SUPPORTING INFORMATION FOR

$CuNiO_2$ Nanocatalyst for Csp^2–S Cross-Coupling in Water: A Green Approach to Synthesizing Bioactive Molecules

1.General Information

All reactions were conducted in a preheated oil bath in vials and round bottom flasks(size: 5/10 mL) sealed with a septum. Flash column chromatography was performed using silica gel (230-400 mesh). Thin-layer chromatography was performed using Merck silica gel GF_{254} plates. All known products were characterized via nuclear magnetic resonance (NMR) spectroscopy and high-resolution mass spectroscopy (HRMS), and the data were compared to the previously reported data. Proton, carbon, and fluorine nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR, and ^{19}F NMR) were recorded on a Bruker AVANCE III 400 instrument with tetramethyl silane (TMS) as the internal reference. Data for ^{1}H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; dd = doublet of doublet; dt = doublet of triplet), coupling constants, J, in (Hz), and integration. Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (ppm). IR spectra are reported in cm^{-1} with Bruker Alpha-II compact FT-IR. High-resolution mass spectra were obtained in ESI mode (QTOF-ESI). XPS is with Al-Kα line. TEM, SEM, EDX, Powdered XRD data is recorded from central facility IIT Patna. Single XRD structure is recorded in NIT Rourkela. Melting points were determined by digital melting point apparatus and were uncorrected. Quantum-chemical calculations are carried out with the Gaussian 16 program to examine the reaction mechanism. The equilibrium geometry of all species studied in this work and their vibrational frequency calculations were calculated with the B3LYP density functional theory, and the LANL2DZ basis set. We constructed a reaction pathway scheme (RPS) for possible reaction channels. All equilibrium geometries showed no imaginary frequencies, confirming their identity as true local minima. The energies are corrected for vibrational zero-point energy (ZPE). Solvent effects were included using the Polarizable Continuum Model (PCM), with water. This was implemented using the SCRF=(SMD, solvent=water) as keywords. Thermochemical corrections, including Gibbs free energy and enthalpy, were computed.

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2: Materials

All starting materials and reagents are commercially available and used as received. Solvents such as DMSO (99.9%), Toluene (99.8%), DMF (99.8%), Acetonitrile (99.8%), DMA (99.9%), THF (99.9%) and $CDCl_3$ (99.8%) is purchased from Sigma-Aldrich. All other solvents are purchased from Merck of high purity grade. DMSO and acetonitrile was sparged with nitrogen (N_2) for 5 min at room temperature and stored under nitrogen atmosphere. All haloarenes such as 1-Iodo-3,5-dimethylbenzene(99%), 4-Methoxyiodobenzene(98%), 2-Bromoquinoline(97%), 4-Iodobenzotrifluoride(97%),4-Bromoacetophenone(99%), 4-Cyano benzonitrile (99%), 4-nitroiodobenzene (98%), and all thiols such as Thiophenol(98%), Cyclohexane thiol(97%), 1-Adamantanethiol(99%),2-Mercaptoethanol(99%), 2-Chlorobenzene thiol(97%), 2-Bromobenzenethiol(95%), 4-Methoxybenzene thiol(97%),4-Mercaptophenol (97%)1-Octanethiol(98%), metals such as $Cu(CO_2CH_3)_2 \cdot H_2O$ (98%), $NiCl_2.6H_2O$(98%), and $Cs2CO_3$ (*Reagent Plus*®, 99%) and KOH (99%), K_2CO_3 (99%), Na_2CO_3(99%) KO^{t}Bu (99%) were purchased from Sigma Aldrich. Organic solutions were concentrated on a Büchi Rotavapour R-100 rotary evaporator using a water bath.

3.Synthesis of Bimetallic $CuNiO_2$ Nano Catalyst:

$Cu(OAc)_2{\cdot}H_2O$ (1 mmol, 199 mg) is dissolved in 50 mL of warm distilled water. In another beaker $NiCl_2.6H_2O$ (1 mmol, 236 mg) is dissolved in 50 mL of warm distilled water. The later solution was added dropwise to first beaker dropwise· The solution was heated at 50 ℃ for 10 minutes to get a sky colour gummy solution. Next, 25mL of 2N KOH solution was added drop wise till the pH of solution is 11. The colour of solution gradually changed to black colour. The whole solution transferred into a Teflon lined hydrothermal autoclave and that kept in an oven at 150 ℃ for 24 h. The catalyst was washed repeatedly with 100 mL of distilled water and then 50 mL of ethanol by using REMI C-24 centrifuge instrument and then dried in an oven at 70 ^{o}C for 12 h. The catalyst was characterized in TEM, SEM, EDX, IR, Powder XRD and XPS (Figure 1).

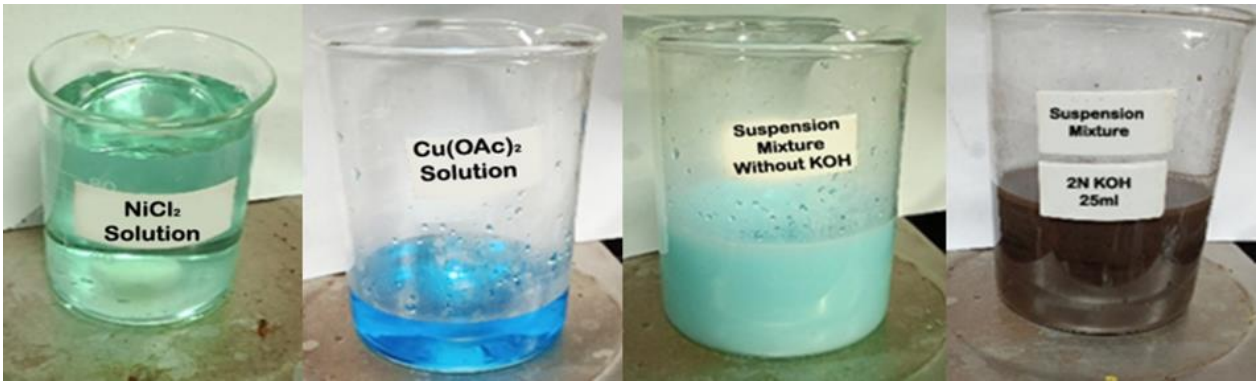


Figure 1: Synthesis of $CuNiO_2$ catalyst

4.Catalyst Characterization:

The catalyst was dried in a heating oven at 80 ^{o}C for 6h then followed by different characterisation techniques such as TEM, SEM, EDX, XPS, IR, and powder XRD (**Figure 2-8**). The particle looks like smoky black colour with thickness range from 25-100 nm which is confirmed from SEM analysis. The EDX analysis of catalyst shows that the atomic percentage of Copper and Nickel are same and that of Oxygen is three times of the metals **(Table 1)**. The high-resolution XPS spectrum of Cu2p demonstrated that presence of Cu^{2+} peaks at the binding energy of 932.78 eV for 2p3/2 and 953.05 eV for 2p1/2 as shown in **Figure 8.** Additionally, the satellite peaks were appeared at around the binding energy of 940.16 and 960.63 eV for 2p3/2 and 2p1/2, respectively. **Figure 9** shows high-resolution spectrum of Ni2p, the peaks appeared at 855 eV and 873 eV for 2p3/2 and 2p1/2 respectively indicates the presence of Ni^{+2} in the catalyst. The peaks are appeared at 861.5 and 879.9 eV, representing the satellite peaks for 2p3/2 and 2p1/2 respectively.[38a] **Figure 10** shows the high-resolution spectrum of O1s, the peak appeared at the binding energy of 531 eV represents O-Ni bonding. Similarly peak at 529 and 530 eV shows O-Cu bonding. 529.09 eV is assigned to lattice O^{2-} in metal oxide, while the intermediate 530.00 eV shift is related to lattice oxide and 531 eV is related to surface hydrolysis. This evidence suggests that oxygen in a mixed Cu-Ni environment [Cu-O-Ni bridging]. [38b]

IR spectra revealed that there is no direct metal-metal Ni-Cu bond but instead a Cu-O-Ni [IR 681 cm^{-1}] bond is there Along with this Ni-O [IR 611cm^{-1}], Cu-O [IR 513.88 cm^{-1}] **(Figure 11).** The powdered XRD data of catalyst of catalyst reveals that there is strong XRD peaks position with corresponding planes at 33.03° (110), 35.49° (-111), 38.72° (111), 48.68° (-202), and 61.46° (-113) confirms the formation of Cu-O-Ni **(Figure 12).** [38a,39] Hence, the whole characterisation

process clearly justifies the composition, structure, bonding, and morphology of the $CuNiO_2$ catalyst.

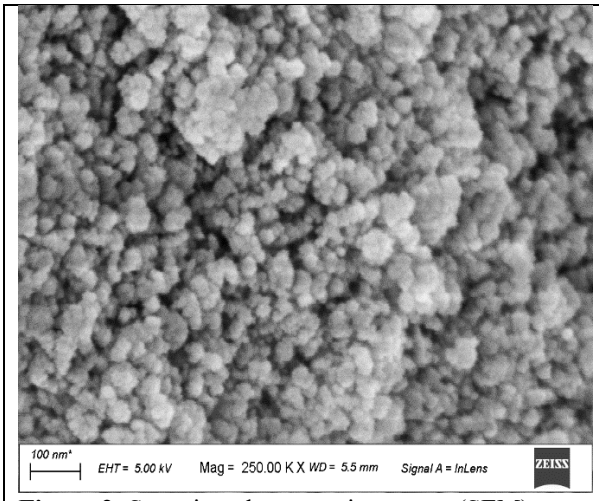


Figure 2: Scanning electron microscopy (SEM) analysis of $CuNiO_2$ Catalyst.

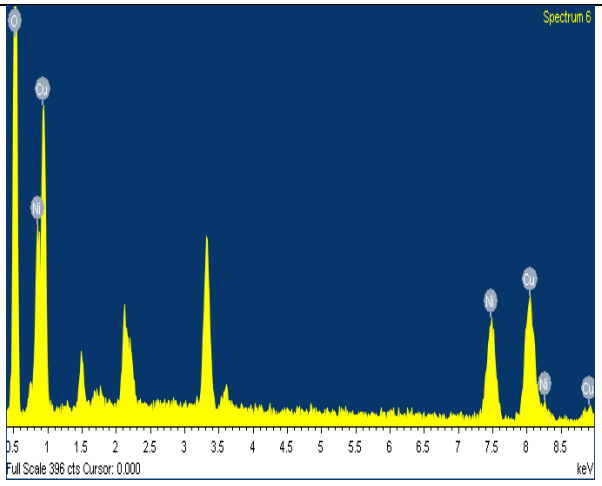


Figure 3: Energy Dispersive X-Ray (**EDX**) analysis of $CuNiO_2$ catalyst.

Table 1: Details of Elemental Analysis of catalyst.

Element	**App Conc.**	**Intensity Corrn.**	**Weight%**	**Weight% Sigma**	**Atomic%**
O K	29.64	1.5623	27.57	0.74	59.29
Ni K	21.73	0.9457	33.39	0.99	19.57
Cu L	9.72	0.3616	39.04	1.10	21.14
Totals			100.00		

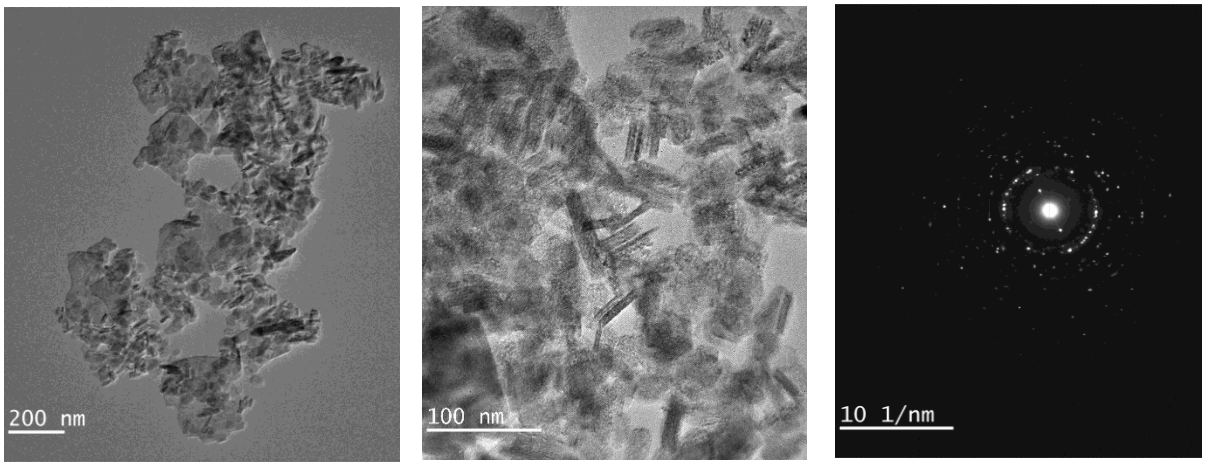


Figure 4: TEM images and electron diffraction pattern of $CuNiO_2$ nanoparticles.

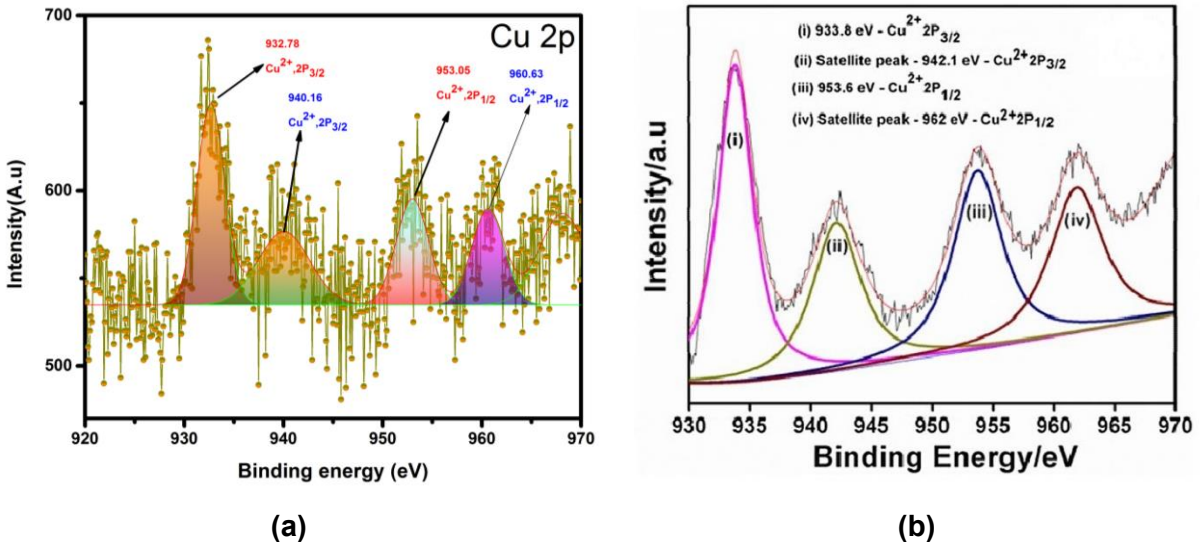


Figure 5: (a) X-ray photoelectron spectroscopy (XPS) spectra of Cu^{+2} in $CuNiO_2$ catalyst.

(b) Refenence XPS data of Cu^{+2} in CuO.[38a]

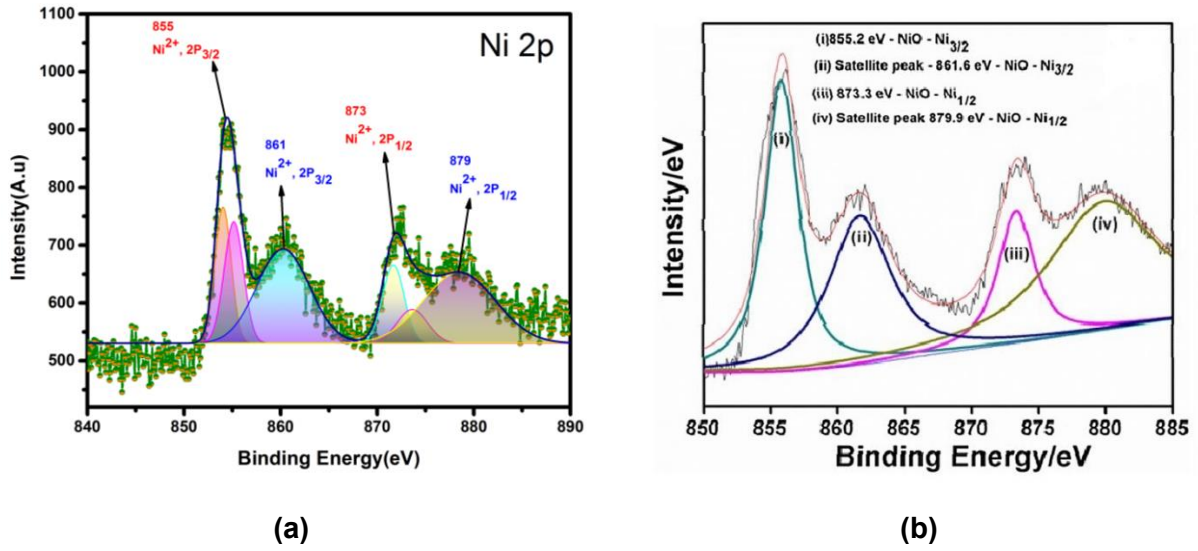
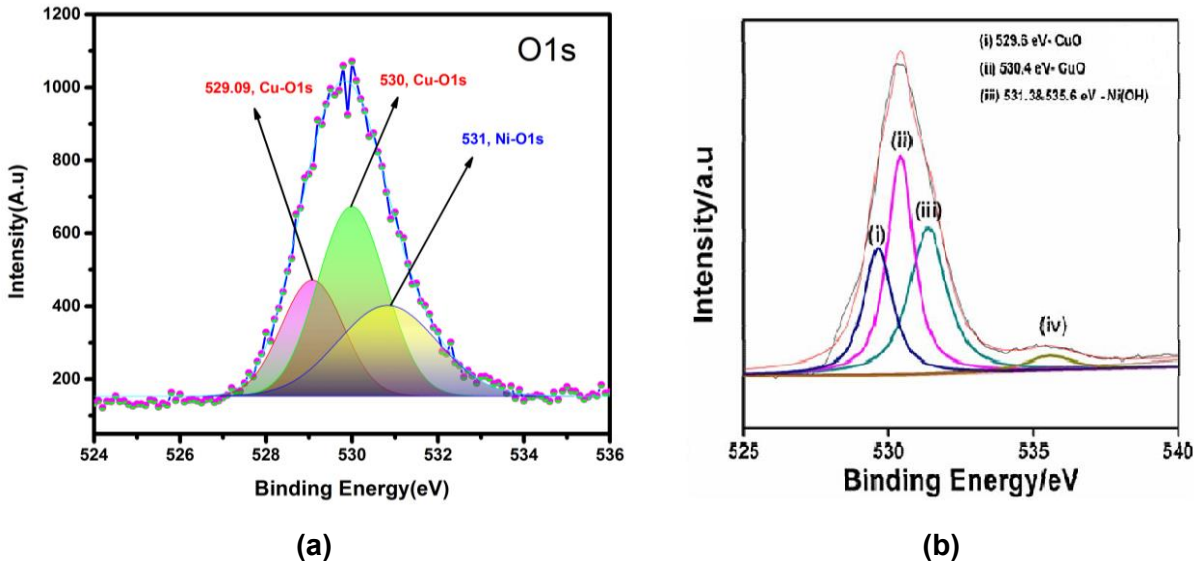


Figure 6: (a) X-ray photoelectron spectroscopy (XPS) spectra of Ni^{+2} in $CuNiO_2$ catalyst.

(b) Refenence XPS data of Ni^{+2} in NiO. [38a]



(a) (b)

Figure 7: (a)X-ray photoelectron spectroscopy (XPS) spectra of O^{2-} in $CuNiO_2$ catalyst. **(b)** Refenence XPS data of oxygen binding to Nickel and copper. [38a]

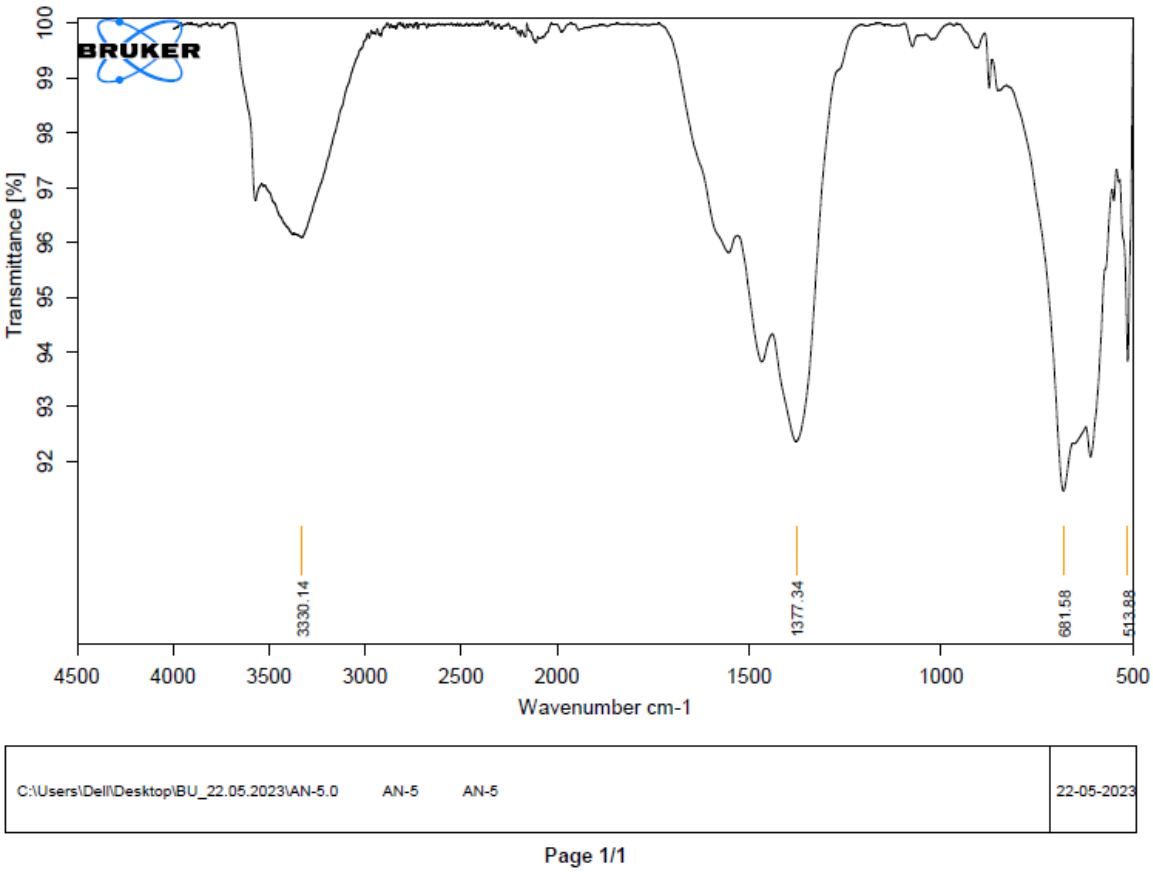


Figure 8: IR Spectra of $CuNiO_2$ Catalyst.

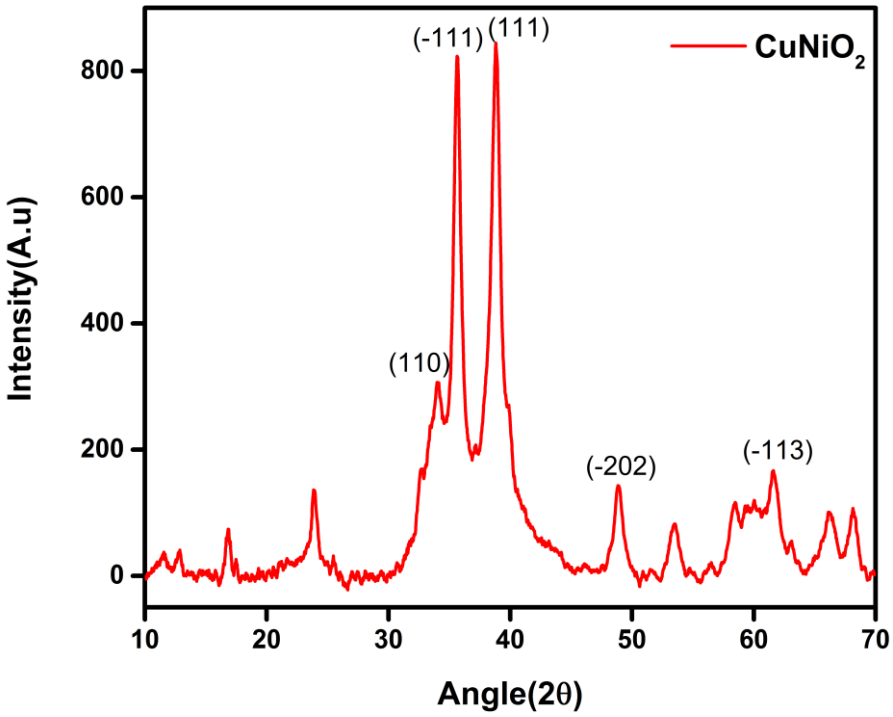
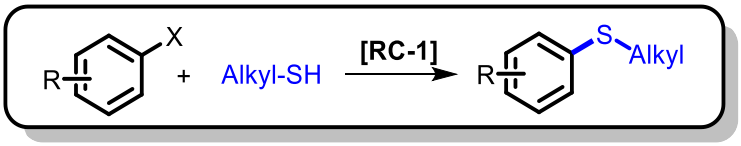


Figure 9: Powdered X-ray diffraction (XRD) analysis of $CuNiO_2$ Catalyst.

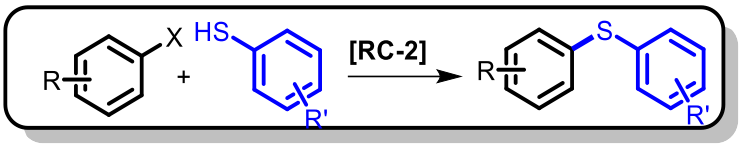
5. General Experimental procedure

(a) Reaction Condition 1: (RC-1)



A 5 mL glass vial equipped with a magnetic stir bar was charged with catalyst $CuNiO_2$ (5 mol%), distilled water (1 mL), TBAB (1 equiv.), haloarenes (1 mmol), thiols (1.2 equiv.) and base K_2CO_3 (1.5 equiv.) in air (The adding sequence should be followed strictly). The reaction mixture was then placed in a preheated oil bath with stirring maintained at 80 °C. The reaction is monitored after every 2 h with the help of TLC and $KMnO_4$ stain. After the time specified in the reaction schemes, the reaction mixture was quenched with NH_4Cl solution (5 mL) and extracted with EtOAc (3 × 10 mL). The organic layer was dried over sodium sulfate and filtered. After evaporation of the solvent under reduced pressure, the residue was purified via flash column chromatography (*n*-hexane/EtOAc).

(b) Reaction Condition 2: (RC-2)



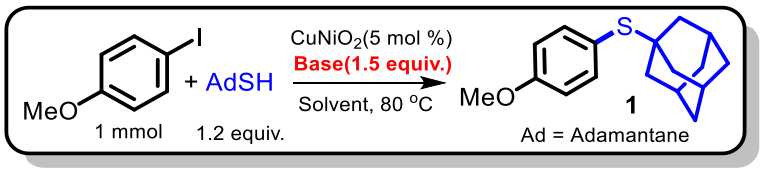
A 5 mL glass vial equipped with a magnetic stir bar was charged with catalyst $CuNiO_2$ (5 mol%), distilled water: DMSO (4:1), TBAB (1 equiv.), respective haloarenes (1 mmol), corresponding thiols (1.2 equiv.) and base K_2CO_3 (1.5 equiv.) in air (The adding sequence should be followed strictly). The reaction mixture was then placed in a preheated oil bath with stirring maintained at 80 °C. The reaction is monitored after every 2 hr with the help of TLC and $KMnO_4$ stain. Figure: 12. All reactions were carried out at Central Instrumentation Centre, Berhampur University, Odisha, India. After the time specified in the reaction schemes, the reaction mixture was quenched with NH_4Cl solution (3 mL) and extracted with EtOAc (3 x 10 mL) The organic layer was dried over sodium sulfate and filtered. After evaporation of the solvent by Rotavapor, the residue was purified via flash column chromatography (n-hexane/EtOAc).

(c) Reaction Condition 3: (RC-3)

Synthesis of aryl sulfones from aryl sulfides by using H_2O_2:[28] To a solution of the Aryl sulfide (1 mmol) in 5 mL glacial acetic acid was added dropwise a solution of 30% H_2O_2 (6 equiv.). The reaction mixture was stirred at 60 °C for 4-5 h. In the reaction mixture, 10 mL of CH_2Cl_2 was added. Then the reaction mixture was washed with saturated $NaHCO_3$ and brine and dried over Na_2SO4. The solvent was removed in vacuo, and the residue was purified by distillation or recrystallization after column chromatography.

6. Optimization of reaction condition

Table 1. Effect of base in the reaction of 4-iodoanisole and adamantane-1-thiol with $CuNiO_2$ catalyst

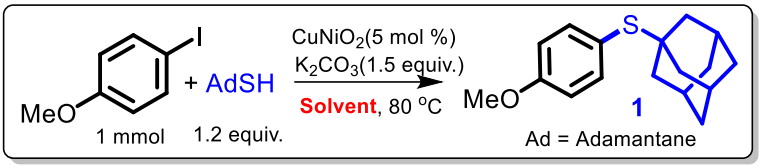


Entry	Catalyst	Base	Solvent	Yield(%)[a,b]
1	$CuNiO_2$	KOH	H_2O	70
2	$CuNiO_2$	NaOH	H_2O	40
3	$CuNiO_2$	NaH	H_2O	50
4	$CuNiO_2$	KOAc	H_2O	40
5	$CuNiO_2$	KO^{t}Bu	H_2O	35

6	$CuNiO_2$	Cs_2CO_3	H_2O	30
7	$CuNiO_2$	Na_2CO_3	H_2O	70
8	$CuNiO_2$	K_2CO_3	H_2O	77*

[a]Reaction condition: catalyst (5 mol%), 4-iodoanisole (1 mmol), adamantane-1-thiol (1.2 equiv.), base (1.5 equiv.), H_2O (1 mL), at 80 °C for 10 h [b]Isolated yield, *<5% disulfide observed. AdSH: adamantane-1-thiol.

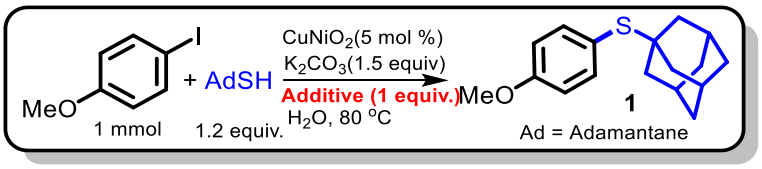
Table 2. Effect of solvent in the reaction of 4-iodoanisole and adamantane-1-thiol with $CuNiO_2$ catalyst.



Entry	Catalyst	Base	Additive	Solvent	Yield(%)[a, b,c]
1	$CuNiO_2$	K_2CO_3	None	THF	13
2	$CuNiO_2$	K_2CO_3	None	DMSO	21
3	$CuNiO_2$	K_2CO_3	None	Toluene	14
4	$CuNiO_2$	K_2CO_3	None	CH_3CN	32
5	$CuNiO_2$	K_2CO_3	None	EtOH	nd
6	$CuNiO_2$	K_2CO_3	None	DMF	50
7	$CuNiO_2$	K_2CO_3	None	DMA	40
8	$CuNiO_2$	K_2CO_3	None	H_2O	77
9	$CuNiO_2$	K_2CO_3	TBAB	H_2O	93[b]

[a]Reaction condition: catalyst(5 mol%),4-iodoanisole (1 mmol), adamantane-1-thiol (1.2 equiv.), K_2CO_3 (1.5 equiv.),[b] with TBAB (1 equiv.) solvent (1 mL) were stirred at 80 °C for 10 h [c] Isolated yield, AdSH: adamantane-1-thiol.

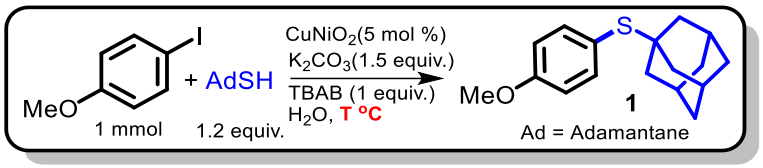
Table 3. Effect of additive in the reaction of 4-iodoanisole and adamantane-1-thiol with $CuNiO_2$ catalyst.



Entry	Catalyst	Base	Solvent	Additives	Yield(%)[a,b]
1	$CuNiO_2$	K_2CO_3	H_2O	None	77
2	$CuNiO_2$	K_2CO_3	H_2O	PEG-8000	25
3	$CuNiO_2$	K_2CO_3	H_2O	TBAF	79
4	$CuNiO_2$	K_2CO_3	H_2O	TBAB	93*

[a]Reaction condition: catalyst (5 mol%), 4-iodoanisole (1 mmol), adamantane-1-thiol (1.2 equiv.), K_2CO_3 (1.5 equiv.), Additive (1 equiv.) H_2O (1 mL) were stirred at 80 °C for 10 h. [b]Isolated yield, *<5% disulfide observed without an additive. AdSH: adamantane-1-thiol.

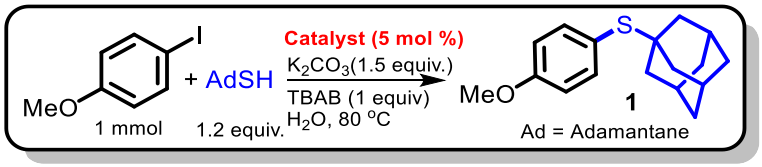
Table 4. Effect of temperature in the reaction of 4-iodoanisole and adamantane-1-thiol with $CuNiO_2$ catalyst



Entry	Catalyst	Base	Solvent	Additive	Temperature(T)	Yield(%)[a,b]
1	$CuNiO_2$	K_2CO_3	H_2O	TBAB	80 ºC	93 *
2	$CuNiO_2$	K_2CO_3	H_2O	TBAB	65 ºC	70
3	$CuNiO_2$	K_2CO_3	H_2O	TBAB	50 ºC	50
4	$CuNiO_2$	K_2CO_3	H_2O	TBAB	25 ºC	0
5	$CuNiO_2$	K_2CO_3	4:1 H_2O/DMSO	TBAB	50 ºC	25

[a]Reaction condition: catalyst (5 mol%), 4-iodoanisole (1 mmol), adamantane-1-thiol (1.2 equiv), K_2CO_3 (1.5 equiv), H_2O (1 mL) were stirred at said temperature ℃ for 10 h. [b]Isolated yield, AdSH: adamantane-1-thiol.

Table 5. Control Experiment.



Entry	Catalyst	Yield(%)[a,b]
1	None	0
2	$CuNiO_2$	93*
3	$Cu(OAc)_2.H_2O$	62
4	$NiCl_2.6H_2O$	10
5	$NiCl_2.6H_2O$ + $Cu(OAc)_2.H_2O$	90

[a]Reaction condition: catalyst (5 mol%),4-Iodoanisole (1 mmol), adamantane-1-thiol (1.2 equiv.), K_2CO_3 (1.5 equiv.), TBAB (1 equiv.), and H_2O (1 mL) were stirred at 80 ºC. [b] Isolated yield.

7. Failed Attempt to synthesize Cathepsin D (49a, 49b)

Attempt to synthesize cathepsin D precursor[40] **49a, 49b** failed by coupling of 4-bromoaniline with benzothiazole-2-thiol, instead afforded symmetrical dithioacetals in good yield (structure confirmed by XRD, CCDC 2377843 and 2377844) [41]

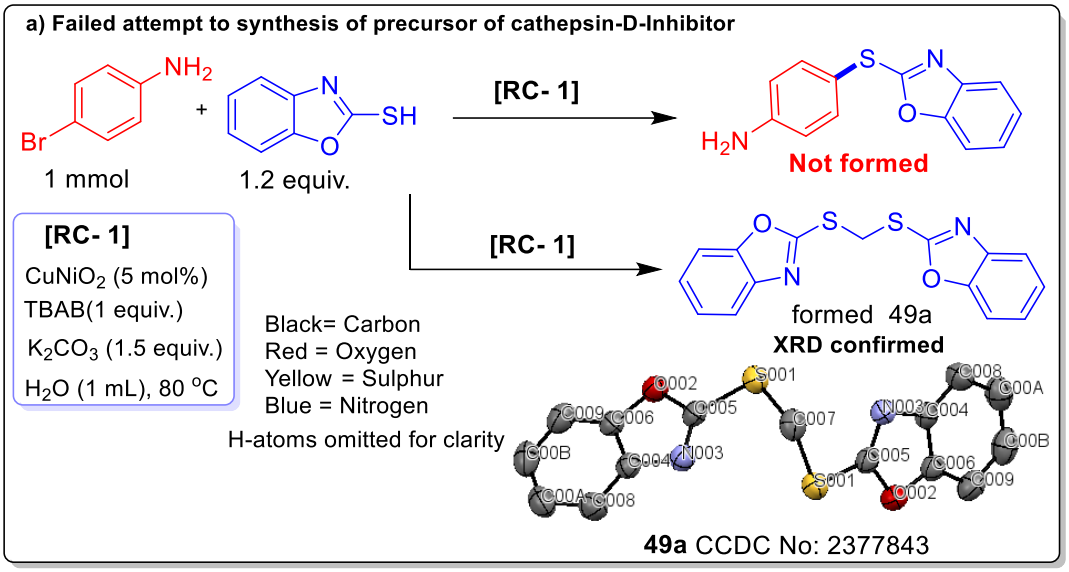


Figure 10a: ORTEP diagram of dithioacetal 49a; Grey Carbon, Red Oxygen, Yellow Sulfur, Blue Nitrogen.

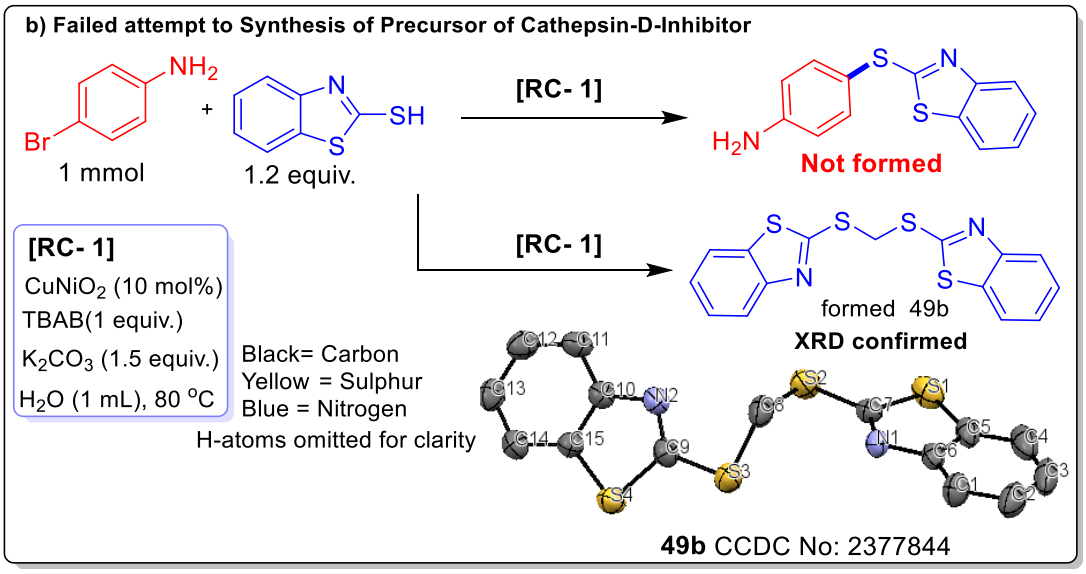
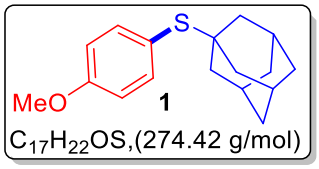


Figure 10b: ORTEP diagram of dithioacetal 49 b; Grey Carbon, Yellow Sulfur, Blue Nitrogen.

8. Characterization of Products

(3s,5s,7s)-Adamantan-1-yl(4-methoxyphenyl)sulfane (1)

Following **RC-1, 1** was synthesized using 4-Iodo anisole (234 mg, 1 mmol) and Adamantane-1-thiol (200 mg,1.2 mmol,1.2 equiv.). Purification by FC (SiO_2 :230 - 400 mesh, pure hexane) afforded **1** (255 mg, 93%) as white solid. Conforms to reported analytical data.[1]

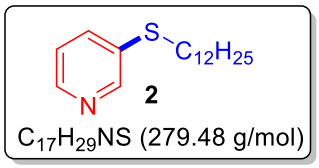


Rf: 0.30 (pure hexane)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.75 (s, 3H), 1.93 (s, 3H), 1.71 (d, *J* = 2.1 Hz, 6H), 1.56 (s, 2H), 1.53 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.13, 138.97, 121.38, 113.80, 55.26, 47.42, 43.44, 36.18, 29.93. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2911, 2857, 1597, 1496, 1246, 1038, 832, 533.

3-(Dodecylthio) pyridine (2)

Following **RC-1, 2** was synthesized using 3-iodopyridine (204 mg, 1 mmol) and dodecane thiol (288 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2 :230 - 400 mesh, n-hexane/ EtOAc 98:2) afforded **2** (245 mg, 88%) as yellow solid. Conforms to reported analytical data.[2]

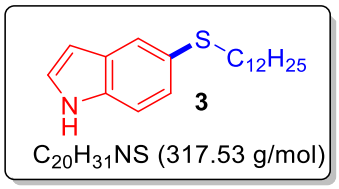


R_f: 0.40 (hexane/EtOAc = 95:5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.41 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.22 (dd, *J* = 7.8, 4.9 Hz, 1H), 2.98 – 2.86 (m, 2H), 1.64 (dt, *J* = 15.0, 7.4 Hz, 2H), 1.40 (dd, *J* = 14.1, 7.3 Hz, 2H), 1.27 (d, *J* = 17.3 Hz, 15H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.69, 146.58, 136.69, 132.13, 33.69, 31.89, 29.52, 29.09, 28.65, 22.66, 22.01, 14.09. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2931, 2861, 1469, 1263, 1019, 797, 707.

5-(Dodecylthio)-1H-indole (3)

Following **RC-1, 3** was synthesized using 5-iodo-1*H*-indole (244 mg, 1 mmol) and Dodecanethiol(288 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 98:2) afforded **3** (301 mg, 95%) as brown solid. Compared with the reported analytical data.



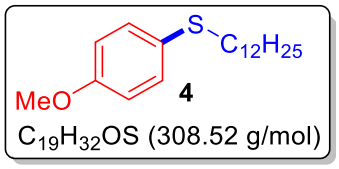
R_f: 0.48 (hexane/EtOAc 95:5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.39 – 6.90 (m, 3H), 6.42 (s, 1H), 2.80 (t, *J* = 7.4 Hz, 2H), 1.53 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.19 (d, *J* = 21.0 Hz, 18H), 0.80 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.94, 128.61, 126.26, 126.0, 124.89, 124.35, 111.49, 102.38,36.43, 31.95, 30.04.82, 22.73, 14.16. **ν_{max}** (CH_2Cl_2, cm^{-1}):3423, 2930, 2860, 1458, 1310, 1097, 723.

HRMS (ESI) Calcd for $C_{20}H_{32}NS$ $[M+H]^+$: 318.2255; found: 318.2256. Mp: 45 °C-46 °C, (new compound)

Dodecyl(4-methoxyphenyl)sulfane (4)

Following **RC-1, 4** was synthesized using 4-iodo anisole (234 mg, 1 mmol) and dodecanethiol (288 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, pure hexane) afforded **4** (293 mg, 95%) as white solid. Compared with the reported analytical data.[21]

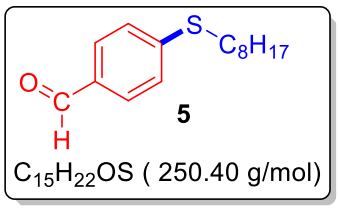


R_f: 0.40 (hexane/EtOAc = 99:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 3.72 (s, 3H), 2.74 (t, *J* = 7.3 Hz, 2H), 1.55 – 1.46 (m, 2H), 1.19 (s, 18H), 0.81 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.68, 132.86, 126.97, 114.45, 55.28, 35.80, 31.89, 29.72 – 29.06, 28.69, 22.66, 14.09. **ν_{max}** (CH_2Cl_2, cm^{-1}):2926, 2855, 1600, 1577, 1248, 1030, 816.

4-(Octylthio)benzaldehyde (5)

Following **RC-1, 5** was synthesized using 4-iodo benzaldehyde (232 mg, 1 mmol) and octanethiol (208 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 99:1) afforded **5** (237 mg, 95%) as yellow liquid. Conforms to reported analytical data.[21]

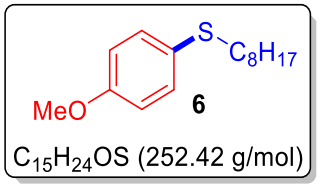


R_f: 0.50, hexane/EtOAc = 49:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 2.96 – 2.89 (m, 2H), 1.65 (dd, *J* = 14.9, 7.3 Hz, 2H), 1.43 – 1.34 (m, 2H), 1.21 (dt, *J* = 11.4, 7.8 Hz, 7H), 0.81 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.18, 147.14, 133.04, 130.18, 129.96, 126.23, 124.63, 57.03, 31.70, 29.65, 28.97, 28.59, 22.55, 21.93, 14.01. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2935, 2862, 1702, 1595, 1090, 813.

(4-Methoxyphenyl)(octyl)sulfane (6)

Following **RC-1, 6** was synthesized using 4-iodo anisole (234 mg, 1 mmol) and octanethiol (208 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, pure hexane) afforded **6** (226 mg, 90%) as yellow liquid. Conforms to reported analytical data.[22]

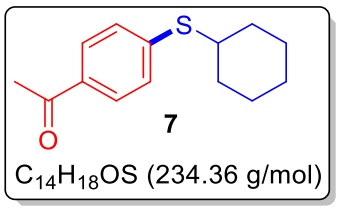


Rf: 0.50 (hexane/EtOAc 99:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 3.73 (s, 3H), 2.74 (t, *J* = 7.4 Hz, 2H), 1.50 (dd, *J* = 14.9, 7.6 Hz, 2H), 1.19 (s, 10H), 0.80 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.69, 132.88, 126.97, 114.47, 55.31, 35.82, 31.78, 29.51, 29.14, 28.69, 22.62, 14.07. **ν_{max}** (CH_2Cl_2, cm^{-1}):2933, 2861, 1598, 1497, 1246, 1035, 799.

1-(4-(Cyclohexylthio)phenyl)ethenone (7)

Following **RC-1, 7** was synthesized using 4-bromo acetophenone (199 mg, 1 mmol) and cyclohexanethiol (148 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 99:1) afforded **7** (200 mg, 85%) as white solid. Conforms to reported analytical data.[14]

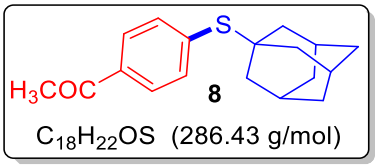


Rf: 0.40 (hexane/EtOAc = 49:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 8H), 7.28 (d, *J* = 7.8 Hz, 8H), 3.23 (t, *J* = 9.6 Hz, 4H), 2.49 (s, 12H), 1.97 (d, *J* = 10.8 Hz, 8H), 1.73 (d, *J* = 8.9 Hz, 9H), 1.62 – 1.55 (m, 5H), 1.42 – 1.25 (m, 19H), 1.18 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.22, 143.54, 134.15, 128.65, 128.34, 44.92, 33.04, 26.41, 25.89, 25.64. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2937, 2861, 1683, 1593, 1264, 1099, 818.

1-(4-((3s,5s,7s)-Adamantan-1-ylthio)phenyl)ethenone (8)

Following **RC-1, 8** was synthesized using 4-iodo acetophenone (248 mg, 1 mmol) and adamantane-1-thiol (200 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 49:1) afforded **8** (251 mg, 88%) as white solid. Compared with the reported analytical data.[23]

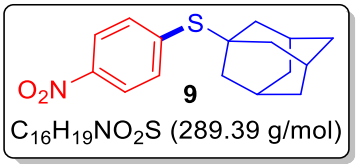


Rf: 0.40 (hexane/EtOAc = 95:5)

^{1}H NMR (400 MHz, CDCl3) δ 7.81 – 7.78 (m, 2H), 7.63 (d, *J* = 7.7 Hz, 2H), 2.55 (d, *J* = 0.6 Hz, 3H), 2.00 (s, 3H), 1.81 (s, 6H), 1.60 (dd, *J* = 24.0, 11.9 Hz, 6H). **^{13}C NMR** (100 MHz, CDCl3) δ 134.94, 128.61, 126.26, 126.05, 124.89, 124.35, 111.49, 102.38, 36.43, 31.95, 30.04 – 29.06, 28.82, 22.73, 14.16. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2912, 1687, 1586, 1455, 1263, 1008, 817, 589.

(3s,5s,7s)-Adamantan-1-yl(4-nitrophenyl)sulfane (9)

Following **RC-1, 9** was synthesized using 4-Bromo nitrobenzene (202 mg, 1 mmol) and Adamantane-1-thiol (200 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 49:1) afforded **9** (251 mg, 87%) as yellow solid. Conforms to reported analytical data.[1]

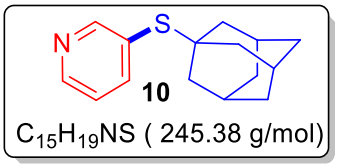


Rf: 0.50 (hexane/EtOAc = 95:5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 4H), 7.57 (d, *J* = 8.5 Hz, 4H), 1.97 (s, 6H), 1.78 (s, 12H), 1.57 (q, *J* = 12.3 Hz, 13H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.80, 140.23, 137.42, 123.11, 49.89, 43.75, 35.96, 30.01. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2918, 1527, 1347, 1268, 1040, 734.

3-((3s,5s,7s)-Adamantan-1-ylthio)pyridine (10)

Following **RC-1, 10** was synthesized using 3-iodo pyridine (204 mg, 1 mmol) and adamantane-1-thiol (200 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 49:1) afforded **10** (220 mg, 90%) as white solid. Compared with the reported analytical data.[32]



Rf: 0.50 (hexane/EtOAc = 95:5)

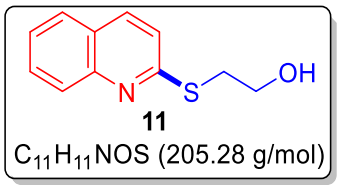
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.55 (d, *J* = 3.8 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 9.0 Hz, 1H), 2.00 (s, 3H), 1.77 (s, 6H), 1.60 (q, *J* = 12.3 Hz, 6H). **^{13}C NMR** (100

MHz, $CDCl_3$) δ 156.86, 149.31, 144.85, 123.28, 48.46, 43.52, 35.99, 29.92. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2911, 2857, 1571, 1456, 1405, 1302, 1021, 709.

2-(Quinolin-2-ylthio)ethanol (11)

Following **RC-1, 11** was synthesized using 2-bromoquinoline (208 mg, 1 mmol) and 2-mercaptoethanol (84 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 49:1) afforded **11** (112 mg, 55%) as yellow solid (new compound).

Mp: 73 °C



11

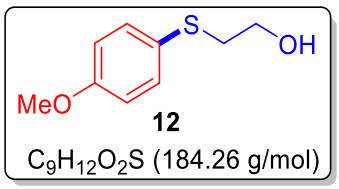
$C_{11}H_{11}NOS$ (205.28 g/mol)

R_f: 0.48 (hexane/EtOAc 95:5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 4.74 (t, *J* = 6.5 Hz, 2H), 3.16 (t, *J* = 6.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.49, 145.22, 138.00, 128.58, 126.40, 126.16, 124.12, 123.16, 112.02, 63.04, 36.96. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2931, 1609, 1431, 1260, 1242, 1007, 821, 756.

2-((4-Methoxyphenyl)thio)ethanol (12)

Following **RC-1, 12** was synthesized using 4-iodo anisole (234 mg, 1 mmol) and 2-mercaptoethanol (84 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2 :230 - 400 mesh, hexane/EtOAc = 9:1) afforded **12** (174 mg, 95%) as colourless liquid. Conforms to reported analytical data.[24]



12

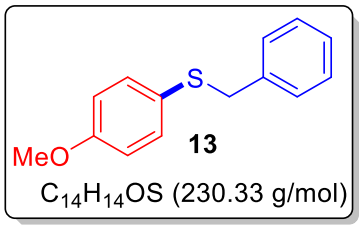
$C_9H_{12}O_2S$ (184.26 g/mol)

R_f: 0.40 (hexane/EtOAc = 85:15)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 3.72 (s, 3H), 3.60 (t, *J* = 5.9 Hz, 2H), 2.92 (t, *J* = 5.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.30, 133.98, 114.94, 114.68, 60.01, 55.30, 39.21, 29.63. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2935, 1597, 1497, 1287, 1245, 1031, 826, 736.

Benzyl(4-methoxyphenyl)sulfane (13)

Following **RC-1, 13** was synthesized using 4-iodoanisole (234 mg, 1 mmol) and benzyl mercaptan (140 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, pure hexane) afforded **13** (202 mg, 88%) as white solid. Compared with the reported analytical data.[19]

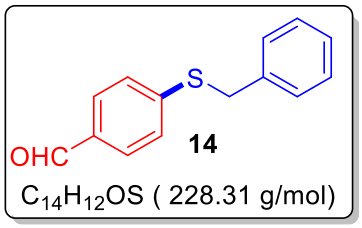


R_f: 0.48 (hexane/EtOAc = 99:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.07 (m, 7H), 6.71 (d, *J* = 8.3 Hz, 2H), 3.91 (s, 2H), 3.70 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.19, 138.10, 134.05, 128.86, 128.33, 126.95, 126.04, 114.40, 55.27, 41.21. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2933, 1595, 1496, 1246, 1030, 800, 698, 639.

4-(Benzylthio)benzaldehyde (14)

Following **RC-1, 14** was synthesized using 4-Iodo benzaldehyde (232 mg, 1 mmol) and Benzyl mercaptan (140 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 49:1) afforded **14** (209 mg, 92%) as white solid. Compared with the reported analytical data.[20]

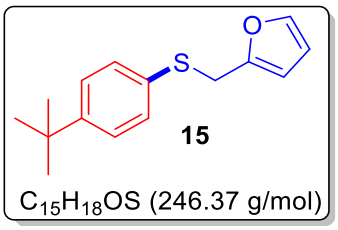


R_f: 0.40 (hexane/EtOAc 95:5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.16 (m, 7H), 4.16 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.21, 146.29, 135.92, 133.49, 129.99, 128.73, 127.61, 126.87, 36.96. **ν_{max}** (CH_2Cl_2, cm^{-1}): 1701, 1594, 1268, 1093, 734, 485.

2-(((4-(*tert*-Butyl)phenyl)thio)methyl)furan (15)

Following **RC-1, 15** was synthesized using 4-tert-Butyl iodobenzene (176 µL, 1 mmol) and 2-Furan methanethiol (120 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, pure hexane) afforded **15** (172 mg, 70%) as colourless liquid. Conforms to reported analytical data (new compound).

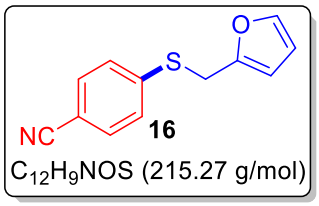


R_f: 0.48 (hexane)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.25 – 7.17 (m, 4H), 6.20 (s, 1H), 6.03 (d, *J* = 3.0 Hz, 1H), 4.00 (s, 2H), 1.22 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.27, 150.12, 142.06, 110.44, 107.74, 34.49, 32.02, 31.24, 29.68. **ν max** (CH_2Cl_2, cm^{-1}):2968, 1722, 1598, 1013, 825, 734, 550. **HRMS** (ESI) Calcd for $C_{15}H_{19}OS$ $[M+H]^+$: 247.1156; found: 247.1157.

4-((Furan-2-ylmethyl)thio)benzonitrile (16)

Following **RC-1, 16** was synthesized using 4-Bromobenzonitrile (180 mg, 1 mmol) and 2-Furanmethanethiol (120 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2 :230 - 400 mesh, hexane/EtOAc = 49:1) afforded **16** (180 mg, 84%) as dark brown solid. Compared with the reported analytical data. [25]

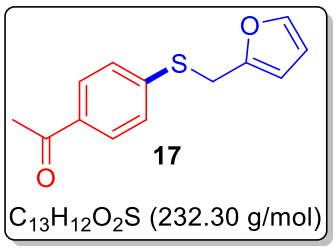


R_f: 0.39 (hexane/EtOAc = 95:5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 3H), 7.29 – 7.25 (m, 4H), 6.21 (s, 1H), 6.13 (d, *J* = 2.5 Hz, 1H), 4.11 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.55, 143.39, 142.42, 132.11, 127.77, 118.61, 110.55, 108.82, 108.29, 29.50. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2232, 1596, 1490, 1090, 1014, 820, 734, 544.

1-(4-((Furan-2-ylmethyl)thio)phenyl)ethenone (17)

Following **RC-1, 17** was synthesized using 4-Iodo acetophenone (200 mg, 1 mmol) and 2-Furanmethanethiol (120 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 24:1) afforded **17** (208 mg, 90%) as yellow solid. Compared with the reported analytical data.



R_f: 0.50 (hexane/EtOAc 95:5)

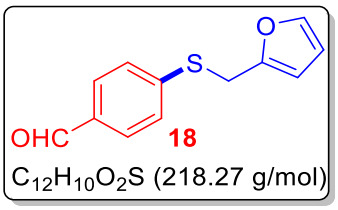
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.25 (m, 3H), 6.28 – 5.99 (m, 2H), 4.13 (s, 2H), 2.49 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.16, 150.10, 143.13, 142.37, 134.50, 128.72, 127.54, 110.58, 108.17, 29.77, 26.43. **ν_{max}** (CH_2Cl_2, cm^{-1}): 1673, 1590, 1249, 1193, 816, 742, 591. **HRMS** (ESI) Calcd for $C_{13}H_{13}O_2S$ $[M+H]^+$: 233.0636; found: 233.0634

Mp: 63 ºC-64 ºC (new compound).

4-((Furan-2-ylmethyl)thio)benzaldehyde (18)

Following **RC-1, 18** was synthesized using 4-Iodobenzaldehyde (232mg, 1 mmol) and 2-Furanmethanethiol (120 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc 98:2) afforded **18** (200 mg, 92%) as dark brown solid. Compared with the reported analytical data.

Mp: >250 ºC

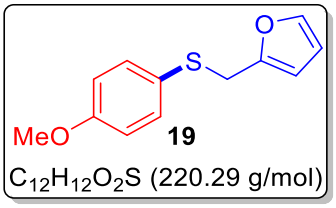


R_f: 0.40 (hexane/EtOAc = 19:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.26 (m, 3H), 6.27 – 6.11 (m, 2H), 4.15 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 191.19, 149.83, 145.20, 142.43, 133.73, 129.96, 127.41, 110.60, 108.27, 29.49. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2155, 2027, 1702, 1594, 1092, 813.

2-(((4-Methoxyphenyl)thio)methyl)furan (19)

Following **RC-1, 19** was synthesized using 4-Iodo anisole (234 mg, 1 mmol) and 2-Furanmethanethiol (120 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 99:1) afforded **19** (193 mg, 88%) as a liquid. Compared with the reported analytical data.[26]

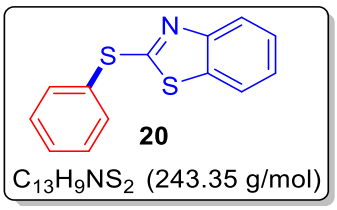


R_f: 0.40 (hexane/EtOAc 98:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 21.0, 13.1 Hz, 3H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.17 (s, 1H), 5.91 (s,1H), 3.89 (s, 2H), 3.71 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.43, 151.31, 142.0, 134.61, 125.42, 114.39, 110.33, 107.77, 55.24, 33.55. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2934, 1596, 1497, 1245, 1032, 735.

2-(Phenylthio)benzo[d]thiazole (20)

Following **RC-1, 20** was synthesized using iodobenzene (112 µL, 1 mmol) and 2-mercaptobenzothiazole (200 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 49:1) afforded **20** (170 mg, 70%) as a white solid. Compared with the reported analytical data.[13]

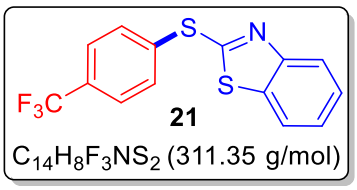


R_f: 0.5 (hexane/EtOAc = 19:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.4 Hz, 1H), 7.63 (dd, *J* = 35.8, 6.2 Hz, 3H), 7.49 – 7.29 (m, 4H), 7.19 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.37, 130.47, 129.93, 126.17, 124.33, 121.96, 120.78. **ν_{max}** (CH_2Cl_2, cm^{-1}):2931, 1713, 1460, 1428, 996, 754.

2-((4-(Trifluoromethyl)phenyl)thio)benzo[d]thiazole (21)

Following **RC-1, 21** was synthesized using 4-iodobenzotrifluoride (148 µL, 1 mmol) and 2-mercaptobenzothiazole (200 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 49:1) afforded **21** (217 mg, 70%) as a white solid. Compared with the reported analytical data.[10]

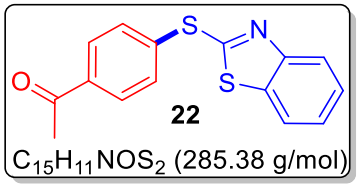


R_f: 0.5 (hexane/EtOAc = 19:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.64 (dd, *J* = 11.7, 8.2 Hz, 3H), 7.41 – 7.35 (m, 1H), 7.29 – 7.24 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.75, 153.57, 135.84, 135.29, 134.11, 131.11 (q, *J* = 33 Hz), 126.57 (q, *J* = 3.9 Hz), 126.44, 125.00, 122.42, 120.99. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.87(s). **ν_{max}** (CH_2Cl_2, cm^{-1}): 1611, 1326, 1167, 1121, 1096, 825, 737.

1-(4-(Benzo[d]thiazol-2-ylthio)phenyl)ethenone (22)

Following **RC-1, 22** was synthesized using 4-Iodoacetophenone (248 mg, 1 mmol) and 2-Mercaptobenzothiazole (200 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 19:1) afforded **22** (205 mg, 72%) as pale yellow solid. Compared with the reported analytical data.[15]

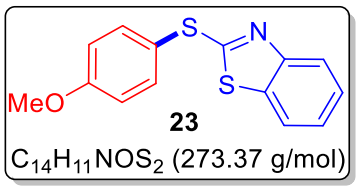


Rf: 0.48 (hexane/EtOAc = 9:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 2.62 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.96, 165.73, 153.48, 137.56, 136.49, 135.79, 133.54, 129.31, 126.34, 124.90, 122.31, 120.91, 26.61. **ν_{max}** (CH_2Cl_2, cm^{-1}): 1688, 1594, 1429, 959, 728, 590.

2-((4-Methoxyphenyl)thio)benzo[d]thiazole (23)

Following **RC-1, 23** was synthesized using 4-iodo anisole (234 mg, 0.25 mmol) and 2-mercaptobenzothiazole (200 mg, 0.30 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 49:1) afforded **23** (204 mg, 75%) as white solid. Compared with the reported analytical data.[16]

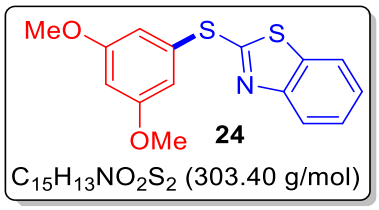


Rf: 0.48 (hexane/EtOAc 95:5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.65 (dd, *J* = 12.9, 8.0 Hz, 3H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 2H), 3.88 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.72, 154.16, 137.59, 135.40, 126.09, 124.07, 121.76, 120.73, 120.22, 115.51, 55.47. **ν_{max}** (CH_2Cl_2, cm^{-1}):2932, 1742, 1595, 1429, 1254, 1006, 800, 728.

2-((3,5-Dimethoxyphenyl)thio)benzo[d]thiazole (24)

Following **RC-1, 24** was synthesized using 1-iodo-3,5-dimethoxybenzene (264 mg, 1 mmol) and 2-mercaptobenzothiazole (200 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 49:1) afforded **24** (227 mg, 75%) as a yellow liquid (new compound).

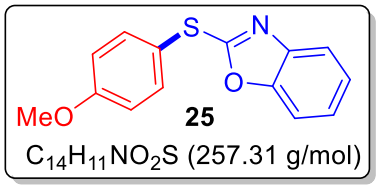


R_f: 0.48 (hexane/EtOAc 95:5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.34 – 7.28 (m, 1H), 7.21 – 7.14 (m, 1H), 6.79 (d, *J* = 2.2 Hz, 2H), 6.48 (t, *J* = 2.2 Hz, 1H), 3.71 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.16, 161.32, 153.75, 135.55, 131.19, 126.10, 124.34, 121.91, 120.77, 112.54, 102.87, 55.54. **ν $_{max}$** (CH_2Cl_2, cm^{-1}):1585, 1495, 1426, 1158, 730. **HRMS** (ESI) Calcd for $C_{15}H_{14}NO_2S_2$ $[M+H]^+$: 304.0466; found: 304.0484.

2-((4-Methoxyphenyl)thio)benzo[d]oxazole (25)

Following **RC-1, 25** was synthesized using 4-iodoanisole (234 mg, 1 mmol) and 2-mercaptobenzoxazole (184 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2 :230 - 400 mesh, hexane/EtOAc 98:2) afforded **25** (154 mg, 60%) as a yellow liquid. Compared with the reported analytical data.[14]



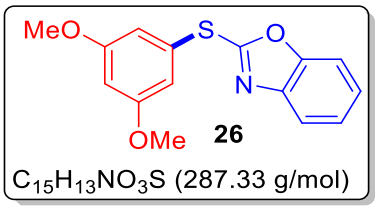
R_f: 0.48 (hexane/EtOAc = 19:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.53 – 7.49 (m, 1H), 7.35 – 7.31 (m, 1H), 7.19 (d, *J* = 1.7 Hz, 1H), 7.17 (dd, *J* = 2.1, 1.5 Hz, 1H), 6.94 – 6.89 (m, 2H), 3.79 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.21, 151.88, 136.75, 124.28, 124.04, 118.94, 115.30, 109.95, 55.42.

2-((3,5-Dimethoxyphenyl)thio)benzo[d]oxazole (26)

Following **RC-1, 26** was synthesized using 1-iodo-3,5-dimethoxybenzene (264 mg, 0.25 mmol) and 2-mercaptobenzoxazole (184 mg, 0.30 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 49:1) afforded **26** (258 mg, 90%) as a white solid (new compound).

Mp: 85 ºC-86 ºC.

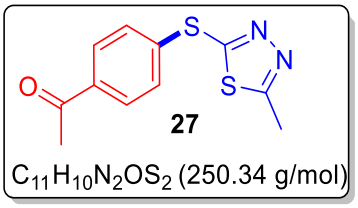


Rf: 0.48 (hexane/EtOAc 95:5)

^{1}H NMR (400 MHz, CDCl3) δ 7.58 – 7.51 (m, 1H), 7.39 – 7.31 (m, 1H), 7.21 – 7.15 (m, 2H), 6.76 (d, *J* = 2.3 Hz, 2H), 6.45 (t, *J* = 2.2 Hz, 1H), 3.72 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.43, 137.30,132.68, 114.89, 114.62, 77.34, 77.03, 76.71, 55.40. **ν max** (CH_2Cl_2, cm^{-1}):2933, 1601, 1455, 1156, 1128, 806, 741. **HRMS** (ESI) Calcd for $C_{15}H_{14}NO_3S$ $[M+H]^+$: 288.0695; found: 288.0705.

1-(4-((5-Methyl-1,3,4-thiadiazol-2-yl)thio)phenyl)ethenone (27)

Following **RC-1, 27** was synthesized using 4-Iodo acetophenone (246 mg, 1 mmol) and 5-methyl-1,3,4-thiadiazole-2-thiol (160 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 85:15) afforded **27** (212 mg, 85%) as yellow solid. Compared with the reported analytical data.[17]

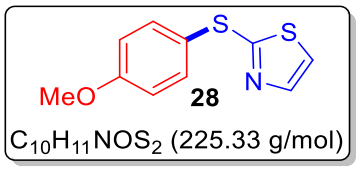


Rf: 0.50 (hexane/EtOAc 80:20)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 2.67 (s, 3H), 2.53 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.94, 167.68, 163.86, 137.65, 137.14, 131.78, 129.36, 26.61, 15.81. **ν max** (CH_2Cl_2, cm^{-1}):2933, 1742, 1595, 1431, 1261, 1196, 836, 626. **HRMS** (ESI) Calcd for $C_{16}H_{16}NO_4S$ $[M+H]^+$: 251.03129; found: 251.0326.

2-((4-Methoxyphenyl)thio)-4,5-dihydrothiazole (28)

Following **RC-1, 28** was synthesized using 4-iodoanisole (234 mg, 1 mmol) and 4,5-dihydrothiazole-2-thiol (144 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 99:1) afforded **28** (135 mg, 60%) as yellow liquid. Compared with the reported analytical data.[18]

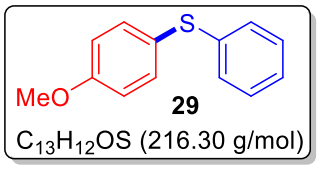


Rf: 0.50 (hexane/EtOAc 98:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.2 Hz, 2H), 6.92 (d, *J* = 7.3 Hz, 2H), 4.28 (t, *J* = 7.4 Hz, 2H), 3.83 (s, 3H), 3.29 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.86, 161.07, 151.84, 141.92, 128.50, 124.38, 119.12, 111.86, 110.07, 102.34, 55.51. **ν_{max}** (CH_2Cl_2, cm^{-1}):2935, 1687, 1594, 1495, 1248, 1175, 1029, 826. **HRMS** (ESI) Calcd for $C_{16}H_{16}NO_4S$ $[M+H]^+$: 226.0360; found: 226.0371.

(4-Methoxyphenyl)(phenyl)sulfane (29)

Following **RC-2, 29** was synthesized using 4-methoxy iodobenzene (234 mg, 1 mmol) and thiophenol (124 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2 :230 - 400 mesh, n-hexane/ EtOAc 99:1) afforded **29** (205 mg, 95%) as colorless oil. Compared with the reported analytical data.[3]

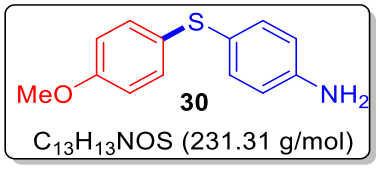


Rf: 0.3 (pure hexane)

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 2H), 7.26 (dt, *J* = 9.1, 1.7 Hz, 2H), 7.21 – 7.14 (m, 3H), 6.95 – 6.91 (m, 2H), 3.85 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.82, 135.34, 128.91, 128.21, 125.75, 114.97, 55.36. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2932, 1743, 1596, 1482, 1248, 1030, 829, 740.

4-((4-Methoxyphenyl)thio)aniline (30)

Following **RC-2, 30** was synthesized using 4-methoxy iodobenzene (234 mg, 1 mmol) and 4-amino thiophenol (148 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, *n*-hexane/ EtOAc = 88:12) afforded **30** (203 mg, 88%) as brown solid. Compared with the reported analytical data.[4]

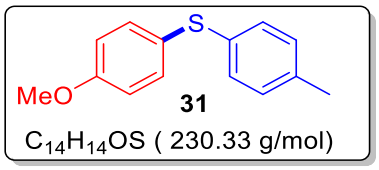


Rf: 0.48 (hexane/EtOAc = 85:15)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.20 (m, 4H), 6.81 (d, *J* = 7.5 Hz, 2H), 6.63 (d, *J* = 7.5 Hz, 2H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158, 146.06, 133.90, 131.43, 128.75, 123.53, 115.77, 114.58, 55.30. **ν_{max}** (CH_2Cl_2, cm^{-1}): 3379, 2935, 1624, 1596, 1493, 1242, 1175, 1028, 821, 507.

(4-Methoxyphenyl)(*p*-tolyl)sulfane (31)

Following **RC-2, 31** was synthesized using 4-methoxy iodobenzene (234 mg, 1 mmol) and 4-methyl thiophenol (149 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 225-400 mesh, pure hexane) afforded **31** (207 mg, 90%) as yellow liquid. Compared with the reported analytical data.[3]

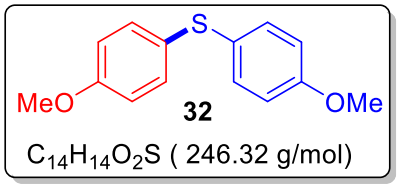


R_f: 0.5 (hexane/EtOAc 99:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 1H), 7.09 – 7.04 (m, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.82 – 6.77 (m, 1H), 3.74 (s, 3H), 2.23 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.12, 134.33, 129.75, 129.37, 114.85, 77.32, 77.00, 76.68, 55.35, 29.69. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2931, 2861, 1597, 1496, 1249, 1085, 803, 700.

Bis(4-methoxyphenyl)sulfane (32)

Following **RC-2, 32** was synthesized using 4-methoxy iodobenzene (234 mg, 1 mmol) and 4-mMethoxy thiophenol (148 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2 :230 - 400 mesh, *n*-hexane/ EtOAc = 49:1) afforded **32** (197 mg, 80%) as yellow liquid. Compared with the reported analytical data.[5]

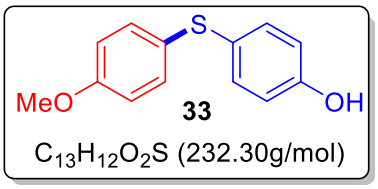


R_f: 0.6 (hexane/EtOAc 95:5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 2H), 7.30 (s, 2H), 6.75 (s, 2H), 6.73 (s, 2H), 3.70 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.94 (s), 159.00, 132.85 – 132.58, 128.45,127.45, 114.71, 77.38, 77.06, 76.75, 55.37. **ν_{max}** (CH_2Cl_2, cm^{-1}): 1594, 1494, 1245, 1174, 1032, 826, 734.

4-((4-Methoxyphenyl)thio)phenol (33)

Following **RC-2, 33** was synthesized using 4-Iodo anisole (234 mg, 1 mmol) and 4-mercaptophenol (152 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 9:1) afforded **33** (208 mg, 90%) as white solid. Compared with the reported analytical data.[30]

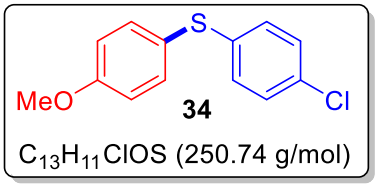


Rf: 0.48 (hexane/EtOAc 85:15)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 6.75 (d, *J* = 8.1 Hz, 2H), 6.67 (d, *J* = 7.8 Hz, 2H), 3.69 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.92, 155.02, 132.89, 127.47, 116.33, 114.88, 55.47. **ν_{max}** (CH_2Cl_2, cm^{-1}): 1595, 1495, 1267, 1172, 826, 734.

(4-Chlorophenyl)(4-methoxyphenyl)sulfane (34)

Following **RC-2, 34** was synthesized using 4-Iodoanisole (234 mg, 1 mmol) and 4-Chloro thiophenol (172 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, pure hexane) afforded **34** (225 mg, 90%) as white solid. Compared with the reported analytical data.[3]

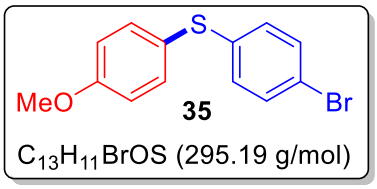


Rf: 0.6 (hexane/EtOAc 99:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.04, 137.35, 135.48, 131.58, 129.29, 128.98, 123.74, 115.11, 55.35. **ν_{max}** (CH_2Cl_2, cm^{-1}): 3423, 2930, 2860, 1458, 1310, 1097, 723.

(4-Bromophenyl)(4-methoxyphenyl)sulfane (35)

Following **RC-2, 35** was synthesized using 4-iodoanisole (234 mg, 1 mmol) and 4-bromo thiophenol (228 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, pure hexane) afforded **35** (259 mg, 88%) as white solid. Compared with the reported analytical data.[3]

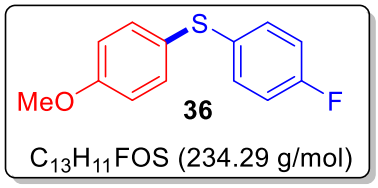


R_f: 0.3 (pure hexane)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.55 (, 3H), 7.51 (s, 1H), 7.41 – 7.28 (m, 4H), 7.20 (d, *J* = 8.6 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.73 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.09, 138.14, 135.60, 131.86, 129.42, 123.46, 119.34, 115.12, 55.34. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2934, 1595, 1576, 1290, 1032, 807, 495.

(4-Fluorophenyl)(4-methoxyphenyl)sulfane (36)

Following **RC-2, 36** was synthesized using 4-Iodoanisole (234 mg, 1 mmol) and 4-Fluoro thiophenol (128 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, pure hexane) afforded **36** (222 mg, 95%) as pale-yellow liquid. Compared with the reported analytical data.[3]

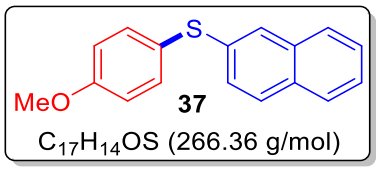


R_f: 0.3 (pure hexane)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.20 (dd, *J* = 7.2, 5.3 Hz, 2H), 6.96 (t, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 7.5 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.85, 159.66, 134.46, 133.11, 131.08, 125.29, 116.03 (d, $J_{(C-F)}$ = 22.7 Hz), 114.97, 55.34. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -116.13 (s). **ν_{max}** (CH_2Cl_2, cm^{-1}): 2935, 1593, 1491, 1247, 1032, 824, 532.

(4-Methoxyphenyl)(naphthalen-2-yl)sulfane (37)

Following **RC-2, 37** was synthesized using 4-iodoanisole (234 mg, 1 mmol) and 2-napthalenethiol (192 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, pure hexane) afforded **37** (210 mg, 79%) as yellow solid. Compared with the reported analytical data.[3]

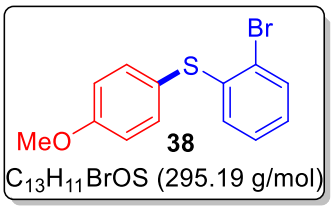


R_f: 0.48 (hexane/EtOAc 99:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.55 (m, 3H), 7.51 (s, 1H), 7.41 – 7.28 (m, 4H), 7.20 (d, *J* = 8.6 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.73 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.81, 135.18, 133.72, 131.68, 128.50, 127.10, 126.67, 126.40, 125.58, 124.36, 115.01, 55.31. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2969, 1595, 1496, 1247, 1031, 811, 744, 472.

(2-Bromophenyl)(4-methoxyphenyl)sulfane (38)

Following **RC-2, 38** was synthesized using 4-Iodoanisole (234 mg, 1 mmol) and 2-Bromo thiophenol (144 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, pure hexane) afforded **38** (236 mg, 80%) as white solid. Compared with the reported analytical data.[9]

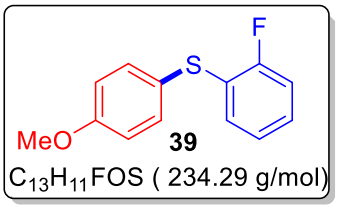


R_f: 0.6 (hexane/EtOAc 99:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 13.5, 8.0 Hz, 3H), 7.01 (t, J = 7.6 Hz, 1H), 6.87 (t, J = 7.5 Hz, 3H), 6.60 (d, J = 8.0 Hz, 1H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.57, 140.83, 136.95, 132.67, 127.59, 127.37, 126.12, 122.01, 120.69, 115.37, 55.36. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2933, 1594, 1576, 1496, 1249, 1020, 800, 711, 502.

(2-Fluorophenyl)(4-methoxyphenyl)sulfane (39)

Following **RC-2, 39** was synthesized using 4-Iodoanisole (234 mg, 1 mmol) and 2-Fluoro thiophenol (128 µL1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, pure hexane) afforded **39** (222 mg, 95%) as white solid. Compared with the reported analytical data.[8]

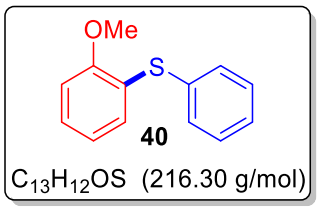


R_f: 0.5 (hexane/EtOAc 99:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.19 – 7.11 (m, 1H), 7.01 (ddt, J = 9.5, 7.8, 6.9 Hz, 3H), 6.95 – 6.87 (m, 2H), 3.82 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.04, 160.06, 158.60, 135.50, 130.50, 127.7 (d, $J_{(C-F)}$ = 7.5 Hz), 125.72 (d, $J_{(C-F)}$ = 17.1 Hz), 124.52 (d, $J_{(C-F)}$ = 3.6 Hz), 122.63, 115.51 (d, $J_{(C-F)}$ = 21.7 Hz), 115.12, 55.38. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -111.04 (s). **ν_{max}** (CH_2Cl_2, cm^{-1}): 1597, 1497, 1248, 1032, 829, 751.

