Research Article

Stereoselective Synthesis of (4E,6Z)-Hexadecadien-1-ol, (4E,6Z)-Hexadecadienyl Acetate and (4E,6Z)-Hexadecadienal, the Pheromone Components of the Persimmon Fruit Moth, *Stathmopoda masinissa*

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Abstract

The sex pheromone components of the Persimmon Fruit Moth (PFM) *Stathmopoda masinissa*, a dangerous persimmon pest in eastern Asia, (4E,6Z)-Hexadeca-4,6-dien-1-ol, (4E,6E)-Hexadeca-4,6-dienyl acetate and (4E,6Z)-Hexadeca-4,6-dienal, were synthesized stereoselectively and efficiently starting from commercially available starting materials. The stereoselective formation of (4E) double bond based on Hydroxymethylation of 4-(2 -tetrahyd- pyranyloxy)-1-pentyn prepared from commercially available 4-Pentynol, while the 6Z-double bond was formed by Wittig reaction of 6-(2-Tetrahydropyranyloxy)-hex-2(E)-en-1-al and n-decyltriphenylphosphonium bromide. The overall GC purities of the final alcohol, acetate, and aldehyde is 95.23%, 98.16% and 94.03% respectively while isomeric purities are more than 99%. Green metrics calculation gives a new insight towards the multistep pheromone synthesis.

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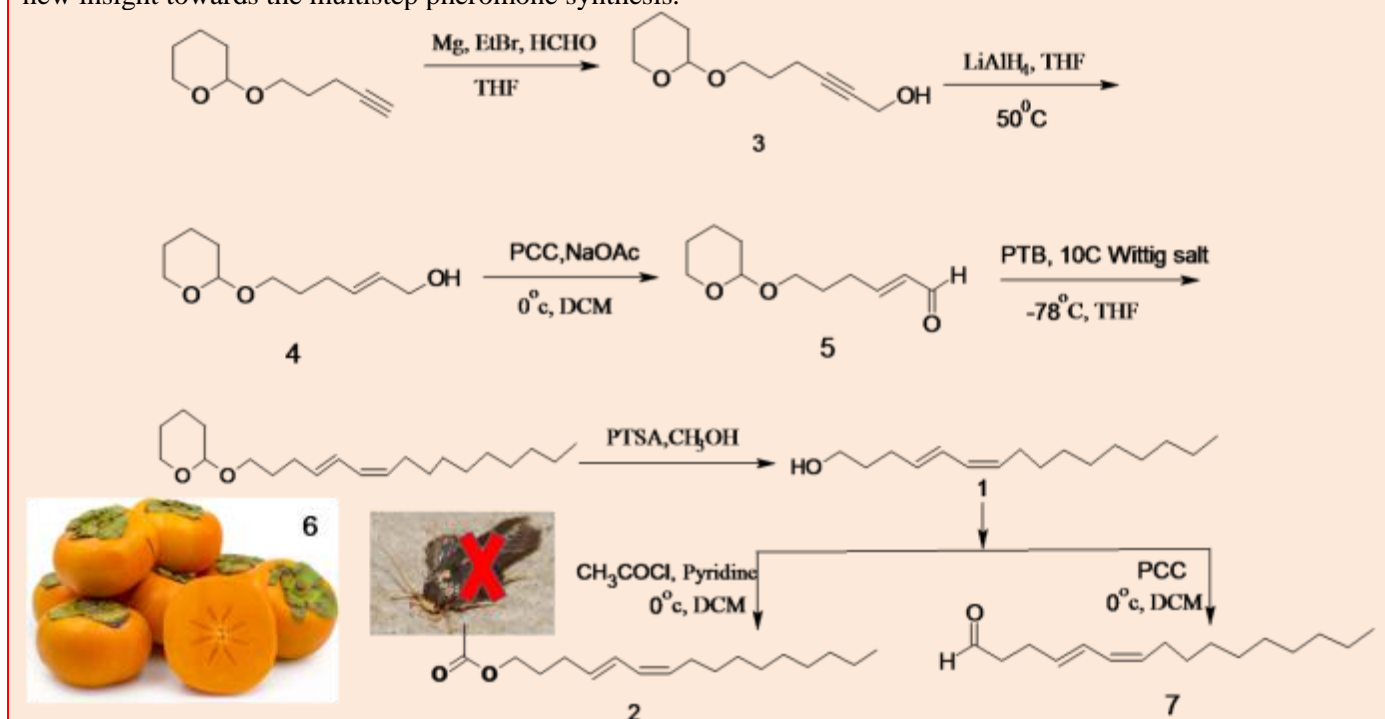
Introduction

The persimmon (Persimon) is an edible fruit of trees in the genus Diospyros. Persimmon (Diospyros kaki Thumb) is an important tree fruit belongs to family Ebenaceae [1]. This is the most significant deciduous fruit tree and the major producers are China, Korea, Japan, Brazil and Italy while U.S.A, India and Australia are the minor producers. In the midst of tree a fruit Persimmon is ranked first in Korea in terms of harvest area literature data reveals that in the year of 2012 almost 30,264 ha land was occupied [2].

Persimmon fruit appears like ripened tomatoes. The fruits are sugar rich with excellent flavor, fragrance and pleasant in terms of texture. Persimmon fruit tree is cost effective, having compact spreading growth habit and an ornamental beauty of orange colored fruit with bright red foliage, and widely attractive in architectural landscape. Persimmon fruit not only attractive but also have a premium source of various minerals, antioxidants, and vitamins especially vitamin-C and dietary fibers with, low calories (70cal/100g) and fats [3]. This sweet and non-astringent persimmon fruit is exported to Southeast Asia, Canada, Russian and Spain and total export value reached about US $12 million in 2012 [4]. Persimmon Fruit Moth (PFM) *Stathmopoda masinissa* Meyrick (Lepidoptera: Oecophoridae) is the most damage causing pest of persimmon (Diospyros kaki Thumb) [5]. This fruit moth is also programmed as a quarantine pest of persimmon to the USA [6]. The PFM is distributed in East Asia particularly Korea, Japan, China and Thailand. In Korea this moth has two generations per year [7]. The adults appear in late spring and summer while the fifth instars overwinter. The early instars feed inside the shoots, and the third to last (fifth) instars bore into the core of the persimmon fruit around the calyx, and subsequently the damaged fruits rot and drop to the ground [8, 9].

To control this notorious insect species, use of insecticide is most common but in the limited period as the larvae migrates from the shoots to the fruits. An effective monitoring of this insect population efficiently is very crucial in decisive proper timing for control applications as well as assessing the effects [10]. Sex pheromone baited traps could provide an effective method of controlling of PFM.

The pheromone composition of *S. masinissa* of Japanese population has been identified and synthesized as (E4,Z6)-4,6-Hexadecadienyl acetate (E4,Z6-16Ac) [8]. However, in the field studies of Korean population monitored by using E4,Z6-16Ac in the year of 2011-12 given less adequate results. Therefore, the sex pheromone components in the abdominal extract of the moth of PFM were identified and synthesized in Korea as Hexadecadien-1-ol and its derivatives (acetate and aldehyde) with a conjugated diene system, (E4,Z6)-4,6-Hexadecadienyl acetate (E4,Z6-16Ac) and (E4,Z6)-4,6-Hexadecadien-1-ol (E4,Z6-16OH), as well as (E4,Z6)-4,6-Hexadecadienal (E4,Z6-16Ald) [11].

In case of Japanese population, the pheromone lure baited with the 1:1:1 mixture of E4, Z6-16Ac, E4,Z6-16OH, and E4,Z6-16Ald was less attractive than that baited with only E4,Z6-16Ac. In Korean population, addition of 10% of E4,Z6-16Ald to E4,Z6-16Ac increased the attraction of male PFM than other combination. Among the most important groups, more than 500 species of Lepidopteran sex pheromones compounds have been chemically defined having a conjugated diene system especially C10-C18 straight chain compounds. Furthermore the 4,6-diene structure is not entirely exceptional, because 4,6,10- or 4,6,11-trienols, acetates, and aldehydes have been identified and synthesized as pheromone components of the cocoa pod borer moth (*Conopomorpha cramerella,* Snellen) (Beevor et al., 1986), and also the eri-silkworm (*Samia cynthia ricini* Donovan). There are possibilities that of these 4,6-dienes and 4,6,10-trienes can be produced by similar synthetic pathways [12, 13].

Scheme 1
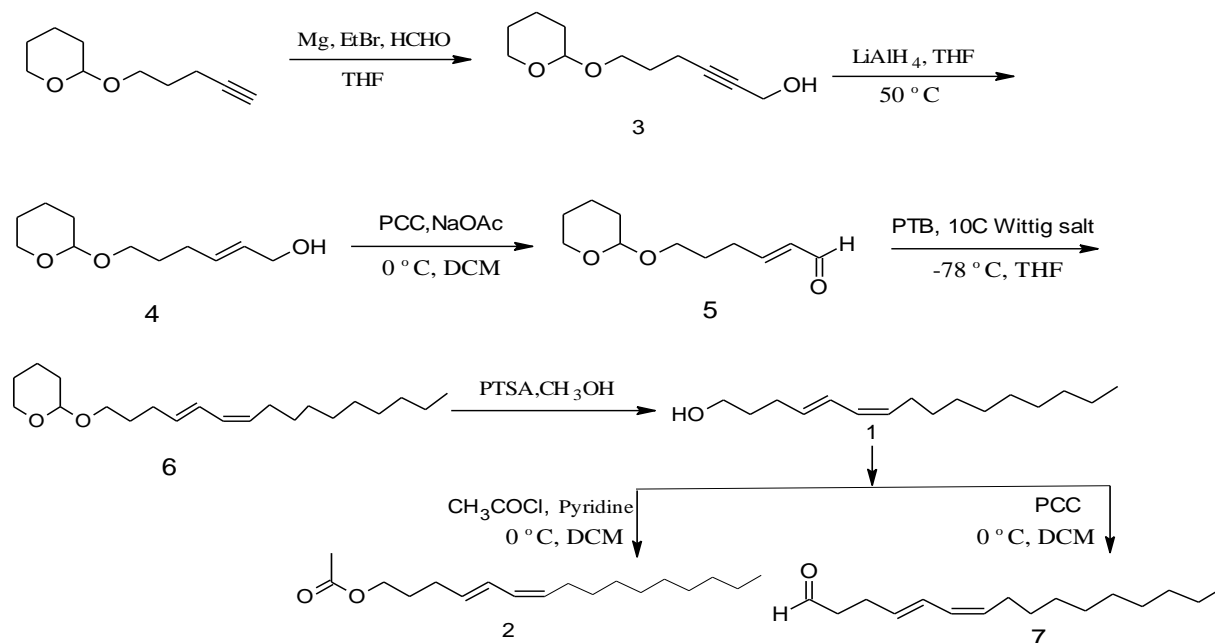
Quite recently Park, C. G. *et al.*, [14] Ando. T. *et al.*, [15, 16] Nishida. T. *et al.*, [17] and Tomida *et al.*, [18], Shakhmaev *et al.*, [19] was successfully synthesized these three conjugated diene molecules with certain modification in various synthetic steps like alkylation [20, 21], acetylation [11], reduction [22, 23], oxidation [24, 25], protection and deprotection [26] with numerous catalysts and named reactions like Grignard [27], Wittig [28], etc. A literature

reveals that these synthetic steps are commonly used for pheromone synthesis. Taking consideration of these scientific works and best of our knowledge in the previous success in synthetic chemistry [29, 30] in this communication, we address first time accomplished synthesis of stereo-specific Hexadecadien-1-ol and the derivatives (acetate and aldehyde) with green metrics calculation for total synthesis, which is eco-friendly, cost effective and useful for an industrial scale. The synthetic route is mentioned in Scheme 1.

The target structures, stereochemical purity, and configurations of substituents on the double bonds, Spin spin coupling constant for cis double bond and for trans double bond of the synthesized molecules were confirmed by spectroscopic and chromatographic techniques such as IR, ^{1}H and ^{13}C NMR, DEPT, GC-MS, all spectroscopic analysis illustrate a good accord with corresponding pheromone structure[19].

Materials and Methods

All chemicals used were purchased from Sigma-Aldrich and used as such. The ^{1}H and ^{13}C-NMR spectra were recorded in DMSO-d_6 on a Bruker instrument (300 MHz for ^{1}H NMR, 75MHz for ^{13}C NMR, DEPT) using TMS as an internal standard. Chemical shifts (δ) are expressed in ppm. IR spectra (KBr) were recorded on a Bruker FT-IR spectrometer expressed in cm^{-1}.

Gas Chromatography-Mass Spectrometric (GC-MS) analyses were carried out with a Hewlett-Packard 5890-5970 system, equipped with a SPB-1 capillary column (20 m × 0.25 mm, 0.33 μm film thickness, Supelco, Sigma-Aldrich Ltd., Greece); carrier gas, helium, 1 mL/min; injector temperature, 230˚C; oven temperature, 50˚C for 5 min isothermal and then raised to 250˚C at a rate of 4˚C /min and then held for 10 min; ion source temperature, 220˚C; interface temperature, 250˚C; mass range, 40-500 amu; and EI, 70 eV. GC analyses were carried out with Agilent 6890 N chromatograph either in a polar capillary column CP-Wax 52 CB (30 m × 0.32 mm, 0.25 μm film thickness, Varian Inc., CA) or in a nonpolar capillary column SPB1 (20 m × 0.32 mm, 1.0 μm film thickness, Supelco, Sigma-Aldrich Ltd.): carrier gas, helium, 1mL/min; injector temperature, 200˚C; oven temperature, 60˚C for 5 min isothermal and then raised to 250˚C at a rate of 4˚C /min and then held for 15 min. Thin-Layer Chromatography (TLC) was performed on 0.25 mm precoated silica gel 60 F 254 glass plates and column chromatography on silica gel 60-120 mesh size (Merck & Co., Darmstadt, Germany).

All commercial reagents and solvents were used as supplied. All reactions of air-and water-sensitive materials were run in oven-dried glassware under nitrogen. Air-sensitive solutions or liquids were transferred with glass syringes and canula. Decyltriphenylphosphonium bromide was prepared by treatment of 1-bromodecane with triphenyl phosphine in methyl cyanide. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Paraformaldehyde was dried to constant mass in a desiccator over Phosphorus pentoxide for 4 days before use. All other chemicals were used as purchased.

Experimental Data
6-(2-Tetrahydropyranyloxy)-2-hexyn-1-ol (3)

A solution of 4-(2-tetrahyd- pyranyloxy)-1-pentyn (100g, 595mmol) in THF (100mL) was added at 5˚C to a solution of ethyl magnesium bromide, prepared from ethyl bromide (57mL, 773mmol) and magnesium turnings (15.71g, 654mmol) in THF (400mL). The reaction mixture was refluxed for 1h, and then cooled to room temperature, and paraformaldehyde (36g, 1190mmol) was added slowly. The resultant mixture was refluxed with stirring for 2h. Then the reaction was quenched with saturated NH₄Cl (100mL) and it was extracted with diethyl ether (3 X 200mL), and then the combined organic layer was washed with water followed by brine (50mL), dried over sodium sulphate. The solvent was removed under vacuum and subjected for evaporated flash chromatography to gave 3 (89 g, 76%) as a colourless liquid.

6-(Tetrahydro-2H-pyran-2-yloxy) hex-2-yn-1-ol

IR (KBr, vmax, cm^{-1}): 3439 (-OH), 2939 (-CH), ^{1}H NMR (CDCl₃, 300MHz δ ppm): 0.74-1.15 (m, 2H-CH₂), 1.58-1.59 (d, 4H, J =3.0MHz, -2CH₂), 1.67-1.74 (m, 3H, -CH₂, -OH), -3.21-2.2 (d, 2H, J =3.0MHz, -CH₂), 3.35-3.39 (s, 2H, -CH₂), 3.68-3.74 (m, 2H, -CH₂), 4.09-4.10 (d, J =3.0MHz, 2H, -CH₂), 4. 95 (s, 1H, -CH), GC (Purity) = 94.86%, Calculated m/z = 198.25 Observed GC-MS m/z = [M-1] = 197.10

6-(2-Tetrahydropyranyloxy)-hex-2(E)-en-1-ol (4)

Lithium aluminium Hydride (21.1g, 555mmol) was added slowly with stirring to an ice-cold solution of THF (250mL) followed by alkylated product 3 (100g, 505mmol) in THF (100mL). Then the reaction mixture was heated at

50˚C for 2hrs. It was allowed to cool to room temperature and the reaction mixture was carefully decomposed by the addition of cold water (5mL), then with 10% sodium hydroxide (25mL). Then the solution was filtered and precipitate was extracted with diethyl ether (3 X 200mL). The combined filtrates were washed water followed by brine (50mL) and then dried with sodium sulphate (50g). The organic layer was evaporated under vacuum and the crude reaction mixture was purified by column chromatography to give trans alcohol 4 (89 g, 88%)

6-(2-Tetrahydropyranyloxy)-hex-2(E)-en-1-ol

IR (KBr, νmax, cm^{-1}): 3425 (-OH), 2938 (-CH), ^{1}H NMR (CDCl$_3$, 300MHz δ ppm): 1.40-1.43 (m, 3H, -CH$_2$, -OH), 1.51-1.58 (m, 6H, -3CH$_2$), 1.99 (s, 2H, -CH$_2$), 3.25- 3.36 (s, 2H, -CH$_2$), 3.60 -3.72 (m, 2H, -CH$_2$), 3.89 (m, 2H, -CH$_2$), 4.43 (br. s, 1H, -CH), 5.49- 5.52 (m, 2H, -2CH), GC (Purity) = 98.41%, Calculated m/z = 200.27 Observed GC-MS m/z = [M-1] = 199.10

6-(2-Tetrahydropyranyloxy)-hex-2(E)-en-1-al (5)

Pyridinium chlorochromate (161.3g, 750mmol) and sodium acetate (20.5 g, 250mmol) were added in dichloromethane (1400mL), and cooled to 0˚C. Then the trans alcohol 4 (100 g, 500mmol) was added slowly along with dichloromethane (100mL) and then the reaction mixture was stirred for 2hrs at room temperature. After completion of the process, it was diluted with dry diethyl ether (200mL), and filtered through a pad of celite. The solvent was evaporated under vacuum and the crude aldehyde was purified by flash chromatography to give aldehyde 5 (63.5 g, 64%).

