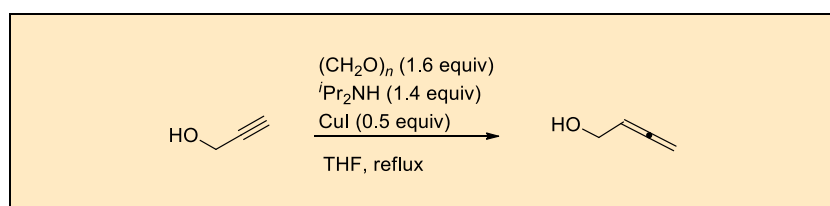


Buta-2,3-dien-1-ol

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Checked by Carl A. Busacca and Chris Senanayake



Procedure

Buta-2,3-dien-1-ol. A 2-L oven-dried, four-necked, round-bottomed flask is equipped with a mechanical stirrer, a 30-cm reflux condenser (open to the air), two septa, and a thermocouple (Note 1), and the flask is placed in a heating mantle. To this flask are added CuI (38.1 g, 0.20 mol, 0.5 equiv), paraformaldehyde (20.5 g, 0.64 mol, 1.6 equiv), and THF (800 mL), and stirring with the mechanical stirrer is initiated. Diisopropylamine (56.7 g, 78.5 mL, 0.56 mol, 1.4 equiv) is added in one portion by graduated cylinder, followed by the addition of propargyl alcohol (22.5 g, 23.4 mL, 0.40 mol, 1.0 equiv) by syringe (Notes 2, 3 and 4). The mixture turns from a greenish suspension to a yellow suspension when the propargyl alcohol is added. The mixture initially became thicker, and a rapid exotherm from 21 °C to 27 °C is observed, and an orange suspension is present (Figure 1). After the



Figure 1. Appearance of Reaction at the Initiation of Reflux

addition of the propargyl alcohol, the resulting mixture is heated to reflux (66 °C) for 24 h in a heating mantle without protection with an inert atmosphere (Notes 5 and 6) (Figures 1 and 2). After being allowed to cool to room temperature, the dark-brown solution is transferred to a 3-L flask and the solution is concentrated under reduced pressure with a rotary evaporator (water bath: 20 °C/75 mmHg) (Note 7).



Figure 2. Reaction after 24 h under Reflux

The original 2-L flask is equipped with a mechanical stirrer and thermocouple, charged with a cold solution (2 °C) of diethyl ether (500 mL) and 12 N HCl (50 mL), and agitation is started. The stirring solution is cooled to ca. -10 °C in a salt/ice bath, at which time the concentrated solution, which has a mass of ca. 185 g, is slowly and cautiously poured into the cold acidic mixture in five portions approximately 3 minutes apart (Note 8). The immediate formation of a thick, dark brown, oily precipitate and an

exotherm to a maximum of 4.0 °C are observed. Agitation is stopped and the mixture is allowed to settle for 5 min. The supernatant yellow solution is carefully decanted onto a short column of silica gel (50 g) in a 150-mL medium-fritted filter funnel positioned above a 1-L filtration flask (Notes 9 and 10). A vacuum is applied briefly to move the solution through the silica gel (Figure 3).



Figure 3. Yellow Solution after Initial Filtration

To the reddish-brown residue in the 2-L flask is added diethyl ether (100 mL), mechanical stirring is used for 3 min, and the solution is allowed to settle for 3 min. The supernatant liquid is carefully decanted onto the same

short silica gel column and filtered through the silica gel pad by briefly applying vacuum. The ether extraction (100 mL), settling, decantation and filtration process is repeated twice more (Figure 4).



Figure 4. Silica Gel Pad after all Filtrations

The clear, light yellow filtrate (~ 850 mL) is transferred to a 1-L separatory funnel and washed with saturated NaCl (2 x 100 mL). The aq. phases are combined and then back-extracted with diethyl ether (2 x 100 mL). All organic phases are combined, dried with anhydrous sodium sulfate (40 g), and filtered into 2-L flask with a 45/50 center joint. The solution is concentrated using a rotary evaporator (20 °C/65 mmHg), which facilitated the removal of ca. 820 mL of clear, colorless distillate. The residual yellow solution is transferred to a 250 mL flask, using ~ 50 mL MTBE to

quantitatively transfer the mixture, and further concentrated in vacuo (20 °C/65 mmHg) to provide 23.5 g of a crude yellow oil (Note 11).

