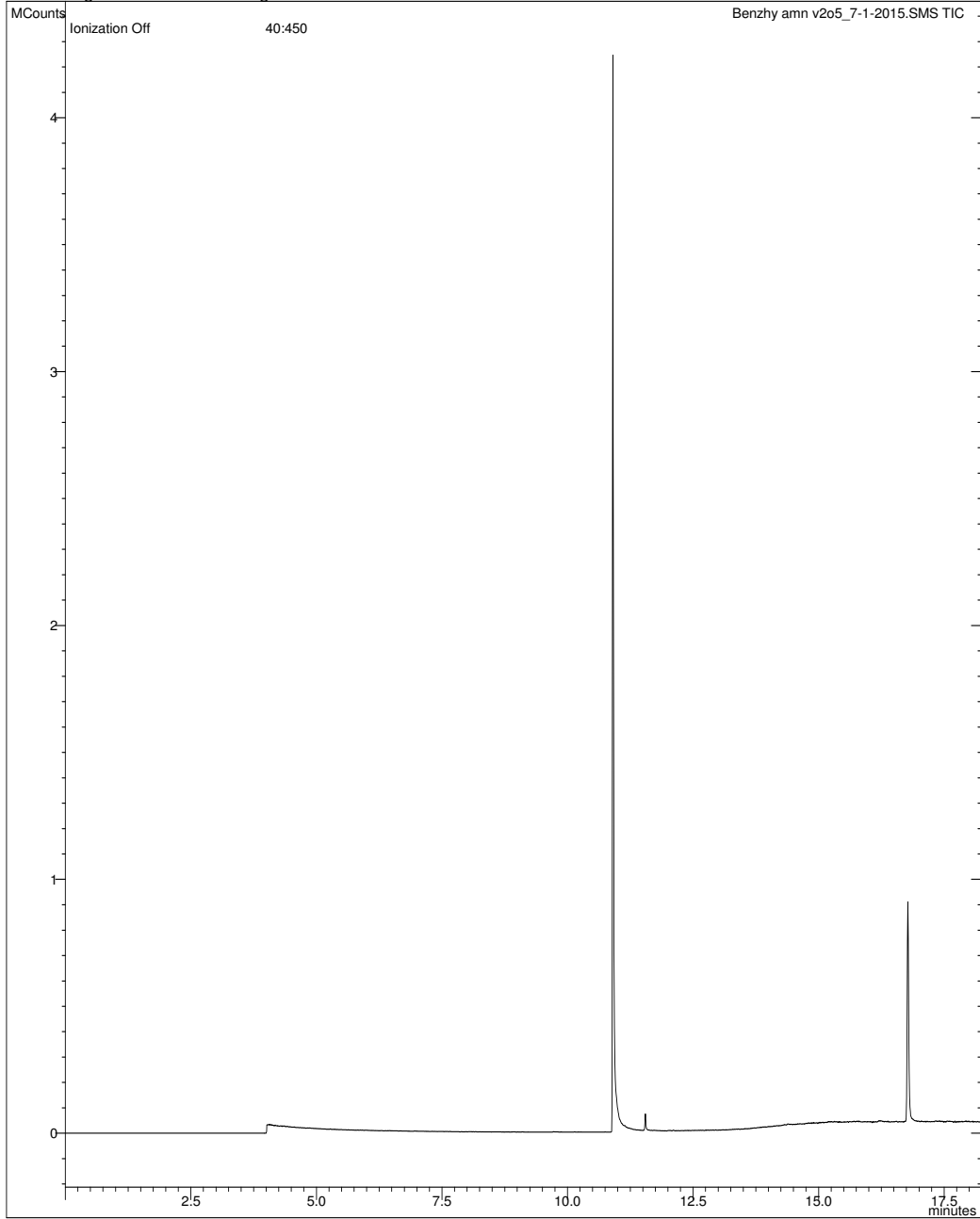
File: ...eb\oberst research\vanadium oxide rxns\benzhy amn v2o5\_7-1-2015.sms

Sample: Benzhy amn v2o5

Operator: jab

Scan Range: 1 - 2142 Time Range: 0.00 - 18.24 min.

