Supporting Information

From Symmetrical Tetrasulfide to Trisulfides Dioxides via Photocatalysis

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I. General Information

NMR Spectrum:

^{1}H and **^{13}C** spectra were collected on 300 MHz, 400 MHz or 500 MHz NMR spectrometers (Bruker AVANCE). Chemical shifts for protons are reported in parts per million (ppm) downfield and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield and are referenced to the carbon resonances of solvent ($CHCl_3$ = δ 77.00). Dates are represented as follows: chemical shift, multiplicity (brs = broad single, s = singlet, d = double, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration.

Mass Spectroscopy:

Mass spectra were in general recorded on a Shimadzu GCMS-QP2010 Ultra and a HP 5989A mass selective detector; Thermo Fisher Scientific LTQ FTICR-MS; Thermo Scientific Q Exactive HF Orbitrap-FTMS.

Chromatography:

Column chromatography was performed with silica gel (300 – 400 mesh ASTM).

IR:

SHIMADZU IR Tracer-100 Spectrometers.

Solvent:

Ethyl acetate (EA, 99.9%, Extra Dry, with molecular sleves) and Tetrahydrofuran (THF, 99.9%, Extra Dry, with molecular sleves) were bought and directly used without further purification.

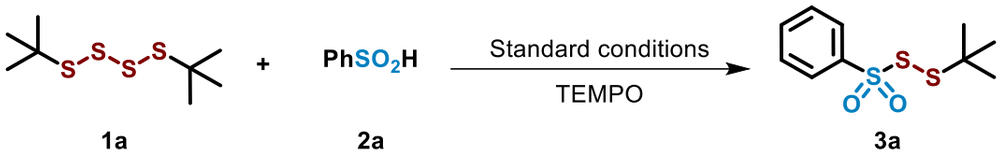
Starting Materials:

Starting materials including the tetrasulfides and the sulfinic acids were prepared adopting the reported procedures[1,7] expect for special emphasis.

II. Mechanistic Study

(a) Radical Quenching Experiments.

All reactions were operated under standard conditions with extra 2,2,6,6-tetramethyl-1-piperinedinyloxy (TEMPO). The yields were collected by isolating. ND = Not detected.



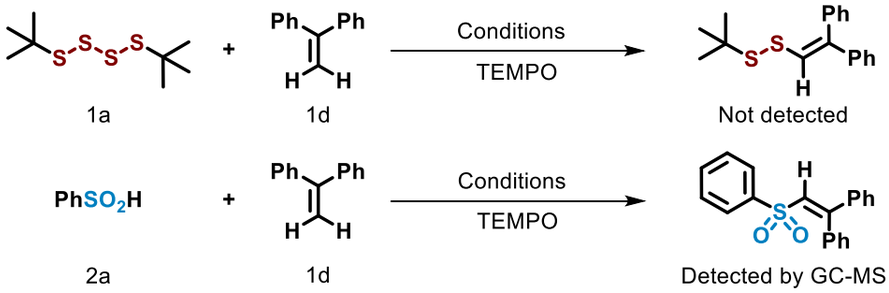
1a 2a 3a

Entry	TEMPO	Yield (%)
1	—	90%
2	1 equiv.	23%
3	2 equiv.	ND

*Radical quenching experiments revealed that TEMPO could efficiently quench the process of the formation of compound **3a**, suggested the radical property of this system.*

(b) Radical Capture Experiments

Radical capture experiments were performed using a Shimadzu GCMS-QP2010 Ultra and a HP 5989A mass selective detector. Follow the reaction conditions: **1a** (0.2 mmol, 48.4 mg), **2a** (0.2 mmol, 28.4 mg), **1d** (0.1 mmol, 18.0 mg), TEMPO (0.1 mmol, 15.6 mg) $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$ (1 mol%, 1.1 mg), ethyl acetate (1 mL) was stirred at room temperature under N_2 atmosphere and blue LEDs (460 nm, 6 W) for 6 h.



1a 1d Not detected

PhSO2H 1d Detected by GC-MS

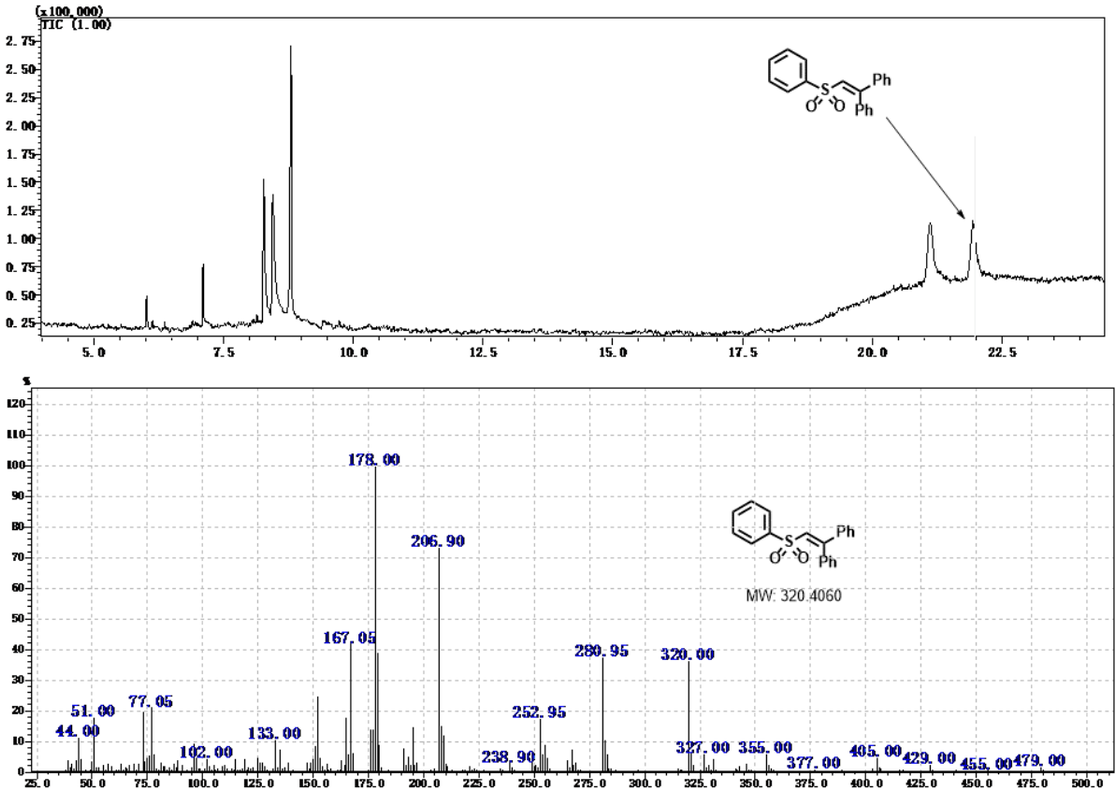


Figure S1. The capture of free radical B

(c) Ultraviolet-Visible Absorption Experiments

Ultraviolet-visible absorption experiments were performed using a Shimadzu UV-2700 UV-visible spectrophotometer. In each experiment, the varying samples were combined in ethyl acetate in screw-top 1.0 cm quartz cuvettes. The concentration of $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$ was 8.91×10^{-4} M, the concentration of 1,4-di-tert-butyltetrasulfane and benzenesulfinic acid were 0.1 M.

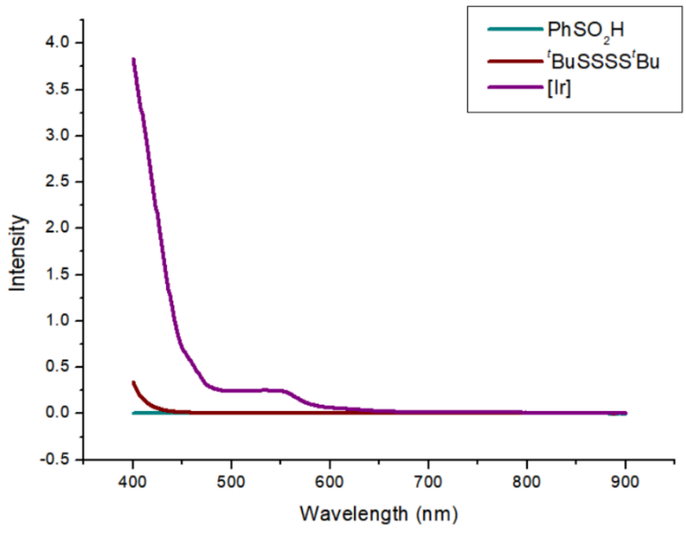


Figure S2. UV-Vis experiments of [Ir], ^{t}BuSSSS^{t}Bu and $PhSO_2H$.

Ir catalyst was approved to serve as photosensor at 530 nm.

(d) Stern–Volmer Fluorescence Quenching Experiments with [Ir(dF(CF$_3$)ppy)$_2$-(dtbbpy)]·PF$_6$]

Fluorescence quenching studies were performed using a Shimadzu RF-6000 Fluorescence Spectrophotometer. In each experiment, the photoredox catalyst and varying concentrations of quencher were combined in ethyl acetate in screw-top 1.0 cm quartz cuvettes. For the emission quenching of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]·PF$_6$], the concentration was 2.67 $\times 10^{-3}$ M, the solution was irradiated at 530 nm.

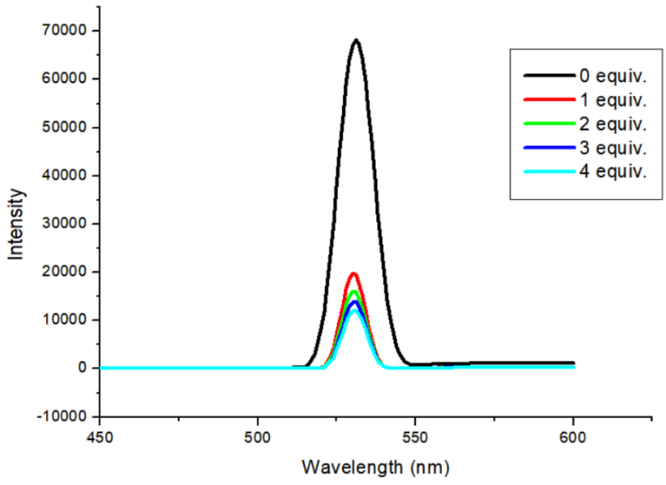


Figure S3. Quenching experiments of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]·PF$_6$] with PhSO$_2$H.

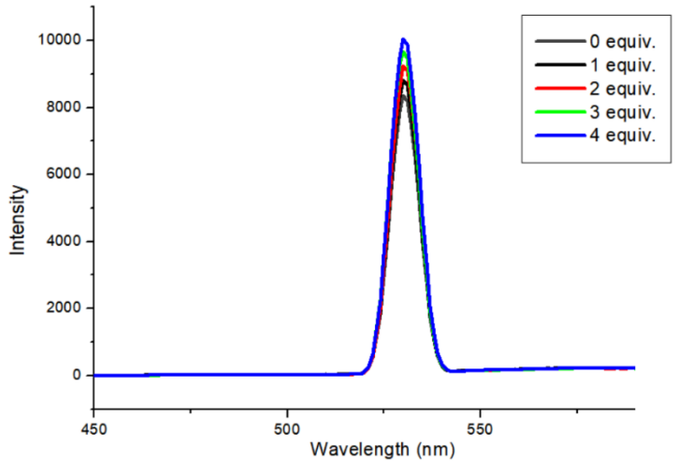


Figure S4. Quenching experiments of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]·PF$_6$] with ^{t}BuSSSS^{t}Bu

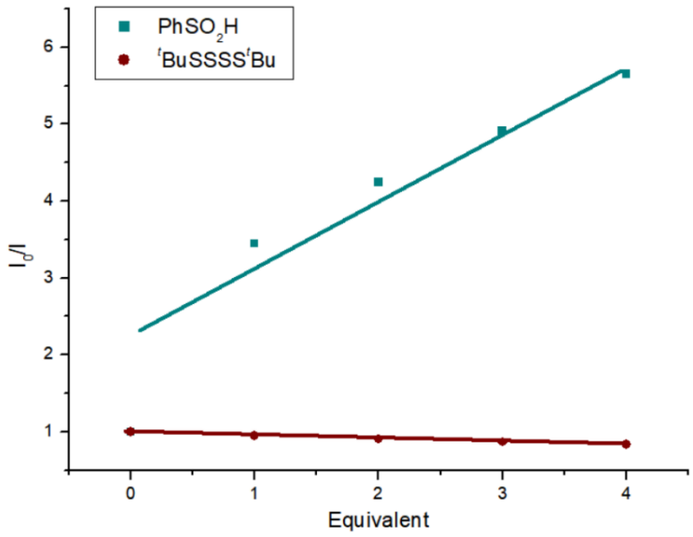


Figure S5. Stern-Volmer Plot of Fluorescence Quenching Experiments

The Stern-Volmer analysis revealed that the excited state of [Ir(dF(CF3)ppy)2(dtbbpy)]·PF6 photoredox catalysis is efficiently quenched by PhSO2H in ethyl acetate at room temperature.

III. The Analysis of By-products.

GC-MS of compound **a**

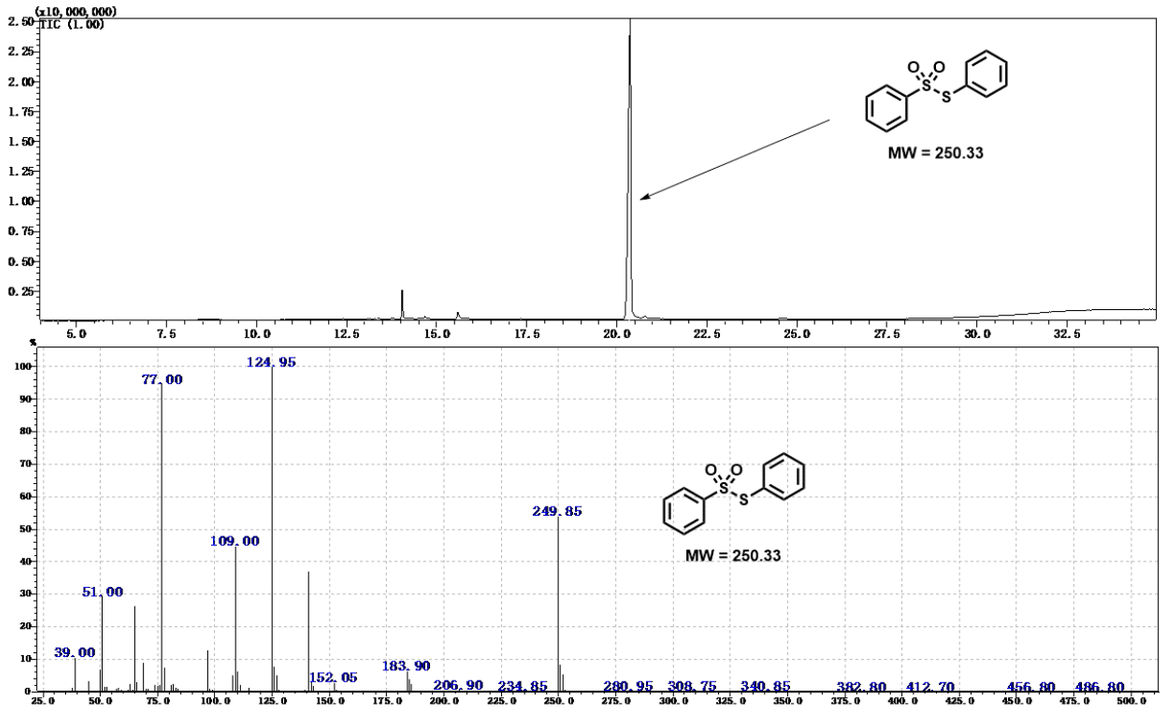


Figure S6. The detection of self-disproportionation product of benzenesulfinic acid **a**

GC-MS of compound **b**

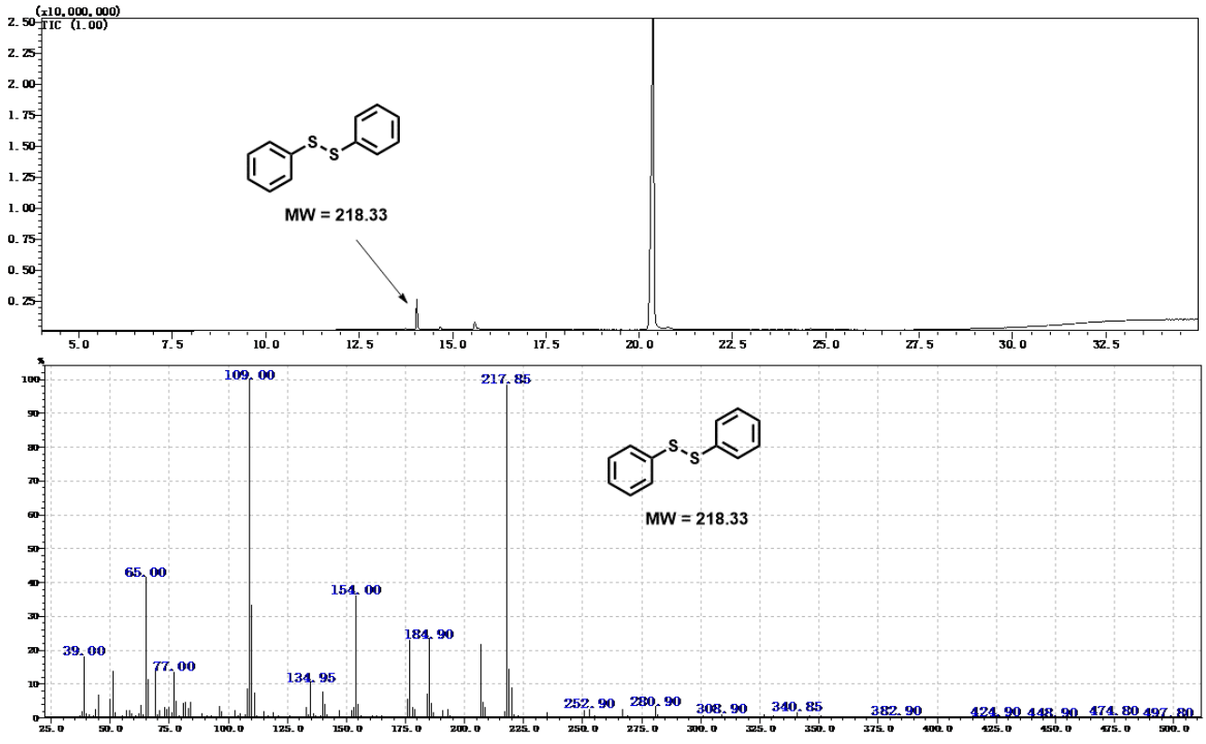


Figure S7. The detection of compound **b**

IV. The General Synthetic Procedure and Data for Starting Materials.

1. Typical procedure for the preparation of tetrasulfide substrates 1

Thiol (1.0 equiv.) and base (1.0 equiv.) were added to anhydrous solvent (30 mL) in an oven-dried round bottom flask under nitrogen. The solution was cooled to -78 °C for 1 hour, after which sulfur monochloride (0.6 equiv.) was added dropwise. The reaction was stirred for 2 hours and then quenched with saturated sodium bicarbonate solution (30 mL), and the aqueous layer was discarded. The organic layer was washed with deionized water (30 mL) and brine (30 mL). The organic layer was dried over sodium sulfate, the residue was purified by column chromatography on silica gel using PE or PE/EA and concentrated in vacuo to afford the required compounds. Compounds **1a**[1], **1b**[2], **1c**[1], **1g**[3], **1h**[4], **1i**[5], **1j**[3], **1k**[3], **1l**[6] **and 1o**[3] have been reported previously. [1]

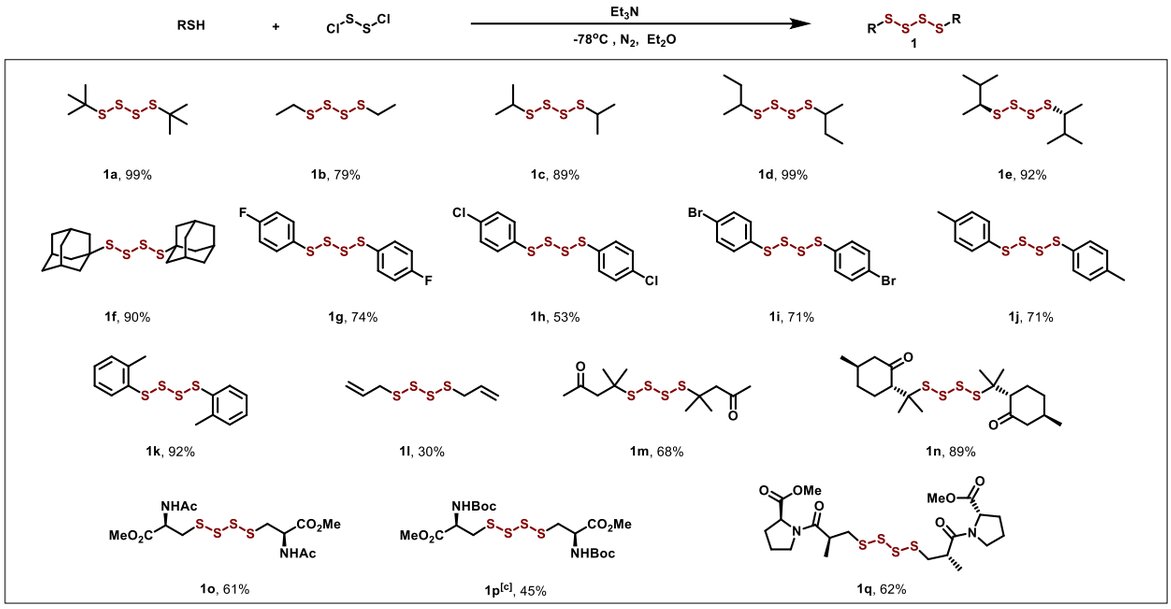
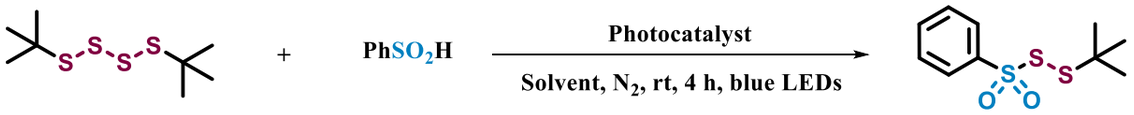


Figure S8. The synthesis of tetrasulfide substrates **1.** [a][b] [a]Reaction conditions: RSH (2 mmol), S_2Cl_2 (1.2 mmol), Et_3N (2 mmol), and Et_2O (15 mL) were stirred at -78 °C under N_2 atmosphere for 1.5-6 h. [b]Isolated yield. [c]Pyridine (2 mmol), dichloromethane (15 mL).

2. Typical procedure for the preparation of sulfinic acids 2

To a 50 mL flask, Na_2SO_3 (3.8 g, 30.0 mmol) was dissolved in 20 mL pure water. Then aryl or alkyl sulfonyl chloride (10.0 mmol) was added into reaction system. The mixture was stirred at 75 °C for 5 h and returned to room temperature. This aqueous solution was washed with chloroform twice, acidified by dripping excess diluent H_2SO_4 solution at 0 °C. The mixture was stirred and kept at 0 °C for 1 h, extracted with dichloromethane and concentrated in vacuo to afford the sulfinic acids in 40-70% yields.[7]

V. Optimization of reaction conditions[a]

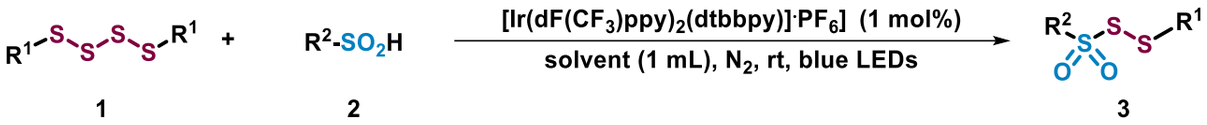


1a **2a** **3a**

Entry	Photocatalyst	Solvent	Yield[b] (%)
1	Eosin B	EA	Trace
2	$UO_2(NO_3)_2{\cdot}6H_2O$	EA	Trace
3	Methylene	EA	NR
4	Eosin Y	EA	56
5	$Ir(ppy)_3$	EA	41
6	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]{\cdot}PF_6$	EA	80
7	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]{\cdot}PF_6$	DCE	54
8	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]{\cdot}PF_6$	THF	63
9	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]{\cdot}PF_6$	DMF	40
10	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]{\cdot}PF_6$	Acetone	55
11	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]{\cdot}PF_6$	DCM	20
12[c]	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]{\cdot}PF_6$	EA	73
13[d]	**$[Ir(dF(CF_3)ppy)_2(dtbbpy)]{\cdot}PF_6$**	**EA**	**90**
14	—	EA	NR
15[e]	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]{\cdot}PF_6$	EA	NR
16[f]	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]{\cdot}PF_6$	EA	7
17[g]	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]{\cdot}PF_6$	EA	Messy

Figure S9. [a]Reaction conditions: **1a** (0.1 mmol, 24.2 mg), **2a** (0.3 mmol, 42.6 mg), catalyst (1 mol%) and solvent (1 mL) were stirred at room temperature under N_2 atmosphere and blue LEDs (460 nm, 6 W) for 4 h. [b]Isolated yields. [c]**2a** (0.2 mmol, 28.4 mg). [d]**2a** (0.1 mmol, 14.2 mg). [e]Without blue LEDs. [f]**2a** (0.1 mmol, 14.2 mg), without blue LEDs but at 60 °C. [g]Under air.

VI. General Procedures



1 2 3

A mixture of tetrasulfide **1** (1 equivalent, 1 mmol), sulfinic acid **2** (1 equivalent, 1 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) was added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL solvent was added and the mixture was stirred for 3-20 h under blue LEDs (460 nm, 5-8 W) in a paralleled reactor. After evaporation of solvent, the residue was purified by column chromatography on silica gel using PE/EA or hexane/EA and concentrated in vacuo to afford the required compound **3**. For detailed modification, please follow the corresponding procedures.

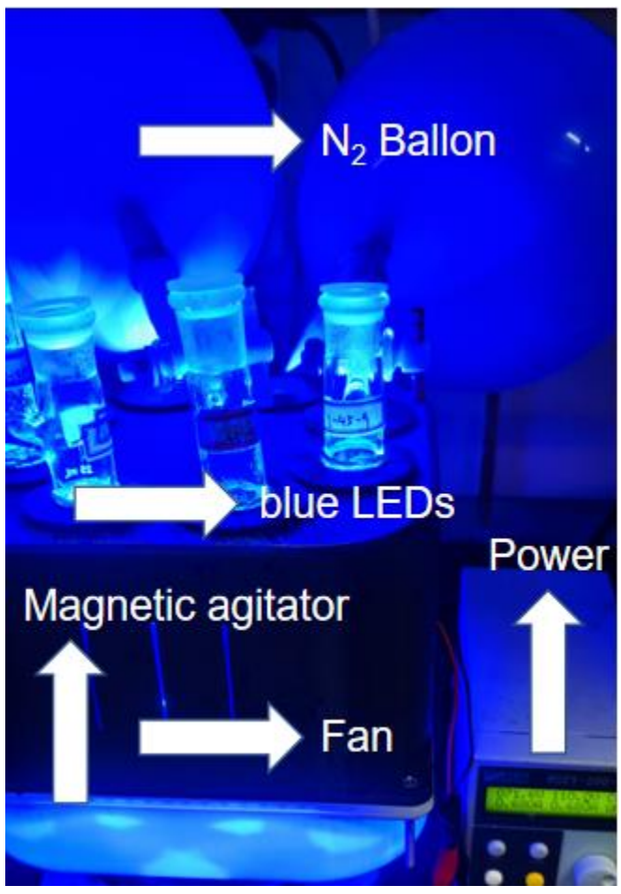
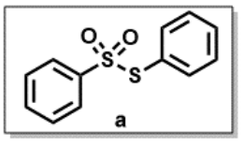


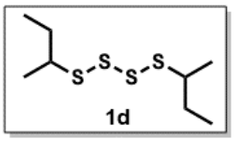
Figure S10: Parallel Photoreactor

[a]There are three LEDs in each cell. Two LEDs are on the opposite sides with the third one on the bottom part of the cell.

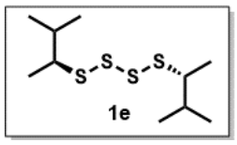
VII. Procedures and Data



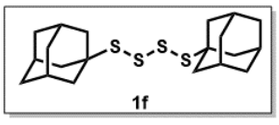
By-product: S-phenyl benzenesulfonothioate **a**[8]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59-7.54 (dd, J = 12.2, 4.8 Hz, 3H), 7.48-7.44 (m, J = 8.7, 4.3, 2.4 Hz, 1H), 7.36-7.38 (m, 1H), 7.36-7.30 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.9, 136.5, 133.5, 131.3, 129.3, 128.7, 127.7, 127.4.