6-(2-Tetrahydropyranyloxy)-hex-2(E)-en-1-al

IR (KBr, νmax, cm^{-1}): 2940 (-CH), 1687 (-C=O), ^{1}H NMR (CDCl$_3$, 300MHz δ ppm): 1.42 (m, 4H, 2CH$_2$), 1.71 (m, 4H, -2CH$_2$), 2.36(m, 2H, -CH$_2$), 3.33- 3.38 (m, 2H, -CH$_2$), 3.69-3.70 (m, 2H, -CH$_2$), 4.46 (s, 1H, -CH), 5.97- 6.04 (m, 1H, -CH), 9.38- 9.40 (d, 1H, -CHO), GC (Purity) = 94.03%, Calculated m/z = 198.25 Observed GC-MS m/z = [M-1] = 197.10

16-(2-Tetrahydropyranyloxy)-hexadeca-4(E)-6(Z)-dien (6)

The freshly prepared solution of ylide of n-Decylidenetriphenylphosphorane (It was prepared by the addition of a solution of Potassium Ter. Butoxide (46.4g, 414mmol) in THF (100mL) to suspension of n-Decyltriphenyl phosphonium bromide (100g, 207 mmol) in THF (300ml) and stirred for 2hrs at room temperature. Then the orange coloured ylide was cooled to -78˚C and then the Aldehyde 5 (39g, 196mmol) was dissolved in THF (50mL) and added slowly. After the addition, the reaction mixture was stirred at the room temperature for 2 hrs. Then the reaction mixture was quenched with saturated ammonium chloride solution (100mL) and then it was extracted in diethyl ether (3 X 200mL), washed with water followed by brine (50mL) and dried over sodium sulphate (50g). Then the evaporation of the solvent under vacuum and flash chromatography afforded the pure Wittig compound 6 (50.1g 79% yield based on Aldehyde).

16-(2-Tetrahydropyranyloxy)-hexadeca-4(E)-6(Z)-dien

IR (KBr, νmax, cm^{-1}): 1540 (C=C), 1028,1074 (C-O), 2922 (-CH), ^{1}H NMR (CDCl$_3$, 300MHz δ ppm): 0.86 (s, 3H, -CH$_3$), 1.25 (br. s, 12H, -6CH$_2$), 1.50 (m, 4H, -2CH$_2$), 1.67-2.15 (m, 10H, -5CH$_2$), 3.46 (s, 2H, -CH$_2$), 3.82 (s, 2H, -CH$_2$), 4.55 (s, 1H, -CH), 5.29 (s, 1H, -CH), 5.63 (s, 1H, -CH), 5.93 (s, 1H, -CH), 6.32 (s, 1H, -CH), GC (Purity) = 88.00%, Calculated m/z = 322.52 Observed GC-MS m/z = [M$^+$] = 322.30

(4E,6Z)-Hexadeca-4,6-dien-1-ol (1)

A solution of Wittig product 6 (100g) and methanol (100mL) was taken in flask and 4-toluene-sulphonic acid (0.5g) added and the reaction mixture was stirred for 1h at room temperature. After complete consumption of the starting material, sodium bicarbonate (2g) was added to the reaction mixture, and methanol was removed under vacuum. The residue was extracted with diethyl ether (3 X 200mL), and then organic layer was washed with water followed by brine (50mL) and dried over sodium sulphate (50g). The solution was evaporated in vacuum, and the residue was subjected for the column chromatography to give alcohol 1 (59.1 g, 80%).

(4E,6Z)-Hexadeca-4,6-dien-1-ol

IR (KBr, vmax, cm^{-1}): 3332 (-OH), 2922 (-CH), 1699,1651 (C=C), 1374 (C-O), ^{1}H NMR (CDCl$_3$, 300MHz δ ppm): 0.86-0.90 (M, 5H), 1.62-1.71 (m, 5H), 2.14-2.22 (m, 10H), 3.61-3.66 (m, 3H), 5.36 (m, Jcis = 9, 2H), 5.67 (m, J$trans$ = 15, 2H), 5.97 (m, Jcis = 9, 2H), 6.38 (m, J$trans$ = 15, 2H), ^{13}C NMR (CDCl$_3$, 300MHz δ ppm): 133.39, 130.29, 128.44, 126.23, 61.91, 31.98, 29.58, 29.39, 28.277, 27.71, 22.40, 14.11, ^{13}C DEPT NMR (CDCl$_3$, 300MHz δ ppm): 14.05, 126.22, 128.43, 130.28, 133.38, GC (Purity) = 95.23%, Calculated m/z = 238.40 Observed GC-MS m/z = [M$^+$] = 238.3

(4E,6Z)-Hexadeca-4,6-dienyl acetate (2)

A solution of alcohol 1 (50g, 210mmol) and dichloromethane 100mL, pyridine (22mL, 273mmol) was added slowly. Then the mixture was cooled to 0˚C and acetyl chloride (16.5mL, 231mmol) was added dropwise. Then the ice water (50mL) was added to the reaction mixture and shaken, and the layers separated. The aqueous layer was extracted with diethyl ether (3 X 100mL). The combined organic layers were washed with water followed by brine and then dried with Sodium sulphate (20g). Solvent was evaporated under vacuum and purification carried out by column chromatography to afford acetate 2, (55.9g, 95%).

(4E,6Z)-Hexadeca-4,6-dienyl acetate

IR (KBr, vmax, cm^{-1}): 2923 (-CH), 1741 (-C=O), 1233 (-C-O) ^{1}H NMR (CDCl$_3$, 300MHz δ ppm): 0.89 – 0.84 (t, 3H, -CH$_3$), 1.26 (m, 14H, -7CH$_2$), 1.77 – 1.69 (m, 2H, -CH$_2$), 2.10 (s, 3H, -CH$_3$), 4.08- 4.04 (q, 2H, -CH$_2$), 5.35 – 5.26 (m, 1H, Jcis = 9, -CH), 5.65 – 5.55 (m, 1H, J$trans$ = 15, -CH), 5.9 (t, 1H, Jcis = 9, -CH), 6.36 (q, 1H, J$trans$ = 15, -CH), ^{13}C NMR (CDCl$_3$, 300MHz δ ppm): 14.06, 20.78, 22.67, 27.70, 28.34, 29.23, 29.56, 31.88, 63.78, 126.56, 128.30, 130.55, 132.43, 170.73, ^{13}C DEPT NMR (CDCl$_3$, 300MHz δ ppm): 14.00, 17.80, 126.57, 128.33, 130.59, 131.11, 132.46 GC (Purity) = 98.16%, Calculated m/z = 280.44 Observed GC-MS m/z = [M$^+$] = 280.30

(4E,6Z)-Hexadeca-4,6-dienal (7)

Pyridinium chlorochromate (33.9g, 157mmol) and sodium acetate (4.3g, 52mmol) were suspended in anhydrous dichloromethane (300mL) and cooled to 0˚C and alcohol (25g, 105mmol) in dichloromethane (25mL) was added slowly to the mechanically stirred solution. After 15 minutes the cooling bath was removed and then resultant mixture was stirred for 2h at room temperature. It was diluted with dry Ether (100mL), filtered through a pad of celite. The filtrate was concentrated in vacuum and the crude was purified by column chromatography to give aldehyde 7 as colourless oil (15.6g, 63 %).

(4E,6Z)-Hexadeca-4,6-dienal

IR (KBr, vmax, cm^{-1}): 2922 (-CH), 1727 (-C=O), 1461 (C=C) ^{1}H NMR (CDCl$_3$, 300MHz δ ppm): 0.84-0.80 (s, 7H, -2CH$_3$), 2.09-2.07 (m, 4H, -2CH$_2$), 2.34-2.39 (m, 3H, -3CH$_2$), 2.48-2.44 (m, 3H, -3CH$_2$), 5.31 (m, 2H, Jcis = 9, -CH$_2$), 5.59 (m, 2H, J$trans$ = 12, -CH$_2$), 5.88 (t, 2H, Jcis = 9, -CH$_2$), 6.33 (t, 2H, J$trans$ = 12, -CH$_2$), 9.68 (s, 1H, -CHO), ^{13}C NMR (CDCl$_3$, 300MHz δ ppm): 13.94, 22.59, 25.22, 27.57, 29.18, 29.28, 29.47, 29.54, 29.61, 31.83, 43.16, 126.73, 128.10, 130.75, 131.28, 200.52, ^{13}C DEPT NMR (CDCl$_3$, 300MHz δ ppm): 15.09, 126.43, 128.22, 128.34, 130.23, 131.45, 131.55, 200.64, GC (Purity) = 94.03%, Calculated m/z = 236.39 Observed GC-MS m/z = [M$^+$] = 236.20

Results and Discussion

4-(2-Tetrahydropyranyloxy)-1-pentyn (4-pentyn-1-OTHP) used as starting material, it was synthesized by reported method [26]. Herein, we report a simpler and cheaper stereospecific synthesis of the pheromone from 4-pentyn-1-OTHP. Hydroxymethylation of 4-pentyn-1-OTHP was carried out by the Grignard reagent of the terminal alkyne using ethylmagnesium bromide in THF solvent and paraformaldehyde, afforded alcohol 3 in 71% yield. Furthermore, stereospecific formation of the trans (E) double bond was carried out by using a specific reducing agent LiAlH$_4$ in THF at 50˚C, here stereospecific conversion of compound 3 to (E)-enol (4) with no evidence of Z-isomer were formed which is confirmed by Gas Chromatography. Ones the stereospecific reduction carried out, the oxidation of (E)-enol (4) was carried out with pyridinium chlorochromate (PCC) in dichloromethane to afford the corresponding aldehyde (5). This aldehyde (5) was subjected to Wittig olefination with the wittig salt n-decylidene triphenylphosphorane (The salt was prepared from n-decyl bromide and triphenyl phosphine in refluxing with acetonitrile) with the base potassium ter-butoxide (PTB) in THF at -78˚C. The compound 6 contains a highly (Z)-stereoselectivity with 80% yield after column chromatography. Then the depyranylation was carried out by using of 4-toluenesulphonic acid (PTSA) in methanol, to give one of the pheromone component (E4,Z6)-4,6-Hexadecadien-1-

ol (1) in 80% yield. Then compound (1) was converted to (E4,Z6)-4,6-Hexadecadien-1-ol acetate (2) by treating with acetyl chloride and pyridine in dichloromethane which yields 95% yield of compound (2). The subsequent compound 1 was oxidized in presence of Pyridinium Chlorochromate (PCC) and sodium acetate in dichloromethane at 0°C which yields (E4,Z6)-4,6-Hexadecadienal (7) with 63% yield.

Green Metrics Calculations

The concept of green chemistry is widely recognized in chemical laboratories and industries to measure properly an environmental impact of chemical processes as well as committed assessment. It has become a tool for promoting sustainable development in laboratories and the evaluation of the greenness of chemical processes. It is an important in green organic synthesis is the reduction of energy use, which is possible through replacing traditional reaction conditions with alternative less energy sources [31-34].

In the synthesis of most of the sex pheromones multistep processes are involved in achieving the final molecules, hence it becomes a challenging to follow the green chemistry principles. The green metrics have been accepted as an evaluator of environmental sustainability in diminishing the amount of theoretical waste and it consists of many parameters such as Mass Intensity (MI), Reaction Mass Efficiency (RME), Carbon Efficiency (CE), and Atom Economy (AE). The MI is the yield stoichiometry and solvent, RME is the reaction mass balance of a chemical process and stands for yield and excess catalytic amount of reactant excluding solvent. The CE is the carbon efficiency idea regarding the use of gain or loss of carbon atoms while conversion of reactant to product and finally AE stands for the idea of the theoretical calculation of the process and environmental efficiency. One of the most important tools which can be considered as a fundamental green chemistry metrics that forms the basis for all of the other metrics is Atom Economy. The standard values of green metrics at ideal conditions are MI ≈ 1%, RME ≈ 100%, %CE ≈ 100 and %AE ≈ 100. To explain the greenness of the present synthesis, we have presented the results in terms of green metric calculations (**Figure 1**). An experiential value of green metrics shows the synthesized route obeys the greener approach for pheromone synthesis which is one of the unique characteristic of this work.
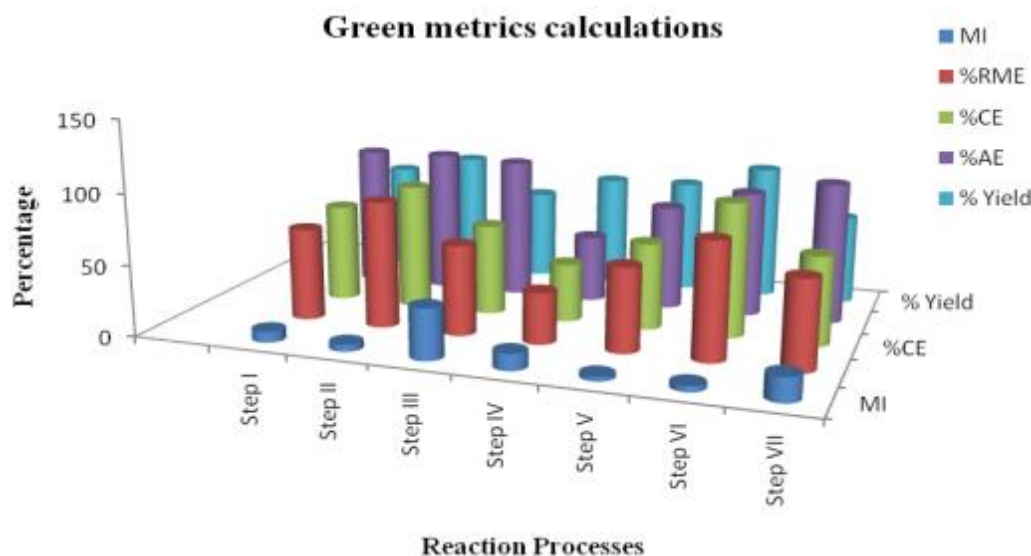
Figure 1 Green Metrics Calculation of (4E, 6Z)-4, 6-Hexadecadienol, Acetate and Aldehyde

Conclusion

In conclusion, we presented methodology for the synthesis of the stereoselective,(4E,6Z)-Hexadeca-4,6-dien-1-ol, (4E,6E)-Hexadeca-4,6-dienyl acetate and (4E,6Z)-Hexadeca-4,6-dienal, the sex pheromone of the PFM, through simple and efficient synthetic process. The present protocol gives the targeted stereoselective compounds with more than 95% isomeric purity. The isomeric purity and green metrics calculation gives a characteristic feature for pheromone synthetic chemistry.