Date: 7/1/2015 2:51 PM





*Reaction 13: Benzhydryl amine with V<sub>2</sub>O<sub>5</sub> and CuSO<sub>4</sub>•H<sub>2</sub>O – 1.5 hours*

**MS Data Review Active Chromatogram Plot - 4/20/2016 11:35 AM**

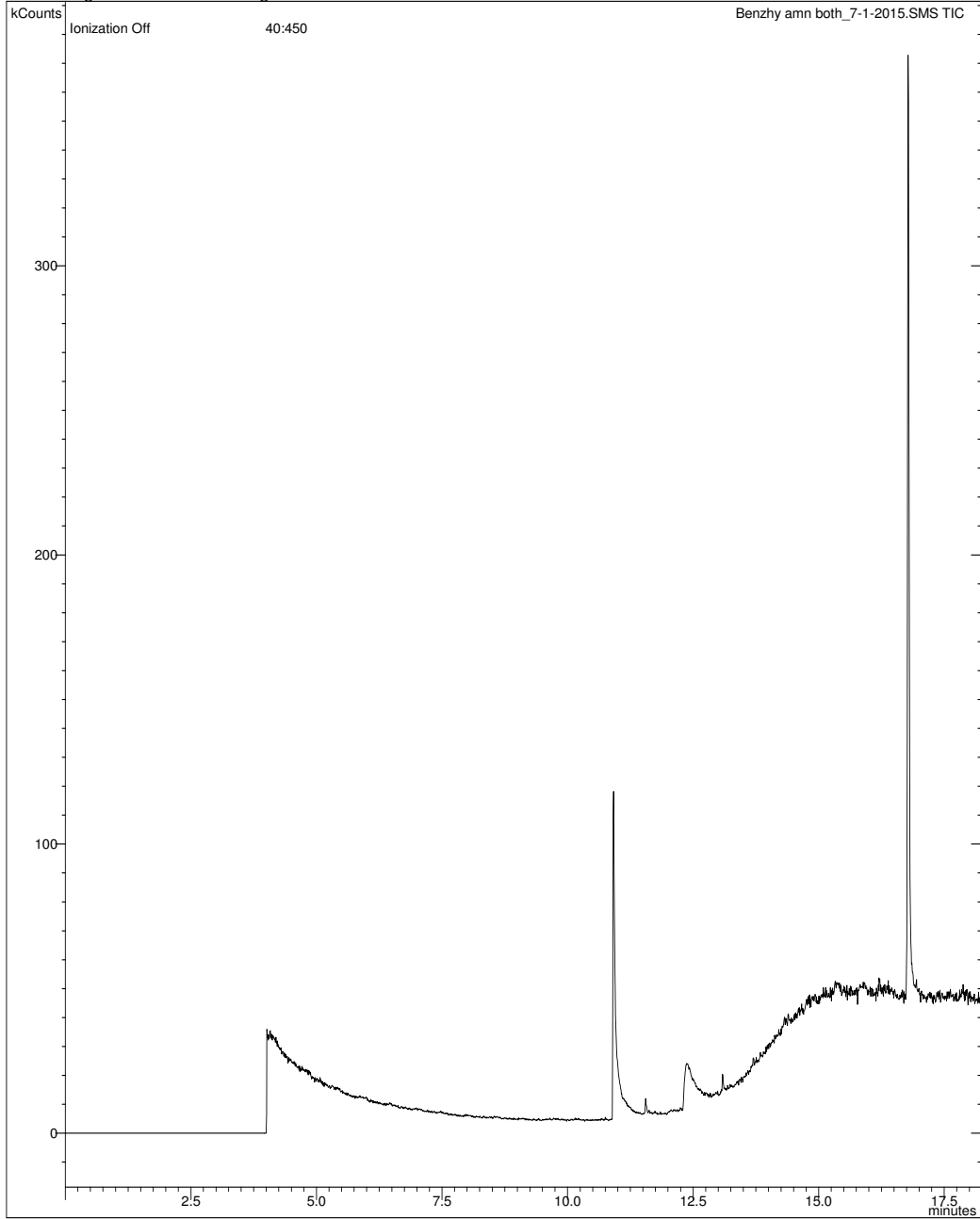
File: ...eb\oberst research\vanadium oxide rxns\benzhy amn both\_7-1-2015.sms

Sample: Benzhy amn both

Operator: jab

Scan Range: 1 - 2144 Time Range: 0.00 - 18.24 min.