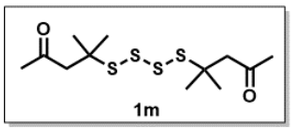
1,4-di-sec-butyltetrasulfane (**1d,** Yellow liquid, 99%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.08-2.94 (m, 1H), 1.80-1.57 (m, J = 28.3, 14.1, 6.9 Hz, 2H), 1.37-1.35 (d, J = 6.9 Hz, 3H), 0.99 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 48.9, 29.0, 20.2, 11.4. **IR** (neat) 3173, 2963, 2920, 2872, 1449, 1373, 1219, 716, 1146, 789, 513 cm^{-1}. **HRMS** (EI) Calcd for $C_8H_{18}S_4$ 242.0291, found 242.0290.



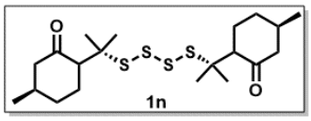
1,4-bis(3-methylbutan-2-yl) tetrasulfane (**1e,** Yellow liquid, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.16-3.09 (m, 1H), 2.14-1.96 (m, 1H), 1.37-1.29 (m, 3H), 1.05-0.91 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 54.3 (d, J = 2.7 Hz), 32.0 (d, J = 1.2 Hz), 20.2, 18.1, 16.5. **IR** (neat) 2961, 2928, 2870, 1713, 1265, 741, 507 cm^{-1}. **HRMS** (EI) Calcd for $C_{10}H_{22}S_4$ 270.0604, found 270.0602.



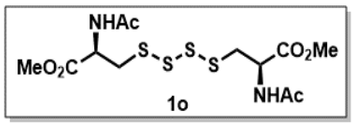
1,4-di((3S,5S,7S)-adamantan-1-yl) tetrasulfane (**1f,** White solid, 90%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.11 (s, 3H), 1.92 (s, 6H), 1.70 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 50.7, 42.8, 36.0, 29.9. **IR** (neat) 2901, 2920, 2847, 2673, 2654, 1451, 1341, 1296, 1040, 741, 513 cm^{-1}. **HRMS** (EI) Calcd for $C_{20}H_{30}S_4$ 398.1230, found 398.1226.



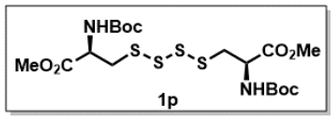
4,4'-tetrasulfanediylbis(4-methylpentan-2-one) (**1m,** Yellow liquid, 68%) 5-methyl-5-((2-methyl-4-oxopentan-2-yl) tetrasulfanyl) hexan-2-one. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.76-2.66(m, 2H), 2.07-2,01 (dd, *J* = 16.1, 11.1 Hz, 3H), 1.36 (m, *J* = 22.4, 15.8, 9.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.3, 53.2, 50.0, 31.7, 27.1. **IR** (neat) 3173, 2967, 2924, 2361, 1709, 1462, 1377, 1358, 1333, 1113, 943, 546 cm^{-1}. **HRMS** (EI) Calcd for $C_{12}H_{22}O_2S_4$ 326.0503, found 326.0498.



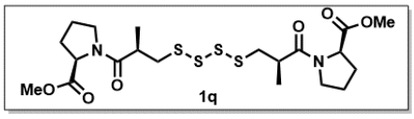
6,6'-(tetrasulfanediylbis(propane-2,2-diyl)) bis(3-methylcyclohexan-1-one) (**1n,** Yellow liquid, 89%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.74-2.70 (m, 1H), 2.45-2.42 (m, 2H), 2.26-2.25 (m, *J* = 12.1, 3.7, 2.2 Hz, 3H), 2.11-1.84 (m, 3H), 1.94-1.82 (m, 2H), 1.53 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.2 Hz, 2H), 0.90 (d, *J* = 7.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.5, 56.7, 54.1, 52.3, 36.7, 34.1, 29.7, 27.0, 23.1, 22.2. **IR** (neat) 2959, 2926, 2868, 1709, 1454, 1360, 1119, 733, 548 cm^{-1}. **HRMS** (EI) Calcd for $C_{20}H_{34}O_2S_4$ 434.1442, found 434.1438.



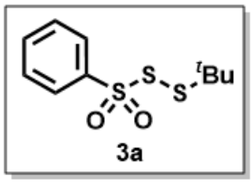
Dimethyl 3,3'-tetrasulfanediyl(2R,2'R)-bis(2-acetamidopropanoate) (**1o^{3}**, Yellow solid, 61%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.04-4.99 (m, 1H), 3.76 (s, 3H), 3.60-3.46 (m, *J* = 34.0, 11.2, 9.4 Hz, 2H), 2.23-2.22 (d, *J* = 1.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.1, 170.0, 77.9, 52.5, 36.0, 20.1. **IR (neat)** 3410, 2953, 2361, 1736, 1626, 1229, 1202, 1157, 621, 604, 592 cm^{-1}.



Dimethyl 3,3'-tetrasulfanediyl(2R,2'R)-bis(2-((tert-butoxycarbonyl) amino) propanoate) (**1p,** White powder, 45%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.41 (d, *J* = 6.5 Hz, 1H), 4.67 (d, *J* = 5.0 Hz, 1H), 3.78 (s, 4H), 3.44 (m, *J* = 19.5, 14.0, 5.0 Hz, 3H), 1.45 (s, 13H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.8, 154.9, 99.9, 80.3, 52.9, 52.7, 41.4, 28.3. **IR (neat)** 3431, 3420, 3055, 2984, 2957, 1746, 1713, 1499, 1265, 1163, 735, 704 cm^{-1}. **HRMS** (EI) Calcd for $C_{18}H_{32}N_2O_8S_4$ 532.1042, found 532.1028.



Dimethyl ((2S,2'S)-3,3'-tetrasulfanediylbis(2-methylpropanoyl)) (S)-di-L-prolinate (**1q,** White power, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.52-4.48 (dt, J = 8.8, 4.4 Hz, 1H), 3.72-3.72 (d, J = 1.8 Hz, 3H), 3.69-3.67 (d, J = 6.3 Hz, 1H), 3.24-3.16 (m, J = 11.3, 9.9, 6.7 Hz, 1H), 3.06-3.00 (dt, J = 12.5, 5.5 Hz, 1H), 2.87-2.82 (dd, J = 12.8, 4.9 Hz, 1H), 2.63-2.58 (dt, J = 9.7, 3.9 Hz, 1H), 2.21 (m, J = 10.6, 6.8, 3.8 Hz, 1H), 2.01 (dd, J = 11.1, 5.1 Hz, 3H), 1.23 (m, J = 15.0, 10.7, 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.37 (d, J = 31.1 Hz), 172.7, 58.67 (d, J = 3.9 Hz), 52.1, 46.9 (d, J = 3.4 Hz), 41.4 (d, J = 45.6 Hz), 29.0, 24.8 (d, J = 3.7 Hz), 16.8 (d, J = 8.0 Hz). **IR (neat)** 2972, 2878, 2361, 2243, 1742, 1639, 1431, 1196, 1173, 914, 727 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{20}H_{33}N_2O_6S_4$ $[M+H]^+$: Calcd 525.1221, found 525.1207.



A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg), benzenesulfinic acid (1 equivalent, 1 mmol, 14.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 5 h under blue LEDs (460 nm, 6 W) in a paralleled reactor. **3a**[9] (23.6 mg, 90%) was obtained through column chromatography (V_{PE}/V_{EA} = 60/1) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94-7.92 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.67-7.53 (m, *J* = 33.9, 15.2, 4.2 Hz, 3H), 1.38 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 133.9, 129.1, 127.8, 50.3, 30.2.

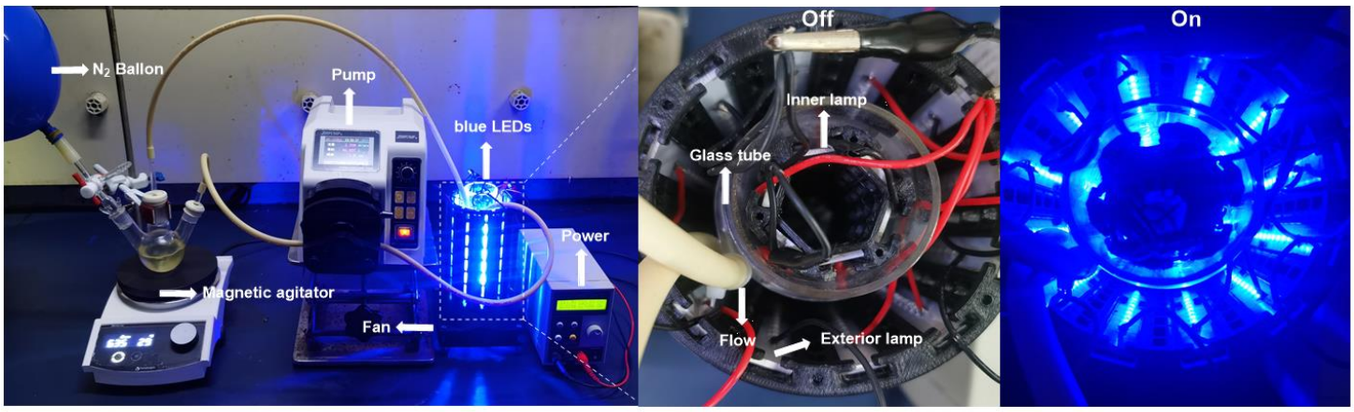
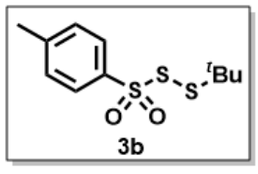


Figure S11. Flow Reaction Photoreactor.

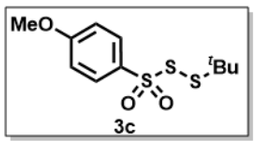
Flow reaction: A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 6 mmol, 1.45 g), benzenesulfinic acid (1 equivalent, 6 mmol, 0.85 g), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$ (1 mol%, 60 mg) was added into a 250 mL three-necked flask. The flask along with the micro cube were evacuated and filled with N_2 three times at room temperture. Then ethyl acetate (60 mL) was added and the mixture was stirred for 6.5 h under blue LEDs (430 nm, 85 W totally) in a paralleled reactor. The flask was equipped with rubber plugs, with inlet and outlet of micro tube, which was made of grass tubing (O.D. = 5 mm, I.D. = 2 mm, length = 2.42 m, volume = 39.9 mL). The solution was pumped by a pump (0.5 mL/min) into the micro tube, then returned to flask. This circulatory system was irradiated by blue LEDs. After the reaction, ethyl acetate (10 mL) was pumped into the tube to flush out residual fluid. After evaporation of solvent, the residue was purified by column chromatography on silica gel (PE/EA= 60:1) and concentrated in vacuo to afford the required compound **3a** (76%, 1.196 g).



3b

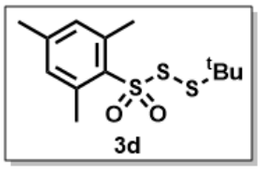
A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg),4-methyl-benzene-sulfinic acid (3 equivalent, 3 mmol, 46.8 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs

(460 nm, 5 W) in a paralleled reactor. **3b** (52.0 mg, 93%) was obtained through column chromatography (V_{PE}/V_{EA} = 50/1) as a colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.82-7.79 (d, *J* = 8.1 Hz, 2H), 7.36-7.33 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 1.37 (s, 9H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.0, 140.2, 129.6, 127.9, 50.2, 30.2, 21.6. **IR** (neat) 3051, 2963, 2857, 1591, 1469, 1460, 1366, 1329, 1125, 1329, 1125, 812, 652 cm^{-1}. **HRMS** (EI) Calcd for $C_{11}H_{16}O_2S_3$ 276.0312, found 276.0316.



3c

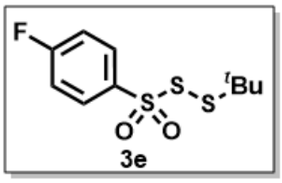
A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg), 4-methoxybenzenesulfinic acid (1 equivalent, 1 mmol, 10.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 8 W) in a paralleled reactor. **3c** (26.3 mg, 90%) was obtained through column chromatography (V_{PE}/V_{EA} = 60/1) as a colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.87-7.84 (d, *J* = 9.0 Hz, 2H), 7.01-6.98 (d, *J* = 9.0 Hz, 2H), 3.89 (s, 3H), 1.37 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.9, 134.7, 130.2, 114.1, 55.7, 50.2, 30.2. **IR** (neat) 3051, 2965, 2940, 2922, 2898, 1591, 1495, 1327, 1261, 1134, 1159, 1076, 1022, 656, 575, 529 cm^{-1}. **HRMS** (EI) Calcd for $C_{11}H_{16}O_3S_3$ 292.0262, found 292.0258.



3d

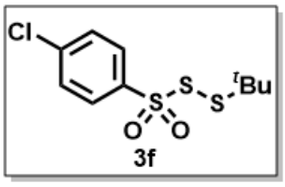
A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg),2,4,6-trimethyl-benzenesulfinic acid (1 equivalent, 1 mmol, 18.4 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 8 W) in a paralleled reactor. **3d** (19.6 mg, 64%) was obtained through column chromatography (V_{PE}/V_{EA} = 20/1) as a colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.26-6.96 (d, 2H), 2.73 (s, 6H), 2.31 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.8,

139.9, 138.2, 132.0, 50.1, 30.2, 23.3, 21.0. **IR** (neat) 3011, 2967, 2850, 2743, 1751, 1456, 1366, 1323, 1140, 716, 640, 586, 509 cm^{-1}. **HRMS** (EI) Calcd for $C_{13}H_{20}O_2S_3$ 304.0625, found 304.0631.



3e

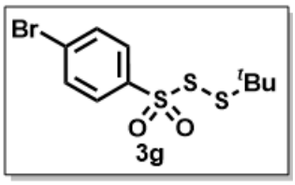
A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg), 4-fluorobenzenesulfinic acid (1 equivalent, 1 mmol, 16.0 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 8 W) in a paralleled reactor. **3e** (21.0 mg, 75%) was obtained through column chromatography (V_{PE}/V_{EA} = 60/1) as a colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.97-7.92 (m, 2H), 7.23-7.20 (d, 2H), 1.39 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8-164.5 (d, *J* = 257.2 Hz), 139.0-139.0 (d, *J* = 3.2 Hz), 130.8-130.7 (d, *J* = 9.7 Hz), 116.5-116.3 (d, *J* = 22.8 Hz), 50.5, 30.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.57 (s). **IR** (neat) 3048, 2965, 1466, 1366, 1327, 1144, 1366, 799, 750, 716, 687, 592, 538 cm^{-1}. **HRMS** (EI) Calcd for $C_{10}H_{13}FO_2S_3$ 280.0062, found 280.0060.



3f

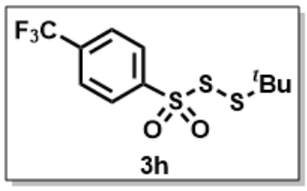
A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg), 4-chlorobenzenesulfinic acid (1 equivalent, 1 mmol, 17.7 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 8 W) in a paralleled reactor. **3f** (24.0 mg, 81%) was obtained through column chromatography (V_{PE}/V_{EA} = 60/1) as a colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.89-7.83 (m, 2H), 7.55-7.51 (m, 2H), 1.39 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4, 140.6, 129.4,

129.2, 50.5, 30.2. **IR** (neat) 3051, 2965, 2359, 1753, 1611, 1470, 1327, 1446, 1092, 602, 592, 822 cm^{-1}. **HRMS** (EI) Calcd for $C_{10}H_{13}O_2S_3$ 295.9766, found 295.9763.



3g

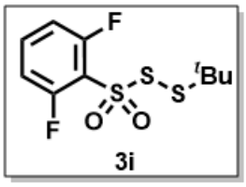
A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg), 4 -bromobenzene-sulfinic acid (1 equivalent, 1 mmol, 22.1 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 8 W) in a paralleled reactor. **3g** (28.4 mg, 83%) was obtained through column chromatography (V_{PE}/V_{EA} = 20/1) as a colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.70-7.67 (d, *J* = 8.8 Hz, 2H), 1.38 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 141.5, 132.4, 129.2, 50.5, 30.2. **IR** (neat) 3090, 2963, 1470, 1456, 1389, 1366, 1329, 1140, 1074, 737, 594, 550 cm^{-1}. **HRMS** (EI) Calcd for $C_{10}H_{13}BrO_2S_3$ 339.9261, found 339.9260.



3h

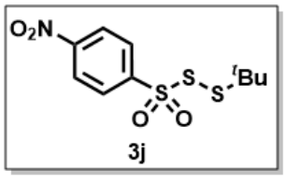
A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg), 4-(trifluoromethyl) benzenesulfinic acid (1 equivalent, 1 mmol, 21.0 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 8 W) in a paralleled reactor. **3h** (21.5 mg, 67%) was obtained through column chromatography (V_{PE}/V_{EA} = 60/1) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06-8.04 (d, *J* = 8.2 Hz, 2H), 7.84-7.81(d, *J* = 8.4 Hz, 2H), 1.40 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.3, 135.9-134.9 (q, *J* = 33.2 Hz), 128.8, 128.3, 127.1, 126.5-126.4 (d, *J* = 3.7 Hz), 126.5-126.3 (q, *J* = 3.7 Hz), 124.4, 121.6, 118.9, 50.7, 30.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.20 (s). **IR** (neat)

3031, 2968, 2930, 2864, 1461, 1404, 1368, 1323, 1146, 1061, 710, 610, 588 cm^{-1}. **HRMS** (EI) Calcd for $C_{11}H_{13}F_3O_2S_3$ 330.0030, found 330.0028.



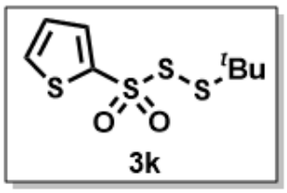
3i

A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg), 2,6-difluorobenzenesulfinic acid (1 equivalent, 1 mmol, 17.8 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 6 W) in a paralleled reactor. **3i** (19.1 mg, 60%) was obtained through column chromatography (V_{Hexane}/V_{EA} = 20/1) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62-7.55 (m, 1H), 7.07-7.03 (dd, *J* = 9.6, 7.1 Hz, 2H), 1.39 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.9-169.8 (d, *J* = 3.3 Hz), 136.1-135.9 (t, *J* = 11.0 Hz), 120.9-120.6 (t, *J* = 15.6 Hz), 113.3-113.1 (dd, *J* = 23.2, 3.4 Hz), 50.8, 30.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.85 (s). **IR** (neat) 3096, 2963, 2924, 1609, 1585, 1468, 1346, 1148, 1005, 791, 621, 577, 511 cm^{-1}. **HRMS** (EI) Calcd for $C_{10}H_{12}F_2O_2S_3$ 297.9968, found 297.9971.



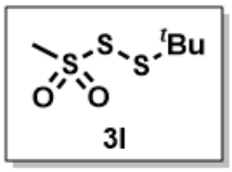
3j

A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg), 4-nitrobenzenesulfinic acid (1 equivalent, 1 mmol, 18.7 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 5 W) in a paralleled reactor. **3j** (14.0 mg, 46%) was obtained through column chromatography (V_{PE}/V_{EA} = 50/1) as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41-8.39 (d, *J* = 8.9 Hz, 2H), 8.12-8.10 (d, *J* = 8.9 Hz, 2H), 1.42 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.6, 148.0, 129.0, 124.4, 51.0, 30.2. **IR** (neat) 3103, 2965, 2924, 2864, 1529, 1346, 1312, 1140, 1074, 853, 745, 733, 681, 596, 554 cm^{-1}. **HRMS** (EI) Calcd for $C_{10}H_{13}NO_4S_3$ 307.0007, found 307.0005.



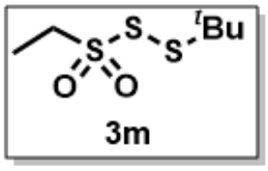
3k

A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg), thiophene-2-sulfinic acid (1 equivalent, 1 mmol, 14.9 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 5 W) in a paralleled reactor. **3k** (13.4 mg, 50%) was obtained through column chromatography (V_{PE}/V_{EA} = 20/1) as a colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.73-7.71 (m, 2H), 7.26-7.13(m, 1H), 1.40 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.2, 134.3, 134.2, 127.4, 50.6, 30.2. **IR** (neat) 3102, 2963, 2938, 2922, 2897, 1503, 1472, 1396, 1327, 1134, 1009, 721, 664, 554 cm^{-1}. **HRMS** (EI) Calcd for $C_8H_{12}O_2S_4$ 267.9720, found 267.9723.



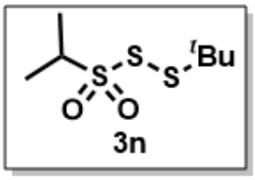
3l

A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg), sodium methanesulfinate (1 equivalent, 1 mmol, 10.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 8 W) in a paralleled reactor. **3l** (13.4 mg, 67%) was obtained through column chromatography (V_{PE}/V_{EA} = 60/1) as a colorless liquid**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.29 (s, 3H), 1.43 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 50.5, 47.1, 30.1. **IR** (neat) 2963, 2928, 2853, 2361, 1366, 1327, 1146, 1078, 716, 604, 592 cm^{-1}. **HRMS** (EI) calcd for $C_5H_{12}O_2S_3$ 199.9999, found 199.9997.



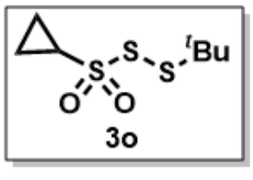
3m

A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg), sodium ethanesulfinate (1 equivalent, 1 mmol, 11.6 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 8 W) in a paralleled reactor. **3m** (19.3 mg, 90%) was obtained through column chromatography (V_{PE}/V_{EA} = 60/1) as a yellow oily liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.41-3.35 (q, *J* = 7.4 Hz, 3H), 1.48-1.44 (dt, *J* = 10.0, 3.2 Hz, 2H), 1.42 (s, *J* = 3.5 Hz, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 54.1, 50.2, 30.0, 8.2. **IR** (neat) 2965, 2940, 2924, 1472, 1456, 1366, 1323, 1126, 700 cm^{-1}. **HRMS** (EI) Calcd for $C_6H_{14}O_2S_3$ 214.0156, found 214.0152.



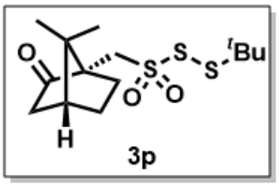
3n

A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg), propane-2-sulfinic acid (1 equivalent, 1 mmol, 10.8 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 6 W) in a paralleled reactor. **3n** (20.6 mg, 90%) was obtained through column chromatography (V_{PE}/V_{EA} = 60/1) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.58-3.51 (dt, *J* = 13.7, 6.8 Hz, 1H), 1.47 (s, 3H), 1.45 (s, 3H), 1.41 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 61.9, 50.1, 29.9, 16.5. **IR** (neat) 2968, 2938, 1468, 1458, 1368, 1323, 1256, 1161, 1144, 1126, 716, 664, 588 cm^{-1}. **HRMS** (EI) Calcd for $C_7H_{16}O_2S_3$ 228.0312, found 228.0313.



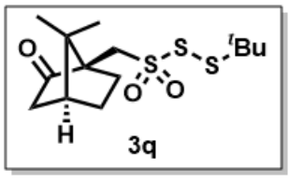
3o

A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg), cyclopropanesulfinic acid (1 equivalent, 1 mmol, 17.0 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 5 W) in a paralleled reactor. **3o** (25.6 mg, 88%) was obtained through column chromatography (V_{PE}/V_{EA} = 50/1) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.97-2.91 (tt, *J* = 7.9, 4.7 Hz, 1H), 1.42 (s, 9H), 1.41-1.40 (dd, *J* = 4.9, 2.0 Hz, 2H), 1.16-1.10 (qd, *J* = 6.2, 1.3 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 50.1, 38.1, 30.0, 6.8. **IR** (neat) 3021, 2965, 2940, 2922, 2867, 2864, 1456, 1323, 1226, 876, 683, 583 cm^{-1}. **HRMS** (EI) Calcd for $C_7H_{14}O_2S_3$ 226.0156, found 226.0156.



3p

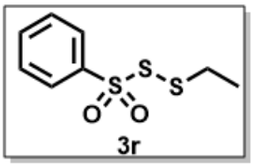
A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg), ((1S,4R)-7,7-dimethyl-2-oxobicyclo [2.2.1] heptan-1-yl) methanesulfinic acid (1 equivalent, 1 mmol, 21.7 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 5 h under blue LEDs (460 nm, 8 W) in a paralleled reactor. **3p** (21.2 mg, 63%) was obtained through column chromatography (V_{PE}/V_{EA} = 20/1) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.95-3.92 (d, *J* = 14.6 Hz, 1H), 3.32-3.28 (d, *J* = 14.6 Hz, 1H), 2.54-2.37 (m, 2H), 2.12– 2.02 (m, 2H), 1.97-1.93 (d, *J* = 18.5 Hz, 1H), 1.79-1.72(m, *J* = 13.9, 9.3, 4.6 Hz, 1H), 1.46 (dd, *J* = 9.1, 3.6 Hz, 1H), 1.42 (s, 9H), 1.13 (s, 3H), 0.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.8, 59.5, 57.5, 50.3, 48.1, 42.7, 42.5, 30.1, 26.9, 25.2, 19.9, 19.7. **IR** (neat) 2963, 2922, 2895, 2257, 1746, 1366, 1327, 1161, 1128, 1051, 735, 519 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{14}H_{24}O_3S_3Na$ $[M+Na]^+$: Calcd 359.0785, Found 359.0804.



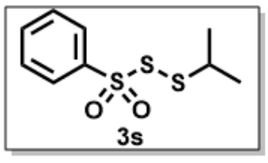
3q

A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent,1 mmol, 24.2 mg), ((1R,4S)-7,7-dimethyl-2-oxobicyclo [2.2.1] heptan-1-yl) methanesulfinic acid (1 equivalent, 1 mmol, 21.7 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 5 h under blue LEDs (460 nm, 7 W) in a paralleled reactor. **3q** (17.2 mg, 51%) was obtained through column chromatography (V_{PE}/V_{EA} = 20/1) as a colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.96-3.91 (d, *J* = 14.6 Hz, 1H), 3.32-3.27 (d, *J* = 14.6 Hz, 1H), 2.55 -2.36 (m, 2H), 2.13-2.01 (m, 2H), 1.98-1.92 (d, *J* = 18.5 Hz, 1H), 1.75 (m, *J* = 13.6, 9.2, 4.3 Hz, 1H), 1.47 (d, *J* = 3.6 Hz, 1H), 1.42 (s, 8H), 1.13 (s, 3H), 0.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.8, 59.5, 57.5, 50.3, 48.1, 42.7, 42.5, 30.1, 26.9, 25.2, 19.9, 19.7. **IR** (neat) 2963, 2941, 2897,

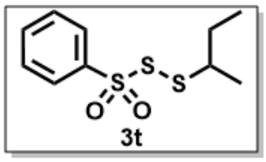
2257, 1748, 1719, 1456, 1325, 1161, 1128, 754, 731, 596, 557 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{14}H_{24}O_3S_3Na$ $[M+Na]^+$: Calcd 359.0785, Found 359.0804.



A mixture of 1,4-diethyltetrasulfane (1 equivalent, 1 mmol, 15.7 mg), benzenesulfinic acid (1 equivalent, 1 mmol, 14.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 7 W) in a paralleled reactor. **3r** (10.1 mg, 43%) was obtained through column chromatography (V_{hexane}/V_{EA} = 20/1) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98-7.93(m, 2H), 7.68- 7.55(m, 3H), 3.05-2.87 (m, 2H), 1.36-1.27 (m, 3H). **^{13}C NMR** 101 MHz, $CDCl_3$) δ 142.4, 134.0, 129.1, 127.9, 33.7, 13.9. **IR** (neat) 3037, 2968, 2932, 2359, 1449, 1327, 1144, 1078, 716, 685, 602, 592, 538 cm^{-1}. **HRMS** (EI) Calcd for $C_8H_{10}O_2S_3$ 233.9843, found 233.9840.

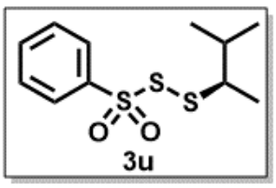


A mixture of 1,4-diisopropyltetrasulfane (1 equivalent, 1 mmol, 21.4 mg), benzenesulfinic acid (1 equivalent, 1 mmol, 14.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 5 h under blue LEDs (460 nm, 6 W) in a paralleled reactor. **3s** (16.1 mg, 65%) was obtained through column chromatography (PE→V_{PE}/V_{EA} = 20/1) as a colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.97-7.94 (m, 2H), 7.66 -7.54 (m, 3H), 3.29-3.20 (dt, *J* = 16.3, 6.8 Hz, 1H), 1.33 (s, 3H), 1.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.6, 134.0, 129.1, 127.9, 42.7, 22.2. **IR** (neat) 3067, 2965, 2928, 2866, 1458, 1387, 1366, 1323, 1142, 1076, 754, 739, 716, 685, 588, 536 cm^{-1}. **HRMS** (EI) Calcd for $C_9H_{12}O_2S_3$ 247.9999, found 247.9995.



