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A Publication
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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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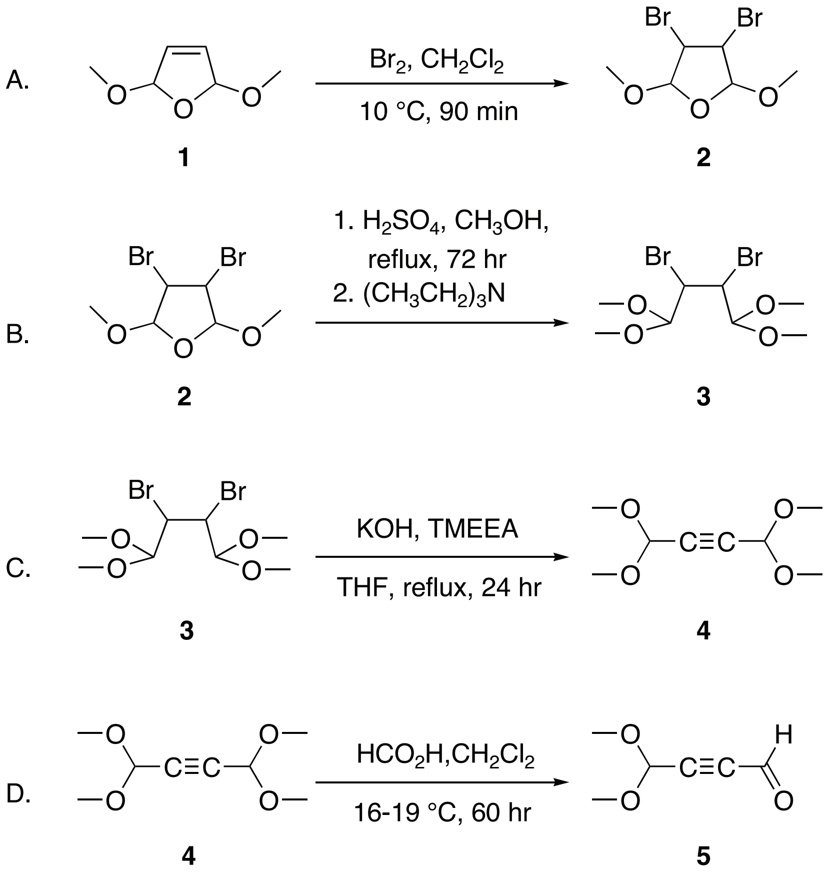
ALKYNE *via* SOLID-LIQUID PHASE-TRANSFER CATALYZED DEHYDROHALOGENATION: ACETYLENE DICARBOXALDEHYDE TETRAMETHYL ACETAL AND ACETYLENE DICARBOXALDEHYDE DIMETHYL ACETAL

[1,1,4,4-Tetramethoxy-2-butyne and 4,4-Dimethoxy-2-Butynal]



Submitted by Rufine Akué-Gédu and Benoît Rigo.[1]
Checked by Shigeki Matsunaga and Masakatsu Shibasaki.

1. Procedure

A. 3,4-Dibromo-2,5-dimethoxytetrahydrofuran (**2**). A 1-L three-necked, round-bottomed flask, equipped with a magnetic stirring bar, thermometer, pressure-equalizing addition funnel and water condenser connected to nitrogen, is loaded with dichloromethane (150 mL) (Note 2) and 2,5-dimethoxy-2,5-dihydrofuran (**1**) (50 g, 0.384 mol) (Note 3). The flask is cooled to 10 °C by using an ice bath. Bromine (61.4 g, 0.384 mol) is added over 120 min, while keeping the reaction temperature below 15 °C. After addition is complete, the reaction mixture is stirred at 10 °C until the bromine color disappears. The solution is concentrated on a rotary evaporator while keeping the bath temperature below 20 °C (Note 4). 3,4-Dibromo-2,5-dimethoxytetrahydrofuran (**2**) is obtained as a light colored semi-solid mass (110-111 g, 99%, mixtures of isomers) (Note 5, 6).

B. 2,3-Dibromo-1,1,4,4-tetramethoxybutane (**3**). A 3-L three-necked, round-bottomed flask, equipped with a heating mantle, a pressure-equalizing addition funnel and a water condenser connected to nitrogen, is loaded with crude 3,4-dibromo-2,5-dimethoxytetrahydrofuran (**1**) prepared in Step A (110-111 g), methanol (2 L) and boiling chips. The solution is heated to reflux, at which time 96% sulfuric acid (37.7 g, 0.384 mol) is added over 30 min (Notes 7, 8). The solution is refluxed for 72 h, then cooled at room temperature. Triethylamine (49 mL, 0.352 mol) is added (Notes 9, 10), then the solution is concentrated on a rotary evaporator. Heptane (250 mL) is added and the residue is stirred and refluxed for 20 min. The lightly colored heptane phase is separated using a separatory funnel. The heptane extraction step is repeated three times. The combined heptane solutions are concentrated on a rotary evaporator to give 2,3-dibromo-1,1,4,4-tetramethoxybutane (**3**) as a yellow oil (99-100 g including inpurities, < 79%) (Note 11).

