Supplementary Information

Diastereoselectivity thia-[3+2] cyclization of acetylpyranuloses and *β*-oxodithioesters

Shihao Cheng, †[ab] Xiao Ni, †[a] Guanyou Cui, [b] Chenhu Dong,[a] Yujie Ma,[a] Jinlong Li,[a] Xiaofeng Bao*[a] and Yu Zhao*[a]

[a] School of Pharmacy, Nantong University, Nantong 226001, China.

[b] Jiangsu Key Laboratory of Bioactive Natural Product Research, State Key Laboratory of Natural Medicines, Department of Natural Medicinal Chemistry, China Pharmaceutical University, Nanjing 210009, People's Republic of China.

E-mail: zhaoyu@ntu.edu.cn.

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General information

All reactions in non-aqueous media were conducted under a positive pressure of dry nitrogen in glassware that had been dried in an oven prior to use, unless noted otherwise. All anhydrous solvents were purchased from Shanghai Titan Technology Co., Ltd. Thin layer chromatography (Spec). A silica gel plate (100×25mm, GF254, 0.23mm, 5-20μm) was purchased from Yantai Huayang New Material Technology Co., Ltd. Flash column chromatography was performed using silica gel (200-300 mesh). The Phosphomolybdic acid (5% phosphomolybdic acid + 95% ethanol) was utilized for color development, and the light absorption effect of the product was observed using a portable UV analyzer. ^{1}H and ^{13}C nuclear magnetic resonance spectra (NMR) were obtained on a Bruker 400 MHz spectrometer. The spectra were recorded in parts per million (ppm) downfield of tetramethylsilane (TMS) (δ = 0) in $CDCl_3$ and DMSO-d_6, unless otherwise specified. Signal splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), or multiplet (m), with coupling constants (J) in hertz. High-resolution mass spectra (HRMS) and X-ray single crystal diffraction were performed by Sanguan Technology Service (Guangzhou) Co., Ltd. HMRS data for new compounds were acquired in the mass spectrometer equipped with TOF analyzer. High-resolution mass spectra (HRMS) were recorded using Electron Impact (EI), Fast Atom Bombardment (FAB) or Electrospray Ionization (ESI) techniques. The parent ion $[M]^+$ is quoted with the indicated cation.

Complete compounds set

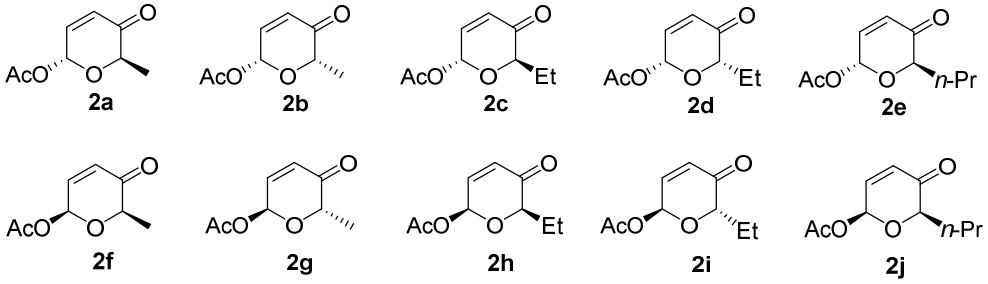


Figure S1 Acetylpyranulose substrates **2a-2j.**

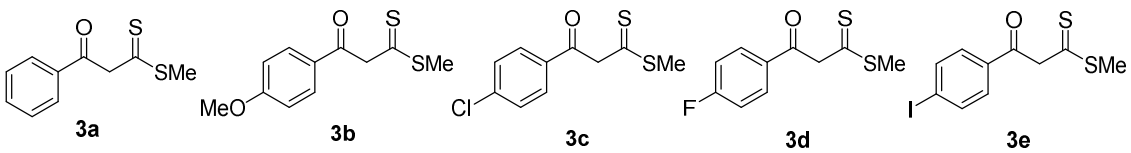


Figure S2 β-oxodithioester substrates **3a-3e.**

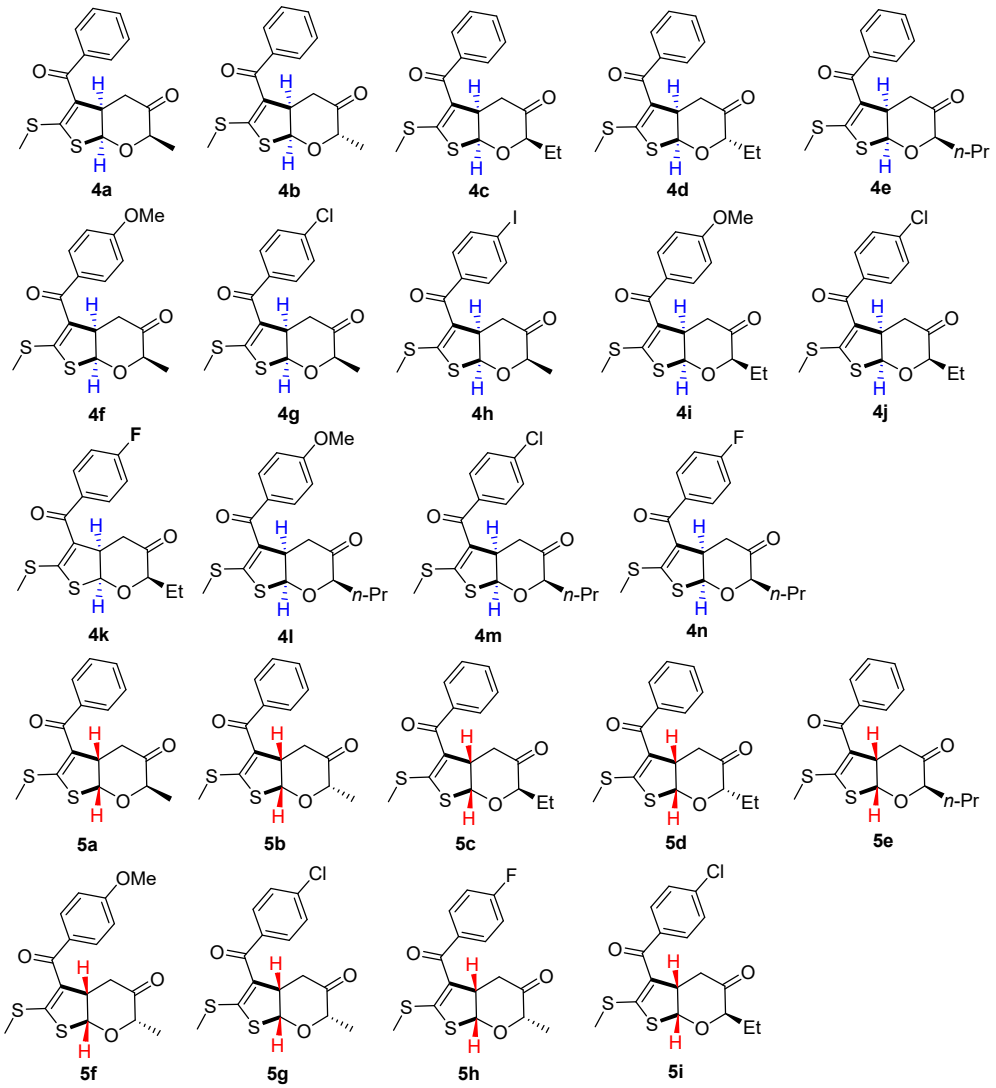
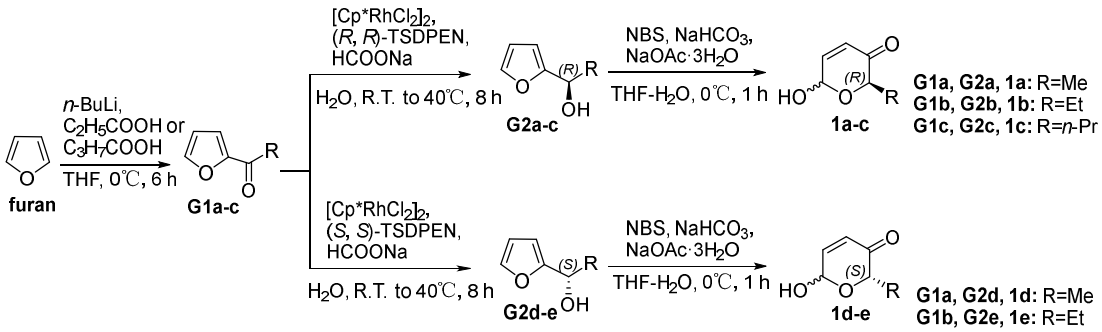


Figure S3 Thieno[2, 3-*b*]pyran products **4a-4n** and **5a-5i.**

General procedures for the synthesis of acetylpyranuloses 1a-e and 2a-2j [1]



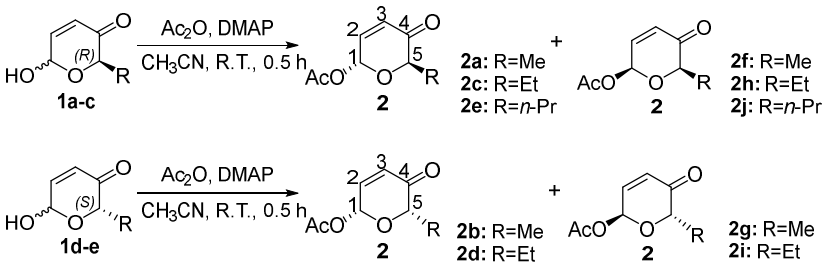
Scheme S1 Synthesis of substrates **1a-e**. (**1b** as an example)

Step 1: n-Butyllithium (33 mL, 80 mmol, 3.0 eq.) was added dropwise to furan (20.7 mL, 287 mmol, 11.0 eq.) at 0°C and stirred for 3 hours. Then, 25 mL anhydrous tetrahydrofuran and propanoic acid (1.97 mL, 26 mmol, 1.0 eq.) were slowly added at 0°C. After stirring for 30 minutes, the mixture was allowed to gradually return to room temperature and stirred for another 3 hours. After the reaction was complete, quenched with water and extracted with EA (20 mL×3). The organic layer was dried over

Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (PE:EA=30:1) to obtain **G1b** (yellow oil, 2.1 g, yield 64%).

Step 2: $[Cp^*RhCl_2]_2$ (10 mg, 0.1% mmol) and (*R*, *R*)-TSDPEN (44 mg, 1% mmol) were added in water (50 mL) and the mixture was stirred for 1.5 hours at 40°C. **G1b** (1.1 g, 10 mmol, 1.0 eq.) and sodium formate (13.5 g, 20 mmol, 2.0 eq.) were added to the mixture and stirred for 12 hours. The crude reaction mixture was extracted with EA (20 mL×3) and the organic layer was dried over Na_2SO_4, concentrated under vacuum. The residue was purified by column chromatography (PE:EA=40:1) to get **G2b** (colorless oil, 0.9 g, yield 81.2%).

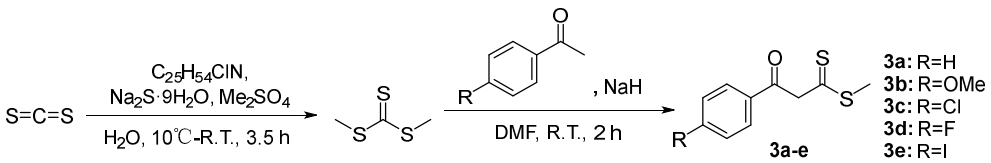
Step 3: To a solution of **G2b** (1.06 g, 10 mmol, 1.0 eq.) in THF-H_2O (40 mL, THF:H_2O=3:1), $NaHCO_3$ (1.62 g, 20 mmol, 2.0 eq.), $NaOAc·3H_2O$ (1.3 g, 10 mmol, 1.0 eq.), and NBS (1.71 g, 10 mmol, 1.0 eq.) were added and the mixture was stirred for 1 hour. After the reaction was complete, the crude reaction mixture was quenched with water, extracted with EA (20 mL×3), and the organic layer was dried over Na_2SO_4, concentrated under vacuum. The residue was purified by column chromatography (PE:EA=40:1) to get **1b** (light yellow oil, 0.85 g, yield 69%) .



Scheme S2 Synthesis of substrates **2a-j**. (**2c** as an example)

Step 4: To a solution of **1b** (1 g, 7.03 mmol, 1.0 eq.) in ethanol (20 mL), Ac_2O (1.08 g, 10.55 mmol, 1.0 eq.) and DMAP (99 mg, 0.7 mmol, 0.1 eq.) were added and the mixture was stirred for 30 minutes at 40°C. After the reaction was complete, the crude reaction mixture was extracted with EA (20 mL×3), the organic layer was dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (PE:EA=30:1) to obtain **2c** and **2h** (**2c**:**2h**=3:1).

General procedures for the synthesis of *β*-oxodithioesters 3a-3e



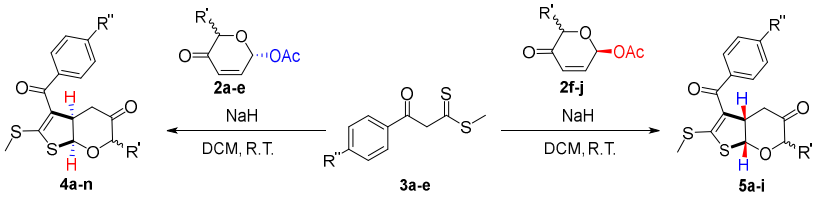
Scheme S3 Synthesis of substrates **3a-e**. (**3a** as an example)

Step1: $Na_2S·9H_2O$ (6.31 g, 26.27 mmol, 1.0 eq.), CS_2 (2.0 g, 26.27 mmol, 1.0 eq.) and methyl trioctylammonium chloride (0.05 g, 0.26 mmol, 1.0 eq.) were dissolved in water and then the mixture was stirred for 1.5 hours at room temperature. Subsequently, Me_2SO_4 (6.63 g, 52.56 mmol, 2.0 eq.) was added to the mixture and stirred for another 1 hour at 10℃, 1 hour at room temperature. After the reaction was complete, the crude reaction mixture was extracted with EA (20 mL×3), the organic layer was dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (petroleum ether) to get dimethyl carbonotrithioate (yellow oil, 0.72 g, yield 51.4%).

Step2: To a solution of dimethyl carbonotrithioate (0.58 g, 4.16mmol, 1.0 eq.) in anhydrous DMF, NaH (0.20 g, 8.32 mmol, 2.0 eq.) and C_8H_8O (0.50 g, 4.16 mmol, 1.0 eq.) were added at room temperature,

and the mixture was stirred for 2 hours. After the reaction was complete, the reaction mixture was subsequently acidified with 5N HCl, pH 2-3. The resulting mixture was extracted with EA (20 mL×3), the organic layer was dried over Na_2SO_4 and concentrated under vacuum. The residue was purified through column chromatography (petroleum ether) to get **3a** (yellow solid, 0.62 g, yield 81%).

General procedures for the synthesis of thieno[2, 3-*b*]pyran 4a-n and 5a-i



Scheme S4 Synthesis of substrates **4a-n** and **5a-i**. (**4a** as an example)

To a solution of **3a** (0.10g, 0.47mmol, 1.0 eq.) and **2a** (0.08g, 0.47 mmol, 1.0 eq.) in anhydrous DCM (3.0 mL), NaH (0.01g, 0.47 mmol, 1.0 eq.) was added slowly under nitrogen atmosphere, and the resulting mixture was stirred for ten minutes at 0°C, then allowed to return to room temperature and stirred for 12 hours. After the reaction was complete, the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography (PE:EA=30:1, R_f=0.1) to obtain **4a** (white powder, 0.06 g, yield 60.4%).

Crystallographic data and molecular structure of enantiomer 4 (Deposition Number 2402947**)**

The crystal of **4** for X-ray diffraction study has been obtained through the dissolving of compound in PE-EA, followed by slow evaporation of the solvent at room temperature. The crystal was kept at 150 K during data collection.

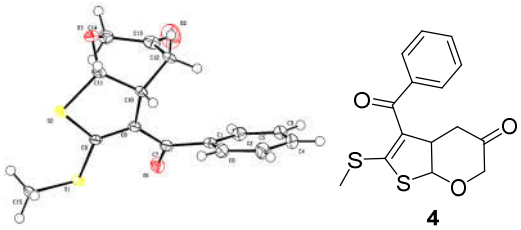


Figure S4 X-ray crystal structure of **4**; the ellipsoids depicted at the 50% probability level.

Table S1 Crystal data and structure refinement for 4.

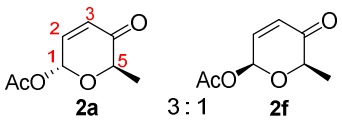
Identification code	**4**
Empirical formula	$C_{15}H_{14}O_3S_2$
Formula weight	306.38
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	6.1960(3)
b/Å	10.6217(6)
c/Å	11.3470(6)
α/°	82.619(4)
β/°	74.785(5)
γ/°	73.760(5)
Volume/Å^3	690.62(7)
Z	2

ρ_{calc}g/cm^3	1.473
μ/mm^{-1}	3.536
F(000)	320.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.09 to 148.326
Index ranges	-6 ≤ h ≤ 7, -13 ≤ k ≤ 13, -14 ≤ l ≤ 13
Reflections collected	4814
Independent reflections	2708 [R_{int} = 0.0381, R_{sigma} = 0.0375]
Data/restraints/parameters	2708/0/183
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0574, wR_2 = 0.1588
Final R indexes [all data]	R_1 = 0.0586, wR_2 = 0.1612
Largest diff. peak/hole / e Å^{-3}	0.51/-0.66

Crystal structure determination of 4

Crystal Data for $C_{15}H_{14}O_3S_2$ (*M* =306.38 g/mol): triclinic, space group P-1 (no. 2), *a* = 6.1960(3) Å, *b* = 10.6217(6) Å, *c* = 11.3470(6) Å, *α* = 82.619(4)°, *β* = 74.785(5)°, *γ* = 73.760(5)°, *V* = 690.62(7) Å^3, *Z* = 2, *T* = 149.99(10) K, μ(Cu Kα) = 3.536 mm^{-1}, *Dcalc* = 1.473 g/cm^3, 4814 reflections measured (8.09° ≤ 2Θ ≤ 148.326°), 2708 unique (R_{int} = 0.0381, R_{sigma} = 0.0375) which were used in all calculations. The final R_1 was 0.0574 (I > 2σ(I)) and wR_2 was 0.1612 (all data).

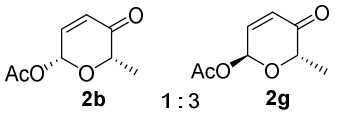
Characterization data of the obtained compounds



2a 3 : 1 **2f**

(2*R*,6*R*)-6-methyl-5-oxo-5,6-dihydro-2*H*-pyran-2-yl acetate (**2a**): colorless oil, 0.85 g, 66.7% yield, R_f =0.6 (PE:EA=2:1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 6.89 (dd, *J* = 10.2, 3.7 Hz, 1H, H-2), 6.49 (d, *J* = 3.6 Hz, 1H, H-1), 6.22 (d, *J* = 10.2 Hz, 1H, H-3), 4.61 (q, *J* = 6.7 Hz, 1H, H-5), 2.15 (s, 3H, $COCH_3$), 1.42 (d, *J* = 6.8 Hz, 3H, 5-CH_3). The data of ^{1}H NMR is consistent with the literature.[1]

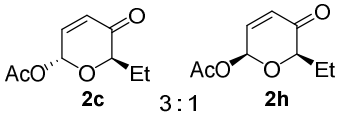
(2*S*,6*R*)-6-methyl-5-oxo-5,6-dihydro-2*H*-pyran-2-yl acetate (**2f**): colorless oil, 0.42 g, 33.3% yield, R_f =0.7 (PE:EA=2:1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 6.88 (dd, *J* = 10.3, 2.4 Hz, 1H, H-2), 6.56 (d, *J* = 2.4, 1H, H-1), 6.24 (d, *J* = 10.3 Hz, 1H, H-3), 4.38 (q, *J* = 7.0 Hz, 1H, H-5), 2.16 (s, 3H, $COCH_3$), 1.50 (d, *J* = 7.0 Hz, 3H, 5-CH_3). The data of ^{1}H NMR is consistent with the literatures.[1]



2b 1 : 3 **2g**

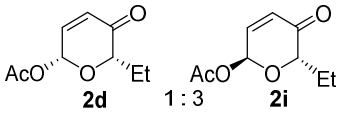
(2*R*,6*S*)-6-methyl-5-oxo-5,6-dihydro-2*H*-pyran-2-yl acetate (**2b**): colorless oil, 0.88 g, 31.8% yield, R_f =0.7 (PE:EA=1:1). ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 6.89 (dd, *J* = 10.4, 2.4 Hz, 1H, H-2), 6.56 (d, *J* = 2.4 Hz, 1H, H-1), 6.24 (d, *J* = 10.4 Hz, 1H, H-3), 4.38 (q, *J* = 7.0 Hz, 1H, H-5), 2.16 (s, 3H, $COCH_3$), 1.50 (d, *J* = 7.0 Hz, 3H, 5-CH_3).

(2*S*,6*S*)-6-methyl-5-oxo-5,6-dihydro-2*H*-pyran-2-yl acetate (**2g**): colorless oil, 0.41 g, 68.2% yield, R_f =0.6 (PE:EA=1:1) ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 6.88 (dd, *J* = 10.2, 3.7 Hz, 1H, H-2), 6.48 (d, *J* = 3.7 Hz, 1H, H-1), 6.21 (d, *J* = 10.2 Hz, 1H, H-3), 4.60 (q, *J* = 6.7 Hz, 1H, H-5), 2.14 (s, 3H, $COCH_3$), 1.41 (d, *J* = 6.7 Hz, 3H, 5-CH_3). The data of ^{1}H NMR is consistent with the literature.[0]



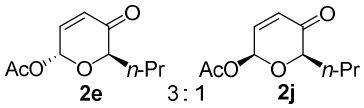
(2*R*,6*R*)-6-ethyl-5-oxo-5,6-dihydro-2*H*-pyran-2-yl acetate (**2c**): colorless oil, 1.15 g, 65.6% yield, R_f =0.7 (PE:EA=2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (dd, J = 10.2, 3.7 Hz, 1H, H-2), 6.52 (d, J = 3.6 Hz, 1H, H-1), 6.21 (d, J = 10.2 Hz, 1H, H-3), 4.43 (dd, J = 6.9, 4.0 Hz, 1H, H-5), 2.14 (s, 3H, $COCH_3$), 1.96 (dqd, J = 15.1, 7.6, 4.2 Hz, 1H, $\underline{CH_2}CH_3$), 1.81 (dp, J = 14.4, 7.3 Hz, 1H, $\underline{CH_2}CH_3$), 0.97 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 169.6, 141.6, 128.8, 87.1, 76.8, 23.0, 21.0, 9.0.

(2*S*,6*R*)-6-ethyl-5-oxo-5,6-dihydro-2*H*-pyran-2-yl acetate (**2h**): colorless oil, 0.60 g, 34.4% yield, R_f =0.6 (PE:EA=2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (dt, J = 10.4, 2.6 Hz, 1H, H-2), 6.56 (dd, J = 2.8, 1.3 Hz, 1H, H-1), 6.22 (d, J = 10.4, 1H, H-3), 4.15 (dd, J = 7.8, 6.2 Hz, 1H, H-5), 2.15 (s, J = 1.2 Hz, 3H, $COCH_3$), 1.89 (p, J = 7.4 Hz, 2H, $\underline{CH_2}CH_3$), 1.03 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 169.6, 141.6, 128.8, 87.1, 76.9, 23.0, 21.0, 9.0.



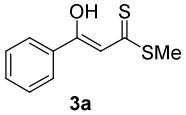
(2*R*,6*S*)-6-ethyl-5-oxo-5,6-dihydro-2*H*-pyran-2-yl acetate (**2d**): colorless oil, 0.48 g, 32.8% yield, R_f =0.6 (PE:EA=2:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.84 (dd, J = 10.4, 2.7 Hz, 1H, H-2), 6.55 (d, J = 2.7 Hz, 1H, H-1), 6.21 (d, J = 10.4 Hz, 1H, H-3), 4.14 (dd, J = 7.8, 6.2 Hz, 1H, H-5), 2.14 (s, 3H, $COCH_3$), 1.88 (p, J = 7.4 Hz, 2H, $\underline{CH_2}CH_3$), 1.02 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 169.4, 142.8, 128.4, 87.6, 80.9, 26.3, 21.1, 9.9.

(2*S*,6*S*)-6-ethyl-5-oxo-5,6-dihydro-2*H*-pyran-2-yl acetate (**2i**): colorless oil, 0.98 g, 67.2% yield, R_f =0.7 (PE:EA=2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (dd, J = 10.2, 3.7 Hz, 1H, H-2), 6.52 (d, J = 3.7 Hz, 1H, H-1), 6.22 (d, J = 10.2 Hz, 1H, H-3), 4.43 (dd, J = 6.9, 4.1 Hz, 1H, H-5), 2.14 (s, 3H, $COCH_3$), 1.96 (ddd, J = 14.6, 7.4, 4.1 Hz, 1H, $\underline{CH_2}CH_3$), 1.81 (dp, J = 14.4, 7.2 Hz, 1H, $\underline{CH_2}CH_3$), 1.65 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 169.6, 141.6, 128.7, 87.1, 76.8, 23.0, 20.9, 8.9.



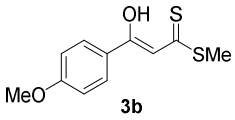
(2*R*,6*R*)-5-oxo-6-propyl-5,6-dihydro-2*H*-pyran-2-yl acetate (**2e**), colorless oil, 0.60 g, 66.7% yield, R_f =0.7 (PE:EA=2:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.10 (dd, J = 10.2, 3.7 Hz, 1H, H-2), 6.46 (d, J = 3.7 Hz, 1H, H-1), 6.25 (d, J = 10.3 Hz, 1H, H-3), 4.48 (dd, J = 7.7, 3.8 Hz, 1H, H-5), 2.10 (s, 3H, $COCH_3$), 1.84 – 1.70 (m, 1H), 1.58 (dtd, J = 14.1, 8.3, 6.1 Hz, 1H), 1.40 – 1.28 (m, 2H), 0.86 (t, J = 7.4 Hz, 3H, CH3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 169.6, 141.5, 128.7, 87.2, 75.6, 31.7, 21.3, 17.5, 13.8.

(2*S*,6*R*)-5-oxo-6-propyl-5,6-dihydro-2*H*-pyran-2-yl acetate (**2j**), colorless oil, 1.22 g, 33.3% yield, R_f =0.6 (PE:EA=2:1). ^{1}H NMR (400 MHz, DMSO) δ 7.09 (dd, J = 10.3, 2.5 Hz, 1H, H-2), 6.53 (d, J = 2.5, 1.4 Hz, 1H, H-1), 6.25 (d, J = 10.3 , 1H, H-3), 4.30 (dd, J = 8.6, 5.2 Hz, 1H, H-5), 2.10 (s, 3H, $COCH_3$), 1.74 – 1.64 (m, 2H), 1.37 (dhept, J = 13.2, 6.8, 6.4 Hz, 2H), 0.88 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 169.6, 141.2, 128.7, 87.3, 75.9, 31.7, 21.0, 17.9, 14.0.



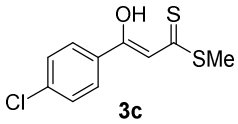
methyl (*Z*)-3-hydroxy-3-phenylprop-2-enedithioate (**3a**), yellow solid, 425.4 mg, 80.4% yield. R_f=0.4

(PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.10 (s, 1H, Bn-OH), 7.88 (d, J = 7.3 Hz, 2H, ArH), 7.54 – 7.48 (m, 1H, ArH), 7.44 (dd, J = 8.3, 6.5 Hz, 2H, ArH), 6.96 (s, 1H, CH), 2.65 (s, 3H, SCH_3). The data of ^{1}H NMR is consistent with the literature.[3]



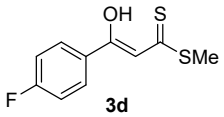
3b

methyl (*Z*)-3-hydroxy-3-(4-methoxyphenyl)prop-2-enedithioate (**3b**), yellow solid, 393.8 mg, 78.8% yield. R_f=0.5 (PE), ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.19 (s, 1H, Bn-OH), 7.86 (d, J = 8.8 Hz, 2H, ArH), 6.94 (s, 1H, CH), 6.97 – 6.92 (m, 2H, ArH), 3.87 (s, 3H, OCH_3), 2.65 (s, 3H, CH_3). The data of ^{1}H NMR is consistent with the literature.[3]



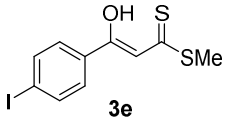
3c

methyl (*Z*)-3-(4-chlorophenyl)-3-hydroxyprop-2-enedithioate (**3c**), yellow solid, 434.7 mg, 82.4% yield. R_f=0.4 (PE), ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.07 (s, 1H, Bn-OH), 7.85 – 7.78 (m, 2H, ArH), 7.47 – 7.38 (m, 2H, ArH), 6.91 (s, 1H, CH), 2.66 (s, 3H, CH_3). The data of ^{1}H NMR is consistent with the literature.[3]



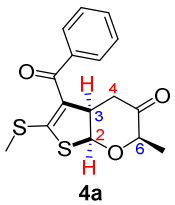
3d

methyl (*Z*)-3-(4-fluorophenyl)-3-hydroxyprop-2-enedithioate (**3d**), yellow solid, 419.5 mg, 81.7% yield. R_f=0.61 (PE), ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.11 (s, 1H, Bn-OH), 7.94 – 7.85 (m, 2H, ArH), 7.19 – 7.09 (m, 2H, ArH), 6.90 (s, 1H, CH), 2.66 (s, 3H, CH_3). The data of ^{1}H NMR is consistent with the literature.[4]



3e

methyl (*Z*)-3-hydroxy-3-(4-iodophenyl)prop-2-enedithioate (**3e**), yellow solid, 398.7 mg, 77.6% yield，R_f=0.8 (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.04 (s, 1H, Bn-OH), 7.87 – 7.76 (m, 2H, ArH), 7.63 – 7.56 (m, 2H, ArH), 6.91 (s, 1H, CH), 2.66 (s, 3H, CH_3). The data of ^{1}H NMR is consistent with the literature.[3]

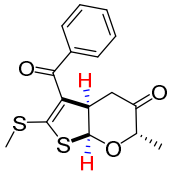


4a

(2*R*,4*aR*,7*aS*)-5-benzoyl-2-methyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**4a**):

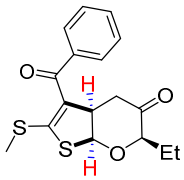
White powder, R_f =0.3 (PE:EA=6:1), 48.9 mg, 60.4% yield. m.p. 149–151°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H, ArH), 7.55 – 7.49 (m, 1H, ArH), 7.43 (dd, J = 8.2, 6.7 Hz, 2H, ArH), 5.57 (d, J = 7.4 Hz, 1H, H-2), 4.25 (dt, J = 9.5, 7.3 Hz, 1H, H-3), 3.99 (q, J = 7.0 Hz, 1H, H-6), 2.67 (dd, J = 14.6, 9.6 Hz, 1H, H-4), 2.50 (dd, J = 14.7, 7.1 Hz, 1H, H-4), 2.45 (s, 3H, SCH_3), 1.38 (d, J = 6.9 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1, 190.2, 156.4, 139.7, 132.0, 128.7, 128.2,

127.7, 83.7, 80.9, 51.1, 38.3, 17.6, 16.7. HRMS (ESI): *m/z* calcd for $C_{16}H_{16}O_3S_2Na$: 343.0439; found: 343.0444 $[M+Na]^+$.



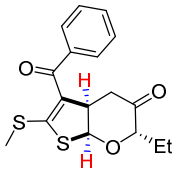
4b

(2*S,*4*aR,*7*aS*)-5-benzoyl-2-methyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**4b**): White powder, R_f=0.3 (PE:EA=6:1), 50.1 mg, 62.3% yield. m.p. 159–160°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.46 (m, 3H, ArH), 7.46 – 7.39 (m, 2H, ArH) 6.27 (d, J = 8.8 Hz, 1H, H-2), 4.57 (ddd, J = 8.5, 5.4, 2.6 Hz, 1H, H-3), 4.23 (q, J = 6.8 Hz, 1H, H-6), 2.85 (dd, J = 15.7, 5.4 Hz, 1H, H-4), 2.57 (dd, J = 15.7, 2.7 Hz, 1H, H-4), 2.41 (s, 3H, SCH_3), 1.37 (d, J = 6.9 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 210.8, 190.1, 157.5, 139.6, 132.1, 128.7, 128.1, 127.8, 84.7, 73.5, 49.6, 36.5, 17.8, 15.6. HRMS (ESI): *m/z* calcd for $C_{16}H_{16}O_3S_2Na$: 343.0439; found: 343.0443 $[M+Na]^+$.



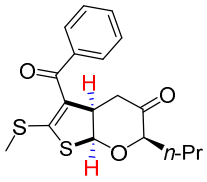
4c

(2*R,*4*aR,*7*aS*)-5-benzoyl-2-ethyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**4c**): White powder, R_f=0.3 (PE:EA=6:1), 56.1 mg, 70.4% yield. m.p. 149–151°C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.58 (m, 2H, ArH), 7.58 – 7.48 (m, 1H, ArH), 7.48 – 7.37 (m, 2H, ArH), 5.54 (d, J = 7.4 Hz, 1H, H-2), 4.23 (dt, J = 9.8, 7.3 Hz, 1H, H-3), 3.80 (dd, J = 7.7, 4.7 Hz, 1H, H-6), 2.60 (dd, J = 14.4, 9.9 Hz, 1H, H-4), 2.48 (dd, J = 14.4, 7.2 Hz, 1H, H-4), 2.46 (s, 3H, SCH_3), 1.92 – 1.66 (m, 2H, $\underline{CH_2}CH_3$), 1.00 (t, J = 7.4 Hz, 3H, $CH_2\underline{CH_3}$).^{13}C NMR (100 MHz, $CDCl_3$) δ 211.3, 190.2, 156.8, 139.7, 131.9, 128.7, 128.1, 127.7, 85.9, 83.8, 51.9, 39.4, 24.8, 17.6, 9.7. HRMS (ESI): *m/z* calcd for $C_{17}H_{18}O_3S_2Na$: 357.0595; found: 357.0600 $[M+Na]^+$.



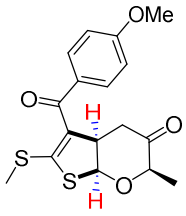
4d

(2*S,*4*aR,*7*aS)*-5-benzoyl-2-ethyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[*2,3-b*]pyran-3(4*H*)-one (**4d**): White powder, R_f=0.3 (PE:EA=6:1), 52.3 mg, 65.4% yield. m.p. 137–139°C. ^{1}H NMR (400 MHz,) δ 7.55 – 7.47 (m, 3H, ArH), 7.45 – 7.38 (m, 2H, ArH), 6.31 (d, J = 8.8 Hz, 1H, H-2), 4.58 (ddd, J = 8.8, 5.3, 2.5 Hz, 1H, H-3), 4.05 (dd, J = 7.5, 3.8 Hz, 1H, , H-6), 2.80 (dd, J = 15.4, 5.3 Hz, 1H, H-4), 2.56 (dd, J = 15.4, 2.5 Hz, 1H, H-4), 2.40 (s, 3H, , SCH_3), 1.92 (dqd, J = 14.9, 7.5, 3.9 Hz, 1H, $\underline{CH_2}CH_3$), 1.74 (dt, J = 14.4, 7.3 Hz, 1H, $\underline{CH_2}CH_3$), 0.96 (t, J = 7.4 Hz, 3H, $CH_2\underline{CH_3}$).^{13}C NMR (100 MHz, $CDCl_3$) δ 210.74, 190.1, 157.4, 139.6, 132.1, 128.6, 128.1, 127.9, 84.7, 78.1, 49.7, 37.4, 23.3, 17.8, 9.4. HRMS (ESI): *m/z* calcd for $C_{17}H_{18}O_3S_2Na$: 357.0595; found: 357.0599 $[M+Na]^+$.



4e

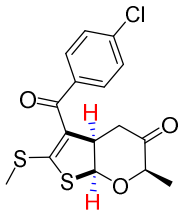
(2*R*,4*aR*,7*aS*)-5-benzoyl-6-(methylthio)-2-propyl-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**4e**): White powder, R_f=0.3 (PE:EA=6:1), 54.8 mg, 68.5% yield. m.p. 104–106℃. ^{1}H NMR (400 MHz,) δ 7.63 – 7.59 (m, 2H, ArH), 7.56 – 7.49 (m, 1H, ArH), 7.47 – 7.40 (m, 2H, ArH), 5.53 (d, J = 7.5 Hz, 1H, H-2), 4.23 (dt, J = 9.8, 7.3 Hz, 1H, H-3), 3.86 (dd, J = 7.0, 5.6 Hz, 1H, H-6), 2.61 (dd, J = 14.5, 10.0 Hz, 1H, H-4), 2.49 (dd, J = 14.5, 7.1 Hz, 1H, H-4), 2.46 (s, 3H, SCH_3), 1.74 – 1.66 (m, 2H), 1.55 – 1.41 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.4, 190.2, 156.7, 139.7, 131.9, 128.7, 128.1, 127.7, 84.7, 83.8, 51.1, 39.1, 33.4, 18.5, 17.6, 13.7. HRMS (ESI): *m/z* calcd for $C_{18}H_{20}O_3S_2Na$: 371.0752; found: 371.0756 $[M+Na]^+$.



4f

(2*R*,4*aR*,7*aS*)-5-(4-methoxybenzoyl)-2-methyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**4f**):

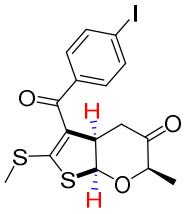
White powder, R_f=0.4 (PE:EA=6:1), 62.7 mg, 62.7% yield. m.p. 149–151℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J =8.7Hz, 2H, ArH), 6.93 (d, J = 8.8 Hz, 2H, ArH), 5.54 (d, J = 7.3 Hz, 1H, H-2), 4.26 (dt, J = 9.1, 7.3 Hz, 1H, H-3),4.01 (q, J = 6.8 Hz, 1H, H-6), 3.87 (s, 3H, OCH_3), 2.69 (dd, J = 14.7, 9.2 Hz, 1H, H-4), 2.62 (dd, J = 14.7, 7.4 Hz, 1H, H-4), 2.42 (s, 3H, SCH_3), 1.39 (d, J = 7.0 Hz, 3H, CH_3). ^{13}C NMR (100 MzHz, $CDCl_3$) δ 211.3, 189.5, 163.1, 151.9, 131.8, 130.7, 129.2, 113.9, 83.6, 80.9, 55.5, 51.7, 38.1, 17.5, 16.8. HRMS (ESI): *m/z* calcd for $C_{17}H_{18}O_4S_2Na$: 373.0544; found: 373.0548 $[M+Na]^+$.



4g

(2*R*,4*aR*,7*aS*)-5-(4-chlorobenzoyl)-2-methyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**4g**):

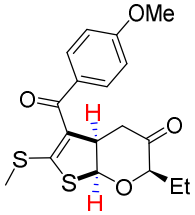
White powder, R_f=0.3 (PE:EA=6:1), 64.3 mg, 80.4% yield. m.p. 155–157℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H, ArH), 7.45 – 7.39 (m, 2H, ArH), 5.57 (d, J = 7.4 Hz, 1H, H-2), 4.23 (dt, J = 9.4, 7.3 Hz, 1H, H-3), 4.01 (q, J = 7.0 Hz, 1H, H-6), 2.68 (dd, J = 14.6, 9.4 Hz, 1H, H-4), 2.58 (dd, J = 14.6, 7.2 Hz, 1H, H-4), 2.46 (s, 3H, SCH_3), 1.39 (d, J = 7.0 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.9, 189.0, 156.8, 138.4, 137.9, 129.4, 129.0, 128.0, 83.6, 80.9, 51.1, 38.3, 17.7, 16.8. HRMS (ESI): *m/z* calcd for $C_{16}H_{15}ClO_3S_2Na$: 377.0049; found: 377.0053 $[M+Na]^+$.



4h

(2*R*,4*aR*,7*aS*)-5-(4-iodobenzoyl)-2-methyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**4h**):

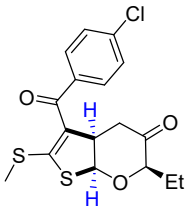
White powder, R_f=0.3 (PE:EA=6:1), 56.9 mg, 70.7% yield. m.p. 190–191°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.73 (m, 2H, ArH), 7.39 – 7.30 (m, 2H, ArH), 5.57 (d, J = 7.4 Hz, 1H, H-2), 4.22 (dt, J = 9.4, 7.3 Hz, 1H, H-3), 4.01 (q, J = 7.0 Hz, 1H, H-6), 2.67 (dd, J = 14.6, 9.4 Hz, 1H, H-4), 2.62 – 2.55 (d, 1H, H-4), 2.46 (s, 3H, SCH_3), 1.39 (d, J = 7.0 Hz, 3H, 6-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.9, 189.2, 157.2, 138.9, 137.9, 129.4, 127.8, 99.3, 83.6, 80.9, 51.1, 38.3, 17.6, 16.7. HRMS (ESI): *m/z* calcd for $C_{16}H_{15}IO_3S_2Na$: 468.9405; found: 468.9407 $[M+Na]^+$.



4i

(2*R*,4*aR*,7*aS*)-2-ethyl-5-(4-methoxybenzoyl)-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**4i**):

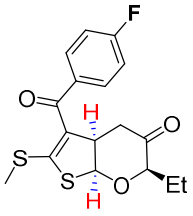
Wihte powder, R_f=0.3 (PE:EA=6:1), 62.2 mg, 77.8% yield. m.p. 99–100°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H, ArH), 6.98-6.85 (m, 2H, ArH), 5.52 (d, J = 7.4 Hz, 1H, H-2), 4.24 (q, J = 8.1 Hz, 1H, H-3), 3.87 (s, 3H, OCH_3), 3.82 (dd, J = 7.4, 4.5 Hz, 1H, H-6), 2.61 (d, J = 8.5 Hz, 2H, H-4), 2.43 (s, 3H, SCH_3), 1.78 (m, 2H, $\underline{CH_2}CH_3$), 1.01 (t, J = 7.4 Hz, 3H, $CH_2\underline{CH_3}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.4, 189.4, 163.0, 131.9, 130.5, 129.1, 113.9, 85.9, 83.7, 55.4, 51.6, 39.2, 24.8, 17.5, 9.7. HRMS (ESI): *m/z* calcd for $C_{18}H_{20}O_4S_2Na$: 387.0701; found: 387.0705 $[M+Na]^+$.



4j

(2*R*,4*aR*,7*aS*)-5-(4-chlorobenzoyl)-2-ethyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**4j**):

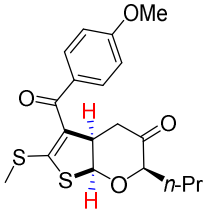
White powder, R_f=0.4 (PE:EA=6:1), 63.7 mg, 79.6% yield. m.p. 114–116°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.4 Hz, 2H, ArH), 7.41 (d, J = 8.4 Hz, 2H, ArH), 5.54 (d, J = 7.4 Hz, 1H, H-2), 4.21 (dt, J = 9.4, 7.5 Hz, 1H, H-3), 3.82 (dd, J = 7.7, 4.6 Hz, 1H, H-6), 2.58 (dd, J = 8.4, 6.9 Hz, 2H, H-4), 2.46 (s, 3H, SCH_3), 1.86 – 1.71 (dq, 2H), 1.00 (t, J = 7.4 Hz, 3H, $CH_2\underline{CH_3}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.0, 188.9, 157.1, 138.2, 137.9, 129.3, 129.1, 127.9, 85.9, 83.7, 51.1, 39.3, 24.8, 17.6, 9.7. HRMS (ESI): m/z calcd for $C_{17}H_{17}ClO_3S_2Na$: 391.0205; found: 391.0209 $[M+Na]^+$.



4k

(2*R*,4*aR*,7*aS*)-2-ethyl-5-(4-fluorobenzoyl)-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**4k**):

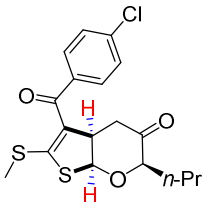
White powder, R_f=0.4 (PE:EA=6:1), 60.3 mg, 75.4% yield. m.p. 119–120°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.61 (m, 2H, ArH), 7.17 – 7.07 (m, 2H, ArH), 5.54 (d, J = 7.4 Hz, 1H, H-2), 4.22 (dt, J = 9.3, 7.5 Hz, 1H, H-3), 3.82 (dd, J = 7.7, 4.6 Hz, 1H, H-6), 2.59 (dd, J = 8.4, 5.6 Hz, 2H, H-4), 2.46 (s, 3H, SCH_3), 1.90 – 1.67 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1, 188.9, 165.1 (d, J = 253.4 Hz), 156.1, 135.8, 130.5, 130.5, 128.2, 116.0, 115.8, 86.0, 83.7, 51.3, 39.3, 24.8, 17.6, 9.8. HRMS (ESI): *m/z* calcd for $C_{17}H_{17}FO_3S_2Na$: 375.0501; found: 375.0504 $[M+Na]^+$.



4l

(2*R*,4*aR*,7*aS*)-5-(4-methoxybenzoyl)-6-(methylthio)-2-propyl-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**4l**):

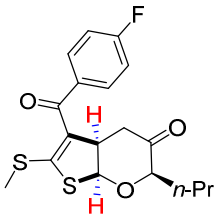
White powder, R_f=0.5 (PE:EA=6:1), 58.7 mg, 73.4% yield. m.p. 109–110°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 2H, ArH), 6.98 – 6.89 (m, 2H, ArH), 5.51 (d, J = 7.4 Hz, 1H, H-2), 4.24 (dt, J = 9.2, 7.5 Hz, 1H, H-3), 3.90 – 3.84 (m, 1H, H-6), 3.87 (s, 3H, OCH_3), 2.69 – 2.54 (m, 2H, H-4), 2.43 (s, 3H, SCH_3), 1.78 – 1.63 (m, 2H), 1.53 – 1.42 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.5, 189.4, 163.0, 152.3, 131.9, 130.5, 129.1, 113.9, 84.7, 83.6, 55.4, 51.6, 39.0, 33.4, 18.5, 17.5, 13.7. HRMS (ESI): *m/z* calcd for $C_{19}H_{22}O_4S_2Na$: 401.0857; found: 401.0858 $[M+Na]^+$.



4m

(2*R*,4*aR*,7*aS*)-5-(4-chlorobenzoyl)-6-(methylthio)-2-propyl-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**4m**):

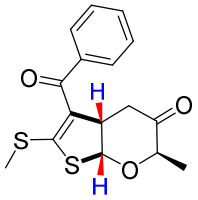
White powder, R_f=0.5 (PE:EA=6:1), 61.2 mg, 76.5% yield. m.p. 104–106°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H, ArH), 7.46-7.39 (m, 2H, ArH), 6.30 (d, J = 8.9 Hz, 1H, H-2), 4.58 (dt, J = 8.6, 5.3, 2.6 Hz, 1H, H-3), 4.14 – 4.06 (dd, 1H, H-6), 2.82 (dd, J = 15.4, 5.4 Hz, 1H, H-4), 2.55 (dd, J = 15.4, 2.7 Hz, 1H, H-4), 2.40 (s, 3H, SCH_3), 1.92 – 1.79 (m, 1H), 1.71 – 1.57 (m, 1H), 1.43 (dq, J = 7.4 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.2, 188.9, 157.2, 138.2, 137.9, 129.3, 129.0, 127.9, 84.7, 83.7, 51.1, 39.1, 33.4, 18.5, 17.6, 14.1, 13.7. HRMS (ESI): *m/z* calcd for $C_{18}H_{19}ClO_3S_2Na$: 405.0362; found: 405.0366 $[M+Na]^+$.



4n

(2*R*,4*aR*,7*aS*)-5-(4-fluorobenzoyl)-6-(methylthio)-2-propyl-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**4n**):

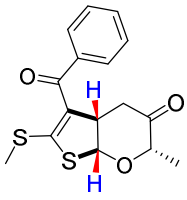
White yield, 65.1 mg, R_f=0.5 (PE:EA=6:1), 81.4% yield. m.p. 104–105℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 2H, ArH), 7.16 – 7.09 (m, 2H, ArH), 5.54 (d, J = 7.5 Hz, 1H, H-2), 4.22 (dt, J = 9.6, 7.5 Hz, 1H, H-3), 3.88 (dd, J = 7.2, 5.4 Hz, 1H, H-6), 2.63 (dd, J = 14.4, 9.5 Hz, 1H, H-4), 2.56 (dd, J = 14.4, 7.3 Hz, 1H, H-4), 2.45 (s, 3H, SCH_3), 1.71 (dq, J = 7.7, 5.6, 2.1 Hz, 2H), 1.46 (dt, J = 15.1, 7.7 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.2, 188.8, 165.1 (d, J = 253.3 Hz), 156.1, 135.8, 130.5, 130.4, 128.1, 115.9, 115.8, 84.7, 83.7, 51.3, 39.1, 33.4, 18.6, 17.6, 13.37. HRMS (ESI): *m/z* calcd for $C_{18}H_{19}FO_3S_2Na$: 389.0657; found: 389.0660 $[M+Na]^+$.



5a

(2*R*,4*aS*,7*aR*)-5-benzoyl-2-methyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**5a**):

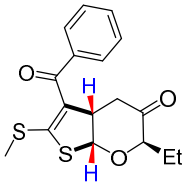
White powder, 63.8 mg, R_f=0.29 (PE:EA=6:1), 79.8% yield. m.p. 163–165 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 3H, ArH), 7.44-7.39 (m, 2H, ArH), 6.27 (dd, J = 8.8, 0.9 Hz, 1H, H-2), 4.57 (ddd, J = 8.2, 5.2, 2.5 Hz, 1H, H-3), 4.23 (q, J = 6.8 Hz, 1H, H-6), 2.85 (dd, J = 15.7, 5.3 Hz, 1H, H-4), 2.57 (dd, J = 15.7, 2.6 Hz, 1H, H-4), 2.41 (s, 3H, CH_3), 1.37 (d, J = 6.9 Hz, 3H, 6-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 190.0, 157.4, 139.6, 132.0, 128.9, 128.1, 127.9, 84.2, 73.4, 49.6, 36.5, 17.8, 15.6. HRMS (ESI): *m/z* calcd for $C_{16}H_{16}O_3S_2Na$: 343.0439; found: 343.0441 $[M+Na]^+$.



5b

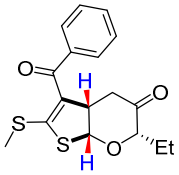
(2*S*,4*aS*,7*aR*)-5-benzoyl-2-methyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**5b**):

White powder, 60.0 mg, R_f=0.3 (PE:EA=6:1), 74.7% yield. m.p. 154–156℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 2H, ArH), 7.56 – 7.50 (m, 1H, ArH), 7.46 – 7.40 (m, 2H, ArH), 5.57 (d, J = 7.3 Hz, 1H, H-2), 4.25 (dt, J = 9.5, 7.2 Hz, 1H, H-3), 3.99 (q, J = 7.0 Hz, 1H, H-6), 2.67 (dd, J = 14.5, 9.6 Hz, 1H, H-4), 2.50 (dd, J = 14.6, 7.2 Hz, 1H, H-4), 2.45 (s, 3H, SCH_3), 1.38 (d, J = 6.9 Hz, 3H, 6-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.2, 190.2, 156.5, 139.7, 132.1, 128.1, 128.9, 128.1, 127.8, 83.7, 80.9, 77.2, 51.0, 38.3, 17.6, 16.7. HRMS (ESI): *m/z* calcd for $C_{16}H_{16}O_3S_2Na$: 343.0439; found: 343.0440 $[M+Na]^+$.



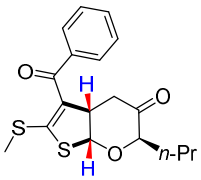
5c

(2*R*,4*aS*,7*aR*)-5-benzoyl-2-ethyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**5c**): white powder, R_f=0.44 (PE:EA=6:1), 60.6 mg, 75.7% yield. m.p. 139–141 ℃. ^{1}H NMR (400 MHz,) δ 7.56 – 7.47 (m, 3H, ArH), 7.45 – 7.38 (m, 2H, ArH), 6.31 (d, J = 8.9 Hz, 1H, H-2), 4.58 (ddd, J = 8.7, 5.3, 2.6 Hz, 1H, H-3), 4.05 (dd, J = 7.6, 3.9 Hz, 1H, H-6), 2.81 (dd, J = 15.4, 5.4 Hz, 1H, H-4), 2.56 (dd, J = 15.5, 2.6 Hz, 1H, H-4), 2.40 (s, 3H, SCH_3) 1.92 (dqd, J = 14.9, 7.5, 3.8 Hz, 1H), 1.72 (dt, J = 14.6, 7.3 Hz, 1H), 0.96 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 190.1, 157.4, 139.7, 132.1, 128.7, 128.1, 128.0, 84.8, 78.1, 49.8, 37.4, 23.4, 17.9, 9.4. HRMS (ESI): m/z calcd for $C_{17}H_{18}O_3S_2Na$: 357.0595; found: 357.0599 $[M+Na]^+$.



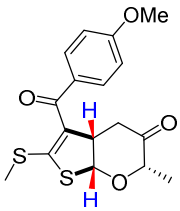
5d

(2*S*,4*aS*,7*aR*)-5-benzoyl-2-ethyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**5d**): White powder, R_f=0.5 (PE:EA=6:1), 48.3 mg, 60.4% yield. m.p. 151–153℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H, ArH), 7.56 – 7.47 (m, 1H, ArH), 7.47 – 7.39 (m, 2H, ArH), 5.54 (d, J = 7.5 Hz, 1H, H-2), 4.23 (dt, J = 9.8, 7.3 Hz, 1H, H-3), 3.80 (dd, J = 7.6, 4.7 Hz, 1H, H-6), 2.59 (dd, J = 14.3, 9.9 Hz, 1H, H-4), 2.47 (dd, J = 14.2, 8.9 Hz, 1H, H-4), 2.47 (s, 3H, SCH_3), 1.89 – 1.66 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.3, 190.3, 156.9, 139.7, 131.9, 128.1, 128.1, 127.7, 85.9, 83.8, 51.0, 39.4, 24.8, 17.6, 9.7. HRMS (ESI): *m/z* calcd for $C_{17}H_{18}O_3S_2Na$: 357.0595; found: 357.0599 $[M+Na]^+$.



