Supporting Information

Total synthesis of C_{37} alken-2-one temperature geomarkers

Anna Alcaide,[a] Carme Serra,[a] Juanlo Catena,[a,b] Lourdes Muñoz[a] and Amadeu Llebaria*[a,b]

[a] Synthesis of High Added Value Molecules (SIMChem), Institute for Advanced Chemistry of Catalonia (IQAC-CSIC), Jordi Girona 18-26, Barcelona, 08034, Spain.

[b] Medicinal Chemistry and Synthesis (MCS), Institute for Advanced Chemistry of Catalonia (IQAC-CSIC), Jordi Girona 18-26, Barcelona, 08034, Spain.

* Corresponding author. Tel. +34 934006100; Fax +34 932045904; E-mail: amadeu.llebaria@iqac.csic.es

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1. Experimental Section

1.1. General information

All moisture-sensitive reactions were carried out under Argon. All glassware used to prepare the Grignard reagents was flame-dried under vacuum and back-filled with nitrogen. Activation of 3Å molecular sieves involved heating in an oven at 400 ºC at least 4h or overnight. Commercially available chemicals were used without further purification. Solvents were dried prior to use with Pure Solv-ENTM system or distilled and dried by standard methods. Thin-layer chromatography (TLC) was performed on silica gel (Alugram Sil G/UV) and flash chromatography was done using silica gel 60 (40-63 microns, Panreac) or Biotage® SNAP Cartridges when using Biotage® Isolera PrimeTM flash purification system. Flash chromatography purifications using $AgNO_3$ adsorbed on silica[1] were performed in the dark and TLC plates impregnated in 20% $AgNO_3$ were used to identify the compounds. These plates were commercially available and a solution of phosphomolybdic acid monohydrate was used as a dye. Analytical samples were homogeneous as confirmed by TLC and afforded spectroscopic results consistent with the assigned structures. For GC-MS analysis, 2 µL of samples were injected in splitless mode into a Finnigan Trace 2000 GC system (Thermo Scientific) coupled to a Trace MS quadrupole mass spectrometer (Thermo Scientific). The analyses were implemented in HP-5MS (30m x 0.25 mm x 0.25 µm) capillary columns (Agilent Technologies) in electron impact (EI) mode. The oven programme was 50 ºC for 5 min, then raised to 280 ºC (10 ºC/min) and maintained at this temperature for 10 min. Helium (1 mL/min) was used as carrier gas. Mass range was m/z 50–700, with a scan time of 1.0 s. Alternatively, an Agilent 7890A gas chromatograph coupled to an Agilent 5975 inert XL EI/CI MSD with triple-axis detector was used under positive chemical ionization conditions in methane. The analysis was implemented in a CP-Sil 5 DB column (50m x 0.32mm x 0.12µm) from Agilent Technologies. The oven program started at 90 ºC, immediately raised to 170 ºC (20ºC/min), maintained for 1ºC and then raised to 280 ºC (6ºC/min), maintained for 35 min and raised again to 320ºC (10ºC/min) and finally maintained for 20 min. Helium was used as the carrier gas at a constant column flow of 3ml/min. The injector temperature was set at 320 ºC. Mass range was m/z 70-750 Identification of compounds was done by comparison of their MS and RT values with those of synthetic chemicals and/or previous isolated compounds. All NMR spectra were acquired at 25°C on a Varian VNMRS 400 MHz (^{1}H at 400.10 MHz and ^{13}C at 100.62 MHz), equipped with a OneNMR probe and ProTune system. Chemical shifts are reported in δ (ppm) relative to the singlet at δ = 7.26 ppm of $CDCl_3$ for ^{1}H NMR, and to the center line of the triplet at δ = 77.16 ppm of $CDCl_3$ for ^{13}C-NMR. ESI/HRMS were recorded with a Waters LCT Premier mass spectrometer.

1.2. Synthesis of bromide 3

1.2.1. Undeca-2,9-diyne-1,11-diol (9)

A solution of prop-2-yn-1-ol (7.51 mL, 128 mmol) in anhydrous THF (250 mL) was cooled to -20ºC, then butyllithium (2.5 M in hexanes, 100 mL, 250 mmol) was added and the resulting solution was stirred at this temperature for 30 minutes. To the previous solution was added HMPA (37.4 mL, 213 mmol) and 1,5-dibromopentane (**11**, 7.47 mL, 53.2 mmol). The resulting mixture was allowed to reach room temperature and stirred for 3 days. After that, the reaction mixture was quenched by adding sat. aq. NH_4Cl (75 mL) and extracted with Et_2O (3 x 75 mL). Then, the collected organic layers were dried over $MgSO_4$, filtered and the solvent of the filtrate was removed under reduced pressure to afford a pale yellow oil that was purified by *flash* chromatography on silica gel (hexane-EtOAc 7:1, isocratic) to afford pure product **9** (8.8 g, 92%) as a colorless oil. Characterization data obtained for diol **9** were identical with the described in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (s, 4H), 2.24 (s, 4H), 1.52 (s, 6H).

1.2.2. (2*E*,9*E*)-undeca-2,9-diene-1,11-diol (16)

A solution of undeca-2,9-diyne-1,11-diol (**9**, 2.00 g, 11.1 mmol) in anhydrous THF (110 mL) was cooled to 0ºC and, then, $LiAlH_4$ (927 mg, 24.4 mmol) was added in one portion. The resulting suspension was heated at reflux and stirred at this temperature for 3h. This reaction was monitored by ^{1}H-NMR until no starting material remained. After that, the reaction mixture was quenched with sat. aq. NH_4Cl (3 mL), dried over $MgSO_4$, filtered and the solvent of the filtrate was removed under reduced pressure to afford the desired diol **16** (2.05 g, 100%) as a colorless oil. Characterization data obtained for compound **16** were identical with the described in the literature.[31] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82–5.55 (m, 4H), 4.10 (d, *J* = 4.8 Hz, 4H), 2.06 (q, *J* = 6.5 Hz, 4H), 1.45–1.27 (m, 6H).

1.2.3. (2*E*,9*E*)-11-bromoundeca-2,9-dien-1-ol (7)

To a solution of (2*E*,9*E*)-undeca-2,9-diene-1,11-diol (**16**, 2.37 g, 12.86 mmol) in anhydrous DCM (130 mL), was added DIPEA (2.26 mL, 12.9 mmol). The resulting solution was cooled to 0ºC and then, MsBr (800 μL, 9.65 mmol) was added. This mixture was allowed to reach room temperature and stirred overnight. The reaction mixture was diluted with water (30 mL) and extracted with DCM (3 x 30 mL). The collected organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered and the solvent of the filtrate was removed under reduced pressure to give a residue that was purified by *flash* chromatography (silica gel, hexane-EtOAc 8:2 to 1:1, gradient) to afford (2*E*,9*E*)-11-bromoundeca-2,9-dien-1-ol (**7**, 1.77 g, 56%), accompanied of the (2*E*,9*E*)-1,11-dibromoundeca-2,9-diene (510 mg, 13%) as colorless oil and the starting material (2*E*,9*E*)-undeca-2,9-diene-1,11-diol. **(2*E*,9*E*)-11-bromoundeca-2,9-dien-1-ol (7).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80–5.58 (m, 4H), 4.08 (d, *J* = 4.9 Hz, 2H), 3.94 (d, *J* = 7.2 Hz, 2H), 2.09–1.99 (m, 4H), 1.43–1.26 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 133.4, 129.1, 126.5, 63.9, 33.8, 32.2, 32.1, 29.0, 28.7, 28.7. GC-MS (EI): m/z (%) = 246.1 $[M]^+$ (1), 202.0 (1), 167.1 (2), 149.1 (36), 135.0 (18), 123.1 (24), 107.1 (64), 93.1 (79), 81.0 (94), 67.0 (100), 55.1 (85), 43.0 (61).

1.2.4. Tridecylmagnesium bromide (8)

A suspension of magnesium (905 mg, 37.2 mmol) in anhydrous THF (3 mL) was heated to 50ºC. Then, 1,2-dibromoethane (162 μl, 1.86 mmol) was added and the resulting solution was heated to 50ºC and stirred at this temperature for 30 minutes. Then, the solvent of the suspension was removed by syringe suction and Mg turnings were resuspended in anhydrous THF (7.45 mL). After that, 1-bromotridecane (971 μl, 3.72 mmol) was added and the resulting solution was stirred at this temperature for 2h, when the starting 1-bromotridecane was almost consumed. At this point the next reaction step was carried out (see preparation of product **17**) by using the necessary amount of Grignard reagent, considering that the final concentration of tridecylmagnesium bromide was 0.44M in THF.

1.2.5. (2*E*,9*E*)-tetracosa-2,9-dien-1-ol (17)

To a solution of (2*E*,9*E*)-11-bromoundeca-2,9-dien-1-ol (**7**, 400 mg, 1.62 mmol) in anhydrous THF (16 mL), was added 0.1 M Li_2CuCl_4 in THF (809 μL, 0.081 mmol). The resulting solution was cooled to -70ºC and then, a freshly prepared solution of tridecylmagnesium bromide **8** (0.44 M, 11.0 mL, 4.85 mmol) in THF was quickly added (see preparation of product **8**). The resulting mixture was allowed to reach room temperature and stirred overnight. After that, the reaction mixture was quenched with sat. aq. NH_4Cl (50 mL) and then extractions with Et_2O (3 x 50 mL) were done. The collected organic layers were dried over $MgSO_4$, filtered

and the solvent of the filtrate was removed under reduced pressure to afford a residue that was purified by *flash* chromatography (20% $AgNO_3$ adsorbed on silica gel[1], hexane-EtOAc 99:1 to 97:3, gradient) to afford product **17** (163 mg, 29%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74–5.58 (m, 2H), 5.41–5.35 (m, 2H), 4.08 (br d, *J* = 5.4 Hz, 2H), 2.09–2.00 (m, 2H), 2.00–1.89 (m, 4H), 1.43–1.20 (m, 30H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.7, 130.7, 130.3, 129.0, 64.0, 32.8, 32.7, 32.3, 32.1, 31.8, 29.9, 29.8, 29.7, 29.6, 29.5, 29.3, 29.2, 28.8, 22.9, 14.3. GC-MS (EI): m/z (%) = 351.4[M]$^+$ (1), 333.3 (21), 331.3 (23), 151.1 (24), 137.1 (43), 123.1 (58), 111.1 (64), 97.1 (100), 83.1 (68).

1.2.6. (2*E*,9*E*)-1-bromotetracosa-2,9-diene (3)

To a solution of (2*E*,9*E*)-tetracosa-2,9-dien-1-ol (**17**, 156 mg, 0.450 mmol) in anhydrous DCM (5 mL), was added DIPEA (274 µl, 1.56 mmol) and then, MsBr (92 µl, 1.11 mmol). The resulting solution was stirred at room temperature overnight. The reaction mixture was quenched with water (25 mL) and extracted with DCM (3 x 25 mL). After that, the collected organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered and the solvent of the filtrate was removed under reduced pressure to afford pure bromide **3** (180 mg, 98%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82–5.60 (m, 2H), 5.39–5.33 (m, 2H), 3.93 (dd, *J* = 7.3, 0.7 Hz, 2H), 2.04 (q, *J* = 6.9 Hz, 2H), 1.95 (q, *J* = 6.1 Hz, 4H), 1.24 (s, 30H), 0.86 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 131.1, 130.6, 126.7, 34.1, 33.1, 32.9, 32.0, 31.9, 30.2, 30.2, 30.1, 30.0, 29.9, 29.3, 29.8, 29.1, 20.1, 23.2, 14.6. GC-MS (EI): m/z (%) 333.4 (39), 332.5 (19), 331.5 (100), 135.4 (13), 123.1 (18), 109.2 (29), 97.1 (16), 95.3 (18).

1.3. Synthesis of Grignard reagent 13

1.3.1. Ethyl 4-(2-methyl-1,3-dioxolan-2-yl)butanoate (22)

To a solution of 4-methylbenzenesulfonic acid hydrate (37 mg, 0.190 mmol) in toluene (218 mL) was added ethyl 5-oxohexanoate (**21**, 3 mL, 18.8 mmol) and ethane-1,2-diol (5.2 mL, 94.0 mmol). The resulting solution was heated at reflux overnight with continuous removal of water by using 3Å molecular sieves (50 g) placed in an addition funnel, coupled to a refrigerant. The reaction mixture was allowed to reach room temperature and neutralized by adding solid Na_2CO_3 until reaching pH 5-6. After that, the resulting solution was filtered and the filtrate was diluted with Et_2O (75 mL). The organic layer was washed with sat. aq. $NaHCO_3$ (3 x 75 mL) and brine (75 mL), and it was dried over $MgSO_4$, filtered and the solvent of the filtrate was removed under reduced pressure to afford a pale yellow oil (3.41 g, 90%) that was used without further purification in the next reaction step. Characterization data obtained for compound **22** were identical with the described in the literature.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (q, *J* = 7.1 Hz, 2H), 3.99–3.86 (m, 4H), 2.33 (dd, *J* = 13.6, 6.6 Hz, 2H), 1.78–1.63 (m, 4H), 1.32 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).

1.3.2. 4-(2-methyl-1,3-dioxolan-2-yl)butan-1-ol (23)

A solution of ethyl 4-(2-methyl-1,3-dioxolan-2-yl)butanoate (**22**, 217 mg, 1.07 mmol) in anhydrous THF (3.5 mL) was cooled to 0ºC. Then, 1 M DIBALH in THF (2.7 mL, 2.68 mmol) was added. The resulting solution was stirred at 0ºC for 10 minutes and then, at room temperature for 3h. After that, the reaction mixture was cooled to 0ºC and water (2-3 mL) was added dropwise. When no reaction was observed, $MgSO_4$ was added and this suspension was stirred for 1h, filtered and the solvent of the filtrate was removed under reduced pressure to give a residue that was purified by *flash* chromatography (silica gel, hexane-EtOAc 7:3 to 1:1, gradient) to afford alcohol **23** (143 mg, 83%). Characterization data obtained for compound **23** were identical with the described in the literature.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99–3.88 (m, 4H), 3.65 (t, *J* = 6.4 Hz, 2H), 1.71–1.64 (m, 2H), 1.62–1.53 (m, 2H), 1.52–1.43 (m, 2H), 1.31 (s, 3H).

1.3.3. 4-(2-methyl-1,3-dioxolan-2-yl)butyl methanesulfonate (24)

To a solution of 4-(2-methyl-1,3-dioxolan-2-yl)butan-1-ol (**23**, 1.20 g, 7.49 mmol) in anhydrous DCM (75 mL), was added TEA (3.5 mL, 24.7 mmol). The resulting solution was cooled to 0ºC and then, MsCl (1.5 mL, 18.7 mmol) was added. This mixture was allowed to reach room temperature and stirred overnight. The reaction mixture was diluted with DCM (25 mL) and it was washed with sat. aq. $NaHCO_3$ (3 x 100 mL). Then, was filtered and the solvent of the filtrate was removed under pressure to give mesylate **24** (1.76 g, 99%) as a red oil. This product was used without further purification in the next reaction step. Characterization data obtained for compound **26** were identical with the described in the literature.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (t, *J* = 6.5 Hz, 2H), 3.99–3.86 (m, 4H), 3.00 (s, 3H), 1.82–1.73 (m, 2H), 1.71–1.63 (m, 2H), 1.57–1.48 (m, 2H), 1.31 (s, 3H).

1.3.4. 2-(4-bromobutyl)-2-methyl-1,3-dioxolane (25)

A solution of lithium bromide (437 mg, 5.04 mmol) in anhydrous THF (8 mL) was dried with 3Å molecular sieves (5 g) placed inside the reaction flask. After stirring this solution for 20 minutes, a solution of 4-(2-methyl-1,3-dioxolan-2-yl)butyl methanesulfonate (**24**, 600 mg, 2.52 mmol) in anhydrous THF (4 mL) was added to the previous reaction flask. This solution was stirred at 50ºC overnight. Next day, lithium bromide (437 mg, 5.04 mmol) was added and heating again 3h at 50ºC. Then, the reaction mixture was allowed to reach room temperature and it was diluted with AcOEt (60 mL). The organic layer was washed with sat. aq. $NaHCO_3$, dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to afford bromide **25** (500 mg, 89%) as a yellow oil. Characterization data obtained for compound **25** were identical with the described in the literature.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99–3.88 (m, 4H), 3.41 (t, *J* = 6.8 Hz, 2H), 1.88 (dt, *J* = 14.1, 6.9 Hz, 2H), 1.69–1.64 (m, 2H), 1.59–1.51 (m, 2H), 1.32 (s, 3H).

1.3.5. (4-(2-methyl-1,3-dioxolan-2-yl)butyl)magnesium bromide (13)

A suspension of magnesium (2.71 g, 112 mmol) in anhydrous THF (45 mL) was heated to 50ºC. Then, 1,2-dibromoethane (485 µl, 5.58 mmol) was added and the resulting suspension was stirred at this temperature for 30 minutes. After this period, a solution of 2-(4-bromobutyl)-2-methyl-1,3-dioxolane (**25**, 2.49 g, 11.2 mmol) in THF (25 mL) was added and this mixture was heated at 50ºC for 15 min, when TLC depicted full conversion to the Grignard reagent **13**. This solution was reacted with bromide **12** to prepare acetal **6**.

1.4. Synthesis of Grignard reagents 4 and 5

1.4.1. *tert*-butyl(hex-5-yn-1-yloxy)diphenylsilane (18)

A solution of hex-5-yn-1-ol (**14**, 549 µl, 4.84 mmol) and 1*H*-imidazole (659 mg, 9.68 mmol) in anhydrous DMF (6 mL) was cooled to 0ºC. Then, TBDPSCl (1.90 mL, 7.26 mmol) was added in one portion. The resulting solution was allowed to reach room temperature and stirred overnight. The reaction mixture was quenched with brine (30 mL) and diluted with Et_2O (25 mL). After that, extractions with Et_2O (3 x 25 mL) were done and the collected organic layers were washed with brine (25 mL). Then, the resulting organic layer was dried over $MgSO_4$, filtered and the solvent of the filtrate was removed under reduced pressure to afford a residue that was purified by *flash* chromatography (silica gel, hexane-EtOAc 95:5 to 9:1) to afford tert-butyl(hex-5-yn-1-yloxy)diphenylsilane **18** (1.59 g, 98%) as a colorless oil. Characterization data obtained for compound **18** were identical with the described in the literature.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.64 (m, 4H), 7.46–7.35 (m, 6H), 3.68 (t, *J* = 6.0 Hz, 2H), 2.19 (td, *J* = 6.8, 2.6 Hz, 2H), 1.93 (t, *J* = 2.6 Hz, 1H), 1.72–1.60 (m, 4H), 1.05 (s, 9H).

1.4.2. 7-((*tert*-butyldiphenylsilyl)oxy)hept-2-yn-1-ol (19)

A solution of tert-butyl(hex-5-yn-1-yloxy)diphenylsilane (**18**, 1.58 g, 4.69 mmol) in anhydrous THF (47 mL) was cooled to -78ºC. Then butyllithium (2.30 mL, 5.63 mmol) was added and this solution was stirred at this temperature for 30 minutes. Then, *p*-formaldehyde (previously dried under vacuum for a few hours, 564 mg, 18.8 mmol) was added in one portion and the reaction mixture was stirred and allowed to reach room temperature overnight. The reaction mixture was quenched with sat. aq. NH_4Cl (40 mL) and extracted with Et_2O (3 x 40 mL). The collected organic layers were dried over $MgSO_4$, filtered and the solvent of the filtrate was removed under reduced pressure to give a residue that was purified by *flash* chromatography (silica gel, hexane-EtOAc 95:5 to 7:3, gradient). 7-((tert-butyldiphenylsilyl)oxy)hept-2-yn-1-ol **19** (1.41 g, 82%) was isolated as a colorless oil. Characterization data obtained for compound **19** were identical with the described in the literature.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.9, 1.6 Hz, 4H), 7.46–7.34 (m, 6H), 4.23 (dt, *J* = 6.0, 2.2 Hz, 2H), 3.68 (t, *J* = 6.0 Hz, 2H), 2.22 (tt, *J* = 6.7, 2.2 Hz, 2H), 1.68–1.59 (m, 4H), 1.05 (s, 9H).

1.4.3. (*E*)-7-((*tert*-butyldiphenylsilyl)oxy)hept-2-en-1-ol (20)

A solution of 7-((tert-butyldiphenylsilyl)oxy)hept-2-yn-1-ol (**19**, 500 mg, 1.36 mmol) in anhydrous Et_2O (14 mL) was cooled to 0ºC. Then, Red-Al® (1.20 mL, 4.09 mmol) was added slowly and the resulting solution was stirred at 0ºC for a few minutes. Then, the reaction mixture was stirred at room temperature for 4h. After this period, the reaction mixture was cooled to 0ºC and quenched by adding sat. aq. NH_4Cl (75 mL) dropwise. Then, extractions with Et_2O (3 x 75 mL) were done and the collected organic layers were dried over Na_2SO_4, filtered and the solvent of the filtrate was removed under reduced pressure to afford a residue that was purified by *flash* chromatography (silica gel, hexane-EtOAc 9:1 to 8:2, gradient) to afford the desired alcohol **20** (332 mg, 66%) as a colorless oil. Characterization data obtained for compound **20** were identical with the described in the literature.[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.63 (m, 4H), 7.46–7.33 (m, 6H), 5.72–5.57 (m, 2H), 4.08 (t, *J* = 5.6 Hz, 2H), 3.66 (t, *J* = 6.3 Hz, 2H), 2.07–2.01 (m, 2H), 1.61–1.53 (m, 2H), 1.51–1.42 (m, 2H), 1.05 (s, 9H).

1.4.4. (*E*)-((7-bromohept-5-en-1-yl)oxy)(*tert*-butyl)diphenylsilane (12)

To a solution of (*E*)-7-((*tert*-butyldiphenylsilyl)oxy)hept-2-en-1-ol (**20**, 309 mg, 0.837 mmol) in anhydrous DCM (8.4 mL), was added DIPEA (516 µl, 2.93 mmol). The resulting solution was cooled to 0ºC and then, MsBr (174 µl, 2.09 mmol) was added (green colored solution). The resulting solution was allowed to reach room temperature and stirred overnight. The reaction mixture was quenched by adding water (40 mL) and extracted with DCM (3 x 40 mL). The collected organic layers were dried over Na_2SO_4, filtered and the solvent of the filtrate was removed under reduced pressure to afford a brown-orange oil that was purified by *flash* chromatography (silica gel, hexane-EtOAc 9:1, isocratic) to afford the silane **12** (300 mg, 83%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (br d, *J* = 7.0 Hz, 4H), 7.47–7.34 (m, 6H), 5.81–5.61 (m, 2H), 3.94 (d, *J* = 7.2 Hz, 2H), 3.66 (t, *J* = 6.3 Hz, 2H), 2.06 (dd, *J* = 13.9, 7.0 Hz, 2H), 1.62–1.52 (m, 2H), 1.51–1.42 (m, 2H), 1.05 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 135.7, 134.2, 129.7, 127.7, 126.6, 63.8, 33.7, 32.1, 31.9, 27.0, 25.2, 19.4. GC-MS (EI): m/z (%) = 351 (6), 293 (11), 273 (28), 135 (5), 123 (11), 95 (100).

1.4.5. (*E*)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-ol (6)

A solution of (*E*)-((7-bromohept-5-en-1-yl)oxy)(tert-butyl)diphenylsilane (**12**, 1.93 g, 4.46 mmol) in anhydrous THF (80 mL) was cooled to 0ºC and 3Å molecular sieves (2 g) were added. The resulting mixture was stirred at this temperature for 30 minutes, and then 0.1M Li_2CuCl_4 in THF (1.79 mL, 0.178 mmol) was added. After 10 minutes, freshly prepared (4-(2-methyl-1,3-dioxolan-

2-yl)butyl)magnesium bromide (**13**, 74.4 mL, 11.2 mmol) was added quickly and this mixture was allowed to reach room temperature over 1.5h. The reaction mixture was quenched with sat. aq. NH_4Cl (30 mL), diluted with Et_2O (30 mL), and extracted with Et_2O (3 x 30 mL). Then, the collected organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered and the solvent of the filtrate was removed under reduced pressure to get a residue that was purified by *flash* chromatography (silica gel, hexane-EtOAc 15:1, isocratic) to afford a pure mixture of the α and γ addition products (2.16 g, 4.37 mmol, 98%), that was dissolved in anhydrous THF (70 mL). Then, 1M TBAF in THF (17.5 ml, 17.5 mmol) was added and the resulting solution was stirred at room temperature overnight. The reaction mixture was diluted with Et_2O (30 mL) and brine (30 mL), then, extractions with Et_2O (3 x 30 mL) were done. The collected organic layers were dried over $MgSO_4$, filtered and the solvent of the filtrate was removed under reduced pressure to give a residue that was purified by *flash* chromatography (30% $AgNO_3$ adsorbed on silica gel,[1] hexane-EtOAc 6:1 to 5:1, gradient) to afford products **6** (399 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43–5.31 (m, 2H), 3.96–3.86 (m, 4H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.02–1.91 (m, 4H), 1.64–1.51 (m, 4H), 1.44–1.22 (m, 8H), 1.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.9, 130.0, 110.3, 64.8, 63.1, 39.4, 32.6, 32.4, 32.4, 29.7, 29.5, 25.8, 24.1, 23.9. GC-MS (EI): m/z (%) = 257.3 (1) $[M+1]^+$, 241.3 (42) $[M-15]^+$, 211.3 (10), 169.2 (30), 141.2 (18), 115.2 (36), 98.2 (40), 86.9 (100), 55.2 (40).

1.4.6. (*E*)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-yl methanesulfonate (26)

To a solution of ((*E*)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-ol (**6**, 210 mg, 0.819 mmol) in anhydrous DCM (8 mL), was added DIPEA (504 µl, 2.87 mmol) and MsCl (127 µl, 1.64 mmol). The resulting solution was stirred at room temperature overnight. The reaction mixture was diluted with DCM (100 mL) and washed with sat. aq. $NaHCO_3$ (3 x 50 mL) and brine (50 mL). Then, the organic layer was dried over Na_2SO_4, filtered and the solvent of the filtrate was removed *in vacuo* to get pure product **26** (259 mg, 94%) that was used without further purification in the next reaction step (see preparation of product **27**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45–5.27 (m, 2H), 4.21 (t, *J* = 6.5 Hz, 2H), 3.97–3.86 (m, 4H), 2.99 (s, 3H), 1.98 (dq, *J* = 19.8, 6.7 Hz, 4H), 1.73 (dt, *J* = 14.3, 6.6 Hz, 2H), 1.64–1.19 (m, 10H), 1.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.4, 129.1, 110.1, 70.0, 64.6, 39.2, 37.4, 32.4, 31.8, 29.5, 29.3, 28.5, 25.3, 23.9, 23.7. HRMS (ESI^+) m/z $[M + H]^+$ calculated for $C_{16}H_{31}O_5S$ 335.1892, found 335.1881. GC-MS (EI): m/z (%): 336.5 (22), 335.3 (95), 291.6 (26), 239.4 (21), 195.2 (9), 177.4 (100), 87.2 (32).

1.4.7. (*E*)-2-(11-bromoundec-6-en-1-yl)-2-methyl-1,3-dioxolane (27)

A solution of lithium bromide (134 mg, 1.54 mmol) in anhydrous THF (2 mL) was dried with 3Å molecular sieves (300 mg). After stirring this solution for 20 minutes, a solution of (*E*)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-yl methanesulfonate (**26**, 258 mg, 0.771 mmol) in anhydrous THF (4 mL) was added to the previous reaction flask. This solution was stirred at reflux for 6h. Then, the reaction mixture was diluted with EtOAc (25 mL) and the organic layer was washed with sat. aq. $NaHCO_3$ (25 mL), dried over Na_2SO_4, filtered and the solvent of the filtrate was removed under reduced pressure to afford bromide **27** (210 mg, 85%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46–5.30 (m, 2H), 3.97–3.86 (m, 4H), 3.39 (t, *J* = 6.9 Hz, 2H), 2.05–1.92 (m, 4H), 1.84 (dt, *J* = 14.5, 6.9 Hz, 2H), 1.64–1.55 (m, 2H), 1.47 (p, *J* = 7.5 Hz, 2H), 1.42–1.21 (m, 6H) 1.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.1, 129.4, 110.1, 64.6, 39.2, 33.8, 32.4, 32.2, 31.6, 29.5, 29.3, 28.0, 23.9, 23.7. GC-MS (EI): m/z (%): 321.2 (94), 319.2 (93), 259.1 (18), 257.3 (22), 239.3 (47), 177.3 (85), 143.2 (40), 95.2 (33), 87.1 (100).

1.4.8. (*E*)-(11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-yl)magnesium bromide (4)

A suspension of magnesium (160 mg, 6.58 mmol) in anhydrous THF (6 mL) was heated to 50ºC. Then, 1,2-dibromoethane (58 µL, 0.658 mmol) was added and the resulting solution was heated at reflux and stirred for 50 minutes. Then, the solvent of the

suspension was removed by syringe suction and, a solution of (*E*)-2-(11-bromoundec-6-en-1-yl)-2-methyl-1,3-dioxolane (**27**, 210 mg, 0.658 mmol) in THF (6 mL) was added. The resulting mixture was heated at reflux for 45 min, when additional 1,2-dibromoethane (29 µl, 0.329 mmol) was added in order to promote the total completion of the reaction. After 1h, this solution was allowed to reach room temperature and it was reacted with bromide **3** to prepare ketone **1** (see preparation of product **1**).

1.4.9. 11-(2-methyl-1,3-dioxolan-2-yl)undecan-1-ol (28)

A solution of (*E*)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-ol (**6**, 189 mg, 0.737 mmol) in a mixture of MeOH (3.7 mL) and ACN (3.7 mL) was added to Pd/C (95 mg, 0.802 mmol) under inert atmosphere. The reaction tube was repeatedly filled and evacuated with H_2, and the mixture was vigorously stirred at room temperature overnight under H_2 (1 atm). After this period, the reaction mixture was filtered through a plug of Celite, and the filtrate was washed with ACN (3 × 3 mL). Then, the solvent of the filtrate was removed under reduced pressure to give a white waxy solid (186 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97–3.88 (m, 4H), 3.63 (t, *J* = 6.6 Hz, 2H), 1.65–1.59 (m, 2H), 1.59–1.52 (m, 2H), 1.34–1.22 (m, 16H), 1.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 110.4, 64.8, 63.2, 39.4, 33.0, 30.0, 29.7, 29.7, 29.6, 25.9, 24.3, 23.9. GC-MS (EI): m/z (%) 259.3 (100), 257.3 (23), 243.4 (17), 197.3 (23), 87.2 (24).

1.4.10. 11-(2-methyl-1,3-dioxolan-2-yl)undecyl methanesulfonate (29)

To a solution of 11-(2-methyl-1,3-dioxolan-2-yl)undecan-1-ol (**28**, 210 mg, 0.819 mmol) in anhydrous DCM (8.2 mL), was added DIPEA (504 µl, 2.87 mmol). The resulting solution was cooled to 0ºC and then, MsCl (127 µl, 1.64 mmol) was added. The resulting mixture was allowed to reach room temperature and stirred overnight. The reaction mixture was diluted with DCM (100 mL), washed with sat. aq. $NaHCO_3$ (3 x 50 mL) and brine (50 mL). Then, the organic layer was dried over Na_2SO_4, filtered and the solvent of the filtrate was removed under pressure to give pure product **29** (258 mg, 94%) as a colorless oil. This product was used without further purification in the next reaction step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20 (t, *J* = 6.6 Hz, 2H), 3.97–3.85 (m, 4H), 2.98 (s, 3H), 1.77–1.67 (m, 2H), 1.63–1.57 (m, 4H), 1.40–1.23 (m, 14H), 1.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 110.2, 70.2 , 64.6 , 39.2, 37.3, 29.8, 29.5, 29.5, 29.4, 29.4, 29.1, 29.0, 25.4, 24.1, 23.7. GC-MS (EI): m/z 337.3, 293.3, 241.4, 197.3, 179.3, 87.2. HRMS (ESI+) m/z $[M + H]^+$ calculated for $C_{16}H_{33}O_5S$ 337.2049; found 337.2070. GC-MS (EI): m/z (%) 337.3 (100), 293.3 (31), 241.4 (26), 197.3 (32), 87.2 (21).

1.4.11. 2-(11-bromoundecyl)-2-methyl-1,3-dioxolane (30)

A solution of lithium bromide (120 mg, 1.39 mmol) in anhydrous THF (2 mL) was dried with 3Å molecular sieves (300 mg). After stirring this solution for 20 minutes, a solution of 11-(2-methyl-1,3-dioxolan-2-yl)undecyl methanesulfonate (**29**,233 mg, 0.693 mmol) in anhydrous THF (4 mL) was added to the previous reaction flask, and the resulting mixture was heated to reflux and stirred for 4h. Then, the reaction mixture was allowed to reach room temperature and it was diluted with EtOAc(25 mL). The organic layer was washed with sat. aq. $NaHCO_3$(25 mL), dried over Na_2SO_4, filtered and the solvent of the filtrate was removed under reduced pressure to afford a residue that was purified by flashchromatography (silica gel, hexane-EtOAc 20:1, isocratic) to afford bromide **30** (165 mg, 74%) as a colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96–3.86 (m, 4H), 3.39 (t, *J* = 6.9 Hz, 2H), 1.83 (dq, *J* = 8.7, 6.9 Hz, 2H), 1.63–1.57 (m, 2H), 1.44–1.32 (m, 4H), 1.32–1.20 (m, 12H), 1.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 110.2, 64.6, 39.2, 34.0, 32.8, 29.8, 29.5, 29.5, 29.5, 29.4, 28.7, 28.1, 24.1, 23.7.GC-MS (EI): m/z323.3 (69), 321.2 (92), 277.3 (7), 241.4 (100), 197.4 (8), 179.3 (20), 87.2 (66).

1.4.12. (11-(2-methyl-1,3-dioxolan-2-yl)undecyl)magnesium bromide (5)

A suspension of magnesium (117 mg, 4.82 mmol) in anhydrous THF (4.4 mL) was heated to 50 ºC. Then, 1,2-dibromoethane (42 µl, 0.482 mmol) was added and the resulting solution was heated at reflux and stirred for 50 minutes. Then, the solvent of the suspension was removed by syringe suction and, a solution of 2-(11-bromoundecyl)-2-methyl-1,3-dioxolane (**30**, 155 mg, 0.482 mmol) in THF (4.4 mL) was added. The resulting mixture was heated at reflux for 45 min, when additional 1,2-dibromoethane (21 µl, 0.241 mmol) was added in order to promote the total completion of the reaction. After 1h, this solution was allowed to reach room temperature and reacted with bromide **3** to prepare ketone **2** (see preparation of product **2**).

1.5. Synthesis of alkenones 1 and 2

1.5.1. (8*E*,15*E*,22*E*)-heptatriaconta-8, 15, 22-trien-2-one (1)

A solution of (2*E*,9*E*)-1-bromotetracosa-2,9-diene (**3**, 108 mg, 0.261 mmol) in THF (3.7 mL) was cooled to 0 ºC. Then, 0.1M Li_2CuCl_4 in THF (131 µl, 0.013 mmol) was added and the resulting orange solution was stirred at this temperature for 10 minutes. After that, freshly prepared (*E*)-(11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-yl)magnesium bromide (**4**, 237 mg, 0.689 mmol) was added and the mixture was allowed to reach room temperature and stirred for 3 h. After this period, the reaction mixture was quenched with sat. aq. NH_4Cl (25 mL) and diluted with Et_2O (25 mL), then, extractions with Et_2O (3 x 25 mL) were done. The collected organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered and the solvent of the filtrate was removed under reduced pressure to give a residue that was purified by flash chromatography (silica gel, hexane-EtOAc 30:1, isocratic) to afford a mixture of alcohols resulting from the the α and γ alcohols (100 mg, 0.175mmol) that was dissolved in acetone (10 mL). This solution was treated with Amberlyst-15 (strongly acidic resin, 4.7 mmol/g, previously washed with 1N HCl, H_2O, MeOH and acetone, 186 mg, 0.873 mmol) and stirred for 5h at room temperature. After this period, the reaction mixture was filtered and the resin was washed with H_2O (10 mL) and EtOAc (10 mL). Then, the organic layer was isolated, dried with anhydrous Na_2SO_4, filtered, and the solvent of the filtrate was removed under reduced pressure to get a residue that was purified by flash chromatography (42% $AgNO_3$ adsorbed on silica gel,[1] hexane-EtOAc 70:1, isocratic) to afford separately the pure α-addition product **1** (41 mg, 29% yield, two steps). Characterization data obtained for compound **1** were identical with the described in the literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45–5.31 (m, 6H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.13 (s, 3H), 2.02–1.89 (m, 12H), 1.59–1.53 (m, 2H), 1.34–1.26 (m, 40H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.4, 130.8, 130.6, 130.5, 130.5, 130.4, 130.1, 43.9, 32.8, 32.7, 32.7, 32.5, 32.1, 29.9, 29.9, 29.8, 29.8, 29,8, 29.7, 29.7, 29.6, 29.5, 29.3, 28.9, 28.8, 28,8, 23.9, 22.8, 14.3. HRMS (ESI+) m/z $[M + H]^+$ calculated for $C_{37}H_{69}O$ 529.5348; found 529.5370. GC-MS (EI): m/z (%) = 529.7 $[M]^+$ (100), 527.7 (74), 511.7 (32), 509.6 (20), 415.5 (10), 319.4 (12), 305.3 (15), 291.4 (15), 263.2 (12), 235.2 (18), 221.2 (22), 177.2 (24), 163.1 (26), 125.1 (32), 111.1 (43), 109.1 (48), 97.1 (68).

1.5.2. (15*E*,22*E*)-heptatriaconta-15,22-dien-2-one (2)

A solution of (2*E*,9*E*)-1-bromotetracosa-2,9-diene (**3**, 119 mg, 0.288 mmol) in THF (4.1 mL) was cooled to 0ºC. Then, 0.1M Li_2CuCl_4 in THF (144 µl, 14 µmol) was added and the resulting orange solution was stirred at this temperature for 10 minutes. After that, (11-(2-methyl-1,3-dioxolan-2-yl)undecyl)magnesium bromide (**5**, 248 mg, 0.719 mmol) was added and the mixture was allowed to reach room temperature and stirred for 3h. After this period, the reaction mixture was quenched with sat. aq. NH_4Cl (20 mL) and diluted with Et_2O (15 mL), then, extractions with Et_2O (3 x 15 mL) were done. The collected organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and the solvent of the filtrate was removed under reduced pressure to give a residue that was purified by flash chromatography (silica gel, hexane-EtOAc 30:1, isocratic) to afford a mixture of the α and γ acetals (50.9 mg, 0.087 mmol) that was dissolved in acetone (6.2 mL) and treated with Amberlyst-15 (strongly acidic resin, 4.7

mmol/g, previously washed with 1N HCl, H_2O, MeOH and acetone, 93 mg, 0.435 mmol). After stirring for 3h at room temperature, the reaction mixture was filtered and the resin was washed with H_2O (2 x 5 mL) and EtOAc (2 x 5 mL). Then, the organic layer was isolated, dried with anhydrous Na_2SO_4, filtered, and the solvent of the filtrate was removed under reduced pressure to get a residue that was purified by flash chromatography (42% $AgNO_3$ adsorbed on silica gel,[1] hexane-EtOAc 70:1, isocratic) to afford separately the α-addition product **2** (14.0 mg, 7% yield, two steps). Characterization data obtained for compound **2** were identical with the described in the literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39-5.37 (m, 4H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.13 (s, 3H), 1.99–1.93 (m, 8H), 1.60-1.53 (m, 2H), 1.28–1.18 (m, 48H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.6, 130.6, 130.6, 130.5, 44.0, 32.6, 32.6, 31.9, 30.9, 30.0, 29.9, 29.8, 29.8, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.3, 28.8, 24.0, 22.8, 14.3. HRMS (ESI+) m/z $[M + H]^+$ calculated for $C_{37}H_{71}O$ 531.5505; found 531.5484. GC-MS (EI): m/z (%) = 531 (100), 530 (90), 513 (25), 511 (30), 459 (5), 433 (8), 417 (10), 333 (10), 307 (15), 293 (25), 279 (25), 125 (35), 111 (62), 97 (93), 83 (60), 71 (70).

