Synthesis and Photochromism of Some Bis(Thienyl) Substituted Oxathiine 2,2-dioxides

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Experimental

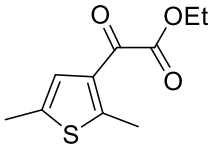
Equipment and materials

Unless otherwise stated, reagents and solvents were purchased from major chemical catalogue companies and were used as supplied. Routine ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on either a Bruker Avance DPX400 instrument or a Bruker Fourier 300 instrument for solutions in $CDCl_3$. Chemical shifts are provided in parts per million (ppm) referenced against either the residual solvent peak or TMS as the internal reference. Coupling constants (*J*) are provided in Hz and where applicable, in order to resolve close signals and extract valuable coupling information, the raw FID data was processed using a Gaussian multiplication in place of the more usual exponential multiplication. It should be noted that in the ^{13}C NMR spectra for some of the enaminoketones the N-C carbon resonances were too broad and the chemical shift was inferred from HSQC cross peaks. All FT-IR spectra were recorded on a Nicolet 380 FTIR spectrophotometer equipped with a diamond ATR attachment (neat sample). Flash column chromatography was performed on chromatography silica gel (Fluorochem, 40-63 micron particle size distribution). All final compounds were homogeneous by TLC using a range of eluent systems of differing polarity (Merck TLC aluminium sheets silica gel 60 F254 (cat. No 105554)) with visualisation provided by a TLC inspection lamp (Spectroline E Series 254 nm and 365 nm, 8 Watt). High resolution mass spectra were recorded on an Agilent 6210 1200 SL TOF spectrometer within the IPOS centre at the University of Huddersfield.

UV-visible spectra were recorded for either spectroscopic grade PhMe or DCM or hexane solutions of the samples (10 mm path length quartz cuvette, PTFE capped, concentration in the range $1 \times 10^{-4} - 10^{-6}$ moldm^{-3}). A bespoke Shimadzu UV-3600 Plus UV-Vis-NIR spectrophotometer was used that was equipped with a single cell Peltier temperature controlled (20 ^{o}C) stirred fluorescence cell holder attachment. The spectrophotometer sample chamber door was modified to accept activating irradiation delivered from the light source by liquid light guides (Newport 77557, Newport 77569). Irradiation was provided by a xenon ozone free arc lamp (Newport 6255) powered by an Oriel 300-Watt xenon arc lamp source (Newport 66906) with power manually limited to 120 - 150 Watts. An in-line distilled water liquid filter (Newport 6177), multiple filter holder (Newport 62020), UG11 filter (Newport FSO-UG11), fibre optic coupler (Newport 77799) completed the irradiation equipment. Spectra (350 – 750 nm) were recorded prior to (ground state) and immediately after cessation of activating irradiation to a steady state (25 – 150 min irradiation). Activation of the colourless forms of the series of **13-open** and **14-open** was achieved using UV irradiation in the range 255 – 390 nm (filters Newport FSQ-UG11). Bleaching of the coloured forms of the series of **13-closed** and **14-closed** was effected by irradiation with visible light > 455 nm (filters Newport FSQ-GG455).

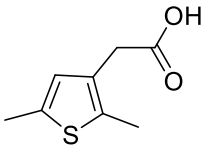
(*E*)-3-(dimethylamino)-1,2-diphenylprop-2-en-1-one (**11d**)[1] was obtained in 62 % yield by refluxing deoxybenzoin in neat *N,N*-dimethylformamide dimethylacetal (DMFDMA) (2.5 eq.) until TLC examination of the reaction mixture indicated that no starting material remained.

Ethyl 2,5-dimethylthiophene-3-glyoxylate (3)



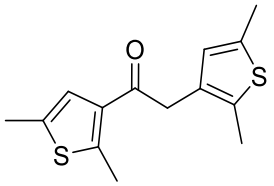
2,5-Dimethylthiophene (10.0 g, 89.0 mmol) was dissolved in $MeNO_2$ (40 mL), followed by the addition of ethyl oxalyl chloride (11.90 mL, 107 mmol, 1.2 eq.). The mixture was cooled down to 0 - 5° C in an acetone-ice bath and a solution of anhydrous $AlCl_3$ (14.3 g, 106.8 mmol, 1.2 eq.) in dry $MeNO_2$ (25 mL) was added dropwise with the temperature maintained below 5° C. An anhydrous $CaCl_2$ drying tube was used during the addition to create a dry atmosphere and allow for a smooth HCl release. Upon completion of the addition, the reaction mixture reached room temperature over 2 h, after which time it was slowly poured into ice (approx. 100 mL). The product was extracted with Et_2O (2 × 100 mL, 50 mL) and washed with H_2O (3 × 100 mL) and then aqueous $NaHCO_3$ solution (1M, 2 × 40 mL). The organic phase was dried (anhyd. Na_2SO_4), the solvent was removed under reduced pressure and the crude product was purified by Kugelrohr distillation (product distils at 150°- 160° C) to afford the title ester **3** (13.22 g, 70 %) as a yellow oil, bp = 140-145 °C (52 Torr) [lit. bp 110 °C (1 Torr)[2]]; R_f = 0.7 (10 % EtOAc / hexane); ν_{max} (neat): 2982, 2923, 1732 (OC=O), 1668 (C=O), 1549, 1477, 1446, 1378, 1284, 1207, 1116, 1013 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 1.40 (t, *J* = 7 Hz, 3H, OCH_2CH_3), 2.41 (m, 3H, thienyl-CH_3), 2.70 (m, 3H, thienyl-CH_3), 4.39 (q, *J* = 7 Hz, 2H, OCH_2CH_3), 7.09 (app. s, 1H, thienyl-H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 14.0, 14.8, 15.9, 62.1, 126.8, 131.2, 135.9, 152.5, 164.0, 180.6.

2-(2,5-Dimethylthiophen-3-yl)acetic acid (4)



Ethyl 2,5-dimethylthiophene-3-glyoxylate (12 g, 56.6 mmol) was slowly dissolved in ethylene glycol (50 mL). Upon complete dissolution, hydrazine monohydrate (4.87 mL, 62.3 mmol, 1.1 eq.) was added with vigorous stirring, prompting a change the colour of the mixture from orange to yellow and, subsequently, the formation of yellow crystals. The reaction mixture was heated for 1 h at 70 °C and then allowed to reach room temperature, before the swift addition of KOH (8.07 g, 143.8 mmol, 2.5 eq.), followed by heating the reaction mixture at reflux for 1 h, during which time the colour changed from yellow to orange. The H_2O thus formed was removed azeotropically over 4 h and 30 min. The reaction mixture was, afterwards, allowed to reach room temperature and poured into H_2O (50 mL). The pH was adjusted to approx. 2 and the solid that formed was extracted with EtOAc (2 × 100 mL). After it was washed with brine (100 mL) and H_2O (100 mL), the organic layer was dried (anhyd. Na_2SO_4) and the solvent was removed in vacuo to afford the acid **4** as a pale brown-orange solid (8.88 g, 92 %), mp = 67 - 69 °C [lit. mp : 67.5 - 68 °C (from EtOH)[3]]; R_f = 0.5 (50 % EtOAc / hexane); ν_{max} (neat): 2917, 2669, 2566, 2360, 1822, 1690 (C=O), 1573, 1496, 1437, 1409, 1303, 1276, 1213, 1198, 1144, 1122, 1075, 1037; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 2.33 (s, 3H, thienyl-CH_3), 2.40 (s, 3H, thienyl-CH_3), 3.50 (s, 2H, CH_2), 6.55 (s, 1H, thienyl-H), 10.94 (br, 1H, COOH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 12.9, 15.1, 33.8, 127.1, 128.0, 133.6, 135.8, 177.9.

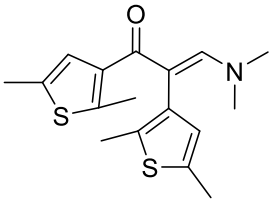
1,2-Bis(2,5-dimethylthiophen-3-yl)ethan-1-one (6)



2-(2,5-Dimethylthiophen-3-yl)acetic acid **4** (10.00 g, 58.8 mmol) was dissolved in DCM (100 mL) and $SOCl_2$ (6.40 mL, 88.2 mmol, 1.5 eq.) added. After the addition of DMF (0.05 mL, 0.06 mmol), at which point the colour started turning from orange to brown, the reaction mixture was stirred at room temperature for 1 h. After evaporation of the volatile components, the resulting acid chloride **5**, as a mobile brown oil (12.06 g), was used directly in the next step without further purification.

Dimethylthiophene (5.60 mL, 48.9 mmol, 1 eq.) was dissolved in $MeNO_2$ (50 mL) and mixed with the foregoing acid chloride **5**. The solution was cooled down to 0 - 5 ^oC and $AlCl_3$ (6.52 g, 48.9 mmol, 1.0 eq.) added in small portions over 20 min maintaining the temperature to below 5 ^oC. The resulting mixture was stirred at room temperature. After 2 h the resulting mixture was poured into ice water (approx. 150 mL), containing aq. HCl (2M, 30 mL) and extracted with DCM (2 × 200 mL, 50 mL). The combined organic phase was, washed with H_2O (2 × 100 mL), aqueous Na_2CO_3 (2 × 100 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was distilled under reduced pressure to give a colourless oil which solidified on standing. The solid was chromatographed on silica (10% EtOAc in hexane). The solvent was removed under reduced pressure and the residue triturated with n-pentane to give **6** (5.97g, 47 %) as off-white crystals, mp = 48 - 50 ^oC (from EtOAc/ hexane) [lit. mp: 44 - 46 ^oC (from EtOH)[4]]; R_f = 0.5 (10 % EtOAc/ hexane); ν_{max} (neat): 2949, 2915, 2872, 1666 (C=O), 1548, 1478, 1445, 1417, 1373, 1355, 1313, 1221, 1167, 1125, 1038 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 2.31 (s, 3H, thienyl-CH_3), 2.38 (s, 3H, thienyl-CH_3), 2.42 (s, 3H, thienyl-CH_3), 2.66 (s, 3H, thienyl-CH_3), 3.92 (s, 2H, CH_2CO), 6.48 (s, 1H, thienyl-H), 7.05 (s, 1H, thienyl-H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 13.1, 15.1, 15.2, 16.1, 41.1, 125.9, 127.3, 129.6, 132.6, 135.0, 135.2, 135.5, 148.4, 193.2. HRMS: Found $[M+H]^+$= 265.0729, $C_{14}H_{16}OS_2$ requires $[M+H]^+$= 265.0715.

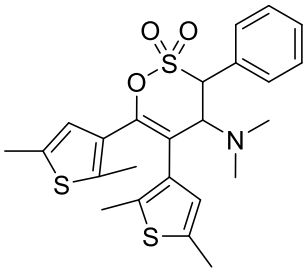
(*E*)-3-(Dimethylamino)-1,2-bis(1,5-dimethylthiophen-3-yl)prop-2-en-1-one (12a)



1,2-Bis(2,5-dimethylthiophen-3-yl)ethan-1-one **6** (5.00 g, 18.9 mmol) was dissolved in DMFDMA (6.29 mL, 47.3 mmol, 2.5 eq.) and stirred at reflux overnight (mixture colour changed from pale yellow to red-black). The solvent was removed under reduced pressure, the residue mixed with brine and extracted with EtOAc (3 × 50 mL). The combined organic phase was washed with H_2O (40 mL), dried over anhyd. Na_2SO_4 and the solvent removed under reduced pressure. The residue was purified by column chromatography (neutral alumina, 10 % to 50 % EtOAc in hexane/DCM). The enaminoketone **12a** was thus obtained (3.62 g, 60 %) as a viscous red-orange liquid, R_f = 0.4 (50% EtOAc / Hexane); ν_{max} (neat): 2914, 2858, 1628 (C=O), 1578, 1553, 1488, 1424, 1390, 1313, 1224, 1205, 1179, 1116, 1060, 1014 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 2.12 (s, 3H, thienyl-CH_3), 2.33 (s, 3H, thienyl-CH_3), 2.37 (s, 3H, thienyl-CH_3), 2.42 (s, 3H, thienyl-CH_3), 2.77 (s, 6H, $N(CH_3)_2$), 6.43 (s, 1H, thienyl-H), 6.45 (s, 1H, thienyl-H), 7.30 (s, 1H, vinyl-H); ^{13}C-NMR (100

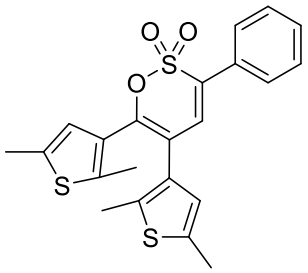
MHz, $CDCl_3$): δ_C 13.8, 14.4, 15.0, 15.3, 42.4, 107.2, 126.5, 129.7, 132.8, 133.8, 134.4, 134.7, 137.6, 139.4, 154.2, 190.4. HRMS: Found $[M+H]^+$= 320.1149, $C_{17}H_{21}NOS_2$ requires $[M+H]^+$= 320.1137.

4-(Dimethylamino)-5,6-bis-(2,5-dimethylthiophen-3-yl)-3-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide (13a-open)



A solution of phenylmethanesulfonyl chloride (1.44g, 7.56 mmol, 1.2 eq.) in THF (20 mL) was added dropwise to a cold (0 - 5 ^oC) stirred solution of 3-(dimethylamino)-1,2-bis(1,5-dimethylthiophen-3-yl)prop-2-en-1-one **12a** (2.00 g, 6.3 mmol) in THF (25 mL) containing Et_3N (1.05 mL, 7.56 mmol, 1.2 eq.) under a N_2 atmosphere. Upon complete addition the mixture was allowed to reach room temperature over 4h (reaction completion was achieved after the addition of an extra 0.3 eq. of the chloride and the base). The resulting mixture was filtered through a short plug of alumina (ca. 5 mm) and the solvent removed under reduced pressure. The resulting oil was dissolved in EtOAc (50 mL), washed with H_2O (2 × 25 mL), dried over anhyd. Na_2SO_4 and the solvent removed under reduced pressure. The residue was crystallised from EtOAc / hexane afforded the title product **13a-open** as an off-white solid (1.57 g, 53 %), R_f = 0.8 (DCM); mp = 135 - 138 ^oC (from EtOAc/ Hexane); ν_{max} (neat): 2915, 2857, 2836, 2785, 1645, 1496, 1440, 1367 (O-SO_2), 1287, 1244, 1181, 1157 (O-SO_2), 1136, 1110, 1055, 1035 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 2.01 (s, 3H, thienyl-CH_3), 2.21 (s, 3H, thienyl-CH_3), 2.23 (s, 6H, $N(CH_3)_2$), 2.28 (s, 3H, thienyl-CH_3), 2.38 (s, 3H, thienyl-CH_3), 4.32 (d, *J* = 7.8 Hz, 1H, 4-H), 4.85 (d, *J* = 7.8 Hz, 1H, 3-H), 6.32 (s, 1H, thienyl-H), 6.67 (s, 1H, thienyl-H), 7.42 - 7.43 (m, 3H, ArH), 7.55 - 7.57 (m, 2H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 13.9, 14.6, 15.0, 15.3, 40.7, 62.1, 71.0, 118.0, 126.0, 126.7, 129.2, 129.4, 129.6, 129.9, 131.9, 132.3, 134.9, 135.0, 135.3, 138.4, 145.4. HRMS: Found $[M+H]^+$= 474.1236, $C_{24}H_{27}NO_3S_3$ requires $[M+H]^+$= 474.1226.

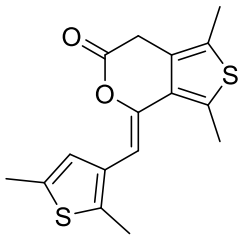
5,6-Bis-(2,5-dimethylthiophen-3-yl)-3-phenyl-1,2-oxathiine 2,2-dioxide (14a-open)



A solution of *m*-CPBA (0.68 g, 2.97 mmol, 1.1 eq.) in DCM (20 mL) was added dropwise over 10 min. to a cold (ca. 5 ^oC) stirred solution of 4-(dimethylamino)-5,6-bis-(2,5-dimethylthiophen-3-yl)-3-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide **13a-open** (1.30 g, 2.7 mmol) in DCM (20 mL). Upon completion of the addition the mixture was then allowed to reach room temperature over 1.5 h (reaction completion was achieved after the addition of an extra 1.3 eq. of *m*-CPBA). The resulting mixture was washed with H_2O (15 mL), aqueous Na_2SO_3 (0.667 M, 2 × 15 mL), NaOH solution (1 M, 15 mL) and H_2O (10 mL). The organic phase was dried over Na_2SO_4 and the solvent removed under reduced pressure. The resulting crude

material was purified by silica column chromatography (10 % EtOAc/Hexane) and the solvent removed under reduced pressure to afford the title product **14a-open** as pale brown crystals (0.96 g, 84 %), mp = 132 - 134 ^{o}C (from EtOAc / Hexane); R_f = 0.4 (10 % EtOAc / hexane); ν_{max} (neat): 2910, 2853, 1627, 1556, 1494, 1433, 1358 (O-SO_2), 1342, 1319, 1259, 1231, 1182, 1166 (O-SO_2), 1142, 1132, 1062, 1036 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 1.96 (s, 3H, thienyl-CH_3), 2.30 (s, 3H, thienyl-CH_3), 2.35 (s, 3H, thienyl-CH_3), 2.42 (s, 3H, thienyl-CH_3), 6.29 (s, 1H, thienyl-H), 6.56 (s, 1H, thienyl-H), 6.89 (s, 1H, 4-H), 7.43 - 7.46 (m, 3H, ArH), 7.62 - 7.65 (m, 2H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 13.7, 14.8, 15.1, 15.3, 114.1, 125.2, 125.5, 127.7, 128.3, 129.0, 129.7, 130.1, 130.9, 133.2, 133.6, 135.1, 136.0, 137.2, 141.4, 149.6. HRMS: Found $[M+Na]^+$ = 451.0467, $[C_{22}H_{20}O_3S_3]^+$ requires $[M+Na]^+$ = 451.0467.

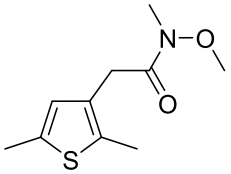
(*Z*)-4-((2,5-Dimethylthiophen-3-yl)methylene)-1,3-dimethyl-4*H*-thieno[3,4-*c*]pyran-6(7*H*)-one (7)



2-(2,5-Dimethylthiophen-3-yl)acetic acid **4** (4.00 g, 23.5 mmol) was dissolved in DCM (40 mL) and mixed with $SOCl_2$ (2.55 mL, 35.3 mmol, 1.5 eq.). DMF (6 drops) was subsequently added and the mixture was stirred at room temperature for 1h. Upon evaporation of the volatile components, the crude acid chloride **5** (4.57 g) was used directly in the next step without further purification.

Benzene (1.53 g, 19.6 mmol) was dissolved in $MeNO_2$ (30 mL), mixed with the crude acid chloride **5** and cooled to 5 ^{o}C. Anhydrous $AlCl_3$ (3.13 g, 23.5 mmol, 1.2 eq.) was then added portion wise over 10 min, maintaining the temperature between 5 - 10 ^{o}C. Upon complete addition, the reaction mixture was allowed to reach room temperature over 2h, before being poured into ice water (approx. 50 mL). The resulting mixture was extracted with Et_2O (2 × 100 mL) and EtOAc (50 mL). The combined organic phase was washed with aq. sat. $NaHCO_3$ (3 × 50 mL) and H_2O (2 × 75 mL), dried over anhyd. Na_2SO_4 and the solvent removed under reduced pressure. Purification by flash chromatography on silica (0 % to 15 % EtOAc in hexane) afforded the title product as light brown crystals (0.32 g, 11 %) after recrystallization from EtOAc / hexane, mp = 144 - 147 ^{o}C; R_f = 0.6 (20 % EtOAc / hexane); ν_{max} (neat): 2914, 2357, 1756 (OC=O), 1637, 1581, 1556, 1494, 1446, 1383, 1311, 1257, 1207, 1145, 1074, 1039 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 2.30 (s, 3H, thienyl-CH_3), 2.42 (s, 3H, thienyl-CH_3), 2.44 (s, 3H, thienyl-CH_3), 2.56 (s, 3H, thienyl-CH_3), 3.67 (s, 2H, CH_2CO), 5.85 (s, 1H, thienyl-H), 7.41 (s, 1H, C=CH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 12.1, 13.4, 15.1, 15.3, 31.9, 104.4, 126.1, 126.5, 126.7, 128.6, 130.6, 131.4, 134.9, 135.6, 141.0, 166.4. HRMS: Found $[M+H]^+$= 305.0660, $[C_{16}H_{16}O_2S_2]^+$ requires $[M+H]^+$= 305.0664.

2-(2,5-Dimethylthiophen-3-yl)-*N*-methoxy-*N*-methylacetamide (8)

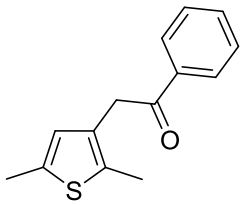


In a three neck flask fitted with a $CaCl_2$ drying tube, 2-(2,5-dimethylthiophen-3-yl)acetic acid **4** (7.00 g, 41.2 mmol) was dissolved in DCM (70 mL) and mixed with $SOCl_2$ (4.48 mL, 61.8 mmol, 1.5 eq.). DMF (10 drops) was added and the mixture stirred at room temperature. The volatile components were removed

under reduced pressure and the crude acid chloride **5** (7.93 g) was used directly without further purification.

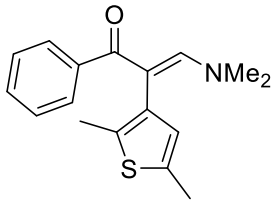
A solution of *N,O*-dimethylhydroxylamine hydrochloride (5.22 g, 45.32 mmol, 1.3 eq.) in pyridine (7.33 mL, 90.64 mmol, 2.2 eq.) under N_2 was cooled down at 0 - 4 ^oC was added drop wise to a solution of the foregoing acid chloride **5** (7.93 g, 41.2 mmol) in DCM (110 mL) over 45 min, maintaining the temperature below 5 ^oC. Upon complete addition, the reaction mixture was allowed to warm to room temperature and diluted with DCM (200 mL). The resulting solution was washed with water (3 × 100 mL), saturated aqueous $NaHCO_3$ (125 mL), dried over anhyd. Na_2SO_4 and the solvent removed under reduced pressure. The residue was purified by column chromatography (0 to 1 % EtOAc in DCM) to afford the title amide **8** as a red-orange oil (5.69 g, 65 %), R_f = 0.5 (DCM); ν_{max} (neat): 2918, 2361, 1665 (C=O), 1576, 1413, 1378, 1285, 1176, 1144, 1097, 1002 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 2.32 (s, 3H, thienyl-CH_3), 2.37 (s, 3H, thienyl-CH_3), 3.18 (s, 3H, NCH_3), 3.59 (s, 2H, CH_2CO), 3.60 (s, 3H, OCH_3), 6.56 (s, 1H, thienyl-H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 13.0, 15.2, 32.26, 32.32, 61.2, 127.2, 129.6, 132.5, 135.4, 172.3. HRMS: Found $[M+H]^+$= 214.0893, $[C_{10}H_{15}NO_2S]^+$ requires $[M+H]^+$= 214.0896.

1-Phenyl-2-(2,5-dimethylthiophen-3-yl)-ethanone (9)



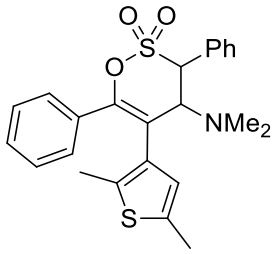
2-(2,5-Dimethylthiophen-3-yl)-*N*-methoxy-*N*-methylacetamide **8** (5.00 g, 23.5 mmol) was dissolved in dry THF (140 mL) under N_2 and cooled down to -78 ^oC. A solution of phenyllithium in Bu_2O (43.30 mL, 1.9 M, 82.25 mmol, 3.5 eq.) was added dropwise over 20 min with the temperature maintained below -70 ^oC. After the addition was complete, the reaction mixture was stirred at -70 ^oC for 1 h, before being quenched with aqueous NH_4Cl (160 mL). The pH was adjusted to 7 - 8 and the product was extracted with DCM (3 × 100 mL). The combined organic phase was washed with brine (300 mL), dried over anhyd. Na_2SO_4 and the solvent was removed *in vacuo*. The resulting crude product was purified by column chromatography (50 to 60 % DCM in petroleum ether) to yield the title ketone **9** as a pale green solid (3.56 g, 66 %), mp = 52 - 54 ^oC [lit. mp: 55 - 57 ^oC (from MeOH / H_2O)[4]]; R_f = 0.6 (50 % DCM / hexane); ν_{max} (neat): 2916, 2875, 2356, 1683 (C=O), 1593, 1578, 1444, 1399, 1336, 1215, 1204, 1182, 1140, 1075, 1028 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 2.34 (s, 3H, thienyl-CH_3), 2.37 (s, 3H, thienyl-CH_3), 4.12 (s, 2H, CH_2CO), 6.49 (s, 1H, thienyl-H), 7.46-7.49 (m, 2H, ArH), 7.55-7.59 (m, 1H, ArH), 7.99-8.01 (m, 2H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 13.2, 15.2, 38.4, 127.2, 128.5, 128.7, 129.3, 132.7, 133.2, 135.7, 136.7, 197.3.

(*E*)-3-(Dimethylamino)-2-(2,5-dimethylthiophen-3-yl)-1-phenylprop-2-en-1-one (12b)



In a flame-dried flask, 1-phenyl-2-(2,5-dmethylthiophen-3-yl)-ethanone **9** (2.5 g, 10.9 mmol) was dissolved in PhMe (60 mL) and mixed with DMFDMA (1.6 mL, 12.0 mmol, 1.1 eq.) under a N_2 atmosphere. The resulting solution was stirred at reflux for 2 h 30 min, after which time it was poured into H_2O (100 mL) and the organic phase was separated and the aqueous phase extracted with EtOAc (2 × 25 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to yield the pure product **12b** as a pale pink solid(2.65 g, 86 %) was obtained as a pink solid, R_f = 0.3 (50 % EtOAc / hexane); mp = 102 - 105 °C (from EtOAc and hexane); ν_{max} (neat): 2913, 1599, 1581 (C=O), 1557, 1492, 1442, 1393, 1317, 1301, 1289, 1227, 1205, 1176, 1155, 1135, 1111m 1037, 1022 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 2.09 (s, 3H, thienyl-CH_3), 2.36 (s, 3H, thienyl-CH_3), 2.79 (s, 6H, N(CH_3)$_2$), 6.44 (s, 1H, thienyl-H), 7.26 - 7.32 (m, 2H, ArH), 7.42 - 7.43 (m, 3H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 13.8, 15.4, 42.8 (br), 105.3, 127.5, 128.4, 129.3, 129.8, 133.2, 133.8, 134.6, 141.9, 154.2, 194.4; HRMS: Found $[M+H]^+$= 286.1266, $[C_{17}H_{19}NOS]^+$ requires $[M+H]^+$= 286.126.

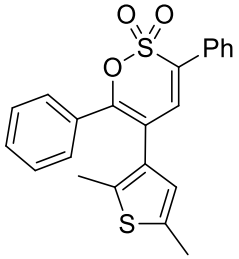
4-(Dimethylamino)-5-(2,5-dimethylthiophen-3-yl)-3,6-diphenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide (13b-open)



A solution of phenylmethanesulfonyl chloride (1.73 g, 9.1 mmol, 1.3 eq.) in THF (25 mL) was added dropwise over 10 min, to a cold (ca. 5 °C) stirred solution of (*E*)-3-(dimethylamino)-2-(2,5-dimethylthiophen-3-yl)-1-phenylprop-2-en-1-one **12b** (2.00 g, 7.0 mmol) in dry THF (25 mL), containing Et_3N (1.27 mL, 9.1 mmol, 1.3 eq.) under a N_2 atmosphere. Upon completion of the addition, the reaction mixture was allowed to warm to room temperature over 3 h. A further portion of Et_3N (0.3 eq) and phenylmethanesulfonyl chloride (0.3 eq) was added at this time and the reaction was stirred at room temperature for a further 1.5 h to ensure complete consumption of the starting enaminoketone. The reaction mixture was filtered through a plug of alumina and the solvent was evaporated *in vacuo*. The residue was chromatographed on silica (50 % to 75 % DCM in hexane) and the solvent removed under reduced pressure. The residue was recrystallized from EtOAc / Hexane to afford the pure product **13b-open** (1.62 g, 53 %) as colourless crystals, R_f = 0.3 (50 % DCM / Hexane); mp = 133 - 135 °C (from EtOAc / hexane); ν_{max} (neat): 2941, 2832, 1495, 1446, 1369 (O-SO_2), 1339, 1317, 1266, 1240, 1225, 1178 (O-SO_2), 1152, 1134, 1099, 1061, 1050, 1037, 1025, 1000 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 1.93 (s, 3H, thienyl-CH_3), 2.26 (s, 6H, N(CH_3)$_2$), 2.42 (s, 3H, thienyl-CH_3), 4.28 (d, *J* = 8.1 Hz, 1H, 4-H), 4.92 (d, *J* = 8.1 Hz, 1H, 3-H), 6.72 (s, 1H, thienyl-H), 7.22 - 7.26 (m, 5H, ArH), 7.42 - 7.45 (m, 3H, ArH), 7.56 - 7.58 (m, 2H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 13.5, 15.4, 40.8, 61.9, 71.3, 117.4, 127.4, 127.9, 128.3, 129.0, 129.2, 129.5,

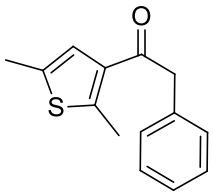
129.9, 131.8, 132.4, 133.1, 134.5, 135.6, 148.6; HRMS: Found $[M+H]^+$= 440.1335, $[C_{24}H_{25}NO_3S_2]^+$ requires 440.1349.

5-(2,5-Dimethylthiophen-3-yl)-3,6-diphenyl-1,2-oxathiine 2,2-dioxide (14b-open)



A solution of *m*-CPBA (0.68 g, 2.96 mmol, 1.3 eq.) in DCM (25 mL) was added dropwise over 5 min, to a cold (ca. 5 °C) stirred solution of 4-(dimethylamino)-5-(2,5-dimethylthiophen-3-yl)-3,6-diphenyl-1,2-oxathiine 2.2-dioxide **13b-open** (1.00 g, 2.3 mmol) dissolved in DCM (20 mL). Upon completion of the addition, the mixture was allowed to warm to room temperature over 2 h The resulting mixture was washed sequentially with H_2O (15 mL), aqueous Na_2SO_3 (0.7 M, 2 × 15 mL), aqueous NaOH (1 M, 15 mL) and H_2O (10 mL). The organic phase was dried over anhyd. $NaSO_4$ and the solvent was removed under reduced pressure, affording the pure product **14b-open** (0.71 g, 78 %) as a pale yellow solid. R_f = 0.8 (60 % DCM / hexane), mp = 126 - 128 °C; ν_{max} (neat): 3025, 2914, 1625, 1577, 1552, 1488, 1446, 1363 (O-SO_2), 1321, 1264, 1223, 1182 (O-SO_2), 1170, 1153, 1139, 1086, 1067, 1035, 1009 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 1.93 (s, 3H, thienyl-CH_3), 2.45 (s, 3H, thienyl-CH_3), 6.63 (s, 1H, thienyl-H), 6.89 (s, 1H, 4-H), 7.29 - 7.37 (m, 3H, ArH), 7.40 - 7.47 (m, 5H, ArH), 7.64 - 7.67 (m, 2H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 13.5, 15.3, 113.8, 125.3, 127.7, 128.3, 128.4, 129.0, 129.9, 129.9, 130.2, 130.9, 131.5, 133.7, 134.0, 134.8, 138.0, 152.1. HRMS: Found $[M+H]^+$ = 395.0768, $[C_{22}H_{18}O_3S_2]^+$ requires $[M+H]^+$ = 395.077.

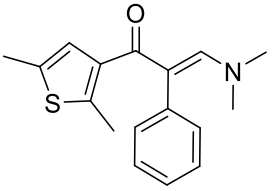
1-(2,5-Dimethylthiophen-3-yl)-2-phenylethanone (10)



2,5-Dimethylthiophene (10.0 g, 89.1 mmol) was dissolved in DCM (30 mL) and mixed with phenylacetyl chloride (14.15 mL, 106.9 mmol, 1.2 eq.). The mixture was cooled down to 0-5 °C and a solution of $AlCl_3$ (14.25 g, 106.9 mmol, 1.2 eq.) in DCM (30 mL) and $MeNO_2$ (10 mL) was added dropwise over 20 min, while the temperature was maintained below 5 °C. Upon completion of the addition, the reaction mixture was allowed to reach room temperature over 2.5 h, before being poured into ice (approx. 60 mL). The organic layer was separated and the aqueous phase was extracted with DCM (3 × 80 mL). The combined organic phase were sequentially washed with H_2O (2 × 100 mL), aq. sat. $NaHCO_3$ (6 × 50 mL) and H_2O (50 mL) then dried with anhyd. Na_2SO_4 and the solvent removed under reduced pressure. Short path length Kugelrohr distillation gave the title product **10** (15.83 g, 77 %) as a dark red oil, b.p. 130 - 135 °C (0.06 mbar); R_f = 0.5 (10 % EtOAc / Hexane); ν_{max} (neat): 3028, 2919, 1736, 1663 (C=O), 1602, 1548, 1477, 1452, 1358, 1307, 1247, 1222, 1186, 1162, 1125, 1073, 1030 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 2.42 (app. s, 3H, thienyl-CH_3), 2.68 (app. s, 3H, thienyl-CH_3), 4.11 (s, 2H, CH_2CO), 7.09 (app. s, 1H, thienyl-H), 7.25 - 7.29 (m, 3H,

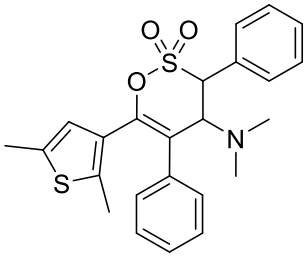
ArH), 7.33 - 7.38 (m, 2H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 15.1, 16.2, 48.4, 126.2, 126.8, 128.6, 129.6, 134.8, 135.1, 135.2, 148.6, 193.6. HRMS: Found $[M+H]^+$ = 231.0840, $C_{14}H_{14}OS$ requires $[M+H]^+$ = 231.0838.

(*E*)-(Dimethylamino)-1-(2,5-dimethylthiophen-3-yl)-2-phenylprop-2-en-1-one (12c)



1-(2,5-Dimethylthiophen-3-yl)-2-phenylethanone **10** (10.0 g, 43.4 mmol) was dissolved in DMFDMA (14.91 mL, 108.5 mmol, 2.5 eq.) and the solution was stirred at reflux overnight. After removal of the volatile components under reduced pressure, the orange-brown oil so obtained turned into a solid after 1 h at room temperature. Recrystallization from EtOAc / hexane afforded the title product **12c** (10.17 g, 82 %) as pale yellow crystals, mp = 85 - 87 ^oC (from EtOAc / Hexane); R_f = 0.2 (50 % EtOAc/ Hexane); ν_{max} (neat): 3048, 2911, 1620 (C=O), 1563, 1494, 1482, 1431, 1388, 1371, 1342, 1318, 1285, 1221, 1197, 1157, 1142, 1106, 1071, 1057, 1037, 1022 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 2.32 (app. s, 3H, thienyl-CH_3), 2.41 (app. s, 3H, thienyl-CH_3), 2.72 (s, 6H, $N(CH_3)_2$), 6.49 (m, 1H, thienyl-H), 7.14 - 7.21 (m, 3H, ArH), 7.25 - 7.29 (m, 2H, ArH), 7.28 (s, 1H, vinyl-H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 14.4, 15.0, 43.6, 113.6, 126.3, 126.7, 127.6, 131.9, 135.0, 136.9, 137.5, 139.3, 153.6, 190.9. HRMS: Found $[M+H]^+$= 286.1268, $C_{17}H_{19}NOS$ requires $[M+H]^+$= 286.126.

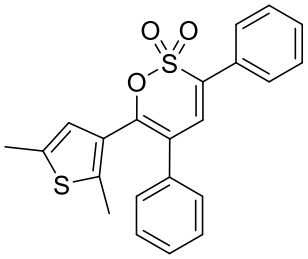
6-(2,5-Dimethylthiophen-3-yl)-4-(dimethylamino)-3,4-dihydro-3,5-diphenyl-1,2-oxathiine 2,2 dioxide (13c-open)



A solution of $PhCH_2SO_2Cl$ (4.80 g, 25.2 mmol, 1.2 eq.) in THF (50 mL) was added dropwise over 20 min to a cold (0 - 5 ^oC) vigorously stirred solution of 3-(dimethylamino)-1-(2,5-dimethylthiophen-3-yl)-2-phenylprop-2-en-1-one **12c** (6.00 g, 21.0 mmol) in anhydrous THF (70 mL) containing Et_3N (3.51 mL, 25.2 mmol, 1.2 eq.). Upon completion of the addition, the reaction mixture was allowed to warm to room temperature overnight. A further portion of Et_3N (0.4 eq) and phenylmethanesulfonyl chloride (0.4 eq) was added at this time and the reaction was stirred at room temperature for a further 1.5 h to ensure complete consumption of the starting enaminoketone. The mixture was filtered through a short plug of alumina and the solvent removed under reduced pressure. The residue was dissolved in EtOAc (120 mL), washed with H_2O (2 × 60 mL), dried over anhyd. Na_2SO_4 and the solvent was removed under reduced pressure. The residue was crystallized from EtOAc / hexane to give the **13c-open** as colourless microcrystals (6.57 g, 71 %), mp= 146 - 150 ^oC (from EtOAc); R_f = 0.9 (50 % EtOAc / hexane); ν_{max} (neat): 2913, 2859, 2824, 2782, 1650, 1496, 1479, 1441, 1363 (O-SO_2), 1285, 1216, 1183 (O-SO_2), 1167, 1126, 1086, 1073, 1054, 1038, 1027 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 2.02 (app. s, 3H, thienyl-CH_3), 2.20 (app. s, 6H, $N(CH_3)_2$), 2.31 (s, 3H, thienyl-CH_3), 4.56 (d, *J* = 7.8 Hz, 1H, 4-H), 4.89 (d, *J* = 7.8 Hz, 1H, 3-H), 6.50 – 6.51 (m, 1H, thienyl-H), 7.21 - 7.28 (m, 5H, ArH), 7.42 - 7.44 (m, 2H, ArH), 7.58 - 7.61 (m, 3H, ArH); ^{13}C-

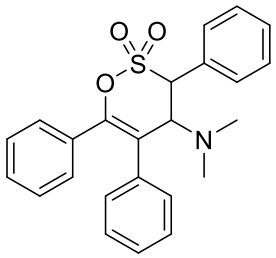
NMR (100 MHz, $CDCl_3$): δ_C 14.2, 15.1, 40.6, 62.3, 71.0, 123.9, 126.1, 127.5, 128.0, 129.2, 129.3, 129.5, 129.5, 129.9, 131.9, 136.1, 137.2, 138.3, 144.90. HRMS: Found $[M+H]^+$= 440.1345, $C_{24}H_{25}NO_3S_2$ requires $[M+H]^+$= 440.1349.

6-(2,5-Dimethylthiophen-yl)-3,5-diphenyl-1,2-oxathiine 2,2-dioxide (14c-open)



A solution of *m*-CPBA (1.12 g, 6.50 mmol, 1.9 eq.) in DCM (15 mL) was added dropwise over 10 min to a stirred solution of 6-(2,5-dimethylthiophen-3-yl)-4-(dimethylamino)-3,4-dihydro-3,5-diphenyl-1,2-oxathiine 2,2 dioxide **13c-open** in DCM (25 mL) at 0 - 5 ^oC. Upon completion of the addition the reaction mixture was allowed to reach room temperature overnight. The resulting mixture was sequentially washed with H_2O (15 mL), aqueous Na_2SO_3 (0.7 M, 2 × 15 mL), aqueous NaOH (1M, 15 mL) and H_2O (12 mL), followed by drying over anhyd. Na_2SO_4 and the solvent removed under reduced pressure. The residue was crystallized from EtOAc to afford the pure product **14c-open** as yellow crystals (0.96 g, 71 %), mp = 143 - 145 ^oC (from DCM); R_f = 0.9 (DCM); ν_{max} (neat): 3062, 2961, 1613, 1537, 1494, 1442, 1359 (O-SO_2), 1284, 1270, 1228, 1178 (O-SO_2), 1146, 1113, 1075, 1035, 1003 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 2.15 (app. s, 3H, thienyl-CH_3), 2.29 (app. s, 3H, thienyl-CH_3), 6.38 (app. s, 1H, thienyl-H), 7.04 (s, 1H, 4-H), 7.22-7.34 (m, 5H, ArH), 7.44-7.46 (m, 3H, ArH), 7.65-7.67 (m, 2H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 14.6, 15.0, 119.5, 125.9, 127.7, 127.9, 128.0, 128.7, 128.9, 129.0, 129.8, 130.1, 133.5, 133.9, 135.7, 136.4, 141.1, 149.5. HRMS: Found $[M+H]^+$= 395.0777, $C_{22}H_{18}O_3S_2$ requires $[M+H]^+$= 395.077.

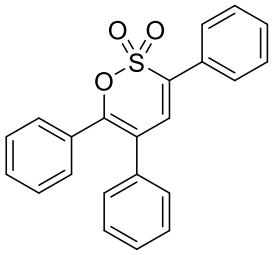
4-(Dimethylamino)-3,5,6-triphenyl-3,4-dihydro-1,2-oxathiine 2,2 dioxide (**13d-open**)



Under an N_2 atmosphere, (*E*)-(dimethylamino)-1,2-diphenylprop-2-en-1-one **12d** (10.0 g, 39.7 mmol) was dissolved in THF (120 mL), warmed up to facilitate dissolution and mixed with triethylamine (6.17 mL, 44.5 mmol). The mixture was stirred vigorously at approx. 5 ^oC, before the dropwise addition of a solution of phenylmethanesulfonyl chloride (8.48 g, 44.5 mmol) in THF (80 mL) over *ca*. 25 min. The reaction mixture was allowed to reach room temperature overnight. The resulting mixture was filtered through a short plug of alumina and the solvent removed under reduced pressure. The residual oily mass was diluted with EtOAc (100 mL) and washed with water (50 mL). Removal of the dried solvent gave the crude product which was crystallised from EtOH / hexane to afford the title dihydrooxathiine **13d-open** as colourless microcrystals (12.52 g, 77 %), mp = 139 - 142 ^oC (from EtOH / hexane); R_f = 0.9, (10 % EtOAc in hexane); ν_{max} (neat): 2972, 2938, 2899, 1644, 1494, 1455, 1446, 1365 (O-SO_2), 1332, 1266, 1227, 1182 (O-SO_2), 1169, 1154, 1102, 1093, 1071, 1036, 1025, 1001 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 2.23 (s, 6H, N(CH_3)$_2$),

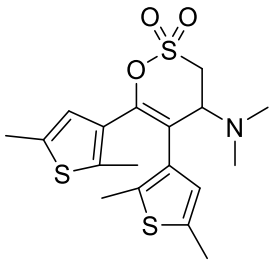
4.49 (d, *J* = 8.0 Hz, 1H, 4-H), 4.96 (d, *J* = 8.0 Hz, 1H, 3-H), 7.17 - 7.31 (m, 10H, ArH), 7.42 - 7.45 (m, 3H, ArH), 7.59 - 7.61 (m, 2H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 40.7, 62.3, 71.7, 122.8, 127.7, 127.9, 128.2, 129.0, 129.1, 129.3, 129.5, 129.9, 130.0, 131.7, 132.8, 137.3, 148.3. HRMS: Found $[M+H]^+$ = 406.1471, $[C_{24}H_{23}NO_3S]^+$ requires $[M+H]^+$ = 406.1471.

3,4,6-(Triphenyl)-1,2-oxathiine 2,2-dioxide (14d-open)



4-(Dimethylamino)-3,5,6-triphenyl-3,4-dihydro-1,2-oxatlhiine 2,2 dioxide **13d-open** (5.54 g, 13.7 mmol) was dissolved in DCM (70 mL) and the solution was cooled to 0 - 5 ^oC. A solution of *m*-chloroperoxybenzoic acid (4.18 g, 24.2 mmol, 1.7 eq.) in DCM (40 mL) was added dropwise over 15 min, while the temperature was maintained below 5 ^oC. The reaction mixture was left to warm to room temperature over 4 h. The resulting mixture was washed sequentially with H_2O (75 mL), aqueous Na_2SO_3 (0.7 M, 110 mL), aqueous NaOH (1 M, 50 mL) and H_2O (60 mL). The organic phase was dried with anhyd. Na_2SO_4 and the solvent was removed under reduced pressure. The residue was chromatographed on silica (40 % DCM in hexane) gave **14d-open** as yellow needles (3.05 g, 62 %), mp = 158 - 160 ^oC (from DCM / hexane); R_f = 0.7 (20 % DCM / hexane); ν_{max} (neat): 3060, 3028, 2919, 1621, 1575, 1541, 1488, 1445, 1368 (O-SO_2), 1350, 1286, 1270, 1231, 1186 (O-SO_2), 1130, 1073, 1033, 1011, 1000 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.01 (s, 1H, 4-H), 7.23 - 7.37 (m, 10H, ArH) 7.44 - 7.48 (m, 3H, ArH), 7.66 - 7.69 (m, 2H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 119.0, 127.7, 128.2, 128.3, 129.1, 129.1, 129.2, 129.3, 129.9, 130.0, 130.3, 131.1, 134.0, 134.1, 135,8, 152.1. HRMS: Found $[M+Na]^+$ = 383.0712, $[C_{22}H_{16}O_3S]^+$ requires $[M+Na]^+$ = 383.0712.