5e

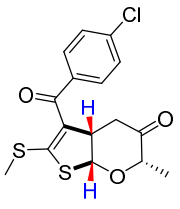
(2*R*,4*aS*,7*aR*)-5-benzoyl-6-(methylthio)-2-propyl-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**5e**): White powder, R_f=0.5 (PE:EA=6:1), 49.9 mg, 83.2% yield. m.p. 139–141℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 3H, ArH), 7.46 – 7.38 (m, 2H, ArH), 6.30 (d, J = 8.9 Hz, 1H, H-2), 4.58 (ddd, J = 8.5, 5.4, 2.6 Hz, 1H, H-3), 4.10 (dd, J = 8.4, 3.6 Hz, 1H, H-6), 2.82 (dd, J = 15.4, 5.4 Hz, 1H, H-4), 2.55 (dd, J = 15.5, 2.6 Hz, 1H, H-4), 2.40 (s, 3H, SCH_3), 1.92 – 1.79 (m, 1H), 1.71 – 1.57 (m, 1H), 1.43 (h, J = 7.4 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.9, 190.1, 157.4, 139.7, 132.1, 128.7, 128.1, 128.0, 84.8, 76.9, 49.8, 37.2, 31.9, 18.3, 17.9, 13.8. HRMS (ESI): *m/z* calcd for $C_{18}H_{20}O_3S_2Na$: 371.0752; found: 371.0756 $[M+Na]^+$.



5f

(2*S*,4a*S*,7a*R*)-5-(4-methoxybenzoyl)-2-methyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**5f**):

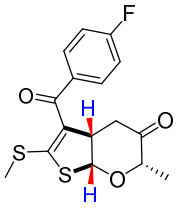
White powder, R_f=0.3 (PE:EA=6:1), 63.4 mg, 79.2% yield. m.p. 150–152°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 2H, ArH), 6.96 – 6.90 (m, 2H, ArH), 5.57 – 5.51 (d, J = 7.3 Hz, 1H, H-2), 4.26 (dt, J = 8.6, 7.1 Hz, 1H, H-3), 4.01 (q, J = 7.0 Hz, 1H, H-6), 3.87 (s, 3H, OCH_3), 2.71 – 2.59 (m, 2H, H-4), 2.42 (s, 3H, SCH_3), 1.61 (d, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.2, 189.5, 163.1, 131.8, 130.9, 130.6, 129.1, 113.9, 83.5, 80.9, 55.5, 51.6, 38.1, 17.5, 16.8. HRMS (ESI): *m/z* calcd for $C_{17}H_{18}O_4S_2Na$: 373.0544; found: 373.0548 $[M+Na]^+$.



5g

(2*S*,4*aS*,7*aR*)-5-(4-chlorobenzoyl)-2-methyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**5g**):

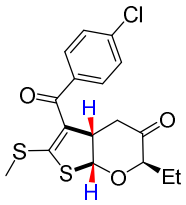
White powder, R_f=0.3 (PE:EA=6:1), 61.3 mg, 74.7% yield. m.p. 166–168°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.2 Hz, 2H, ArH), 7.42 (d, J = 8.1 Hz, 2H, ArH), 5.57 (d, J = 7.4 Hz, 1H, H-2), 4.23 (dt, J = 9.1, 7.6 Hz, 1H, H-3), 4.01 (q, J = 6.9 Hz, 1H, H-6), 2.68 (dd, J = 14.6, 9.3 Hz, 1H, H-4), 2.58 (dd, J = 14.6, 7.2 Hz, 1H, H-4), 2.46 (d, J = 1.0 Hz, 3H, SCH_3), 1.39 (d, J = 7.0 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.0, 189.0, 156.9, 138.3, 137.9, 129.4, 129.0, 128.0, 83.6, 80.9, 51.1, 38.3, 17.7, 16.7. HRMS (ESI): m/z calcd for $C_{16}H_{15}ClO_3S_2Na$: 377.0046; found: 377.0049 $[M+Na]^+$.



5h

(2*S*,4*aS*,7*aR*)-5-(4-fluorobenzoyl)-2-methyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**5h**):

White powder, R_f=0.3 (PE:EA=6:1), 62.5 mg, 78.1% yield. m.p. 126–128°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 2H, ArH), 7.17 – 7.07 (m, 2H, ArH), 5.57 (d, J = 7.2 Hz, 1H, H-2), 4.24 (dt, J = 9.3, 7.3 Hz, 1H, H-3), 4.01 (q, J = 7.0 Hz, 1H, H-6), 2.69 (dd, J = 14.6, 9.3 Hz, 1H, H-4), 2.59 (dd, J = 14.6, 7.2 Hz, 1H, H-4), 2.45 (s, 3H, SCH_3), 1.39 (d, J = 7.0 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.0, 188.9, 165.1 (d, J = 253.5 Hz), 155.7, 135.7, 130.6, 130.5, 128.2, 115.9, 115.7, 83.5, 80.9, 51.2, 38.2, 17.6. HRMS (ESI): *m/z* calcd for $C_{16}H_{15}FO_3S_2Na$: 361.0344; found: 361.0347 $[M+Na]^+$.



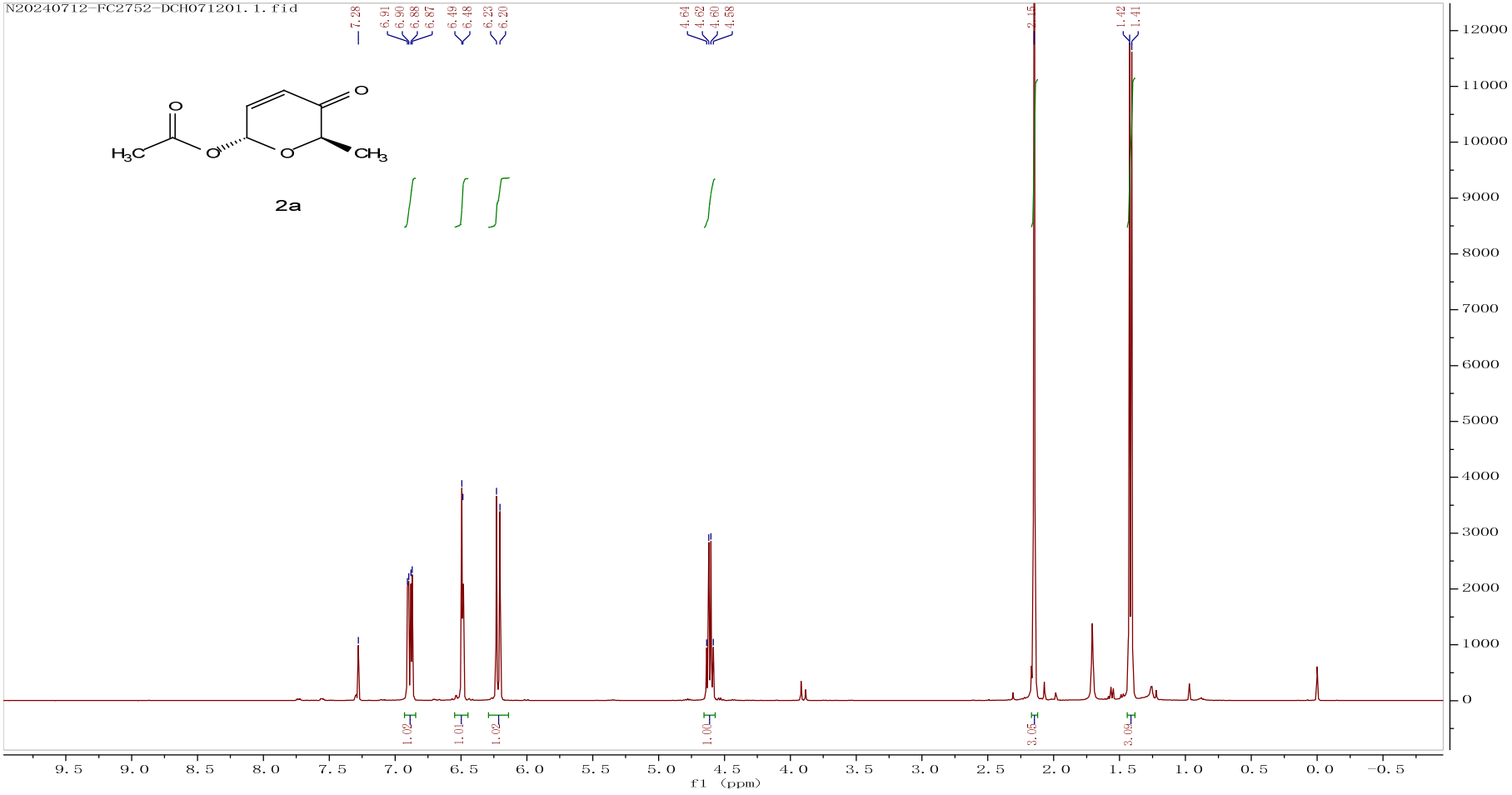
5i

(2*R*,4*aS*,7*aR*)-5-(4-chlorobenzoyl)-2-ethyl-6-(methylthio)-4a,7a-dihydro-2*H*-thieno[2,3-*b*]pyran-3(4*H*)-one (**5i**):

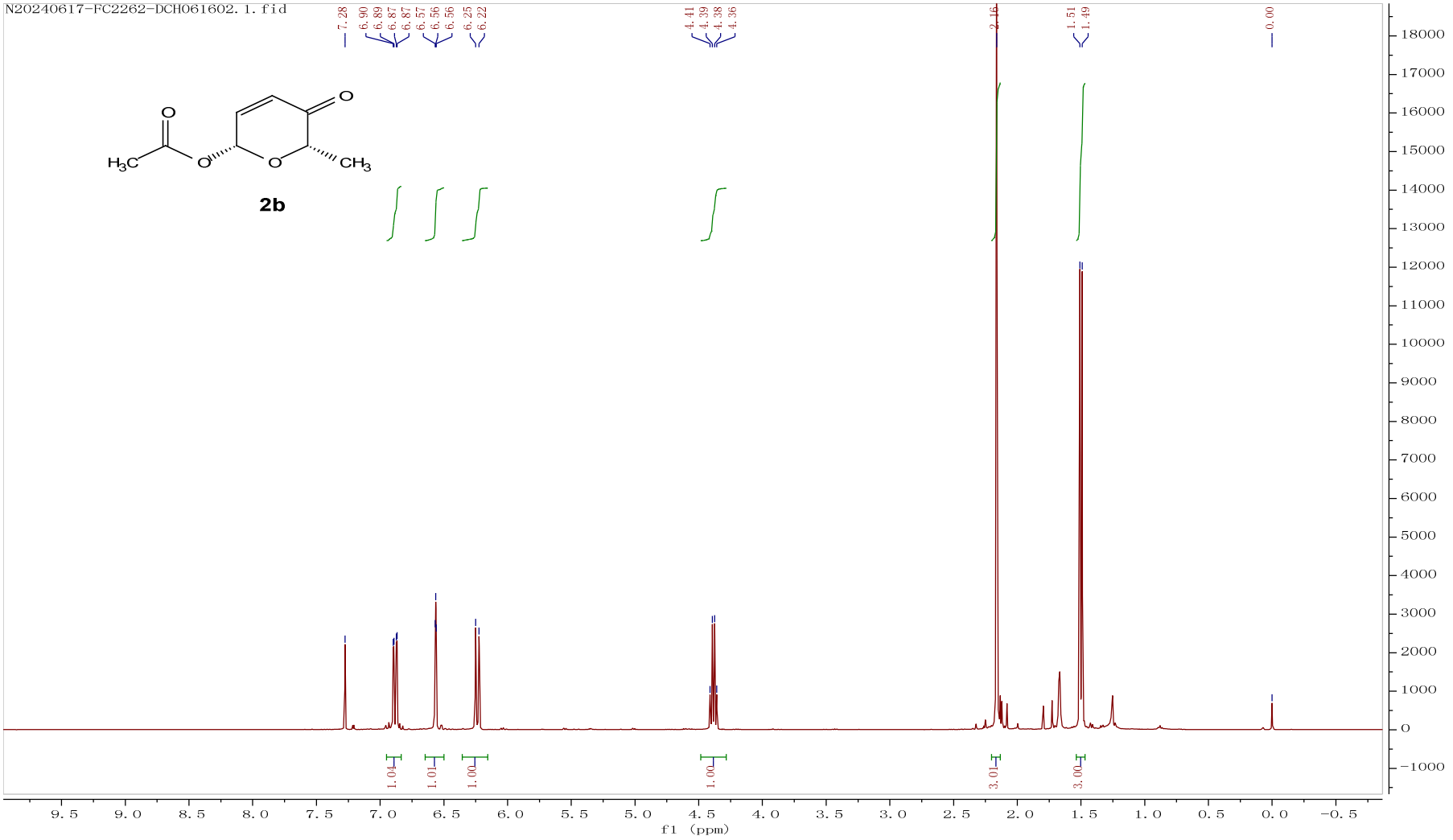
White powder, R_f=0.4 (PE:EA=6:1), 57.0 mg, 71.6% yield. m.p. 119–121℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.5 Hz, 2H, ArH), 7.39 (d, J = 8.5 Hz, 2H, ArH), 6.31 (dd, J = 8.9, 0.8 Hz, 1H, H-2), 4.56 (ddd, J = 8.4, 5.3, 2.6 Hz, 1H, H-3), 4.04 (dd, J = 7.5, 3.9 Hz, 1H, H-6), 2.83 (dd, J = 15.2, 5.3 Hz, 1H, H-4), 2.58 (dd, J = 15.3, 2.7 Hz, 1H, H-4), 2.41 (s, 3H, SCH_3), 1.92 (dqd, J = 15.0, 7.5, 3.9 Hz, 1H), 1.73 (dq, J = 14.6, 7.4 Hz, 1H), 0.97 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.8, 188.8, 157.7, 138.4, 137.8, 129.6, 129.0, 127.7, 84.7, 78.7, 49.8, 37.4, 23.4, 17.8, 9.4. HRMS (ESI): *m/z* calcd for $C_{17}H_{17}ClO_3S_2Na$: 391.0205; found: 391.0209 $[M+Na]^+$.

NMR spectra

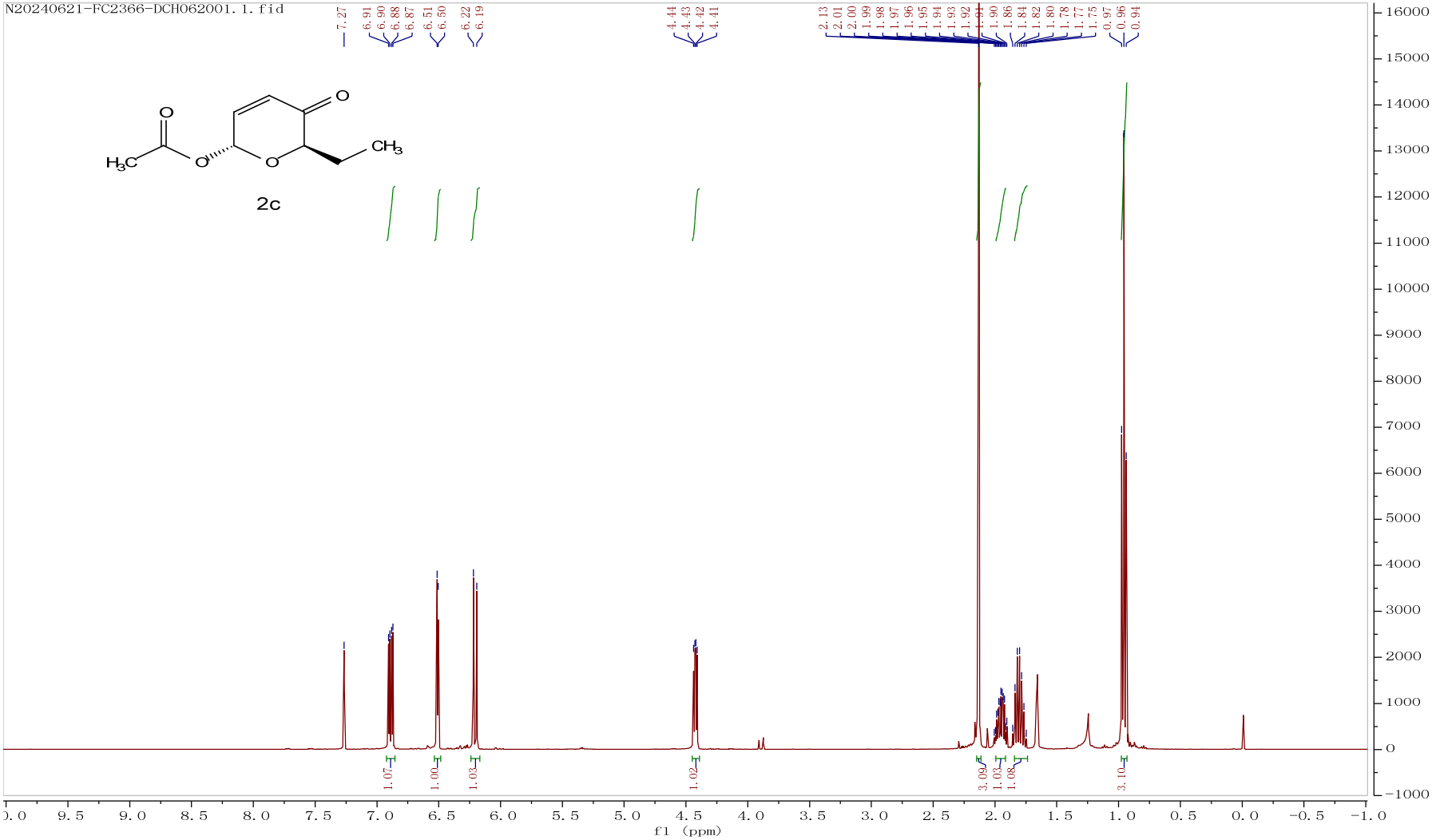
^{1}H spectra of **2a**.



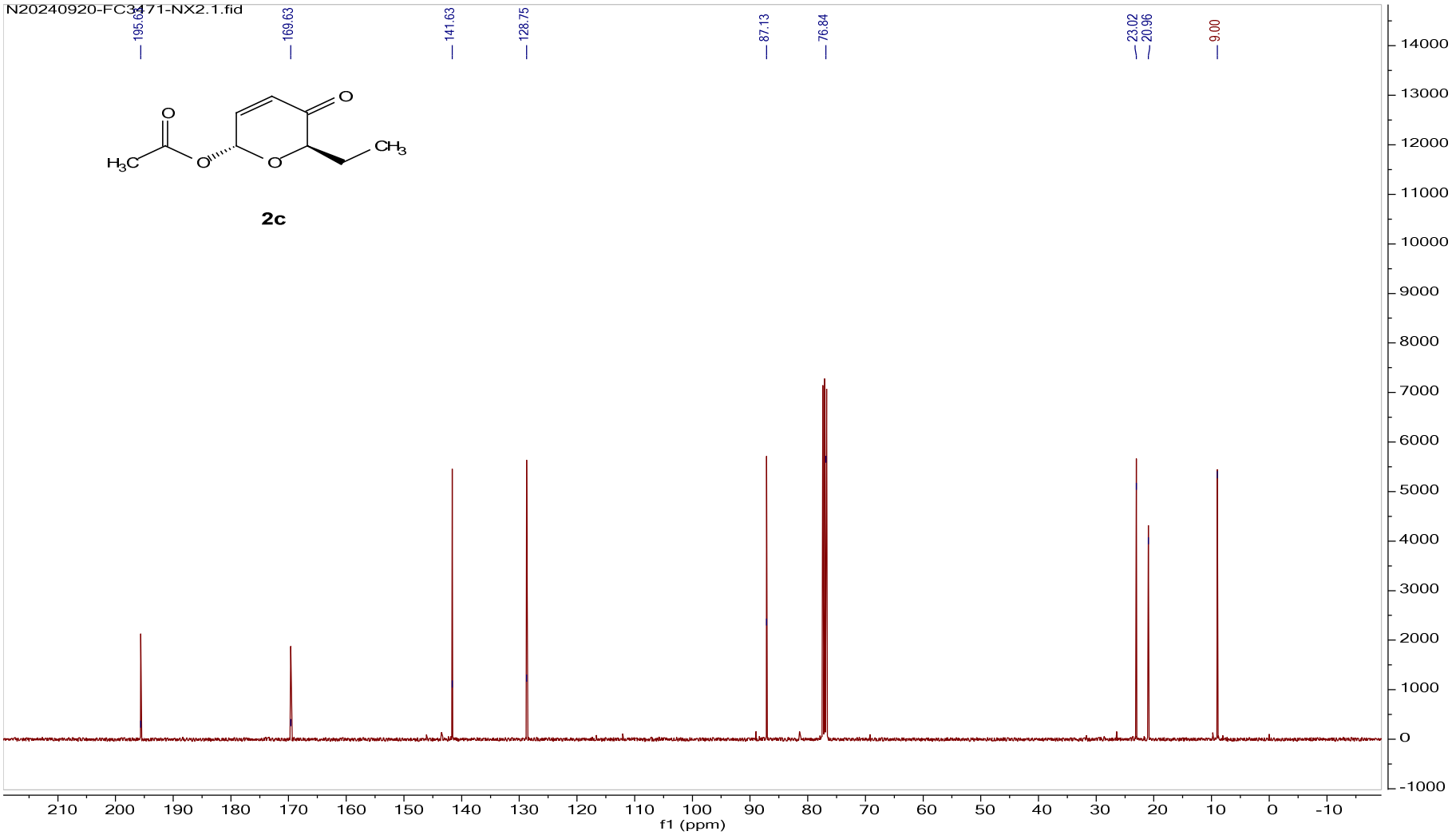
^{1}H spectra of **2b**.



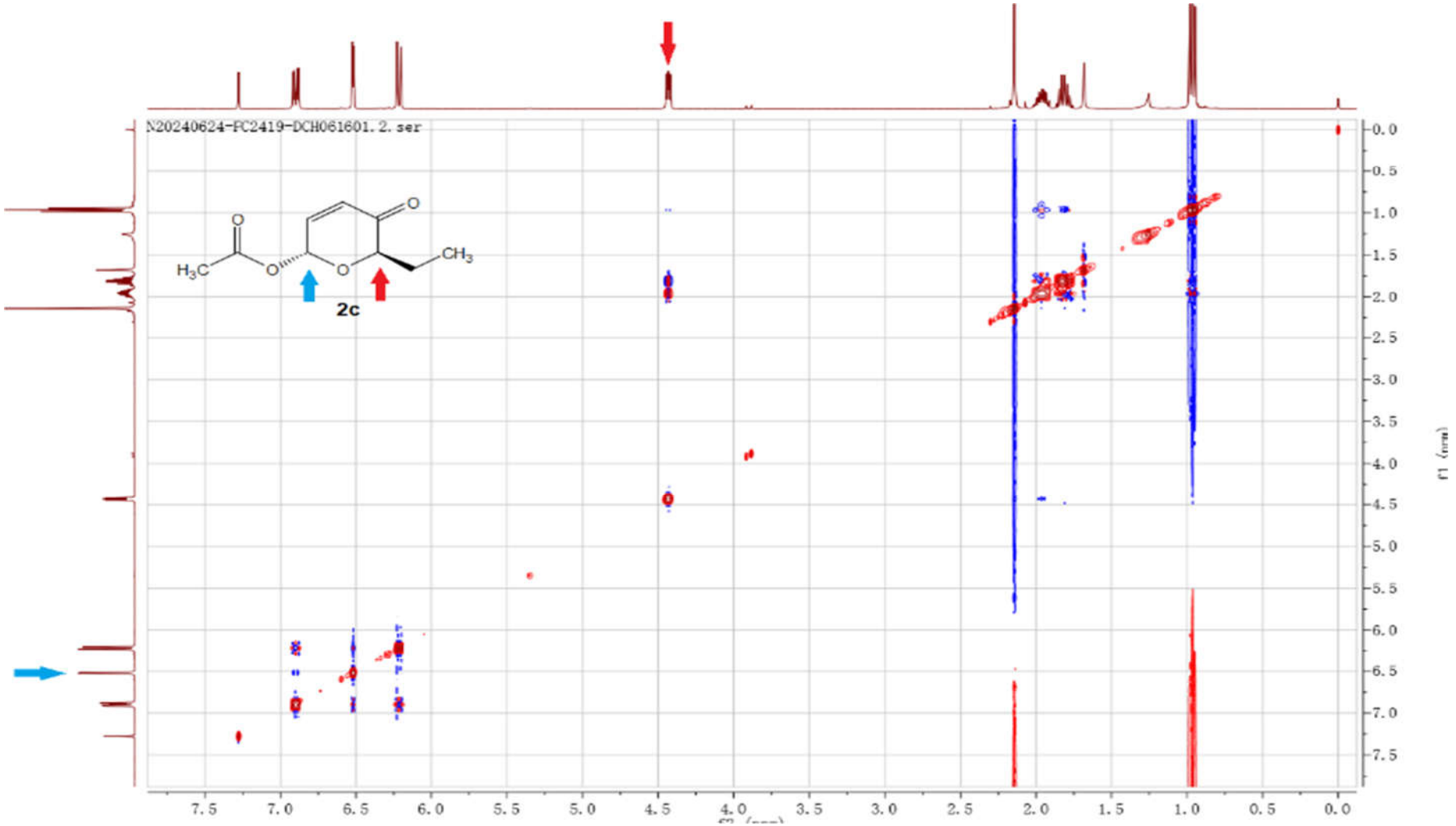
^{1}H spectra of **2c**.



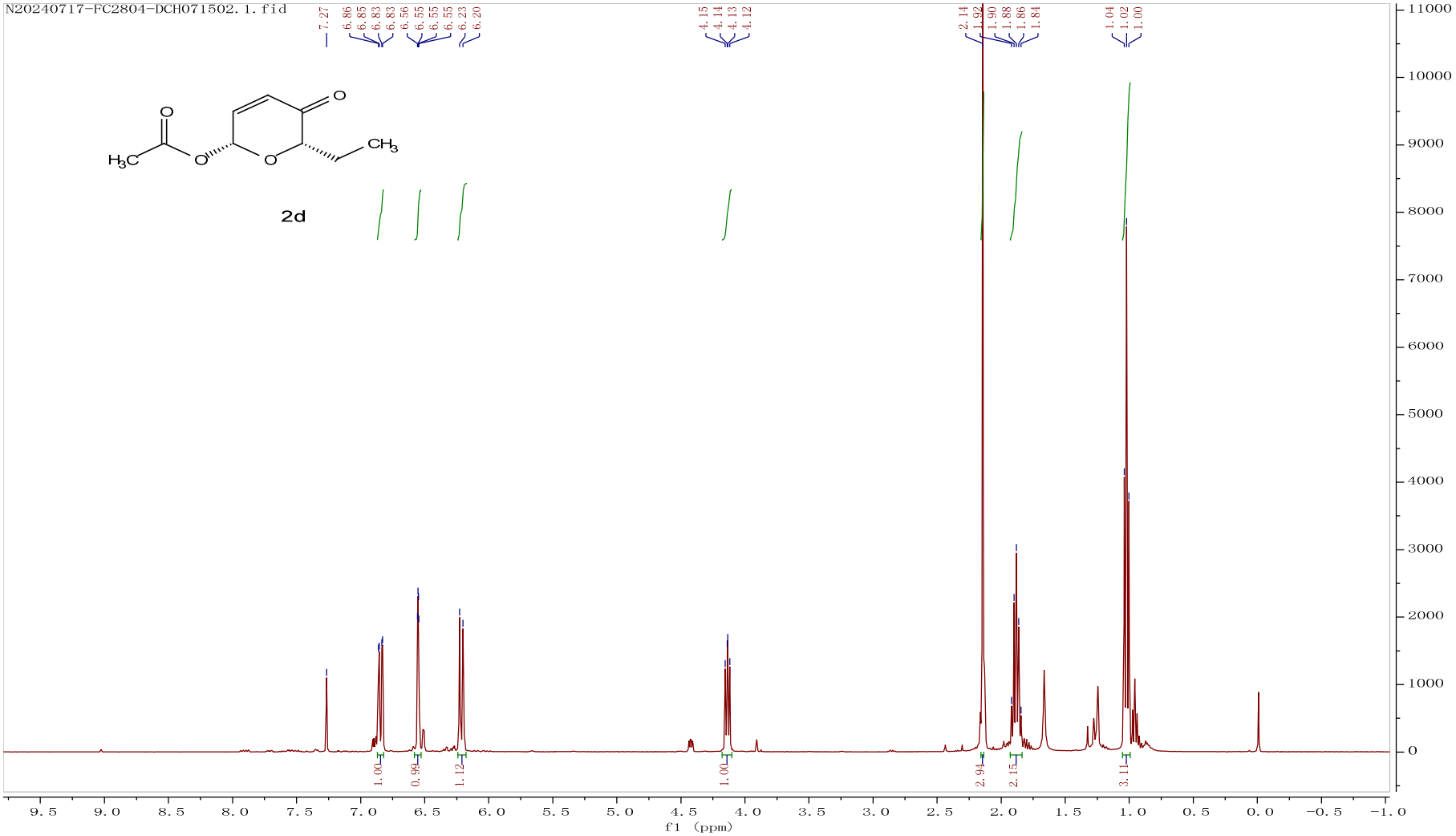
^{13}C spectra of **2c**.



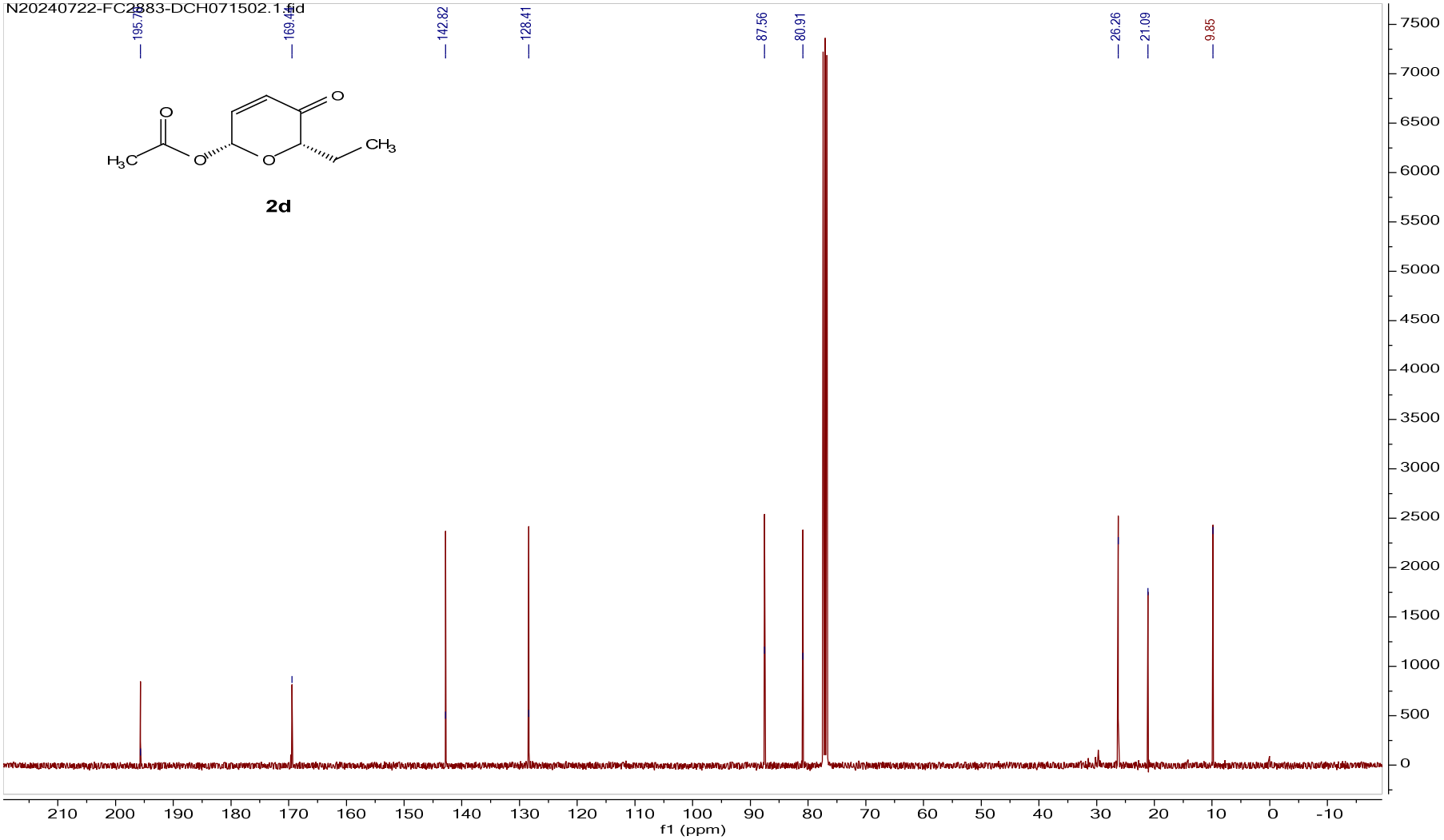
NOESY spectra of **2c**.



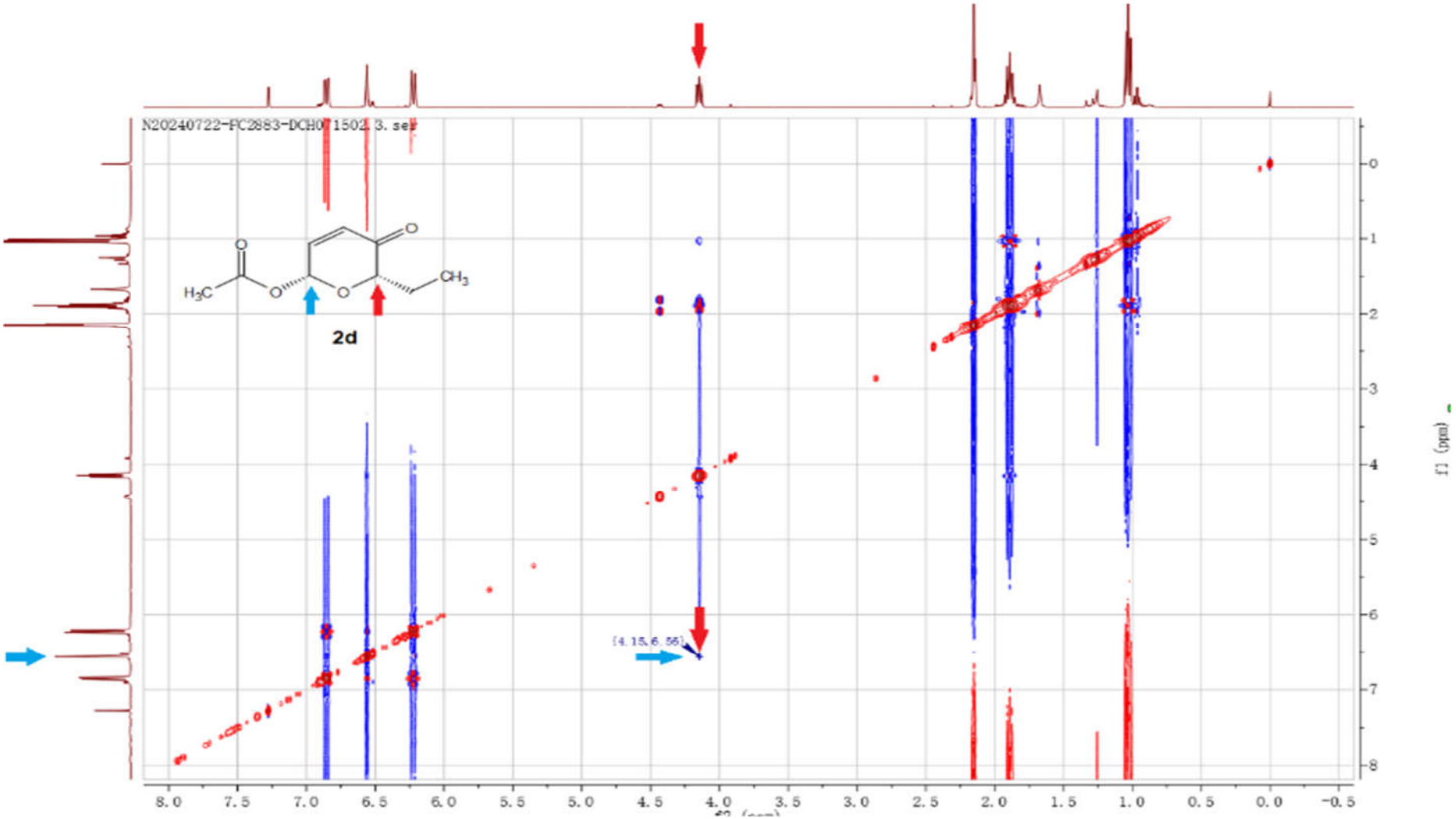
^{1}H spectra of **2d**.



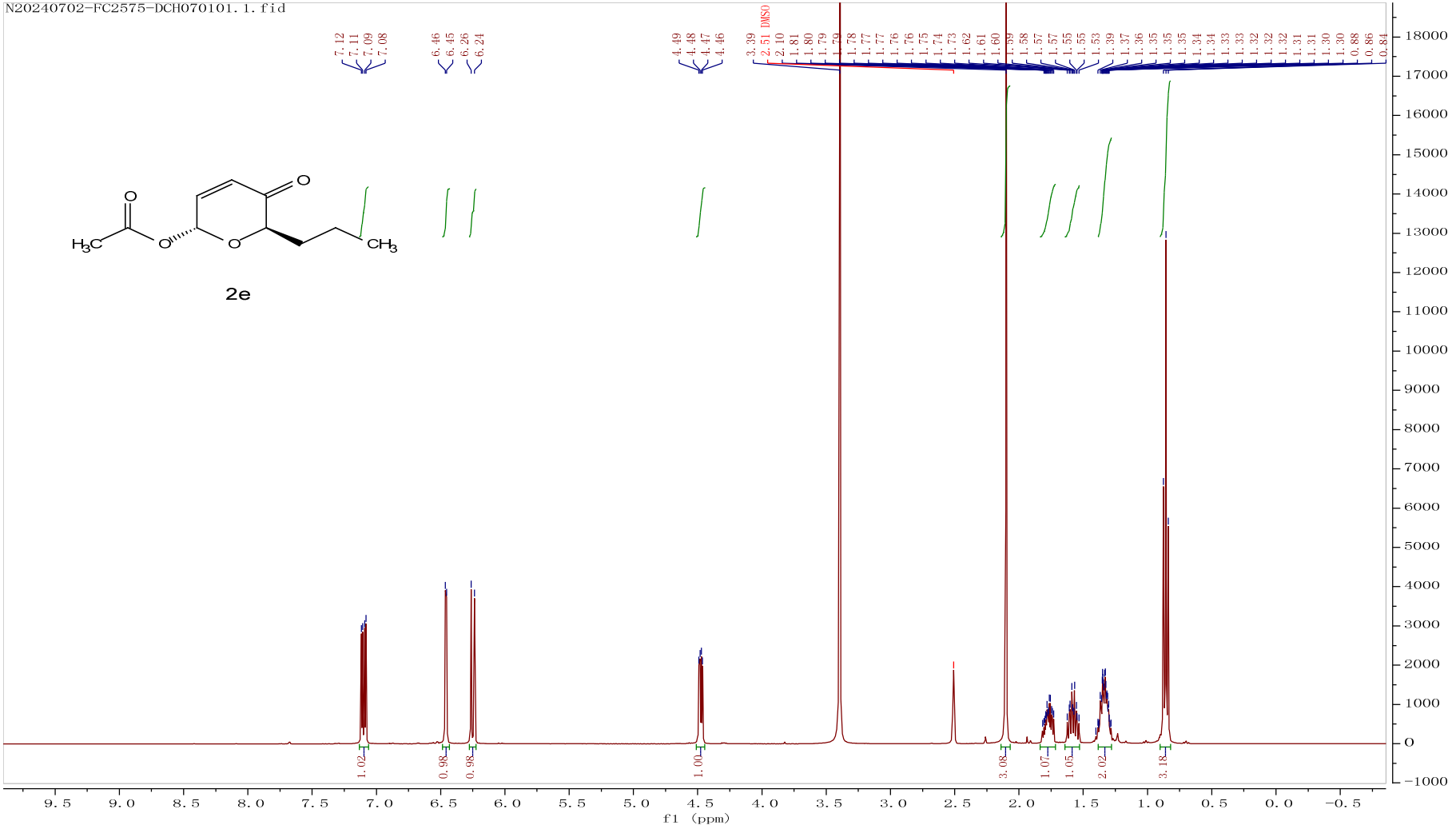
^{13}C spectra of **2d**.



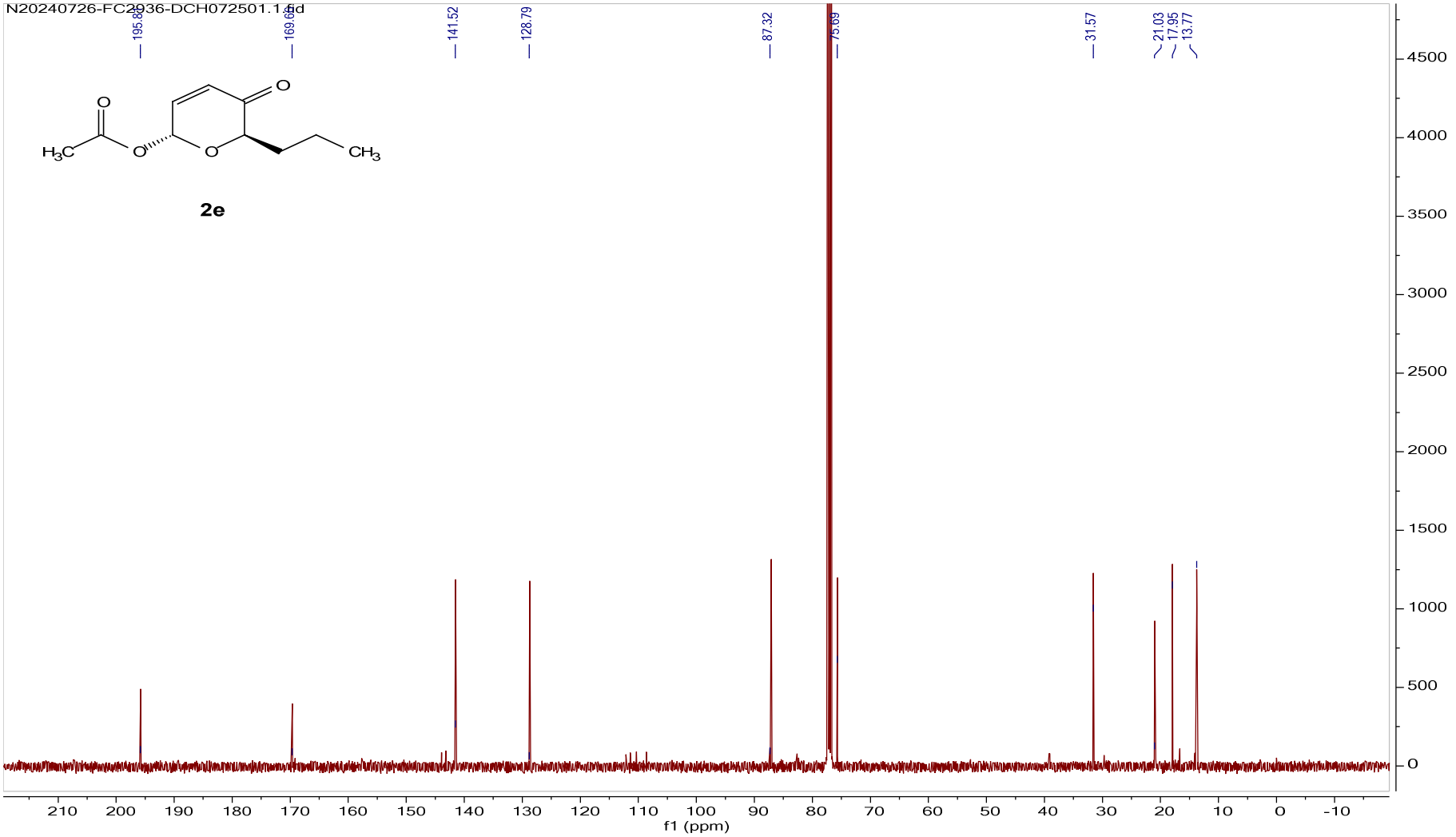
NOESY spectra of **2d**.



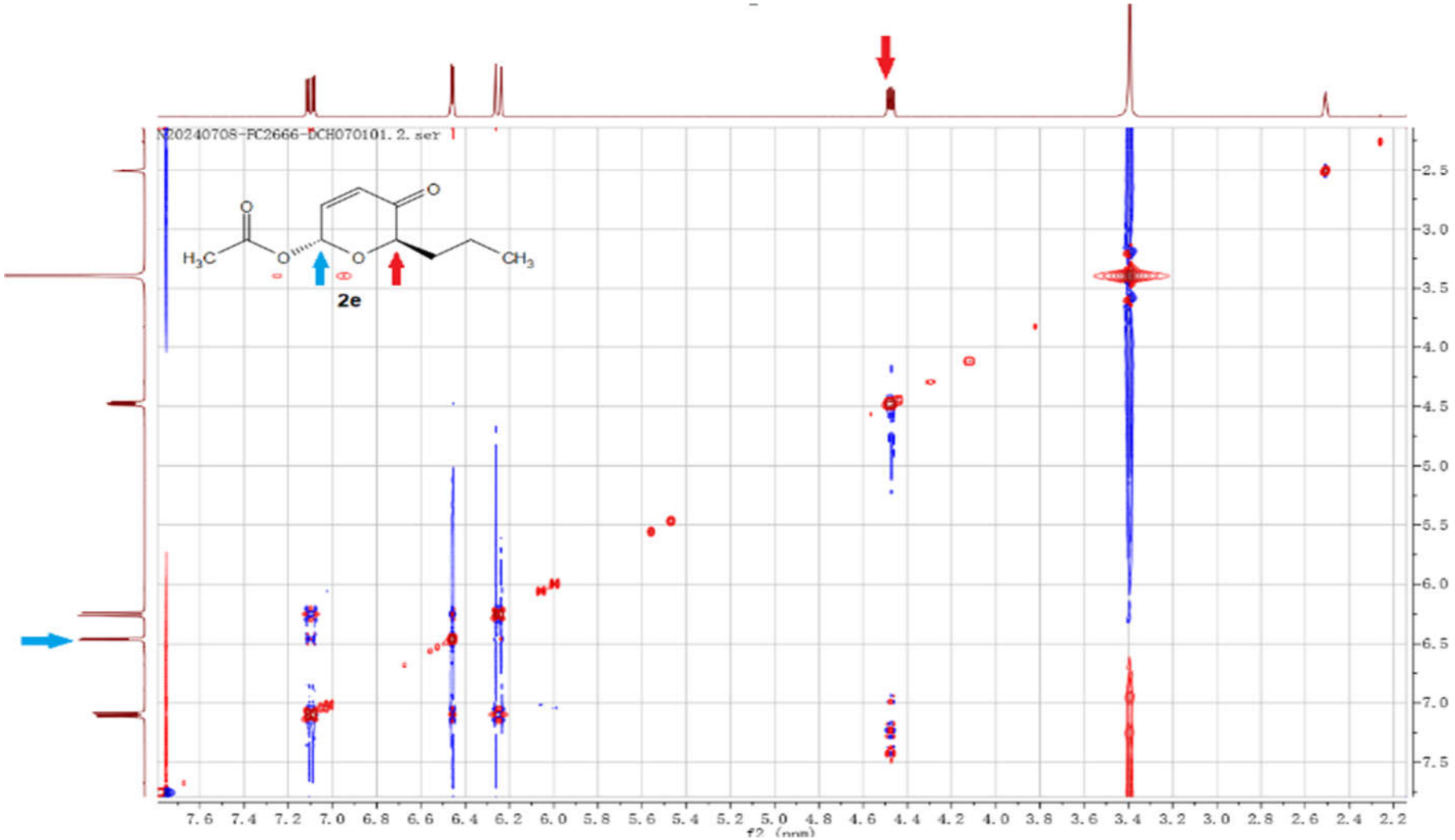
[1]H spectra of **2e**.



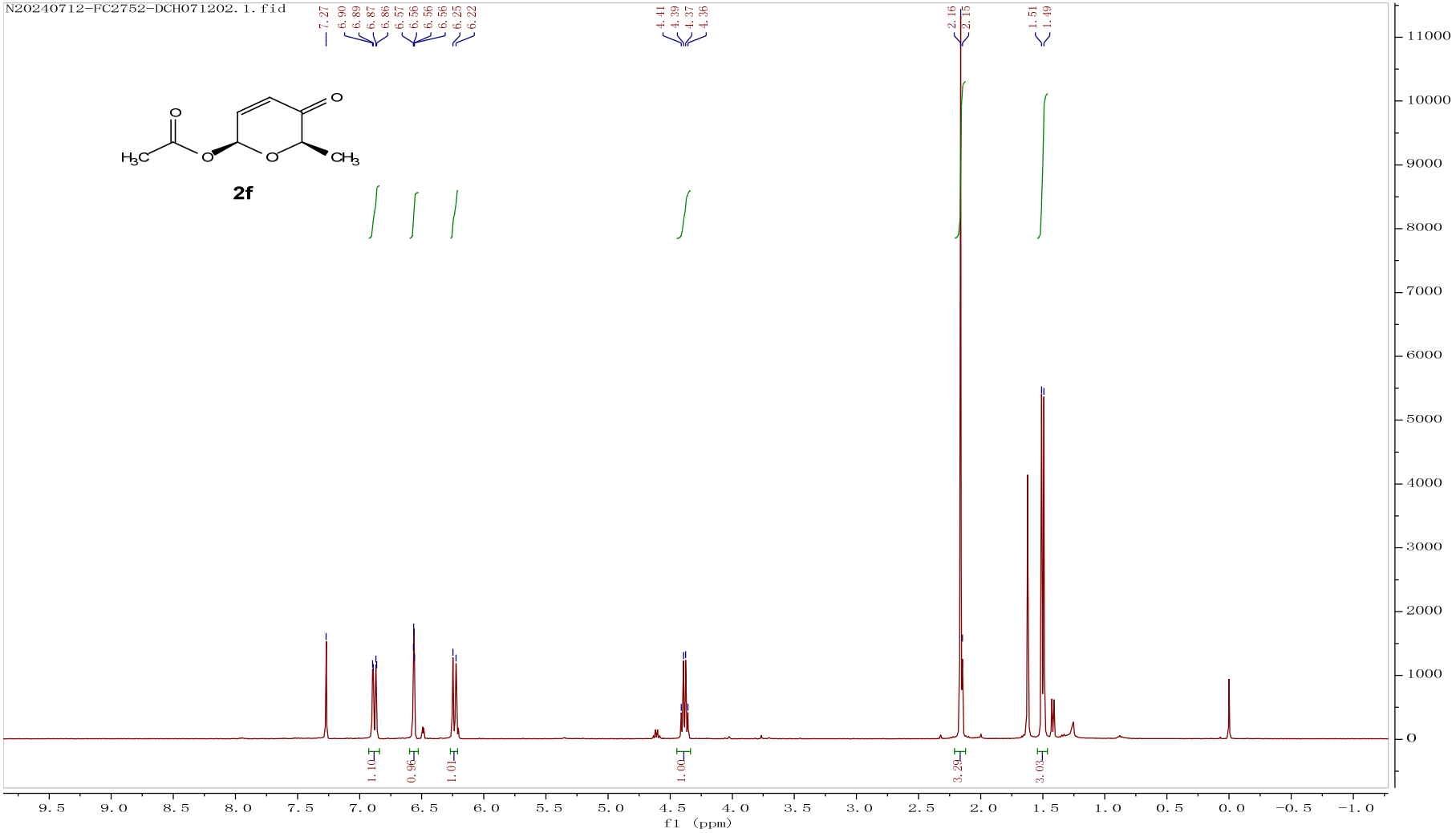
^{13}C spectra of **2e**.



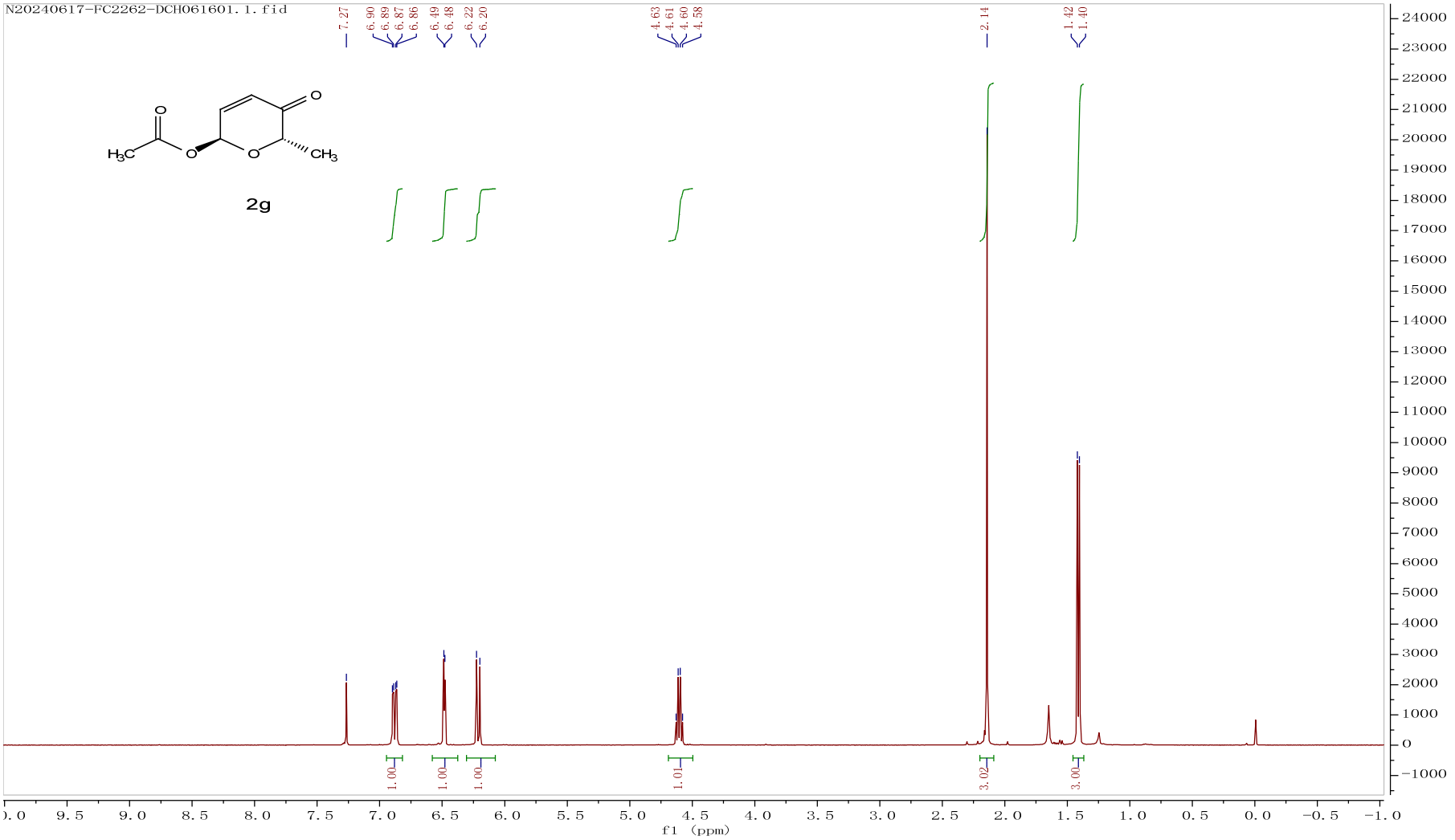
NOESY spectra of **2e**.



