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Development of a [2]-Catenane Synthetic Method and a Student Beliefs Survey for a Hybrid Organometallics Course

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BY

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Abstract

In this study, the value-added of a new upper-level chemistry course, CHEM 372 - Organometallics, was defined using a Student Beliefs Survey that was answered by students in CHEM 372 and by faculty who teach upper-level chemistry courses at Coastal Carolina University. The laboratory portion of CHEM 372 focused on the synthesis of a [2]-catenane, which is a molecularly interlocked molecule (MIM). The intention was to give the CHEM 372 students a goal to work toward over the course of the semester instead of different, unrelated, experiments each week. Using this style of lab teaching, the students were introduced to graduate school-level research and real-world application of laboratory technique. From the survey, the course was found to be 85% valuable, based on the similar responses between the experts and students. This indicates that CHEM 372 is a value-added, studio-based (laboratory-based) course that should be kept in the Coastal Carolina University's Chemistry Department as an upper-level course option for chemistry students.

Introduction

Interest in involving undergraduate students in research has continued to grow over the years in response to initiatives from the National Science Foundation (NSF) [1a], the Council of Undergraduate Research (CUR) [1b], the National Conferences on Undergraduate Research (NCUR) [1c], and other organizations, as well as faculty desires to enhance the undergraduate experience and preparedness for future endeavors. In fact, the ACS Committee on Professional Training (CPT) Supplement states, "research can be the most rewarding aspect of an undergraduate degree" [2]. Although many institutions,

including our own (Coastal Carolina University), have promoted participation in undergraduate research, whether it be through summer internship/research or elective courses, few actually require a research experience of all chemistry majors. This limited, or less-structured, approach seldom provides the full benefits of an in-depth research experience to a large majority of students [3].

So, how can Coastal Carolina University's Chemistry Department engage its students, both to improve learning and to teach them real-world chemistry skills? Many important questions, such as this one, drive reform-minded instructional development in higher education [4]. One such resolution to this question is the design and implementation of a studio-based upper-level chemistry course. In designing this course, the primary goal is to create a value-added chemistry experience by enhancing students' scientific literacy and critical-thinking skills, appreciation and understanding of the scientific method, and ability to apply their chemical knowledge to assessing real-world problems [4].

Now the issue that faced the department was developing an upper-level chemistry course that fulfilled all of the benefits of a studio-based course. The main idea was to design an upper-level chemistry course that could expose chemistry students to research techniques that would be useful to them in their future. Some of these research techniques would include exposing students to scientific instruments, such as Proton Nuclear Magnetic Resonance (^{1}H NMR), basic synthetic techniques, literature searches, and molecular modeling. Molecular modeling, in particular, is becoming an increasingly important tool to stimulate, explain, and predict phenomena in chemistry [5]. The role modeling plays in the development of new materials was recently highlighted by the

Materials Genome Initiative for Global Competitiveness, which hypothesized that the synergy between computation, experiment, and digital data will drastically accelerate materials development from initial discovery to deployment [6]. In order to prepare the University's chemistry students for future careers where the integration of theory, computation, and experimentation, it is important for them to be exposed to molecular modeling in their undergraduate curriculum [5]. To this end, an upper-level undergraduate computational and experimental chemistry laboratory course was recently implemented this year (January, 2016).

Herein, a newly developed experimental course that deals with a class of molecules that undergraduate students are seldom exposed to, that of molecularly interlocked molecules (MIMs), is described. Much attention has been given to the synthesis of MIMs [5]. Interest in MIMs stems from their potential use as building blocks in artificial molecular machines. MIMs include catenanes, rotaxanes, and pretzelanes, to name a few. The newly developed experimental course described herein focuses on synthesizing a simple catenane, which is composed of two interlocked rings/macrocycles.

The students performed a step-wise synthesis of the first macrocycle, and a separate step-wise synthesis of the diyne linker, which threads through the first macrocycle to form the second macrocycle. Accompanying the synthesis of the [2]-catenane itself, a student beliefs survey was implemented to determine the "value-added" of this newly designed course (CHEM 372 – Organometallics).

Materials and Methods

Lecture.

The lecture portion of the upper-level chemistry course, Organometallics, comprised of equal parts literature search, presentation, up-keep of an electronic lab notebook, and molecular modeling assignments. There were two literature-based presentations, one with a 1) classical paper, and another with a 2) current paper. As a part of preparing for these two presentations, literature searches - using the Inter Library Loan System at Coastal Carolina University, or database finders such as ACS or SciFinder - were required.

The other presentation undertaken in the lecture portion of Organometallics was an instrument presentation. For this presentation, the students worked in pairs to create an educational video on the principles behind, and the operating procedures of, an assigned instrument, such as: ^{1}H NMR, infrared-spectroscopy (IR), crystal growing, and gas chromatography with mass spectrometry (GC-MS). The students were exposed to molecular modeling using two programs, 1) Marvin Sketch and 2) GaussView 5. The Marvin Sketch program was used, primarily for the 2D representation of lab protocol mechanisms, while the GaussView 5 was used to determine the lowest energy level of the structures, and for the 3D representation of the main structures of both the macrocycle and the diyne linker throughout the synthesizing process. The electronic laboratory notebook (ELN) that students were exposed to was the Docollabs system. All of the protocols were uploaded to the ELN and individual experiments were made for each trial of each protocol that was run during the class duration (January – May 2016).

Laboratory Protocols.

Protocol 1 (Synthesis of 2-(4-methoxyphenyl)-1,10-phenanthroline)[7]*:* A 62 mL portion (100 mmol) of a 1.6 M n-butyllithium solution in hexane was rapidly added to a degassed solution of p-bromoanisole (26.0 g, 110 mmol) in anhydrous diethyl ether (Et_2O) (150 mL) at room temperature. Then 210 mL (63 mmol) of the 0.3 M p-bromophenyl-lithium solution thus obtained was slowly added, by the means of a graduated addition funnel, to a degassed suspension of 1,10-phenanthroline monohydrate (4.95 g, 25 mmol) in 180 mL of anhydrous Et_2O kept at 0 °C. After the resulting dark red solution was stirred for 2 h 30 min under nitrogen at 2 °C, it was hydrolyzed with water at 0 °C. The bright yellow Et_2O layer was decanted and the aqueous layer extracted three times with 200 mL portions of dichloromethane (CH_2Cl_2). The combined organic layers were thereafter re-aromatized by successive additions of manganese dioxide (MnO_2) under effective magnetic stirring. This re-oxidation, easily followed by TLC and the disappearance of the yellow color, was ended after the addition of 73 g of MnO_2. After the mixture was dried over magnesium sulfate ($MgSO_4$), the black slurry could be easily filtered on a sintered glass and the filtrate evaporated to dryness. ^{1}H NMR (200 MHz, $CDCl_3$): 9.23 (dd, 1H, *H*9, *J*1) 4.4 Hz, *J*2) 1.8 Hz), 8.29 (d, 1H, *H*4, *J*)8.4Hz),8.25(dd,1H,*H*7,*J*1)8.4Hz,*J*2)1.8Hz),8.22(d,1H, *H*0-1, *J*) 8.2 Hz), 8.04 (d, 1H, *H*3, *J*) 8.4 Hz), 7.78 (AB, 2H, *H*5,6, *J*) 10.2 Hz), 7.66 (d, 2H, *H*m-1, *J*) 8.8 Hz) [8]. [Figure 1]

Protocol 1a (Synthesis of 2,9-Bis(p-methoxyphenyl)-1,10-phenanthroline): A 16 mL sample of an etheral solution of p-bromophenyllithium (prepared as above from 0.954mL, 7.6 mmol of p-bromoanisole, and 5mL, 7.6 mmol of n-Buli) was slowly added,

by means of a graduated addition funnel, to a degassed suspension of 2-(4-methoxyphenyl)-1,10-phenanthroline in 35 mL of anhydrous Et_2O maintained at 2°C. The resulting dark purple solution was stirred during three further hours at 3°C. After hydrolysis at 0°C, decantation, three extractions with CH_2Cl_2, and rearomatization with 5.0 g of MnO_2, a crude mixture was obtained as a pale yellow solid. ^{1}H NMR (200 MHz, $CDCl_3$): 8.33 (d, 4H, *H*o-1, *J*) 8.8 Hz), 8.33 (d, 2H, *H*4,7, *J*) 8.8 Hz), 8.12 (d, 2H, *H*3,8, *J*) 8.4 Hz), 7.81 (s, 2H, *H*5,6), 7.73 (d, 4H, *H*m-1, *J*) 8.8 Hz) [8].