A short path distillation head is attached and the 10 mL receiving flask is chilled to -78 °C. The flask is immersed in an oil bath, and distillation is initiated at 25 °C (65 mmHg). A forerun of 2.0 mL is collected at 45 °C, at which point the distillation temperature dropped and distillation of the forerun stopped. A 25 mL receiver flask is then installed and chilled to -78 °C, and the distillation re-started. With the pot temperature at 65 °C, the main fraction (12.5 g, 45%, 98% purity) is collected (55 °C/30-33 mmHg) as a colorless oil (Note 12).

Notes

1. All glassware were thoroughly washed and dried in oven.
2. CuI ($\geq 99.5\%$), paraformaldehyde ($\geq 94.0\%$), diisopropylamine ($\geq 99.0\%$), THF ($\geq 99.0\%$), and diethyl ether ($\geq 98.5\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and used as received. Propargyl alcohol ($\geq 99\%$) was purchased from AstaTech Pharmaceutical Co., Ltd. (Chengdu, China) and distilled before use.
3. The ratio of starting materials has been studied. The use of 1.6 equiv of paraformaldehyde and 1.4 equiv of diisopropylamine is optimal. See ref. 28 and 29.
4. The mixture will turn sticky after the addition of propargyl alcohol, it needs a rapid stirring to avoid congelation of reaction system.
5. The orange reaction mixture turned reddish-brown slowly during the reaction.
6. The reaction was monitored by GC, which revealed complete consumption of propargyl alcohol in 24 h. A reaction mixture aliquot was withdrawn and filtered through a 0.45 micron syringe tip filter into a GC vial, then diluted with THF and injected. Gas Chromatography conditions: Column: DB-1701, 30 m x 250 μm , film 0.15 μm ; Flow rate 1.2-mL/min; Injector temperature 240 °C; Oven Temp: 50 °C to 150 °C at 15 °C/min; 150 °C to 280 °C at 20 °C/min, hold at 280 °C for 2 min. FID Detector Temp: 280 °C; Retention times: propargyl alcohol = 2.18 min, Buta-2,3-dien-1-ol = 2.55 min.

7. Significant foaming is observed at the beginning of the distillation, although the foaming is confined to the 3 L flask. Approximately 720 mL of liquid is removed by distillation.
8. White smoke was observed inside the flask during the addition of the concentrated solution. The work-up should be conducted in the fume hood.
9. Silica gel: 10-40 μ m. The column: h = 3.0 cm, ϕ = 6.5 cm
10. The reddish brown residue has a pungent smell, and the residue can easily clog the filter funnel; therefore, care should be taken to decant only the liquid and leave the residue in the flask.
11. Analysis of the crude liquid by ^1H NMR indicated the presence of the desired product, THF, and MTBE.
12. A second run on the same scale provided 12.8 g (46%) of the identical product. The spectral properties of buta-2,3-dien-1-ol are as follows : ^1H NMR (500 MHz, CDCl_3) δ : 1.60 (brs, 1 H, OH), 4.15 (dt, J = 6.1, 3.0 Hz, 2 H), 4.85 (dt, J = 6.5, 3.0 Hz, 2 H), 5.35 (quint, J = 6.4 Hz, 1 H), dilute and concentrated samples of the pure, distilled material showed slightly different proton resonances; ^{13}C NMR (125 MHz, CDCl_3) δ : 60.0, 76.7, 90.6, 207.8; MS (EI) m/z 70 (M^+ , 18.11), 55 (100); IR (neat): ν 3333, 1956, 1046, 1010 cm^{-1} . Buta-2,3-dien-1-ol (98% purity by 500 MHz ^1H NMR analysis using dimethyl fumarate as the internal standard) was colorless right after distillation, but slowly took on a light yellow color. The product should be stored below -30 $^\circ\text{C}$.