Acknowledgement

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Appendix

Copies of ^{1}H NMR and ^{13}C NMR of synthesized compounds
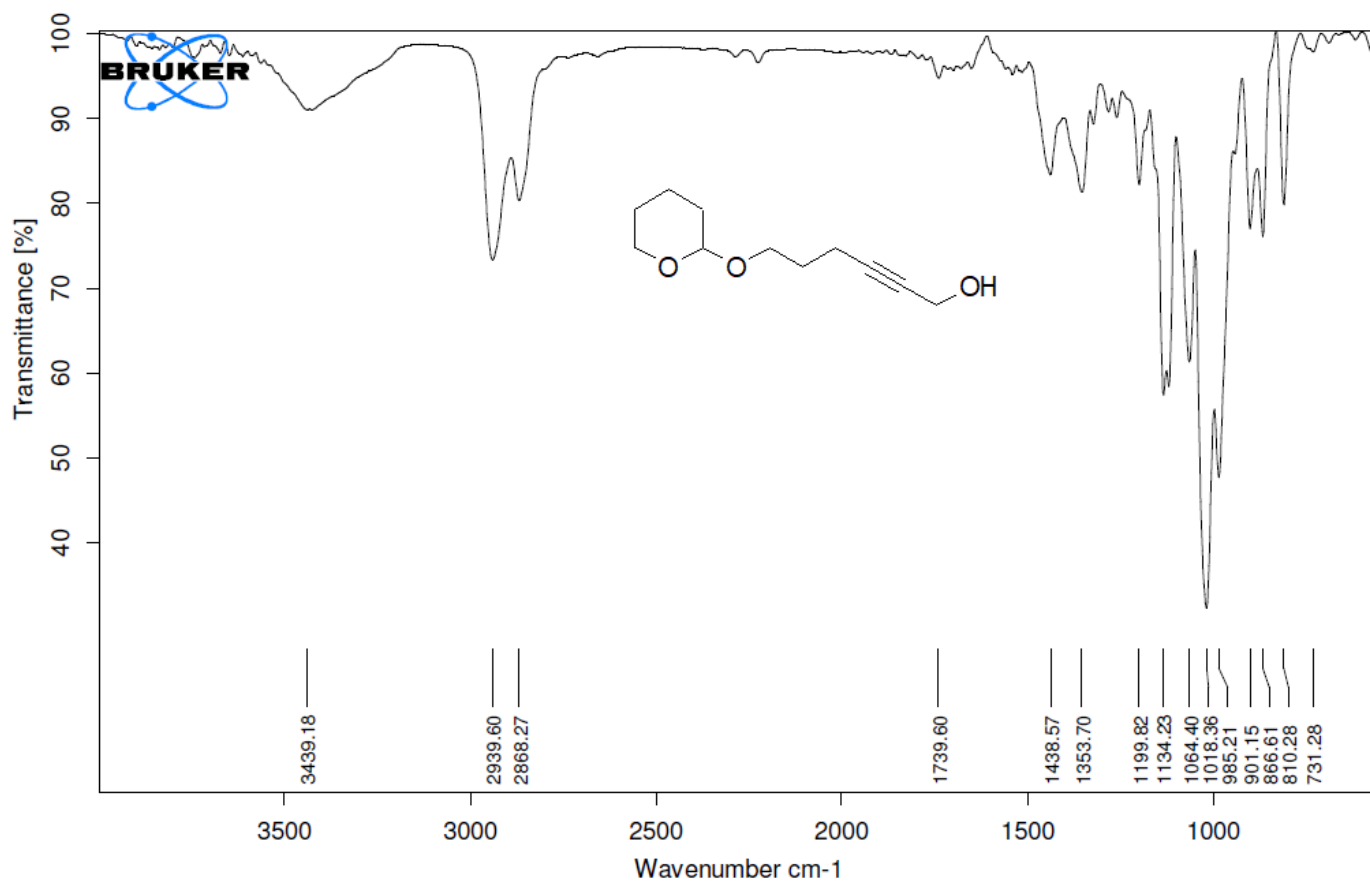
Figure 1 IR-6-(tetrahydro-2*H*-pyran-2-yloxy) hex-2-yn-1-ol
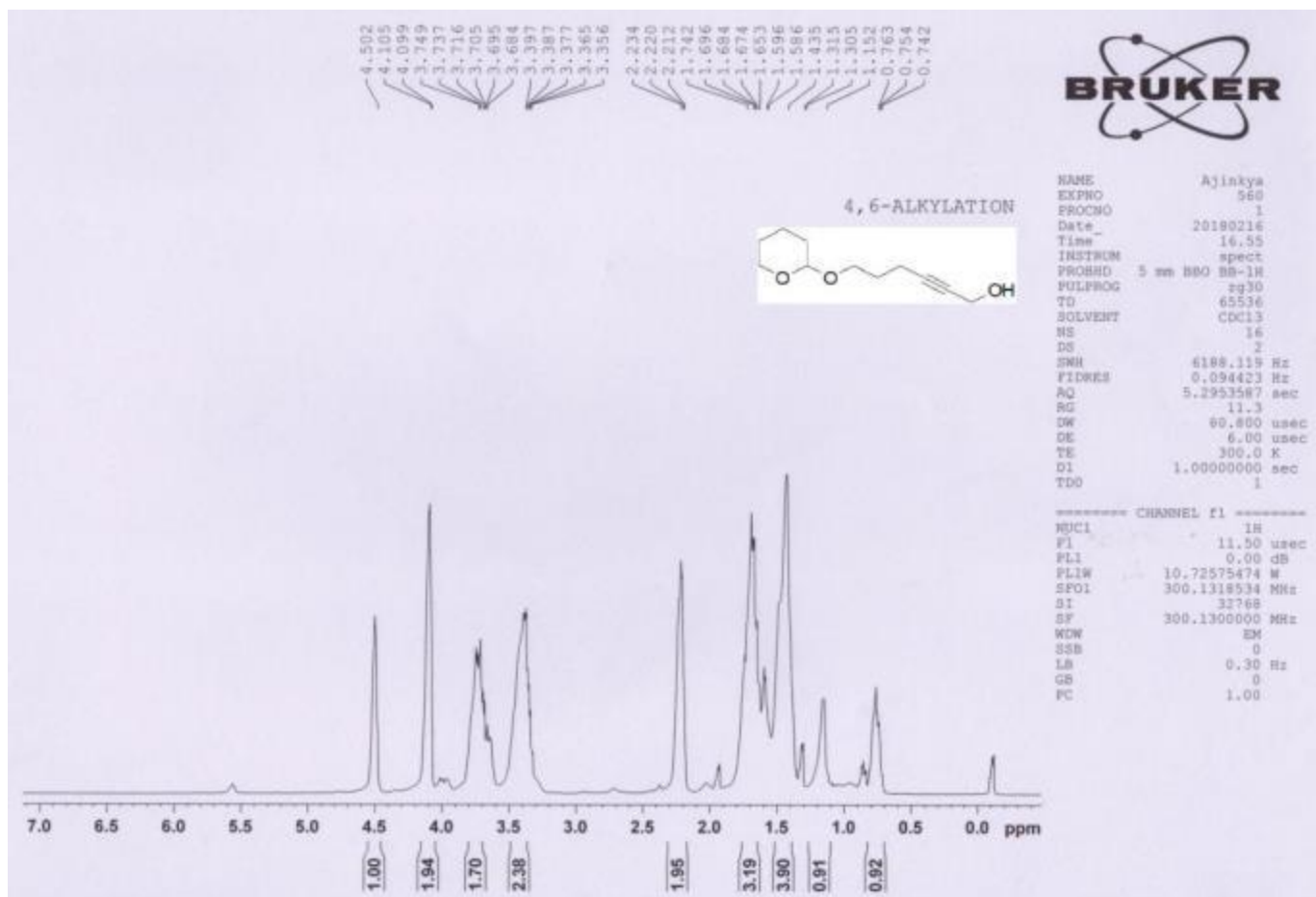
Figure 2 ^{1}H NMR -6-(tetrahydro-2*H*-pyran-2-yloxy) hex-2-yn-1-ol
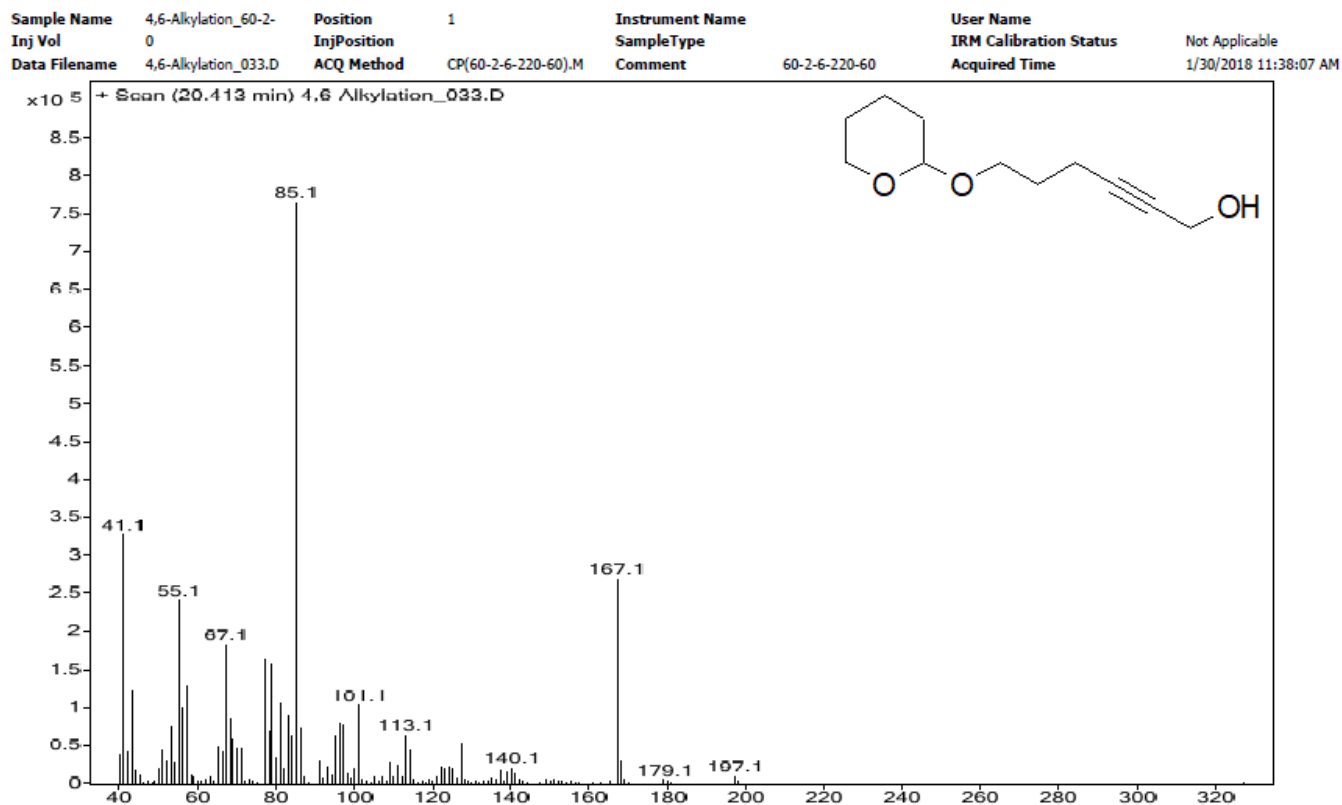
Figure 3 MS-6-(tetrahydro-2*H*-pyran-2-yloxy) hex-2-yn-1-ol
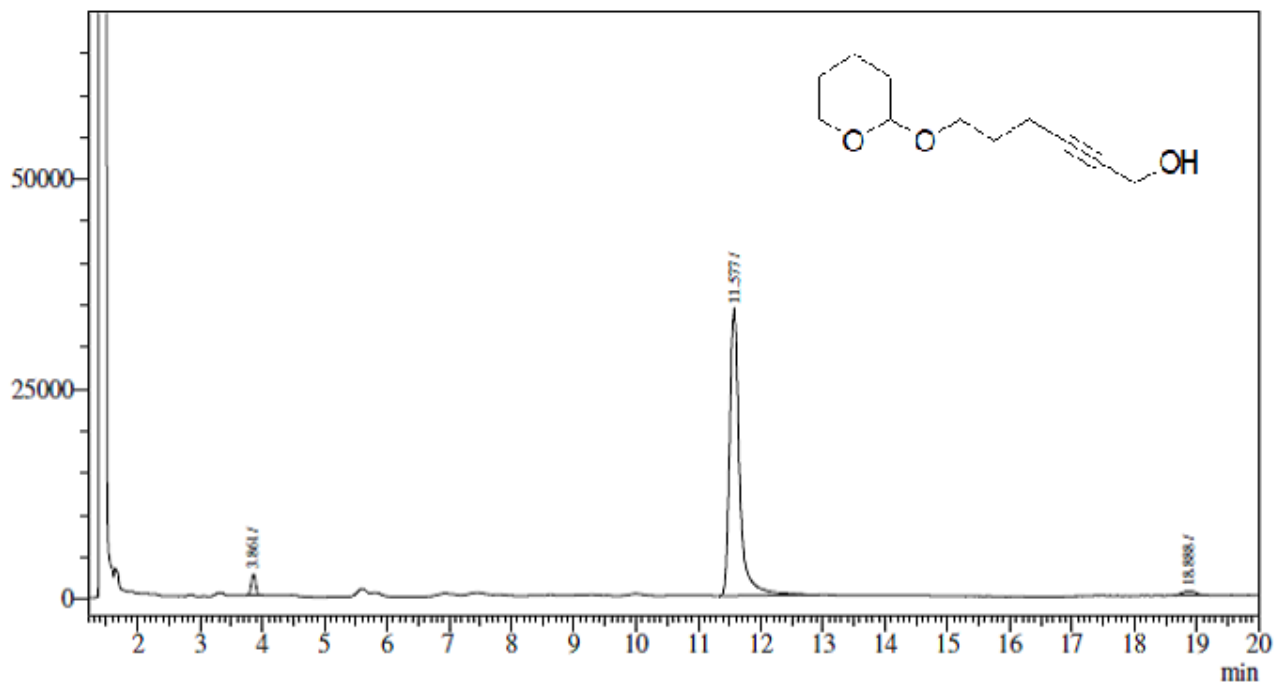
Peak Table - Channel 1

Peak#	Ret. Time	Height	Area	Height%	Area%
1	3.861	2558	12872	6.8586	3.2185
2	11.577	34228	379397	91.7816	94.8667
3	18.888	507	7658	1.3598	1.9148
Total		37293	399927	100.0000	100.0000

Figure 4: GC-6-(tetrahydro-2*H*-pyran-2-yloxy) hex-2-yn-1-ol
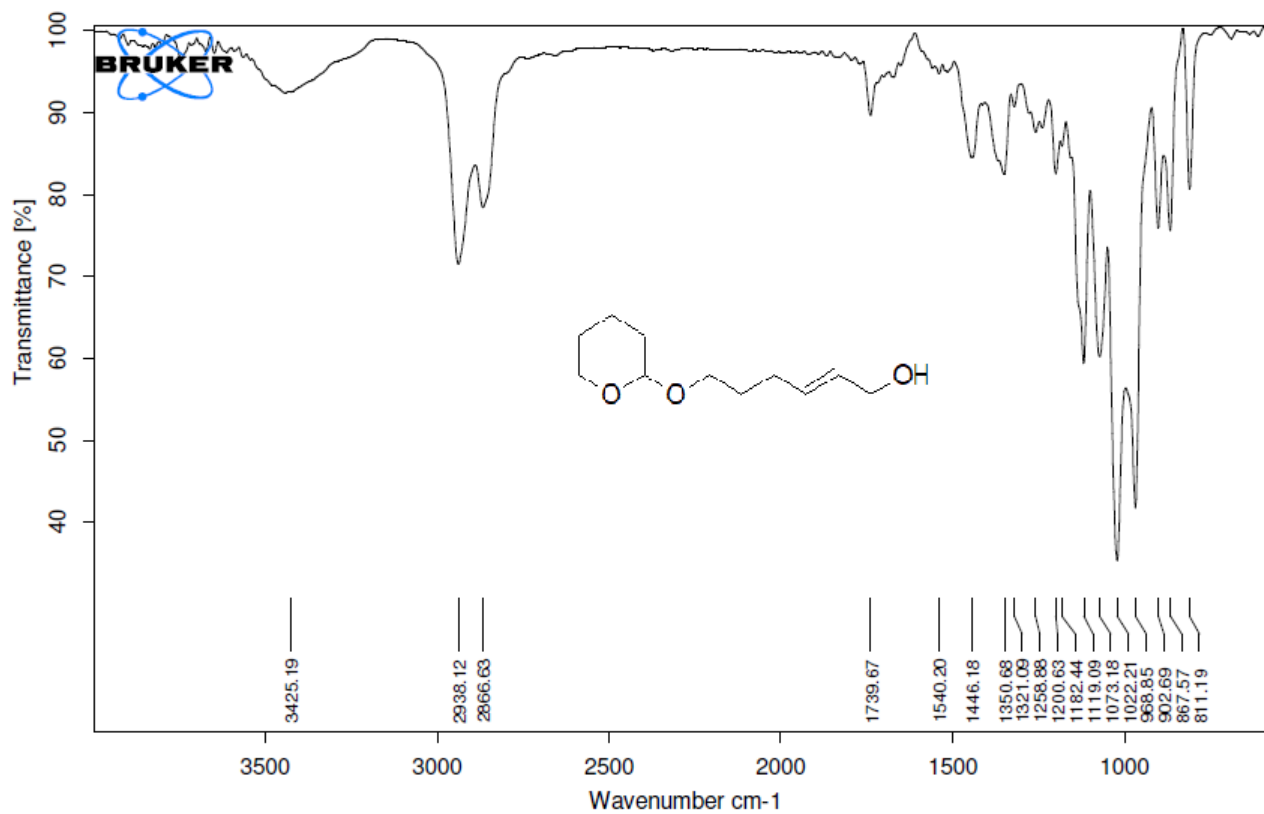
Figure 5 IR-(2*E*)-6-(tetrahydro-2*H*-pyran-2-yloxy) hex-2-en-1-ol
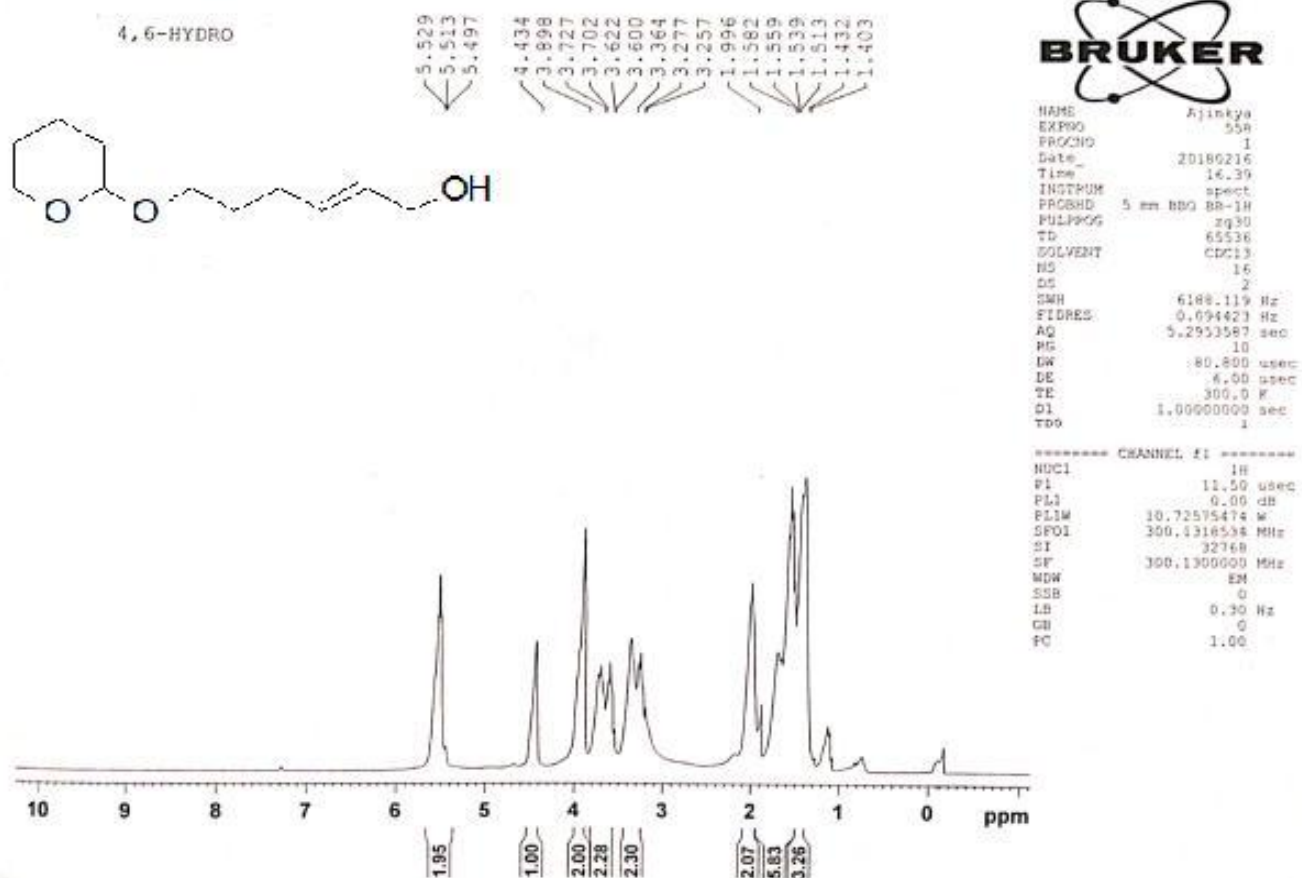
Figure 6 ^{1}H NMR - (2*E*)-6-(tetrahydro-2*H*-pyran-2-yloxy) hex-2-en-1-ol