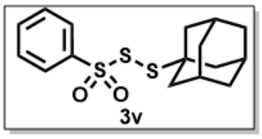
3t

A mixture of 1,4-di-sec-butyltetrasulfane (1 equivalent, 1 mmol, 24.2 mg), benzene sulfinicacid (1 equivalent,1 mmol,14.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 5 h under blue LEDs (460 nm, 5 W) in a paralleled reactor. **3t** (19.7 mg, 75%) was obtained through column chromatography (V_{PE}/V_{EA} = 50/1) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.94 (m, 2H), 7.68-7.55 (dt, *J* = 15.2, 7.4 Hz, 3H), 3.07 – 2.98 (m, 1H), 1.76-1.50 (m, 1H), 1.30 (d, *J* = 6.8 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.6, 133.9, 129.1, 127.9, 49.5, 28.8, 19.6, 11.2. **IR** (neat) 3067, 2965, 2924, 2874, 1458, 1447, 1325, 1140, 1076, 752, 714, 683 cm^{-1}. **HRMS** (EI) Calcd for $C_{10}H_{14}O_2S_3$ 262.0156, found 262.0151.

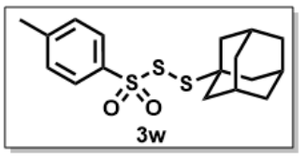


3u

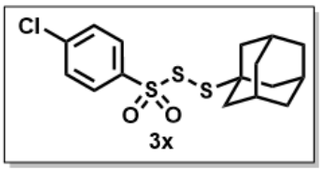
A mixture of 1,4-bis(3-methylbutan-2-yl) tetrasulfane (1 equivalent, 1 mmol, 27.7 mg), benzenesulfinic acid (1 equivalent, 1 mmol, 14.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 5 h under blue LEDs (460 nm, 8 W) in a paralleled reactor. **3u** (21.0 mg, 75%) was obtained through column chromatography (V_{PE}/V_{EA} = 100/1) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98-7.95 (m, 2H), 7.71- 7.64 (m, 1H), 7.61-7.55 (m, *J* = 7.2, 1.9 Hz, 2H), 3.09-3.02 (m, *J* = 7.0, 4.8 Hz, 1H), 12.01-1.93 (m, *J* = 13.6, 6.8, 4.7 Hz, 3H), 1.45-1.21 (m, 3H), 1.02- 0.83 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 133.9, 129.1, 128.0, 77.3, 77.0, 76.6, 54.8, 32.1, 19.9, 17.9, 16.0. **IR** (neat) 3067, 2963, 2909, 2872, 1447, 1325, 1310, 1140, 1076, 752, 714, 683, 584, 532 cm^{-1}. **HRMS** (EI) Calcd for $C_{11}H_{16}O_2S_3$ 276.0312, found 276.0313.



A mixture of 1,4-di((3S,5S,7S)-adamantan-1-yl) tetrasulfane (1 equivalent, 1 mmol, 39.8 mg), benzenesulfinic acid (3 equivalent, 3 mmol, 42.6 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$] (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 5 W) in a paralleled reactor. **3v** (62.0 mg, 91%) was obtained through column chromatography (V_{PE}/V_{EA} = 100/1) as a white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.94-7.91 (d, *J* = 7.8 Hz, 2H), 7.67-7.65 (dt, *J* = 27.1, 7.4 Hz, 3H), 2.10 (s, 3H), 1.87 (s,6H), 1.72- 1.62 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 133.8, 129.0, 127.8, 51.9, 42.6, 35.7, 30.0. **IR** (neat) 3061, 2907, 2851, 1582, 1449, 1323, 1265, 1142, 1076, 748, 714, 683, 641, 536 cm^{-1}. **HRMS** (EI) Calcd for $C_{16}H_{20}O_2S_3$ 340.0625, found 340.0618.

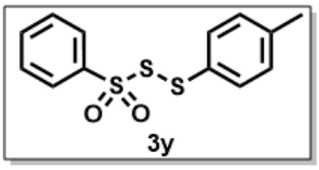


A mixture of 1,4-di((3S,5S,7S)-adamantan-1-yl) tetrasulfane (1 equivalent, 1 mmol, 39.8 mg),4-methylbenzenesulfinic acid (3 equivalent, 3 mmol, 46.8 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$] (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4.5 h under blue LEDs (460 nm, 5 W) in a paralleled reactor. **3w** (49.2 mg, 69%) was obtained through column chromatography (V_{PE}/V_{EA} = 100/1) as a white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.94-7.79 (m, 2H), 7.42-7.33(t, *J* = 14.5 Hz, 2H), 2.49- 2.45 (m, 3H), 2.10 (s, 3H), 1.88 -1.80 (m, 6H), 1.72-1.63 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.9, 140.3, 129.6, 127.9, 51.8, 42.6, 35.7, 30.1, 21.6. **IR** (neat) 2914, 2853, 1449, 1325, 1265, 1142, 812, 748, 702, 652, 593 cm^{-1}. **HRMS** (EI) Calcd for $C_{17}H_{22}O_2S_3$ 354.0782, found 354.0774.



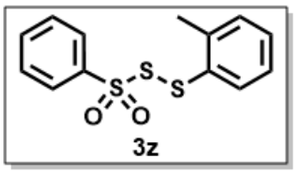
3x

A mixture of 1,4-di((3S,5S,7S)-adamantan-1-yl) tetrasulfane (1 equivalent, 1 mmol, 39.8 mg), 4-chlorobenzenesulfinic acid (1 equivalent, 1 mmol, 17.7 mg), [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]·PF_6] (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4.3 h under blue LEDs (460 nm, 8 W) in a paralleled reactor. **3x** (34.4 mg, 92%) was obtained through column chromatography (V_{PE}/V_{EA} = 100/1) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91-7.84 (m, 2H), 7.56-7.51 (m, 2H), 2.12 (s, 3H), 1.89-1.88 (d, *J* = 2.7 Hz, 6H), 1.72-1.65 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4, 140.5, 129.3, 129.2, 52.1, 42.6, 35.7, 30.1. **IR** (neat) 3021, 2905, 2851, 1474, 1395, 1331, 1267, 1144, 1090, 1076, 752, 606, 559 cm^{-1}. **HRMS** (EI) Calcd for $C_{16}H_{19}ClO_2S_3$ 374.0236, found 374.0241.



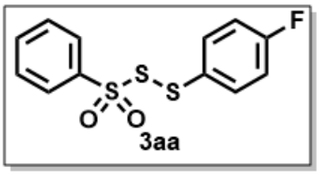
3y

A mixture of 1,4-di-p-tolyltetrasulfane (1 equivalent, 1 mmol, 31.04 mg), benzenesulfinic acid (1 equivalent, 1mmol, 14.2 mg), [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]·PF_6] (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 5 h under blue LEDs (460 nm, 6 W) in a paralleled reactor. **3y** (21.1 mg, 71%) was obtained through column chromatography (V_{PE}/V_{EA} = 50/1) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59-7.56 (m, 3H), 7.45-7.41 (m, 2H), 7.26-7.22 (dd, *J* = 11.7, 5.3 Hz, 2H), 7.15-7.13 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 142.1, 136.4, 133.5, 130.2, 128.7, 127.5, 124.4, 21.4. **IR** (neat) 3061, 2963, 2922, 2859, 1971, 1911, 1447, 1323, 1142, 716, 683, 588, 536 cm^{-1}. **HRMS** (EI) Calcd for $C_{13}H_{12}O_2S_3$ 295.9999, found 295.9995.



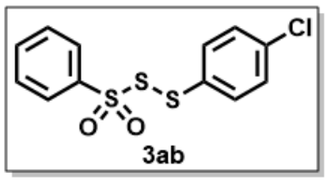
3z

A mixture of 1,4-di-o-tolyltetrasulfane (1 equivalent, 1 mmol, 31.1 mg), benzenesulfinic acid (1 equivalent, 1 mmol, 14.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 5.5 h under blue LEDs (460 nm, 6 W) in a paralleled reactor. **3z** (19.9 mg, 67%) was obtained through column chromatography (V_{PE}/V_{EA} = 10/1) as a yellow oily liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.54 (m, 3H), 7.44-7.33 (m, 4H), 7.23-7.22 (d, *J* = 7.5 Hz, 1H), 7.18-7.14 (t, *J* = 7.6 Hz, 1H), 2.14 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.2, 143.4, 138.3, 133.5, 131.8, 130.9, 128.8, 127.4, 127.1, 126.9, 20.5. **IR** (neat) 3061, 2970, 2928, 1582, 1470, 1447, 1325, 1144, 1078, 752, 716, 685, 590, 536 cm^{-1}. **HRMS** (EI) Calcd for $C_{13}H_{12}O_2S_3$ 295.9999, found 296.0003.



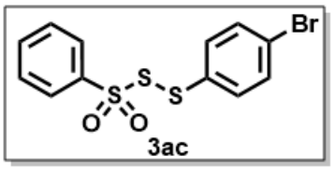
3aa

A mixture of 1,4-bis(4-fluorophenyl) tetrasulfane (1 equivalent, 1 mmol, 31.9 mg), benzenesulfinic acid (1 equivalent, 1 mmol, 14.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 5 h under blue LEDs (460 nm, 6 W) in a paralleled reactor. **3aa** (22.3 mg, 74%) was obtained through column chromatography (V_{PE}/V_{EA} = 20/1) as a yellow oily liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.57 (m, 3H), 7.46-7.43(m, 2H), 7.37-7.32 (m, 2H), 7.06-7.01 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.7, 163.7, 142.6, 138.85-138.78 (d, *J* = 9.1 Hz), 133.7, 128.8, 127.5, 123.36-123.33 (d, *J* = 3.4 Hz), 116.87-116.70 (d, *J* = 22.3 Hz).**^{19}F NMR** (376 MHz, $CDCl_3$) δ -107.22 (s). **IR** (neat) 3096, 3069, 1587, 1325, 1233, 1144, 833, 716, 685, 590 cm^{-1}. **HRMS** (EI) Calcd for $C_{12}H_9FO_2S_3$ 299.9749, found 299.9744.



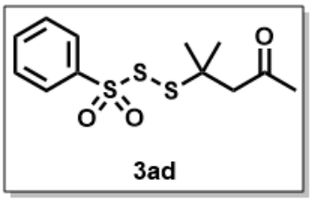
3ab

A mixture of 1,4-bis(4-chlorophenyl) tetrasulfane (1 equivalent, 1 mmol, 35.2 mg), benzenesulfinic acid (1 equivalent, 1 mmol, 14.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 6 W) in a paralleled reactor. **3ab** (22.4 mg, 71%) was obtained through column chromatography (PE→V_{PE}/V_{EA} = 20/1) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62-7.58(m, 3H), 7.47-7.43 (m, 2H), 7.33-7.27 (m, 4H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.8, 138.2, 137.6, 133.8, 129.7, 128.9, 127.5, 126.3. **IR** (neat) 3031, 2963, 2924, 2857, 1609, 1468, 1346, 1148, 1096, 1005, 791, 770, 621, 577, 511 cm^{-1}. **HRMS** (EI) Calcd for $C_{12}H_9ClO_2S_3$ 315.9453, found 315.9448.

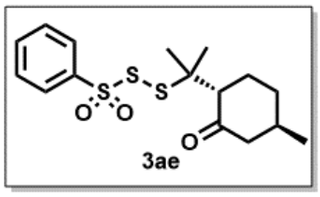


3ac

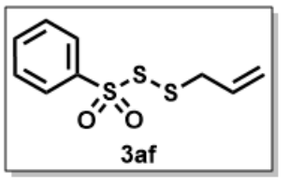
A mixture of 1,4-bis(4-bromophenyl) tetrasulfane (1 equivalent, 1 mmol, 44.0 mg), benzenesulfinic acid (1 equivalent, 1 mmol, 14.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 3 h under blue LEDs (460 nm, 6 W) in a paralleled reactor. **4ac** (22.7 mg, 63%) was obtained through column chromatography (V_{PE}/V_{EA} = 40/1) as a white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.66-7.55 (m, 1H), 7.52-7.41 (m, 1H), 7.21 (d, J = 8.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.8, 137.8, 133.8, 132.7, 128.9, 127.5, 126.9, 126.7. **IR** (neat) 3031, 2955,2924, 2853, 1560, 1472, 1447, 1327, 1144, 1009, 716, 683, 590, 536, 515 cm^{-1}. **HRMS** (EI) Calcd for $C_{12}H_9BrO_2S_3$ 359.8948, found 359.8954.



A mixture of 4,4'-tetrasulfanediylbis(4-methylpentan-2-one) (1 equivalent, 1 mmol, 32.7 mg), benzenesulfinic acid (1 equivalent, 1 mmol, 14.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 5 h under blue LEDs (460 nm, 7 W) in a paralleled reactor. **3ad** (13.8 mg, 48%) was obtained through column chromatography (V_{PE}/V_{EA} = 5/1) as a yellow oily liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90-7.88 (d, *J* = 7.6 Hz, 2H), 7.65-7.54 (m, 3H), 2.90 (s, 2H), 2.17 (s, 3H), 1.48 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.5, 142.7, 134.0, 129.1, 127.8, 53.4, 50.5, 31.2, 27.6. **IR** (neat) 3014, 2941, 1713, 1447, 1364, 1323, 1140, 1076, 754, 714, 583, 532 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{12}H_{16}O_3S_3Na$ $[M+Na]^+$: Calcd 327.0159, Found 327.0189.



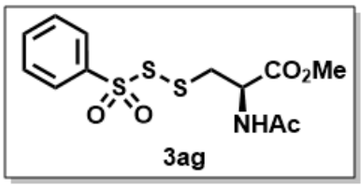
A mixture of 1,4-di-tert-butyltetrasulfane (1 equivalent, 1 mmol, 43.5 mg), benzenesulfinic acid (1 equivalent, 1 mmol, 14.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 8 W) in a paralleled reactor. **3ae**[9] (30.0 mg, 84%) was obtained through column chromatography (V_{PE}/V_{EA} = 50/1→2/1) as a colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.89-7.87 (m, 2H), 7.67-7.53(m, 3H), 2.88-2.83 (m, 1H), 2.39-2.31 (m, 2H), 1.97-1.85 (ddd, *J* = 16.7, 9.8, 6.3 Hz, 2H), 1.57-1.49 (m, 6H), 1.43 (s, 3H), 1.04-1.02 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.5, 142.7, 133.9, 127.8, 57.6, 54.3, 51.7, 36.4, 34.0, 29.6, 25.7, 25.6, 22.2.



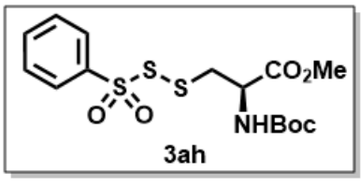
3af

A mixture of 1,4-diallyltetrasulfane (1 equivalent, 1 mmol, 21.1 mg), benzenesulfinic acid (1 equivalent, 1 mmol, 14.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL ethyl acetate was added and the mixture was stirred for 10 h under blue LEDs (460 nm, 6 W) in a paralleled reactor. **3af** (13.4 mg, 62%) was obtained through column chromatography (V_{PE}/V_{EA} = 60/1) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88-7.86 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.67 -7.62(m, 1H), 7.57-7.53(dd, *J* = 10.5, 4.7 Hz, 2H), 5.84-5.73 (m, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.34-5.31 (dd, *J* = 10.1, 0.5 Hz, 1H), 5.16-5.12 (dd, *J* = 17.1, 1.1 Hz, 2H), 3.81- 3.80(d, *J* = 7.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.2, 133.7, 129.0, 128.4, 124.63 (d, *J* = 8.0 Hz), 60.8. **IR** (neat) 3630, 3090, 2976, 2920, 1447, 1317, 1308, 1292, 1142, 1084, 689, 623, 532 cm^{-1}. **HRMS** (EI) Calcd for $C_9H_{10}O_2S_3$ 245.9843, found 245.9845.

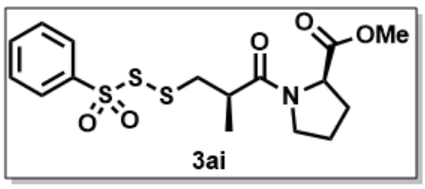
Flow reaction: A mixture of 1,4-diallyltetrasulfane (1 equivalent, 6 mmol, 1.26 g), benzenesulfinic acid (1 equivalent, 6 mmol, 0.85 g), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$ (1 mol%, 60 mg) was added into a 250 mL three-necked flask. The flask along with the micro cube were evacuated and filled with N_2 three times at room temperture. Then ethyl acetate (80 mL) was added and the mixture was stirred for 13 h under blue LEDs (430 nm, 118 W totally) in a paralleled reactor. The flask was equipped with rubber plugs, with inlet and outlet of micro tube, which was made of grass tubing (O.D. = 5 mm, I.D. = 2 mm, length = 2.88 m, volume = 4.45 mL). The solution was pumped by a pump (0.5 mL/min) into the micro tube, then returned to flask. This circulatory system was irradiated by Blue LEDs. After the reaction, ethyl acetate (10 mL) was pumped into the tube to flush out residual fluid. After evaporation of solvent, the residue was purified by column chromatography on silica gel (PE/EA= 60:1) and concentrated in vacuo to afford the required compound **3af** (69%, 1.020 g).



A mixture of dimethyl 3,3'-tetrasulfanediyl (2R,2'R) -bis (2 - acetamidopropanoate) (1 equivalent, 1 mmol, 41.7 mg), benzenesulfinic acid (1 equivalent, 1 mmol, 14.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL tetrahydrofuran was added and the mixture was stirred for 12 h under blue LEDs (460 nm, 6 W) in a paralleled reactor. **3ag** (15.3 mg, 44%) was obtained through column chromatography (V_{PE}/V_{EA} = 10/1→2/1) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.50(m, 2H), 7.37-7.33 (m, 2H), 7.29-7.27 (dd, *J* = 4.8, 3.7 Hz, 1H), 6.21-6.20 (d, *J* = 6.1 Hz, 1H), 4.90-4.88 (dt, *J* = 7.5, 4.9 Hz, 1H), 3.76 (s, 3H), 3.26-3.24 (m, 2H), 1.94 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.7, 169.7, 136.6, 129.2, 128.3, 127.5, 52.7, 51.6, 40.6, 23.0. **IR** (neat) 3059, 2967, 2938, 2866, 2361, 1468, 1368, 1321, 1144, 1125, 1051, 748, 662, 588 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{12}H_{16}NO_5S_3$ $[M+H]^+$: Calcd 350.0191, found 350.0183.



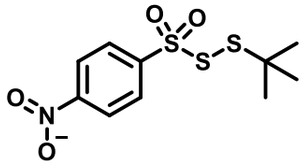
A mixture of dimethyl 3,3'-tetra-sulfanediyl(2R,2'R)-bis(2-((tert-butoxycarbonyl) amino) propanoate) (1 equivalent, 1 mmol, 52.7 mg), benzenesulfinic acid (1 equivalent, 1 mmol, 14.2 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6]$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL tetrahydrofuran was added and the mixture was stirred for 4 h under blue LEDs (460 nm, 7 W) in a paralleled reactor. **3ah** (16.1 mg, 40%) was obtained through column chromatography (V_{PE}/V_{EA} =100/1→ 5/1) as a colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54-7.51(dd, *J* = 5.3, 3.3 Hz, 2H), 7.37-7.28 (m, 3H), 5.31-5.29 (d, *J* = 7.2 Hz, 1H), 4.63 (s, 1H), 3.74 (s, 3H), 3.26-2.98 (m, 2H), 1.44 (s, 9H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.0, 154.9, 129.1, 128.3, 127.8, 127.4, 80.2, 52.8, 52.6, 40.9, 28.2. **IR** (neat) 3049, 2928, 1468, 1458, 1368, 1323, 1256, 1161, 1144, 1126, 716, 664, 588 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{15}H_{21}NO_6S_3Na$ $[M+Na]^+$: Calcd 430.0423, found 430.0421.



3ai

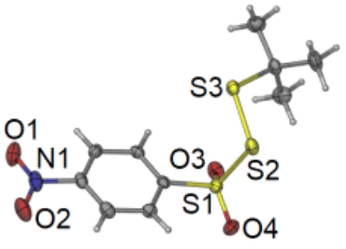
A mixture of dimethyl ((2R,2'R)-3,3'-tetrasulfanediylbis (2- methylpentanoyl)) (2'R)-di-D-prolinate (1 equivalent, 1 mmol, 52.5 mg), benzenesulfinic acid (3 equivalent, 3 mmol, 42.6 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]\cdot PF_6$ (1 mol%, 1.1 mg) were added into a reaction tube. The tube was evacuated and inflated with N_2 ballon for three times. Then 1 mL tetrahydrofuran was added and the mixture was stirred for 11 h under blue LEDs (460 nm, 6 W) in a paralleled reactor. **3ai** (26.5 mg, 33%) was obtained through column chromatography (V_{PE}/V_{EA} = 60/1) as a colorless liquid. **^{1}H NMR** (501 MHz, $CDCl_3$) δ 7.53-7.52 (m, 2H), 7.33-7.30 (t, *J* = 7.7 Hz, 2H), 7.23-7.20 (t, *J* = 7.4 Hz, 1H), 4.50-4.48 (dd, *J* = 8.6, 3.9 Hz, 1H), 3.71 (s, 3H), 3.55-3.50 (m, *J* = 9.4, 7.8, 5.0 Hz, 1H), 3.29-3.25 (dt, *J* = 9.6, 7.1 Hz, 1H), 3.14-3.10 (dd, *J* = 13.4, 8.6 Hz, 1H), 3.02-2.93 (m, 1H), 2.71-2.66 (m, 1H), 2.18-2.11 (m, *J* = 16.5, 9.6, 7.0 Hz, 1H), 2.03-1.88 (m, 3H), 1.21-1.19 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.2, 172.7, 137.3, 128.9, 127.4, 126.8, 58.5, 52.1, 46.5, 41.7, 37.3, 28.9, 24.7, 16.7. **IR** (neat) 3069, 2972, 2851, 2359, 1744,1641, 1433, 1327, 1196, 1172, 1146, 741, 689, 592 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{16}H_{22}NO_5S_3$ $[M+H]^+$: Calcd 404.0660, found 404.0652.

VIII. X-ray Crystallography Analysis



3j

≡



X-ray 3j
CDCC: 2105227

solvent system: DCM/hexane; method for crystal growth: volatilization at rt;

Datablock: exp_936

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Bond precision:       C-C = 0.0019 A              Wavelength=1.54184
Cell:          a=12.5171(1)     b=6.9957(1)      c=22.7966(2)
               alpha=90         beta=100.667(1)  gamma=90
Temperature: 100 K
                    Calculated                   Reported
Volume              1961.71(4)                   1961.71(4)
Space group         P 21/n                       P 1 21/n 1
Hall group          -P 2yn                       -P 2yn
Moiety formula      C20 H20 N 04, C2 F3 02       C20 H20 N 04, C2 F3 02
Sum formula         C22 H20 F3 N 06              C22 H20 F3 N 06
Mr                  451.39                       451.39
Dx, g cm-3          1.528                        1.528
Z                   4                            4
Mu (mm-1)           1.118                        1.118
F000                936.0                        936.0
F000'               939.65
h, k, lmax          15, 8, 28                    15, 8, 28
Nref                4004                         3978
Tmin, Tmax          0.741, 0.782                 0.014, 1.000
Tmin'               0.596
Correction method= # Reported T Limits: Tmin=0.014 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 0.994          Theta(max)= 74.395
R(reflections)= 0.0429( 3684)       wR2(reflections)= 0.1196( 3978)
S = 1.058              Npar= 321
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

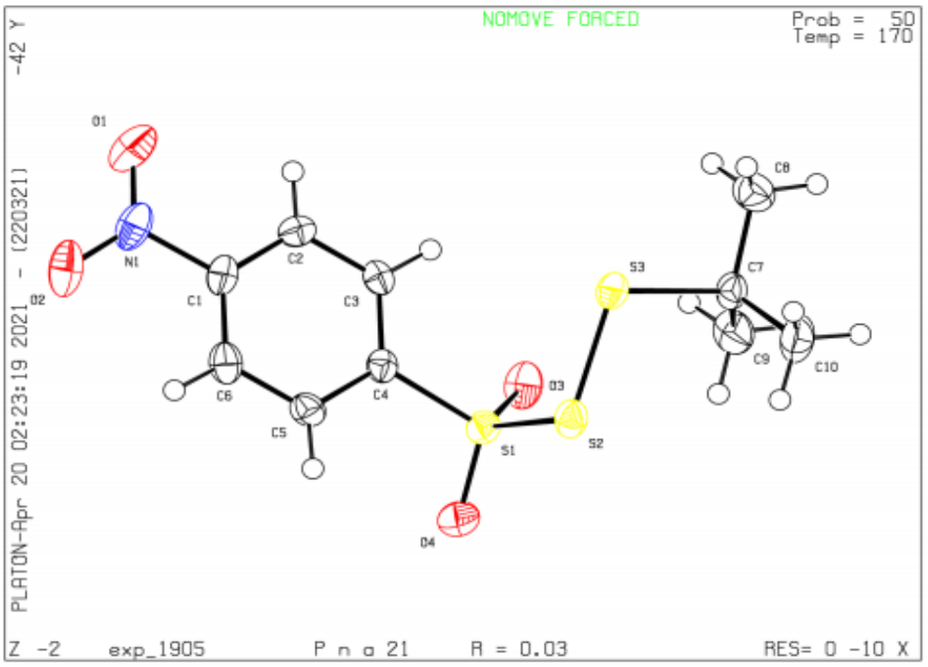
Alert level C

PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 3.2 Note
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 2.775 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 6 Report

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 7 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 6 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 1 Report
PLAT143_ALERT_4_G s.u. on c - Axis Small or Missing ..... 0.00020 Ang.
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records 4 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records 1 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records 1 Report
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records 1 Report
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F3' --C22 . 6.5 s.u.
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of C22 Check
PLAT300_ALERT_4_G Atom Site Occupancy of F1 Constrained at 0.5 Check

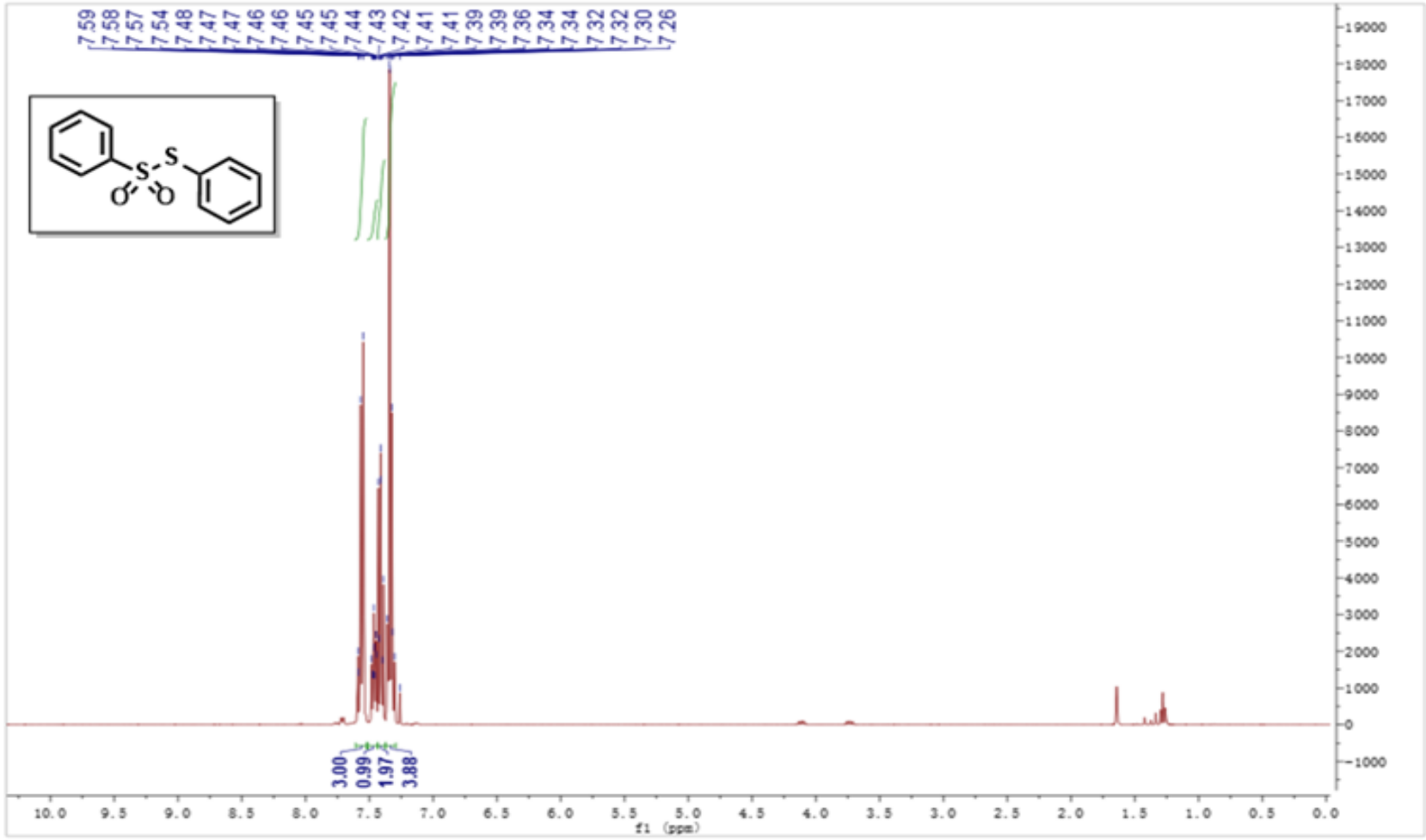
Datablock exp_1905 - ellipsoid plot



IX. References

1. Z. Wu, D. A. Pratt, *J. Am. Chem. Soc.,* 2020, **142,** 10284.
2. G. Barany, A. L. Schroll, A. W. Mott, D. A. Halsrud, *J. Org. Chem.,* 1983, **48,** 4750.
3. M. M. Cerda, M. D. Hammers, M. S. Earp, L. N. Zakharov, M. D. Pluth, *Org. Lett.,* 2017, **19,** 2314.
4. M. Arisawa, K. Tanaka, M. Yamaguchi, *Tetrahedron Lett.,* 2005, **46,** 4797.
5. E. Zysman-Colman, D. N. Harpp, *J. Org. Chem.,* 2003, **68,** 2487.
6. R. Kaur, A. Tiwari, M. Manish, I. K. Maurya, R. Bhatnagar, S. Singh, *J. Ethnopharmacol,* 2021, **264,** 113230.
7. P. Qian, Y. Deng, H. Mei, J. Han, J. Zhou, Y. Pan, *Org. Lett.,* 2017, **19,** 4798.
8. L. Cao, S.H. Luo, K. Jiang, Z. F. Hao, B. W. Wang, C. M. Pang, Z. Y. Wang , *Org. Lett.,* 2018, **20,** 4754.
9. Z. Wu, D. A. Pratt, *Angew. Chem., Int. Ed.,* 2021, **60,** 15598.