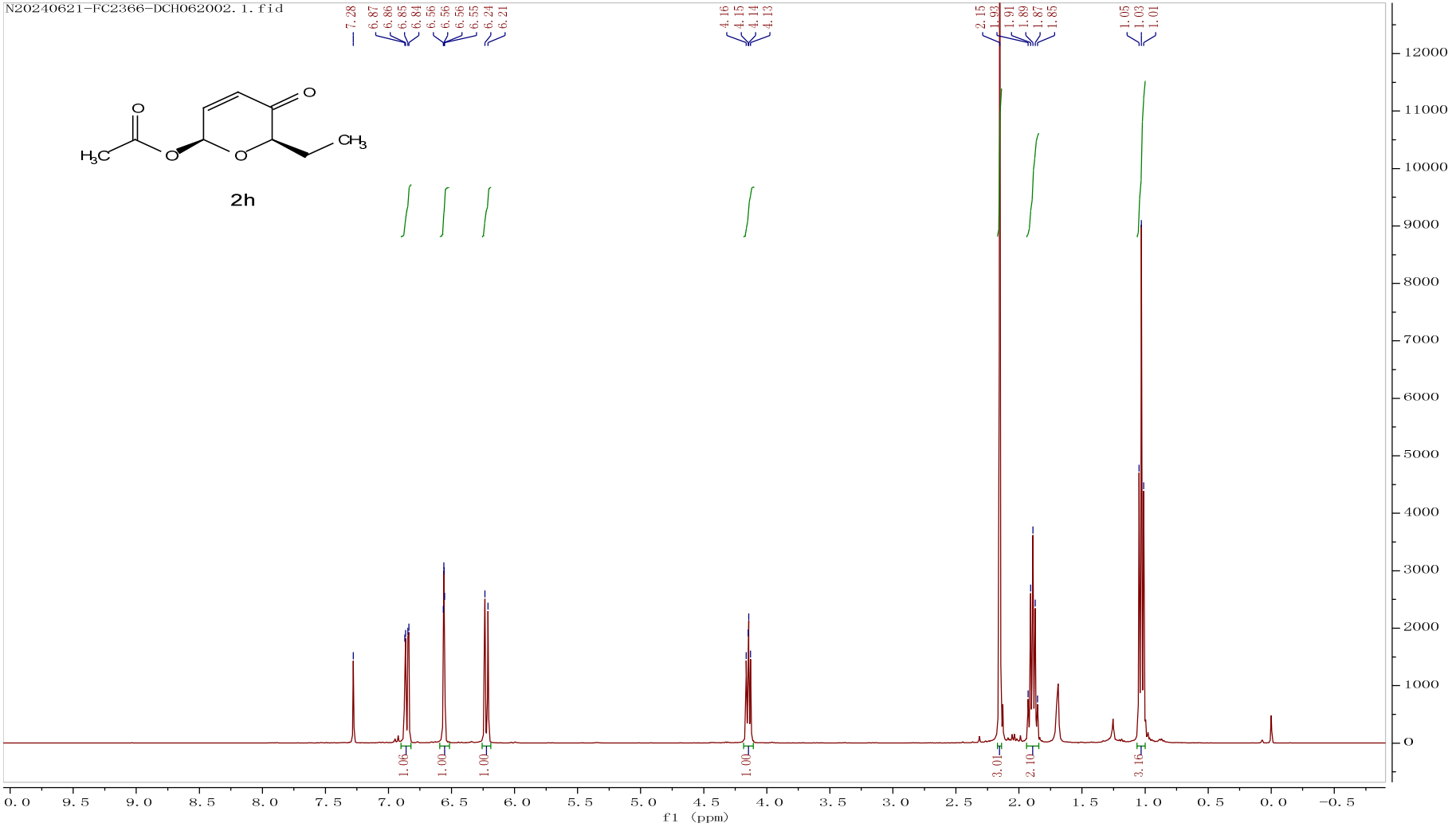
^{1}H spectra of **2f**.



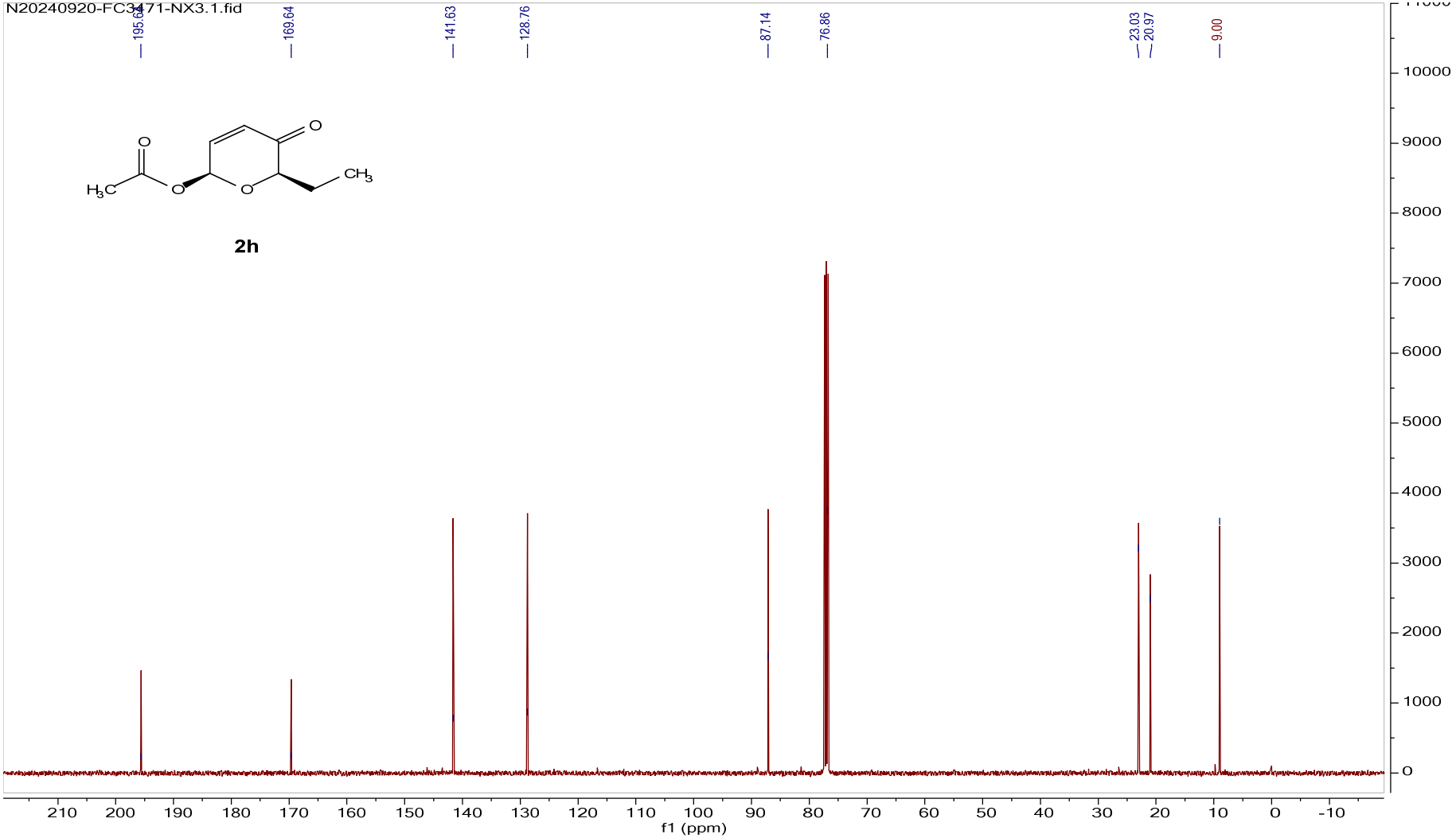
^{1}H spectra of **2g**.



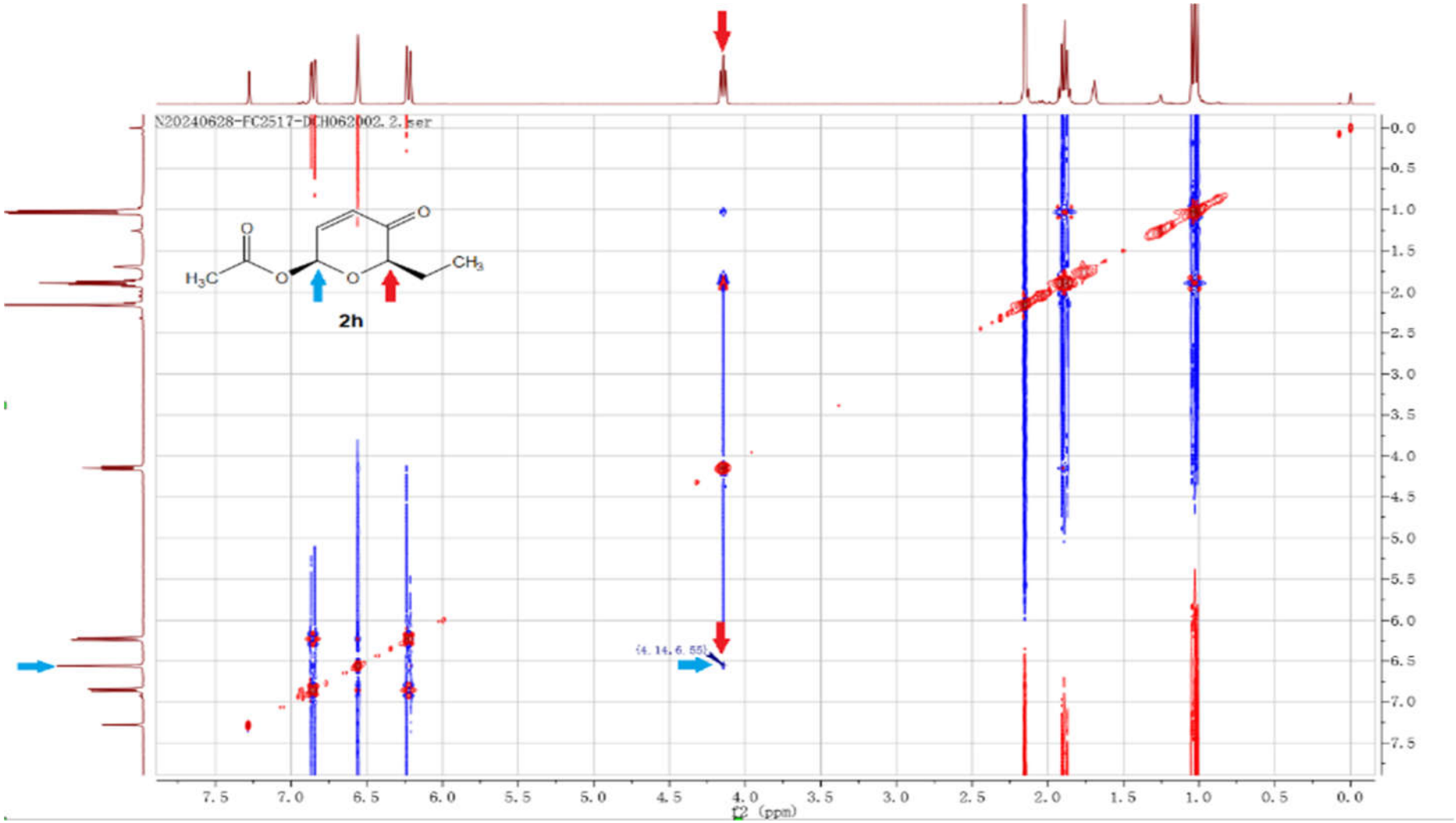
^{1}H spectra of **2h**.



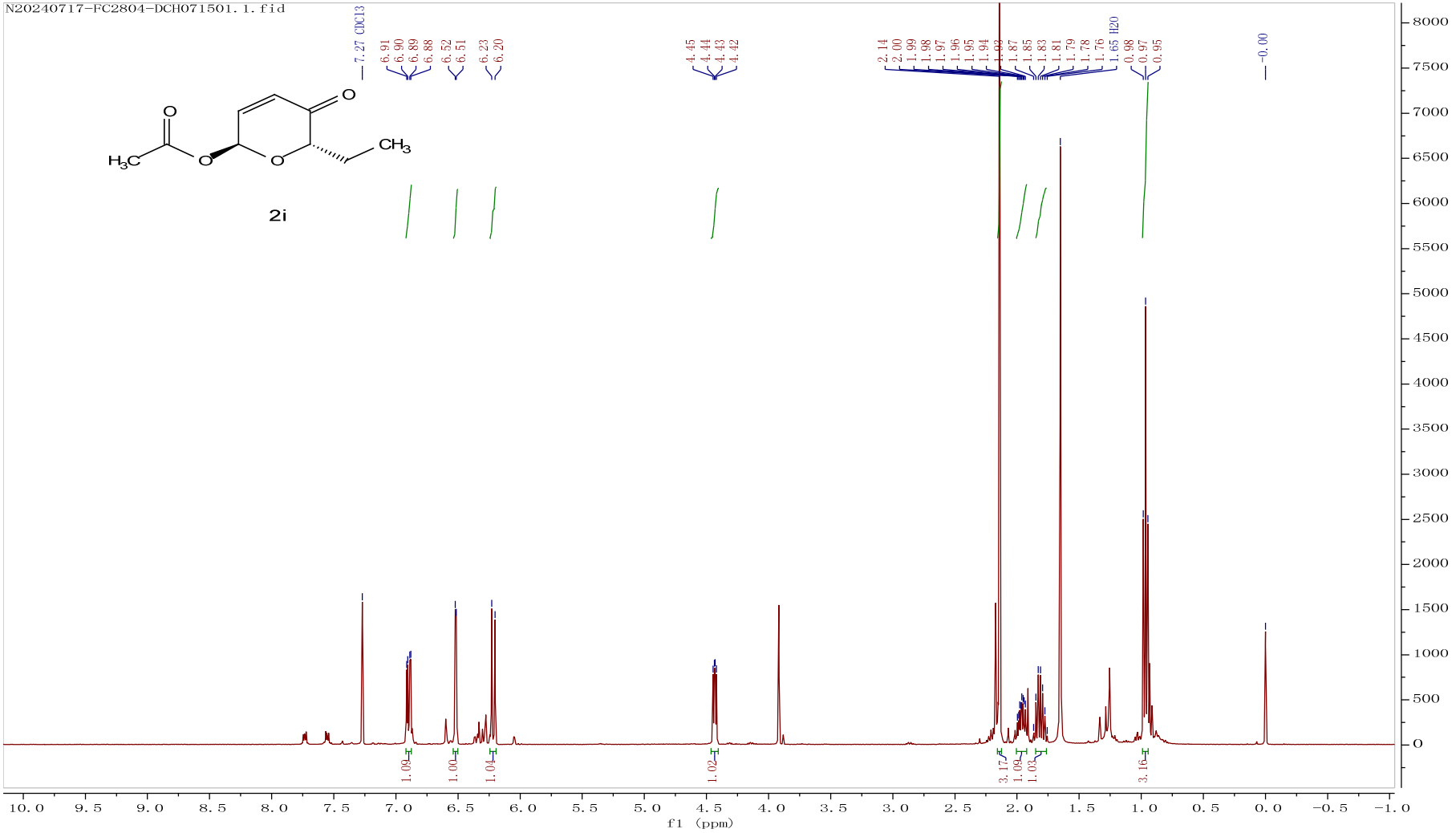
^{13}C spectra of **2h**.



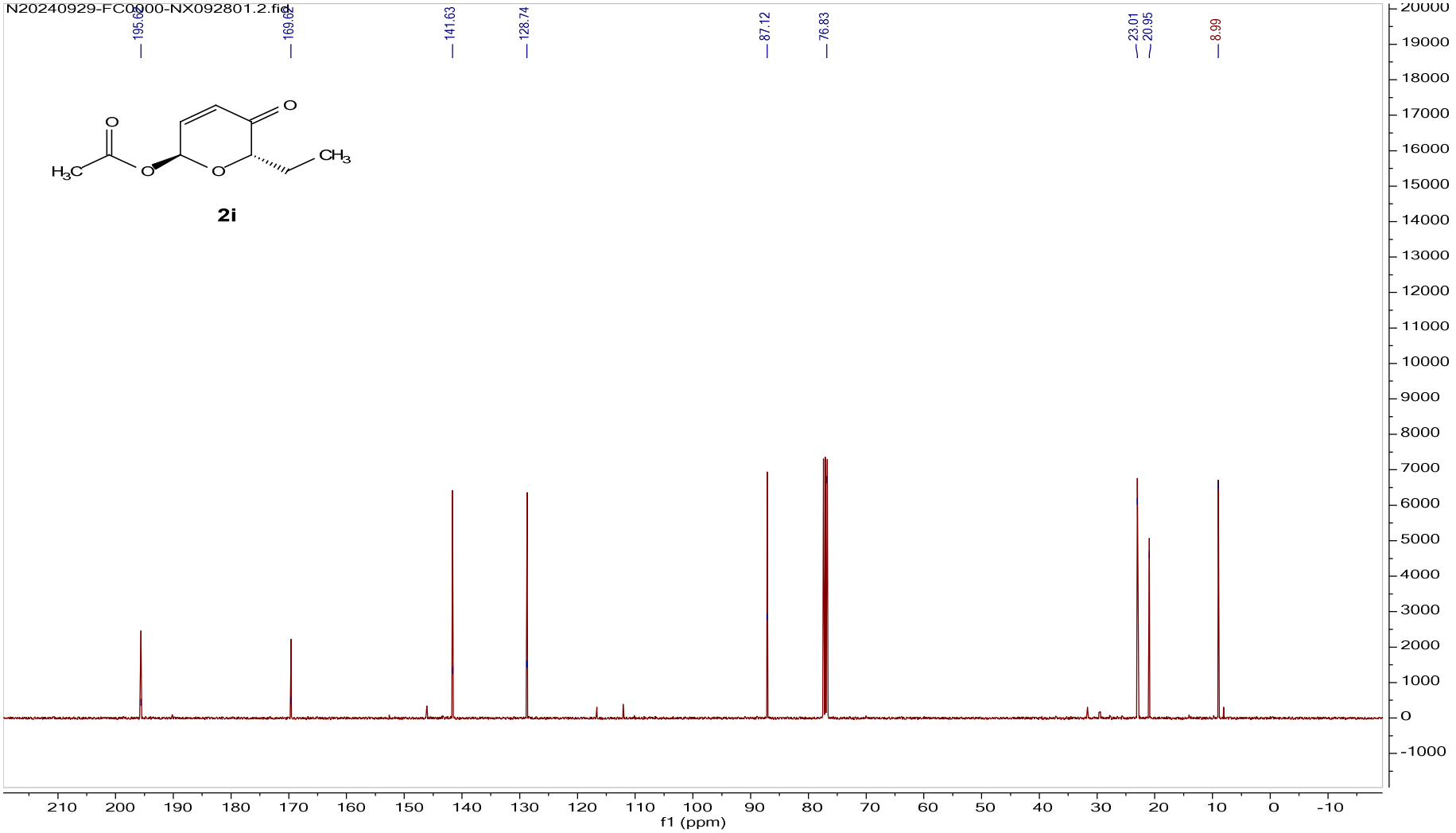
NOESY spectra of **2h**.



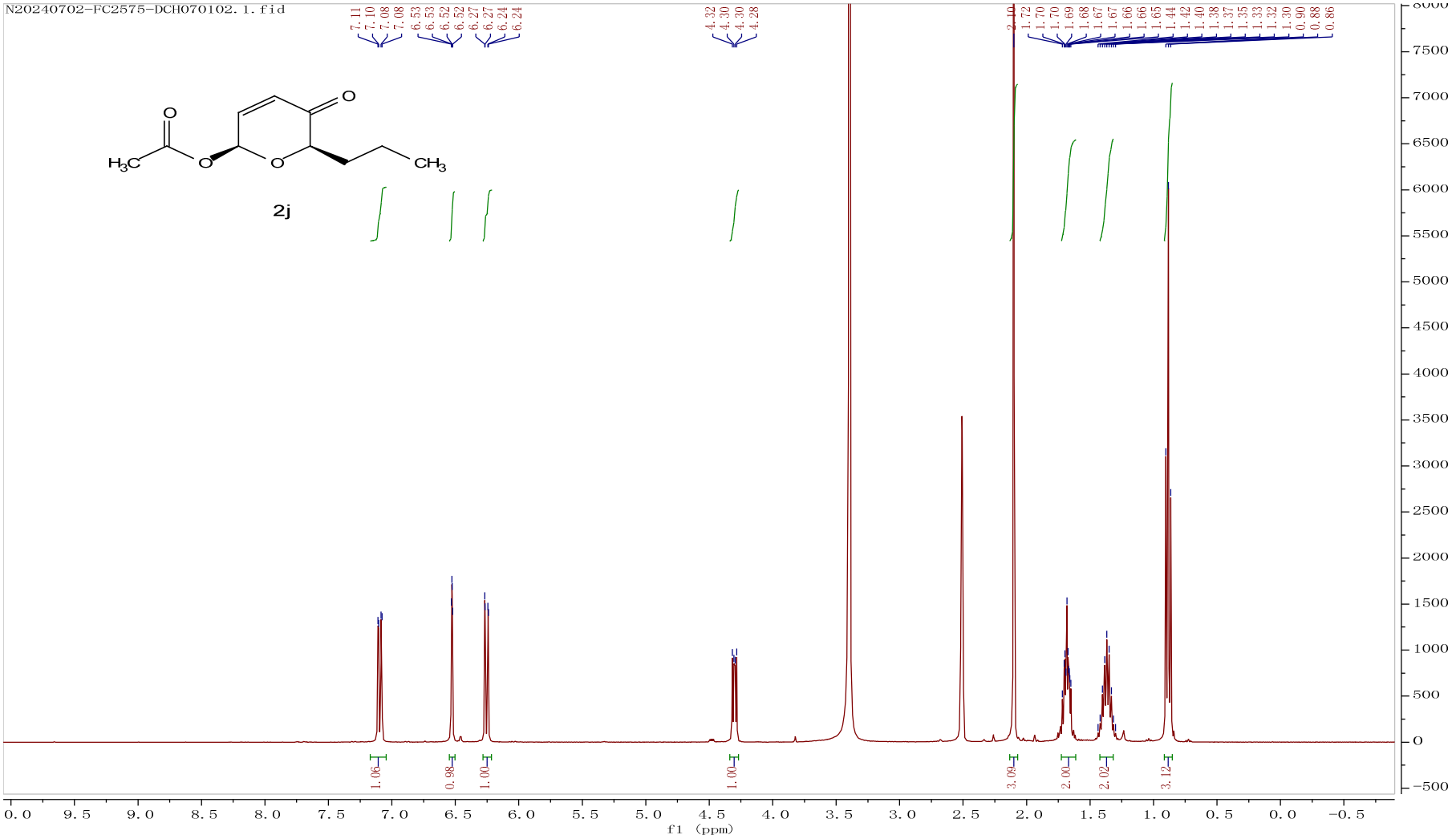
^{1}H spectra of **2i**.



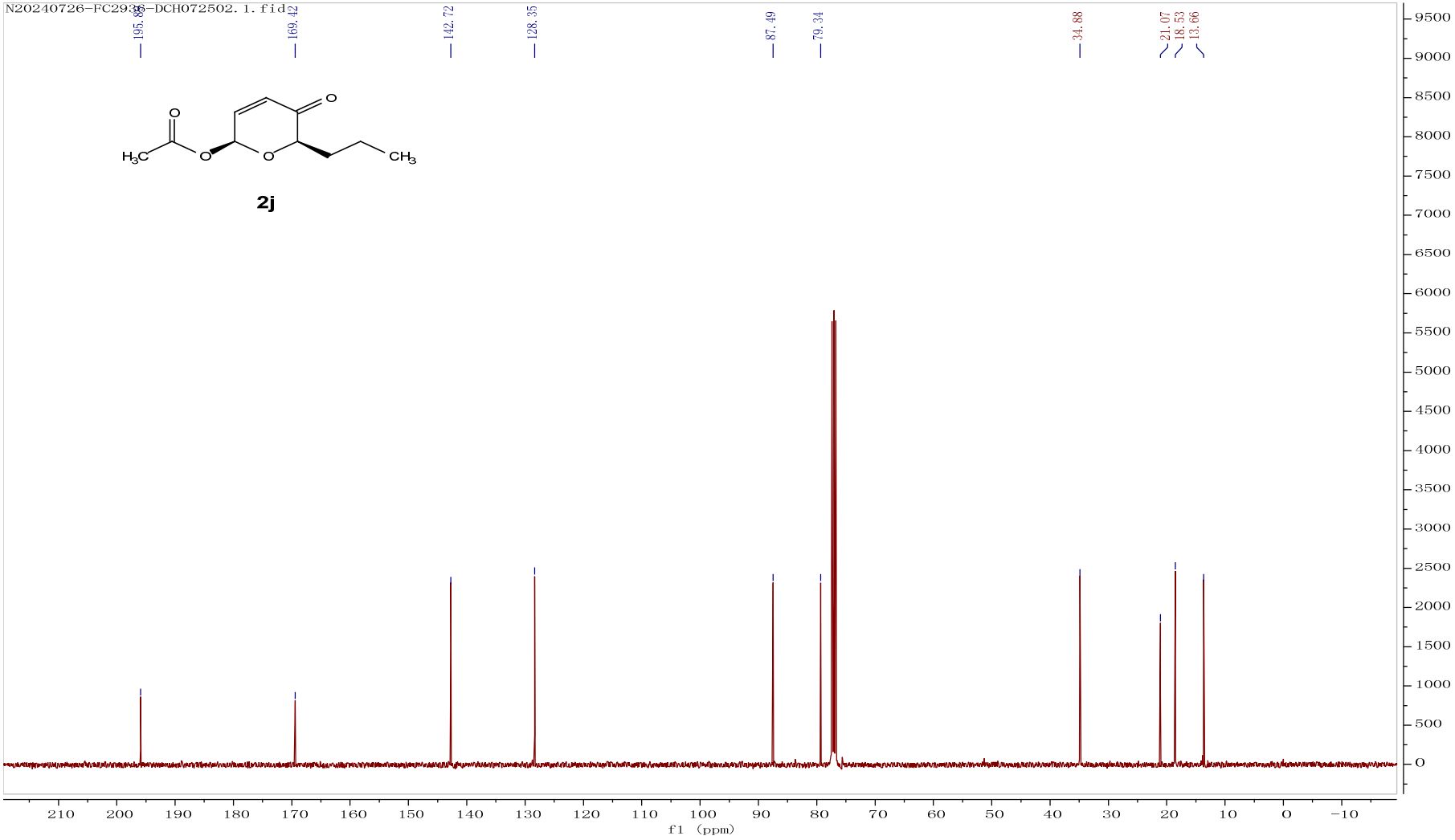
^{13}C spectra of **2i**.



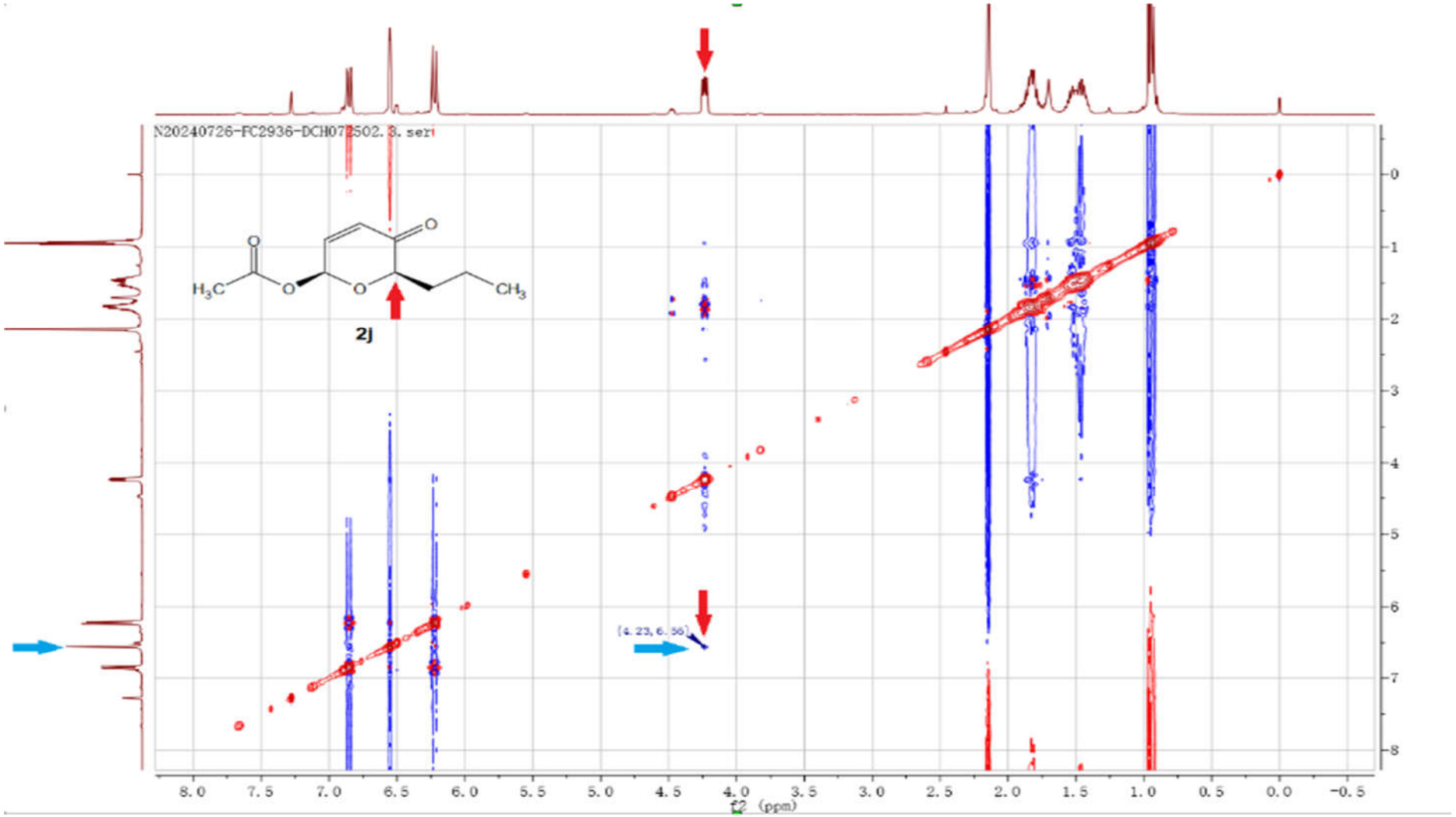
^{1}H spectra of **2j**.



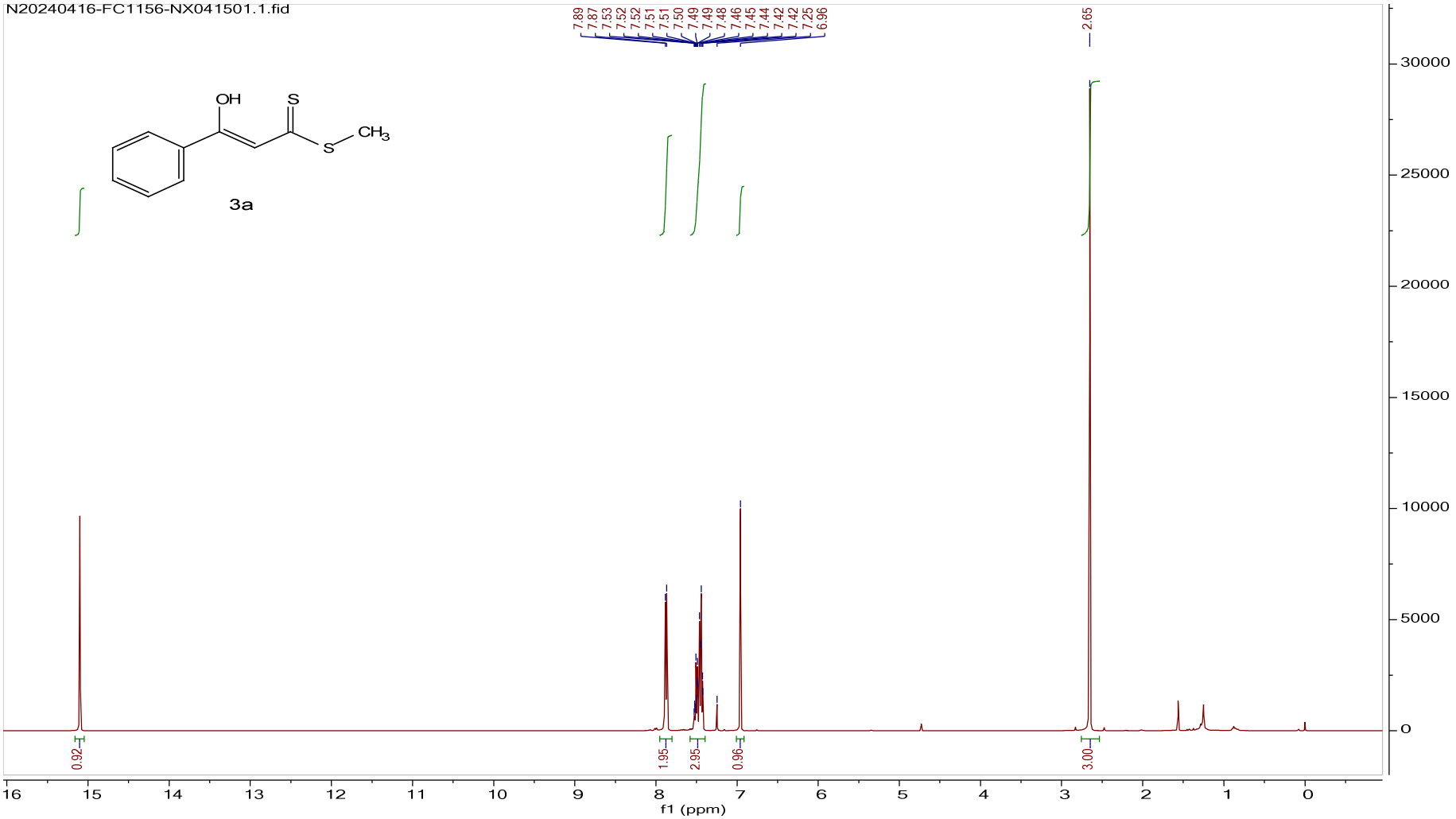
^{13}C spectra of **2j**.



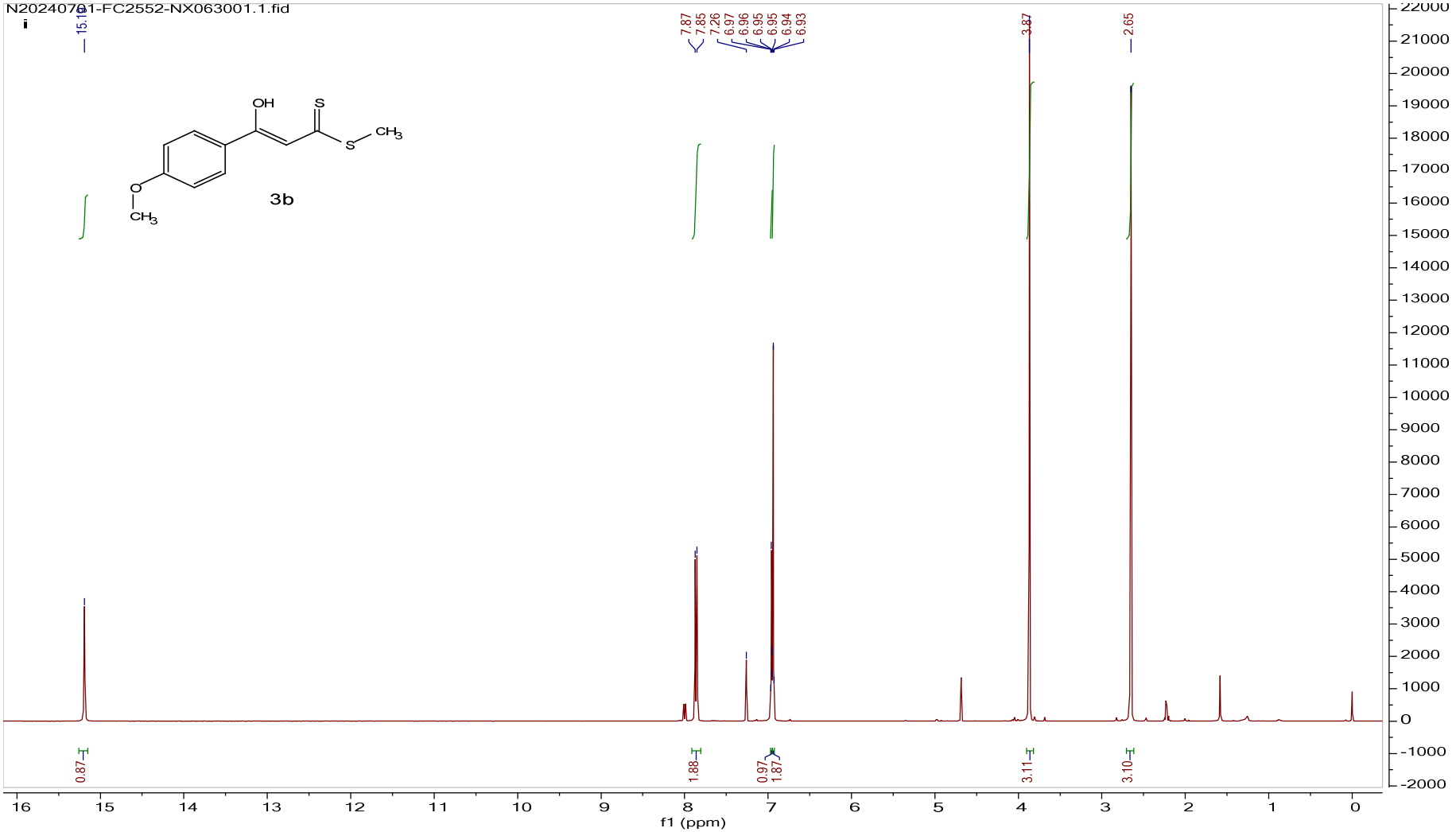
NOESY spectra of **2j**.



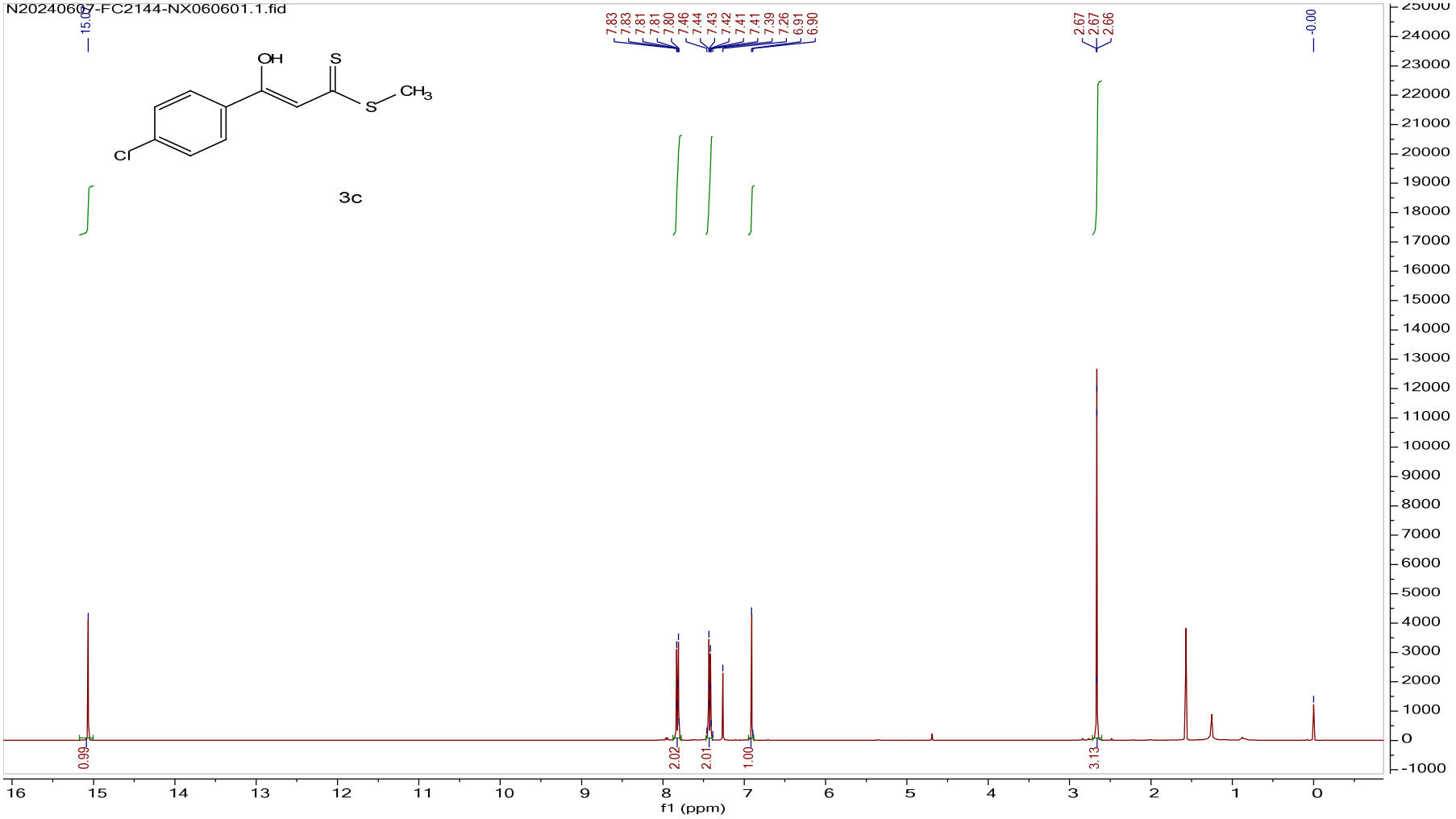
^{1}H spectra of **3a**.



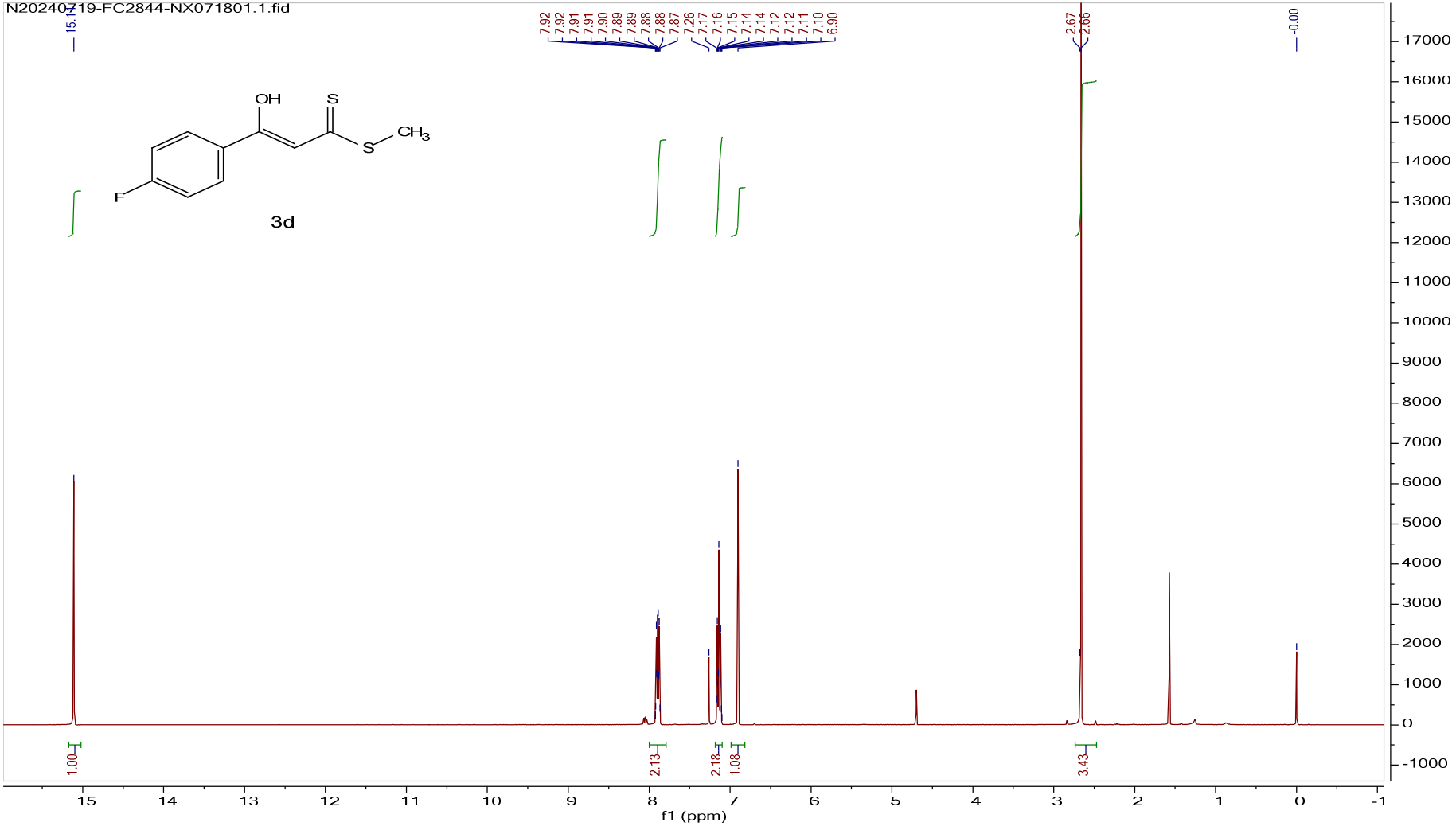
^{1}H spectra of **3b.**



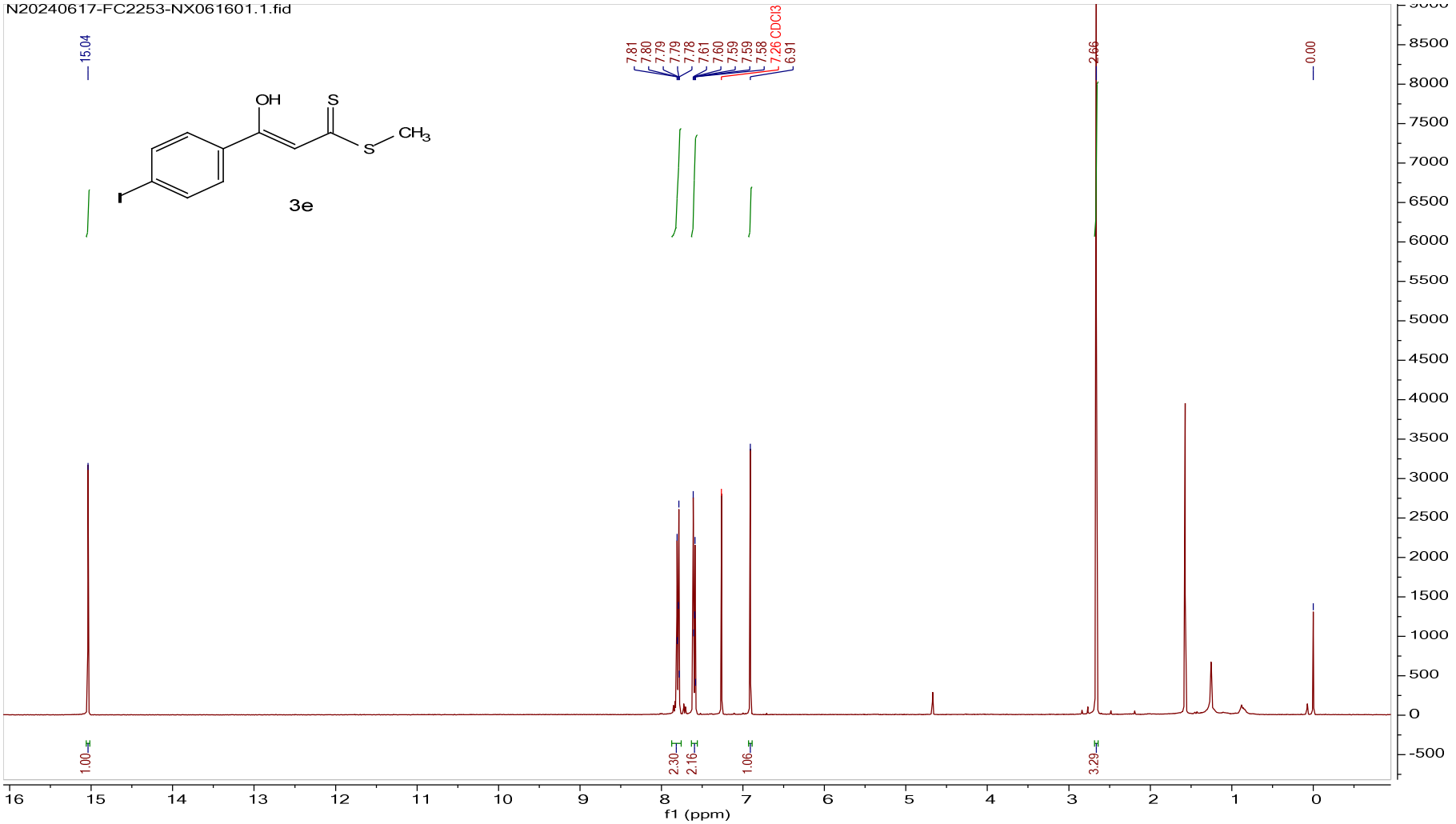
^{1}H spectra of **3c.**



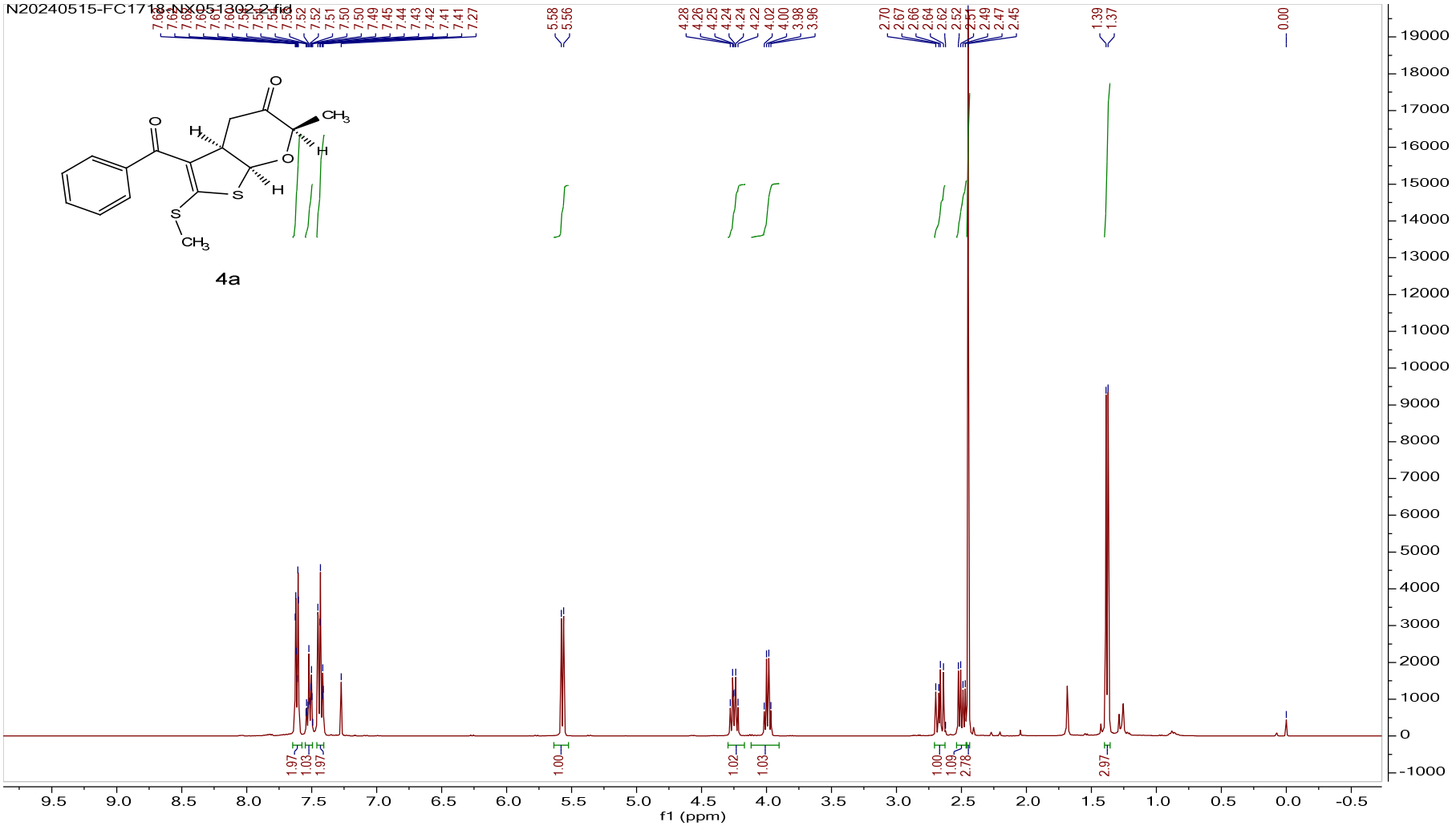
^{1}H spectra of **3d.**



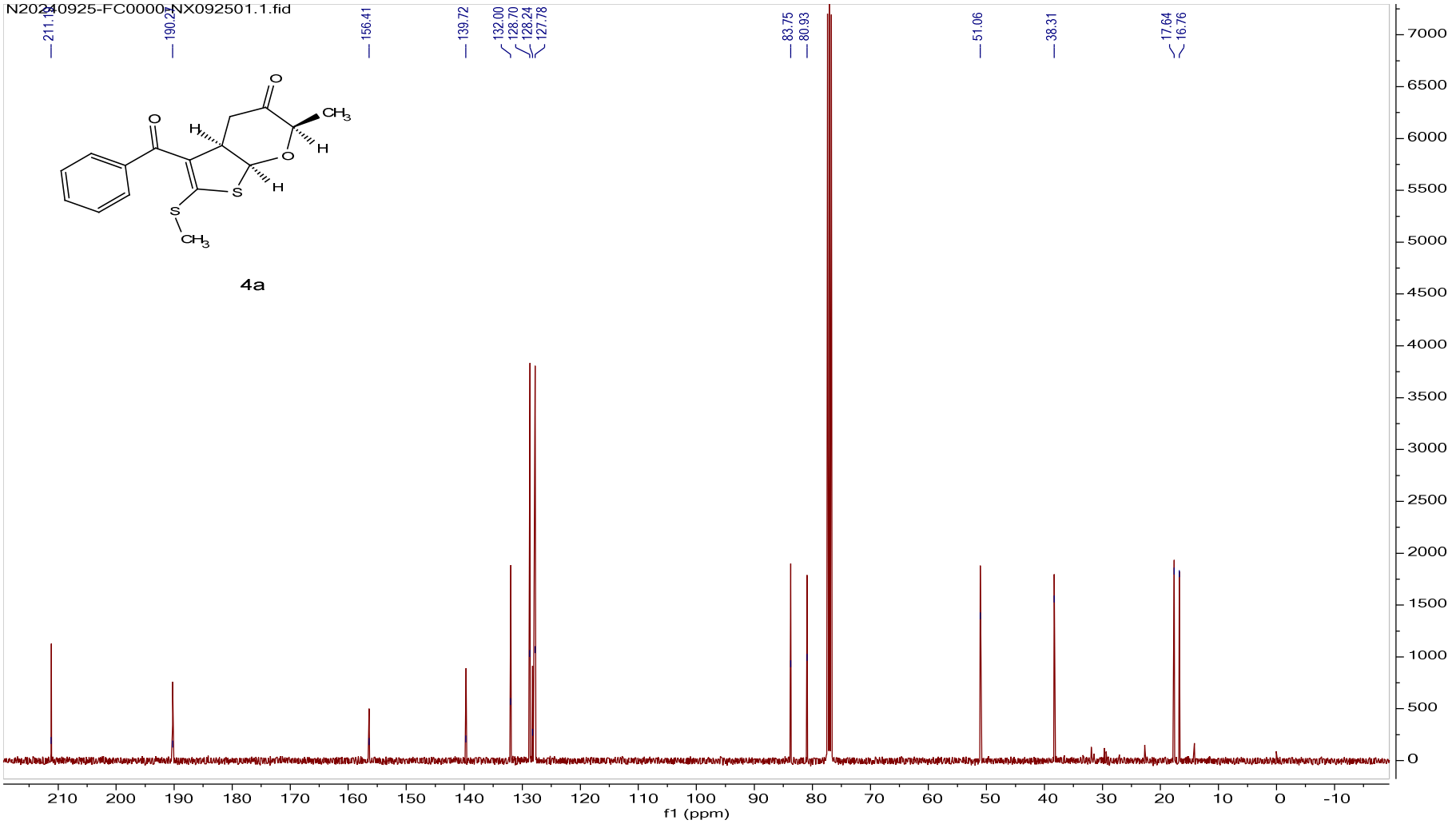
[1]H spectra of **3e.**



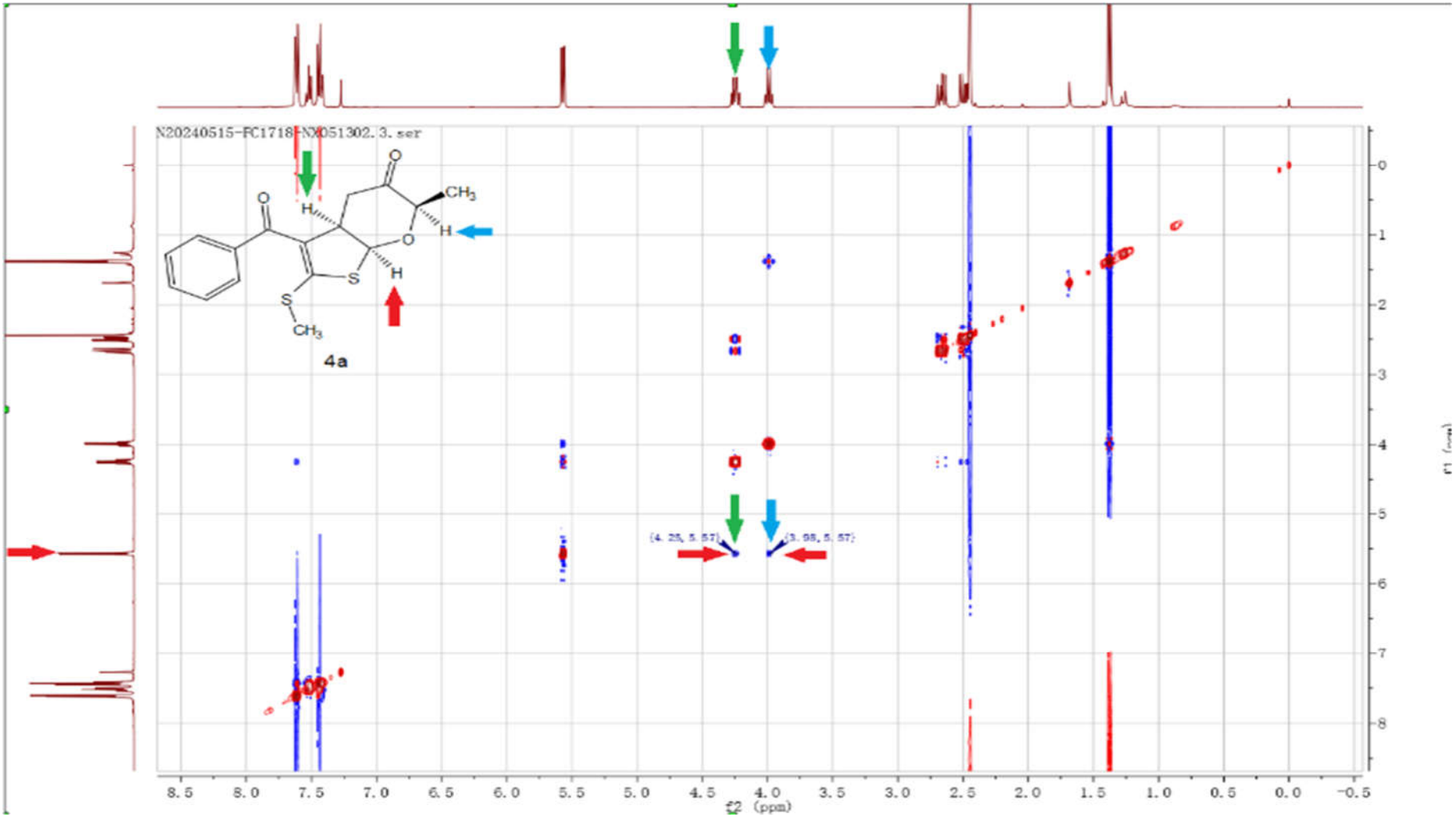
^{1}H spectra of **4a**.



