

EFFECT OF ARYLDIMETHYLPHOSPHINE ELECTRONICS ON RATE OF  
OXIDATIVE ADDITION OF ARYL ELECTROPHILES AT Ni<sup>0</sup>

by

Michael James Giroux

A thesis submitted in partial fulfillment  
of the requirements for the degree

of

Master of Science

in

Chemistry

MONTANA STATE UNIVERSITY  
Bozeman, Montana

April 2019

©COPYRIGHT

by

Michael James Giroux

2019

All Rights Reserved

## ACKNOWLEDGEMENTS

This project could not have been completed without the aid of Mary Cloninger, Matthew Cook, Thomas Livinghouse, and Sharon Neufeldt. Their guidance as my committee was crucial to the success of my research presented in this document. I would also like to give special thanks to Brian Tripet, for his extensive assistance and expertise with the operation of the 500 MHz NMR. The copious amount of N<sub>2</sub> used to facilitate the temperature of my kinetic experiments was not in vain. Additionally, I would like to give special thanks to Thomas Livinghouse, for the usage of various gaseous canisters and laboratory equipment essential for this project.

## TABLE OF CONTENTS

|                                                                           |    |
|---------------------------------------------------------------------------|----|
| 1. INTRODUCTION .....                                                     | 1  |
| A General Introduction to Transition-Metal Catalysis .....                | 1  |
| Selectivity between Electrophiles in Cross-Coupling reactions .....       | 4  |
| Recent Findings within our Research Group .....                           | 6  |
| Hammett Plots, Describing a Linear Free-Energy Relationship.....          | 9  |
| 2. RESULTS AND DISCUSSION .....                                           | 15 |
| Selection of Phosphine Ligands for Hammett Analyses.....                  | 15 |
| Initial Synthetic Efforts: Lithiation of Bromobenzenes.....               | 17 |
| Revised Synthetic procedure Involving Air-Stable Intermediates.....       | 20 |
| Kinetic Studies of Aryldimethylphosphine Ligands.....                     | 26 |
| Hammett Analysis of Aryldimethylphosphine Ligands .....                   | 37 |
| 3. EXPERIMENTAL METHODOLOGY .....                                         | 42 |
| Synthesis of Phosphine-Borane Precursors .....                            | 42 |
| Synthesis of Dichloro(bisethylammino)phosphine.....                       | 42 |
| Synthesis of P, P-Dimethyl(bisethylammino)phosphine-borane.....           | 44 |
| Synthesis of Chlorodimethylphosphine-borane .....                         | 45 |
| Synthesis of Aryldimethylphosphines .....                                 | 46 |
| General Procedure for the Synthesis of Aryldimethylphosphine-borane ..... | 46 |
| 3-methoxyaryldimethylphosphine-borane .....                               | 47 |
| 4-methoxyaryldimethylphosphine-borane .....                               | 49 |
| 4-methylaryldimethylphosphine-borane .....                                | 49 |
| 3-fluoroaryldimethylphosphine-borane .....                                | 50 |
| General Procedure for the synthesis of Aryldimethylphosphines.....        | 51 |
| Phenyldimethylphosphine.....                                              | 52 |
| 3-methoxyaryldimethylphosphine .....                                      | 53 |
| 4-methoxyaryldimethylphosphine .....                                      | 54 |
| 4-methylaryldimethylphosphine .....                                       | 54 |
| Synthesis of Additional Compounds .....                                   | 55 |
| Synthesis of Tosylate Substrate .....                                     | 55 |

## TABLE OF CONTENTS CONTINUED

|                                                                |    |
|----------------------------------------------------------------|----|
| Kinetic Analyses Conditions.....                               | 56 |
| General Procedure for Determining Ligand Equilibrium .....     | 56 |
| General Procedure for Kinetic Analysis of Ligands .....        | 57 |
| Kinetic Analysis of Tosylate Substrate Oxidative Addition..... | 58 |
| Kinetic Analysis of Chloride Substrate Oxidative Addition..... | 54 |
| General Procedure for the Calculation of Rate Constants .....  | 58 |
| REFERENCES CITED.....                                          | 60 |
| APPENDICES .....                                               | 61 |
| APPENDIX A: NMR Spectra of Synthesized Compounds .....         | 62 |
| APPENDIX B: Graphs of Kinetic Analyses.....                    | 97 |

## LIST OF TABLES

| Table                                                                 | Page |
|-----------------------------------------------------------------------|------|
| 1. Previous Cross-Coupling Results .....                              | 8    |
| 2. $\sigma$ Constants of Common Substituents .....                    | 11   |
| 3. Average Rate Constants Calculated from Synthesized Ligands .....   | 36   |
| 4. Acquisition Parameters for Qualitative NMR analyses .....          | 63   |
| 5. Acquisition Parameters for Quantitative Kinetic NMR analyses ..... | 98   |

## LIST OF FIGURES

| Figure                                                                       | Page |
|------------------------------------------------------------------------------|------|
| 1. Typical Energy Diagram Comparing Catalyzed vs Noncatalyzed .....          | 2    |
| 2. Transition Metal Catalyzed Cross-Coupling Energy Diagram .....            | 3    |
| 3. General Nickel-catalyzed cross-coupling .....                             | 4    |
| 4. Selectivity of Palladium Catalysts Demonstrated by Fu <i>et al.</i> ..... | 5    |
| 5. Benzoic Acid Derivatives used to Formulate the Hammett Equation .....     | 10   |
| 6. Influence of Electron Density on an Example Reaction .....                | 10   |
| 7. Hypothetical Hammett Plots with Established $\rho$ Values .....           | 12   |
| 8. Hypothetical Hammett Plots with Alternative $\rho$ Values .....           | 13   |
| 9. Ligand Synthetic Targets .....                                            | 16   |
| 10. Aryldimethylphosphine Synthesis Lithiation Route .....                   | 17   |
| 11. Lithiation Synthetic Route Mixed Success .....                           | 18   |
| 12. Lithiation Synthetic Impurities Examples .....                           | 19   |
| 13. Aryldimethylphosphine Synthesis Borane Route .....                       | 21   |
| 14. Aryldimethylphosphine Synthesis Grignard success .....                   | 22   |
| 15. Aryldimethylphosphine Synthesis Anhydrous Decomplexation .....           | 23   |
| 16. Aryldimethylphosphine Synthesis Hydrous Decomplexation .....             | 24   |
| 17. Re-purified 4-Methylaryldimethylphosphine .....                          | 25   |
| 18. Re-purified 3-Fluoroaryldimethylphosphine .....                          | 26   |
| 19. Initial Procedures for Kinetic Analyses .....                            | 27   |
| 20. Kinetic Time Evaluation .....                                            | 28   |

## LIST OF FIGURES CONTINUED

| Figure                                             | Page |
|----------------------------------------------------|------|
| 21. Equilibrium Time Evaluation .....              | 30   |
| 22. Internal Standard Mixing Comparison.....       | 32   |
| 23. Kinetic Trial Graphical Example .....          | 33   |
| 24. Optimized Procedures for Kinetic Analyses..... | 34   |
| 25. Tosylate Oxidative Addition Hammett Plot ..... | 37   |
| 26. Chloride Oxidative Addition Hammett Plot ..... | 38   |
| 27. Two-Step Oxidative Addition.....               | 39   |

## ABSTRACT

An analysis of kinetics related to the selectivity of aryldimethylphosphine-nickel complexes for reaction at carbon—chlorine versus carbon—tosylate bonds is reported. A series of aryldimethylphosphine ligands bearing electronically-varied substituents were investigated. The rate constants for oxidative addition of ligand-nickel complexes to either aryl chloride or aryl tosylate substrates were calculated. These rate constants were used to construct Hammett plots describing the susceptibility of oxidative addition at both types of electrophiles to electronic influence from the ligand. Oxidation of catalyst to aryl tosylates yields a plot with a negative slope, while addition to aryl chlorides produces a positive slope. With this, we see that electron donating groups accelerate the addition of catalyst to aryl tosylates, while electron withdrawing groups may change the rate determining step of addition to aryl chlorides.

## INTRODUCTION

A General Introduction to Transition-Metal Catalysis

The synthesis of macromolecules at the pharmaceutical scale requires the use of efficient stereo- and regioselective reactions that afford high yields of product. To this end, many synthetic strategies rely on joining smaller chemical fragments to produce a more complex compound. Transition-metal catalyzed cross-couplings are some of the most prolific reactions utilized to form carbon-carbon and carbon-heteroatom bonds.<sup>1</sup> These techniques employ transition-metal catalysts to facilitate the coupling of an organic halide or pseudohalide with a nucleophilic organometallic species. Such catalysts greatly expand a synthetic chemist's repertoire, unlocking more accessible pathways, lowered costs, and expedited syntheses.

Transition-metal catalyzed coupling reactions have changed greatly since the earliest examples. Initial use of transition metals for coupling reactions typically involved the joining of two identical fragments in a homocoupling.<sup>1</sup> The following years saw the maturation of modern coupling strategies. Transition-metal catalyzed cross-couplings have been refined for specific transition metals, multi-dentate ligands, and a multitude of cross-coupling partners.<sup>1</sup>

A typical transition metal catalyst for cross-coupling consists of one or more ligands coordinated around a central transition metal atom, most commonly palladium or nickel.<sup>1</sup> Because of their d orbitals, transition metals are usually capable of rapidly associating and dissociating ligands.<sup>2</sup> The electrons inhabiting the filled or partially-filled

d-orbitals of transition metals allow for the rapid bond-formation and breakage necessary for catalytic activity.

As with any catalyst, transition metal catalysts facilitate chemical reactions by lowering the energy barriers for a reaction (*Figure 1*). It should be noted that lowering the energy barrier of the transition state in a reaction does not affect thermodynamics.

Transition metal-catalyzed cross-coupling reactions (especially C—C bond-forming reactions) are perhaps better represented by *Figure 2*, in which the reversion of product into reagents is too energetically demanding to be reasonably expected.

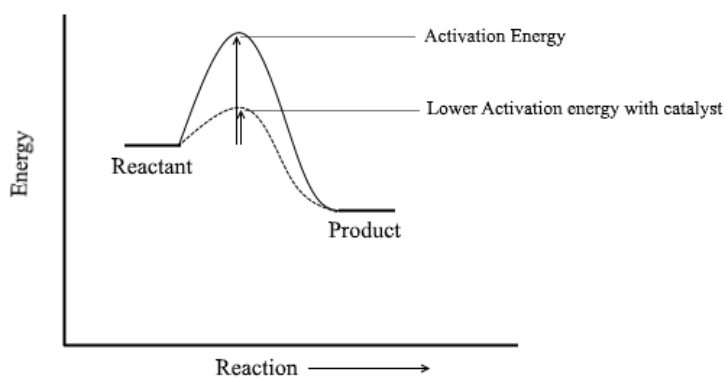


Figure 1. Energy diagram comparing an uncatalyzed (solid line) and catalyzed (dashed line) reaction.

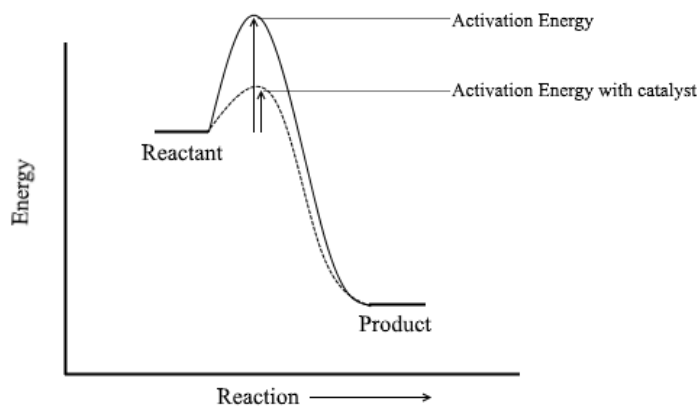


Figure 2. Simplified energy diagram representative of an irreversible transition metal-catalyzed cross-coupling. Note that transition-metal catalyzed cross-couplings are multi-step reactions, so this diagram is a simplification.

A general cycle typical of a nickel-catalyzed C—C bond-forming cross-coupling reaction is displayed in *Figure 3*. Located at the top, the most “electron rich” species of catalyst ( $\text{Ni}^0$ ) is ripe to proceed to the first step of a cross-coupling. The “capture” of a carbon-heteroatom bond initiates the cycle with an oxidative addition of the nickel complex into an electrophilic C-X bond.

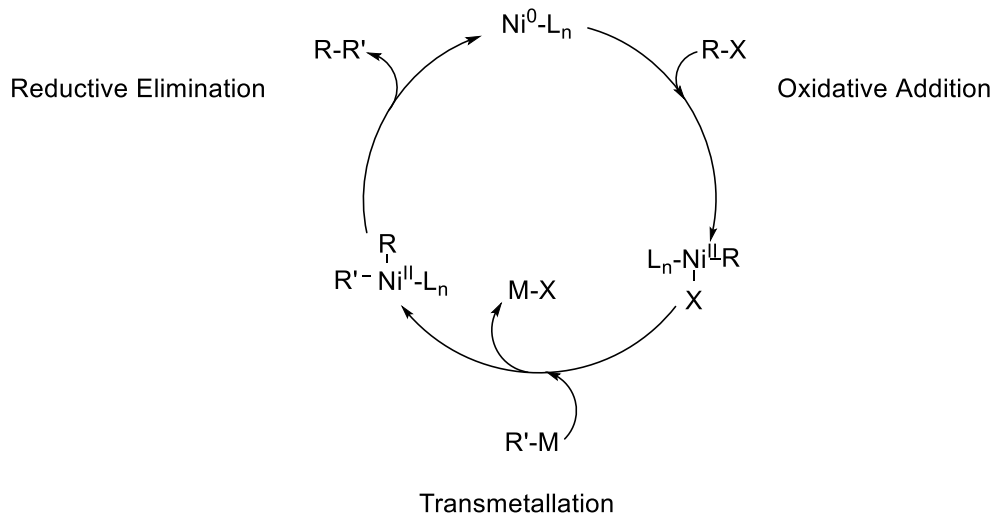


Figure 3. General catalytic cycle of a nickel-catalyzed cross-coupling.

The now electron-deficient  $\text{Ni}^{\text{II}}$  species is then attacked by the carbon nucleophile cross-coupling partner ( $\text{R'-M}$ ). Transmetalation between nickel and the coupling partner places  $\text{R'}$  onto nickel. In the final step, C—C bond-forming reductive elimination discards the product from the catalyst and regenerates  $\text{Ni}^0$  to begin cross-coupling anew.

### Selectivity Between Electrophiles in Cross-coupling Reactions

A pharmaceutically-desirable compound can consist of complicated structures constructed from multiple moieties.<sup>3</sup> To build these large molecules requires specific connections formed in a particular sequence. This often requires the utilization of protecting groups and complicated synthetic pathways to prevent forming mixtures of products when multiple reactive sites are present. In cross-coupling reactions, it can be

difficult to control selectivity between similar halide or pseudohalide substituents. A site-selective catalyst that displays high selectivity could circumvent the time-consuming or costly procedures needed when multiple reactive sites are present. The development of site-selective catalysts presents an efficient solution when these scenarios appear.

Prior publications have explored site- or chemoselective transition metal catalysts for cross-coupling.<sup>4</sup> There exist a few examples of catalysts that preferentially effect coupling at specific carbon-heteroatom bonds while ignoring other potential reactive sites.<sup>4</sup> As shown in *Figure 4*, palladium/phosphine catalysts can exhibit selectivity between chloride and triflate heteroatom bonds.<sup>4</sup>

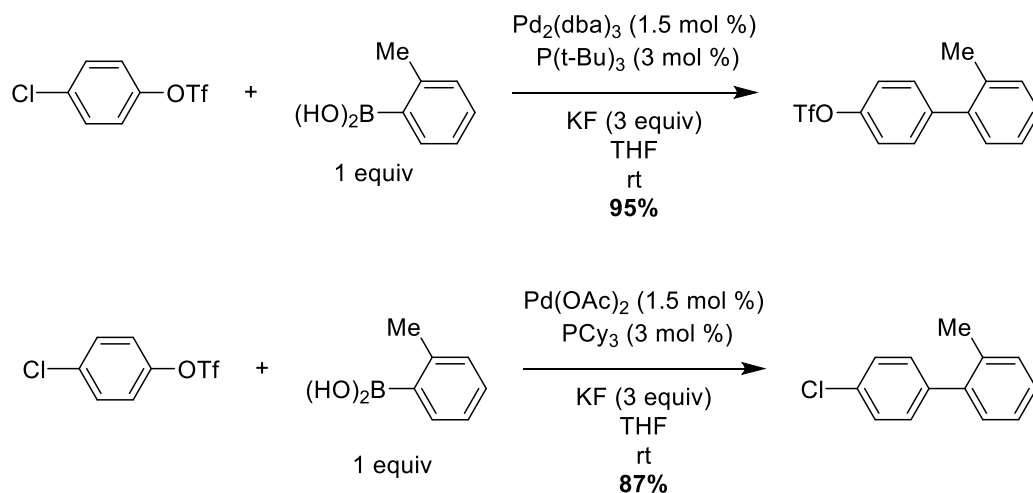


Figure 4. Phosphine ligand-mediated selectivity of palladium catalysts demonstrated by Fu and coworkers.<sup>4</sup>

In these examples, the choice of either tri-*tert*-butylphosphine or tricyclohexylphosphine is the determining factor in cross-coupling selectivity. This study suggests that the type of ligand coordinating palladium during oxidative addition influences selectivity.<sup>4</sup> Later computational analyses by Houk and Schoenebeck showed

that during oxidative addition palladium is coordinated by either a single large tri-*tert*-butylphosphine or by two smaller tricyclohexylphosphine ligands.<sup>4</sup> The different ligation states result in different amounts of electron density around palladium. The more electron-rich bisligated species prefers to react with the more electrophilic C—OTf, whereas the less electron-rich monoligated species prefers to react with the weaker C—Cl bond.

### Recent Findings within our Research Group

A primary research goal of the Neufeldt Lab is to use ancillary ligands to control cross-coupling site selectivity. Whereas phosphine ligands have been studied in selective Pd-catalyzed cross-couplings (*Figure 4*), the use of phosphine ligands to control selectivity between C—X and C—O electrophiles in nickel-catalyzed couplings has not been reported. Because of differences between nickel and palladium, it is possible that different phosphine ligand features will be necessary to control selectivity in nickel catalysis compared to palladium catalysis. When nickel is compared to its larger group 10 cousin, palladium, the smaller atomic radius provides much less space for ligand binding.

It is theorized that the restricted space available for ligands and the more concentrated electronic density of nickel makes it a better nucleophile for oxidative addition.<sup>1</sup> At the atomic scale, the smaller size of nickel allows for much closer association with its ligands and cross-coupling targets. Consequently, nickel is better able to react with strong bonds (such as C—O) when compared to palladium. For example,

nickel can more readily effect cross-couplings of aryl tosylates, mesylates, sulfamates, esters, ethers, and other phenol-derived electrophiles than palladium.<sup>1</sup> However, a challenge in these Ni-catalyzed cross-couplings of phenol-derived electrophiles is that halides, if present, generally react faster or competitively with the C—O electrophile.

To understand the relationship between phosphine ligands and selectivity for C—Cl vs. C—OTs in Ni-catalyzed Suzuki cross-couplings, other lab members (primarily Leidy Hooker) performed many screening reactions (*Table 1*). With most phosphine ligands, the Suzuki coupling is selective for reaction of the C—Cl bond of an aryl compound that contains both C—Cl and C—OTs reactive sites (entries 1–8). But two ligands, PMe<sub>3</sub> and PPhMe<sub>2</sub>, provide the opposite selectivity, favoring coupling at the C-OTs reaction site (entries 9-10).

Table 1. Previous results from our group: comparison of cross-coupling selectivity at chloride versus tosylate with different phosphine ligands. Only PPhMe<sub>2</sub> and PMe<sub>3</sub> (entries 9-10) favor reaction at OTs.

| Entry | Ligand                                                       | Reaction at Cl<br>(A, %) | Reaction at OTs<br>(B, %) | A : B     |
|-------|--------------------------------------------------------------|--------------------------|---------------------------|-----------|
| 1     | PPh <sub>3</sub>                                             | 85                       | 14                        | 6.07 : 1  |
| 2     | PPh <sub>2</sub> Me                                          | 37                       | 35                        | 1.06 : 1  |
| 3     | P( <i>n</i> -Bu) <sub>3</sub>                                | 59                       | 34                        | 1.74 : 1  |
| 4     | P(2-furyl) <sub>3</sub>                                      | 8                        | 0                         | >20 : 1   |
| 5     | dcypf                                                        | 12                       | 14                        | 1 : 1.17  |
| 6     | PPhEt <sub>2</sub>                                           | 52                       | 34                        | 1.53 : 1  |
| 7     | P( <i>p</i> -C <sub>6</sub> H <sub>4</sub> F) <sub>3</sub>   | 96                       | 9                         | 10.67 : 1 |
| 8     | P( <i>p</i> -C <sub>6</sub> H <sub>4</sub> OMe) <sub>3</sub> | 78                       | 36                        | 2.17 : 1  |
| 9     | PPhMe <sub>2</sub>                                           | 15                       | 65                        | 1 : 4.33  |
| 10    | PMe <sub>3</sub>                                             | 10                       | 60                        | 1 : 6     |

As a weaker bond, it is expected that cross-coupling will usually be more facile at C—Cl. This selectivity is exhibited with all ligands except PMe<sub>3</sub> and PPhMe<sub>2</sub> (Table 1). However, the higher electronegativity of oxygen compared to chloride gives the carbon attached to oxygen a more electrophilic profile. We hypothesize that PMe<sub>3</sub> and PPhMe<sub>2</sub> are uniquely capable of making nickel particularly electron-rich, therefore favoring its interaction with the more electrophilic C—OTs site. The unique reactivity of aryl dimethylphosphines provides an opportunity to study the effect of ligand electronics

on selectivity, by modulating the substituents on the ligand aryl ring as described in Chapter 2.

### Hammett Plots, Describing a Linear Free-energy Relationship

The study of the kinetics of chemical reactions requires a great degree of precision and determination. Originally conceptualized in 1936 by Louis P. Hammett, the Hammett equation was developed to describe the effect of aryl electronics on the equilibrium or rate of a reaction.<sup>4</sup> As shown in *Figure 5*, the original equation was developed using benzoic acid derivatives. By measuring the equilibrium between the benzoic acid and its conjugate base, the (de)stabilization of charge by substituents is evaluated. The effect of a substituent on rate or equilibrium can be described by the equation shown in *Figure 5*. The substituent constant,  $\sigma$ , reflects the electronic character of the substituent (the degree to which it is electron-donating or -withdrawing). The constant  $\rho$  describes the sensitivity of the equilibrium to electronics ( $\rho$  is defined as 1 for the reaction shown in *Figure 5*).

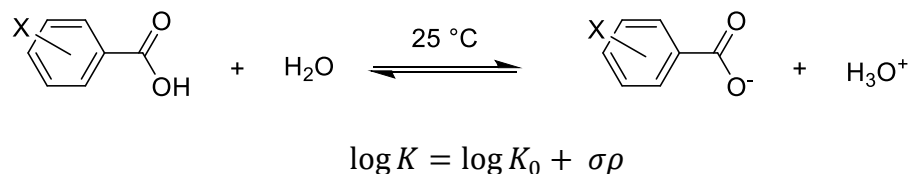


Figure 5. Benzoic acid/benzoate equilibrium used to formulate the Hammett equation, depicted underneath.

As exemplified in *Figure 6* for electrophilic aromatic substitution, when a transition state for a rate-determining step builds up positive charge, electron donating groups accelerate the rate of reaction. Conversely, when a transition state builds negative charge, electron withdrawing groups stabilize and accelerate the rate of reaction. By analyzing a reaction performed with a series of different substituents, the susceptibility of the rate-limiting transition state to electronic influence can be measured.<sup>4</sup>

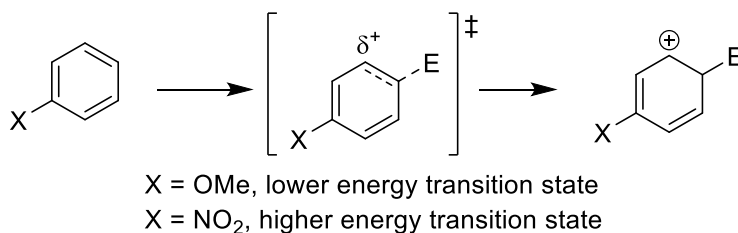


Figure 6. Electrophilic aromatic substitutions are accelerated by the presence of electron-donating substituents at the *para* position, which stabilizes buildup of positive charge in the TS, but decelerated by electron-withdrawing substituents.

Different substituents confer differing electronic influence on an aryl ring. As shown in *Table 2*, substituents at the *meta*- or *para*- position of a substituted arene have a measurable  $\sigma$  constant that denotes how much electron density they donate or withdraw.<sup>4</sup> As determined originally by Hammett, these values range from about -1 to +1, with new

$\sigma$  values for substituents being experimentally determined and computationally calculated since the original publication.<sup>4</sup> Originally calculated from the ionization of organic acids in solution,  $\sigma$  values are an effective method for describing electronic influence on an aryl ring.

Table 2.  $\sigma$  constants for some common substituents. Substituents with negative  $\sigma$  values donate electron density to the aryl ring, while those with positive values withdraw.<sup>5</sup>

| Group                                         | $\sigma_m$ | $\sigma_p$ |
|-----------------------------------------------|------------|------------|
| H                                             | 0.0        | 0.0        |
| CH <sub>3</sub>                               | -0.07      | -0.17      |
| CN                                            | 0.56       | 0.66       |
| CHO                                           | 0.35       | 0.42       |
| CO <sub>2</sub> H                             | 0.37       | 0.45       |
| F                                             | 0.34       | 0.06       |
| Br                                            | 0.39       | 0.23       |
| OCH <sub>3</sub>                              | 0.12       | -0.27      |
| SH                                            | 0.25       | 0.15       |
| NO <sub>2</sub>                               | 0.71       | 0.78       |
| N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> | 0.88       | 0.82       |

Once either equilibrium or rate constants have been calculated, these values are integrated into a Hammett plot as demonstrated in *Figure 7*. From this, a conclusion is made based on any trend that manifests. In the most optimal scenario where a linear trend develops, the slope is known as the  $\rho$  value. Illustrated in *Figure 7A*, the Hammett plot displays a negative  $\rho$  value, revealing that the representative reaction is accelerated by electron-donating groups. The Hammett plot in *Figure 7B* shows the opposite scenario, where a positive  $\rho$  value indicates the reaction is accelerated by electron-withdrawing groups. Beyond these outcomes, there are other trends that may develop from a Hammett study. A  $\rho$  value of 0 (a horizontal line, *Figure 8A*) indicates that electronics do not have

a significant influence on the reaction rate. Nonlinearity (*Figure 8B*) supports the notion that the reaction mechanism changes with different substituents, and thus alternative methods of analysis are necessary.

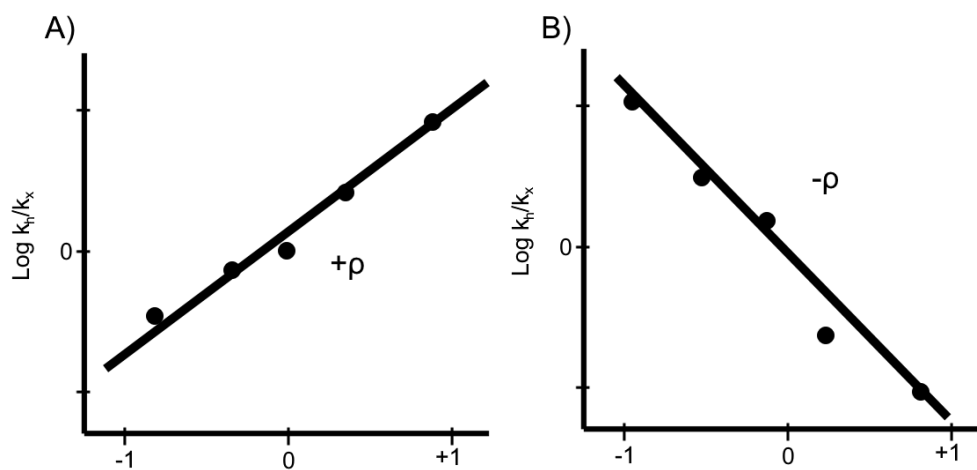


Figure 7. A) A hypothetical Hammett plot depicting a negative  $\rho$  value, where electron-donating groups accelerate the reaction. B) A hypothetical Hammett plot depicting a positive  $\rho$  value, where electron-withdrawing groups accelerate the reaction.

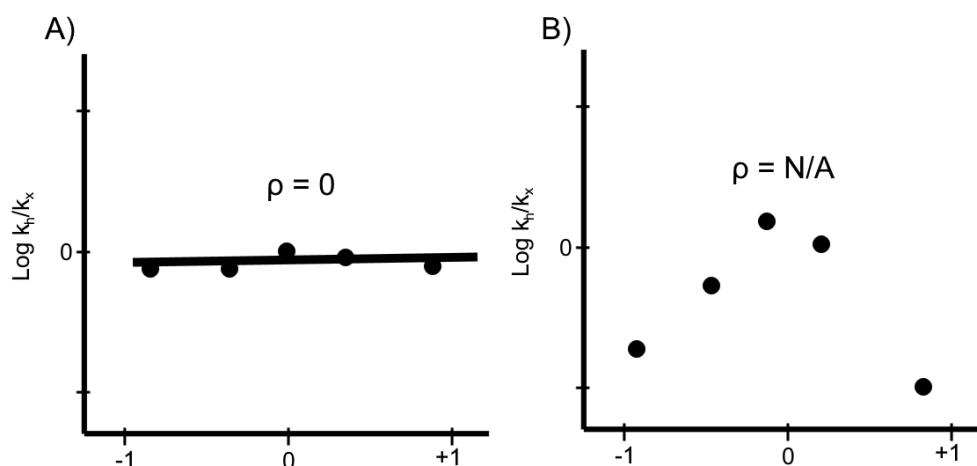


Figure 8. A) A hypothetical Hammett plot depicting a  $\rho$  value of zero, where the reaction rate is insensitive to electronic effects. B) A hypothetical Hammett plot depicting a nonlinear trend, which may suggest a change in mechanism.

To explore the origins behind the observed selectivity for cross-coupling at tosylate using  $\text{PPhMe}_2$  (Table 1, entry 9), the synthesis and analysis of new substituted aryl dimethylphosphine ligands is reported herein. It is hypothesized that cross-coupling selectivity is determined in the oxidative addition step. By modulating aryl substituents and conferring changes to the electronic environment about phosphorus, the electronic environment of a coordinated transition metal is similarly modulated. By measuring the kinetics of oxidative addition at  $\text{C—Cl}$  or at  $\text{C—OTs}$  using various  $\text{PArMe}_2$  ligands, Hammett plots can be constructed that investigate the role of electronics in selectivity towards cross-coupling targets.

We hypothesized that the Hammett plots for oxidative addition of nickel-phosphine complexes into both tosylate and chloride substrates should exhibit a negative

$\rho$  value. For both reactions, oxidative addition of the nickel catalyst was expected to be accelerated as its nucleophilicity is enhanced by greater electron density around the nickel atom. Further, based on the greater electrophilicity of the C—OTs bond, we hypothesized that the Hammett plot of tosylate addition should show a steeper slope than for the C—Cl addition. If the rate of oxidative addition is influenced by the favorable interaction between nickel (as a nucleophile) and carbon (as an electrophile), then the more electrophilic substrate should be more sensitive to electron-modulating substituents on the phosphine ligand.

## RESULTS AND DISCUSSION

Selection of Phosphine Ligands for Hammett Analysis

The goal of this project was to synthesize a series of aryl dimethylphosphine ligands, each with a different substituent on the aryl ring. As previously shown in *Table 2*, there are a great variety of substituents with published  $\sigma$  values. Substituents with positive  $\sigma$  values withdraw while those with negative values donate electron density, and the strength of these effects relates to the magnitude of their  $\sigma$  value. An effective Hammett plot contains a wide range of  $\sigma$  values to best illustrate a potential reactivity trend. The inherent difficulty in designing a set of ligands ( $\text{PArMe}_2$ ) for a Hammett plot is that each substituent on the aryl rings must be stable to the synthetic processes required to prepare the ligands, and the substituents also must not interfere with oxidative addition. Many of the published  $\sigma$  values, such as the bromide and ammonium groups in *Table 2*, are potentially susceptible to undesirable side reactions. As such, we chose to focus on the ligands displayed in *Figure 9* based on the inert character of their substituents while also retaining a wide range of  $\sigma$  values.

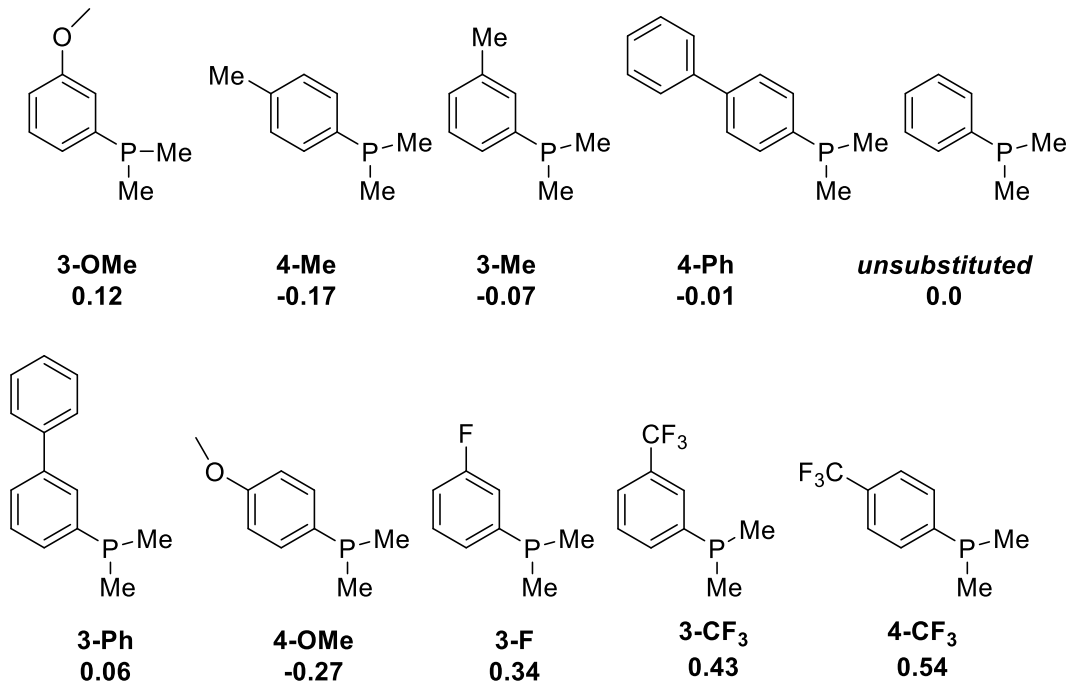


Figure 9. Ligand synthetic targets and their substituent  $\sigma$  values.

With the ligand targets selected, we turned to ligand synthesis. A major challenge related to the synthesis of many alkyl phosphines is that they are susceptible to oxidation. The same electron pair that makes tertiary phosphines such effective ligands in organometallic catalysis is also detrimental to their stability in air. That is, exposure to oxygen results in the rapid oxidation of these ligands to form phosphine oxides. Even further, those ligands with electron-donating substituents are potentially even more likely to oxidize based on the increased electron density about the phosphorus atom. In order to avoid this outcome, reactions had to be carried out under rigorously air-free conditions. The Schlenk line used in this project was filled with argon, and anaerobic flushing techniques were performed with care.

### Initial Synthetic Efforts: Lithiation of Bromobenzenes

In order to prepare these tertiary phosphines, a few different synthetic strategies were explored. Initially, the synthetic scheme adapted from Wright *et al.* was chosen based on its quick synthetic timetable and reported effectiveness.<sup>6</sup> In this synthesis, a bromobenzene derivative undergoes lithium-halogen exchange to provide a highly reactive aryllithium reagent (*Figure 10*). This intermediate is transformed into an arylzinc nucleophile when treated with zinc(II) chloride. This nucleophile is then exposed to phosphorus trichloride, resulting in a replacement of a single chloride on the phosphorus to yield the aryldichlorophosphine product. As a highly toxic substance, phosphorous trichloride was handled with extreme care, and cleanup of exposed equipment included bleaching and exposure to air in the fume hood for several days. Still vulnerable to oxidation, this aryldichlorophosphine is then treated with methyllithium in a further reaction to produce the final aryldimethylphosphine ligand.

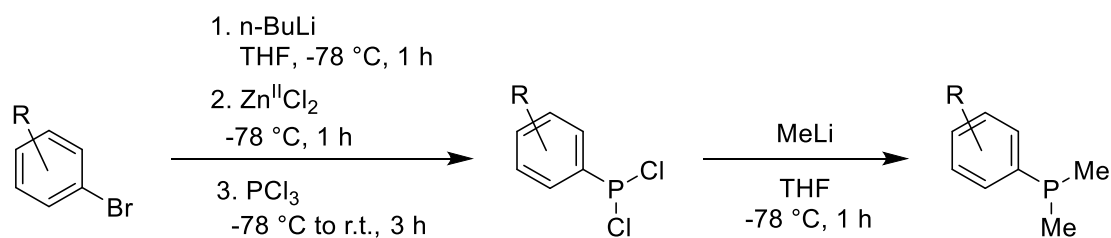


Figure 10. Synthesis of aryldimethylphosphine ligands through a route that installs the aryl onto phosphorus before installing the methyl groups.<sup>6</sup>

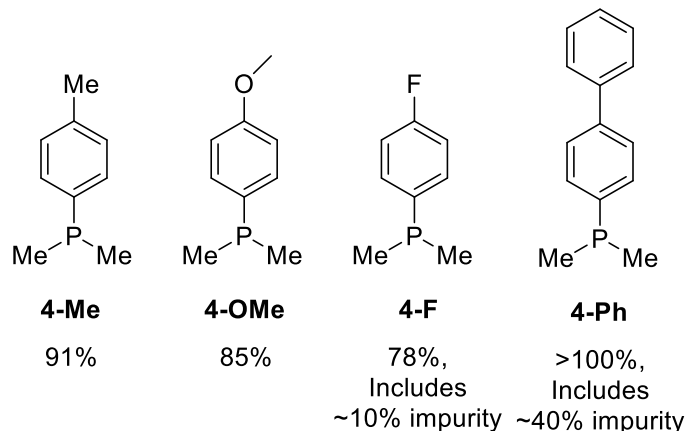


Figure 11. Final yields of aryldimethylphosphine ligands synthesized through the route shown in *Figure 10*. Note the impurities estimated by NMR for both **4-F** and **4-Ph**.

Using this synthetic methodology, a series of aryldimethylphosphine ligands were synthesized, and the reaction yields are shown in *Figure 11*. For some aryl substituents (**4-Me**, **4-OMe**),  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectra were clean and indicated highly pure phosphine ligand product. A problem began to arise, however, with other substituents. As shown in *Figure 12*, the 4-fluoro- and 4-phenyl-substituted ligands prepared by this method exhibit various impurities. 4-fluoro contained impurities by  $^{31}\text{P}$  NMR and  $^1\text{H}$  NMR, while 4-phenyl contained impurities only visible by  $^1\text{H}$  NMR. Even with a few different purification attempts, it was not possible to obtain clean products.

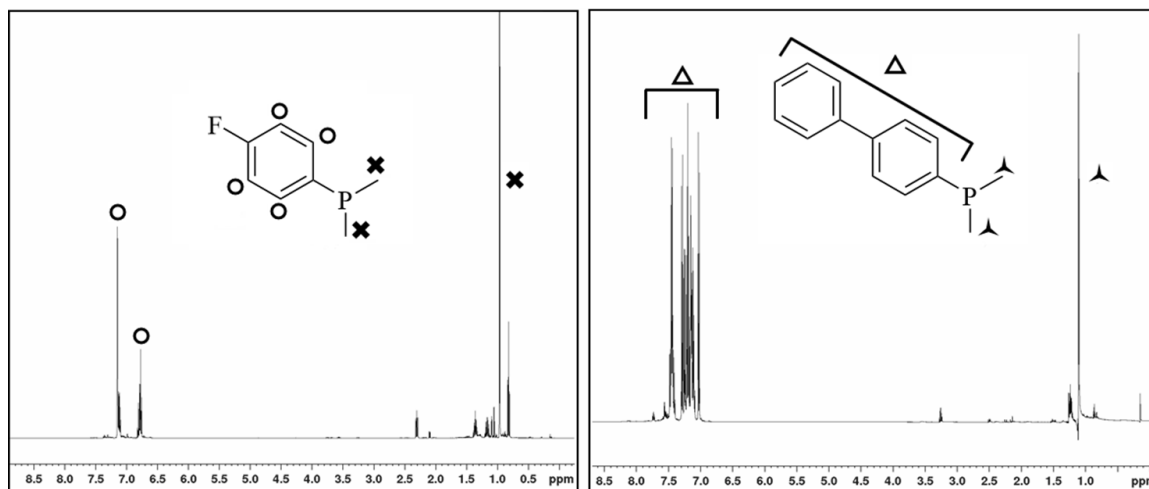


Figure 12.  $^1\text{H}$  NMR spectra of **4-F** (left) and **4-Ph** (right) with contaminants persistent after purification attempts. Proton signals corresponding to desired product signals have been labelled with symbols.

Due to the persistence of these impurities, a different synthetic method was sought. A more desirable method would be one that minimizes the risk of phosphine oxidation and that involves intermediates that can be more effectively purified by conventional distillation and chromatographic methods.

### Revised Synthetic Procedure Involving Air-Stable Intermediates

To synthesize ligands through a route involving air-stable intermediates, a few potential solutions were explored. We eventually settled on a method adapted from the doctoral thesis of Holly Heath from the research group of Prof. Tom Livinghouse.<sup>7</sup> As shown in *Figure 13*, constructing the dimethylated core of the phosphine ligand before finally attaching an aryl group provides a more divergent synthetic pathway. In this strategy, methylmagnesium chloride is first prepared from chloromethane gas. To the Grignard reagent is added compound **1** (prepared from diethylamine and  $\text{PCl}_3$ ) by slow drop-wise addition over a period of several hours with constant observation to produce dimethyl(diethylamino)phosphine. Borane dimethylsulfide is then added to the reaction mixture. Dimethylsulfide is displaced from boron by (diethylamino)dimethylphosphine to form an air-stable phosphine-borane complex **2**. This compound was synthesized at a large scale, as it is the precursor for all the targeted phosphine ligand.

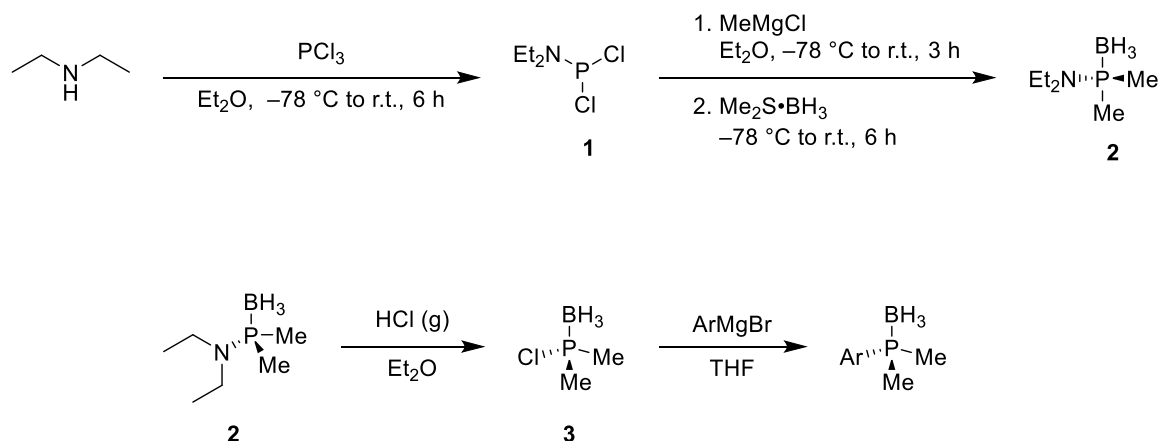


Figure 13. Synthesis of aryl dimethylphosphines via phosphine-borane intermediates.<sup>7</sup>

Acidification of complex **2** with hydrogen chloride gas effectively replaces the diethylamino group with a chloride. Product **3** is easily purified by flash-vacuum distillation, but it is much more vulnerable to hydrolysis than its diethylamino precursor. Through replacement of the labile chloride, this phosphine species can be diversified into the target aryl dimethylphosphine ligand.

In the next stage of synthesis, the substituted aryl group is attached. Initial synthetic efforts used aryllithium reagents as previously described to attach aryl groups to phosphorous trichloride.<sup>7</sup> When this reaction was performed with  $\text{PhLi}$  prepared from unsubstituted bromobenzene and compound **3**, a wide variety of products were formed in significant quantities. Based on crude  $^{31}\text{P}$  NMR, none of these products appeared to correspond to the desired target. After multiple efforts to refine and tune these conditions, we determined that a less reactive nucleophile was needed. In the original thesis by Holly, these aryl rings were attached directly to phosphorous trichloride, prior to methylation or borane decomplexation. This may explain the poorer results with our

synthetic efforts. Consequently, we turned to aryl Grignard reagents, which are less reactive nucleophiles than aryllithium reagents. The first attempt to synthesize the **3-OMe** ligand using a Grignard reagent proved to be highly successful after purification and decomplexation. This Grignard method produced the desired borane complex as the major product, with a single significant side product and a cluster of trace contaminants that were removed via column chromatography and distillation to produce a purer form of the ligand (*Figure 14*). In most cases, the crude products could be purified by column chromatography to yield the desired aryl dimethylphosphine-borane as a single species by  $^{31}\text{P}$  NMR spectroscopy.

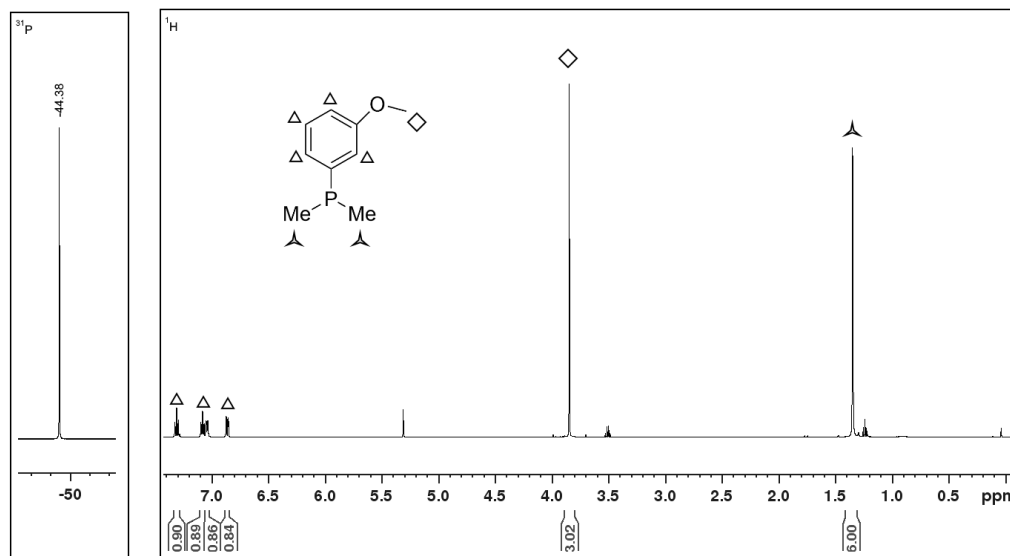


Figure 14.  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectrum of the complex of **3-OMe** after preparation with an aryl Grignard reagent.

The borane complexes of **3-OMe** and **3-F** remained impure after multiple attempts at column chromatography with varying solvent systems. Eventually, these

complexes were purified with additional flash-vacuum distillations that effectively separated the desired phosphine-borane complex from the associated impurities.

With the successful syntheses of a few phosphine-borane complexes, the next step was to strip off the borane complex to yield the free phosphine ligand. This stage proved exceptionally challenging for these compounds and was explored with multiple strategies. Adapted from Livinghouse *et al.* for the decomplexation of diphosphine-diborane complexes, there are both aqueous and anhydrous methods to decomplex boron from the phosphine.<sup>8</sup> The first of these methodologies to be explored was anhydrous, involving treatment of the phosphine-borane with  $\text{HBF}_4 \cdot \text{OMe}_2$  (or in our case,  $\text{HBF}_4 \cdot \text{OEt}_2$ ) followed by anhydrous  $\text{K}_2\text{CO}_3$  (Figure 15).

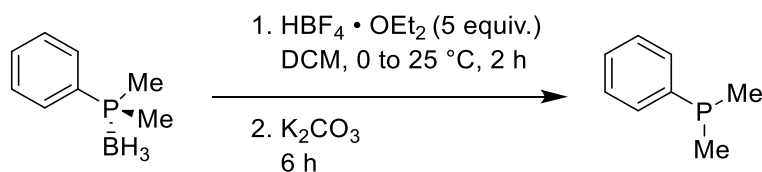


Figure 15. Method for decomplexation of phosphine-boranes under anhydrous conditions.<sup>8</sup>

This reaction was attempted numerous times with  $\text{PPhMe}_2 \cdot \text{BH}_3$ , which was prepared by treating commercially available  $\text{PPhMe}_2$  with  $\text{BH}_3 \cdot \text{Me}_2\text{S}$ . Despite trying different solvents, alternative bases (including sodium and potassium hydride), and extended reaction times; the protonated form of the ligand remained. Eventually, the aqueous alternative described in Livinghouse *et al.* was explored and adapted for use with aryldimethylphosphines (Figure 16).<sup>8</sup> The acidification of

PhPMe<sub>2</sub>•BH<sub>3</sub> with 5 equivalents of HBF<sub>4</sub>•OMe<sub>2</sub> yielded the protonated form of the desired phosphine as before. When treated with 6 equivalents of aqueous potassium hydroxide (degassed by sparging with argon for 2 h), a ~1:3 mixture of free phosphine and protonated phosphine was observed by <sup>31</sup>P NMR. This and other similar results suggest that even an excess of base (as much as 10 equivalents) is insufficient for fully deprotonating phosphine. As such, the organic phase was transferred to a new flask via cannula and re-treated with an additional 3 equivalents of degassed aqueous potassium hydroxide. The first iteration of this procedure produced a low yield (14%) of free PhPMe<sub>2</sub> that contained ~6% of the corresponding phosphine oxide impurity by <sup>31</sup>P NMR. However, by further optimizing the reaction technique, including using stronger argon flow and extended degassing procedures, we were able to obtain PhPMe<sub>2</sub> in ~60% yield with less than 2% of the corresponding oxide visible by <sup>31</sup>P NMR.

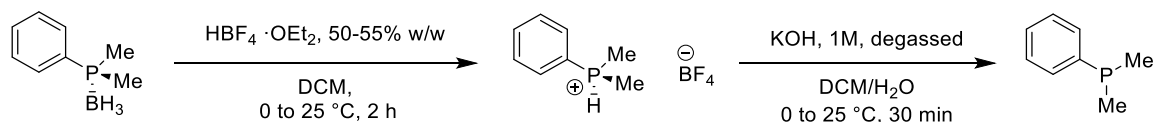


Figure 16. Method for decomplexation of phosphine-boranes under aqueous conditions.<sup>8</sup>

Ligands **3-OMe** and **4-OMe** were successfully synthesized by this method, as shown in *Figure 14* for a higher purity form of **3-OMe** than for the lithiation attempts of other ligands. In addition, the borane complexes of **3-F** and **4-Me** were synthesized. Unfortunately, during the decomplexation procedure of these latter two ligands, an unknown contaminant was introduced and remained persistent in the final products after decomplexation. The only significant difference in the procedure to prepare these two

ligands was that the final products were dissolved in pentane prior to filtration through celite, as opposed to the use of diethyl ether in the preparation of compounds **3-OMe** and **4-OMe**. As shown in the  $^1\text{H}$  NMR spectrum for **4-Me** (Figure 17) contaminants mainly exist in both the alkyl and aryl regions. The signal for the dimethyl group on phosphorus gives incorrect integration relative to the methyl signal on the aryl ring and depicts singlet multiplicity when compared to the doublet seen for other ligands. For **3-F**, a contaminant is clearly visible near 2.35 ppm (Figure 18), and a similar contaminant appears to be present in the spectrum of **4-Me** (immediately downfield of the benzylic methyl signal). Later, careful anaerobic distillation of the **4-Me** product yielded the desired **4-Me** ligand as compound **12**.

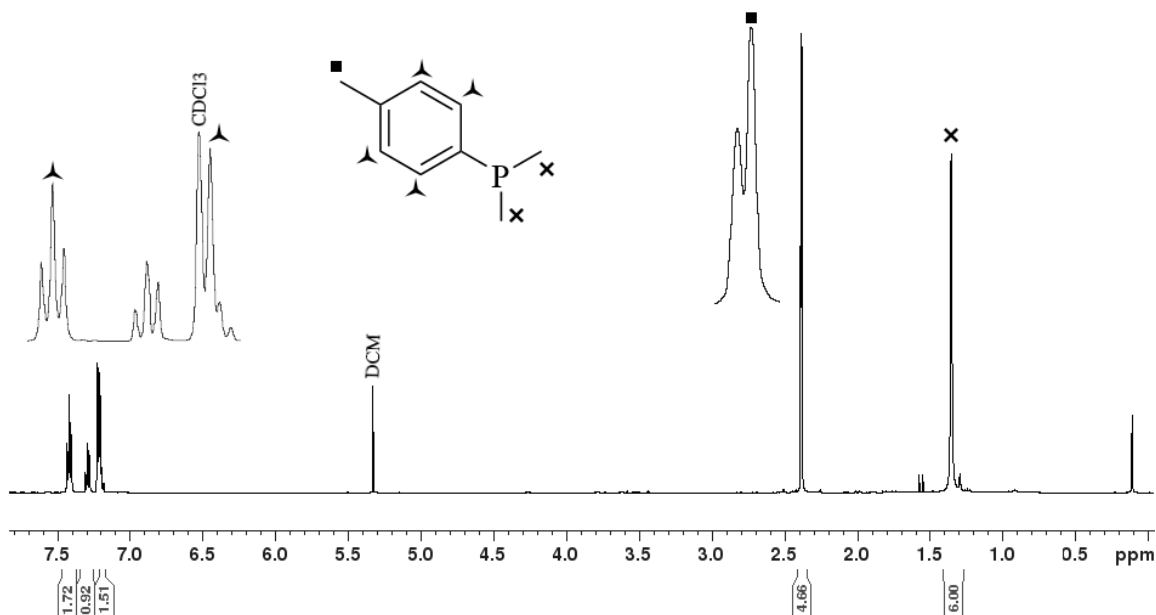


Figure 17.  $^1\text{H}$  NMR spectrum of re-purified **4-Me**.

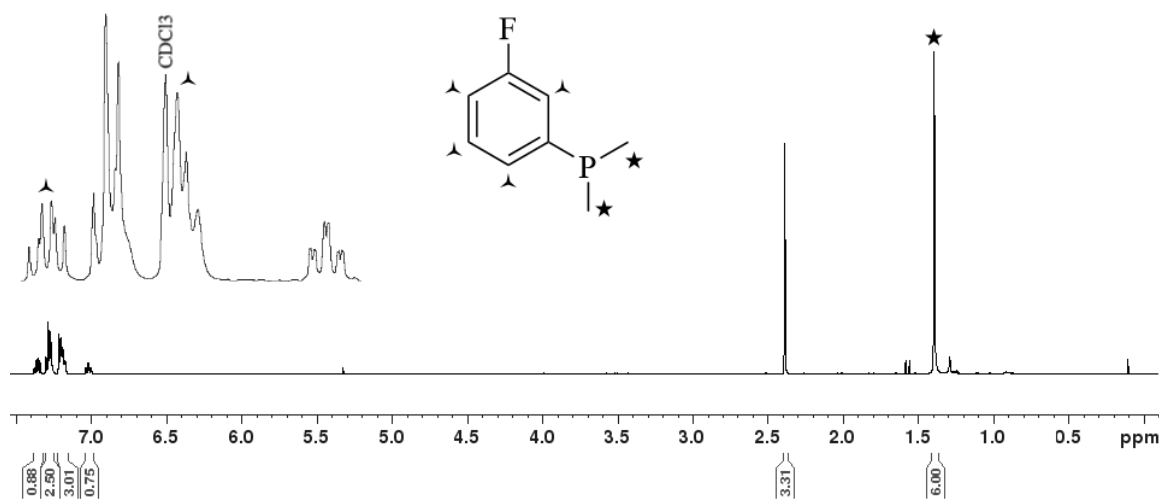
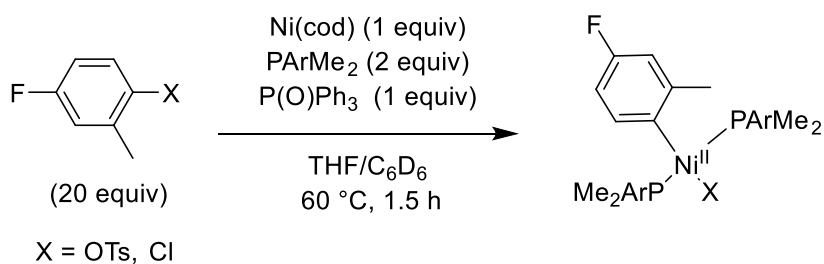


Figure 18.  $^1\text{H}$  NMR spectrum of re-purified **3-F**.

### Kinetic Studies of Aryldimethylphosphine Ligands

Having prepared some of the necessary phosphine ligands in high purity, the next stage of this project focused on acquiring kinetic data on oxidative addition of nickel/phosphine complexes into C—OTs and C—Cl bonds. Each ligand needed to be tested under identical conditions. Our goal was to analyze the oxidative addition of an aryl tosylate substrate, and separately an aryl chloride substrate, at nickel in the presence of each different phosphine ligand (Figure 19). Substrates were chosen that contain a *para*-fluoro substituent (to enable analysis by  $^{19}\text{F}$  NMR if needed) and an *ortho*-methyl group to help stabilize against decomposition of  $\text{Ni}^{\text{II}}$  to  $\text{Ni}^{\text{I}}$  decomposition.<sup>9</sup> Kinetic trials were performed in triplicate and the results were averaged together to generate more accurate rate constants for each reaction. This portion of the project was the most time

intensive and it required significant optimization of the procedure for running the kinetic trials in order to achieve good reproducibility.



13

Figure 19. Initial protocol for kinetic studies on the reaction of aryl tosylate or chloride substrates with Ni(cod)<sub>2</sub> and PArMe<sub>2</sub>.

The first stage of kinetic analyses used commercially available PPhMe<sub>2</sub>. It should be noted that over many kinetic trials, no significant difference was found between the reactivity of commercially acquired PPhMe<sub>2</sub> and the same ligand decomplexed from the corresponding PPhMe<sub>2</sub>•BH<sub>3</sub> complex. In initial trials, Ni(cod)<sub>2</sub>, phosphine ligand, triphenylphosphine oxide standard, and the aryl tosylate substrate were combined in an NMR tube inside an N<sub>2</sub>-atmosphere glovebox. The NMR tube was capped, removed from the glovebox, and immediately immersed in liquid nitrogen in an attempt to standardize the start time of all kinetic trials.

The next immediate step was to begin NMR analysis of the catalyst solution. Before inserting the sample into the instrument, frost needed to be removed from the outside of the NMR tube. Loading the cleaned tube into the autosampler, <sup>31</sup>P NMR spectra were collected over a period of 1.5 h according to standard collection procedures. Observation of spectra showed the initial presence of signals at 3.10 and -10.13 ppm.

Further observation over time shows the gradual disappearance of the two signals at 3.10 and -10.13 ppm along with the growth of a signal at -9.10 ppm. Shown in *Figure 19*, the signal growing at -9.10 ppm was assigned to the Ni<sup>II</sup> oxidative addition complex **13** based on analogy to related complexes prepared in our lab;<sup>10</sup> in addition, this signal only appears in the presence of substrate.

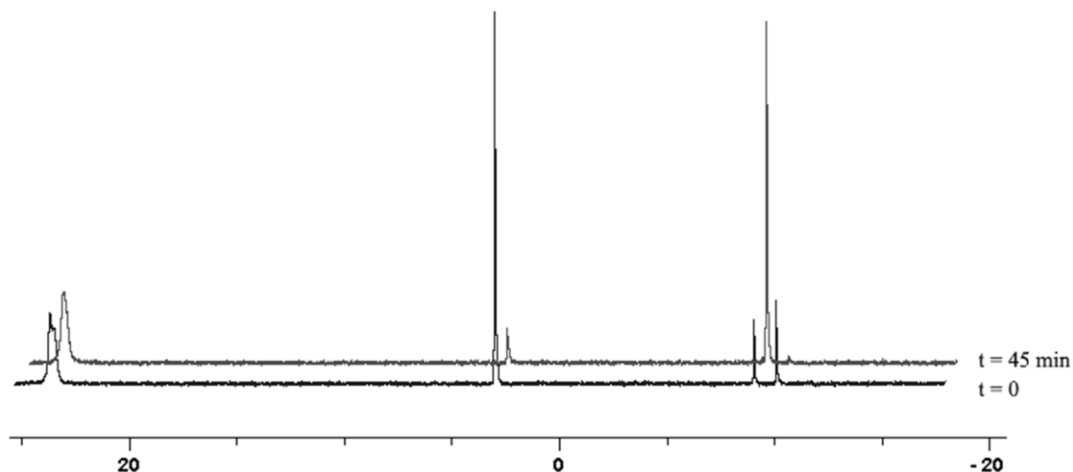


Figure 20. <sup>31</sup>P NMR spectra at t = 0 and t = 45 min for one of the first kinetic studies performed with PPhMe<sub>2</sub> ligand. Note the change over time for signals at 3.10, -9.10, and -10.13 ppm.

However, despite the initial success of being able to observe formation of an oxidative addition complex, after a few trials, it became apparent that this procedure was unsuitable for collecting accurate kinetic data due to poor reproducibility. Accordingly, we next attempted to adapt a protocol from Sproules *et al.*<sup>9</sup> Instead of freezing the NMR tube to arrest catalytic activity, the substrate was injected by syringe through a septum in

a final step immediately prior to collecting data. This modification circumvented the temperature variability that could be encountered in the procedure involving freezing the sample prior to data collection. Furthermore, this modified procedure allowed data to be collected very close to the time that the substrate was combined with the nickel/phosphine solution.

We made a second major change to the original kinetic procedure in response to the observation that two major phosphine species at -3.10 and -10.13 ppm ( $^{31}\text{P}$  NMR) are formed upon combining  $\text{Ni}(\text{cod})_2$  and phosphine, prior to the appearance of an oxidative addition complex. Further evaluation revealed that these two species begin forming immediately when  $\text{Ni}(\text{cod})_2$  and  $\text{PPhMe}_2$  are combined in the absence of substrate. The exact identities of these species cannot be determined at the current time but are hypothesized to be  $\text{Ni}(0)$  species with different numbers of coordinated phosphines. When substrate is added, the signal at 3.10 ppm appears to disappear much more rapidly than the signal at -10.13 ppm, suggesting that the former signal may correspond to the species that reacts with substrate to form the oxidative addition complex. In the absence of substrate, the ratio of the two  $\text{Ni}(0)$ /phosphine species was observed to change over time as analyzed by  $^{31}\text{P}$  NMR, so it became necessary to identify a suitable equilibrium timepoint where the ratio of the two signals became approximately constant. By reaching a suitable equilibrium timepoint, the presence of each species could be better normalized between successive kinetic trials. Evaluation of the reaction of  $\text{PPhMe}_2$ , **4-OMe**, and **3-OMe** with  $\text{Ni}(\text{cod})_2$  showed that the integration of the  $\text{Ni}(0)$ /phosphine signal at about ~3.10 ppm became approximately stable at the 30-minute mark (*Figure 21*). Based on

this, the procedure for oxidative addition kinetic analyses was adjusted so that the substrate was injected 30 minutes after the initial metal-ligand mixing.

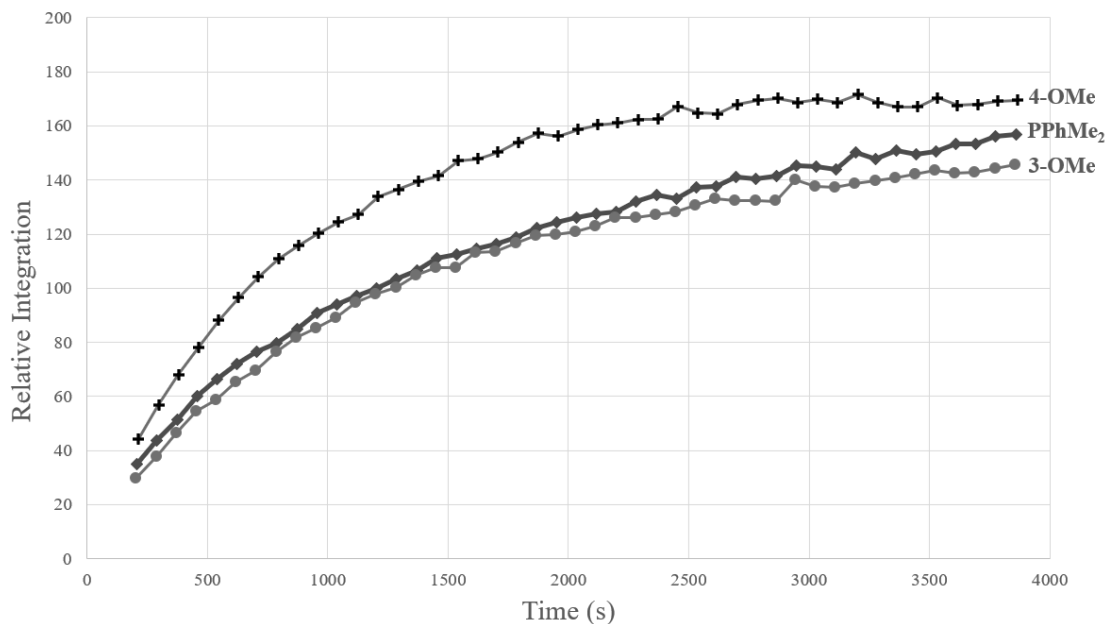


Figure 21. Growth of the Ni(0)/phosphine species at 3.10 ppm over time for **4-OMe**, PPhMe<sub>2</sub>, and **3-OMe** ligands. At approximately 2000 seconds (~30 minutes), growth of this signal starts to level off. Similar trend was observed for **4-Me** ligand.

With this modified protocol, rate constants could be calculated based on disappearance of the signal at 3.10 ppm. In order to calculate these values, we made use of integrated rate laws. The oxidative addition reaction relies on the joining of two fragments, both the catalyst and the substrate in what appears to be a second order reaction on first observation. To approximate first order kinetics, a large excess (20 equivalents) of substrate was used. These conditions mean that for the oxidative addition, the reaction rate is approximately independent of the concentration of substrate and can be described with a pseudo first-order equation as shown below (eq 1), where “Ni·P”

represents the nickel/phosphine species that reacts with substrate. It is important to note that a negative rate constant is calculated in this manner, as the disappearance of this species is being recorded over time. The opposites of these values are noted in *Table 3* for final calculations. The differential form of this rate law (eq 2) represents the first derivative with respect to time. By integrating this equation with respect to time (eq 3), the equation can then be rearranged to a linear form. In our experiments, taking the natural log of the concentration of the reaction over time should produce a straight line if the reaction is first order.

$$rate = -k[Ni \cdot P] \quad (1)$$

$$rate = d[Ni \cdot P]/dt = -k[Ni \cdot P] \quad (2)$$

$$\ln[Ni \cdot P] = -kt + \ln[Ni \cdot P]_o \quad (3)$$

*Figure 22* shows a plot of the natural log of the three changing signals seen for a kinetics trial of the oxidative addition into C—OTs. The linear nature of the trend marked with crosses in *Figures 22* and *24* shows that the disappearance of the signal at ~3.10 ppm follows first-order kinetics with a consistent linear trend exhibited over each kinetic trial.

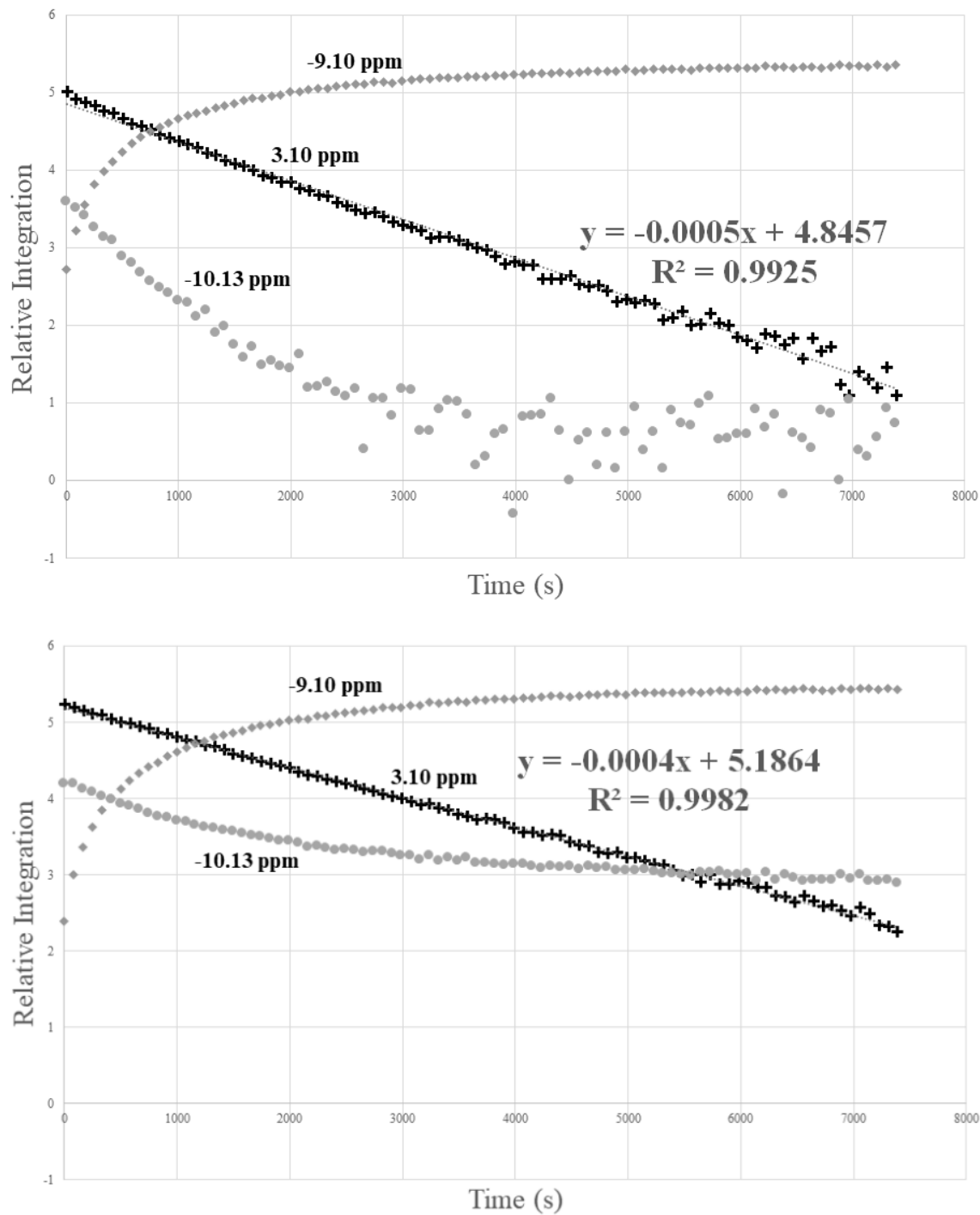


Figure 22. Results of two studies illustrating different behavior when triphenylphosphine oxide is (A) in the reaction solution or (B) segregated in a sealed capillary. Change over time of signals at 3.10 (cross), -9.10 (diamond), and -10.13 ppm (circle).