C. 1,1,4,4-Tetramethoxybut-2-yne (**4**). A 1-L one-necked, round-bottomed flask is equipped with a powerful magnetic stirrer, a large rugby ball-shaped stirring bar, and a water condenser equipped with a nitrogen inlet. The flask is charged with tetrahydrofuran (300 mL) (Note 3), tris[2-(2-methoxyethoxy)-ethyl]amine (TMEEA, 10.1 g, 31.2 mmol) (Note 3) and crude 2,3-dibromo-1,1,4,4-tetramethoxybutane (**3**) prepared in Step B (99 g). Potassium hydroxide pellets (85%) (70 g, 1.06 mol) (Note 12) are then added to the homogenous solution, and the stirred mixture is refluxed for 24 h using an oil-bath. Solvent is evaporated on a rotary evaporator, water (250 mL) is added, and the solution is partitioned three times with ether (250 mL) (Note 13). The combined ether phases are washed three times with water (100 mL). After the solution is dried over $MgSO_4$, the solution is concentrated on a rotary evaporator to give 1,1,4,4-tetramethoxybut-2-yne (**4**) as a yellow oil (50-51 g, 97-99%) (Note 14, 15, 16).

D. 4,4-Dimethoxybut-2-ynal (**5**). A 1-L round-bottomed flask, charged with dichloromethane (150 mL) (Note 2) and crude 1,1,4,4-tetramethoxybut-

2-yne (**4**) (50 g, 287 mmol) prepared in Step C is cooled to 0 °C in an ice bath. Another flask charged with formic acid (280 g, 6 mol), dichloromethane (150 mL), and H_2O (1.5 mL) is also cooled to 0 °C. The cooled solution of formic acid is then rapidly added to the diacetal solution. The neck is sealed with a rubber septum equipped with a stainless steel syringe needle (Note 17). The flask is rapidly covered by a large opaque towel, and the reaction is stirred in the dark at 16-19 °C using a temperature regulated water bath for 60 h (Note 18). The dark brown solution is partitioned three times with ice cooled water (200 mL x 1, then 150 mL x 2). The aqueous phases are combined and extracted three times with dichloromethane (100 mL). The dichloromethane extracts are combined, washed with ice-cooled water (100 mL), and then dried with a mixture of Na_2SO_4 /$NaHCO_3$ (10/1). The solution is concentrated on a rotary evaporator while keeping the bath temperature below 25 °C (Note 4), to give 4,4-dimethoxybut-2-ynal (**5**) (25.5 g, 69% from **4**, 52% from **1**) as a brown oil (Note 19, 20, 21, 22, 23).

2. Notes

1. This procedure is an adaptation of a procedure published earlier by our group.[2]

2. Dichloromethane was distilled from P_2O_5.

3. 2,5-Dimethoxy-2,5-dihydrofuran (99%) was purchased from Alfa Aesar; triethylamine (99.5%) was purchased from Aldrich; tetrahydrofuran (99+%) was purchased from Acros; TMEEA, (tris[2-(2-methoxyethoxy)ethyl]amine) (99%) was purchased from Alfa Aesar; formic acid (95-97%) was purchased from Aldrich. These compounds were used as received.

4. Heating the oil bath of the rotary evaporator leads to a more colored, less pure product.

5. While the product was sufficiently pure for the subsequent step, ^{1}H NMR indicated the presence of undetermined impurities and showed that a mixture of the three isomers of 3,4-dibromo-2,5-dimethoxytetrahydrofuran was obtained in a ratio depending mainly on the temperature and length of the evaporation of solvent (The ratio of products as determined by ^{1}H NMR 43/17/40 (submitters), 46/12/42 (checkers); Isomer 1 (46% of the mass, mp 88 °C) ^{1}H NMR ($CDCl_3$) δ: 3.48 (s, 3H), 3.50 (s, 3H), 4.16 (dd, *J* = 9.6, 3.9

Hz, 1H), 4.26 (dd, *J* =9.6, 3.9 Hz, 1H), 4.94 (d, *J* = 3.9 Hz, 1H), 5.21 (d, *J* = 3.9 Hz, 1H); Isomer 2 (12% of the mass, mp 56 °C) ^{1}H NMR ($CDCl_3$) δ: 3.47 (s, 6H), 4.42 (dd, *J* = 1.9, 0.7 Hz, 2H), 5.23 (dd, *J* = 1.9, 0.7 Hz, 2H); Isomer 3 ^{1}H NMR ($CDCl_3$) δ: (42% of the mass, mp 72 °C) 3.50 (s, 6H), 4.18 (dd, *J* = 1.9, 1.3 Hz, 2H), 5.29 (dd, *J* = 1.9, 1.3 Hz, 2H).