2. References

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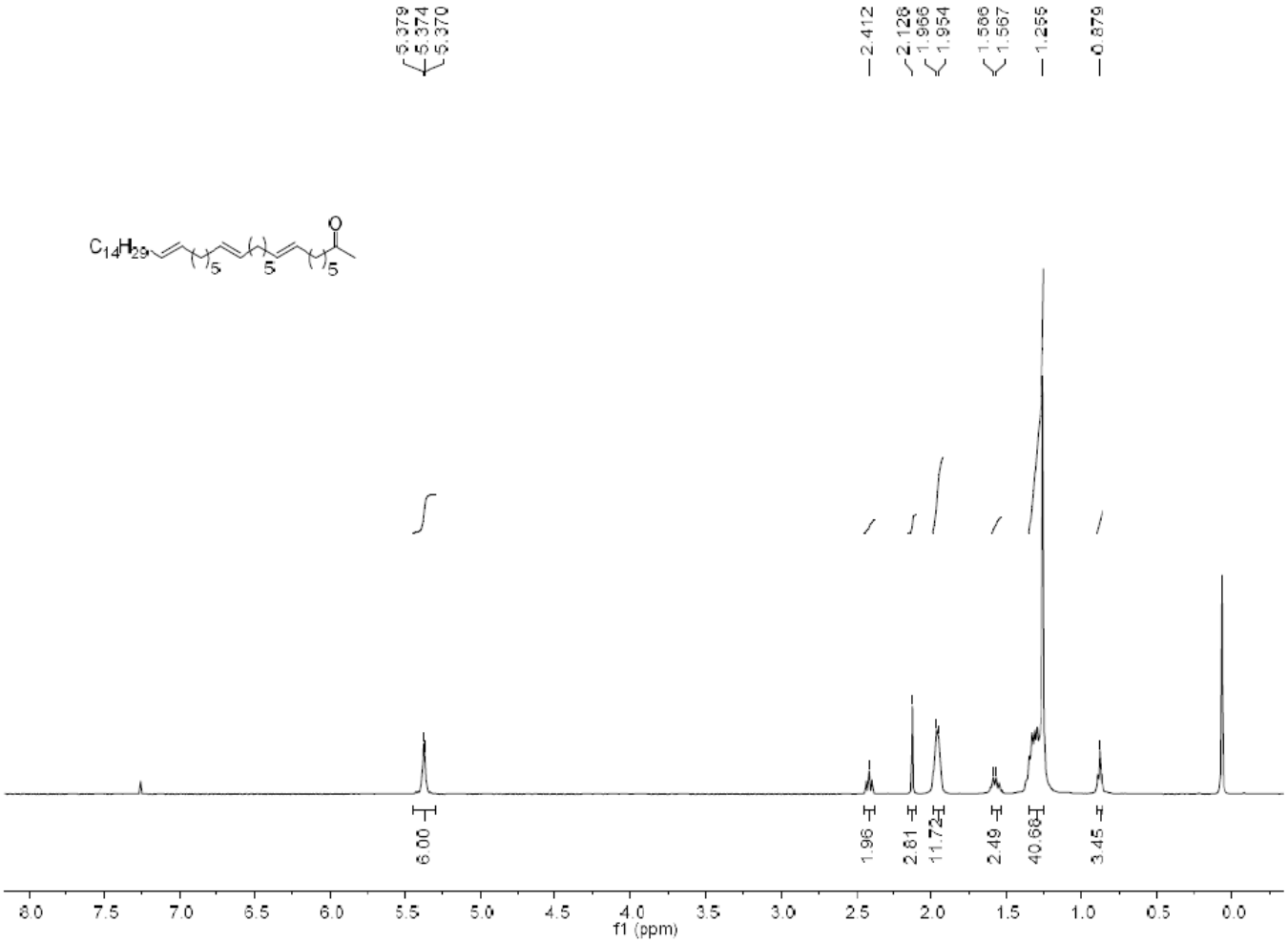
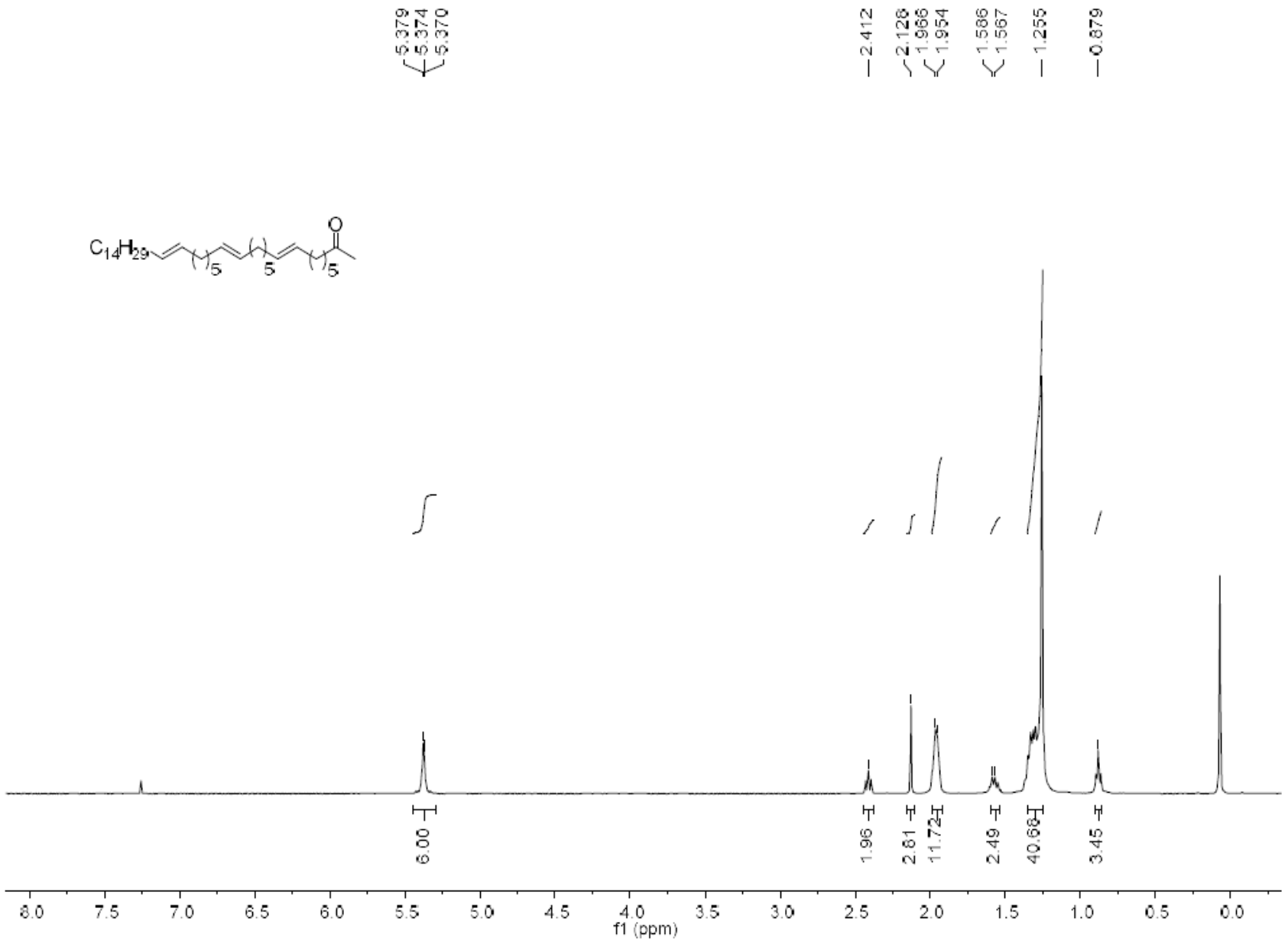
3. Characterization data

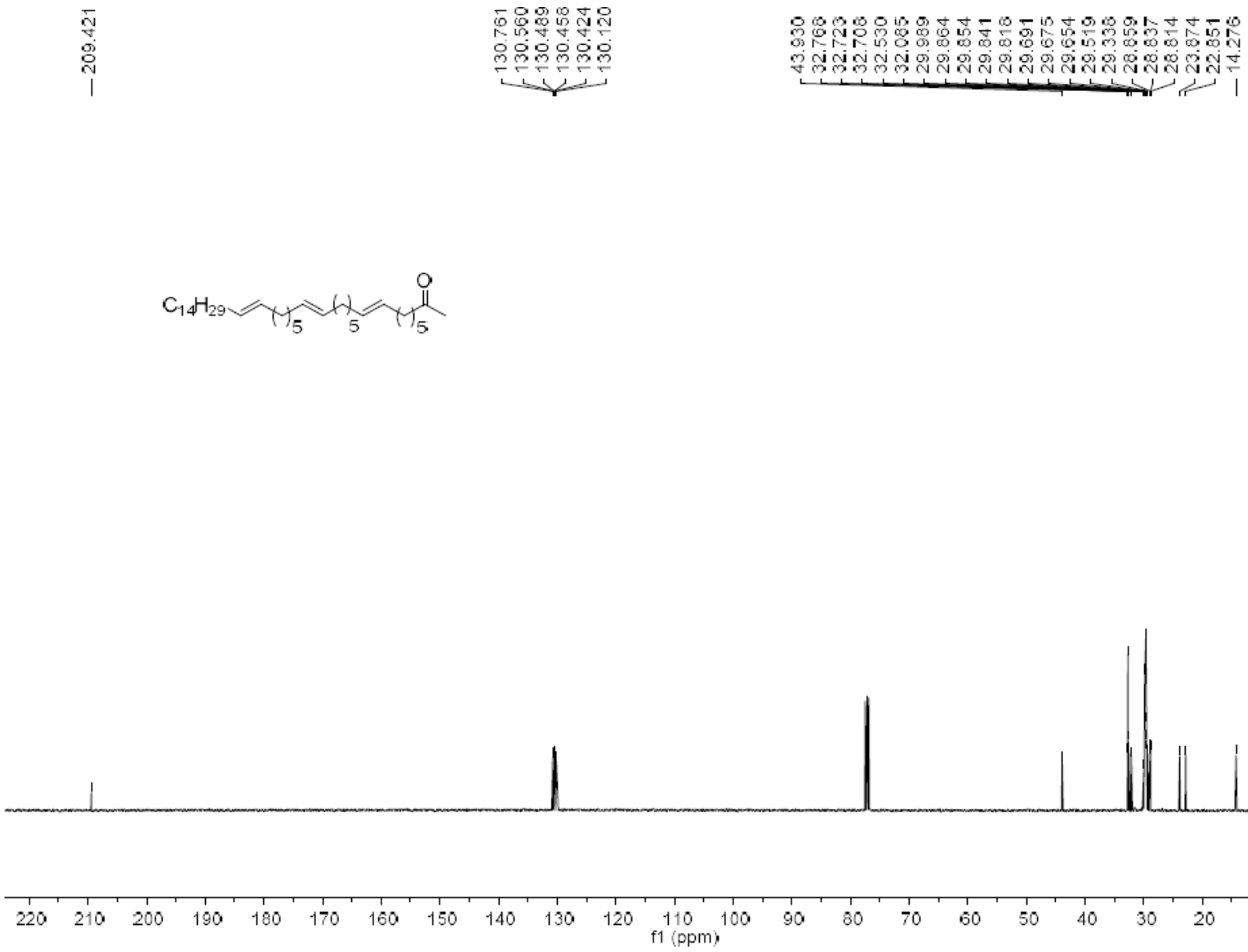
^{1}H-NMR spectrum of (8*E*,15*E*,22*E*)-heptatriaconta-8, 15, 22-trien-2-one (1) (400 MHz, $CDCl_3$)



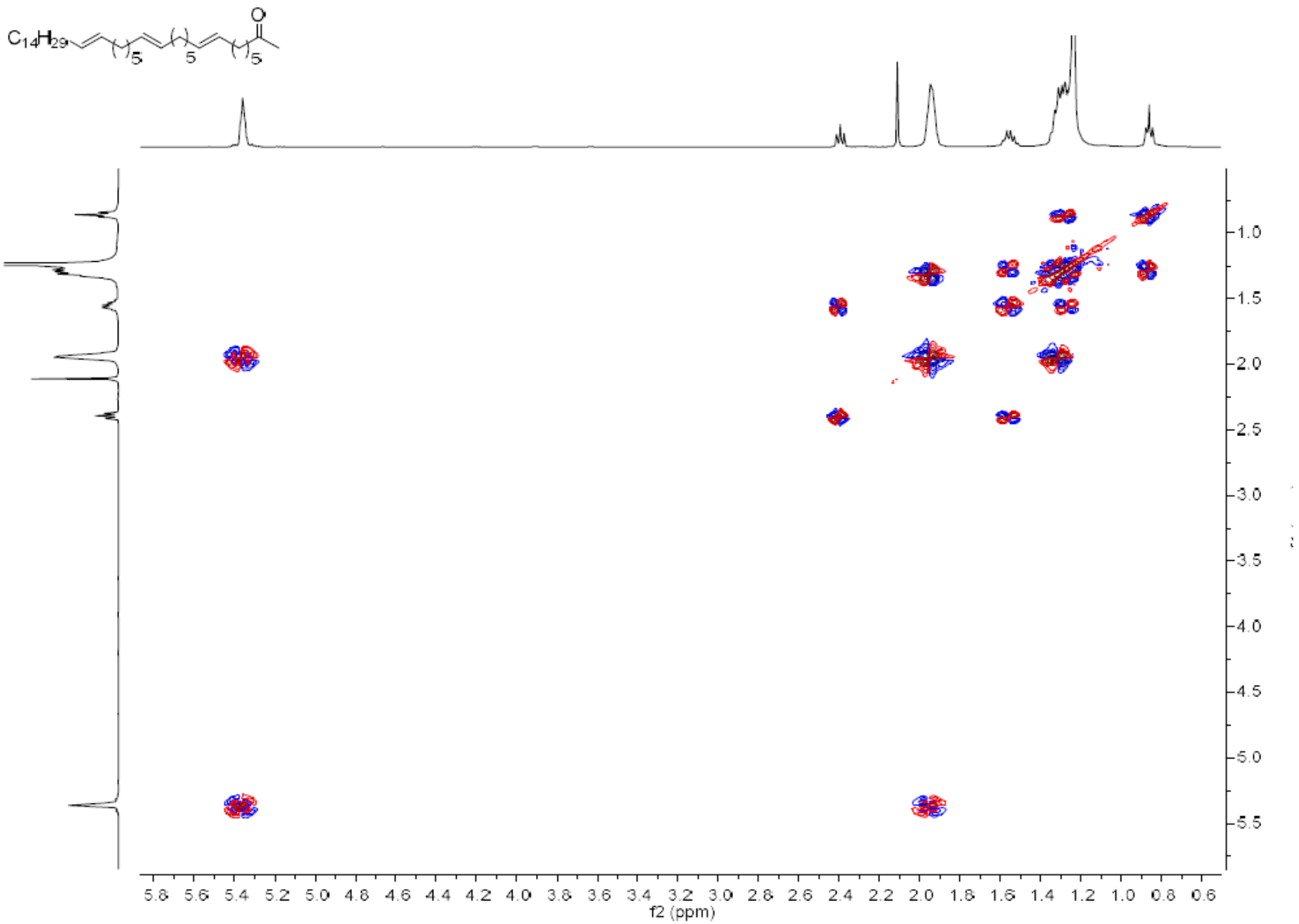
^{1}H-NMR spectrum of (8*E*,15*E*,22*E*)-heptatriaconta-8, 15, 22-trien-2-one (1) (400 MHz, $CDCl_3$)



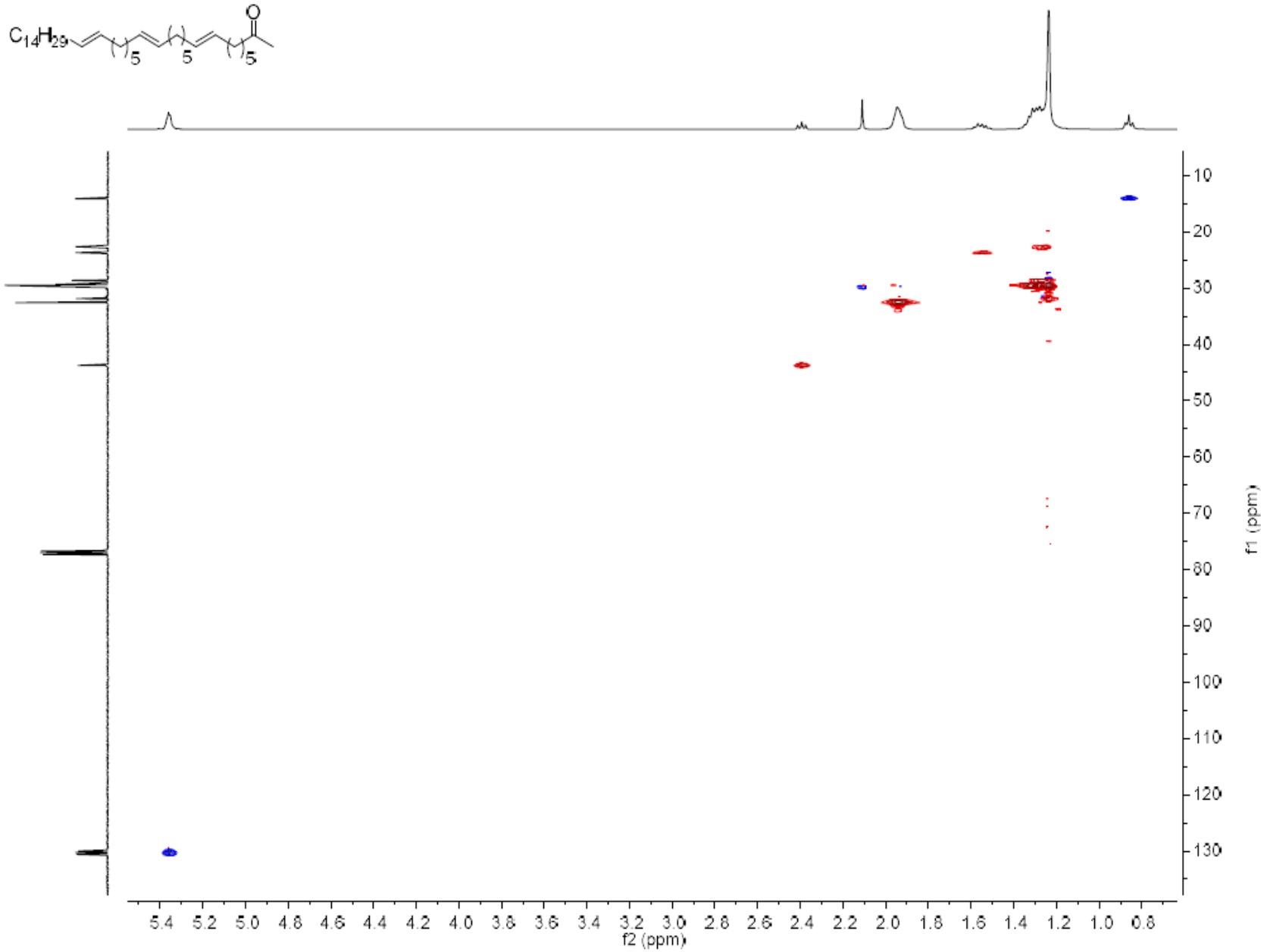
^{13}C-NMR spectrum of (8*E*,15*E*,22*E*)-heptatriaconta-8, 15, 22-trien-2-one (1) (101 MHz, $CDCl_3$)



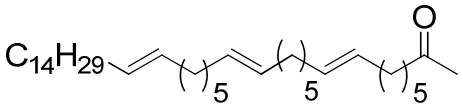
*g*DQCOSY spectrum of (8*E*,15*E*,22*E*)-heptatriaconta-8, 15, 22-trien-2-one (1) (400 MHz, $CDCl_3$)



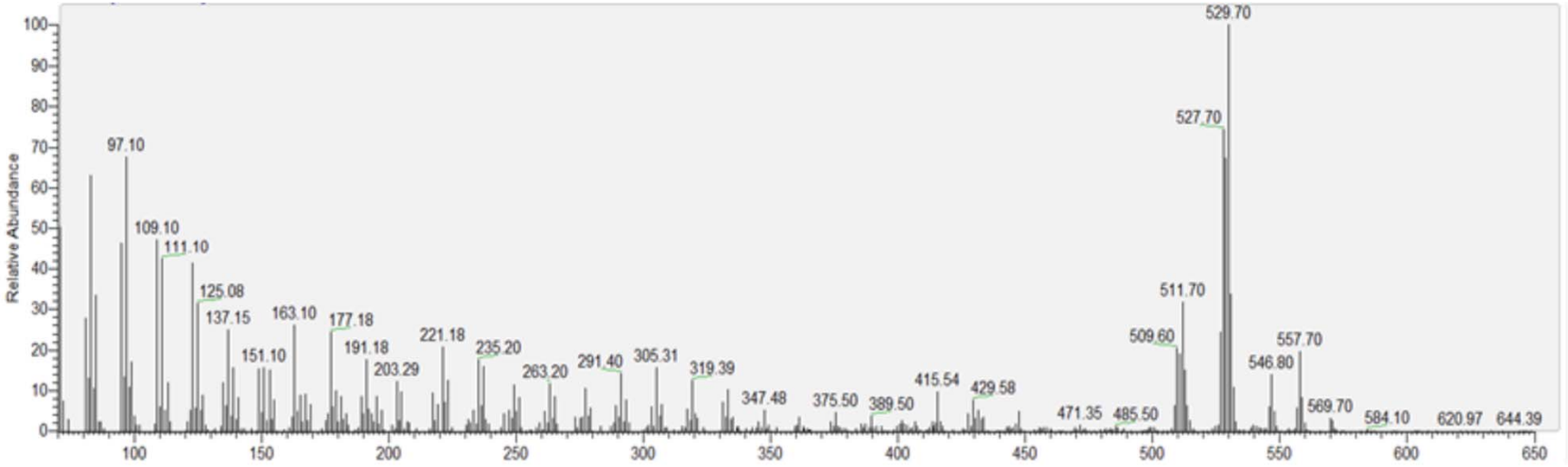
*g*HSQC spectrum of (8*E*,15*E*,22*E*)-heptatriaconta-8, 15, 22-trien-2-one (1) (400 MHz,101 MHz; $CDCl_3$)



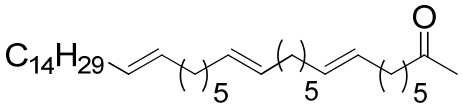
GC-MS chromatogram and fragmentations of (8*E*,15*E*,22*E*)-heptatriaconta-8, 15, 22-trien-2-one (1)



Chemical Formula: $C_{37}H_{68}O$
Exact Mass: 528.53
Molecular Weight: 528.94



Exact Mass chromatogram of (8*E*,15*E*,22*E*)-heptatriaconta-8, 15, 22-trien-2-one (1)



Chemical Formula: $C_{37}H_{68}O$
Exact Mass: 528.53

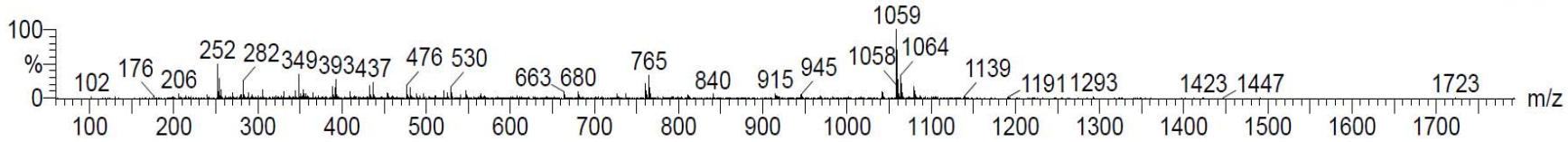
Single Mass Analysis

Tolerance = 15.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
202 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 50-200 O: 0-4 Cl: 0-2 Br: 0-2

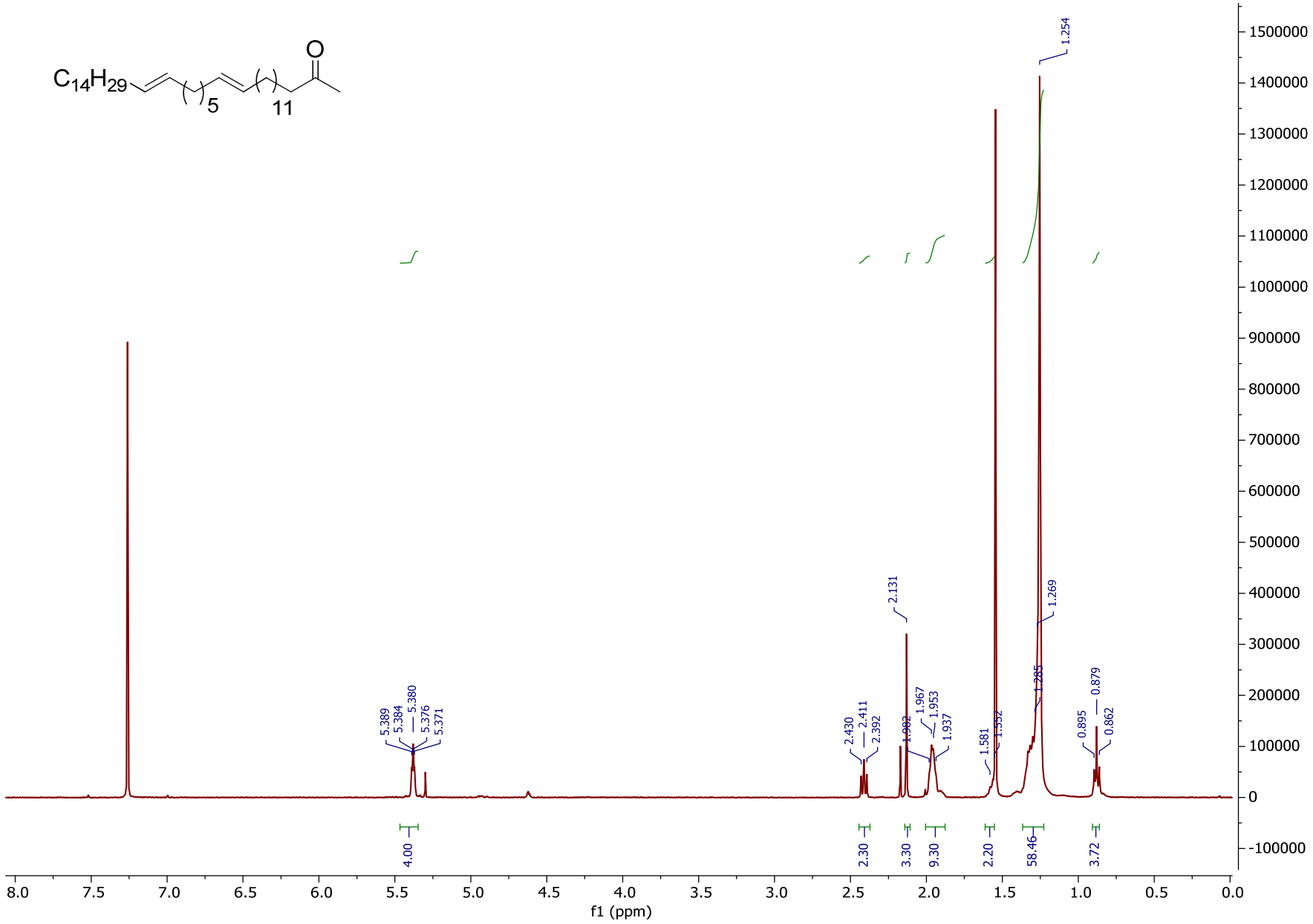
Carme SimChem
Compuesto_1alfa 12 (0.633)

1: TOF MS ES+
1.13e+003

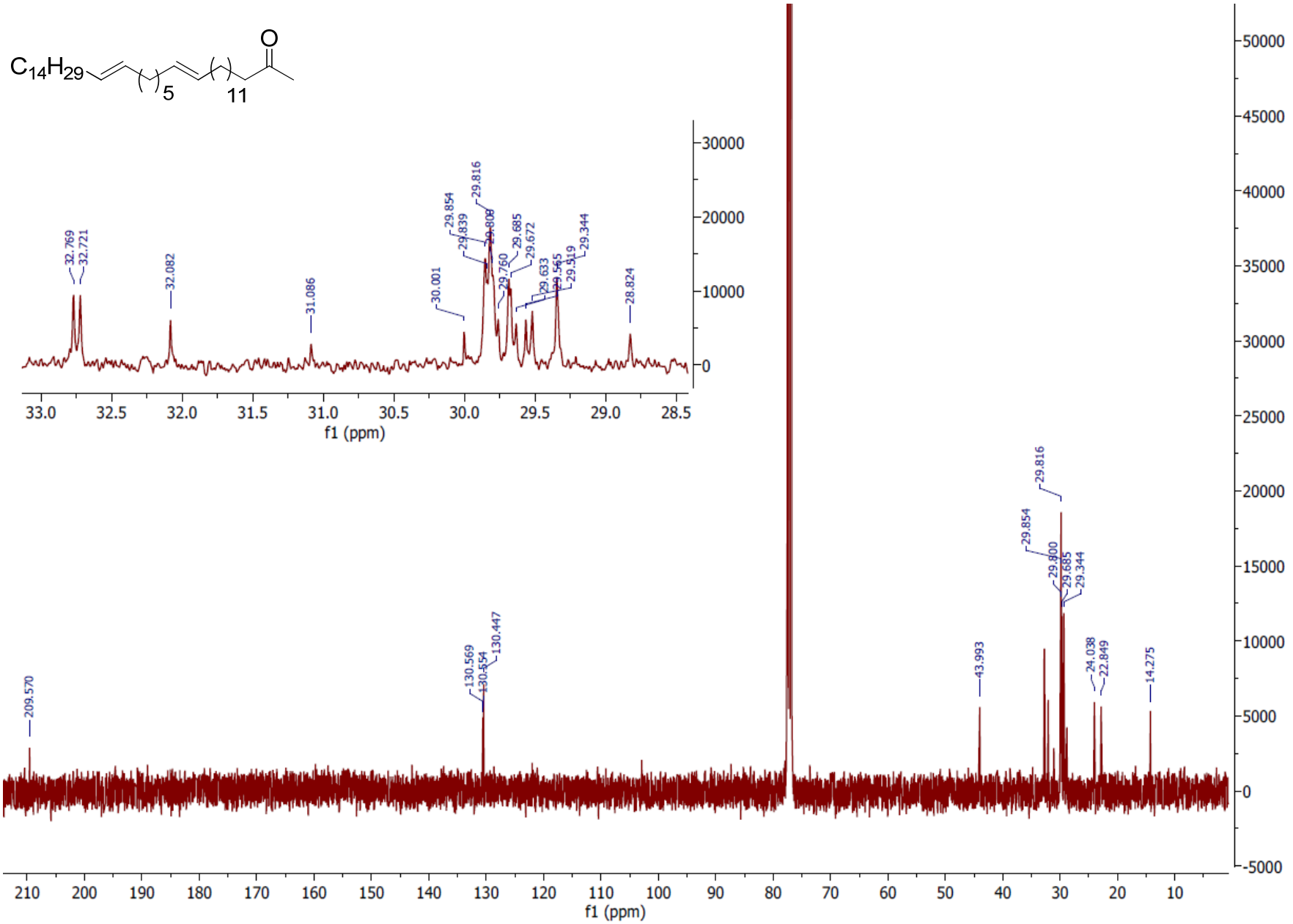


Minimum:				-1.5			
Maximum:		5.0	15.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
529.5370	529.5348	2.2	4.2	3.5	27.8	0.0	C37 H69 O

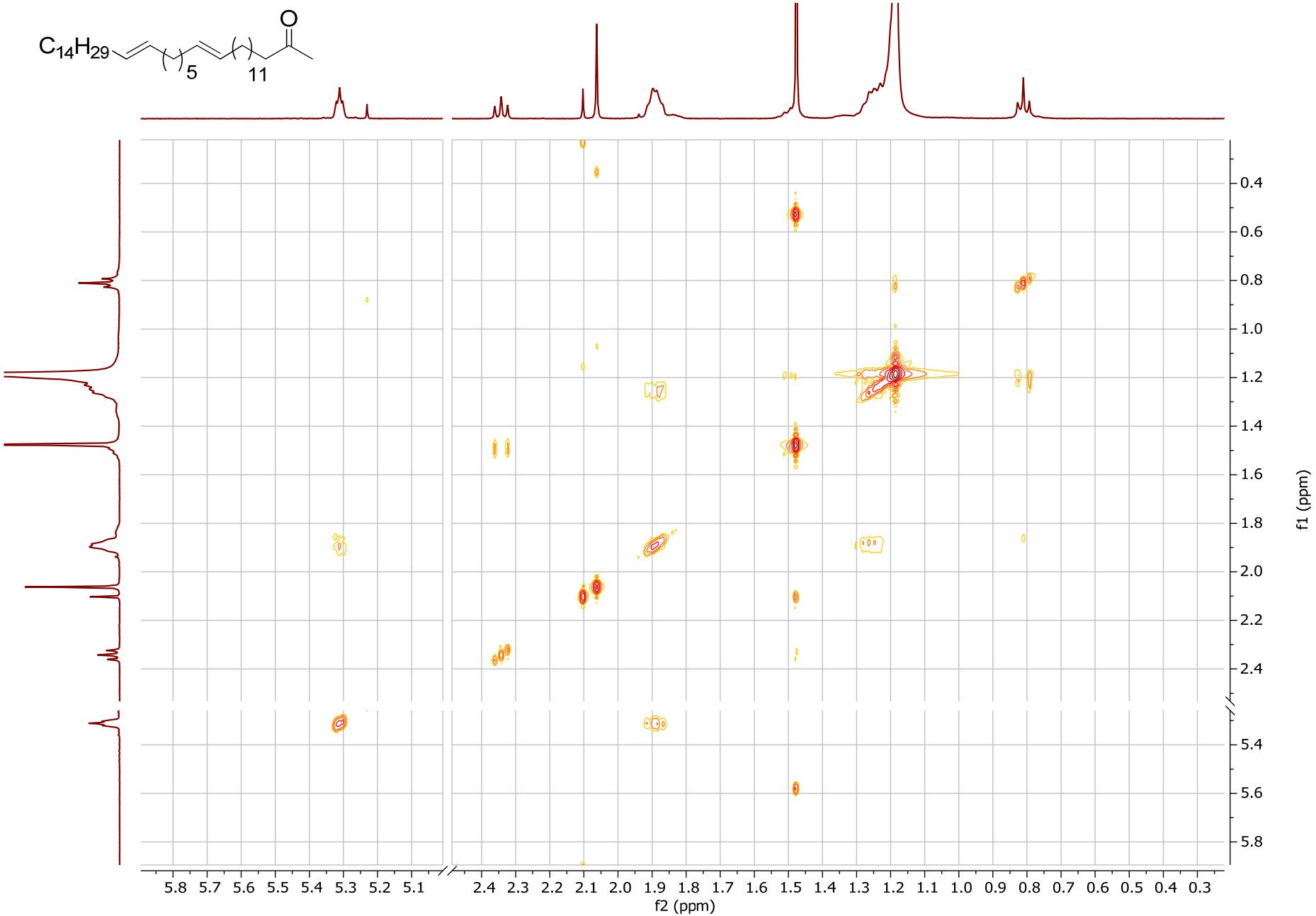
^{1}H-NMR spectrum of (15*E*,22*E*)-heptatriaconta-15,22-dien-2-one (2) (400 MHz, $CDCl_3$)



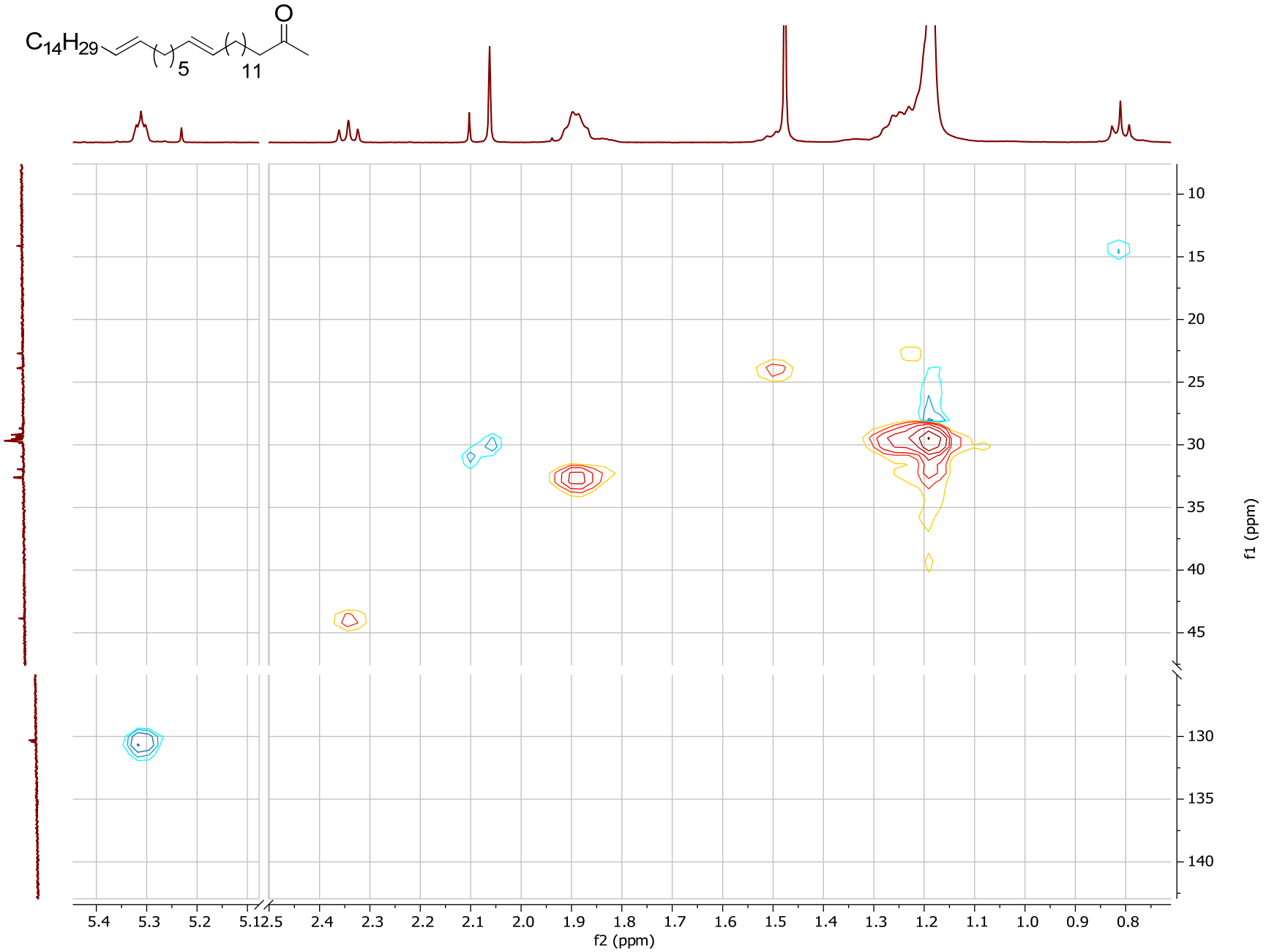
^{13}C-NMR spectrum of (15*E*,22*E*)-heptatriaconta-15,22-dien-2-one (2) (101 MHz, $CDCl_3$)



*g*DQCOSY spectrum of (15*E*,22*E*)-heptatriaconta-15,22-dien-2-one (2) (400 MHz, $CDCl_3$)

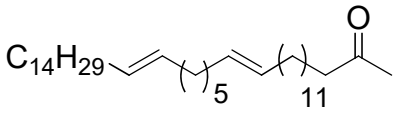


*g*HSQC spectrum (15*E*,22*E*)-heptatriaconta-15,22-dien-2-one (2) (400 MHz,101 MHz; $CDCl_3$)



u1

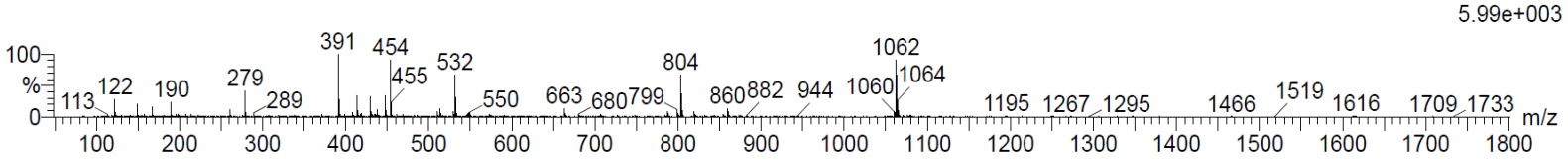
Exact Mass chromatogram of (15*E*,22*E*)-heptatriaconta-15,22-dien-2-one (2)