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The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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Discussion

Buta-2,3-dien-1-ol is the most simple allenol. A highly useful reagent²⁻²¹ due to the presence of the allene and hydroxyl functionality, this molecule can participate in many types of reactions and act as a very versatile intermediate in organic synthesis (Figure 5).²²

Several methods for synthesizing buta-2,3-dien-1-ol are listed in Figure 6. It should be noted that multi-step manipulations are needed to synthesize this compound from readily available materials, and all the methods require the use of LiAlH_4 or MeLi as the reducing reagent in the last step. The use of pyridine, benzene, LiAlH_4 or MeLi on a large scale can be harmful and dangerous. Furthermore, the intermediate 4-chlorobut-2-yn-1-ol in Figure 6 is highly explosive and a severe skin irritant. Thus, a facile and safe procedure suitable for large-scale synthesis of buta-2,3-dien-1-ol is highly desirable.²⁵

A synthesis of terminal allenes from terminal alkynes, paraformaldehyde, CuBr , and diisopropylamine in dioxane was developed,²⁶ which was later modified by the use of CuI and Cy_2NH instead of CuBr and diisopropylamine to afford the allene products with substantially improved yields.²⁷ However, neither procedure is practical for the large scale synthesis of buta-2,3-dien-1-ol due to the workup and separation problem. Recently,

after extensive screening, we developed a practical large-scale procedure for the synthesis of terminal allenes with THF as the optimal solvent.²⁸ Based on this observation, a procedure was established for the practical synthesis of buta-2,3-dien-1-ol on a 0.4 mol scale: under refluxing conditions, 0.4 mol of propargyl alcohol proceeds smoothly to afford 38-45% yield of the product in the presence of 0.5 equiv of CuI.