6. The submitter describes the following unchecked procedure to separate three isomers; the mixture of three isomers of **2** can be partially separated by cooling the crude semisolid mass at 0 °C overnight. Filtration of the solid and washing with cold (0 °C) heptane, gave 78 g of isomer with mp 88-89 °C. Heptane was added to the residue, and the solution was cooled at 0 °C. Filtration and washing of the solid with cold (0 °C) heptane, gave isomer with mp 72-74 °C. Chromatography of the residue on alumina can give the third isomer (mp 56-58 °C).[3]

7. If a lesser amount of sulfuric acid is used, the reaction takes a longer time and leads to less pure product.

8. Slow addition of sulfuric acid to the hot reaction mixture allows for better control of the exothermicity of the addition, and provides a less colored final product.

9. Neutralization of sulfuric acid before evaporation of methanol avoids decomposition and colorization of diacetal **3**.

10. Triethylamine was selected for the neutralization because it decomposes the methyl sulfate formed from reaction of sulfuric acid with methanol.

11. Product **3** is difficult to purify, but remaining impurities are removed during the treatment of the next step. ^{1}H NMR ($CDCl_3$) δ: 3.44 (two singlet peaks overlapped with impurities, 12 H), 4.34 (d, *J* = 7.9 Hz, 2H), 4.58 (d, *J* = 7.9 Hz, 2H).

12. Potassium hydroxide pellets are better than finely ground powder, because the powder readily solidifies into a mass causing the reaction to slow down.

13. It was necessary to use diethyl ether instead of CH_2Cl_2 to avoid extraction of the phase transfer agent.

14. It was possible to perform the dehydrobromination step with potassium *tert*-butoxide in DMSO (2 h, 20 °C in a smaller scale), but treatment of the reaction mixture was less efficient and the purity of the product was lower.

15. While the product was sufficiently pure for the subsequent step, ^{1}H NMR indicated the presence of a small amount of undetermined impurities. If very pure product is needed for another use, compound **4** can be purified by distillation through a 10-cm Vigreux column: bp 55-59 °C (0.5 mmHg) [bp = 70-73 °C (1 mmHg),[4] bp = 101-103 °C (13 mmHg)[5]] to give a colorless liquid. ^{1}H NMR ($CDCl_3$) δ ppm: 3.40 (s, 12H), 5.21 (s, 2H).

16. Alternatively, it was not necessary to perform heptane extraction of compound **3**: the solution obtained after neutralization **3** with triethylamine (Step B) was evaporated on a rotary evaporator. Tetrahydrofuran (250 mL) (Note 2), TMEEA (0.03 mol, 10.1 g) (Note 2) and pellets of 85% potassium hydroxide (110 g, 1065 mol) (Note 11) were added. The mixture was refluxed for 24 h, and then part of THF was evaporated. Water was added and the mixture was extracted with ether, leading to 56 g of **4**. The weight of diacetal **4,** including impurities, is higher with no heptane extraction (56 g for Steps B and C); however, the purity of **4** is higher using the heptane extraction procedure.

17. The syringe needle is used for carbon dioxide evolution from the reaction mixture containing formic acid and acetal **4**.

18. It is important to perform the deprotection step below 20 °C in the dark, because exposure of the reaction mixture to a higher temperature or to light can lead to a lower yield through formation of a highly colored by-product. The reaction time and yield of Step D strongly depended on the quality of formic acid used. 95-97% formic acid from Aldrich gave best results. Drier formic acids: 99% from Acros Organics (Cat. No. 14793), 98% (Cat. No. 8841) from Lancaster, 97% from Avocado (Cat. No. 13285), gave decomposition of the monoacetal and formation of black tars. Even using 95-97% formic acid from Aldrich, difference in lot number may cause different yield and reaction time. Although addition of a small amount of H_2O (1.5 mL) was not a part of the submitter's original procedure, the isolated yield of **5** by the checkers is slightly improved by addition of a small amount of H_2O to the reaction mixture. Loss of product during work-up can also be problematic. It is necessary to wash the organic extracts with ice-cooled water quickly to avoid decomposition of product during extraction and washing. The temperature of the water bath also affected the reaction time significantly. The reaction was judged to be complete after 60 h at 16-19 °C (by the checkers), after 32 h at 17-20 °C (by the checkers), and after 20 h at 20-21 °C (by the submitters).