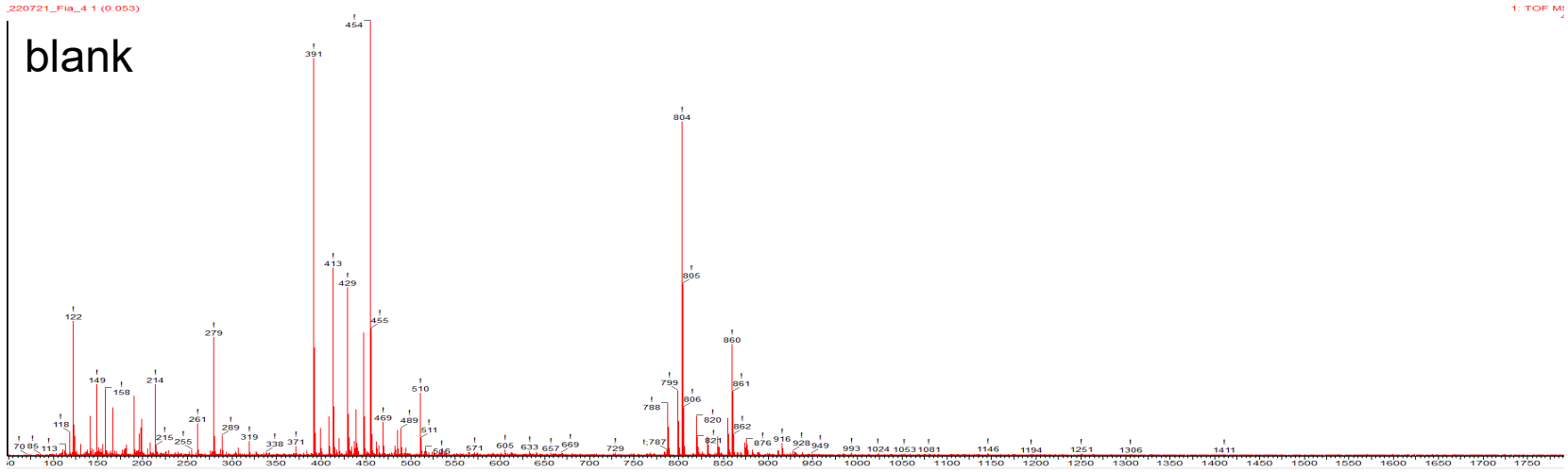
Chemical Formula: $C_{37}H_{70}O$
Exact Mass: 530.54
Molecular Weight: 530.95

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

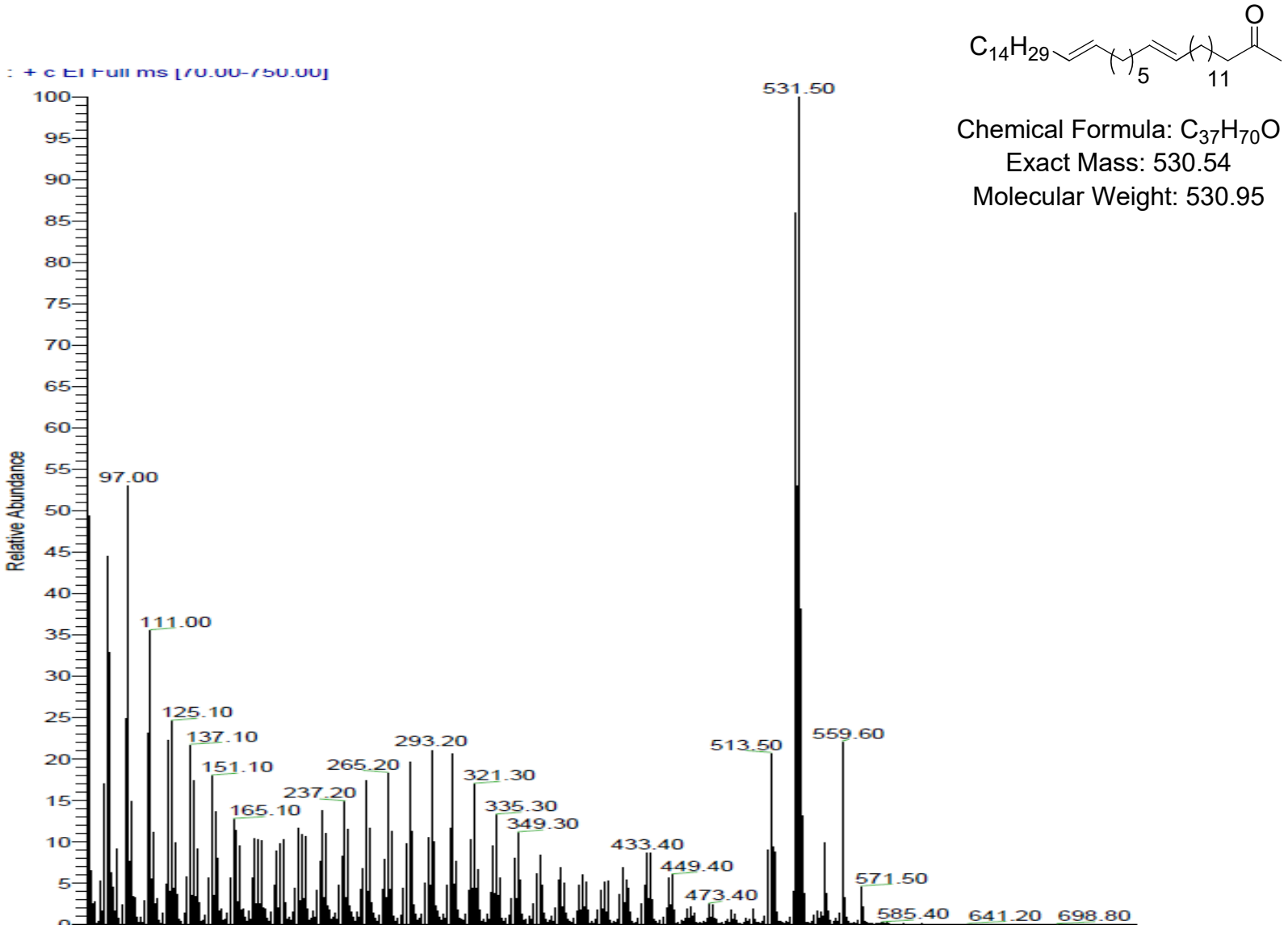
Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 37-37 H: 71-71 Li: 0-1 O: 1-1



Minimum:				-1.5			
Maximum:		5.0	100.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
531.5484	531.5505	-2.1	-4.0	2.5	98.1	0.0	C37 H71 O

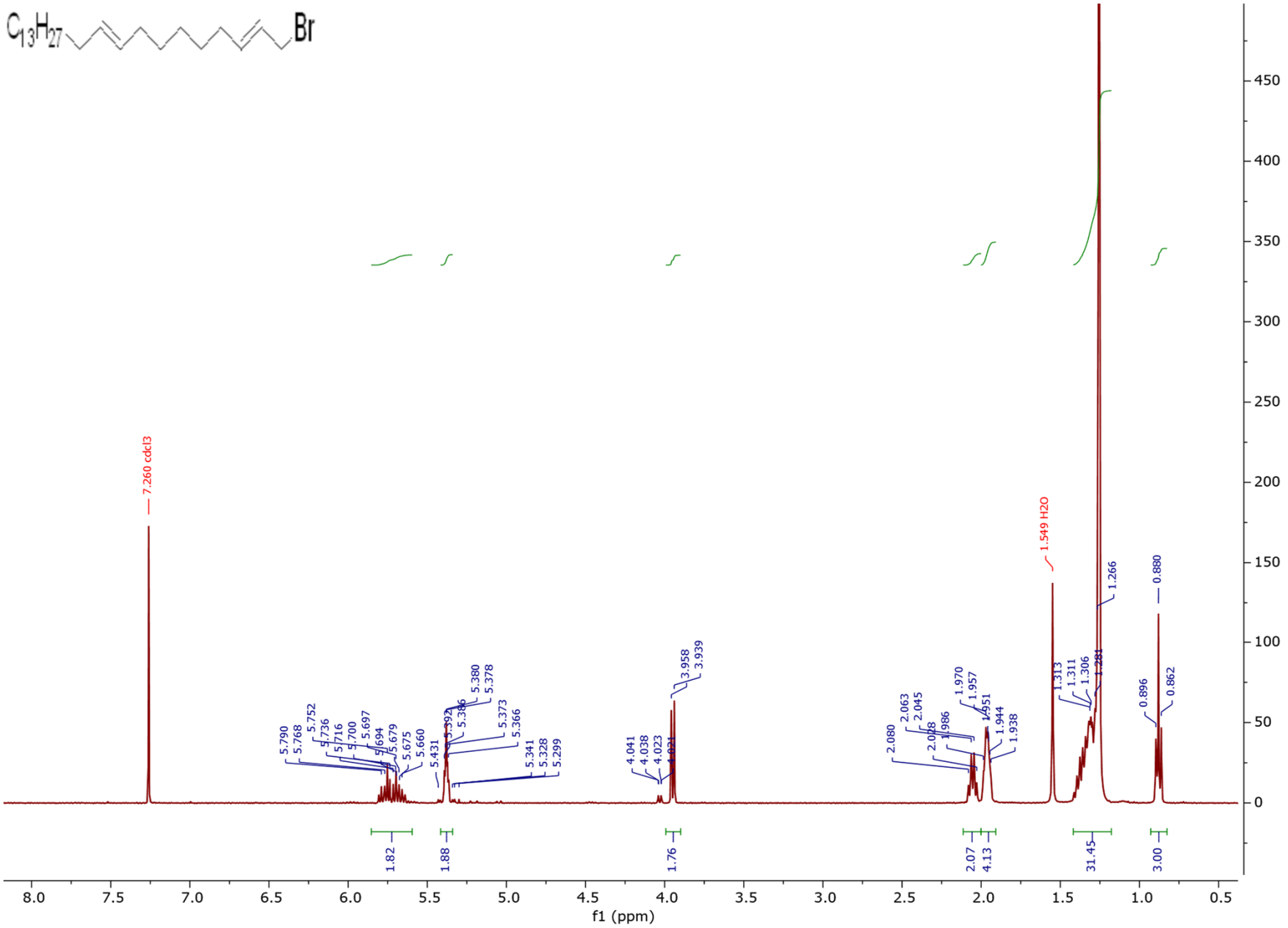


GC-MS chromatogram and fragmentations of (15*E*,22*E*)-heptatriaconta-15,22-dien-2-one (2)

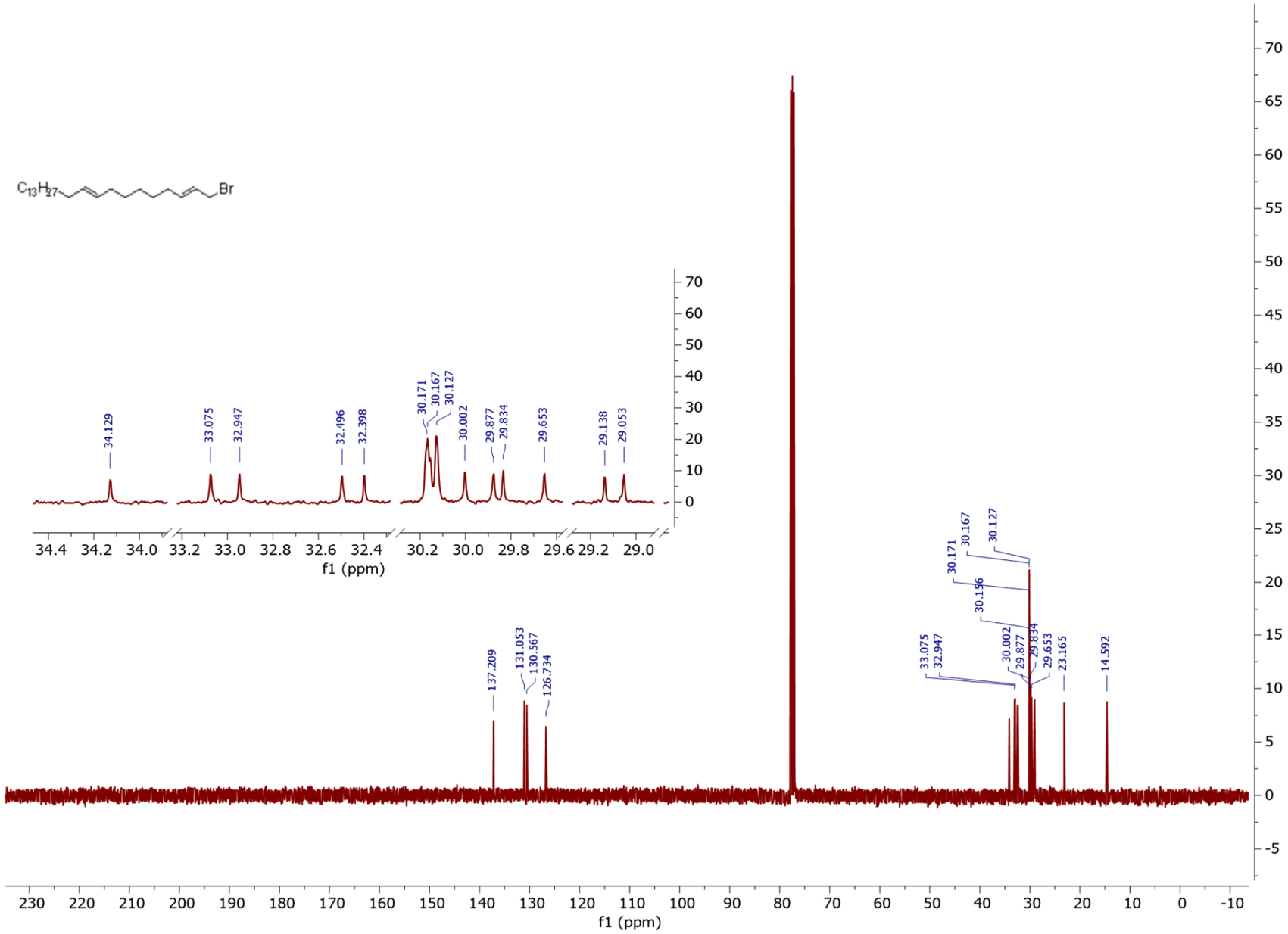


Chemical Formula: $C_{37}H_{70}O$
Exact Mass: 530.54
Molecular Weight: 530.95

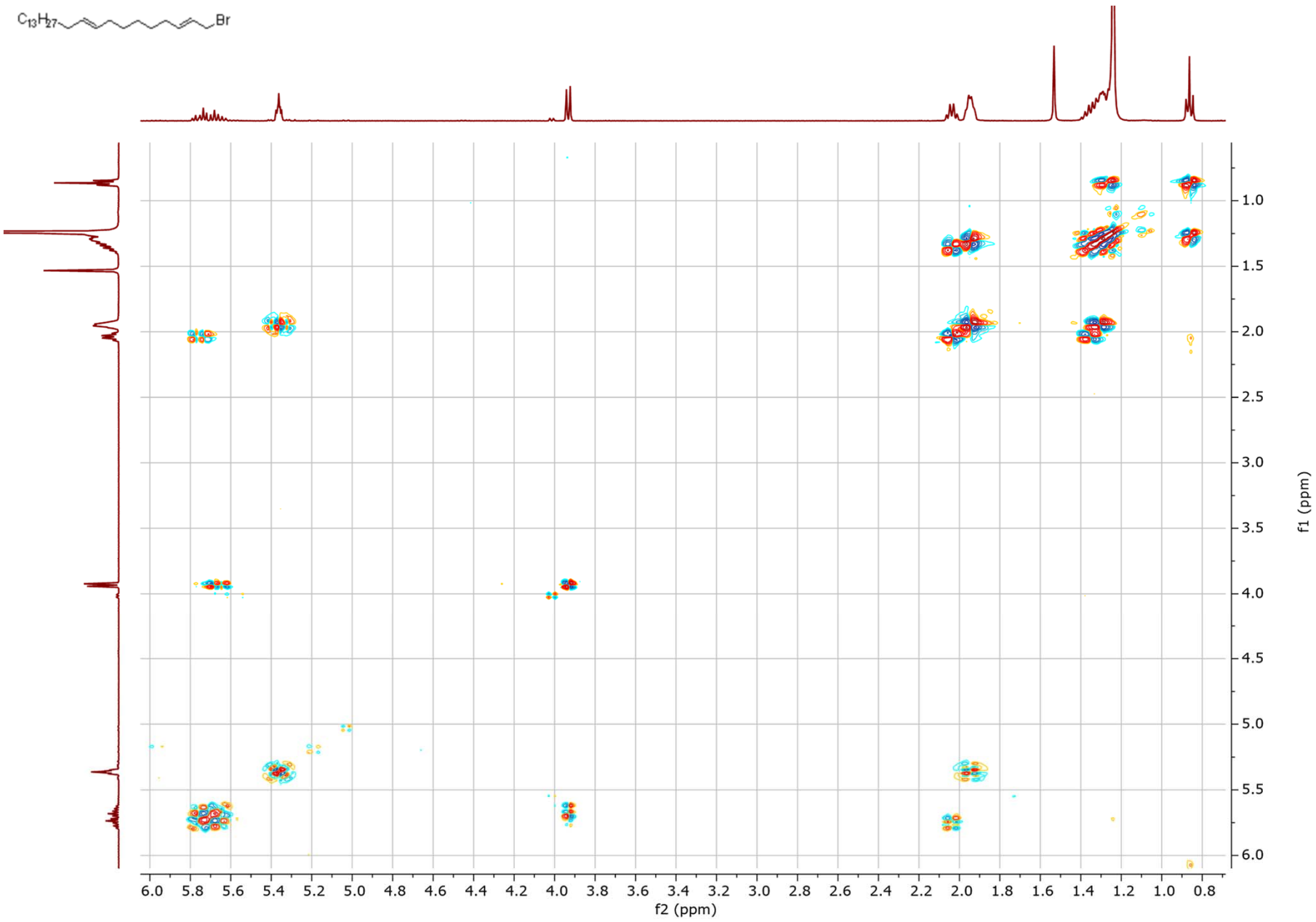
^{1}H-NMR spectrum of (2*E*,9*E*)-1-bromotetracosa-2,9-diene (3) (400 MHz, $CDCl_3$)



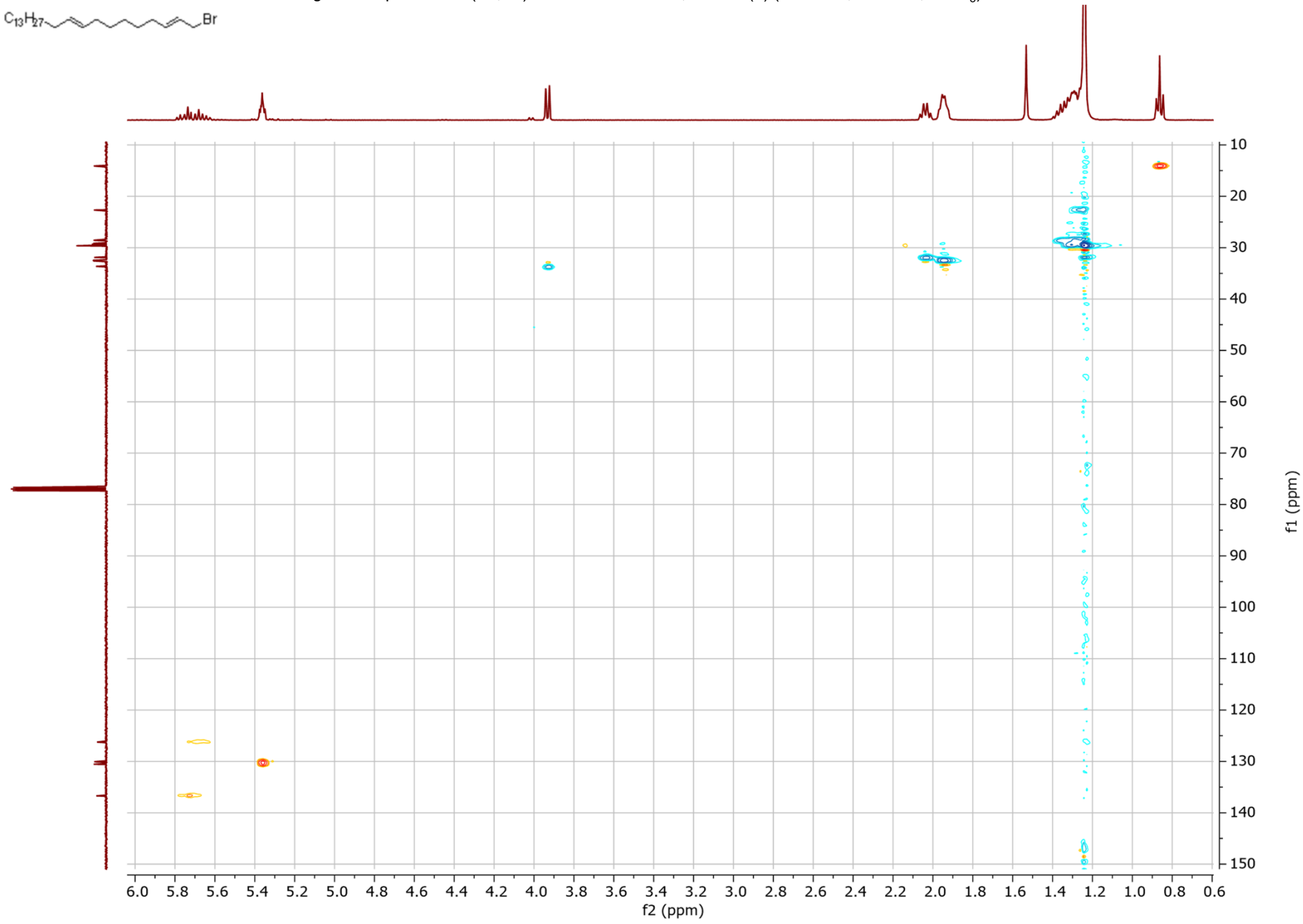
^{13}C-NMR spectrum of ((2*E*,9*E*)-1-bromotetracosa-2,9-diene (3) (101 MHz, $CDCl_3$)



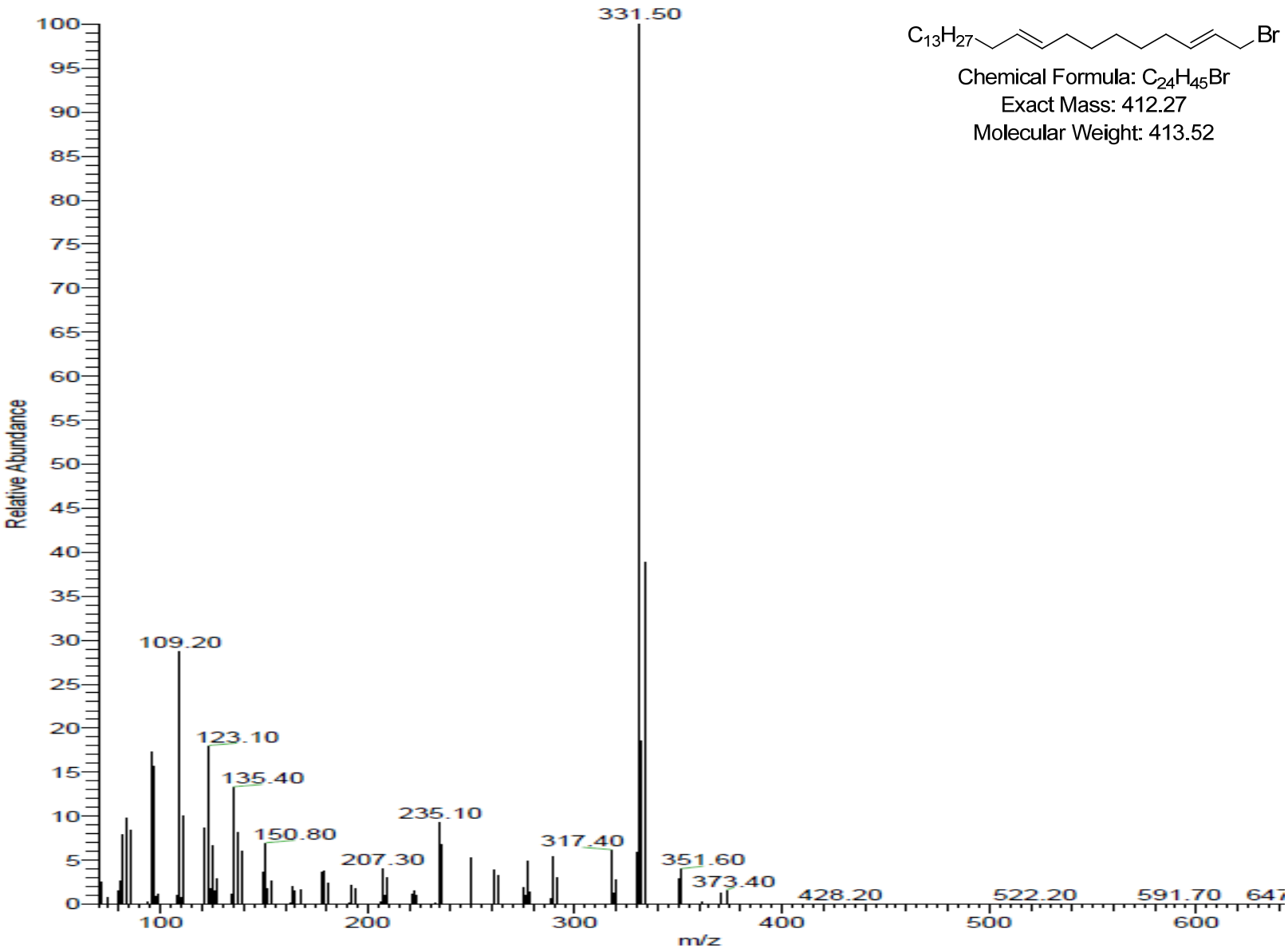
*g*DQCOSY of ((2*E*,9*E*)-1-bromotetracosa-2,9-diene (3) (400 MHz, $CDCl_3$)



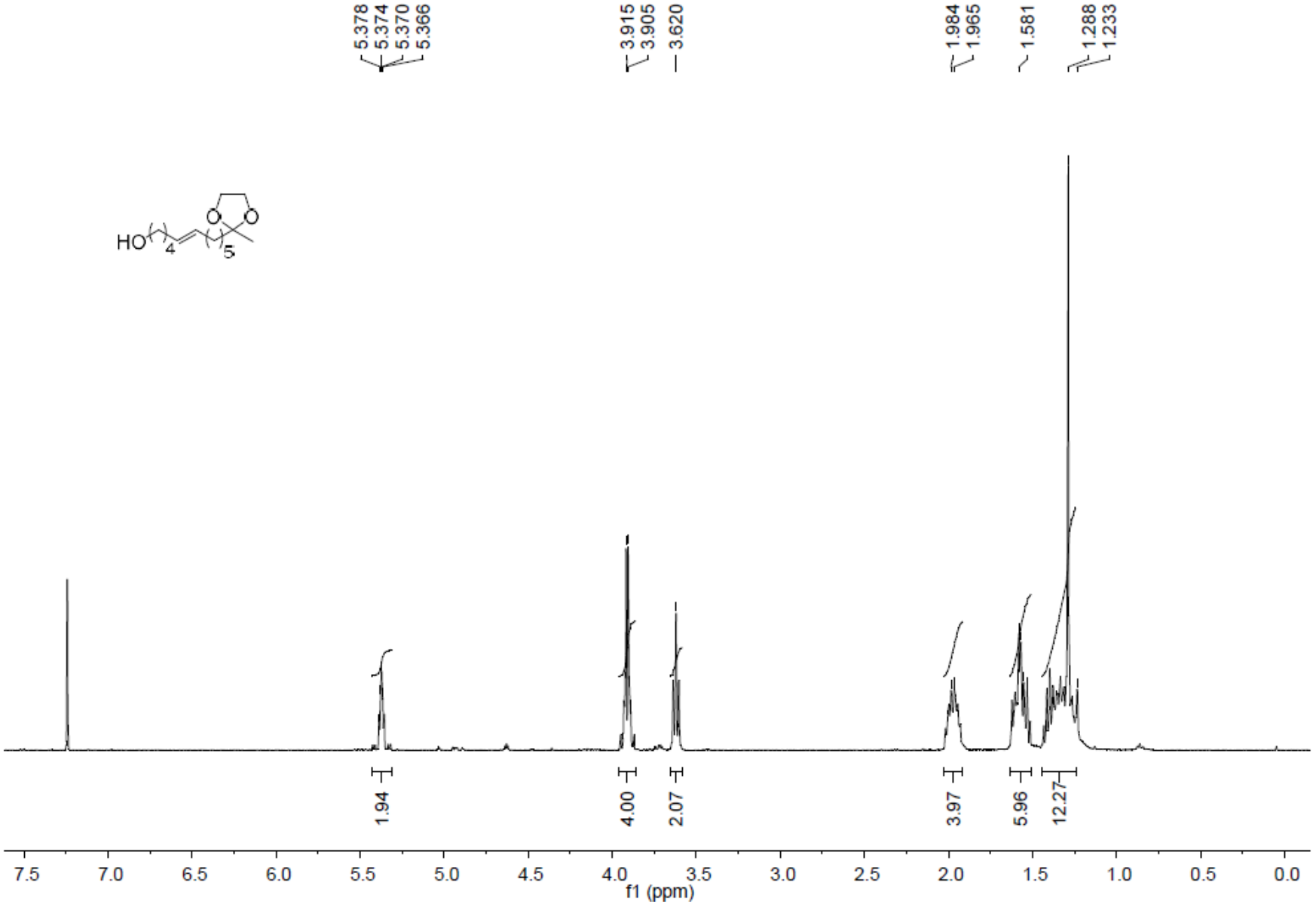
*g*HSQC spectrum of (2*E*,9*E*)-1-bromotetracosa-2,9-diene (3) (400 MHz,101 MHz; $CDCl_3$)



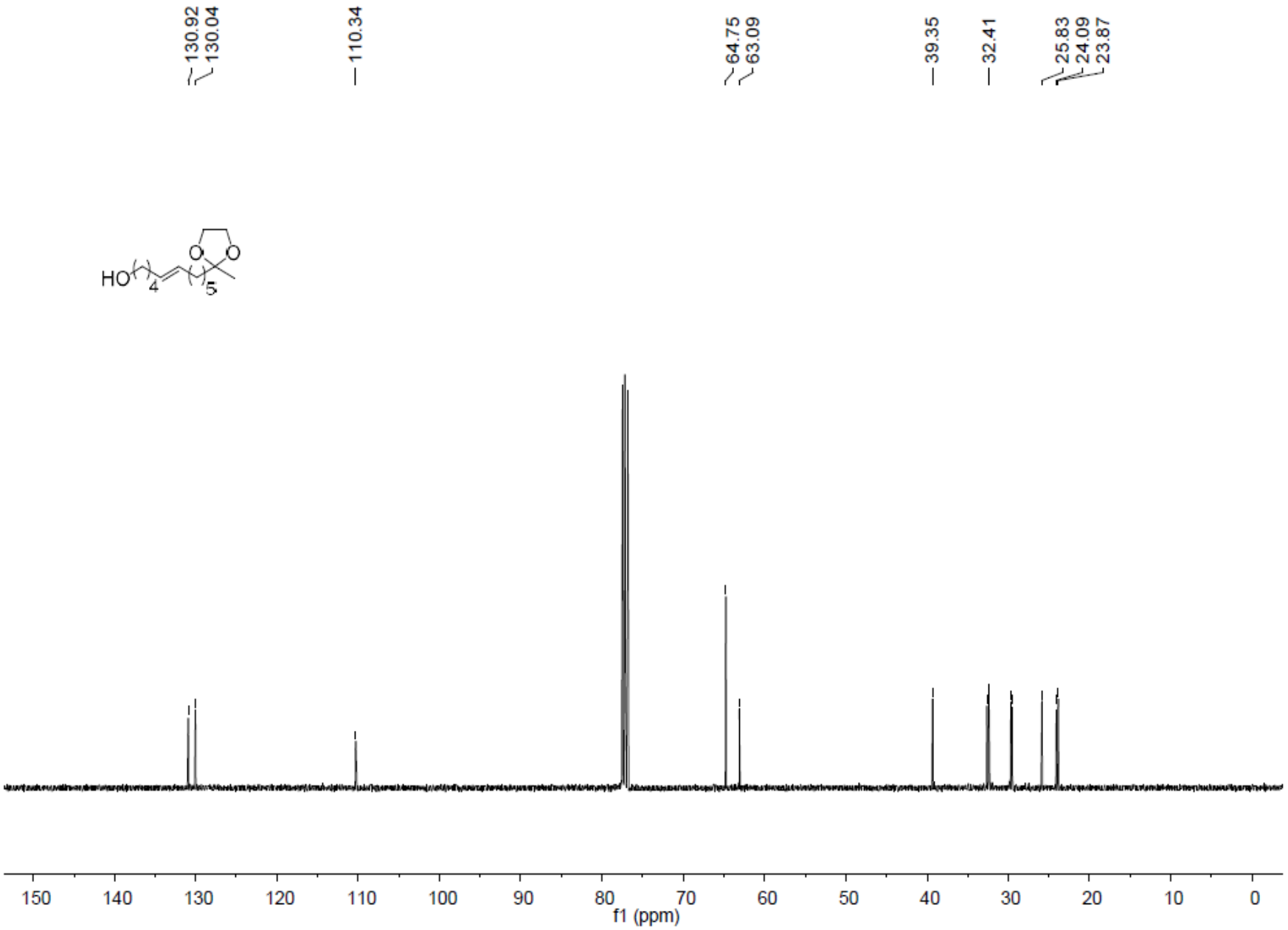
GC-MS chromatogram and fragmentations of (2*E*,9*E*)-1-bromotetracosa-2,9-diene (3)



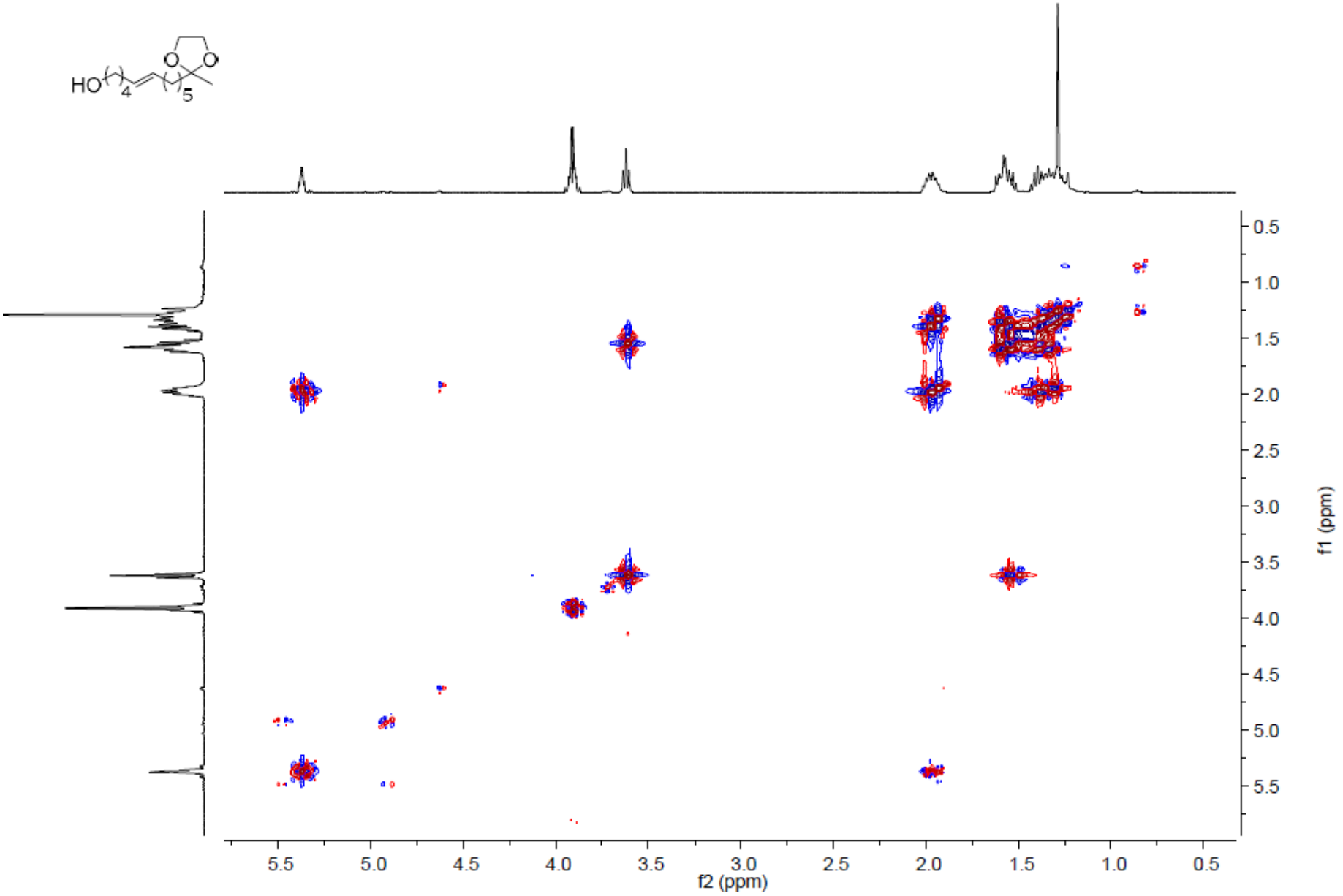
^{1}H-NMR spectrum of (*E*)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-ol (6) (400 MHz, $CDCl_3$)



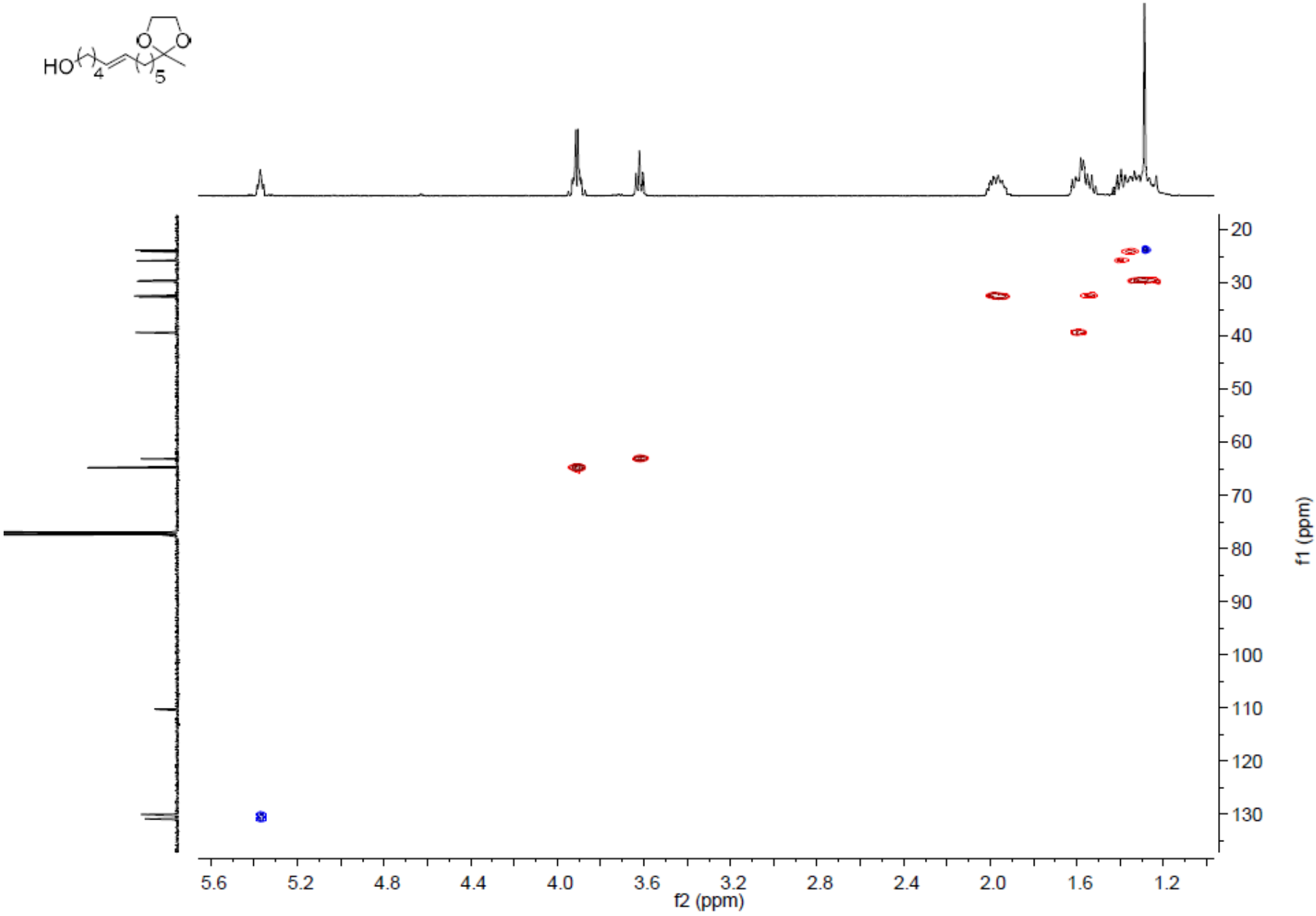
^{13}C-NMR spectrum of (*E*)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-ol (6) (101 MHz, $CDCl_3$)



