Electronic Supporting Information

A Regioselective and Sustainable Approach to the Synthesis of Substituted Thieno[2,3-*b*]chromen-4-ones with Pendant Imine Groups *via* Base-Promoted Multicomponent Reaction

Ujjwal Jyoti Goswami,[a] Anjela Xalxo, [a] and Abu Taleb Khan*[a]

[a]*Department of Chemistry, Indian Institute of Technology, Guwahati 781039, Assam, India.*

Content **Page No**

1. General information and methods

Melting points were determined using a melting point apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 MHz, 500 MHz and 600 MHz NMR spectrometers and 100 MHz, 125 MHz and 150 MHz NMR spectrometers, respectively. Tetramethyl silane (TMS) was used as an internal reference; chemical shifts (δ scale) are reported in ppm. ^{1}H NMR spectra are reported following standard conventions for multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet; br s, broad singlet), coupling constants (*J* in Hz), and number of protons. IR spectra were recorded on a Perkin Elmer Spectrum FT-IR spectrophotometer. HRMS data were acquired using an ESI mass spectrometer.

2. Crystal data and structure refinement for compound 4abf

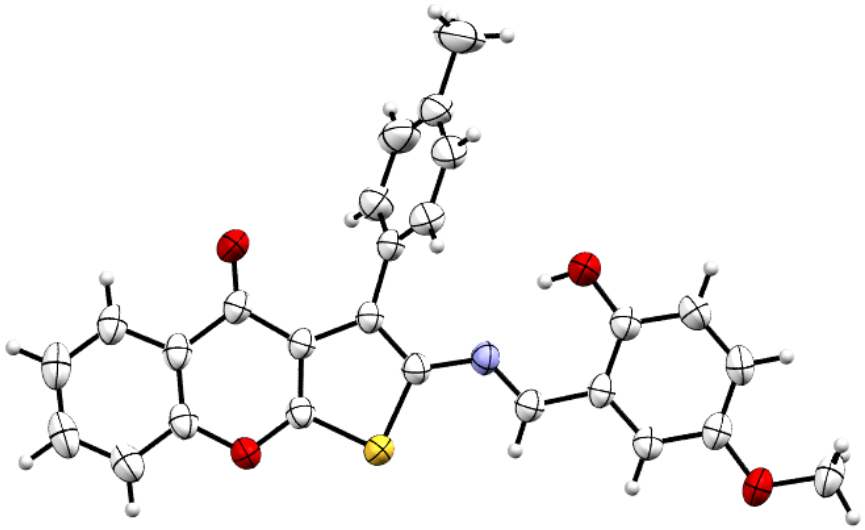


Figure S1. ORTEP Diagrams of compound **4abf**

Table S1. Crystal data and structure refinement for compound **4abf**

Entry	Identification Code	Compound 10a
01	Empirical formula	$C_{26}H_{19}NO_4S$
02	Formula weight	441.48
03	Temperature	295 K
04	Wavelength	0.71073 Å
05	Radiation type	Mo K\α
06	Radiation system	Fine-focus sealed tube
07	Crystal system	Monoclinic
08	Space group	$P2_1/n$
09	Cell length	a 7.1781 (12) Å b 25.329 (4) Å c 11.7749 (18) Å
10	Cell angle	α 90° β 92.840 (4)° γ 90°
11	Cell volume	2138.2 (6) $Å^3$
12	Density	1.371 Mg m^{-3}
13	Completeness to theta	99.6
14	Absorption correction	multi-scan
15	Refinement method	Full-matrix least-squares on F2
16	Index ranges	-8<=h<=8, -31<=k<=31, -14<=l<=14
17	Reflection number	4187

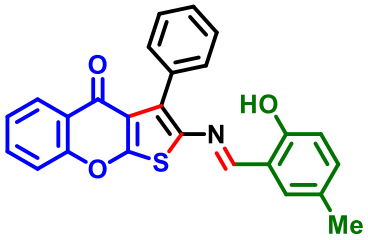
18	Theta range	2.4–27.7°
19	Cell formula units Z	4
20	CCDC no	2418286

3. Experimental Section and Compound Characterization Data

General procedure for synthesis of (*E*)-2-((2-hydroxy-5-methylbenzylidene)amino)-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4aab-gca)

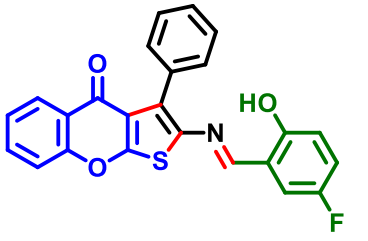
A 10 mL round-bottomed flask is charged with 4-hydroxythiocoumarin **1a** (0.1 mmol), *trans*-β-nitrostyrene **2a** (0.1 mmol) and 4-methyl-2-hydroxybenzaldehyde **3a** (0.05 mmol) in ethanol (0.5 ml). DABCO (40 mol%) and L-proline (10 mol%) are added to the mixture. The mixture is refluxed in a preheated oil bath at 78 °C for 24 hours. As the reaction progresses, the product is precipitated out of the solvent. The progress of the reaction was monitored by thin-layer chromatography (TLC) using 9.5:0.5 EtOAC/hexane as the mobile phase. Once the starting materials are consumed, as indicated by TLC, the reaction mixture is brought to room temperature. The precipitate is filtered and washed multiple times with ethanol to obtain the analytically pure product **4aab.** Other derivatives (**4aac-gca**) are synthesized following the same general protocol.

(*E*)-2-((2-hydroxy-5-methylbenzylidene)amino)-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4aab)



Yellow Solid (17 mg, 82%); **mp** 260-262 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.34 (s, 1H), 8.38 (s, 1H), 8.27 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.69 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.55 – 7.50 (m, 5H), 7.49 – 7.45 (m, 1H), 7.44 – 7.39 (m, 1H), 7.13 – 7.10 (m, 2H), 6.81 (d, *J* = 9.0 Hz, 1H), 2.28 (s, 3H); **^{13}C NMR (125 MHz, CDCl3)** δ 172.02, 165.12, 157.86, 157.82, 156.30, 137.17, 134.52, 133.49, 133.31, 133.15, 131.96, 130.23, 128.57, 128.35, 127.79, 126.90, 125.26, 123.56, 121.14, 118.58, 117.35, 117.13, 20.27; **IR (KBr) ν_{max}/cm^{-1}** 2958, 2924, 1654, 1612, 1575, 1460, 1261; **HRMS (ESI)** calcd for $C_{25}H_{18}NO_3S$ 412.1002 (M + H^+); found 412.0994.

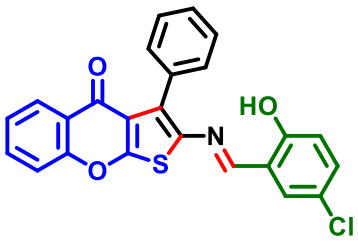
(*E*)-2-((5-fluoro-2-hydroxybenzylidene)amino)-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4aac)



Yellow Solid (17 mg, 83%); **mp** 258-260 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.34 (s, 1H), 8.36 (s, 1H), 8.27 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.70 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.56 – 7.47 (m, 6H), 7.45 – 7.41 (m, 1H), 7.05 – 7.01 (m, 2H), 6.88 – 6.83 (m, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 172.00, 165.41, 156.33, 156.26 (d, *J* = 3.1 Hz), 156.13 (d, *J* = 1.4 Hz), 155.69 (d, *J*

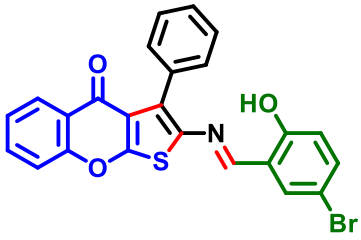
= 238.0 Hz), 136.47, 134.56, 133.63, 132.99, 130.16, 128.51, 127.87, 126.93, 125.38, 123.54, 121.17, 120.58 (d, *J* = 23.5 Hz), 118.74 (d, *J* = 7.4 Hz), 118.51 (d, *J* = 7.4 Hz), 117.39, 116.67 (d, *J* = 23.4 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -124.86; **IR (KBr) ν_{max}/cm^{-1}** 2958, 2924, 1656, 1611, 1459, 1275; **HRMS (ESI)** calcd for $C_{24}H_{15}FNO_3S$ 416.0757 ($M + H^+$); found 416.0725.

(*E*)-2-((5-chloro-2-hydroxybenzylidene)amino)-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4aad)



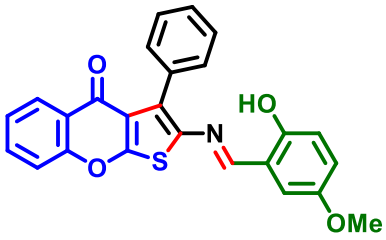
Yellow Solid (18 mg, 82%); **mp** 286-288 ° C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.51 (s, 1H), 8.33 (s, 1H), 8.26 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.69 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.55 – 7.47 (m, 6H), 7.45 – 7.38 (m, 1H), 7.29 (d, *J* = 2.5 Hz, 1H), 7.24 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 171.96, 165.40, 158.41, 156.28, 156.03, 136.41, 134.61, 133.63, 133.13, 132.93, 130.81, 130.14, 128.51, 127.87, 126.89, 125.37, 124.09, 123.49, 121.12, 119.75, 118.88, 117.38; **IR (KBr) ν_{max}/cm^{-1}** 2955, 2924, 1655, 1611, 1458, 1276; **HRMS (ESI)** calcd for $C_{24}H_{15}ClNO_3S$ 432.0461 ($M + H^+$); found 432.0438.

(*E*)-2-((5-bromo-2-hydroxybenzylidene)amino)-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4aae)



Yellow Solid (20 mg, 82%); **mp** 279-280 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.53 (s, 1H), 8.34 (s, 1H), 8.27 (d, *J* = 7.3 Hz, 1H), 7.70 (t, *J* = 7.3 Hz, 1H), 7.55 – 7.49 (m, 5H), 7.46 – 7.40 (m, 2H), 7.37 (dd, *J* = 8.9, 1.9 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 172.00, 165.43, 158.88, 156.30, 155.94, 136.40, 135.93, 134.65, 133.84, 133.65, 132.94, 130.14, 128.52, 127.88, 126.91, 125.39, 123.50, 121.14, 120.41, 119.30, 117.39, 110.95; **IR (KBr) ν_{max}/cm^{-1}** 2957, 2924, 1655, 1612, 1459, 1276; **HRMS (ESI)** calcd for $C_{24}H_{15}BrNO_3S$ 475.9951 ($M + H^+$); found 475.9921.

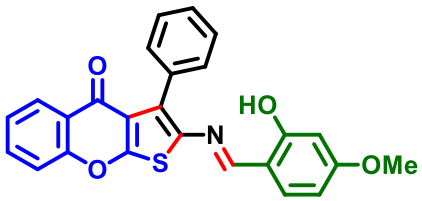
(*E*)-2-((2-hydroxy-5-methoxybenzylidene)amino)-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4aaf)



Yellow solid (17 mg, 79%); **mp** 271-272 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.15 (s, 1H), 8.37 (s, 1H), 8.26 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.68 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.55 – 7.50 (m, 5H), 7.49 – 7.46 (m, 1H), 7.44 – 7.39 (m, 1H), 6.93 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 1H), 6.81 (d, *J* = 3.0 Hz, 1H), 3.78 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 172.00, 165.20, 157.37, 156.31, 154.37, 152.49, 136.99, 133.69, 133.52, 133.13, 130.22, 128.39, 127.82, 126.91, 125.28, 123.57, 121.17, 121.06, 118.56, 118.23, 117.36, 114.73, 55.89; **IR (KBr)**

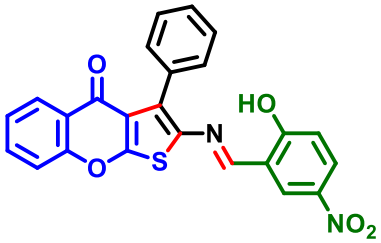
ν_{max}/cm^{-1} 2955, 2924, 1654, 1572, 1459, 1268; **HRMS (ESI)** calcd for $C_{25}H_{18}NO_4S$ 428.0951 (M + Na^+); found 428.0934.

(*E*)-2-((2-hydroxy-4-methoxybenzylidene)amino)-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4aag)



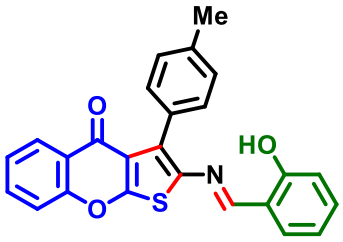
Yellow Solid (16 mg, 77%); **mp** 278-279 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.95 (s, 1H), 8.33 (s, 1H), 8.27 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.67 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.55 – 7.49 (m, 5H), 7.49 – 7.44 (m, 1H), 7.43 – 7.38 (m, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 6.47 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.40 (d, *J* = 2.4 Hz, 1H), 3.79 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 172.02, 164.70, 164.25, 162.30, 157.10, 156.29, 137.46, 133.39, 133.32, 131.84, 130.27, 128.18, 127.75, 126.87, 125.17, 123.56, 121.13, 117.34, 112.85, 107.71, 101.12, 55.46; **IR (KBr) ν_{max}/cm^{-1}** 2955, 2923, 1631, 1600, 1464, 1276; **HRMS (ESI)** calcd for $C_{25}H_{18}NO_4S$ 428.0957 (M + H^+); found 428.0940.

(*E*)-2-((2-hydroxy-5-nitrobenzylidene)amino)-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4aah)



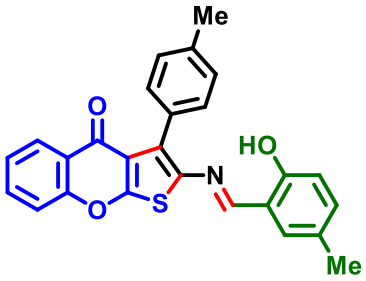
Yellow Solid (19 mg, 86%); **mp** 266-267 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 12.44 (s, 1H), 8.49 (s, 1H), 8.33 (d, *J* = 2.6 Hz, 1H), 8.27 (dd, *J* = 7.9, 1.3 Hz, 1H), 8.19 (dd, *J* = 9.1, 2.7 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.50 (m, 5H), 7.47 – 7.43 (m, 1H), 6.97 (d, *J* = 9.1 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 172.00, 156.33, 155.12, 140.36, 135.54, 133.85, 132.74, 130.05, 128.72, 128.27, 128.00, 127.76, 126.92, 125.55, 123.45, 121.15, 118.32, 118.21, 117.45; **IR (KBr) ν_{max}**/cm^{-1} 3055, 2960, 2924, 1651, 1611, 1461, 1275; **HRMS (ESI)** calcd for $C_{24}H_{15}N_2O_4S$ 443.0696 (M + H^+); found 443.0680.

(*E*)-2-((2-hydroxybenzylidene)amino)-3-(*p*-tolyl)-4*H*-thieno[2,3-*b*]chromen-4-one (4aba)



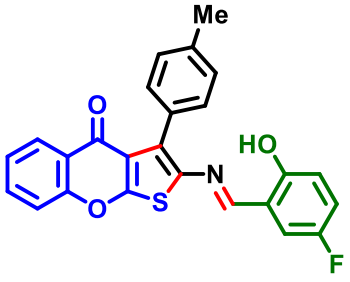
Yellow Solid (15 mg, 73%); **mp** 246-247 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 11.63 (s, 1H), 8.43 (s, 1H), 8.27 (d, *J* = 6.9 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.32 (t, *J* = 9.0 Hz, 4H), 6.92 (dt, *J* = 7.0, 2.7 Hz, 2H), 2.45 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 172.03, 165.21, 159.94, 157.61, 156.29, 138.10, 136.65, 133.70, 133.48, 133.44, 132.01, 130.11, 130.05, 128.57, 126.94, 125.26, 123.61, 121.21, 119.47, 119.00, 117.33, 117.33, 21.53; **IR (KBr) ν_{max}**/cm^{-1} 3053, 2964, 2926, 1656, 1611, 1553, 1461, 1220; **HRMS (ESI)** calcd for $C_{25}H_{18}NO_3S$ 412.1002 (M + H^+); found 412.1002.+

(*E*)-2-((2-hydroxy-5-methylbenzylidene)amino)-3-(*p*-tolyl)-4*H*-thieno[2,3-*b*]chromen-4-one (4abb)



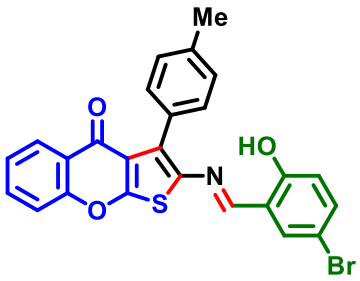
Yellow Solid (16 mg, 74%); **mp** 312-314 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.41 (s, 1H), 8.38 (s, 1H), 8.26 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.68 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.38 (m, 4H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.14 – 7.09 (m, 2H), 6.82 (d, *J* = 9.0 Hz, 1H), 2.44 (s, 3H), 2.29 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 172.00, 165.14, 157.81, 157.68, 156.27, 138.04, 136.86, 134.43, 133.45, 133.43, 131.94, 130.11, 130.08, 128.57, 128.54, 126.92, 125.22, 123.61, 121.20, 118.63, 117.32, 117.09, 21.53, 20.27; **IR (KBr) ν_{max}/cm^{-1}** 2961, 2923, 1654, 1611, 1460, 1276; HRMS (ESI) calcd for $C_{26}H_{20}NO_3S$ 426.1158 (M + H$^+$); found 426.1167.

(*E*)-2-((5-fluoro-2-hydroxybenzylidene)amino)-3-(*p*-tolyl)-4*H*-thieno[2,3-*b*]chromen-4-one (4abc)



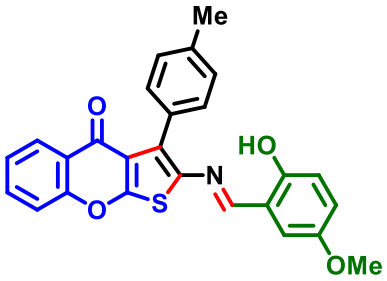
Yellow Solid (16 mg, 75%); **mp** 254-256 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.41 (s, 1H), 8.34 (s, 1H), 8.26 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.86 (dd, *J* = 8.5, 4.4 Hz, 1H), 2.45 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 171.97, 165.42, 156.26, 156.08 (d, *J* = 2.9 Hz), 156.04 (d, *J* = 1.4 Hz), 155.68 (d, *J* = 237.8 Hz), 138.26, 136.15, 134.65, 133.56, 130.04, 129.89, 128.60, 126.91, 125.32, 123.56, 121.18, 120.46 (d, *J* = 23.4 Hz), 118.78 (d, *J* = 7.4 Hz), 118.43 (d, *J* = 7.5 Hz), 117.34, 116.65 (d, *J* = 23.5 Hz), 21.53; ^{19}F NMR (471 MHz, $CDCl_3$) δ -124.86; **IR (KBr) ν_{max}/cm^{-1}** 2958, 2925, 1661, 1612, 1460, 1248; HRMS (ESI) calcd for $C_{25}H_{17}FNO_3S$ 430.0908 (M + H$^+$); found 430.0915.

(*E*)-2-((5-bromo-2-hydroxybenzylidene)amino)-3-(*p*-tolyl)-4*H*-thieno[2,3-*b*]chromen-4-one (4abe)



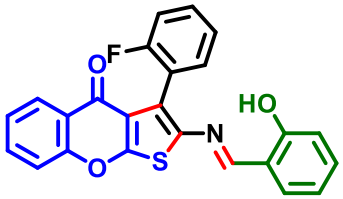
Yellow Solid (18 mg, 75%); **mp** 270-272 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.61 (s, 1H), 8.33 (s, 1H), 8.26 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 2.3 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 3H), 7.37 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 1H), 2.45 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 171.97, 165.45, 158.82, 156.25, 155.77, 138.29, 136.08, 135.84, 134.77, 133.81, 133.59, 130.03, 129.85, 128.61, 126.91, 125.35, 123.54, 121.16, 120.45, 119.24, 117.35, 110.95, 77.25, 77.00, 76.75, 21.54; IR (KBr) ν_{max}/cm^{-1} 2958, 2925, 2854, 1662, 1612, 1460, 1277; HRMS (ESI) calcd for $C_{25}H_{17}BrNO_3S$ 490.0107 (M + H$^+$); found 490.0091.

(*E*)-2-((2-hydroxy-5-methoxybenzylidene)amino)-3-(*p*-tolyl)-4*H*-thieno[2,3-*b*]chromen-4-one (4abf)



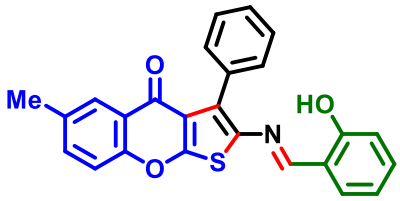
Yellow Solid (16 mg, 72%); **mp** 230-232 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.22 (s, 1H), 8.39 (s, 1H), 8.27 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.69 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.45 – 7.40 (m, 3H), 7.31 (d, *J* = 7.9 Hz, 2H), 6.94 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.82 (d, *J* = 3.0 Hz, 1H), 3.80 (s, 3H), 2.44 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 172.02, 165.24, 157.22, 156.27, 154.27, 152.46, 138.12, 136.65, 133.83, 133.49, 130.08, 130.02, 128.56, 126.93, 125.26, 123.59, 121.20, 120.94, 118.59, 118.19, 117.33, 114.66, 55.88, 21.54; IR (KBr) ν_{max}/cm^{-1} 2962, 2924, 2855, 1653, 1610, 1571, 1458, 1267; HRMS (ESI) calcd for $C_{26}H_{20}NO_4S$ 442.1108 (M + H$^+$); found 442.1109.

(*E*)-3-(2-fluorophenyl)-2-((2-hydroxybenzylidene)amino)-4*H*-thieno[2,3-*b*]chromen-4-one (4ada)



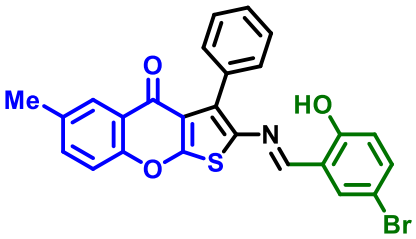
Yellow Solid (15 mg, 72%); **mp** 239-240 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 11.54 (s, 1H), 8.45 (s, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 6.9 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 9.3 Hz, 1H), 6.94 – 6.90 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 171.99, 164.64, 160.21 (d, *J* = 247.5 Hz), 160.14, 158.28, 156.46, 137.91, 133.65 (d, *J* = 19.7 Hz), 132.17, 131.82 (d, *J* = 2.9 Hz), 130.57 (d, *J* = 8.3 Hz), 126.85, 126.55, 125.32, 123.74 (d, *J* = 3.4 Hz), 123.41, 121.56, 121.37 (d, *J* = 16.0 Hz), 119.55, 118.82, 117.40 (d, *J* = 11.7 Hz), 115.55 (d, *J* = 21.7 Hz); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -112.68; **IR (KBr) ν_{max}**/cm^{-1} 2963, 2924, 2853, 1659, 1615, 1553, 1461, 1275; **HRMS (ESI)** calcd for $C_{24}H_{15}FNO_3S$ 416.0757 (M + H$^+$); found 416.0751.

(*E*)-2-((2-hydroxybenzylidene)amino)-6-methyl-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4baa)



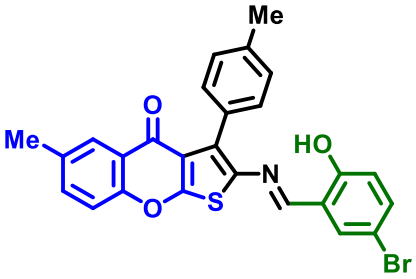
Yield Solid (17 mg, 81%); **mp** 233-235 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.55 (s, 1H), 8.37 (s, 1H), 8.02 (d, *J* = 1.0 Hz, 1H), 7.54 – 7.50 (m, 3H), 7.50 – 7.48 (m, 1H), 7.47 – 7.46 (m, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.30 (ddd, *J* = 7.3, 3.8, 1.6 Hz, 2H), 6.92 – 6.87 (m, 2H), 2.41 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 172.11, 165.14, 159.90, 157.51, 154.56, 136.76, 135.22, 134.65, 133.55, 133.42, 133.13, 131.98, 130.23, 128.33, 127.76, 126.24, 123.13, 120.95, 119.43, 118.93, 117.30, 117.07, 20.91; **IR (KBr) ν_{max}/cm^{-1}** 2961, 2925, 2856, 1660, 1618, 1471, 1276; **HRMS (ESI)** calcd for $C_{25}H_{18}NO_3S$ 412.1002 (M + H$^+$); found 412.1005.

(*E*)-2-((5-bromo-2-hydroxybenzylidene)amino)-6-methyl-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4bae)



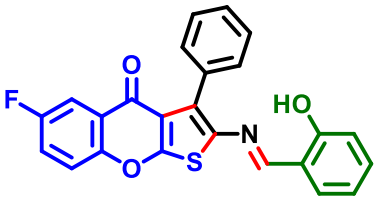
Yellow Solid (21 mg, 85%); **mp** 274-275 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.52 (s, 1H), 8.26 (s, 1H), 8.01 (d, *J* = 1.0 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 2H), 7.50 (s, 2H), 7.49 – 7.46 (m, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.35 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 1H), 2.41 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 172.08, 165.41, 158.82, 155.76, 154.57, 136.23, 135.84, 135.35, 134.76, 134.65, 133.80, 132.97, 130.17, 128.46, 127.83, 126.27, 123.10, 120.97, 120.41, 119.25, 117.09, 110.93, 20.93; **IR (KBr) ν_{max}/cm^{-1}** 2960, 2924, 1656, 1616, 1469, 1276; **HRMS (ESI)** calcd for $C_{25}H_{17}BrNO_3S$ 490.0107 (M + H^+); found 490.0080.

(*E*)-2-((5-bromo-2-hydroxybenzylidene)amino)-6-methyl-3-(*p*-tolyl)-4*H*-thieno[2,3-*b*]chromen-4-one (4bbe)



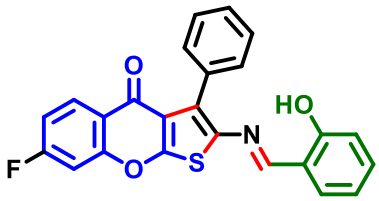
Yellow Solid (19 mg, 76%); **mp** 272-273 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.61 (s, 1H), 8.31 (s, 1H), 8.03 (s, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.43 (dd, *J* = 10.7, 1.6 Hz, 3H), 7.40 – 7.36 (m, 2H), 7.30 (d, *J* = 7.7 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 1H), 2.44 (s, 3H), 2.44 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 172.10, 165.46, 158.83, 155.65, 154.59, 138.24, 135.93, 135.79, 135.31, 134.86, 134.71, 133.80, 130.07, 129.93, 128.59, 126.34, 123.22, 121.07, 120.51, 119.25, 117.08, 110.94, 21.53, 20.96; **IR (KBr) ν_{max}**/cm^{-1} 2961, 2924, 1658, 1616, 1470, 1275; **HRMS (ESI)** calcd for $C_{26}H_{19}BrNO_3S$ 504.0264 (M + H^+); found 504.0236.

(*E*)-6-fluoro-2-((2-hydroxybenzylidene)amino)-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4caa)



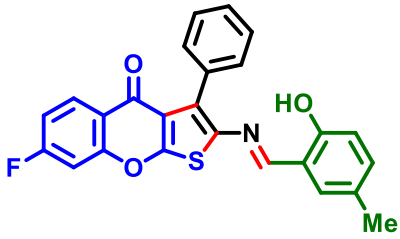
Yellow Solid (13 mg, 63%); **mp** 237-239 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.51 (s, 1H), 8.41 (s, 1H), 7.89 (dd, *J* = 8.2, 3.0 Hz, 1H), 7.56 – 7.47 (m, 6H), 7.43 – 7.36 (m, 1H), 7.34 – 7.28 (m, 2H), 6.93 – 6.88 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 171.09, 165.39, 160.00, 159.52 (d, *J* = 246.9 Hz), 157.98, 152.40 (d, *J* = 1.7 Hz), 137.24, 133.63, 133.20, 132.90, 132.07, 130.19, 128.49, 127.85, 124.81 (d, *J* = 7.1 Hz), 121.53 (d, *J* = 25.6 Hz), 120.52, 119.50, 119.35 (d, *J* = 8.1 Hz), 118.86, 117.37, 111.87 (d, *J* = 24.2 Hz); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -114.87; **IR (KBr) ν_{max}/cm^{-1}** 3060, 2956, 2925, 1659, 1622, 1469, 1277; **HRMS (ESI)** calcd for $C_{24}H_{15}FNO_3S$ 416.0757 (M + H^+); found 416.0734.

(*E*)-7-fluoro-2-((2-hydroxybenzylidene)amino)-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4daa)



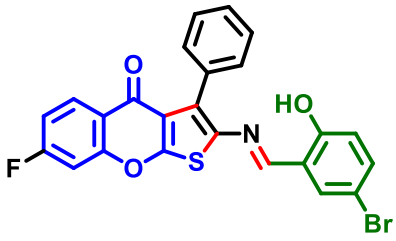
Yellow Solid (14 mg, 65%); **mp** 278-280 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.52 (s, 1H), 8.44 (s, 1H), 8.28 (dd, *J* = 8.8, 6.3 Hz, 1H), 7.54 – 7.45 (m, 5H), 7.35 – 7.30 (m, 2H), 7.23 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.15 (td, *J* = 8.7, 2.3 Hz, 1H), 6.95 – 6.89 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 171.11, 165.40 (d, *J* = 255.8 Hz), 165.02, 160.04, 157.96, 157.10 (d, *J* = 13.2 Hz), 137.26, 133.64, 133.41, 132.96, 132.08, 130.19, 129.33 (d, *J* = 10.6 Hz), 128.47, 127.85, 121.18, 120.39 (d, *J* = 2.4 Hz), 119.50, 118.88, 117.40, 113.93 (d, *J* = 22.5 Hz), 104.34 (d, *J* = 25.9 Hz); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -102.77; **IR (KBr) ν_{max}**/cm^{-1} 3057, 2958, 2925, 2854, 1662, 1615, 1567, 1436, 1277; **HRMS (ESI)** calcd for $C_{24}H_{15}FNO_3S$ 416.0757 (M + H$^+$); found 416.0727.

(*E*)-7-fluoro-2-((2-hydroxy-5-methoxybenzylidene)amino)-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4dab)



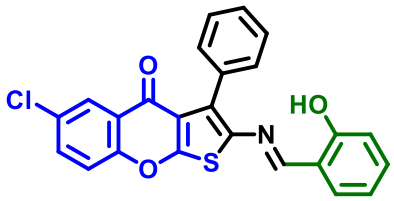
Yellow Solid (14 mg, 66%); **mp** 266-267 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 11.30 (s, 1H), 8.26 (dd, *J* = 8.4, 6.5 Hz, 1H), 7.53 – 7.43 (m, 5H), 7.20 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.16 – 7.10 (m, 2H), 7.09 (s, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 2.27 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 171.07, 165.34 (d, *J* = 255.8 Hz), 164.94, 157.97, 157.85, 157.03 (d, *J* = 13.2 Hz), 137.46, 134.62, 133.08, 132.96, 131.98, 130.19, 129.26 (d, *J* = 10.6 Hz), 128.60, 128.41, 127.81, 121.10, 120.33 (d, *J* = 2.6 Hz), 118.46, 117.11, 113.86 (d, *J* = 22.5 Hz), 104.30 (d, *J* = 26.0 Hz), 20.24; **IR (KBr) ν_{max}**/cm^{-1} 3062, 2961, 2925, 2860, 1660, 1615, 1576, 1434, 1278; **HRMS (ESI)** calcd for $C_{25}H_{17}FNO_3S$ 430.0908 (M + H$^+$); found 430.0911.

(*E*)-2-((5-bromo-2-hydroxybenzylidene)amino)-7-fluoro-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4dae)



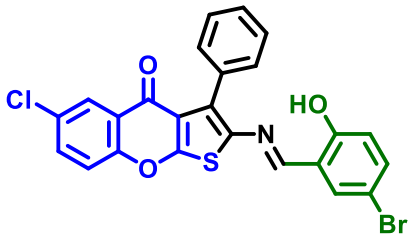
Yellow Solid (17 mg, 68%); **mp** 284-285 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 11.49 (s, 1H), 8.34 (s, 1H), 8.30 – 8.24 (m, 1H), 7.54 – 7.47 (m, 5H), 7.45 (s, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 8.7 Hz, 1H), 7.15 (t, *J* = 8.2 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 171.08, 165.48 (d, *J* = 255.8 Hz), 165.30, 158.96, 157.12 (d, *J* = 14.0 Hz), 156.20, 136.73, 136.08, 134.52, 133.91, 132.81, 130.14, 129.37 (d, *J* = 10.6 Hz), 128.62, 127.93, 121.20, 120.37, 119.35, 114.05 (d, *J* = 22.9 Hz), 111.01, 104.41 (d, *J* = 25.9 Hz); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -102.48; **IR (KBr) ν_{max}**/cm^{-1} 3053, 2961, 2924, 1658, 1615, 1571, 1435, 1276; **HRMS (ESI)** calcd for $C_{24}H_{14}BrFNO_3S$ 493.9856 (M + H$^+$); found 493.9830.

(*E*)-6-chloro-2-((2-hydroxybenzylidene)amino)-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4eaa)



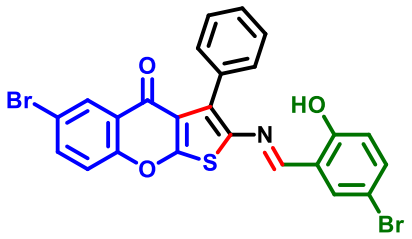
Yellow Solid (13 mg, 60%); **mp** 224-226 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.52 (s, 1H), 8.44 (s, 1H), 8.22 (d, *J* = 2.6 Hz, 1H), 7.63 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.52 – 7.50 (m, 4H), 7.49 (t, *J* = 2.5 Hz, 1H), 7.32 (td, *J* = 6.7, 5.9, 1.7 Hz, 3H), 6.94 – 6.88 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 170.78, 165.24, 160.03, 158.09, 154.58, 137.33, 133.69, 133.65, 133.28, 132.83, 132.10, 131.21, 130.20, 128.51, 127.86, 126.34, 124.56, 121.00, 119.53, 119.04, 118.86, 117.40; **IR (KBr) ν_{max}/cm^{-1}** 3053, 2963, 2926, 2855, 1661, 1611, 1465, 1277; **HRMS (ESI)** calcd for $C_{24}H_{15}ClNO_3S$ 432.0461 (M + H^+); found 432.0436.

(*E*)-2-((5-bromo-2-hydroxybenzylidene)amino)-6-chloro-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4eae)



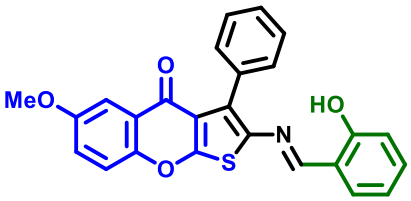
Yellow Solid (17 mg, 65%); **mp** 227-229 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.49 (s, 1H), 8.34 (s, 1H), 8.21 (d, *J* = 2.5 Hz, 1H), 7.63 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.53 – 7.47 (m, 6H), 7.45 (d, *J* = 2.4 Hz, 1H), 7.38 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.72, 165.47, 158.93, 156.31, 154.56, 136.77, 136.10, 134.35, 133.91, 133.76, 132.66, 131.33, 130.13, 128.64, 127.92, 126.34, 124.52, 120.99, 120.32, 119.33, 119.06, 111.01; **IR (KBr) ν_{max}/cm^{-1}** 3055, 2957, 2924, 2854, 1658, 1604, 1460, 1275; **HRMS (ESI)** calcd for $C_{24}H_{14}BrClNO_3S$ 509.9561 (M + H^+); found 509.9530.

(*E*)-6-bromo-2-((5-bromo-2-hydroxybenzylidene)amino)-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4fae)



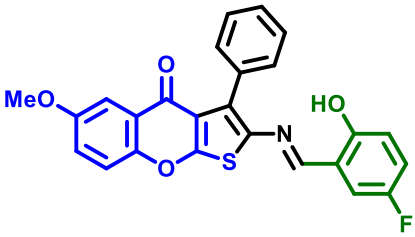
Yellow Solid (17 mg, 62%); **mp** 285-287 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.49 (s, 1H), 8.36 (d, *J* = 2.4 Hz, 1H), 8.33 (s, 1H), 7.77 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.50 (s, 5H), 7.44 (d, *J* = 2.4 Hz, 1H), 7.43 (d, *J* = 9.0 Hz, 1H), 7.38 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 170.59, 165.43, 158.92, 156.33, 155.02, 136.78, 136.54, 136.11, 134.35, 133.91, 132.63, 130.13, 129.53, 128.64, 127.91, 124.85, 121.03, 120.31, 119.33, 119.29, 118.73, 111.01; **IR (KBr) ν_{max}/cm^{-1}** 3060, 2956, 2925, 2854, 1656, 1611, 1464, 1277; **HRMS (ESI)** calcd for $C_{24}H_{14}Br_2NO_3S$ 553.9056 (M + H^+); found 553.9042.

(*E*)-2-((2-hydroxybenzylidene)amino)-6-methoxy-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4gaa)



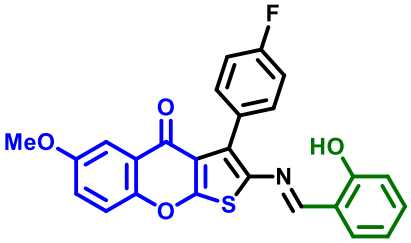
Yellow Solid (18 mg, 86%); **mp** 274-275 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.58 (s, 1H), 8.42 (s, 1H), 7.65 (d, *J* = 3.1 Hz, 1H), 7.54 – 7.51 (m, 4H), 7.49 – 7.45 (m, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 3.1 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.96, 165.15, 159.99, 157.66, 156.95, 151.14, 136.87, 133.51, 133.48, 133.19, 132.01, 130.22, 128.33, 127.78, 124.11, 123.24, 120.54, 119.46, 118.97, 118.69, 117.36, 106.25, 55.85; **IR (KBr) ν_{max}/cm^{-1}** 3059, 2959, 2925, 2854, 1653, 1618, 1473, 1276; **HRMS (ESI)** calcd for $C_{25}H_{18}NO_4S$ 428.0951 ($M + H^+$); found 428.0950.

(*E*)-2-((5-fluoro-2-hydroxybenzylidene)amino)-6-methoxy-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4gac)



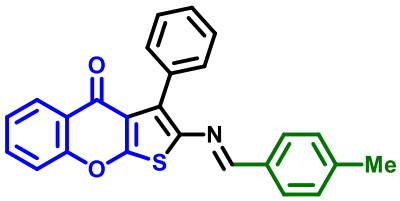
Yellow Solid (19 mg, 87%); **mp** 268-269 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.35 (s, 1H), 8.33 (s, 1H), 7.65 (d, *J* = 3.1 Hz, 1H), 7.52 (s, 2H), 7.51 (s, 2H), 7.48 (t, *J* = 2.2 Hz, 1H), 7.45 (s, 1H), 7.28 (d, *J* = 3.1 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.85 (dd, *J* = 9.0, 4.4 Hz, 1H), 3.85 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 171.95, 165.37, 156.97, 156.15 (d, *J* = 3.0 Hz), 156.08 (d, *J* = 1.3 Hz), 155.67 (d, *J* = 237.8 Hz), 151.12, 136.37, 134.46, 133.03, 130.15, 128.45, 127.82, 124.05, 123.34, 120.63, 120.48 (d, *J* = 8.2 Hz), 118.76, 118.71, 118.48 (d, *J* = 7.5 Hz), 116.65 (d, *J* = 23.5 Hz), 106.19, 55.85; ^{19}F NMR (471 MHz, $CDCl_3$) δ -124.85; **IR (KBr) ν_{max}/cm^{-1}** 3059, 2958, 2925, 2853, 1655, 1613, 1471, 1274; **HRMS (ESI)** calcd for $C_{25}H_{17}FNO_4S$ 446.0857 ($M + H^+$); found 446.0851.

(*E*)-3-(4-fluorophenyl)-2-((2-hydroxybenzylidene)amino)-6-methoxy-4*H*-thieno[2,3-*b*]chromen-4-one (4gca)



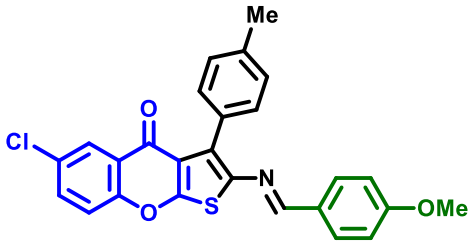
Yellow Solid (18 mg, 81%); **mp** 255-256 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.57 (s, 1H), 8.42 (s, 1H), 7.64 (d, *J* = 3.1 Hz, 1H), 7.51 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.46 (d, *J* = 9.1 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.28 (d, *J* = 3.2 Hz, 1H), 7.20 (t, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 2H), 3.86 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 172.04, 165.10, 162.67 (d, *J* = 247.9 Hz), 159.96, 157.98, 156.97, 151.09, 137.02, 133.66, 132.13 (d, *J* = 8.4 Hz), 132.08, 128.97 (d, *J* = 3.4 Hz), 123.98, 123.36, 120.34, 119.56, 118.85, 118.71, 117.31, 114.87 (d, *J* = 21.7 Hz), 106.09, 55.84; ^{19}F NMR (471 MHz, $CDCl_3$) δ -113.06; **IR (KBr) ν_{max}/cm^{-1}** 2960, 2925, 2853, 1650, 1612, 1473, 1276; **HRMS (ESI)** calcd for $C_{25}H_{17}FNO_4S$ 446.0857 ($M + H^+$); found 446.0852.

(*E*)-2-((4-methylbenzylidene)amino)-3-phenyl-4*H*-thieno[2,3-*b*]chromen-4-one (4abi)



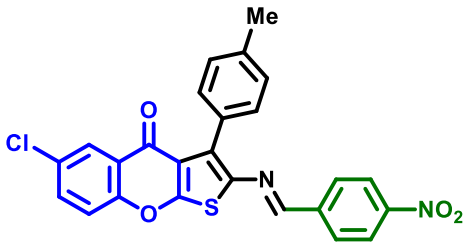
Yellow Solid (15 mg, 74%); **mp** 251-253 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.35 (s, 1H), 8.29 (d, *J* = 7.4 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.60 (dd, *J* = 18.7, 7.1 Hz, 4H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.44 – 7.38 (m, 2H), 7.20 (d, *J* = 7.1 Hz, 2H), 2.37 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 172.09, 165.35, 156.21, 155.87, 142.12, 139.48, 133.35, 133.25, 133.07, 133.01, 131.49, 129.53, 128.98, 127.61, 126.88, 125.04, 123.65, 121.09, 117.28, 21.65; **IR (KBr) ν_{max}/cm^{-1}** 2956, 2925, 2853, 1662, 1605, 1473, 1267; **HRMS (ESI)** calcd for $C_{25}H_{18}NO_2S$ 396.1053 (M + H^+); found 396.1050.

(*E*)-6-chloro-2-((4-methoxybenzylidene)amino)-3-(*p*-tolyl)-4*H*-thieno[2,3-*b*]chromen-4-one (4ebj)



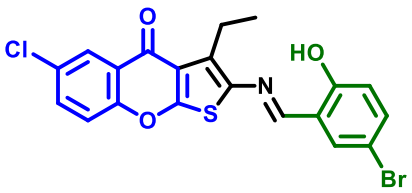
Yellow Solid (14 mg, 62%); **mp** 235-236 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.30 (s, 1H), 8.22 (d, *J* = 2.5 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 2H), 7.60 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 3H), 7.28 (s, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H), 2.45 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 170.80, 165.24, 162.43, 155.38, 154.43, 139.74, 137.37, 133.27, 131.32, 130.80, 130.15, 128.56, 127.73, 126.31, 124.69, 120.96, 118.93, 114.27, 55.41, 21.48; **IR (KBr) ν_{max}/cm^{-1}** 3069, 2954, 2924, 2852, 1676, 1603, 1462, 1257; **HRMS (ESI)** calcd for $C_{26}H_{19}ClNO_3S$ 460.0769 (M + H^+); found 460.0760.

(*E*)-6-chloro-2-((4-nitrobenzylidene)amino)-3-(*p*-tolyl)-4*H*-thieno[2,3-*b*]chromen-4-one (4ebk)



Yellow Solid (19 mg, 81%); **mp** 241-243 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.41 (s, 1H), 8.26 (d, *J* = 8.6 Hz, 2H), 8.23 (d, *J* = 2.4 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 2H), 7.63 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.49 (d, *J* = 8.9 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 2.47 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 170.78, 166.43, 154.48, 152.30, 149.04, 141.01, 138.20, 136.67, 133.69, 131.26, 129.67, 129.35, 127.90, 126.42, 124.65, 124.07, 121.06, 119.00, 21.51; **IR (KBr) ν_{max}/cm^{-1}** 3092, 2957, 2924, 2855, 1660, 1605, 1520, 1455, 1344; **HRMS (ESI)** calcd for $C_{25}H_{16}ClN_2O_4S$ 475.0514 (M + H^+); found 475.0513.

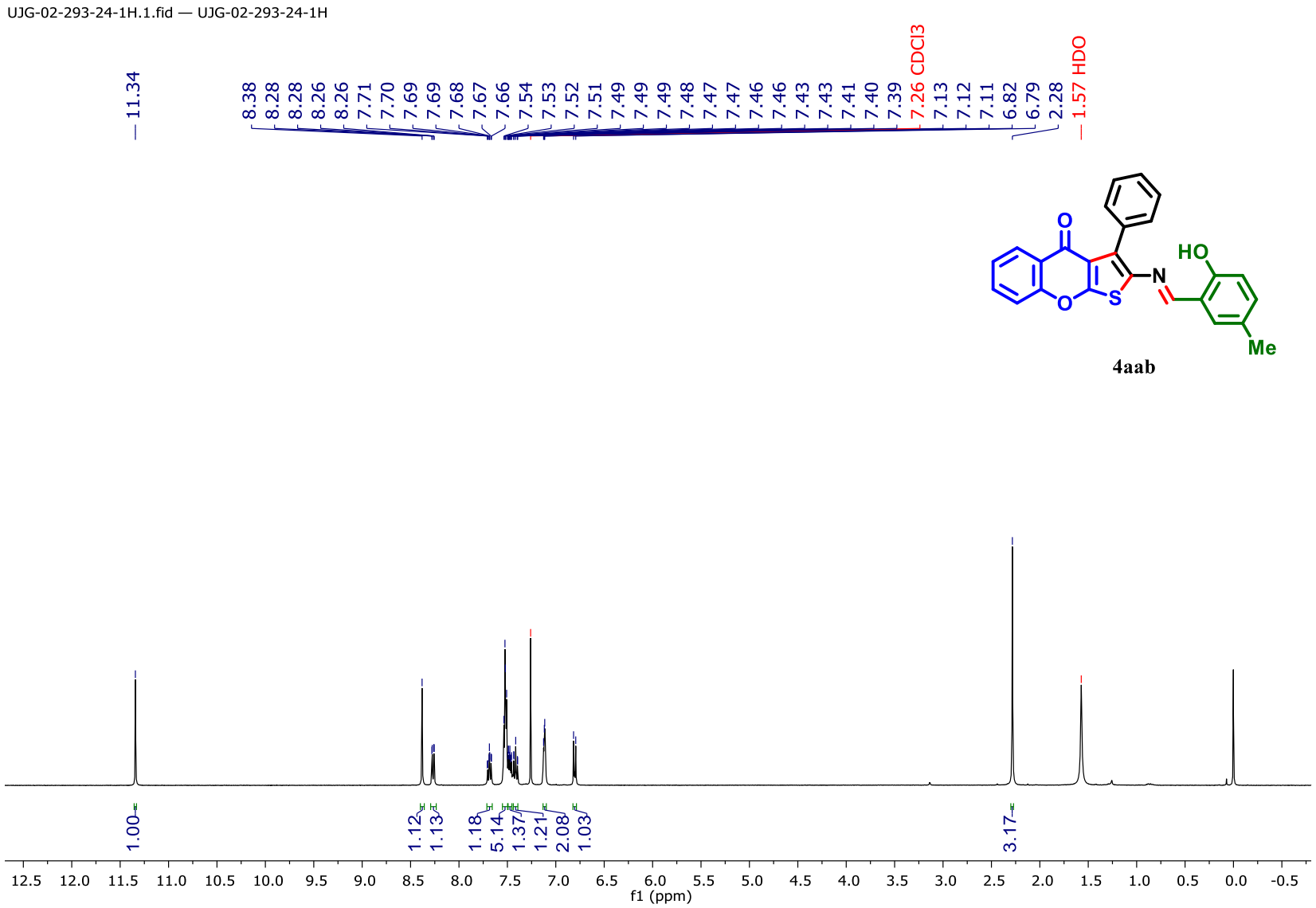
(*E*)-2-((5-bromo-2-hydroxybenzylidene)amino)-6-chloro-3-ethyl-4*H*-thieno[2,3-*b*]chromen-4-one (4eee)



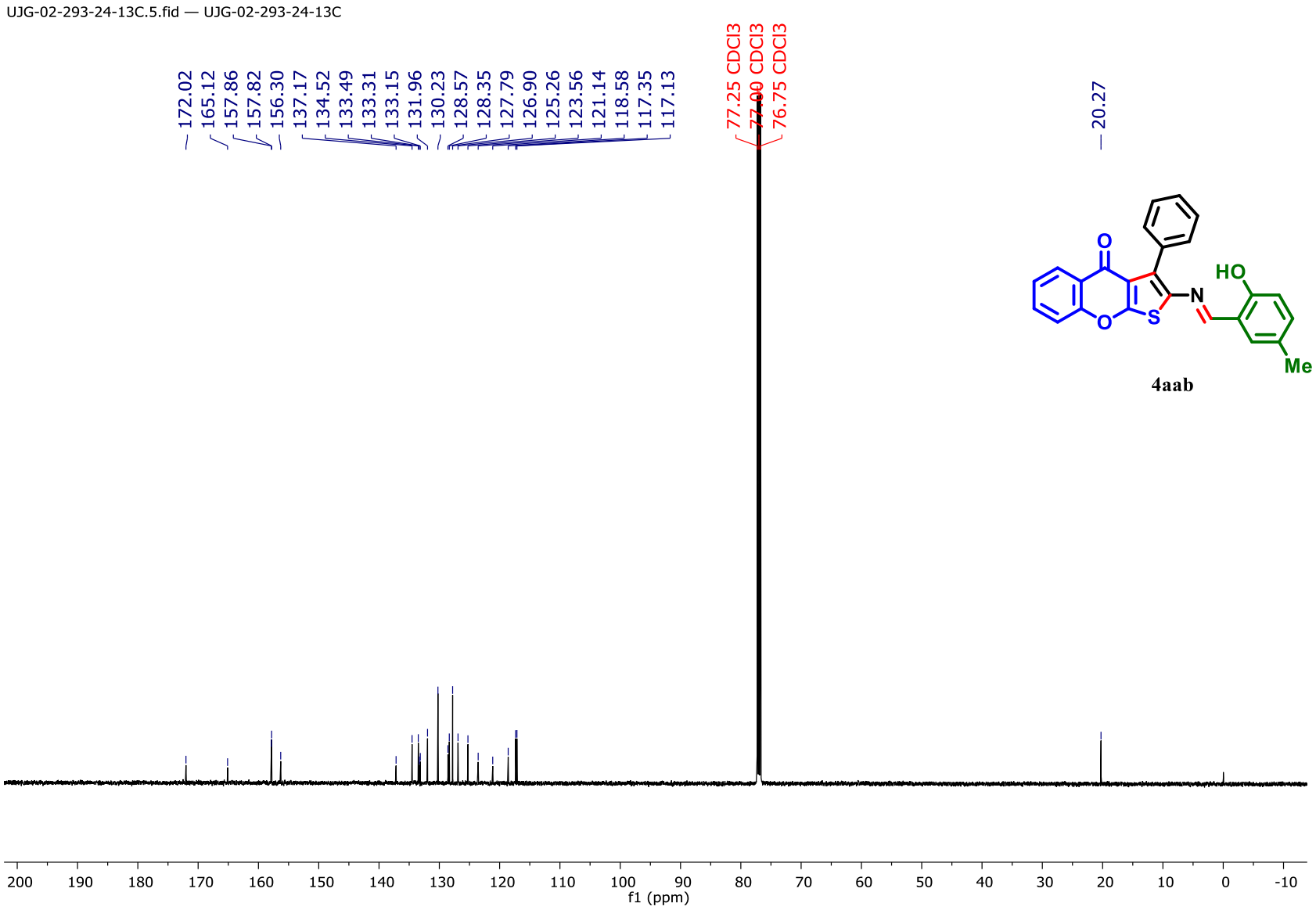
Yellow Solid (12 mg, 54%); **mp** 212-213 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 12.21 (s, 1H), 8.29 (s, 1H), 8.28 (d, *J* = 2.5 Hz, 1H), 7.63 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.45 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 3.25 (q, *J* = 7.5 Hz, 2H), 1.30 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 171.62, 165.91, 159.17, 155.27, 154.69, 138.01, 135.85, 134.63, 133.81, 133.68, 131.21, 126.22, 124.46, 121.44, 120.42, 119.21, 119.12, 111.14, 21.23, 14.77; **IR (KBr) ν_{max}/cm^{-1}** 2957, 2925, 2854, 1646, 1605, 1460, 1297, 1278; **HRMS (ESI)** calcd for $C_{20}H_{14}BrClNO_3S$ 461.9561 ($M + H^+$); found 461.9547.