^{1}H NMR of By-product a



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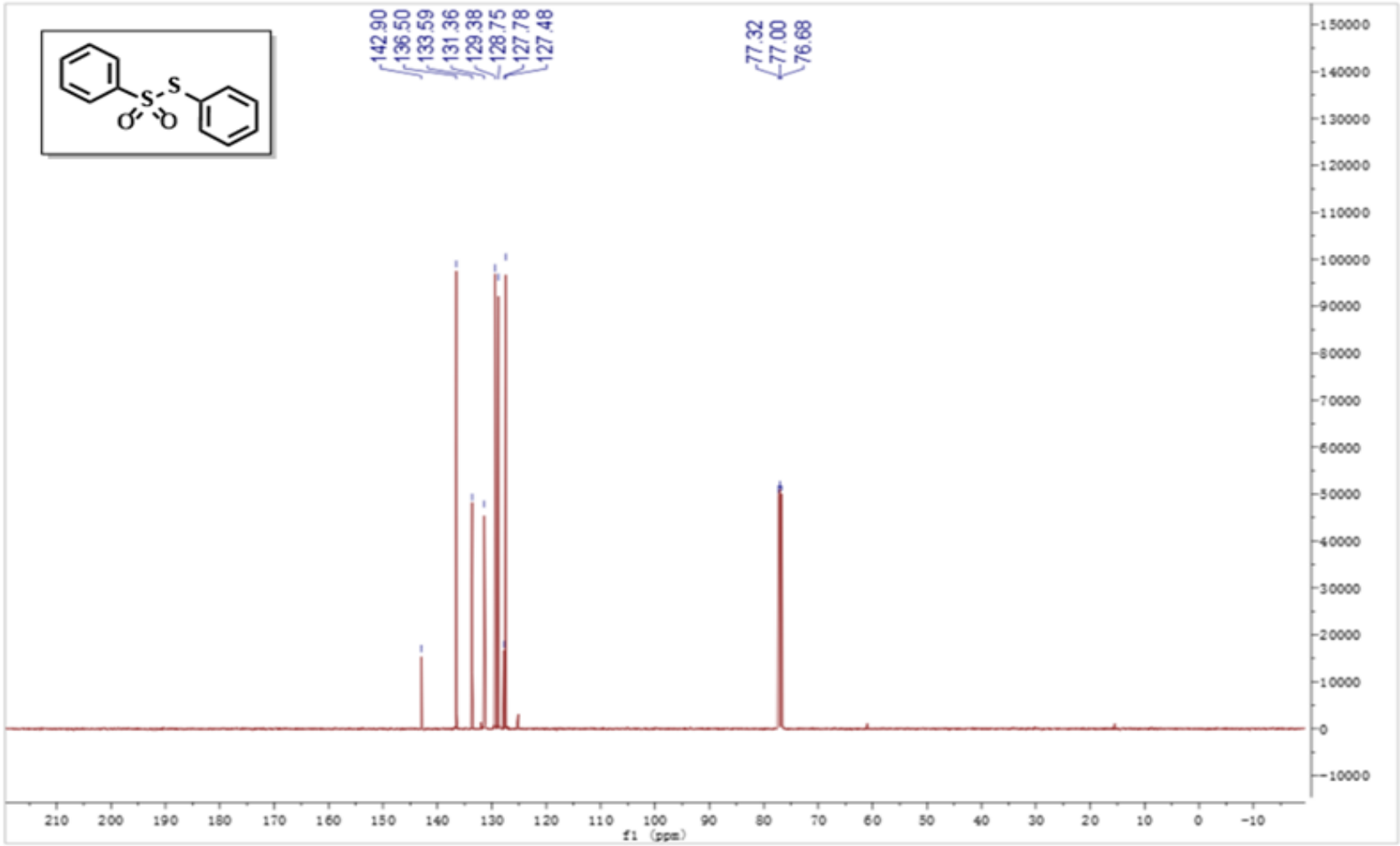

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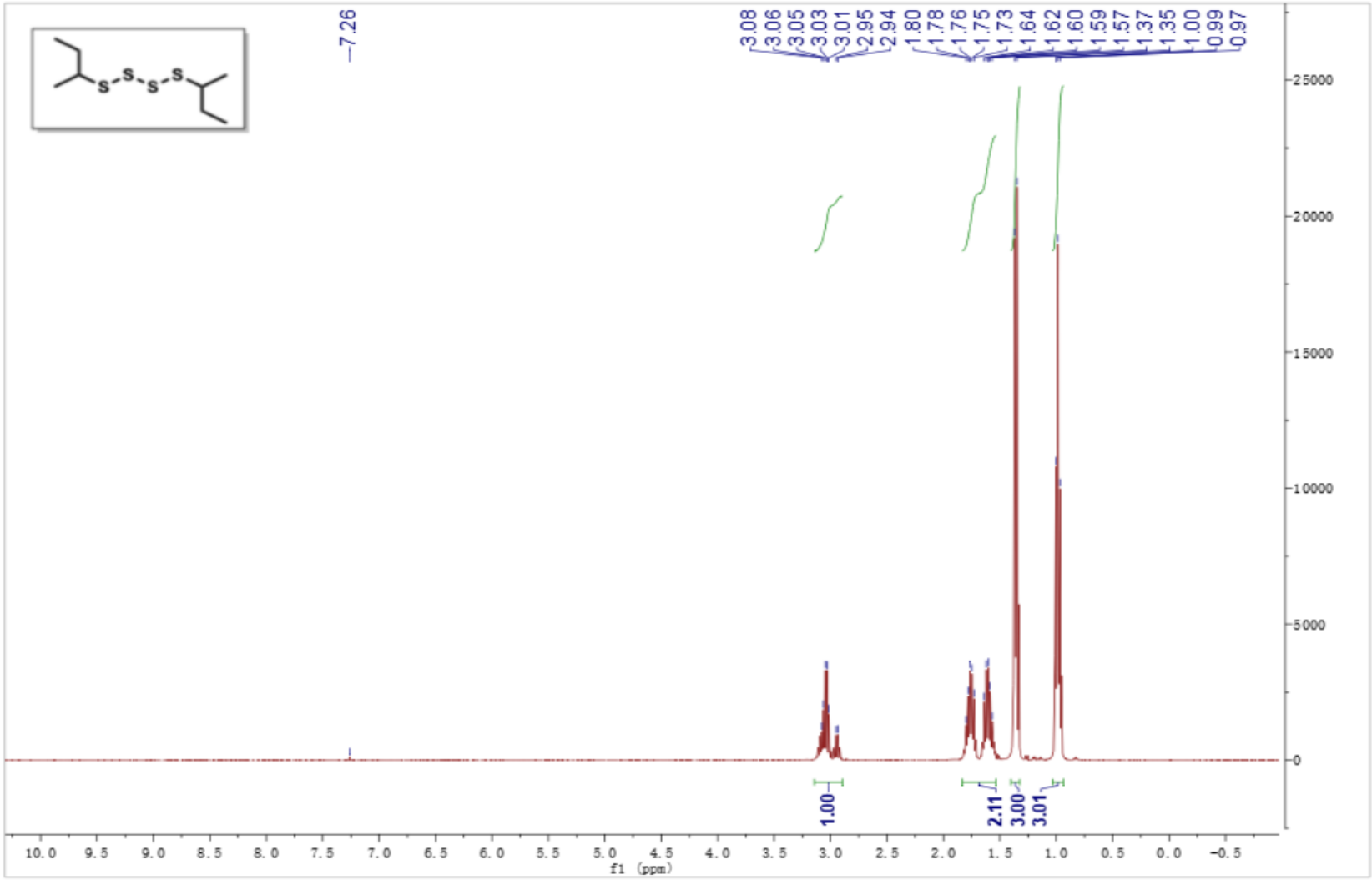
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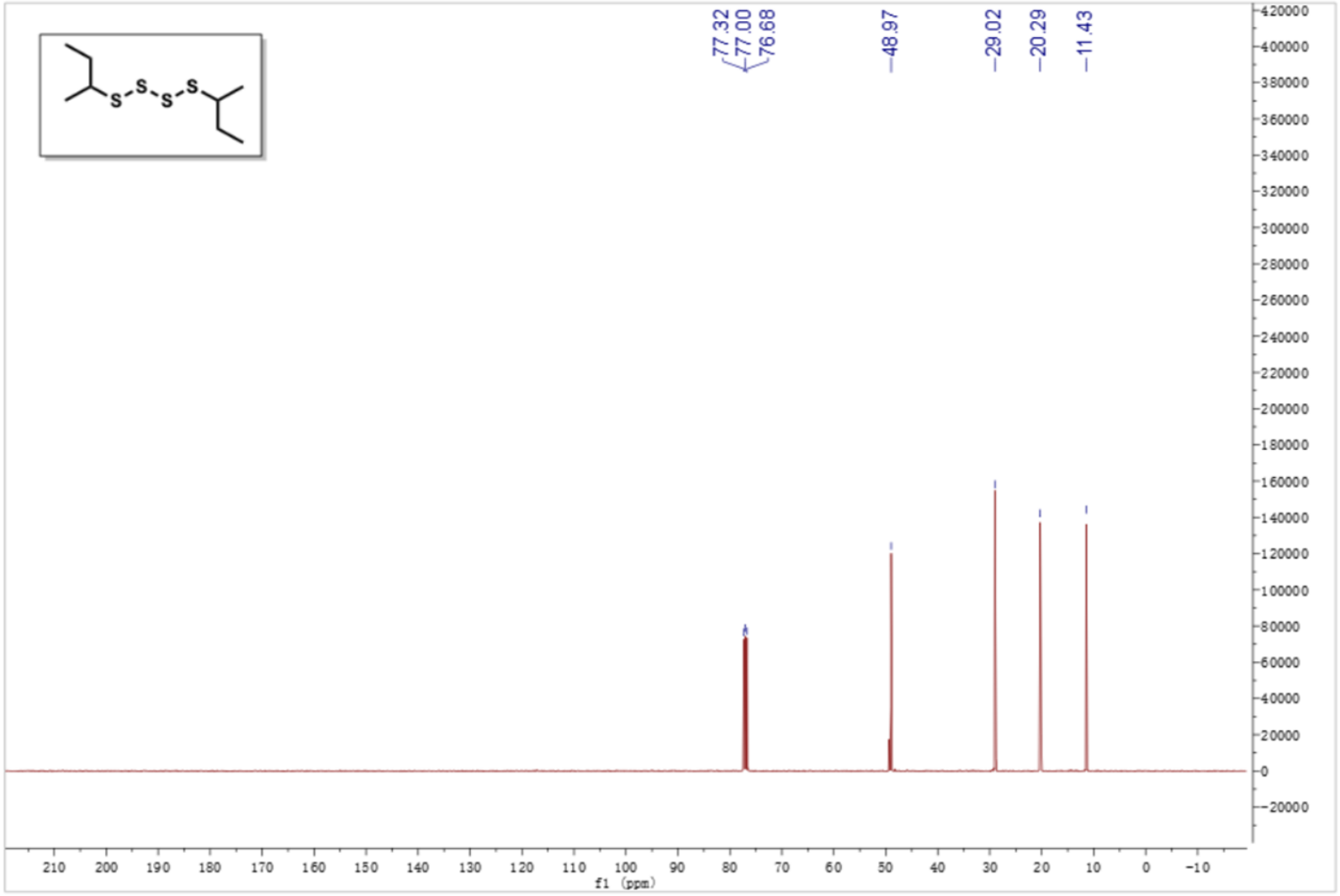
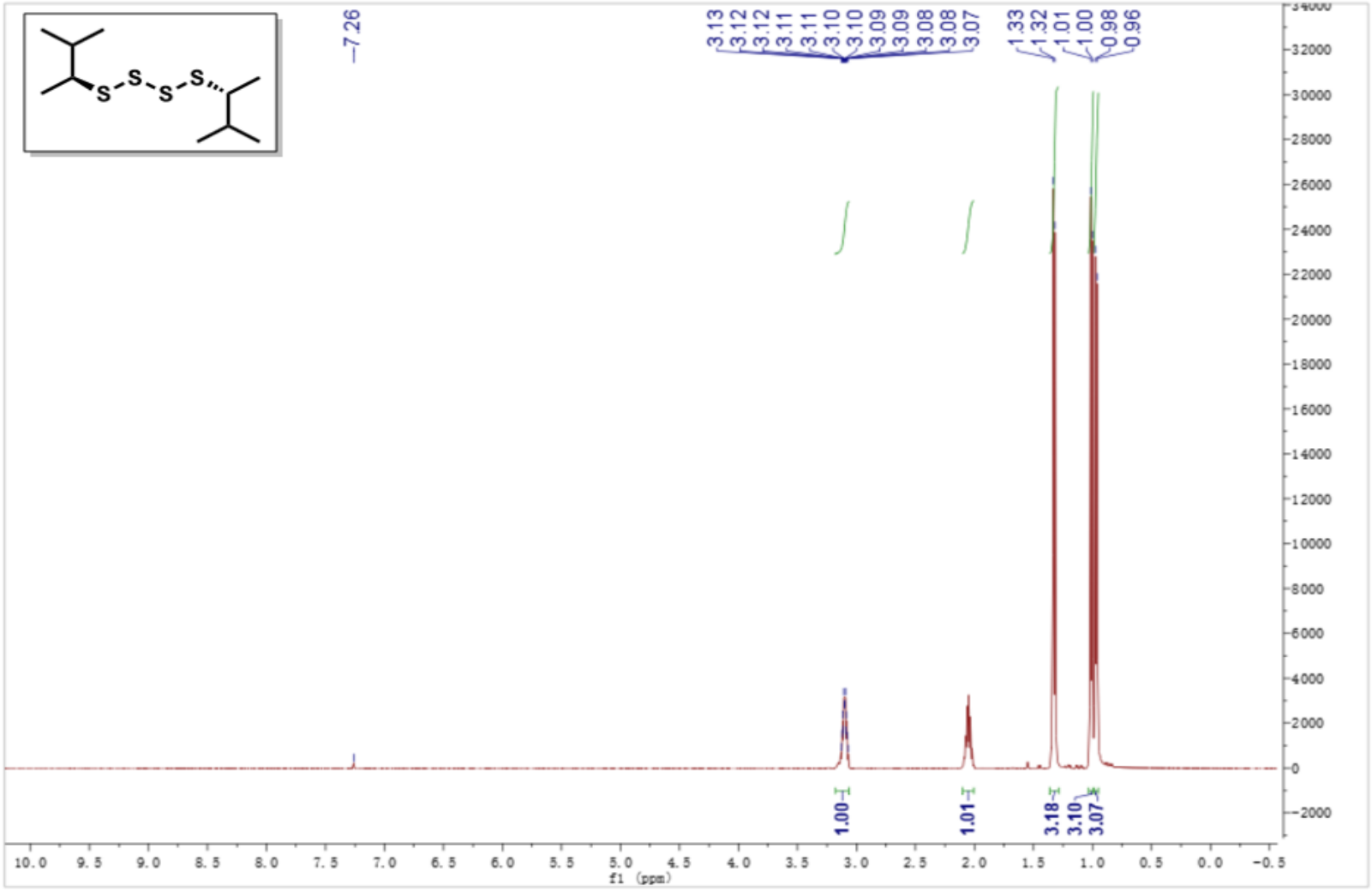
−0.5
f1 (ppm)

^{13}C NMR of 2d



^{1}H NMR of 2e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1.33
1.32
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1.01
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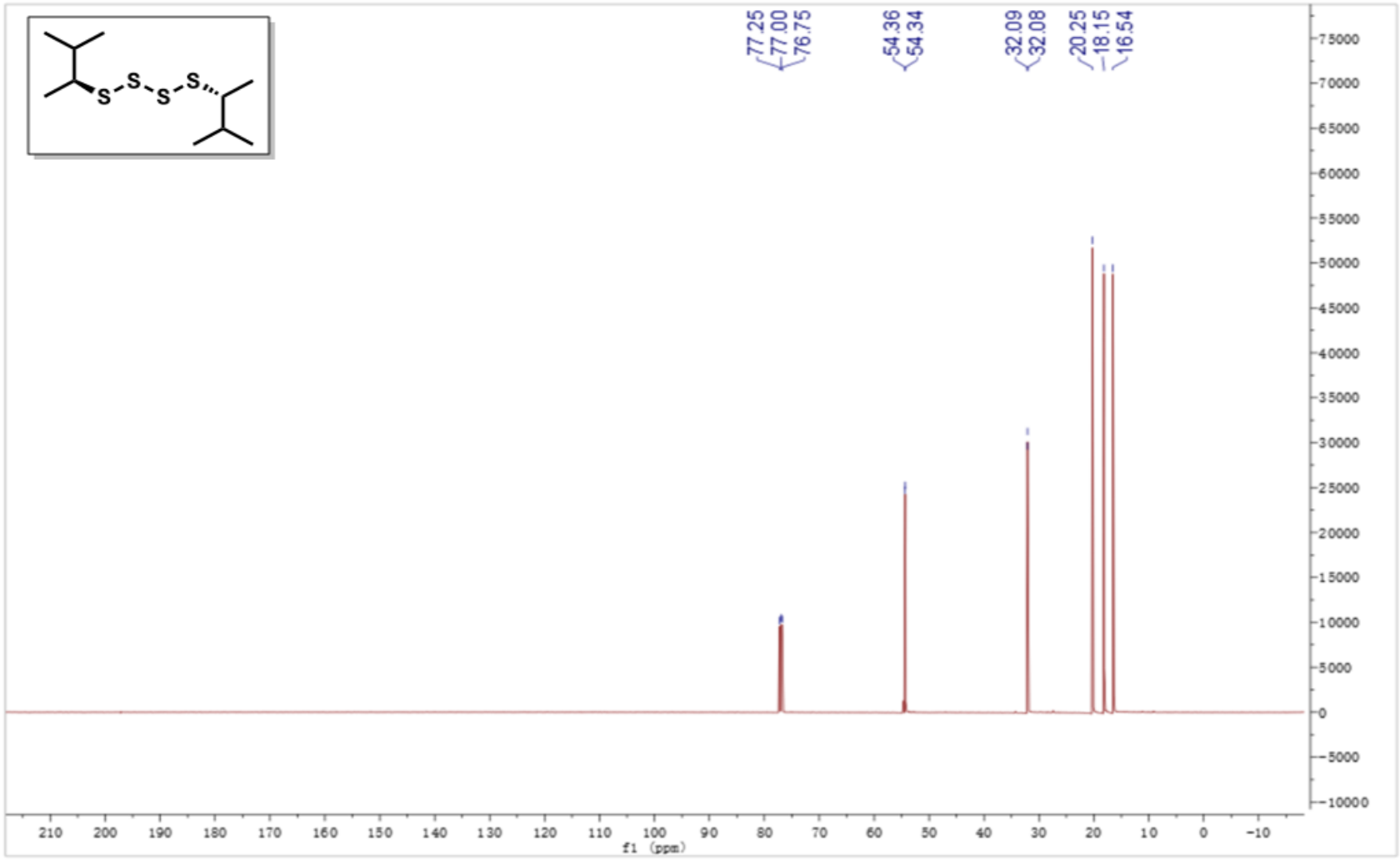
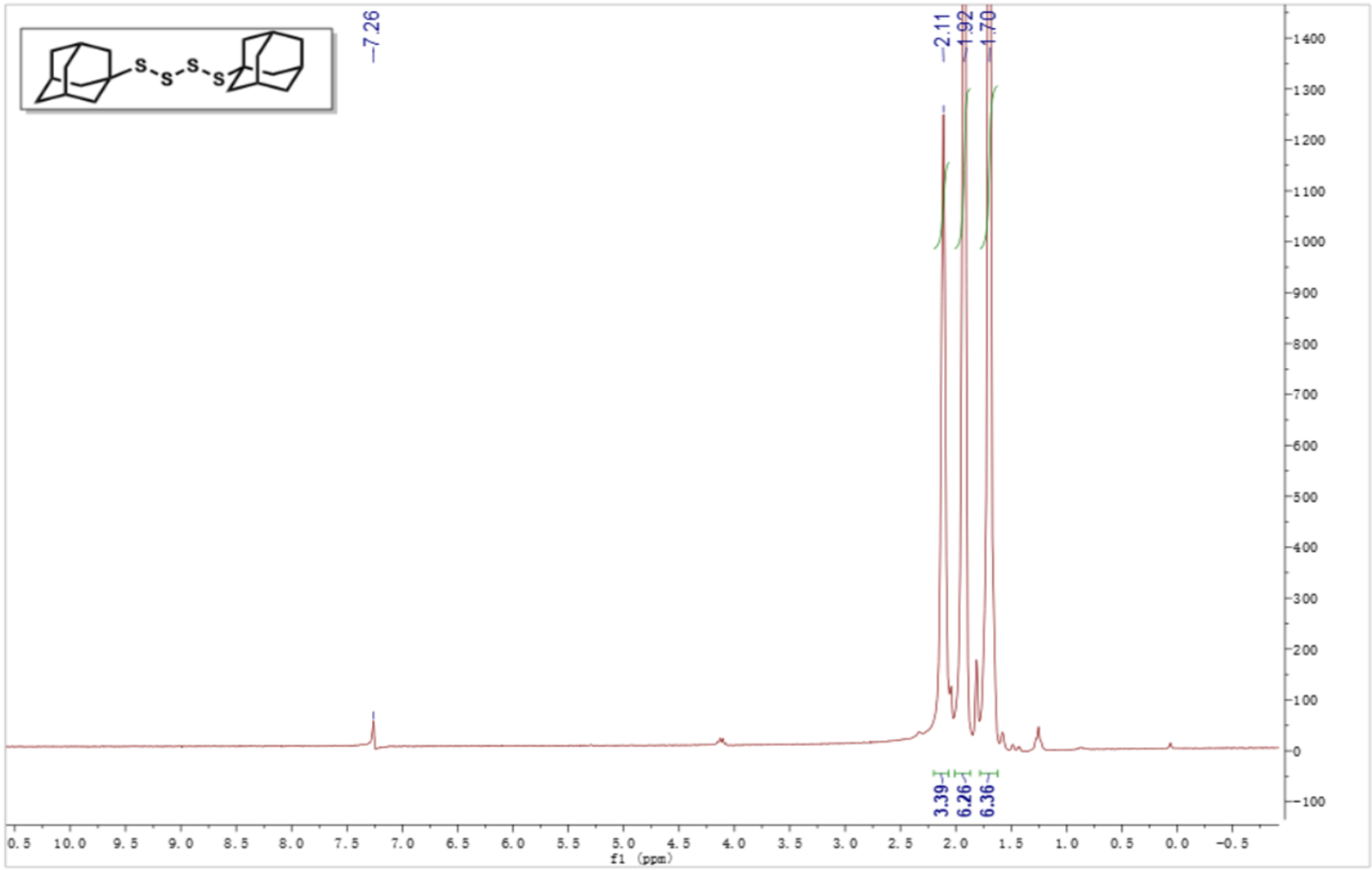
f1 (ppm)