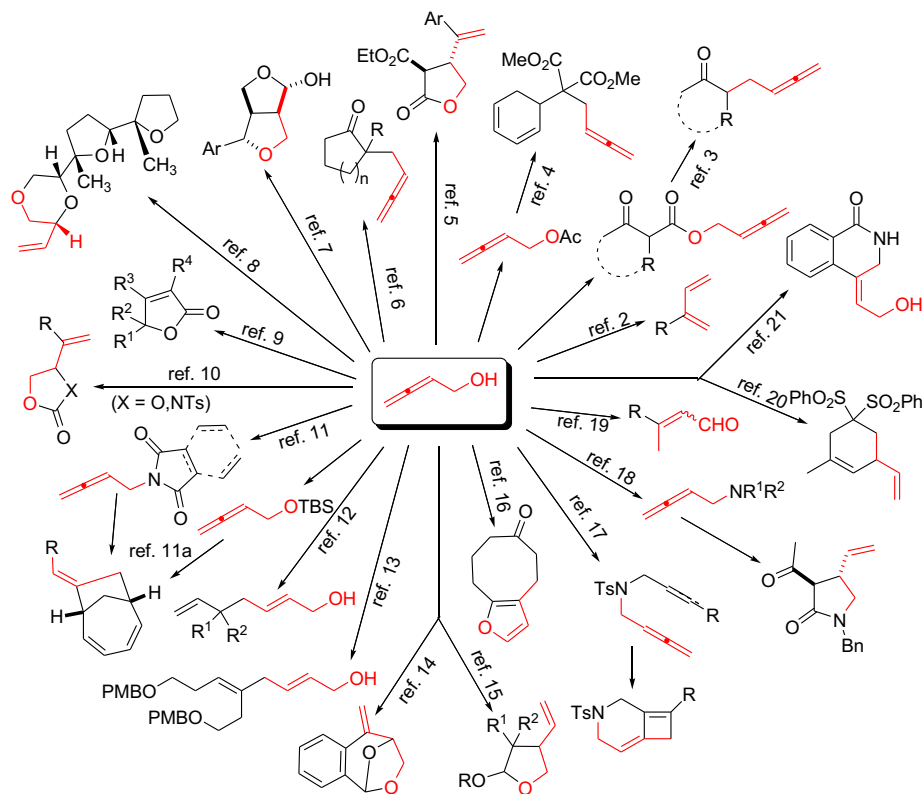


Figure 5. Selected Examples of the Applications of Buta-2,3-dien-1-ol

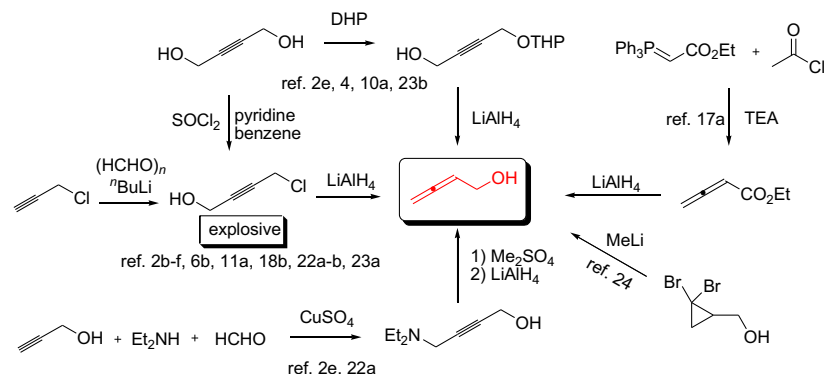


Figure 6. Reported Methods for the Synthesis of Buta-2,3-dien-1-ol

References

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Appendix

Chemical Abstracts Nomenclature (Registry Number)

Copper iodide (CuI); (7681-65-4)

Paraformaldehyde; (30525-89-4)

2-Propanamine, N-(1-methylethyl)-; (108-18-9)

2-Propyn-1-ol; (107-19-7)

2,3-Butadien-1-ol; (18913-31-0)



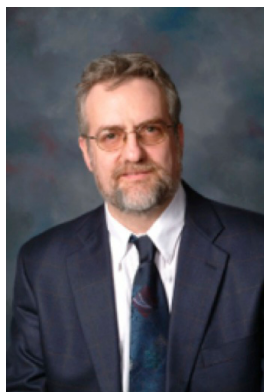
Prof. Shengming Ma was born in 1965 in Zhejiang, China. He graduated from Hangzhou University (1986) and received his Ph.D. degree from Shanghai Institute of Organic Chemistry (1990). He became an assistant professor in 1991 at SIOC. After his postdoctoral appointments at ETH with Prof. Venanzi and Purdue University with Prof. Negishi from 1992–1997, he joined the faculty of SIOC in 1997. From February 2003 to September 2007, he was jointly appointed by SIOC and Zhejiang University. From September 2007 to September 2014, he was a professor at ECNU and SIOC and Adjunct Professor at Zhejiang University. Currently he is a professor at Fudan University and SIOC and Adjunct Professor at Zhejiang University.



Hongwen Luo was born in Hunan, China, in 1989. He received his B.S. degree from University of Science and Technology of China (USTC) in 2011. He is currently pursuing his Ph. D. degree in the research group of Professor Ma.