4. Copies of ^{1}H NMR, ^{13}C NMR and HRMS spectra of Compounds

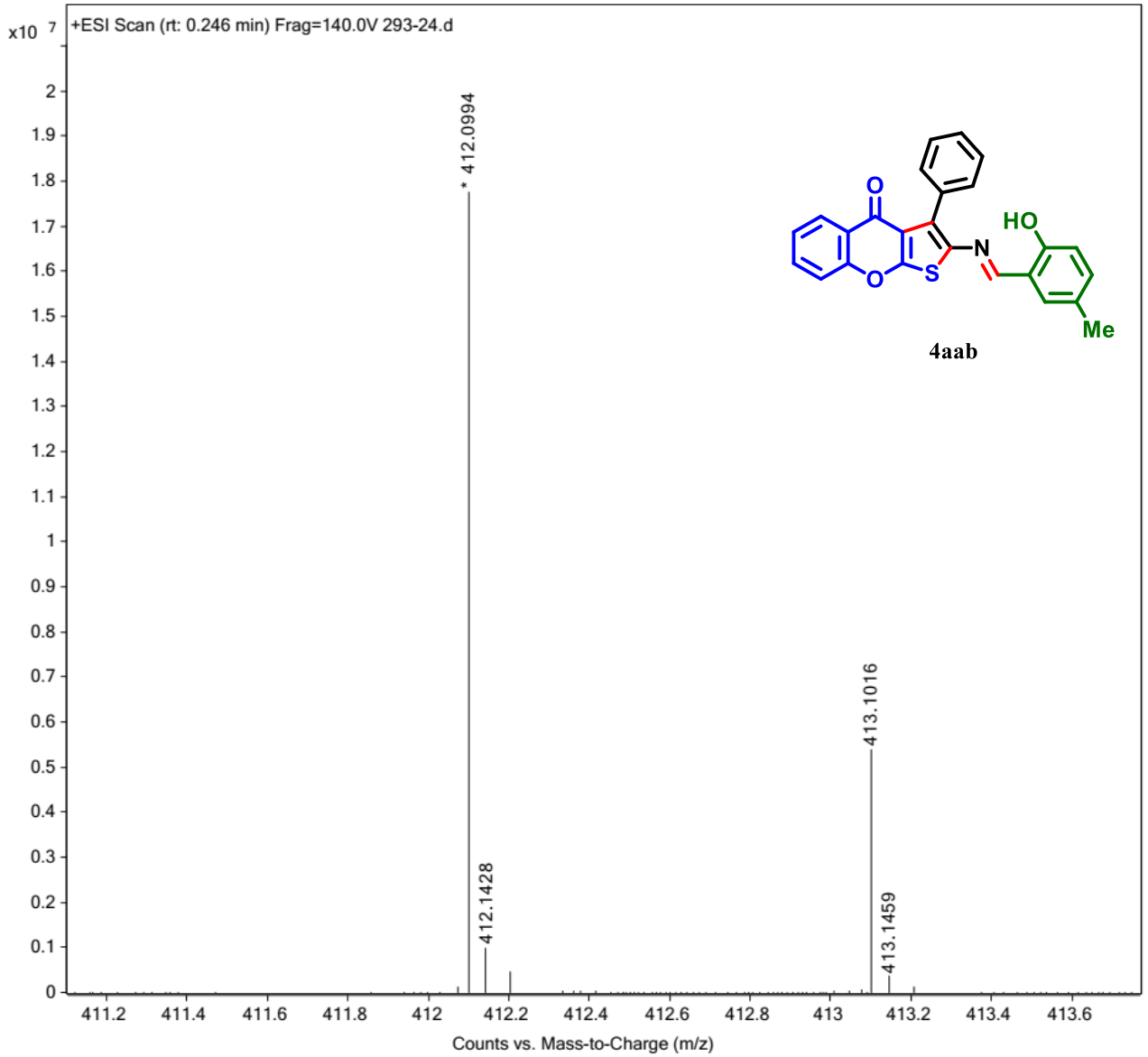
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4aab



^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4aab

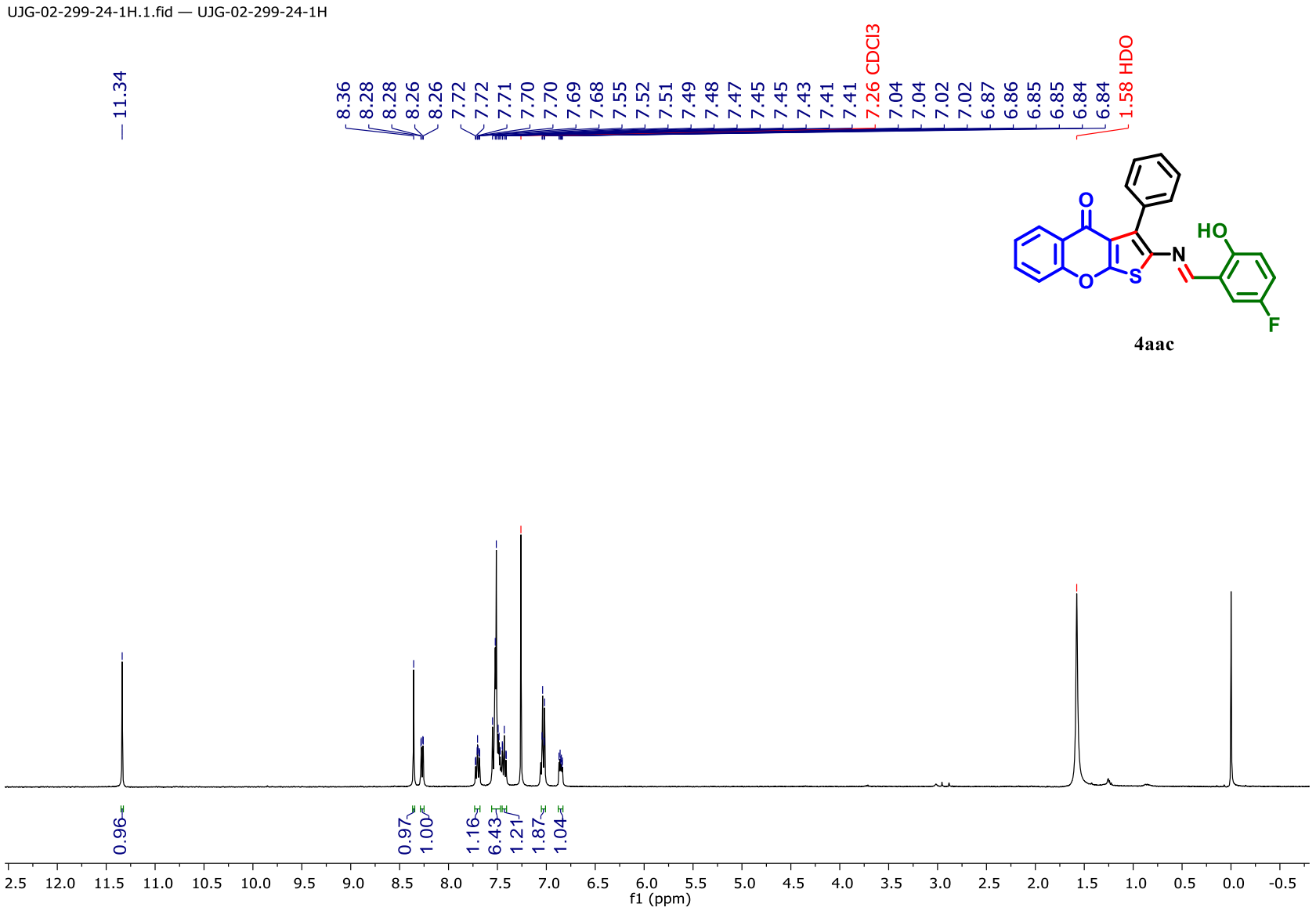


HRMS Spectrum of Compound 4aab



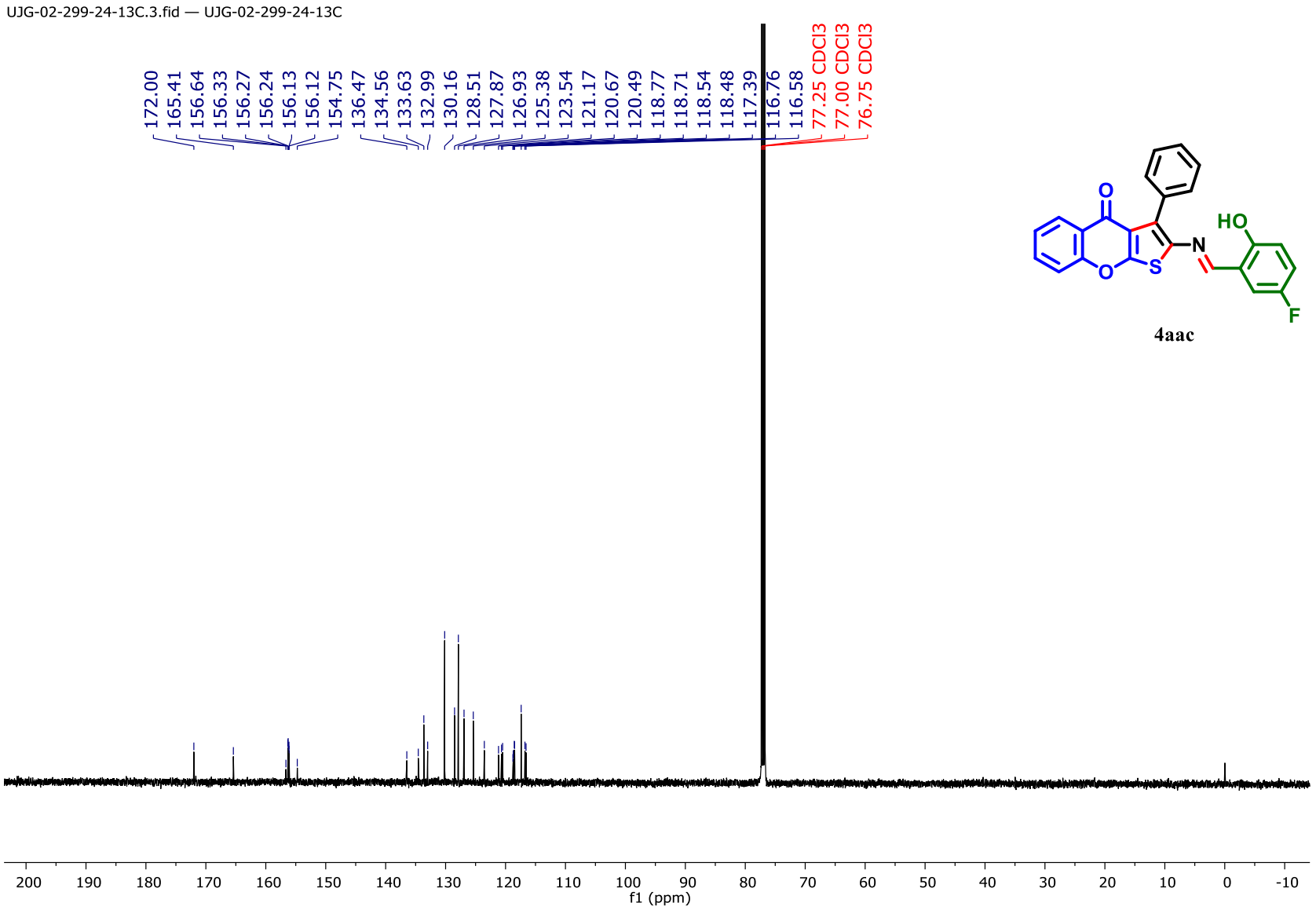
4aab

^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4aac

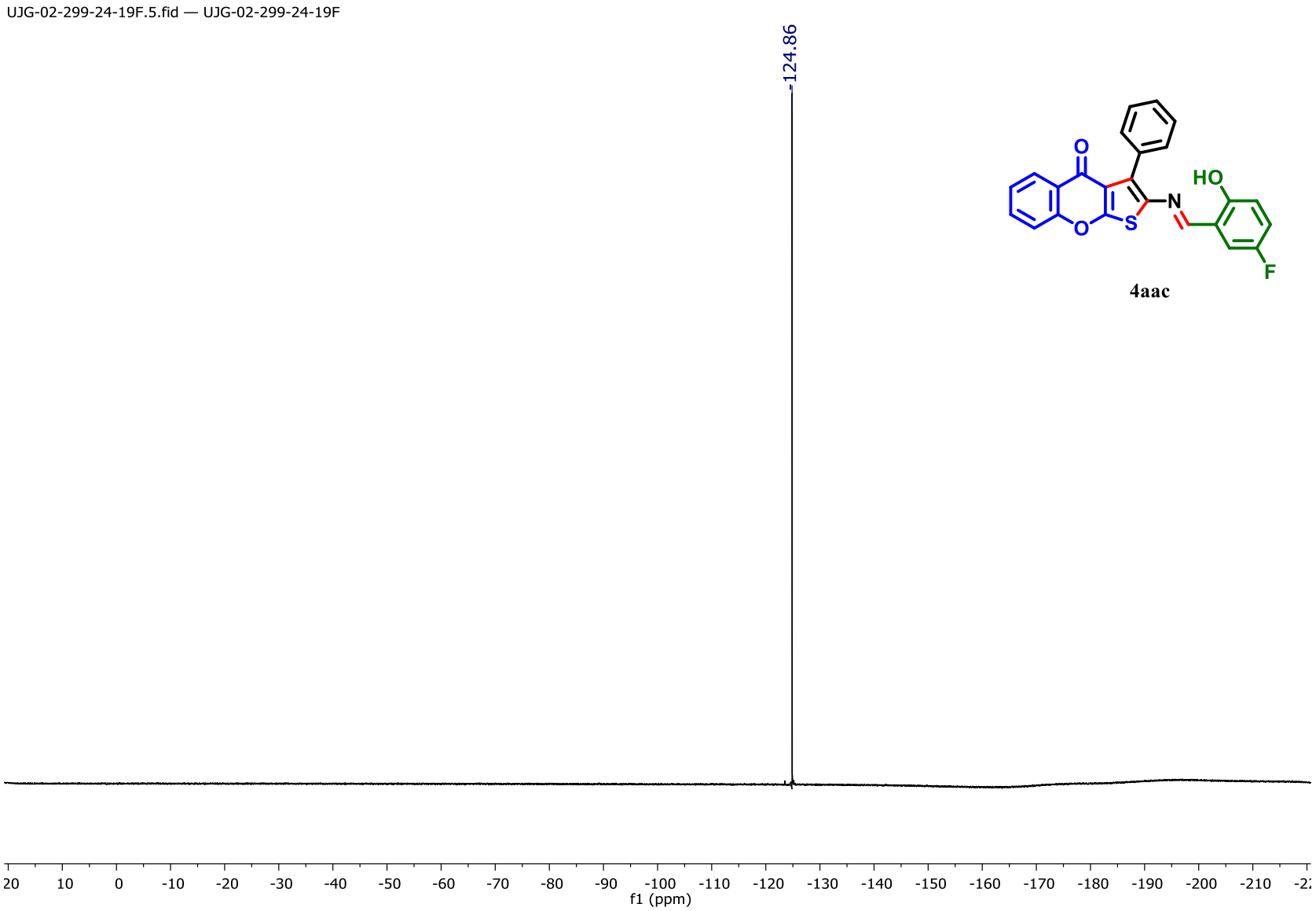


4aac

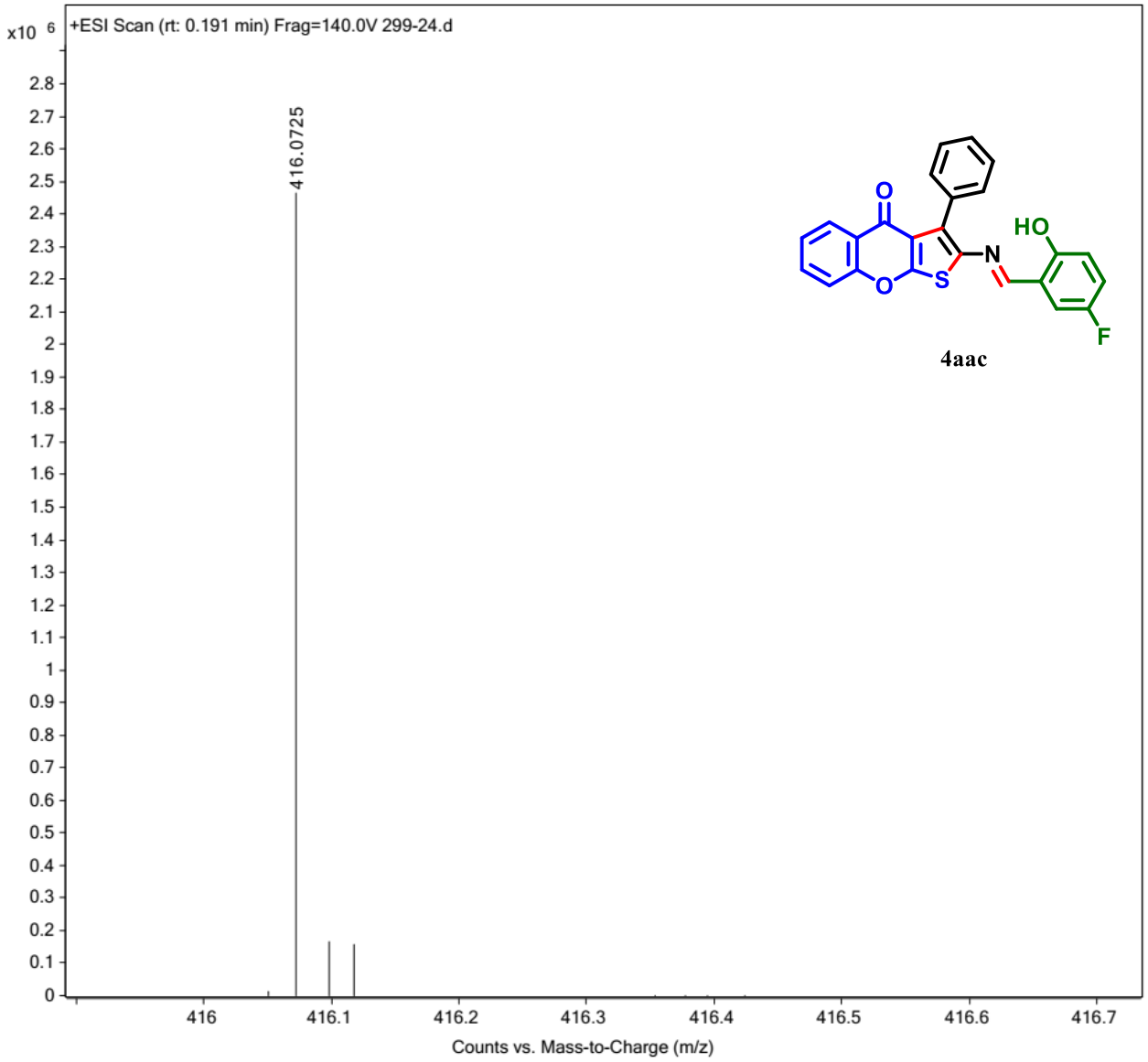
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4aac



^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound 4aac

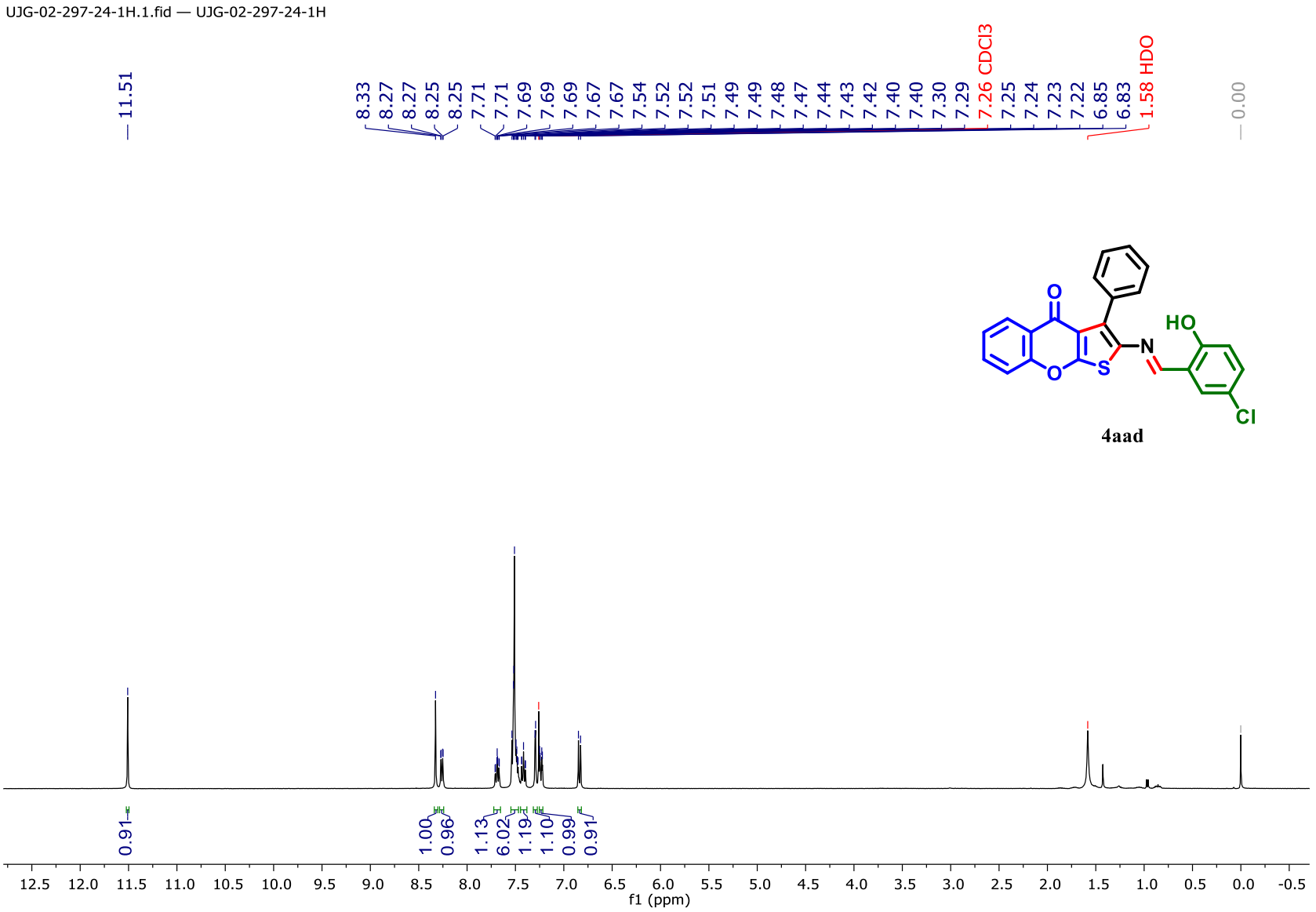


HRMS Spectrum of Compound 4aac

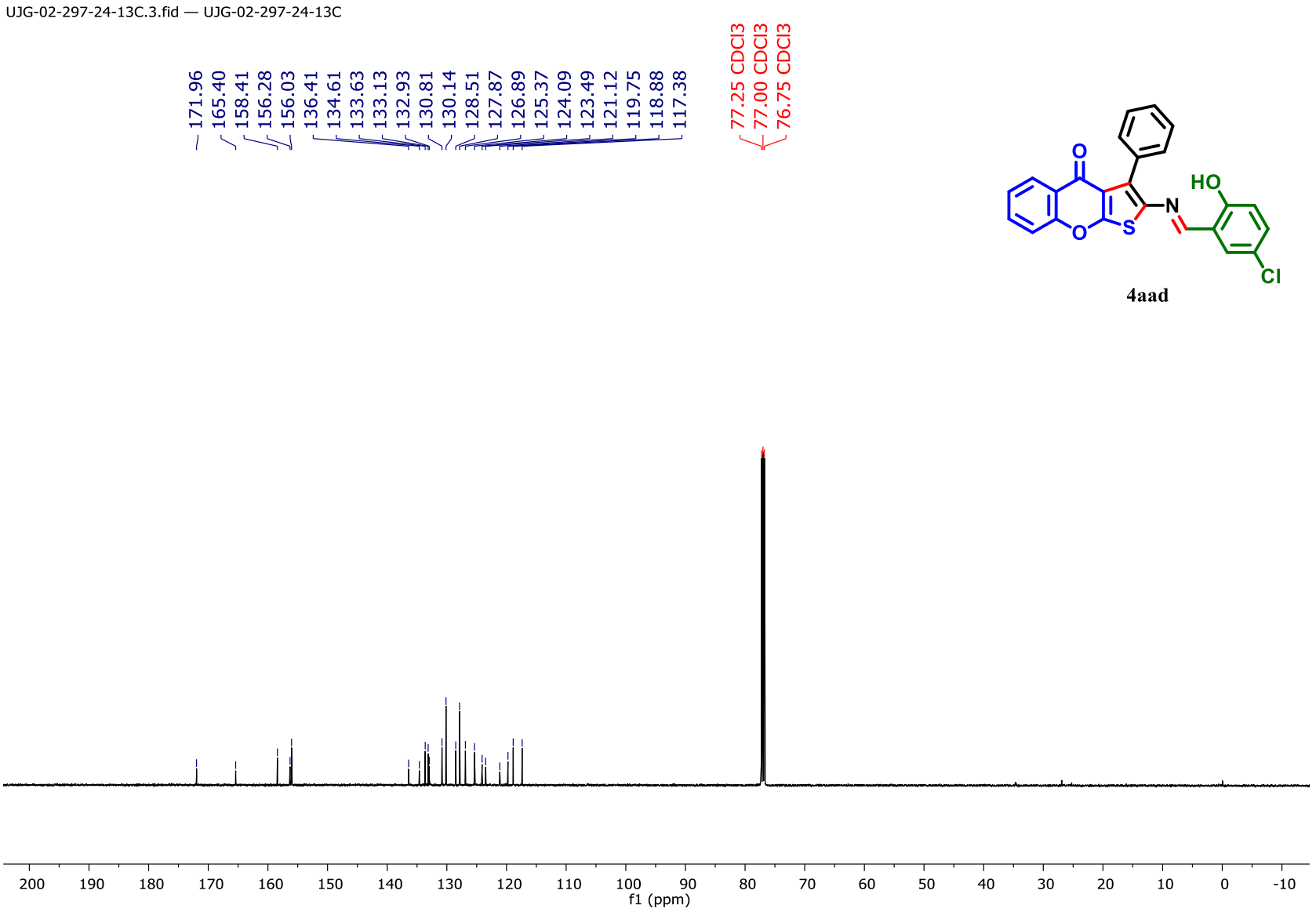


4aac

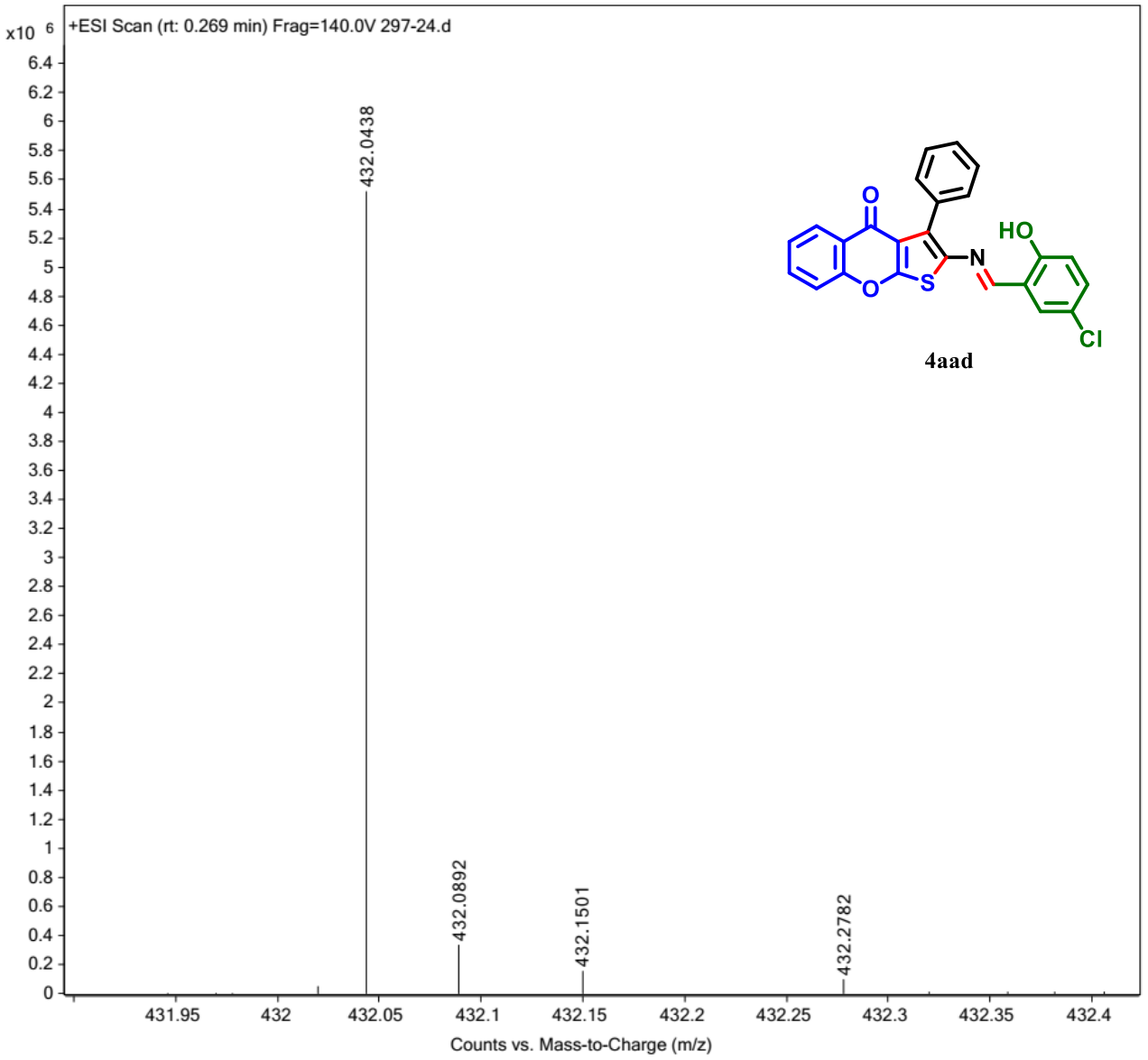
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4aad



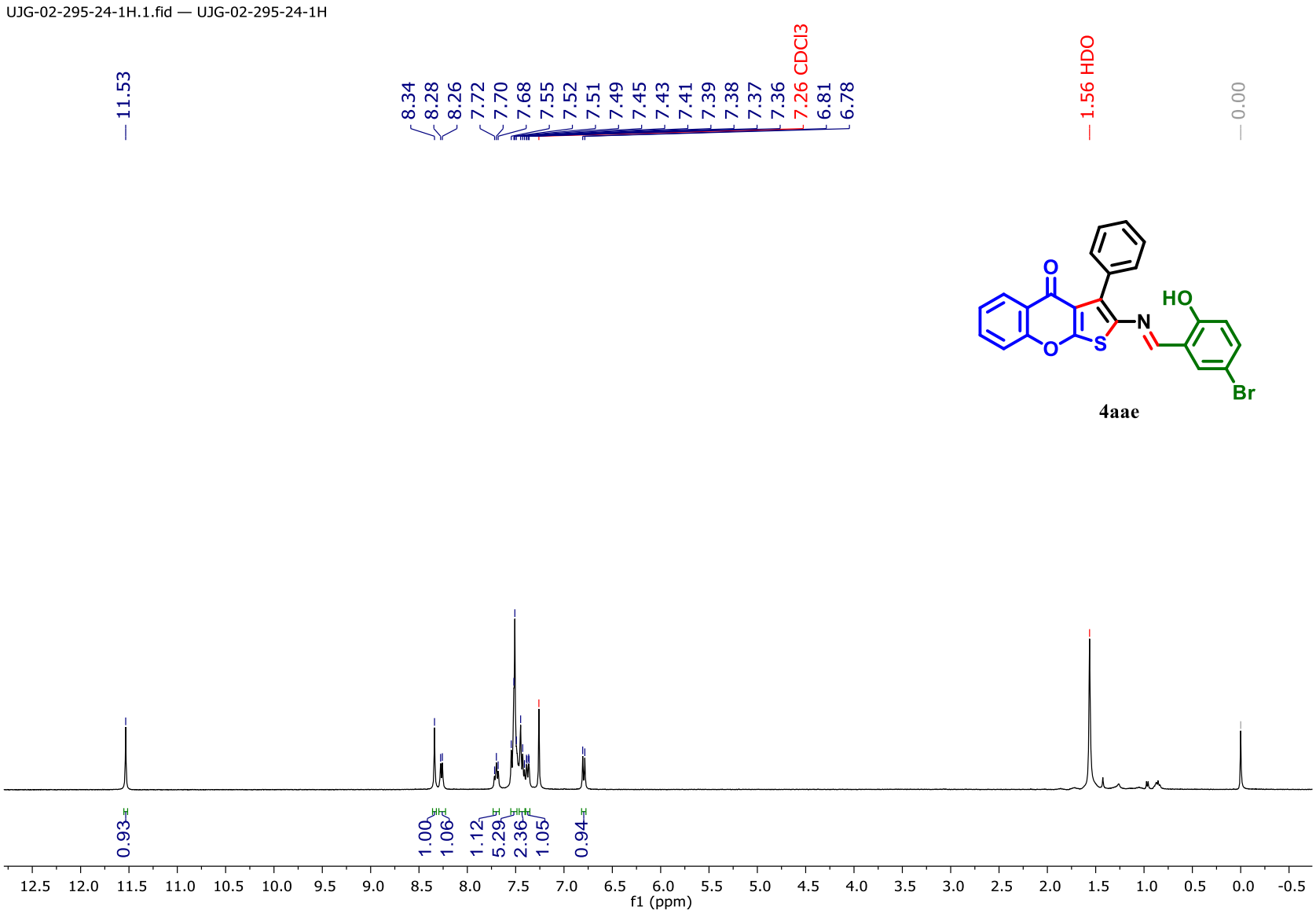
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4aad



HRMS Spectrum of Compound 4aad

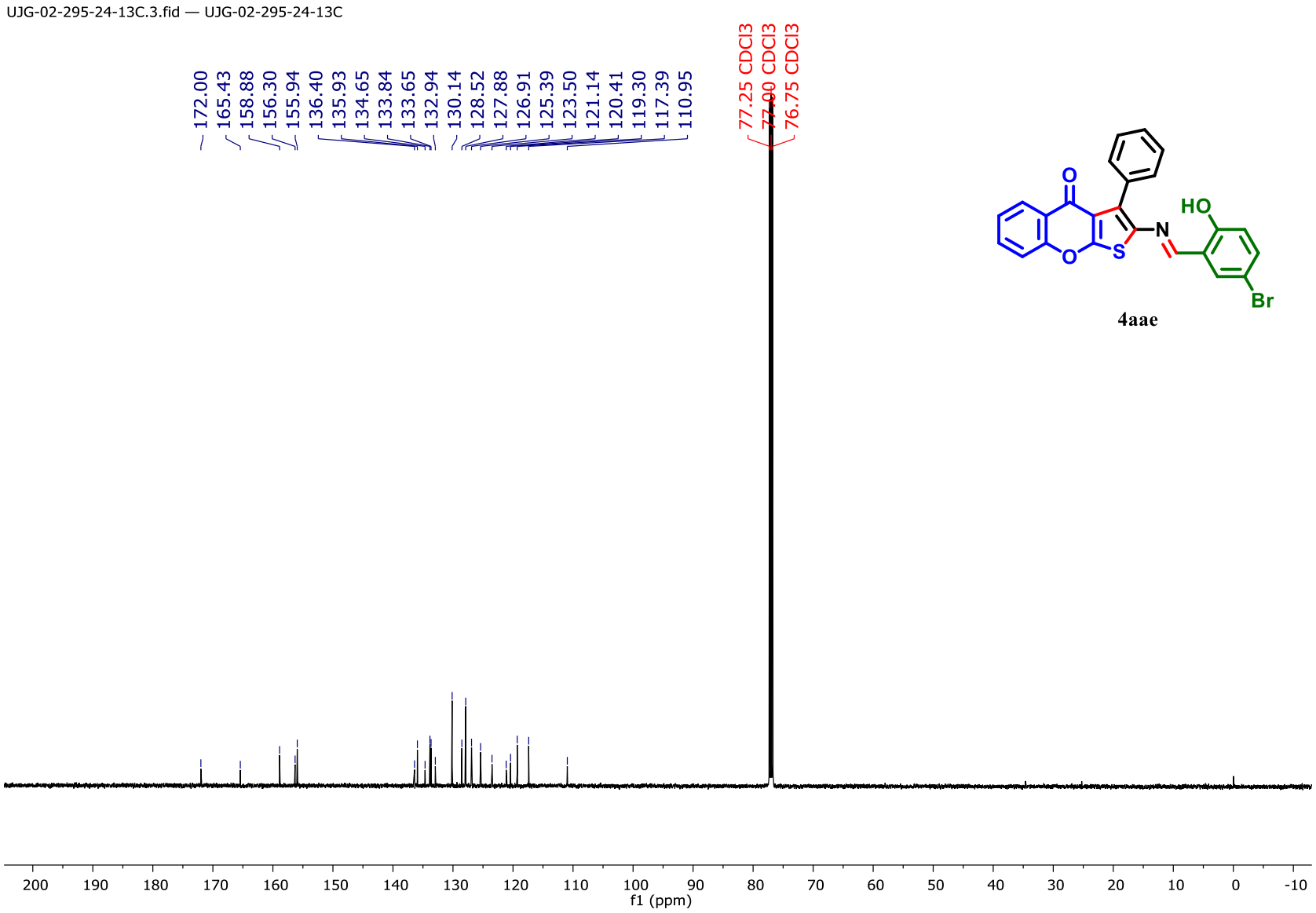


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4aae

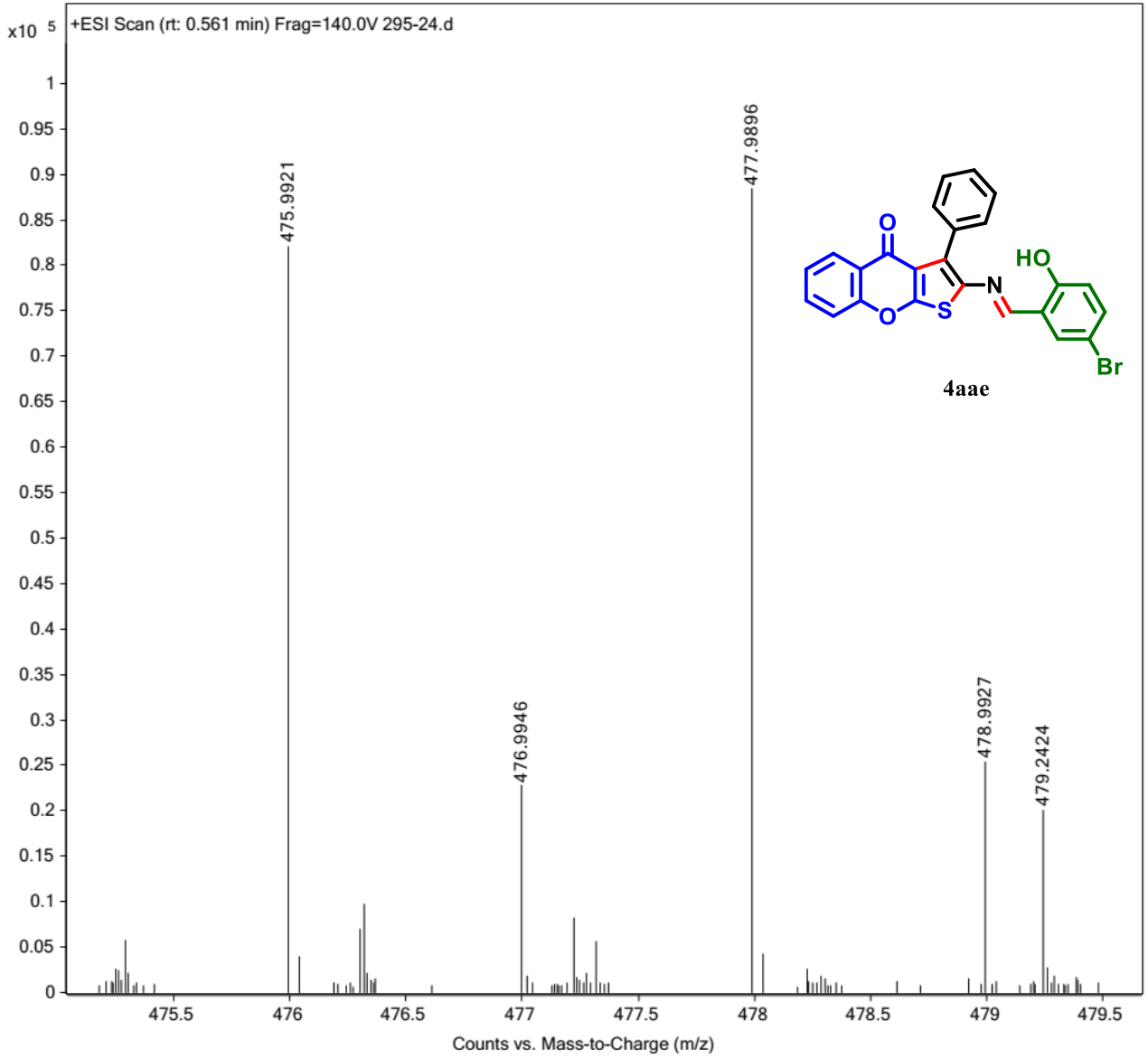


4aae

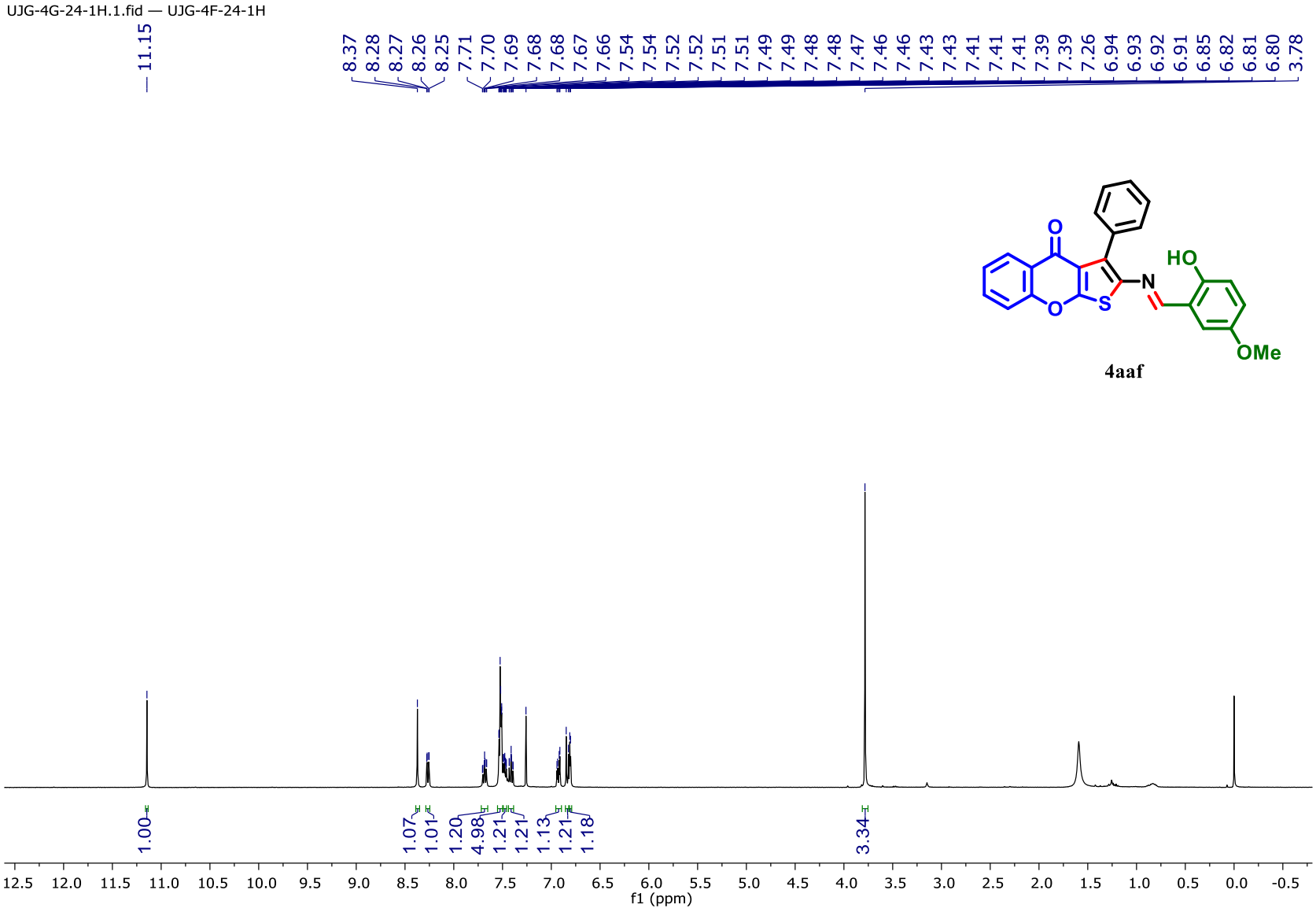
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4aae



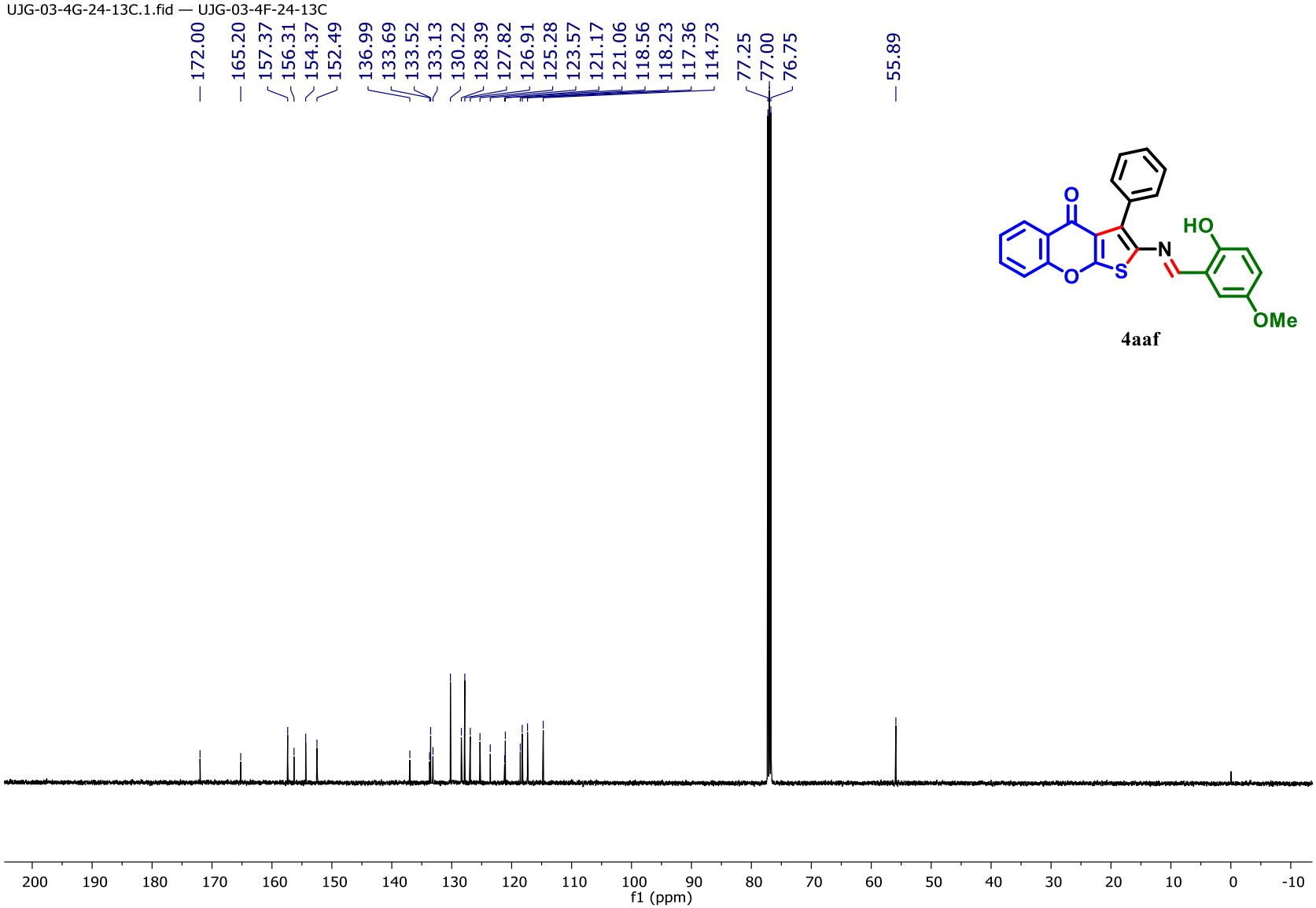
HRMS Spectrum of Compound 4aae



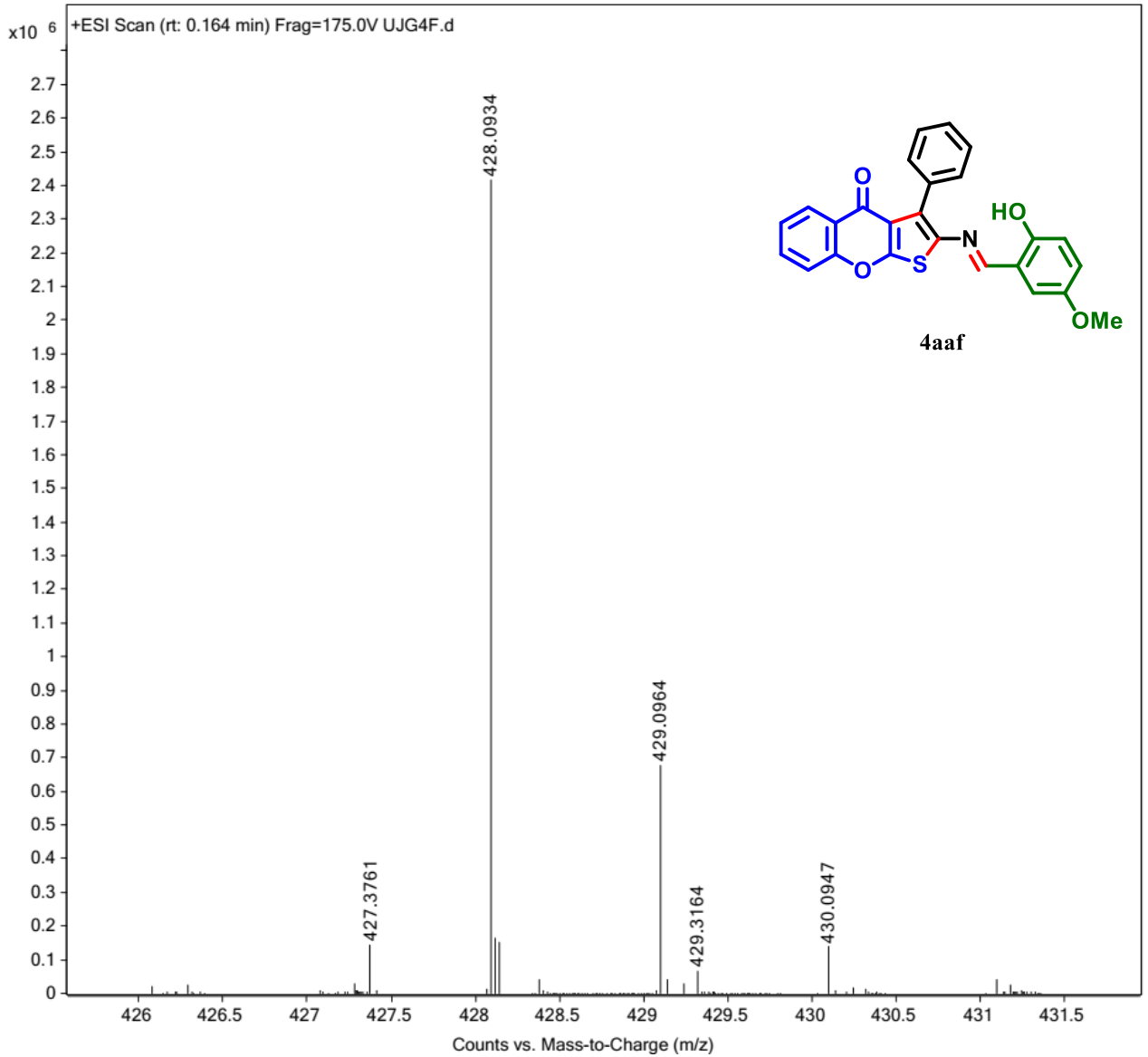
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4aaf