^{13}C spectra of **4a**.



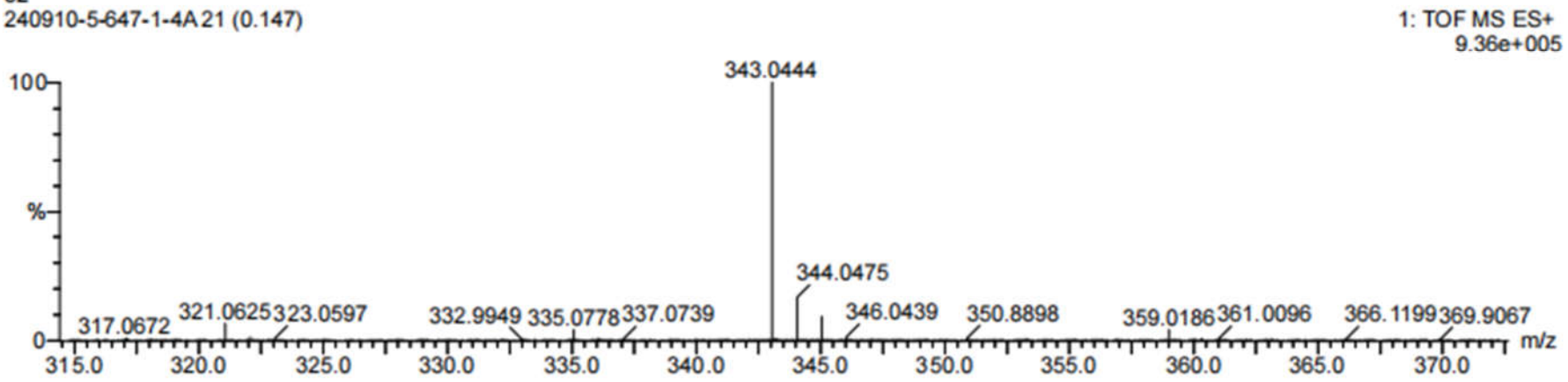
NOESY spectra of **4a**.



HRMS of **4a**.

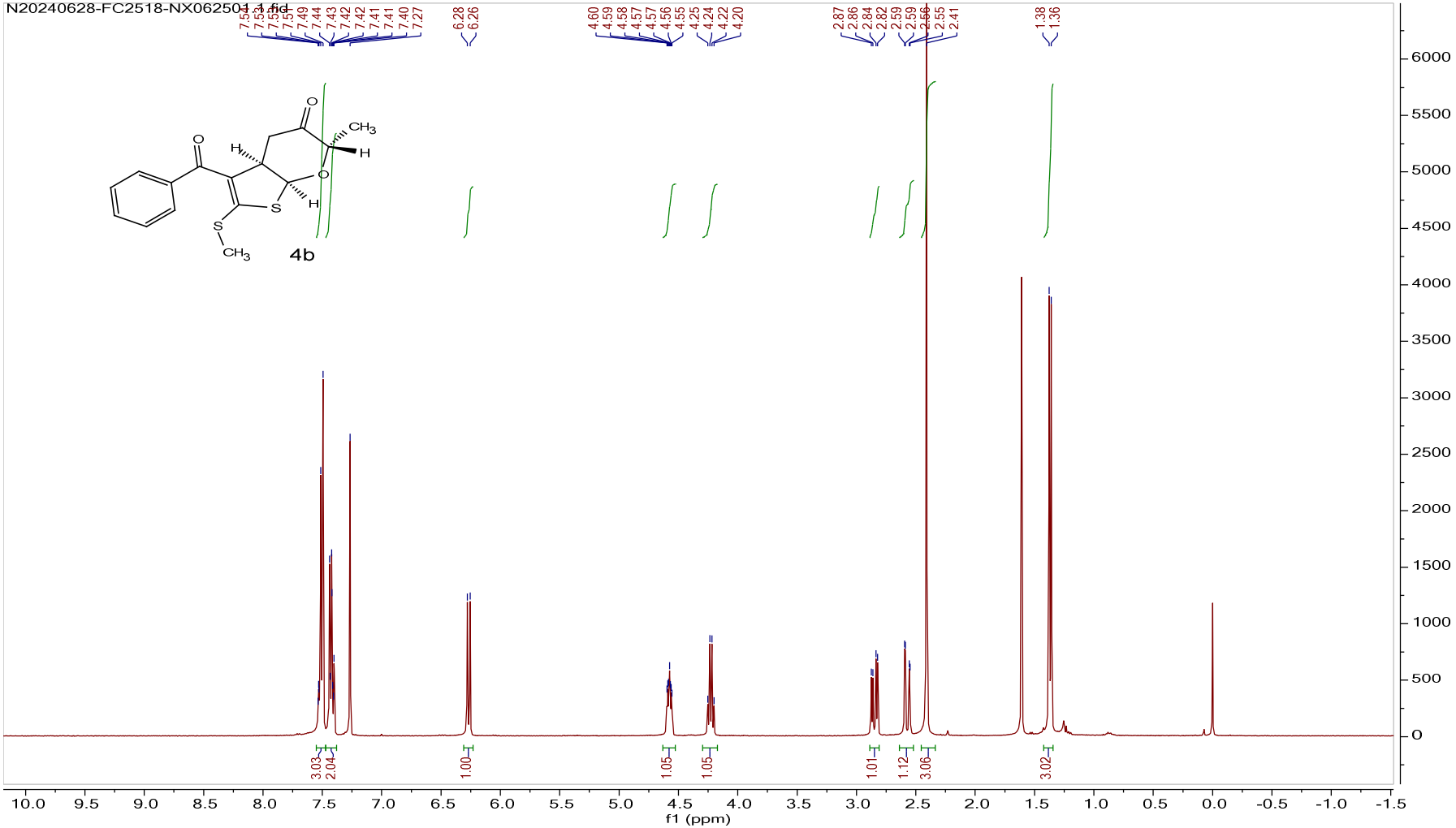
Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2354 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 16-16 H: 16-16 N: 0-100 O: 0-100 Na: 0-4 S: 1-4
32
240910-5-647-1-4A 21 (0.147)

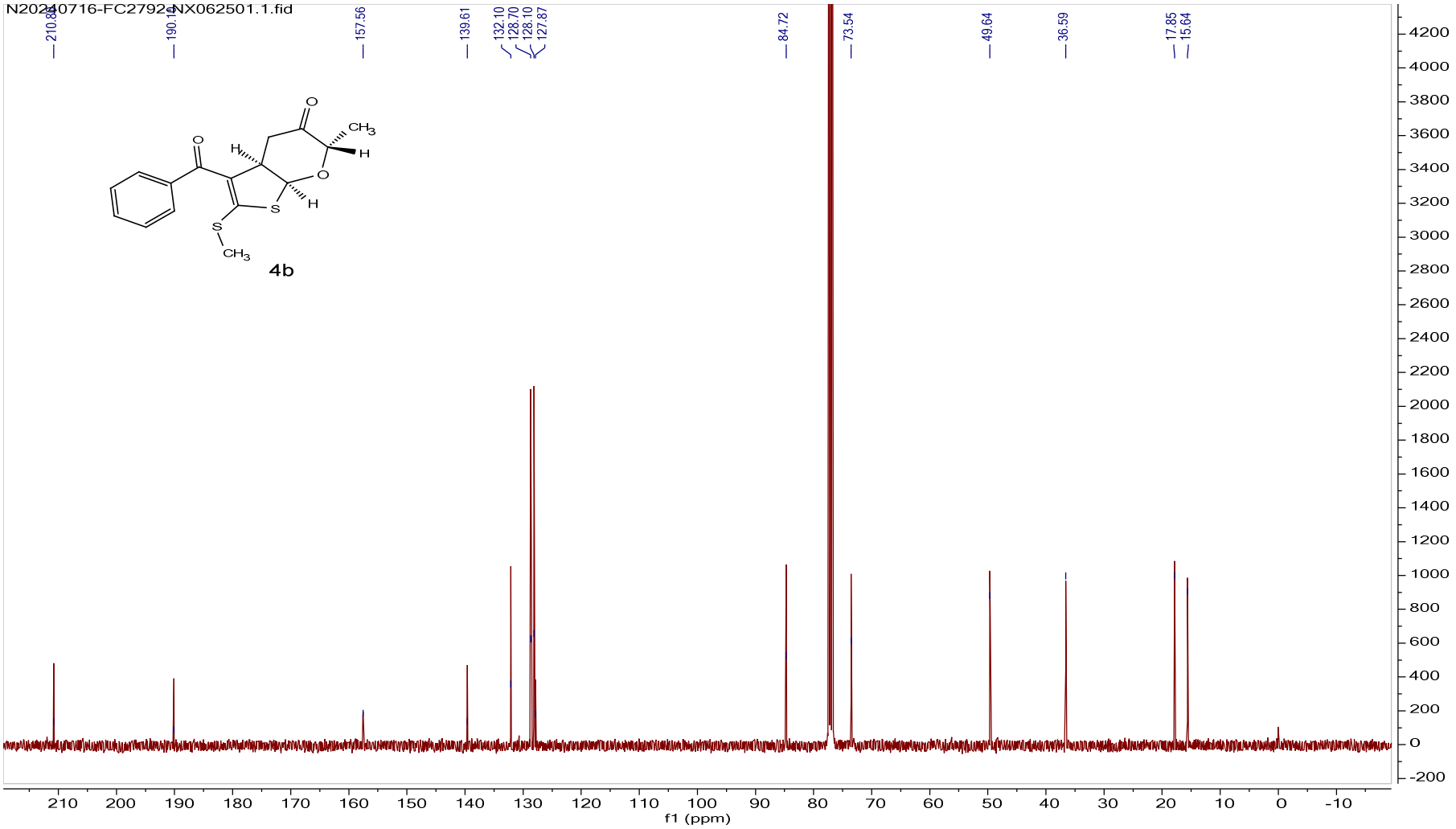


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
343.0444	343.0439	0.5	1.5	8.5	1018.9	n/a	n/a	C16 H16 O3 Na S2

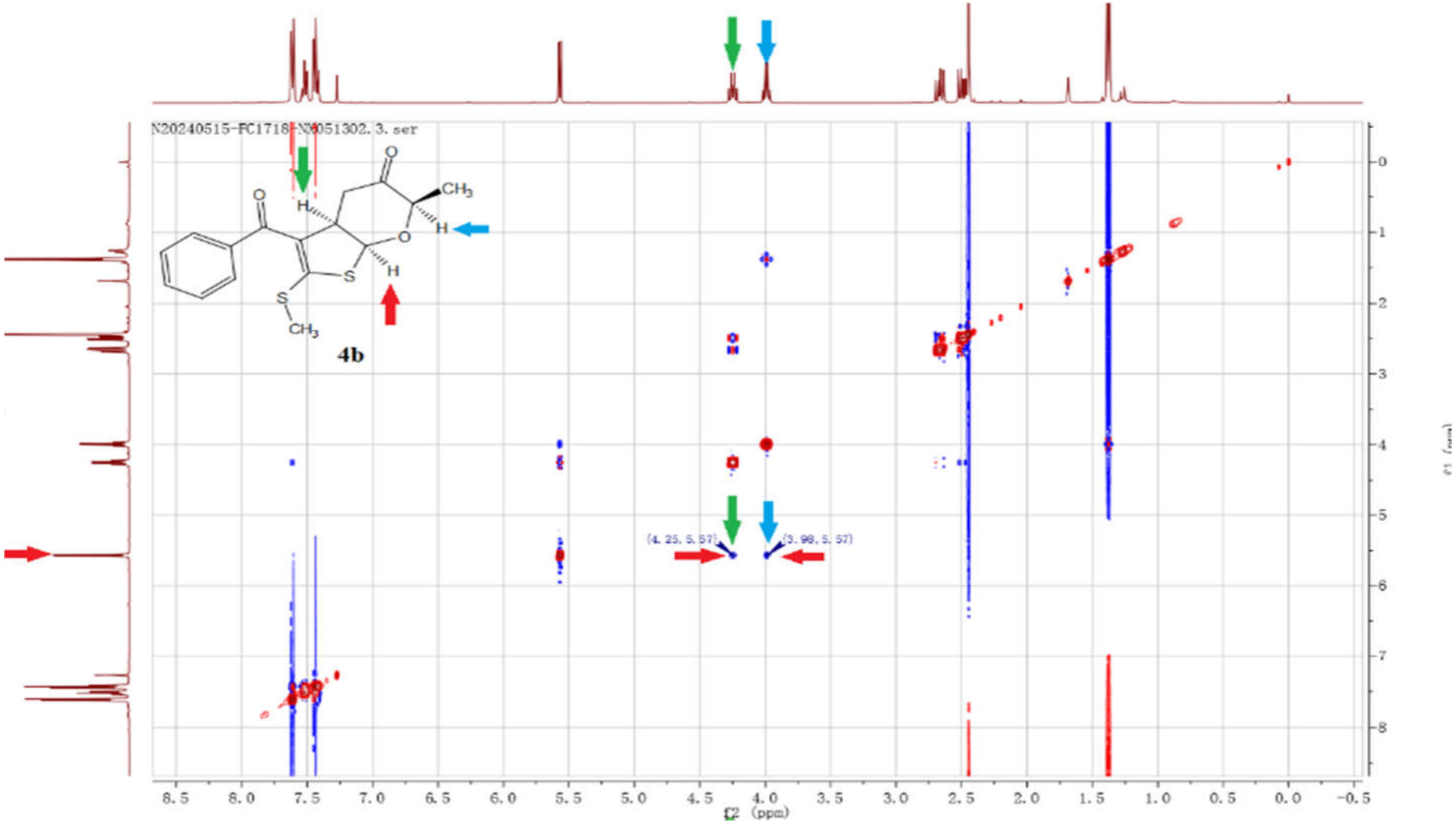
^{1}H spectra of **4b**.



^{13}C spectra **4b**.



NOESY spectra of **4b**.



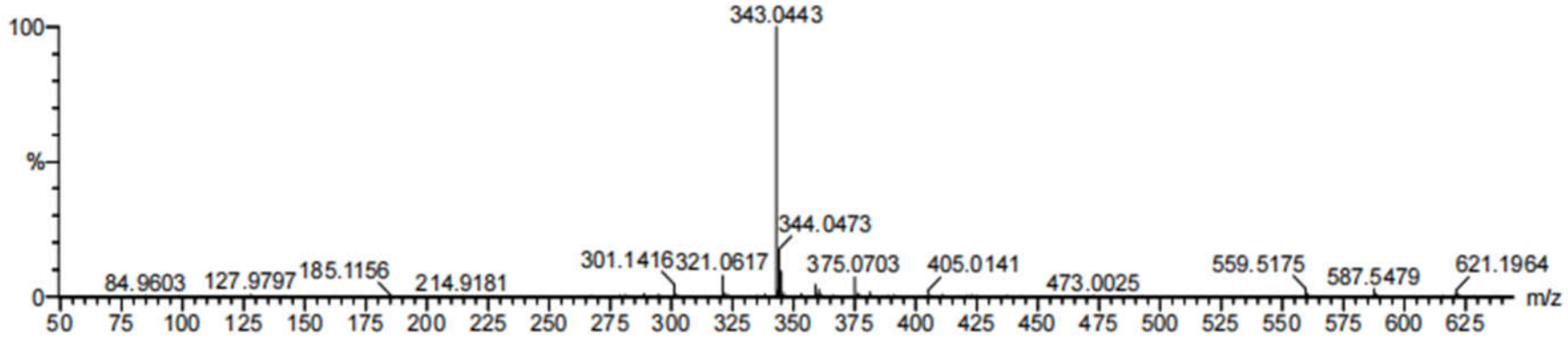
HRMS of **4b**.

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
2354 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 16-16 H: 16-16 N: 0-100 O: 0-100 Na: 0-4 S: 1-4

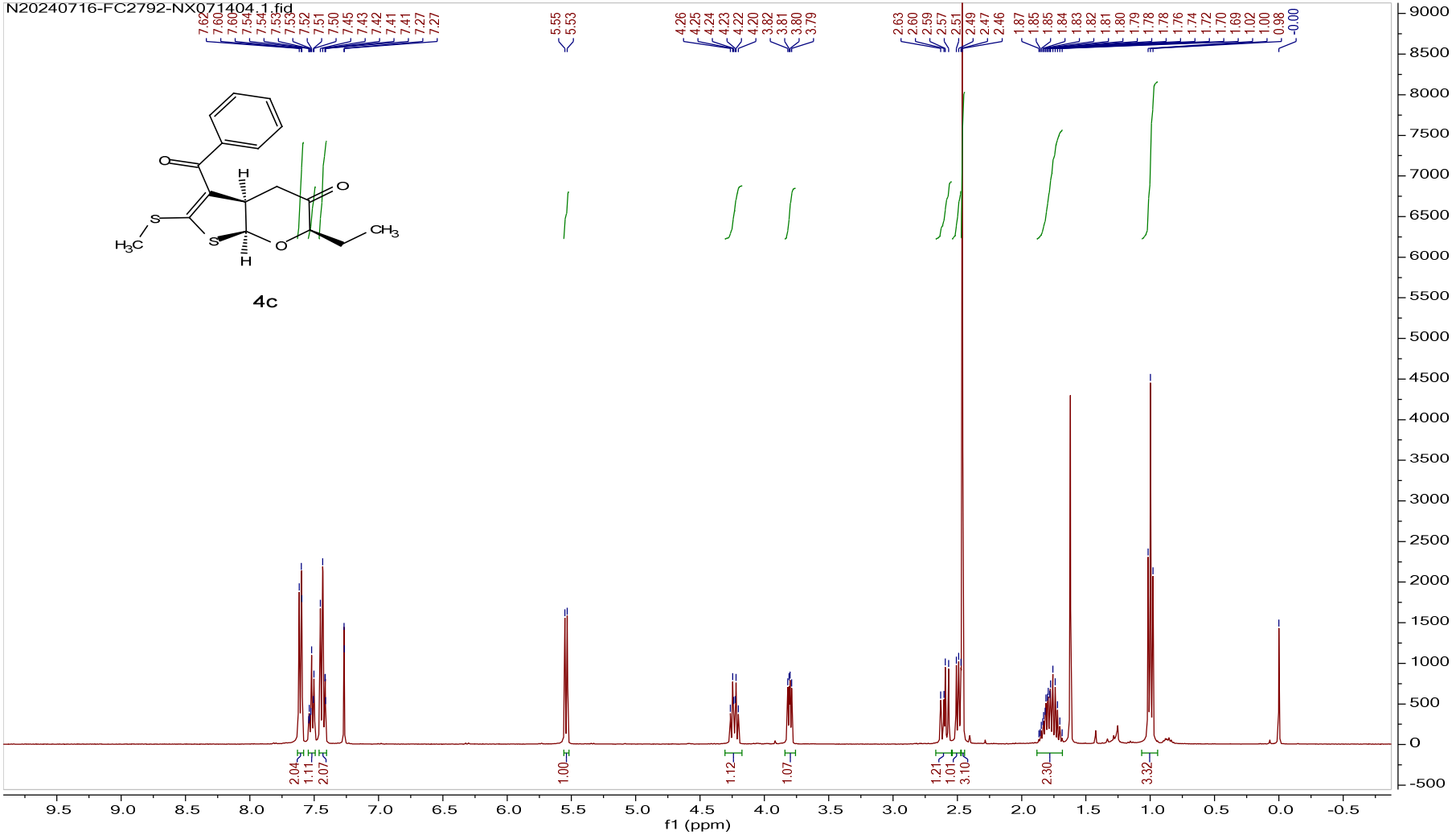
32
240910-5-647-1-4B 16 (0.121)

1: TOF MS ES+
2.13e+006

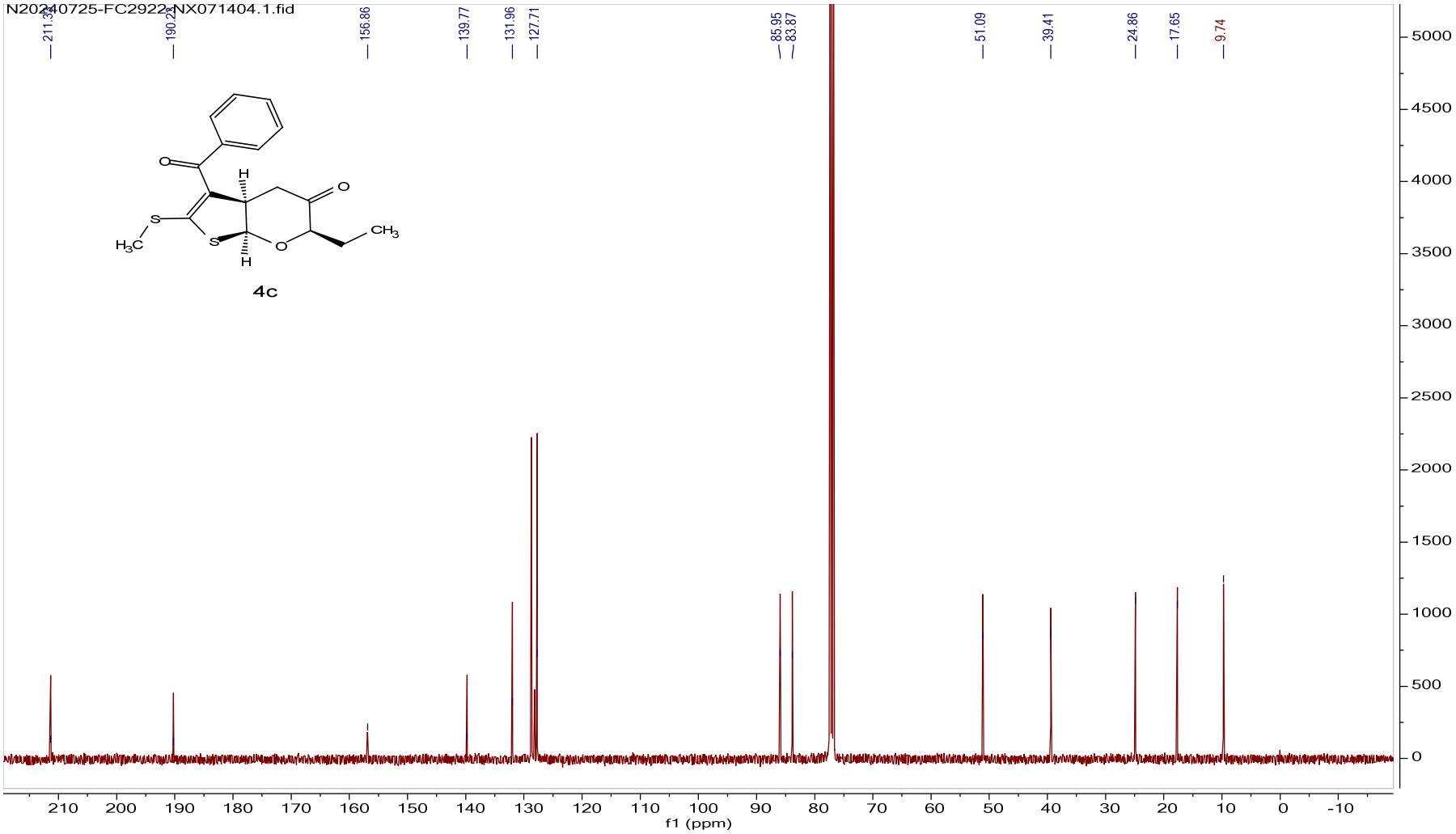


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
343.0443	343.0439	0.4	1.2	8.5	1088.2	n/a	n/a	C16 H16 O3 Na S2

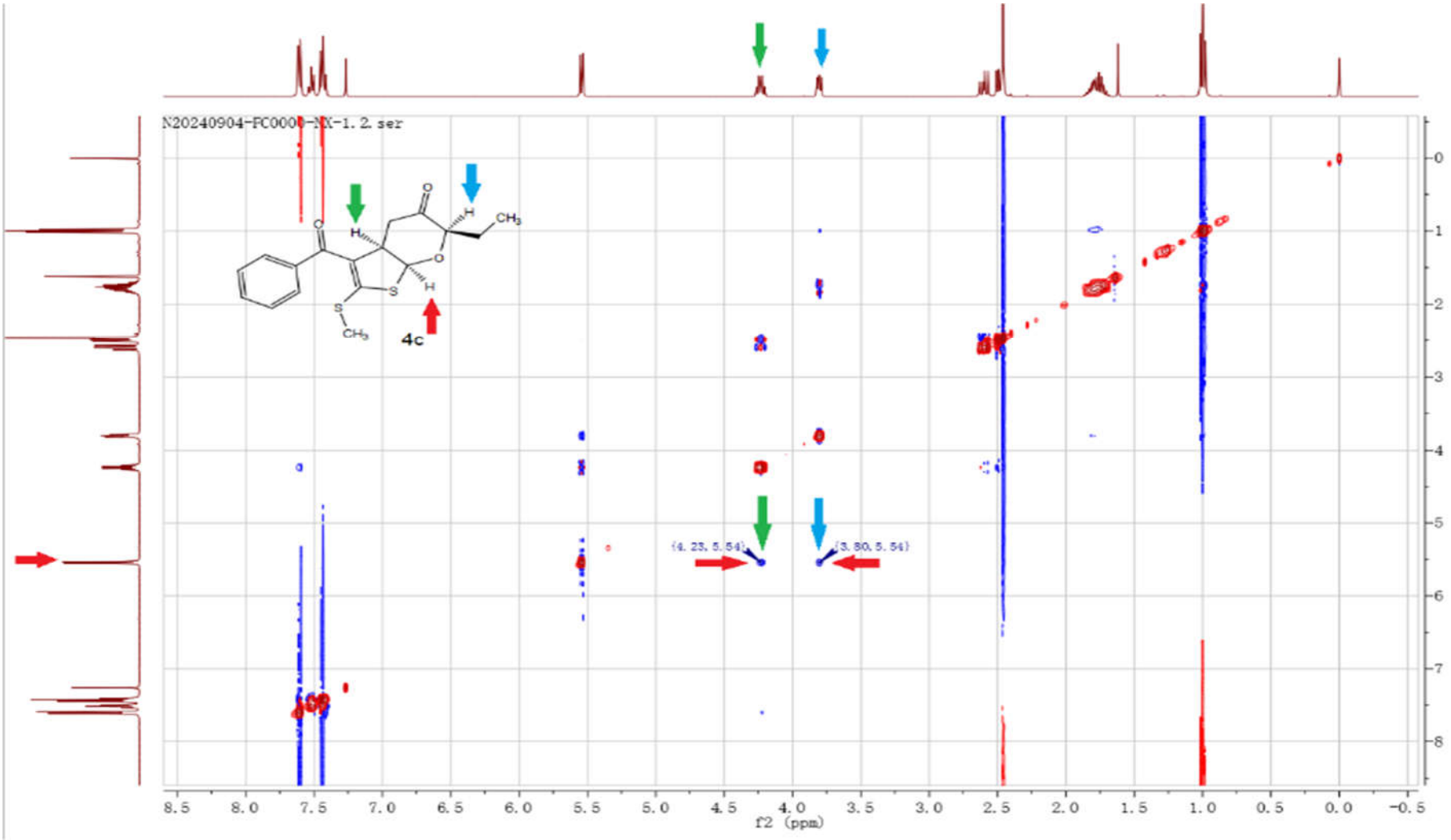
^{1}H spectra of **4c**.



^{13}C spectra **4c.**



NOESY spectra of **4c.**



HRMS of **4c.**

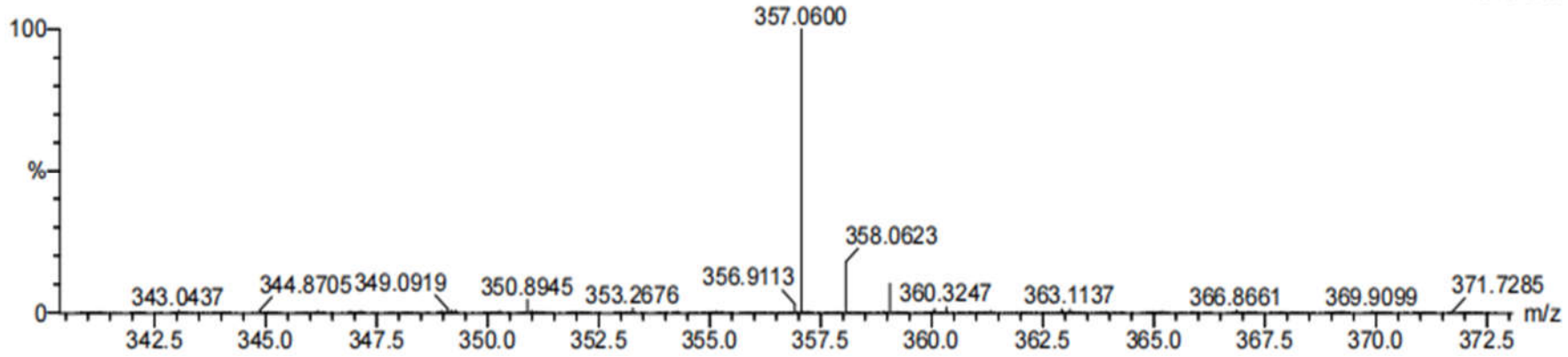
Single Mass Analysis

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
2640 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 17-17 H: 18-18 N: 0-100 O: 0-100 Na: 0-4 S: 1-4

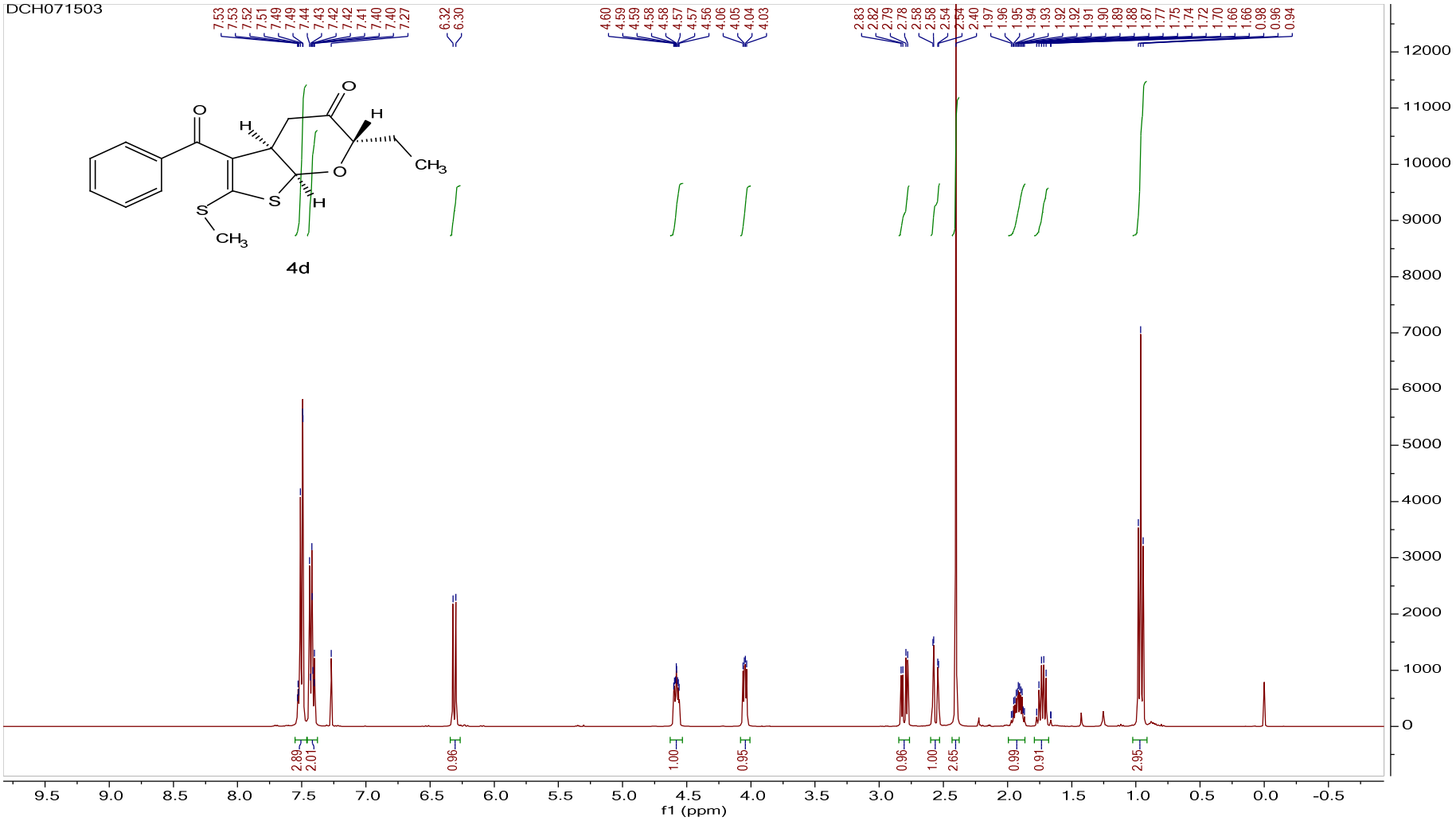
32
240910-5-647-1-4C 33 (0.229)

1: TOF MS ES+
1.94e+005

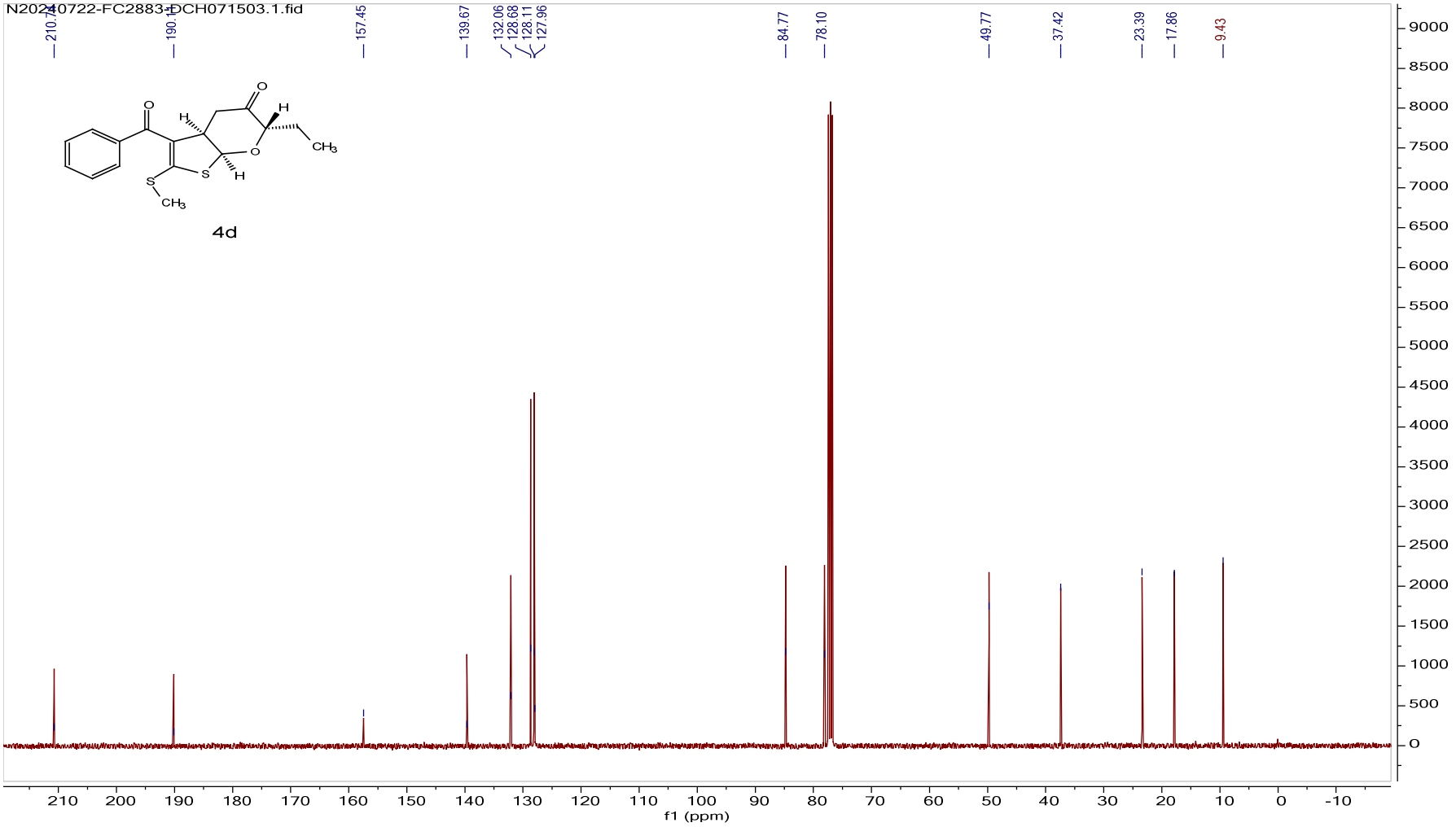


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
357.0600	357.0595	0.5	1.4	8.5	698.9	n/a	n/a	C17 H18 O3 Na S2

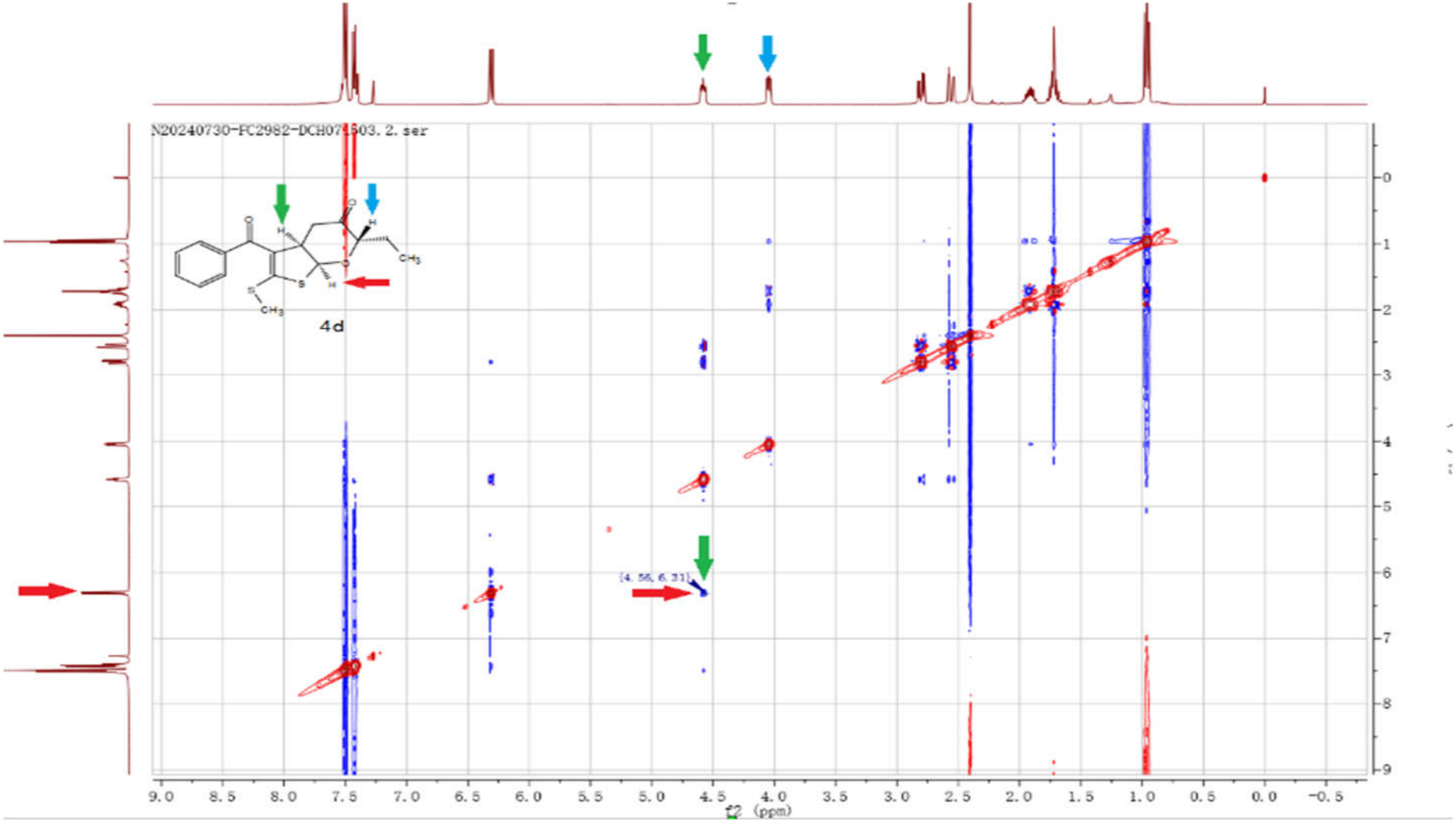
^{1}H spectra of **4d.**



^{13}C spectra of **4d.**



NOESY spectra of **4d.**



HRMS of **4d.**

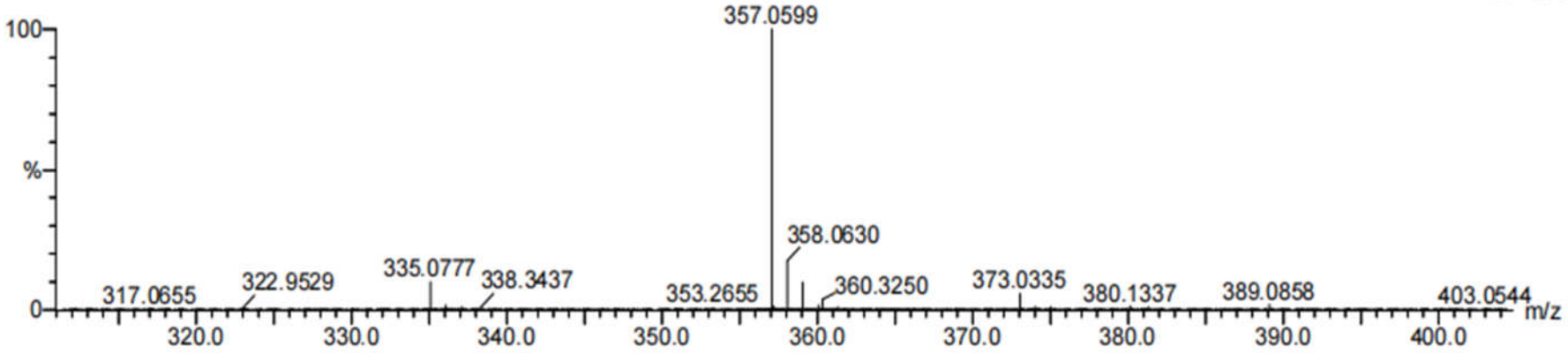
Single Mass Analysis

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
2640 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 17-17 H: 18-18 N: 0-100 O: 0-100 Na: 0-4 S: 1-4

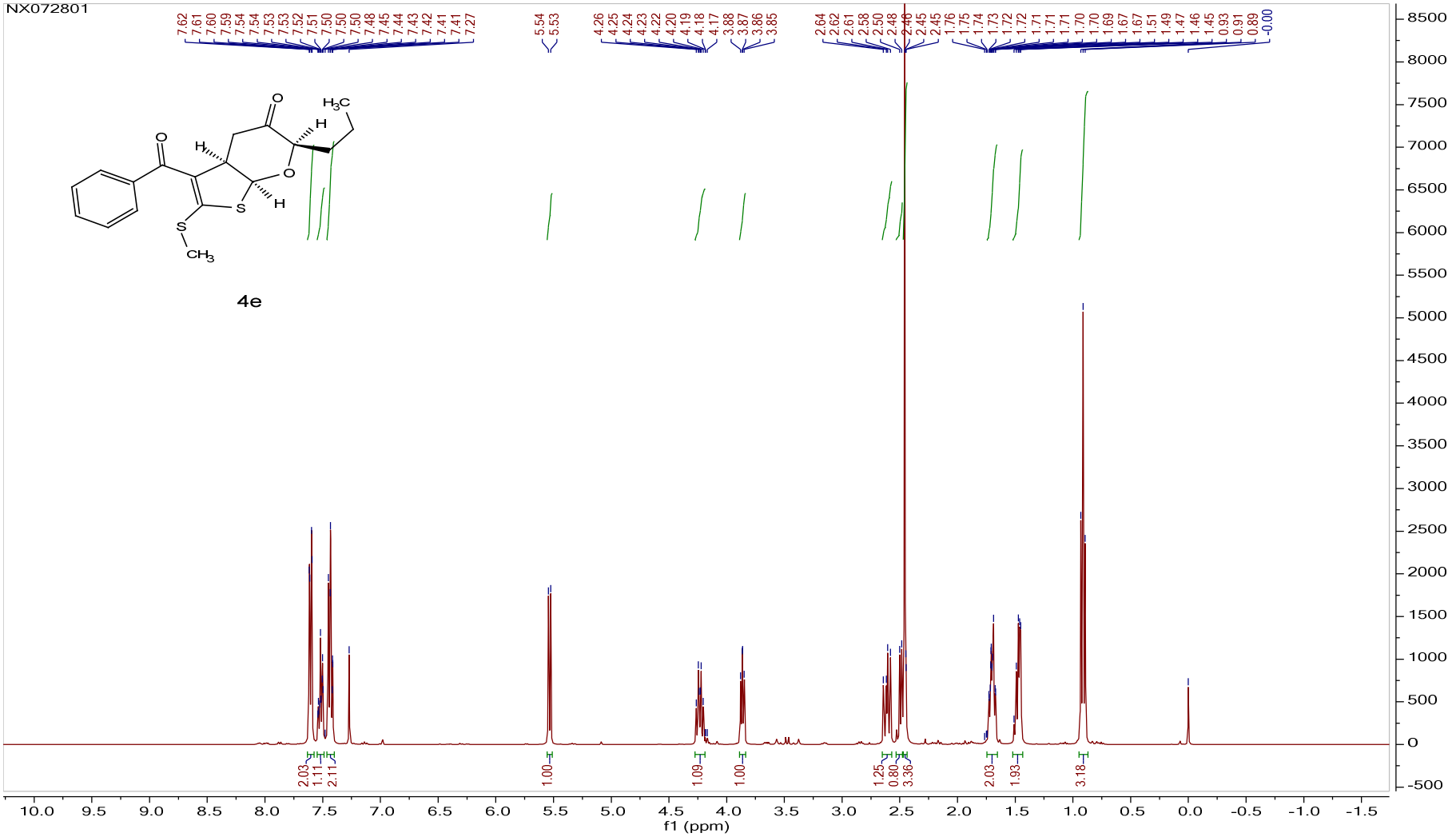
32
240910-5-647-1-4D 19 (0.136)

1: TOF MS ES+
1.20e+006

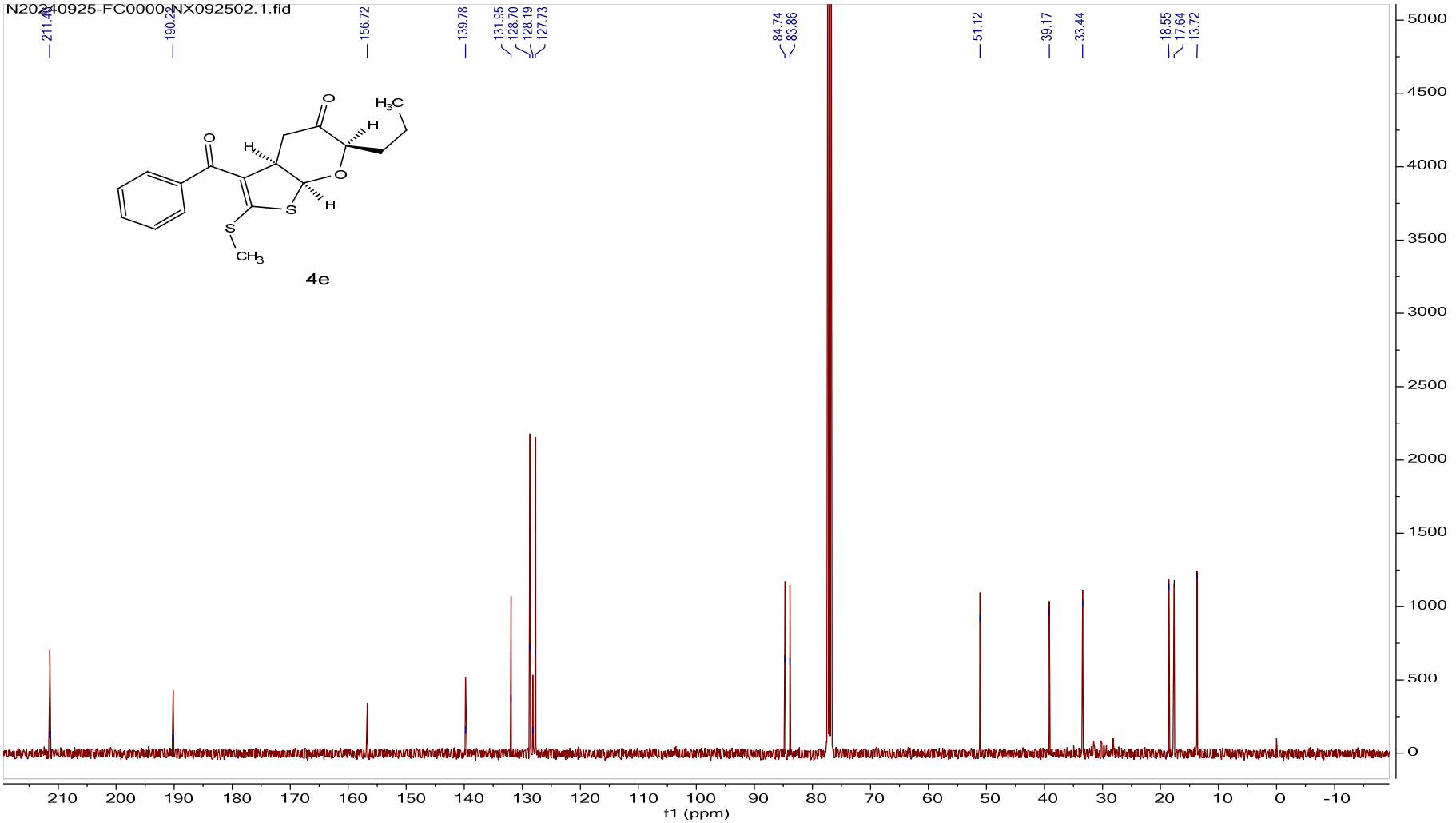


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
357.0599	357.0595	0.4	1.1	8.5	961.4	n/a	n/a	C17 H18 O3 Na S2

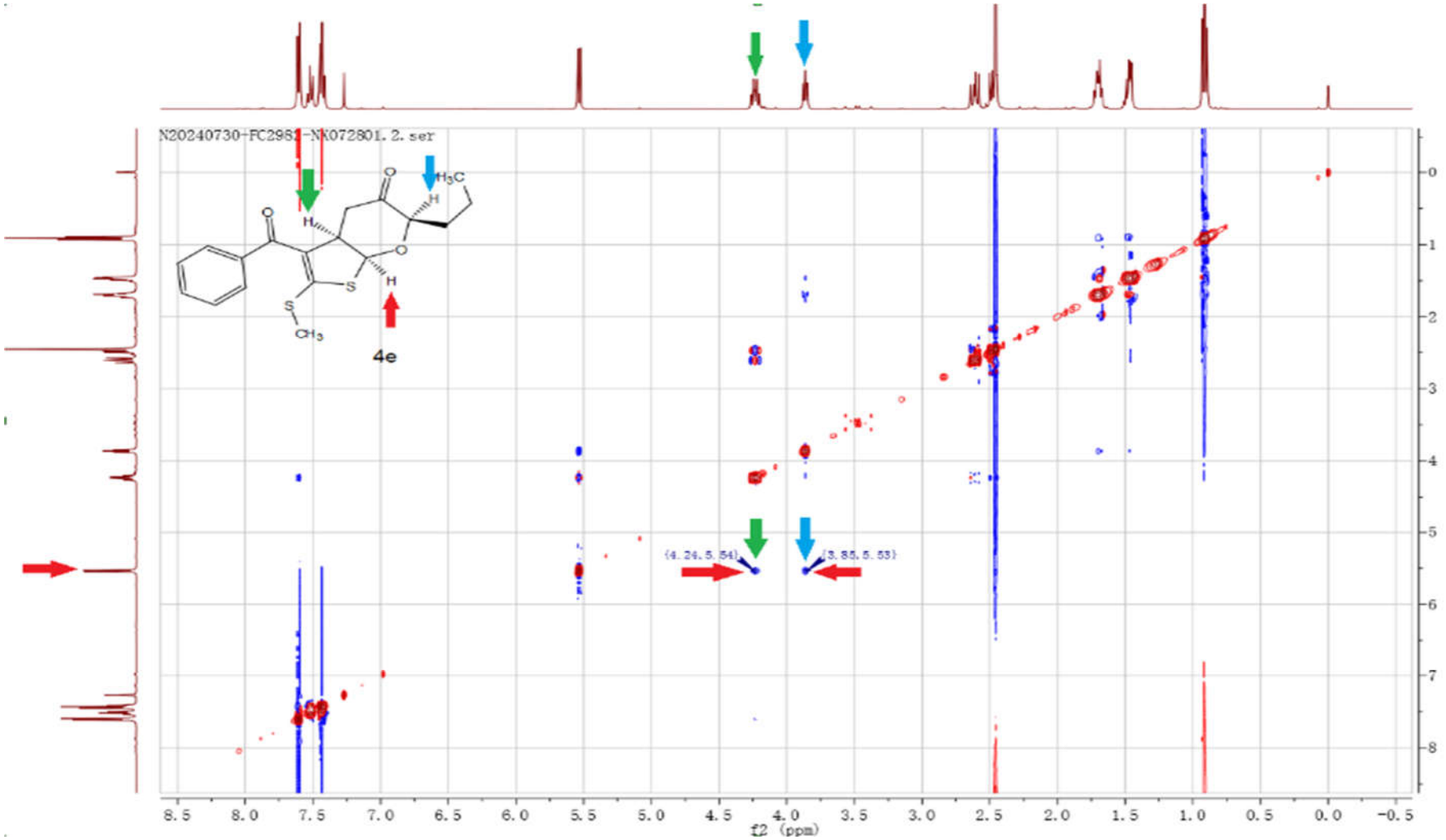
^{1}H spectra of **4e**.