(2-Methoxyphenyl)(phenyl)sulfane (40)

Following **RC-2, 40** was synthesized using 2-iodoanisole (132 µL, 1 mmol) and Thiophenol (124 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 99:1) afforded **40** (205 mg, 95%) as yellow liquid. Compared with the reported analytical data.[6]

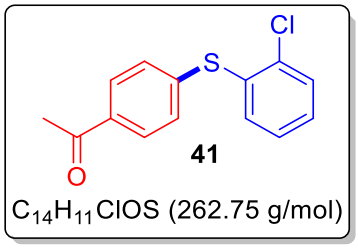


Rf: 0.4 (hexane/EtOAc 99:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.1 Hz, 2H), 7.17 – 7.11 (m, 2H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.78 (dd, *J* = 16.3, 8.1 Hz, 2H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.29, 134.47,131.59,131.43, 129.10, 128.31, 127.02, 124.04, 121.21, 110.84, 55.85. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2971, 1582, 1479, 1263, 1024, 797, 742.

1-(4-((2-Chlorophenyl)thio)phenyl)ethenone (41)

Following **RC-2, 41** was synthesized using 4-iodo acetophenone (246 mg, 1 mmol) and 2-chloro thiophenol (172 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 99:1) afforded **41** (235 mg, 90%) as white solid. Compared with the reported analytical data.[11]

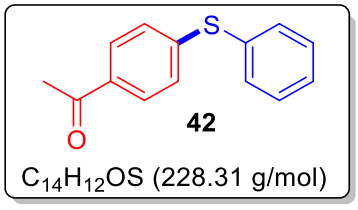


Rf: 0.48 (hexane/EtOAc 98:2)

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.78 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.13 (m, 4H), 2.48 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.04, 141.96, 136.94, 135.13, 134.49, 132.10, 130.36, 129.69, 129.02, 128.74, 127.60, 26.44.

1-(4-(Phenylthio)phenyl)ethenone (42)

Following **RC-2, 42** was synthesized using 4-iodoacetophenone (246 mg, 1 mmol) and thiophenol (124 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 49:1) afforded **42** (193 mg, 85%) as pale yellow solid. Compared with the reported analytical data.[13]

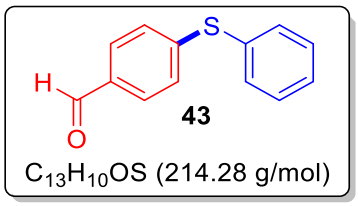


R_f: 0.48 (hexane/EtOAc = 19:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.2 Hz, 2H), 7.54 – 7.35 (m, 5H), 7.21 (d, *J* = 7.2 Hz, 2H), 2.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.09, 144.87, 134.45, 133.83, 132.06, 129.64, 128.80, 127.44, 26.42.**ν_{max}** (CH_2Cl_2, cm^{-1}): 1682, 1593, 1360, 1263, 1088, 820, 691, 590.

4-(Phenylthio)benzaldehyde (43)

Following **RC-2, 43** was synthesized using 4-iodobenzaldehyde (232 mg, 1 mmol) and thiophenol (124 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 99:1) afforded **43** (192 mg, 90%) as white solid. Compared with the reported analytical data.[12]

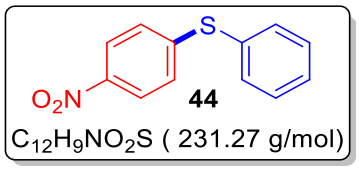


R_f: 0.4 (hexane/EtOAc 98:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.67 – 7.61 (m, 2H), 7.48 – 7.42 (m, 2H), 7.35 (dd, *J* = 6.4, 2.7 Hz, 3H), 7.17 (dd, *J* = 7.3, 5.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.12, 147.18, 134.31, 133.67, 131.26, 130.08, 129.76, 129.12, 127.18. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2933, 2800, 1699, 1594, 1479, 1213, 1170, 1026, 836, 692, 507.

(4-Nitrophenyl)(phenyl)sulfane (44)

Following **RC-2, 44** was synthesized using 4-iodo-4-nitrobenzene (248 mg, 1 mmol) and Thiophenol (124 µL, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, pure hexane) afforded **44** (212 mg, 92%) as yellow liquid. Compared with the reported analytical data.[14]

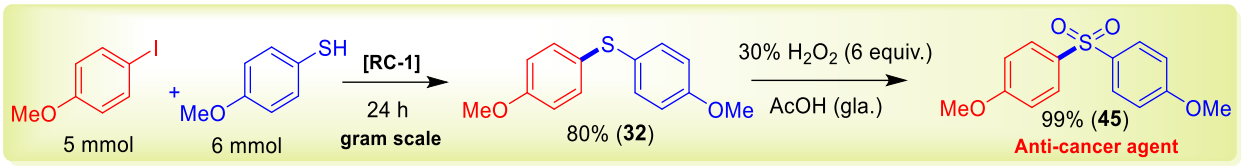


R_f: 0.40 (hexane/EtOAc 99:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.61 – 7.41 (m, 5H), 7.18 (d, *J* = 7.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.71, 130.00, 129.63, 126.66, 124.00. **ν_{max}** (CH_2Cl_2, cm^{-1}): 1580, 1338, 1267, 1085, 737.

9: Application of Methodology for the Synthesis of Important Thioether Derivatives

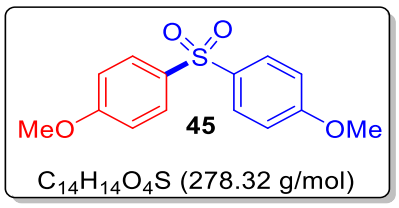
Gram-Scale Synthesis of Anti-Cancer Molecule (45):



Step 1: Following **RC-1**, **32** was synthesized in 1 g scale by using 4-iodoanisole (1.17 g, 5 mmol) and 4-methoxy thiophenol (740 µL, 6 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, n-hexane/ EtOAc = 49:1) afforded **32** (984 mg, 80%) as a yellow liquid.

Step 2: Synthesis of 4,4'-sulfonylbis(methoxybenzene) (45)

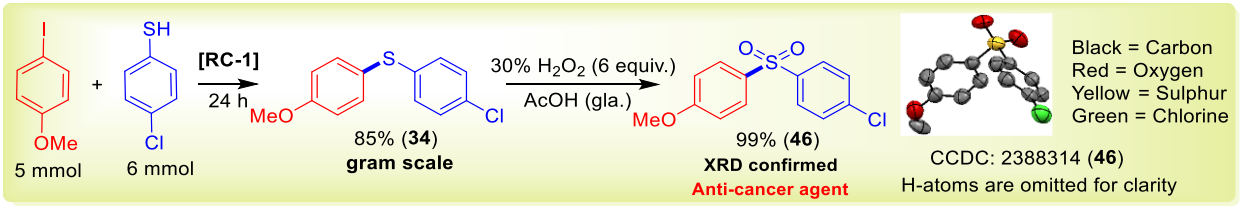
Following **RC-3** [28], **45** was synthesized using **32** (1.23 g, 5 mmol) and 30% H_2O_2 solution (6 equiv.; 1.12 mL). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 9:1) afforded **45** (1.37 g, 99%) as white solid. Compared with the reported analytical data.[35]



R_f: 0.40 (hexane/EtOAc = 85:15)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.9 Hz, 3H), 6.88 (d, J = 8.9 Hz, 3H), 3.77 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.08, 129.50, 114.40, 55.60. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2931, 1735, 1598, 1500, 1260, 1150, 1108, 1024, 806, 684, 558. **HRMS** (ESI) Calcd for $C_{14}H_{15}O_4S$ $[M+H]^+$: 279.0691; found: 279.0691.

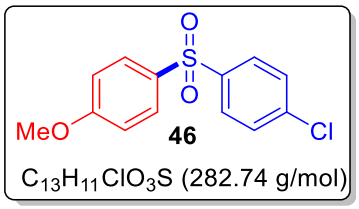
Gram-Scale Synthesis of Anti-Cancer Molecule (46):



Step 1: Following **RC-1, 34** was synthesized using 4-iodoanisole (1.17 g, 5 mmol) and 4-chloro thiophenol (860 mg, 6 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, pure hexane) afforded **34** (1.12 g, 90%) as white solid.

Step 2: Synthesis of 1-chloro-4-((4-methoxyphenyl)sulfonyl)benzene (46)

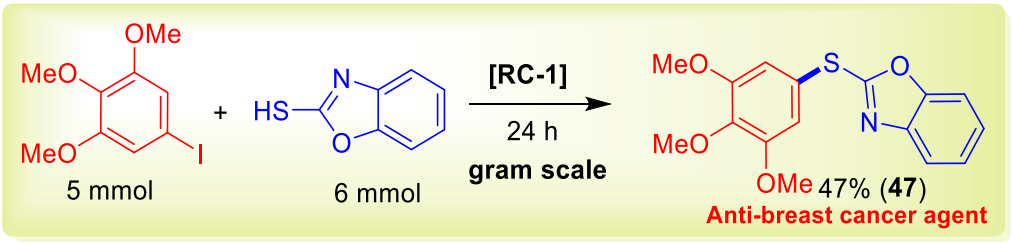
Following **RC-3** [28]**, 46** was synthesized using **34** (1.253 g, 5 mmol) and 30% H_2O_2 solution (6 equiv.; 1.12 mL). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 9:1) afforded **46** (1.39 g, 99%) as white solid. Compared with the reported analytical data.[36]



Rf: 0.50 (hexane/EtOAc 85:15)

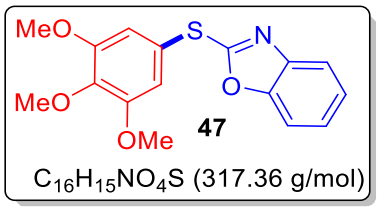
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.86 (t, *J* = 8.4 Hz, 4H), 7.46 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 163.54, 140.83, 139.42, 132.55, 129.84, 129.47, 128.73, 114.61, 55.64. **ν_{max}** (CH_2Cl_2, cm^{-1}): 1599, 1502, 1264, 1110, 1016, 706, 556. **HRMS** (ESI) Calcd for $C_{13}H_{12}ClO_3S$ $[M+H]^+$: 283.0196; found: 283.0201.

Gram-Scale Synthesis of Anti-Breast Cancer Agent (47):



2-((3,4,5-Trimethoxyphenyl)thio)benzo[d]oxazole (47)

Following **RC-1, 47** was synthesized using 5-iodo-1,2,3-trimethoxybenzene (1.48 g, 5 mmol) and 2-mercaptobenzoxazole (920 mg, 6 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 3:1) afforded **47** (744 mg, 47%) as white solid. Compared with the reported analytical data. [27]

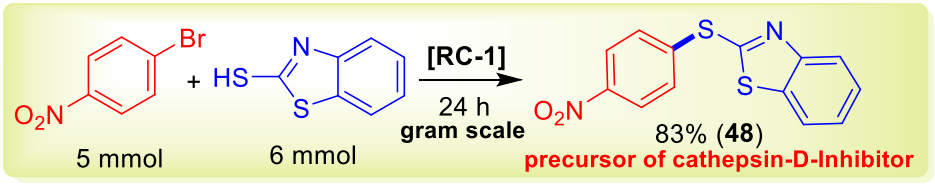


Rf: 0.40 (hexane/EtOAc 70:30)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 1H), 7.39 – 7.35 (m, 1H), 7.20 (d, *J* = 5.0 Hz, 2H), 6.87 (s, 2H), 3.83 (s, 3H), 3.81 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.46, 153.67, 151.87, 141.97, 139.69, 124.37, 121.04, 119.10, 111.96, 110.06, 60.89, 56.30. **ν_{max}** (CH_2Cl_2,

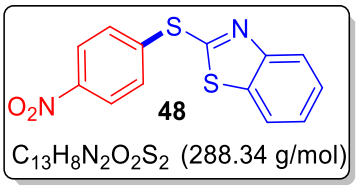
cm^{-1}): 2927, 1588, 1493, 1455, 1313, 1235, 1123, 751. **HRMS** (ESI) Calcd for $C_{16}H_{16}NO_4S$ $[M+H]^+$: 318.0800; found: 318.0814.

Gram-Scale Synthesis of Precursor of Cathepsin-D-Inhibitor (48):



2-((4-Nitrophenyl)thio)benzo[d]thiazole (48)

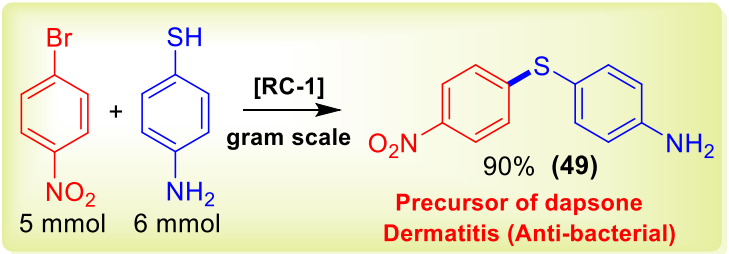
Following **RC-1, 48** was synthesized using 4-bromo nitrobenzene (1.01 g, 5 mmol) and 2-mercaptobenzothiazole (1.0 g, 6 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 19:1) afforded **48** (1.29 g, 90%) as yellow solid. Compared with the reported analytical data.[33]



R_f: 0.50 (hexane/EtOAc 90:10)

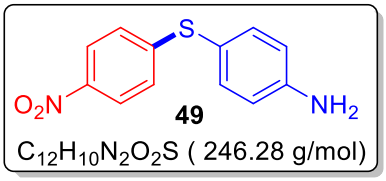
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.29 – 8.22 (m, 2H), 7.99 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.4 Hz, 3H), 7.51 (t, J = 7.7 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 162.74, 153.34, 147.83, 139.99, 136.14, 132.62, 126.62, 125.50, 124.44, 122.76, 121.13. **ν_{max}** (CH_2Cl_2, cm^{-1}): 1602, 1521, 1343, 1004, 845, 742, 479.

Gram Scale Synthesis of Precursor of Anti-Bacterial Agent Dapsone (49): -



4-((4-Nitrophenyl)thio)aniline (49)

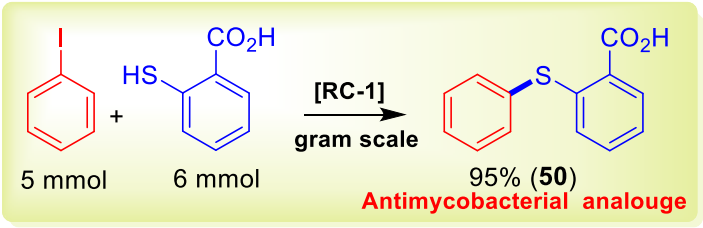
Following **RC-1, 49** was synthesized using 1-bromo-4-nitro benzene (1 g, 5 mmol) and 4-aminothiophenol (888 mg, 6 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 9:1) afforded **49** (1.1 g, 90%) as yellow solid. Compared with the reported analytical data.[34]



Rf: 0.50 (hexane/EtOAc 85:15)

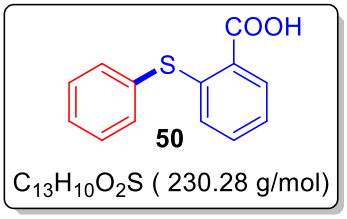
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.2 Hz, 2H), 3.88 (s, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 151.02, 148.32, 144.76, 137.20, 125.19, 123.85, 116.11. **ν_{max}** (CH_2Cl_2, cm^{-1}): 3387, 2926, 2858, 1622, 1578, 1495, 1335, 1121, 824, 515.

Gram-Scale Synthesis of Precursor of Anti-Mycobacterial Analogue (50):



2-(Phenylthio)benzoic acid (50)

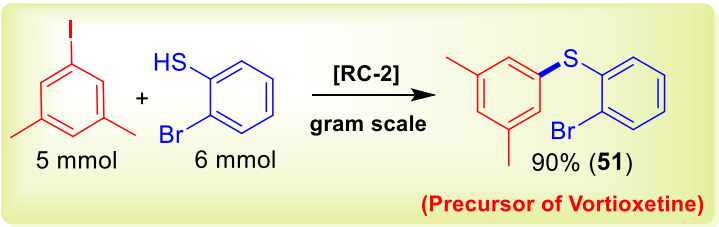
Following **RC-1, 50** was synthesized using iodobenzne(560 µL, 5 mmol) and 2-mercaptobenzoic acid (1.104 g, 6 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 4:1) afforded **50** (1.09 g, 95%) as white crystalline solid. Compared with the reported analytical data.[31]



Rf: 0.48 (hexane/EtOAc = 3:1)

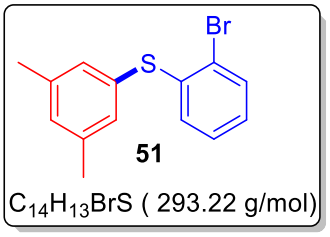
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 1H), 7.51 (dd, *J* = 6.3, 2.9 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.19 (dd, *J* = 13.2, 5.4 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.78, 144.64, 135.81, 133.15, 132.11, 129.80, 129.28, 127.18, 125.27, 124.25. **ν_{max}** (CH_2Cl_2, cm^{-1}): 2929, 1682, 1420, 1260, 746, 688.

Gram-Scale Synthesis of Precursor of Anti-Depressant Vortioxetine (51):



(2-Bromophenyl)(3,5-dimethyl phenyl) sulfane (51)

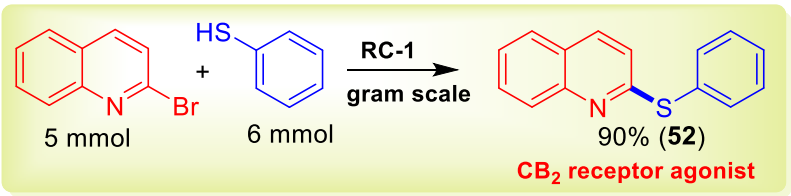
Following **RC-1, 51** was synthesized using 3,5-dimethyl iodobenzene (720 µL, 5 mmol) and 2-bromo thiophenol (720 µL, 0.30 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, pure hexane) afforded **51** (1.32 g, 90%) as colorless liquid. Compared with the reported analytical data.[10]



R_f: 0.6 (pure hexane)

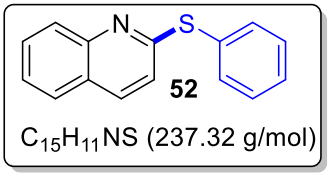
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.9 Hz, 1H), 7.09 – 7.02 (m, 3H), 6.98 – 6.90 (m, 2H), 6.81 (dd, J = 7.9, 1.2 Hz, 1H), 2.24 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.33, 132.78, 131.79, 131.45, 130.43, 129.14, 127.64, 126.73, 122.32, 21.11. **ν_{max}** (CH_2Cl_2, cm^{-1}): 1579, 1449, 1021, 849, 744. **HRMS** (ESI) Calcd for $C_{15}H_{12}NS$ $[M+H]^+$: 294.9921; found: 294.9947.

Synthesis of CB2 Receptor Agonist (52):



2-(Phenylthio)quinoline (52)

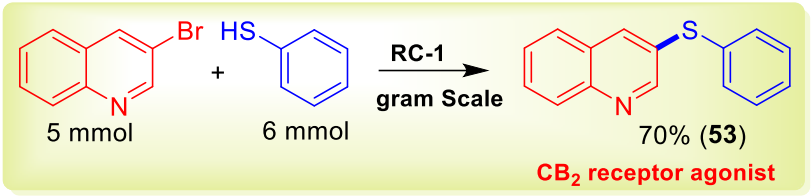
Following **RC-1, 52** was synthesized using 2-bromoquinoliene (1.04 g, 5 mmol) and thiophenol (620 µL, 6 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc 98:2) afforded **52** (1.06 g, 90%) as yellow liquid. Compared with the reported analytical data. [29]



R_f: 0.60 (hexane/EtOAc = 19:1)

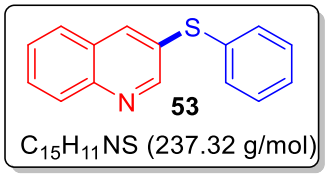
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 7.64 – 7.54 (m, 4H), 7.39 – 7.32 (m, 4H), 6.90 (d, J = 8.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.57, 147.96, 136.46, 135.10, 130.80, 130.01, 129.60, 129.20, 128.26, 127.52, 125.78, 119.49. **ν_{max}** (CH_2Cl_2, cm^{-1}): 1593, 1267, 1085, 734, 691. **HRMS** (ESI) Calcd for $C_{15}H_{12}NS$ $[M+H]^+$: 238.0690; found: 238.0705.

Synthesis of CB2 Receptor Agonist (53):



3-(Phenylthio)quinoline (53)

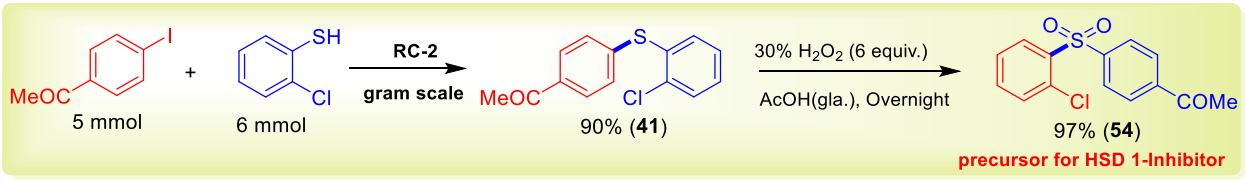
Following **GP-A, 53** was synthesized using 3-bromoquinoliene (700 µL, 5 mmol) and thiophenol (620 µL, 6 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc 98:2) afforded **53** (830 mg, 70%) as a yellow solid. Conforms to reported analytical data.[29]



Rf: 0.60 (hexane/EtOAc = 19:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 2.0 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.69 (t, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.37 – 7.27 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.05, 146.52, 137.07, 134.23, 131.34, 130.04, 129.54, 129.21, 128.18, 127.72, 127.24. ν_{max} (CH_2Cl_2, cm^{-1}): 3200, 1584, 1358, 866, 739, 691, 472.

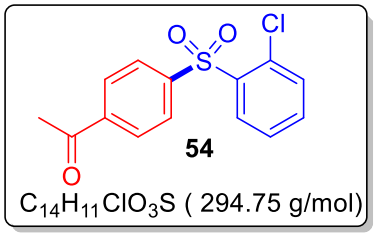
Synthesis of Precursor for HSD 1-Inhibitor (54):



Step:1 Following **RC-1, 41** was synthesized using 4-iodo acetophenone (1.24 g, 5 mmol) and 2-chloro thiophenol (860 mg, 6 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 99:1) afforded **41** (1.18 g, 90%) as white solid. Conforms to reported analytical data.[11]

Step 2. Synthesis of 1-(4-((2-chlorophenyl)sulfonyl)phenyl)ethenone (54)

Following **RC-3,**[28] **54** was synthesized using **41** (1.31 g, 5 mmol) and 30% H_2O_2 solution (6 equiv.; 1.12 mL). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 9:1) afforded **54** (1.429 g, 97%) as white solid. Conforms to reported analytical data.[37]

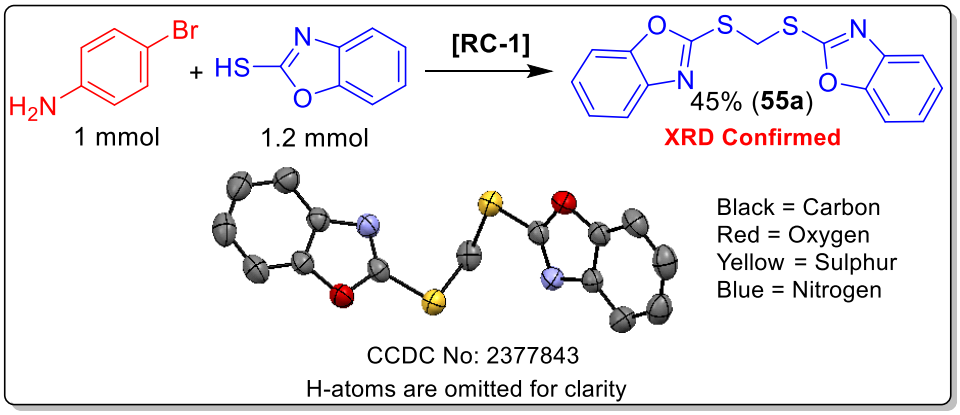


Rf: 0.48 (hexane/EtOAc = 85:15)

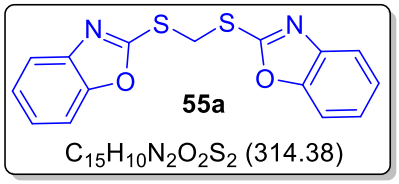
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.09 – 8.01 (m, 4H), 7.56 (dtd, *J* = 28.3, 7.6, 1.4 Hz, 2H), 7.45 (dd, *J* = 7.8, 1.1 Hz, 1H), 2.65 (s, 3H). **^{13}C NMR** (100 MHz, CDCl3) δ 196.7, 143.86, 140.48, 137.62, 135.06, 132.92, 132.08, 131.1, 128.67, 127.44, 26.84. **ν max** (CH_2Cl_2, cm^{-1}):1688, 1322, 1161, 771, 633, 598. **HRMS** (ESI) Calcd for $C_{14}H_{11}ClO_3S$ $[M+H]^+$: 295.0195; found: 295.0196.

Failed Attempt to Synthesize Precursor of Cathepsin-D-Inhibitor:

Synthesis of bis(benzo[d]oxazol-2-ylthio)methane (55a):



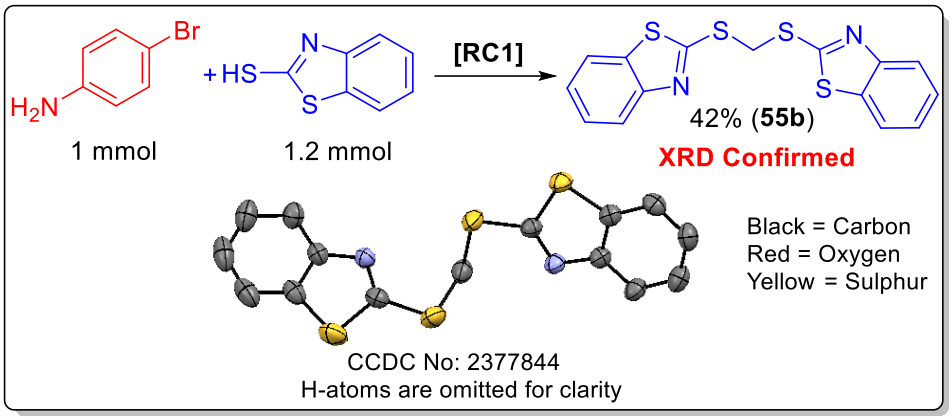
Following **RC-1, 55a** was synthesized using 4-bromoaniline (172 mg, 1mmol) and 2-mercaptobenzoxazole (181 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 49:1) afforded **55a** (141 mg, 45%) as white solid. Conforms to reported analytical data.[41]



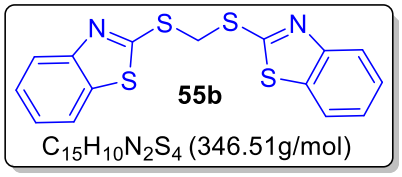
Rf: 0.50 (hexane/EtOAc 95:5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.27 – 7.16 (m, 4H), 5.11 (s, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 163.37, 152.26, 141.65, 124.37, 118.74, 110.11, 35.41. **ν_{max}** (CH_2Cl_2, cm^{-1}): 1505, 1456, 1210, 1138, 891, 738. **HRMS** (ESI) Calcd for $C_{15}H_{11}N_2O_2S_2$ $[M+H]^+$: 315.0262; found: 315.0273.

Synthesis of bis(benzo[d]thiazol-2-ylthio)methane (55b):



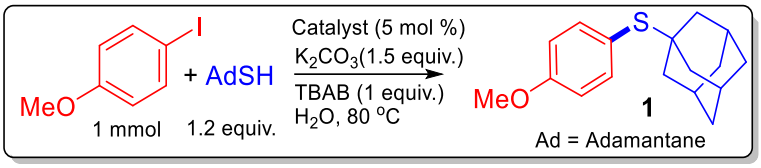
Following **RC-1, 55b** was synthesized using 4-bromoaniline (172 mg, 1mmol) and 2-mercaptobenzothiazole (200 mg, 1.2 mmol, 1.2 equiv.). Purification by FC (SiO_2: 230-400 mesh, hexane/EtOAc = 99:1) afforded **55b** (145 mg, 42%) as white solid. Conforms to reported analytical data.[41]



R_f: 0.50 (hexane/EtOAc 98:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.43 – 7.32 (m, 2H), 7.28 – 7.19 (m, 2H), 5.25 (s, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 164.78, 152.83, 135.55, 126.13, 124.51, 121.82, 121.08, 36.45. **ν_{max}** (CH_2Cl_2, cm^{-1}): 1461, 1429, 1266, 996, 726. **HRMS** (ESI) Calcd for $C_{15}H_{11}N_2O_2S_2$ $[M+H]^+$: 346.9805; found: 346.9816.

10: Recyclability Experiments:



Initial reaction. A 5 mL glass vial equipped with a magnetic stir bar was charged with catalyst $CuNiO_2$ (10 mol%), distilled water (1 mL), TBAB (1 equiv.), respective haloarenes (1 mmol), corresponding thiols (1.2 equiv.) and base K_2CO_3 (1.5 equiv.) in air. The reaction mixture was then placed in a preheated oil bath with stirring maintained at 80 °C for 10 h. After the reaction 5-10 mL of ethyl acetate was added and with the aid of centrifuge the organic layer was separated. The organic layer was then evaporated to dryness and to yield the desired product (255 mg, 93%).

Thereafter the water layer containing catalyst was heated at 50 ℃ for 2-3 h after adding KOH (to reach the pH to 11). The catalyst regenerated as black powder and ready for reuse. **The 1st recycle.** **To a new** 5 mL glass vial equipped with a magnetic stir bar was charged with recycled catalyst $CuNiO_2$, distilled water (1 mL), TBAB (1 equiv.), respective haloarenes (1 mmol), corresponding thiols (1.2 equiv.) and base K_2CO_3 (1.5 equiv.) in air. The reaction mixture was then placed in a preheated oil bath with stirring maintained at 80 ℃ for 10 h. After the reaction 5-10 mL of ethyl acetate was added and with the aid of centrifuge the organic layer was separated. The organic layer was then evaporated to dryness and to yield the desired product (254 mg, 93%). Thereafter the water layer containing catalyst was heated at 80 ℃ for 2-3 h after adding KOH (to reach the *pH* to 11). The catalyst regenerated as black powder and ready for reuse.

Further recycling. The same procedure from the **1st recycle** was repeated for the **2nd recycle** (yield 252 mg, 92%) and the **3rd recycle** (yield 249 mg, 91%).

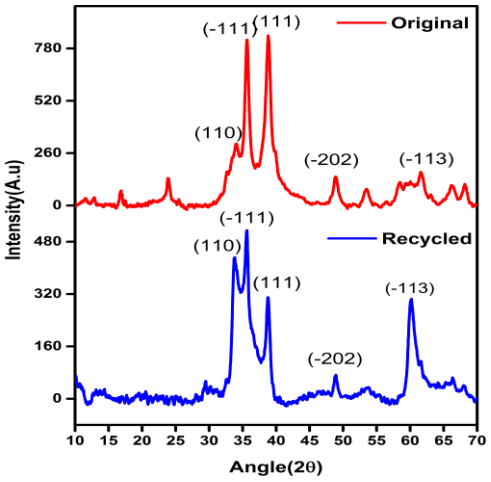
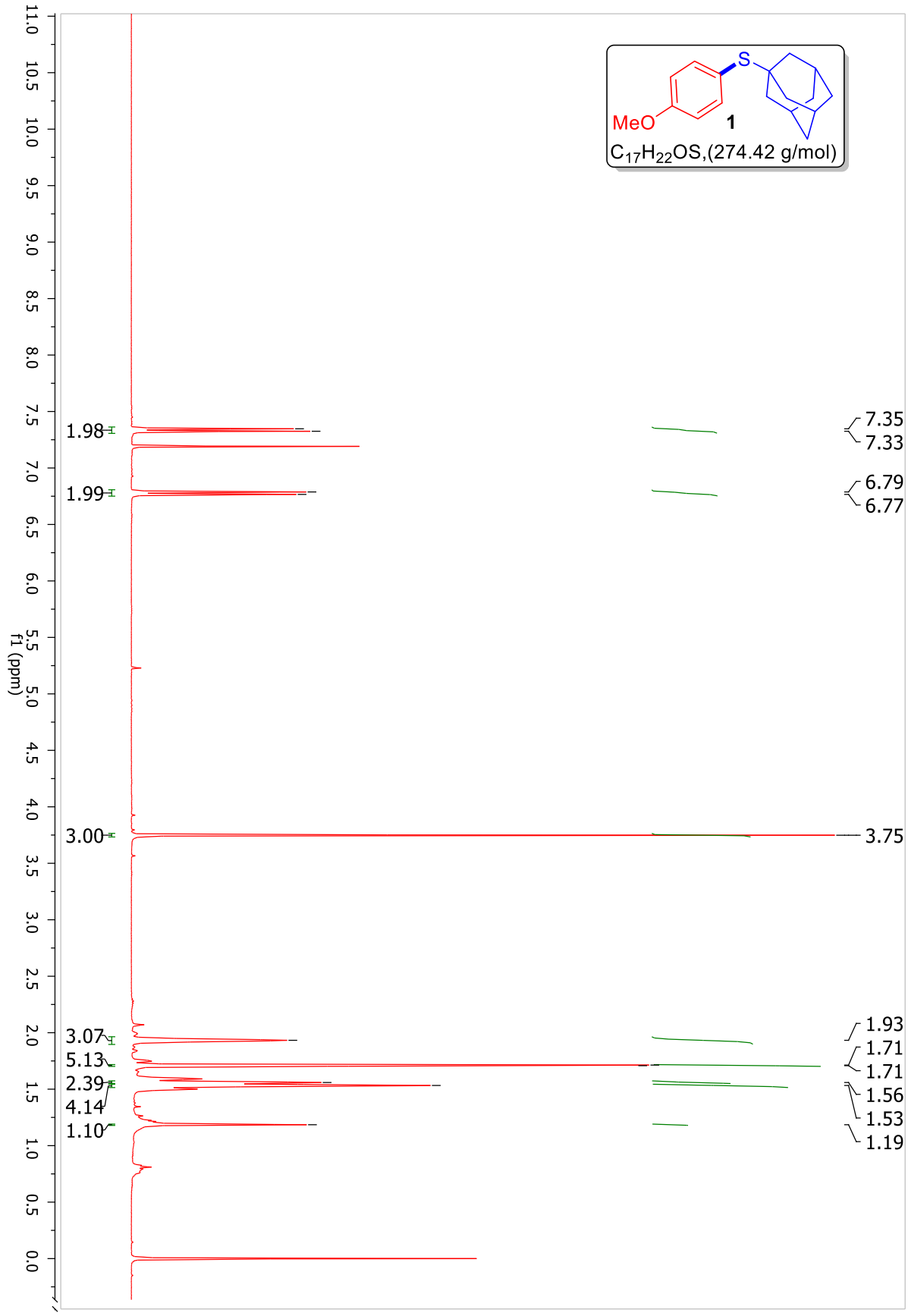


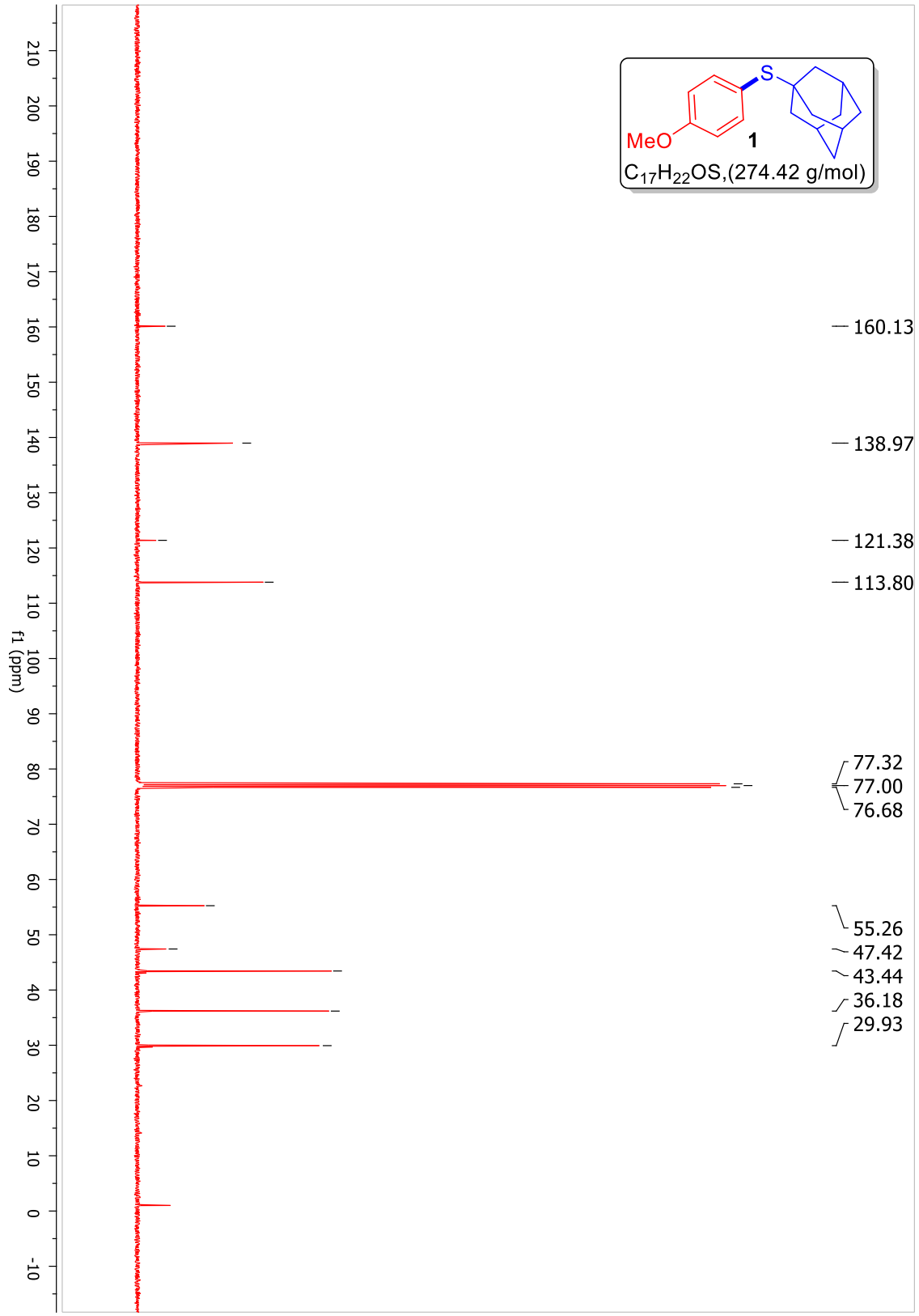
Figure 11: Powdered X-ray diffraction (XRD) analysis of $CuNiO_2$ of Recycled Catalyst

11: NMR Spectra of Compounds pp

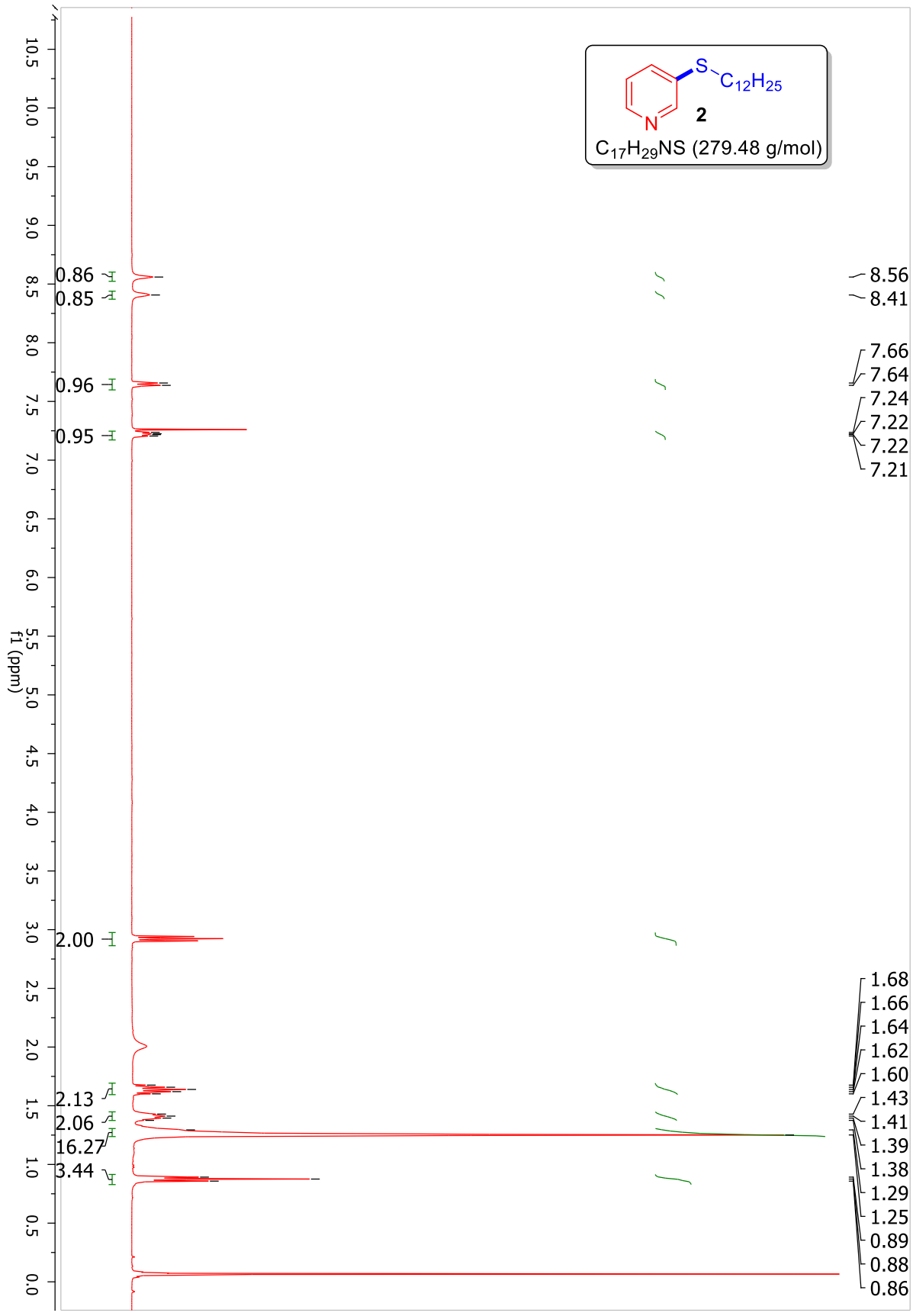
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **1:**



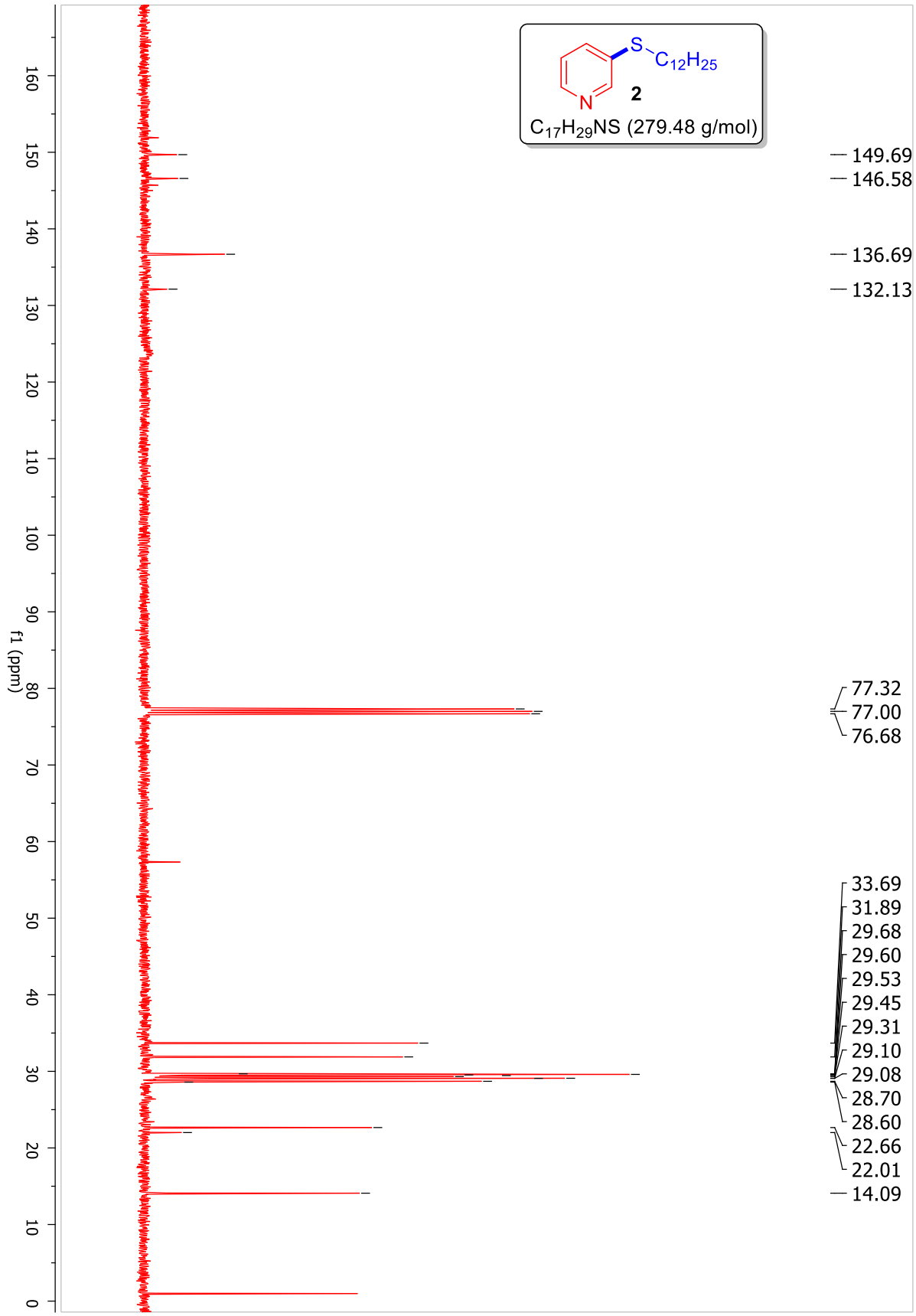
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **1:**



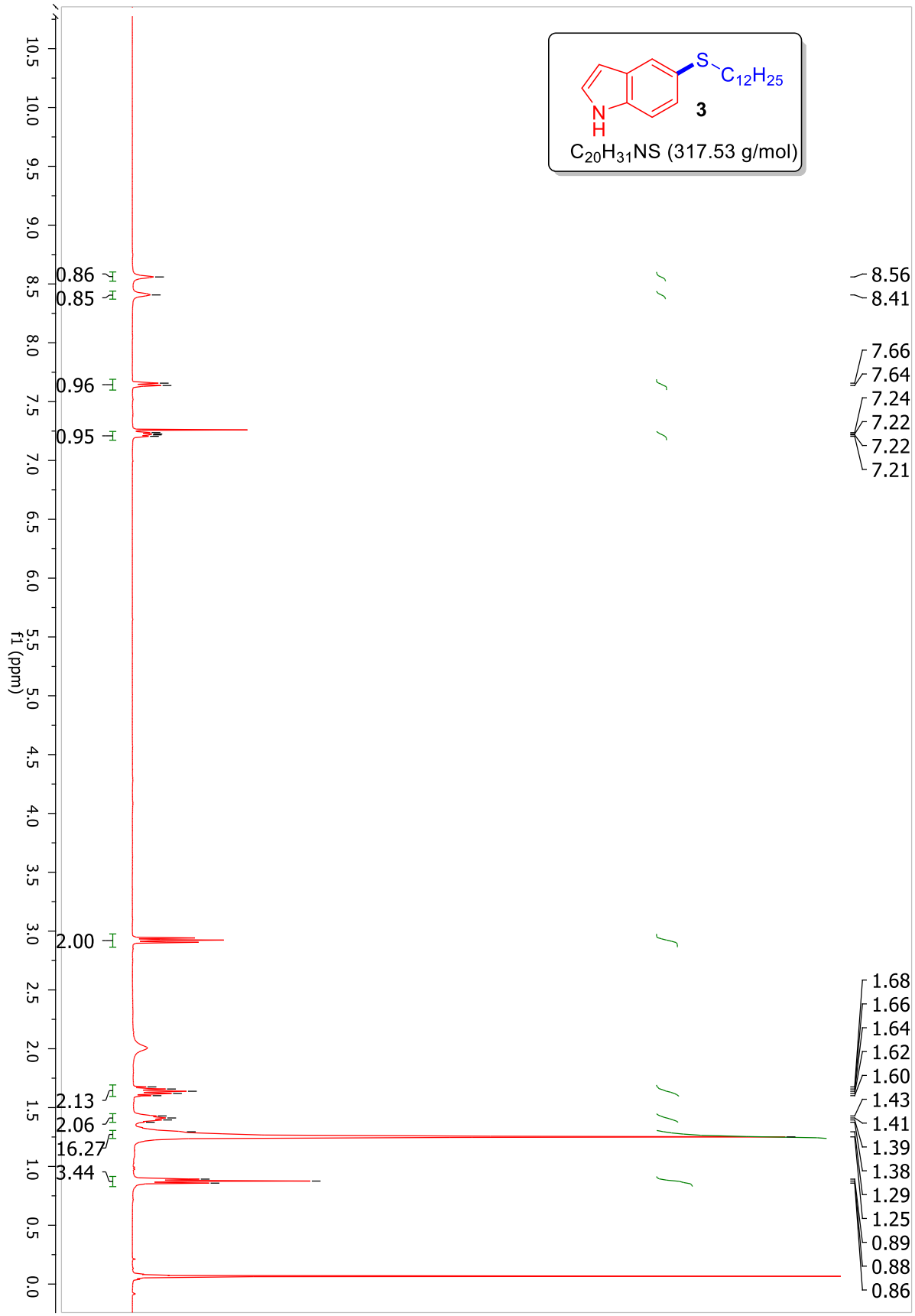
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **2:**



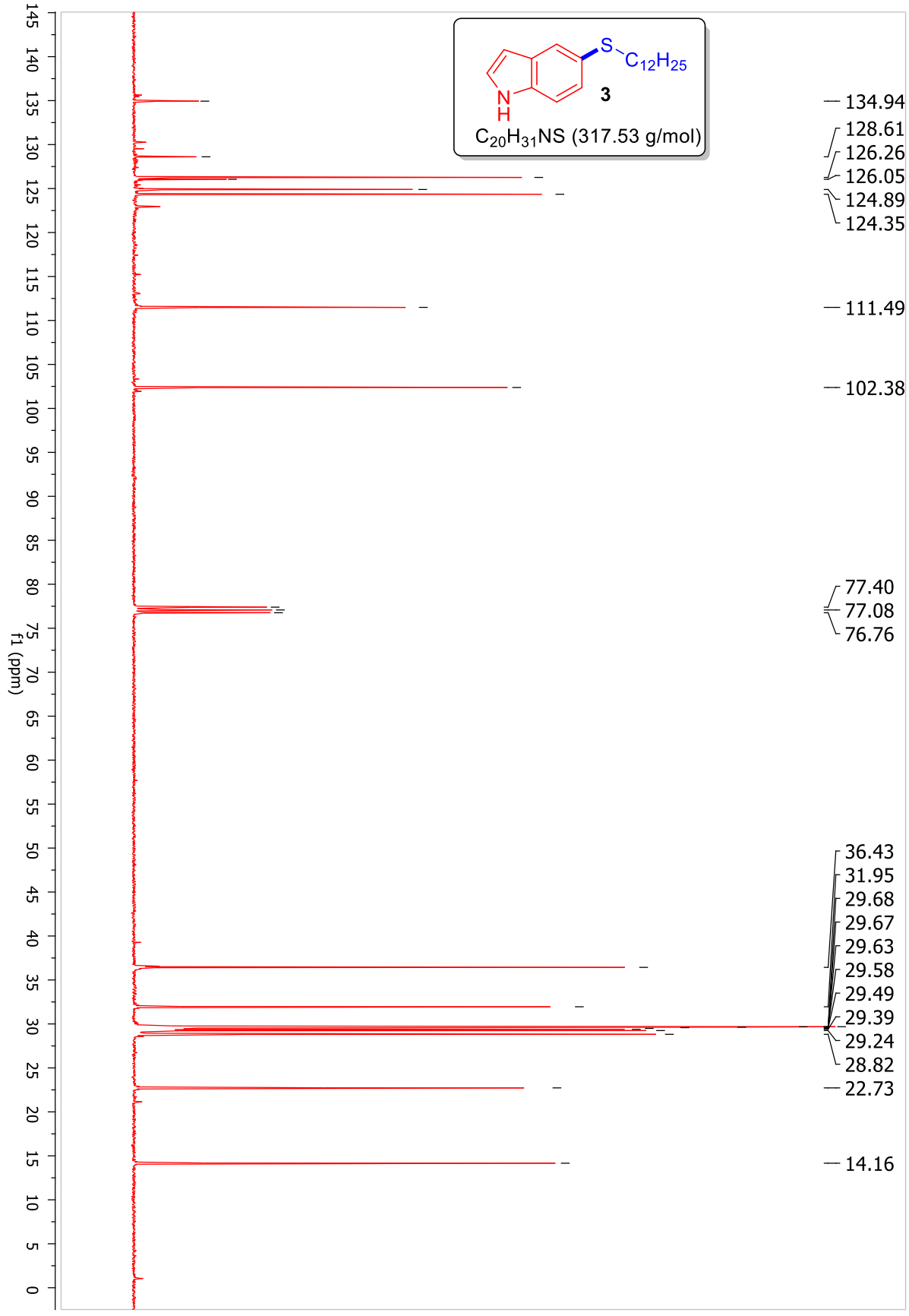
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **2:**



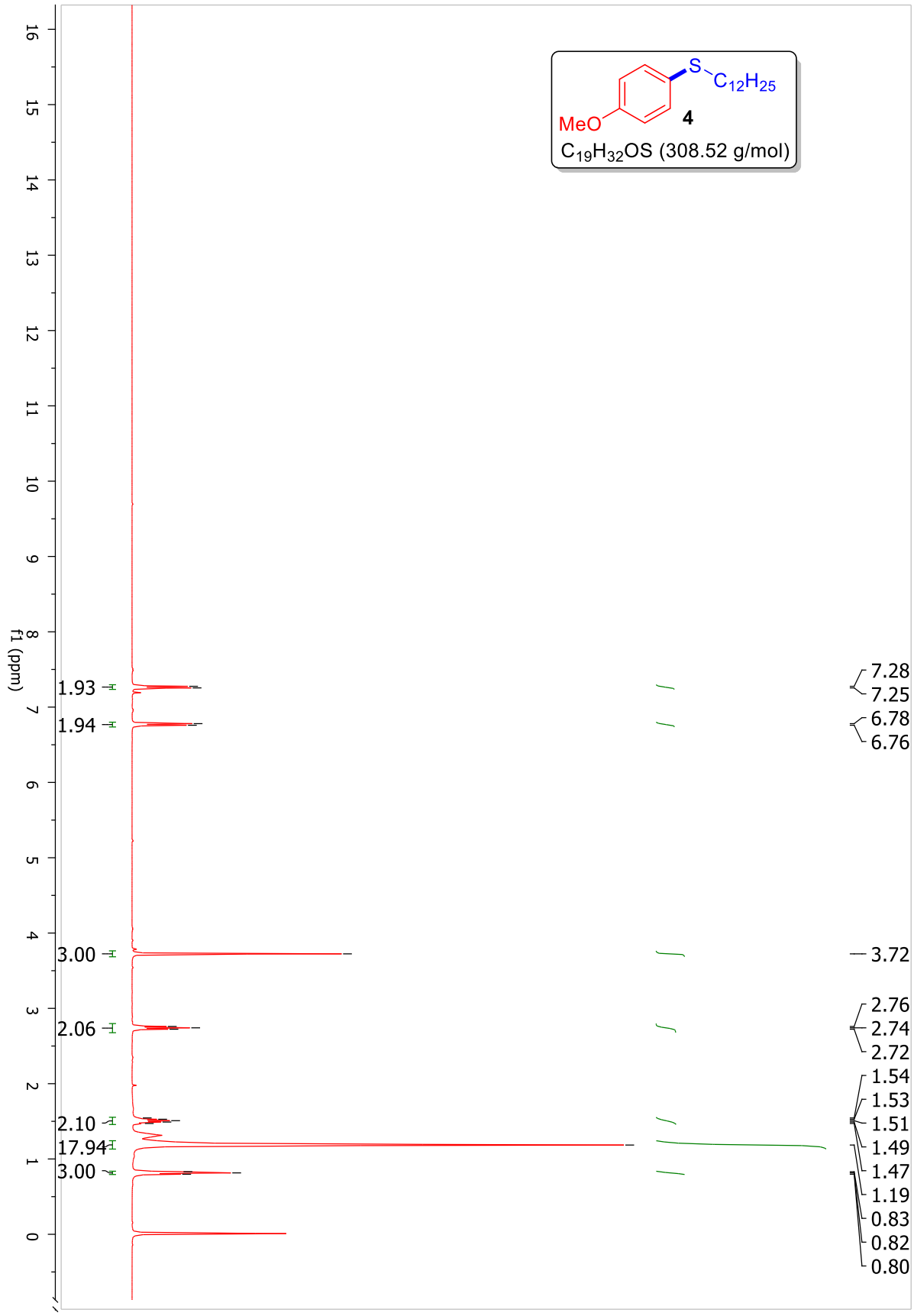
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **3:**



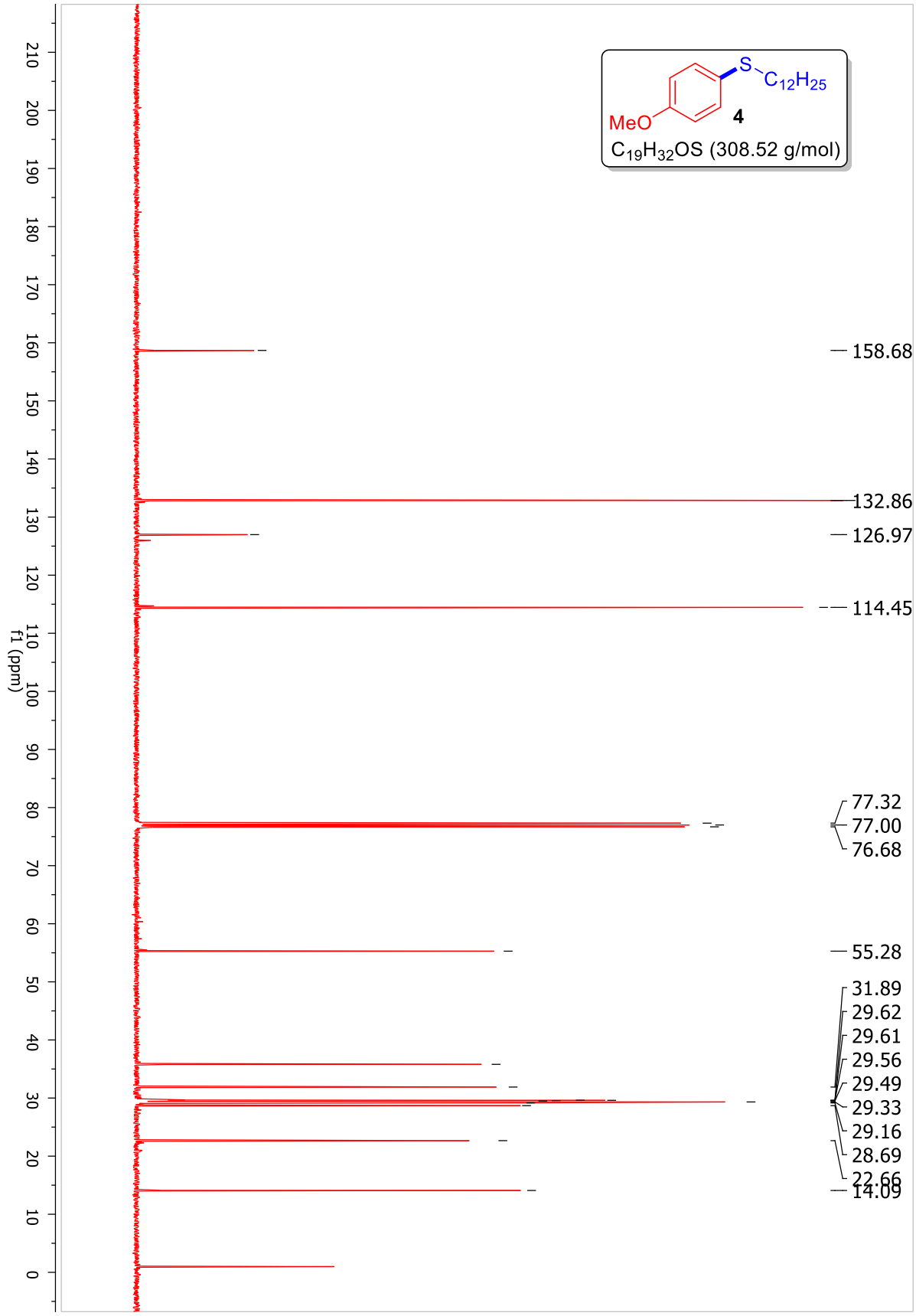
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **3:**



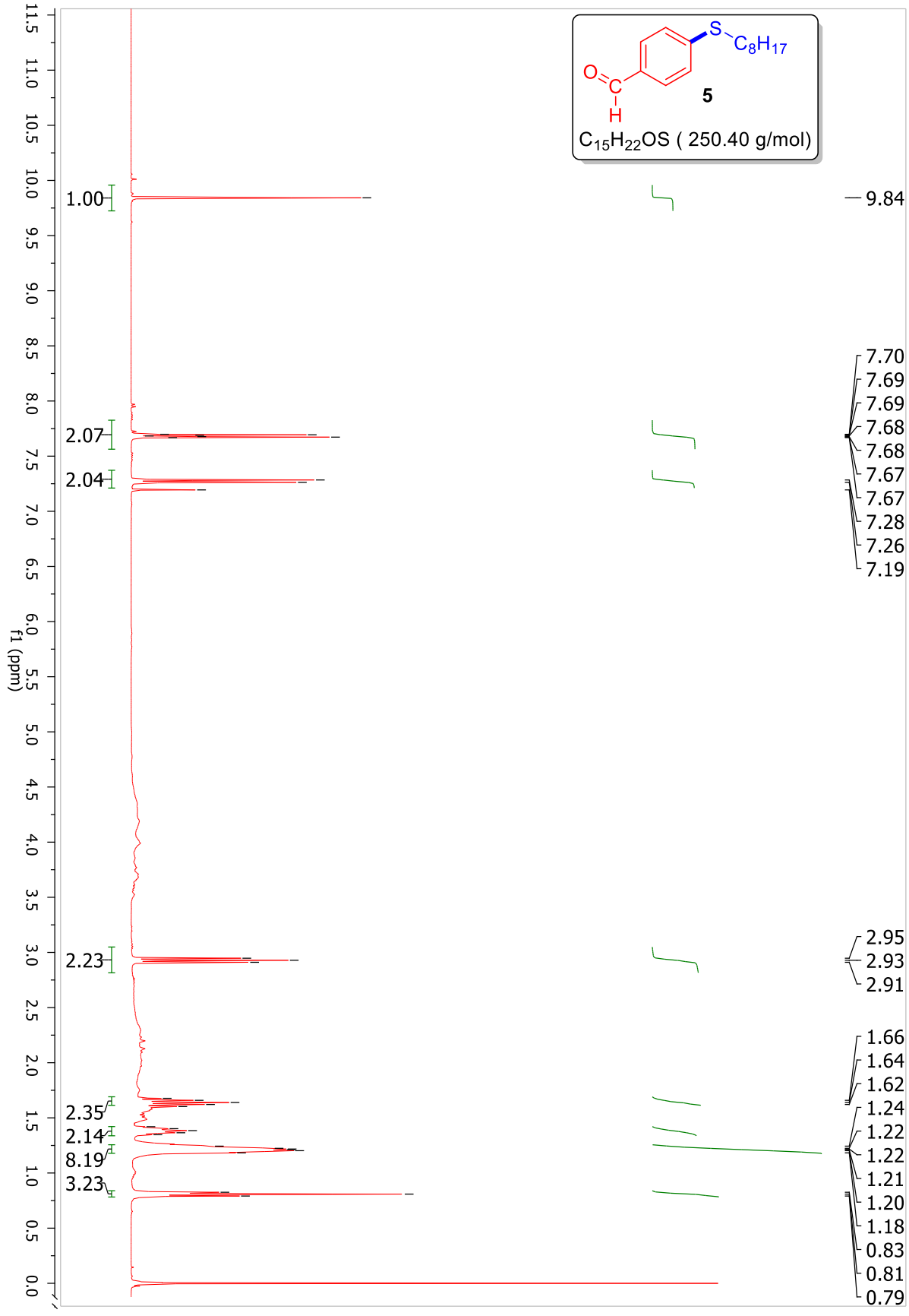
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **4:**



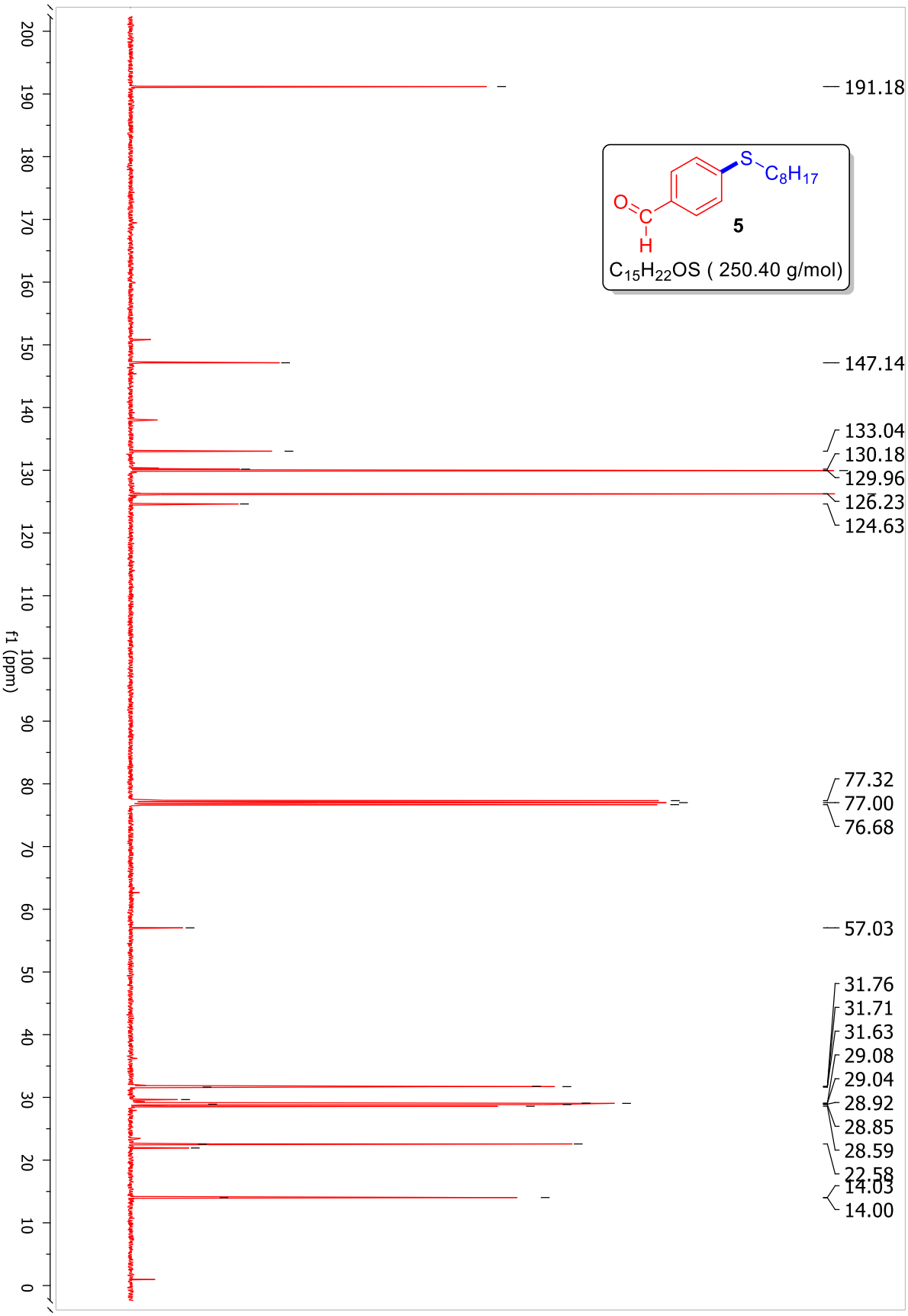
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **4:**



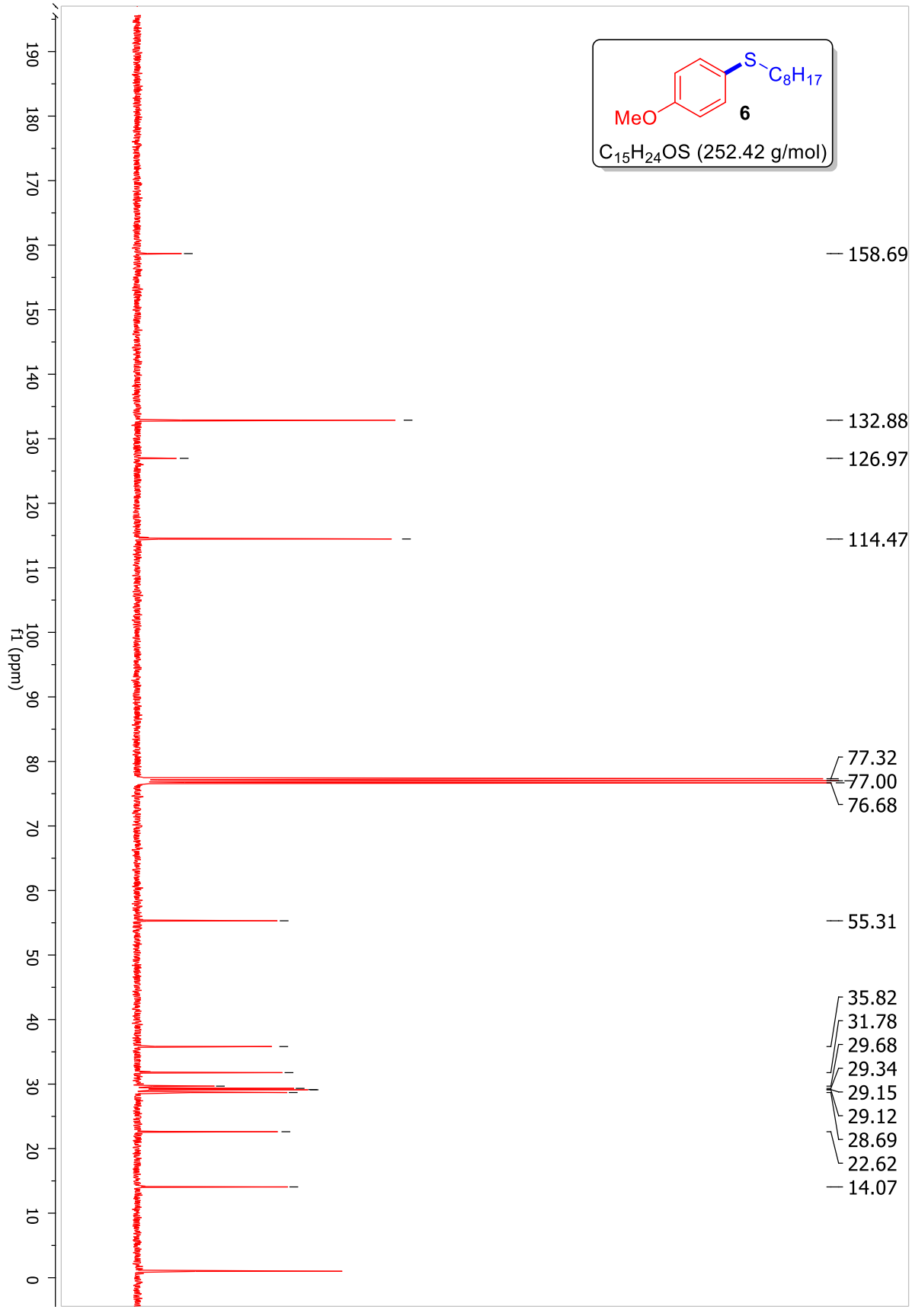
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **5:**



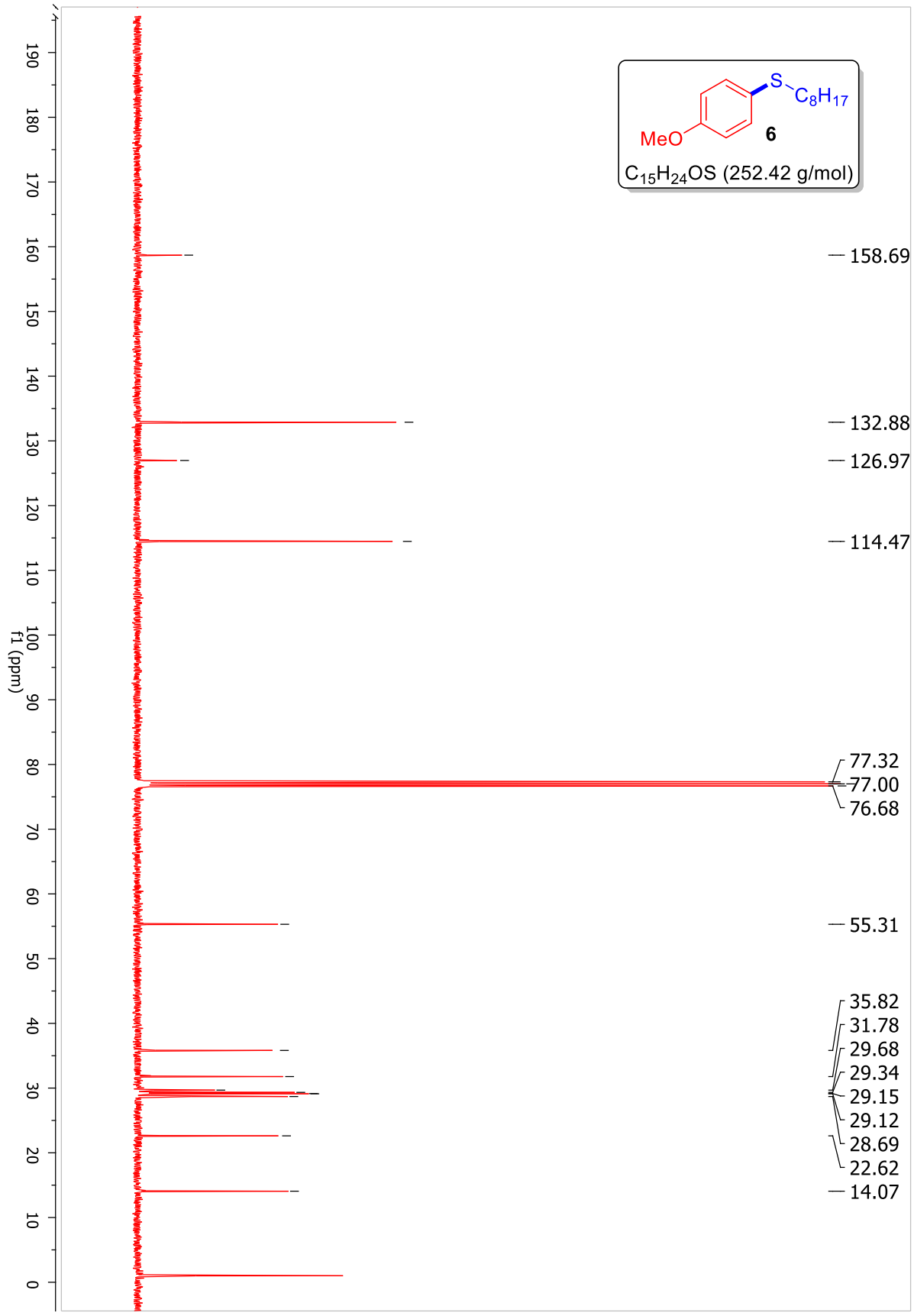
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **5:**



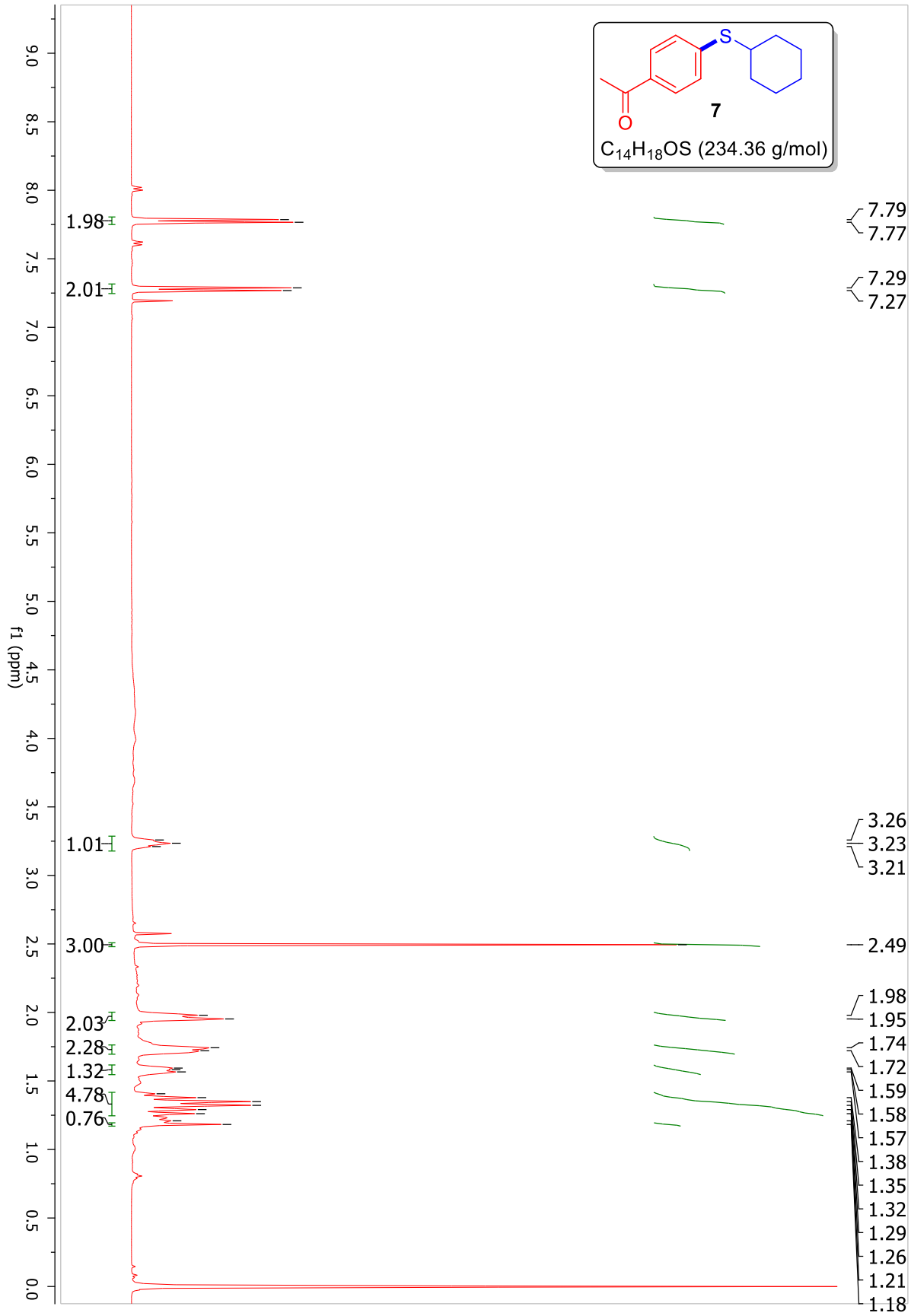
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **6:**