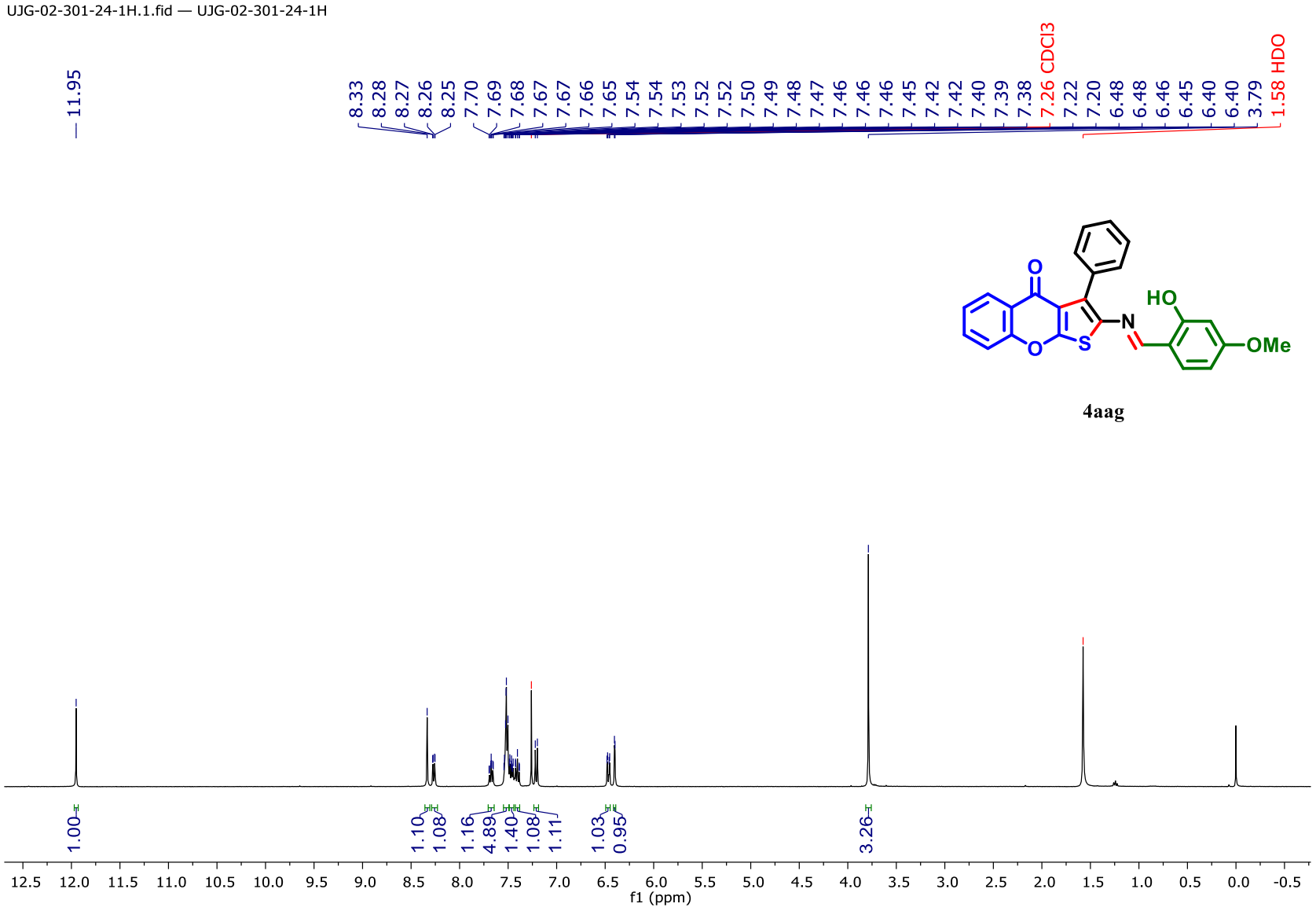
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4aaf



HRMS Spectrum of Compound 4aaf

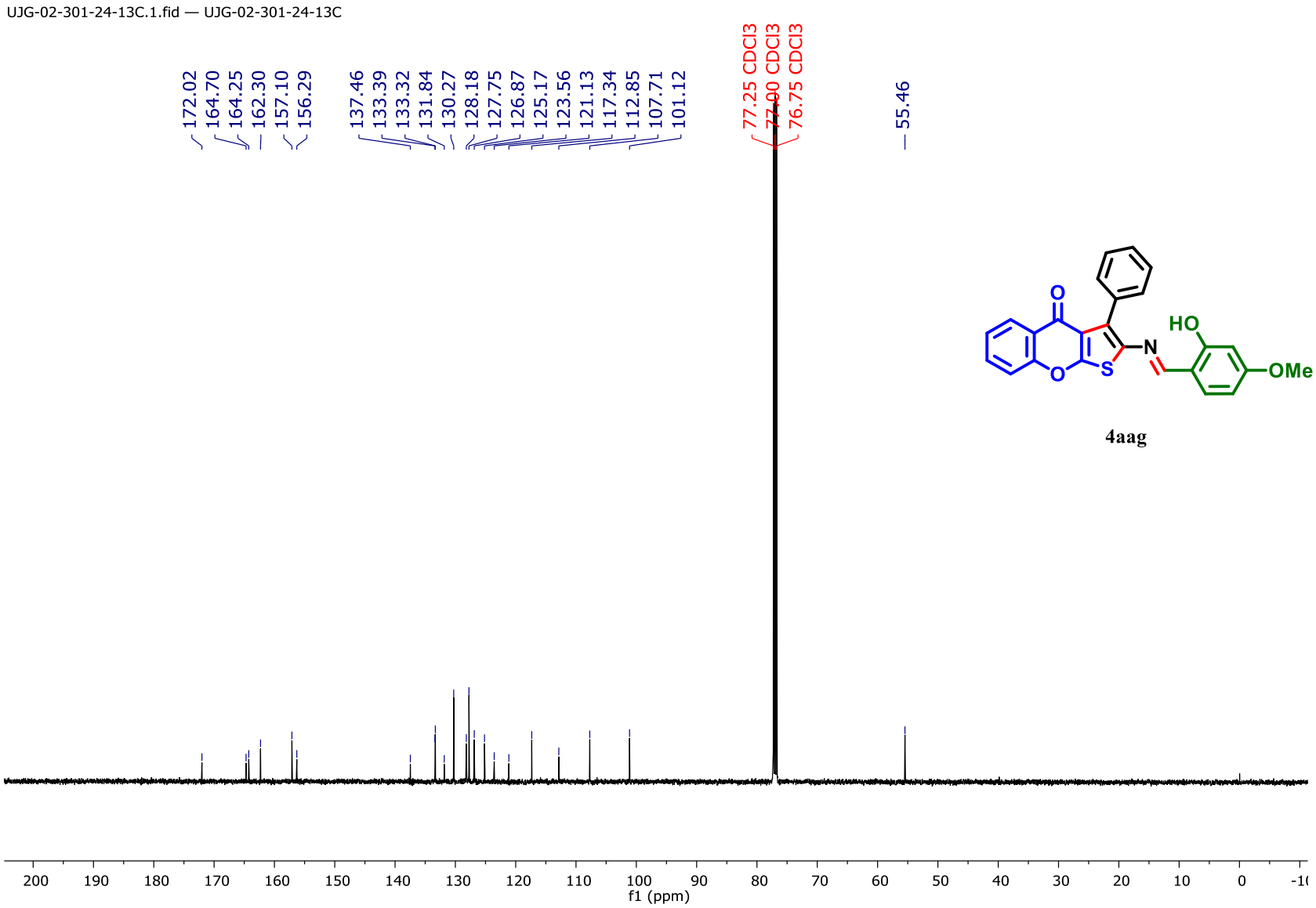


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4aag



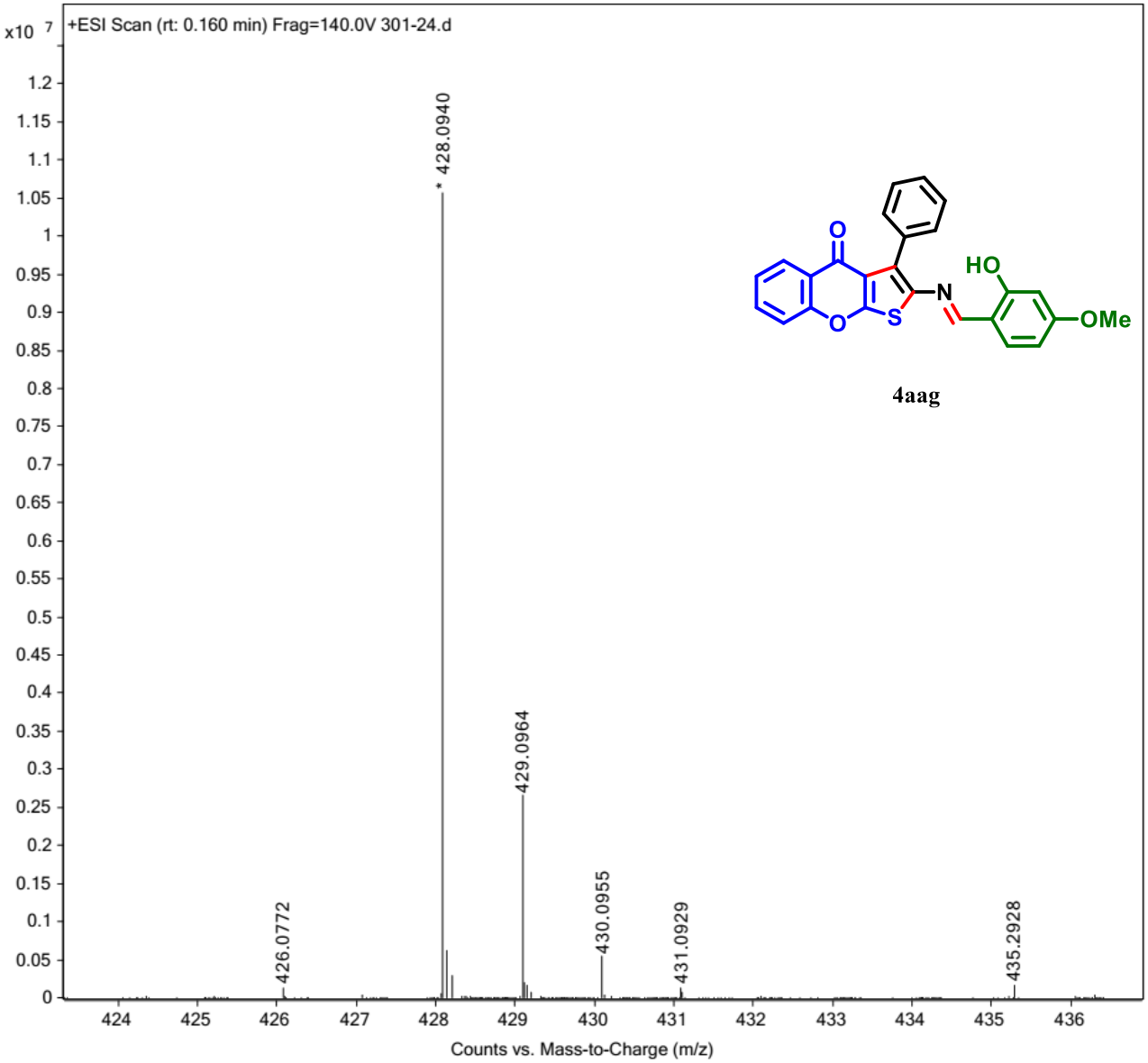
4aag

^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4aag



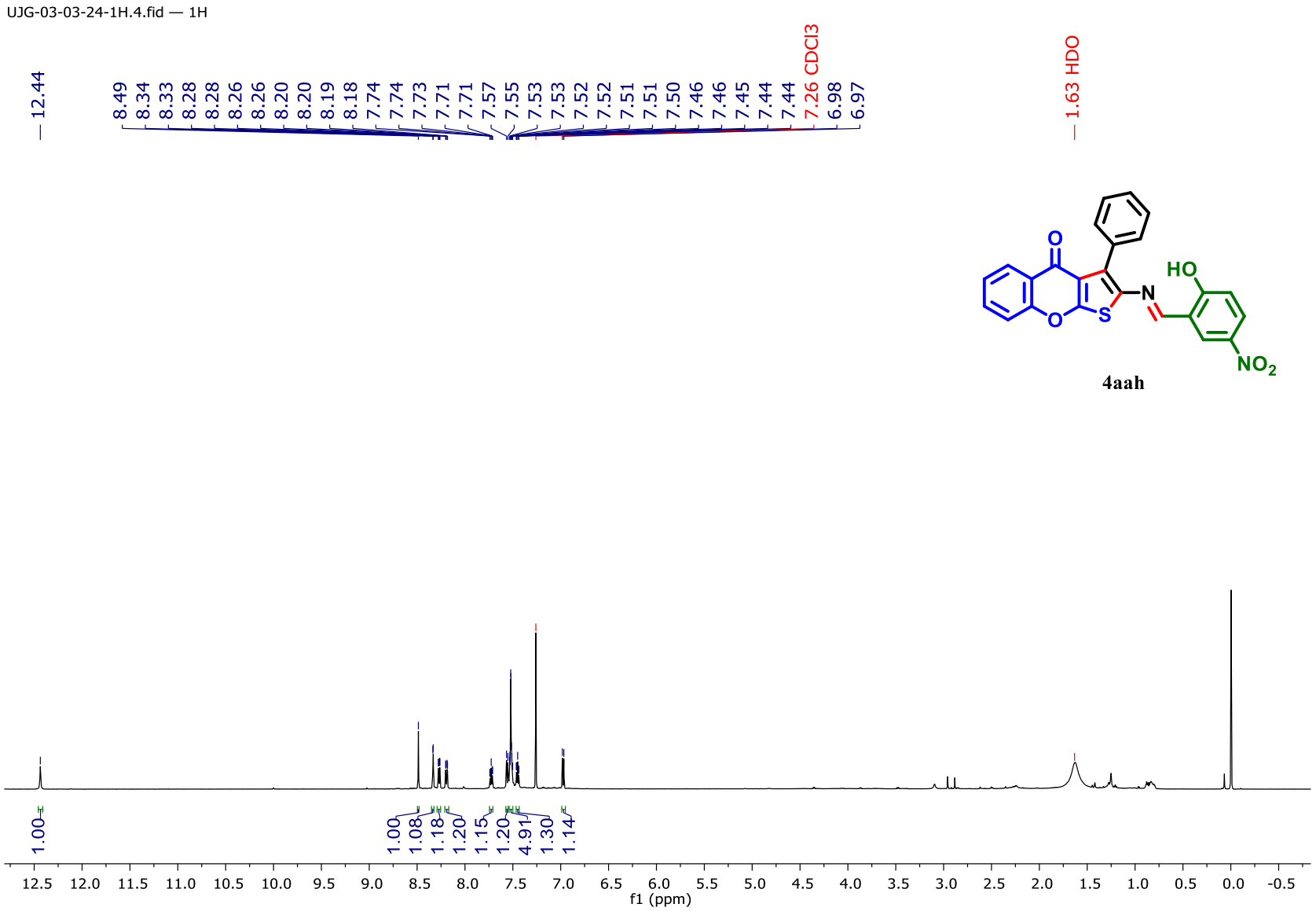
4aag

HRMS Spectrum of Compound 4aag

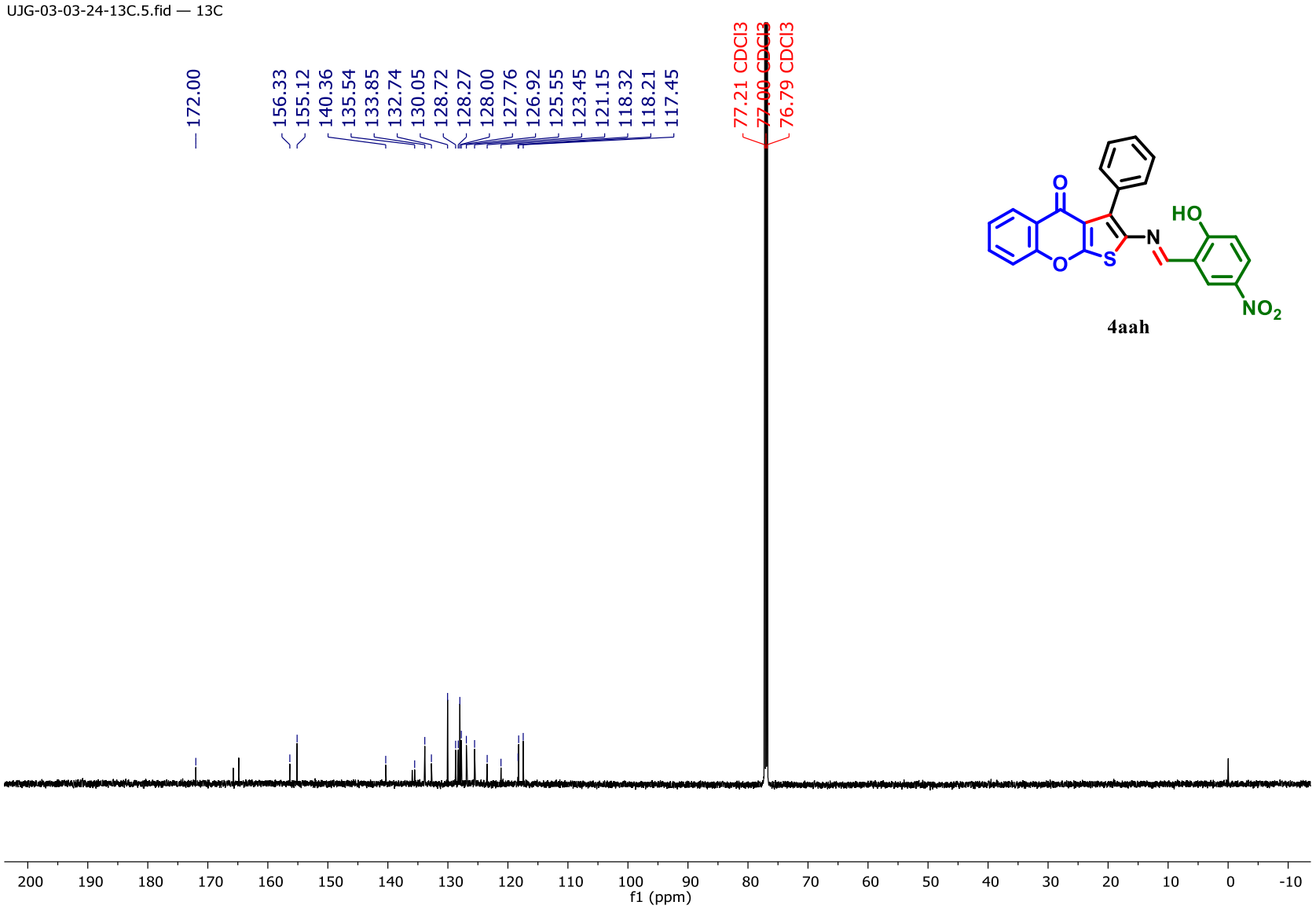


4aag

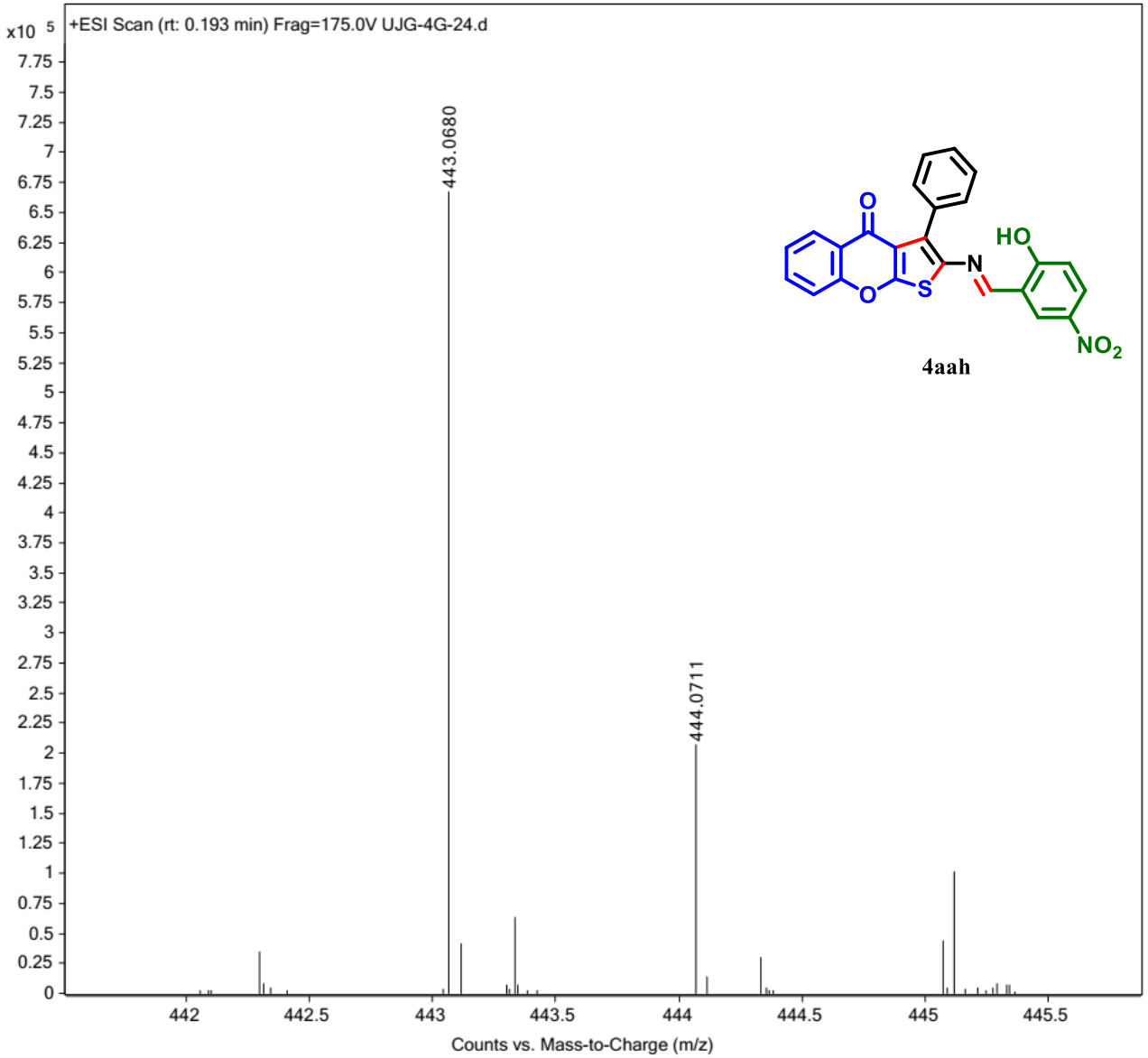
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound 4aah



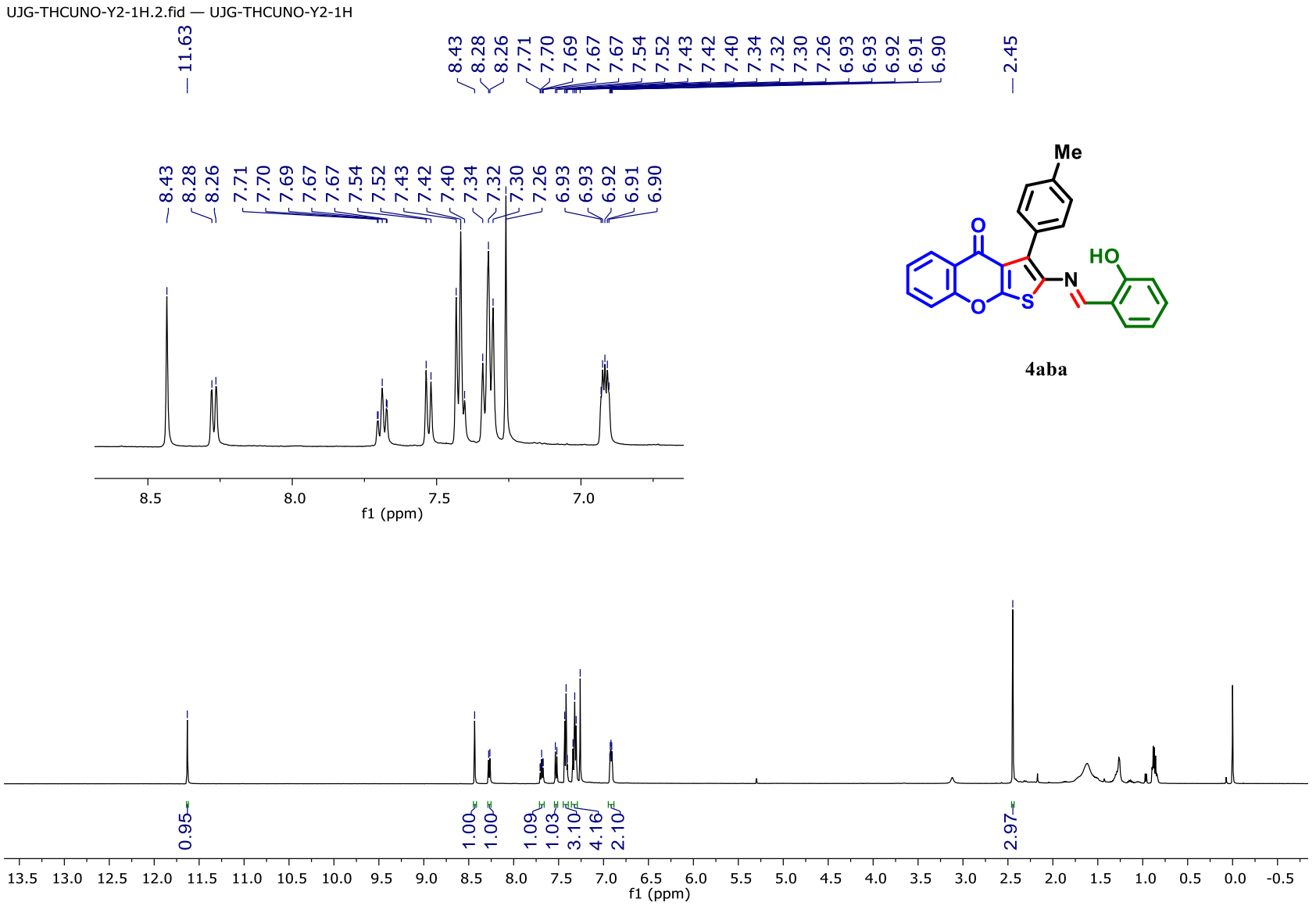
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound 4aah



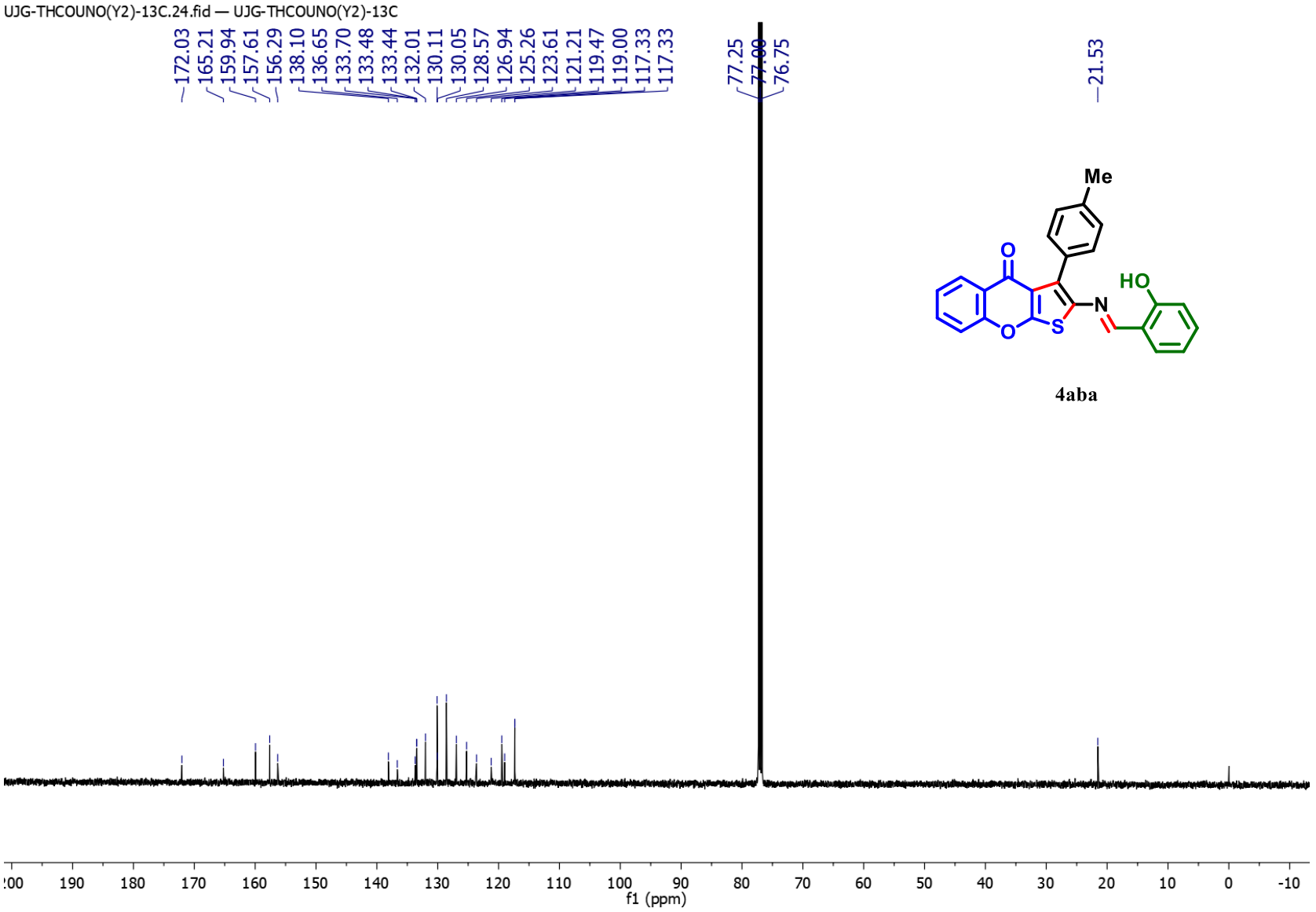
HRMS Spectrum of Compound 4aah



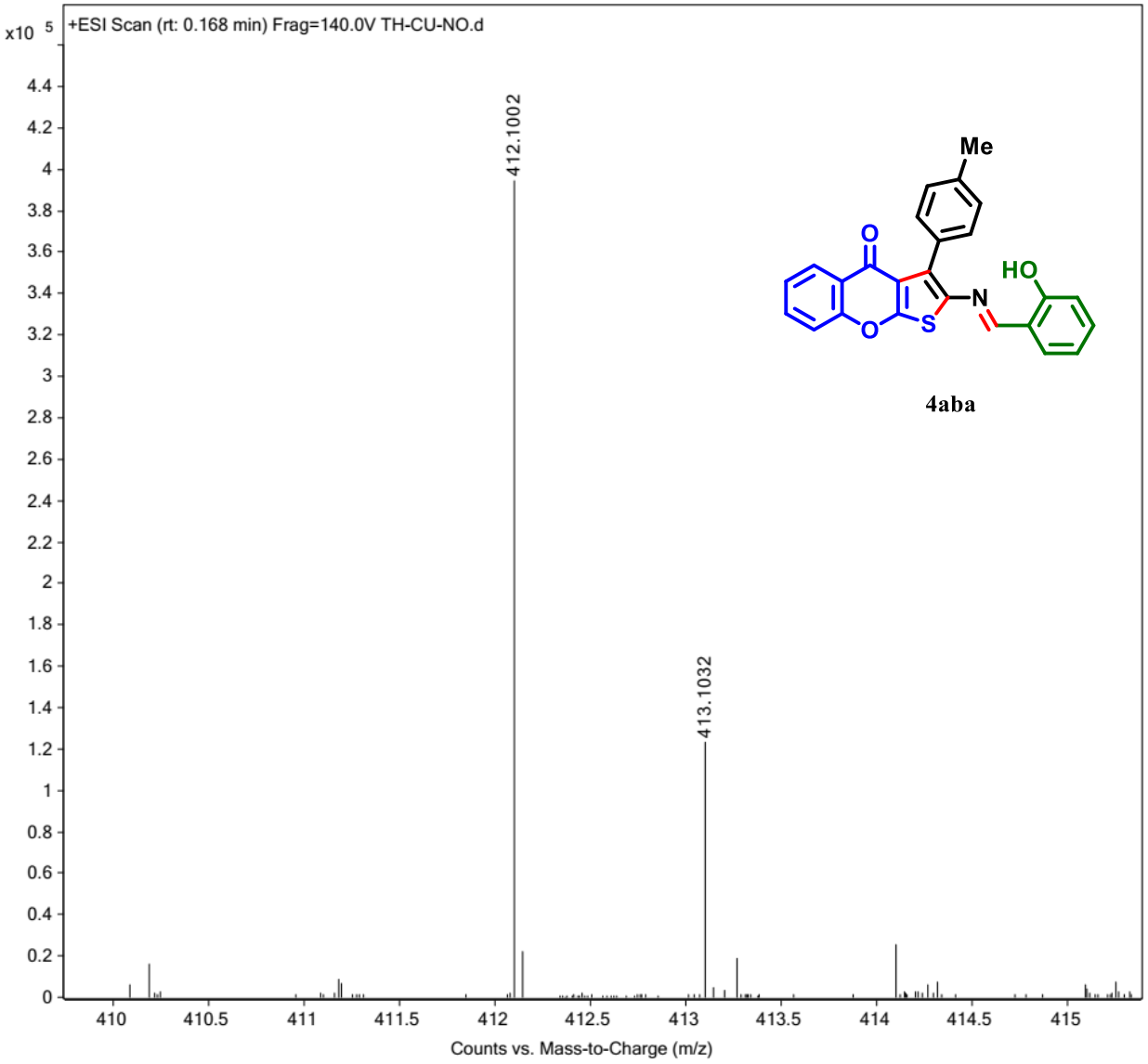
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound 4aba



^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4aba

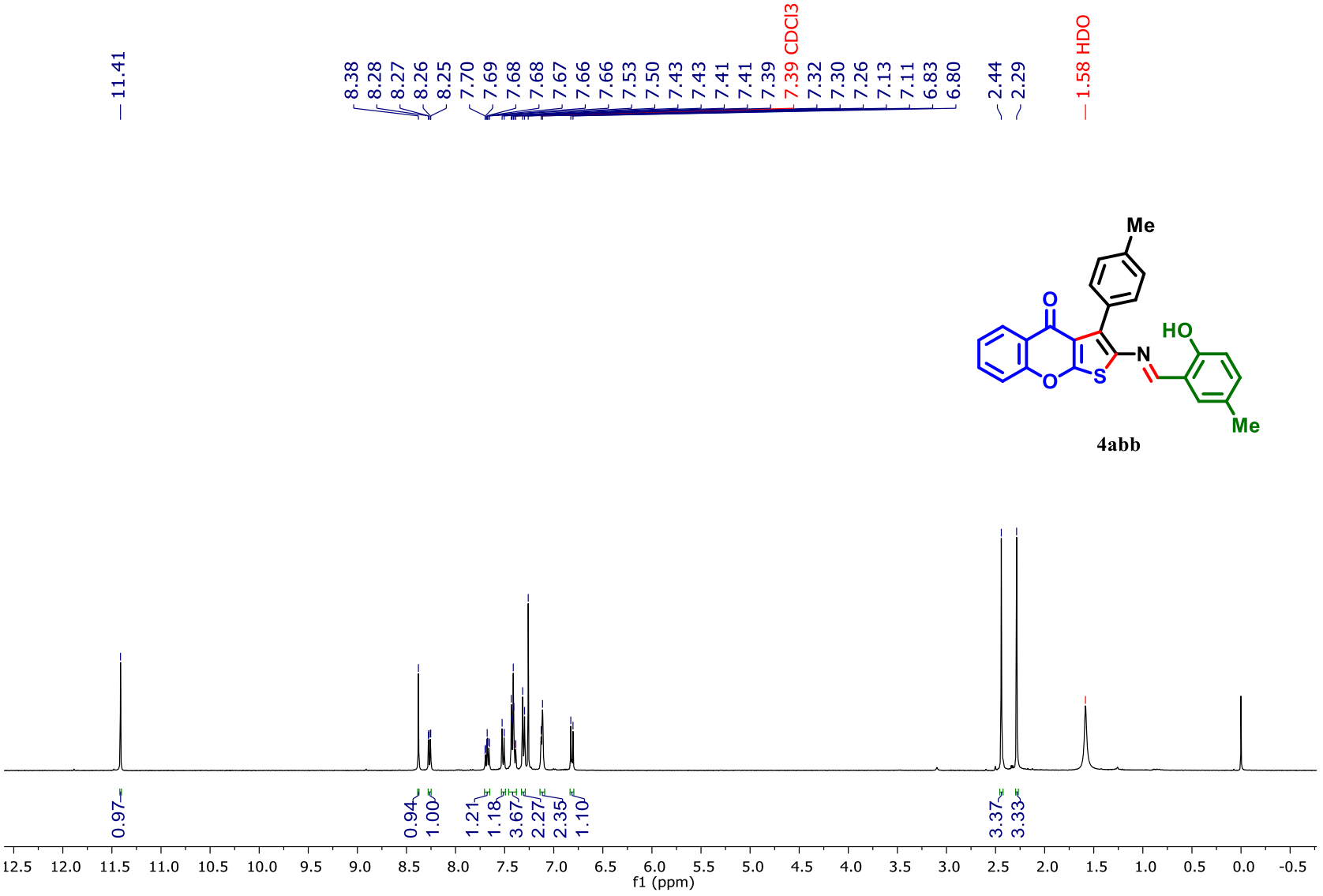


HRMS Spectrum of Compound 4aba

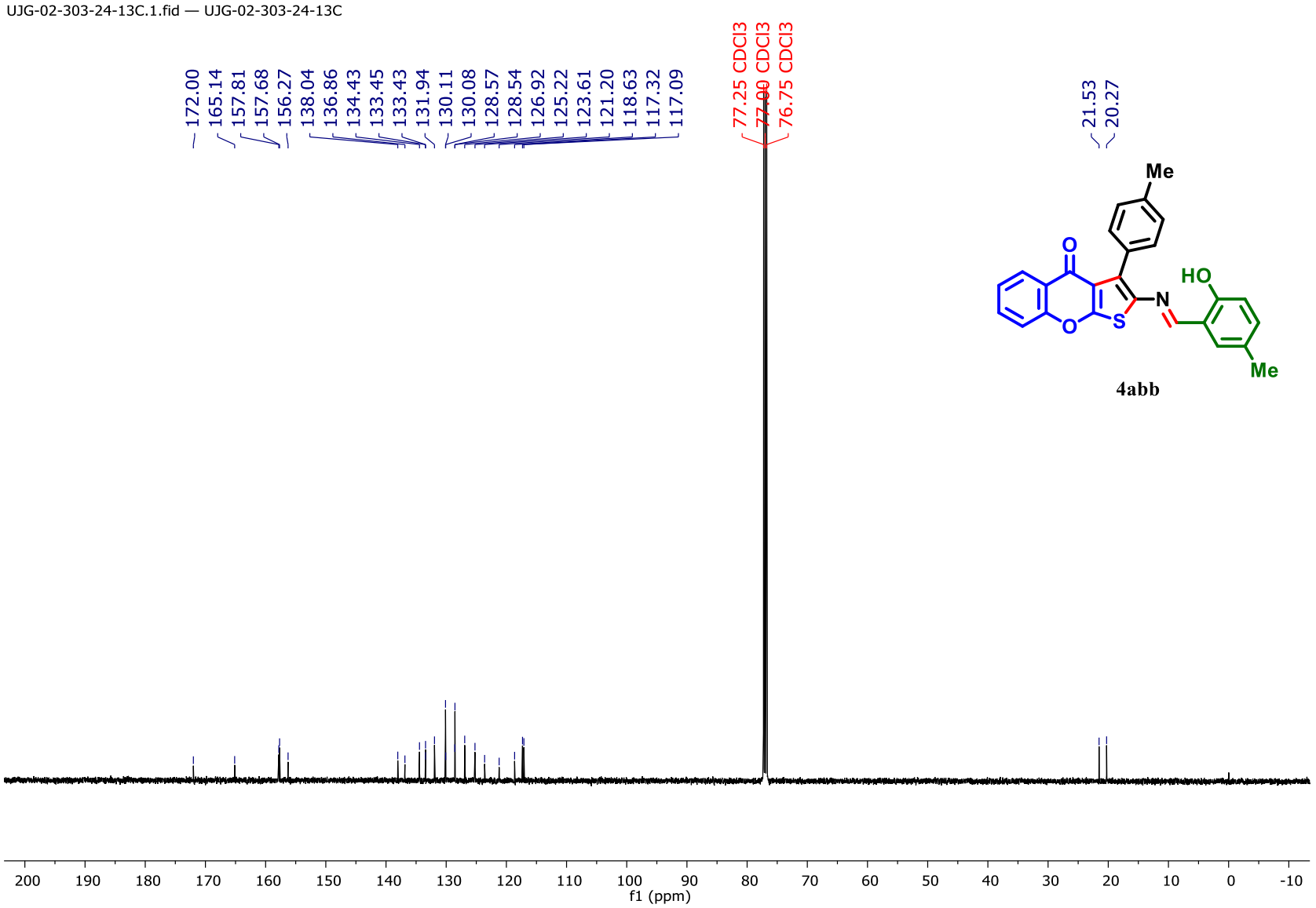


4aba

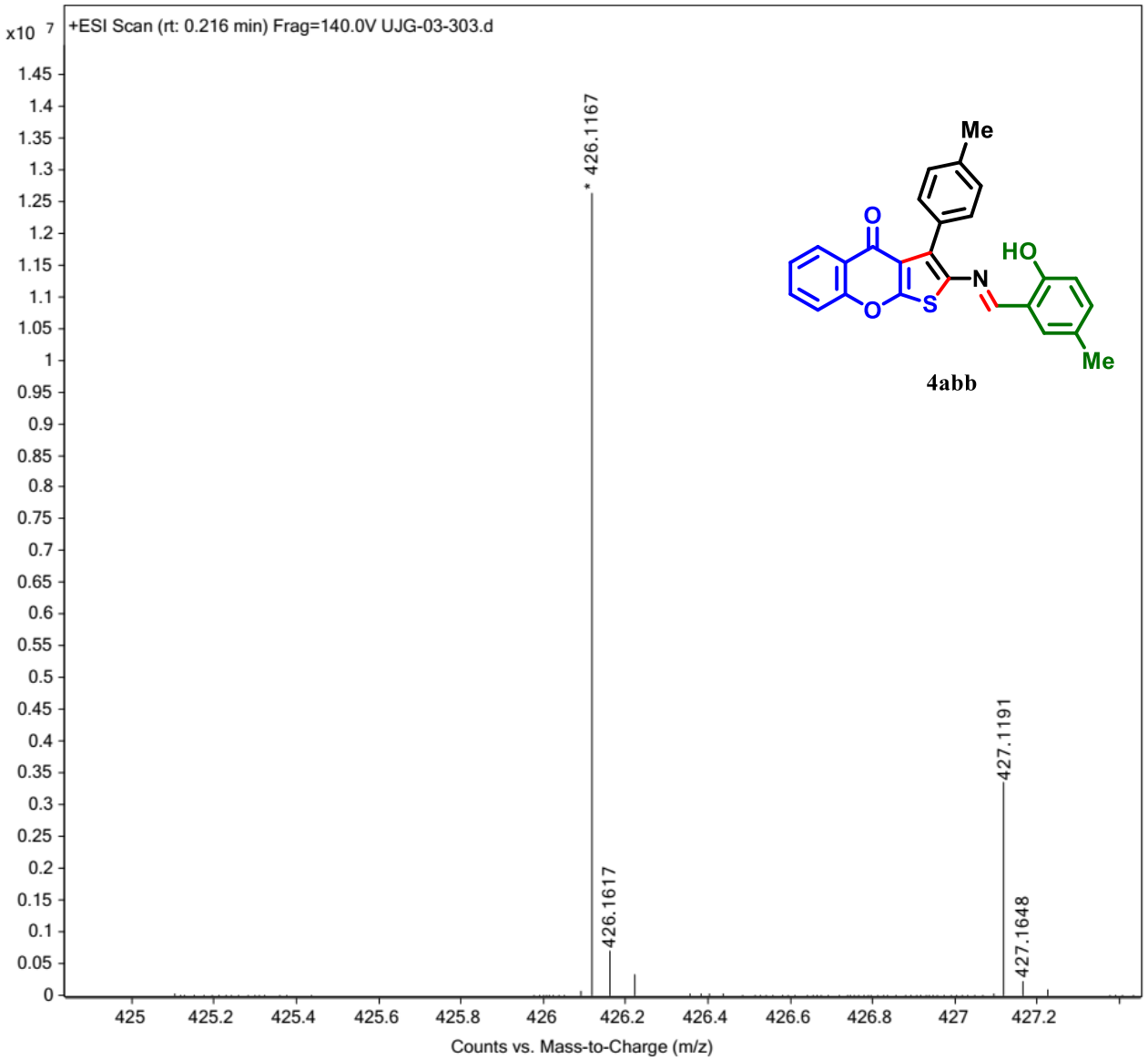
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4abb



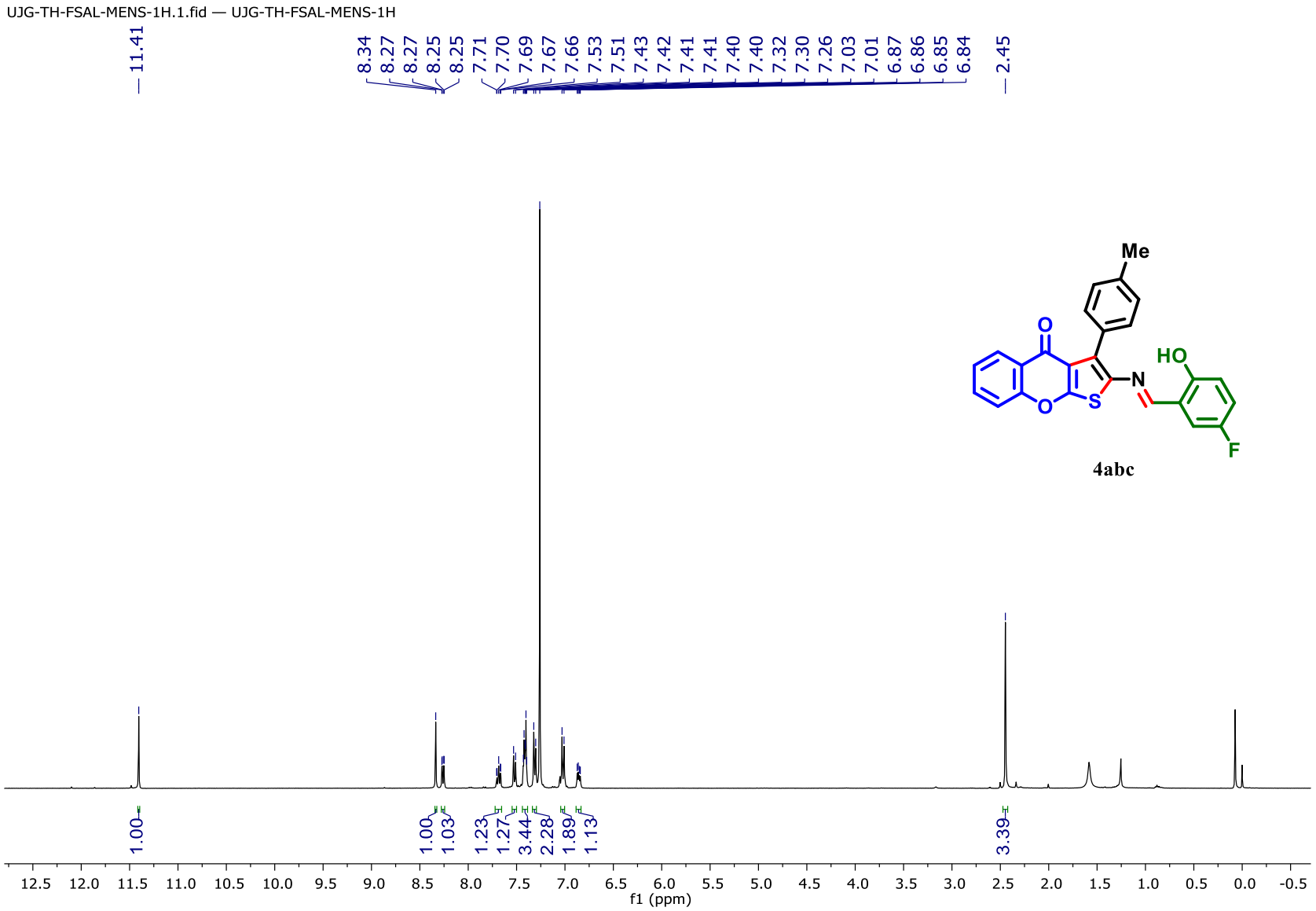
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4abb



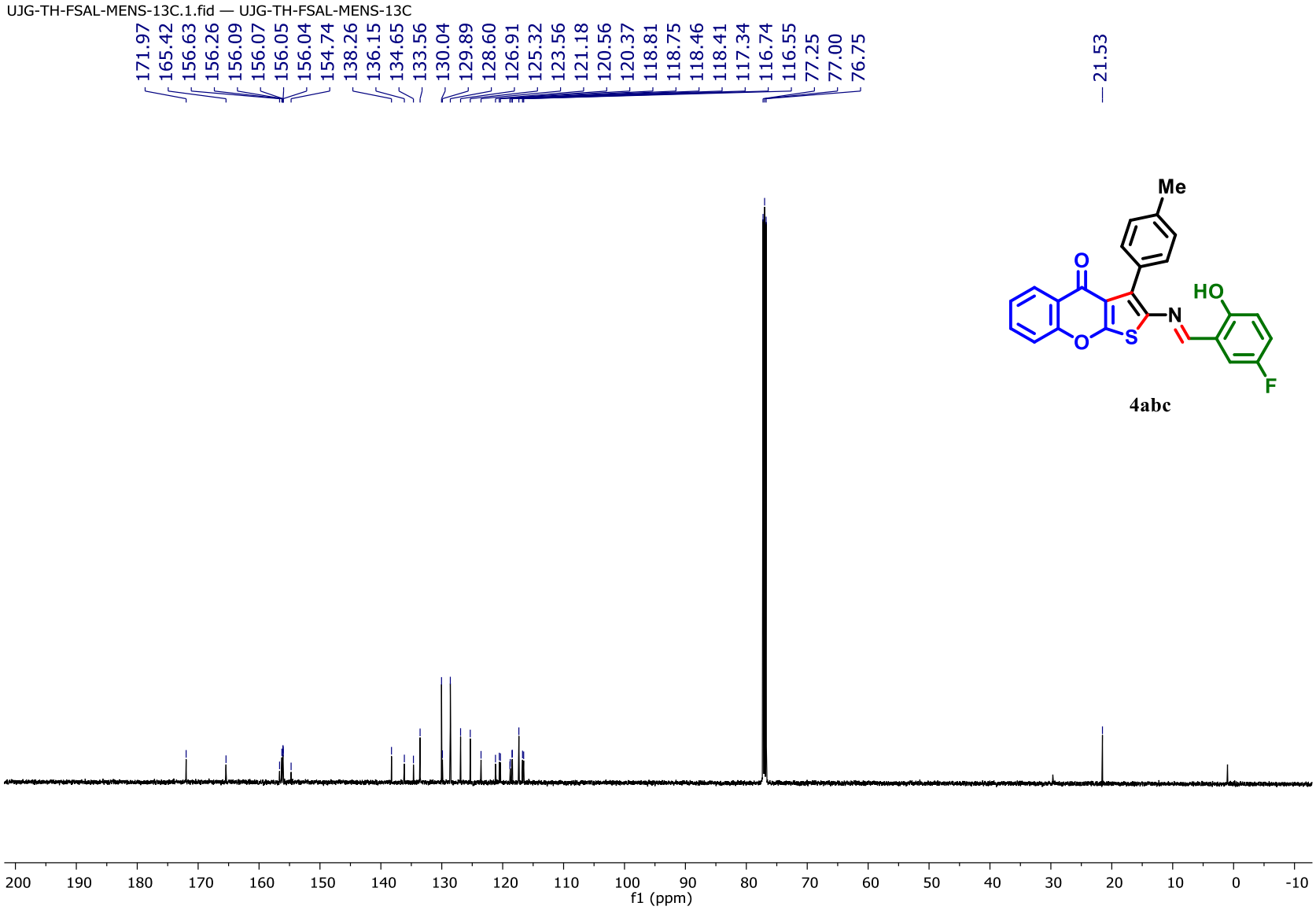
HRMS Spectrum of Compound 4abb



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4abc



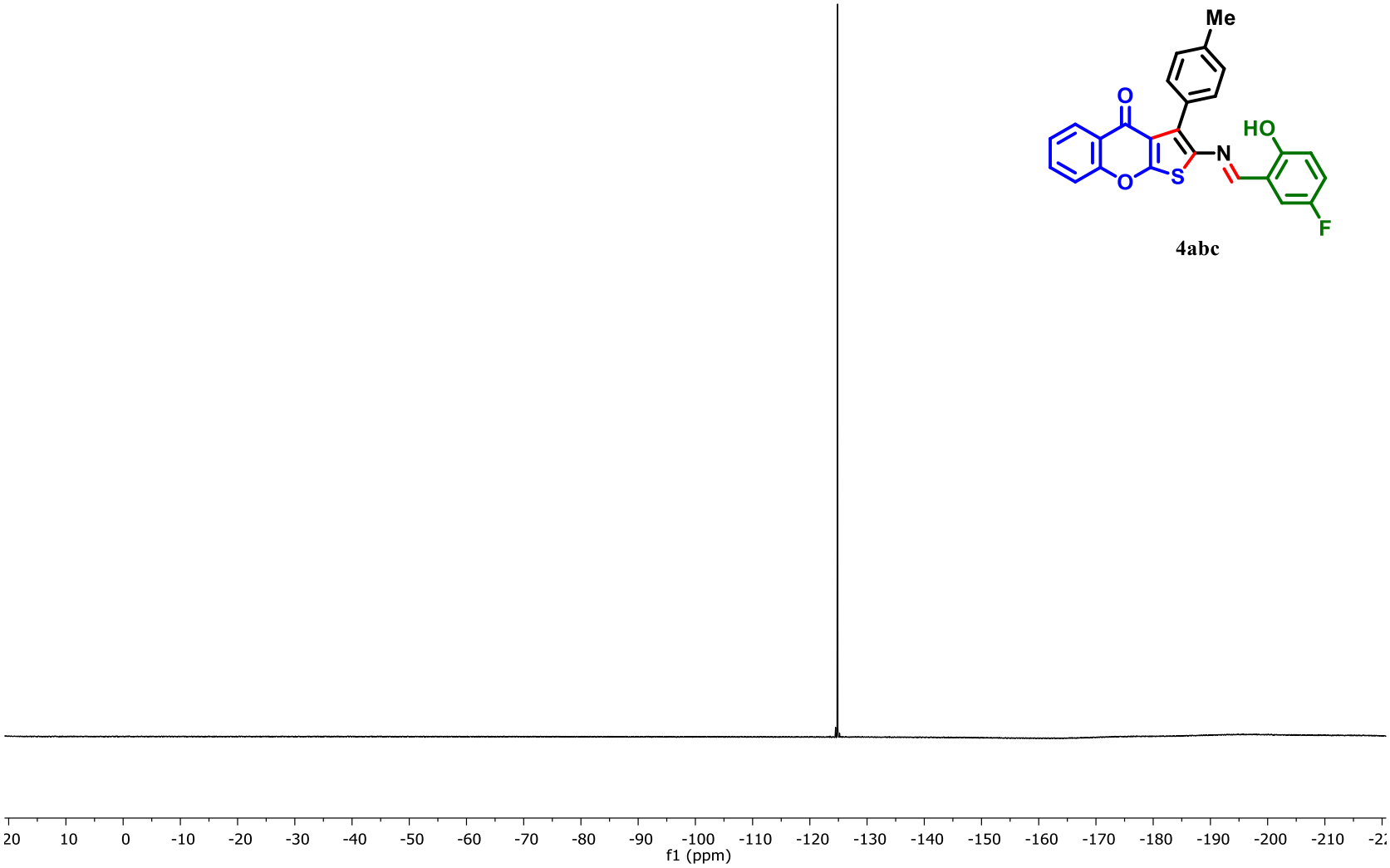
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4abc