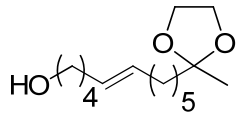
*g*DQCOSY of (*E*)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-ol (6) (400 MHz, $CDCl_3$)



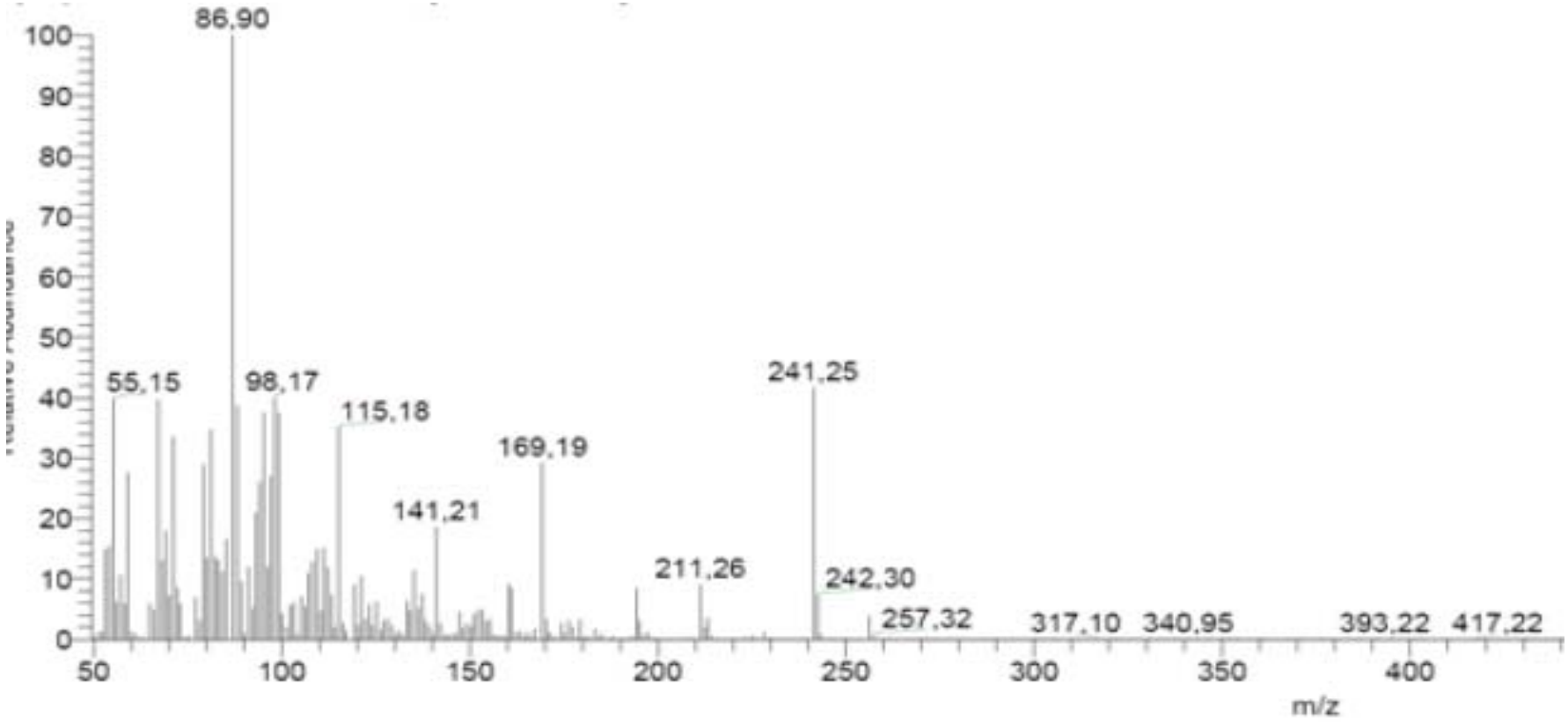
*g*HSQC spectrum of (*E*)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-ol (6) (400 MHz,101 MHz; $CDCl_3$)



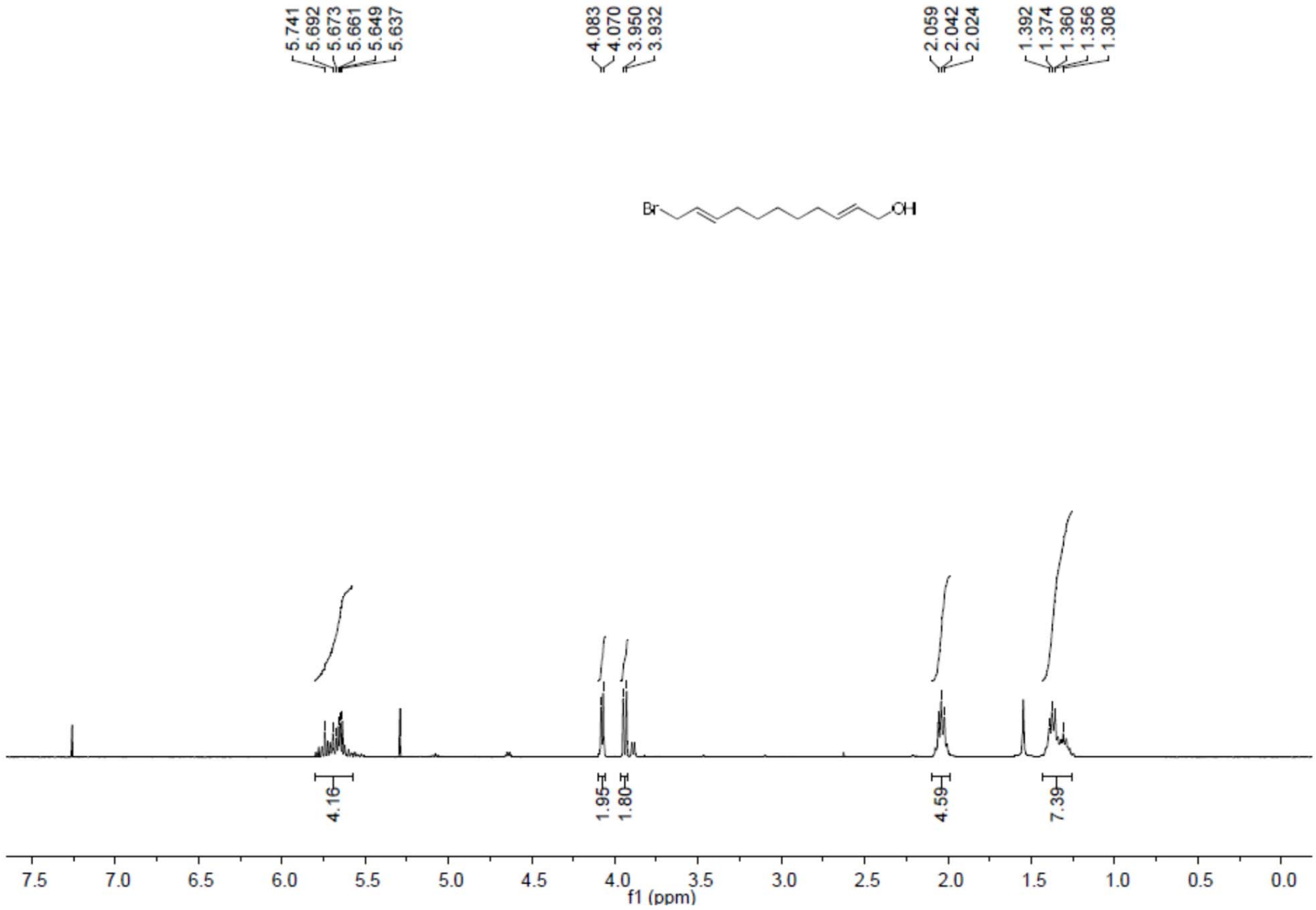
GC-MS chromatogram and fragmentations (*E*)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-ol (6)



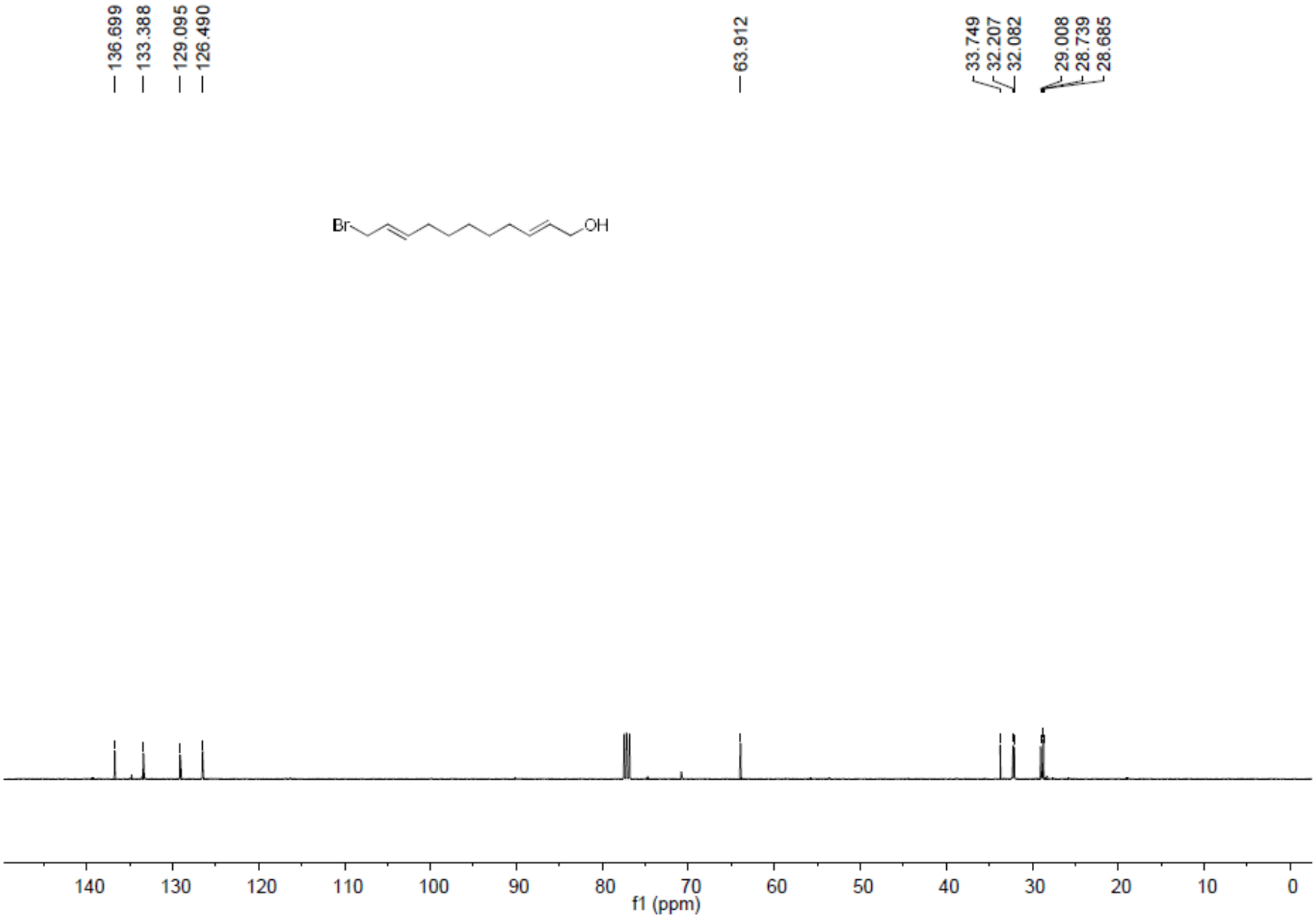
Chemical Formula: $C_{15}H_{28}O_3$
Exact Mass: 256.20
Molecular Weight: 256.38



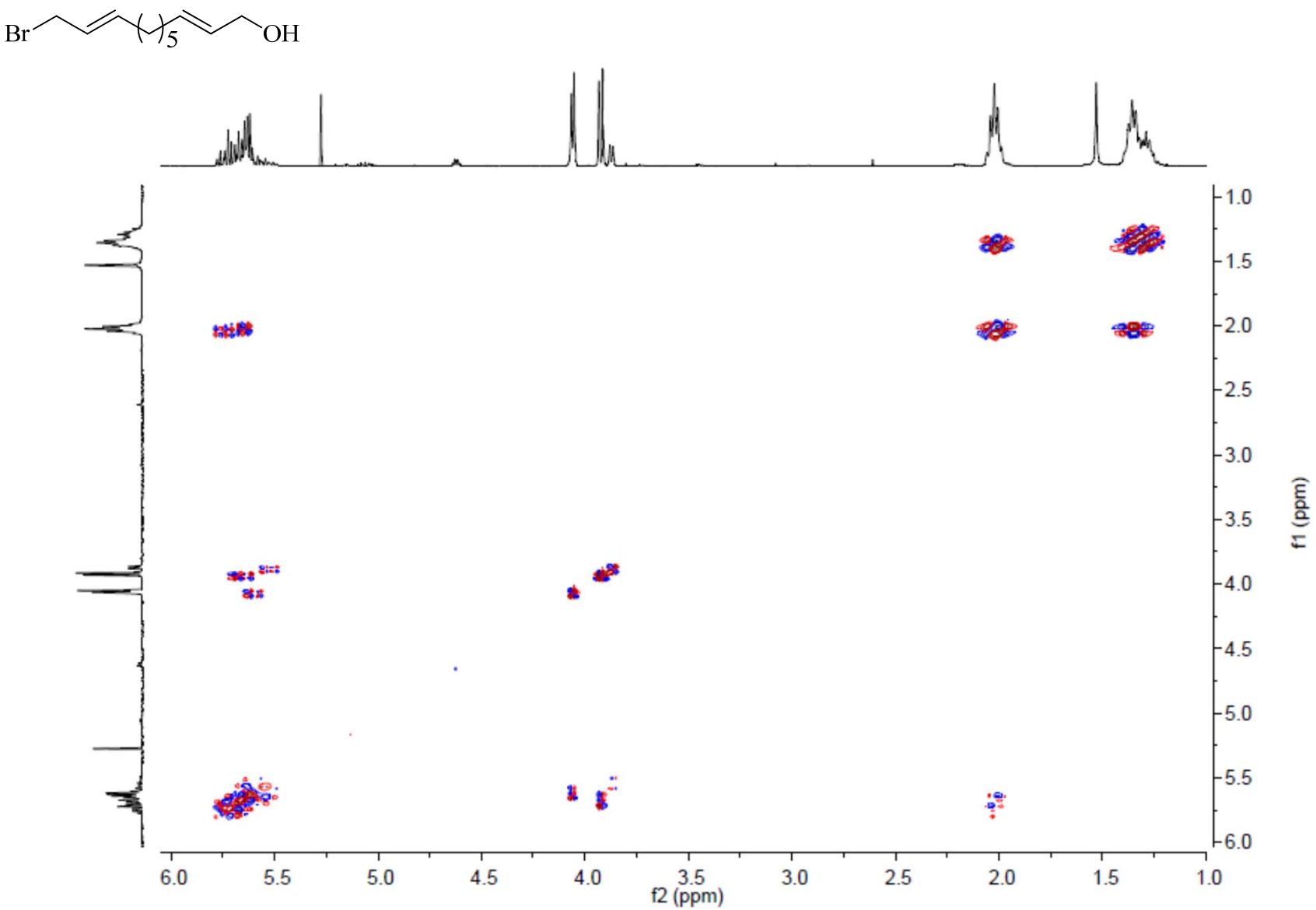
^{1}H-NMR spectrum of (2*E*,9*E*)-1-bromoundeca-2,9-dien-1-ol (7) (400 MHz, $CDCl_3$)



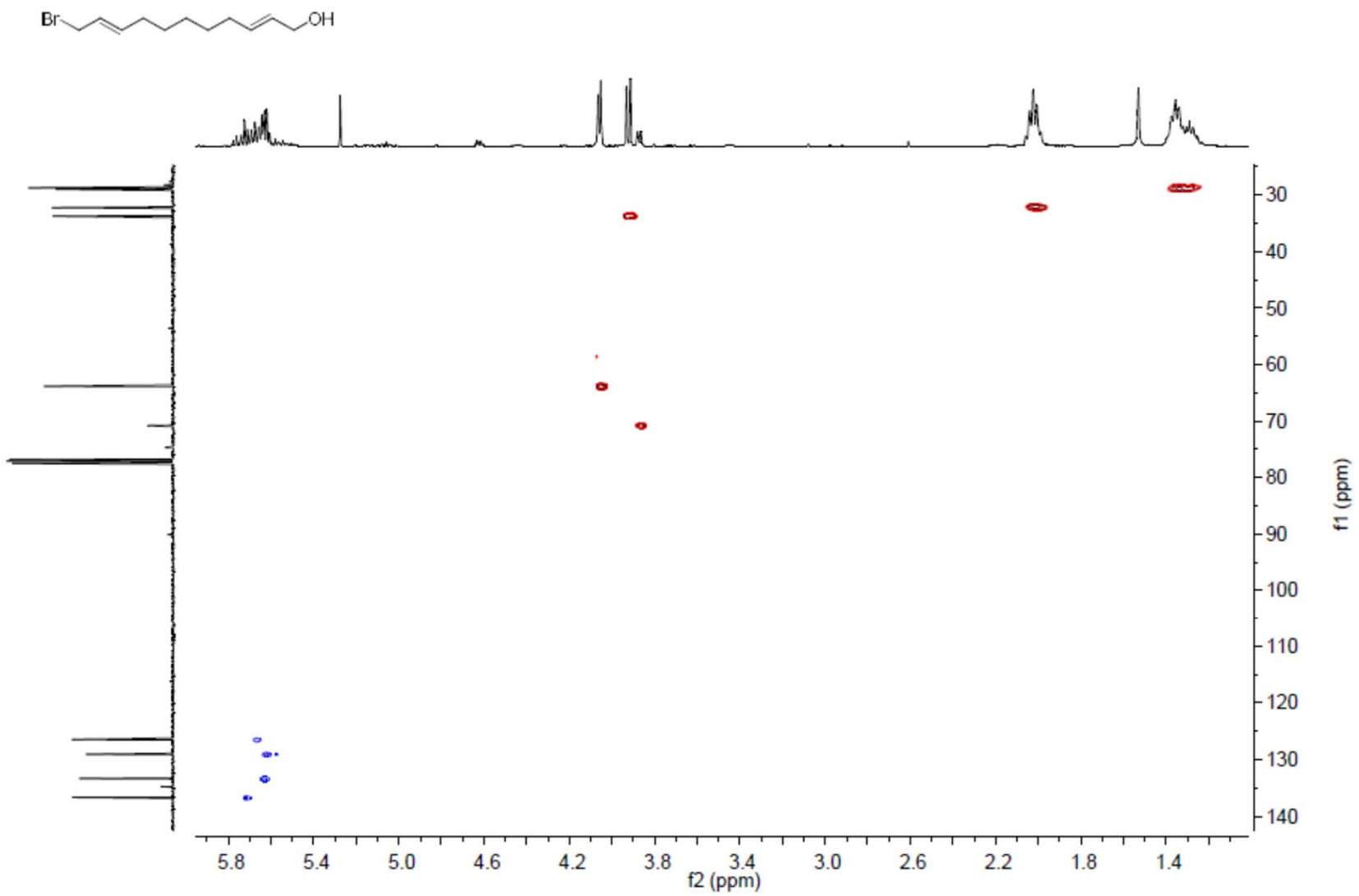
^{13}C-NMR spectrum of (2*E*,9*E*)-1-bromoundeca-2,9-dien-1-ol (7) (101 MHz, $CDCl_3$)



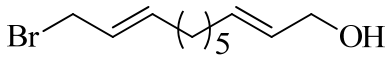
*g*DQCOSY spectrum of (2*E*,9*E*)-1-bromoundeca-2,9-dien-1-ol (7) (400 MHz, $CDCl_3$)



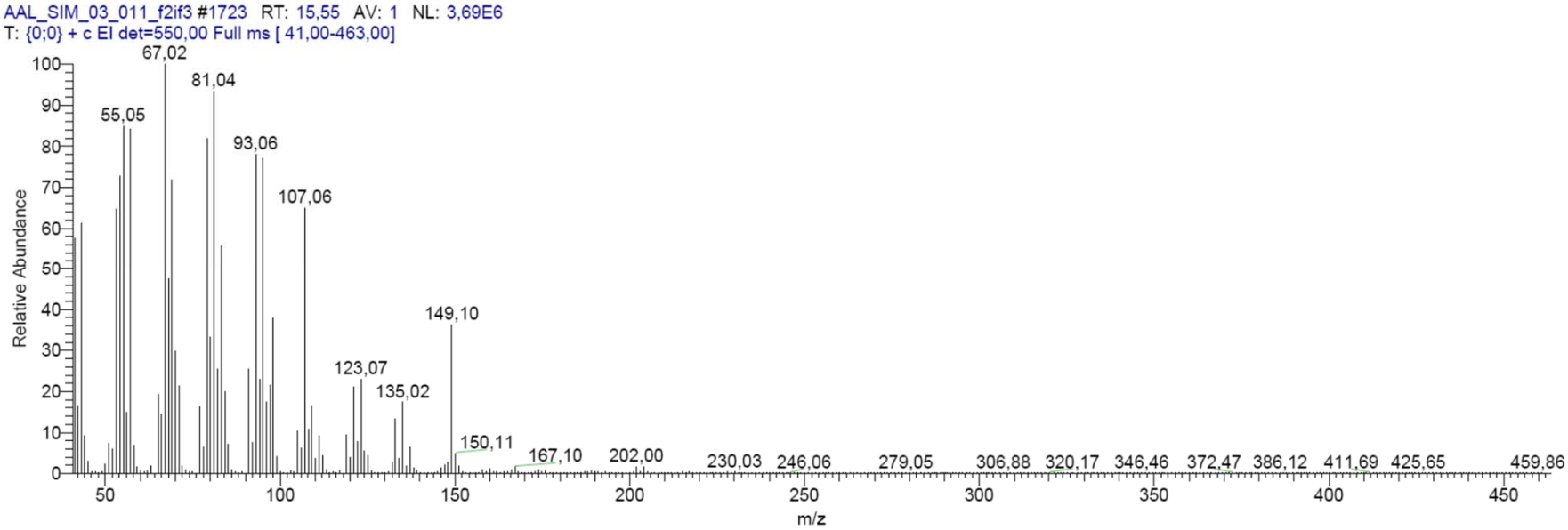
*g*HSQC spectrum (2*E*,9*E*)-1-bromoundeca-2,9-dien-1-ol (7) (400 MHz,101 MHz; $CDCl_3$)



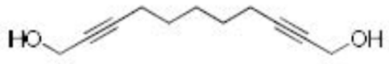
GC-MS chromatogram and fragmentations of (2*E*,9*E*)-1-bromoundeca-2,9-dien-1-ol (7)

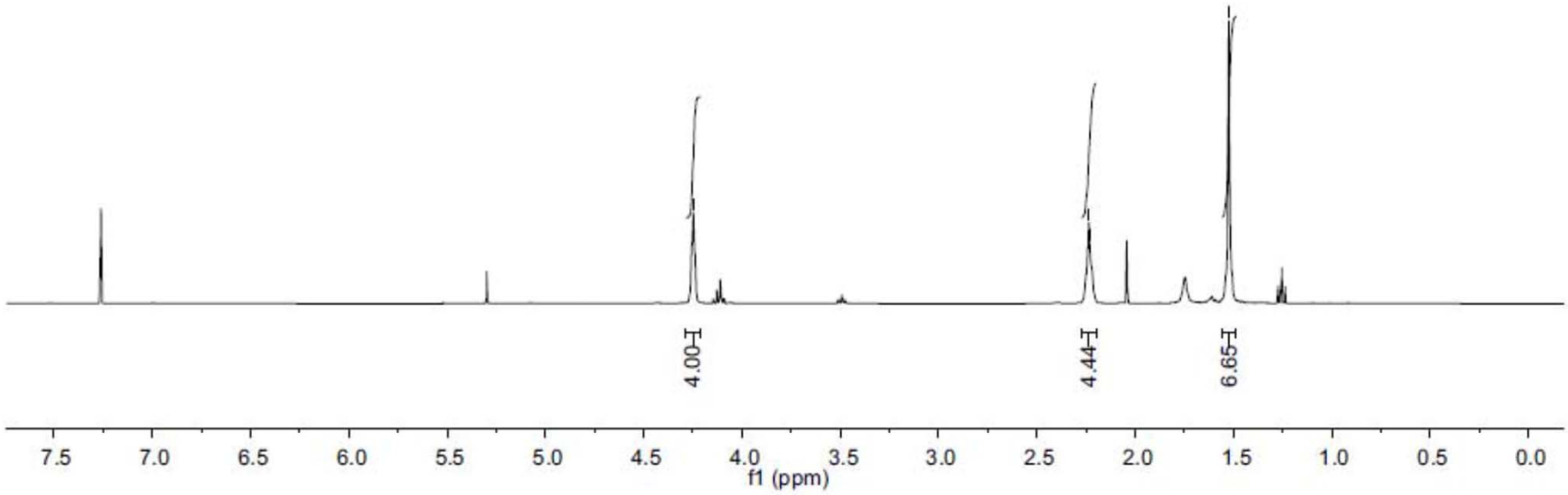


Chemical Formula: $C_{37}H_{68}O$
Exact Mass: 528,53
Molecular Weight: 528,95

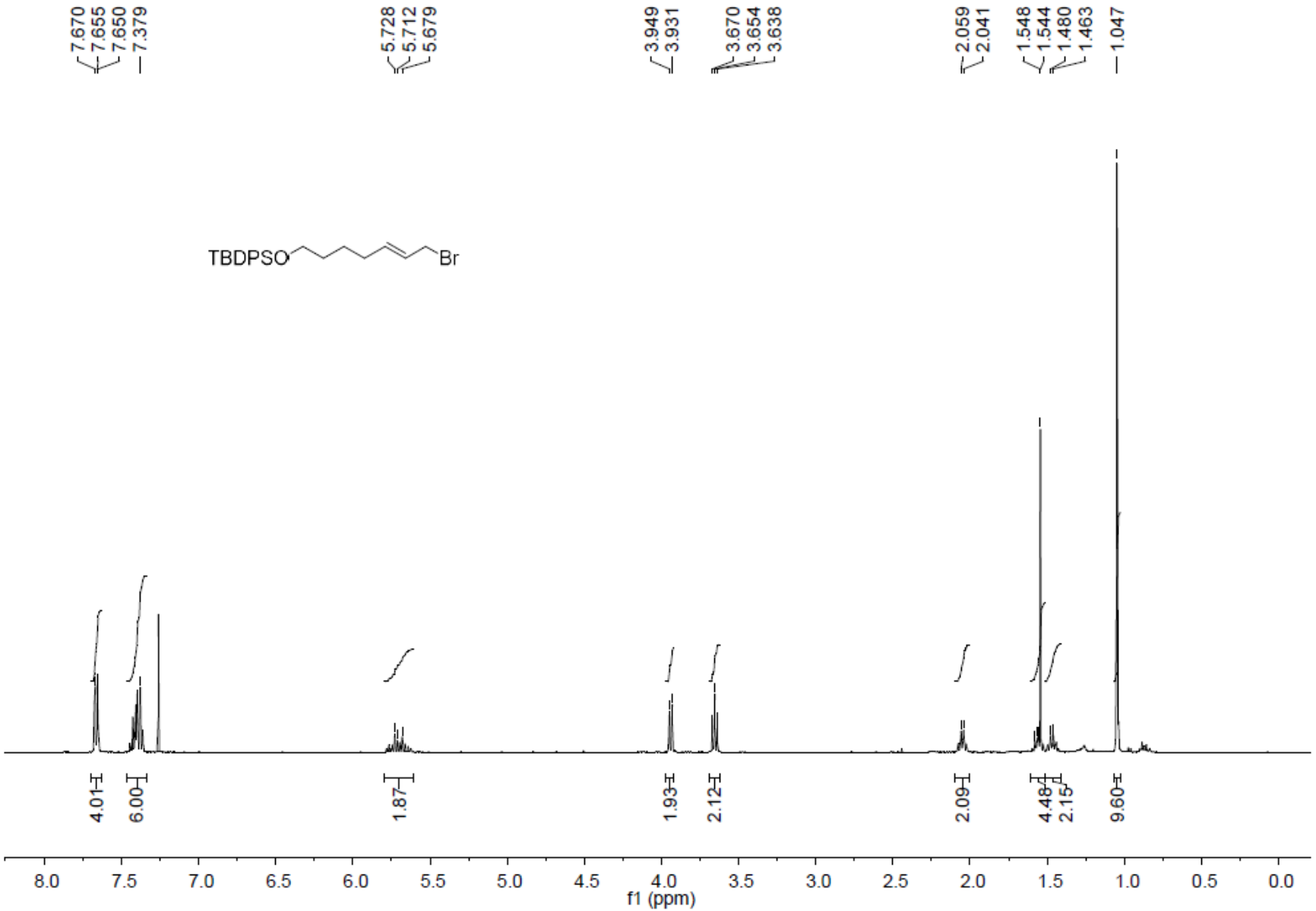


^{1}H-NMR spectrum of Undeca-2,9-diyne-1,11-diol (9) (400 MHz, $CDCl_3$)

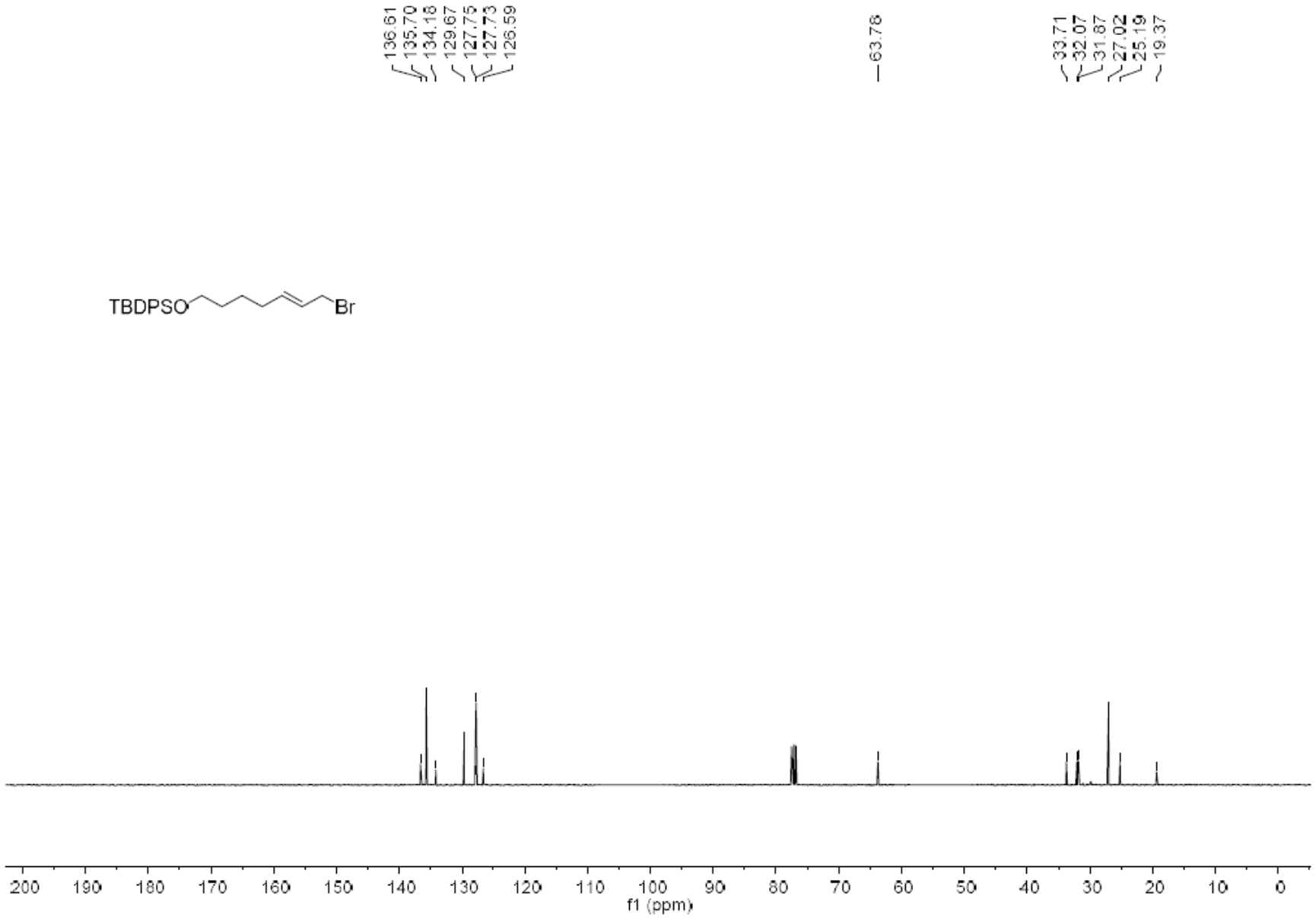




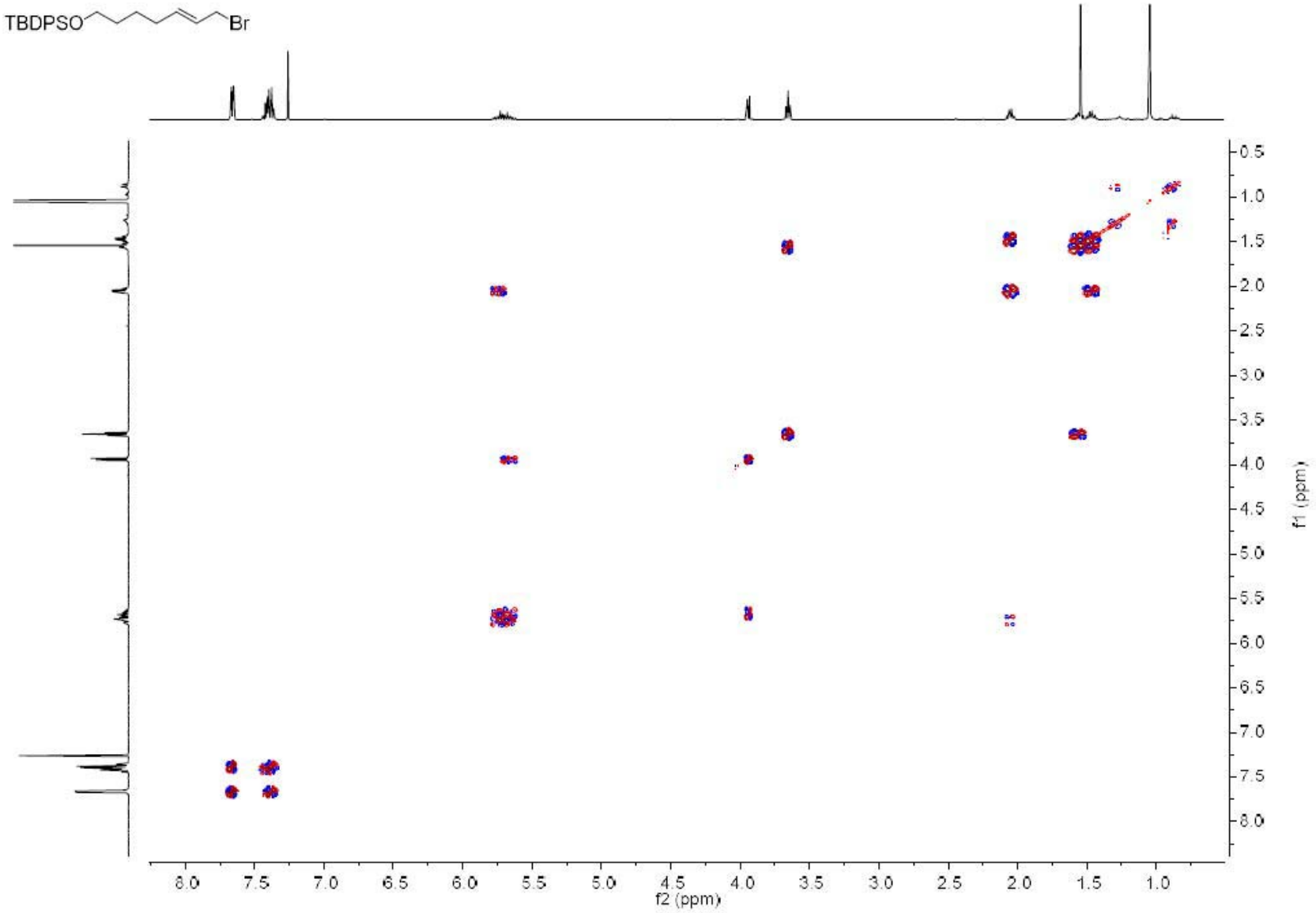
^{1}H-NMR spectrum of (*E*)-((7-bromohept-5-en-1-yl)oxy)(tert-butyl)diphenylsilane (12) (400 MHz, $CDCl_3$)



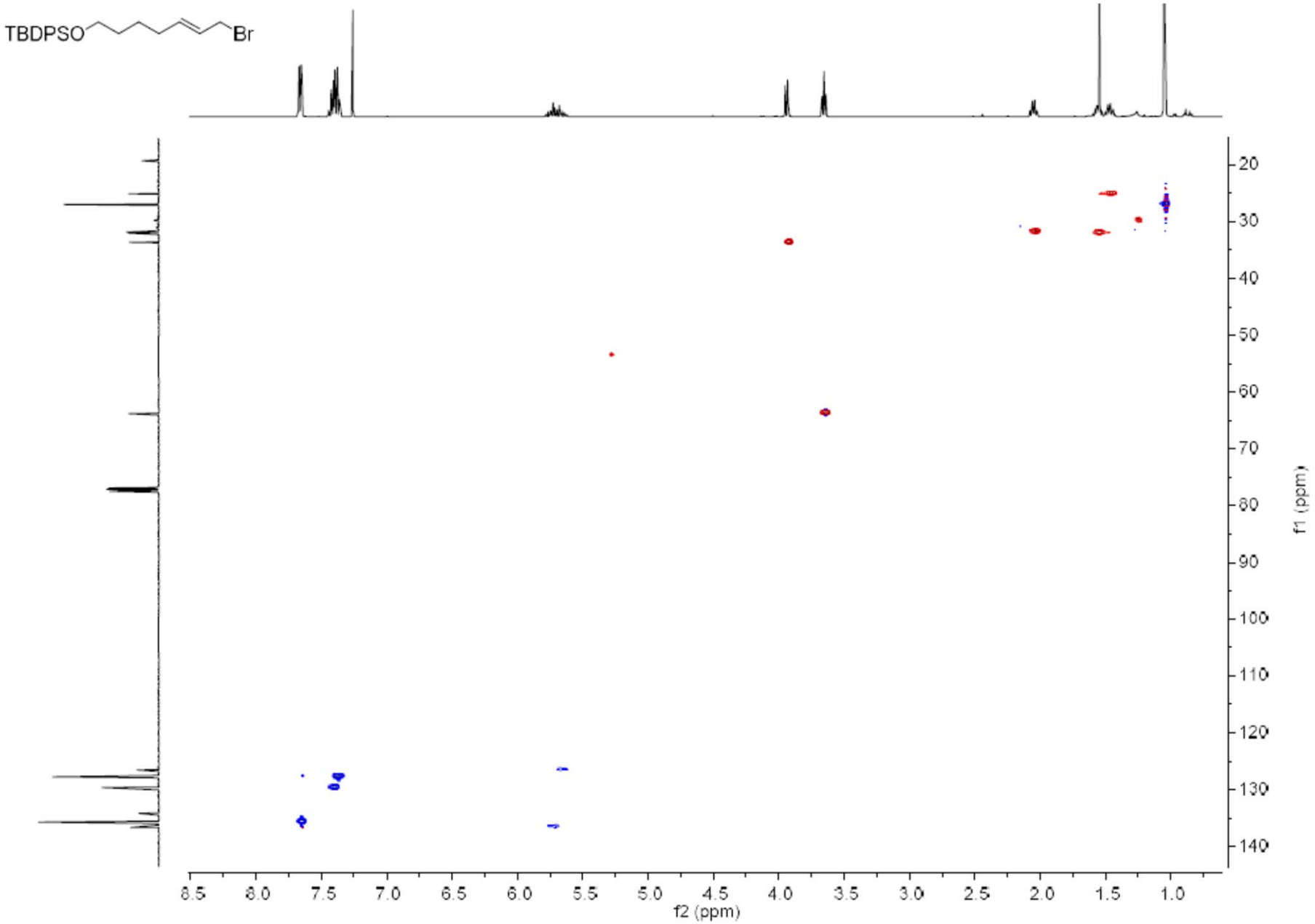
^{13}C-NMR spectrum of (*E*)-((7-bromohept-5-en-1-yl)oxy)(tert-butyl)diphenylsilane (12) (101 MHz, $CDCl_3$)