19. Because the formic acid quality, the reaction temperature, the quality of crude **4**, and the amount of water greatly influence the reaction time and isolated yield, it is essential to follow the reaction by NMR analysis of the crude reaction mixture. A 0.5 mL sample of the reaction mixture is evaporated under reduced pressure (2 mmHg) below 20 °C and dissolved in $CDCl_3$. A resonance at 5.20 ppm ($CH(OMe)_2$ of dialdehyde) is compared with resonances at 5.31 ppm {$CH(OMe)_2$} and 9.27 ppm {(CHO) of the monoaldehyde}.

20. ^1H NMR spectrum of 4,4-dimethoxybut-2-ynal (**5**) indicated the presence of tiny amount of undetermined impurities. ^1H NMR ($CDCl_3$) δ: 3.41 (s, 6H), 5.31 (s, 1H), 9.27 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 53.0, 83.0, 88.3, 92.7, 176.0. Purity of this crude compound is sufficient for participation in Michael reactions with nucleophiles. Aldehyde **5** remains unaltered when kept for years at -40 °C.

21. While the brown color of the crude compound can be removed by filtration on silica, most impurities remain in the product. [A solution of the product in CH_2Cl_2 was applied to the top of a short column of flash-grade silica gel (200 g, 10-cm diam x 4 cm) loaded with CH_2Cl_2. The brown color remains on the top of the column upon washing with CH_2Cl_2. Last traces of solvent were removed at 0.5 mmHg to afford **5** as a slighly yellow liquid.]

22. If one needs a purer product, compound **5** can be purified by distillation: 24 g of aldehyde **5** and a rugby ball-shaped stirring bar were introduced in a 50-mL one-neck flask immersed in an oil-bath, and fitted with a 10-cm Vigreux column, a water condenser cooled at –10 to –20 °C by a cooling regulator, and a receiving flask cooled at –40 °C by cooling bath. Aldehyde **5** was distilled under vacuum (0.2 mmHg), while the temperature of the oil-bath was slowly raised from 25 °C to 60 °C by using a temperature regulator. Aldehyde **5** (17.3 g (72 %), bp 34-37 °C (0.2 mmHg) [bp = 75-78 °C (14 mm)].)[4] was obtained as a slightly yellow liquid.

23. While working in a 20 to 50 g scale of diacetal **4**, compound **5** was obtained in 85-92 % yields (by the submitters) and in 72% (by the checkers in 25 g scale).

Safety and Waste Disposal Information

All hazardous materials should be handled and disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

This procedure describes the synthesis of acetylene dicarboxaldehyde mono and bis *dimethyl* acetals. It was reported[4,6] that acetylene dicarboxaldehyde *dimethyl* acetals are less reactive than their *diethyl* analogs**.** The new procedure takes advantages of this slightly lower reactivity and higher stability of the *dimethyl* acetals (Reaction time for the formic acid hydrolysis described in Step D is 20-60 h when using *dimethyl* acetals whereas it is 10 h when using *diethyl* acetals). Acetylene dicarboxaldehyde[4-15] and its precursors mono and bis *diethyl* acetals are useful starting materials, which have found many applications in dipolar cycloaddition,[7-11] Diels-Alder,[4,6,7,12,13] Michael,[4,6,7,13] or Wittig[15] reactions.

A major drawback for a larger use of these compounds is their high price[16] or difficulties in their preparation, which preclude a large-scale synthesis. Two main procedures for the synthesis of these compounds are described in the literature. In a first reaction sequence, addition of bromine to acrolein followed by a dehydrobromination step leads to acetylene carboxaldehyde diethyl acetal. Reaction of this compound with triethyl orthoformate using $ZnCl_2$ afforded the ethyl analog of acetal **4**.[2] In order to obtain 50 g of diacetal using this method,[2,6,17] it would be necessary to use 175 g of triethyl orthoformate, 345 g of KOH and 575 g of tetrabutylammonium hydrogen sulfate. In another approach, acetylene was reacted with ethyl magnesium bromide to give a bis magnesium salt. Reaction of this salt with triethyl orthoformate yields the ethyl analog of acetal **4**. In order to obtain 50 g of the diacetal using this second method,[4,6] it would be necessary to use 200 g of triethyl orthoformate, 19 g of magnesium and 260 L of gaseous acetylene. During this last procedure, it is necessary to avoid precipitation of the intermediate bis-magnesium salt of acetylene, which due to difficulties in stirring can lead to poor yields.[4]

The use of 99% formic acid to perform hydrolysis of one functional group of acetylene dicarboxaldehyde tetramethyl acetal is an adaptation of a method from Gorgues.[4,5,18]

The procedure described above reports an easy, high yielding, large-scale preparation of dimethyl acetals **4** from inexpensive 2,5-dimethoxy-2,5-dihydrofuran (**1**), a compound that contains all the carbon atoms of acetylene dicarboxaldehyde. The use of the phase transfer agent TMEEA is very important for this reaction,[19] because TMEEA enables the use of KOH and THF instead of DMSO and potassium *tert*-butoxide in the dehydrobromination step.