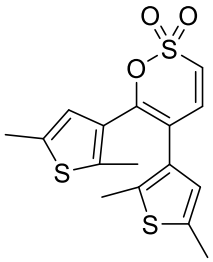
4-(Dimethylamino)-5,6-bis(2,5-dimethylthiophen-3-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (13e-open)



(*E*)-3-(Dimethylamino)-1,2-bis(1,5-dimethylthiophen-3-yl)prop-2-en-1-one **12a** (1.01 g, 3.2 mmol) was dissolved in THF (20 mL), containing Et_3N (0.57 mL, 4.1 mmol, 1.3 eq) under a N_2 atmosphere and then cooled to *circa* 0 ^oC. A solution of CH_3SO_2Cl (0.47 mL, 4.1 mmol, 1.3 eq.) in THF (10 mL) was added dropwise over 10 min with the temperature maintained below 2 ^oC. The resulting mixture was warmed to room temperature over 3h. A further portion of Et_3N (0.4 eq.) and methanesulfonyl chloride (0.4 eq.) was added at this time and the reaction was stirred at room temperature for a further 1.5 h to ensure complete consumption of the starting enaminoketone. The resulting mixture was filtered through a short plug of alumina and the solvent was removed under reduced pressure. The residue was triturated with EtOAc, dissolved in DCM and filtered through a short plug of alumina. The solvent was removed under reduced

pressure to give **13e-open** as a colourless solid (0.70 g, 55 %), mp = 144 - 146° C (from DCM); R_f= 0.5 (30 % EtOAc / hexane); ν_{max} (neat): 2984, 2916, 2602, 2490, 2360, 1475, 1440, 1385 (O-SO_2), 1346, 1289, 1252, 1235, 1200, 1153 (O-SO_2), 1129, 1112, 1066, 1031, 1002 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.92 (app. s, 3H, thienyl-CH_3), 2.17 (app. s, 3H, thienyl-CH_3), 2.26 (app. s, 3H, thienyl-CH_3), 2.30 (s, 6H, N(CH_3)$_2$), 2.38 (app. s, 3H, thienyl-CH_3), 3.52 (dd, *J* = 9.1 Hz, 13.8 Hz, 1H, 3-H), 3.57 (d, *J* = 7.8 Hz, 13.8 Hz, 1H, 3-H), 4.17 (dd, *J* = 7.8 Hz, 9.1 Hz, 1H, 4-H), 6.23 (app. s, 1H, thienyl-H), 6.55 (app. s, 1H, thienyl-H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 13.7, 14.4, 15.0, 15.3, 40.3, 42.5, 63.3, 117.1, 125.9, 126.6, 129.6, 131.4, 134.8, 134.9, 135.3, 138.3, 145.5; HRMS: Found $[M+H]^+$ = 398.0910, $[C_{18}H_{23}NO_3S_3]^+$ requires $[M+H]^+$ = 398.0913.

5,6-Bis(2,5-dimethylthiophen-3-yl)-1,2-oxathiine 2,2-dioxide (14e-open)



4-(Dimethylamino)-5,6-bis(2,5-dimethylthiophen-3-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide **13e-open** (0.40 g, 1.0 mmol) was dissolved in DCM (10 mL) and cooled to 2° C. A solution of *m*-chloroperoxybenzoic acid (0.30 g, 1.3 mmol, 1.3 eq) in DCM (15 mL) was added drop wise over 15 min, with the temperature maintained between 0 °C and 3 °C. The resulting mixture was warmed to room temperature over 3h. A further portion of *m*-CPBA (0.6 eq) was added at this time and the reaction was stirred at room temperature for a further 1.5 h to ensure complete consumption of the starting 3,4-dihyro-1,2-oxathiine. The resulting mixture was washed sequentially with H_2O (10 mL), aqueous Na_2SO_3 (0.667 M, 15 mL), aqueous NaOH (1 M, 10 mL) and H_2O (10 mL). The organic phase was dried using Na_2SO_4 and the solvent removed under reduced pressure to give **14e-open** as a pale pink solid (0.27 g, 78 %), mp = 145 - 146° C (from DCM); R_f = 0.2 (30 % EtOAc / Hexane); ν_{max} (neat): 3064, 2916, 1622, 1557, 1545, 1494, 1442, 1363 (O-SO_2), 1249, 1223, 1186, 1174 (O-SO_2), 1141, 1115, 1055 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.90 (app. s, 3H, thienyl-CH_3), 2.28 (app. s, 3H, thienyl-CH_3), 2.32(app. s, 3H, thienyl-CH_3), 2.40 (app. s, 3H, thienyl-CH_3), 6.22 (app. s, 1H, thienyl-H), 6.48 (app. s, 1H, thienyl-H), 6.61 (d, *J* = 10.2 Hz, 1H, 4-H), 6.90 (d, *J* = 10.2 Hz, 1H, 3-H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 13.6, 14.7, 15.0, 15.3, 112.7, 118.1, 125.0, 125.5, 128.3, 130.4, 135.1, 136.0, 137.3, 139.0, 141.8, 150.8; HRMS: Found $[M+NH_4]^+$= 370.0587, $[C_{16}H_{16}O_3S_3]^+$ requires $[M+NH_4]^+$= 370.0600.

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2. B. Unterhalt, P. Gores, *Arch Pharm*., 1989, **322**, 839–840.
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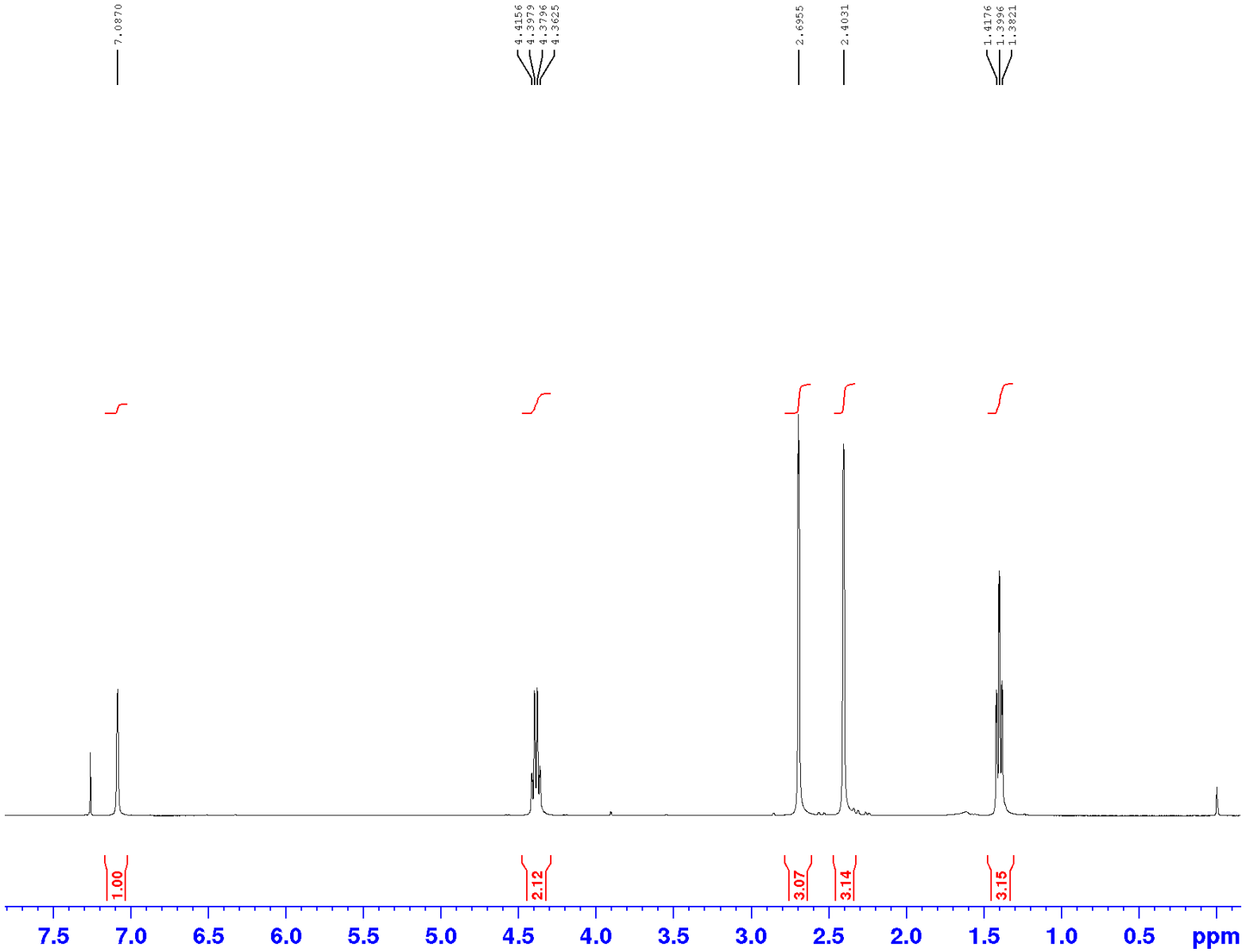
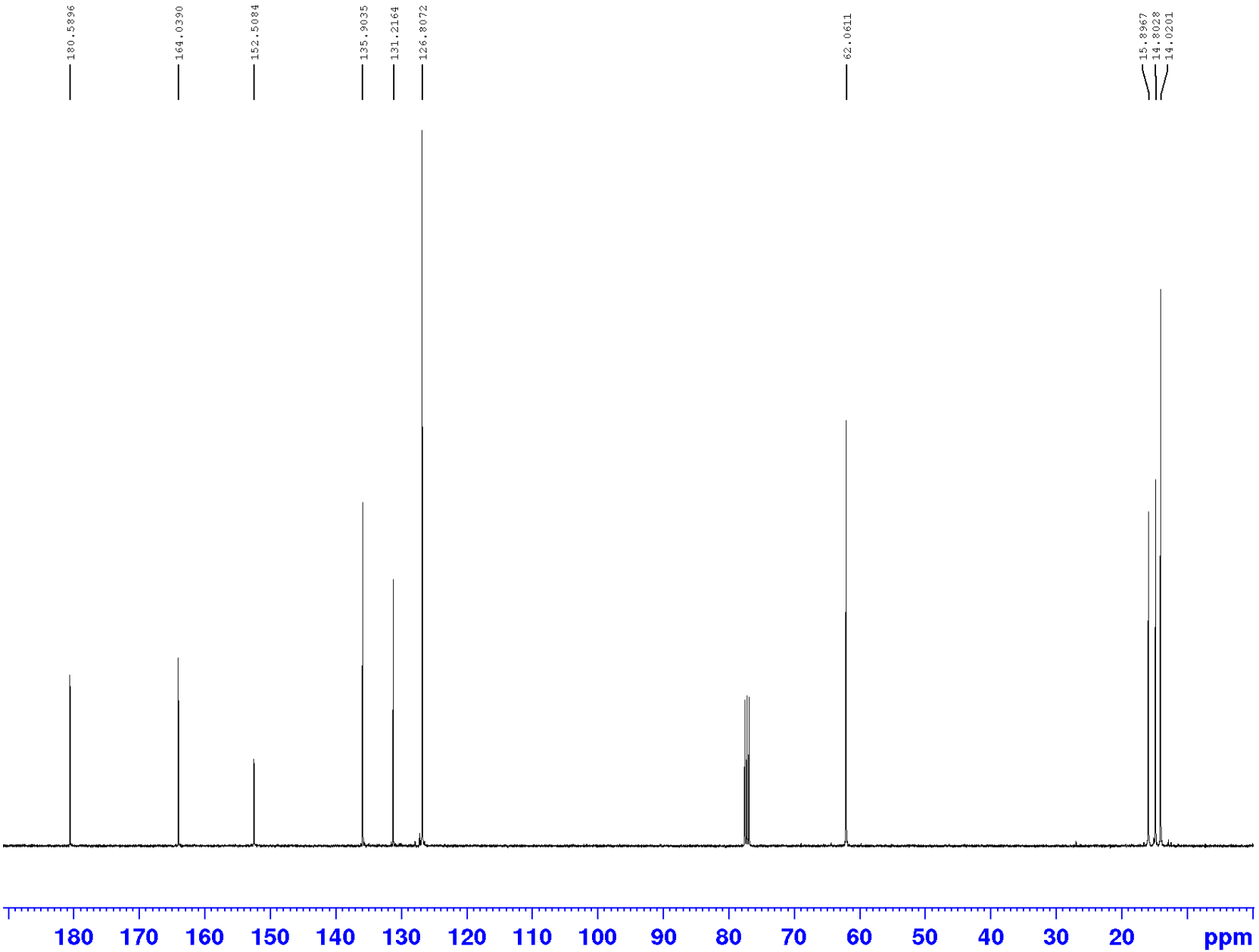
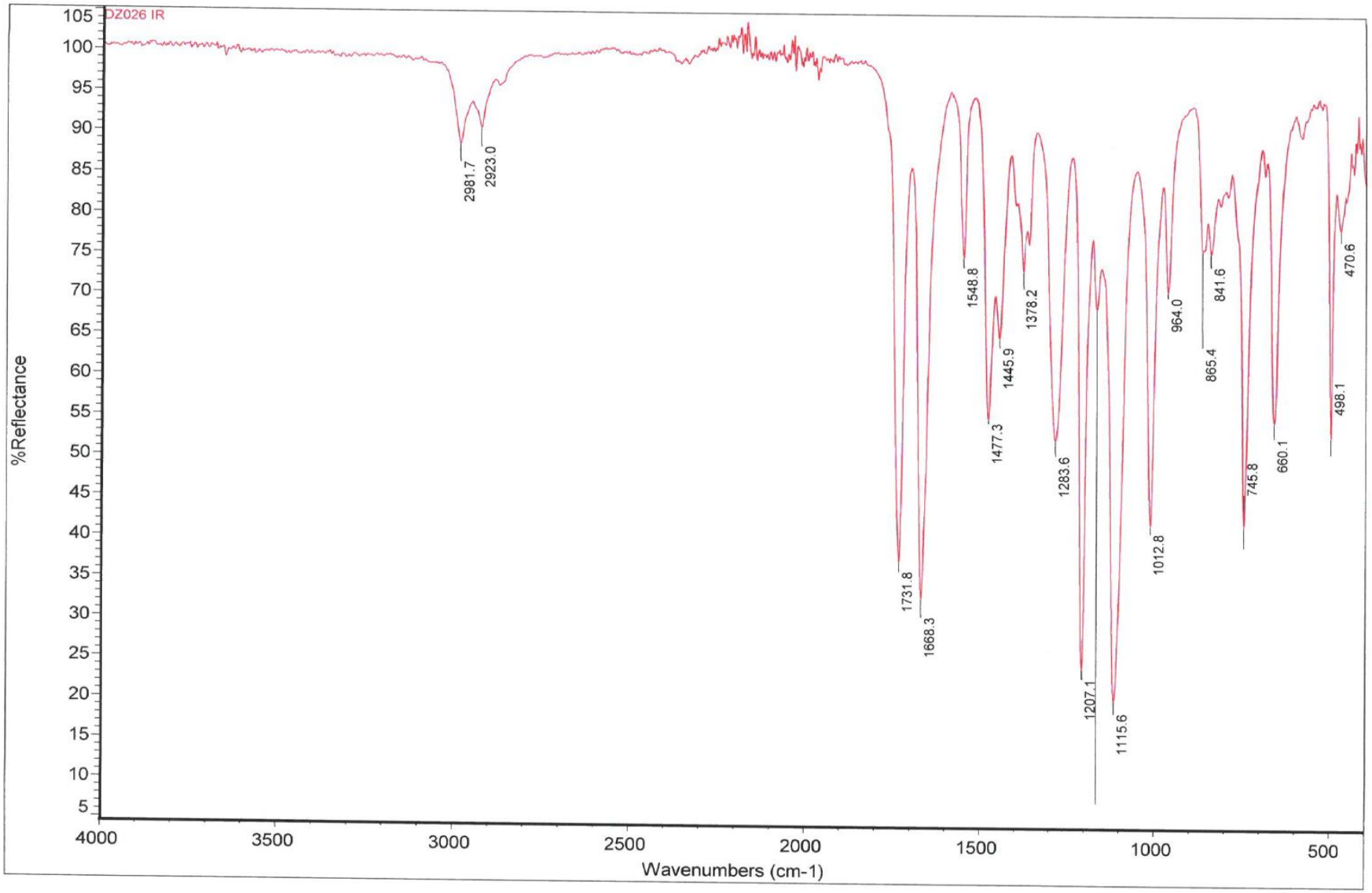
^{1}H-NMR spectrum of 3



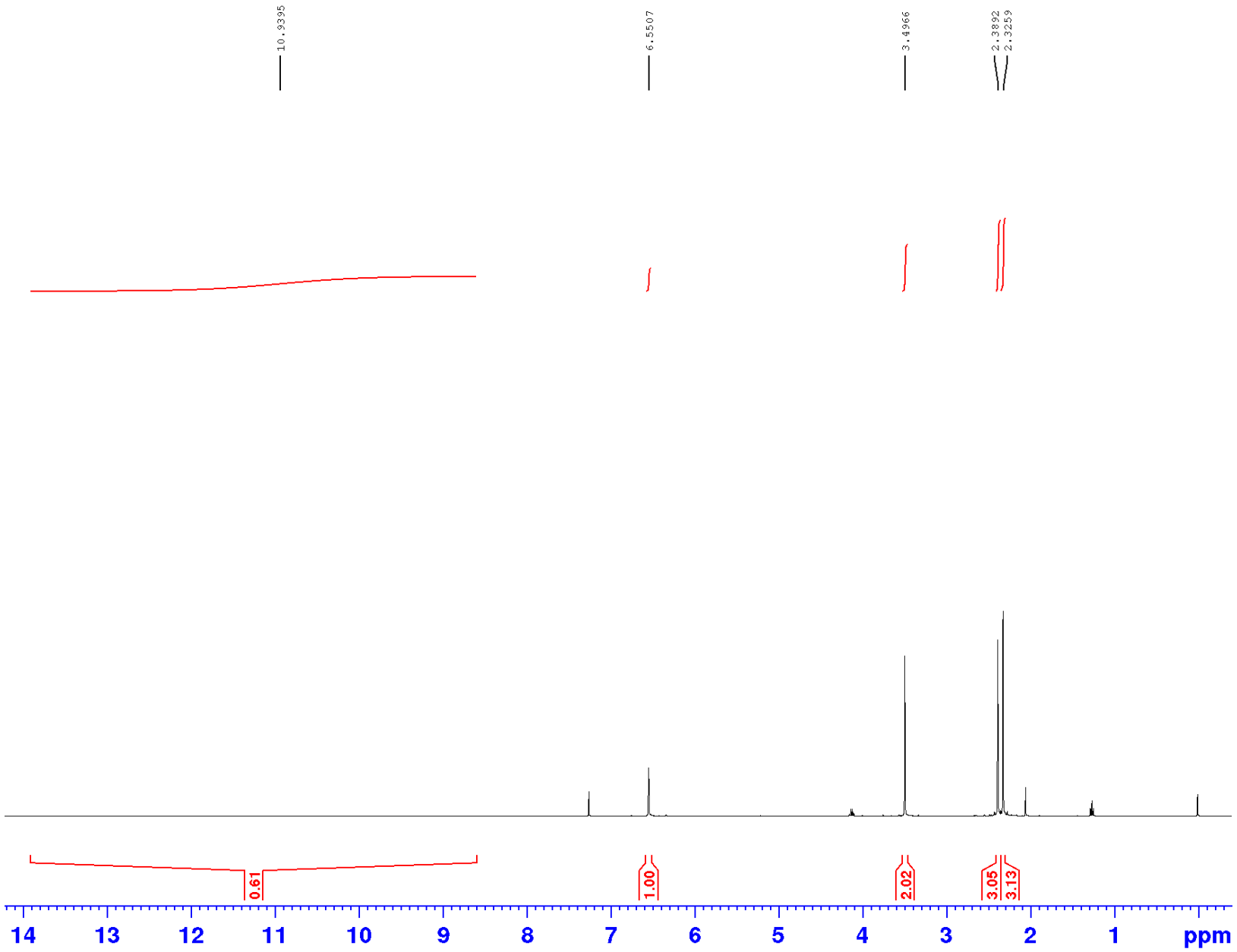
^{13}C-NMR spectrum of 3



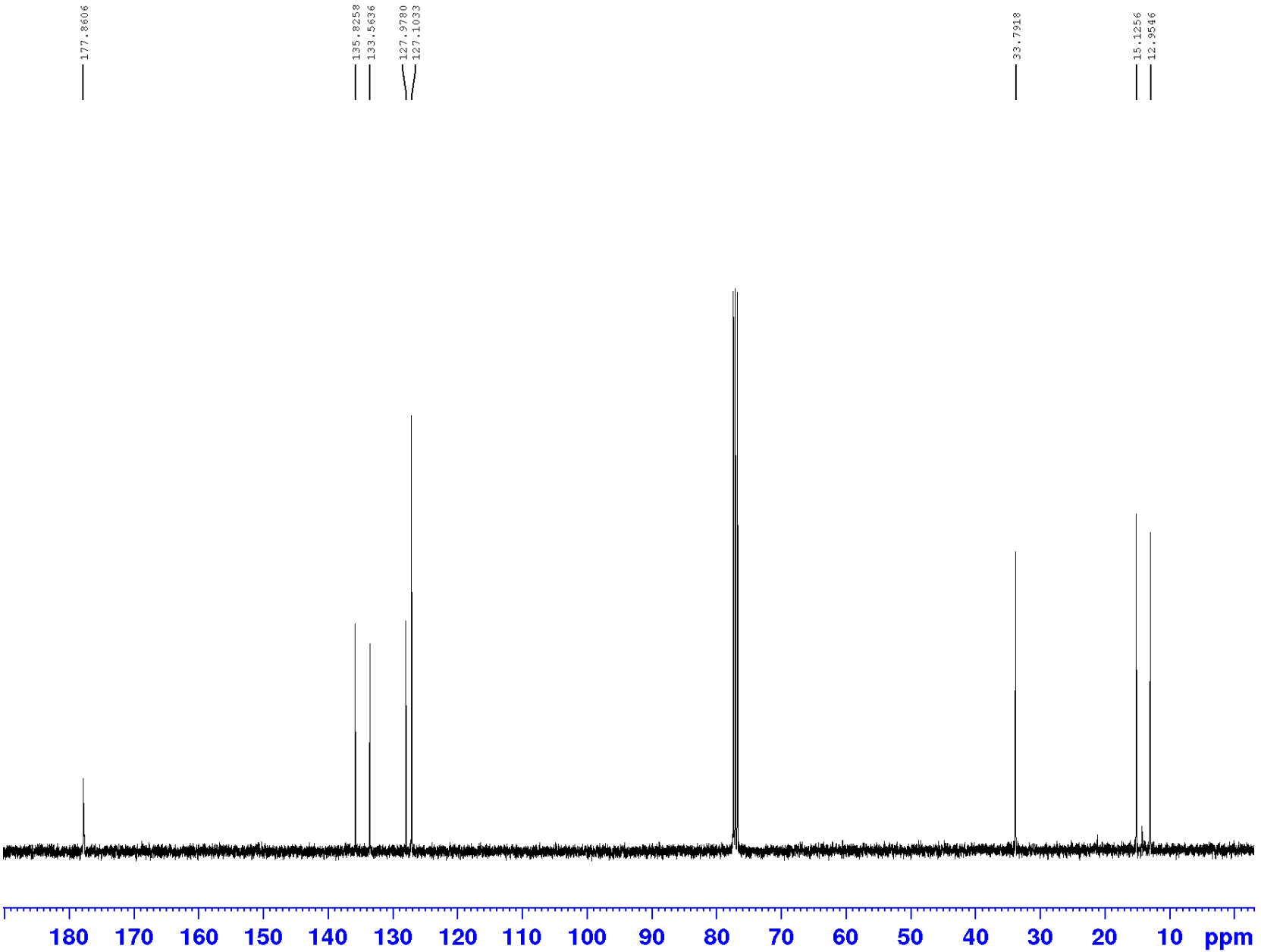
IR spectrum of 3



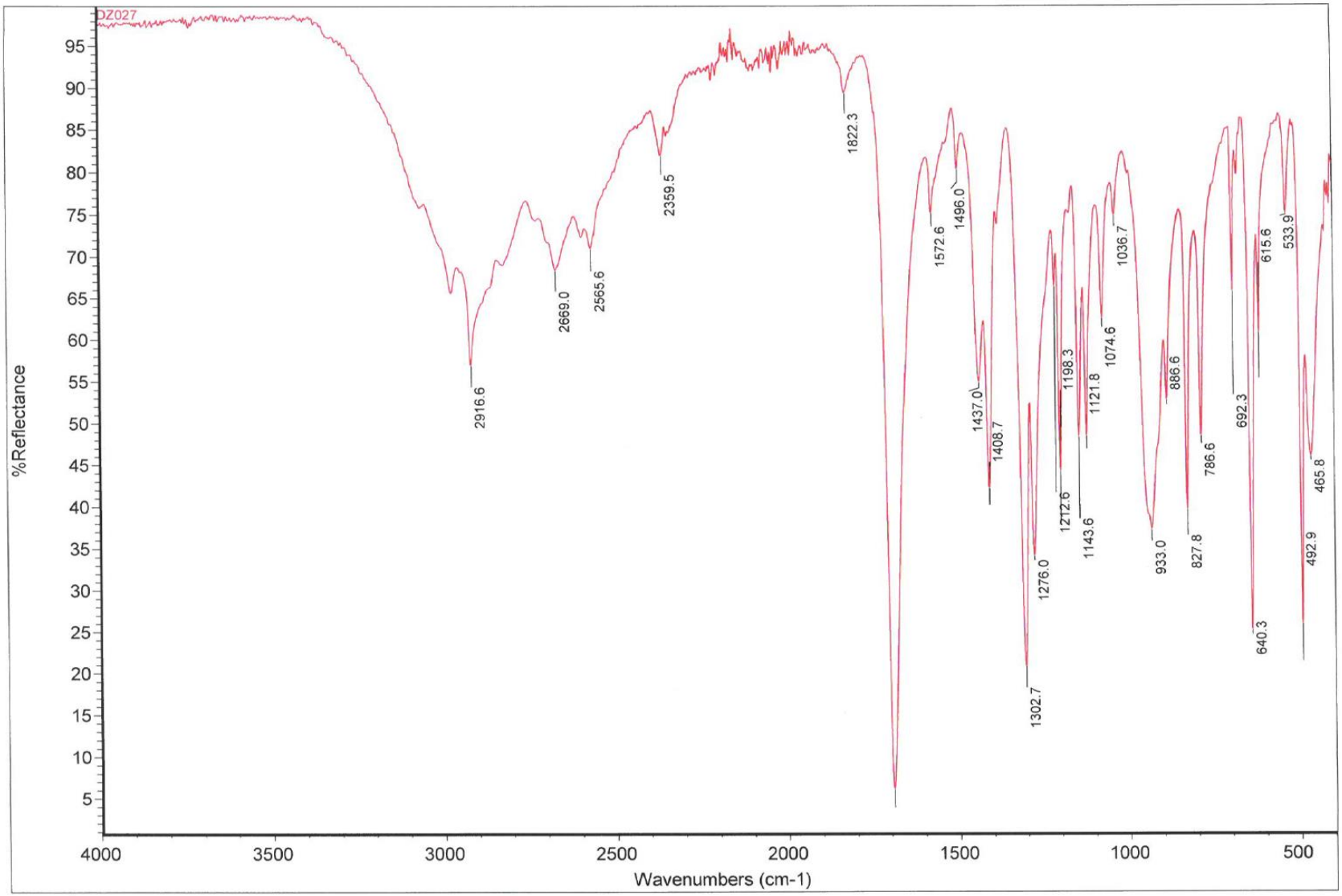
^{1}H-NMR spectrum of 4



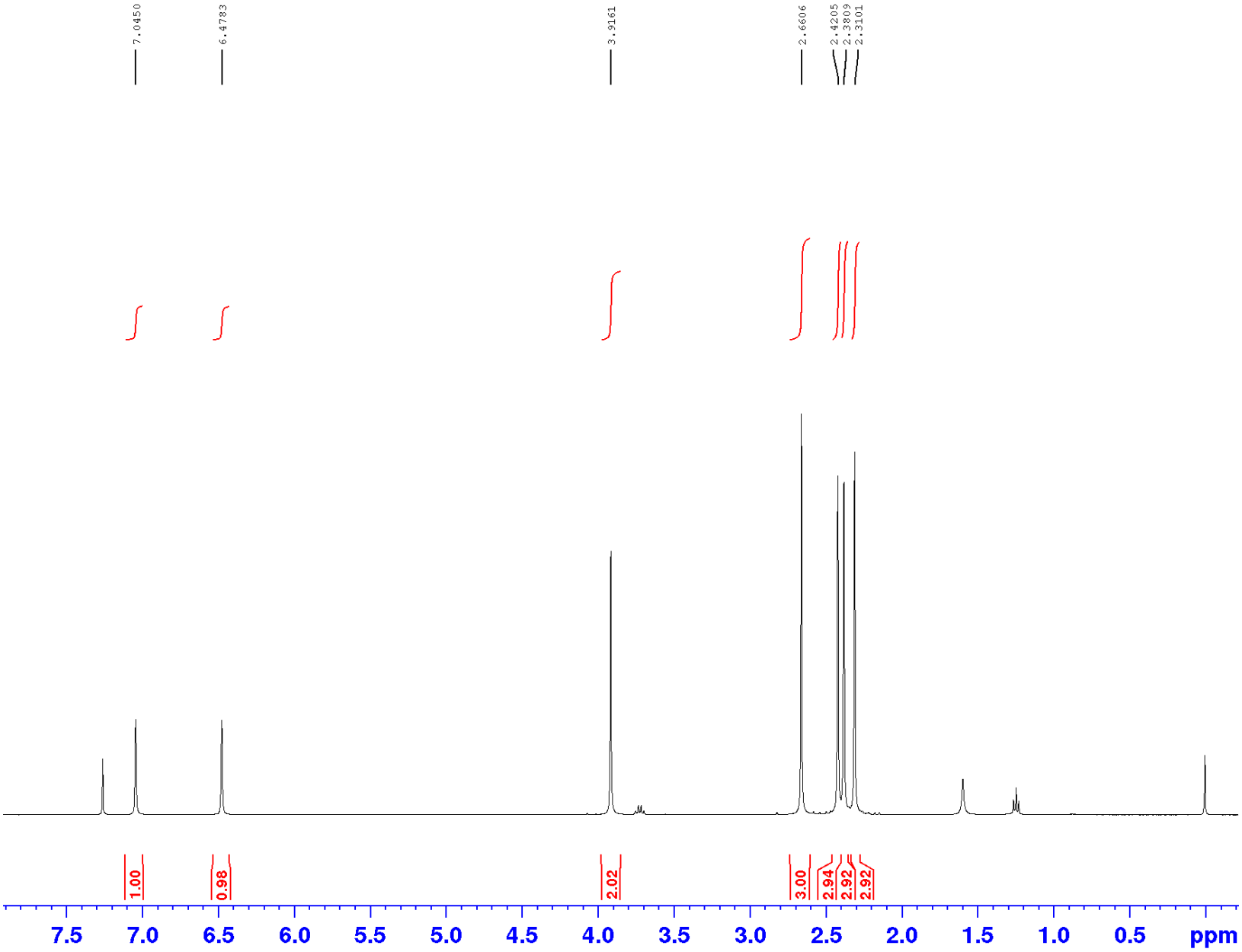
^{13}C-NMR spectrum of 4



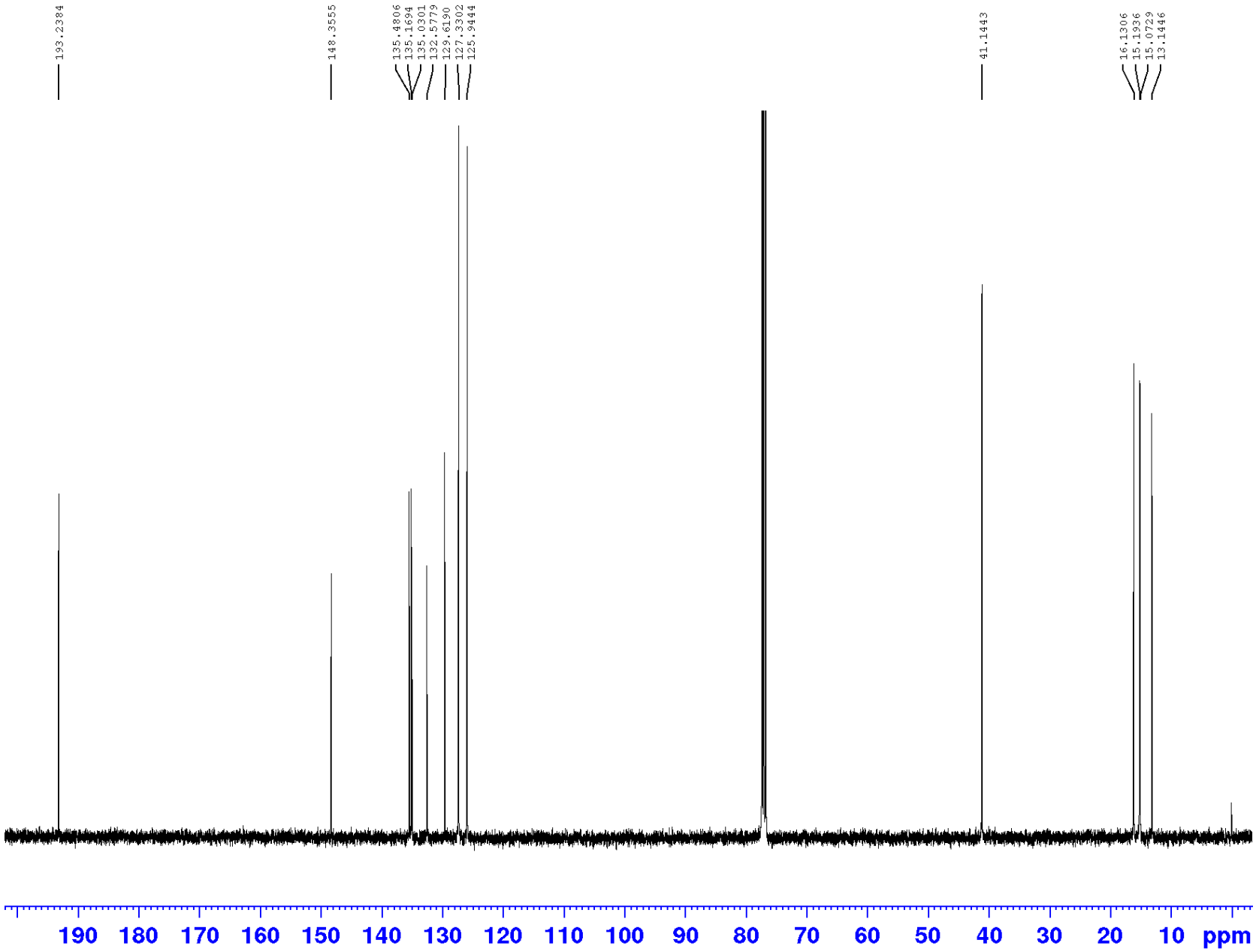
IR spectrum of 4



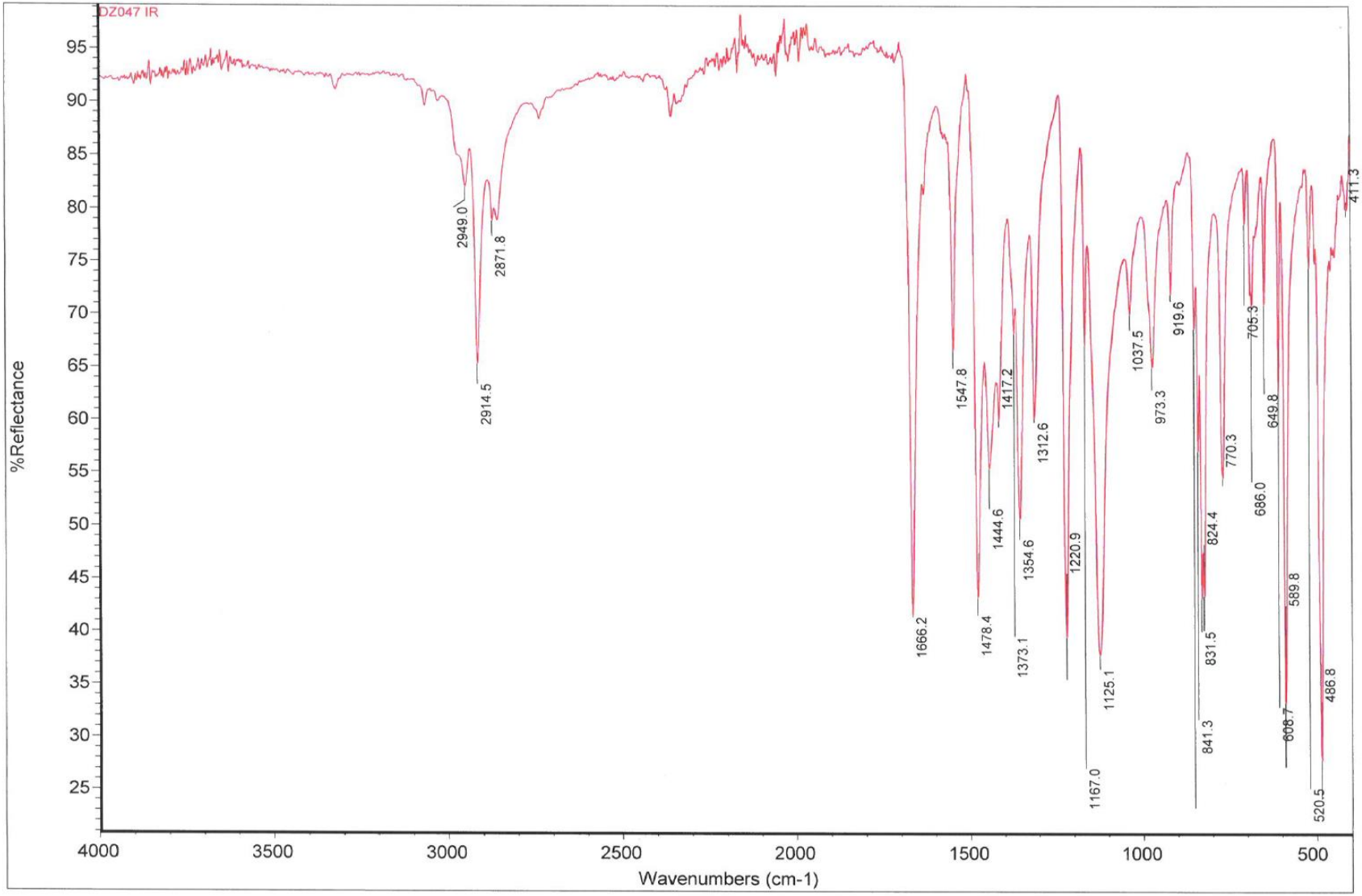
^{1}H-NMR spectrum of 6



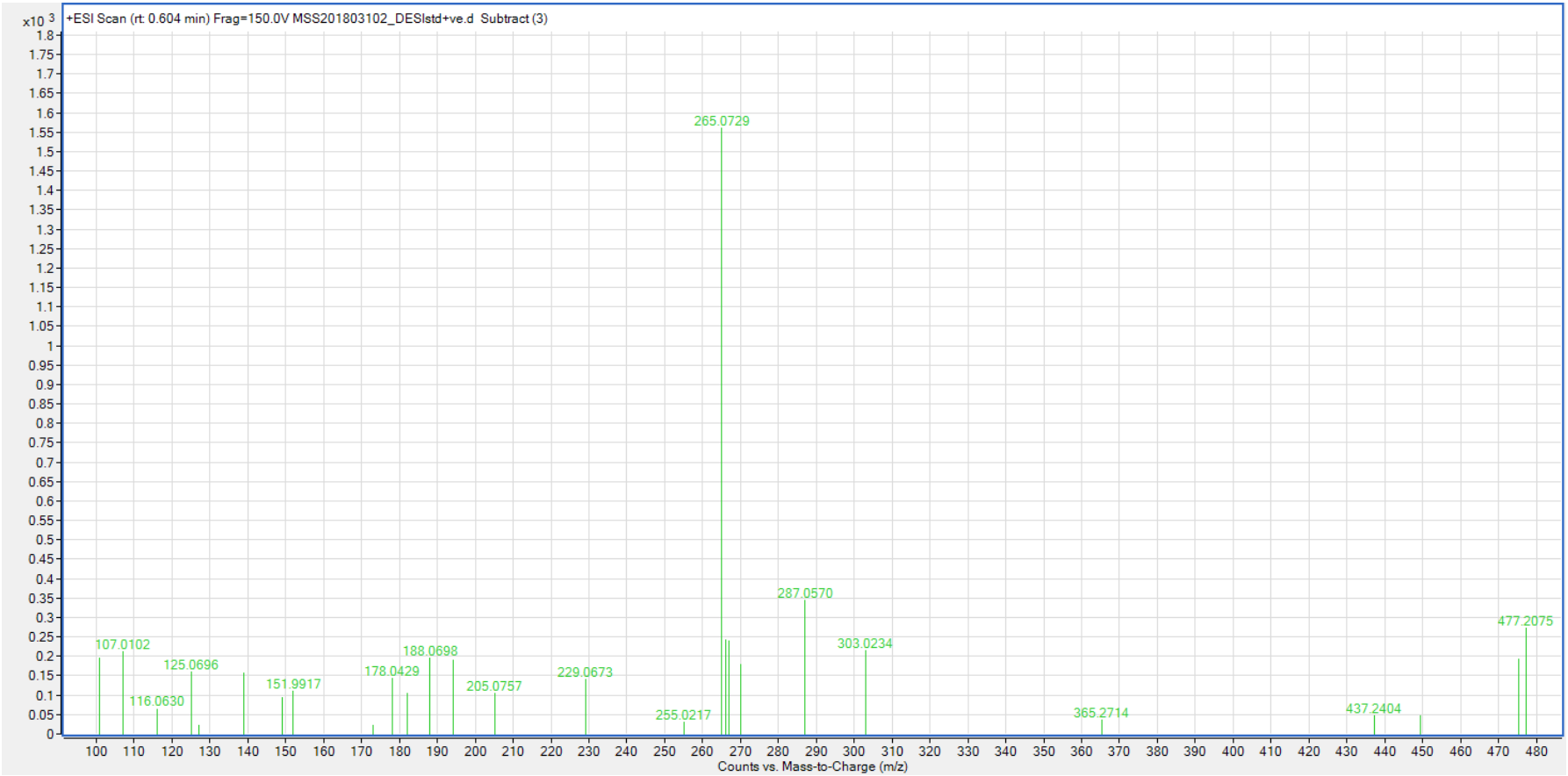
^{13}C-NMR spectrum of 6



IR spectrum of 6

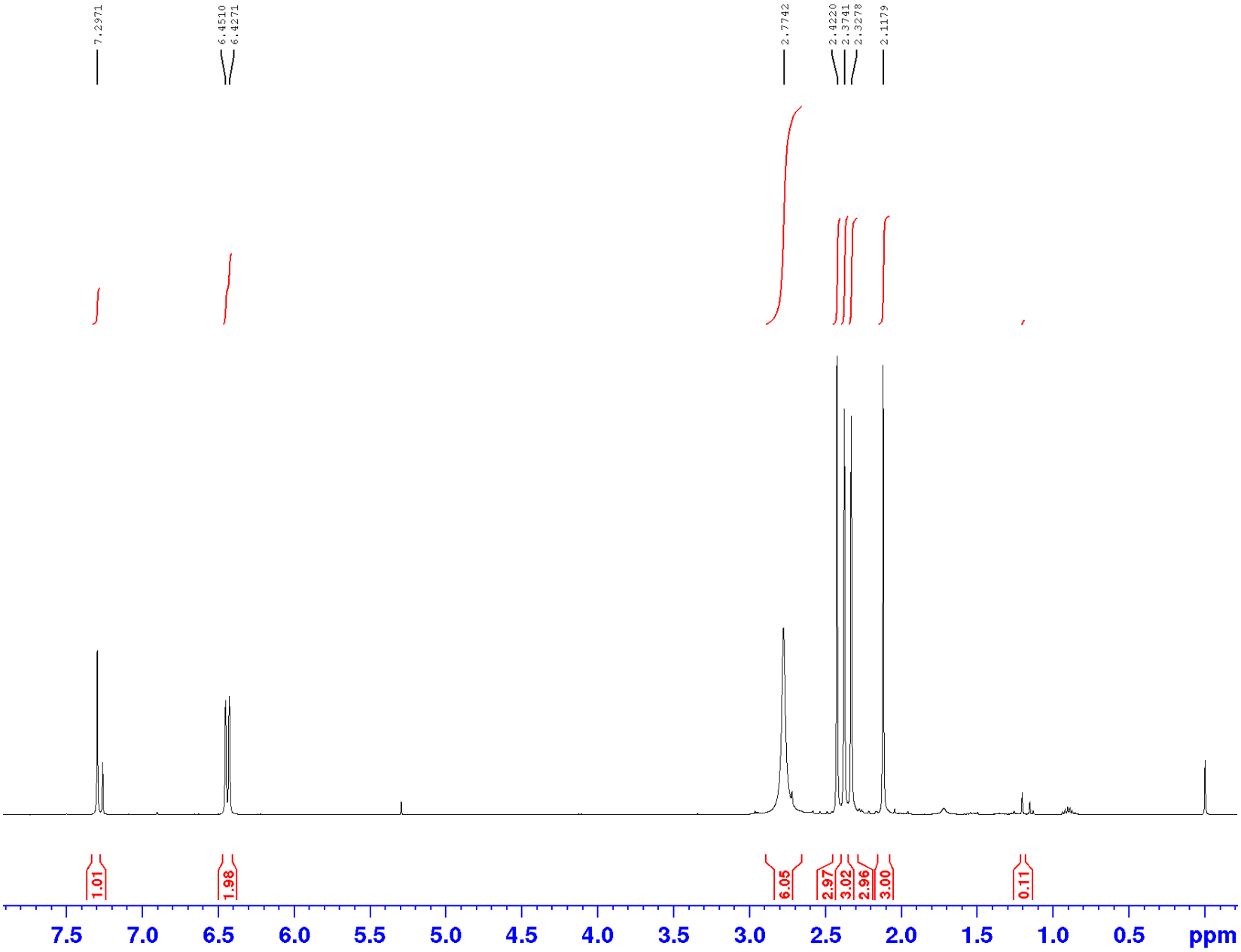


Mass spectrum of 6

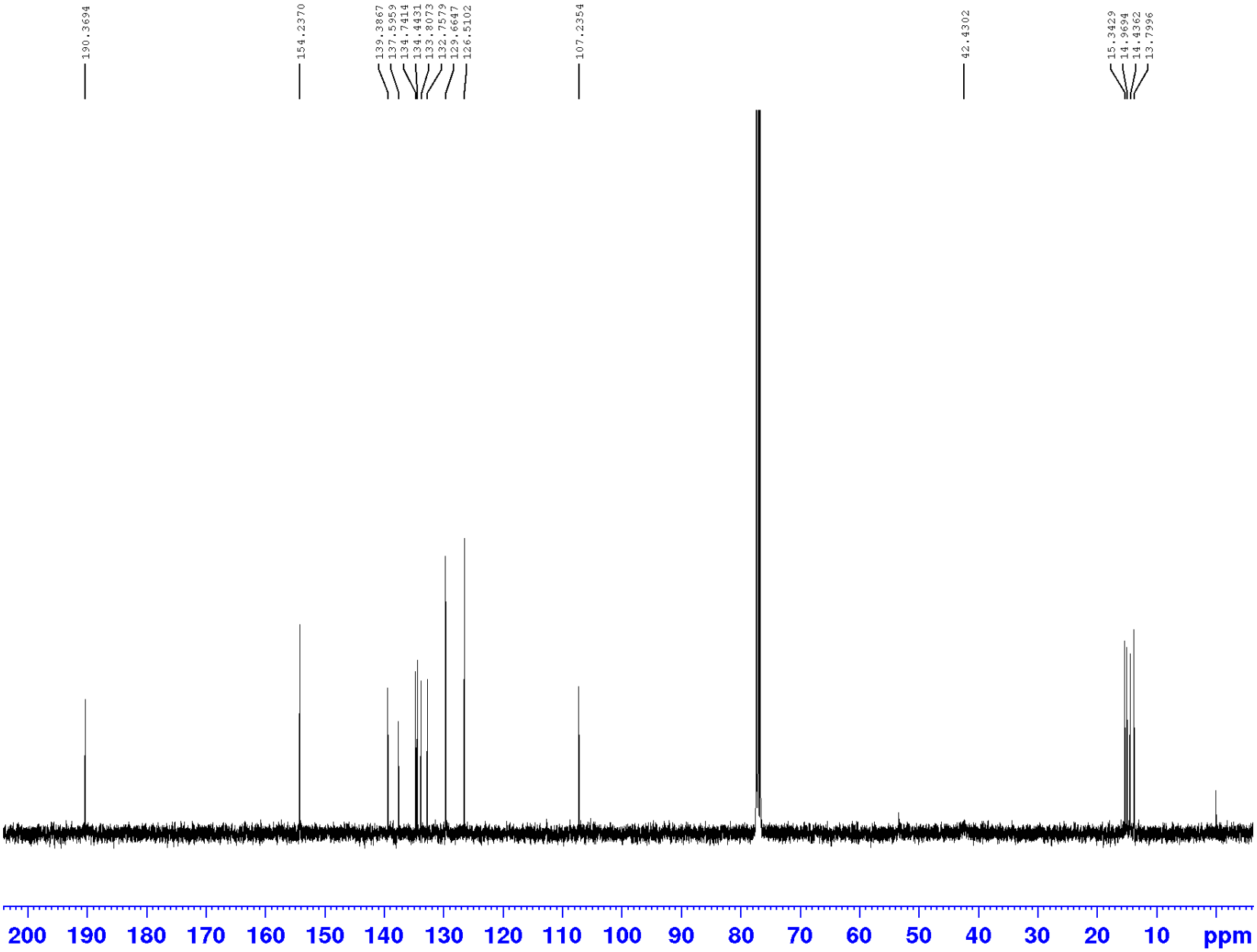


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C14 H16 O S2	(M+H)+	265.0729	264.065	264.0643	78.68	-2.69
C8 H14 N3 O5 S	(M+H)+	265.0729	264.0649	264.0654	67.97	1.81
C12 H14 N3 S2	(M+H)+	265.0729	264.0651	264.0629	64.13	-8.16
C13 H12 O6	(M+H)+	265.0729	264.064	264.0634	63.77	-2.2
C14 H8 N4 O2	(M+H)+	265.0729	264.064	264.0647	60.4	2.57
C10 H16 O6 S	(M+H)+	265.0729	264.0648	264.0668	59.47	7.41
C16 H10 N O3	(M+H)+	265.0729	264.0639	264.0661	48.79	8.1
C11 H12 N4 O2 S	(M+H)+	265.0729	264.065	264.0681	42.96	11.91
C19 H8 N2	(M+H)+	265.0729	264.0639	264.0687	21.35	18.4