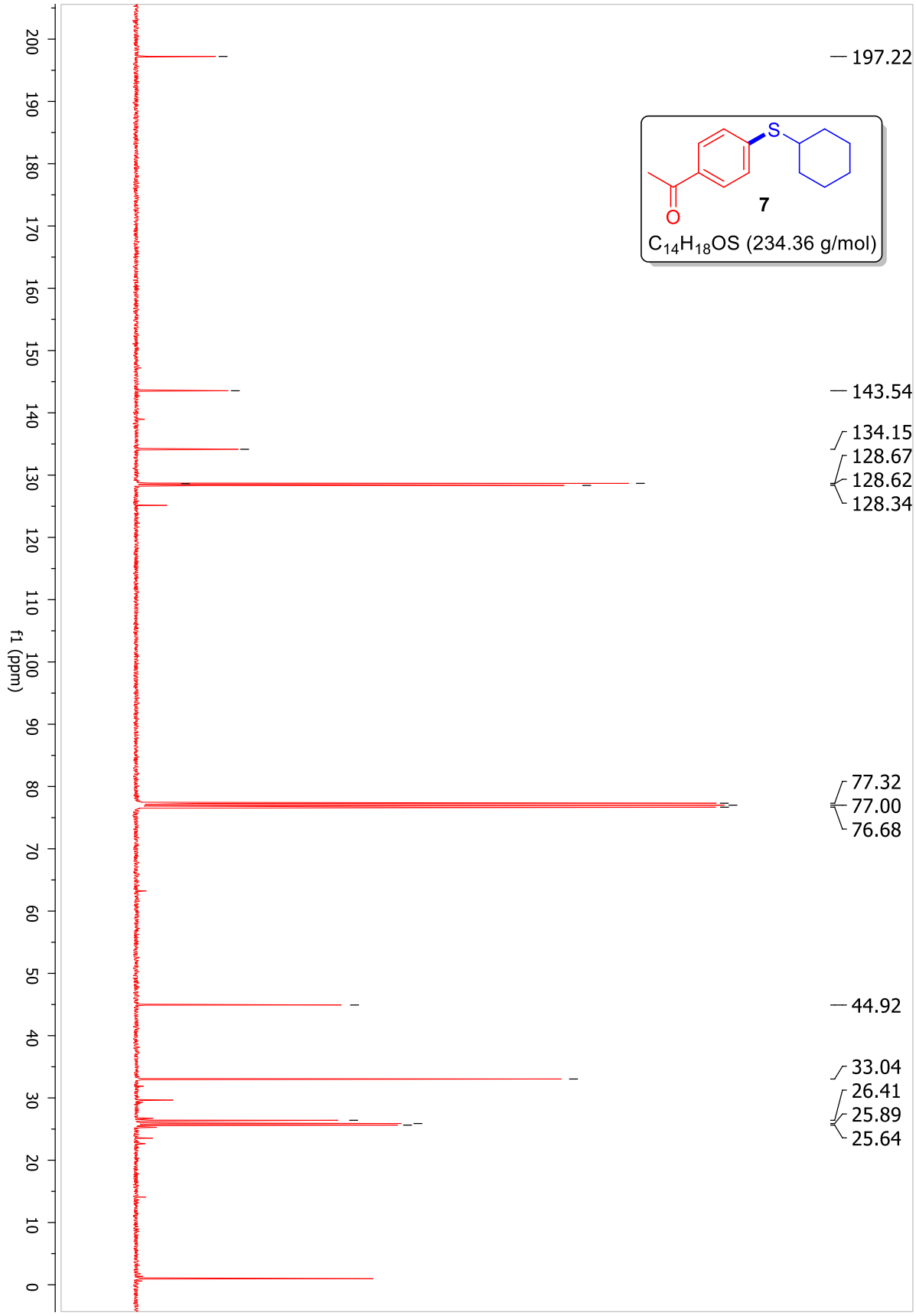
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **6:**



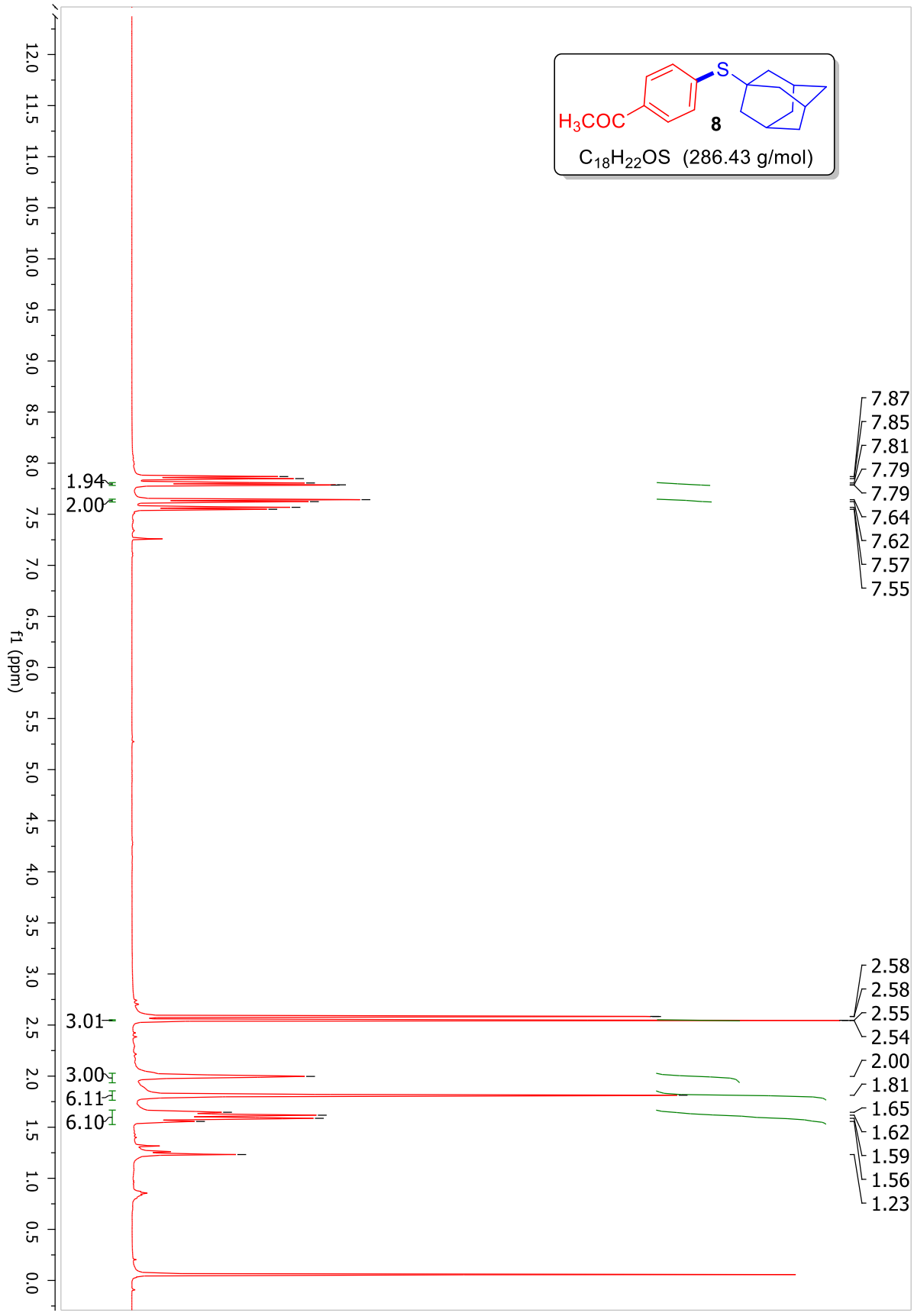
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **7:**



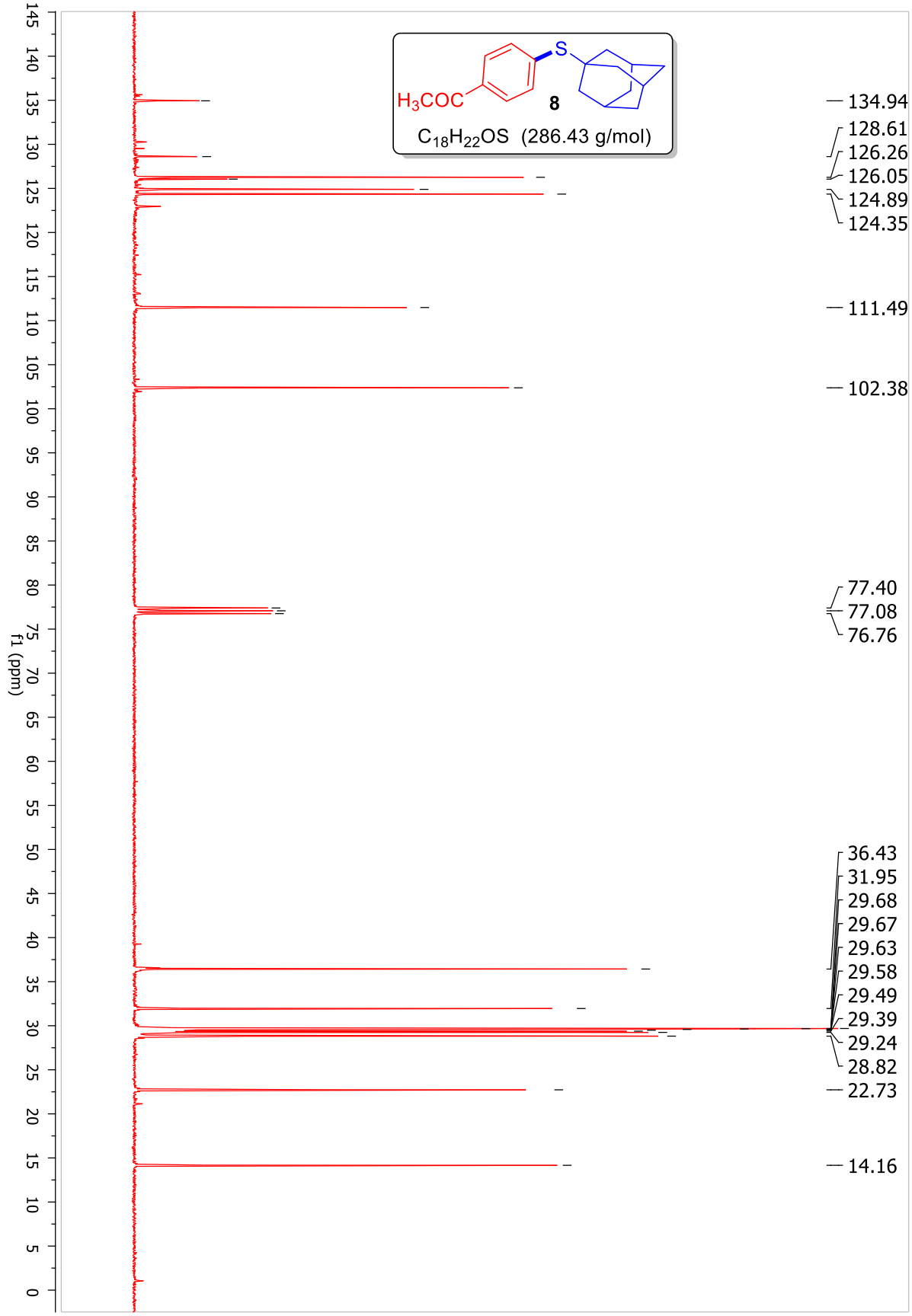
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **7:**



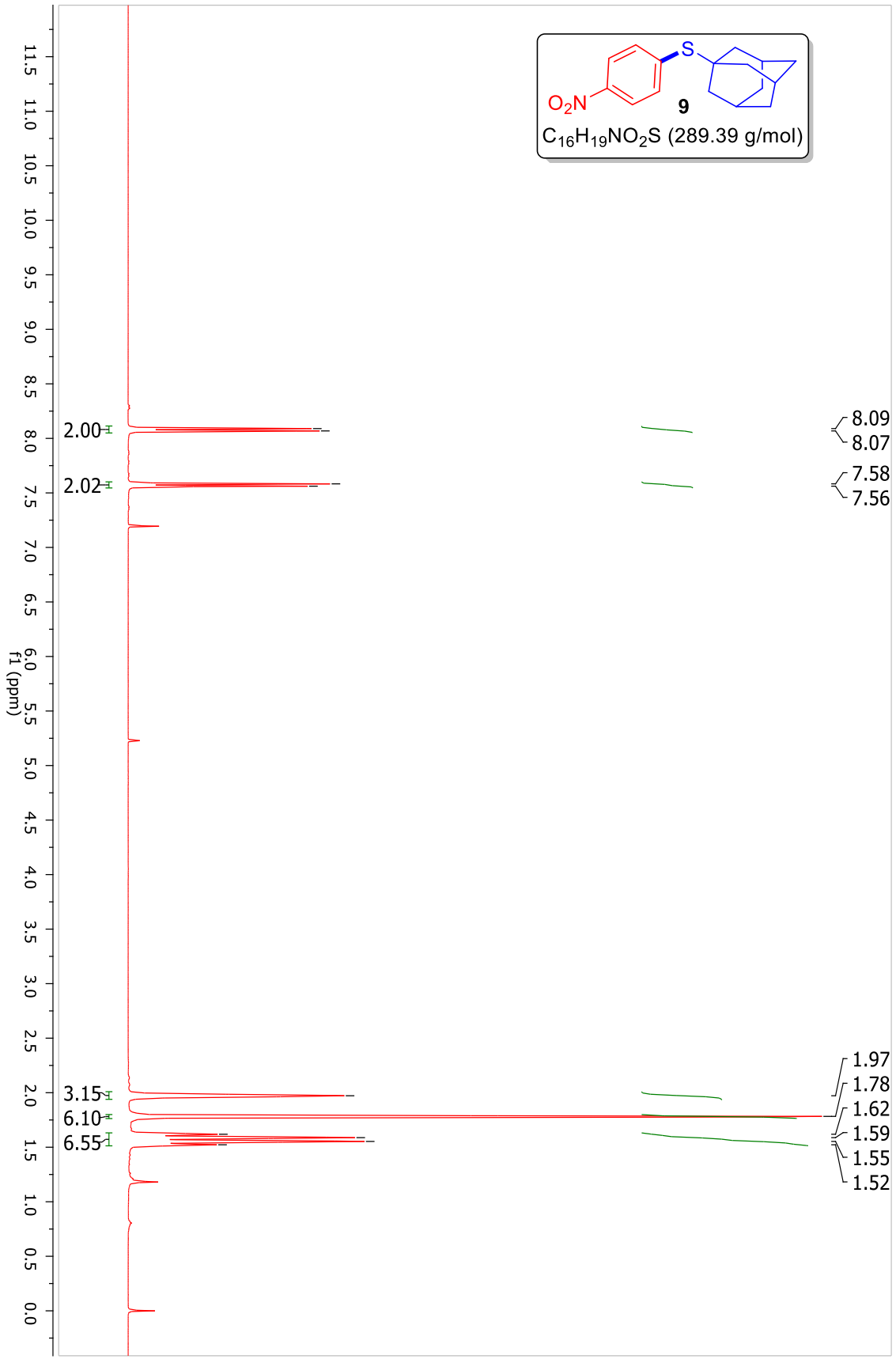
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **8:**



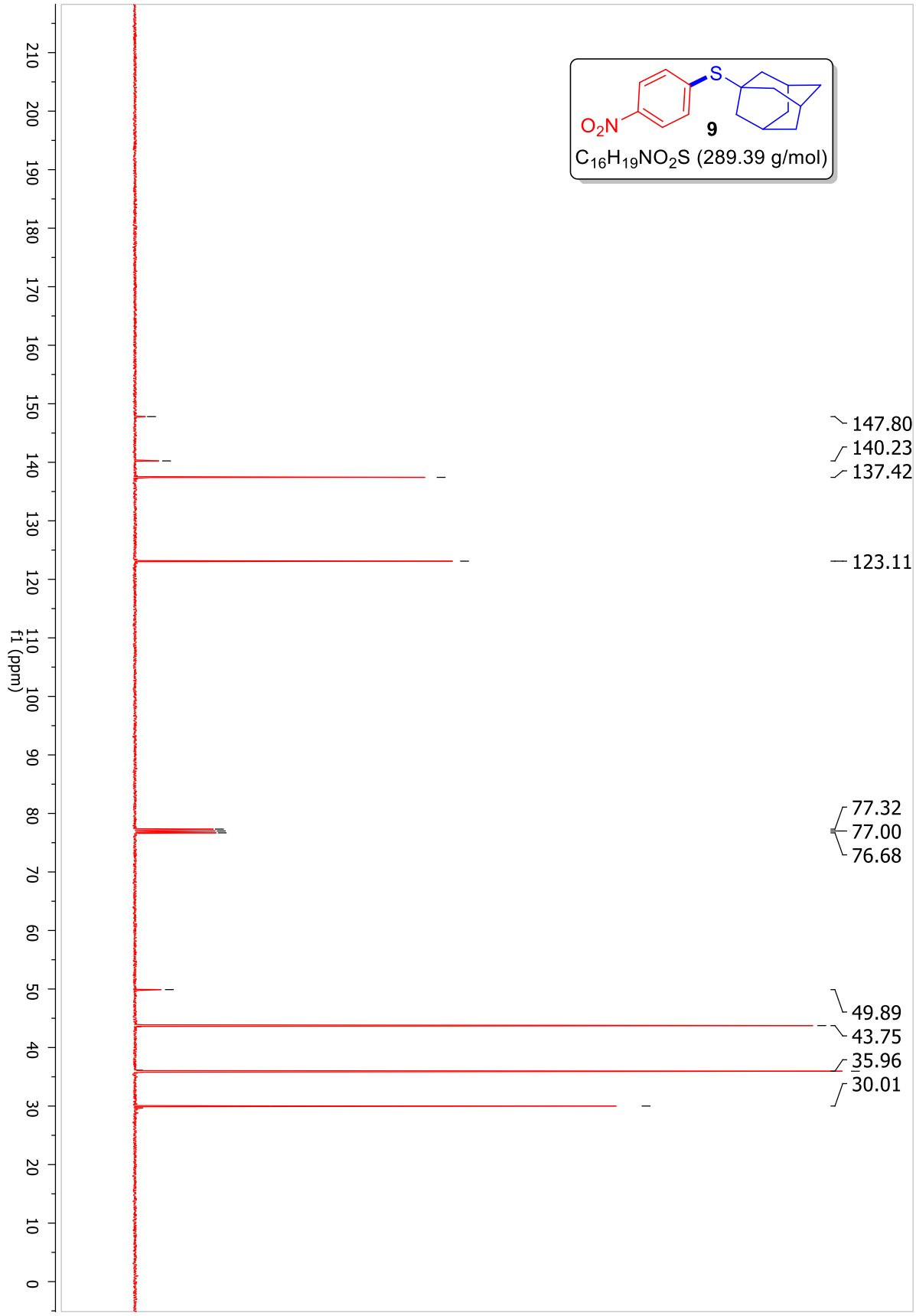
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **8:**



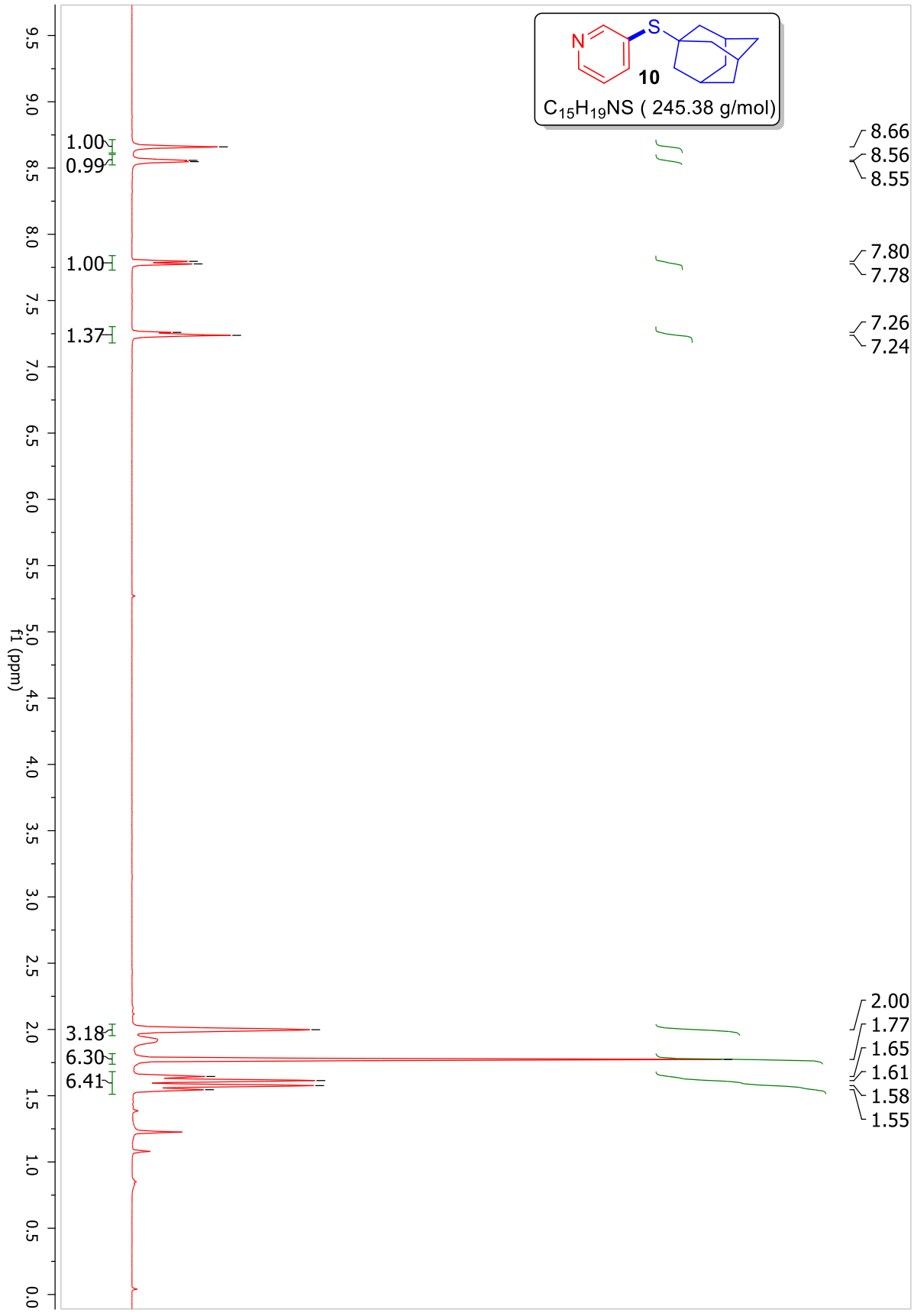
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **9:**



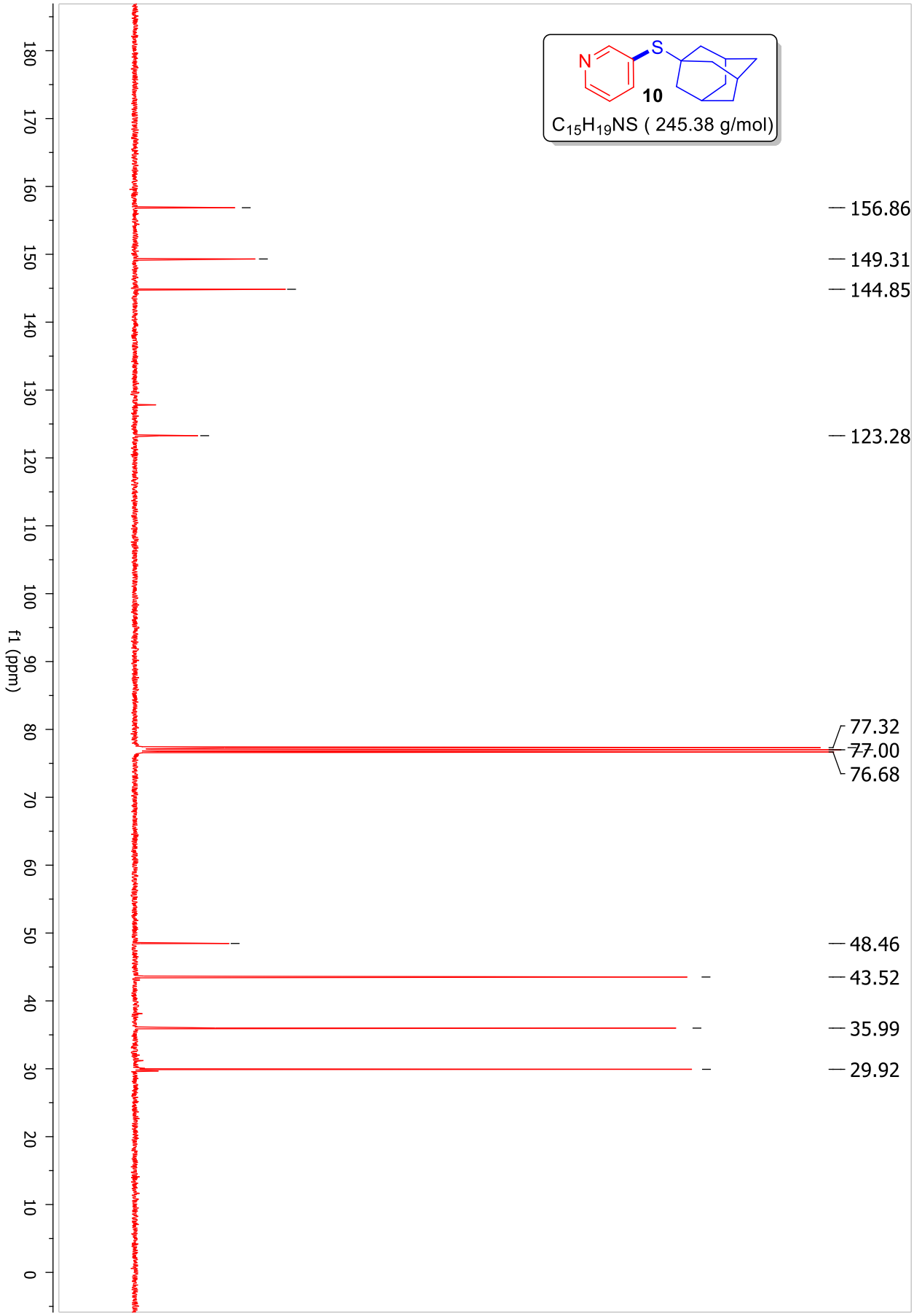
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **9:**



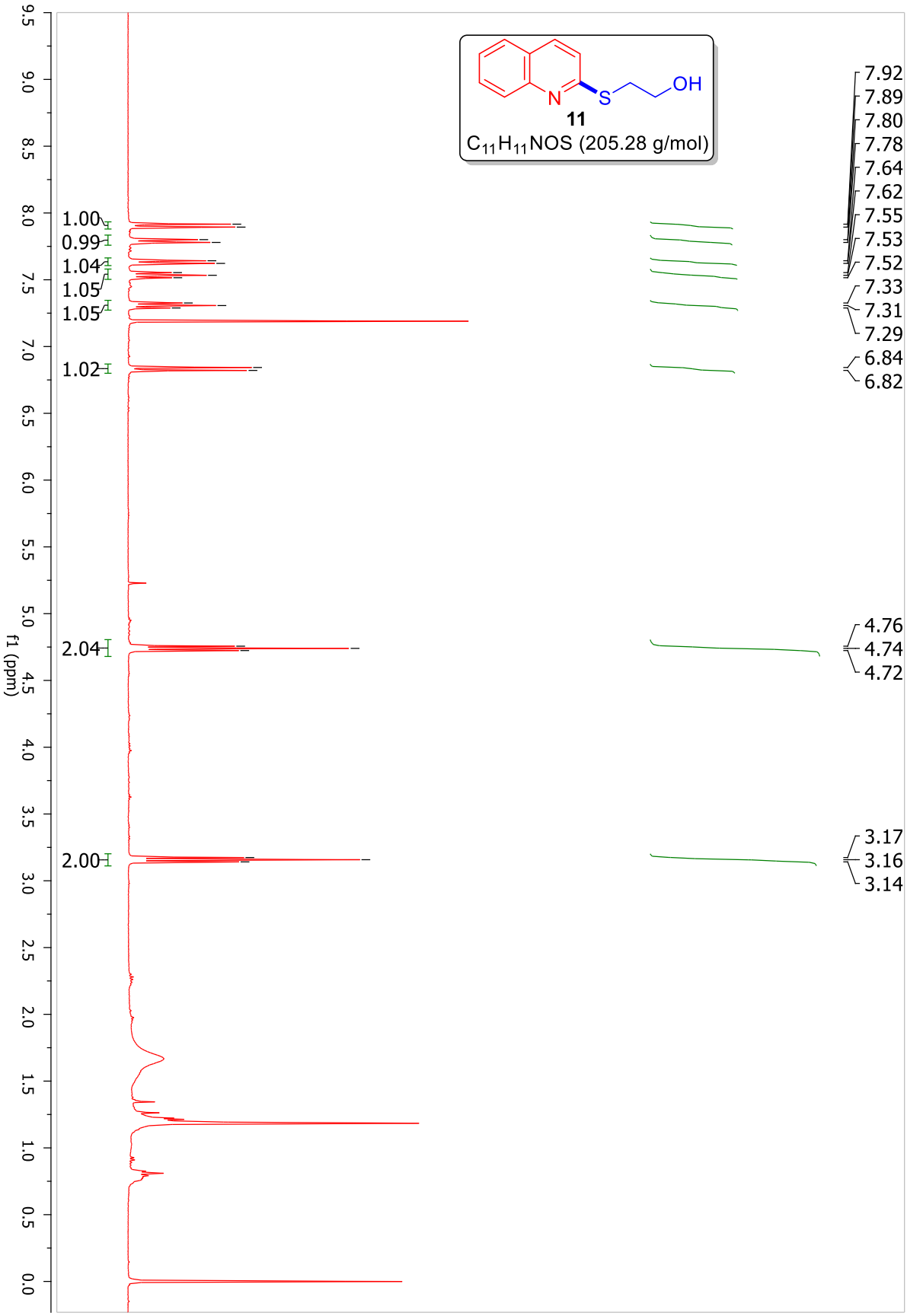
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **10:**



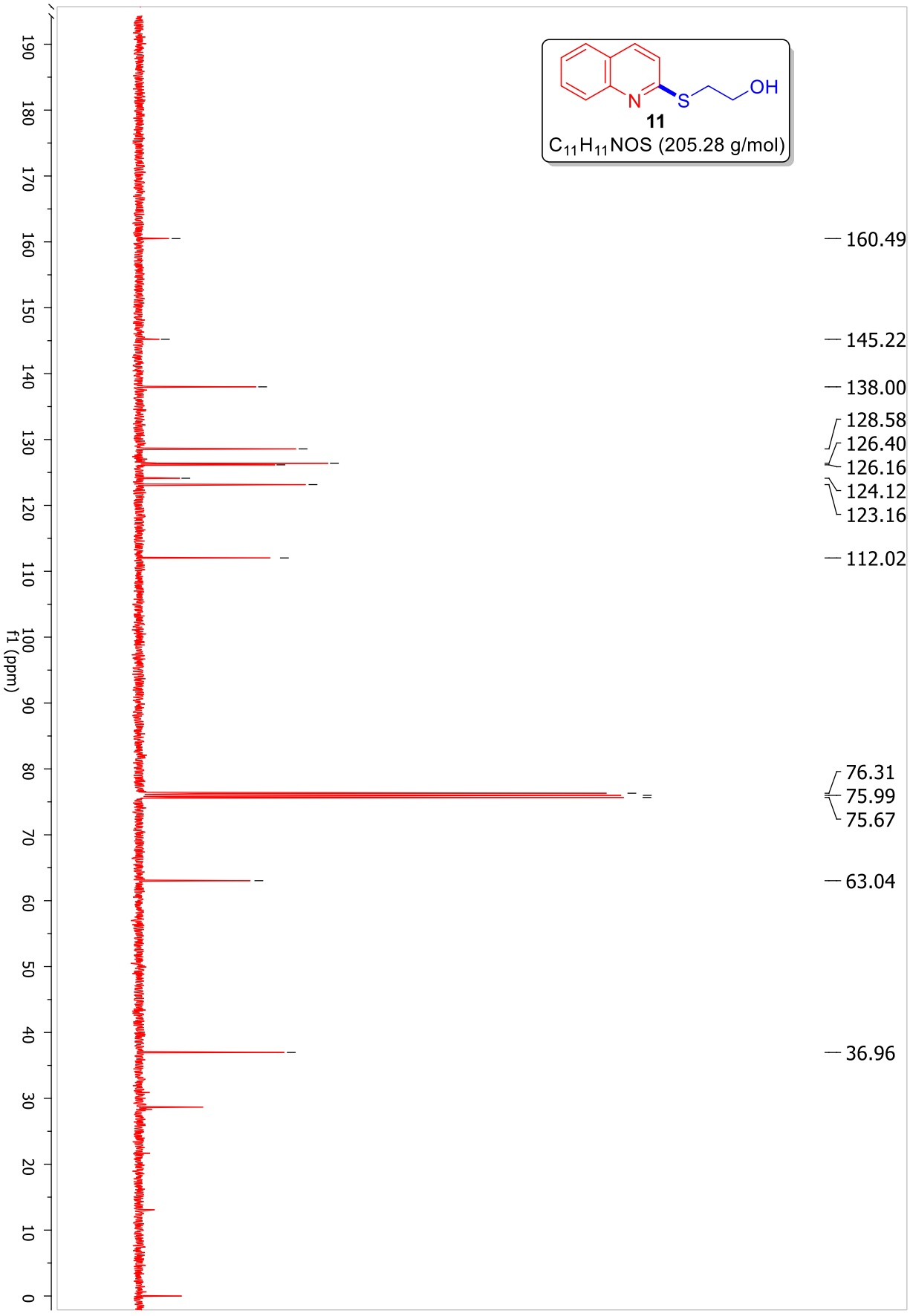
^{13}CNMR (101 MHz, $CDCl_3$) of compound **10:**



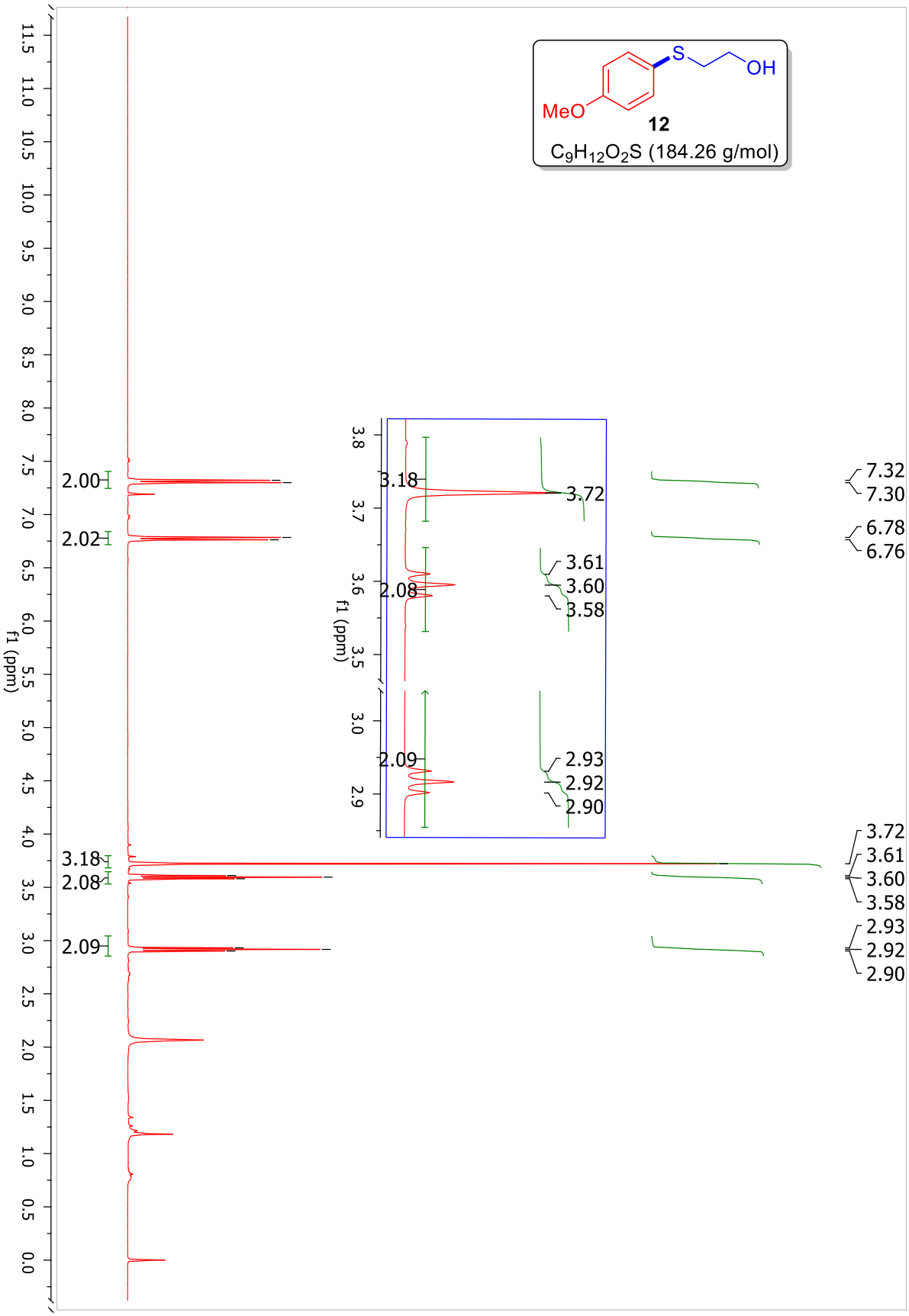
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **11:**



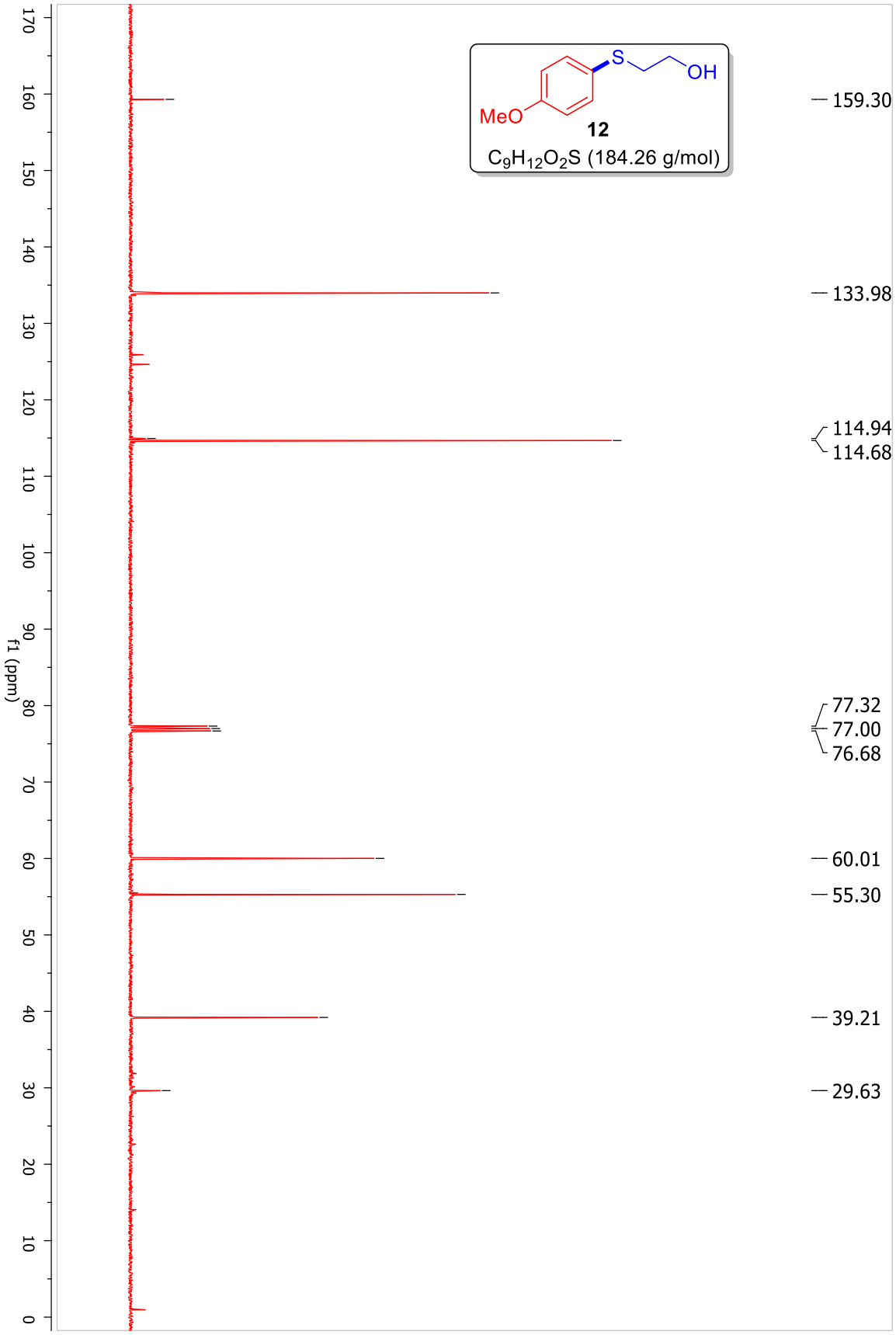
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **11:**



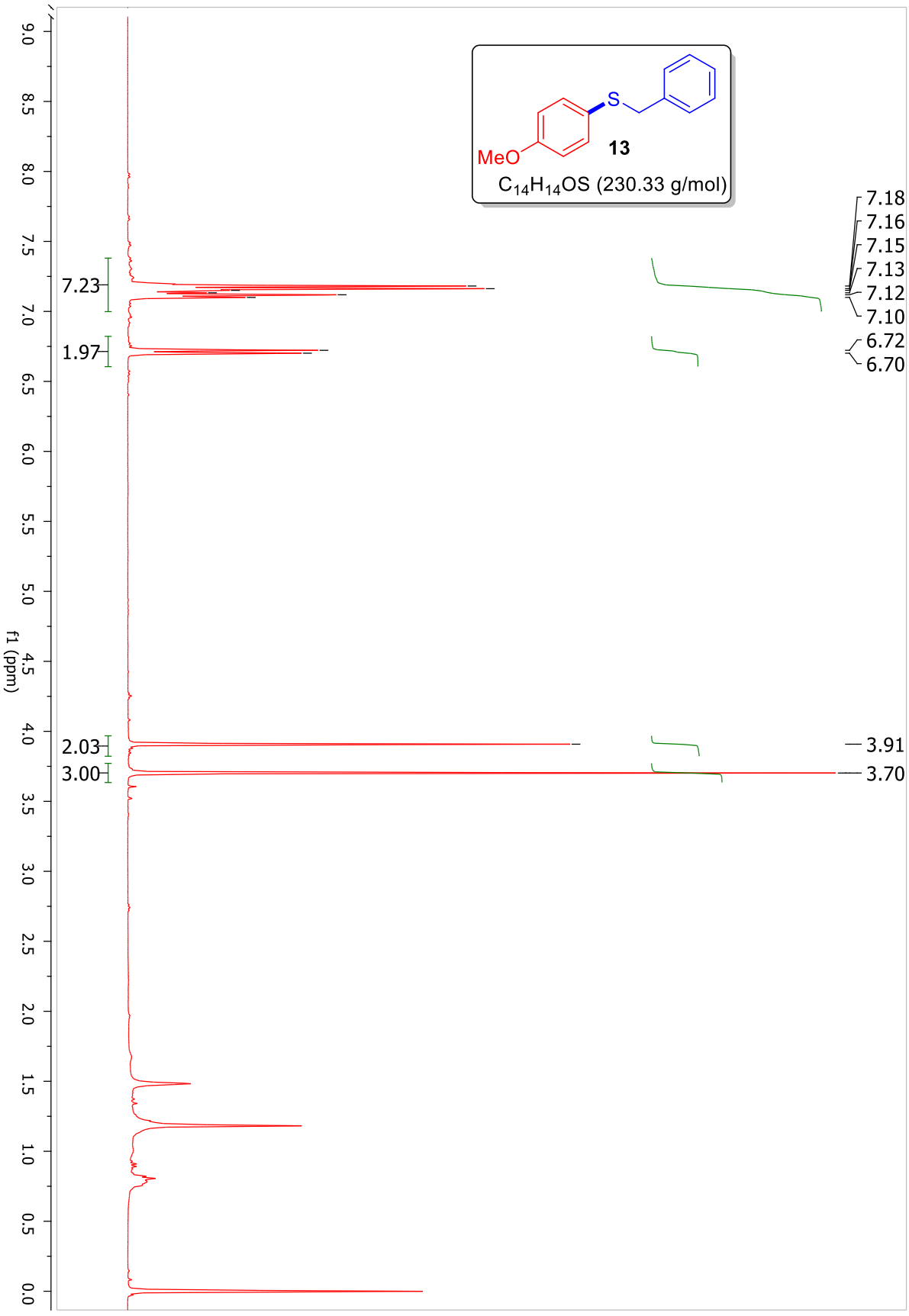
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **12:**



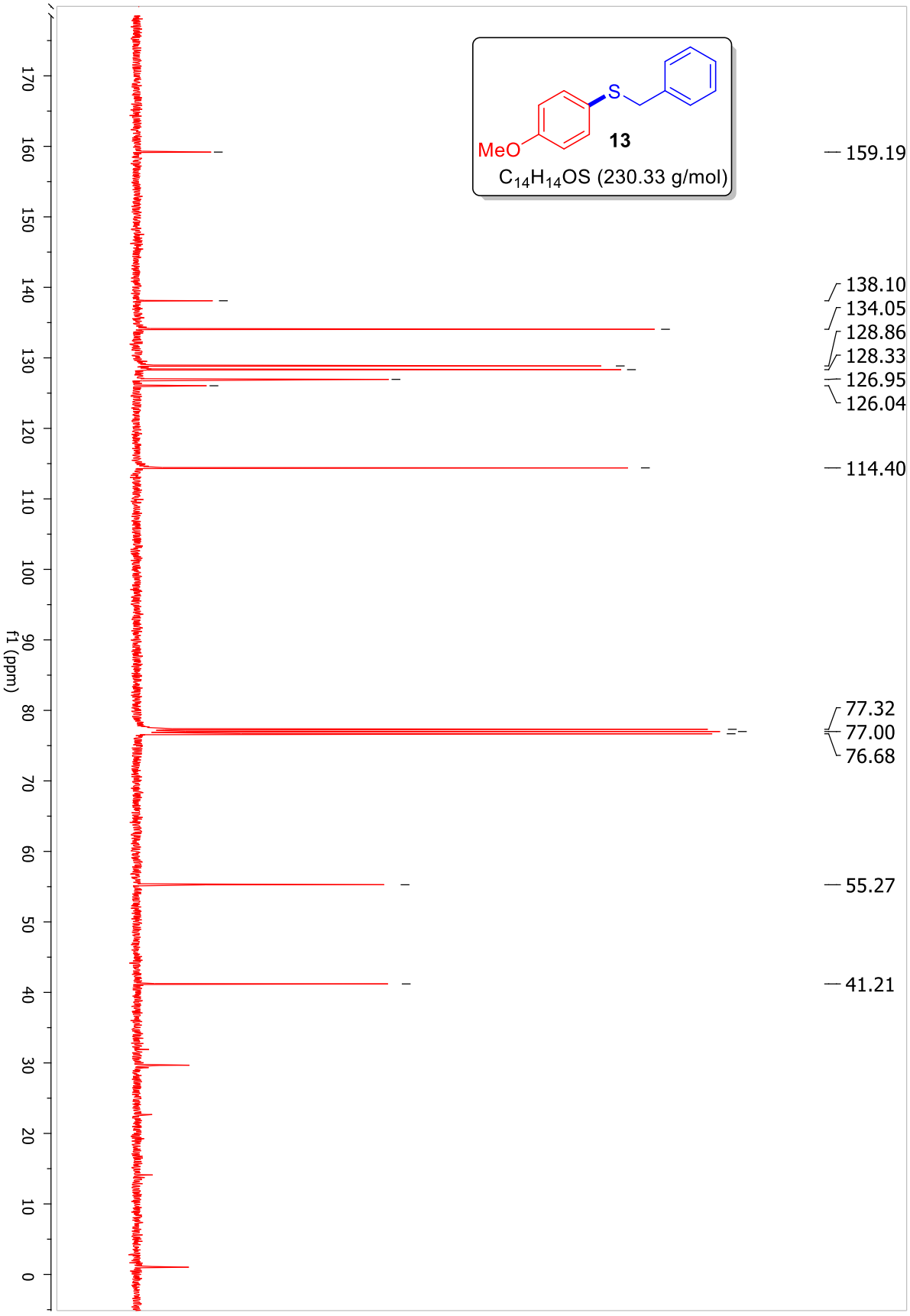
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **12:**



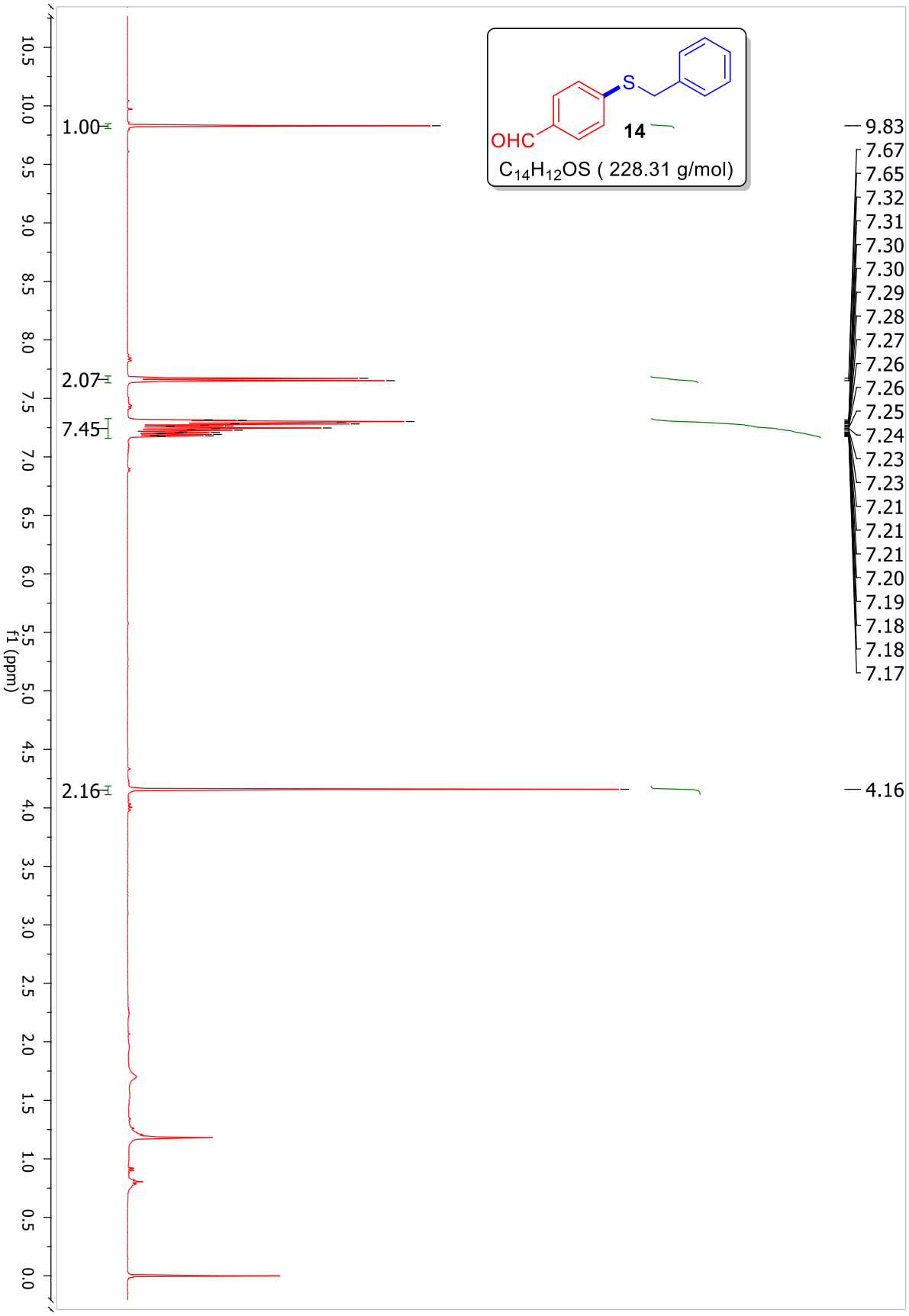
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **13:**



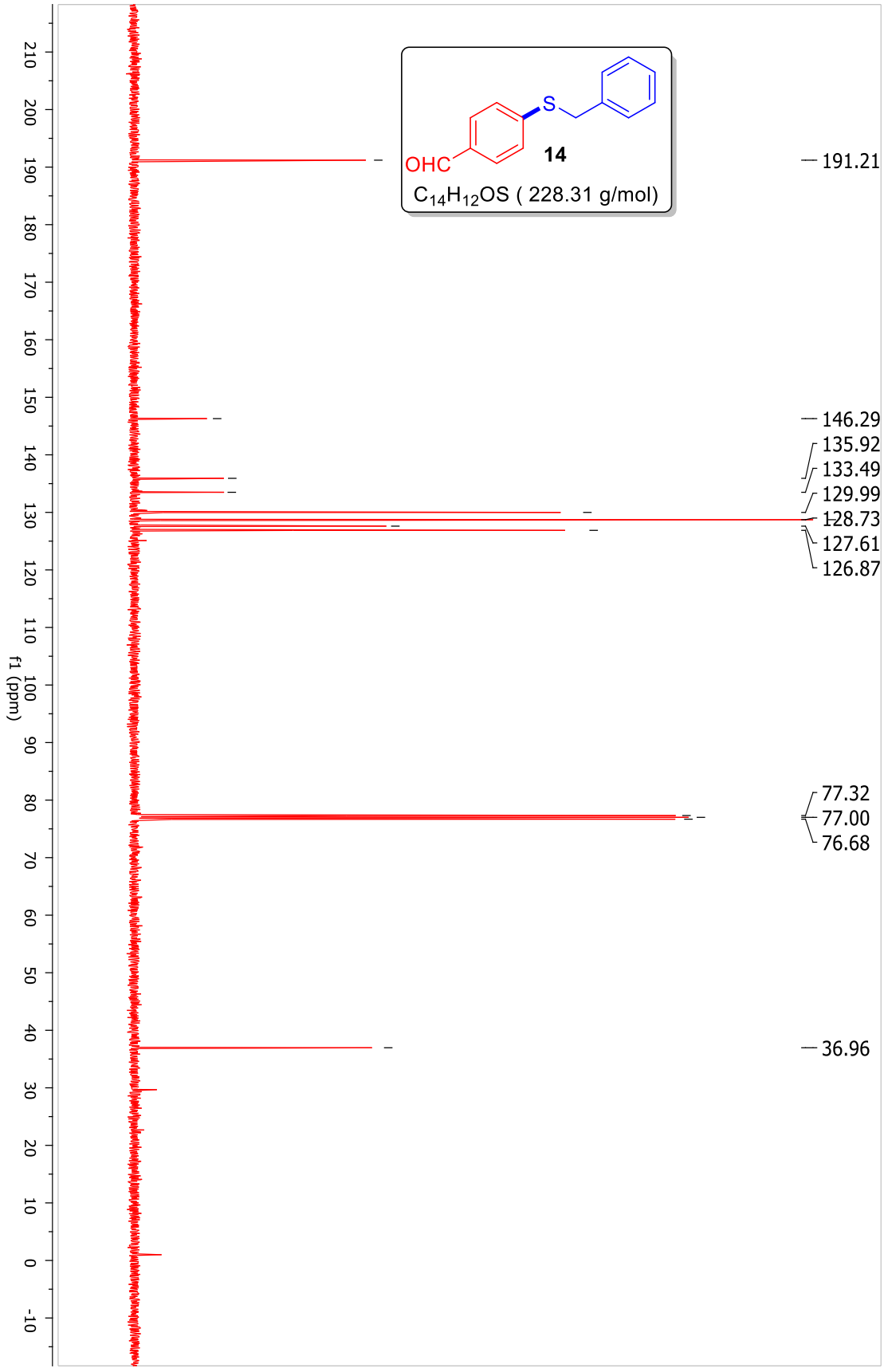
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **13:**



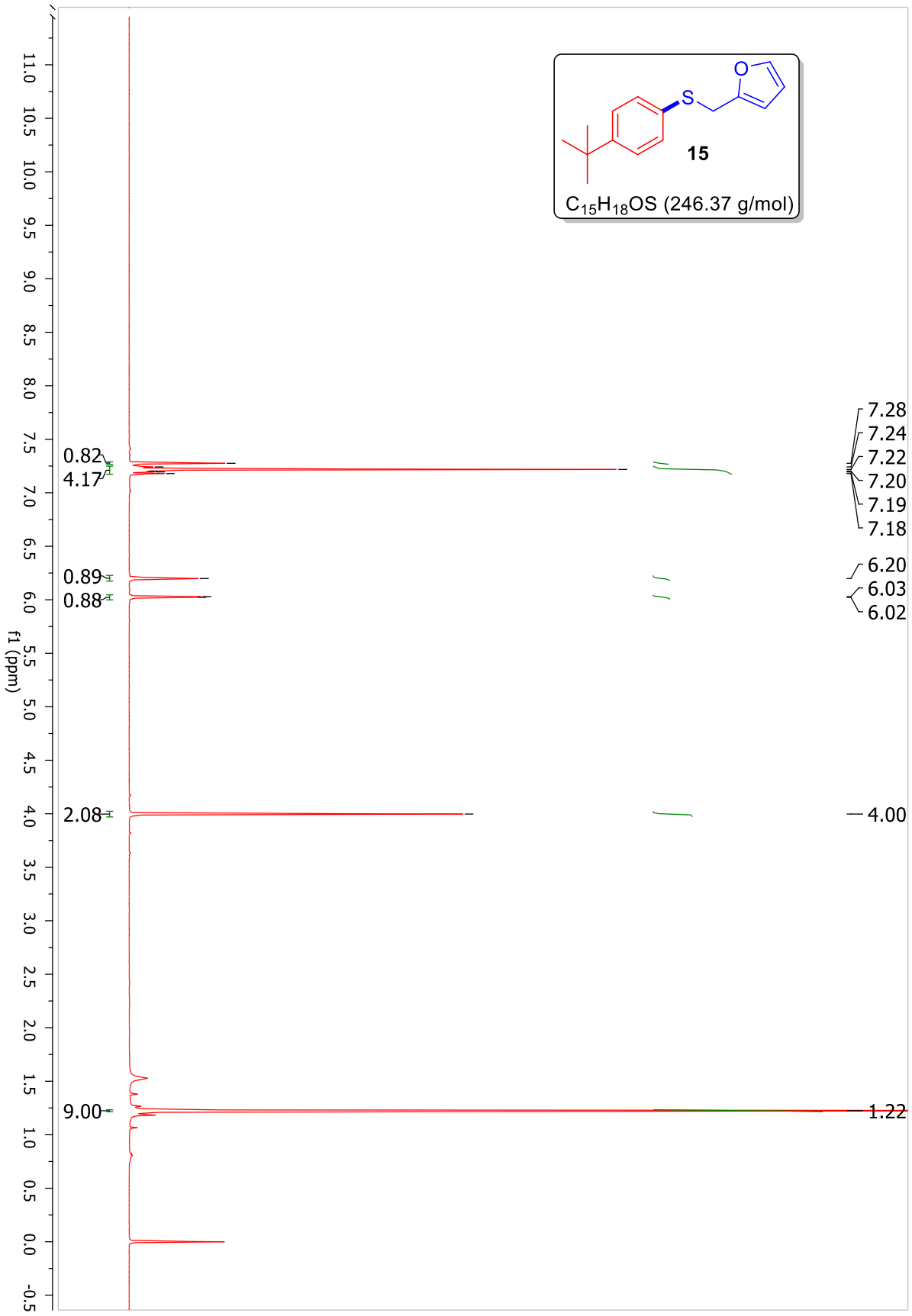
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **14:**



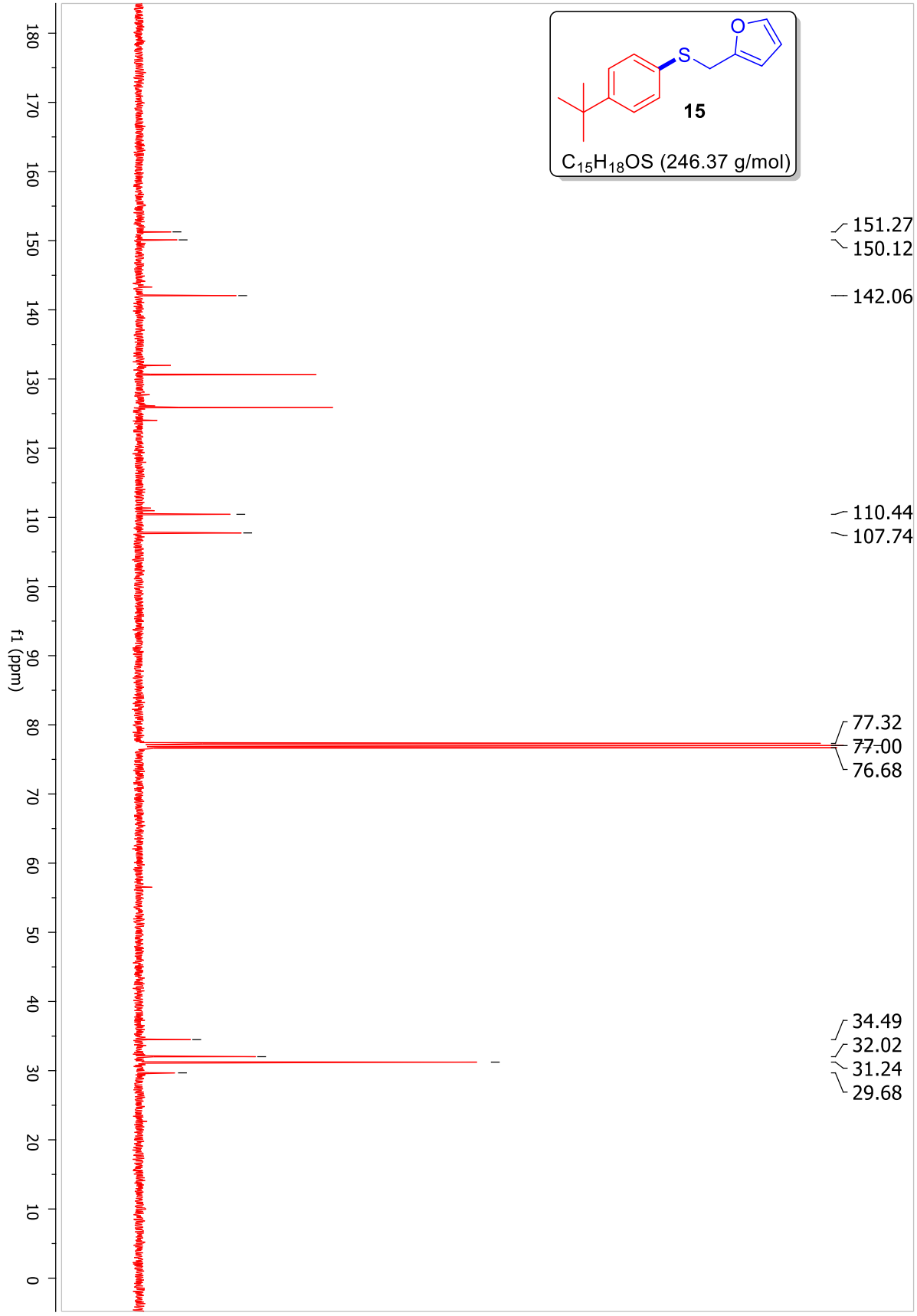
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **14:**



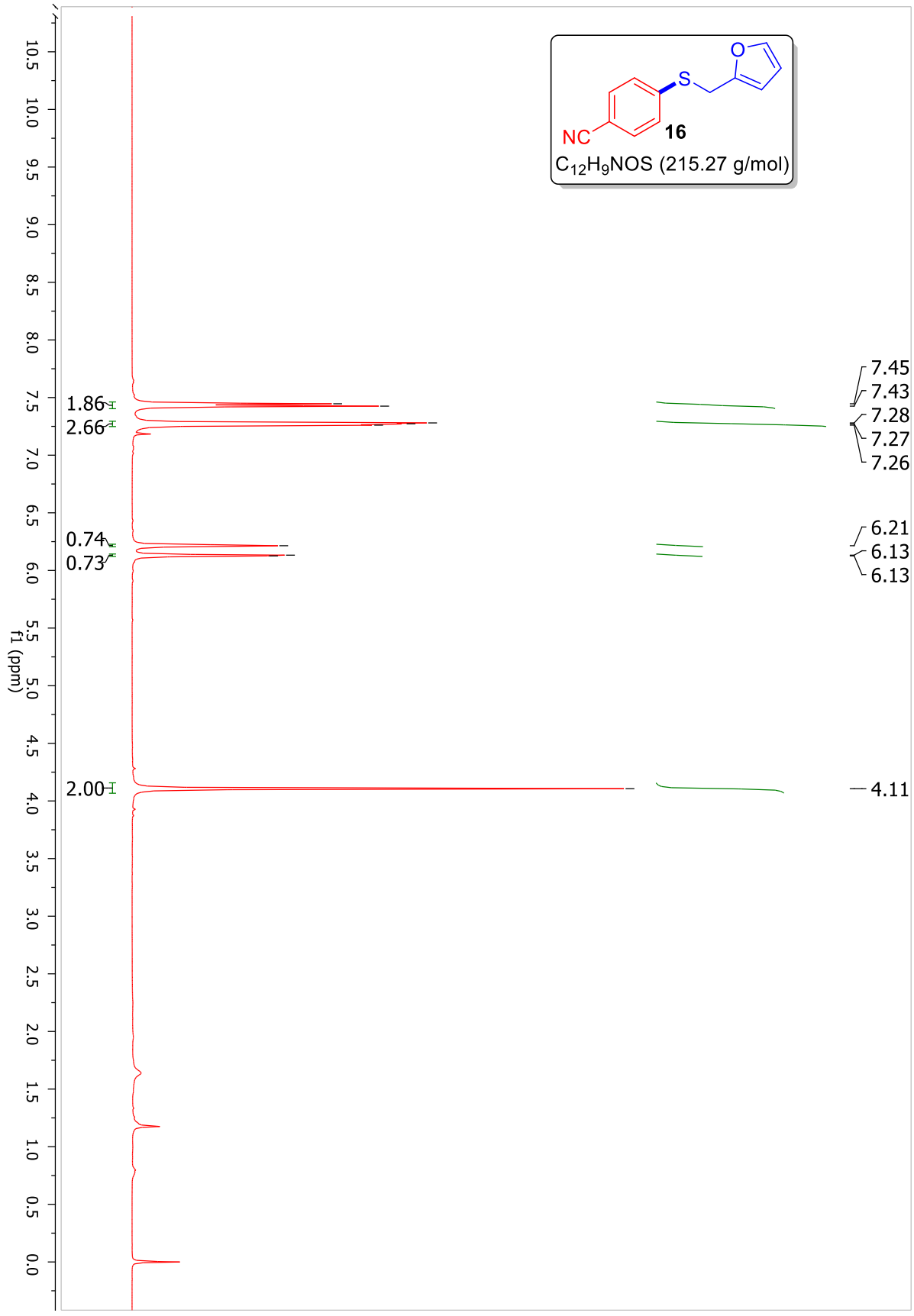
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **15:**



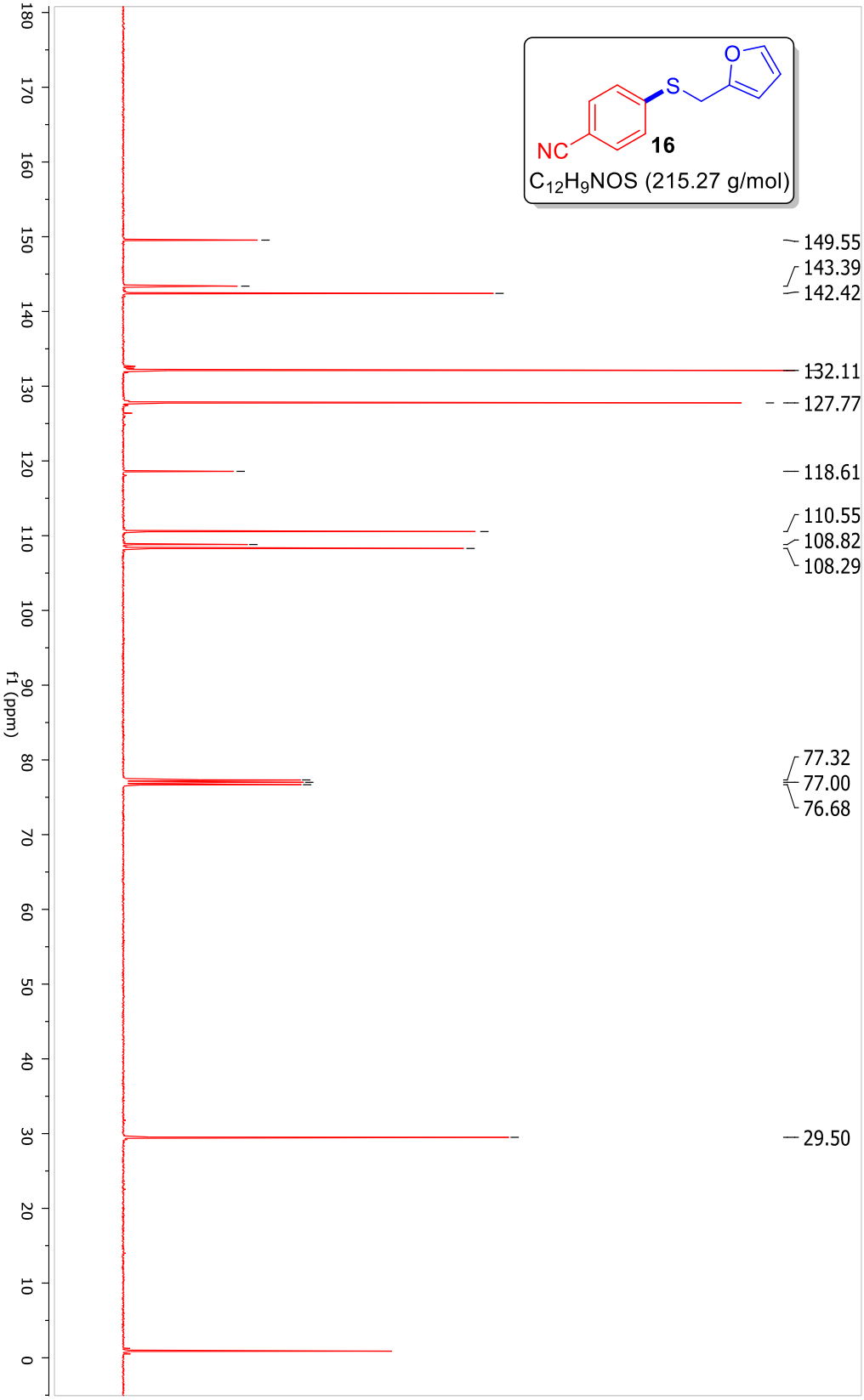
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **15:**



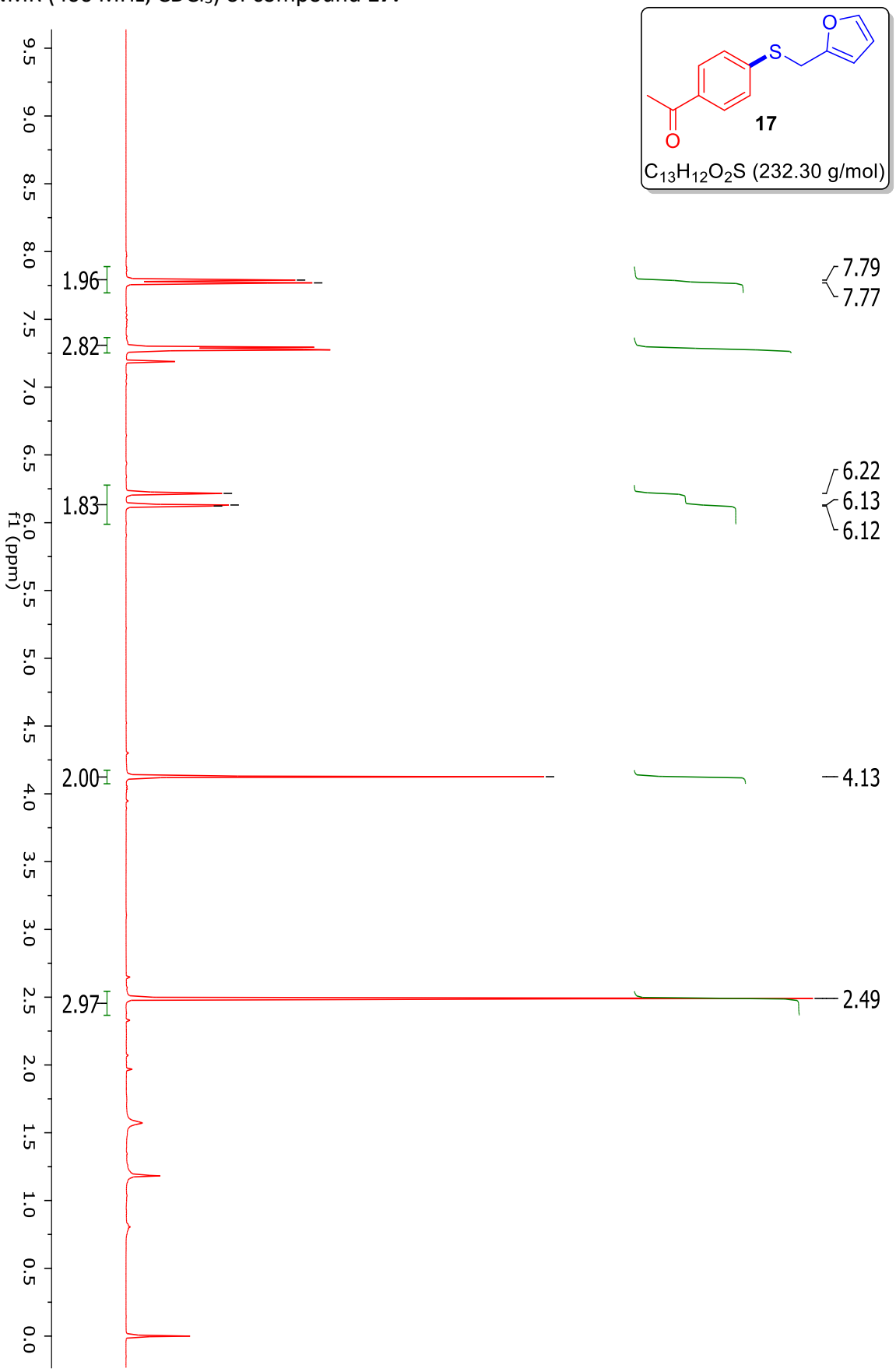
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **16:**



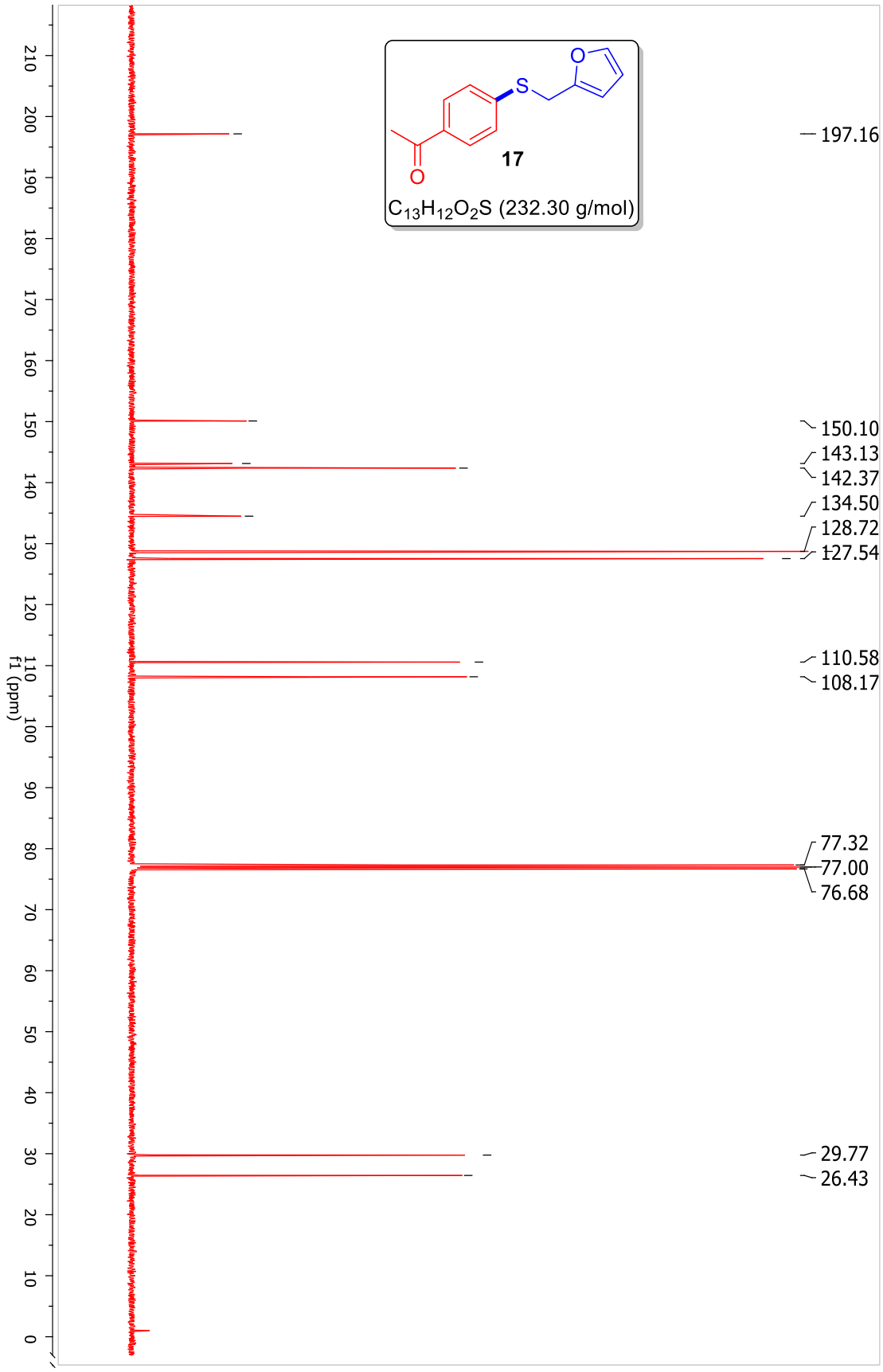
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **16:**



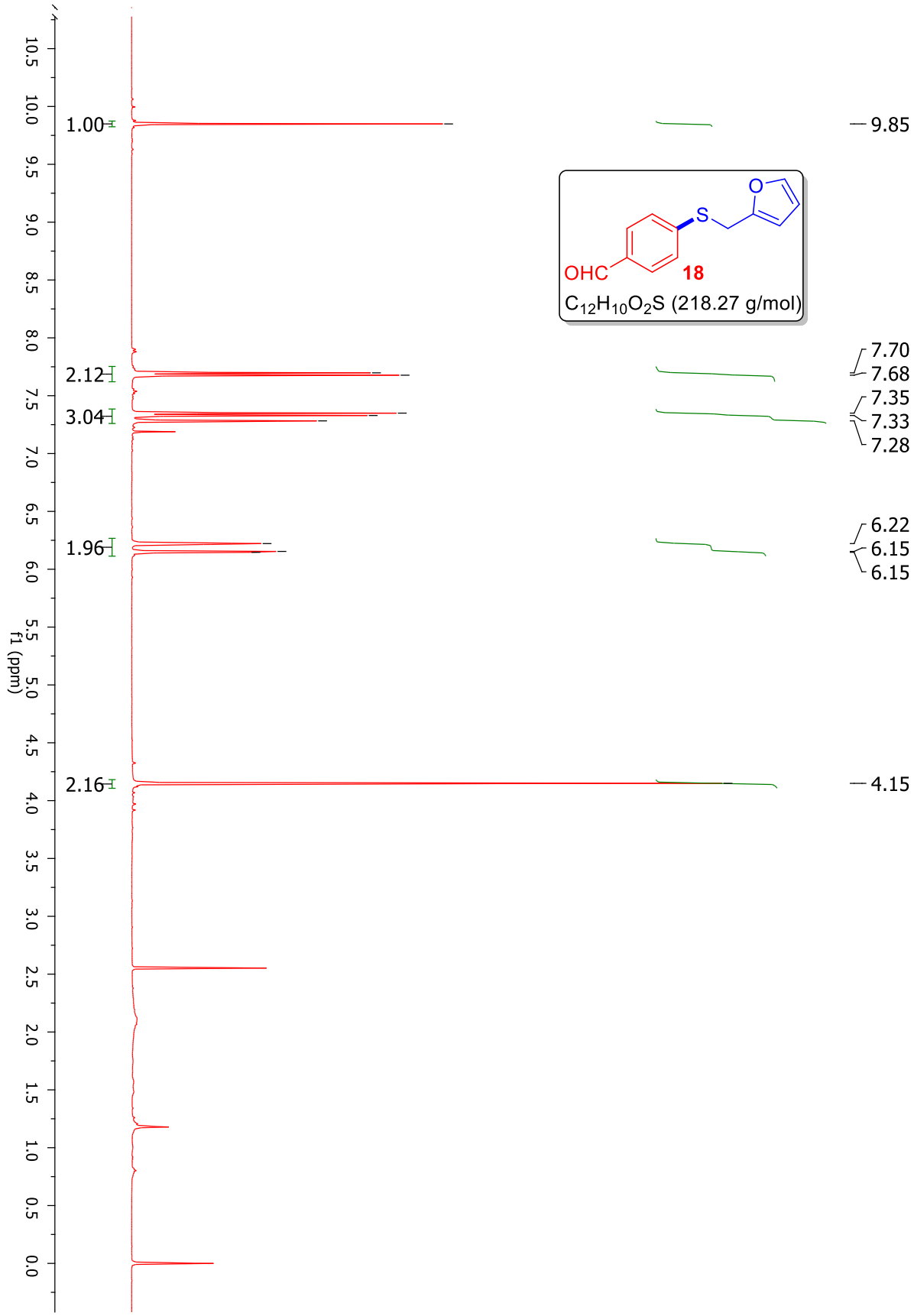
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **17:**