1. Groupe de Recherche sur l'Inhibition de la Prolifération Cellulaire (EA 2692), Ecole des Hautes Etudes Industrielles, 13 rue de Toul, 59046 Lille, France.

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16. 3,3-Diethoxy-1-propyne: 329 €/25 g (Lancaster); acetylene-dicarboxaldehyde tetraethyldiacetals: 75 €/1 g (Acros); acetylene-dicarboxaldehyde monodiethylacetal: 78 €/1 g (Acros); 2,5-dimethoxy-2,5-dihydrofuran (**1**): 191 €/1000 g (Alfa Aesar).

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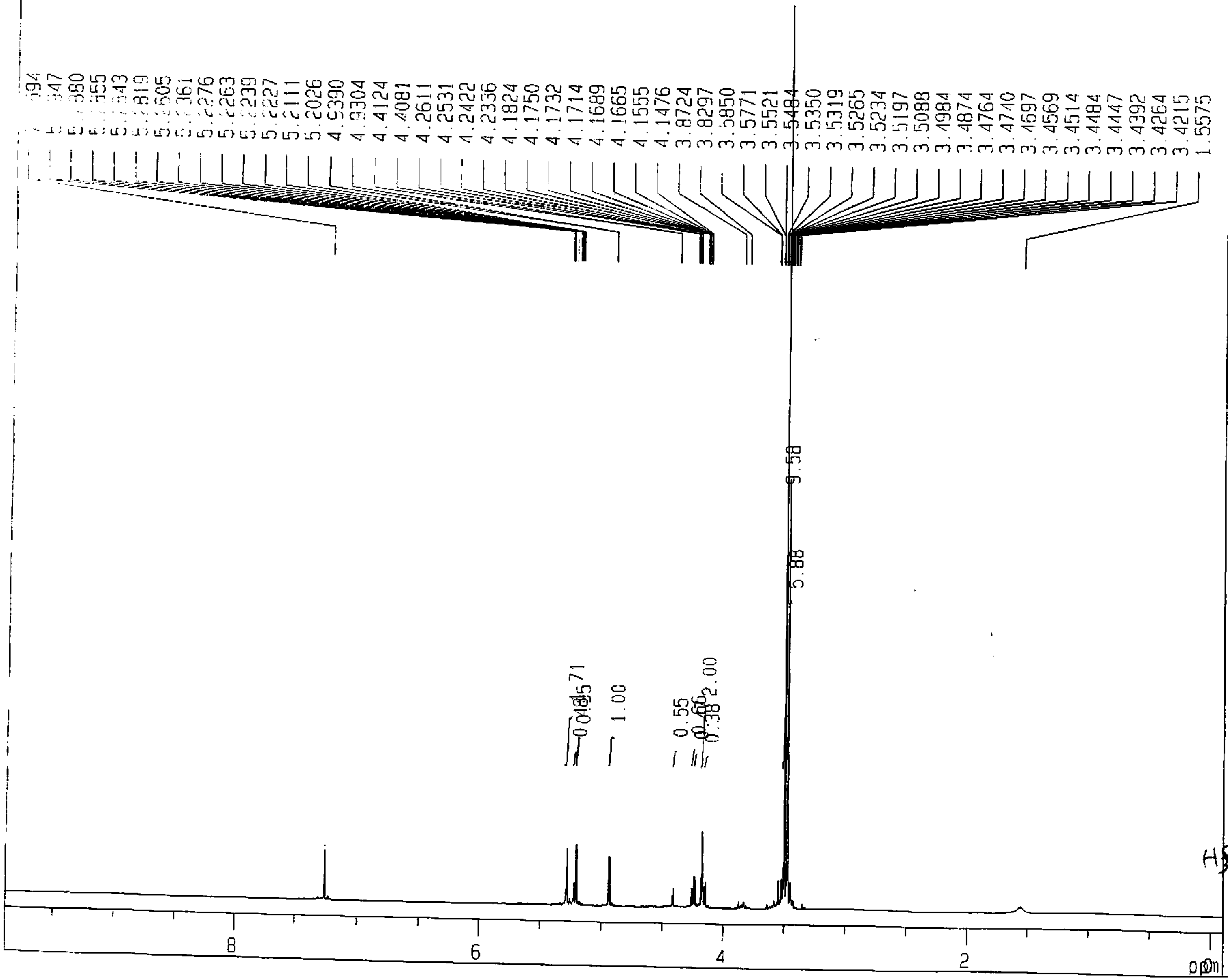
Appendix
Chemical Abstracts Nomenclature; (Registry Number)