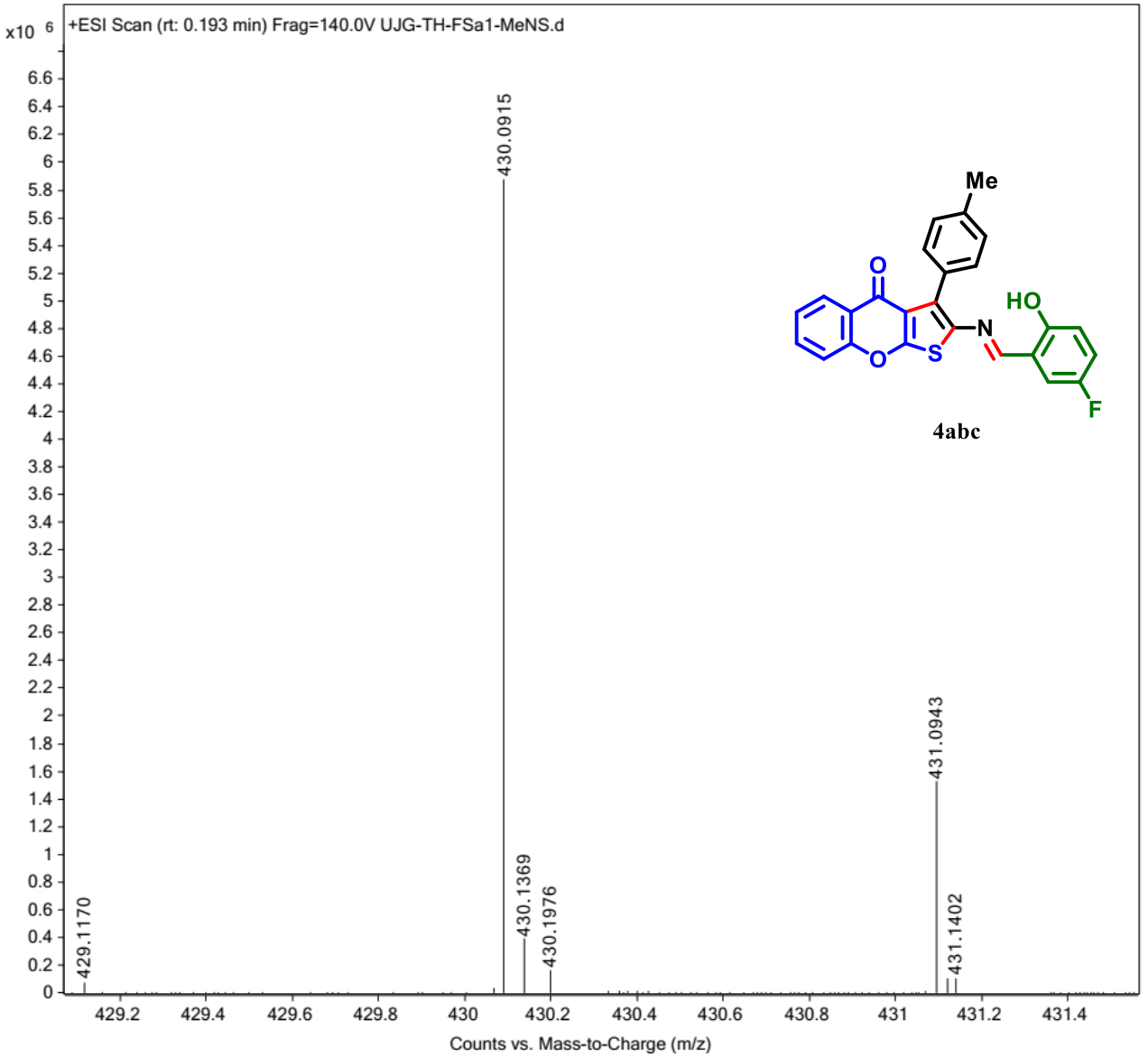
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound 4abc

UJG-TH-FSAL-MENS-19F.3.fid — UJG-TH-FSAL-MENS-19F

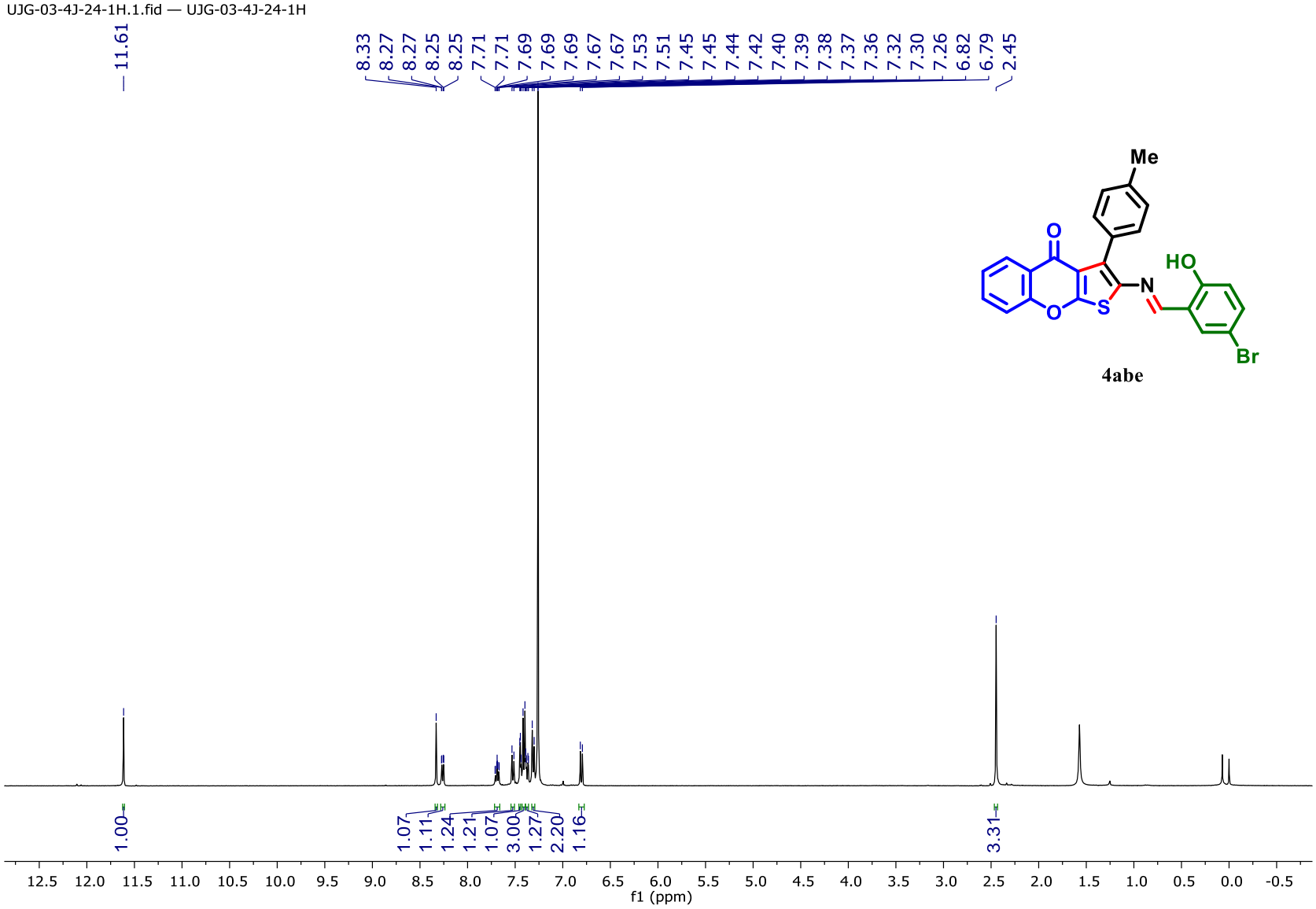
4abc



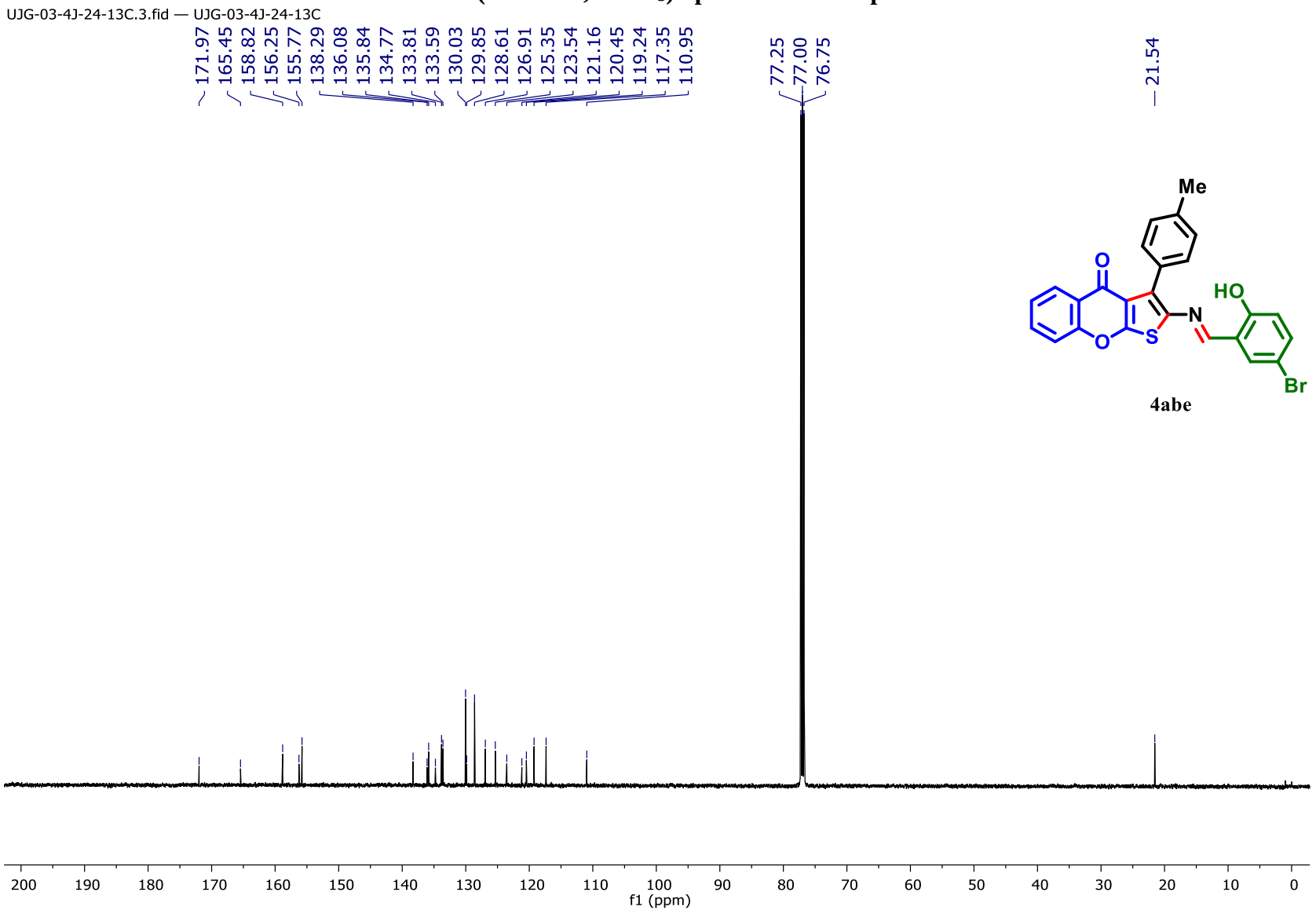
HRMS Spectrum of Compound 4abc



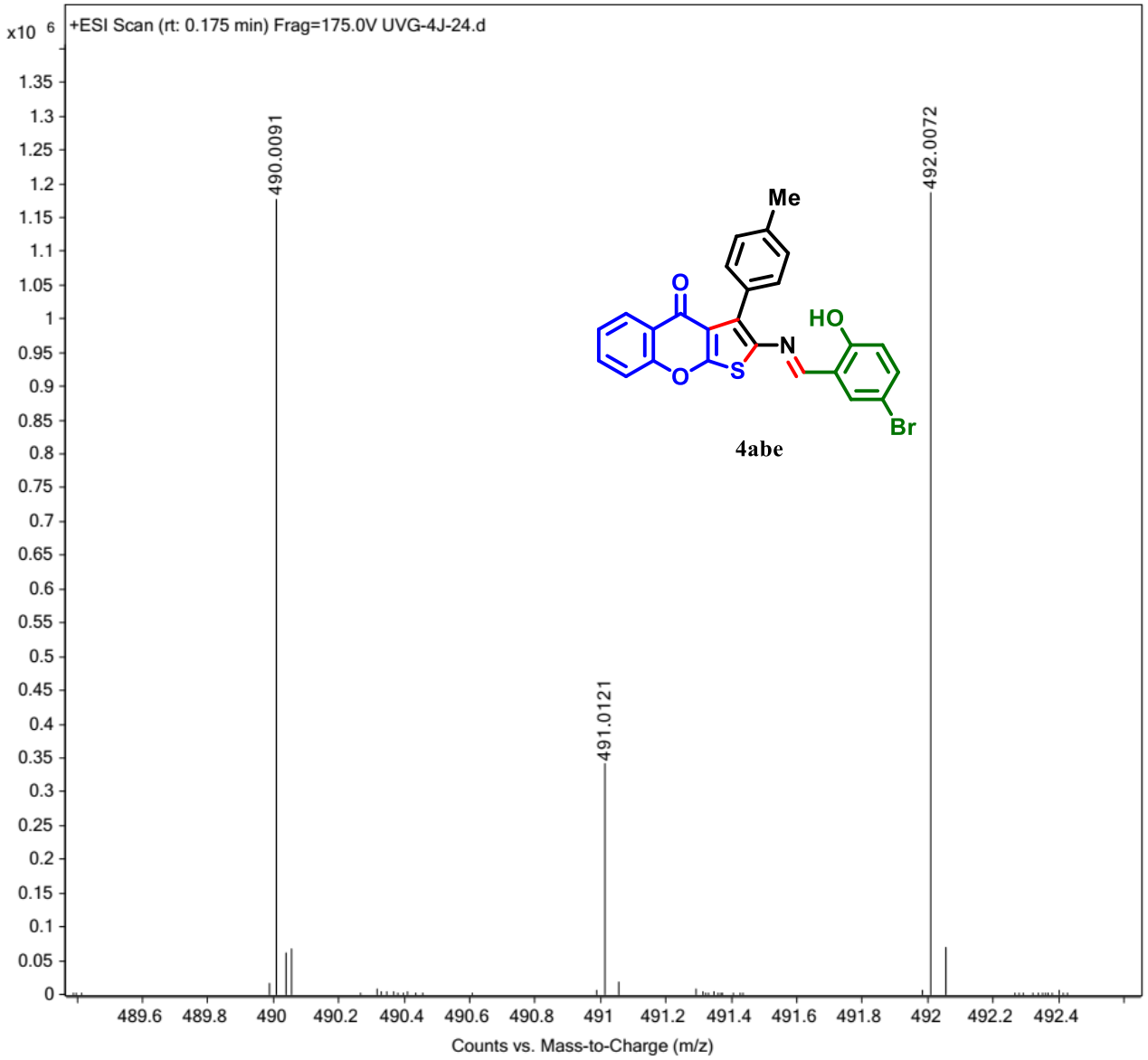
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4abe



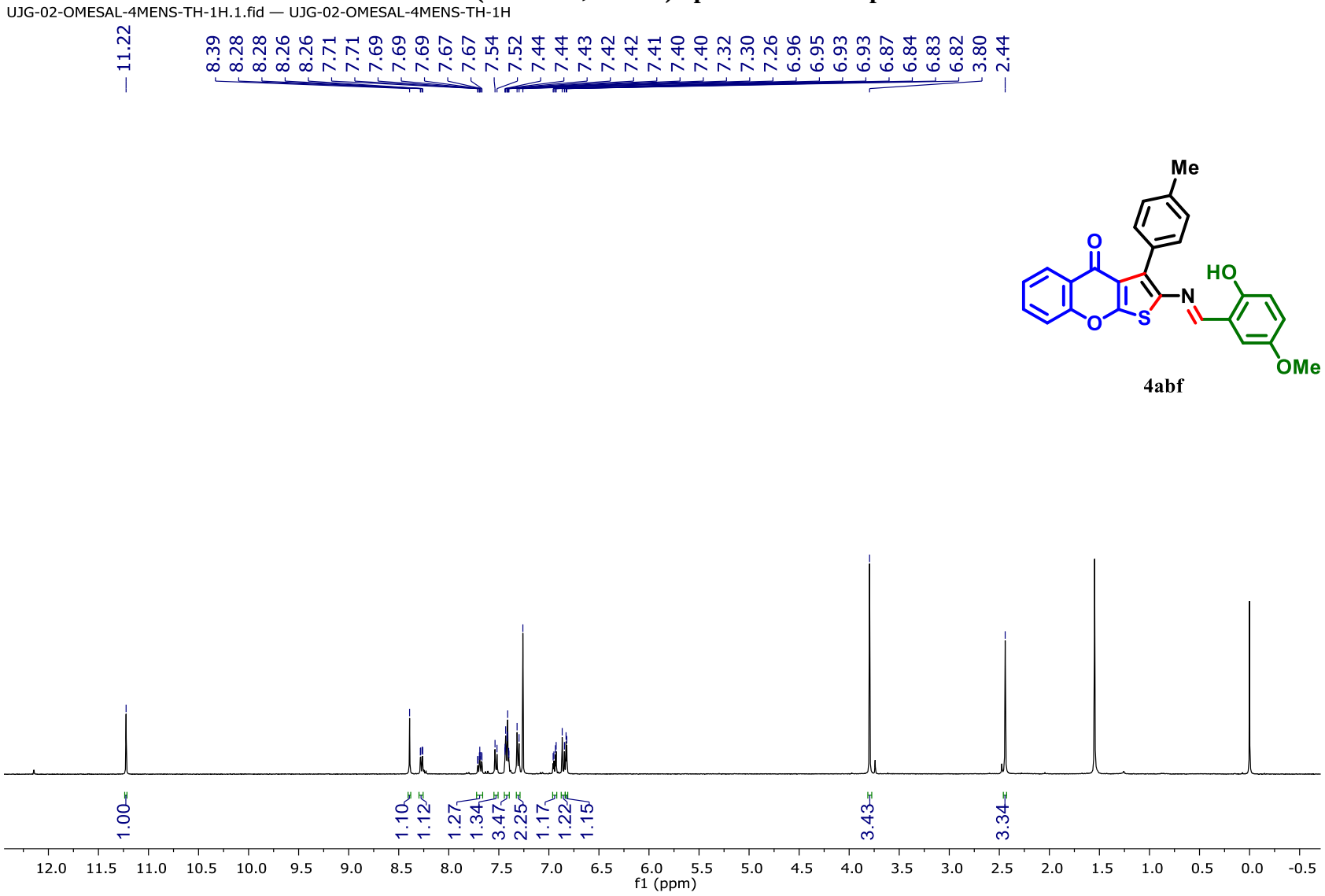
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4abe



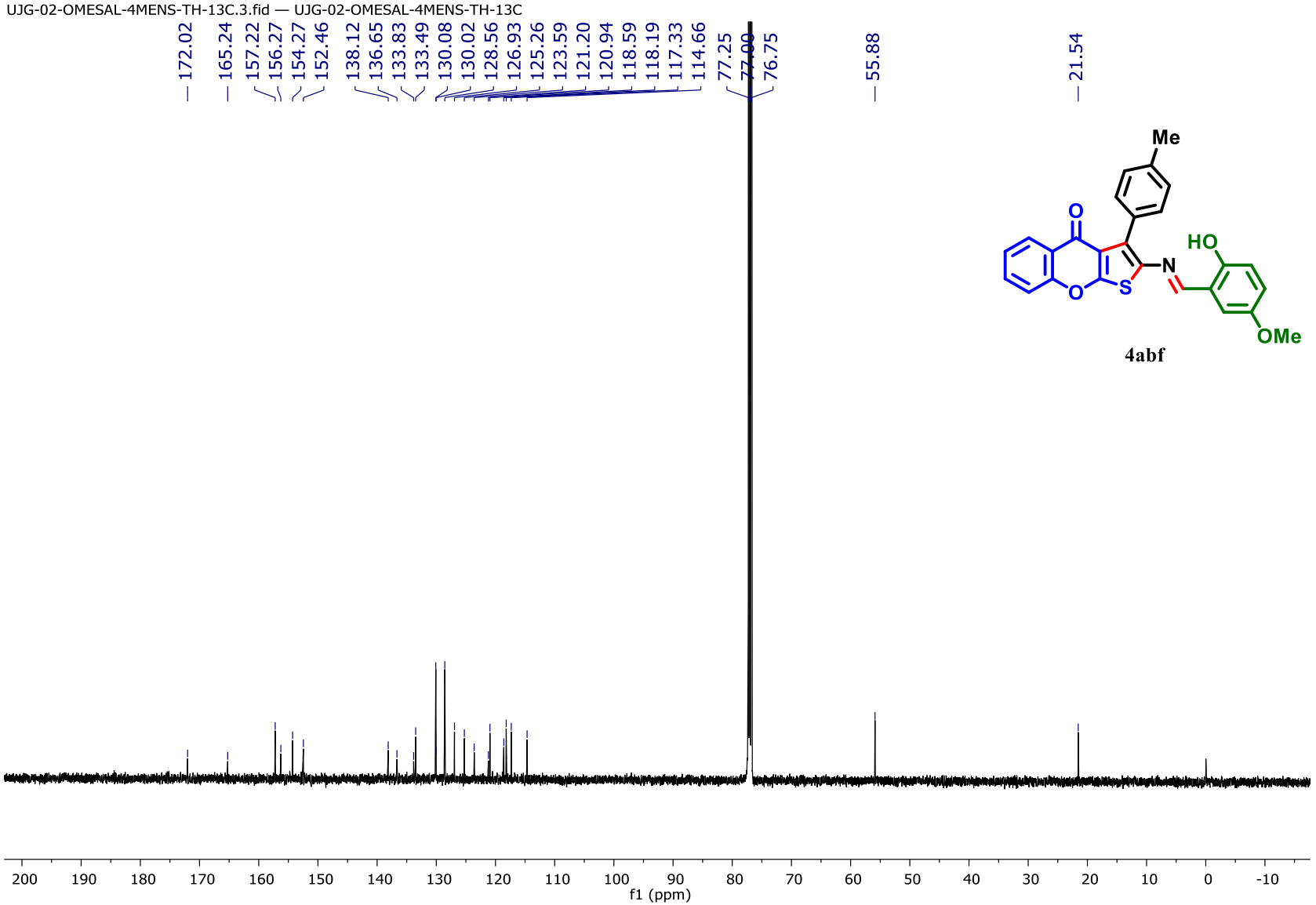
HRMS Spectrum of Compound 4abe



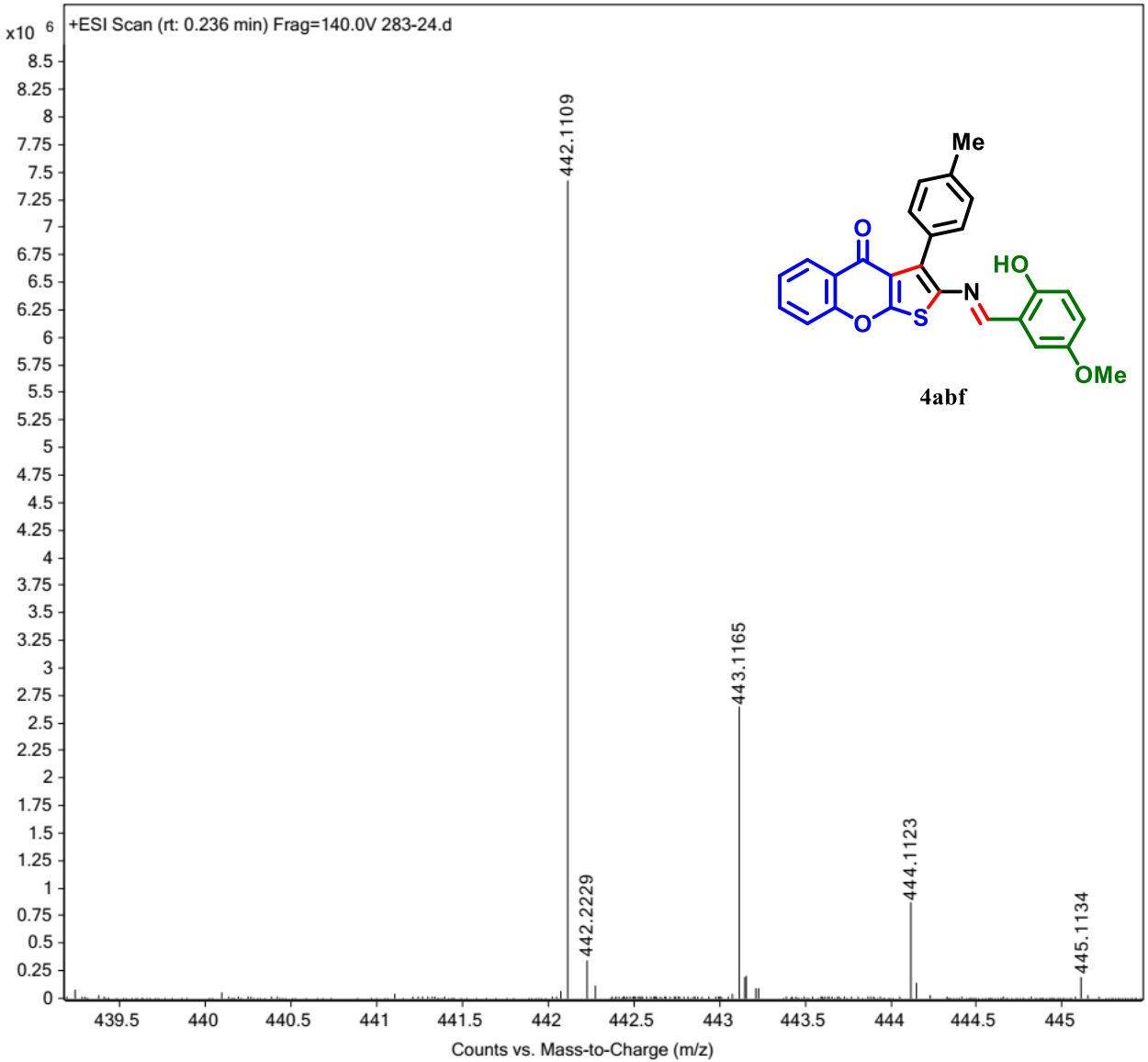
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4abf



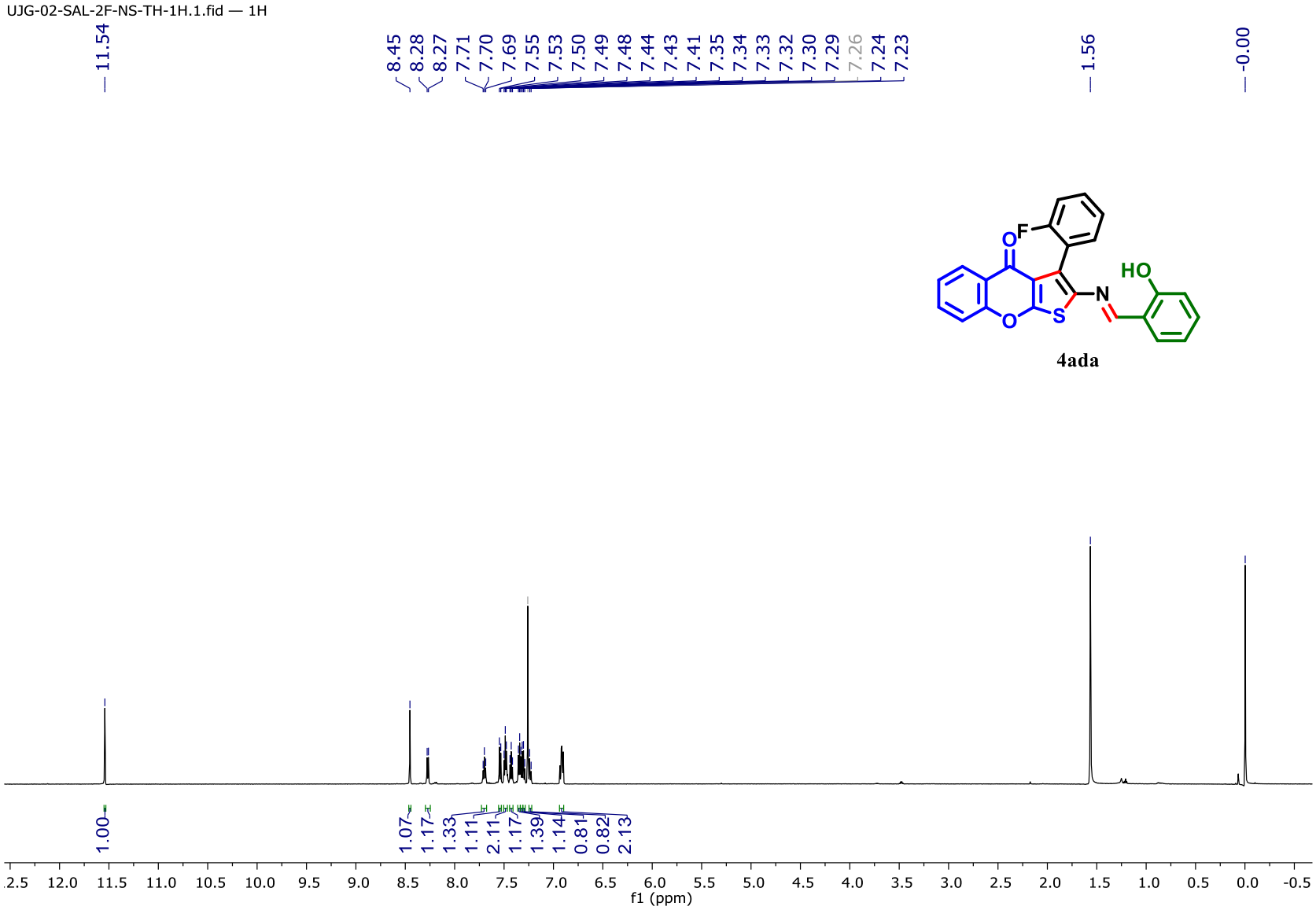
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4abf



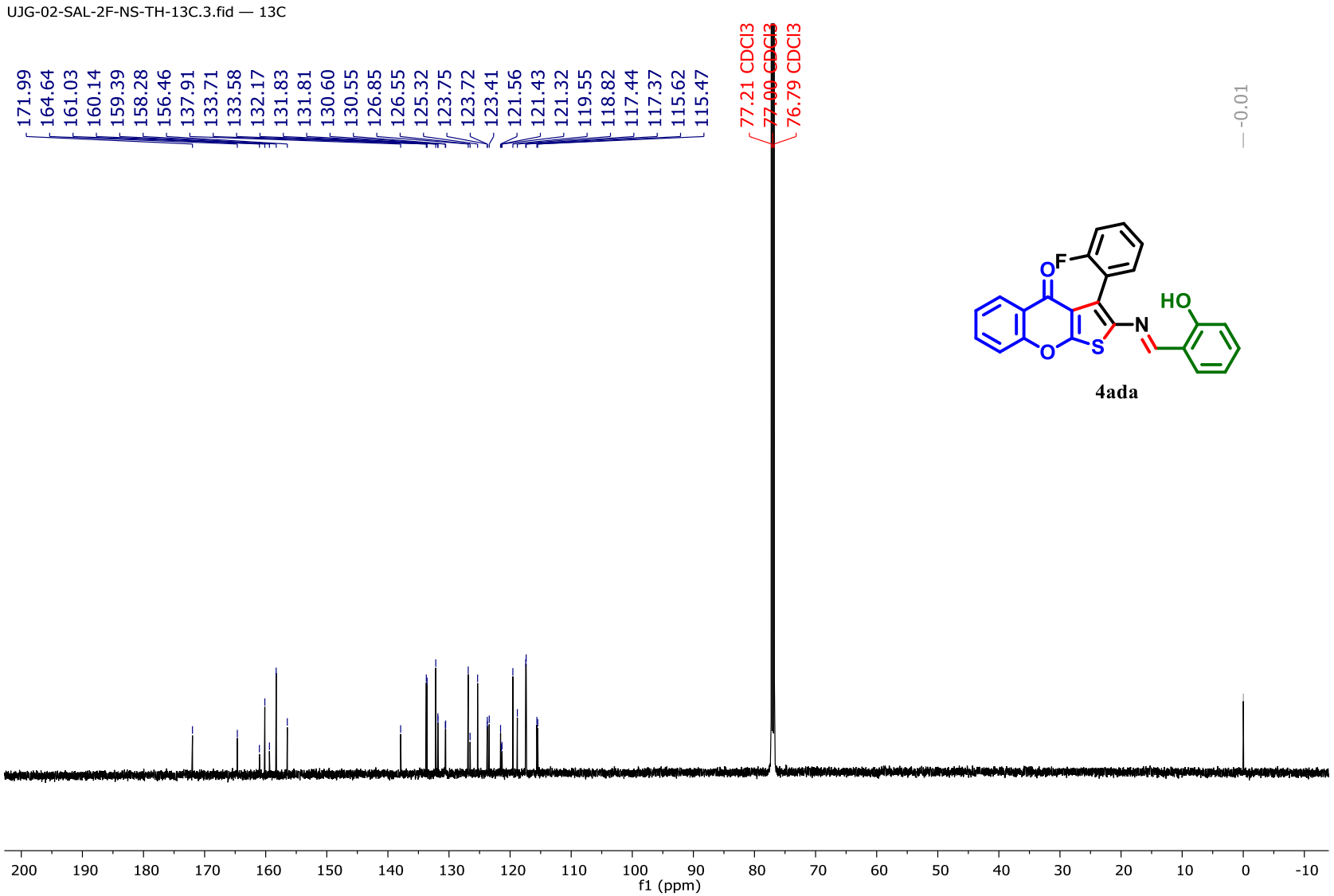
HRMS Spectrum of Compound 4abf



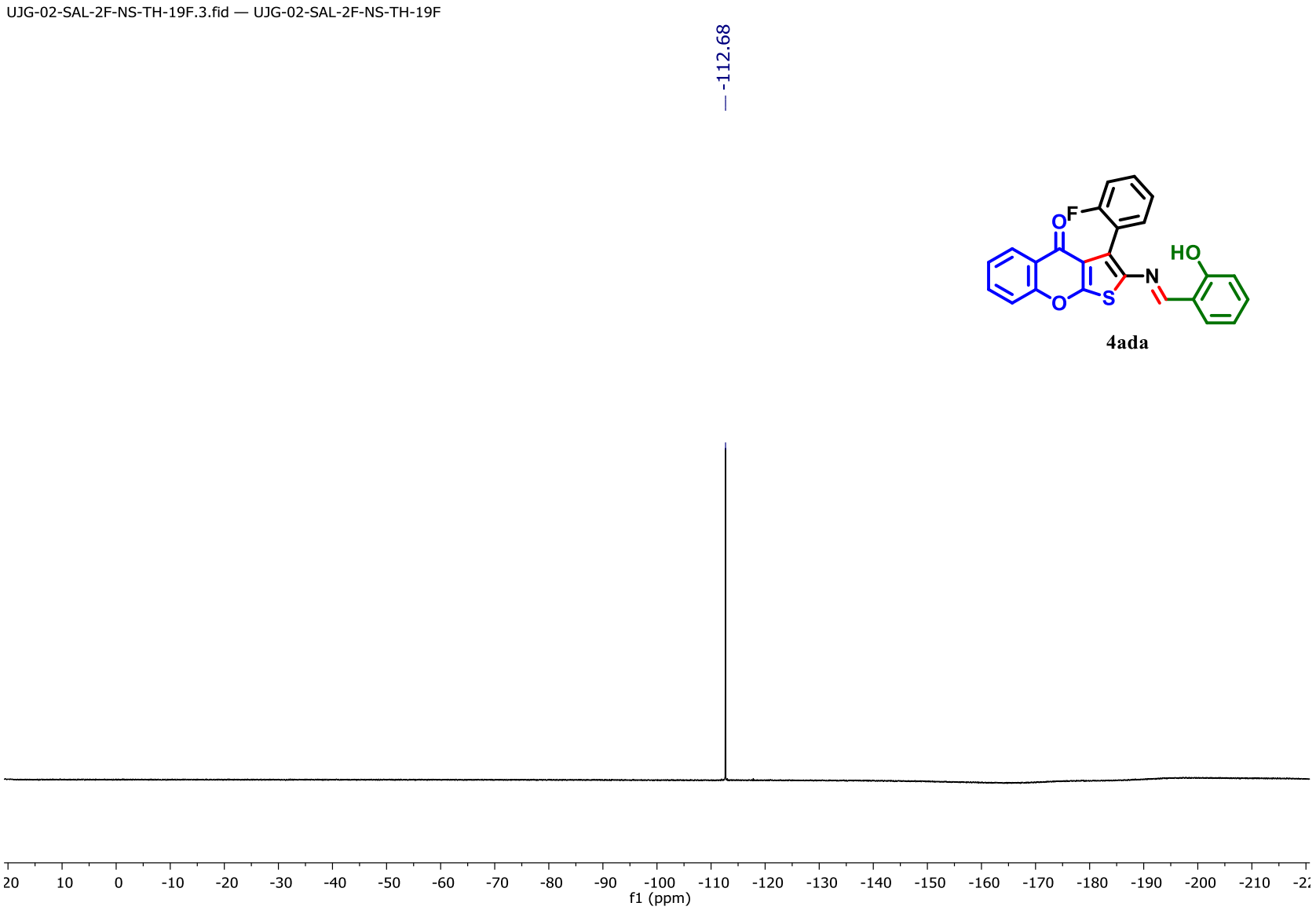
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound 4ada



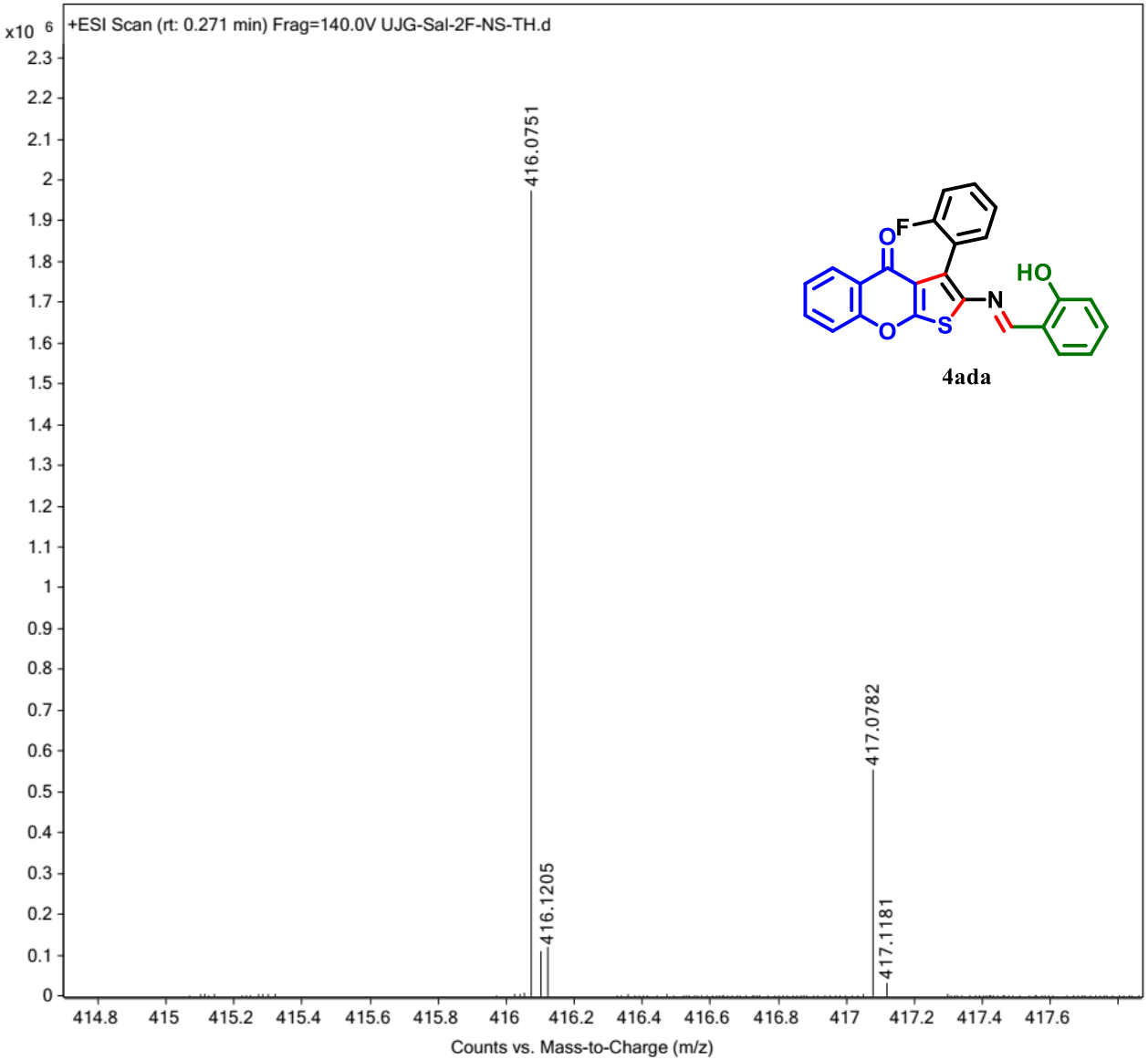
^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound 4ada