Figure 7 MS-(2*E*)-6-(tetrahydro-2*H*-pyran-2-yloxy) hex-2-en-1-ol

Figure 8 GC-(2*E*)-6-(tetrahydro-2*H*-pyran-2-yloxy) hex-2-en-1-ol
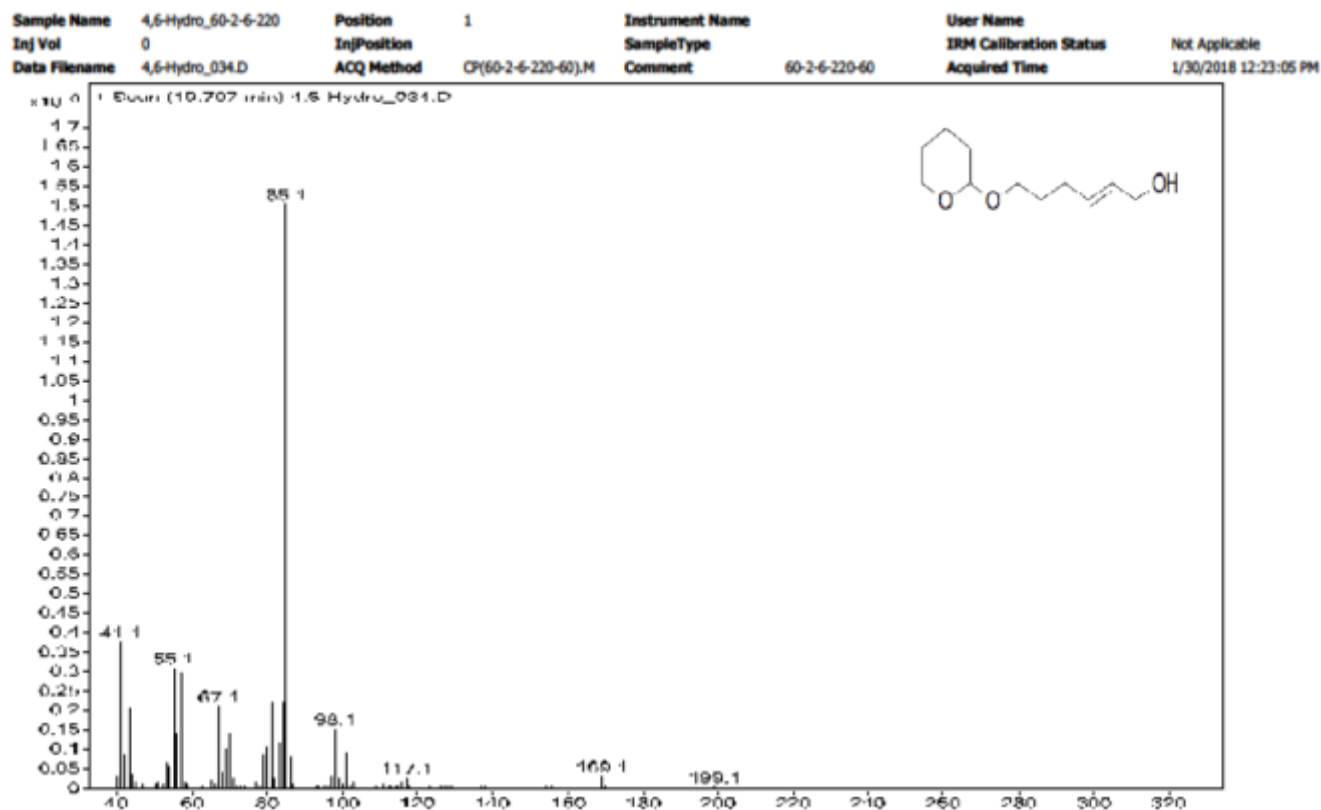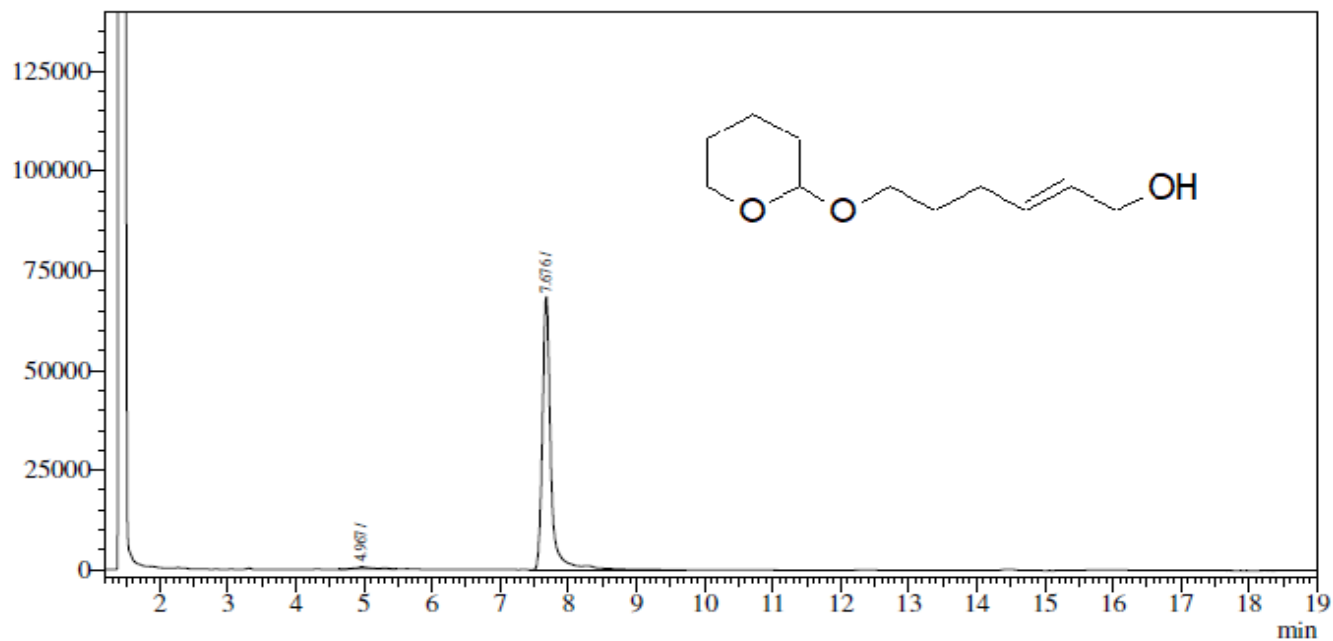
Peak Table - Channel 1

Peak#	Ret.Time	Height	Area	Height%	Area%
1	4.967	584	9663	0.8452	1.5842
2	7.676	68493	600275	99.1548	98.4158
Total		69077	609938	100.0000	100.0000
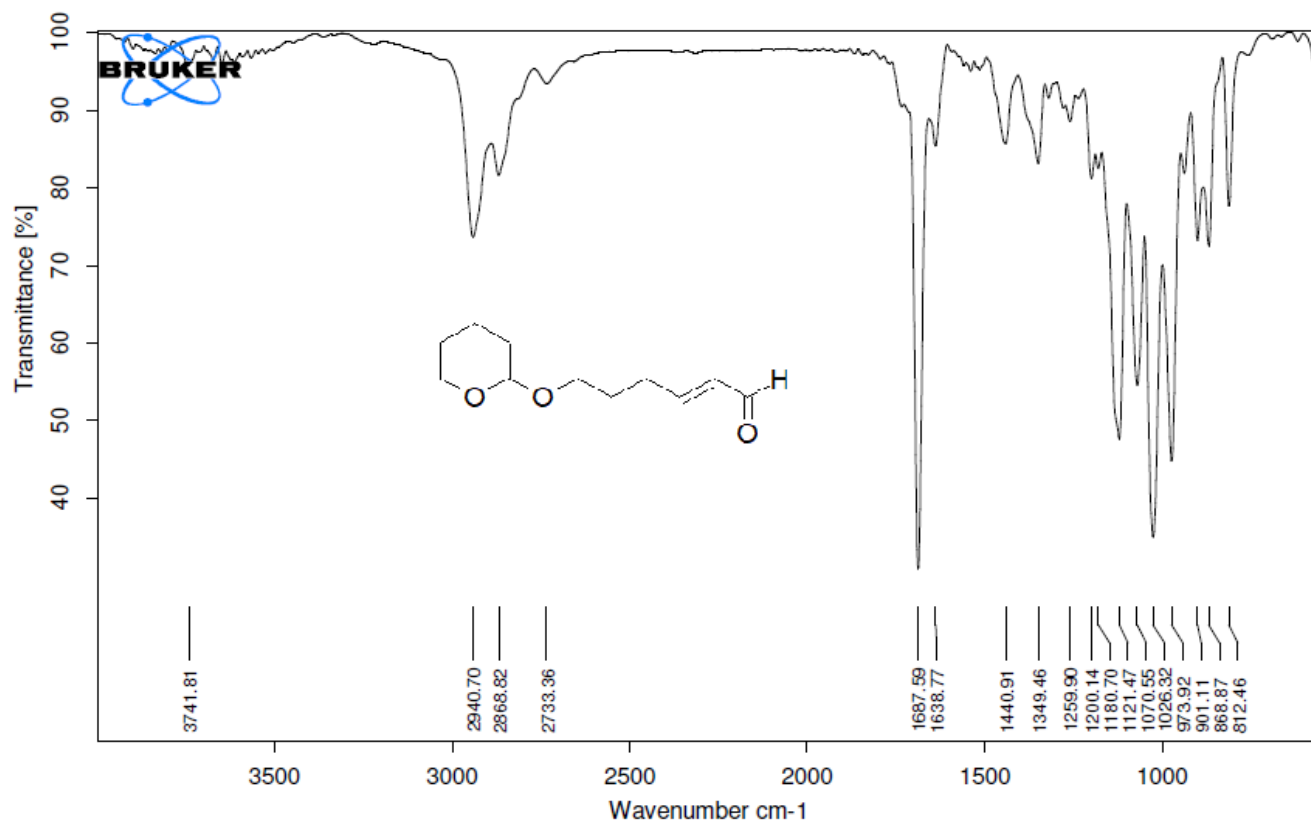
Figure 9 IR-(2*E*)-6-(tetrahydro-2*H*-pyran-2-yloxy) hex-2-enal
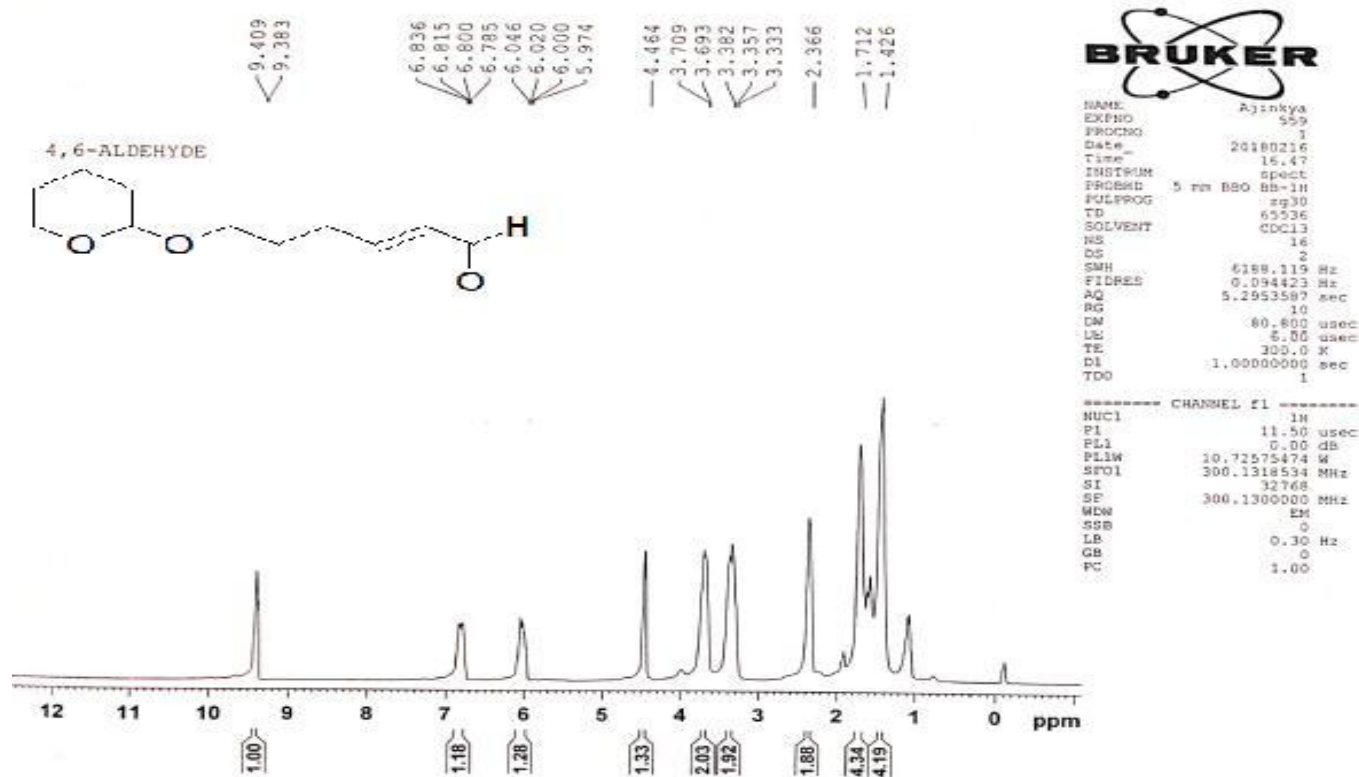
Figure 10 ^{1}H NMR - (2E)-6-(tetrahydro-2H-pyran-2-yloxy) hex-2-enal
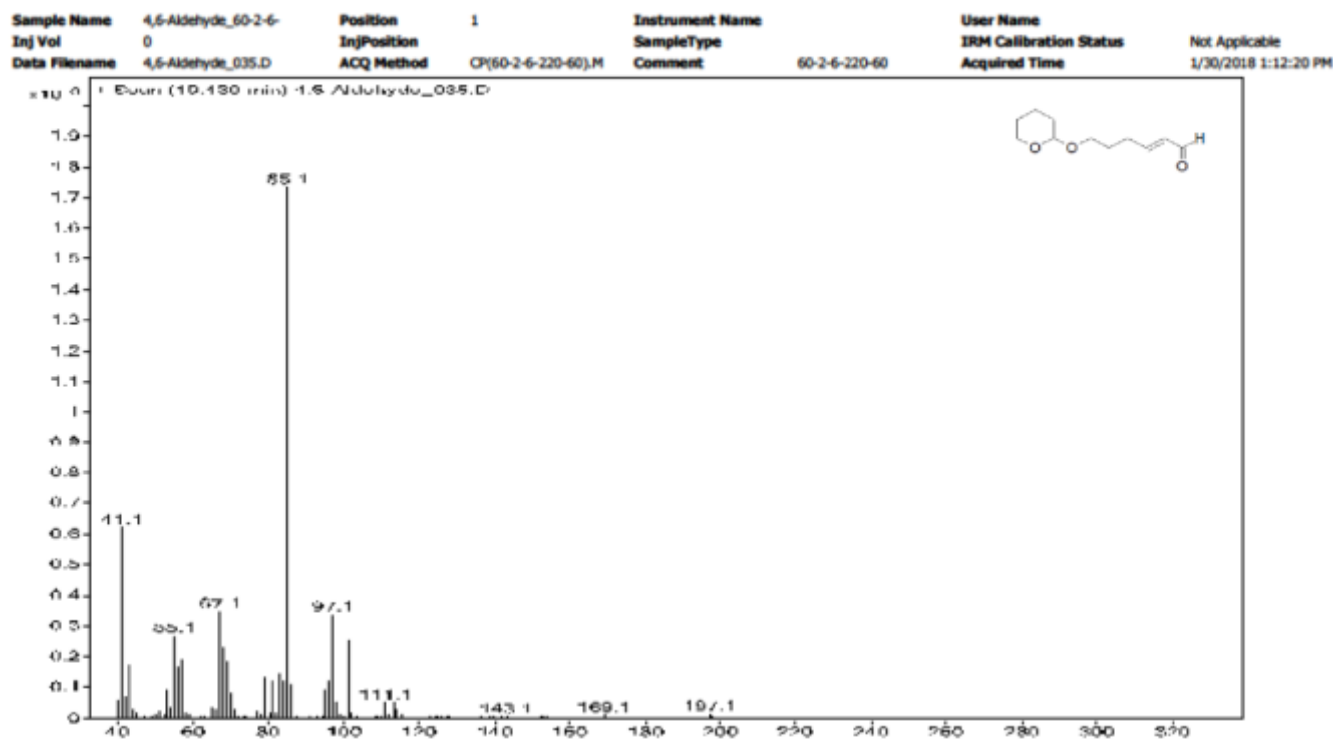
Figure 11 MS-(2E)-6-(tetrahydro-2H-pyran-2-yloxy) hex-2-enal

| Peak Table - Channel 1 | | | | | |
Peak#	Ret. Time	Height	Area	Height%	Area%
1	2.421	1967	7367	1.1622	0.5553
2	2.715	2999	10560	1.7717	0.7960
3	3.575	1676	8720	0.9900	0.6573
4	3.892	1777	8125	1.0500	0.6125
5	5.867	154485	1247431	91.2709	94.0320
6	6.494	6356	44399	3.7551	3.3468
Total		169260	1326602	100.0000	100.0000