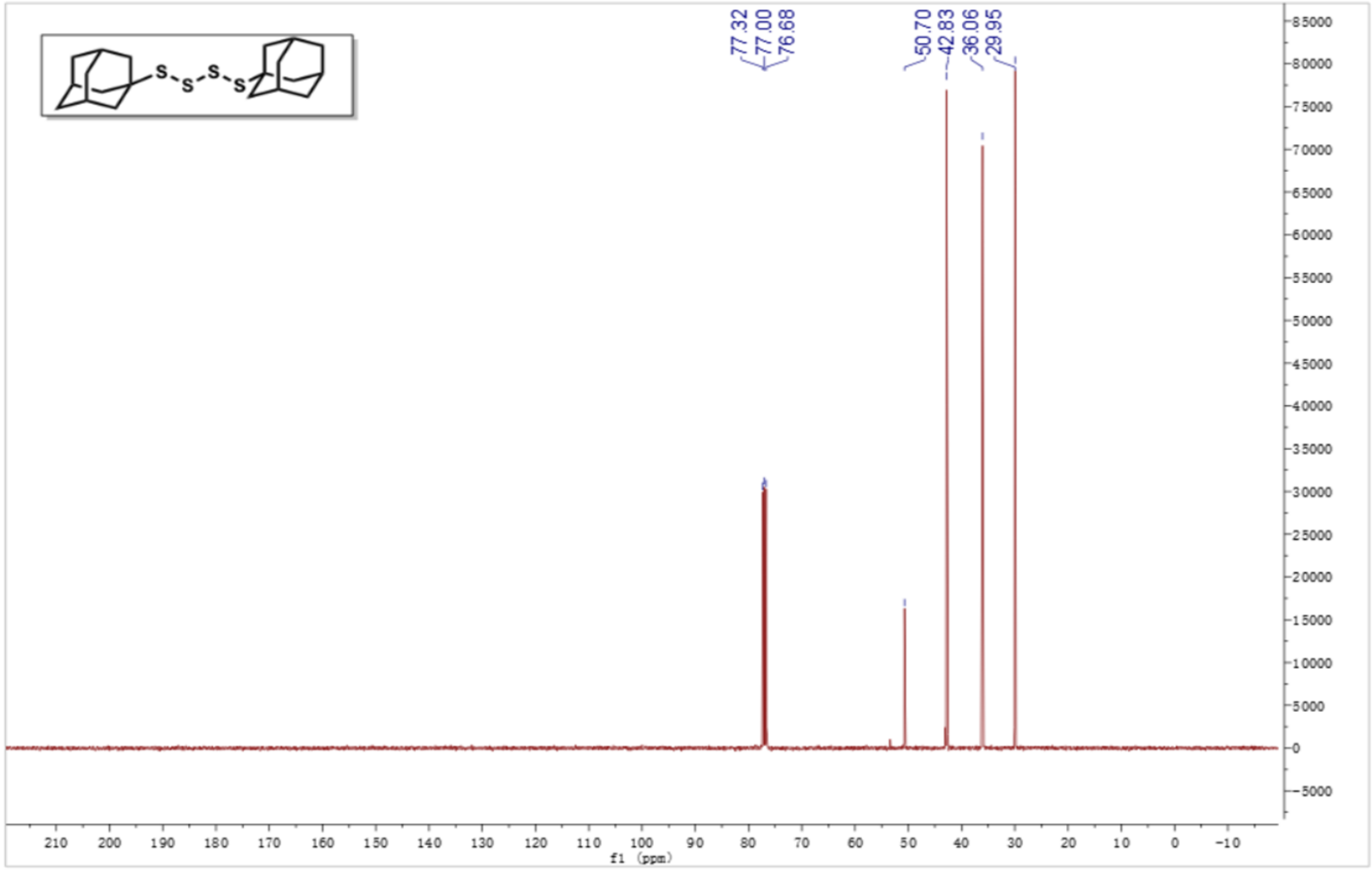
^{13}C NMR of 2e



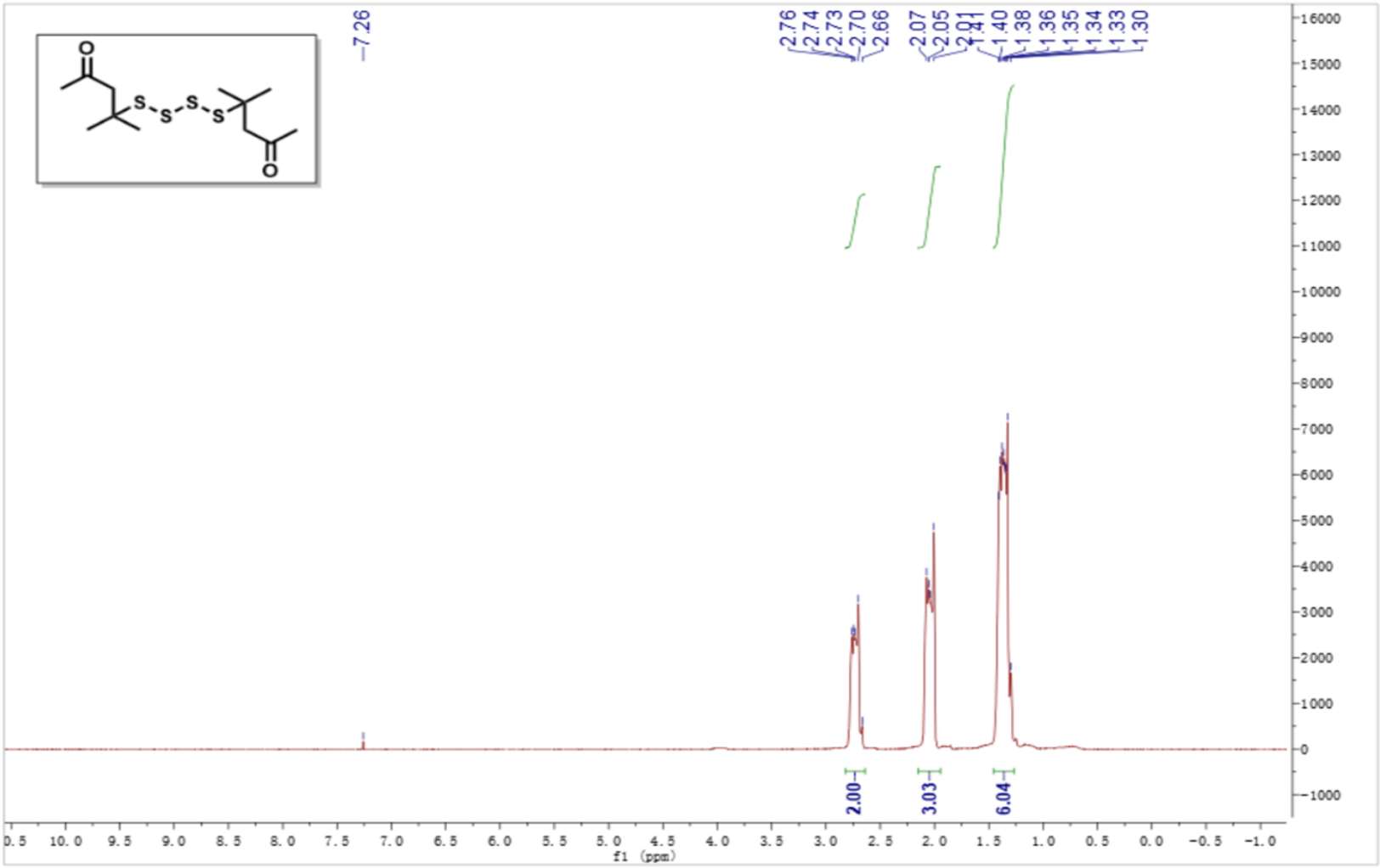
^{1}H NMR of 2f



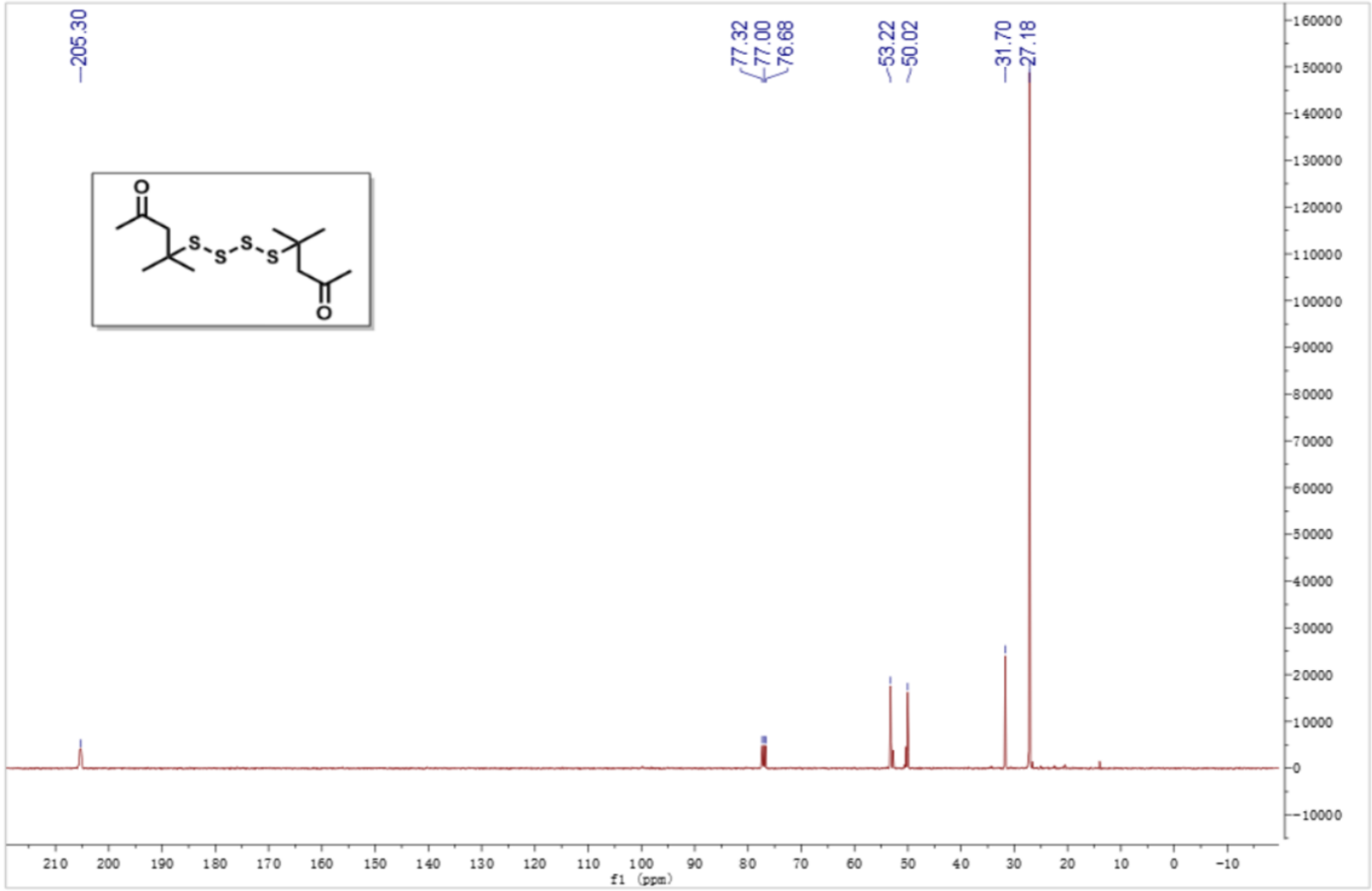
^{13}C NMR of 2f



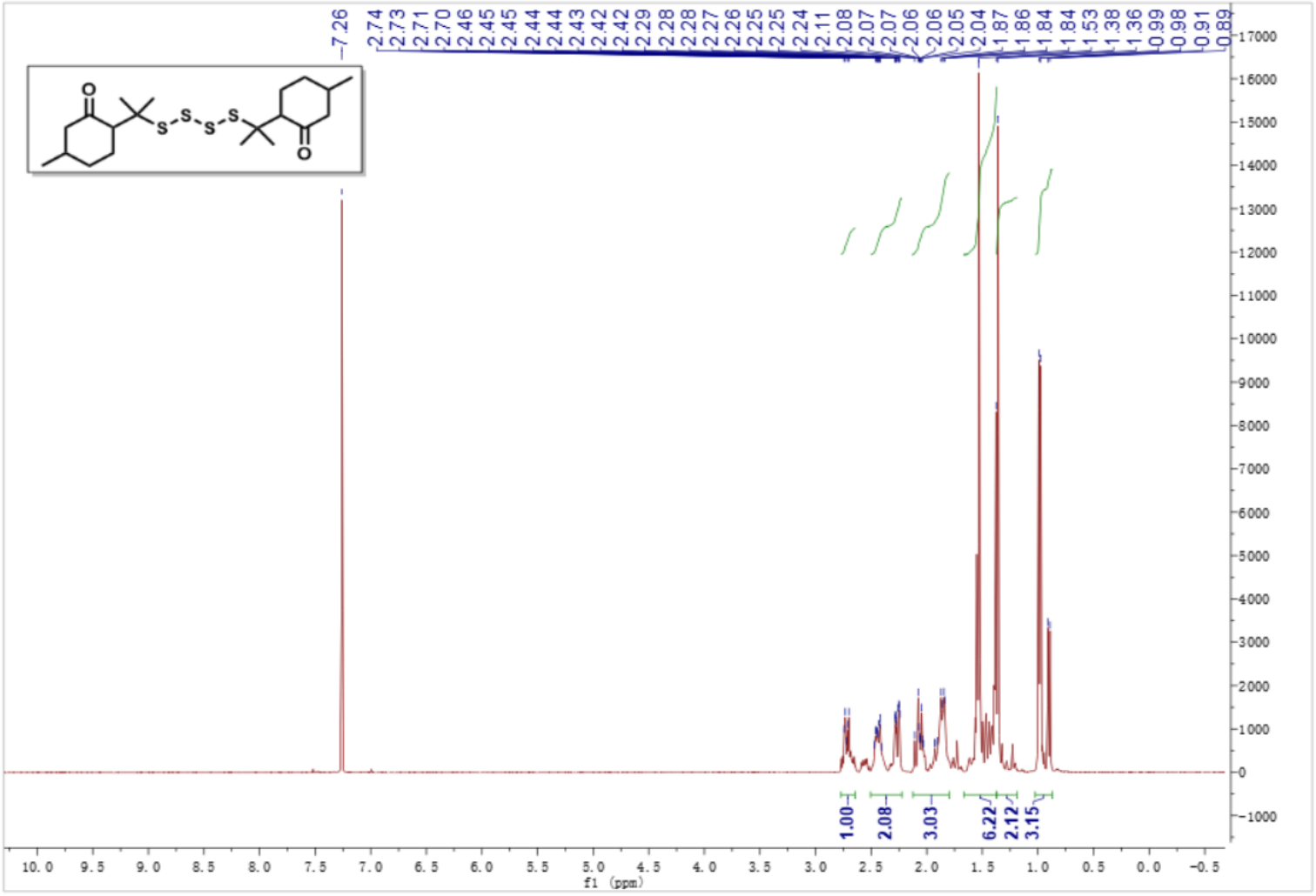
^{1}H NMR of 2m


7.26
2.76
2.74
2.73
2.70
2.66
2.07
2.05
2.01
1.41
1.40
1.38
1.36
1.35
1.34
1.33
1.30
2.00
3.03
6.04
f1 (ppm)

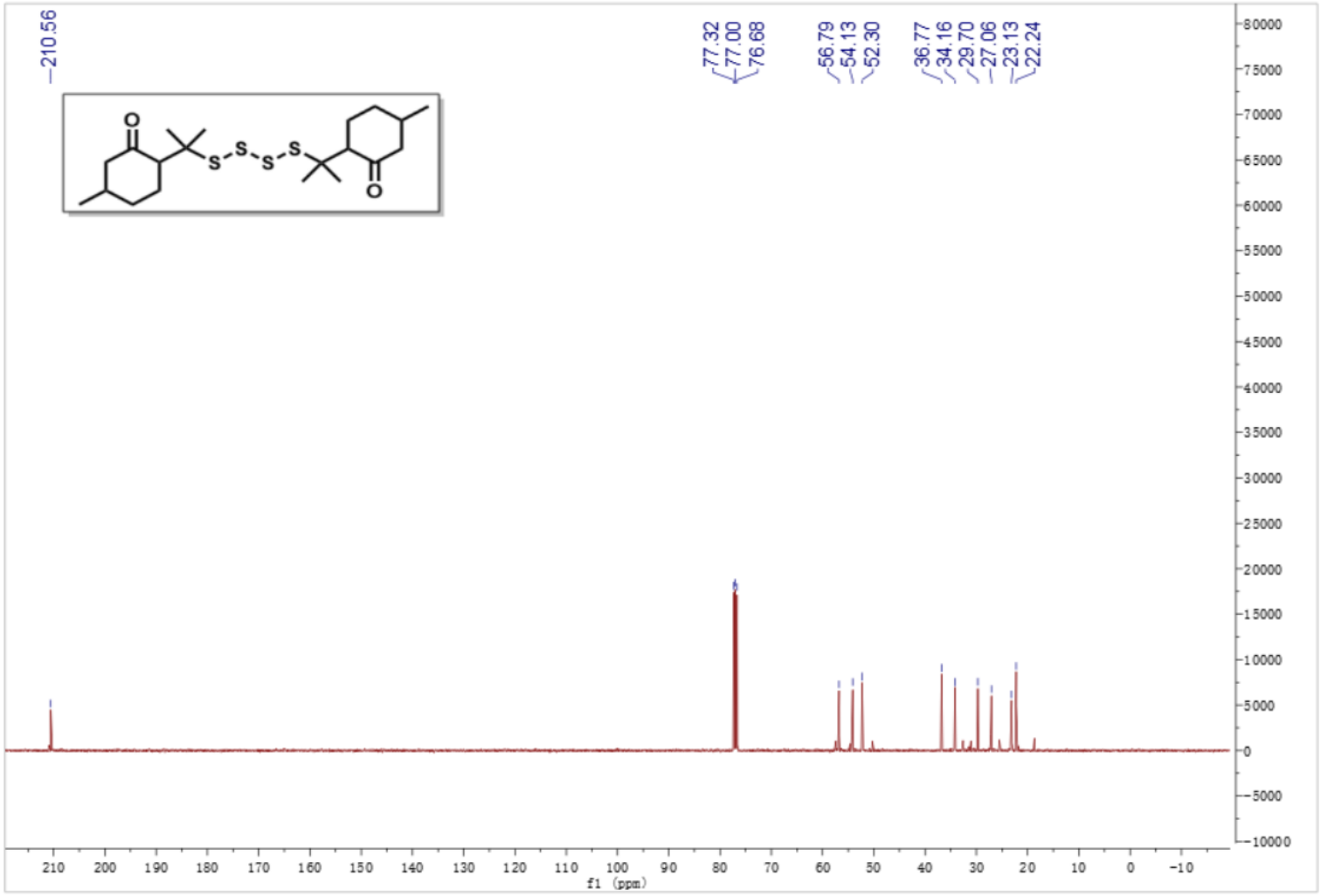
^{13}C NMR of 2m



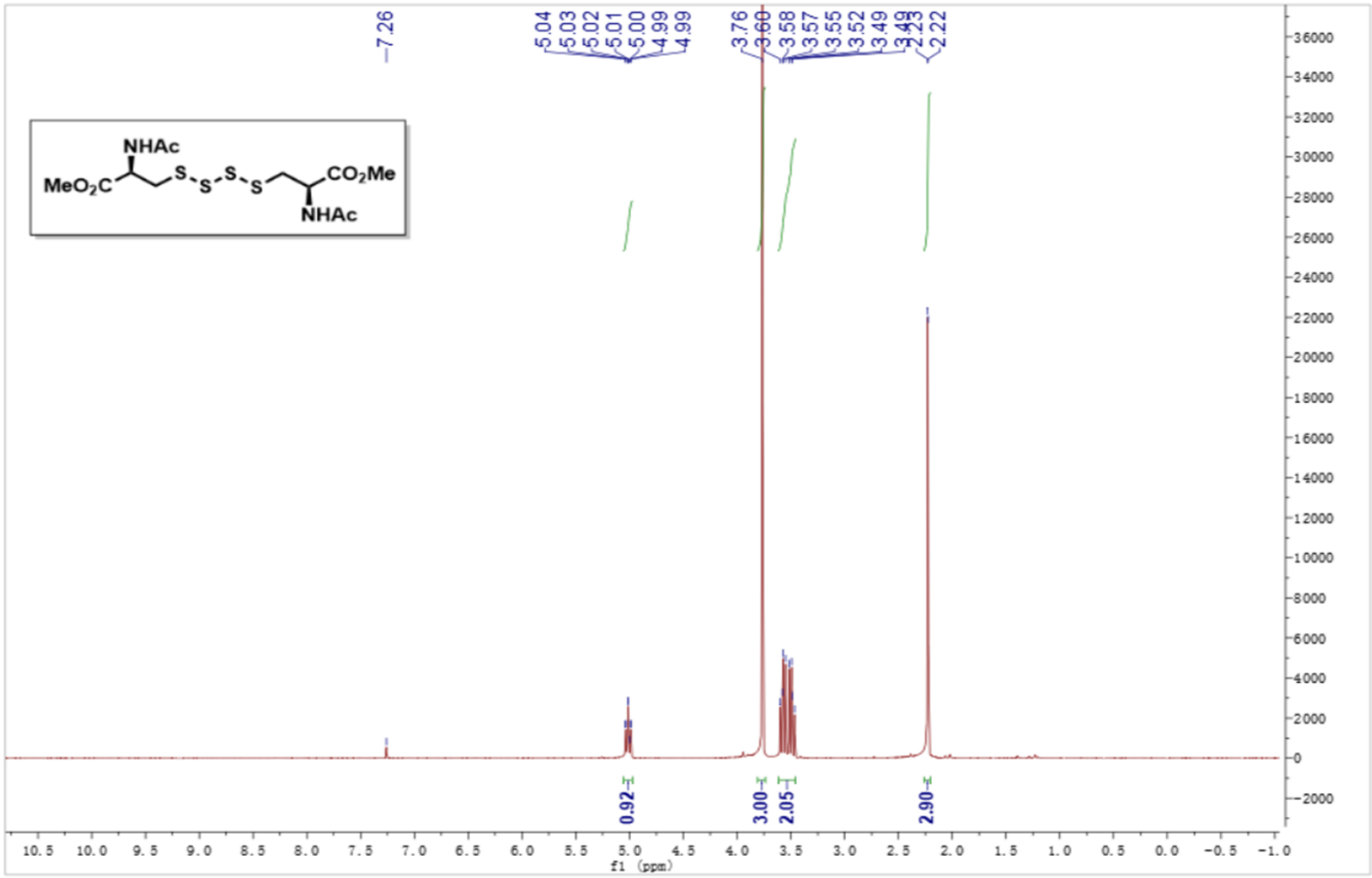
^{1}H NMR of 2n


7.26
2.74
2.73
2.71
2.70
2.46
2.45
2.45
2.44
2.44
2.43
2.42
2.42
2.29
2.28
2.28
2.27
2.26
2.25
2.25
2.24
2.11
2.08
2.07
2.07
2.06
2.06
2.05
2.04
1.87
1.86
1.84
1.84
1.53
1.38
1.36
0.99
0.98
0.91
0.89
1.00
2.08
3.03
6.22
2.12
3.15
f1 (ppm)

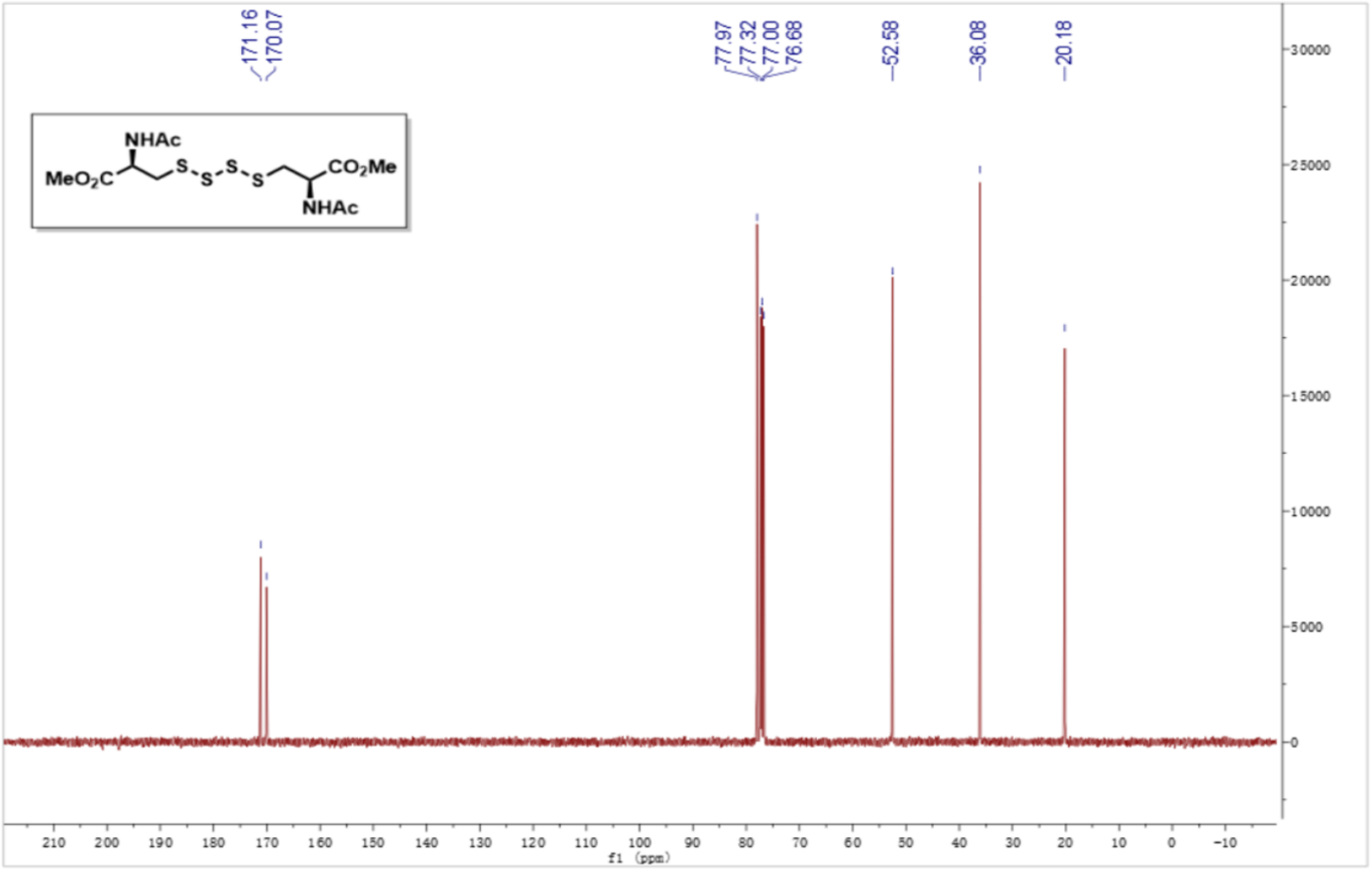
^{13}C NMR of 2n


210.56
77.32
77.00
76.68
56.79
54.13
52.30
36.77
34.16
29.70
27.06
23.13
22.24
O
S
S
S
S
O
f1 (ppm)

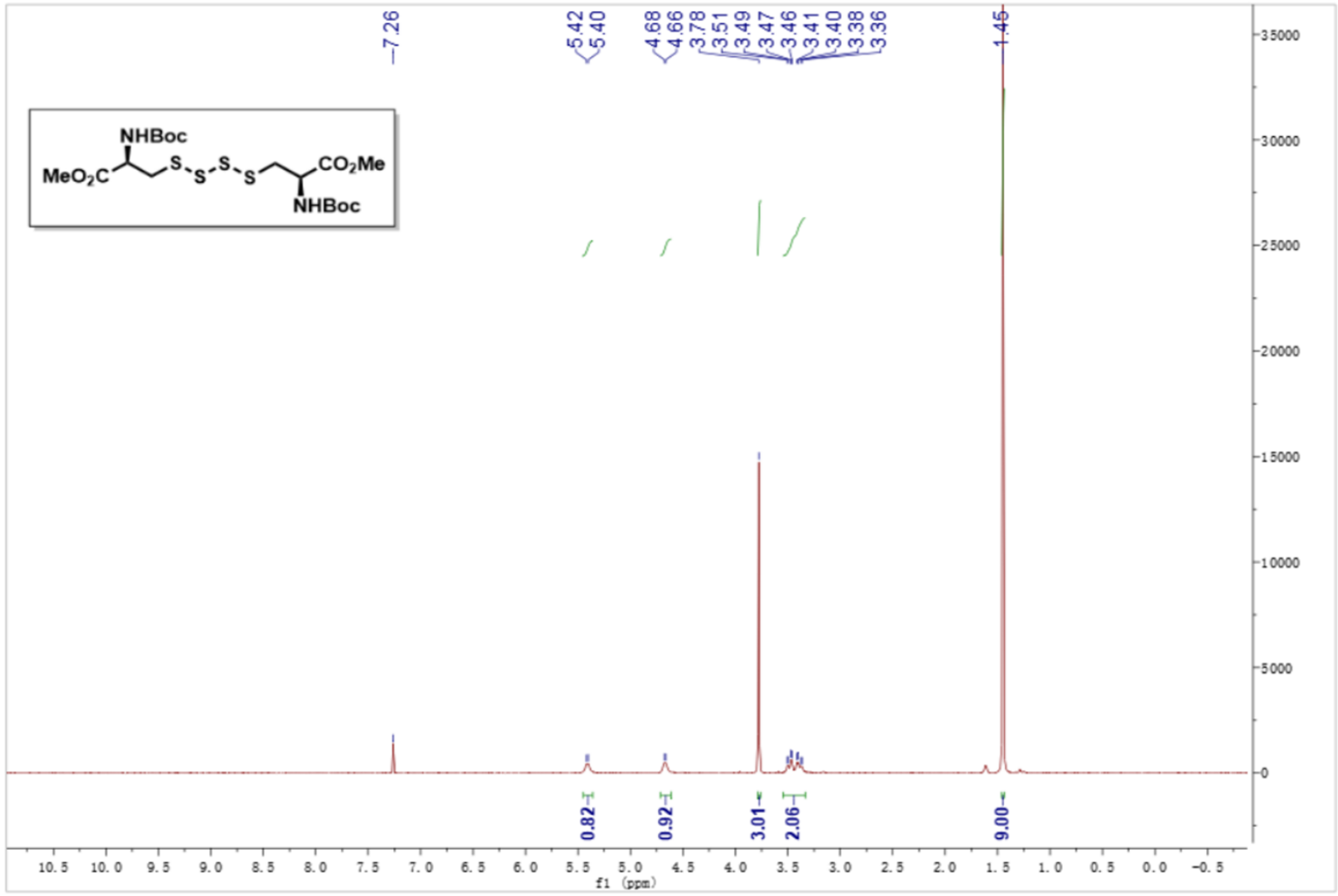
^{1}H NMR of 2o


7.26
5.04
5.03
5.02
5.01
5.00
4.99
4.99
3.76
3.60
3.58
3.57
3.55
3.52
3.49
3.49
2.23
2.22
NHAc
MeO2C
S
S
S
S
CO2Me
NHAc
0.92
3.00
2.05
2.90
f1 (ppm)