It is important to clarify that the slope in *Figure 23* representing the species at -3.10 ppm is a negative value. This is because we are observing the disappearance of a species over time, as opposed to the growth of a product signal. We chose this method of analysis because the growing signal at -9.10 ppm, assigned to the oxidative addition product, does not display a linear trend. We hypothesize that the nonlinearity of the latter signal is due to decomposition of the Ni<sup>II</sup> species into NMR-silent Ni<sup>I</sup> species.

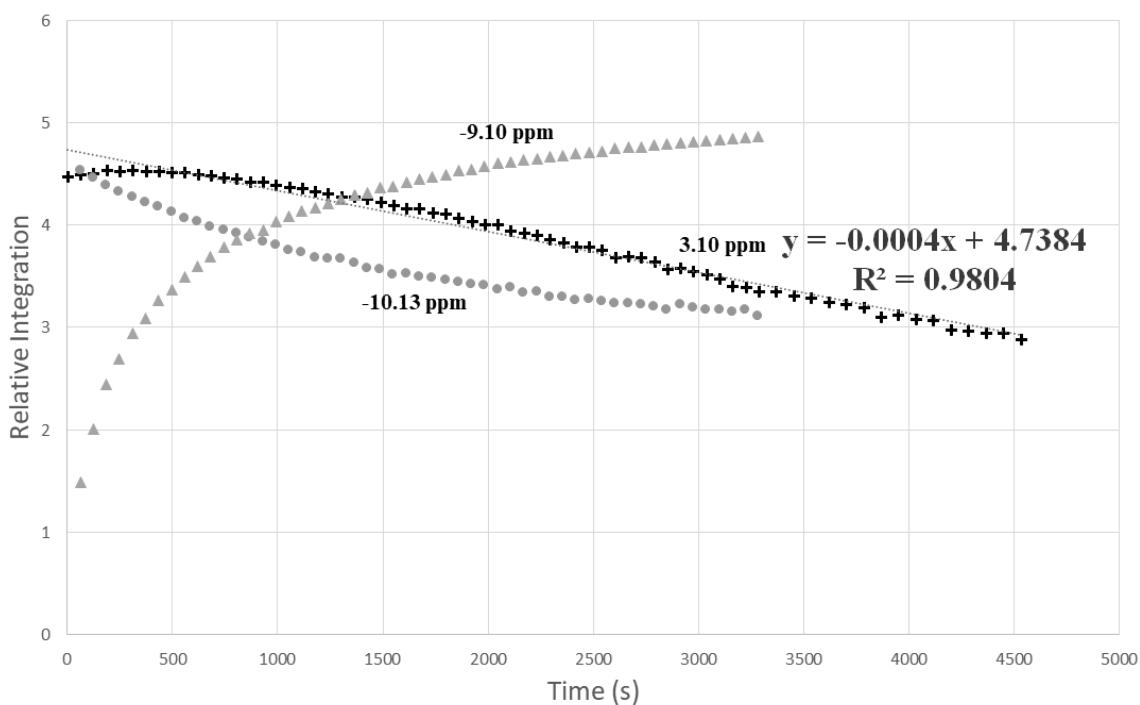


Figure 23. Results of kinetic studies on the reaction of Ni(cod)<sub>2</sub> and PPhMe<sub>2</sub> with the aryl tosylate substrate under the optimized protocol.

One additional obstacle became apparent related to the triphenylphosphine oxide standard. Because it is a poor ligand relative to trivalent phosphine, triphenylphosphine oxide was expected to be inert during these kinetic analyses. However, as shown in the

series of analyses in *Figure 22*, the inclusion of triphenylphosphine oxide directly in solution in the NMR tube consistently resulted in a different trend for the disappearance of the signal at -10.13 ppm when compared to segregating the standard in a glass capillary insert. In addition, the overall data collected with  $\text{P}(\text{O})\text{Ph}_3$  in solution was more scattered, especially with respect to the signal at -10.13 ppm. This observation suggests that triphenylphosphine oxide is a non-innocent additive. This complication was remedied with the use of sealed glass capillaries containing the standard for future kinetic trials.

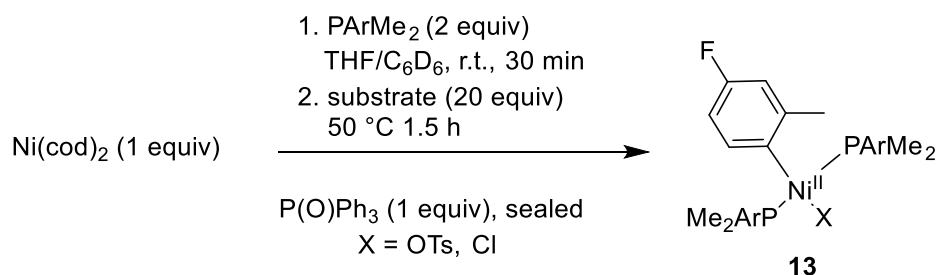


Figure 24. Optimized protocol for kinetic studies on the reaction of aryl tosylate or chloride substrates with  $\text{Ni}(\text{cod})_2$  and  $\text{ArPMe}_2$ .

The final optimizations implemented were a series of small but significant changes for data collection. The first of these was to lower the NMR probe temperature. Although kinetic trials were initially conducted at 60 °C to replicate typical catalytic reaction conditions, the oxidative addition proved too fast at this temperature, preventing a significant time range of catalytic activity data to be collected in the beginning of kinetic trials (see *Figure 22*). A series of temperature experiments determined that a reaction temperature of 50 °C provided oxidative addition at a suitably slow rate to allow

enough data collection in a reasonable amount of time. Beyond this adjustment, we also coordinated with the NMR lab technician to set new data-collecting adjustments for the Bruker Topspin Software, such as reducing scan times, abolishing dummy scans, and modifying spectral width, to allow data to be collected at a more rapid and consistent pace. *Figure 24* illustrates the final optimized protocol for the kinetic experiments, and *Figure 23* shows an example of the data collected under these conditions using PPhMe<sub>2</sub>.

With the entire kinetic trial process streamlined, kinetic experiments were carried out with PPhMe<sub>2</sub>, **4-OMe**, **4-Me**, and **3-OMe**. Rate constants were calculated for the 3 viable ligands based on the slope of the line corresponding to disappearance of the signal at ~3.10 ppm as detailed in *Figure 23*, *24*, and *Table 3*. These experiments were done in triplicate, and the results were averaged to determine rate constants for each ligand, with the occasional outliers for rate constants omitted from final calculations. As described in section 2.3, significant unknown contaminants prevented the analysis of **3-F**.

Table 3. Average rate constants obtained using PPhMe<sub>2</sub>, **4-OMe**, **4-Me**, and **3-OMe** for the reaction shown in Figure 24. Note that a single extreme outlier of a triplicate study was omitted from some calculations, and the raw data for these values can be viewed in *Appendix B*.

| Ligand             | Sigma Value | OTs Average $k_x$ (M s <sup>-1</sup> ) (std. dev) | Cl Average $k_x$ (Ms <sup>-1</sup> ) (std. dev) |
|--------------------|-------------|---------------------------------------------------|-------------------------------------------------|
| PPhMe <sub>2</sub> | 0           | 2.33 E-06 (9.91 E-07)                             | 1.83 E-06 (6.20 E-07)                           |
| <b>4-Me</b>        | -0.17       | 7.10 E-06 (3.54 E-06)                             | 1.36 E-06 (9.94 E-08)                           |
| <b>4-OMe</b>       | -0.27       | 8.06 E-06 (5.65 E-07)                             | 2.38 E-06 (2.71 E-07)                           |
| <b>3-OMe</b>       | 0.12        | 2.42 E-06 (1.78 E-07)                             | 4.87 E-06 (6.41 E-07)                           |

### Hammett Analysis of Aryldimethylphosphine Ligands

Hammett plots were next constructed using PPhMe<sub>2</sub>, **4-OMe**, and **3-OMe**.

Hammett plots for the aryl tosylate and aryl chloride substrates are shown in *Figures 25* and *26*, respectively. Because these preliminary plots only contain three data points each, it is not possible to firmly establish  $\rho$  values but they appear approximately linear. Importantly, the trends in these two plots are clearly different for the two substrates.

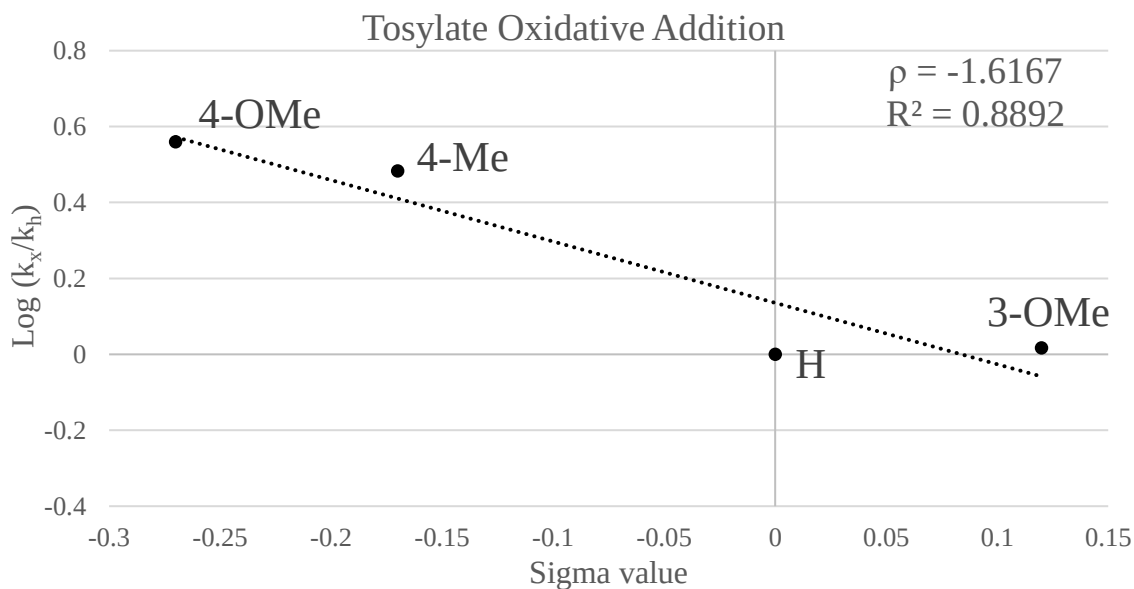


Figure 25. Kinetic Hammett plot generated for the oxidative addition of tosylate substrate at Ni/ArPMe<sub>3</sub>.

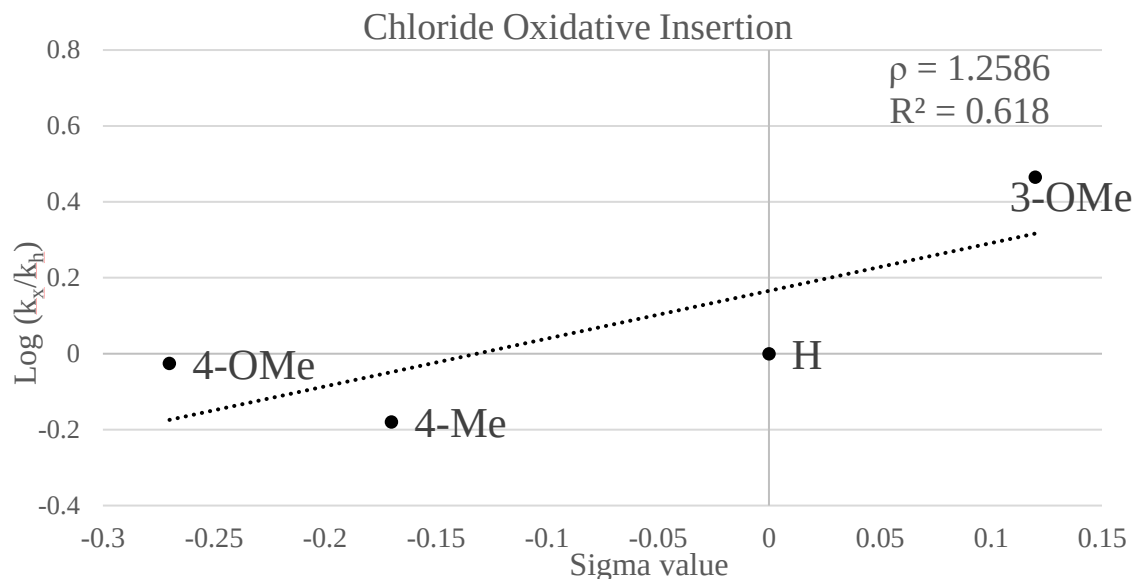


Figure 26. Kinetic Hammett plot generated for the oxidative addition of chloride substrate at Ni/ArPMe<sub>3</sub>.

C—OTs and C—Cl oxidative addition appear to show opposing trends for the electronic influence from substituents. In our original hypothesis, we expected both plots to have negative  $\rho$  values, indicating that electron donating groups on the arylphosphine accelerate the reaction. We hypothesized that the Hammett plot for the tosylate substrate, which has a more electrophilic carbon, should have a steeper slope than seen with the chloride substrate, signifying that the rate of oxidative addition into C—OTs is more susceptible to electronic influence from the phosphine ligand. In contrast, although the hypothesis holds for the tosylate substrate, the opposite trend is seen for the chloride substrate. While the tosylate substrate shows the expected negative  $\rho$  value, the chloride substrate appears to have a positive  $\rho$  value. Though these results are only preliminary due to the small number of data points, it appears that the electronics of a Ni/ArPMe<sub>2</sub> catalyst may influence the rate of oxidation of these two substrates in opposite ways.

The differences between these two Hammett plots can be rationalized by considering that oxidative addition involves at least two elementary steps (*Figure 27*). The first step of an oxidative addition is an initial close association of aryl substrate to nickel complex. This close-association occurs when  $\pi$  electrons of the aryl ring donate into nickel (Ni acts as an electrophile). The acceptance of these  $\pi$  electrons by nickel is supported by the ability of its associated ligand(s) to accept  $\pi$  backbonding. The nickel catalyst can then ring walk around the aryl until it is close to the C—X bond. In the next step, the catalyst acts as a nucleophile and inserts into the C—X bond.

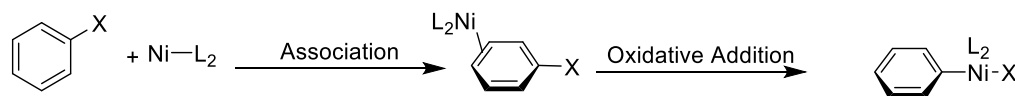


Figure 26. Representation of oxidative addition separated into two distinct steps

Each of these two steps in oxidative addition can be influenced by the ligands around a transition metal catalyst. Metal-to-ligand  $\pi$  backbonding takes place during the initial association established between an arene and the catalyst. A ligand's ability to accept  $\pi$ -backbonding will influence how quickly this association is established. In contrast, the  $\sigma$ -donating ability of a ligand comes into effect when the catalyst begins acting as a nucleophile. The ligand's ability to donate electron density towards the nucleophilic catalyst will influence how fast the metal can be oxidized during insertion into a heteroatom bond. The presence of electron withdrawing groups should decrease the  $\sigma$ -donating ability of the phosphine, and therefore potentially slow down the rate of insertion of the metal into C—X.<sup>11</sup> However, electron-withdrawing groups lower the

energy levels of the  $\pi^*$  orbitals on phosphine ligands, which facilitates metal-to-ligand backbonding.<sup>11</sup> This increased backbonding ability can stabilize and accelerate the rate of formation of metal/arene  $\pi$  complexes.<sup>12</sup>

The data show that oxidative addition of a Ni/ArPMe<sub>2</sub> complex into C—OTs is most strongly accelerated by the presence of electron donating groups attached to the aryl ring. This is most likely due to the stronger  $\sigma$  donation of the catalyst which imparts greater electron density around nickel, facilitating insertion of nickel into the C—OTs bond. For oxidative addition to C—Cl, we instead see that electron-withdrawing groups on the arylphosphine are better at accelerating the reaction than electron-donating groups. This may signify that, for aryl chlorides, the rate-limiting step of oxidative addition at Ni/PArMe<sub>2</sub> is coordination between the arene  $\pi$  system and nickel.

A second, but related, interpretation of the Hammett plot results is that both plots reflect a change in the mechanism (a change in the rate determining step) when ligand electronics are varied. The (*Figures 25 and 26*). This could be interpreted to mean that, for both substrates,  $\pi$  complexation is rate-determining. However, as described above, the reaction rate with the tosylate substrate is more strongly accelerated with **4-OMe** and **4-Me** (more electron-rich ligands), while the rate of reaction of the aryl chloride is more strongly accelerated with **3-OMe** (more electron-deficient ligand).

It bears repeating that there are not yet enough points on either Hammett plot of *Figures 25 or 26* to make firm conclusions. An alternative interpretation of the preliminary data could be that both plots reflect a change in mechanism when ligand electronics are varied, since the reactions of both substrates using both **4-OMe** and **3-**

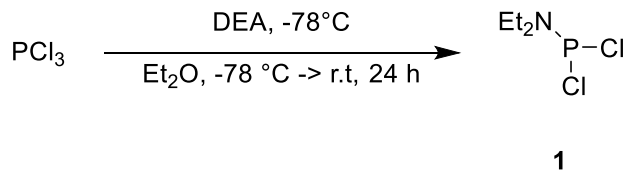
**OMe** are at least slightly faster than the corresponding reactions with  $\text{PPhMe}_2$ . Future work on this project should aim to add more data points to both Hammett plots. These additional data points will be useful for gathering more solid evidence as to the effect of  $\text{PArMe}_2$  electronics on the rate of oxidative addition of aryl electrophiles at  $\text{Ni}^0$ .

## EXPERIMENTAL METHODOLOGY

One of the primary difficulties in handling catalytically reactive phosphines is their susceptibility to oxidation. Unless otherwise noted, reactions were carried out under Argon using Schlenk technique. NMR spectra were acquired on a Bruker 500 MHz instrument.

Synthesis of Phosphine-Borane Precursors

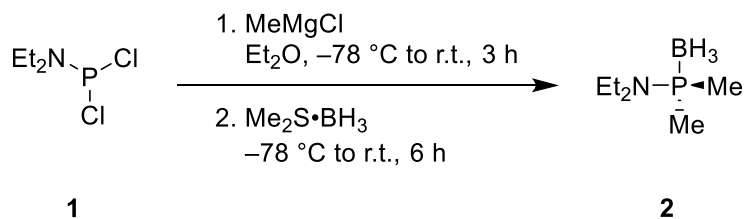
The synthesis of aryldimethylphosphine-borane complexes was adapted from prior phosphine ligand syntheses methodologies.<sup>7</sup>

Synthesis of Dichloro(bisethylammino)phosphine

A 500 L dried round-bottomed flask equipped with a magnetic teflon-coated stir bar was brought into a N<sub>2</sub>-filled glovebox. To this flask was added Et<sub>2</sub>O (250 mL). The flask was removed from the glovebox and connected to an Ar-equipped Schlenk line. The flask was charged with PCl<sub>3</sub> (11.805 g, 86.04 mmol, 1 equiv) and cooled to -78 °C. To this flask was then added diethylamine that had previously been purged with Ar (12.57 g, 172 mmol, 2 equiv) dropwise. The reaction mixture was allowed to stir and warm to

room temperature over a period of 18 hours. The flask was then brought into a N<sub>2</sub>-filled glovebox, where the white precipitate was removed with a frit and washed with 3 x 50 mL Et<sub>2</sub>O into a 500mL Schlenk flask. The Schlenk flask was removed from the glovebox, and the solvent was removed under vacuum on the Schlenk line to give the crude product as a yellow oil. The Schlenk flask was brought back into glovebox, and the crude product was transferred to a 50 mL Schlenk flask with small amounts of Et<sub>2</sub>O. The 50 mL Schlenk flask was again brought out of glovebox, and the solvent was removed under vacuum. The flask was then attached to an Ar-purged, oven-dried short path distillation apparatus, and the product was purified by distillation under vacuum (300 micron, 79 °C) to yield product **1** as a clear oil (11.58 g, 77.3%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 3.34 (dq, J = 13.9 Hz, 4H), 1.15 (t, J = 7.2 Hz, 6H); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>, δ): 162.7; <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>, δ): 41.7 (d, J<sub>CP</sub> = 22.9 Hz), 14.1 (d, J<sub>CP</sub> = 5.0 Hz).

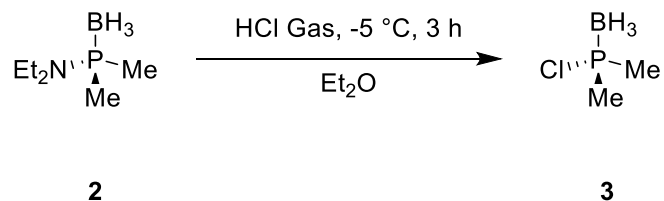
Synthesis of P, P-Dimethyl(bisethylammino)phosphine-borane



A 250 L dried 3-necked round-bottomed flask was equipped with a magnetic teflon-coated stir bar, a -78 °C cold finger (center), and a 100 mL pressure equalizing addition funnel (right) was charged with magnesium turnings (6.95 g, 285.6 mmol, 2 equiv) and fitted with a rubber septum. The flask was purged with Argon, and Et<sub>2</sub>O (180 mL) was subsequently added. Chloromethane gas was added dropwise through a syringe inlet over a period of 4 h while maintaining gentle reflux until ~95% of the magnesium metal had been consumed. The Grignard reagent was cooled to 0 °C followed by the addition of dichlorobis(diethylamino)phosphine **1** (25 g, 142.83 mmol, 1 equiv) in Et<sub>2</sub>O (43 mL) dropwise from a constant rate addition funnel over a 3 h period. The resulting suspension was warmed to ambient temperature and stirred for an additional 4 h. The reaction mixture was cooled to -78 °C and borane-methyl sulfide complex (0.801g/mL, 12.216 mL, 135.6 mol, 0.95 equiv) was added dropwise from the constant rate addition funnel over a 30 min period. The suspension was warmed to ambient temperature and stirred overnight. The grey precipitate was filtered and washed with 3 x 150 mL portions of anhydrous Et<sub>2</sub>O through a 100 mL frit. the organic layers were combined and concentrated in vacuo. The resulting orange suspension was filtered through a pad of

florisil (benzene for elution). The yellow solution was concentrated in vacuo and the residue was purified by fractional distillation (61 °C, 300 micron) to provide product **2** (16.359 g, 78%%) as a colorless oil. Spectral data consistent with those previously reported<sup>7</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 3.05 (dq, J<sub>PH</sub> = 10.9 Hz, J<sub>HH</sub> = 7.1 Hz, 4H), 1.36 (d, J = 9.3 Hz, 6H), 1.08 (t, J = 6.9 Hz, 6H), 0.57 (qd, J<sub>BH</sub> = 93.5, J<sub>PH</sub> = 14.7 Hz, 3H); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>, δ): 59.5 (q, J = 74.2); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>, δ): 40.2 (d, J<sub>CP</sub> = 3.1 Hz), 15.0, 14.6 (d, J<sub>CP</sub> = 8.3 Hz), 14.5 (d, J<sub>CB</sub> = 1.7 Hz).

#### Synthesis of Chlorodimethylphosphine-borane



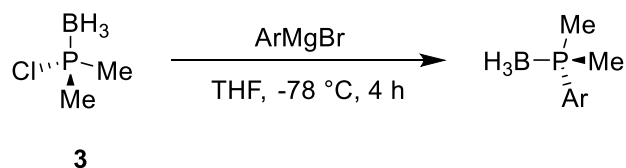
A dried 50 mL round-bottom flask equipped with a magnetic teflon-coated stir bar was fitted with a rubber septum and purged with Argon. The flask was charged with Et<sub>2</sub>O (25 mL), cooled to 0 °C and then tarred. Hydrogen chloride gas (2.18 g, 60 mmol, 2 equiv) was dissolved into the tarred flask of Et<sub>2</sub>O at 0 °C until the necessary mass was injected. The resulting solution was cooled to -78 °C and dimethyl(bisethylammino)phosphine-borane **2** (4.41 g, 30 mmol, 1 equiv) was added dropwise via syringe. Once the addition was complete the reaction mixture was stirred for 3 h at 0 °C. The precipitate was filtered and washed with anhydrous Et<sub>2</sub>O (3 x 20 mL) through a 60 mL frit. The organic layers were combined and concentrated with vacuo.

The residue was purified by flash vacuum distillation (300 micron) to provide product **3** (2.74 g, 83%) as a clear oil. Spectral data consistent with those previously reported<sup>7</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 1.92 (d, J = 8.41 Hz, 6H), 0.92 (qd, J<sub>BH</sub> = 98.92 Hz, J<sub>PH</sub> = 10.34 Hz, 3H); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>, δ): 102.8 (q, J = 43.2); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>, δ): 19.9 (d, J<sub>CP</sub> = 28.1 Hz).

### Synthesis of Aryldimethylphosphines

The decomplexation of aryldimethylphosphine ligands was adapted from prior phosphine ligand synthetic methodologies.<sup>8</sup>

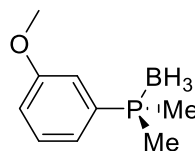
### General Procedure for the Synthesis of Aryldimethylphosphine



A dried 100 mL round-bottom flask equipped with a magnetic teflon-coated stir bar was fitted with a rubber septum and purged with Argon. Flask was charged with chlorodimethylphosphine-borane **3** (6.5 mmol, 1 equiv) and anhydrous THF (25mL). A separate 50 mL round-bottom flask was equipped with a magnetic teflon-coated spinbar, water-cooled condenser, and purged with Ar. To this flask was added Mg turnings (0.36 g, 15 mmol), anhydrous THF (15 mL), and a crystal of iodine. This solution was allowed

to stir for 30 min to activate Mg. To this solution was added the corresponding Bromobenzene derivative (15 mmol) dropwise. Unless spontaneous, solution was heated with a heat gun until Grignard reagent began to form. Grignard was allowed to form over a period of 2 h, or until Mg was ~95% consumed. Original 100 mL reagent was cooled to -78 °C, and Grignard reagent was slowly added dropwise (9 mmol, 1.5 equiv). Solution was allowed to stir for 4 h while gradually warming up to room temperature. Once at room temperature, reaction was quenched with 50 mL ice water.

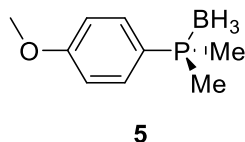
#### 3-methoxyaryldimethylphosphine-borane



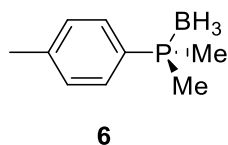
**4**

3-methoxyaryldimethylphosphine-borane was prepared according to the general procedure using 3-bromoanisole (2.7 g, 15 mmol) to create the Grignard reagent. The crude product was purified on a silica column using hexanes. Crude product was heated under vacuum to remove impurities and yield the product **4** as a cloudy oil (1.18 g, 94.5%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 7.41 (tod, J<sub>HH</sub> = 8.2, J<sub>PH</sub> = 3.0, 1H), 7.30 (m, 2H), 7.04 (d, J<sub>PH</sub> = 7.8 Hz, 1H), 3.87 (s, 3H), 1.58 (d, J = 10.4, 6H), 0.79 (qd, J<sub>BH</sub> = 94.1 Hz, J<sub>PH</sub> = 13.5 Hz, 3H); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>, δ): 3.6 (q, J = 58); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>, δ): 159.7 (d, J<sub>CP</sub> = 12.3 Hz), 132.6, 132.2, 130.1 (d, J<sub>CP</sub> = 11.5

Hz), 122.8 ( $J_{\text{CP}} = 8.7$  Hz), 116.7 (d,  $J_{\text{BC}} = 2.3$  Hz), 116.6 (d,  $J_{\text{CP}} = 11.6$  Hz), 55.4, 13.1 (d,  $J_{\text{CP}} = 39$  Hz).

4-methoxyaryldimethylphosphine-borane

4-methoxyaryldimethylphosphine-borane was prepared according to the general procedure using 4-methoxybromobenzene (2.7 g, 15 mmol) to create the Grignard reagent. The crude product was purified on a silica column using a 90:10 hexanes/EtoAc solution to yield product **5** as a colorless oil (0.343 g, 36%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.68 (dd  $J_{\text{HH}} = 9.6$  Hz,  $J_{\text{PH}} = 4.8$  Hz,  $J_{\text{BH}} = 2.7$  Hz, 2H), 7.00 (dd,  $J_{\text{HH}} = 4.0$  Hz,  $J = 1.8$  Hz, 2H), 3.87 (s, 3H), 1.56 (d,  $J = 10.4$ , 6H), 0.77 (qd,  $J_{\text{CB}} = 94.3$  Hz,  $J_{\text{CP}} = 13.9$  Hz 3H);  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.98 (q,  $J = 59.6$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 162.1 (d,  $J_{\text{CP}} = 2.2$  Hz), 132.7 (d,  $J_{\text{CP}} = 10.8$ ), 121.9, 121.4, 114.5 (d,  $J_{\text{CP}} = 10.9$  Hz), 55.4, 13.4 (d,  $J_{\text{CP}} = 39.5$  Hz).

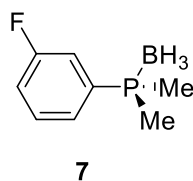
4-methylaryldimethylphosphine-borane

4-tolylaryldimethylphosphine-borane was prepared according to the general procedure using 4-bromotoluene (2.57 g, 15 mmol) to create the Grignard reagent. The

crude product was purified on a silica column using a 90:10 hexanes/EtoAc solution.

Crude product was heated under vacuum to remove impurities and yield the product 6 as cloudy oil (.479 g, 47.4%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.63 (dod,  $J_{\text{HH}} = 10.9$ ,  $J_{\text{PH}} = 8.0$  Hz, 2H), 7.29 (d,  $J_{\text{HH}} = 7.9$  Hz, 2H), 2.39 (s, 3H), 1.57 (d,  $J = 10.6$  Hz, 6H), 0.77 (qd,  $J_{\text{BH}} = 94.8$  Hz,  $J_{\text{PH}} = 15.0$  Hz, 3H);  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ): 1.8 (q,  $J = 60.2$  Hz, 1P);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 141.7 (d,  $J_{\text{CP}} = 2.0$  Hz), 130.9 (d,  $J_{\text{CP}} = 9.8$  Hz), 129.6 (d,  $J_{\text{CP}} = 10.4$  Hz), 127.7, 127.3, 21.5, 13.3 (d,  $J_{\text{CP}} = 39.1$  Hz).

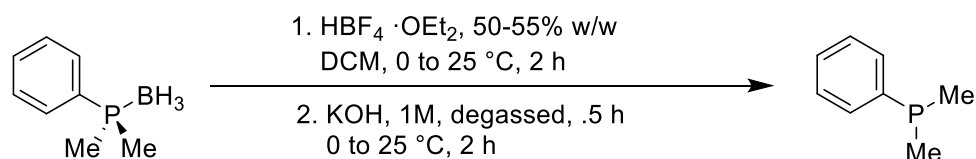
### 3-fluoroaryldimethylphosphine-borane



3-fluoroaryldimethylphosphine-borane was prepared according to the general procedure using 3-bromo-4-fluorobenzene (2.63 g, 15 mmol) to create the Grignard reagent. The crude product was purified on a silica column using a 50:50 hexanes/EtoAc solution. Colorless oil was treated with heat under vacuum to remove impurities to yield **7** as colorless oil (0.259 g, 17%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.49 (m, 3H), 7.21 (t,  $J_{\text{PH}} = 8.37$  Hz, 1H), 1.59 (d,  $J = 10.4$  Hz, 6H), 0.78 (qd,  $J_{\text{BH}} = 95.4$  Hz,  $J_{\text{PH}} = 14.7$  Hz, 3H);  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 4.37 (q,  $J = 58.3$ ),  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 163.7 (d,  $J_{\text{CP}} = 13.5$  Hz), 161.7 (d,  $J_{\text{CP}} = 13.1$  Hz), 134.0 (d,  $J_{\text{CP}} = 6.3$  Hz), 133.7 (d,  $J_{\text{CP}} = 6.31$  Hz), 130.8 (dot,  $J_{\text{CP}} = 9.0$  Hz,  $J_{\text{CF}} = 3.61$  Hz), 126.6 (dod,  $J_{\text{CP}} = 8.6$

Hz,  $J_{\text{CF}} = 2.9$  Hz), 118.5 (dod,  $J_{\text{CP}} = 21.0$  Hz,  $J_{\text{CF}} = 2.1$  Hz), 117.9 (dod,  $J_{\text{CP}} = 22.6$  Hz,  $J_{\text{CF}} = 10.7$  Hz), 12.9 (d,  $J_{\text{CP}} = 36.4$  Hz).

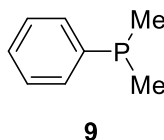
General Procedure for the synthesis of Aryldimethylphosphine-boranes



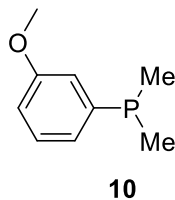
Three dried 100 mL conical-bottom flasks, a dried 100 mL round-bottom flask, and a dried 250 mL round-bottom flask equipped with magnetic teflon-coated stir bars were taken into an  $\text{N}_2$  glovebox. The first conical flask was charged with corresponding aryl dimethylphosphine-borane (1 equiv) and 25 mL DCM. The second conical flask was sealed with septa, the third charged with ~4g oven-dried  $\text{NaSO}_4$  and sealed with septa. The 100 mL round-bottom flask was charged with 90 mL DCM, and the 250 mL round-bottom flask was sealed with a septum. All four flasks were removed from glovebox. To the phosphine-containing flask was added tetrafluoroboric acid diethyl ether complex (1.19 g/mL, 4.47 mL, 16.45 mmol, 5 equiv) at 0 °C with Schlenk technique. This solution was allowed to stir for 2 h, taking a small aliquot and analyzing  $^{31}\text{P}$  NMR to check for the presence of phosphine-borane complex. Once full disappearance of phosphine-borane confirmed, to this flask was added degassed KOH solution (1 M, 20 mmol, ~6 equiv) at 0 °C. Solution was allowed to stir for 30 min. The organic layer was transferred via cannula to second conical flask. The remaining aqueous solution washed with 3 x 10 mL

degassed DCM and transferred to second conical flask. To this second conical flask was added degassed KOH solution (1 M, 5 mmol, ~1 equiv). This solution was allowed to stir for an additional 30 mins. Aqueous layer transferred via cannula to third conical flask containing oven-dried NaSO<sub>4</sub>. Second aqueous phase again washed with 3 x 10 mL degassed DCM and transferred to the third conical flask containing oven-dried NaSO<sub>4</sub>. This solution was allowed to stir for 1 h, and then was cannula transferred the sealed 250 mL round-bottom flask. The flask with NaSO<sub>4</sub> was washed with 3 x 10 mL degassed DCM, which was transferred to the 250 mL round-bottom flask. The 250 mL round-bottom flask was transferred to N<sub>2</sub> Glovebox, and solvent was removed under vacuum to yield cloudy oil. Flask was rinsed with DCM and solution was filtered through a plug of celite into a storage vial.

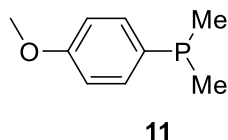
#### Phenyldimethylphosphine



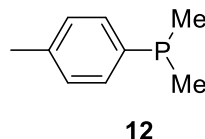
Aryldimethylphosphine was prepared according to the general procedure using phenyldimethylphosphine-borane from commercial phenyldimethylphosphine (514.2 mg, 3.38 mmol, 1 equiv). Solvent removed with vacuo to yield product 9 as a slightly cloudy oil (0.106 g, 22.7%). Spectral data are consistent with those previously reported.<sup>13</sup>

3-methoxyaryldimethylphosphine

3-methoxyaryldimethylphosphine was prepared according to the general procedure using 3-methoxyaryldimethylphosphine-borane (599.0 mg, 3.29 mmol, 1 equiv). Solvent removed with vacuo to yield product **10** as a cloudy slightly yellow oil (0.401 g, 72.4%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.29 (t,  $J_{\text{HH}} = 4.2$  Hz, 1H), 7.06 (t,  $J_{\text{HH}} = 7.18$  Hz, 1H), 7.02 (d,  $J_{\text{HH}} = 7.6$  Hz, 1H), 7.84 (dd,  $J_{\text{PH}} = 8.2$  Hz,  $J_{\text{HH}} = 2.6$  Hz,  $J_{\text{HH}} = 0.7$  Hz, 1H), 3.85 (s, 3H), 1.35 (d,  $J_{\text{PH}} = 2.7$  Hz, 6H);  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): -44.4;  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 159.4 (d,  $J_{\text{CP}} = 7.0$  Hz), 144.3 (d,  $J_{\text{CP}} = 14.0$  Hz), 129.4 (d,  $J_{\text{CP}} = 7.0$  Hz), 122.7 (d,  $J_{\text{CP}} = 16.8$  Hz), 116.2 (d,  $J_{\text{CP}} = 18.1$  Hz), 113.3, 55.2, 14.5 (d,  $J_{\text{CP}} = 12.6$  Hz).

4-methoxyaryldimethylphosphine

4-methoxyaryldimethylphosphine was prepared according to the general procedure using 4-methoxyaryldimethylphosphine-borane (343.1 mg, 1.89 mmol, 1 equiv). Solvent removed via vacuum to yield product **11** as a mild green cloudy oil (113.56 mg, 0.675 mmol, 36%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.4 (t,  $J_{\text{HH}} = 7.8$  Hz, 2H), 6.9 (d,  $J_{\text{HH}} = 6.7$  Hz, 2H), 3.84 (s, 3H), 1.30 (d,  $J_{\text{PH}} = 2.5$  Hz, 6H);  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): -47.6;  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 159.9, 132.8 (d,  $J_{\text{CP}} = 10.7$  Hz), 132.3 (d,  $J_{\text{CP}} = 19.7$  Hz), 114.0 (d,  $J_{\text{CP}} = 7.3$  Hz), 65.9, 55.2, 53.4, 15.2, 15.1 (d,  $J_{\text{CP}} = 12.0$  Hz).

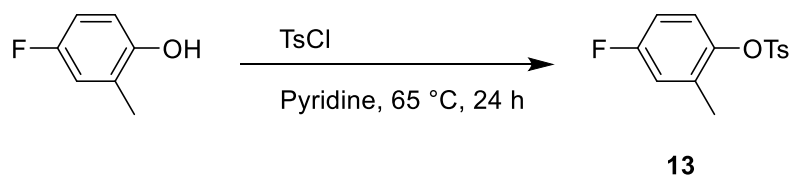
4-methylaryldimethylphosphine

4-methylaryldimethylphosphine was prepared according to the general procedure using 4-methylaryldimethylphosphine-borane (478.7 mg, 2.88 mmol, 1 equiv). Colorless oil was treated with heat under vacuum to remove impurities and yield **12** as colorless oil

yield product **12** as a clear oil (48.2 mg, 0.317 mmol, 11%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.38 (t,  $J_{\text{HH}} = 7.3$  Hz, 2H), 7.18 (d,  $J_{\text{HH}} = 7.7$  Hz, 2H), 2.35 (s, 3H), 1.32 (s, 6H);  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): -46.53;  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 138.1, 130.7 (d,  $J_{\text{CP}} = 16.8$  Hz), 129.2 (d,  $J_{\text{CP}} = 5.6$  Hz), 129.0, 128.2, 125.3.

### Synthesis of Additional Compounds

#### Synthesis of Tosylate Substrate

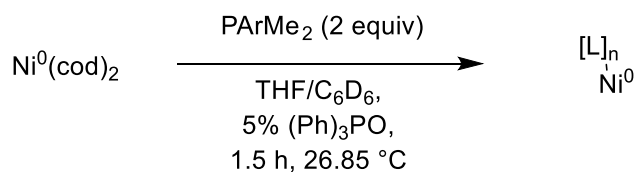


To a 500 mL round-bottom flask was added tosyl chloride (4.772 g, 25.02 mmol, 1.8 equiv) and 4-fluoro-2-tolylphenol (7.750 g, 13.88 mmol, 1 equiv) along with 250 mL pyridine and a Teflon-coated stir bar. Solution was allowed to stir for 24 h at 65 °C. To this solution was added 150 mL  $\text{dH}_2\text{O}$ , and the organic product was extracted with hexanes using a separatory funnel. Solvent removed in vacuo to yield crude product as a white crystalline solid. Solid was recrystallized with 2/1 Hexanes/EtoAc. NMR consistent with prior spectra.<sup>14</sup>

### Kinetic Analysis Conditions

The development of these conditions for testing ligand kinetics were developed with consideration to the conditions used in Sproules *et al.*<sup>9</sup> Unless otherwise noted, experimental set up was completed within an N<sub>2</sub> glovebox. NMR scans were performed on a Bruker 500 MHz NMR using Bruker Topspin software for data processing.

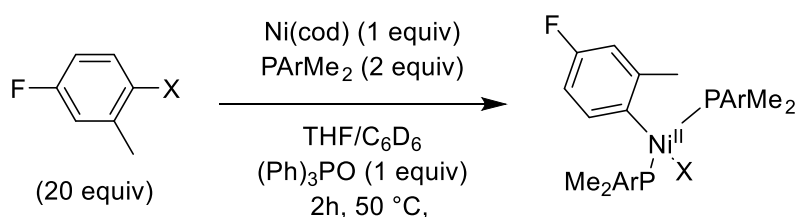
### General Procedure for Determining Ligand Equilibrium



Within an N<sub>2</sub> glovebox, Ni(cod)<sub>2</sub> (5.5 mg, 0.02 mmol, 1 equiv) and the Aryldimethylphosphphine (0.04 mmol, 2 equiv) were placed in separate vials. To the phopshine vial was added 600 uL THF and 100 uL C<sub>6</sub>D<sub>6</sub>. These vials were sealed with septa and were removed from the glovebox along with a septa-sealed NMR tube containing a sealed capillary with triphenylphosphine oxide internal standard (5.57 mg, 0.02 mmol, 1 equiv). In the NMR room, the phosphine solution was injected into the nickel-containing vial with a degassed syringe. Solution was allowed to mix for 1.5 min to allow nickel to dissolve into solution. Using manual experimental preparation, the NMR tube was inserted into the NMR and manual tuning procedures were applied (solvent lock/tune/shimming) to obtain an initial scan. NMR experiment was then started, and scans were taken for 1 h. Results interpreted based on appearance of different

phosphine signals over time representing nickel-phosphine complexes, such as in *Figure 21*. For each applicable ligand, equilibrium of species was reached at approximately 30 min of reaction time.

#### General procedure for Kinetic Analysis of Ligands



Within an  $\text{N}_2$  glovebox,  $\text{Ni(cod)}_2$  (5.5 mg, 0.02 mmol, 1 equiv) and the Aryldimethylphosphine (0.04 mmol, 2 equiv) were combined in a vial with 600  $\mu\text{L}$  THF and 100  $\mu\text{L}$   $\text{C}_6\text{D}_6$  and allowed to stir according to previously established equilibrium time to pre-mix the metal and ligand. In a separate vial, substrate (20 equiv) was dissolved into 200  $\mu\text{L}$  THF, and then taken up into 1 mL syringe which was then inserted into a septum sealed round bottom flask. 10 min prior to established equilibrium point, nickel-phosphine solution was injected into NMR tube containing a sealed capillary tube with triphenylphosphine oxide (5.57 mg, 0.02 mmol, 1 equiv) internal standard and sealed with an NMR tube septum. Both NMR tube, and syringe-flask were removed from the glovebox and taken into the NMR room. Using manual experimental preparation, the NMR tube was inserted into the NMR and manual tuning procedures were applied (solvent lock/tune/shimming) to obtain an initial scan. At the equilibrium mark of 29 min,

probe temperature was adjusted to 323.1 K (50 °C) and the tube was ejected from the NMR probe. At the 30 min mark, substrate was injected into the NMR tube, which was inverted once and inserted back into the NMR. At 31 min,  $^{31}\text{P}$  NMR experiment begun using previously optimized parameters (16 scans,  $d_0$ , etc.) to reduce the time between spectra to 1:02 min. In total, experiments ran for 1.5 and the appearance of phosphine signals at approximately 3.10, -9.10. and -10.13 ppm were identified based on previous scans during nickel-phosphine equilibrium determination.

Kinetic Analysis of Tosylate Substrate Oxidative Addition Kinetic analysis was prepared according to the general procedure, and the addition of tosylate substrate **12** (112.12 mg, 0.4 mmol, 20 equiv) from stock solution immediately before data collection.

Kinetic Analysis of Chloride Substrate Oxidative Addition Kinetic analysis was prepared according to the general procedure, and the addition of chloride substrate (57.8 mg, 0.4 mmol, 20 equiv) from stock solution immediately before data collection.

#### General Procedure for the Calculation of Rate Constants

To analyze the kinetics of oxidative addition for these nickel-ligand catalysts, the  $^{31}\text{P}$  NMR signals are analyzed over time as adapted from Sproules *et al.*<sup>9</sup> The natural log of signal change over time for a pseudo first-order reaction will produce a straight line<sup>2</sup>. The slope of this line represents the rate constant of a reaction and allows us to identify a species that is displaying a pseudo first-order rate reaction as described in *Section 2.4*. By

converting integration signals to  $\text{Ms}^{-1}$  based on the internal standard (having contained 0.02 mmol of triphenylphosphine oxide), the rate of change over time for individual phosphine signals can be calculated. As shown in *Figure 22*, there are multiple phosphine signals in each spectra, by calculating the natural log of these signals over time, the signal at  $\sim 3.10$  ppm displays a linear trend.

Shown in *Figure 23*, the natural log of a particular species' signal over time reveals a linear segment most likely identified as the catalytically active nickel-phosphine complex. The slope of this linear segment is calculated at -0.0004 as  $-k$ , producing a rate constant for this trial of  $1.93443\text{E-}06 \text{ M}\cdot\text{s}^{-1}$  from the signal of the internal standard. For compounds **4-OMe**, **4-Me**, **3-OMe**, and commercially-sourced  $\text{ArPMe}_2$ ; triplicate kinetic analyses were performed for both tosylate substrate **12** and commercially available chloride substrate with the calculated rate constants for these trials shown in *Table 3*.

## 4. REFERENCES CITED

- (1) Garg, N. K.; Percec, V.; Rosen, B. M.; Wilson, D. A.; Quasdorf, K. W.; Resmerita, A.-M.; Zhang, N. *Chem. Rev.* **2010**, *111* (3), 1346–1416.
- (2) Anslyn, E. V.; Dougherty, D. A. *Modern physical organic chemistry*; University Science, 2006.
- (3) Dreher, S. D.; Terrett, N. K.; Alvarez, J. C.; Parmee, E. R.; Coleman, P. J.; Truppo, M. D.; Campos, K. R.; Garbaccio, R. M.; Tillyer, R. D. *Science* (80-. ). **2019**, 363 (6424), eaat0805.
- (4) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122* (17), 4020–4028.
- (5) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91* (2), 165–195.
- (6) Solomon, S. A.; Allen, L. K.; Dane, S. B. J.; Wright, D. S. *Eur. J. Inorg. Chem.* **2014**, *2014* (10), 1615–1619.
- (7) Heath, H. A. Synthesis of C2-symmetric P-chiral bis(phosphine borane)s and their application in rhodium(I) catalyzed asymmetric transformation, Montana State University, 2001.
- (8) Mckinstry, L.; Livinghouse, T. *Tetrahedron Lett.* **1994**, *35* (50), 9319–9322.
- (9) Bajo, S.; Laidlaw, G.; Kennedy, A. R.; Sproules, S.; Nelson, D. J. *Organometallics* **2017**, *36* (8), 1662–1672.
- (10) Russell, J. E. A.; Entz, E. D.; Joyce, I. M.; Neufeldt, S. R. *ACS Catal.* **2019**, 3304–3310.
- (11) Organometallic HyperTextBook: Phosphine Complexes  
<http://www.ilpi.com/organomet/phosphine.html> (accessed Jul 31, 2017).
- (12) Dunne, B. J.; Morris, R. B.; Orpen, A. G. *J. Chem. Soc. Dalt. Trans.* **1991**, 0 (S), 653.
- (13) Mika, L. T.; Orha, L.; Farkas, N.; Horváth, I. T. *Organometallics* **2009**, *28* (5), 1593–1596.
- (14) Hooker, L. V.; Neufeldt, S. R. *Tetrahedron* **2018**.

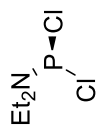
## APPENDICES

APPENDIX A

NMR SPECTRA OF SYNTHESIZED COMPOUNDS

Table 4. Acquisition parameters for qualitative NMR analysis of synthesized compounds

| <b>Parameter</b>      | <b><sup>1</sup>H</b> | <b><sup>31</sup>P</b> | <b><sup>13</sup>C</b> |
|-----------------------|----------------------|-----------------------|-----------------------|
| NS                    | 64                   | 16                    | 1024                  |
| AQ [Sec]              | 3.2767999            | 0.4019541             | 1.1010048             |
| Pulse Angle [deg]     | 30                   | 30                    | 30                    |
| SW [ppm]              | 19.9907              | 402.6030              | 236.5896              |
| O1P [ppm]             | 6.175                | -50.000               | 100.000               |
| Td                    | 65536                | 65536                 | 65536                 |
| ds                    | 2                    | 4                     | 4                     |
| D1 [sec]              | 2.0                  | 2.0                   | 2.0                   |
| CPDPRG                | ~                    | waltz16               | waltz16               |
| PULPROG               | Zg30                 | zgpg30                | zgpg30                |
| Powergated Decoupling | N                    | Y                     | Y                     |



1

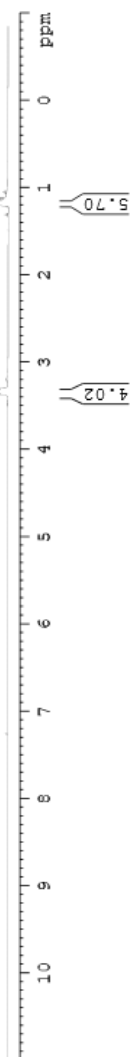
3.46  
3.38  
3.37  
3.36  
3.34  
3.33  
1.22  
1.21  
1.20

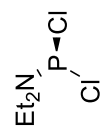


Current Data Parameters  
NAME 2-MJG-1921\_1H  
EXPNO 10  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20180706  
Time 8.48 h  
INSTRUM spect  
PROBHD Z125869.0055 (H30)  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 64  
DS 2  
SWH 7002.801 Hz  
FIDRES 0.213709 Hz  
AQ 4.6792703 sec  
RG 320.54  
LW 71.400 usec  
DE 16.00 usec  
TE 300.0 K  
D1 2.00000000 sec  
ID0 1  
SFO1 500.2330889 MHz  
NUC1 1H  
P1 12.00 usec  
PLW1 11.4468955 W

F2 - Processing parameters  
SI 65536  
SF 500.230123 MHz  
WDW EM  
SSB 0  
RB 0  
GB 0  
PC 1.00





1

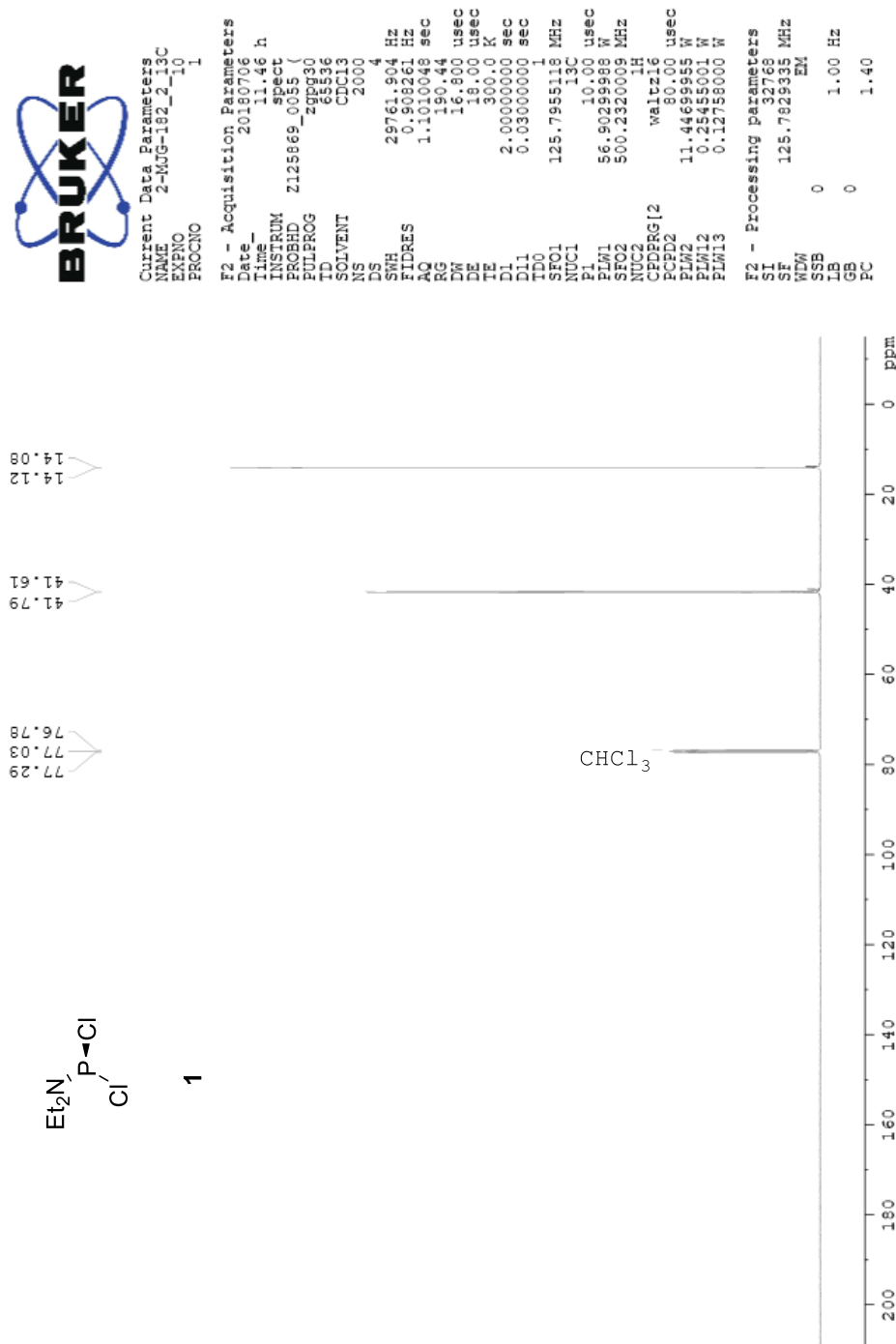
154.60  
154.42  
156.49  
160.09  
162.43

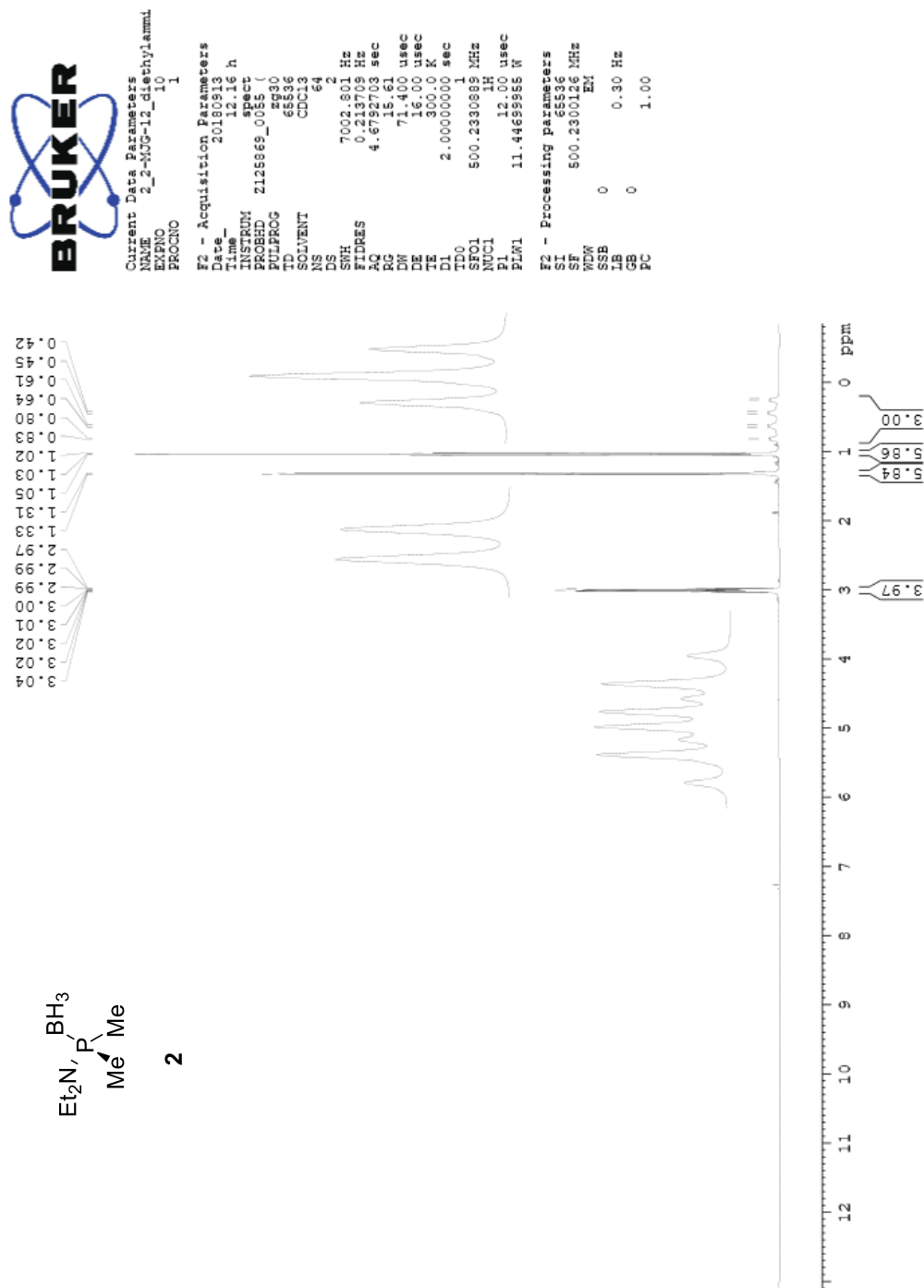


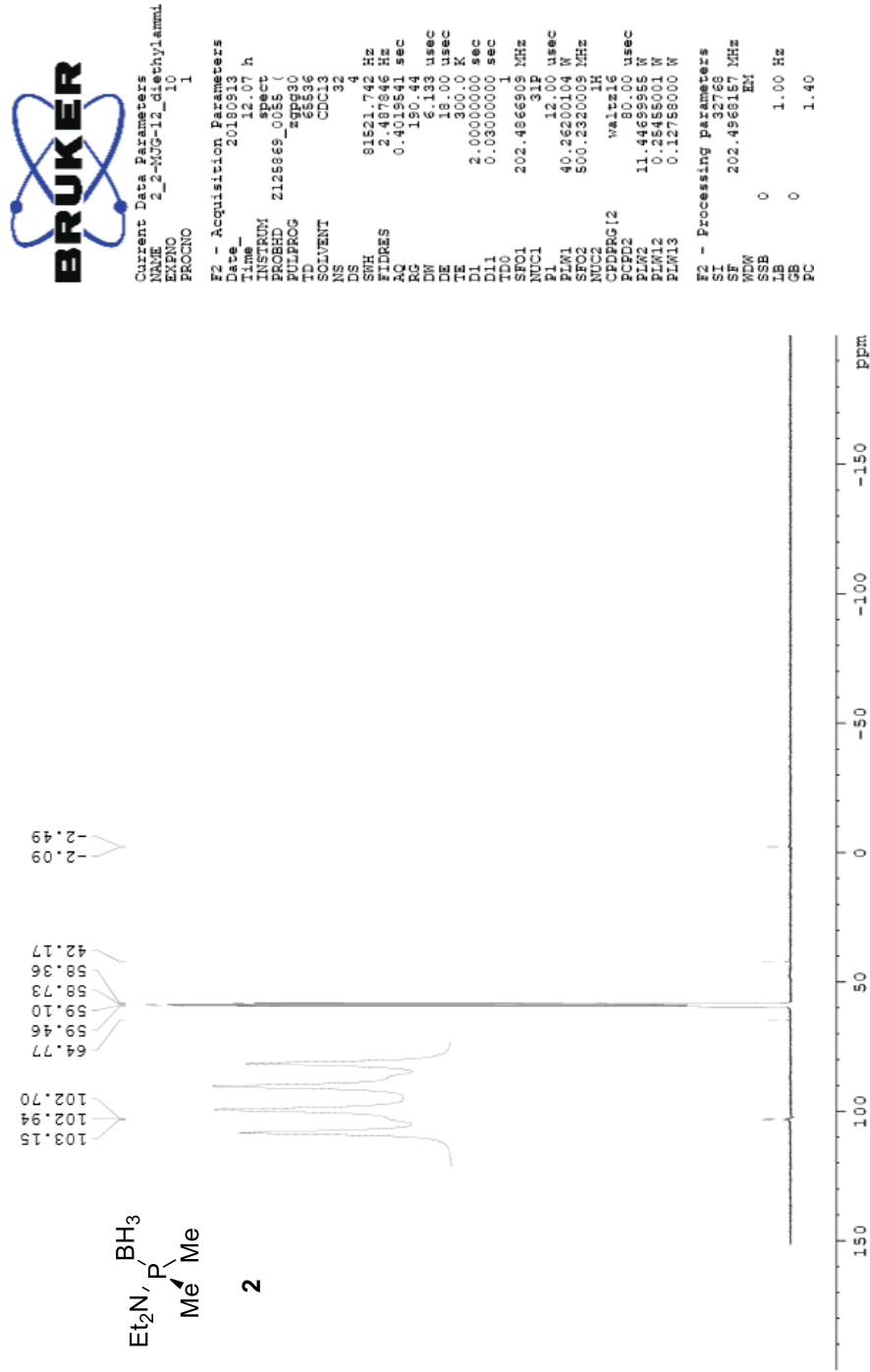
Current Data Parameters  
NAME 2-nujg-192-150ppm  
EXPNO 10  
PROCNO 1

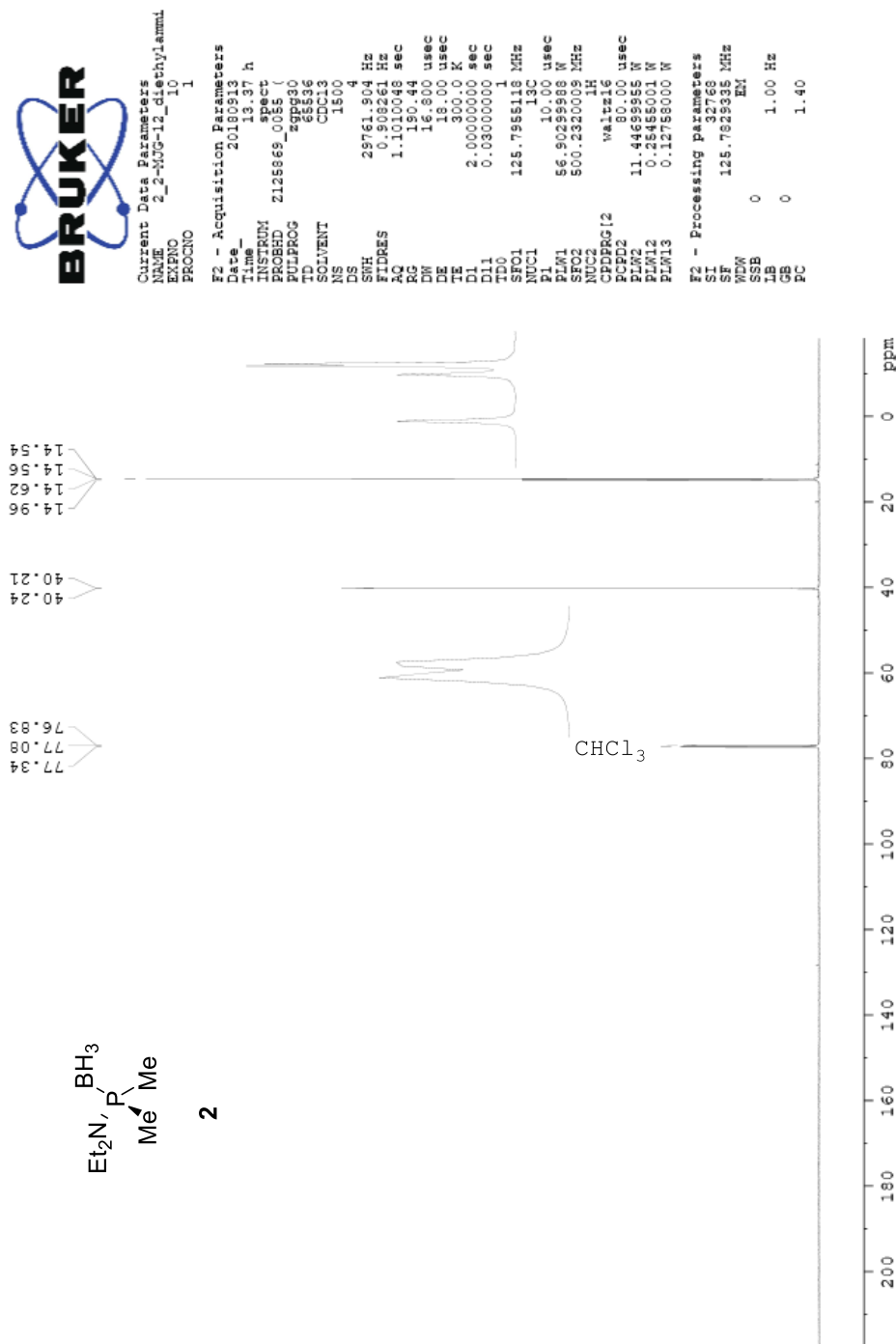
F2 - Acquisition Parameters  
Date\_ 20180701  
Time 13.40 h  
INSTRUM spect  
PROBHD Z125869.0085 (H30)  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 32  
DS 4  
SWH 81521.742 Hz  
FIDRES 2.467646 Hz  
AQ 0.4019541 sec  
RG 190.44  
LW 61.33 usec  
DE 18.00 usec  
TE 300.0 K  
D1 2.00000000 sec  
ID0 1  
SFO1 202.4968157 MHz  
NUC1 31P  
P1 12.00 usec  
PLW1 40.26200104 W  
F2 - Processing Parameters  
SI 32768  
SF 202.4968157 MHz  
WDW EM  
SSB 0  
RB 0  
GB 0  
PC 1.40