Protocol 2 (Synthesis of 4,6-bis(trimethylsilyl)dibenzofuran)[9]: To a solution of dibenzofuran (5.05 g, 30 mmol) and tetramethylethylenediamine (TMEDA) (9.0 ml, 60 mmol) in dry ether (120 mL) and dry hexane (180 mL) was added *n*-BuLi (1.65 M hexane solution, 43.6 mL, 72 mmol) for 10 min, and the mixture was heated to 40°C for 3 h. The mixture was cooled to 0°C and Me_3SiCl (7.6 mL, 60 mmol) was added over 10 min, then the mixture was warmed to room temperature and stirred for 19.5 h followed by the addition of water. The organic layer was dried over $MgSO_4$, and concentrated. Purification of the residue by silica gel column chromatography using hexane as eluent afforded the title product (4.80 g, 51%) as a colorless crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96-7.93 (dd, J = 7.5, 1.2 Hz, 2H), 7.52-7.49 (dd, J = 7.2, 1.2 Hz, 2H), 7.33-7.26 (t, J = 7.5 Hz, 2H), 0.45 (s, 18H) [10]. [Figure 2]

Protocol 3 (Synthesis of 8-bromooctanol)[11]: To a mixture of 1,8-octanediol (30g 0.205 mol) and toluene (600ml) add a concentration of hydrobromic acid [27ml of a 48% (9 M) aqueous solution, 0.24 mol] . The heterogeneous mixture is stirred and heated at reflux (110°C for 36h. Chong (2000), found that after 36 h, substantial amounts of 1,8-octanediol still remained. Thus a further quantity of hydrobromic acid (10ml, 0.09 mol)

was added, and the mixture was heated at reflux for another 36 h. The mixture is then cooled to room temperature and the phases were separated. The organic layer is then diluted with ether and washed with 1 M sodium hydroxide brine and phosphate buffer (3 M, pH 7). Drying sodium sulfate and concentration of the organic layer gave a yellow oil which is distilled (Kugelrohr, bath temp 110-1200°C, 0.2 Torr. This provides 42g of 8-bromooctanol. ^{1}H NMR ($CDCl_3$): 3.6232 ppm (t, 2H) 3.3869 ppm (t, 2H) 1.8358 ppm (m, 2H) 1.55 ppm (m, 2H) 1.32 ppm (m, 8H) [12]. [Figure 3]

Protocol 4 (Synthesis of dibenzofuran-4,6-diboronic acid)[13]*:* Diboronic acid was prepared by the hydrolysis of 4,6-bis(dibromoboryl)dibenzofuran. To a solution of 4,6-bis(trimethylsilyl)dibenzofuran (0.156 g, 0.50 mmol) in dry CH_2Cl_2 (8.0 mL) was added BBr_3 (0.12 mL, 1.2 mmol), and stirred at room temperature for 14 h. Water was added to the solution, and white precipitate formed. The precipitate was collected by filtration, and washed with water and CH_2Cl_2. The product was dried under reduced pressure to afford the title product (0.120 g, 94%) as a white solid: Spectroscopic properties were in agreement with the literature. ^{1}H NMR (DMSO): 8.1990, 8.1697 ppm (d, 2H) 7.7858, 7.7650 ppm (d, 2H) 7.4052, 7.3557, 7.3517 ppm (t, 2H) 4.8377 ppm (bs, 4H) [10]. [Figure 4]

Protocol 5 (Synthesis of 4,6-dihydroxydibenzofuran): A mixture of dibenzofuran-4,6-diboronic acid, 35% hydrogen peroxide (0.20 mL, 7.0 mmol), 2% aqueous sodium hydroxide solution (6 mL) in dry THF (6.67 mL) was stirred at room temperature for 25 h. The solvent was removed under reduced pressure, and the residue was taken up in diethyl ether and acidified with 2M HCl aq. (2.67 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was

dried over Na_2SO_4 and evaporated to dryness to afford the title product as a gray solid. ^1H NMR (300MHz, DMSO-d6) δ 7.47-7.45 (d, J = 7.8 Hz, 2H), 7.17-7.11 (t, J = 7.8 Hz, 2H), 6.94-6.92 (d, J = 7.8 Hz, 2H) [10]. [Figure 5]

Protocol 7 (Synthesis of 2-[2-(trimethylsilylethynyl)]phenol): $Pd(PPh_3)_4$ (51 mg, 0.04 mmol), CuI (15 mg, 0.08 mmol) and Et_3N (0.417 mL, 3.0 mmol) were combined in THF (5.0 mL) under a N_2 atmosphere. Substituted 2-iodophenol (0.3 mL, 2.0 mmol) was added and the reaction mixture was cooled to 0°C. After stirring for 10 min, trimethylsilylacetylene (206 mg, 2.1 mmol) was added drop-wise over 30 min. The reaction mixture stirred at room temperature overnight and was filtered through celite to remove Pd and Cu catalysts. ^1H NMR (300 MHz, $CDCl_3$) δ 7.41-7.38 (dd, J = 7.5, 1.8 Hz, 1H), 7.26-7.02 (m, 1H), 6.88-6.79 (m, 2H), 4.02-3.98 (t, J = 6.0 Hz, 2H), 3.45-3.43 (t, J = 6.9 Hz, 2H), 1.99-1.65 (m, 12H), 0.23 (s, 9H) [10]. [Figure 6]

Quantifying Value. In order to establish a method to quantify the worth of the studio-based Organometallics course, a Student Beliefs Survey [Attachment 1] was partly designed based off the CLASS Survey [14] developed by Dr. Jack Barbera at the University of Colorado, Boulder. In the survey, students responded to each statement using a five-point Likert scale (strongly agree to strongly disagree). An individual's "Overall percent favorable" score was the percentage of responses for which the student agrees with the expert (faculty at Coastal Carolina that teach upper-level chemistry courses) response. The "Overall percent unfavorable" score was the percentage of responses for which the student disagrees with the expert response. A choice of neutral is grouped in neither category. The individual scores were averaged to determine the "Overall percent favorable/unfavorable" for all students whom participated [14]. The

rejection of a completed survey was determined by two factors: 1) The same answer was chosen for most (>80%) statements, and 2) Statement 10 was answered incorrectly (see Attachment 1).

An interview portion was also set up for both the students and faculty who would participate in the survey (Attachment 1). The interview questions for the students were used to show that the wording and meaning of the statements within the survey were clear and that their responses were consistent with their explanations. While the faculty interview questions were used as a means to gage consistent responses by experts, and as a means to better define the expert response.

Results

Protocols.

Protocol 1: Trial 1 of Protocol 1 was followed at half reaction quantities listed above in the Materials and Methods section. It was completed in three, 2 hr 50 min lab periods, and resulted in the formation of an orange oil. This oil, upon sitting for ~4 days, began to form pale-orange crystals (crude mass 1.0965g). Trial 2 and 5, followed this trend as well. However, Trial 4 resulted in a dark orange oil, which remained an oil through the entire length of the 2016 semester, beginning in January. Trial 2 resulted in 1.3957g of pale-yellow solid. Trial 3 was thrown out, due to formation of a product that completely evaporated off, and Trial 4 yielded no solid.

Protocol 1a: Trial 1 of Protocol 1a used the crystallized product (1.0965g) of Protocol 1 Trial 1 as the reagent. This reaction was done at half scale. The resulting product, upon rotovaping, was a pale yellow oil, which after ~1 week of sitting, formed crystals of the

same color. The ^{1}H NMR spectrum for Protocol 1a was not obtained during the study duration.

Protocol 2: Trial 1 of Protocol 2 was followed at quarter-scale reaction quantities, as listed above in the Materials and Methods section. It was completed in two, 2 hr 50 min lab periods, and resulted in the formation of pale yellow crystals (crude mass 0.8095g). Trial 4 and the full-scale reaction (Trial 5) followed this trend, and formed pale yellow crystals as well. Trial 4 yielded 0.2803g of pale-yellow crystals, and Trial 5 yielded 5.3302g of yellow crystals. However, Trials 2-3 resulted in an orange oil, which had not formed crystals during the entire duration of the 2016-Spring semester, beginning in January.

Protocol 3: Trial 1 of Protocol 3 was followed at half-scale reaction quantities, as listed above in the Materials and Methods section. It was completed in ~ two 2 hr 50min lab periods, and resulted in the formation of a clear oil, which was the desired product of the reaction. Trial 2 of Protocol 3, carried out at the same scale as Trial 1, resulted in 3.1770g of fine, white crystals. Trial 3 of Protocol 3 was run at full-scale reaction quantities, and resulted in a clear oil.

Protocol 4: Trial 2 of Protocol 4 was followed at quarter-scale reaction quantities, as listed above in the Materials and Methods section. It was completed in ~two 2 hr 50 min lab periods, and resulted in a fine powder (crude mass 0.081g). Trial 3 of Protocol 4 was carried out at the same scale as Trial 2, and resulted in the formation of 0.0257g of crude solid. Trial 1 of Protocol 4 resulted in an oil, which did not crystallize at any point during the study period length.

Protocol 5: Trial 1 (only Trial done) of Protocol 5 was run at third-reaction quantities, as seen above in the Materials and Methods section. It was completed in ~two 2 hr 50 min lab periods, and resulted in a brown film around the flask (a mass could not be obtained).

Protocol 7: Trial 1 (only Trial done) of Protocol 7 was done at full-scale reaction quantities, as noted above in the Materials and Methods section. It was completed in ~two 2 hr 50 min lab periods, and resulted in a dark brown oil.

Quantifying Value. The students answered 76.9% of the questions positively with a minimum of a 60% positive response rate for those questions (Questions 2, 3, 5 – 9, and 11 – 14). The experts answered 76.9% of the questions positively with a minimum of a 67% positive response rate for the same 11 questions as the students. Of the 13 questions answered by the students and experts, 11 (Questions 2, 3, 5 – 9, and 11 – 14) of those questions had identical responses between the experts and students (85% similar). Question #10 is excluded from these statistics because it was the throwaway question.

Discussion

The first class of students to complete the new upper-level chemistry course (CHEM 372 - Organometallics) did so in May 2016. Overall, student opinions of CHEM 372 have been positive, as evidenced by exit-interviews and the Student Beliefs Survey. The main negative comment from the students has been regarding the technical malfunctions of the e-notebook, Docollabs, which was used alongside a hardcopy lab notebook. However, the students have given overwhelmingly positive feedback about their laboratory experiences, particularly regarding the introduction to new lab technique and instrumentation.