2,5-Dimethoxy-2,5-dihydrofuran: Furan, 2,5-dihydro-2,5-dimethoxy-; (332-77-4)
Bromine; (7726-95-6)
Dibromo-2,5-dimethoxytetrahydrofuran: Furan, 3,4-dibromotetrahydro-2,5-dimethoxy-; (91468-55-2)
Methanol; (67-56-1)
Triethylamine: Ethanamine, *N,N*-diethyl-: (121-44-8)
2,3-Dibromo-1,1,4,4-tetramethoxybutane: Butane, 2,3-dibromo-1,1,4,4-tetramethoxy-; (25537-21-7)
Tris[2-(2-methoxyethoxy)-ethyl]amine: Ethanamine, 2-(2-methoxyethoxy)-*N,N*-bis[2-(2-methoxyethoxy)ethyl]-; (70384-51-9)
Potassium hydroxide: (1310-58-3)
1,1,4,4-tetramethoxybut-2-yne: 2-Butyne, 1,1,4,4-tetramethoxy-; (53281-53-1)
Formic acid; (64-18-6)
4,4-Dimethoxybut-2-ynal: 2-Butynal, 4,4-dimethoxy-; (124744-10-1)

Step A



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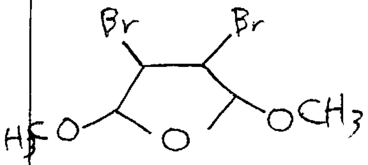
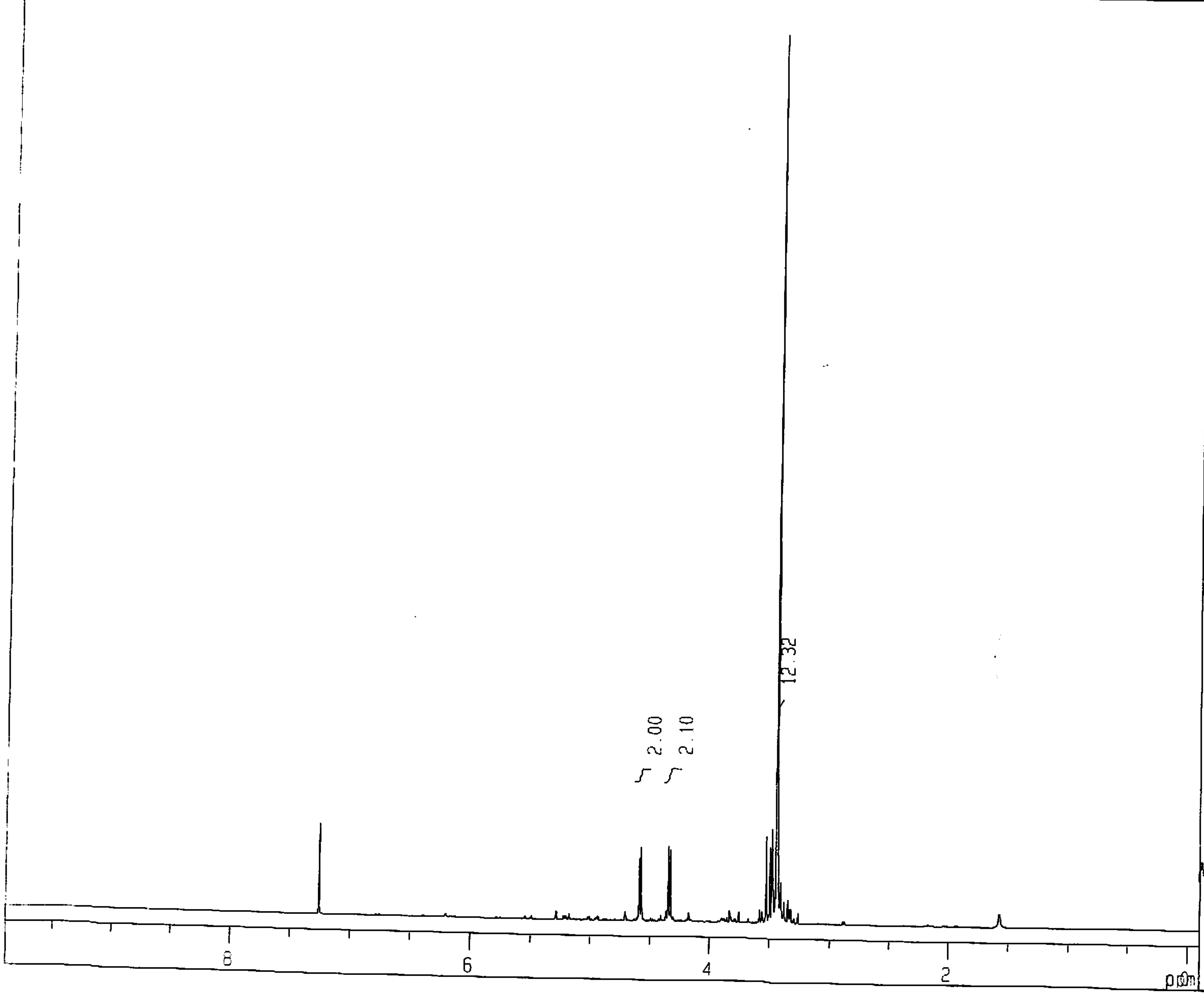