Figure 12 GC-(2*E*)-6-(tetrahydro-2*H*-pyran-2-yloxy) hex-2-enal
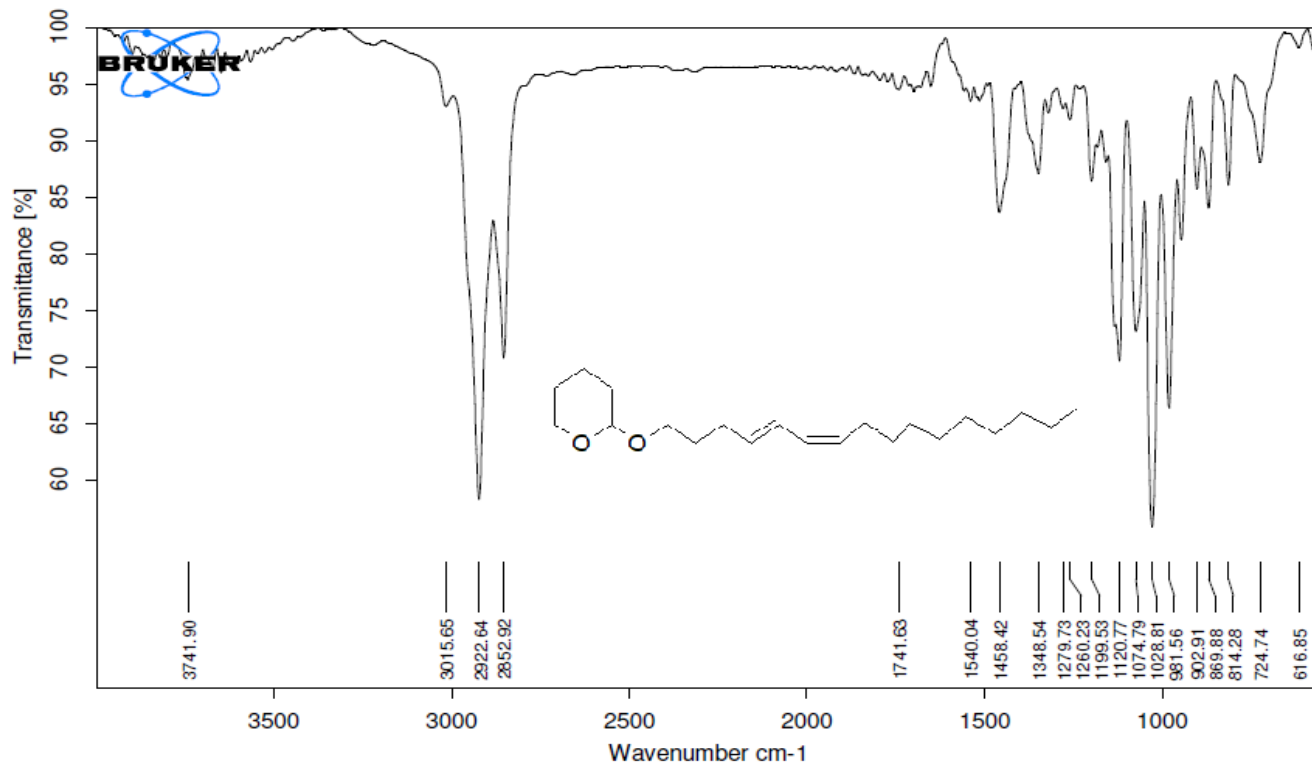
Figure 13 IR-16-(2-Tetrahydropyranyloxy)-hexadeca-4(E)-6(Z)-dien
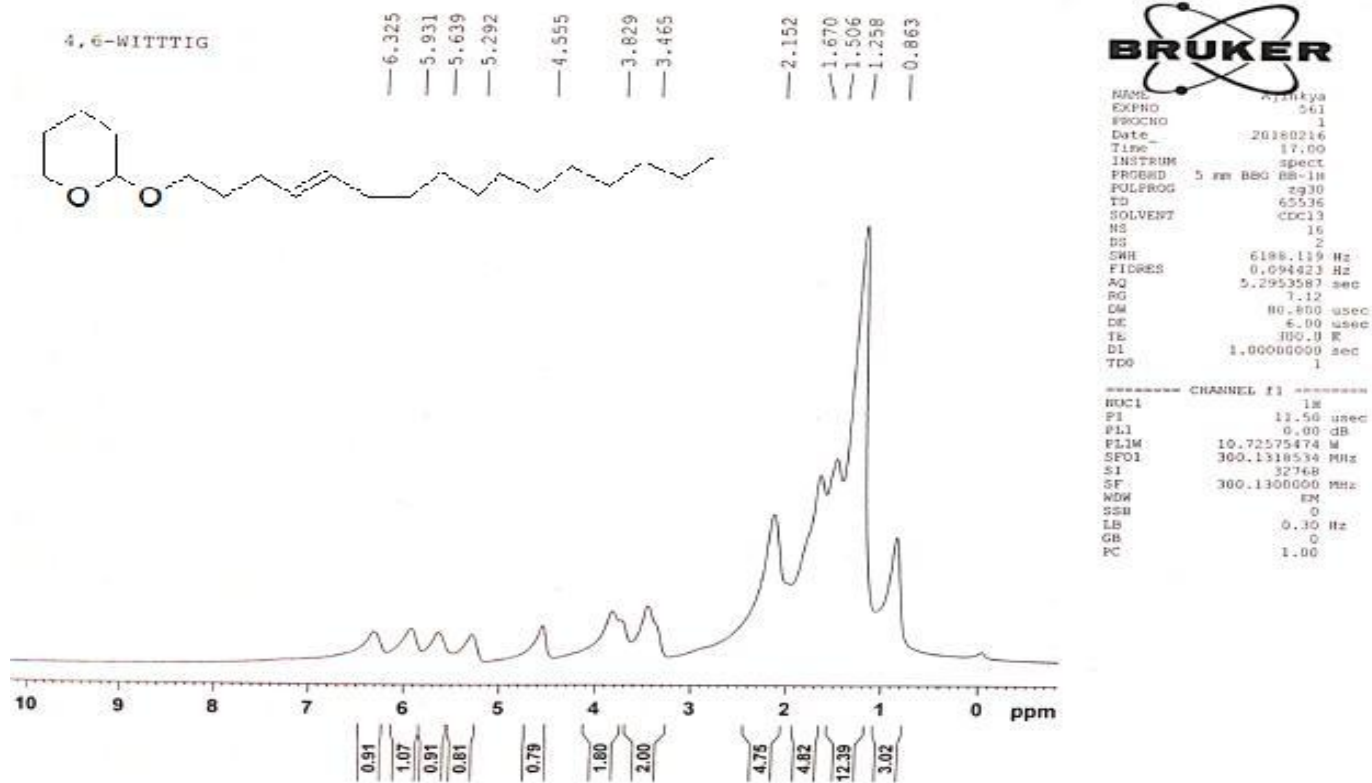
Figure 14 ^{1}H NMR -16-(2-Tetrahydropyranyloxy)-hexadeca-4(E)-6(Z)-dien
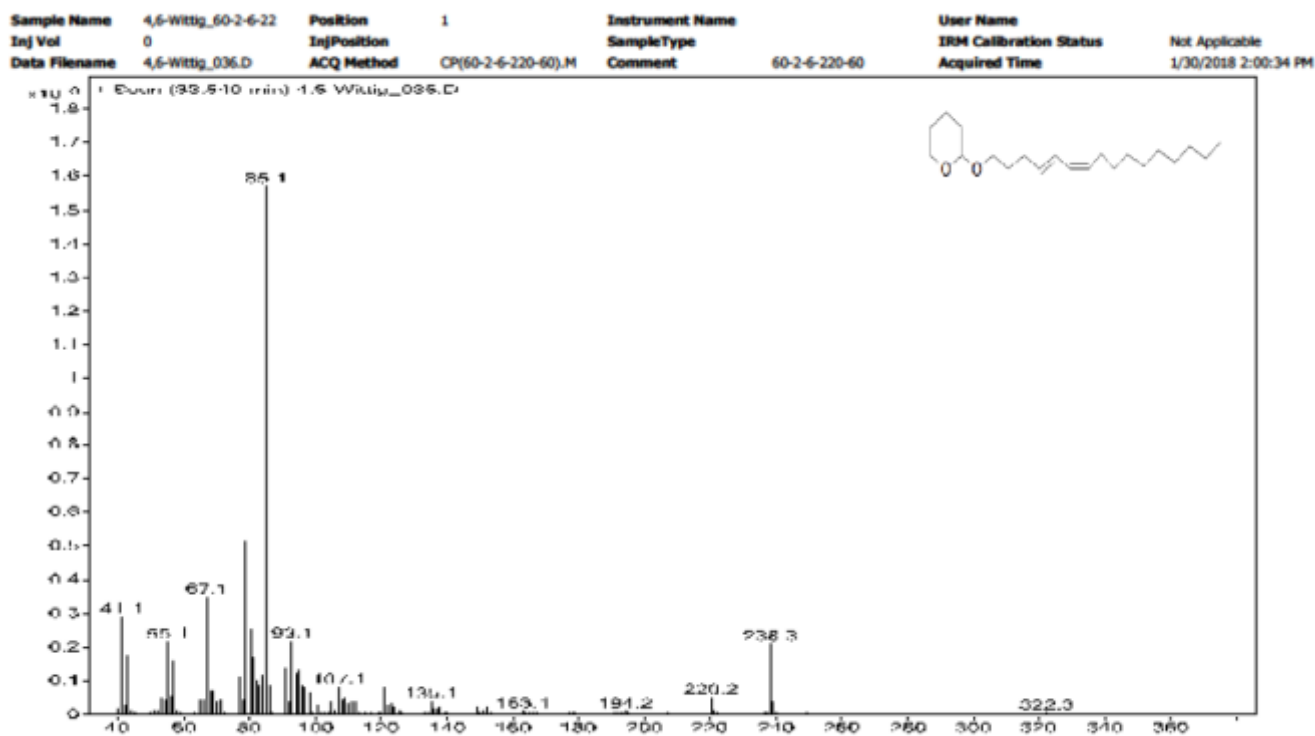
Figure 15 MS-16-(2-Tetrahydropyranyloxy)-hexadeca-4(E)-6(Z)-dien
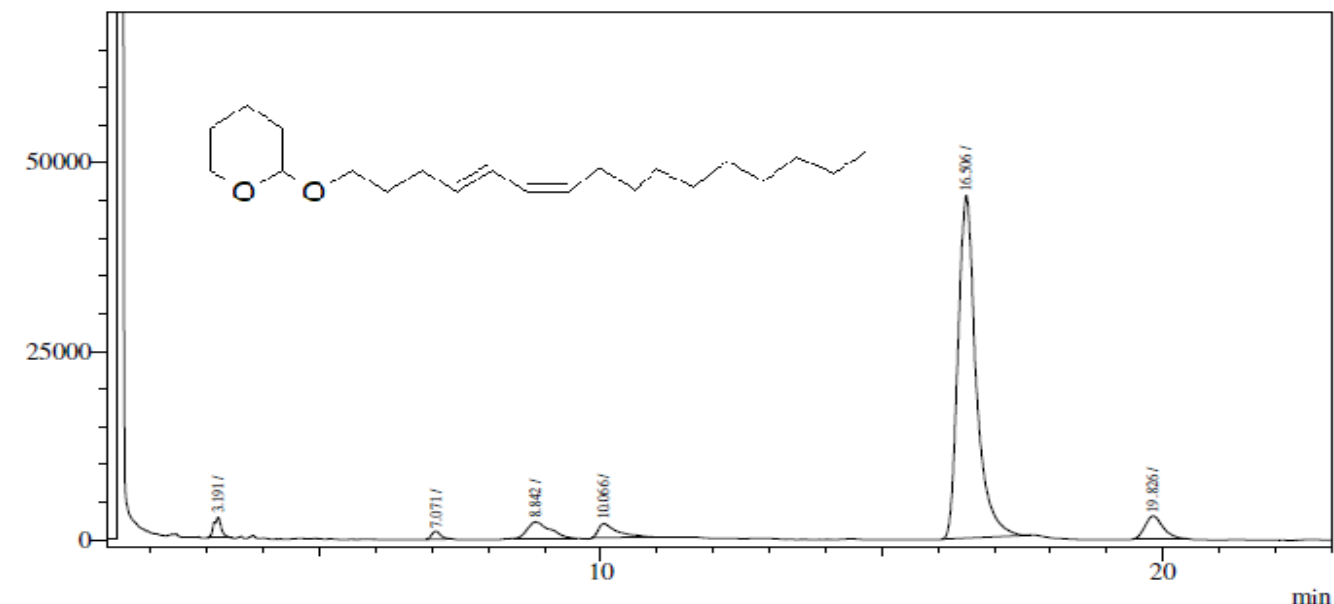
| Peak Table - Channel 1 | | | | | |
Peak#	Ret.Time	Height	Area	Height%	Area%
1	3.191	2735	25668	4.8557	2.0912
2	7.071	1067	11510	1.8938	0.9377
3	8.842	2203	61337	3.9119	4.9971
4	10.066	1845	42661	3.2759	3.4755
5	16.506	45411	1018449	80.6279	82.9725
6	19.826	3061	67828	5.4347	5.5259
Total		56322	1227453	100.0000	100.0000