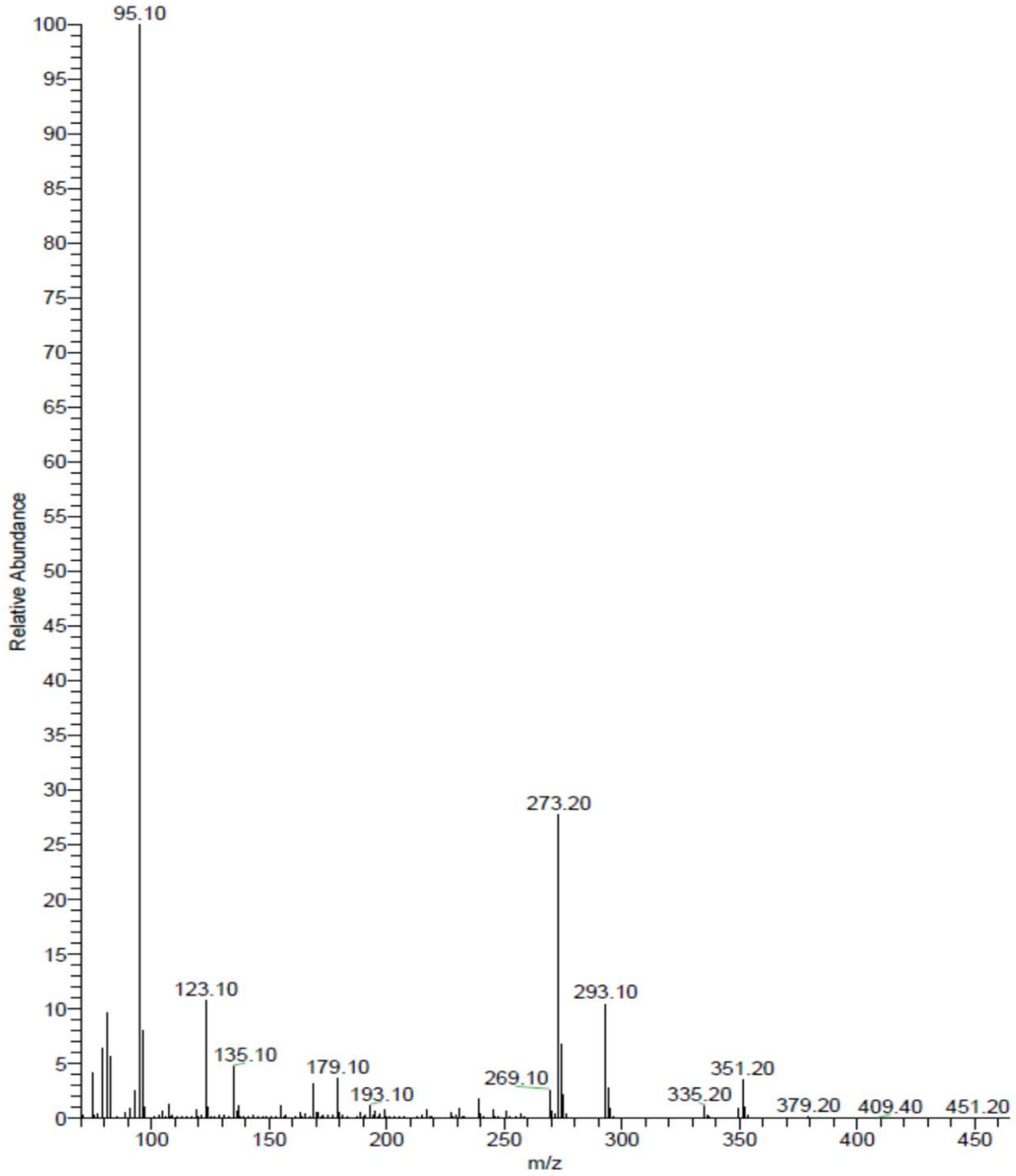
*g*DQCOSY spectrum of (*E*)-((7-bromohept-5-en-1-yl)oxy)(tert-butyl)diphenylsilane (12) (400 MHz, $CDCl_3$)

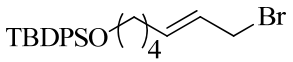


*g*HSQC spectrum of (*E*)-((7-bromohept-5-en-1-yl)oxy)(tert-butyl)diphenylsilane (12) (400 MHz,101 MHz; $CDCl_3$)



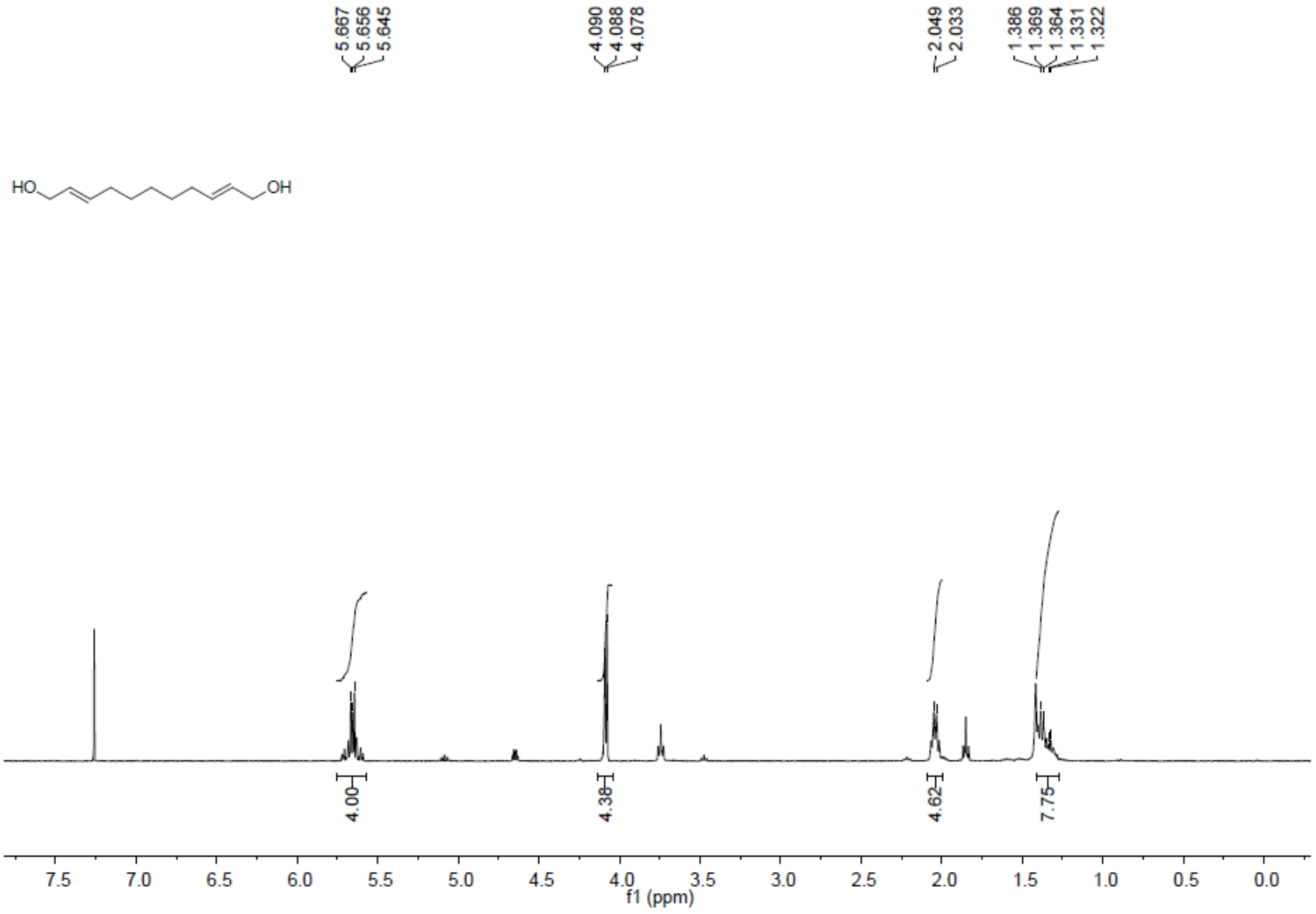
GC-MS chromatogram and fragmentations of (*E*)-((7-bromohept-5-en-1-yl)oxy)(tert-butyl)diphenylsilane (12)



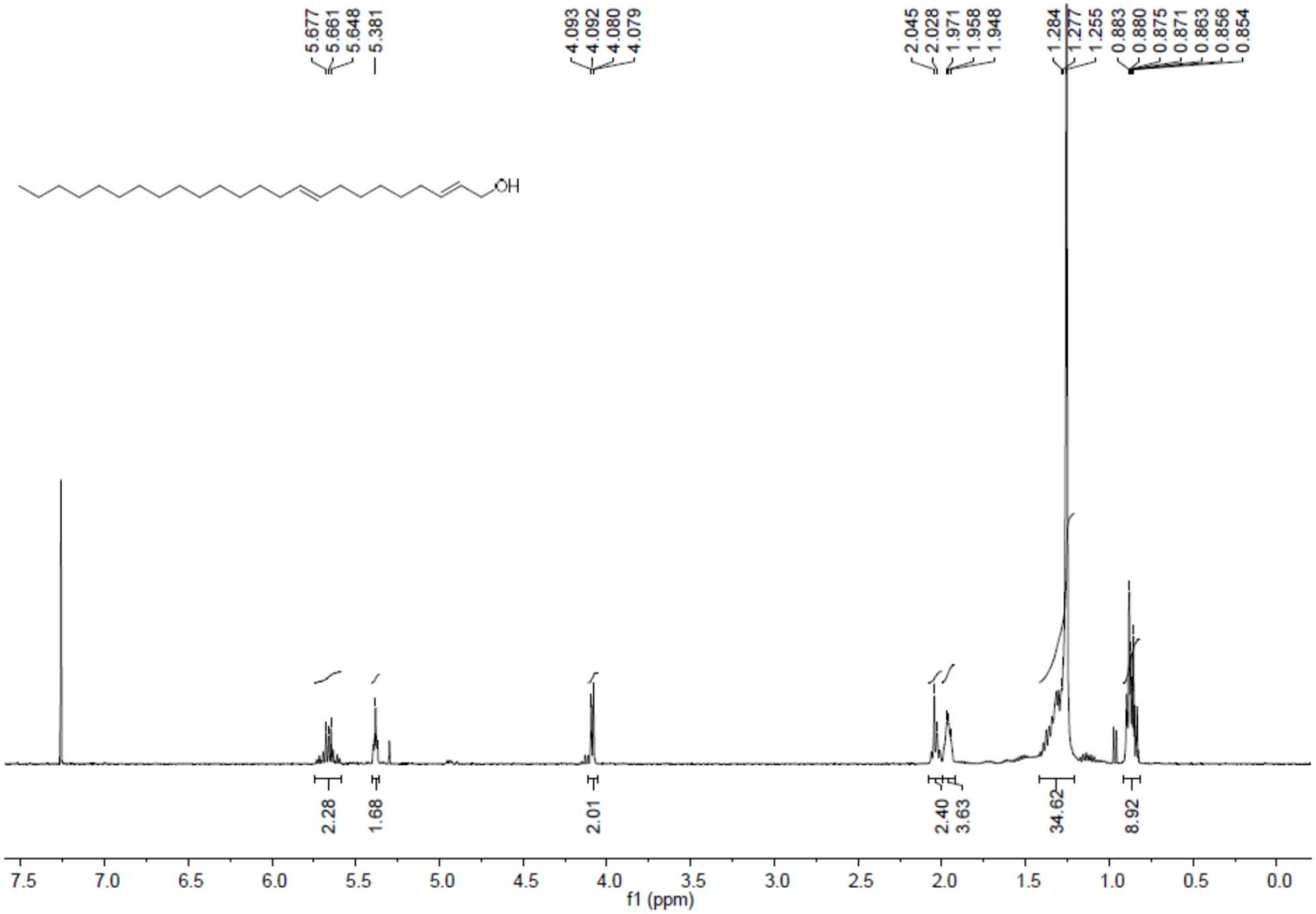


Chemical Formula: $C_{23}H_{31}BrOSi$
Exact Mass: 430.13
Molecular Weight: 431.48

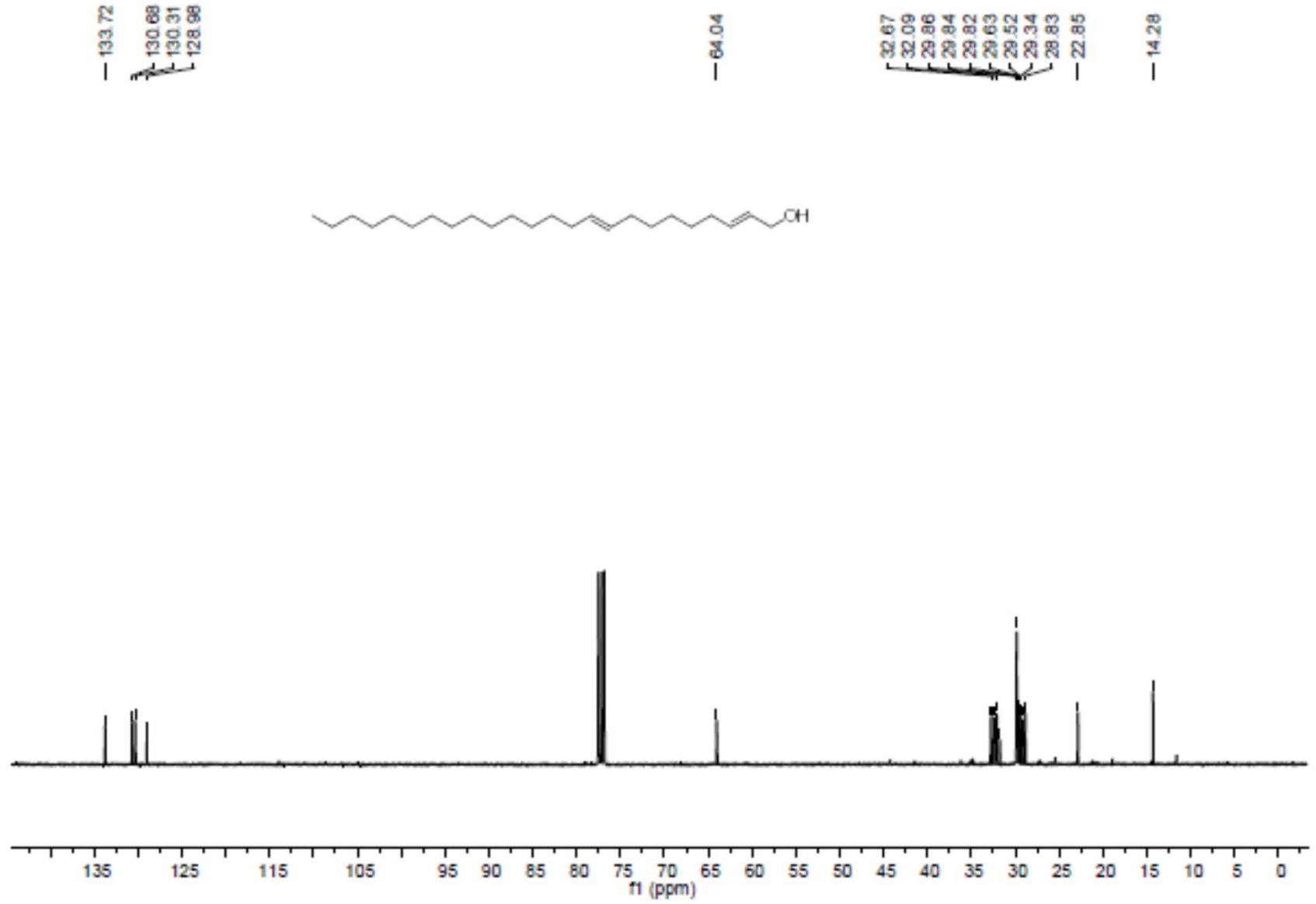
^{1}H-NMR spectrum of (2*E*,9*E*)-undeca-2,9-diene-1,11-diol (16) (400 MHz, $CDCl_3$)



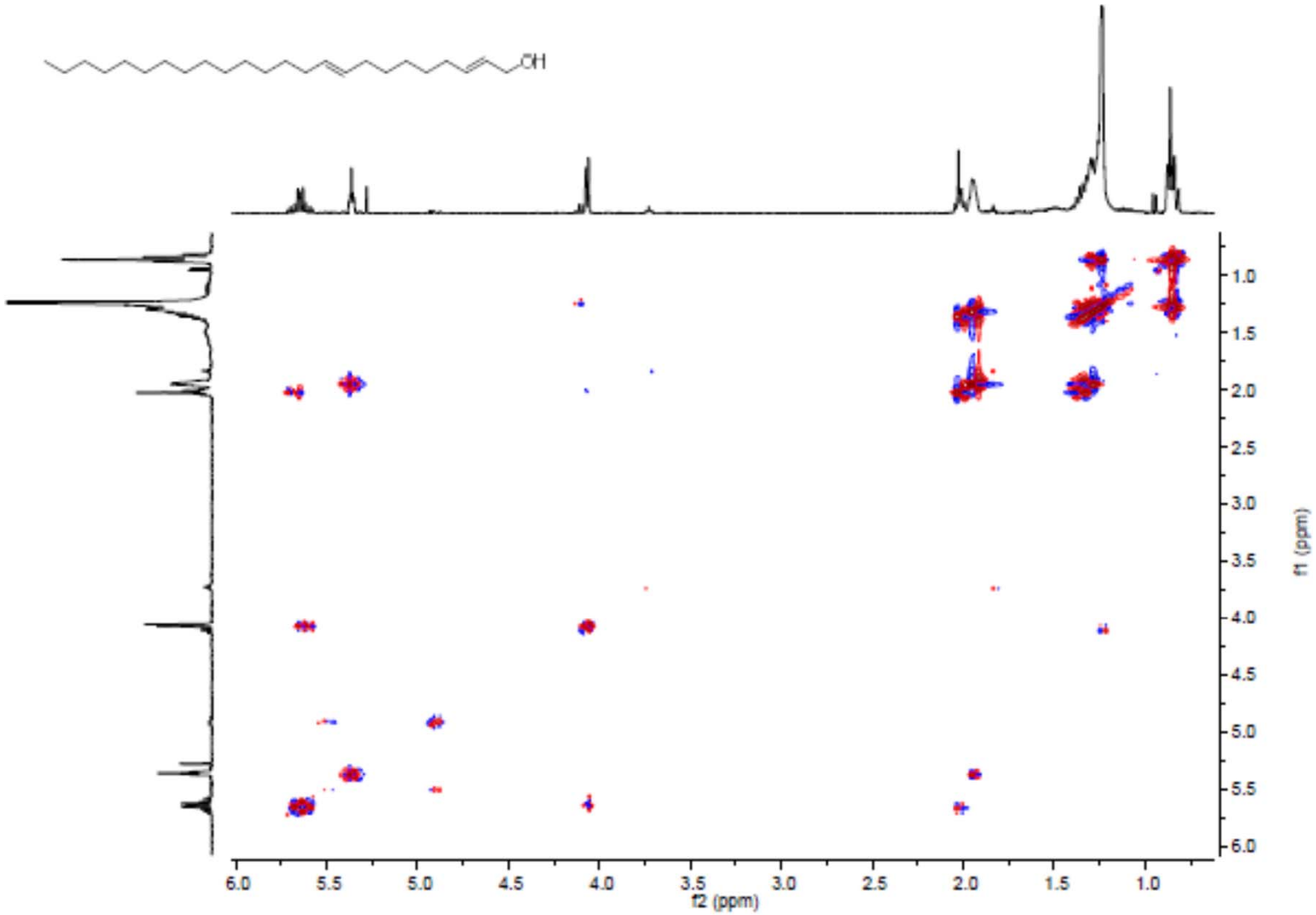
^{1}H-NMR spectrum of (2*E*,9*E*)-tetracosa-2,9-dien-1-ol (17) (400 MHz, $CDCl_3$)



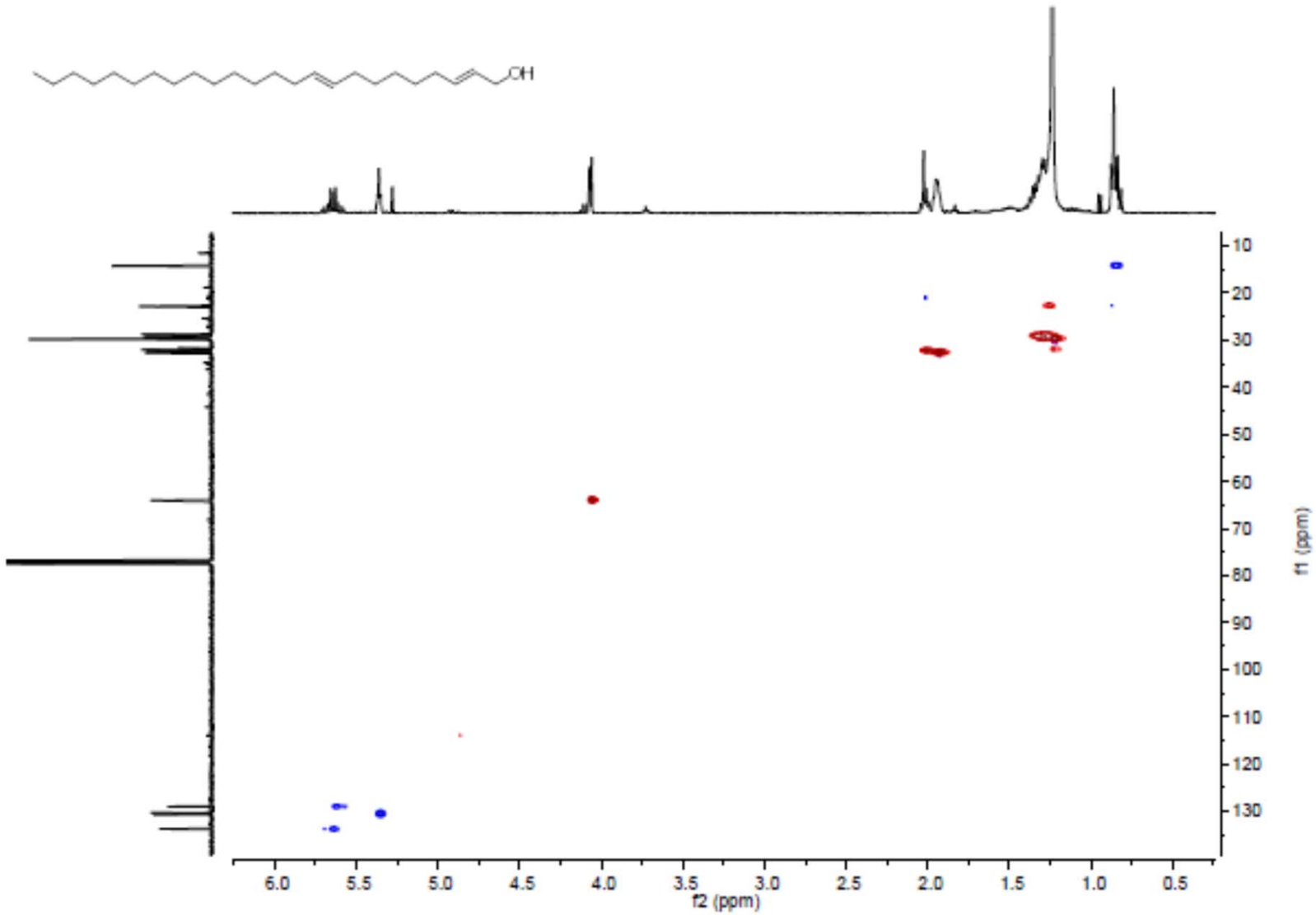
^{13}C-NMR spectrum of (2*E*,9*E*)-tetracosa-2,9-dien-1-ol (17) (101 MHz, $CDCl_3$)



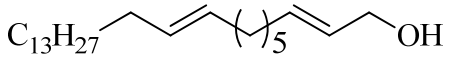
*g*DQCOSY spectrum of (2*E*,9*E*)-tetracosa-2,9-dien-1-ol (17) (400 MHz, $CDCl_3$)



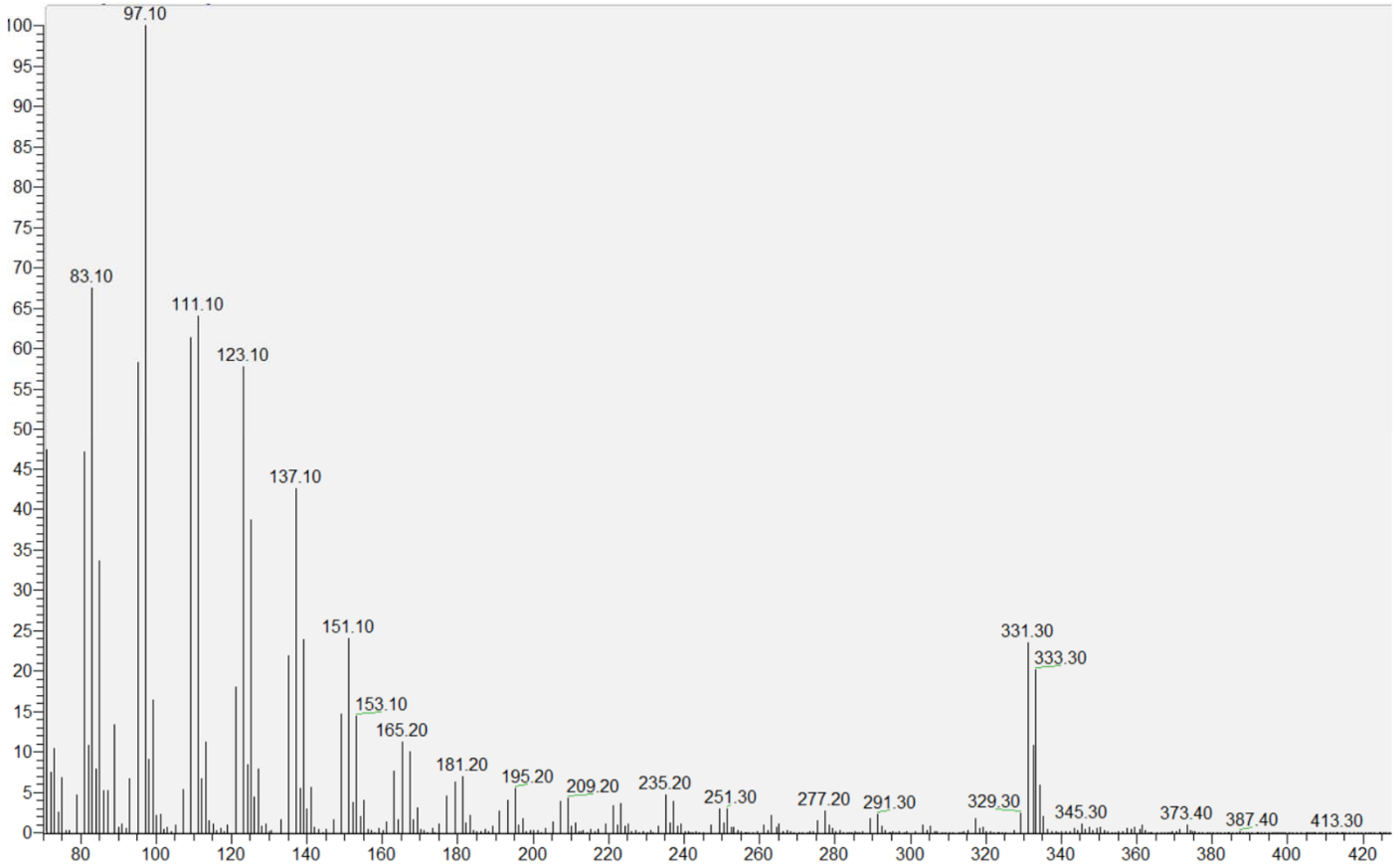
*g*HSQC spectrum (2*E*,9*E*)-tetracosa-2,9-dien-1-ol (17) (400 MHz,101 MHz; $CDCl_3$)



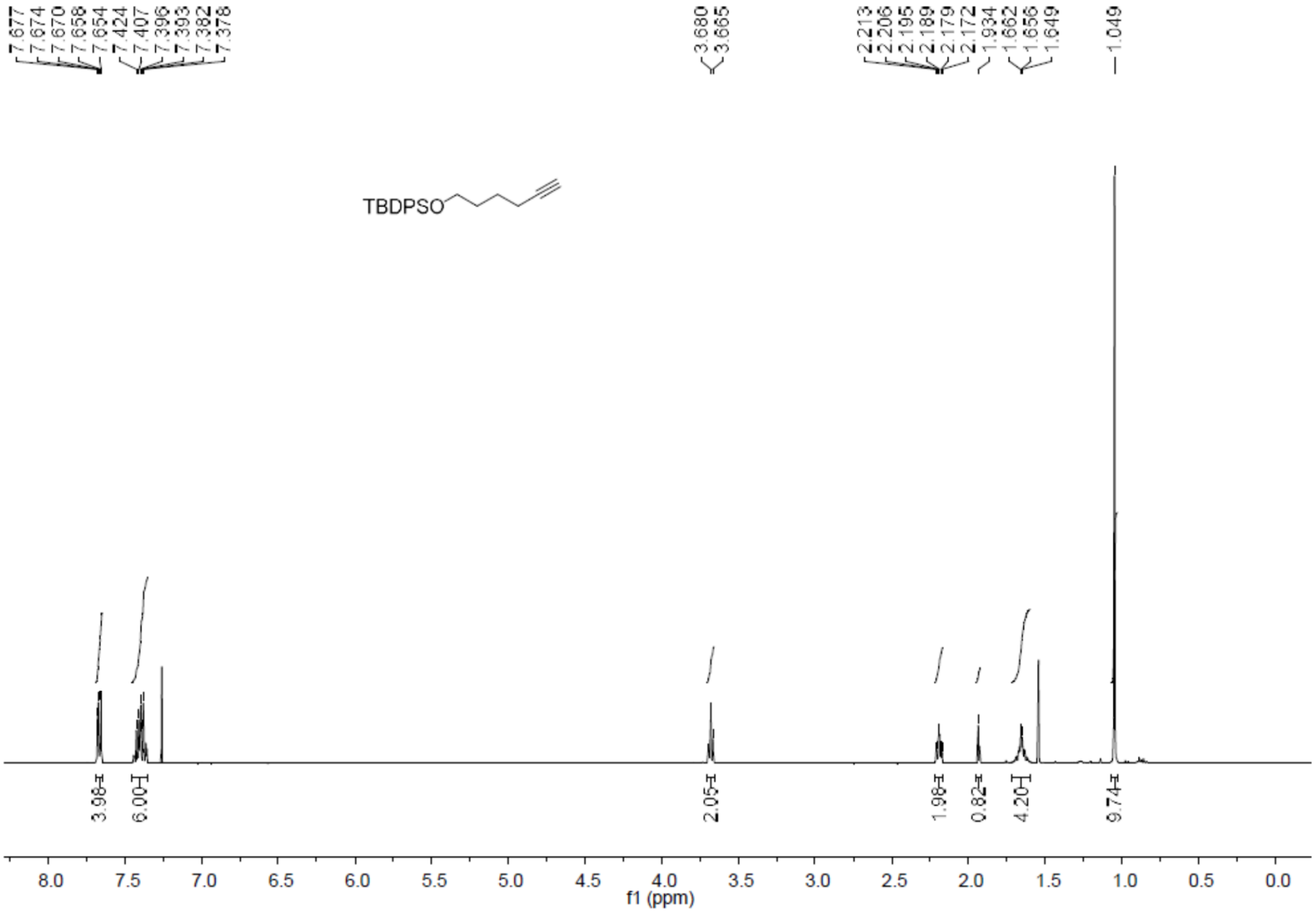
GC-MS chromatogram and fragmentations of (2*E*,9*E*)-tetracosa-2,9-dien-1-ol (17)



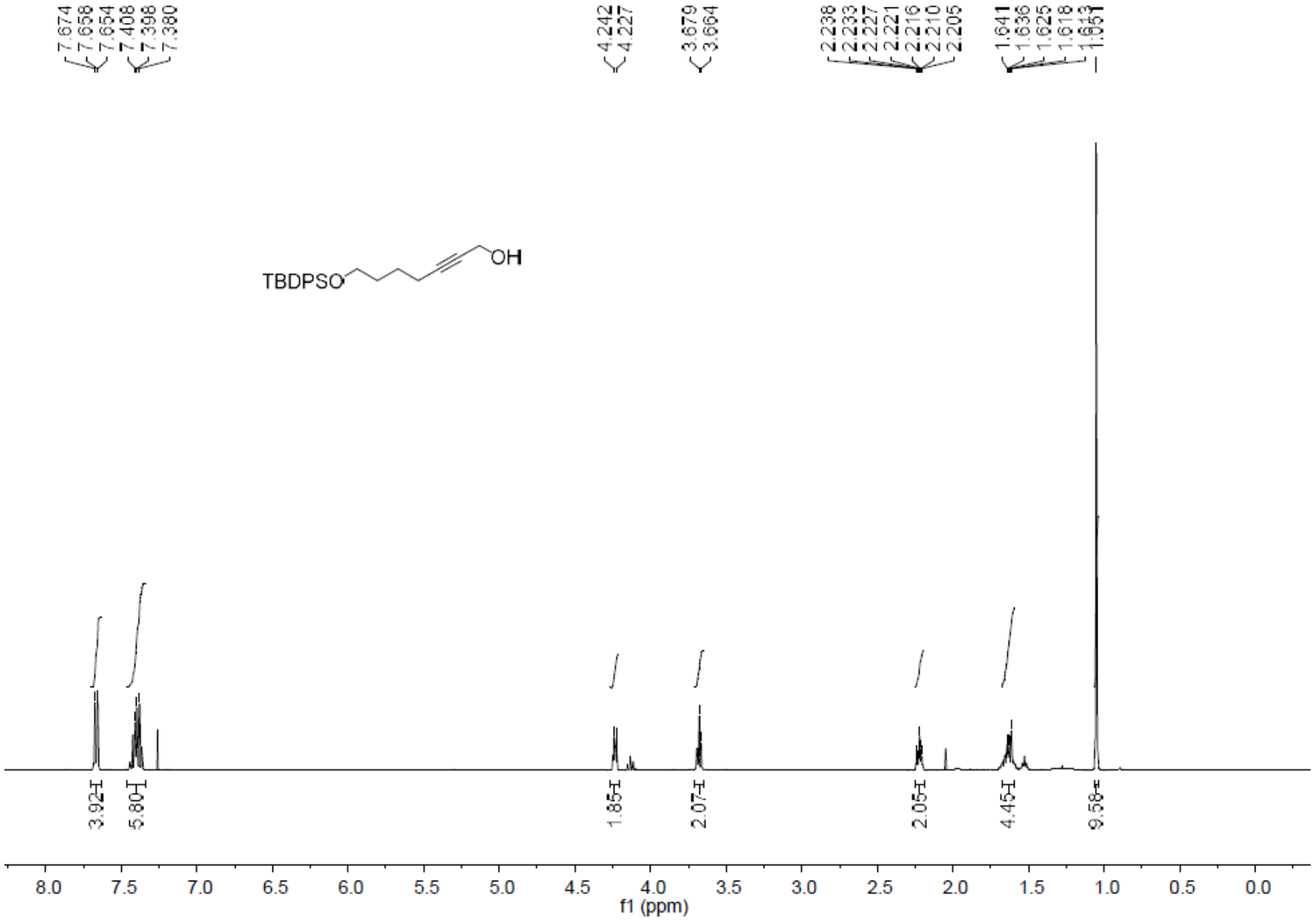
Chemical Formula: $C_{24}H_{46}O$
Exact Mass: 350.35
Molecular Weight: 350.62



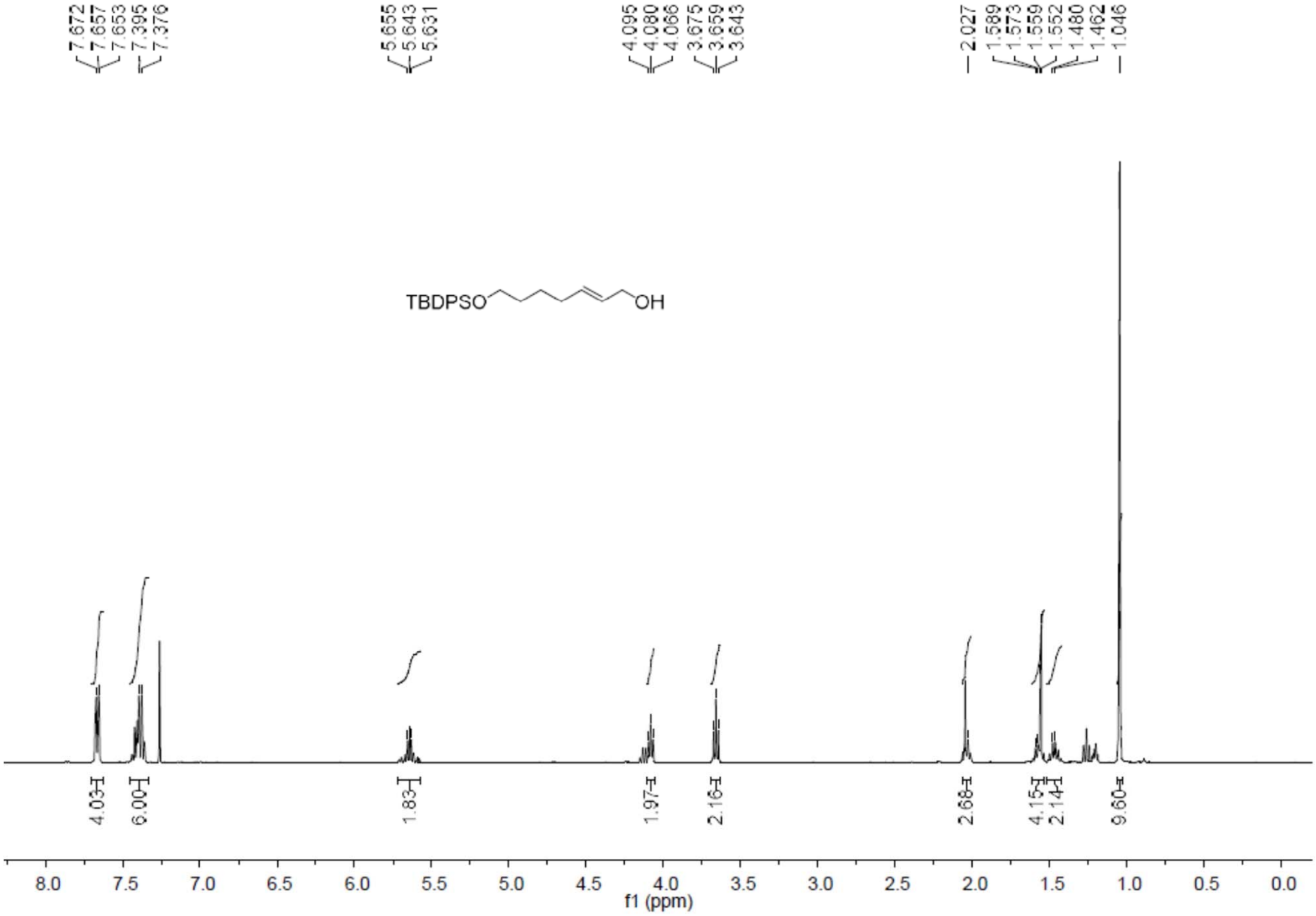
^{1}H-NMR spectrum of tert-butyl(hex-5-yn-1-yloxy)diphenylsilane (18) (400 MHz, $CDCl_3$)