Based on the results of the Student Beliefs Survey, 85% of the student and expert responses match up (Questions 2, 3, 5 – 9, and 11 – 14). In the expert responses, there were 8 questions out of the 13 (excluding #10) that were answered 100% positively, which includes "strongly agree" and "agree" answer choices. These questions were numbers 2, 3, 5, 6, 9, and 11 – 14. Whereas, the students answered 6 of the 13 questions 100% positively, including "strongly agree" and "agree" answer choices. Those questions were numbers 2, 3, 6, and 11 – 13. The other two questions answered positively by experts were numbers 5 and 11. They had positive response rates of >60%, which is why they were included in the 11 questions compared between experts and students. The other questions answered positively by students were numbers 5, 7 – 9, and 14. They had positive responses by >60% of the students, which is why they were included in the 11 questions compared between the students and experts.

It can be concluded that there was an overall agreement between faculty and students with respect to individual questions concerning the course, with the exception of two questions where the responses differed (Questions 1 and 4). In these questions, experts had a tendency to disagree with the statement, while the majority of the student either agreed with the statement (Question 1) or give split responses between agreeing and disagreeing with the statement (Question 4). A possible explanation for the discrepancy could be that these two questions are a matter of opinion (see Attachment 1), where an expert opinion may differ enough from a student opinion to result in a discrepancy. These results indicate that the new studio-based course (CHEM 372) can be classified as a value-added upper-level chemistry course at Coastal Carolina University, and should continue to be taught.

In the laboratory, all seven protocols (Protocols 1-5, 7, and 1a) ran during the semester were completed. The ^{1}H NMR results of Trials 1 and 2 (Figures 7, and 8) demonstrate that the desired product of Protocol 1, 2-(4-methoxyphenyl)-1,10-phenanthroline, was obtained. While the ^{1}H NMR spectra generated from the oil product synthesized during Trials 4 and 5 (Figures 9 and 10) demonstrated that the desired product was not obtained. For Protocol 2, the ^{1}H NMR results of Trials 1 and 5 (Figures 11 and 12) demonstrate that the desired product, 4,6-bis(trimethylsilyl)dibenzofuran, was obtained. Whereas, the ^{1}H NMR results of Trials 2 and 3 (Figures 13 and 14) demonstrate that the product was not obtained and that solvent was still present in the oil. The ^{1}H NMR spectrum was not obtained for Trial 4, during the given data collection time. For Protocol 3, the ^{1}H NMR results of Trial 1 (Figure 15) demonstrate that the desired product, 8-bromooctanol, was obtained. Whereas, the ^{1}H NMR results of Trial 2 (Figure16) demonstrate that some initial reactants may have still been present in the mixture. For Protocol 4 trials, ^{1}H NMR spectra for Trial 1 was generated (Figure 17), and demonstrates that the desired product (dibenzofuran-4,6-diboronic acid) had been obtained. The ^{1}H NMR results of the remaining trials were not obtained during the study time. For the sole trial ran of Protocol 5, the ^{1}H NMR (Figure 18), thus obtained, demonstrates that the desired product, 4,6-dihydroxydibenzofuran, was obtained, despite the low product yield.

Therefore, assessments on the (un)successful formation of product could not be determined. Out of the protocols ran in the laboratory during the study period, a number of trials within Protocols 1, 2, 3, and 5 had confirmed successes. For Protocol 1, Trials 1 and 2 had product formation successes, which were confirmed by their ^{1}H NMR spectra.

Of the trials done for Protocol 2, Trials 1 and 5 had confirmed product formation successes by the same means as Trial 1 and 2 of Protocol 1. Trial1 of Protocol 3 was also a confirmed success based on its ^{1}H NMR spectra. The last confirmed success of the research period was the only Trial ran of Protocol 5.

However, where there were successes, there were also failures. Protocol 1 had two confirmed failures, Trial 4 and 5. These failures were confirmed by their ^{1}H NMR spectra. Protocol 2 also had product formation failures in Trials 2 and 3. The last confirmed failure of the study period was Trial 2 of Protocol 3. Protocol 7 and Protocol 1a had products form, however, neither of them had ^{1}H NMR spectra obtained for these products.

Despite the failures and success, the laboratory portion was meant to introduce chemistry students to new lab instrumentation and technique. It was also meant as an introduction to graduate school and what careers in the chemistry field would be like. The laboratory portion of the CHEM 372 course was set up so the students had an end goal (the [2]-catenane) to work towards instead of various lab assignments each week that did not relate to one another. Students were to be exposed to experiment successes and failures as a means of exposing them to the realities of chemical research, so they were not having these experiences for the first time in their careers or graduate programs.

In the future, the students taking CHEM 372 will continue to move towards an end goal, whether it be the synthesis of the [2]-catenane or, once the catenane has been synthesized, the addition of functional groups onto the catenane itself. Future classes will continue where the Spring 2016 students left off, i.e. Protocol 6 and 8, until the [2]-catenane is synthesized, and then they will continue in the aforementioned fashion.

Citations

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[1b] Council on Undergraduate Research. http://www.cur.org/ (accessed Jan 2016).

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[3] Dillner, D. K.; Ferrante, R. F.; Fitzgerald, J. P.; Schroeder, M. J. *J. Chem. Educ.* **2011**, 88, 1623 – 1629.

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[7] Trials 1-4 out of 5 were run at half scale to what is shown. This protocol is shown with full-scale reaction quantities.

[8] Sauvage, J.P.; et al. *J. Am. Chem. Soc.* **2003**, 125, 5717 – 5725.

[9] Trials 1-4 out of 5 were run at quarter scale to what is shown.

[10] Saito, S.; et al. *Angew. Chem. Int. Ed.* **2009**, 48, 504 – SI.

[11] Trials 1 and 2 were run at half-scale, and Trial 3 was run at full scale-quantities as shown in the protocol description.

[12] Chong, J.M.; et al. *J. Org. Chem.* **2000**, 65, 5837 – 5838.

[13] Three trials of this protocol were run, all of which were done at quarter-scale reaction quantities.

[14] Barbera, J., Adams, W.K., Wieman, C.E., Perkins, K.K. *J. Chem. Educ.* **2008**, 85, 1435 – 1439.

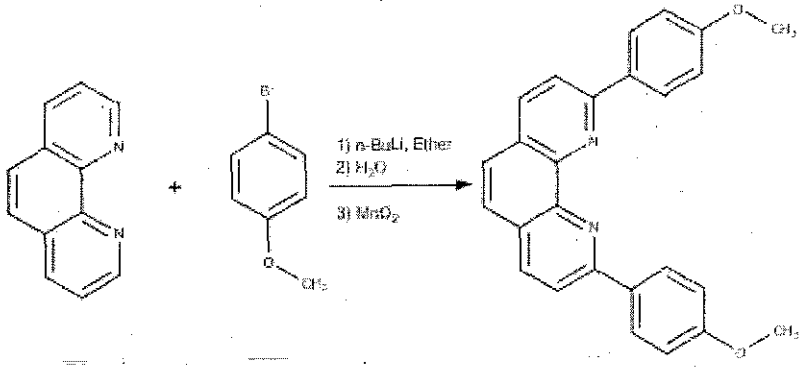

Figure 1. This represents the synthetic route of Protocol 1: conversion of 1,10-phenanthroline to 2-(4-methoxyphenyl)-1,10-phenanthroline. It also represents the synthetic route of Protocol 1a: conversion of 2,9-bis(4-methoxyphenyl)-1,10-phenanthroline.

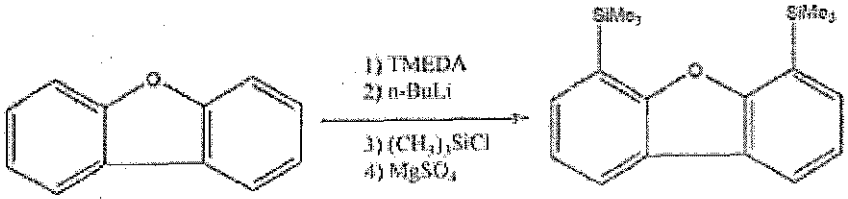

Figure 2. This figure represents the synthetic route of Protocol 2: conversion of dibenzofuran to 4,6-bis(trimethylsilyl)dibenzofuran.

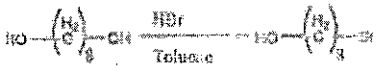

Figure 3. This figure represents the synthetic route for Protocol 3: conversion of 1,8-octanediol to 8-bromooctanol.

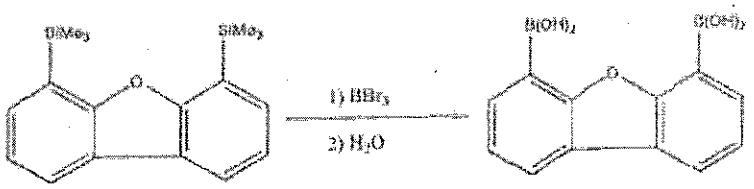

Figure 4. This figure demonstrates the synthetic route taken by Protocol 4: conversion of 4,6-bis(trimethylsilyl)dibenzofuran to dibenzofuran-4,6-diboronic acid.

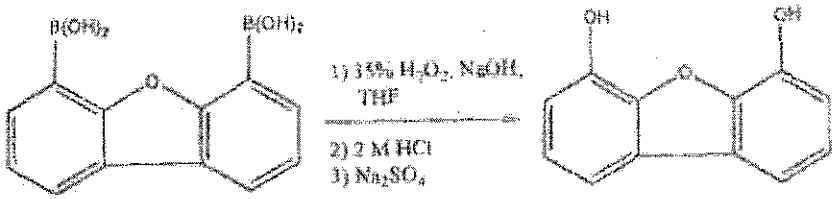

Figure 5. This figure demonstrates the synthetic pathway taken in Protocol 5: conversion of dibenzofuran-4,6-diboronic acid to 4,6-dihydroxydibenzofuran.