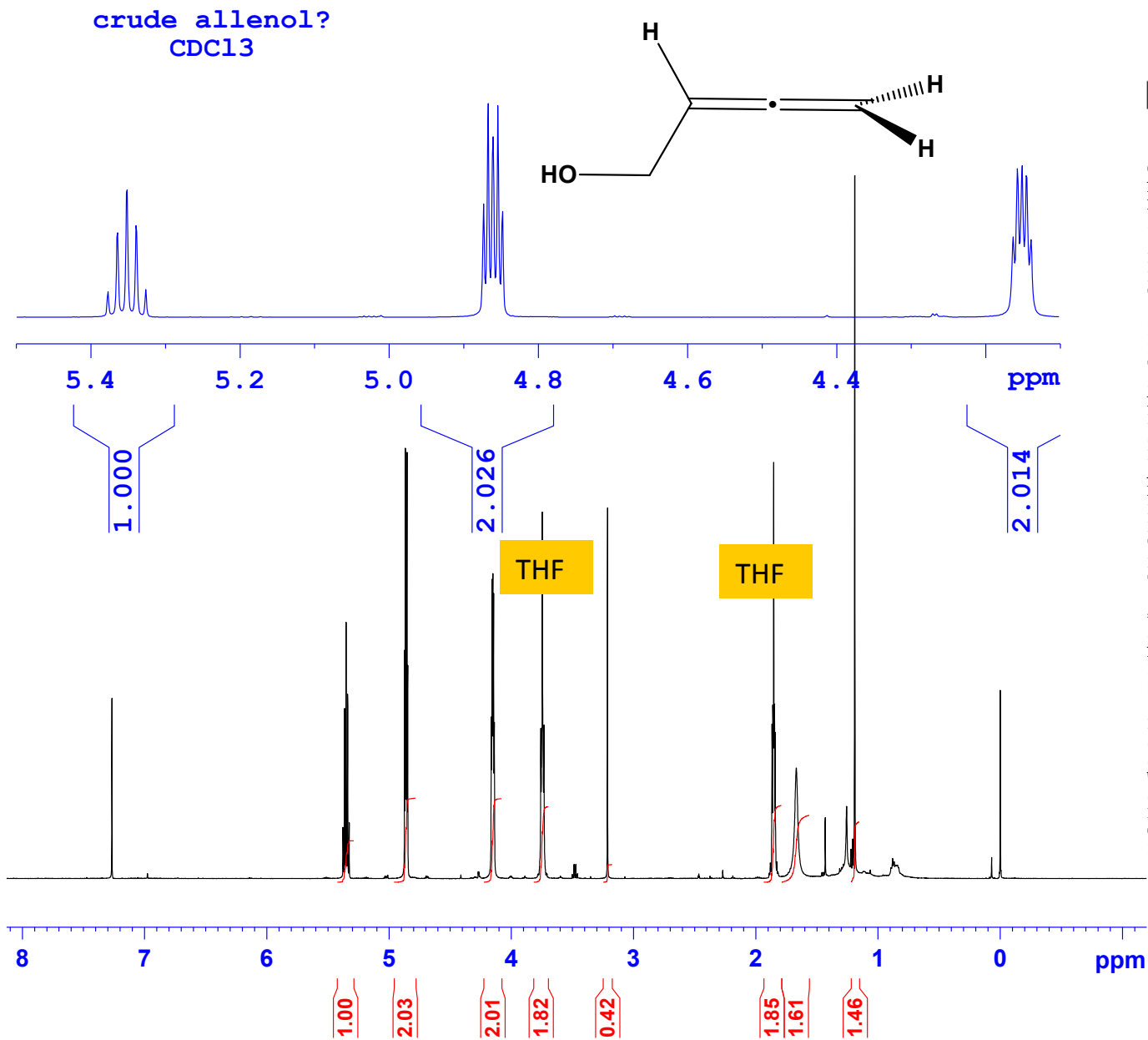


Dengke Ma was born in Henan, China, in 1988. He received his B. S. degree from Zhengzhou University in 2012. He is currently pursuing his Ph. D. degree in the research group of Professor Ma.



Dr. Carl Busacca received his B. S. in Chemistry from North Carolina State University, and did undergraduate research in Raman spectroscopy and ^{60}Co radiolyses. After three years with Union Carbide, he moved to the labs of A. I. Meyers at Colorado State University, earning his Ph. D. in 1989 studying asymmetric cycloadditions. He worked first for Sterling Winthrop before joining Boehringer-Ingelheim in 1994. He has worked extensively with anti-virals, and done research in organopalladium chemistry, ligand design, organophosphorus chemistry, asymmetric catalysis, NMR spectroscopy, and the design of efficient chemical processes. He is deeply interested in the nucleosynthesis of transition metals in supernovae.

