SUPPORTING INFORMATION

Phase-Vanishing Reactions with PTFE (Teflon®) as a Phase Screen

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(1) General experimental methods.

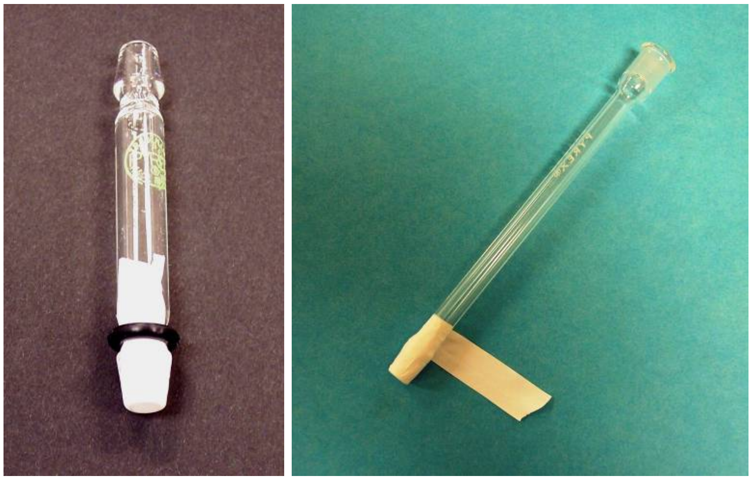
All of the commercially available reagents (bromine, FC-72, cyclohexane, 4-pentenoic acid, vinylacetic acid, phenol, L-menthol, oxalyl chloride, propionyl chloride, aluminum chloride, titanium tetrachloride, dichloromethane, ethyl acetate, hexanes, benzene, acetonitrile, ethanol) were used as supplied without further purification.

Separations of the reaction products were done either by column chromatography or by preparative radial thin layer chromatography (Harrison Chromatotron). GC-MS analyses were performed by means of an Agilent 6890N Gas Chromatograph equipped with an HP-5MS 30 m x 0.25 mm column and an Agilent 5973N MSD. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer in $CDCl_3$ solutions. Temperature measurements were recorded using a Vernier Stainless-Steel Temperature Probe connected to a Texas Instruments TI-83 calculator by means of the Vernier LabPro^{TM} interface. Data were transferred to a PC as an Excel file. All of the isolated products were known compounds and gave satisfactory GC-MS and ^{1}H NMR data. Compounds **9, 12 and 13** are commercially available and were identified by comparison with samples purchased from Aldrich. ^{1}H NMR spectra of the compounds (**2**,[1] **3**,[1] **5**,[2] **16**,[3] and **17**[4] have been reported in the literature. Compounds **6**[5] and **15**[6] have been reported. However, it appears that their ^{1}H NMR spectra have not been reported so far.

Various PTFE-sealed tubes were used to deliver the reagent (Figure 1). Tubes we most frequently used were an inverted disposable pipette, a disposable syringe barrel, and a burette funnel. After the reaction, any remaining traces of the reagent and solvent quickly evaporate and the tube could be reused (Figure 2). In some cases, particularly when the reaction was done under a reflux, PTFE tape had to be secured with an O-ring to prevent it from coming off (Figure 3). If use of an O-ring is not compatible with the reaction conditions, additional wrap of PTFE could be used to secure PTFE phase screen (Figure 3b). While quality and thickness of the PTFE wrap was not important, quality and thickness of a PTFE phase screen was crucial for success of a reaction (page S4). At the end of the reaction, the delivery tube was empty (Figure 4). An exception were reactions in dichloromethane where the solvent was often drawn into the delivery tube and, at the end of the reaction, one had to either collect solutions from both the reaction flask and the delivery tube or lift the delivery tube above the level of the solvent and allow the solution to drip into the flask. A way to prevent dichloromethane from being drawn into the delivery tube is to either provide a pressure outlet, or to carry out a tetraphasic reaction (page S9, figure 14).

Figure 1. Various tubes used to deliver the reagent.

Figure 2. At the end of reaction the PTFE tape was undamaged and the tube could be reused.



a) b)

Figure 3. In some cases the PTFE tape had to be secured with a) an O-ring, or b) an additional PTFE wrap.

Figure 4. At the end of reaction, the delivery tube was empty (two different reactions in ethyl acetate are shown).

(2) Thickness of PTFE tape

PTFE tape was commercially available Teflon tape (Mil. Spec. T-27730A) purchased in hardware stores or Taega Technologies' High Density PTFE tape purchased from Fisher Scientific. Tapes were of different thickness (Figure 5), which for hardware store tapes was not provided. We measured the thickness of each tape. First, ten strips of the tape to be measured were cut (Figure 6a). Next, the strips were stacked and a weight was applied to expel any air that may have been trapped between the strips (Figure 6b). Finally, the thickness was measured with calipers (Figure 6c). Reported thickness of the tape was an average of six measurements (three in the direction of the tape and three perpendicular to it). PTFE tape commonly sold in hardware and plumbing stores had a thickness of 0.05 and 0.06 mm. Interestingly, there was a considerable difference between the two. Thinner tape (0.05 mm) was not suitable for any of the reactions, while the slightly thicker tape (0.06 mm) could be used with less vigorous reagents (e.g. oxalyl chloride in dichloromethane). Taega Technologies' High Density PTFE tape was best suited for PV-PTFE reactions. According to the manufacturer, this tape is 0.08-0.09 mm thick. Our measurements indicated thickness of 0.11 mm. It can be purchased in 1/2 and 1 inch widths. The 1 inch tape, used in our work, was purchased from Fisher Scientific (catalog #14-610-121). The PTFE tape should be applied in the direction of the tape to avoid any stretching. If more than one layer of PTFE tape is used, the tape should be applied perpendicular to each other to create a "mesh" of tape. Layering of the thin tape did not give good results. Very thin tape (red roll shown below) did not provide much of a barrier and, in most cases, was not suitable. Thicker tapes (blue rolls) worked well and, if necessary, two layers of tape were used.

Figure 5. Various types of PTFE tape used in this project.

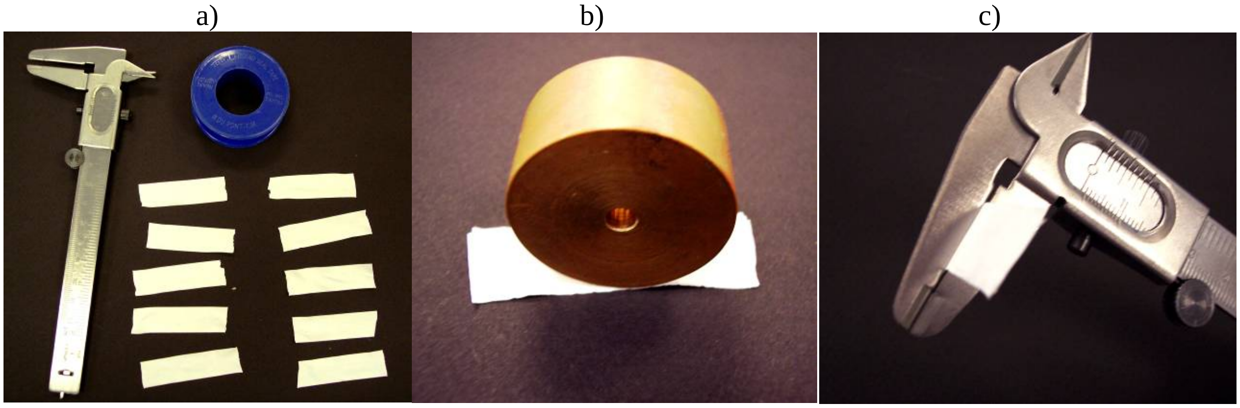

a) b) c)

Figure 6. Measurement of the thickness of PTFE tape.

(3) Mechanical Properties of PTFE tape

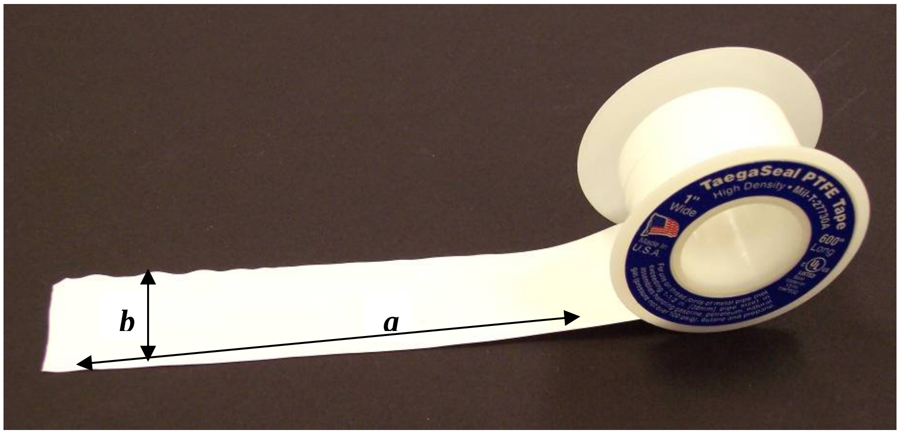
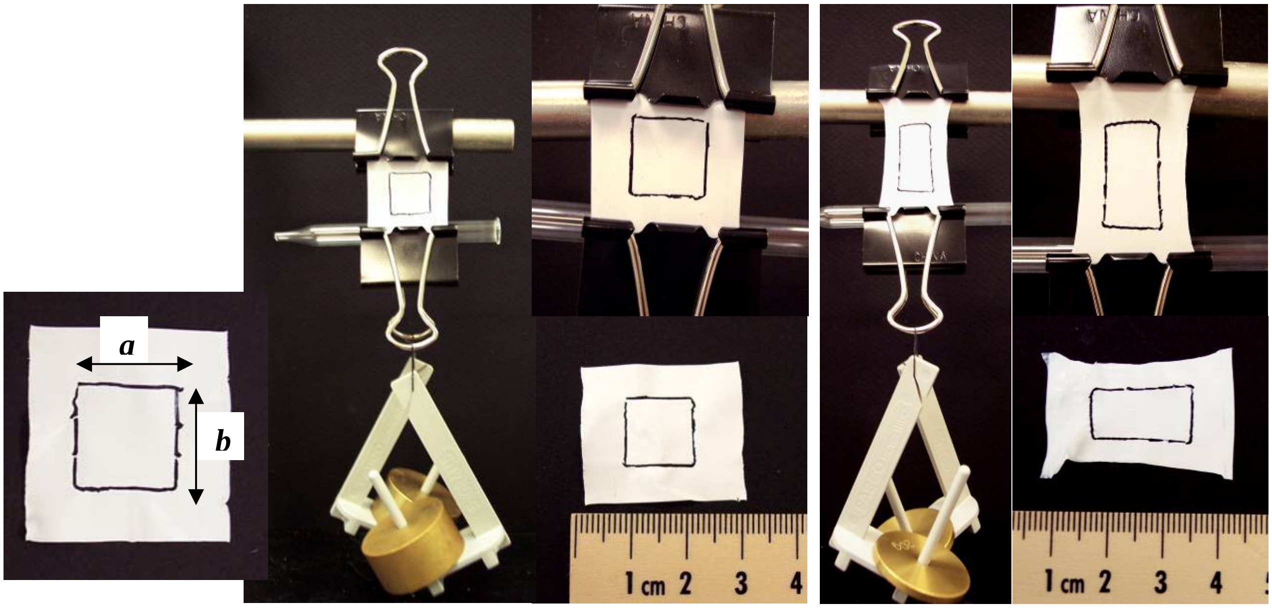


Figure 7. PTFE tape exhibits different mechanical properties in the direction of the tape (***a***) and perpendicular to it (***b***).



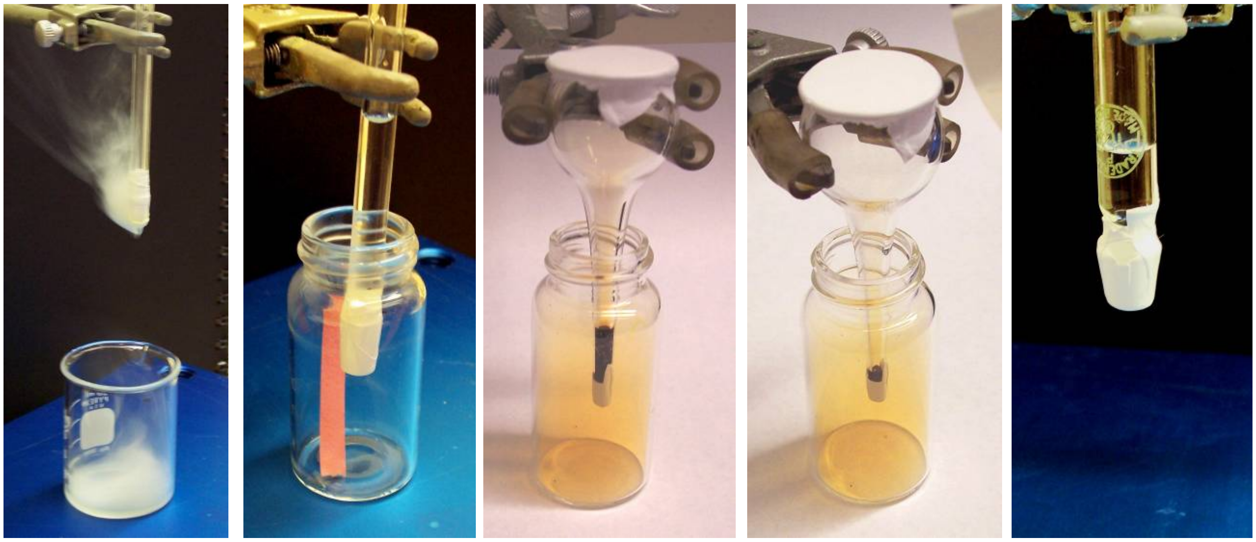
a) b) c)

Figure 8. a) A square was drawn on PTFE tape; b) the tape did not stretch when force was applied in the direction of the tape (direction ***a***), and c) stretched when a moderate force was applied perpendicular to it (direction ***b***).