a mixture of three isomers

Step A

Step B



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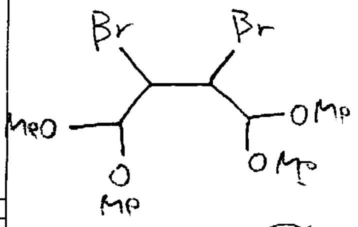

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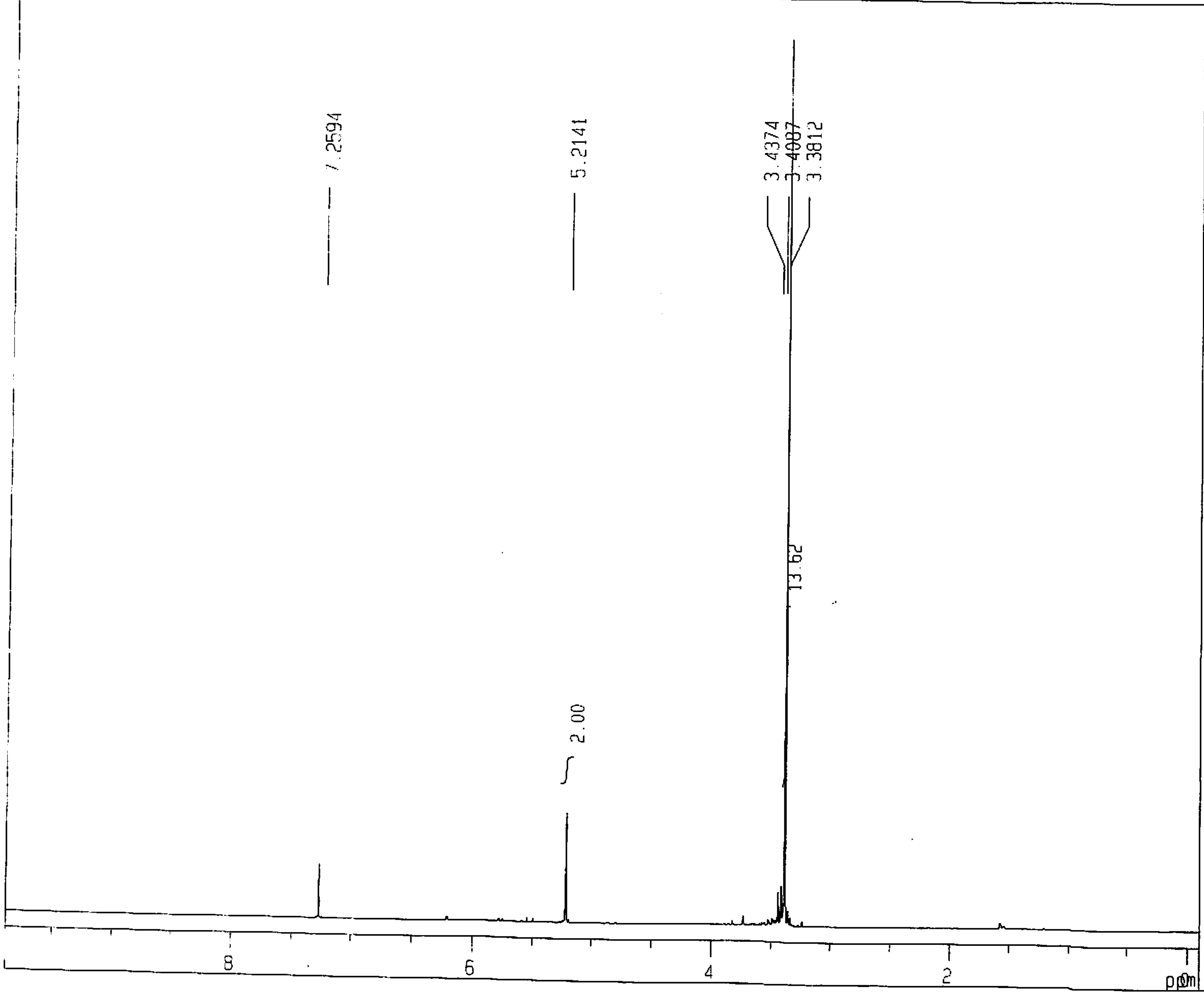