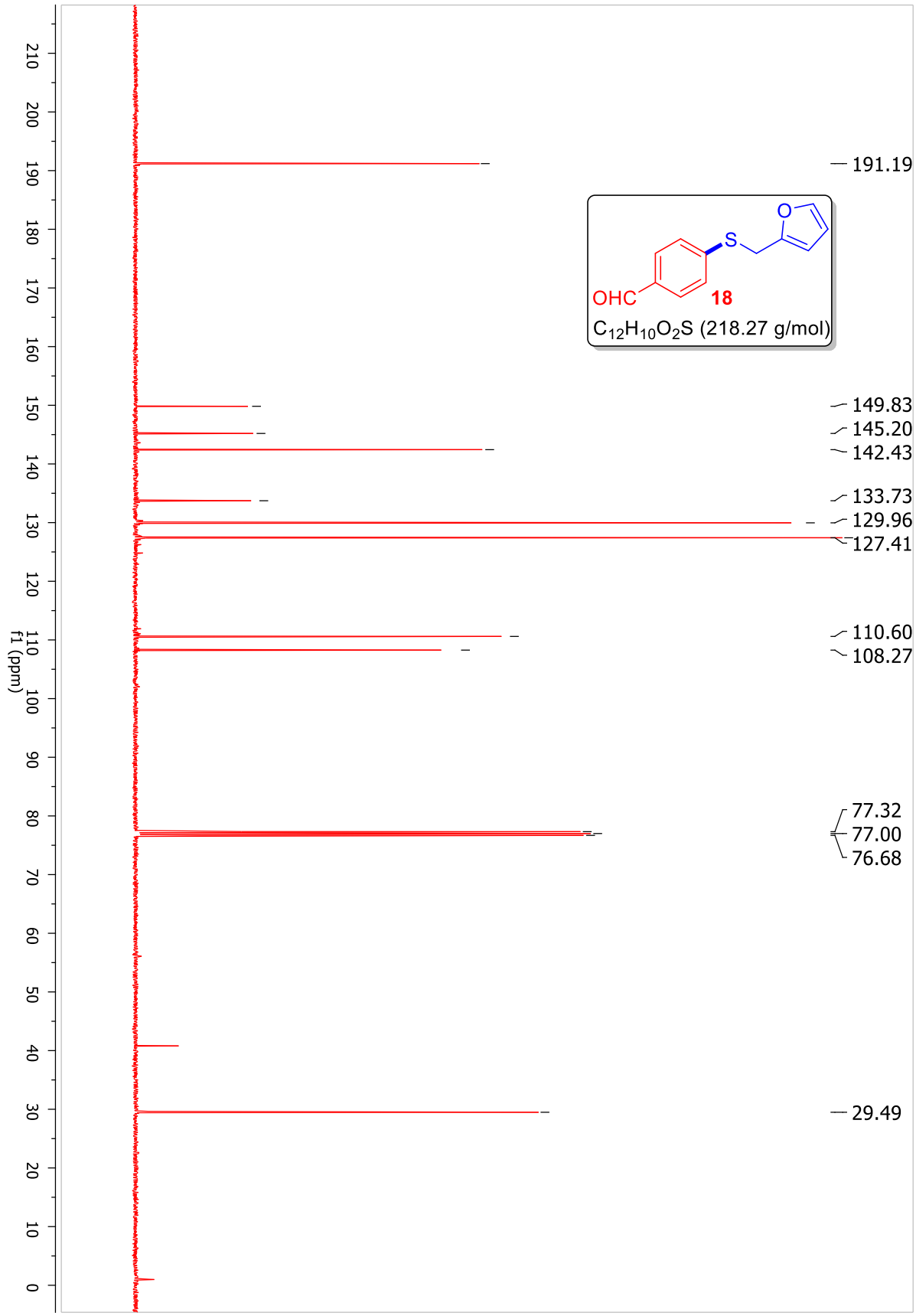
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **17:**



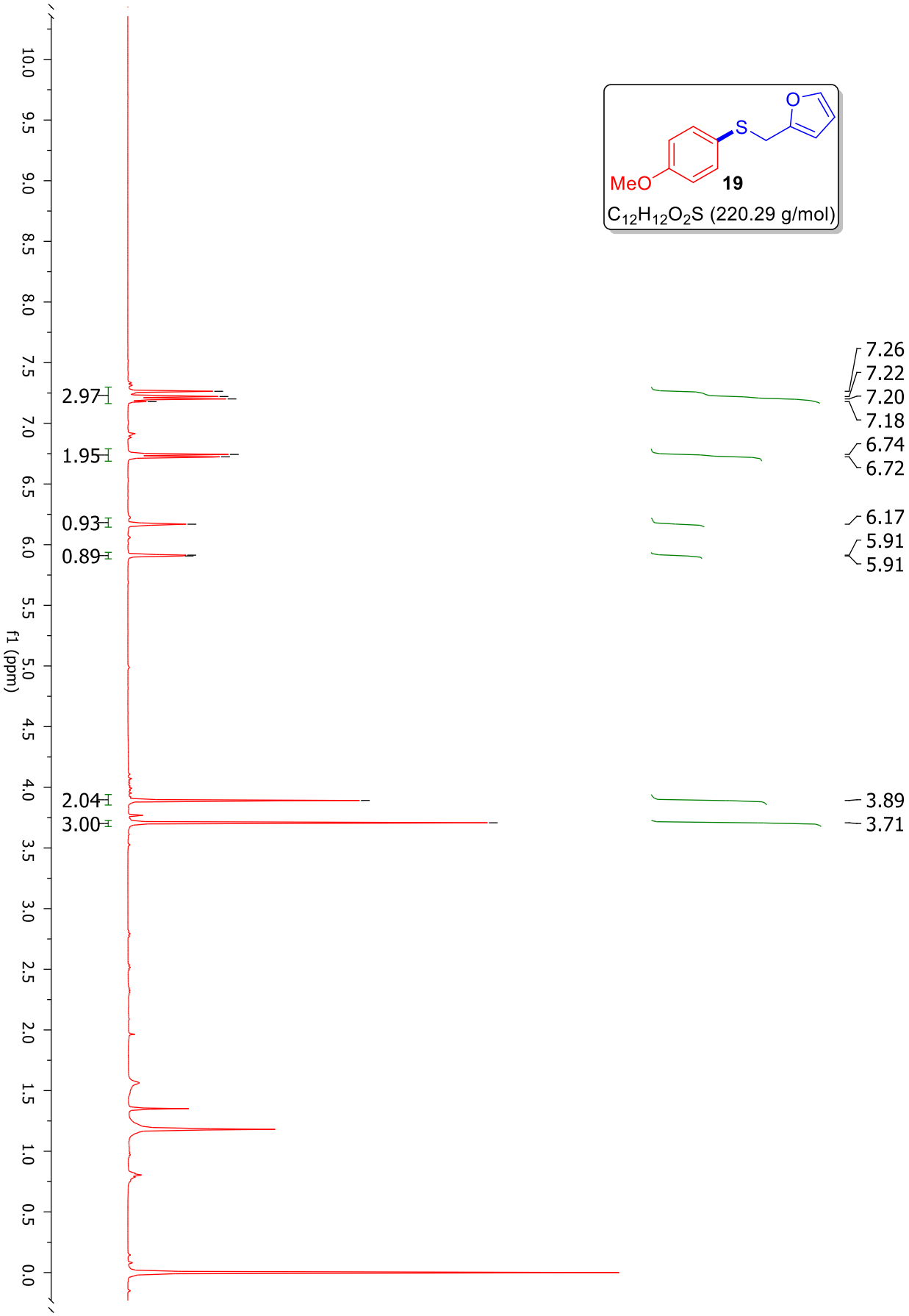
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **18:**



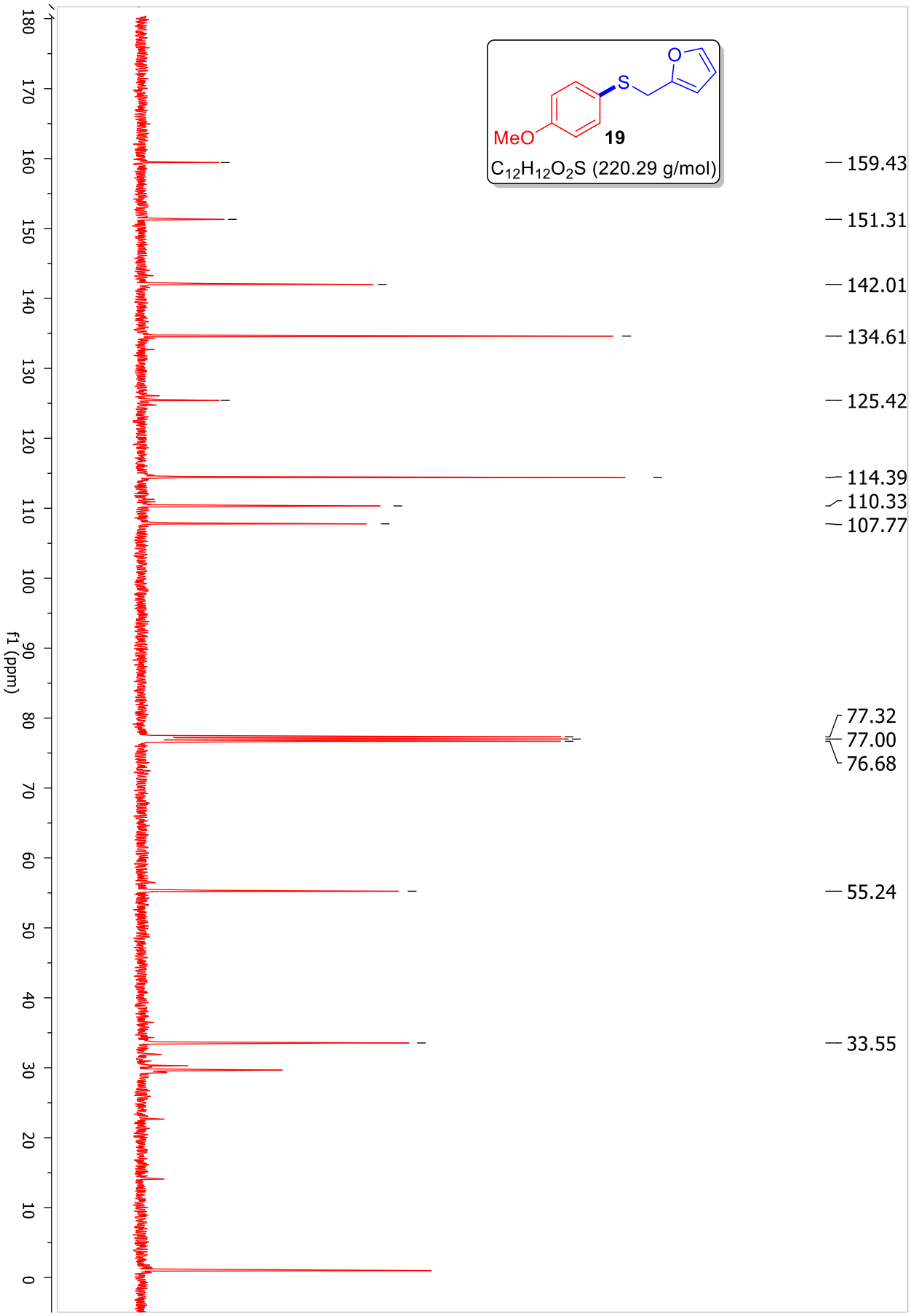
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **18:**



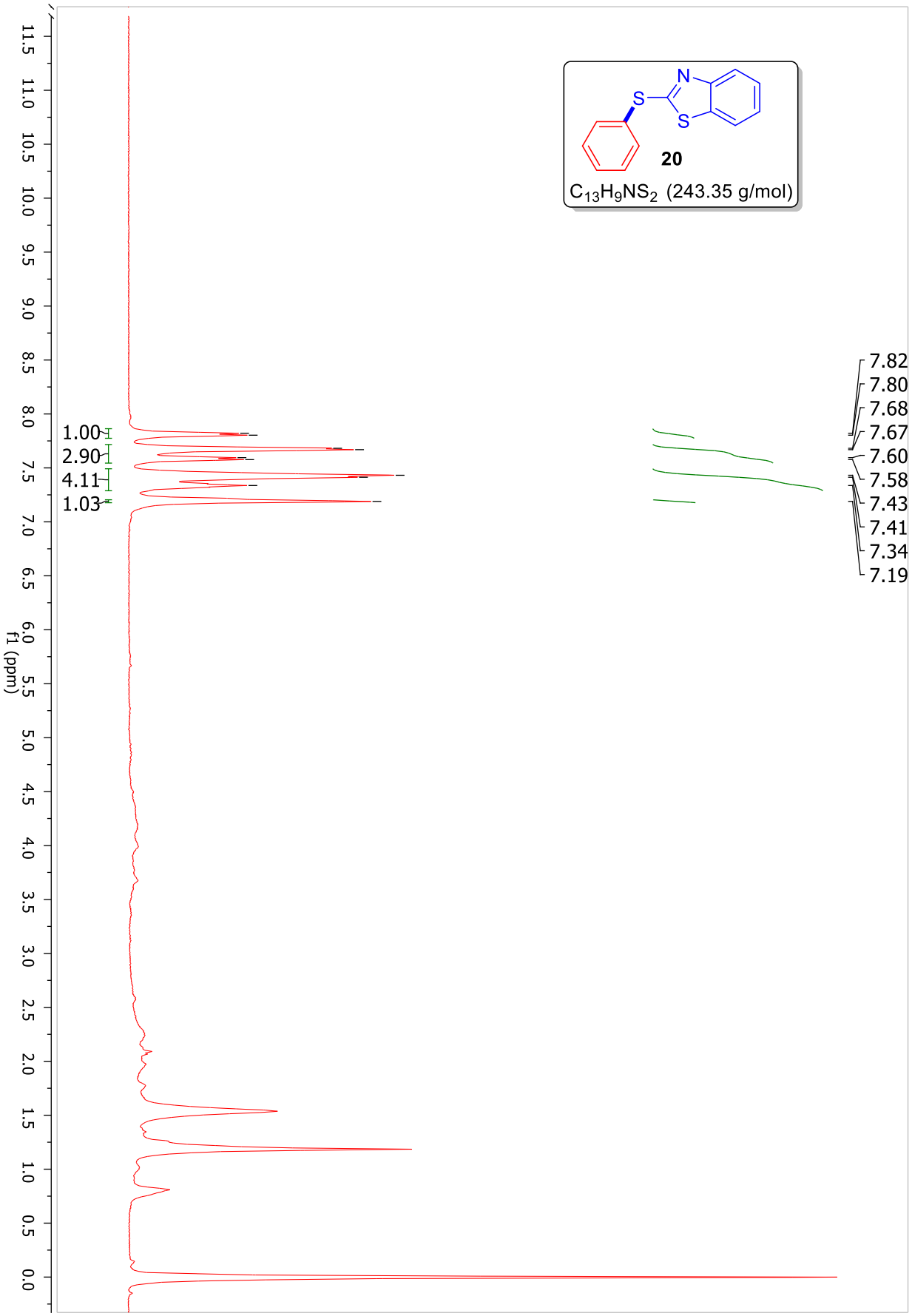
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **19:**



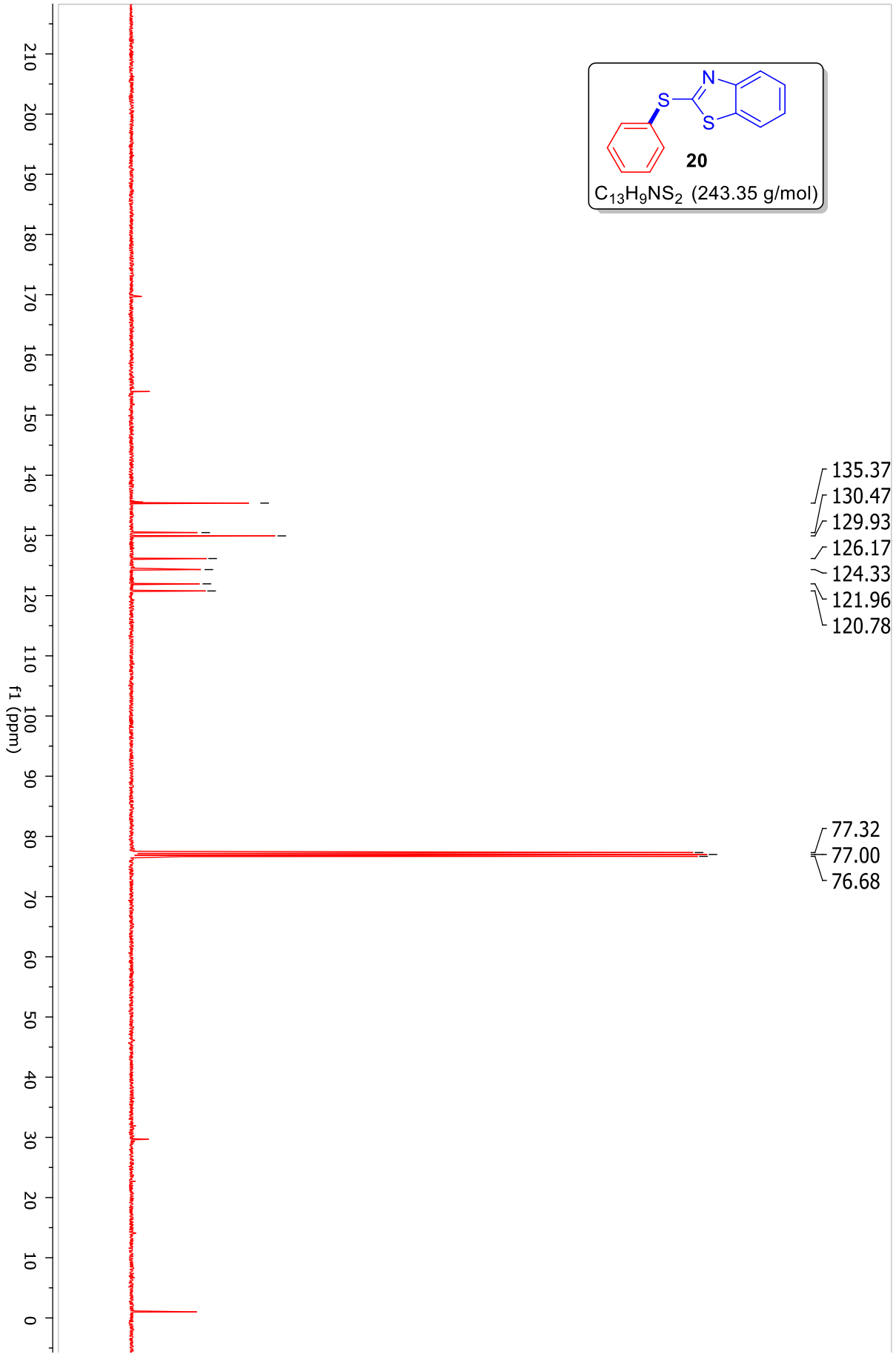
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **19:**



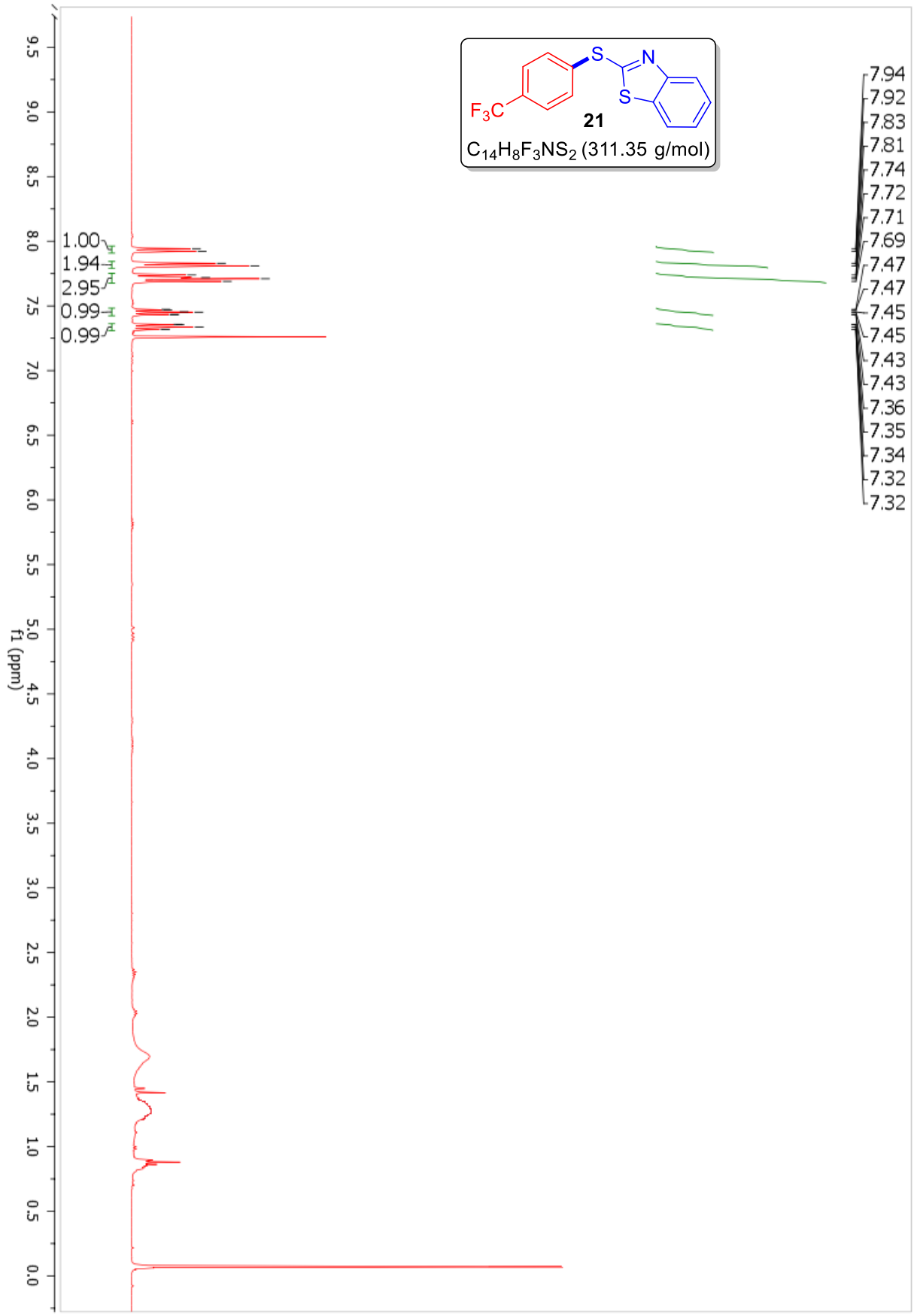
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **20:**



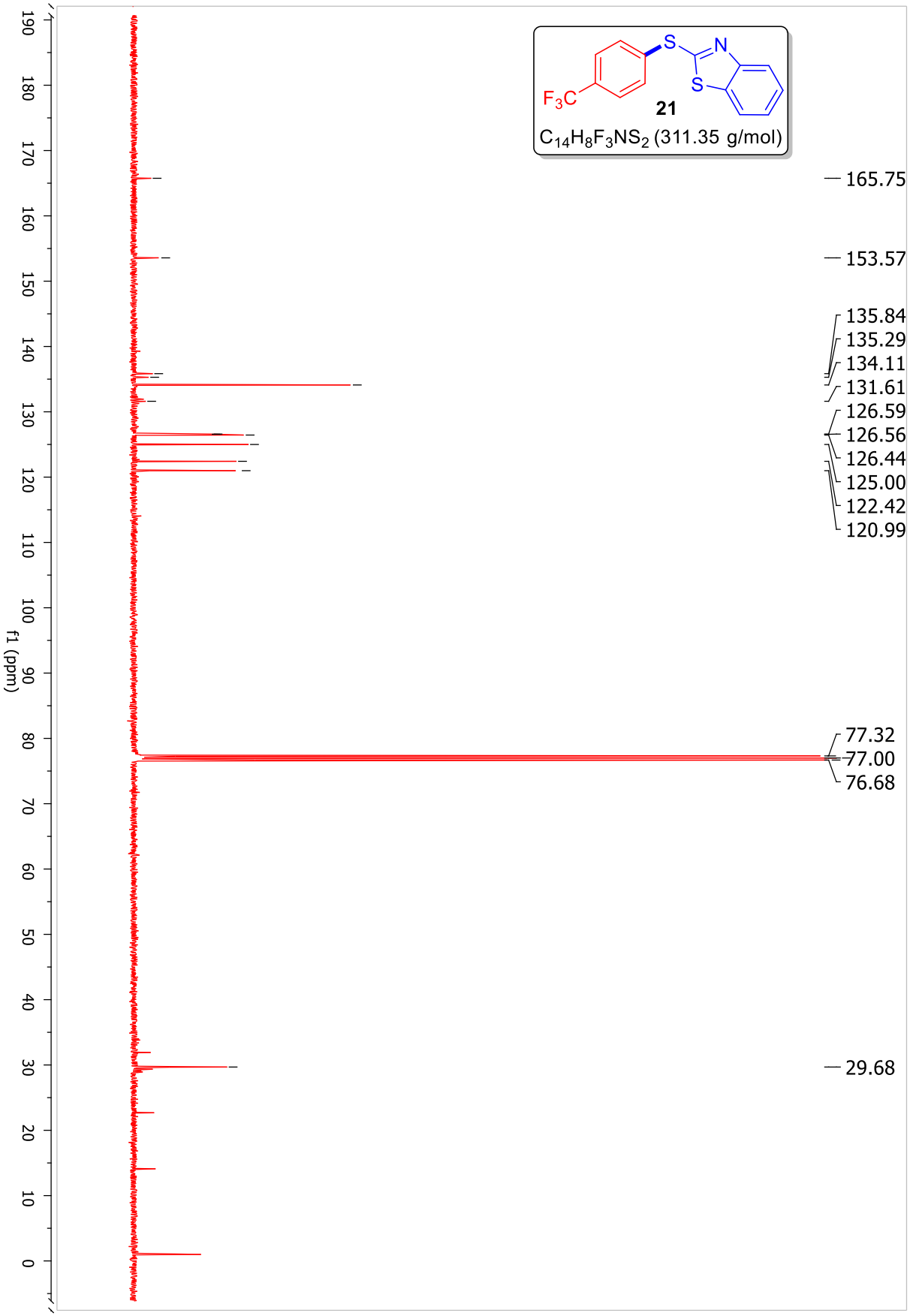
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **20:**



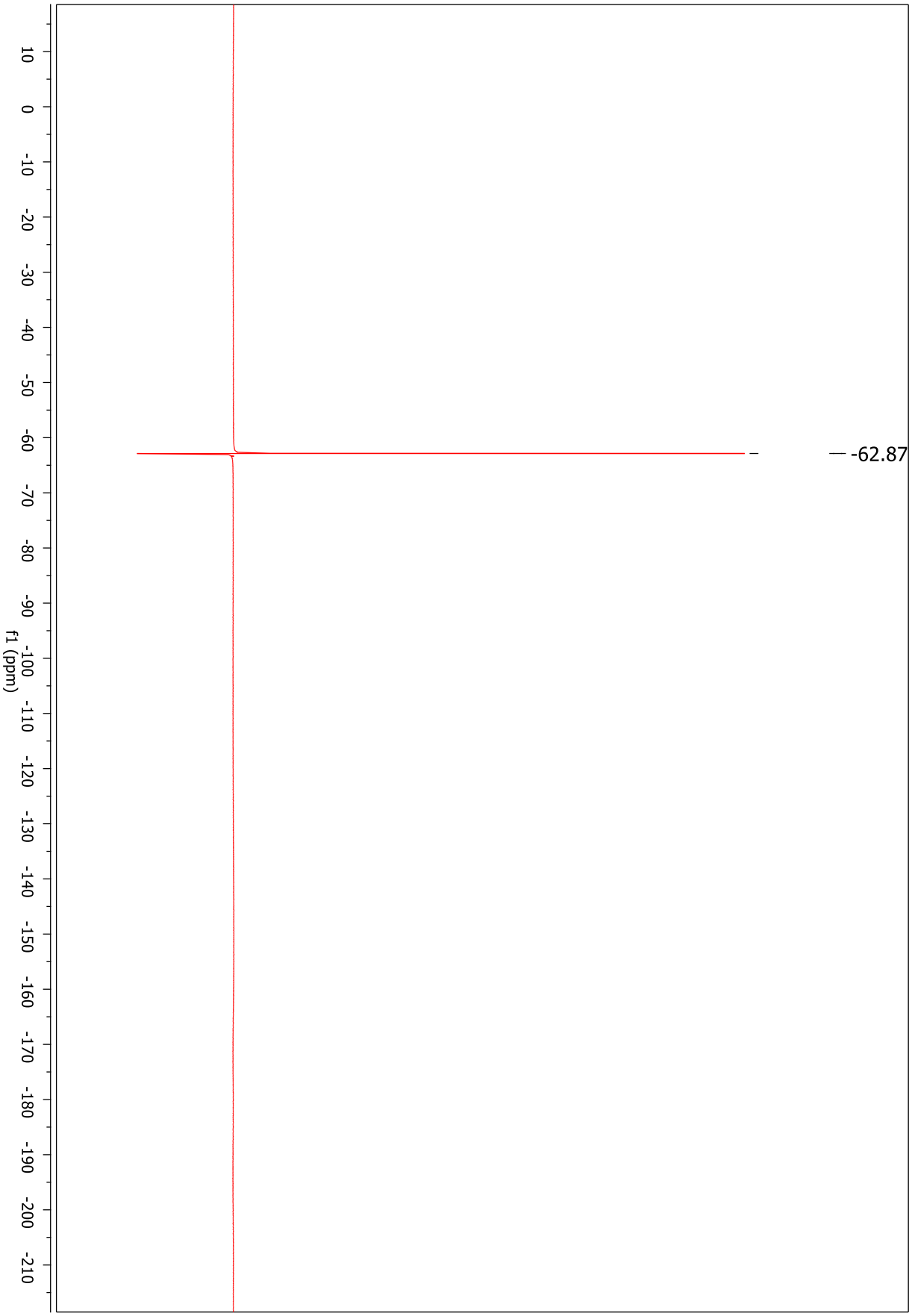
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **21:**



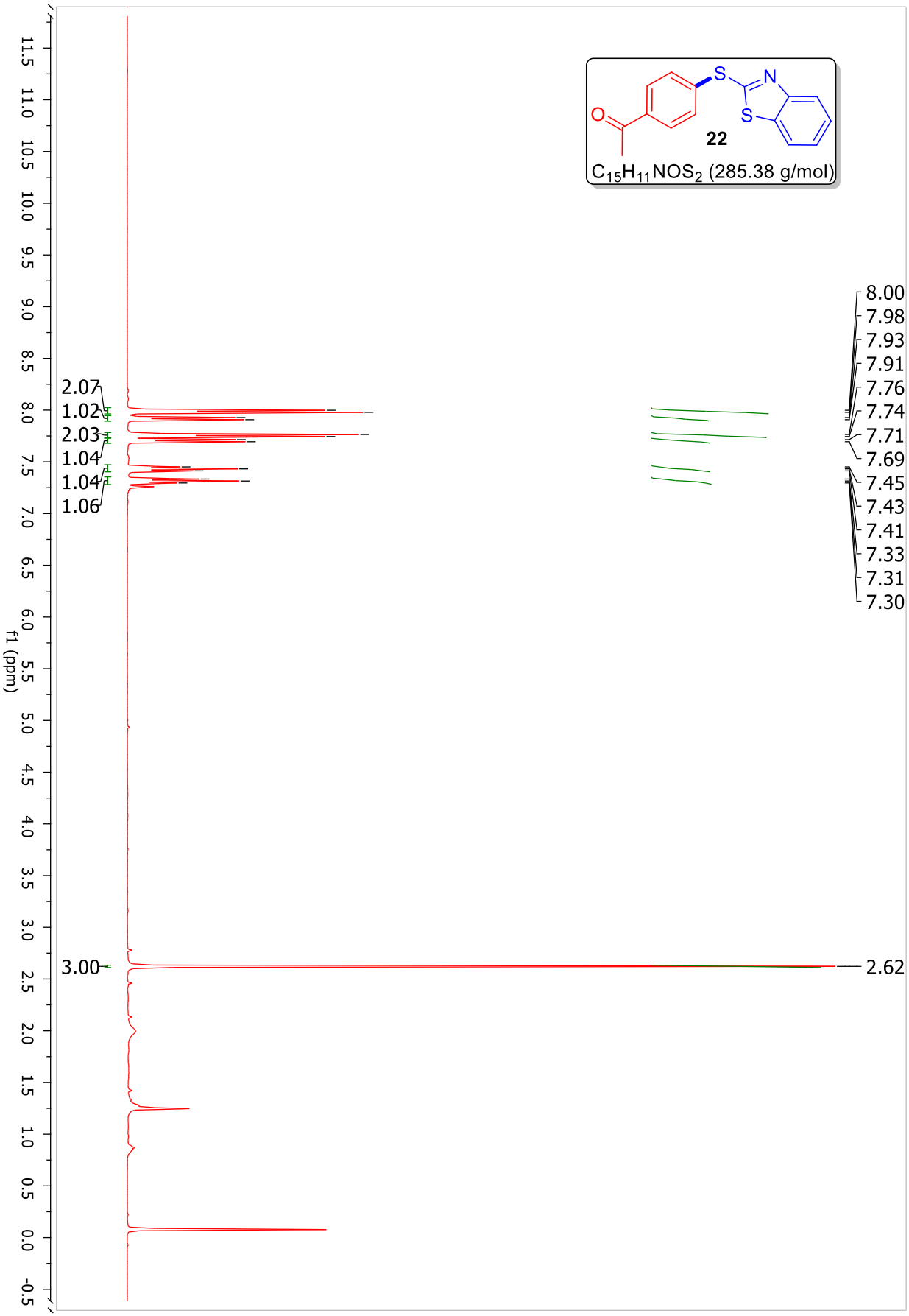
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **21:**



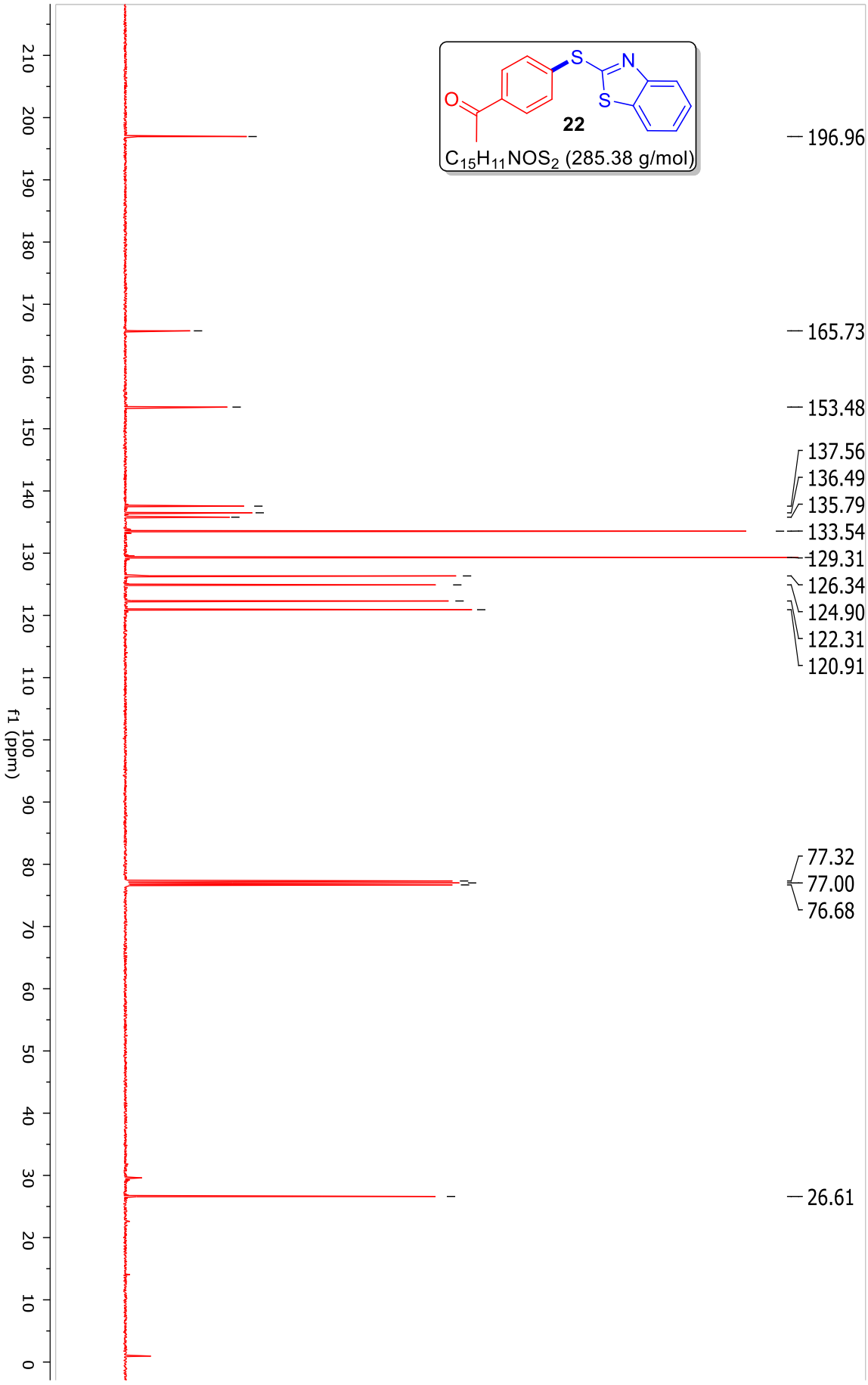
^{19}F-NMR (377 MHz, $CDCl_3$) of Compound **21:**



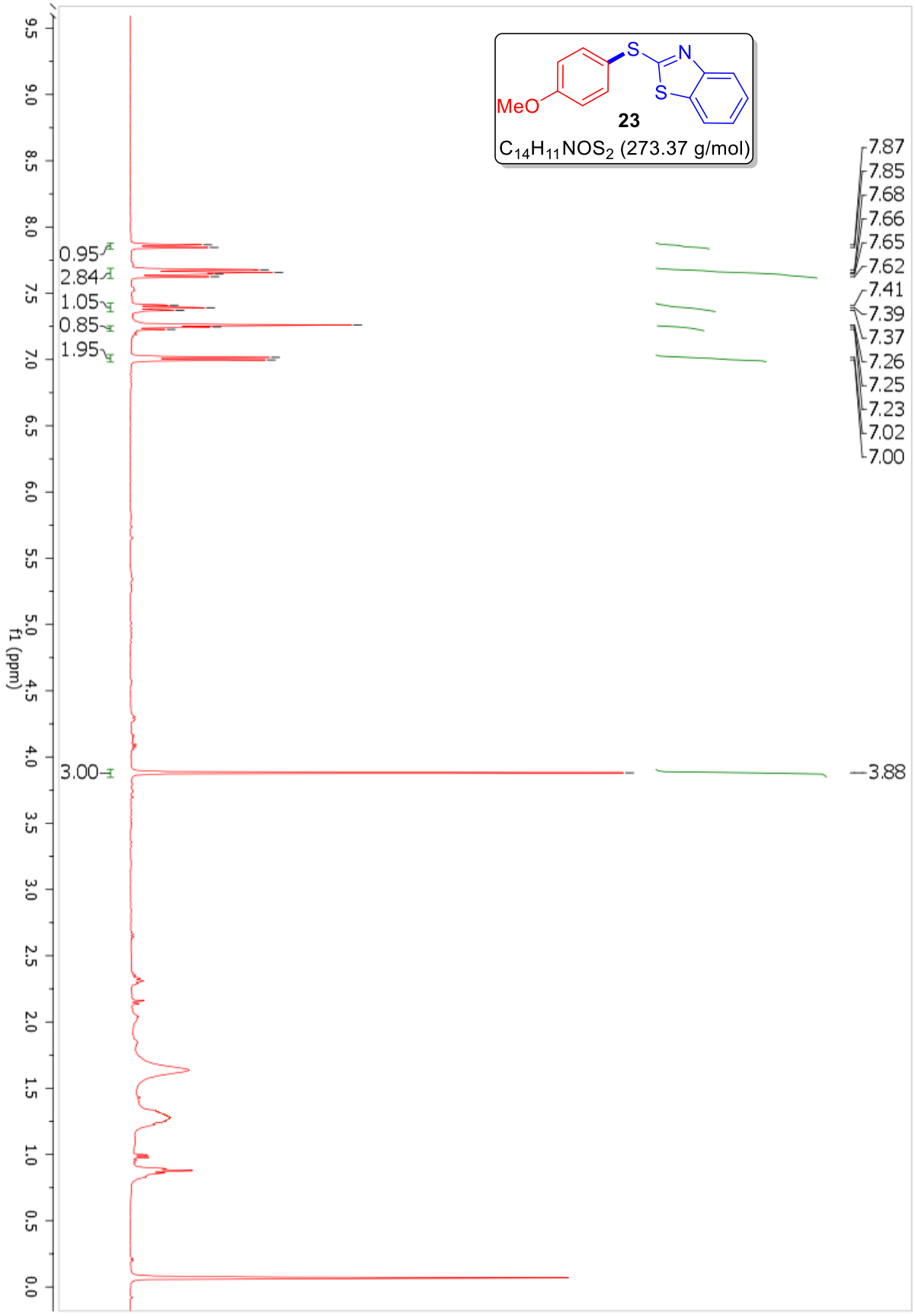
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **22:**



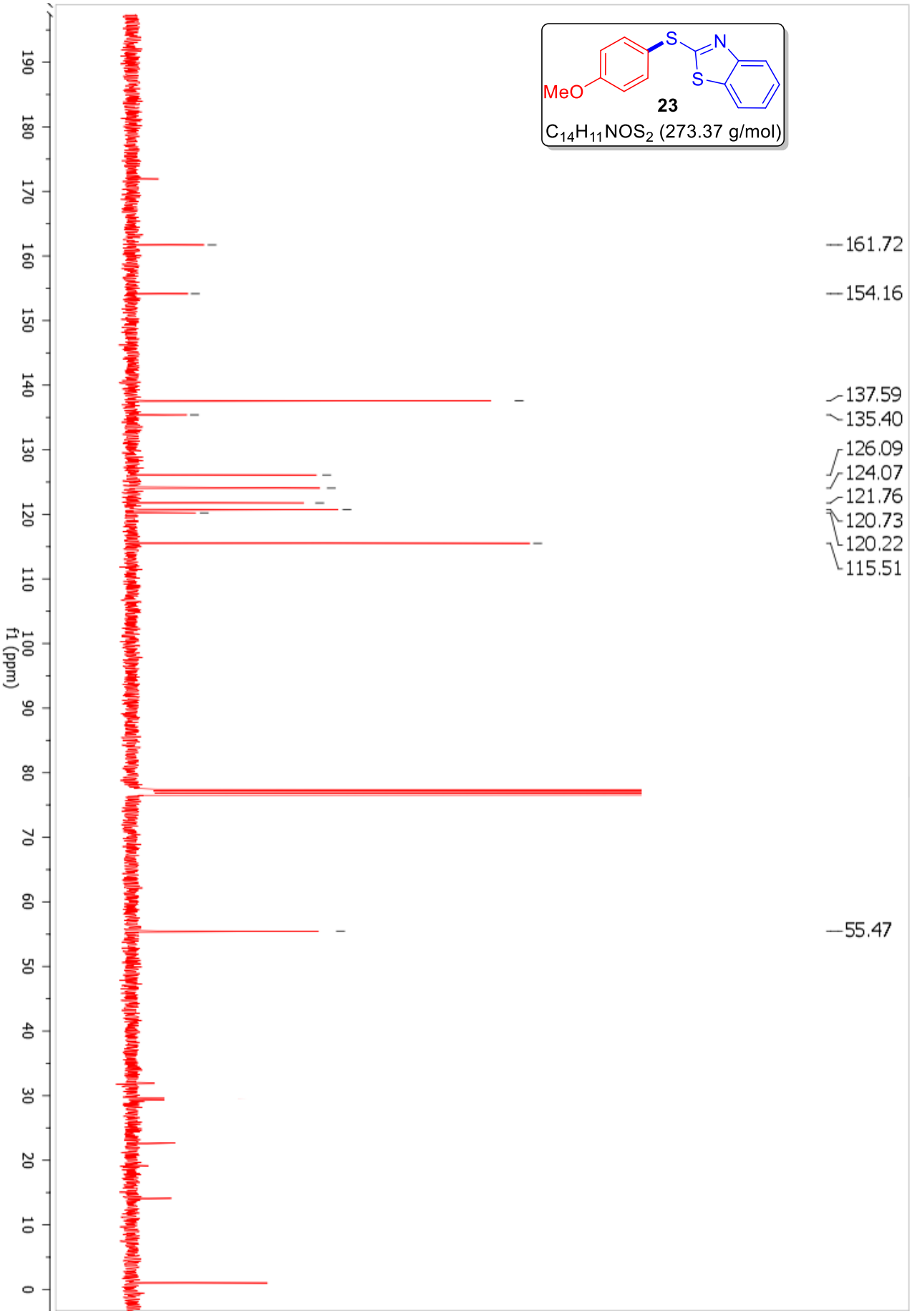
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **22:**



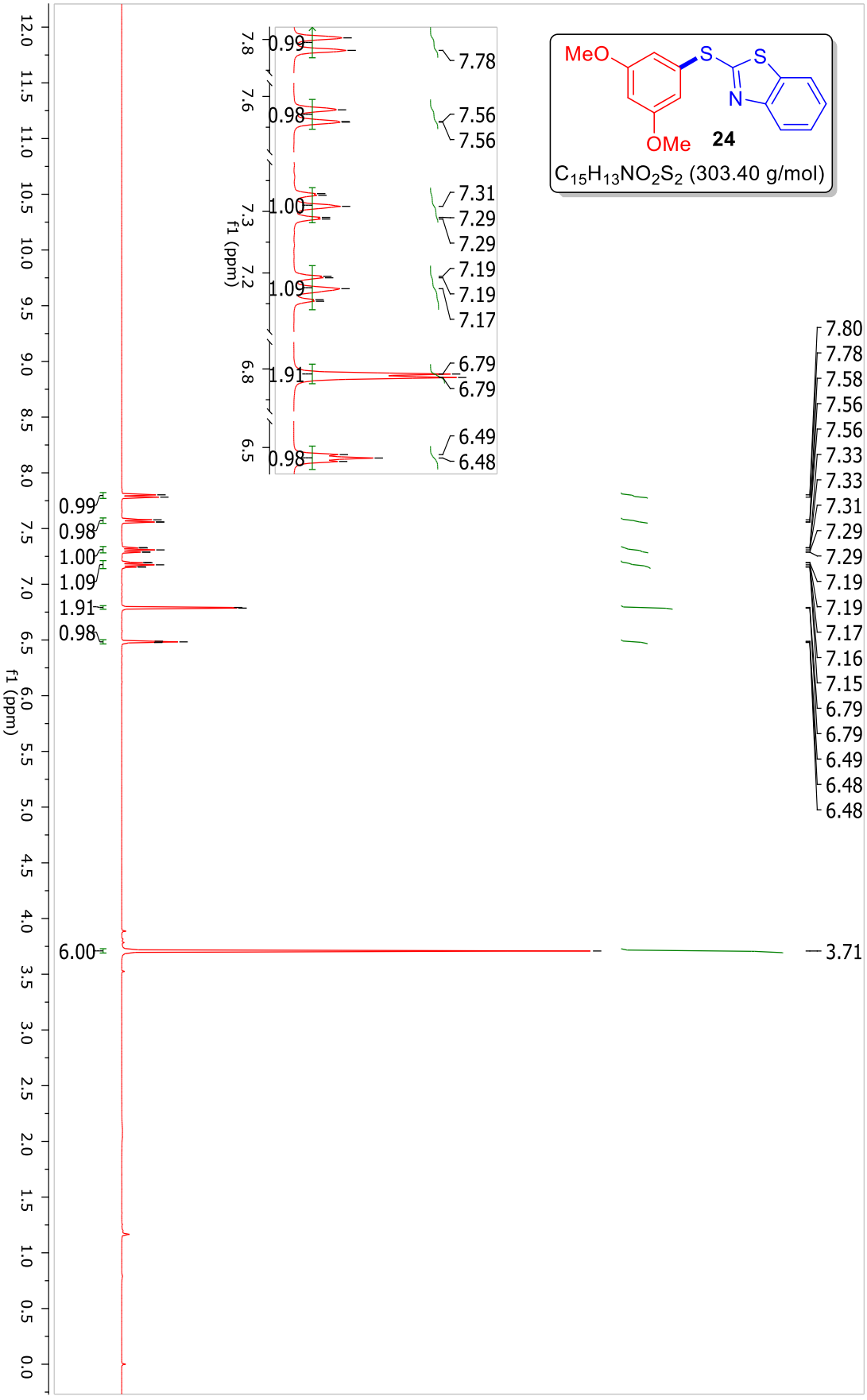
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **23:**



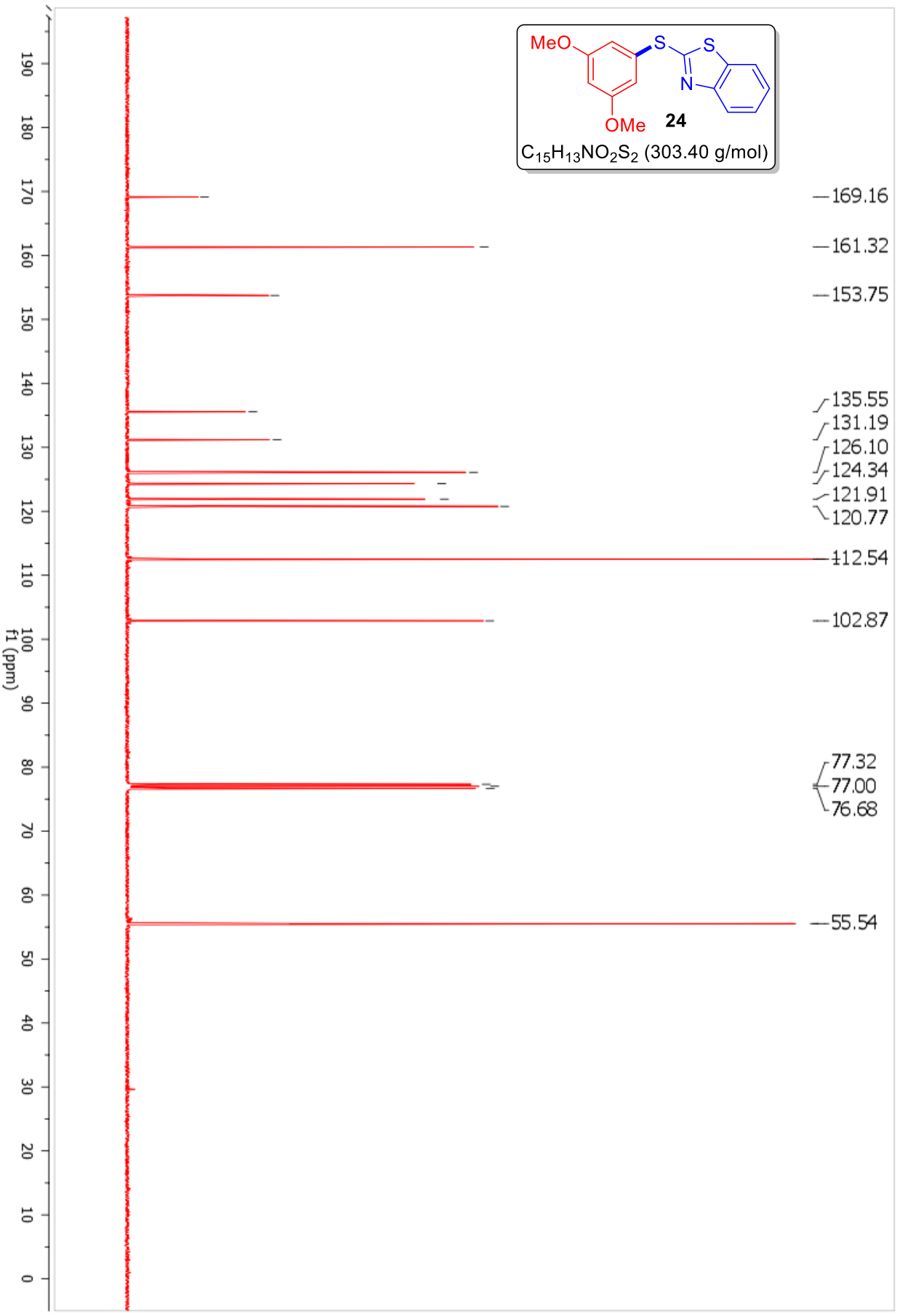
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **23:**



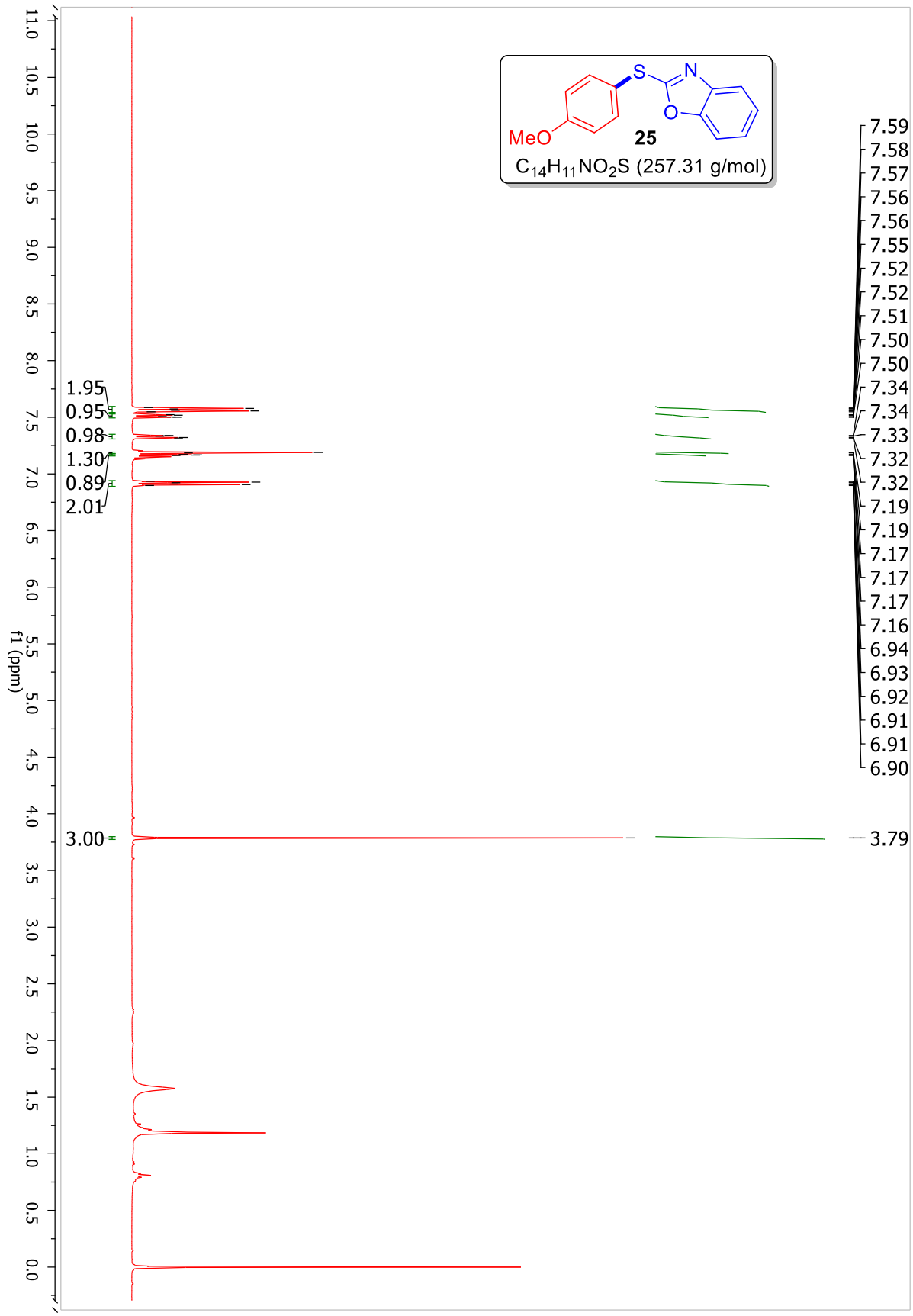
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **24:**



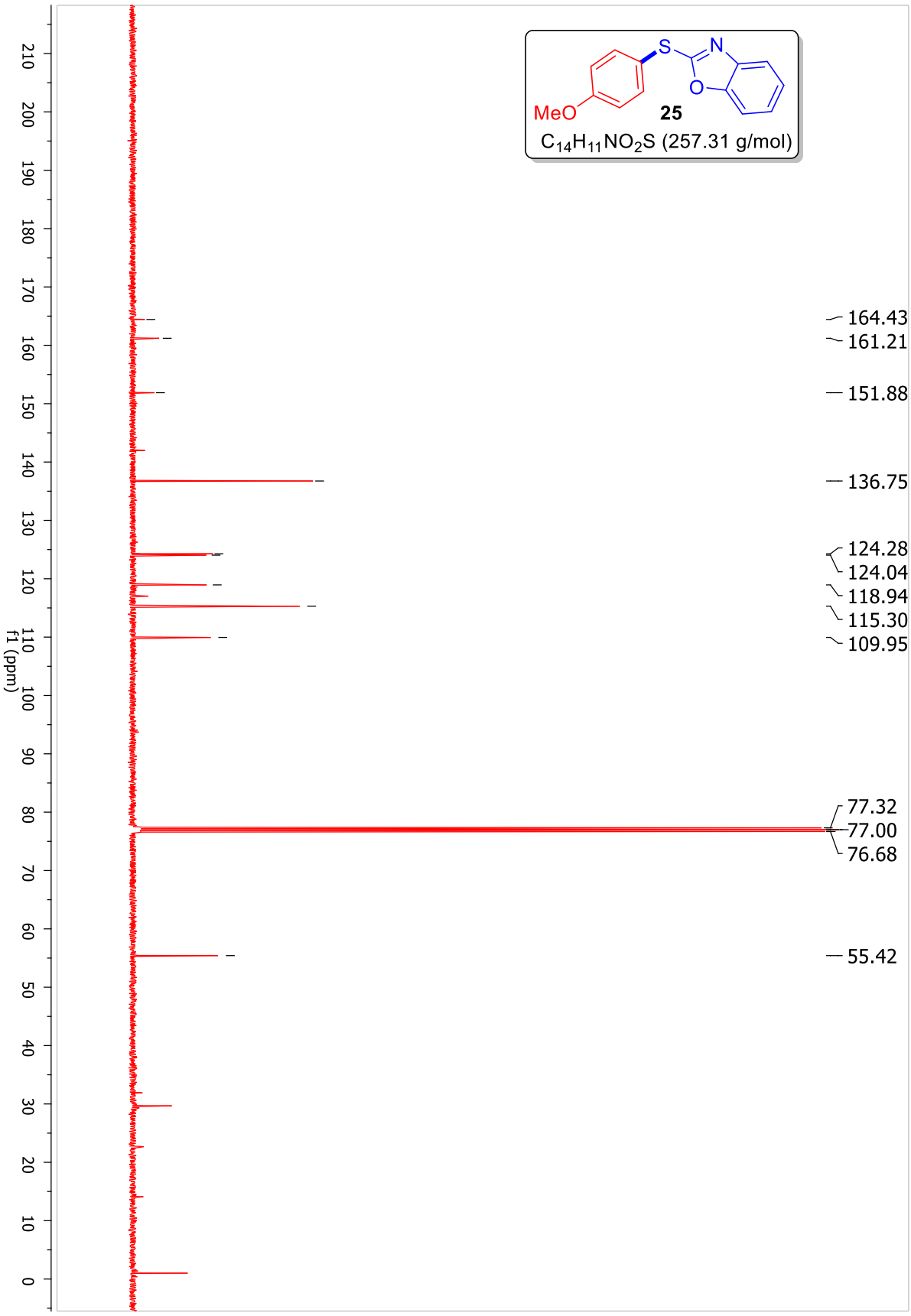
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **24:**



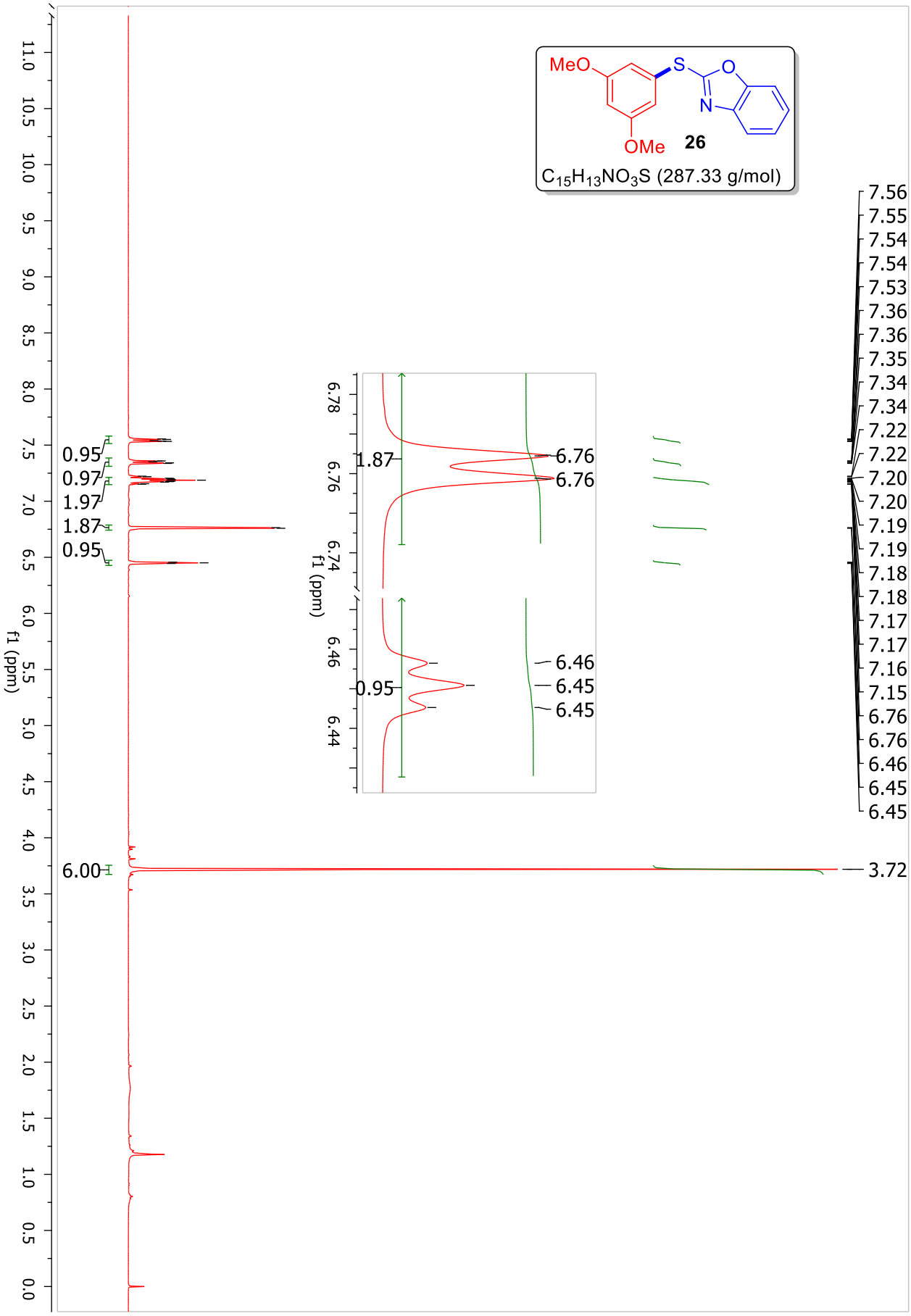
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **25:**



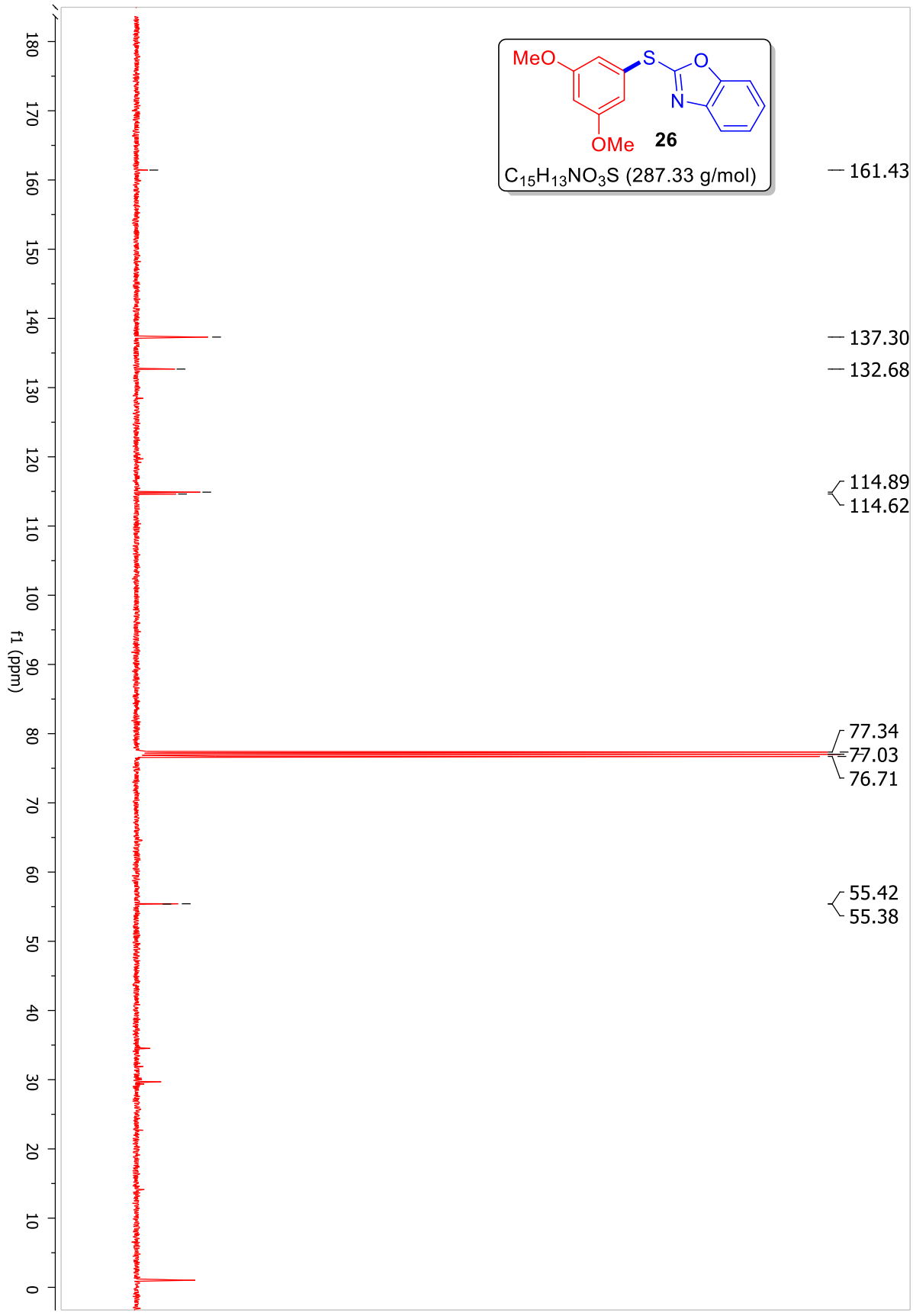
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **25:**



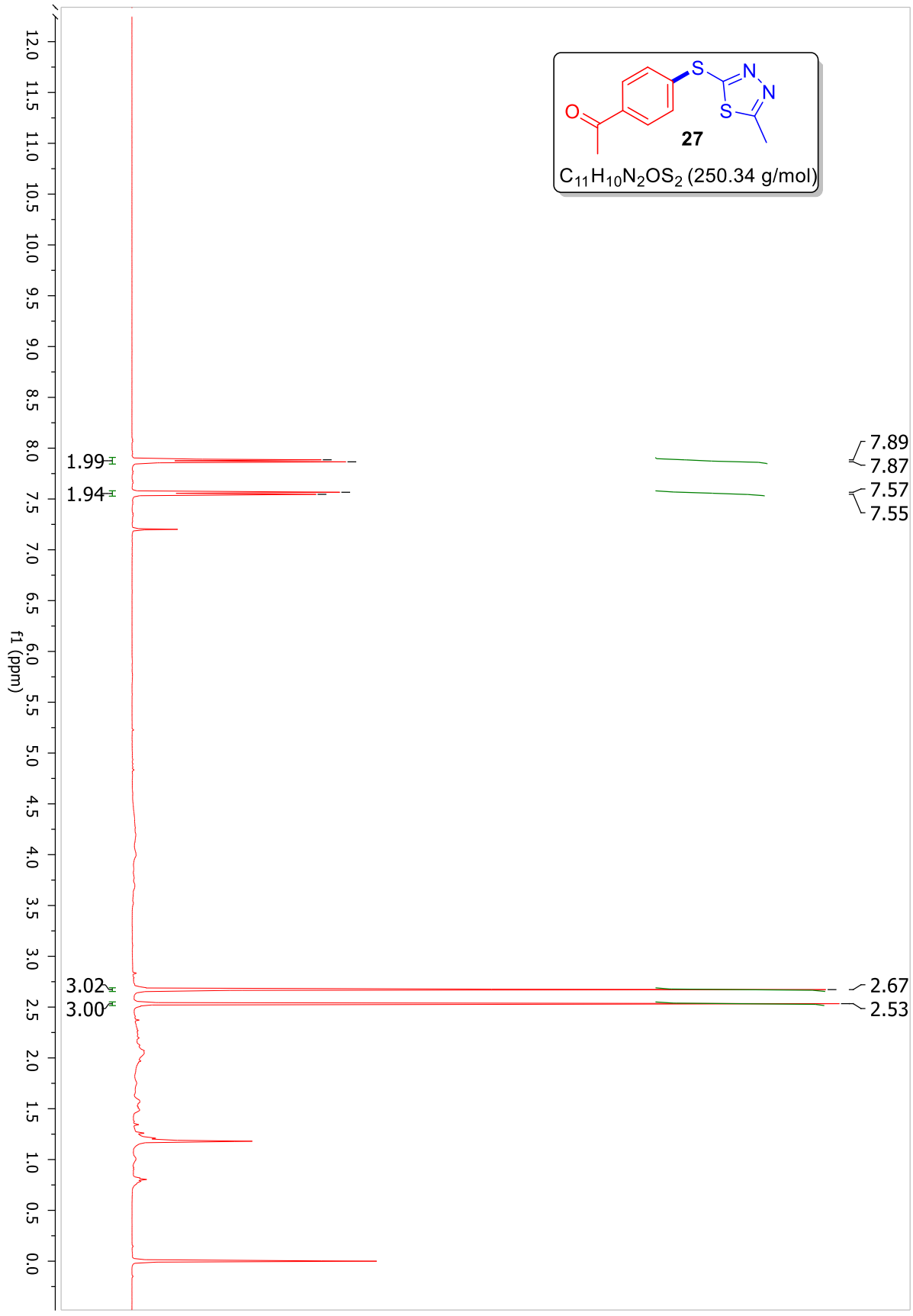
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **26:**



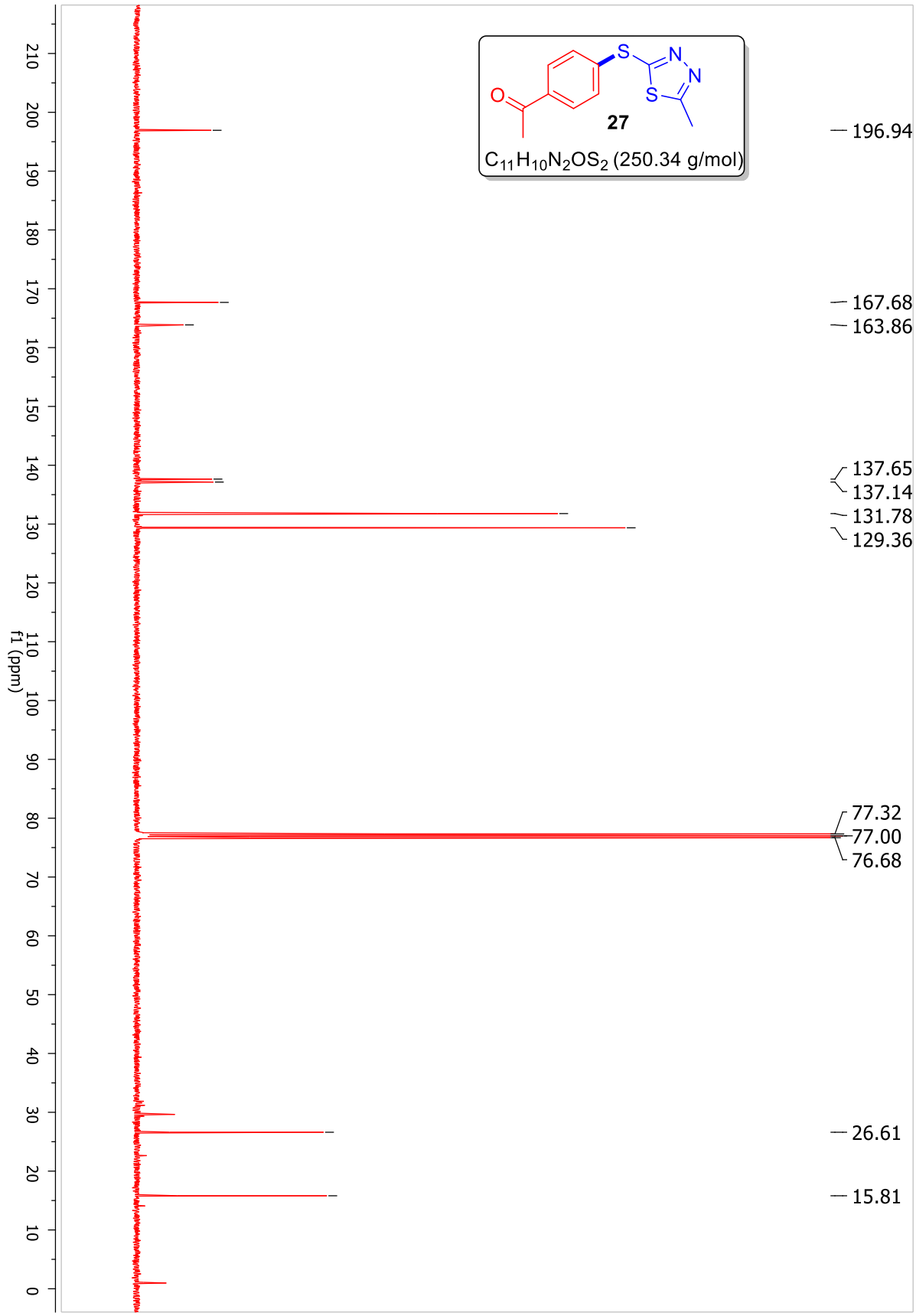
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **26:**



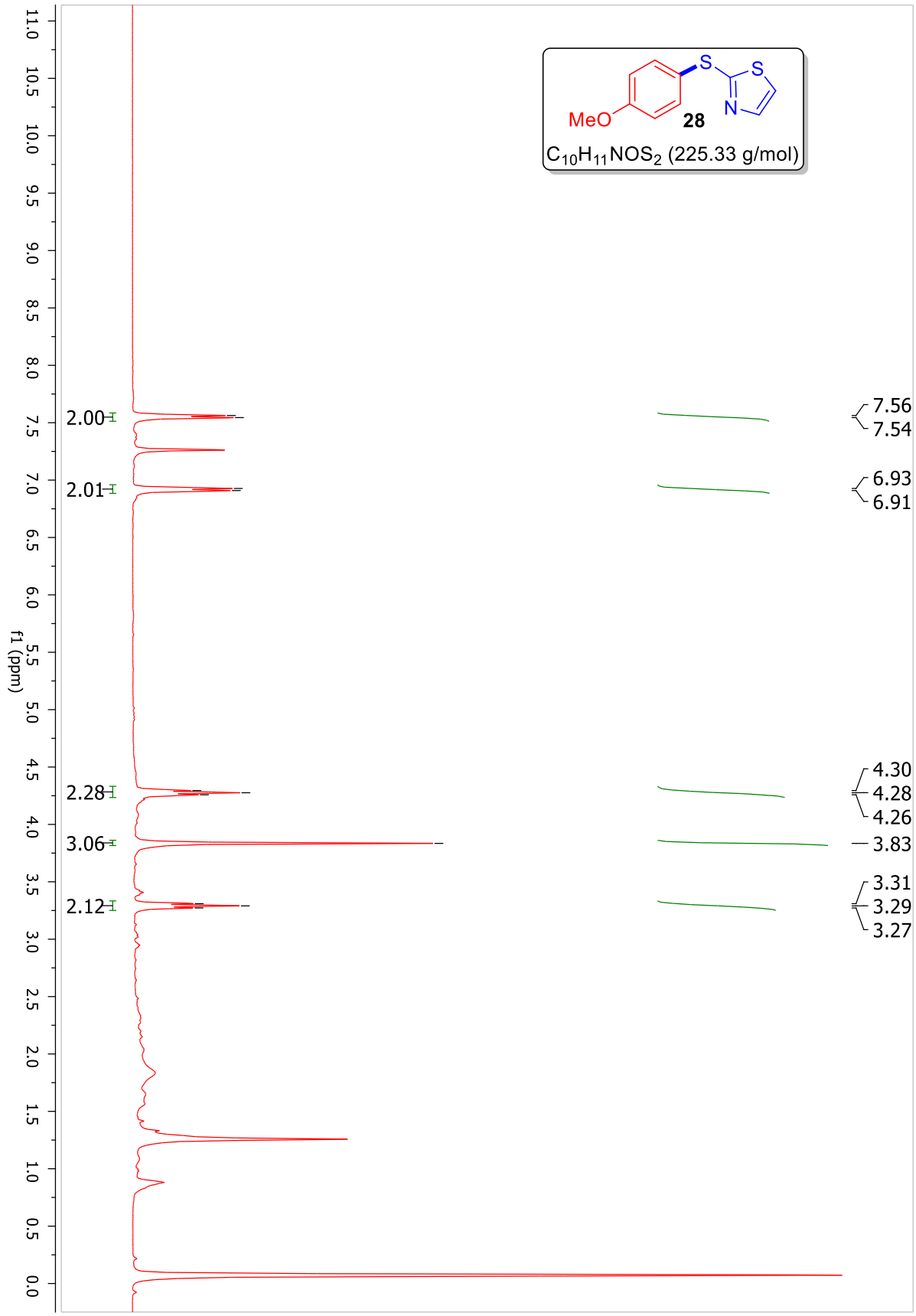
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **27:**



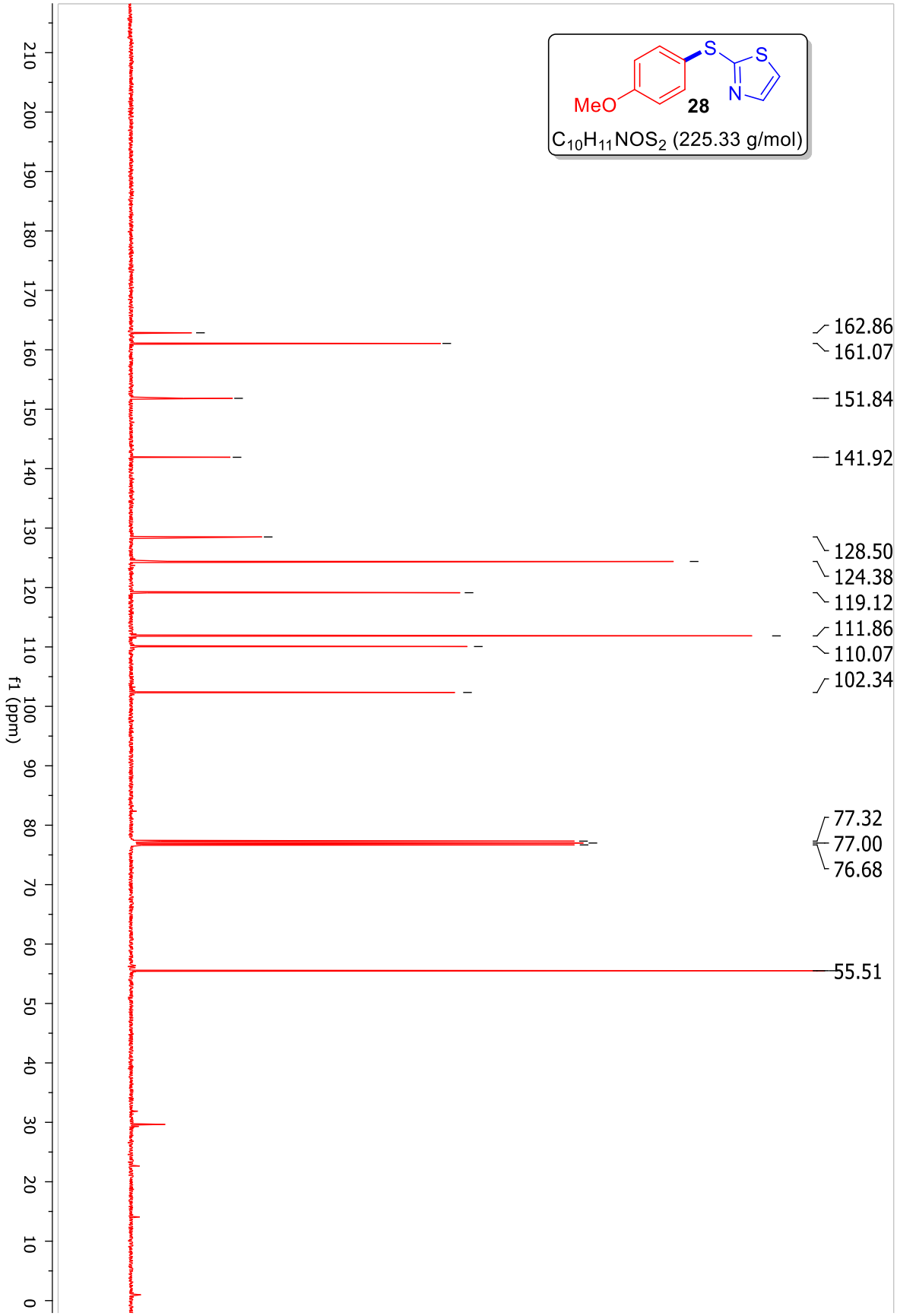
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **27:**