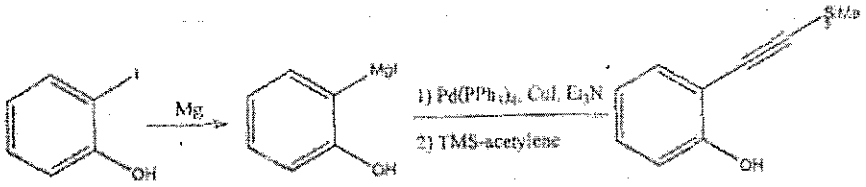

Figure 6. This figure demonstrates the synthetic pathway taken in Protocol 7: conversion from 2-iodophenol and magnesium to 2-[2-(trimethylsilylethynyl)]phenol.

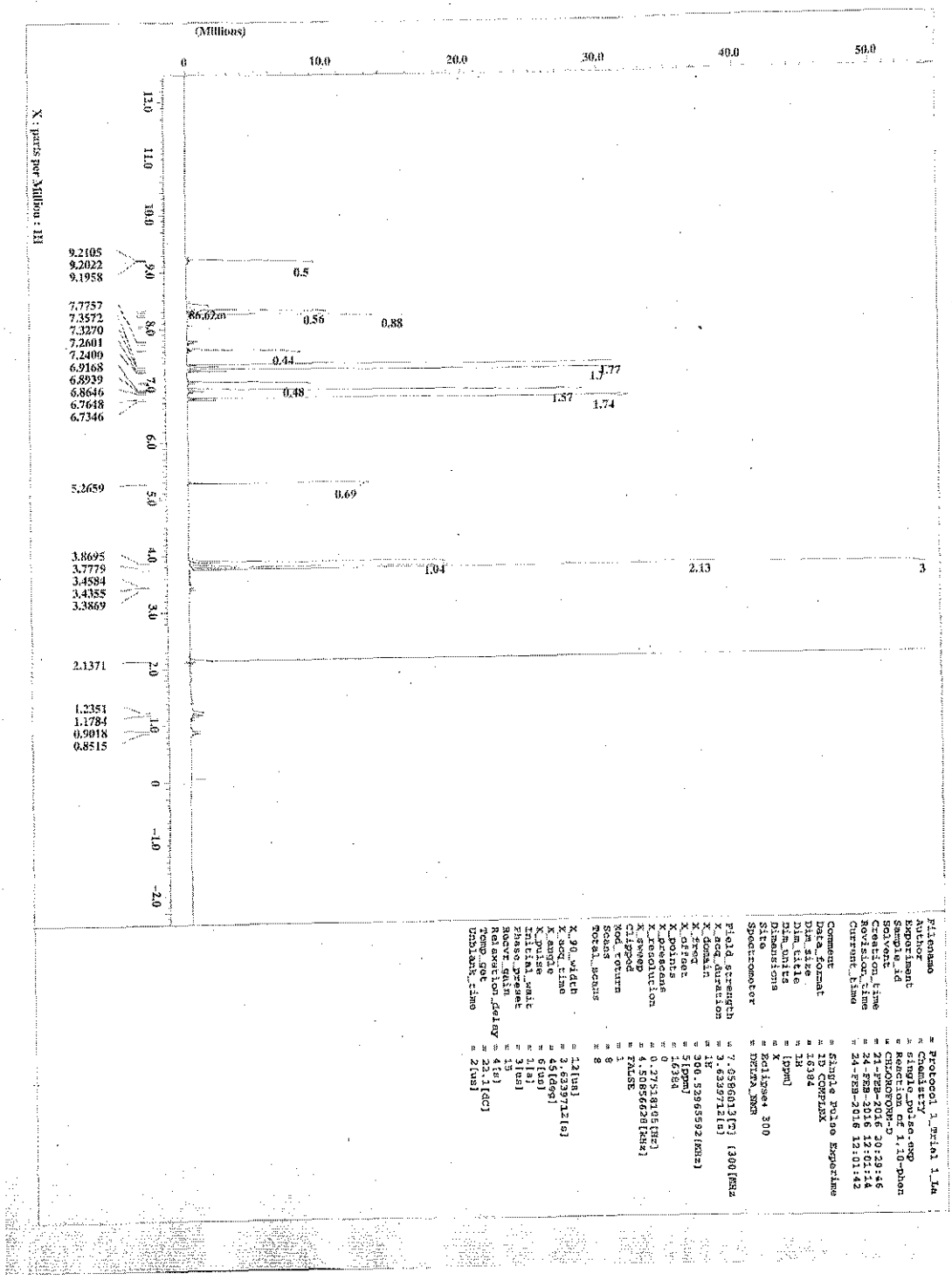

Figure 7. This figure is the ^{1}H NMR spectrum of the isolated, pure, product from Trial 1 of Protocol 1. See Protocol #1 in Materials and Methods section for proper peak assignments.

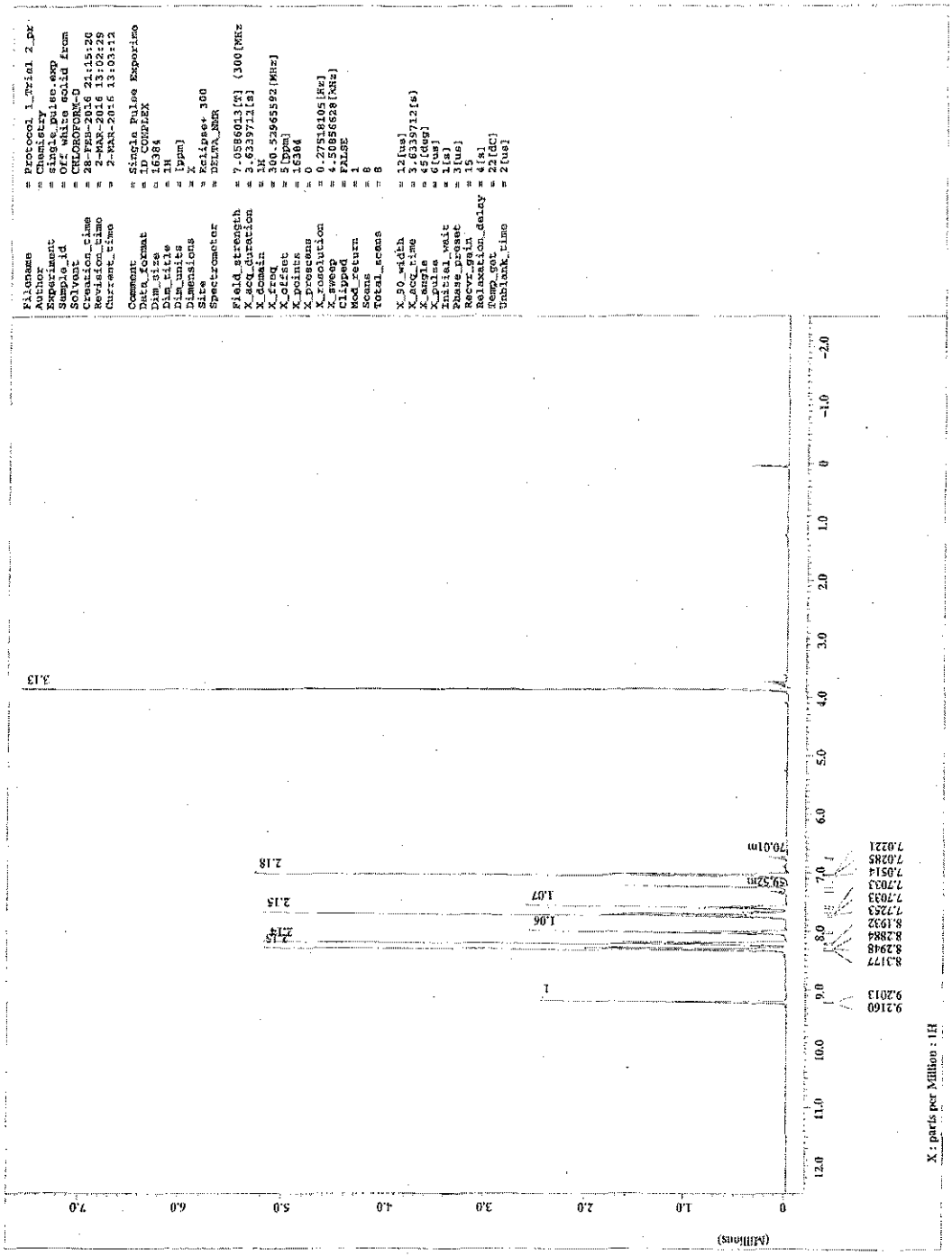

Figure 8. This figure is the ^{1}H NMR spectrum of the isolated, pure, product from Trial 2 of Protocol 1. See Protocol #1 in Materials and Methods section for proper peak assignments.