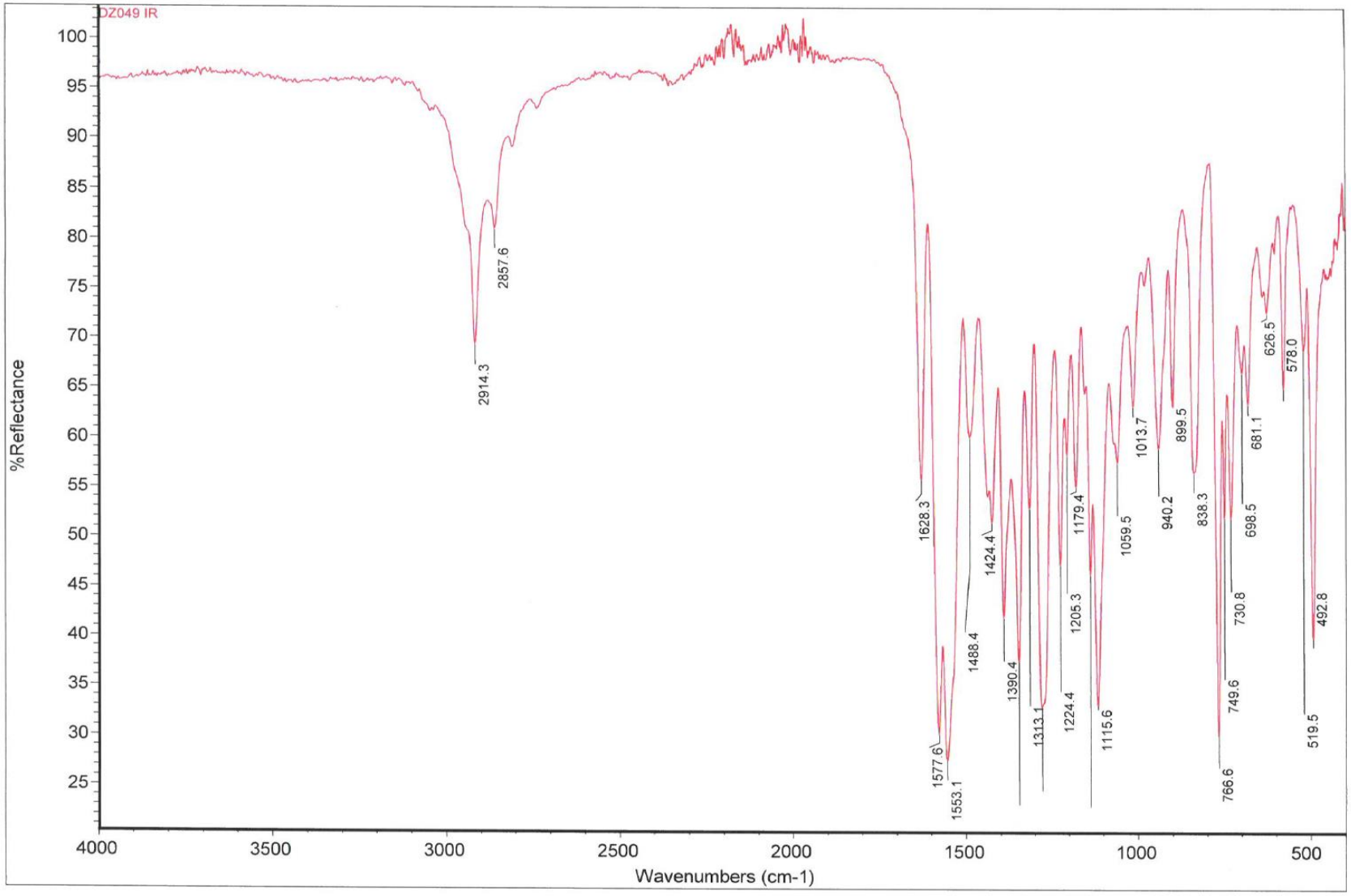
^{1}H-NMR spectrum of 12a



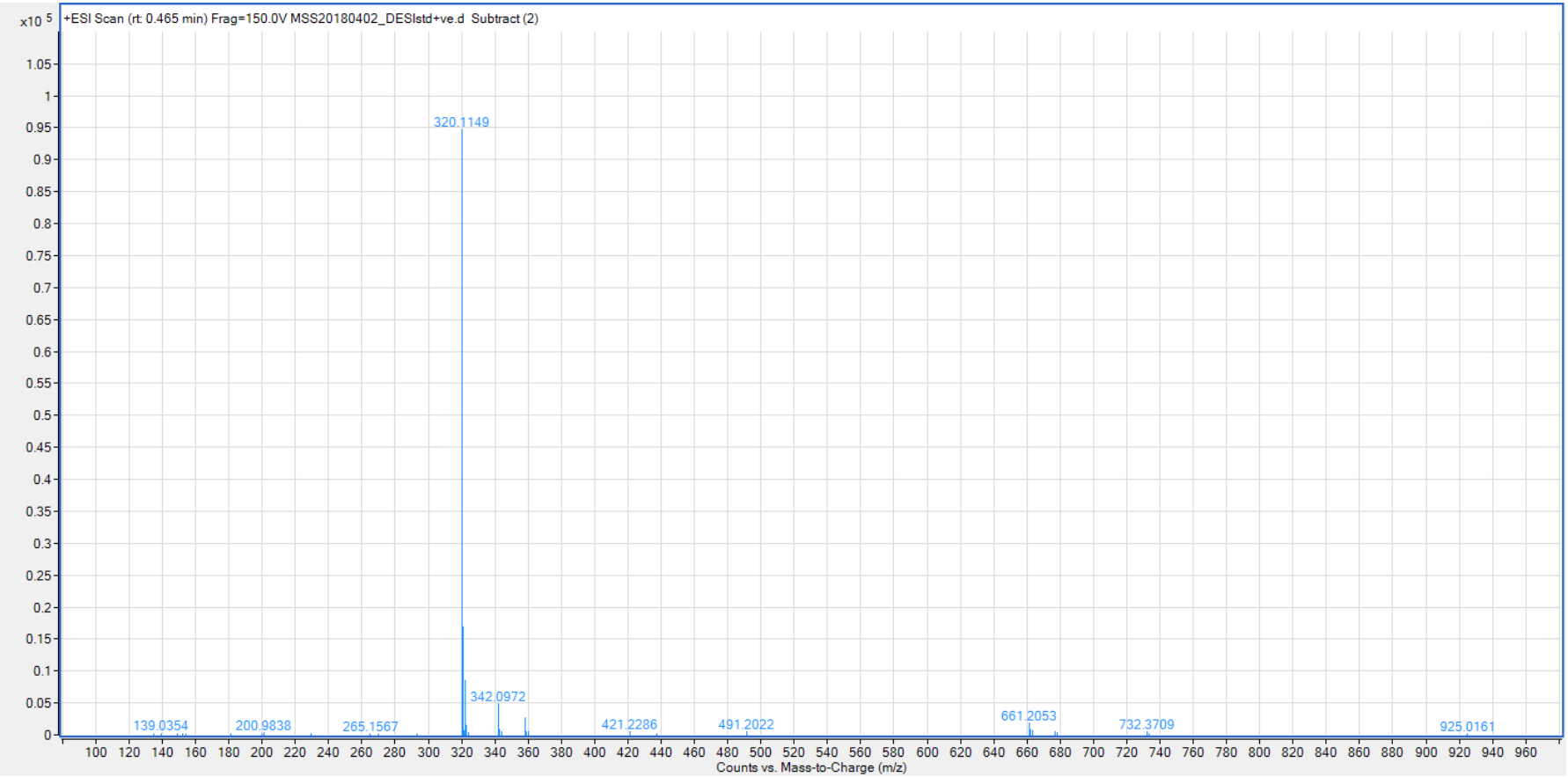
^{13}C-NMR spectrum of 12a



IR spectrum of 12a

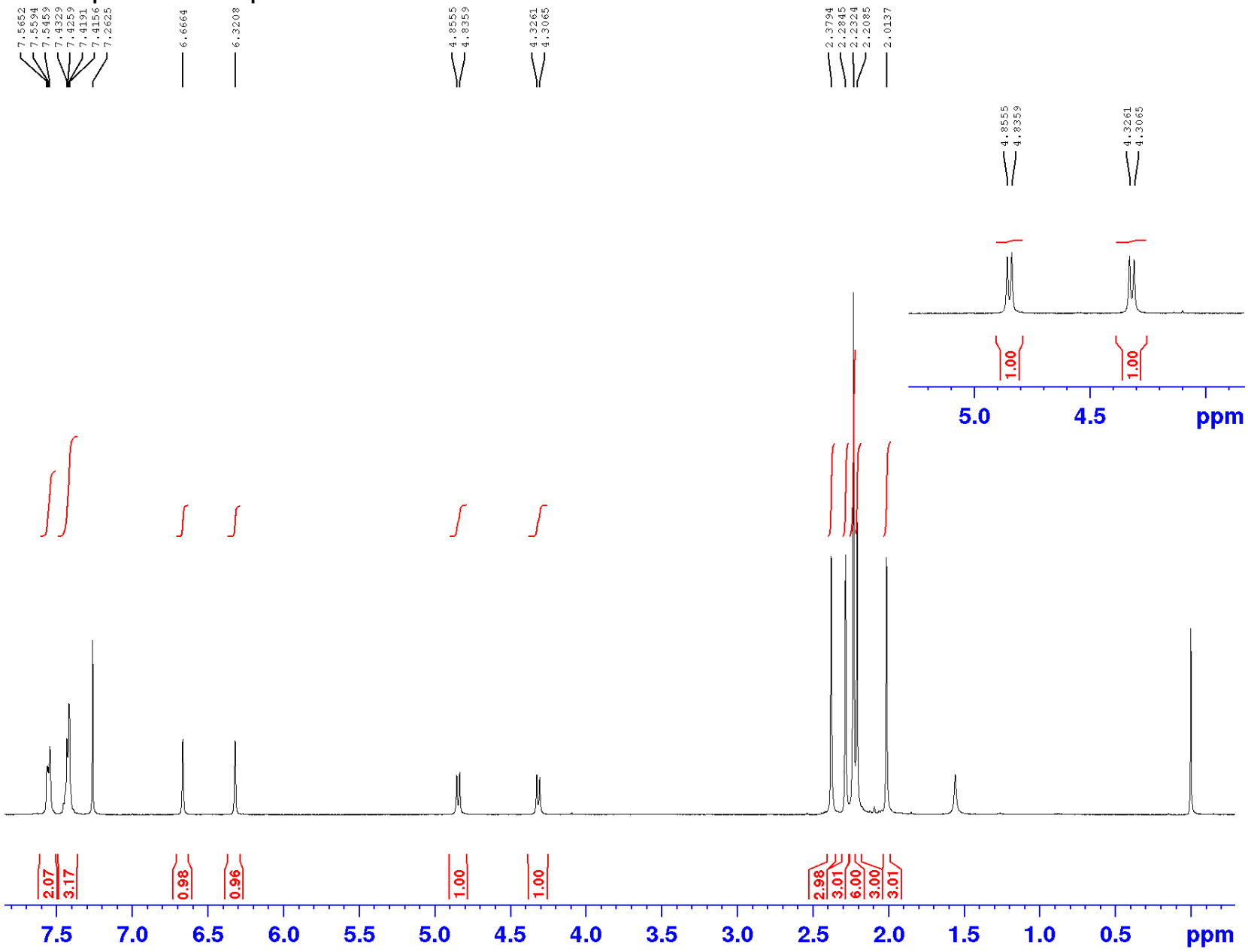


Mass spectrum of 12a

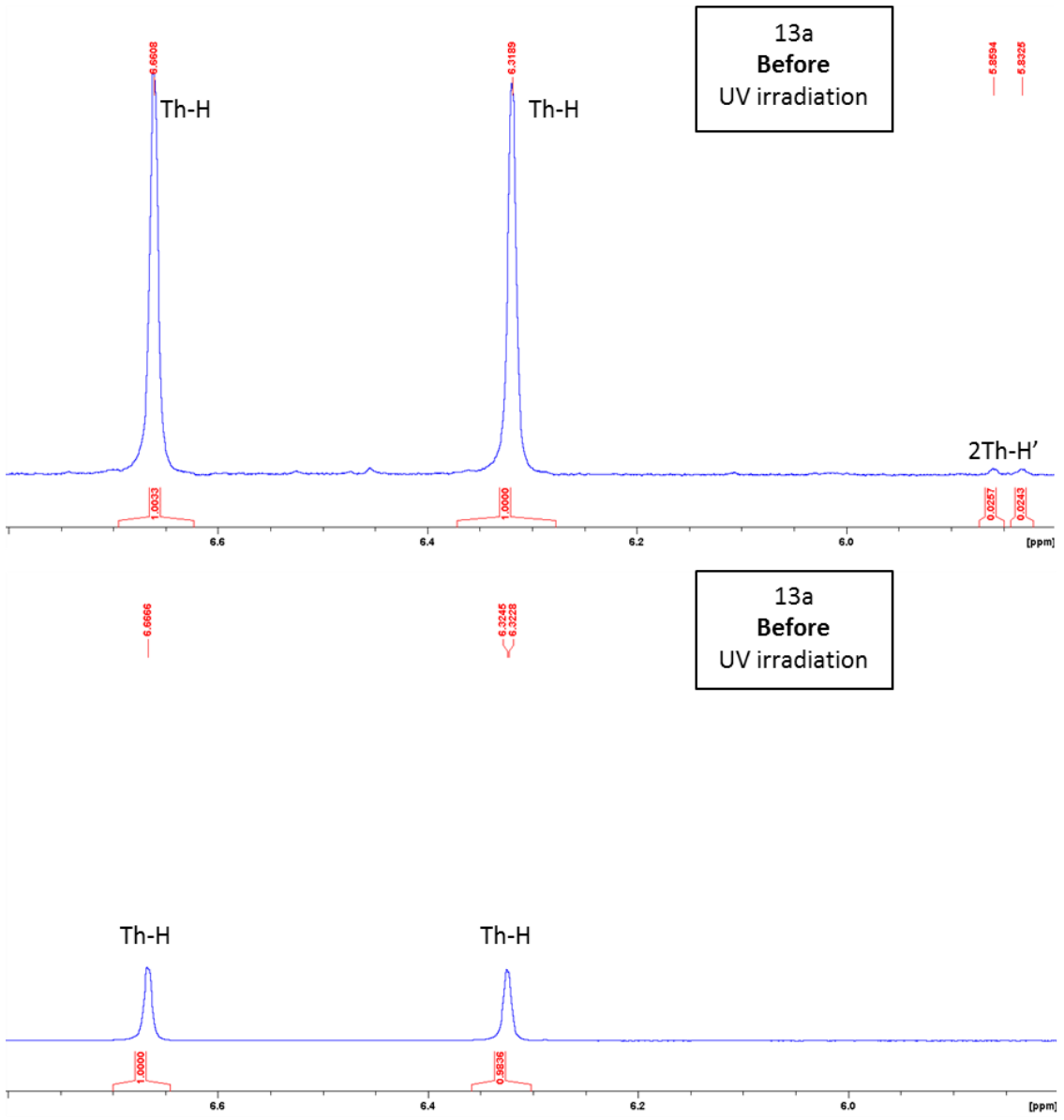


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C11 H19 N4 O5 S	(M+H)+	320.1149	319.1077	319.1076	47.61	-0.13
C19 H15 N2 O3	(M+H)+	320.1149	319.1077	319.1083	46.4	1.91
C17 H21 N O S2	(M+H)+	320.1149	319.1077	319.1065	43.07	-3.77
C13 H21 N O6 S	(M+H)+	320.1149	319.1077	319.109	42.34	4.07
C10 H23 O9 S	(M+H)+	320.1149	319.1077	319.1063	41.72	-4.32
C16 H17 N O6	(M+H)+	320.1149	319.1077	319.1056	35.35	-6.49
C15 H19 N4 S2	(M+H)+	320.1149	319.1077	319.1051	30.36	-7.97
C23 H43	(M+H)+	320.3400	319.3324	319.3365	29.44	12.67
C8 H21 N3 O8 S	(M+H)+	320.1149	319.1077	319.1049	28.44	-8.53

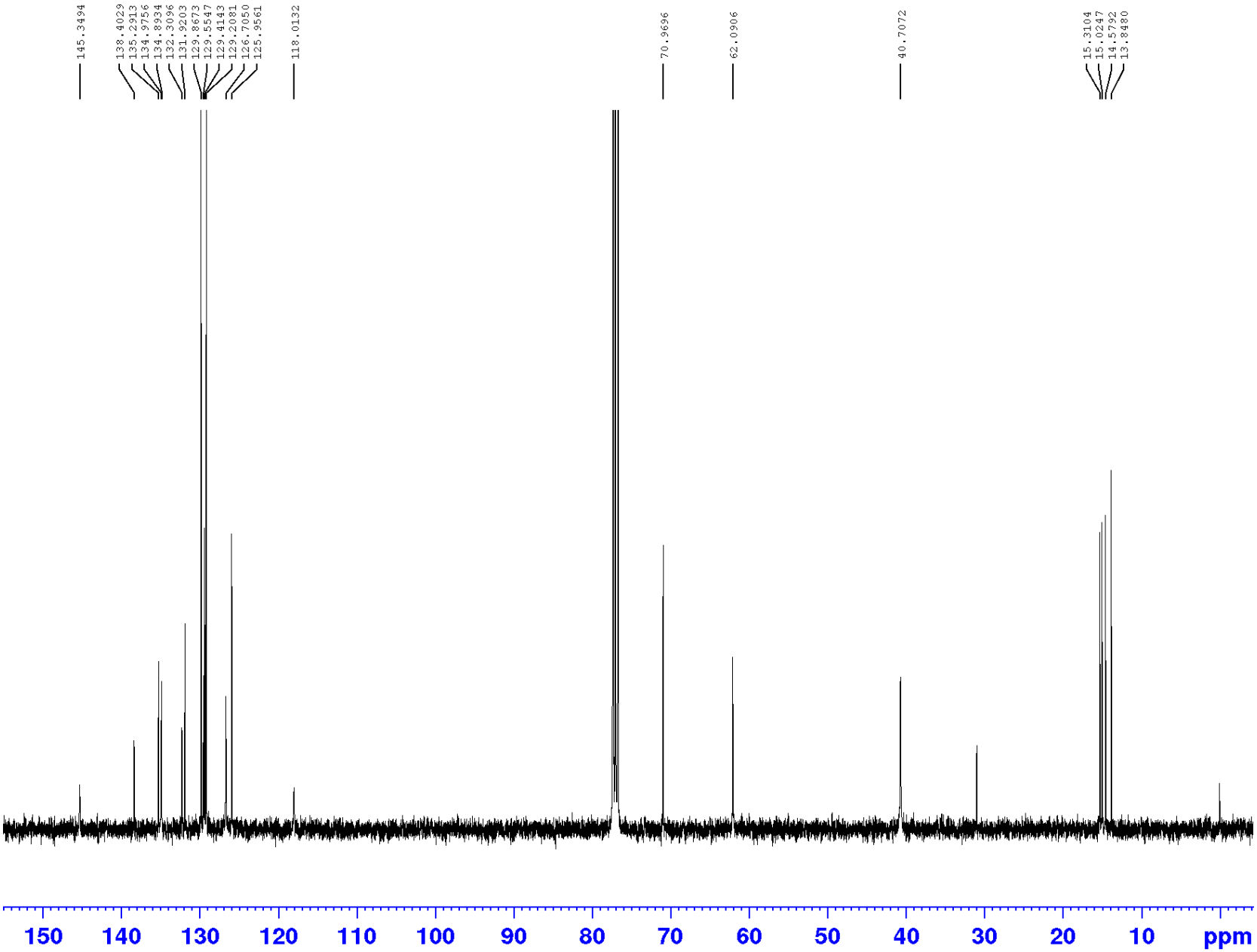
^{1}H-NMR spectrum of 13a-open



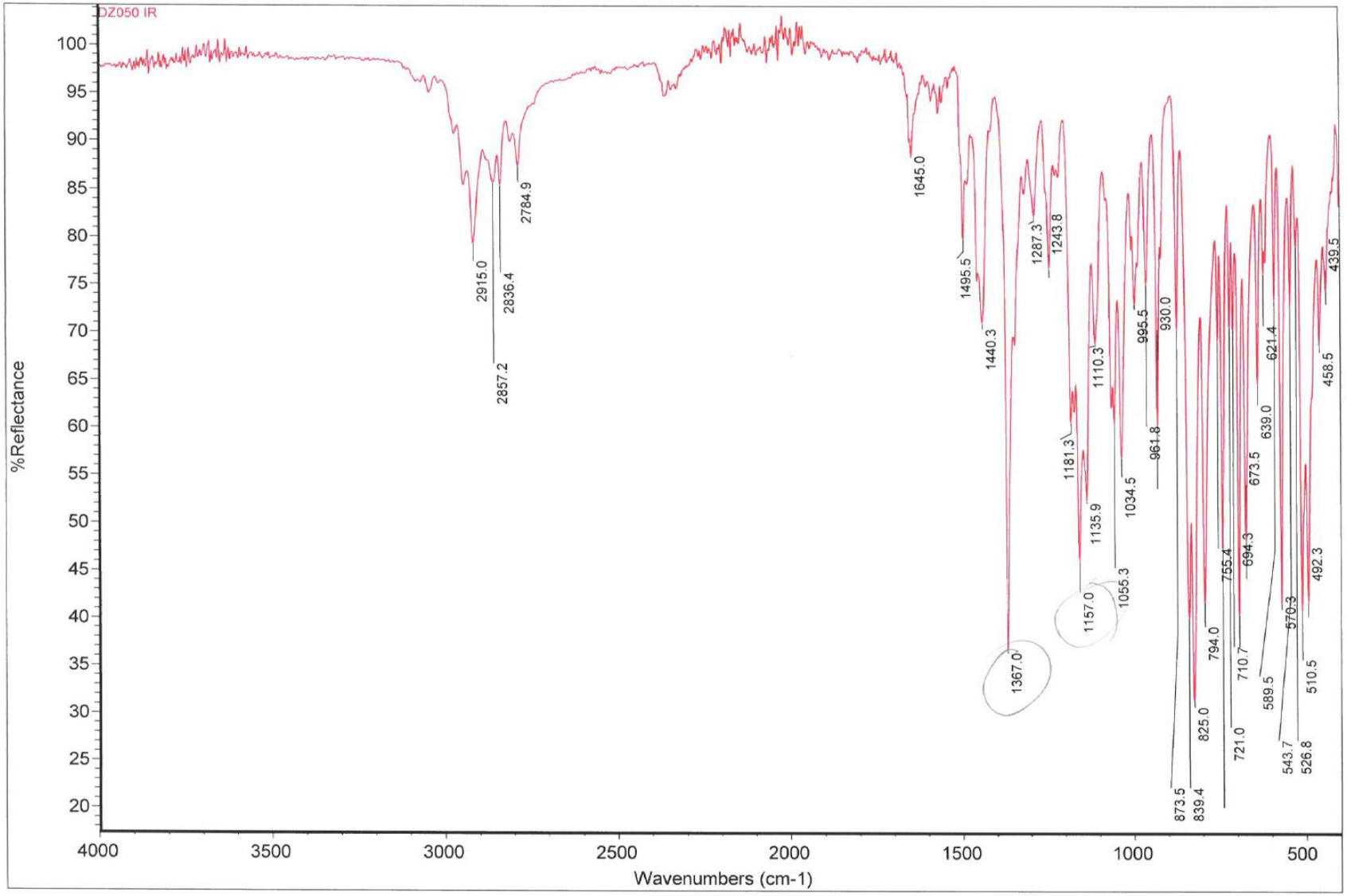
^{1}H NMR spectra (δ 4.8 – 7.8, $CDCl_3$) showing signals for evolution of 13a-closed from 13a-open.



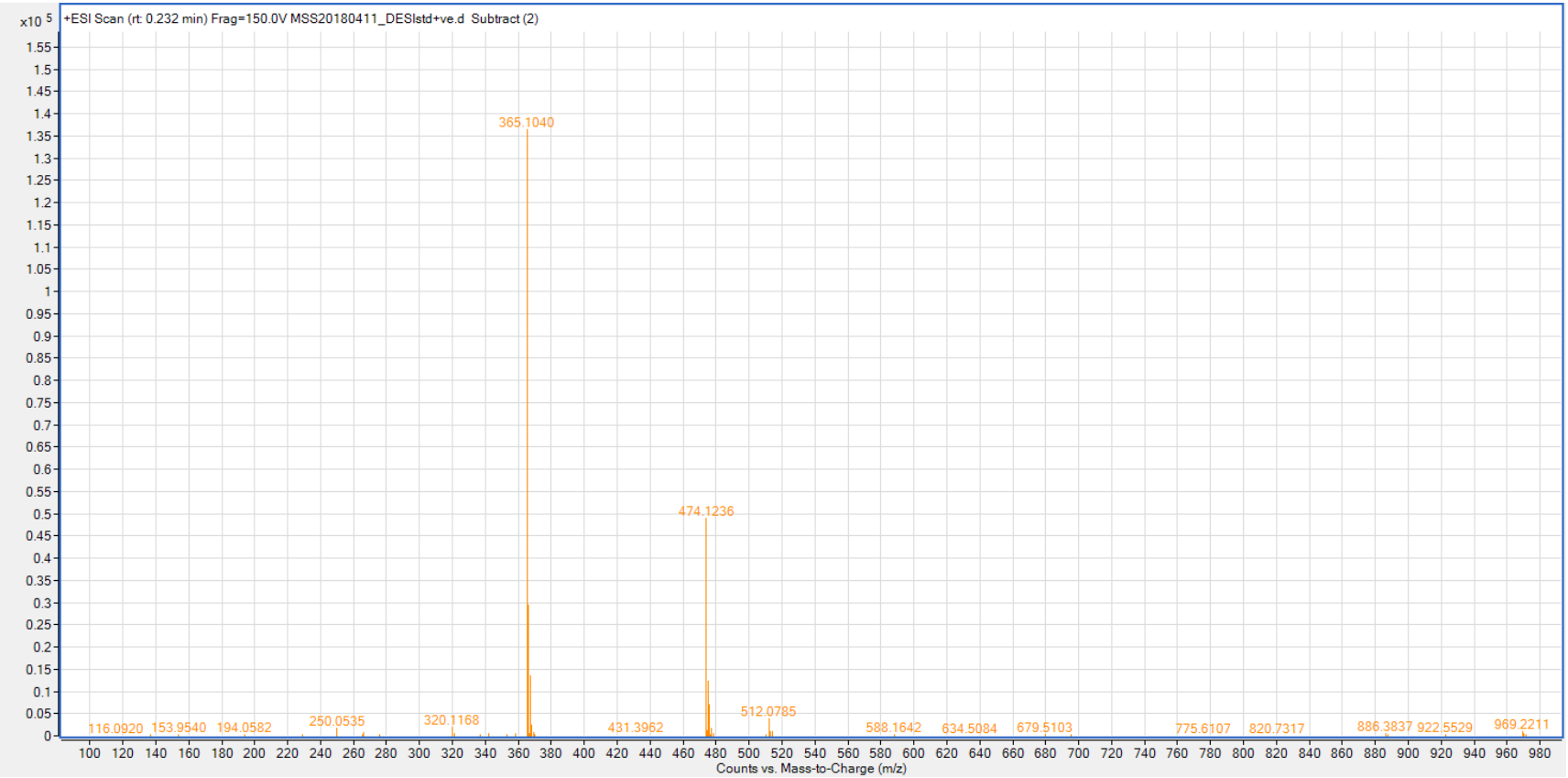
^{13}C-NMR spectrum of 13a-open



IR spectrum of 13a-open

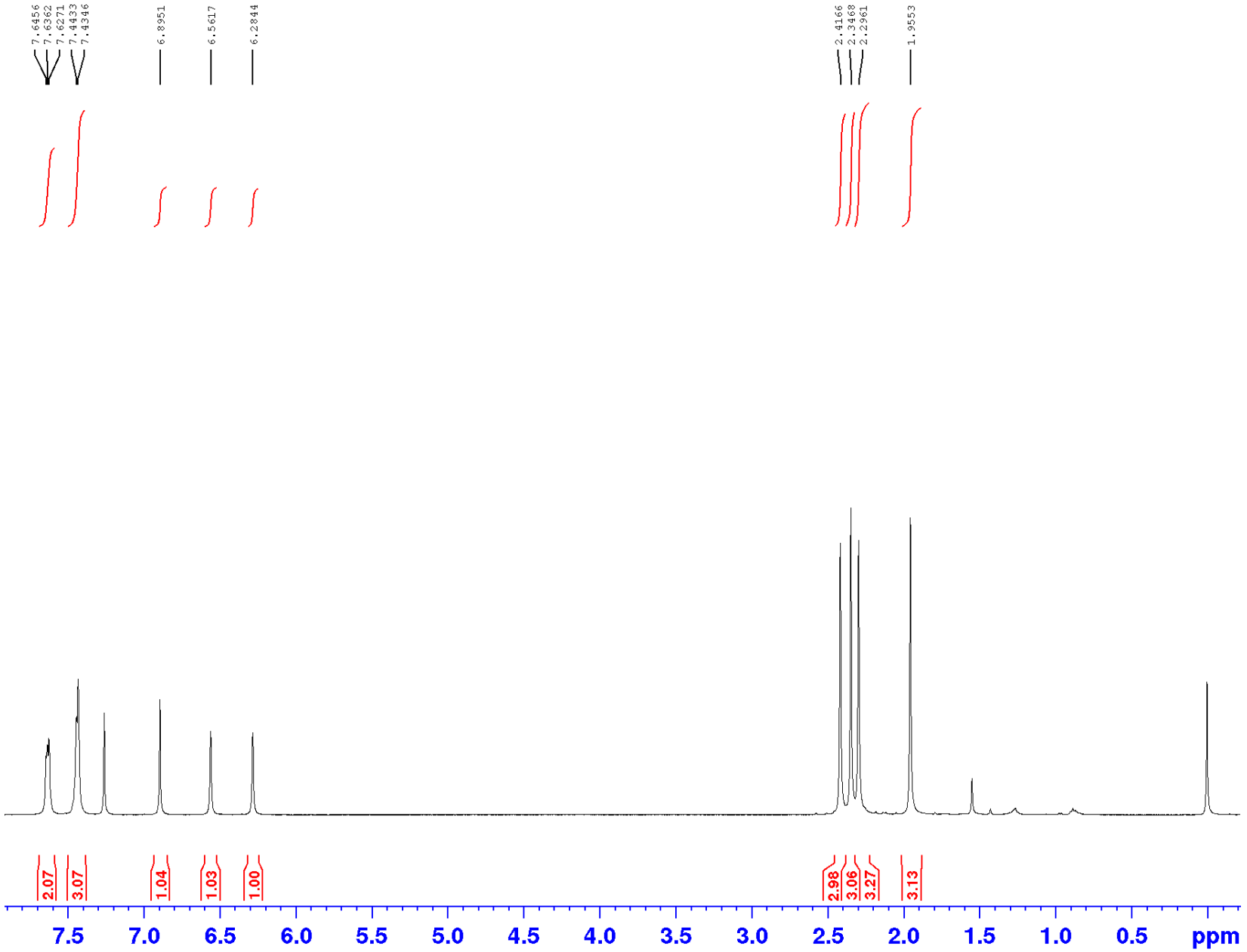


Mass spectrum of 13a-open

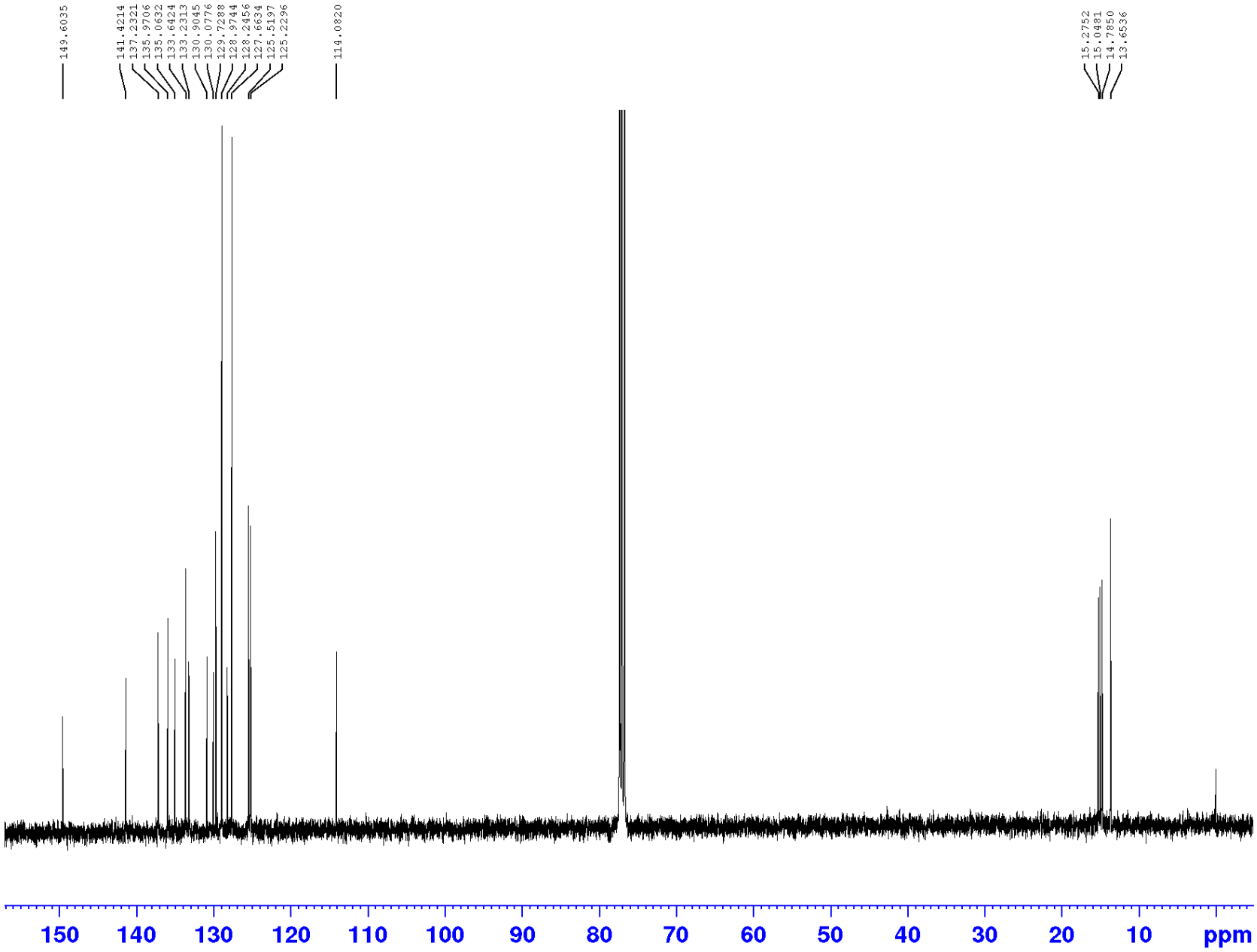


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C18 H25 N4 O7 S2	(M+H)+	474.1236	473.1165	473.1165	95.62	-0.06
C20 H27 N O8 S2	(M+H)+	474.1236	473.1164	473.1178	92.3	2.97
C24 H27 N O3 S3	(M+H)+	474.1236	473.1165	473.1153	90.3	-2.47
C19 H29 N4 O2 S4	(M+H)+	474.1236	473.1167	473.1173	86.45	1.42
C18 H33 O6 S4	(M+H)+	474.1236	473.1166	473.116	85.31	-1.25
C27 H25 N2 S3	(M+H)+	474.1236	473.1165	473.118	85.13	3.23
C26 H21 N2 O5 S	(M+H)+	474.1236	473.1162	473.1171	83.98	2.04
C23 H23 N O8 S	(M+H)+	474.1236	473.1162	473.1144	83.47	-3.65
C22 H25 N4 O2 S3	(M+H)+	474.1236	473.1166	473.114	81.1	-5.48
C30 H21 N2 S2	(M+H)+	474.1236	473.1163	473.1146	80.22	-3.57