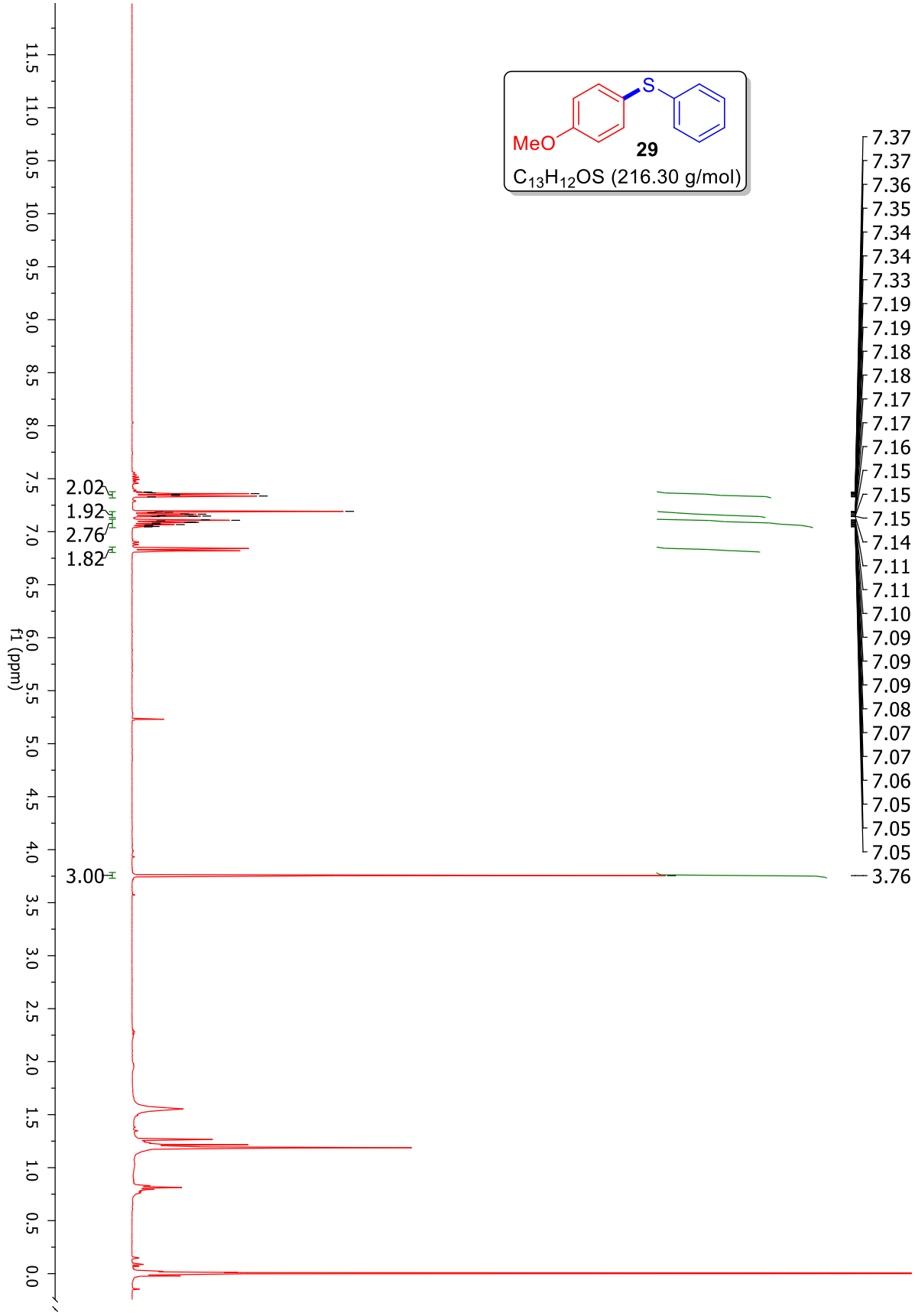
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **28:**



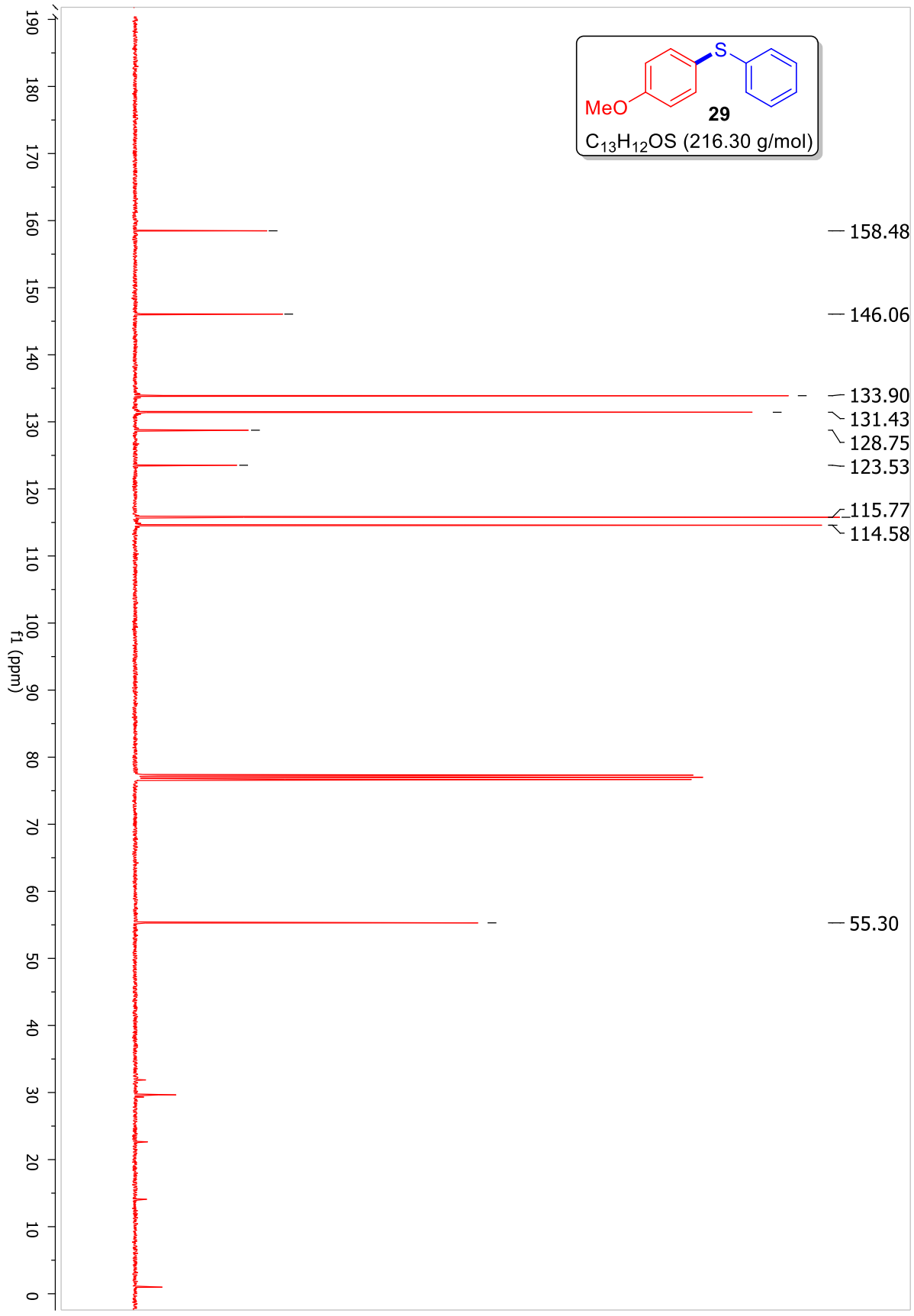
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **28:**



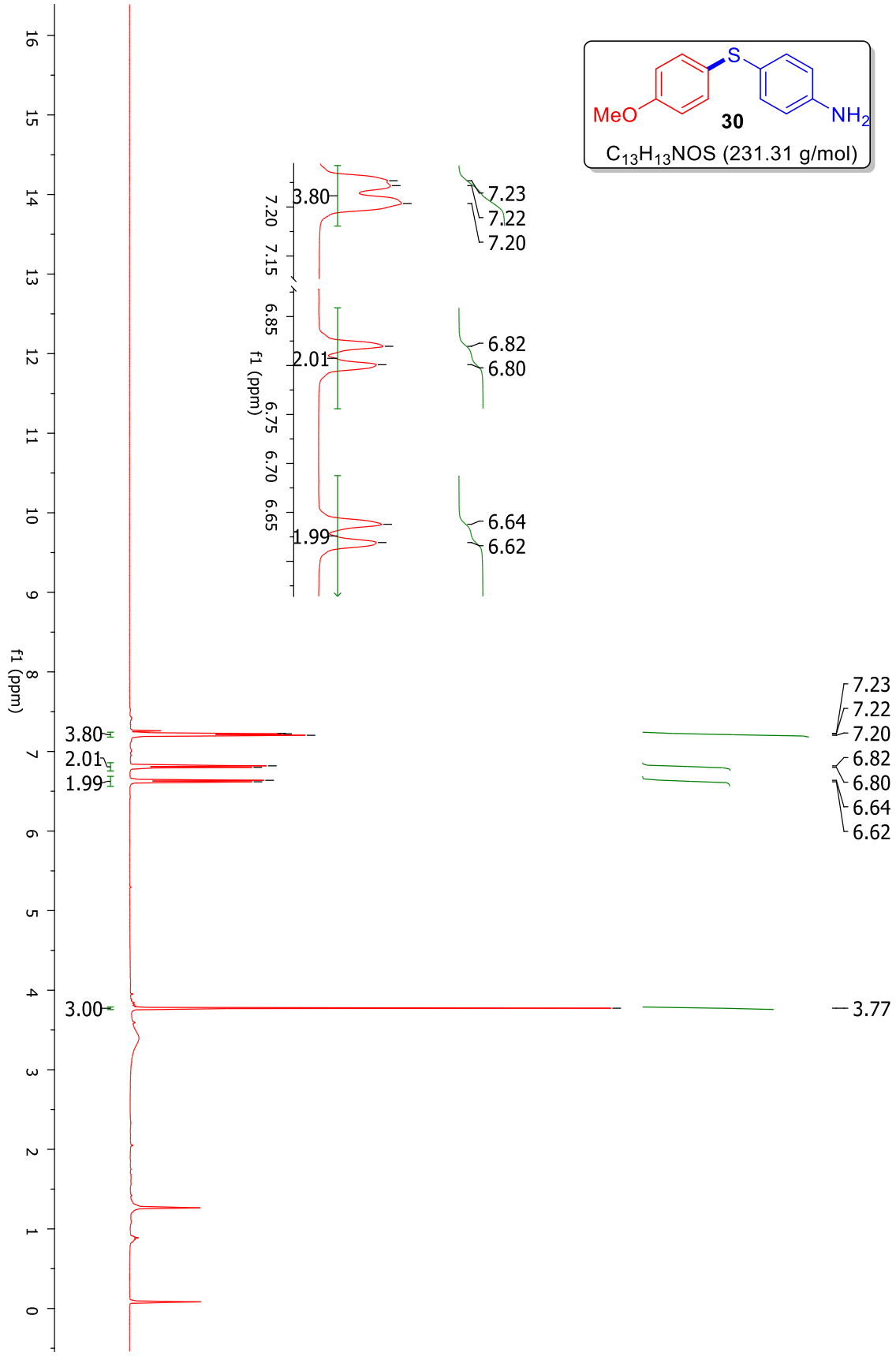
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **29:**



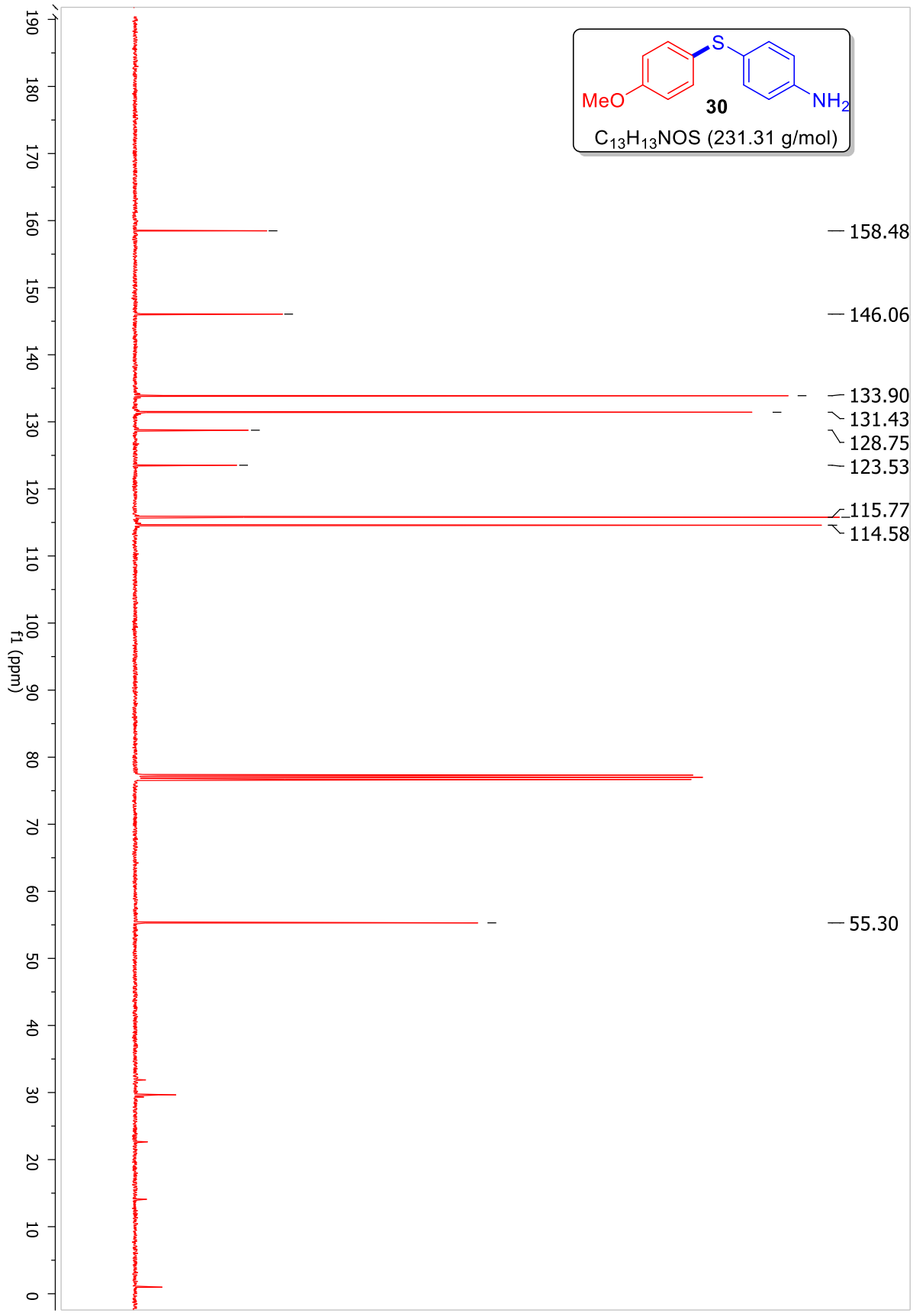
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **29:**



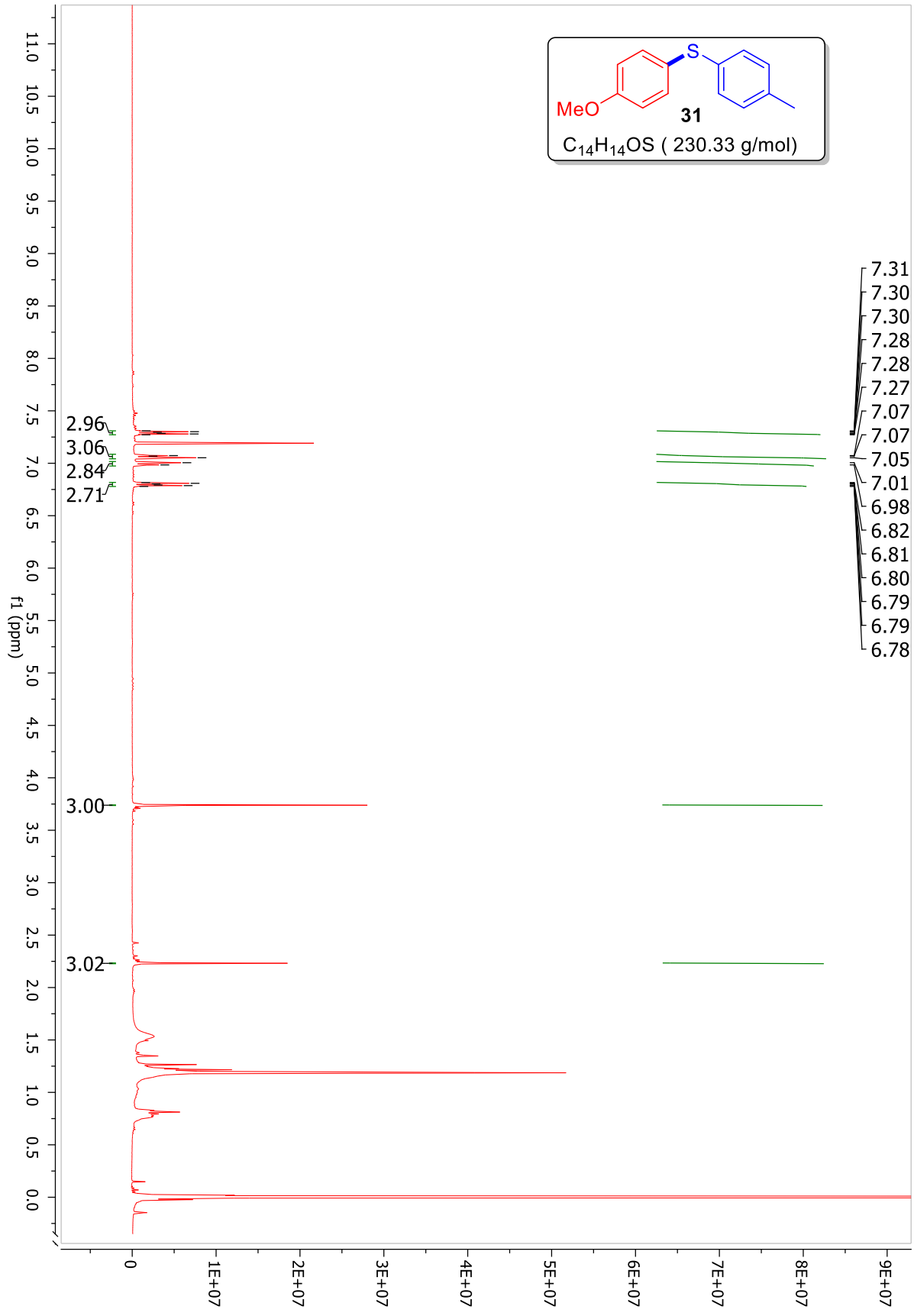
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **30:**



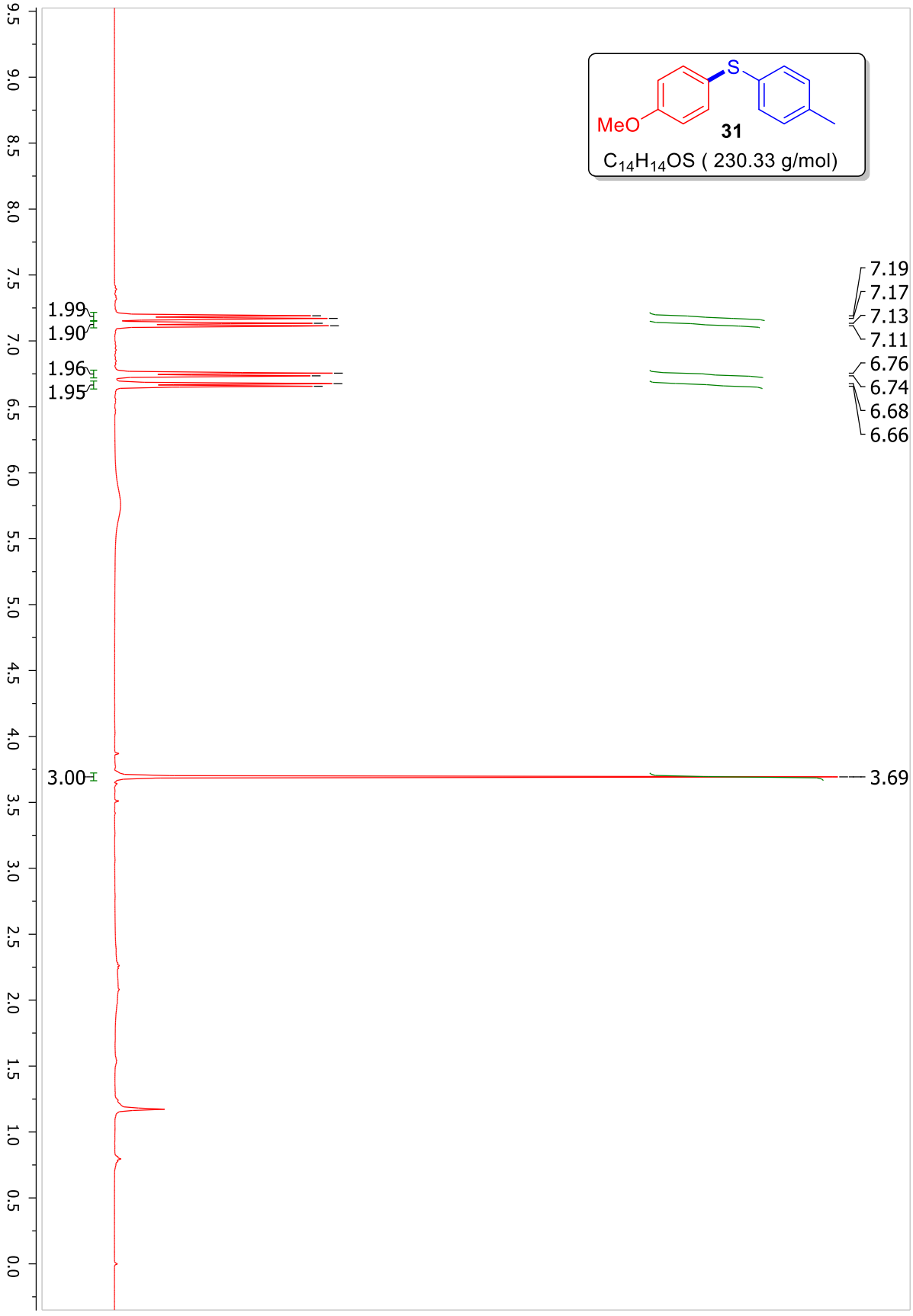
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **30:**



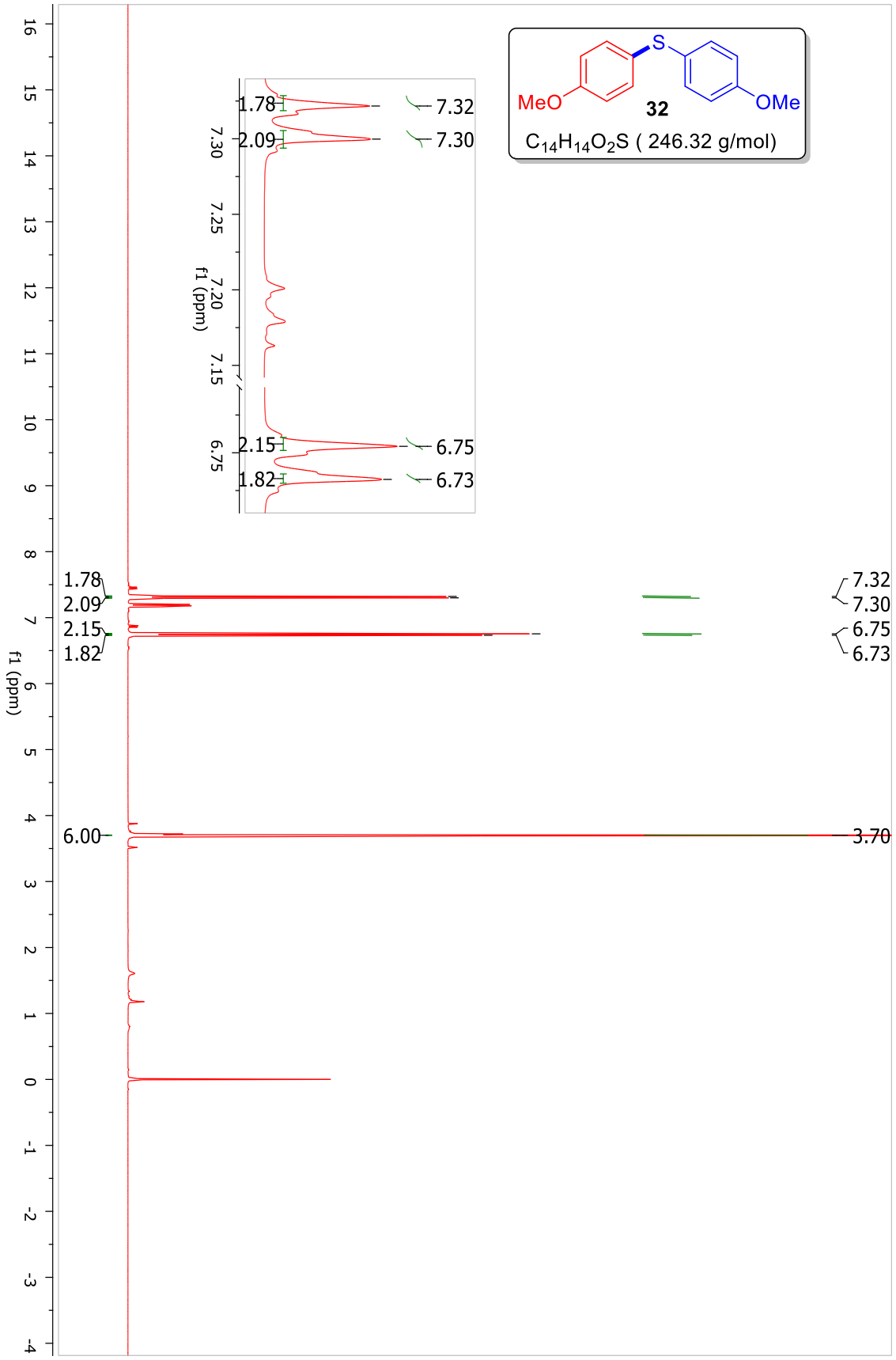
^{1}H-NMR (101 MHz, $CDCl_3$) of compound **31:**



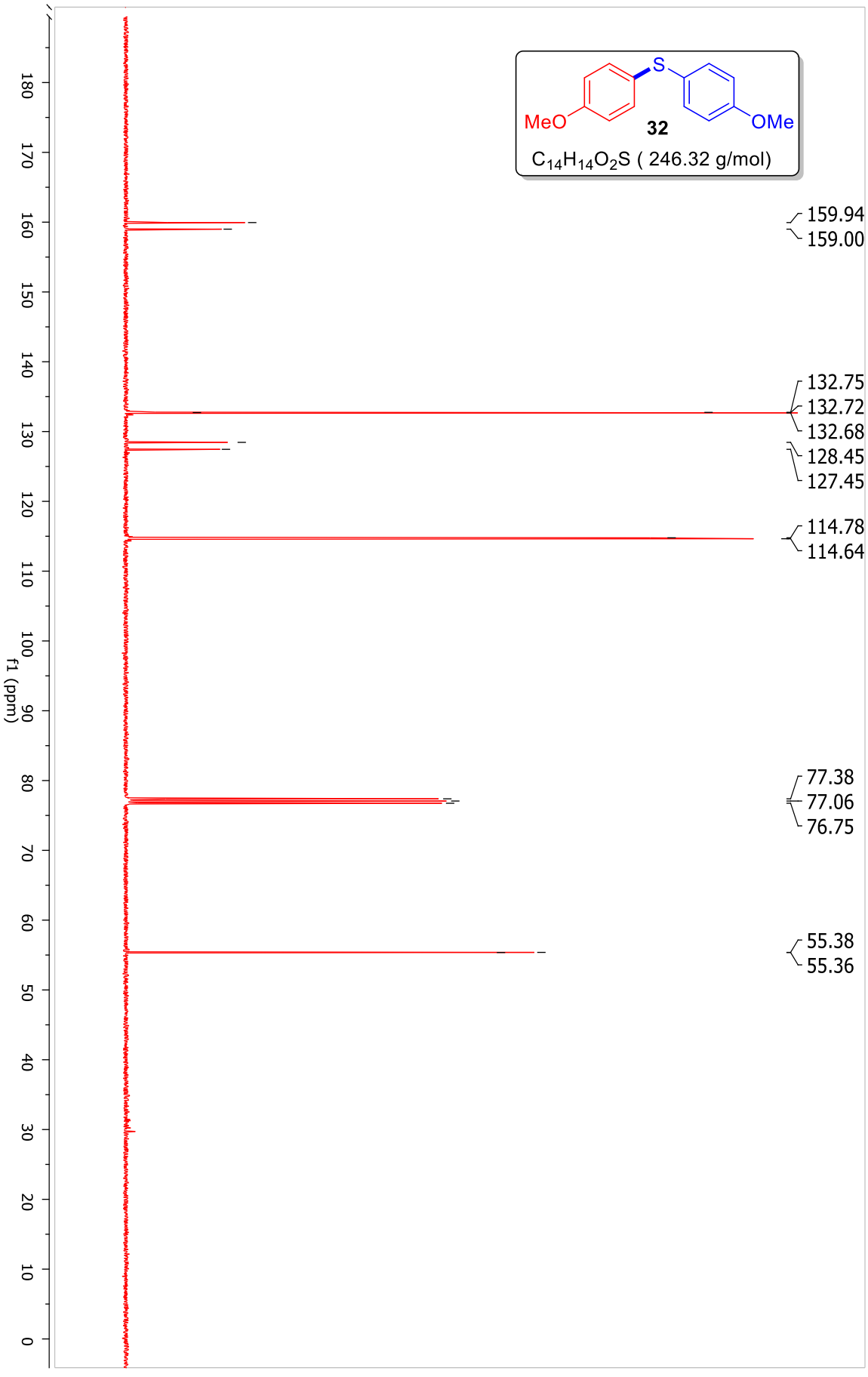
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **31:**



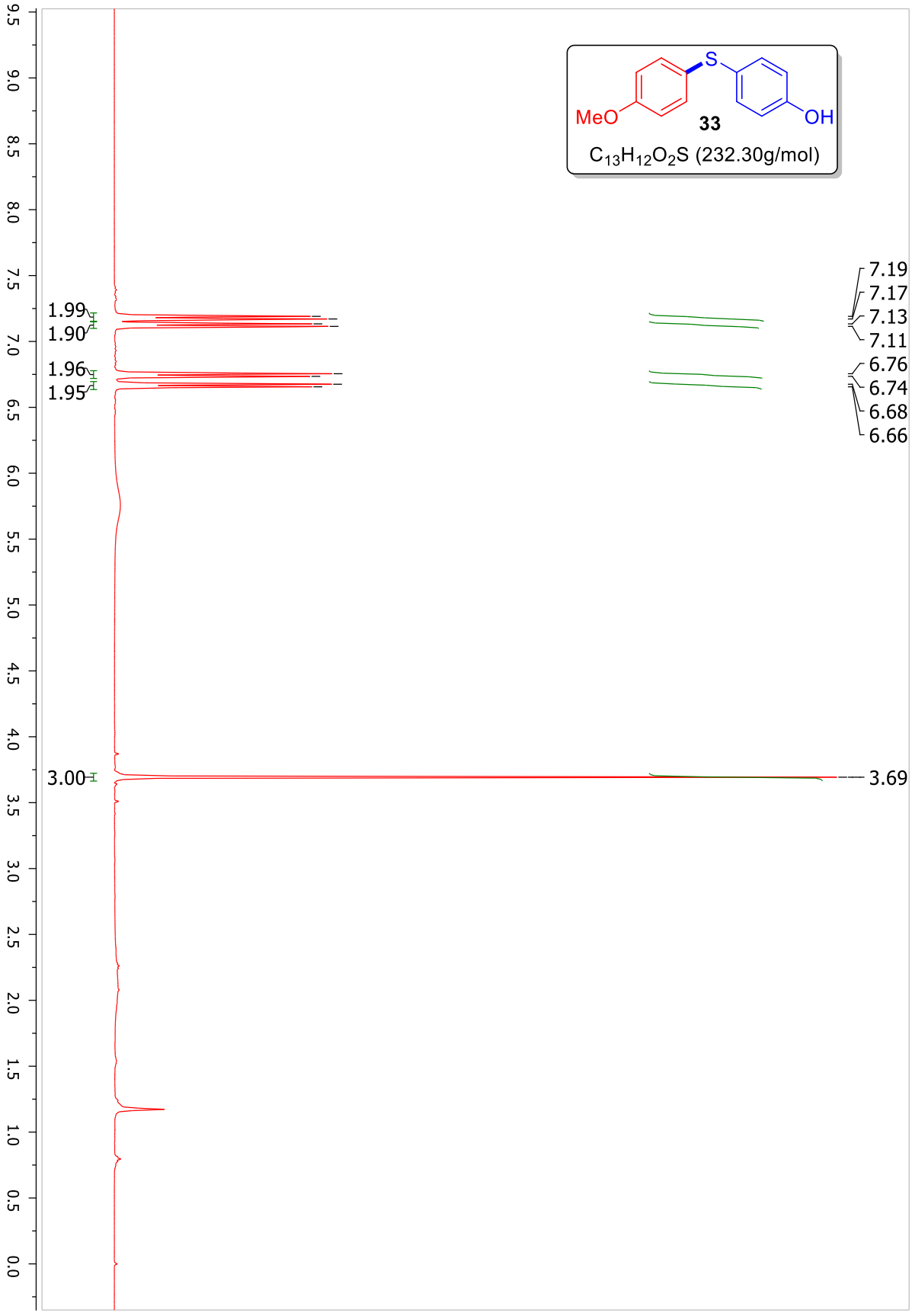
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **32:**



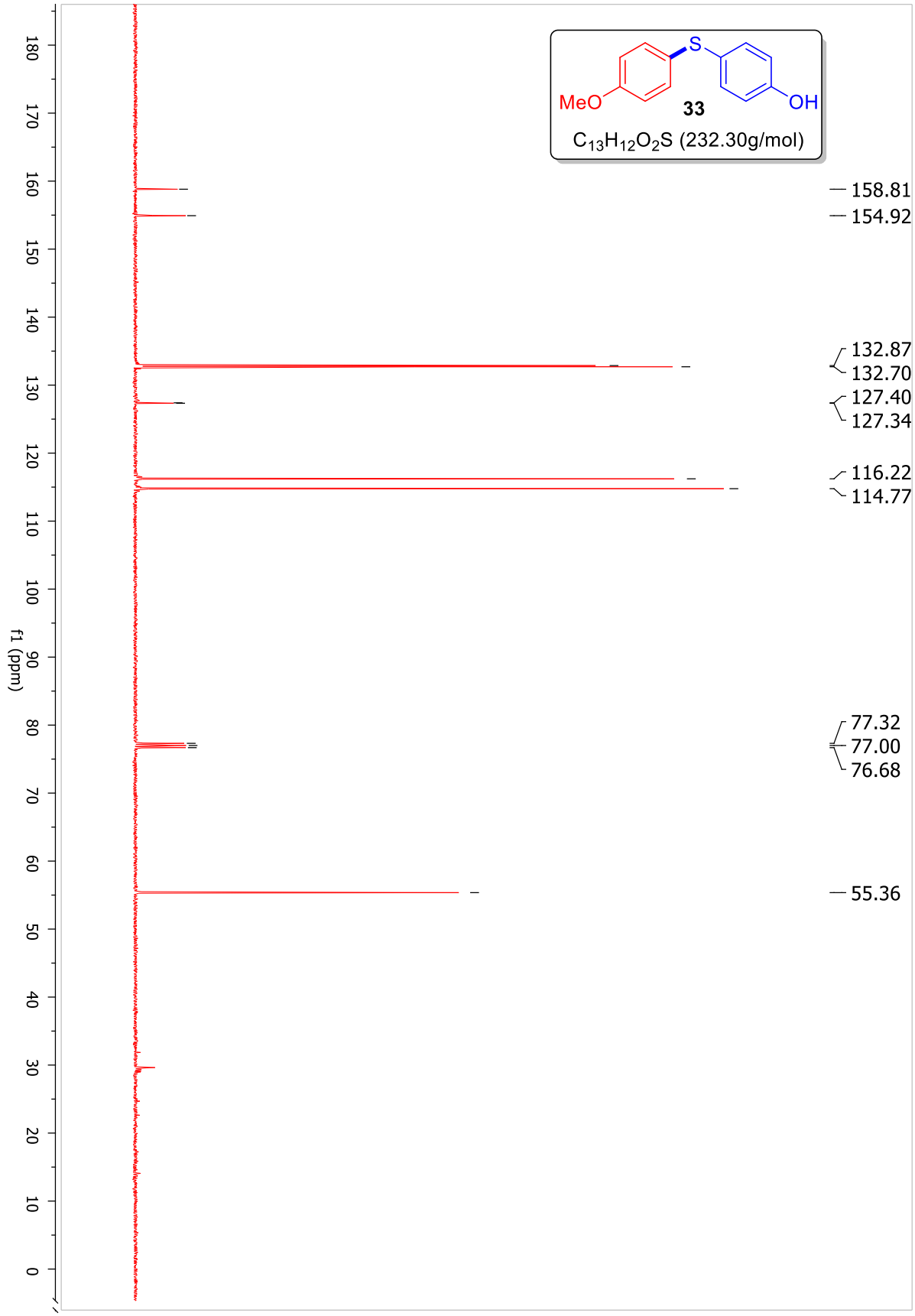
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **32:**



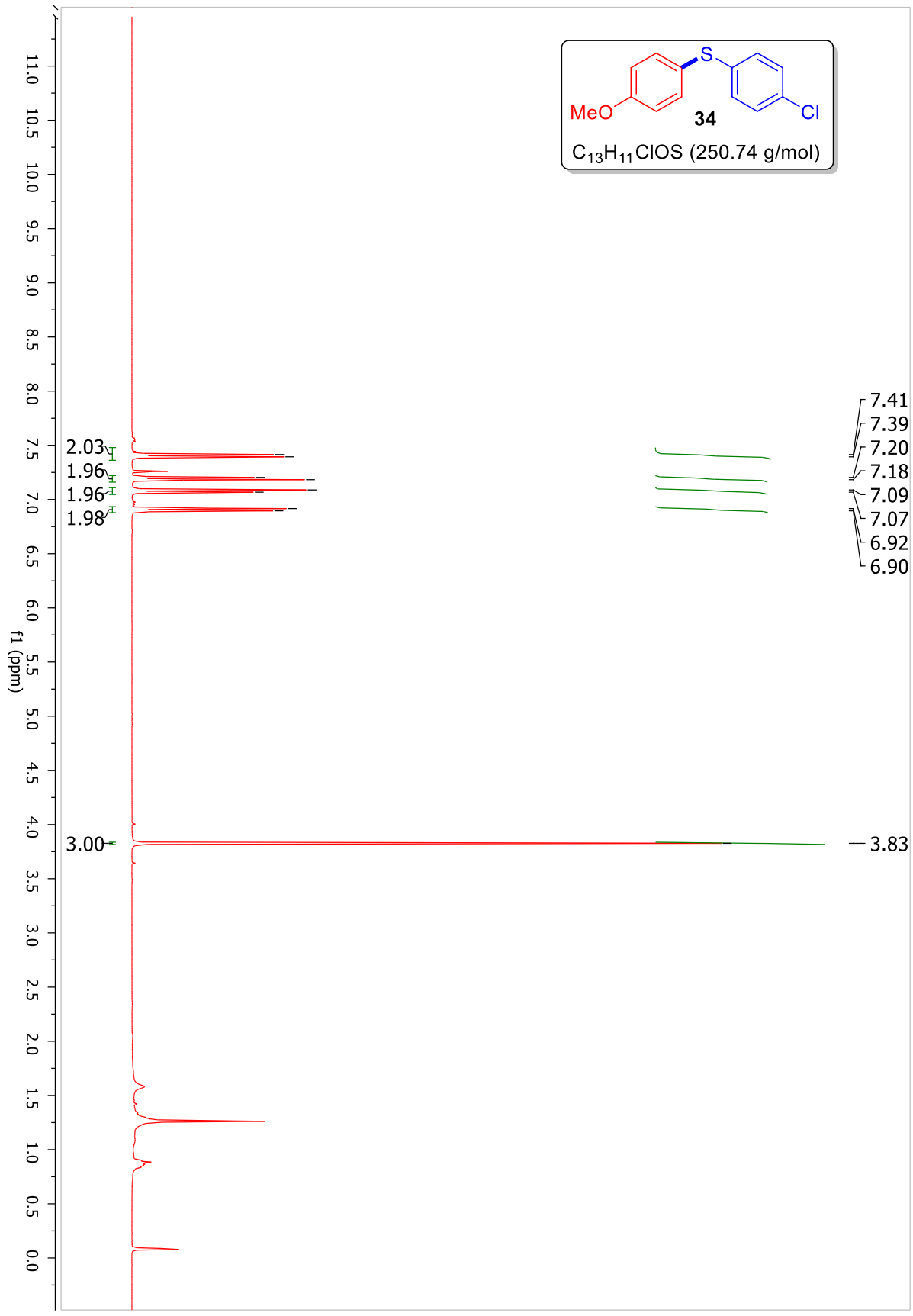
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **33:**



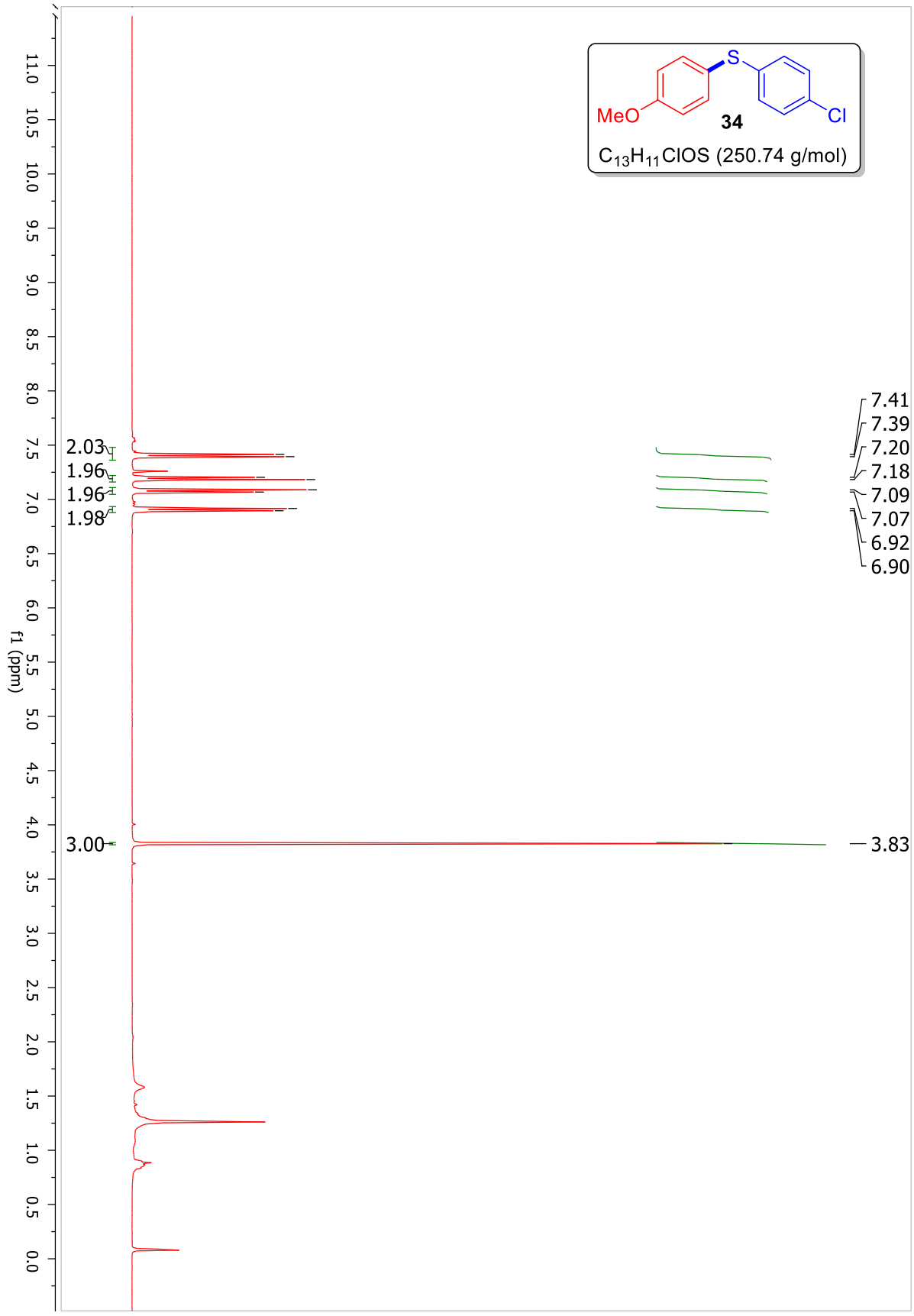
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **33:**



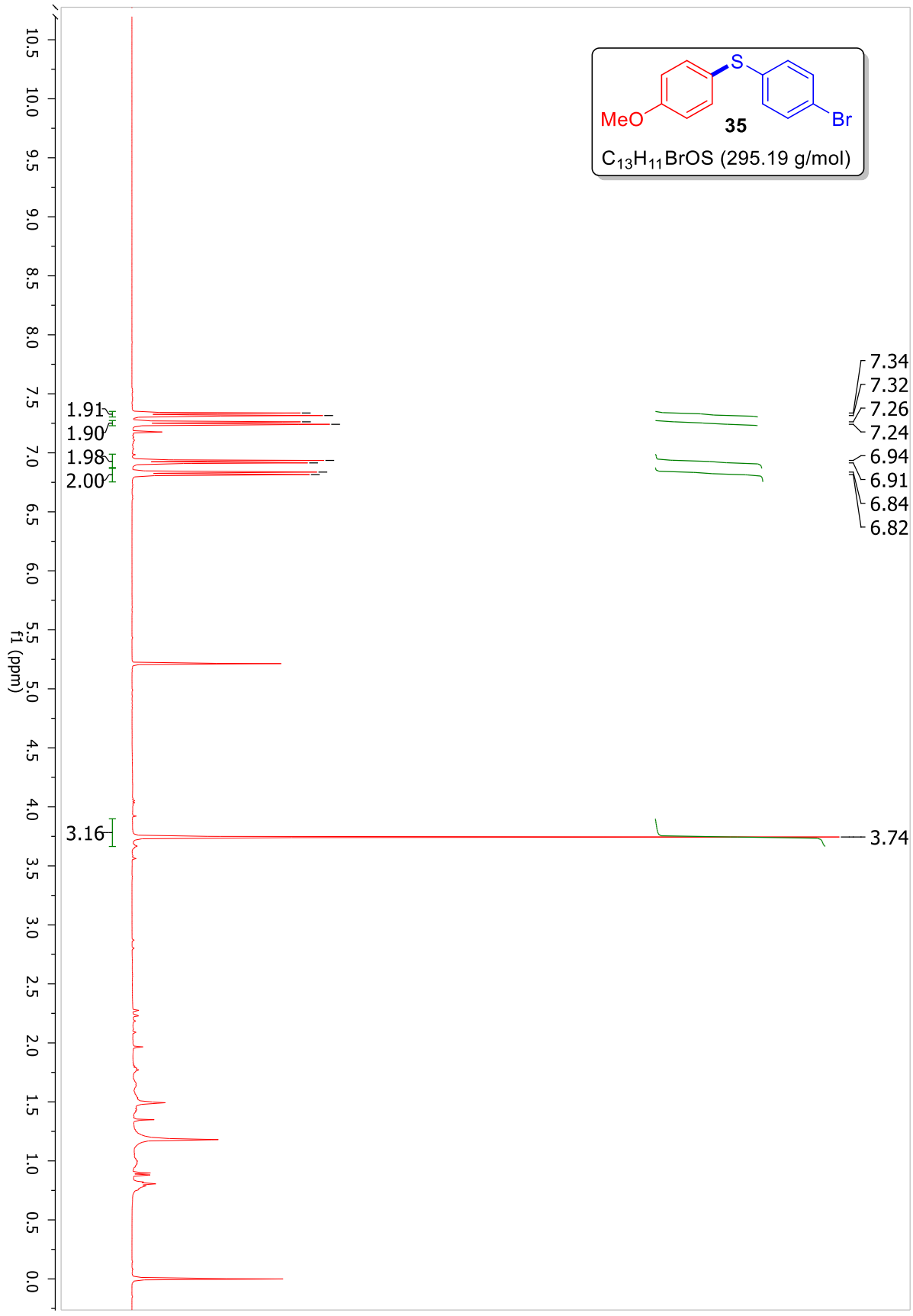
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **34:**



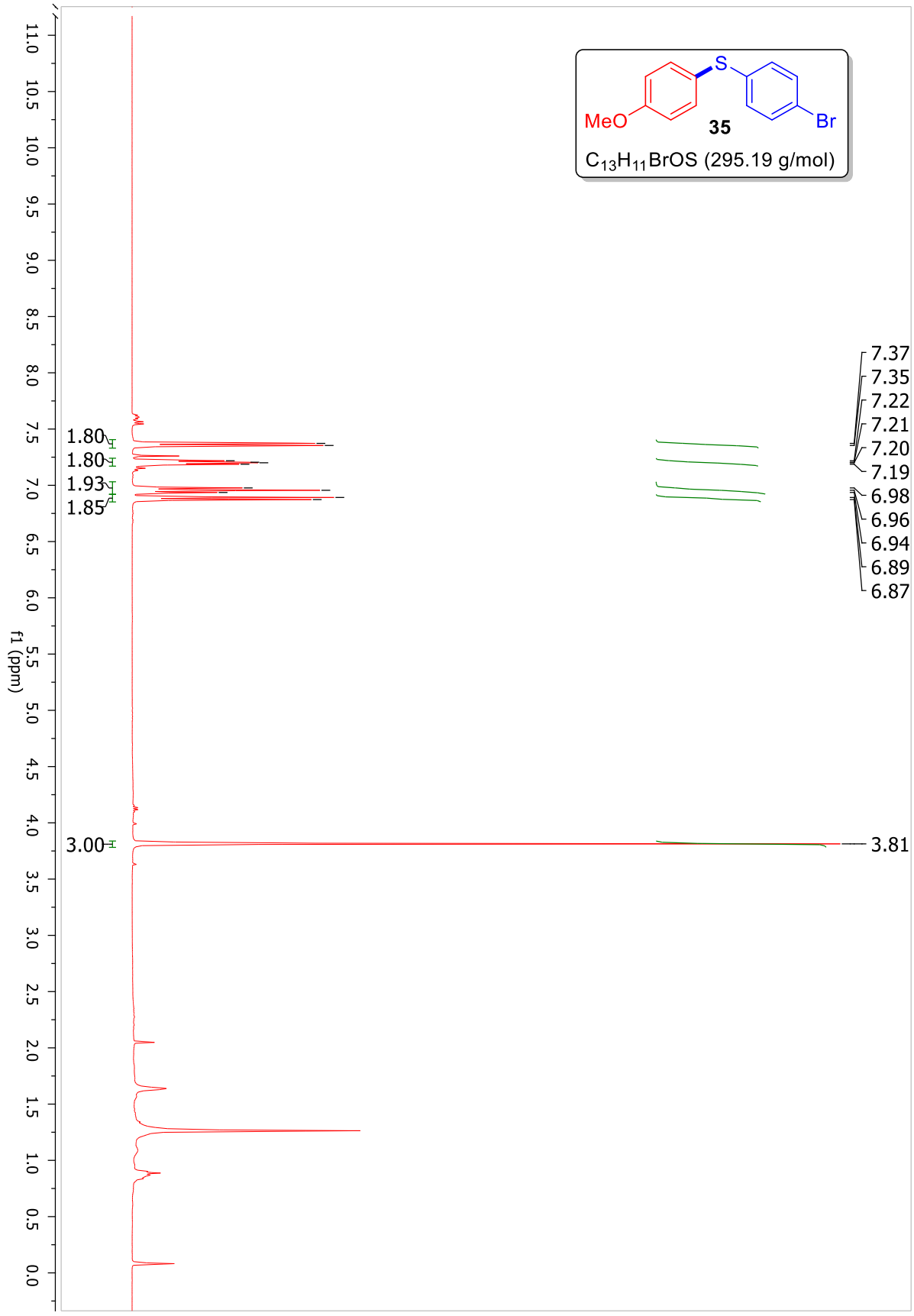
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **34:**



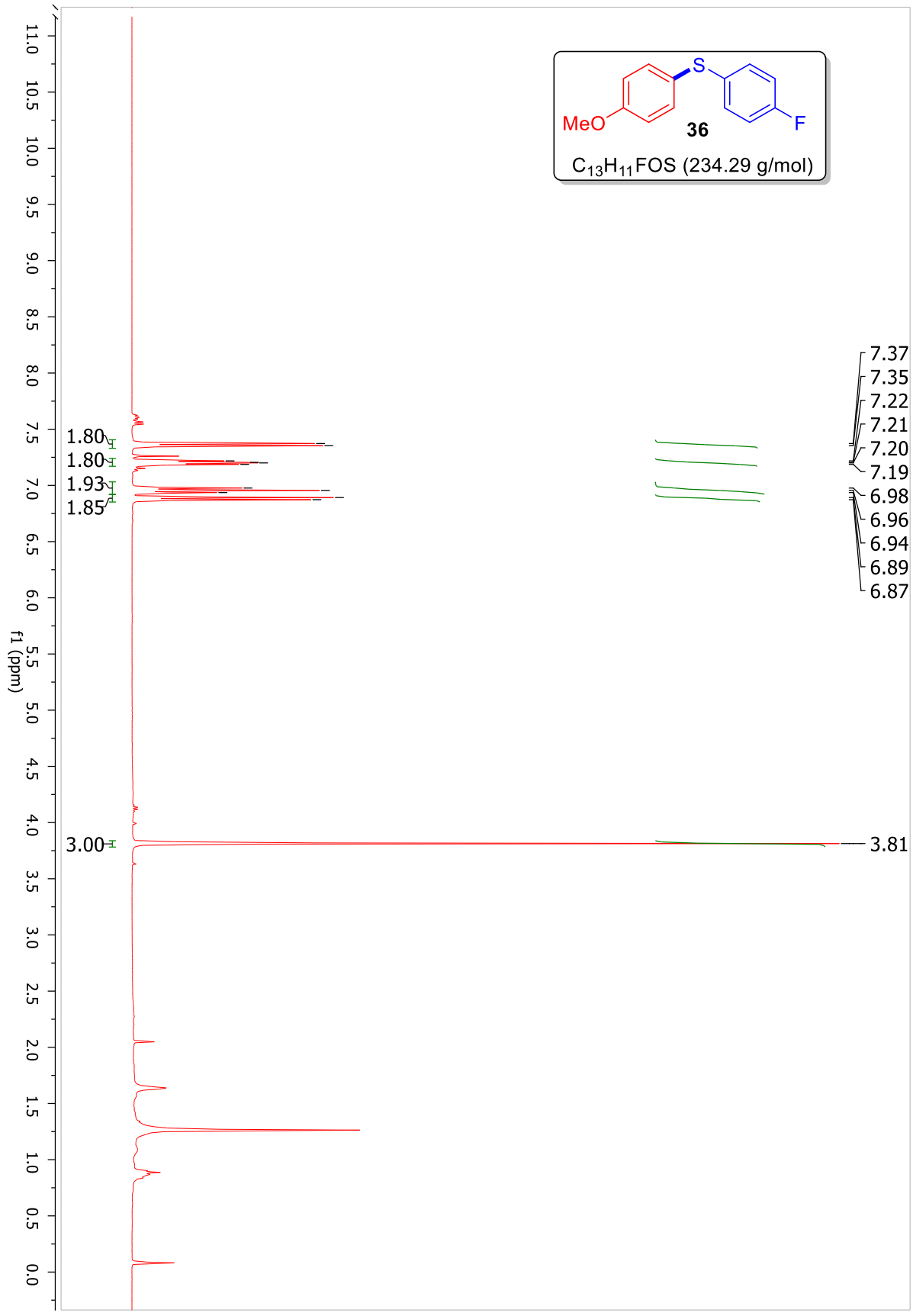
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **35:**



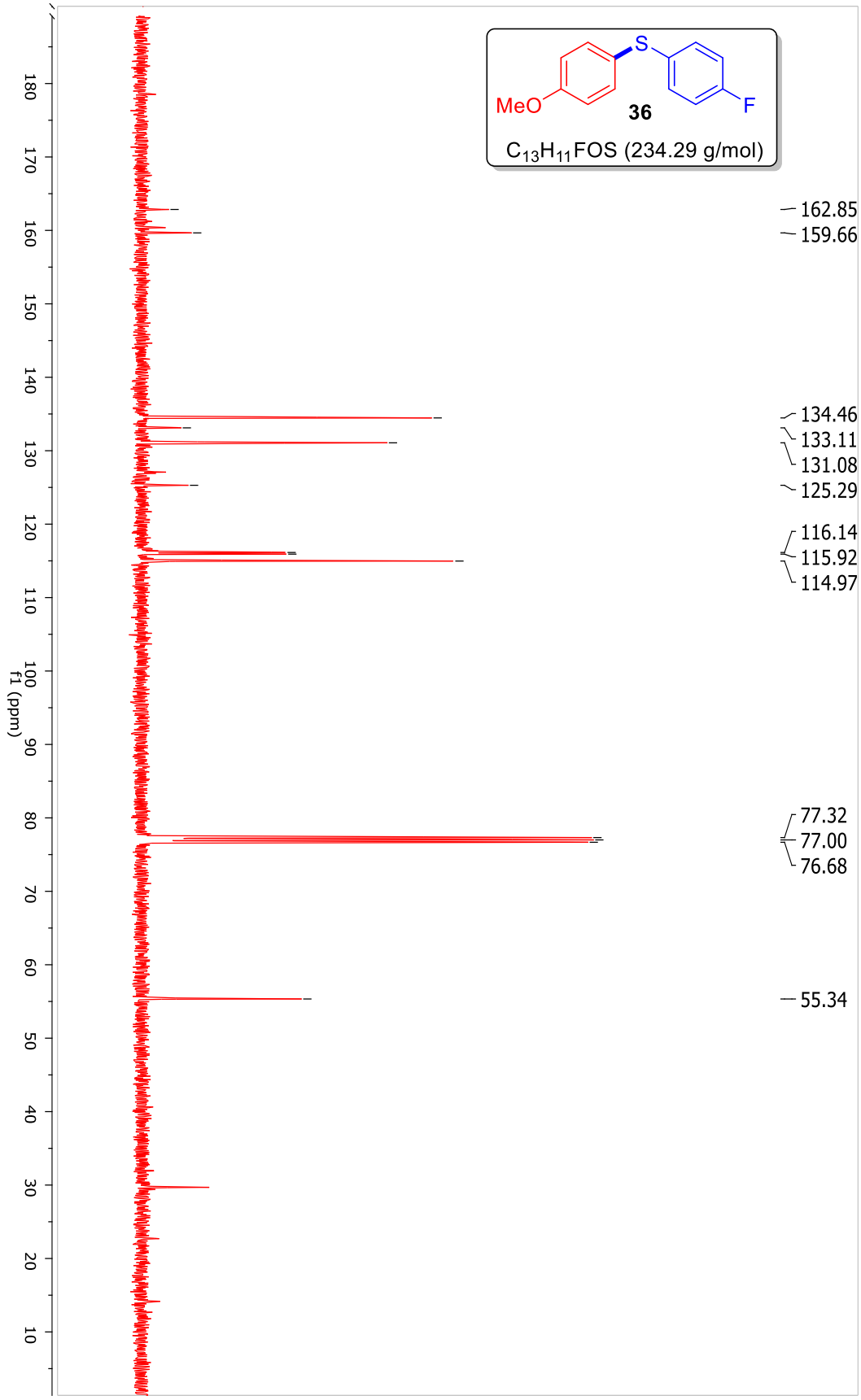
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **35:**



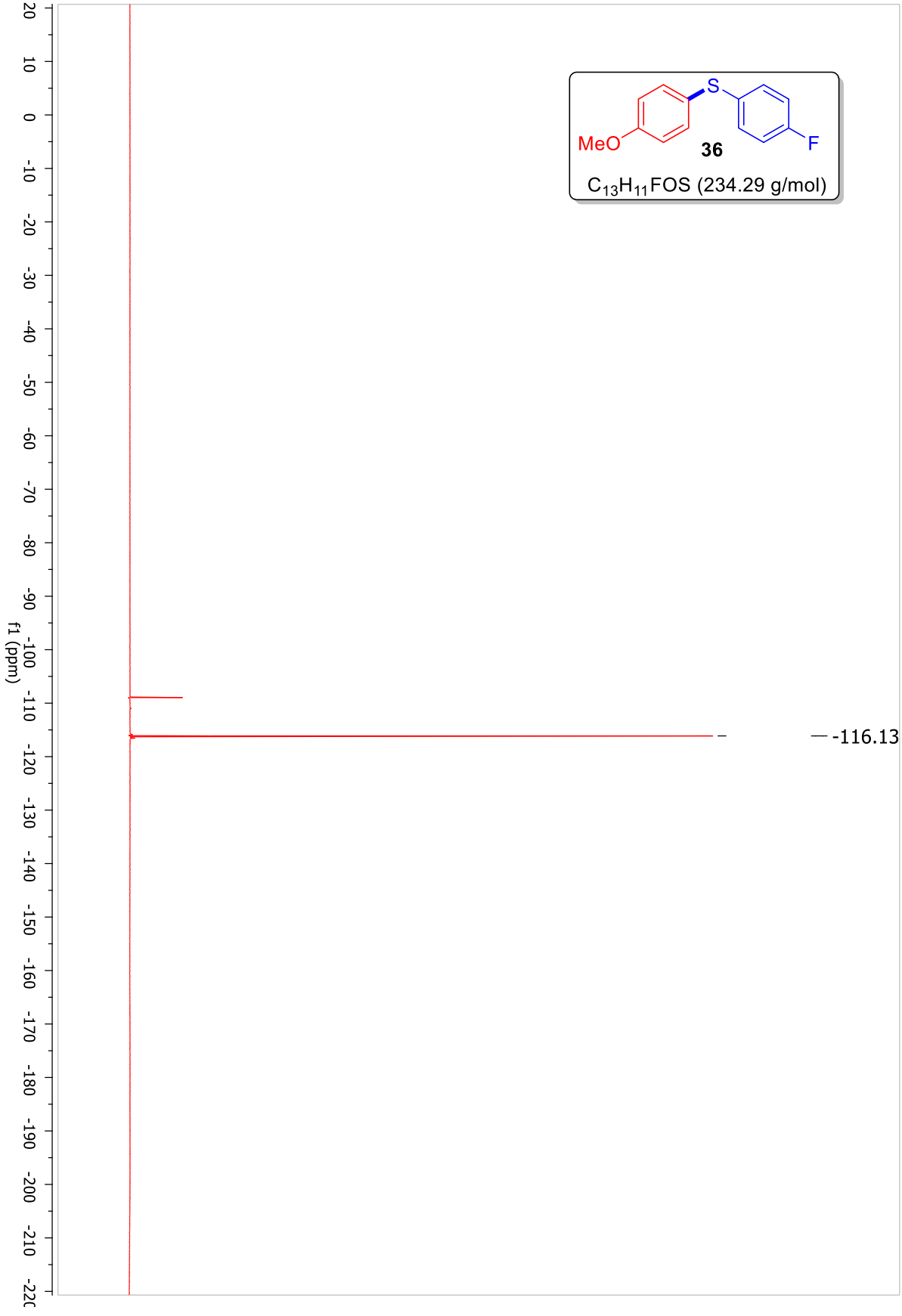
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **36:**



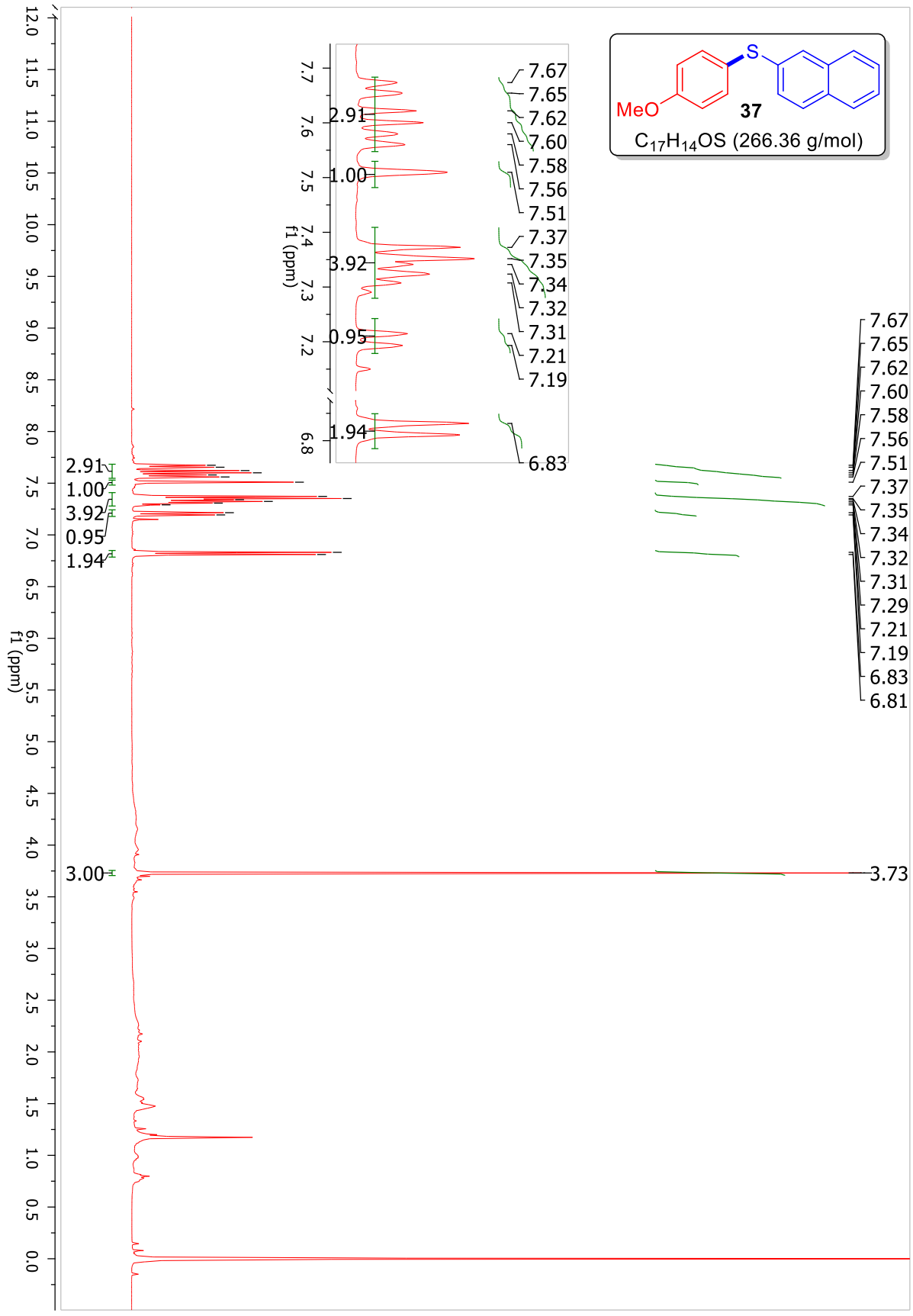
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **36:**



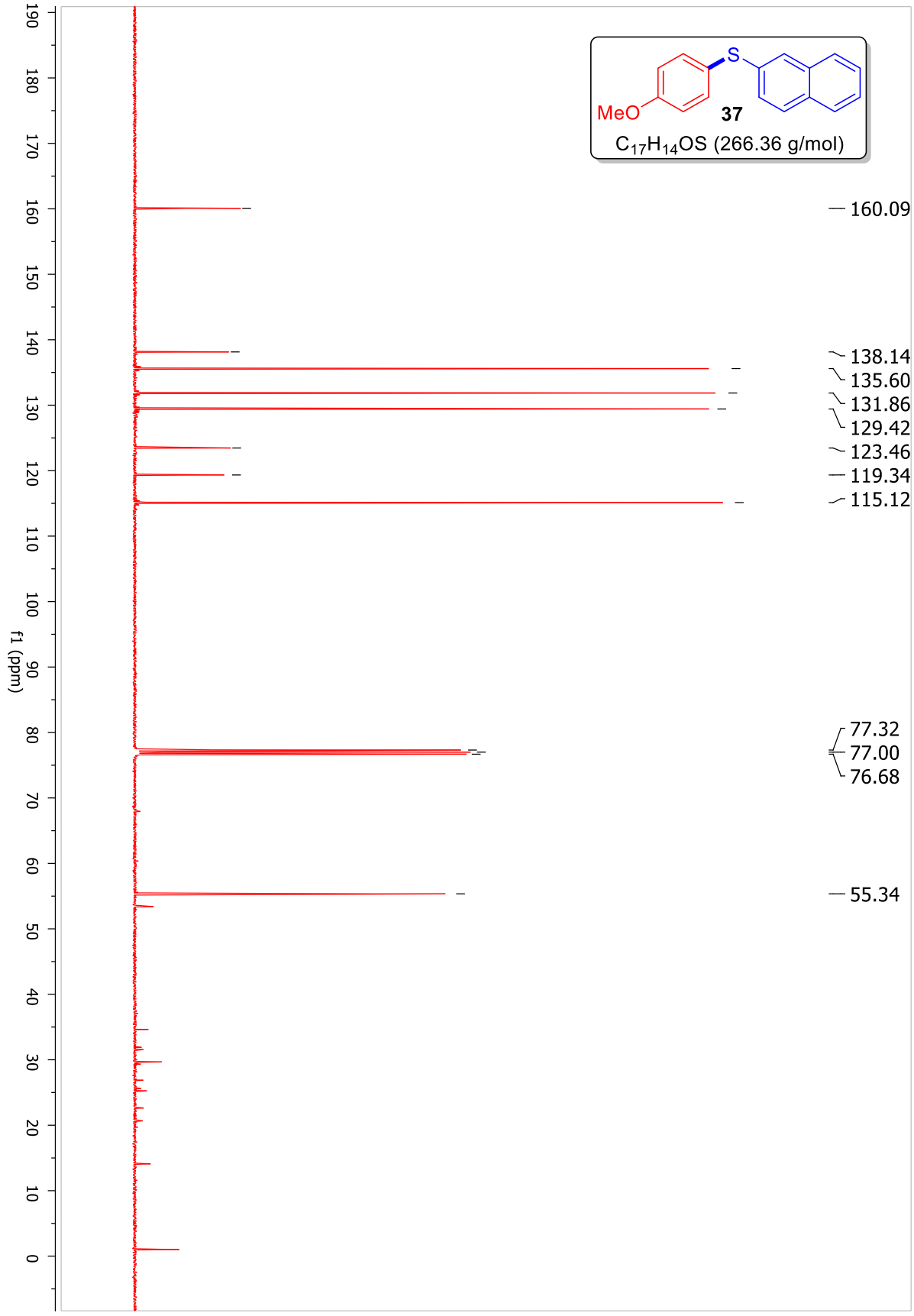
^{19}F-NMR of Compound **36:**



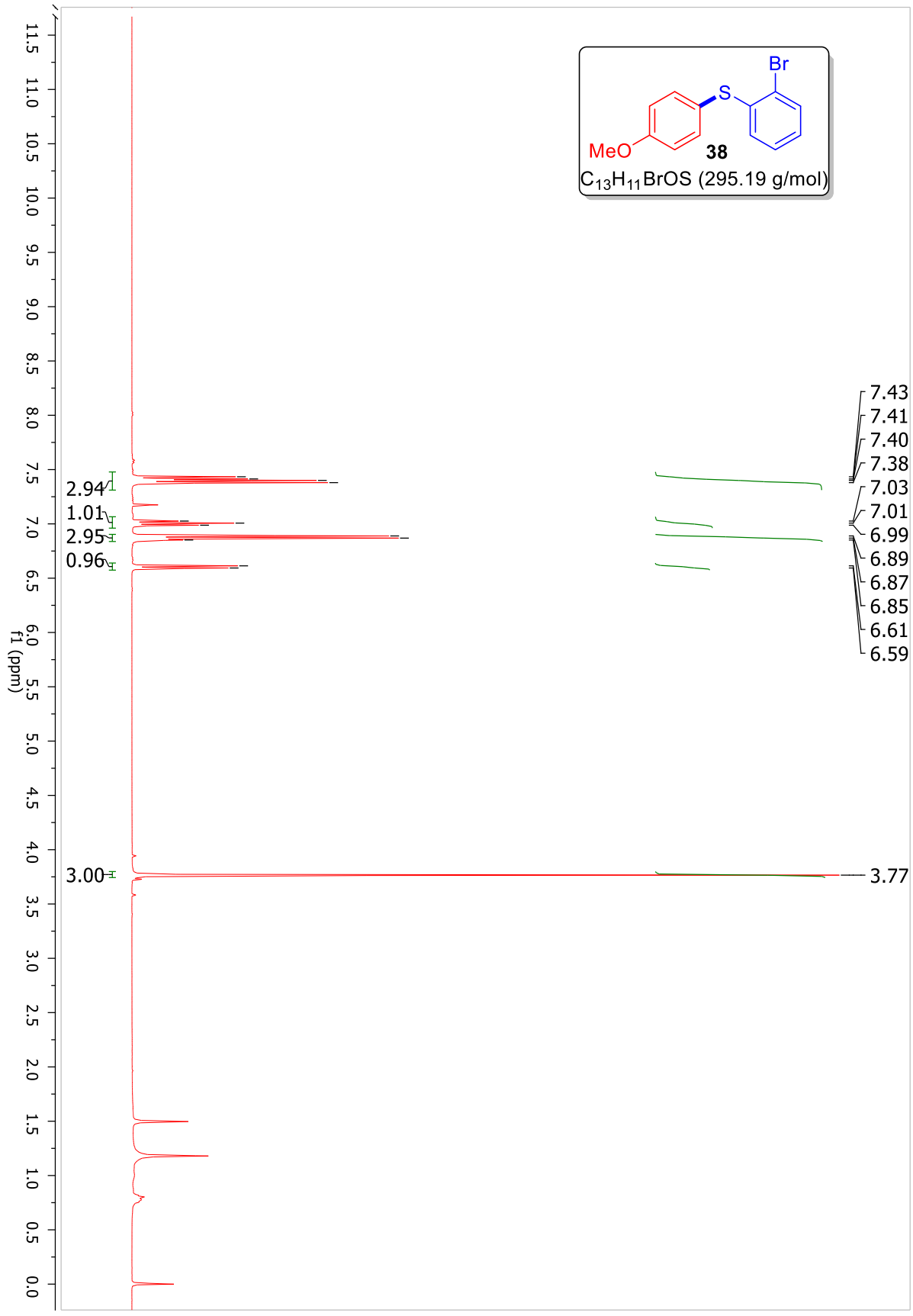
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **37:**



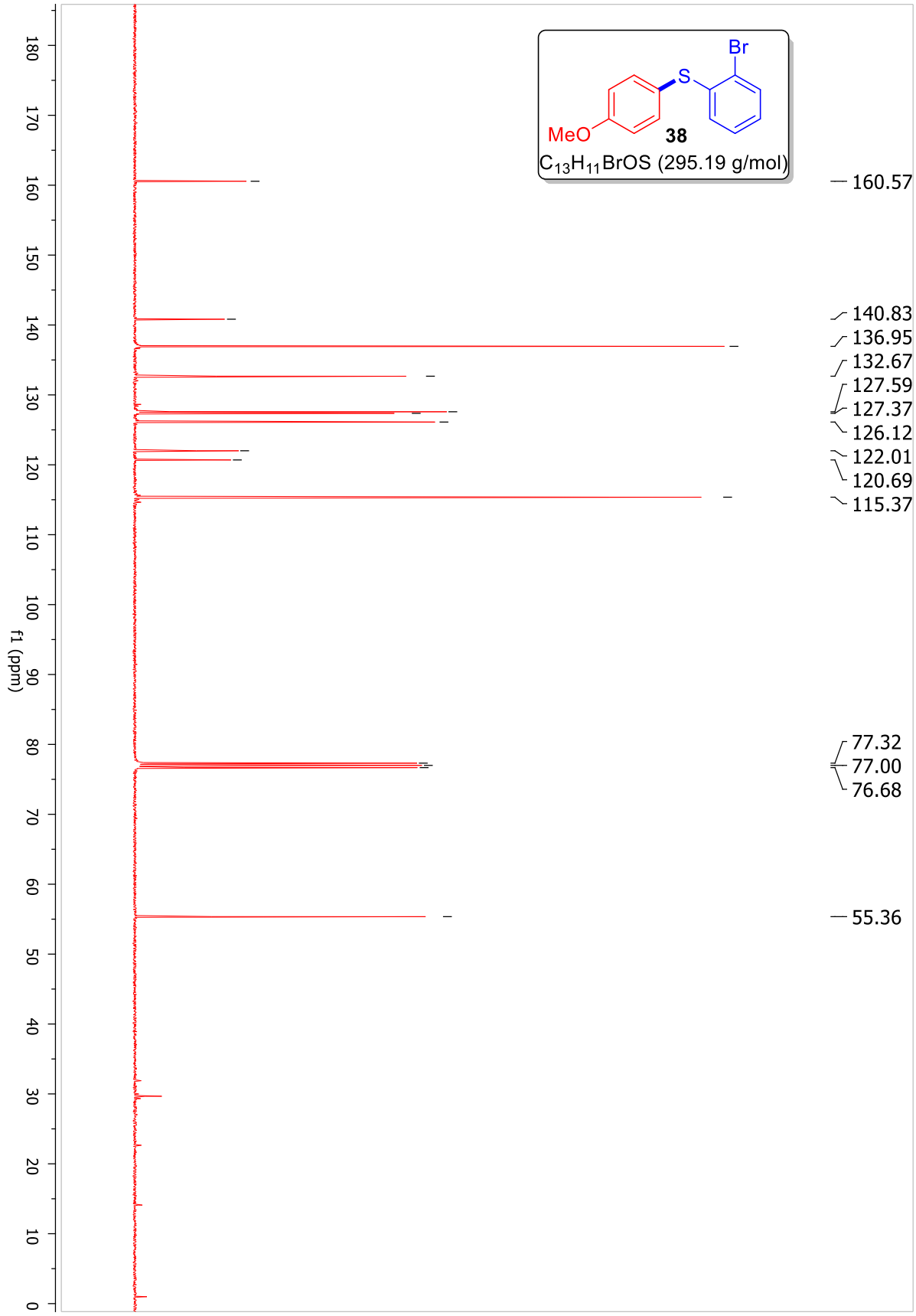
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **37:**