^{13}C spectra of **4e**.



NOESY spectra of **4e**.



HRMS of **4e**.

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

2943 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

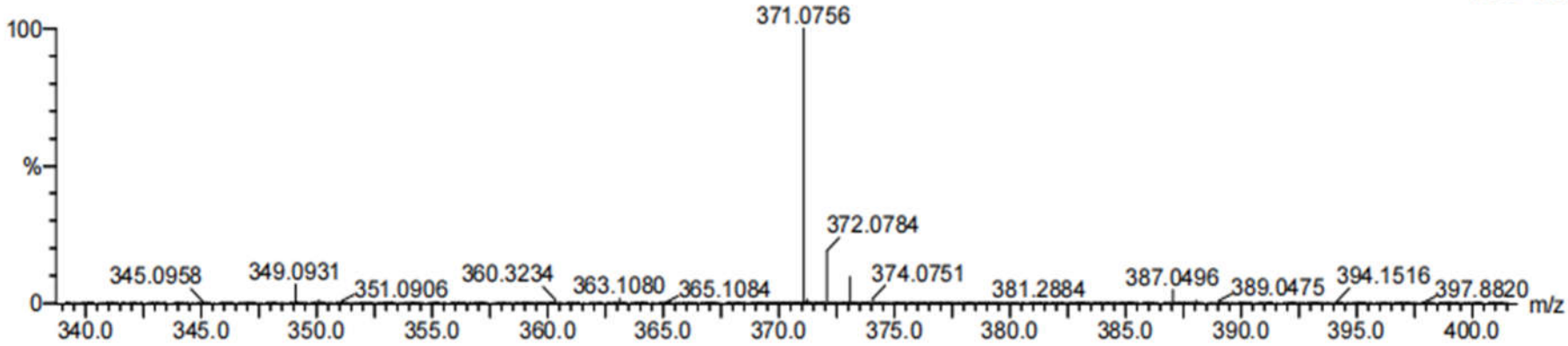
C: 18-18 H: 20-20 N: 0-100 O: 0-100 Na: 0-4 S: 1-4

32

240910-5-647-1-4E 25 (0.168)

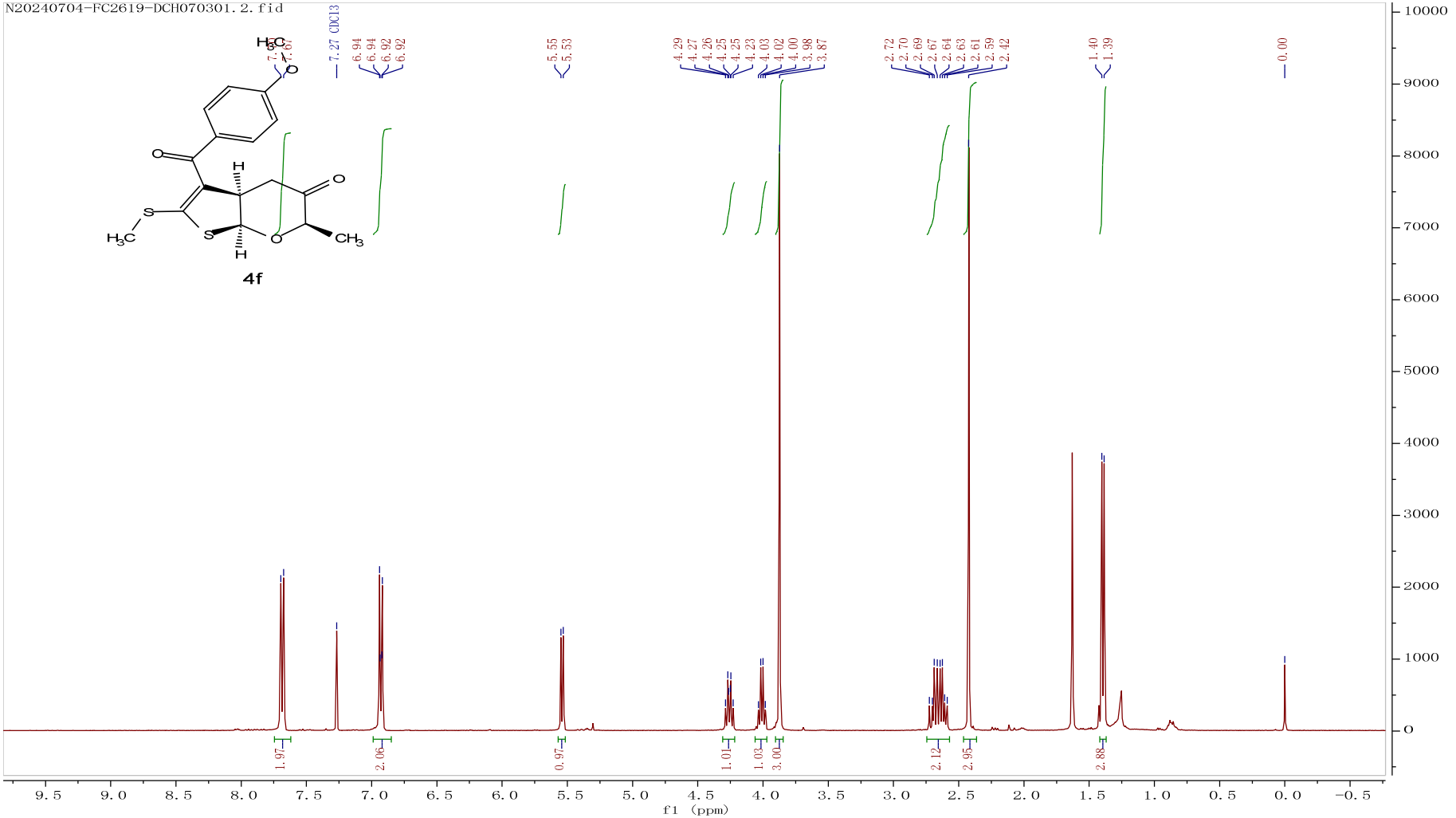
1: TOF MS ES+

1.31e+006

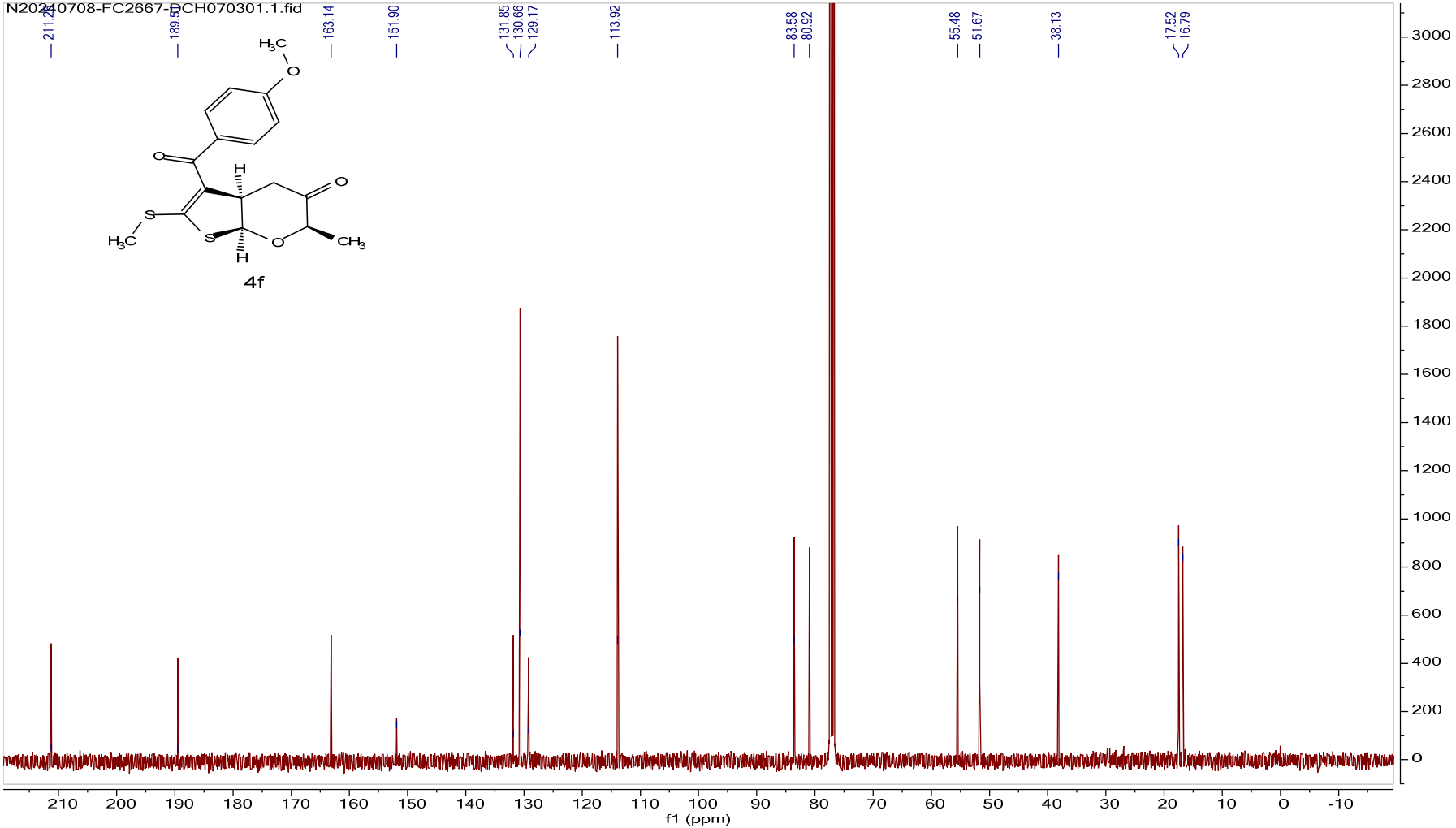


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
371.0756	371.0752	0.4	1.1	8.5	963.9	n/a	n/a	C18 H20 O3 Na S2

^{1}H spectra of **4f**.



^{13}C spectra of **4f**.



HRMS of **4f**.

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

2940 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

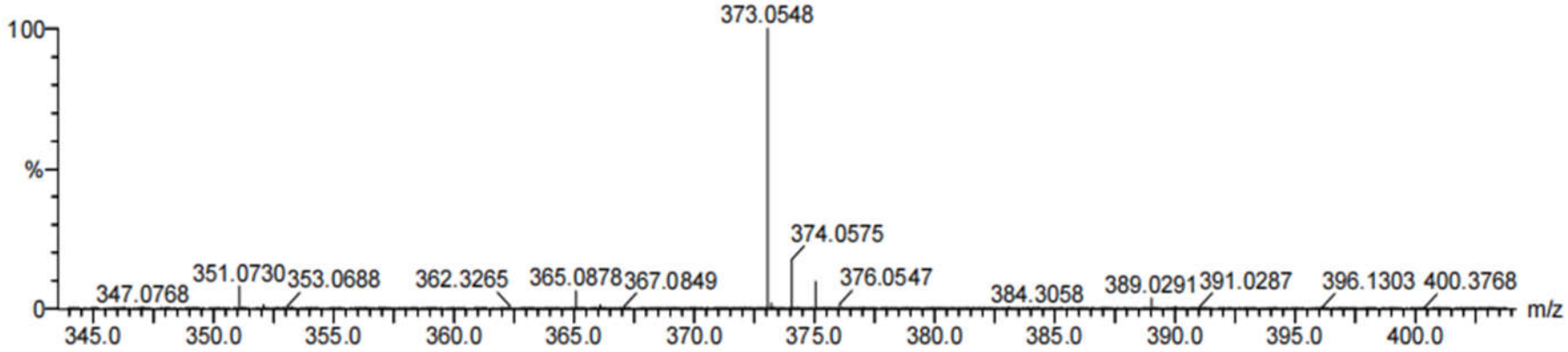
C: 17-17 H: 18-18 N: 0-100 O: 0-100 Na: 0-4 S: 1-4

29

240910-5-647-1-4F 10 (0.089)

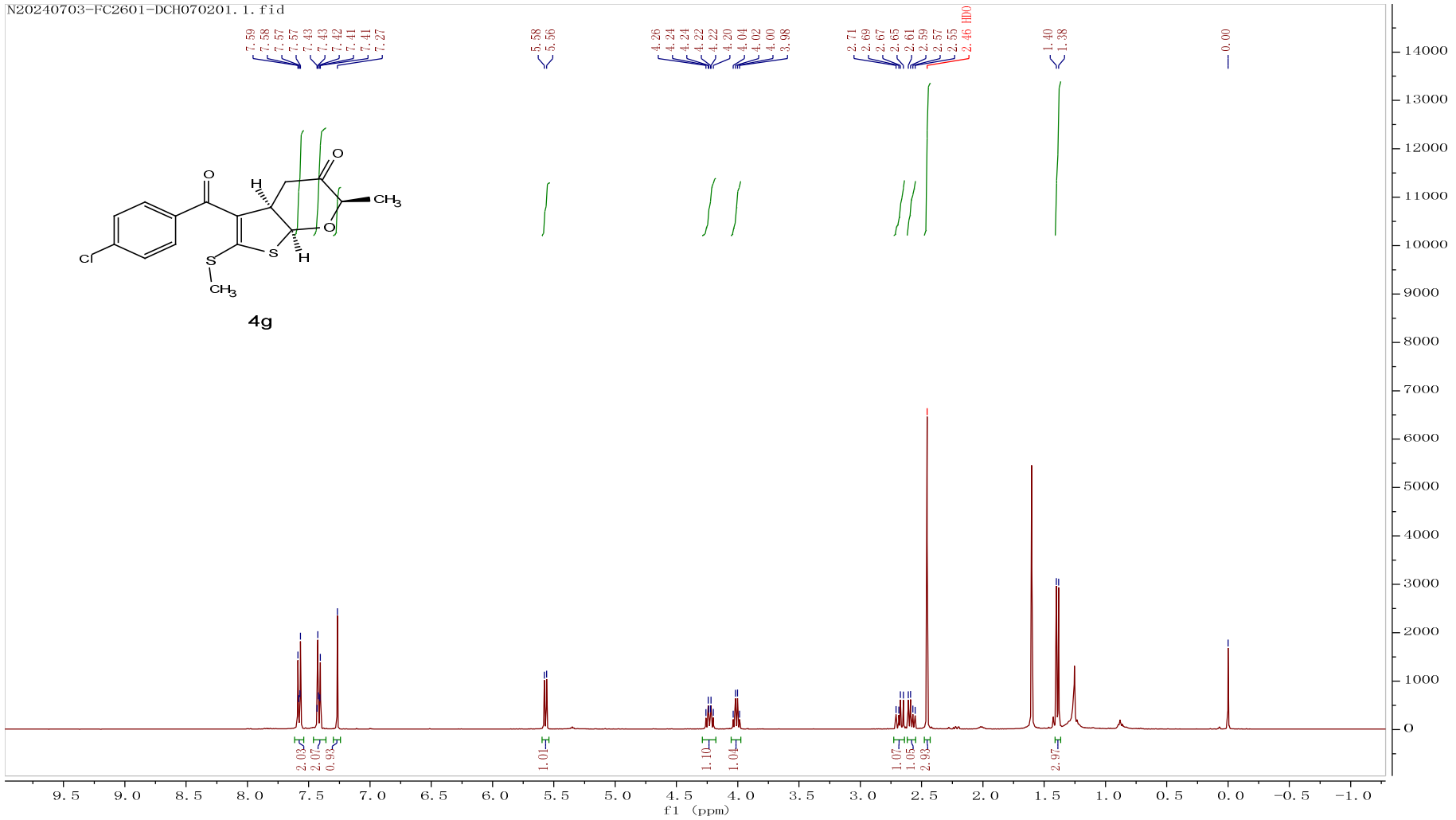
1: TOF MS ES+

1.72e+006

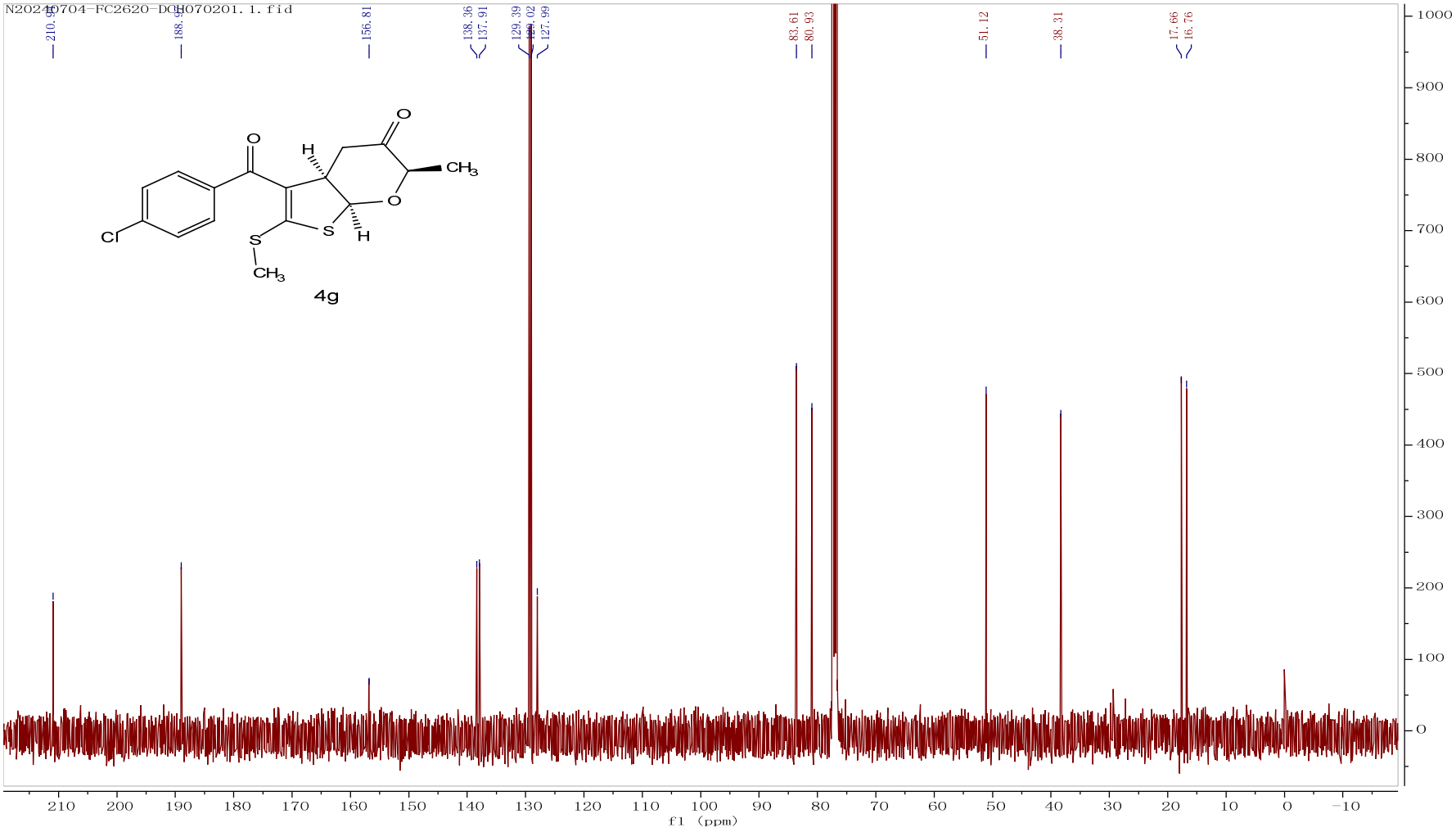


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
373.0548	373.0544	0.4	1.1	8.5	1022.7	n/a	n/a	C17 H18 O4 Na S2

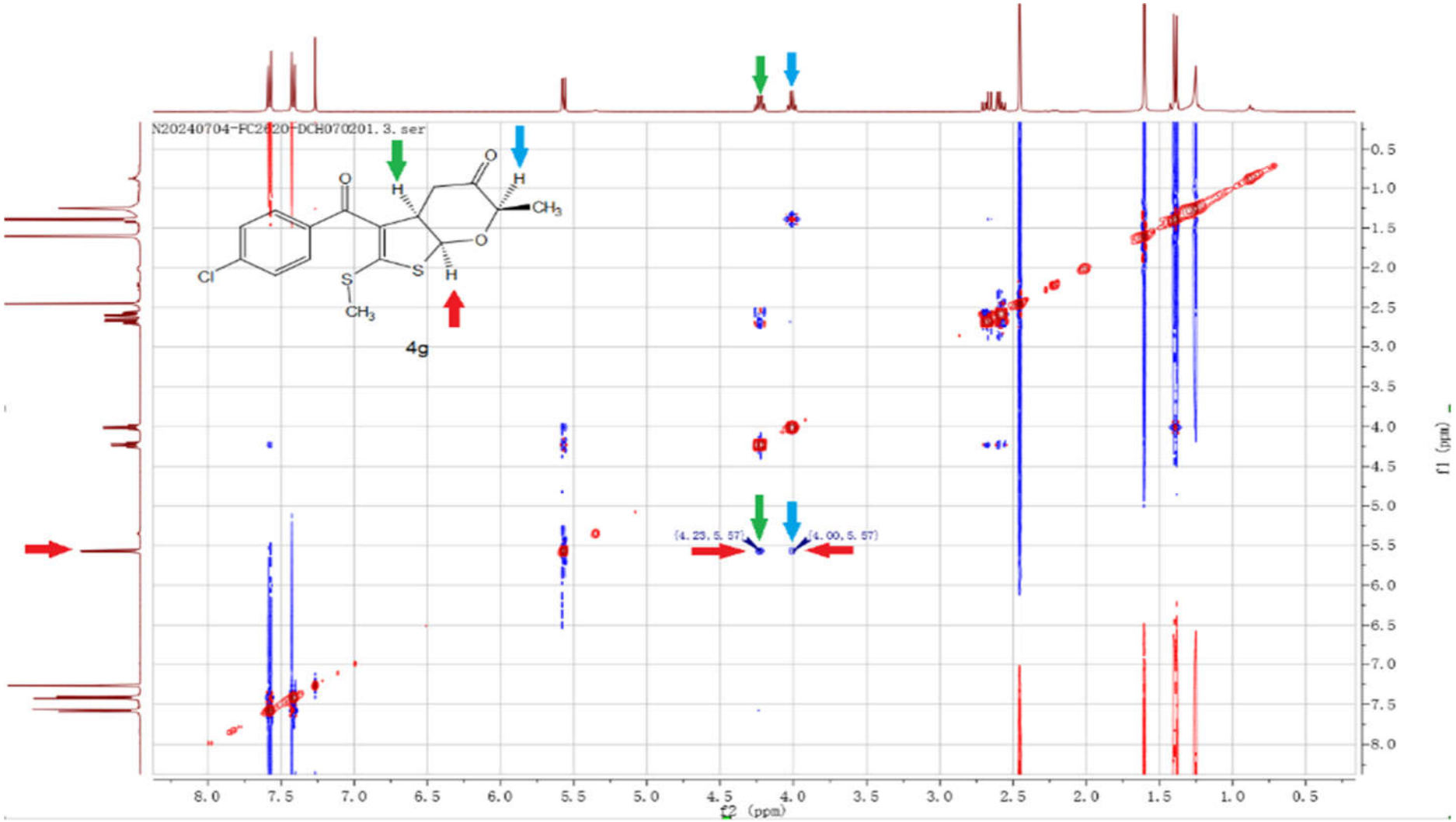
^{1}H spectra of **4g.**



^{13}C spectra of **4g.**



NOESY spectra of **4g.**



HRMS of **4g.**

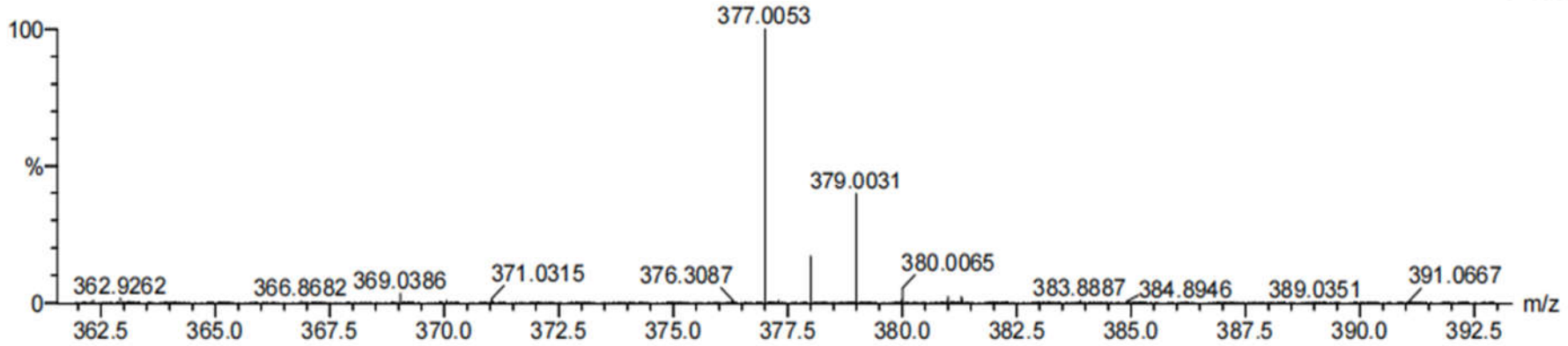
Single Mass Analysis

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
5349 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 16-16 H: 15-15 N: 0-100 O: 0-100 Na: 0-4 S: 1-4 Cl: 1-3

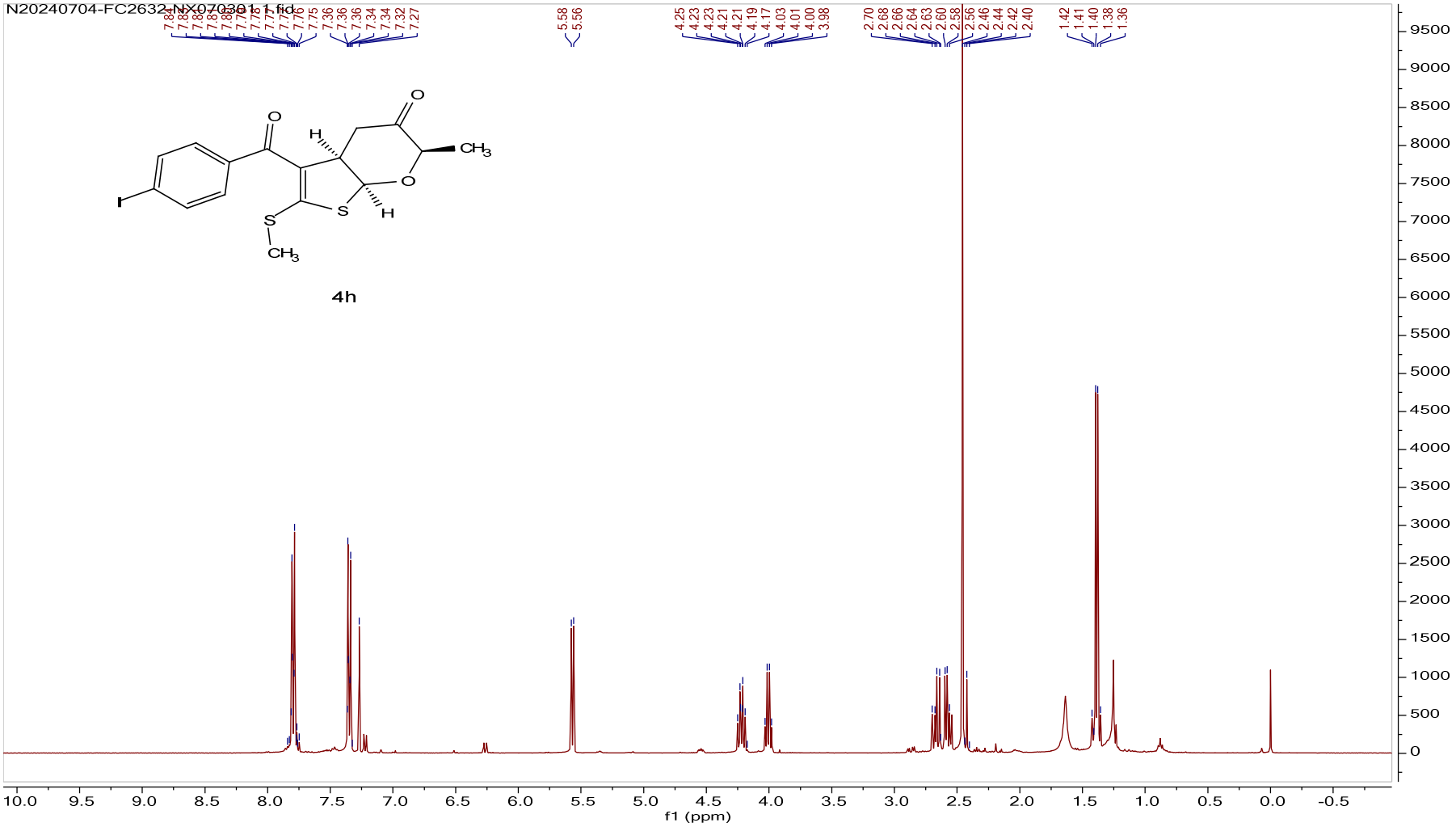
29
240910-5-647-1-4G 27 (0.178)

1: TOF MS ES+
1.77e+005

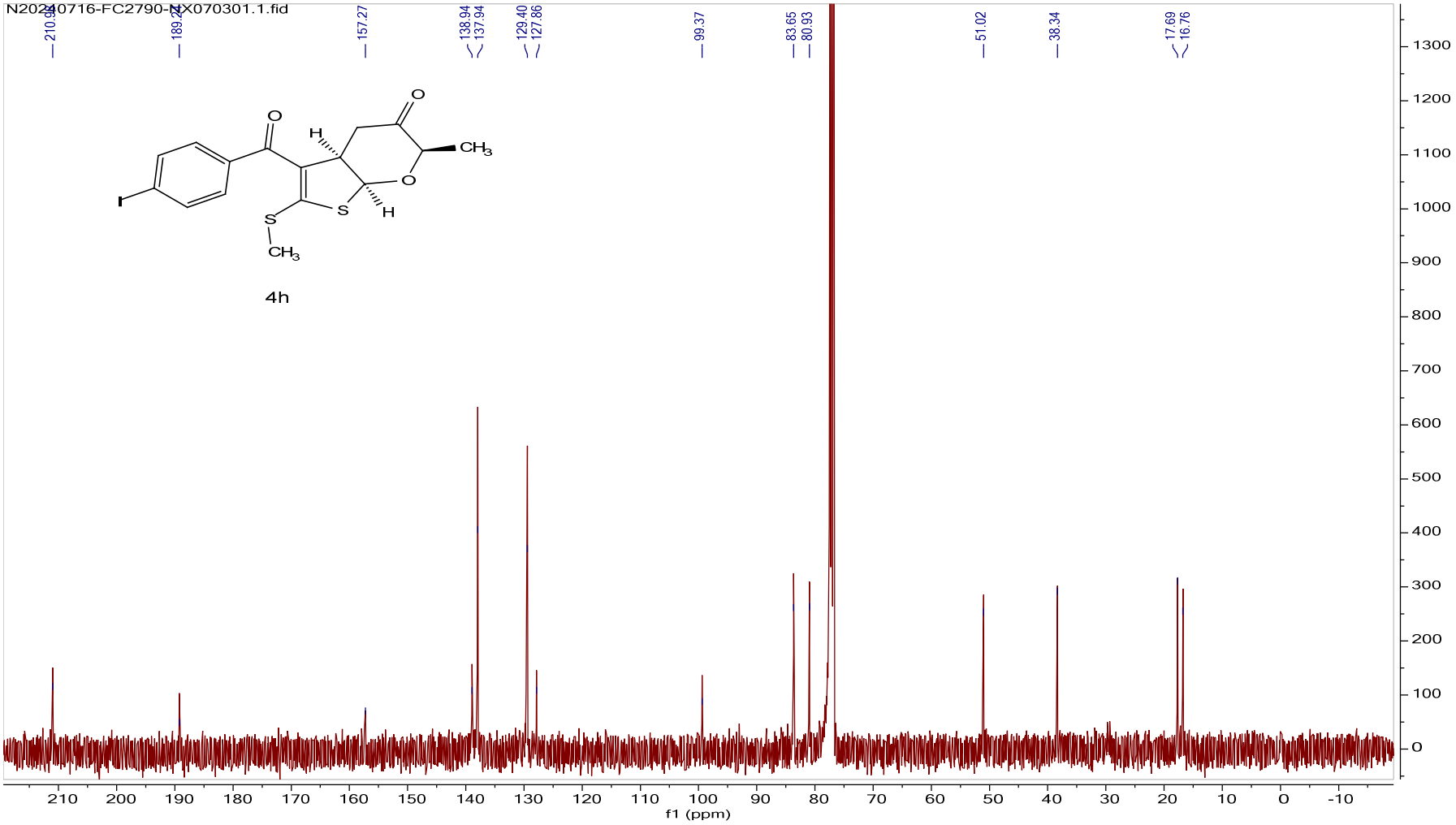


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
377.0053	377.0049	0.4	1.1	8.5	720.8	n/a	n/a	C16 H15 O3 Na S2 Cl

[1]H spectra of **4h.**



^{13}C spectra of **4h.**



HRMS of **4h.**

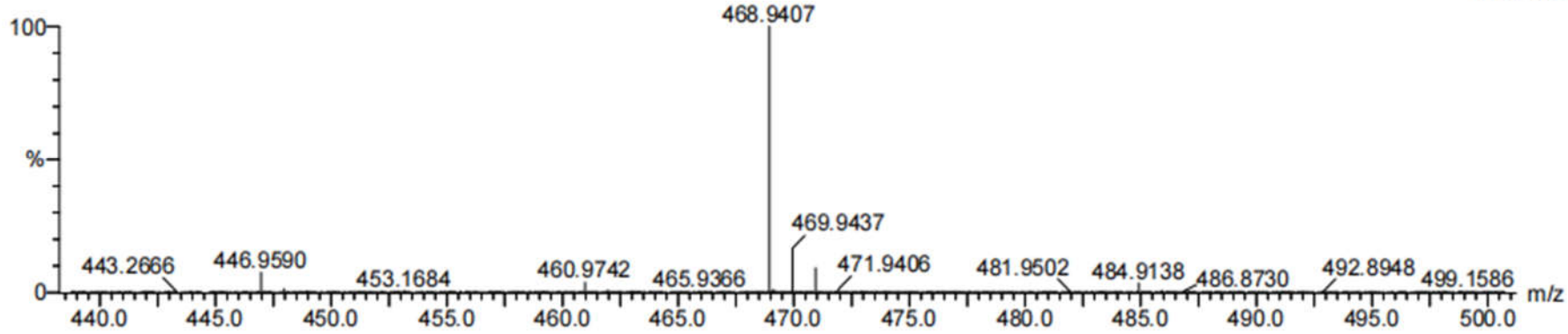
Single Mass Analysis

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
2951 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 16-16 H: 15-15 N: 0-100 O: 0-100 Na: 0-4 S: 1-4 I: 1-3

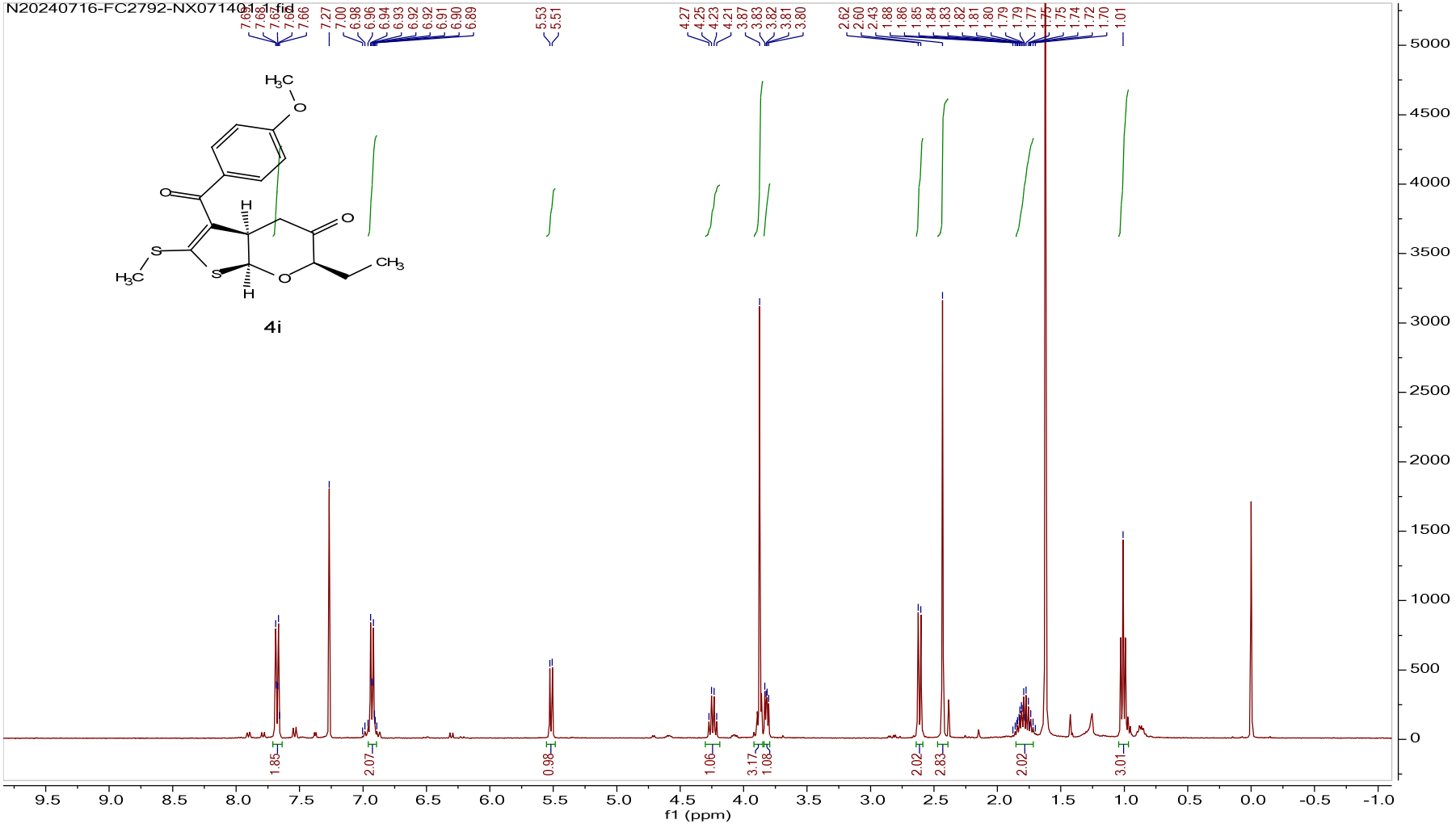
29
240910-5-647-1-4I 12 (0.100)

1: TOF MS ES+
1.16e+006

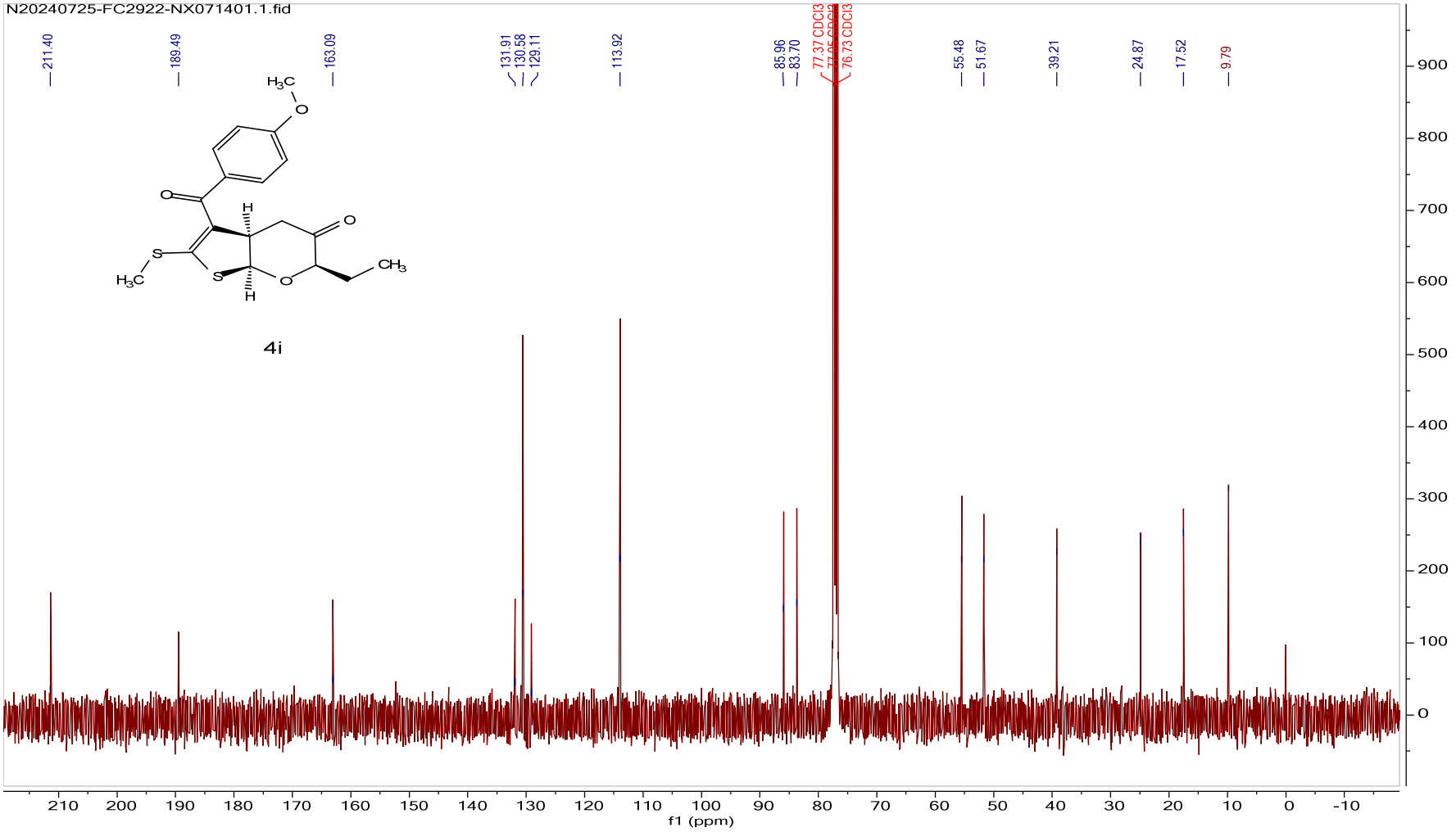


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
468.9407	468.9405	0.2	0.4	8.5	856.8	n/a	n/a	C16 H15 O3 Na S2 I

^{1}H spectra of **4i.**



^{13}C spectra of **4i.**



HRMS of **4i.**

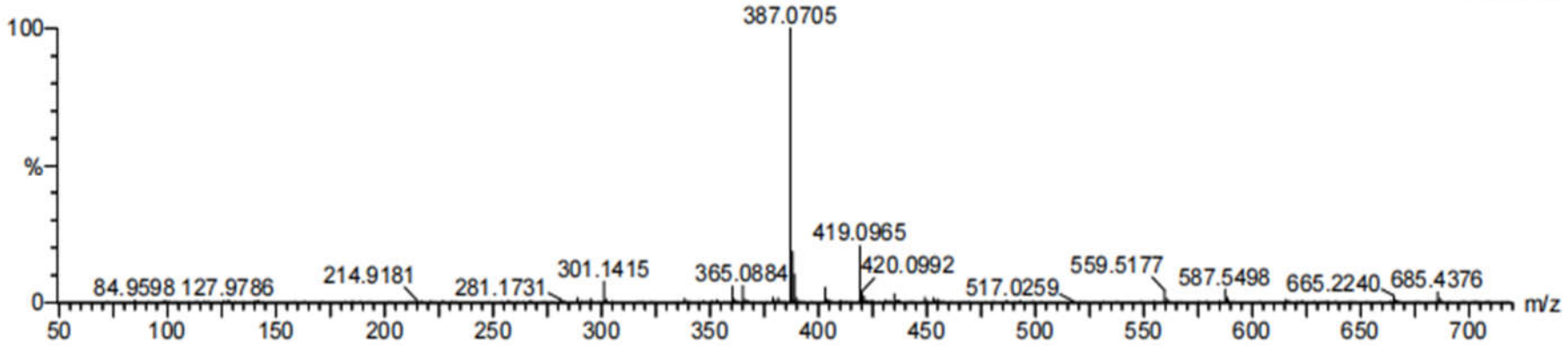
Single Mass Analysis

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
3261 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 18-18 H: 20-20 N: 0-100 O: 0-100 Na: 0-4 S: 1-4

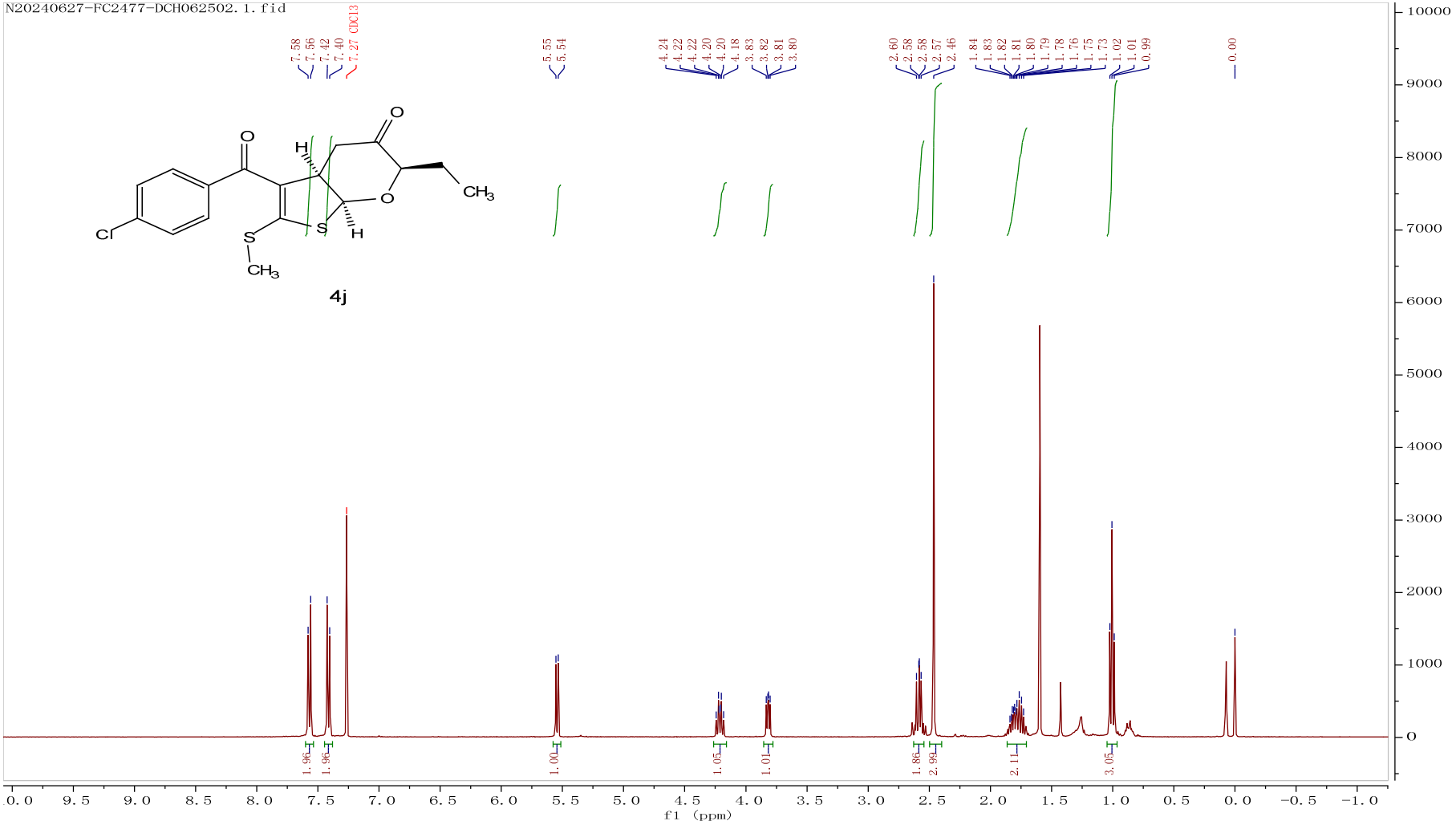
29
240910-5-647-1-4J 17 (0.126)