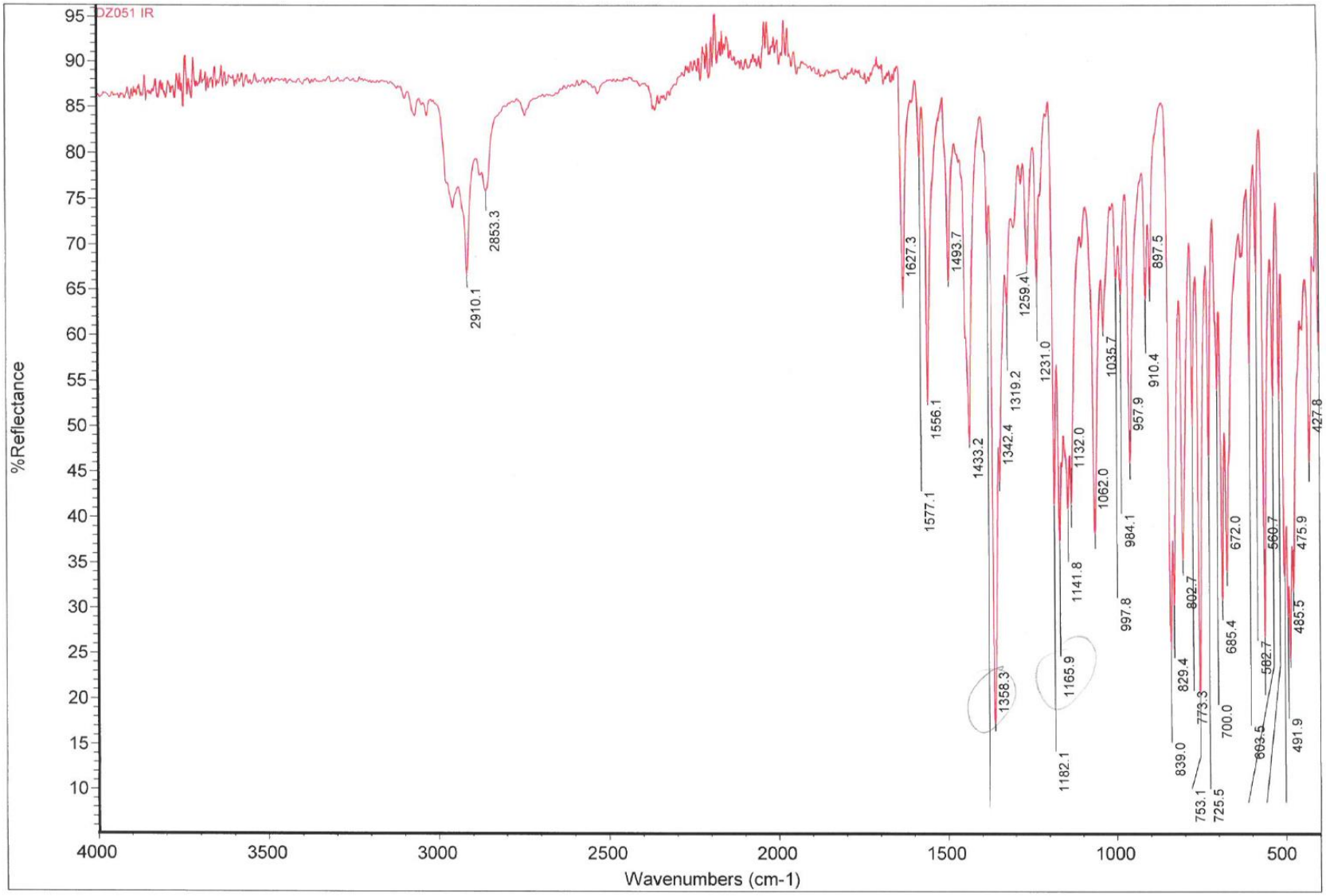
^{1}H-NMR spectrum of 14a-open



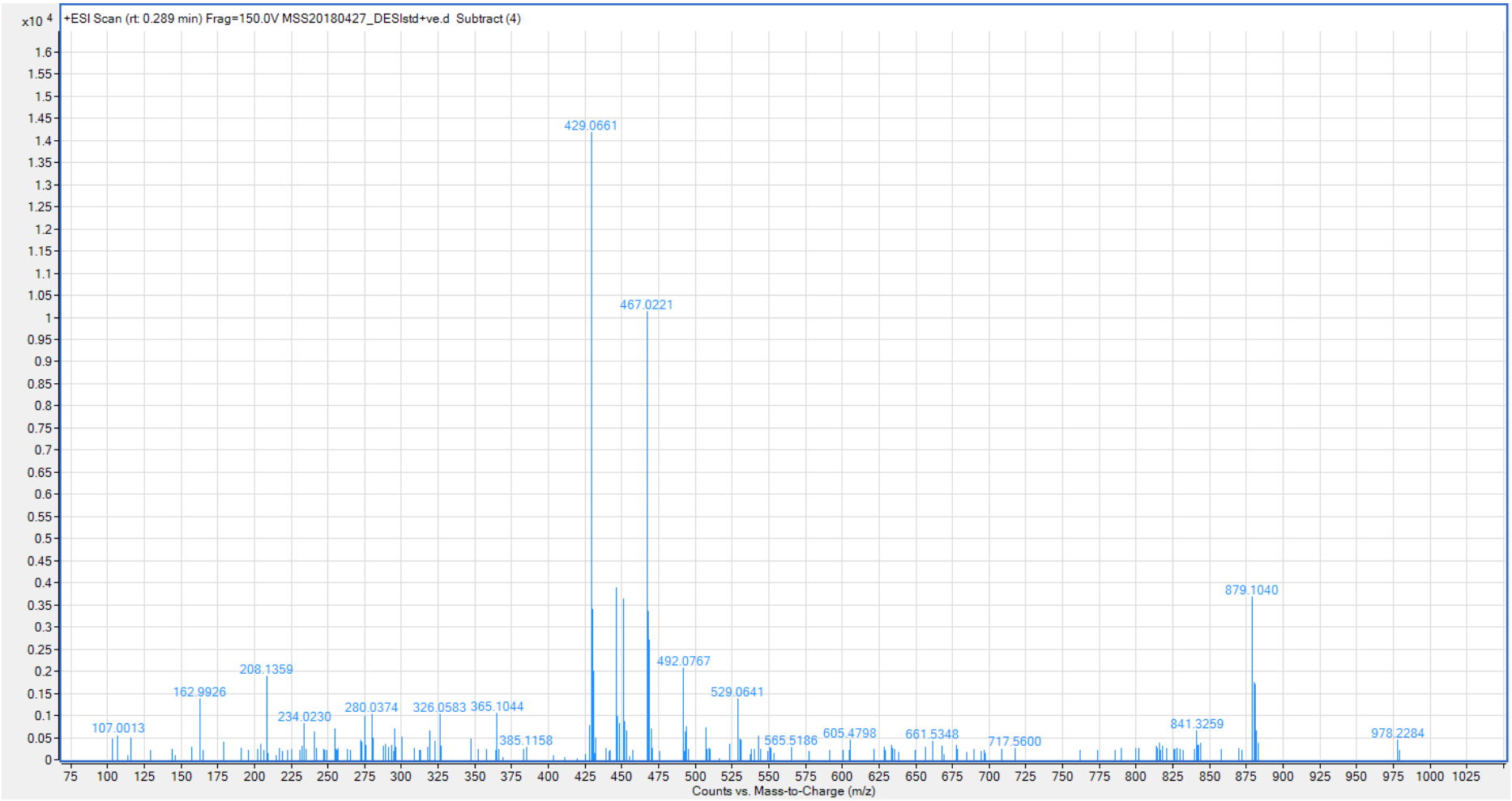
^{13}C-NMR spectrum of 14a-open



IR spectrum of 14a-open

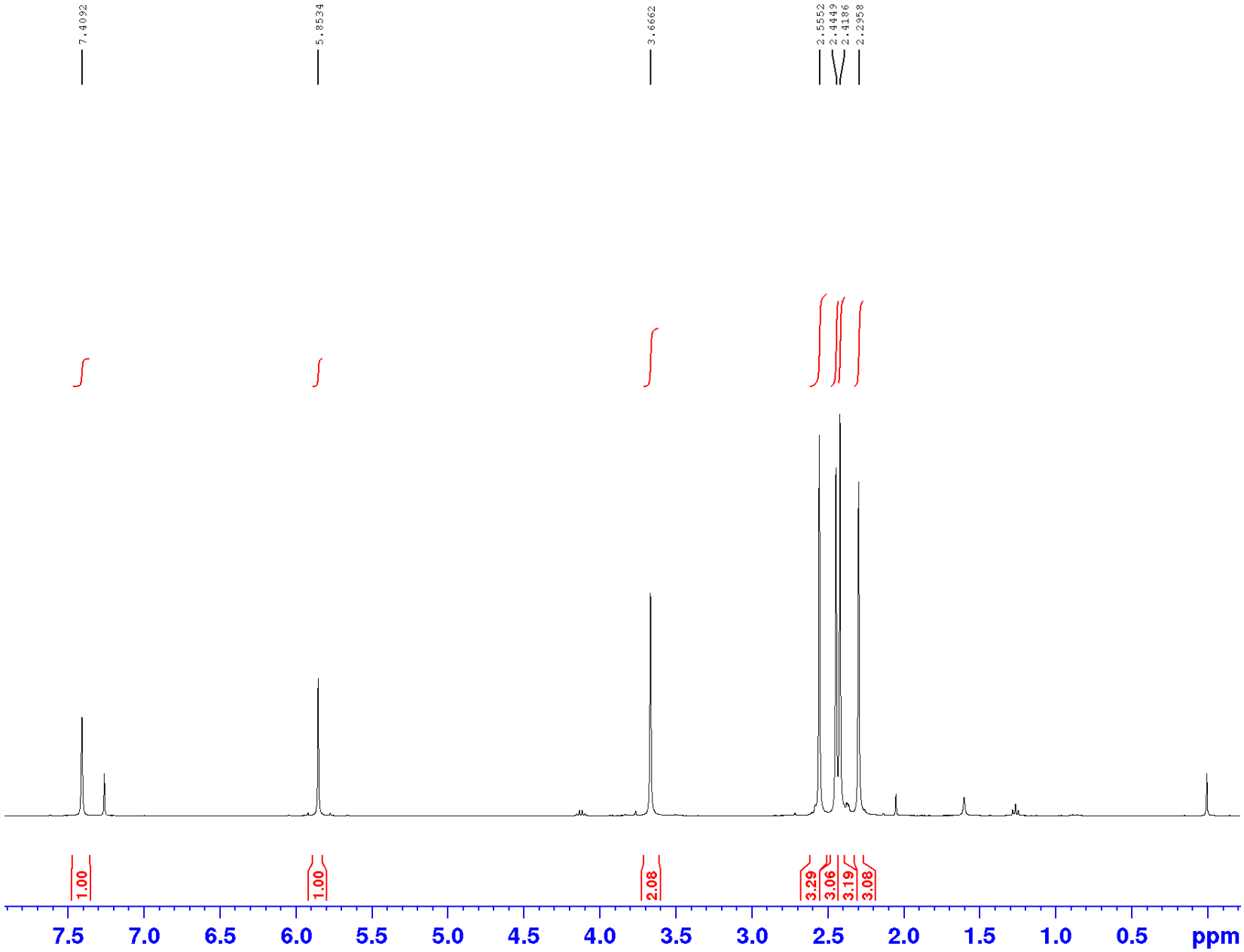


Mass spectrum of 14a-open

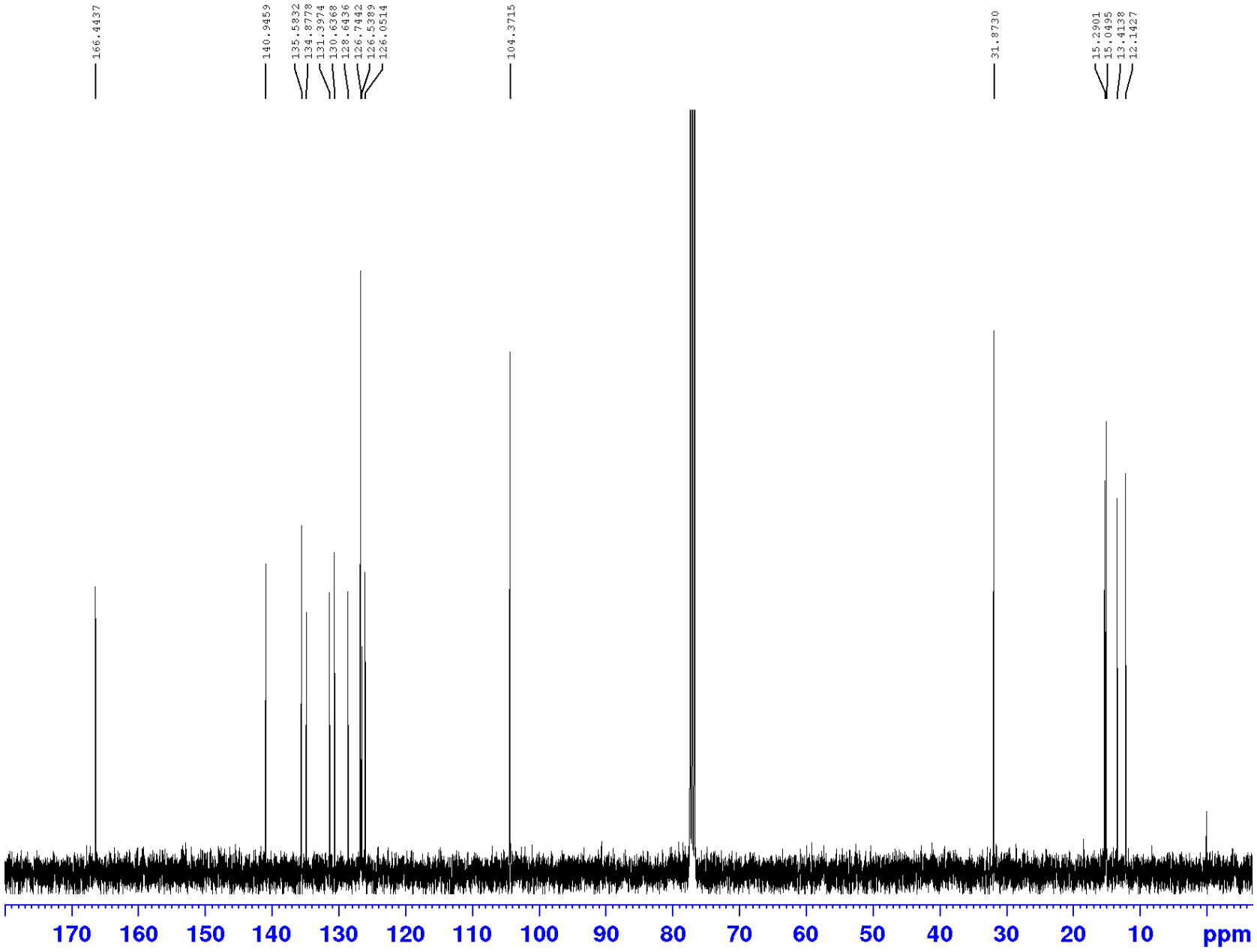


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C22 H20 O3 S3	(M+H)+	429.0661	428.0589	428.0575	89.79	-3.48
C19 H24 O3 S4	(M+H)+	429.0661	428.059	428.0608	80.74	4.16
C35 H8	(M+H)+	429.0661	428.058	428.0626	35.1	10.75

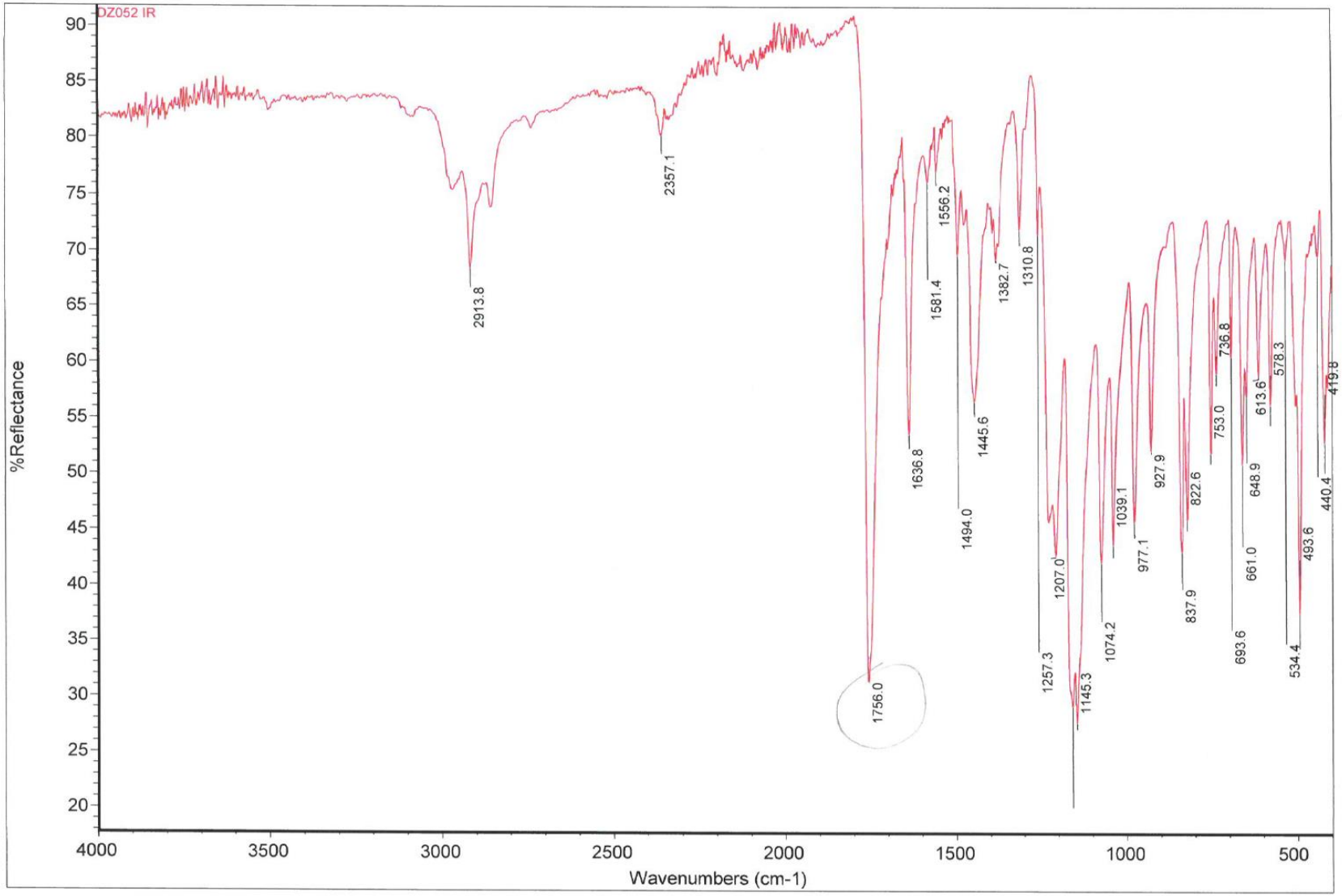
^{1}H-NMR spectrum of 7



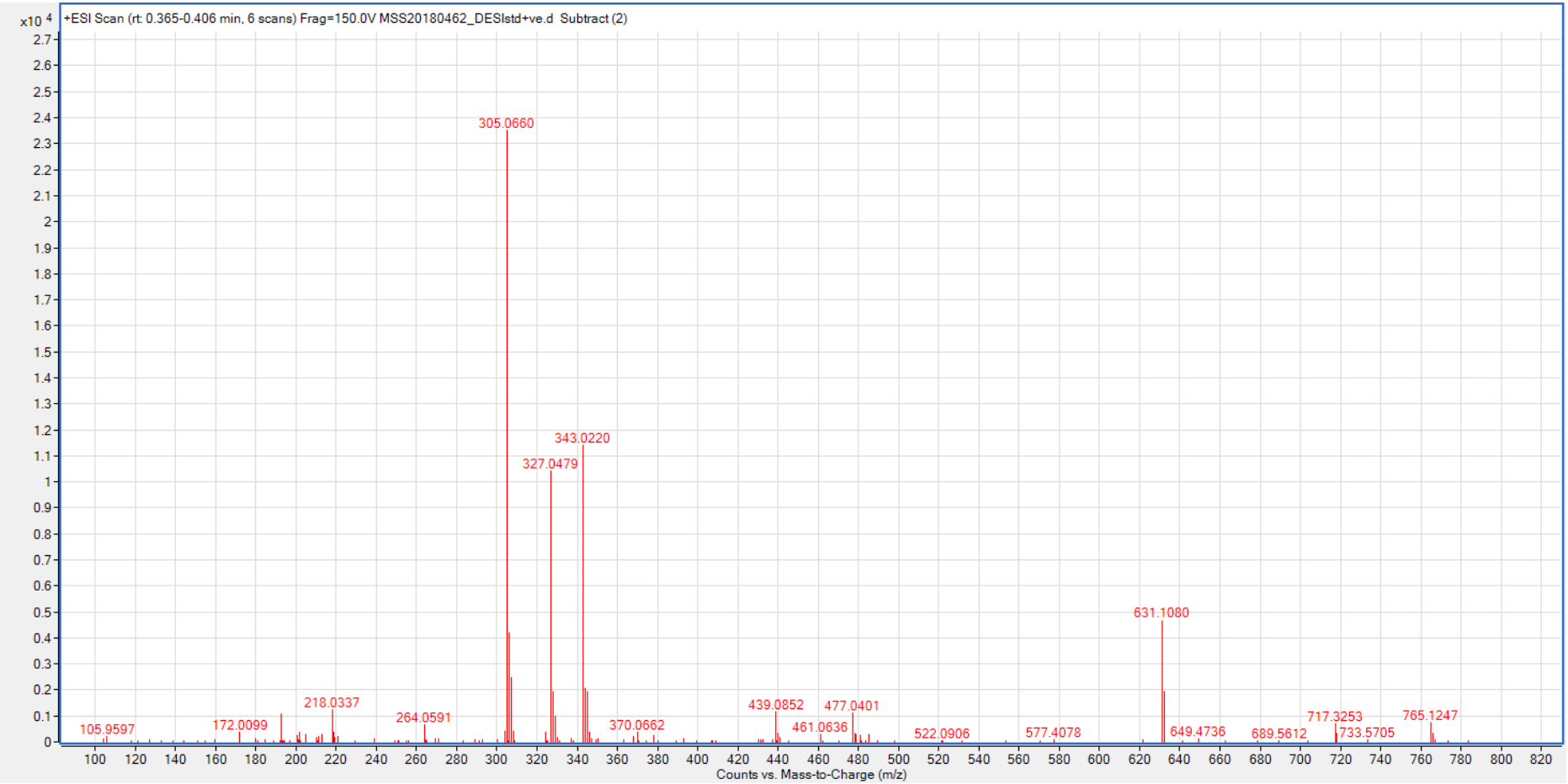
^{13}C-NMR spectrum of 7



IR spectrum of 7

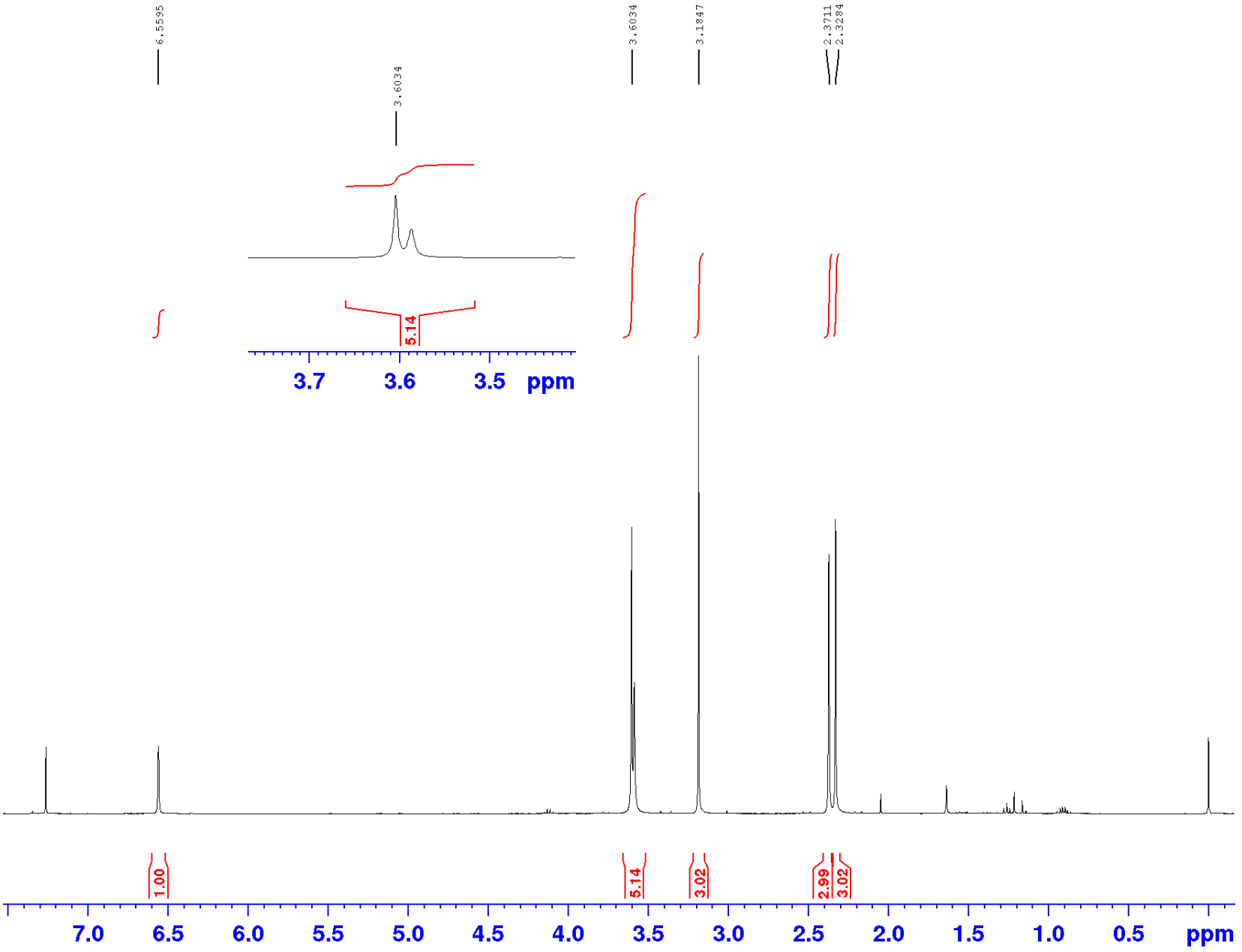


Mass spectrum of 7

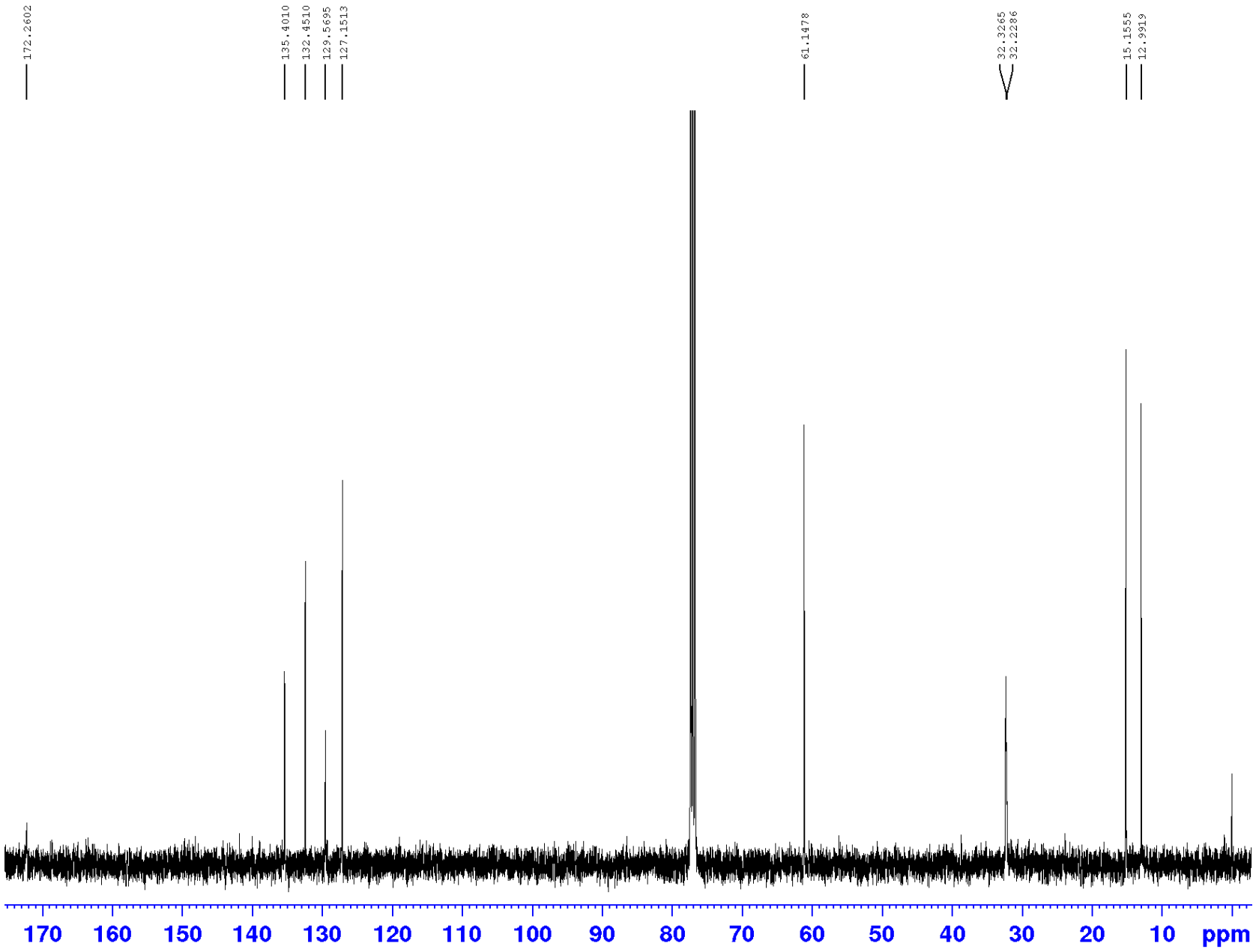


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C16 H16 O2 S2	(M+H)+	305.0660	304.0587	304.0592	98.17	1.41
C19 H12 O2 S	(M+H)+	305.0660	304.0586	304.0558	71.13	-9.09

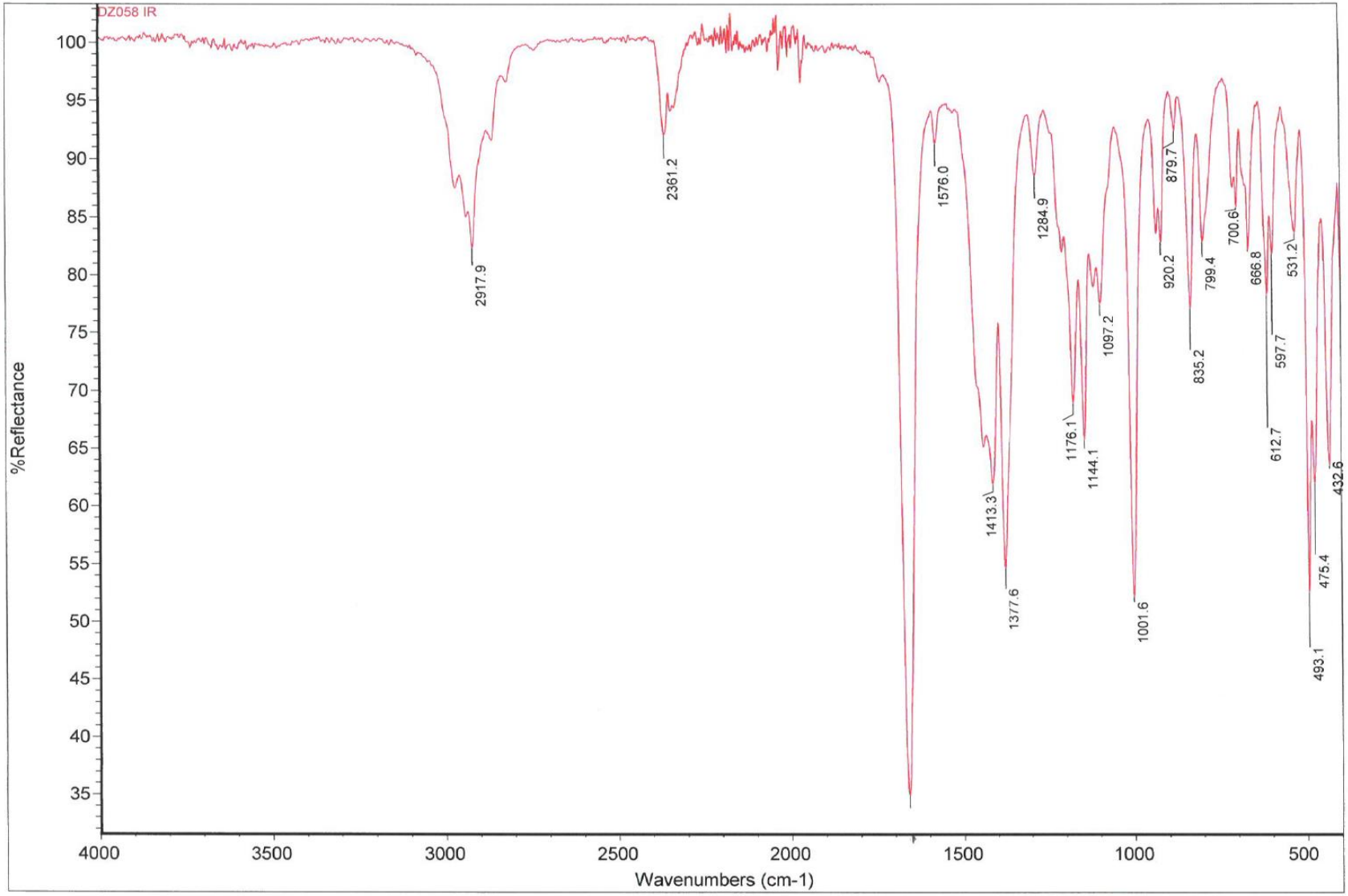
^{1}H-NMR spectrum of 8



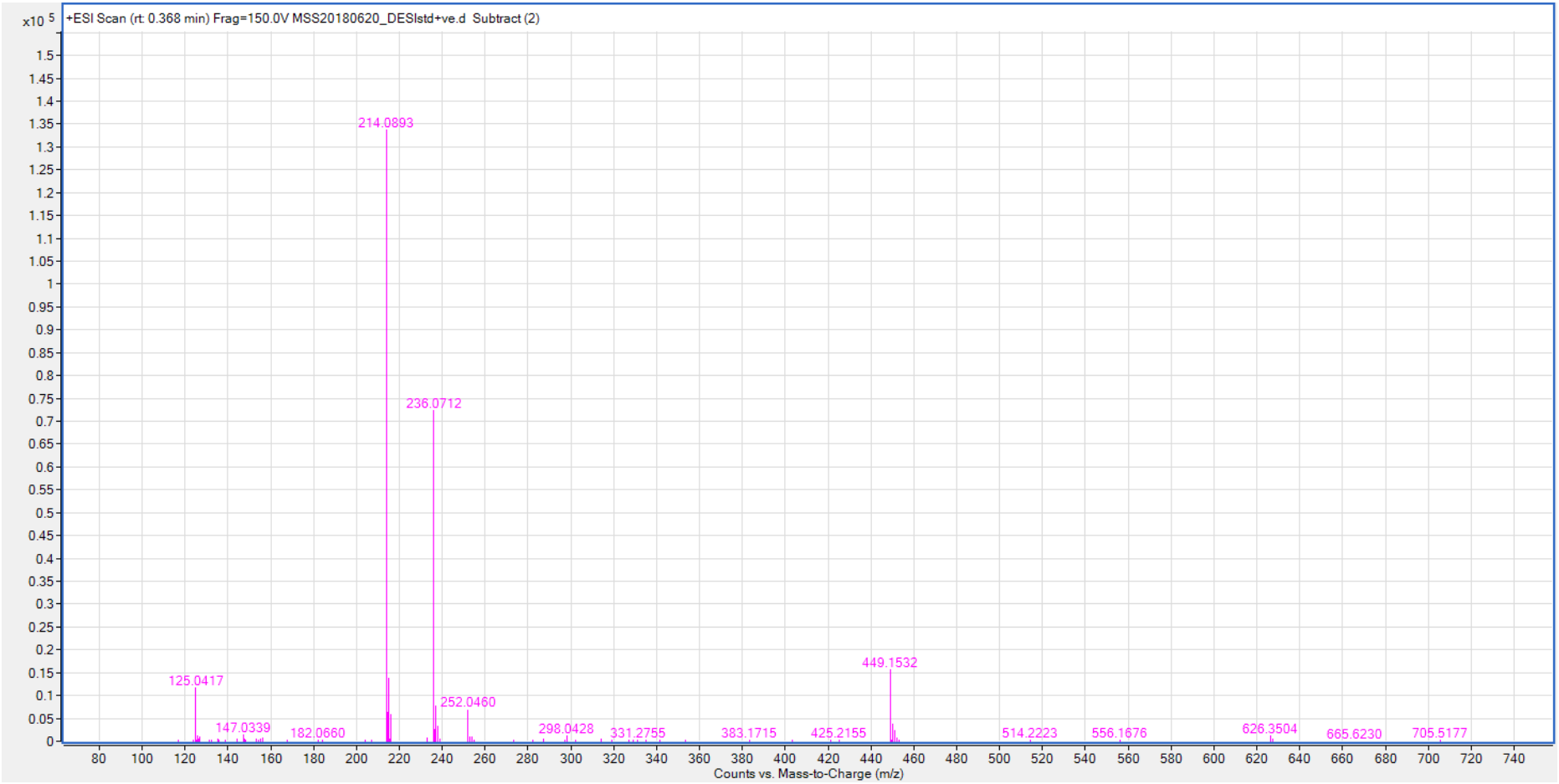
^{13}C-NMR spectrum of 8



IR spectrum of 8

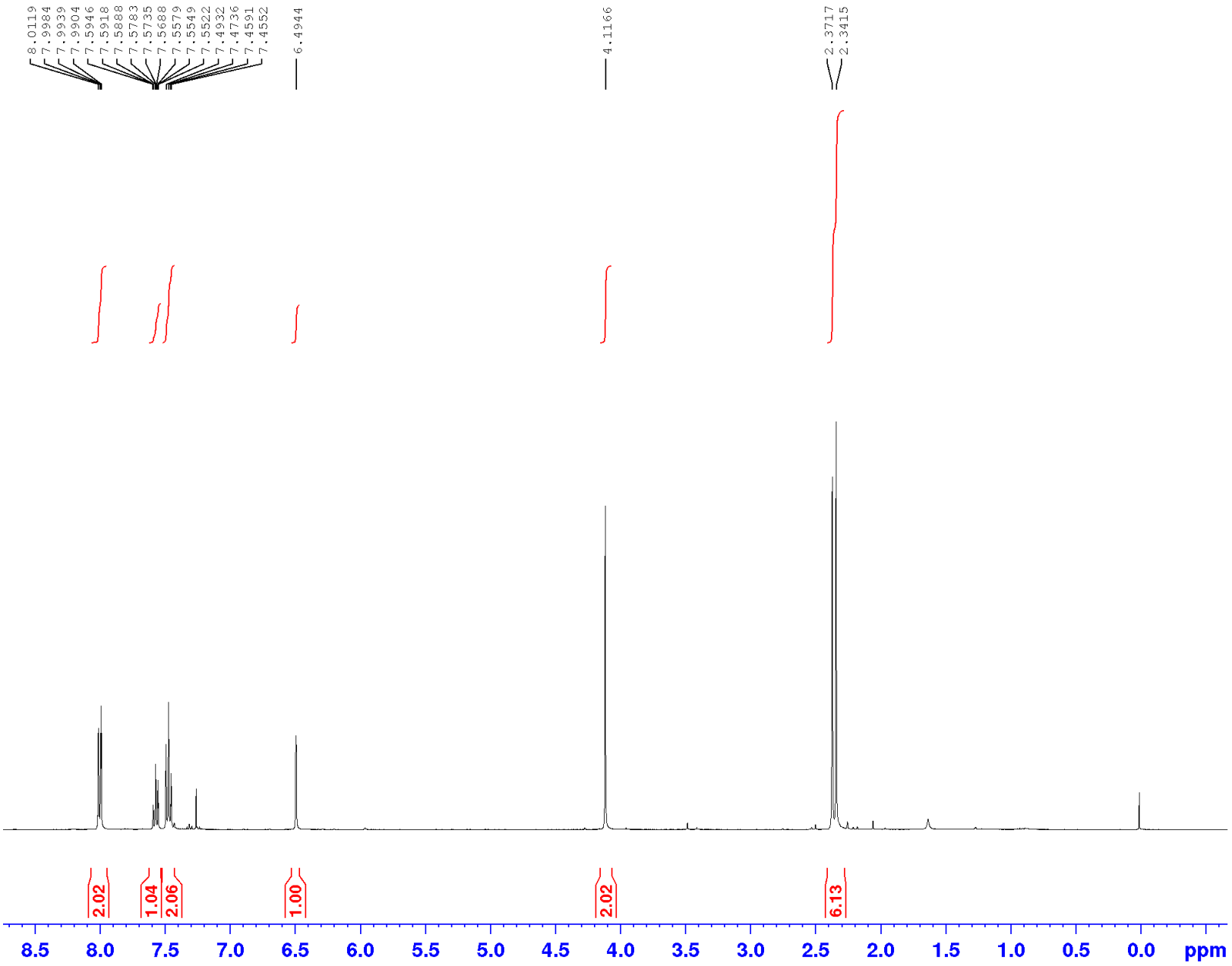


Mass spectrum of 8

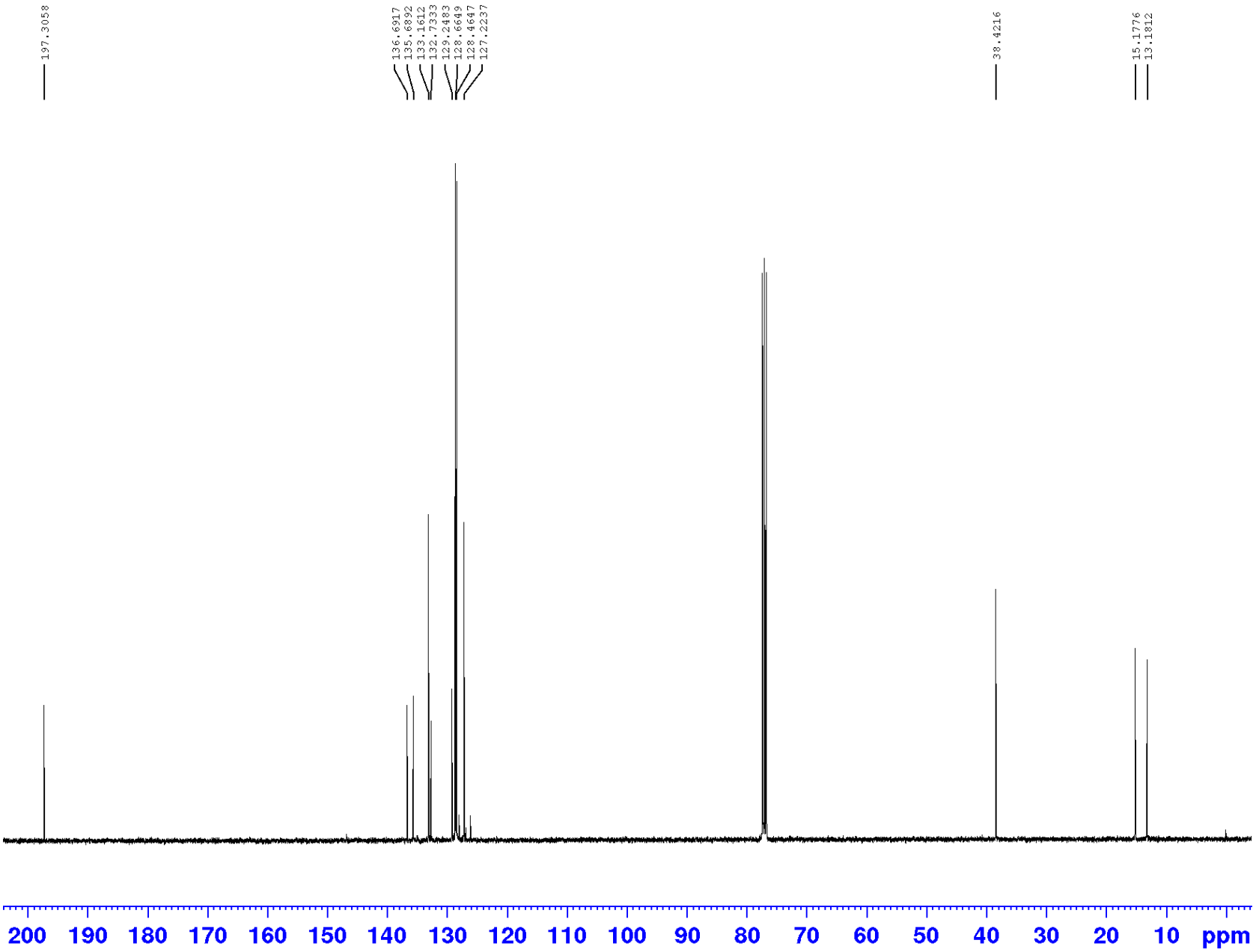


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C10 H15 N O2 S	(M+H)+	214.0893	213.0821	213.0823	97.89	1.2
C8 H13 N4 O S	(M+H)+	214.0893	213.0822	213.081	91.51	-5.49
C7 H17 O5 S	(M+H)+	214.0893	213.0821	213.0797	77.61	-11.28
C6 H15 N O7	(M+H)+	214.0893	213.0818	213.0849	61.51	14.26
C13 H11 N O2	(M+H)+	214.0893	213.0818	213.079	59.52	-13.04