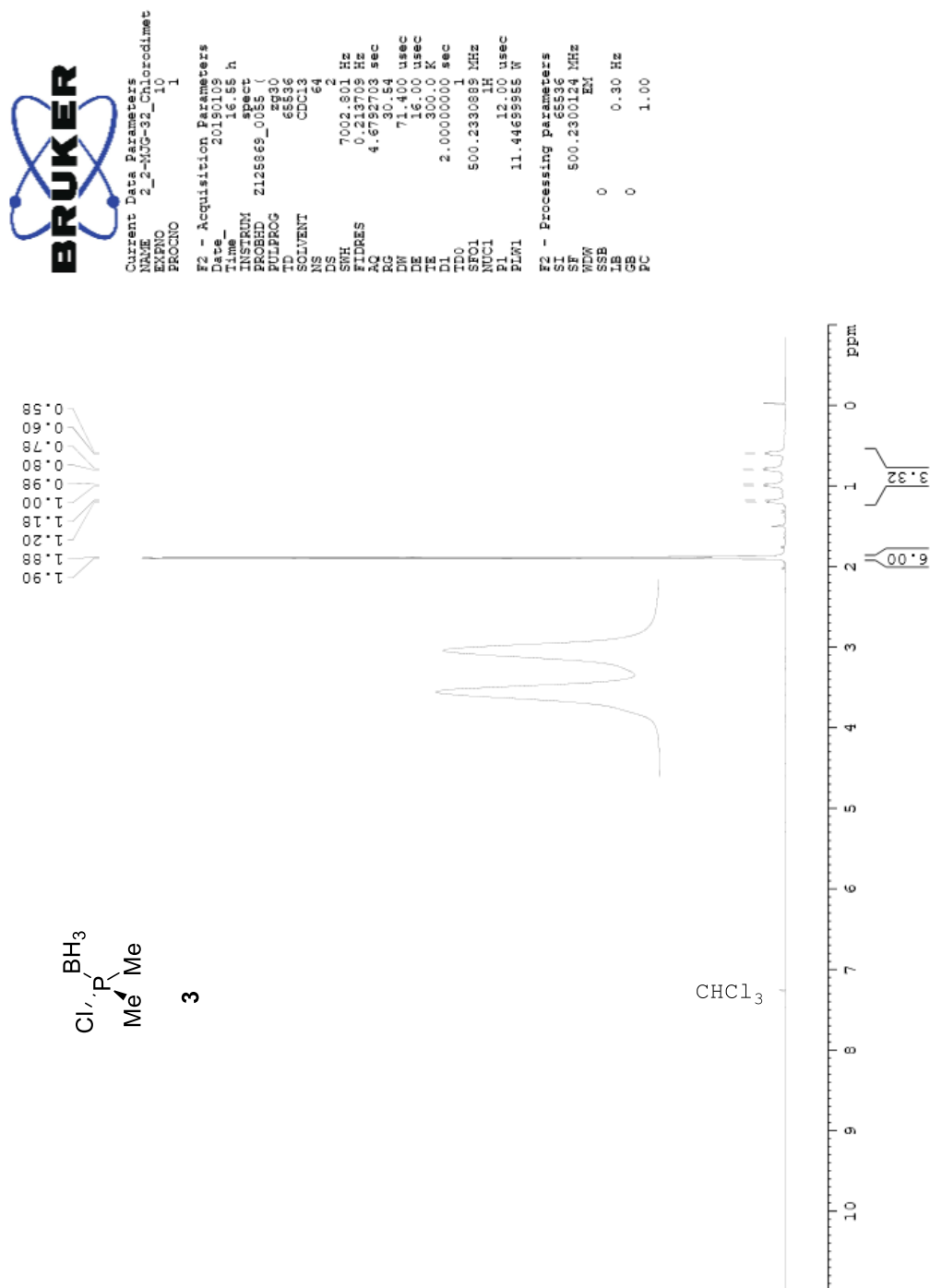


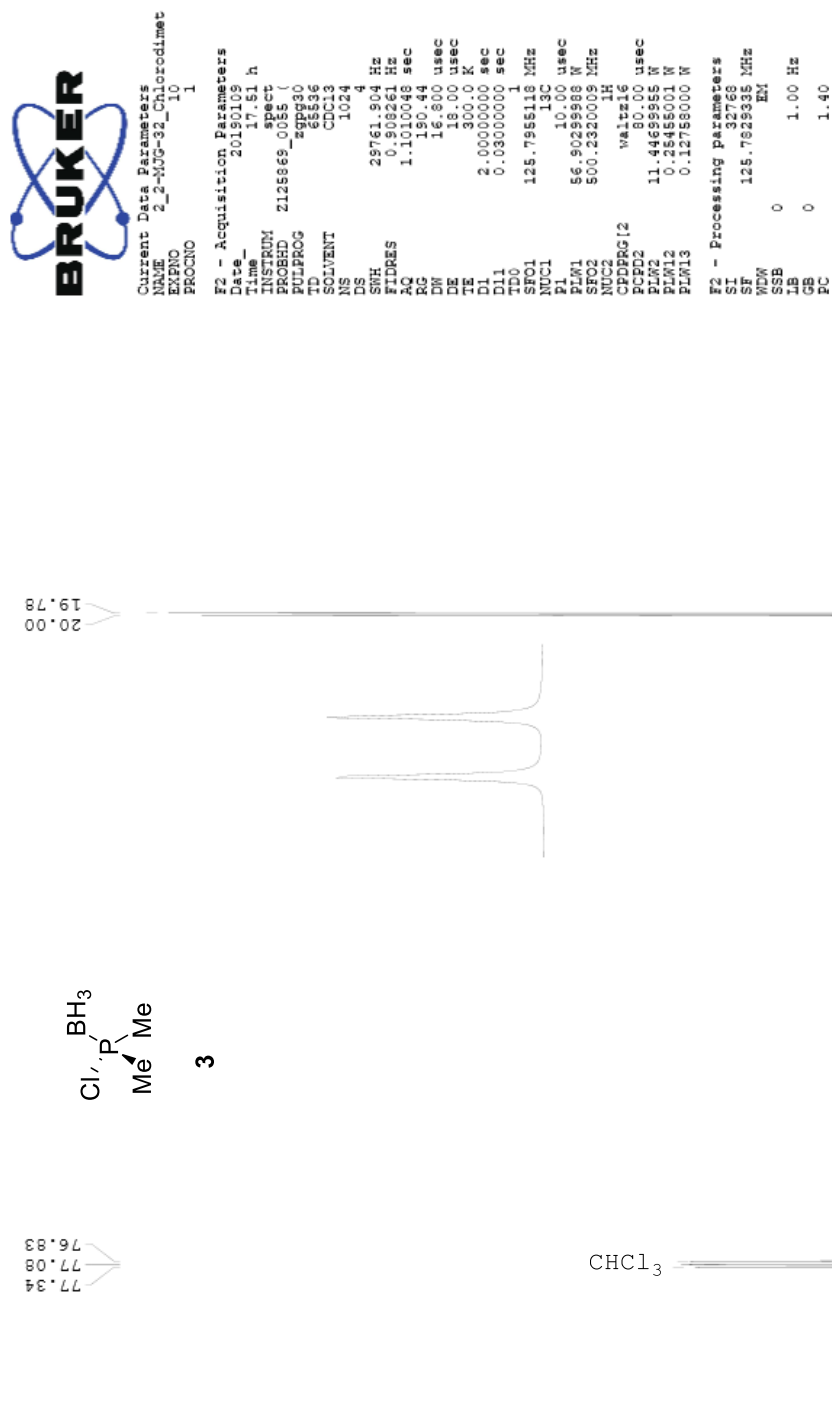


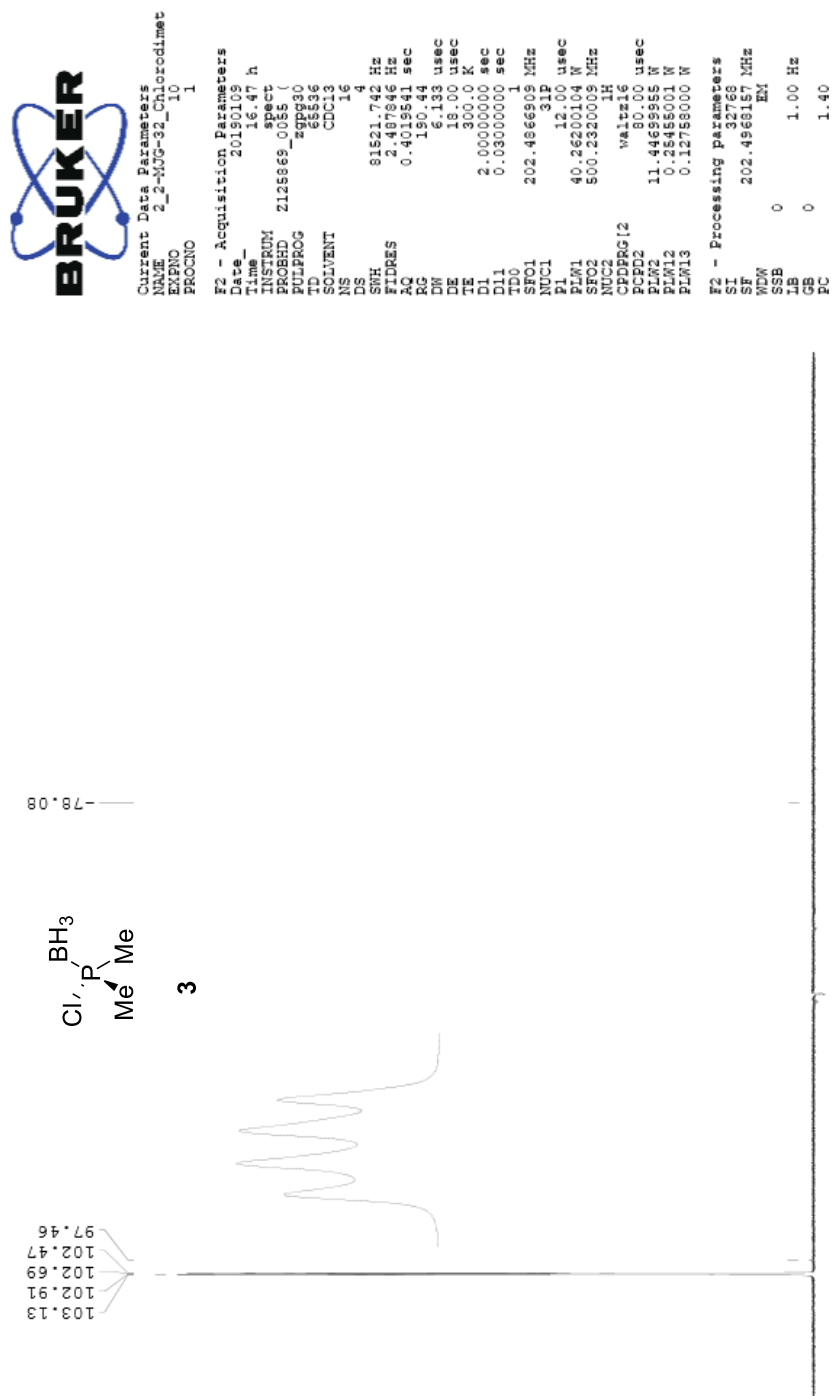


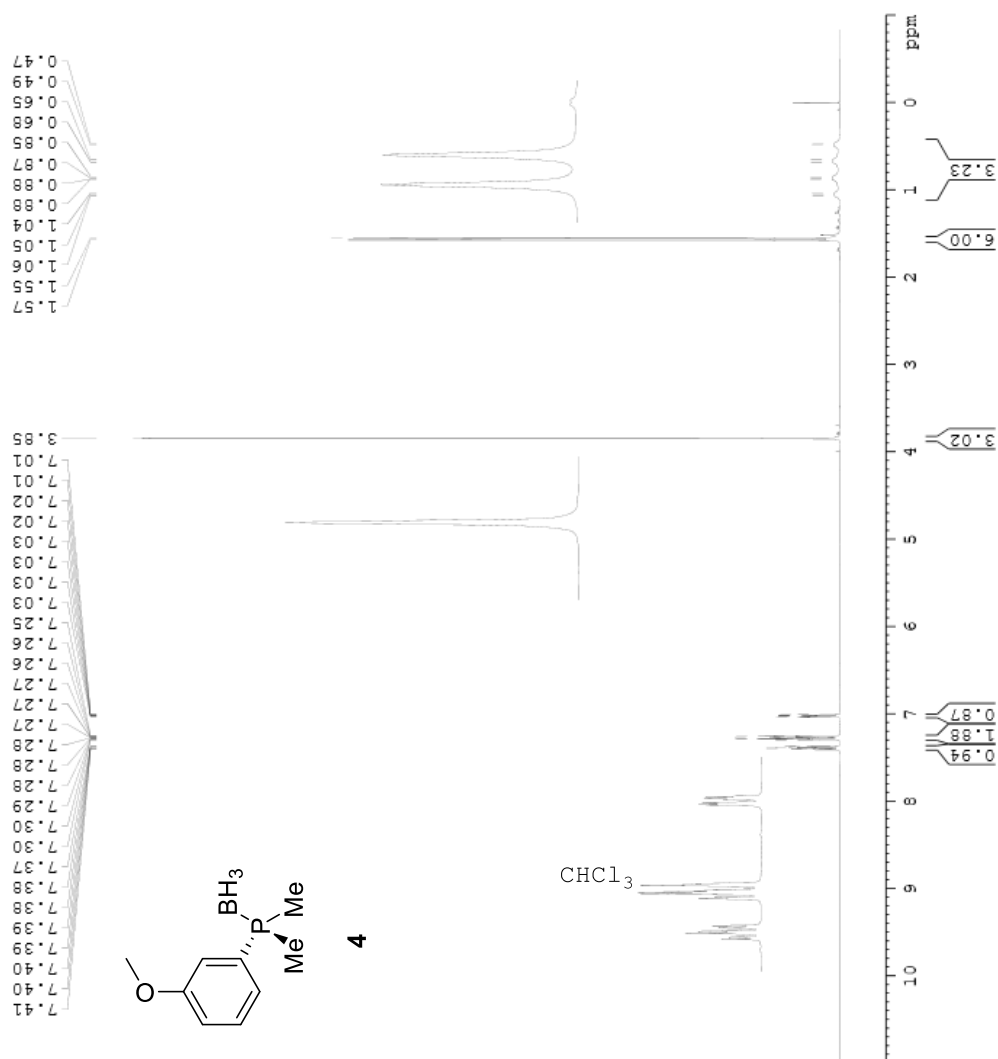










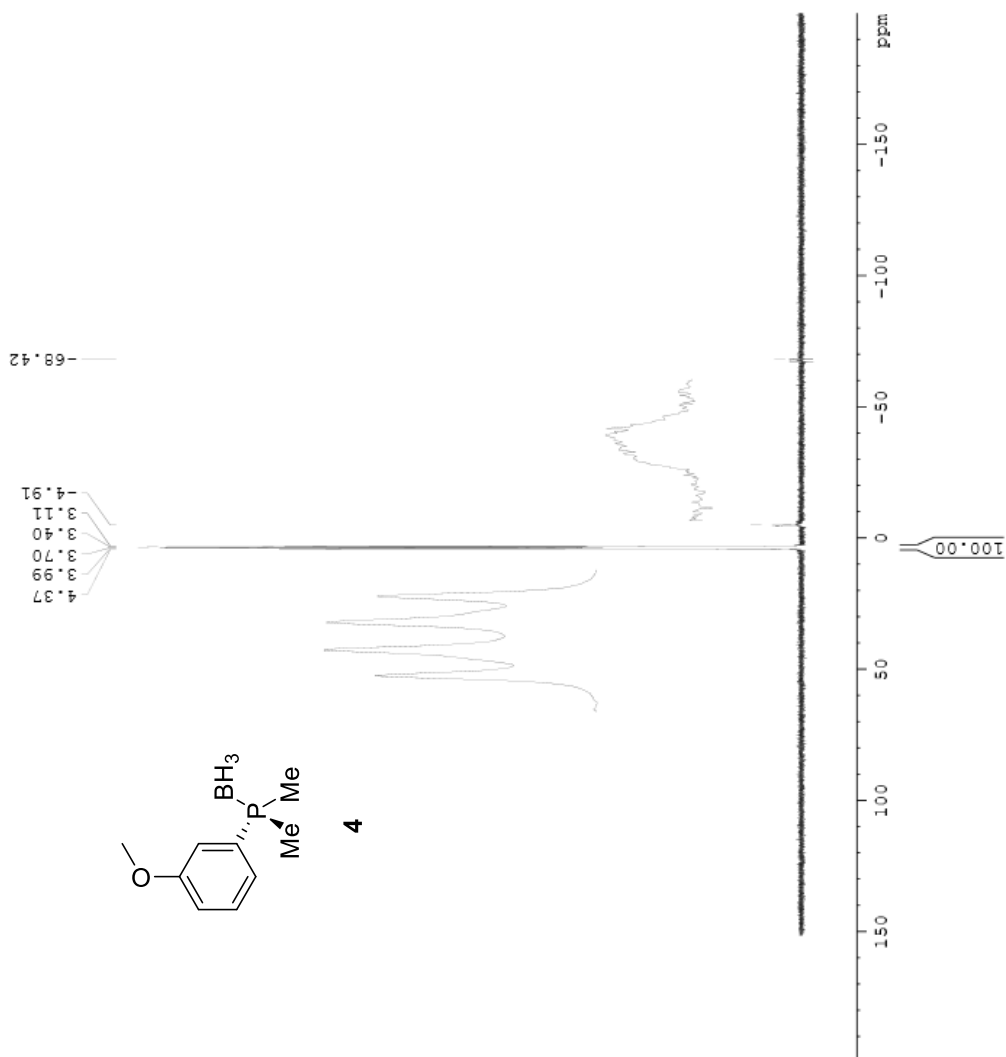


**BRUKER**

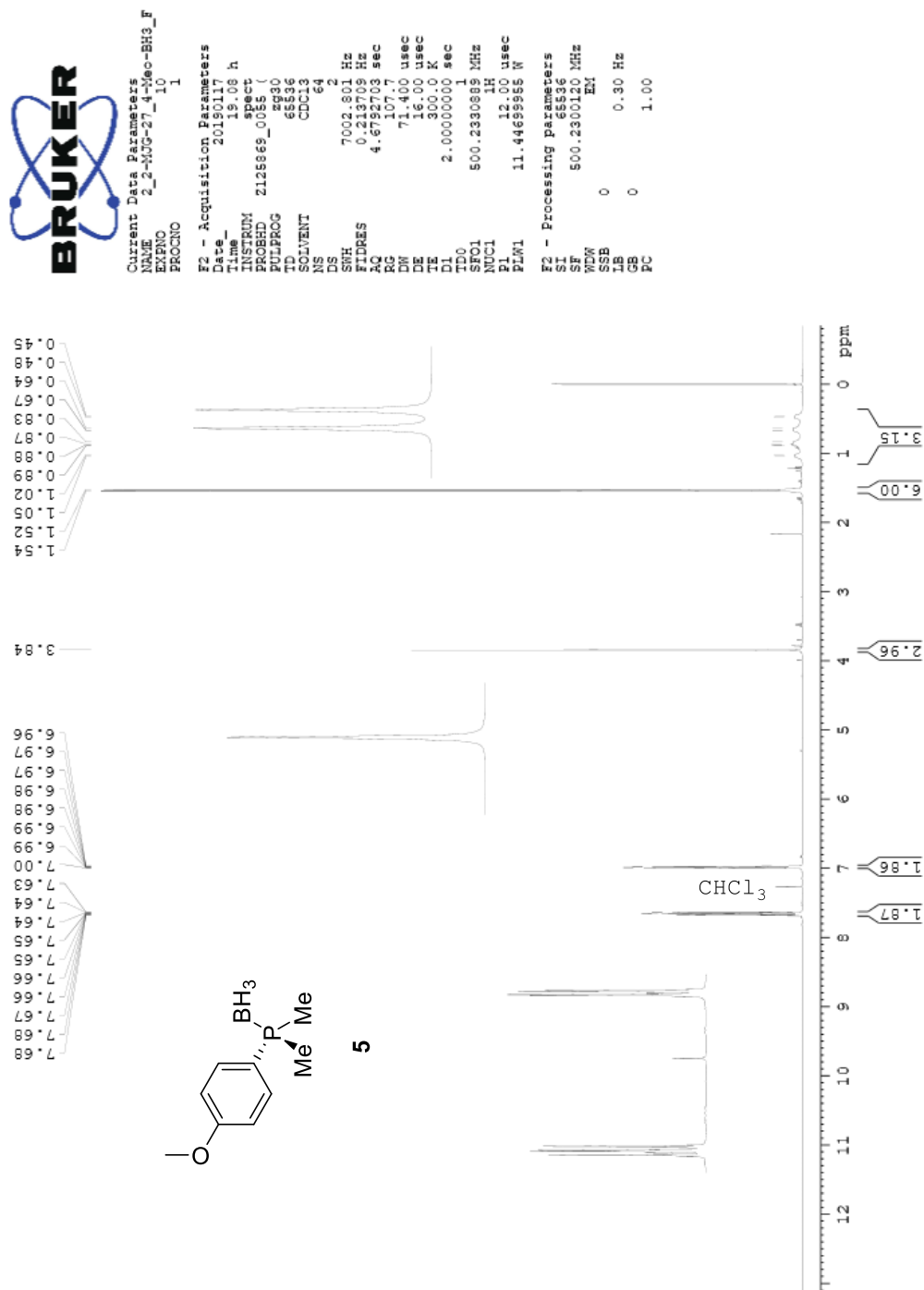
Current Data Parameters  
 NAME 2\_2-MUG-3-Me-BH3\_FP\_  
 EXPNO 10  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20190117  
 Time\_ 17.49 h  
 INSTRUM spect  
 PROBHD Z128889\_0085 (zgr30)  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 4  
 SWH 91621.742 Hz  
 FIDRES 2.487846 Hz  
 AQ 0.4018541 sec  
 RG 130.44  
 DW 6.133 usec  
 DE 18.00 usec  
 TE 300.0 K  
 D1 2.0000000 sec  
 T1 0.0300000 sec  
 T11 1.0000000 sec  
 SFO1 202.486698 MHz  
 NUC1 31P  
 P1 12.00 usec  
 PL1 40.26200104 W  
 SFO2 500.322008 MHz  
 NUC2 1H  
 CPDPRG12waltz16  
 PCPD2 80.00 usec  
 PLM2 11.44689955 W  
 PLM12 0.2645501 W  
 PLM13 0.1275800 W

F2 - Processing parameters  
 SI 32768  
 SF 202.4866157 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40





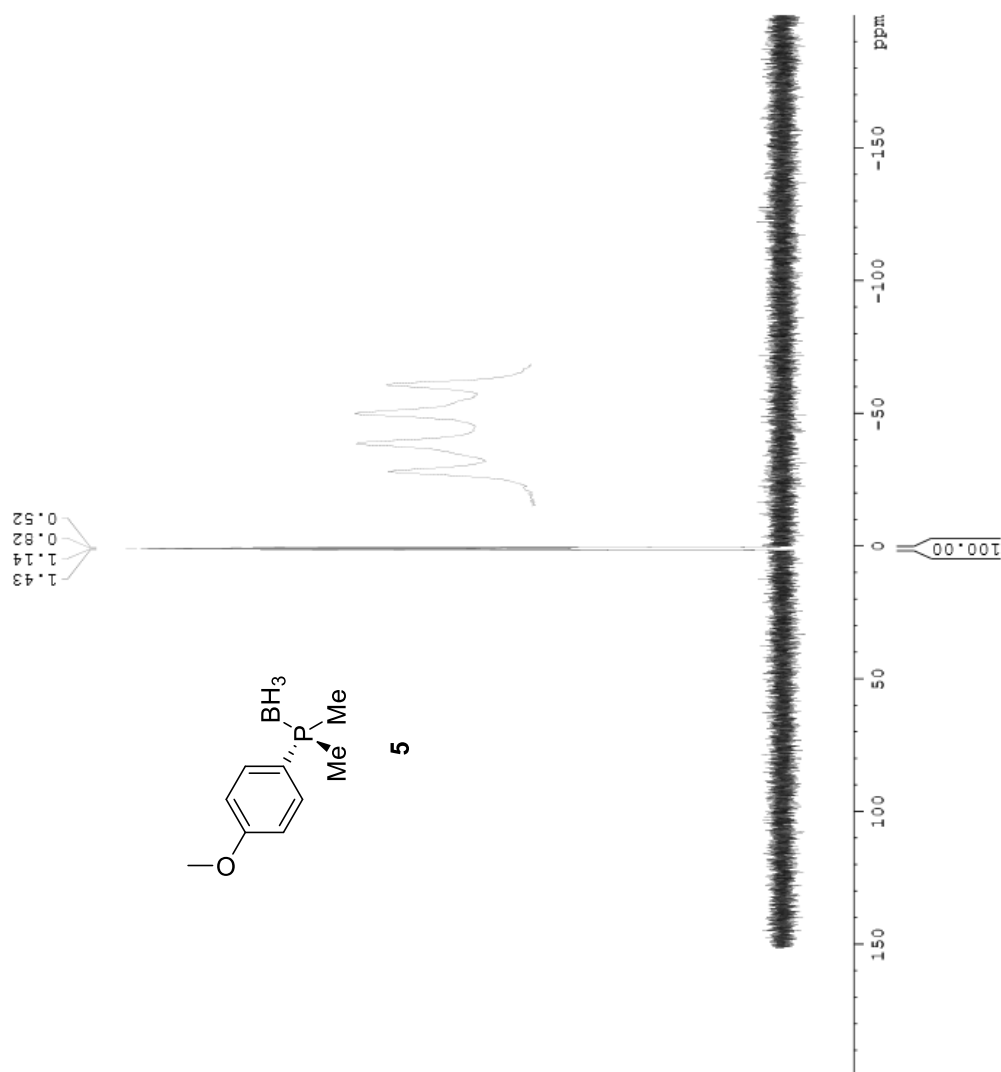


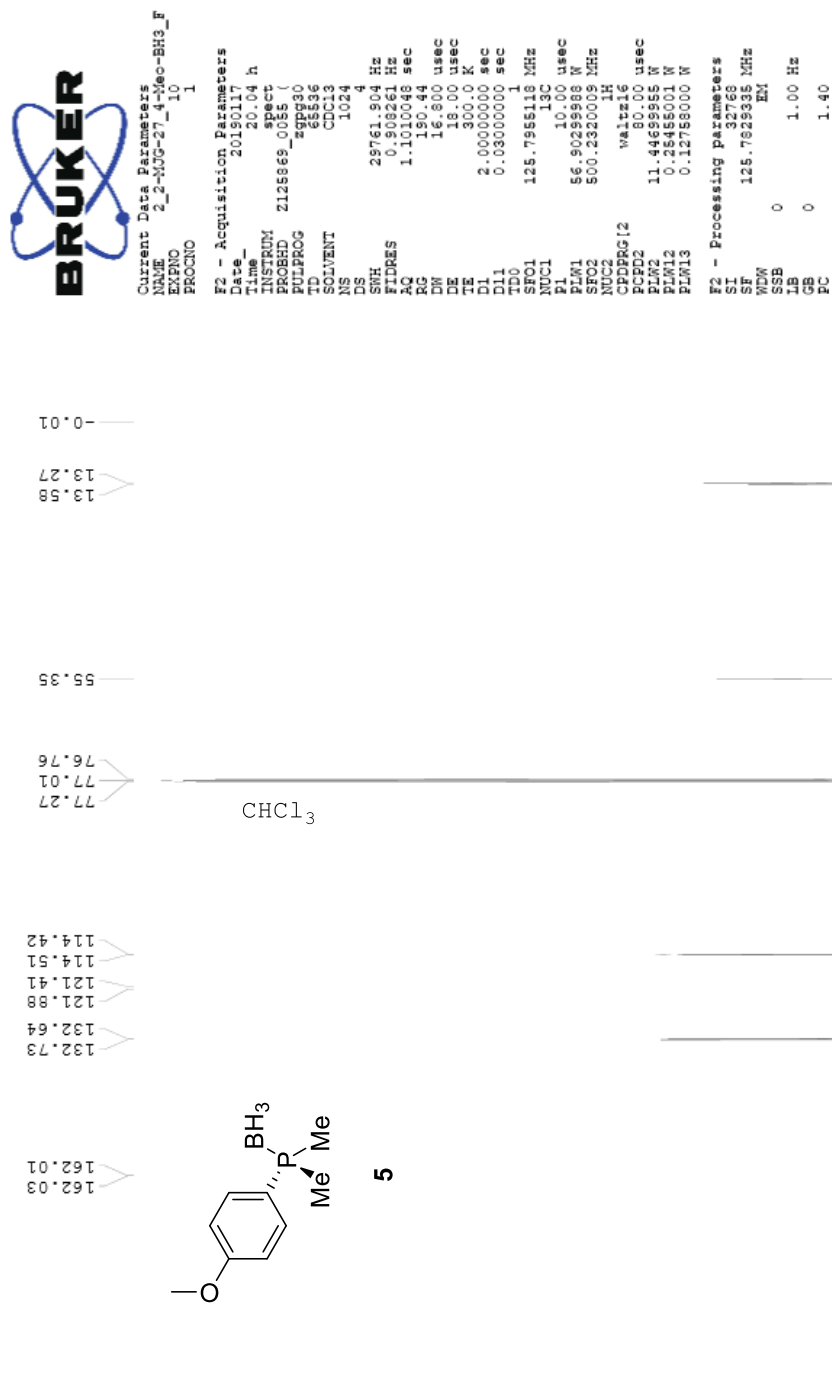
**BRUKER**

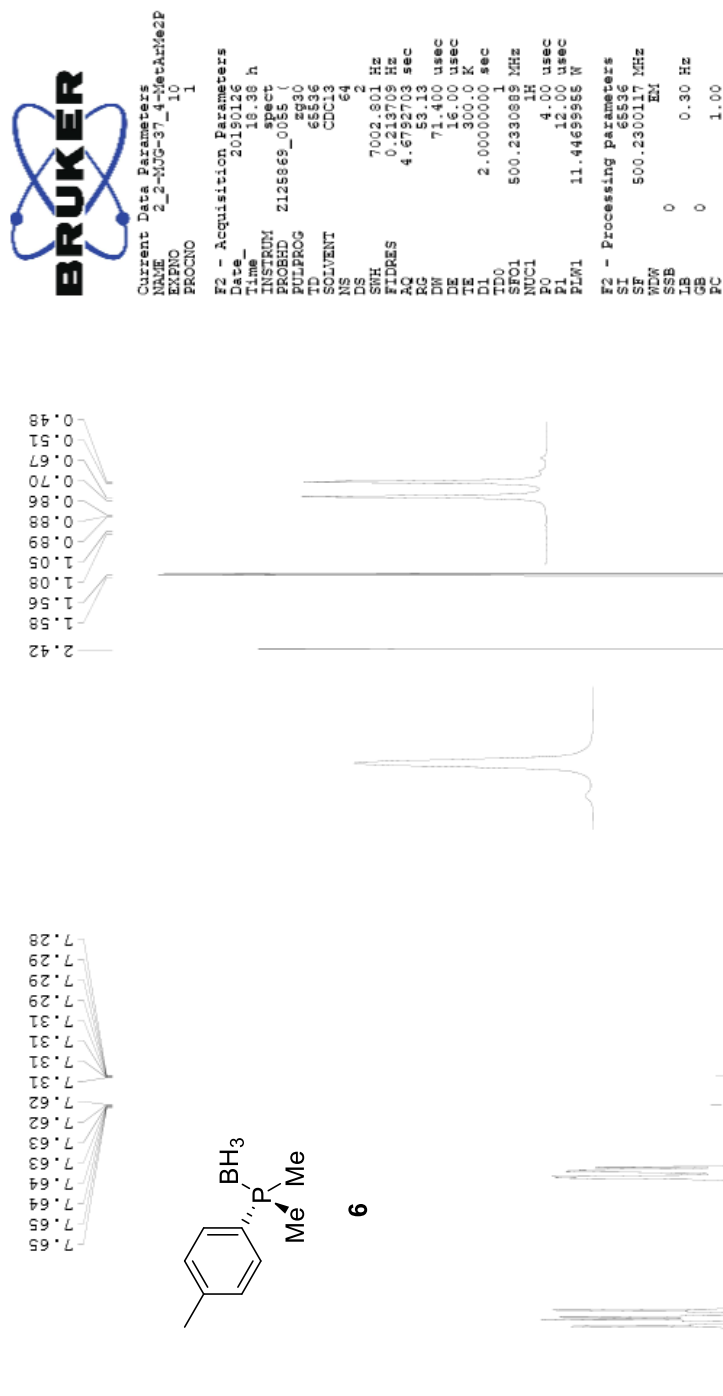
Current Data Parameters  
 NAME 2\_2-MG-27\_4-Me-BH3\_F  
 EXPNO 10  
 PROCNO 1

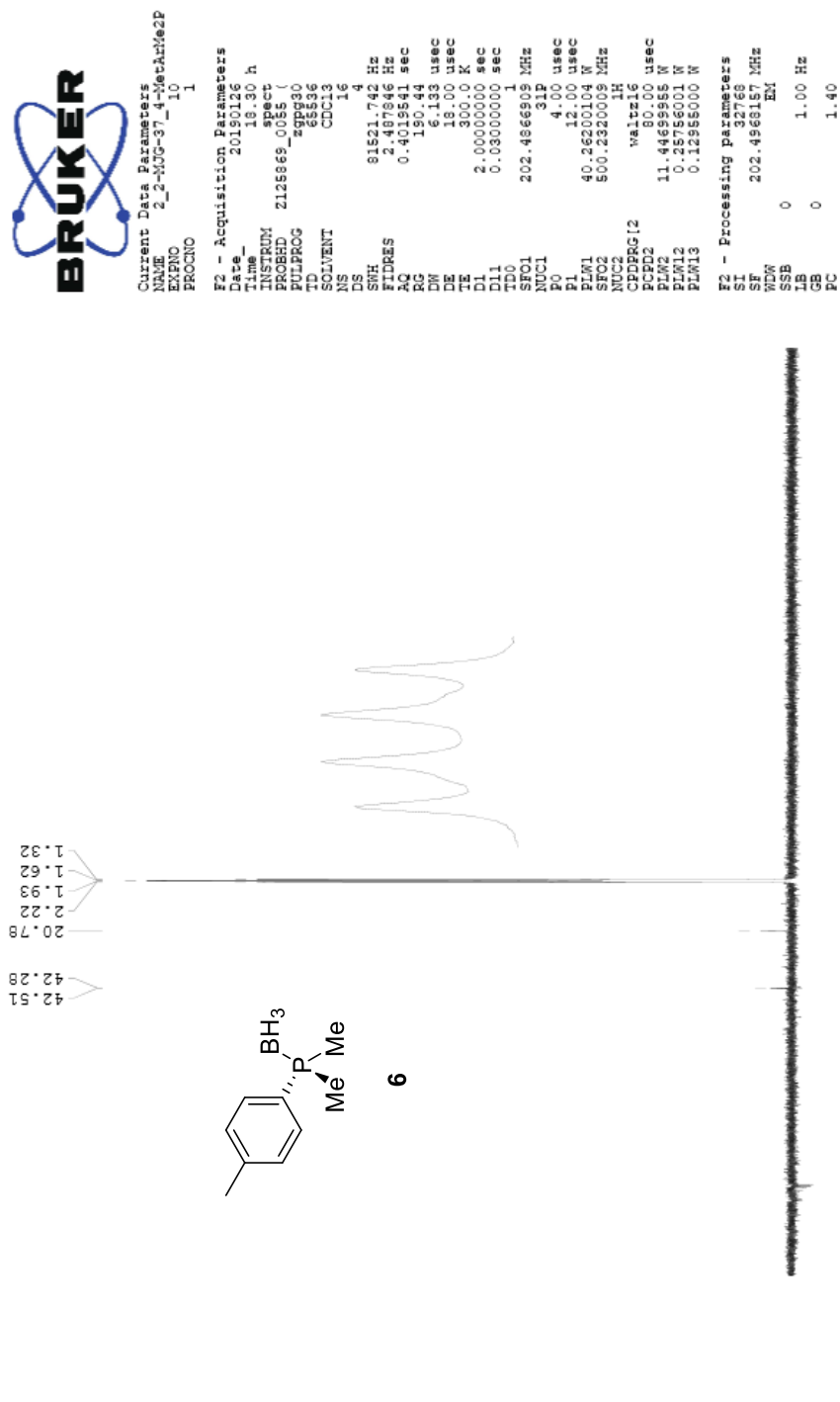
F2 - Acquisition Parameters  
 Date\_ 20190117  
 Time\_ 19.00 h  
 INSTRUM spect  
 PROBD 2128889\_0055 ( zgr930  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 4  
 SWH 81621.742 Hz  
 FIDRES 2.487846 Hz  
 AQ 0.4018541 sec  
 RG 130.44  
 DW 6.133 usec  
 DE 18.00 usec  
 TE 300.0 K  
 D1 2.0000000 sec  
 T1 0.0300000 sec  
 T11 1.0000000 sec  
 SFO1 202.486698 MHz  
 NUC1 31P  
 P1 12.00 usec  
 PL1 40.26200104 W  
 SFO2 500.322008 MHz  
 NUC2 1H  
 CPDPRG12waltz16  
 PCPD2 80.00 usec  
 PLM2 11.44689955 W  
 PLM12 0.2545501 W  
 PLM13 0.1275800 W

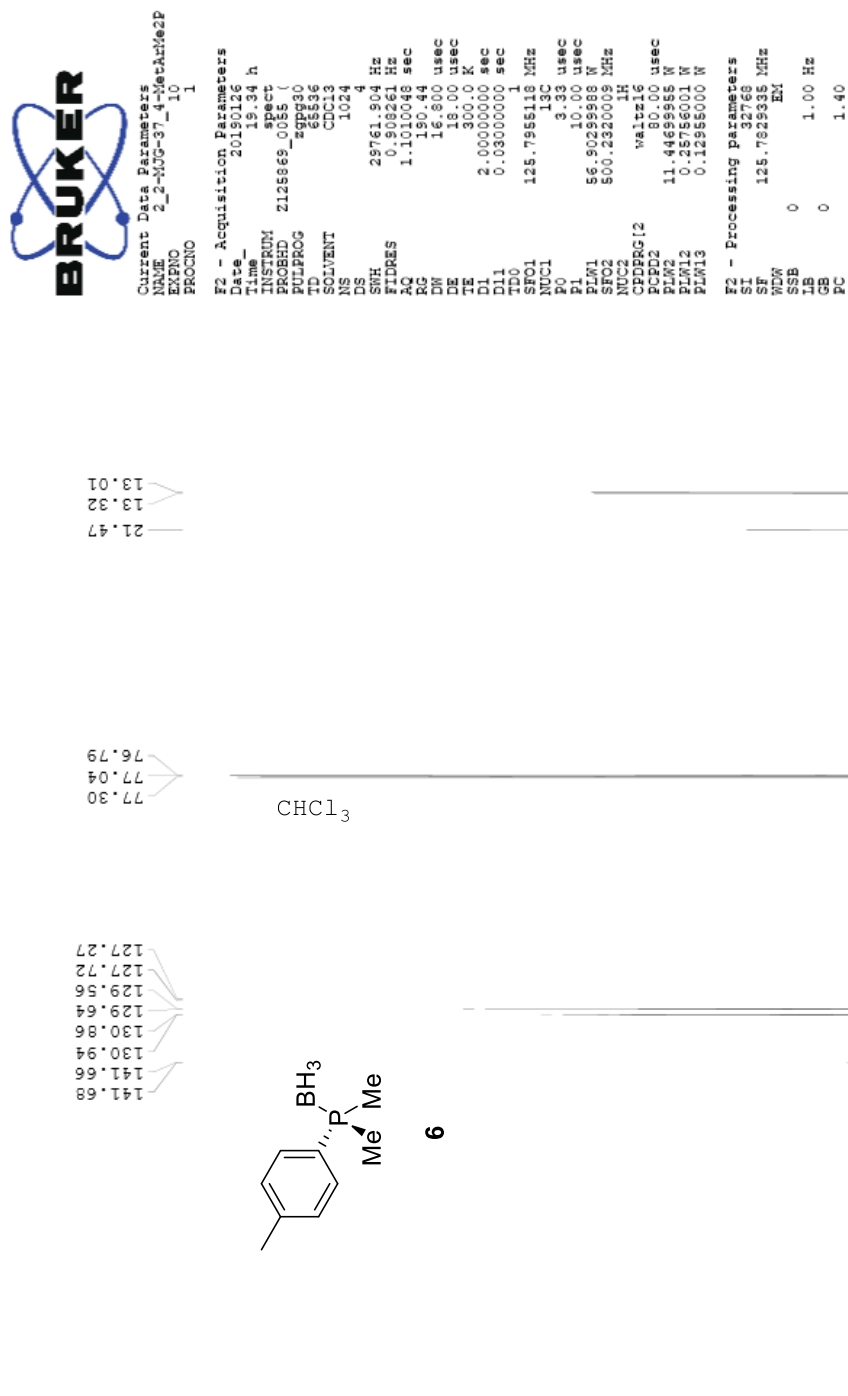
F2 - Processing parameters  
 SI 32768  
 SF 202.4866157 MHz  
 WDW EX  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

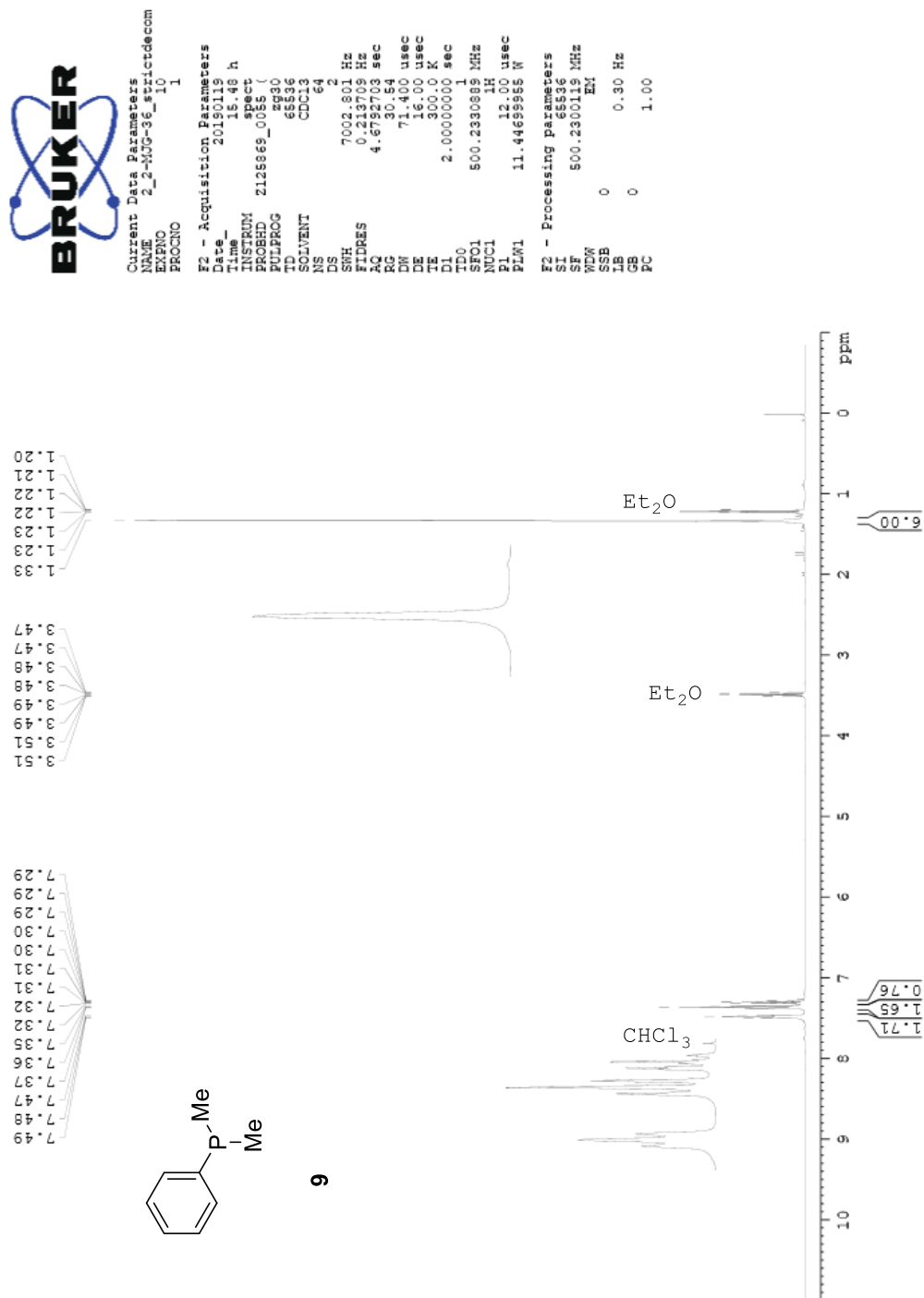


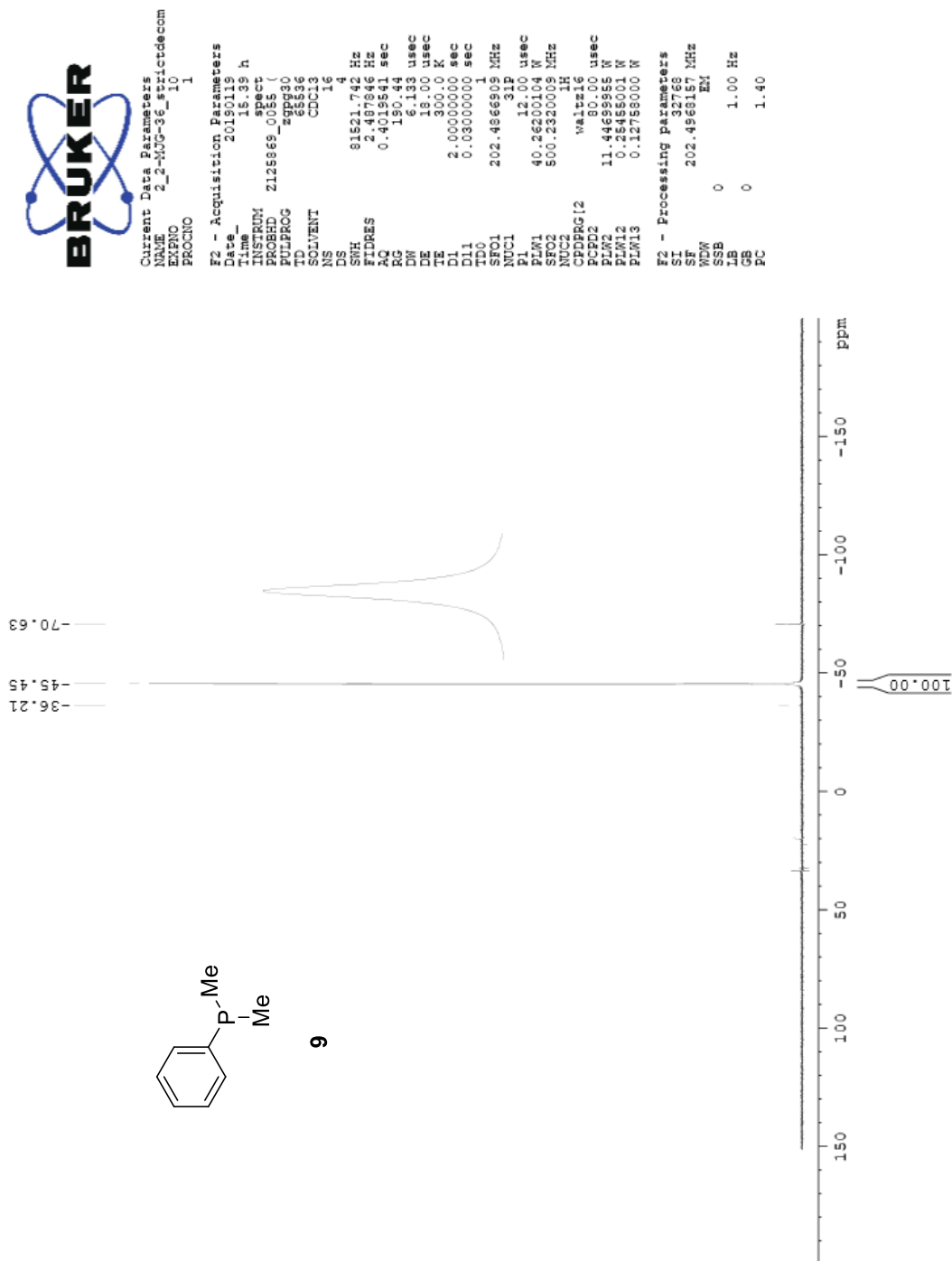


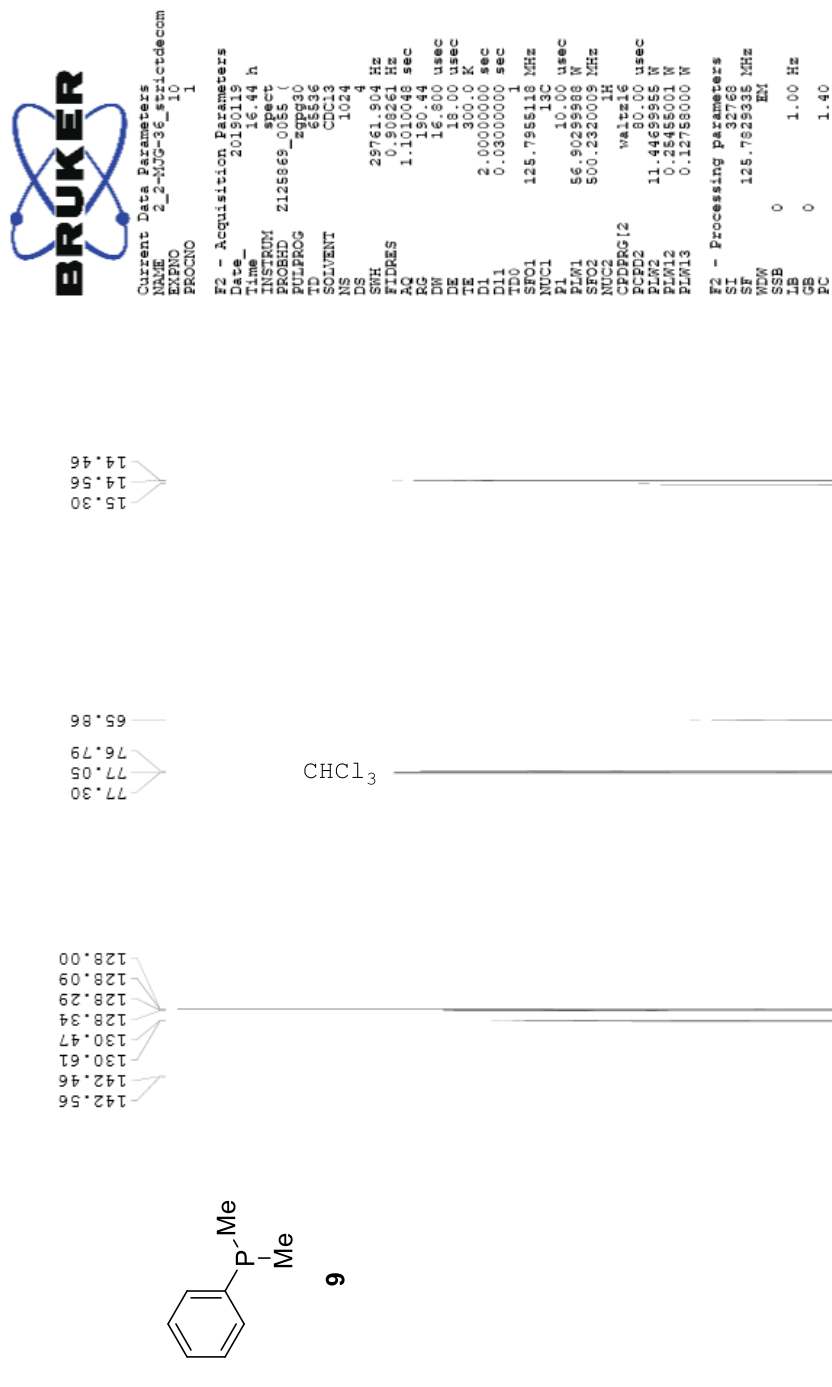


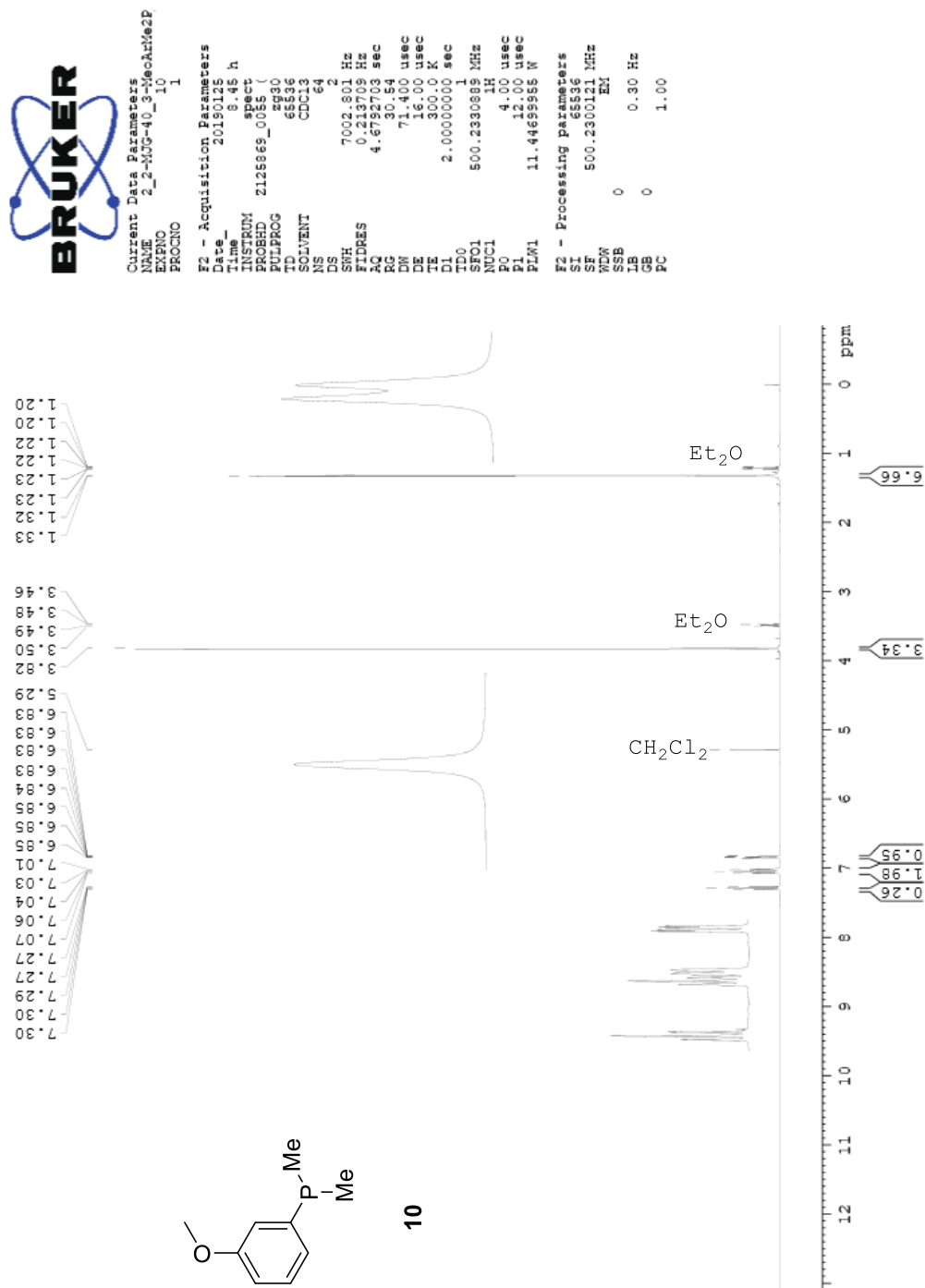










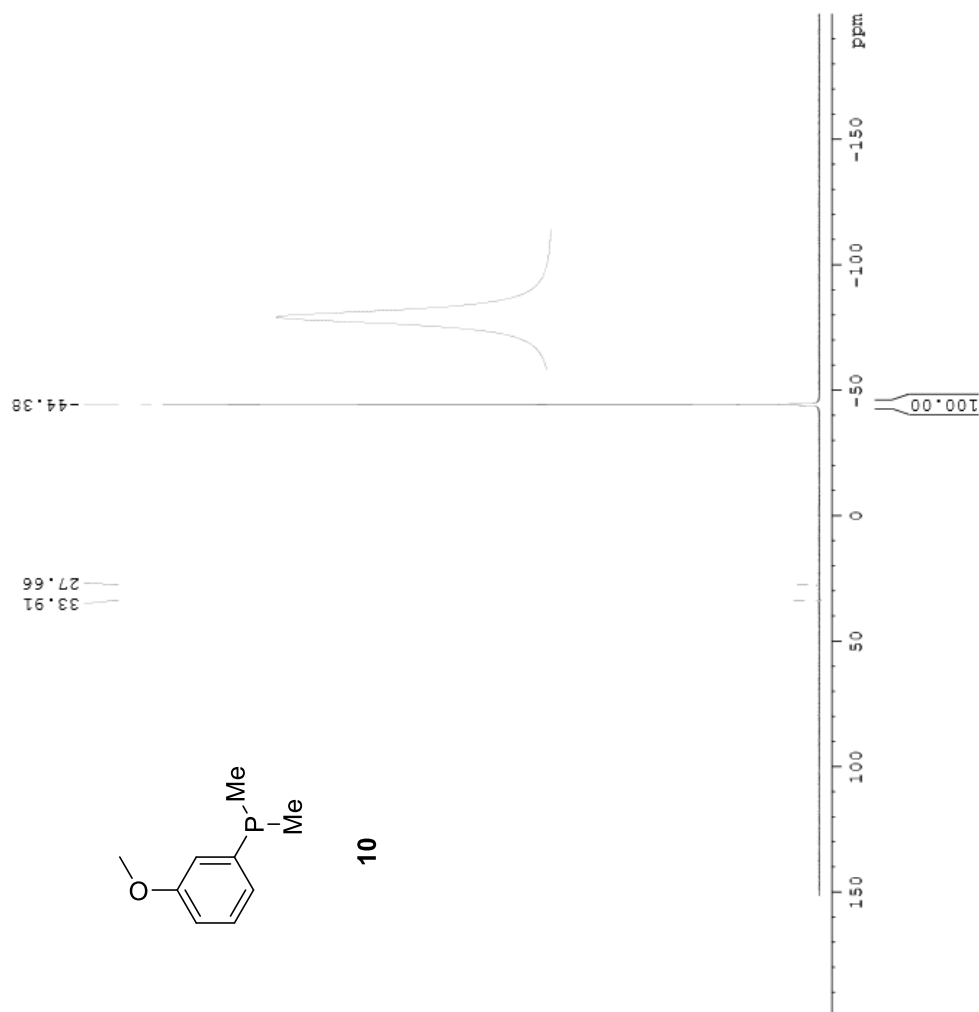


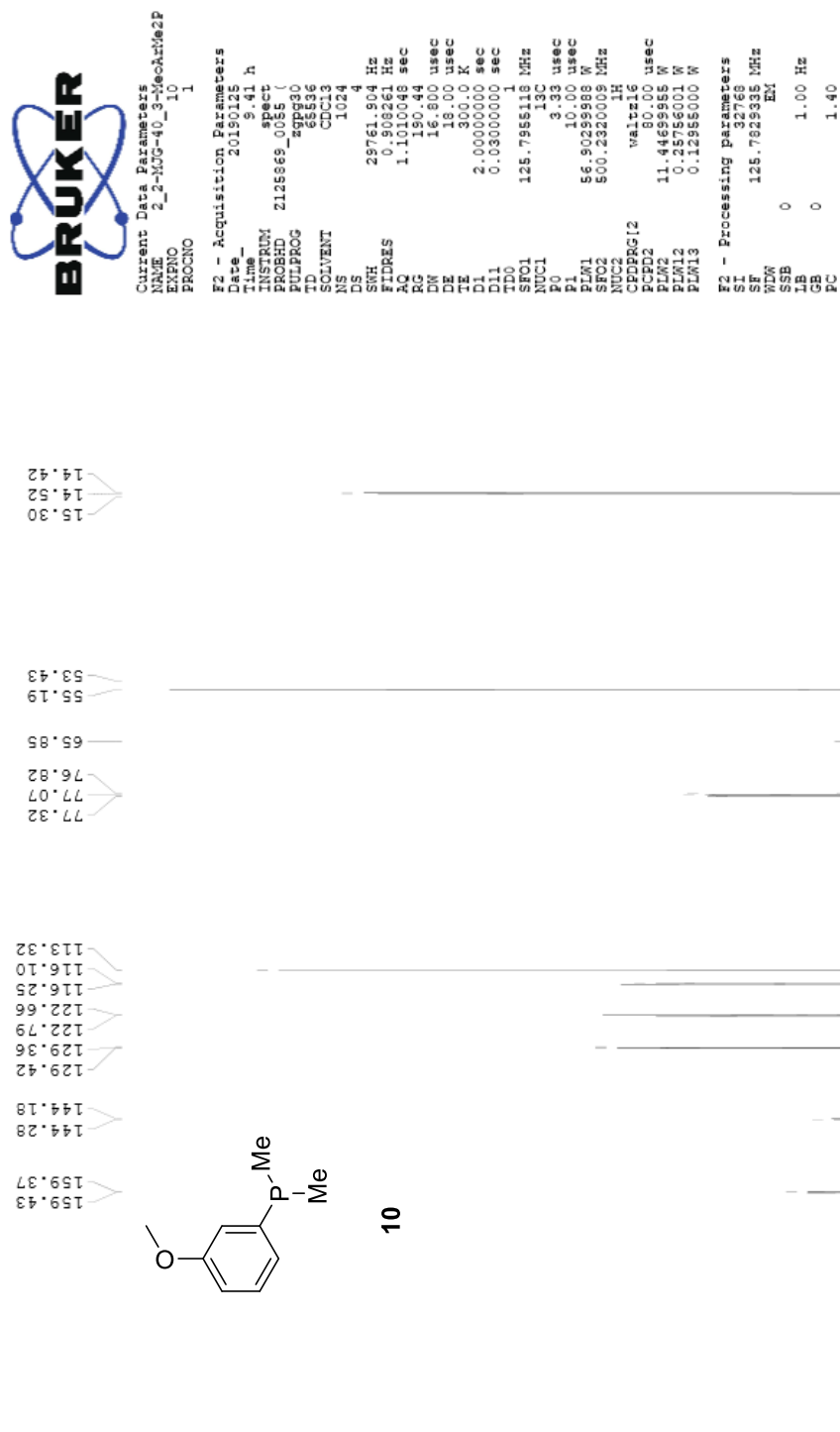
**BRUKER**

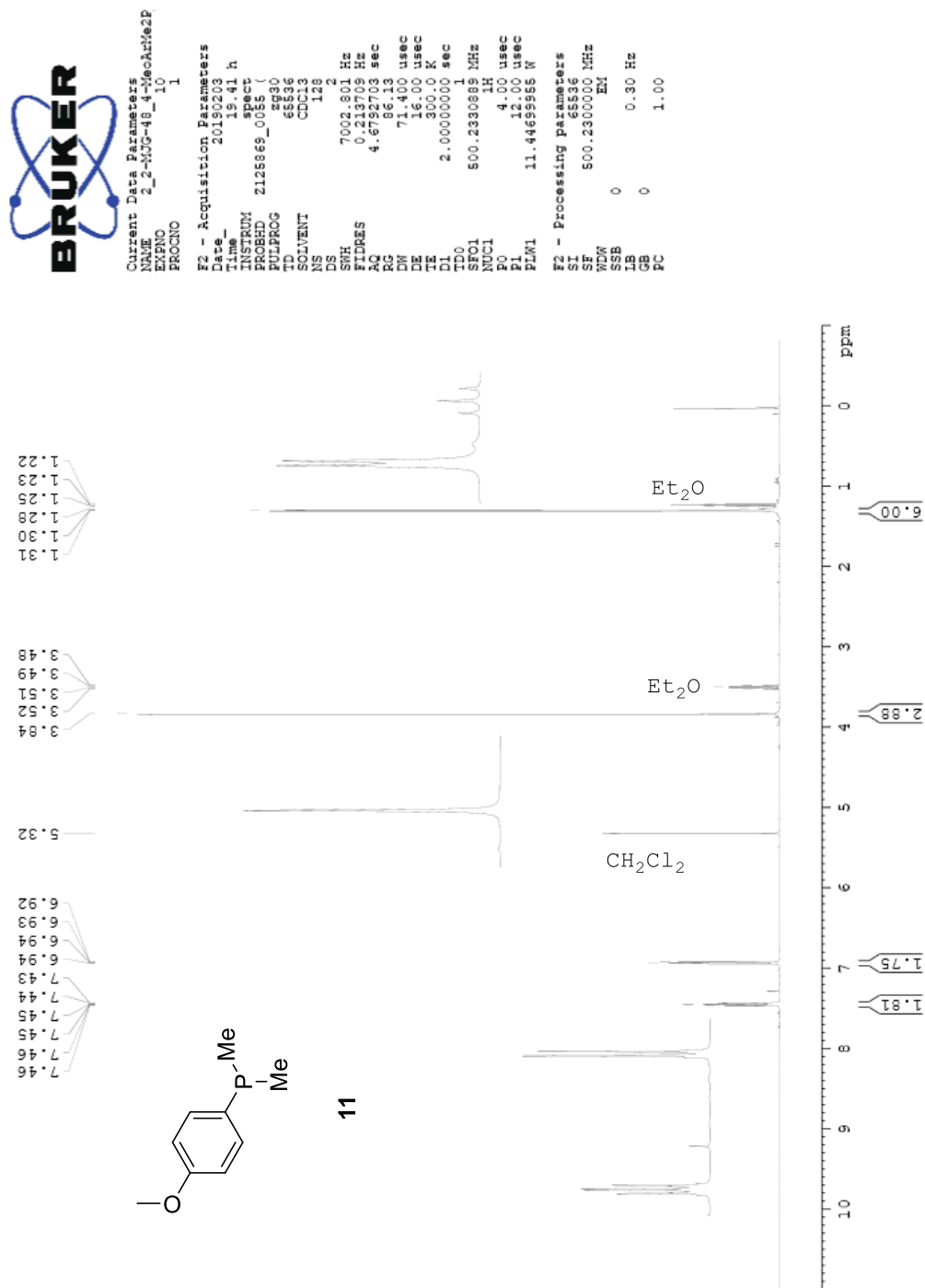
Current Data Parameters  
 NAME 2\_2-MJG-40\_3-MeCMe2P  
 EXPNO 10  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20190105  
 Time\_ 8.37 h  
 INSTRUM spect  
 PROBHD Z128889\_0055 (zgr30)  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 4  
 SWH 91621.742 Hz  
 FIDRES 2.487846 Hz  
 AQ 0.4018541 sec  
 RG 130.44  
 DW 6.133 usec  
 DE 18.00 usec  
 TE 300.0 K  
 D1 2.00000000 sec  
 T1 0.03000000 sec  
 T11 1.00000000 sec  
 SFO1 202.486698 MHz  
 NUC1 31P  
 P1 4.00 usec  
 PL1 12.00 usec  
 SFO2 40.26200104 MHz  
 NUC2 1H  
 SFO2 500.232008 MHz  
 P2 1.00 usec  
 PL2 0.28756001 W  
 SFO2 11.44659555 MHz  
 P2 0.12955000 W  
 PL2 0.12955000 W

F2 - Processing parameters  
 SI 32768  
 SF 202.486698 MHz  
 WDW EM  
 SSB 0  
 LB 0  
 GB 0  
 PC 1.40





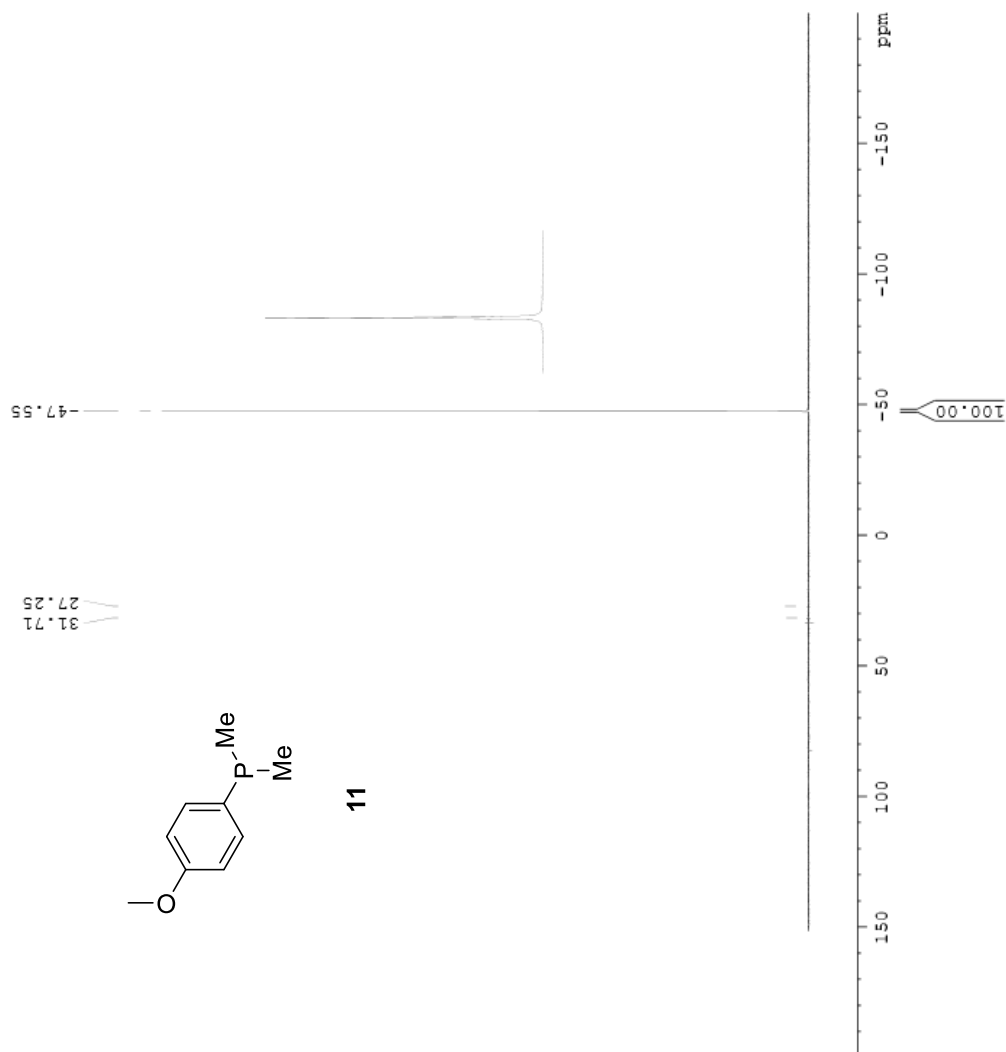


**BRUKER**

Current Data Parameters  
 NAME 2\_2-MG-48\_4-MeAcMe2P  
 EXPNO 10  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20190203  
 Time\_ 19.45 h  
 INSTRUM spect  
 PROBHD Z128869\_0055 (zgr30)  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 4  
 SWH 91621.742 Hz  
 FIDRES 2.487846 Hz  
 AQ 0.4018541 sec  
 RG 130.44  
 DW 6.133 usec  
 DE 18.00 usec  
 TE 300.0 K  
 D1 2.0000000 sec  
 T1 0.0300000 sec  
 T11 1.10 sec  
 SFO1 202.486698 MHz  
 NUC1 31P  
 P0 4.00 usec  
 PL1 17.00 usec  
 PL11 40.26200104 W  
 SFO2 500.232008 MHz  
 NUC2 1H  
 CPDPRG12 waltz16  
 PCPD2 80.00 usec  
 PL12 11.4465555 W  
 PL112 0.25756001 W  
 PL113 0.12955000 W

F2 - Processing parameters  
 SI 32768  
 SF 202.486157 MHz  
 WDW EM  
 SSB 0  
 LB 0  
 GB 0  
 PC 1.40





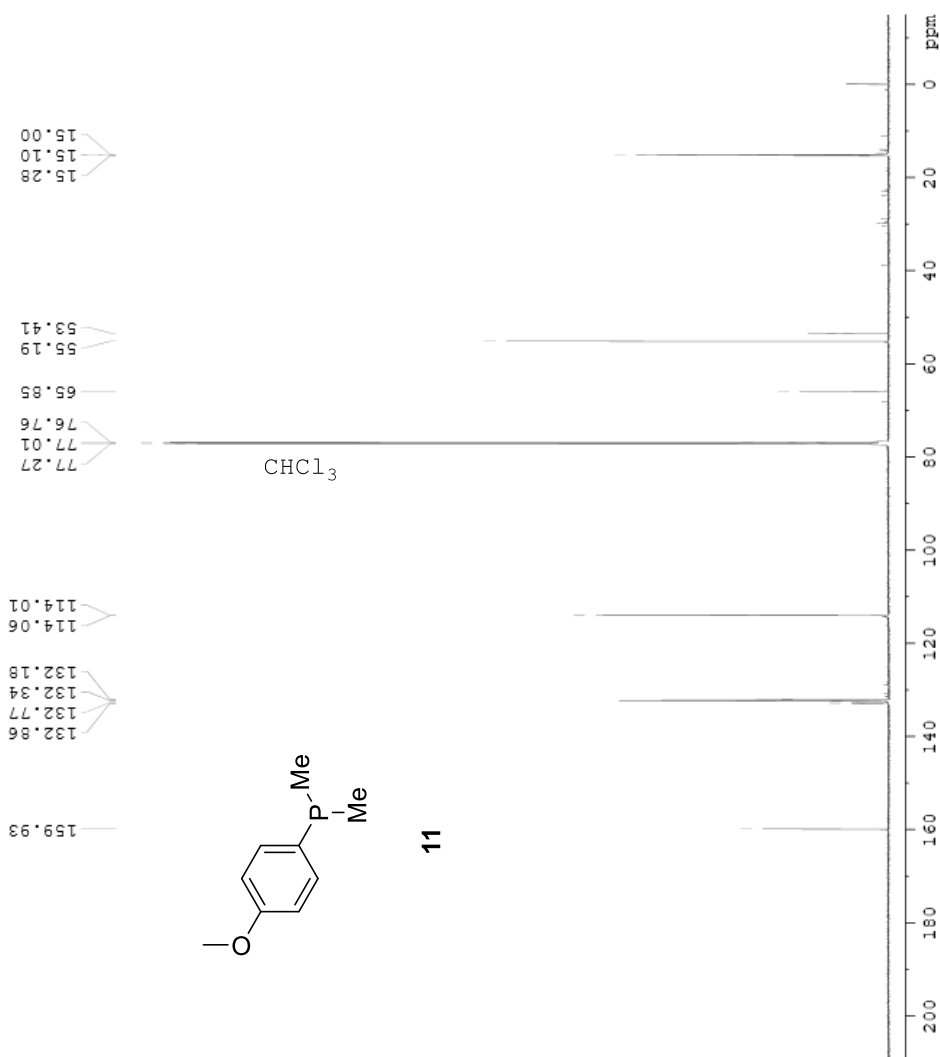
Current Data Parameters  
 NAME 2\_2-MG-48\_4-MeAcMe2P  
 EXPNO 10  
 PROCNO 1