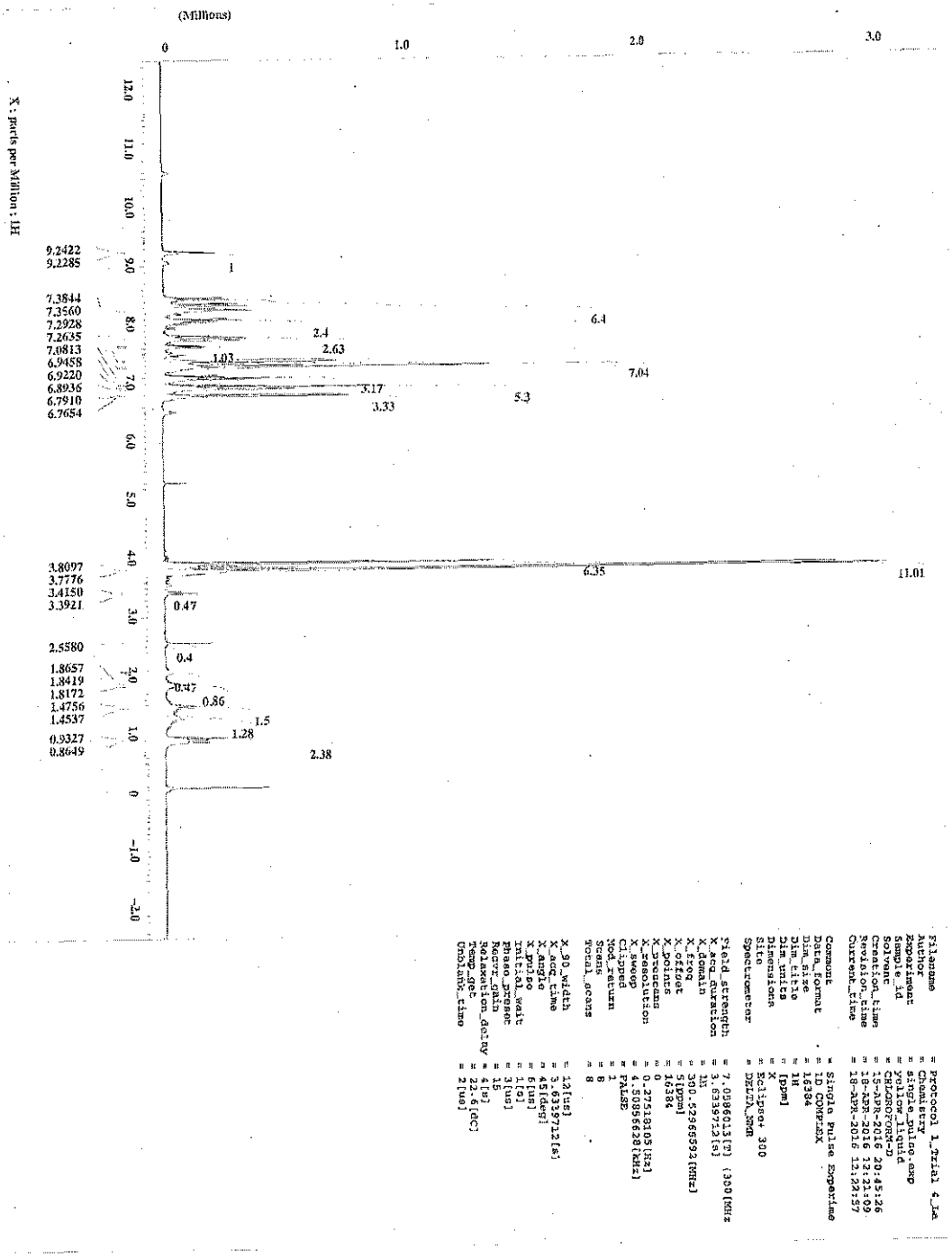

Figure 9. This figure demonstrates the ^{1}H NMR spectrum of the isolated, impure, product from Trial 4 of Protocol 1.

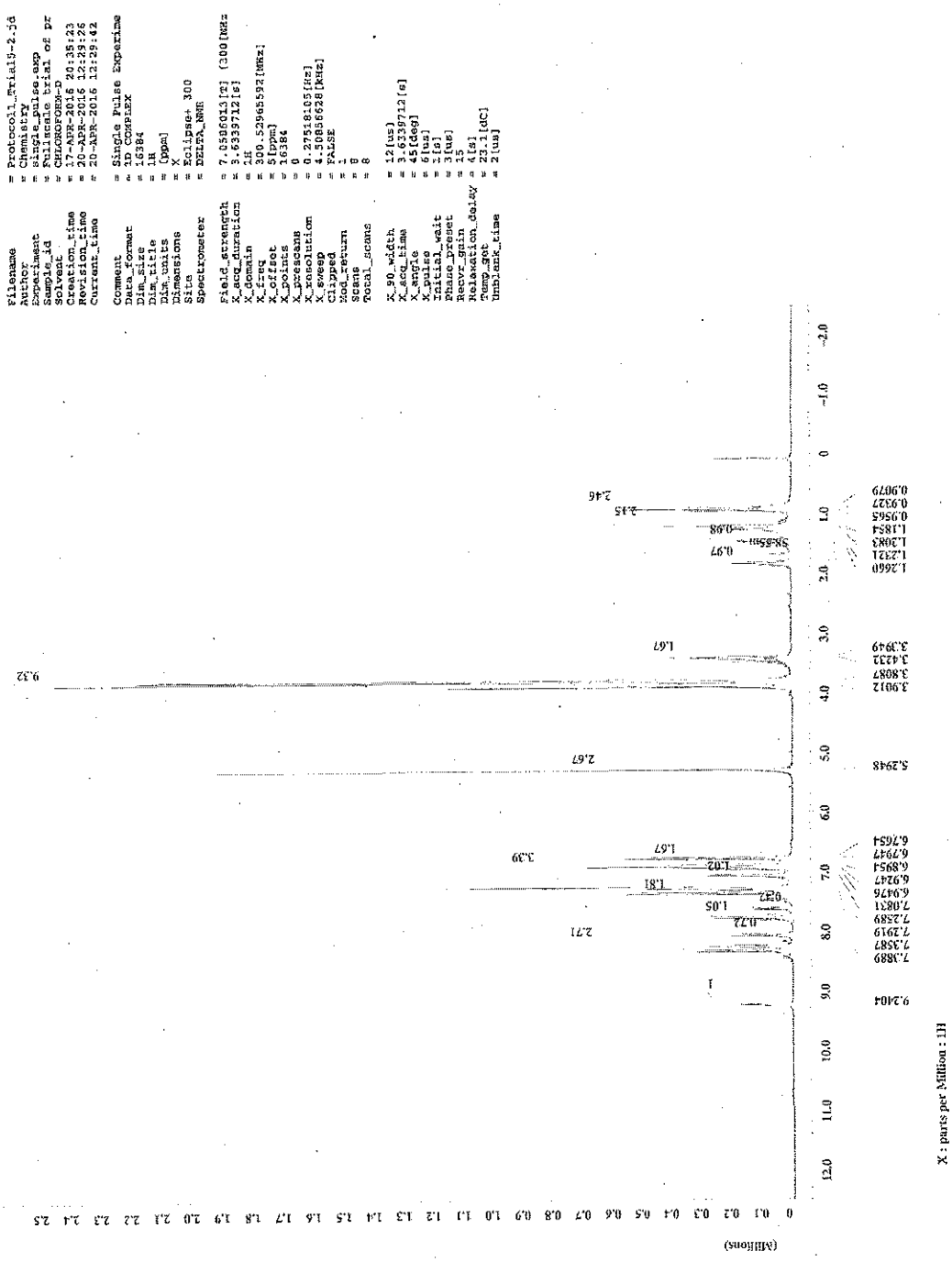

Figure 10. This figure demonstrates the ^{1}H NMR spectrum of the isolated, impure, product from Trial 5 of Protocol 1.

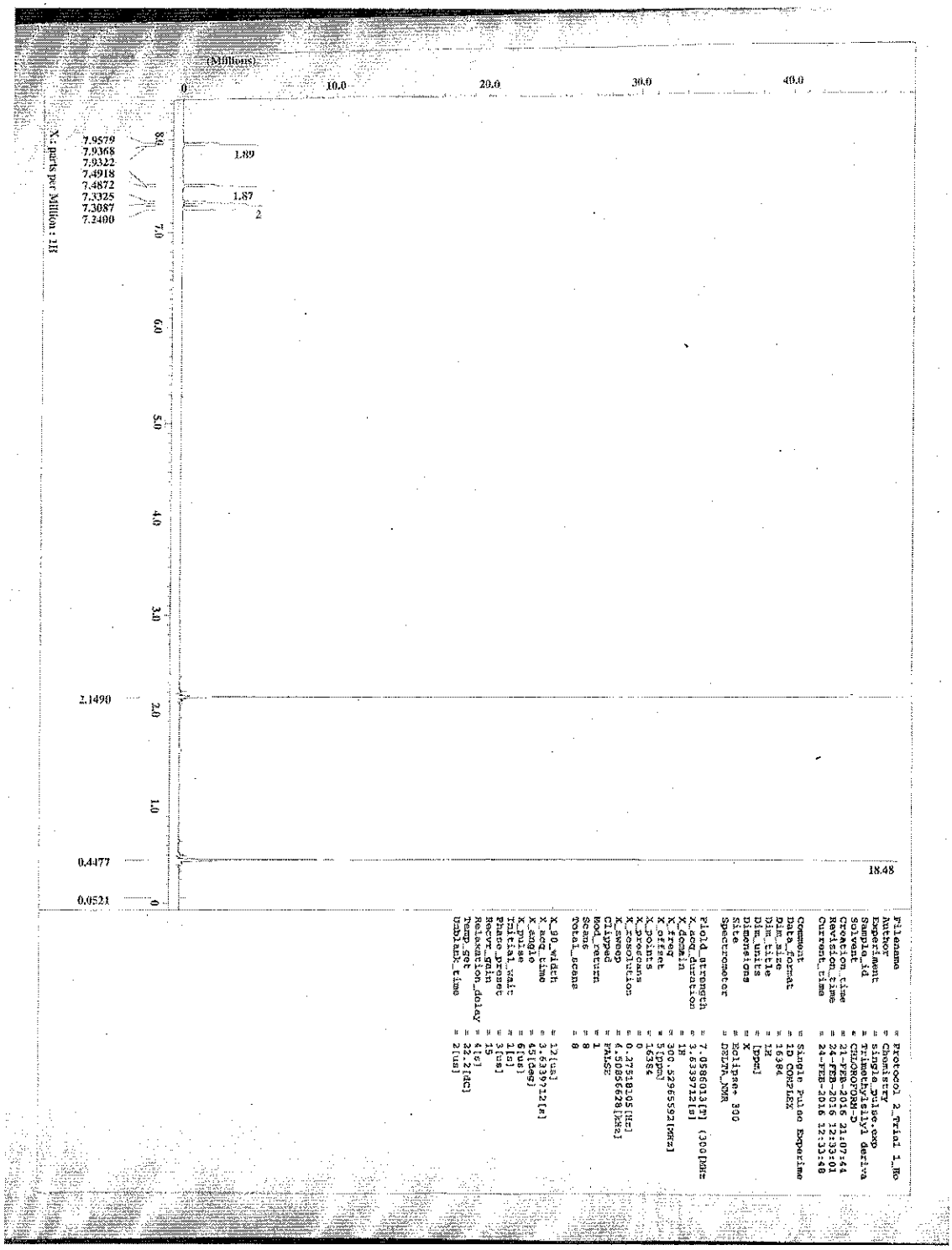

Figure 11. This figure shows the ^{1}H NMR spectrum of the isolated, pure, product from Trial 1 of Protocol 2. See Protocol #2 in Materials and Methods section for proper peak assignments.