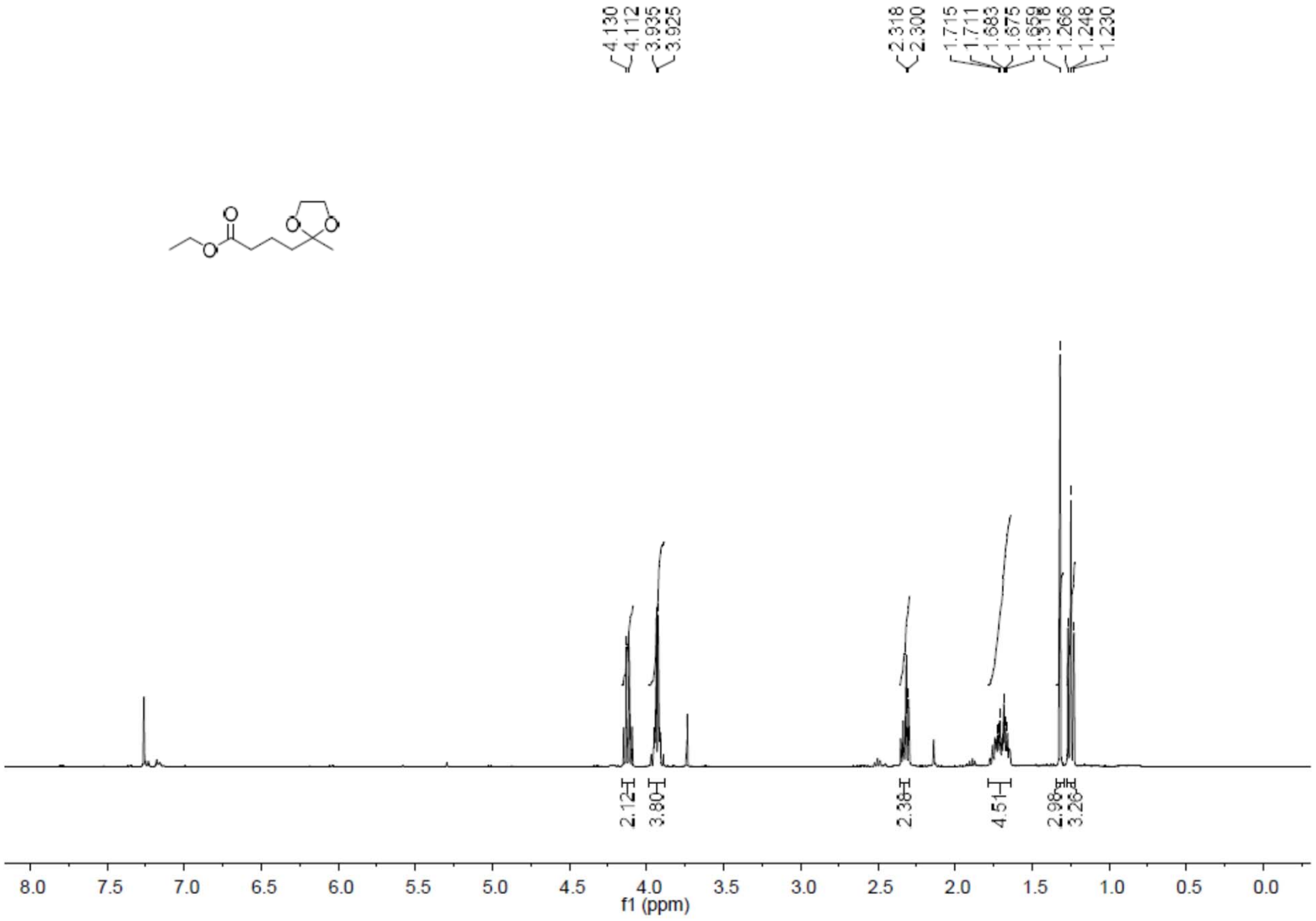
^{1}H-NMR spectrum of 7-((tert-butyldiphenylsilyl)oxy)hept-2-yn-1-ol (19) (400 MHz, $CDCl_3$)



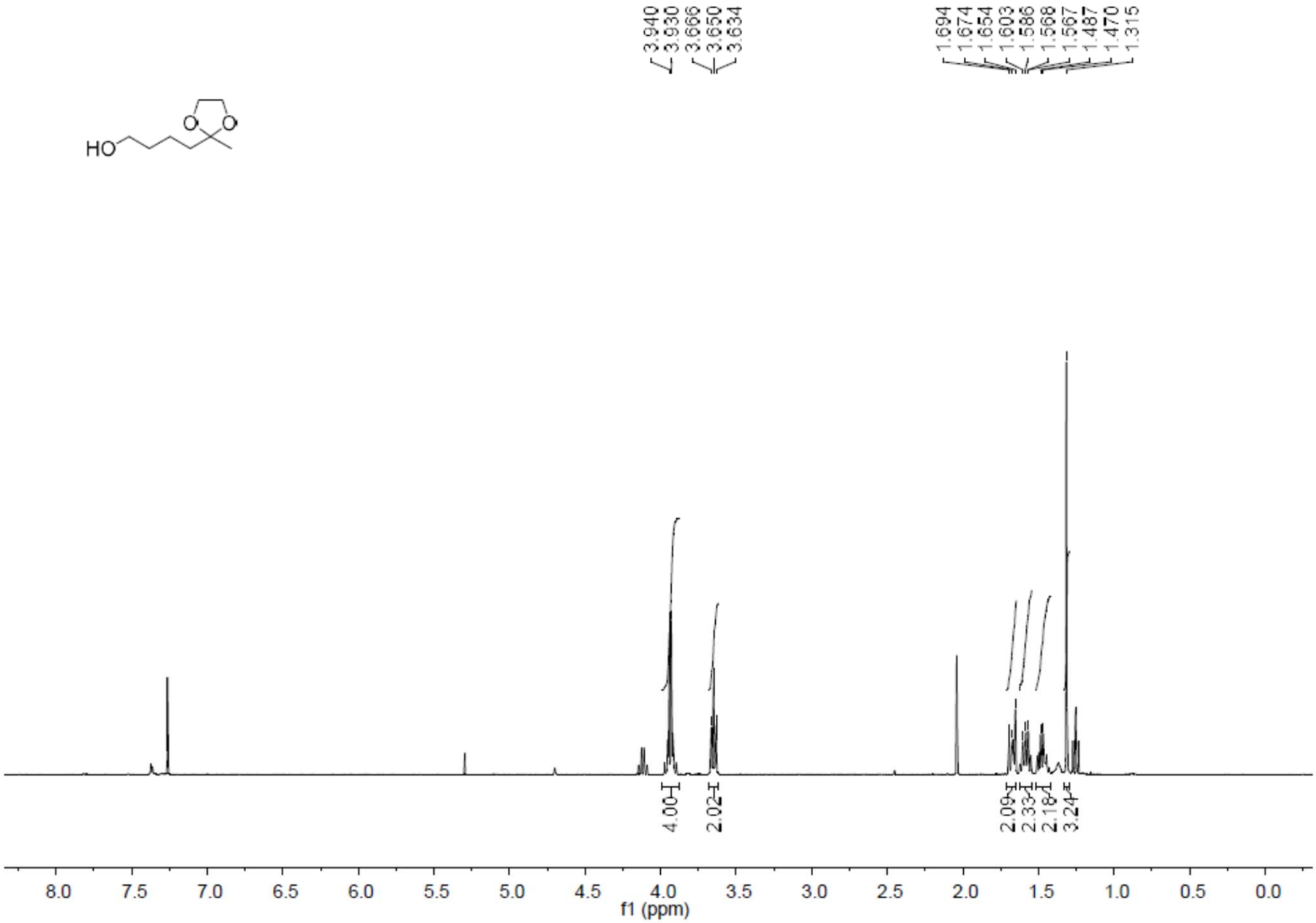
^{1}H-NMR spectrum of (*E*)-7-((tert-butyldiphenylsilyl)oxy)hept-2-en-1-ol (20) (400 MHz, $CDCl_3$)



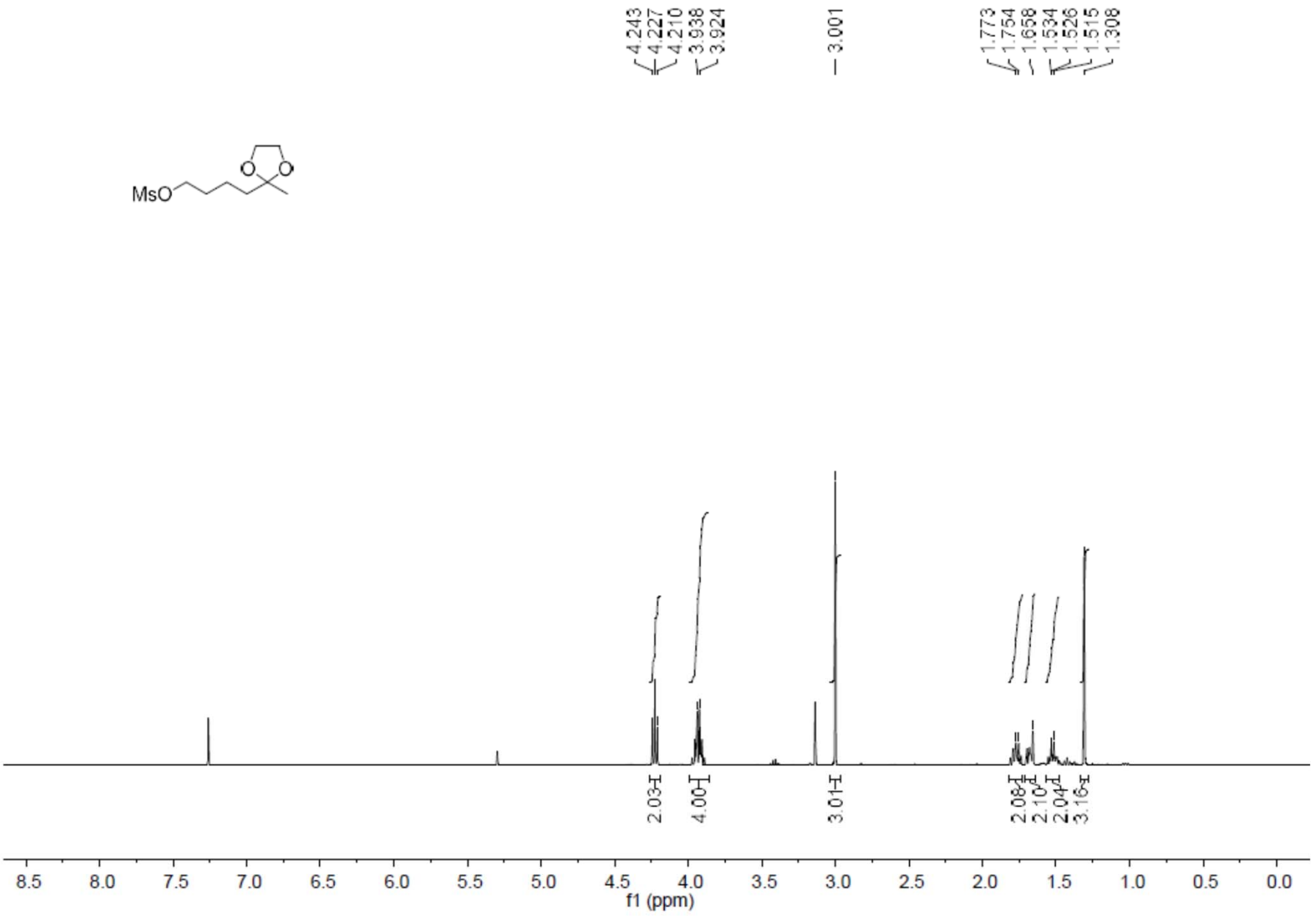
^{1}H-NMR spectrum of Ethyl 4-(2-methyl-1,3-dioxolan-2-yl)butanoate (22) (400 MHz, $CDCl_3$)



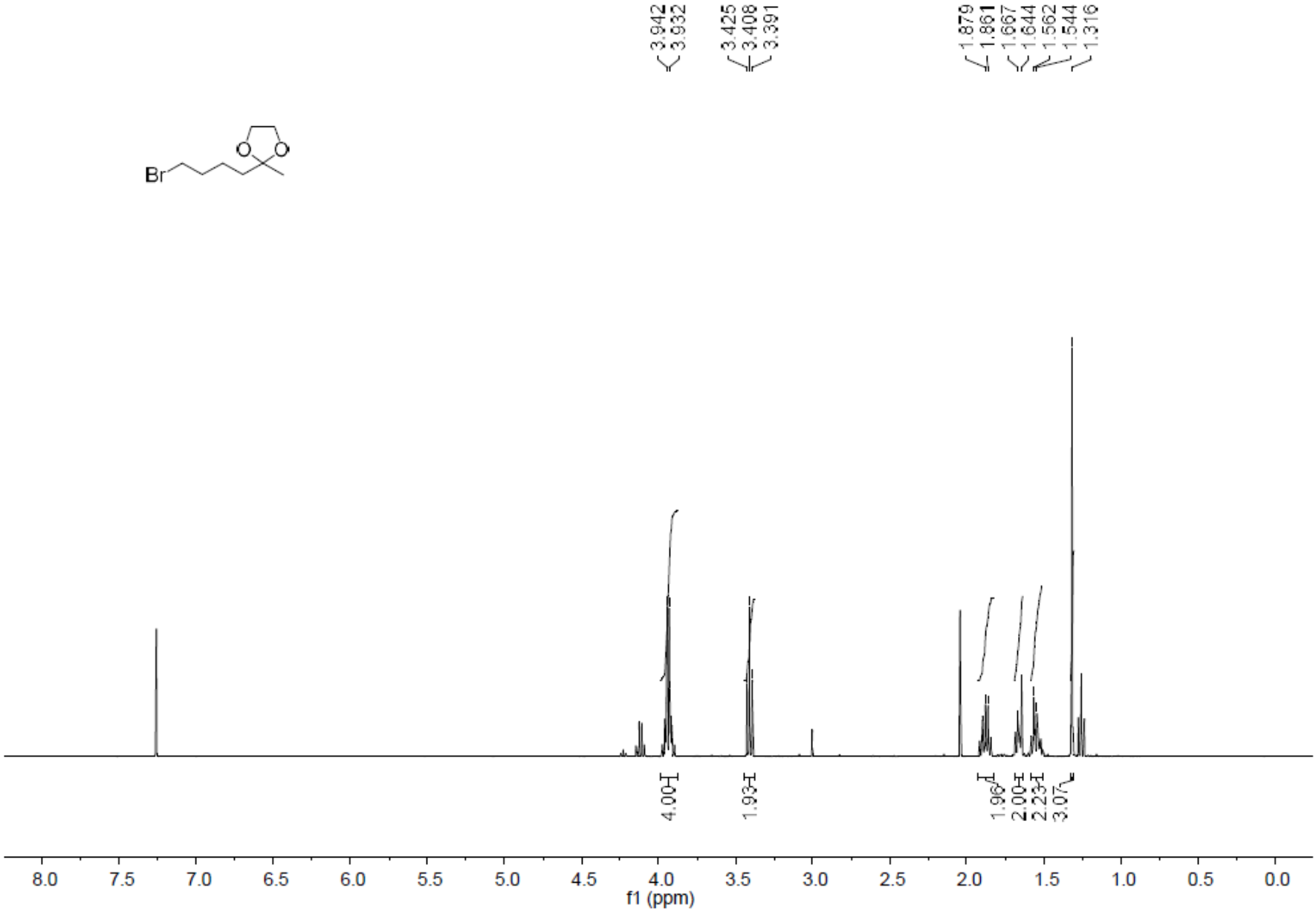
^{1}H-NMR spectrum of 4-(2-methyl-1,3-dioxolan-2-yl)butan-1-ol (23) (400 MHz, $CDCl_3$)



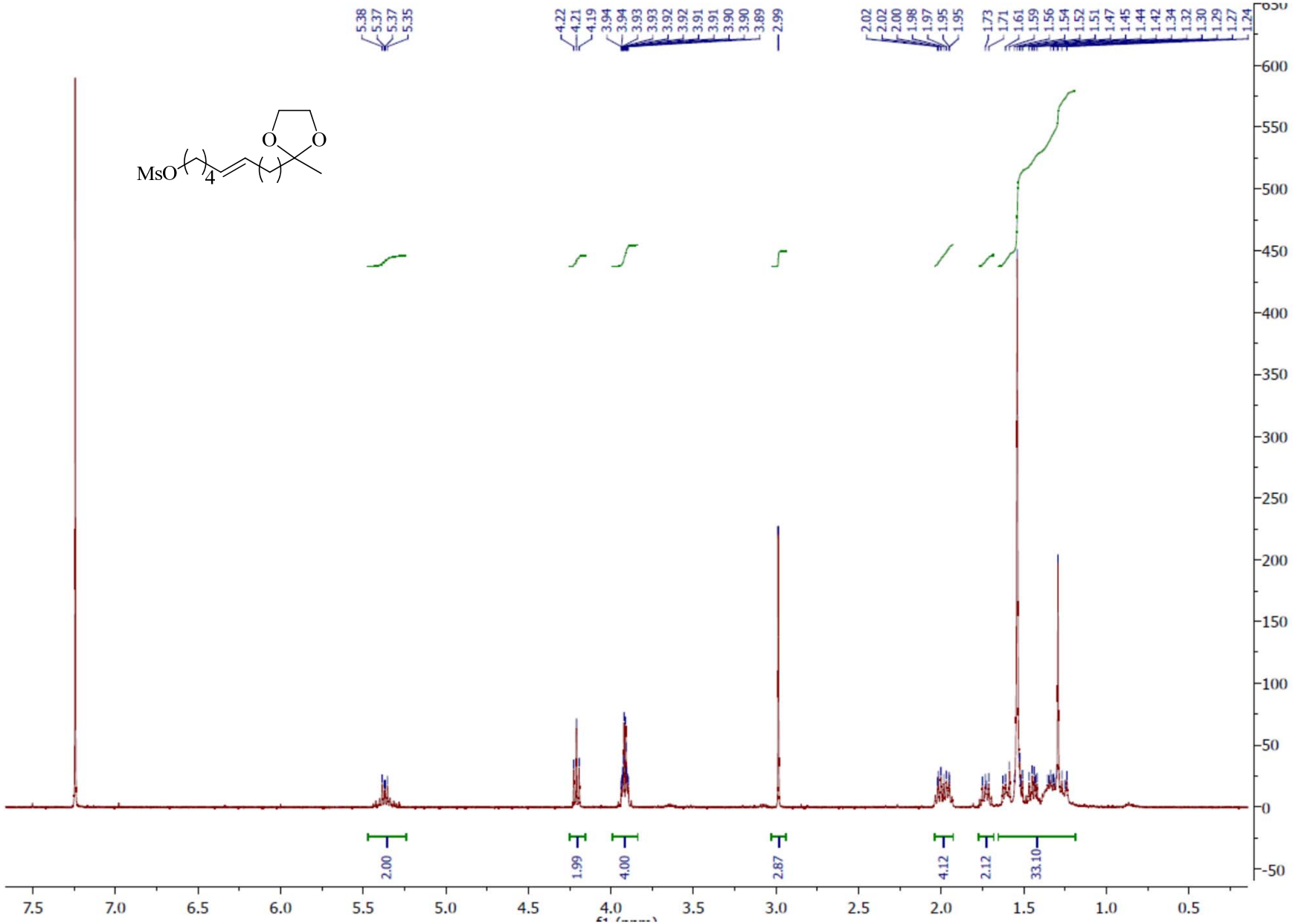
^{1}H-NMR spectrum of 4-(2-methyl-1,3-dioxolan-2-yl)butyl methanesulfonate (24) (400 MHz, $CDCl_3$)



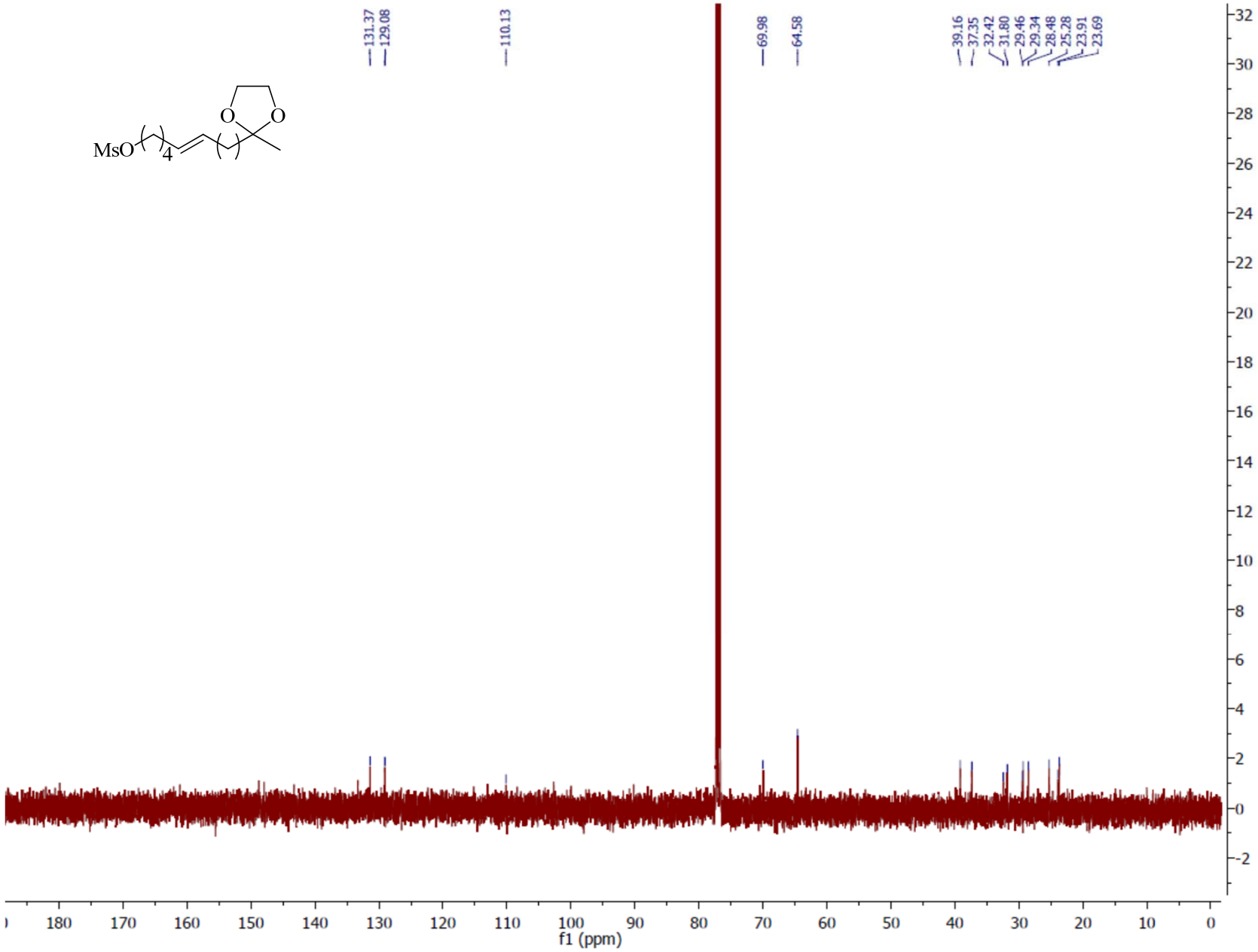
^{1}H-NMR spectrum of 2-(4-bromobutyl)-2-methyl-1,3-dioxolane (25) (400 MHz, $CDCl_3$)



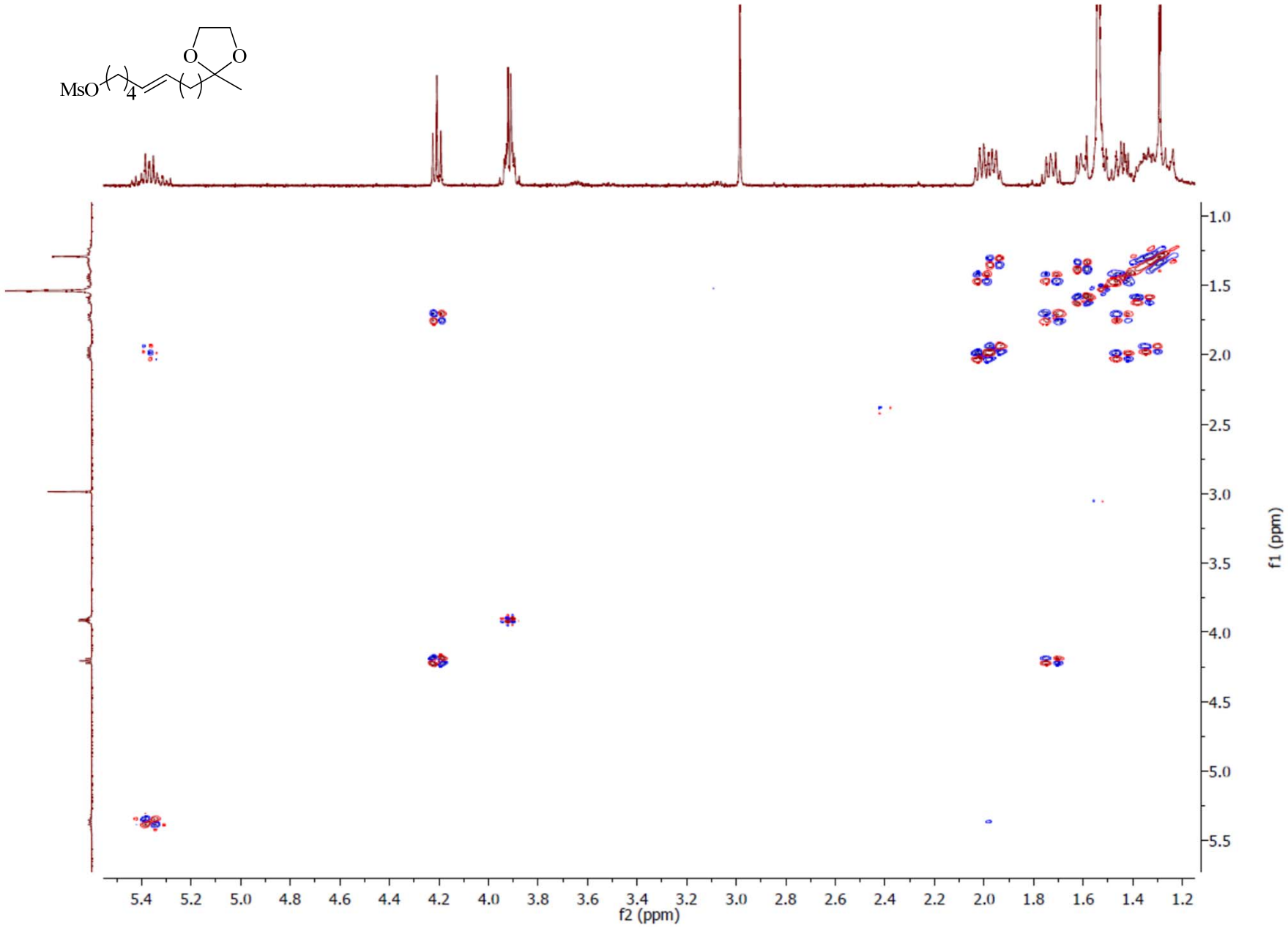
^{1}H-NMR spectrum of (*E*)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-yl methanesulfonate (26) (400 MHz, $CDCl_3$)



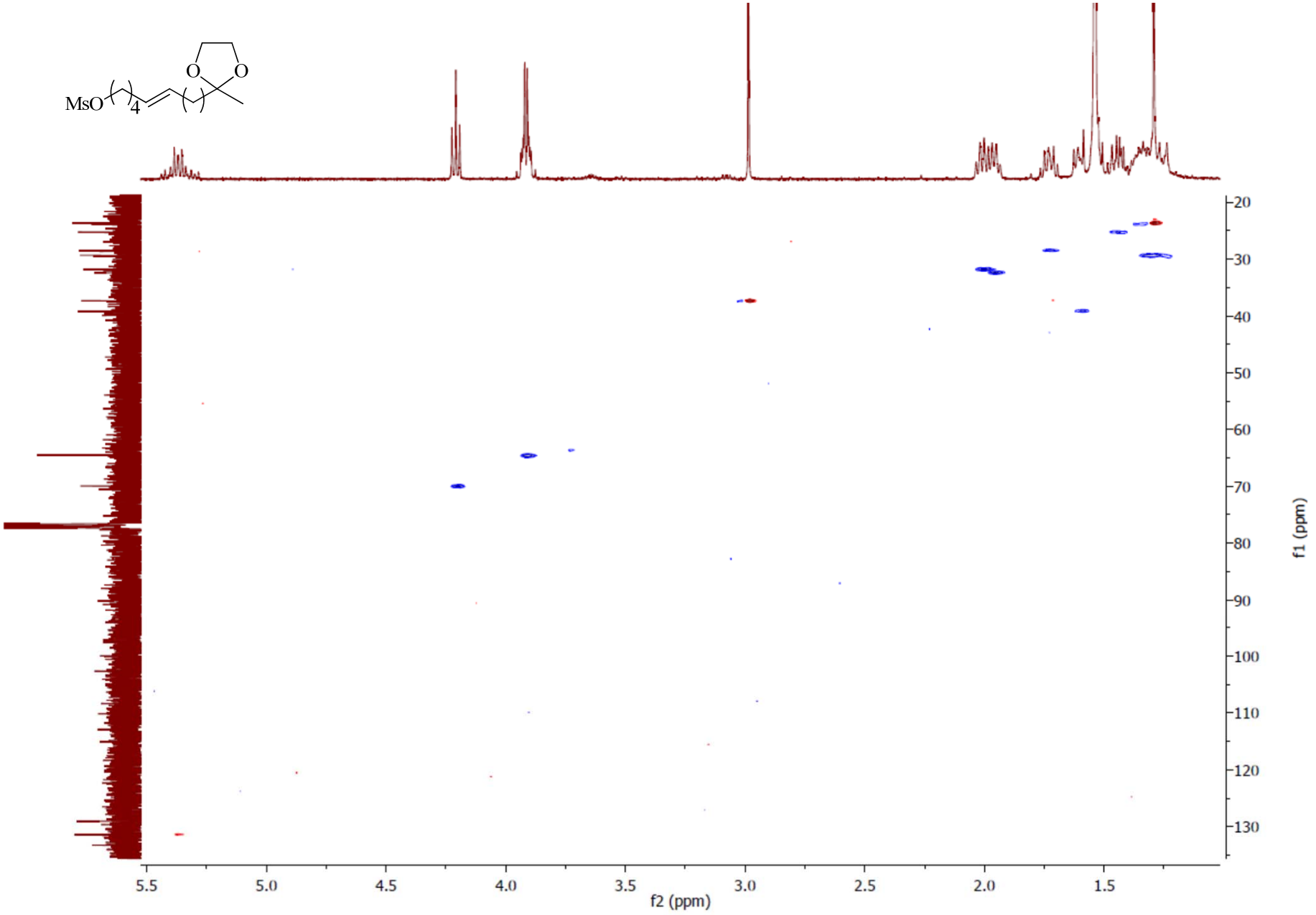
^{13}C-NMR spectrum of (*E*)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-yl methanesulfonate (26) (101 MHz, $CDCl_3$)



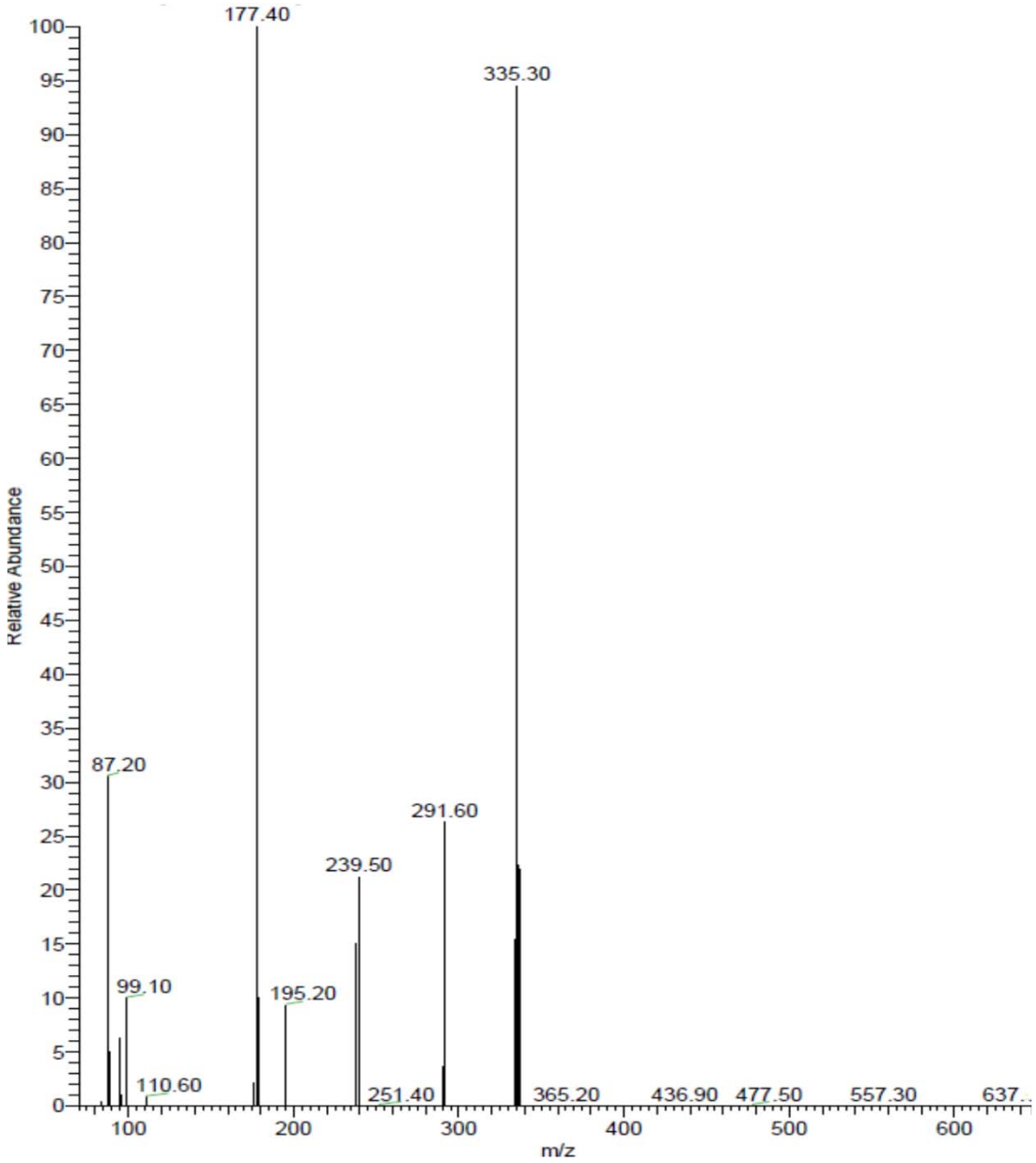
*g*DQCOSY spectrum of (*E*)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-yl methanesulfonate (26) (400 MHz, $CDCl_3$)

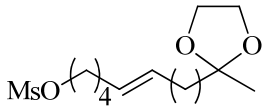


*g*HSQC spectrum of (*E*)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-yl methanesulfonate (26) (400 MHz,101 MHz; $CDCl_3$)



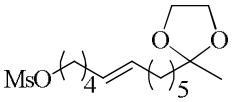
GC-MS chromatogram and fragmentations of (*E*)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-yl methanesulfonate (26)





Chemical Formula: $C_{16}H_{30}O_5S$
Exact Mass: 334.18
Molecular Weight: 334.47

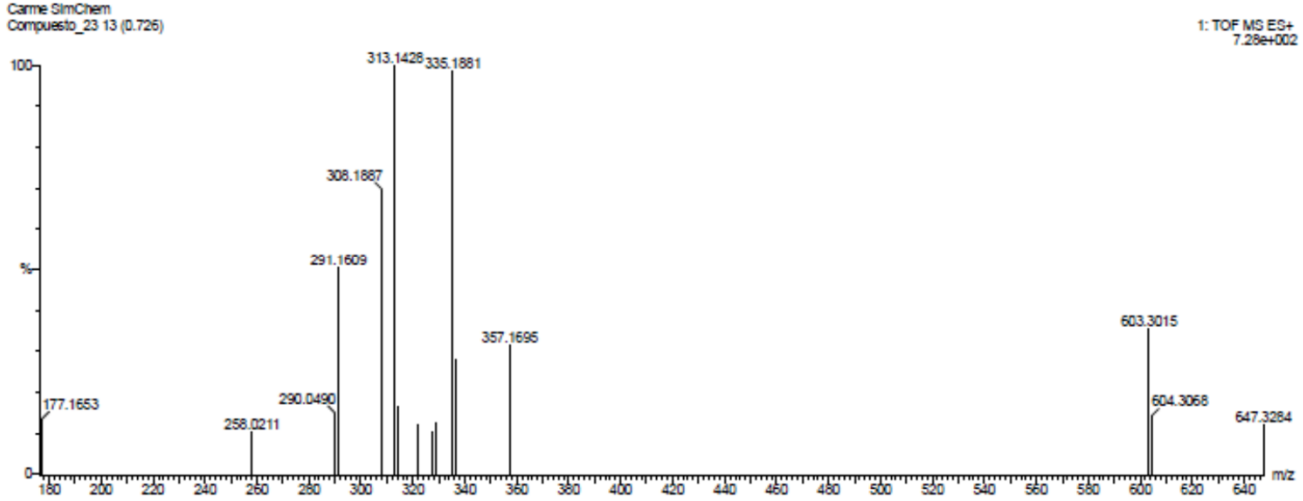
Exact Mass chromatogram of (E)-11-(2-methyl-1,3-dioxolan-2-yl)undec-5-en-1-yl methanesulfonate (26)



Chemical Formula: $C_{16}H_{30}O_5S$
Exact Mass: 334.18

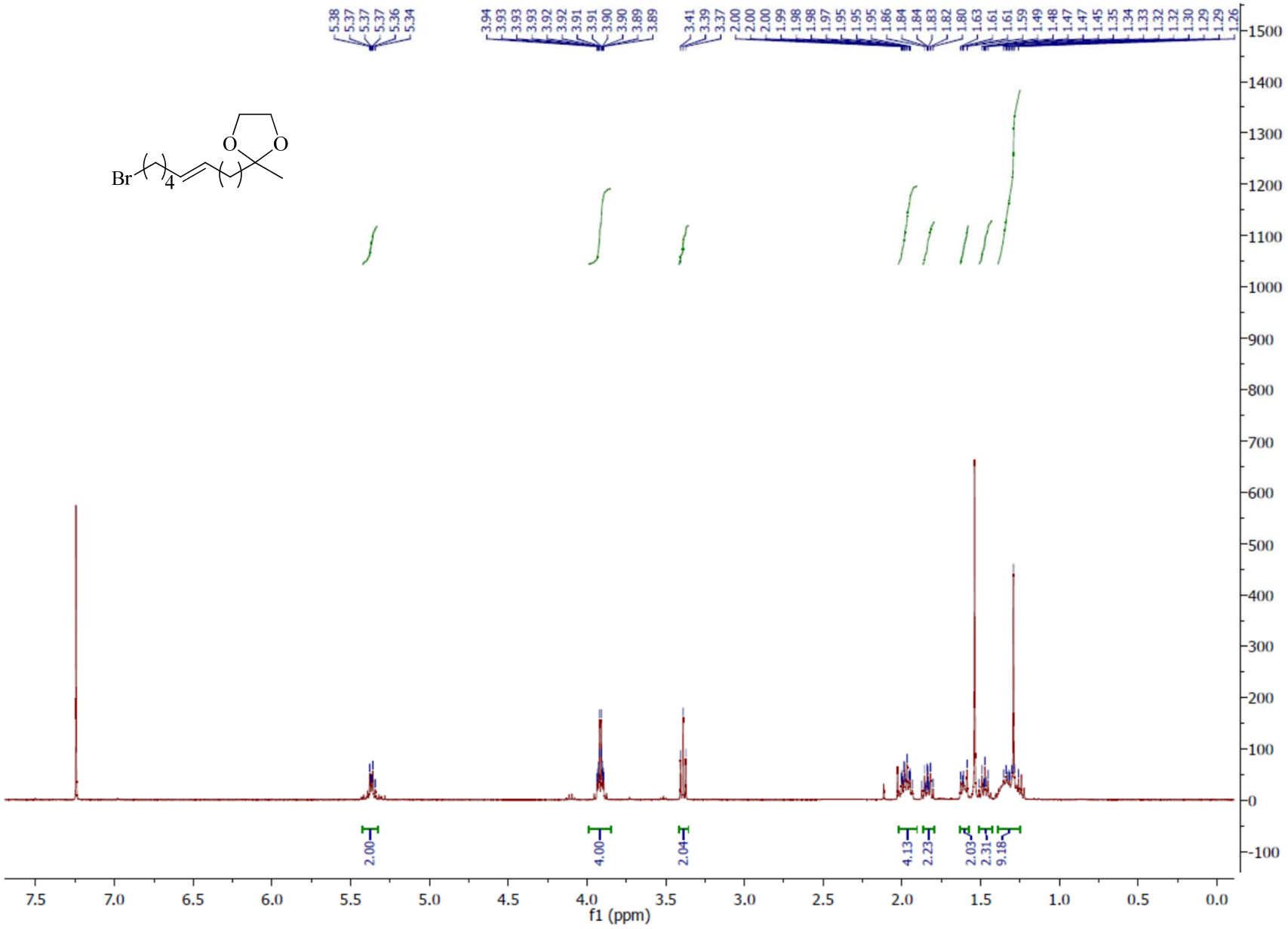
Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 15-20 H: 30-40 O: 5-6 S: 0-1
Carme SimChem
Compuesto_23 13 (0.726)