^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound 4ada

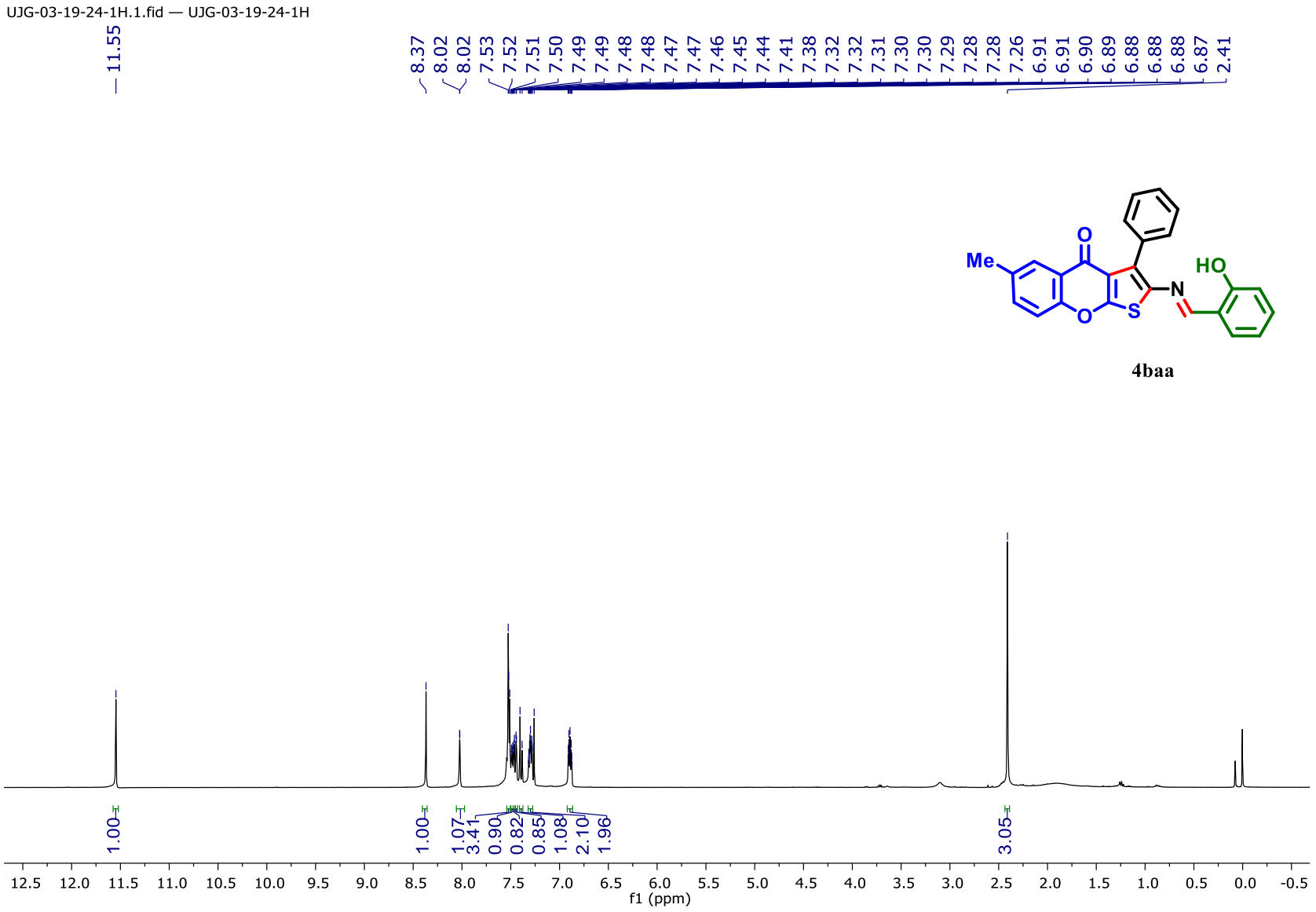


HRMS Spectrum of Compound 4ada



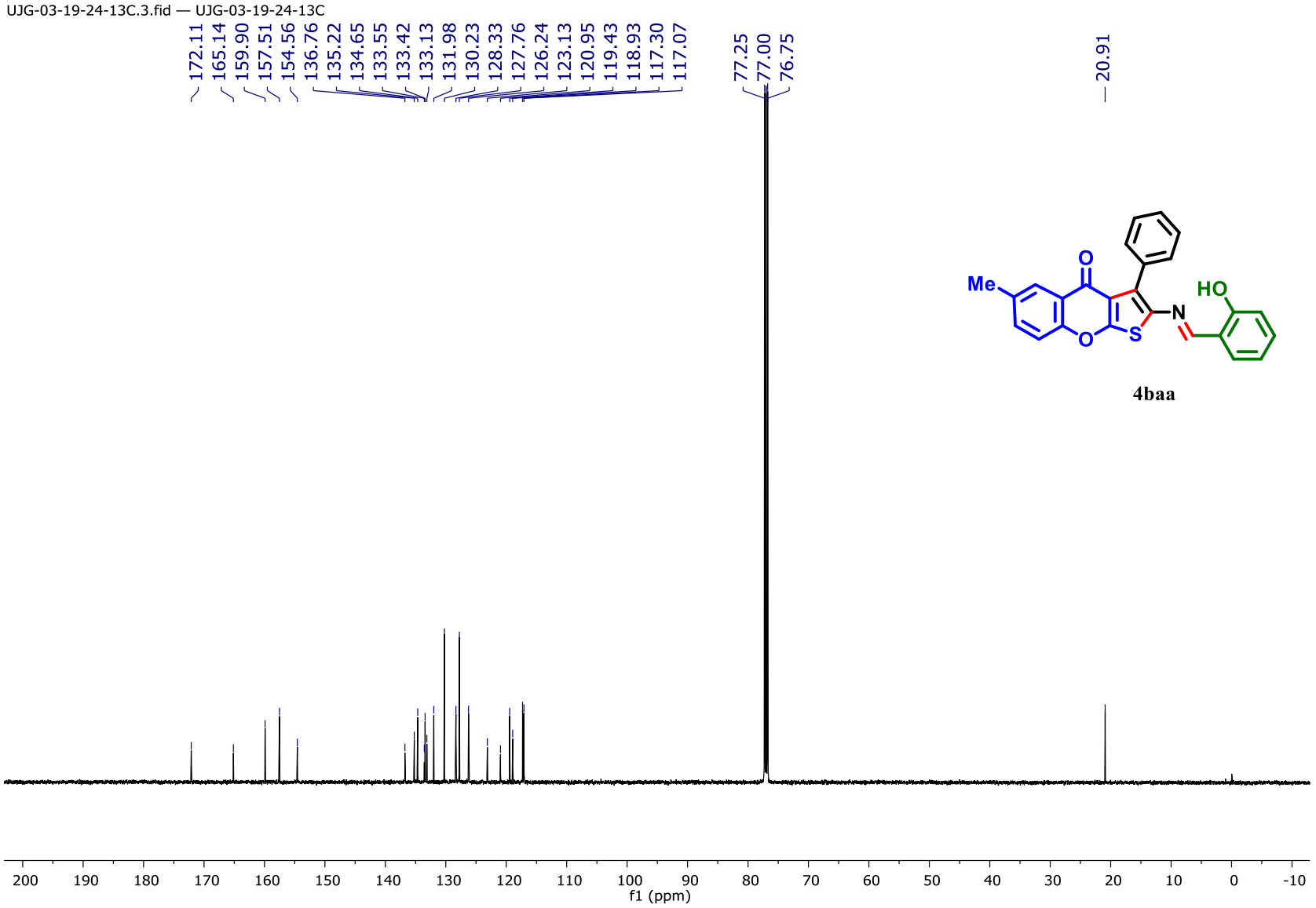
4ada

^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4baa

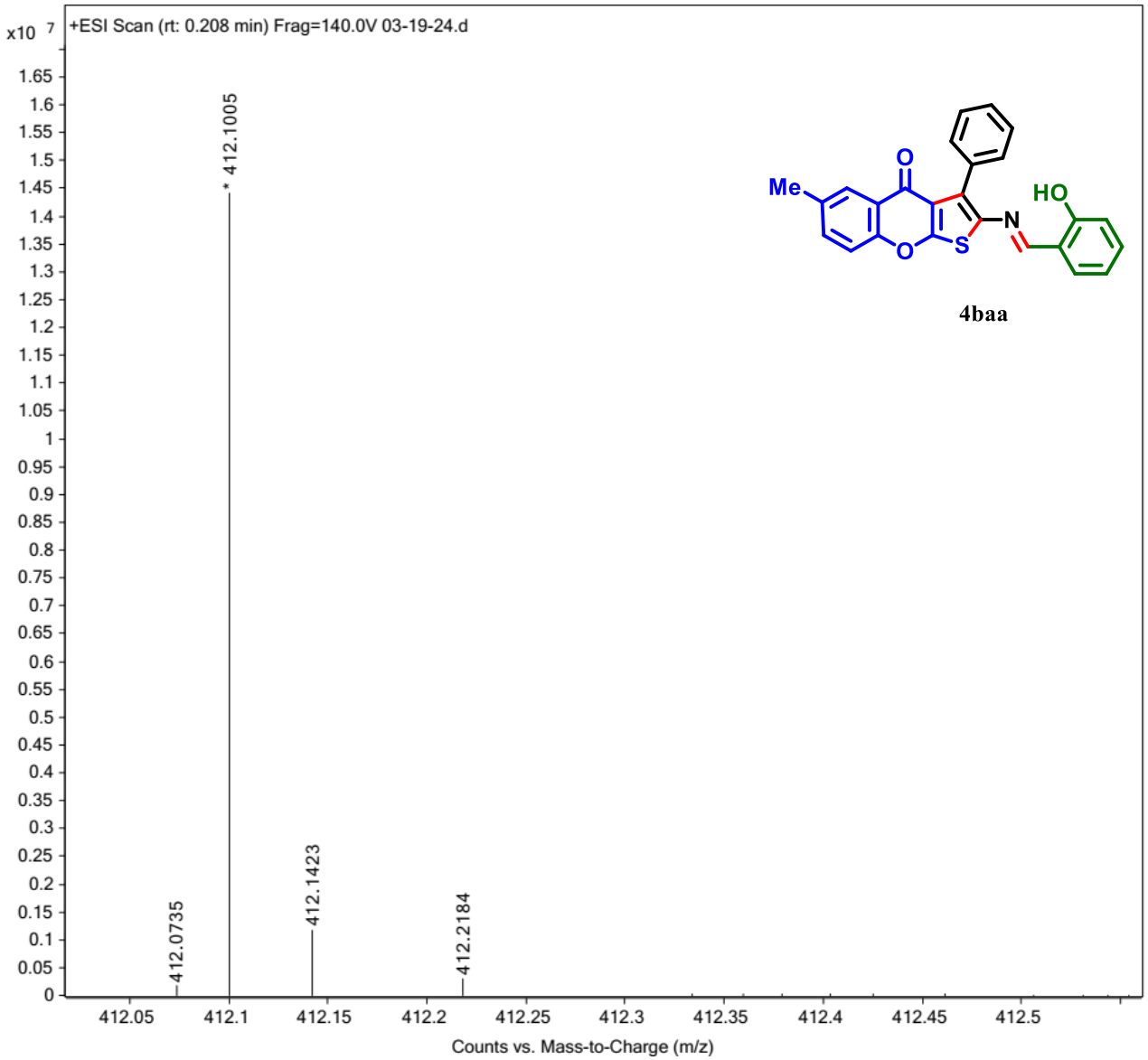


4baa

^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4baa

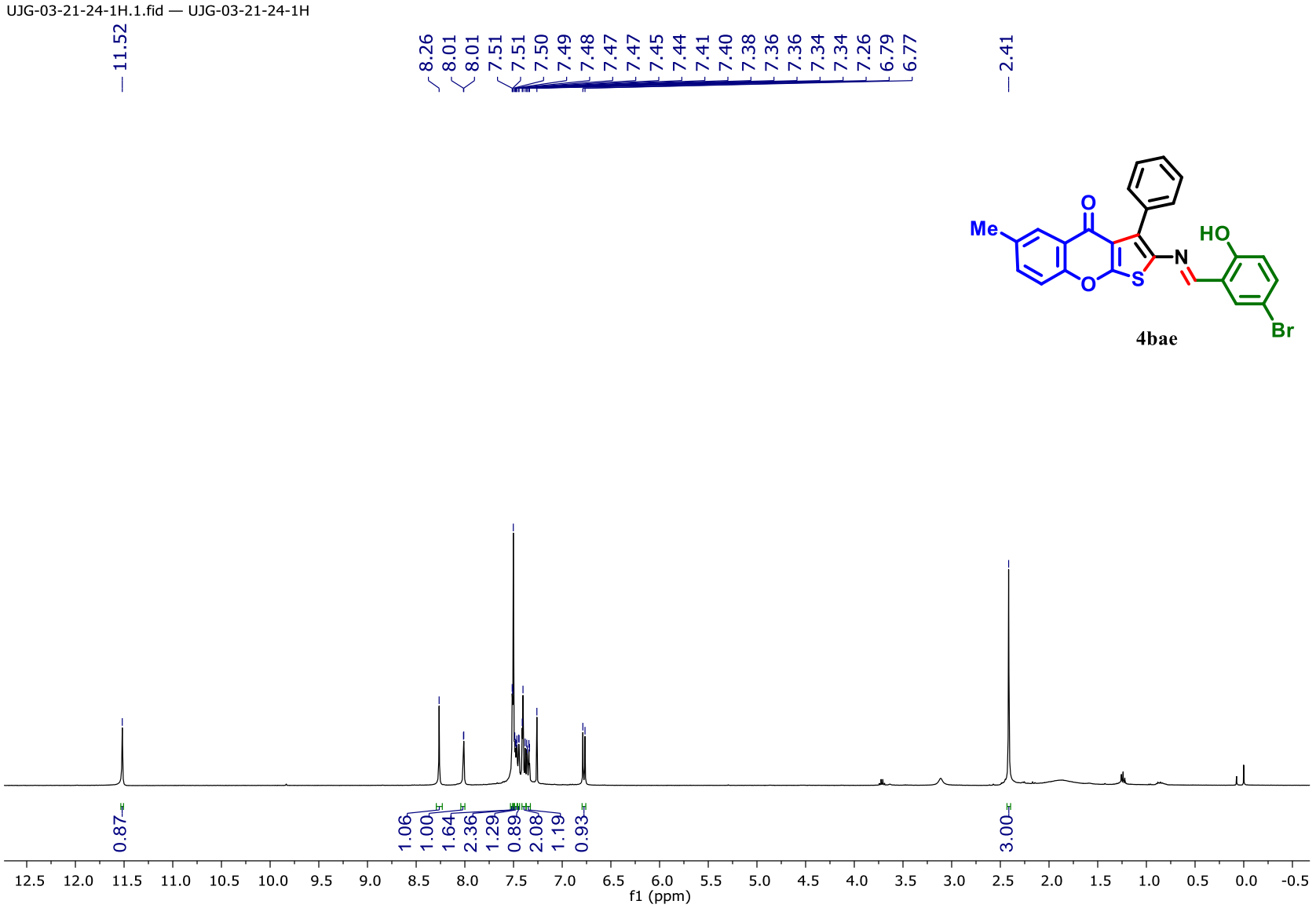


HRMS Spectrum of Compound 4baa

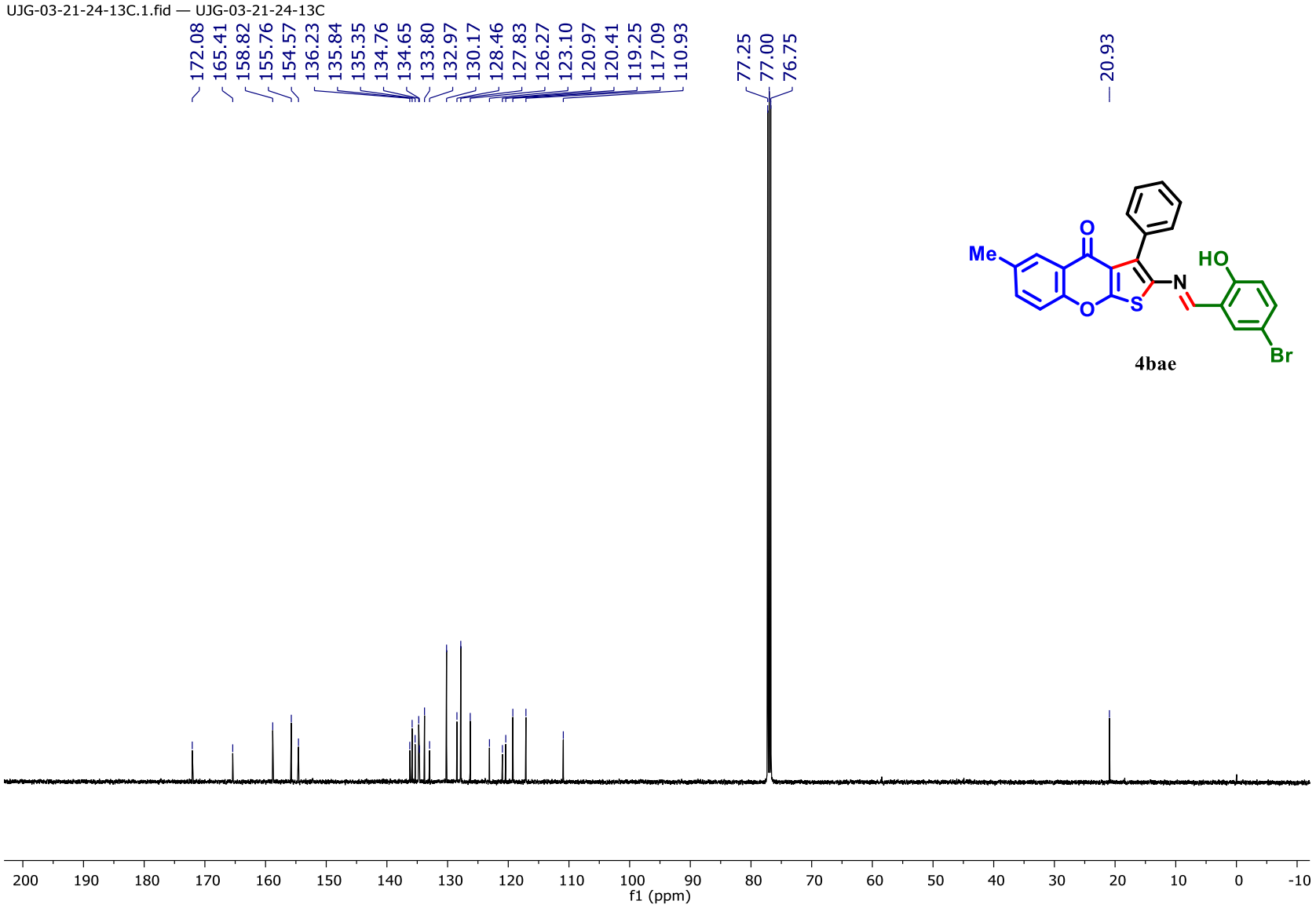


4baa

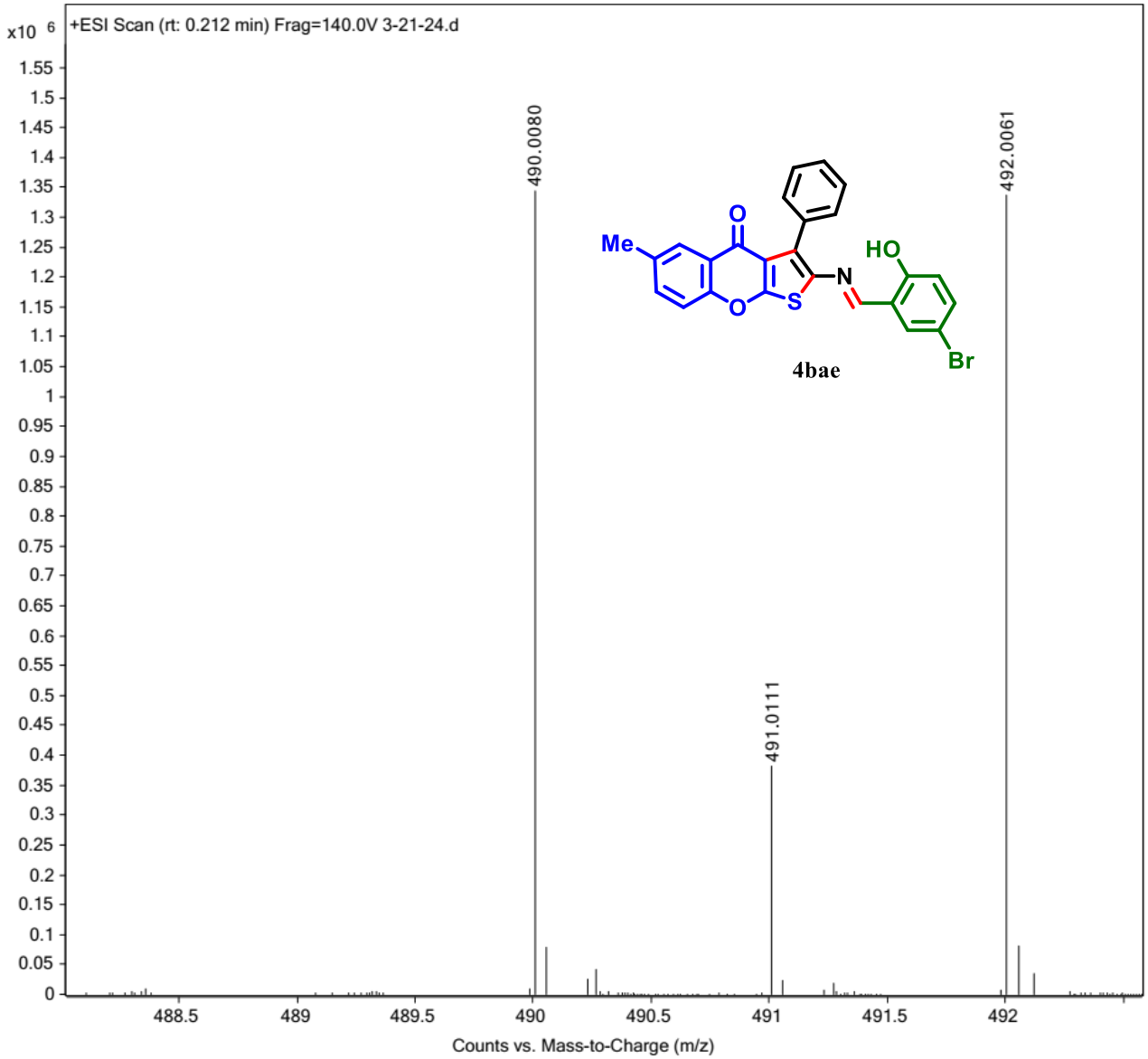
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4bae



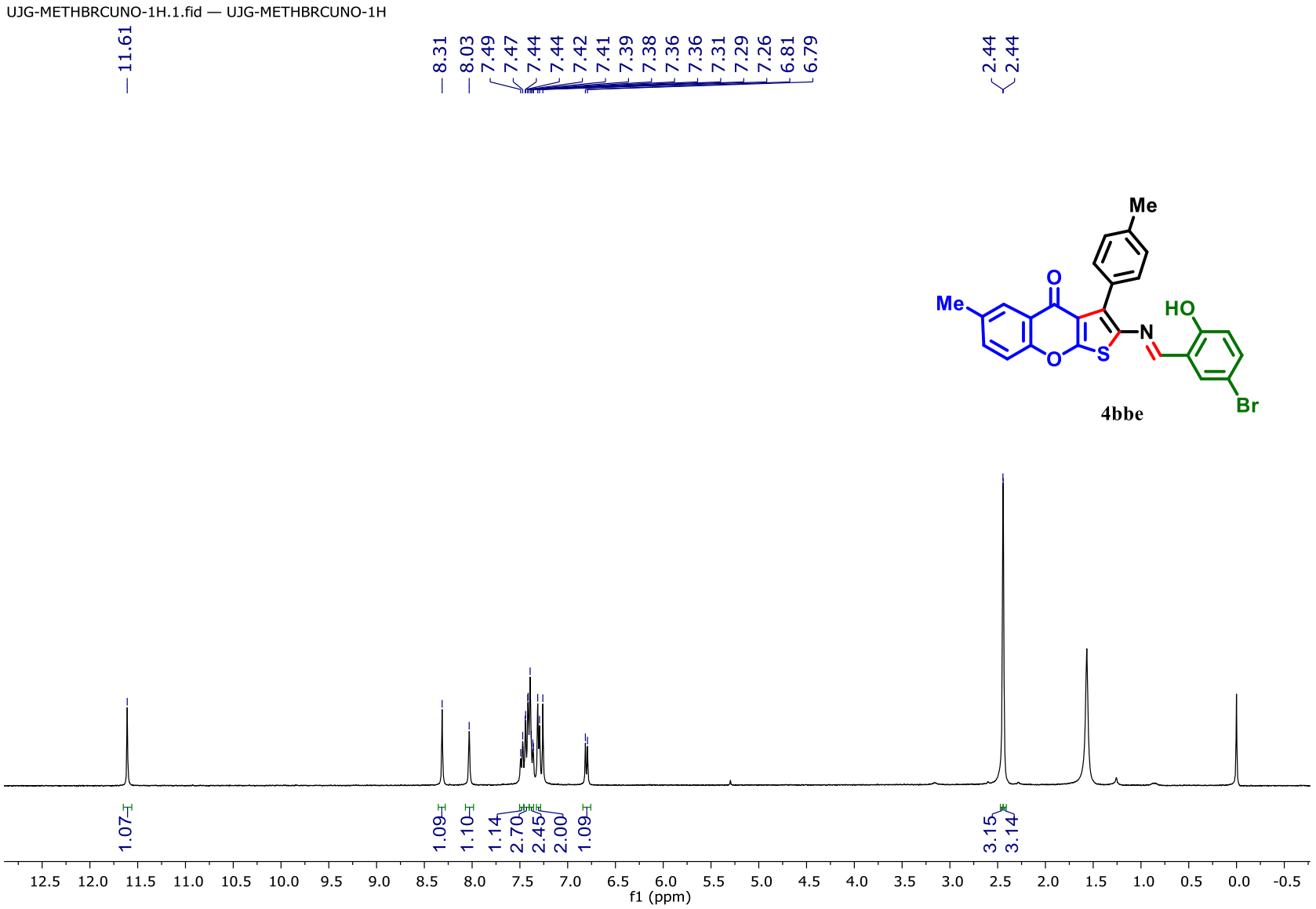
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4bae



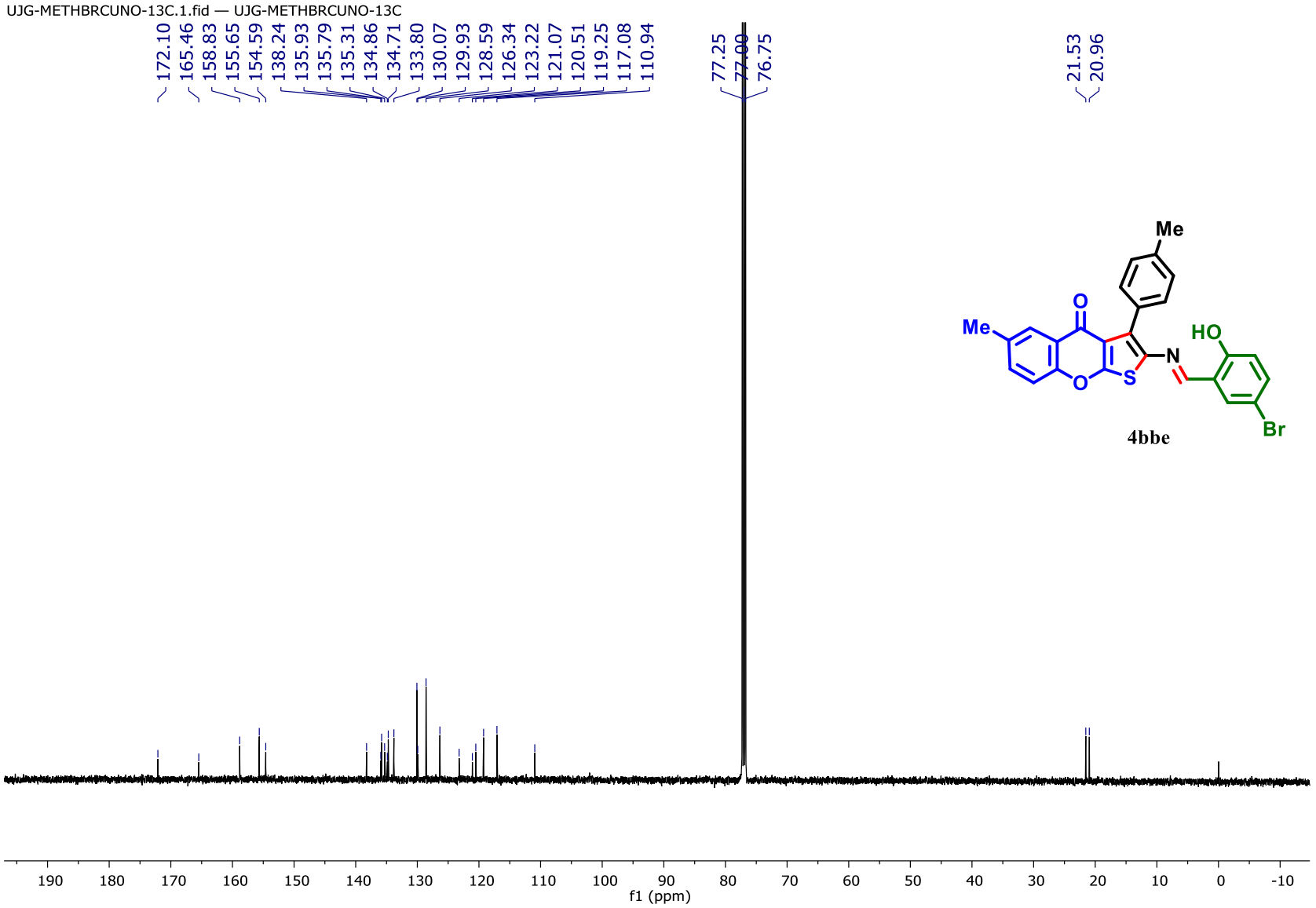
HRMS Spectrum of Compound 4bae



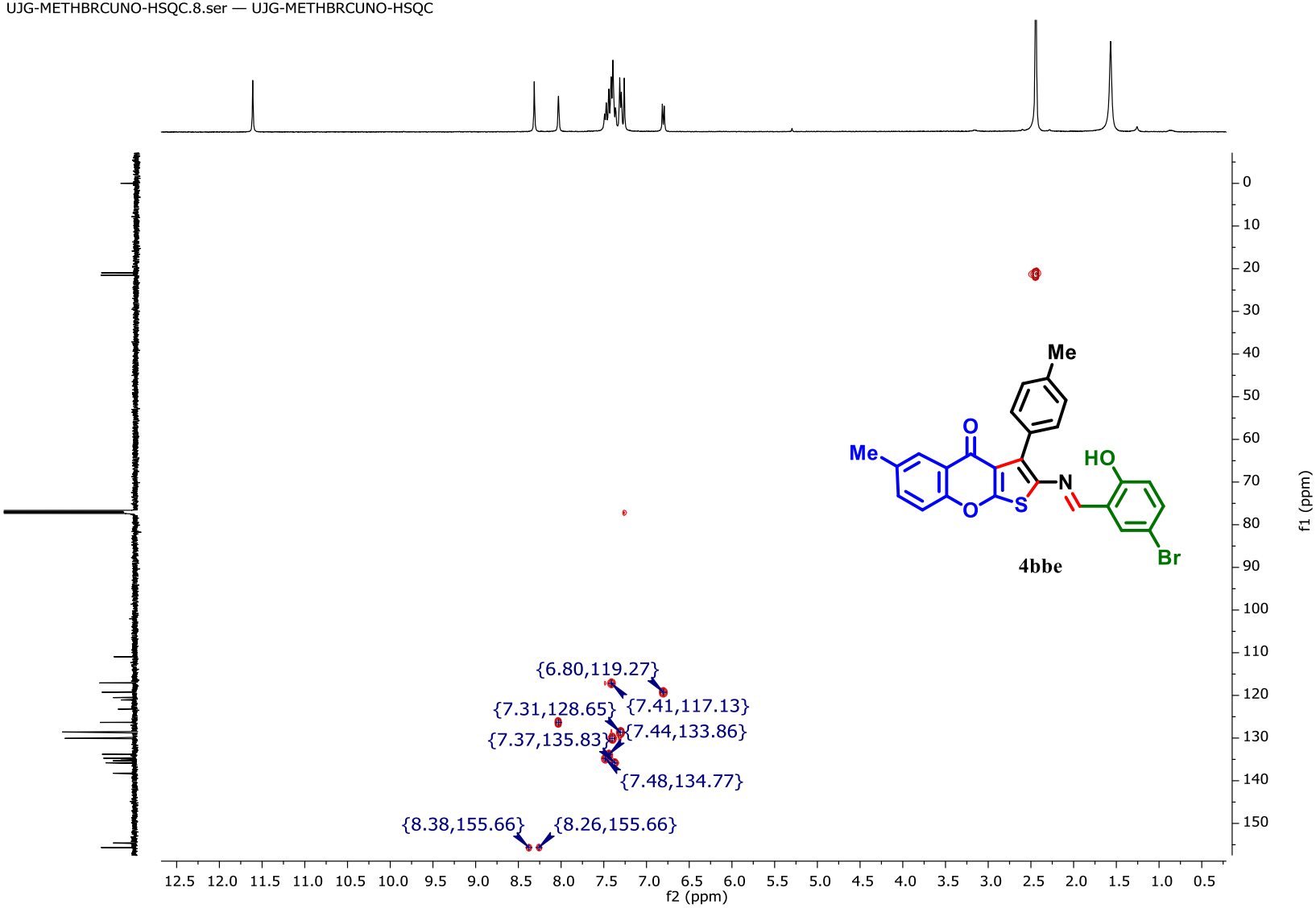
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4bbe



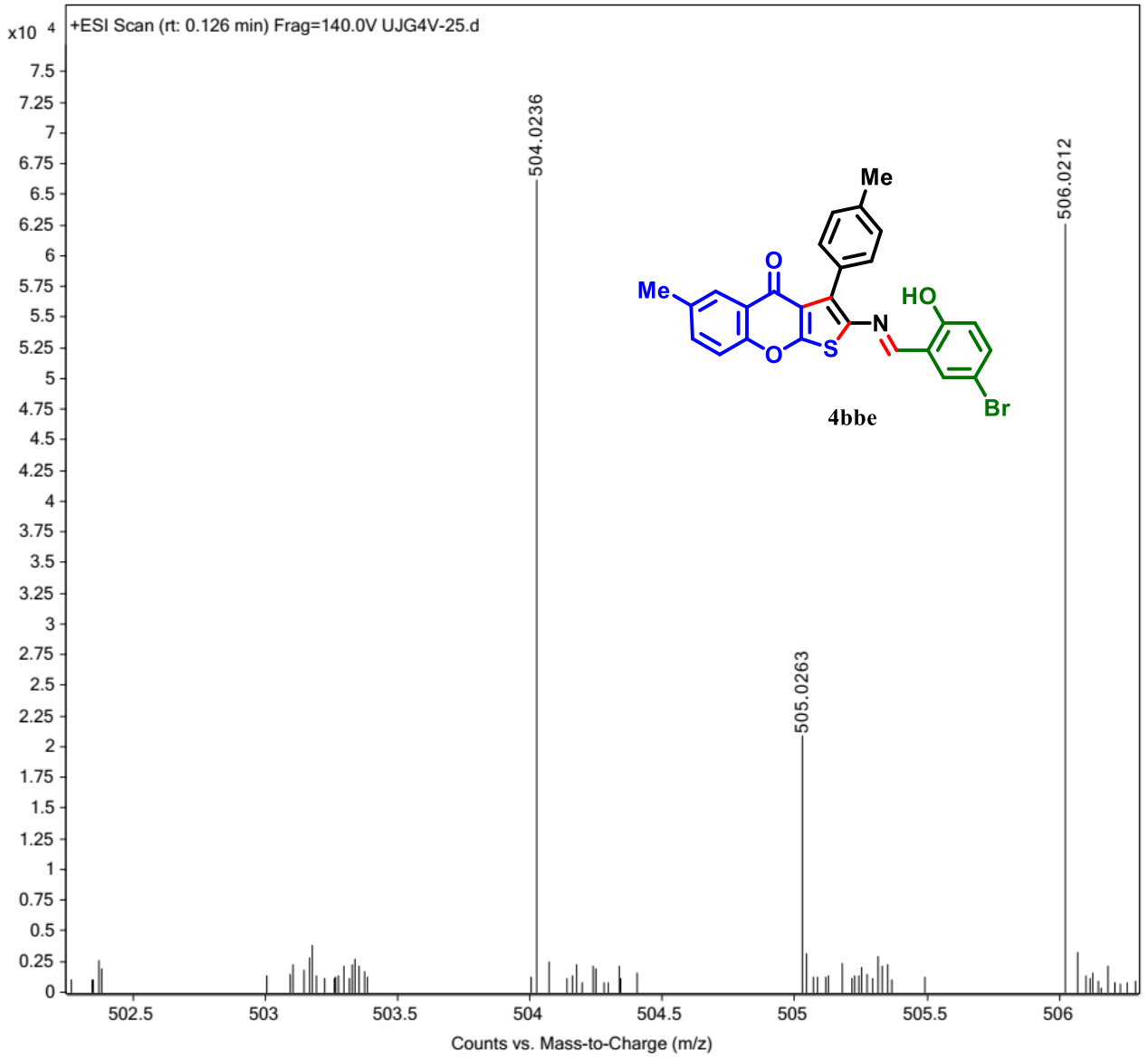
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4bbe