F2 - Acquisition Parameters

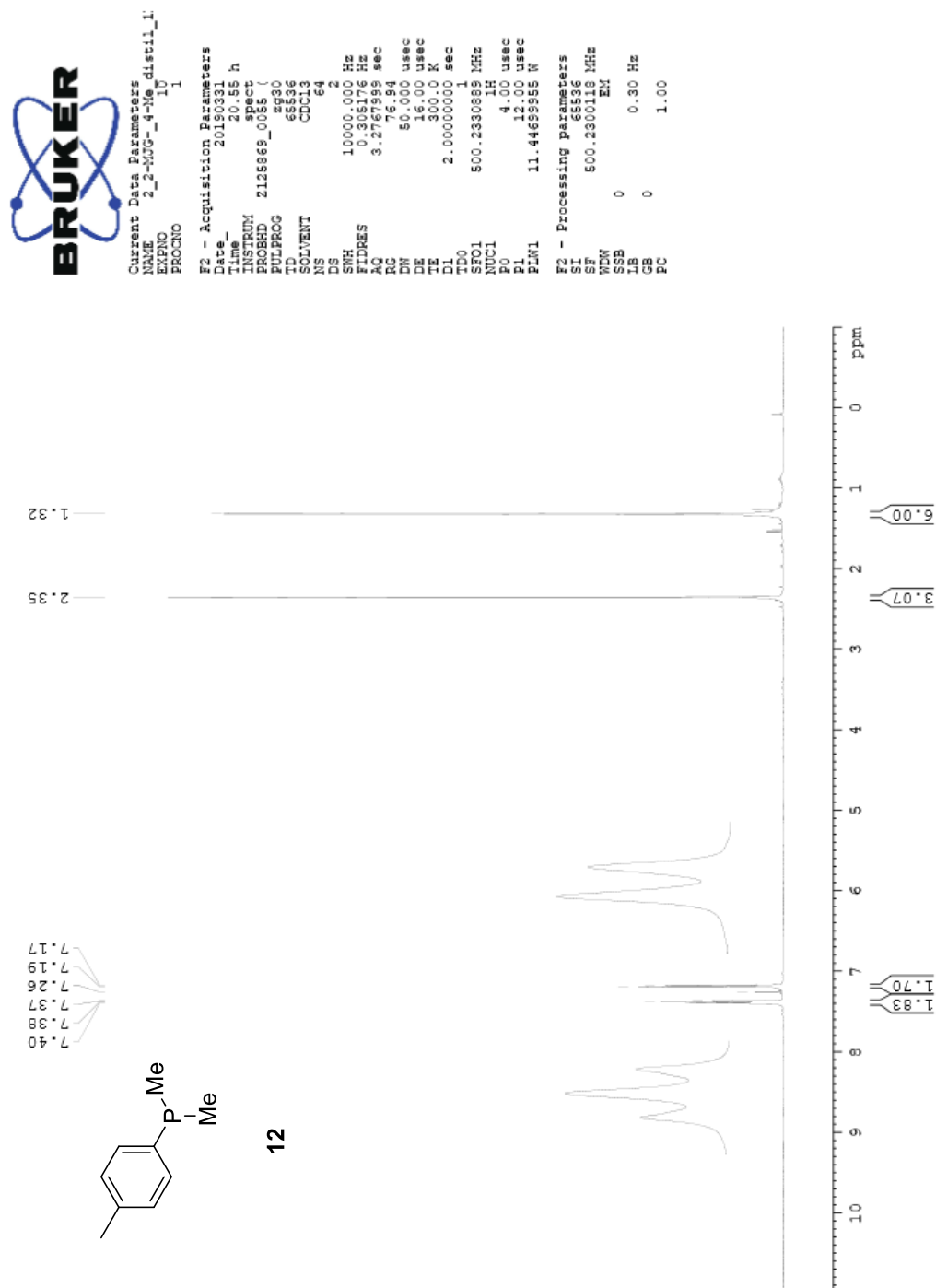
Date\_ 20190203  
 Time\_ 21.48 h  
 INSTRUM spect  
 PROBHD Z128869\_0055 (zgg930)  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 2000  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.908261 Hz  
 AQ 1.1010048 sec  
 RG 190.44  
 DW 16.800 usec  
 DE 18.00 usec  
 TE 300.0 K  
 D1 2.00000000 sec  
 T1 0.03000000 sec  
 T1 1.10000000 sec  
 SFO1 125.755518 MHz  
 NUC1 13C  
 P0 3.33 usec  
 PL1 10.00 usec  
 SFO2 56.9028388 MHz  
 NUC2 1H  
 CDEPRG12 waltz16  
 PCPD2 80.00 usec  
 PLM2 11.4465955 W  
 PLM12 0.2575601 W  
 PLM13 0.1295500 W

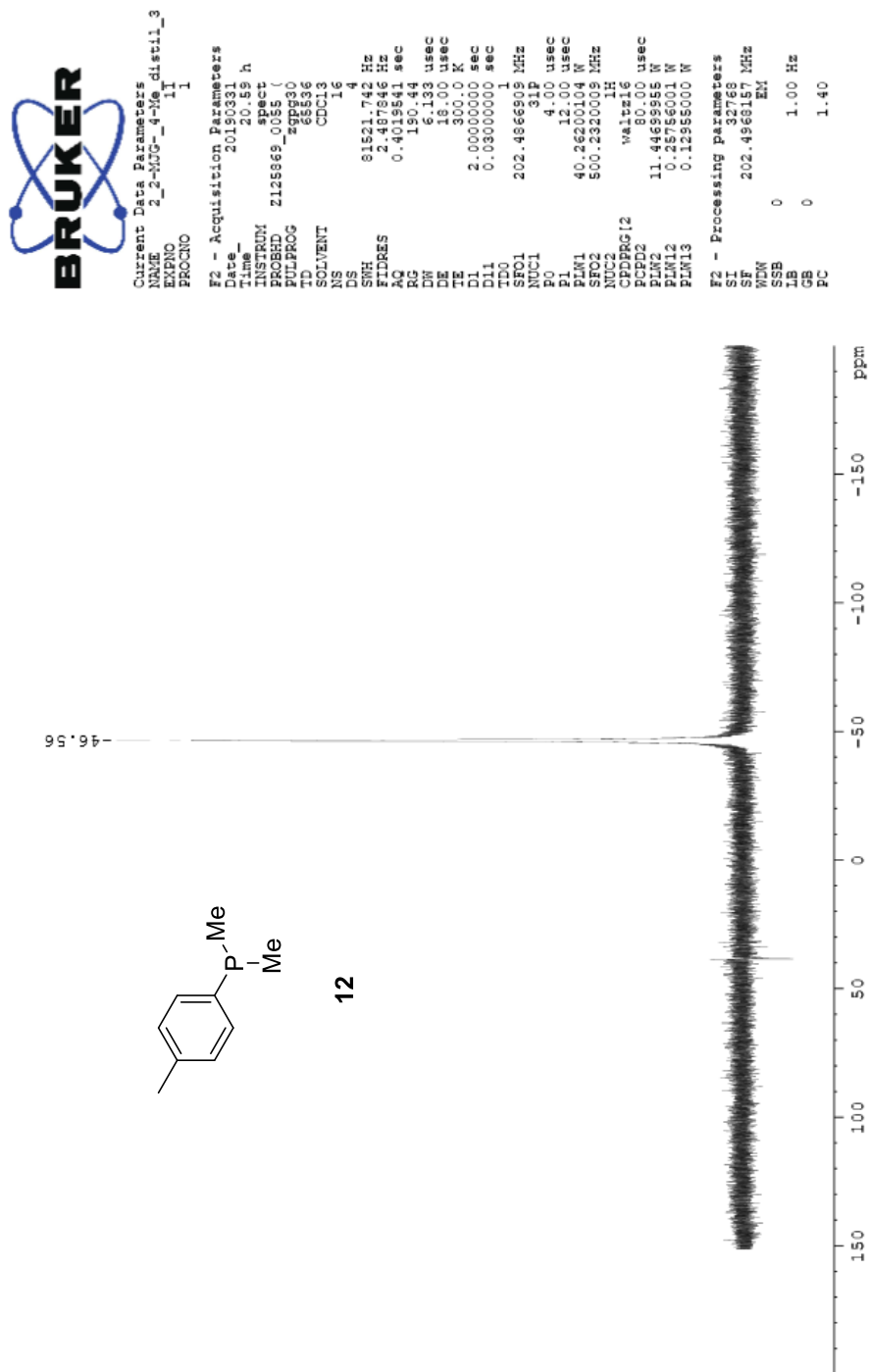
F2 - Processing parameters

SI 32768  
 SF 125.752338 MHz  
 WDW EX  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40



11



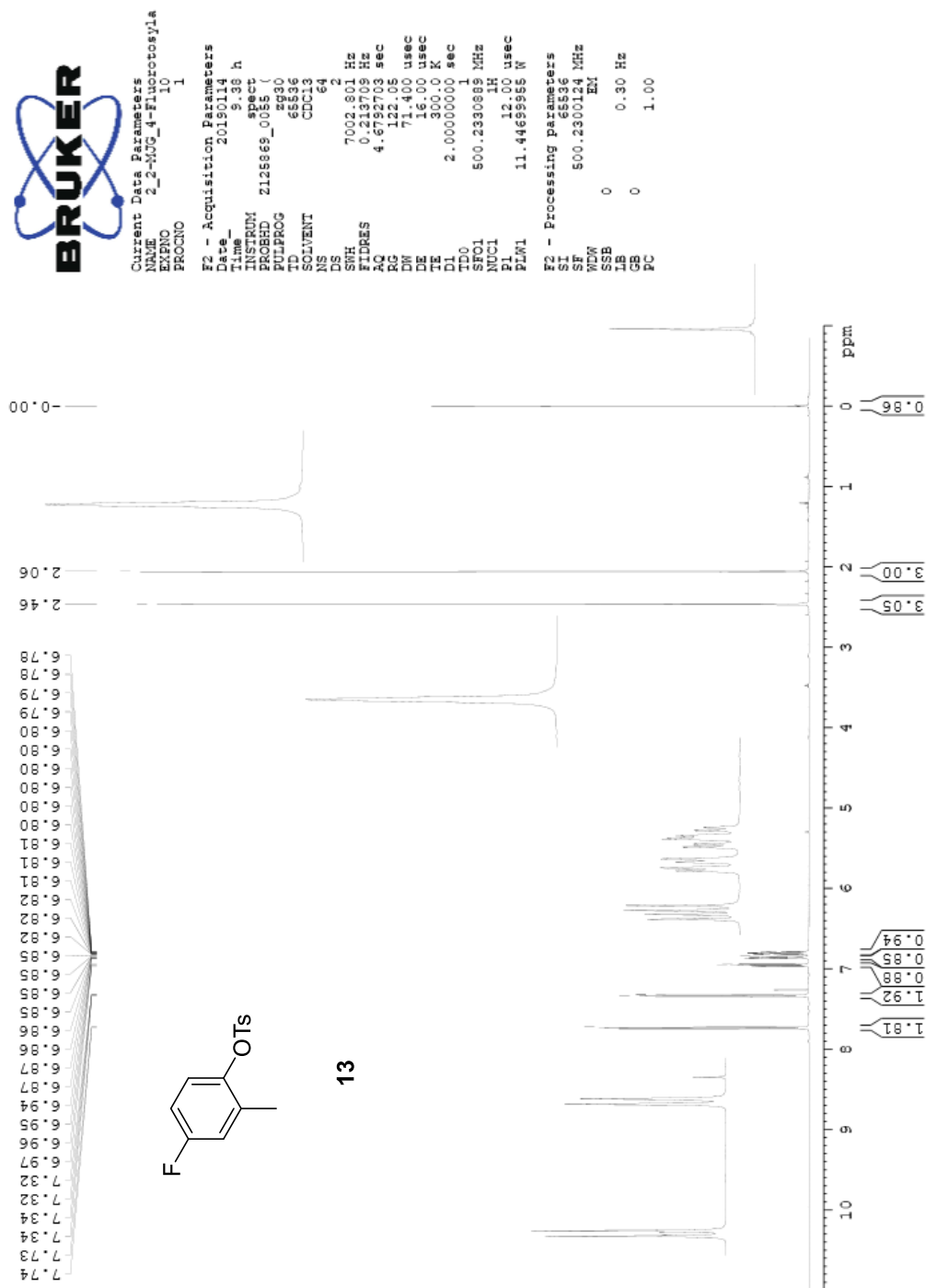




Current Data Parameters  
 NAME 2\_2-MG-4-Me distill\_1  
 EXPNO 11  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20190331  
 Time\_ 22.04 h  
 INSTRUM spect  
 PROBD 2128889\_0015 ( 4  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 1024  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.90261 Hz  
 AQ 1.1010048 sec  
 RG 190.44  
 DW 16.800 usec  
 DE 18.00 usec  
 TE 300.0 K  
 TL 2.00000000 sec  
 TLI 0.03000000 sec  
 SFO1 125.76113 MHz  
 SFO2 125.76113 MHz  
 NUC1 13C  
 P1 1.00 usec  
 PL1 56.90233888 W  
 SFO2 500.232008 MHz  
 NUC2 1H  
 P2 16.00 usec  
 PL2 11.4483955 W  
 SFO2 0.25756001 W  
 PL13 0.1255600 W  
 F2 - Processing parameters  
 SI 32768  
 SF 125.7623335 MHz  
 WTW 0  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40







Current Data Parameters

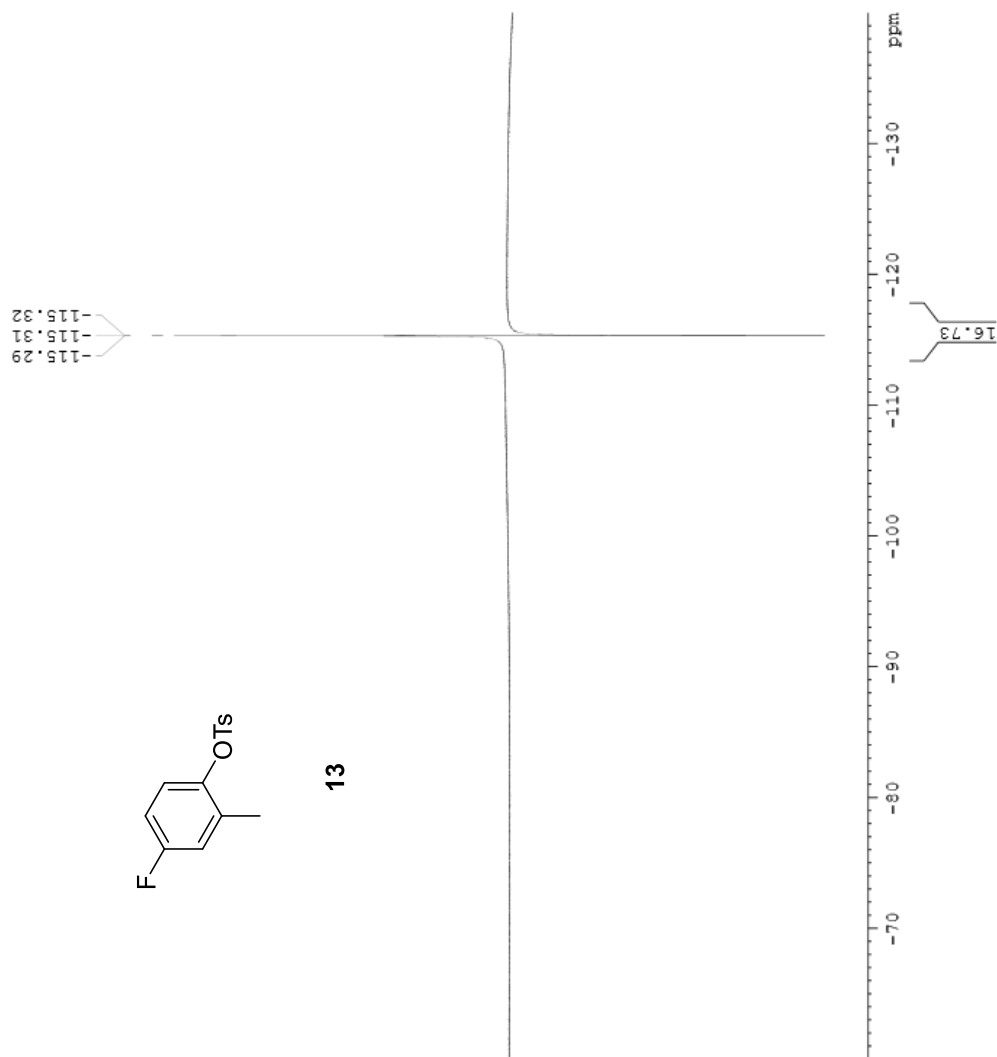
NAME 2,2-MG-4-Fluorotostyla  
EXPNO 10  
PROCNO 1

F2 - Acquisition Parameters

Date\_ 20190114  
Time 10.36 h  
INSTRUM spect  
PROBHD 2128869\_0085 (zgpg30)  
PULPROG zgpg30  
TD 131072  
SOLVENT CDCl3  
NS 16  
DS 4  
SWH 113636.367 Hz  
FIDRES 1.733963 Hz  
AQ 0.5767168 sec  
RG 14.14  
DW 4.400 usec  
DE 18.000 usec  
TE 300.0 K  
D1 1.00000000 sec  
D2 1.00000000 sec  
D3 1.00000000 sec  
SFO1 470.6394032 MHz  
NUC1 13C  
P1 15.00 usec  
PL1 11.70600018 W

F2 - Processing parameters

SI 65536  
SF 470.6394032 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00





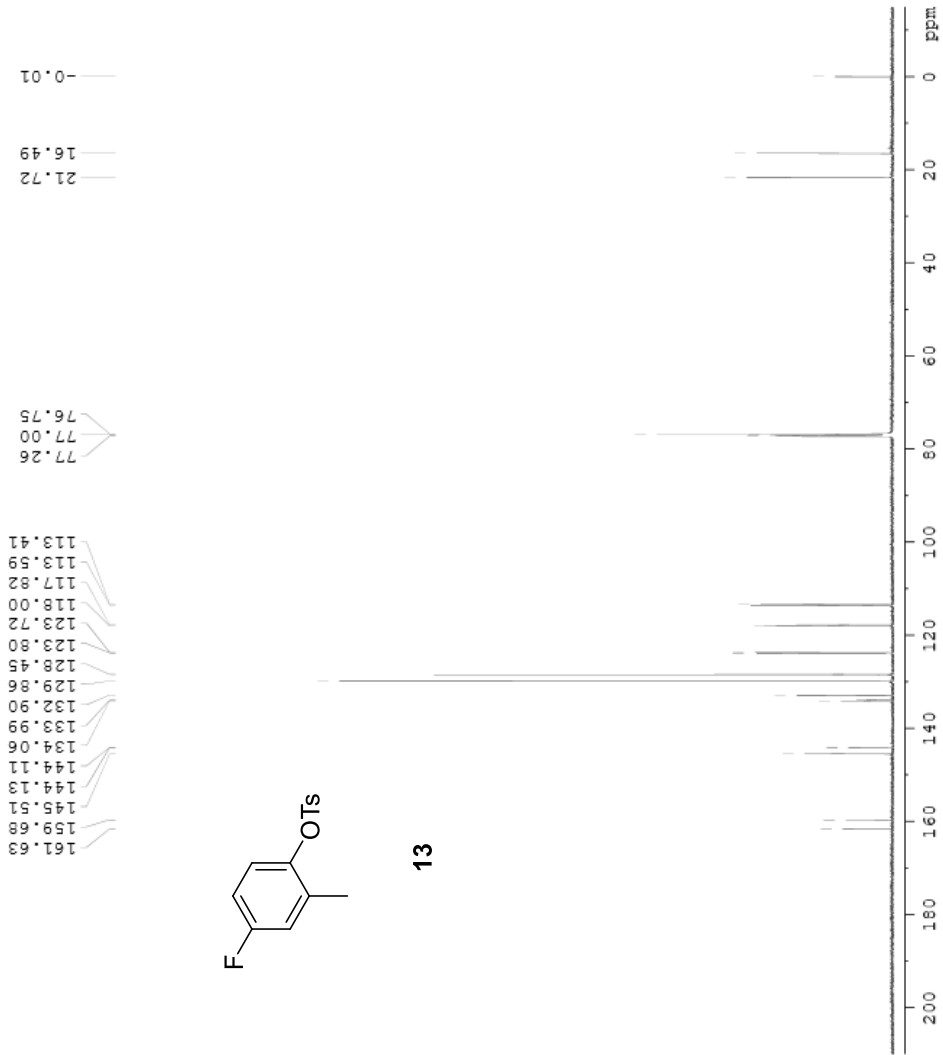
Current Data Parameters  
 NAME 2\_2-MUG\_4-Fluorotostyla  
 EXPNO 10  
 PROCNO 1

# F2 - Acquisition Parameters

Date\_ 20190114  
 Time\_ 10.33 h  
 INSTRUM spect  
 PROBD 2128889\_0055 ( zgr930  
 PULPROG zgpg30  
 TD 65536  
 SFO1 125.755518 MHz  
 SFO2 56.90233588 MHz  
 SFO3 500.232009 MHz  
 NUC1 13C  
 NUC2 1H  
 PCPD2 80.00 usec  
 PLM2 11.44833355 W  
 PLM12 0.2545501 W  
 PLM13 0.1275800 W

# F2 - Processing parameters

SI 32768  
 SF 125.7523338 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40



13

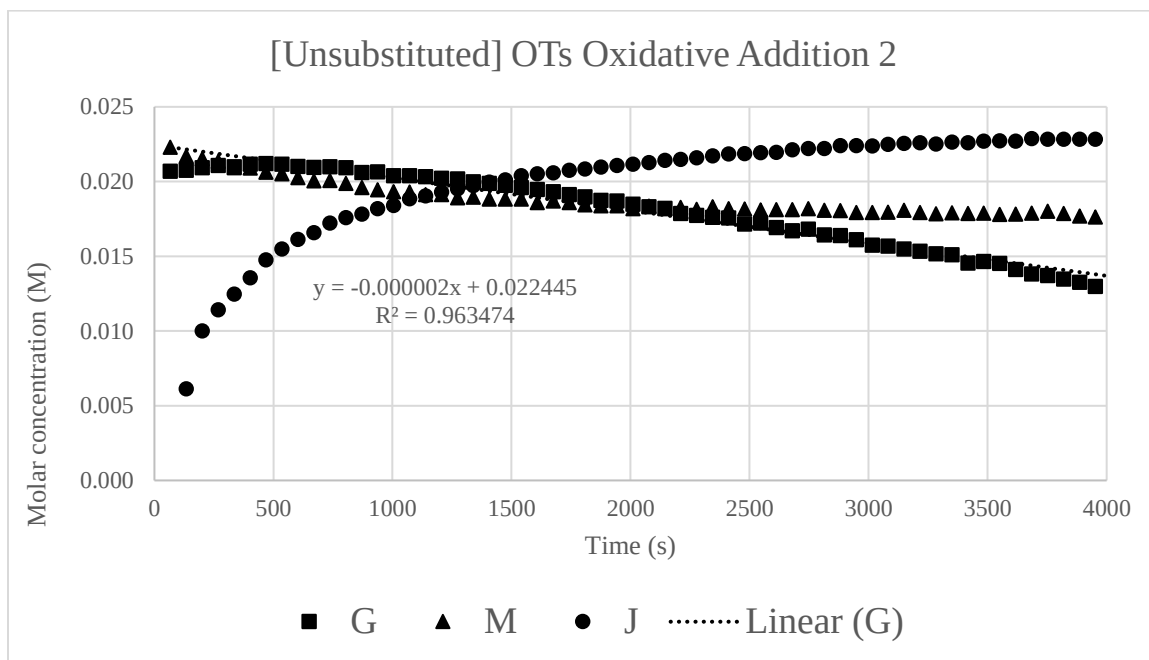
APPENDIX B

GRAPHS OF KINETIC ANALYSES

Note that for Graphs where linear trends are not marked, that rate constants were calculated from the most linear portions of those trends.

Table 5. NMR acquisition parameters for quantitative NMR analysis of synthesized compounds

| <b>Parameter</b>      | <b><sup>31</sup>P</b> |
|-----------------------|-----------------------|
| NS                    | 16                    |
| AQ [Sec]              | 1.8350080             |
| Pulse Angle           | 30                    |
| SW [ppm]              | 88.1845               |
| O1P [ppm]             | 3.161                 |
| TD                    | 65536                 |
| DS                    | 0                     |
| D1 [sec]              | 2.0                   |
| CPDPRG                | waltz16               |
| PULPROG               | zgpg30                |
| Powergated Decoupling | Y                     |

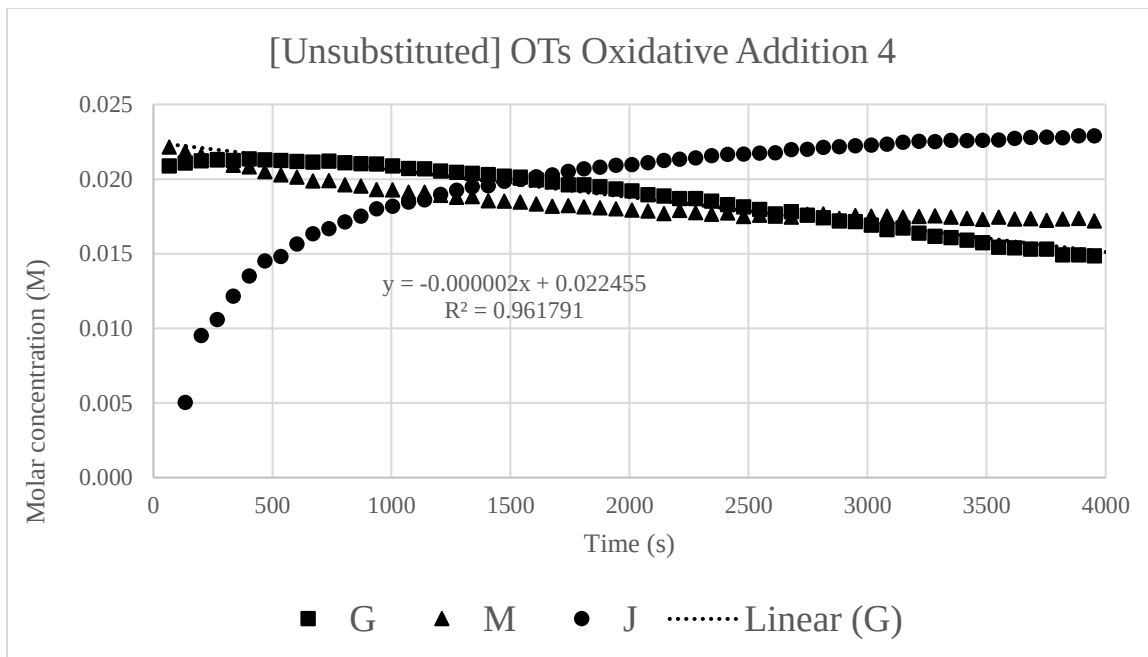
Table: Raw Data For [Unsubstituted] OTs Oxidative Addition 2<sup>1</sup>

| A  | B    | C   | D     | E      | F     | G     | H      | I      | J      | K       | L     | M     |
|----|------|-----|-------|--------|-------|-------|--------|--------|--------|---------|-------|-------|
| 1  | 67   | 100 | 4.605 | 72.733 | 4.287 | 0.021 | 0.354  | -1.039 | -0.005 | 101.525 | 4.620 | 0.022 |
| 2  | 134  | 100 | 4.605 | 73.739 | 4.301 | 0.021 | 3.556  | 1.269  | 0.006  | 89.553  | 4.495 | 0.022 |
| 3  | 201  | 100 | 4.605 | 76.510 | 4.337 | 0.021 | 7.951  | 2.073  | 0.010  | 86.394  | 4.459 | 0.022 |
| 4  | 268  | 100 | 4.605 | 78.750 | 4.366 | 0.021 | 10.680 | 2.368  | 0.011  | 83.452  | 4.424 | 0.021 |
| 5  | 335  | 100 | 4.605 | 77.501 | 4.350 | 0.021 | 13.257 | 2.585  | 0.012  | 76.617  | 4.339 | 0.021 |
| 6  | 402  | 100 | 4.605 | 80.279 | 4.386 | 0.021 | 16.606 | 2.810  | 0.014  | 76.075  | 4.332 | 0.021 |
| 7  | 469  | 100 | 4.605 | 80.833 | 4.392 | 0.021 | 21.323 | 3.060  | 0.015  | 71.991  | 4.277 | 0.021 |
| 8  | 536  | 100 | 4.605 | 80.135 | 4.384 | 0.021 | 24.772 | 3.210  | 0.015  | 70.318  | 4.253 | 0.021 |
| 9  | 603  | 100 | 4.605 | 77.669 | 4.352 | 0.021 | 28.250 | 3.341  | 0.016  | 66.482  | 4.197 | 0.020 |
| 10 | 670  | 100 | 4.605 | 76.917 | 4.343 | 0.021 | 31.051 | 3.436  | 0.017  | 63.734  | 4.155 | 0.020 |
| 11 | 737  | 100 | 4.605 | 77.560 | 4.351 | 0.021 | 35.547 | 3.571  | 0.017  | 64.061  | 4.160 | 0.020 |
| 12 | 804  | 100 | 4.605 | 76.589 | 4.338 | 0.021 | 38.250 | 3.644  | 0.018  | 61.457  | 4.118 | 0.020 |
| 13 | 871  | 100 | 4.605 | 71.675 | 4.272 | 0.021 | 40.209 | 3.694  | 0.018  | 58.167  | 4.063 | 0.020 |
| 14 | 938  | 100 | 4.605 | 72.184 | 4.279 | 0.021 | 43.269 | 3.767  | 0.018  | 56.304  | 4.031 | 0.019 |
| 15 | 1005 | 100 | 4.605 | 68.286 | 4.224 | 0.020 | 45.248 | 3.812  | 0.018  | 54.838  | 4.004 | 0.019 |
| 16 | 1072 | 100 | 4.605 | 68.463 | 4.226 | 0.020 | 49.734 | 3.907  | 0.019  | 54.674  | 4.001 | 0.019 |
| 17 | 1139 | 100 | 4.605 | 67.409 | 4.211 | 0.020 | 51.672 | 3.945  | 0.019  | 52.643  | 3.964 | 0.019 |

<sup>1</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~-10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |     |       |        |       |       |         |       |       |        |       |       |
|----|------|-----|-------|--------|-------|-------|---------|-------|-------|--------|-------|-------|
| 18 | 1206 | 100 | 4.605 | 65.956 | 4.189 | 0.020 | 54.594  | 4.000 | 0.019 | 52.724 | 3.965 | 0.019 |
| 19 | 1273 | 100 | 4.605 | 65.420 | 4.181 | 0.020 | 56.920  | 4.042 | 0.020 | 50.341 | 3.919 | 0.019 |
| 20 | 1340 | 100 | 4.605 | 62.827 | 4.140 | 0.020 | 59.565  | 4.087 | 0.020 | 50.888 | 3.930 | 0.019 |
| 21 | 1407 | 100 | 4.605 | 61.591 | 4.121 | 0.020 | 62.506  | 4.135 | 0.020 | 49.380 | 3.900 | 0.019 |
| 22 | 1474 | 100 | 4.605 | 60.016 | 4.095 | 0.020 | 64.716  | 4.170 | 0.020 | 49.565 | 3.903 | 0.019 |
| 23 | 1541 | 100 | 4.605 | 58.001 | 4.060 | 0.020 | 68.368  | 4.225 | 0.020 | 49.474 | 3.901 | 0.019 |
| 24 | 1608 | 100 | 4.605 | 56.428 | 4.033 | 0.019 | 70.226  | 4.252 | 0.021 | 47.120 | 3.853 | 0.019 |
| 25 | 1675 | 100 | 4.605 | 54.827 | 4.004 | 0.019 | 71.146  | 4.265 | 0.021 | 48.196 | 3.875 | 0.019 |
| 26 | 1742 | 100 | 4.605 | 52.660 | 3.964 | 0.019 | 73.881  | 4.302 | 0.021 | 47.065 | 3.852 | 0.019 |
| 27 | 1809 | 100 | 4.605 | 51.067 | 3.933 | 0.019 | 75.207  | 4.320 | 0.021 | 45.693 | 3.822 | 0.018 |
| 28 | 1876 | 100 | 4.605 | 48.627 | 3.884 | 0.019 | 76.979  | 4.344 | 0.021 | 45.172 | 3.810 | 0.018 |
| 29 | 1943 | 100 | 4.605 | 48.107 | 3.873 | 0.019 | 78.872  | 4.368 | 0.021 | 45.022 | 3.807 | 0.018 |
| 30 | 2010 | 100 | 4.605 | 46.089 | 3.831 | 0.018 | 80.248  | 4.385 | 0.021 | 43.403 | 3.771 | 0.018 |
| 31 | 2077 | 100 | 4.605 | 44.558 | 3.797 | 0.018 | 82.166  | 4.409 | 0.021 | 44.798 | 3.802 | 0.018 |
| 32 | 2144 | 100 | 4.605 | 43.455 | 3.772 | 0.018 | 84.714  | 4.439 | 0.021 | 43.399 | 3.770 | 0.018 |
| 33 | 2211 | 100 | 4.605 | 40.442 | 3.700 | 0.018 | 85.848  | 4.453 | 0.021 | 44.012 | 3.784 | 0.018 |
| 34 | 2278 | 100 | 4.605 | 39.380 | 3.673 | 0.018 | 87.701  | 4.474 | 0.022 | 42.950 | 3.760 | 0.018 |
| 35 | 2345 | 100 | 4.605 | 38.447 | 3.649 | 0.018 | 90.208  | 4.502 | 0.022 | 44.454 | 3.794 | 0.018 |
| 36 | 2412 | 100 | 4.605 | 38.160 | 3.642 | 0.018 | 92.337  | 4.525 | 0.022 | 43.400 | 3.770 | 0.018 |
| 37 | 2479 | 100 | 4.605 | 34.985 | 3.555 | 0.017 | 93.022  | 4.533 | 0.022 | 43.143 | 3.765 | 0.018 |
| 38 | 2546 | 100 | 4.605 | 35.432 | 3.568 | 0.017 | 94.170  | 4.545 | 0.022 | 42.549 | 3.751 | 0.018 |
| 39 | 2613 | 100 | 4.605 | 33.312 | 3.506 | 0.017 | 94.631  | 4.550 | 0.022 | 42.741 | 3.755 | 0.018 |
| 40 | 2680 | 100 | 4.605 | 31.865 | 3.461 | 0.017 | 97.803  | 4.583 | 0.022 | 42.778 | 3.756 | 0.018 |
| 41 | 2747 | 100 | 4.605 | 32.609 | 3.485 | 0.017 | 99.687  | 4.602 | 0.022 | 43.353 | 3.769 | 0.018 |
| 42 | 2814 | 100 | 4.605 | 30.099 | 3.404 | 0.016 | 99.904  | 4.604 | 0.022 | 42.445 | 3.748 | 0.018 |
| 43 | 2881 | 100 | 4.605 | 29.887 | 3.397 | 0.016 | 103.639 | 4.641 | 0.022 | 42.189 | 3.742 | 0.018 |
| 44 | 2948 | 100 | 4.605 | 28.110 | 3.336 | 0.016 | 103.631 | 4.641 | 0.022 | 41.086 | 3.716 | 0.018 |
| 45 | 3015 | 100 | 4.605 | 26.172 | 3.265 | 0.016 | 103.282 | 4.637 | 0.022 | 41.121 | 3.717 | 0.018 |
| 46 | 3082 | 100 | 4.605 | 25.817 | 3.251 | 0.016 | 105.641 | 4.660 | 0.022 | 41.249 | 3.720 | 0.018 |
| 47 | 3149 | 100 | 4.605 | 24.720 | 3.208 | 0.015 | 107.035 | 4.673 | 0.023 | 42.459 | 3.749 | 0.018 |
| 48 | 3216 | 100 | 4.605 | 23.966 | 3.177 | 0.015 | 107.848 | 4.681 | 0.023 | 41.040 | 3.715 | 0.018 |
| 49 | 3283 | 100 | 4.605 | 23.128 | 3.141 | 0.015 | 106.016 | 4.664 | 0.023 | 40.309 | 3.697 | 0.018 |
| 50 | 3350 | 100 | 4.605 | 22.819 | 3.128 | 0.015 | 109.019 | 4.692 | 0.023 | 40.893 | 3.711 | 0.018 |
| 51 | 3417 | 100 | 4.605 | 20.384 | 3.015 | 0.015 | 108.066 | 4.683 | 0.023 | 40.579 | 3.703 | 0.018 |
| 52 | 3484 | 100 | 4.605 | 20.864 | 3.038 | 0.015 | 110.457 | 4.705 | 0.023 | 40.675 | 3.706 | 0.018 |
| 53 | 3551 | 100 | 4.605 | 20.256 | 3.008 | 0.015 | 110.794 | 4.708 | 0.023 | 40.070 | 3.691 | 0.018 |
| 54 | 3618 | 100 | 4.605 | 18.621 | 2.924 | 0.014 | 110.543 | 4.705 | 0.023 | 40.129 | 3.692 | 0.018 |
| 55 | 3685 | 100 | 4.605 | 17.484 | 2.861 | 0.014 | 114.571 | 4.741 | 0.023 | 40.725 | 3.707 | 0.018 |
| 56 | 3752 | 100 | 4.605 | 17.164 | 2.843 | 0.014 | 113.646 | 4.733 | 0.023 | 41.765 | 3.732 | 0.018 |

|    |      |     |       |        |       |       |         |       |       |        |       |       |
|----|------|-----|-------|--------|-------|-------|---------|-------|-------|--------|-------|-------|
| 57 | 3819 | 100 | 4.605 | 16.323 | 2.793 | 0.013 | 113.380 | 4.731 | 0.023 | 40.481 | 3.701 | 0.018 |
| 58 | 3886 | 100 | 4.605 | 15.599 | 2.747 | 0.013 | 113.268 | 4.730 | 0.023 | 39.078 | 3.666 | 0.018 |
| 59 | 3953 | 100 | 4.605 | 14.762 | 2.692 | 0.013 | 113.324 | 4.730 | 0.023 | 38.600 | 3.653 | 0.018 |
| 60 | 4020 | 100 | 4.605 | 15.060 | 2.712 | 0.013 | 115.613 | 4.750 | 0.023 | 40.805 | 3.709 | 0.018 |

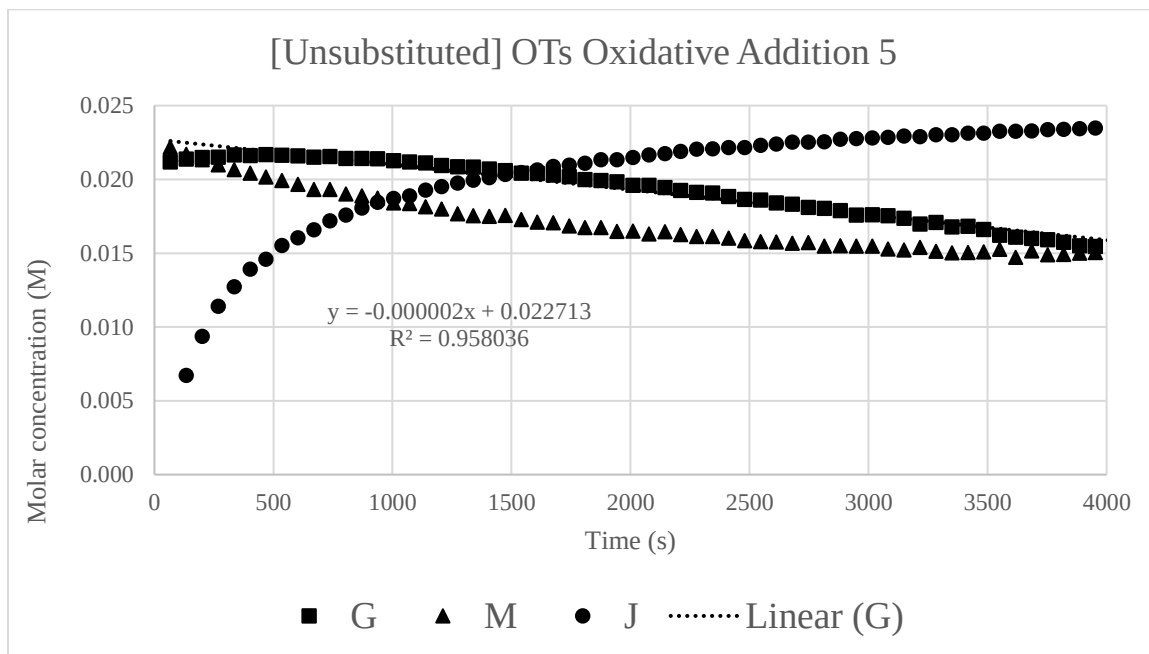
Table: Raw Data For [Unsubstituted] OTs Oxidative Addition 4<sup>2</sup>

| A  | B   | C   | D     | E      | F     | G     | H      | I      | J      | K      | L     | M     |
|----|-----|-----|-------|--------|-------|-------|--------|--------|--------|--------|-------|-------|
| 1  | 67  | 100 | 4.605 | 75.844 | 4.329 | 0.021 | 0.783  | -0.244 | -0.001 | 98.792 | 4.593 | 0.022 |
| 2  | 134 | 100 | 4.605 | 78.865 | 4.368 | 0.021 | 2.851  | 1.048  | 0.005  | 92.804 | 4.530 | 0.022 |
| 3  | 201 | 100 | 4.605 | 81.581 | 4.402 | 0.021 | 7.187  | 1.972  | 0.010  | 87.662 | 4.473 | 0.022 |
| 4  | 268 | 100 | 4.605 | 82.762 | 4.416 | 0.021 | 8.988  | 2.196  | 0.011  | 82.565 | 4.414 | 0.021 |
| 5  | 335 | 100 | 4.605 | 81.831 | 4.405 | 0.021 | 12.422 | 2.519  | 0.012  | 76.601 | 4.339 | 0.021 |
| 6  | 402 | 100 | 4.605 | 83.551 | 4.425 | 0.021 | 16.488 | 2.803  | 0.014  | 74.834 | 4.315 | 0.021 |
| 7  | 469 | 100 | 4.605 | 82.573 | 4.414 | 0.021 | 20.278 | 3.010  | 0.015  | 70.067 | 4.249 | 0.021 |
| 8  | 536 | 100 | 4.605 | 81.917 | 4.406 | 0.021 | 21.556 | 3.071  | 0.015  | 67.011 | 4.205 | 0.020 |
| 9  | 603 | 100 | 4.605 | 80.834 | 4.392 | 0.021 | 25.670 | 3.245  | 0.016  | 64.864 | 4.172 | 0.020 |
| 10 | 670 | 100 | 4.605 | 79.993 | 4.382 | 0.021 | 29.643 | 3.389  | 0.016  | 61.529 | 4.120 | 0.020 |
| 11 | 737 | 100 | 4.605 | 81.266 | 4.398 | 0.021 | 31.808 | 3.460  | 0.017  | 61.720 | 4.123 | 0.020 |

<sup>2</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~-10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |     |       |        |       |       |         |       |       |        |       |       |
|----|------|-----|-------|--------|-------|-------|---------|-------|-------|--------|-------|-------|
| 12 | 804  | 100 | 4.605 | 79.380 | 4.374 | 0.021 | 34.849  | 3.551 | 0.017 | 58.345 | 4.066 | 0.020 |
| 13 | 871  | 100 | 4.605 | 78.088 | 4.358 | 0.021 | 37.760  | 3.631 | 0.018 | 57.413 | 4.050 | 0.020 |
| 14 | 938  | 100 | 4.605 | 77.928 | 4.356 | 0.021 | 41.837  | 3.734 | 0.018 | 54.709 | 4.002 | 0.019 |
| 15 | 1005 | 100 | 4.605 | 75.889 | 4.329 | 0.021 | 43.250  | 3.767 | 0.018 | 54.258 | 3.994 | 0.019 |
| 16 | 1072 | 100 | 4.605 | 73.305 | 4.295 | 0.021 | 45.937  | 3.827 | 0.018 | 52.616 | 3.963 | 0.019 |
| 17 | 1139 | 100 | 4.605 | 72.942 | 4.290 | 0.021 | 47.370  | 3.858 | 0.019 | 52.652 | 3.964 | 0.019 |
| 18 | 1206 | 100 | 4.605 | 70.771 | 4.259 | 0.021 | 51.016  | 3.932 | 0.019 | 50.385 | 3.920 | 0.019 |
| 19 | 1273 | 100 | 4.605 | 69.529 | 4.242 | 0.020 | 54.216  | 3.993 | 0.019 | 49.109 | 3.894 | 0.019 |
| 20 | 1340 | 100 | 4.605 | 68.610 | 4.228 | 0.020 | 56.762  | 4.039 | 0.019 | 49.608 | 3.904 | 0.019 |
| 21 | 1407 | 100 | 4.605 | 67.274 | 4.209 | 0.020 | 57.520  | 4.052 | 0.020 | 46.742 | 3.845 | 0.019 |
| 22 | 1474 | 100 | 4.605 | 65.796 | 4.187 | 0.020 | 61.323  | 4.116 | 0.020 | 46.590 | 3.841 | 0.019 |
| 23 | 1541 | 100 | 4.605 | 65.045 | 4.175 | 0.020 | 63.035  | 4.144 | 0.020 | 46.018 | 3.829 | 0.018 |
| 24 | 1608 | 100 | 4.605 | 62.354 | 4.133 | 0.020 | 65.290  | 4.179 | 0.020 | 44.790 | 3.802 | 0.018 |
| 25 | 1675 | 100 | 4.605 | 60.791 | 4.107 | 0.020 | 67.068  | 4.206 | 0.020 | 43.293 | 3.768 | 0.018 |
| 26 | 1742 | 100 | 4.605 | 58.247 | 4.065 | 0.020 | 70.497  | 4.256 | 0.021 | 43.775 | 3.779 | 0.018 |
| 27 | 1809 | 100 | 4.605 | 58.389 | 4.067 | 0.020 | 72.836  | 4.288 | 0.021 | 42.991 | 3.761 | 0.018 |
| 28 | 1876 | 100 | 4.605 | 56.911 | 4.041 | 0.020 | 74.655  | 4.313 | 0.021 | 42.393 | 3.747 | 0.018 |
| 29 | 1943 | 100 | 4.605 | 55.115 | 4.009 | 0.019 | 76.414  | 4.336 | 0.021 | 41.787 | 3.733 | 0.018 |
| 30 | 2010 | 100 | 4.605 | 53.694 | 3.983 | 0.019 | 77.201  | 4.346 | 0.021 | 41.008 | 3.714 | 0.018 |
| 31 | 2077 | 100 | 4.605 | 50.869 | 3.929 | 0.019 | 79.355  | 4.374 | 0.021 | 40.519 | 3.702 | 0.018 |
| 32 | 2144 | 100 | 4.605 | 50.066 | 3.913 | 0.019 | 81.680  | 4.403 | 0.021 | 39.084 | 3.666 | 0.018 |
| 33 | 2211 | 100 | 4.605 | 48.275 | 3.877 | 0.019 | 83.430  | 4.424 | 0.021 | 40.992 | 3.713 | 0.018 |
| 34 | 2278 | 100 | 4.605 | 48.164 | 3.875 | 0.019 | 84.838  | 4.441 | 0.021 | 39.572 | 3.678 | 0.018 |
| 35 | 2345 | 100 | 4.605 | 46.588 | 3.841 | 0.019 | 87.474  | 4.471 | 0.022 | 38.800 | 3.658 | 0.018 |
| 36 | 2412 | 100 | 4.605 | 44.262 | 3.790 | 0.018 | 88.894  | 4.487 | 0.022 | 39.484 | 3.676 | 0.018 |
| 37 | 2479 | 100 | 4.605 | 42.998 | 3.761 | 0.018 | 89.512  | 4.494 | 0.022 | 37.537 | 3.625 | 0.017 |
| 38 | 2546 | 100 | 4.605 | 41.542 | 3.727 | 0.018 | 90.570  | 4.506 | 0.022 | 38.191 | 3.643 | 0.018 |
| 39 | 2613 | 100 | 4.605 | 39.000 | 3.664 | 0.018 | 90.958  | 4.510 | 0.022 | 37.684 | 3.629 | 0.018 |
| 40 | 2680 | 100 | 4.605 | 40.161 | 3.693 | 0.018 | 95.345  | 4.557 | 0.022 | 37.266 | 3.618 | 0.017 |
| 41 | 2747 | 100 | 4.605 | 38.345 | 3.647 | 0.018 | 95.577  | 4.560 | 0.022 | 38.748 | 3.657 | 0.018 |
| 42 | 2814 | 100 | 4.605 | 36.919 | 3.609 | 0.017 | 98.237  | 4.587 | 0.022 | 38.874 | 3.660 | 0.018 |
| 43 | 2881 | 100 | 4.605 | 35.306 | 3.564 | 0.017 | 99.011  | 4.595 | 0.022 | 36.570 | 3.599 | 0.017 |
| 44 | 2948 | 100 | 4.605 | 35.007 | 3.556 | 0.017 | 100.156 | 4.607 | 0.022 | 38.067 | 3.639 | 0.018 |
| 45 | 3015 | 100 | 4.605 | 33.367 | 3.508 | 0.017 | 101.258 | 4.618 | 0.022 | 37.690 | 3.629 | 0.018 |
| 46 | 3082 | 100 | 4.605 | 31.321 | 3.444 | 0.017 | 102.398 | 4.629 | 0.022 | 37.709 | 3.630 | 0.018 |
| 47 | 3149 | 100 | 4.605 | 32.036 | 3.467 | 0.017 | 105.305 | 4.657 | 0.022 | 37.215 | 3.617 | 0.017 |
| 48 | 3216 | 100 | 4.605 | 29.862 | 3.397 | 0.016 | 106.785 | 4.671 | 0.023 | 37.577 | 3.626 | 0.017 |
| 49 | 3283 | 100 | 4.605 | 28.602 | 3.353 | 0.016 | 106.374 | 4.667 | 0.023 | 37.852 | 3.634 | 0.018 |
| 50 | 3350 | 100 | 4.605 | 28.016 | 3.333 | 0.016 | 108.292 | 4.685 | 0.023 | 37.211 | 3.617 | 0.017 |

|    |      |     |       |        |       |       |         |       |       |        |       |       |
|----|------|-----|-------|--------|-------|-------|---------|-------|-------|--------|-------|-------|
| 51 | 3417 | 100 | 4.605 | 27.035 | 3.297 | 0.016 | 107.915 | 4.681 | 0.023 | 36.545 | 3.599 | 0.017 |
| 52 | 3484 | 100 | 4.605 | 26.165 | 3.264 | 0.016 | 108.364 | 4.685 | 0.023 | 36.165 | 3.588 | 0.017 |
| 53 | 3551 | 100 | 4.605 | 24.580 | 3.202 | 0.015 | 108.643 | 4.688 | 0.023 | 37.190 | 3.616 | 0.017 |
| 54 | 3618 | 100 | 4.605 | 24.330 | 3.192 | 0.015 | 111.007 | 4.710 | 0.023 | 36.326 | 3.593 | 0.017 |
| 55 | 3685 | 100 | 4.605 | 23.853 | 3.172 | 0.015 | 112.767 | 4.725 | 0.023 | 36.514 | 3.598 | 0.017 |
| 56 | 3752 | 100 | 4.605 | 23.879 | 3.173 | 0.015 | 112.923 | 4.727 | 0.023 | 35.692 | 3.575 | 0.017 |
| 57 | 3819 | 100 | 4.605 | 22.074 | 3.094 | 0.015 | 111.961 | 4.718 | 0.023 | 36.265 | 3.591 | 0.017 |
| 58 | 3886 | 100 | 4.605 | 22.063 | 3.094 | 0.015 | 115.067 | 4.746 | 0.023 | 36.569 | 3.599 | 0.017 |
| 59 | 3953 | 100 | 4.605 | 21.724 | 3.078 | 0.015 | 114.965 | 4.745 | 0.023 | 35.311 | 3.564 | 0.017 |
| 60 | 4020 | 100 | 4.605 | 20.161 | 3.004 | 0.014 | 115.683 | 4.751 | 0.023 | 35.686 | 3.575 | 0.017 |
| 61 | 4087 | 100 | 4.605 | 19.646 | 2.978 | 0.014 | 115.713 | 4.751 | 0.023 | 35.591 | 3.572 | 0.017 |
| 62 | 4154 | 100 | 4.605 | 18.507 | 2.918 | 0.014 | 116.948 | 4.762 | 0.023 | 34.884 | 3.552 | 0.017 |
| 63 | 4221 | 100 | 4.605 | 18.046 | 2.893 | 0.014 | 119.695 | 4.785 | 0.023 | 36.389 | 3.594 | 0.017 |
| 64 | 4288 | 100 | 4.605 | 17.186 | 2.844 | 0.014 | 118.516 | 4.775 | 0.023 | 34.704 | 3.547 | 0.017 |
| 65 | 4355 | 100 | 4.605 | 16.541 | 2.806 | 0.014 | 121.179 | 4.797 | 0.023 | 36.386 | 3.594 | 0.017 |
| 66 | 4422 | 100 | 4.605 | 18.672 | 2.927 | 0.014 | 134.691 | 4.903 | 0.024 | 36.499 | 3.597 | 0.017 |
| 67 | 4489 | 100 | 4.605 | 19.076 | 2.948 | 0.014 | 136.179 | 4.914 | 0.024 | 35.773 | 3.577 | 0.017 |
| 68 | 4556 | 100 | 4.605 | 17.299 | 2.851 | 0.014 | 137.282 | 4.922 | 0.024 | 36.127 | 3.587 | 0.017 |
| 69 | 4623 | 100 | 4.605 | 18.336 | 2.909 | 0.014 | 136.577 | 4.917 | 0.024 | 35.554 | 3.571 | 0.017 |
| 70 | 4690 | 100 | 4.605 | 17.844 | 2.882 | 0.014 | 136.372 | 4.915 | 0.024 | 36.198 | 3.589 | 0.017 |

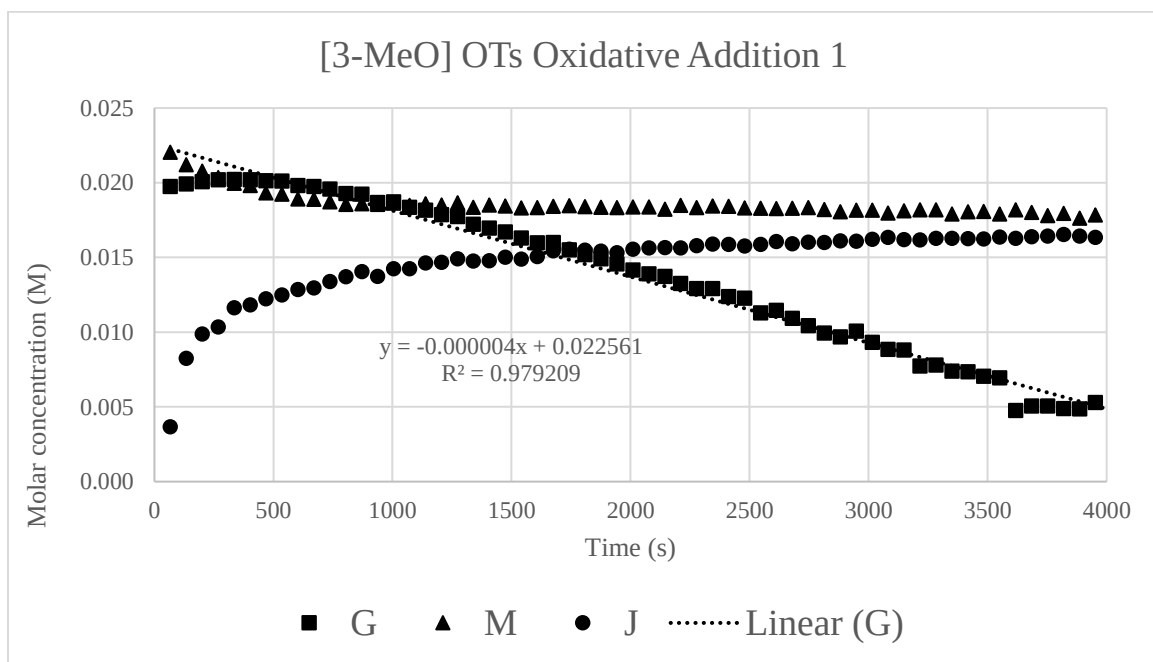
Table: Raw Data For [Unsubstituted] OTs Oxidative Addition 5<sup>3</sup>

| A  | B    | C       | D     | E      | F     | G     | H      | I      | J      | K      | L     | M     |
|----|------|---------|-------|--------|-------|-------|--------|--------|--------|--------|-------|-------|
| 1  | 67   | 100.000 | 4.605 | 80.703 | 4.391 | 0.021 | 0.371  | -0.992 | -0.005 | 99.052 | 4.596 | 0.022 |
| 2  | 134  | 100.000 | 4.605 | 84.173 | 4.433 | 0.021 | 4.035  | 1.395  | 0.007  | 89.961 | 4.499 | 0.022 |
| 3  | 201  | 100.000 | 4.605 | 85.807 | 4.452 | 0.021 | 6.979  | 1.943  | 0.009  | 83.440 | 4.424 | 0.021 |
| 4  | 268  | 100.000 | 4.605 | 86.259 | 4.457 | 0.022 | 10.651 | 2.366  | 0.011  | 77.415 | 4.349 | 0.021 |
| 5  | 335  | 100.000 | 4.605 | 88.975 | 4.488 | 0.022 | 13.989 | 2.638  | 0.013  | 72.535 | 4.284 | 0.021 |
| 6  | 402  | 100.000 | 4.605 | 88.452 | 4.482 | 0.022 | 17.913 | 2.886  | 0.014  | 69.041 | 4.235 | 0.020 |
| 7  | 469  | 100.000 | 4.605 | 89.332 | 4.492 | 0.022 | 20.567 | 3.024  | 0.015  | 65.270 | 4.179 | 0.020 |
| 8  | 536  | 100.000 | 4.605 | 88.860 | 4.487 | 0.022 | 25.015 | 3.219  | 0.016  | 62.191 | 4.130 | 0.020 |
| 9  | 603  | 100.000 | 4.605 | 87.911 | 4.476 | 0.022 | 27.821 | 3.326  | 0.016  | 59.072 | 4.079 | 0.020 |
| 10 | 670  | 100.000 | 4.605 | 86.466 | 4.460 | 0.022 | 31.155 | 3.439  | 0.017  | 54.950 | 4.006 | 0.019 |
| 11 | 737  | 100.000 | 4.605 | 87.116 | 4.467 | 0.022 | 35.352 | 3.565  | 0.017  | 54.755 | 4.003 | 0.019 |
| 12 | 804  | 100.000 | 4.605 | 84.802 | 4.440 | 0.021 | 38.294 | 3.645  | 0.018  | 51.417 | 3.940 | 0.019 |
| 13 | 871  | 100.000 | 4.605 | 84.756 | 4.440 | 0.021 | 42.285 | 3.744  | 0.018  | 50.029 | 3.913 | 0.019 |
| 14 | 938  | 100.000 | 4.605 | 84.251 | 4.434 | 0.021 | 45.797 | 3.824  | 0.018  | 48.543 | 3.882 | 0.019 |
| 15 | 1005 | 100.000 | 4.605 | 82.020 | 4.407 | 0.021 | 48.303 | 3.877  | 0.019  | 45.451 | 3.817 | 0.018 |
| 16 | 1072 | 100.000 | 4.605 | 80.564 | 4.389 | 0.021 | 50.116 | 3.914  | 0.019  | 44.956 | 3.806 | 0.018 |
| 17 | 1139 | 100.000 | 4.605 | 79.483 | 4.376 | 0.021 | 54.355 | 3.996  | 0.019  | 43.026 | 3.762 | 0.018 |

<sup>3</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~-9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~-10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |         |       |        |       |       |         |       |       |        |       |       |
|----|------|---------|-------|--------|-------|-------|---------|-------|-------|--------|-------|-------|
| 18 | 1206 | 100.000 | 4.605 | 76.747 | 4.341 | 0.021 | 57.123  | 4.045 | 0.020 | 41.771 | 3.732 | 0.018 |
| 19 | 1273 | 100.000 | 4.605 | 75.347 | 4.322 | 0.021 | 59.967  | 4.094 | 0.020 | 39.031 | 3.664 | 0.018 |
| 20 | 1340 | 100.000 | 4.605 | 75.156 | 4.320 | 0.021 | 62.407  | 4.134 | 0.020 | 37.900 | 3.635 | 0.018 |
| 21 | 1407 | 100.000 | 4.605 | 73.223 | 4.294 | 0.021 | 64.686  | 4.170 | 0.020 | 37.565 | 3.626 | 0.017 |
| 22 | 1474 | 100.000 | 4.605 | 71.391 | 4.268 | 0.021 | 67.751  | 4.216 | 0.020 | 38.158 | 3.642 | 0.018 |
| 23 | 1541 | 100.000 | 4.605 | 68.836 | 4.232 | 0.020 | 69.576  | 4.242 | 0.020 | 36.026 | 3.584 | 0.017 |
| 24 | 1608 | 100.000 | 4.605 | 68.782 | 4.231 | 0.020 | 71.985  | 4.276 | 0.021 | 34.655 | 3.545 | 0.017 |
| 25 | 1675 | 100.000 | 4.605 | 67.263 | 4.209 | 0.020 | 75.683  | 4.327 | 0.021 | 34.419 | 3.539 | 0.017 |
| 26 | 1742 | 100.000 | 4.605 | 65.778 | 4.186 | 0.020 | 77.056  | 4.345 | 0.021 | 32.852 | 3.492 | 0.017 |
| 27 | 1809 | 100.000 | 4.605 | 63.007 | 4.143 | 0.020 | 79.255  | 4.373 | 0.021 | 32.086 | 3.468 | 0.017 |
| 28 | 1876 | 100.000 | 4.605 | 62.270 | 4.131 | 0.020 | 83.359  | 4.423 | 0.021 | 32.160 | 3.471 | 0.017 |
| 29 | 1943 | 100.000 | 4.605 | 61.083 | 4.112 | 0.020 | 83.289  | 4.422 | 0.021 | 30.484 | 3.417 | 0.016 |
| 30 | 2010 | 100.000 | 4.605 | 58.278 | 4.065 | 0.020 | 86.100  | 4.456 | 0.022 | 30.538 | 3.419 | 0.016 |
| 31 | 2077 | 100.000 | 4.605 | 58.118 | 4.062 | 0.020 | 88.960  | 4.488 | 0.022 | 29.417 | 3.382 | 0.016 |
| 32 | 2144 | 100.000 | 4.605 | 56.387 | 4.032 | 0.019 | 90.917  | 4.510 | 0.022 | 30.342 | 3.413 | 0.016 |
| 33 | 2211 | 100.000 | 4.605 | 54.072 | 3.990 | 0.019 | 93.566  | 4.539 | 0.022 | 29.076 | 3.370 | 0.016 |
| 34 | 2278 | 100.000 | 4.605 | 52.661 | 3.964 | 0.019 | 96.627  | 4.571 | 0.022 | 28.279 | 3.342 | 0.016 |
| 35 | 2345 | 100.000 | 4.605 | 52.212 | 3.955 | 0.019 | 96.866  | 4.573 | 0.022 | 28.334 | 3.344 | 0.016 |
| 36 | 2412 | 100.000 | 4.605 | 49.754 | 3.907 | 0.019 | 98.752  | 4.593 | 0.022 | 27.766 | 3.324 | 0.016 |
| 37 | 2479 | 100.000 | 4.605 | 47.820 | 3.867 | 0.019 | 98.822  | 4.593 | 0.022 | 26.739 | 3.286 | 0.016 |
| 38 | 2546 | 100.000 | 4.605 | 47.391 | 3.858 | 0.019 | 101.769 | 4.623 | 0.022 | 26.352 | 3.272 | 0.016 |
| 39 | 2613 | 100.000 | 4.605 | 45.423 | 3.816 | 0.018 | 104.019 | 4.645 | 0.022 | 26.218 | 3.266 | 0.016 |
| 40 | 2680 | 100.000 | 4.605 | 44.646 | 3.799 | 0.018 | 106.670 | 4.670 | 0.023 | 25.770 | 3.249 | 0.016 |
| 41 | 2747 | 100.000 | 4.605 | 42.602 | 3.752 | 0.018 | 106.797 | 4.671 | 0.023 | 26.008 | 3.258 | 0.016 |
| 42 | 2814 | 100.000 | 4.605 | 42.009 | 3.738 | 0.018 | 106.927 | 4.672 | 0.023 | 24.770 | 3.210 | 0.015 |
| 43 | 2881 | 100.000 | 4.605 | 40.795 | 3.709 | 0.018 | 110.915 | 4.709 | 0.023 | 24.835 | 3.212 | 0.016 |
| 44 | 2948 | 100.000 | 4.605 | 38.292 | 3.645 | 0.018 | 111.934 | 4.718 | 0.023 | 24.734 | 3.208 | 0.015 |
| 45 | 3015 | 100.000 | 4.605 | 38.536 | 3.652 | 0.018 | 112.814 | 4.726 | 0.023 | 24.725 | 3.208 | 0.015 |
| 46 | 3082 | 100.000 | 4.605 | 37.963 | 3.637 | 0.018 | 114.115 | 4.737 | 0.023 | 23.781 | 3.169 | 0.015 |
| 47 | 3149 | 100.000 | 4.605 | 36.657 | 3.602 | 0.017 | 116.096 | 4.754 | 0.023 | 23.487 | 3.156 | 0.015 |
| 48 | 3216 | 100.000 | 4.605 | 33.769 | 3.520 | 0.017 | 114.988 | 4.745 | 0.023 | 24.316 | 3.191 | 0.015 |
| 49 | 3283 | 100.000 | 4.605 | 34.472 | 3.540 | 0.017 | 118.229 | 4.773 | 0.023 | 23.073 | 3.139 | 0.015 |
| 50 | 3350 | 100.000 | 4.605 | 32.435 | 3.479 | 0.017 | 118.427 | 4.774 | 0.023 | 22.556 | 3.116 | 0.015 |
| 51 | 3417 | 100.000 | 4.605 | 32.657 | 3.486 | 0.017 | 120.897 | 4.795 | 0.023 | 22.678 | 3.121 | 0.015 |
| 52 | 3484 | 100.000 | 4.605 | 31.336 | 3.445 | 0.017 | 121.043 | 4.796 | 0.023 | 22.830 | 3.128 | 0.015 |
| 53 | 3551 | 100.000 | 4.605 | 28.862 | 3.363 | 0.016 | 124.367 | 4.823 | 0.023 | 23.719 | 3.166 | 0.015 |
| 54 | 3618 | 100.000 | 4.605 | 28.136 | 3.337 | 0.016 | 124.280 | 4.823 | 0.023 | 21.162 | 3.052 | 0.015 |
| 55 | 3685 | 100.000 | 4.605 | 27.575 | 3.317 | 0.016 | 124.926 | 4.828 | 0.023 | 23.142 | 3.142 | 0.015 |
| 56 | 3752 | 100.000 | 4.605 | 27.129 | 3.301 | 0.016 | 127.267 | 4.846 | 0.023 | 21.903 | 3.087 | 0.015 |

|    |      |         |       |        |       |       |         |       |       |        |       |       |
|----|------|---------|-------|--------|-------|-------|---------|-------|-------|--------|-------|-------|
| 57 | 3819 | 100.000 | 4.605 | 26.082 | 3.261 | 0.016 | 127.488 | 4.848 | 0.023 | 22.035 | 3.093 | 0.015 |
| 58 | 3886 | 100.000 | 4.605 | 24.930 | 3.216 | 0.016 | 128.915 | 4.859 | 0.023 | 22.442 | 3.111 | 0.015 |
| 59 | 3953 | 100.000 | 4.605 | 24.709 | 3.207 | 0.015 | 130.237 | 4.869 | 0.023 | 22.609 | 3.118 | 0.015 |
| 60 | 4020 | 100.000 | 4.605 | 23.901 | 3.174 | 0.015 | 129.288 | 4.862 | 0.023 | 21.555 | 3.071 | 0.015 |
| 61 | 4087 | 100.000 | 4.605 | 23.546 | 3.159 | 0.015 | 132.519 | 4.887 | 0.024 | 21.805 | 3.082 | 0.015 |
| 62 | 4154 | 100.000 | 4.605 | 21.018 | 3.045 | 0.015 | 133.627 | 4.895 | 0.024 | 21.453 | 3.066 | 0.015 |
| 63 | 4221 | 100.000 | 4.605 | 21.977 | 3.090 | 0.015 | 134.748 | 4.903 | 0.024 | 22.268 | 3.103 | 0.015 |
| 64 | 4288 | 100.000 | 4.605 | 21.150 | 3.052 | 0.015 | 134.429 | 4.901 | 0.024 | 20.054 | 2.998 | 0.014 |
| 65 | 4355 | 100.000 | 4.605 | 20.344 | 3.013 | 0.015 | 134.624 | 4.902 | 0.024 | 20.531 | 3.022 | 0.015 |
| 66 | 4422 | 100.000 | 4.605 | 18.894 | 2.939 | 0.014 | 133.225 | 4.892 | 0.024 | 21.393 | 3.063 | 0.015 |
| 67 | 4489 | 100.000 | 4.605 | 18.951 | 2.942 | 0.014 | 136.442 | 4.916 | 0.024 | 20.844 | 3.037 | 0.015 |
| 68 | 4556 | 100.000 | 4.605 | 18.025 | 2.892 | 0.014 | 137.860 | 4.926 | 0.024 | 18.895 | 2.939 | 0.014 |
| 69 | 4623 | 100.000 | 4.605 | 17.775 | 2.878 | 0.014 | 136.876 | 4.919 | 0.024 | 21.200 | 3.054 | 0.015 |
| 70 | 4690 | 100.000 | 4.605 | 16.764 | 2.819 | 0.014 | 137.017 | 4.920 | 0.024 | 21.165 | 3.052 | 0.015 |

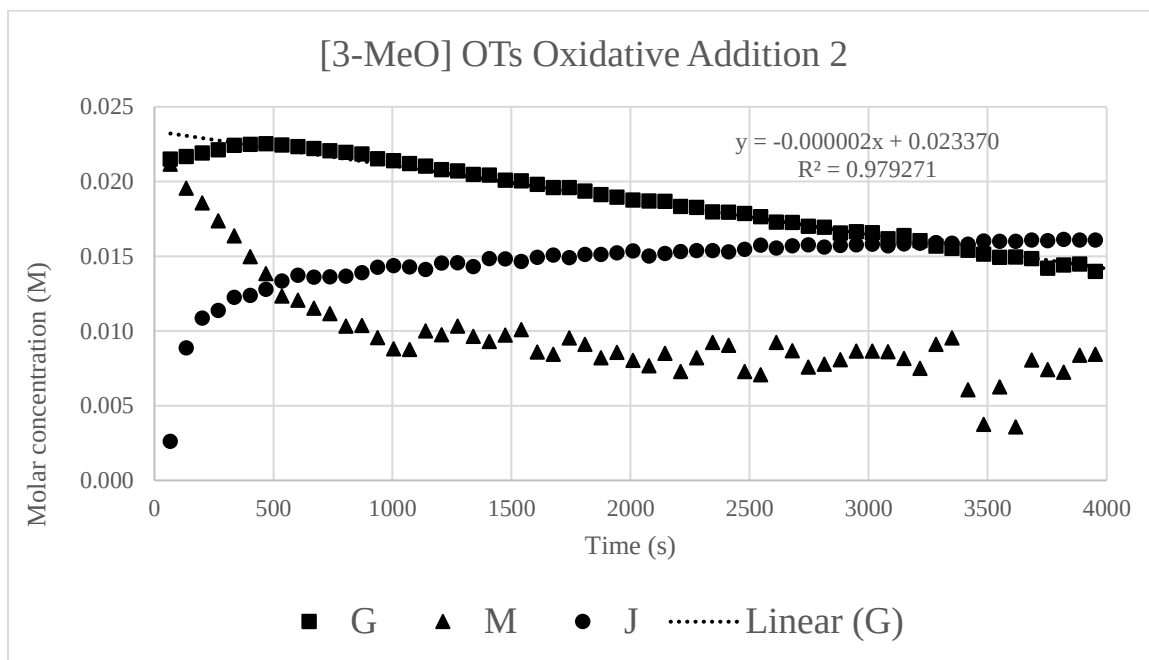
Table: Raw Data For [3-MeO] OTs Oxidative Addition 1<sup>4</sup>

| A | B  | C   | D     | E      | F     | G     | H     | I     | J     | K      | L     | M     |
|---|----|-----|-------|--------|-------|-------|-------|-------|-------|--------|-------|-------|
| 1 | 67 | 100 | 4.605 | 59.906 | 4.093 | 0.020 | 2.132 | 0.757 | 0.004 | 96.378 | 4.568 | 0.022 |