1: TOF MS ES+
1.31e+006

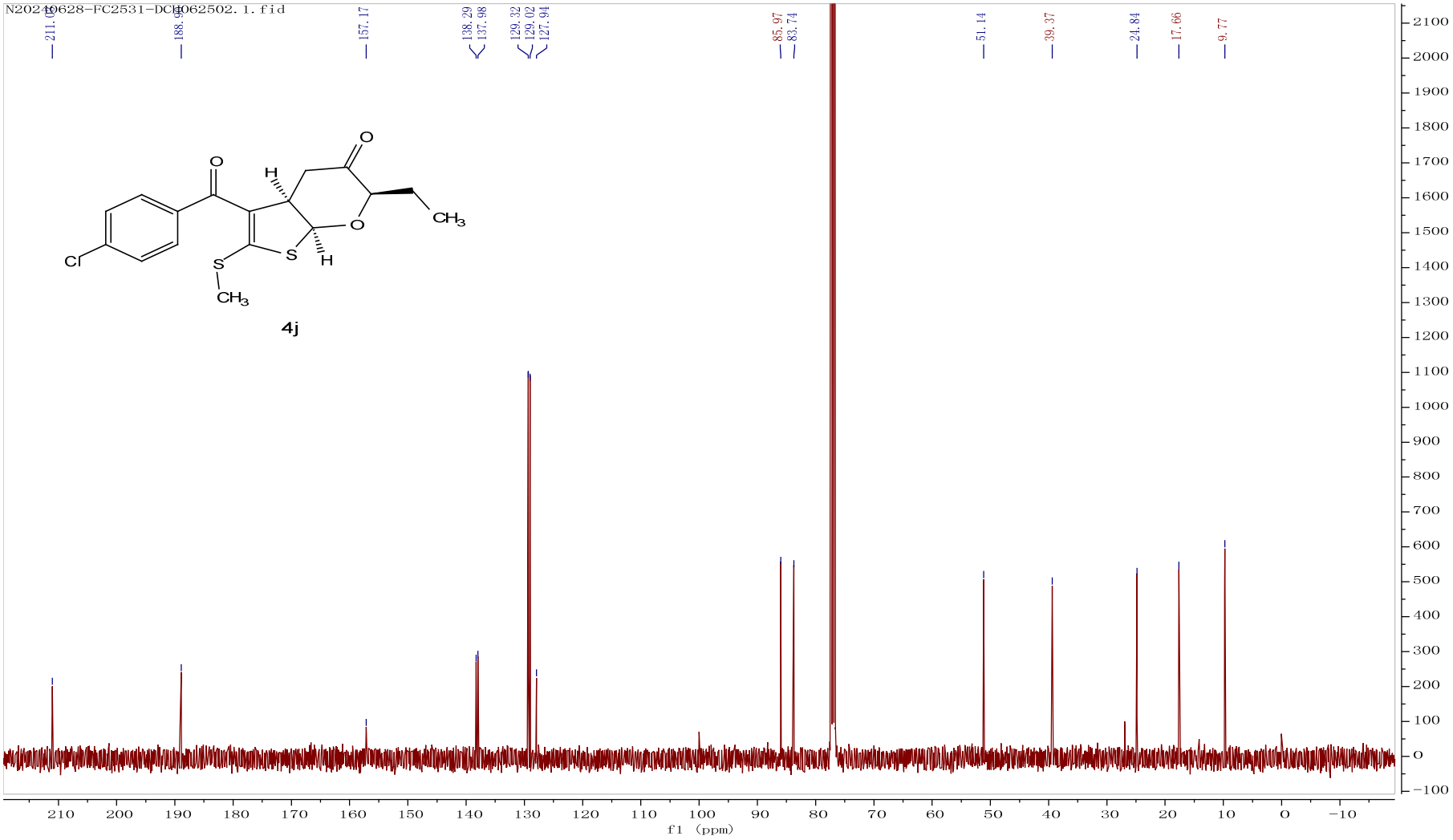


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
387.0705	387.0701	0.4	1.0	8.5	1001.3	n/a	n/a	C18 H20 O4 Na S2

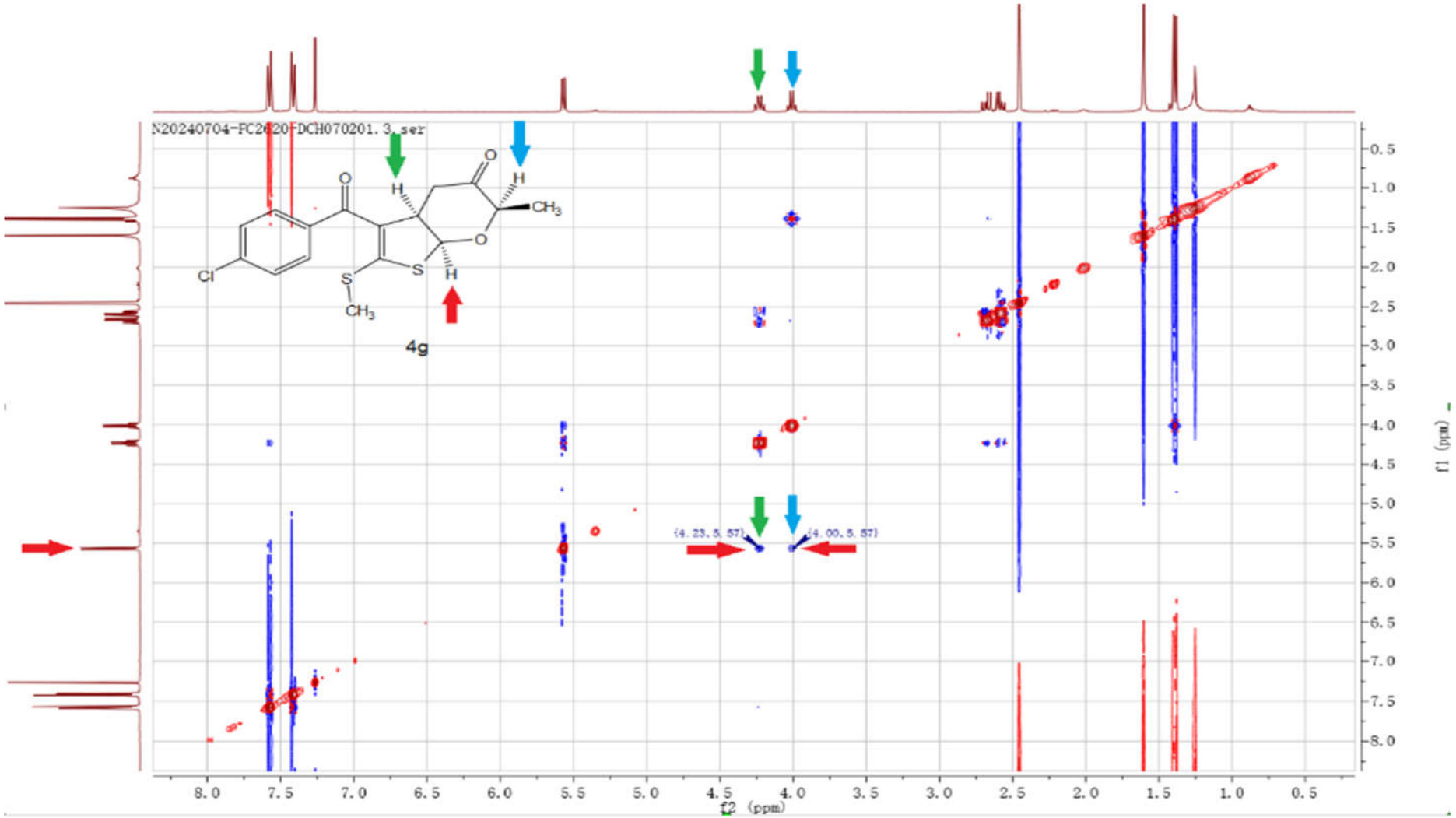
^{1}H spectra of **4j.**



^{13}C spectra of **4j.**



NOESY spectra of **4j.**



HRMS of **4j.**

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

6092 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

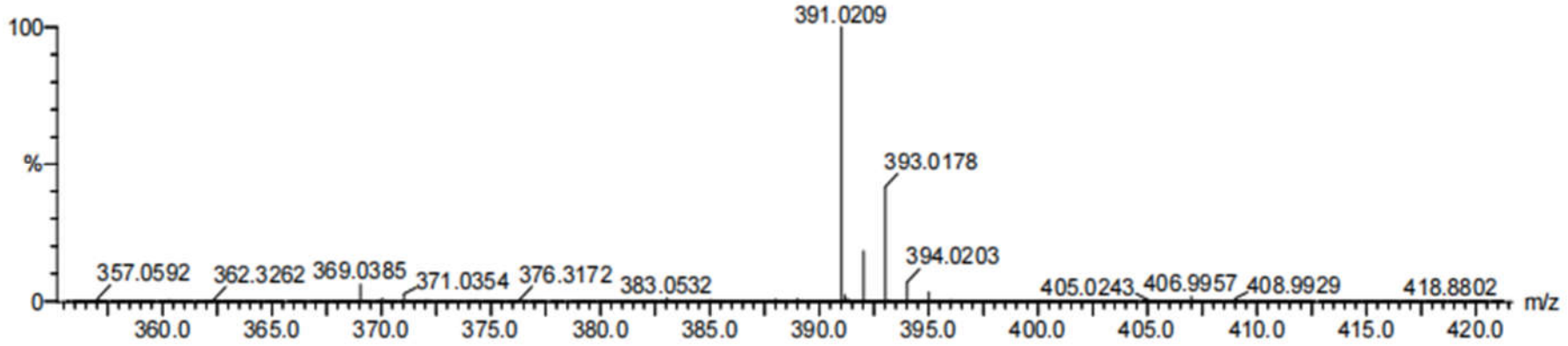
C: 17-17 H: 17-17 N: 0-100 O: 0-100 Na: 0-4 S: 1-4 Cl: 1-3

29

240910-5-647-1-4K 11 (0.094)

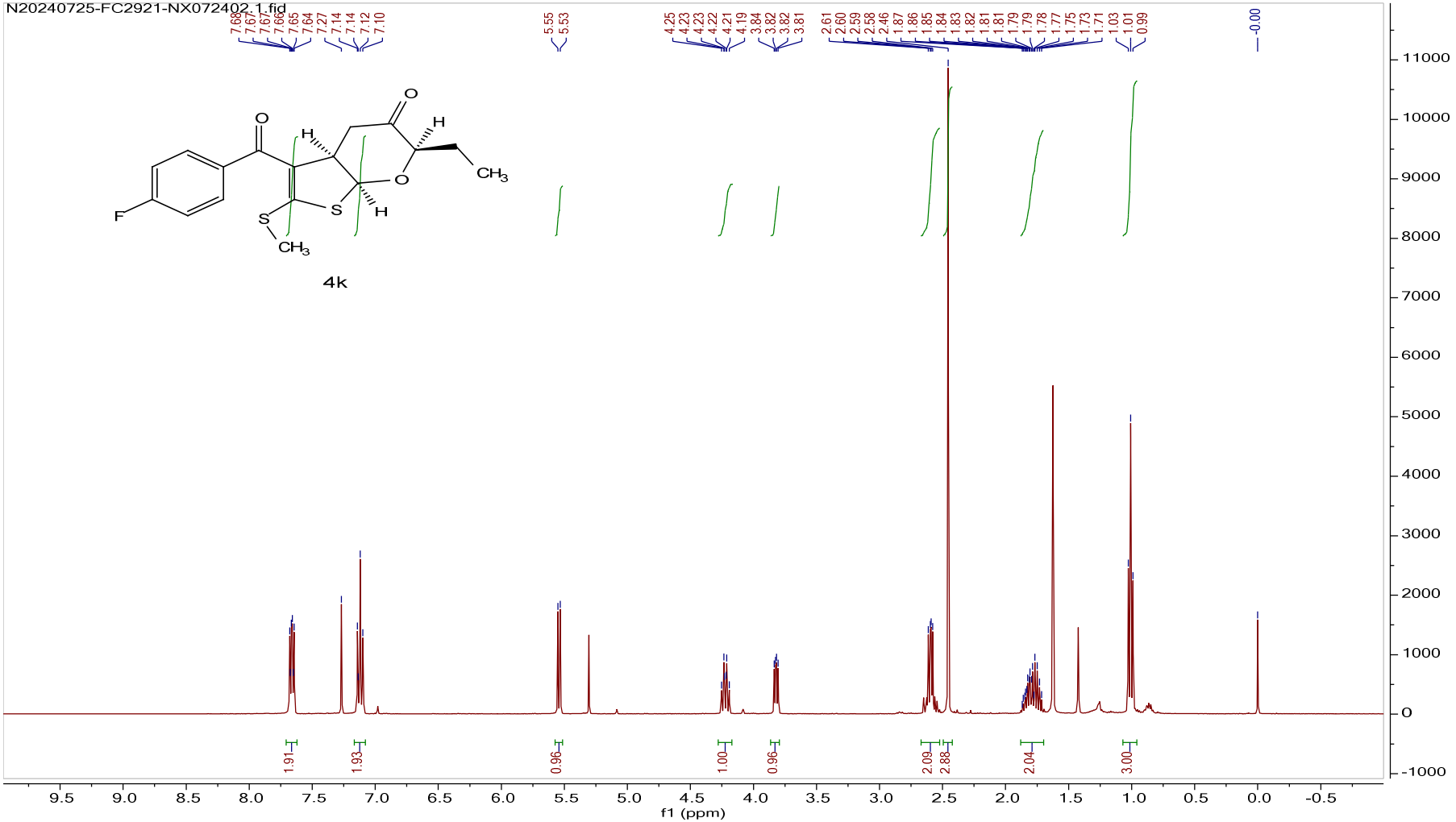
1: TOF MS ES+

2.40e+006

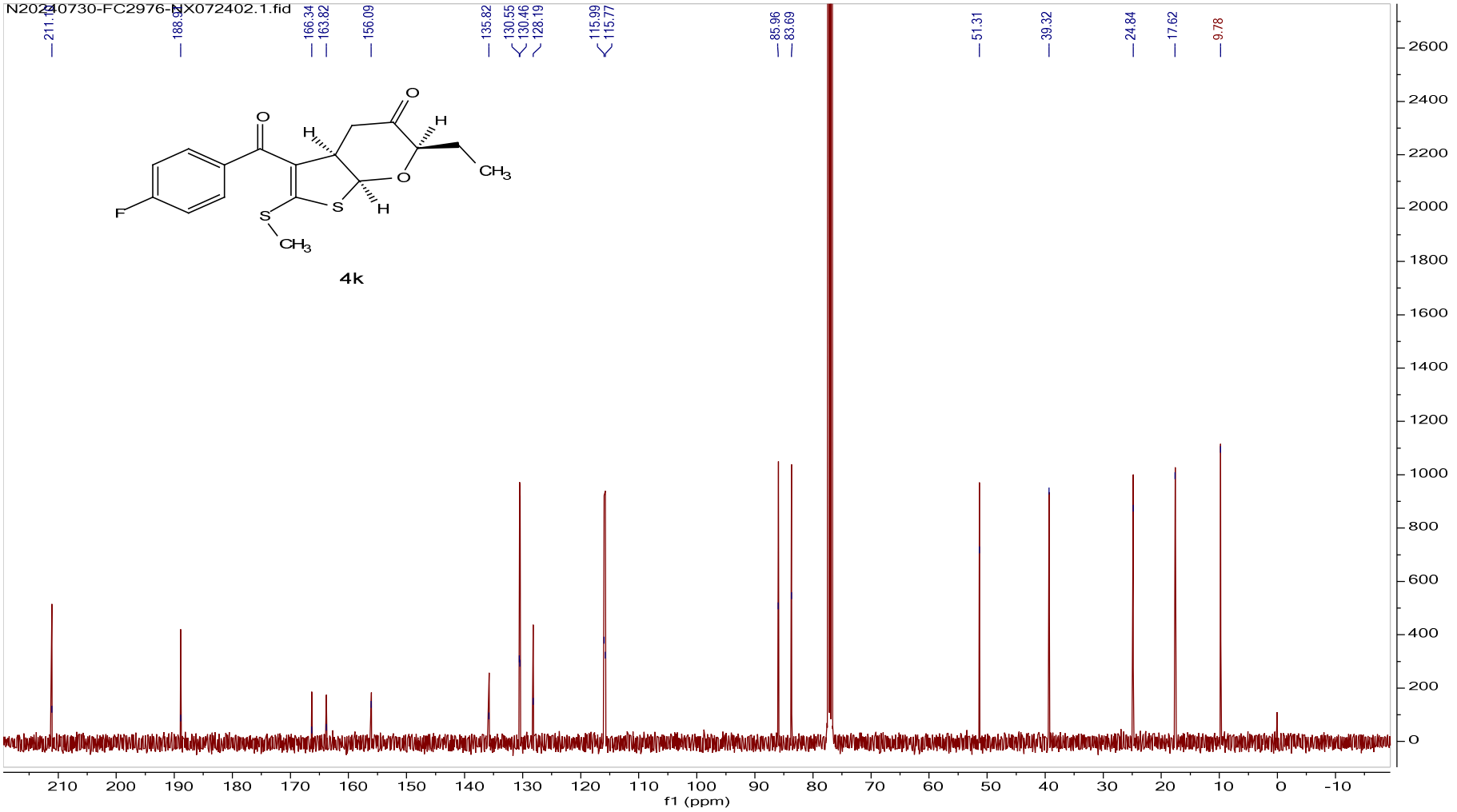


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
391.0209	391.0205	0.4	1.0	8.5	1125.0	n/a	n/a	C17 H17 O3 Na S2 Cl

[1]Hspectra of **4k.**



^{13}C spectra of **4k.**



HRMS of **4k.**

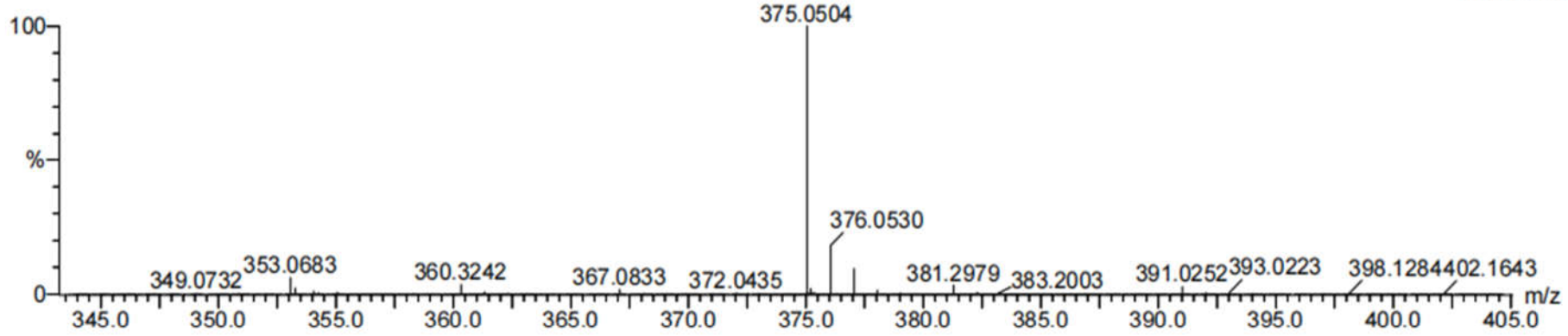
Single Mass Analysis

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
2622 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 17-17 H: 17-17 N: 0-100 O: 0-100 Na: 0-4 S: 1-4 F: 1-1

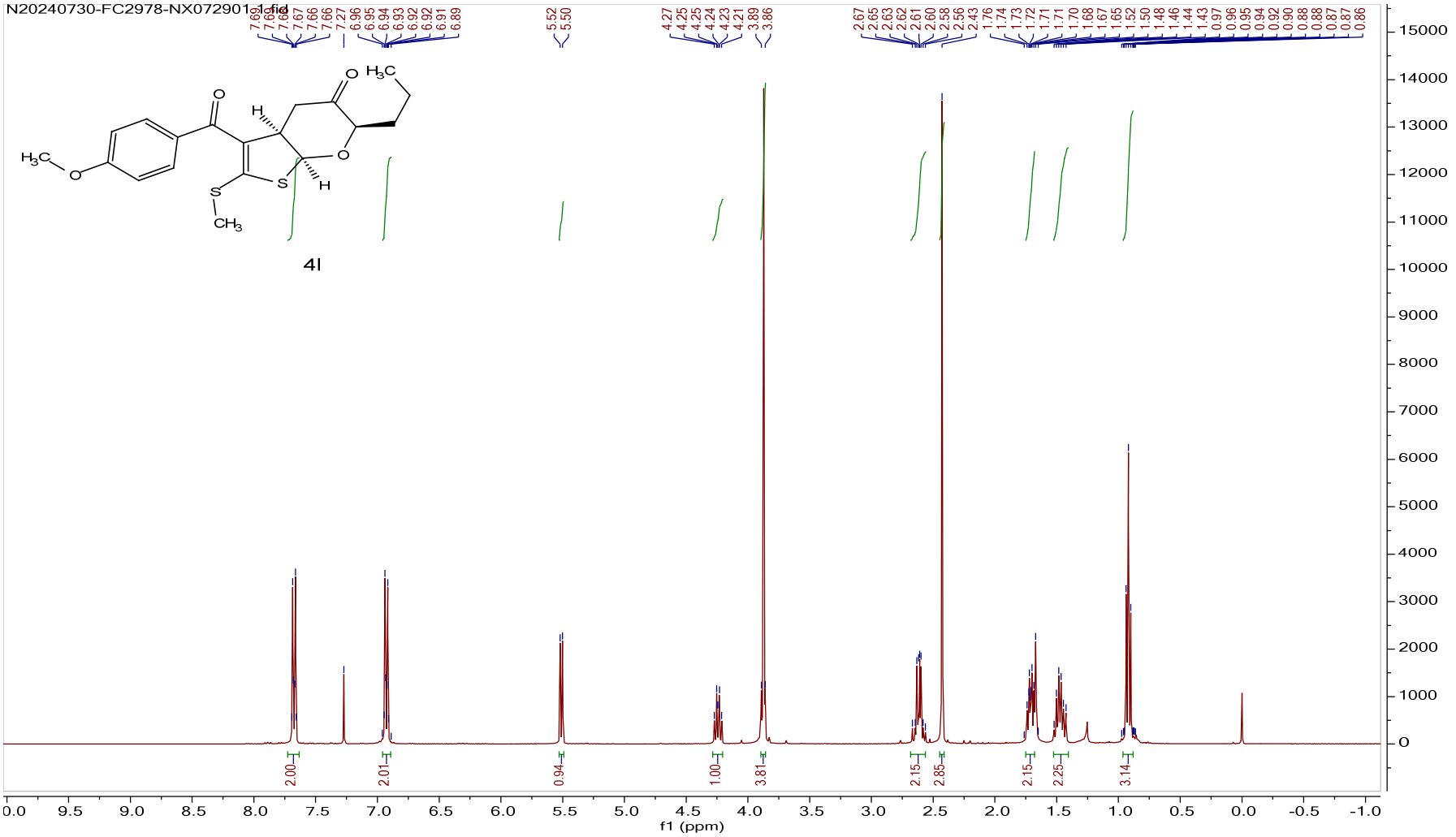
29
240910-5-647-1-4L 14 (0.110)

1: TOF MS ES+
2.07e+006

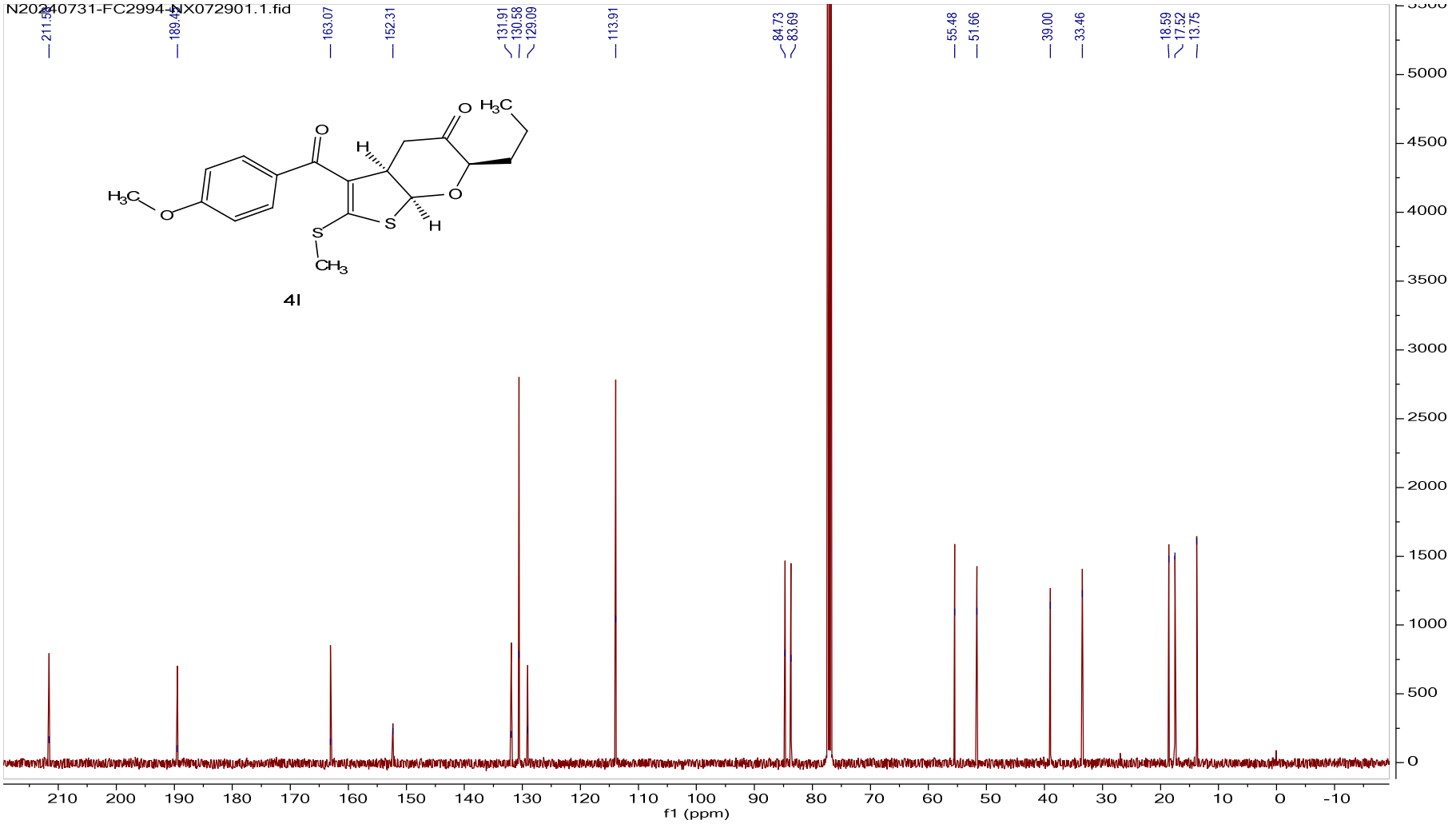


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
375.0504	375.0501	0.3	0.8	8.5	1104.1	n/a	n/a	C17 H17 O3 Na S2 F

^{1}H spectra of **4l.**



^{13}C spectra of **4l.**



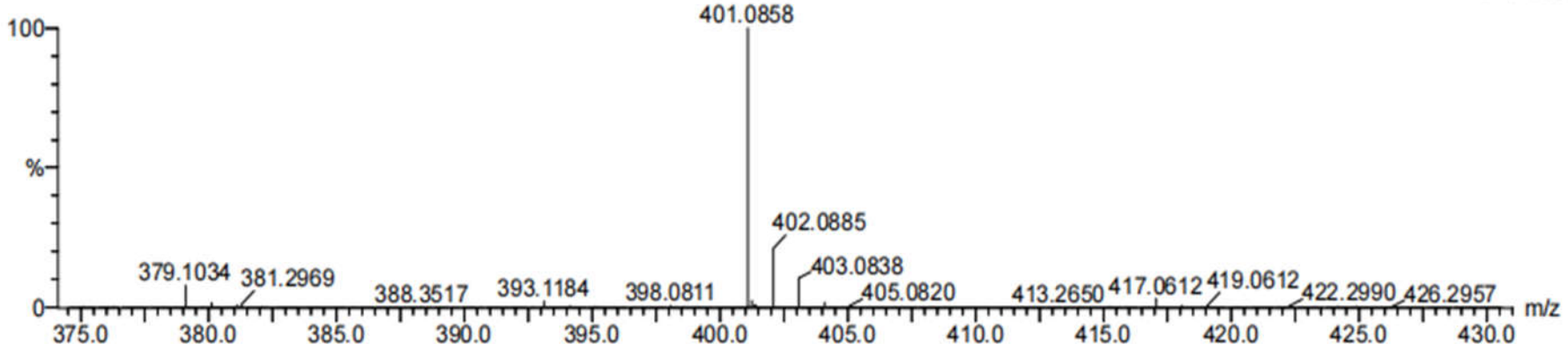
HRMS of **4l.**

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

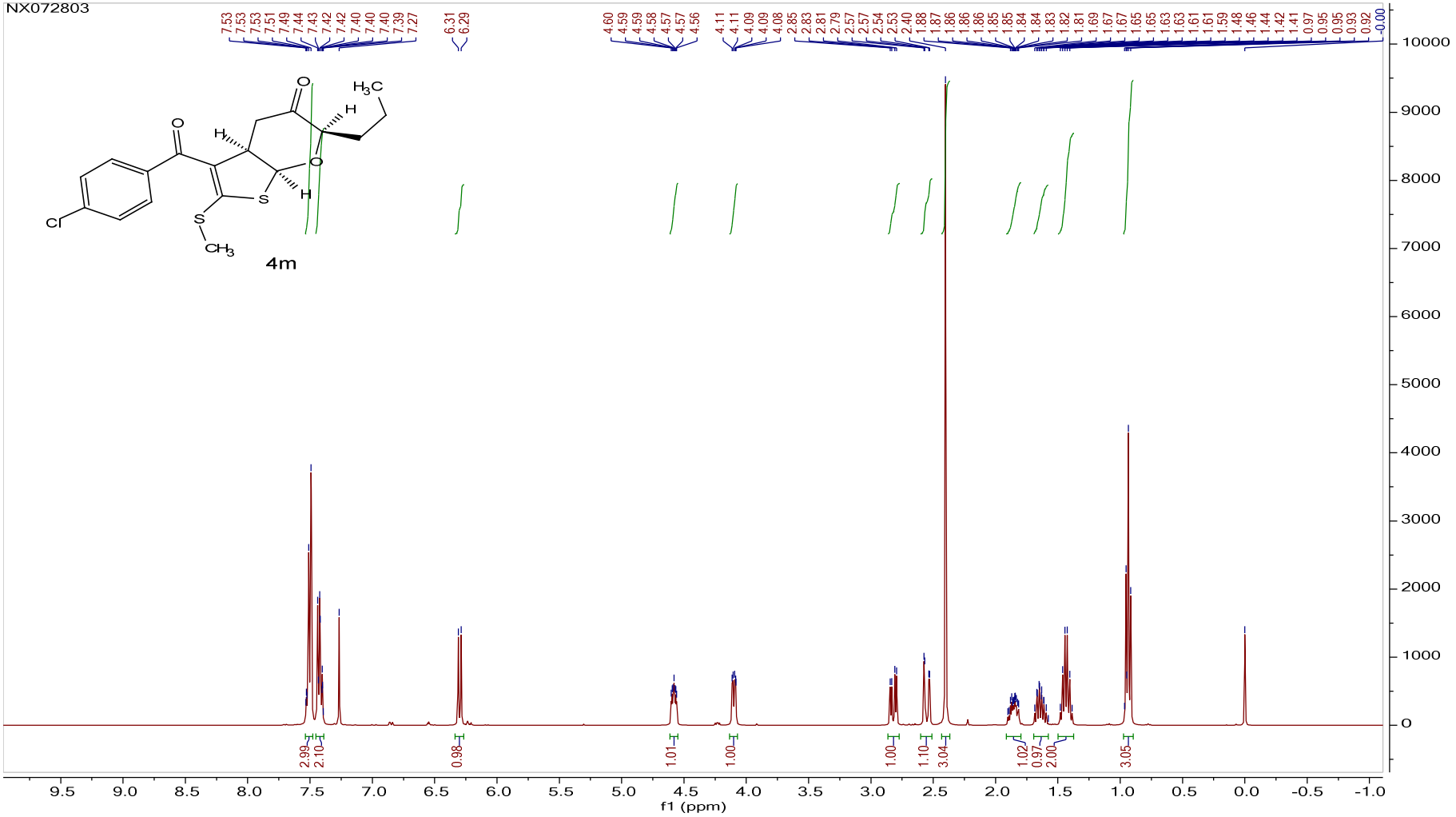
Monoisotopic Mass, Even Electron Ions
3604 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 19-19 H: 22-22 N: 0-100 O: 0-100 Na: 0-4 S: 1-4
29
240910-5-647-1-4M 16 (0.121)

1: TOF MS ES+
2.64e+006

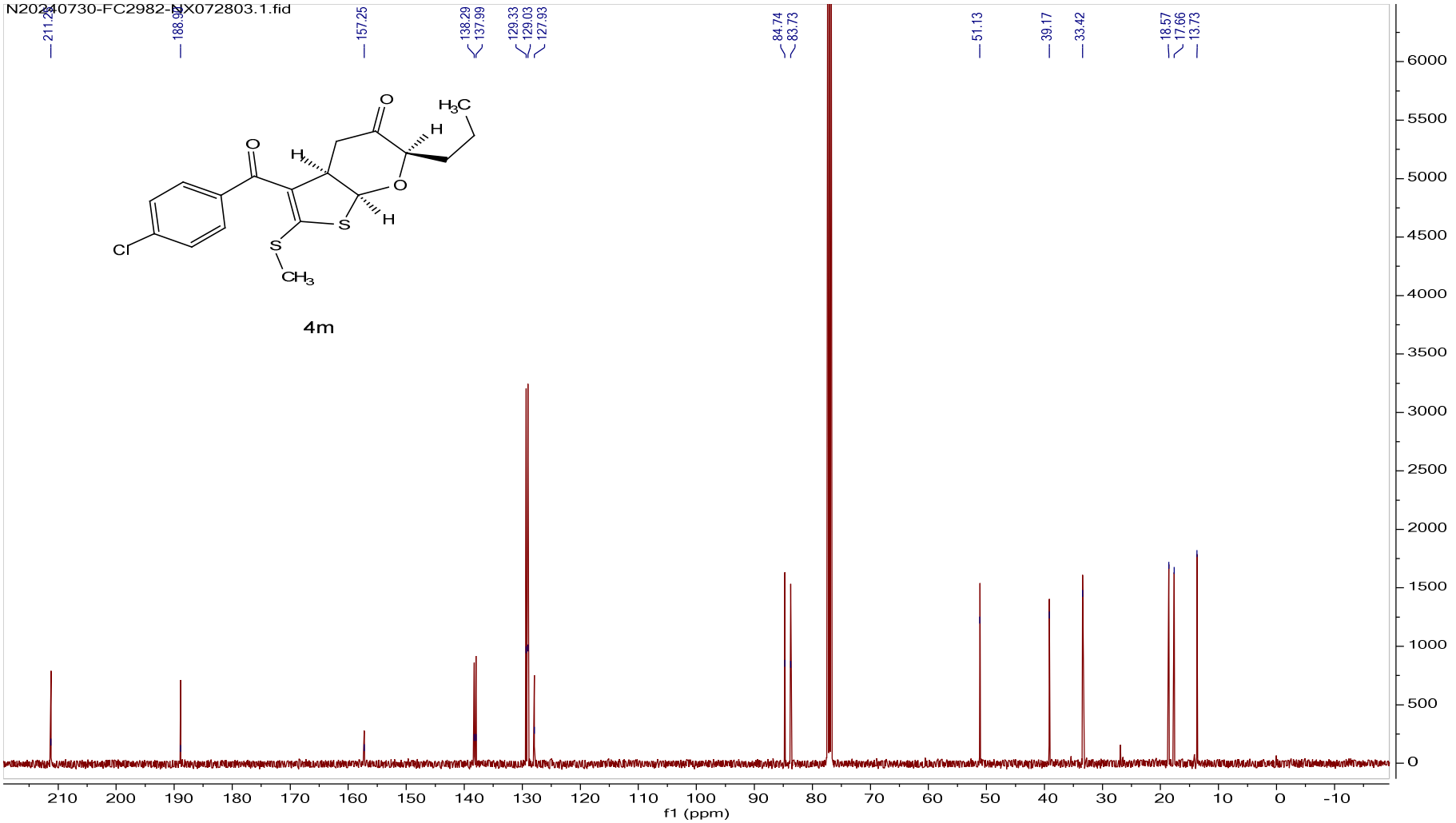


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
401.0858	401.0857	0.1	0.2	8.5	1075.3	n/a	n/a	C19 H22 O4 Na S2

^{1}H spectra of **4m.**



^{13}C spectra of **4m.**



HRMS of **4m.**

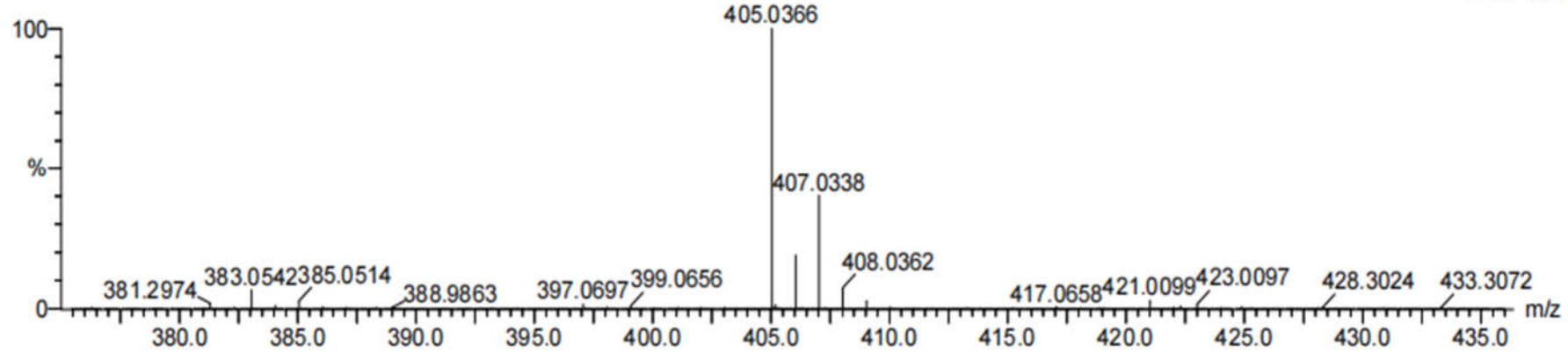
Single Mass Analysis

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
6889 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 18-18 H: 19-19 N: 0-100 O: 0-100 Na: 0-4 S: 1-4 Cl: 1-3

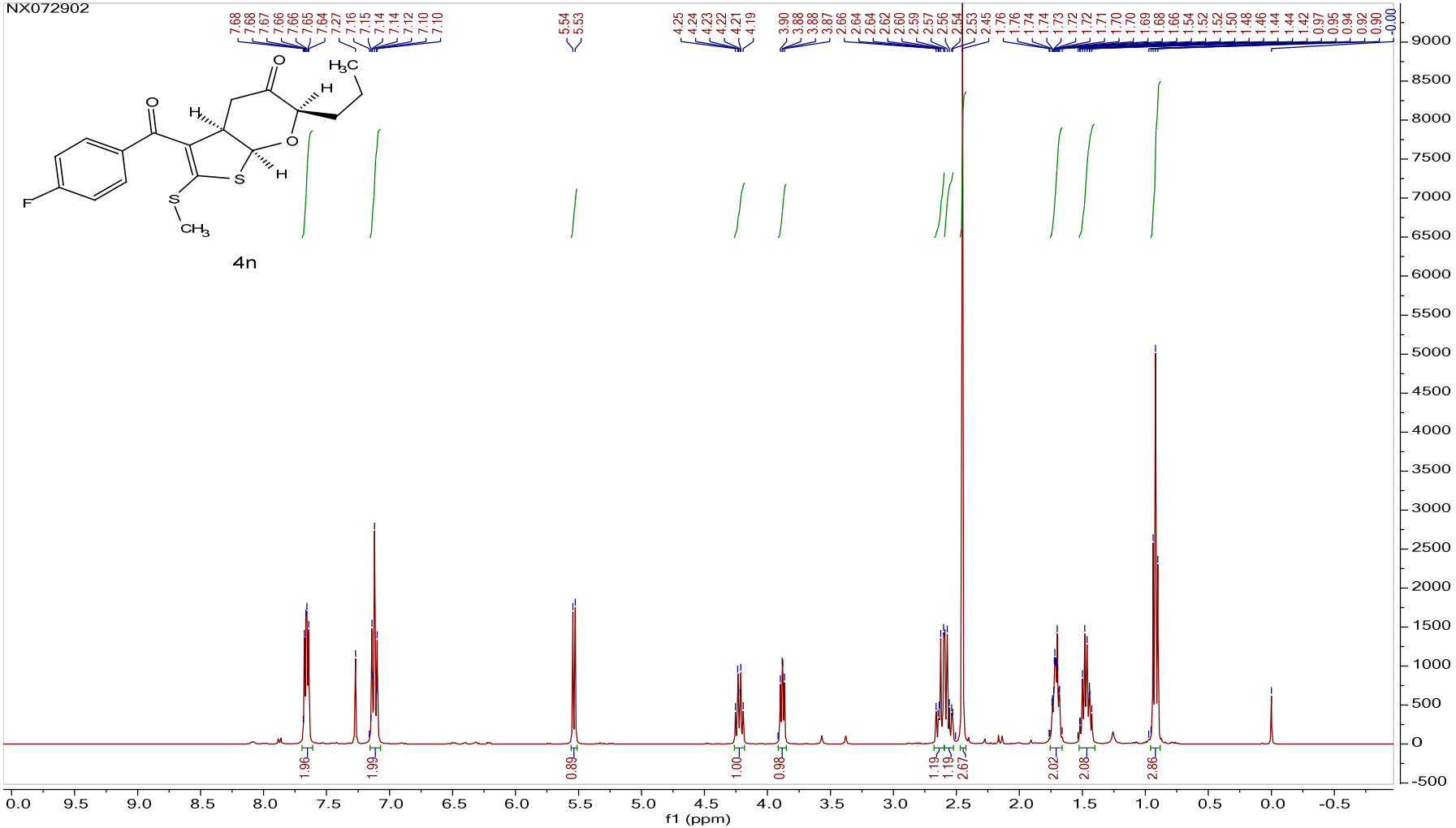
29
240910-5-647-1-4N 17 (0.126)

1: TOF MS ES+
1.28e+006

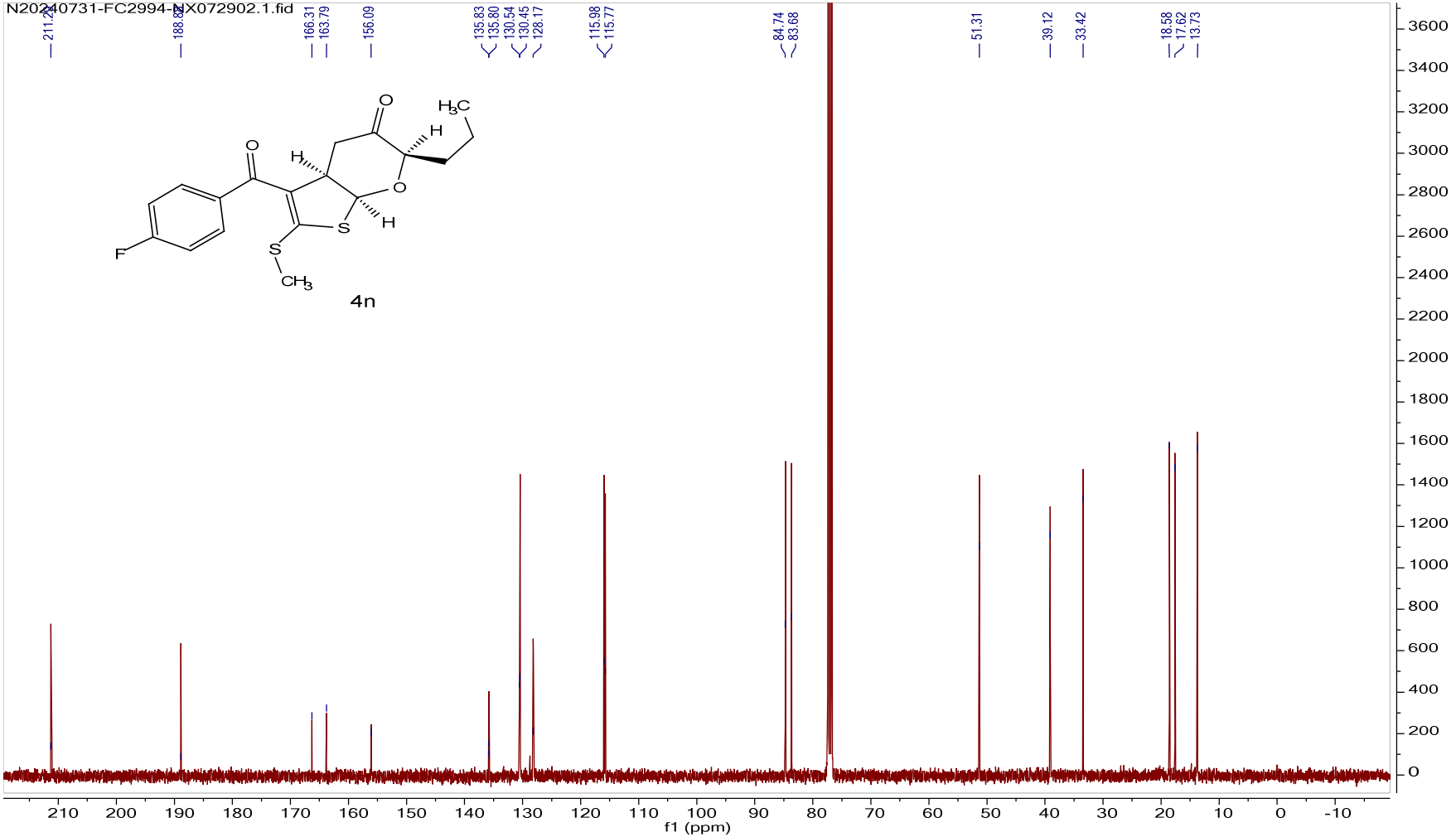


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
405.0366	405.0362	0.4	1.0	8.5	1064.8	n/a	n/a	C18 H19 O3 Na S2 Cl

^{1}H spectra of **4n.**



^{13}C spectra of **4n.**

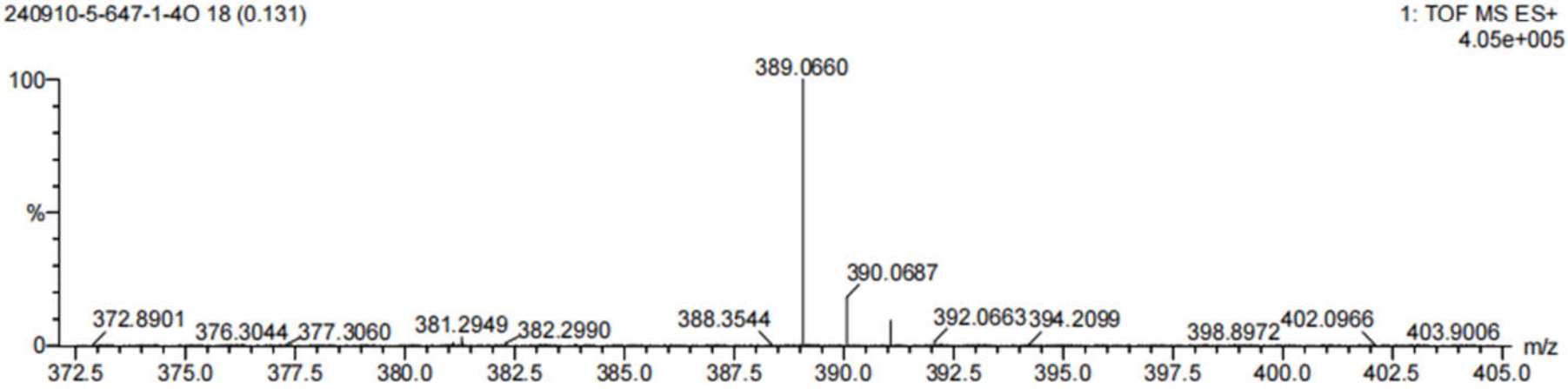


HRMS of **4n.**

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

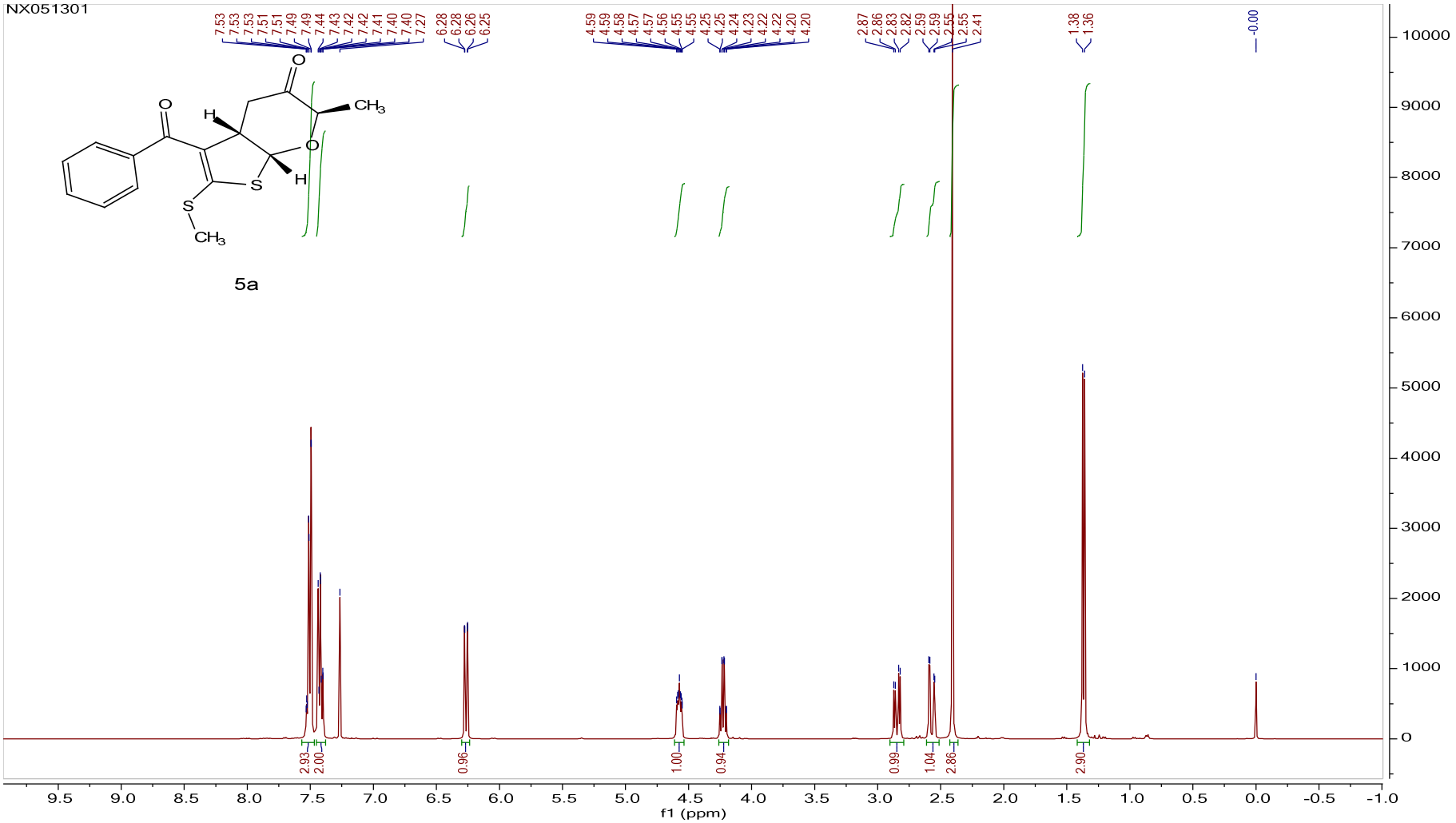
Monoisotopic Mass, Even Electron Ions
2927 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 18-18 H: 19-19 N: 0-100 O: 0-100 Na: 0-4 S: 1-4 F: 1-1

29
240910-5-647-1-4O 18 (0.131)