Crude allenol, prior to final distillation



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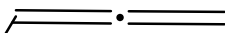
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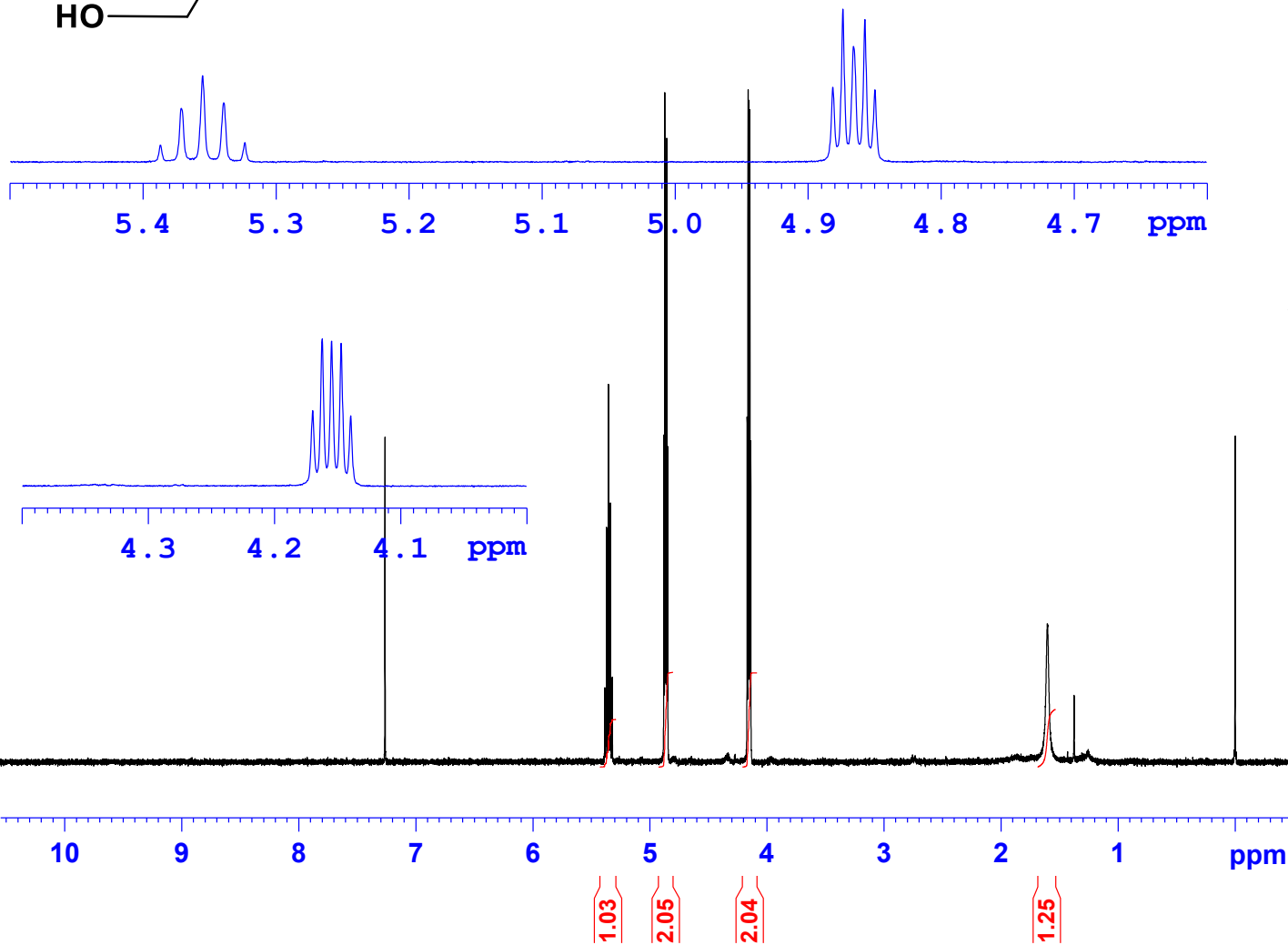
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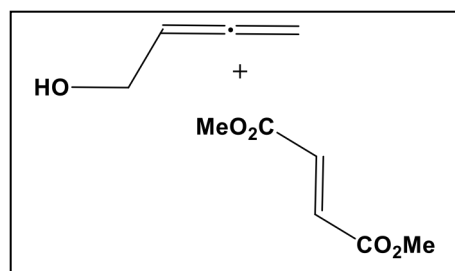
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PLW1 10.50000000 W