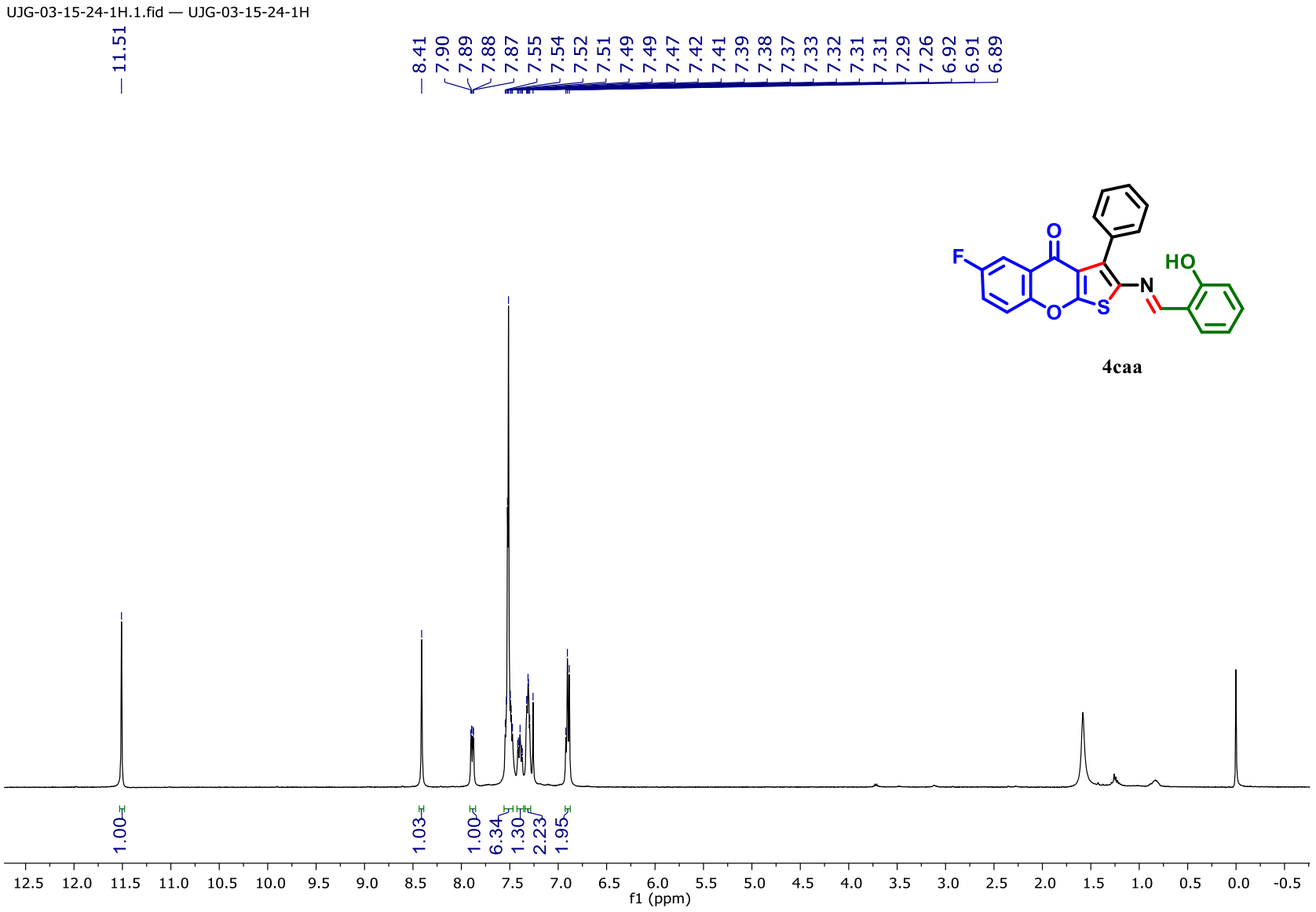
HSQC Spectrum of Compound 4bbe



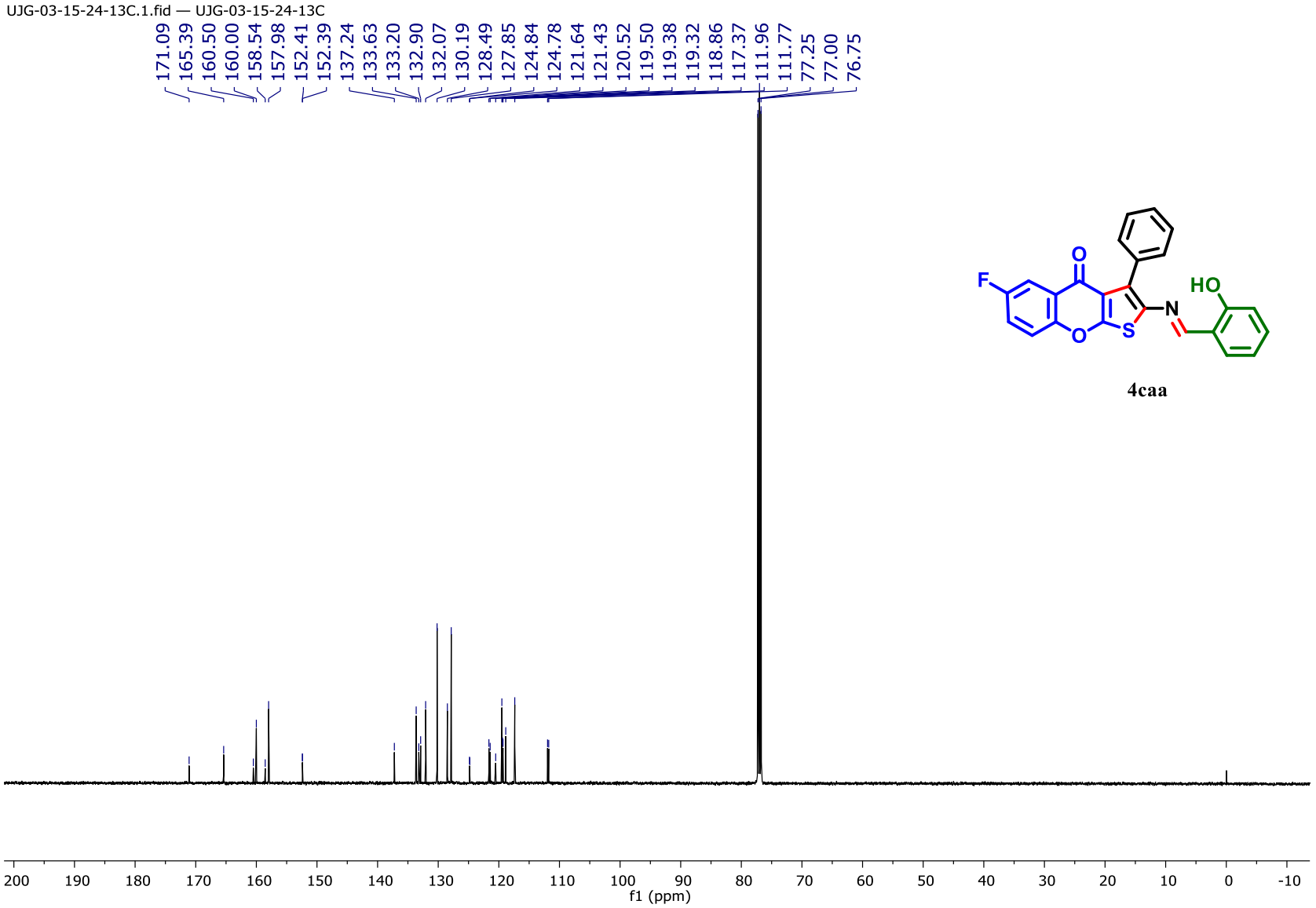
HRMS Spectrum of Compound 4bbe



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4caa

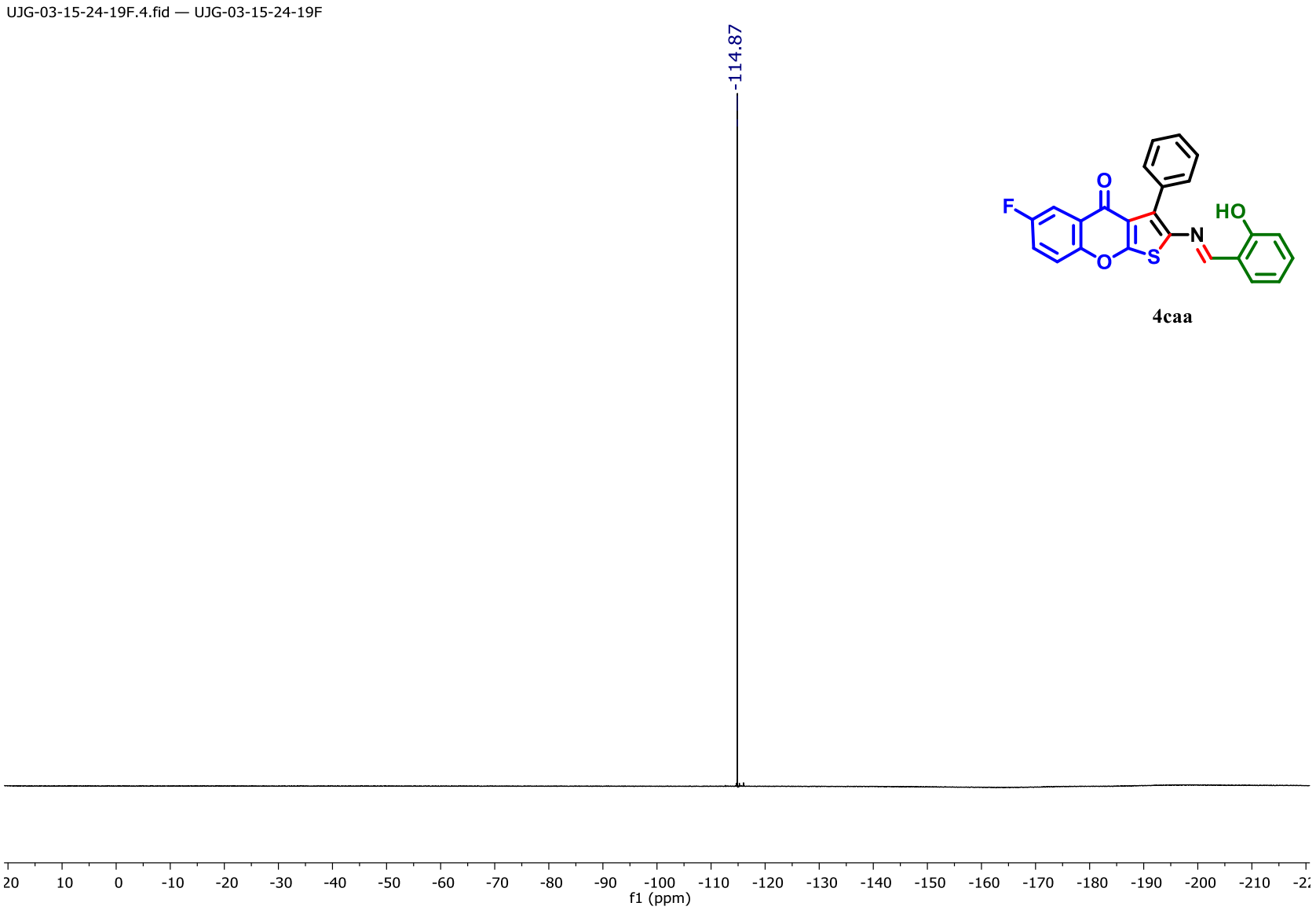


^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4caa



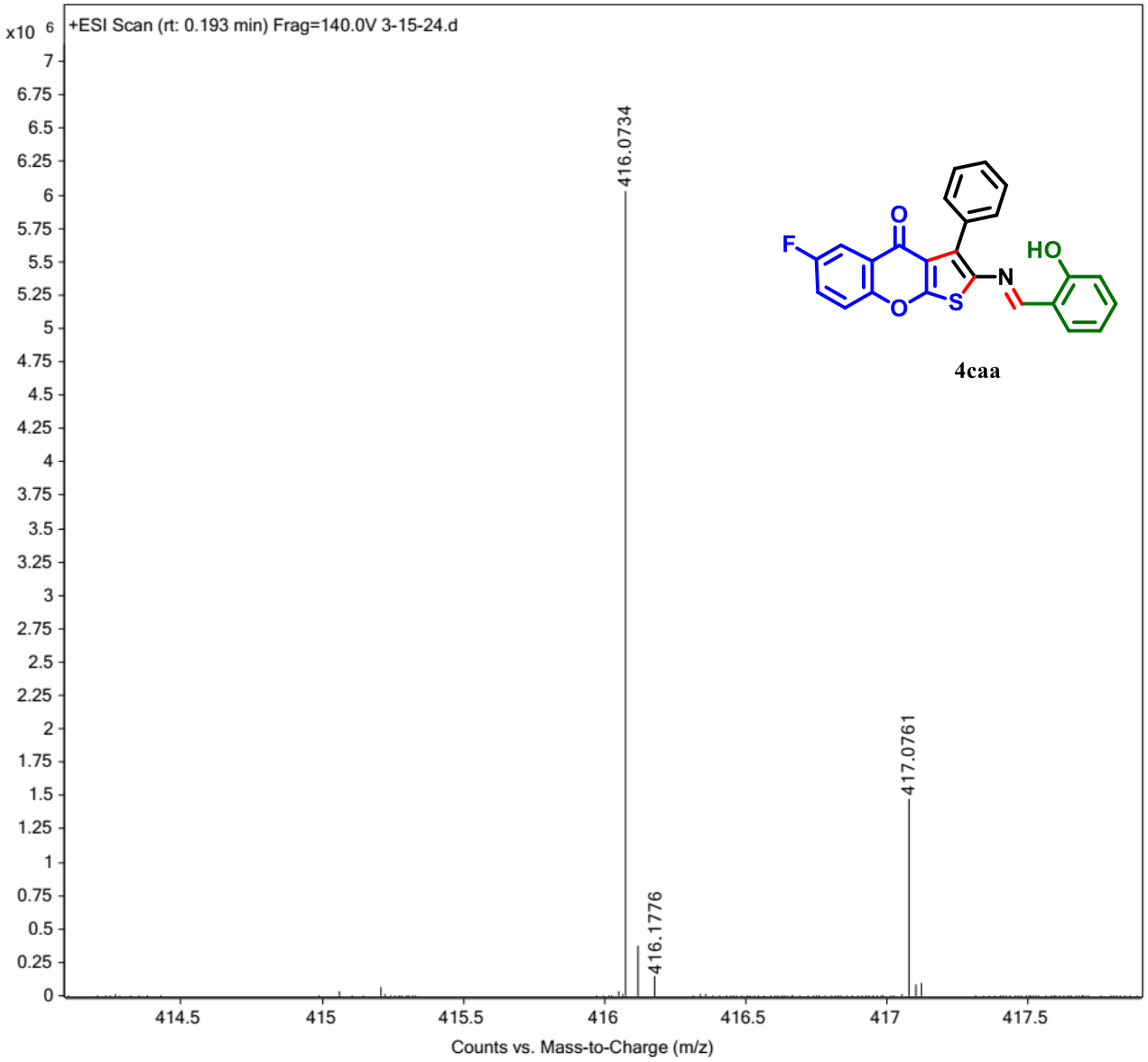
4caa

^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound 4caa



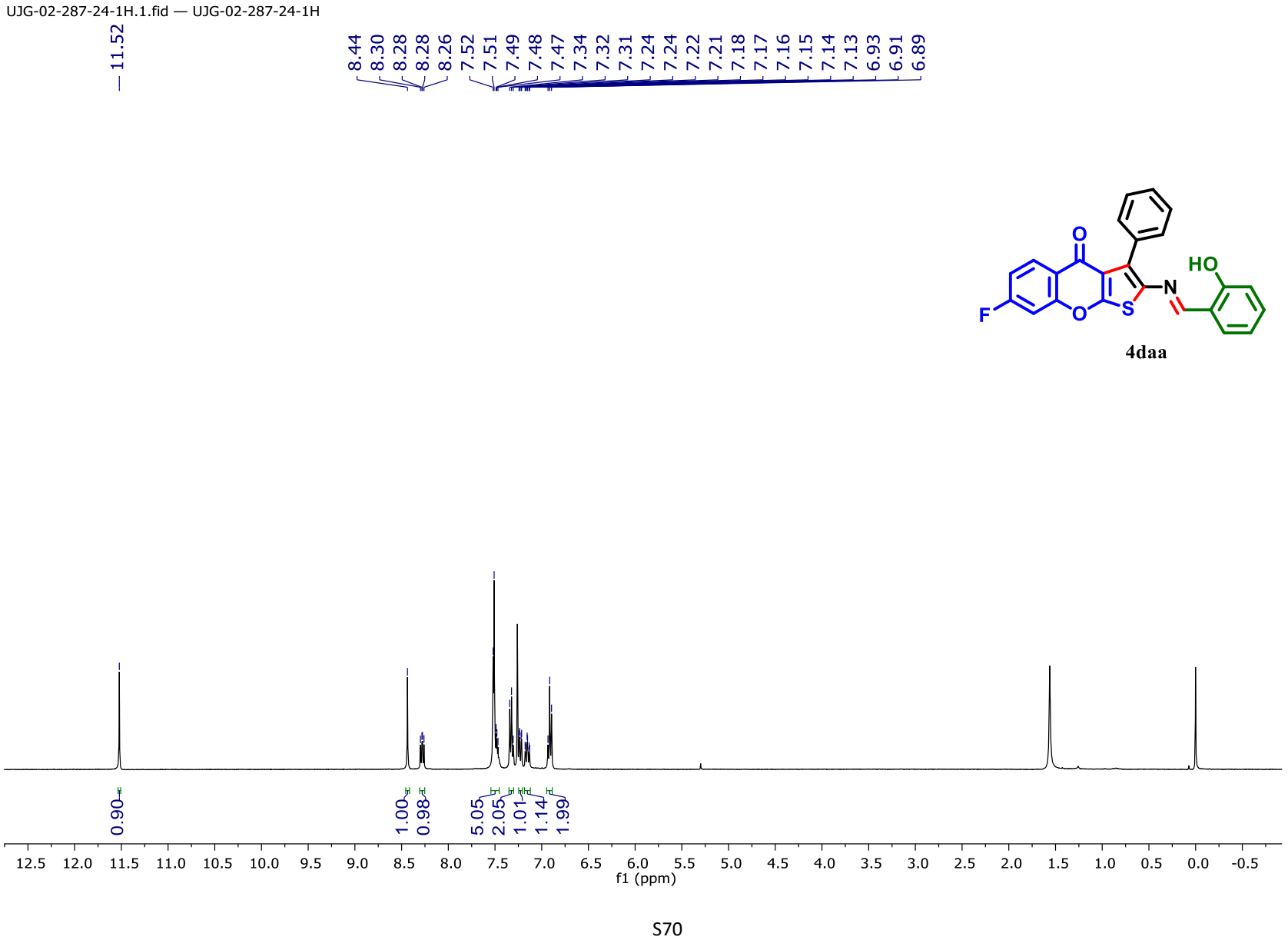
4caa

HRMS Spectrum of Compound 4caa

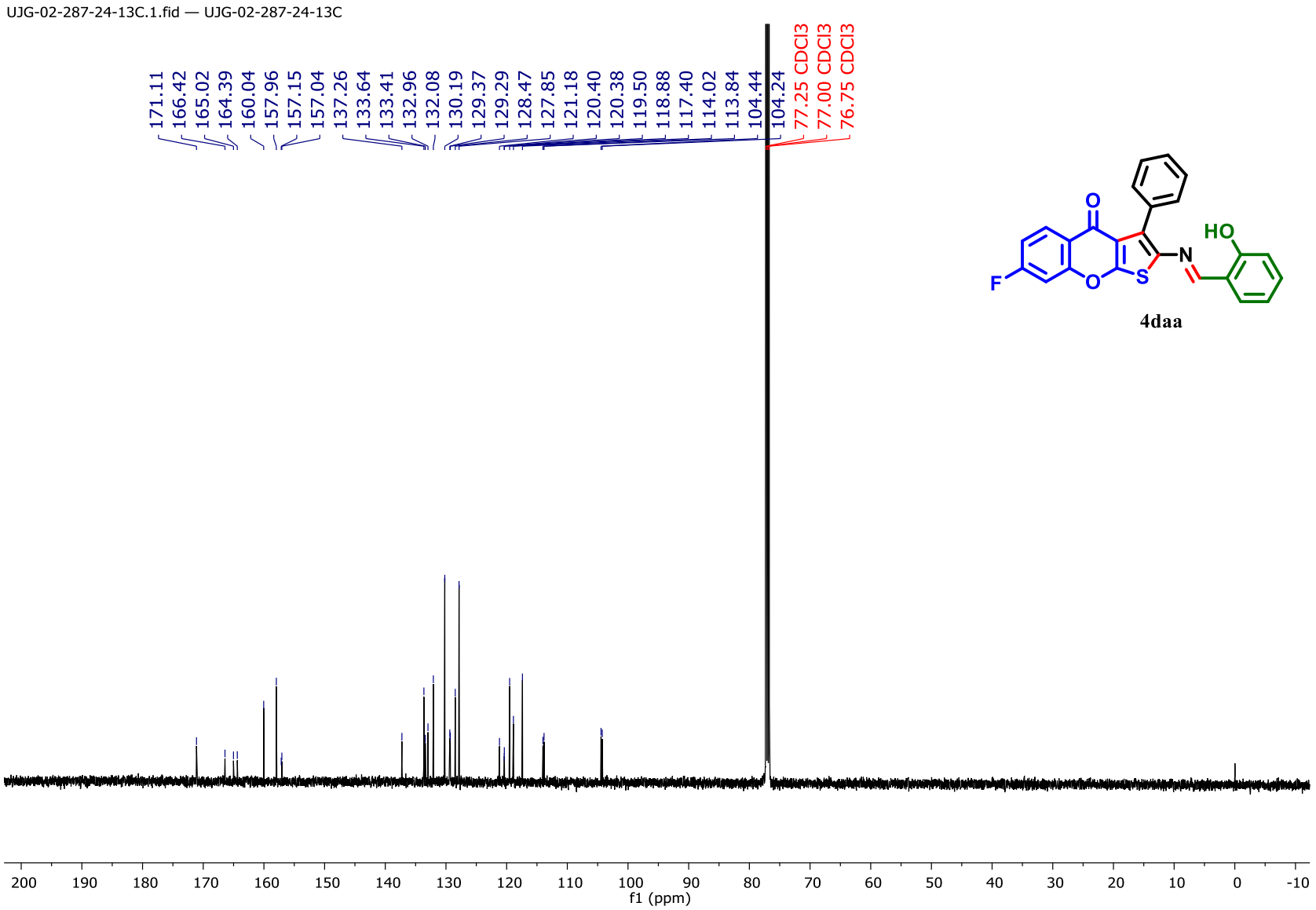


4caa

^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4daa

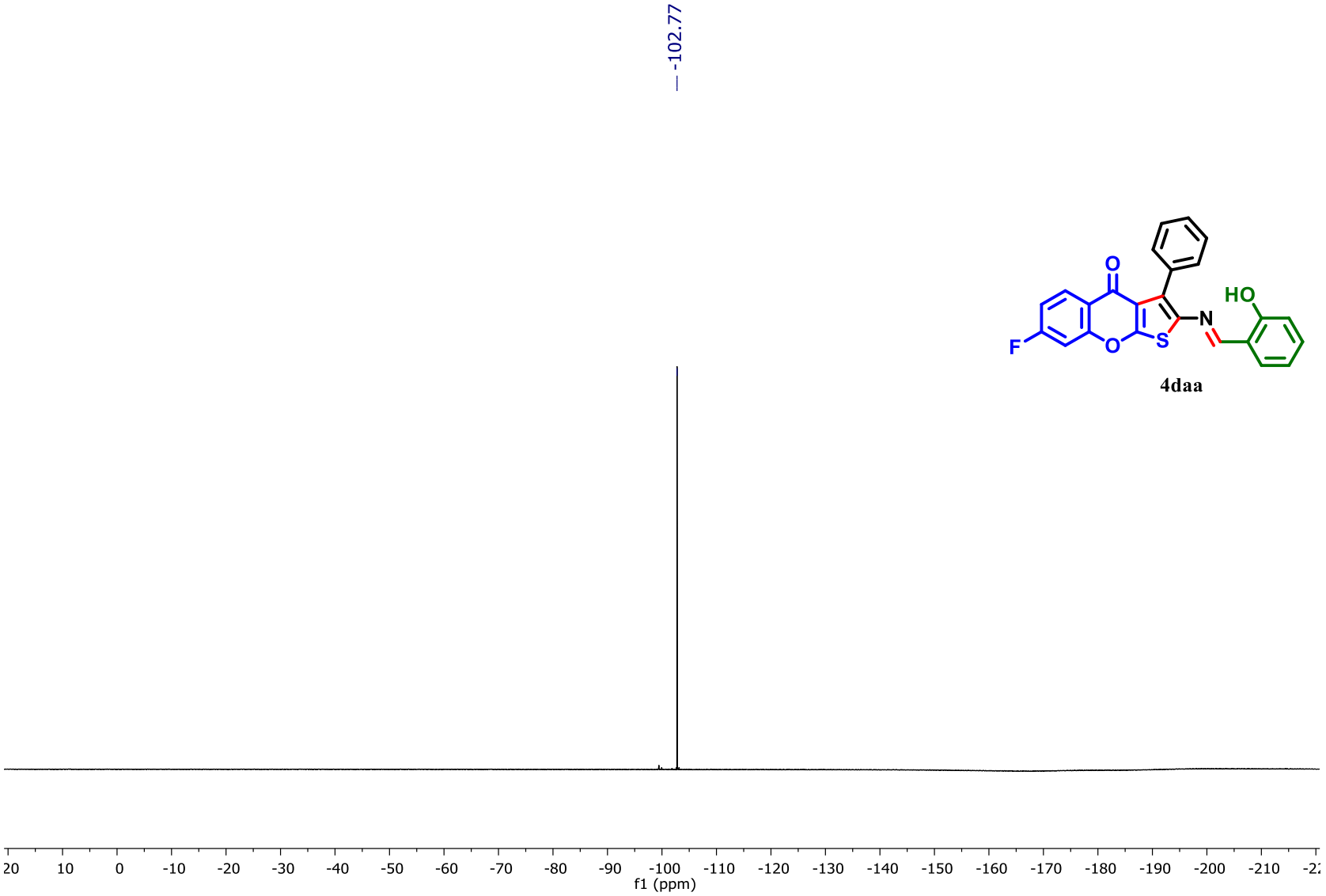


^{13}H NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4daa

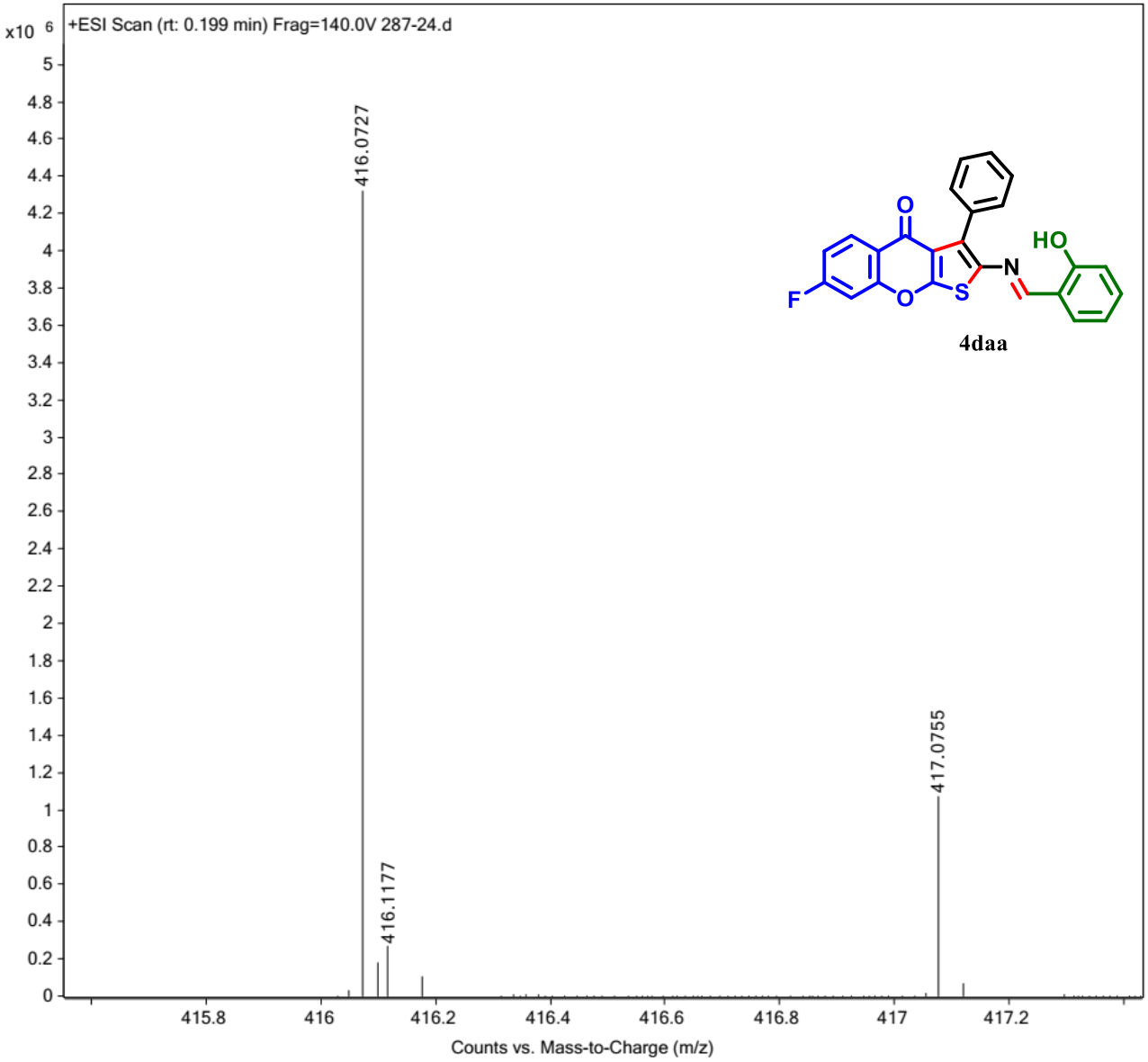


^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound 4daa

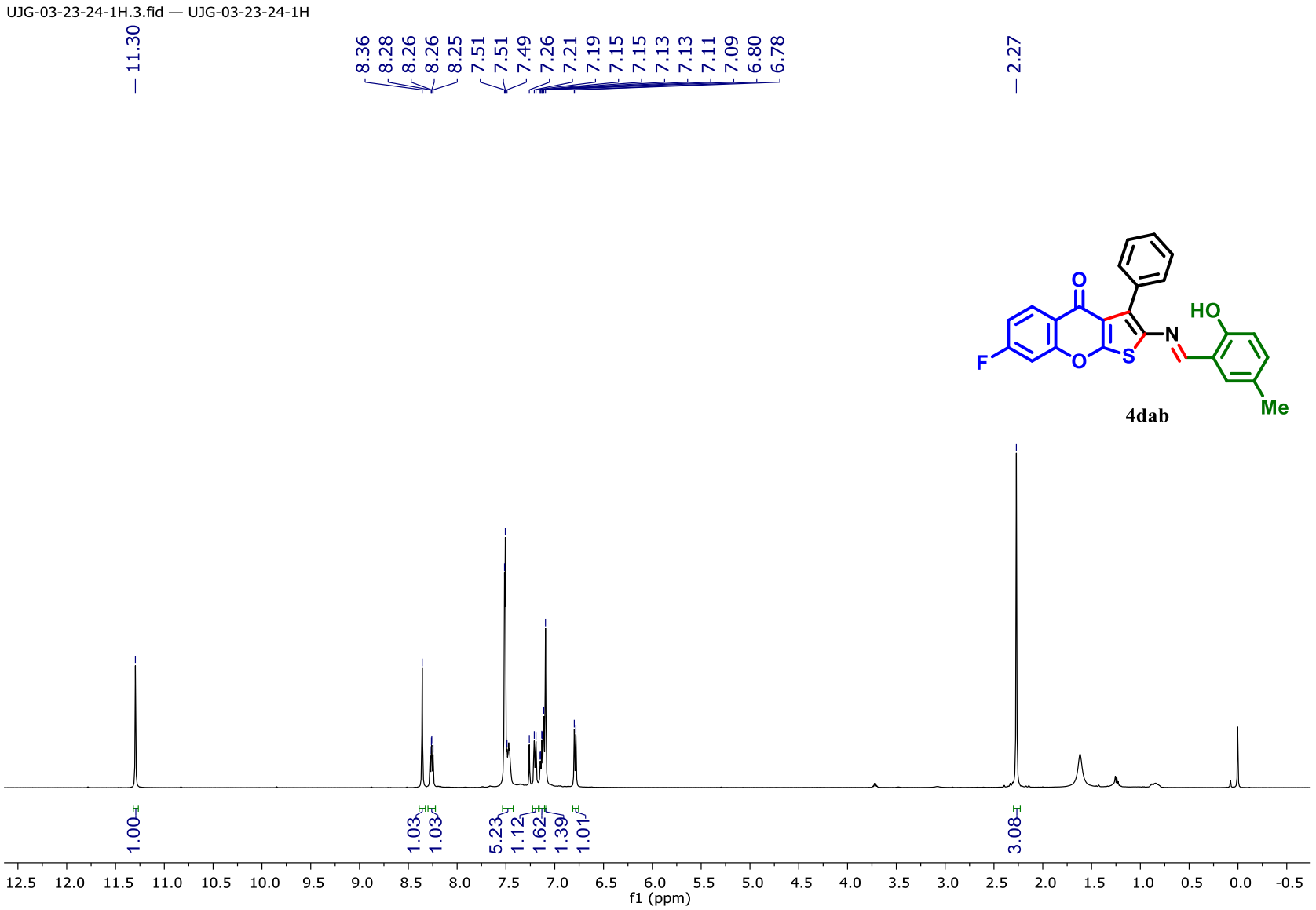
UJG-02-287-24-19F.5.fid — UJG-02-287-24-19F



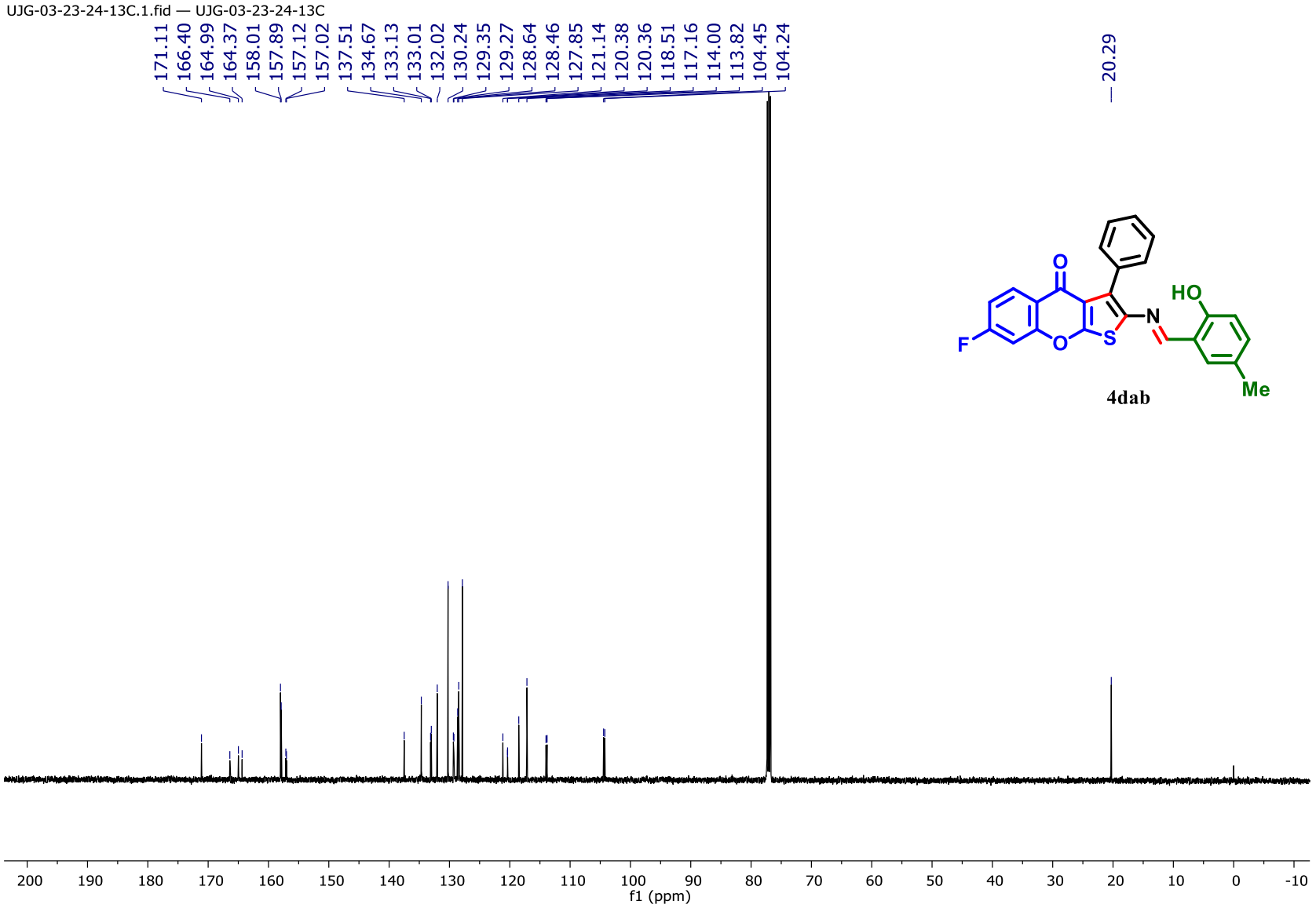
HRMS Spectrum of Compound 4daa



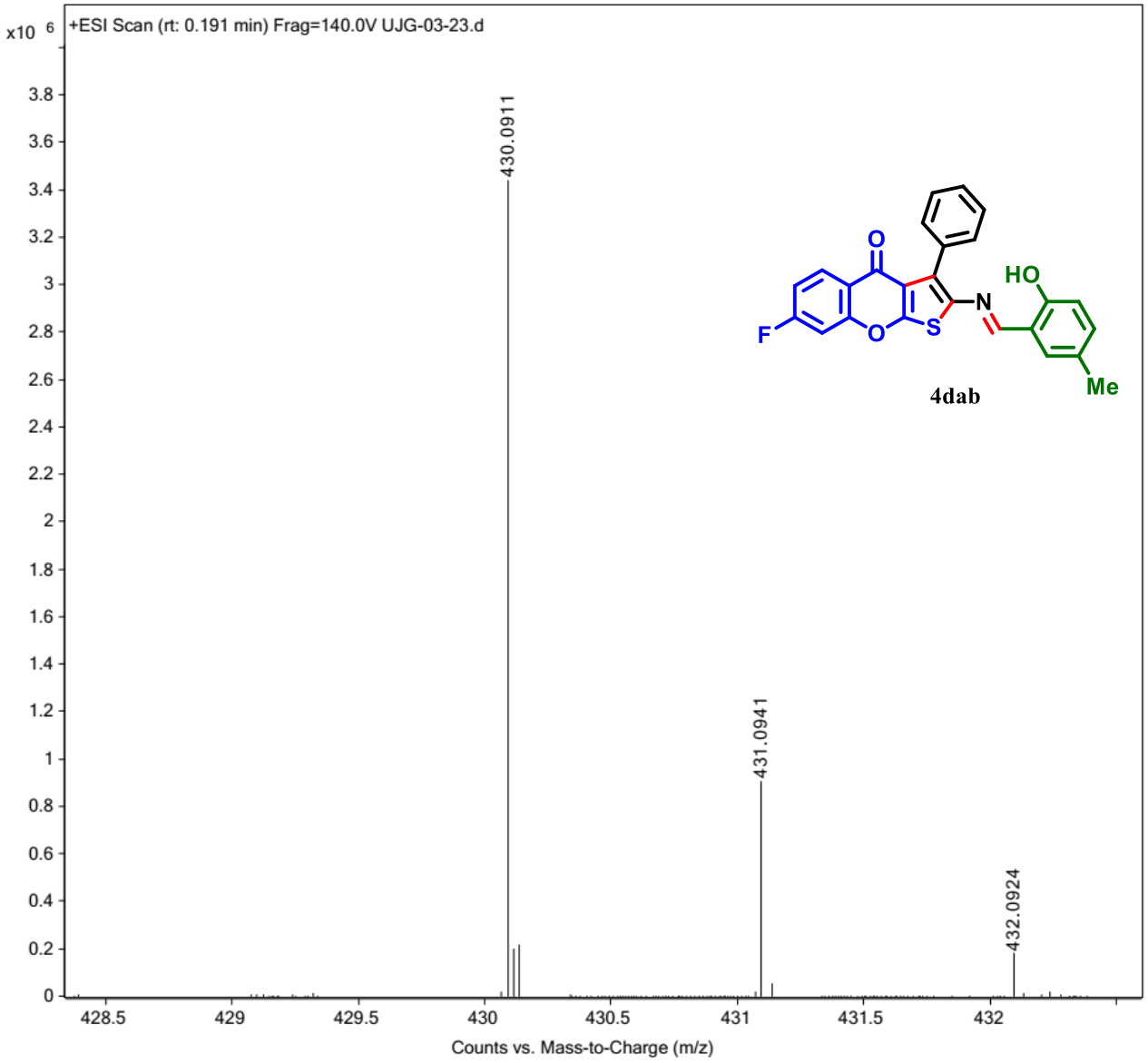
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound 4dab



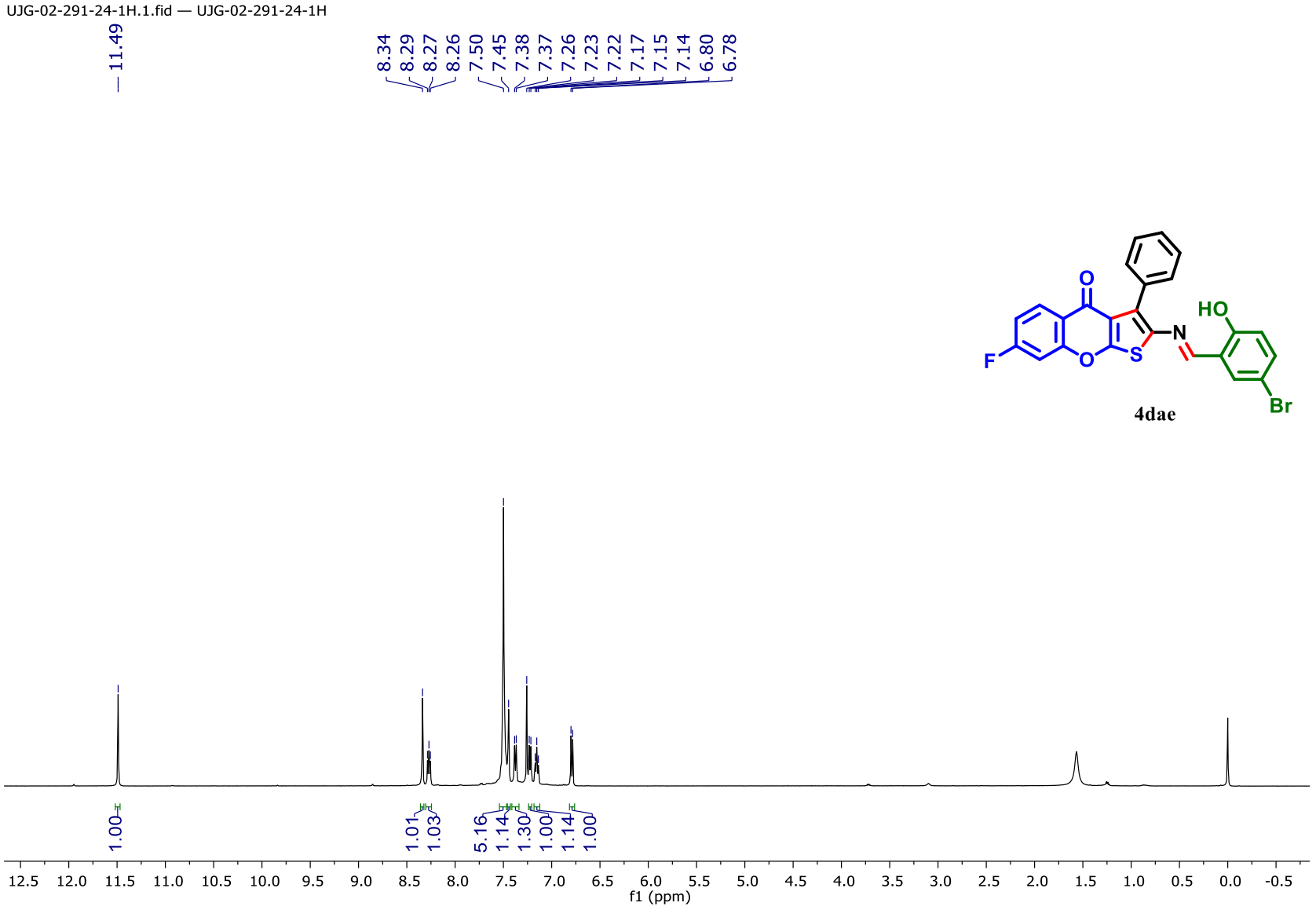
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4dab



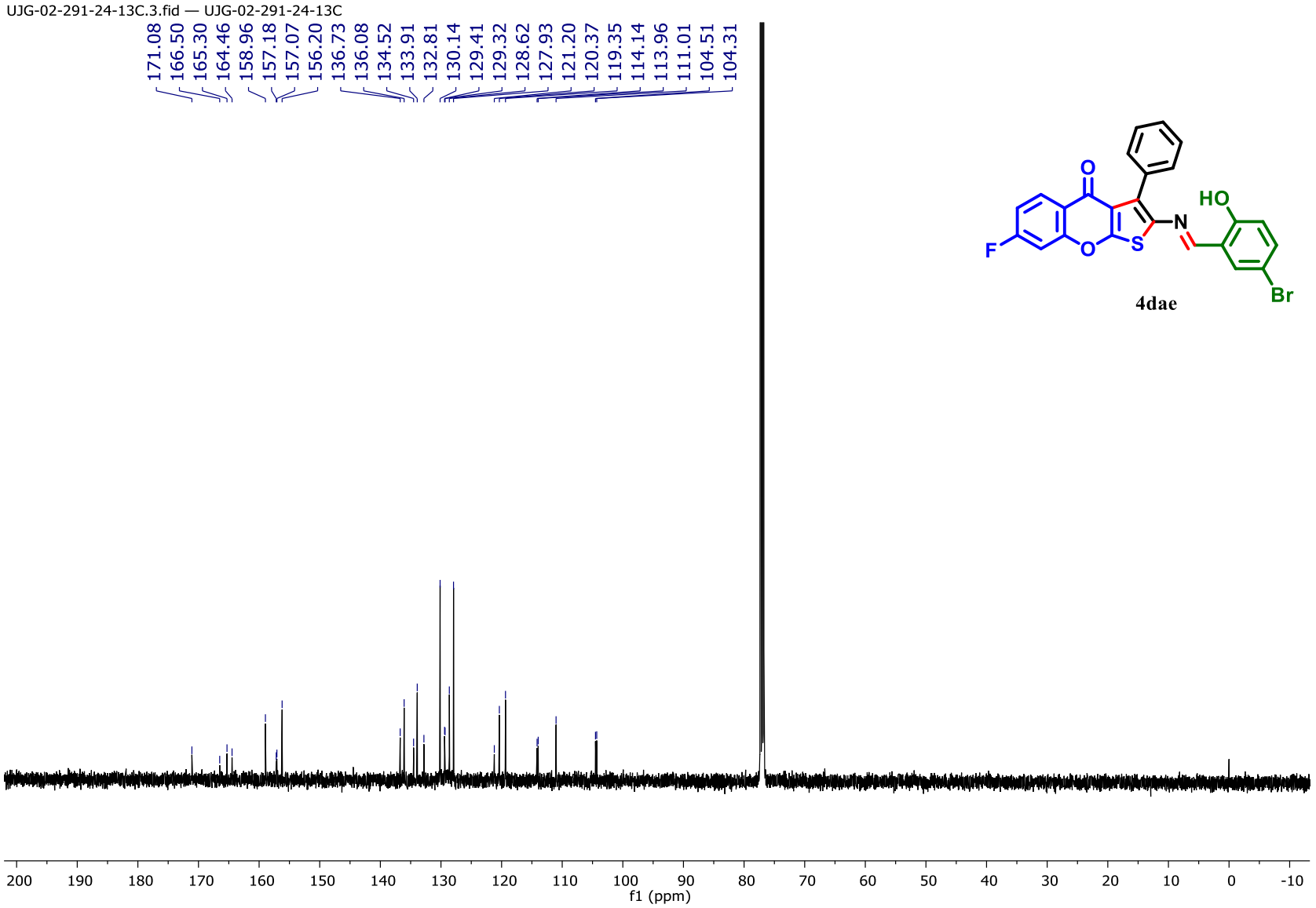
HRMS Spectrum of Compound 4dab



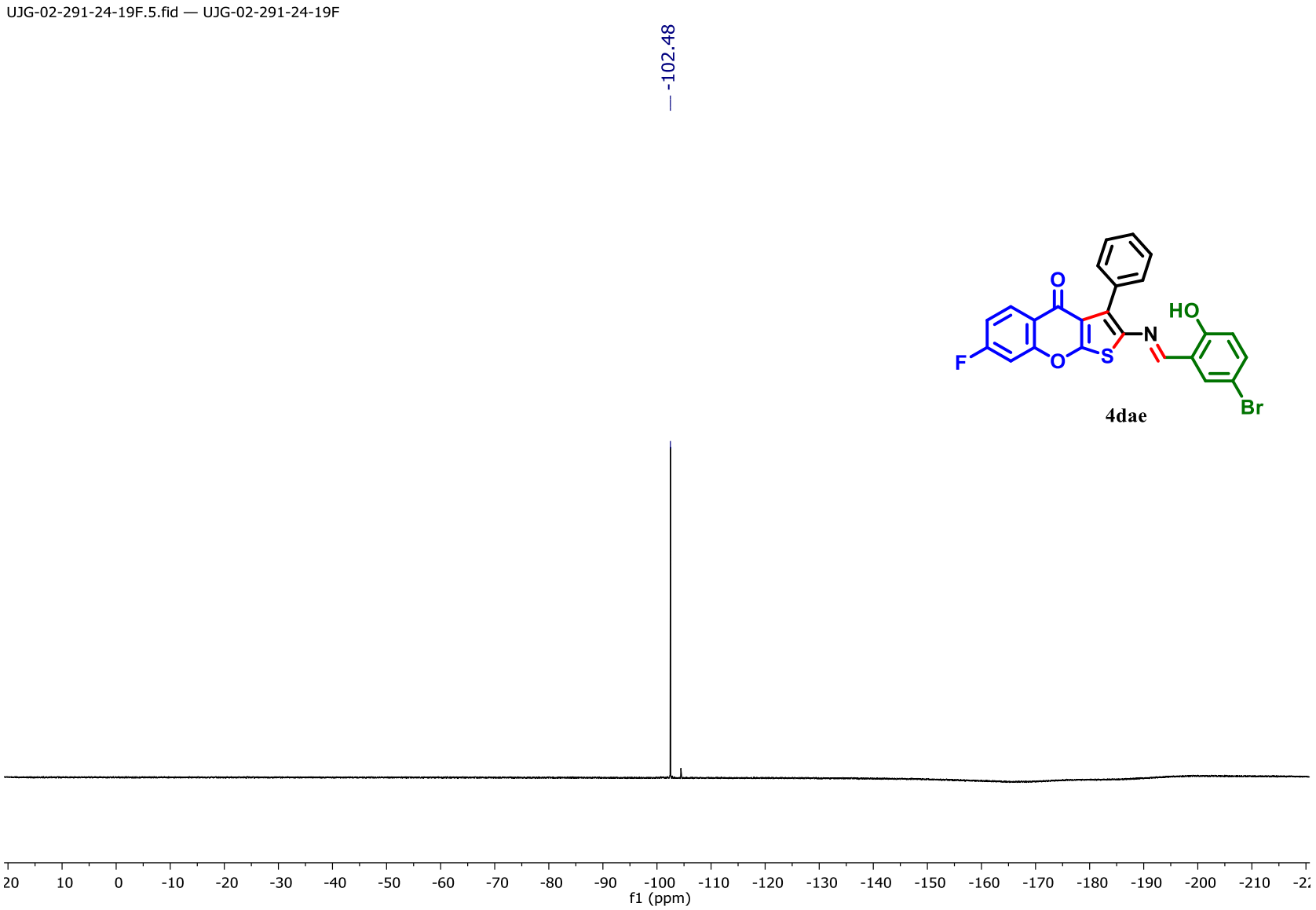
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound 4dae



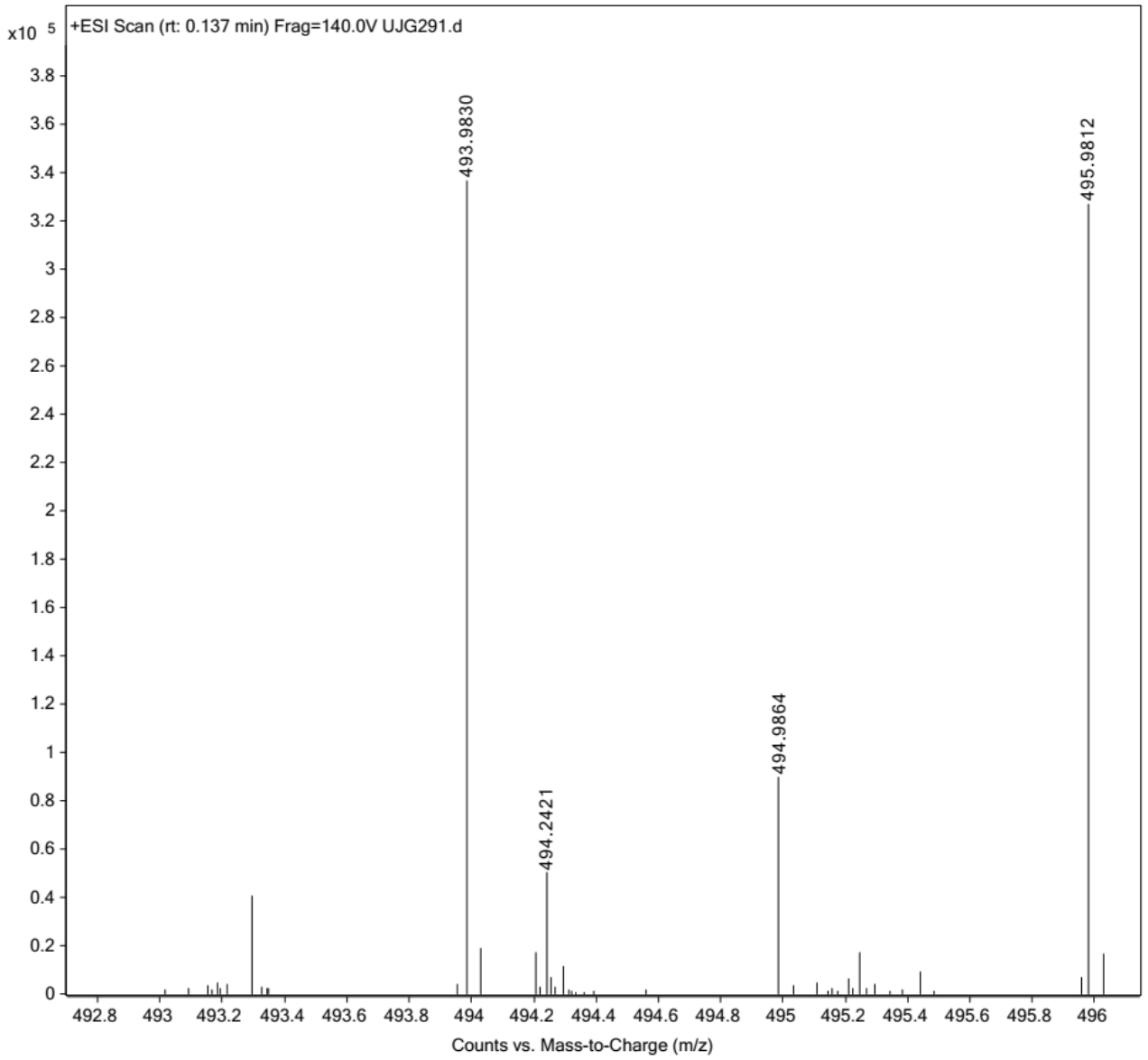
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4dae



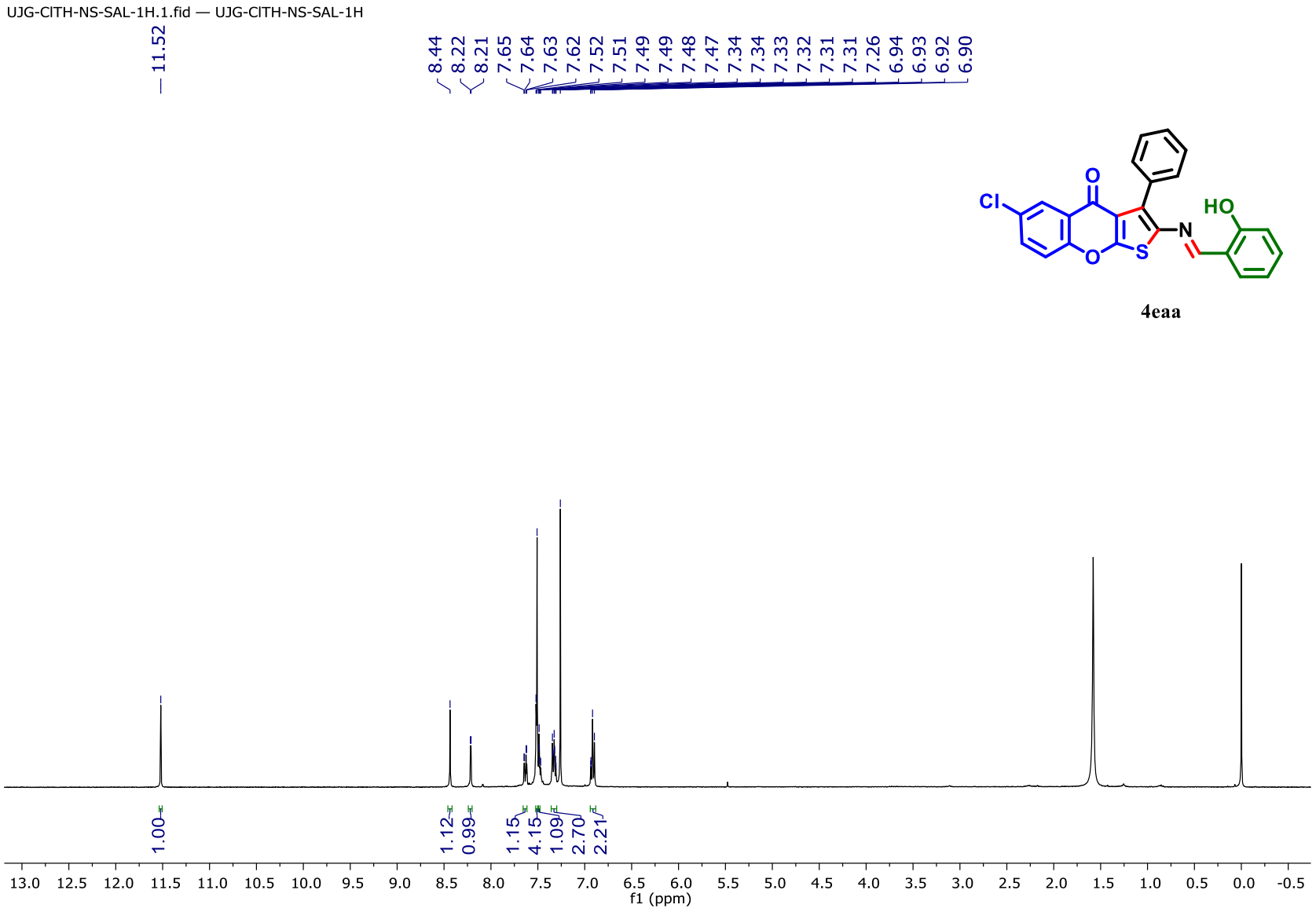
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound 4dae



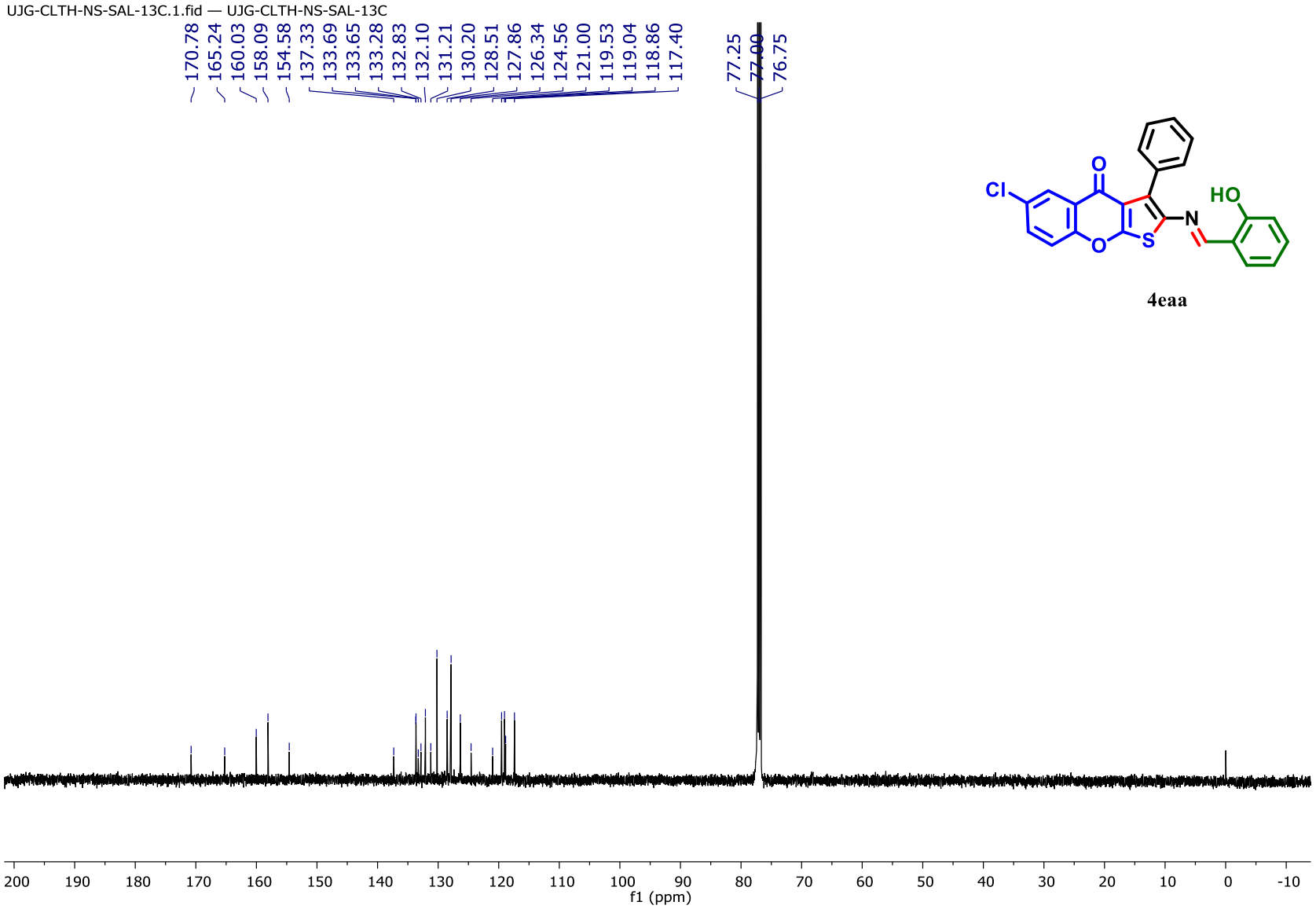
HRMS Spectrum of Compound 4dae



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4eaa

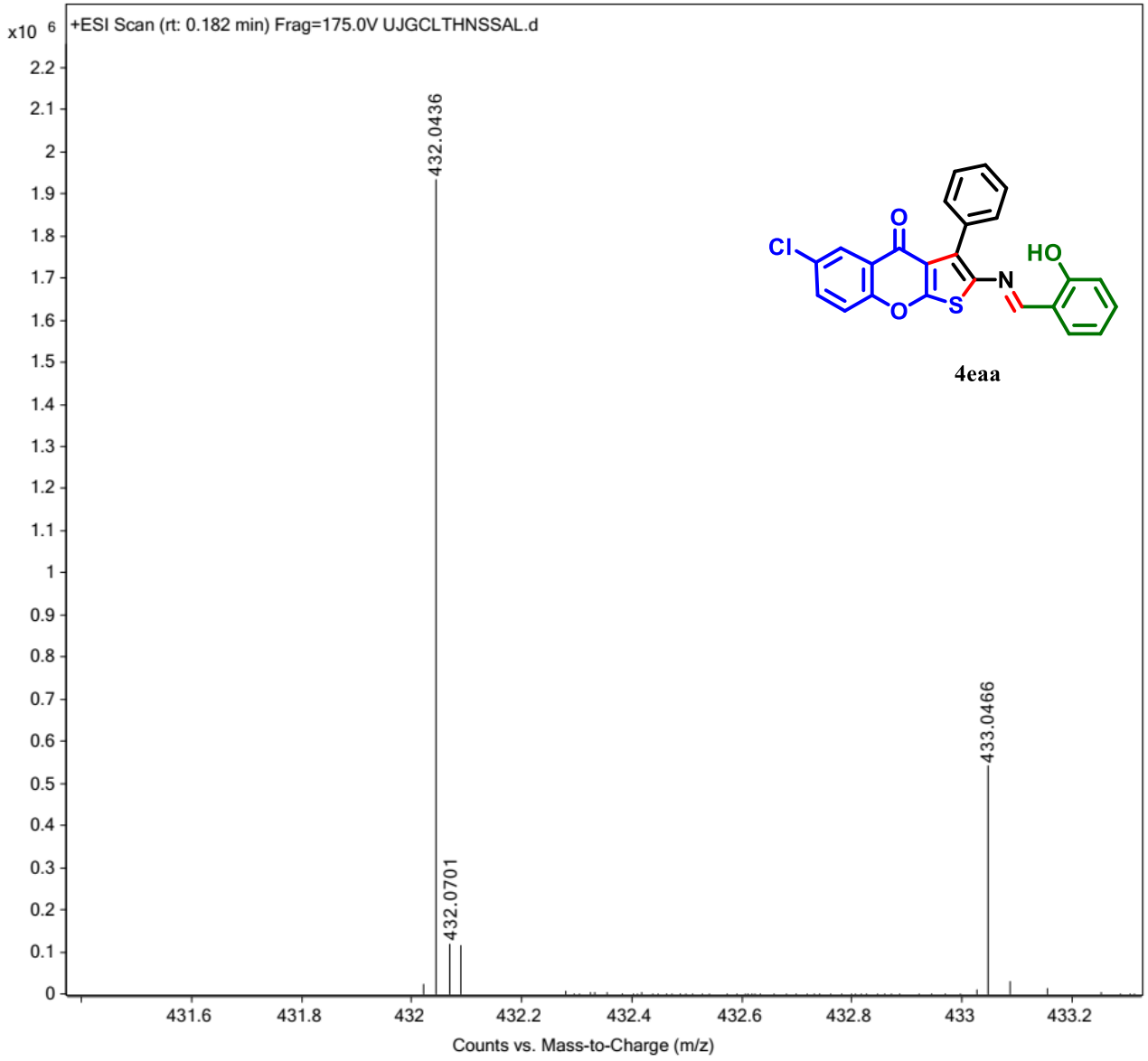


^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4eaa



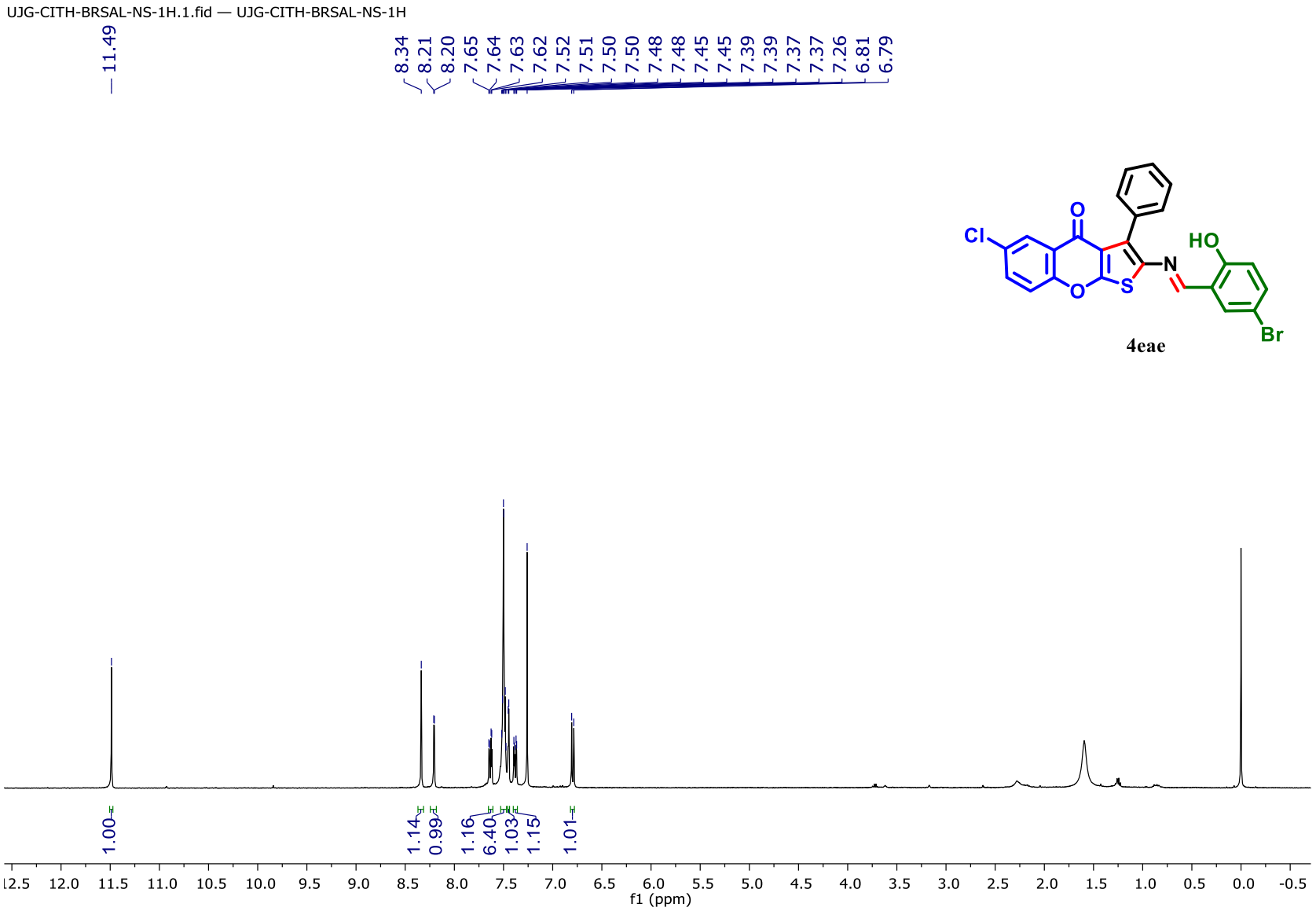
4eaa

HRMS Spectrum of Compound 4eaa

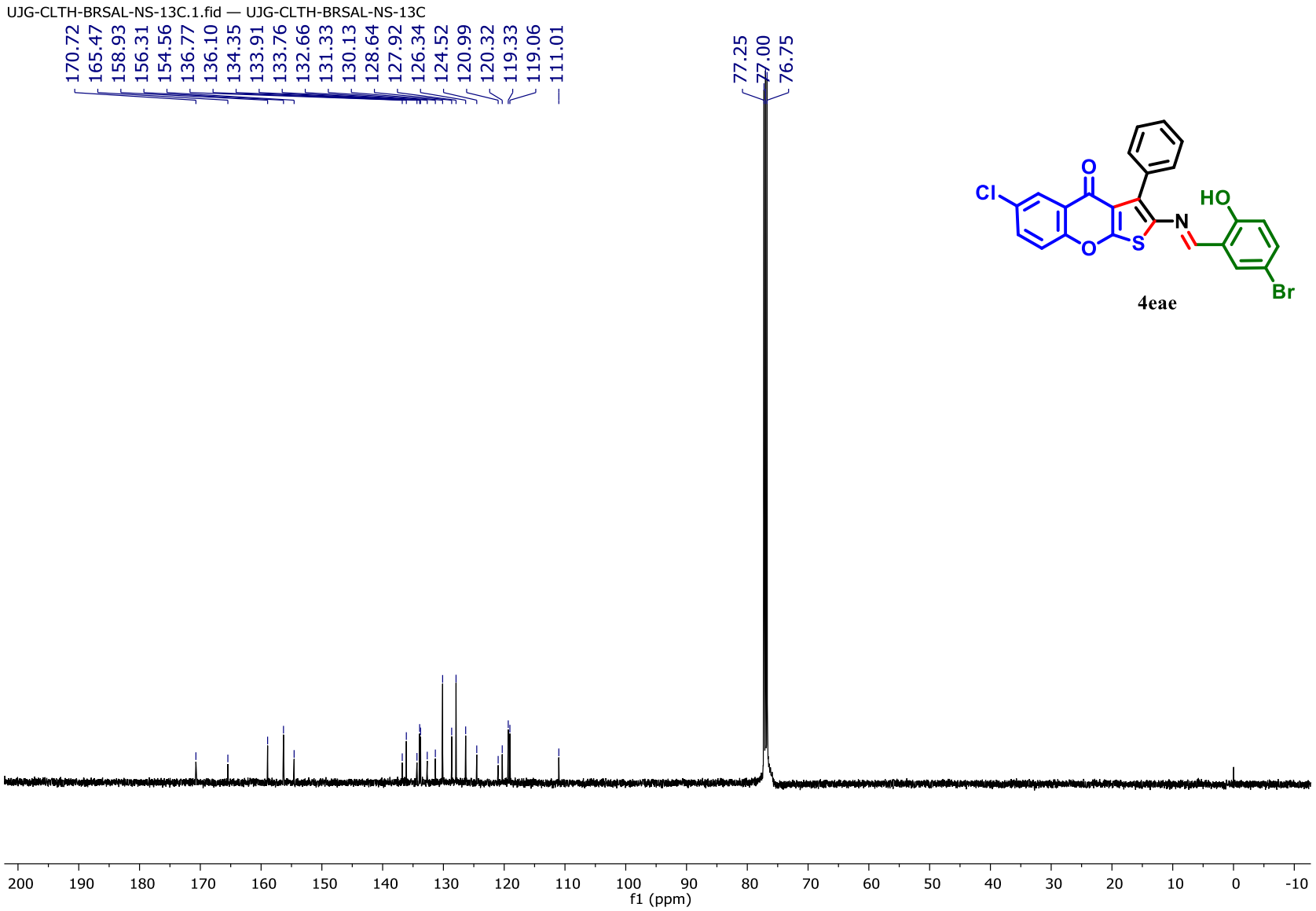


4eaa

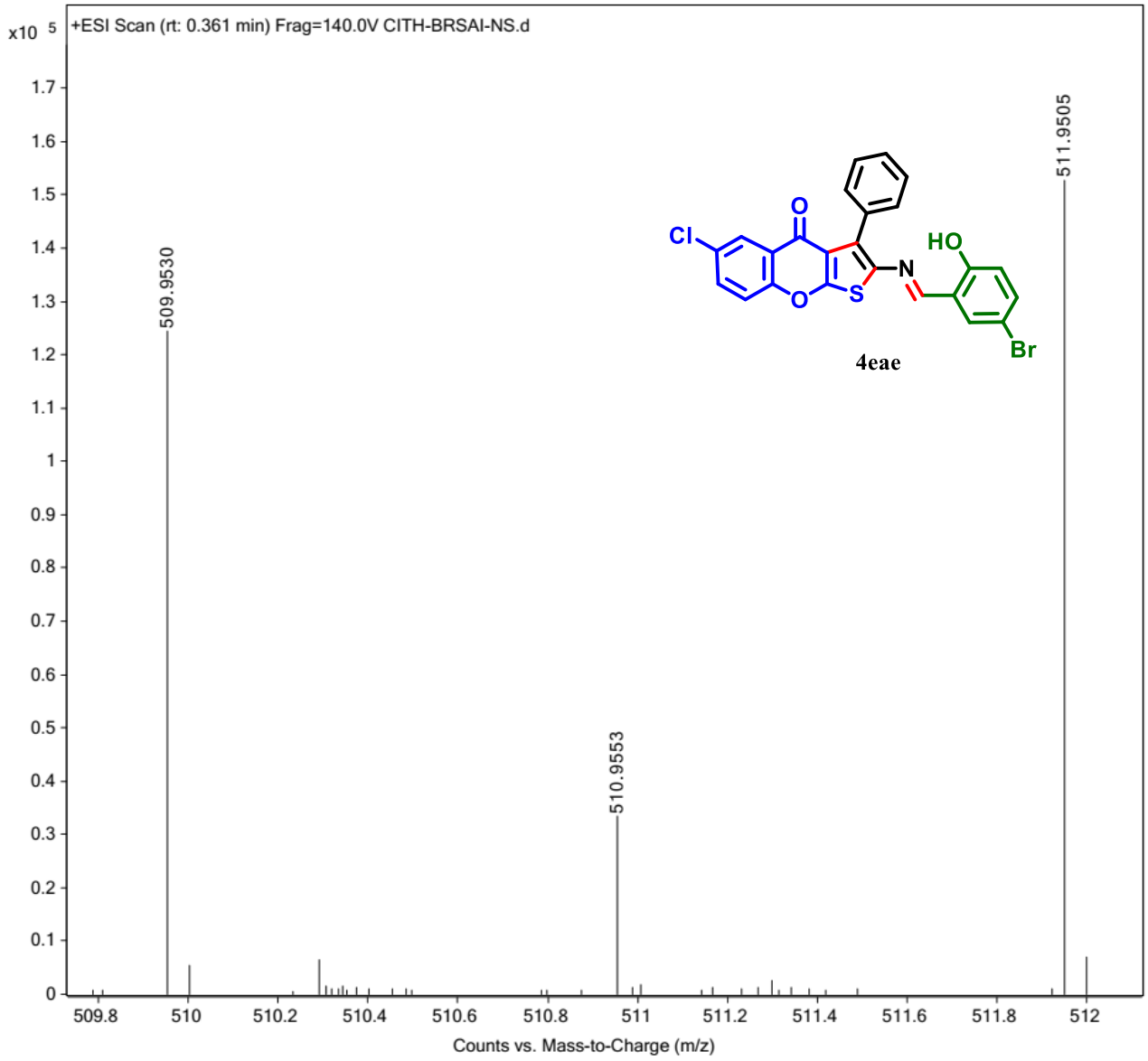
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4eae