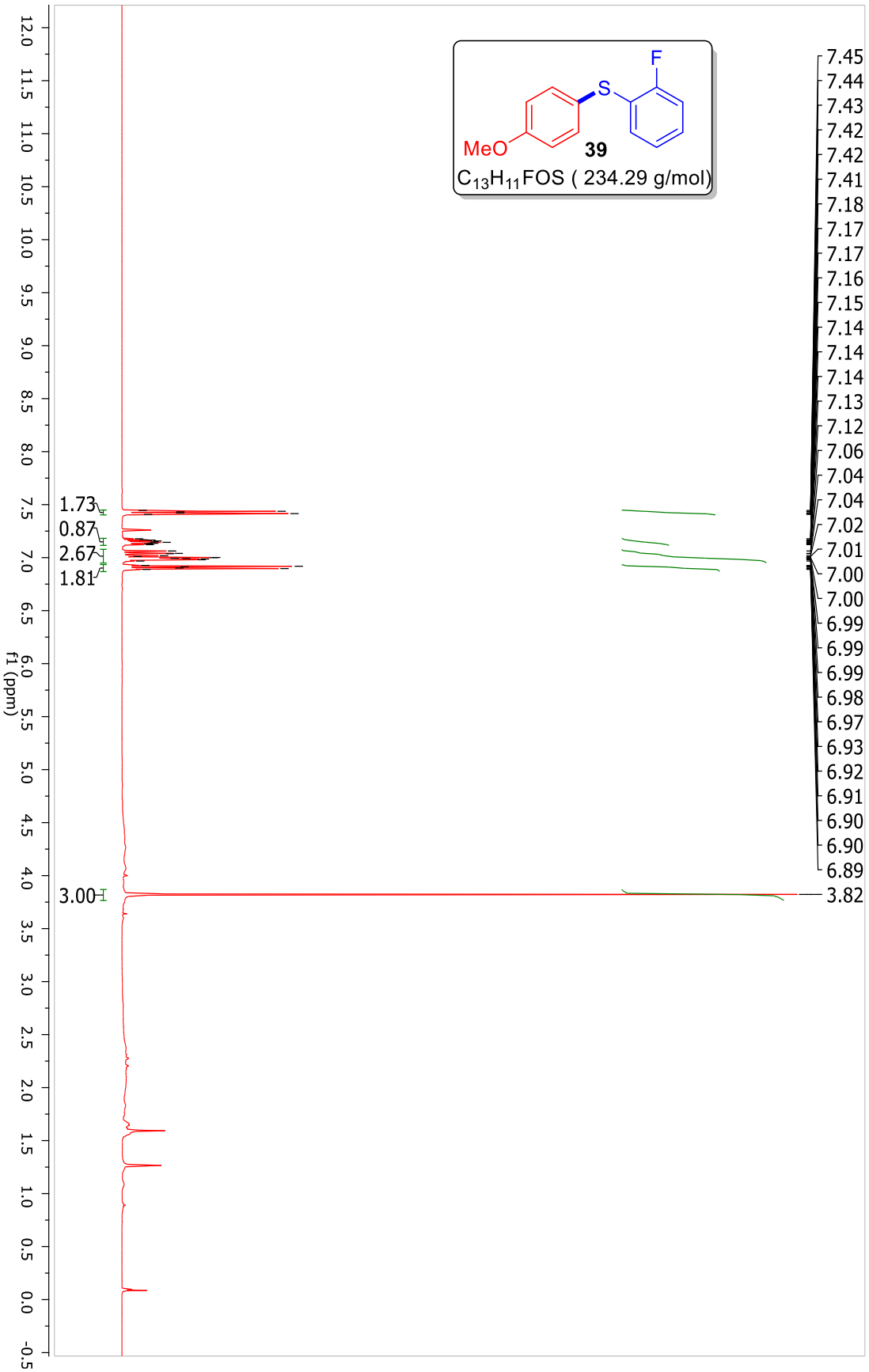
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **38:**



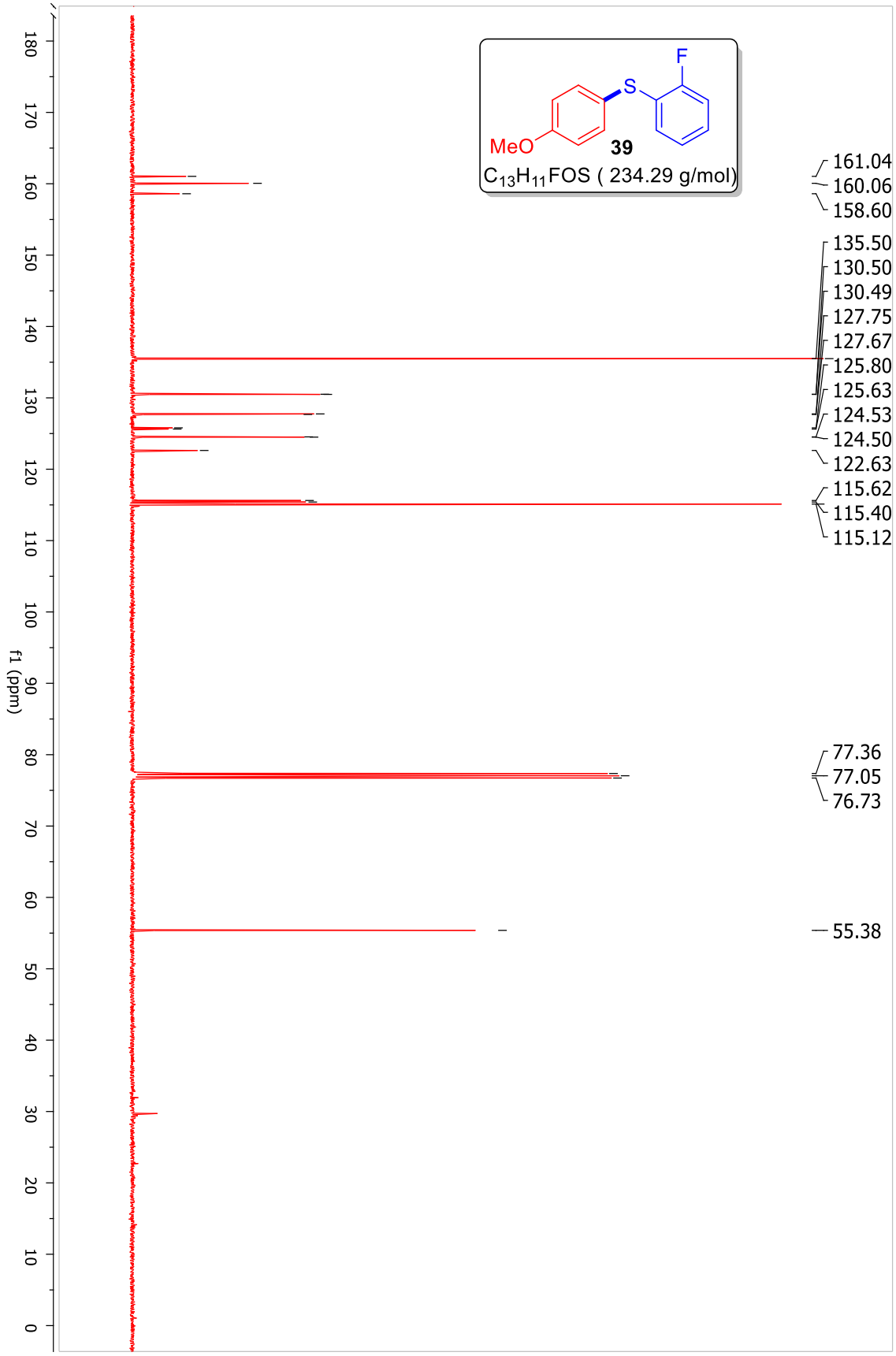
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **38:**



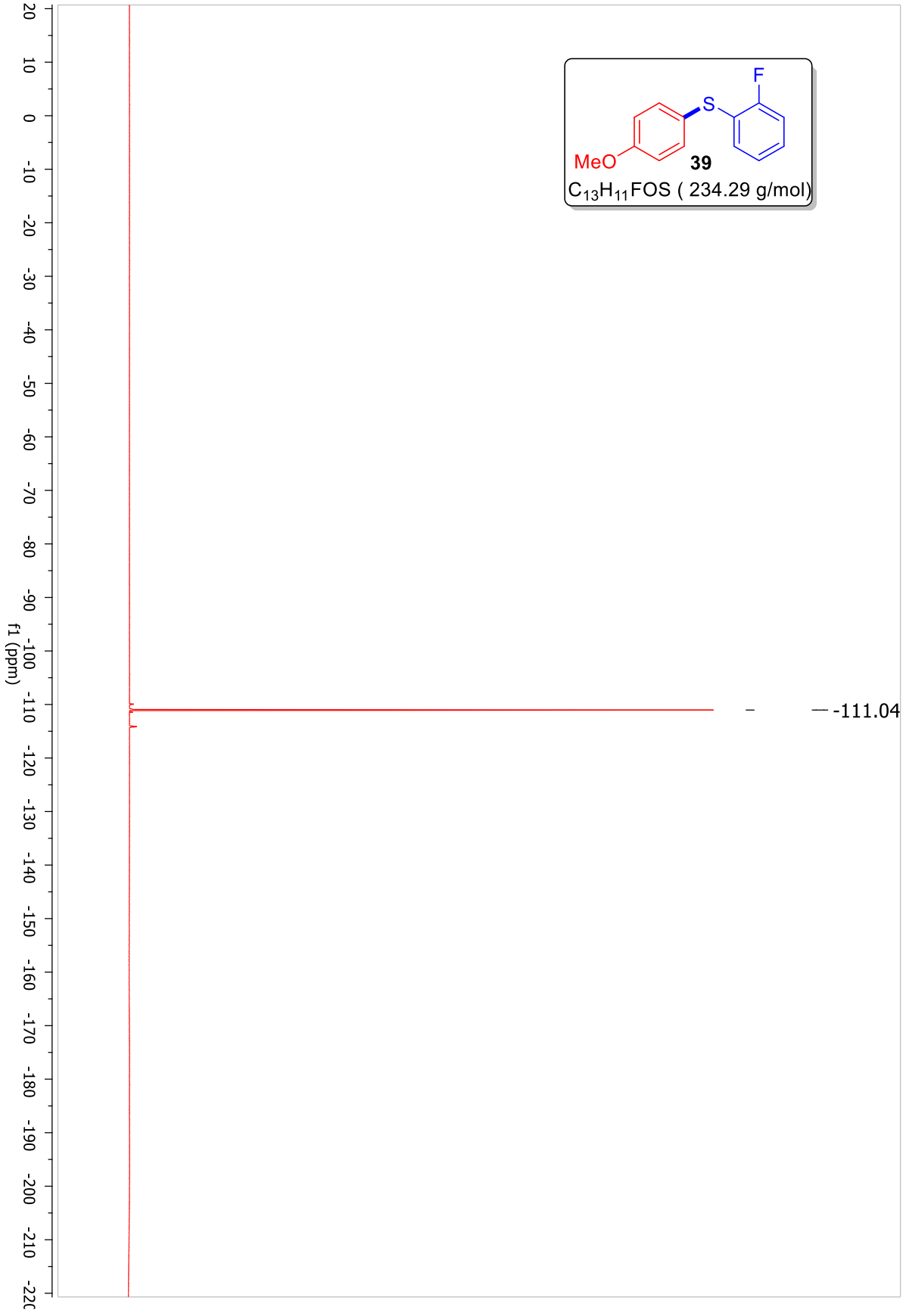
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **39:**



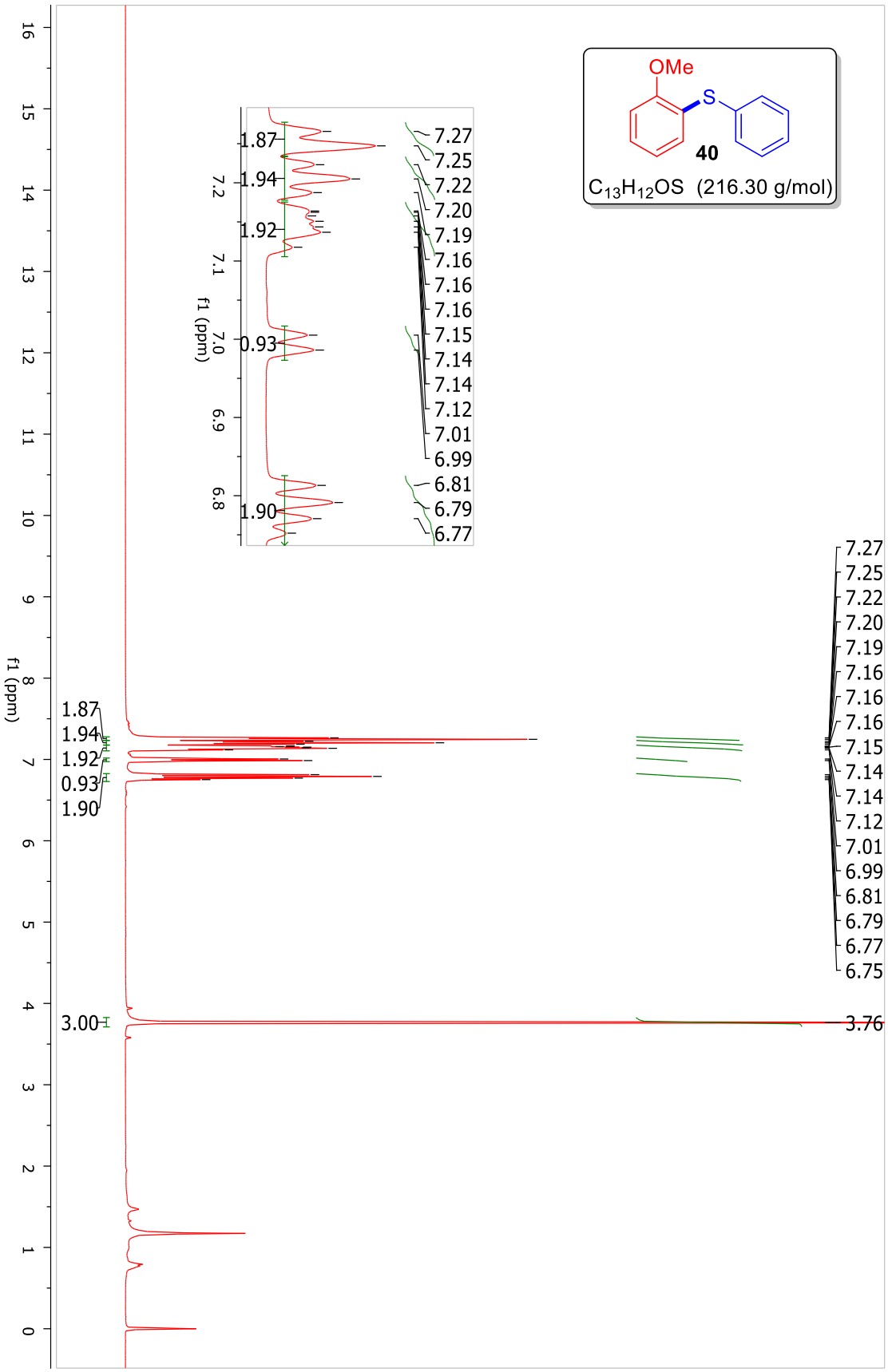
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **39:**



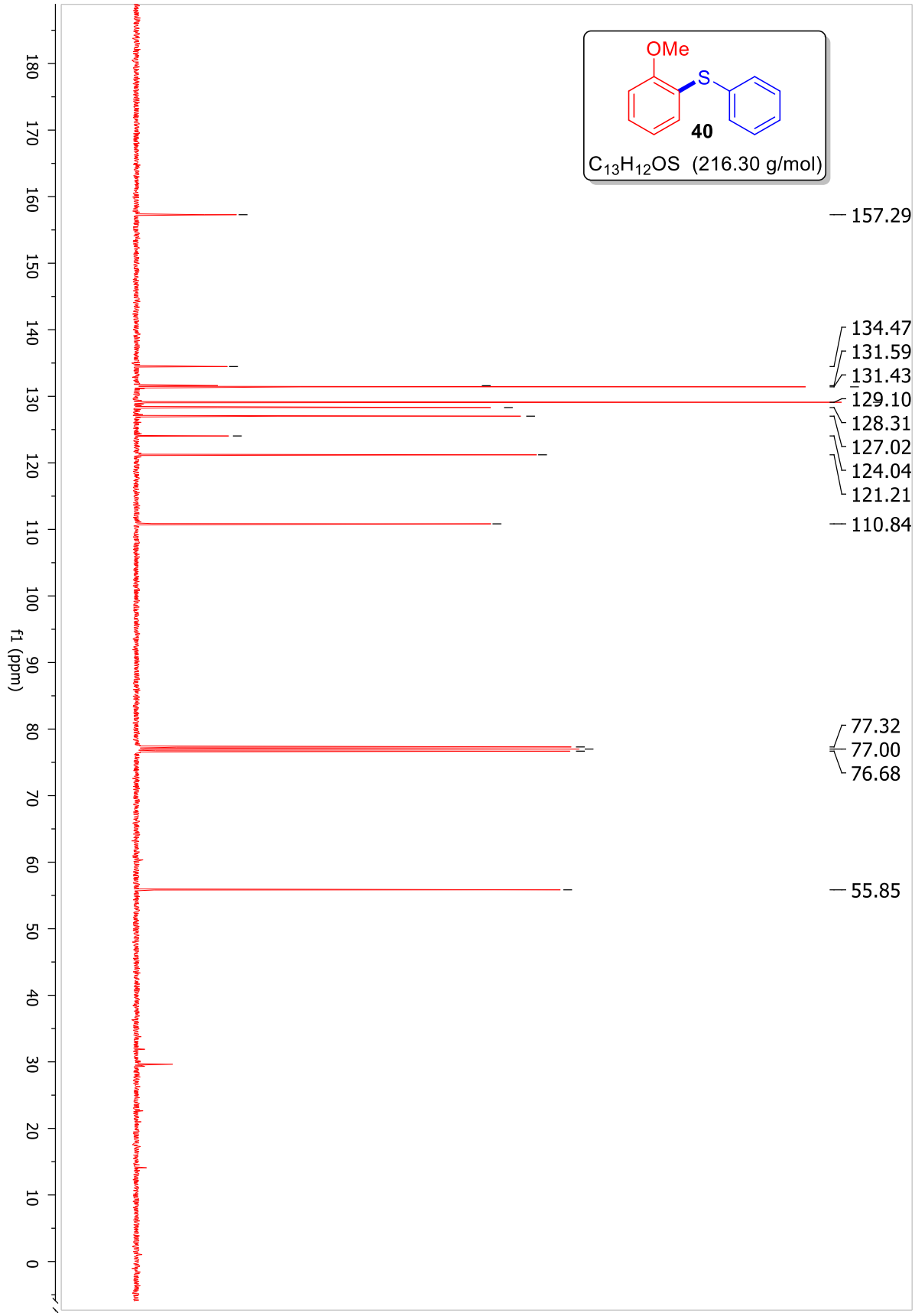
^{19}F NMR of Compound **39:**



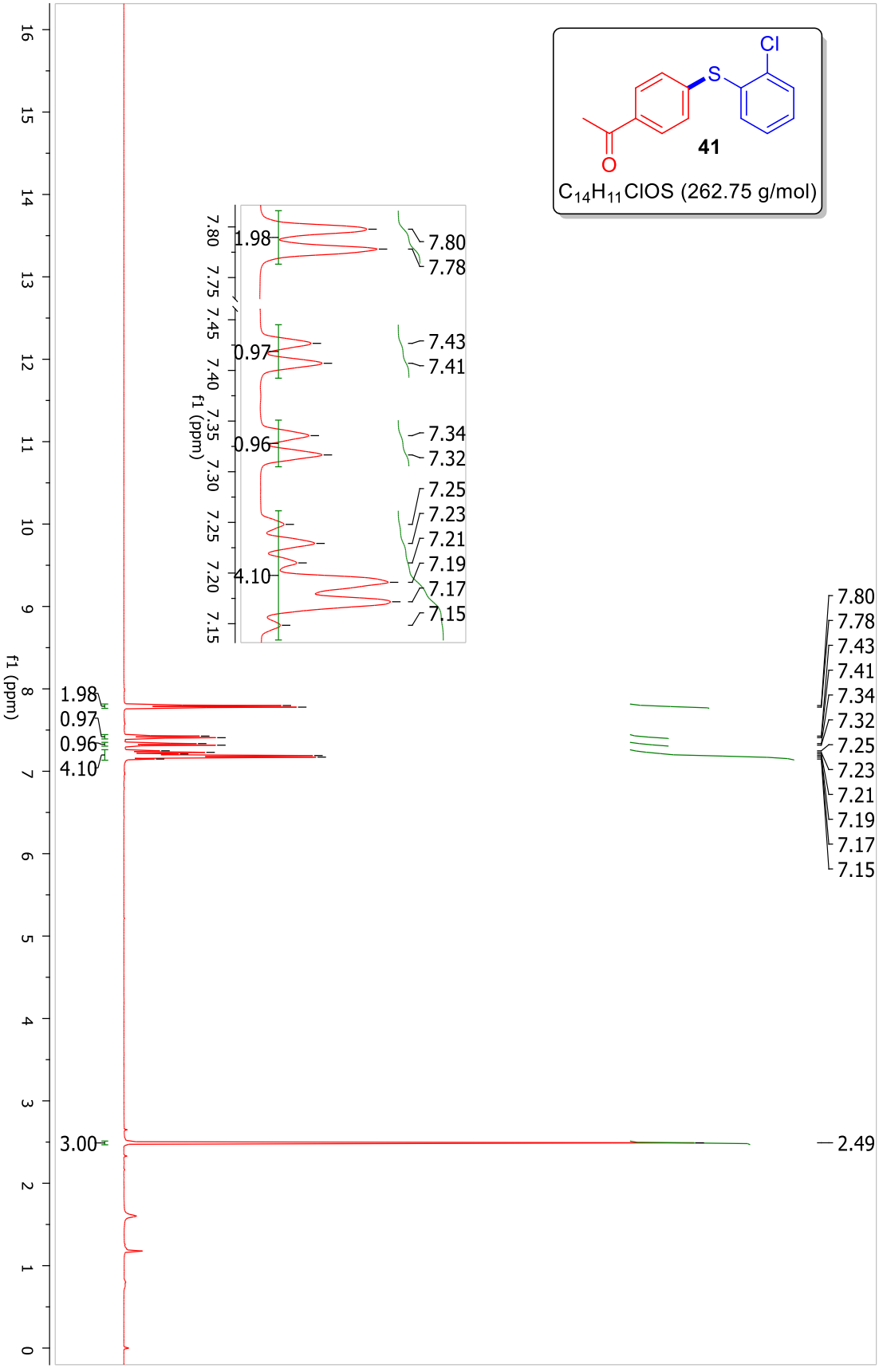
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **40:**



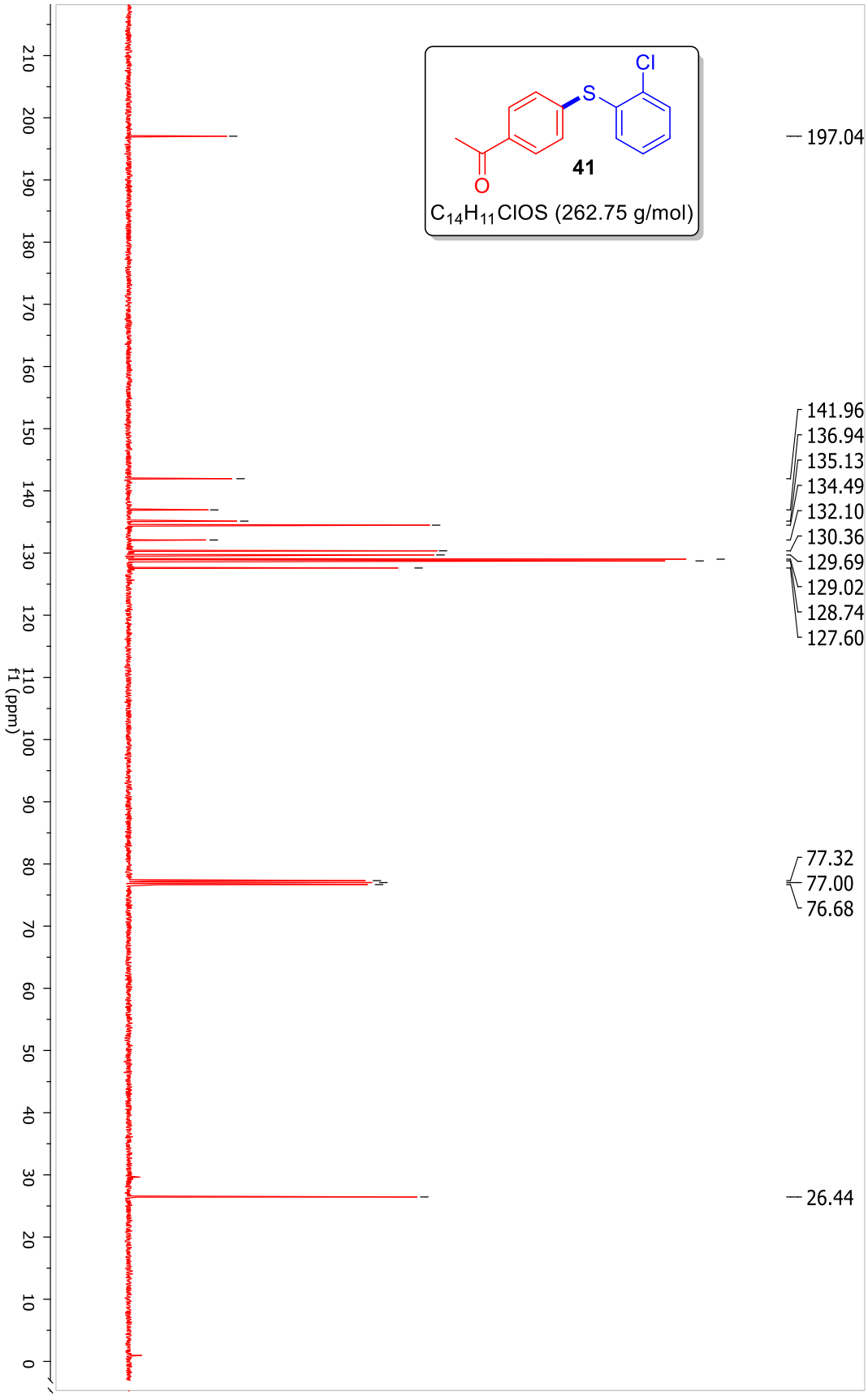
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **40:**



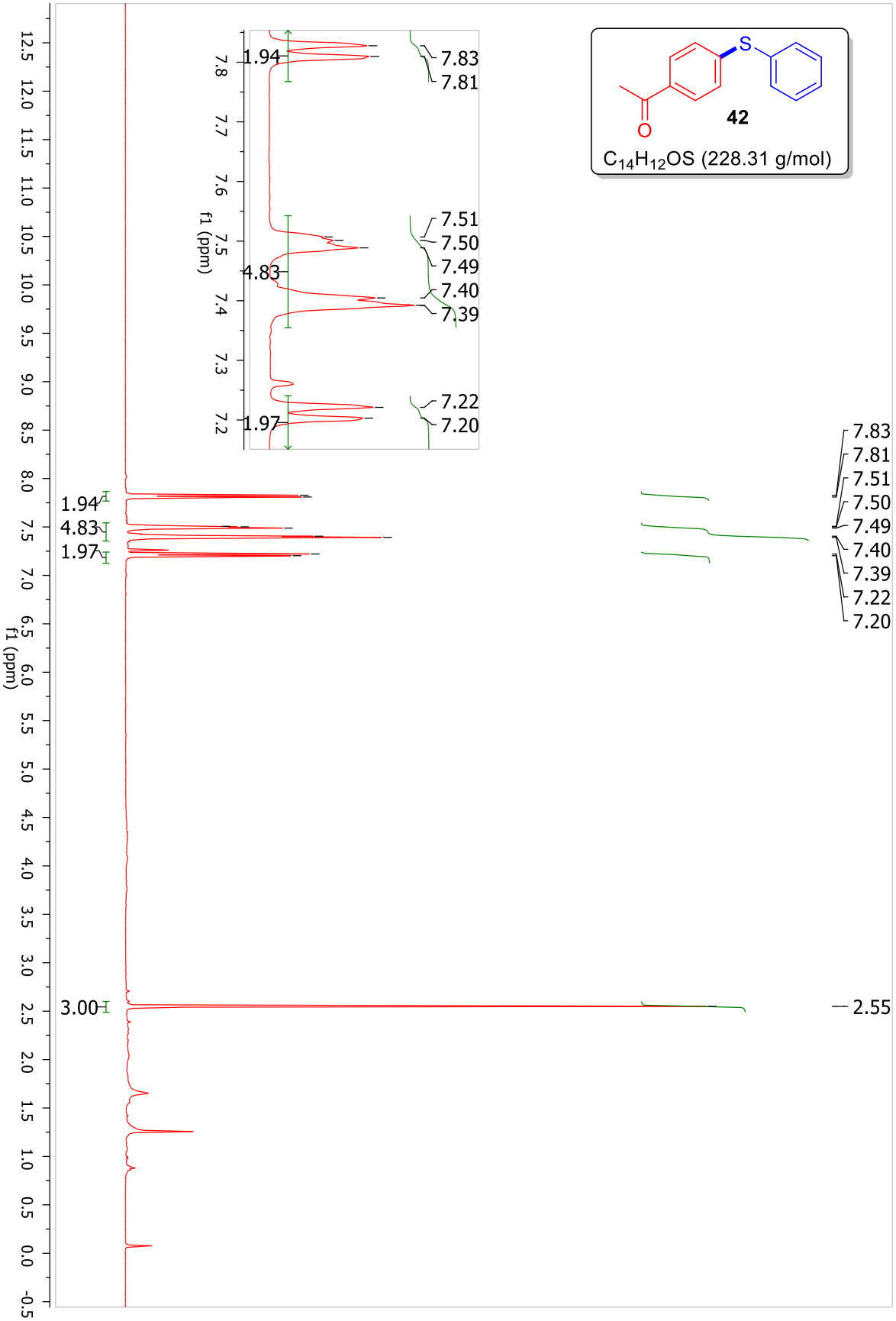
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **41:**



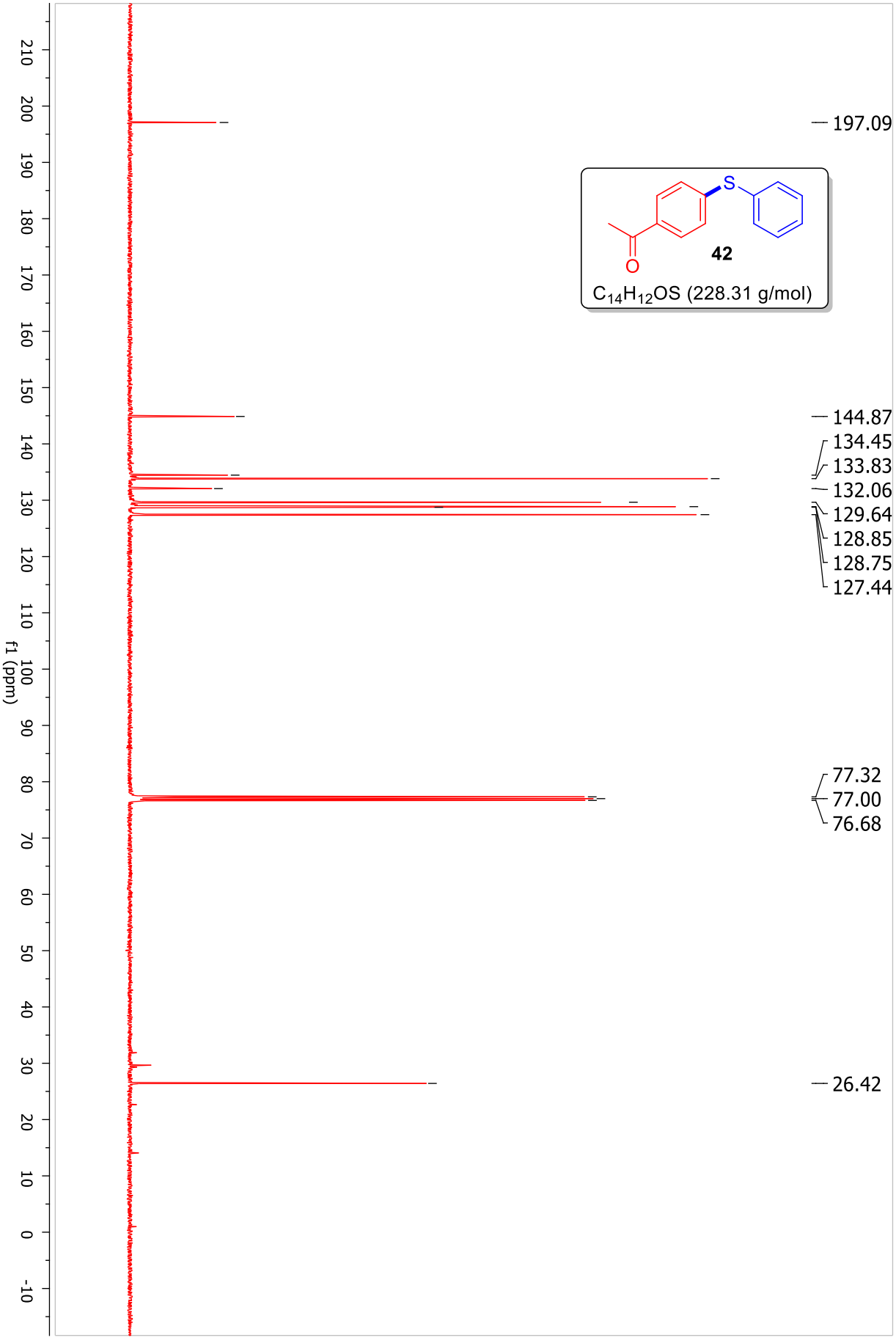
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **41:**



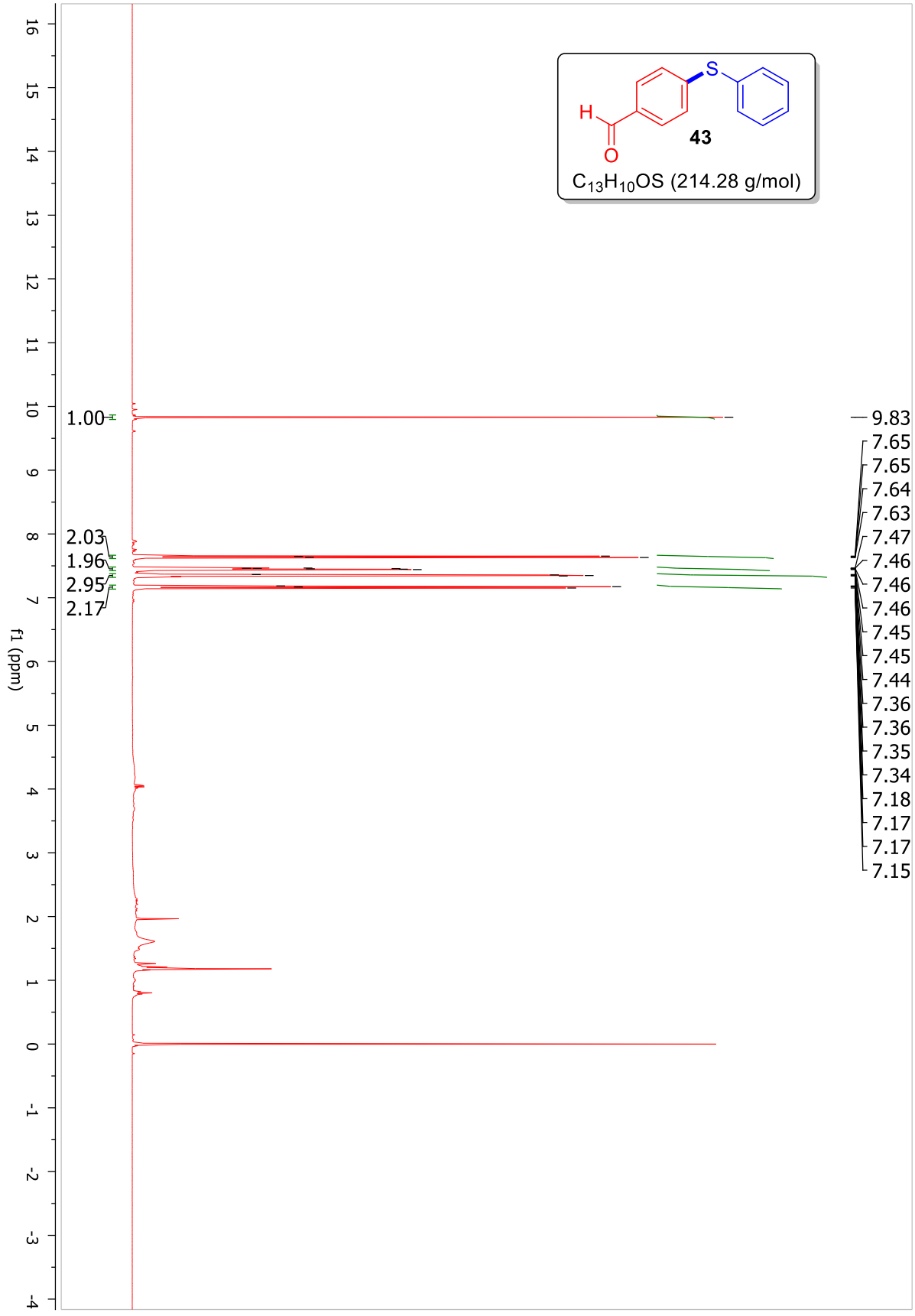
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **42:**



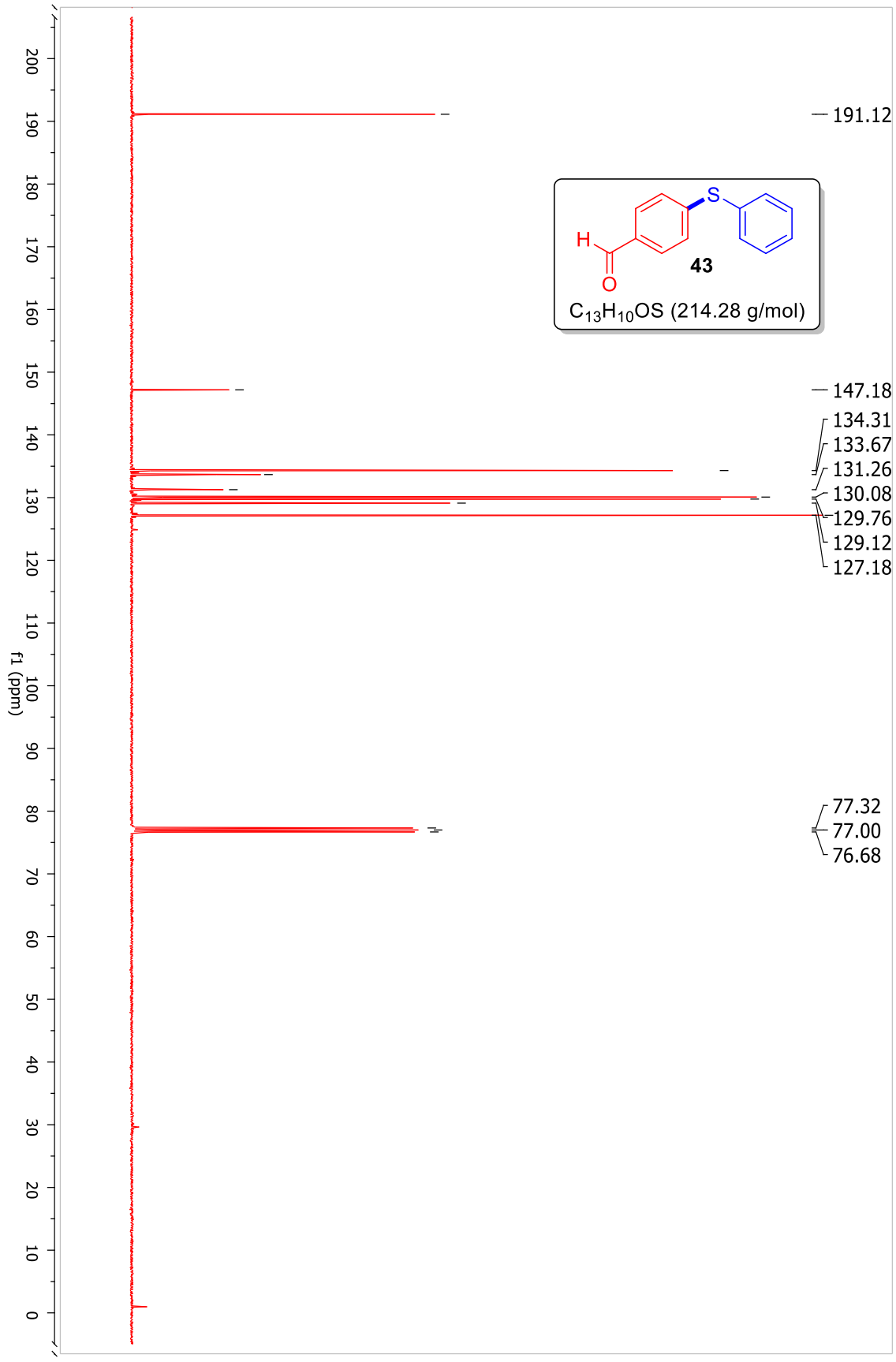
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **42:**



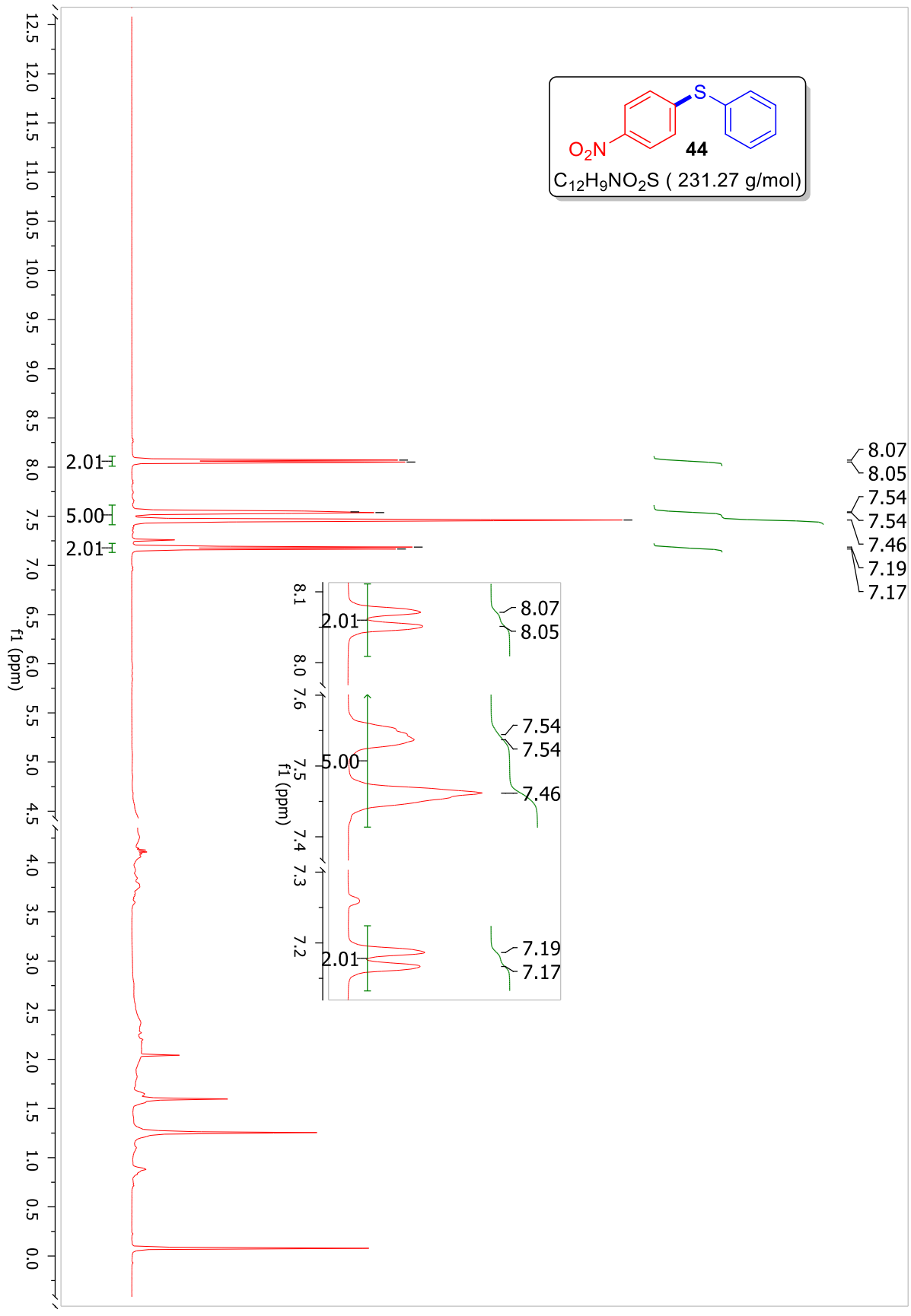
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **43:**



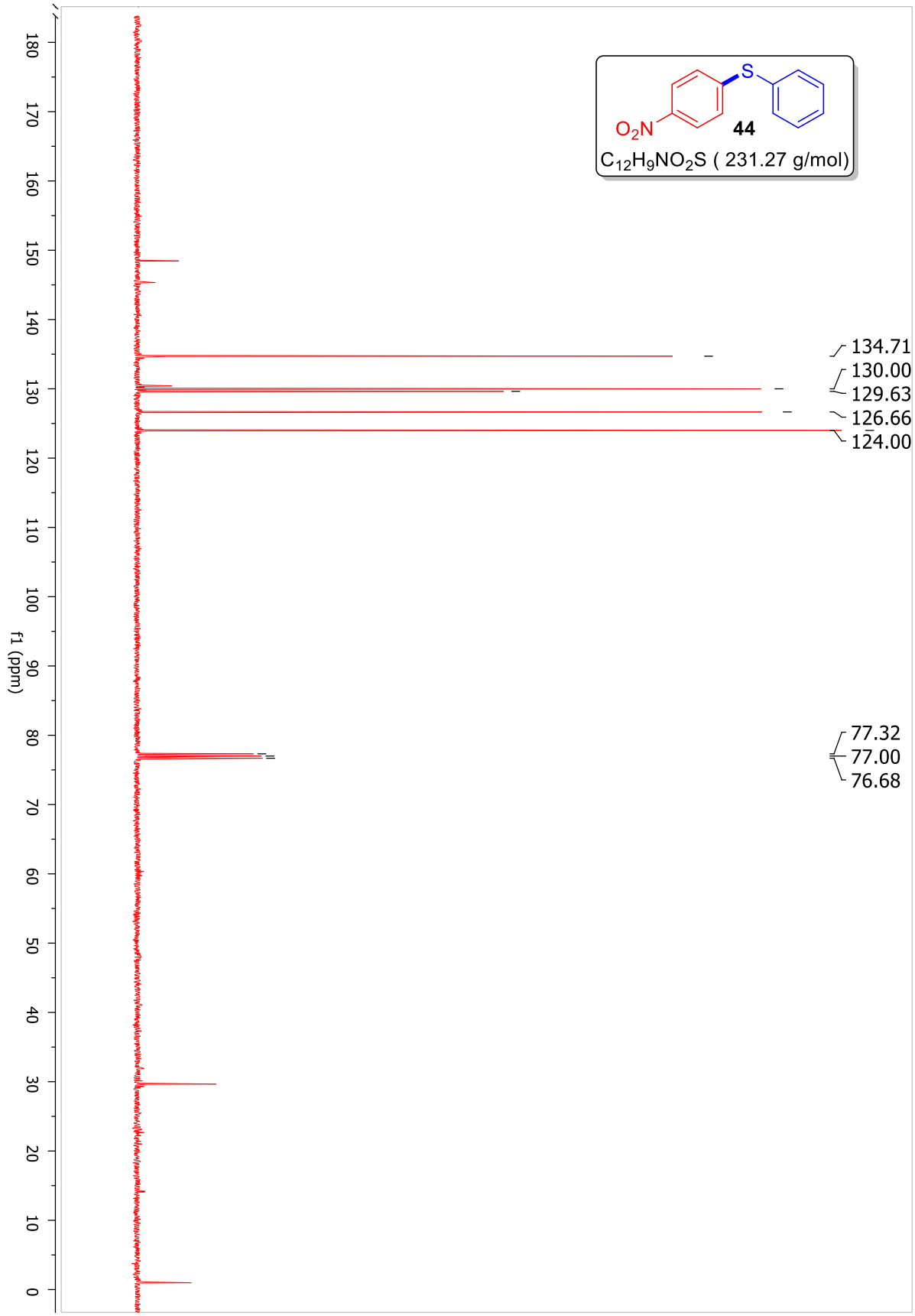
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **43:**



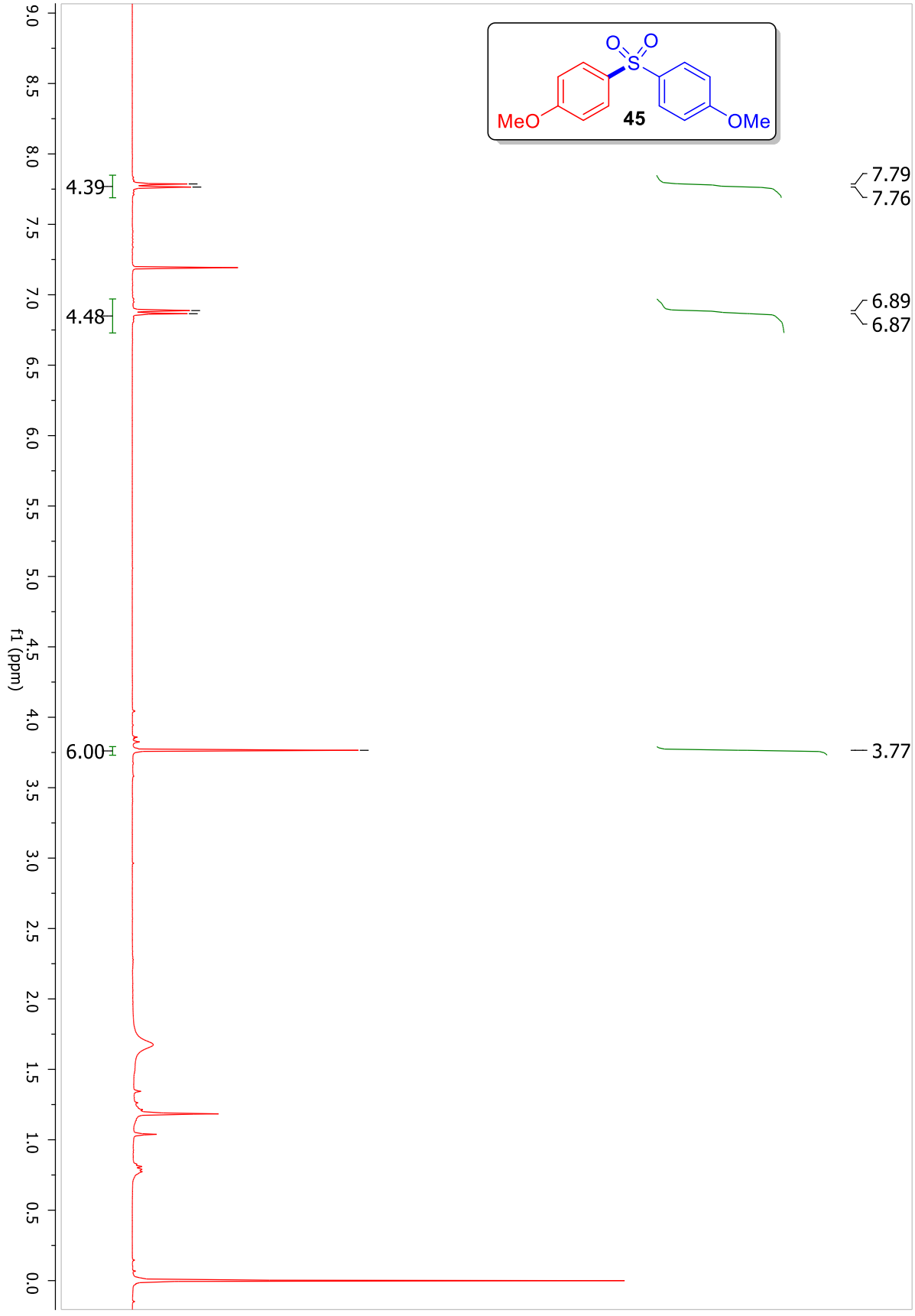
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **44:**



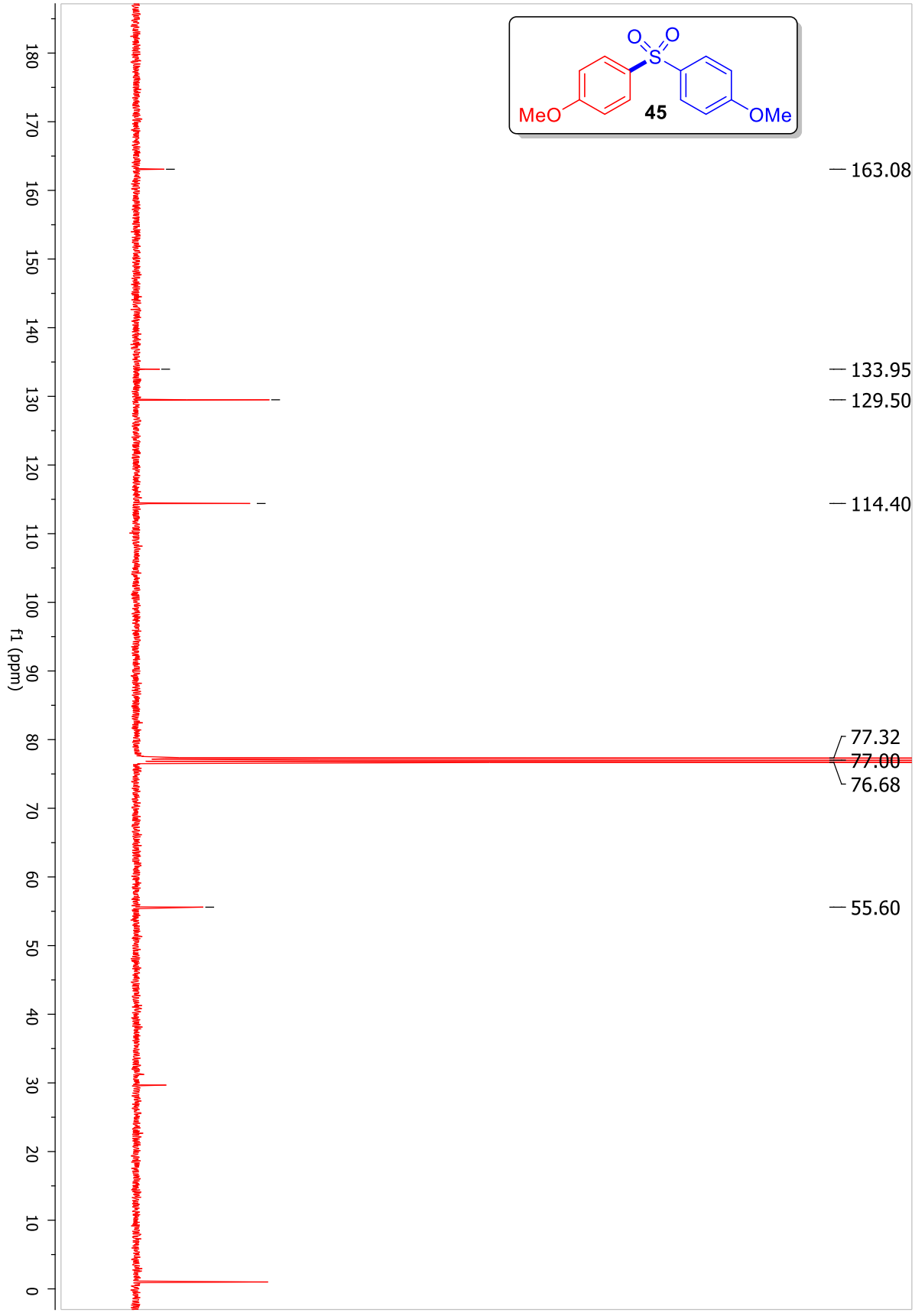
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **44:**



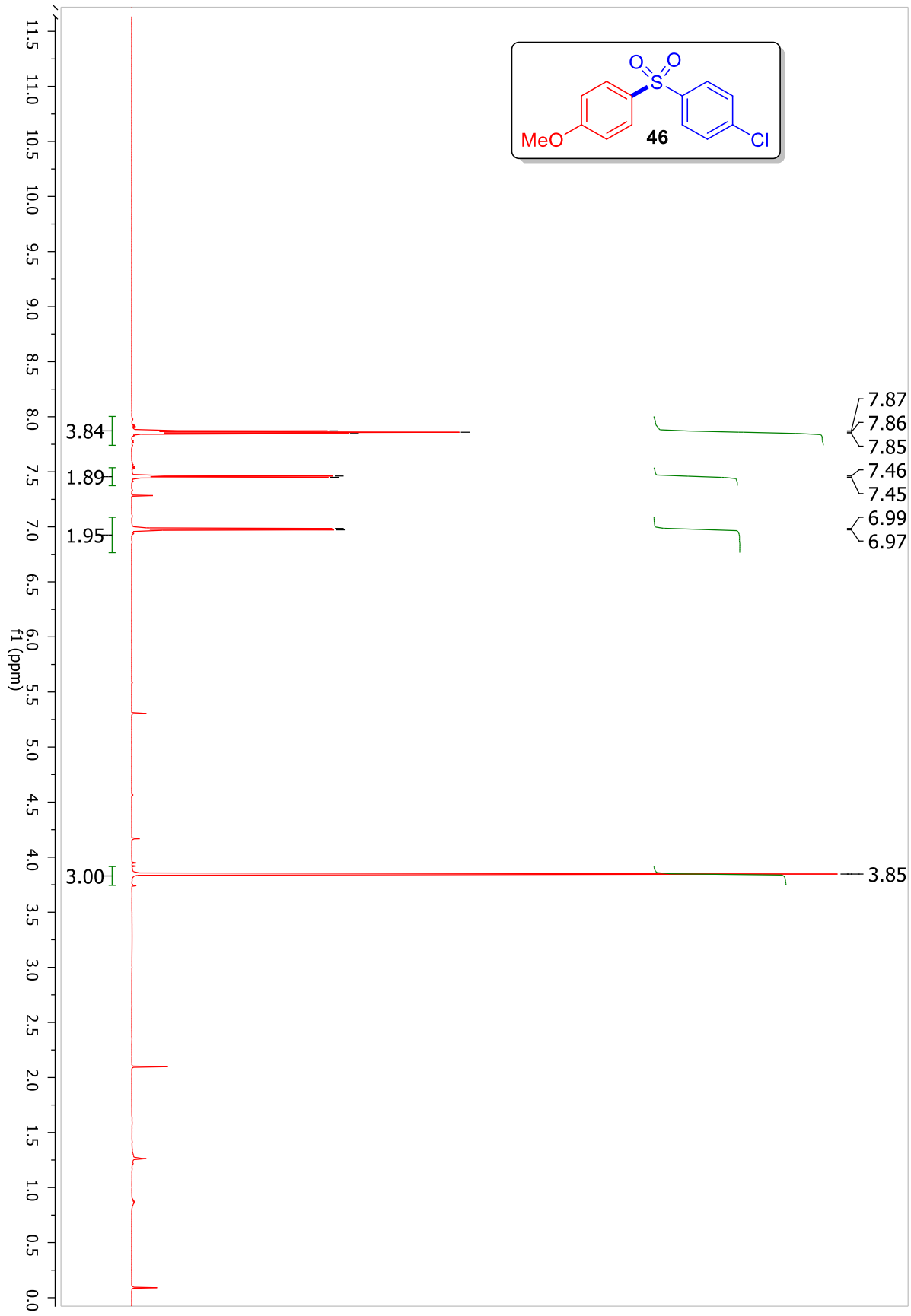
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **45:**



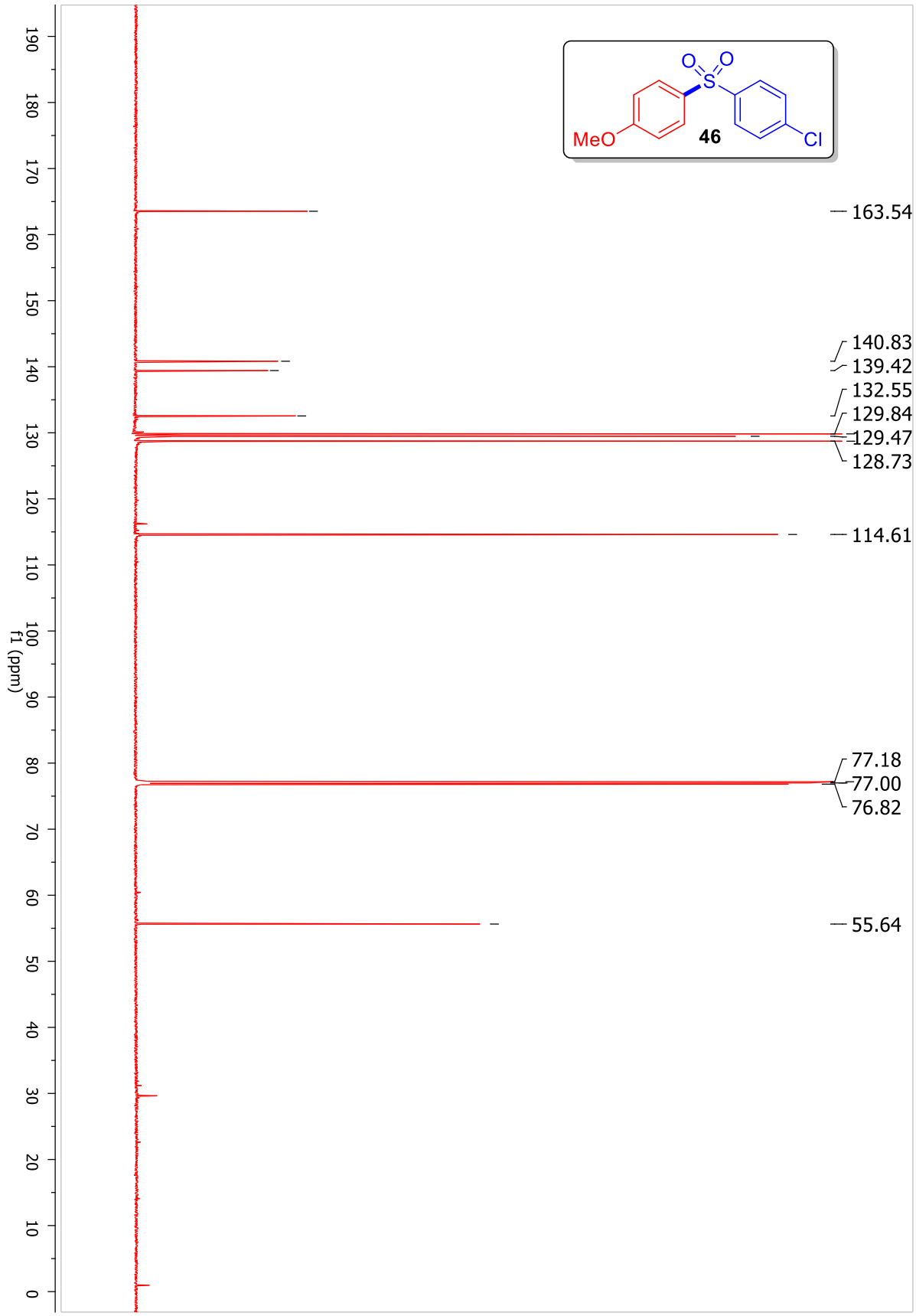
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **45:**



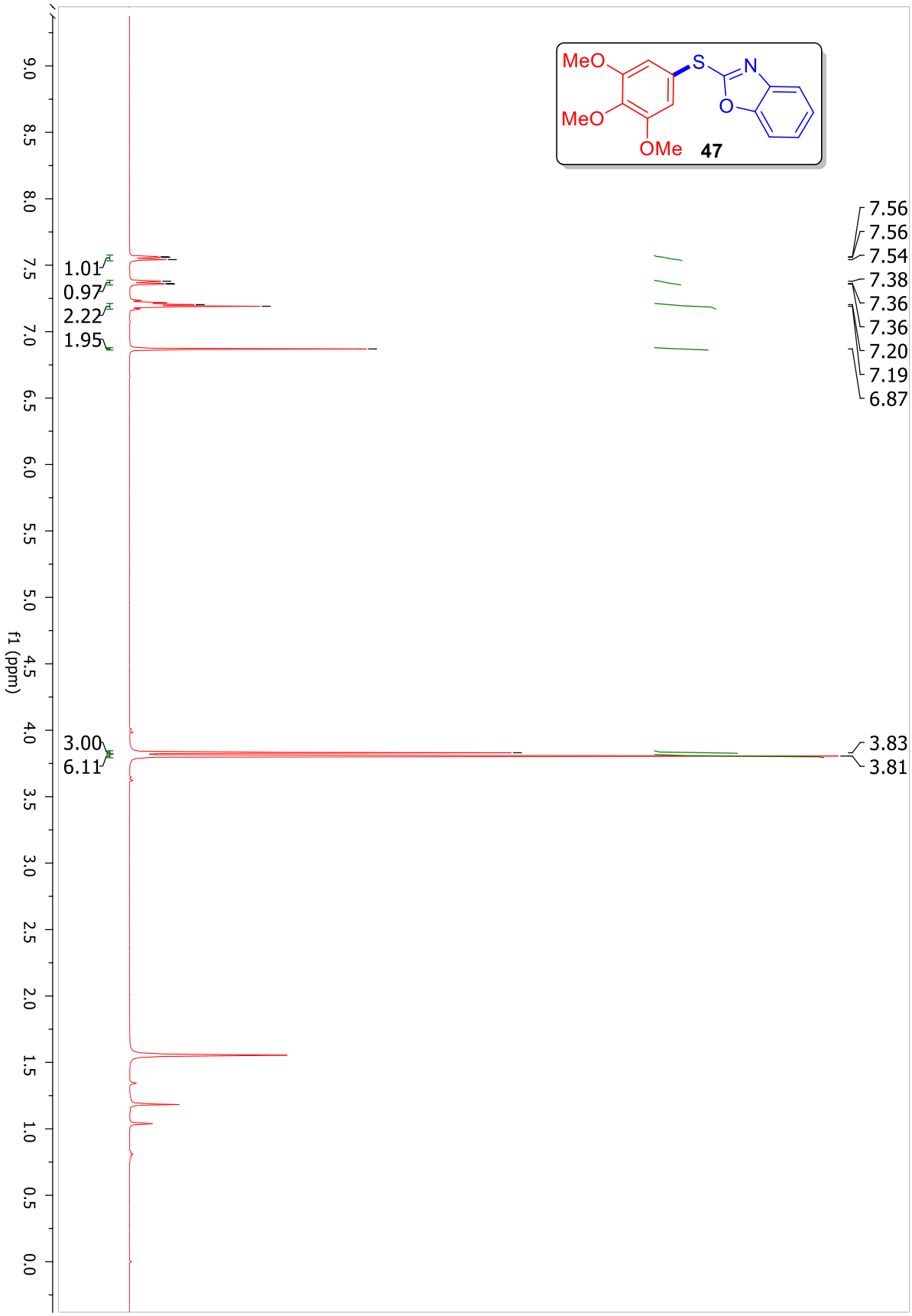
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **46:**



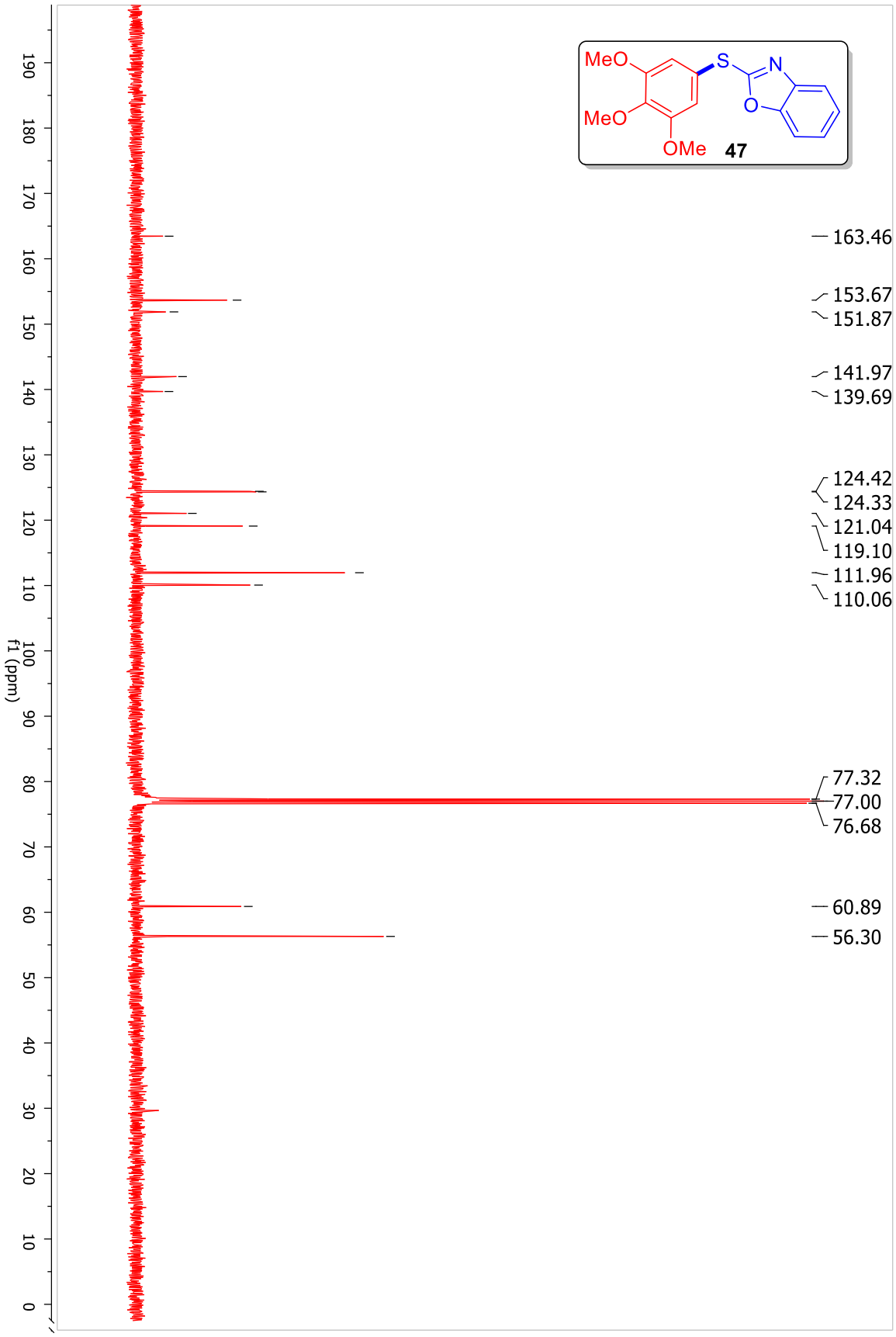
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **46:**



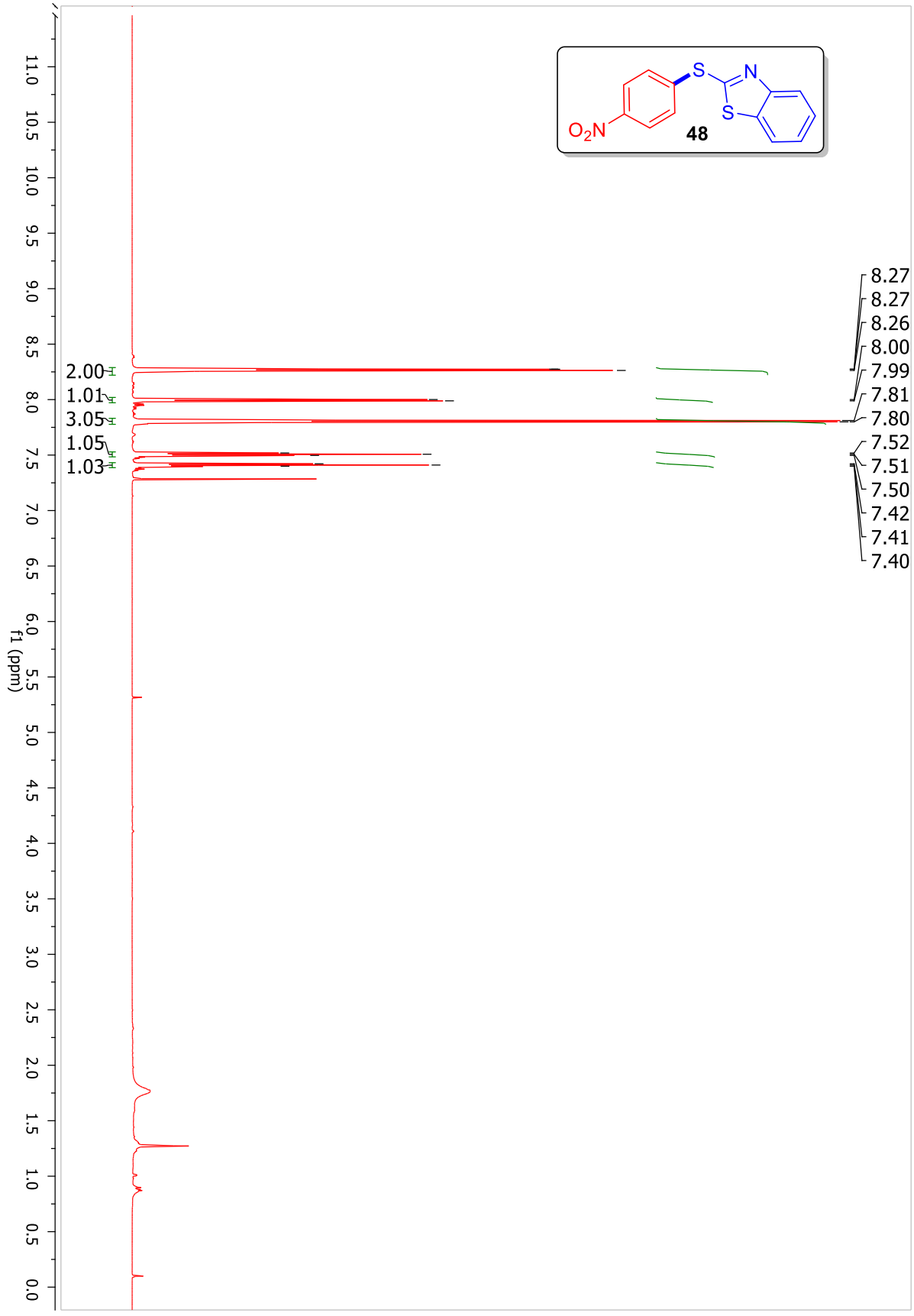
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **47:**



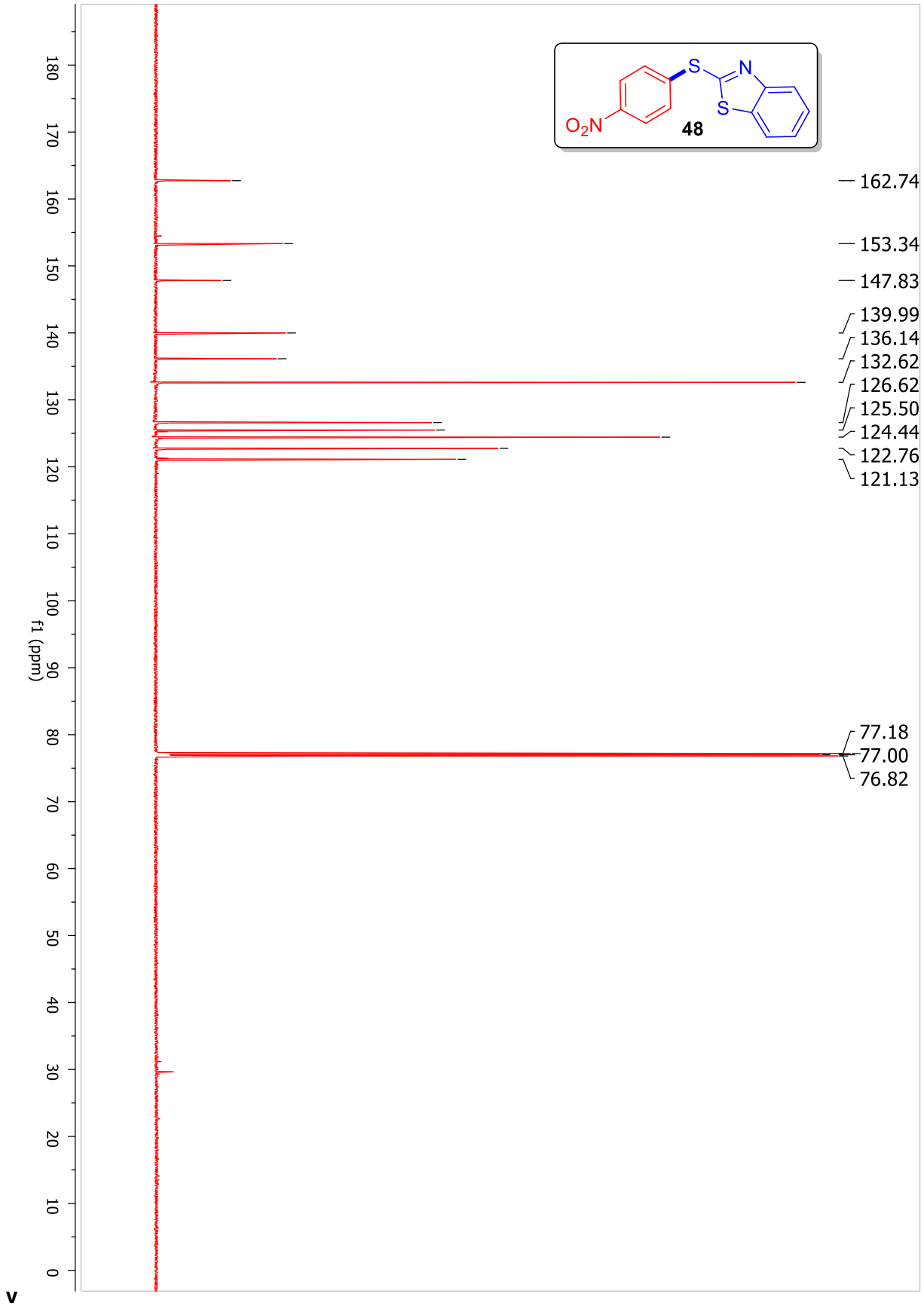
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **47:**