<sup>4</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |     |       |        |       |       |        |       |       |        |       |       |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|--------|-------|-------|
| 2  | 134  | 100 | 4.605 | 62.017 | 4.127 | 0.020 | 5.516  | 1.708 | 0.008 | 81.002 | 4.394 | 0.021 |
| 3  | 201  | 100 | 4.605 | 63.820 | 4.156 | 0.020 | 7.728  | 2.045 | 0.010 | 73.858 | 4.302 | 0.021 |
| 4  | 268  | 100 | 4.605 | 65.691 | 4.185 | 0.020 | 8.522  | 2.143 | 0.010 | 67.711 | 4.215 | 0.020 |
| 5  | 335  | 100 | 4.605 | 65.906 | 4.188 | 0.020 | 11.123 | 2.409 | 0.012 | 62.538 | 4.136 | 0.020 |
| 6  | 402  | 100 | 4.605 | 65.653 | 4.184 | 0.020 | 11.581 | 2.449 | 0.012 | 60.529 | 4.103 | 0.020 |
| 7  | 469  | 100 | 4.605 | 64.935 | 4.173 | 0.020 | 12.576 | 2.532 | 0.012 | 54.751 | 4.003 | 0.019 |
| 8  | 536  | 100 | 4.605 | 64.628 | 4.169 | 0.020 | 13.273 | 2.586 | 0.012 | 53.754 | 3.984 | 0.019 |
| 9  | 603  | 100 | 4.605 | 60.716 | 4.106 | 0.020 | 14.345 | 2.663 | 0.013 | 50.346 | 3.919 | 0.019 |
| 10 | 670  | 100 | 4.605 | 59.880 | 4.092 | 0.020 | 14.641 | 2.684 | 0.013 | 50.115 | 3.914 | 0.019 |
| 11 | 737  | 100 | 4.605 | 57.662 | 4.055 | 0.020 | 16.015 | 2.774 | 0.013 | 48.284 | 3.877 | 0.019 |
| 12 | 804  | 100 | 4.605 | 54.319 | 3.995 | 0.019 | 17.083 | 2.838 | 0.014 | 46.702 | 3.844 | 0.019 |
| 13 | 871  | 100 | 4.605 | 53.833 | 3.986 | 0.019 | 18.405 | 2.913 | 0.014 | 47.073 | 3.852 | 0.019 |
| 14 | 938  | 100 | 4.605 | 47.986 | 3.871 | 0.019 | 17.166 | 2.843 | 0.014 | 46.676 | 3.843 | 0.019 |
| 15 | 1005 | 100 | 4.605 | 48.246 | 3.876 | 0.019 | 19.158 | 2.953 | 0.014 | 47.419 | 3.859 | 0.019 |
| 16 | 1072 | 100 | 4.605 | 44.894 | 3.804 | 0.018 | 19.152 | 2.952 | 0.014 | 45.957 | 3.828 | 0.018 |
| 17 | 1139 | 100 | 4.605 | 43.126 | 3.764 | 0.018 | 20.683 | 3.029 | 0.015 | 46.999 | 3.850 | 0.019 |
| 18 | 1206 | 100 | 4.605 | 40.537 | 3.702 | 0.018 | 20.892 | 3.039 | 0.015 | 46.311 | 3.835 | 0.019 |
| 19 | 1273 | 100 | 4.605 | 39.342 | 3.672 | 0.018 | 21.959 | 3.089 | 0.015 | 47.631 | 3.863 | 0.019 |
| 20 | 1340 | 100 | 4.605 | 35.445 | 3.568 | 0.017 | 21.282 | 3.058 | 0.015 | 44.762 | 3.801 | 0.018 |
| 21 | 1407 | 100 | 4.605 | 33.641 | 3.516 | 0.017 | 21.327 | 3.060 | 0.015 | 46.265 | 3.834 | 0.019 |
| 22 | 1474 | 100 | 4.605 | 31.843 | 3.461 | 0.017 | 22.460 | 3.112 | 0.015 | 45.626 | 3.820 | 0.018 |
| 23 | 1541 | 100 | 4.605 | 29.307 | 3.378 | 0.016 | 21.886 | 3.086 | 0.015 | 44.467 | 3.795 | 0.018 |
| 24 | 1608 | 100 | 4.605 | 27.336 | 3.308 | 0.016 | 22.621 | 3.119 | 0.015 | 44.553 | 3.797 | 0.018 |
| 25 | 1675 | 100 | 4.605 | 27.558 | 3.316 | 0.016 | 24.544 | 3.200 | 0.015 | 45.396 | 3.815 | 0.018 |
| 26 | 1742 | 100 | 4.605 | 24.806 | 3.211 | 0.015 | 25.077 | 3.222 | 0.016 | 45.784 | 3.824 | 0.018 |
| 27 | 1809 | 100 | 4.605 | 23.277 | 3.147 | 0.015 | 24.750 | 3.209 | 0.015 | 45.319 | 3.814 | 0.018 |
| 28 | 1876 | 100 | 4.605 | 21.955 | 3.089 | 0.015 | 24.418 | 3.195 | 0.015 | 44.752 | 3.801 | 0.018 |
| 29 | 1943 | 100 | 4.605 | 20.474 | 3.019 | 0.015 | 23.864 | 3.172 | 0.015 | 44.606 | 3.798 | 0.018 |
| 30 | 2010 | 100 | 4.605 | 18.825 | 2.935 | 0.014 | 25.057 | 3.221 | 0.016 | 45.080 | 3.808 | 0.018 |
| 31 | 2077 | 100 | 4.605 | 17.845 | 2.882 | 0.014 | 25.557 | 3.241 | 0.016 | 45.062 | 3.808 | 0.018 |
| 32 | 2144 | 100 | 4.605 | 17.153 | 2.842 | 0.014 | 25.657 | 3.245 | 0.016 | 43.677 | 3.777 | 0.018 |
| 33 | 2211 | 100 | 4.605 | 15.622 | 2.749 | 0.013 | 25.565 | 3.241 | 0.016 | 46.082 | 3.830 | 0.018 |
| 34 | 2278 | 100 | 4.605 | 14.502 | 2.674 | 0.013 | 26.355 | 3.272 | 0.016 | 44.675 | 3.799 | 0.018 |
| 35 | 2345 | 100 | 4.605 | 14.519 | 2.675 | 0.013 | 26.927 | 3.293 | 0.016 | 45.666 | 3.821 | 0.018 |
| 36 | 2412 | 100 | 4.605 | 13.004 | 2.565 | 0.012 | 26.788 | 3.288 | 0.016 | 45.395 | 3.815 | 0.018 |
| 37 | 2479 | 100 | 4.605 | 12.702 | 2.542 | 0.012 | 26.180 | 3.265 | 0.016 | 44.492 | 3.795 | 0.018 |
| 38 | 2546 | 100 | 4.605 | 10.371 | 2.339 | 0.011 | 26.826 | 3.289 | 0.016 | 44.212 | 3.789 | 0.018 |
| 39 | 2613 | 100 | 4.605 | 10.733 | 2.373 | 0.011 | 27.900 | 3.329 | 0.016 | 43.946 | 3.783 | 0.018 |
| 40 | 2680 | 100 | 4.605 | 9.599  | 2.262 | 0.011 | 27.085 | 3.299 | 0.016 | 44.262 | 3.790 | 0.018 |

|    |      |     |       |       |        |        |        |       |       |        |       |       |
|----|------|-----|-------|-------|--------|--------|--------|-------|-------|--------|-------|-------|
| 41 | 2747 | 100 | 4.605 | 8.692 | 2.162  | 0.010  | 27.607 | 3.318 | 0.016 | 44.617 | 3.798 | 0.018 |
| 42 | 2814 | 100 | 4.605 | 7.827 | 2.058  | 0.010  | 27.501 | 3.314 | 0.016 | 43.555 | 3.774 | 0.018 |
| 43 | 2881 | 100 | 4.605 | 7.445 | 2.008  | 0.010  | 28.078 | 3.335 | 0.016 | 42.067 | 3.739 | 0.018 |
| 44 | 2948 | 100 | 4.605 | 8.045 | 2.085  | 0.010  | 27.964 | 3.331 | 0.016 | 43.169 | 3.765 | 0.018 |
| 45 | 3015 | 100 | 4.605 | 6.893 | 1.931  | 0.009  | 28.766 | 3.359 | 0.016 | 43.090 | 3.763 | 0.018 |
| 46 | 3082 | 100 | 4.605 | 6.260 | 1.834  | 0.009  | 29.492 | 3.384 | 0.016 | 41.356 | 3.722 | 0.018 |
| 47 | 3149 | 100 | 4.605 | 6.204 | 1.825  | 0.009  | 28.649 | 3.355 | 0.016 | 42.779 | 3.756 | 0.018 |
| 48 | 3216 | 100 | 4.605 | 4.968 | 1.603  | 0.008  | 28.489 | 3.350 | 0.016 | 43.189 | 3.766 | 0.018 |
| 49 | 3283 | 100 | 4.605 | 5.038 | 1.617  | 0.008  | 29.212 | 3.375 | 0.016 | 43.180 | 3.765 | 0.018 |
| 50 | 3350 | 100 | 4.605 | 4.620 | 1.530  | 0.007  | 29.133 | 3.372 | 0.016 | 40.867 | 3.710 | 0.018 |
| 51 | 3417 | 100 | 4.605 | 4.575 | 1.521  | 0.007  | 29.036 | 3.369 | 0.016 | 42.044 | 3.739 | 0.018 |
| 52 | 3484 | 100 | 4.605 | 4.309 | 1.461  | 0.007  | 28.852 | 3.362 | 0.016 | 42.395 | 3.747 | 0.018 |
| 53 | 3551 | 100 | 4.605 | 4.205 | 1.436  | 0.007  | 29.694 | 3.391 | 0.016 | 40.801 | 3.709 | 0.018 |
| 54 | 3618 | 100 | 4.605 | 2.674 | 0.984  | 0.005  | 29.144 | 3.372 | 0.016 | 43.263 | 3.767 | 0.018 |
| 55 | 3685 | 100 | 4.605 | 2.851 | 1.048  | 0.005  | 29.809 | 3.395 | 0.016 | 41.682 | 3.730 | 0.018 |
| 56 | 3752 | 100 | 4.605 | 2.846 | 1.046  | 0.005  | 30.025 | 3.402 | 0.016 | 39.858 | 3.685 | 0.018 |
| 57 | 3819 | 100 | 4.605 | 2.755 | 1.013  | 0.005  | 30.808 | 3.428 | 0.017 | 41.171 | 3.718 | 0.018 |
| 58 | 3886 | 100 | 4.605 | 2.742 | 1.009  | 0.005  | 30.063 | 3.403 | 0.016 | 38.633 | 3.654 | 0.018 |
| 59 | 3953 | 100 | 4.605 | 2.991 | 1.096  | 0.005  | 29.506 | 3.385 | 0.016 | 40.304 | 3.696 | 0.018 |
| 60 | 4020 | 100 | 4.605 | 2.210 | 0.793  | 0.004  | 29.673 | 3.390 | 0.016 | 39.358 | 3.673 | 0.018 |
| 61 | 4087 | 100 | 4.605 | 2.484 | 0.910  | 0.004  | 30.102 | 3.405 | 0.016 | 39.536 | 3.677 | 0.018 |
| 62 | 4154 | 100 | 4.605 | 2.714 | 0.999  | 0.005  | 30.525 | 3.419 | 0.016 | 38.799 | 3.658 | 0.018 |
| 63 | 4221 | 100 | 4.605 | 2.407 | 0.879  | 0.004  | 30.714 | 3.425 | 0.017 | 40.010 | 3.689 | 0.018 |
| 64 | 4288 | 100 | 4.605 | 1.623 | 0.484  | 0.002  | 30.387 | 3.414 | 0.016 | 38.491 | 3.650 | 0.018 |
| 65 | 4355 | 100 | 4.605 | 0.929 | -0.074 | 0.000  | 30.787 | 3.427 | 0.017 | 36.728 | 3.604 | 0.017 |
| 66 | 4422 | 100 | 4.605 | 1.065 | 0.063  | 0.000  | 29.897 | 3.398 | 0.016 | 36.581 | 3.600 | 0.017 |
| 67 | 4489 | 100 | 4.605 | 0.834 | -0.181 | -0.001 | 30.173 | 3.407 | 0.016 | 39.692 | 3.681 | 0.018 |
| 68 | 4556 | 100 | 4.605 | 2.261 | 0.816  | 0.004  | 31.757 | 3.458 | 0.017 | 35.877 | 3.580 | 0.017 |
| 69 | 4623 | 100 | 4.605 | 1.553 | 0.440  | 0.002  | 31.511 | 3.450 | 0.017 | 37.944 | 3.636 | 0.018 |
| 70 | 4690 | 100 | 4.605 | 0.572 | -0.558 | -0.003 | 31.142 | 3.439 | 0.017 | 37.736 | 3.631 | 0.018 |

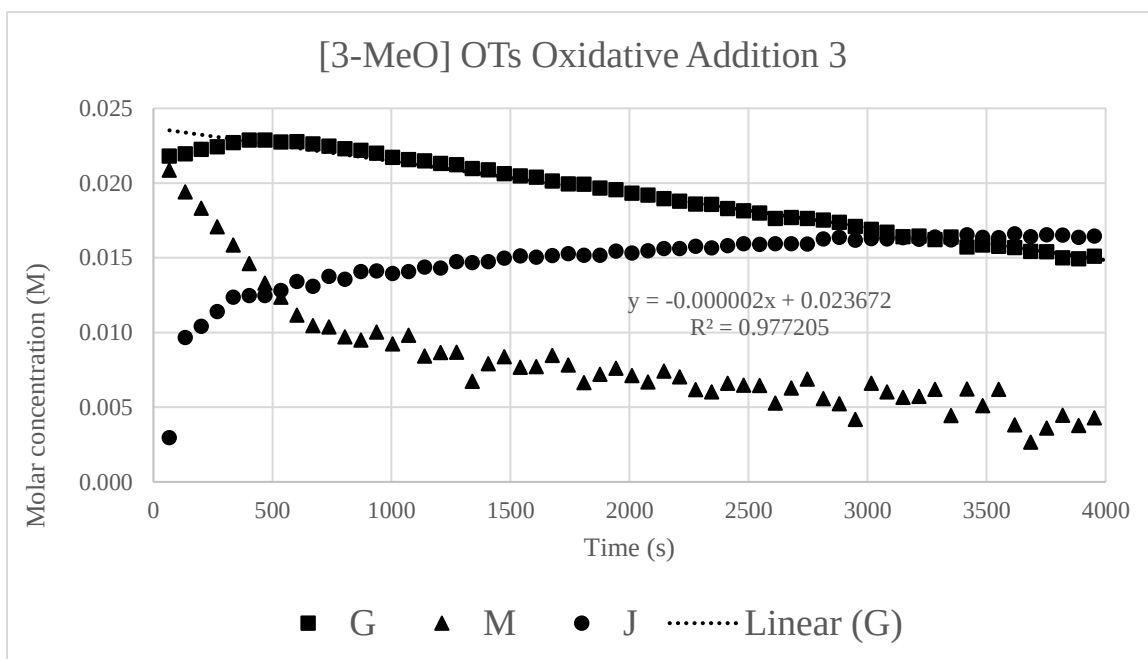
Table: Raw Data For [3-MeO] OTs Oxidative Addition 2<sup>5</sup>

| A  | B    | C       | D     | E       | F     | G     | H      | I     | J     | K      | L     | M     |
|----|------|---------|-------|---------|-------|-------|--------|-------|-------|--------|-------|-------|
| 1  | 67   | 100.000 | 4.605 | 86.326  | 4.458 | 0.022 | 1.721  | 0.543 | 0.003 | 80.231 | 4.385 | 0.021 |
| 2  | 134  | 100.000 | 4.605 | 89.414  | 4.493 | 0.022 | 6.274  | 1.836 | 0.009 | 57.509 | 4.052 | 0.020 |
| 3  | 201  | 100.000 | 4.605 | 93.838  | 4.542 | 0.022 | 9.496  | 2.251 | 0.011 | 46.899 | 3.848 | 0.019 |
| 4  | 268  | 100.000 | 4.605 | 98.136  | 4.586 | 0.022 | 10.541 | 2.355 | 0.011 | 36.652 | 3.601 | 0.017 |
| 5  | 335  | 100.000 | 4.605 | 104.524 | 4.649 | 0.022 | 12.683 | 2.540 | 0.012 | 29.692 | 3.391 | 0.016 |
| 6  | 402  | 100.000 | 4.605 | 105.902 | 4.663 | 0.022 | 13.041 | 2.568 | 0.012 | 22.264 | 3.103 | 0.015 |
| 7  | 469  | 100.000 | 4.605 | 106.663 | 4.670 | 0.023 | 14.166 | 2.651 | 0.013 | 17.589 | 2.867 | 0.014 |
| 8  | 536  | 100.000 | 4.605 | 104.874 | 4.653 | 0.022 | 15.906 | 2.767 | 0.013 | 12.912 | 2.558 | 0.012 |
| 9  | 603  | 100.000 | 4.605 | 102.478 | 4.630 | 0.022 | 17.213 | 2.846 | 0.014 | 12.164 | 2.499 | 0.012 |
| 10 | 670  | 100.000 | 4.605 | 99.580  | 4.601 | 0.022 | 16.747 | 2.818 | 0.014 | 10.909 | 2.390 | 0.012 |
| 11 | 737  | 100.000 | 4.605 | 96.764  | 4.572 | 0.022 | 16.811 | 2.822 | 0.014 | 10.084 | 2.311 | 0.011 |
| 12 | 804  | 100.000 | 4.605 | 94.716  | 4.551 | 0.022 | 16.951 | 2.830 | 0.014 | 8.483  | 2.138 | 0.010 |
| 13 | 871  | 100.000 | 4.605 | 92.488  | 4.527 | 0.022 | 17.836 | 2.881 | 0.014 | 8.587  | 2.150 | 0.010 |
| 14 | 938  | 100.000 | 4.605 | 86.635  | 4.462 | 0.022 | 19.221 | 2.956 | 0.014 | 7.250  | 1.981 | 0.010 |
| 15 | 1005 | 100.000 | 4.605 | 84.439  | 4.436 | 0.021 | 19.671 | 2.979 | 0.014 | 6.196  | 1.824 | 0.009 |
| 16 | 1072 | 100.000 | 4.605 | 81.094  | 4.396 | 0.021 | 19.282 | 2.959 | 0.014 | 6.135  | 1.814 | 0.009 |
| 17 | 1139 | 100.000 | 4.605 | 78.153  | 4.359 | 0.021 | 18.645 | 2.926 | 0.014 | 7.955  | 2.074 | 0.010 |

<sup>5</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |         |       |        |       |       |        |       |       |       |       |       |
|----|------|---------|-------|--------|-------|-------|--------|-------|-------|-------|-------|-------|
| 18 | 1206 | 100.000 | 4.605 | 74.594 | 4.312 | 0.021 | 20.411 | 3.016 | 0.015 | 7.530 | 2.019 | 0.010 |
| 19 | 1273 | 100.000 | 4.605 | 73.193 | 4.293 | 0.021 | 20.500 | 3.020 | 0.015 | 8.482 | 2.138 | 0.010 |
| 20 | 1340 | 100.000 | 4.605 | 69.685 | 4.244 | 0.020 | 19.432 | 2.967 | 0.014 | 7.368 | 1.997 | 0.010 |
| 21 | 1407 | 100.000 | 4.605 | 68.926 | 4.233 | 0.020 | 21.654 | 3.075 | 0.015 | 6.854 | 1.925 | 0.009 |
| 22 | 1474 | 100.000 | 4.605 | 64.272 | 4.163 | 0.020 | 21.572 | 3.071 | 0.015 | 7.495 | 2.014 | 0.010 |
| 23 | 1541 | 100.000 | 4.605 | 63.667 | 4.154 | 0.020 | 20.820 | 3.036 | 0.015 | 8.079 | 2.089 | 0.010 |
| 24 | 1608 | 100.000 | 4.605 | 60.623 | 4.105 | 0.020 | 22.068 | 3.094 | 0.015 | 5.923 | 1.779 | 0.009 |
| 25 | 1675 | 100.000 | 4.605 | 57.995 | 4.060 | 0.020 | 22.745 | 3.124 | 0.015 | 5.760 | 1.751 | 0.008 |
| 26 | 1742 | 100.000 | 4.605 | 58.133 | 4.063 | 0.020 | 22.014 | 3.092 | 0.015 | 7.202 | 1.974 | 0.010 |
| 27 | 1809 | 100.000 | 4.605 | 55.333 | 4.013 | 0.019 | 22.925 | 3.132 | 0.015 | 6.586 | 1.885 | 0.009 |
| 28 | 1876 | 100.000 | 4.605 | 52.690 | 3.964 | 0.019 | 23.005 | 3.136 | 0.015 | 5.478 | 1.701 | 0.008 |
| 29 | 1943 | 100.000 | 4.605 | 50.864 | 3.929 | 0.019 | 23.444 | 3.155 | 0.015 | 5.919 | 1.778 | 0.009 |
| 30 | 2010 | 100.000 | 4.605 | 48.874 | 3.889 | 0.019 | 24.163 | 3.185 | 0.015 | 5.286 | 1.665 | 0.008 |
| 31 | 2077 | 100.000 | 4.605 | 48.151 | 3.874 | 0.019 | 22.419 | 3.110 | 0.015 | 4.897 | 1.589 | 0.008 |
| 32 | 2144 | 100.000 | 4.605 | 48.055 | 3.872 | 0.019 | 23.273 | 3.147 | 0.015 | 5.827 | 1.763 | 0.009 |
| 33 | 2211 | 100.000 | 4.605 | 44.642 | 3.799 | 0.018 | 23.905 | 3.174 | 0.015 | 4.524 | 1.509 | 0.007 |
| 34 | 2278 | 100.000 | 4.605 | 44.181 | 3.788 | 0.018 | 24.274 | 3.189 | 0.015 | 5.487 | 1.702 | 0.008 |
| 35 | 2345 | 100.000 | 4.605 | 41.442 | 3.724 | 0.018 | 24.259 | 3.189 | 0.015 | 6.771 | 1.913 | 0.009 |
| 36 | 2412 | 100.000 | 4.605 | 41.190 | 3.718 | 0.018 | 23.832 | 3.171 | 0.015 | 6.514 | 1.874 | 0.009 |
| 37 | 2479 | 100.000 | 4.605 | 40.598 | 3.704 | 0.018 | 24.708 | 3.207 | 0.015 | 4.519 | 1.508 | 0.007 |
| 38 | 2546 | 100.000 | 4.605 | 38.720 | 3.656 | 0.018 | 26.116 | 3.263 | 0.016 | 4.325 | 1.464 | 0.007 |
| 39 | 2613 | 100.000 | 4.605 | 35.982 | 3.583 | 0.017 | 25.059 | 3.221 | 0.016 | 6.765 | 1.912 | 0.009 |
| 40 | 2680 | 100.000 | 4.605 | 35.816 | 3.578 | 0.017 | 25.894 | 3.254 | 0.016 | 6.039 | 1.798 | 0.009 |
| 41 | 2747 | 100.000 | 4.605 | 34.005 | 3.527 | 0.017 | 26.211 | 3.266 | 0.016 | 4.815 | 1.572 | 0.008 |
| 42 | 2814 | 100.000 | 4.605 | 33.498 | 3.511 | 0.017 | 25.457 | 3.237 | 0.016 | 5.006 | 1.611 | 0.008 |
| 43 | 2881 | 100.000 | 4.605 | 30.934 | 3.432 | 0.017 | 26.058 | 3.260 | 0.016 | 5.336 | 1.674 | 0.008 |
| 44 | 2948 | 100.000 | 4.605 | 31.459 | 3.449 | 0.017 | 26.248 | 3.268 | 0.016 | 6.013 | 1.794 | 0.009 |
| 45 | 3015 | 100.000 | 4.605 | 31.065 | 3.436 | 0.017 | 26.480 | 3.276 | 0.016 | 6.025 | 1.796 | 0.009 |
| 46 | 3082 | 100.000 | 4.605 | 28.572 | 3.352 | 0.016 | 25.893 | 3.254 | 0.016 | 5.950 | 1.783 | 0.009 |
| 47 | 3149 | 100.000 | 4.605 | 29.859 | 3.396 | 0.016 | 26.562 | 3.279 | 0.016 | 5.427 | 1.691 | 0.008 |
| 48 | 3216 | 100.000 | 4.605 | 27.791 | 3.325 | 0.016 | 26.798 | 3.288 | 0.016 | 4.728 | 1.554 | 0.007 |
| 49 | 3283 | 100.000 | 4.605 | 25.810 | 3.251 | 0.016 | 27.022 | 3.297 | 0.016 | 6.603 | 1.888 | 0.009 |
| 50 | 3350 | 100.000 | 4.605 | 25.018 | 3.220 | 0.016 | 26.808 | 3.289 | 0.016 | 7.206 | 1.975 | 0.010 |
| 51 | 3417 | 100.000 | 4.605 | 24.314 | 3.191 | 0.015 | 26.451 | 3.275 | 0.016 | 3.519 | 1.258 | 0.006 |
| 52 | 3484 | 100.000 | 4.605 | 23.056 | 3.138 | 0.015 | 27.622 | 3.319 | 0.016 | 2.177 | 0.778 | 0.004 |
| 53 | 3551 | 100.000 | 4.605 | 22.046 | 3.093 | 0.015 | 27.606 | 3.318 | 0.016 | 3.662 | 1.298 | 0.006 |
| 54 | 3618 | 100.000 | 4.605 | 22.154 | 3.098 | 0.015 | 27.536 | 3.316 | 0.016 | 2.098 | 0.741 | 0.004 |
| 55 | 3685 | 100.000 | 4.605 | 21.675 | 3.076 | 0.015 | 28.028 | 3.333 | 0.016 | 5.305 | 1.669 | 0.008 |
| 56 | 3752 | 100.000 | 4.605 | 18.966 | 2.943 | 0.014 | 27.749 | 3.323 | 0.016 | 4.646 | 1.536 | 0.007 |

|    |      |         |       |        |       |       |        |       |       |       |       |       |
|----|------|---------|-------|--------|-------|-------|--------|-------|-------|-------|-------|-------|
| 57 | 3819 | 100.000 | 4.605 | 19.804 | 2.986 | 0.014 | 28.242 | 3.341 | 0.016 | 4.477 | 1.499 | 0.007 |
| 58 | 3886 | 100.000 | 4.605 | 20.126 | 3.002 | 0.014 | 28.003 | 3.332 | 0.016 | 5.680 | 1.737 | 0.008 |
| 59 | 3953 | 100.000 | 4.605 | 18.157 | 2.899 | 0.014 | 28.024 | 3.333 | 0.016 | 5.742 | 1.748 | 0.008 |
| 60 | 4020 | 100.000 | 4.605 | 17.437 | 2.859 | 0.014 | 27.965 | 3.331 | 0.016 | 5.256 | 1.659 | 0.008 |
| 61 | 4087 | 100.000 | 4.605 | 18.626 | 2.925 | 0.014 | 28.727 | 3.358 | 0.016 | 7.611 | 2.030 | 0.010 |
| 62 | 4154 | 100.000 | 4.605 | 17.593 | 2.868 | 0.014 | 28.347 | 3.345 | 0.016 | 2.783 | 1.024 | 0.005 |
| 63 | 4221 | 100.000 | 4.605 | 14.972 | 2.706 | 0.013 | 28.399 | 3.346 | 0.016 | 3.364 | 1.213 | 0.006 |
| 64 | 4288 | 100.000 | 4.605 | 16.199 | 2.785 | 0.013 | 28.055 | 3.334 | 0.016 | 5.014 | 1.612 | 0.008 |
| 65 | 4355 | 100.000 | 4.605 | 14.460 | 2.671 | 0.013 | 28.680 | 3.356 | 0.016 | 4.640 | 1.535 | 0.007 |
| 66 | 4422 | 100.000 | 4.605 | 13.638 | 2.613 | 0.013 | 28.971 | 3.366 | 0.016 | 6.275 | 1.837 | 0.009 |
| 67 | 4489 | 100.000 | 4.605 | 13.912 | 2.633 | 0.013 | 28.193 | 3.339 | 0.016 | 4.787 | 1.566 | 0.008 |
| 68 | 4556 | 100.000 | 4.605 | 13.724 | 2.619 | 0.013 | 28.064 | 3.334 | 0.016 | 3.760 | 1.324 | 0.006 |
| 69 | 4623 | 100.000 | 4.605 | 13.562 | 2.607 | 0.013 | 27.646 | 3.319 | 0.016 | 6.642 | 1.893 | 0.009 |
| 70 | 4690 | 100.000 | 4.605 | 13.806 | 2.625 | 0.013 | 29.758 | 3.393 | 0.016 | 3.969 | 1.378 | 0.007 |

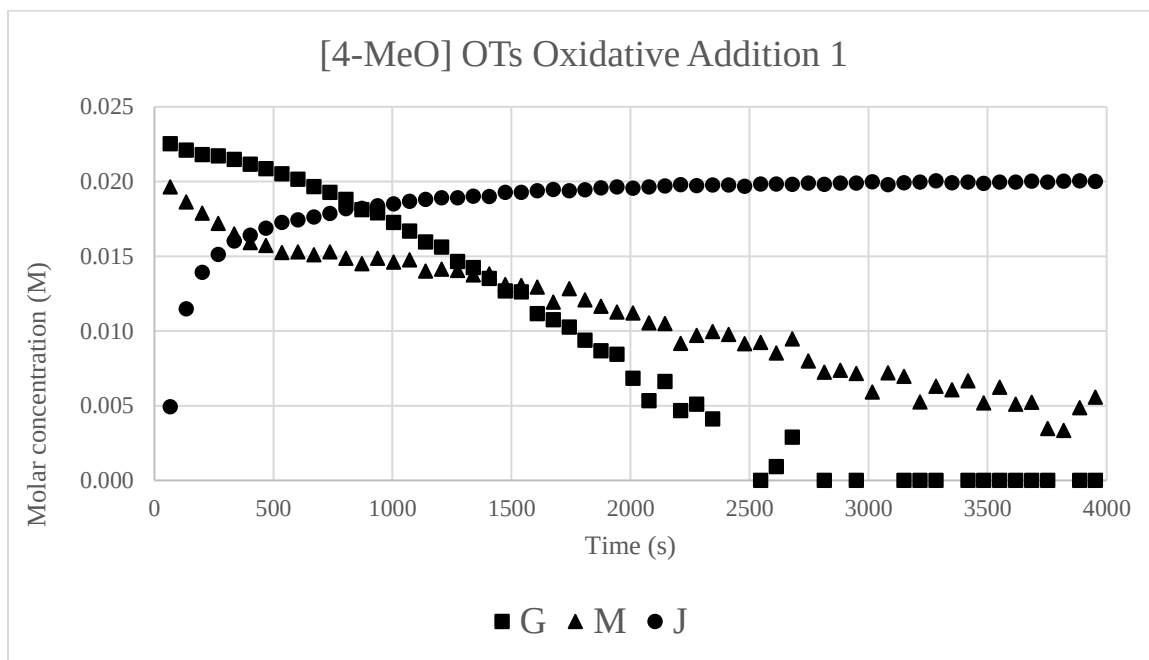
Table: Raw Data For [3-MeO] OTs Oxidative Addition 3<sup>6</sup>

| A | B  | C       | D     | E      | F     | G     | H     | I     | J     | K      | L     | M     |
|---|----|---------|-------|--------|-------|-------|-------|-------|-------|--------|-------|-------|
| 1 | 67 | 100.000 | 4.605 | 91.989 | 4.522 | 0.022 | 1.849 | 0.615 | 0.003 | 75.487 | 4.324 | 0.021 |

<sup>6</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |         |       |         |       |       |        |       |       |        |       |       |
|----|------|---------|-------|---------|-------|-------|--------|-------|-------|--------|-------|-------|
| 2  | 134  | 100.000 | 4.605 | 94.847  | 4.552 | 0.022 | 7.430  | 2.006 | 0.010 | 55.775 | 4.021 | 0.019 |
| 3  | 201  | 100.000 | 4.605 | 100.907 | 4.614 | 0.022 | 8.660  | 2.159 | 0.010 | 44.541 | 3.796 | 0.018 |
| 4  | 268  | 100.000 | 4.605 | 104.507 | 4.649 | 0.022 | 10.645 | 2.365 | 0.011 | 34.463 | 3.540 | 0.017 |
| 5  | 335  | 100.000 | 4.605 | 110.738 | 4.707 | 0.023 | 12.971 | 2.563 | 0.012 | 26.733 | 3.286 | 0.016 |
| 6  | 402  | 100.000 | 4.605 | 114.726 | 4.743 | 0.023 | 13.280 | 2.586 | 0.012 | 20.630 | 3.027 | 0.015 |
| 7  | 469  | 100.000 | 4.605 | 114.775 | 4.743 | 0.023 | 13.272 | 2.586 | 0.012 | 15.750 | 2.757 | 0.013 |
| 8  | 536  | 100.000 | 4.605 | 111.428 | 4.713 | 0.023 | 14.253 | 2.657 | 0.013 | 12.949 | 2.561 | 0.012 |
| 9  | 603  | 100.000 | 4.605 | 111.893 | 4.718 | 0.023 | 16.159 | 2.782 | 0.013 | 10.128 | 2.315 | 0.011 |
| 10 | 670  | 100.000 | 4.605 | 108.540 | 4.687 | 0.023 | 15.104 | 2.715 | 0.013 | 8.730  | 2.167 | 0.010 |
| 11 | 737  | 100.000 | 4.605 | 105.392 | 4.658 | 0.022 | 17.333 | 2.853 | 0.014 | 8.599  | 2.152 | 0.010 |
| 12 | 804  | 100.000 | 4.605 | 101.805 | 4.623 | 0.022 | 16.659 | 2.813 | 0.014 | 7.494  | 2.014 | 0.010 |
| 13 | 871  | 100.000 | 4.605 | 99.631  | 4.601 | 0.022 | 18.512 | 2.918 | 0.014 | 7.165  | 1.969 | 0.010 |
| 14 | 938  | 100.000 | 4.605 | 95.439  | 4.558 | 0.022 | 18.639 | 2.925 | 0.014 | 7.993  | 2.079 | 0.010 |
| 15 | 1005 | 100.000 | 4.605 | 90.366  | 4.504 | 0.022 | 18.030 | 2.892 | 0.014 | 6.773  | 1.913 | 0.009 |
| 16 | 1072 | 100.000 | 4.605 | 87.280  | 4.469 | 0.022 | 18.527 | 2.919 | 0.014 | 7.657  | 2.036 | 0.010 |
| 17 | 1139 | 100.000 | 4.605 | 86.064  | 4.455 | 0.021 | 19.702 | 2.981 | 0.014 | 5.745  | 1.748 | 0.008 |
| 18 | 1206 | 100.000 | 4.605 | 82.930  | 4.418 | 0.021 | 19.464 | 2.969 | 0.014 | 6.022  | 1.795 | 0.009 |
| 19 | 1273 | 100.000 | 4.605 | 81.440  | 4.400 | 0.021 | 21.228 | 3.055 | 0.015 | 6.036  | 1.798 | 0.009 |
| 20 | 1340 | 100.000 | 4.605 | 77.071  | 4.345 | 0.021 | 20.994 | 3.044 | 0.015 | 4.032  | 1.394 | 0.007 |
| 21 | 1407 | 100.000 | 4.605 | 75.854  | 4.329 | 0.021 | 21.267 | 3.057 | 0.015 | 5.161  | 1.641 | 0.008 |
| 22 | 1474 | 100.000 | 4.605 | 71.873  | 4.275 | 0.021 | 22.252 | 3.102 | 0.015 | 5.679  | 1.737 | 0.008 |
| 23 | 1541 | 100.000 | 4.605 | 69.780  | 4.245 | 0.020 | 22.968 | 3.134 | 0.015 | 4.899  | 1.589 | 0.008 |
| 24 | 1608 | 100.000 | 4.605 | 68.430  | 4.226 | 0.020 | 22.591 | 3.118 | 0.015 | 4.947  | 1.599 | 0.008 |
| 25 | 1675 | 100.000 | 4.605 | 65.063  | 4.175 | 0.020 | 23.066 | 3.138 | 0.015 | 5.780  | 1.754 | 0.008 |
| 26 | 1742 | 100.000 | 4.605 | 62.412  | 4.134 | 0.020 | 23.762 | 3.168 | 0.015 | 5.060  | 1.621 | 0.008 |
| 27 | 1809 | 100.000 | 4.605 | 62.233  | 4.131 | 0.020 | 23.229 | 3.145 | 0.015 | 3.965  | 1.378 | 0.007 |
| 28 | 1876 | 100.000 | 4.605 | 58.982  | 4.077 | 0.020 | 23.244 | 3.146 | 0.015 | 4.450  | 1.493 | 0.007 |
| 29 | 1943 | 100.000 | 4.605 | 57.599  | 4.054 | 0.020 | 24.598 | 3.203 | 0.015 | 4.847  | 1.578 | 0.008 |
| 30 | 2010 | 100.000 | 4.605 | 54.846  | 4.005 | 0.019 | 23.913 | 3.174 | 0.015 | 4.371  | 1.475 | 0.007 |
| 31 | 2077 | 100.000 | 4.605 | 53.356  | 3.977 | 0.019 | 24.671 | 3.206 | 0.015 | 4.009  | 1.389 | 0.007 |
| 32 | 2144 | 100.000 | 4.605 | 50.962  | 3.931 | 0.019 | 25.518 | 3.239 | 0.016 | 4.657  | 1.538 | 0.007 |
| 33 | 2211 | 100.000 | 4.605 | 49.095  | 3.894 | 0.019 | 25.435 | 3.236 | 0.016 | 4.305  | 1.460 | 0.007 |
| 34 | 2278 | 100.000 | 4.605 | 47.274  | 3.856 | 0.019 | 26.315 | 3.270 | 0.016 | 3.602  | 1.282 | 0.006 |
| 35 | 2345 | 100.000 | 4.605 | 46.962  | 3.849 | 0.019 | 25.753 | 3.249 | 0.016 | 3.486  | 1.249 | 0.006 |
| 36 | 2412 | 100.000 | 4.605 | 44.390  | 3.793 | 0.018 | 26.455 | 3.275 | 0.016 | 3.934  | 1.370 | 0.007 |
| 37 | 2479 | 100.000 | 4.605 | 42.962  | 3.760 | 0.018 | 27.248 | 3.305 | 0.016 | 3.832  | 1.343 | 0.006 |
| 38 | 2546 | 100.000 | 4.605 | 41.737  | 3.731 | 0.018 | 26.967 | 3.295 | 0.016 | 3.815  | 1.339 | 0.006 |
| 39 | 2613 | 100.000 | 4.605 | 38.643  | 3.654 | 0.018 | 27.233 | 3.304 | 0.016 | 2.989  | 1.095 | 0.005 |
| 40 | 2680 | 100.000 | 4.605 | 39.118  | 3.667 | 0.018 | 27.251 | 3.305 | 0.016 | 3.680  | 1.303 | 0.006 |

|    |      |         |       |        |       |       |        |       |       |       |       |       |
|----|------|---------|-------|--------|-------|-------|--------|-------|-------|-------|-------|-------|
| 41 | 2747 | 100.000 | 4.605 | 38.612 | 3.654 | 0.018 | 27.048 | 3.298 | 0.016 | 4.173 | 1.429 | 0.007 |
| 42 | 2814 | 100.000 | 4.605 | 37.733 | 3.631 | 0.018 | 29.117 | 3.371 | 0.016 | 3.180 | 1.157 | 0.006 |
| 43 | 2881 | 100.000 | 4.605 | 36.648 | 3.601 | 0.017 | 29.718 | 3.392 | 0.016 | 2.956 | 1.084 | 0.005 |
| 44 | 2948 | 100.000 | 4.605 | 34.643 | 3.545 | 0.017 | 28.625 | 3.354 | 0.016 | 2.383 | 0.868 | 0.004 |
| 45 | 3015 | 100.000 | 4.605 | 33.259 | 3.504 | 0.017 | 29.287 | 3.377 | 0.016 | 3.932 | 1.369 | 0.007 |
| 46 | 3082 | 100.000 | 4.605 | 31.959 | 3.464 | 0.017 | 29.121 | 3.371 | 0.016 | 3.494 | 1.251 | 0.006 |
| 47 | 3149 | 100.000 | 4.605 | 29.998 | 3.401 | 0.016 | 29.563 | 3.387 | 0.016 | 3.235 | 1.174 | 0.006 |
| 48 | 3216 | 100.000 | 4.605 | 30.293 | 3.411 | 0.016 | 28.919 | 3.364 | 0.016 | 3.284 | 1.189 | 0.006 |
| 49 | 3283 | 100.000 | 4.605 | 28.824 | 3.361 | 0.016 | 29.925 | 3.399 | 0.016 | 3.622 | 1.287 | 0.006 |
| 50 | 3350 | 100.000 | 4.605 | 29.932 | 3.399 | 0.016 | 28.758 | 3.359 | 0.016 | 2.511 | 0.921 | 0.004 |
| 51 | 3417 | 100.000 | 4.605 | 26.038 | 3.260 | 0.016 | 30.862 | 3.430 | 0.017 | 3.634 | 1.290 | 0.006 |
| 52 | 3484 | 100.000 | 4.605 | 26.763 | 3.287 | 0.016 | 29.762 | 3.393 | 0.016 | 2.886 | 1.060 | 0.005 |
| 53 | 3551 | 100.000 | 4.605 | 26.268 | 3.268 | 0.016 | 29.587 | 3.387 | 0.016 | 3.609 | 1.284 | 0.006 |
| 54 | 3618 | 100.000 | 4.605 | 25.772 | 3.249 | 0.016 | 31.189 | 3.440 | 0.017 | 2.205 | 0.791 | 0.004 |
| 55 | 3685 | 100.000 | 4.605 | 24.428 | 3.196 | 0.015 | 29.963 | 3.400 | 0.016 | 1.735 | 0.551 | 0.003 |
| 56 | 3752 | 100.000 | 4.605 | 24.402 | 3.195 | 0.015 | 30.850 | 3.429 | 0.017 | 2.111 | 0.747 | 0.004 |
| 57 | 3819 | 100.000 | 4.605 | 22.441 | 3.111 | 0.015 | 30.750 | 3.426 | 0.017 | 2.526 | 0.927 | 0.004 |
| 58 | 3886 | 100.000 | 4.605 | 22.069 | 3.094 | 0.015 | 29.813 | 3.395 | 0.016 | 2.186 | 0.782 | 0.004 |
| 59 | 3953 | 100.000 | 4.605 | 22.903 | 3.131 | 0.015 | 30.320 | 3.412 | 0.016 | 2.431 | 0.888 | 0.004 |
| 60 | 4020 | 100.000 | 4.605 | 20.202 | 3.006 | 0.015 | 31.627 | 3.454 | 0.017 | 3.999 | 1.386 | 0.007 |
| 61 | 4087 | 100.000 | 4.605 | 20.213 | 3.006 | 0.015 | 31.931 | 3.464 | 0.017 | 2.210 | 0.793 | 0.004 |
| 62 | 4154 | 100.000 | 4.605 | 19.276 | 2.959 | 0.014 | 29.948 | 3.399 | 0.016 | 2.955 | 1.084 | 0.005 |
| 63 | 4221 | 100.000 | 4.605 | 17.896 | 2.885 | 0.014 | 32.722 | 3.488 | 0.017 | 3.142 | 1.145 | 0.006 |
| 64 | 4288 | 100.000 | 4.605 | 17.416 | 2.857 | 0.014 | 32.620 | 3.485 | 0.017 | 1.259 | 0.230 | 0.001 |
| 65 | 4355 | 100.000 | 4.605 | 17.315 | 2.852 | 0.014 | 31.703 | 3.456 | 0.017 | 1.659 | 0.506 | 0.002 |
| 66 | 4422 | 100.000 | 4.605 | 18.347 | 2.909 | 0.014 | 32.896 | 3.493 | 0.017 | 2.311 | 0.838 | 0.004 |
| 67 | 4489 | 100.000 | 4.605 | 15.347 | 2.731 | 0.013 | 32.037 | 3.467 | 0.017 | 1.160 | 0.149 | 0.001 |
| 68 | 4556 | 100.000 | 4.605 | 14.431 | 2.669 | 0.013 | 33.293 | 3.505 | 0.017 | 2.075 | 0.730 | 0.004 |
| 69 | 4623 | 100.000 | 4.605 | 14.269 | 2.658 | 0.013 | 33.493 | 3.511 | 0.017 | 2.170 | 0.775 | 0.004 |
| 70 | 4690 | 100.000 | 4.605 | 15.646 | 2.750 | 0.013 | 33.416 | 3.509 | 0.017 | 2.768 | 1.018 | 0.005 |

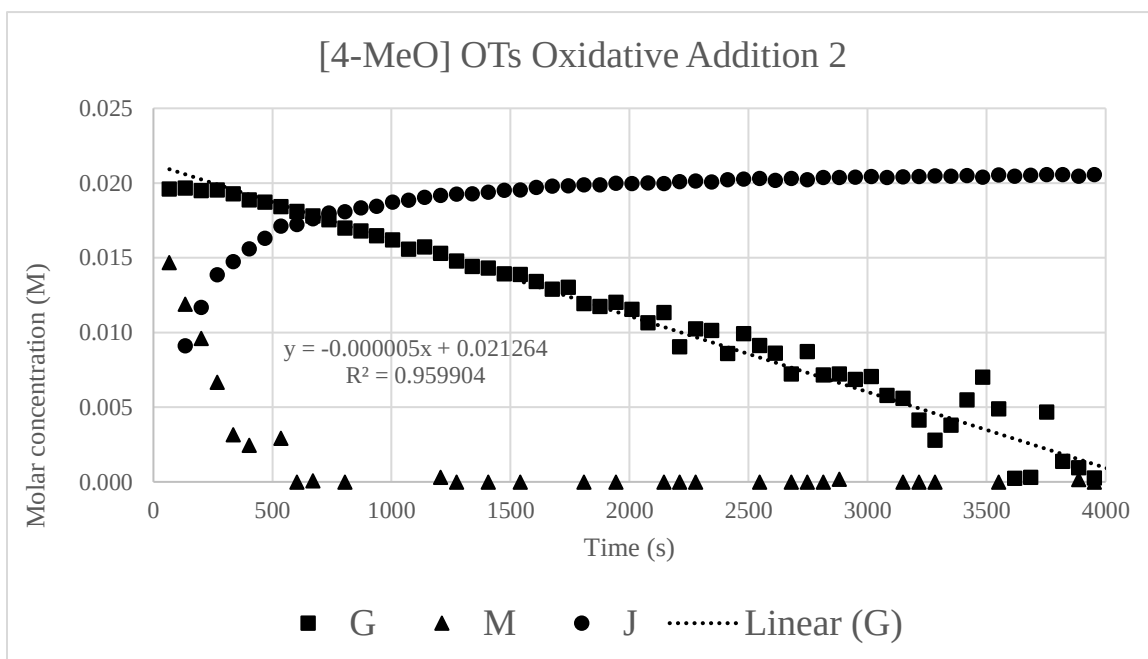
Table: Raw Data For [4-MeO] OTs Oxidative Addition 1<sup>7</sup>

| A  | B    | C   | D     | E       | F     | G     | H      | I     | J     | K      | L     | M     |
|----|------|-----|-------|---------|-------|-------|--------|-------|-------|--------|-------|-------|
| 1  | 67   | 100 | 4.605 | 106.471 | 4.668 | 0.023 | 2.781  | 1.023 | 0.005 | 58.695 | 4.072 | 0.020 |
| 2  | 134  | 100 | 4.605 | 97.433  | 4.579 | 0.022 | 10.799 | 2.379 | 0.011 | 47.480 | 3.860 | 0.019 |
| 3  | 201  | 100 | 4.605 | 91.543  | 4.517 | 0.022 | 17.938 | 2.887 | 0.014 | 40.714 | 3.707 | 0.018 |
| 4  | 268  | 100 | 4.605 | 89.931  | 4.499 | 0.022 | 22.923 | 3.132 | 0.015 | 35.364 | 3.566 | 0.017 |
| 5  | 335  | 100 | 4.605 | 85.680  | 4.451 | 0.021 | 27.680 | 3.321 | 0.016 | 30.511 | 3.418 | 0.016 |
| 6  | 402  | 100 | 4.605 | 80.326  | 4.386 | 0.021 | 29.984 | 3.401 | 0.016 | 27.103 | 3.300 | 0.016 |
| 7  | 469  | 100 | 4.605 | 75.421  | 4.323 | 0.021 | 33.033 | 3.498 | 0.017 | 25.998 | 3.258 | 0.016 |
| 8  | 536  | 100 | 4.605 | 70.259  | 4.252 | 0.021 | 35.771 | 3.577 | 0.017 | 23.618 | 3.162 | 0.015 |
| 9  | 603  | 100 | 4.605 | 65.179  | 4.177 | 0.020 | 37.150 | 3.615 | 0.017 | 23.840 | 3.171 | 0.015 |
| 10 | 670  | 100 | 4.605 | 58.898  | 4.076 | 0.020 | 38.605 | 3.653 | 0.018 | 22.873 | 3.130 | 0.015 |
| 11 | 737  | 100 | 4.605 | 54.226  | 3.993 | 0.019 | 40.501 | 3.701 | 0.018 | 23.809 | 3.170 | 0.015 |
| 12 | 804  | 100 | 4.605 | 49.197  | 3.896 | 0.019 | 43.375 | 3.770 | 0.018 | 21.769 | 3.081 | 0.015 |
| 13 | 871  | 100 | 4.605 | 42.746  | 3.755 | 0.018 | 43.463 | 3.772 | 0.018 | 20.202 | 3.006 | 0.015 |
| 14 | 938  | 100 | 4.605 | 40.945  | 3.712 | 0.018 | 45.036 | 3.807 | 0.018 | 21.758 | 3.080 | 0.015 |
| 15 | 1005 | 100 | 4.605 | 35.758  | 3.577 | 0.017 | 46.288 | 3.835 | 0.019 | 20.614 | 3.026 | 0.015 |
| 16 | 1072 | 100 | 4.605 | 31.696  | 3.456 | 0.017 | 48.031 | 3.872 | 0.019 | 21.340 | 3.061 | 0.015 |
| 17 | 1139 | 100 | 4.605 | 27.277  | 3.306 | 0.016 | 49.256 | 3.897 | 0.019 | 18.224 | 2.903 | 0.014 |

<sup>7</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~-10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |     |       |        |        |        |        |       |       |        |       |       |
|----|------|-----|-------|--------|--------|--------|--------|-------|-------|--------|-------|-------|
| 18 | 1206 | 100 | 4.605 | 25.470 | 3.238  | 0.016  | 50.324 | 3.918 | 0.019 | 18.753 | 2.931 | 0.014 |
| 19 | 1273 | 100 | 4.605 | 20.852 | 3.037  | 0.015  | 50.385 | 3.920 | 0.019 | 18.379 | 2.911 | 0.014 |
| 20 | 1340 | 100 | 4.605 | 19.181 | 2.954  | 0.014  | 51.612 | 3.944 | 0.019 | 17.310 | 2.851 | 0.014 |
| 21 | 1407 | 100 | 4.605 | 16.438 | 2.800  | 0.014  | 51.250 | 3.937 | 0.019 | 17.534 | 2.864 | 0.014 |
| 22 | 1474 | 100 | 4.605 | 13.821 | 2.626  | 0.013  | 54.421 | 3.997 | 0.019 | 15.131 | 2.717 | 0.013 |
| 23 | 1541 | 100 | 4.605 | 13.692 | 2.617  | 0.013  | 54.370 | 3.996 | 0.019 | 14.919 | 2.703 | 0.013 |
| 24 | 1608 | 100 | 4.605 | 10.109 | 2.313  | 0.011  | 55.460 | 4.016 | 0.019 | 14.588 | 2.680 | 0.013 |
| 25 | 1675 | 100 | 4.605 | 9.282  | 2.228  | 0.011  | 56.590 | 4.036 | 0.019 | 11.863 | 2.473 | 0.012 |
| 26 | 1742 | 100 | 4.605 | 8.399  | 2.128  | 0.010  | 55.612 | 4.018 | 0.019 | 14.287 | 2.659 | 0.013 |
| 27 | 1809 | 100 | 4.605 | 6.992  | 1.945  | 0.009  | 56.337 | 4.031 | 0.019 | 12.237 | 2.505 | 0.012 |
| 28 | 1876 | 100 | 4.605 | 6.033  | 1.797  | 0.009  | 57.893 | 4.059 | 0.020 | 11.192 | 2.415 | 0.012 |
| 29 | 1943 | 100 | 4.605 | 5.739  | 1.747  | 0.008  | 58.624 | 4.071 | 0.020 | 10.314 | 2.334 | 0.011 |
| 30 | 2010 | 100 | 4.605 | 4.122  | 1.416  | 0.007  | 57.559 | 4.053 | 0.020 | 10.203 | 2.323 | 0.011 |
| 31 | 2077 | 100 | 4.605 | 3.023  | 1.106  | 0.005  | 58.489 | 4.069 | 0.020 | 8.882  | 2.184 | 0.011 |
| 32 | 2144 | 100 | 4.605 | 3.939  | 1.371  | 0.007  | 59.304 | 4.083 | 0.020 | 8.817  | 2.177 | 0.011 |
| 33 | 2211 | 100 | 4.605 | 2.630  | 0.967  | 0.005  | 60.430 | 4.101 | 0.020 | 6.680  | 1.899 | 0.009 |
| 34 | 2278 | 100 | 4.605 | 2.880  | 1.058  | 0.005  | 59.582 | 4.087 | 0.020 | 7.468  | 2.011 | 0.010 |
| 35 | 2345 | 100 | 4.605 | 2.348  | 0.854  | 0.004  | 60.226 | 4.098 | 0.020 | 7.871  | 2.063 | 0.010 |
| 36 | 2412 | 100 | 4.605 | 0.840  | -0.174 | -0.001 | 60.249 | 4.098 | 0.020 | 7.561  | 2.023 | 0.010 |
| 37 | 2479 | 100 | 4.605 | 0.895  | -0.111 | -0.001 | 59.119 | 4.080 | 0.020 | 6.667  | 1.897 | 0.009 |
| 38 | 2546 | 100 | 4.605 | -0.075 | #NUM!  | #NUM!  | 61.081 | 4.112 | 0.020 | 6.763  | 1.911 | 0.009 |
| 39 | 2613 | 100 | 4.605 | 1.211  | 0.192  | 0.001  | 60.839 | 4.108 | 0.020 | 5.847  | 1.766 | 0.009 |
| 40 | 2680 | 100 | 4.605 | 1.823  | 0.601  | 0.003  | 60.601 | 4.104 | 0.020 | 7.107  | 1.961 | 0.009 |
| 41 | 2747 | 100 | 4.605 | 0.203  | -1.594 | -0.008 | 61.790 | 4.124 | 0.020 | 5.230  | 1.654 | 0.008 |
| 42 | 2814 | 100 | 4.605 | -0.672 | #NUM!  | #NUM!  | 60.586 | 4.104 | 0.020 | 4.487  | 1.501 | 0.007 |
| 43 | 2881 | 100 | 4.605 | 0.395  | -0.930 | -0.004 | 61.648 | 4.121 | 0.020 | 4.611  | 1.528 | 0.007 |
| 44 | 2948 | 100 | 4.605 | -0.476 | #NUM!  | #NUM!  | 61.725 | 4.123 | 0.020 | 4.409  | 1.484 | 0.007 |
| 45 | 3015 | 100 | 4.605 | 0.886  | -0.121 | -0.001 | 62.939 | 4.142 | 0.020 | 3.407  | 1.226 | 0.006 |
| 46 | 3082 | 100 | 4.605 | 0.256  | -1.364 | -0.007 | 60.378 | 4.101 | 0.020 | 4.449  | 1.493 | 0.007 |
| 47 | 3149 | 100 | 4.605 | -0.661 | #NUM!  | #NUM!  | 62.121 | 4.129 | 0.020 | 4.226  | 1.441 | 0.007 |
| 48 | 3216 | 100 | 4.605 | -0.227 | #NUM!  | #NUM!  | 62.496 | 4.135 | 0.020 | 2.969  | 1.088 | 0.005 |
| 49 | 3283 | 100 | 4.605 | -0.046 | #NUM!  | #NUM!  | 63.597 | 4.153 | 0.020 | 3.686  | 1.305 | 0.006 |
| 50 | 3350 | 100 | 4.605 | 0.299  | -1.208 | -0.006 | 61.942 | 4.126 | 0.020 | 3.513  | 1.257 | 0.006 |
| 51 | 3417 | 100 | 4.605 | -0.463 | #NUM!  | #NUM!  | 62.647 | 4.138 | 0.020 | 3.973  | 1.380 | 0.007 |
| 52 | 3484 | 100 | 4.605 | -0.455 | #NUM!  | #NUM!  | 61.583 | 4.120 | 0.020 | 2.928  | 1.074 | 0.005 |
| 53 | 3551 | 100 | 4.605 | -0.475 | #NUM!  | #NUM!  | 62.481 | 4.135 | 0.020 | 3.639  | 1.292 | 0.006 |
| 54 | 3618 | 100 | 4.605 | -0.441 | #NUM!  | #NUM!  | 62.665 | 4.138 | 0.020 | 2.874  | 1.056 | 0.005 |
| 55 | 3685 | 100 | 4.605 | -0.486 | #NUM!  | #NUM!  | 63.521 | 4.151 | 0.020 | 2.959  | 1.085 | 0.005 |
| 56 | 3752 | 100 | 4.605 | -0.441 | #NUM!  | #NUM!  | 62.693 | 4.138 | 0.020 | 2.052  | 0.719 | 0.003 |

|    |      |     |       |        |        |        |        |       |       |       |       |       |
|----|------|-----|-------|--------|--------|--------|--------|-------|-------|-------|-------|-------|
| 57 | 3819 | 100 | 4.605 | 0.538  | -0.621 | -0.003 | 63.345 | 4.149 | 0.020 | 2.003 | 0.695 | 0.003 |
| 58 | 3886 | 100 | 4.605 | -0.162 | #NUM!  | #NUM!  | 63.769 | 4.155 | 0.020 | 2.739 | 1.008 | 0.005 |
| 59 | 3953 | 100 | 4.605 | -0.012 | #NUM!  | #NUM!  | 63.278 | 4.148 | 0.020 | 3.175 | 1.155 | 0.006 |
| 60 | 4020 | 100 | 4.605 | -0.833 | #NUM!  | #NUM!  | 62.580 | 4.136 | 0.020 | 2.567 | 0.943 | 0.005 |
| 61 | 4087 | 100 | 4.605 | -0.785 | #NUM!  | #NUM!  | 64.210 | 4.162 | 0.020 | 2.876 | 1.056 | 0.005 |
| 62 | 4154 | 100 | 4.605 | -0.663 | #NUM!  | #NUM!  | 63.857 | 4.157 | 0.020 | 3.156 | 1.149 | 0.006 |
| 63 | 4221 | 100 | 4.605 | 0.593  | -0.523 | -0.003 | 63.360 | 4.149 | 0.020 | 1.266 | 0.236 | 0.001 |
| 64 | 4288 | 100 | 4.605 | 0.531  | -0.633 | -0.003 | 63.539 | 4.152 | 0.020 | 2.967 | 1.088 | 0.005 |
| 65 | 4355 | 100 | 4.605 | 0.722  | -0.326 | -0.002 | 63.713 | 4.154 | 0.020 | 1.855 | 0.618 | 0.003 |
| 66 | 4422 | 100 | 4.605 | -0.559 | #NUM!  | #NUM!  | 64.762 | 4.171 | 0.020 | 3.812 | 1.338 | 0.006 |
| 67 | 4489 | 100 | 4.605 | -1.769 | #NUM!  | #NUM!  | 62.804 | 4.140 | 0.020 | 3.348 | 1.208 | 0.006 |
| 68 | 4556 | 100 | 4.605 | -1.034 | #NUM!  | #NUM!  | 64.056 | 4.160 | 0.020 | 2.513 | 0.922 | 0.004 |
| 69 | 4623 | 100 | 4.605 | 0.351  | -1.048 | -0.005 | 63.576 | 4.152 | 0.020 | 2.123 | 0.753 | 0.004 |
| 70 | 4690 | 100 | 4.605 | 1.074  | 0.071  | 0.000  | 65.154 | 4.177 | 0.020 | 2.759 | 1.015 | 0.005 |

Table: Raw Data For [4-MeO] OTs Oxidative Addition 2<sup>8</sup>

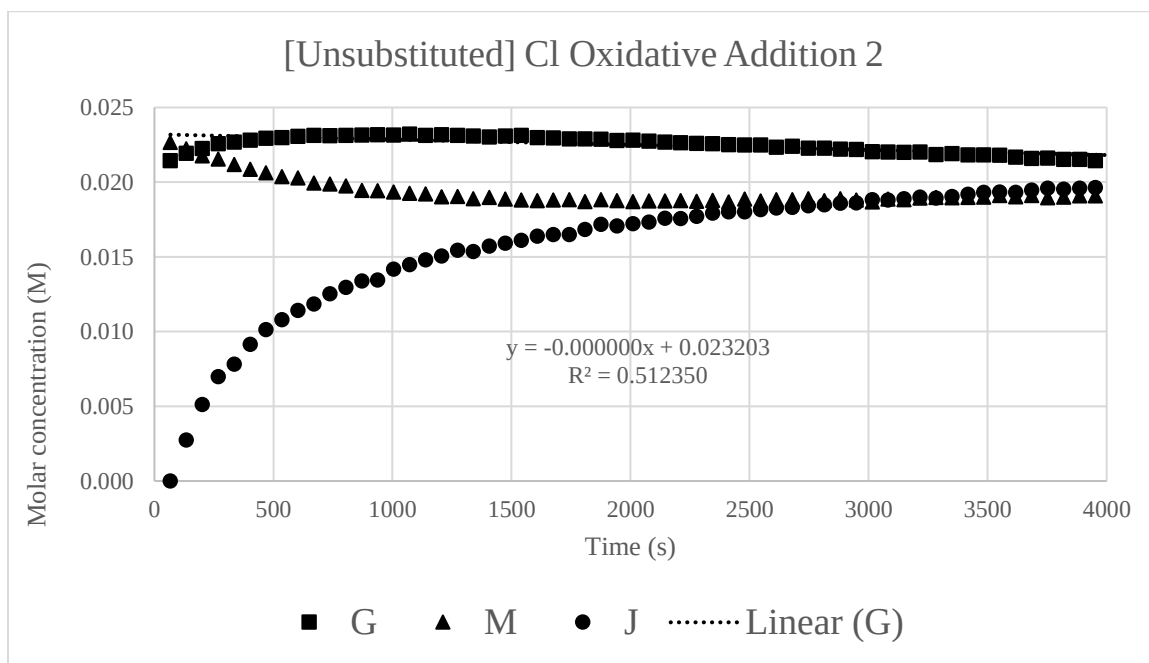
| A | B  | C       | D         | E          | F     | G     | H     | I | J | K          | L     | M     |
|---|----|---------|-----------|------------|-------|-------|-------|---|---|------------|-------|-------|
| 1 | 67 | 10<br>0 | 4.60<br>5 | 58.18<br>7 | 4.064 | 0.020 | 0.585 | - | - | 20.99<br>2 | 3.044 | 0.015 |