Taega Technologies' High Density PTFE tape was used in most of the experiments described in this manuscript and its mechanical properties were tested. The tape exhibited different mechanical properties in the direction of the tape (***a***) and perpendicular to it (***b***). A square with 1 cm sides was drawn on an approximately square piece of PTFE tape (Figure 8a) and various weights (20 g, 100 g and 21 g weight of the assembly) were applied in the directions ***a*** and ***b***. There was no noticeable stretching when a considerable force (221 g) was applied in the direction of the tape (Figure 8b) for a period of 10 minutes or longer. On the other hand, when only a moderate force (61 g) was applied perpendicular to the direction of the tape for a few seconds, it stretched to approximately double its length (Figure 8c). Thus, it was possible to apply the tape to the end of a tube without stretching it.

(4) Permeability of PTFE tape

Permeability of PTFE tape was determined only qualitatively as being high, when the liquid passes through it without any resistance, medium, when it was observed that a liquid passed through after some delay (30-60 min) and low, when no liquid passes through after several hours. Thus, PTFE tape was highly permeable towards $(COCl)_2$ and $TiCl_4$. $TiCl_4$ easily and instantaneously passed through two layers of PTFE (Figure 9a). Oxalyl chloride passed through two layers as shown by the color change of the pH indicator paper (Figure 9b). Permeability was moderate towards reagents such as bromine, which passed through a single PTFE layer after ~45 min. Bromine vapors were observed immediately (Figure 9c), while most of the bromine passed through after ~30 min (Figure 9d). When the tube was immersed in a solvent, diffusion of bromine was much faster. It appears that an equilibrium is established between liquid bromine in the delivery tube and bromine vapors in the vessel. If a bromine vapors are removed, either by dissolving them in a solvent or by blowing them away with nitrogen, additional bromine diffuses into the vessel. The faster the vapors were removed the faster the bromine diffused through PTFE. When a delivery tube was placed in an empty sealed vessel with no leaks, the vessel filled with bromine vapors and liquid bromine remained in the tube for several days. Permeability was low towards reagents, such as phthalates, which did not pass through a single layer of PTFE tape after a period of several hours (Figure 9e).



a) b) c) d) e)

Figure 9. Permeability of PTFE.

(5) Reaction under a reflux

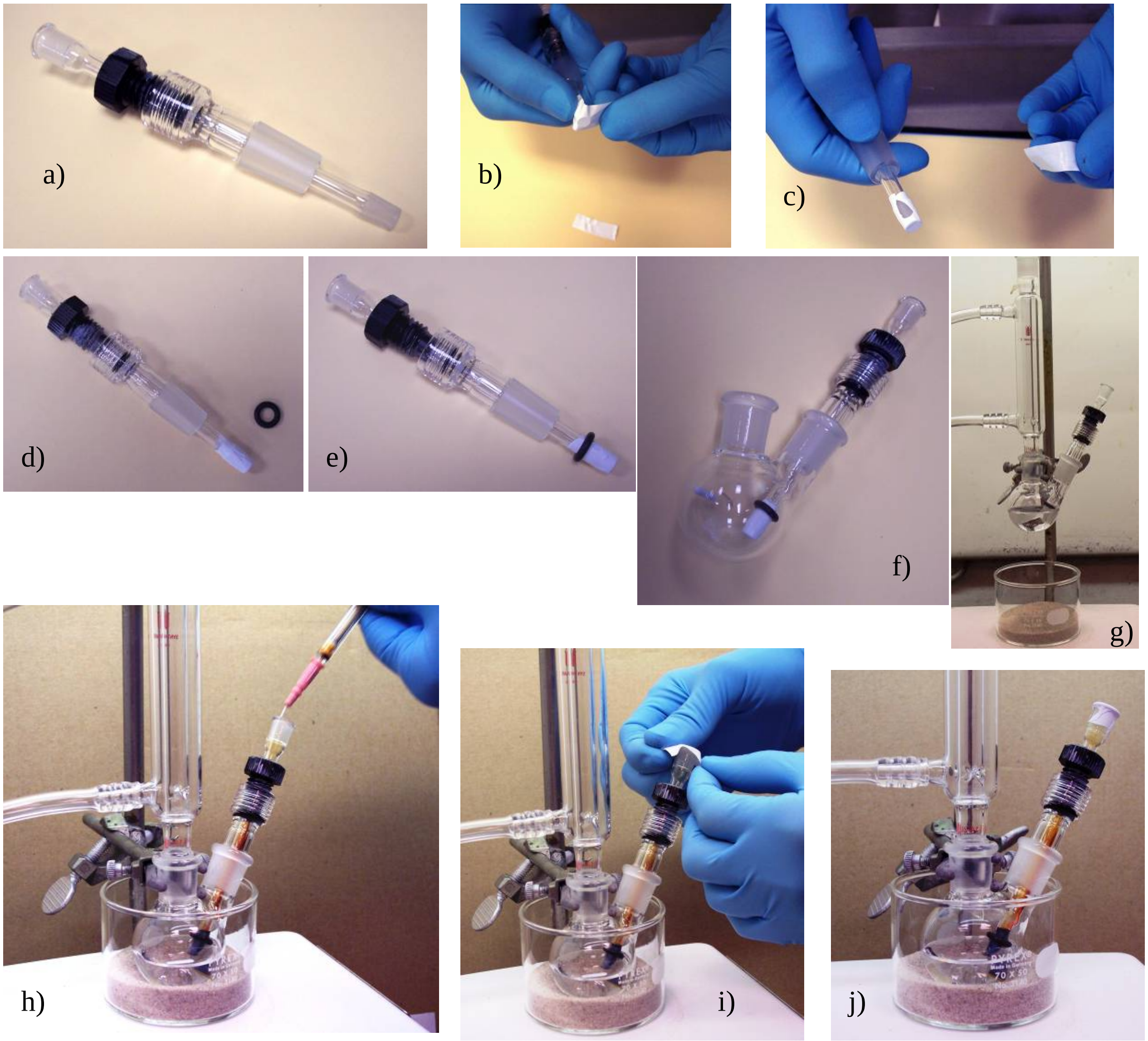


Figure 10. Setting up of a reaction under a reflux.

The most complex PV-PTFE reaction set up involved reaction under a reflux. The procedure for preparation and filling of the reagent tube is identical to that carried out in other PV-PTFE experiments.

A thermometer adapter and a tube of suitable diameter that fits the adapter were used (Figure 10a). The first layer of PTFE tape was applied in the direction of the tape to avoid any stretching (Figure 10b). Another layer of PTFE tape was applied on the top of the first one (Figure 10c). The second layer was applied in the direction of the tape and perpendicular to the first layer. The PTFE tape was secured with an O-ring (Figures 10d and e). The tube set up was inserted into a two-neck round bottom flask (Figure 10f), and a reflux condenser was placed on the flask (Figure 10g). Reagent (bromine) was added to the tube (Figure 10h), and PTFE tape was used to cover the top of the tube to prevent any evaporation of the reagent (Figures 10i and 10j). A photograph and a scheme of the assembled reflux apparatus are shown in the Figures 11 and 12, respectively.

Figure 11. A reflux set up.

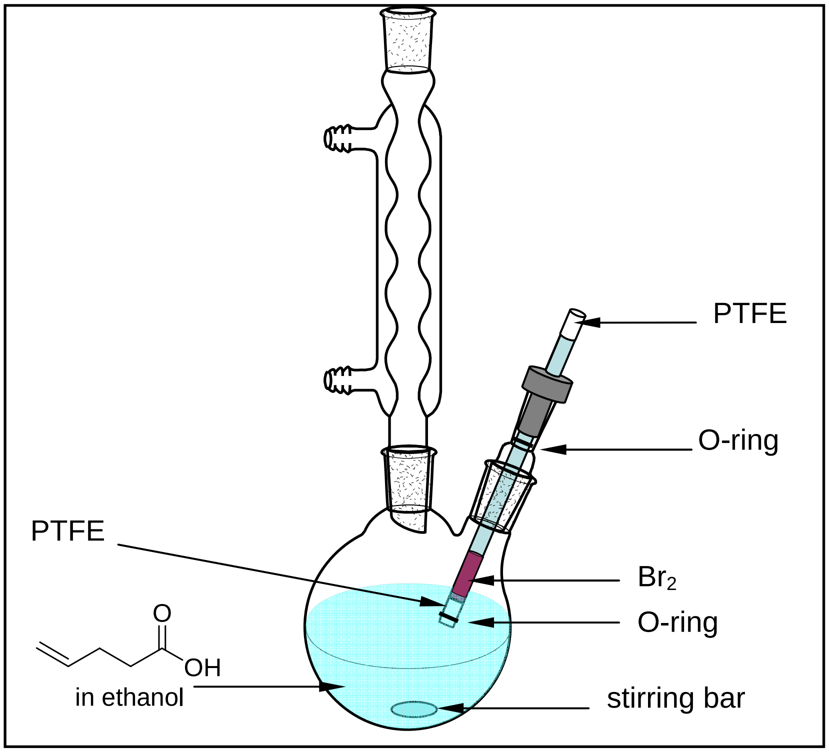


Figure 12. Scheme of a reflux set up.

(6) Tetraphasic reactions

Two tetraphasic reactions of different design were carried out.

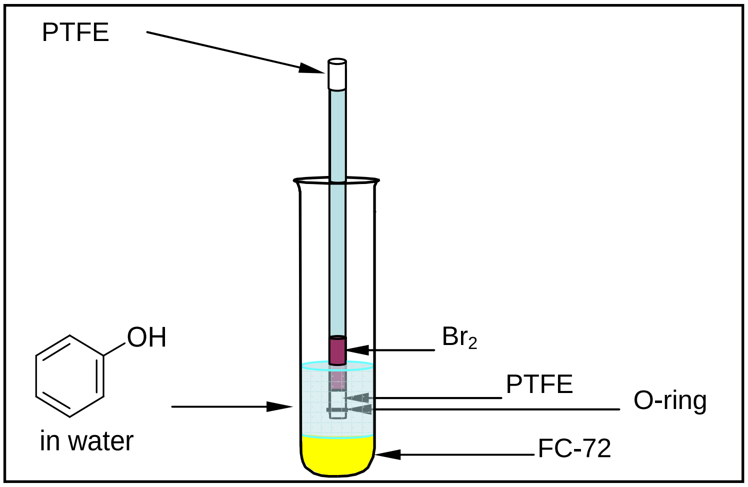


Figure 13. Tetraphasic PV-PTFE bromination of phenol.

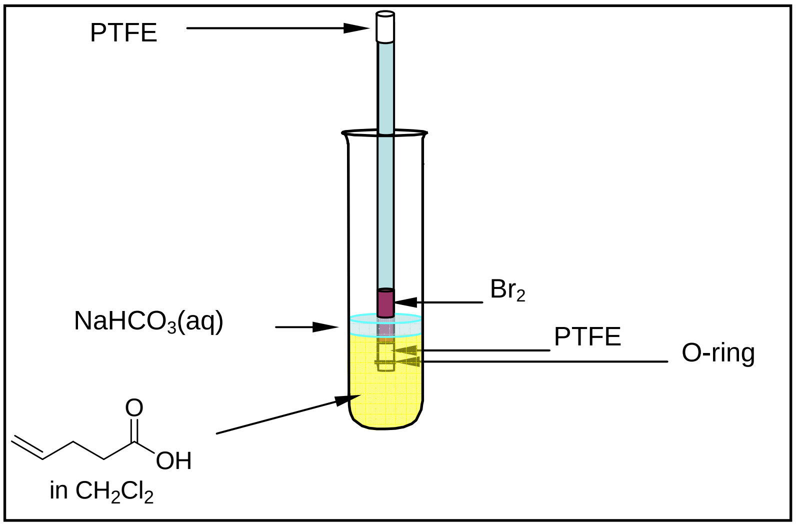
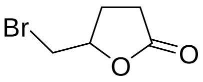


Figure 14. Tetraphasic bromolactonization of 4-pentenoic acid.

Tetraphasic PV-PTFE bromination of phenol (Figure 13) was carried out in water as a solvent and involved addition of the additional heavier phase (perfluorohexane, FC-72). That phase was added to the reaction vessel first. The purpose of it was to purify the reaction product. Impurities (mainly 2,4-dibromophenol) diffused through FC-72 and collected on the bottom, while 2,4,6-tribromophenol solidified at the interface of water and FC-72.