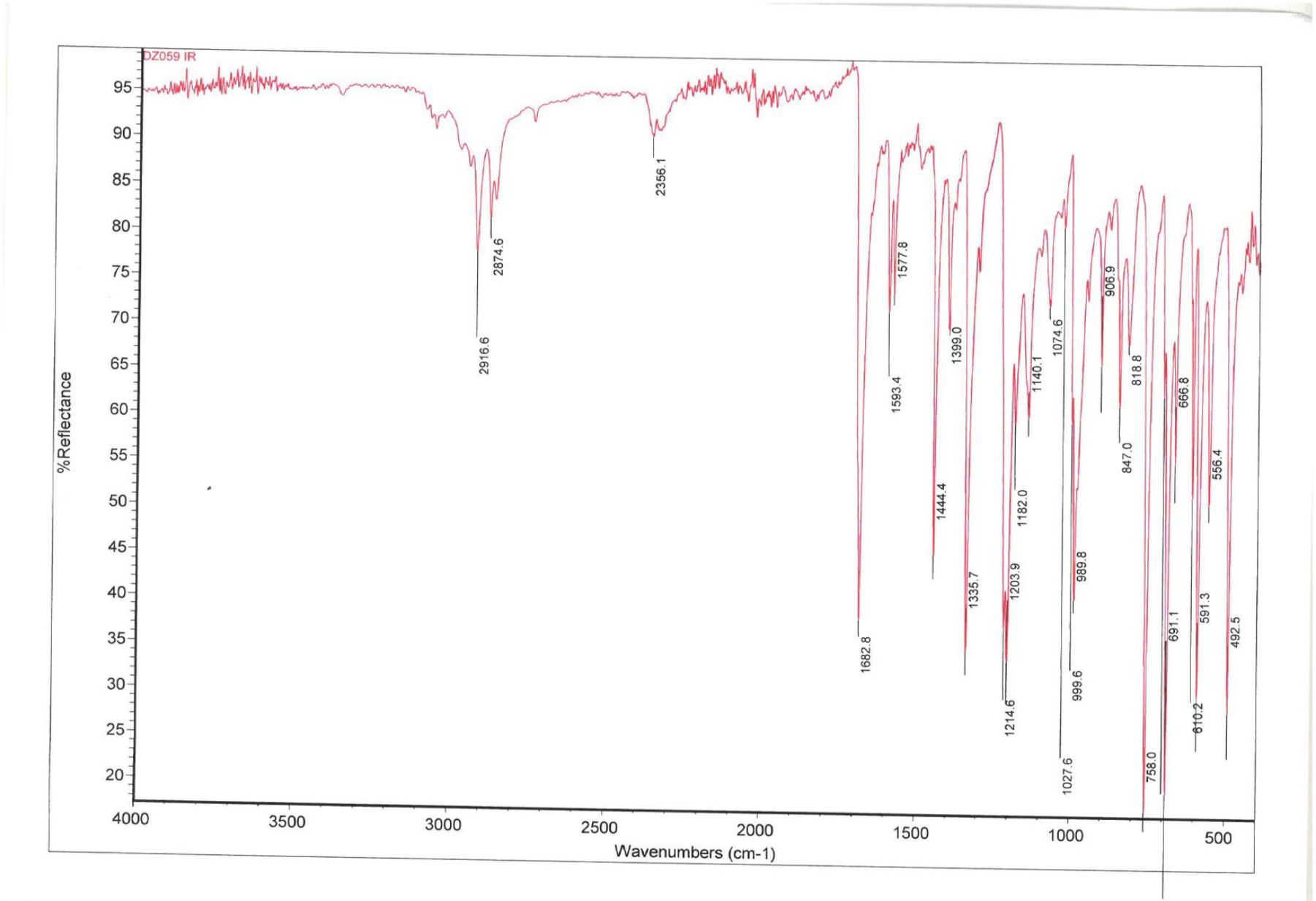
^{1}H-NMR spectrum of 9



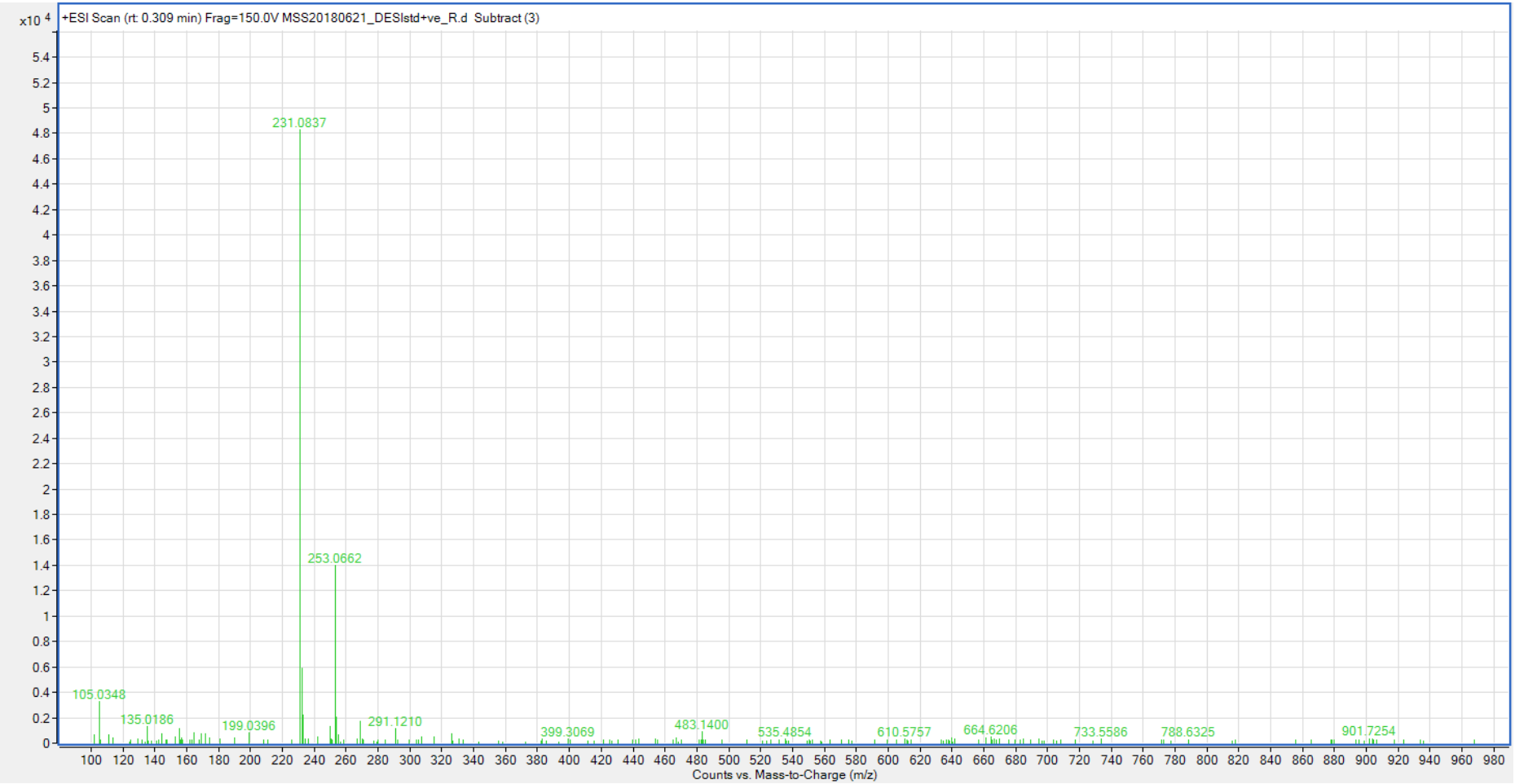
^{13}C-NMR spectrum of 9



IR spectrum of 9

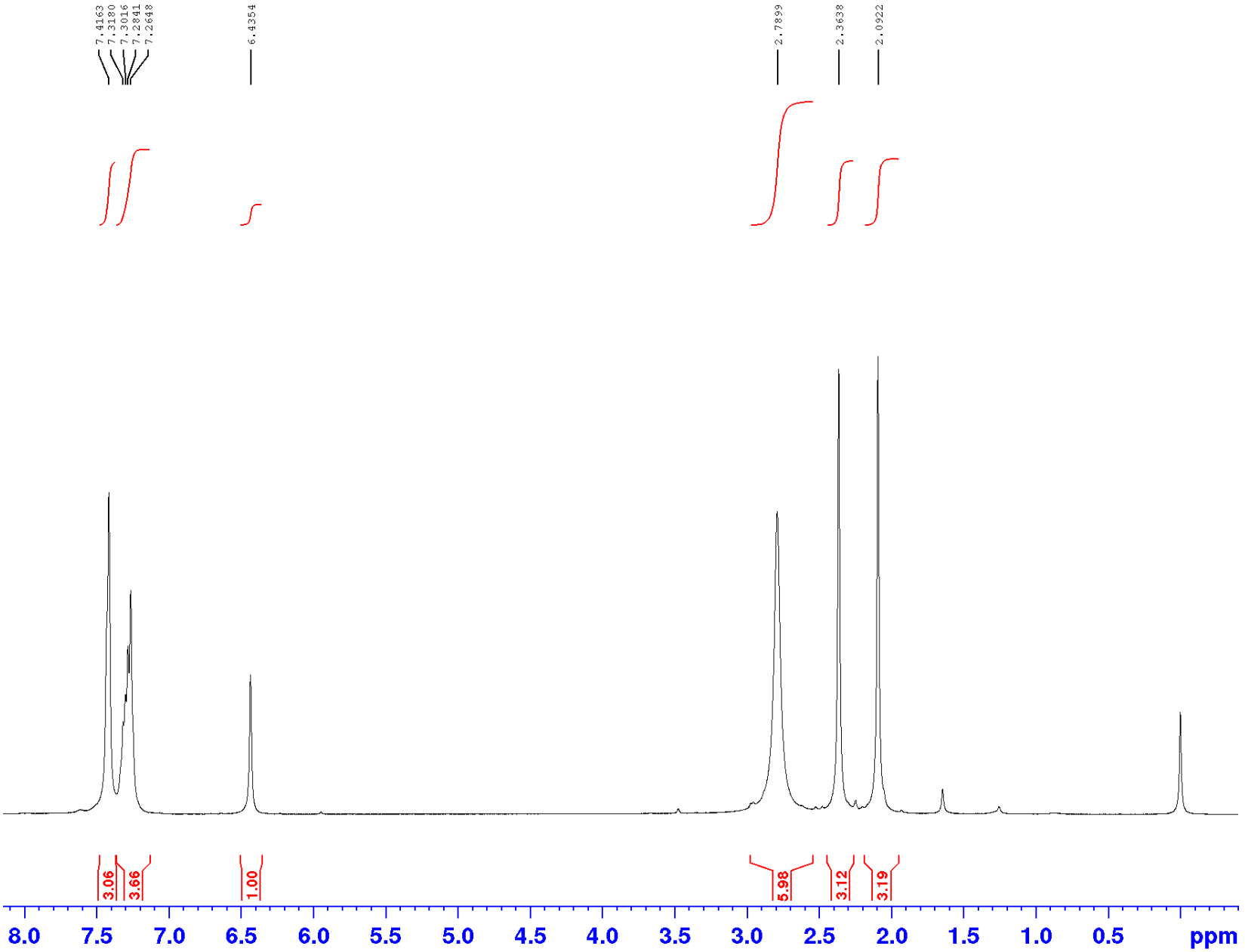


Mass spectrum of 9

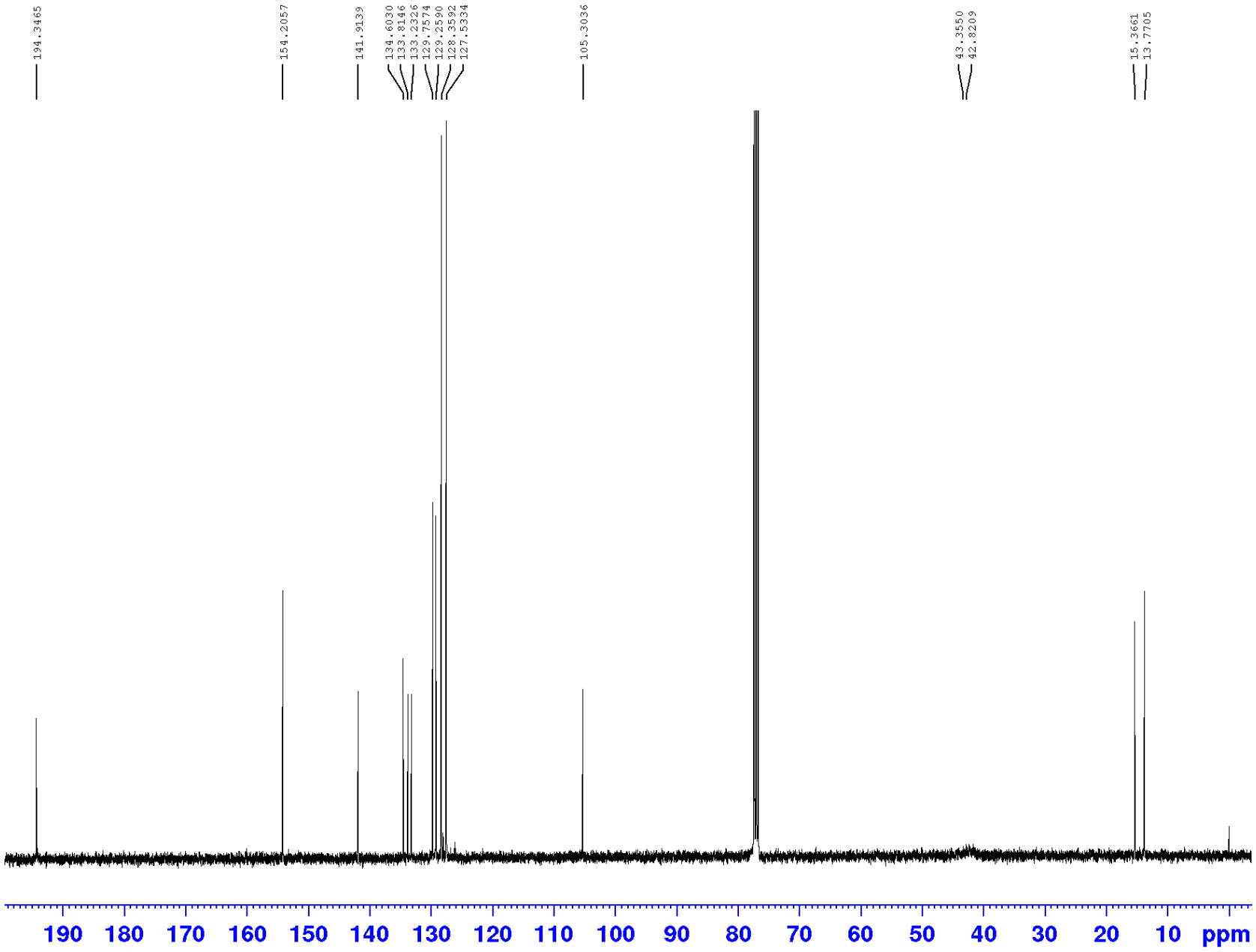


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C14 H14 O S	(M+H)+	231.0837	230.0764	230.0765	95.41	0.46
C12 H16 O S	(M+Na)+	231.0837	208.0945	208.0922	79.61	-11.14
C9 H20 O2 S	(M+K)+	231.0837	192.1206	192.1184	67.27	-11.3

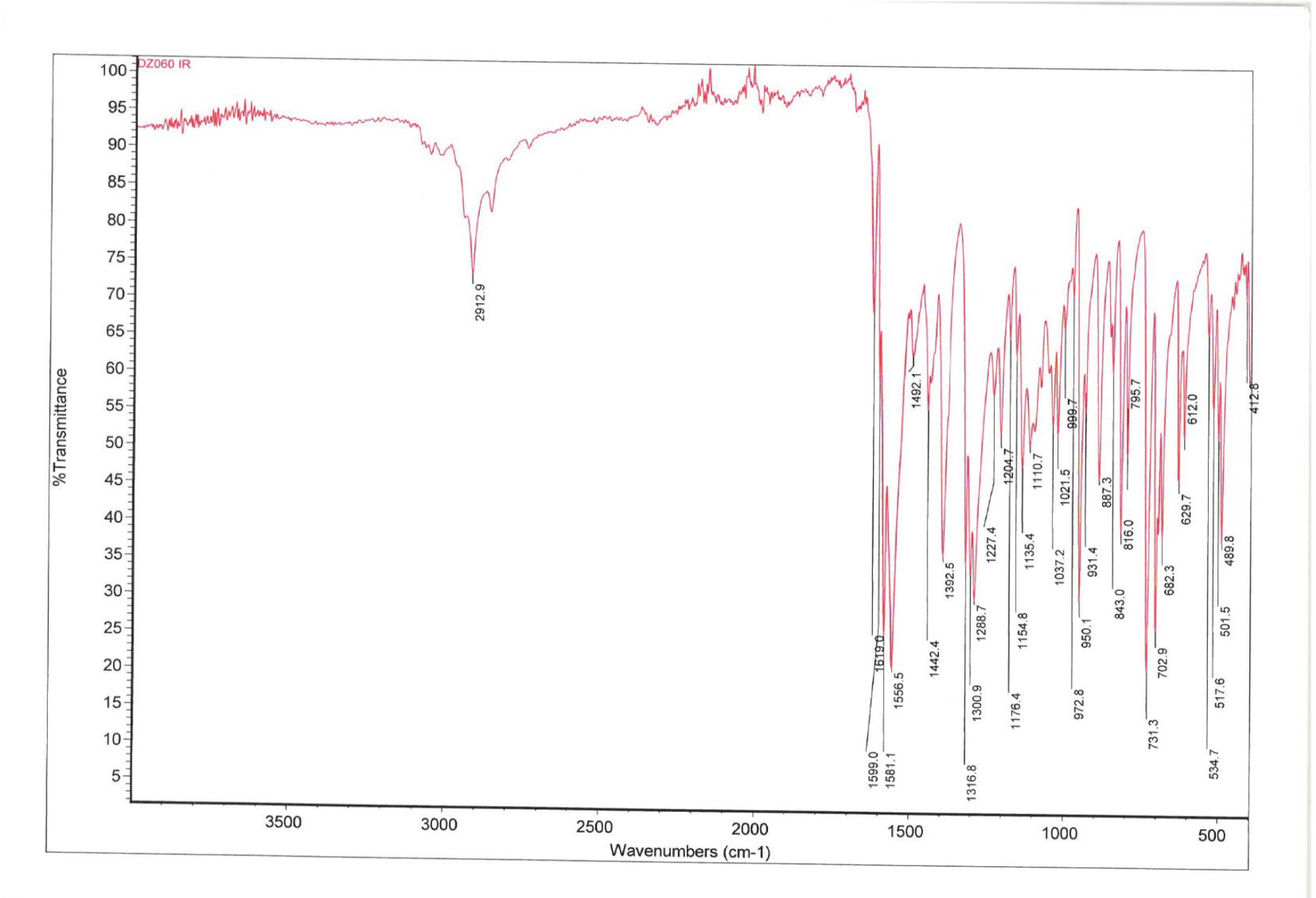
^{1}H-NMR spectrum of 12b



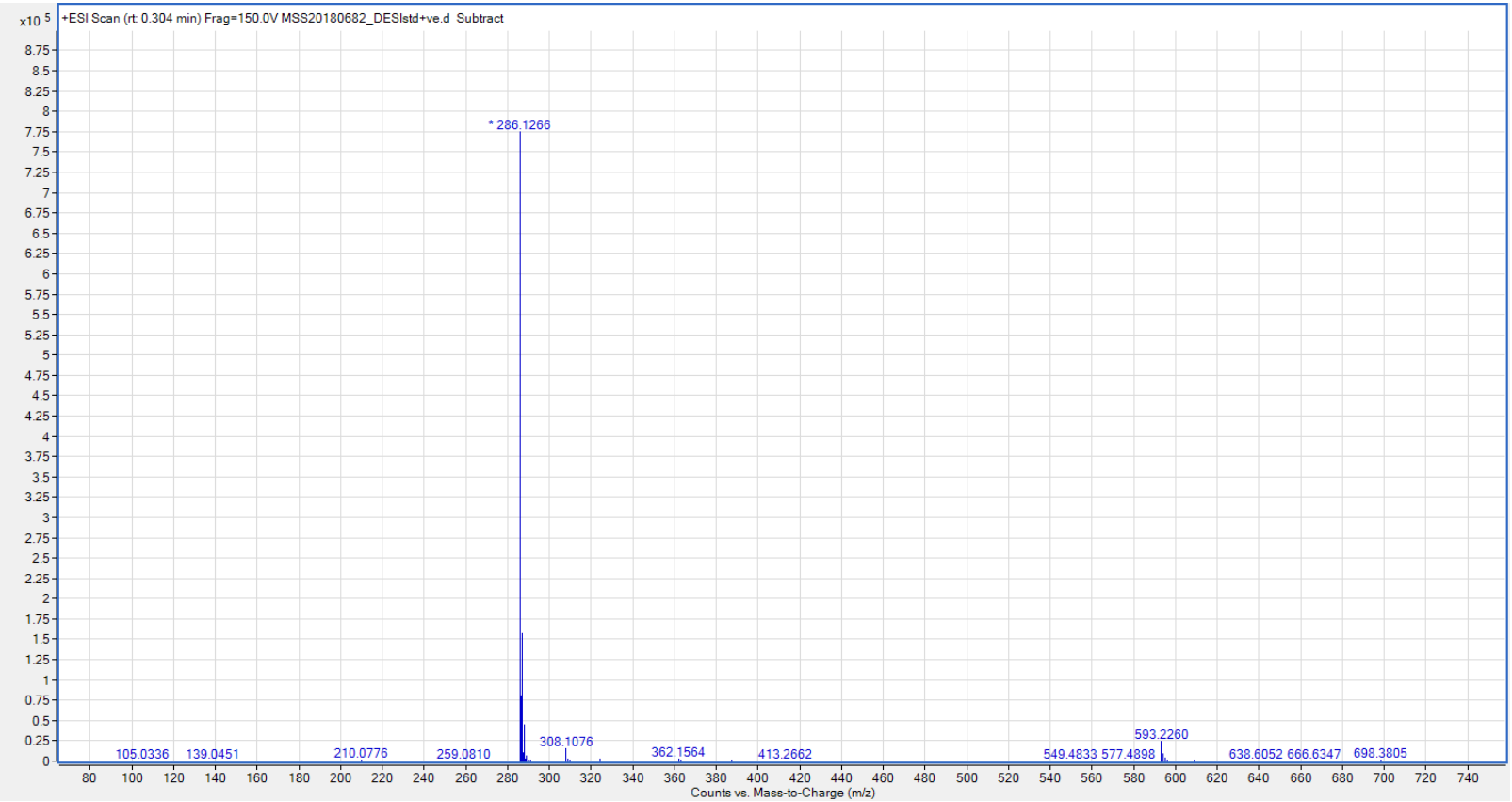
^{13}C-NMR spectrum of 12b



IR spectrum of 12b

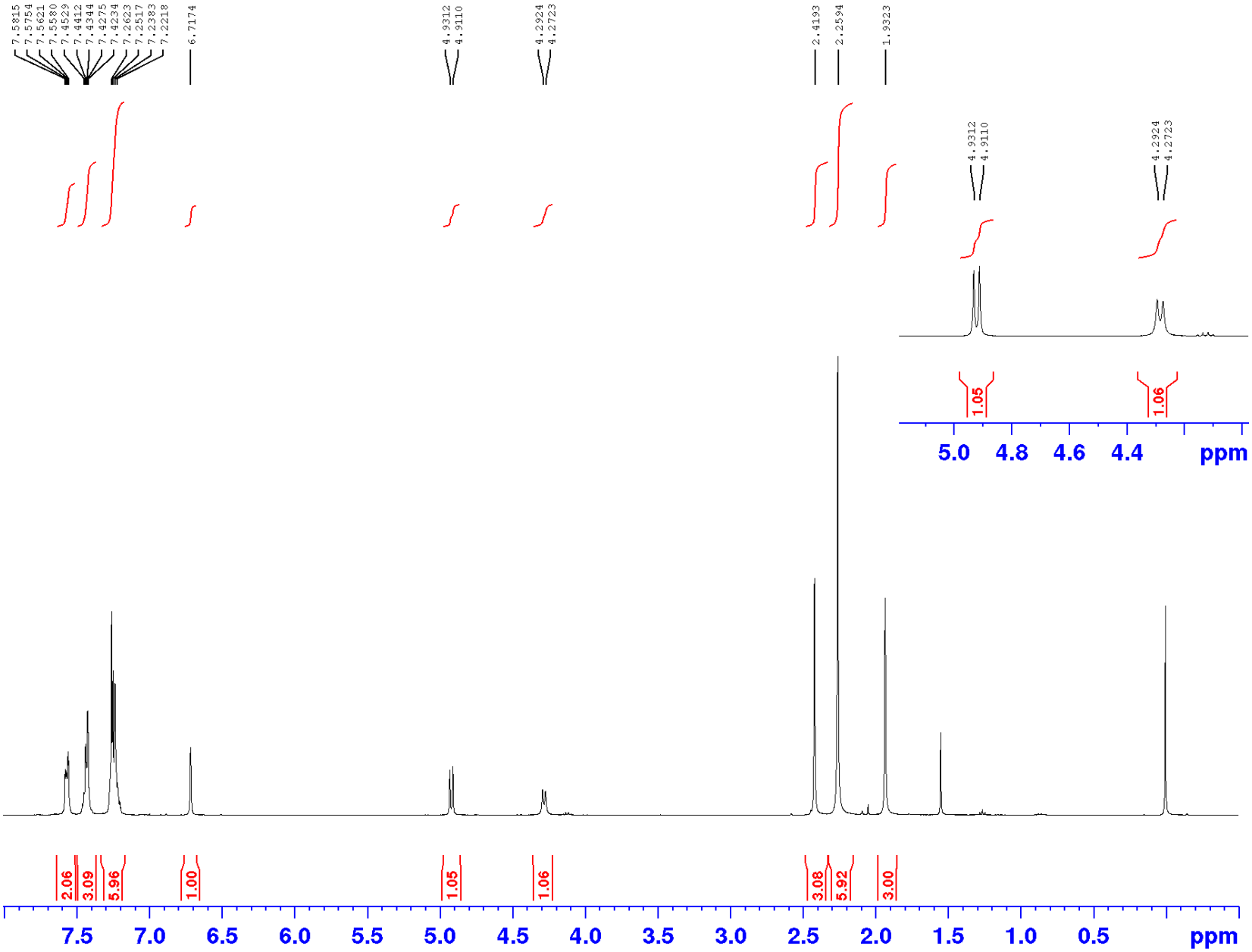


Mass spectrum of 12b

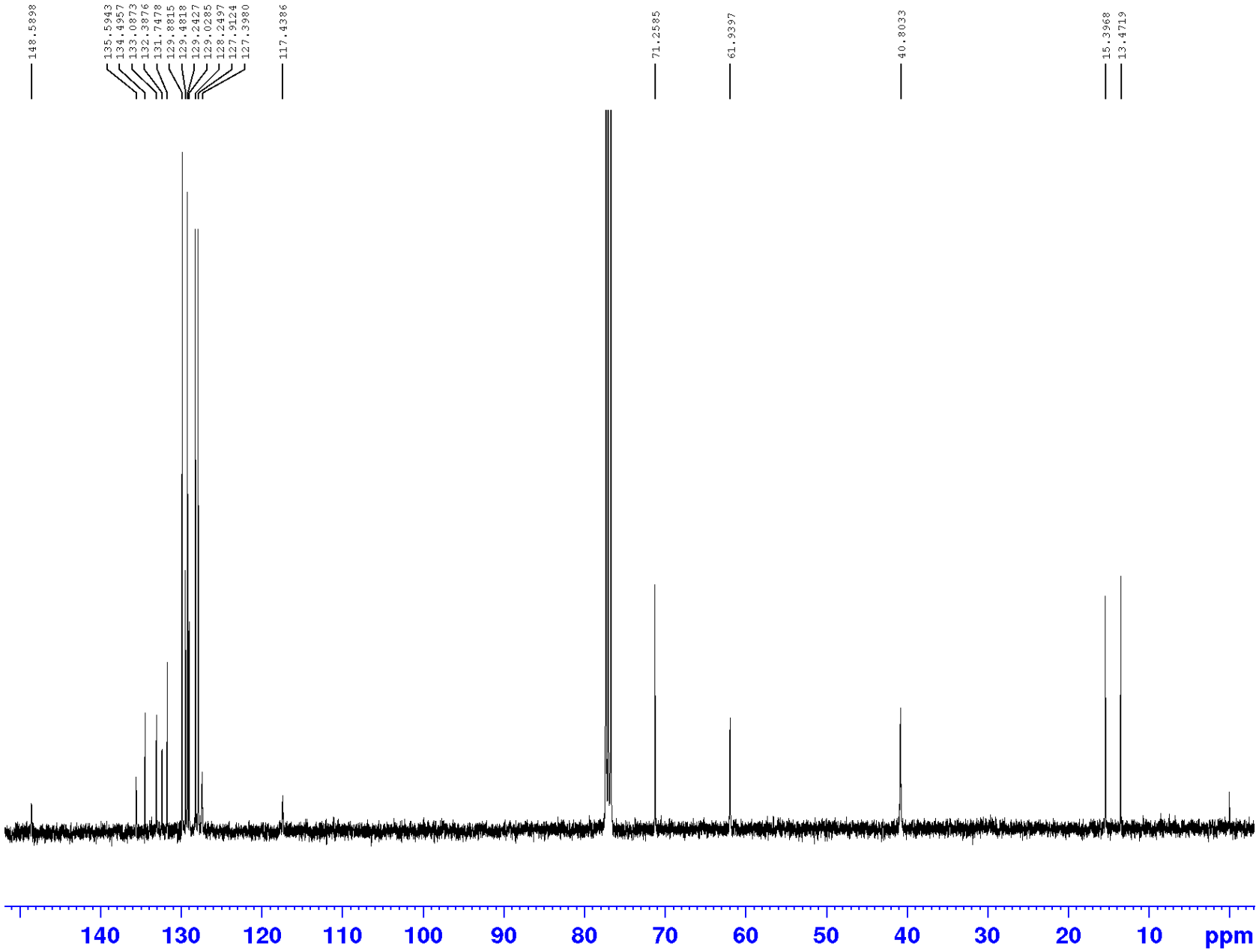


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C17 H19 N O S	(M+H)+	286.1266	285.1191	285.1187	97.2	-1.28
C15 H17 N4 S	(M+H)+	286.1266	285.1192	285.1174	87.75	-6.31
C11 H25 O4 S2	(M+H)+	286.1266	285.1192	285.1194	83.49	0.79
C12 H21 N4 S2	(M+H)+	286.1266	285.1193	285.1208	82.22	5.11
C9 H15 N7 O4	(M+H)+	286.1266	285.119	285.1186	80.16	-1.65
C11 H17 N4 O5	(M+H)+	286.1266	285.1189	285.1199	78.87	3.5
C9 H23 N3 O3 S2	(M+H)+	286.1266	285.1193	285.1181	77.75	-4.31
C10 H21 O9	(M+H)+	286.1266	285.1188	285.1186	75.72	-0.77
C12 H13 N8 O	(M+H)+	286.1266	285.119	285.1212	71.46	7.84
C14 H21 O4 S	(M+H)+	286.1266	285.1191	285.1161	69.41	-10.64

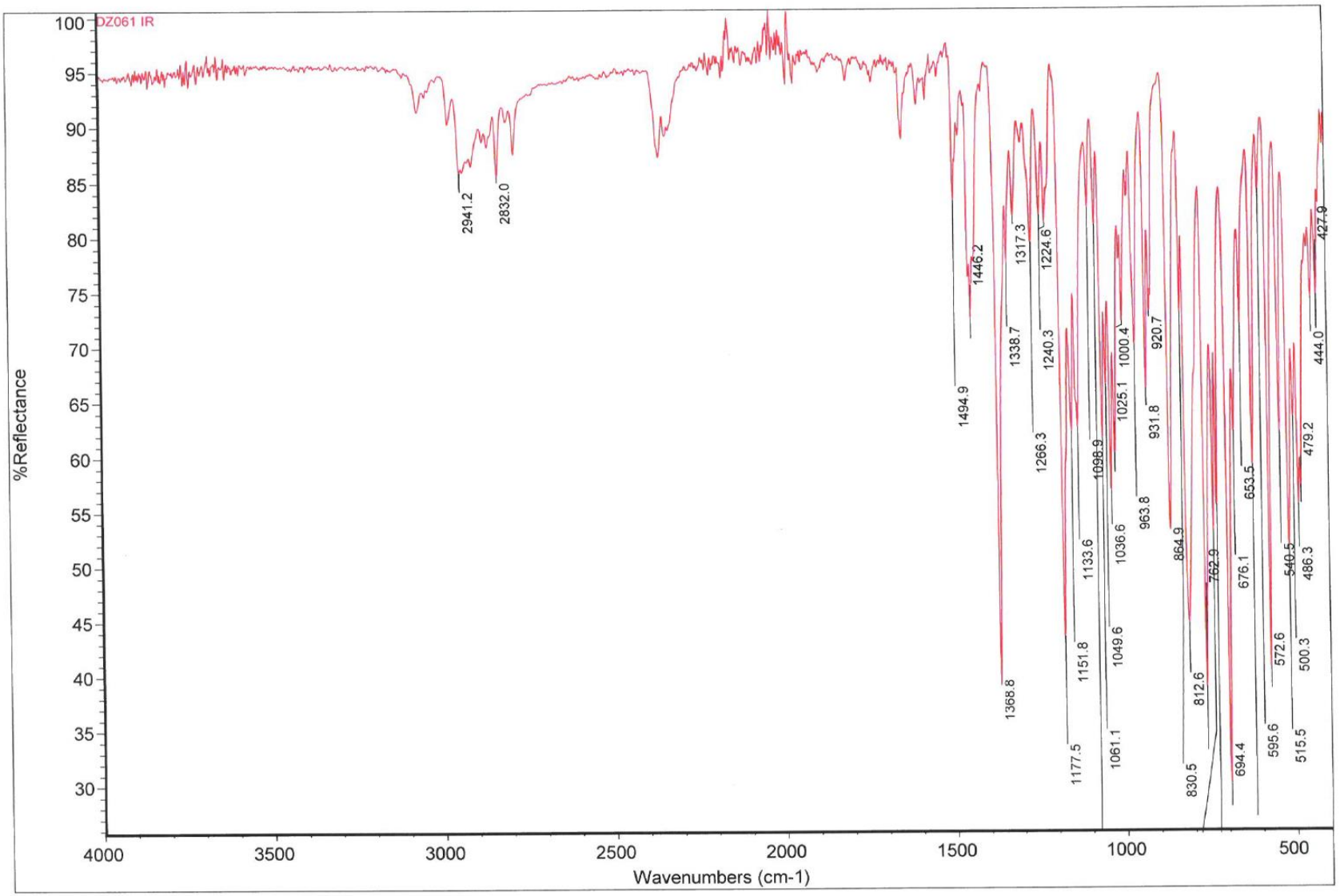
^{1}H-NMR spectrum of 13b-open



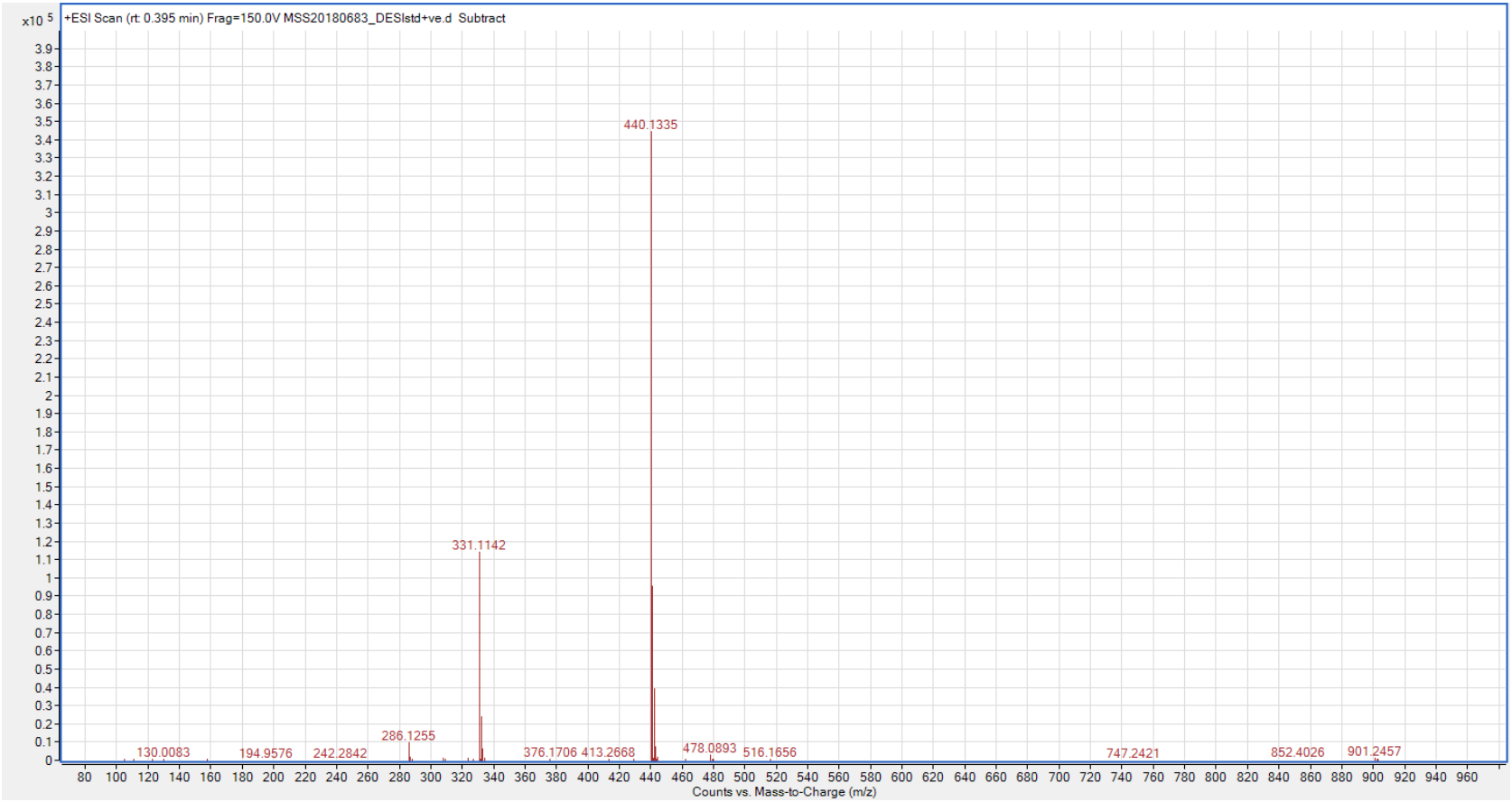
^{13}C-NMR spectrum of 13b-open



IR spectrum of 13b-open

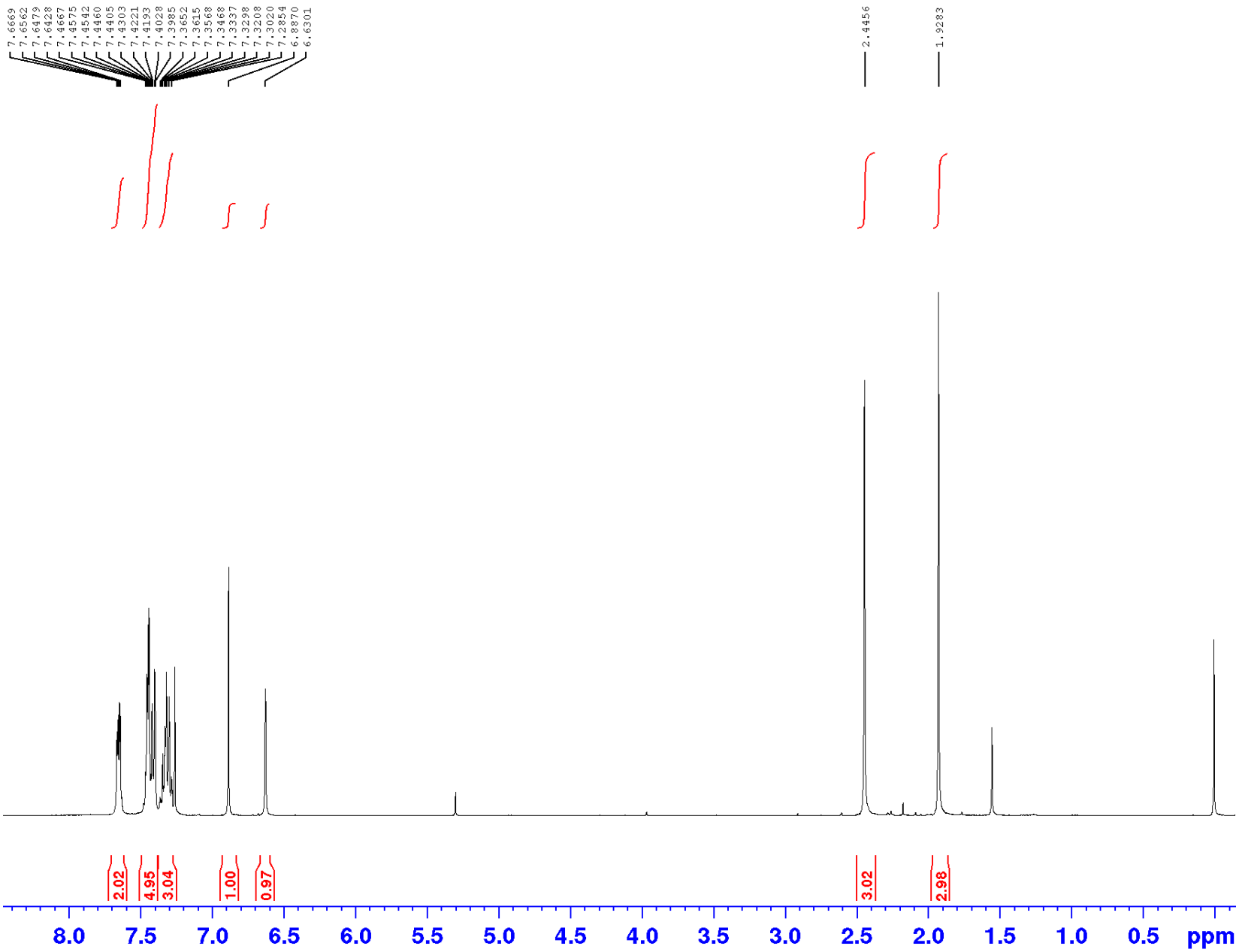


Mass spectrum of 13b-open

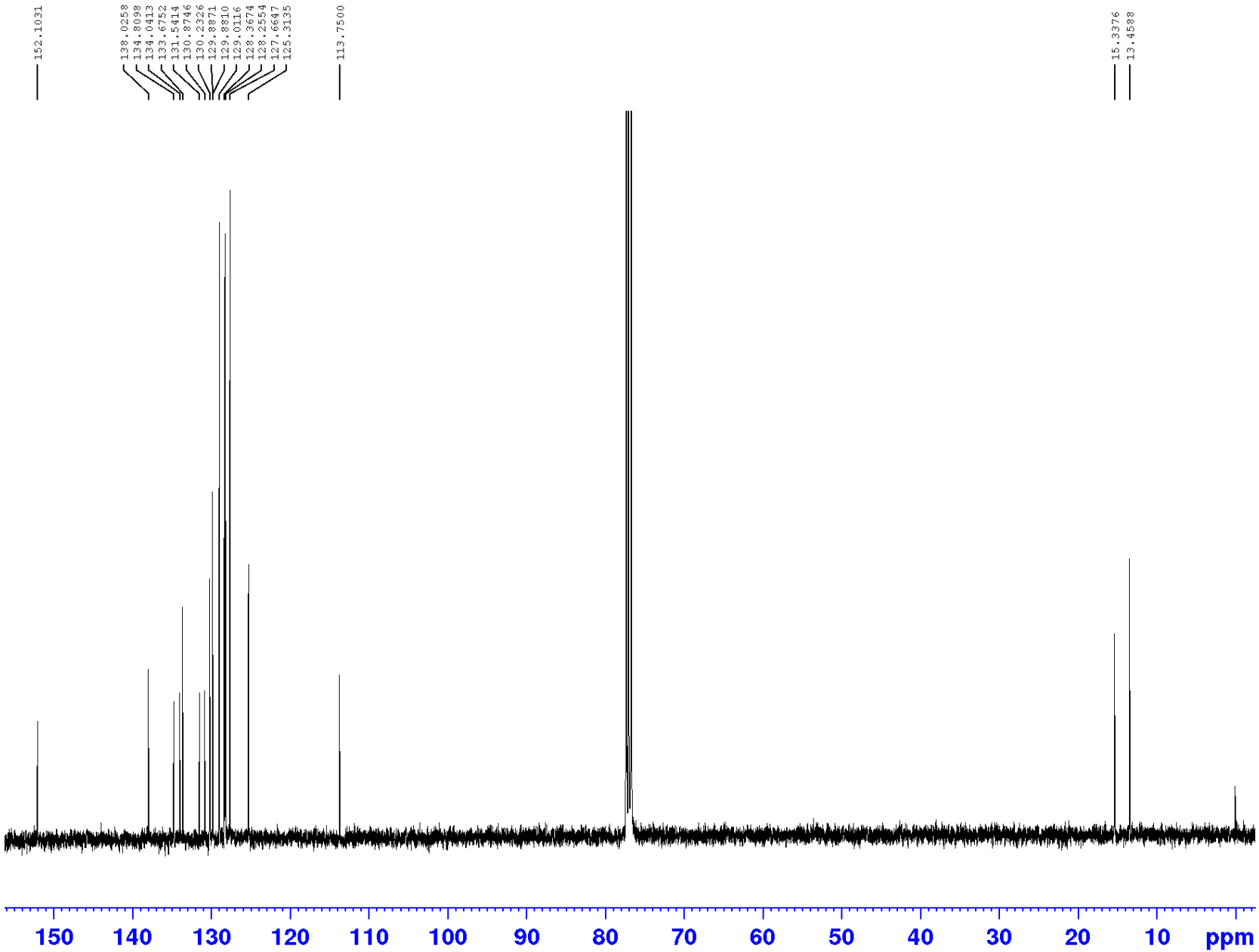


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C22 H23 N4 O2 S2	(M+H)+	440.1335	439.1264	439.1262	96.93	-0.4
C24 H25 N O3 S2	(M+H)+	440.1335	439.1263	439.1276	93.59	2.86
C21 H27 O6 S2	(M+H)+	440.1335	439.1263	439.1249	90.61	-3.26
C20 H21 N7 O S2	(M+H)+	440.1335	439.1265	439.1249	90.35	-3.66
C30 H19 N2 S	(M+H)+	440.1335	439.1261	439.1269	89.32	1.78
C16 H21 N7 O6 S	(M+H)+	440.1335	439.1264	439.1274	88.58	2.25
C14 H19 N10 O5 S	(M+H)+	440.1335	439.1265	439.1261	87.44	-1.08
C15 H25 N3 O10 S	(M+H)+	440.1335	439.1263	439.1261	87.04	-0.55
C27 H21 N O3 S	(M+H)+	440.1335	439.1261	439.1242	86.97	-4.36