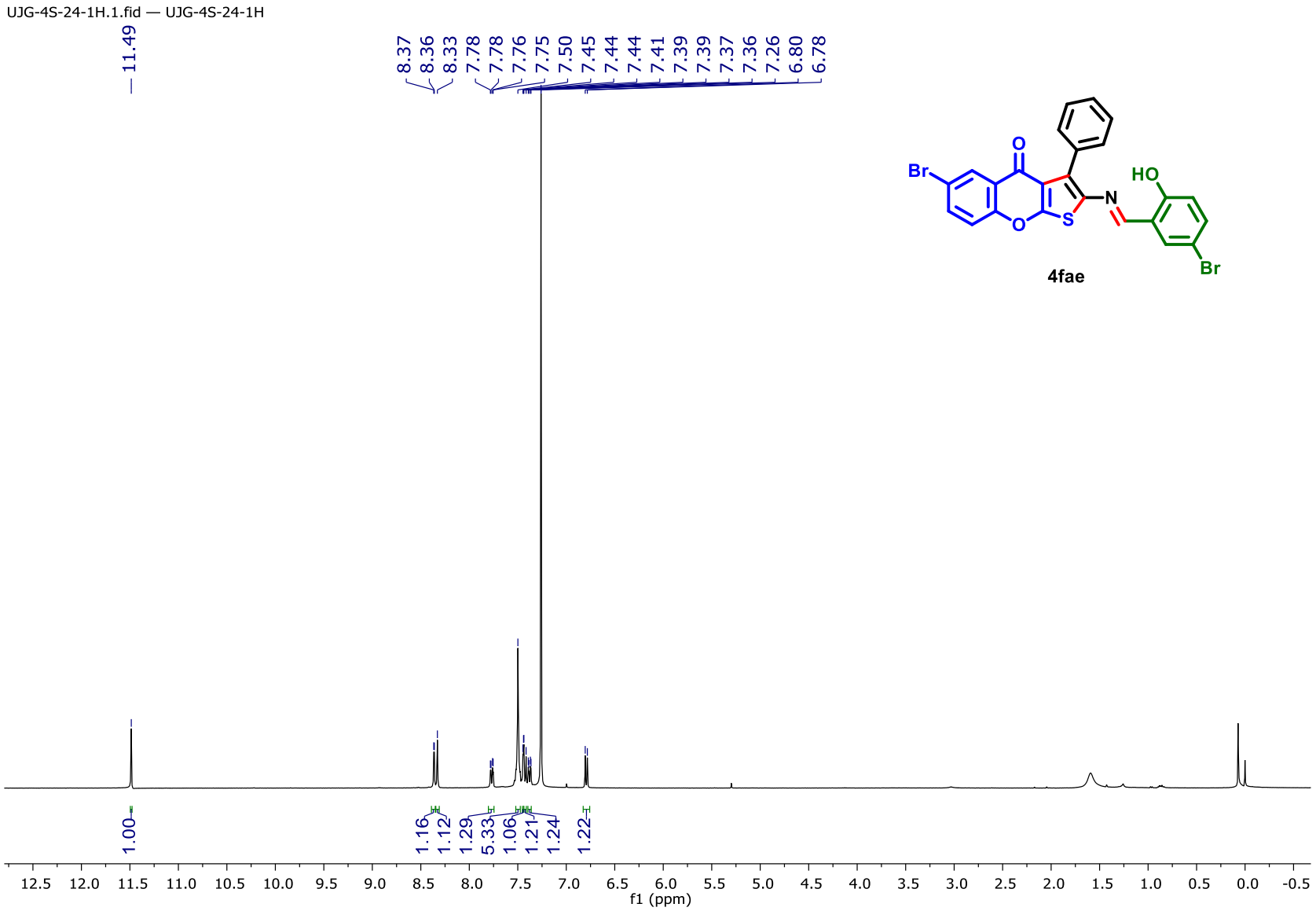
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4eae



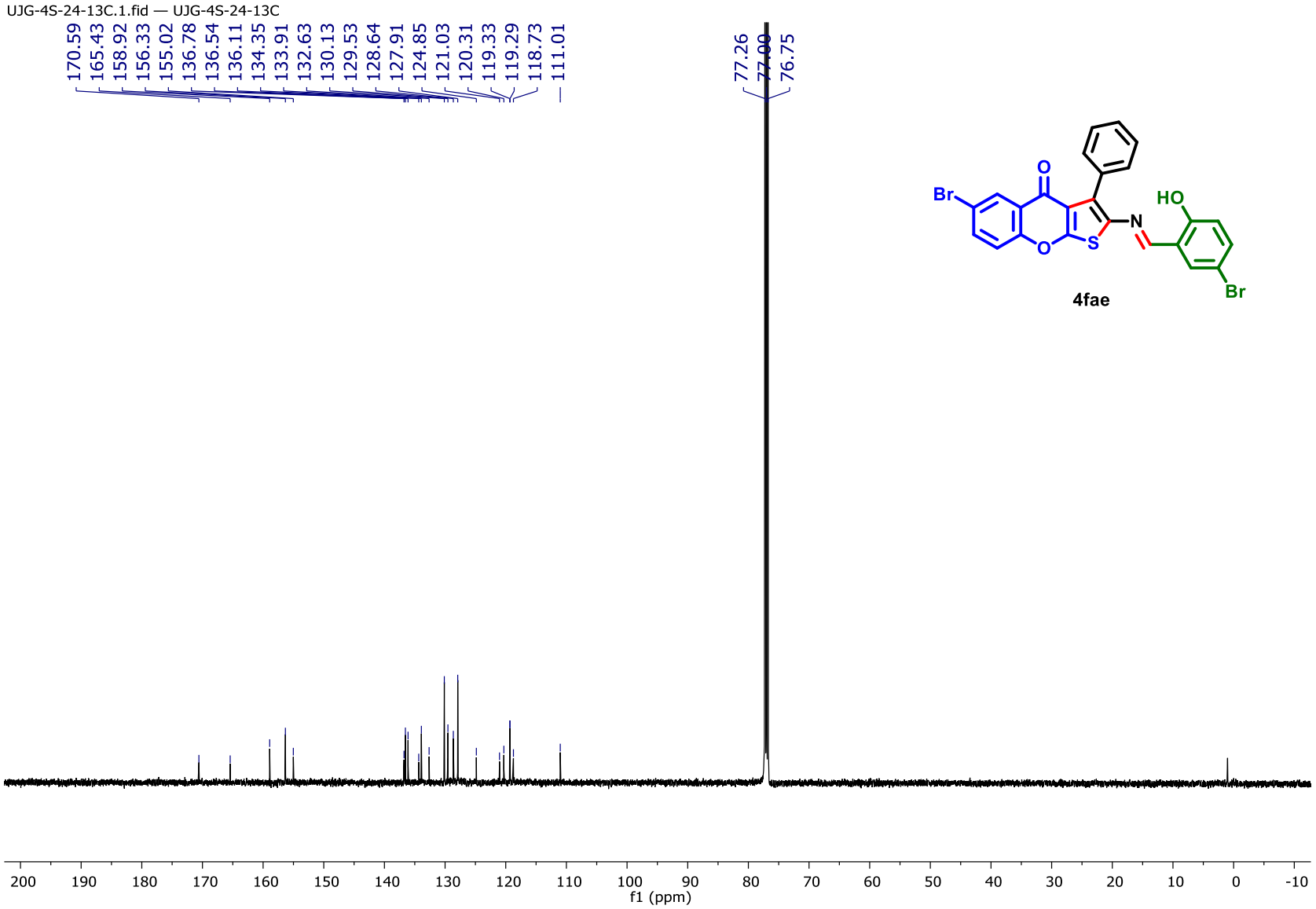
HRMS Spectrum of Compound 4eae



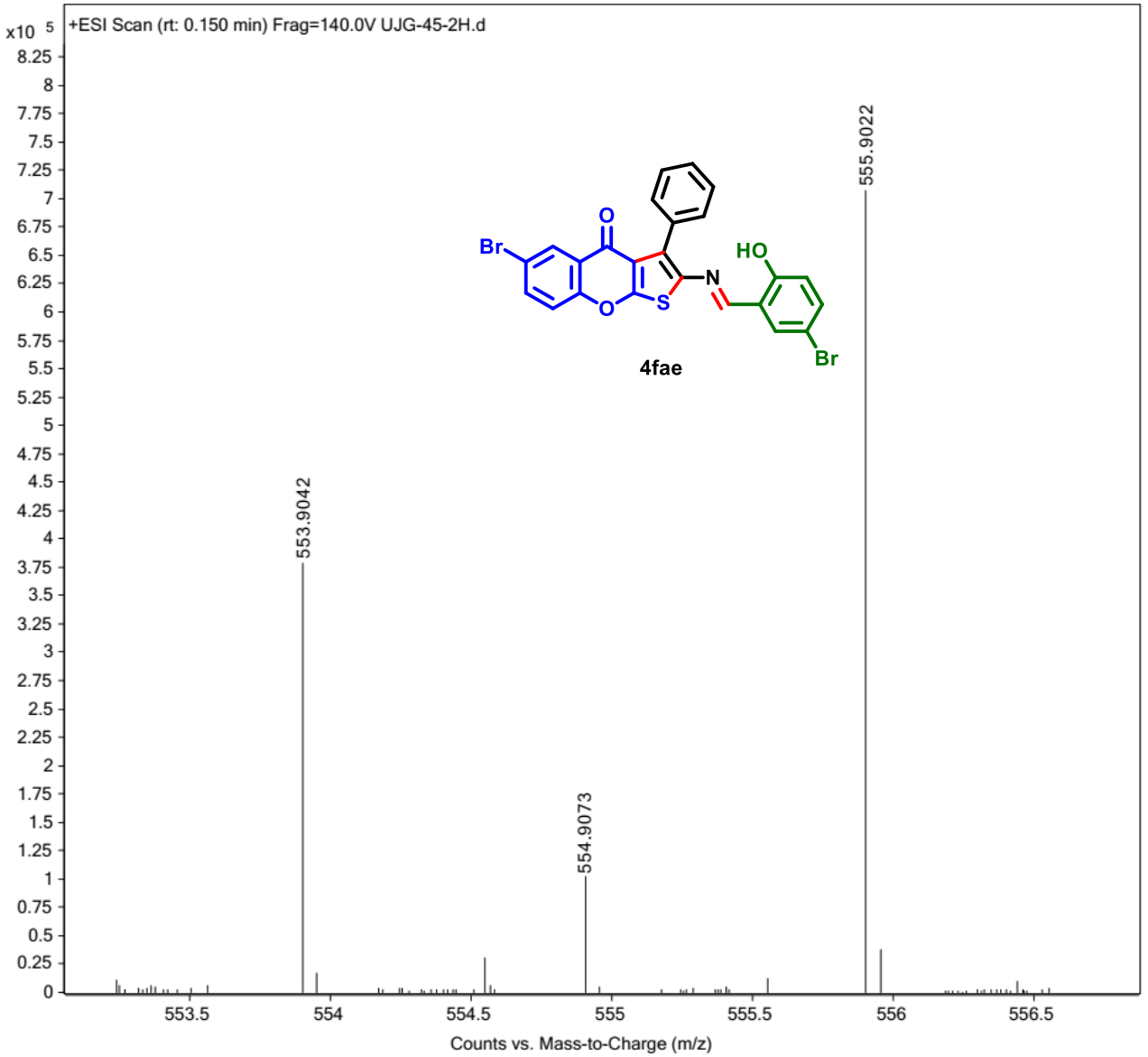
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4fae



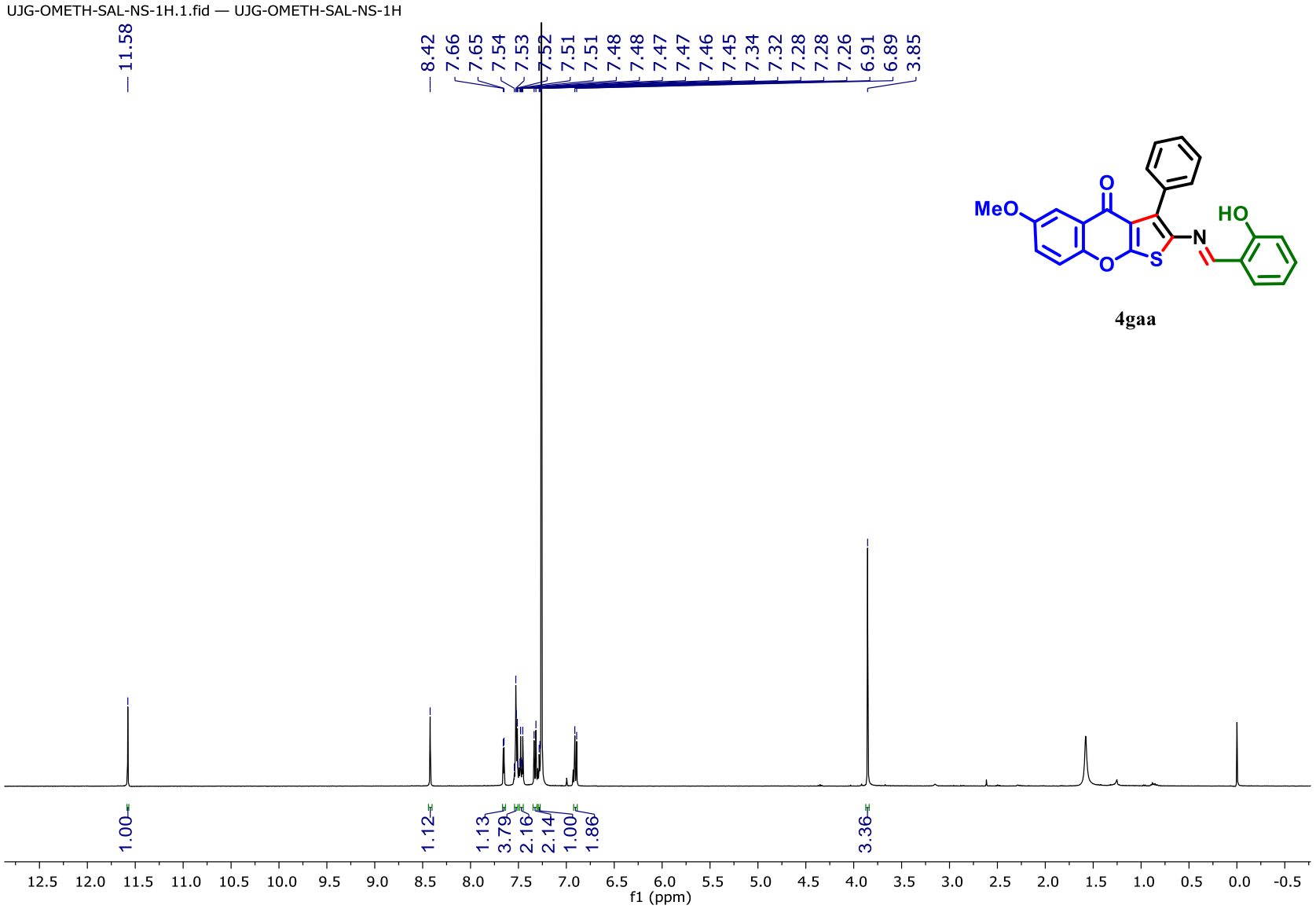
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4fae



HRMS Spectrum of Compound 4fae

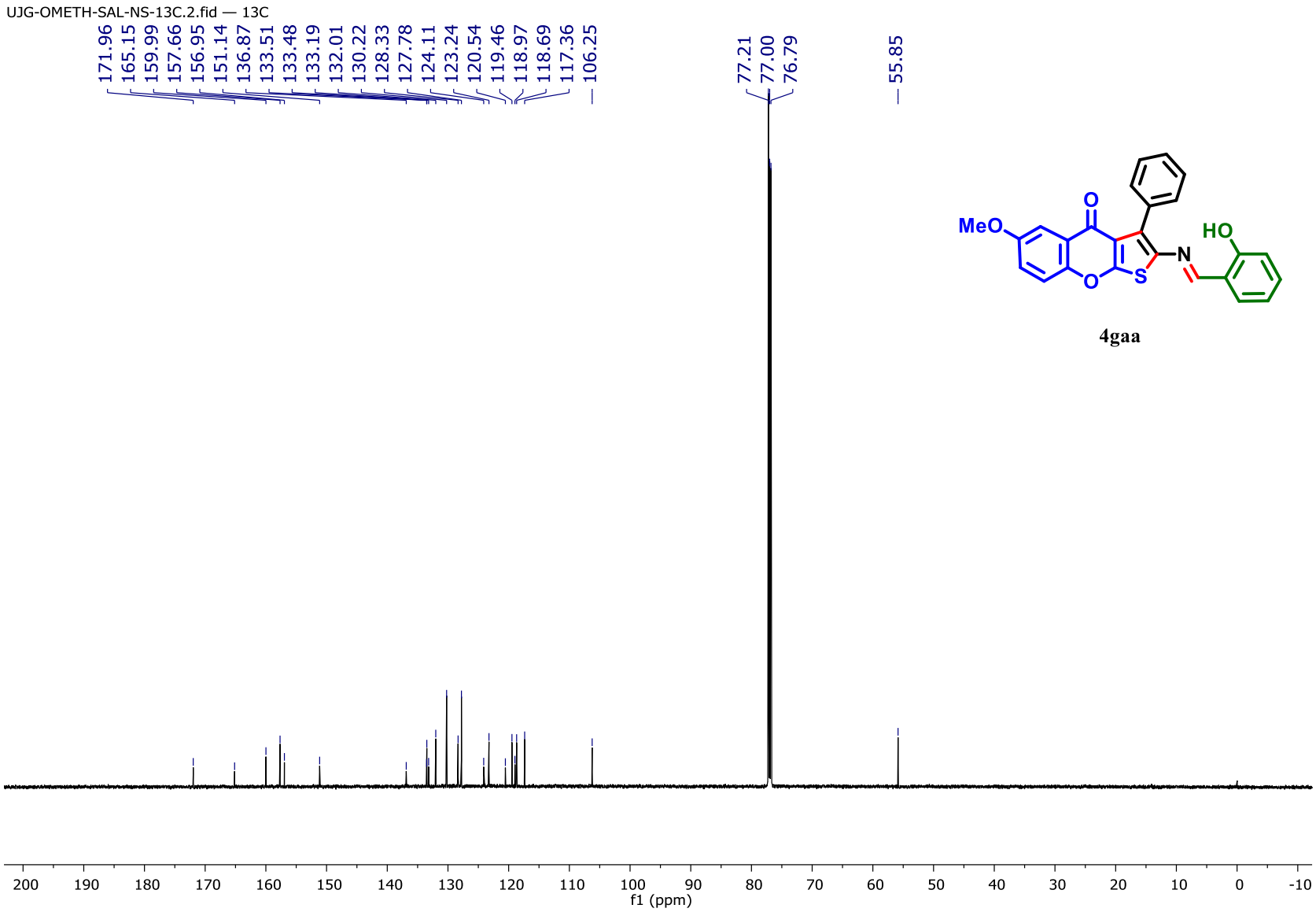


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4gaa



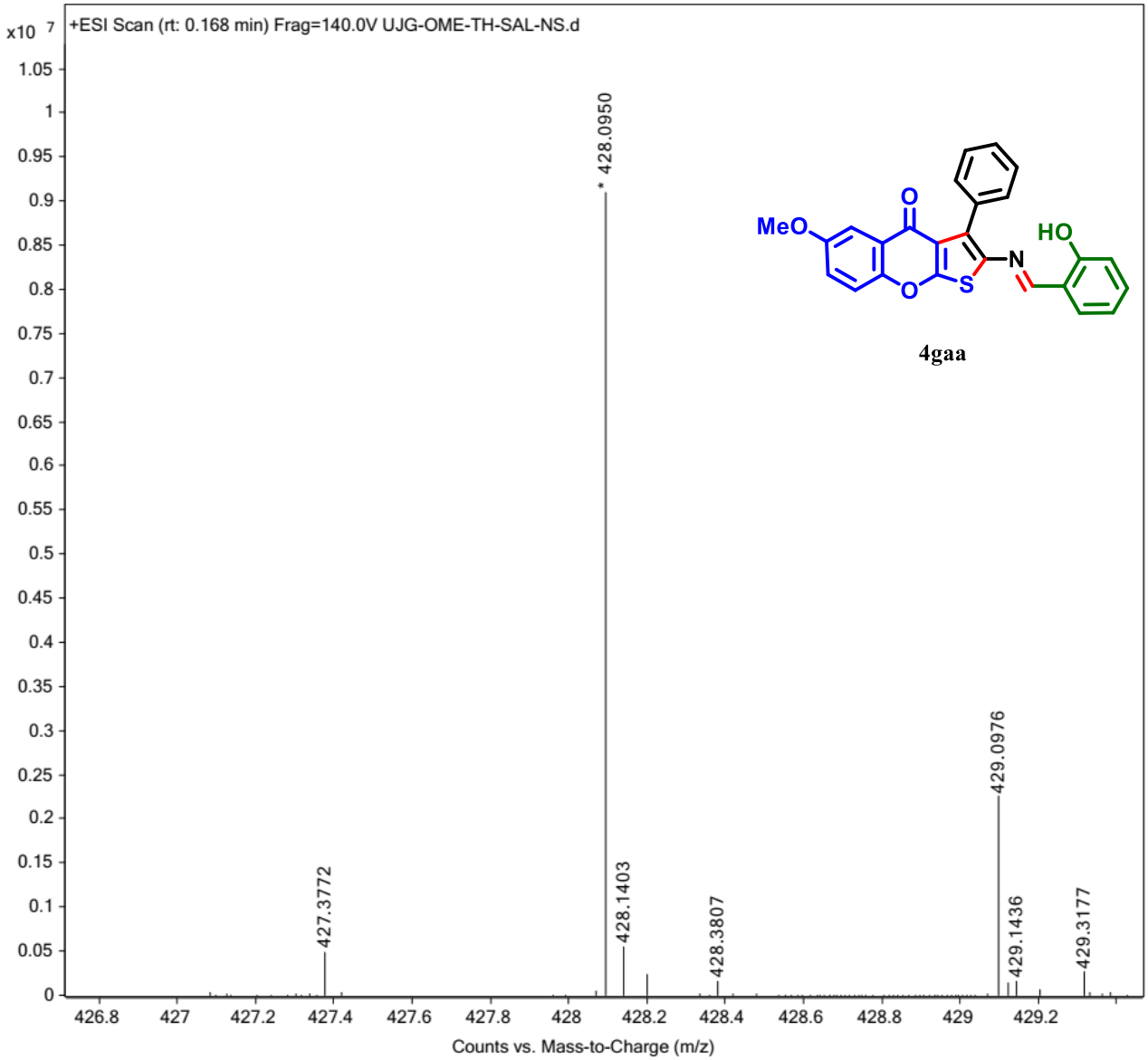
4gaa

^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound 4gaa



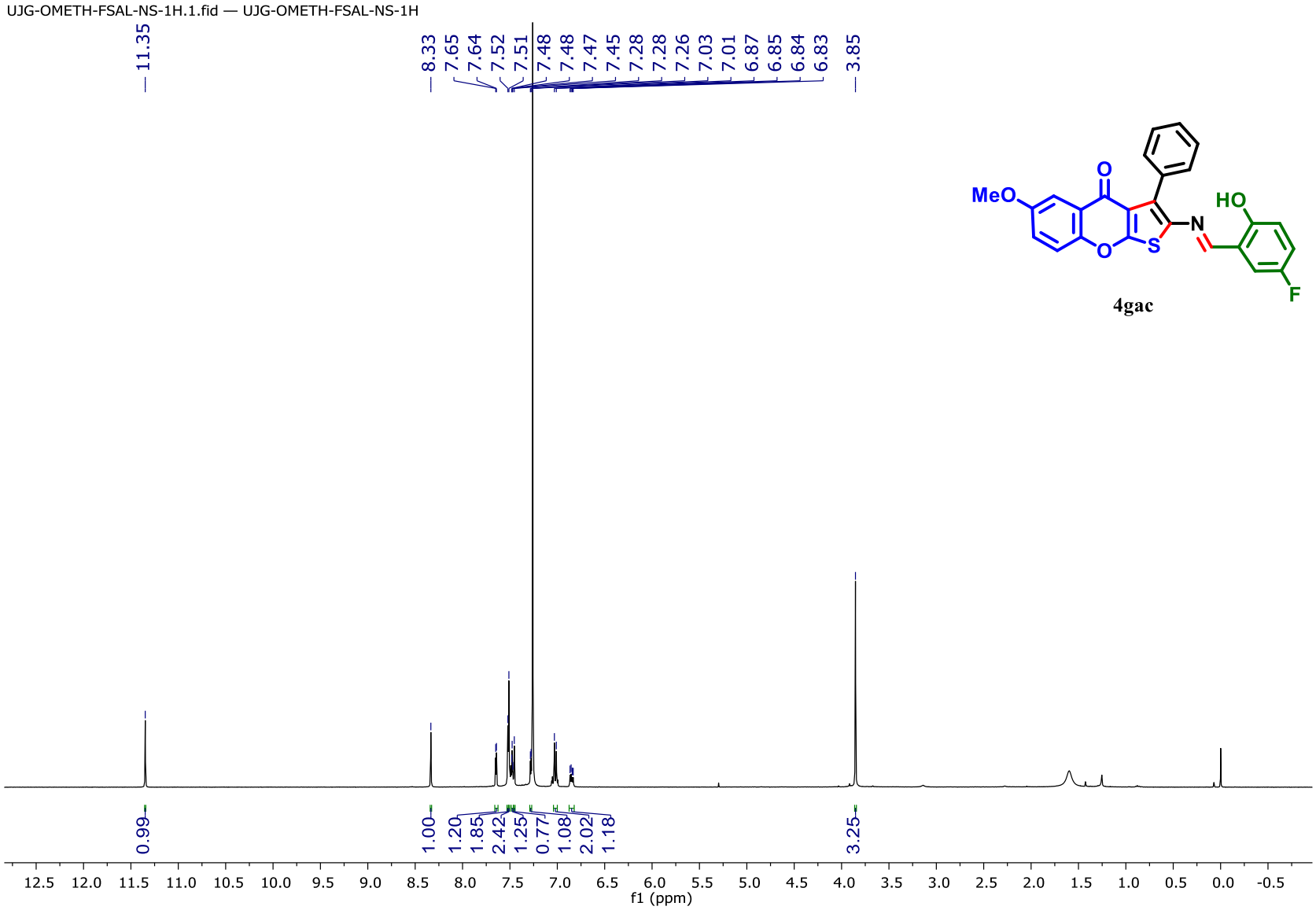
4gaa

HRMS Spectrum of Compound 4gaa

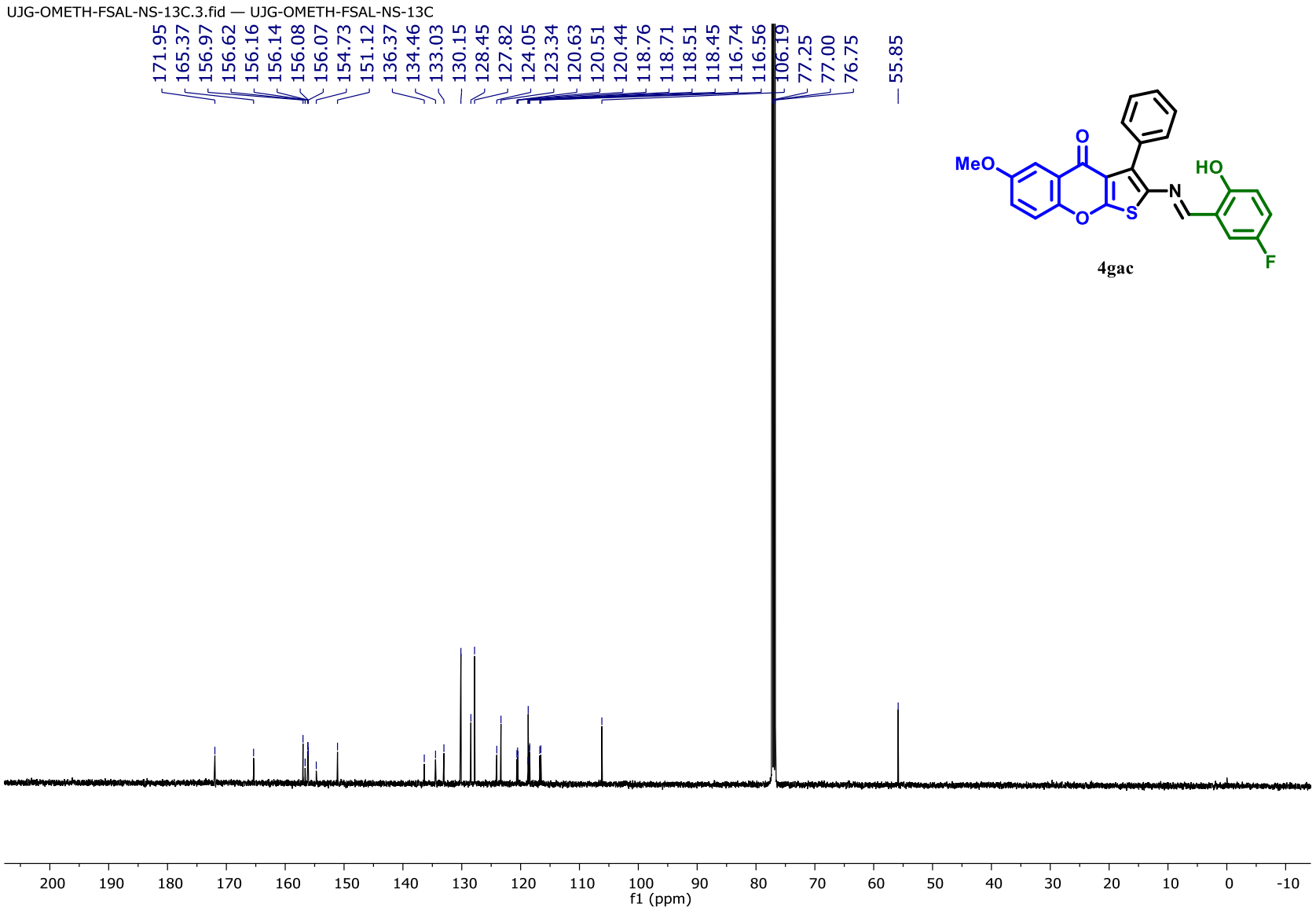


4gaa

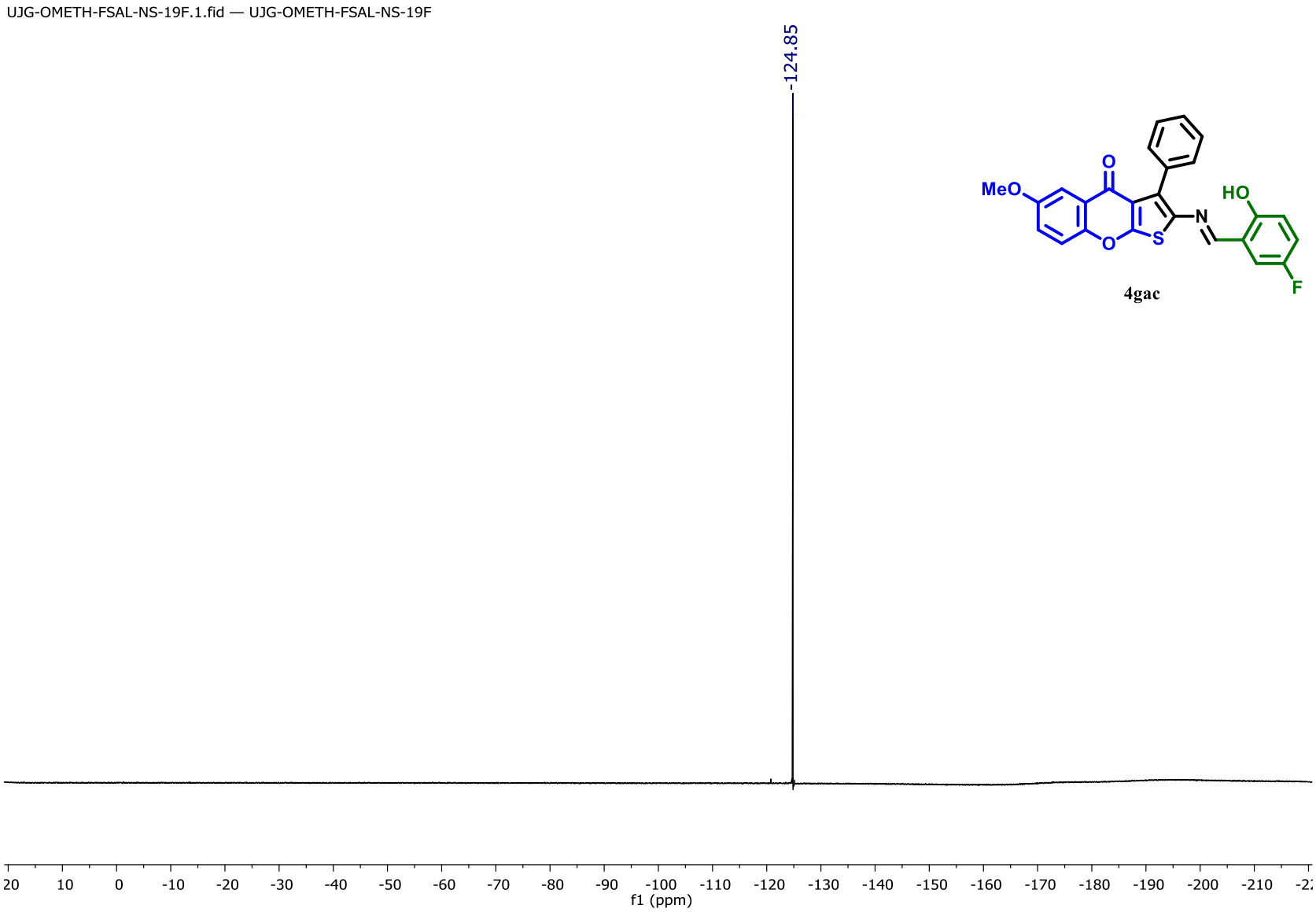
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4gac



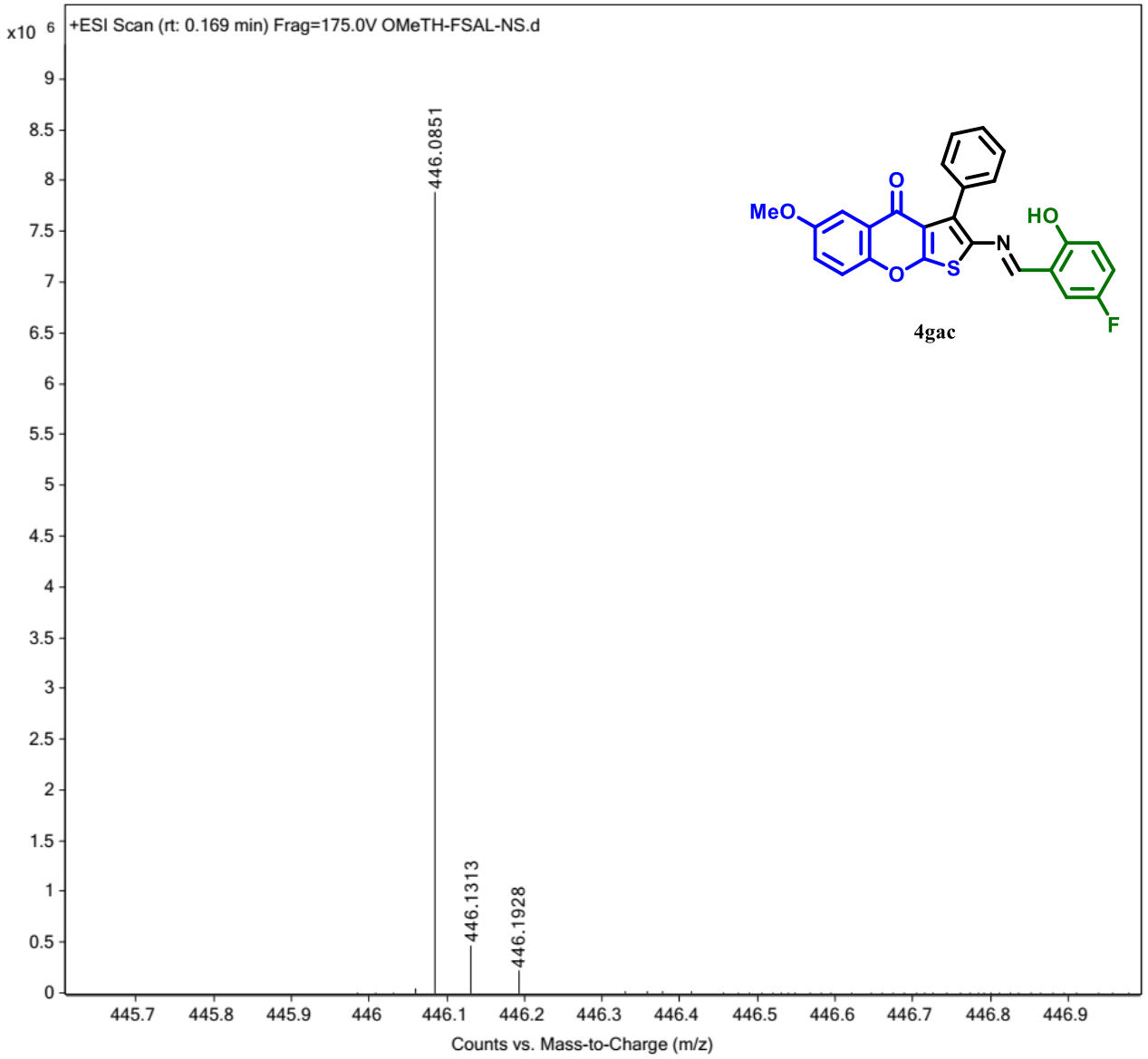
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4gac



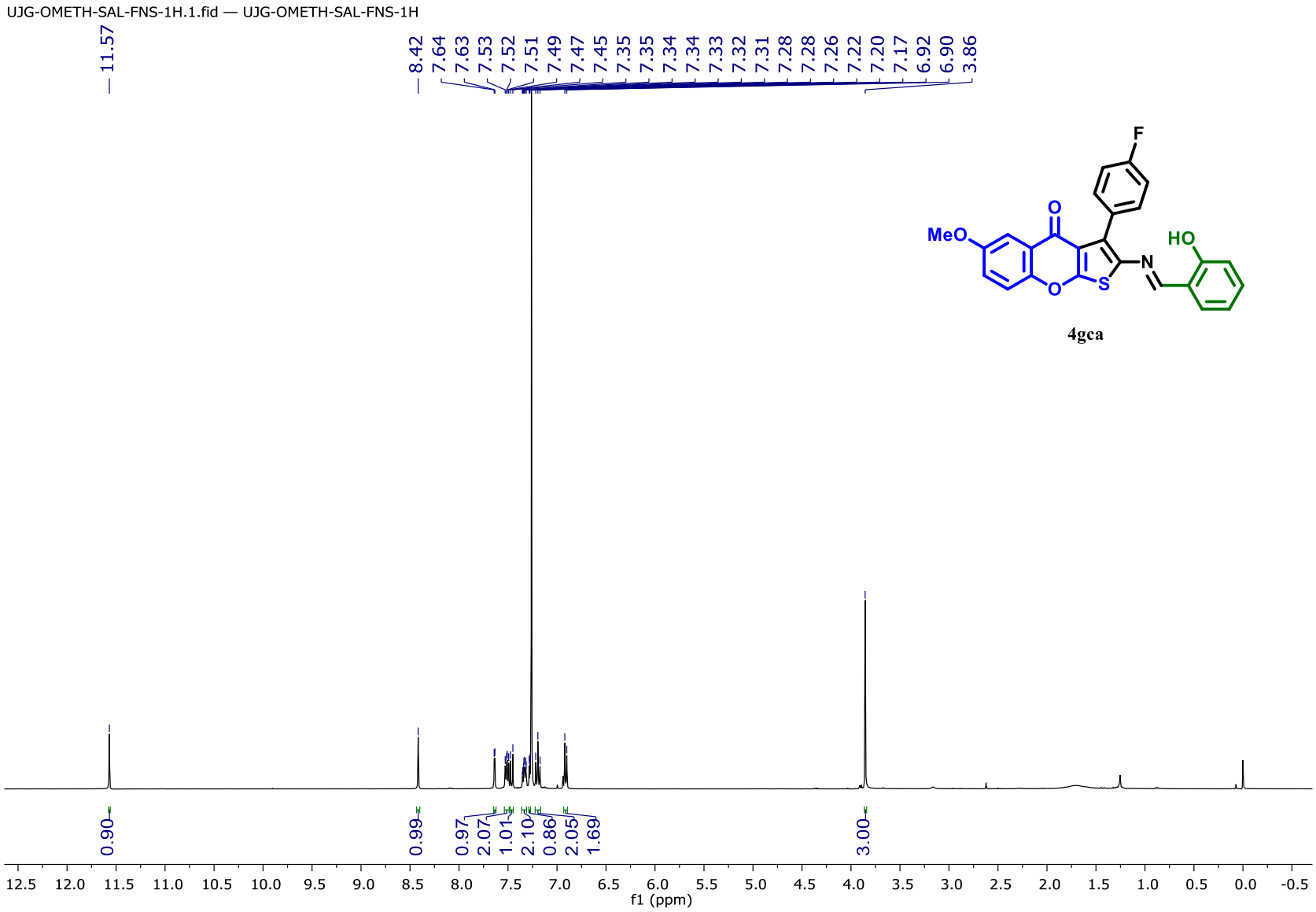
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound 4gac



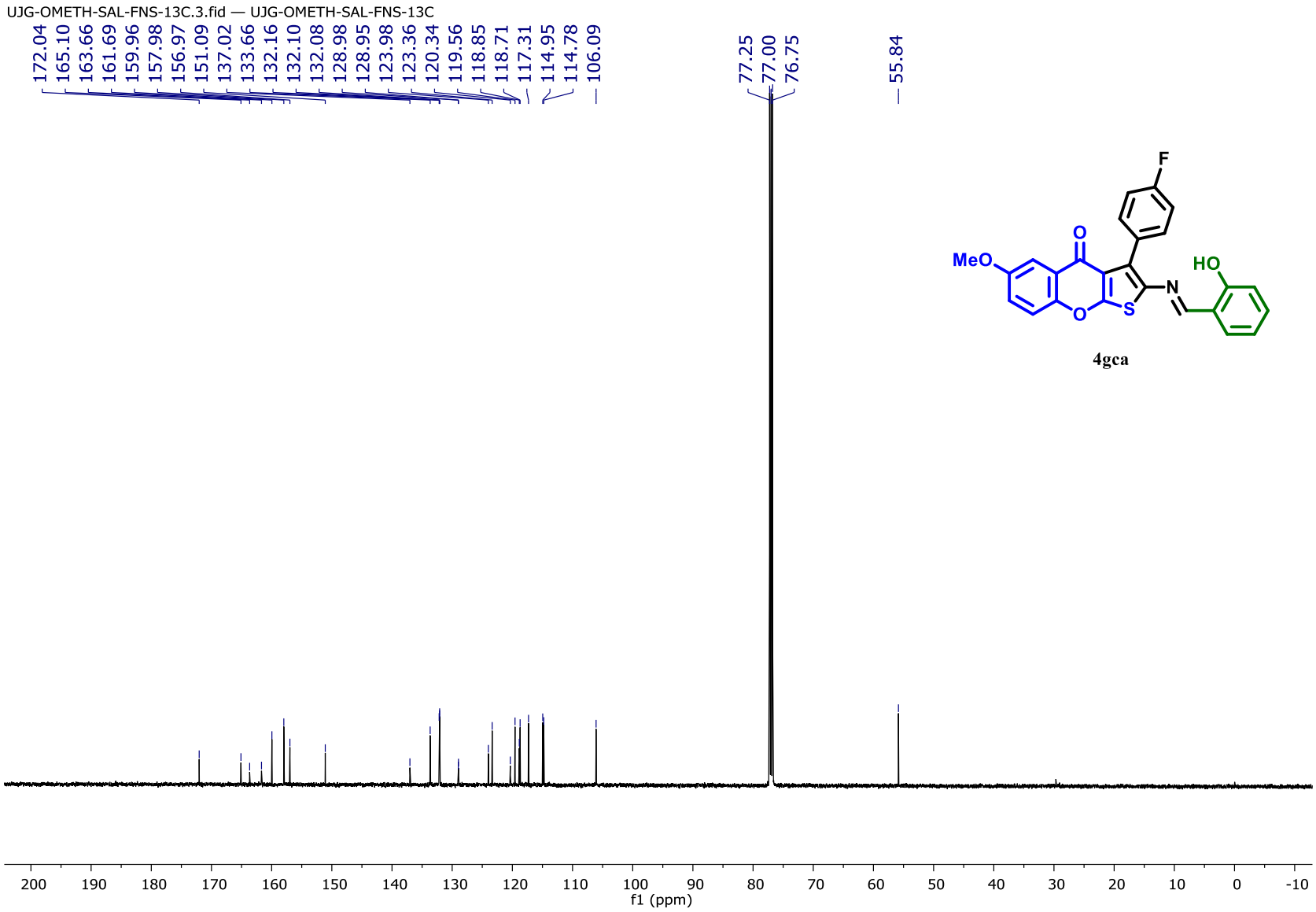
HRMS Spectrum of Compound 4gac



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4gca

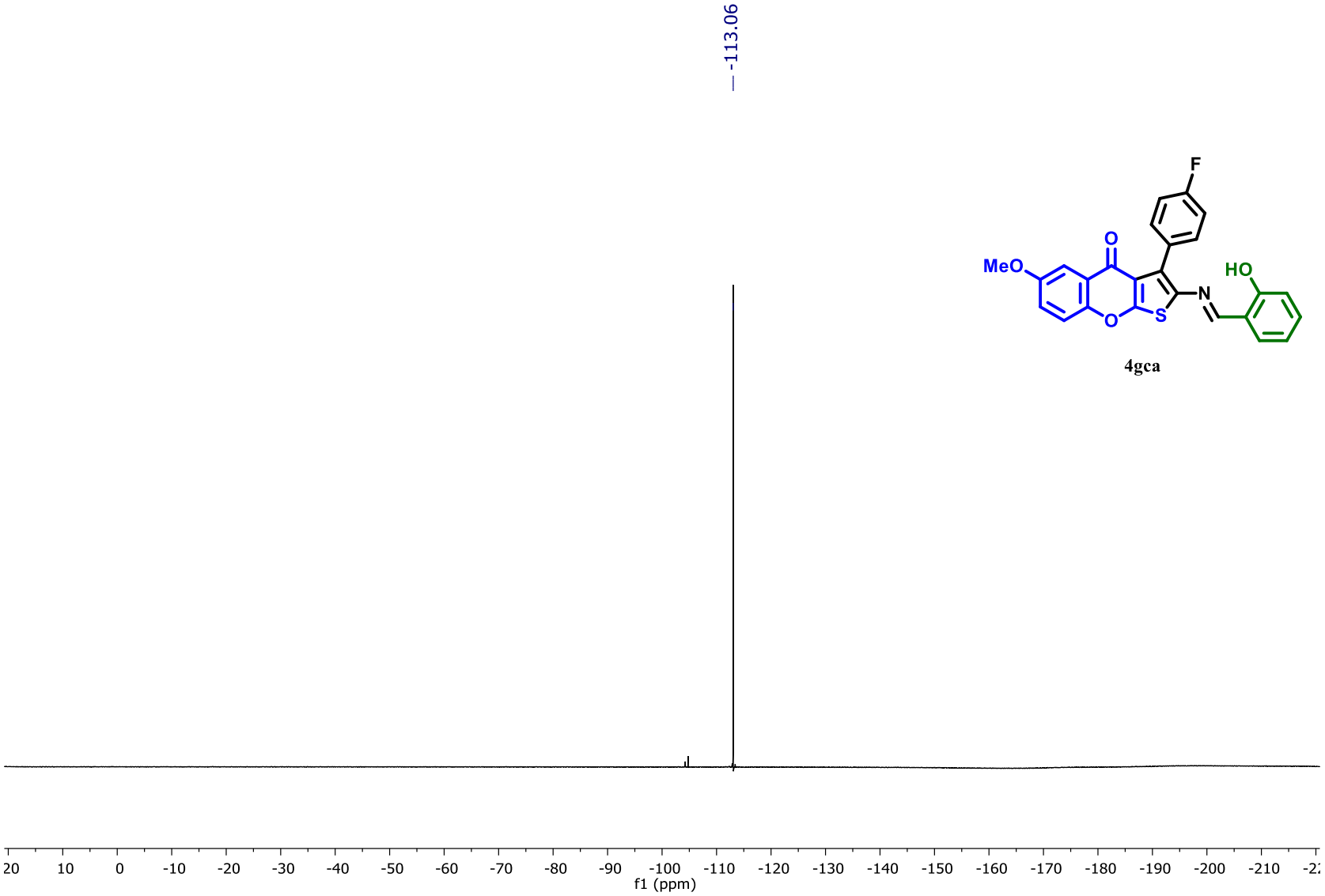


^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4gca



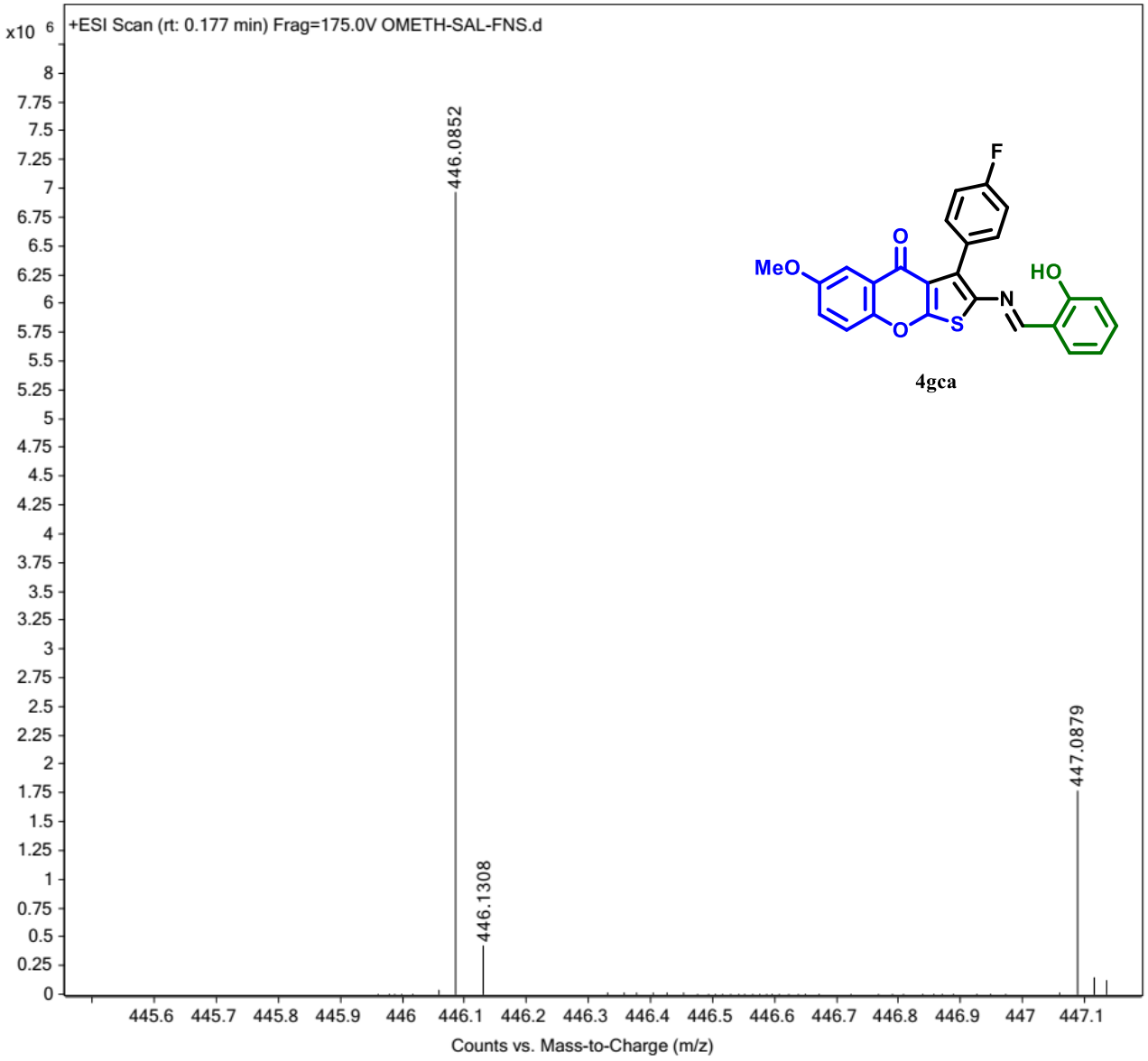
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound 4gca