Figure 16 GC-16-(2-Tetrahydropyranyloxy)-hexadeca-4(E)-6(Z)-dien
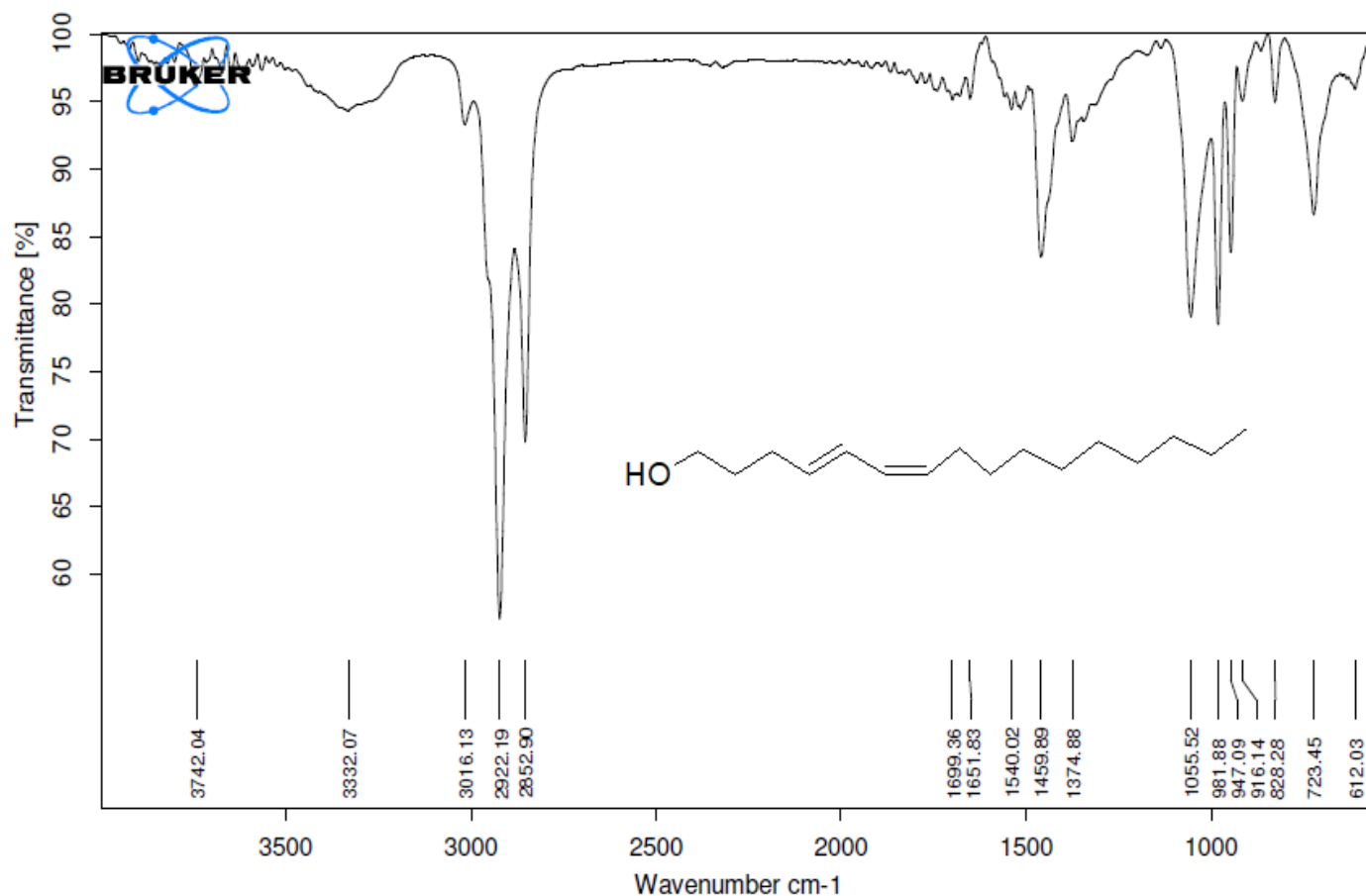
Figure 17 IR- (4E,6Z)-hexadeca-4,6-dien-1- ol
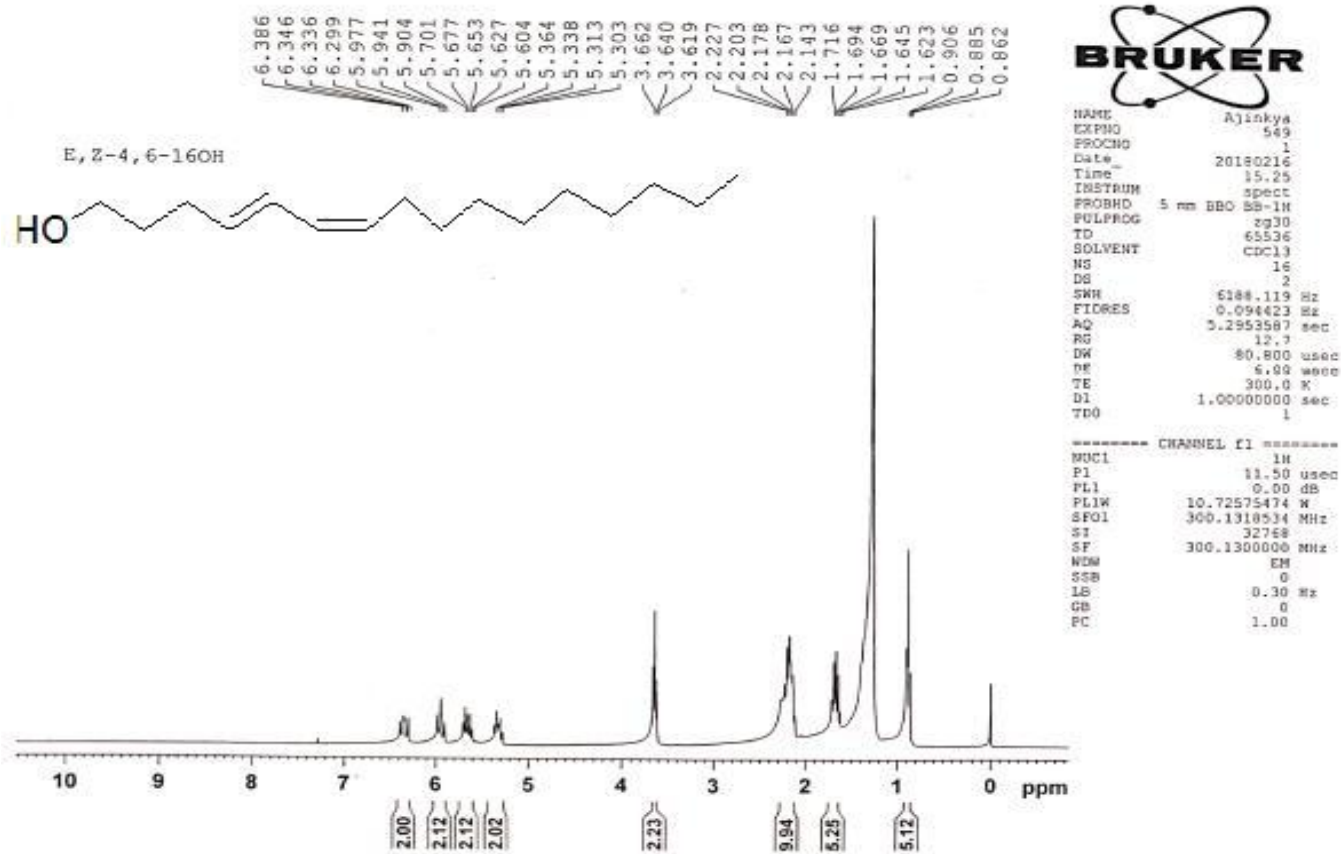
Figure 18 ^{1}H NMR - (4E,6Z)-hexadeca-4,6-dien-1- ol
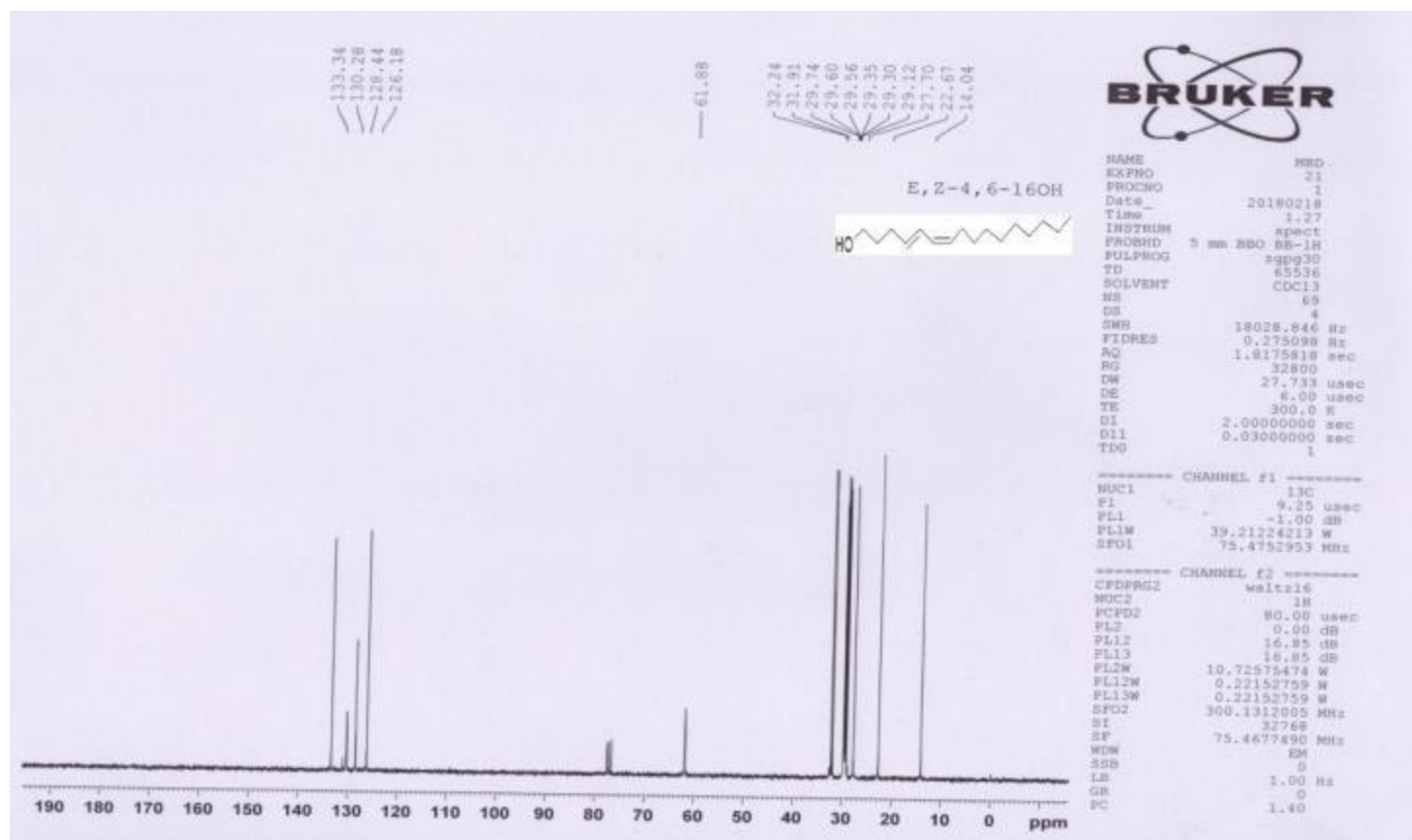
Figure 19 ^{13}C NMR-(4E,6Z) -hexadeca-4,6-dien-1-ol
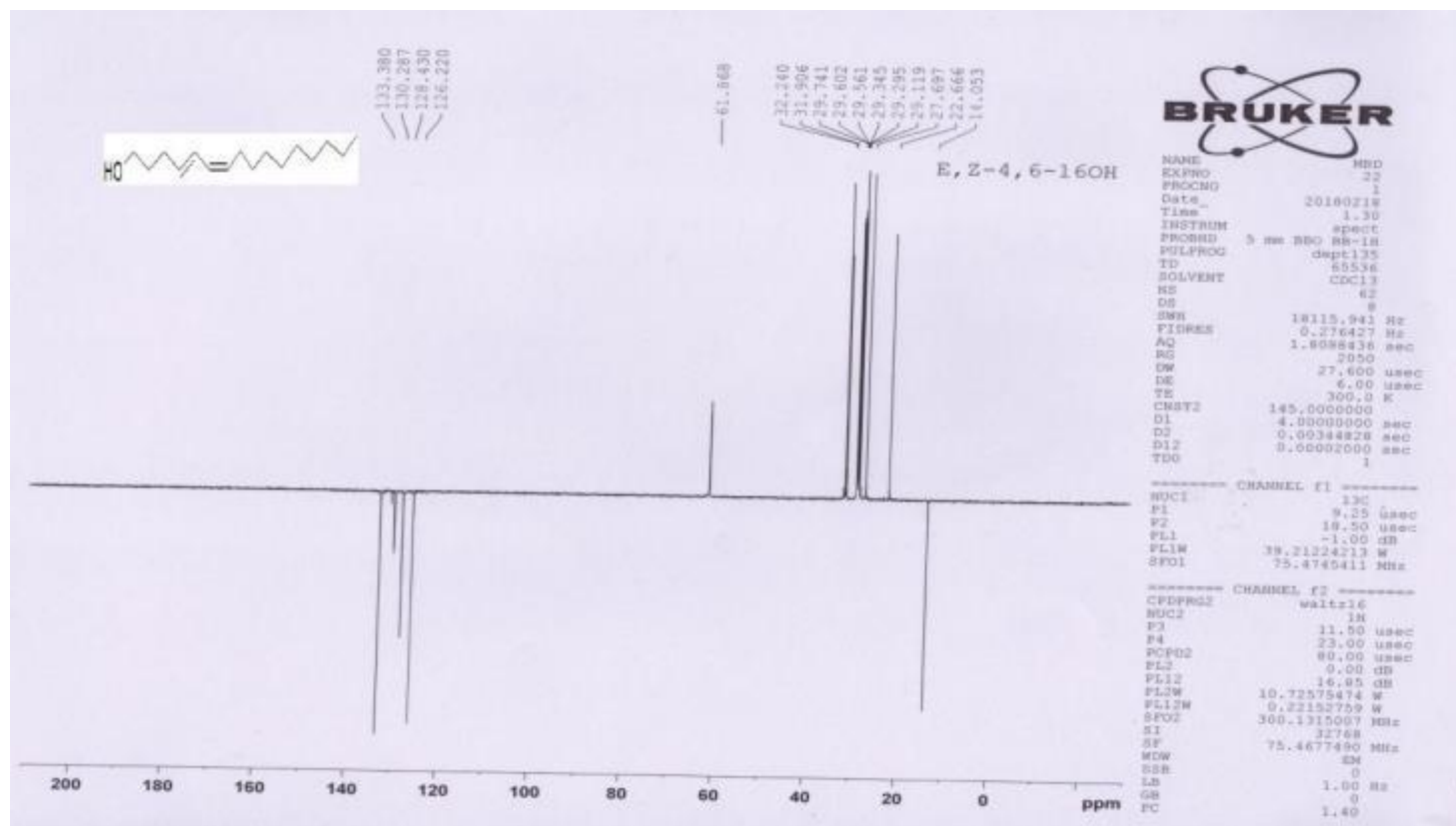
Figure 20 ^{13}C DEPT NMR-(4E,6Z) -hexadeca-4,6-dien-1-ol
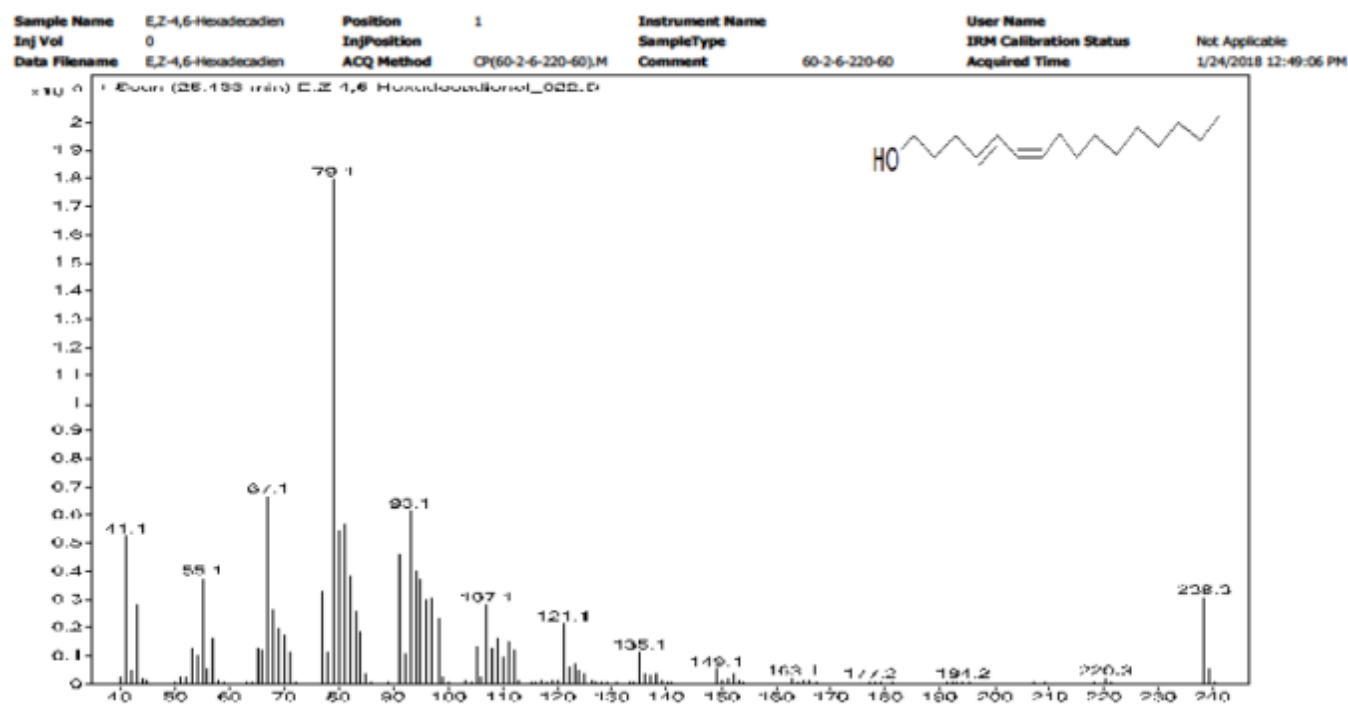
Figure 21 MS-(4E,6Z) -hexadeca-4,6-dien-1-ol
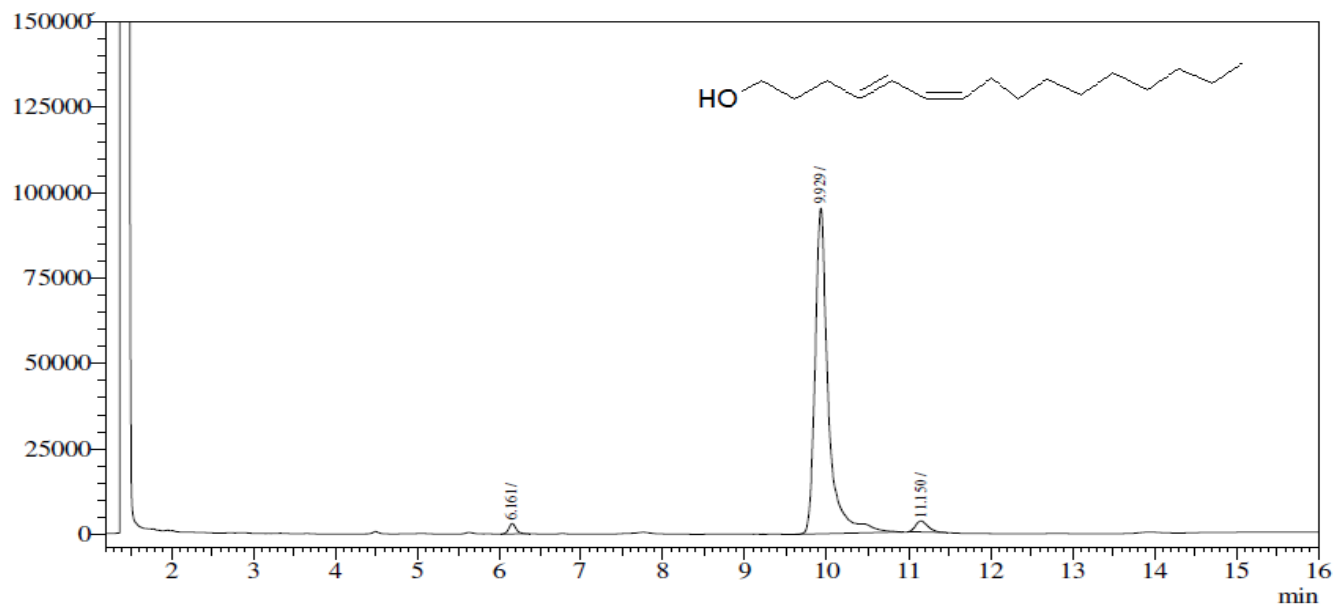
Peak Table - Channel 1

Peak#	Ret.Time	Height	Area	Height%	Area%
1	6.161	3058	18901	3.0103	1.6790
2	9.929	95226	1072007	93.7339	95.2313
3	11.150	3308	34780	3.2558	3.0896
Total		101592	1125688	100.0000	100.0000