F2 - Processing parameters
SI 65536
SF 400.1300080 MHz
WDW EM
SSB 0
LB -0.05 Hz
GB 0
PC 1.00

distilled allenol
+ DMF
CDCl3

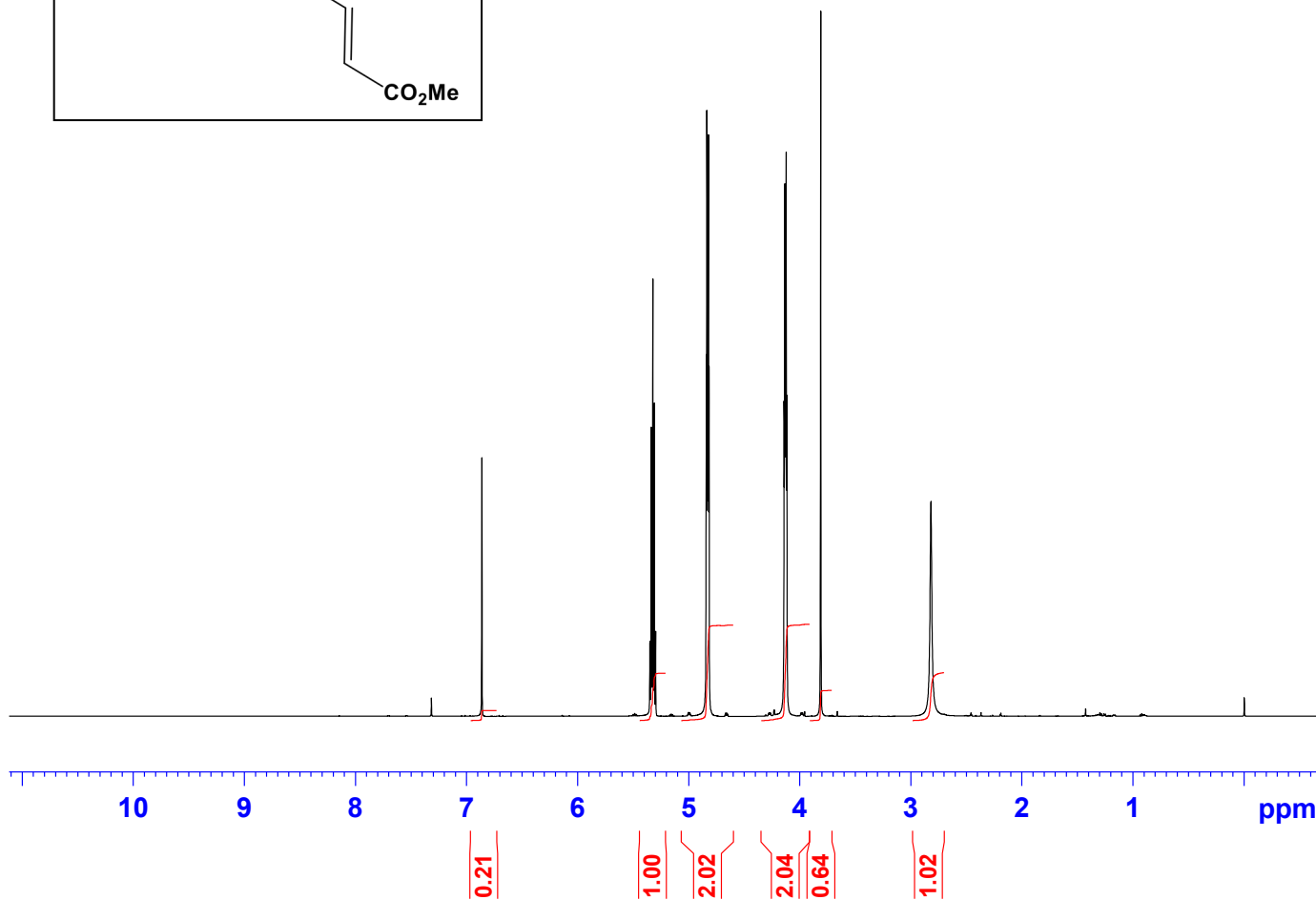


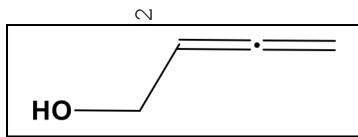
Current Data Parameters
NAME cab1-00043-5q
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170331
Time_ 17.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG q_zg10
TD 32768
SOLVENT CDCl3
NS 128
DS 0
SWH 9014.423 Hz
FIDRES 0.275098 Hz
AQ 1.8175317 sec
RG 64
DW 55.467 usec
DE 6.50 usec
TE 299.0 K
D1 2.0000000 sec
TD0 1