UJG-OMETH-SAL-FNS-19F.1.fid — UJG-OMETH-SAL-FNS-19F



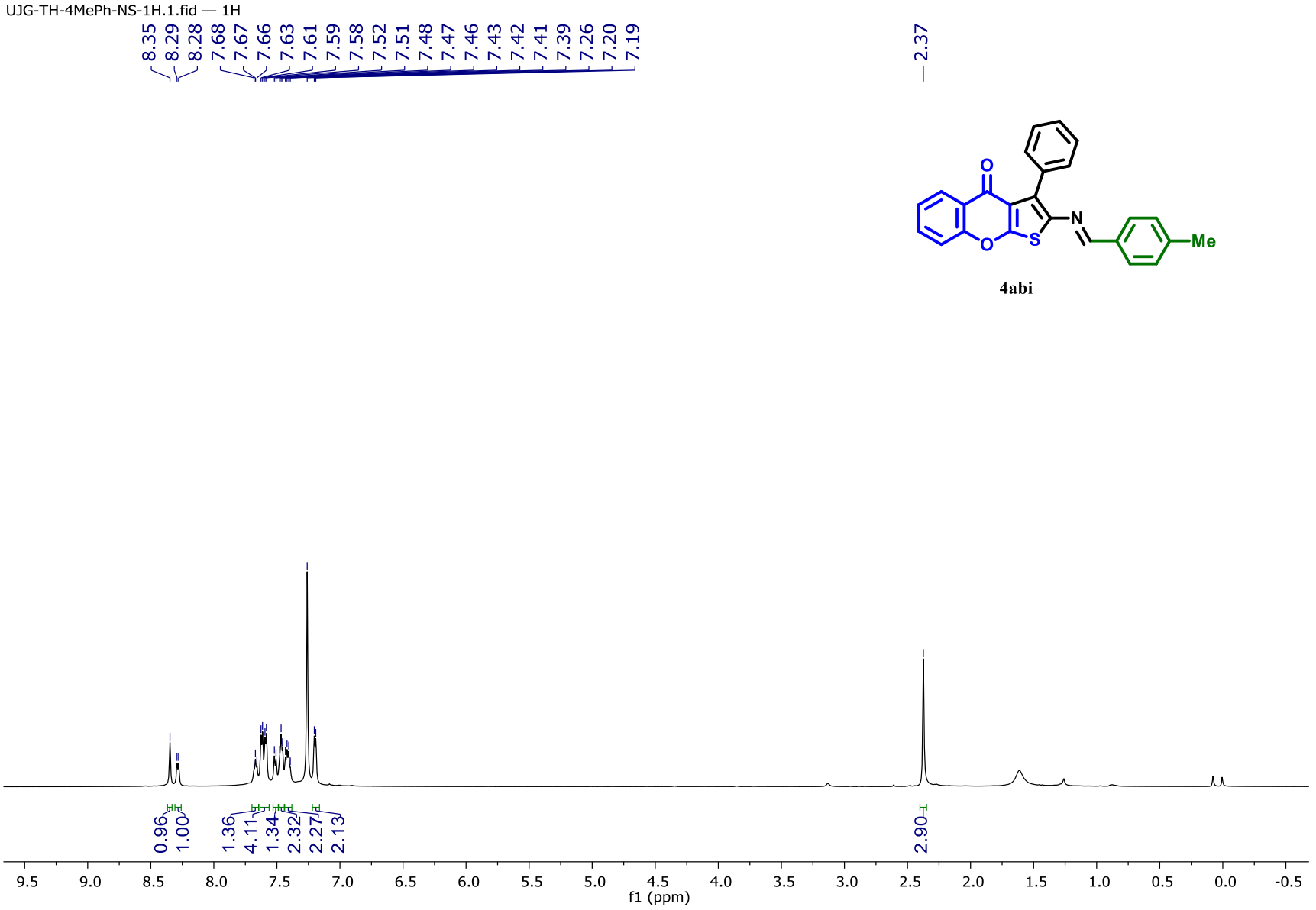
4gca

HRMS Spectrum of Compound 4gca



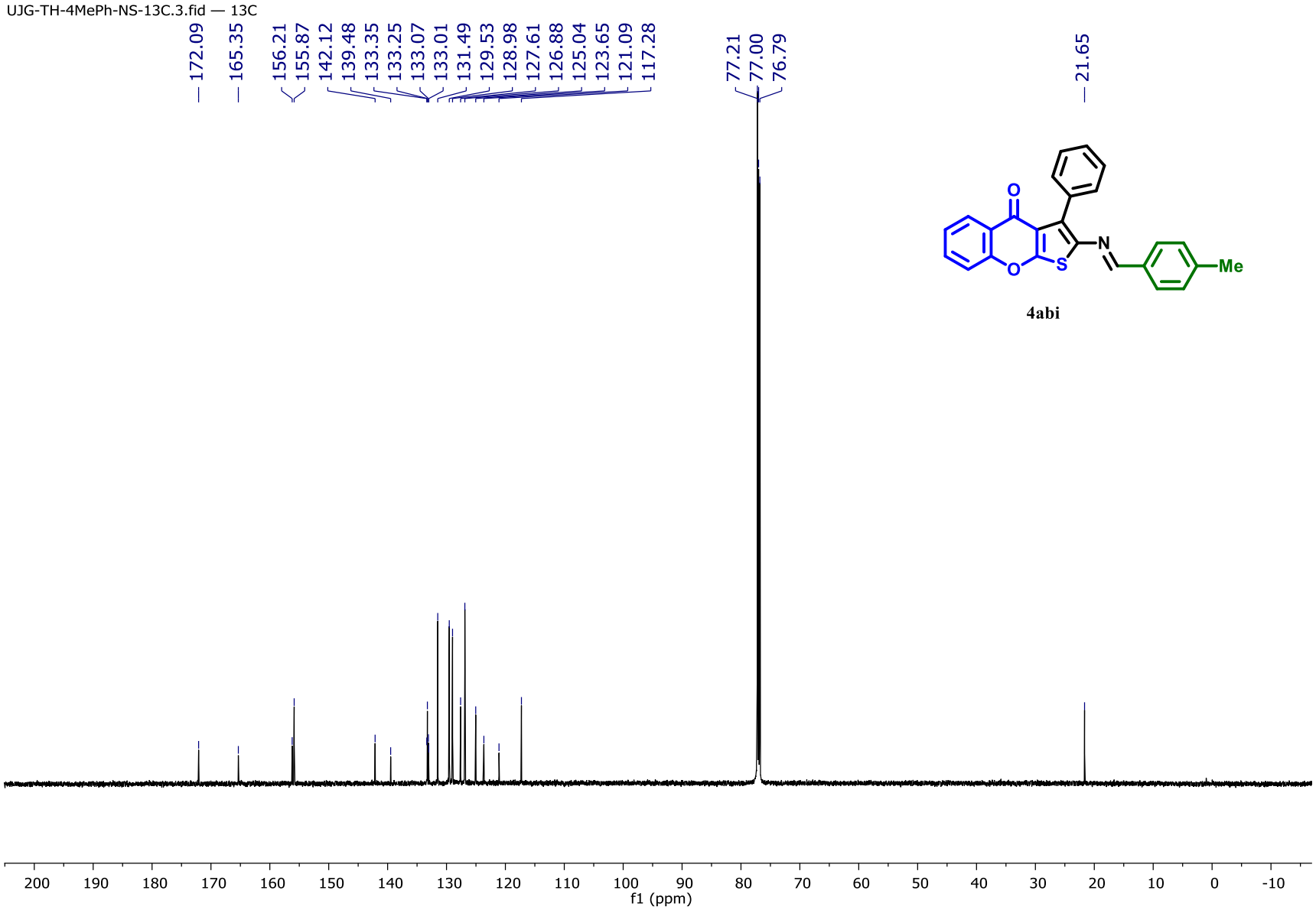
4gca

^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound 4abi

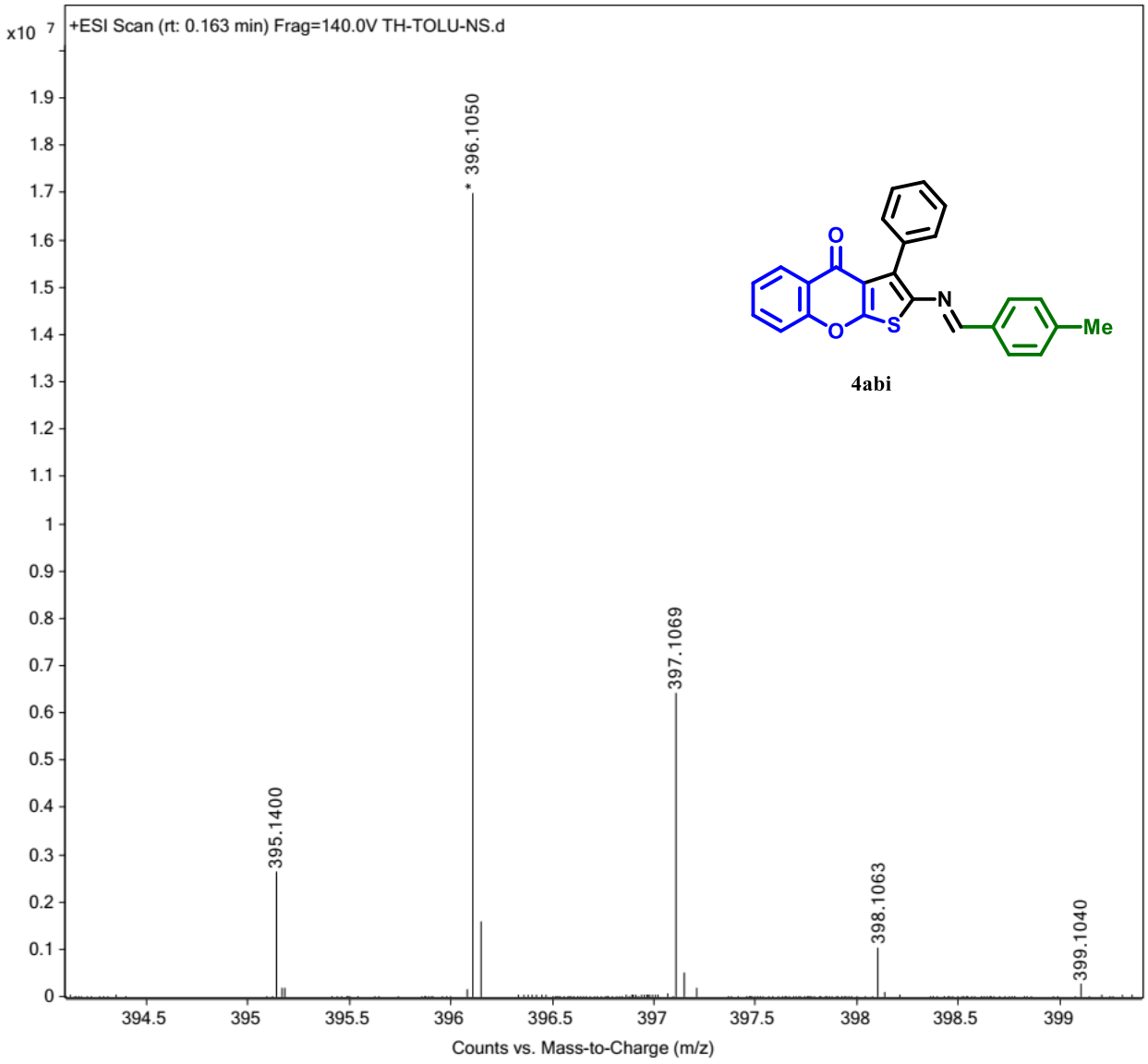


4abi

^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound 4abi

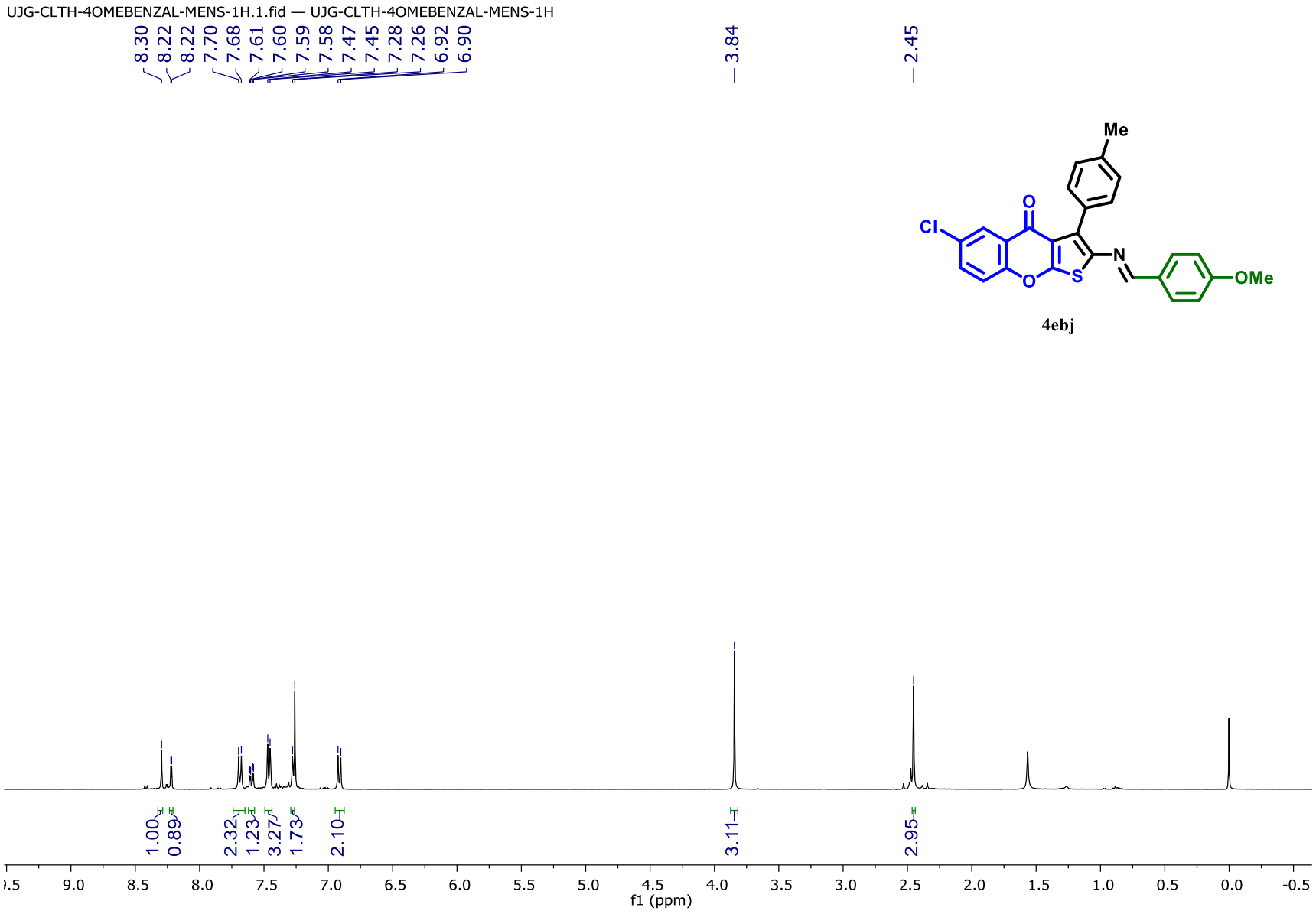


HRMS Spectrum of Compound 4abi



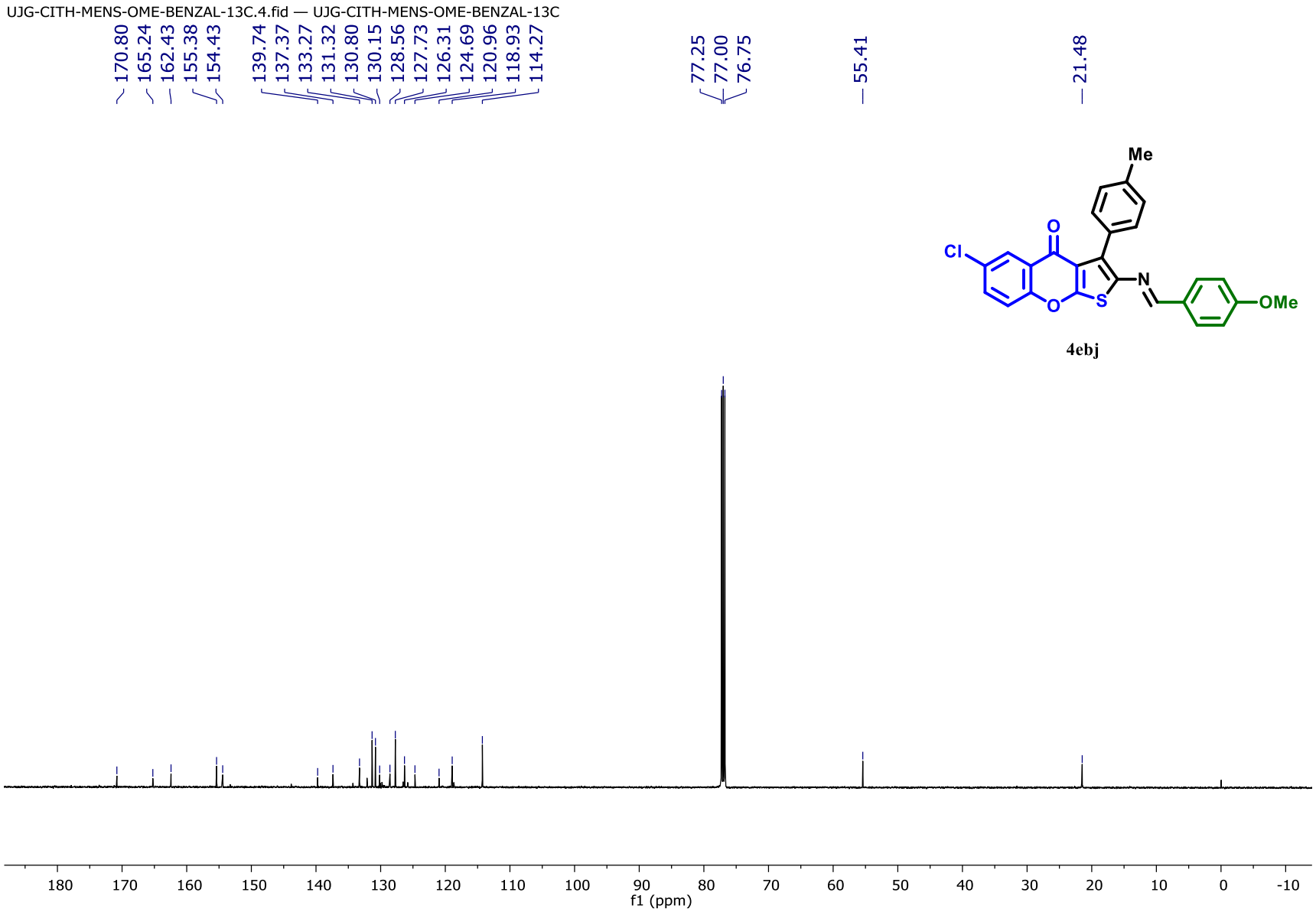
4abi

^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4ebj

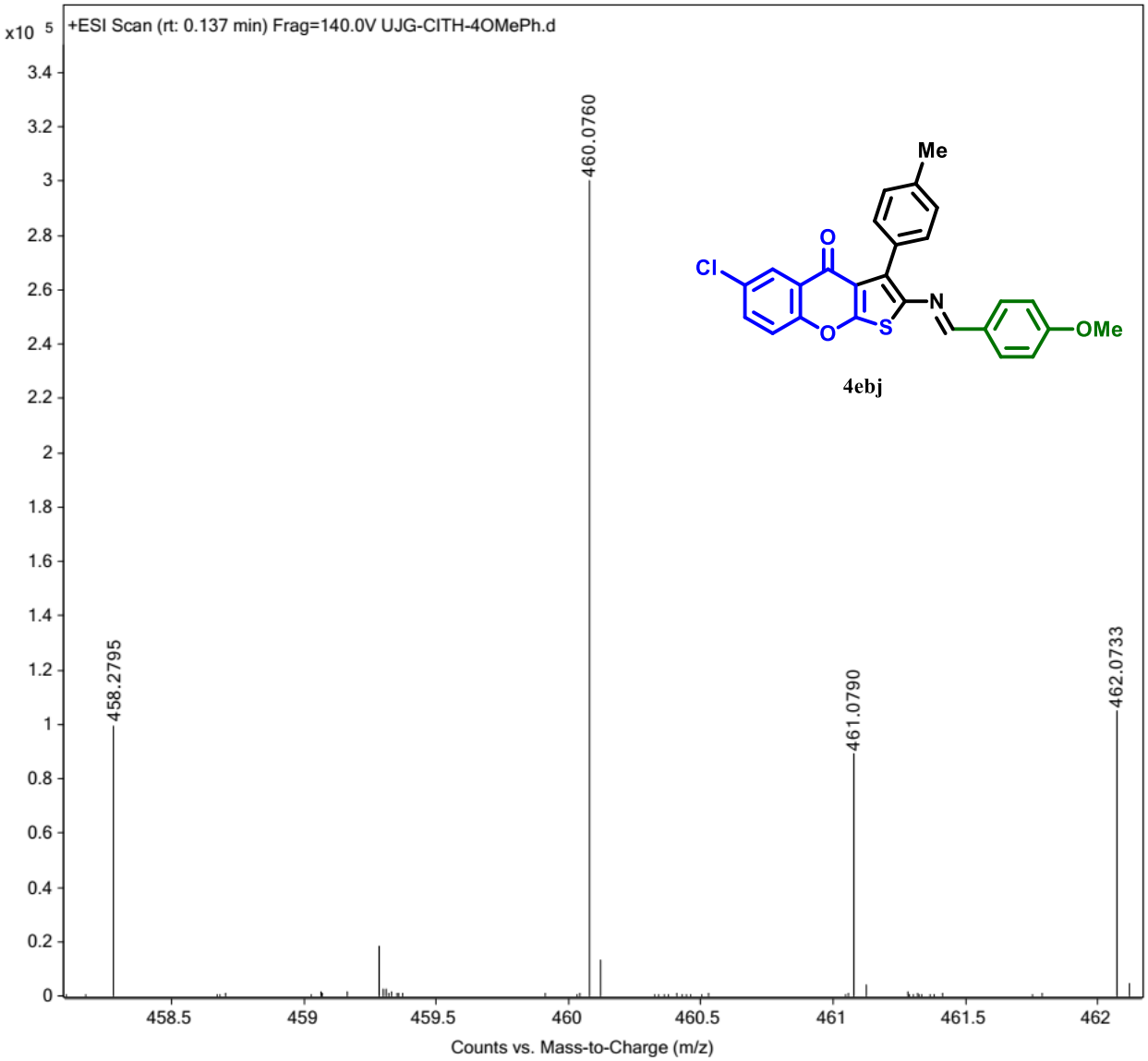


4ebj

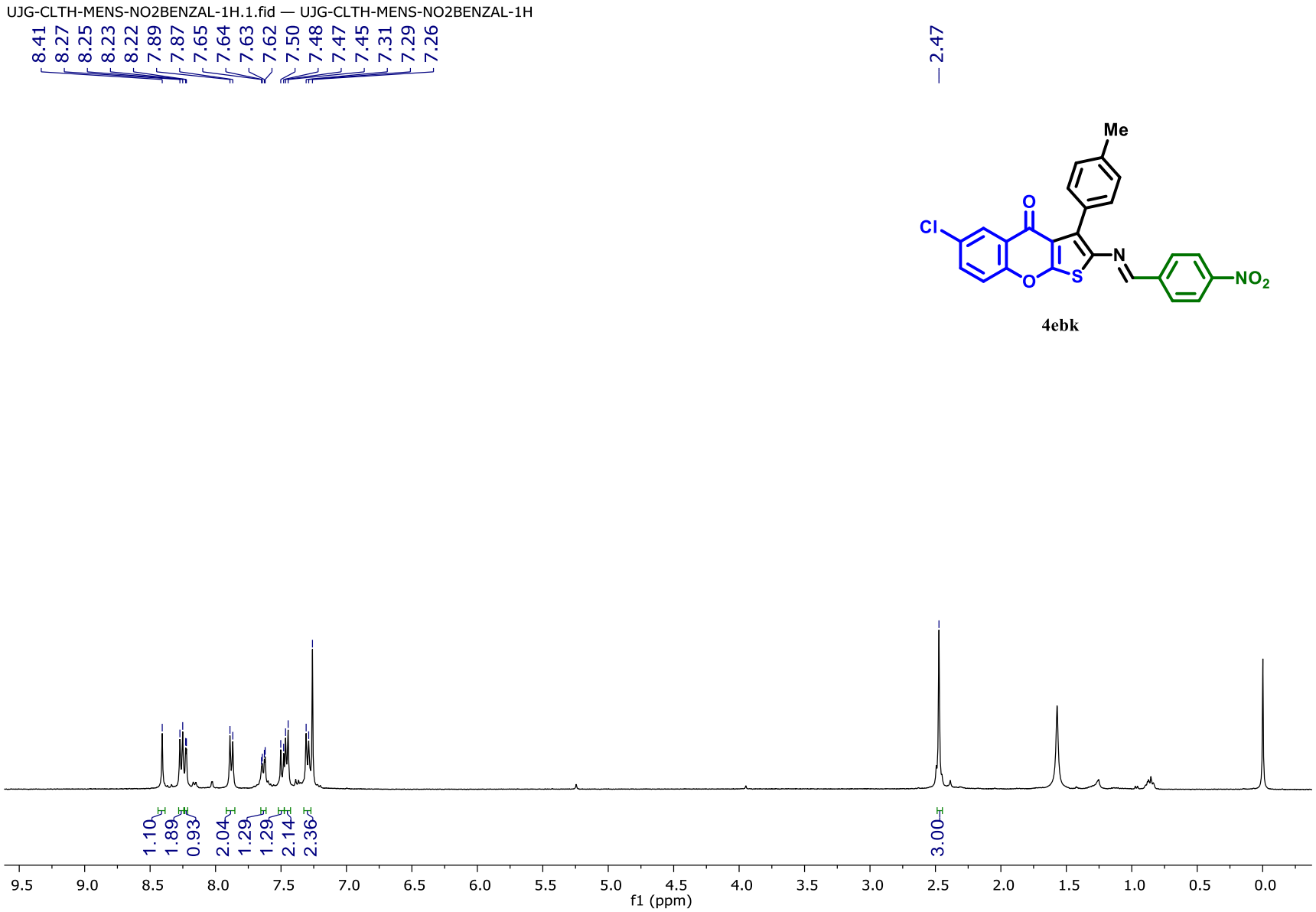
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4ebj



HRMS Spectrum of Compound 4ebj

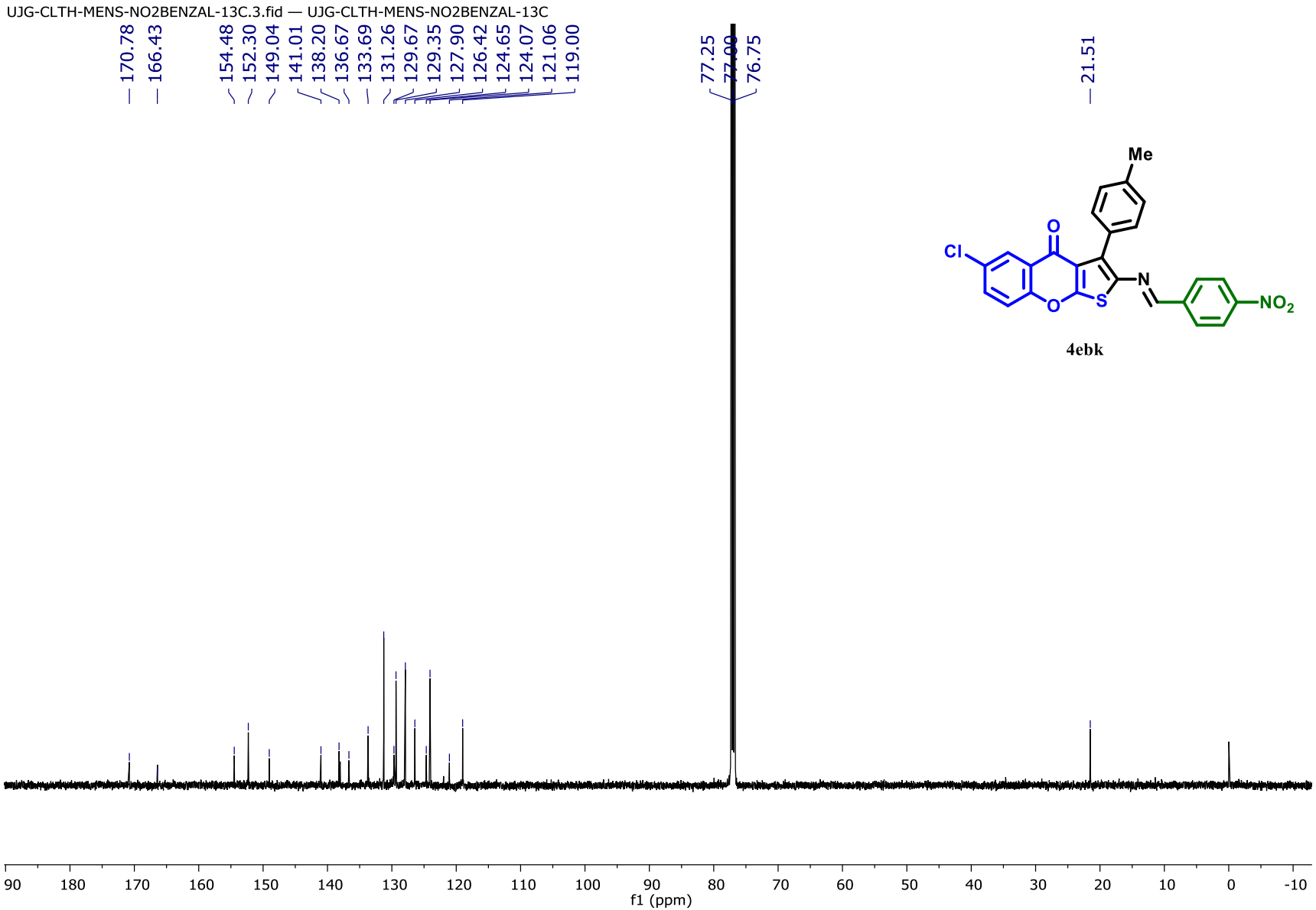


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound 4ebk

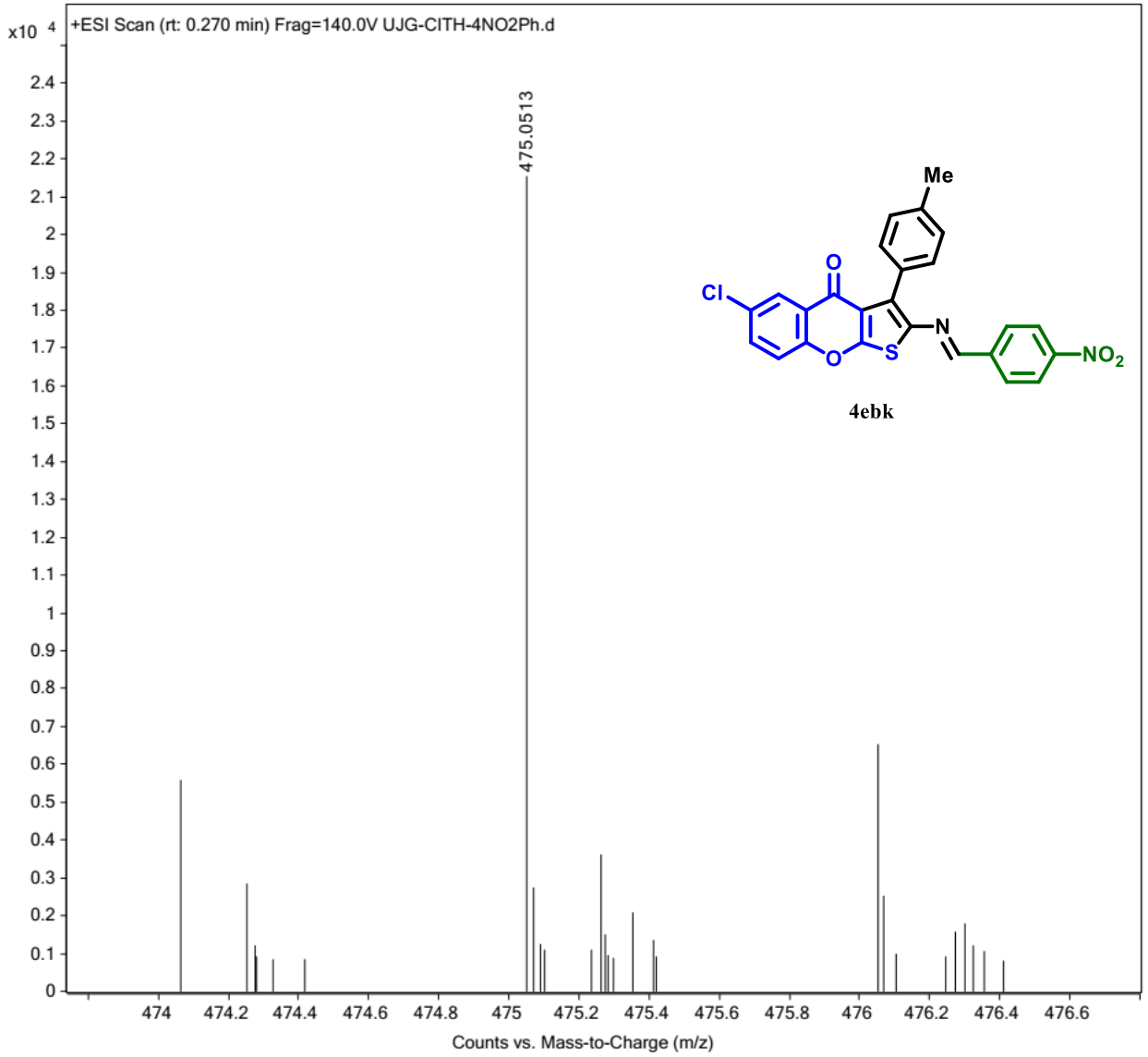


4ebk

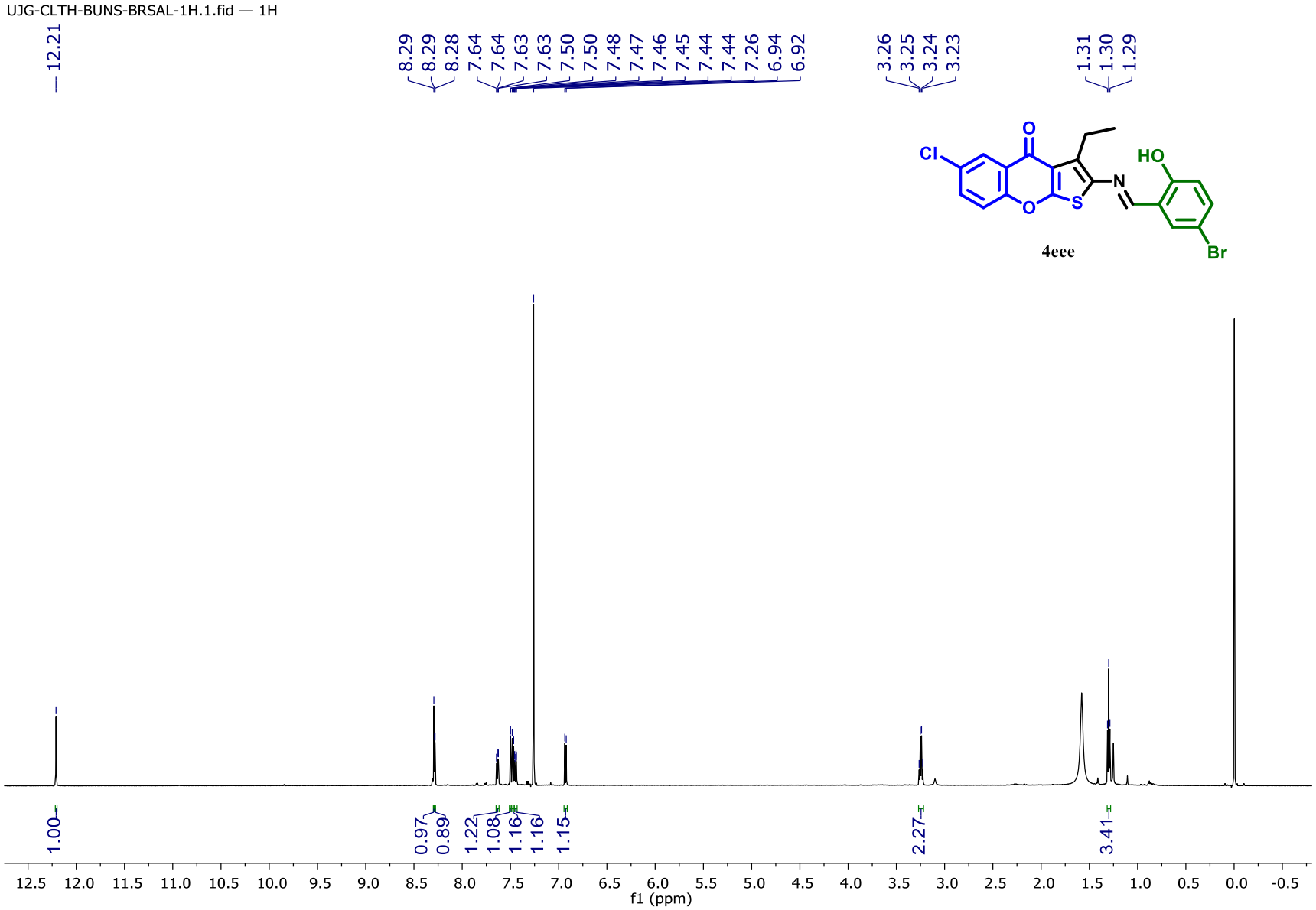
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Compound 4ebk



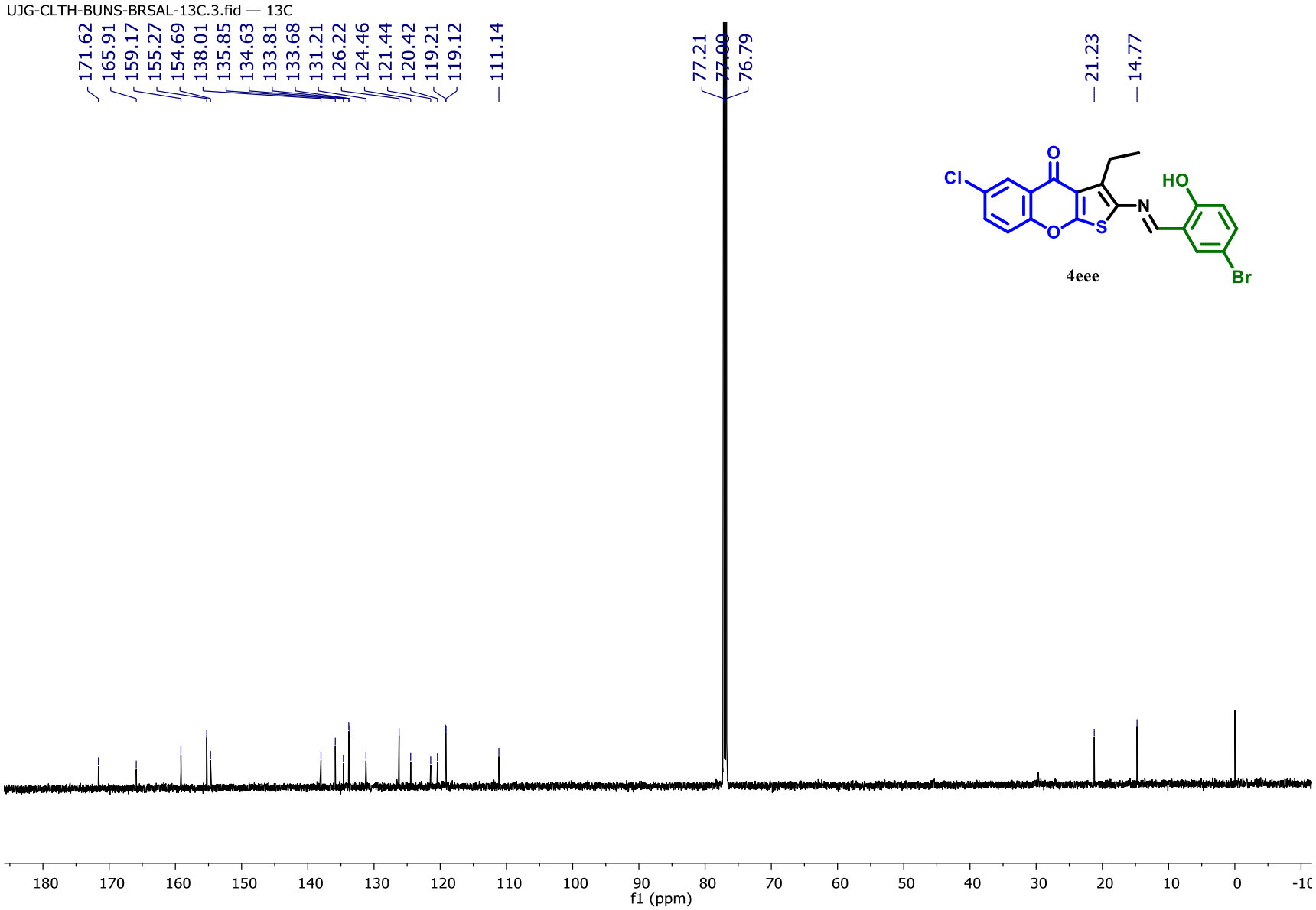
HRMS Spectrum of Compound 4ebk



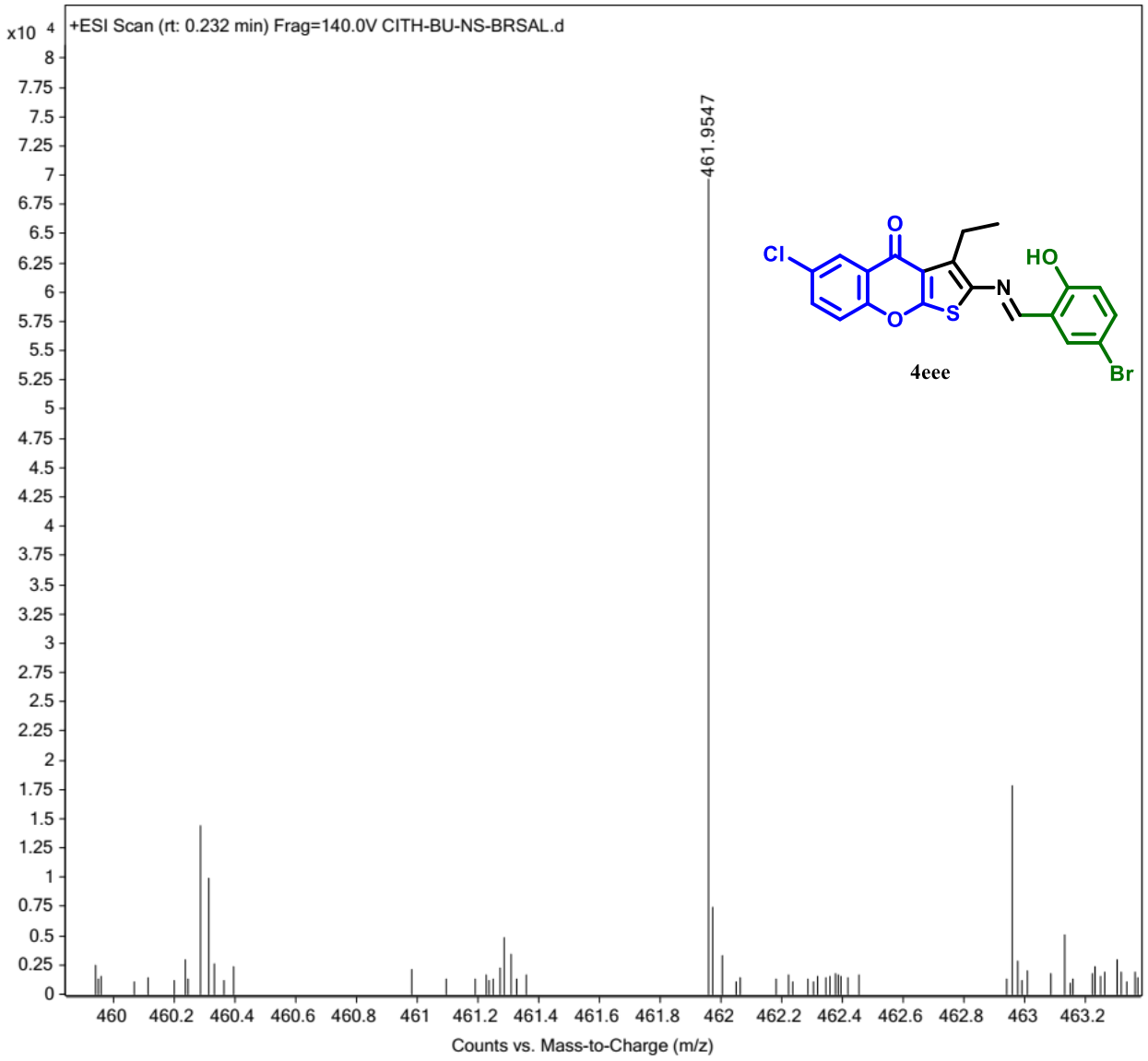
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound 4eee



^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound 4eee



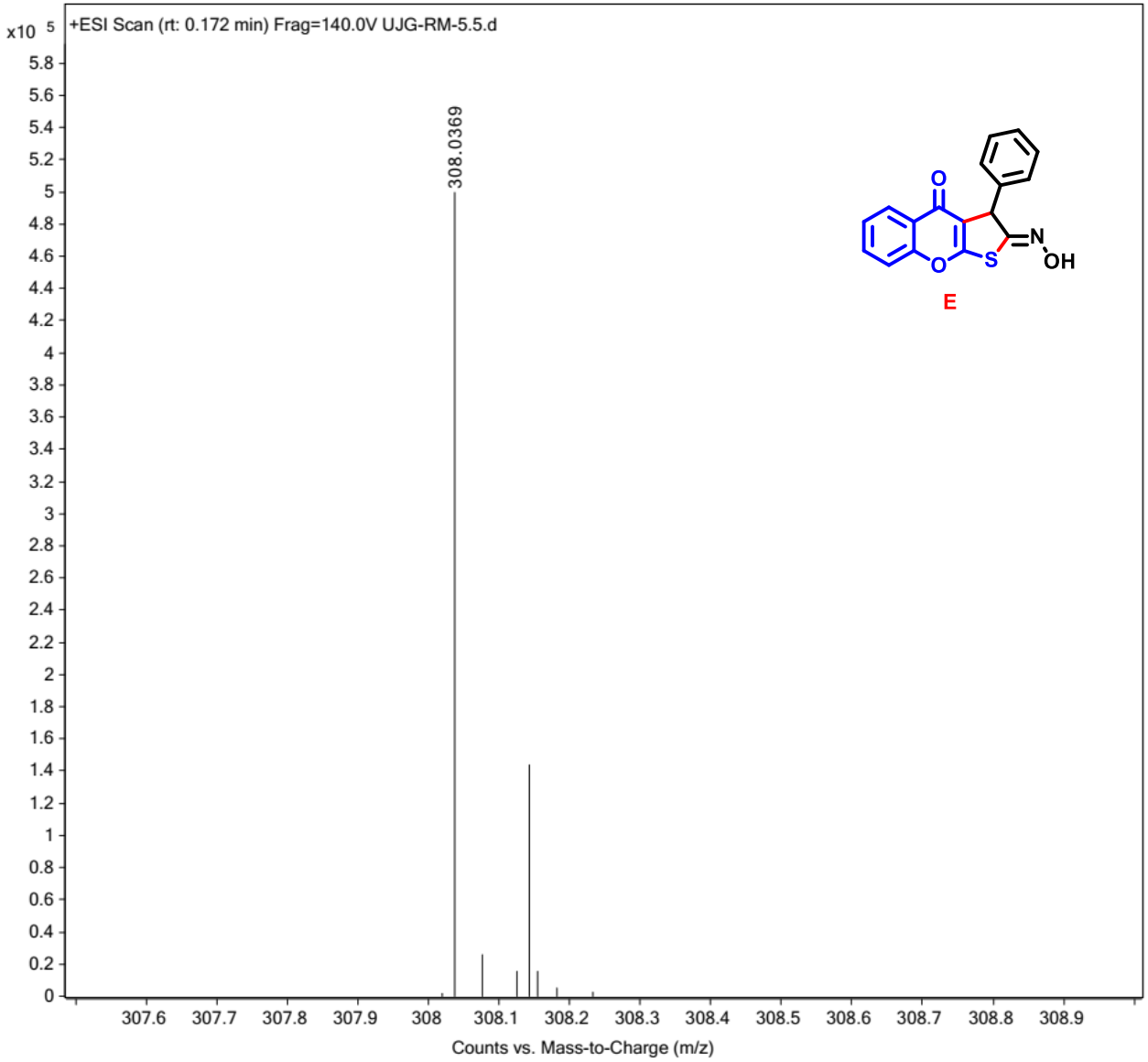
HRMS Spectrum of Compound 4eee



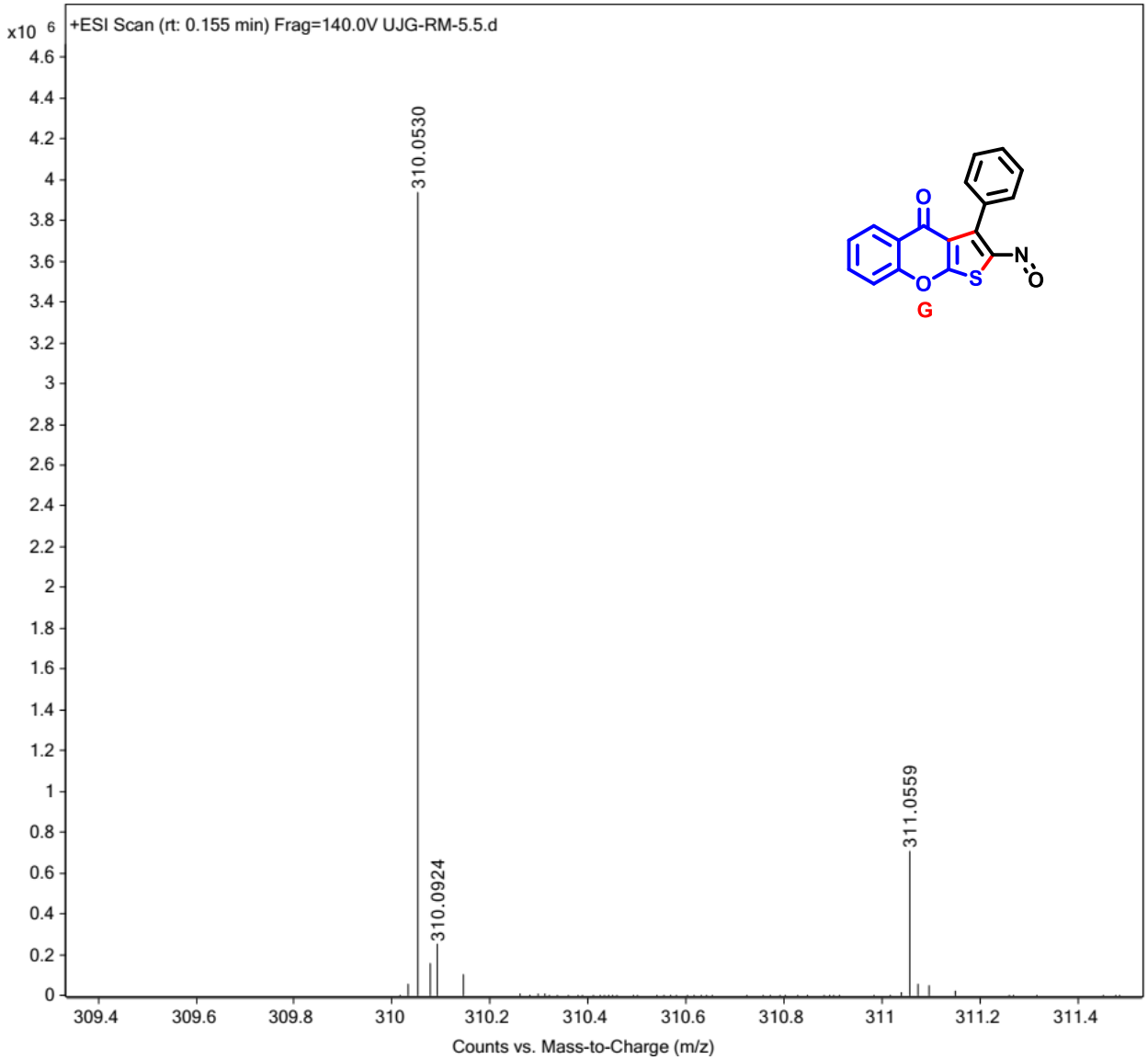
Detection of intermediates in HRMS

0.10 mmol of 4-hydroxythiocoumarin **1a** and *trans*-β-nitrostyrene **2a** and 0.05 mmol of 4-methyl-2-hydroxybenzaldehyde **3a** was stirred in Ethanol in a 10 mL round bottom flask at reflux temperature. After 5.5 h. the reaction mixture was subjected to ESI-MS mass experiment, and the intermediates **E**, **G**, **H** and **I** were detected by HRMS values. The observed m/z values are as follows: intermediate **E**: 310.0530 (expected 310.0532); intermediate **G**: 308.0369 (expected 308.0376); intermediate **H** or **I**: 294.0577 (expected 294.0583).

HRMS Spectrum of intermediate E



HRMS Spectrum of intermediate E



HRMS Spectrum of intermediate H or I