Tetraphasic bromolactonization of 4-pentenoic acid (Figure 14) was carried out in dichloromethane as a solvent and involved addition of a lighter phase (aqueous NaHCO$_3$). That phase was added to the reaction vessel last. The purpose of it was to convert the acid into the corresponding anion and facilitate the bromolactonization reaction.

(7) Experimental procedures



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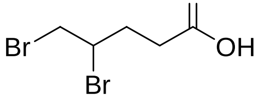
5-(Bromomethyl)-dihydrofuran-2(3*H*)-one (**2**) **from a tetraphasic reaction**. A stirring bar, 0.200 g (2.0 mmol) of 4-pentenoic acid and 2.0 mL of dichloromethane were placed into a 20 mL vial (***note: The reaction is very vigorous accompanied by effervescence and foaming. The reaction vessel must be large to avoid losses.***). A PTFE sealed tube filled with 0.11 mL of bromine was inserted into the dichloromethane solution. 1 mL of a saturated aqueous solution of $NaHCO_3$ was added to the top of dichloromethane layer. Reaction was completed within 5 minutes. The layers were separated and the aqueous layer was extracted with dichloromethane. Dichloromethane extracts were combined, extracted with saturated aqueous $NaHCO_3$ and dried (anhyd $MgSO_4$). Evaporation of dichloromethane under a reduced pressure gave 0.294 g (82%) of 5-(bromomethyl)-dihydrofuran-2(3*H*)-one (**2**). Aqueous bicarbonate extracts were combined, acidified and extracted with ethyl acetate. Ethyl acetate extract was dried (anhyd $MgSO_4$) and ethyl acetate was removed under a reduced pressure to gave 0.021 g (4%) of 4,5-dibromopentanoic acid (**3**).

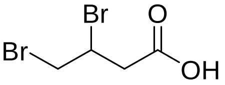
5-(Bromomethyl)-dihydrofuran-2(3*H*)-one (**2**) **from sodium 4-pentenoate**. 4-pentenoic acid (0.200 g; 2.0 mmol) was added to a suspension of Na_2CO_3 (0.120 g) in acetonitrile (2.0 mL) in a 10 mL RB flask. The suspension was stirred for 15 minutes and then a PTFE sealed tube with 0.12 mL (2.4 mmol) of bromine was inserted into the solution. The reaction was continued for 1 hour. The product was partitioned between water and dichloromethane. Aqueous layer was extracted with dichloromethane. Extracts were combined, rinsed with aqueous bicarbonate, dried and dichlormethane was evaporated under a reduced pressure. Yield of 5-(bromomethyl)-dihydrofuran-2(3*H*)-one (**2**) was 0.265 g (74%). A trace of 4,5-dibromopentanoic acid (**3**) was detected by GC-MS after the aqueous layer was acidified and extracted with ethyl acetate. Acid **3** was neither isolated nor quantified.

5-(Bromomethyl)-dihydrofuran-2(3*H*)-one (**2**) **from a reaction in ethyl acetate**. A stirring bar, 0.200 g (2.0 mmol) of 4-pentenoic acid and 5.0 mL of ethyl acetate were placed into a two-neck 25 mL RB flask. The solution was heated to reflux and a PTFE (2 layers) sealed tube filled with 0.12 mL (2.4 mmol) of bromine was inserted into the flask. Bromine was consumed rapidly and the reaction was allowed to proceed for a total of 15 min. Ethyl acetate was evaporated under a reduced pressure and the residue was chromatographed (Harrison Chromatotron, eluting with 4:1 hexanes/ethyl acetate) to give 0.258 g (72%) of 5-(bromomethyl)-dihydrofuran-2(3*H*)-one (**2**) and 0.047 g (9%) of 4,5-dibromopentanoic acid (**3**).



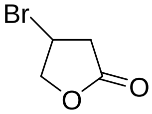
3

4,5-Dibromopentanoic acid (**3**). A stirring bar, 0.200 g (2.0 mmol) of 4-pentenoic acid and 2.0 mL of dichloromethane were placed into a 4 mL vial. A PTFE sealed tube filled with 0.11 mL (2.2 mmol) of bromine was inserted into the solution. Dichloromethane solution was quickly drawn into the tube. Discoloration of bromine was completed within 5 minutes. Evaporation of dichloromethane under a reduced pressure gave 0.489 g (94%) of 4,5-dibromopentanoic acid (**3**). The crude product gave a satisfactory ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (m, 1H), 2.54-2.73 (m, 3H), 3.62 (t, 1H, *J* = 10.0), 3.87 (dd, *J* = 10.0, 4.0), 4.25 (m, 1H).



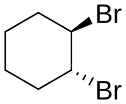
5

3,4-Dibromobutanoic acid (**5**). A stirring bar, 0.175 g (2.0 mmol) of vinylacetic acid and 2.0 mL of dichloromethane were placed into a 4 mL vial. A PTFE sealed tube filled with 0.12 mL (2.4 mmol) of bromine was inserted into the solution. Dichloromethane solution was quickly drawn into the tube. Discoloration of bromine was completed within 5 minutes. Evaporation of ethyl acetate under reduced pressure gave 0.408 g (83%) of 3,4-dibromobutanoic acid (**5**). The crude product gave a satisfactory ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90 (dd, 1H, *J* = 16.8, 9.2), 3.28 (dd, 1H, *J* = 16.8, 4.0), 3.88 (dd, 1H, *J* = 10.4, 8.0), 3.97 (dd, *J* = 10.4, 4.8), 4.56 (m, 1H).



6

5-Bromodihydrofuran-2(3*H*)-one (**6**). A stirring bar, 0.1750 g (2.0 mmol) of vinylacetic acid and 2.0 mL of dichloromethane were placed into a 20 mL vial (***note: The reaction is very vigorous accompanied by effervescence and foaming. The reaction vessel must be large to avoid losses.***). A PTFE sealed tube filled with 0.11 mL (2.2 mmol) of bromine was inserted into the dichloromethane solution. 1.0 mL of a saturated aqueous solution of $NaHCO_3$ was added to the top of dichloromethane layer. Reaction was completed within 5 minutes. The layers were separated and the aqueous layer was extracted with dichloromethane. Dichloromethane extracts were combined, extracted with saturated aqueous $NaHCO_3$ and dried (anhyd $MgSO_4$). Evaporation of dichloromethane under a reduced pressure gave 0.1056 g (32%) of 5-bromodihydrofuran-2(3*H*)-one (**6**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.92 (dd, 1H, *J* = 17.2, 9.2), 3.43 (dd, 1H, *J* = 17.2, 3.6), 3.72 (t, 1H, *J* = 10.4), 3.91 (dd, *J* = 10.4, 4.4), 4.47 (m, 1H). Aqueous bicarbonate extracts were combined, acidified and extracted with ethyl acetate. Ethyl acetate extract was dried (anhyd $MgSO_4$) and ethyl acetate was removed under a reduced pressure gave 0.2313 g (47%) of 3,4-dibromobutanoic acid (**5**).

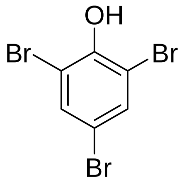


9

***trans*-1,2-Dibromocyclohexane** (**9**) **from a reaction in dichloromethane**. A stirring bar, 0.17 mL (2.0 mmol) of cyclohexene and 2.0 mL of dichloromethane were placed into a 4 mL brown vial. A PTFE sealed tube filled with 0.11 mL (2.2 mmol) of bromine was inserted into the solution. It took about 5 minutes for bromine to diffuse into the solution. Evaporation of dichloromethane gave 0.45 g (93%) of crude *trans*-1,2-dibromocyclohexane (**9**). Bulb-to-bulb distillation under a reduced pressure gave 0.34 g (70%) of pure *trans*-1,2-dibromocyclohexane (**9**).

***trans*-1,2-Dibromocyclohexane** (**9**) **from a reaction in ethyl acetate.** A stirring bar, 0.17 mL (2.0 mmol) of cyclohexene and 2.0 mL of EtOAc were placed into a 4 mL vial. A PTFE sealed tube filled with 0.11

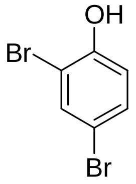
mL (2.2 mmol) of bromine was inserted into the solution. It took about 10 minutes for bromine to diffuse into the solution. Evaporation of EtOAc gave 0.42 g of the product. GC-MS analysis showed that it was 9:1 mixture of *trans*-1,2-dibromocyclohexane (**9**) and 3-bromocyclohexene (**10**).



12

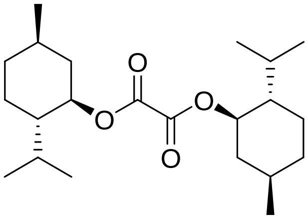
2,4,6-Tribromophenol (**12**). A stirring bar, 0.188 g (2.0 mmol) of phenol and 2.0 mL of water were placed into a 10 mL RB flask. A PTFE sealed tube filled with 0.32 mL (6.4 mmol) of bromine was inserted into the flask. Bromine was consumed rapidly and the reaction was allowed to proceed until all of it was consumed (less than 10 min). Stirring was continued for another 20 min and the white solid was filtered and rinsed with a small amount of water to give 0.642 g (97%) of 2,4,6-tribromophenol (**12**), which according to ^{1}H NMR analysis was impure. GC-MS analysis revealed that the major impurities were 2,4-dibromophenol, 4-bromophenol, 2,6-dibromophenol and 2-bromophenol.

2,4,6-Tribromophenol (**12**). A stirring bar, 2.0 mL of FC-72 and a solution of 0.188 g (2.0 mmol) of phenol in 2.0 mL of water were placed into a 10 mL RB flask. A PTFE sealed tube filled with 0.32 mL (6.4 mmol) of bromine was inserted into the aqueous layer. The reaction was allowed to proceed for 3 h. A layer of white solid formed on the top of FC-72 layer, while a brown liquid settled below it. White solid was filtered and rinsed with a small amount of water to give 0.576 g (87%) of 2,4,6-tribromophenol (**12**), which according to ^{1}H NMR analysis was pure. GC-MS analysis of the brown liquid revealed that the major component was 2,4-dibromophenol accompanied by some 2,4,6-tribromophenol and minor amounts of 4-bromophenol, 2,6-dibromophenol and 2-bromophenol.



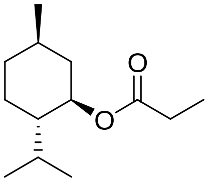
13

2,4-Dibromophenol (**13**). A stirring bar, 0.094 g (1.0 mmol) of phenol and 2.0 mL of dichloromethane were placed into a 4 mL vial. A PTFE sealed tube filled with 0.15 mL (3.0 mmol) of bromine was inserted into the flask. Bromine was consumed rapidly and the reaction was allowed to proceed for 1 hour. Solution was rinsed with aqueous sodium bisulfate, dichloromethane was removed under a reduced pressure and the residue was chromatographed (Harrison Chromatotron, eluting with 3:1 hexanes/ethyl acetate) to give 0.373 g (74%) of 2,4-dibromophenol (**13**).



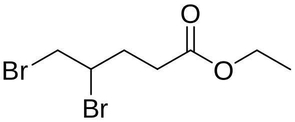
15

Dimenthyl oxalate (**15**). A stirring bar, 0.624 g (4.0 mmol) of menthol and 4.0 mL of dichloromethane were placed into a 10 mL RB flask. A PTFE sealed tube filled with a solution of 0.20 mL (2.3 mmol) of oxalyl chloride in 0.5 mL of dichloromethane was inserted into the flask. The reaction was allowed to proceed until all of oxalyl chloride solution diffused into the vial (less than 10 min). Stirring was continued for total of 1 hour. The solution was rinsed with a small amount of water, dried (anhyd $MgSO_4$) and dichloromethane was removed under a reduced pressure to give 0.660 g (90%) of dimenthyl oxalate (**15**). ^1H NMR (400 MHz, $CDCl_3$) δ 0.85 (d, 3H, *J* = 6.8), 1.00 (dd, 6H, *J* = 6.8 and 9.6), 1.00 (m, 1H), 1.15 (m, 1H), 1.23 (q, 1H, *J* = 11.2), 1.62 (m, 2H), 1.80 (m, 2H), 1.95 (m, 1H), 2.15 (m, 1H), 4.94 (dt, 1H, *J* = 10.8 and 4.8).



16

Menthyl propionate (**16**). A stirring bar, 0.312 g (2.0 mmol) of menthol and 2.0 mL of dichloromethane were placed into a 4 mL vial. A PTFE sealed tube filled with 0.20 mL (2.3 mmol) of propionyl chloride was inserted into the flask. The reaction was allowed to proceed until all of the propionyl chloride solution diffused into the vial (less than 10 min). Stirring was continued for a total of 30 minutes. Dichloromethane was removed under a reduced pressure to give 0.391 g (92%) of menthyl propionate (**16**). ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.3; 16.3; 20.8; 22.0; 23.4; 26.2; 27.9; 31.3; 34.2; 40.9; 47.0; 73.9; 174.1.