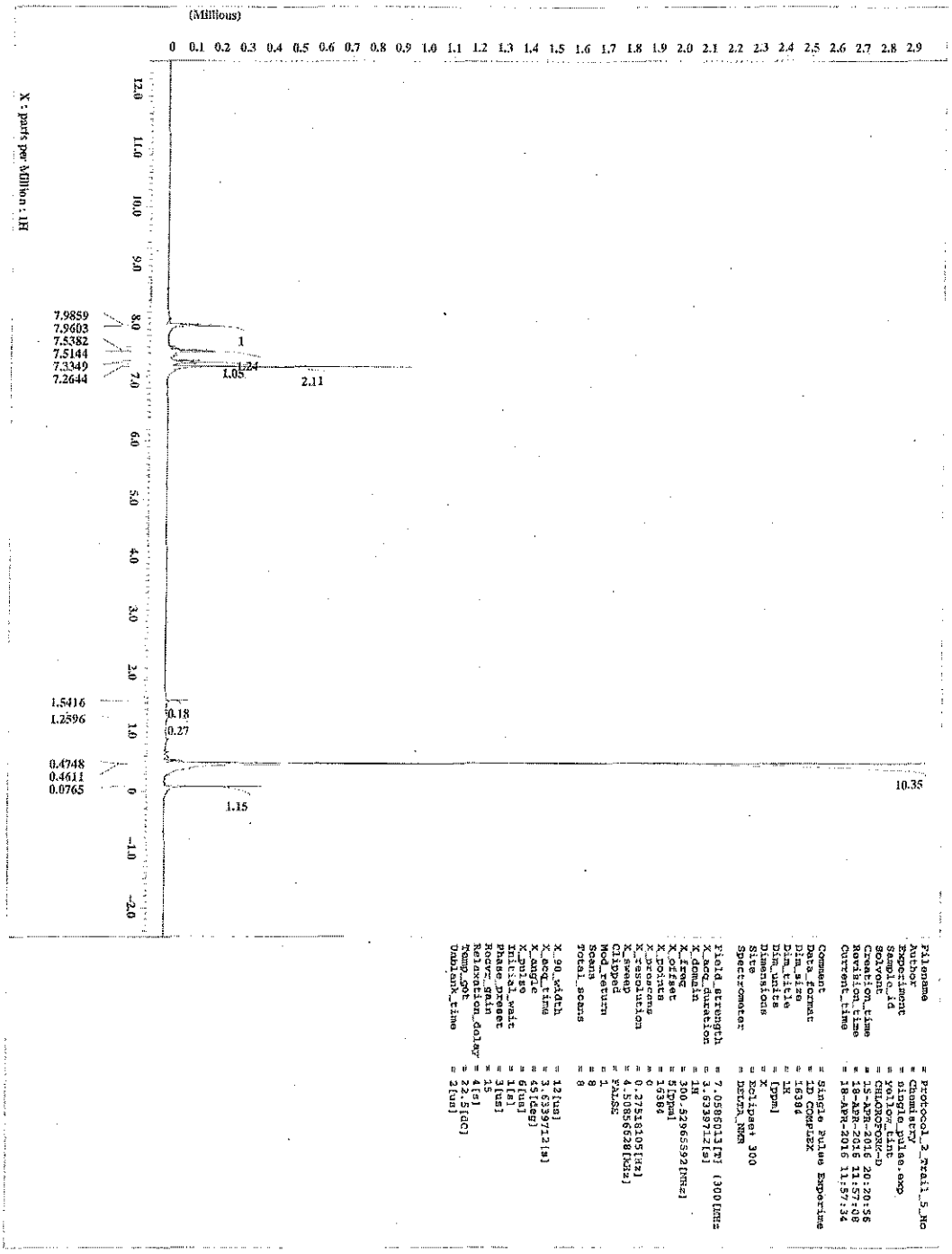

Figure 12. This figure shows the ^{1}H NMR spectrum of the isolated, pure, product from Trial 5 of Protocol 2. See Protocol #2 in Materials and Methods section for proper peak assignments.

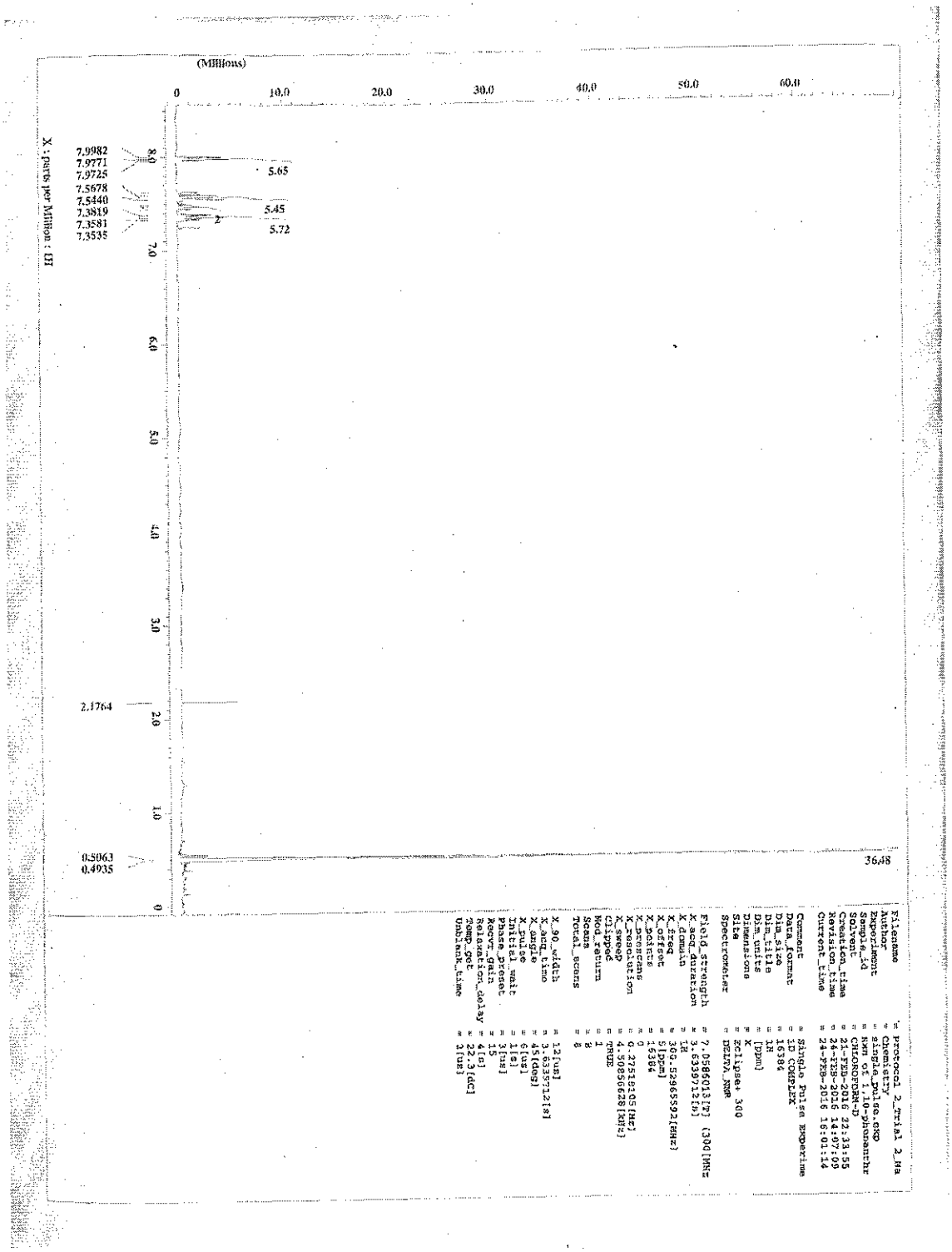

Figure 13. This shows the ^{1}H NMR spectrum of the isolated, impure, product from Trial 2 of Protocol 2.