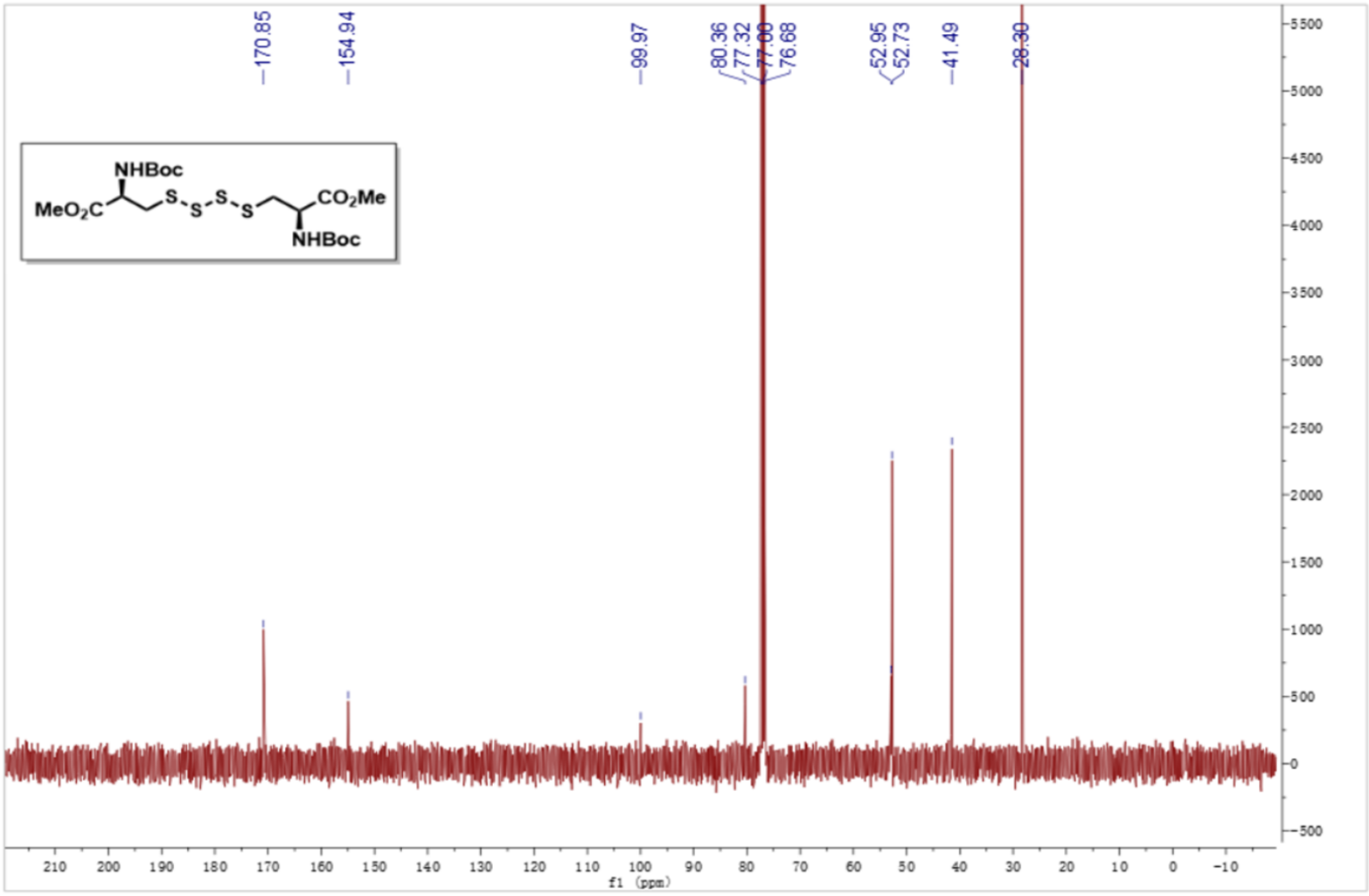
^{13}C NMR of 2o


171.16
170.07
77.97
77.32
77.00
76.68
52.58
36.08
20.18
NHAc
MeO2C
S
S
S
S
CO2Me
NHAc
30000
25000
20000
15000
10000
5000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

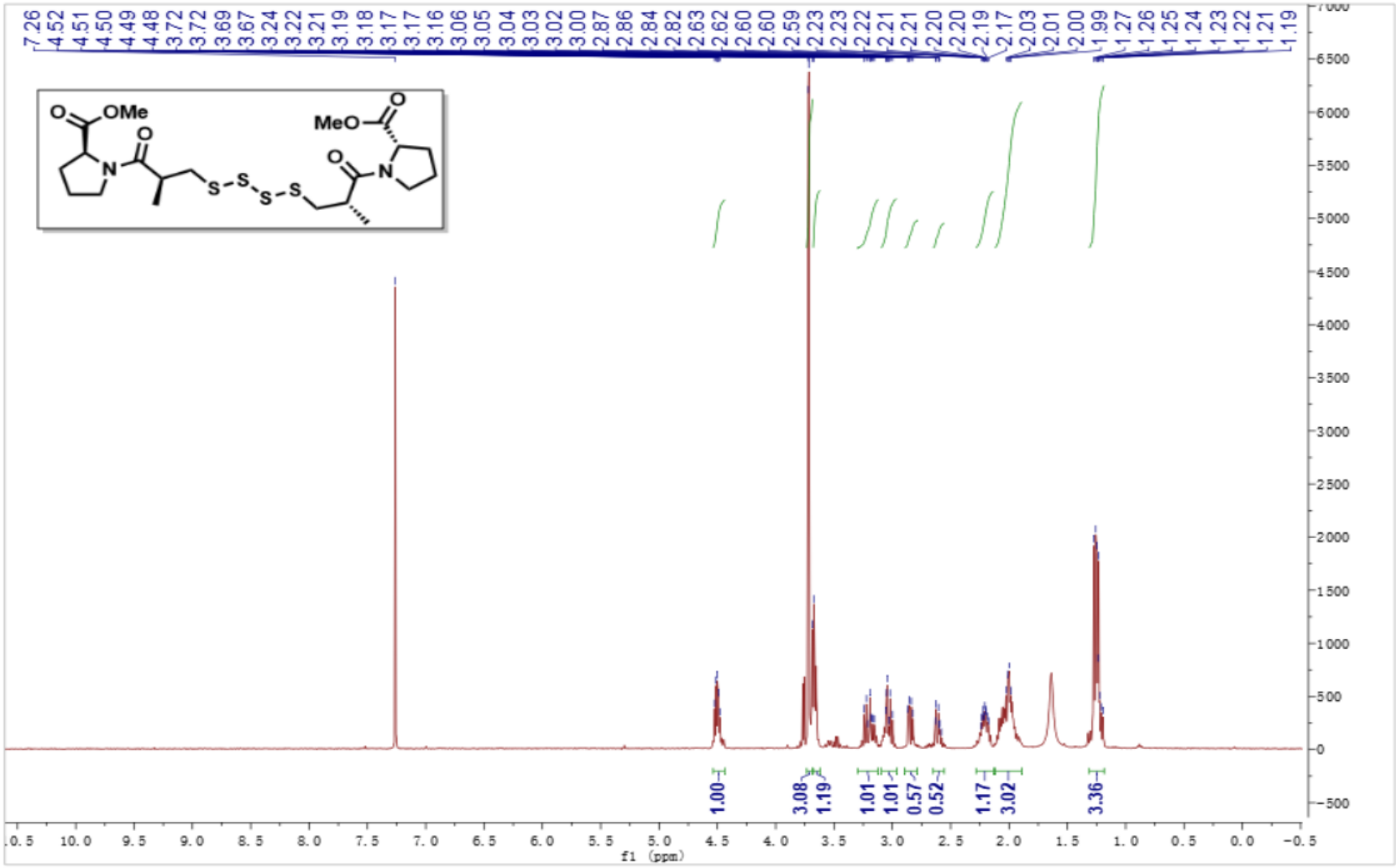
^{1}H NMR of 2p


7.26
5.42
5.40
4.68
4.66
3.78
3.51
3.49
3.47
3.46
3.41
3.40
3.38
3.36
1.45
NHBoc
MeO2C
S
S
S
S
CO2Me
NHBoc
0.82
0.92
3.01
2.06
9.00
f1 (ppm)

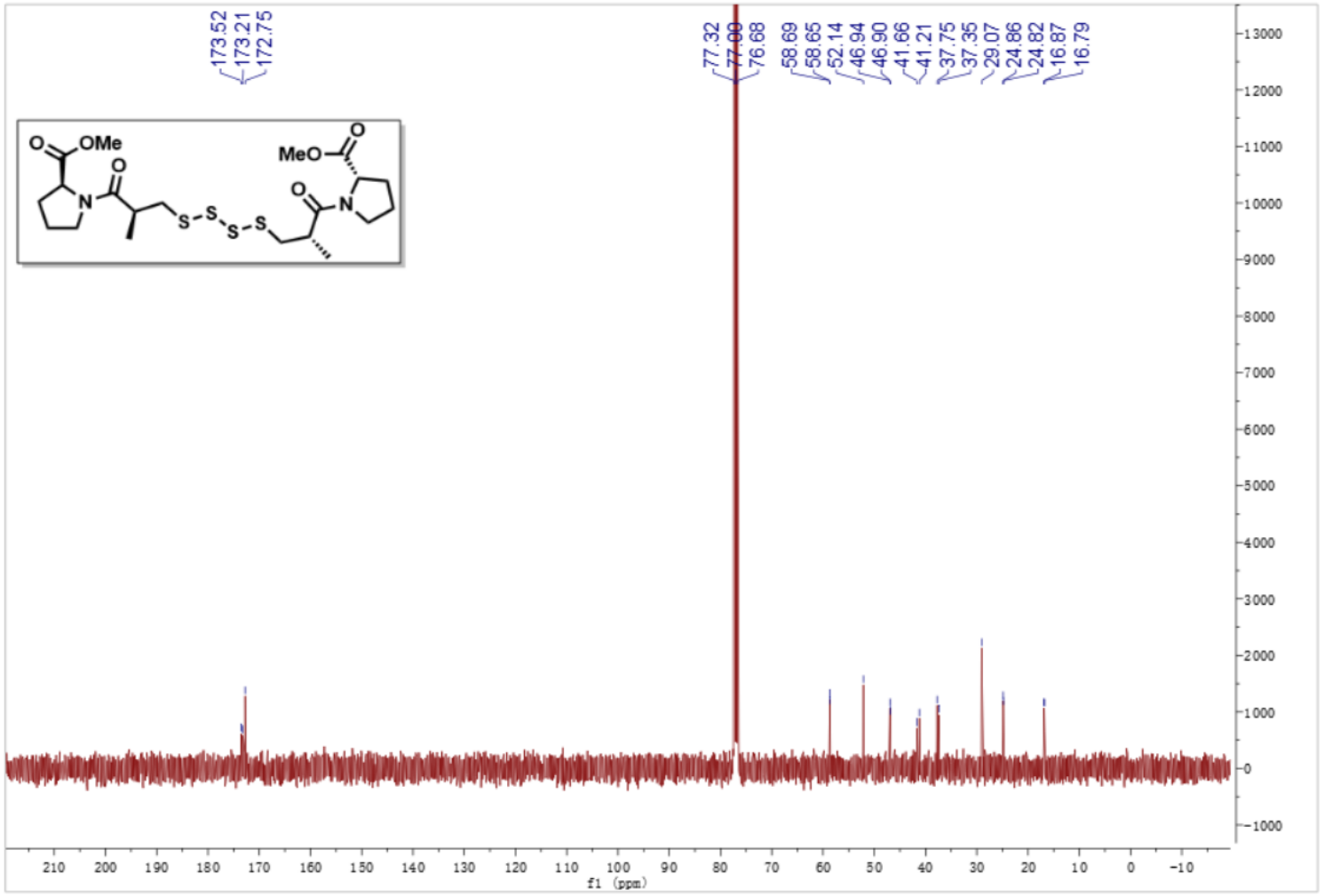
^{13}C NMR of 2p


170.85
154.94
99.97
80.36
77.32
77.00
76.68
52.95
52.73
41.49
28.30
NHBoc
MeO2C
S
S
S
S
CO2Me
NHBoc
f1 (ppm)

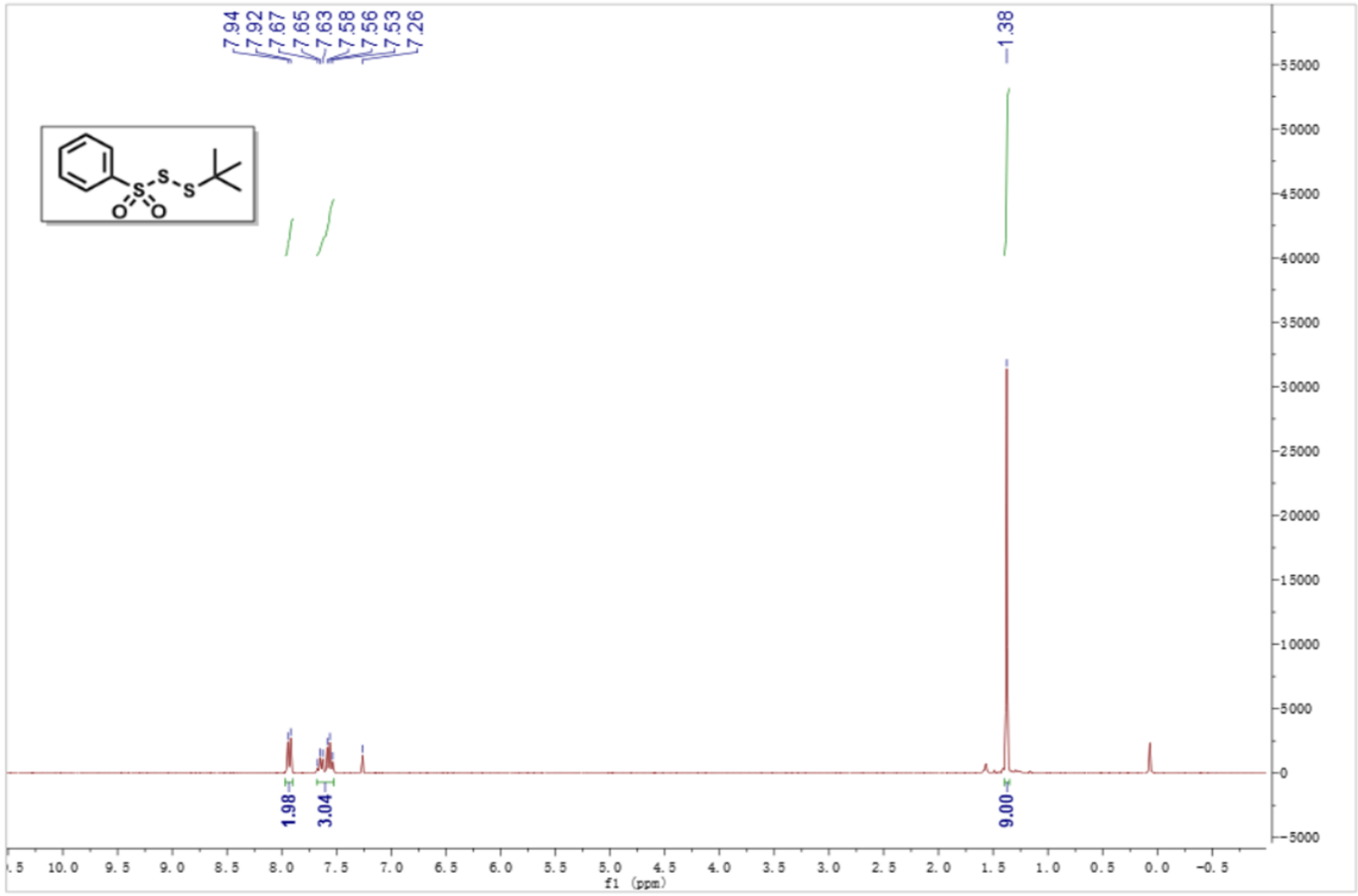
^{1}H NMR of 2q


7.26 4.52 4.51 4.50 4.49 4.48 3.72 3.72 3.69 3.67 3.24 3.22 3.21 3.19 3.18 3.17 3.17 3.16 3.06 3.05 3.04 3.03 3.02 3.00 2.87 2.86 2.84 2.82 2.63 2.62 2.60 2.60 2.59 2.23 2.23 2.22 2.21 2.21 2.20 2.20 2.19 2.17 2.03 2.01 2.00 1.99 1.27 1.26 1.25 1.24 1.23 1.22 1.21 1.19
OMe
MeO
1.00 3.08 1.19 1.01 1.01 0.57 0.52 1.17 3.02 3.36
f1 (ppm)

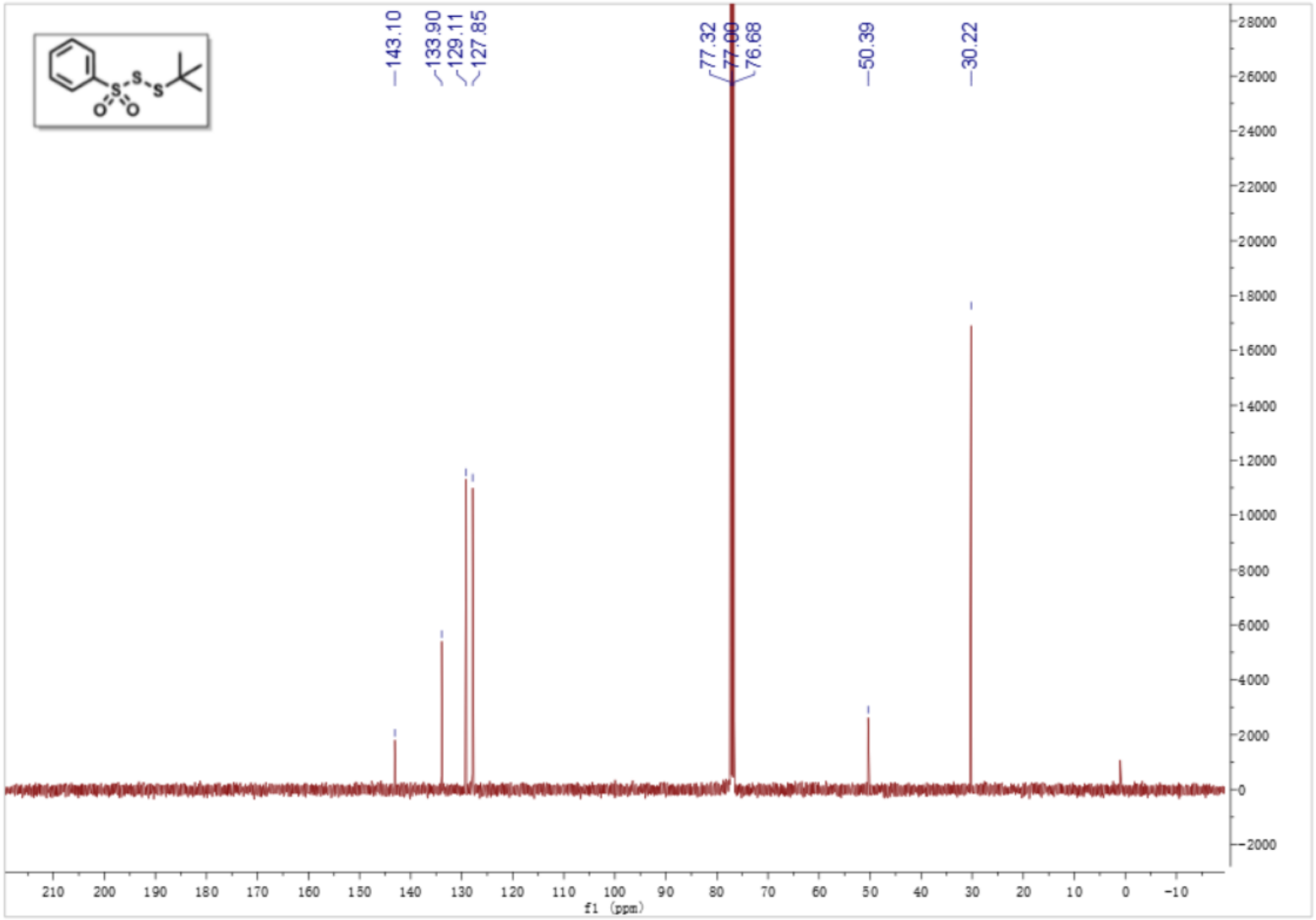
^{13}C NMR of 2q


173.52
173.21
172.75
77.32
77.00
76.68
58.69
58.65
52.14
46.94
46.90
41.66
41.21
37.75
37.35
29.07
24.86
24.82
16.87
16.79
OMe
MeO
f1 (ppm)