Date: 7/1/2015 3:19 PM



*Reaction 14: Benzyl Alcohol with V<sub>2</sub>O<sub>5</sub> and CuSO<sub>4</sub>•H<sub>2</sub>O – 1.5 hours*

**MS Data Review Active Chromatogram Plot - 4/20/2016 11:39 AM**

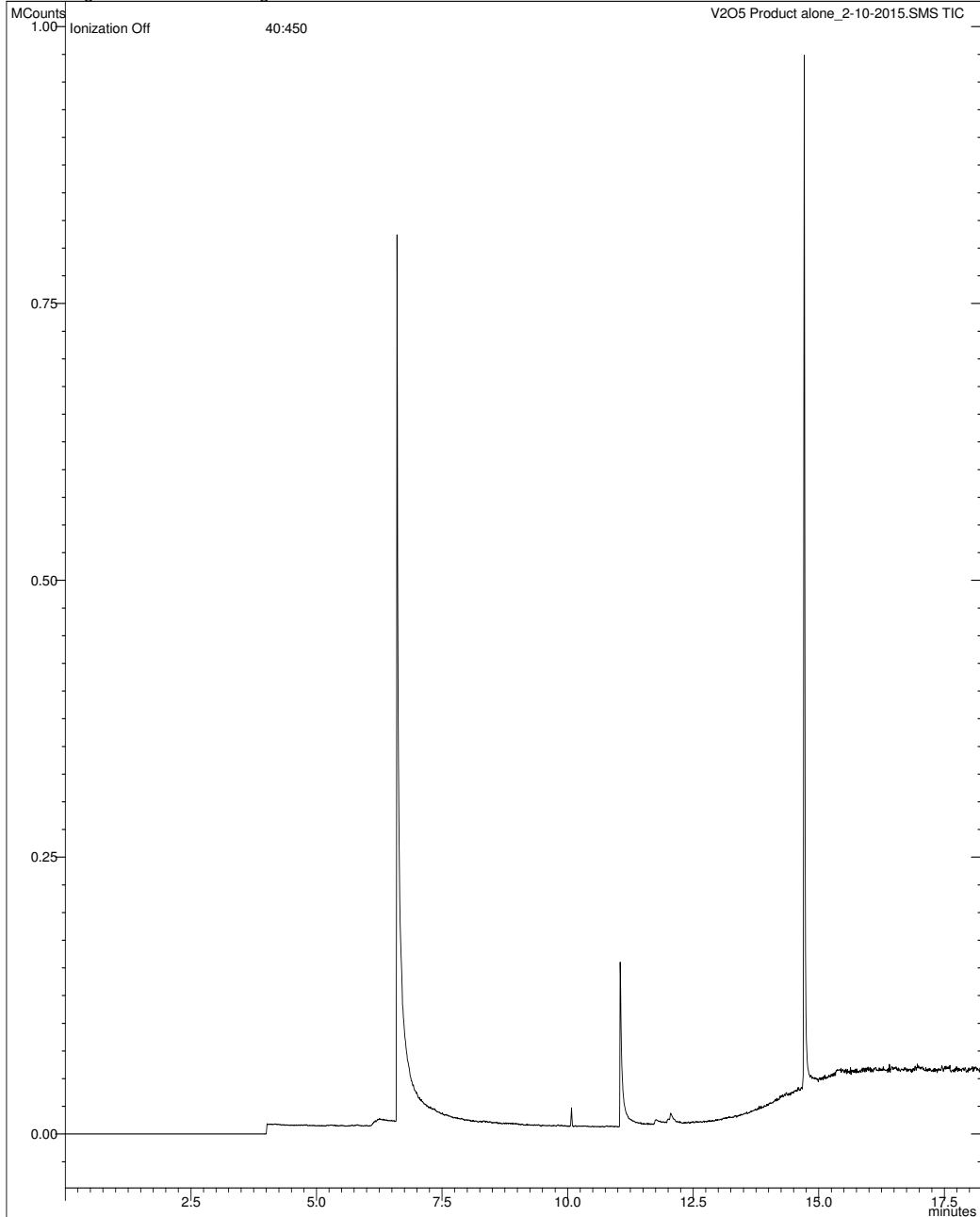
File: ...berst research\vanadium oxide rxns\v2o5 product alone\_2-10-2015.sms

Sample: V2O5 Product alone

Operator: jab

Scan Range: 1 - 2120 Time Range: 0.00 - 18.23 min.