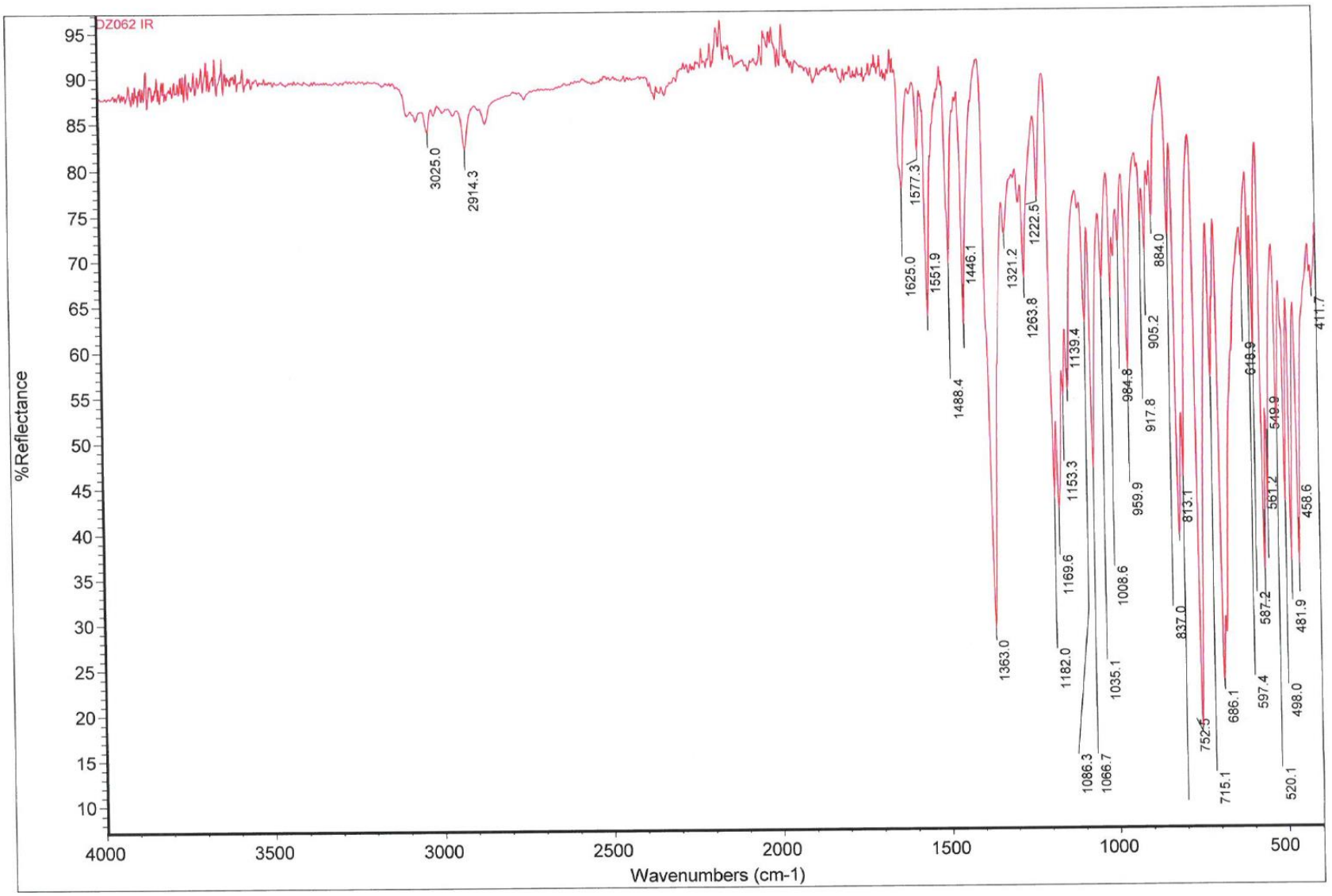
^{1}H-NMR spectrum of 14b-open



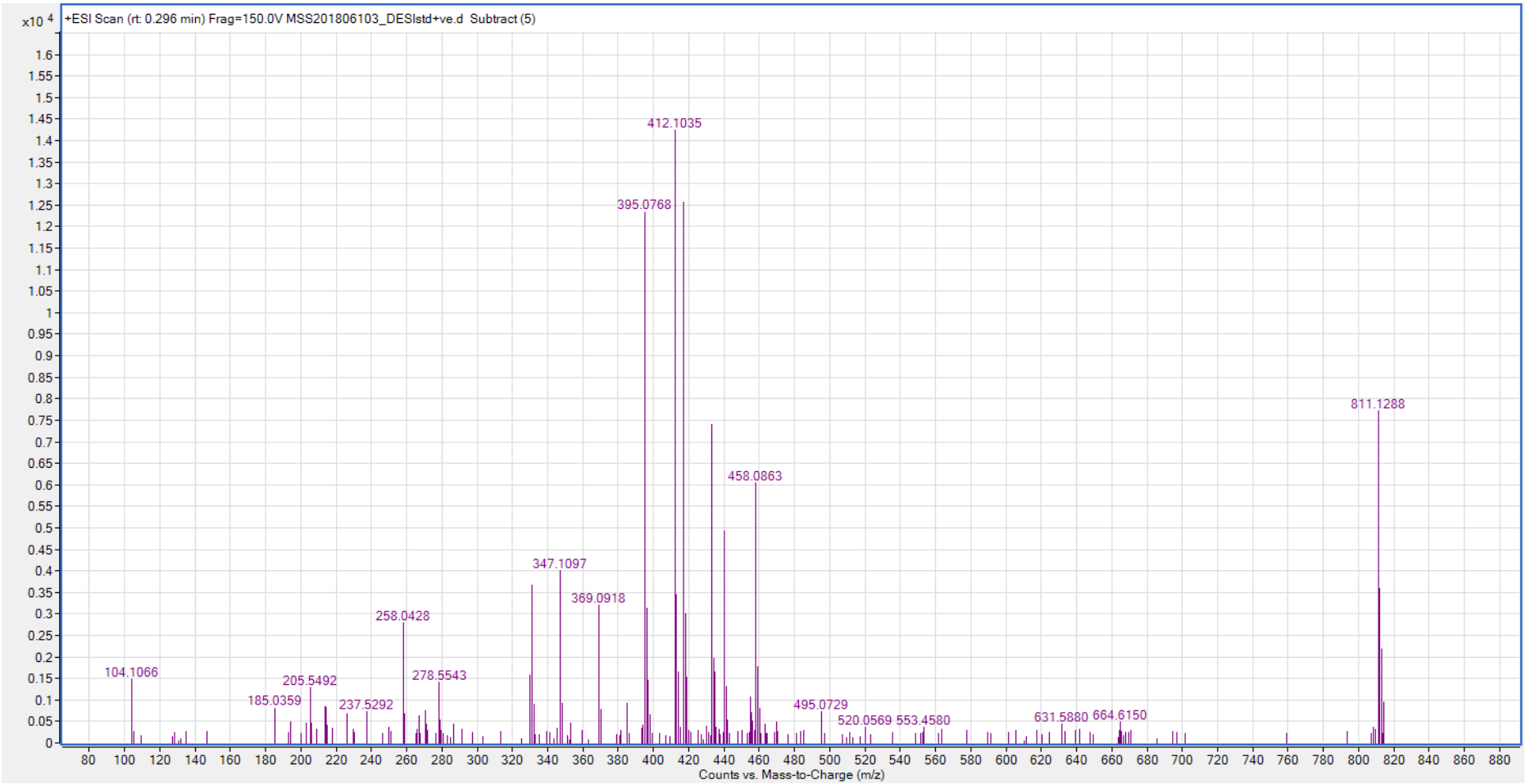
^{13}C-NMR spectrum of 14b-open



IR spectrum of 14b-open

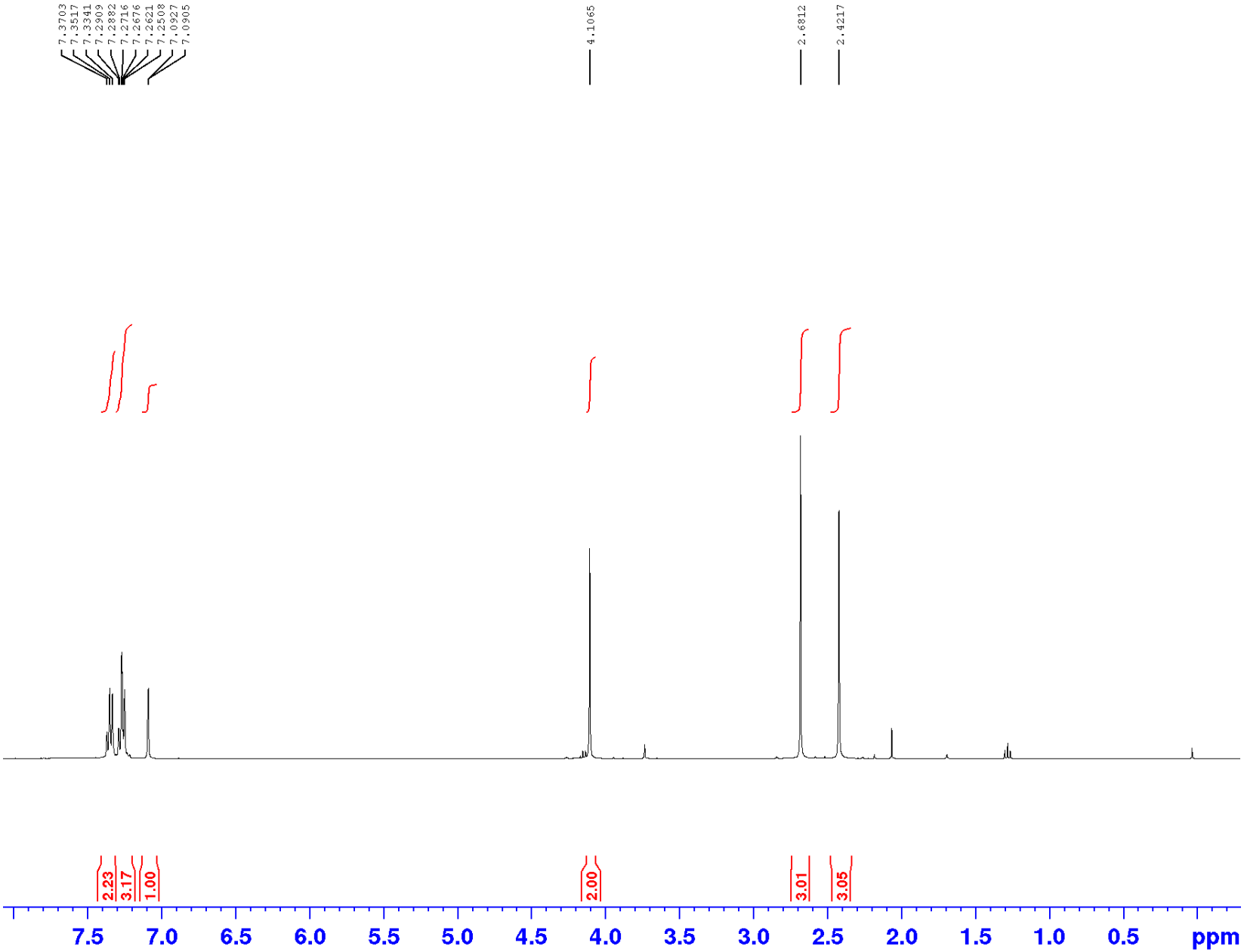


Mass spectrum of 14b-open

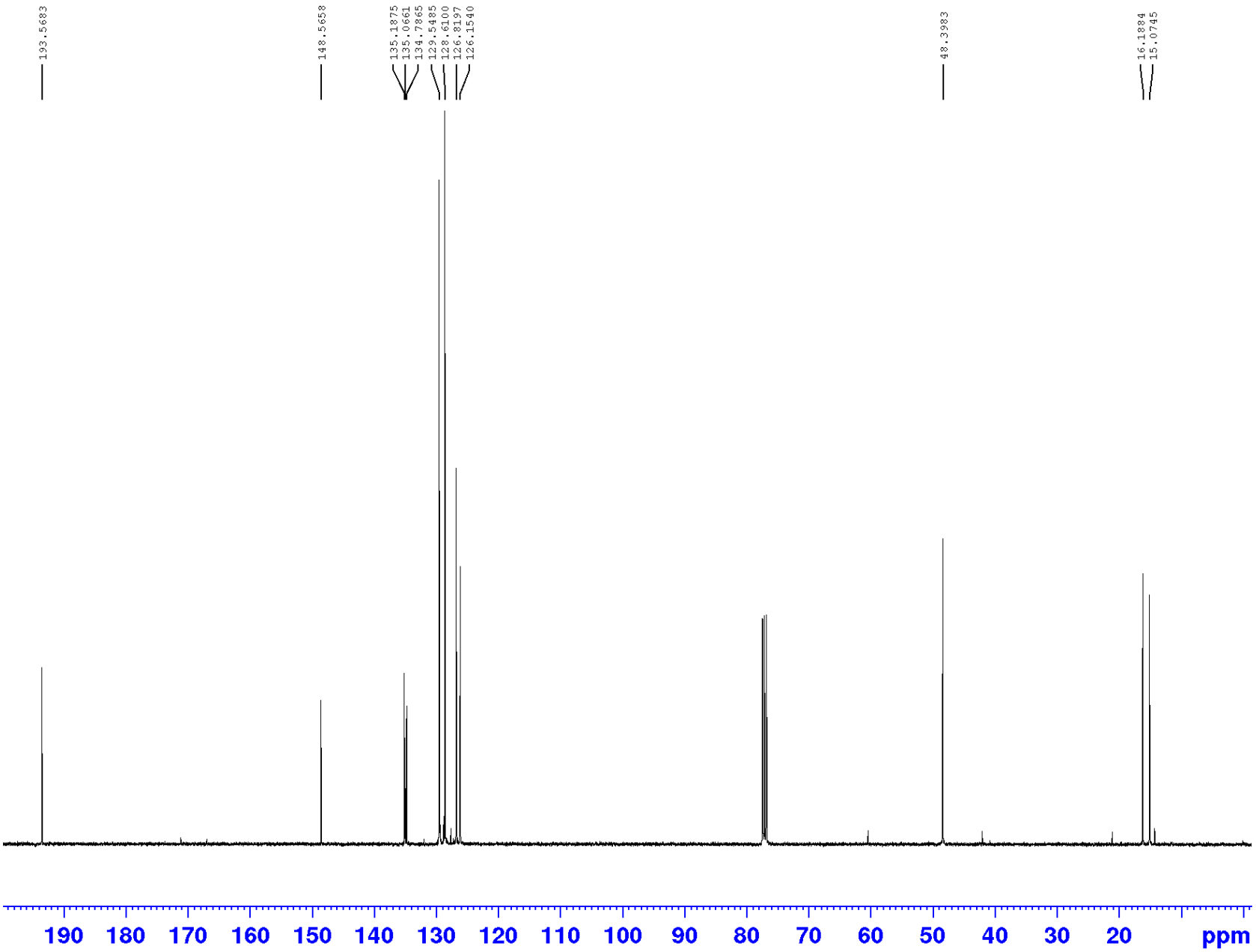


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C22 H18 O3 S2	(M+H)+	395.0768	394.0699	394.0697	94.62	-0.37
C20 H16 N3 O2 S2	(M+H)+	395.0768	394.07	394.0684	87.37	-4
C28 H12 N S	(M+H)+	395.0768	394.0697	394.069	85.4	-1.55
C16 H16 N3 O7 S	(M+H)+	395.0768	394.0699	394.0709	85	2.65
C15 H10 N10 O2 S	(M+H)+	395.0768	394.0701	394.0709	84.79	2.08

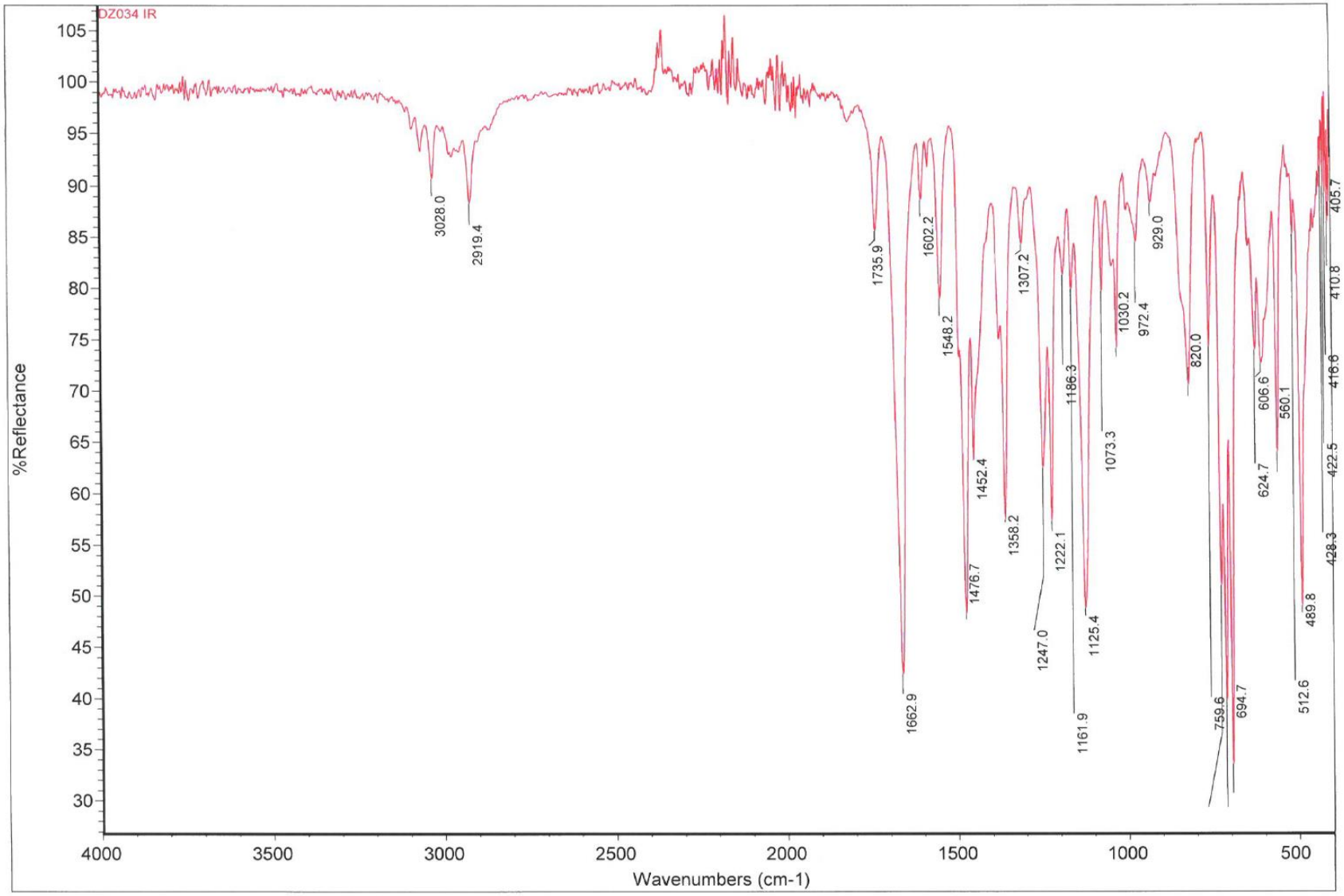
^{1}H-NMR spectrum of 10



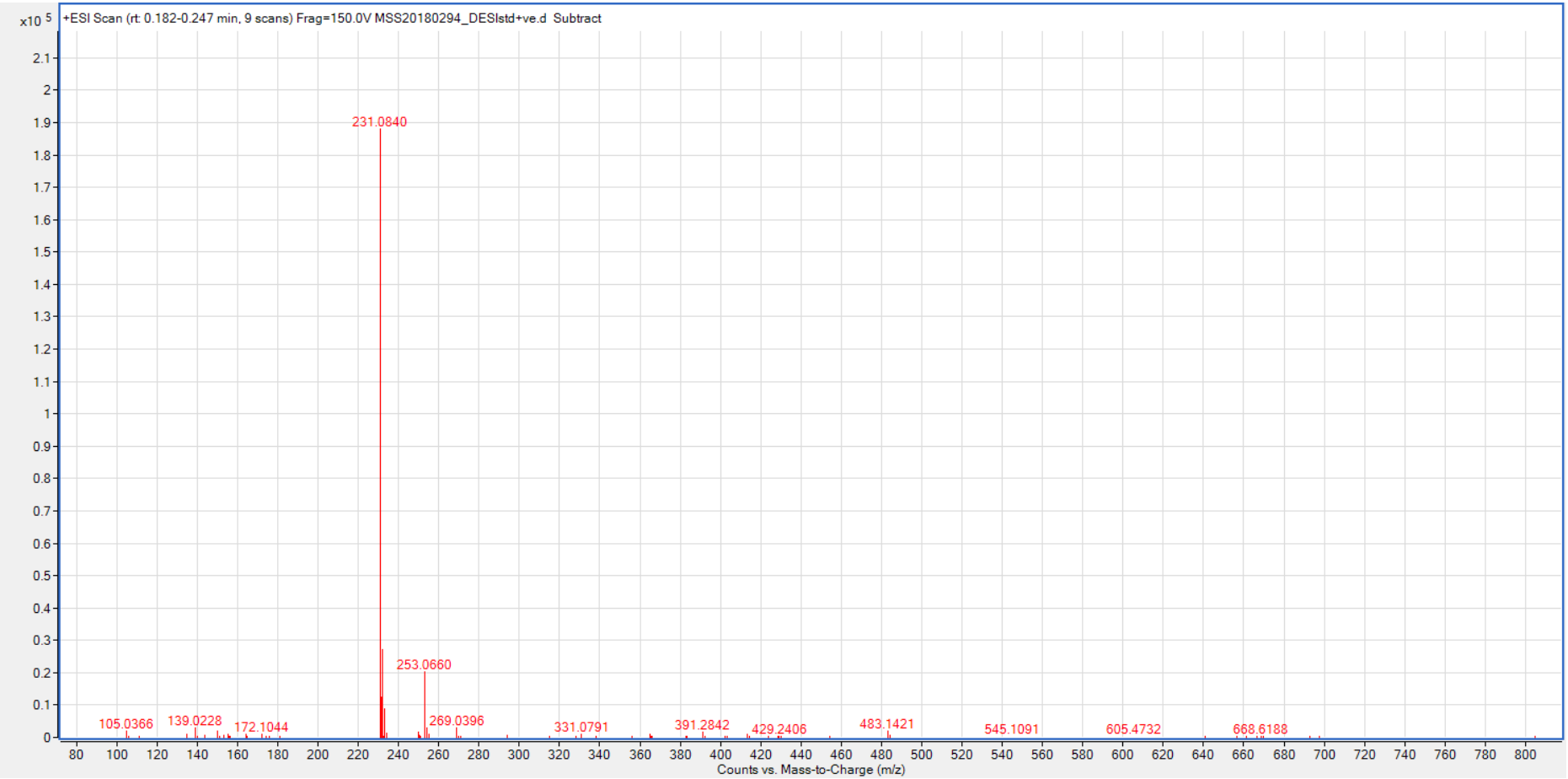
^{13}C-NMR spectrum of 10



IR spectrum of 10

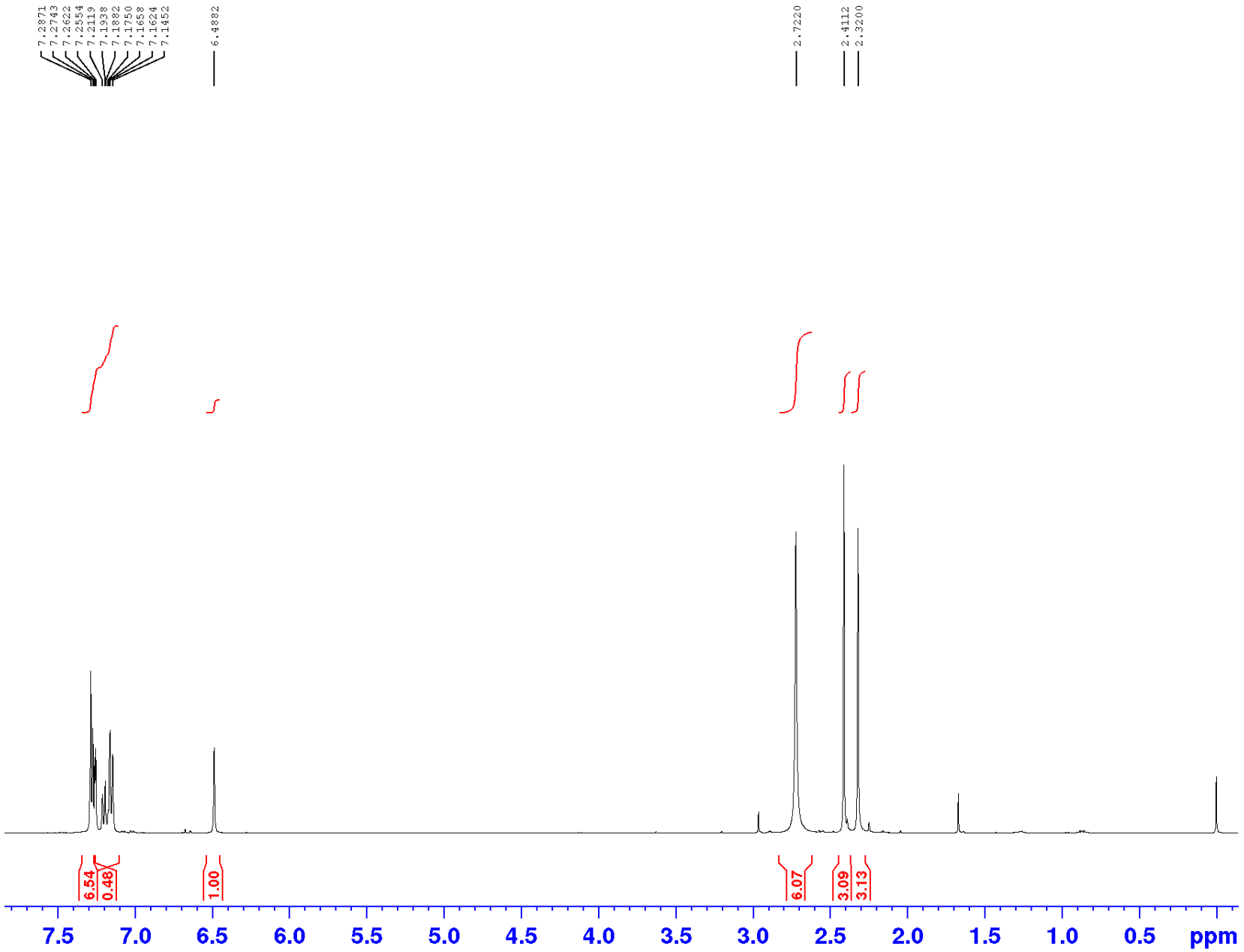


Mass spectrum of 10

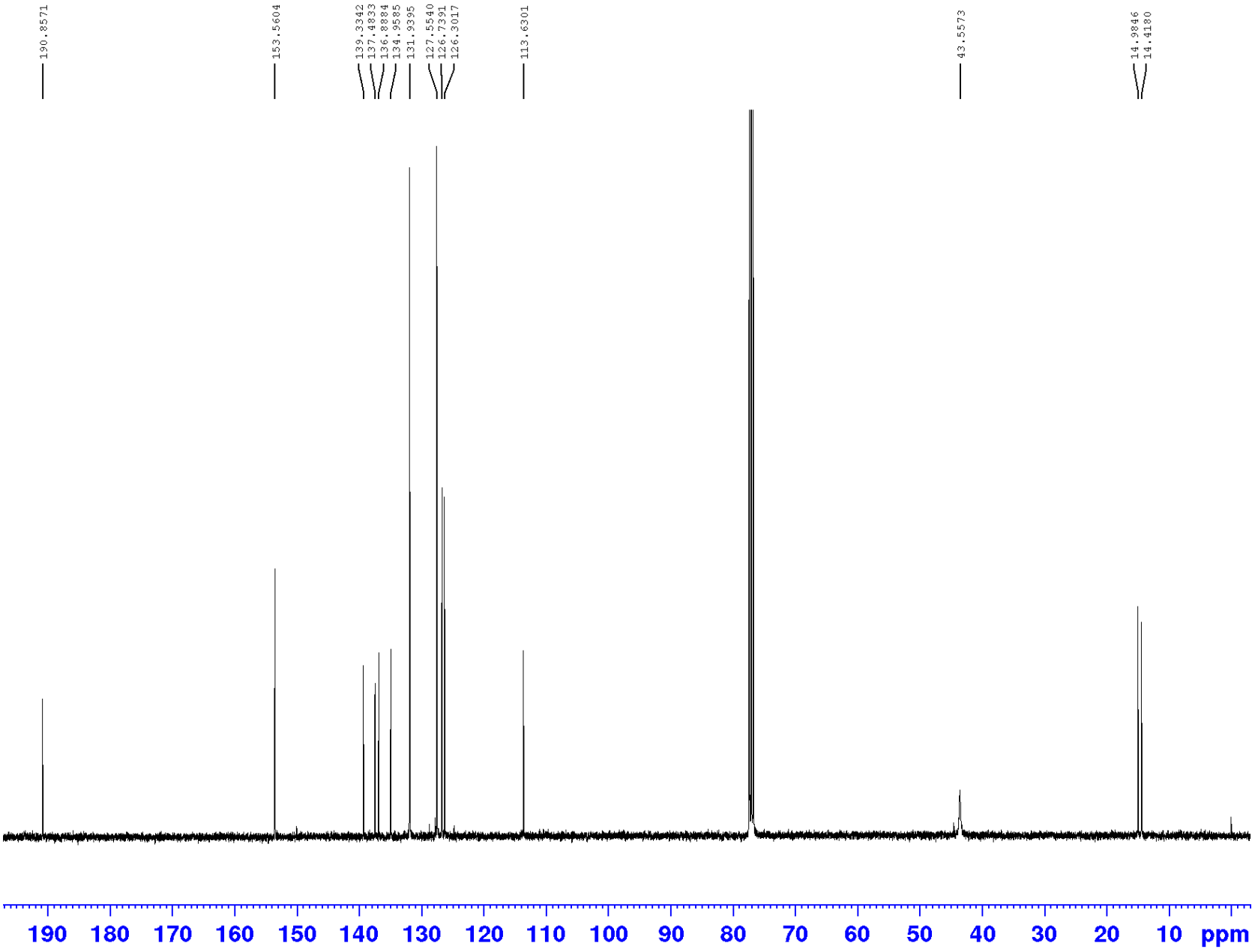


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C14 H14 O S	(M+H)+	231.0840	230.0768	230.0765	47.39	-0.98
C10 H14 O6	(M+H)+	231.0840	230.0768	230.079	29.55	9.89
C11 H18 O S2	(M+H)+	231.0840	230.0768	230.0799	19.15	13.67

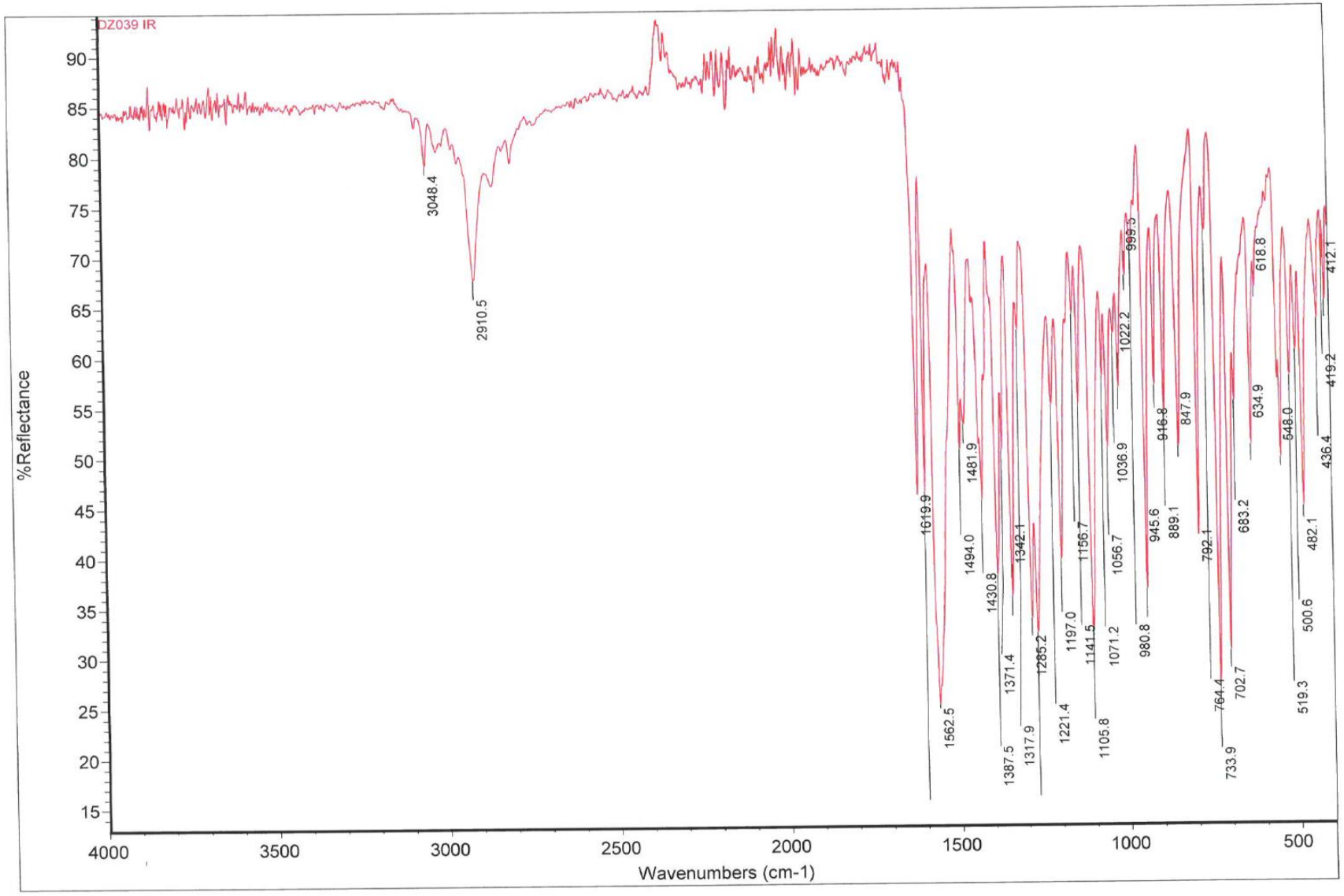
^{1}H-NMR spectrum of 12c



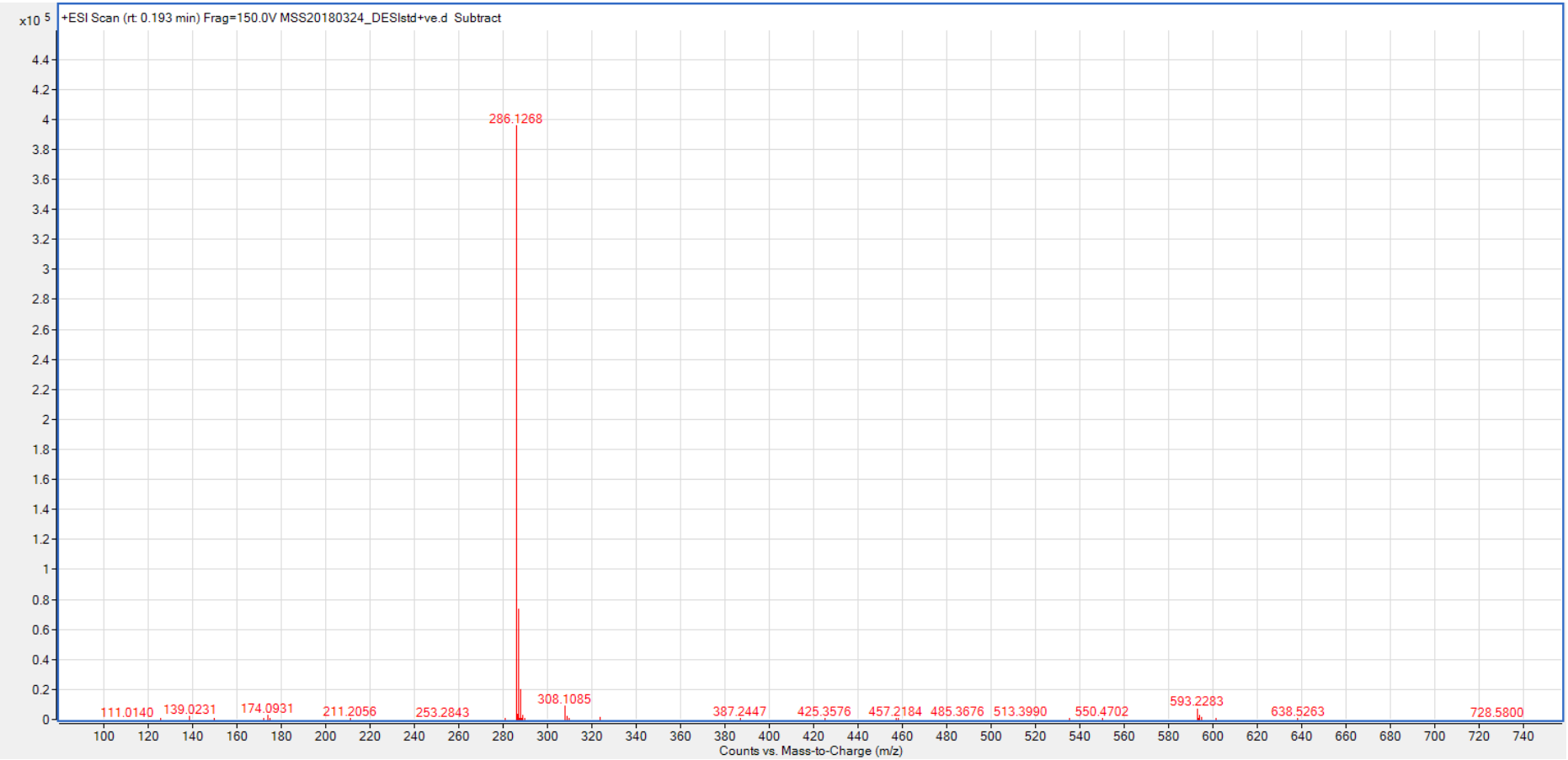
^{13}C-NMR spectrum of 12c



IR spectrum of 12c

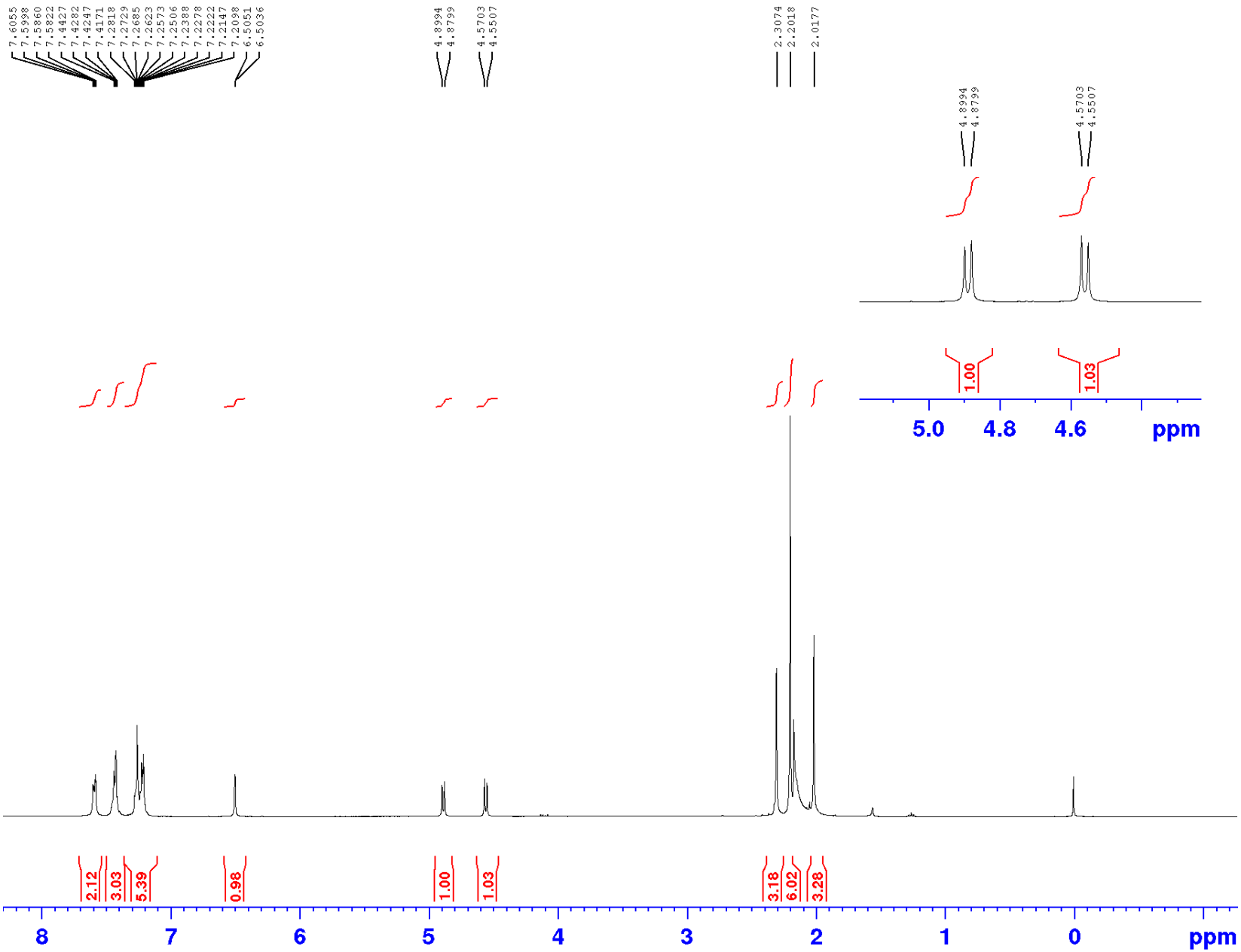


Mass spectrum of 12c

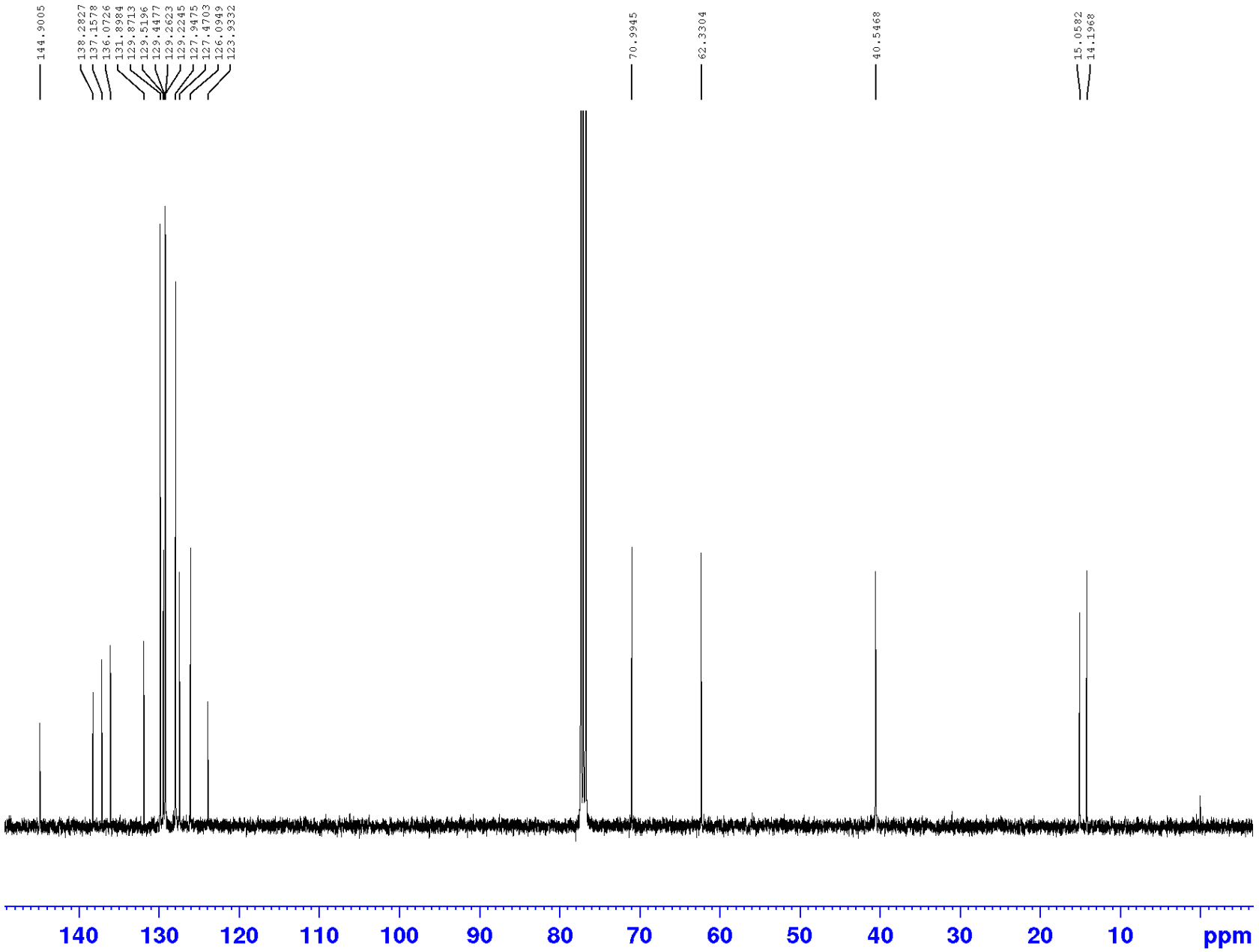


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C17 H19 N O S	(M+H)+	286.1268	285.1195	285.1187	97.02	-2.51
C11 H17 N4 O5	(M+H)+	286.1268	285.1193	285.1199	87.31	2.18
C11 H25 O4 S2	(M+H)+	286.1268	285.1195	285.1194	85.72	-0.41
C12 H21 N4 S2	(M+H)+	286.1268	285.1196	285.1208	85.41	3.94
C15 H17 N4 S	(M+H)+	286.1268	285.1195	285.1174	85.1	-7.52
C9 H15 N7 O4	(M+H)+	286.1268	285.1194	285.1186	83.59	-2.93
C10 H21 O9	(M+H)+	286.1268	285.1192	285.1186	82.13	-2.12
C12 H13 N8 O	(M+H)+	286.1268	285.1194	285.1212	79.92	6.55