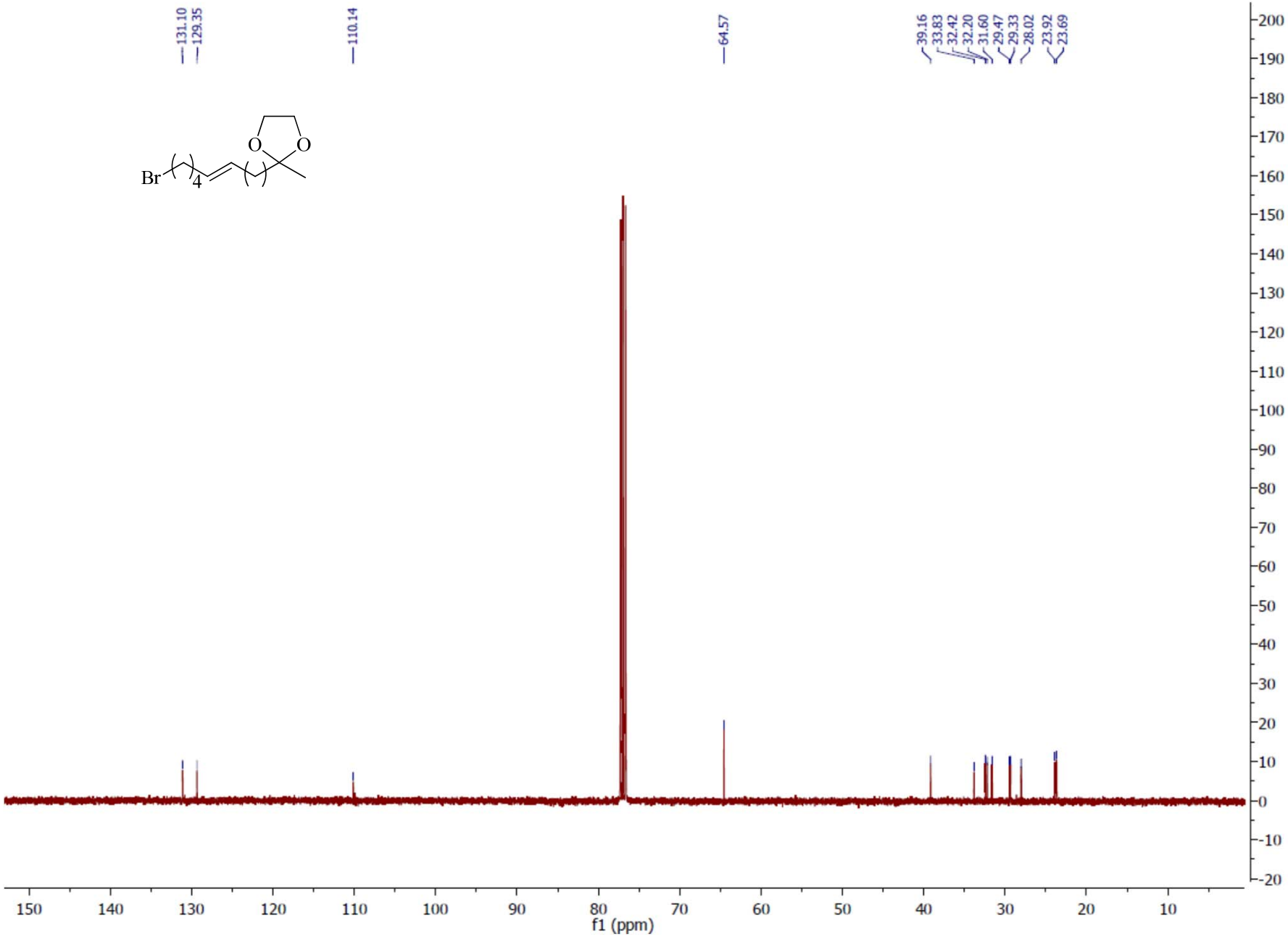


Minimum:		5.0	10.0	-1.5			
Maximum:				50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
335.1881	335.1892	-1.1	-3.3	1.5	24.5	0.0	C16 H31 O5 S

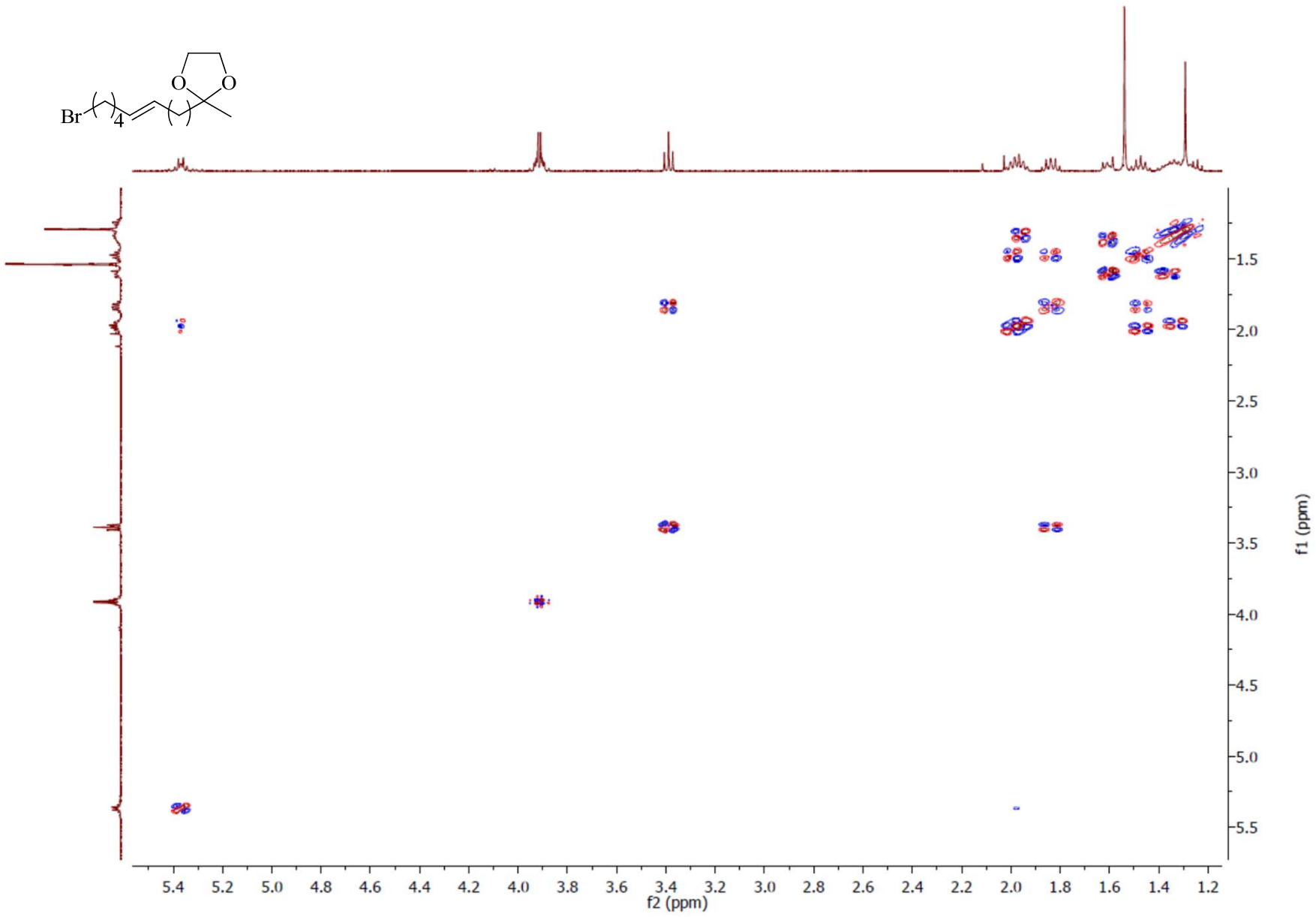
^{1}H-NMR spectrum of (*E*)-2-(11-bromoundec-6-en-1-yl)-2-methyl-1,3-dioxolane (27) (400 MHz, $CDCl_3$)



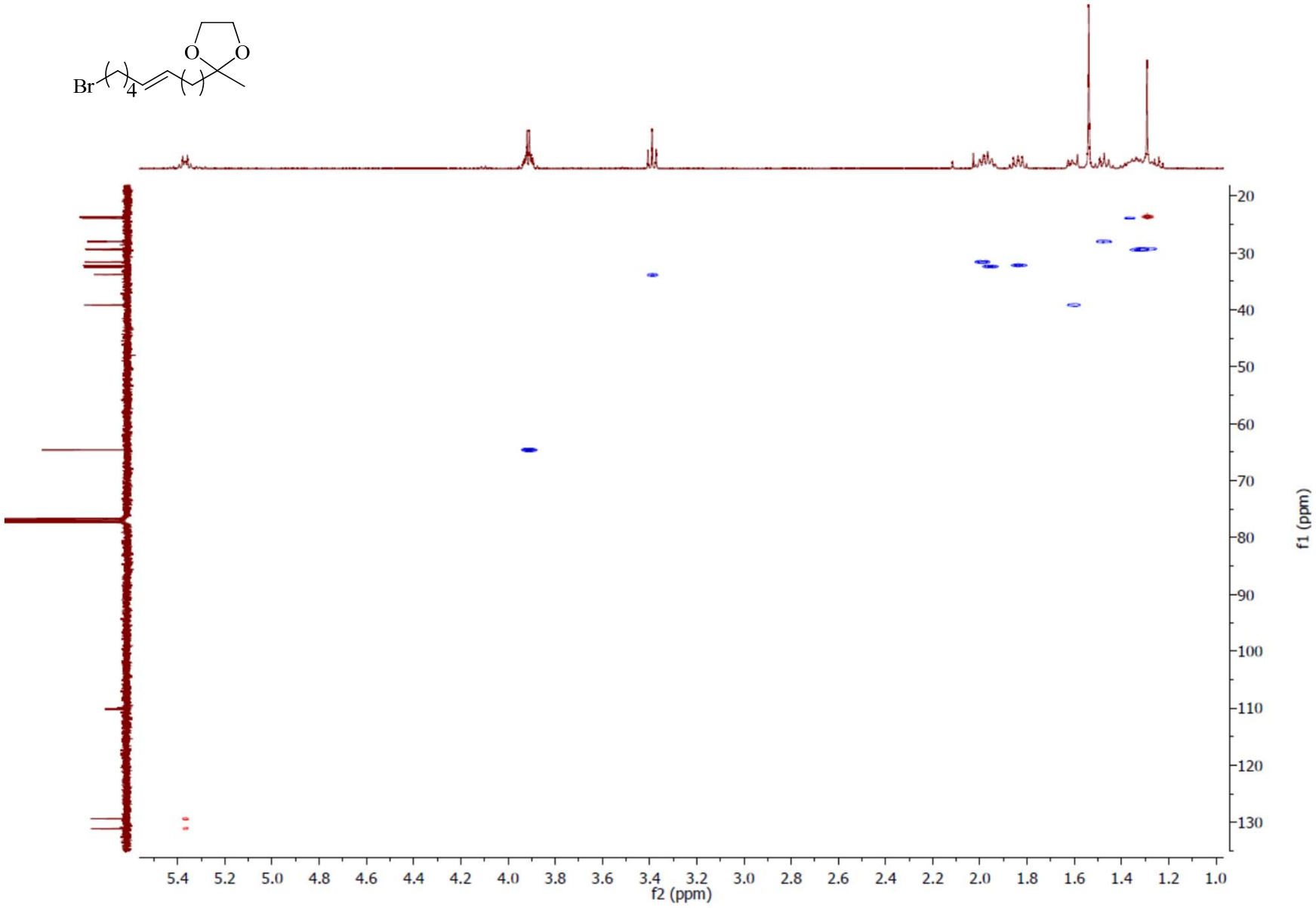
^{13}C-NMR spectrum of (*E*)-2-(11-bromoundec-6-en-1-yl)-2-methyl-1,3-dioxolane (27) (101 MHz, $CDCl_3$)



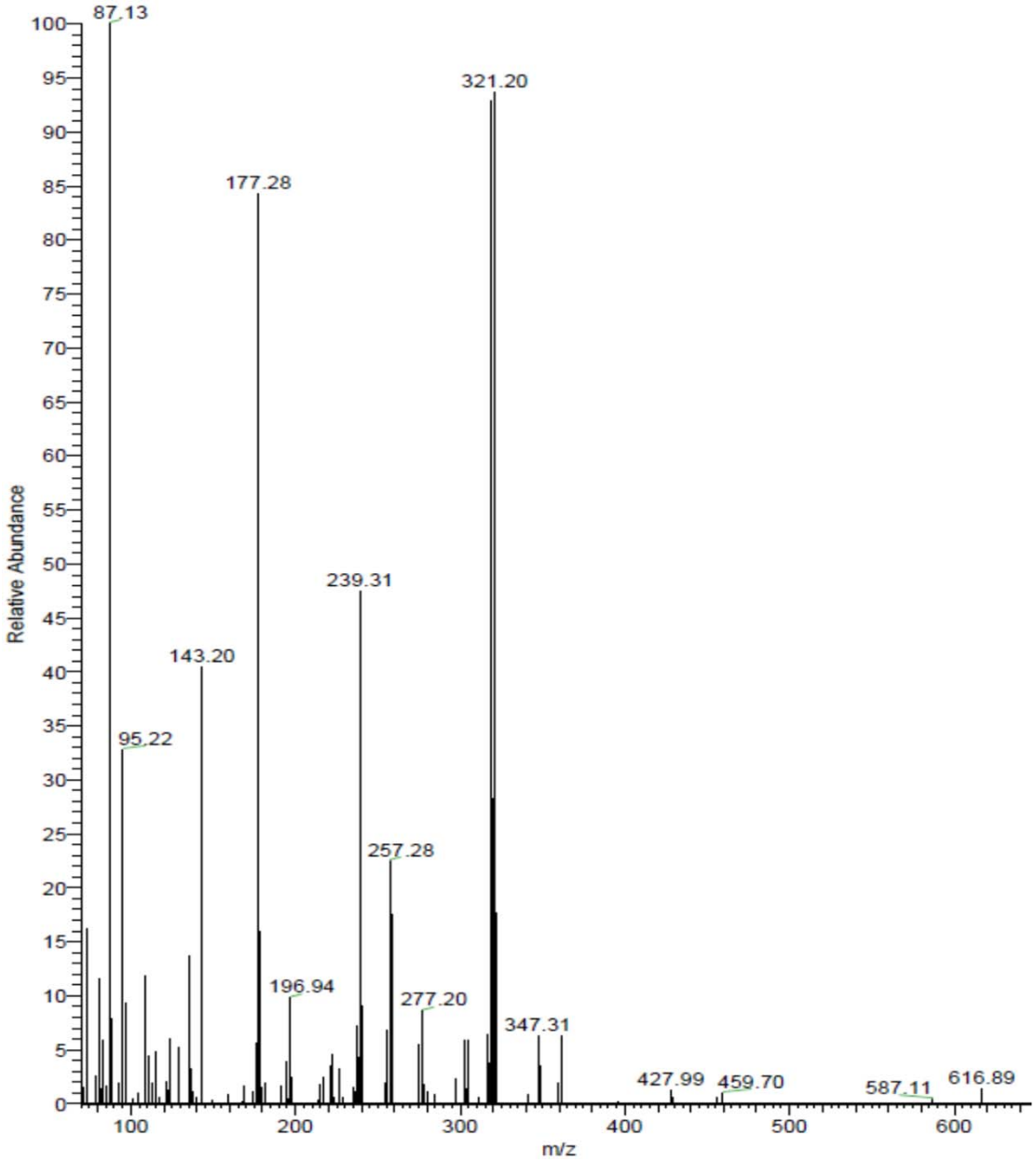
*g*DQCOSY spectrum of (*E*)-2-(11-bromoundec-6-en-1-yl)-2-methyl-1,3-dioxolane (27) (400 MHz, $CDCl_3$)

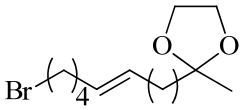


*g*HSQC spectrum of (*E*)-2-(11-bromoundec-6-en-1-yl)-2-methyl-1,3-dioxolane (27) (400 MHz,101 MHz; $CDCl_3$)



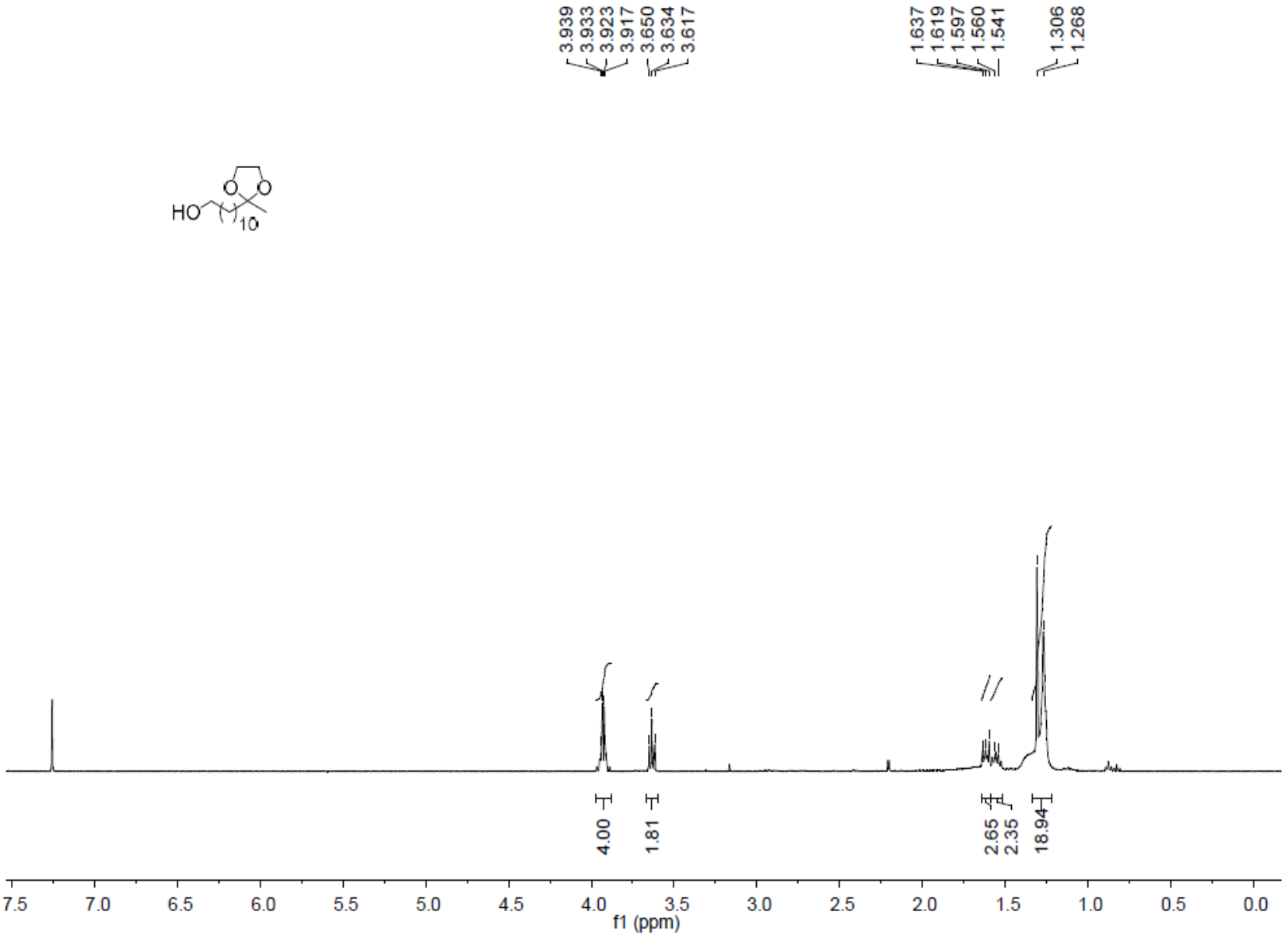
GC-MS chromatogram and fragmentations of (*E*)-2-(11-bromoundec-6-en-1-yl)-2-methyl-1,3-dioxolane (27)



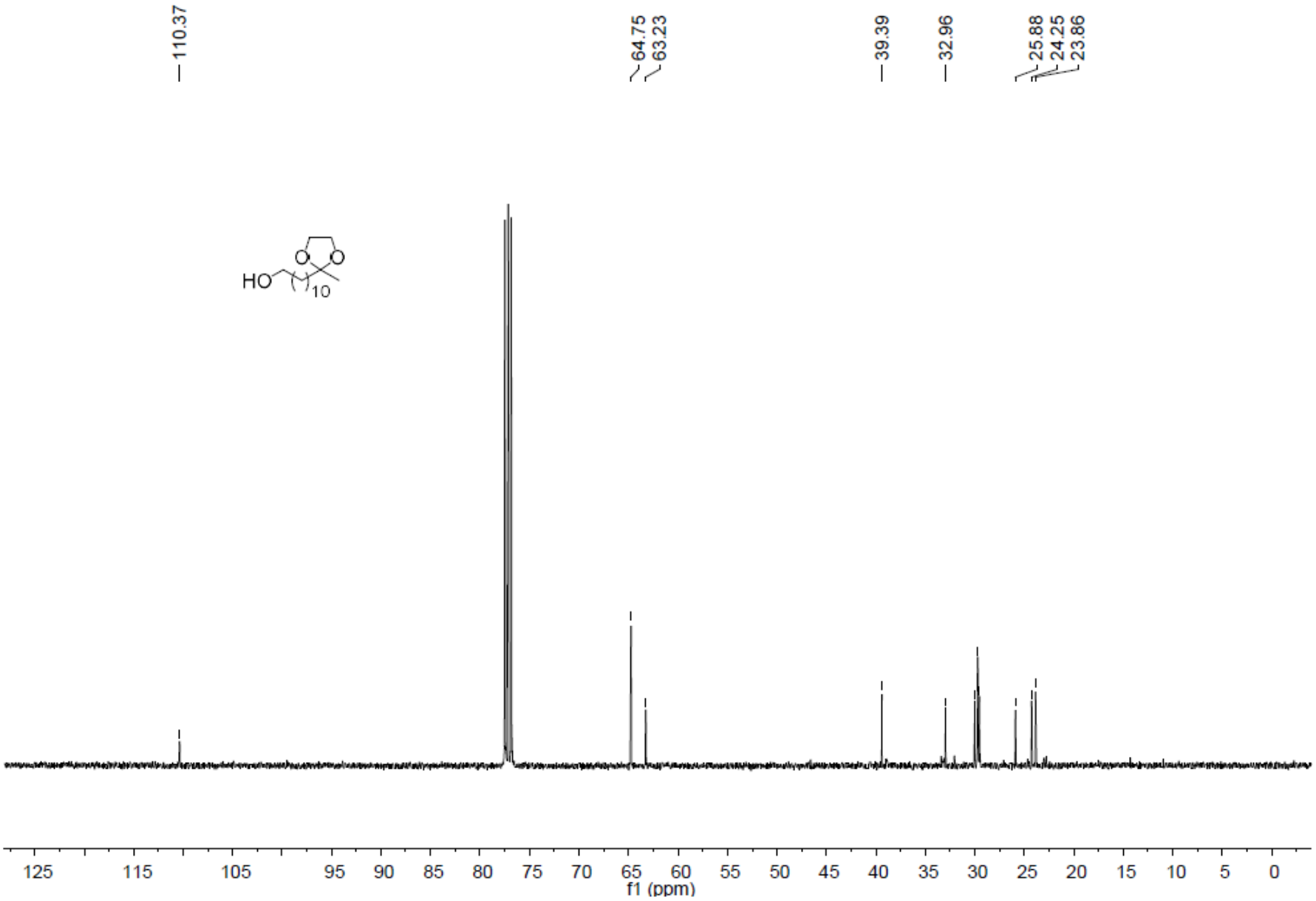


Chemical Formula: $C_{15}H_{27}BrO_2$
Exact Mass: 318.12
Molecular Weight: 319.28

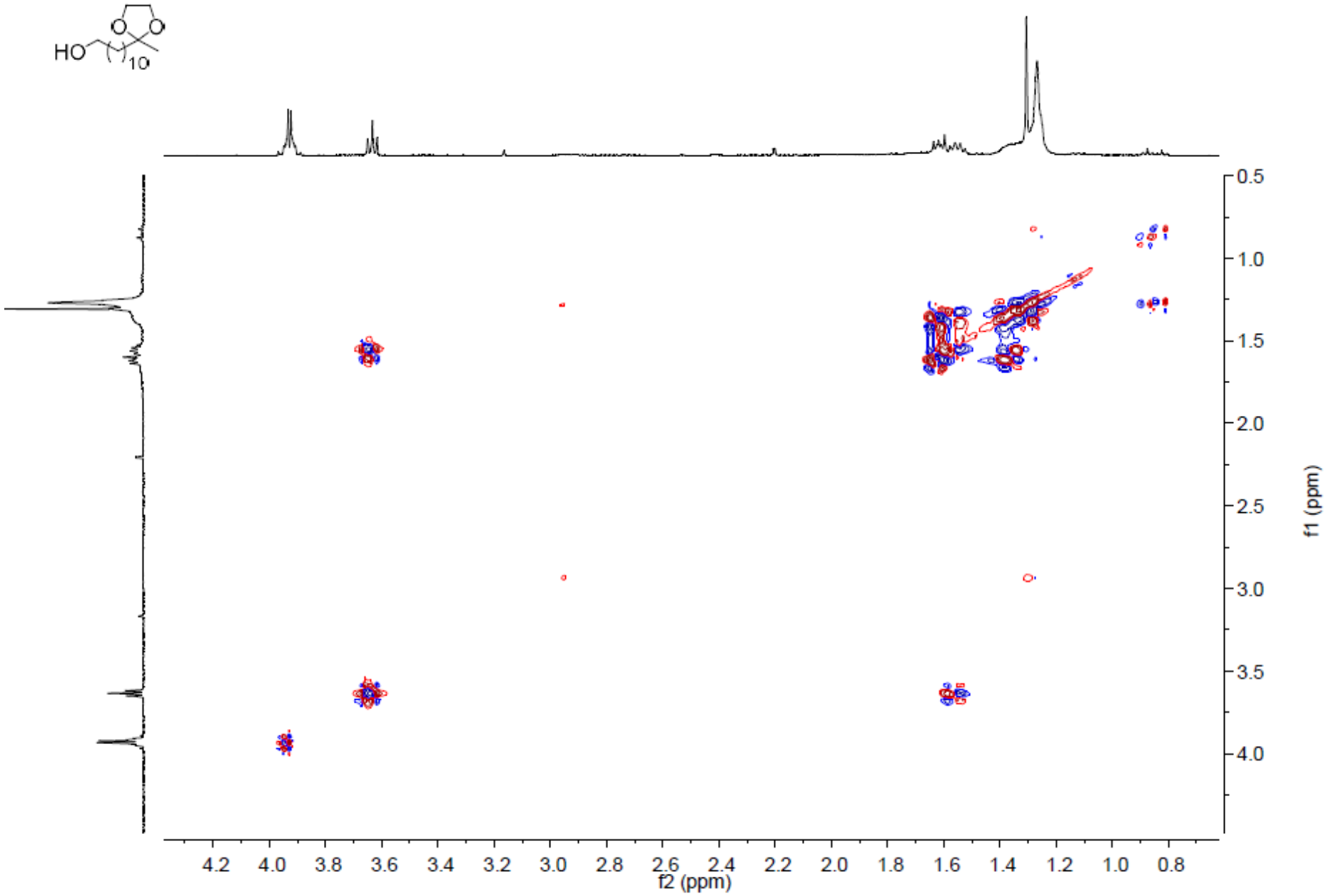
^{1}H-NMR spectrum of 11-(2-methyl-1,3-dioxolan-2-yl)undecan-1-ol (28) (400 MHz, $CDCl_3$)



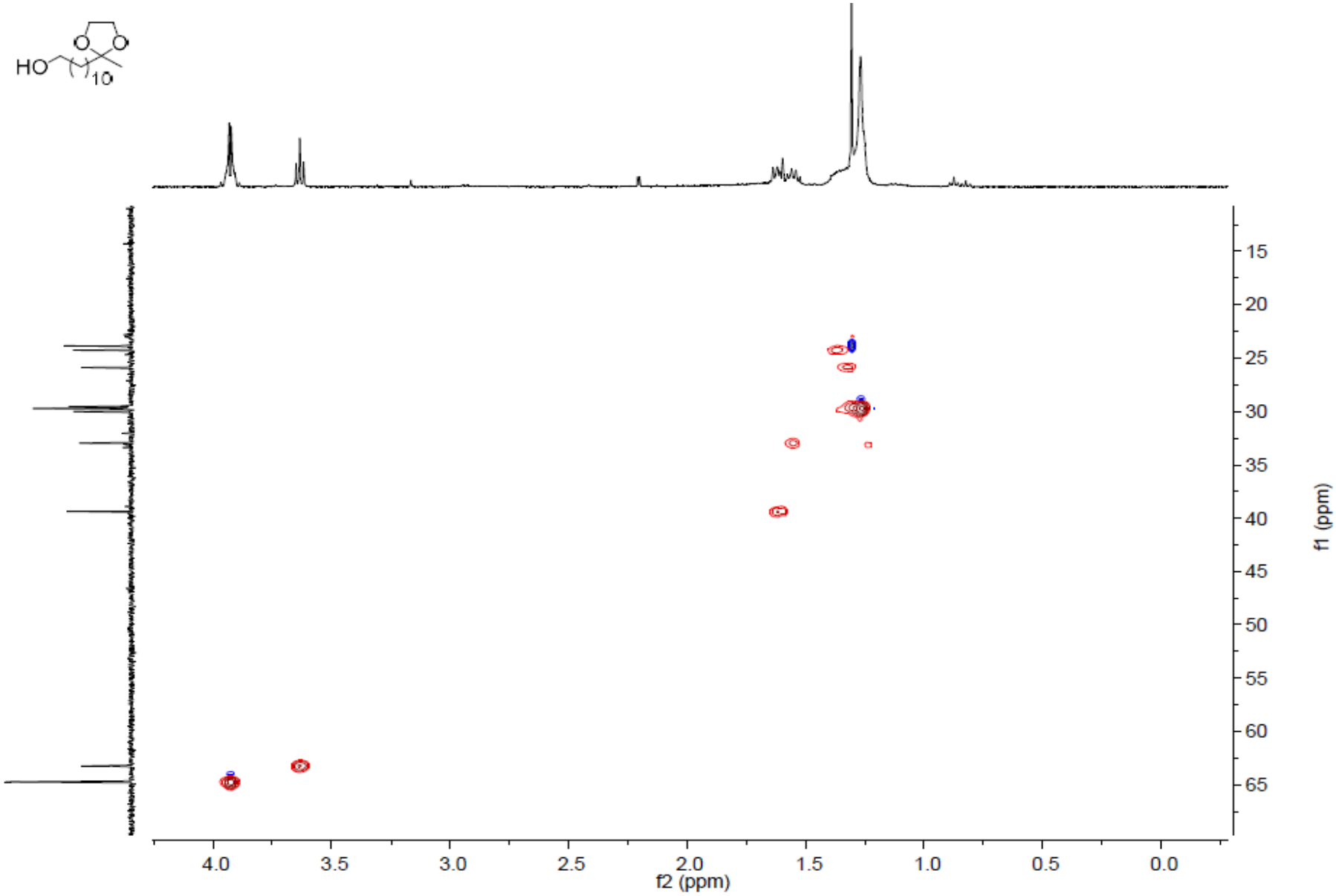
^{13}C-NMR spectrum of 11-(2-methyl-1,3-dioxolan-2-yl)undecan-1-ol (28) (101 MHz, $CDCl_3$)



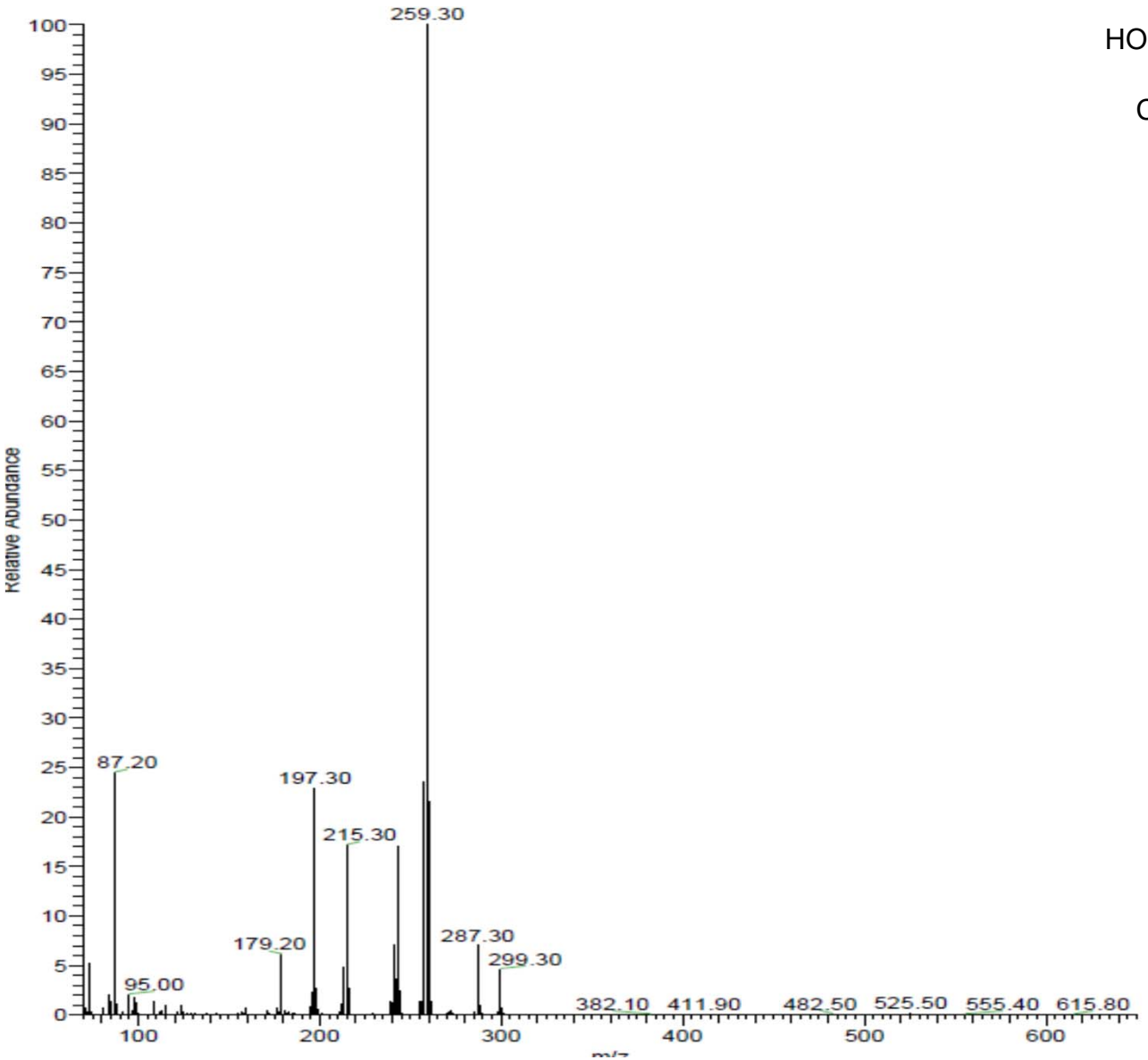
*g*DQCOSY of 11-(2-methyl-1,3-dioxolan-2-yl)undecan-1-ol (28) (400 MHz, $CDCl_3$)

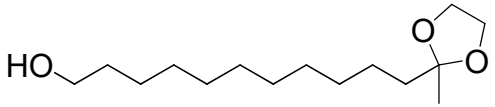


*g*HSQC spectrum of 11-(2-methyl-1,3-dioxolan-2-yl)undecan-1-ol (28) (400 MHz,101 MHz; $CDCl_3$)



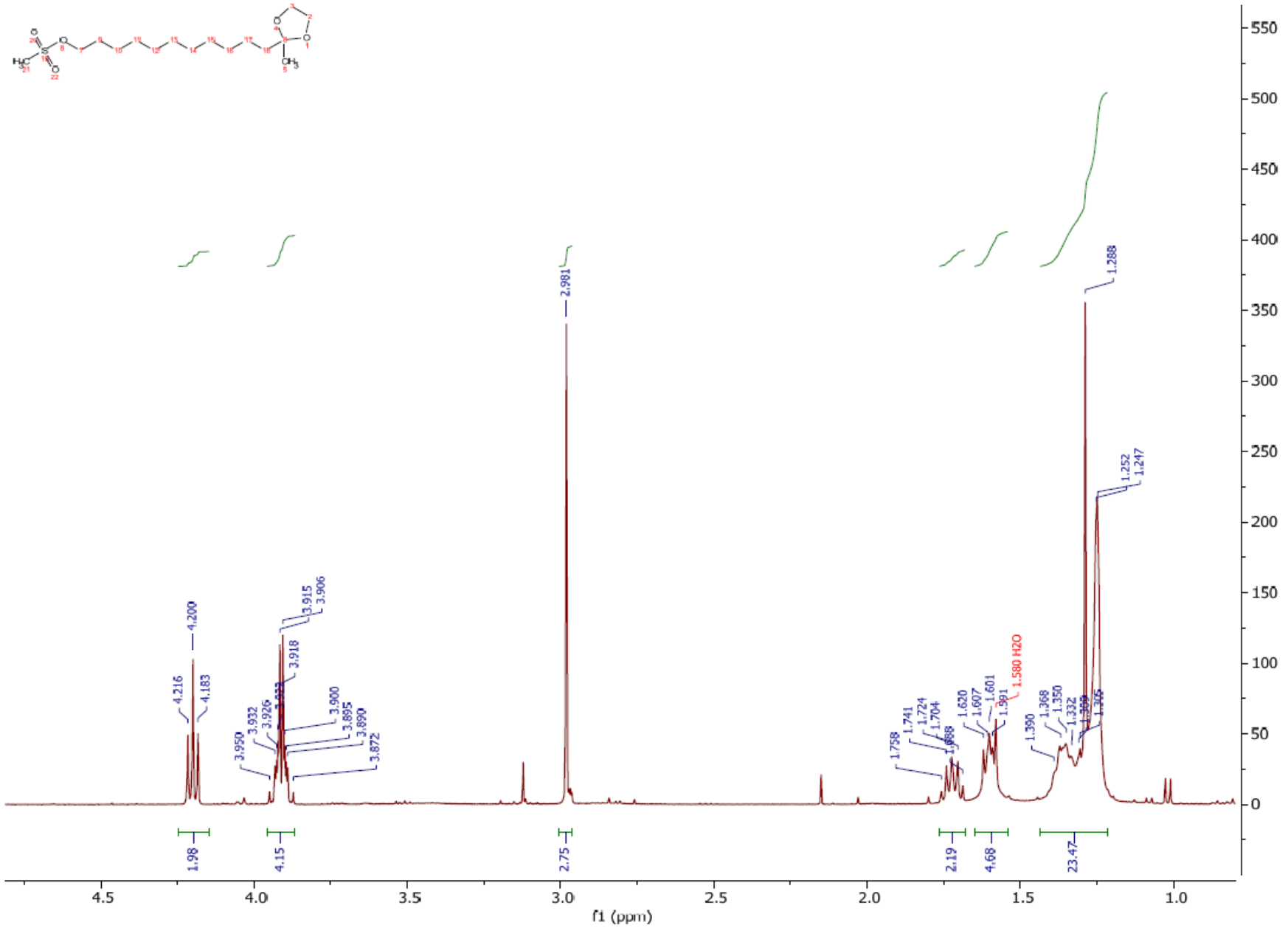
GC-MS chromatogram and 11-(2-methyl-1,3-dioxolan-2-yl)undecan-1-ol (28)