^{1}H-NMR (400 MHz, $CDCl_3$) of compound **48:**

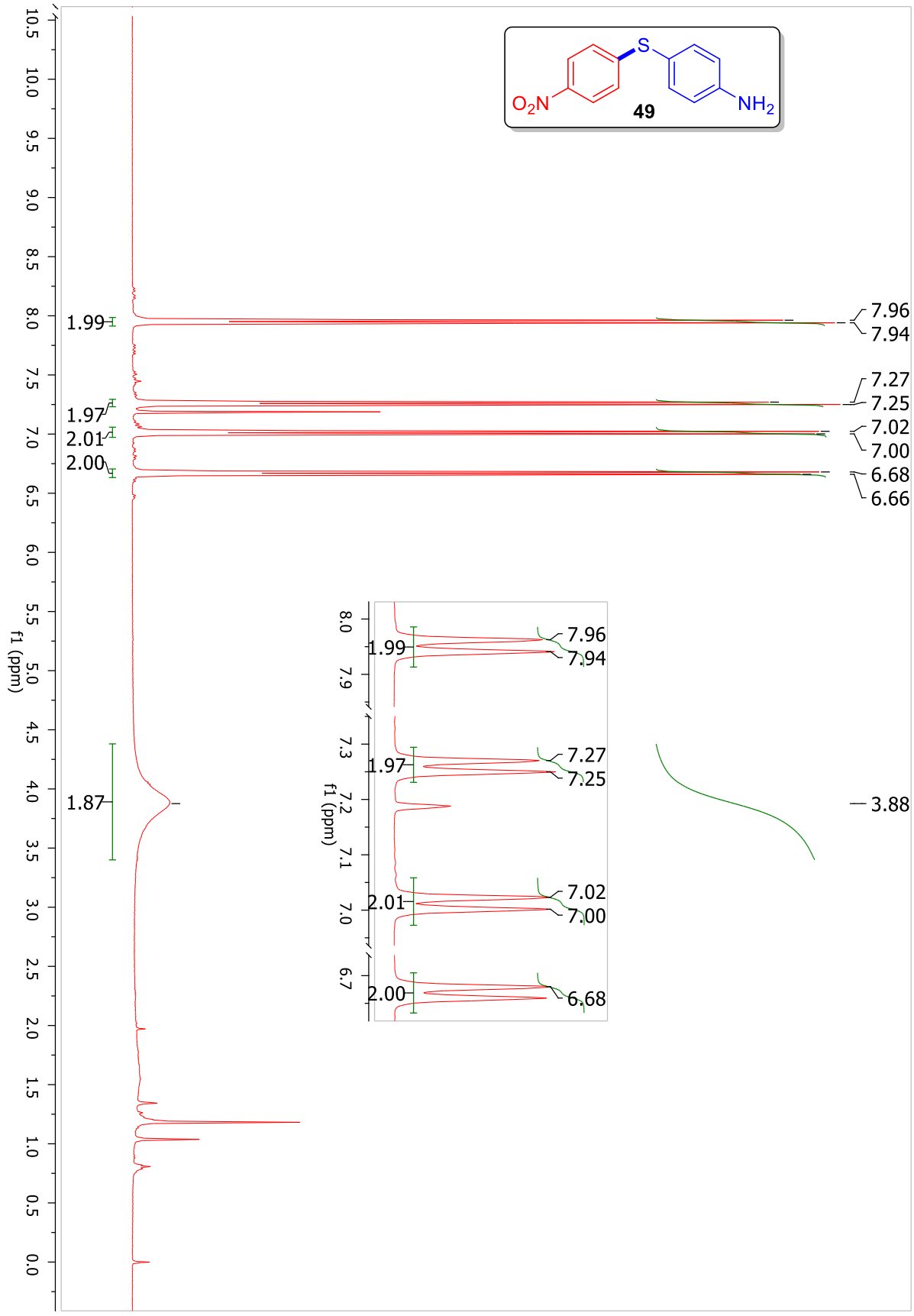


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **48:**

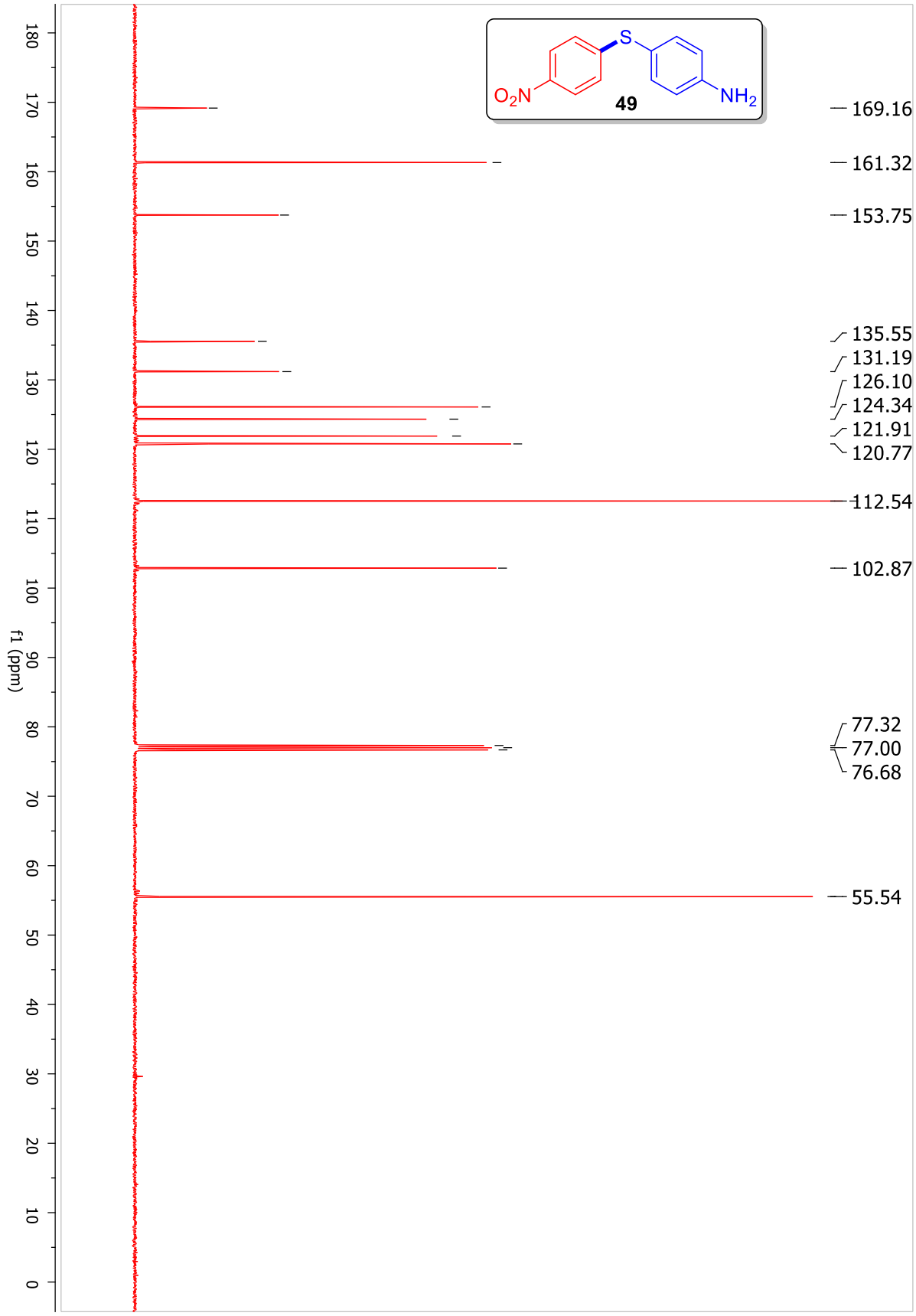


v

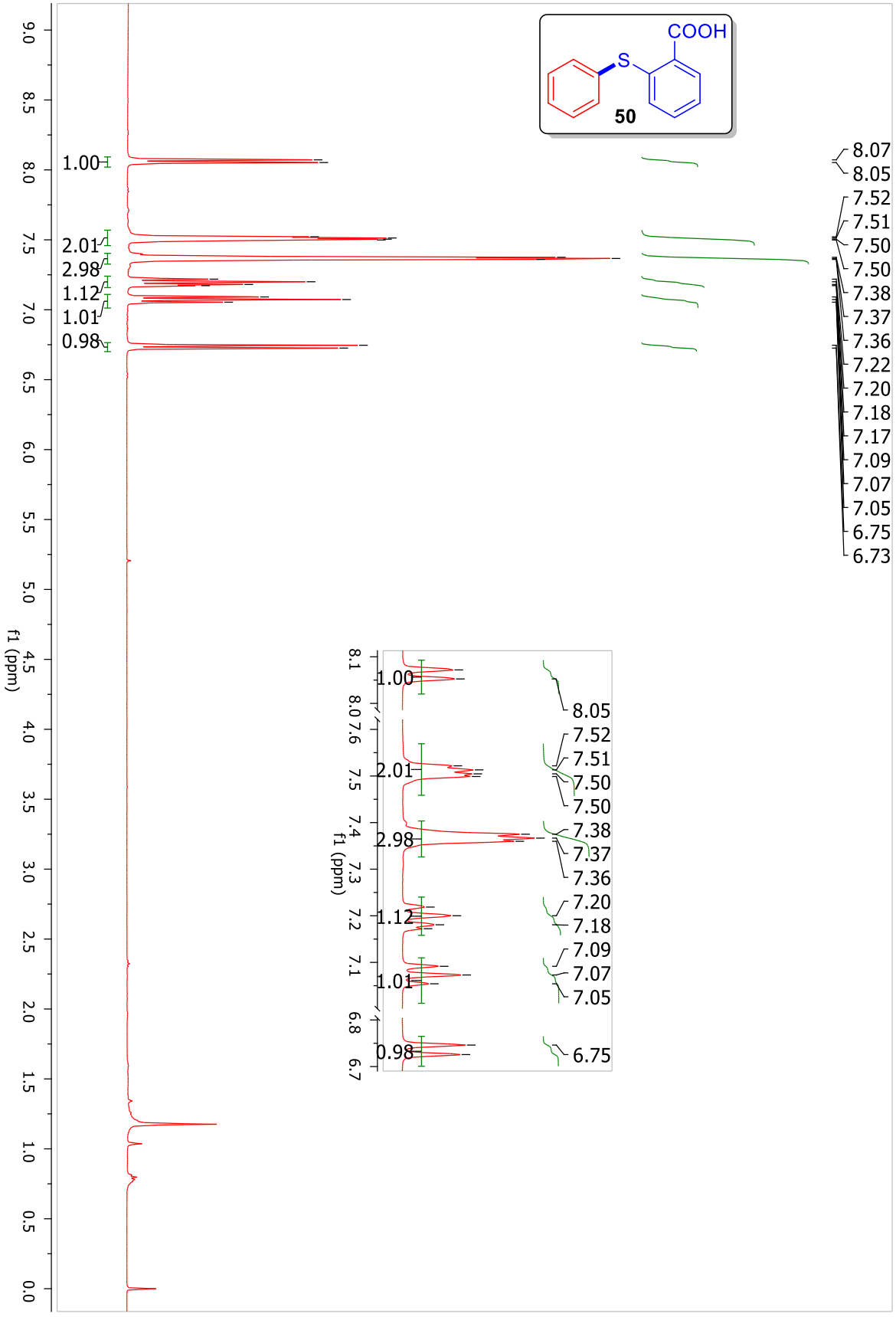
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **49:**



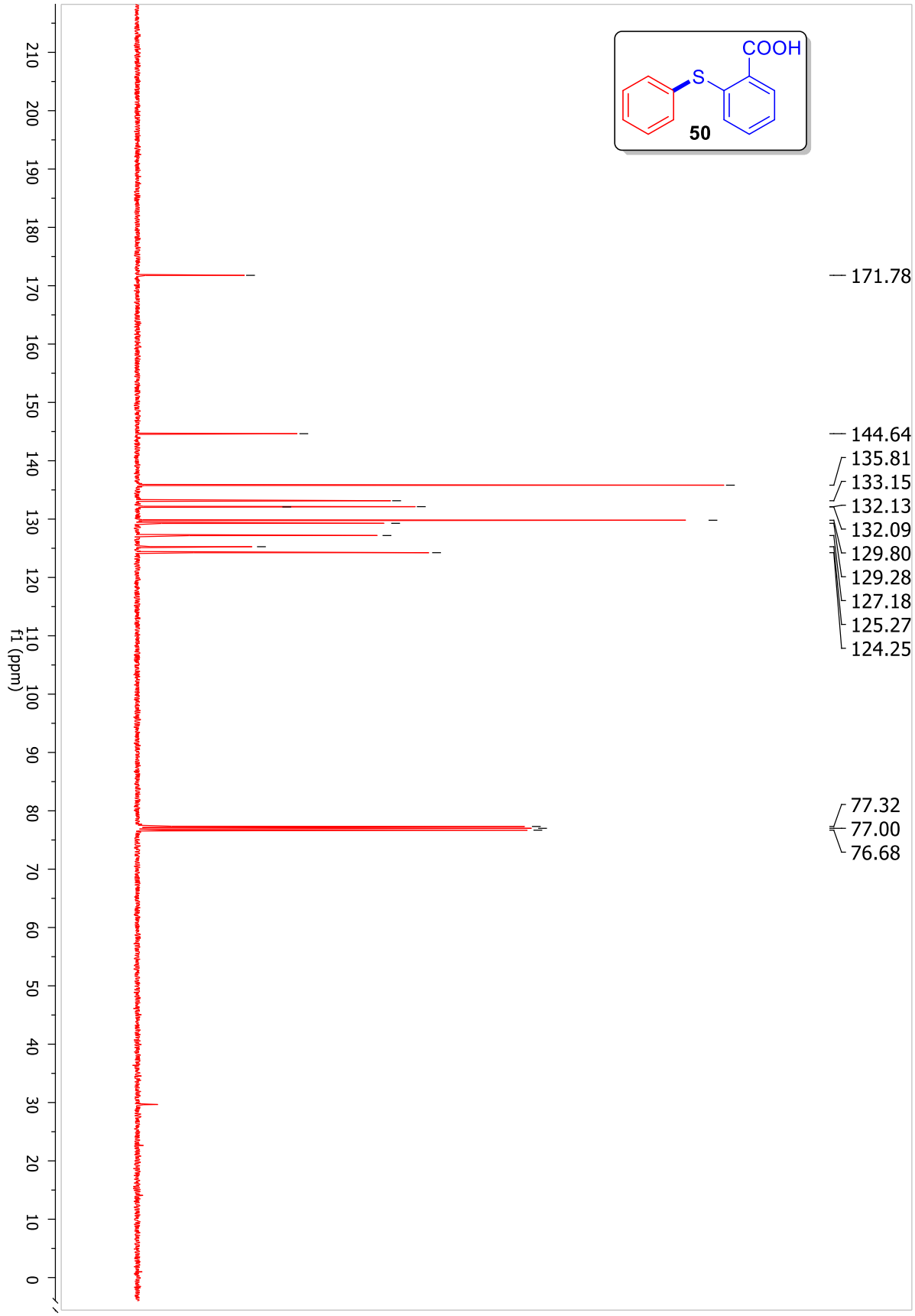
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **49:**



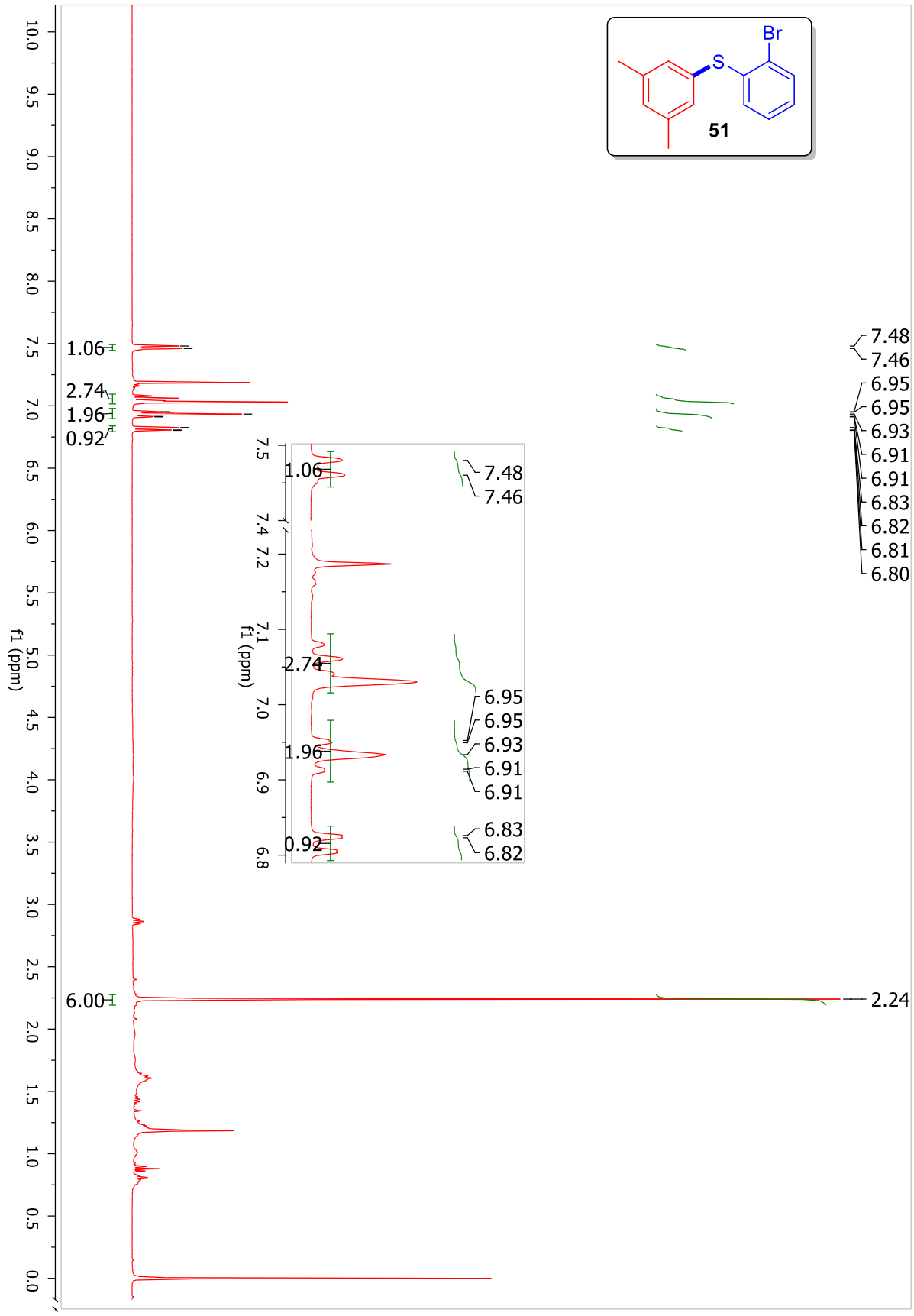
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **50:**



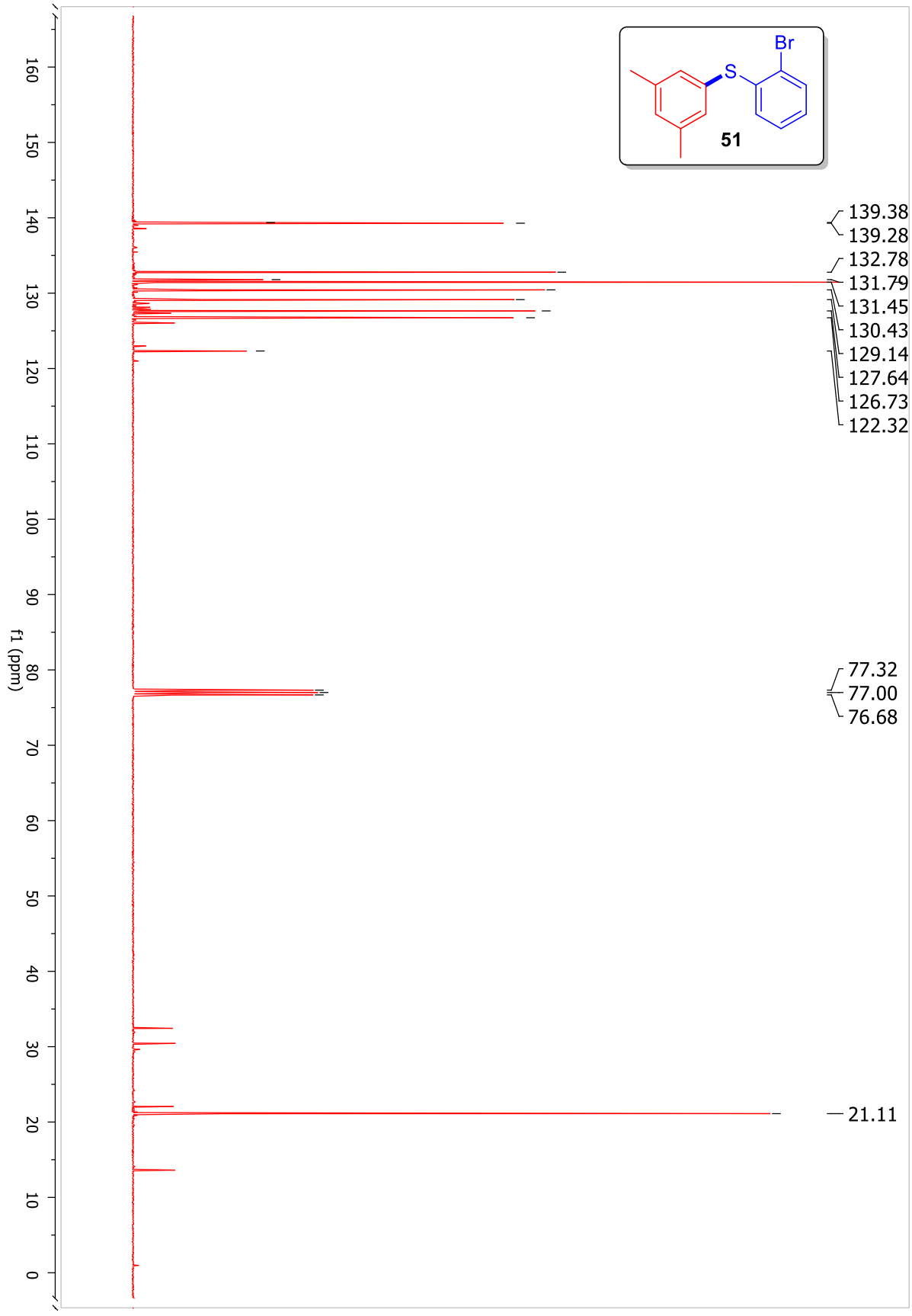
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **50:**



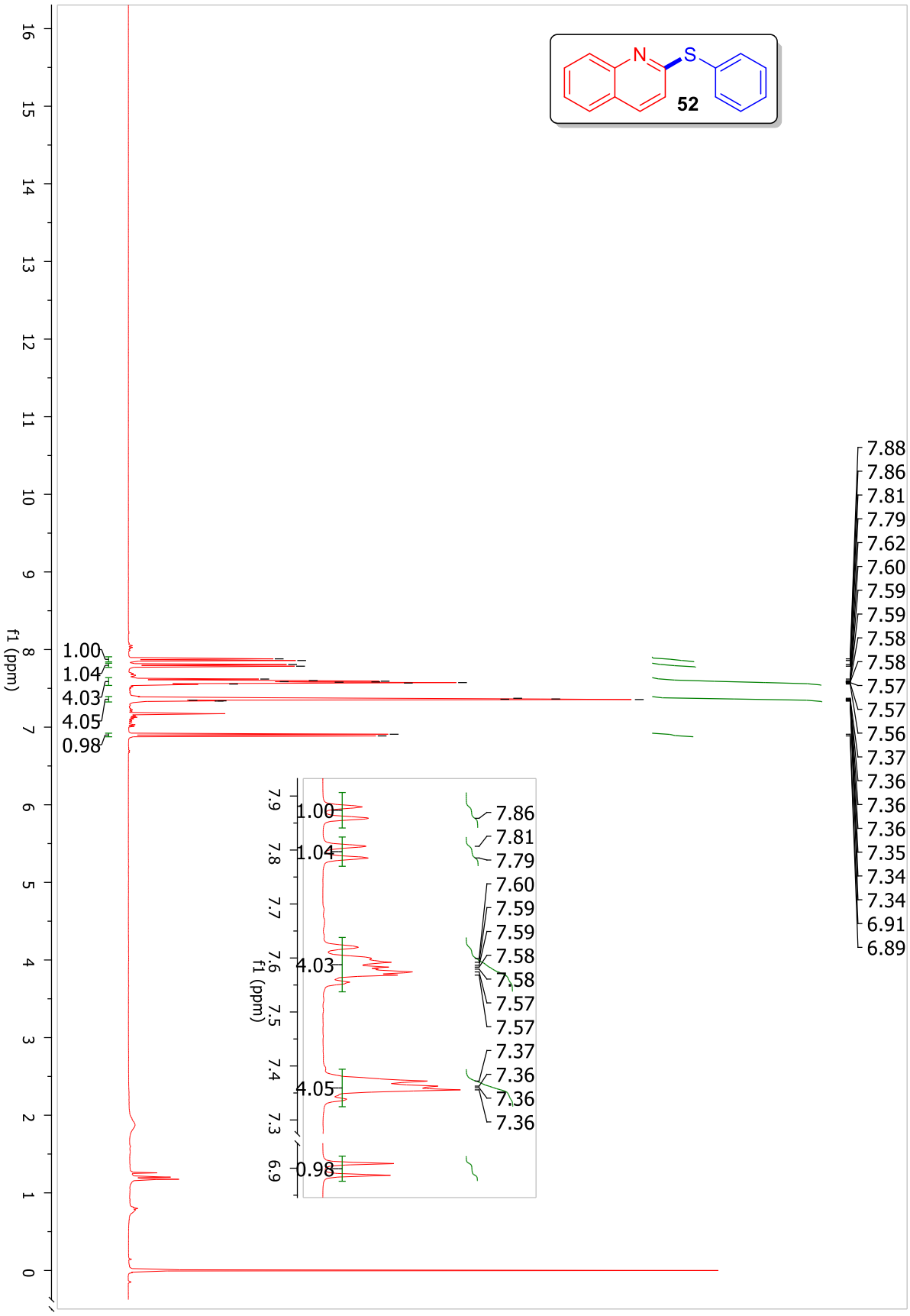
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **51:**



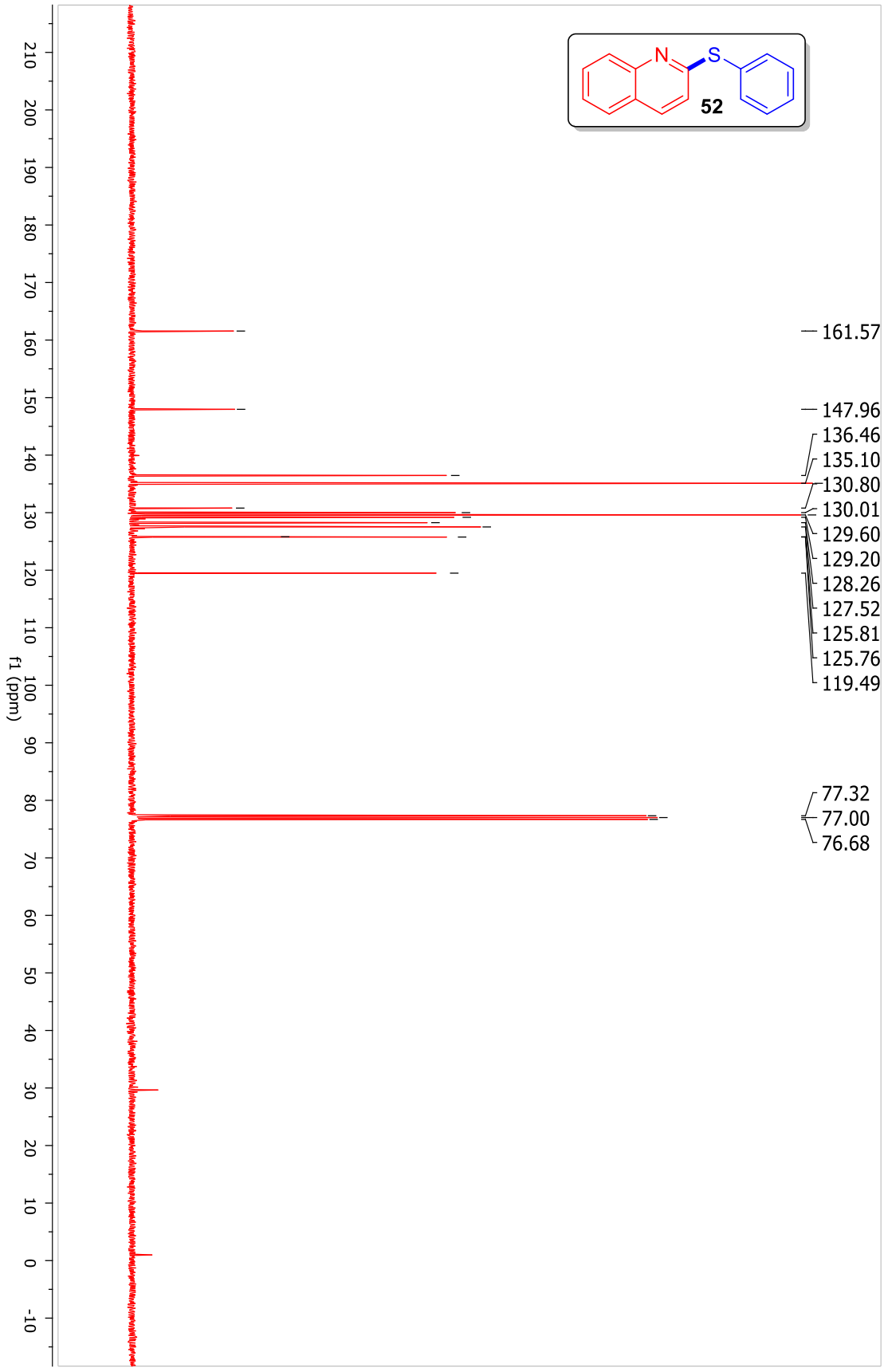
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **51:**



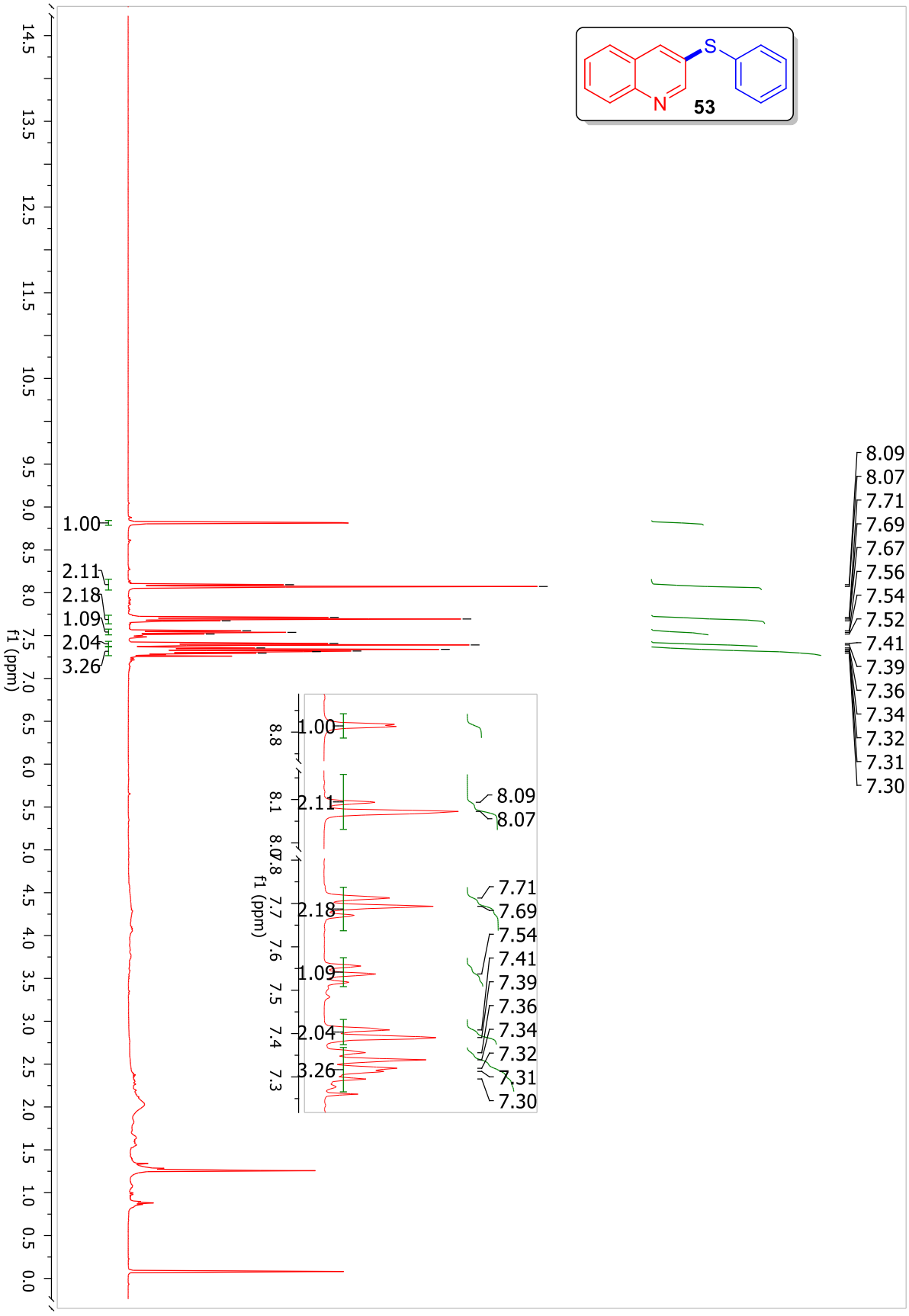
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **52:**



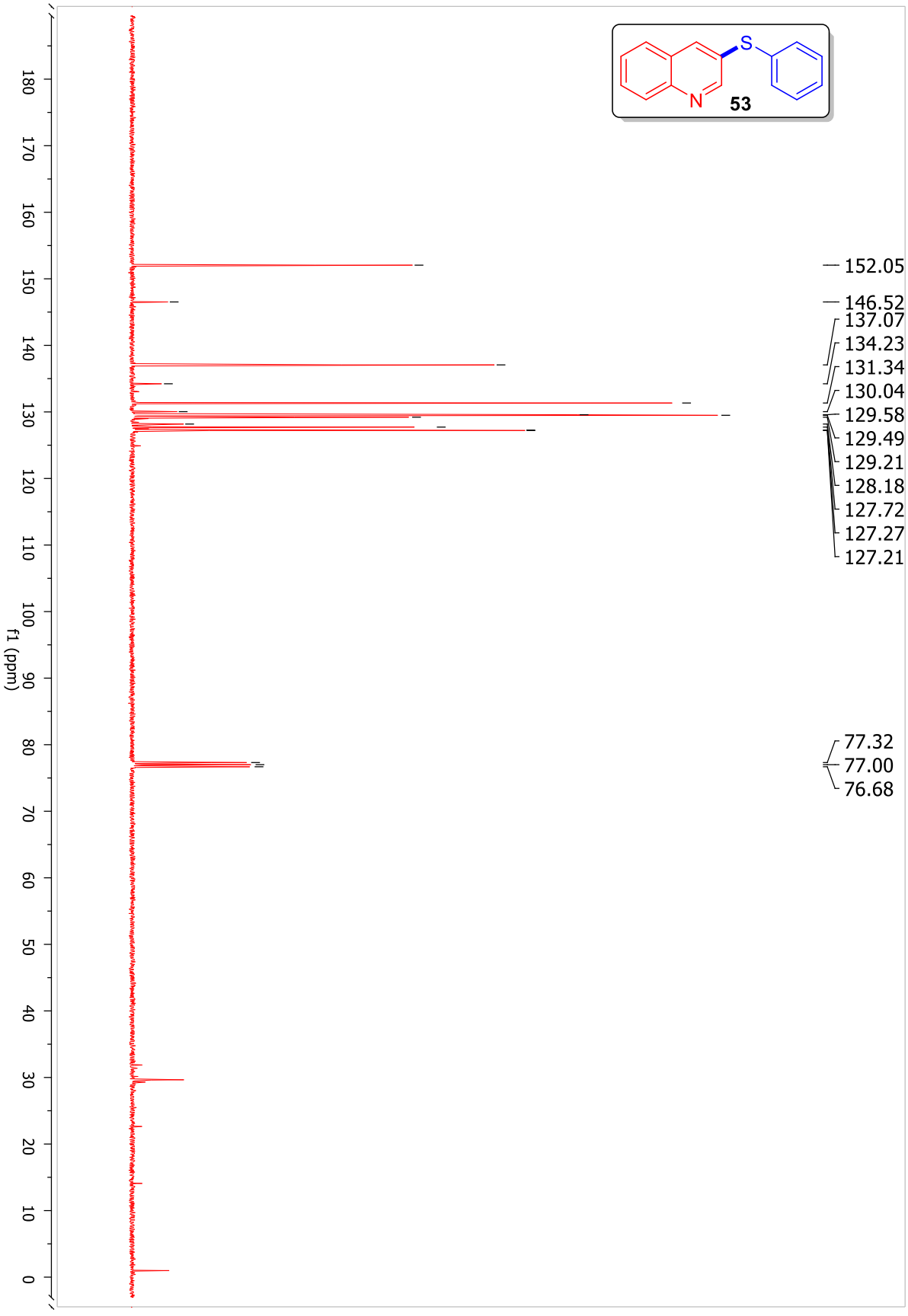
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **52:**



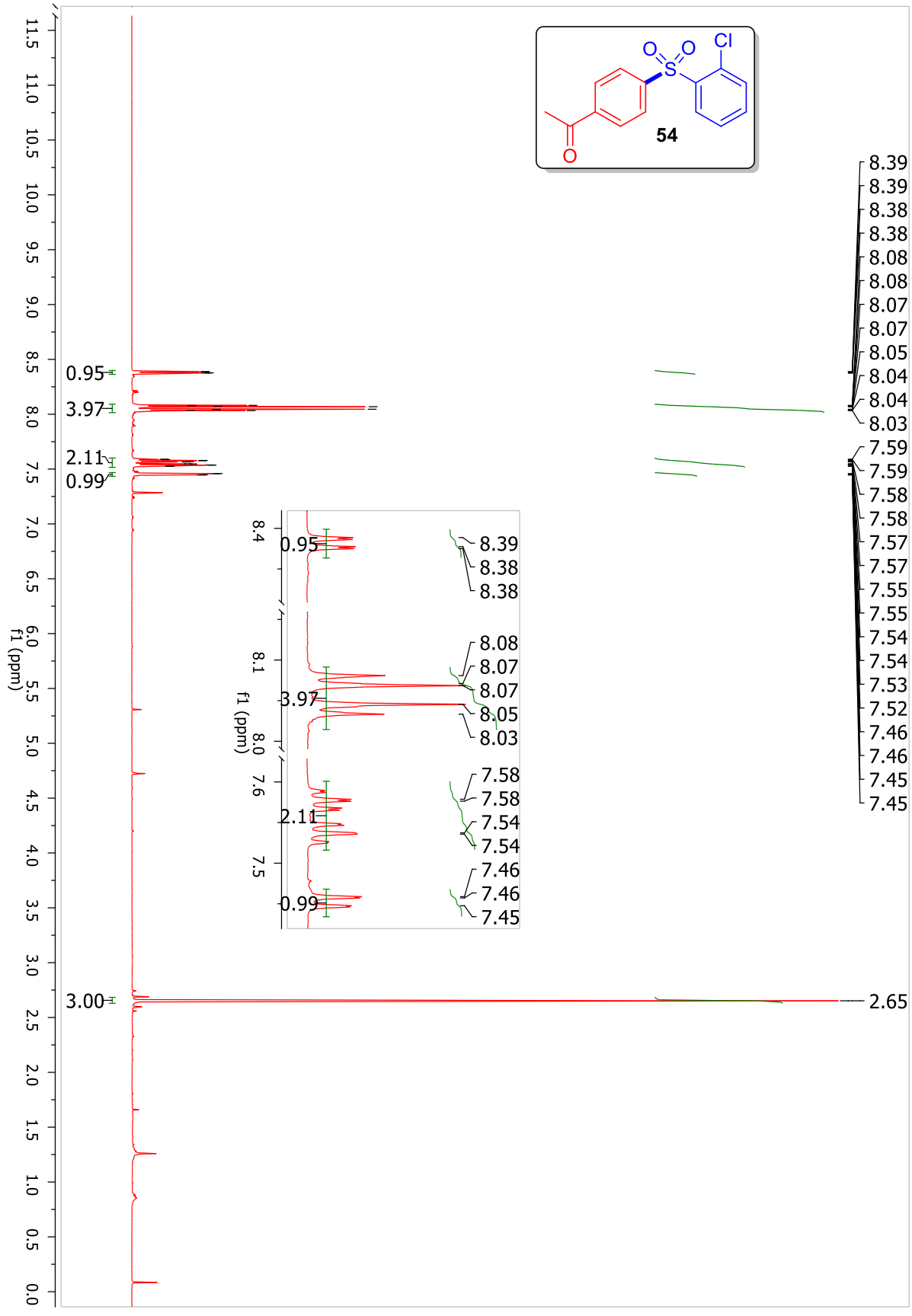
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **53:**



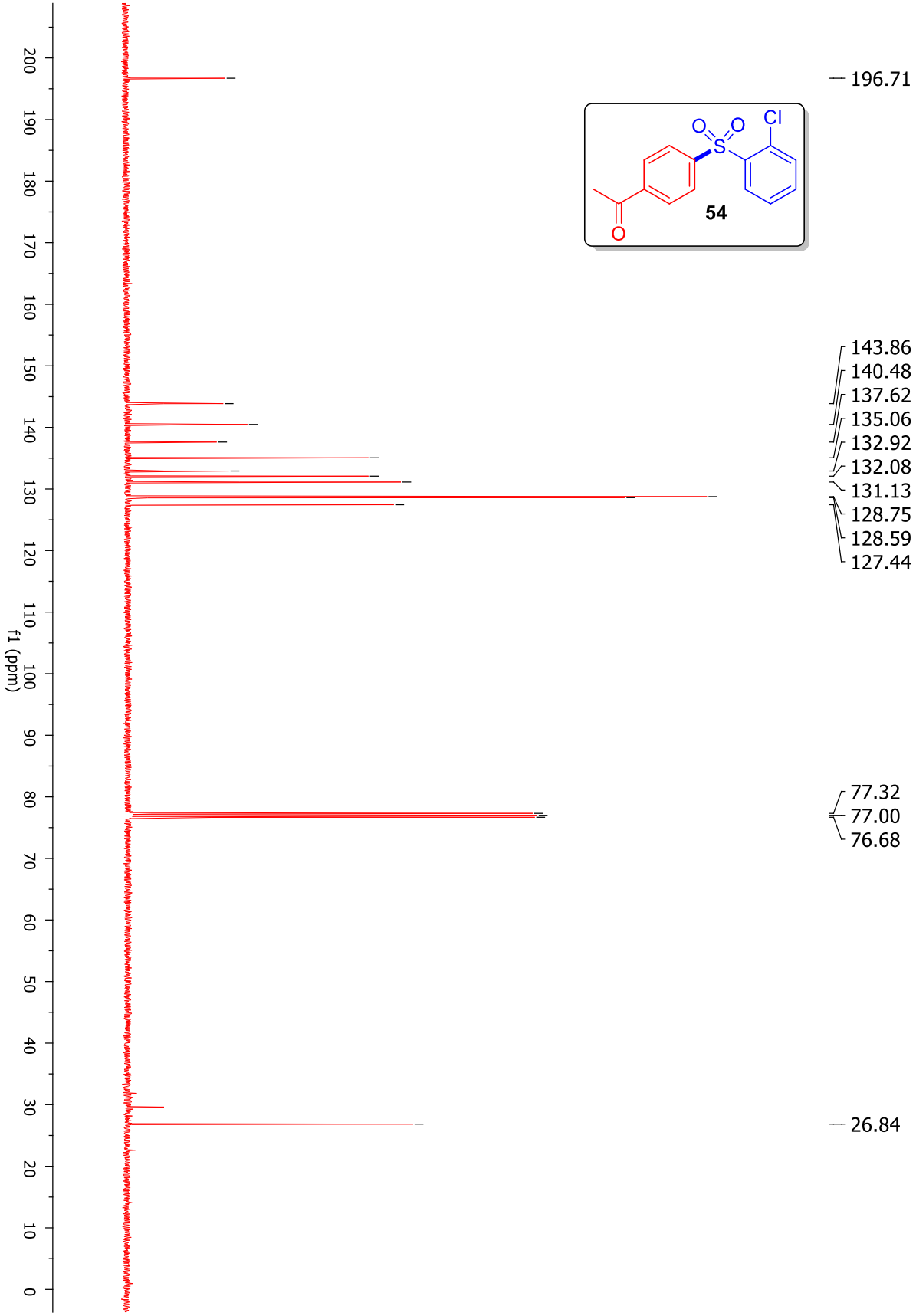
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **53:**



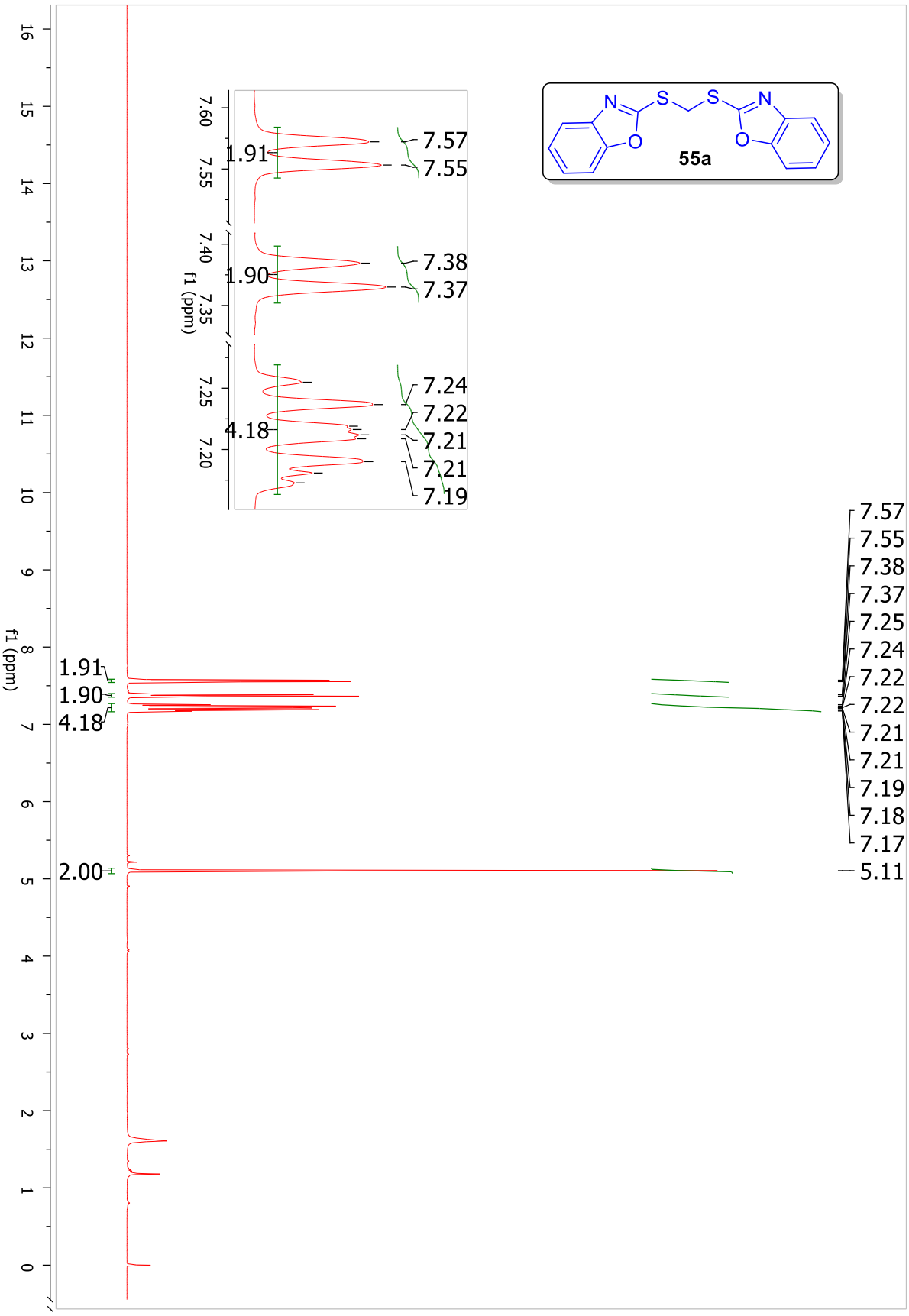
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **54:**



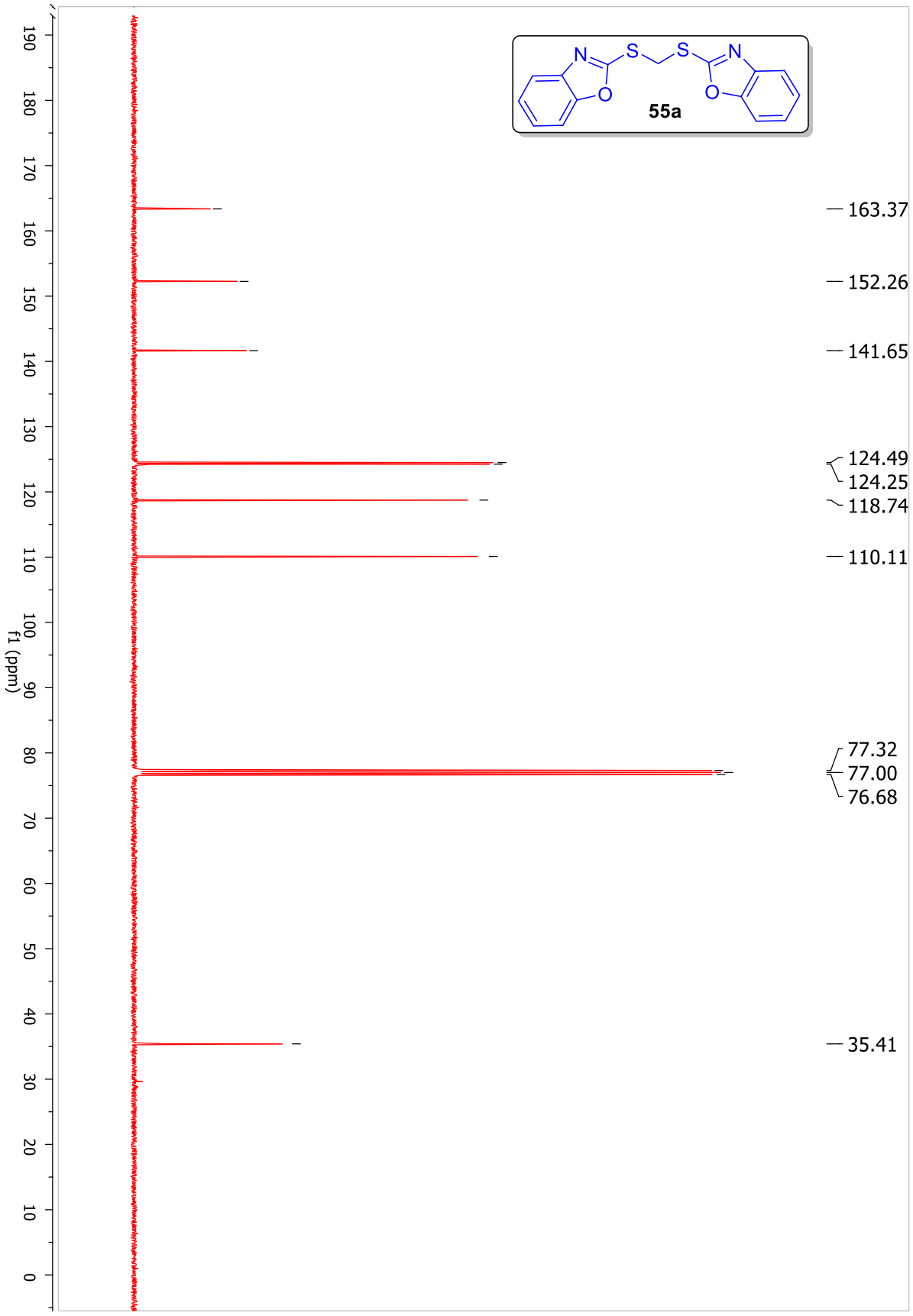
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **54:**



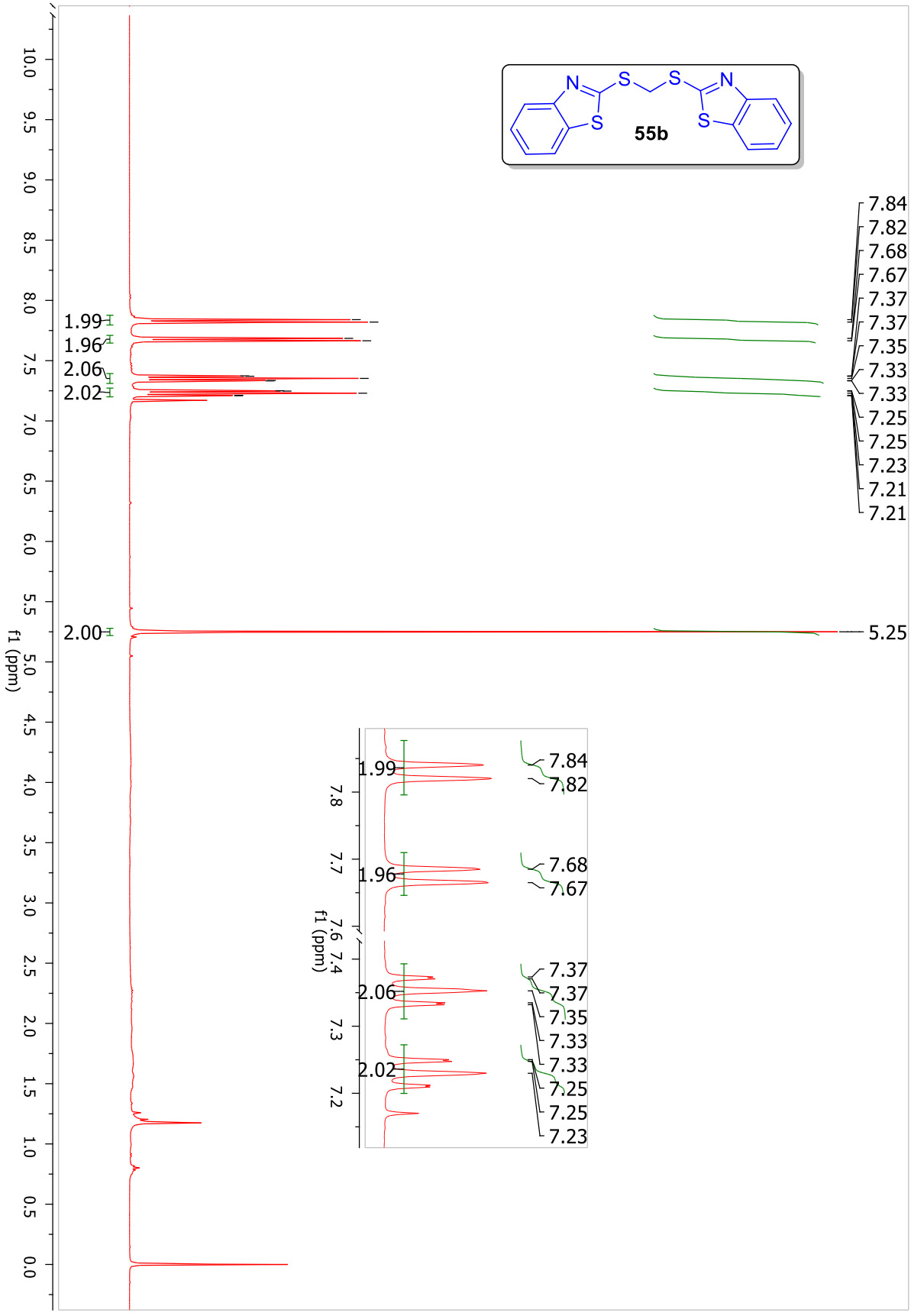
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **55a:**



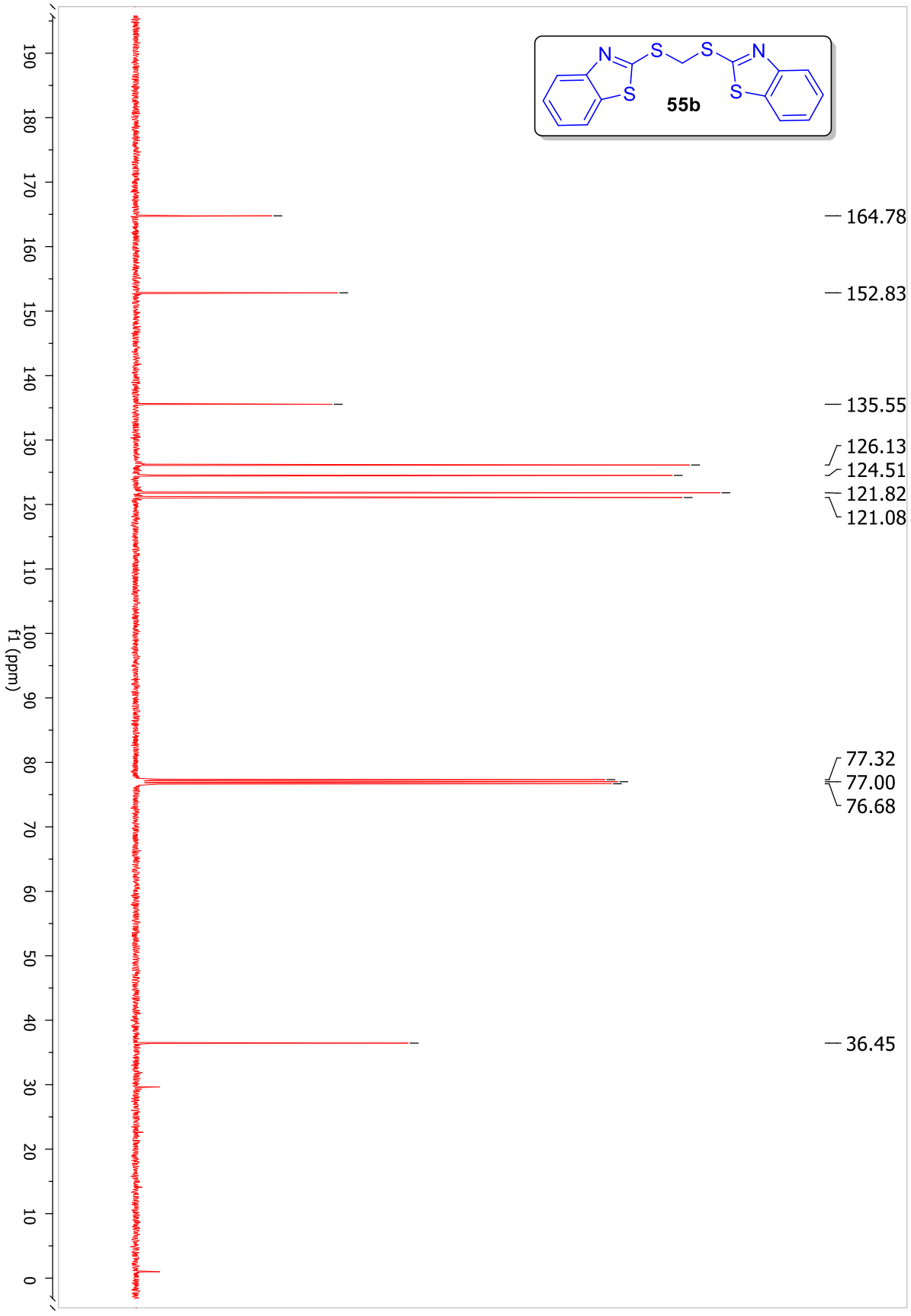
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **55a:**



^{1}H-NMR (400 MHz, $CDCl_3$) of compound **55b:**

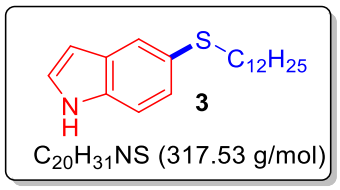


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **55b:**

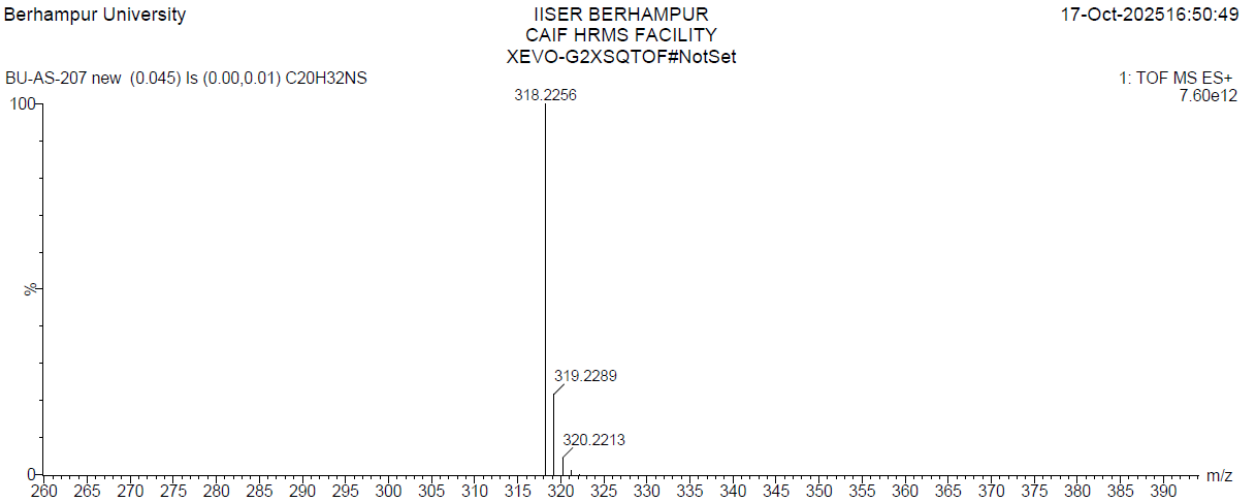


12:HRMS spectra of new compounds:

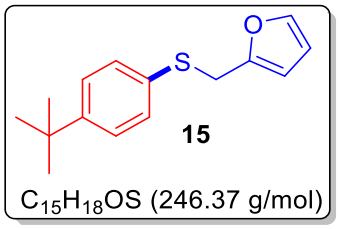
HRMS analysis of compound 3:



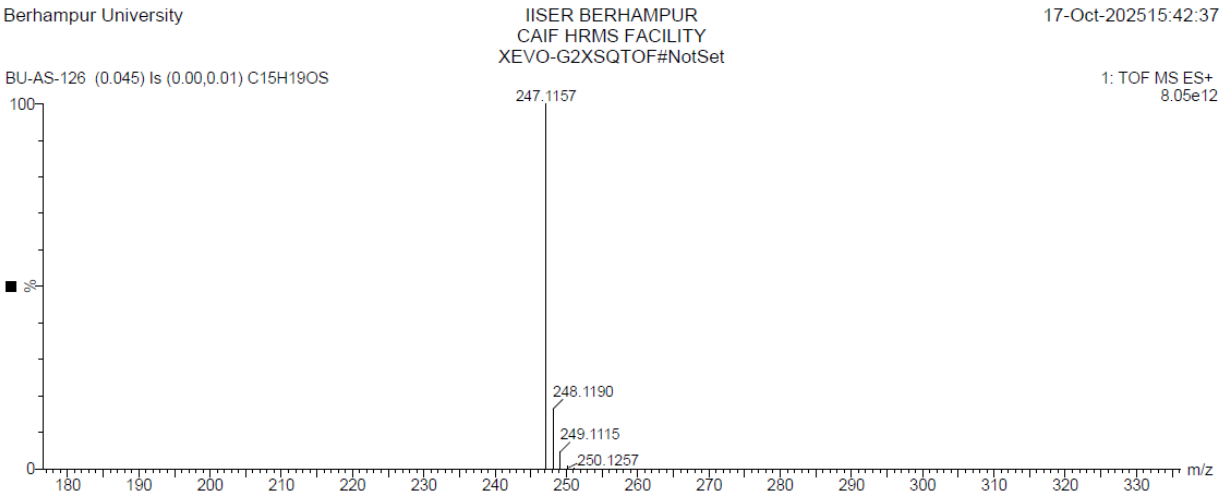
HRMS (ESI) Calcd for $C_{20}H_{32}NS$ $[M+H]^+$: 318.2255; found: 318.2256.



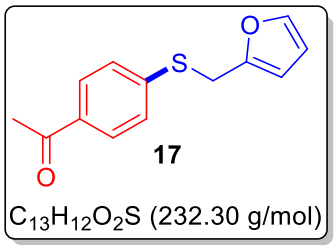
HRMS analysis of compound 15:



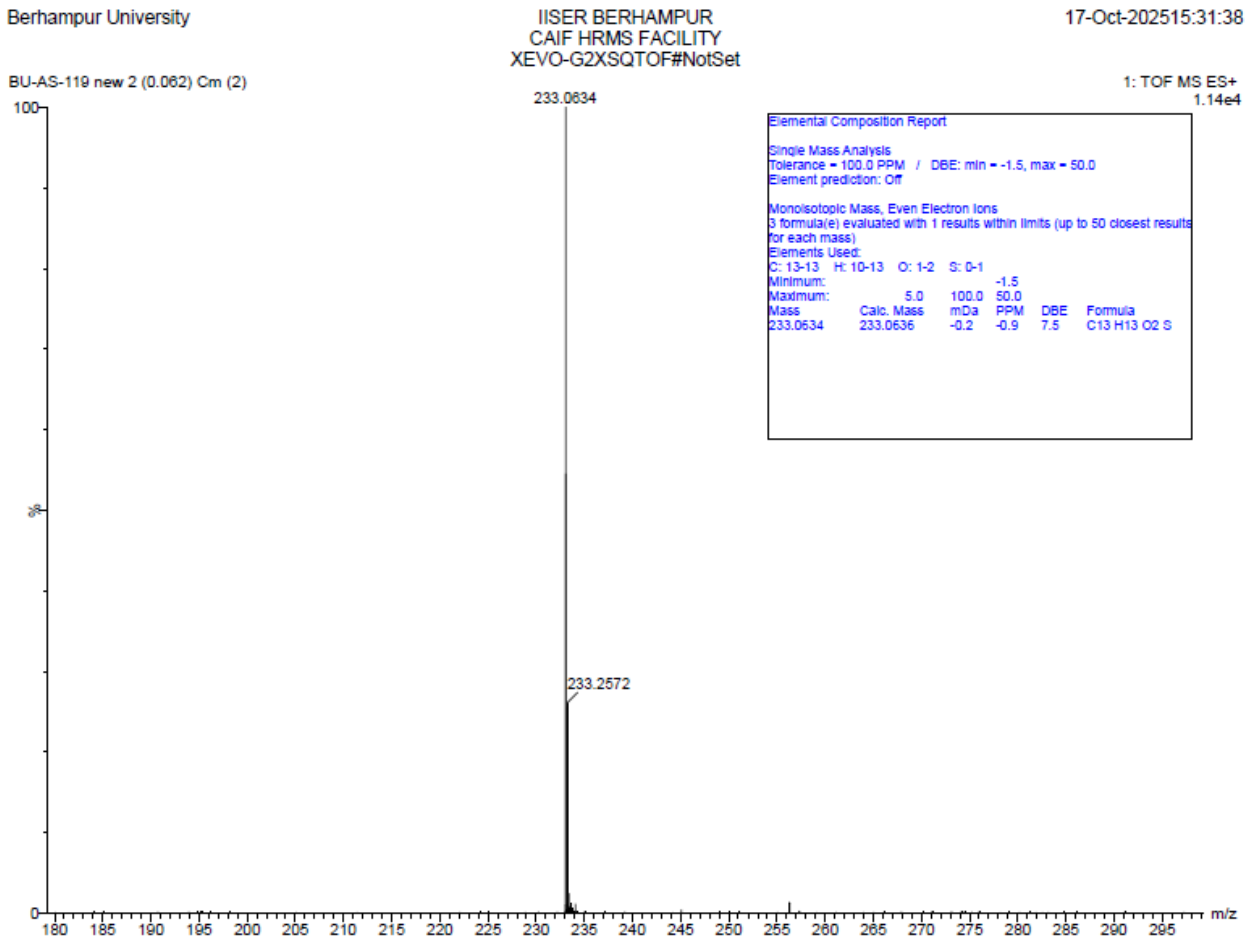
HRMS (ESI) Calcd for $C_{15}H_{19}OS$ $[M+H]^+$: 247.11567; found: 247.1157. new compound.



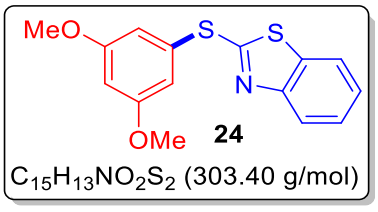
HRMS analysis of compound 17:



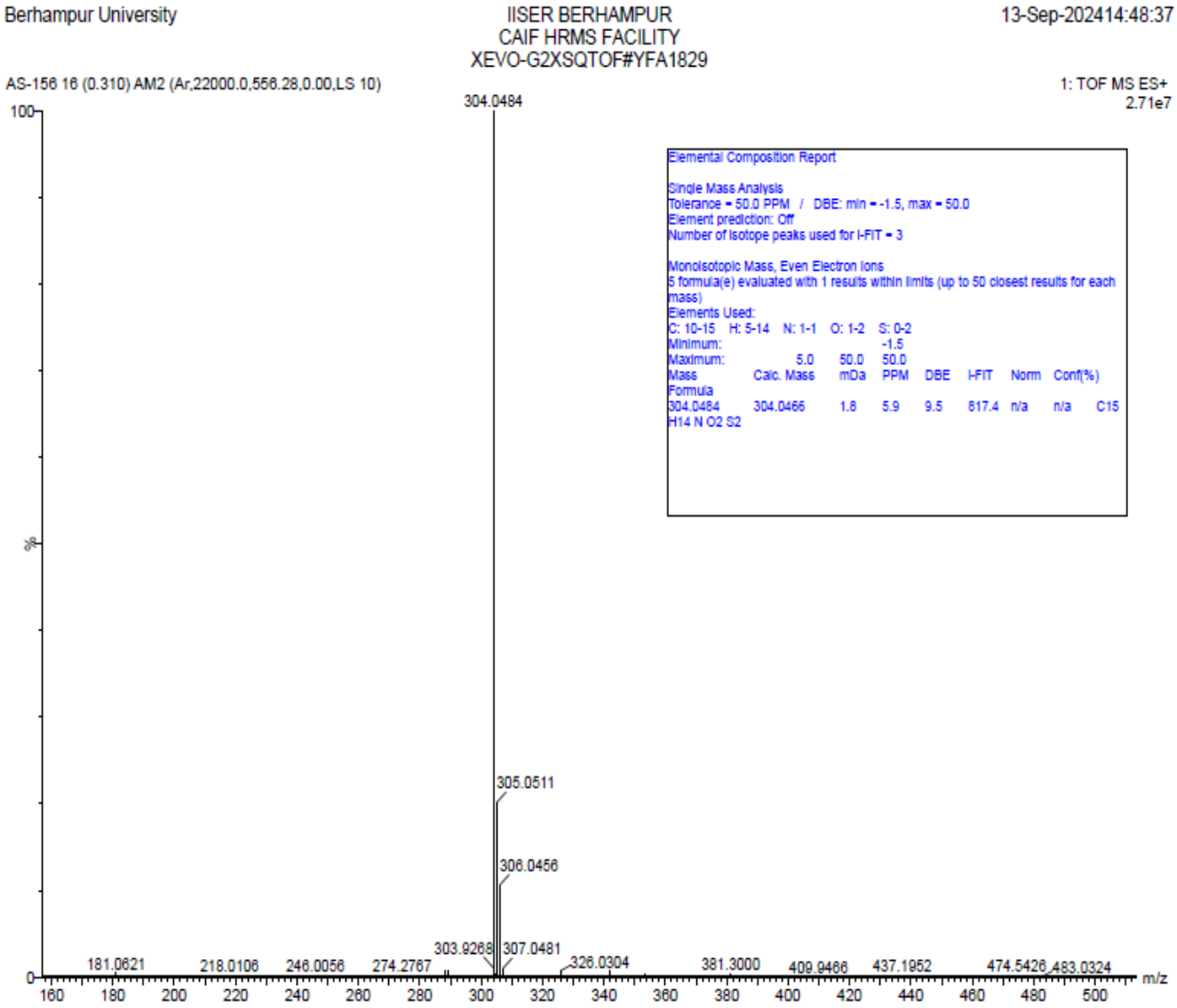
HRMS (ESI) Calcd for $C_{13}H_{13}O_2S$ $[M+H]^+$: 233.0636; found: 233.0634



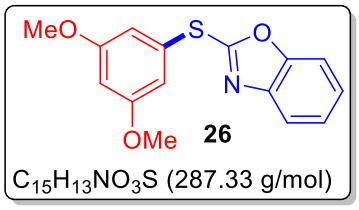
HRMS analysis of compound 24:



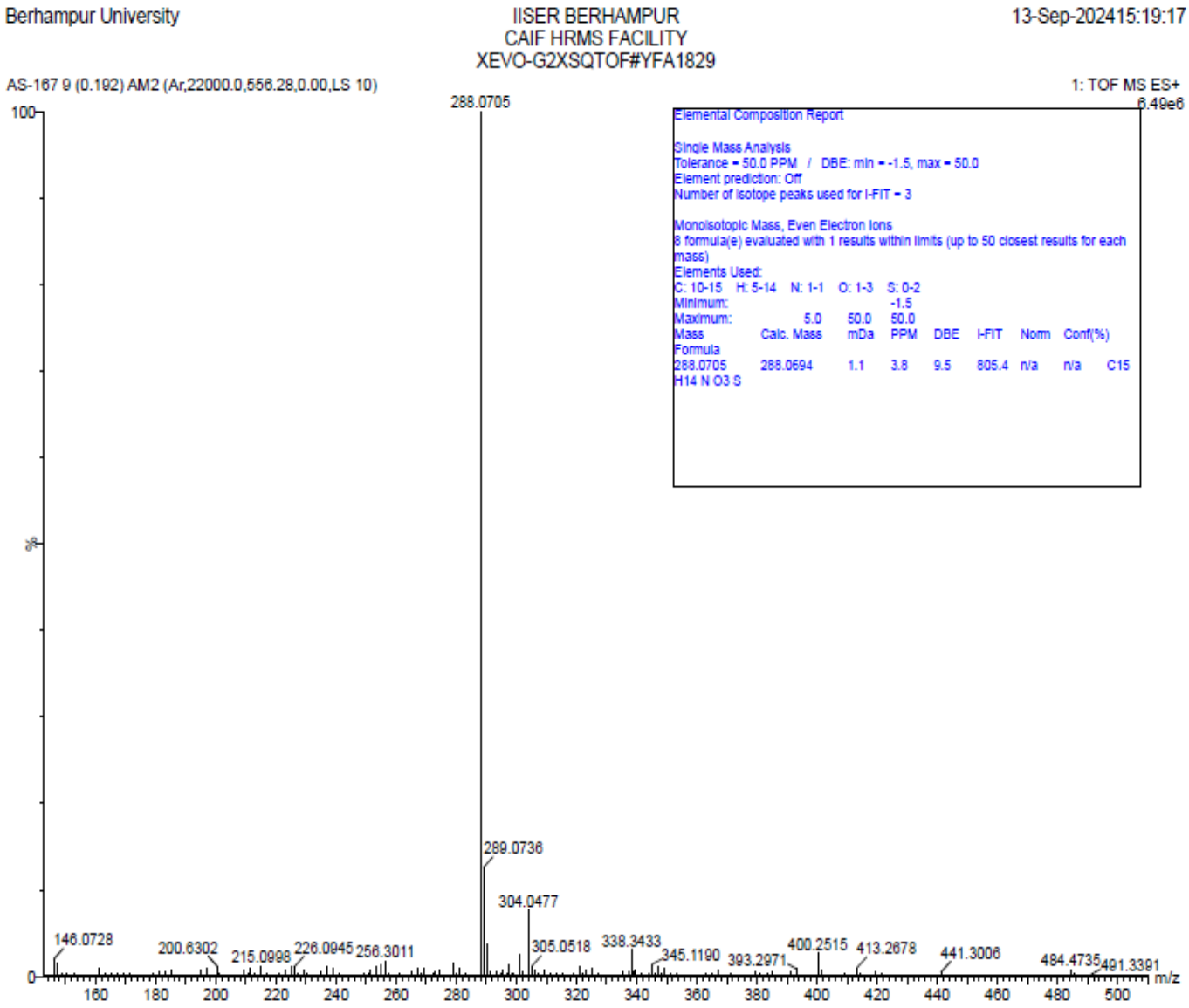
TOF MS ES$^+$ m/z Calculated MF $C_{15}H_{13}NO_2S_2$ H [M+H] $^+$: **304.0466**; found: **304.0484**



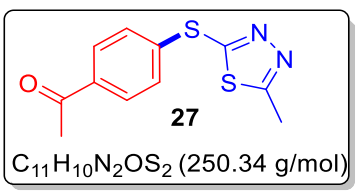
HRMS analysis of compound 26:



TOF MS ES$^+$ m/z Calculated MF $C_{15}H_{13}NO_3S$ H [M+H] $^+$: **288.06945**; found: **288.0705**



HRMS analysis of compound 27:



TOF MS ES$^+$ m/z Calculated MF $C_{16}H_{15}NO_4S$ H [M+H] $^+$: **251.03129**; found: **251.0326**

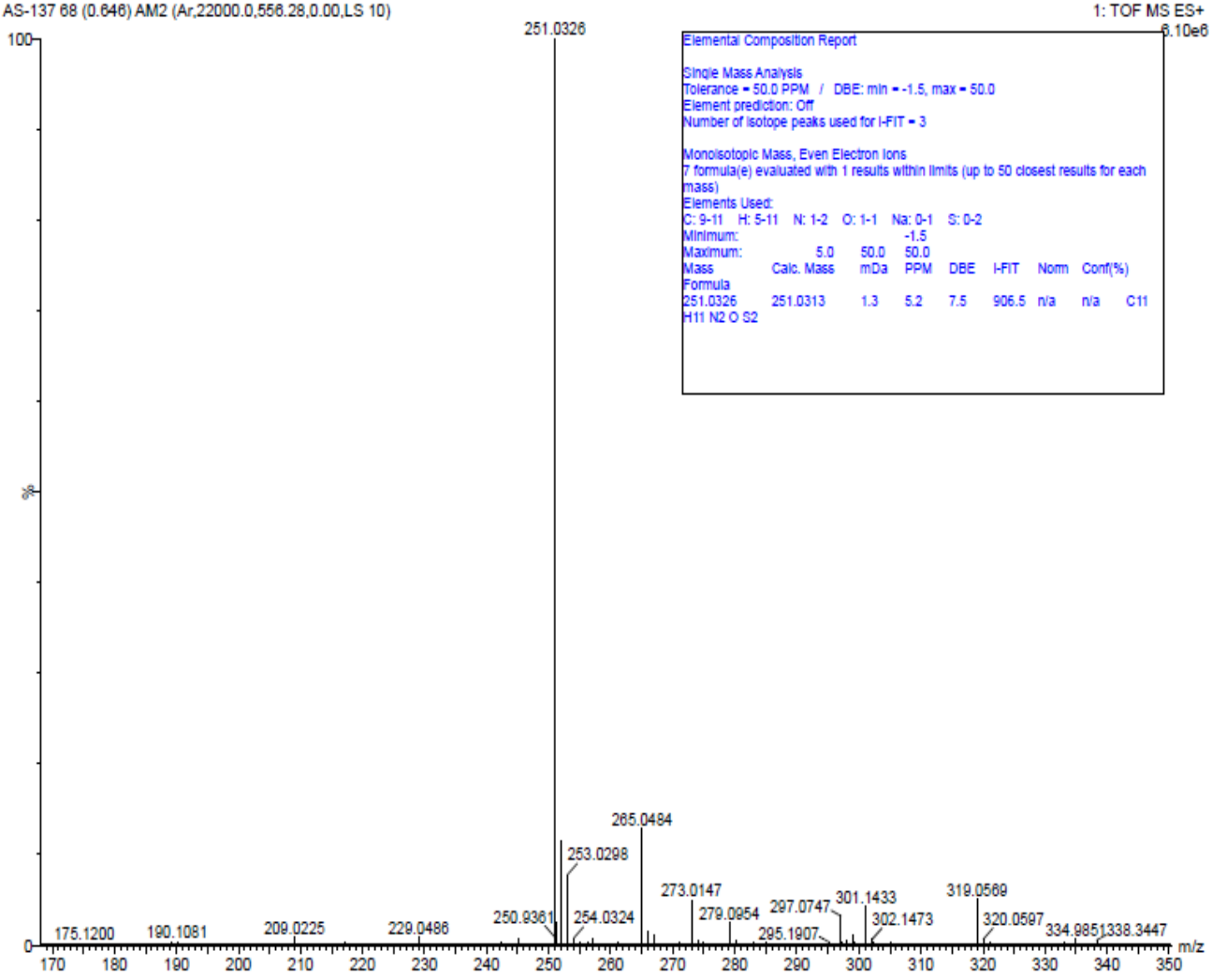
Berhampur University

IISER BERHAMPUR
CAIF HRMS FACILITY
XEVO-G2XSQTOF#YFA1829

28-Oct-202412:14:55

AS-137 68 (0.646) AM2 (Ar,22000.0,556.28,0.00,LS 10)

1: TOF MS ES+
6.10e6



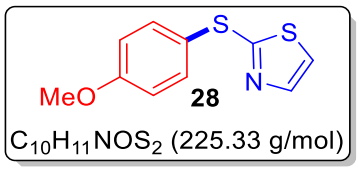
Elemental Composition Report

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

Monoisotopic Mass, Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 9-11 H: 5-11 N: 1-2 O: 1-1 Na: 0-1 S: 0-2

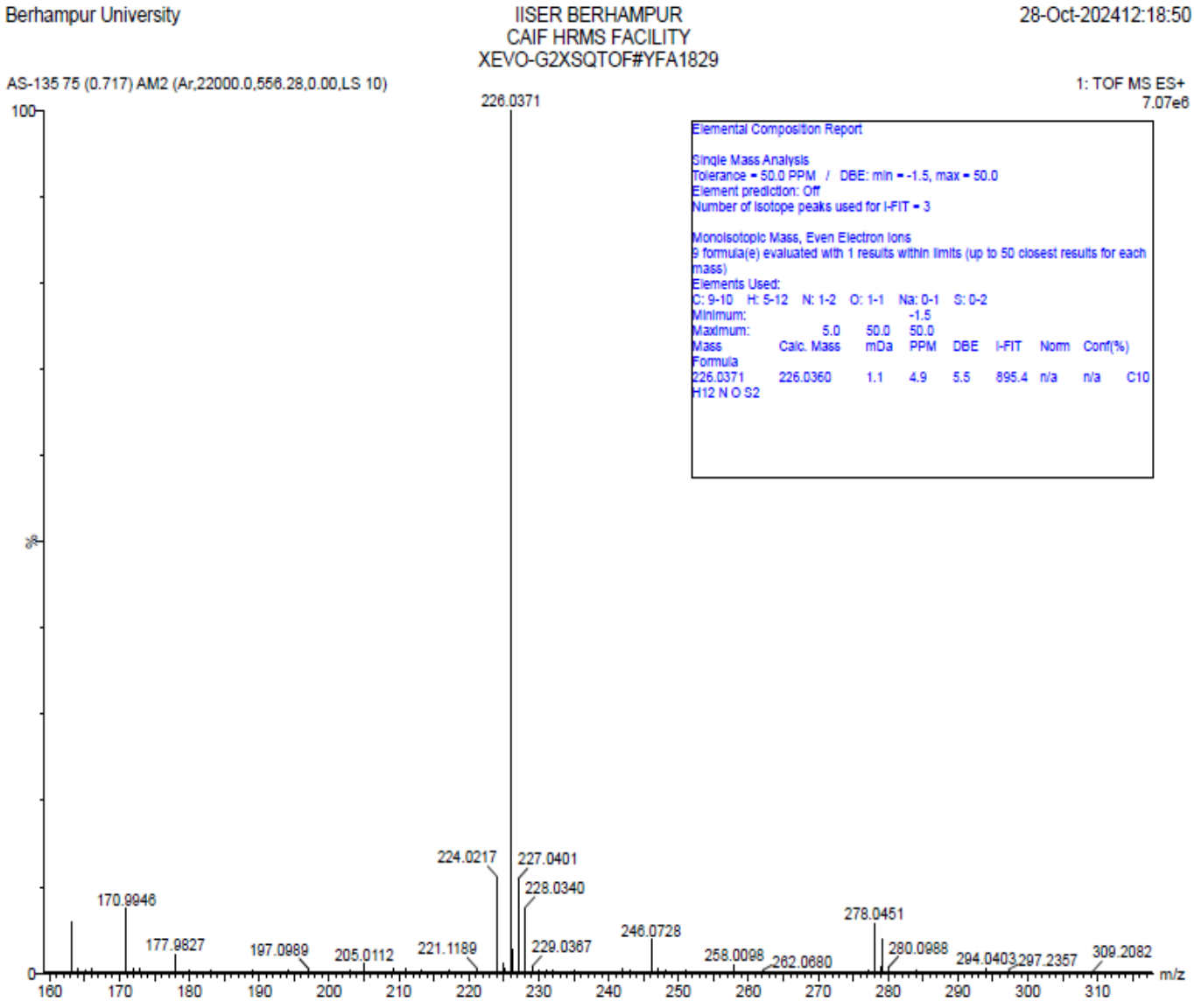
Minimum:				-1.5				
Maximum:		5.0	50.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
251.0326	251.0313	1.3	5.2	7.5	906.5	n/a	n/a	C11 H11 N2 O S2