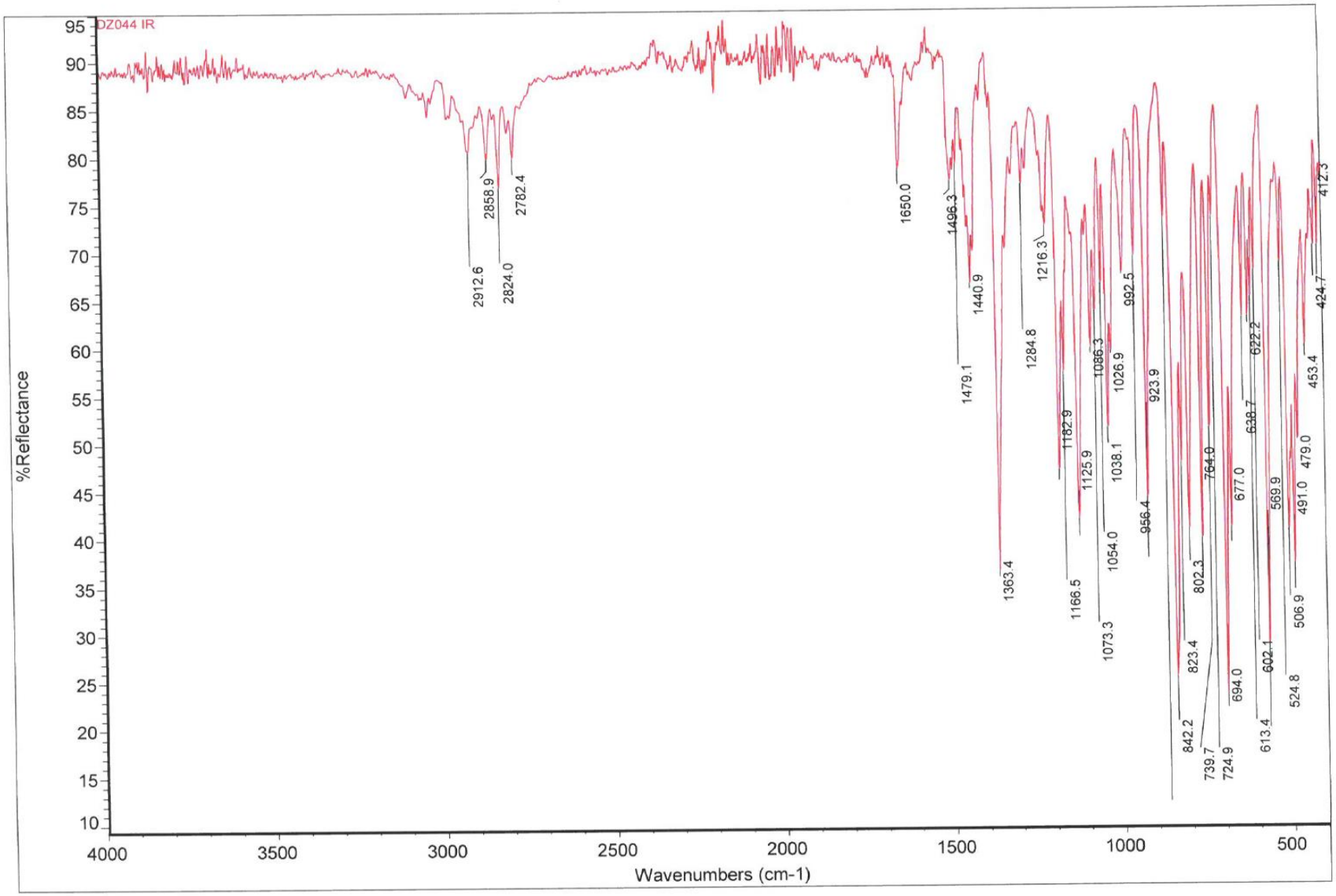
^{1}H-NMR spectrum of 13c-open



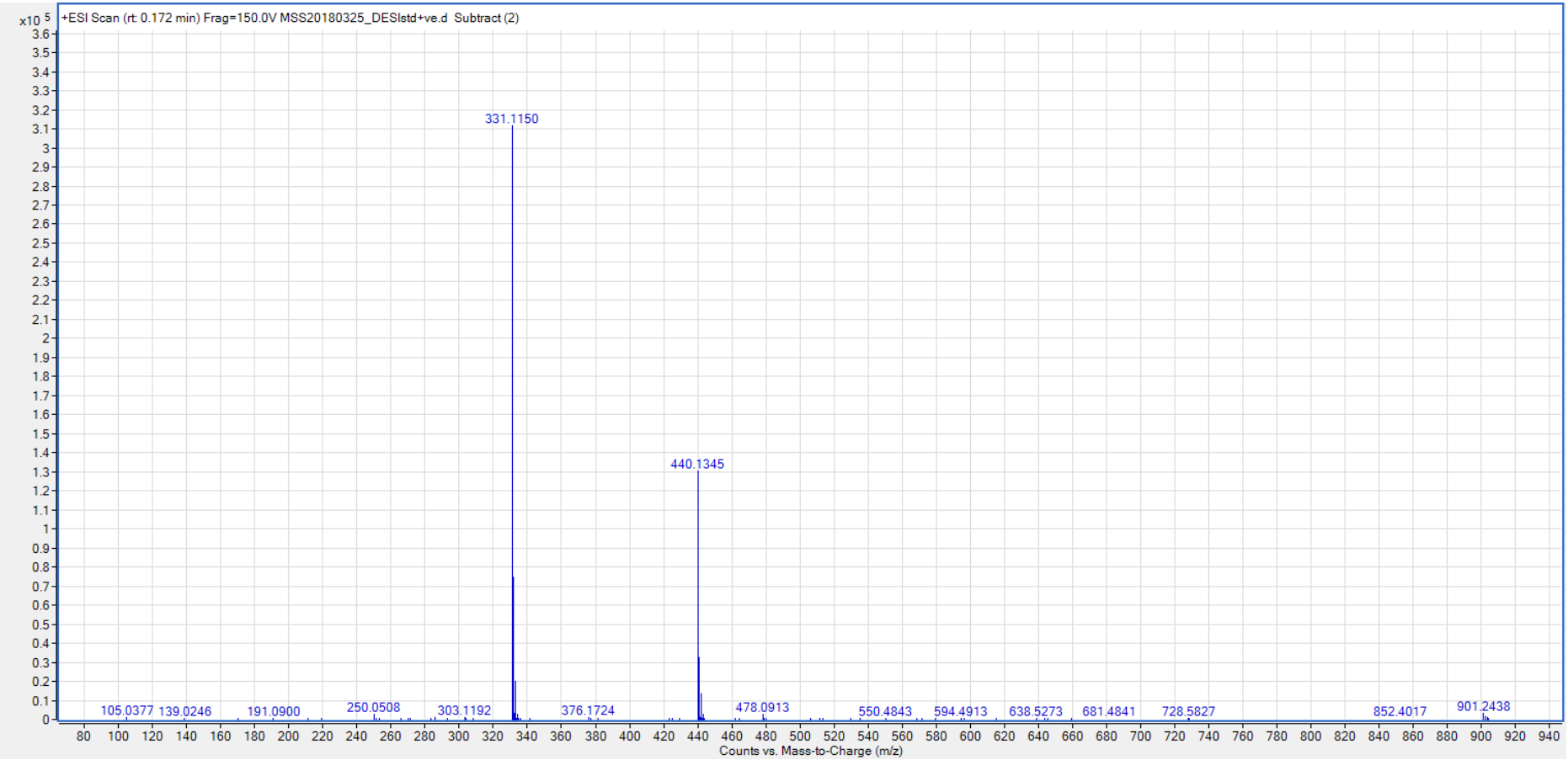
^{13}C-NMR spectrum of 13c-open



IR spectrum of 13c-open

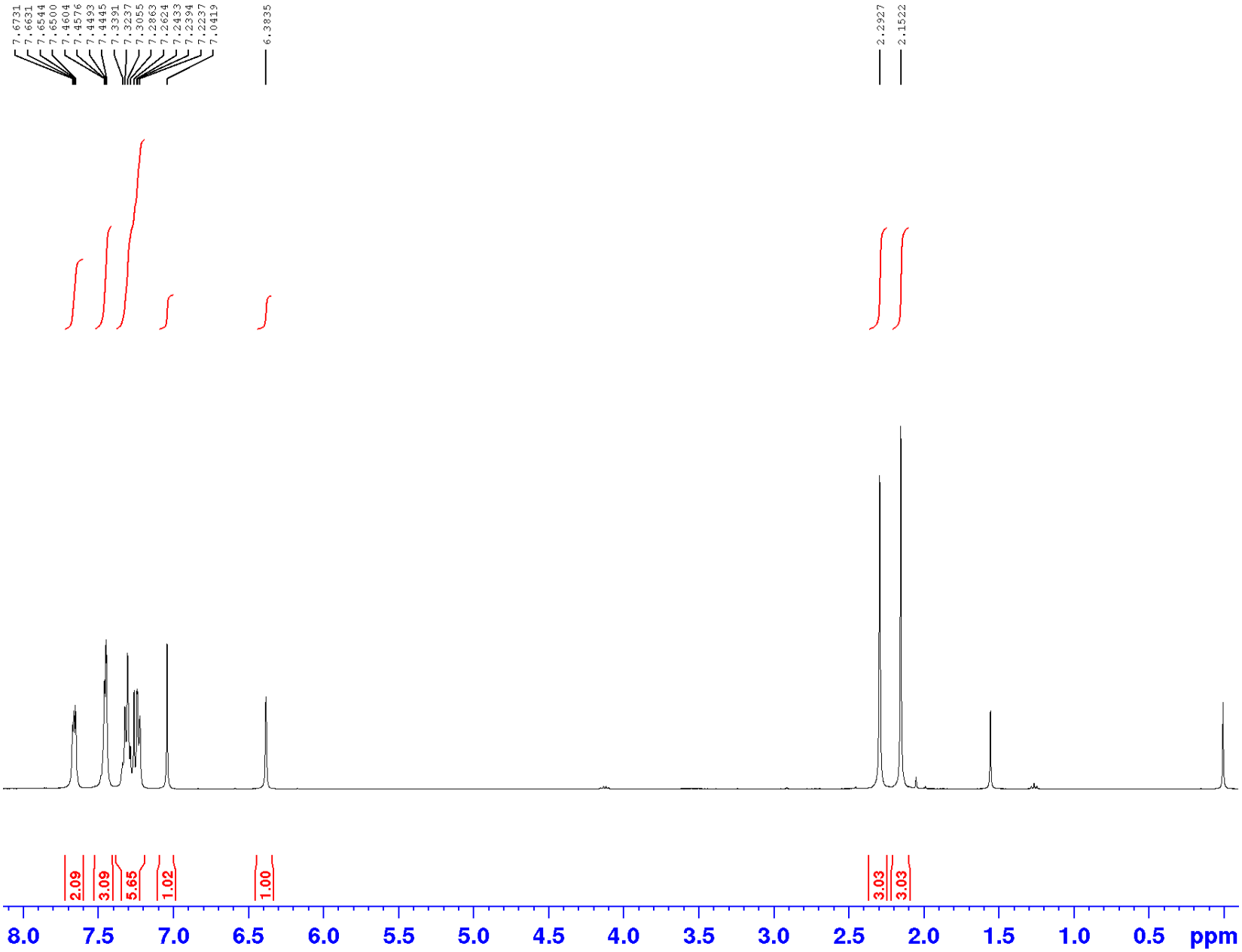


Mass spectrum of 13c-open

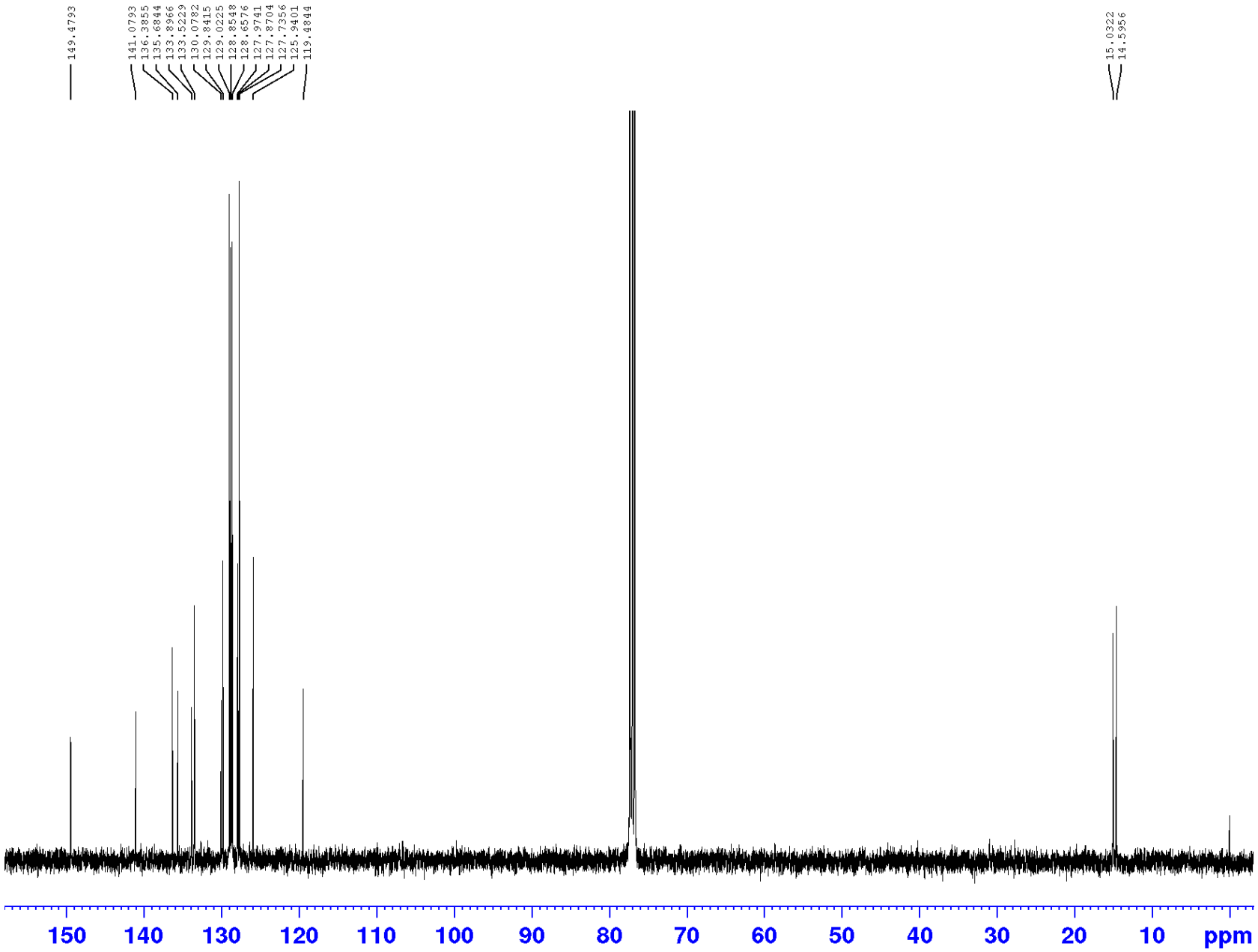


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C24 H25 N O3 S2	(M+H)+	440.1345	439.1273	439.1276	95.54	0.59
C16 H21 N7 O6 S	(M+H)+	440.1345	439.1274	439.1274	95.36	0
C22 H23 N4 O2 S2	(M+H)+	440.1345	439.1274	439.1262	93.02	-2.65
C18 H23 N4 O7 S	(M+H)+	440.1345	439.1273	439.1287	92.44	3.29
C15 H25 N3 O10 S	(M+H)+	440.1345	439.1273	439.1261	89.1	-2.82

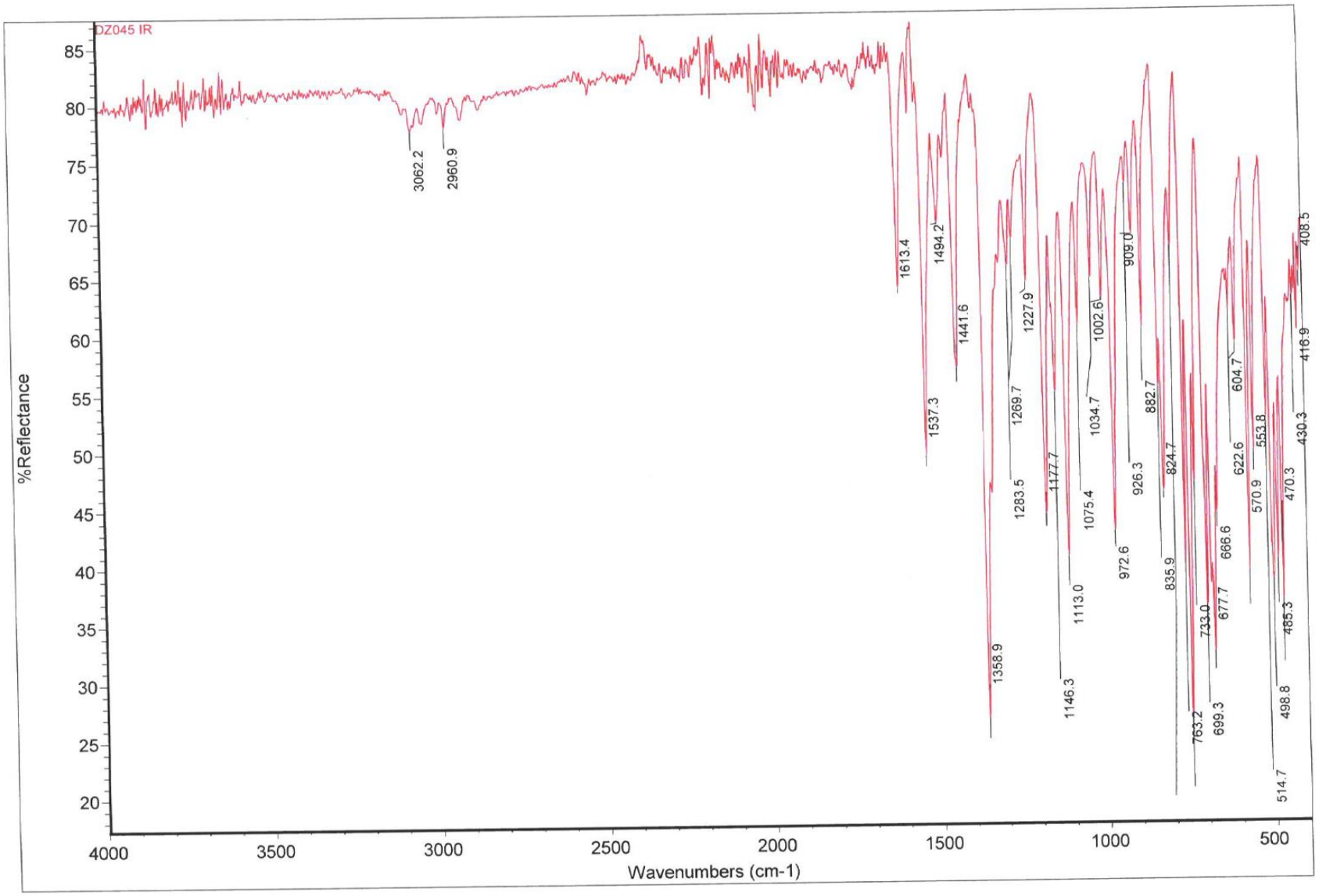
^{1}H-NMR spectrum of 14c-open



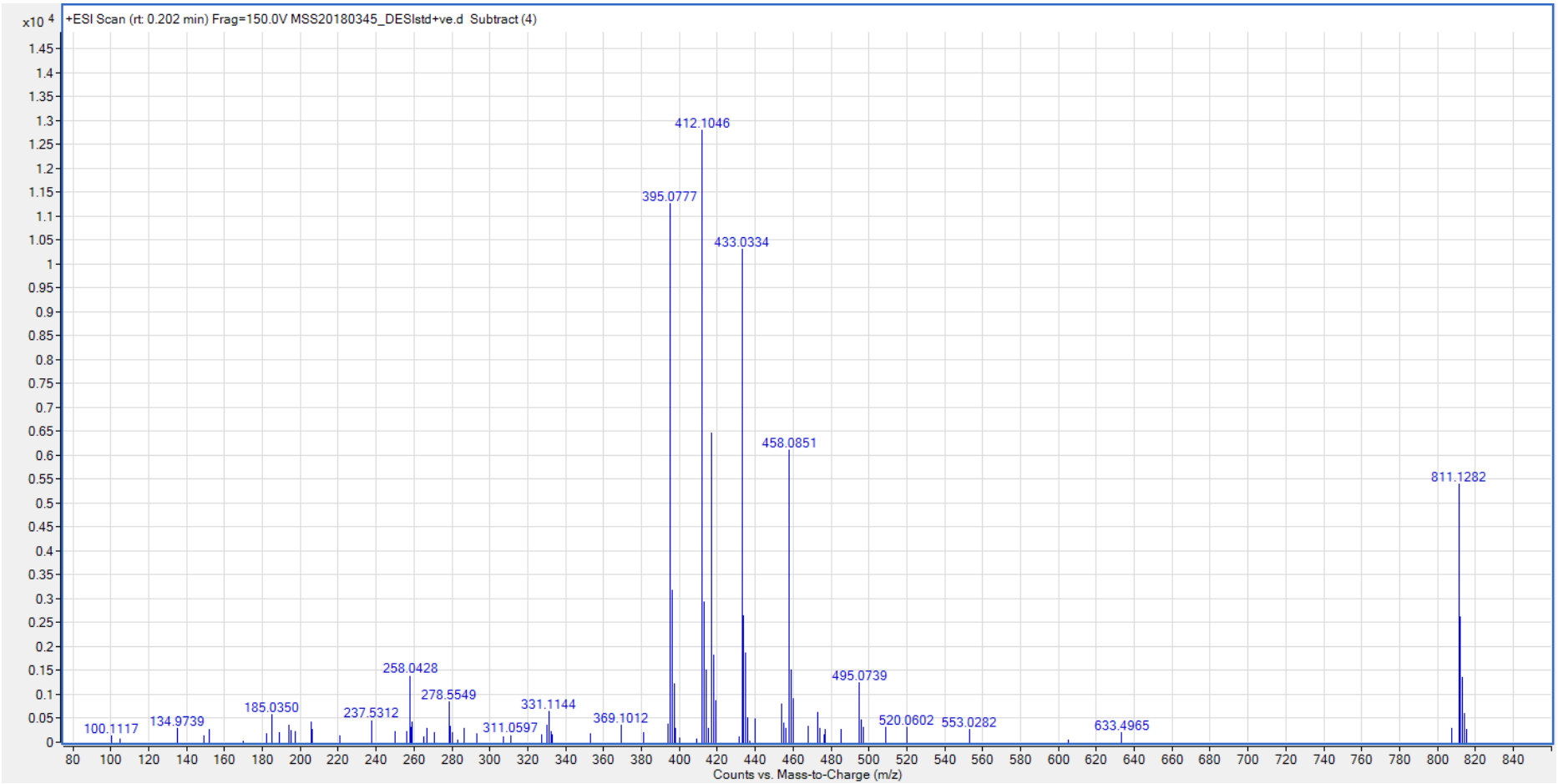
^{13}C-NMR spectrum of 14c-open



IR spectrum of 14c-open

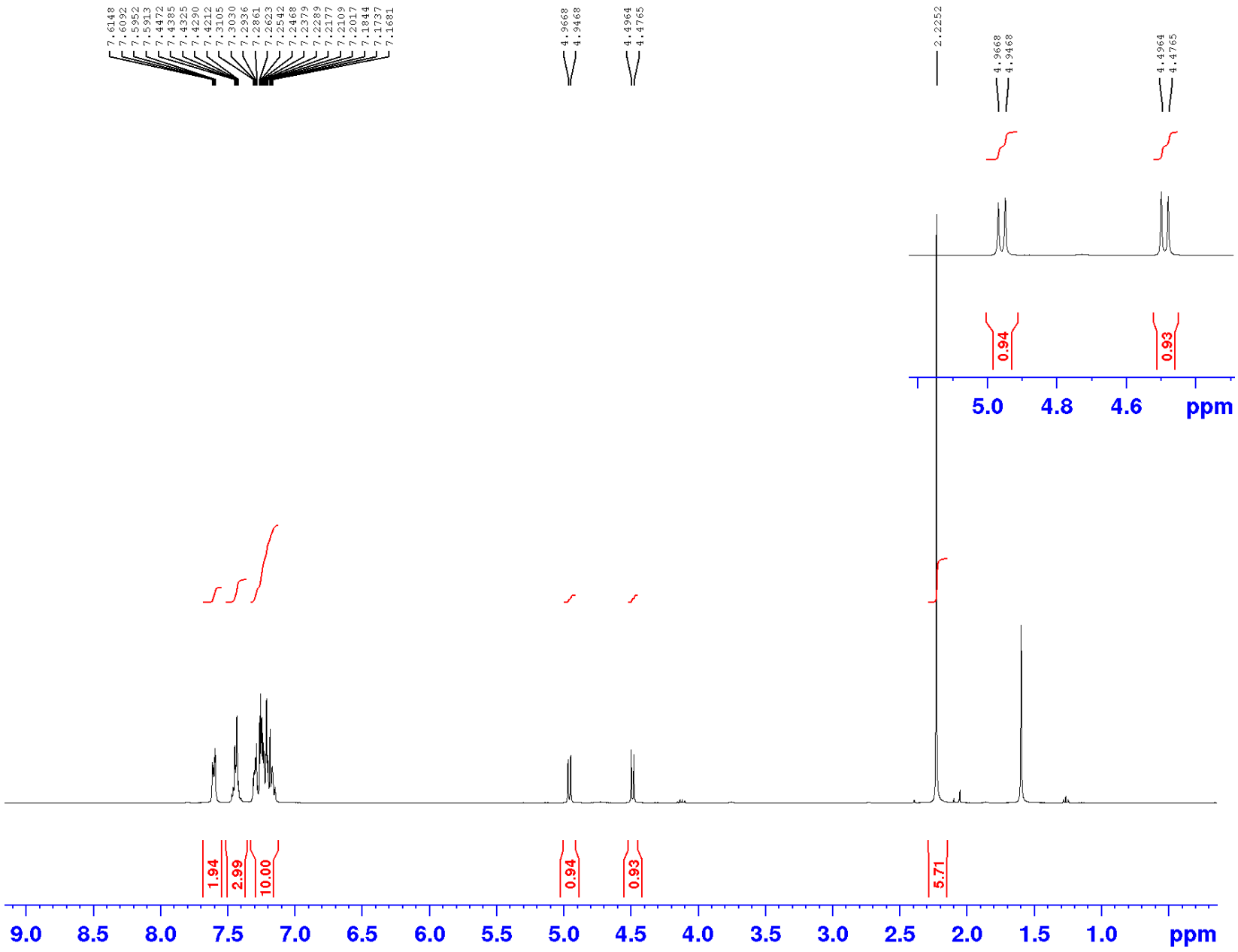


Mass spectrum of 14c-open

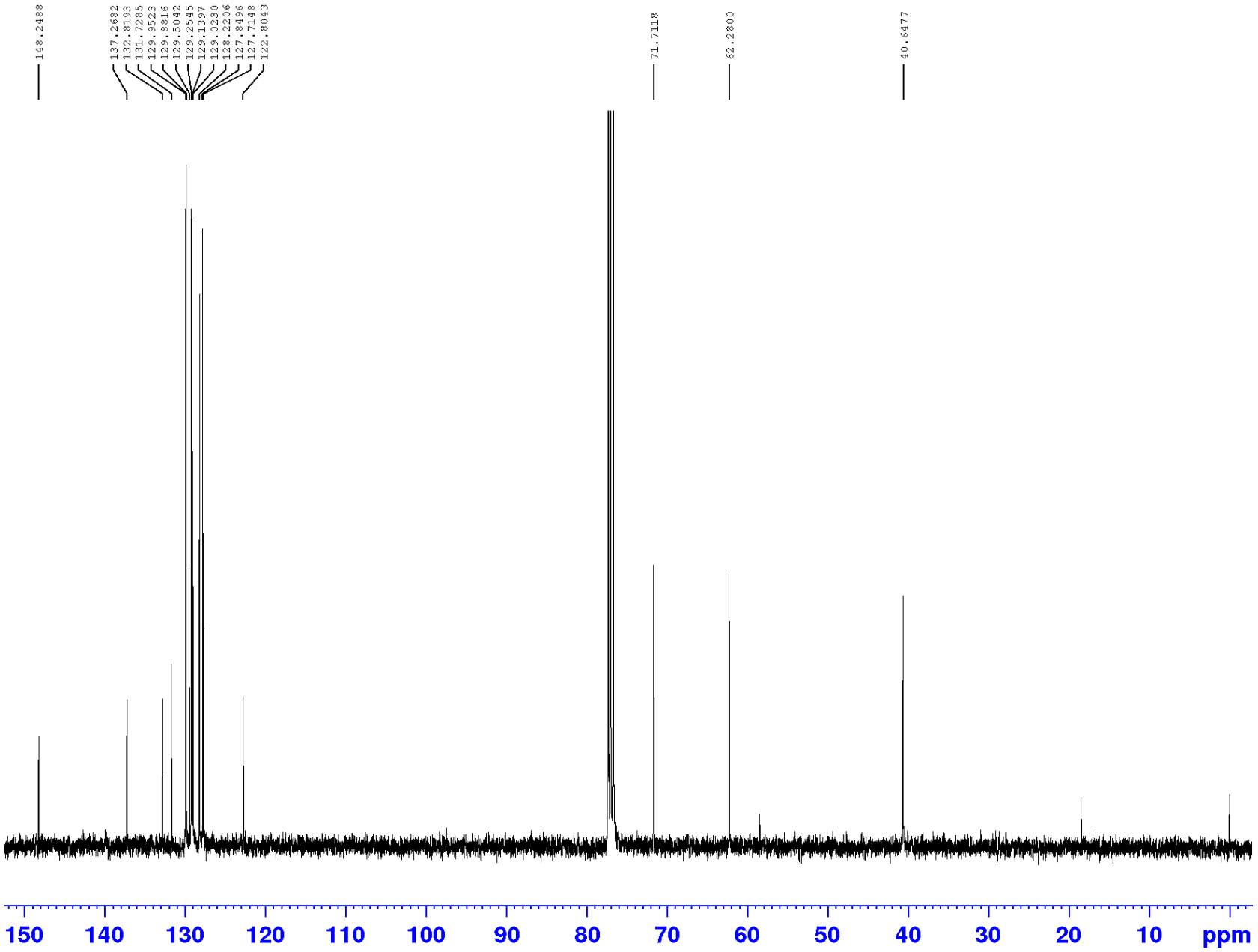


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C22 H18 O3 S2	(M+Na)+	417.0593	394.0697	394.0697	92.93	0.17
C21 H14 O8	(M+Na)+	417.0593	394.069	394.0689	75.25	-0.23
C25 H14 O3 S	(M+Na)+	417.0593	394.0694	394.0664	68.53	-7.8
C19 H22 O3 S3	(M+Na)+	417.0593	394.0698	394.0731	67.54	8.38
C18 H18 O8 S	(M+Na)+	417.0593	394.0695	394.0722	67.33	6.9

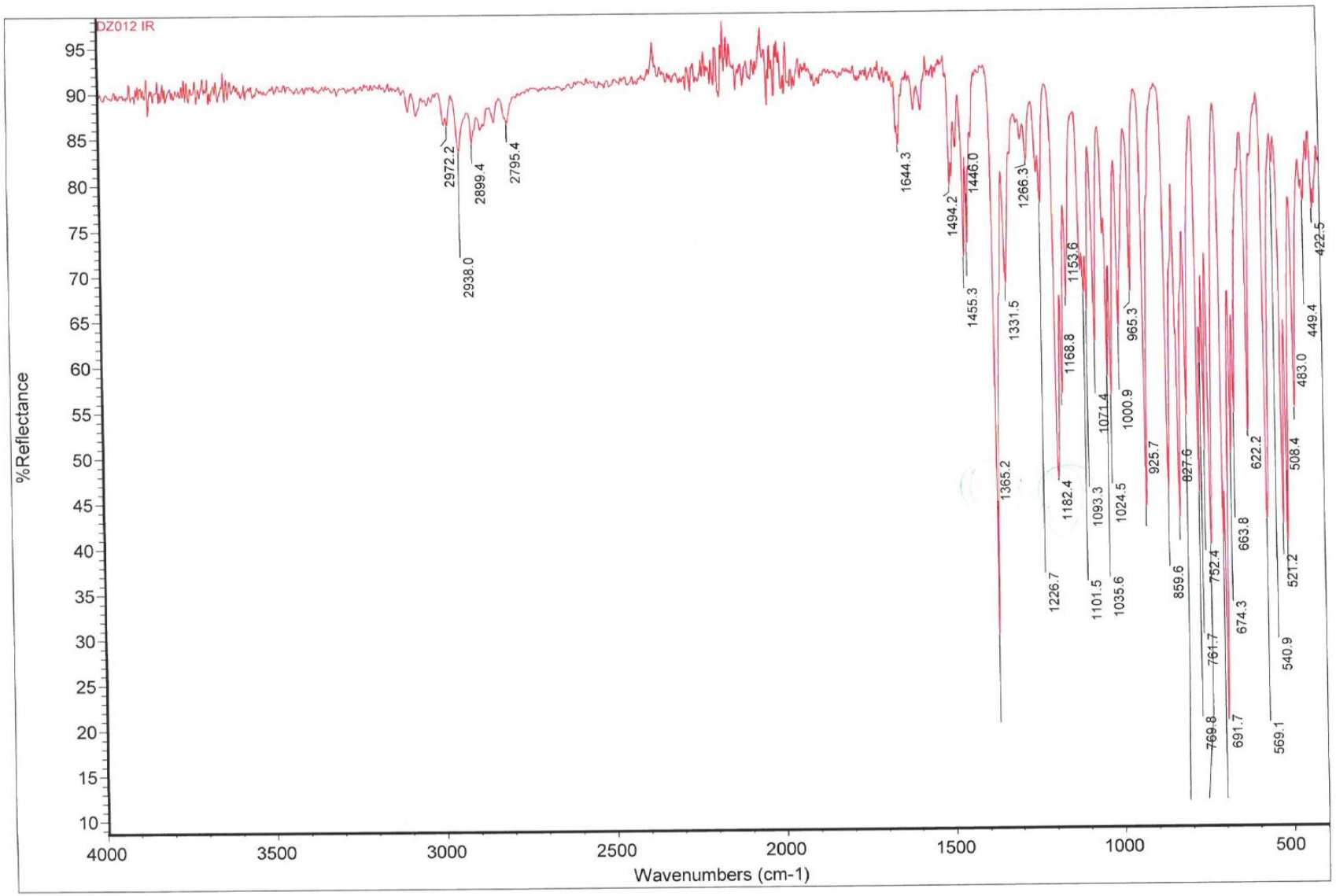
^{1}H-NMR spectrum of 13d-open



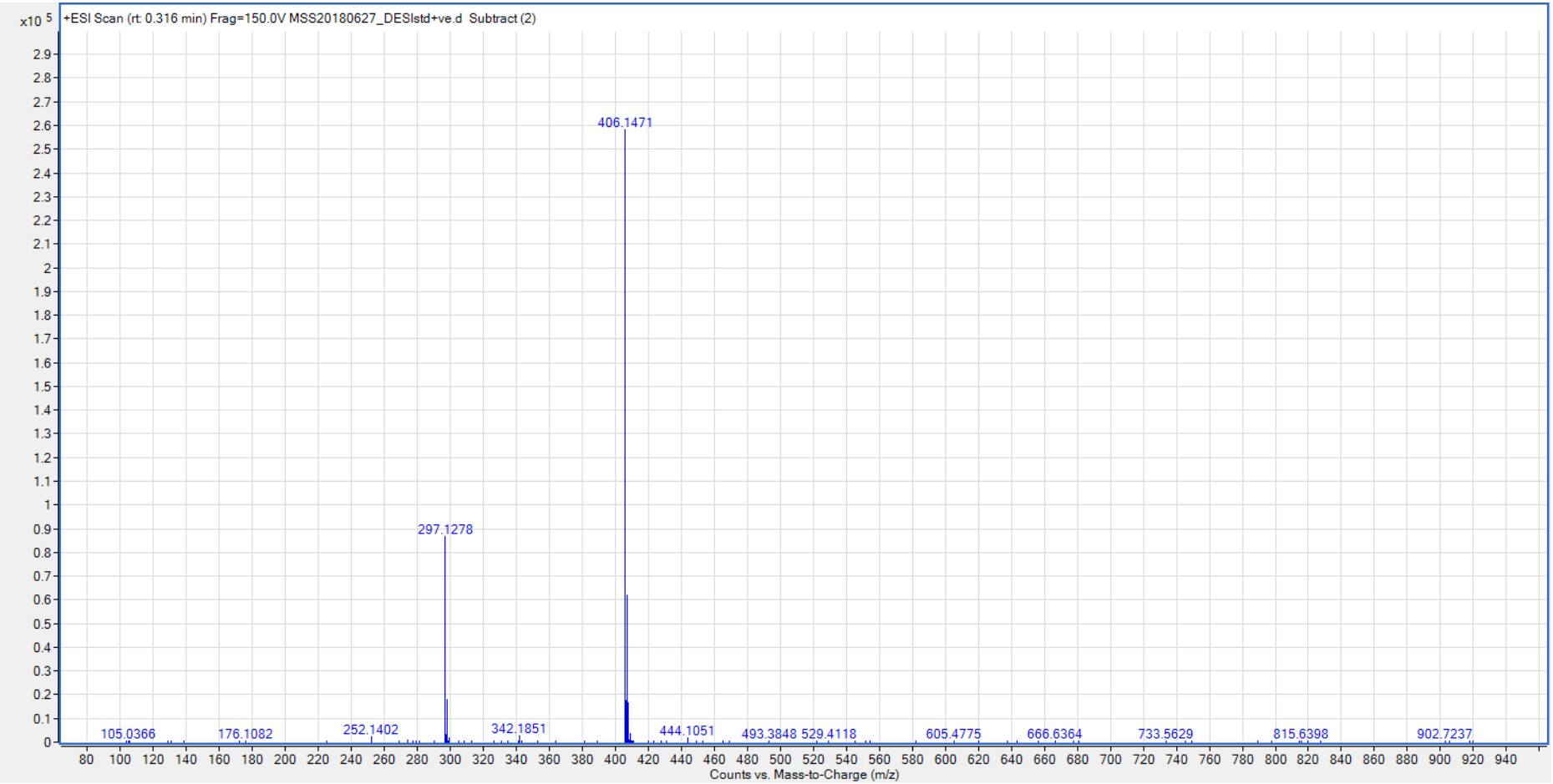
^{13}C-NMR spectrum of 13d-open



IR spectrum of 13d-open

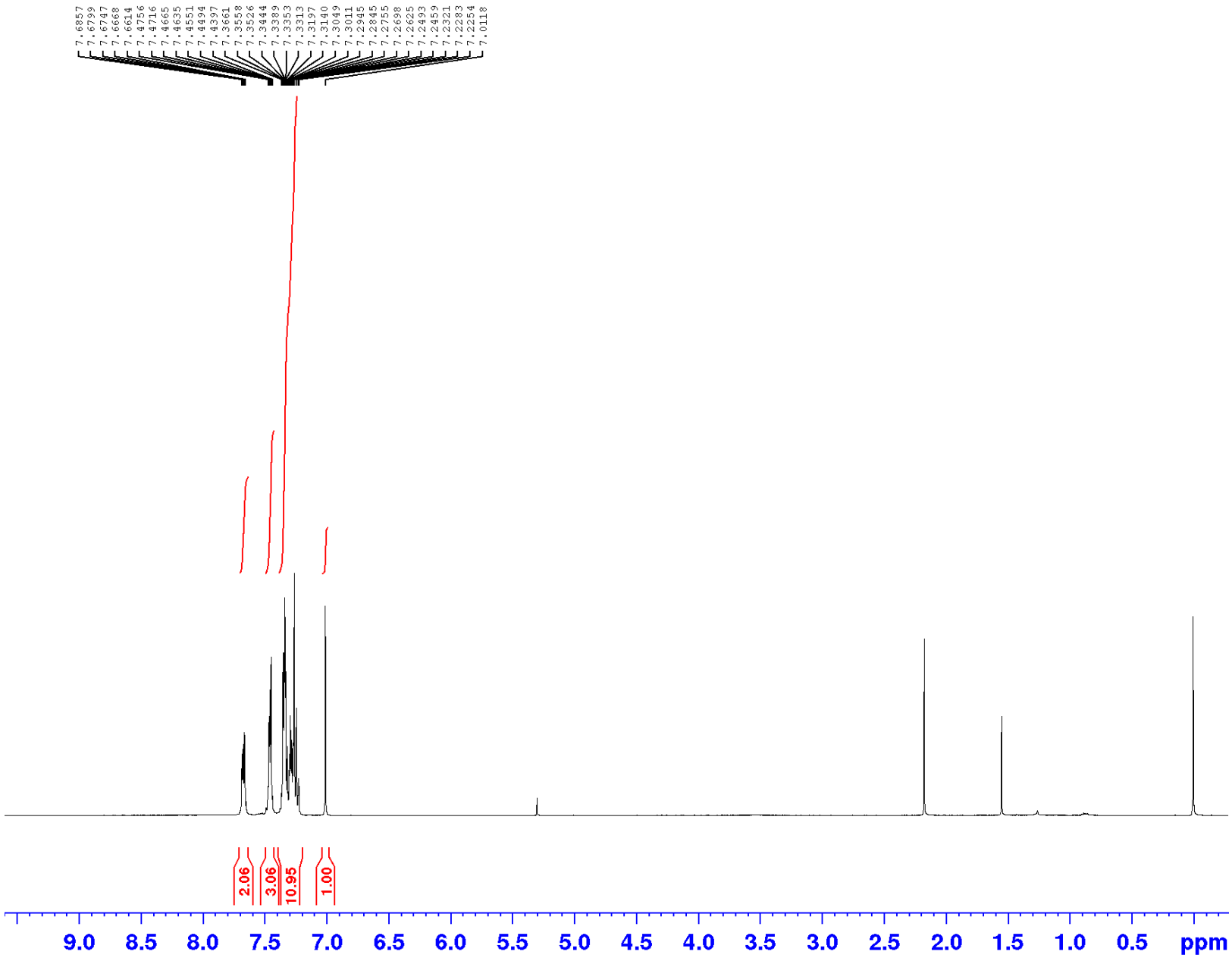


Mass spectrum of 13d-open

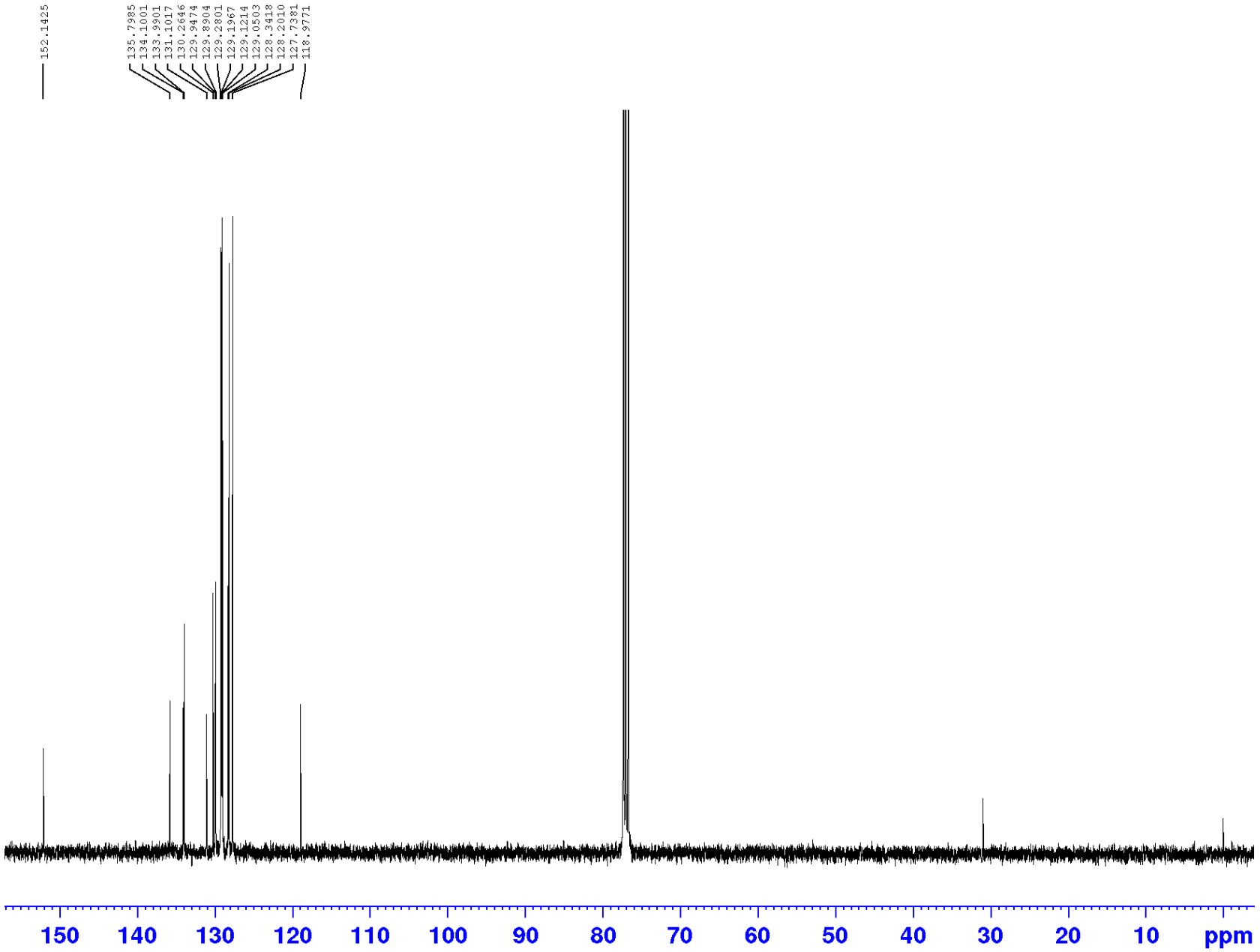


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C24 H23 N O3 S	(M+H)+	406.1471	405.1398	405.1399	97.23	0.06
C22 H21 N4 O2 S	(M+H)+	406.1471	405.1399	405.1385	93.27	-3.44
C30 H17 N2	(M+H)+	406.1471	405.1396	405.1392	82.94	-0.94
C27 H21 N2 S	(M+H)+	406.1471	405.1398	405.1425	77.41	6.68
C27 H19 N O3	(M+H)+	406.1471	405.1395	405.1365	70.03	-7.54