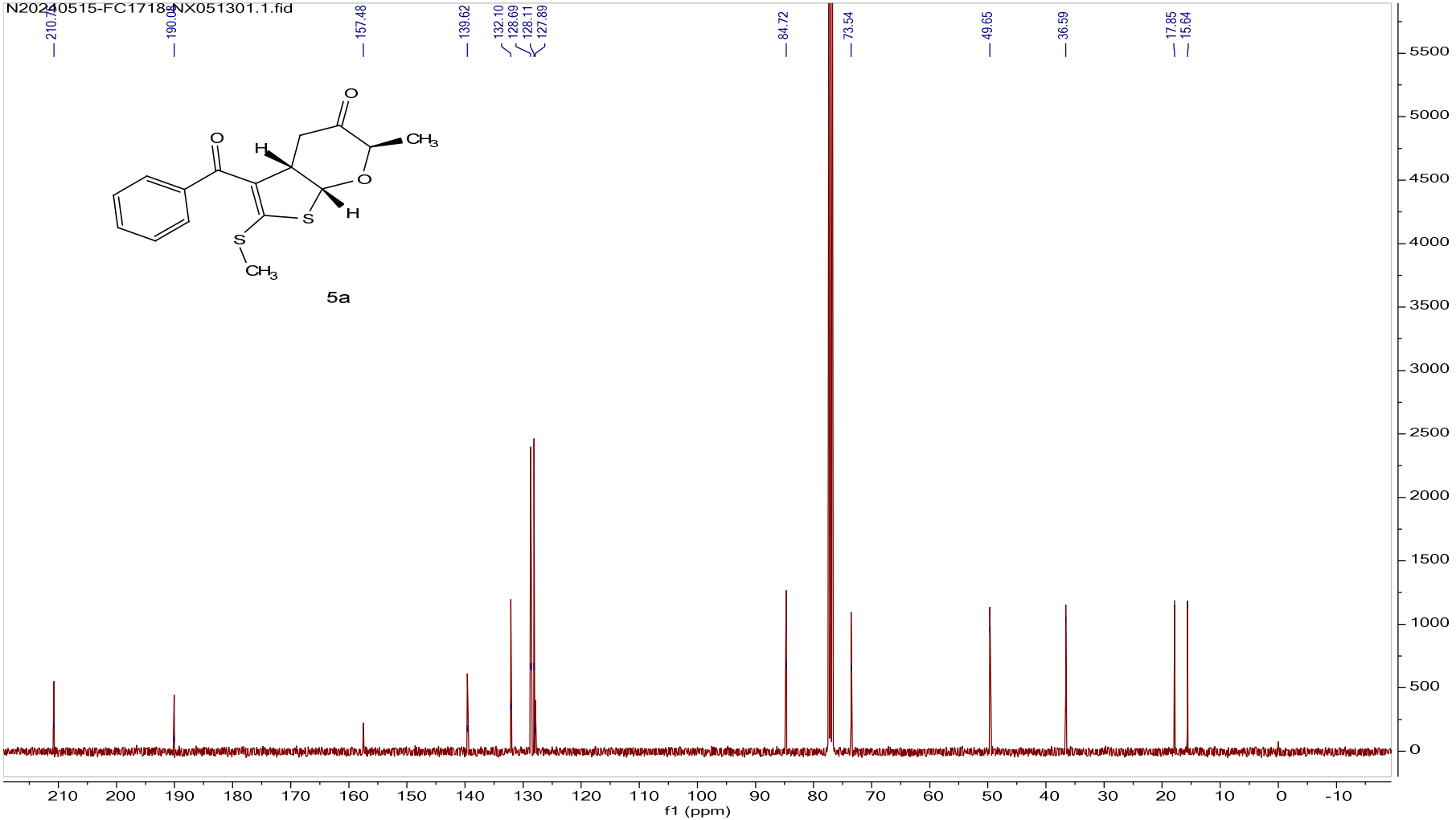


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
389.0660	389.0657	0.3	0.8	8.5	716.3	n/a	n/a	C18 H19 O3 Na S2 F

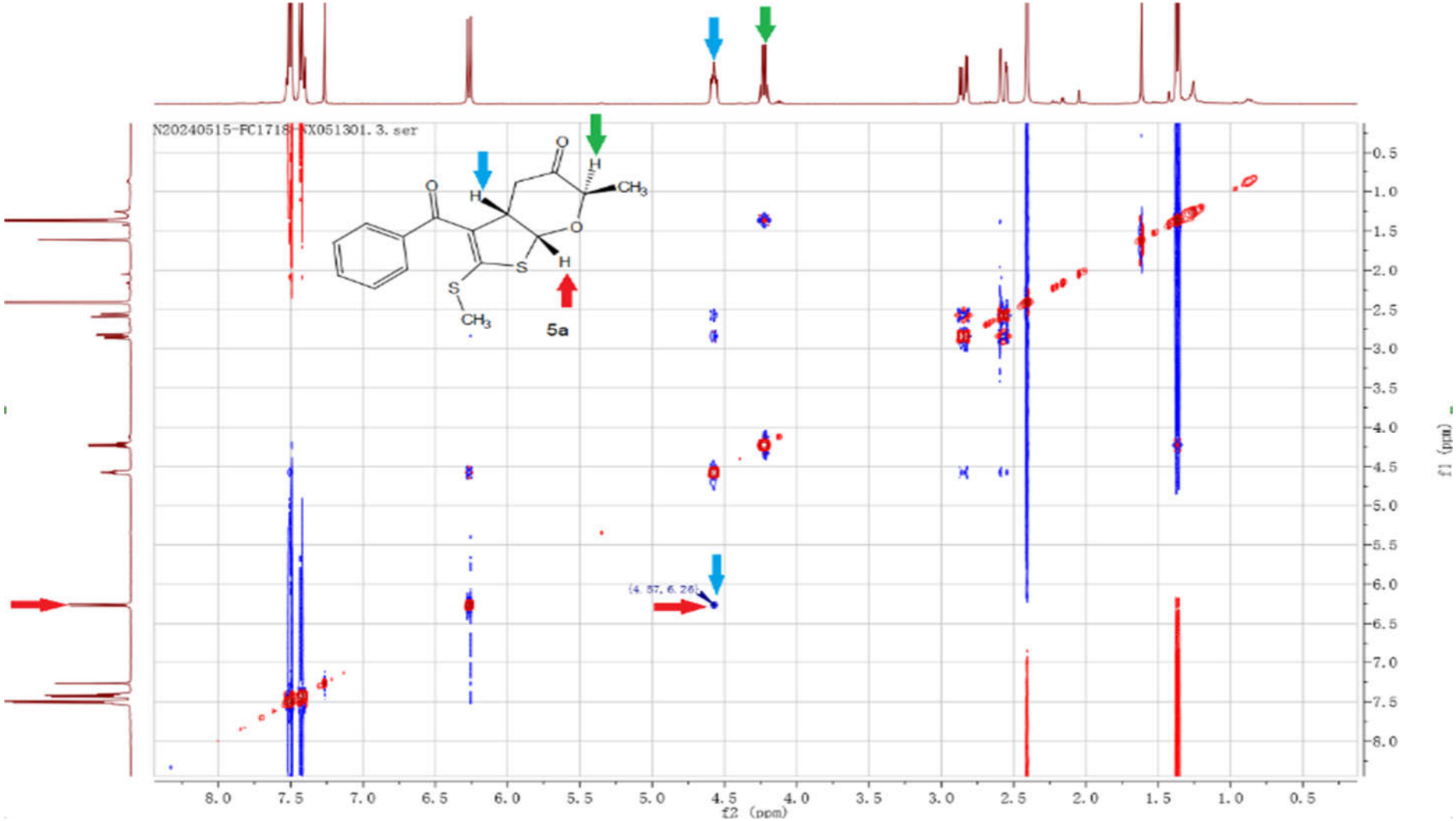
^{1}H spectra of **5a.**



^{13}C spectra of **5a.**



NOSEY spectra of **5a.**



HRMS of **5a.**

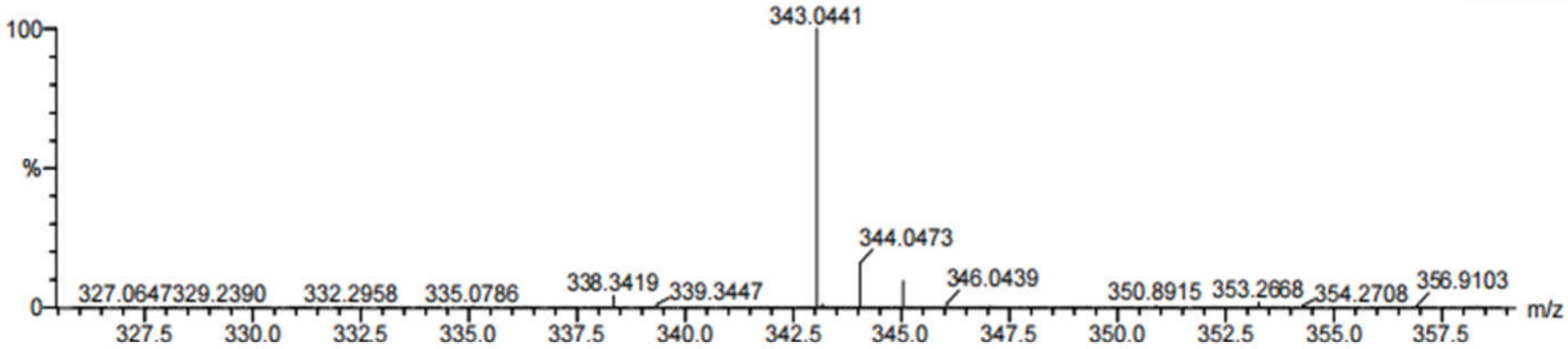
Single Mass Analysis

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
2354 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 16-16 H: 16-16 N: 0-100 O: 0-100 Na: 0-4 S: 1-4

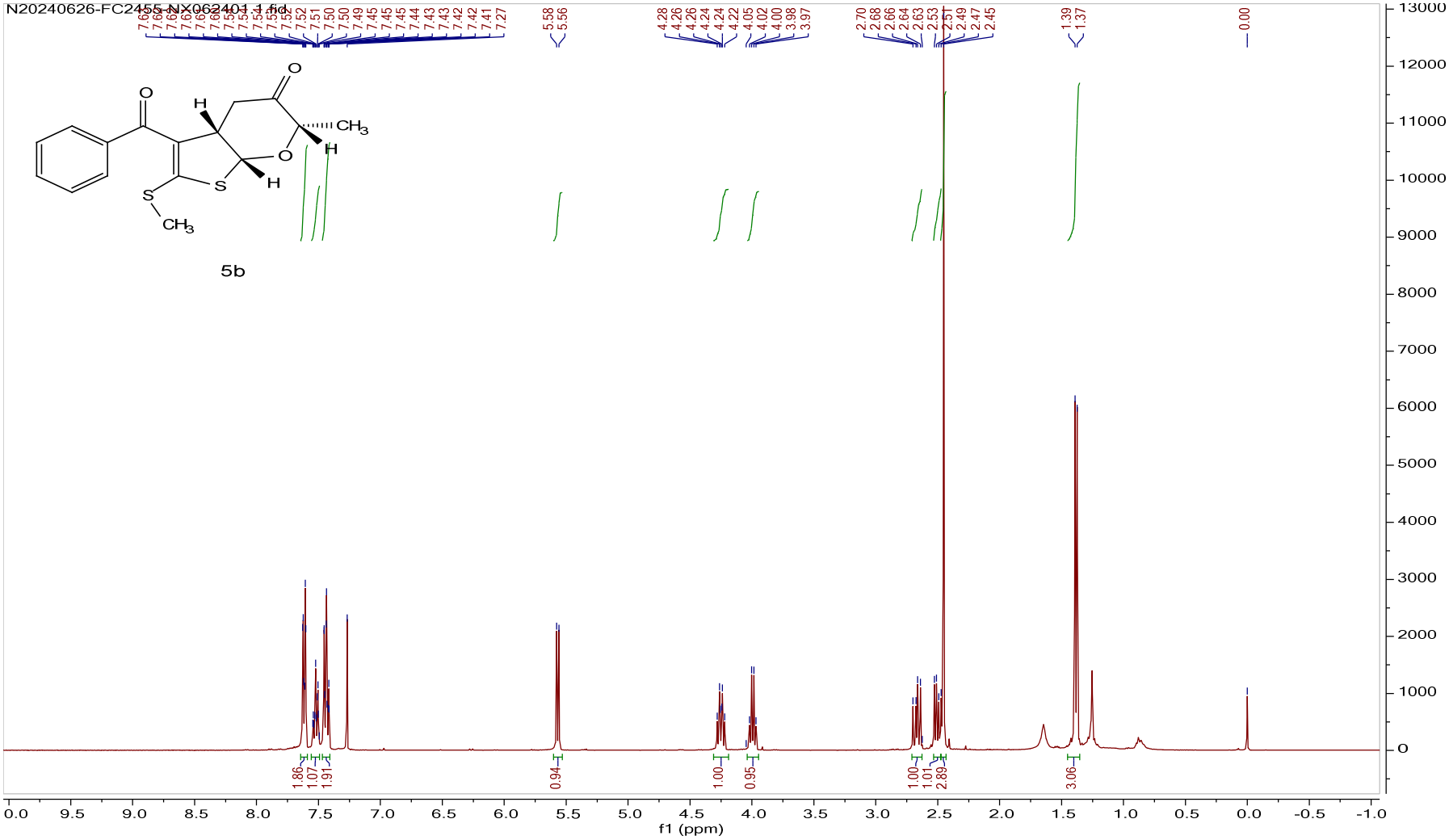
29
240910-5-647-1-5A 17 (0.126)

1: TOF MS ES+
1.11e+006

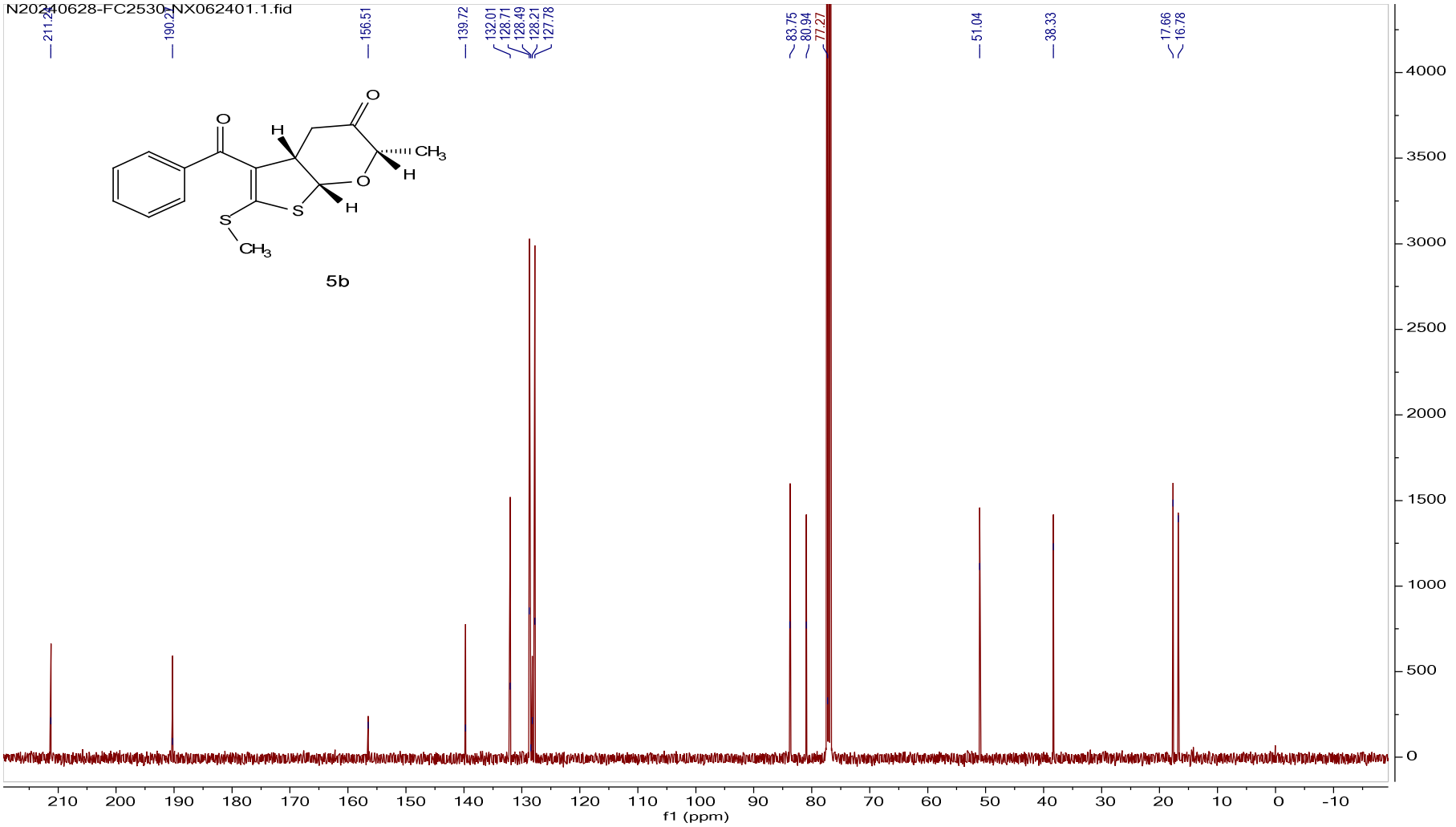


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
343.0441	343.0439	0.2	0.6	8.5	978.3	n/a	n/a	C16 H16 O3 Na S2

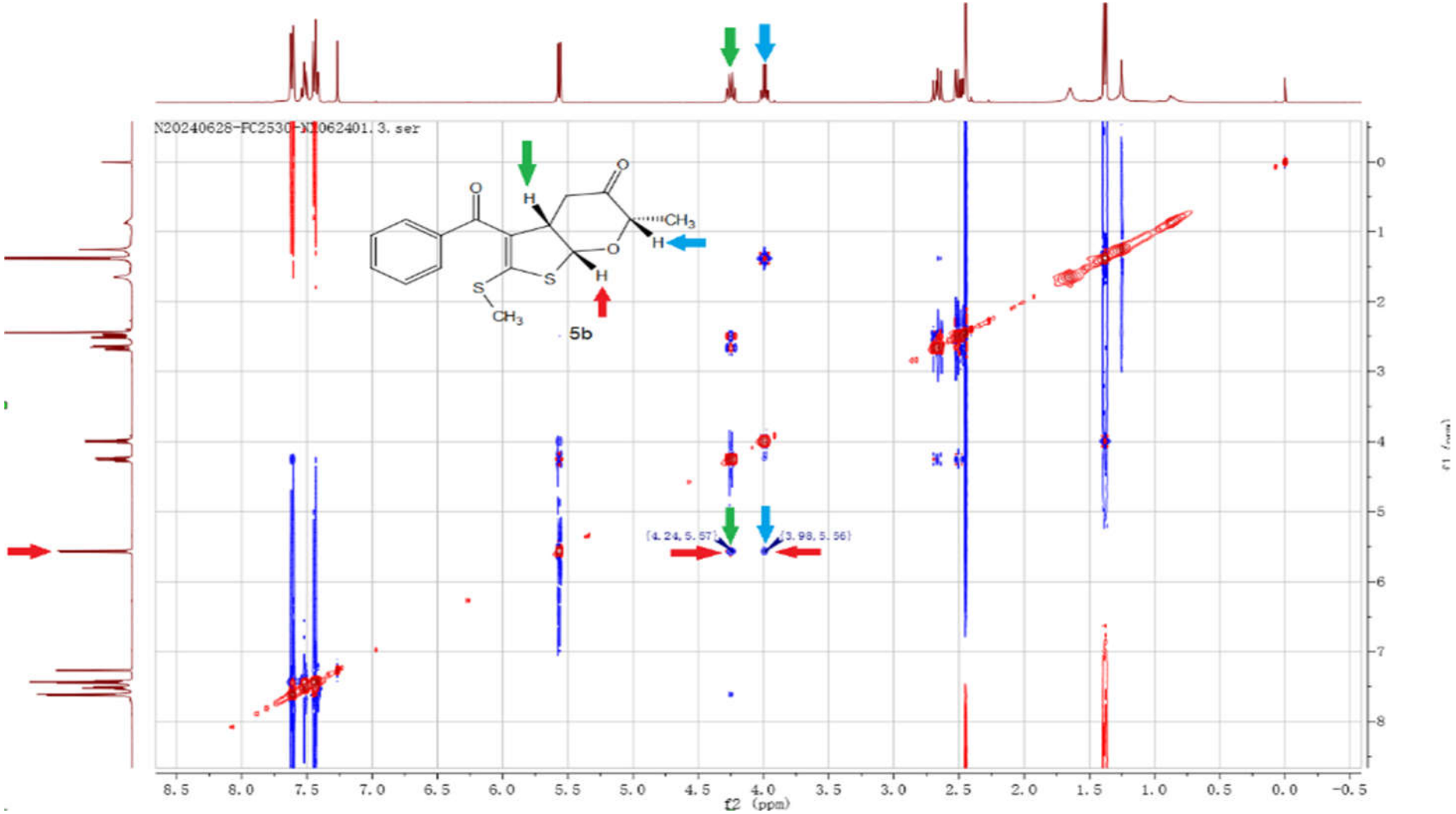
^{1}H spectra of **5b.**



^{13}C spectra of **5b.**



NOESY spectra of **5b.**



HRMS of **5b.**

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

2354 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

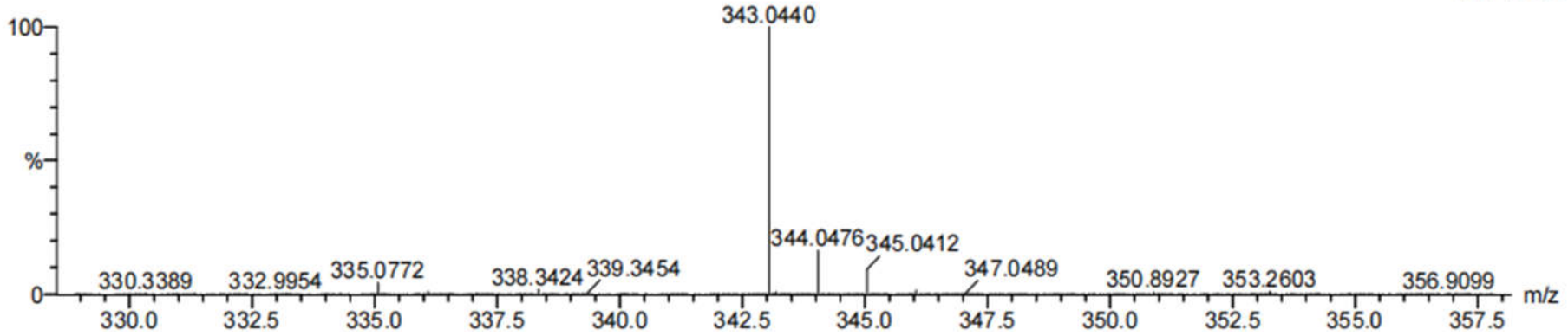
Elements Used:

C: 16-16 H: 16-16 N: 0-100 O: 0-100 Na: 0-4 S: 1-4

29

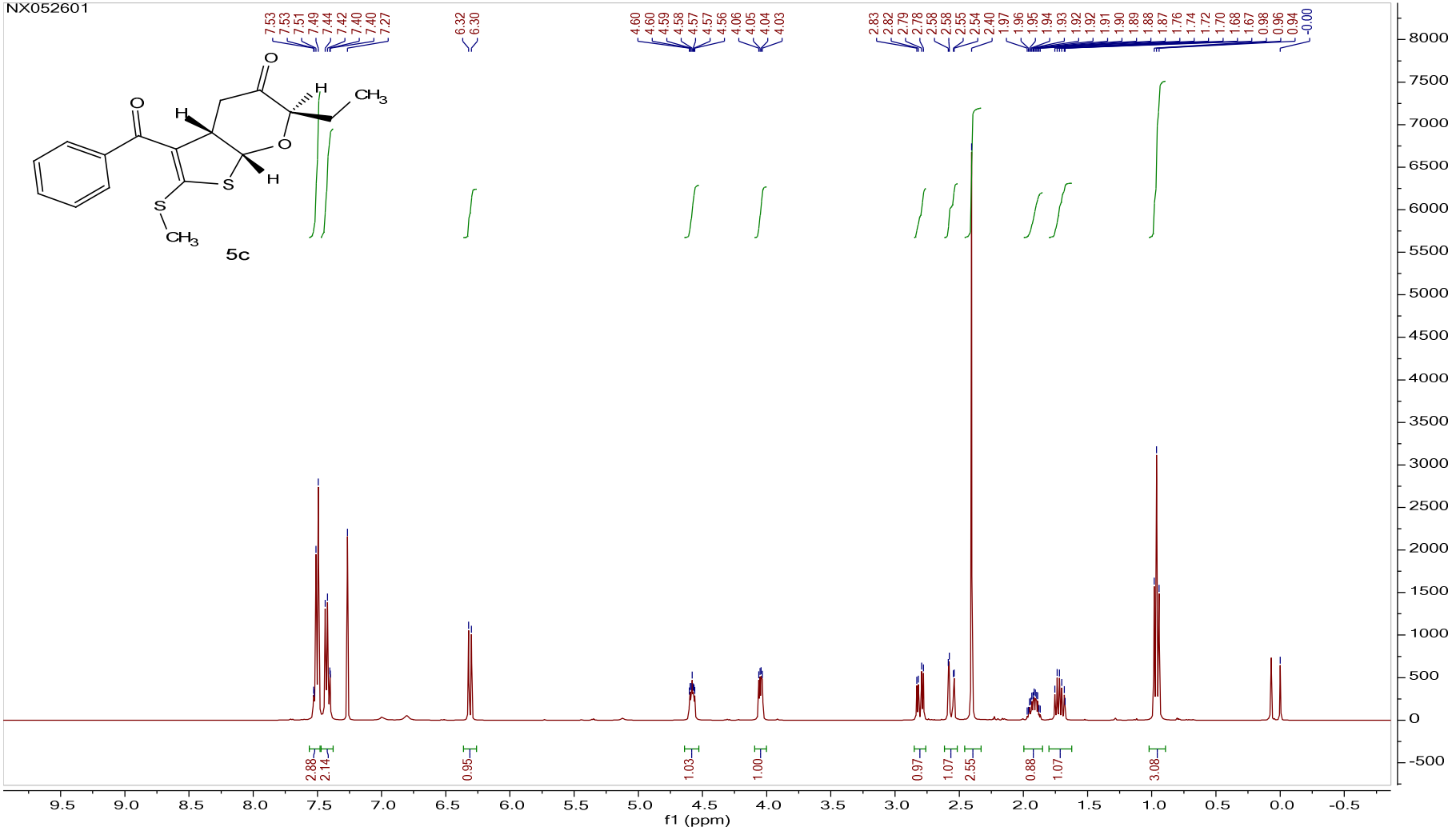
240910-5-647-1-5B 18 (0.131)

1: TOF MS ES+
9.47e+005

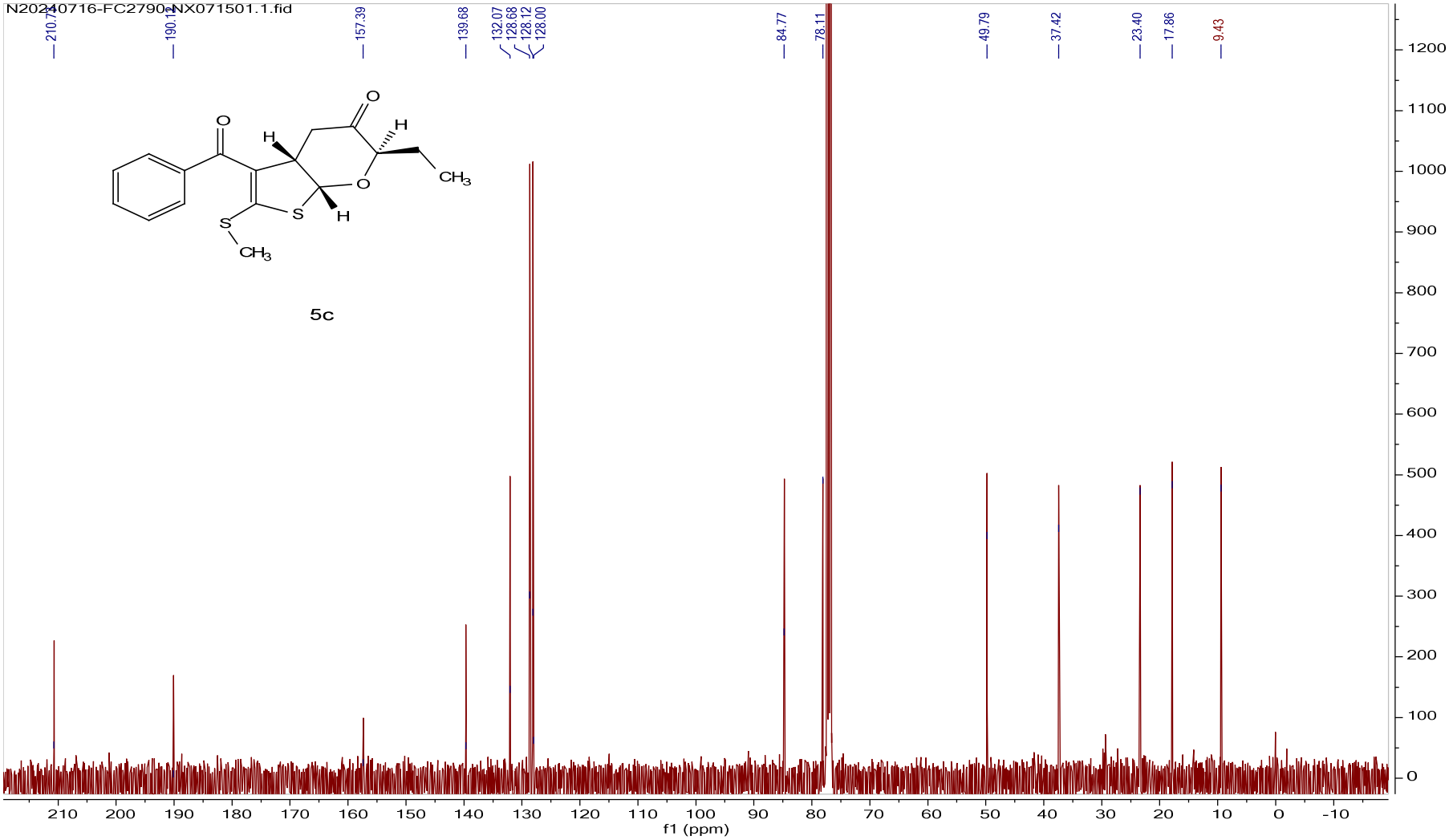


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
343.0440	343.0439	0.1	0.3	8.5	985.3	n/a	n/a	C16 H16 O3 Na S2

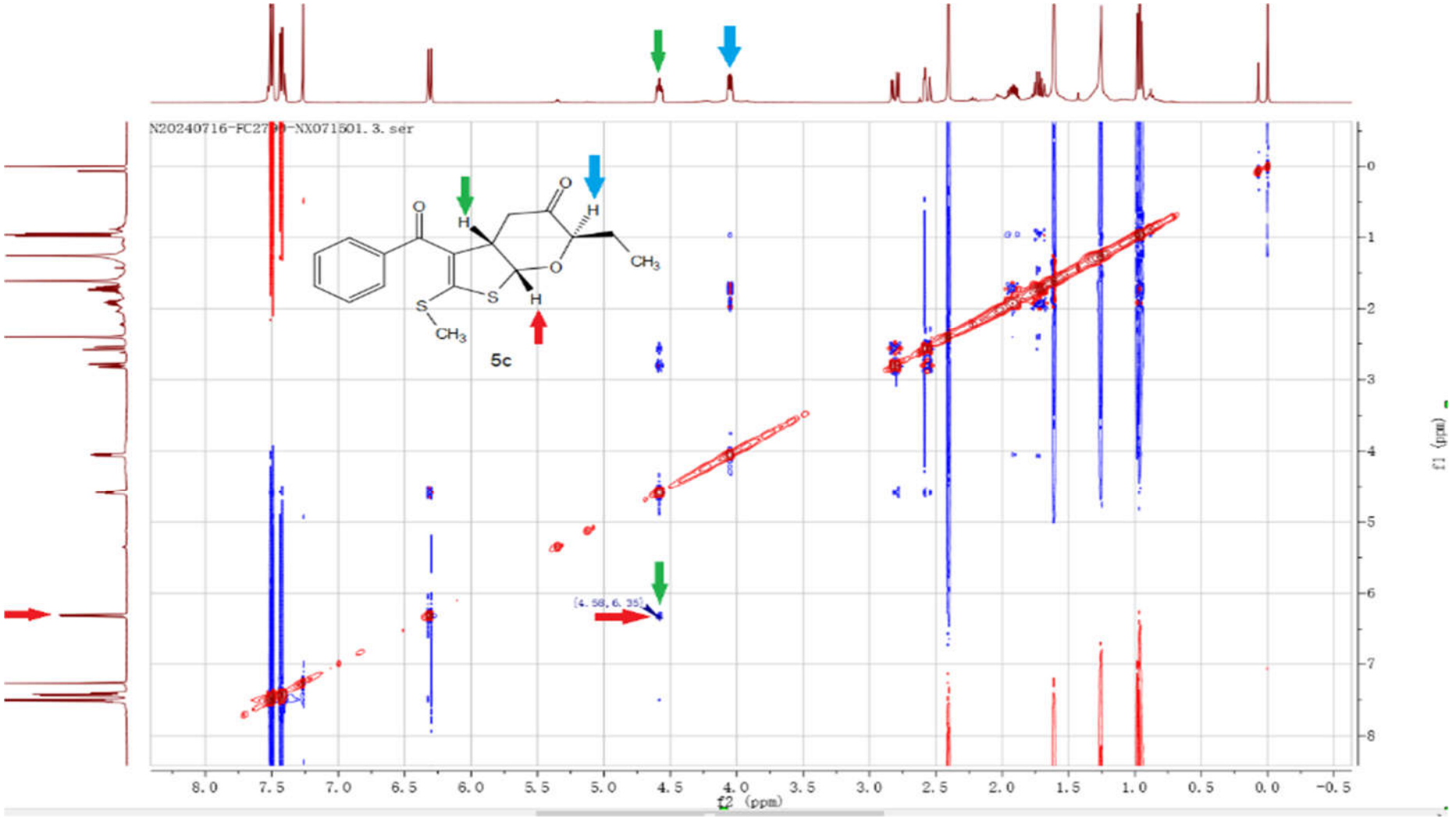
[1]H spectra of **5c.**



^{13}C spectra of **5c.**



NOESY spectra of **5c.**



HRMS of **5c.**

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

2640 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

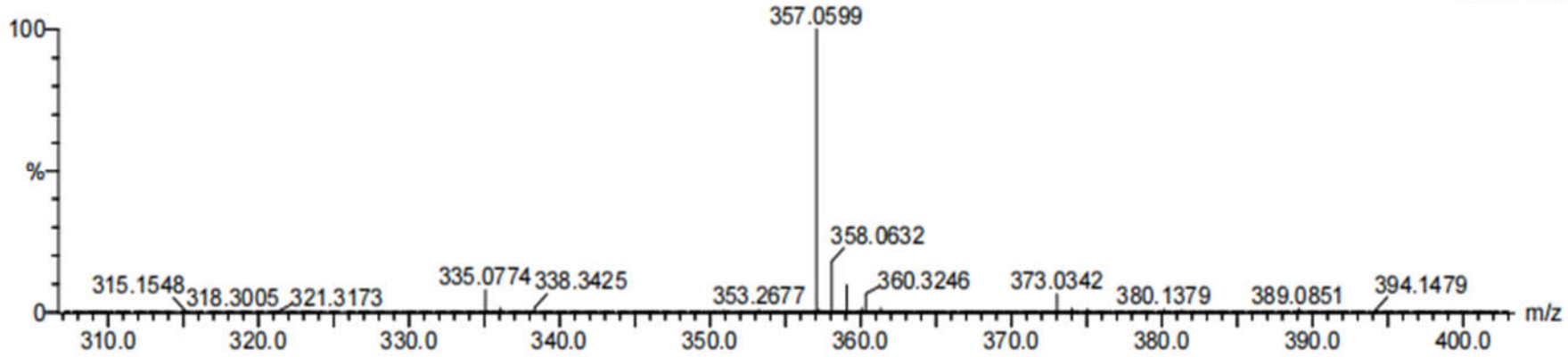
C: 17-17 H: 18-18 N: 0-100 O: 0-100 Na: 0-4 S: 1-4

29

240910-5-647-1-5C 21 (0.147)

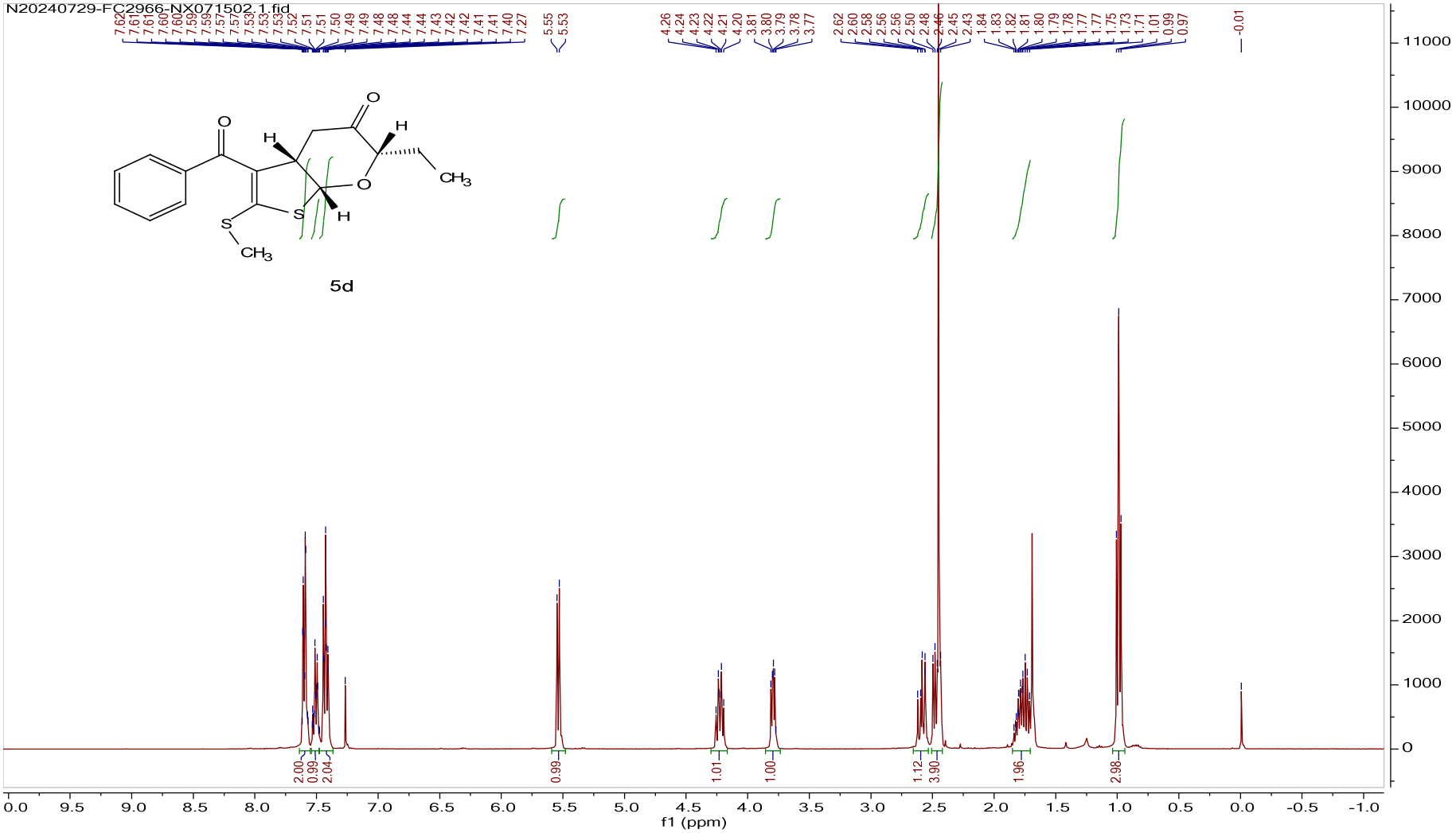
1: TOF MS ES+

9.28e+005

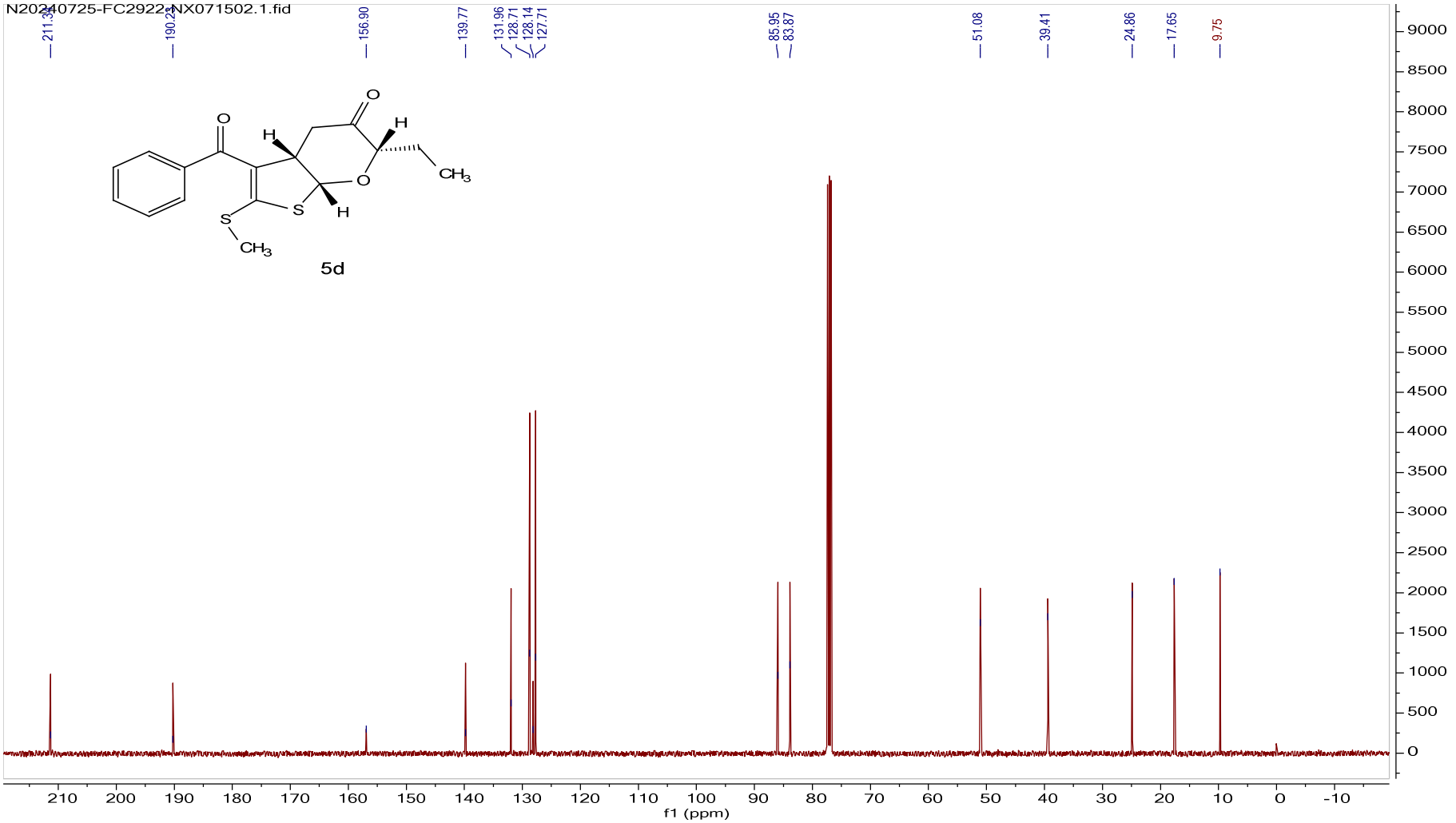


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
357.0599	357.0595	0.4	1.1	8.5	960.6	n/a	n/a	C17 H18 O3 Na S2

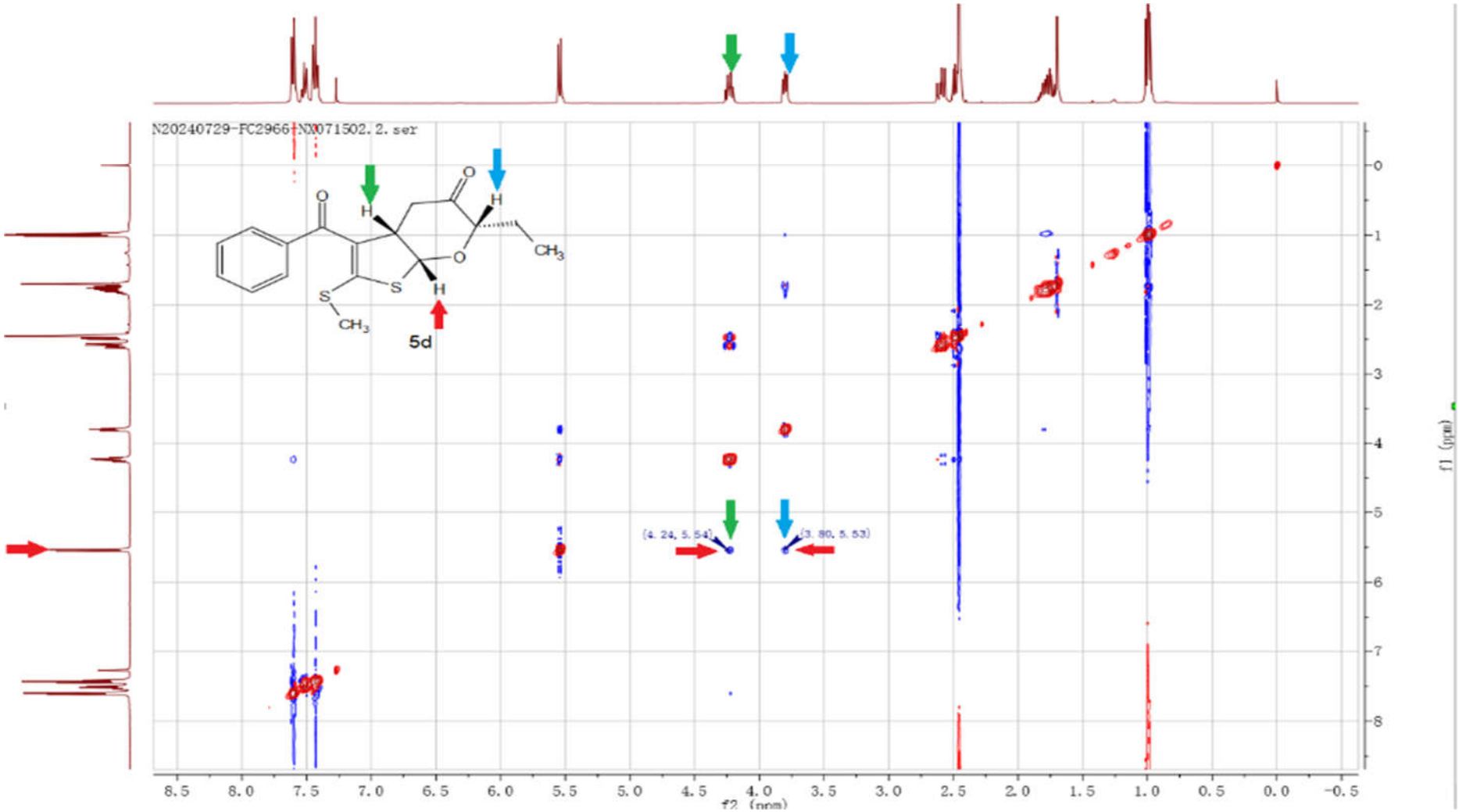
^{1}H spectra of **5d.**



^{13}C spectra of **5d.**



NOESY spectra of **5d.**



HRMS of **5d.**

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

2640 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

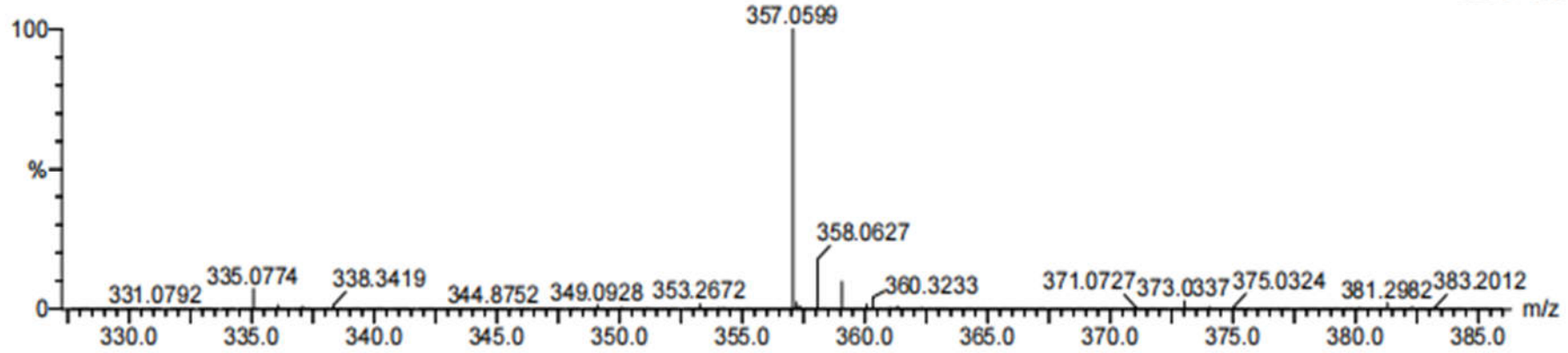
C: 17-17 H: 18-18 N: 0-100 O: 0-100 Na: 0-4 S: 1-4

29

240910-5-647-1-5D 15 (0.115)

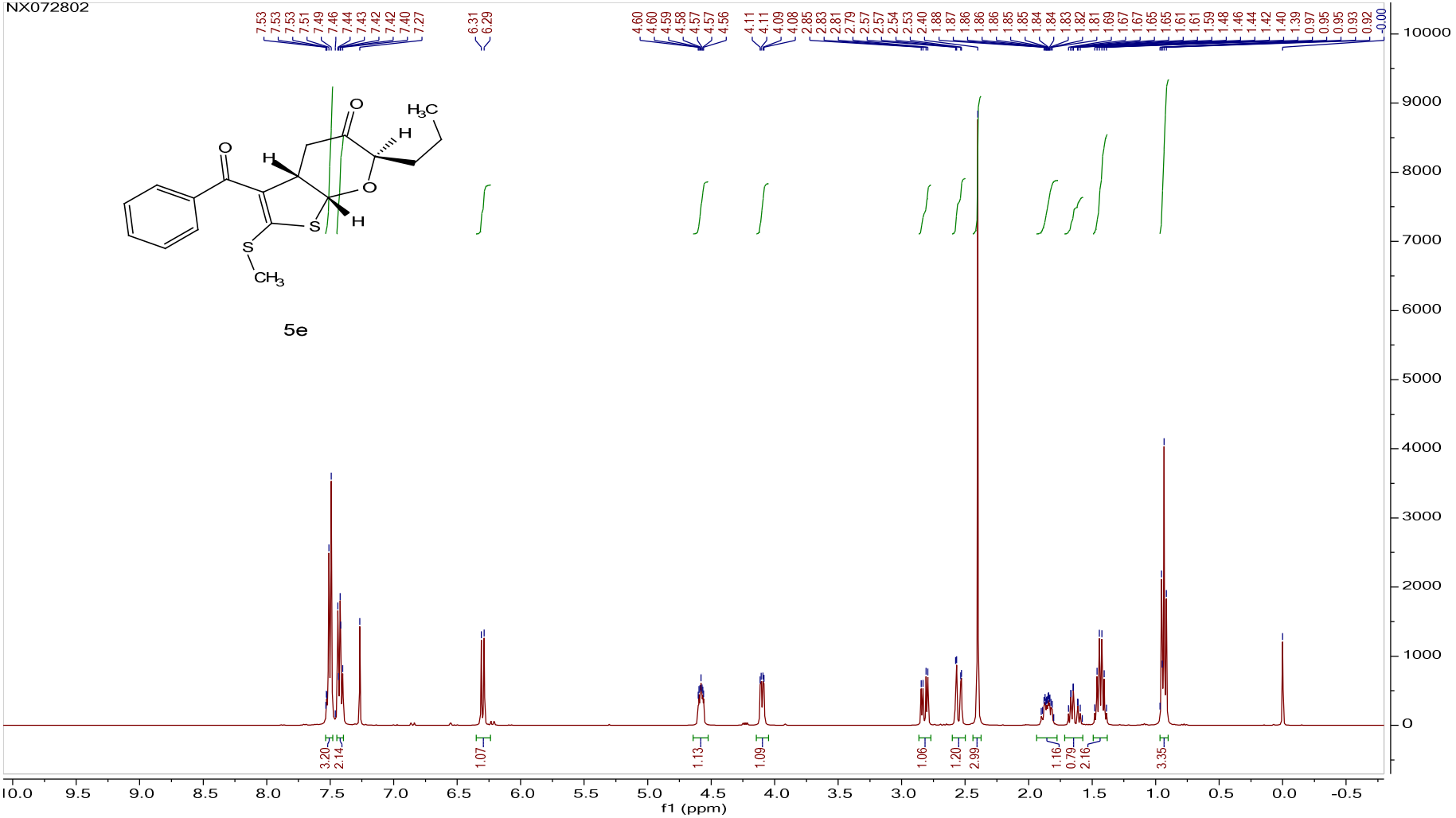
1: TOF MS ES+

2.27e+006

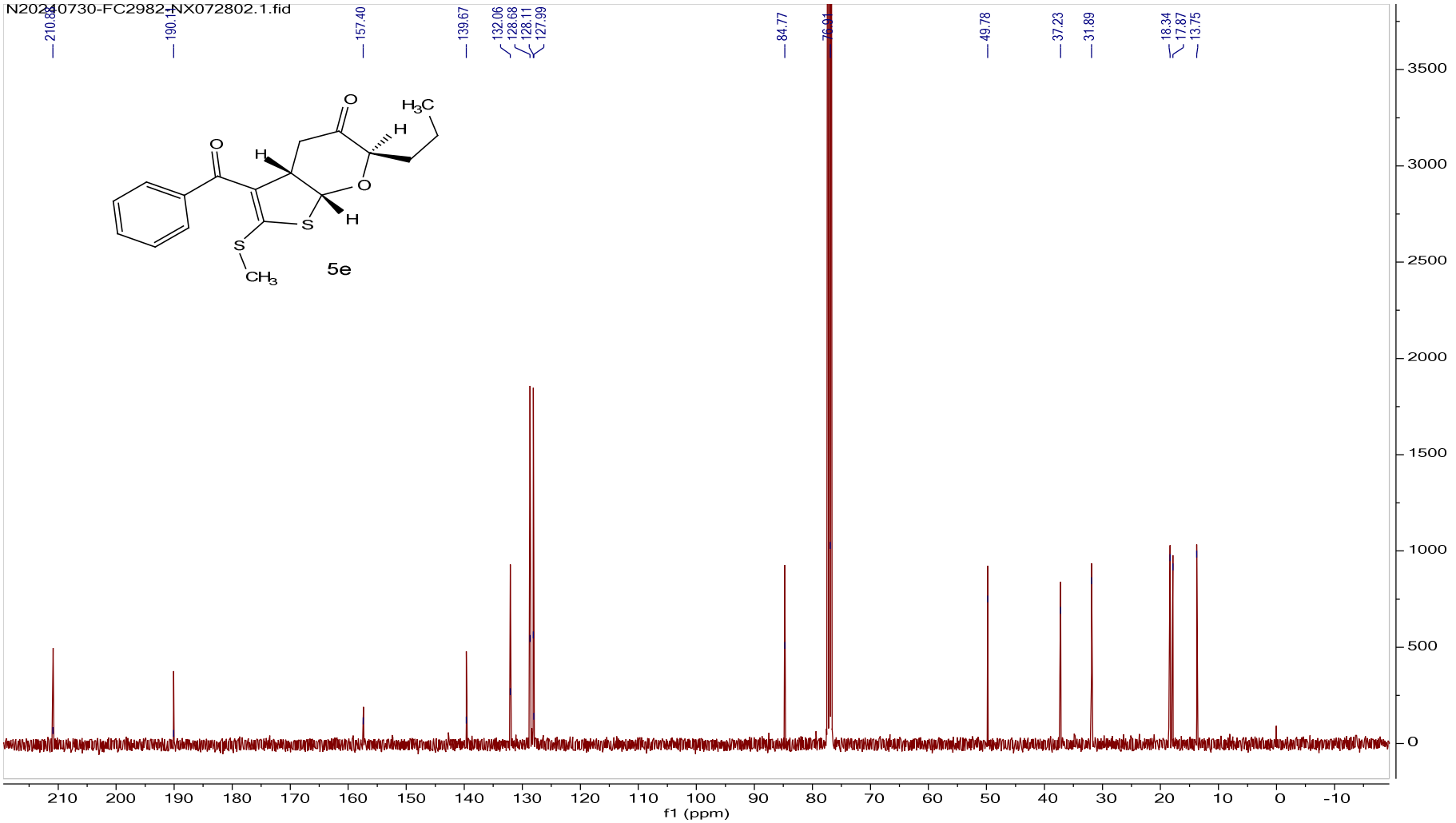


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
357.0599	357.0595	0.4	1.1	8.5	1108.7	n/a	n/a	C17 H18 O3 Na S2