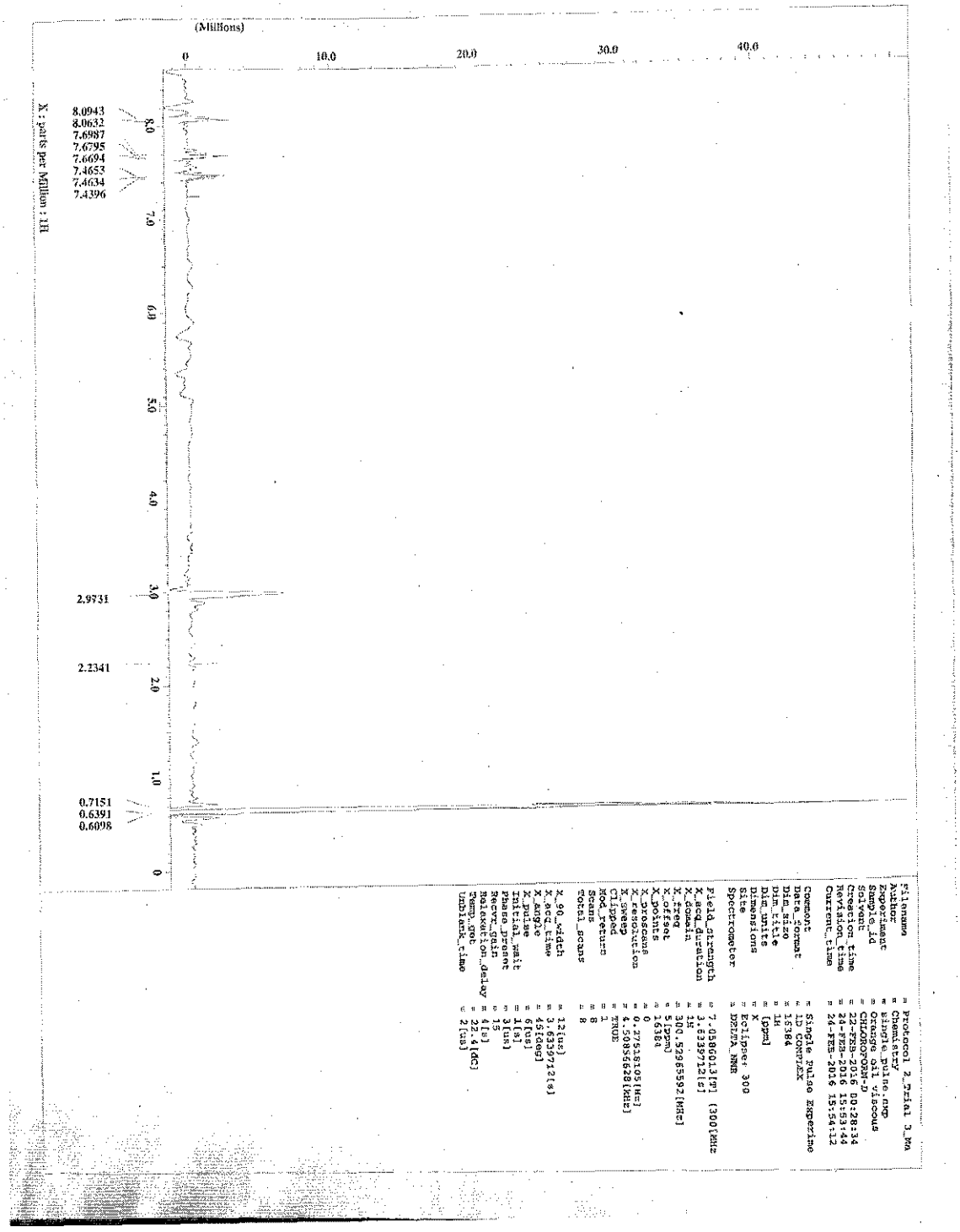

Figure 14. This figure demonstrates the ^{1}H NMR spectrum of the isolated, impure, product from Trial 3 of Protocol 2.

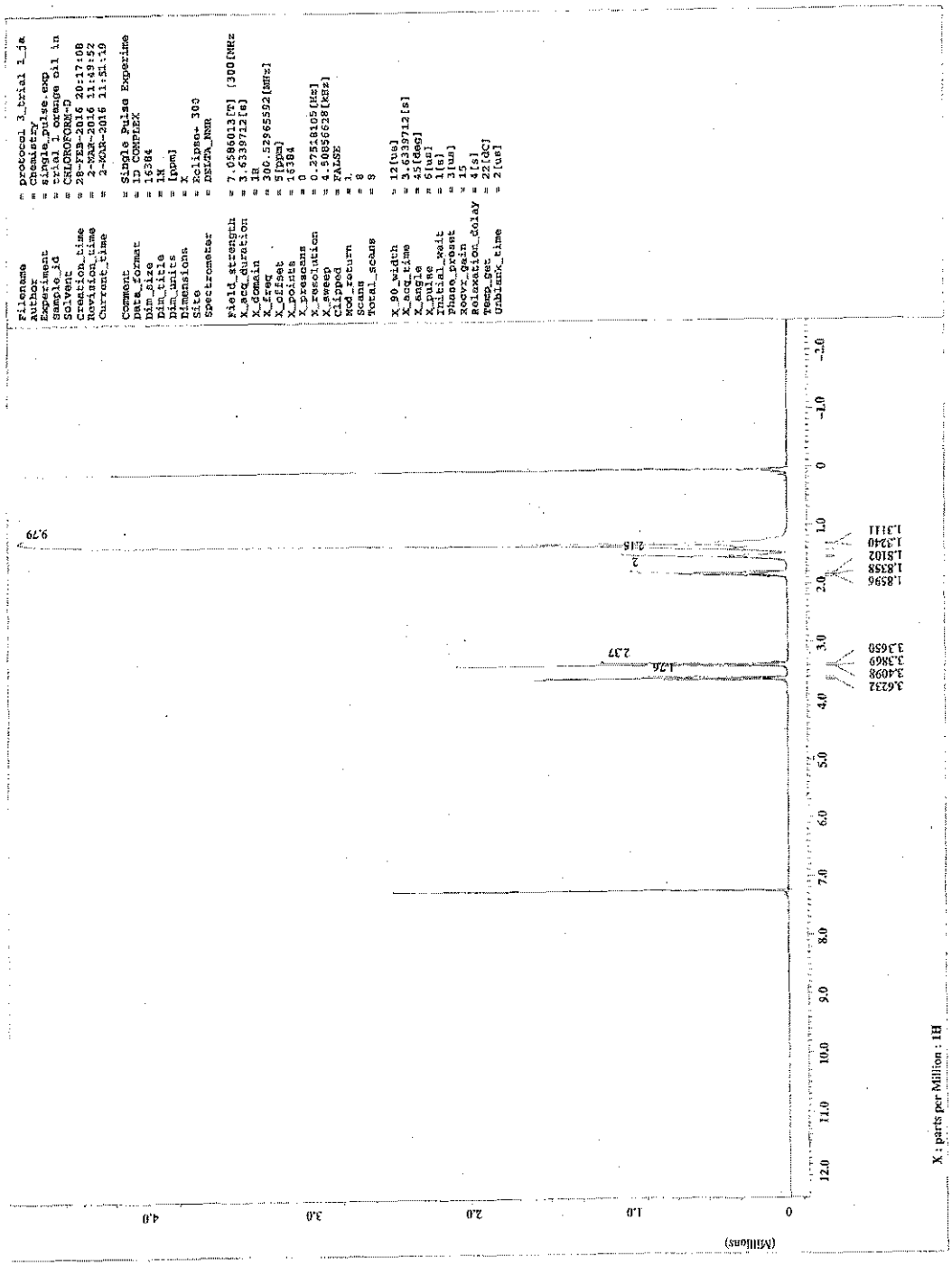

Figure 15. This figure shows the ^{1}H NMR spectrum of the isolated, pure, product from Trial 1 of Protocol 3. See Protocol #3 in Materials and Methods section for proper peak assignments.