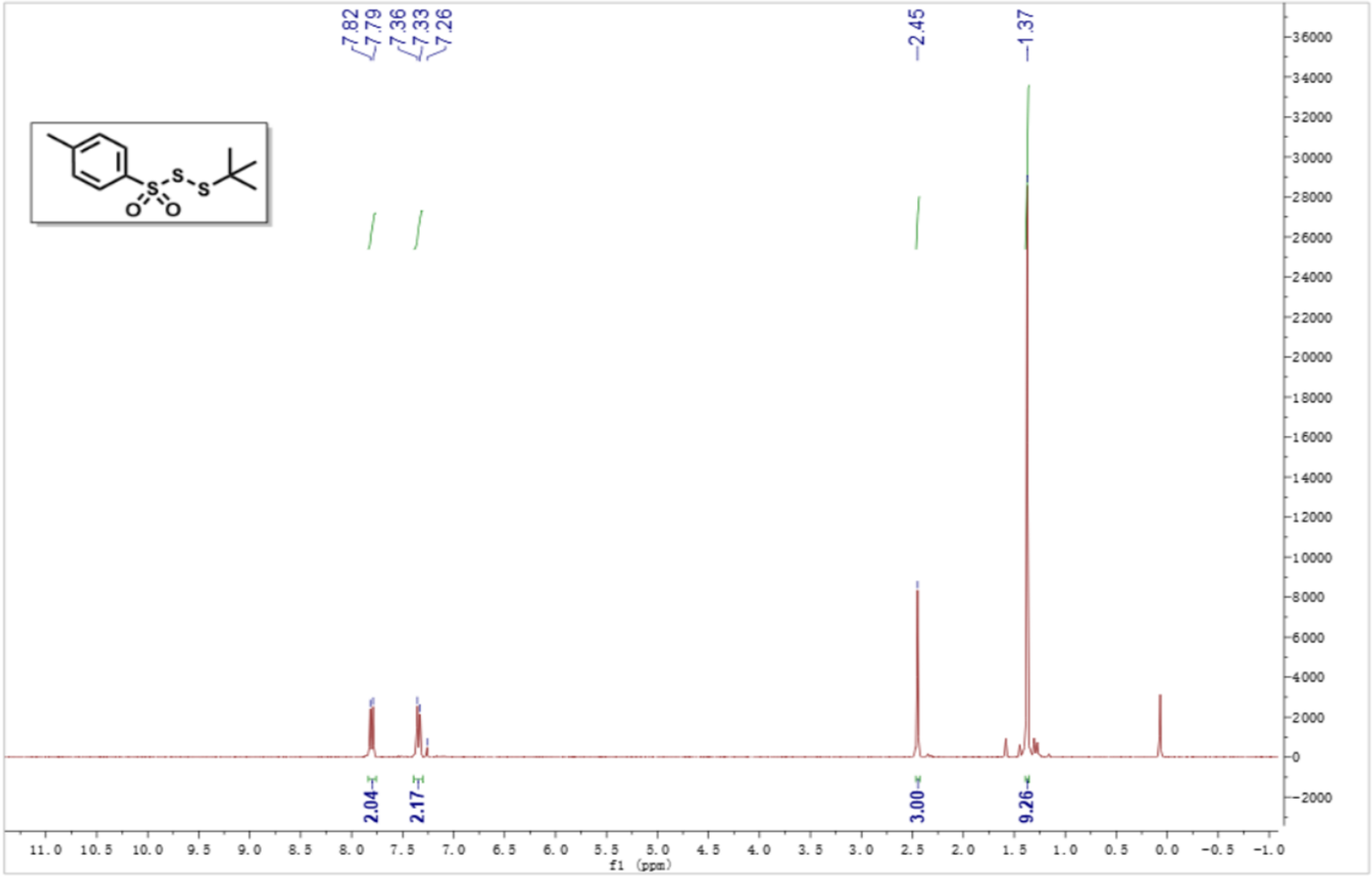
^{1}H NMR of 3a



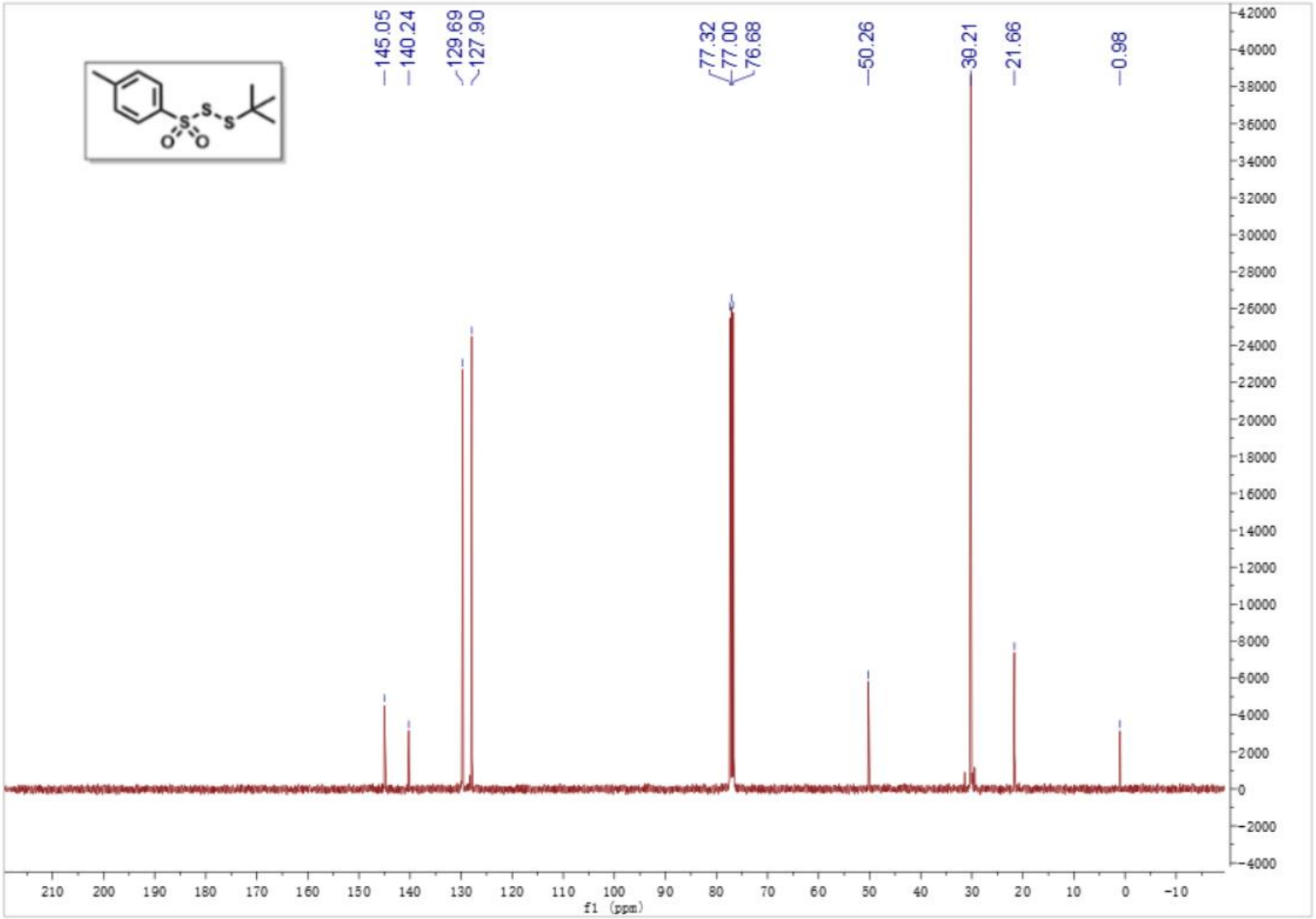
^{13}C NMR of 3a



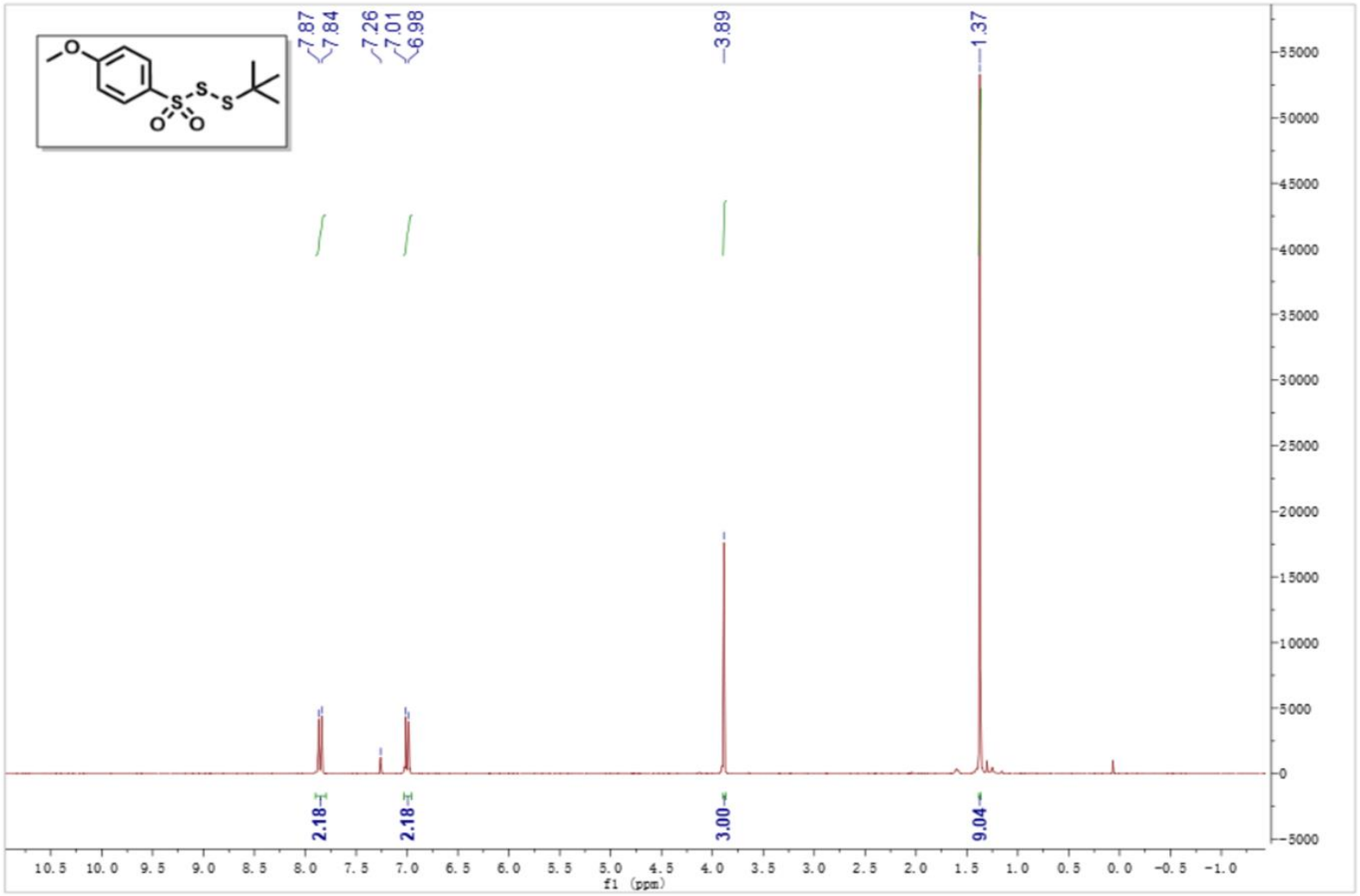
^{1}H NMR of 3b



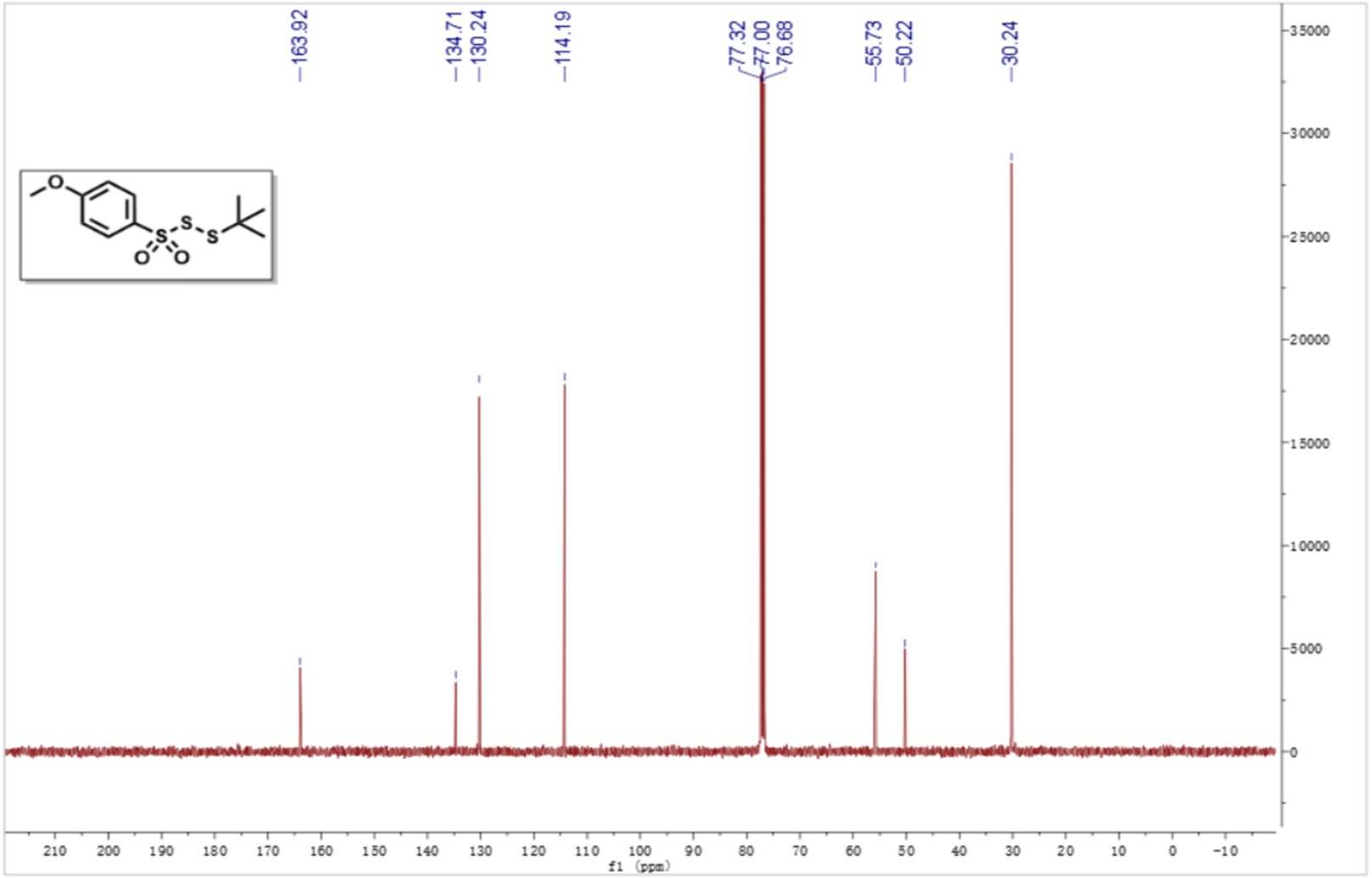
^{13}C NMR of 3b


145.05
140.24
129.69
127.90
77.32
77.00
76.68
50.26
30.21
21.66
0.98
f1 (ppm)

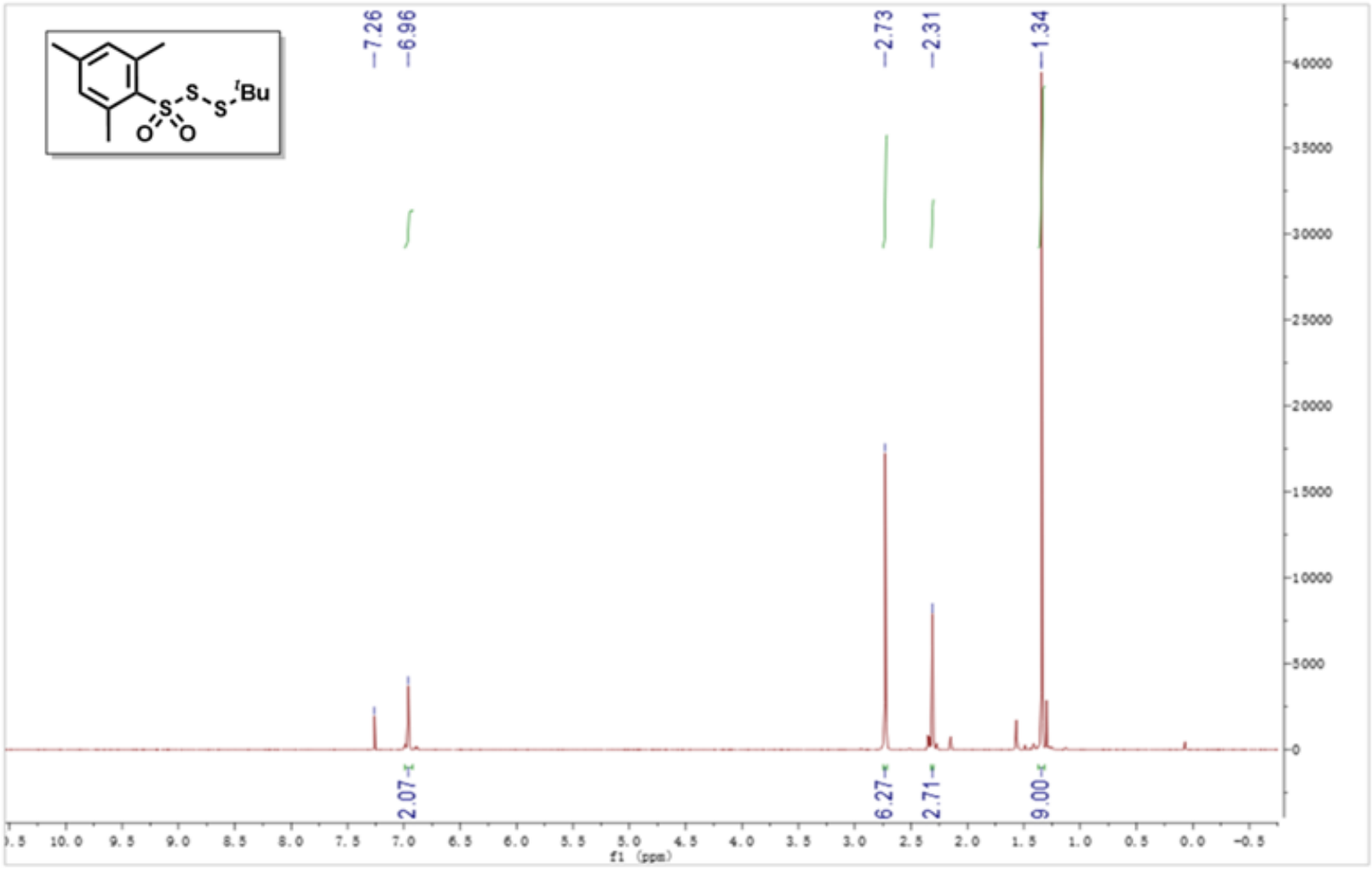
^{1}H NMR of 3c



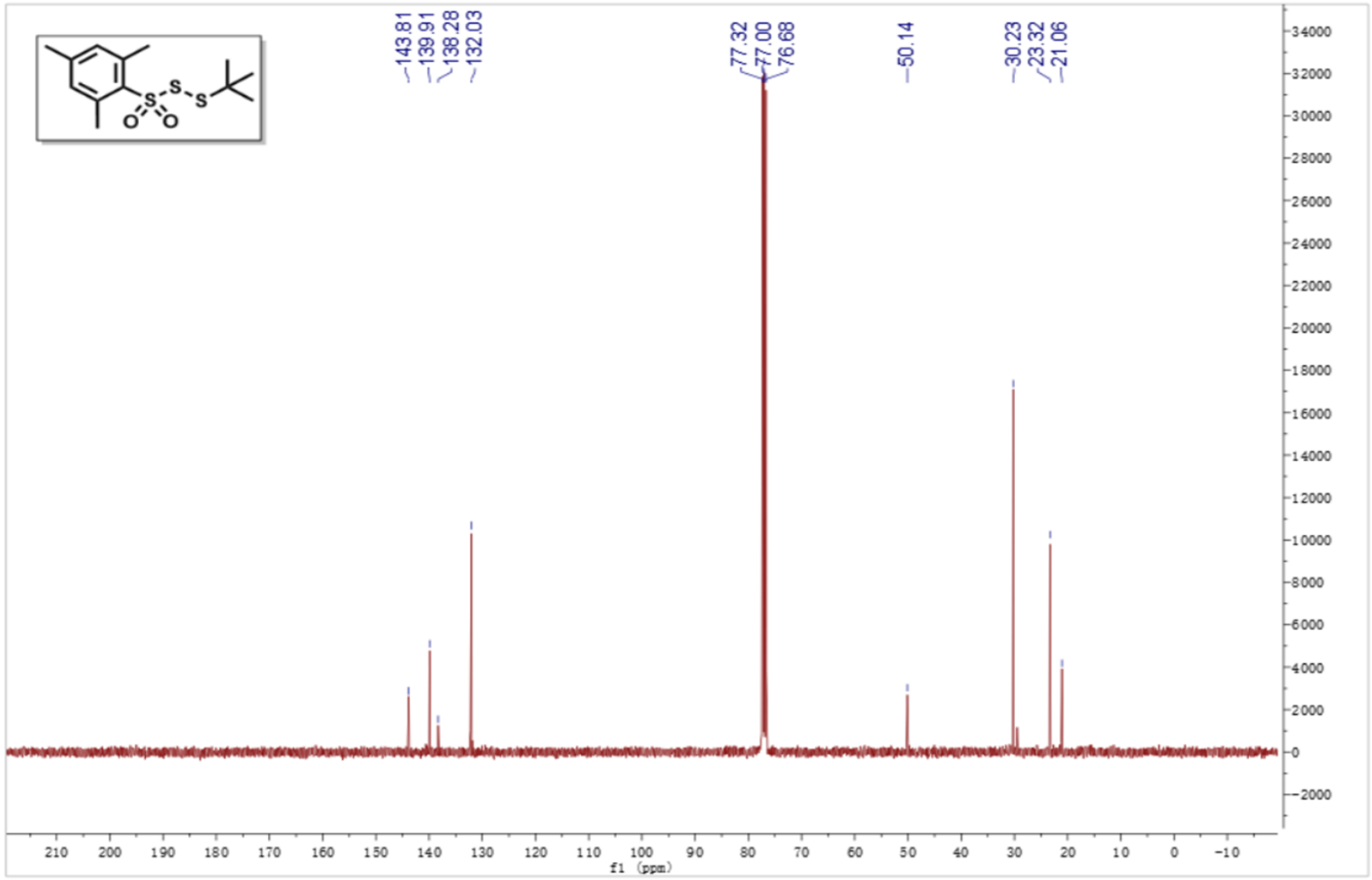
^{13}C NMR of 3c


163.92
134.71
130.24
114.19
77.32
77.00
76.68
55.73
50.22
30.24
35000
30000
25000
20000
15000
10000
5000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

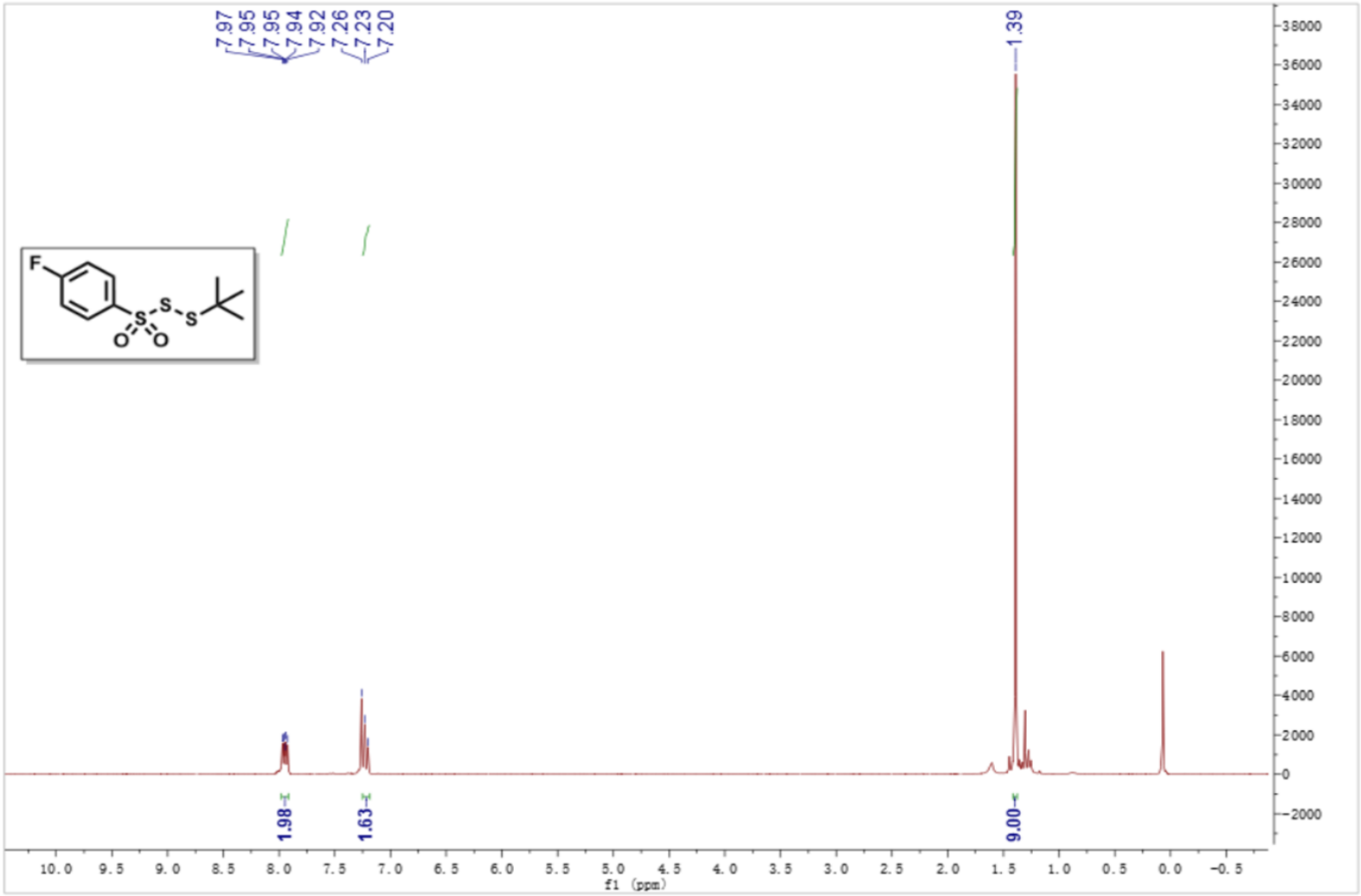
^{1}H NMR of 3d



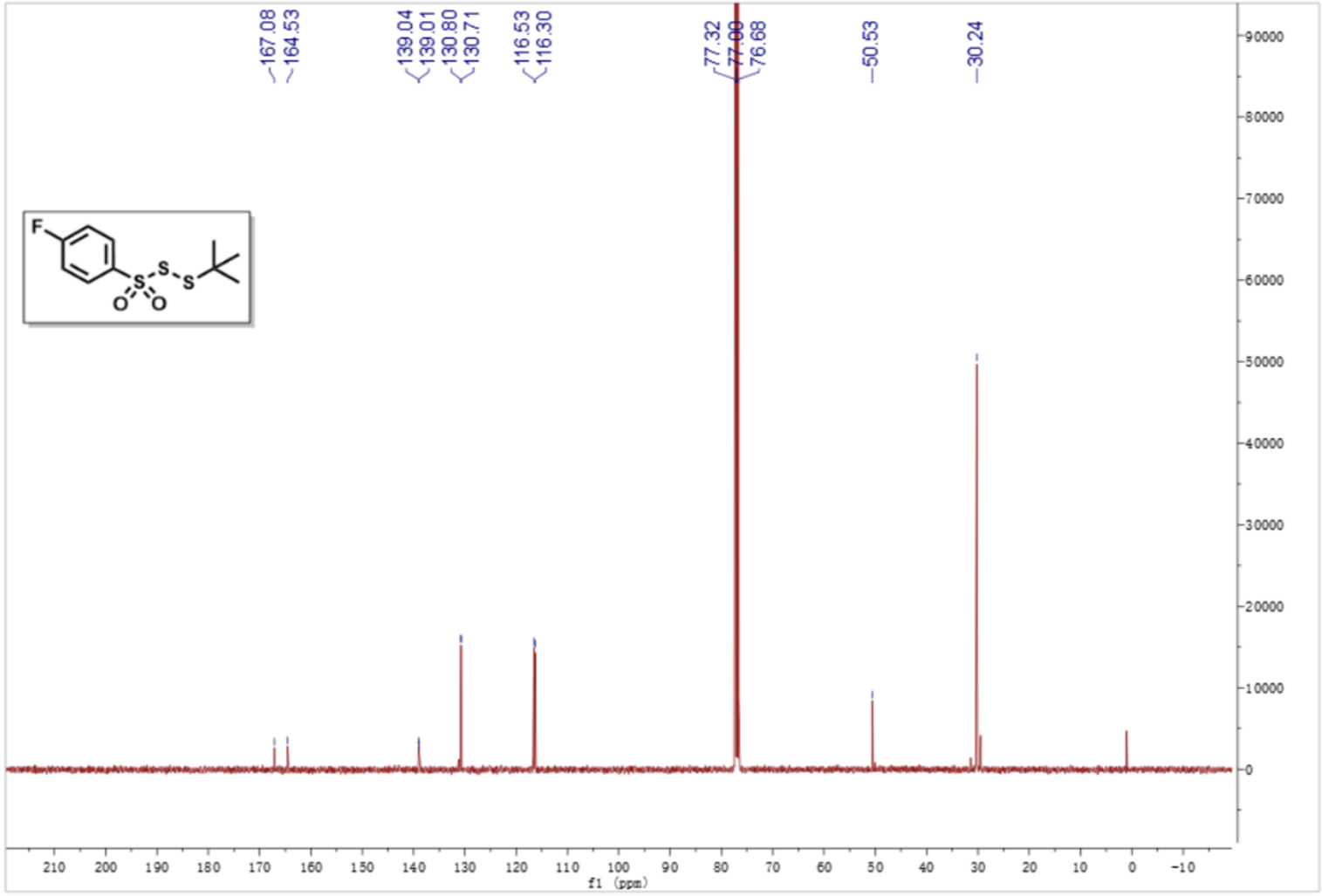
^{13}C NMR of 3d


143.81
139.91
138.28
132.03
77.32
77.00
76.68
50.14
30.23
23.32
21.06
f1 (ppm)

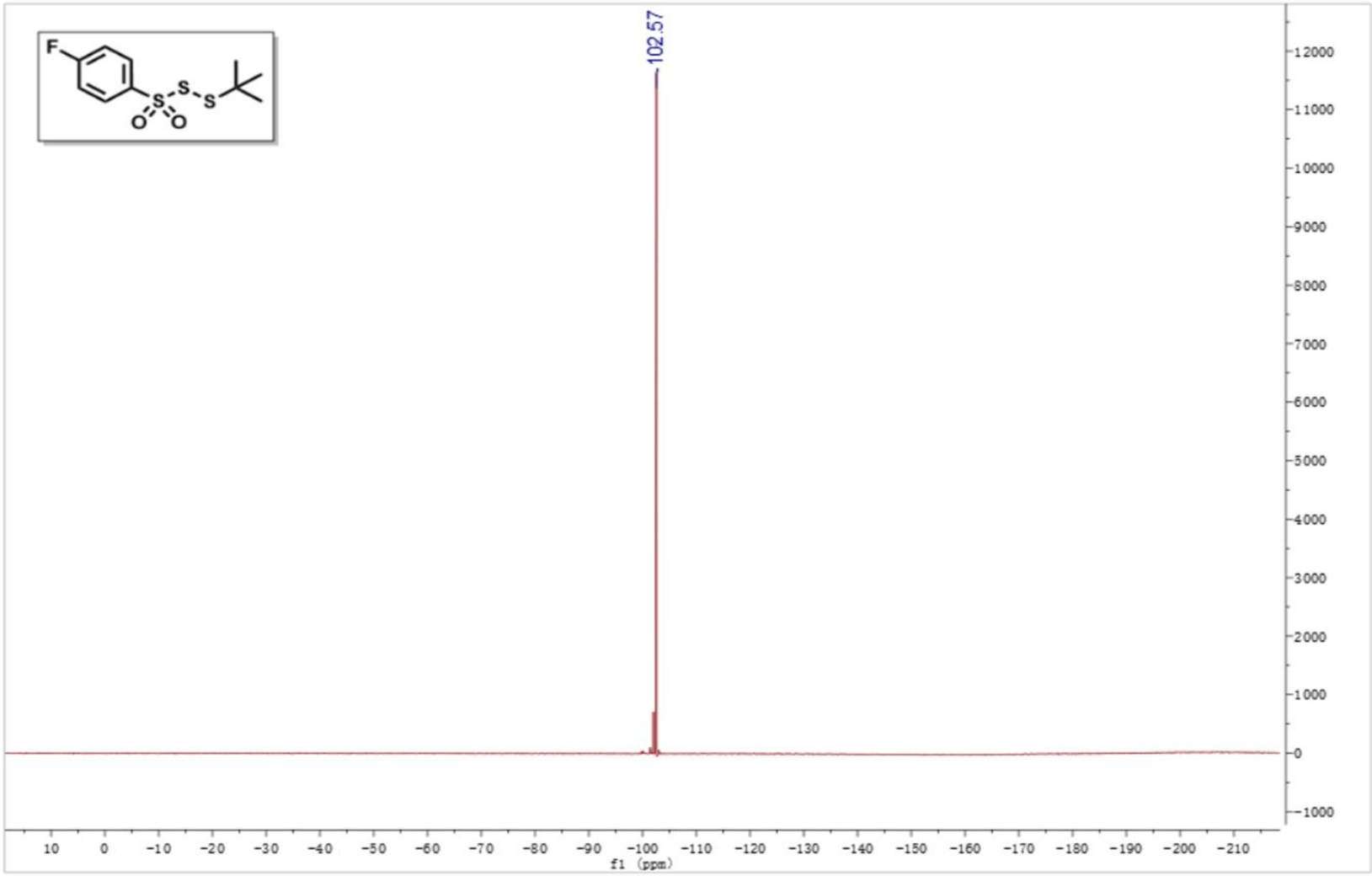
^{1}H NMR of 3e



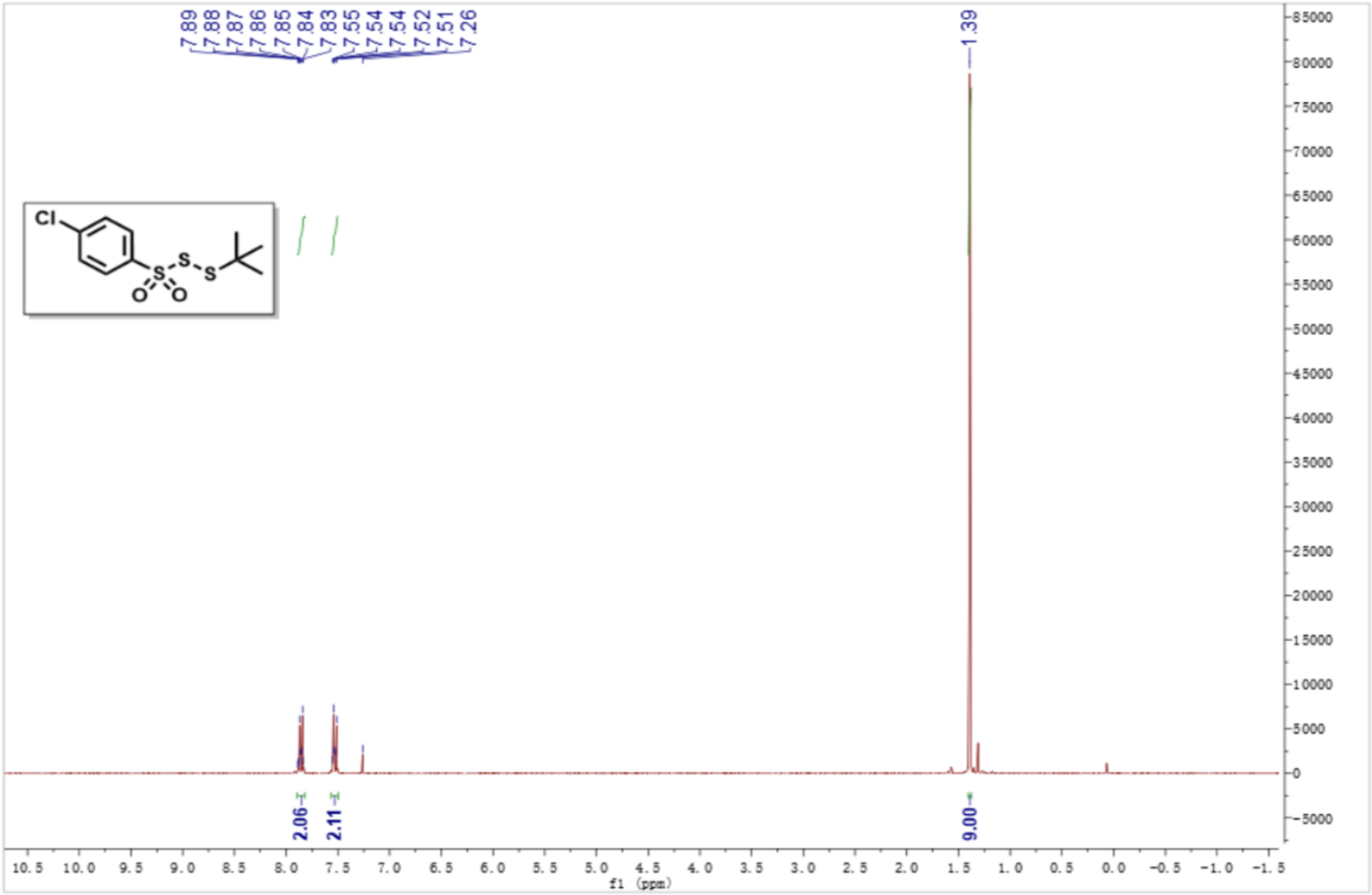
^{13}C NMR of 3e


167.08
164.53
139.04
139.01
130.80
130.71
116.53
116.30
77.32
77.00
76.68
50.53
30.24
F
S
S
S
O
O
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