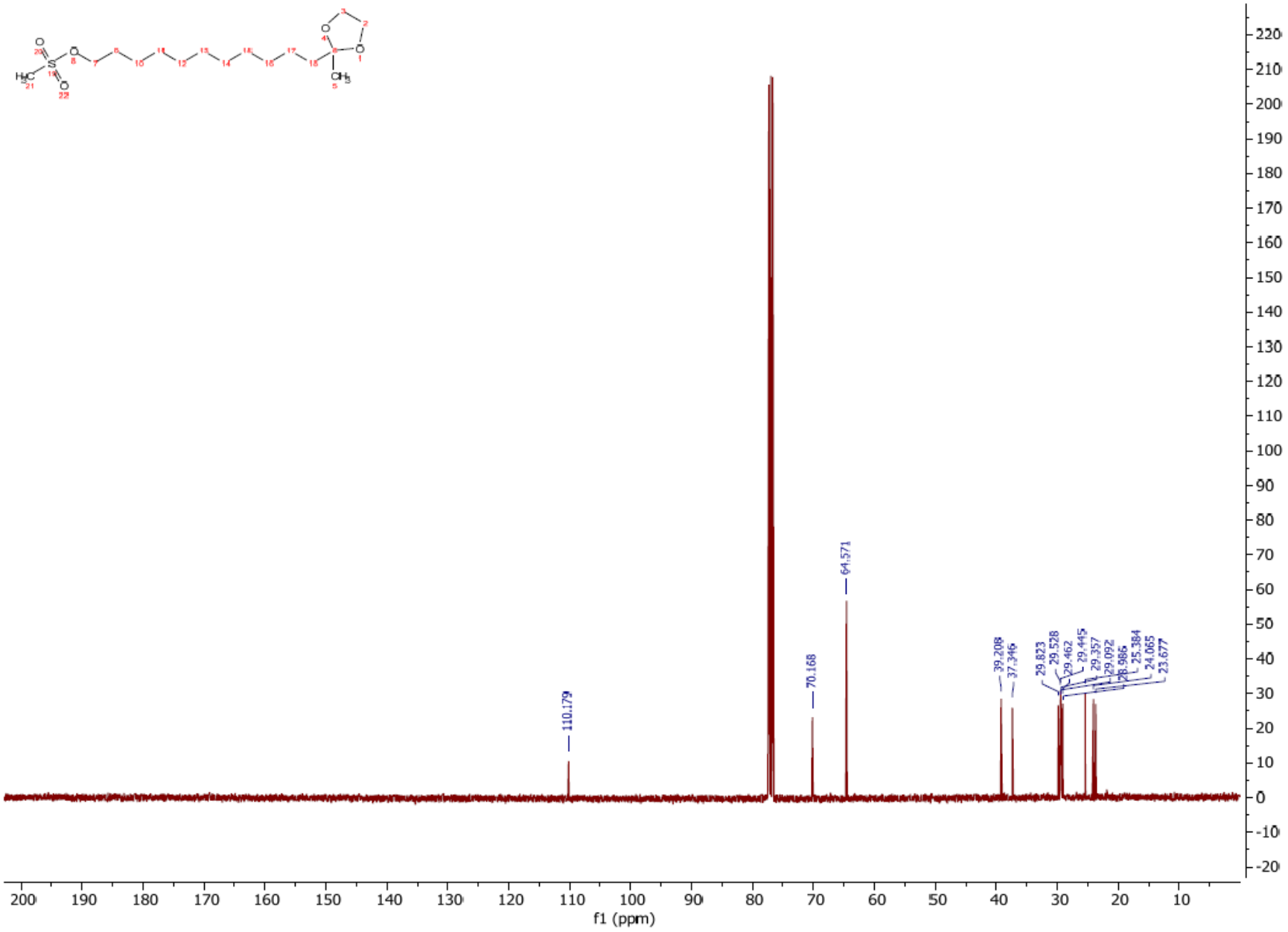


Chemical Formula: $C_{15}H_{30}O_3$
Exact Mass: 258.22
Molecular Weight: 258.40

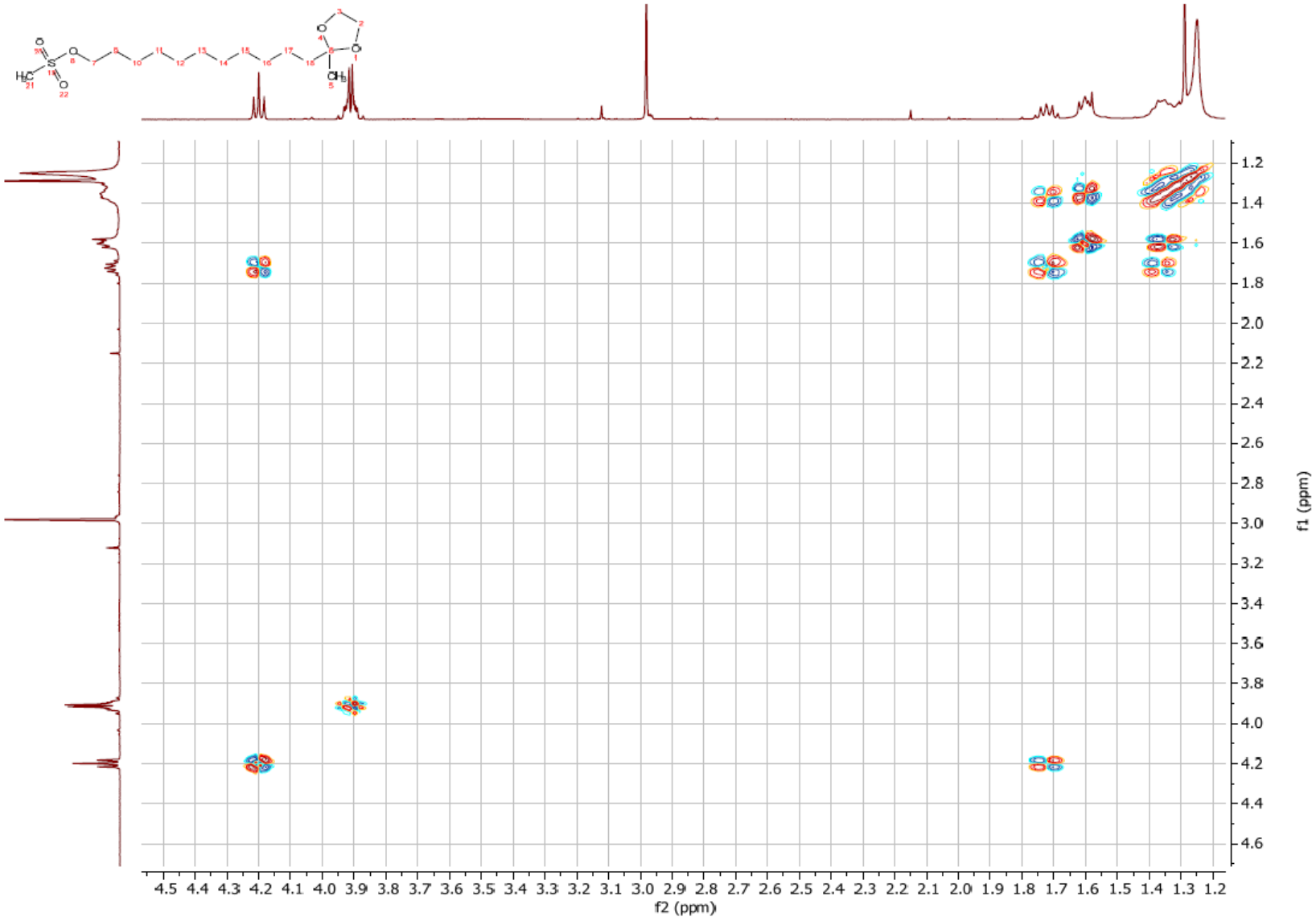
^{1}H-NMR spectrum of 11-(2-methyl-1,3-dioxolan-2-yl)undecyl methanesulfonate (29) (400 MHz, $CDCl_3$)



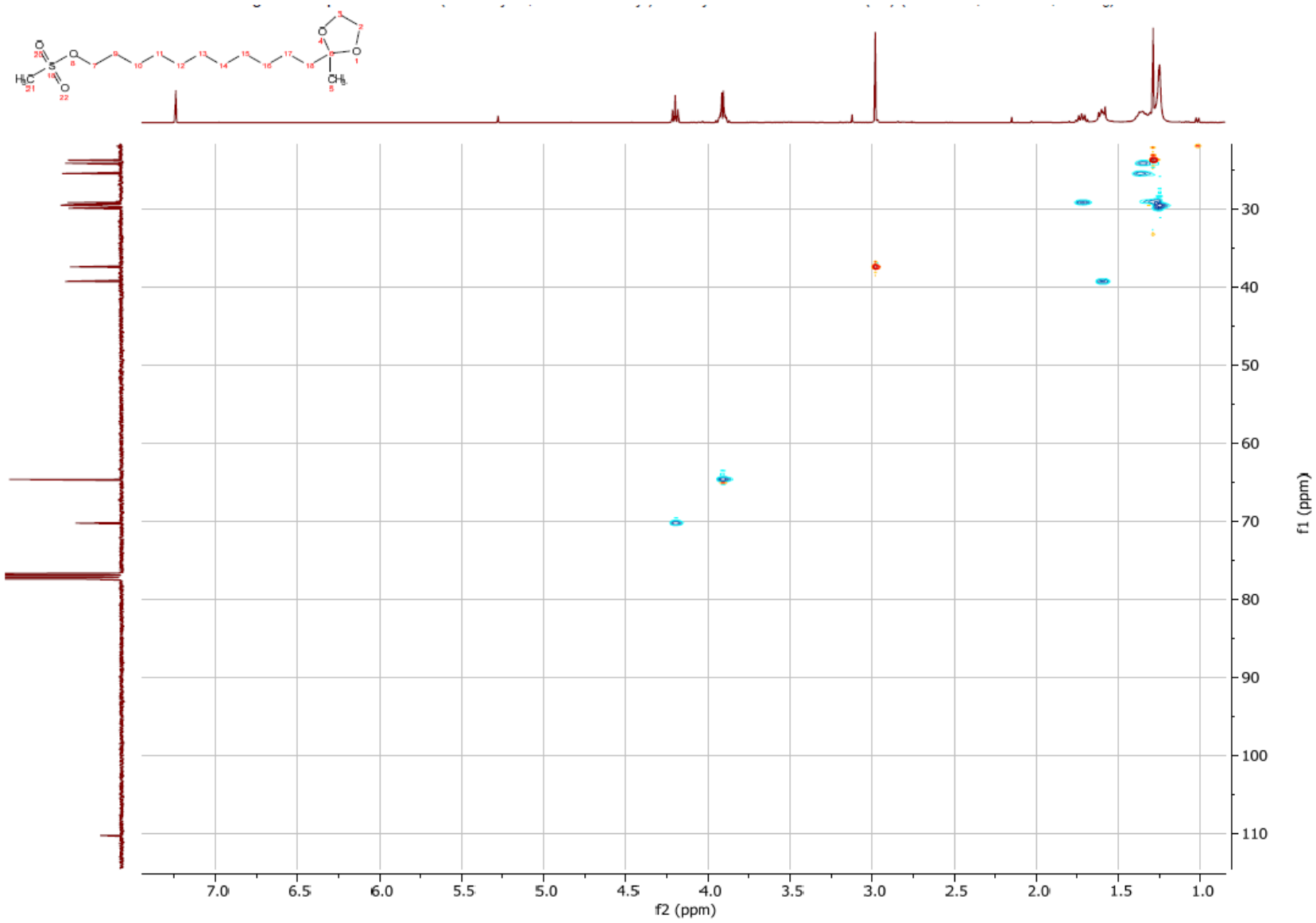
^{13}C-NMR spectrum of 11-(2-methyl-1,3-dioxolan-2-yl)undecyl methanesulfonate (29) (101 MHz, $CDCl_3$)



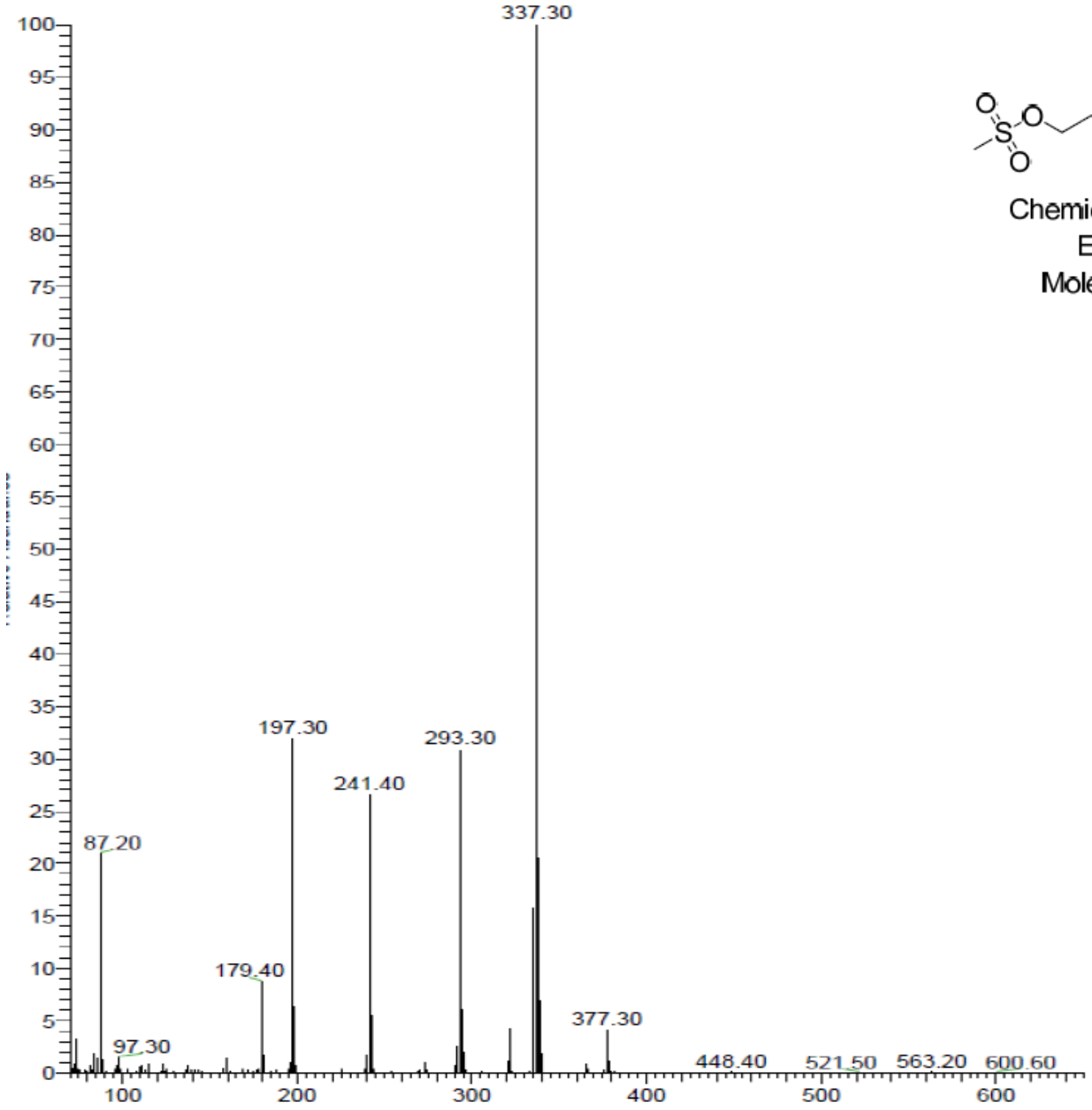
*g*DQCOSY spectrum of 11-(2-methyl-1,3-dioxolan-2-yl)undecyl methanesulfonate (29) (400 MHz, $CDCl_3$)

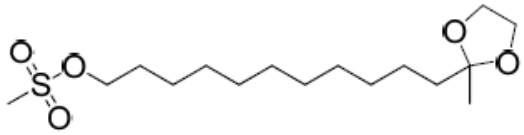


*g*HSQC spectrum of 11-(2-methyl-1,3-dioxolan-2-yl)undecyl methanesulfonate (29) (400 MHz,101 MHz; $CDCl_3$)



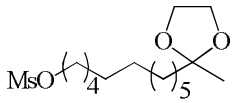
GC-MS chromatogram and fragmentations of 11-(2-methyl-1,3-dioxolan-2-yl)undecyl methanesulfonate (29)





Chemical Formula: $C_{16}H_{32}O_5S$
Exact Mass: 336.20
Molecular Weight: 336.49

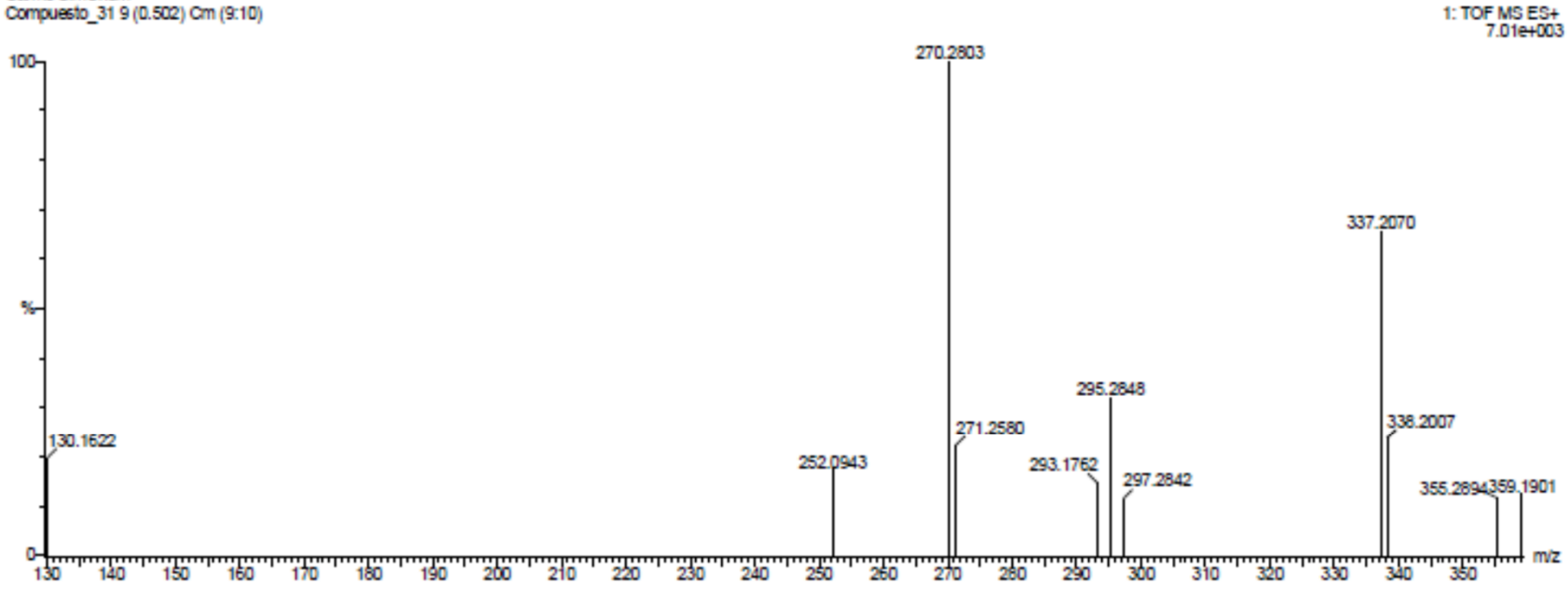
Exact Mass chromatogram of 11-(2-methyl-1,3-dioxolan-2-yl)undecyl methanesulfonate (29)



Chemical Formula: $C_{16}H_{32}O_5S$
Exact Mass: 336.20

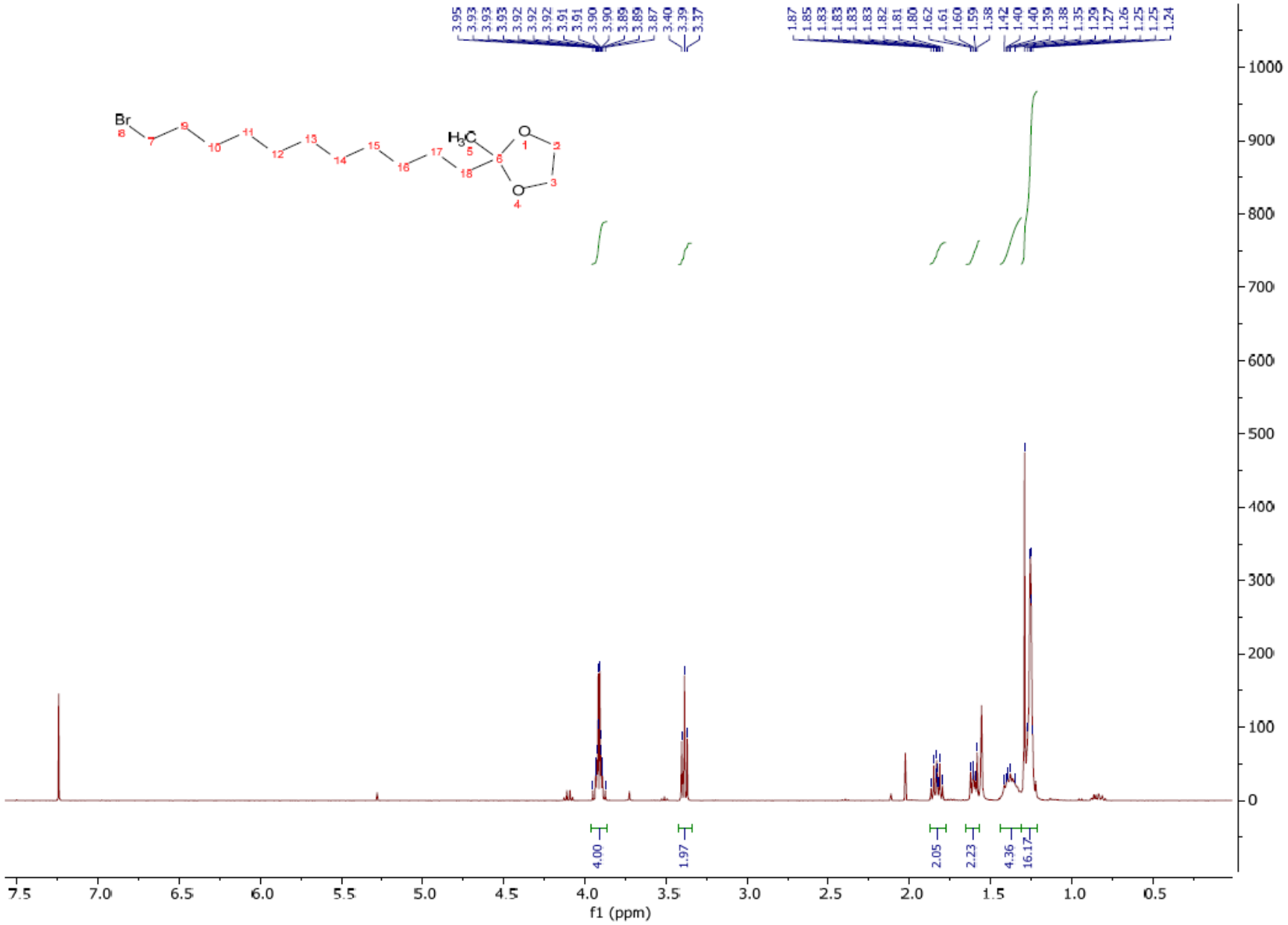
Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 15-20 H: 30-40 O: 5-6 S: 0-1
Carme SimChem
Compuesto_31 9 (0.502) Cm (9:10)

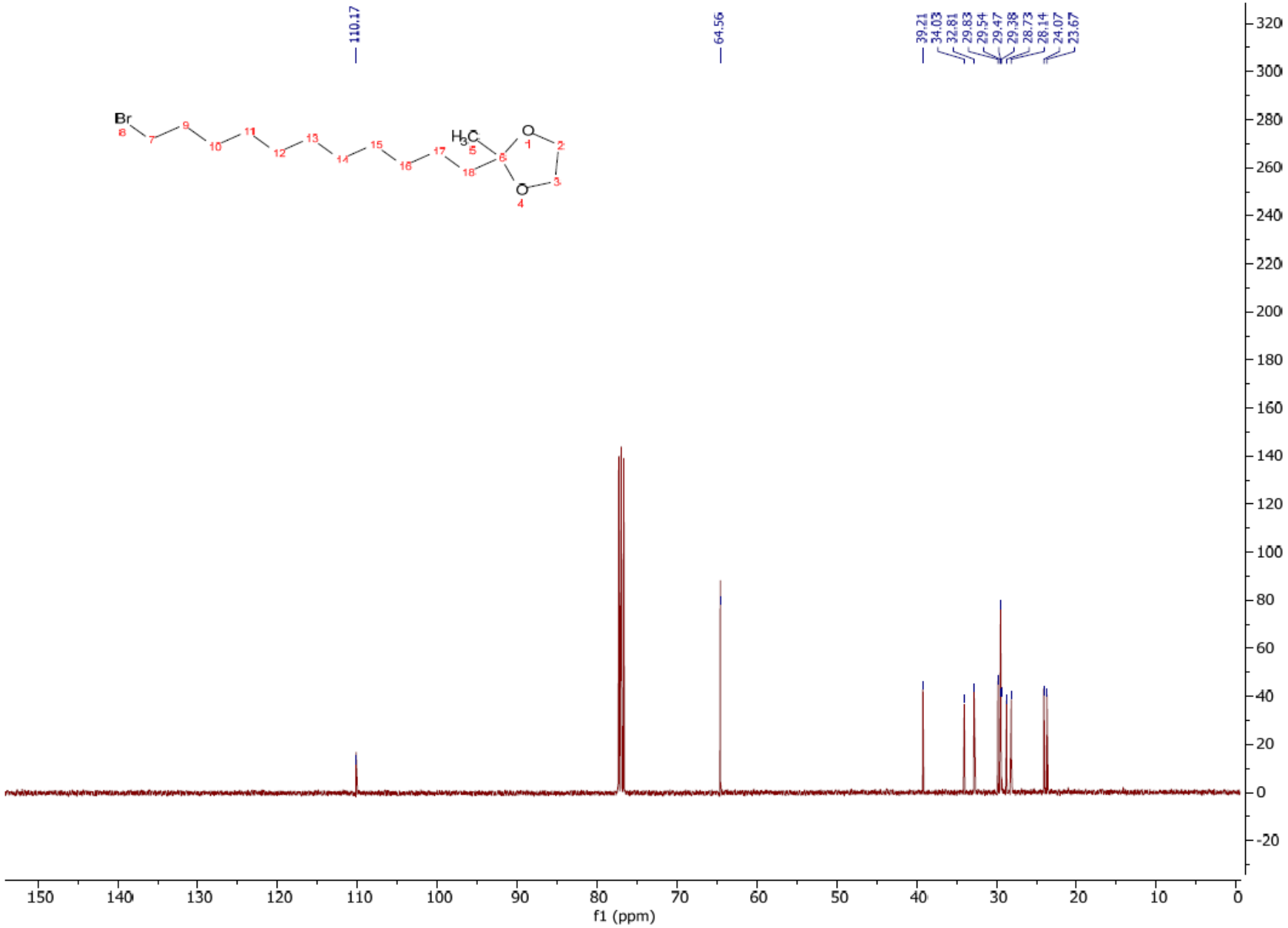


Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
337.2070	337.2049	2.1	6.2	0.5	31.8	0.0	C16 H33 O5 S

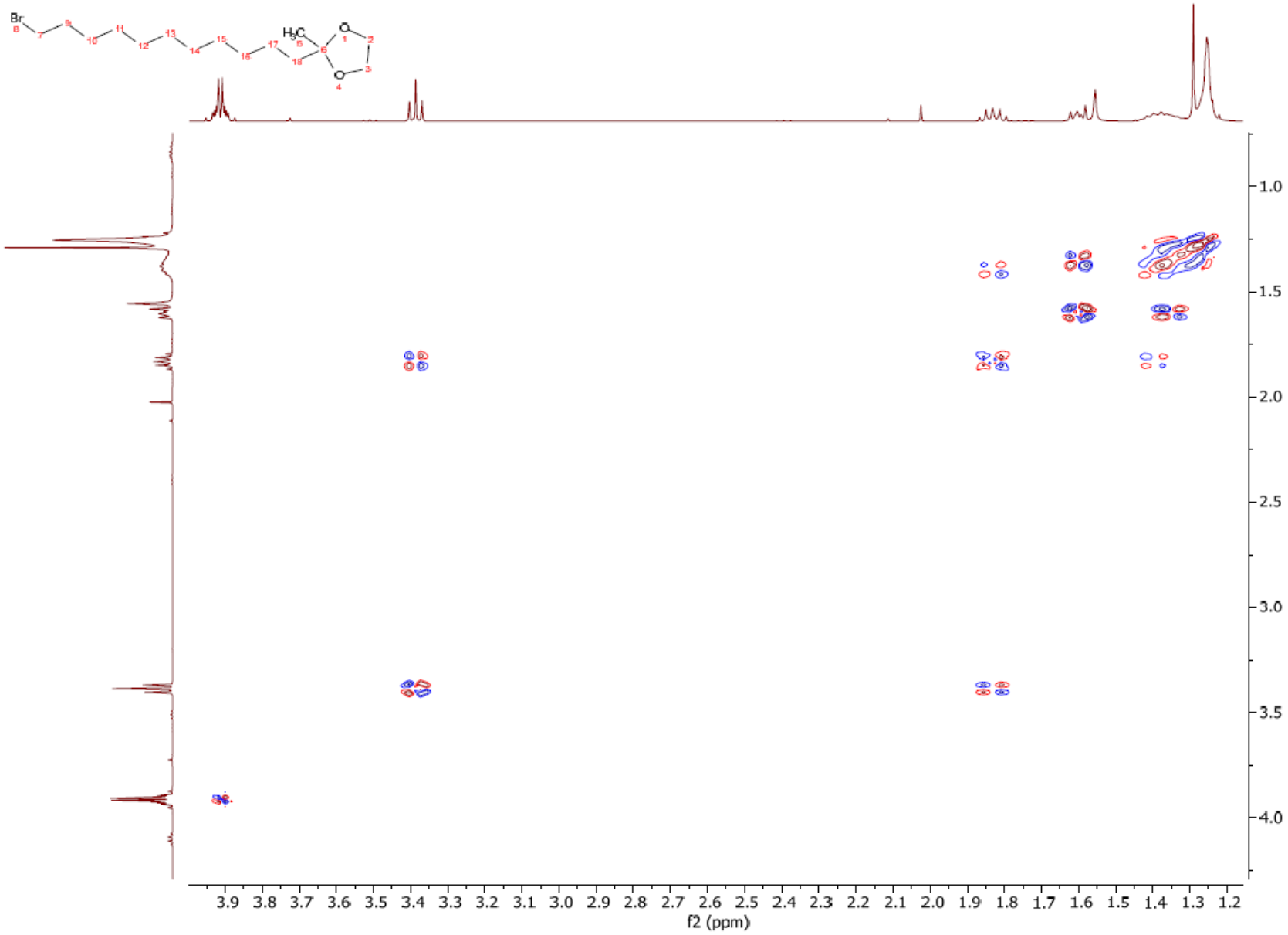
^{1}H-NMR spectrum of 2-(11-bromoundecyl)-2-methyl-1,3-dioxolane (30) (400 MHz, $CDCl_3$)



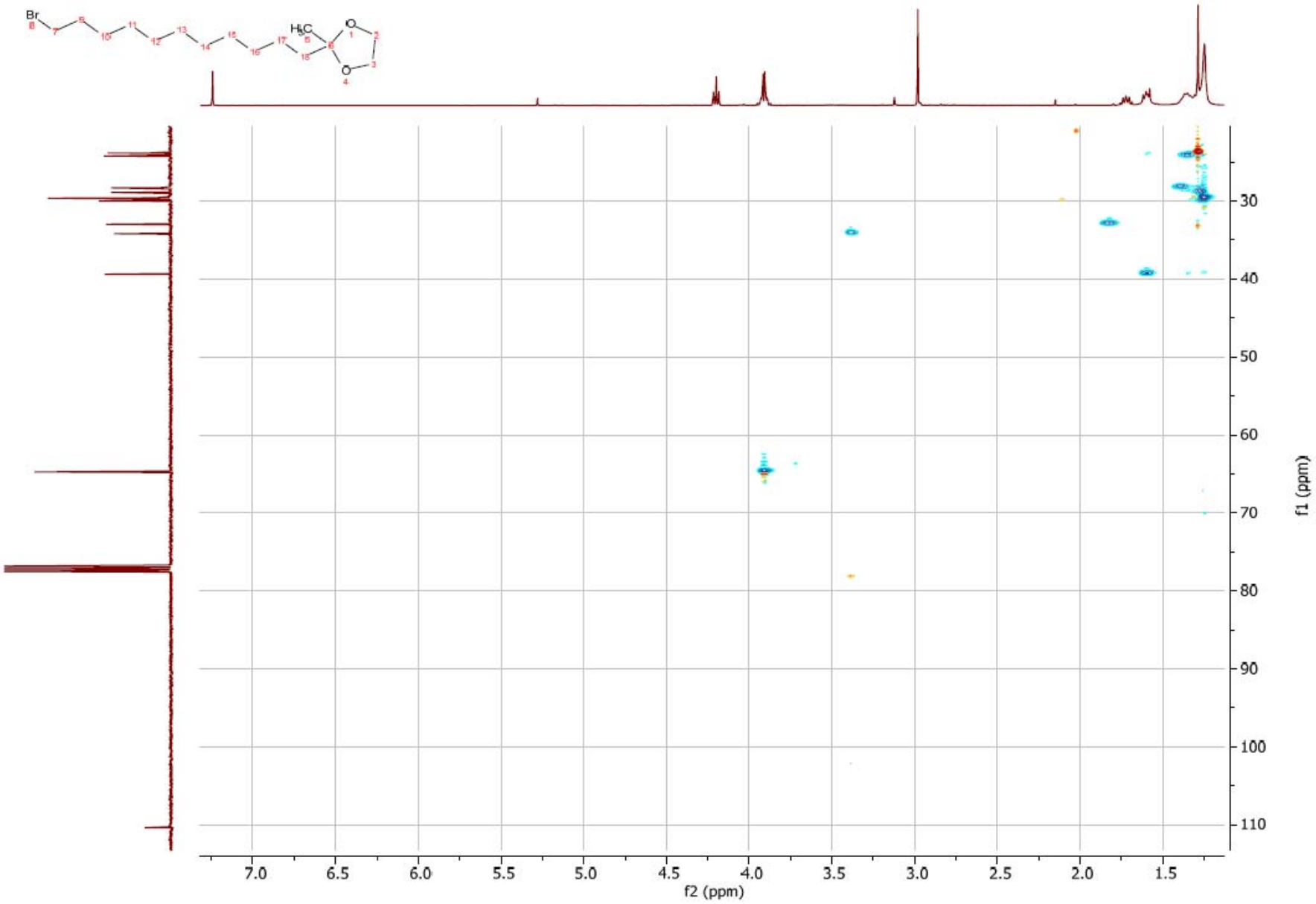
^{13}C-NMR spectrum of 2-(11-bromoundecyl)-2-methyl-1,3-dioxolane (30) (101 MHz, $CDCl_3$)



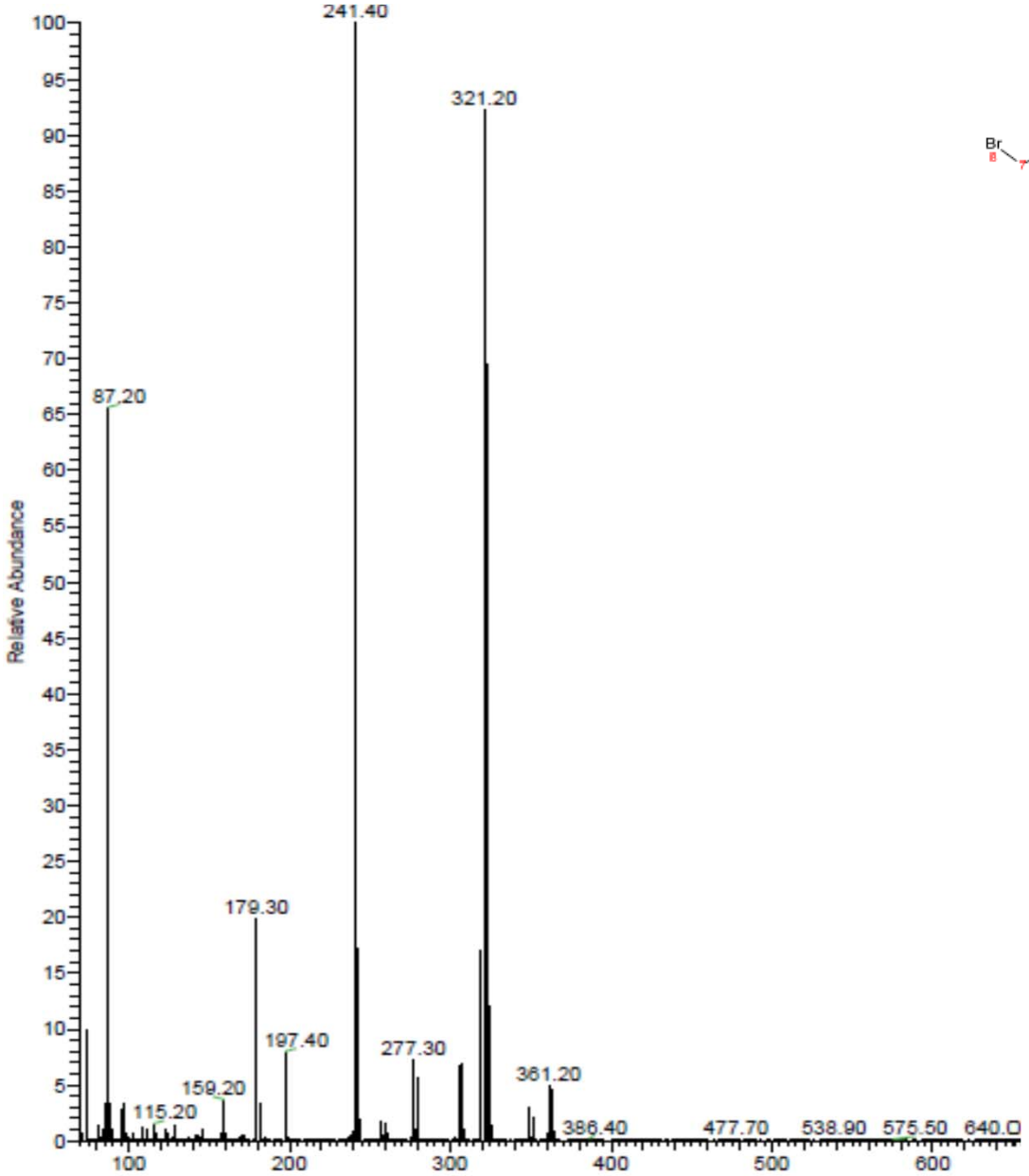
*g*DQCOSY spectrum of 2-(11-bromoundecyl)-2-methyl-1,3-dioxolane (30) (400 MHz, $CDCl_3$)

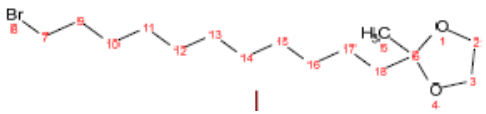


*g*HSQC spectrum of 2-(11-bromoundecyl)-2-methyl-1,3-dioxolane (30) (400 MHz,101 MHz; $CDCl_3$)



GC-MS chromatogram and fragmentations of 2-(11-bromoundecyl)-2-methyl-1,3-dioxolane (30)





Chemical Formula: $C_{15}H_{27}BrO_2$
Exact Mass: 318.12
Molecular Weight: 319.28