17

Ethyl 4,5-dibromopentanoate (**17**). A stirring bar, 0.200 g (2.0 mmol) of 4-pentenoic acid and 5.0 mL of ethanol were placed into a two-neck 25 mL RB flask. The solution was heated to reflux and a PTFE (2 layers) sealed tube filled with 0.12 mL (2.4 mmol) of bromine was inserted into the flask. Bromine was consumed rapidly and the reaction was allowed to proceed for a total of 15 min. Ethanol was evaporated under a reduced pressure and the residue was chromatographed (Harrison Chromatotron, eluting with 4:1 hexanes/ethyl acetate) to give 0.432 g (75%) of ethyl 4,5-dibromopentanoate (**17**). ^1H NMR (400 MHZ, $CDCl_3$) δ: 1.25 (t, 3H, *J* = 7.1 Hz), 2.01 (m, 2H), 2.55 (m, 3H), 3.62 (dd, 1H, *J* = 10.4, 9.8), 3.85 (dd, 1H, *J* = 10.4, 4.5), 4.12 (q, 2H, *J* = 7.1), 4.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2; 31.4; 31.7; 35.9; 51.6; 60.7; 172.3.

MS and NMR spectra

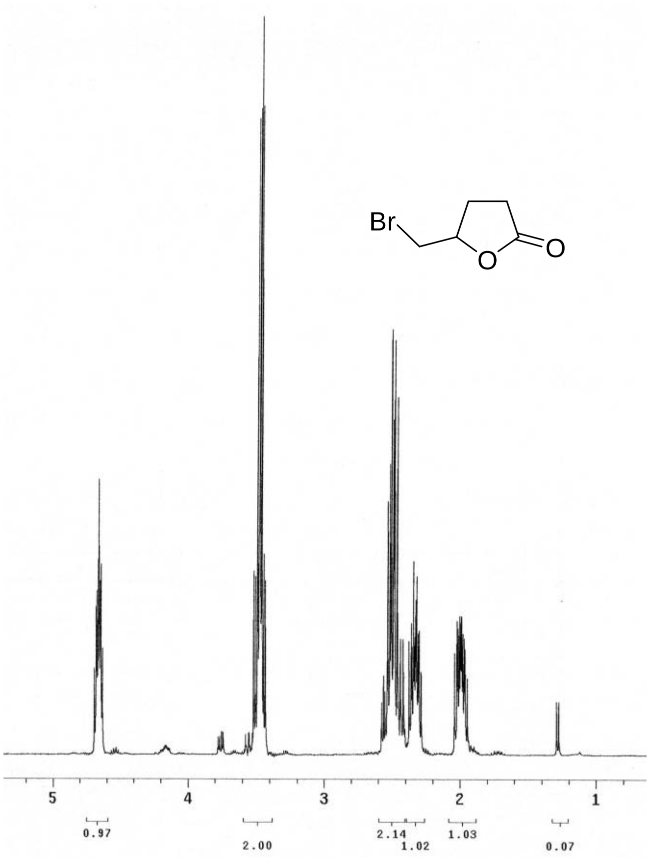
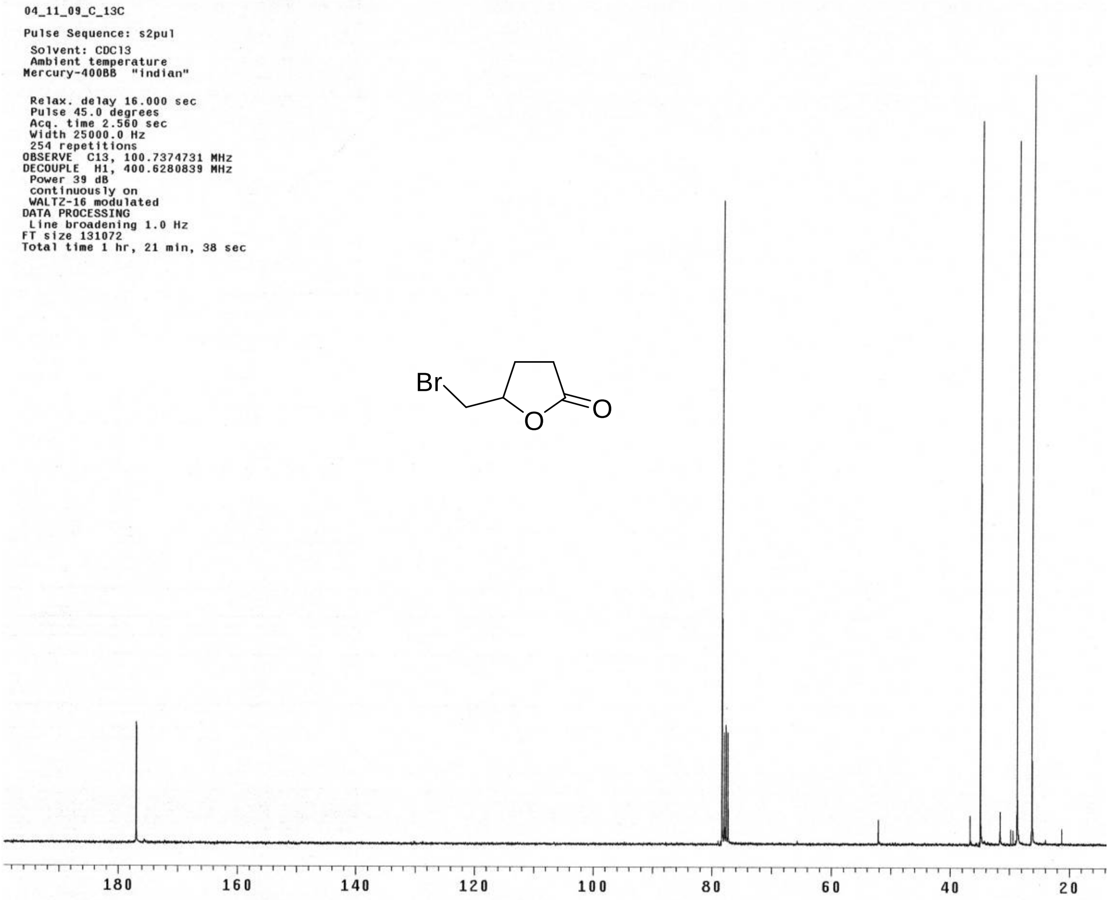


Figure 15. ^{1}H NMR spectrum of 5-(bromomethyl)-dihydrofuran-2(3*H*)-one (**2**).



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DECOUPLE  H1, 400.6280839 MHz
 Power 39 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 21 min, 38 sec
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Figure 16. ^{13}C NMR spectrum of 5-(bromomethyl)-dihydrofuran-2(3*H*)-one (**2**).

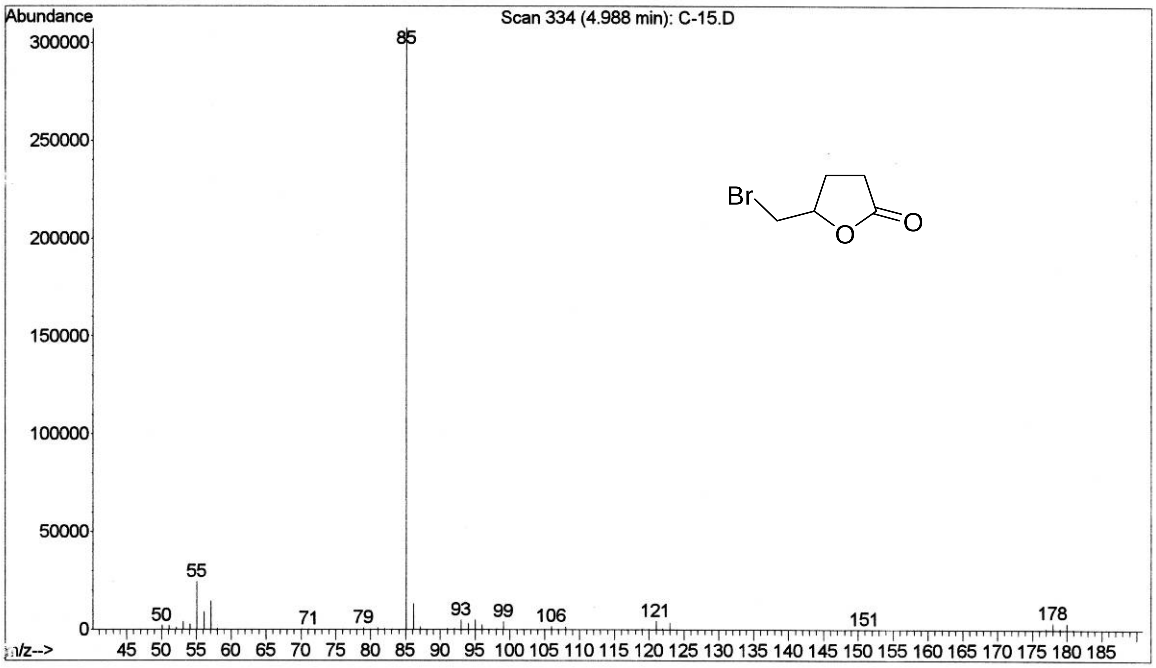


Figure 17. MS of 5-(bromomethyl)-dihydrofuran-2(3*H*)-one (**2**).

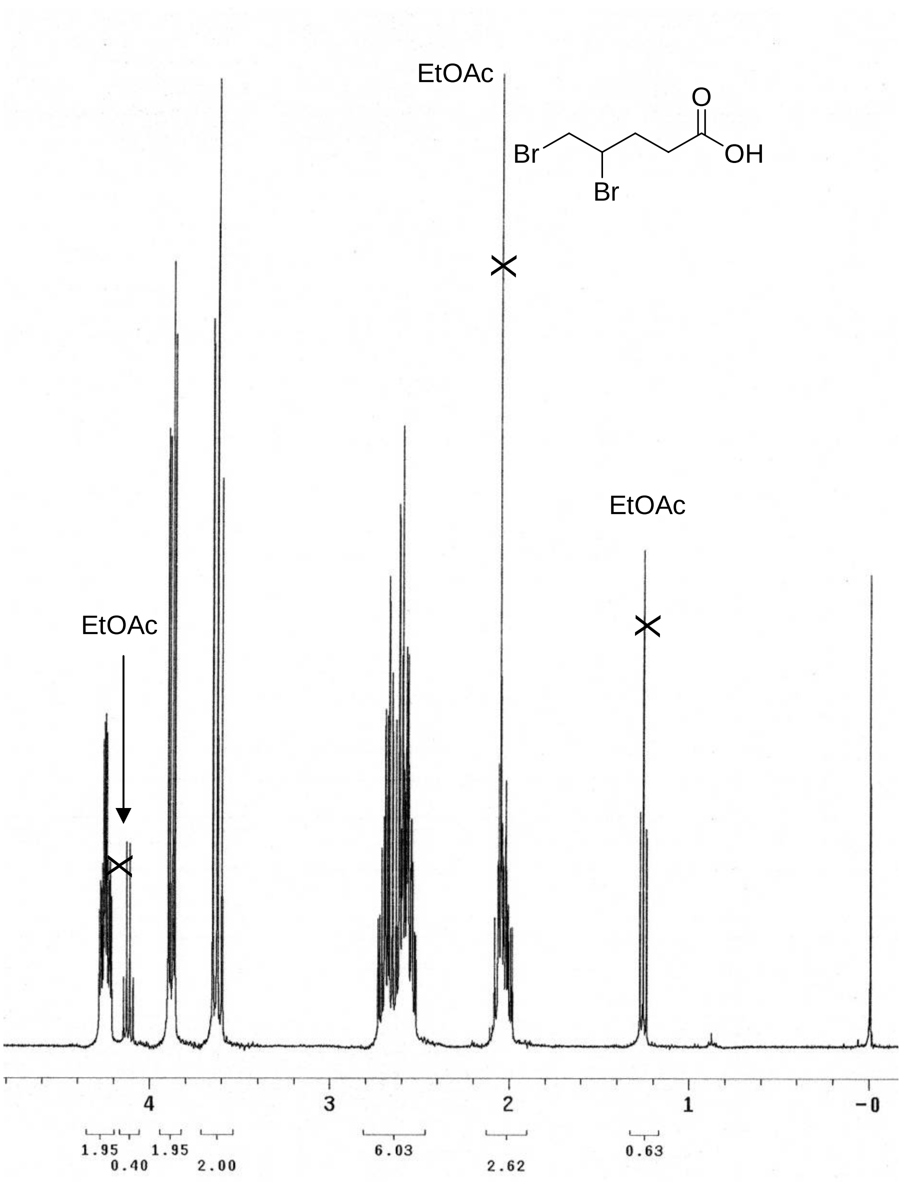


Figure 18. ^{1}H NMR spectrum of 4,5-dibromopentanoic acid (**3**).