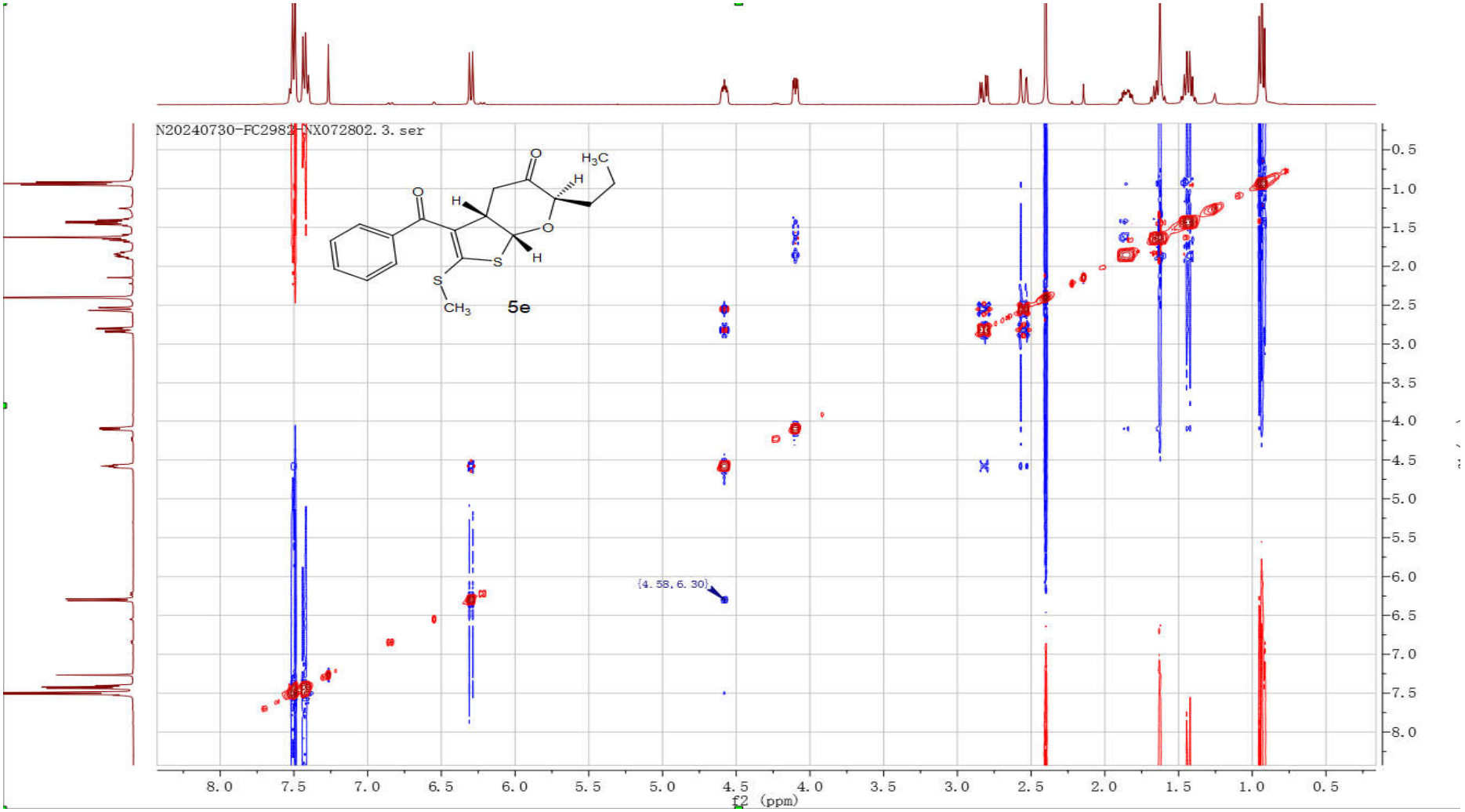
^{1}H spectra of **5e.**



^{13}C spectra of **5e.**



NOESY spectra of **5e.**



HRMS of **5e.**

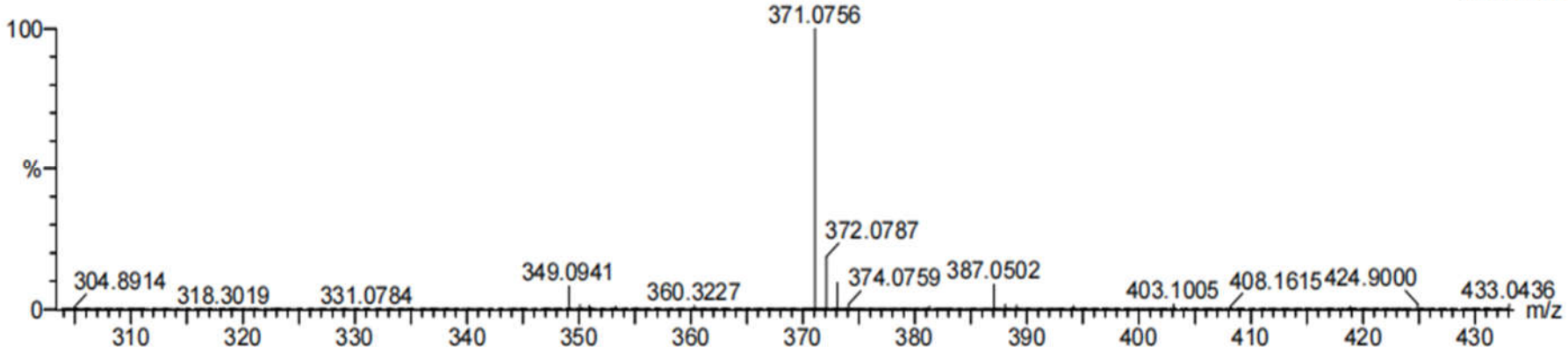
Single Mass Analysis

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
2943 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 18-18 H: 20-20 N: 0-100 O: 0-100 Na: 0-4 S: 1-4

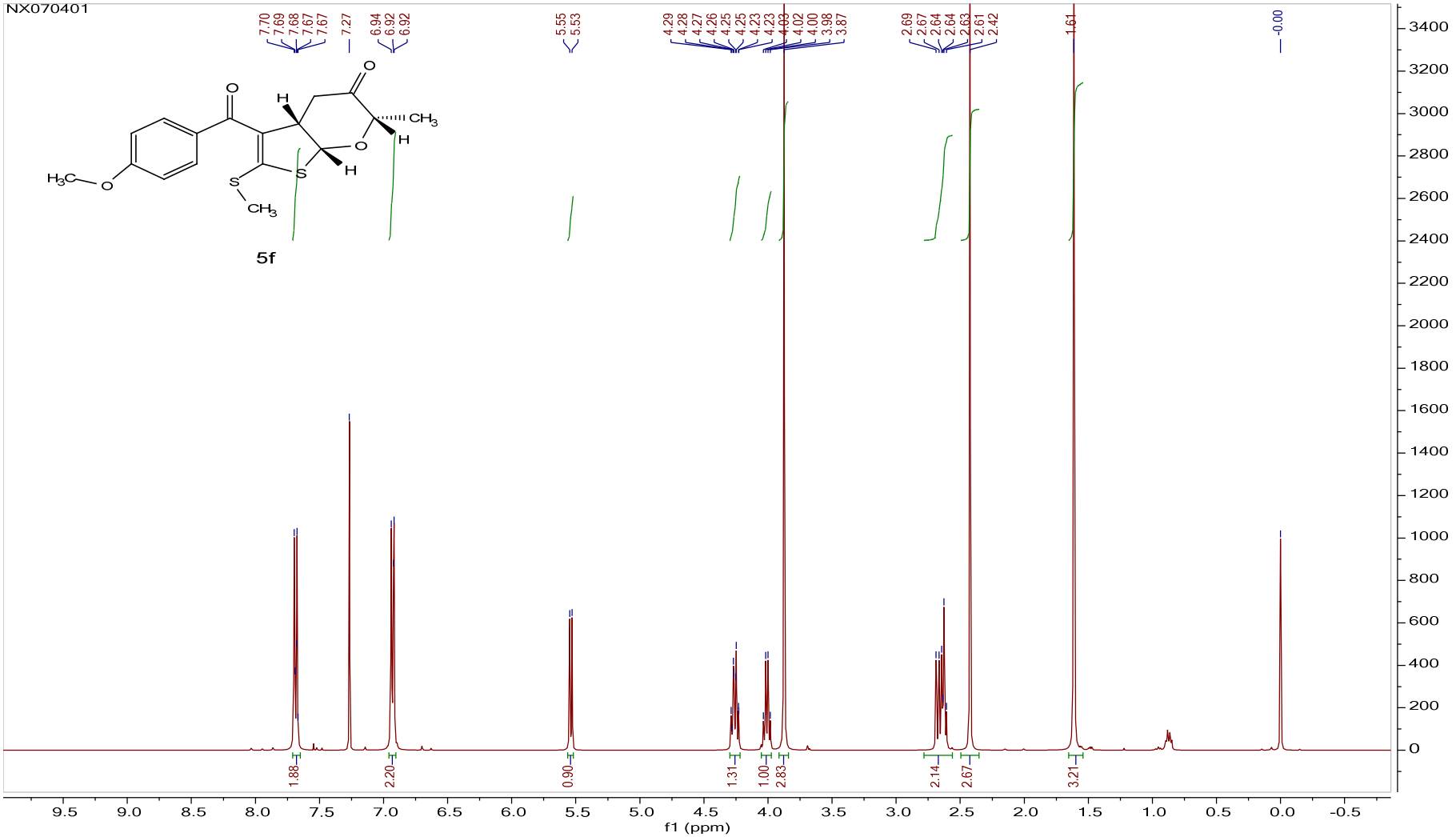
29
240910-5-647-1-5E 22 (0.152)

1: TOF MS ES+
6.02e+005

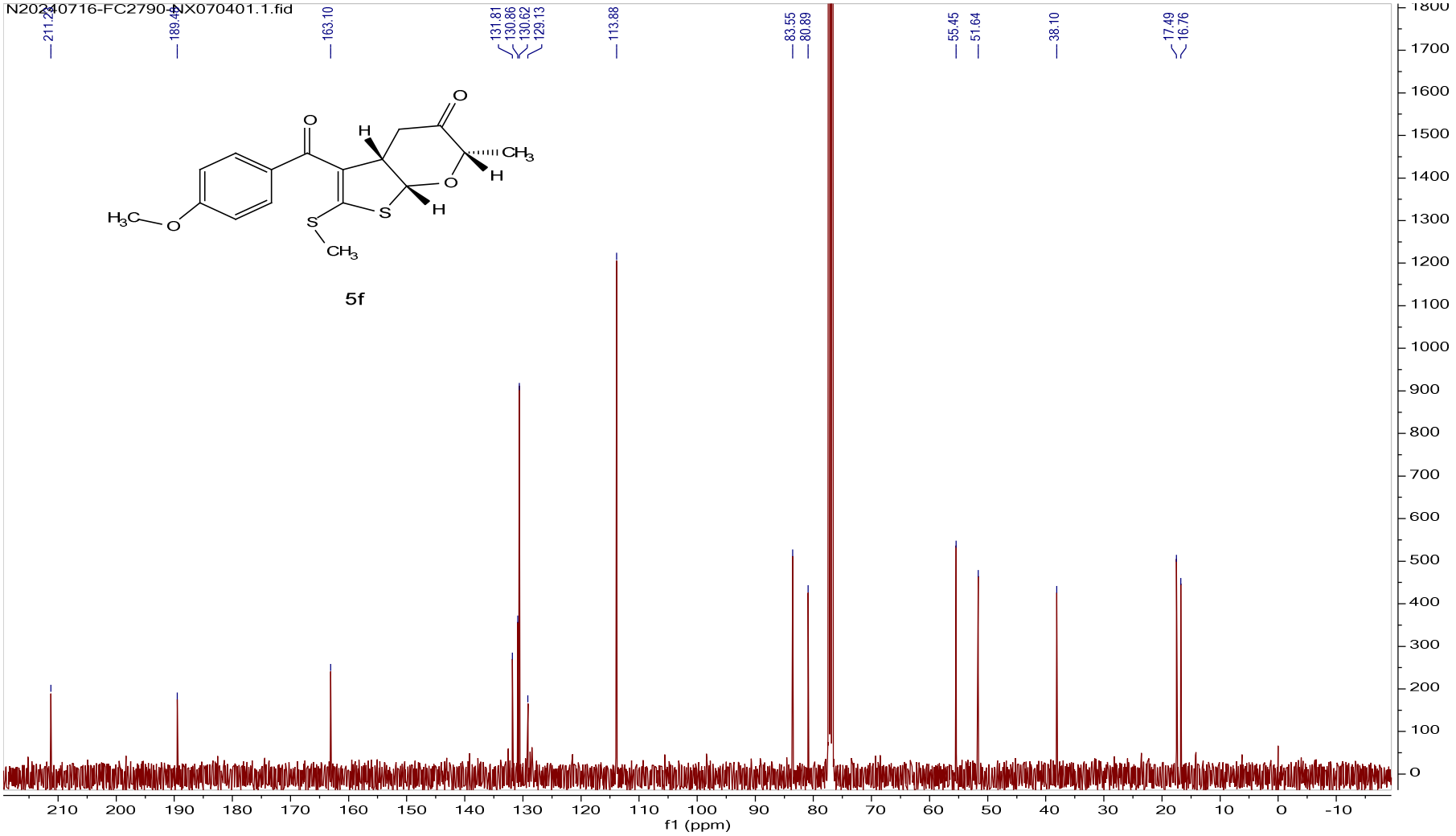


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
371.0756	371.0752	0.4	1.1	8.5	820.1	n/a	n/a	C18 H20 O3 Na S2

^{1}H spectra of **5f.**



^{13}C spectra of **5f.**



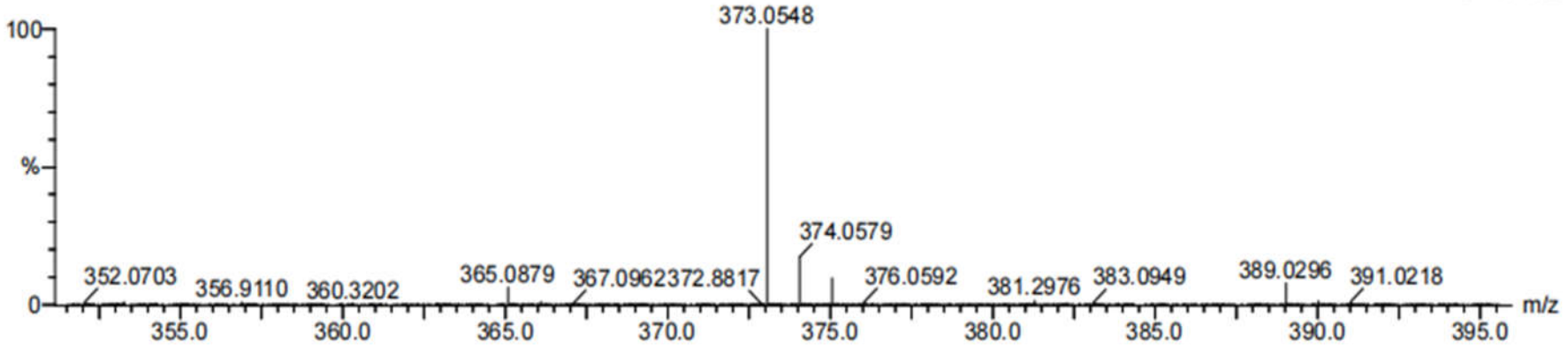
HRMS of **5f.**

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
2940 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 17-17 H: 18-18 N: 0-100 O: 0-100 Na: 0-4 S: 1-4

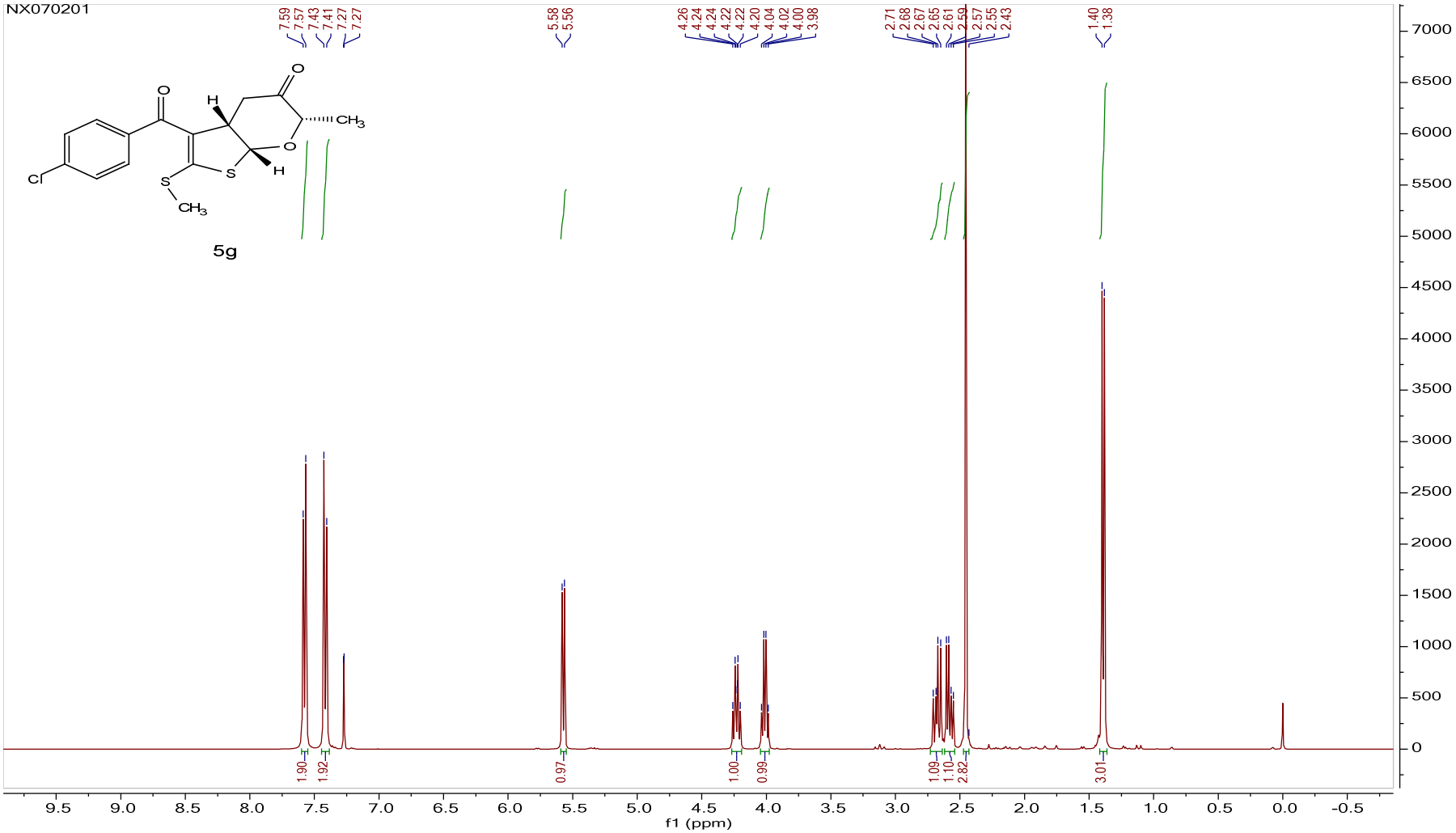
29
240910-5-647-1-5F 21 (0.147)

1: TOF MS ES+
5.14e+005

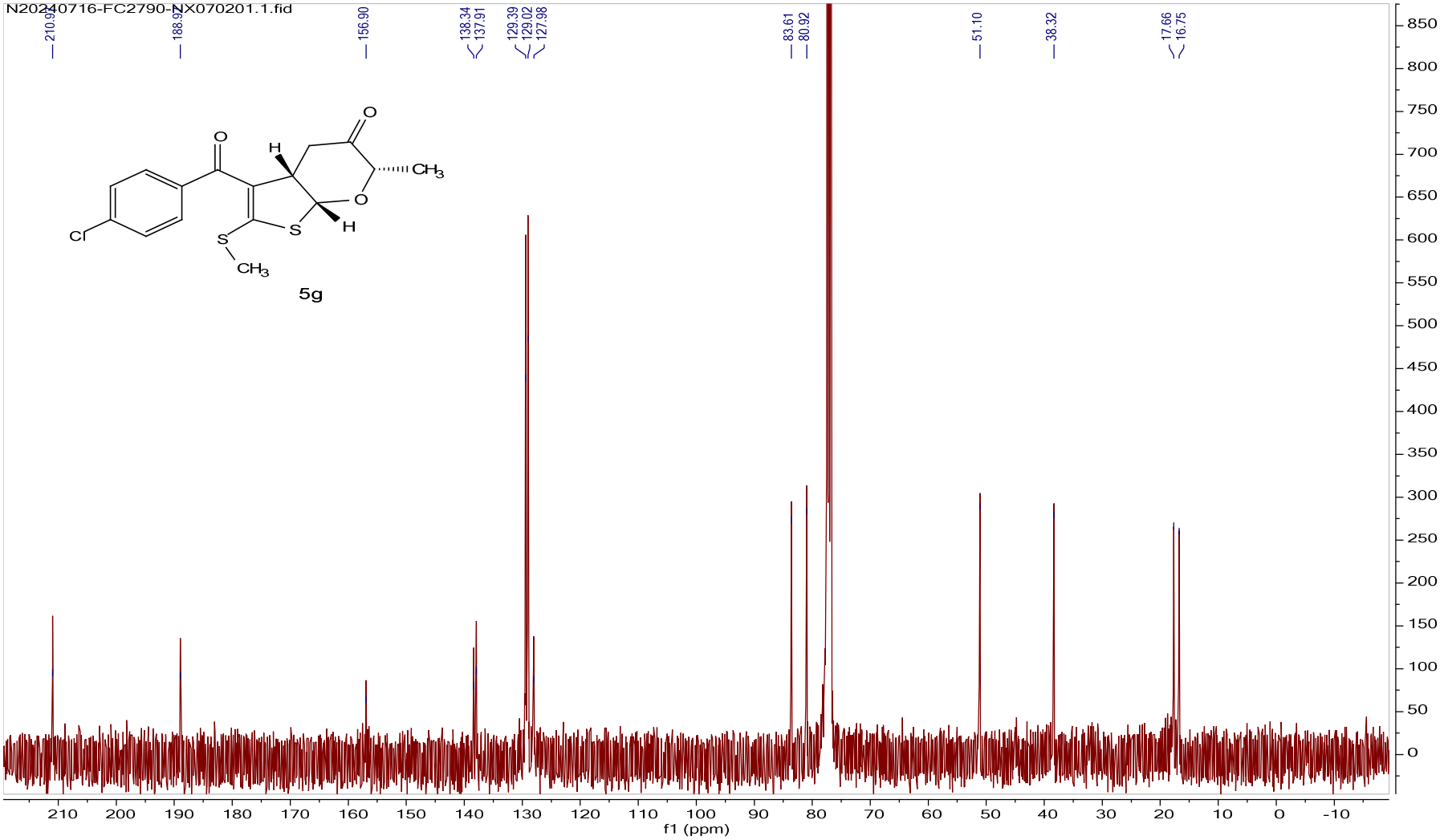


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
373.0548	373.0544	0.4	1.1	8.5	822.0	n/a	n/a	C17 H18 O4 Na S2

^{1}H spectra of **5g.**



^{13}C spectra of **5g.**



HRMS of **5g.**

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

5349 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

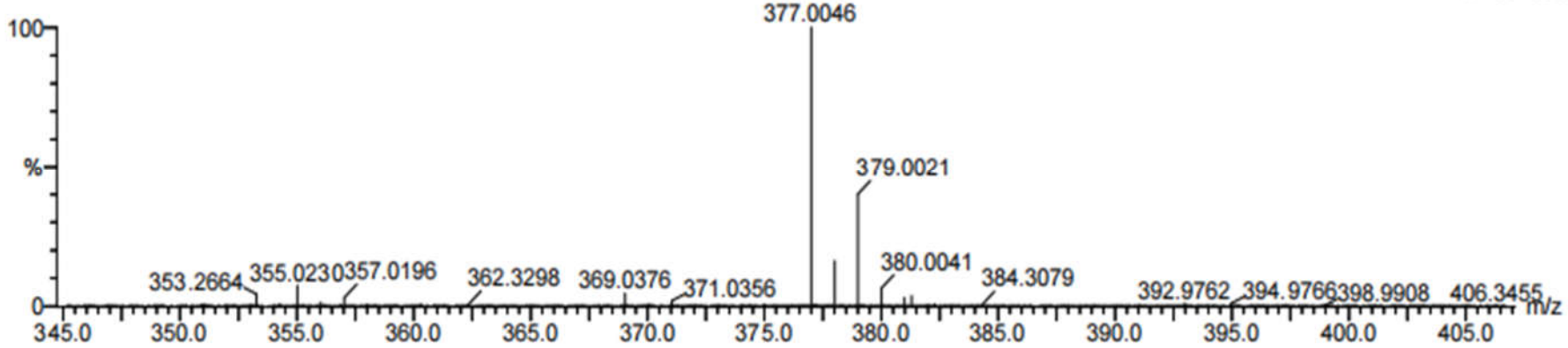
C: 16-16 H: 15-15 N: 0-100 O: 0-100 Na: 0-4 S: 1-4 Cl: 1-3

29

240910-5-647-1-5G 12 (0.100)

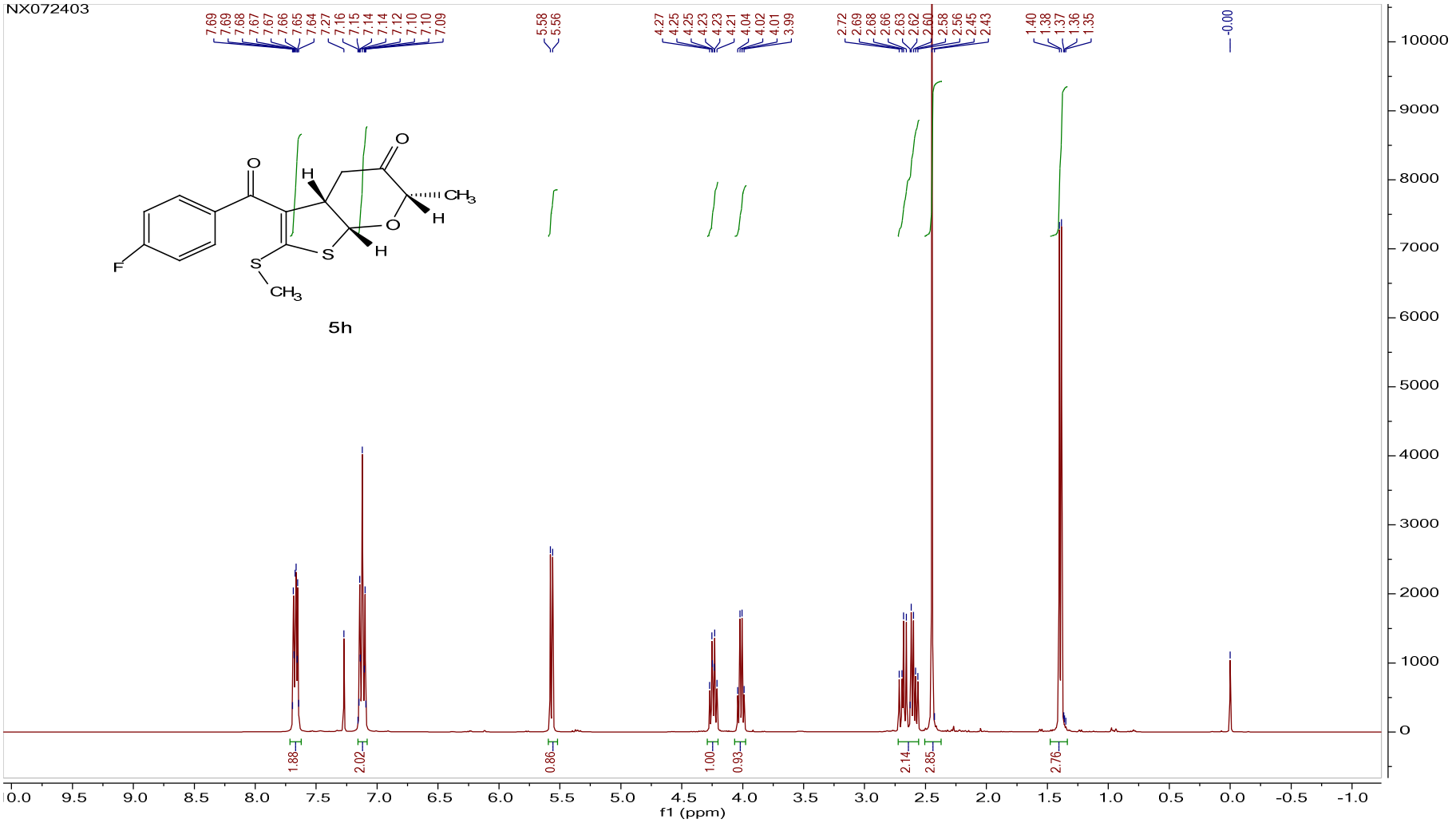
1: TOF MS ES+

9.40e+005

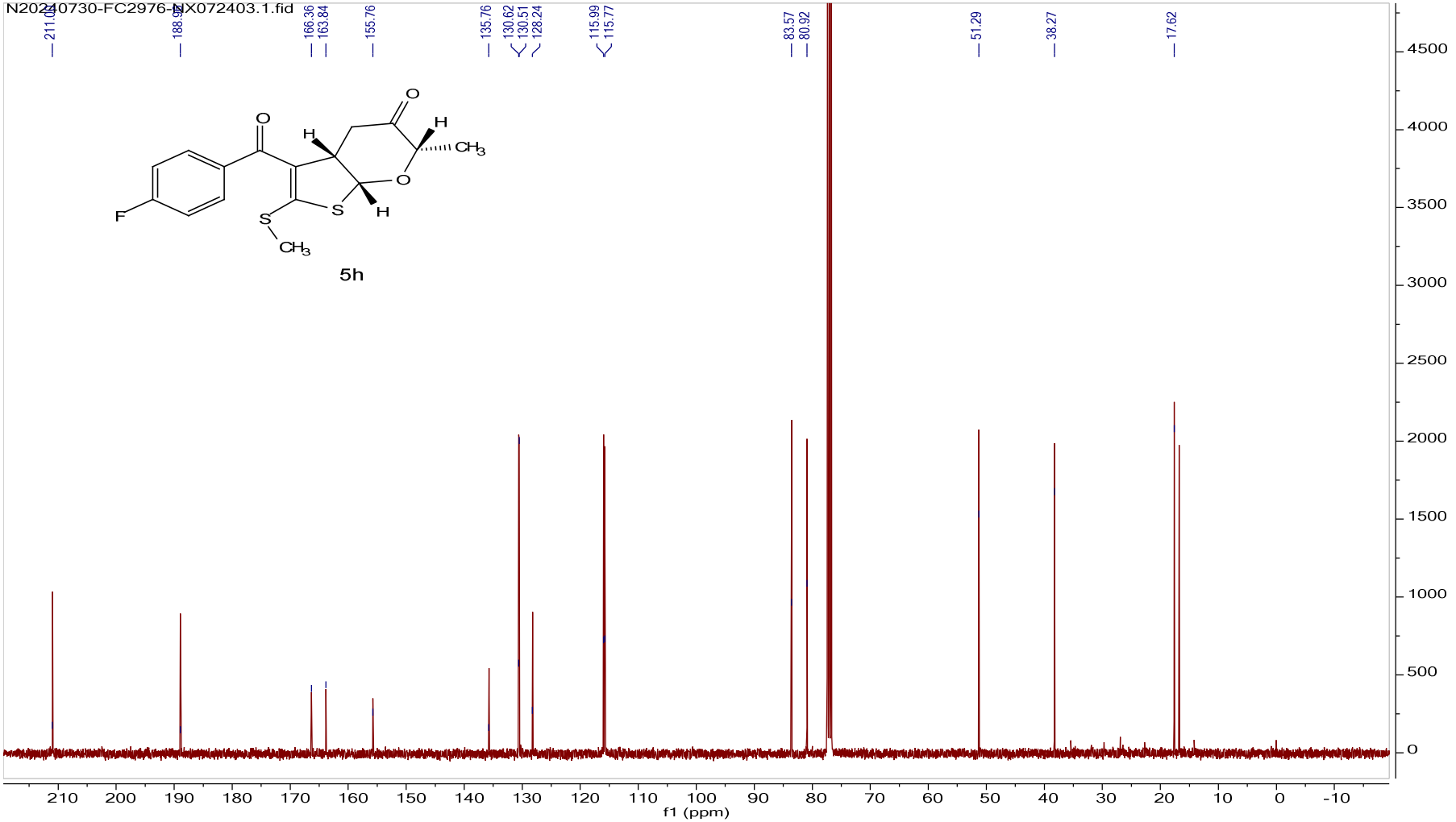


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
377.0046	377.0049	-0.3	-0.8	8.5	1089.0	n/a	n/a	C16 H15 O3 Na S2 Cl

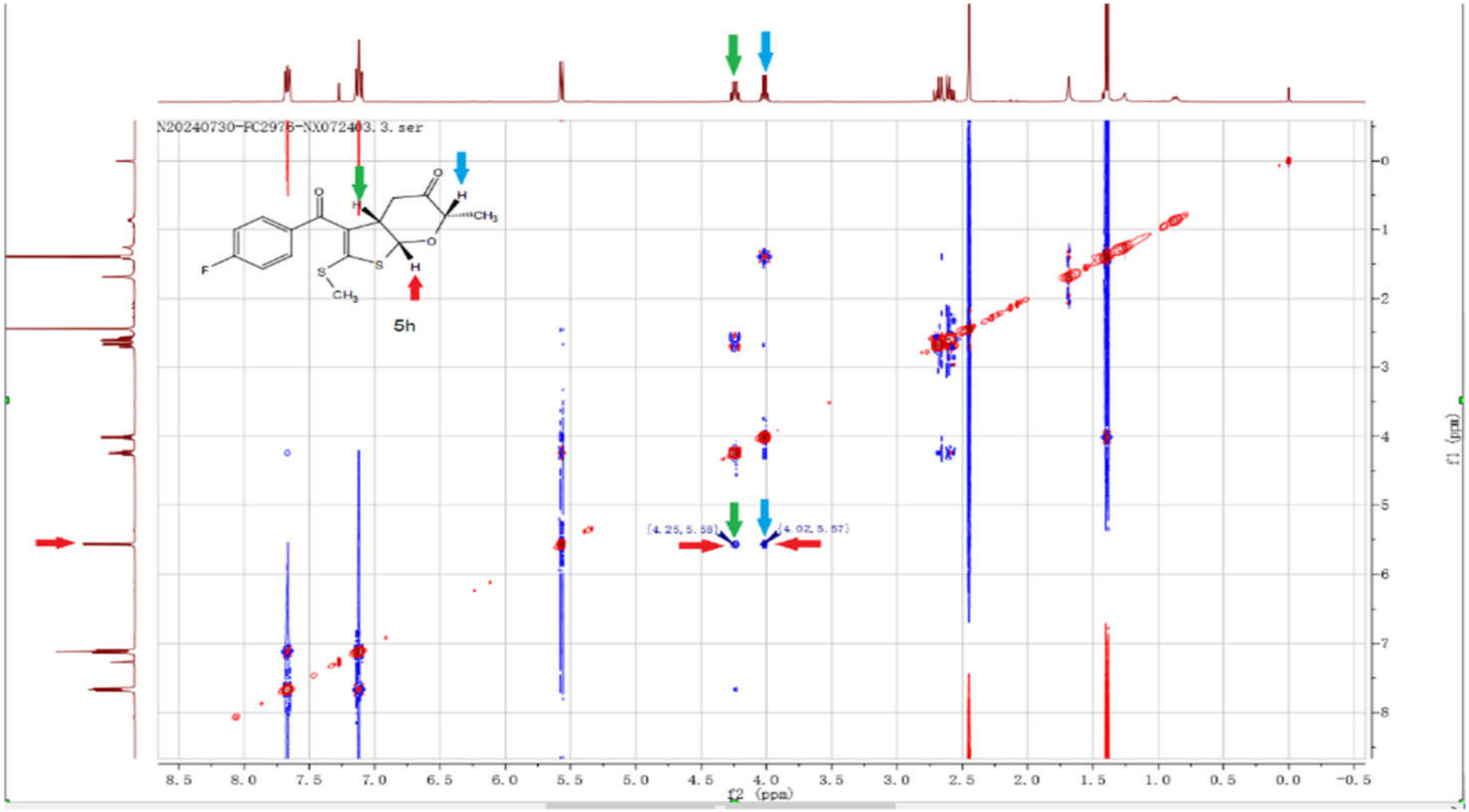
[1]H spectra of **5h.**



^{13}C spectra of **5h.**



NOESY spectra of **5h.**



HRMS of **5h.**

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

2340 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

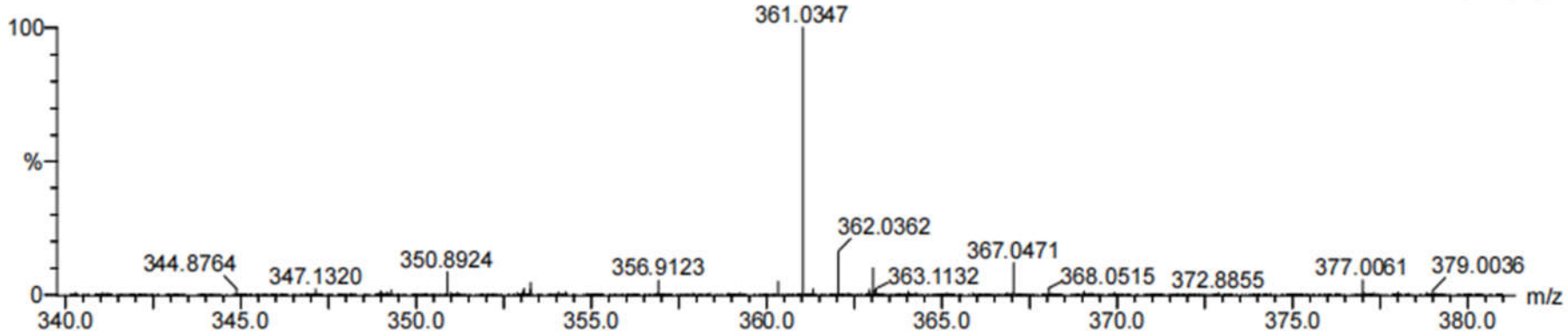
C: 16-16 H: 15-15 N: 0-100 O: 0-100 Na: 0-4 S: 1-4 F: 1-1

29

240910-5-647-1-5H 23 (0.157)

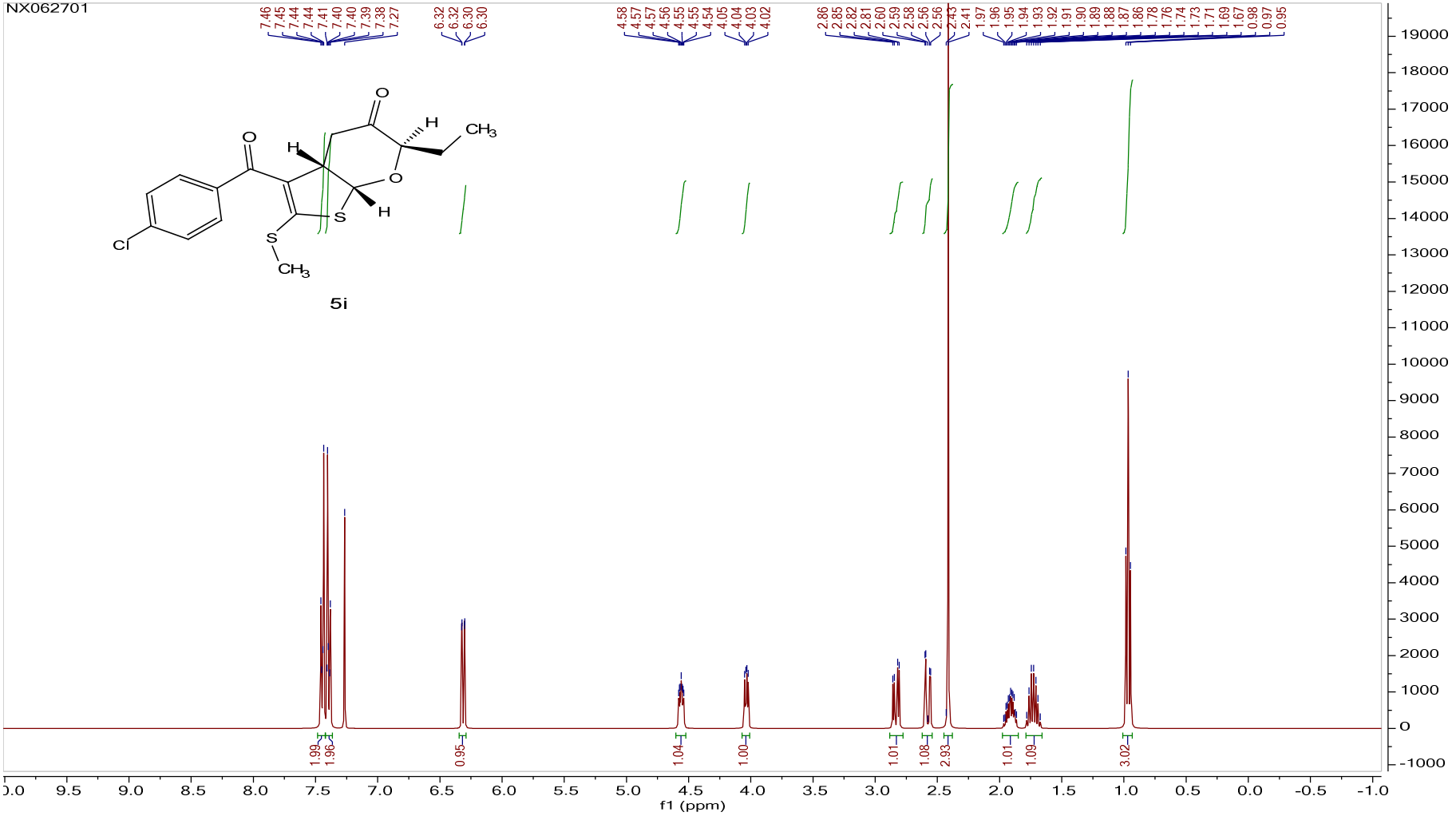
1: TOF MS ES+

9.22e+004

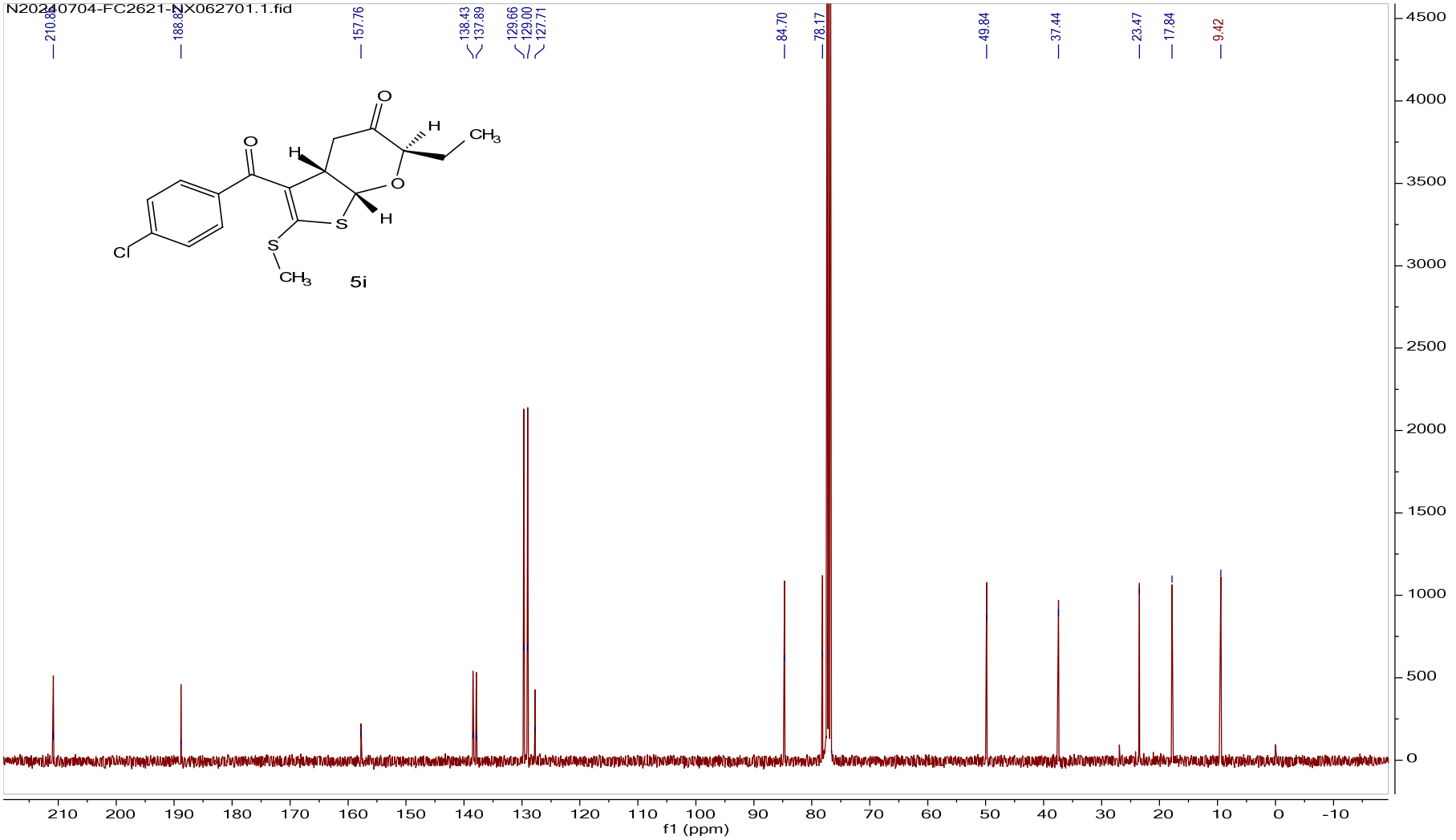


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
361.0347	361.0344	0.3	0.8	8.5	671.5	n/a	n/a	C16 H15 O3 Na S2 F

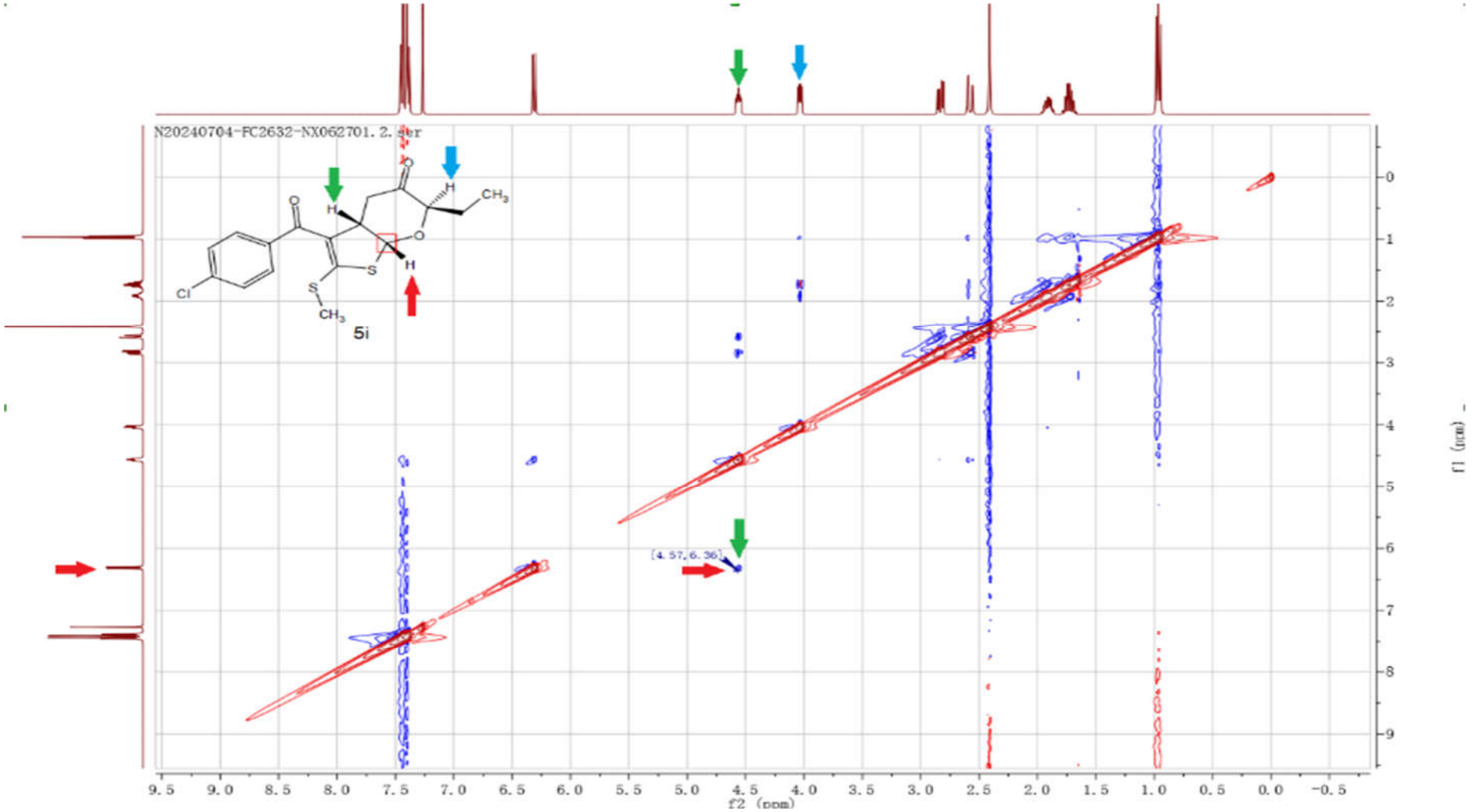
^{1}H spectra of **5i**.



^{13}C spectra of **5i.**



NOSEY spectra of **5i.**



HRMS of **5i.**

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

6092 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

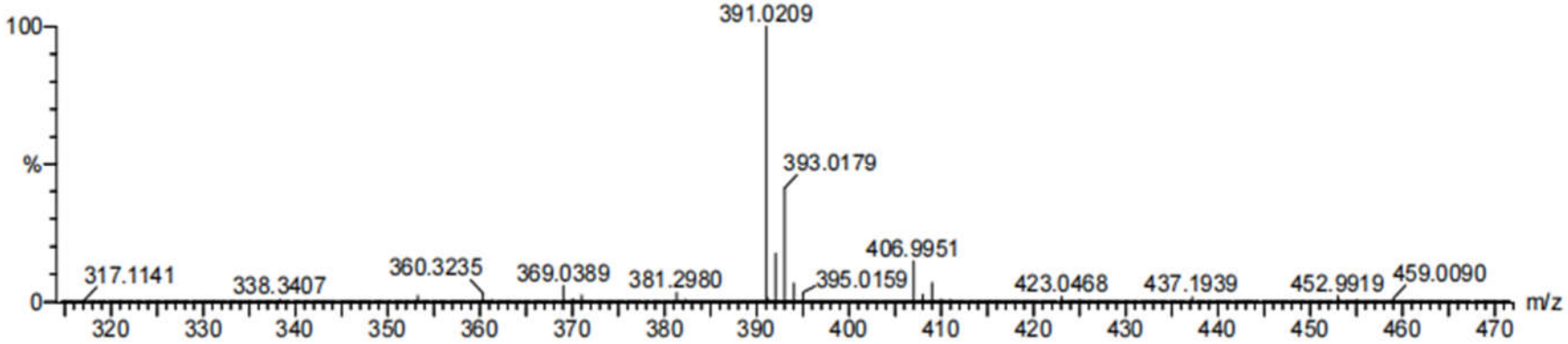
C: 17-17 H: 17-17 N: 0-100 O: 0-100 Na: 0-4 S: 1-4 Cl: 1-3

29

240910-5-647-1-5J 15 (0.115)

1: TOF MS ES+

1.39e+006



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
391.0209	391.0205	0.4	1.0	8.5	1059.6	n/a	n/a	C17 H17 O3 Na S2 Cl

References

[1] (a) S. Borisova, S. Guppi, H. Kim, B. Wu, J. Penn, H. Liu and G. Doherty, *Org. Lett.* 2010, **12**, 5150-5153;
(b) I. Paterson, and G.W. Haslett, *Org. Lett.*, 2013, **15**, 1338-1341.

[2] A. Christoforow, J. Wilke, A. Binici, A. Pahl, C. Ostermann, S. Sievers, and H. Waldmann, *Angew. Chem. Int. Ed.*, 2019, **58**, 14715-14723.

[3] S.T. Bhaskaran, and P. Mathew, *J. Mol. Struct.*, 2022, **1251**, 132071.

[4] L.-R. Wen, W.-K. Yuan, and M. Li, *J. Org. Chem.*, 2015, **80**, 4942-4949.