<sup>8</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|        |          |         |           |            |       |       |            |       |       |            |           |           |
|--------|----------|---------|-----------|------------|-------|-------|------------|-------|-------|------------|-----------|-----------|
| 2      | 134      | 10<br>0 | 4.60<br>5 | 58.86<br>0 | 4.075 | 0.020 | 6.616      | 1.889 | 0.009 | 11.76<br>8 | 2.465     | 0.012     |
| 3      | 201      | 10<br>0 | 4.60<br>5 | 56.79<br>8 | 4.040 | 0.019 | 11.25<br>3 | 2.421 | 0.012 | 7.334      | 1.993     | 0.010     |
| 4      | 268      | 10<br>0 | 4.60<br>5 | 57.33<br>8 | 4.049 | 0.020 | 17.66<br>3 | 2.871 | 0.014 | 3.988      | 1.383     | 0.007     |
| 5      | 335      | 10<br>0 | 4.60<br>5 | 54.49<br>5 | 3.998 | 0.019 | 21.26<br>0 | 3.057 | 0.015 | 1.923      | 0.654     | 0.003     |
| 6      | 402      | 10<br>0 | 4.60<br>5 | 50.02<br>4 | 3.913 | 0.019 | 25.32<br>0 | 3.232 | 0.016 | 1.663      | 0.508     | 0.002     |
| 7      | 469      | 10<br>0 | 4.60<br>5 | 48.53<br>5 | 3.882 | 0.019 | 29.34<br>3 | 3.379 | 0.016 | 0.415      | -0.878    | -0.004    |
| 8      | 536      | 10<br>0 | 4.60<br>5 | 45.52<br>9 | 3.818 | 0.018 | 34.75<br>5 | 3.548 | 0.017 | 1.830      | 0.604     | 0.003     |
| 9      | 603      | 10<br>0 | 4.60<br>5 | 42.65<br>4 | 3.753 | 0.018 | 35.54<br>6 | 3.571 | 0.017 | -0.249     | #NUM<br>! | #NUM<br>! |
| 1<br>0 | 670      | 10<br>0 | 4.60<br>5 | 40.00<br>1 | 3.689 | 0.018 | 38.47<br>6 | 3.650 | 0.018 | 1.015      | 0.015     | 0.000     |
| 1<br>1 | 737      | 10<br>0 | 4.60<br>5 | 37.93<br>4 | 3.636 | 0.018 | 41.65<br>1 | 3.729 | 0.018 | 0.194      | -1.638    | -0.008    |
| 1<br>2 | 804      | 10<br>0 | 4.60<br>5 | 33.82<br>2 | 3.521 | 0.017 | 42.36<br>6 | 3.746 | 0.018 | -0.436     | #NUM<br>! | #NUM<br>! |
| 1<br>3 | 871      | 10<br>0 | 4.60<br>5 | 32.54<br>0 | 3.482 | 0.017 | 44.75<br>1 | 3.801 | 0.018 | 0.228      | -1.477    | -0.007    |
| 1<br>4 | 938      | 10<br>0 | 4.60<br>5 | 30.43<br>5 | 3.416 | 0.016 | 45.83<br>8 | 3.825 | 0.018 | 0.047      | -3.052    | -0.015    |
| 1<br>5 | 100<br>5 | 10<br>0 | 4.60<br>5 | 28.76<br>4 | 3.359 | 0.016 | 48.56<br>6 | 3.883 | 0.019 | 0.186      | -1.682    | -0.008    |
| 1<br>6 | 107<br>2 | 10<br>0 | 4.60<br>5 | 25.21<br>0 | 3.227 | 0.016 | 49.78<br>2 | 3.908 | 0.019 | 0.758      | -0.277    | -0.001    |
| 1<br>7 | 113<br>9 | 10<br>0 | 4.60<br>5 | 26.04<br>6 | 3.260 | 0.016 | 51.70<br>4 | 3.946 | 0.019 | 0.534      | -0.627    | -0.003    |
| 1<br>8 | 120<br>6 | 10<br>0 | 4.60<br>5 | 23.82<br>3 | 3.171 | 0.015 | 53.28<br>1 | 3.976 | 0.019 | 1.067      | 0.065     | 0.000     |
| 1<br>9 | 127<br>3 | 10<br>0 | 4.60<br>5 | 21.38<br>5 | 3.063 | 0.015 | 54.14<br>1 | 3.992 | 0.019 | -0.051     | #NUM<br>! | #NUM<br>! |
| 2<br>0 | 134<br>0 | 10<br>0 | 4.60<br>5 | 19.88<br>8 | 2.990 | 0.014 | 54.46<br>9 | 3.998 | 0.019 | 0.817      | -0.202    | -0.001    |
| 2<br>1 | 140<br>7 | 10<br>0 | 4.60<br>5 | 19.45<br>9 | 2.968 | 0.014 | 55.66<br>3 | 4.019 | 0.019 | -0.766     | #NUM<br>! | #NUM<br>! |
| 2<br>2 | 147<br>4 | 10<br>0 | 4.60<br>5 | 17.97<br>5 | 2.889 | 0.014 | 57.11<br>2 | 4.045 | 0.020 | 0.305      | -1.187    | -0.006    |
| 2<br>3 | 154<br>1 | 10<br>0 | 4.60<br>5 | 17.78<br>1 | 2.878 | 0.014 | 57.46<br>6 | 4.051 | 0.020 | -0.465     | #NUM<br>! | #NUM<br>! |
| 2<br>4 | 160<br>8 | 10<br>0 | 4.60<br>5 | 16.14<br>6 | 2.782 | 0.013 | 59.49<br>4 | 4.086 | 0.020 | 0.177      | -1.734    | -0.008    |
| 2<br>5 | 167<br>5 | 10<br>0 | 4.60<br>5 | 14.52<br>7 | 2.676 | 0.013 | 60.58<br>5 | 4.104 | 0.020 | 0.273      | -1.297    | -0.006    |
| 2<br>6 | 174<br>2 | 10<br>0 | 4.60<br>5 | 14.86<br>8 | 2.699 | 0.013 | 60.84<br>2 | 4.108 | 0.020 | 0.515      | -0.663    | -0.003    |
| 2<br>7 | 180<br>9 | 10<br>0 | 4.60<br>5 | 11.84<br>8 | 2.472 | 0.012 | 61.66<br>3 | 4.122 | 0.020 | -0.632     | #NUM<br>! | #NUM<br>! |
| 2<br>8 | 187<br>6 | 10<br>0 | 4.60<br>5 | 11.38<br>2 | 2.432 | 0.012 | 61.60<br>3 | 4.121 | 0.020 | 0.359      | -1.023    | -0.005    |
| 2<br>9 | 194<br>3 | 10<br>0 | 4.60<br>5 | 12.07<br>8 | 2.491 | 0.012 | 62.98<br>7 | 4.143 | 0.020 | -0.530     | #NUM<br>! | #NUM<br>! |
| 3<br>0 | 201<br>0 | 10<br>0 | 4.60<br>5 | 10.94<br>8 | 2.393 | 0.012 | 62.67<br>0 | 4.138 | 0.020 | 0.438      | -0.826    | -0.004    |

|   |     |    |      |       |       |       |       |       |       |        |        |        |
|---|-----|----|------|-------|-------|-------|-------|-------|-------|--------|--------|--------|
| 3 | 207 | 10 | 4.60 |       |       |       | 63.15 |       |       |        |        |        |
| 1 | 7   | 0  | 5    | 9.094 | 2.208 | 0.011 | 9     | 4.146 | 0.020 | 0.350  | -1.049 | -0.005 |
| 3 | 214 | 10 | 4.60 | 10.47 |       |       | 62.80 |       |       |        | #NUM   | #NUM   |
| 2 | 4   | 0  | 5    | 7     | 2.349 | 0.011 | 1     | 4.140 | 0.020 | -0.138 | !      | !      |
| 3 | 221 | 10 | 4.60 |       |       |       | 64.25 |       |       |        | #NUM   | #NUM   |
| 3 | 1   | 0  | 5    | 6.516 | 1.874 | 0.009 | 5     | 4.163 | 0.020 | -0.161 | !      | !      |
| 3 | 227 | 10 | 4.60 |       |       |       | 65.08 |       |       |        | #NUM   | #NUM   |
| 4 | 8   | 0  | 5    | 8.356 | 2.123 | 0.010 | 7     | 4.176 | 0.020 | -0.132 | !      | !      |
| 3 | 234 | 10 | 4.60 |       |       |       | 64.14 |       |       |        |        |        |
| 5 | 5   | 0  | 5    | 8.166 | 2.100 | 0.010 | 5     | 4.161 | 0.020 | 0.970  | -0.031 | 0.000  |
| 3 | 241 | 10 | 4.60 |       |       |       | 66.15 |       |       |        |        |        |
| 6 | 2   | 0  | 5    | 5.941 | 1.782 | 0.009 | 2     | 4.192 | 0.020 | 0.139  | -1.976 | -0.010 |
| 3 | 247 | 10 | 4.60 |       |       |       | 66.59 |       |       |        |        |        |
| 7 | 9   | 0  | 5    | 7.813 | 2.056 | 0.010 | 8     | 4.199 | 0.020 | 0.699  | -0.358 | -0.002 |
| 3 | 254 | 10 | 4.60 |       |       |       | 67.45 |       |       |        | #NUM   | #NUM   |
| 8 | 6   | 0  | 5    | 6.631 | 1.892 | 0.009 | 2     | 4.211 | 0.020 | -0.443 | !      | !      |
| 3 | 261 | 10 | 4.60 |       |       |       | 65.51 |       |       |        |        |        |
| 9 | 3   | 0  | 5    | 5.966 | 1.786 | 0.009 | 6     | 4.182 | 0.020 | 0.490  | -0.714 | -0.003 |
| 4 | 268 | 10 | 4.60 |       |       |       | 67.20 |       |       |        | #NUM   | #NUM   |
| 0 | 0   | 0  | 5    | 4.482 | 1.500 | 0.007 | 5     | 4.208 | 0.020 | -0.499 | !      | !      |
| 4 | 274 | 10 | 4.60 |       |       |       | 66.21 |       |       |        | #NUM   | #NUM   |
| 1 | 7   | 0  | 5    | 6.108 | 1.810 | 0.009 | 4     | 4.193 | 0.020 | -0.087 | !      | !      |
| 4 | 281 | 10 | 4.60 |       |       |       | 68.16 |       |       |        | #NUM   | #NUM   |
| 2 | 4   | 0  | 5    | 4.409 | 1.484 | 0.007 | 0     | 4.222 | 0.020 | -0.077 | !      | !      |
| 4 | 288 | 10 | 4.60 |       |       |       | 68.14 |       |       |        |        |        |
| 3 | 1   | 0  | 5    | 4.474 | 1.498 | 0.007 | 3     | 4.222 | 0.020 | 1.038  | 0.037  | 0.000  |
| 4 | 294 | 10 | 4.60 |       |       |       | 68.62 |       |       |        |        |        |
| 4 | 8   | 0  | 5    | 4.139 | 1.421 | 0.007 | 5     | 4.229 | 0.020 | 0.861  | -0.150 | -0.001 |
| 4 | 301 | 10 | 4.60 |       |       |       | 69.27 |       |       |        |        |        |
| 5 | 5   | 0  | 5    | 4.311 | 1.461 | 0.007 | 7     | 4.238 | 0.020 | 0.307  | -1.182 | -0.006 |
| 4 | 308 | 10 | 4.60 |       |       |       | 68.27 |       |       |        |        |        |
| 6 | 2   | 0  | 5    | 3.322 | 1.201 | 0.006 | 3     | 4.224 | 0.020 | 0.198  | -1.622 | -0.008 |
| 4 | 314 | 10 | 4.60 |       |       |       | 68.91 |       |       |        | #NUM   | #NUM   |
| 7 | 9   | 0  | 5    | 3.192 | 1.161 | 0.006 | 3     | 4.233 | 0.020 | -0.177 | !      | !      |
| 4 | 321 | 10 | 4.60 |       |       |       | 69.11 |       |       |        | #NUM   | #NUM   |
| 8 | 6   | 0  | 5    | 2.359 | 0.858 | 0.004 | 9     | 4.236 | 0.020 | -0.277 | !      | !      |
| 4 | 328 | 10 | 4.60 |       |       |       | 69.85 |       |       |        | #NUM   | #NUM   |
| 9 | 3   | 0  | 5    | 1.783 | 0.578 | 0.003 | 8     | 4.246 | 0.020 | -0.465 | !      | !      |
| 5 | 335 | 10 | 4.60 |       |       |       | 69.28 |       |       |        |        |        |
| 0 | 0   | 0  | 5    | 2.194 | 0.786 | 0.004 | 4     | 4.238 | 0.020 | 0.371  | -0.991 | -0.005 |
| 5 | 341 | 10 | 4.60 |       |       |       | 70.06 |       |       |        |        |        |
| 1 | 7   | 0  | 5    | 3.126 | 1.140 | 0.006 | 9     | 4.249 | 0.021 | 0.265  | -1.329 | -0.006 |
| 5 | 348 | 10 | 4.60 |       |       |       | 68.54 |       |       |        |        |        |
| 2 | 4   | 0  | 5    | 4.272 | 1.452 | 0.007 | 8     | 4.228 | 0.020 | 0.732  | -0.313 | -0.002 |
| 5 | 355 | 10 | 4.60 |       |       |       | 70.53 |       |       |        | #NUM   | #NUM   |
| 3 | 1   | 0  | 5    | 2.760 | 1.015 | 0.005 | 6     | 4.256 | 0.021 | -0.841 | !      | !      |
| 5 | 361 | 10 | 4.60 |       |       |       | 69.57 |       |       |        |        |        |
| 4 | 8   | 0  | 5    | 1.053 | 0.051 | 0.000 | 9     | 4.242 | 0.020 | 0.169  | -1.781 | -0.009 |
| 5 | 368 | 10 | 4.60 |       |       |       | 70.23 |       |       |        |        |        |
| 5 | 5   | 0  | 5    | 1.065 | 0.063 | 0.000 | 5     | 4.252 | 0.021 | 0.400  | -0.916 | -0.004 |
| 5 | 375 | 10 | 4.60 |       |       |       | 71.04 |       |       |        |        |        |
| 6 | 2   | 0  | 5    | 2.639 | 0.971 | 0.005 | 0     | 4.263 | 0.021 | 0.813  | -0.207 | -0.001 |
| 5 | 381 | 10 | 4.60 |       |       |       | 70.87 |       |       |        |        |        |
| 7 | 9   | 0  | 5    | 1.333 | 0.287 | 0.001 | 9     | 4.261 | 0.021 | 0.062  | -2.785 | -0.013 |
| 5 | 388 | 10 | 4.60 |       |       |       | 69.49 |       |       |        |        |        |
| 8 | 6   | 0  | 5    | 1.219 | 0.198 | 0.001 | 8     | 4.241 | 0.020 | 1.032  | 0.032  | 0.000  |
| 5 | 395 | 10 | 4.60 |       |       |       | 70.86 |       |       |        | #NUM   | #NUM   |
| 9 | 3   | 0  | 5    | 1.055 | 0.054 | 0.000 | 5     | 4.261 | 0.021 | -0.166 | !      | !      |

|    |      |     |       |        |        |        |        |       |       |        |        |        |
|----|------|-----|-------|--------|--------|--------|--------|-------|-------|--------|--------|--------|
| 60 | 4020 | 100 | 4.605 | 0.373  | -0.986 | -0.005 | 71.471 | 4.269 | 0.021 | -0.763 | #NUM!  | #NUM!  |
| 61 | 4087 | 100 | 4.605 | -0.499 | #NUM!  | #NUM!  | 70.553 | 4.256 | 0.021 | -0.036 | #NUM!  | #NUM!  |
| 62 | 4154 | 100 | 4.605 | 2.899  | 1.064  | 0.005  | 71.072 | 4.264 | 0.021 | 0.055  | -2.909 | -0.014 |
| 63 | 4221 | 100 | 4.605 | 2.479  | 0.908  | 0.004  | 71.402 | 4.268 | 0.021 | 0.326  | -1.122 | -0.005 |
| 64 | 4288 | 100 | 4.605 | 0.832  | -0.184 | -0.001 | 71.428 | 4.269 | 0.021 | 0.482  | -0.731 | -0.004 |
| 65 | 4355 | 100 | 4.605 | -0.035 | #NUM!  | #NUM!  | 71.149 | 4.265 | 0.021 | -0.545 | #NUM!  | #NUM!  |
| 66 | 4422 | 100 | 4.605 | 0.102  | -2.286 | -0.011 | 70.431 | 4.255 | 0.021 | 0.656  | -0.421 | -0.002 |
| 67 | 4489 | 100 | 4.605 | 0.858  | -0.153 | -0.001 | 71.735 | 4.273 | 0.021 | 1.291  | 0.255  | 0.001  |
| 68 | 4556 | 100 | 4.605 | 0.483  | -0.728 | -0.004 | 70.821 | 4.260 | 0.021 | 1.317  | 0.276  | 0.001  |
| 69 | 4623 | 100 | 4.605 | 1.824  | 0.601  | 0.003  | 71.248 | 4.266 | 0.021 | -0.470 | #NUM!  | #NUM!  |
| 70 | 4690 | 100 | 4.605 | 0.297  | -1.212 | -0.006 | 70.641 | 4.258 | 0.021 | -0.819 | #NUM!  | #NUM!  |

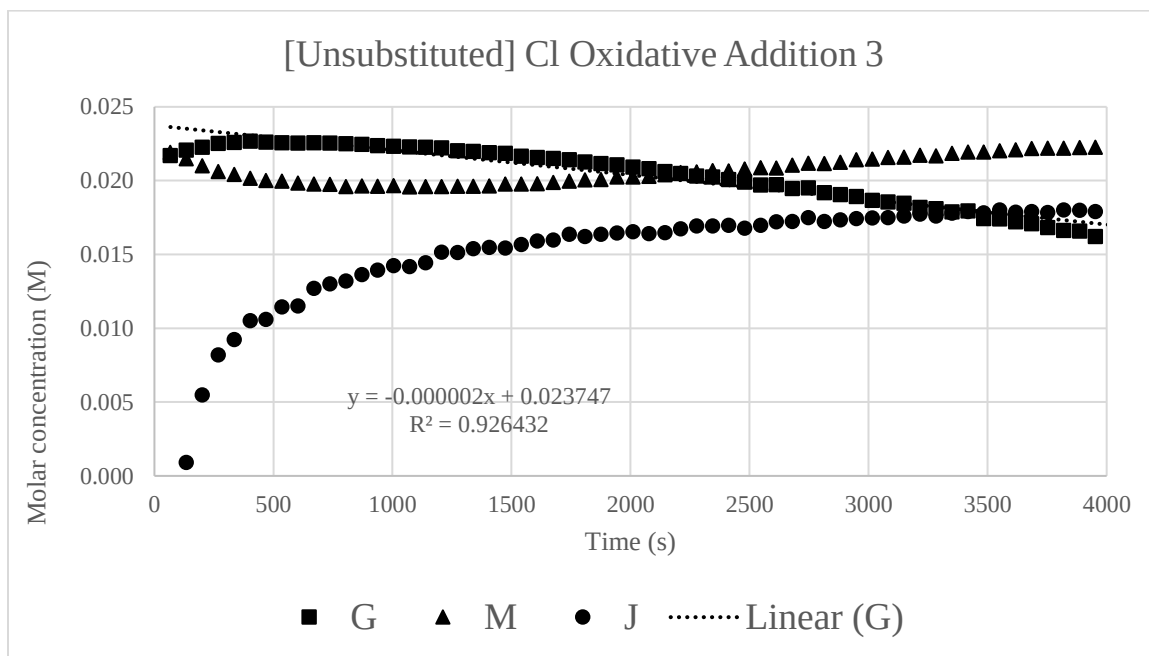
Table: Raw Data For [Unsubstituted] Cl Oxidative Addition 2<sup>9</sup>

| A | B | C | D | E | F | G | H | I | J | K | L | M |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|---|---|---|---|---|---|---|---|---|---|---|---|---|

<sup>9</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~-10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |     |       |         |       |       |        |       |       |         |       |       |
|----|------|-----|-------|---------|-------|-------|--------|-------|-------|---------|-------|-------|
| 1  | 67   | 100 | 4.605 | 85.084  | 4.444 | 0.021 | -0.225 | #NUM! | #NUM! | 109.371 | 4.695 | 0.023 |
| 2  | 134  | 100 | 4.605 | 94.206  | 4.545 | 0.022 | 1.764  | 0.568 | 0.003 | 100.458 | 4.610 | 0.022 |
| 3  | 201  | 100 | 4.605 | 100.892 | 4.614 | 0.022 | 2.892  | 1.062 | 0.005 | 91.016  | 4.511 | 0.022 |
| 4  | 268  | 100 | 4.605 | 107.884 | 4.681 | 0.023 | 4.260  | 1.449 | 0.007 | 87.164  | 4.468 | 0.022 |
| 5  | 335  | 100 | 4.605 | 109.969 | 4.700 | 0.023 | 5.066  | 1.623 | 0.008 | 80.757  | 4.391 | 0.021 |
| 6  | 402  | 100 | 4.605 | 112.827 | 4.726 | 0.023 | 6.673  | 1.898 | 0.009 | 75.468  | 4.324 | 0.021 |
| 7  | 469  | 100 | 4.605 | 116.236 | 4.756 | 0.023 | 8.159  | 2.099 | 0.010 | 71.802  | 4.274 | 0.021 |
| 8  | 536  | 100 | 4.605 | 117.249 | 4.764 | 0.023 | 9.363  | 2.237 | 0.011 | 68.290  | 4.224 | 0.020 |
| 9  | 603  | 100 | 4.605 | 119.353 | 4.782 | 0.023 | 10.658 | 2.366 | 0.011 | 66.898  | 4.203 | 0.020 |
| 10 | 670  | 100 | 4.605 | 120.855 | 4.795 | 0.023 | 11.671 | 2.457 | 0.012 | 62.370  | 4.133 | 0.020 |
| 11 | 737  | 100 | 4.605 | 120.474 | 4.791 | 0.023 | 13.460 | 2.600 | 0.013 | 61.500  | 4.119 | 0.020 |
| 12 | 804  | 100 | 4.605 | 121.081 | 4.796 | 0.023 | 14.693 | 2.687 | 0.013 | 59.831  | 4.092 | 0.020 |
| 13 | 871  | 100 | 4.605 | 121.514 | 4.800 | 0.023 | 16.047 | 2.776 | 0.013 | 56.349  | 4.032 | 0.019 |
| 14 | 938  | 100 | 4.605 | 122.173 | 4.805 | 0.023 | 16.277 | 2.790 | 0.013 | 56.168  | 4.028 | 0.019 |
| 15 | 1005 | 100 | 4.605 | 121.249 | 4.798 | 0.023 | 18.925 | 2.941 | 0.014 | 55.026  | 4.008 | 0.019 |
| 16 | 1072 | 100 | 4.605 | 122.733 | 4.810 | 0.023 | 20.093 | 3.000 | 0.014 | 54.124  | 3.991 | 0.019 |
| 17 | 1139 | 100 | 4.605 | 120.981 | 4.796 | 0.023 | 21.495 | 3.068 | 0.015 | 53.655  | 3.983 | 0.019 |
| 18 | 1206 | 100 | 4.605 | 122.170 | 4.805 | 0.023 | 22.691 | 3.122 | 0.015 | 51.627  | 3.944 | 0.019 |
| 19 | 1273 | 100 | 4.605 | 121.049 | 4.796 | 0.023 | 24.512 | 3.199 | 0.015 | 51.862  | 3.949 | 0.019 |
| 20 | 1340 | 100 | 4.605 | 119.887 | 4.787 | 0.023 | 24.088 | 3.182 | 0.015 | 50.144  | 3.915 | 0.019 |
| 21 | 1407 | 100 | 4.605 | 118.239 | 4.773 | 0.023 | 26.021 | 3.259 | 0.016 | 50.998  | 3.932 | 0.019 |
| 22 | 1474 | 100 | 4.605 | 119.600 | 4.784 | 0.023 | 27.059 | 3.298 | 0.016 | 49.933  | 3.911 | 0.019 |
| 23 | 1541 | 100 | 4.605 | 120.604 | 4.793 | 0.023 | 28.156 | 3.338 | 0.016 | 49.305  | 3.898 | 0.019 |
| 24 | 1608 | 100 | 4.605 | 116.985 | 4.762 | 0.023 | 29.822 | 3.395 | 0.016 | 48.812  | 3.888 | 0.019 |
| 25 | 1675 | 100 | 4.605 | 116.398 | 4.757 | 0.023 | 30.496 | 3.418 | 0.016 | 49.243  | 3.897 | 0.019 |
| 26 | 1742 | 100 | 4.605 | 115.127 | 4.746 | 0.023 | 30.489 | 3.417 | 0.016 | 49.414  | 3.900 | 0.019 |
| 27 | 1809 | 100 | 4.605 | 115.153 | 4.746 | 0.023 | 32.756 | 3.489 | 0.017 | 48.132  | 3.874 | 0.019 |
| 28 | 1876 | 100 | 4.605 | 114.446 | 4.740 | 0.023 | 35.207 | 3.561 | 0.017 | 49.512  | 3.902 | 0.019 |
| 29 | 1943 | 100 | 4.605 | 112.539 | 4.723 | 0.023 | 34.348 | 3.537 | 0.017 | 48.880  | 3.889 | 0.019 |
| 30 | 2010 | 100 | 4.605 | 113.091 | 4.728 | 0.023 | 35.452 | 3.568 | 0.017 | 48.309  | 3.878 | 0.019 |
| 31 | 2077 | 100 | 4.605 | 111.579 | 4.715 | 0.023 | 36.326 | 3.593 | 0.017 | 48.637  | 3.884 | 0.019 |
| 32 | 2144 | 100 | 4.605 | 110.049 | 4.701 | 0.023 | 38.312 | 3.646 | 0.018 | 48.632  | 3.884 | 0.019 |
| 33 | 2211 | 100 | 4.605 | 109.050 | 4.692 | 0.023 | 38.097 | 3.640 | 0.018 | 48.858  | 3.889 | 0.019 |
| 34 | 2278 | 100 | 4.605 | 108.268 | 4.685 | 0.023 | 39.332 | 3.672 | 0.018 | 48.533  | 3.882 | 0.019 |
| 35 | 2345 | 100 | 4.605 | 107.700 | 4.679 | 0.023 | 41.026 | 3.714 | 0.018 | 49.052  | 3.893 | 0.019 |
| 36 | 2412 | 100 | 4.605 | 106.466 | 4.668 | 0.023 | 41.929 | 3.736 | 0.018 | 48.002  | 3.871 | 0.019 |
| 37 | 2479 | 100 | 4.605 | 105.584 | 4.660 | 0.022 | 41.829 | 3.734 | 0.018 | 49.914  | 3.910 | 0.019 |
| 38 | 2546 | 100 | 4.605 | 105.857 | 4.662 | 0.022 | 43.106 | 3.764 | 0.018 | 48.734  | 3.886 | 0.019 |
| 39 | 2613 | 100 | 4.605 | 102.382 | 4.629 | 0.022 | 44.056 | 3.785 | 0.018 | 49.612  | 3.904 | 0.019 |

|    |      |     |       |         |       |       |        |       |       |        |       |       |
|----|------|-----|-------|---------|-------|-------|--------|-------|-------|--------|-------|-------|
| 40 | 2680 | 100 | 4.605 | 103.855 | 4.643 | 0.022 | 44.441 | 3.794 | 0.018 | 49.459 | 3.901 | 0.019 |
| 41 | 2747 | 100 | 4.605 | 101.103 | 4.616 | 0.022 | 45.602 | 3.820 | 0.018 | 50.169 | 3.915 | 0.019 |
| 42 | 2814 | 100 | 4.605 | 101.043 | 4.616 | 0.022 | 46.099 | 3.831 | 0.018 | 48.893 | 3.890 | 0.019 |
| 43 | 2881 | 100 | 4.605 | 100.018 | 4.605 | 0.022 | 47.249 | 3.855 | 0.019 | 50.090 | 3.914 | 0.019 |
| 44 | 2948 | 100 | 4.605 | 99.323  | 4.598 | 0.022 | 47.311 | 3.857 | 0.019 | 49.355 | 3.899 | 0.019 |
| 45 | 3015 | 100 | 4.605 | 96.530  | 4.570 | 0.022 | 49.444 | 3.901 | 0.019 | 47.922 | 3.870 | 0.019 |
| 46 | 3082 | 100 | 4.605 | 96.036  | 4.565 | 0.022 | 49.382 | 3.900 | 0.019 | 49.912 | 3.910 | 0.019 |
| 47 | 3149 | 100 | 4.605 | 95.719  | 4.561 | 0.022 | 50.115 | 3.914 | 0.019 | 49.578 | 3.904 | 0.019 |
| 48 | 3216 | 100 | 4.605 | 95.854  | 4.563 | 0.022 | 51.316 | 3.938 | 0.019 | 50.717 | 3.926 | 0.019 |
| 49 | 3283 | 100 | 4.605 | 92.632  | 4.529 | 0.022 | 50.670 | 3.925 | 0.019 | 51.176 | 3.935 | 0.019 |
| 50 | 3350 | 100 | 4.605 | 93.686  | 4.540 | 0.022 | 51.721 | 3.946 | 0.019 | 50.772 | 3.927 | 0.019 |
| 51 | 3417 | 100 | 4.605 | 92.105  | 4.523 | 0.022 | 53.416 | 3.978 | 0.019 | 50.986 | 3.932 | 0.019 |
| 52 | 3484 | 100 | 4.605 | 92.353  | 4.526 | 0.022 | 54.809 | 4.004 | 0.019 | 51.422 | 3.940 | 0.019 |
| 53 | 3551 | 100 | 4.605 | 91.648  | 4.518 | 0.022 | 55.172 | 4.010 | 0.019 | 52.431 | 3.960 | 0.019 |
| 54 | 3618 | 100 | 4.605 | 89.531  | 4.495 | 0.022 | 54.834 | 4.004 | 0.019 | 51.584 | 3.943 | 0.019 |
| 55 | 3685 | 100 | 4.605 | 87.776  | 4.475 | 0.022 | 56.569 | 4.035 | 0.019 | 52.490 | 3.961 | 0.019 |
| 56 | 3752 | 100 | 4.605 | 88.242  | 4.480 | 0.022 | 58.094 | 4.062 | 0.020 | 50.940 | 3.931 | 0.019 |
| 57 | 3819 | 100 | 4.605 | 86.653  | 4.462 | 0.022 | 57.421 | 4.050 | 0.020 | 51.323 | 3.938 | 0.019 |
| 58 | 3886 | 100 | 4.605 | 86.604  | 4.461 | 0.022 | 58.116 | 4.062 | 0.020 | 52.266 | 3.956 | 0.019 |
| 59 | 3953 | 100 | 4.605 | 85.198  | 4.445 | 0.021 | 58.536 | 4.070 | 0.020 | 52.119 | 3.954 | 0.019 |
| 60 | 4020 | 100 | 4.605 | 85.690  | 4.451 | 0.021 | 58.993 | 4.077 | 0.020 | 52.925 | 3.969 | 0.019 |
| 61 | 4087 | 100 | 4.605 | 83.840  | 4.429 | 0.021 | 60.131 | 4.097 | 0.020 | 52.539 | 3.962 | 0.019 |
| 62 | 4154 | 100 | 4.605 | 84.216  | 4.433 | 0.021 | 61.329 | 4.116 | 0.020 | 53.525 | 3.980 | 0.019 |
| 63 | 4221 | 100 | 4.605 | 83.610  | 4.426 | 0.021 | 61.153 | 4.113 | 0.020 | 53.007 | 3.970 | 0.019 |
| 64 | 4288 | 100 | 4.605 | 82.106  | 4.408 | 0.021 | 63.586 | 4.152 | 0.020 | 53.865 | 3.986 | 0.019 |
| 65 | 4355 | 100 | 4.605 | 81.217  | 4.397 | 0.021 | 64.266 | 4.163 | 0.020 | 54.471 | 3.998 | 0.019 |
| 66 | 4422 | 100 | 4.605 | 81.003  | 4.394 | 0.021 | 64.060 | 4.160 | 0.020 | 54.325 | 3.995 | 0.019 |
| 67 | 4489 | 100 | 4.605 | 80.140  | 4.384 | 0.021 | 62.504 | 4.135 | 0.020 | 54.432 | 3.997 | 0.019 |
| 68 | 4556 | 100 | 4.605 | 79.382  | 4.374 | 0.021 | 64.444 | 4.166 | 0.020 | 54.807 | 4.004 | 0.019 |
| 69 | 4623 | 100 | 4.605 | 77.157  | 4.346 | 0.021 | 64.946 | 4.174 | 0.020 | 53.807 | 3.985 | 0.019 |
| 70 | 4690 | 100 | 4.605 | 78.332  | 4.361 | 0.021 | 65.644 | 4.184 | 0.020 | 56.050 | 4.026 | 0.019 |

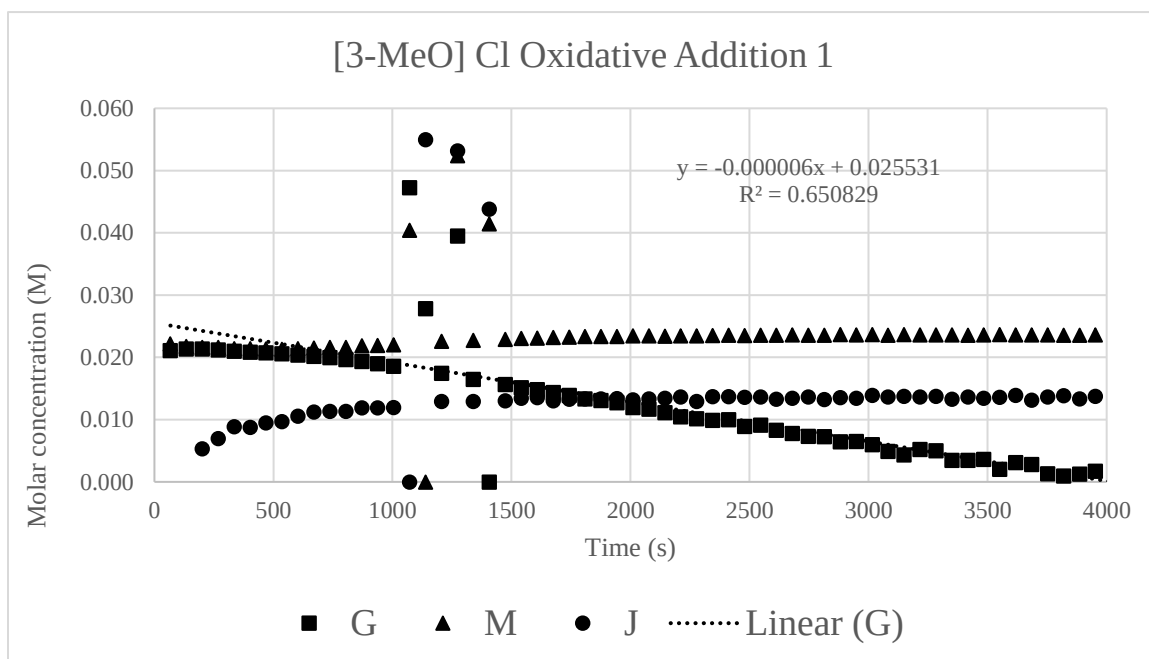
Table: Raw Data For [Unsubstituted] Cl Oxidative Addition 3<sup>10</sup>

| A  | B    | C   | D     | E       | F     | G     | H      | I      | J      | K      | L     | M     |
|----|------|-----|-------|---------|-------|-------|--------|--------|--------|--------|-------|-------|
| 1  | 67   | 100 | 4.605 | 89.851  | 4.498 | 0.022 | 0.398  | -0.921 | -0.004 | 93.835 | 4.542 | 0.022 |
| 2  | 134  | 100 | 4.605 | 96.808  | 4.573 | 0.022 | 1.210  | 0.191  | 0.001  | 85.955 | 4.454 | 0.021 |
| 3  | 201  | 100 | 4.605 | 101.050 | 4.616 | 0.022 | 3.118  | 1.137  | 0.005  | 77.839 | 4.355 | 0.021 |
| 4  | 268  | 100 | 4.605 | 106.416 | 4.667 | 0.023 | 5.471  | 1.700  | 0.008  | 71.792 | 4.274 | 0.021 |
| 5  | 335  | 100 | 4.605 | 107.846 | 4.681 | 0.023 | 6.778  | 1.914  | 0.009  | 68.913 | 4.233 | 0.020 |
| 6  | 402  | 100 | 4.605 | 109.708 | 4.698 | 0.023 | 8.836  | 2.179  | 0.011  | 65.179 | 4.177 | 0.020 |
| 7  | 469  | 100 | 4.605 | 108.520 | 4.687 | 0.023 | 9.008  | 2.198  | 0.011  | 63.183 | 4.146 | 0.020 |
| 8  | 536  | 100 | 4.605 | 107.180 | 4.675 | 0.023 | 10.736 | 2.374  | 0.011  | 62.627 | 4.137 | 0.020 |
| 9  | 603  | 100 | 4.605 | 106.891 | 4.672 | 0.023 | 10.887 | 2.388  | 0.012  | 60.862 | 4.109 | 0.020 |
| 10 | 670  | 100 | 4.605 | 107.205 | 4.675 | 0.023 | 13.912 | 2.633  | 0.013  | 60.229 | 4.098 | 0.020 |
| 11 | 737  | 100 | 4.605 | 107.046 | 4.673 | 0.023 | 14.799 | 2.695  | 0.013  | 59.924 | 4.093 | 0.020 |
| 12 | 804  | 100 | 4.605 | 106.155 | 4.665 | 0.023 | 15.406 | 2.735  | 0.013  | 57.959 | 4.060 | 0.020 |
| 13 | 871  | 100 | 4.605 | 105.176 | 4.656 | 0.022 | 16.898 | 2.827  | 0.014  | 58.628 | 4.071 | 0.020 |
| 14 | 938  | 100 | 4.605 | 103.212 | 4.637 | 0.022 | 17.995 | 2.890  | 0.014  | 58.338 | 4.066 | 0.020 |
| 15 | 1005 | 100 | 4.605 | 102.176 | 4.627 | 0.022 | 19.127 | 2.951  | 0.014  | 58.718 | 4.073 | 0.020 |
| 16 | 1072 | 100 | 4.605 | 101.291 | 4.618 | 0.022 | 18.850 | 2.937  | 0.014  | 57.868 | 4.058 | 0.020 |
| 17 | 1139 | 100 | 4.605 | 100.789 | 4.613 | 0.022 | 19.954 | 2.993  | 0.014  | 57.918 | 4.059 | 0.020 |

<sup>10</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~-10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |     |       |         |       |       |        |       |       |        |       |       |
|----|------|-----|-------|---------|-------|-------|--------|-------|-------|--------|-------|-------|
| 18 | 1206 | 100 | 4.605 | 100.141 | 4.607 | 0.022 | 23.132 | 3.141 | 0.015 | 58.035 | 4.061 | 0.020 |
| 19 | 1273 | 100 | 4.605 | 95.910  | 4.563 | 0.022 | 22.957 | 3.134 | 0.015 | 58.335 | 4.066 | 0.020 |
| 20 | 1340 | 100 | 4.605 | 95.227  | 4.556 | 0.022 | 24.303 | 3.191 | 0.015 | 58.228 | 4.064 | 0.020 |
| 21 | 1407 | 100 | 4.605 | 93.394  | 4.537 | 0.022 | 24.768 | 3.210 | 0.015 | 58.653 | 4.072 | 0.020 |
| 22 | 1474 | 100 | 4.605 | 92.712  | 4.529 | 0.022 | 24.516 | 3.199 | 0.015 | 60.128 | 4.096 | 0.020 |
| 23 | 1541 | 100 | 4.605 | 88.745  | 4.486 | 0.022 | 25.770 | 3.249 | 0.016 | 60.193 | 4.098 | 0.020 |
| 24 | 1608 | 100 | 4.605 | 87.212  | 4.468 | 0.022 | 27.078 | 3.299 | 0.016 | 60.310 | 4.100 | 0.020 |
| 25 | 1675 | 100 | 4.605 | 86.094  | 4.455 | 0.022 | 27.473 | 3.313 | 0.016 | 61.574 | 4.120 | 0.020 |
| 26 | 1742 | 100 | 4.605 | 84.690  | 4.439 | 0.021 | 29.723 | 3.392 | 0.016 | 62.761 | 4.139 | 0.020 |
| 27 | 1809 | 100 | 4.605 | 81.996  | 4.407 | 0.021 | 28.772 | 3.359 | 0.016 | 63.682 | 4.154 | 0.020 |
| 28 | 1876 | 100 | 4.605 | 80.178  | 4.384 | 0.021 | 29.695 | 3.391 | 0.016 | 64.017 | 4.159 | 0.020 |
| 29 | 1943 | 100 | 4.605 | 78.667  | 4.365 | 0.021 | 30.318 | 3.412 | 0.016 | 66.466 | 4.197 | 0.020 |
| 30 | 2010 | 100 | 4.605 | 76.213  | 4.334 | 0.021 | 30.815 | 3.428 | 0.017 | 66.417 | 4.196 | 0.020 |
| 31 | 2077 | 100 | 4.605 | 74.493  | 4.311 | 0.021 | 29.937 | 3.399 | 0.016 | 67.151 | 4.207 | 0.020 |
| 32 | 2144 | 100 | 4.605 | 71.612  | 4.271 | 0.021 | 30.406 | 3.415 | 0.016 | 68.667 | 4.229 | 0.020 |
| 33 | 2211 | 100 | 4.605 | 69.858  | 4.246 | 0.020 | 32.038 | 3.467 | 0.017 | 70.692 | 4.258 | 0.021 |
| 34 | 2278 | 100 | 4.605 | 67.408  | 4.211 | 0.020 | 33.469 | 3.511 | 0.017 | 71.242 | 4.266 | 0.021 |
| 35 | 2345 | 100 | 4.605 | 66.455  | 4.197 | 0.020 | 33.463 | 3.510 | 0.017 | 72.531 | 4.284 | 0.021 |
| 36 | 2412 | 100 | 4.605 | 63.968  | 4.158 | 0.020 | 33.631 | 3.515 | 0.017 | 72.313 | 4.281 | 0.021 |
| 37 | 2479 | 100 | 4.605 | 61.705  | 4.122 | 0.020 | 32.404 | 3.478 | 0.017 | 74.167 | 4.306 | 0.021 |
| 38 | 2546 | 100 | 4.605 | 59.266  | 4.082 | 0.020 | 33.631 | 3.515 | 0.017 | 75.619 | 4.326 | 0.021 |
| 39 | 2613 | 100 | 4.605 | 59.591  | 4.088 | 0.020 | 35.470 | 3.569 | 0.017 | 75.457 | 4.324 | 0.021 |
| 40 | 2680 | 100 | 4.605 | 56.579  | 4.036 | 0.019 | 35.594 | 3.572 | 0.017 | 78.395 | 4.362 | 0.021 |
| 41 | 2747 | 100 | 4.605 | 56.948  | 4.042 | 0.020 | 37.496 | 3.624 | 0.017 | 80.637 | 4.390 | 0.021 |
| 42 | 2814 | 100 | 4.605 | 53.214  | 3.974 | 0.019 | 35.529 | 3.570 | 0.017 | 80.349 | 4.386 | 0.021 |
| 43 | 2881 | 100 | 4.605 | 51.853  | 3.948 | 0.019 | 36.313 | 3.592 | 0.017 | 81.735 | 4.403 | 0.021 |
| 44 | 2948 | 100 | 4.605 | 50.560  | 3.923 | 0.019 | 37.116 | 3.614 | 0.017 | 84.640 | 4.438 | 0.021 |
| 45 | 3015 | 100 | 4.605 | 47.793  | 3.867 | 0.019 | 37.435 | 3.623 | 0.017 | 85.383 | 4.447 | 0.021 |
| 46 | 3082 | 100 | 4.605 | 46.719  | 3.844 | 0.019 | 37.583 | 3.627 | 0.018 | 87.214 | 4.468 | 0.022 |
| 47 | 3149 | 100 | 4.605 | 46.019  | 3.829 | 0.018 | 38.404 | 3.648 | 0.018 | 87.876 | 4.476 | 0.022 |
| 48 | 3216 | 100 | 4.605 | 43.409  | 3.771 | 0.018 | 39.500 | 3.676 | 0.018 | 89.954 | 4.499 | 0.022 |
| 49 | 3283 | 100 | 4.605 | 42.587  | 3.752 | 0.018 | 38.440 | 3.649 | 0.018 | 89.245 | 4.491 | 0.022 |
| 50 | 3350 | 100 | 4.605 | 40.758  | 3.708 | 0.018 | 39.938 | 3.687 | 0.018 | 92.423 | 4.526 | 0.022 |
| 51 | 3417 | 100 | 4.605 | 41.273  | 3.720 | 0.018 | 40.976 | 3.713 | 0.018 | 94.242 | 4.546 | 0.022 |
| 52 | 3484 | 100 | 4.605 | 37.031  | 3.612 | 0.017 | 40.228 | 3.695 | 0.018 | 94.299 | 4.546 | 0.022 |
| 53 | 3551 | 100 | 4.605 | 36.847  | 3.607 | 0.017 | 41.839 | 3.734 | 0.018 | 95.791 | 4.562 | 0.022 |
| 54 | 3618 | 100 | 4.605 | 35.481  | 3.569 | 0.017 | 40.588 | 3.703 | 0.018 | 97.382 | 4.579 | 0.022 |
| 55 | 3685 | 100 | 4.605 | 34.432  | 3.539 | 0.017 | 40.797 | 3.709 | 0.018 | 99.040 | 4.596 | 0.022 |
| 56 | 3752 | 100 | 4.605 | 32.592  | 3.484 | 0.017 | 40.414 | 3.699 | 0.018 | 99.722 | 4.602 | 0.022 |

|    |      |     |       |        |       |       |        |       |       |         |       |       |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|---------|-------|-------|
| 57 | 3819 | 100 | 4.605 | 31.420 | 3.447 | 0.017 | 41.847 | 3.734 | 0.018 | 99.447  | 4.600 | 0.022 |
| 58 | 3886 | 100 | 4.605 | 31.092 | 3.437 | 0.017 | 41.635 | 3.729 | 0.018 | 100.214 | 4.607 | 0.022 |
| 59 | 3953 | 100 | 4.605 | 28.784 | 3.360 | 0.016 | 40.975 | 3.713 | 0.018 | 100.955 | 4.615 | 0.022 |
| 60 | 4020 | 100 | 4.605 | 28.329 | 3.344 | 0.016 | 42.572 | 3.751 | 0.018 | 104.553 | 4.650 | 0.022 |
| 61 | 4087 | 100 | 4.605 | 26.328 | 3.271 | 0.016 | 41.771 | 3.732 | 0.018 | 104.256 | 4.647 | 0.022 |
| 62 | 4154 | 100 | 4.605 | 27.028 | 3.297 | 0.016 | 42.350 | 3.746 | 0.018 | 104.947 | 4.653 | 0.022 |
| 63 | 4221 | 100 | 4.605 | 24.416 | 3.195 | 0.015 | 41.489 | 3.725 | 0.018 | 103.908 | 4.644 | 0.022 |
| 64 | 4288 | 100 | 4.605 | 23.861 | 3.172 | 0.015 | 42.380 | 3.747 | 0.018 | 106.713 | 4.670 | 0.023 |
| 65 | 4355 | 100 | 4.605 | 23.420 | 3.154 | 0.015 | 43.287 | 3.768 | 0.018 | 107.970 | 4.682 | 0.023 |
| 66 | 4422 | 100 | 4.605 | 21.998 | 3.091 | 0.015 | 43.848 | 3.781 | 0.018 | 109.749 | 4.698 | 0.023 |
| 67 | 4489 | 100 | 4.605 | 22.471 | 3.112 | 0.015 | 42.991 | 3.761 | 0.018 | 108.047 | 4.683 | 0.023 |
| 68 | 4556 | 100 | 4.605 | 20.329 | 3.012 | 0.015 | 43.168 | 3.765 | 0.018 | 109.452 | 4.695 | 0.023 |
| 69 | 4623 | 100 | 4.605 | 19.704 | 2.981 | 0.014 | 44.693 | 3.800 | 0.018 | 113.285 | 4.730 | 0.023 |
| 70 | 4690 | 100 | 4.605 | 19.841 | 2.988 | 0.014 | 44.343 | 3.792 | 0.018 | 113.083 | 4.728 | 0.023 |

Table: Raw Data For [3-MeO] Cl Oxidative Addition 1<sup>11</sup>

| A | B  | C       | D         | E      | F     | G     | H     | I      | J      | K      | L     | M     |
|---|----|---------|-----------|--------|-------|-------|-------|--------|--------|--------|-------|-------|
| 1 | 67 | 10<br>0 | 4.60<br>5 | 78.897 | 4.368 | 0.021 | 0.417 | -0.875 | -0.004 | 99.071 | 4.596 | 0.022 |

<sup>11</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~-10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|        |          |         |           |               |           |           |               |            |           |               |            |           |
|--------|----------|---------|-----------|---------------|-----------|-----------|---------------|------------|-----------|---------------|------------|-----------|
| 2      | 134      | 10<br>0 | 4.60<br>5 | 83.312        | 4.423     | 0.021     | 0.628         | -0.465     | -0.002    | 90.999        | 4.511      | 0.022     |
| 3      | 201      | 10<br>0 | 4.60<br>5 | 83.156        | 4.421     | 0.021     | 2.999         | 1.098      | 0.005     | 88.443        | 4.482      | 0.022     |
| 4      | 268      | 10<br>0 | 4.60<br>5 | 80.936        | 4.394     | 0.021     | 4.221         | 1.440      | 0.007     | 87.834        | 4.475      | 0.022     |
| 5      | 335      | 10<br>0 | 4.60<br>5 | 77.546        | 4.351     | 0.021     | 6.280         | 1.837      | 0.009     | 84.265        | 4.434      | 0.021     |
| 6      | 402      | 10<br>0 | 4.60<br>5 | 75.521        | 4.324     | 0.021     | 6.150         | 1.816      | 0.009     | 84.048        | 4.431      | 0.021     |
| 7      | 469      | 10<br>0 | 4.60<br>5 | 73.308        | 4.295     | 0.021     | 7.120         | 1.963      | 0.009     | 83.553        | 4.425      | 0.021     |
| 8      | 536      | 10<br>0 | 4.60<br>5 | 71.073        | 4.264     | 0.021     | 7.454         | 2.009      | 0.010     | 82.693        | 4.415      | 0.021     |
| 9      | 603      | 10<br>0 | 4.60<br>5 | 68.476        | 4.226     | 0.020     | 8.968         | 2.194      | 0.011     | 84.606        | 4.438      | 0.021     |
| 1<br>0 | 670      | 10<br>0 | 4.60<br>5 | 65.733        | 4.186     | 0.020     | 10.217        | 2.324      | 0.011     | 86.215        | 4.457      | 0.022     |
| 1<br>1 | 737      | 10<br>0 | 4.60<br>5 | 62.559        | 4.136     | 0.020     | 10.477        | 2.349      | 0.011     | 88.158        | 4.479      | 0.022     |
| 1<br>2 | 804      | 10<br>0 | 4.60<br>5 | 58.793        | 4.074     | 0.020     | 10.421        | 2.344      | 0.011     | 88.275        | 4.480      | 0.022     |
| 1<br>3 | 871      | 10<br>0 | 4.60<br>5 | 55.262        | 4.012     | 0.019     | 11.728        | 2.462      | 0.012     | 92.864        | 4.531      | 0.022     |
| 1<br>4 | 938      | 10<br>0 | 4.60<br>5 | 51.110        | 3.934     | 0.019     | 11.812        | 2.469      | 0.012     | 94.183        | 4.545      | 0.022     |
| 1<br>5 | 100<br>5 | 10<br>0 | 4.60<br>5 | 46.994        | 3.850     | 0.019     | 11.927        | 2.479      | 0.012     | 96.077        | 4.565      | 0.022     |
| 1<br>6 | 107<br>2 | 10<br>0 | 4.60<br>5 | 17841.8<br>76 | 9.789     | 0.047     | 2169.32<br>2  | #NU<br>M!  | #NU<br>M! | 4325.102      | 8.372      | 0.040     |
| 1<br>7 | 113<br>9 | 10<br>0 | 4.60<br>5 | 320.725       | 5.771     | 0.028     | 88488.2<br>27 | 11.39<br>1 | 0.055     | 12242.67<br>0 | #NU<br>M!  | #NU<br>M! |
| 1<br>8 | 120<br>6 | 10<br>0 | 4.60<br>5 | 37.285        | 3.619     | 0.017     | 14.509        | 2.675      | 0.013     | 107.609       | 4.679      | 0.023     |
| 1<br>9 | 127<br>3 | 10<br>0 | 4.60<br>5 | 3568.97<br>8  | 8.180     | 0.039     | 61211.8<br>76 | 11.02<br>2 | 0.053     | 52049.70<br>7 | 10.86<br>0 | 0.052     |
| 2<br>0 | 134<br>0 | 10<br>0 | 4.60<br>5 | 30.459        | 3.416     | 0.016     | 14.579        | 2.680      | 0.013     | 111.585       | 4.715      | 0.023     |
| 2<br>1 | 140<br>7 | 10<br>0 | 4.60<br>5 | 1317.71<br>5  | #NU<br>M! | #NU<br>M! | 8815.94<br>2  | 9.084      | 0.044     | 5396.608      | 8.594      | 0.041     |
| 2<br>2 | 147<br>4 | 10<br>0 | 4.60<br>5 | 25.611        | 3.243     | 0.016     | 14.919        | 2.703      | 0.013     | 115.396       | 4.748      | 0.023     |
| 2<br>3 | 154<br>1 | 10<br>0 | 4.60<br>5 | 23.008        | 3.136     | 0.015     | 16.252        | 2.788      | 0.013     | 118.216       | 4.773      | 0.023     |
| 2<br>4 | 160<br>8 | 10<br>0 | 4.60<br>5 | 21.580        | 3.072     | 0.015     | 16.498        | 2.803      | 0.014     | 119.442       | 4.783      | 0.023     |
| 2<br>5 | 167<br>5 | 10<br>0 | 4.60<br>5 | 19.661        | 2.979     | 0.014     | 14.923        | 2.703      | 0.013     | 122.218       | 4.806      | 0.023     |
| 2<br>6 | 174<br>2 | 10<br>0 | 4.60<br>5 | 17.839        | 2.881     | 0.014     | 15.697        | 2.753      | 0.013     | 123.983       | 4.820      | 0.023     |
| 2<br>7 | 180<br>9 | 10<br>0 | 4.60<br>5 | 15.861        | 2.764     | 0.013     | 15.830        | 2.762      | 0.013     | 126.800       | 4.843      | 0.023     |
| 2<br>8 | 187<br>6 | 10<br>0 | 4.60<br>5 | 15.012        | 2.709     | 0.013     | 15.877        | 2.765      | 0.013     | 126.022       | 4.836      | 0.023     |

|    |      |     |       |        |       |       |        |       |       |         |       |       |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|---------|-------|-------|
| 29 | 1943 | 100 | 4.605 | 14.018 | 2.640 | 0.013 | 16.074 | 2.777 | 0.013 | 126.273 | 4.838 | 0.023 |
| 30 | 2010 | 100 | 4.605 | 11.898 | 2.476 | 0.012 | 15.336 | 2.730 | 0.013 | 129.210 | 4.861 | 0.023 |
| 31 | 2077 | 100 | 4.605 | 11.231 | 2.419 | 0.012 | 15.887 | 2.766 | 0.013 | 128.963 | 4.860 | 0.023 |
| 32 | 2144 | 100 | 4.605 | 10.069 | 2.309 | 0.011 | 16.188 | 2.784 | 0.013 | 127.962 | 4.852 | 0.023 |
| 33 | 2211 | 100 | 4.605 | 8.728  | 2.167 | 0.010 | 17.003 | 2.833 | 0.014 | 128.796 | 4.858 | 0.023 |
| 34 | 2278 | 100 | 4.605 | 8.191  | 2.103 | 0.010 | 14.609 | 2.682 | 0.013 | 128.931 | 4.859 | 0.023 |
| 35 | 2345 | 100 | 4.605 | 7.799  | 2.054 | 0.010 | 17.030 | 2.835 | 0.014 | 130.701 | 4.873 | 0.024 |
| 36 | 2412 | 100 | 4.605 | 7.900  | 2.067 | 0.010 | 17.013 | 2.834 | 0.014 | 131.905 | 4.882 | 0.024 |
| 37 | 2479 | 100 | 4.605 | 6.380  | 1.853 | 0.009 | 16.653 | 2.813 | 0.014 | 130.979 | 4.875 | 0.024 |
| 38 | 2546 | 100 | 4.605 | 6.648  | 1.894 | 0.009 | 16.848 | 2.824 | 0.014 | 132.451 | 4.886 | 0.024 |
| 39 | 2613 | 100 | 4.605 | 5.580  | 1.719 | 0.008 | 15.747 | 2.757 | 0.013 | 132.564 | 4.887 | 0.024 |
| 40 | 2680 | 100 | 4.605 | 5.030  | 1.615 | 0.008 | 16.133 | 2.781 | 0.013 | 133.562 | 4.895 | 0.024 |
| 41 | 2747 | 100 | 4.605 | 4.577  | 1.521 | 0.007 | 16.852 | 2.824 | 0.014 | 132.752 | 4.888 | 0.024 |
| 42 | 2814 | 100 | 4.605 | 4.495  | 1.503 | 0.007 | 15.487 | 2.740 | 0.013 | 131.947 | 4.882 | 0.024 |
| 43 | 2881 | 100 | 4.605 | 3.802  | 1.335 | 0.006 | 16.638 | 2.812 | 0.014 | 135.247 | 4.907 | 0.024 |
| 44 | 2948 | 100 | 4.605 | 3.863  | 1.351 | 0.007 | 16.292 | 2.791 | 0.013 | 133.775 | 4.896 | 0.024 |
| 45 | 3015 | 100 | 4.605 | 3.454  | 1.240 | 0.006 | 17.920 | 2.886 | 0.014 | 134.240 | 4.900 | 0.024 |
| 46 | 3082 | 100 | 4.605 | 2.757  | 1.014 | 0.005 | 16.862 | 2.825 | 0.014 | 132.324 | 4.885 | 0.024 |
| 47 | 3149 | 100 | 4.605 | 2.464  | 0.902 | 0.004 | 17.313 | 2.851 | 0.014 | 134.245 | 4.900 | 0.024 |
| 48 | 3216 | 100 | 4.605 | 2.939  | 1.078 | 0.005 | 16.986 | 2.832 | 0.014 | 133.276 | 4.892 | 0.024 |
| 49 | 3283 | 100 | 4.605 | 2.838  | 1.043 | 0.005 | 17.246 | 2.848 | 0.014 | 133.940 | 4.897 | 0.024 |
| 50 | 3350 | 100 | 4.605 | 2.047  | 0.717 | 0.003 | 15.767 | 2.758 | 0.013 | 134.043 | 4.898 | 0.024 |
| 51 | 3417 | 100 | 4.605 | 2.060  | 0.722 | 0.003 | 16.878 | 2.826 | 0.014 | 132.771 | 4.889 | 0.024 |
| 52 | 3484 | 100 | 4.605 | 2.122  | 0.752 | 0.004 | 16.286 | 2.790 | 0.013 | 133.993 | 4.898 | 0.024 |
| 53 | 3551 | 100 | 4.605 | 1.530  | 0.425 | 0.002 | 16.783 | 2.820 | 0.014 | 134.474 | 4.901 | 0.024 |
| 54 | 3618 | 100 | 4.605 | 1.915  | 0.650 | 0.003 | 17.917 | 2.886 | 0.014 | 133.912 | 4.897 | 0.024 |
| 55 | 3685 | 100 | 4.605 | 1.796  | 0.586 | 0.003 | 15.267 | 2.726 | 0.013 | 133.008 | 4.890 | 0.024 |
| 56 | 3752 | 100 | 4.605 | 1.308  | 0.268 | 0.001 | 16.887 | 2.827 | 0.014 | 133.406 | 4.893 | 0.024 |
| 57 | 3819 | 100 | 4.605 | 1.223  | 0.202 | 0.001 | 17.618 | 2.869 | 0.014 | 131.703 | 4.881 | 0.024 |

|    |      |     |       |       |        |        |        |       |       |         |       |       |
|----|------|-----|-------|-------|--------|--------|--------|-------|-------|---------|-------|-------|
| 58 | 3886 | 100 | 4.605 | 1.294 | 0.258  | 0.001  | 15.886 | 2.765 | 0.013 | 132.100 | 4.884 | 0.024 |
| 59 | 3953 | 100 | 4.605 | 1.435 | 0.361  | 0.002  | 17.199 | 2.845 | 0.014 | 134.085 | 4.898 | 0.024 |
| 60 | 4020 | 100 | 4.605 | 1.072 | 0.070  | 0.000  | 16.016 | 2.774 | 0.013 | 133.355 | 4.893 | 0.024 |
| 61 | 4087 | 100 | 4.605 | 1.176 | 0.162  | 0.001  | 17.631 | 2.870 | 0.014 | 133.521 | 4.894 | 0.024 |
| 62 | 4154 | 100 | 4.605 | 1.821 | 0.599  | 0.003  | 15.950 | 2.769 | 0.013 | 131.578 | 4.880 | 0.024 |
| 63 | 4221 | 100 | 4.605 | 1.012 | 0.012  | 0.000  | 16.637 | 2.812 | 0.014 | 131.150 | 4.876 | 0.024 |
| 64 | 4288 | 100 | 4.605 | 1.180 | 0.166  | 0.001  | 16.868 | 2.825 | 0.014 | 130.635 | 4.872 | 0.024 |
| 65 | 4355 | 100 | 4.605 | 1.051 | 0.050  | 0.000  | 16.853 | 2.825 | 0.014 | 133.002 | 4.890 | 0.024 |
| 66 | 4422 | 100 | 4.605 | 0.476 | -0.742 | -0.004 | 16.447 | 2.800 | 0.014 | 130.436 | 4.871 | 0.024 |
| 67 | 4489 | 100 | 4.605 | 0.788 | -0.238 | -0.001 | 16.163 | 2.783 | 0.013 | 130.363 | 4.870 | 0.024 |
| 68 | 4556 | 100 | 4.605 | 0.643 | -0.441 | -0.002 | 18.205 | 2.902 | 0.014 | 132.787 | 4.889 | 0.024 |
| 69 | 4623 | 100 | 4.605 | 0.480 | -0.735 | -0.004 | 16.356 | 2.795 | 0.013 | 131.695 | 4.880 | 0.024 |
| 70 | 4690 | 100 | 4.605 | 1.163 | 0.151  | 0.001  | 18.102 | 2.896 | 0.014 | 130.261 | 4.870 | 0.023 |

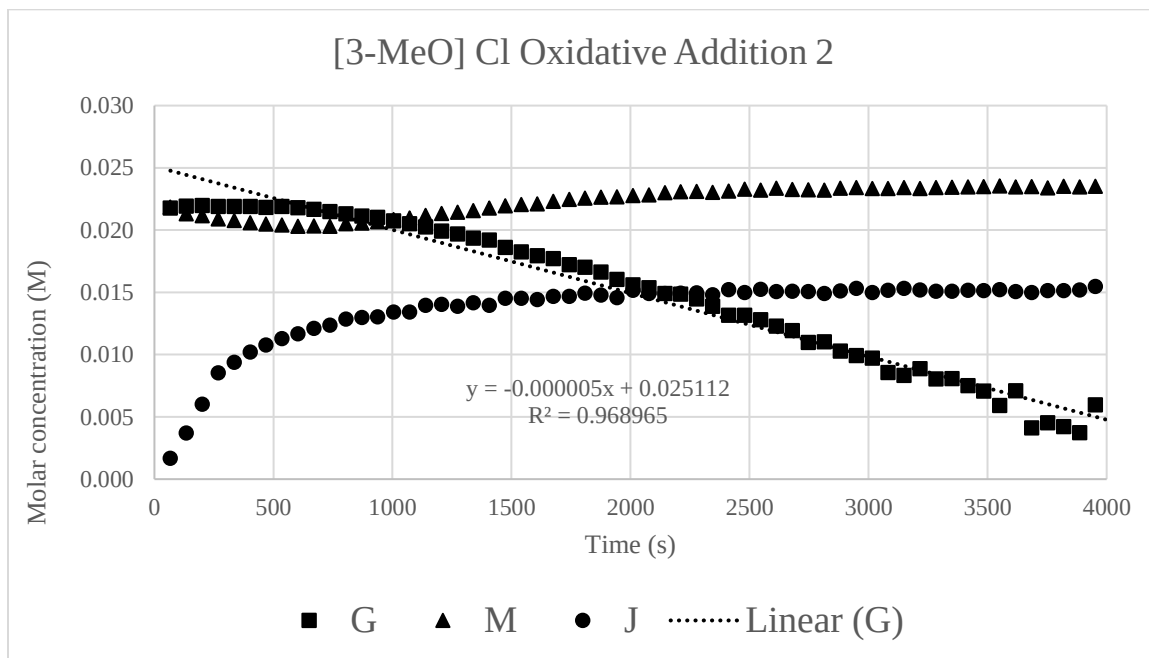


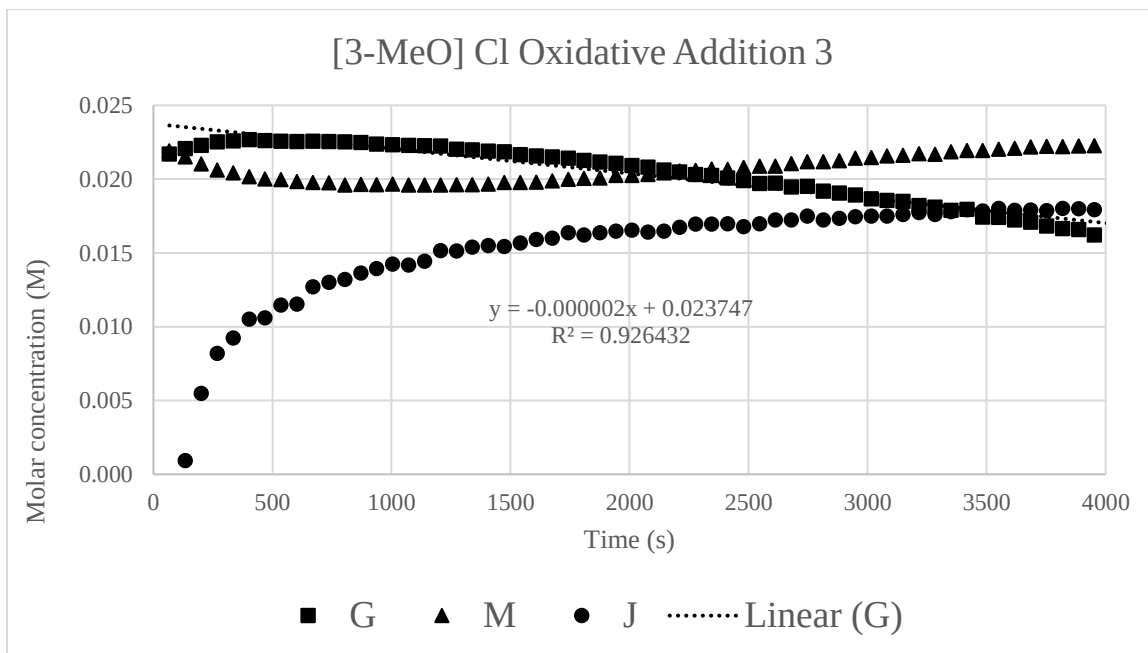
Table: Raw Data For [3-MeO] Cl Oxidative Addition 2<sup>12</sup>

| A  | B    | C   | D     | E      | F     | G     | H      | I     | J     | K      | L     | M     |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|--------|-------|-------|
| 1  | 67   | 100 | 4.605 | 91.268 | 4.514 | 0.022 | 1.421  | 0.352 | 0.002 | 92.688 | 4.529 | 0.022 |
| 2  | 134  | 100 | 4.605 | 94.019 | 4.543 | 0.022 | 2.162  | 0.771 | 0.004 | 83.043 | 4.419 | 0.021 |
| 3  | 201  | 100 | 4.605 | 95.443 | 4.559 | 0.022 | 3.496  | 1.252 | 0.006 | 80.515 | 4.388 | 0.021 |
| 4  | 268  | 100 | 4.605 | 93.960 | 4.543 | 0.022 | 5.892  | 1.774 | 0.009 | 76.130 | 4.332 | 0.021 |
| 5  | 335  | 100 | 4.605 | 93.706 | 4.540 | 0.022 | 7.006  | 1.947 | 0.009 | 74.150 | 4.306 | 0.021 |
| 6  | 402  | 100 | 4.605 | 93.522 | 4.538 | 0.022 | 8.305  | 2.117 | 0.010 | 71.567 | 4.271 | 0.021 |
| 7  | 469  | 100 | 4.605 | 92.349 | 4.526 | 0.022 | 9.345  | 2.235 | 0.011 | 69.861 | 4.247 | 0.020 |
| 8  | 536  | 100 | 4.605 | 93.571 | 4.539 | 0.022 | 10.375 | 2.339 | 0.011 | 68.834 | 4.232 | 0.020 |
| 9  | 603  | 100 | 4.605 | 91.603 | 4.517 | 0.022 | 11.228 | 2.418 | 0.012 | 67.488 | 4.212 | 0.020 |
| 10 | 670  | 100 | 4.605 | 89.401 | 4.493 | 0.022 | 12.299 | 2.510 | 0.012 | 67.894 | 4.218 | 0.020 |
| 11 | 737  | 100 | 4.605 | 86.224 | 4.457 | 0.022 | 12.978 | 2.563 | 0.012 | 67.268 | 4.209 | 0.020 |
| 12 | 804  | 100 | 4.605 | 82.806 | 4.416 | 0.021 | 14.355 | 2.664 | 0.013 | 70.164 | 4.251 | 0.021 |
| 13 | 871  | 100 | 4.605 | 80.013 | 4.382 | 0.021 | 14.809 | 2.695 | 0.013 | 70.896 | 4.261 | 0.021 |
| 14 | 938  | 100 | 4.605 | 78.039 | 4.357 | 0.021 | 14.953 | 2.705 | 0.013 | 72.726 | 4.287 | 0.021 |
| 15 | 1005 | 100 | 4.605 | 73.848 | 4.302 | 0.021 | 16.178 | 2.784 | 0.013 | 75.201 | 4.320 | 0.021 |
| 16 | 1072 | 100 | 4.605 | 70.439 | 4.255 | 0.021 | 16.160 | 2.783 | 0.013 | 77.249 | 4.347 | 0.021 |

<sup>12</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |     |       |        |       |       |        |       |       |         |       |       |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|---------|-------|-------|
| 17 | 1139 | 100 | 4.605 | 66.840 | 4.202 | 0.020 | 18.038 | 2.892 | 0.014 | 80.947  | 4.394 | 0.021 |
| 18 | 1206 | 100 | 4.605 | 62.298 | 4.132 | 0.020 | 18.382 | 2.911 | 0.014 | 83.294  | 4.422 | 0.021 |
| 19 | 1273 | 100 | 4.605 | 59.285 | 4.082 | 0.020 | 17.762 | 2.877 | 0.014 | 84.975  | 4.442 | 0.021 |
| 20 | 1340 | 100 | 4.605 | 55.191 | 4.011 | 0.019 | 18.913 | 2.940 | 0.014 | 87.568  | 4.472 | 0.022 |
| 21 | 1407 | 100 | 4.605 | 53.528 | 3.980 | 0.019 | 18.103 | 2.896 | 0.014 | 91.138  | 4.512 | 0.022 |
| 22 | 1474 | 100 | 4.605 | 47.534 | 3.861 | 0.019 | 20.286 | 3.010 | 0.015 | 94.582  | 4.549 | 0.022 |
| 23 | 1541 | 100 | 4.605 | 44.010 | 3.784 | 0.018 | 20.304 | 3.011 | 0.015 | 96.867  | 4.573 | 0.022 |
| 24 | 1608 | 100 | 4.605 | 41.268 | 3.720 | 0.018 | 19.879 | 2.990 | 0.014 | 97.627  | 4.581 | 0.022 |
| 25 | 1675 | 100 | 4.605 | 39.349 | 3.672 | 0.018 | 20.981 | 3.044 | 0.015 | 102.254 | 4.627 | 0.022 |
| 26 | 1742 | 100 | 4.605 | 35.553 | 3.571 | 0.017 | 21.008 | 3.045 | 0.015 | 105.147 | 4.655 | 0.022 |
| 27 | 1809 | 100 | 4.605 | 34.125 | 3.530 | 0.017 | 22.188 | 3.100 | 0.015 | 107.883 | 4.681 | 0.023 |
| 28 | 1876 | 100 | 4.605 | 31.515 | 3.450 | 0.017 | 21.403 | 3.064 | 0.015 | 109.388 | 4.695 | 0.023 |
| 29 | 1943 | 100 | 4.605 | 27.875 | 3.328 | 0.016 | 20.587 | 3.025 | 0.015 | 109.832 | 4.699 | 0.023 |
| 30 | 2010 | 100 | 4.605 | 25.436 | 3.236 | 0.016 | 23.169 | 3.143 | 0.015 | 112.056 | 4.719 | 0.023 |
| 31 | 2077 | 100 | 4.605 | 24.226 | 3.187 | 0.015 | 22.068 | 3.094 | 0.015 | 113.414 | 4.731 | 0.023 |
| 32 | 2144 | 100 | 4.605 | 22.057 | 3.094 | 0.015 | 21.990 | 3.091 | 0.015 | 117.807 | 4.769 | 0.023 |
| 33 | 2211 | 100 | 4.605 | 21.791 | 3.082 | 0.015 | 22.172 | 3.099 | 0.015 | 119.548 | 4.784 | 0.023 |
| 34 | 2278 | 100 | 4.605 | 20.072 | 2.999 | 0.014 | 22.240 | 3.102 | 0.015 | 120.223 | 4.789 | 0.023 |
| 35 | 2345 | 100 | 4.605 | 17.810 | 2.880 | 0.014 | 21.528 | 3.069 | 0.015 | 118.688 | 4.777 | 0.023 |
| 36 | 2412 | 100 | 4.605 | 15.317 | 2.729 | 0.013 | 23.417 | 3.153 | 0.015 | 121.037 | 4.796 | 0.023 |
| 37 | 2479 | 100 | 4.605 | 15.353 | 2.731 | 0.013 | 22.357 | 3.107 | 0.015 | 124.675 | 4.826 | 0.023 |
| 38 | 2546 | 100 | 4.605 | 14.232 | 2.655 | 0.013 | 23.545 | 3.159 | 0.015 | 123.130 | 4.813 | 0.023 |
| 39 | 2613 | 100 | 4.605 | 12.815 | 2.551 | 0.012 | 22.762 | 3.125 | 0.015 | 126.897 | 4.843 | 0.023 |
| 40 | 2680 | 100 | 4.605 | 11.859 | 2.473 | 0.012 | 22.891 | 3.131 | 0.015 | 124.345 | 4.823 | 0.023 |
| 41 | 2747 | 100 | 4.605 | 9.760  | 2.278 | 0.011 | 22.717 | 3.123 | 0.015 | 123.908 | 4.820 | 0.023 |
| 42 | 2814 | 100 | 4.605 | 9.847  | 2.287 | 0.011 | 22.077 | 3.095 | 0.015 | 122.997 | 4.812 | 0.023 |
| 43 | 2881 | 100 | 4.605 | 8.429  | 2.132 | 0.010 | 23.034 | 3.137 | 0.015 | 127.067 | 4.845 | 0.023 |
| 44 | 2948 | 100 | 4.605 | 7.819  | 2.057 | 0.010 | 23.982 | 3.177 | 0.015 | 128.623 | 4.857 | 0.023 |
| 45 | 3015 | 100 | 4.605 | 7.501  | 2.015 | 0.010 | 22.363 | 3.107 | 0.015 | 126.059 | 4.837 | 0.023 |
| 46 | 3082 | 100 | 4.605 | 5.917  | 1.778 | 0.009 | 23.244 | 3.146 | 0.015 | 126.244 | 4.838 | 0.023 |
| 47 | 3149 | 100 | 4.605 | 5.640  | 1.730 | 0.008 | 24.025 | 3.179 | 0.015 | 128.130 | 4.853 | 0.023 |
| 48 | 3216 | 100 | 4.605 | 6.303  | 1.841 | 0.009 | 23.290 | 3.148 | 0.015 | 126.041 | 4.837 | 0.023 |
| 49 | 3283 | 100 | 4.605 | 5.325  | 1.672 | 0.008 | 22.831 | 3.128 | 0.015 | 128.674 | 4.857 | 0.023 |
| 50 | 3350 | 100 | 4.605 | 5.330  | 1.673 | 0.008 | 22.800 | 3.127 | 0.015 | 128.715 | 4.858 | 0.023 |
| 51 | 3417 | 100 | 4.605 | 4.747  | 1.558 | 0.008 | 23.243 | 3.146 | 0.015 | 129.780 | 4.866 | 0.023 |
| 52 | 3484 | 100 | 4.605 | 4.345  | 1.469 | 0.007 | 23.141 | 3.142 | 0.015 | 130.476 | 4.871 | 0.024 |
| 53 | 3551 | 100 | 4.605 | 3.411  | 1.227 | 0.006 | 23.495 | 3.157 | 0.015 | 131.687 | 4.880 | 0.024 |
| 54 | 3618 | 100 | 4.605 | 4.374  | 1.476 | 0.007 | 22.757 | 3.125 | 0.015 | 129.499 | 4.864 | 0.023 |
| 55 | 3685 | 100 | 4.605 | 2.353  | 0.856 | 0.004 | 22.316 | 3.105 | 0.015 | 130.132 | 4.869 | 0.023 |

|    |      |     |       |       |       |       |        |       |       |         |       |       |
|----|------|-----|-------|-------|-------|-------|--------|-------|-------|---------|-------|-------|
| 56 | 3752 | 100 | 4.605 | 2.568 | 0.943 | 0.005 | 23.162 | 3.143 | 0.015 | 127.658 | 4.849 | 0.023 |
| 57 | 3819 | 100 | 4.605 | 2.402 | 0.877 | 0.004 | 23.055 | 3.138 | 0.015 | 131.408 | 4.878 | 0.024 |
| 58 | 3886 | 100 | 4.605 | 2.171 | 0.775 | 0.004 | 23.319 | 3.149 | 0.015 | 129.684 | 4.865 | 0.023 |
| 59 | 3953 | 100 | 4.605 | 3.444 | 1.237 | 0.006 | 24.741 | 3.208 | 0.015 | 131.388 | 4.878 | 0.024 |
| 60 | 4020 | 100 | 4.605 | 2.035 | 0.711 | 0.003 | 23.653 | 3.163 | 0.015 | 133.059 | 4.891 | 0.024 |

Table: Raw Data For [3-MeO] Cl Oxidative Addition 3<sup>13</sup>

| A  | B   | C   | D     | E       | F     | G     | H      | I      | J      | K      | L     | M     |
|----|-----|-----|-------|---------|-------|-------|--------|--------|--------|--------|-------|-------|
| 1  | 67  | 100 | 4.605 | 89.851  | 4.498 | 0.022 | 0.398  | -0.921 | -0.004 | 93.835 | 4.542 | 0.022 |
| 2  | 134 | 100 | 4.605 | 96.808  | 4.573 | 0.022 | 1.210  | 0.191  | 0.001  | 85.955 | 4.454 | 0.021 |
| 3  | 201 | 100 | 4.605 | 101.050 | 4.616 | 0.022 | 3.118  | 1.137  | 0.005  | 77.839 | 4.355 | 0.021 |
| 4  | 268 | 100 | 4.605 | 106.416 | 4.667 | 0.023 | 5.471  | 1.700  | 0.008  | 71.792 | 4.274 | 0.021 |
| 5  | 335 | 100 | 4.605 | 107.846 | 4.681 | 0.023 | 6.778  | 1.914  | 0.009  | 68.913 | 4.233 | 0.020 |
| 6  | 402 | 100 | 4.605 | 109.708 | 4.698 | 0.023 | 8.836  | 2.179  | 0.011  | 65.179 | 4.177 | 0.020 |
| 7  | 469 | 100 | 4.605 | 108.520 | 4.687 | 0.023 | 9.008  | 2.198  | 0.011  | 63.183 | 4.146 | 0.020 |
| 8  | 536 | 100 | 4.605 | 107.180 | 4.675 | 0.023 | 10.736 | 2.374  | 0.011  | 62.627 | 4.137 | 0.020 |
| 9  | 603 | 100 | 4.605 | 106.891 | 4.672 | 0.023 | 10.887 | 2.388  | 0.012  | 60.862 | 4.109 | 0.020 |
| 10 | 670 | 100 | 4.605 | 107.205 | 4.675 | 0.023 | 13.912 | 2.633  | 0.013  | 60.229 | 4.098 | 0.020 |
| 11 | 737 | 100 | 4.605 | 107.046 | 4.673 | 0.023 | 14.799 | 2.695  | 0.013  | 59.924 | 4.093 | 0.020 |