Figure 22 GC-(4E,6Z) -hexadeca-4,6-dien-1-ol
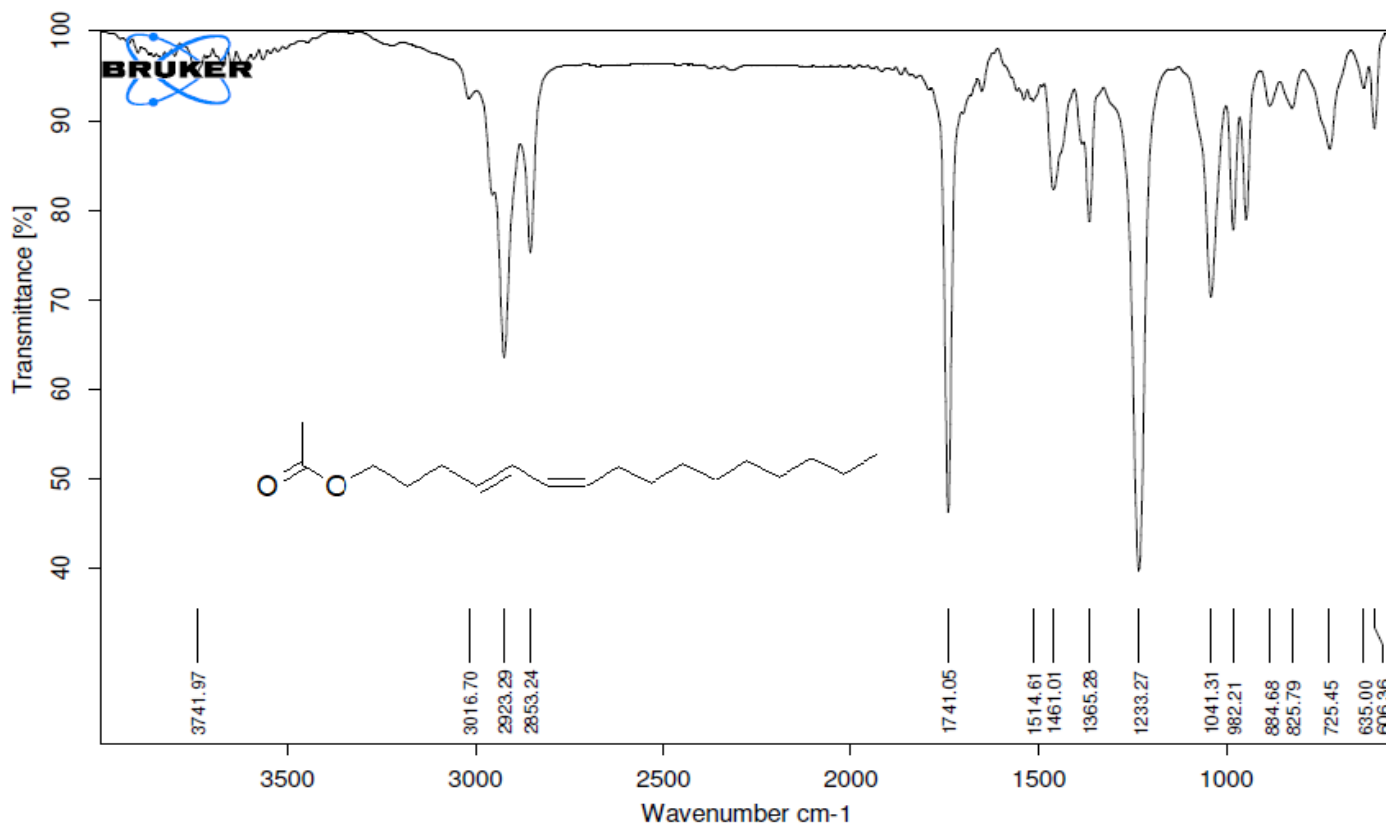
Figure 23 IR- (4E,6Z) -hexadeca-4,6-dienyl acetate
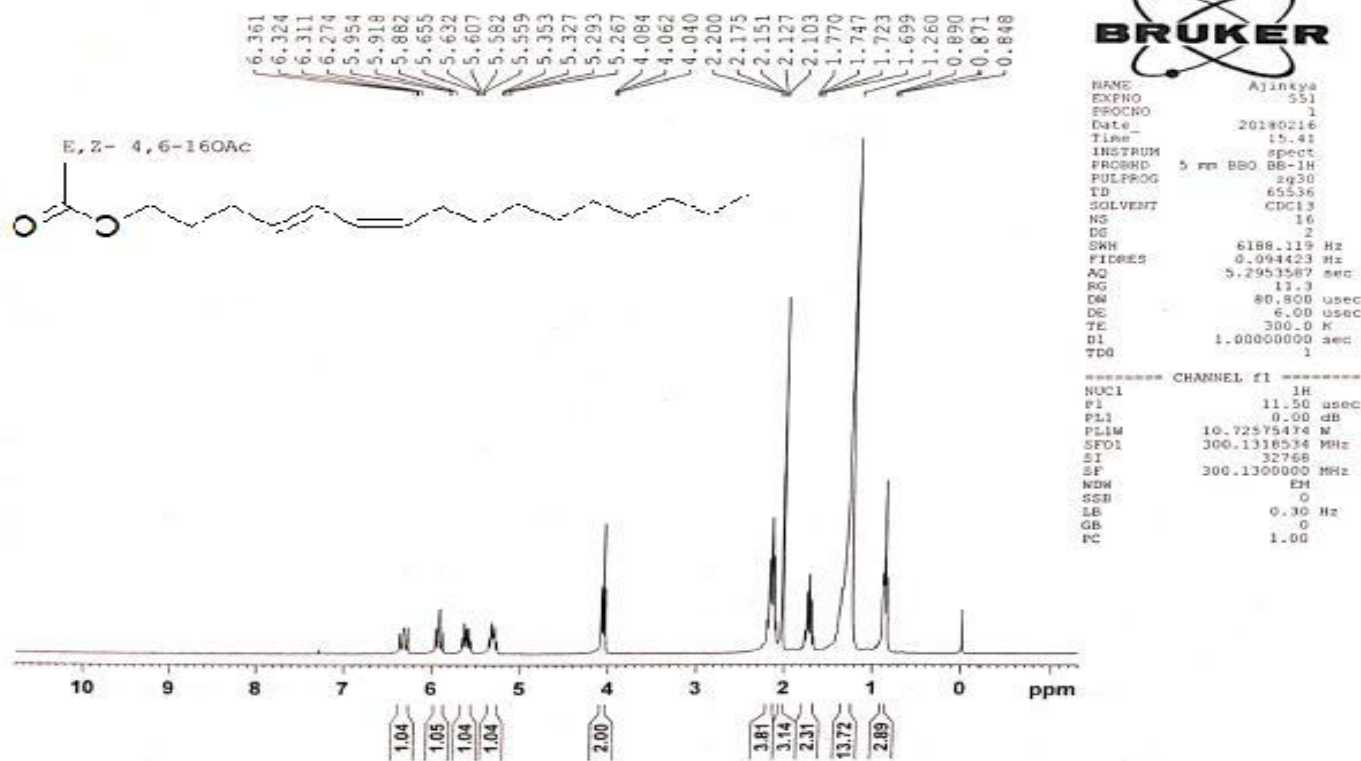
Figure 24 ^{1}H NMR - (4E,6Z) -hexadeca-4,6-dienyl acetate
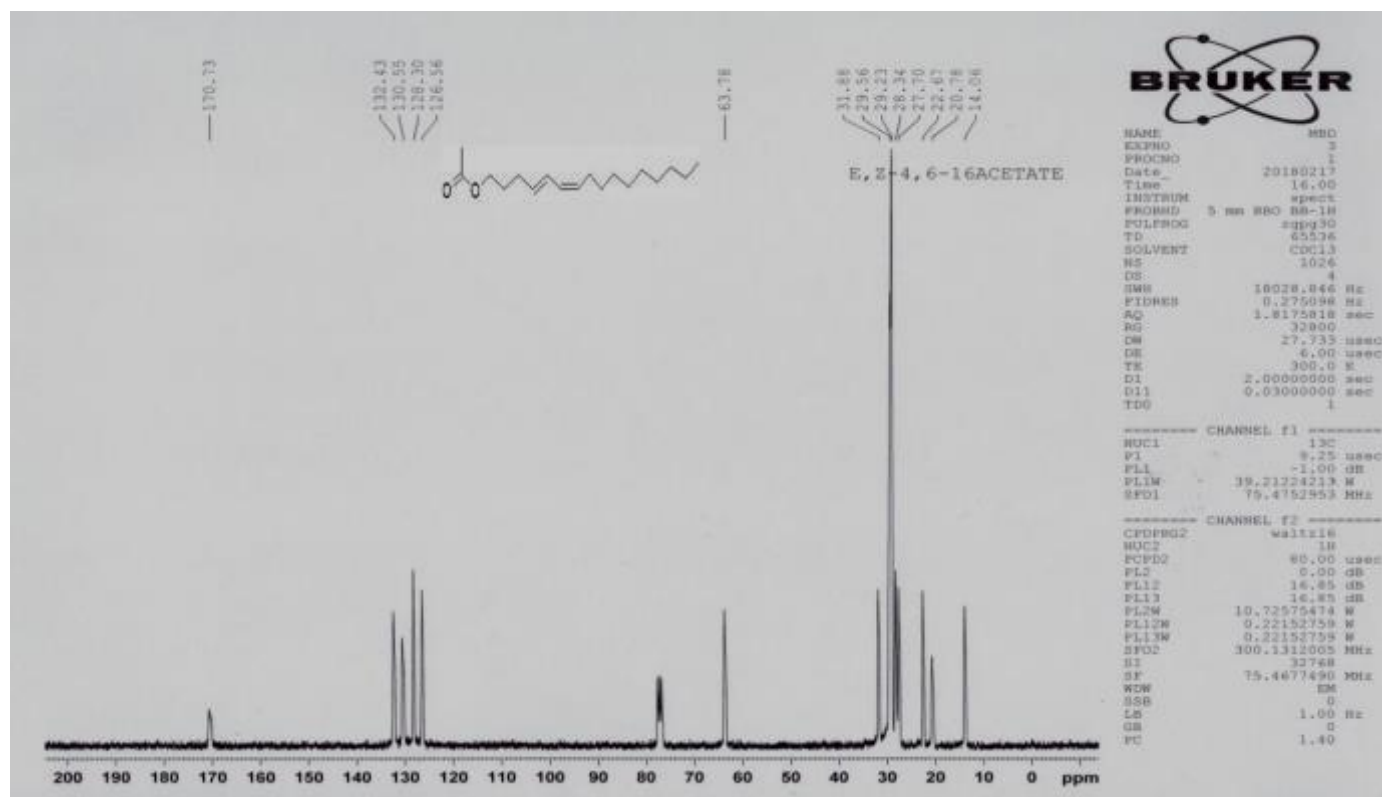
Figure 25 ^{13}CNMR- (4E,6Z) -hexadeca-4,6-dienyl acetate
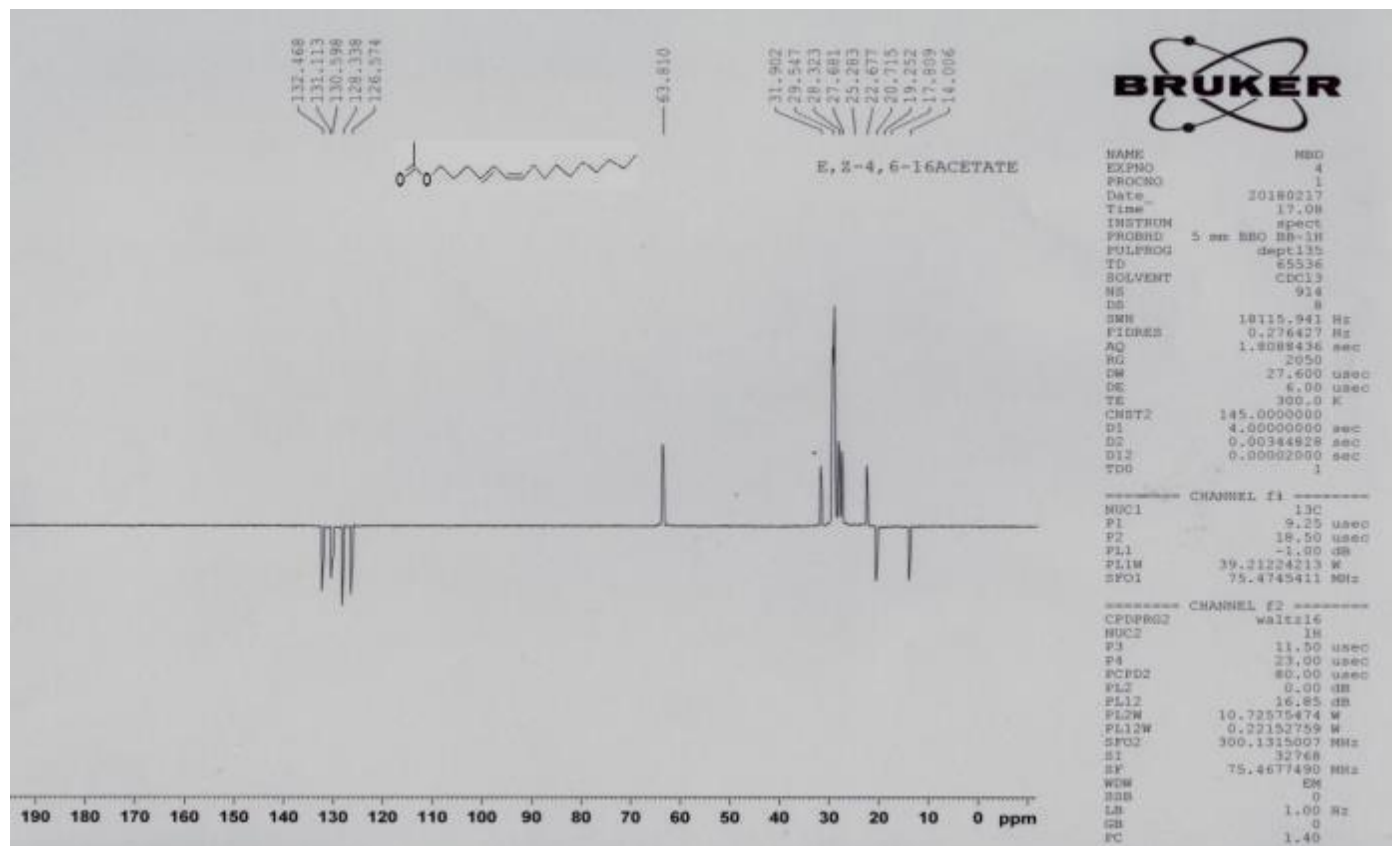
Figure 26 ^{13}C DEPT NMR- (4E,6Z) -hexadeca-4,6-dienyl acetate
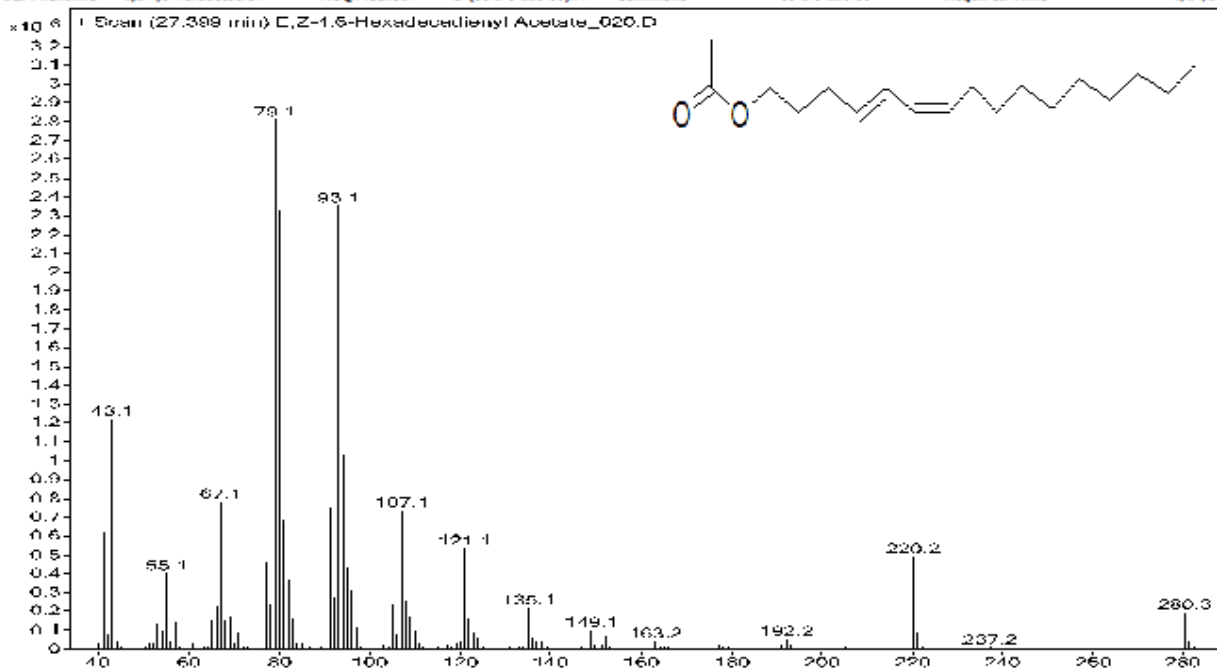
Figure 27 MS-(4E,6Z) -hexadeca-4,6-dienyl acetate

Peak Table - Channel 1

Peak#	Ret. Time	Height	Area	Height%	Area%
1	5.017	2356	13955	1.8480	1.0720
2	7.814	123993	1277886	97.2478	98.1677
3	8.995	1153	9897	0.9042	0.7603
Total		127502	1301738	100.0000	100.0000
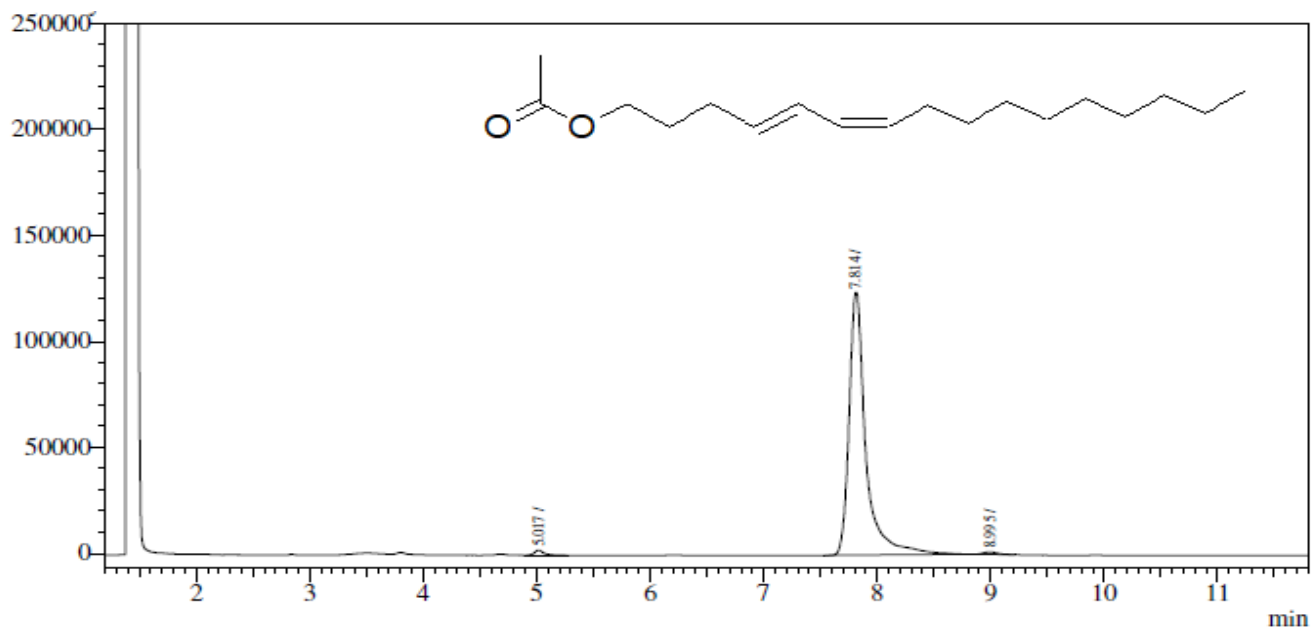
Figure 28 GC-(4E,6Z) -hexadeca-4,6-dienyl acetate
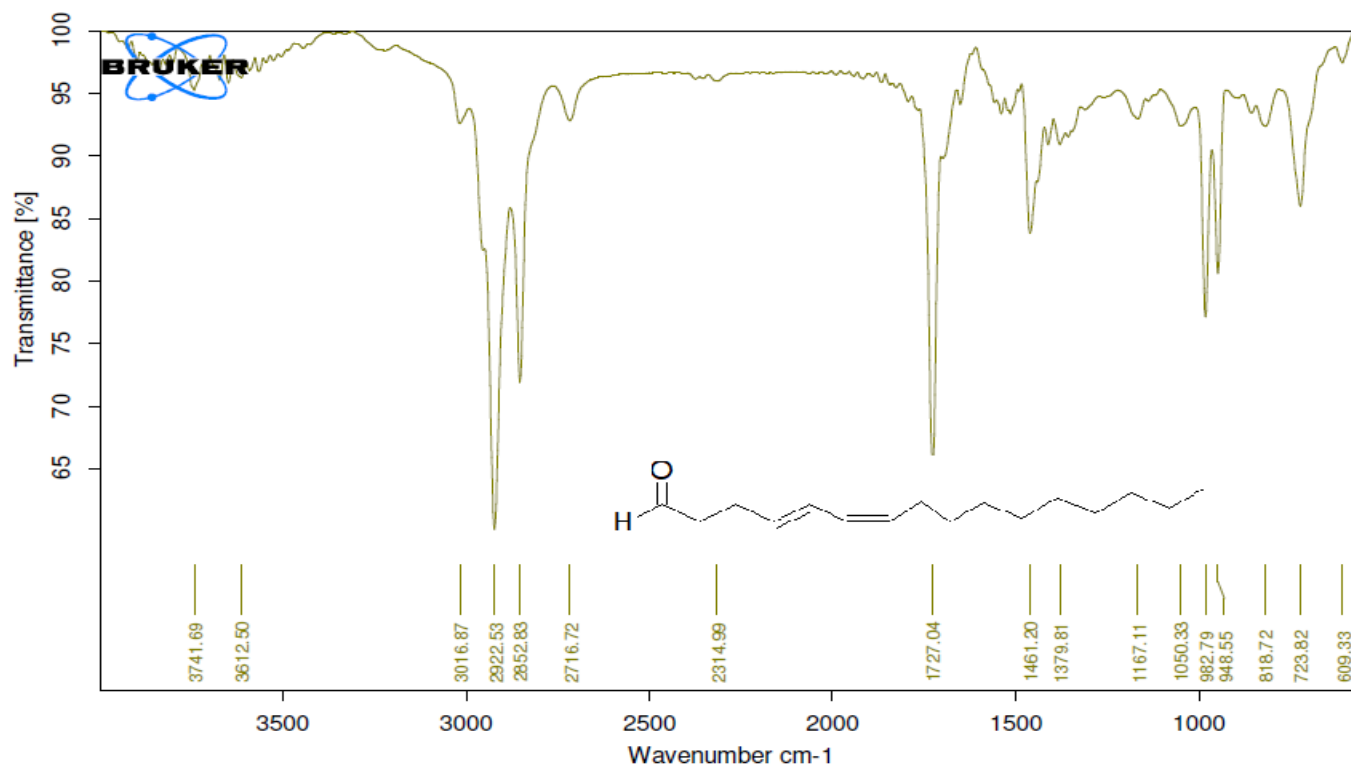