Date: 2/10/2015 1:18 PM



*Reaction 15: 1-Heptanol with V<sub>2</sub>O<sub>5</sub> and CuSO<sub>4</sub>•H<sub>2</sub>O – 16 hours*

**MS Data Review Active Chromatogram Plot - 4/20/2016 11:41 AM**

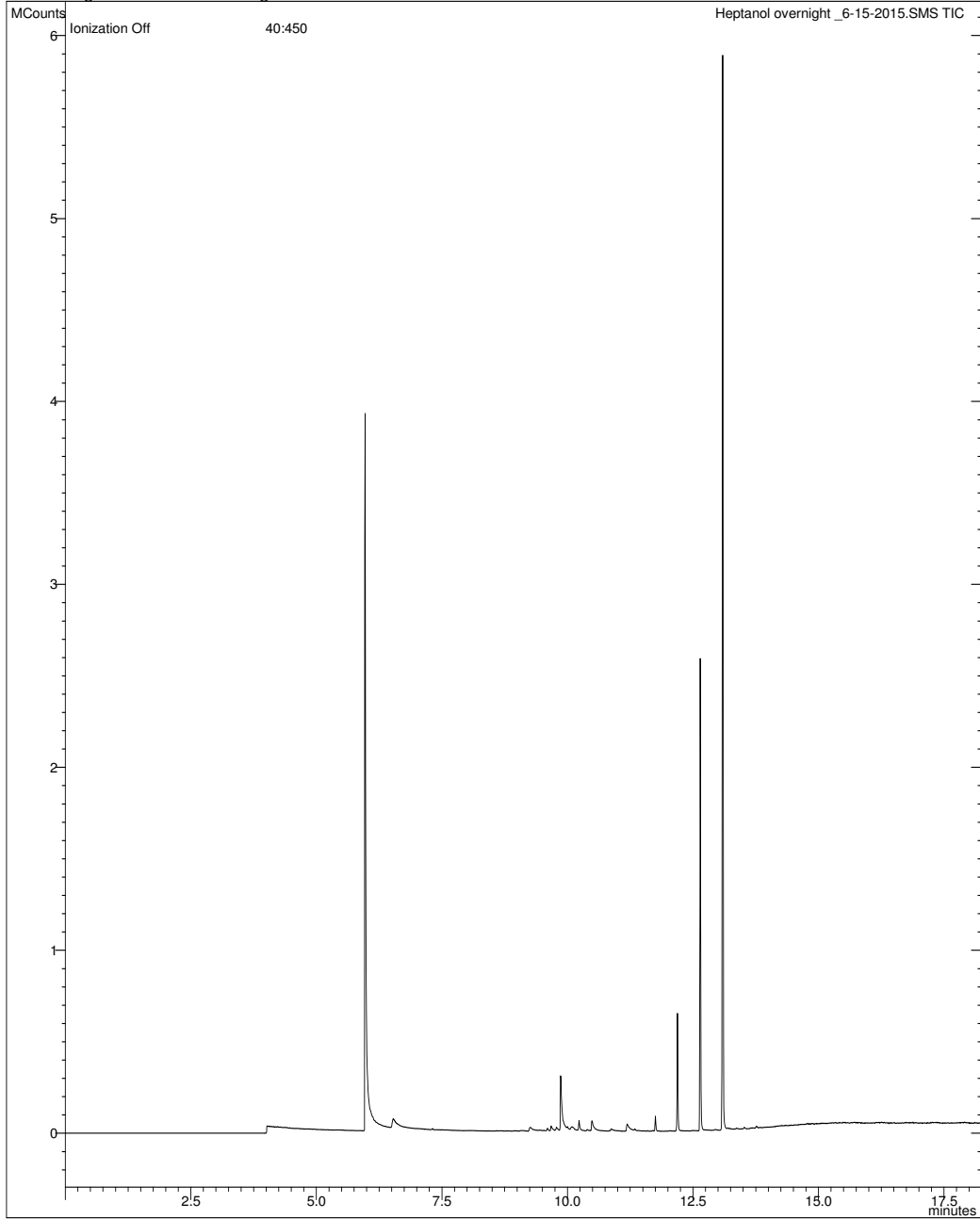
File: ...erst research\vanadium oxide rxns\heptanol overnight \_6-15-2015.sms