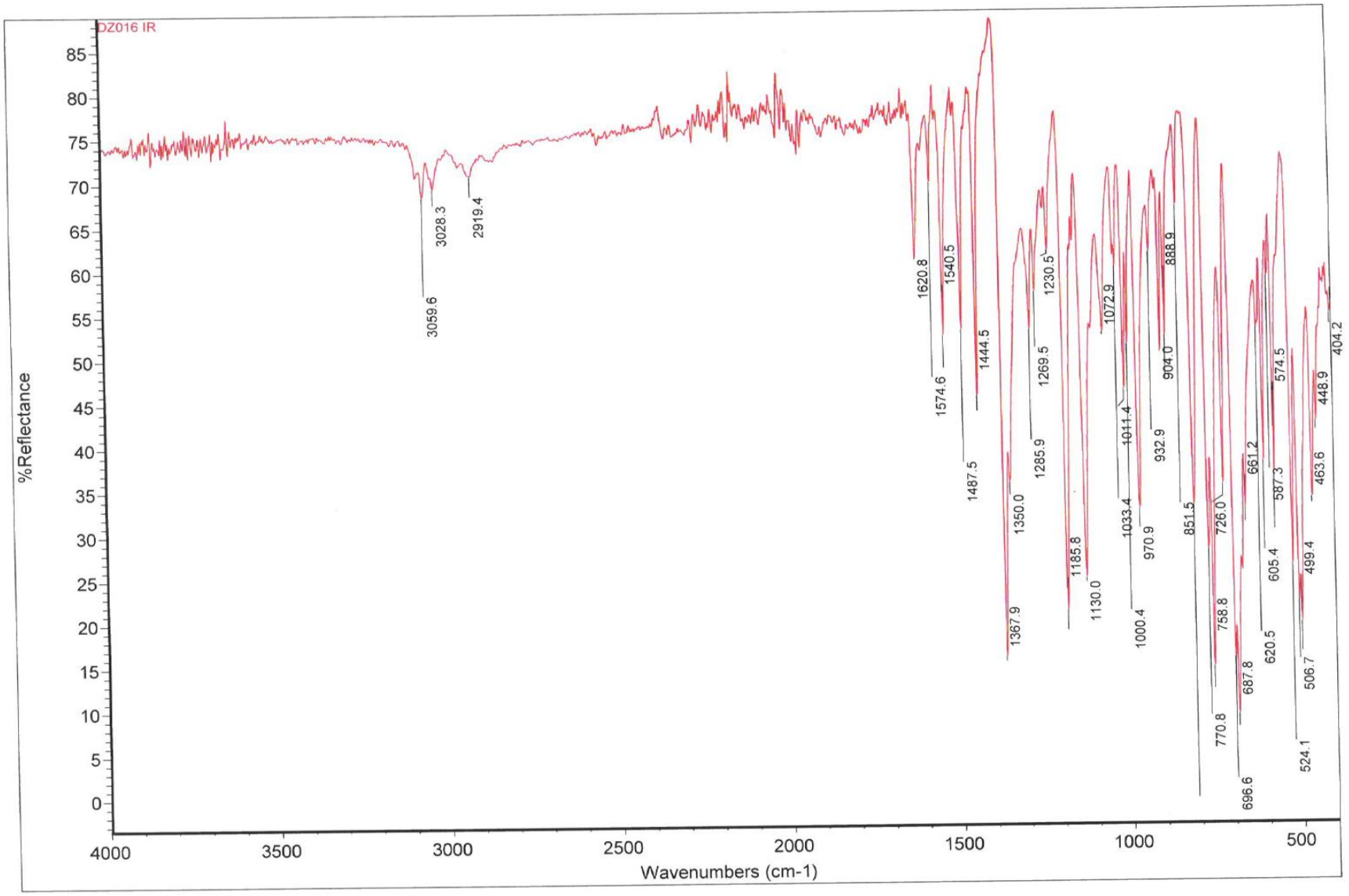
^{1}H-NMR spectrum of 14d-open



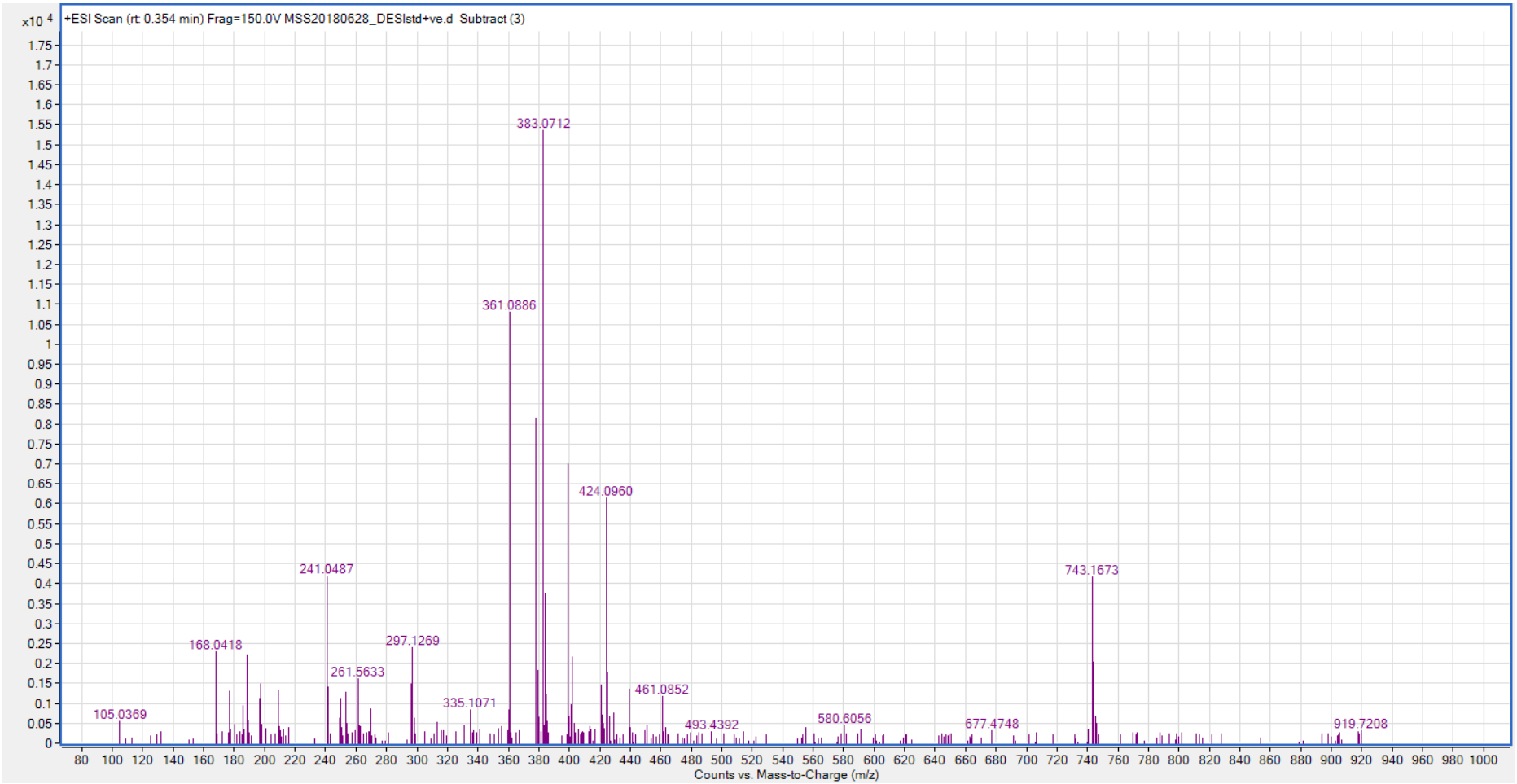
^{13}C-NMR spectrum of 14d-open



IR spectrum of 14d-open

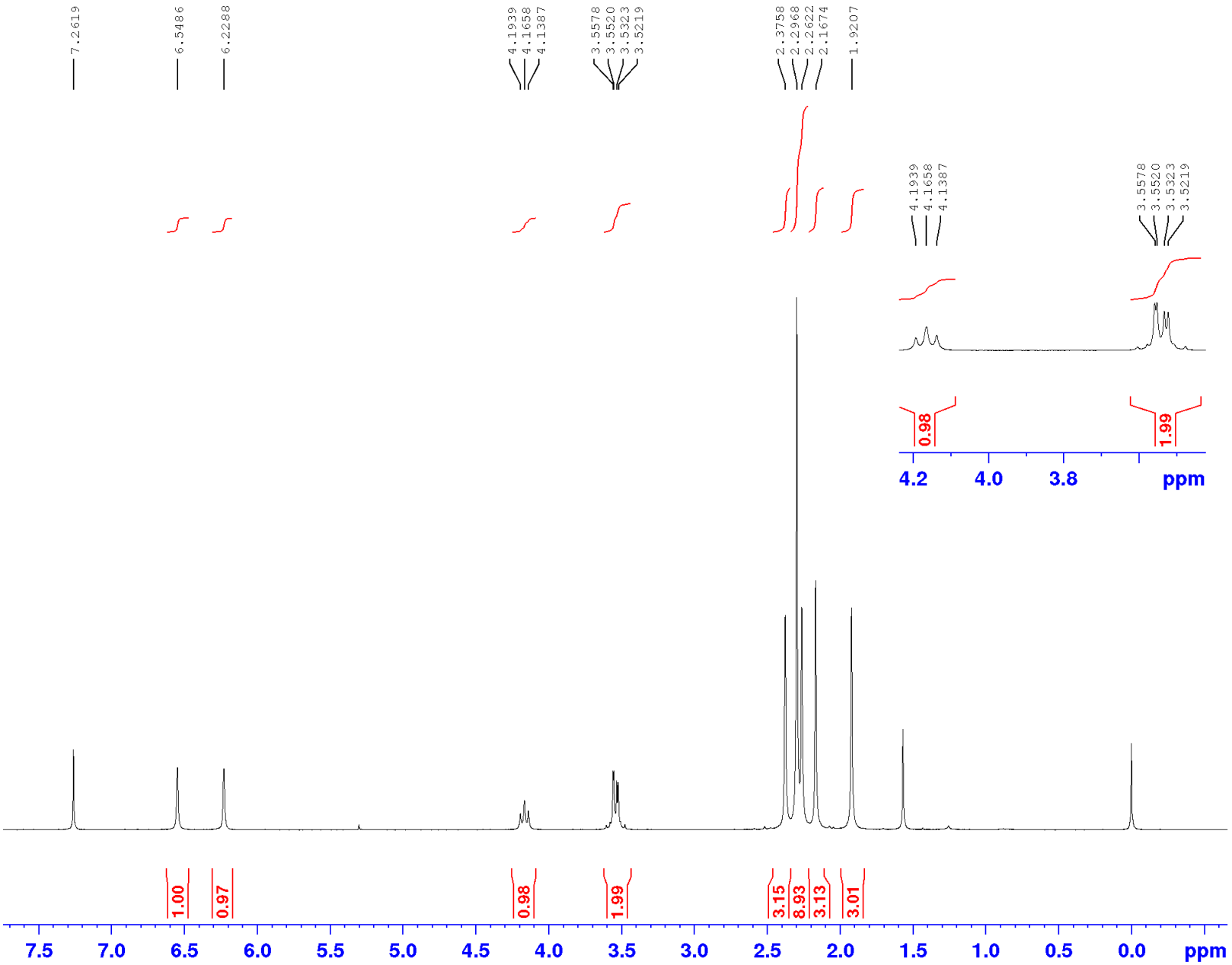


Mass spectrum of 14d-open

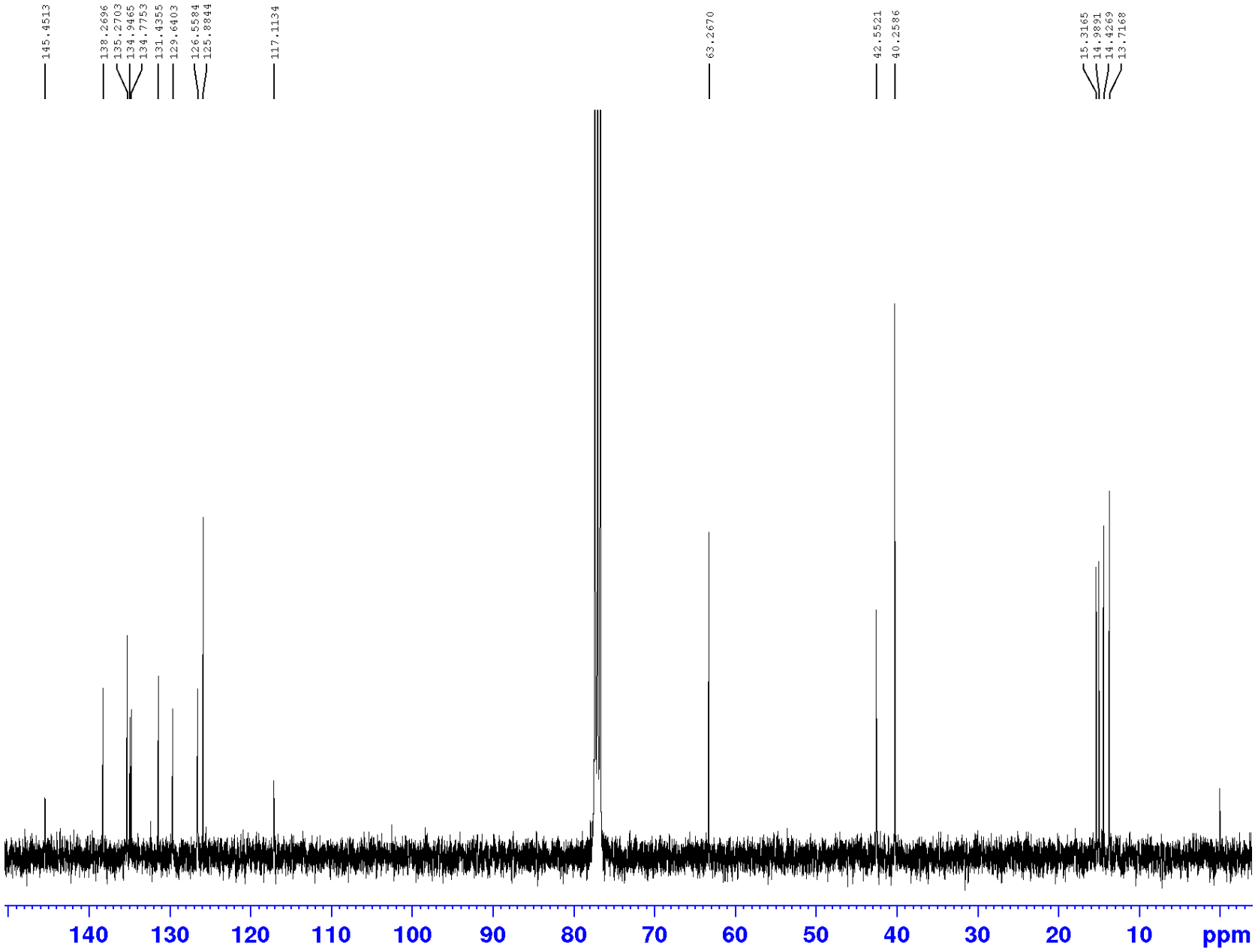


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C22 H16 O3 S	(M+Na)+	383.0712	360.0818	360.082	98.29	0.52
C25 H12 O3	(M+Na)+	383.0712	360.0814	360.0786	69.88	-7.78

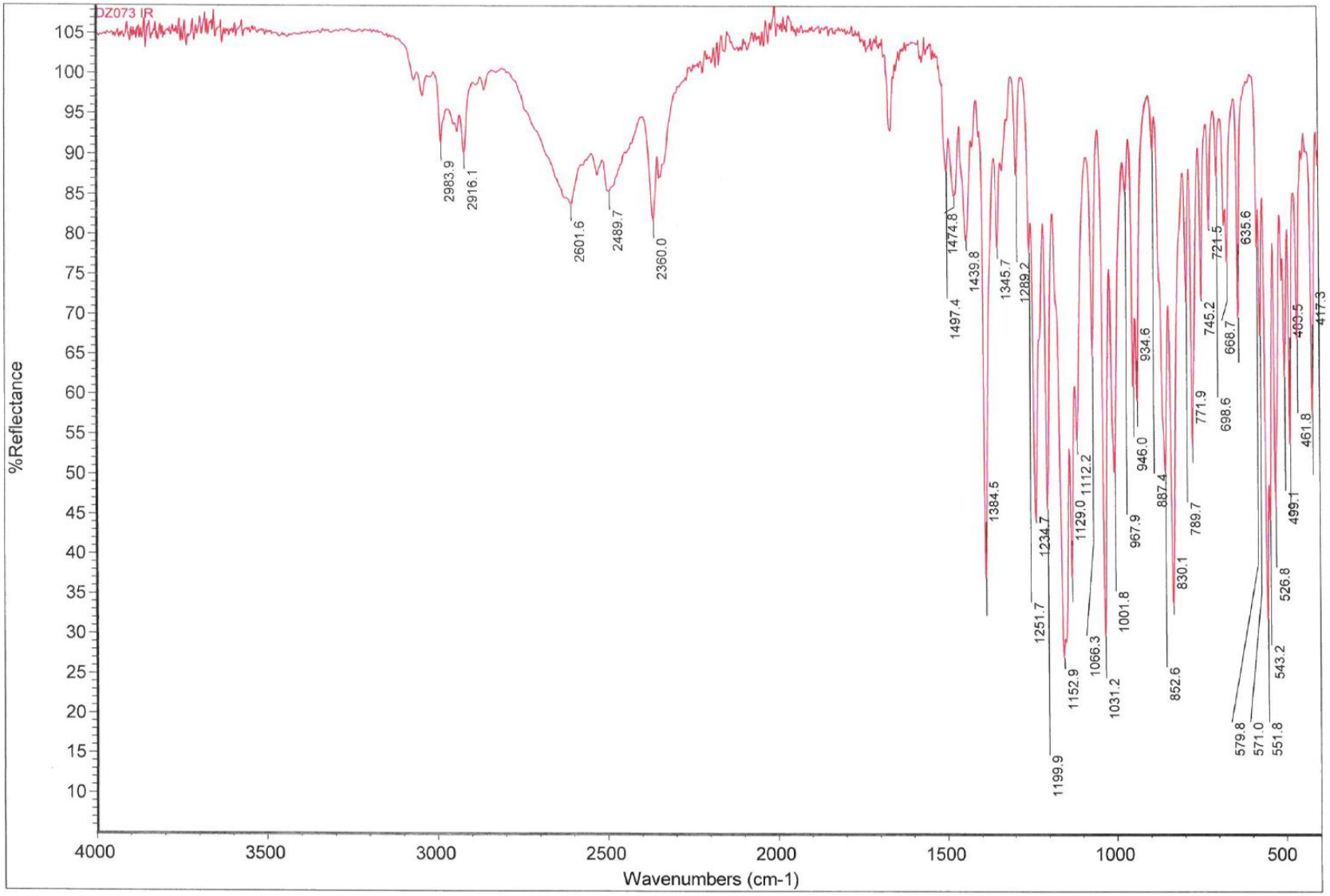
^{1}H-NMR spectrum of 13e-open



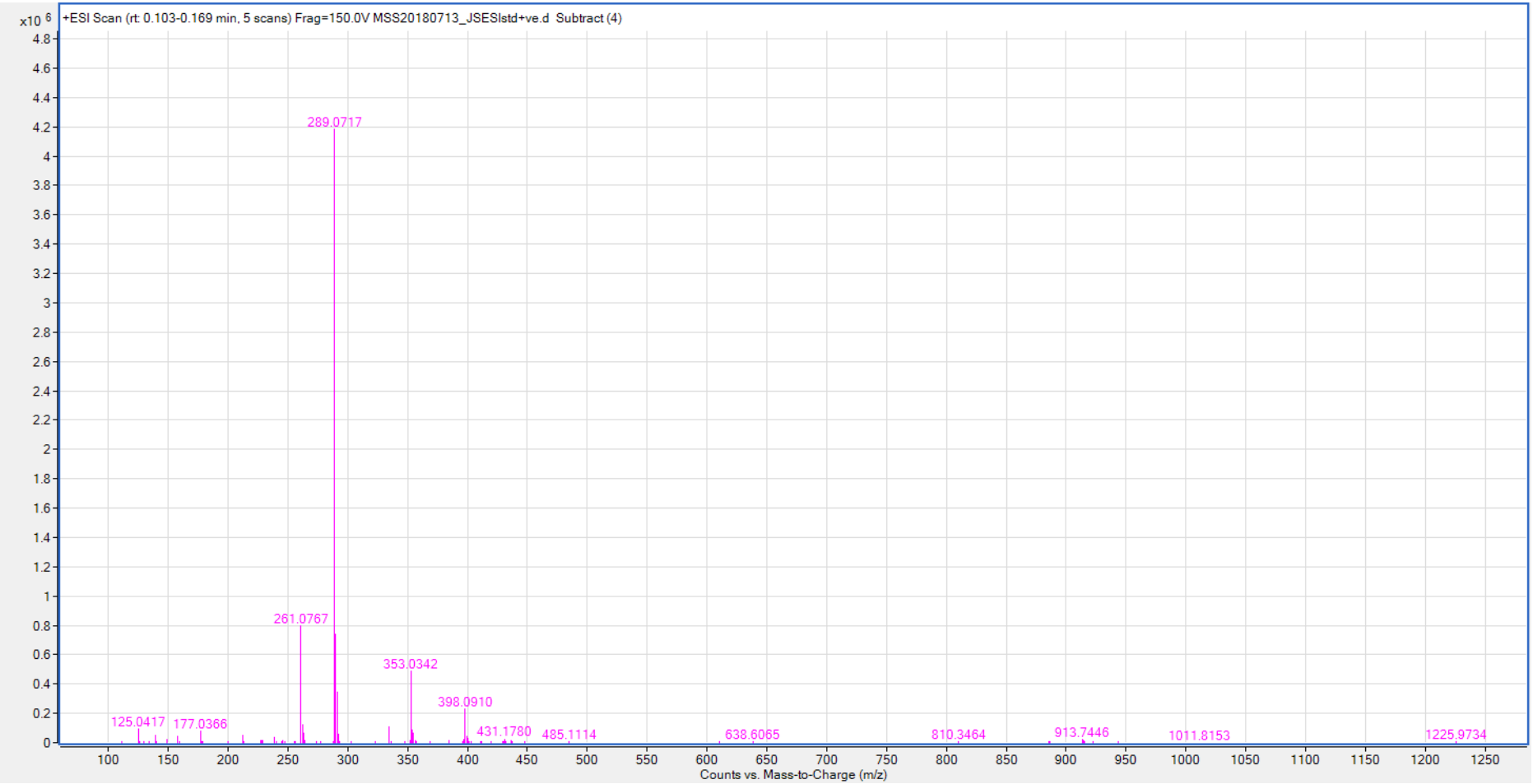
^{13}C-NMR spectrum of 13e-open



IR spectrum of 13e-open

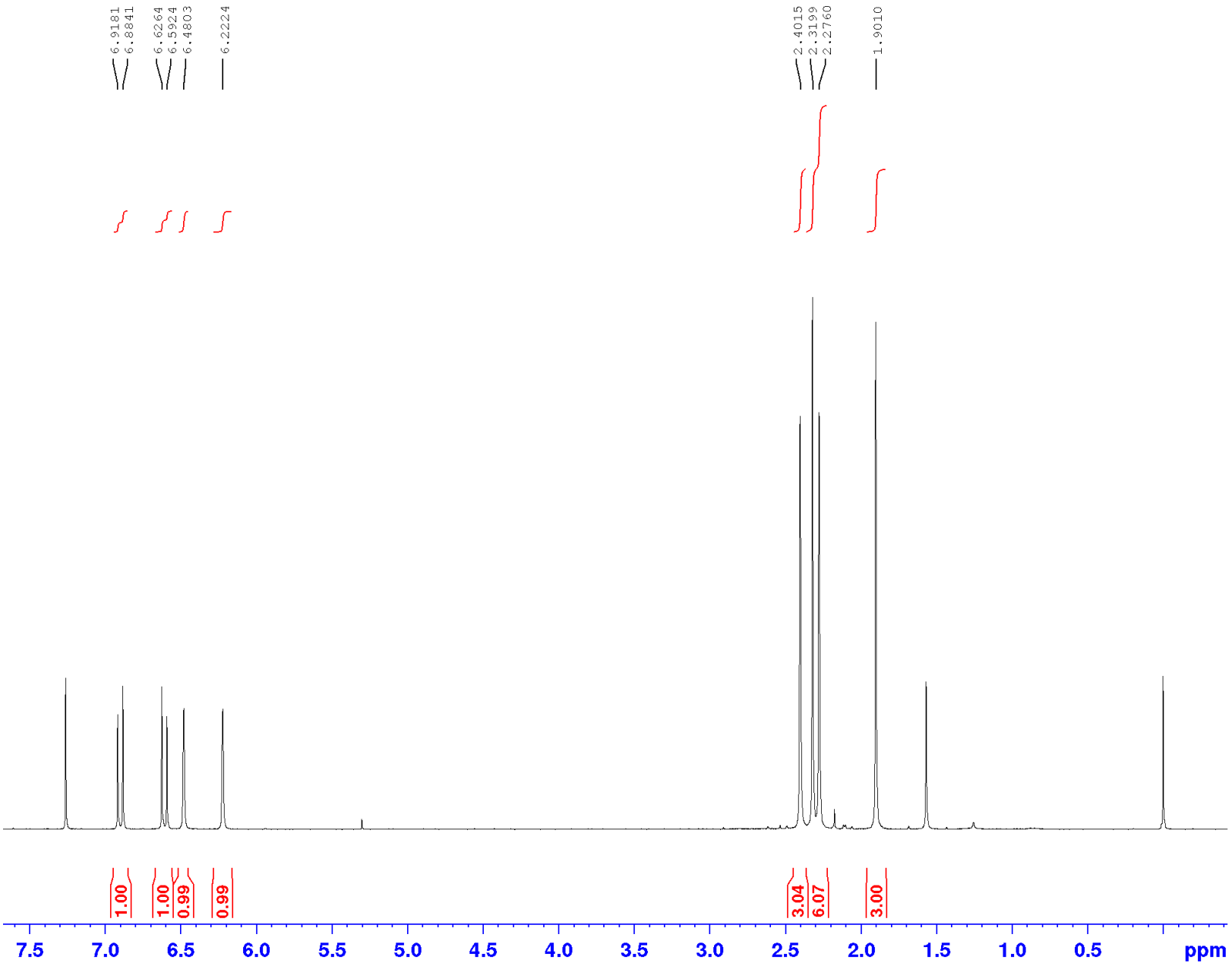


Mass spectrum of 13e-open

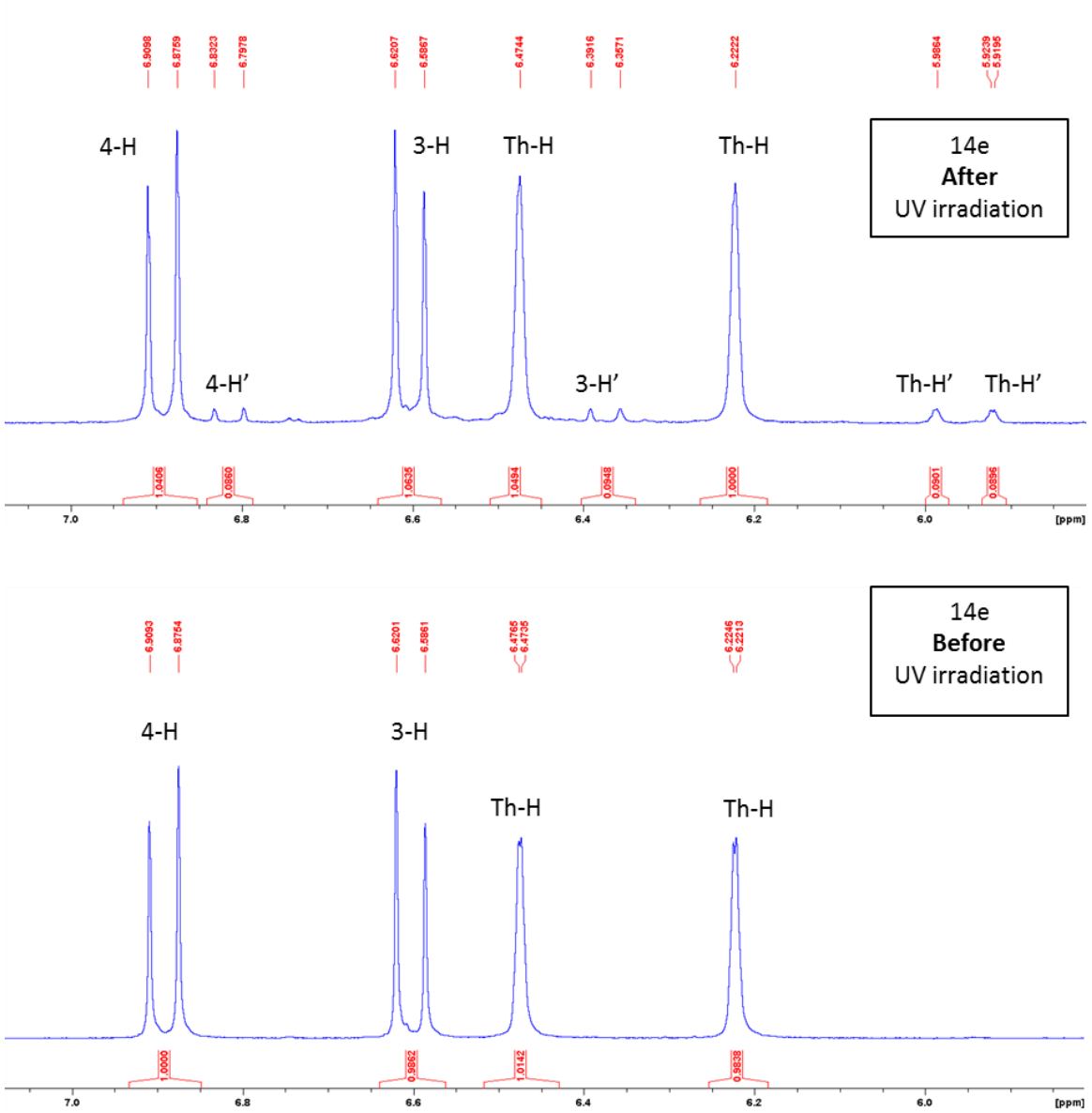


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C10 H19 N7 O6 S2	(M+H)+	398.0910	397.0837	397.0838	95.4	0.39
C16 H21 N4 O2 S3	(M+H)+	398.0910	397.0836	397.0827	93.78	-2.39
C18 H23 N O3 S3	(M+H)+	398.0910	397.0835	397.084	93.73	1.2
C12 H21 N4 O7 S2	(M+H)+	398.0910	397.0836	397.0852	90.02	4.04
C9 H23 N3 O10 S2	(M+H)+	398.0910	397.0836	397.0825	88.75	-2.71
C17 H19 N O8 S	(M+H)+	398.0910	397.0832	397.0831	86.26	-0.27
C16 H13 N8 O3 S	(M+H)+	398.0910	397.0834	397.0831	85.49	-0.78

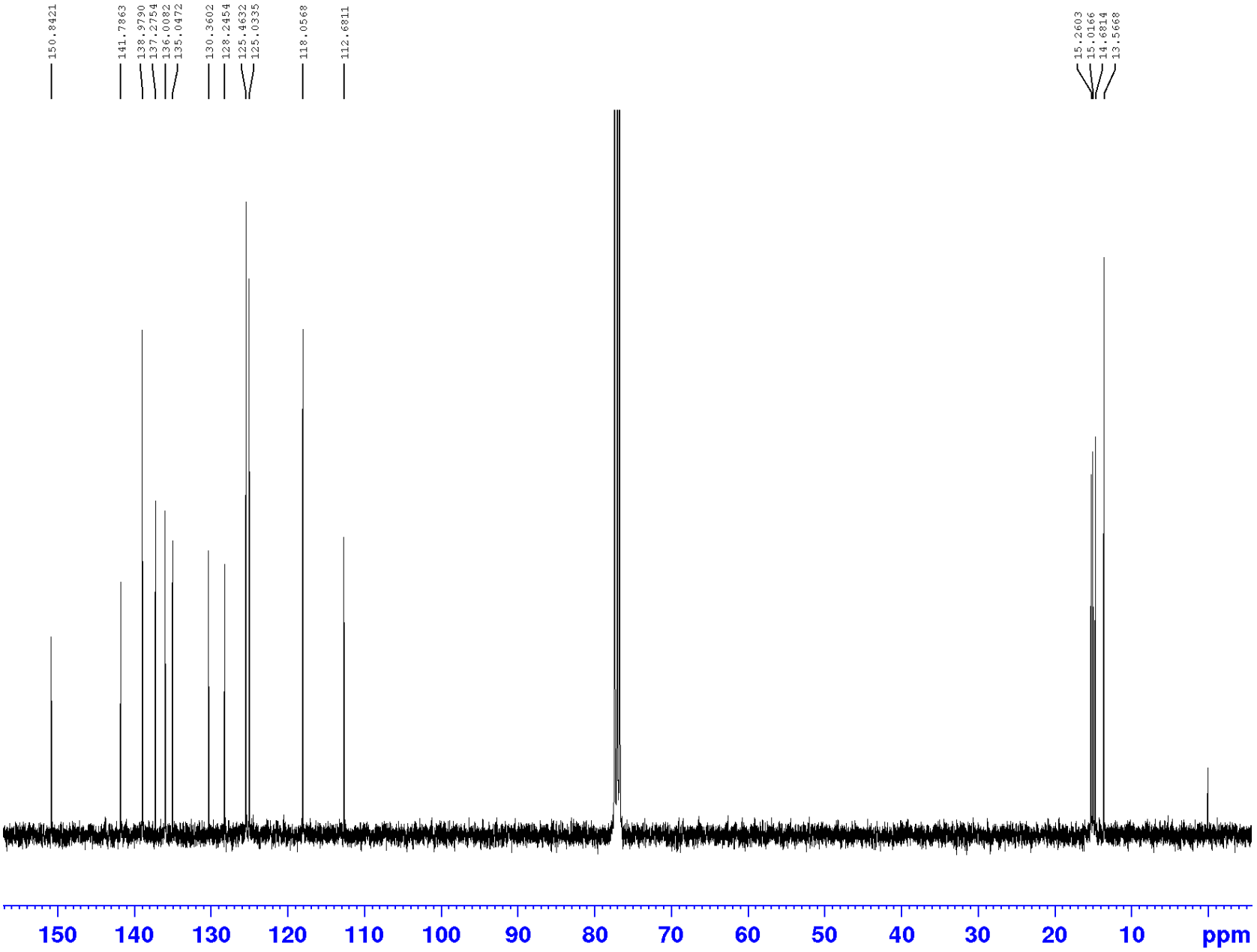
[1]H-NMR spectrum of 14e-open



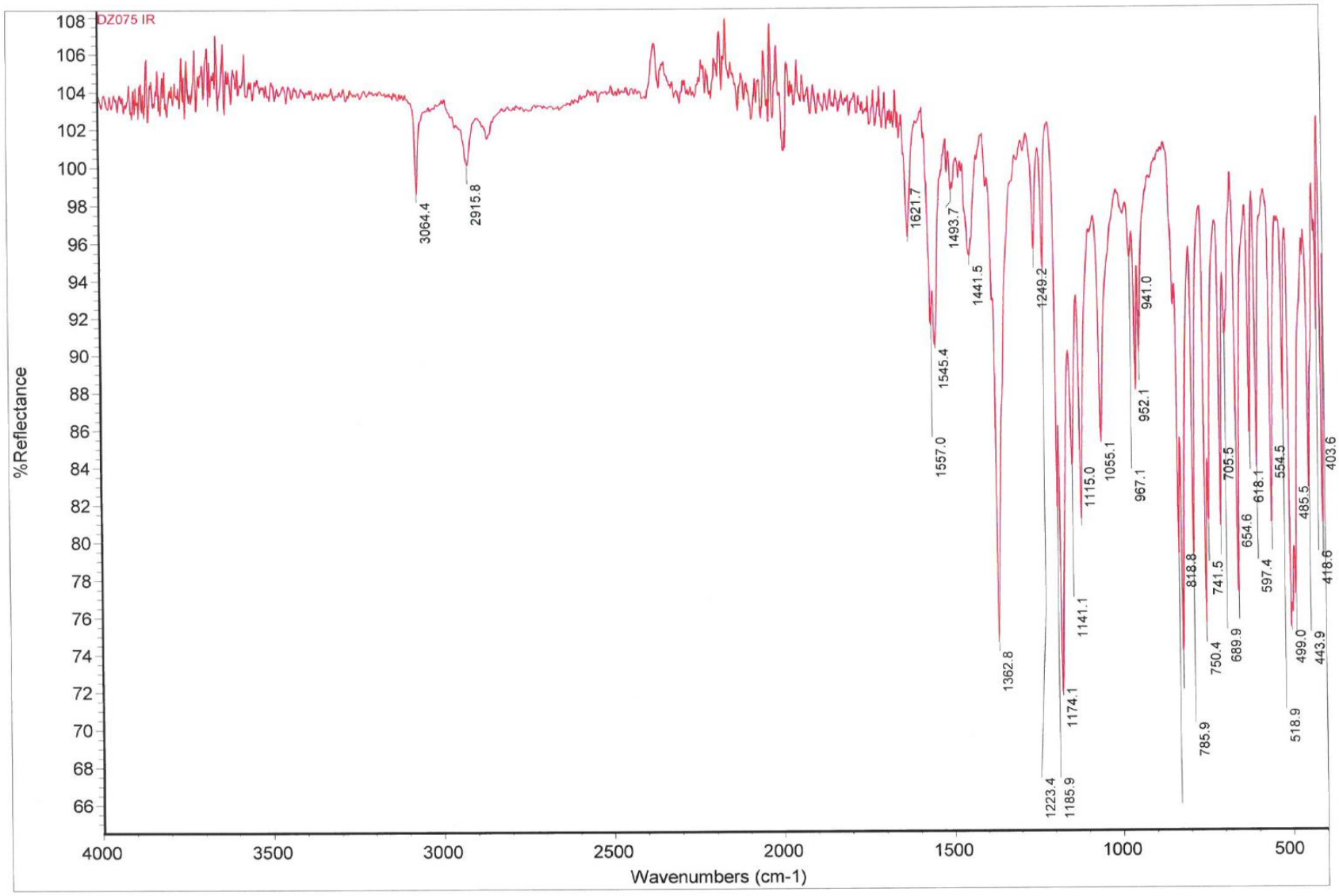
^{1}H NMR spectra (δ 5.8 – 7.2, $CDCl_3$) showing signals for 14e-open (lower) and 14e-closed (upper) at Photostationary state.



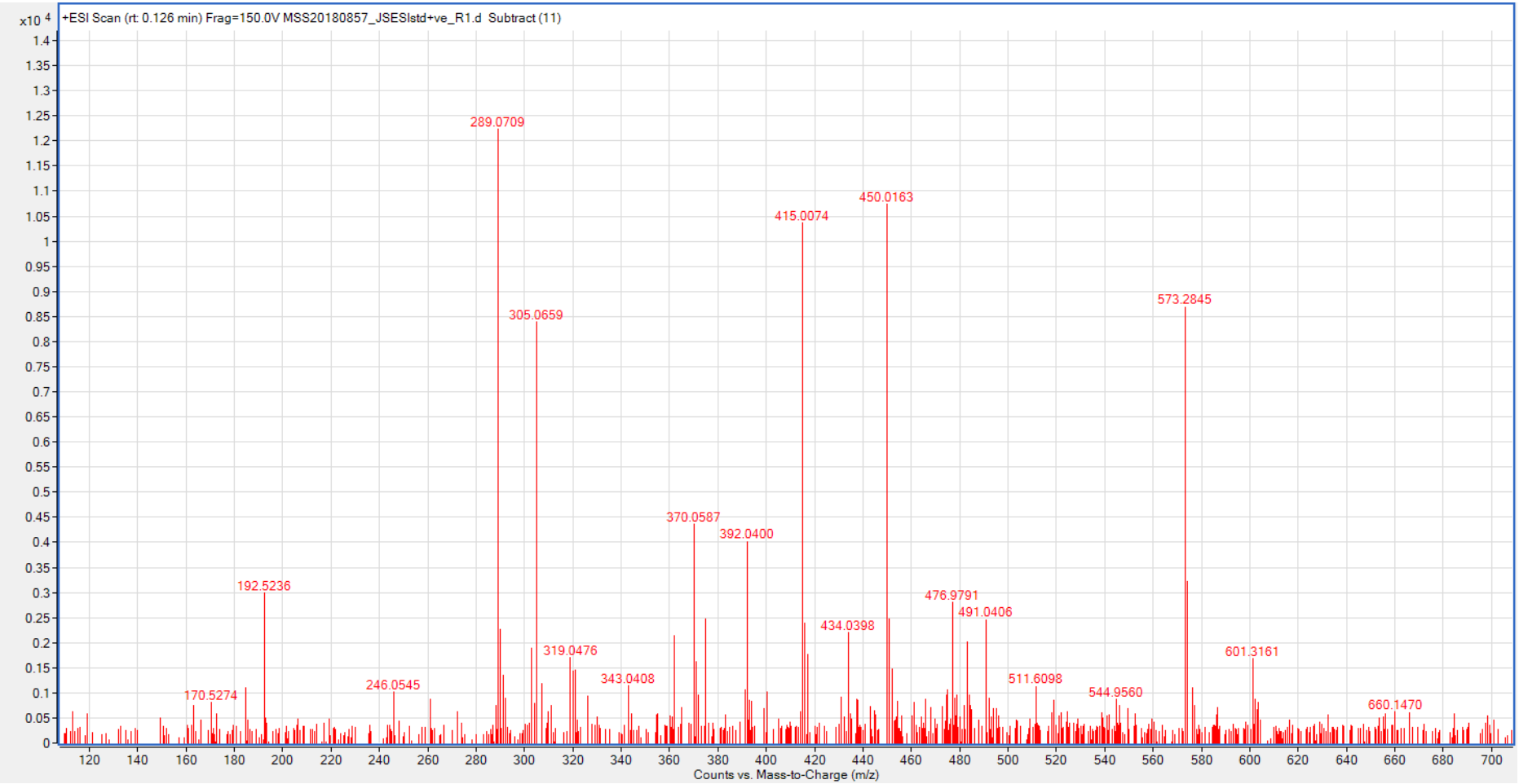
^{13}C-NMR spectrum of 14e-open



IR spectrum of 14e-open



Mass spectrum of 14e-open



Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C16 H16 O3 S3	(M+NH4)+	370.0587	352.0249	352.0262	43.35	3.54
C19 H12 O3 S2	(M+NH4)+	370.0587	352.0249	352.0228	36.28	-6.03

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) ColourChem_DZ050_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: ColourChem_DZ050_0m_a (Compound reference number 13a-open)

```
Bond precision:  C-C = 0.0033          A Wavelength=0.71073

Cell:            a=9.869(5)            b=11.897(5)      c=13.181(5)
                 alpha=113.322(17)     beta=109.14(2)   gamma=90.79(2)
Temperature: 150 K

                 Calculated                  Reported
Volume           1324.1(10)                  1324.1(10)
Space group      P -1                        P -1
Hall group       -P 1                        -P 1
Moiety formula
                 2(C24 H27 N O3 S3), C4 H10
                 O

Sum formula      C52 H64 N2 O7 S6            C26 H32 N O3.50 S3
Mr               1021.41                     510.70
Dx,g cm-3        1.281                       1.281
Z                1                           2
Mu (mm-1)        0.309                       0.309
F000             542.0                       542.0
F000'            542.95
h,k,lmax         14,16,18                    14,16,18
Nref             8086                        8011
Tmin,Tmax        0.939,0.988                 0.710,0.890
Tmin'            0.937

Correction method= # Reported T Limits: Tmin=0.710 Tmax=0.890
AbsCorr = MULTI-SCAN

Data completeness= 0.991               Theta(max)= 30.533

R(reflections)= 0.0519( 5853)          wR2(reflections)= 0.1481( 8011)

S = 1.027        Npar= 331
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT243_ALERT_4_C High 'Solvent' Ueq as Compared to Neighbors of O4 Check

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Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 5 Report
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ... 0.50 Check
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records 1 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records 1 Report
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 2) 80% Note
PLAT395_ALERT_2_G Deviating X-O-Y Angle From 120 for O3 115.6 Degree
PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O4 51.9 Degree
PLAT793_ALERT_4_G Model has Chirality at C3 (Centro SPGR) R Verify
PLAT793_ALERT_4_G Model has Chirality at C4 (Centro SPGR) S Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 54 Note
PLAT883_ALERT_1_G No Info for _atom_sites_solution_primary ..... Please Do !

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
11 **ALERT level G** = General information/check it is not something unexpected
2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
6 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 18/02/2019; check.def file version of 18/02/2019