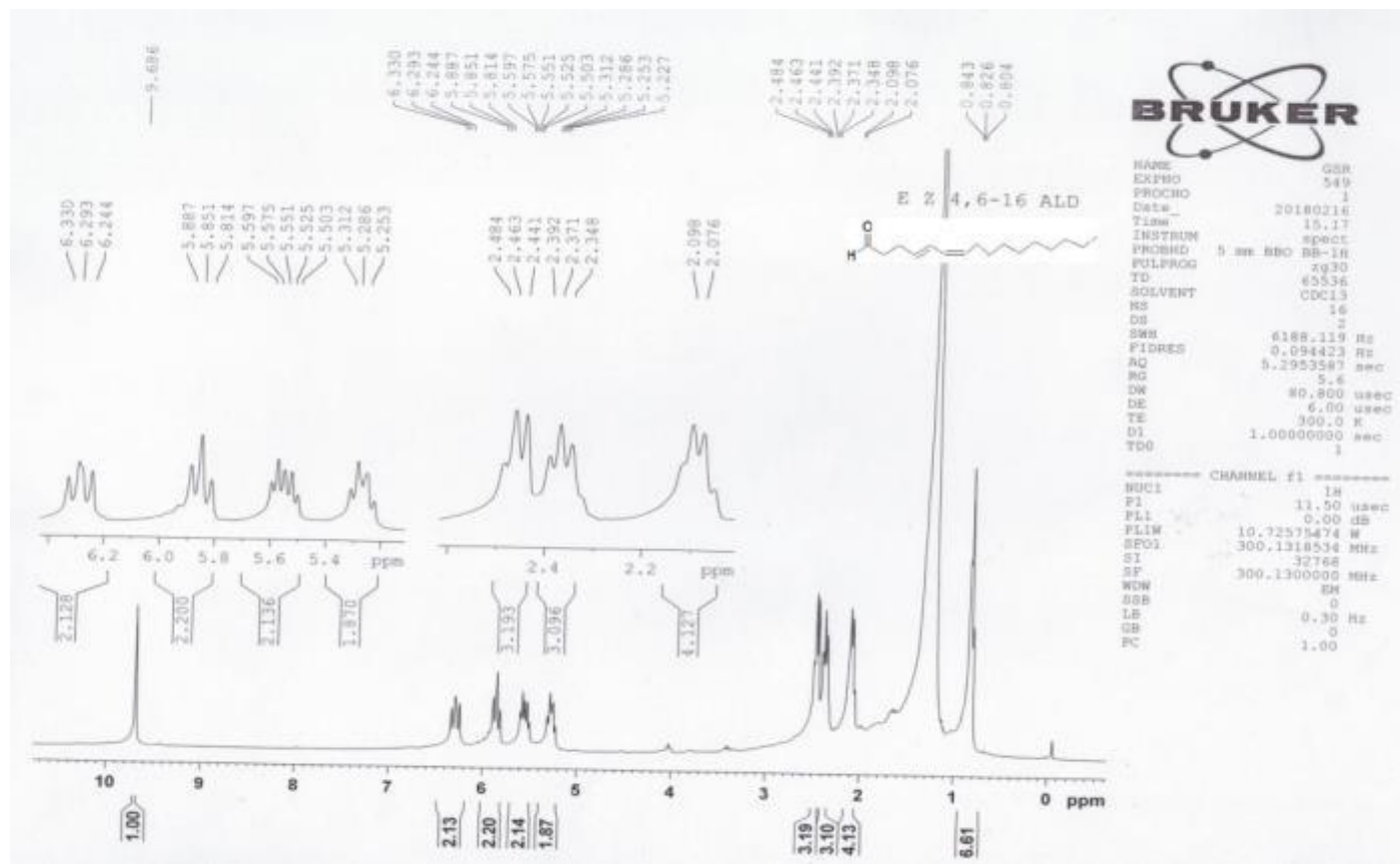**Figure 29** IR -(4E,6Z)-hexadeca-4,6-dienal
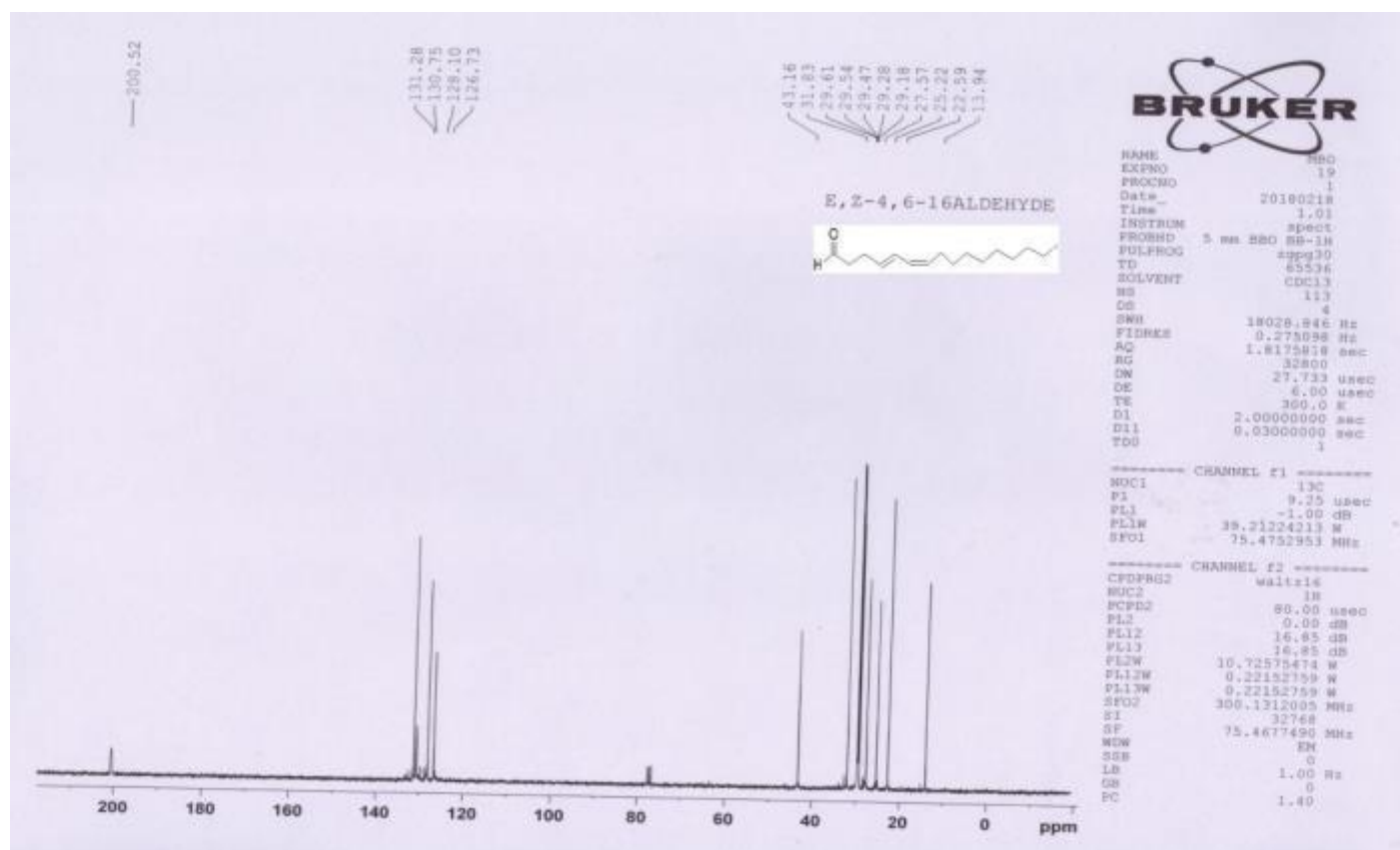
Figure 30 ^{1}H NMR -(4E,6Z)-hexadeca-4,6-dienal

Figure 31 ^{13}CNMR-(4E,6Z) -hexadeca-4,6-dienal
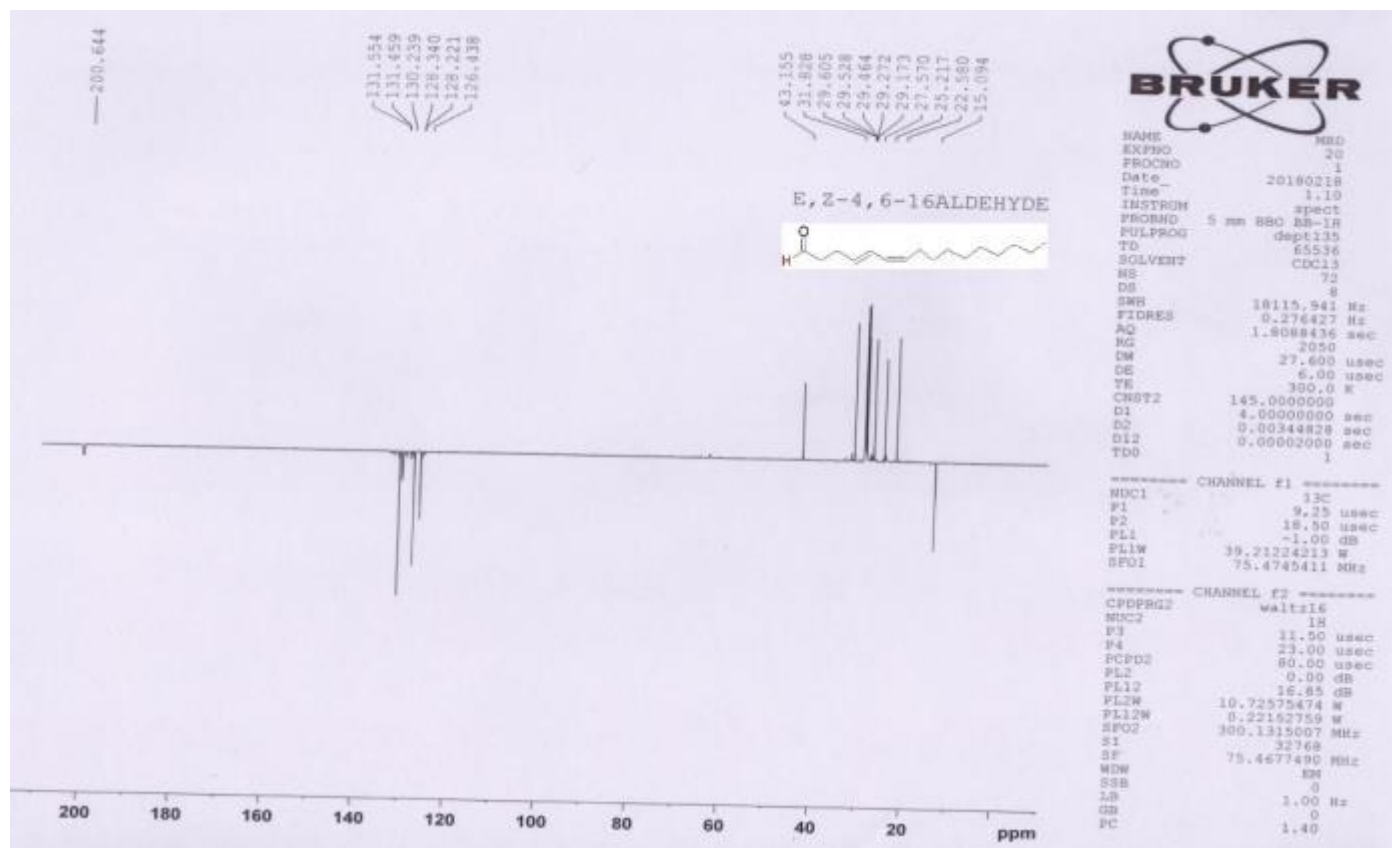
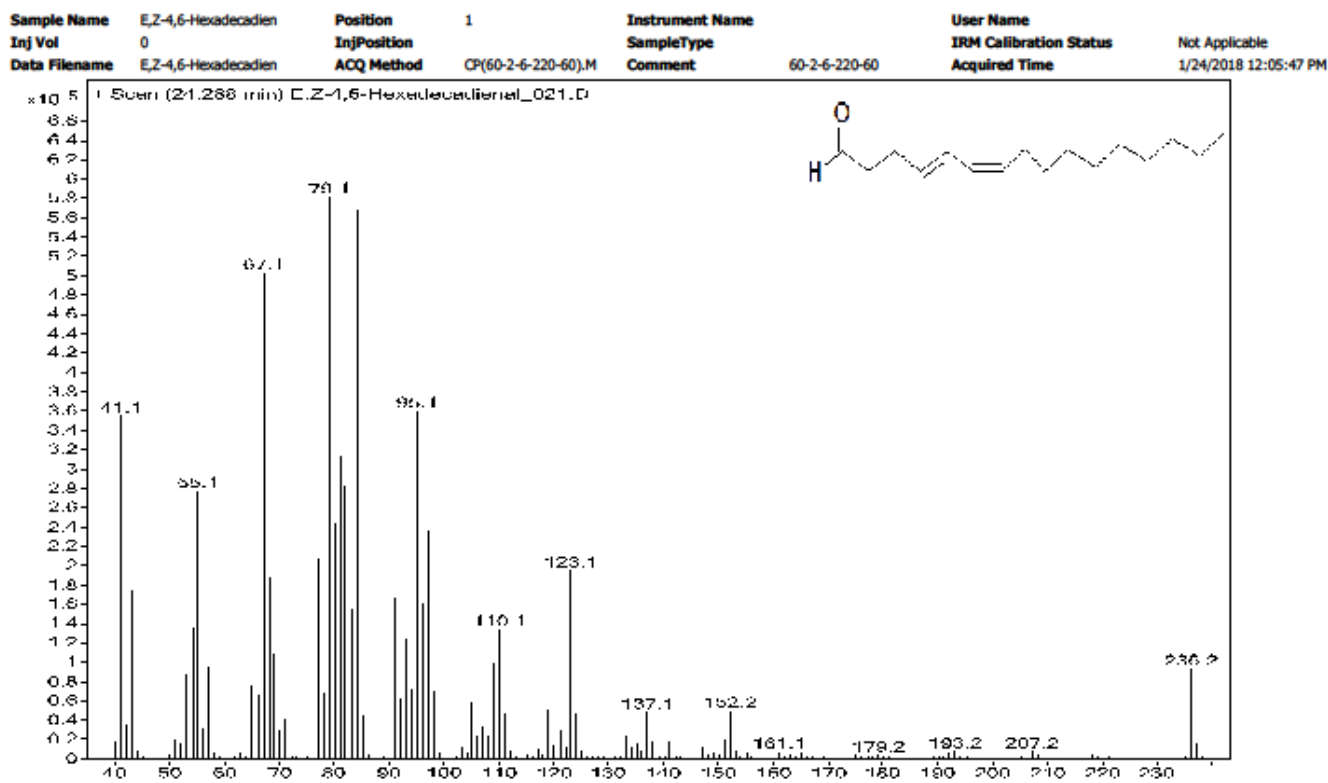**Figure 32** ^{13}C DEPT NMR-(4E,6Z) -hexadeca-4,6-dienal

Figure 33 MS-(4E,6Z)-hexadeca-4,6-dienal
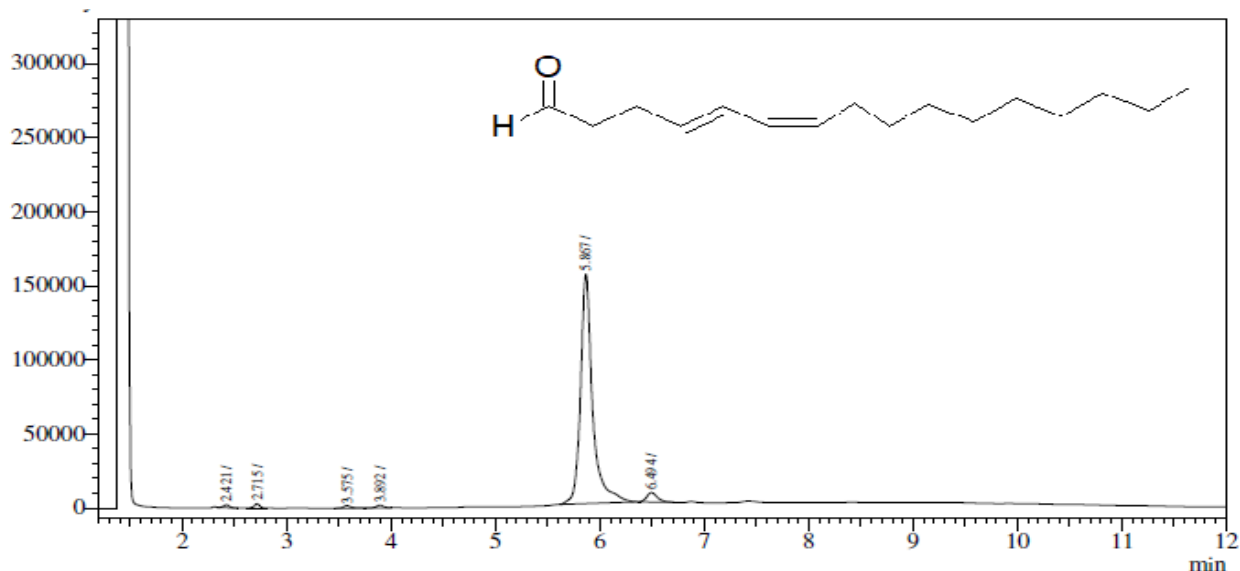
Peak Table - Channel 1

Peak#	Ret.Time	Height	Area	Height%	Area%
1	2.421	1967	7367	1.1622	0.5553
2	2.715	2999	10560	1.7717	0.7960
3	3.575	1676	8720	0.9900	0.6573
4	3.892	1777	8125	1.0500	0.6125
5	5.867	154485	1247431	91.2709	94.0320
6	6.494	6356	44399	3.7551	3.3468
Total		169260	1326602	100.0000	100.0000

Figure 34 GC-(4E,6Z)-hexadeca-4,6-dienal

Green metrics calculations of Persimmon Fruit Moth

Mass Intensity

Σ Reactant Weight/Weight of product in gm (yield)
Reactant weight = All reactants weight in gm included solvent and catalyst
Conversion of ml to gm = volume × Density
Volume = Mol Wt / Density

Reaction Mass Efficiency (RME %)

% RME = Weight of Product (Yield)/ Σ Reactant Weight × 100

Carbon Efficiency (CE):

% CE = Σ Number of moles of product × Number of carbons in product / Σ Number of moles of reactant ×Number of carbons in reactant × 100

For CE calculation, do not take weight of solvent and catalyst.

Atomic Efficiency (AE %)

%AE = Mol. Wt. of product / Σ Mol. Wt. of reactants × 100

For AE calculation, do not take weight of solvent and catalyst.

The greater yields of the product indicate that the significant RME values and moderate yield generate moderate RME values. Furthermore, the percent CE of step1 is 69 % while at step 6 and 7 percent CE is 94.07% and 62.5% respectively, demonstrated a remarkable conversions to the final products. Finally, the percent atom economy of step 1 is 100% and at step 6 and 7 AE is 88.46% and 99.15% respectively, indicates maximum conversion of starting materials into product and minimum waste (Table 1).

The green metrics calculations for compounds were calculated as below.

Table 1 Green metrics calculations

Green metrics calculations of Persimmon Fruit Moth						
Sr. no.	Particulars	MI	%RME	%CE	%AE	% Yield
1	Step I	7.65	65	69	100	76
2	Step II	4.86	89	88.11	101	88
3	Step III	35.76	63.5	64	99.00	64
4	Step IV	11.68	36,04	41,05	47.28	79
5	Step V	3.04	59.1	60.92	73.91	80
6	Step VI	3.97	82.08	94.07	88.46	95
7	Step VII	16.8	62.4	62.5	99.15	63