Sample: Heptanol overnight

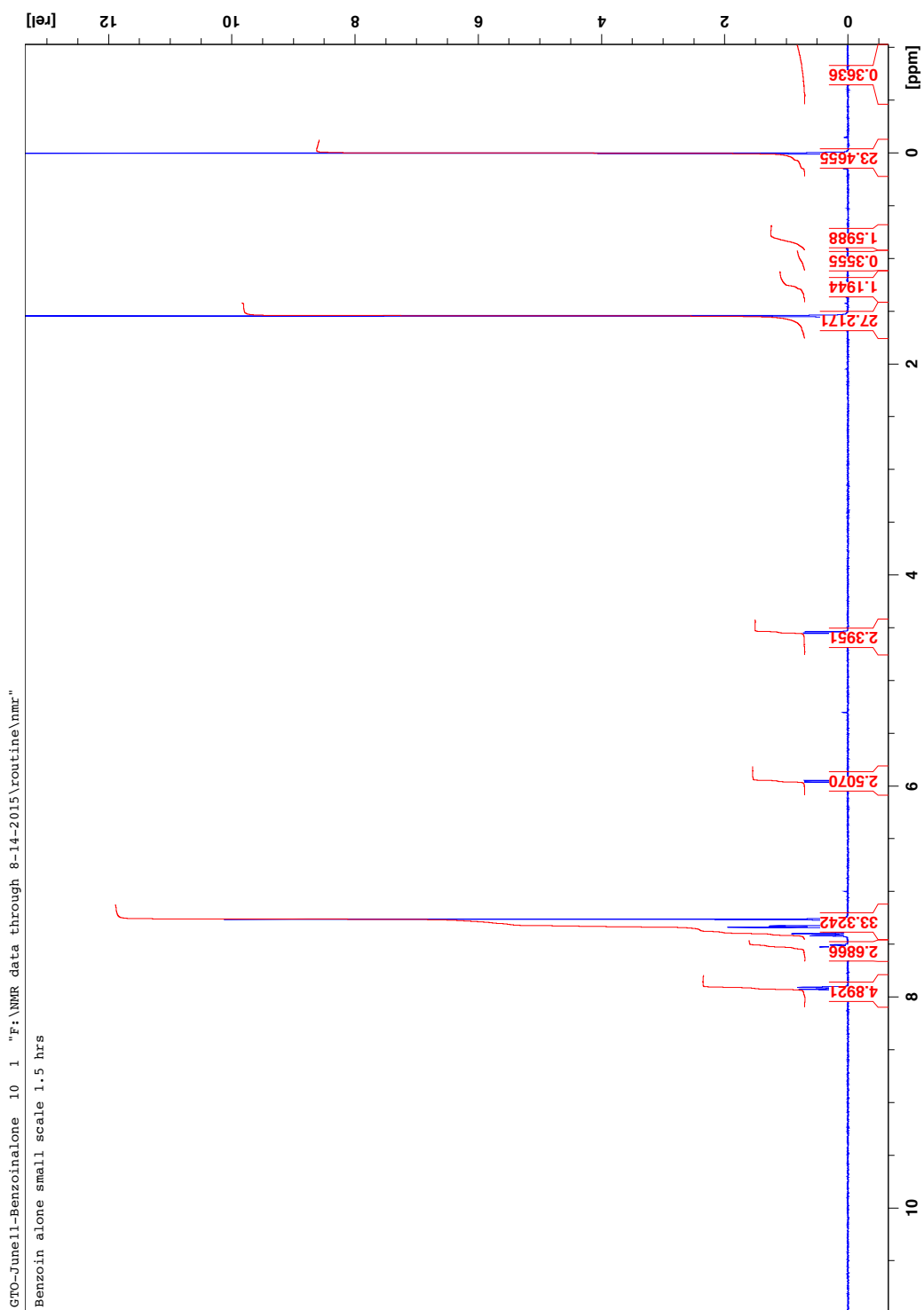
Operator: jab

Scan Range: 1 - 2117 Time Range: 0.00 - 18.24 min.