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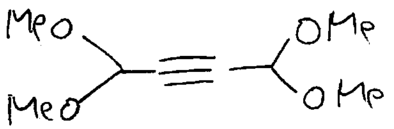

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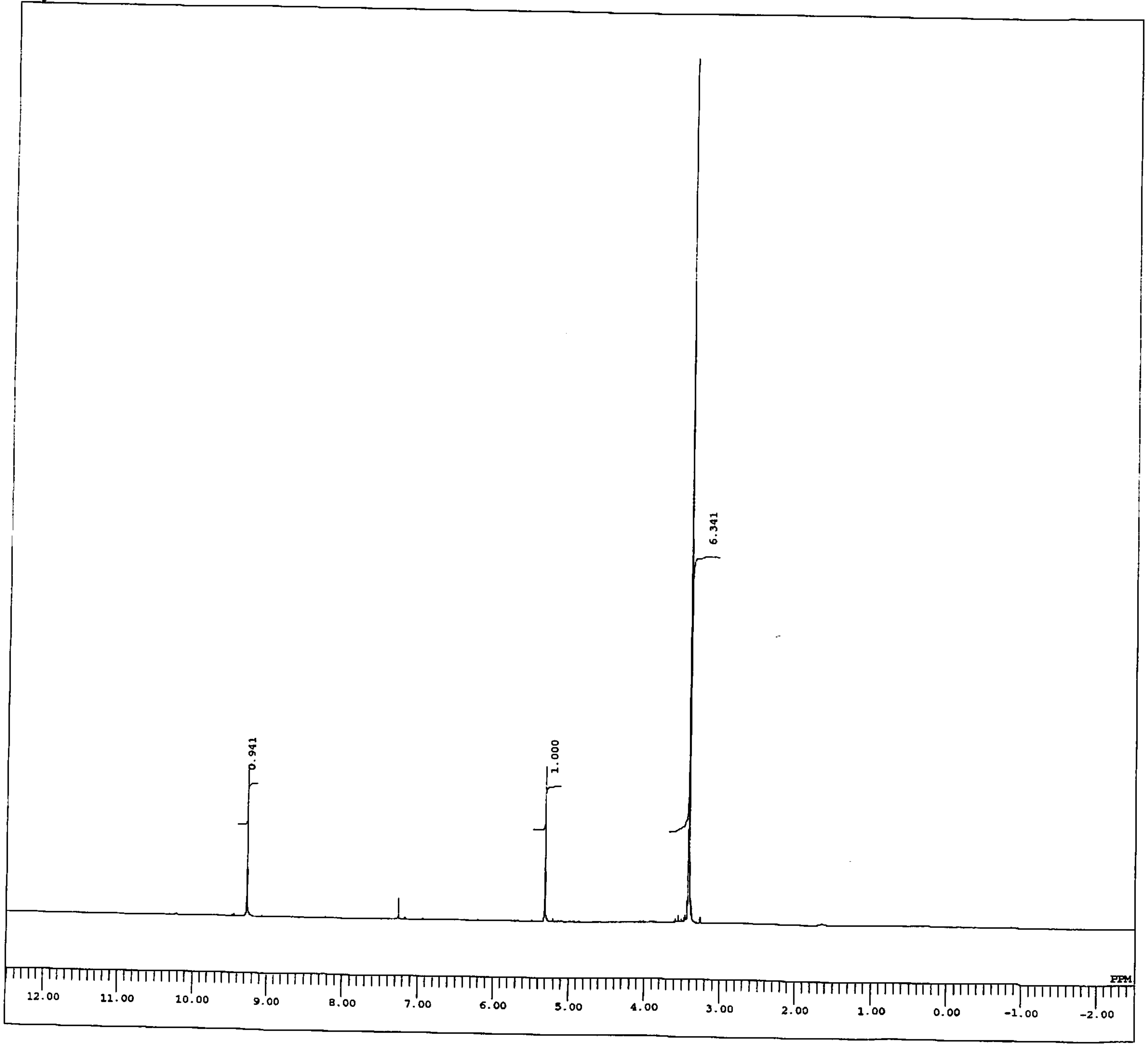

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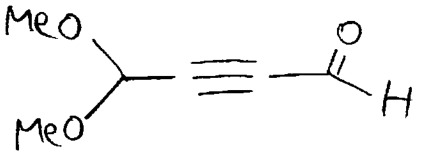
CTEMP         18.9 c
SLVNT  CDCL3
EXREF         7.26 ppm
BF            0.12 Hz
RGAIN           50
```



Step D