<sup>13</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~-10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |     |       |         |       |       |        |       |       |        |       |       |
|----|------|-----|-------|---------|-------|-------|--------|-------|-------|--------|-------|-------|
| 12 | 804  | 100 | 4.605 | 106.155 | 4.665 | 0.023 | 15.406 | 2.735 | 0.013 | 57.959 | 4.060 | 0.020 |
| 13 | 871  | 100 | 4.605 | 105.176 | 4.656 | 0.022 | 16.898 | 2.827 | 0.014 | 58.628 | 4.071 | 0.020 |
| 14 | 938  | 100 | 4.605 | 103.212 | 4.637 | 0.022 | 17.995 | 2.890 | 0.014 | 58.338 | 4.066 | 0.020 |
| 15 | 1005 | 100 | 4.605 | 102.176 | 4.627 | 0.022 | 19.127 | 2.951 | 0.014 | 58.718 | 4.073 | 0.020 |
| 16 | 1072 | 100 | 4.605 | 101.291 | 4.618 | 0.022 | 18.850 | 2.937 | 0.014 | 57.868 | 4.058 | 0.020 |
| 17 | 1139 | 100 | 4.605 | 100.789 | 4.613 | 0.022 | 19.954 | 2.993 | 0.014 | 57.918 | 4.059 | 0.020 |
| 18 | 1206 | 100 | 4.605 | 100.141 | 4.607 | 0.022 | 23.132 | 3.141 | 0.015 | 58.035 | 4.061 | 0.020 |
| 19 | 1273 | 100 | 4.605 | 95.910  | 4.563 | 0.022 | 22.957 | 3.134 | 0.015 | 58.335 | 4.066 | 0.020 |
| 20 | 1340 | 100 | 4.605 | 95.227  | 4.556 | 0.022 | 24.303 | 3.191 | 0.015 | 58.228 | 4.064 | 0.020 |
| 21 | 1407 | 100 | 4.605 | 93.394  | 4.537 | 0.022 | 24.768 | 3.210 | 0.015 | 58.653 | 4.072 | 0.020 |
| 22 | 1474 | 100 | 4.605 | 92.712  | 4.529 | 0.022 | 24.516 | 3.199 | 0.015 | 60.128 | 4.096 | 0.020 |
| 23 | 1541 | 100 | 4.605 | 88.745  | 4.486 | 0.022 | 25.770 | 3.249 | 0.016 | 60.193 | 4.098 | 0.020 |
| 24 | 1608 | 100 | 4.605 | 87.212  | 4.468 | 0.022 | 27.078 | 3.299 | 0.016 | 60.310 | 4.100 | 0.020 |
| 25 | 1675 | 100 | 4.605 | 86.094  | 4.455 | 0.022 | 27.473 | 3.313 | 0.016 | 61.574 | 4.120 | 0.020 |
| 26 | 1742 | 100 | 4.605 | 84.690  | 4.439 | 0.021 | 29.723 | 3.392 | 0.016 | 62.761 | 4.139 | 0.020 |
| 27 | 1809 | 100 | 4.605 | 81.996  | 4.407 | 0.021 | 28.772 | 3.359 | 0.016 | 63.682 | 4.154 | 0.020 |
| 28 | 1876 | 100 | 4.605 | 80.178  | 4.384 | 0.021 | 29.695 | 3.391 | 0.016 | 64.017 | 4.159 | 0.020 |
| 29 | 1943 | 100 | 4.605 | 78.667  | 4.365 | 0.021 | 30.318 | 3.412 | 0.016 | 66.466 | 4.197 | 0.020 |
| 30 | 2010 | 100 | 4.605 | 76.213  | 4.334 | 0.021 | 30.815 | 3.428 | 0.017 | 66.417 | 4.196 | 0.020 |
| 31 | 2077 | 100 | 4.605 | 74.493  | 4.311 | 0.021 | 29.937 | 3.399 | 0.016 | 67.151 | 4.207 | 0.020 |
| 32 | 2144 | 100 | 4.605 | 71.612  | 4.271 | 0.021 | 30.406 | 3.415 | 0.016 | 68.667 | 4.229 | 0.020 |
| 33 | 2211 | 100 | 4.605 | 69.858  | 4.246 | 0.020 | 32.038 | 3.467 | 0.017 | 70.692 | 4.258 | 0.021 |
| 34 | 2278 | 100 | 4.605 | 67.408  | 4.211 | 0.020 | 33.469 | 3.511 | 0.017 | 71.242 | 4.266 | 0.021 |
| 35 | 2345 | 100 | 4.605 | 66.455  | 4.197 | 0.020 | 33.463 | 3.510 | 0.017 | 72.531 | 4.284 | 0.021 |
| 36 | 2412 | 100 | 4.605 | 63.968  | 4.158 | 0.020 | 33.631 | 3.515 | 0.017 | 72.313 | 4.281 | 0.021 |
| 37 | 2479 | 100 | 4.605 | 61.705  | 4.122 | 0.020 | 32.404 | 3.478 | 0.017 | 74.167 | 4.306 | 0.021 |
| 38 | 2546 | 100 | 4.605 | 59.266  | 4.082 | 0.020 | 33.631 | 3.515 | 0.017 | 75.619 | 4.326 | 0.021 |
| 39 | 2613 | 100 | 4.605 | 59.591  | 4.088 | 0.020 | 35.470 | 3.569 | 0.017 | 75.457 | 4.324 | 0.021 |
| 40 | 2680 | 100 | 4.605 | 56.579  | 4.036 | 0.019 | 35.594 | 3.572 | 0.017 | 78.395 | 4.362 | 0.021 |
| 41 | 2747 | 100 | 4.605 | 56.948  | 4.042 | 0.020 | 37.496 | 3.624 | 0.017 | 80.637 | 4.390 | 0.021 |
| 42 | 2814 | 100 | 4.605 | 53.214  | 3.974 | 0.019 | 35.529 | 3.570 | 0.017 | 80.349 | 4.386 | 0.021 |
| 43 | 2881 | 100 | 4.605 | 51.853  | 3.948 | 0.019 | 36.313 | 3.592 | 0.017 | 81.735 | 4.403 | 0.021 |
| 44 | 2948 | 100 | 4.605 | 50.560  | 3.923 | 0.019 | 37.116 | 3.614 | 0.017 | 84.640 | 4.438 | 0.021 |
| 45 | 3015 | 100 | 4.605 | 47.793  | 3.867 | 0.019 | 37.435 | 3.623 | 0.017 | 85.383 | 4.447 | 0.021 |
| 46 | 3082 | 100 | 4.605 | 46.719  | 3.844 | 0.019 | 37.583 | 3.627 | 0.018 | 87.214 | 4.468 | 0.022 |
| 47 | 3149 | 100 | 4.605 | 46.019  | 3.829 | 0.018 | 38.404 | 3.648 | 0.018 | 87.876 | 4.476 | 0.022 |
| 48 | 3216 | 100 | 4.605 | 43.409  | 3.771 | 0.018 | 39.500 | 3.676 | 0.018 | 89.954 | 4.499 | 0.022 |
| 49 | 3283 | 100 | 4.605 | 42.587  | 3.752 | 0.018 | 38.440 | 3.649 | 0.018 | 89.245 | 4.491 | 0.022 |
| 50 | 3350 | 100 | 4.605 | 40.758  | 3.708 | 0.018 | 39.938 | 3.687 | 0.018 | 92.423 | 4.526 | 0.022 |

|    |      |     |       |        |       |       |        |       |       |         |       |       |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|---------|-------|-------|
| 51 | 3417 | 100 | 4.605 | 41.273 | 3.720 | 0.018 | 40.976 | 3.713 | 0.018 | 94.242  | 4.546 | 0.022 |
| 52 | 3484 | 100 | 4.605 | 37.031 | 3.612 | 0.017 | 40.228 | 3.695 | 0.018 | 94.299  | 4.546 | 0.022 |
| 53 | 3551 | 100 | 4.605 | 36.847 | 3.607 | 0.017 | 41.839 | 3.734 | 0.018 | 95.791  | 4.562 | 0.022 |
| 54 | 3618 | 100 | 4.605 | 35.481 | 3.569 | 0.017 | 40.588 | 3.703 | 0.018 | 97.382  | 4.579 | 0.022 |
| 55 | 3685 | 100 | 4.605 | 34.432 | 3.539 | 0.017 | 40.797 | 3.709 | 0.018 | 99.040  | 4.596 | 0.022 |
| 56 | 3752 | 100 | 4.605 | 32.592 | 3.484 | 0.017 | 40.414 | 3.699 | 0.018 | 99.722  | 4.602 | 0.022 |
| 57 | 3819 | 100 | 4.605 | 31.420 | 3.447 | 0.017 | 41.847 | 3.734 | 0.018 | 99.447  | 4.600 | 0.022 |
| 58 | 3886 | 100 | 4.605 | 31.092 | 3.437 | 0.017 | 41.635 | 3.729 | 0.018 | 100.214 | 4.607 | 0.022 |
| 59 | 3953 | 100 | 4.605 | 28.784 | 3.360 | 0.016 | 40.975 | 3.713 | 0.018 | 100.955 | 4.615 | 0.022 |
| 60 | 4020 | 100 | 4.605 | 28.329 | 3.344 | 0.016 | 42.572 | 3.751 | 0.018 | 104.553 | 4.650 | 0.022 |
| 61 | 4087 | 100 | 4.605 | 26.328 | 3.271 | 0.016 | 41.771 | 3.732 | 0.018 | 104.256 | 4.647 | 0.022 |
| 62 | 4154 | 100 | 4.605 | 27.028 | 3.297 | 0.016 | 42.350 | 3.746 | 0.018 | 104.947 | 4.653 | 0.022 |
| 63 | 4221 | 100 | 4.605 | 24.416 | 3.195 | 0.015 | 41.489 | 3.725 | 0.018 | 103.908 | 4.644 | 0.022 |
| 64 | 4288 | 100 | 4.605 | 23.861 | 3.172 | 0.015 | 42.380 | 3.747 | 0.018 | 106.713 | 4.670 | 0.023 |
| 65 | 4355 | 100 | 4.605 | 23.420 | 3.154 | 0.015 | 43.287 | 3.768 | 0.018 | 107.970 | 4.682 | 0.023 |
| 66 | 4422 | 100 | 4.605 | 21.998 | 3.091 | 0.015 | 43.848 | 3.781 | 0.018 | 109.749 | 4.698 | 0.023 |
| 67 | 4489 | 100 | 4.605 | 22.471 | 3.112 | 0.015 | 42.991 | 3.761 | 0.018 | 108.047 | 4.683 | 0.023 |
| 68 | 4556 | 100 | 4.605 | 20.329 | 3.012 | 0.015 | 43.168 | 3.765 | 0.018 | 109.452 | 4.695 | 0.023 |
| 69 | 4623 | 100 | 4.605 | 19.704 | 2.981 | 0.014 | 44.693 | 3.800 | 0.018 | 113.285 | 4.730 | 0.023 |
| 70 | 4690 | 100 | 4.605 | 19.841 | 2.988 | 0.014 | 44.343 | 3.792 | 0.018 | 113.083 | 4.728 | 0.023 |

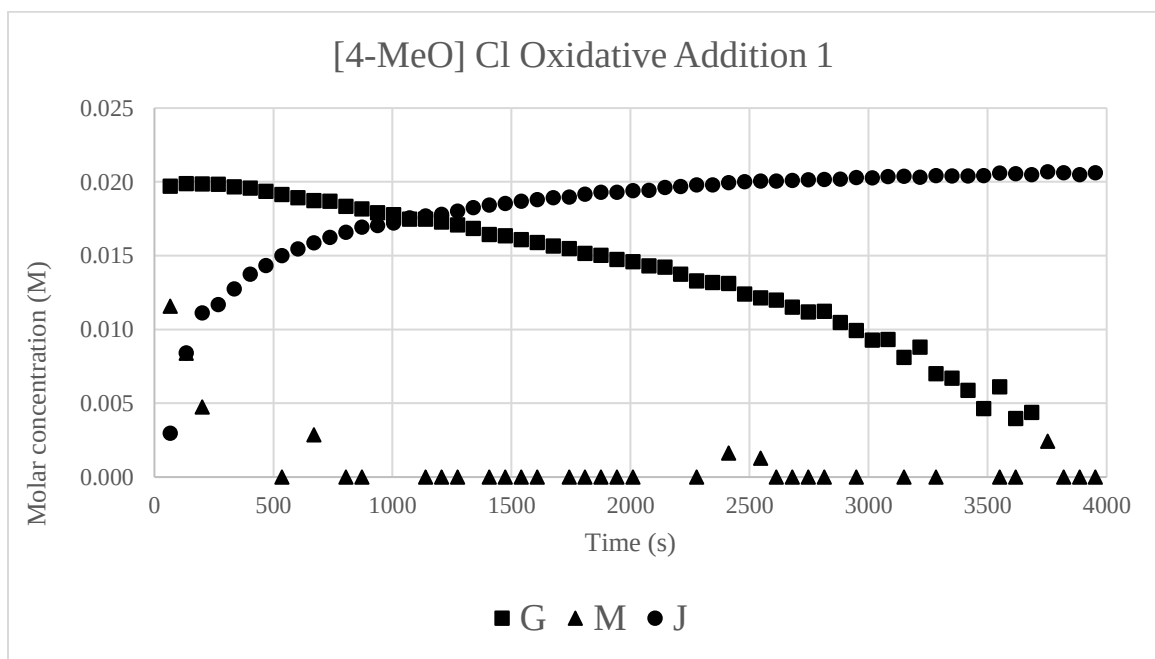


Table: Raw Data For [4-MeO] Cl Oxidative Addition <sup>14</sup>

| A  | B    | C       | D         | E          | F     | G     | H      | I         | J         | K      | L         | M         |
|----|------|---------|-----------|------------|-------|-------|--------|-----------|-----------|--------|-----------|-----------|
| 1  | 67   | 10<br>0 | 4.60<br>5 | 59.29<br>8 | 4.083 | 0.020 | 1.849  | 0.61<br>5 | 0.00<br>3 | 11.022 | 2.400     | 0.012     |
| 2  | 134  | 10<br>0 | 4.60<br>5 | 61.58<br>2 | 4.120 | 0.020 | 5.725  | 1.74<br>5 | 0.00<br>8 | 5.691  | 1.739     | 0.008     |
| 3  | 201  | 10<br>0 | 4.60<br>5 | 61.12<br>7 | 4.113 | 0.020 | 10.022 | 2.30<br>5 | 0.01<br>1 | 2.672  | 0.983     | 0.005     |
| 4  | 268  | 10<br>0 | 4.60<br>5 | 61.00<br>9 | 4.111 | 0.020 | 11.279 | 2.42<br>3 | 0.01<br>2 | 0.700  | -0.357    | -0.002    |
| 5  | 335  | 10<br>0 | 4.60<br>5 | 58.87<br>4 | 4.075 | 0.020 | 14.025 | 2.64<br>1 | 0.01<br>3 | 0.954  | -0.047    | 0.000     |
| 6  | 402  | 10<br>0 | 4.60<br>5 | 57.89<br>6 | 4.059 | 0.020 | 17.250 | 2.84<br>8 | 0.01<br>4 | 0.103  | -2.268    | -0.011    |
| 7  | 469  | 10<br>0 | 4.60<br>5 | 55.13<br>2 | 4.010 | 0.019 | 19.502 | 2.97<br>1 | 0.01<br>4 | 0.536  | -0.623    | -0.003    |
| 8  | 536  | 10<br>0 | 4.60<br>5 | 52.84<br>0 | 3.967 | 0.019 | 22.361 | 3.10<br>7 | 0.01<br>5 | -1.438 | #NUM<br>! | #NUM<br>! |
| 9  | 603  | 10<br>0 | 4.60<br>5 | 50.58<br>2 | 3.924 | 0.019 | 24.592 | 3.20<br>2 | 0.01<br>5 | 0.107  | -2.239    | -0.011    |
| 10 | 670  | 10<br>0 | 4.60<br>5 | 48.53<br>2 | 3.882 | 0.019 | 26.847 | 3.29<br>0 | 0.01<br>6 | 1.809  | 0.593     | 0.003     |
| 11 | 737  | 10<br>0 | 4.60<br>5 | 47.99<br>6 | 3.871 | 0.019 | 28.884 | 3.36<br>3 | 0.01<br>6 | 0.260  | -1.348    | -0.007    |
| 12 | 804  | 10<br>0 | 4.60<br>5 | 44.71<br>1 | 3.800 | 0.018 | 31.021 | 3.43<br>5 | 0.01<br>7 | -0.523 | #NUM<br>! | #NUM<br>! |
| 13 | 871  | 10<br>0 | 4.60<br>5 | 43.09<br>5 | 3.763 | 0.018 | 33.420 | 3.50<br>9 | 0.01<br>7 | -0.296 | #NUM<br>! | #NUM<br>! |
| 14 | 938  | 10<br>0 | 4.60<br>5 | 40.89<br>7 | 3.711 | 0.018 | 34.164 | 3.53<br>1 | 0.01<br>7 | 0.209  | -1.566    | -0.008    |
| 15 | 1005 | 10<br>0 | 4.60<br>5 | 39.80<br>4 | 3.684 | 0.018 | 35.460 | 3.56<br>8 | 0.01<br>7 | 0.028  | -3.560    | -0.017    |
| 16 | 1072 | 10<br>0 | 4.60<br>5 | 37.40<br>9 | 3.622 | 0.017 | 37.998 | 3.63<br>8 | 0.01<br>8 | 0.520  | -0.654    | -0.003    |
| 17 | 1139 | 10<br>0 | 4.60<br>5 | 37.37<br>9 | 3.621 | 0.017 | 39.041 | 3.66<br>5 | 0.01<br>8 | -0.248 | #NUM<br>! | #NUM<br>! |
| 18 | 1206 | 10<br>0 | 4.60<br>5 | 35.91<br>0 | 3.581 | 0.017 | 40.006 | 3.68<br>9 | 0.01<br>8 | -0.190 | #NUM<br>! | #NUM<br>! |
| 19 | 1273 | 10<br>0 | 4.60<br>5 | 34.52<br>6 | 3.542 | 0.017 | 41.776 | 3.73<br>2 | 0.01<br>8 | -0.548 | #NUM<br>! | #NUM<br>! |
| 20 | 1340 | 10<br>0 | 4.60<br>5 | 32.80<br>5 | 3.491 | 0.017 | 43.842 | 3.78<br>1 | 0.01<br>8 | 0.389  | -0.945    | -0.005    |
| 21 | 1407 | 10<br>0 | 4.60<br>5 | 30.16<br>7 | 3.407 | 0.016 | 45.540 | 3.81<br>9 | 0.01<br>8 | -0.465 | #NUM<br>! | #NUM<br>! |
| 22 | 1474 | 10<br>0 | 4.60<br>5 | 29.58<br>4 | 3.387 | 0.016 | 46.667 | 3.84<br>3 | 0.01<br>9 | -1.481 | #NUM<br>! | #NUM<br>! |
| 23 | 1541 | 10<br>0 | 4.60<br>5 | 28.00<br>1 | 3.332 | 0.016 | 48.063 | 3.87<br>3 | 0.01<br>9 | -0.078 | #NUM<br>! | #NUM<br>! |
| 24 | 1608 | 10<br>0 | 4.60<br>5 | 26.95<br>1 | 3.294 | 0.016 | 49.184 | 3.89<br>6 | 0.01<br>9 | -0.330 | #NUM<br>! | #NUM<br>! |
| 25 | 1675 | 10<br>0 | 4.60<br>5 | 25.56<br>9 | 3.241 | 0.016 | 50.434 | 3.92<br>1 | 0.01<br>9 | 0.181  | -1.708    | -0.008    |

<sup>14</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |     |       |        |       |       |        |       |       |        |        |        |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|--------|--------|--------|
| 26 | 1742 | 100 | 4.605 | 24.682 | 3.206 | 0.015 | 50.976 | 3.931 | 0.019 | -0.701 | #NUM!  | #NUM!  |
| 27 | 1809 | 100 | 4.605 | 23.130 | 3.141 | 0.015 | 52.955 | 3.969 | 0.019 | -0.477 | #NUM!  | #NUM!  |
| 28 | 1876 | 100 | 4.605 | 22.512 | 3.114 | 0.015 | 54.412 | 3.997 | 0.019 | -0.522 | #NUM!  | #NUM!  |
| 29 | 1943 | 100 | 4.605 | 21.247 | 3.056 | 0.015 | 54.411 | 3.997 | 0.019 | -0.074 | #NUM!  | #NUM!  |
| 30 | 2010 | 100 | 4.605 | 20.554 | 3.023 | 0.015 | 55.852 | 4.023 | 0.019 | -0.077 | #NUM!  | #NUM!  |
| 31 | 2077 | 100 | 4.605 | 19.404 | 2.966 | 0.014 | 55.946 | 4.024 | 0.019 | 0.016  | -4.106 | -0.020 |
| 32 | 2144 | 100 | 4.605 | 19.062 | 2.948 | 0.014 | 58.270 | 4.065 | 0.020 | 0.253  | -1.376 | -0.007 |
| 33 | 2211 | 100 | 4.605 | 17.284 | 2.850 | 0.014 | 59.029 | 4.078 | 0.020 | 0.370  | -0.993 | -0.005 |
| 34 | 2278 | 100 | 4.605 | 15.732 | 2.756 | 0.013 | 60.366 | 4.100 | 0.020 | -0.282 | #NUM!  | #NUM!  |
| 35 | 2345 | 100 | 4.605 | 15.372 | 2.733 | 0.013 | 60.360 | 4.100 | 0.020 | 0.146  | -1.923 | -0.009 |
| 36 | 2412 | 100 | 4.605 | 15.166 | 2.719 | 0.013 | 62.440 | 4.134 | 0.020 | 1.403  | 0.339  | 0.002  |
| 37 | 2479 | 100 | 4.605 | 13.076 | 2.571 | 0.012 | 63.335 | 4.148 | 0.020 | 0.612  | -0.491 | -0.002 |
| 38 | 2546 | 100 | 4.605 | 12.382 | 2.516 | 0.012 | 63.676 | 4.154 | 0.020 | 1.303  | 0.265  | 0.001  |
| 39 | 2613 | 100 | 4.605 | 12.005 | 2.485 | 0.012 | 63.905 | 4.157 | 0.020 | -0.950 | #NUM!  | #NUM!  |
| 40 | 2680 | 100 | 4.605 | 10.842 | 2.383 | 0.012 | 64.298 | 4.164 | 0.020 | -0.654 | #NUM!  | #NUM!  |
| 41 | 2747 | 100 | 4.605 | 10.177 | 2.320 | 0.011 | 64.847 | 4.172 | 0.020 | -0.446 | #NUM!  | #NUM!  |
| 42 | 2814 | 100 | 4.605 | 10.243 | 2.327 | 0.011 | 65.330 | 4.179 | 0.020 | -0.525 | #NUM!  | #NUM!  |
| 43 | 2881 | 100 | 4.605 | 8.761  | 2.170 | 0.010 | 65.447 | 4.181 | 0.020 | 0.189  | -1.664 | -0.008 |
| 44 | 2948 | 100 | 4.605 | 7.828  | 2.058 | 0.010 | 66.939 | 4.204 | 0.020 | -0.496 | #NUM!  | #NUM!  |
| 45 | 3015 | 100 | 4.605 | 6.853  | 1.925 | 0.009 | 66.669 | 4.200 | 0.020 | 0.295  | -1.221 | -0.006 |
| 46 | 3082 | 100 | 4.605 | 6.897  | 1.931 | 0.009 | 67.772 | 4.216 | 0.020 | 0.088  | -2.429 | -0.012 |
| 47 | 3149 | 100 | 4.605 | 5.376  | 1.682 | 0.008 | 68.149 | 4.222 | 0.020 | -0.899 | #NUM!  | #NUM!  |
| 48 | 3216 | 100 | 4.605 | 6.188  | 1.823 | 0.009 | 67.405 | 4.211 | 0.020 | 0.433  | -0.836 | -0.004 |
| 49 | 3283 | 100 | 4.605 | 4.274  | 1.452 | 0.007 | 68.775 | 4.231 | 0.020 | -0.008 | #NUM!  | #NUM!  |
| 50 | 3350 | 100 | 4.605 | 4.012  | 1.389 | 0.007 | 68.599 | 4.228 | 0.020 | 0.744  | -0.296 | -0.001 |
| 51 | 3417 | 100 | 4.605 | 3.377  | 1.217 | 0.006 | 68.418 | 4.226 | 0.020 | 0.390  | -0.941 | -0.005 |
| 52 | 3484 | 100 | 4.605 | 2.619  | 0.963 | 0.005 | 68.737 | 4.230 | 0.020 | 0.294  | -1.226 | -0.006 |
| 53 | 3551 | 100 | 4.605 | 3.543  | 1.265 | 0.006 | 71.233 | 4.266 | 0.021 | -0.115 | #NUM!  | #NUM!  |
| 54 | 3618 | 100 | 4.605 | 2.277  | 0.823 | 0.004 | 70.878 | 4.261 | 0.021 | -0.043 | #NUM!  | #NUM!  |

|   |     |    |      |        |        |        |        |      |      |        |        |        |
|---|-----|----|------|--------|--------|--------|--------|------|------|--------|--------|--------|
| 5 | 368 | 10 | 4.60 |        |        |        |        | 4.24 | 0.02 |        |        |        |
| 5 | 5   | 0  | 5    | 2.474  | 0.906  | 0.004  | 69.829 | 6    | 0    | 0.013  | -4.323 | -0.021 |
| 5 | 375 | 10 | 4.60 |        |        |        |        | 4.28 | 0.02 |        |        |        |
| 6 | 2   | 0  | 5    | 0.918  | -0.085 | 0.000  | 72.561 | 4    | 1    | 1.653  | 0.502  | 0.002  |
| 5 | 381 | 10 | 4.60 |        |        |        |        | 4.27 | 0.02 |        | #NUM   | #NUM   |
| 7 | 9   | 0  | 5    | 0.877  | -0.132 | -0.001 | 71.778 | 4    | 1    | -0.575 | !      | !      |
| 5 | 388 | 10 | 4.60 |        |        |        |        | 4.24 | 0.02 |        | #NUM   | #NUM   |
| 8 | 6   | 0  | 5    | 0.707  | -0.346 | -0.002 | 69.804 | 6    | 0    | -0.469 | !      | !      |
| 5 | 395 | 10 | 4.60 |        |        |        |        | 4.27 | 0.02 |        | #NUM   | #NUM   |
| 9 | 3   | 0  | 5    | 0.148  | -1.909 | -0.009 | 71.760 | 3    | 1    | -0.082 | !      | !      |
| 6 | 402 | 10 | 4.60 |        |        |        |        | 4.31 | 0.02 |        |        |        |
| 0 | 0   | 0  | 5    | 0.112  | -2.186 | -0.011 | 74.445 | 0    | 1    | 1.302  | 0.264  | 0.001  |
| 6 | 408 | 10 | 4.60 |        |        |        |        | 4.28 | 0.02 |        |        |        |
| 1 | 7   | 0  | 5    | 0.205  | -1.583 | -0.008 | 72.428 | 3    | 1    | 0.506  | -0.680 | -0.003 |
| 6 | 415 | 10 | 4.60 |        |        |        |        | 4.67 | 0.02 |        | #NUM   | #NUM   |
| 2 | 4   | 0  | 5    | -0.801 | !      | !      | 107.16 | 4    | 3    | -1.605 | !      | !      |
| 6 | 422 | 10 | 4.60 |        |        |        |        | 5.30 | 0.02 |        | #NUM   | #NUM   |
| 3 | 1   | 0  | 5    | -3.351 | !      | !      | 201.45 | 6    | 6    | -1.060 | !      | !      |
| 6 | 428 | 10 | 4.60 |        |        |        |        | 5.54 | 0.02 |        |        |        |
| 4 | 8   | 0  | 5    | -0.826 | !      | !      | 254.98 | 1    | 7    | 0.567  | -0.567 | -0.003 |
| 6 | 435 | 10 | 4.60 |        |        |        |        | 5.78 | 0.02 |        | #NUM   | #NUM   |
| 5 | 5   | 0  | 5    | -7.468 | !      | !      | 323.77 | 0    | 8    | -1.405 | !      | !      |
| 6 | 442 | 10 | 4.60 |        |        |        |        | 5.72 | 0.02 |        | #NUM   | #NUM   |
| 6 | 2   | 0  | 5    | -0.255 | !      | !      | 306.76 | 9    | 6    | -3.077 | !      | !      |
| 6 | 448 | 10 | 4.60 |        |        |        |        | 5.70 | 0.02 |        |        |        |
| 7 | 9   | 0  | 5    | -0.676 | !      | !      | 299.67 | 3    | 8    | 4.984  | 1.606  | 0.008  |
| 6 | 455 | 10 | 4.60 |        |        |        |        | 5.61 | 0.02 |        | #NUM   | #NUM   |
| 8 | 6   | 0  | 5    | -6.494 | !      | !      | 274.01 | 1    | 3    | -      | !      | !      |
| 9 | 3   | 0  | 5    | -5.613 | !      | !      | 316.64 | 5    | 8    | 10.144 | !      | !      |
| 7 | 469 | 10 | 4.60 |        |        |        |        | 5.55 | 0.02 |        | #NUM   | #NUM   |
| 0 | 0   | 0  | 5    | -1.656 | !      | !      | 258.07 | 4    | 3    | -2.968 | !      | !      |

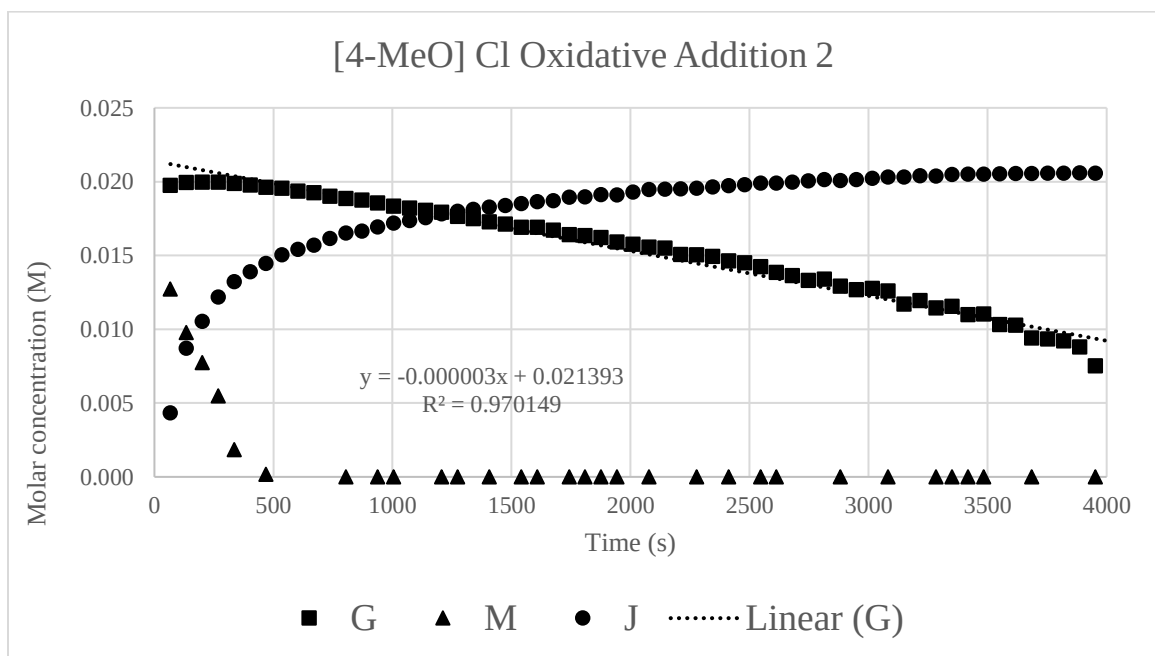
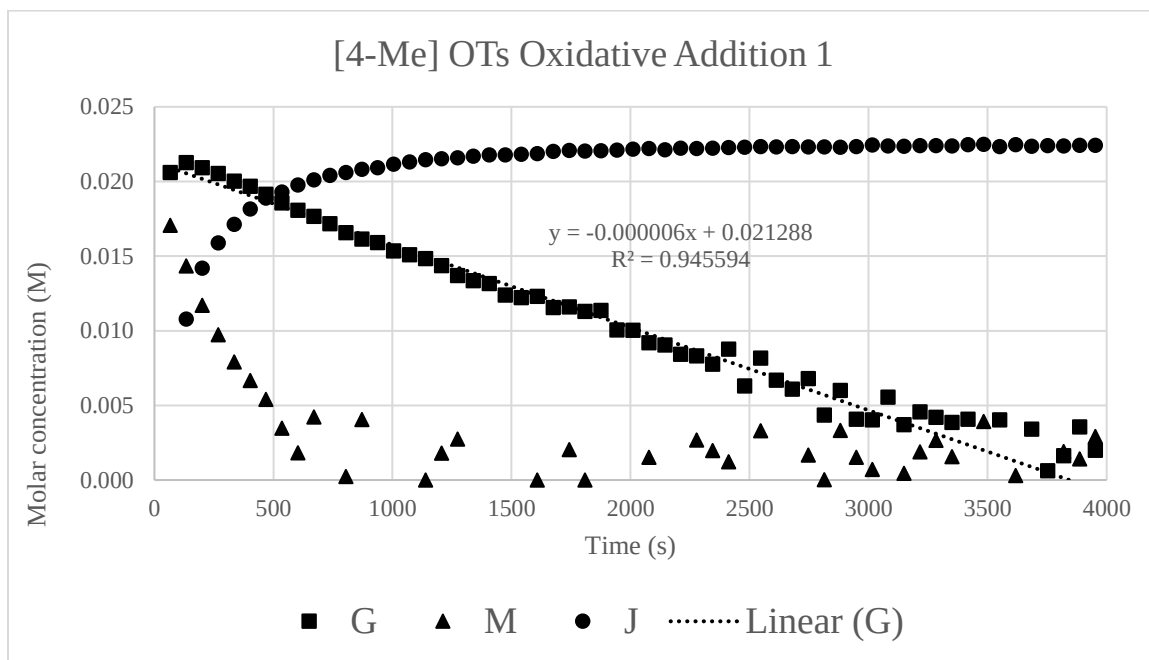


Table: Raw Data For [4-MeO] Cl Oxidative Addition 2<sup>15</sup>

| A  | B    | C   | D     | E      | F     | G     | H      | I     | J     | K      | L      | M      |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|--------|--------|--------|
| 1  | 67   | 100 | 4.605 | 60.024 | 4.095 | 0.020 | 2.461  | 0.901 | 0.004 | 14.006 | 2.639  | 0.013  |
| 2  | 134  | 100 | 4.605 | 62.501 | 4.135 | 0.020 | 6.098  | 1.808 | 0.009 | 7.586  | 2.026  | 0.010  |
| 3  | 201  | 100 | 4.605 | 62.637 | 4.137 | 0.020 | 8.881  | 2.184 | 0.011 | 4.969  | 1.603  | 0.008  |
| 4  | 268  | 100 | 4.605 | 62.736 | 4.139 | 0.020 | 12.480 | 2.524 | 0.012 | 3.116  | 1.137  | 0.005  |
| 5  | 335  | 100 | 4.605 | 61.478 | 4.119 | 0.020 | 15.468 | 2.739 | 0.013 | 1.466  | 0.382  | 0.002  |
| 6  | 402  | 100 | 4.605 | 60.271 | 4.099 | 0.020 | 17.795 | 2.879 | 0.014 | 0.895  | -0.111 | -0.001 |
| 7  | 469  | 100 | 4.605 | 58.377 | 4.067 | 0.020 | 20.009 | 2.996 | 0.014 | 1.038  | 0.037  | 0.000  |
| 8  | 536  | 100 | 4.605 | 57.629 | 4.054 | 0.020 | 22.614 | 3.119 | 0.015 | 0.535  | -0.625 | -0.003 |
| 9  | 603  | 100 | 4.605 | 55.380 | 4.014 | 0.019 | 24.435 | 3.196 | 0.015 | 0.112  | -2.190 | -0.011 |
| 10 | 670  | 100 | 4.605 | 53.999 | 3.989 | 0.019 | 25.915 | 3.255 | 0.016 | 0.587  | -0.533 | -0.003 |
| 11 | 737  | 100 | 4.605 | 51.346 | 3.939 | 0.019 | 28.406 | 3.347 | 0.016 | 0.111  | -2.195 | -0.011 |
| 12 | 804  | 100 | 4.605 | 49.780 | 3.908 | 0.019 | 30.679 | 3.424 | 0.017 | -0.065 | #NUM!  | #NUM!  |
| 13 | 871  | 100 | 4.605 | 48.696 | 3.886 | 0.019 | 31.556 | 3.452 | 0.017 | 0.940  | -0.062 | 0.000  |
| 14 | 938  | 100 | 4.605 | 46.894 | 3.848 | 0.019 | 33.474 | 3.511 | 0.017 | -0.635 | #NUM!  | #NUM!  |
| 15 | 1005 | 100 | 4.605 | 44.797 | 3.802 | 0.018 | 35.253 | 3.563 | 0.017 | -0.035 | #NUM!  | #NUM!  |
| 16 | 1072 | 100 | 4.605 | 43.631 | 3.776 | 0.018 | 36.522 | 3.598 | 0.017 | 0.633  | -0.457 | -0.002 |
| 17 | 1139 | 100 | 4.605 | 42.216 | 3.743 | 0.018 | 38.139 | 3.641 | 0.018 | 0.038  | -3.282 | -0.016 |
| 18 | 1206 | 100 | 4.605 | 41.176 | 3.718 | 0.018 | 40.087 | 3.691 | 0.018 | -0.054 | #NUM!  | #NUM!  |
| 19 | 1273 | 100 | 4.605 | 38.837 | 3.659 | 0.018 | 41.710 | 3.731 | 0.018 | -0.095 | #NUM!  | #NUM!  |
| 20 | 1340 | 100 | 4.605 | 37.536 | 3.625 | 0.017 | 42.733 | 3.755 | 0.018 | 0.112  | -2.193 | -0.011 |
| 21 | 1407 | 100 | 4.605 | 35.828 | 3.579 | 0.017 | 44.109 | 3.787 | 0.018 | -0.038 | #NUM!  | #NUM!  |
| 22 | 1474 | 100 | 4.605 | 34.761 | 3.548 | 0.017 | 45.157 | 3.810 | 0.018 | 0.266  | -1.323 | -0.006 |
| 23 | 1541 | 100 | 4.605 | 33.200 | 3.503 | 0.017 | 46.410 | 3.838 | 0.019 | -0.130 | #NUM!  | #NUM!  |
| 24 | 1608 | 100 | 4.605 | 33.334 | 3.507 | 0.017 | 47.658 | 3.864 | 0.019 | -0.164 | #NUM!  | #NUM!  |
| 25 | 1675 | 100 | 4.605 | 31.933 | 3.464 | 0.017 | 48.277 | 3.877 | 0.019 | 0.071  | -2.640 | -0.013 |
| 26 | 1742 | 100 | 4.605 | 30.028 | 3.402 | 0.016 | 50.657 | 3.925 | 0.019 | -0.011 | #NUM!  | #NUM!  |
| 27 | 1809 | 100 | 4.605 | 29.605 | 3.388 | 0.016 | 50.862 | 3.929 | 0.019 | -0.358 | #NUM!  | #NUM!  |
| 28 | 1876 | 100 | 4.605 | 28.864 | 3.363 | 0.016 | 52.568 | 3.962 | 0.019 | -0.336 | #NUM!  | #NUM!  |
| 29 | 1943 | 100 | 4.605 | 26.998 | 3.296 | 0.016 | 52.313 | 3.957 | 0.019 | -0.069 | #NUM!  | #NUM!  |
| 30 | 2010 | 100 | 4.605 | 26.181 | 3.265 | 0.016 | 54.633 | 4.001 | 0.019 | 0.502  | -0.689 | -0.003 |
| 31 | 2077 | 100 | 4.605 | 25.129 | 3.224 | 0.016 | 56.432 | 4.033 | 0.019 | -0.148 | #NUM!  | #NUM!  |
| 32 | 2144 | 100 | 4.605 | 24.799 | 3.211 | 0.015 | 56.744 | 4.039 | 0.019 | 0.479  | -0.736 | -0.004 |
| 33 | 2211 | 100 | 4.605 | 22.671 | 3.121 | 0.015 | 57.104 | 4.045 | 0.020 | 0.231  | -1.464 | -0.007 |
| 34 | 2278 | 100 | 4.605 | 22.573 | 3.117 | 0.015 | 57.623 | 4.054 | 0.020 | -0.009 | #NUM!  | #NUM!  |
| 35 | 2345 | 100 | 4.605 | 22.142 | 3.097 | 0.015 | 58.481 | 4.069 | 0.020 | 0.481  | -0.731 | -0.004 |

<sup>15</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~-10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |     |       |        |       |       |        |       |       |        |        |        |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|--------|--------|--------|
| 36 | 2412 | 100 | 4.605 | 20.771 | 3.034 | 0.015 | 59.525 | 4.086 | 0.020 | -0.275 | #NUM!  | #NUM!  |
| 37 | 2479 | 100 | 4.605 | 20.165 | 3.004 | 0.014 | 60.451 | 4.102 | 0.020 | 0.060  | -2.809 | -0.014 |
| 38 | 2546 | 100 | 4.605 | 19.113 | 2.950 | 0.014 | 61.815 | 4.124 | 0.020 | -0.522 | #NUM!  | #NUM!  |
| 39 | 2613 | 100 | 4.605 | 17.658 | 2.871 | 0.014 | 61.975 | 4.127 | 0.020 | -0.411 | #NUM!  | #NUM!  |
| 40 | 2680 | 100 | 4.605 | 16.913 | 2.828 | 0.014 | 62.807 | 4.140 | 0.020 | 0.265  | -1.330 | -0.006 |
| 41 | 2747 | 100 | 4.605 | 15.757 | 2.757 | 0.013 | 63.731 | 4.155 | 0.020 | 0.382  | -0.962 | -0.005 |
| 42 | 2814 | 100 | 4.605 | 16.079 | 2.778 | 0.013 | 64.846 | 4.172 | 0.020 | 0.218  | -1.521 | -0.007 |
| 43 | 2881 | 100 | 4.605 | 14.580 | 2.680 | 0.013 | 64.176 | 4.162 | 0.020 | -0.126 | #NUM!  | #NUM!  |
| 44 | 2948 | 100 | 4.605 | 13.831 | 2.627 | 0.013 | 65.053 | 4.175 | 0.020 | 0.093  | -2.379 | -0.011 |
| 45 | 3015 | 100 | 4.605 | 14.094 | 2.646 | 0.013 | 66.141 | 4.192 | 0.020 | 0.074  | -2.609 | -0.013 |
| 46 | 3082 | 100 | 4.605 | 13.596 | 2.610 | 0.013 | 67.367 | 4.210 | 0.020 | -0.182 | #NUM!  | #NUM!  |
| 47 | 3149 | 100 | 4.605 | 11.342 | 2.429 | 0.012 | 67.451 | 4.211 | 0.020 | 0.196  | -1.629 | -0.008 |
| 48 | 3216 | 100 | 4.605 | 11.896 | 2.476 | 0.012 | 68.485 | 4.227 | 0.020 | 0.412  | -0.886 | -0.004 |
| 49 | 3283 | 100 | 4.605 | 10.740 | 2.374 | 0.011 | 68.279 | 4.224 | 0.020 | -0.033 | #NUM!  | #NUM!  |
| 50 | 3350 | 100 | 4.605 | 10.954 | 2.394 | 0.012 | 69.838 | 4.246 | 0.020 | -0.253 | #NUM!  | #NUM!  |
| 51 | 3417 | 100 | 4.605 | 9.741  | 2.276 | 0.011 | 70.012 | 4.249 | 0.021 | -0.448 | #NUM!  | #NUM!  |
| 52 | 3484 | 100 | 4.605 | 9.847  | 2.287 | 0.011 | 70.047 | 4.249 | 0.021 | -0.249 | #NUM!  | #NUM!  |
| 53 | 3551 | 100 | 4.605 | 8.483  | 2.138 | 0.010 | 70.460 | 4.255 | 0.021 | 0.413  | -0.884 | -0.004 |
| 54 | 3618 | 100 | 4.605 | 8.400  | 2.128 | 0.010 | 70.904 | 4.261 | 0.021 | 0.217  | -1.530 | -0.007 |
| 55 | 3685 | 100 | 4.605 | 7.030  | 1.950 | 0.009 | 70.671 | 4.258 | 0.021 | -0.071 | #NUM!  | #NUM!  |
| 56 | 3752 | 100 | 4.605 | 6.949  | 1.939 | 0.009 | 71.104 | 4.264 | 0.021 | 0.122  | -2.101 | -0.010 |
| 57 | 3819 | 100 | 4.605 | 6.740  | 1.908 | 0.009 | 70.952 | 4.262 | 0.021 | 0.004  | -5.468 | -0.026 |
| 58 | 3886 | 100 | 4.605 | 6.210  | 1.826 | 0.009 | 71.288 | 4.267 | 0.021 | 0.129  | -2.050 | -0.010 |
| 59 | 3953 | 100 | 4.605 | 4.750  | 1.558 | 0.008 | 71.157 | 4.265 | 0.021 | -0.260 | #NUM!  | #NUM!  |
| 60 | 4020 | 100 | 4.605 | 3.898  | 1.361 | 0.007 | 71.149 | 4.265 | 0.021 | -0.478 | #NUM!  | #NUM!  |
| 61 | 4087 | 100 | 4.605 | 4.612  | 1.529 | 0.007 | 72.460 | 4.283 | 0.021 | -0.345 | #NUM!  | #NUM!  |
| 62 | 4154 | 100 | 4.605 | 3.354  | 1.210 | 0.006 | 72.152 | 4.279 | 0.021 | 0.446  | -0.808 | -0.004 |
| 63 | 4221 | 100 | 4.605 | 3.093  | 1.129 | 0.005 | 72.185 | 4.279 | 0.021 | -0.464 | #NUM!  | #NUM!  |
| 64 | 4288 | 100 | 4.605 | 3.666  | 1.299 | 0.006 | 72.901 | 4.289 | 0.021 | -0.394 | #NUM!  | #NUM!  |
| 65 | 4355 | 100 | 4.605 | 2.654  | 0.976 | 0.005 | 72.498 | 4.284 | 0.021 | 0.329  | -1.110 | -0.005 |
| 66 | 4422 | 100 | 4.605 | 2.707  | 0.996 | 0.005 | 71.602 | 4.271 | 0.021 | -0.845 | #NUM!  | #NUM!  |
| 67 | 4489 | 100 | 4.605 | 2.405  | 0.878 | 0.004 | 73.965 | 4.304 | 0.021 | -0.135 | #NUM!  | #NUM!  |
| 68 | 4556 | 100 | 4.605 | 1.305  | 0.267 | 0.001 | 72.297 | 4.281 | 0.021 | 0.400  | -0.916 | -0.004 |
| 69 | 4623 | 100 | 4.605 | 1.821  | 0.599 | 0.003 | 71.803 | 4.274 | 0.021 | -0.501 | #NUM!  | #NUM!  |
| 70 | 4690 | 100 | 4.605 | 1.944  | 0.665 | 0.003 | 71.410 | 4.268 | 0.021 | 0.242  | -1.419 | -0.007 |

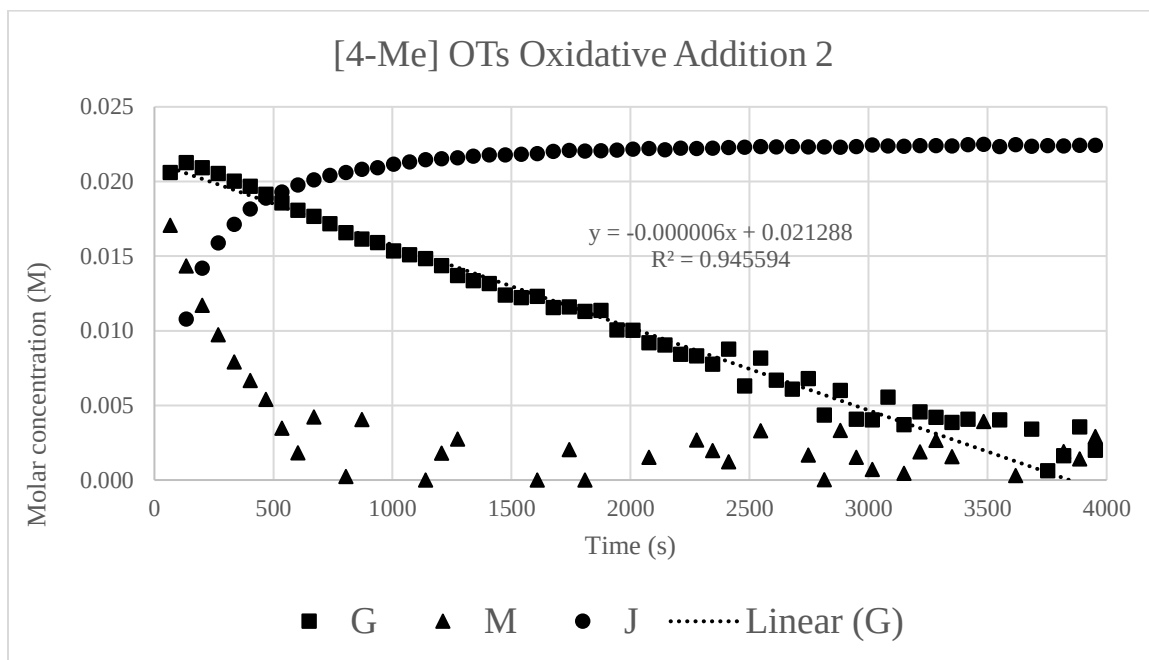
Table: Raw Data For [4-Me] OTs Oxidative Addition 1<sup>16</sup>

| A      | B   | C       | D         | E          | F     | G     | H      | I          | J         | K          | L      | M      |
|--------|-----|---------|-----------|------------|-------|-------|--------|------------|-----------|------------|--------|--------|
| 1      | 67  | 10<br>0 | 4.60<br>5 | 71.60<br>4 | 4.271 | 0.021 | 0.986  | -<br>0.014 | 0.00<br>0 | 34.32<br>5 | 3.536  | 0.017  |
| 2      | 134 | 10<br>0 | 4.60<br>5 | 82.07<br>2 | 4.408 | 0.021 | 9.327  | 2.233      | 0.01<br>1 | 19.49<br>5 | 2.970  | 0.014  |
| 3      | 201 | 10<br>0 | 4.60<br>5 | 76.24<br>4 | 4.334 | 0.021 | 18.955 | 2.942      | 0.01<br>4 | 11.32<br>8 | 2.427  | 0.012  |
| 4      | 268 | 10<br>0 | 4.60<br>5 | 70.65<br>3 | 4.258 | 0.021 | 26.884 | 3.292      | 0.01<br>6 | 7.516      | 2.017  | 0.010  |
| 5      | 335 | 10<br>0 | 4.60<br>5 | 63.34<br>0 | 4.149 | 0.020 | 34.795 | 3.549      | 0.01<br>7 | 5.148      | 1.639  | 0.008  |
| 6      | 402 | 10<br>0 | 4.60<br>5 | 59.08<br>3 | 4.079 | 0.020 | 43.123 | 3.764      | 0.01<br>8 | 3.974      | 1.380  | 0.007  |
| 7      | 469 | 10<br>0 | 4.60<br>5 | 52.82<br>8 | 3.967 | 0.019 | 50.040 | 3.913      | 0.01<br>9 | 3.060      | 1.118  | 0.005  |
| 8      | 536 | 10<br>0 | 4.60<br>5 | 46.83<br>9 | 3.847 | 0.019 | 54.417 | 3.997      | 0.01<br>9 | 2.056      | 0.721  | 0.003  |
| 9      | 603 | 10<br>0 | 4.60<br>5 | 42.35<br>0 | 3.746 | 0.018 | 60.216 | 4.098      | 0.02<br>0 | 1.458      | 0.377  | 0.002  |
| 1<br>0 | 670 | 10<br>0 | 4.60<br>5 | 38.87<br>8 | 3.660 | 0.018 | 64.589 | 4.168      | 0.02<br>0 | 2.394      | 0.873  | 0.004  |
| 1<br>1 | 737 | 10<br>0 | 4.60<br>5 | 35.15<br>2 | 3.560 | 0.017 | 68.570 | 4.228      | 0.02<br>0 | 0.425      | -0.856 | -0.004 |
| 1<br>2 | 804 | 10<br>0 | 4.60<br>5 | 31.04<br>9 | 3.436 | 0.017 | 71.417 | 4.269      | 0.02<br>1 | 1.050      | 0.049  | 0.000  |
| 1<br>3 | 871 | 10<br>0 | 4.60<br>5 | 28.39<br>5 | 3.346 | 0.016 | 74.741 | 4.314      | 0.02<br>1 | 2.316      | 0.840  | 0.004  |

<sup>16</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~-10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |     |       |        |       |       |         |       |       |        |        |        |
|----|------|-----|-------|--------|-------|-------|---------|-------|-------|--------|--------|--------|
| 14 | 938  | 100 | 4.605 | 27.038 | 3.297 | 0.016 | 76.542  | 4.338 | 0.021 | 0.712  | -0.339 | -0.002 |
| 15 | 1005 | 100 | 4.605 | 24.114 | 3.183 | 0.015 | 80.315  | 4.386 | 0.021 | 0.070  | -2.657 | -0.013 |
| 16 | 1072 | 100 | 4.605 | 22.793 | 3.126 | 0.015 | 82.603  | 4.414 | 0.021 | 0.547  | -0.603 | -0.003 |
| 17 | 1139 | 100 | 4.605 | 21.583 | 3.072 | 0.015 | 85.386  | 4.447 | 0.021 | -0.219 | #NUM!  | #NUM!  |
| 18 | 1206 | 100 | 4.605 | 19.594 | 2.975 | 0.014 | 86.611  | 4.461 | 0.022 | 1.451  | 0.372  | 0.002  |
| 19 | 1273 | 100 | 4.605 | 17.103 | 2.839 | 0.014 | 87.685  | 4.474 | 0.022 | 1.769  | 0.571  | 0.003  |
| 20 | 1340 | 100 | 4.605 | 15.935 | 2.769 | 0.013 | 89.532  | 4.495 | 0.022 | 0.935  | -0.067 | 0.000  |
| 21 | 1407 | 100 | 4.605 | 15.301 | 2.728 | 0.013 | 91.201  | 4.513 | 0.022 | 0.482  | -0.730 | -0.004 |
| 22 | 1474 | 100 | 4.605 | 13.042 | 2.568 | 0.012 | 91.300  | 4.514 | 0.022 | 0.542  | -0.613 | -0.003 |
| 23 | 1541 | 100 | 4.605 | 12.601 | 2.534 | 0.012 | 91.979  | 4.522 | 0.022 | 0.778  | -0.251 | -0.001 |
| 24 | 1608 | 100 | 4.605 | 12.800 | 2.549 | 0.012 | 92.704  | 4.529 | 0.022 | -0.029 | #NUM!  | #NUM!  |
| 25 | 1675 | 100 | 4.605 | 10.972 | 2.395 | 0.012 | 95.975  | 4.564 | 0.022 | 0.721  | -0.327 | -0.002 |
| 26 | 1742 | 100 | 4.605 | 11.040 | 2.402 | 0.012 | 96.958  | 4.574 | 0.022 | 1.523  | 0.421  | 0.002  |
| 27 | 1809 | 100 | 4.605 | 10.407 | 2.342 | 0.011 | 96.185  | 4.566 | 0.022 | -0.428 | #NUM!  | #NUM!  |
| 28 | 1876 | 100 | 4.605 | 10.541 | 2.355 | 0.011 | 96.555  | 4.570 | 0.022 | 0.921  | -0.082 | 0.000  |
| 29 | 1943 | 100 | 4.605 | 8.039  | 2.084 | 0.010 | 97.652  | 4.581 | 0.022 | 0.171  | -1.767 | -0.009 |
| 30 | 2010 | 100 | 4.605 | 7.996  | 2.079 | 0.010 | 98.610  | 4.591 | 0.022 | 0.226  | -1.489 | -0.007 |
| 31 | 2077 | 100 | 4.605 | 6.728  | 1.906 | 0.009 | 99.923  | 4.604 | 0.022 | 1.372  | 0.316  | 0.002  |
| 32 | 2144 | 100 | 4.605 | 6.504  | 1.872 | 0.009 | 97.940  | 4.584 | 0.022 | 0.959  | -0.042 | 0.000  |
| 33 | 2211 | 100 | 4.605 | 5.725  | 1.745 | 0.008 | 100.053 | 4.606 | 0.022 | 0.424  | -0.859 | -0.004 |
| 34 | 2278 | 100 | 4.605 | 5.604  | 1.723 | 0.008 | 99.706  | 4.602 | 0.022 | 1.745  | 0.557  | 0.003  |
| 35 | 2345 | 100 | 4.605 | 5.000  | 1.609 | 0.008 | 100.147 | 4.607 | 0.022 | 1.502  | 0.407  | 0.002  |
| 36 | 2412 | 100 | 4.605 | 6.145  | 1.816 | 0.009 | 100.982 | 4.615 | 0.022 | 1.286  | 0.251  | 0.001  |
| 37 | 2479 | 100 | 4.605 | 3.694  | 1.307 | 0.006 | 101.614 | 4.621 | 0.022 | 0.603  | -0.505 | -0.002 |
| 38 | 2546 | 100 | 4.605 | 5.430  | 1.692 | 0.008 | 102.438 | 4.629 | 0.022 | 1.983  | 0.684  | 0.003  |
| 39 | 2613 | 100 | 4.605 | 3.990  | 1.384 | 0.007 | 102.098 | 4.626 | 0.022 | 0.832  | -0.184 | -0.001 |
| 40 | 2680 | 100 | 4.605 | 3.536  | 1.263 | 0.006 | 102.216 | 4.627 | 0.022 | 0.929  | -0.073 | 0.000  |
| 41 | 2747 | 100 | 4.605 | 4.084  | 1.407 | 0.007 | 102.045 | 4.625 | 0.022 | 1.414  | 0.346  | 0.002  |
| 42 | 2814 | 100 | 4.605 | 2.464  | 0.902 | 0.004 | 102.140 | 4.626 | 0.022 | 1.003  | 0.003  | 0.000  |

|        |          |         |           |        |           |           |             |       |           |       |        |        |
|--------|----------|---------|-----------|--------|-----------|-----------|-------------|-------|-----------|-------|--------|--------|
| 4<br>3 | 288<br>1 | 10<br>0 | 4.60<br>5 | 3.474  | 1.245     | 0.006     | 101.39<br>6 | 4.619 | 0.02<br>2 | 1.994 | 0.690  | 0.003  |
| 4<br>4 | 294<br>8 | 10<br>0 | 4.60<br>5 | 2.328  | 0.845     | 0.004     | 102.55<br>5 | 4.630 | 0.02<br>2 | 1.372 | 0.316  | 0.002  |
| 4<br>5 | 301<br>5 | 10<br>0 | 4.60<br>5 | 2.306  | 0.836     | 0.004     | 104.49<br>1 | 4.649 | 0.02<br>2 | 1.155 | 0.144  | 0.001  |
| 4<br>6 | 308<br>2 | 10<br>0 | 4.60<br>5 | 3.155  | 1.149     | 0.006     | 103.52<br>0 | 4.640 | 0.02<br>2 | 0.952 | -0.049 | 0.000  |
| 4<br>7 | 314<br>9 | 10<br>0 | 4.60<br>5 | 2.159  | 0.770     | 0.004     | 103.06<br>9 | 4.635 | 0.02<br>2 | 1.097 | 0.092  | 0.000  |
| 4<br>8 | 321<br>6 | 10<br>0 | 4.60<br>5 | 2.576  | 0.946     | 0.005     | 103.95<br>7 | 4.644 | 0.02<br>2 | 1.478 | 0.391  | 0.002  |
| 4<br>9 | 328<br>3 | 10<br>0 | 4.60<br>5 | 2.384  | 0.869     | 0.004     | 103.61<br>2 | 4.641 | 0.02<br>2 | 1.736 | 0.552  | 0.003  |
| 5<br>0 | 335<br>0 | 10<br>0 | 4.60<br>5 | 2.224  | 0.799     | 0.004     | 103.35<br>2 | 4.638 | 0.02<br>2 | 1.381 | 0.323  | 0.002  |
| 5<br>1 | 341<br>7 | 10<br>0 | 4.60<br>5 | 2.322  | 0.842     | 0.004     | 104.94<br>9 | 4.653 | 0.02<br>2 | 0.595 | -0.519 | -0.003 |
| 5<br>2 | 348<br>4 | 10<br>0 | 4.60<br>5 | 0.897  | -0.109    | -0.001    | 105.55<br>5 | 4.659 | 0.02<br>2 | 2.259 | 0.815  | 0.004  |
| 5<br>3 | 355<br>1 | 10<br>0 | 4.60<br>5 | 2.307  | 0.836     | 0.004     | 102.35<br>6 | 4.628 | 0.02<br>2 | 0.973 | -0.028 | 0.000  |
| 5<br>4 | 361<br>8 | 10<br>0 | 4.60<br>5 | 0.594  | -0.521    | -0.003    | 104.95<br>9 | 4.654 | 0.02<br>2 | 1.063 | 0.061  | 0.000  |
| 5<br>5 | 368<br>5 | 10<br>0 | 4.60<br>5 | 2.024  | 0.705     | 0.003     | 102.95<br>4 | 4.634 | 0.02<br>2 | 0.426 | -0.853 | -0.004 |
| 5<br>6 | 375<br>2 | 10<br>0 | 4.60<br>5 | 1.139  | 0.130     | 0.001     | 103.75<br>3 | 4.642 | 0.02<br>2 | 0.896 | -0.109 | -0.001 |
| 5<br>7 | 381<br>9 | 10<br>0 | 4.60<br>5 | 1.404  | 0.339     | 0.002     | 103.22<br>1 | 4.637 | 0.02<br>2 | 1.483 | 0.394  | 0.002  |
| 5<br>8 | 388<br>6 | 10<br>0 | 4.60<br>5 | 2.091  | 0.738     | 0.004     | 104.14<br>6 | 4.646 | 0.02<br>2 | 1.343 | 0.295  | 0.001  |
| 5<br>9 | 395<br>3 | 10<br>0 | 4.60<br>5 | 1.511  | 0.413     | 0.002     | 104.08<br>7 | 4.645 | 0.02<br>2 | 1.830 | 0.604  | 0.003  |
| 6<br>0 | 402<br>0 | 10<br>0 | 4.60<br>5 | 0.155  | -1.864    | -0.009    | 104.72<br>0 | 4.651 | 0.02<br>2 | 1.120 | 0.113  | 0.001  |
| 6<br>1 | 408<br>7 | 10<br>0 | 4.60<br>5 | 0.992  | -0.008    | 0.000     | 103.29<br>6 | 4.638 | 0.02<br>2 | 1.458 | 0.377  | 0.002  |
| 6<br>2 | 415<br>4 | 10<br>0 | 4.60<br>5 | 1.374  | 0.318     | 0.002     | 105.27<br>0 | 4.657 | 0.02<br>2 | 1.547 | 0.436  | 0.002  |
| 6<br>3 | 422<br>1 | 10<br>0 | 4.60<br>5 | -0.037 | #NUM<br>! | #NUM<br>! | 105.30<br>8 | 4.657 | 0.02<br>2 | 1.113 | 0.107  | 0.001  |
| 6<br>4 | 428<br>8 | 10<br>0 | 4.60<br>5 | 0.541  | -0.614    | -0.003    | 105.82<br>4 | 4.662 | 0.02<br>2 | 1.659 | 0.506  | 0.002  |
| 6<br>5 | 435<br>5 | 10<br>0 | 4.60<br>5 | 0.469  | -0.758    | -0.004    | 106.60<br>6 | 4.669 | 0.02<br>3 | 1.953 | 0.669  | 0.003  |
| 6<br>6 | 442<br>2 | 10<br>0 | 4.60<br>5 | 1.548  | 0.437     | 0.002     | 104.26<br>0 | 4.647 | 0.02<br>2 | 1.882 | 0.632  | 0.003  |
| 6<br>7 | 448<br>9 | 10<br>0 | 4.60<br>5 | -1.029 | #NUM<br>! | #NUM<br>! | 103.56<br>7 | 4.640 | 0.02<br>2 | 1.462 | 0.380  | 0.002  |
| 6<br>8 | 455<br>6 | 10<br>0 | 4.60<br>5 | 1.494  | 0.401     | 0.002     | 104.45<br>8 | 4.649 | 0.02<br>2 | 1.762 | 0.567  | 0.003  |
| 6<br>9 | 462<br>3 | 10<br>0 | 4.60<br>5 | 0.785  | -0.242    | -0.001    | 103.52<br>7 | 4.640 | 0.02<br>2 | 1.496 | 0.403  | 0.002  |
| 7<br>0 | 469<br>0 | 10<br>0 | 4.60<br>5 | -0.496 | #NUM<br>! | #NUM<br>! | 106.20<br>3 | 4.665 | 0.02<br>3 | 2.208 | 0.792  | 0.004  |

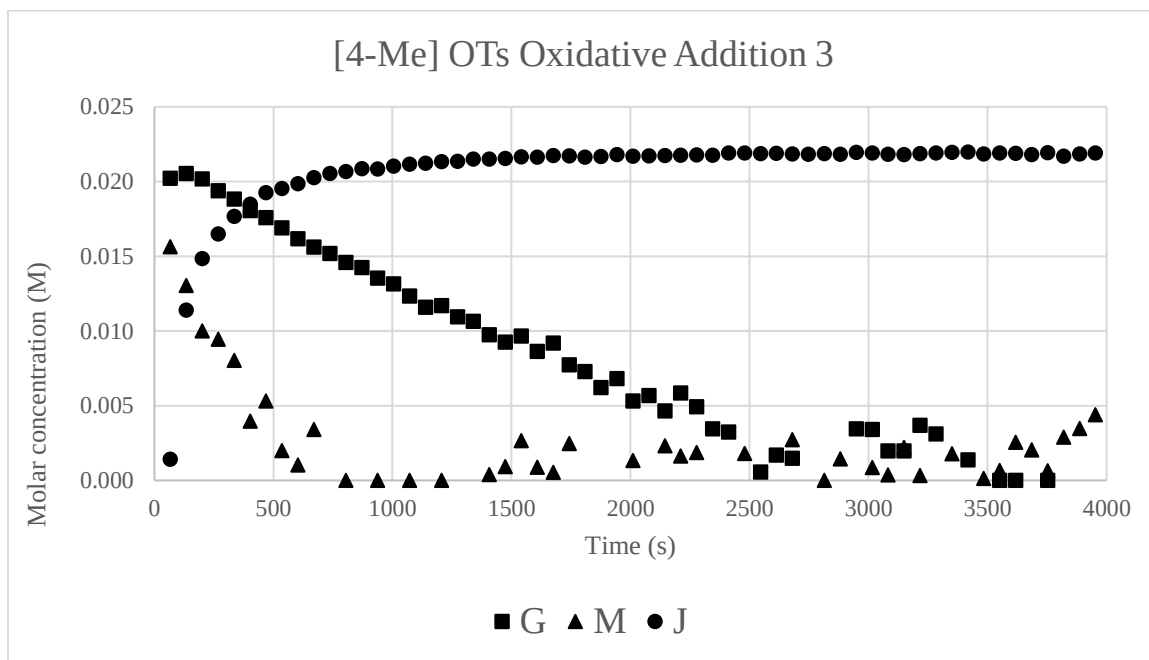
Table: Raw Data For [4-Me] OTs Oxidative Addition 2<sup>17</sup>

| A      | B   | C       | D         | E          | F     | G     | H      | I          | J         | K          | L      | M      |
|--------|-----|---------|-----------|------------|-------|-------|--------|------------|-----------|------------|--------|--------|
| 1      | 67  | 10<br>0 | 4.60<br>5 | 71.60<br>4 | 4.271 | 0.021 | 0.986  | -<br>0.014 | 0.00<br>0 | 34.32<br>5 | 3.536  | 0.017  |
| 2      | 134 | 10<br>0 | 4.60<br>5 | 82.07<br>2 | 4.408 | 0.021 | 9.327  | 2.233      | 0.01<br>1 | 19.49<br>5 | 2.970  | 0.014  |
| 3      | 201 | 10<br>0 | 4.60<br>5 | 76.24<br>4 | 4.334 | 0.021 | 18.955 | 2.942      | 0.01<br>4 | 11.32<br>8 | 2.427  | 0.012  |
| 4      | 268 | 10<br>0 | 4.60<br>5 | 70.65<br>3 | 4.258 | 0.021 | 26.884 | 3.292      | 0.01<br>6 | 7.516      | 2.017  | 0.010  |
| 5      | 335 | 10<br>0 | 4.60<br>5 | 63.34<br>0 | 4.149 | 0.020 | 34.795 | 3.549      | 0.01<br>7 | 5.148      | 1.639  | 0.008  |
| 6      | 402 | 10<br>0 | 4.60<br>5 | 59.08<br>3 | 4.079 | 0.020 | 43.123 | 3.764      | 0.01<br>8 | 3.974      | 1.380  | 0.007  |
| 7      | 469 | 10<br>0 | 4.60<br>5 | 52.82<br>8 | 3.967 | 0.019 | 50.040 | 3.913      | 0.01<br>9 | 3.060      | 1.118  | 0.005  |
| 8      | 536 | 10<br>0 | 4.60<br>5 | 46.83<br>9 | 3.847 | 0.019 | 54.417 | 3.997      | 0.01<br>9 | 2.056      | 0.721  | 0.003  |
| 9      | 603 | 10<br>0 | 4.60<br>5 | 42.35<br>0 | 3.746 | 0.018 | 60.216 | 4.098      | 0.02<br>0 | 1.458      | 0.377  | 0.002  |
| 1<br>0 | 670 | 10<br>0 | 4.60<br>5 | 38.87<br>8 | 3.660 | 0.018 | 64.589 | 4.168      | 0.02<br>0 | 2.394      | 0.873  | 0.004  |
| 1<br>1 | 737 | 10<br>0 | 4.60<br>5 | 35.15<br>2 | 3.560 | 0.017 | 68.570 | 4.228      | 0.02<br>0 | 0.425      | -0.856 | -0.004 |
| 1<br>2 | 804 | 10<br>0 | 4.60<br>5 | 31.04<br>9 | 3.436 | 0.017 | 71.417 | 4.269      | 0.02<br>1 | 1.050      | 0.049  | 0.000  |
| 1<br>3 | 871 | 10<br>0 | 4.60<br>5 | 28.39<br>5 | 3.346 | 0.016 | 74.741 | 4.314      | 0.02<br>1 | 2.316      | 0.840  | 0.004  |