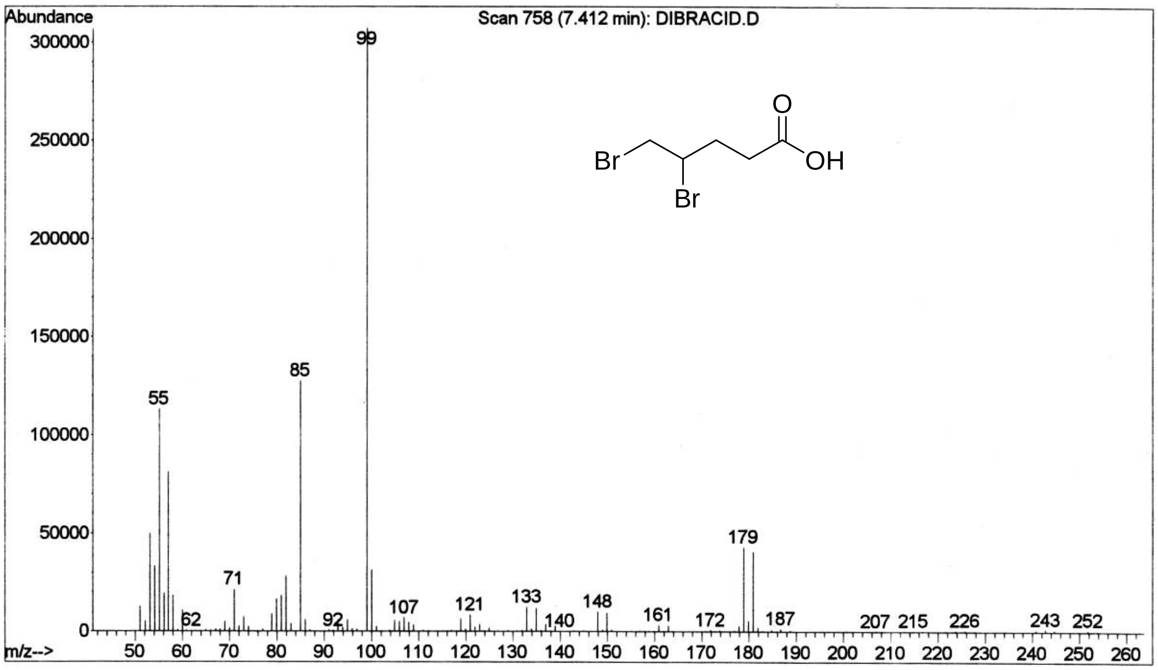
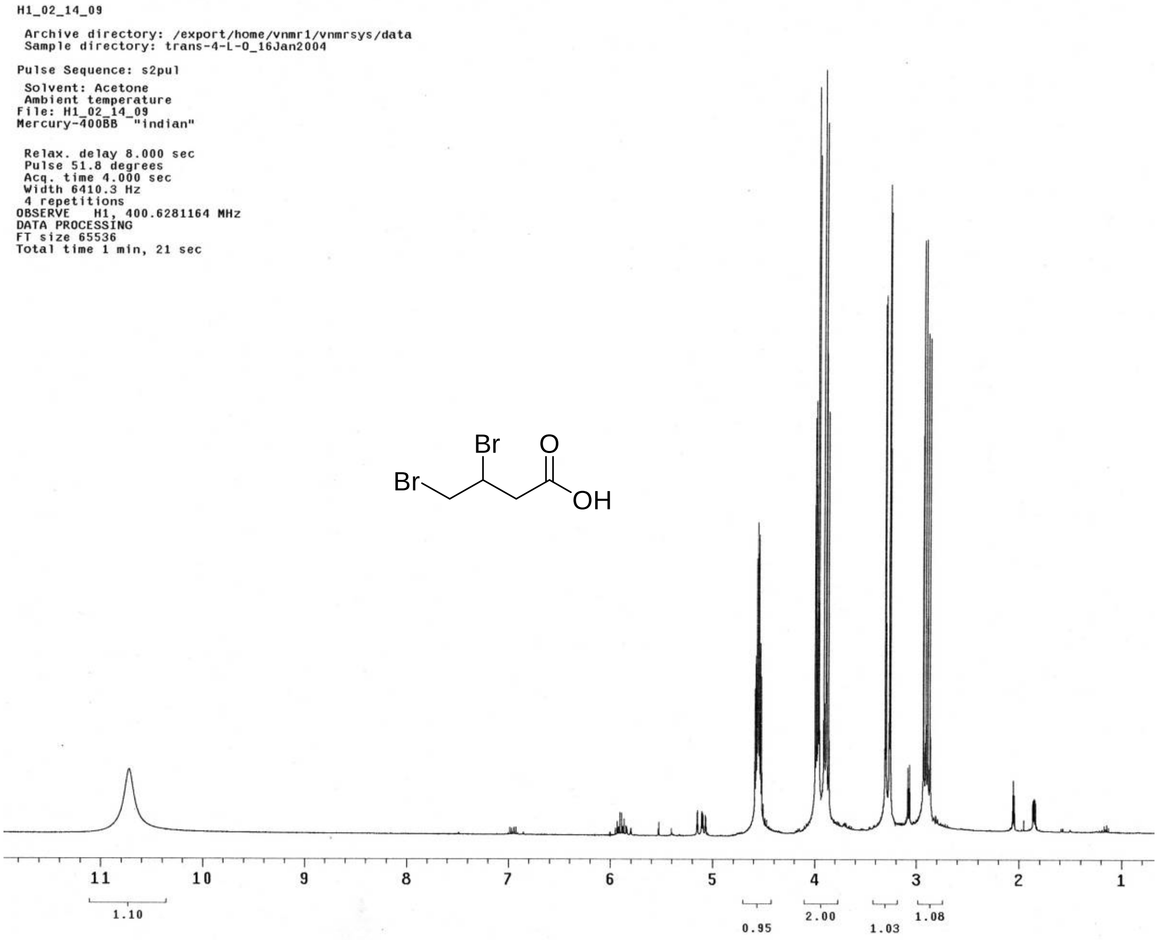


Figure 19. MS of 4,5-dibromopentanoic acid (**3**).



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H1_02_14_09

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DATA PROCESSING
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Total time 1 min, 21 sec
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Figure 20. ^{1}H NMR spectrum of 3,4-dibromobutanoic acid (**5**).

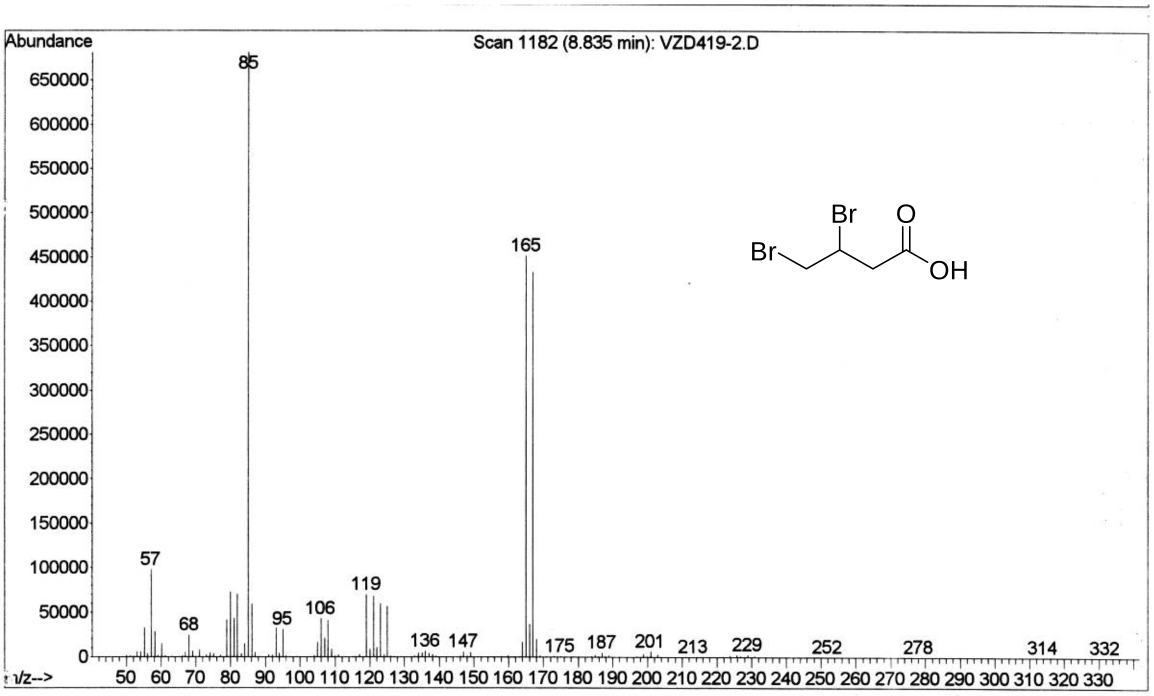
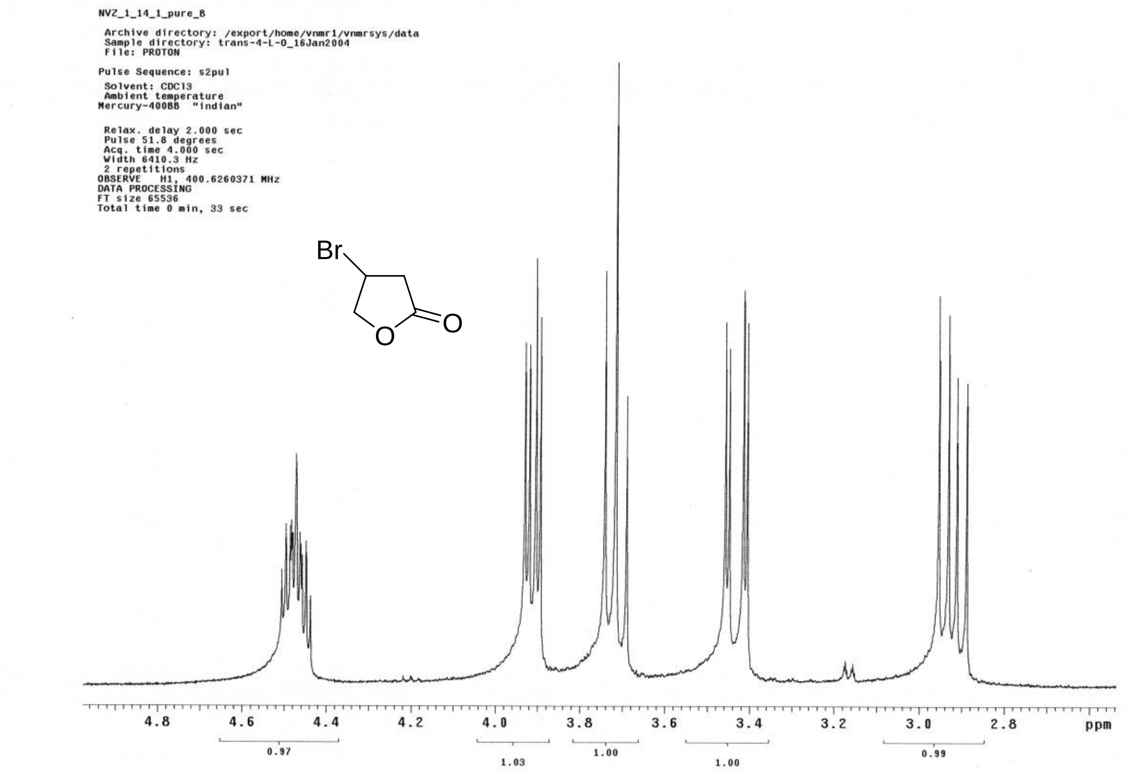


Figure 21. MS of 3,4-dibromobutanoic acid (**5**).



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 File: PROTON

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 Solvent: CDCl3
 Ambient temperature
Mercury-400BB  "indian"

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OBSERVE   H1, 400.6260371 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 33 sec
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Figure 22. ^{1}H NMR spectrum of 5-bromodihydrofuran-2(3*H*)-one (**6**).

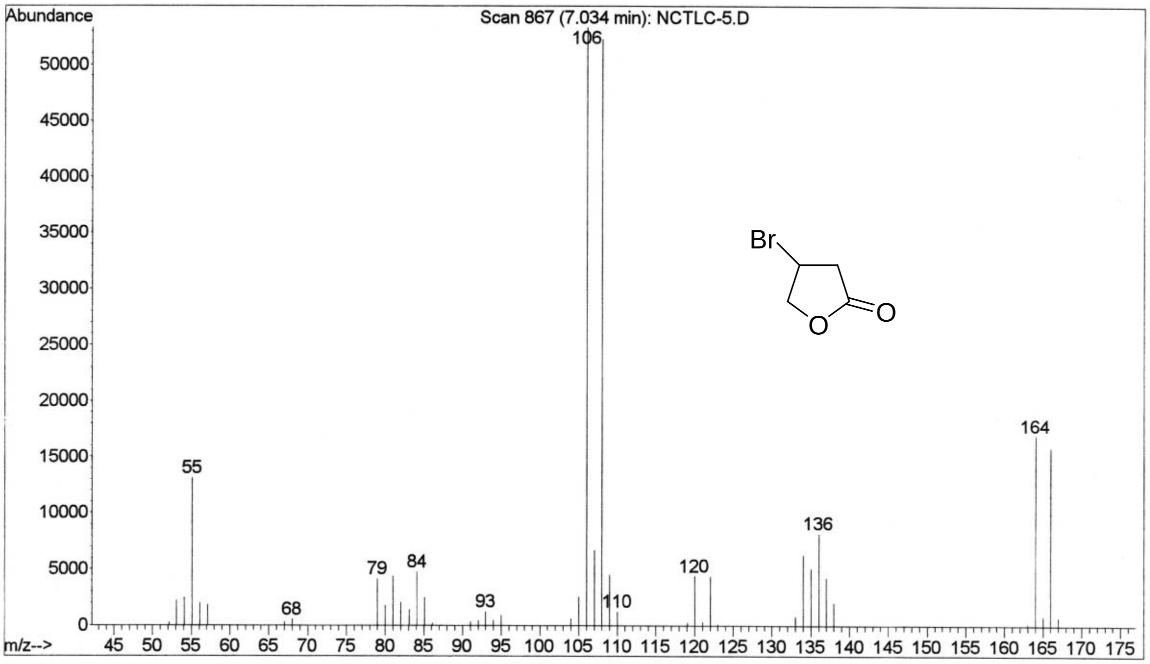


Figure 23. MS of 5-bromodihydrofuran-2(3*H*)-one (**6**).