HRMS analysis of compound 28:

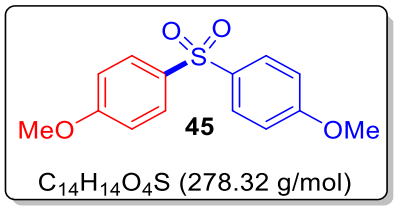


$C_{10}H_{11}NOS_2$ (225.33 g/mol)

TOF *MS ES*$^+$ m/z Calculated MF $C_{16}H_{15}NO_4S$ H [M+H] $^+$: **226.03603**; found: **226.0371**

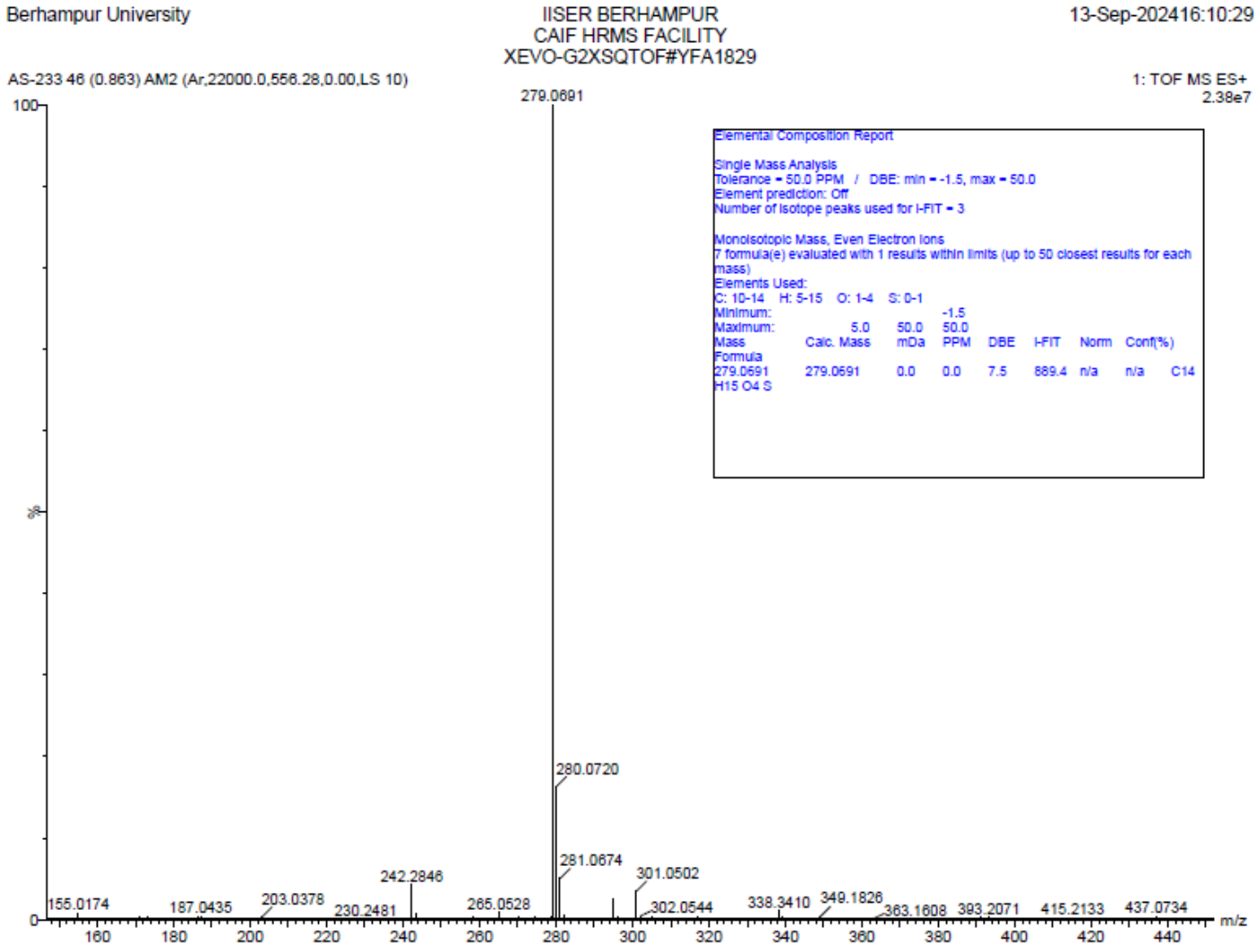


HRMS analysis of compound 45:

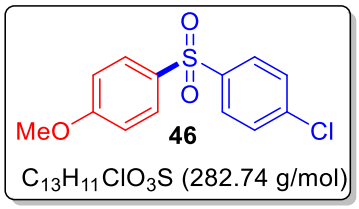


$C_{14}H_{14}O_4S$ (278.32 g/mol)

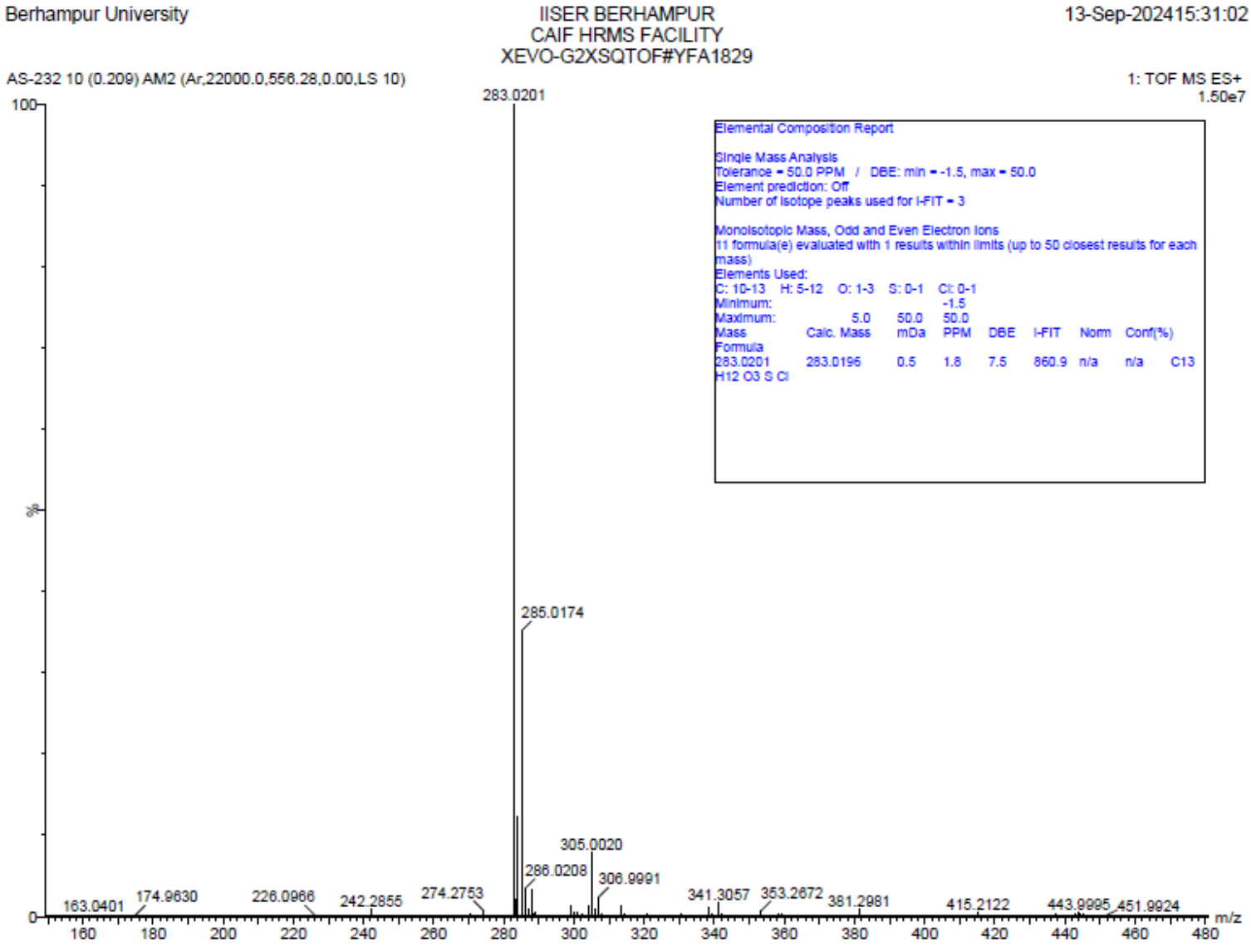
TOF MS ES$^+$ m/z Calculated MF $C_{14}H_{14}O_4S$ H [M+H] $^+$: **279.06913**; found: **279.0691**



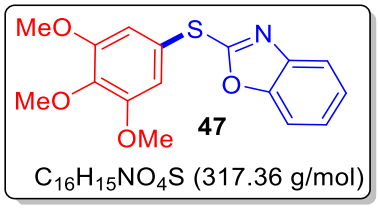
HRMS analysis of compound 46:



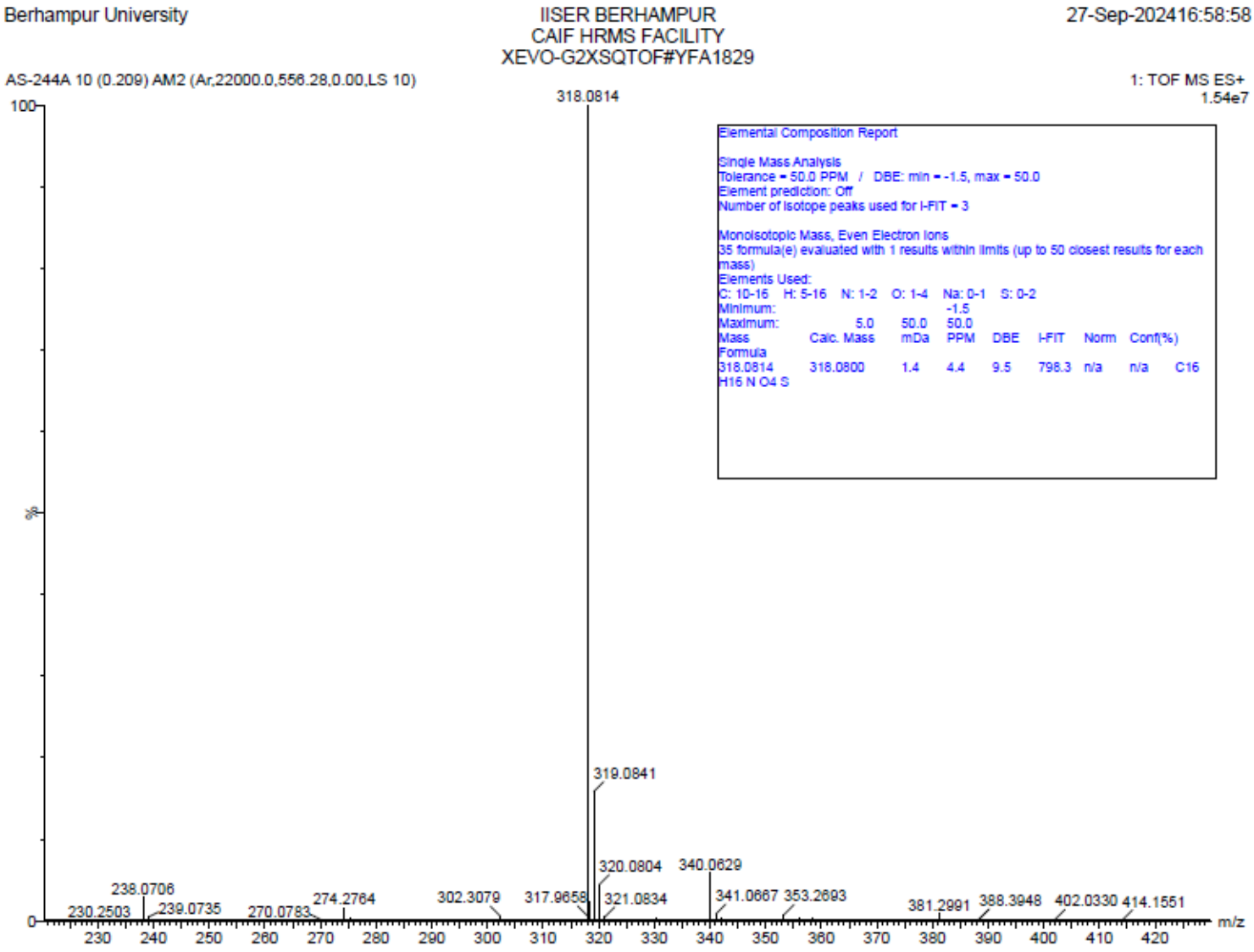
TOF MS ES$^+$ m/z Calculated MF $C_{13}H_{11}ClO_3S$ H [M+H] $^+$: **283.01958**; found: **283.0201**



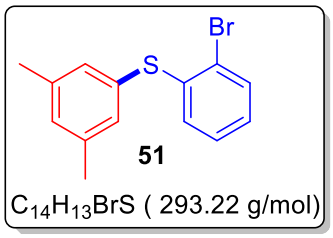
HRMS analysis of compound 47:



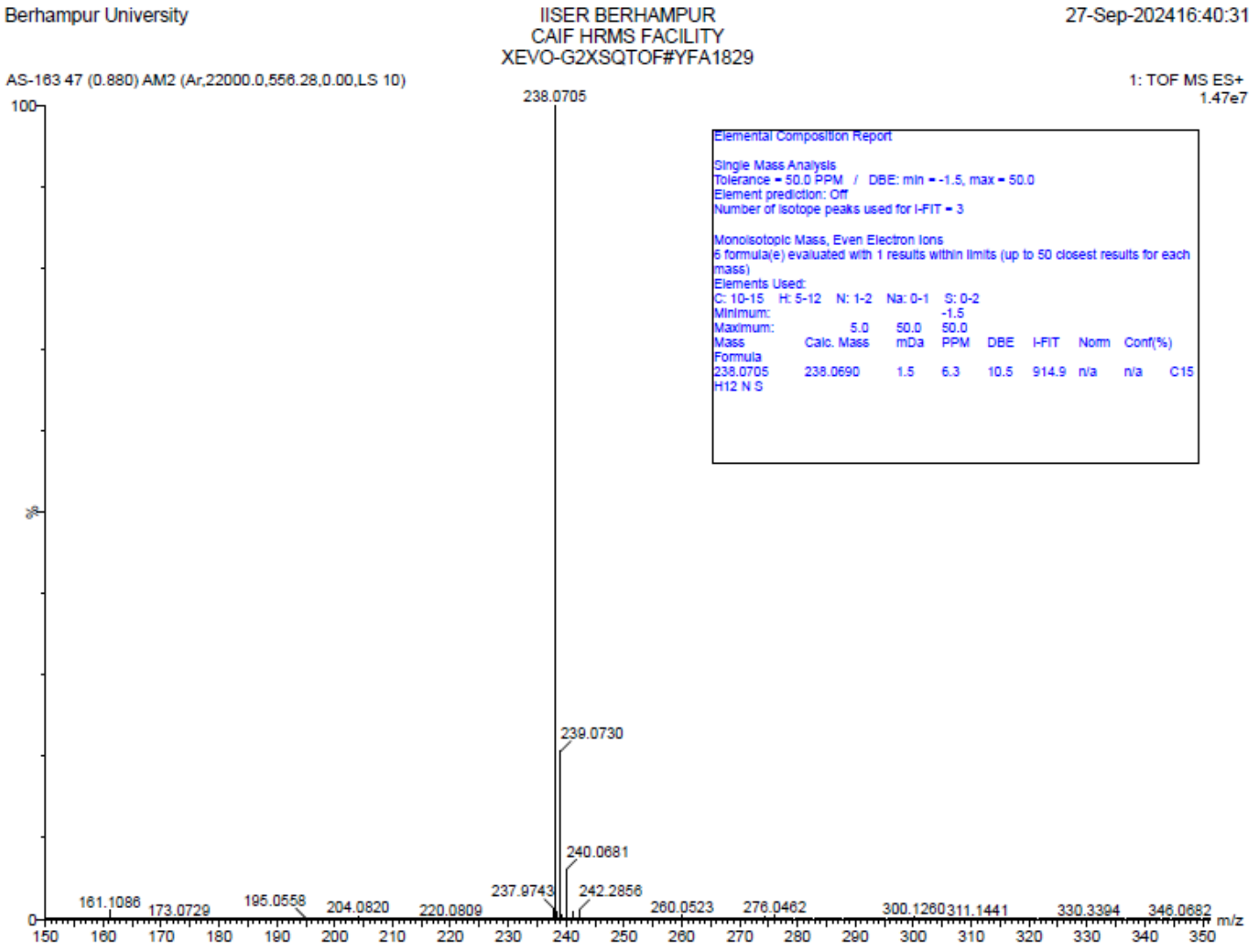
TOF MS ES$^+$ m/z Calculated MF $C_{16}H_{15}NO_4S$ H [M+H] $^+$: **318.08002**; found: **318.0814**



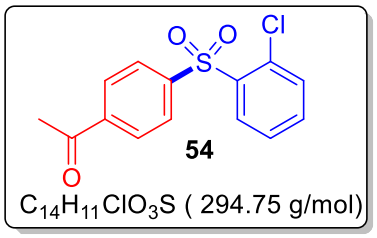
HRMS analysis of compound 51:



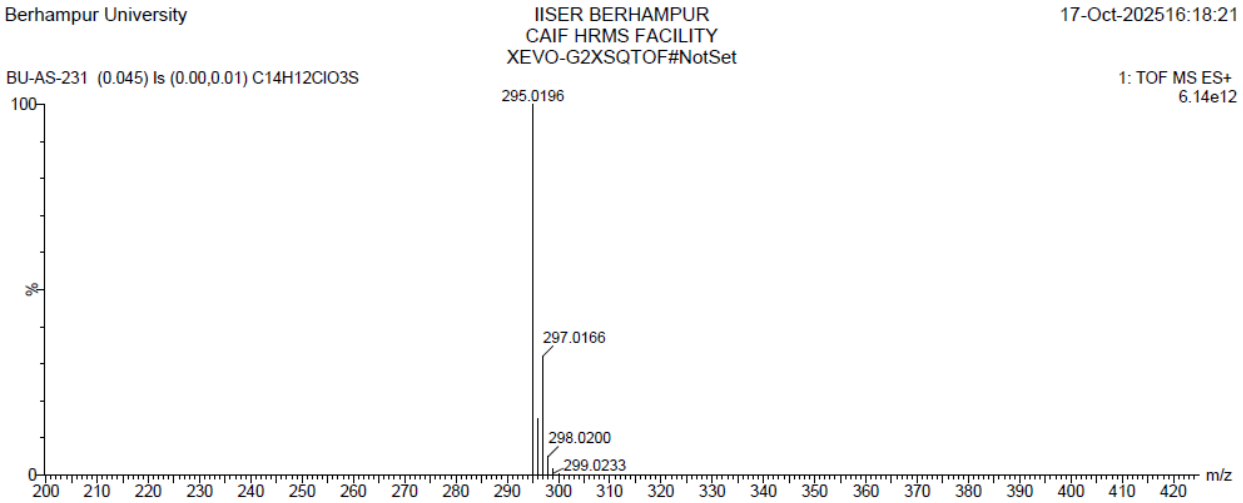
TOF MS ES$^+$ m/z Calculated MF $C_{15}H_{11}NS$ H $[M+H]^+$: **238.06904**; found : **238.0705**



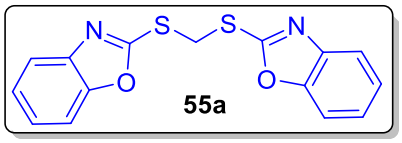
HRMS analysis of compound 54:



HRMS (ESI) Calcd for $C_{14}H_{11}ClO_3S$ $[M+H]^+$: 295.0195; found : 295.0196.

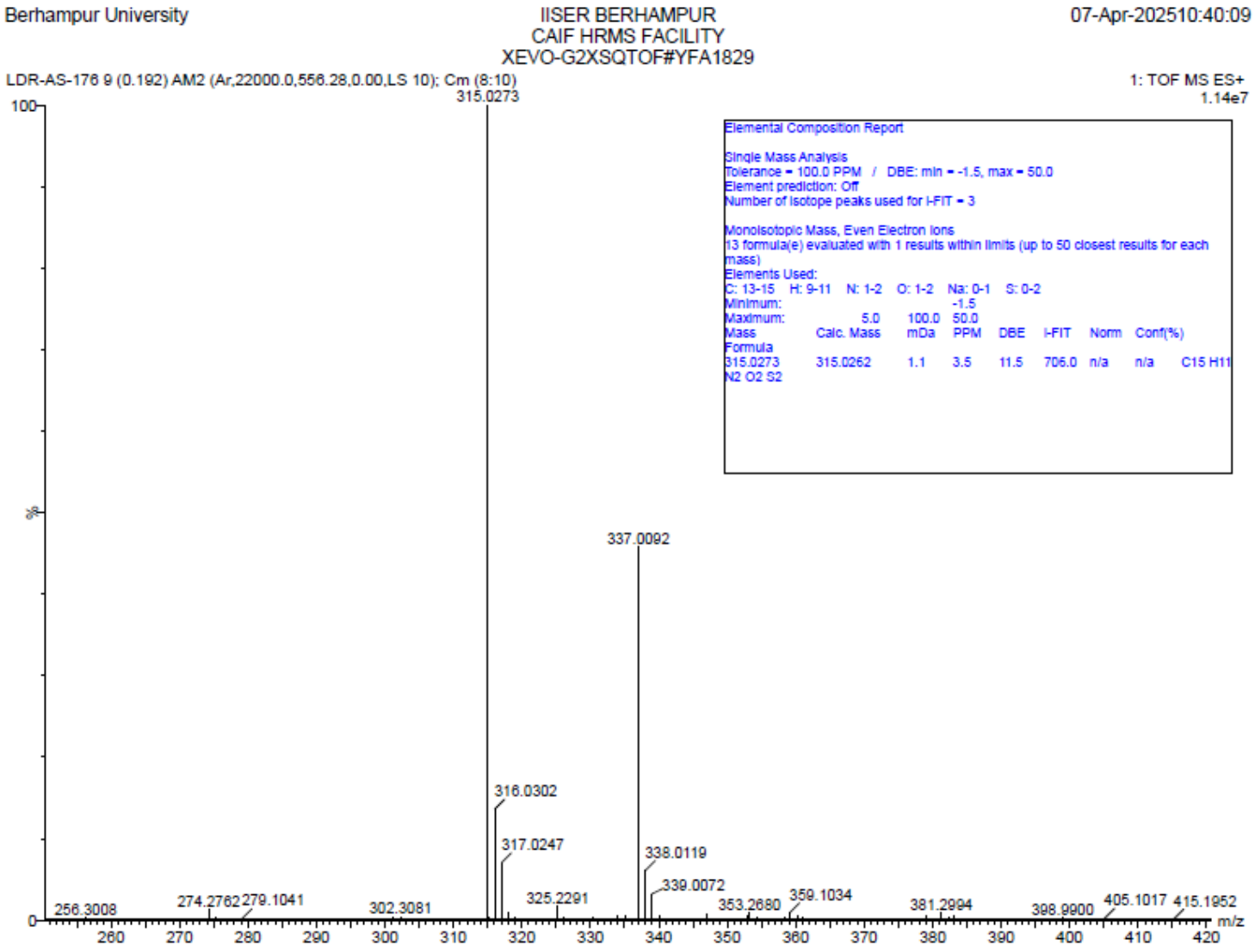


HRMS analysis of compound 55(a):

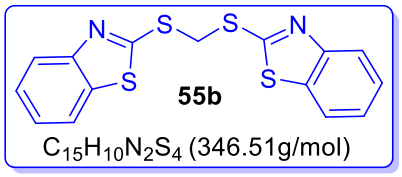


55a

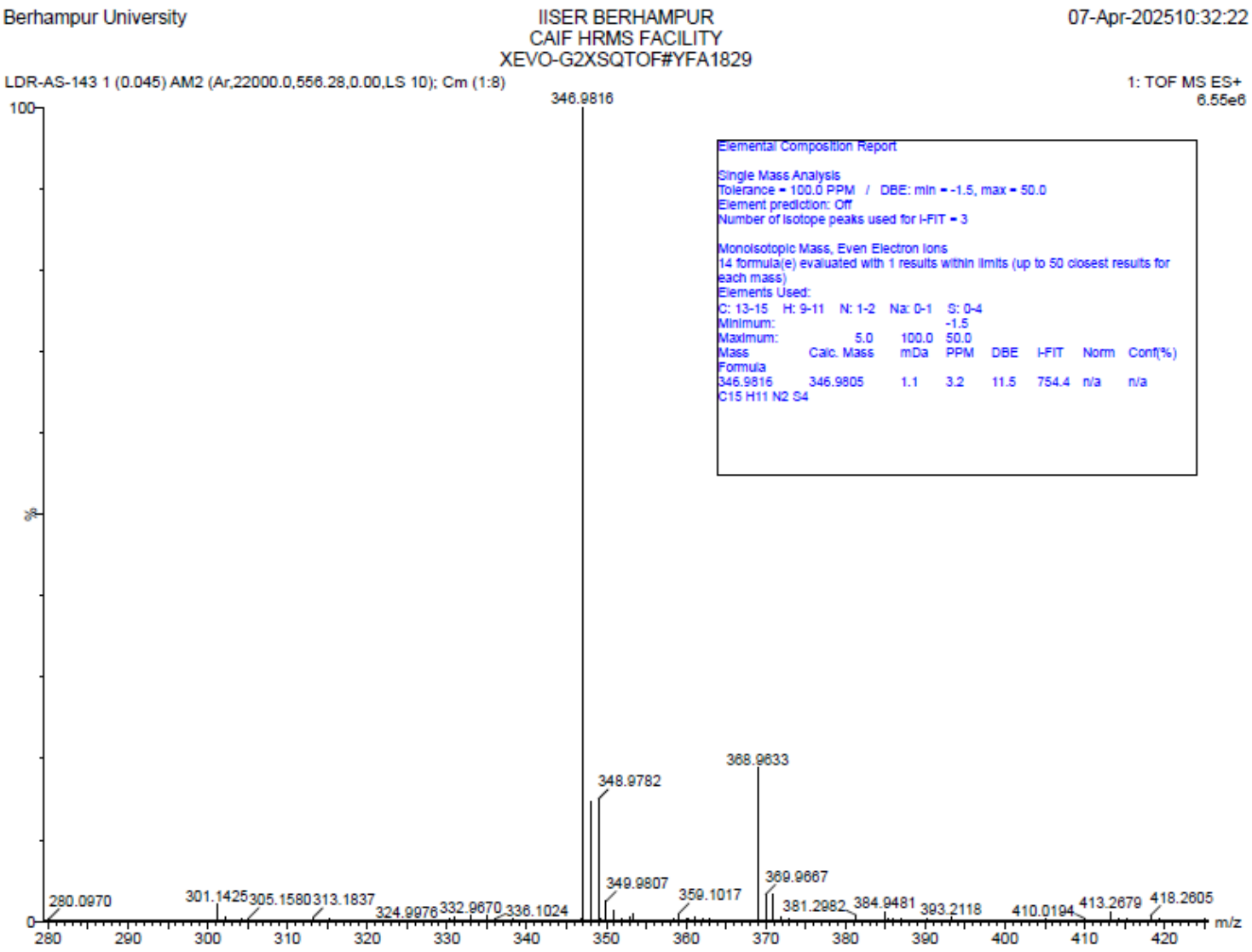
TOF MS ES$^+$ m/z Calculated MF $C_{15}H_{10}N_2O_2S_2$ H [M+H] $^+$: **315.0262**; found: **315.0273**



HRMS analysis of compound 55(b):

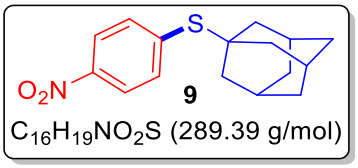


TOF MS ES^{+} m/z Calculated MF $C_{15}H_{10}N_2O_2S_2$ H [M+H] $^{+}$: **346.9805**; found: **346.9816**



13: Single XRD data of new Compounds

XRD data of compound 9: CCDC deposition number: **2388312**



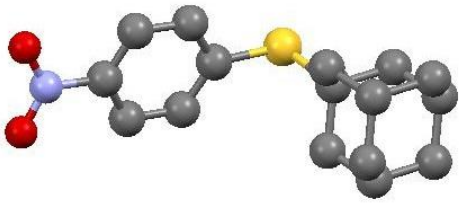
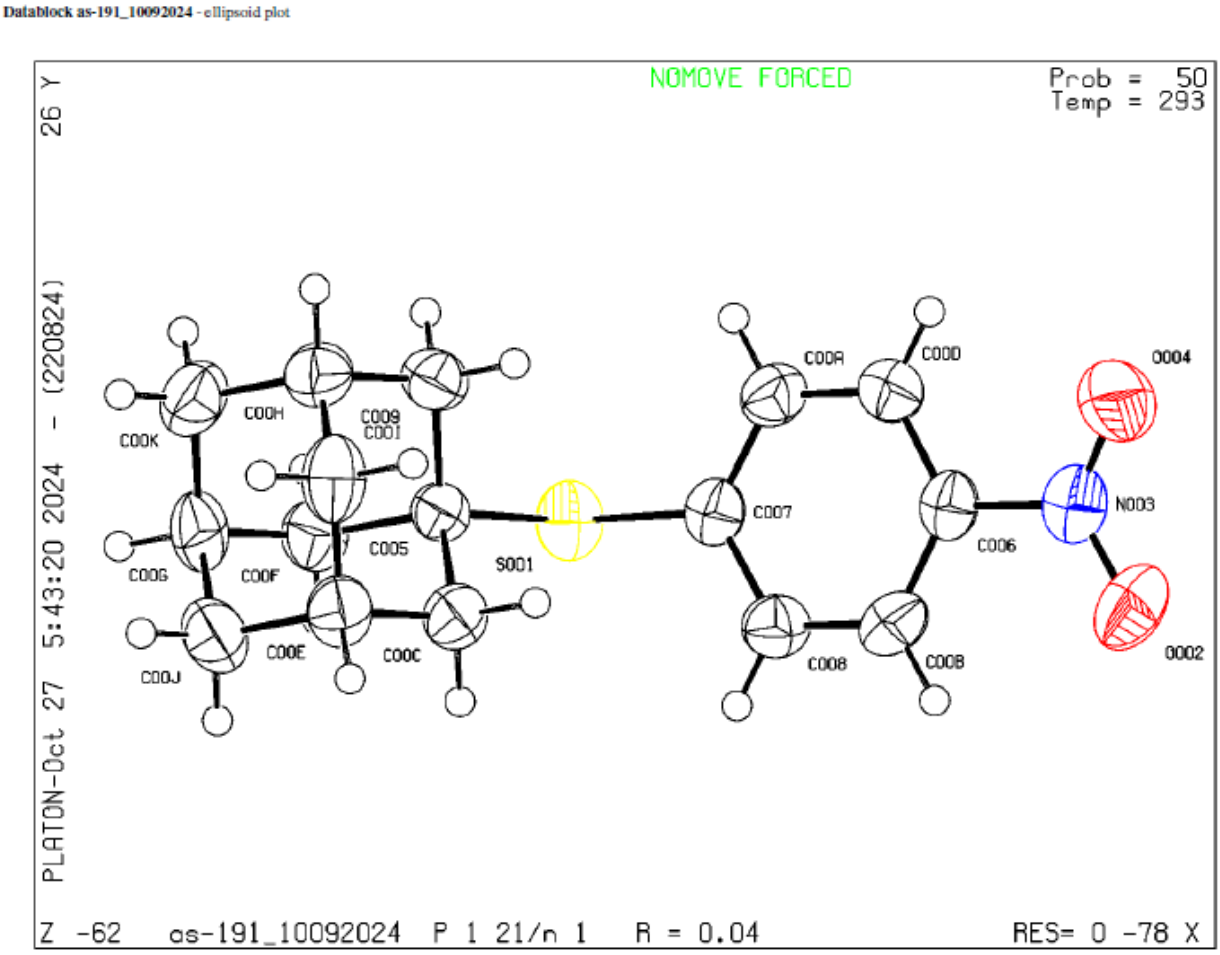


Figure 10: XRD data of compound 9:



Datablock: as-191_10092024

Bond precision: C-C = 0.0021 A Wavelength=0.71073

Cell: a=6.6830(3) b=20.6941(10) c=10.3255(4)
alpha=90 beta=91.252(4) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1427.66(11)	1427.66(11)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C16 H19 N O2 S	C16 H19 N O2 S
Sum formula	C16 H19 N O2 S	C16 H19 N O2 S
Mr	289.38	289.38
Dx,g cm-3	1.346	1.346
Z	4	4
Mu (mm-1)	0.228	0.228
F000	616.0	616.0
F000'	616.74	
h,k,lmax	8,26,13	8,25,12
Nref	3109	2969
Tmin,Tmax	0.968,0.977	0.543,1.000
Tmin'	0.966	

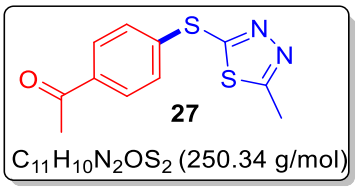
Correction method= # Reported T Limits: Tmin=0.543 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.955 Theta(max)= 26.950

R(reflections)= 0.0412(1950) wR2(reflections)= 0.0955(2969)

S = 1.045 Npar= 181

XRD data of compound 27: CCDC deposition number: **2393839**



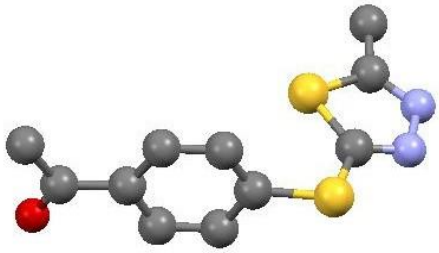
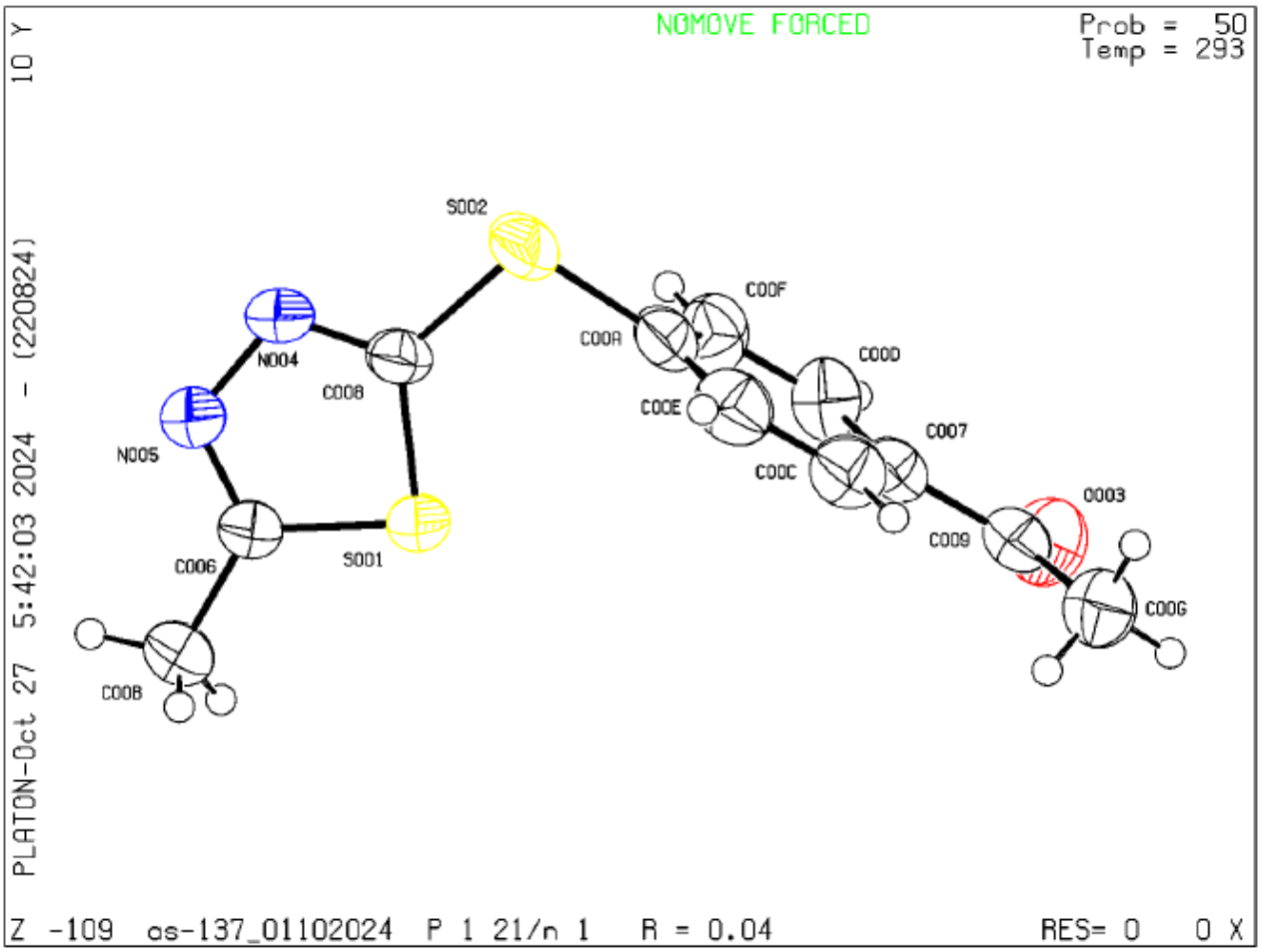


Figure 11: XRD data of compound 27

Datablock as-137_01102024 - ellipsoid plot



Datablock: as-137_01102024

Bond precision: C-C = 0.0026 A Wavelength=0.71073

Cell: a=5.6370(2) b=22.2950(7) c=9.3965(4)
alpha=90 beta=95.349(4) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1175.78(8)	1175.78(8)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C11 H10 N2 O S2	C11 H10 N2 O S2
Sum formula	C11 H10 N2 O S2	C11 H10 N2 O S2
Mr	250.33	250.33
Dx,g cm-3	1.414	1.414
Z	4	4
Mu (mm-1)	0.432	0.432
F000	520.0	520.0
F000'	521.15	
h,k,lmax	7,28,11	7,27,11
Nref	2563	2431
Tmin,Tmax	0.940,0.958	0.443,1.000
Tmin'	0.937	

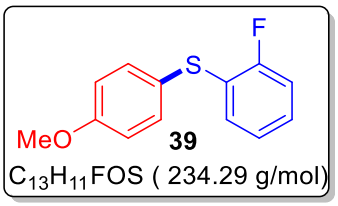
Correction method= # Reported T Limits: Tmin=0.443 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.948 Theta(max)= 26.990

R(reflections)= 0.0356(1869) wR2(reflections)= 0.1021(2431)

S = 1.137 Npar= 147

XRD data of compound 39: CCDC deposition number: **2393842**



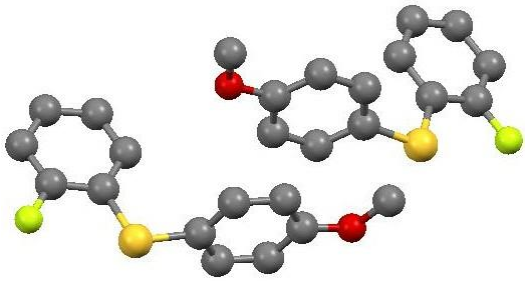
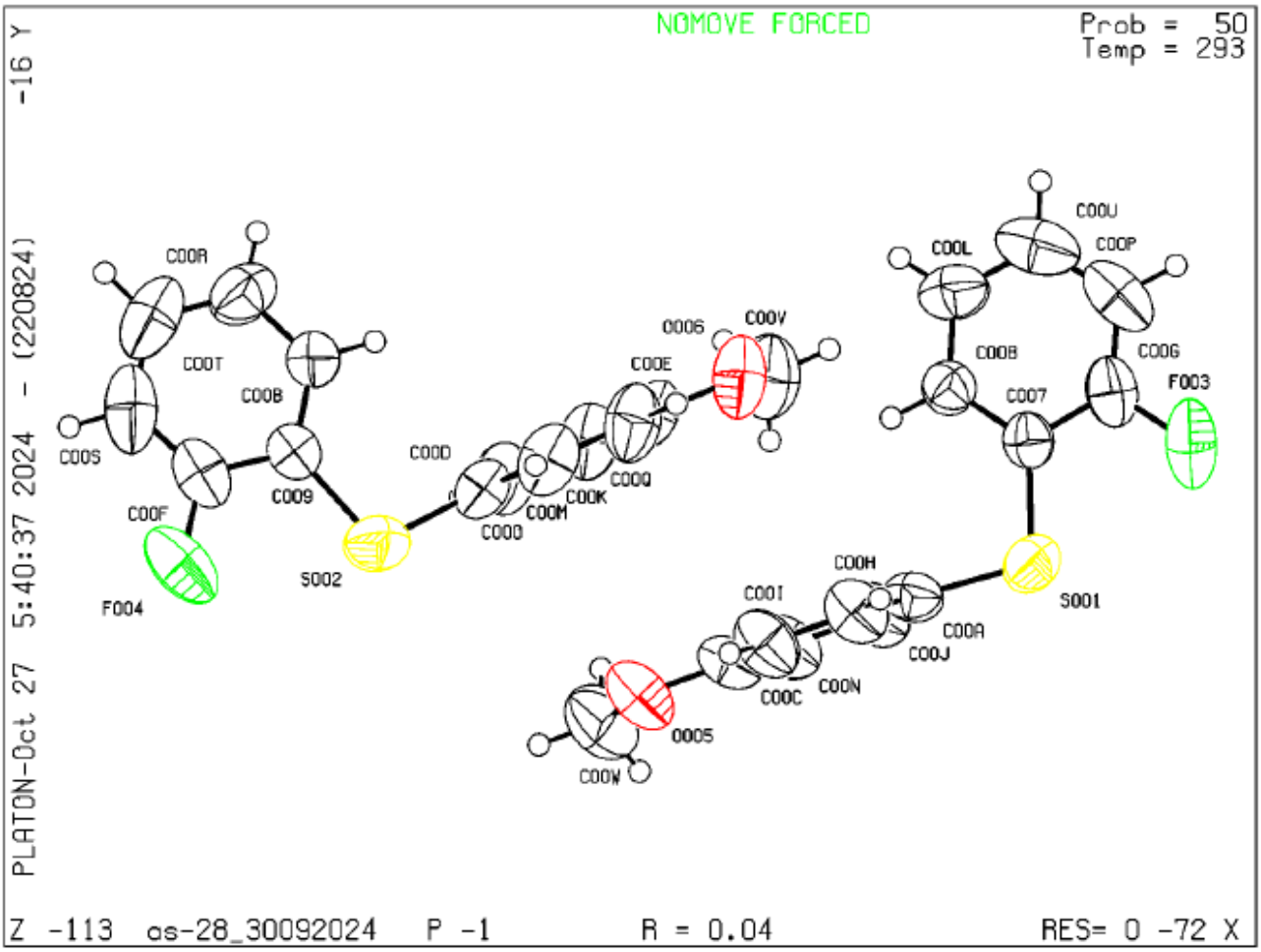


Figure 12: XRD data of compound 39

Datablock as-28_30092024 - ellipsoid plot



Structure factors have been supplied for datablock(s) as-28_30092024

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

No syntax errors found. CIF dictionary Interpreting this report

Datablock: as-28_30092024

Bond precision: C-C = 0.0032 A Wavelength=0.71073

Cell: a=7.6812(2) b=10.0587(2) c=15.6788(3)
alpha=77.844(2) beta=88.357(2) gamma=87.353(2)
Temperature: 293 K

	Calculated	Reported
Volume	1182.74(5)	1182.74(5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C13 H11 F O S	C13 H11 F O S
Sum formula	C13 H11 F O S	C13 H11 F O S
Mr	234.28	234.28
Dx,g cm-3	1.316	1.316
Z	4	4
Mu (mm-1)	0.261	0.261
F000	488.0	488.0
F000'	488.73	
h,k,lmax	9,12,20	9,12,20
Nref	5197	4904
Tmin,Tmax	0.963,0.974	0.849,1.000
Tmin'	0.962	

Correction method= # Reported T Limits: Tmin=0.849 Tmax=1.000
AbsCorr = MULTI-SCAN

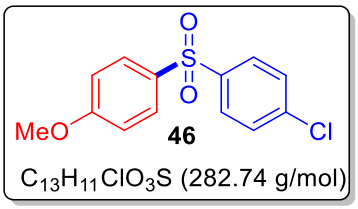
Data completeness= 0.944 Theta(max)= 27.072

R(reflections)= 0.0433(2810) wR2(reflections)= 0.1238(4904)

S = 1.042 Npar= 291

XRD data of compound 46:

CCDC deposition number: **2388314**



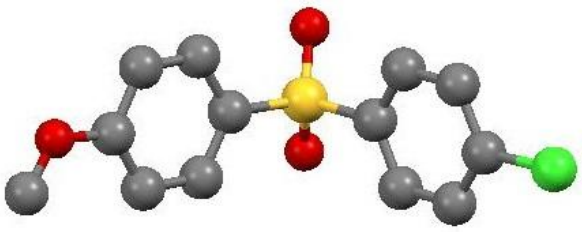
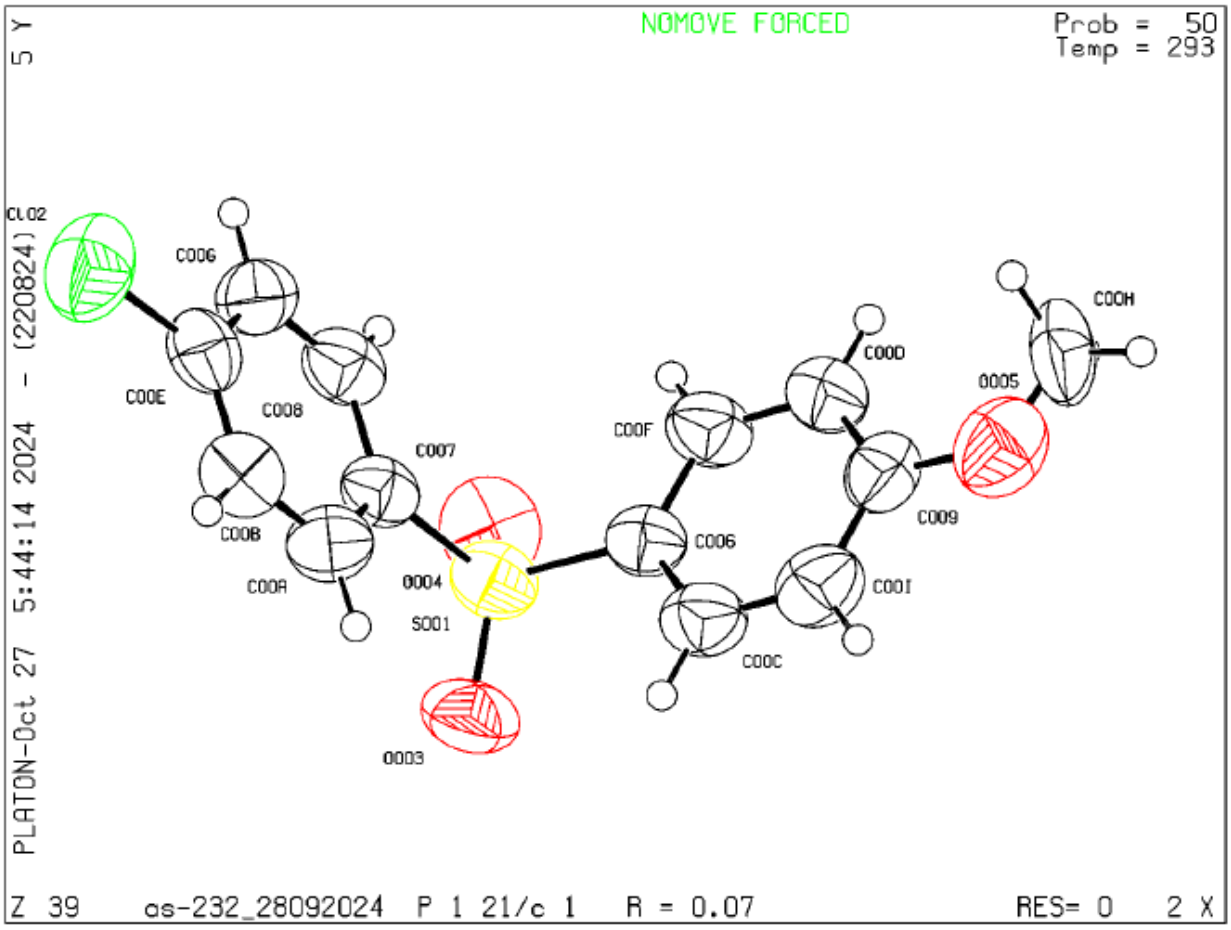


Figure 13: XRD data of compound 46

Datablock as-232_28092024 - ellipsoid plot



Datablock: as-232_28092024

Bond precision: C-C = 0.0069 A Wavelength=0.71073

Cell: a=10.3136(5) b=8.2566(4) c=15.6300(7)
alpha=90 beta=103.712(5) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1293.04(11)	1293.04(11)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C13 H11 Cl O3 S	C13 H11 Cl O3 S
Sum formula	C13 H11 Cl O3 S	C13 H11 Cl O3 S
Mr	282.73	282.73
Dx,g cm-3	1.452	1.452
Z	4	4
Mu (mm-1)	0.453	0.453
F000	584.0	584.0
F000'	585.34	
h,k,lmax	13,10,19	13,10,19
Nref	2826	2706
Tmin,Tmax	0.937,0.956	0.306,1.000
Tmin'	0.934	

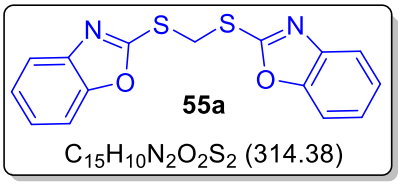
Correction method= # Reported T Limits: Tmin=0.306 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.958 Theta(max)= 27.030

R(reflections)= 0.0732(1547) wR2(reflections)= 0.2429(2706)

S = 1.071 Npar= 163

XRD data of compound 55a: CCDC deposition number: **2377843**



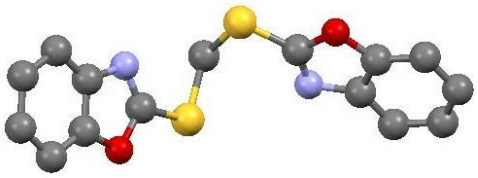
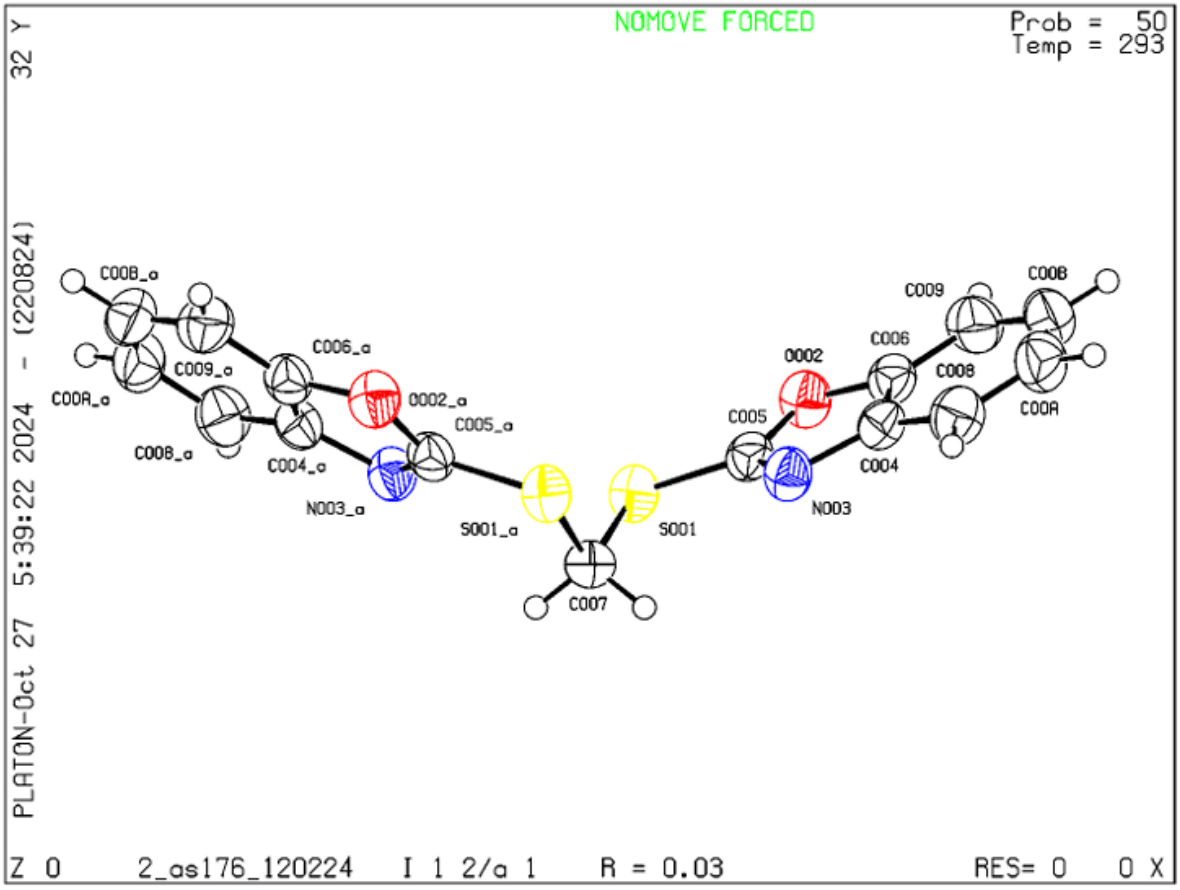


Figure 14: XRD data of compound 55a

Datablock 2_as176_120224 - ellipsoid plot



Datablock: 2_as176_120224

Bond precision: C-C = 0.0028 A Wavelength=0.71073

Cell: a=18.1182(7) b=4.2420(2) c=19.6101(8)
alpha=90 beta=111.198(5) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1405.20(11)	1405.20(11)
Space group	I 2/a	I 1 2/a 1
Hall group	-I 2ya	-I 2ya
Moiety formula	C15 H10 N2 O2 S2	C15 H10 N2 O2 S2
Sum formula	C15 H10 N2 O2 S2	C15 H10 N2 O2 S2
Mr	314.37	314.37
Dx,g cm-3	1.486	1.486
Z	4	4
Mu (mm-1)	0.383	0.383
F000	648.0	648.0
F000'	649.23	
h,k,lmax	23,5,25	22,5,24
Nref	1544	1458
Tmin,Tmax	0.938,0.955	0.594,1.000
Tmin'	0.933	

Correction method= # Reported T Limits: Tmin=0.594 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.944 Theta(max)= 27.042

R(reflections)= 0.0329(1160) wR2(reflections)= 0.0858(1458)

S = 1.035 Npar= 96

XRD data of compound 55b: CCDC deposition number: **2377844**

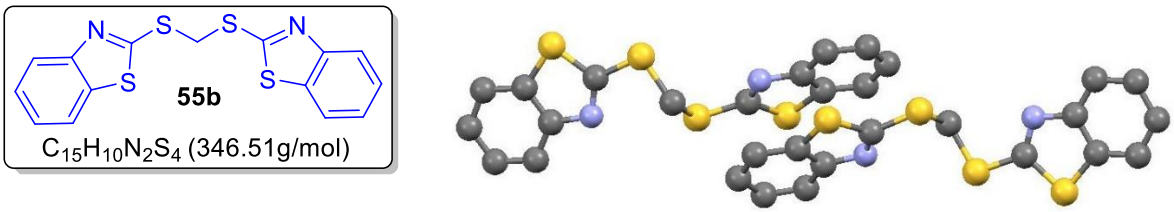
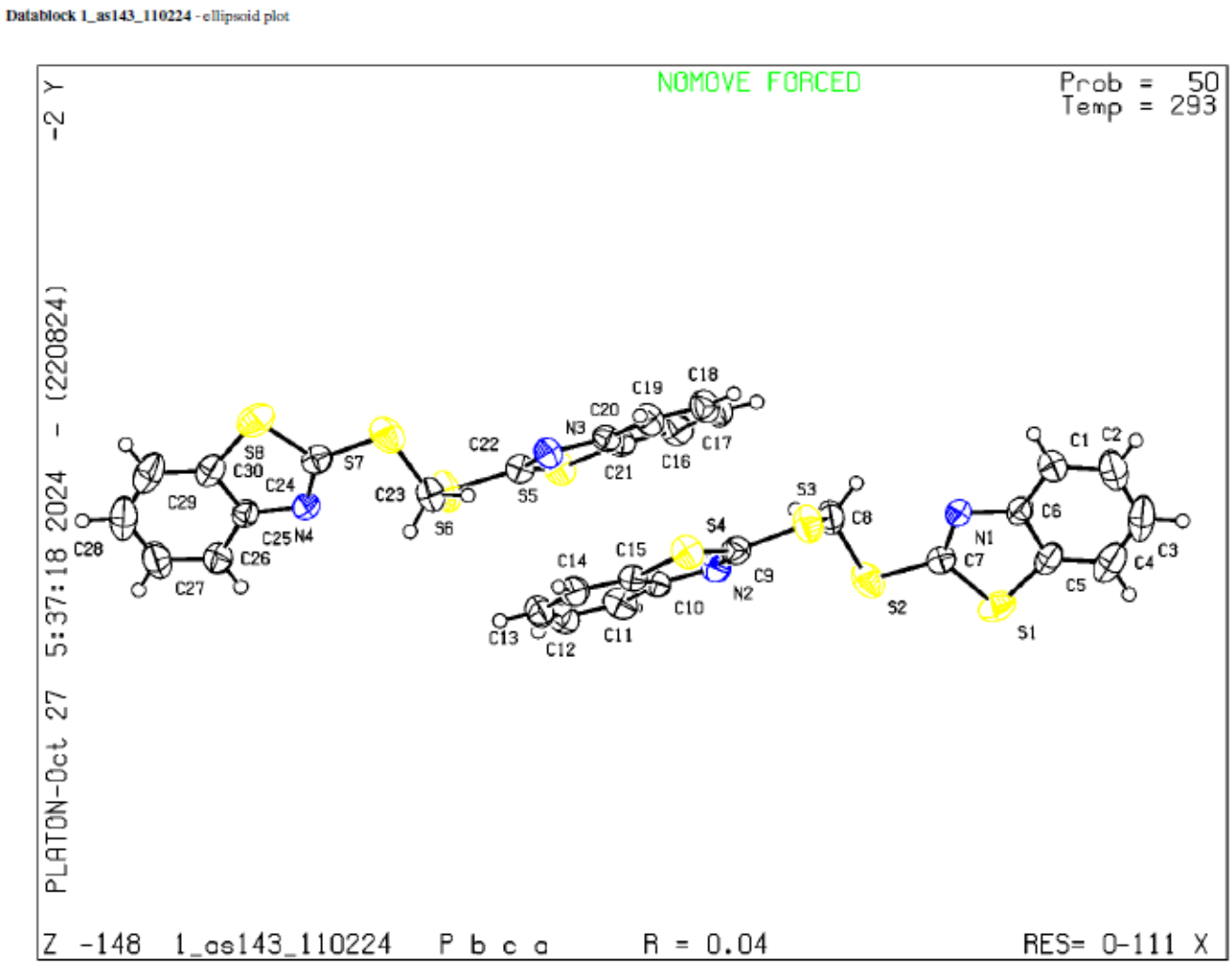


Figure 15: XRD data of compound 55b



Datablock: 1_as143_110224

Bond precision: C-C = 0.0032 A Wavelength=0.71073

Cell: a=12.6019(4) b=21.5377(5) c=22.3675(6)
alpha=90 beta=90 gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	6070.9(3)	6070.9(3)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C15 H10 N2 S4	4(C15 H10 N2 S4)
Sum formula	C15 H10 N2 S4	C60 H40 N8 S16
Mr	346.49	1385.96
Dx,g cm-3	1.516	1.516
Z	16	4
Mu (mm-1)	0.618	0.618
F000	2848.0	2848.0
F000'	2856.59	
h,k,lmax	16,27,28	16,27,28
Nref	6657	6389
Tmin,Tmax	0.895,0.929	0.435,1.000
Tmin'	0.895	

Correction method= # Reported T Limits: Tmin=0.435 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.960 Theta(max)= 27.047

R(reflections)= 0.0428(4075) wR2(reflections)= 0.0910(6389)

S = 1.067 Npar= 379

14: Computational DFT Study

Quantum-chemical calculations were carried out with the Gaussian 16 program to examine the reaction mechanism. The equilibrium geometry of all species studied in this work and their vibrational frequency calculations were calculated with the B3LYP density functional theory, and the LANL2DZ basis set. We constructed a reaction pathway scheme (RPS) for possible reaction channels. All equilibrium geometries showed no imaginary frequencies, confirming their identity as true local minima. The energies are corrected for vibrational zero-point energy (ZPE). Solvent effects were included using the Polarizable Continuum Model (PCM), with water. This was implemented using the SCRF = (SMD, solvent=water) as keywords. Thermochemical corrections, including Gibbs free energy and enthalpy, were computed. [42-52]

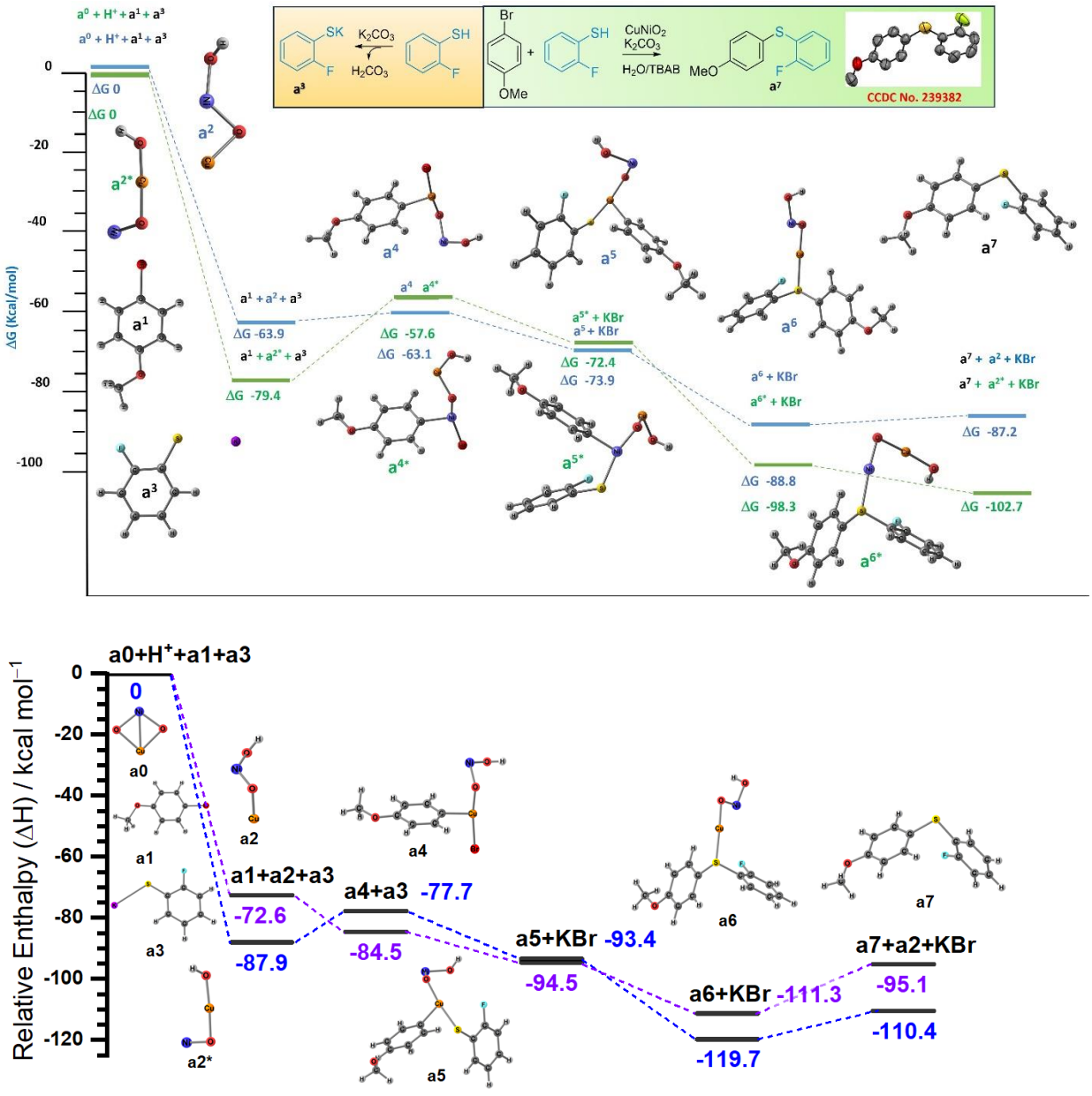
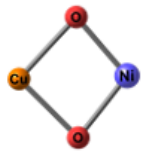
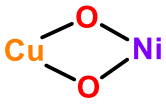
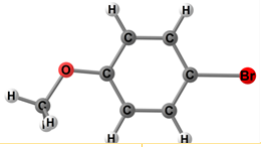
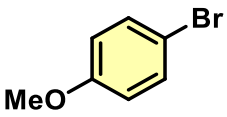
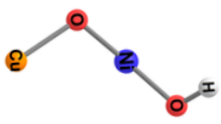
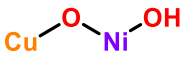
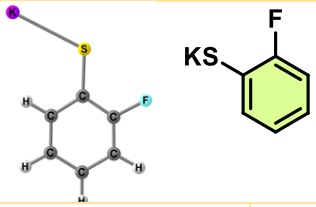
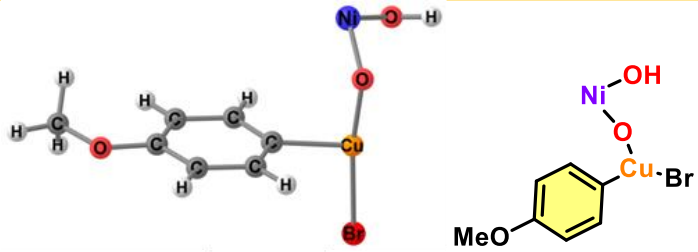
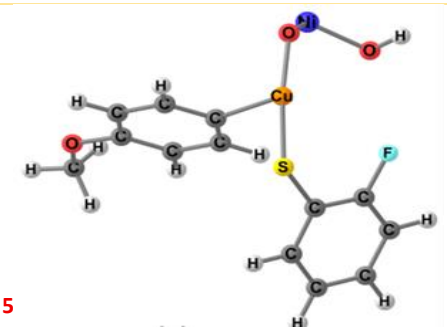


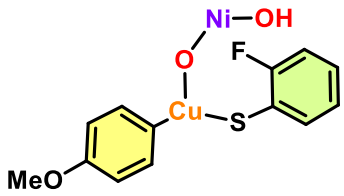
Figure 16: Energy and enthalpy profile of reaction from DFT study

Table 7. Cartesian coordinates of optimized geometries of a1, a2, a3, a4, a5, a6, a7, a2*, a4*, a5*, and a6*. The structures were calculated with the B3LYP/6-311+g* level of theory.

	X	y	z
a^0	 		
28	1.1848	-0.0016	0.0000
8	0.1135	-1.4070	0.0000
29	-1.2073	-0.0005	0.0000
8	0.1161	1.4146	0.0000
a^1	 		
6	-2.0454	0.2836	0.0000
6	-1.4539	-0.9825	0.0000
6	-1.2391	1.4290	0.0000
1	-2.0520	-1.8843	0.0000
1	-1.7059	2.4078	0.0000
6	-0.0613	-1.0984	0.0000
6	0.1451	1.3144	0.0000
1	0.3883	-2.0842	0.0000
1	0.7577	2.2080	0.0000
6	0.7243	0.0459	0.0000
8	-3.3978	0.5026	0.0000
6	-4.2699	-0.6336	0.0000
1	-4.1198	-1.2426	-0.8949
1	-4.1198	-1.2425	0.8949
1	-5.2798	-0.2284	0.0000
35	2.6433	-0.1173	0.0000
a^2	 		
29	1.6136	-0.1330	0.0038
8	0.2466	1.1190	-0.0162
28	-0.8749	-0.1890	0.0038
8	-2.6551	-0.0044	-0.1052
1	-3.0289	0.2337	0.7542

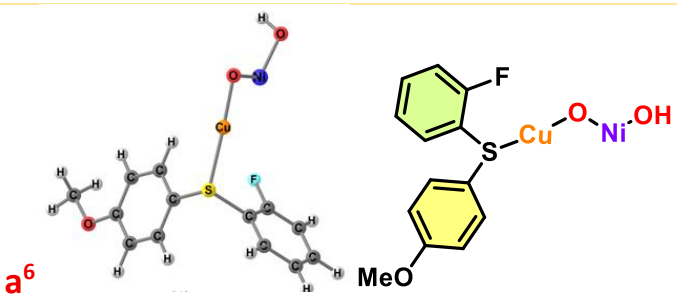
a[3] 			
6	-0.4481	-0.1578	0.0001
6	-0.4477	1.2550	0.0001
6	-1.7270	-0.7379	0.0001
1	0.5059	1.7734	0.0002
6	-1.6214	2.0050	0.0001
6	-2.9124	-0.0218	0.0001
1	-1.5606	3.0888	0.0001
1	-3.8555	-0.5583	0.0001
6	-2.8661	1.3725	0.0001
1	-3.7851	1.9479	0.0001
16	1.0258	-1.1341	0.0002
9	-1.8356	-2.1049	0.0001
19	3.6284	0.4498	-0.0004
a[4] 			
6	3.3595	-0.1179	0.2032
6	2.5781	-0.4865	-0.8948
6	2.7512	0.3572	1.3723
1	3.0248	-0.8641	-1.8054
1	3.3679	0.6358	2.2201
6	1.1820	-0.3678	-0.8280
6	1.3646	0.4771	1.4474
1	0.5823	-0.6525	-1.6837
1	0.9037	0.8466	2.3555
6	0.6221	0.1353	0.3286
8	4.7293	-0.1889	0.2293
6	5.4057	-0.6716	-0.9381
1	5.1166	-1.7016	-1.1603
1	5.2021	-0.0329	-1.8012
1	6.4667	-0.6336	-0.6994
1	-3.7580	-2.2435	-0.6084
8	-2.9211	-2.2709	-1.0930
28	-1.5628	-2.4779	0.0200
8	-1.5111	-1.1476	1.1265
29	-1.2866	0.4647	0.3664
35	-1.3084	2.6702	-0.4071



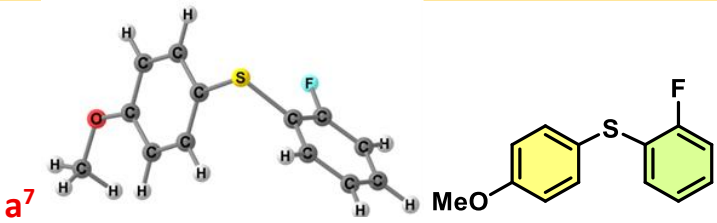


a[5]

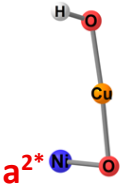
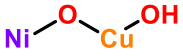
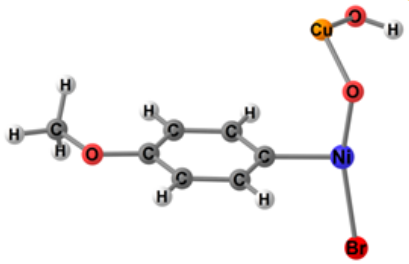
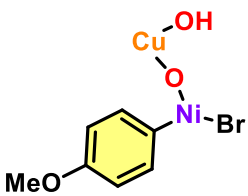
6	-3.5000	-1.0939	-0.0357
6	-2.4000	-1.1447	-0.8946
6	-3.3786	-0.4951	1.2247
1	-2.4681	-1.6044	-1.8722
1	-4.2383	-0.4673	1.8860
6	-1.1762	-0.5936	-0.4885
6	-2.1646	0.0569	1.6279
1	-0.3251	-0.6487	-1.1583
1	-2.0842	0.5139	2.6074
6	-1.0857	0.0116	0.7516
8	-4.7378	-1.6082	-0.3385
6	-4.9135	-2.2404	-1.6114
1	-4.7363	-1.5354	-2.4275
1	-4.2517	-3.1039	-1.7156
1	-5.9500	-2.5711	-1.6353
1	2.0218	3.4262	-1.6423
8	1.3019	2.8343	-1.9013
28	-0.1503	3.1678	-0.9398
8	0.0168	2.7560	0.7257
29	0.4923	1.0398	1.1733
6	3.3384	-1.7832	-1.4557
6	3.0803	-3.1487	-1.5702
6	2.7922	-1.0882	-0.3908
1	3.5022	-3.7051	-2.3996
6	2.2813	-3.7886	-0.6218
6	1.9851	-1.6902	0.5806
1	2.0757	-4.8499	-0.7080
6	1.7365	-3.0657	0.4353
1	1.1102	-3.5626	1.1677
1	3.9554	-1.2582	-2.1762
16	1.3457	-0.8211	1.9902
9	3.0630	0.2421	-0.2976

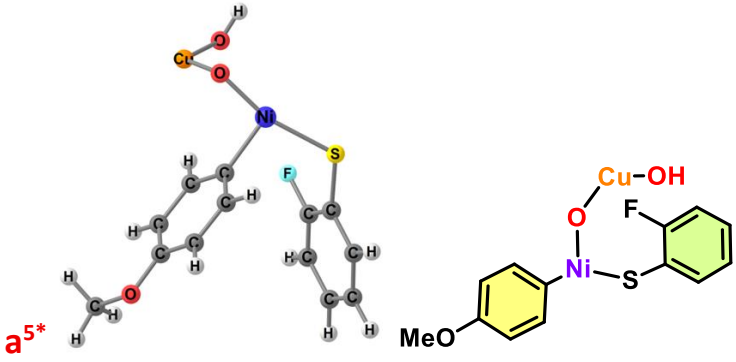


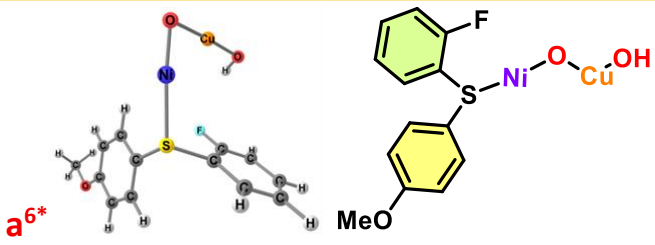
6	-4.0424	-1.1164	0.1616
6	-2.8219	-1.7958	0.2115
6	-4.0981	0.1852	-0.3590
1	-2.7532	-2.8004	0.6069
1	-5.0519	0.6996	-0.3980
6	-1.6642	-1.1676	-0.2483
6	-2.9476	0.7987	-0.8289
1	-0.7180	-1.6955	-0.1978
1	-3.0063	1.8002	-1.2402
6	-1.7225	0.1239	-0.7646
8	-5.2288	-1.6381	0.5925
6	-5.2340	-2.9648	1.1382
1	-4.9000	-3.6936	0.3963
1	-4.6043	-3.0219	2.0291
1	-6.2686	-3.1656	1.4083
1	4.1758	-3.4939	1.3559
8	4.4176	-2.5603	1.2849
28	3.0810	-1.6240	0.5546
8	2.8585	-1.7794	-1.1516
29	1.4725	-0.5465	-1.2370
6	0.6150	3.1112	1.9295
6	0.5690	4.4158	1.4387
6	0.3672	2.0642	1.0596
1	0.7626	5.2439	2.1111
6	0.2768	4.6535	0.0965
6	0.0651	2.2727	-0.2857
1	0.2400	5.6677	-0.2841
6	0.0214	3.5859	-0.7618
1	-0.2142	3.7672	-1.8042
1	0.8426	2.9006	2.9682
16	-0.2478	0.9226	-1.4373
9	0.4228	0.7974	1.5398



6	3.1750	-0.0958	0.0591
6	2.2354	-0.7671	-0.7300

6	2.8307	1.1162	0.6687
1	2.4761	-1.7048	-1.2139
1	3.5632	1.6273	1.2842
6	0.9676	-0.2149	-0.9142
6	1.5580	1.6470	0.5000
1	0.2546	-0.7370	-1.5430
1	1.2990	2.5762	0.9958
6	0.6163	0.9857	-0.2970
8	4.4488	-0.5468	0.2918
6	4.8560	-1.7792	-0.3154
1	4.2373	-2.6105	0.0317
1	4.8126	-1.7121	-1.4052
1	5.8859	-1.9353	-0.0006
6	-3.1586	-1.2217	1.2118
6	-4.0482	-1.5840	0.2003
6	-2.2333	-0.2242	0.9586
1	-4.7804	-2.3616	0.3862
6	-3.9928	-0.9485	-1.0394
6	-2.1376	0.4219	-0.2754
1	-4.6817	-1.2286	-1.8284
6	-3.0398	0.0411	-1.2758
1	-2.9863	0.5247	-2.2447
1	-3.1825	-1.6936	2.1875
16	-0.9858	1.7603	-0.5712
9	-1.3876	0.1340	1.9610
a^8 KBr			
19	0.0000	0.0000	-1.9552
35	0.0000	0.0000	1.0614
a^{2*}	 		
28	1.4361	-0.4076	-0.0028
8	0.7584	1.1808	0.0197
29	-0.8548	0.3117	-0.0007
8	-2.3631	-0.7490	-0.1046
1	-2.5820	-1.0808	0.7753
a^{4*}	 		
6	-3.2419	-0.4789	0.1836
6	-2.5510	0.1452	-0.8563

6	-2.5322	-1.0605	1.2411
1	-3.0746	0.6045	-1.6851
1	-3.0786	-1.5436	2.0447
6	-1.1493	0.1874	-0.8297
6	-1.1399	-1.0204	1.2594
1	-0.6305	0.6810	-1.6443
1	-0.6122	-1.4811	2.0873
6	-0.4479	-0.4020	0.2161
8	-4.6140	-0.5701	0.2574
6	-5.3872	0.0119	-0.7972
1	-5.2123	1.0887	-0.8653
1	-5.1632	-0.4614	-1.7568
1	-6.4278	-0.1712	-0.5360
1	2.6756	2.8441	-1.1099
8	1.7555	3.1145	-1.2299
29	0.7821	2.6969	0.2691
8	1.5251	1.2350	0.9751
28	1.4260	-0.3106	0.2397
35	1.9508	-2.4459	-0.3878
			
6	1.6892	2.8263	-0.3763
6	0.8573	2.4025	0.6611
6	1.6314	2.1859	-1.6193
1	0.8764	2.8843	1.6307
1	2.2808	2.5228	-2.4210
6	-0.0292	1.3368	0.4472
6	0.7542	1.1227	-1.8221
1	-0.6744	1.0289	1.2627
1	0.7339	0.6402	-2.7929
6	-0.0744	0.6888	-0.7834
8	2.5942	3.8601	-0.2729
6	2.6857	4.5566	0.9741
1	1.7362	5.0346	1.2293
1	2.9899	3.8840	1.7801
1	3.4488	5.3196	0.8310
1	-4.3726	-1.2932	1.3468
8	-3.7160	-0.7180	1.7613
29	-3.3729	0.7089	0.6312
8	-2.7387	0.2587	-0.9910

28	-1.3164	-0.6989	-1.0679
6	2.5394	-1.8748	1.9696
6	3.8004	-2.0658	1.4065
6	1.4236	-1.9409	1.1522
1	4.6819	-2.0169	2.0359
6	3.9180	-2.3238	0.0404
6	1.4999	-2.1868	-0.2219
1	4.8953	-2.4765	-0.4042
6	2.7808	-2.3864	-0.7607
1	2.8768	-2.5889	-1.8217
1	2.4128	-1.6815	3.0290
16	0.0606	-2.3459	-1.2558
9	0.2049	-1.7737	1.7335
			
6	-4.2662	-0.2325	0.1730
6	-3.2824	-1.2114	0.3423
6	-3.9551	0.9676	-0.4836
1	-3.4973	-2.1456	0.8439
1	-4.7291	1.7158	-0.6139
6	-1.9916	-0.9797	-0.1340
6	-2.6759	1.1857	-0.9697
1	-1.2285	-1.7367	0.0137
1	-2.4505	2.1119	-1.4867
6	-1.6876	0.2120	-0.7845
8	-5.5544	-0.3551	0.6093
6	-5.9350	-1.5588	1.2904
1	-5.8144	-2.4289	0.6411
1	-5.3521	-1.6903	2.2049
1	-6.9860	-1.4326	1.5416
1	2.4953	-0.6992	2.6919
8	3.2539	-0.7408	2.0971
29	2.8492	-1.7601	0.6104
8	2.3935	-2.6548	-0.9106
28	1.2761	-1.3483	-1.1750
6	1.2662	2.8627	1.6005
6	1.7466	3.9756	0.9112
6	0.7238	1.8144	0.8784
1	2.1769	4.8006	1.4673
6	1.6747	4.0274	-0.4801
6	0.6321	1.8441	-0.5126
1	2.0465	4.8933	-1.0156
6	1.1130	2.9681	-1.1897

1	1.0449	3.0096	-2.2708
1	1.3143	2.7969	2.6813
16	-0.0463	0.4867	-1.4802
9	0.2716	0.7296	1.5518

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