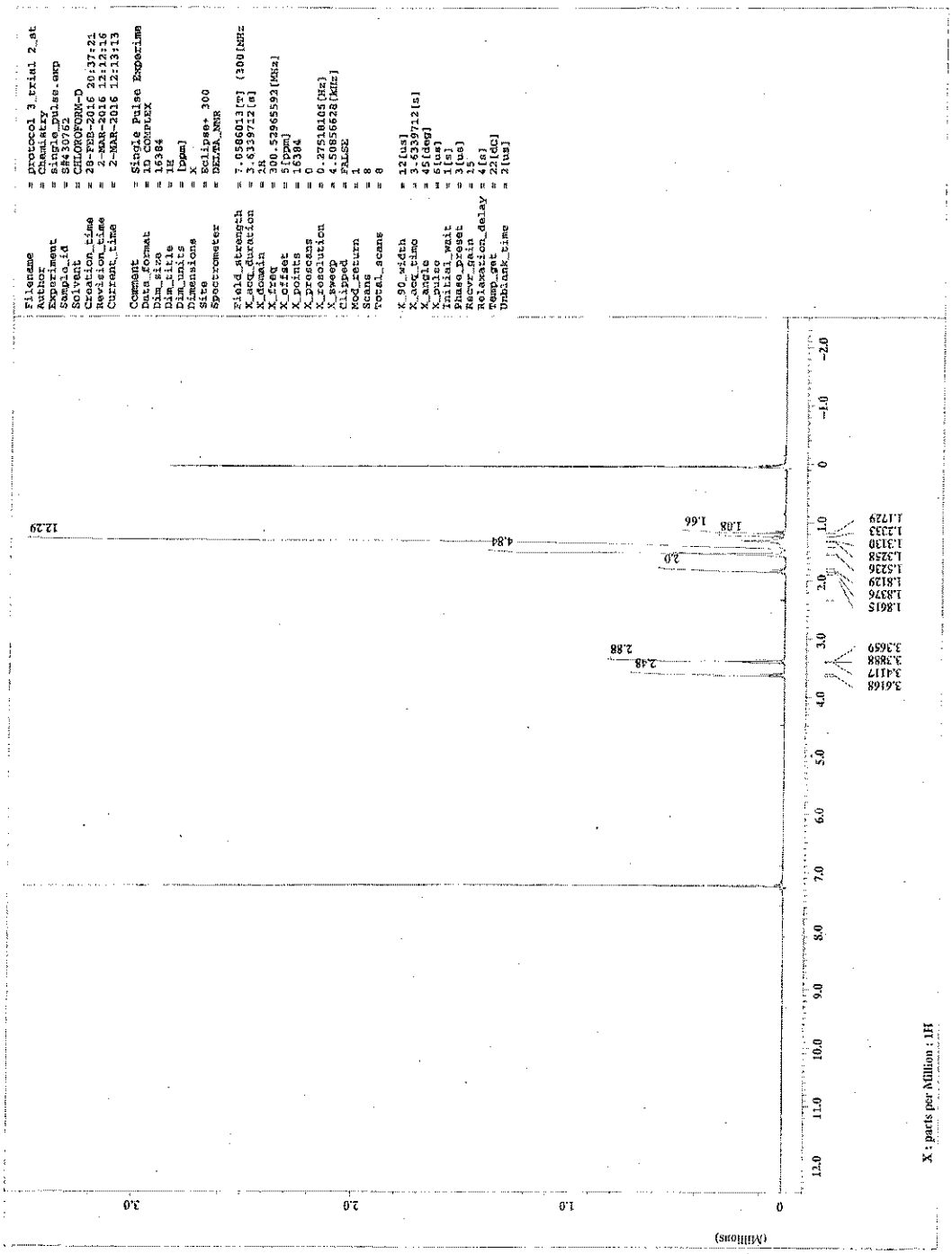

Figure 16. This figure shows the ^{1}H NMR spectrum of the isolated, impure, product from Trial 2 of Protocol 3.

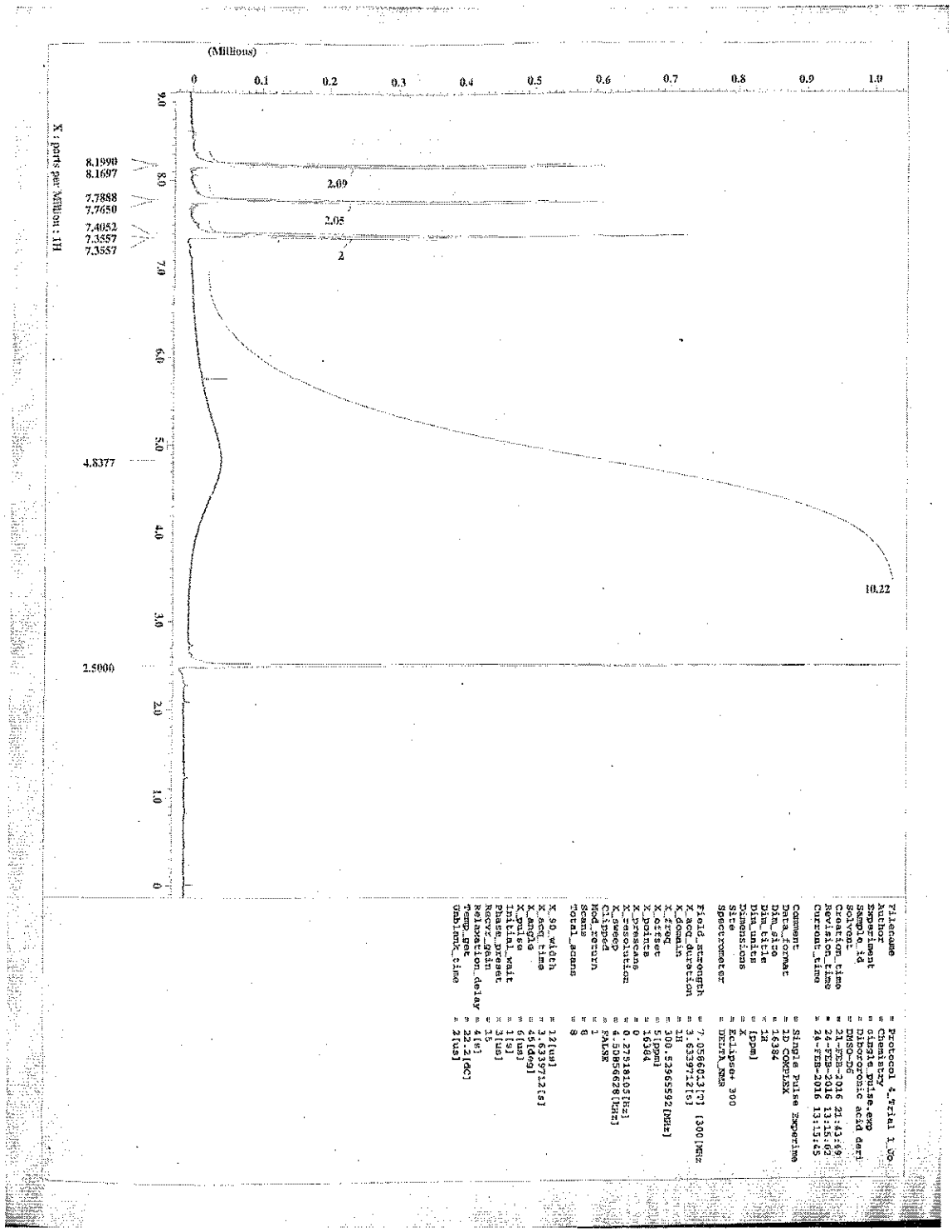

Figure 17. This figure shows the ^{1}H NMR spectrum of the isolated, pure, product from Trial 1 of Protocol 4. See Protocol #4 in Materials and Methods section for proper peak assignments.

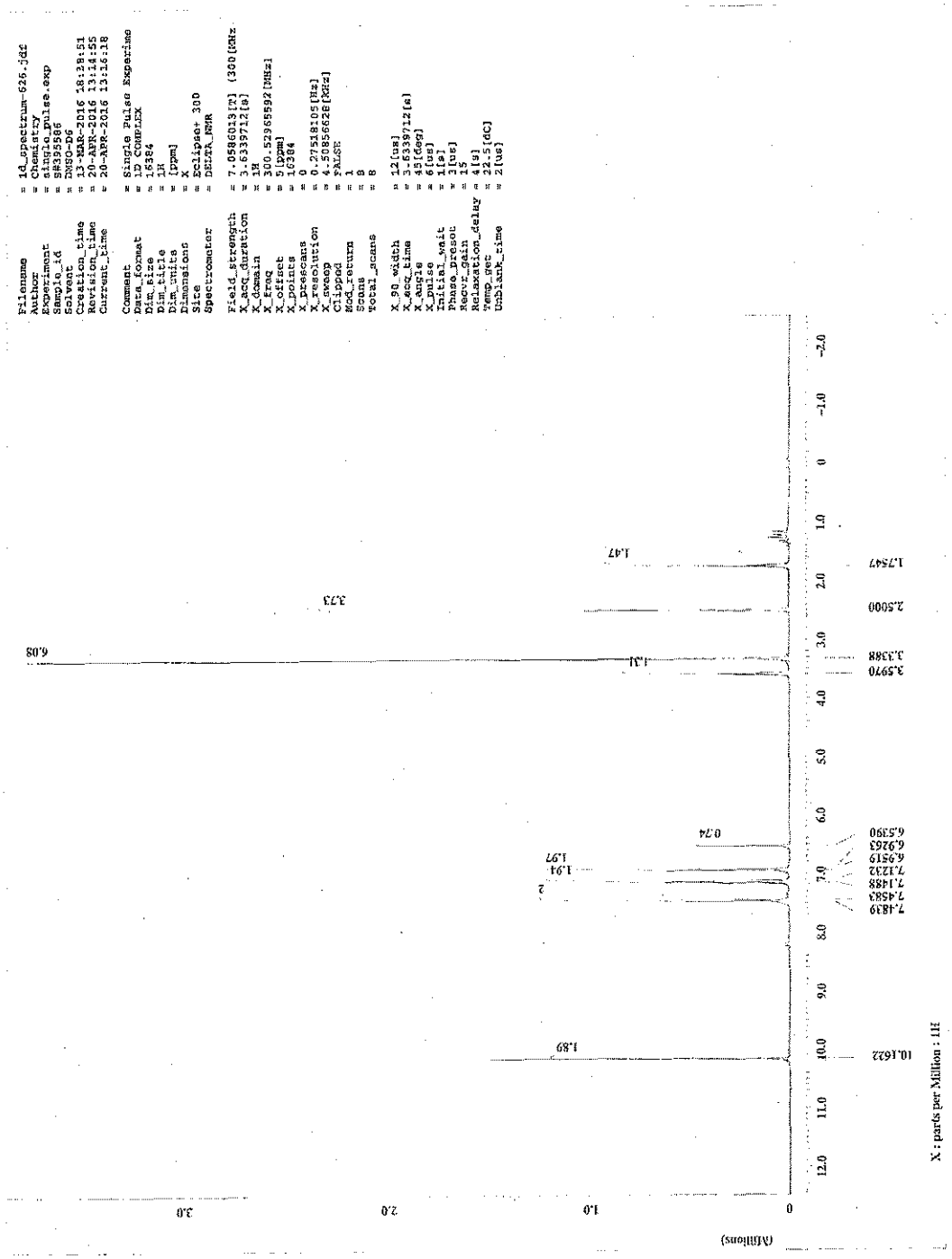

Figure 18. This figure shows the ^{1}H NMR spectrum of the isolated, pure, product from Trial 1 of Protocol 5. See Protocol #5 in Materials and Methods section for proper peak assignments.