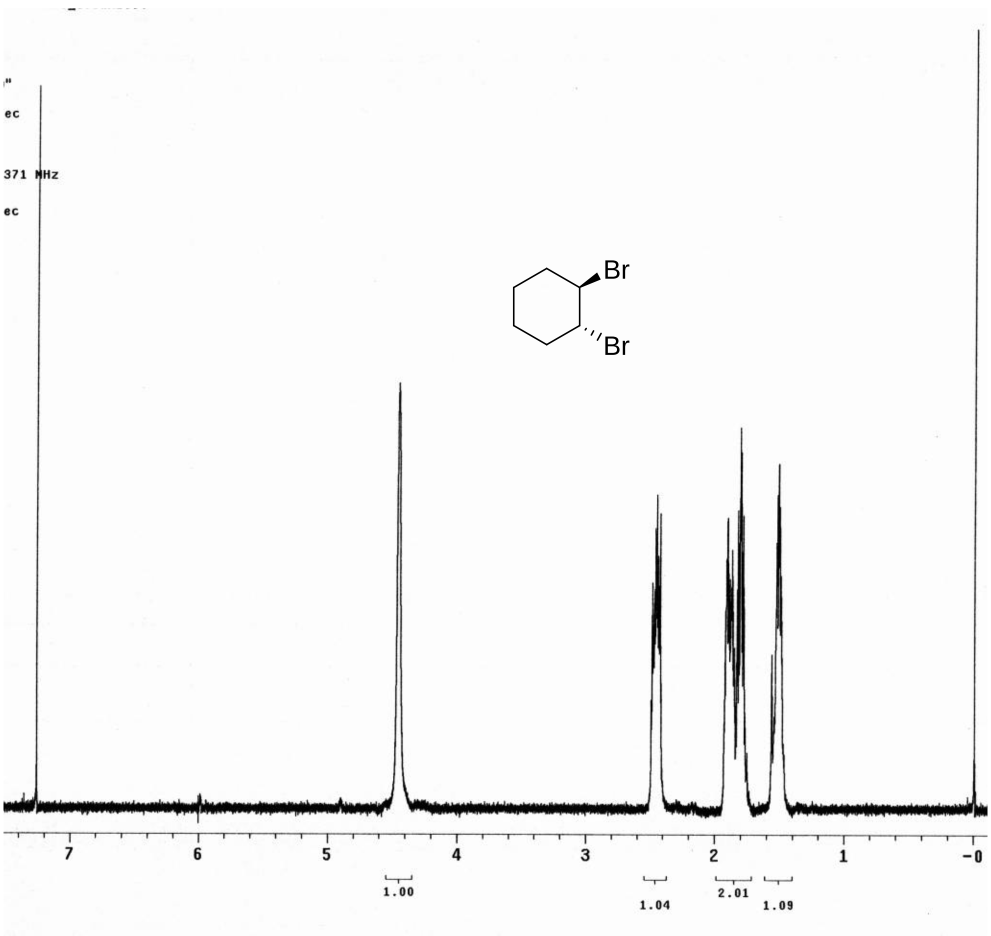


Figure 24. ^{1}H NMR spectrum of *trans*-1,2-dibromocyclohexane (**9**).

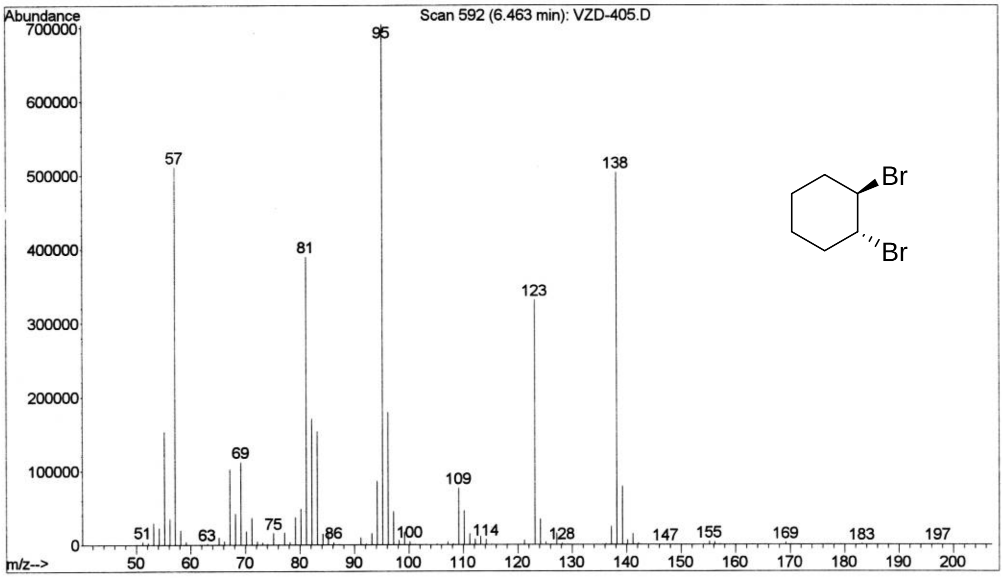


Figure 25. MS of *trans*-1,2-dibromocyclohexane (**9**).

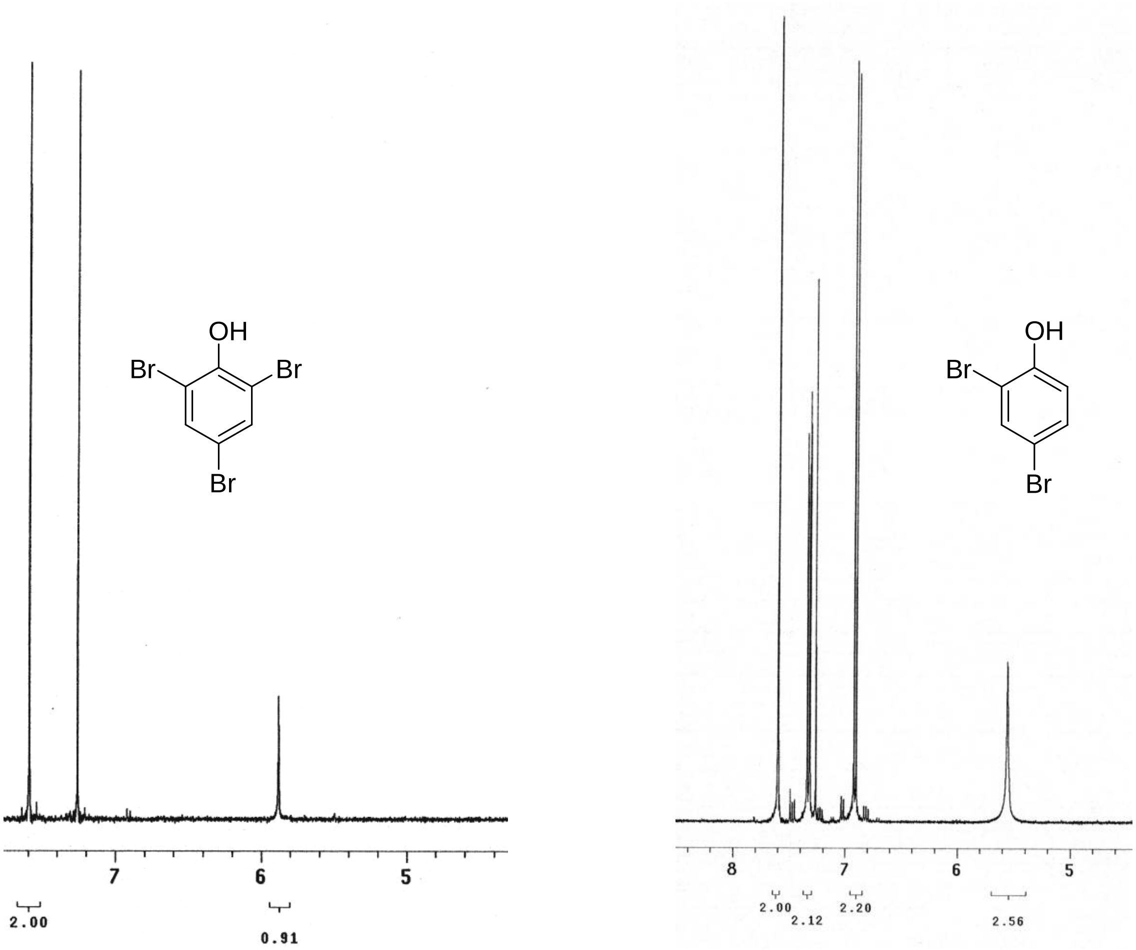


Figure 26. ^{1}H NMR spectra of 2,4,6-tribromophenol (**12**) and 2,4-dibromophenol (**13**).

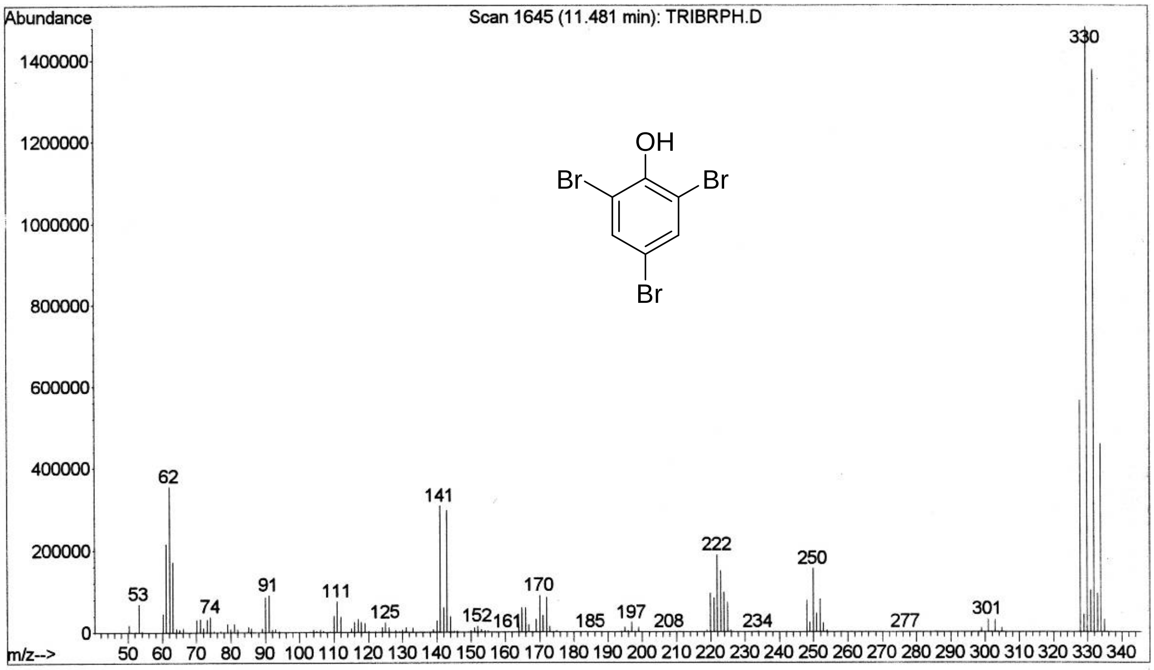


Figure 27. MS of 2,4,6-tribromophenol (**12**).