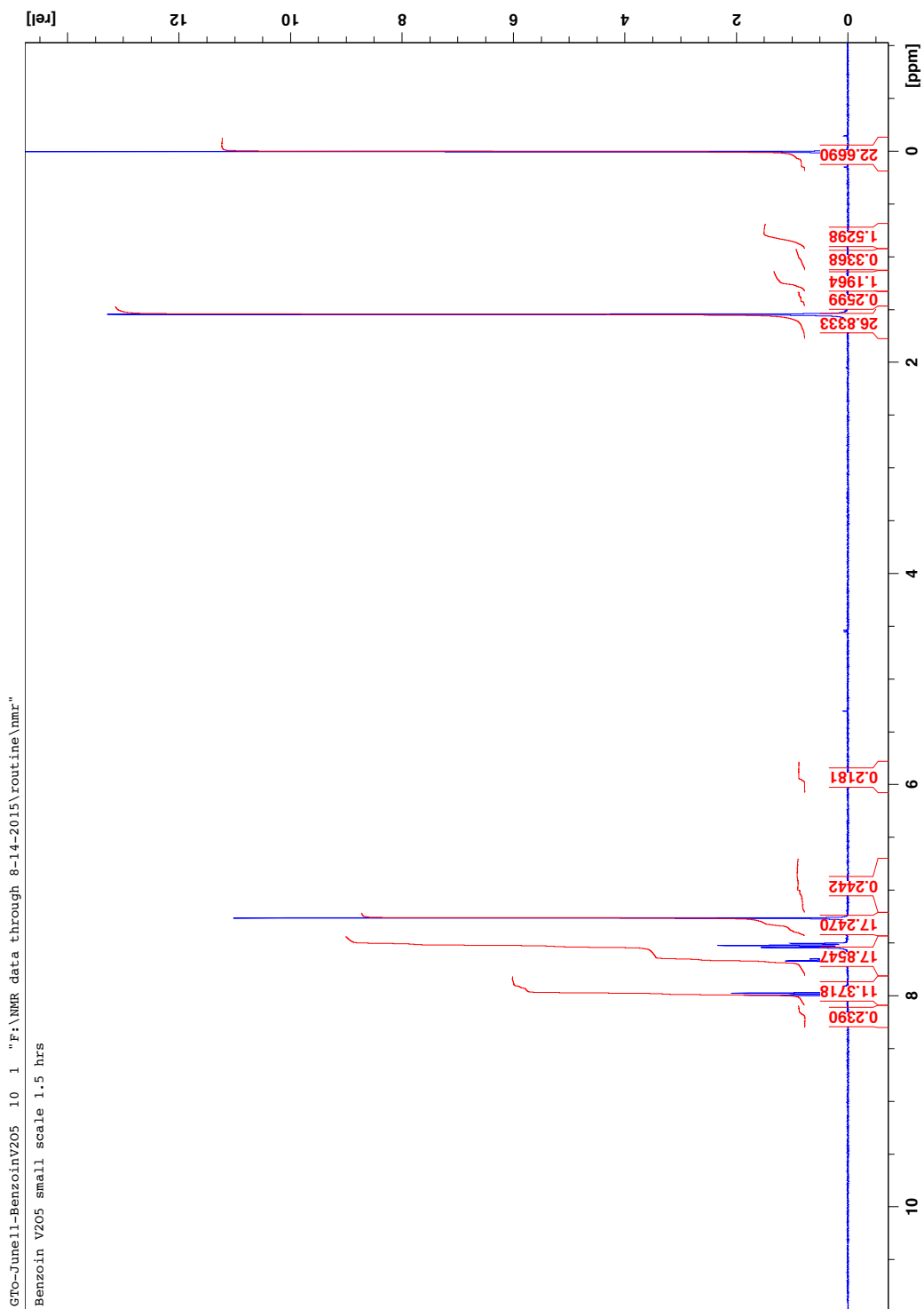
Date: 6/15/2015 12:41 PM



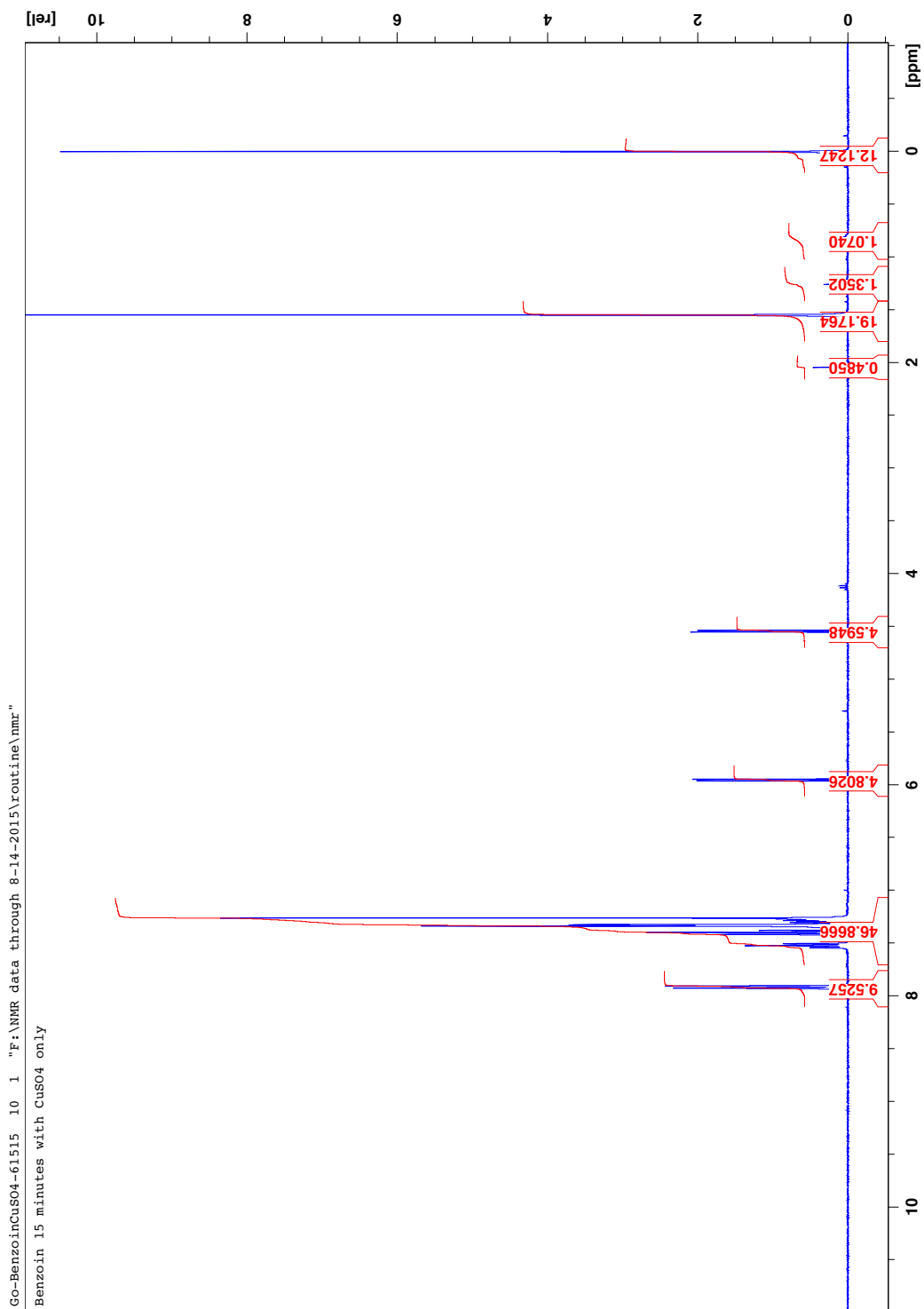
Reaction 16: Benzoin (no catalyst) – 1.5 hours



Reaction 17: Benzoin and V<sub>2</sub>O<sub>5</sub> – 1.5 hours



Reaction 18: Benzoin and  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  – 1.5 hours



Reaction 19: Benzoin with  $V_2O_5$  and  $CuSO_4 \cdot H_2O$  – 1.5 hours