<sup>17</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~-10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|        |          |         |           |            |       |       |             |       |           |        |           |           |
|--------|----------|---------|-----------|------------|-------|-------|-------------|-------|-----------|--------|-----------|-----------|
| 1<br>4 | 938      | 10<br>0 | 4.60<br>5 | 27.03<br>8 | 3.297 | 0.016 | 76.542      | 4.338 | 0.02<br>1 | 0.712  | -0.339    | -0.002    |
| 1<br>5 | 100<br>5 | 10<br>0 | 4.60<br>5 | 24.11<br>4 | 3.183 | 0.015 | 80.315      | 4.386 | 0.02<br>1 | 0.070  | -2.657    | -0.013    |
| 1<br>6 | 107<br>2 | 10<br>0 | 4.60<br>5 | 22.79<br>3 | 3.126 | 0.015 | 82.603      | 4.414 | 0.02<br>1 | 0.547  | -0.603    | -0.003    |
| 1<br>7 | 113<br>9 | 10<br>0 | 4.60<br>5 | 21.58<br>3 | 3.072 | 0.015 | 85.386      | 4.447 | 0.02<br>1 | -0.219 | #NUM<br>! | #NUM<br>! |
| 1<br>8 | 120<br>6 | 10<br>0 | 4.60<br>5 | 19.59<br>4 | 2.975 | 0.014 | 86.611      | 4.461 | 0.02<br>2 | 1.451  | 0.372     | 0.002     |
| 1<br>9 | 127<br>3 | 10<br>0 | 4.60<br>5 | 17.10<br>3 | 2.839 | 0.014 | 87.685      | 4.474 | 0.02<br>2 | 1.769  | 0.571     | 0.003     |
| 2<br>0 | 134<br>0 | 10<br>0 | 4.60<br>5 | 15.93<br>5 | 2.769 | 0.013 | 89.532      | 4.495 | 0.02<br>2 | 0.935  | -0.067    | 0.000     |
| 2<br>1 | 140<br>7 | 10<br>0 | 4.60<br>5 | 15.30<br>1 | 2.728 | 0.013 | 91.201      | 4.513 | 0.02<br>2 | 0.482  | -0.730    | -0.004    |
| 2<br>2 | 147<br>4 | 10<br>0 | 4.60<br>5 | 13.04<br>2 | 2.568 | 0.012 | 91.300      | 4.514 | 0.02<br>2 | 0.542  | -0.613    | -0.003    |
| 2<br>3 | 154<br>1 | 10<br>0 | 4.60<br>5 | 12.60<br>1 | 2.534 | 0.012 | 91.979      | 4.522 | 0.02<br>2 | 0.778  | -0.251    | -0.001    |
| 2<br>4 | 160<br>8 | 10<br>0 | 4.60<br>5 | 12.80<br>0 | 2.549 | 0.012 | 92.704      | 4.529 | 0.02<br>2 | -0.029 | #NUM<br>! | #NUM<br>! |
| 2<br>5 | 167<br>5 | 10<br>0 | 4.60<br>5 | 10.97<br>2 | 2.395 | 0.012 | 95.975      | 4.564 | 0.02<br>2 | 0.721  | -0.327    | -0.002    |
| 2<br>6 | 174<br>2 | 10<br>0 | 4.60<br>5 | 11.04<br>0 | 2.402 | 0.012 | 96.958      | 4.574 | 0.02<br>2 | 1.523  | 0.421     | 0.002     |
| 2<br>7 | 180<br>9 | 10<br>0 | 4.60<br>5 | 10.40<br>7 | 2.342 | 0.011 | 96.185      | 4.566 | 0.02<br>2 | -0.428 | #NUM<br>! | #NUM<br>! |
| 2<br>8 | 187<br>6 | 10<br>0 | 4.60<br>5 | 10.54<br>1 | 2.355 | 0.011 | 96.555      | 4.570 | 0.02<br>2 | 0.921  | -0.082    | 0.000     |
| 2<br>9 | 194<br>3 | 10<br>0 | 4.60<br>5 | 8.039      | 2.084 | 0.010 | 97.652      | 4.581 | 0.02<br>2 | 0.171  | -1.767    | -0.009    |
| 3<br>0 | 201<br>0 | 10<br>0 | 4.60<br>5 | 7.996      | 2.079 | 0.010 | 98.610      | 4.591 | 0.02<br>2 | 0.226  | -1.489    | -0.007    |
| 3<br>1 | 207<br>7 | 10<br>0 | 4.60<br>5 | 6.728      | 1.906 | 0.009 | 99.923      | 4.604 | 0.02<br>2 | 1.372  | 0.316     | 0.002     |
| 3<br>2 | 214<br>4 | 10<br>0 | 4.60<br>5 | 6.504      | 1.872 | 0.009 | 97.940      | 4.584 | 0.02<br>2 | 0.959  | -0.042    | 0.000     |
| 3<br>3 | 221<br>1 | 10<br>0 | 4.60<br>5 | 5.725      | 1.745 | 0.008 | 100.05<br>3 | 4.606 | 0.02<br>2 | 0.424  | -0.859    | -0.004    |
| 3<br>4 | 227<br>8 | 10<br>0 | 4.60<br>5 | 5.604      | 1.723 | 0.008 | 99.706      | 4.602 | 0.02<br>2 | 1.745  | 0.557     | 0.003     |
| 3<br>5 | 234<br>5 | 10<br>0 | 4.60<br>5 | 5.000      | 1.609 | 0.008 | 100.14<br>7 | 4.607 | 0.02<br>2 | 1.502  | 0.407     | 0.002     |
| 3<br>6 | 241<br>2 | 10<br>0 | 4.60<br>5 | 6.145      | 1.816 | 0.009 | 100.98<br>2 | 4.615 | 0.02<br>2 | 1.286  | 0.251     | 0.001     |
| 3<br>7 | 247<br>9 | 10<br>0 | 4.60<br>5 | 3.694      | 1.307 | 0.006 | 101.61<br>4 | 4.621 | 0.02<br>2 | 0.603  | -0.505    | -0.002    |
| 3<br>8 | 254<br>6 | 10<br>0 | 4.60<br>5 | 5.430      | 1.692 | 0.008 | 102.43<br>8 | 4.629 | 0.02<br>2 | 1.983  | 0.684     | 0.003     |
| 3<br>9 | 261<br>3 | 10<br>0 | 4.60<br>5 | 3.990      | 1.384 | 0.007 | 102.09<br>8 | 4.626 | 0.02<br>2 | 0.832  | -0.184    | -0.001    |
| 4<br>0 | 268<br>0 | 10<br>0 | 4.60<br>5 | 3.536      | 1.263 | 0.006 | 102.21<br>6 | 4.627 | 0.02<br>2 | 0.929  | -0.073    | 0.000     |
| 4<br>1 | 274<br>7 | 10<br>0 | 4.60<br>5 | 4.084      | 1.407 | 0.007 | 102.04<br>5 | 4.625 | 0.02<br>2 | 1.414  | 0.346     | 0.002     |
| 4<br>2 | 281<br>4 | 10<br>0 | 4.60<br>5 | 2.464      | 0.902 | 0.004 | 102.14<br>0 | 4.626 | 0.02<br>2 | 1.003  | 0.003     | 0.000     |

|    |      |     |       |        |        |        |         |       |       |       |        |        |
|----|------|-----|-------|--------|--------|--------|---------|-------|-------|-------|--------|--------|
| 43 | 2881 | 100 | 4.605 | 3.474  | 1.245  | 0.006  | 101.396 | 4.619 | 0.022 | 1.994 | 0.690  | 0.003  |
| 44 | 2948 | 100 | 4.605 | 2.328  | 0.845  | 0.004  | 102.555 | 4.630 | 0.022 | 1.372 | 0.316  | 0.002  |
| 45 | 3015 | 100 | 4.605 | 2.306  | 0.836  | 0.004  | 104.491 | 4.649 | 0.022 | 1.155 | 0.144  | 0.001  |
| 46 | 3082 | 100 | 4.605 | 3.155  | 1.149  | 0.006  | 103.520 | 4.640 | 0.022 | 0.952 | -0.049 | 0.000  |
| 47 | 3149 | 100 | 4.605 | 2.159  | 0.770  | 0.004  | 103.069 | 4.635 | 0.022 | 1.097 | 0.092  | 0.000  |
| 48 | 3216 | 100 | 4.605 | 2.576  | 0.946  | 0.005  | 103.957 | 4.644 | 0.022 | 1.478 | 0.391  | 0.002  |
| 49 | 3283 | 100 | 4.605 | 2.384  | 0.869  | 0.004  | 103.612 | 4.641 | 0.022 | 1.736 | 0.552  | 0.003  |
| 50 | 3350 | 100 | 4.605 | 2.224  | 0.799  | 0.004  | 103.352 | 4.638 | 0.022 | 1.381 | 0.323  | 0.002  |
| 51 | 3417 | 100 | 4.605 | 2.322  | 0.842  | 0.004  | 104.949 | 4.653 | 0.022 | 0.595 | -0.519 | -0.003 |
| 52 | 3484 | 100 | 4.605 | 0.897  | -0.109 | -0.001 | 105.555 | 4.659 | 0.022 | 2.259 | 0.815  | 0.004  |
| 53 | 3551 | 100 | 4.605 | 2.307  | 0.836  | 0.004  | 102.356 | 4.628 | 0.022 | 0.973 | -0.028 | 0.000  |
| 54 | 3618 | 100 | 4.605 | 0.594  | -0.521 | -0.003 | 104.959 | 4.654 | 0.022 | 1.063 | 0.061  | 0.000  |
| 55 | 3685 | 100 | 4.605 | 2.024  | 0.705  | 0.003  | 102.954 | 4.634 | 0.022 | 0.426 | -0.853 | -0.004 |
| 56 | 3752 | 100 | 4.605 | 1.139  | 0.130  | 0.001  | 103.753 | 4.642 | 0.022 | 0.896 | -0.109 | -0.001 |
| 57 | 3819 | 100 | 4.605 | 1.404  | 0.339  | 0.002  | 103.221 | 4.637 | 0.022 | 1.483 | 0.394  | 0.002  |
| 58 | 3886 | 100 | 4.605 | 2.091  | 0.738  | 0.004  | 104.146 | 4.646 | 0.022 | 1.343 | 0.295  | 0.001  |
| 59 | 3953 | 100 | 4.605 | 1.511  | 0.413  | 0.002  | 104.087 | 4.645 | 0.022 | 1.830 | 0.604  | 0.003  |
| 60 | 4020 | 100 | 4.605 | 0.155  | -1.864 | -0.009 | 104.720 | 4.651 | 0.022 | 1.120 | 0.113  | 0.001  |
| 61 | 4087 | 100 | 4.605 | 0.992  | -0.008 | 0.000  | 103.296 | 4.638 | 0.022 | 1.458 | 0.377  | 0.002  |
| 62 | 4154 | 100 | 4.605 | 1.374  | 0.318  | 0.002  | 105.270 | 4.657 | 0.022 | 1.547 | 0.436  | 0.002  |
| 63 | 4221 | 100 | 4.605 | -0.037 | #NUM!  | #NUM!  | 105.308 | 4.657 | 0.022 | 1.113 | 0.107  | 0.001  |
| 64 | 4288 | 100 | 4.605 | 0.541  | -0.614 | -0.003 | 105.824 | 4.662 | 0.022 | 1.659 | 0.506  | 0.002  |
| 65 | 4355 | 100 | 4.605 | 0.469  | -0.758 | -0.004 | 106.606 | 4.669 | 0.023 | 1.953 | 0.669  | 0.003  |
| 66 | 4422 | 100 | 4.605 | 1.548  | 0.437  | 0.002  | 104.260 | 4.647 | 0.022 | 1.882 | 0.632  | 0.003  |
| 67 | 4489 | 100 | 4.605 | -1.029 | #NUM!  | #NUM!  | 103.567 | 4.640 | 0.022 | 1.462 | 0.380  | 0.002  |
| 68 | 4556 | 100 | 4.605 | 1.494  | 0.401  | 0.002  | 104.458 | 4.649 | 0.022 | 1.762 | 0.567  | 0.003  |
| 69 | 4623 | 100 | 4.605 | 0.785  | -0.242 | -0.001 | 103.527 | 4.640 | 0.022 | 1.496 | 0.403  | 0.002  |
| 70 | 4690 | 100 | 4.605 | -0.496 | #NUM!  | #NUM!  | 106.203 | 4.665 | 0.023 | 2.208 | 0.792  | 0.004  |

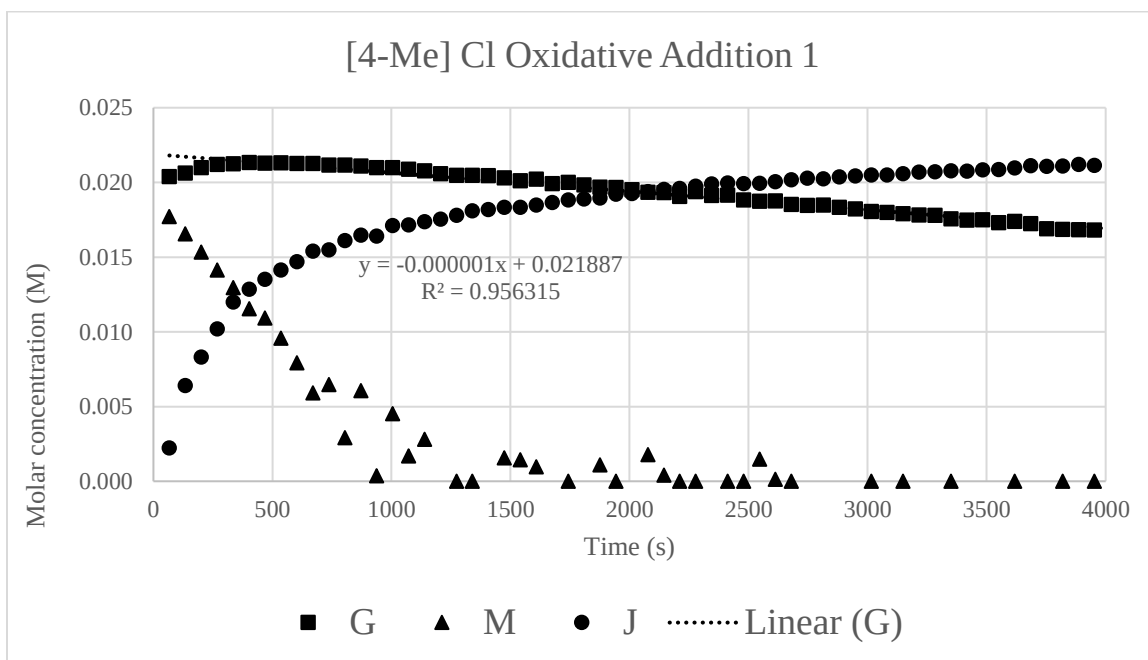
Table: Raw Data For [4-Me] OTs Oxidative Addition 3<sup>18</sup>

| A  | B    | C   | D     | E      | F     | G     | H      | I     | J     | K      | L      | M      |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|--------|--------|--------|
| 1  | 67   | 100 | 4.605 | 66.121 | 4.191 | 0.020 | 1.344  | 0.296 | 0.001 | 25.567 | 3.241  | 0.016  |
| 2  | 134  | 100 | 4.605 | 70.476 | 4.255 | 0.021 | 10.612 | 2.362 | 0.011 | 14.920 | 2.703  | 0.013  |
| 3  | 201  | 100 | 4.605 | 65.534 | 4.183 | 0.020 | 21.650 | 3.075 | 0.015 | 7.942  | 2.072  | 0.010  |
| 4  | 268  | 100 | 4.605 | 55.604 | 4.018 | 0.019 | 30.496 | 3.418 | 0.016 | 7.082  | 1.958  | 0.009  |
| 5  | 335  | 100 | 4.605 | 49.385 | 3.900 | 0.019 | 38.994 | 3.663 | 0.018 | 5.276  | 1.663  | 0.008  |
| 6  | 402  | 100 | 4.605 | 42.227 | 3.743 | 0.018 | 46.182 | 3.833 | 0.018 | 2.270  | 0.820  | 0.004  |
| 7  | 469  | 100 | 4.605 | 38.335 | 3.646 | 0.018 | 53.995 | 3.989 | 0.019 | 3.003  | 1.100  | 0.005  |
| 8  | 536  | 100 | 4.605 | 33.188 | 3.502 | 0.017 | 57.272 | 4.048 | 0.020 | 1.511  | 0.413  | 0.002  |
| 9  | 603  | 100 | 4.605 | 28.512 | 3.350 | 0.016 | 61.123 | 4.113 | 0.020 | 1.236  | 0.212  | 0.001  |
| 10 | 670  | 100 | 4.605 | 25.457 | 3.237 | 0.016 | 66.658 | 4.200 | 0.020 | 2.031  | 0.708  | 0.003  |
| 11 | 737  | 100 | 4.605 | 23.316 | 3.149 | 0.015 | 70.478 | 4.255 | 0.021 | 0.976  | -0.025 | 0.000  |
| 12 | 804  | 100 | 4.605 | 20.515 | 3.021 | 0.015 | 72.334 | 4.281 | 0.021 | -0.025 | #NUM!  | #NUM!  |
| 13 | 871  | 100 | 4.605 | 19.108 | 2.950 | 0.014 | 75.452 | 4.323 | 0.021 | 0.131  | -2.031 | -0.010 |
| 14 | 938  | 100 | 4.605 | 16.558 | 2.807 | 0.014 | 75.197 | 4.320 | 0.021 | -0.011 | #NUM!  | #NUM!  |
| 15 | 1005 | 100 | 4.605 | 15.268 | 2.726 | 0.013 | 78.127 | 4.358 | 0.021 | 0.434  | -0.835 | -0.004 |
| 16 | 1072 | 100 | 4.605 | 12.907 | 2.558 | 0.012 | 80.358 | 4.386 | 0.021 | -0.374 | #NUM!  | #NUM!  |
| 17 | 1139 | 100 | 4.605 | 11.055 | 2.403 | 0.012 | 81.220 | 4.397 | 0.021 | 0.270  | -1.308 | -0.006 |
| 18 | 1206 | 100 | 4.605 | 11.310 | 2.426 | 0.012 | 83.220 | 4.421 | 0.021 | -0.377 | #NUM!  | #NUM!  |

<sup>18</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~-10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |     |       |        |        |        |        |       |       |       |        |        |
|----|------|-----|-------|--------|--------|--------|--------|-------|-------|-------|--------|--------|
| 19 | 1273 | 100 | 4.605 | 9.662  | 2.268  | 0.011  | 83.574 | 4.426 | 0.021 | 0.345 | -1.064 | -0.005 |
| 20 | 1340 | 100 | 4.605 | 9.094  | 2.208  | 0.011  | 86.187 | 4.457 | 0.022 | 0.784 | -0.243 | -0.001 |
| 21 | 1407 | 100 | 4.605 | 7.551  | 2.022  | 0.010  | 86.333 | 4.458 | 0.022 | 1.082 | 0.079  | 0.000  |
| 22 | 1474 | 100 | 4.605 | 6.804  | 1.918  | 0.009  | 87.059 | 4.467 | 0.022 | 1.213 | 0.193  | 0.001  |
| 23 | 1541 | 100 | 4.605 | 7.409  | 2.003  | 0.010  | 89.050 | 4.489 | 0.022 | 1.735 | 0.551  | 0.003  |
| 24 | 1608 | 100 | 4.605 | 5.986  | 1.789  | 0.009  | 88.535 | 4.483 | 0.022 | 1.202 | 0.184  | 0.001  |
| 25 | 1675 | 100 | 4.605 | 6.712  | 1.904  | 0.009  | 90.344 | 4.504 | 0.022 | 1.120 | 0.113  | 0.001  |
| 26 | 1742 | 100 | 4.605 | 4.969  | 1.603  | 0.008  | 90.156 | 4.502 | 0.022 | 1.670 | 0.513  | 0.002  |
| 27 | 1809 | 100 | 4.605 | 4.523  | 1.509  | 0.007  | 88.436 | 4.482 | 0.022 | 0.731 | -0.313 | -0.002 |
| 28 | 1876 | 100 | 4.605 | 3.626  | 1.288  | 0.006  | 89.349 | 4.493 | 0.022 | 0.615 | -0.486 | -0.002 |
| 29 | 1943 | 100 | 4.605 | 4.105  | 1.412  | 0.007  | 91.606 | 4.517 | 0.022 | 0.579 | -0.546 | -0.003 |
| 30 | 2010 | 100 | 4.605 | 3.009  | 1.102  | 0.005  | 89.854 | 4.498 | 0.022 | 1.321 | 0.278  | 0.001  |
| 31 | 2077 | 100 | 4.605 | 3.245  | 1.177  | 0.006  | 90.041 | 4.500 | 0.022 | 0.891 | -0.115 | -0.001 |
| 32 | 2144 | 100 | 4.605 | 2.618  | 0.962  | 0.005  | 90.321 | 4.503 | 0.022 | 1.616 | 0.480  | 0.002  |
| 33 | 2211 | 100 | 4.605 | 3.366  | 1.214  | 0.006  | 90.726 | 4.508 | 0.022 | 1.400 | 0.337  | 0.002  |
| 34 | 2278 | 100 | 4.605 | 2.780  | 1.022  | 0.005  | 91.315 | 4.514 | 0.022 | 1.475 | 0.389  | 0.002  |
| 35 | 2345 | 100 | 4.605 | 2.043  | 0.714  | 0.003  | 91.056 | 4.511 | 0.022 | 0.010 | -4.561 | -0.022 |
| 36 | 2412 | 100 | 4.605 | 1.960  | 0.673  | 0.003  | 93.608 | 4.539 | 0.022 | 0.827 | -0.190 | -0.001 |
| 37 | 2479 | 100 | 4.605 | 0.425  | -0.856 | -0.004 | 93.557 | 4.539 | 0.022 | 1.450 | 0.372  | 0.002  |
| 38 | 2546 | 100 | 4.605 | 1.122  | 0.115  | 0.001  | 92.737 | 4.530 | 0.022 | 0.770 | -0.262 | -0.001 |
| 39 | 2613 | 100 | 4.605 | 1.418  | 0.350  | 0.002  | 93.382 | 4.537 | 0.022 | 0.746 | -0.293 | -0.001 |
| 40 | 2680 | 100 | 4.605 | 1.362  | 0.309  | 0.001  | 92.682 | 4.529 | 0.022 | 1.757 | 0.563  | 0.003  |
| 41 | 2747 | 100 | 4.605 | 0.425  | -0.855 | -0.004 | 92.165 | 4.524 | 0.022 | 0.810 | -0.211 | -0.001 |
| 42 | 2814 | 100 | 4.605 | 0.984  | -0.016 | 0.000  | 92.816 | 4.531 | 0.022 | 1.002 | 0.002  | 0.000  |
| 43 | 2881 | 100 | 4.605 | 0.970  | -0.031 | 0.000  | 92.266 | 4.525 | 0.022 | 1.345 | 0.296  | 0.001  |
| 44 | 2948 | 100 | 4.605 | 2.049  | 0.717  | 0.003  | 94.806 | 4.552 | 0.022 | 0.954 | -0.047 | 0.000  |
| 45 | 3015 | 100 | 4.605 | 2.026  | 0.706  | 0.003  | 93.679 | 4.540 | 0.022 | 1.195 | 0.178  | 0.001  |
| 46 | 3082 | 100 | 4.605 | 1.506  | 0.409  | 0.002  | 91.970 | 4.521 | 0.022 | 1.078 | 0.075  | 0.000  |
| 47 | 3149 | 100 | 4.605 | 1.506  | 0.409  | 0.002  | 91.779 | 4.519 | 0.022 | 1.579 | 0.457  | 0.002  |
| 48 | 3216 | 100 | 4.605 | 2.143  | 0.762  | 0.004  | 92.886 | 4.531 | 0.022 | 1.072 | 0.069  | 0.000  |
| 49 | 3283 | 100 | 4.605 | 1.904  | 0.644  | 0.003  | 93.699 | 4.540 | 0.022 | 0.221 | -1.509 | -0.007 |
| 50 | 3350 | 100 | 4.605 | 0.276  | -1.288 | -0.006 | 94.500 | 4.549 | 0.022 | 1.447 | 0.369  | 0.002  |
| 51 | 3417 | 100 | 4.605 | 1.327  | 0.283  | 0.001  | 94.876 | 4.553 | 0.022 | 0.035 | -3.364 | -0.016 |
| 52 | 3484 | 100 | 4.605 | 0.121  | -2.114 | -0.010 | 92.713 | 4.530 | 0.022 | 1.026 | 0.025  | 0.000  |
| 53 | 3551 | 100 | 4.605 | -0.255 | #NUM!  | #NUM!  | 93.877 | 4.542 | 0.022 | 1.149 | 0.139  | 0.001  |
| 54 | 3618 | 100 | 4.605 | -0.227 | #NUM!  | #NUM!  | 93.252 | 4.535 | 0.022 | 1.696 | 0.529  | 0.003  |
| 55 | 3685 | 100 | 4.605 | 0.458  | -0.780 | -0.004 | 91.652 | 4.518 | 0.022 | 1.528 | 0.424  | 0.002  |
| 56 | 3752 | 100 | 4.605 | -0.013 | #NUM!  | #NUM!  | 94.002 | 4.543 | 0.022 | 1.145 | 0.136  | 0.001  |
| 57 | 3819 | 100 | 4.605 | 0.348  | -1.055 | -0.005 | 89.669 | 4.496 | 0.022 | 1.822 | 0.600  | 0.003  |

|    |      |     |       |        |        |        |        |       |       |       |        |        |
|----|------|-----|-------|--------|--------|--------|--------|-------|-------|-------|--------|--------|
| 58 | 3886 | 100 | 4.605 | 0.513  | -0.668 | -0.003 | 92.466 | 4.527 | 0.022 | 2.056 | 0.721  | 0.003  |
| 59 | 3953 | 100 | 4.605 | 0.737  | -0.305 | -0.001 | 93.635 | 4.539 | 0.022 | 2.482 | 0.909  | 0.004  |
| 60 | 4020 | 100 | 4.605 | 0.054  | -2.914 | -0.014 | 90.838 | 4.509 | 0.022 | 1.406 | 0.341  | 0.002  |
| 61 | 4087 | 100 | 4.605 | 1.156  | 0.145  | 0.001  | 91.899 | 4.521 | 0.022 | 0.715 | -0.335 | -0.002 |
| 62 | 4154 | 100 | 4.605 | 0.208  | -1.568 | -0.008 | 92.337 | 4.525 | 0.022 | 0.432 | -0.839 | -0.004 |
| 63 | 4221 | 100 | 4.605 | -0.046 | #NUM!  | #NUM!  | 92.936 | 4.532 | 0.022 | 1.431 | 0.358  | 0.002  |
| 64 | 4288 | 100 | 4.605 | -0.407 | #NUM!  | #NUM!  | 93.222 | 4.535 | 0.022 | 1.022 | 0.022  | 0.000  |
| 65 | 4355 | 100 | 4.605 | 0.432  | -0.839 | -0.004 | 92.015 | 4.522 | 0.022 | 2.546 | 0.934  | 0.005  |
| 66 | 4422 | 100 | 4.605 | -0.504 | #NUM!  | #NUM!  | 91.822 | 4.520 | 0.022 | 2.509 | 0.920  | 0.004  |
| 67 | 4489 | 100 | 4.605 | 1.229  | 0.206  | 0.001  | 93.522 | 4.538 | 0.022 | 1.252 | 0.225  | 0.001  |
| 68 | 4556 | 100 | 4.605 | -0.740 | #NUM!  | #NUM!  | 93.071 | 4.533 | 0.022 | 1.985 | 0.686  | 0.003  |
| 69 | 4623 | 100 | 4.605 | -0.251 | #NUM!  | #NUM!  | 94.630 | 4.550 | 0.022 | 1.219 | 0.198  | 0.001  |
| 70 | 4690 | 100 | 4.605 | -0.885 | #NUM!  | #NUM!  | 92.030 | 4.522 | 0.022 | 1.764 | 0.567  | 0.003  |

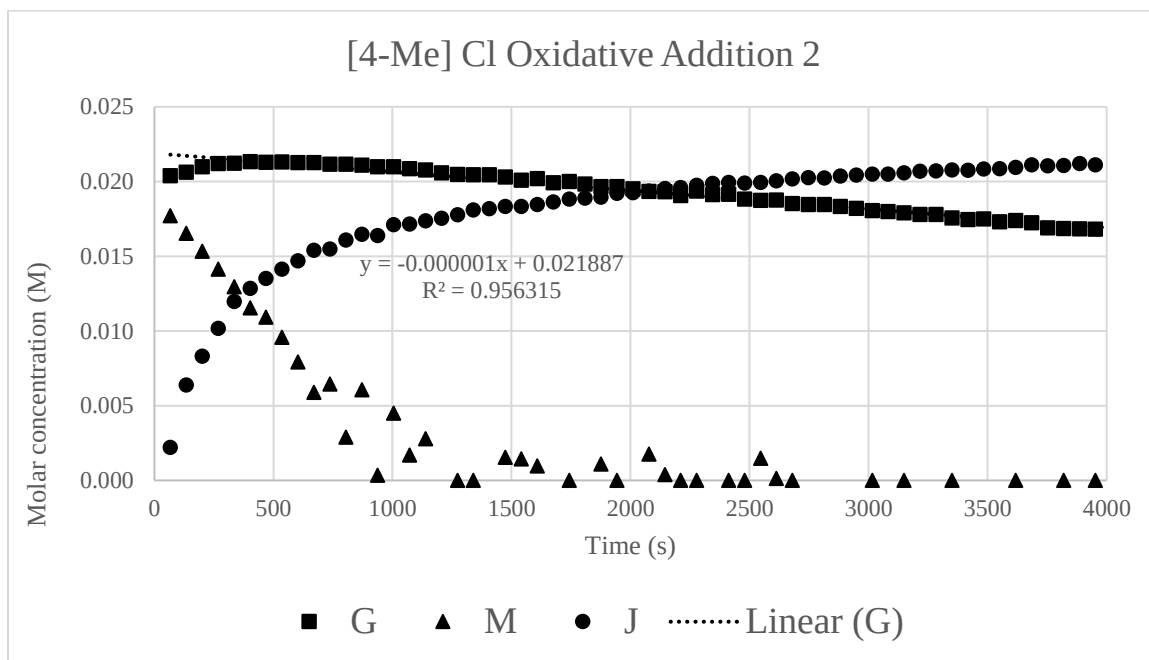
Table: Raw Data For [4-Me] Cl Oxidative Addition 1<sup>19</sup>

| A | B   | C   | D     | E      | F     | G     | H     | I     | J     | K      | L     | M     |
|---|-----|-----|-------|--------|-------|-------|-------|-------|-------|--------|-------|-------|
| 1 | 67  | 100 | 4.605 | 68.403 | 4.225 | 0.020 | 1.584 | 0.460 | 0.002 | 39.235 | 3.670 | 0.018 |
| 2 | 134 | 100 | 4.605 | 71.938 | 4.276 | 0.021 | 3.764 | 1.326 | 0.006 | 30.832 | 3.429 | 0.017 |
| 3 | 201 | 100 | 4.605 | 77.494 | 4.350 | 0.021 | 5.604 | 1.723 | 0.008 | 23.979 | 3.177 | 0.015 |

<sup>19</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |     |       |        |       |       |        |       |       |        |        |        |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|--------|--------|--------|
| 4  | 268  | 100 | 4.605 | 80.986 | 4.394 | 0.021 | 8.256  | 2.111 | 0.010 | 18.751 | 2.931  | 0.014  |
| 5  | 335  | 100 | 4.605 | 81.490 | 4.400 | 0.021 | 11.984 | 2.484 | 0.012 | 14.651 | 2.684  | 0.013  |
| 6  | 402  | 100 | 4.605 | 83.130 | 4.420 | 0.021 | 14.348 | 2.664 | 0.013 | 10.937 | 2.392  | 0.012  |
| 7  | 469  | 100 | 4.605 | 82.326 | 4.411 | 0.021 | 16.456 | 2.801 | 0.014 | 9.618  | 2.264  | 0.011  |
| 8  | 536  | 100 | 4.605 | 82.903 | 4.418 | 0.021 | 18.707 | 2.929 | 0.014 | 7.282  | 1.985  | 0.010  |
| 9  | 603  | 100 | 4.605 | 81.946 | 4.406 | 0.021 | 21.021 | 3.046 | 0.015 | 5.172  | 1.643  | 0.008  |
| 10 | 670  | 100 | 4.605 | 82.023 | 4.407 | 0.021 | 24.333 | 3.192 | 0.015 | 3.398  | 1.223  | 0.006  |
| 11 | 737  | 100 | 4.605 | 80.311 | 4.386 | 0.021 | 24.711 | 3.207 | 0.015 | 3.812  | 1.338  | 0.006  |
| 12 | 804  | 100 | 4.605 | 80.188 | 4.384 | 0.021 | 28.091 | 3.335 | 0.016 | 1.826  | 0.602  | 0.003  |
| 13 | 871  | 100 | 4.605 | 79.301 | 4.373 | 0.021 | 30.334 | 3.412 | 0.016 | 3.511  | 1.256  | 0.006  |
| 14 | 938  | 100 | 4.605 | 77.435 | 4.349 | 0.021 | 29.905 | 3.398 | 0.016 | 1.076  | 0.073  | 0.000  |
| 15 | 1005 | 100 | 4.605 | 77.342 | 4.348 | 0.021 | 34.710 | 3.547 | 0.017 | 2.546  | 0.934  | 0.005  |
| 16 | 1072 | 100 | 4.605 | 75.589 | 4.325 | 0.021 | 35.030 | 3.556 | 0.017 | 1.420  | 0.351  | 0.002  |
| 17 | 1139 | 100 | 4.605 | 74.076 | 4.305 | 0.021 | 36.606 | 3.600 | 0.017 | 1.786  | 0.580  | 0.003  |
| 18 | 1206 | 100 | 4.605 | 71.075 | 4.264 | 0.021 | 37.961 | 3.637 | 0.018 | 0.687  | -0.376 | -0.002 |
| 19 | 1273 | 100 | 4.605 | 69.508 | 4.241 | 0.020 | 39.893 | 3.686 | 0.018 | -0.112 | #NUM!  | #NUM!  |
| 20 | 1340 | 100 | 4.605 | 69.445 | 4.241 | 0.020 | 42.481 | 3.749 | 0.018 | -0.237 | #NUM!  | #NUM!  |
| 21 | 1407 | 100 | 4.605 | 69.204 | 4.237 | 0.020 | 43.369 | 3.770 | 0.018 | 0.254  | -1.369 | -0.007 |
| 22 | 1474 | 100 | 4.605 | 67.182 | 4.207 | 0.020 | 44.673 | 3.799 | 0.018 | 1.381  | 0.323  | 0.002  |
| 23 | 1541 | 100 | 4.605 | 64.410 | 4.165 | 0.020 | 44.729 | 3.801 | 0.018 | 1.349  | 0.299  | 0.001  |
| 24 | 1608 | 100 | 4.605 | 65.867 | 4.188 | 0.020 | 45.978 | 3.828 | 0.018 | 1.223  | 0.201  | 0.001  |
| 25 | 1675 | 100 | 4.605 | 62.091 | 4.129 | 0.020 | 47.636 | 3.864 | 0.019 | 0.991  | -0.009 | 0.000  |
| 26 | 1742 | 100 | 4.605 | 63.078 | 4.144 | 0.020 | 49.391 | 3.900 | 0.019 | -0.151 | #NUM!  | #NUM!  |
| 27 | 1809 | 100 | 4.605 | 60.965 | 4.110 | 0.020 | 50.125 | 3.915 | 0.019 | 0.323  | -1.130 | -0.005 |
| 28 | 1876 | 100 | 4.605 | 58.948 | 4.077 | 0.020 | 50.837 | 3.929 | 0.019 | 1.253  | 0.226  | 0.001  |
| 29 | 1943 | 100 | 4.605 | 58.759 | 4.073 | 0.020 | 53.582 | 3.981 | 0.019 | -0.427 | #NUM!  | #NUM!  |
| 30 | 2010 | 100 | 4.605 | 57.029 | 4.044 | 0.020 | 54.118 | 3.991 | 0.019 | 0.206  | -1.580 | -0.008 |
| 31 | 2077 | 100 | 4.605 | 55.012 | 4.008 | 0.019 | 55.387 | 4.014 | 0.019 | 1.442  | 0.366  | 0.002  |
| 32 | 2144 | 100 | 4.605 | 54.692 | 4.002 | 0.019 | 57.328 | 4.049 | 0.020 | 1.087  | 0.083  | 0.000  |
| 33 | 2211 | 100 | 4.605 | 51.902 | 3.949 | 0.019 | 58.054 | 4.061 | 0.020 | -0.641 | #NUM!  | #NUM!  |
| 34 | 2278 | 100 | 4.605 | 55.374 | 4.014 | 0.019 | 59.920 | 4.093 | 0.020 | -0.307 | #NUM!  | #NUM!  |
| 35 | 2345 | 100 | 4.605 | 52.624 | 3.963 | 0.019 | 61.616 | 4.121 | 0.020 | 0.358  | -1.028 | -0.005 |
| 36 | 2412 | 100 | 4.605 | 52.915 | 3.969 | 0.019 | 62.423 | 4.134 | 0.020 | -0.447 | #NUM!  | #NUM!  |
| 37 | 2479 | 100 | 4.605 | 49.436 | 3.901 | 0.019 | 61.904 | 4.126 | 0.020 | -0.661 | #NUM!  | #NUM!  |
| 38 | 2546 | 100 | 4.605 | 48.536 | 3.882 | 0.019 | 62.405 | 4.134 | 0.020 | 1.361  | 0.308  | 0.001  |
| 39 | 2613 | 100 | 4.605 | 48.828 | 3.888 | 0.019 | 63.665 | 4.154 | 0.020 | 1.028  | 0.028  | 0.000  |
| 40 | 2680 | 100 | 4.605 | 46.560 | 3.841 | 0.019 | 65.462 | 4.181 | 0.020 | -0.263 | #NUM!  | #NUM!  |
| 41 | 2747 | 100 | 4.605 | 45.943 | 3.827 | 0.018 | 66.745 | 4.201 | 0.020 | 0.265  | -1.327 | -0.006 |
| 42 | 2814 | 100 | 4.605 | 45.991 | 3.828 | 0.018 | 66.357 | 4.195 | 0.020 | 0.066  | -2.713 | -0.013 |

|    |      |     |       |        |       |       |        |       |       |        |        |        |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|--------|--------|--------|
| 43 | 2881 | 100 | 4.605 | 44.608 | 3.798 | 0.018 | 68.173 | 4.222 | 0.020 | 0.170  | -1.773 | -0.009 |
| 44 | 2948 | 100 | 4.605 | 43.607 | 3.775 | 0.018 | 69.003 | 4.234 | 0.020 | 0.637  | -0.451 | -0.002 |
| 45 | 3015 | 100 | 4.605 | 42.107 | 3.740 | 0.018 | 69.843 | 4.246 | 0.020 | -0.037 | #NUM!  | #NUM!  |
| 46 | 3082 | 100 | 4.605 | 41.680 | 3.730 | 0.018 | 69.825 | 4.246 | 0.020 | 0.757  | -0.278 | -0.001 |
| 47 | 3149 | 100 | 4.605 | 40.867 | 3.710 | 0.018 | 71.297 | 4.267 | 0.021 | -0.268 | #NUM!  | #NUM!  |
| 48 | 3216 | 100 | 4.605 | 40.070 | 3.691 | 0.018 | 72.856 | 4.288 | 0.021 | 0.019  | -3.988 | -0.019 |
| 49 | 3283 | 100 | 4.605 | 39.929 | 3.687 | 0.018 | 73.162 | 4.293 | 0.021 | 0.683  | -0.381 | -0.002 |
| 50 | 3350 | 100 | 4.605 | 38.019 | 3.638 | 0.018 | 74.081 | 4.305 | 0.021 | -0.494 | #NUM!  | #NUM!  |
| 51 | 3417 | 100 | 4.605 | 37.315 | 3.619 | 0.017 | 73.710 | 4.300 | 0.021 | 0.783  | -0.244 | -0.001 |
| 52 | 3484 | 100 | 4.605 | 37.603 | 3.627 | 0.018 | 75.113 | 4.319 | 0.021 | 0.087  | -2.441 | -0.012 |
| 53 | 3551 | 100 | 4.605 | 36.151 | 3.588 | 0.017 | 75.374 | 4.322 | 0.021 | 0.130  | -2.041 | -0.010 |
| 54 | 3618 | 100 | 4.605 | 36.777 | 3.605 | 0.017 | 76.948 | 4.343 | 0.021 | -0.181 | #NUM!  | #NUM!  |
| 55 | 3685 | 100 | 4.605 | 35.589 | 3.572 | 0.017 | 79.608 | 4.377 | 0.021 | 0.991  | -0.009 | 0.000  |
| 56 | 3752 | 100 | 4.605 | 33.195 | 3.502 | 0.017 | 78.629 | 4.365 | 0.021 | 0.547  | -0.603 | -0.003 |
| 57 | 3819 | 100 | 4.605 | 32.831 | 3.491 | 0.017 | 79.021 | 4.370 | 0.021 | -0.784 | #NUM!  | #NUM!  |
| 58 | 3886 | 100 | 4.605 | 32.711 | 3.488 | 0.017 | 81.049 | 4.395 | 0.021 | 0.198  | -1.618 | -0.008 |
| 59 | 3953 | 100 | 4.605 | 32.651 | 3.486 | 0.017 | 79.700 | 4.378 | 0.021 | -0.040 | #NUM!  | #NUM!  |
| 60 | 4020 | 100 | 4.605 | 31.368 | 3.446 | 0.017 | 81.799 | 4.404 | 0.021 | 0.084  | -2.474 | -0.012 |
| 61 | 4087 | 100 | 4.605 | 32.264 | 3.474 | 0.017 | 81.282 | 4.398 | 0.021 | -0.649 | #NUM!  | #NUM!  |
| 62 | 4154 | 100 | 4.605 | 31.082 | 3.437 | 0.017 | 84.206 | 4.433 | 0.021 | -0.494 | #NUM!  | #NUM!  |
| 63 | 4221 | 100 | 4.605 | 30.270 | 3.410 | 0.016 | 82.984 | 4.419 | 0.021 | -0.112 | #NUM!  | #NUM!  |
| 64 | 4288 | 100 | 4.605 | 29.226 | 3.375 | 0.016 | 85.350 | 4.447 | 0.021 | -1.077 | #NUM!  | #NUM!  |
| 65 | 4355 | 100 | 4.605 | 28.162 | 3.338 | 0.016 | 83.504 | 4.425 | 0.021 | 1.089  | 0.085  | 0.000  |
| 66 | 4422 | 100 | 4.605 | 30.202 | 3.408 | 0.016 | 86.024 | 4.455 | 0.021 | 0.310  | -1.171 | -0.006 |
| 67 | 4489 | 100 | 4.605 | 28.868 | 3.363 | 0.016 | 85.638 | 4.450 | 0.021 | 0.960  | -0.041 | 0.000  |
| 68 | 4556 | 100 | 4.605 | 27.354 | 3.309 | 0.016 | 87.439 | 4.471 | 0.022 | -0.325 | #NUM!  | #NUM!  |
| 69 | 4623 | 100 | 4.605 | 26.386 | 3.273 | 0.016 | 85.719 | 4.451 | 0.021 | -0.462 | #NUM!  | #NUM!  |
| 70 | 4690 | 100 | 4.605 | 26.634 | 3.282 | 0.016 | 88.186 | 4.479 | 0.022 | -0.506 | #NUM!  | #NUM!  |

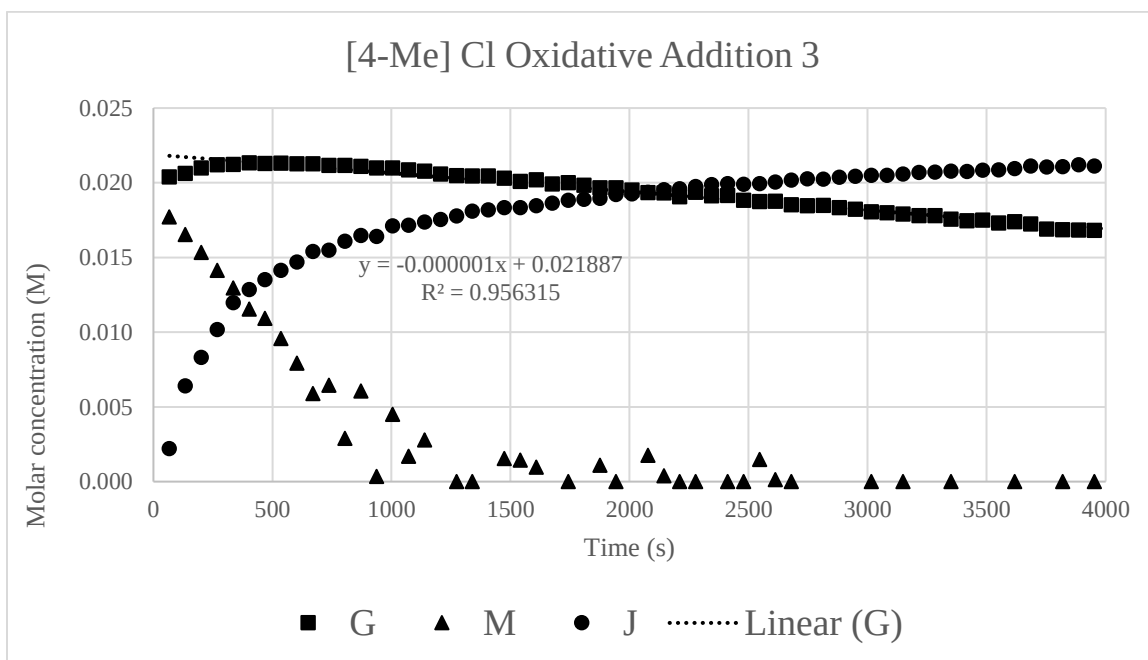
Table: Raw Data For [4-Me] Cl Oxidative Addition 2<sup>20</sup>

| A  | B    | C   | D     | E      | F     | G     | H      | I     | J     | K      | L      | M      |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|--------|--------|--------|
| 1  | 67   | 100 | 4.605 | 68.403 | 4.225 | 0.020 | 1.584  | 0.460 | 0.002 | 39.235 | 3.670  | 0.018  |
| 2  | 134  | 100 | 4.605 | 71.938 | 4.276 | 0.021 | 3.764  | 1.326 | 0.006 | 30.832 | 3.429  | 0.017  |
| 3  | 201  | 100 | 4.605 | 77.494 | 4.350 | 0.021 | 5.604  | 1.723 | 0.008 | 23.979 | 3.177  | 0.015  |
| 4  | 268  | 100 | 4.605 | 80.986 | 4.394 | 0.021 | 8.256  | 2.111 | 0.010 | 18.751 | 2.931  | 0.014  |
| 5  | 335  | 100 | 4.605 | 81.490 | 4.400 | 0.021 | 11.984 | 2.484 | 0.012 | 14.651 | 2.684  | 0.013  |
| 6  | 402  | 100 | 4.605 | 83.130 | 4.420 | 0.021 | 14.348 | 2.664 | 0.013 | 10.937 | 2.392  | 0.012  |
| 7  | 469  | 100 | 4.605 | 82.326 | 4.411 | 0.021 | 16.456 | 2.801 | 0.014 | 9.618  | 2.264  | 0.011  |
| 8  | 536  | 100 | 4.605 | 82.903 | 4.418 | 0.021 | 18.707 | 2.929 | 0.014 | 7.282  | 1.985  | 0.010  |
| 9  | 603  | 100 | 4.605 | 81.946 | 4.406 | 0.021 | 21.021 | 3.046 | 0.015 | 5.172  | 1.643  | 0.008  |
| 10 | 670  | 100 | 4.605 | 82.023 | 4.407 | 0.021 | 24.333 | 3.192 | 0.015 | 3.398  | 1.223  | 0.006  |
| 11 | 737  | 100 | 4.605 | 80.311 | 4.386 | 0.021 | 24.711 | 3.207 | 0.015 | 3.812  | 1.338  | 0.006  |
| 12 | 804  | 100 | 4.605 | 80.188 | 4.384 | 0.021 | 28.091 | 3.335 | 0.016 | 1.826  | 0.602  | 0.003  |
| 13 | 871  | 100 | 4.605 | 79.301 | 4.373 | 0.021 | 30.334 | 3.412 | 0.016 | 3.511  | 1.256  | 0.006  |
| 14 | 938  | 100 | 4.605 | 77.435 | 4.349 | 0.021 | 29.905 | 3.398 | 0.016 | 1.076  | 0.073  | 0.000  |
| 15 | 1005 | 100 | 4.605 | 77.342 | 4.348 | 0.021 | 34.710 | 3.547 | 0.017 | 2.546  | 0.934  | 0.005  |
| 16 | 1072 | 100 | 4.605 | 75.589 | 4.325 | 0.021 | 35.030 | 3.556 | 0.017 | 1.420  | 0.351  | 0.002  |
| 17 | 1139 | 100 | 4.605 | 74.076 | 4.305 | 0.021 | 36.606 | 3.600 | 0.017 | 1.786  | 0.580  | 0.003  |
| 18 | 1206 | 100 | 4.605 | 71.075 | 4.264 | 0.021 | 37.961 | 3.637 | 0.018 | 0.687  | -0.376 | -0.002 |

<sup>20</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~-10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |     |       |        |       |       |        |       |       |        |        |        |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|--------|--------|--------|
| 19 | 1273 | 100 | 4.605 | 69.508 | 4.241 | 0.020 | 39.893 | 3.686 | 0.018 | -0.112 | #NUM!  | #NUM!  |
| 20 | 1340 | 100 | 4.605 | 69.445 | 4.241 | 0.020 | 42.481 | 3.749 | 0.018 | -0.237 | #NUM!  | #NUM!  |
| 21 | 1407 | 100 | 4.605 | 69.204 | 4.237 | 0.020 | 43.369 | 3.770 | 0.018 | 0.254  | -1.369 | -0.007 |
| 22 | 1474 | 100 | 4.605 | 67.182 | 4.207 | 0.020 | 44.673 | 3.799 | 0.018 | 1.381  | 0.323  | 0.002  |
| 23 | 1541 | 100 | 4.605 | 64.410 | 4.165 | 0.020 | 44.729 | 3.801 | 0.018 | 1.349  | 0.299  | 0.001  |
| 24 | 1608 | 100 | 4.605 | 65.867 | 4.188 | 0.020 | 45.978 | 3.828 | 0.018 | 1.223  | 0.201  | 0.001  |
| 25 | 1675 | 100 | 4.605 | 62.091 | 4.129 | 0.020 | 47.636 | 3.864 | 0.019 | 0.991  | -0.009 | 0.000  |
| 26 | 1742 | 100 | 4.605 | 63.078 | 4.144 | 0.020 | 49.391 | 3.900 | 0.019 | -0.151 | #NUM!  | #NUM!  |
| 27 | 1809 | 100 | 4.605 | 60.965 | 4.110 | 0.020 | 50.125 | 3.915 | 0.019 | 0.323  | -1.130 | -0.005 |
| 28 | 1876 | 100 | 4.605 | 58.948 | 4.077 | 0.020 | 50.837 | 3.929 | 0.019 | 1.253  | 0.226  | 0.001  |
| 29 | 1943 | 100 | 4.605 | 58.759 | 4.073 | 0.020 | 53.582 | 3.981 | 0.019 | -0.427 | #NUM!  | #NUM!  |
| 30 | 2010 | 100 | 4.605 | 57.029 | 4.044 | 0.020 | 54.118 | 3.991 | 0.019 | 0.206  | -1.580 | -0.008 |
| 31 | 2077 | 100 | 4.605 | 55.012 | 4.008 | 0.019 | 55.387 | 4.014 | 0.019 | 1.442  | 0.366  | 0.002  |
| 32 | 2144 | 100 | 4.605 | 54.692 | 4.002 | 0.019 | 57.328 | 4.049 | 0.020 | 1.087  | 0.083  | 0.000  |
| 33 | 2211 | 100 | 4.605 | 51.902 | 3.949 | 0.019 | 58.054 | 4.061 | 0.020 | -0.641 | #NUM!  | #NUM!  |
| 34 | 2278 | 100 | 4.605 | 55.374 | 4.014 | 0.019 | 59.920 | 4.093 | 0.020 | -0.307 | #NUM!  | #NUM!  |
| 35 | 2345 | 100 | 4.605 | 52.624 | 3.963 | 0.019 | 61.616 | 4.121 | 0.020 | 0.358  | -1.028 | -0.005 |
| 36 | 2412 | 100 | 4.605 | 52.915 | 3.969 | 0.019 | 62.423 | 4.134 | 0.020 | -0.447 | #NUM!  | #NUM!  |
| 37 | 2479 | 100 | 4.605 | 49.436 | 3.901 | 0.019 | 61.904 | 4.126 | 0.020 | -0.661 | #NUM!  | #NUM!  |
| 38 | 2546 | 100 | 4.605 | 48.536 | 3.882 | 0.019 | 62.405 | 4.134 | 0.020 | 1.361  | 0.308  | 0.001  |
| 39 | 2613 | 100 | 4.605 | 48.828 | 3.888 | 0.019 | 63.665 | 4.154 | 0.020 | 1.028  | 0.028  | 0.000  |
| 40 | 2680 | 100 | 4.605 | 46.560 | 3.841 | 0.019 | 65.462 | 4.181 | 0.020 | -0.263 | #NUM!  | #NUM!  |
| 41 | 2747 | 100 | 4.605 | 45.943 | 3.827 | 0.018 | 66.745 | 4.201 | 0.020 | 0.265  | -1.327 | -0.006 |
| 42 | 2814 | 100 | 4.605 | 45.991 | 3.828 | 0.018 | 66.357 | 4.195 | 0.020 | 0.066  | -2.713 | -0.013 |
| 43 | 2881 | 100 | 4.605 | 44.608 | 3.798 | 0.018 | 68.173 | 4.222 | 0.020 | 0.170  | -1.773 | -0.009 |
| 44 | 2948 | 100 | 4.605 | 43.607 | 3.775 | 0.018 | 69.003 | 4.234 | 0.020 | 0.637  | -0.451 | -0.002 |
| 45 | 3015 | 100 | 4.605 | 42.107 | 3.740 | 0.018 | 69.843 | 4.246 | 0.020 | -0.037 | #NUM!  | #NUM!  |
| 46 | 3082 | 100 | 4.605 | 41.680 | 3.730 | 0.018 | 69.825 | 4.246 | 0.020 | 0.757  | -0.278 | -0.001 |
| 47 | 3149 | 100 | 4.605 | 40.867 | 3.710 | 0.018 | 71.297 | 4.267 | 0.021 | -0.268 | #NUM!  | #NUM!  |
| 48 | 3216 | 100 | 4.605 | 40.070 | 3.691 | 0.018 | 72.856 | 4.288 | 0.021 | 0.019  | -3.988 | -0.019 |
| 49 | 3283 | 100 | 4.605 | 39.929 | 3.687 | 0.018 | 73.162 | 4.293 | 0.021 | 0.683  | -0.381 | -0.002 |
| 50 | 3350 | 100 | 4.605 | 38.019 | 3.638 | 0.018 | 74.081 | 4.305 | 0.021 | -0.494 | #NUM!  | #NUM!  |
| 51 | 3417 | 100 | 4.605 | 37.315 | 3.619 | 0.017 | 73.710 | 4.300 | 0.021 | 0.783  | -0.244 | -0.001 |
| 52 | 3484 | 100 | 4.605 | 37.603 | 3.627 | 0.018 | 75.113 | 4.319 | 0.021 | 0.087  | -2.441 | -0.012 |
| 53 | 3551 | 100 | 4.605 | 36.151 | 3.588 | 0.017 | 75.374 | 4.322 | 0.021 | 0.130  | -2.041 | -0.010 |
| 54 | 3618 | 100 | 4.605 | 36.777 | 3.605 | 0.017 | 76.948 | 4.343 | 0.021 | -0.181 | #NUM!  | #NUM!  |
| 55 | 3685 | 100 | 4.605 | 35.589 | 3.572 | 0.017 | 79.608 | 4.377 | 0.021 | 0.991  | -0.009 | 0.000  |
| 56 | 3752 | 100 | 4.605 | 33.195 | 3.502 | 0.017 | 78.629 | 4.365 | 0.021 | 0.547  | -0.603 | -0.003 |
| 57 | 3819 | 100 | 4.605 | 32.831 | 3.491 | 0.017 | 79.021 | 4.370 | 0.021 | -0.784 | #NUM!  | #NUM!  |

|    |      |     |       |        |       |       |        |       |       |        |        |        |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|--------|--------|--------|
| 58 | 3886 | 100 | 4.605 | 32.711 | 3.488 | 0.017 | 81.049 | 4.395 | 0.021 | 0.198  | -1.618 | -0.008 |
| 59 | 3953 | 100 | 4.605 | 32.651 | 3.486 | 0.017 | 79.700 | 4.378 | 0.021 | -0.040 | #NUM!  | #NUM!  |
| 60 | 4020 | 100 | 4.605 | 31.368 | 3.446 | 0.017 | 81.799 | 4.404 | 0.021 | 0.084  | -2.474 | -0.012 |
| 61 | 4087 | 100 | 4.605 | 32.264 | 3.474 | 0.017 | 81.282 | 4.398 | 0.021 | -0.649 | #NUM!  | #NUM!  |
| 62 | 4154 | 100 | 4.605 | 31.082 | 3.437 | 0.017 | 84.206 | 4.433 | 0.021 | -0.494 | #NUM!  | #NUM!  |
| 63 | 4221 | 100 | 4.605 | 30.270 | 3.410 | 0.016 | 82.984 | 4.419 | 0.021 | -0.112 | #NUM!  | #NUM!  |
| 64 | 4288 | 100 | 4.605 | 29.226 | 3.375 | 0.016 | 85.350 | 4.447 | 0.021 | -1.077 | #NUM!  | #NUM!  |
| 65 | 4355 | 100 | 4.605 | 28.162 | 3.338 | 0.016 | 83.504 | 4.425 | 0.021 | 1.089  | 0.085  | 0.000  |

Table: Raw Data For [4-Me] Cl Oxidative Addition 3<sup>21</sup>

| A | B   | C   | D     | E      | F     | G     | H      | I     | J     | K      | L     | M     |
|---|-----|-----|-------|--------|-------|-------|--------|-------|-------|--------|-------|-------|
| 1 | 67  | 100 | 4.605 | 68.403 | 4.225 | 0.020 | 1.584  | 0.460 | 0.002 | 39.235 | 3.670 | 0.018 |
| 2 | 134 | 100 | 4.605 | 71.938 | 4.276 | 0.021 | 3.764  | 1.326 | 0.006 | 30.832 | 3.429 | 0.017 |
| 3 | 201 | 100 | 4.605 | 77.494 | 4.350 | 0.021 | 5.604  | 1.723 | 0.008 | 23.979 | 3.177 | 0.015 |
| 4 | 268 | 100 | 4.605 | 80.986 | 4.394 | 0.021 | 8.256  | 2.111 | 0.010 | 18.751 | 2.931 | 0.014 |
| 5 | 335 | 100 | 4.605 | 81.490 | 4.400 | 0.021 | 11.984 | 2.484 | 0.012 | 14.651 | 2.684 | 0.013 |
| 6 | 402 | 100 | 4.605 | 83.130 | 4.420 | 0.021 | 14.348 | 2.664 | 0.013 | 10.937 | 2.392 | 0.012 |
| 7 | 469 | 100 | 4.605 | 82.326 | 4.411 | 0.021 | 16.456 | 2.801 | 0.014 | 9.618  | 2.264 | 0.011 |
| 8 | 536 | 100 | 4.605 | 82.903 | 4.418 | 0.021 | 18.707 | 2.929 | 0.014 | 7.282  | 1.985 | 0.010 |

<sup>21</sup> **A:** ExpNo, **B:** Time (s), **C:** Peak 1 (24 ppm), **D:** ln(Peak 1), **E:** Peak 2 (~3.0 ppm), **F:** ln(Peak 2), **G:** Peak 2 (M), **H:** Peak 3 (~9.2 ppm), **I:** ln(Peak 3), **J:** Peak 3 (M), **K:** Peak 4 (~-10.3 ppm), **L:** ln(Peak 4), **M:** Peak 4 (M).

|    |      |     |       |        |       |       |        |       |       |        |        |        |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|--------|--------|--------|
| 9  | 603  | 100 | 4.605 | 81.946 | 4.406 | 0.021 | 21.021 | 3.046 | 0.015 | 5.172  | 1.643  | 0.008  |
| 10 | 670  | 100 | 4.605 | 82.023 | 4.407 | 0.021 | 24.333 | 3.192 | 0.015 | 3.398  | 1.223  | 0.006  |
| 11 | 737  | 100 | 4.605 | 80.311 | 4.386 | 0.021 | 24.711 | 3.207 | 0.015 | 3.812  | 1.338  | 0.006  |
| 12 | 804  | 100 | 4.605 | 80.188 | 4.384 | 0.021 | 28.091 | 3.335 | 0.016 | 1.826  | 0.602  | 0.003  |
| 13 | 871  | 100 | 4.605 | 79.301 | 4.373 | 0.021 | 30.334 | 3.412 | 0.016 | 3.511  | 1.256  | 0.006  |
| 14 | 938  | 100 | 4.605 | 77.435 | 4.349 | 0.021 | 29.905 | 3.398 | 0.016 | 1.076  | 0.073  | 0.000  |
| 15 | 1005 | 100 | 4.605 | 77.342 | 4.348 | 0.021 | 34.710 | 3.547 | 0.017 | 2.546  | 0.934  | 0.005  |
| 16 | 1072 | 100 | 4.605 | 75.589 | 4.325 | 0.021 | 35.030 | 3.556 | 0.017 | 1.420  | 0.351  | 0.002  |
| 17 | 1139 | 100 | 4.605 | 74.076 | 4.305 | 0.021 | 36.606 | 3.600 | 0.017 | 1.786  | 0.580  | 0.003  |
| 18 | 1206 | 100 | 4.605 | 71.075 | 4.264 | 0.021 | 37.961 | 3.637 | 0.018 | 0.687  | -0.376 | -0.002 |
| 19 | 1273 | 100 | 4.605 | 69.508 | 4.241 | 0.020 | 39.893 | 3.686 | 0.018 | -0.112 | #NUM!  | #NUM!  |
| 20 | 1340 | 100 | 4.605 | 69.445 | 4.241 | 0.020 | 42.481 | 3.749 | 0.018 | -0.237 | #NUM!  | #NUM!  |
| 21 | 1407 | 100 | 4.605 | 69.204 | 4.237 | 0.020 | 43.369 | 3.770 | 0.018 | 0.254  | -1.369 | -0.007 |
| 22 | 1474 | 100 | 4.605 | 67.182 | 4.207 | 0.020 | 44.673 | 3.799 | 0.018 | 1.381  | 0.323  | 0.002  |
| 23 | 1541 | 100 | 4.605 | 64.410 | 4.165 | 0.020 | 44.729 | 3.801 | 0.018 | 1.349  | 0.299  | 0.001  |
| 24 | 1608 | 100 | 4.605 | 65.867 | 4.188 | 0.020 | 45.978 | 3.828 | 0.018 | 1.223  | 0.201  | 0.001  |
| 25 | 1675 | 100 | 4.605 | 62.091 | 4.129 | 0.020 | 47.636 | 3.864 | 0.019 | 0.991  | -0.009 | 0.000  |
| 26 | 1742 | 100 | 4.605 | 63.078 | 4.144 | 0.020 | 49.391 | 3.900 | 0.019 | -0.151 | #NUM!  | #NUM!  |
| 27 | 1809 | 100 | 4.605 | 60.965 | 4.110 | 0.020 | 50.125 | 3.915 | 0.019 | 0.323  | -1.130 | -0.005 |
| 28 | 1876 | 100 | 4.605 | 58.948 | 4.077 | 0.020 | 50.837 | 3.929 | 0.019 | 1.253  | 0.226  | 0.001  |
| 29 | 1943 | 100 | 4.605 | 58.759 | 4.073 | 0.020 | 53.582 | 3.981 | 0.019 | -0.427 | #NUM!  | #NUM!  |
| 30 | 2010 | 100 | 4.605 | 57.029 | 4.044 | 0.020 | 54.118 | 3.991 | 0.019 | 0.206  | -1.580 | -0.008 |
| 31 | 2077 | 100 | 4.605 | 55.012 | 4.008 | 0.019 | 55.387 | 4.014 | 0.019 | 1.442  | 0.366  | 0.002  |
| 32 | 2144 | 100 | 4.605 | 54.692 | 4.002 | 0.019 | 57.328 | 4.049 | 0.020 | 1.087  | 0.083  | 0.000  |
| 33 | 2211 | 100 | 4.605 | 51.902 | 3.949 | 0.019 | 58.054 | 4.061 | 0.020 | -0.641 | #NUM!  | #NUM!  |
| 34 | 2278 | 100 | 4.605 | 55.374 | 4.014 | 0.019 | 59.920 | 4.093 | 0.020 | -0.307 | #NUM!  | #NUM!  |
| 35 | 2345 | 100 | 4.605 | 52.624 | 3.963 | 0.019 | 61.616 | 4.121 | 0.020 | 0.358  | -1.028 | -0.005 |
| 36 | 2412 | 100 | 4.605 | 52.915 | 3.969 | 0.019 | 62.423 | 4.134 | 0.020 | -0.447 | #NUM!  | #NUM!  |
| 37 | 2479 | 100 | 4.605 | 49.436 | 3.901 | 0.019 | 61.904 | 4.126 | 0.020 | -0.661 | #NUM!  | #NUM!  |
| 38 | 2546 | 100 | 4.605 | 48.536 | 3.882 | 0.019 | 62.405 | 4.134 | 0.020 | 1.361  | 0.308  | 0.001  |
| 39 | 2613 | 100 | 4.605 | 48.828 | 3.888 | 0.019 | 63.665 | 4.154 | 0.020 | 1.028  | 0.028  | 0.000  |
| 40 | 2680 | 100 | 4.605 | 46.560 | 3.841 | 0.019 | 65.462 | 4.181 | 0.020 | -0.263 | #NUM!  | #NUM!  |
| 41 | 2747 | 100 | 4.605 | 45.943 | 3.827 | 0.018 | 66.745 | 4.201 | 0.020 | 0.265  | -1.327 | -0.006 |
| 42 | 2814 | 100 | 4.605 | 45.991 | 3.828 | 0.018 | 66.357 | 4.195 | 0.020 | 0.066  | -2.713 | -0.013 |
| 43 | 2881 | 100 | 4.605 | 44.608 | 3.798 | 0.018 | 68.173 | 4.222 | 0.020 | 0.170  | -1.773 | -0.009 |
| 44 | 2948 | 100 | 4.605 | 43.607 | 3.775 | 0.018 | 69.003 | 4.234 | 0.020 | 0.637  | -0.451 | -0.002 |
| 45 | 3015 | 100 | 4.605 | 42.107 | 3.740 | 0.018 | 69.843 | 4.246 | 0.020 | -0.037 | #NUM!  | #NUM!  |
| 46 | 3082 | 100 | 4.605 | 41.680 | 3.730 | 0.018 | 69.825 | 4.246 | 0.020 | 0.757  | -0.278 | -0.001 |
| 47 | 3149 | 100 | 4.605 | 40.867 | 3.710 | 0.018 | 71.297 | 4.267 | 0.021 | -0.268 | #NUM!  | #NUM!  |

|    |      |     |       |        |       |       |        |       |       |        |        |        |
|----|------|-----|-------|--------|-------|-------|--------|-------|-------|--------|--------|--------|
| 48 | 3216 | 100 | 4.605 | 40.070 | 3.691 | 0.018 | 72.856 | 4.288 | 0.021 | 0.019  | -3.988 | -0.019 |
| 49 | 3283 | 100 | 4.605 | 39.929 | 3.687 | 0.018 | 73.162 | 4.293 | 0.021 | 0.683  | -0.381 | -0.002 |
| 50 | 3350 | 100 | 4.605 | 38.019 | 3.638 | 0.018 | 74.081 | 4.305 | 0.021 | -0.494 | #NUM!  | #NUM!  |
| 51 | 3417 | 100 | 4.605 | 37.315 | 3.619 | 0.017 | 73.710 | 4.300 | 0.021 | 0.783  | -0.244 | -0.001 |
| 52 | 3484 | 100 | 4.605 | 37.603 | 3.627 | 0.018 | 75.113 | 4.319 | 0.021 | 0.087  | -2.441 | -0.012 |
| 53 | 3551 | 100 | 4.605 | 36.151 | 3.588 | 0.017 | 75.374 | 4.322 | 0.021 | 0.130  | -2.041 | -0.010 |
| 54 | 3618 | 100 | 4.605 | 36.777 | 3.605 | 0.017 | 76.948 | 4.343 | 0.021 | -0.181 | #NUM!  | #NUM!  |
| 55 | 3685 | 100 | 4.605 | 35.589 | 3.572 | 0.017 | 79.608 | 4.377 | 0.021 | 0.991  | -0.009 | 0.000  |
| 56 | 3752 | 100 | 4.605 | 33.195 | 3.502 | 0.017 | 78.629 | 4.365 | 0.021 | 0.547  | -0.603 | -0.003 |
| 57 | 3819 | 100 | 4.605 | 32.831 | 3.491 | 0.017 | 79.021 | 4.370 | 0.021 | -0.784 | #NUM!  | #NUM!  |
| 58 | 3886 | 100 | 4.605 | 32.711 | 3.488 | 0.017 | 81.049 | 4.395 | 0.021 | 0.198  | -1.618 | -0.008 |
| 59 | 3953 | 100 | 4.605 | 32.651 | 3.486 | 0.017 | 79.700 | 4.378 | 0.021 | -0.040 | #NUM!  | #NUM!  |
| 60 | 4020 | 100 | 4.605 | 31.368 | 3.446 | 0.017 | 81.799 | 4.404 | 0.021 | 0.084  | -2.474 | -0.012 |
| 61 | 4087 | 100 | 4.605 | 32.264 | 3.474 | 0.017 | 81.282 | 4.398 | 0.021 | -0.649 | #NUM!  | #NUM!  |
| 62 | 4154 | 100 | 4.605 | 31.082 | 3.437 | 0.017 | 84.206 | 4.433 | 0.021 | -0.494 | #NUM!  | #NUM!  |
| 63 | 4221 | 100 | 4.605 | 30.270 | 3.410 | 0.016 | 82.984 | 4.419 | 0.021 | -0.112 | #NUM!  | #NUM!  |
| 64 | 4288 | 100 | 4.605 | 29.226 | 3.375 | 0.016 | 85.350 | 4.447 | 0.021 | -1.077 | #NUM!  | #NUM!  |
| 65 | 4355 | 100 | 4.605 | 28.162 | 3.338 | 0.016 | 83.504 | 4.425 | 0.021 | 1.089  | 0.085  | 0.000  |
| 66 | 4422 | 100 | 4.605 | 30.202 | 3.408 | 0.016 | 86.024 | 4.455 | 0.021 | 0.310  | -1.171 | -0.006 |
| 67 | 4489 | 100 | 4.605 | 28.868 | 3.363 | 0.016 | 85.638 | 4.450 | 0.021 | 0.960  | -0.041 | 0.000  |
| 68 | 4556 | 100 | 4.605 | 27.354 | 3.309 | 0.016 | 87.439 | 4.471 | 0.022 | -0.325 | #NUM!  | #NUM!  |
| 69 | 4623 | 100 | 4.605 | 26.386 | 3.273 | 0.016 | 85.719 | 4.451 | 0.021 | -0.462 | #NUM!  | #NUM!  |
| 70 | 4690 | 100 | 4.605 | 26.634 | 3.282 | 0.016 | 88.186 | 4.479 | 0.022 | -0.506 | #NUM!  | #NUM!  |