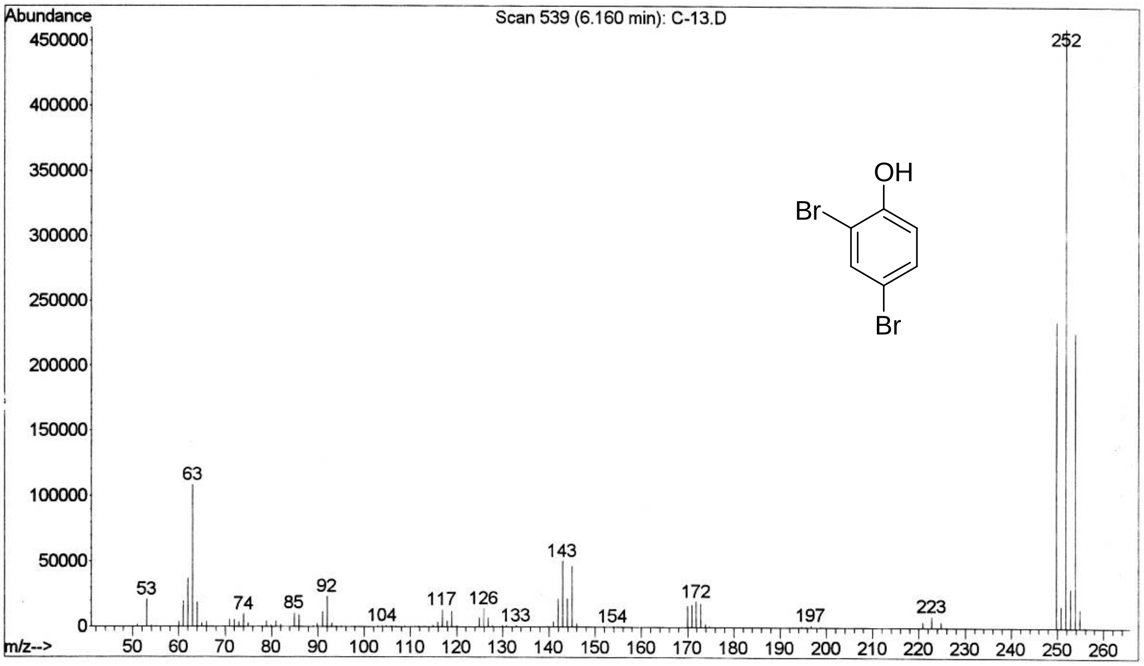


Figure 28. MS of 2,4-dibromophenol (**13**).

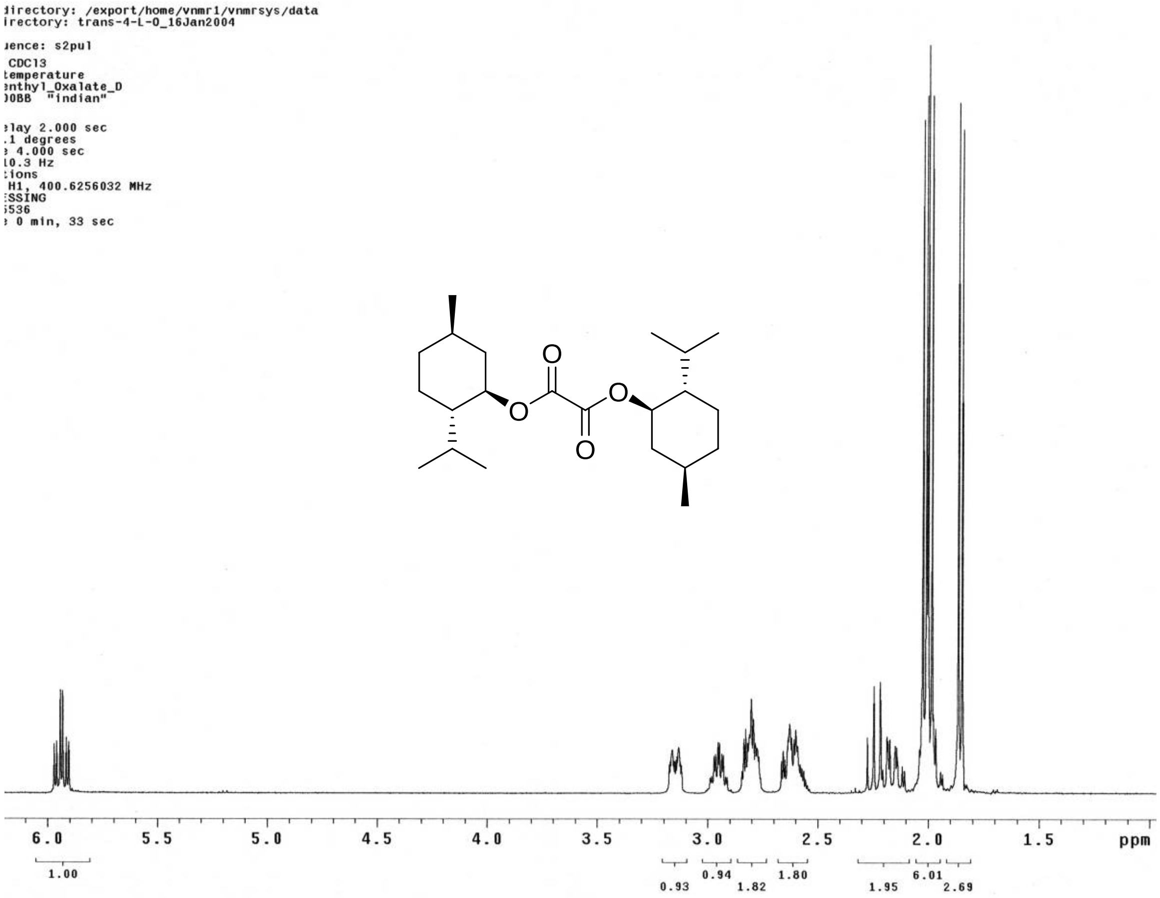


Figure 29. ^{1}H NMR spectrum of dimenthyl oxalate (**15**).

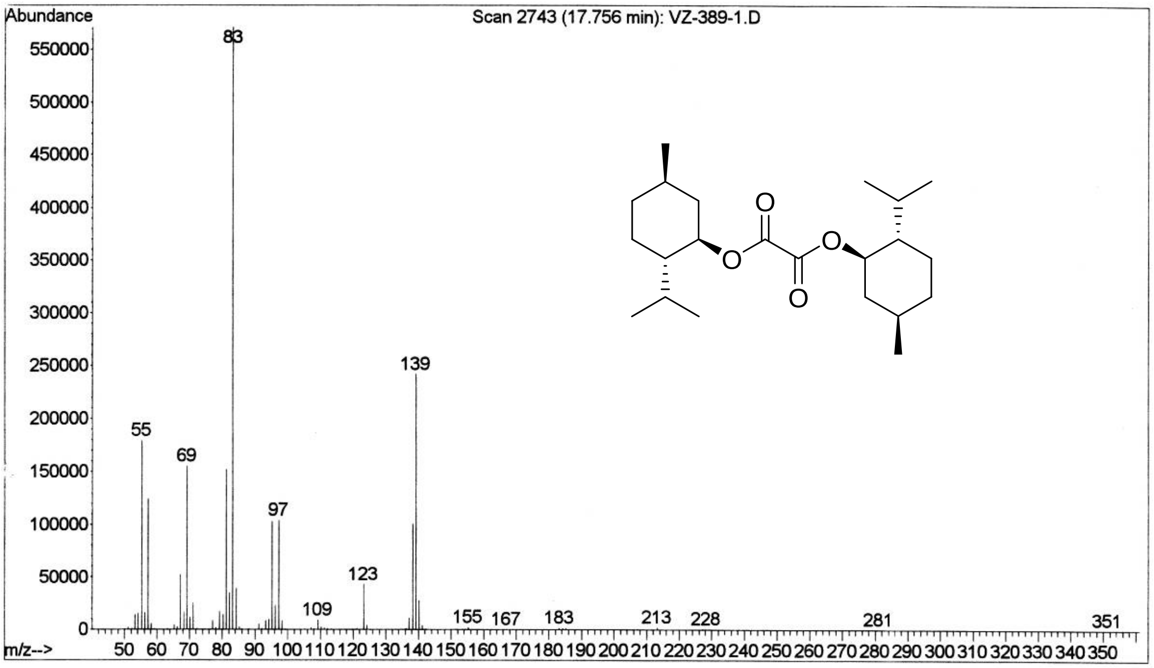


Figure 30. MS of dimenthyl oxalate (**15**).

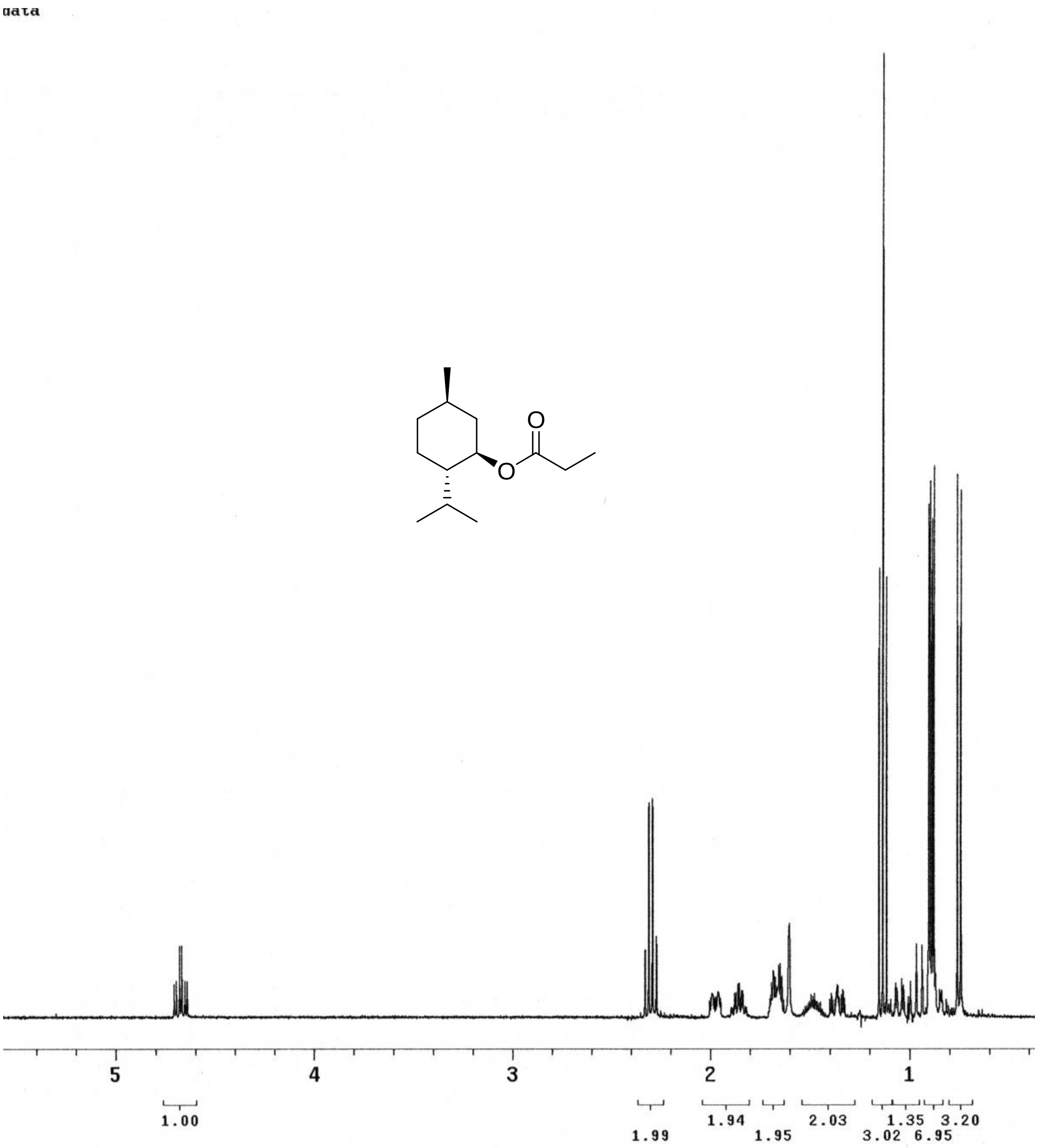


Figure 31. ^{1}H NMR spectrum of menthyl propionate (**16**).