==== CHANNEL f1 =====
SFO1 500.1334009 MHz
NUC1 1H
P1 11.75 usec
PLW1 18.39999962 W

F2 - Processing parameters
SI 16384
SF 500.1299808 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



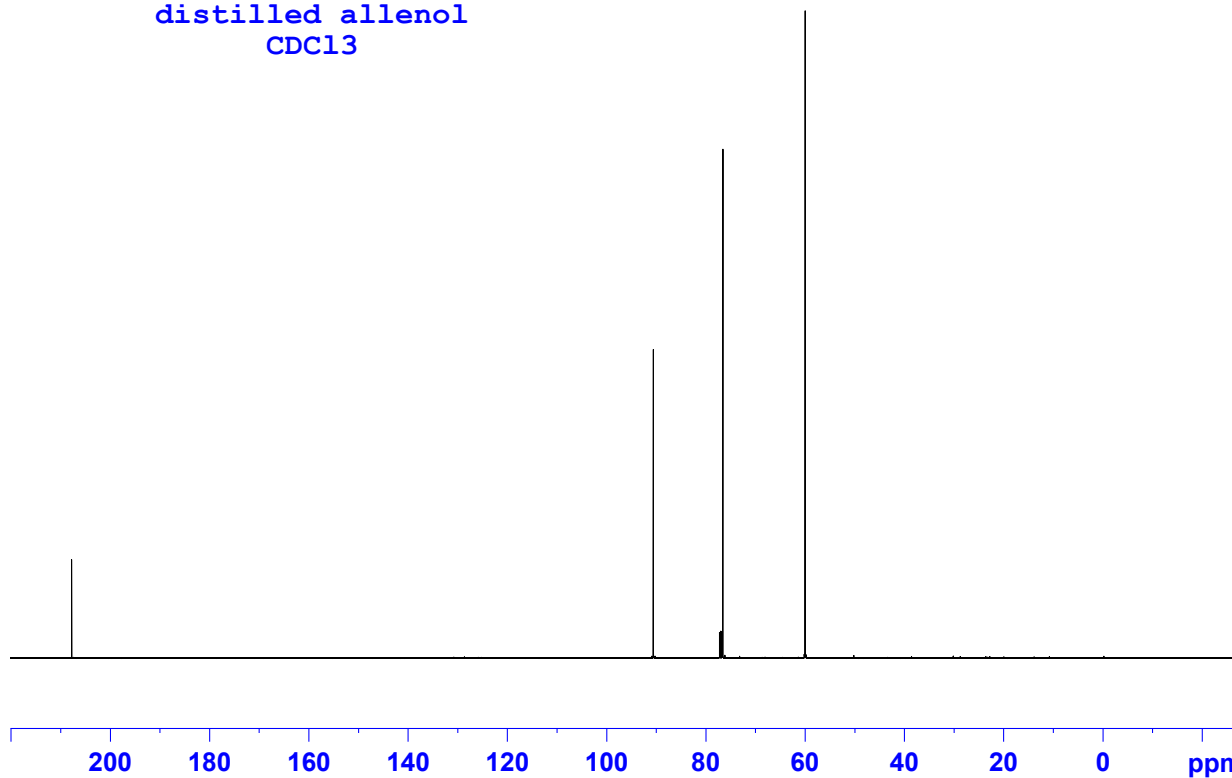


90.60
 77.25
 77.00
 76.74
 60.01



Current Data Parameters
 NAME cab1-00043-5x
 EXPNO 1
 PROCNO 1

distilled allenol
 CDC13



F2 - Acquisition Parameters
 Date_ 20170401
 Time_ 14.22
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg
 TD 262144
 SOLVENT CDC13
 NS 512
 DS 0
 SWH 31250.000 Hz
 FIDRES 0.119209 Hz
 AQ 4.1943040 sec
 RG 2050
 DW 16.000 usec
 DE 6.50 usec
 TE 299.0 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 125.7698617 MHz
 NUC1 13C
 P1 9.75 usec
 PLW1 126.00000000 W

==== CHANNEL f2 =====
 SFO2 500.1325007 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 18.39999962 W
 PLW12 0.41056001 W
 PLW13 0.20651001 W

F2 - Processing parameters
 SI 131072
 SF 125.7578044 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.40