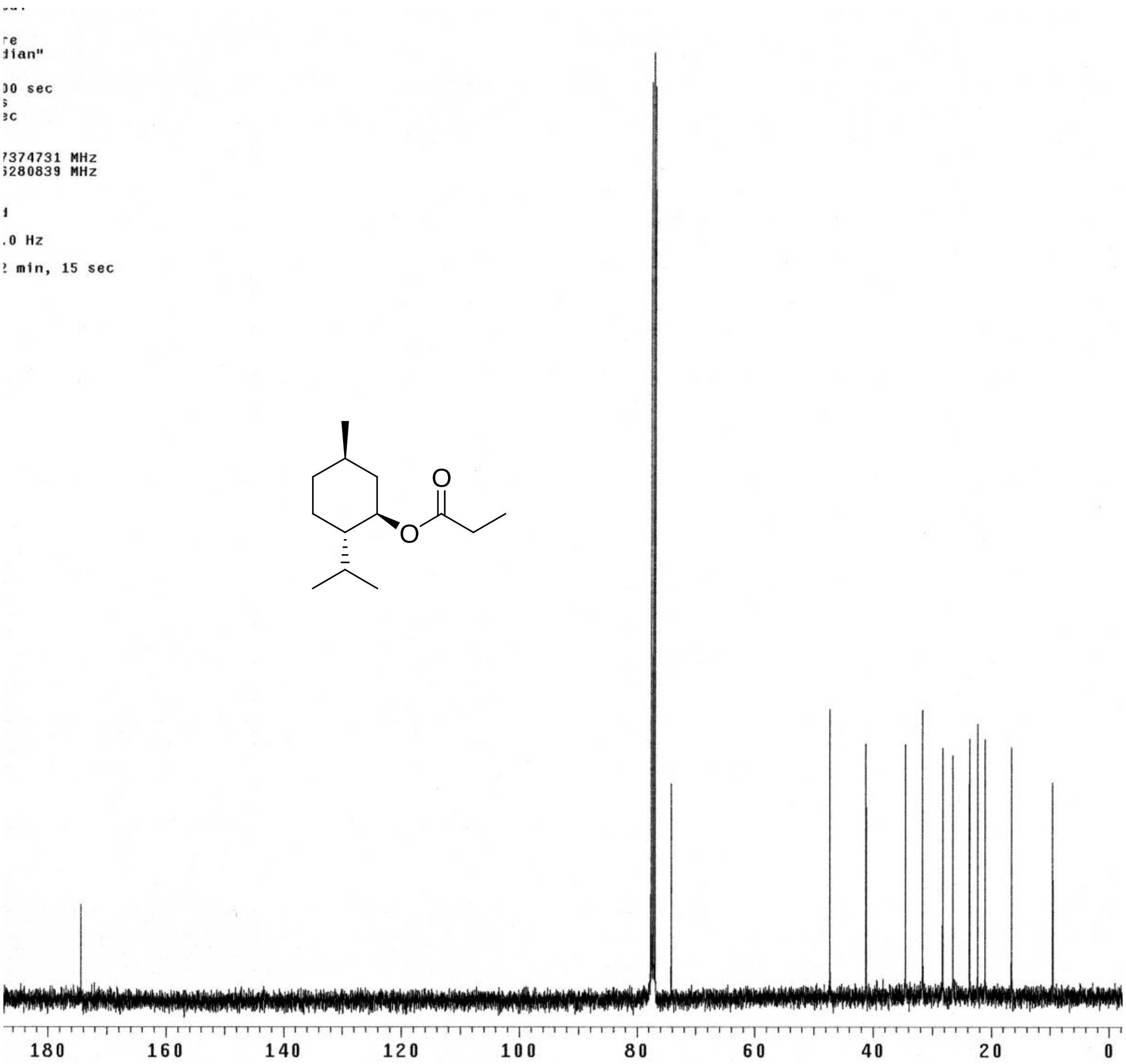


Figure 32. ^{13}C NMR spectrum of menthyl propionate (**16**).

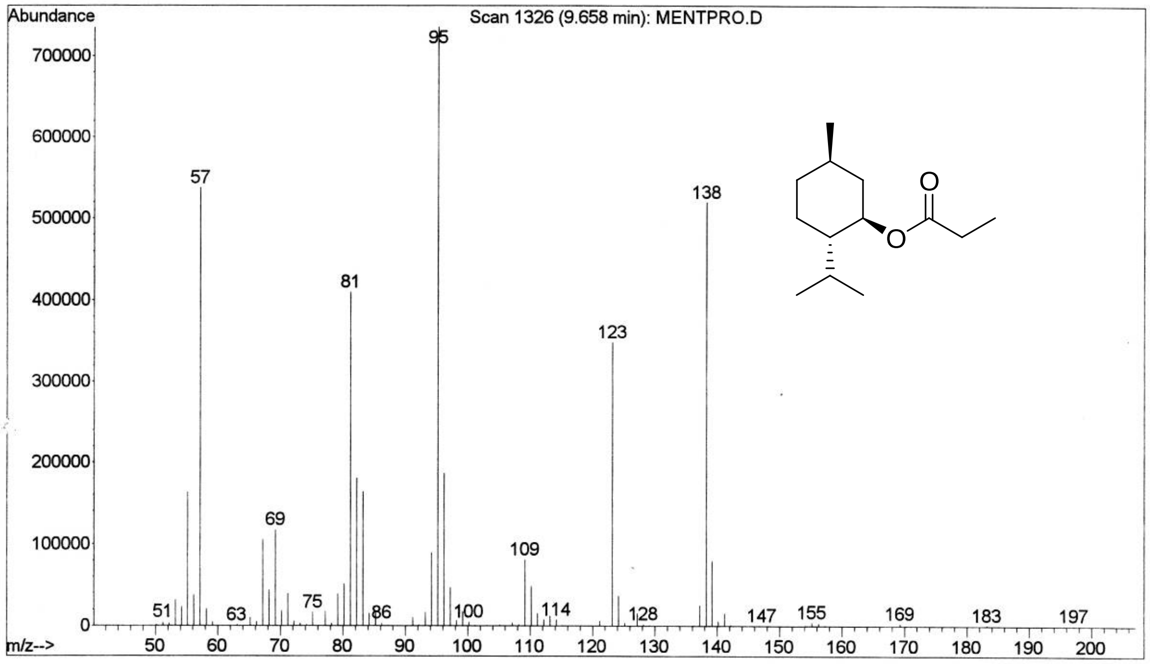
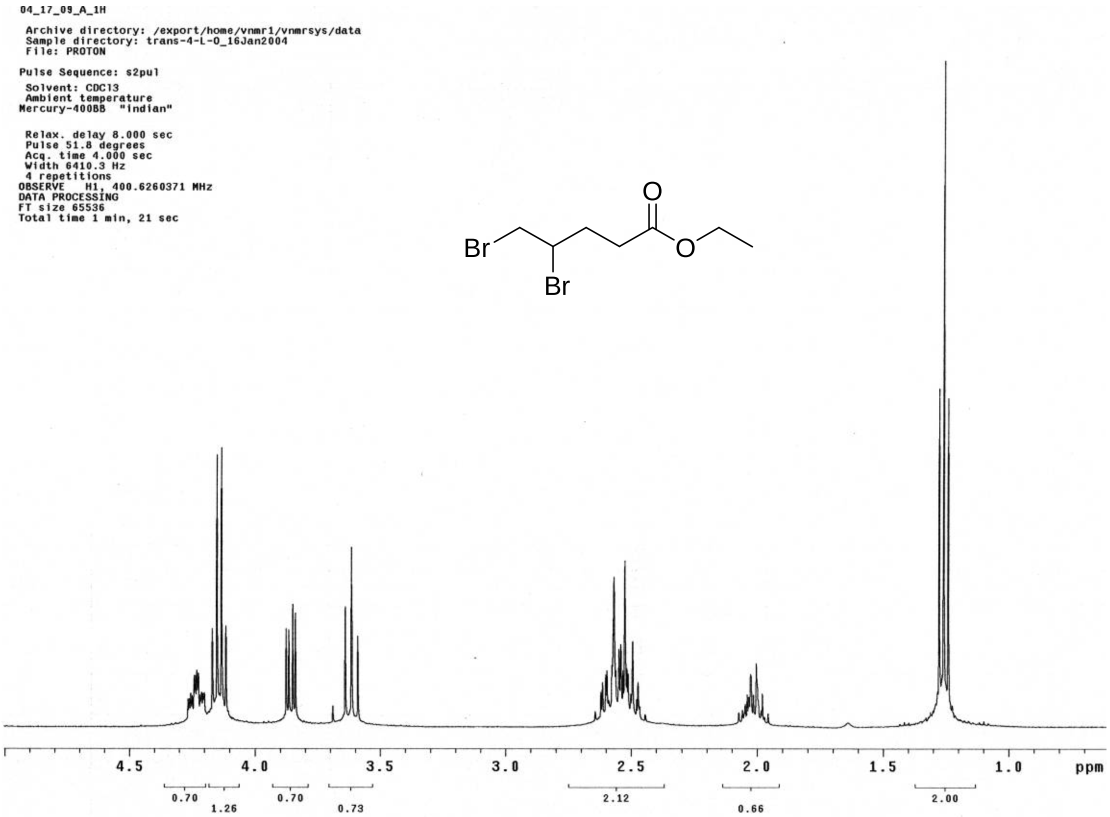


Figure 33. MS of menthyl propionate (**16**).



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04_17_09_A_1H

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 File: PROTON

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 Ambient temperature
Mercury-400BB  "indian"

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 Pulse 51.8 degrees
 Acq. time 4.000 sec
 Width 6410.3 Hz
 4 repetitions
OBSERVE   H1, 400.6260371 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 21 sec
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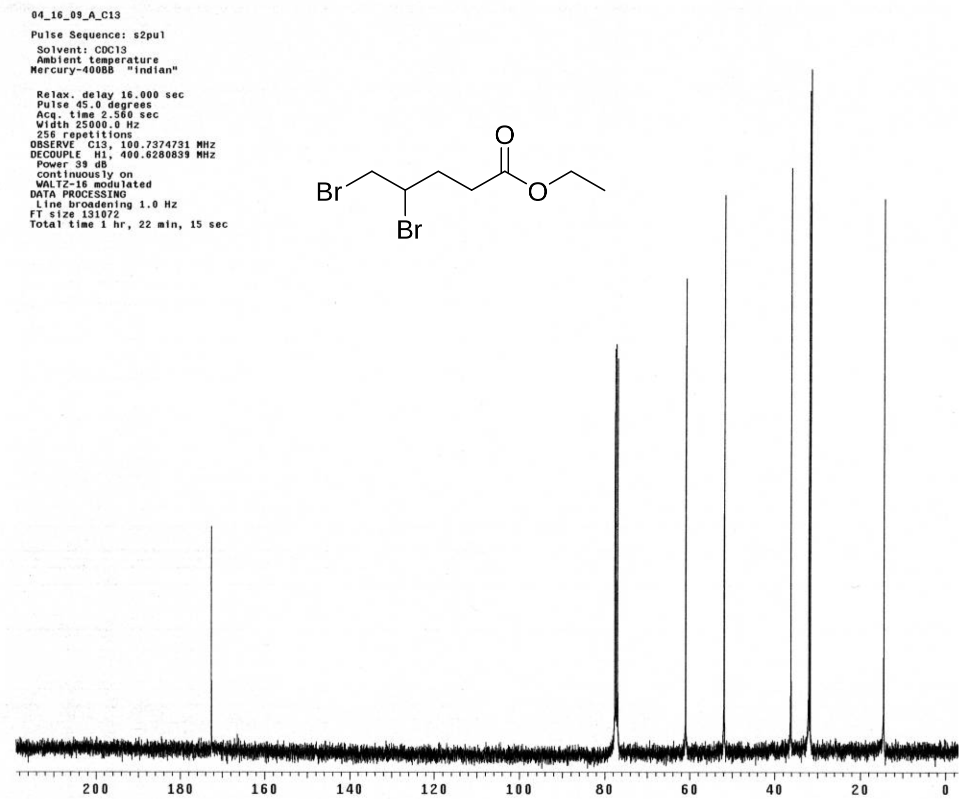
Figure 34. ^{1}H NMR spectrum of ethyl 4,5-dibromopentanoate (**17**).



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04_16_09_A_C13

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Mercury-400BB  "indian"

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 256 repetitions
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DECOUPLE  H1, 400.6280839 MHz
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 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 22 min, 15 sec
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Figure 35. ^{13}C NMR spectrum of ethyl 4,5-dibromopentanoate (**17**).

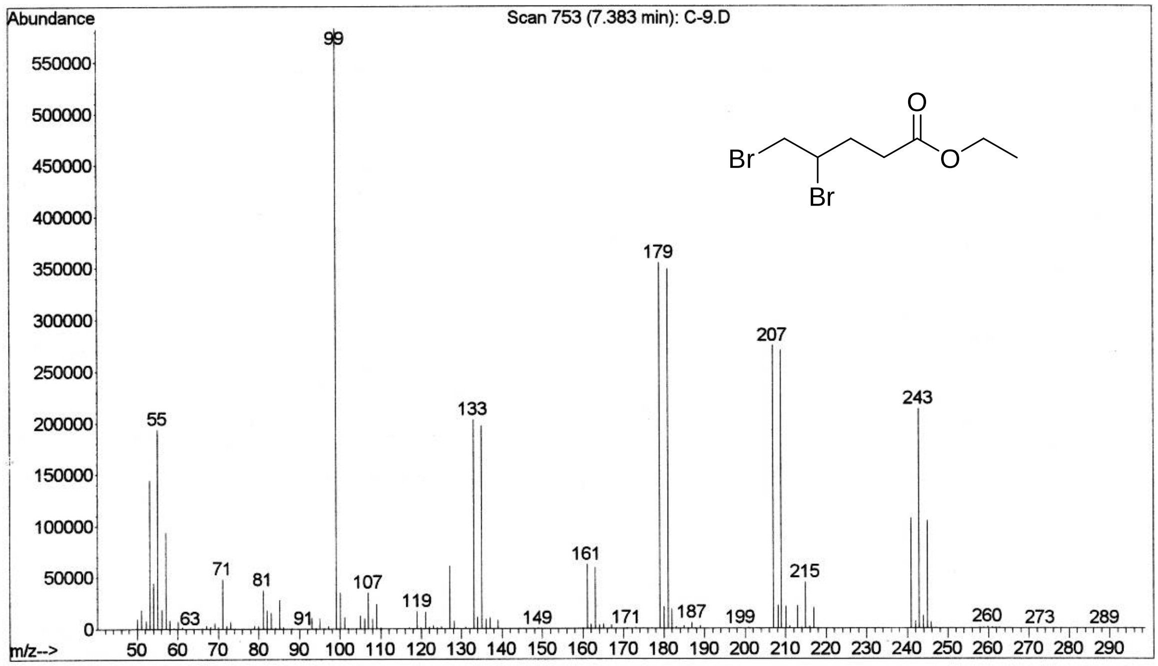

Figure 36. MS of ethyl 4,5-dibromopentanoate (**17**).

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