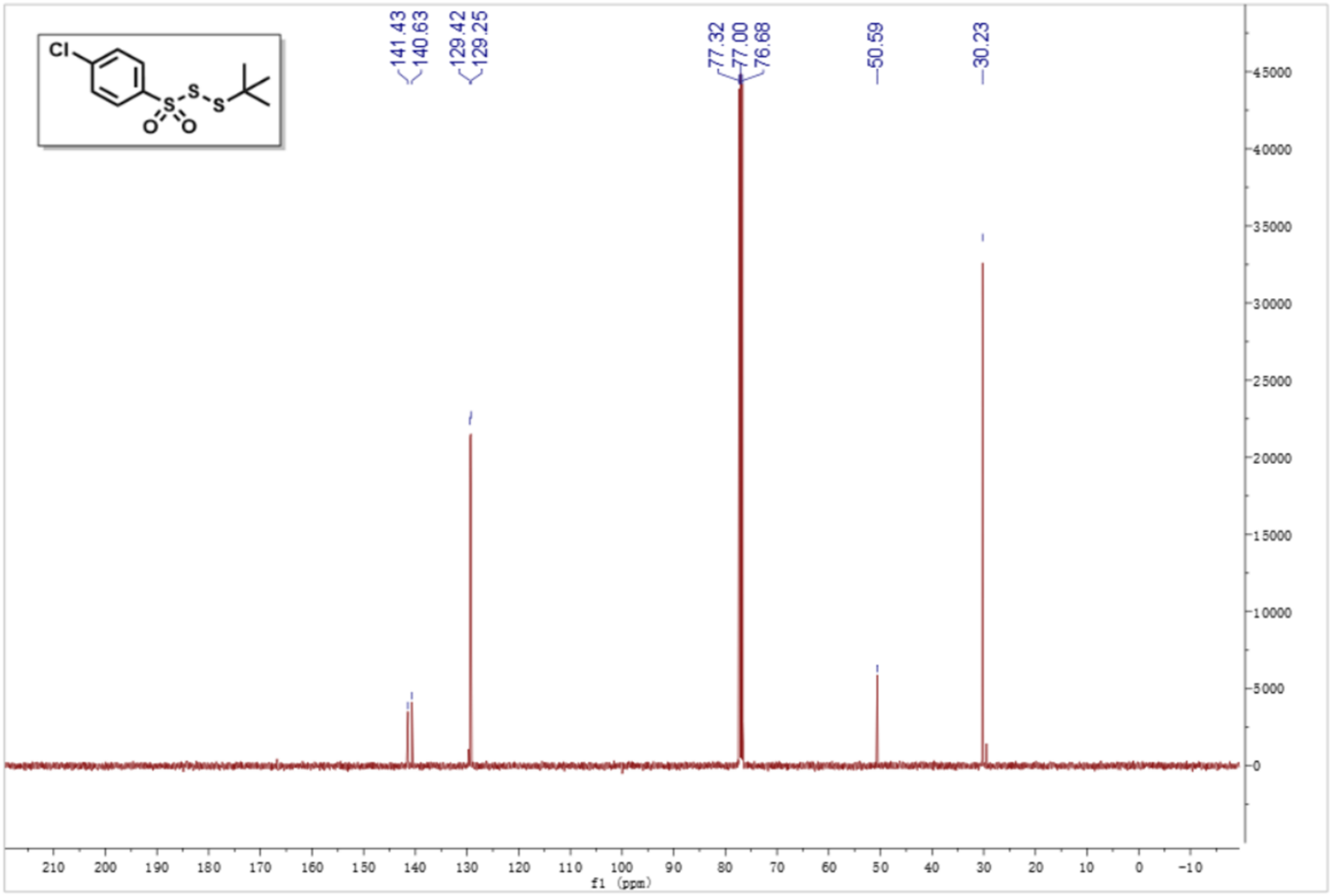
^{19}F NMR of 3e


F
S
S
S
O
O
102.57
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

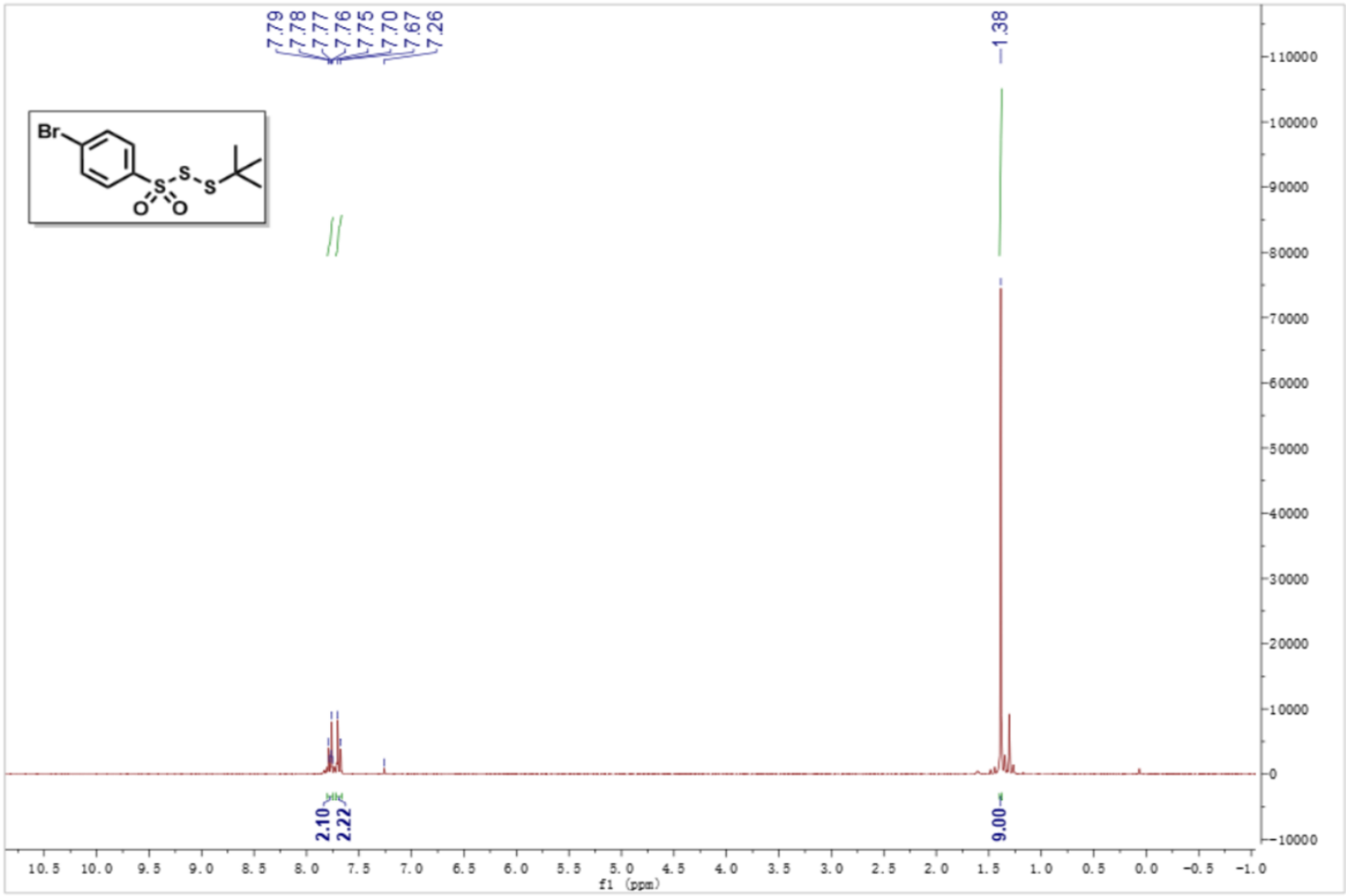
^{1}H NMR of 3f


7.89
7.88
7.87
7.86
7.85
7.84
7.83
7.55
7.54
7.54
7.52
7.51
7.26
1.39
Cl
S
S
S
O
O
2.06
2.11
9.00
f1 (ppm)

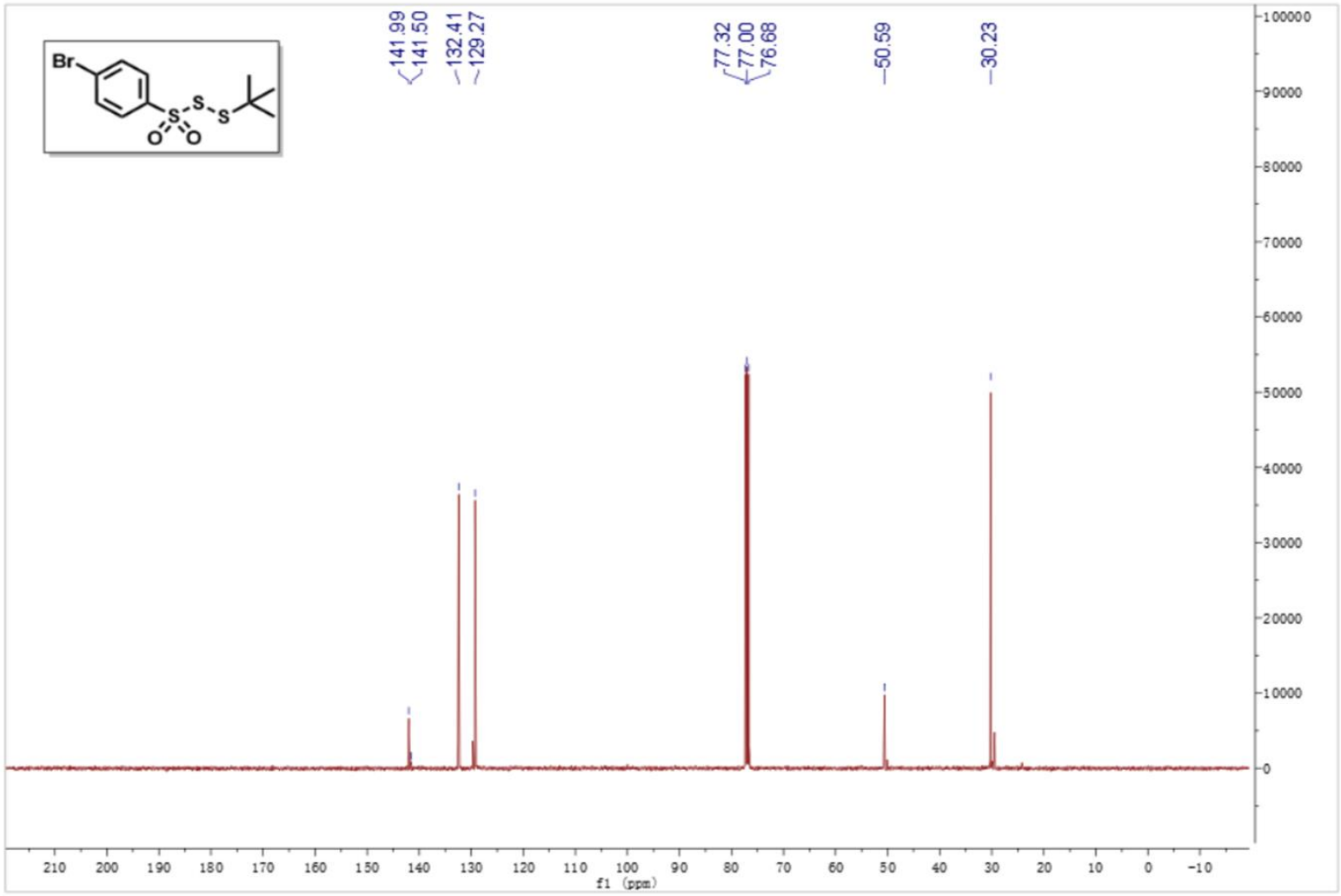
^{13}C NMR of 3f


Cl
S
S
S
O
O
141.43
140.63
129.42
129.25
77.32
77.00
76.68
50.59
30.23
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

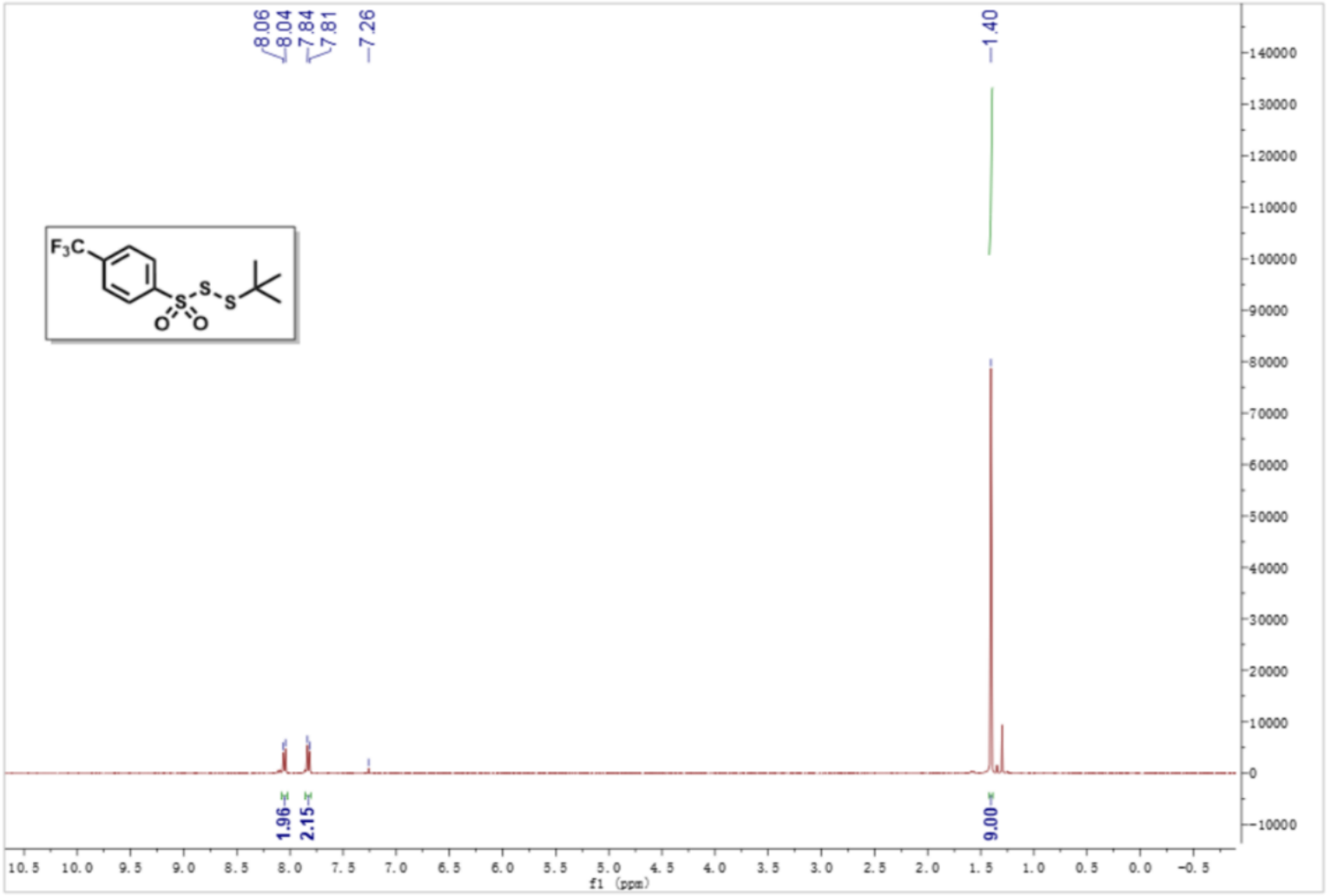
^{1}H NMR of 3g



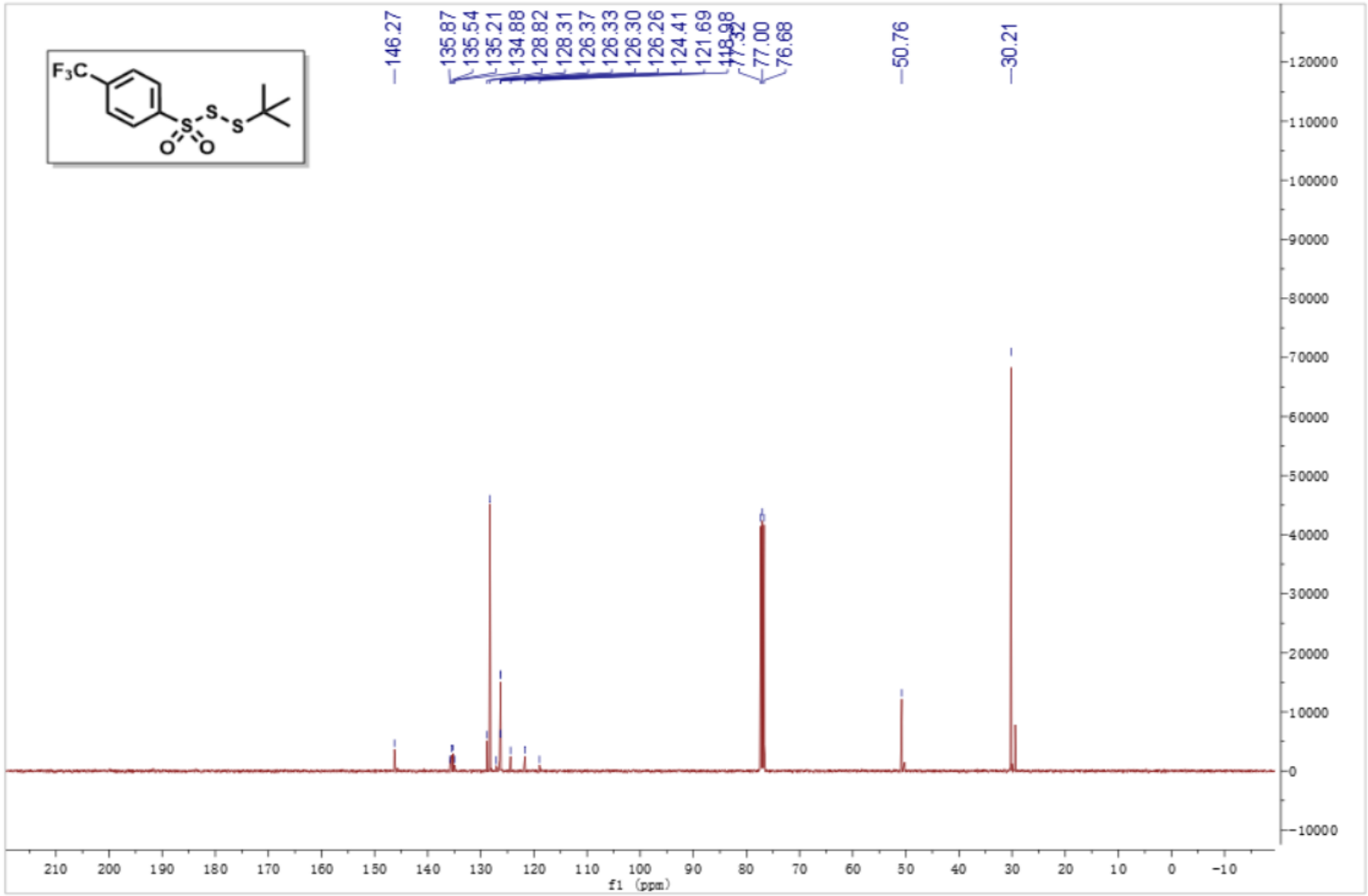
^{13}C NMR of 3g


Br
S
S
S
O
O
141.99
141.50
132.41
129.27
77.32
77.00
76.68
50.59
30.23
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

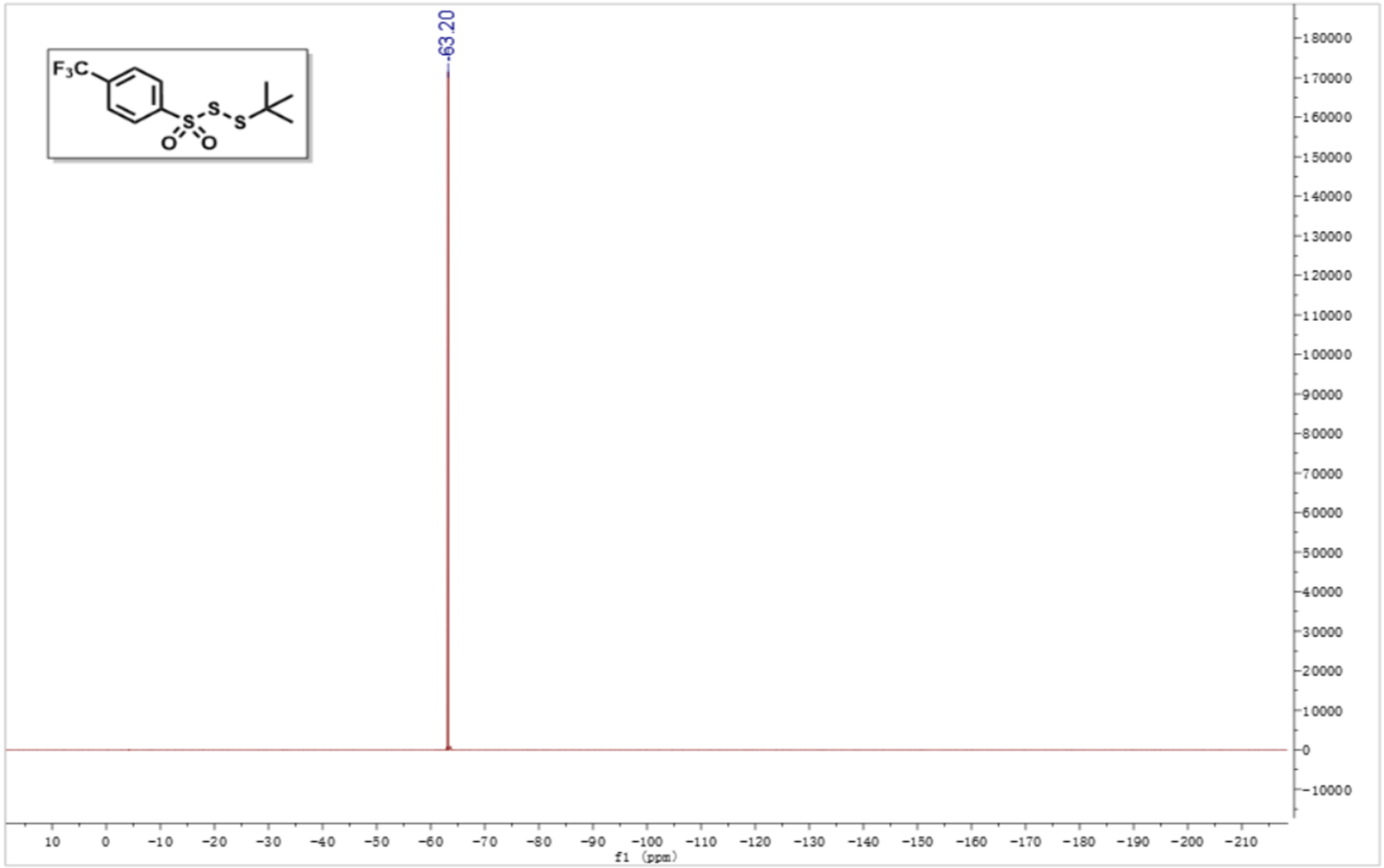
^{1}H NMR of 3h



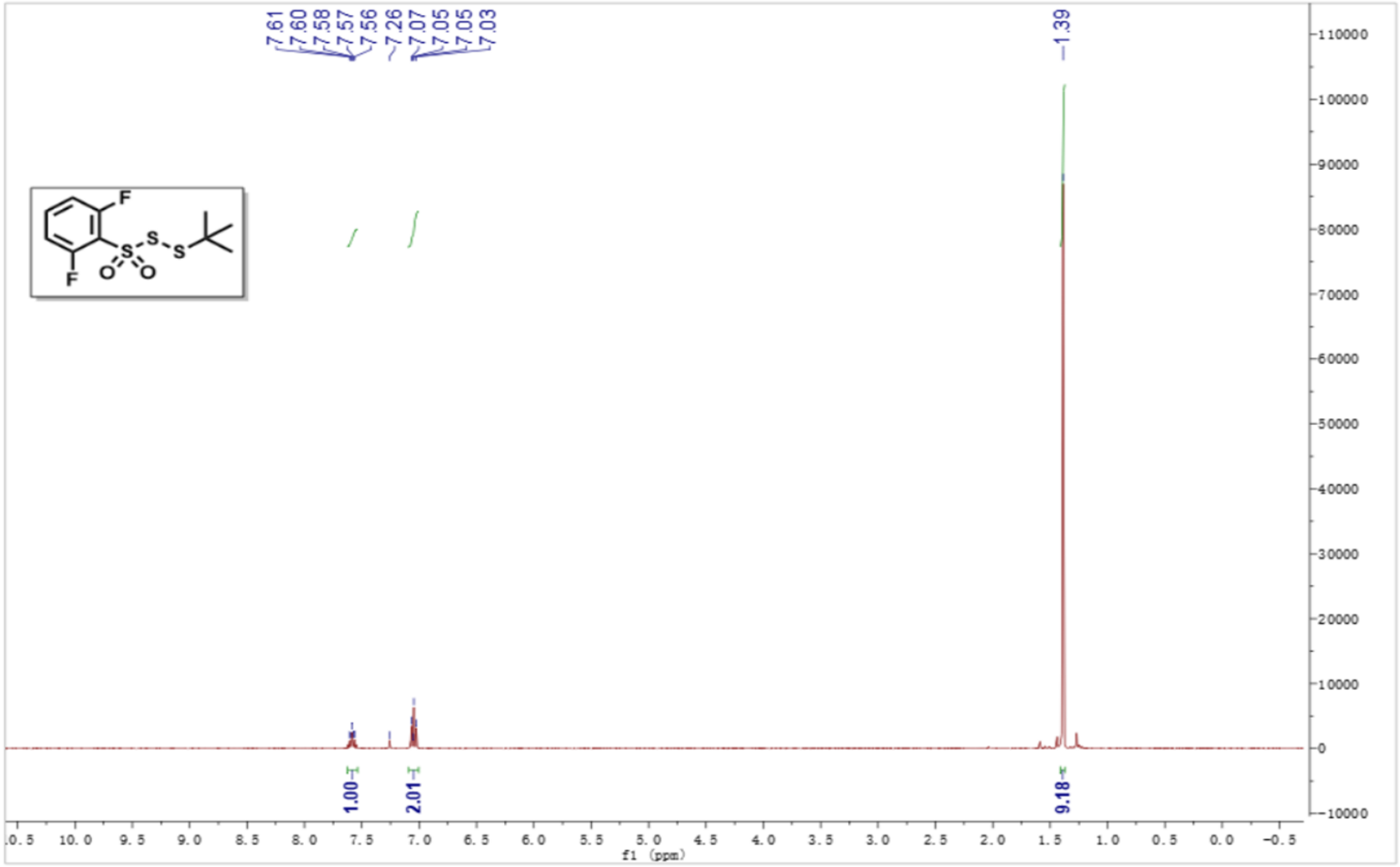
^{13}C NMR of 3h


F3C
S
S
S
O
O
146.27
135.87
135.54
135.21
134.88
128.82
128.31
126.37
126.33
126.30
126.26
124.41
121.69
118.98
77.32
77.00
76.68
50.76
30.21
f1 (ppm)

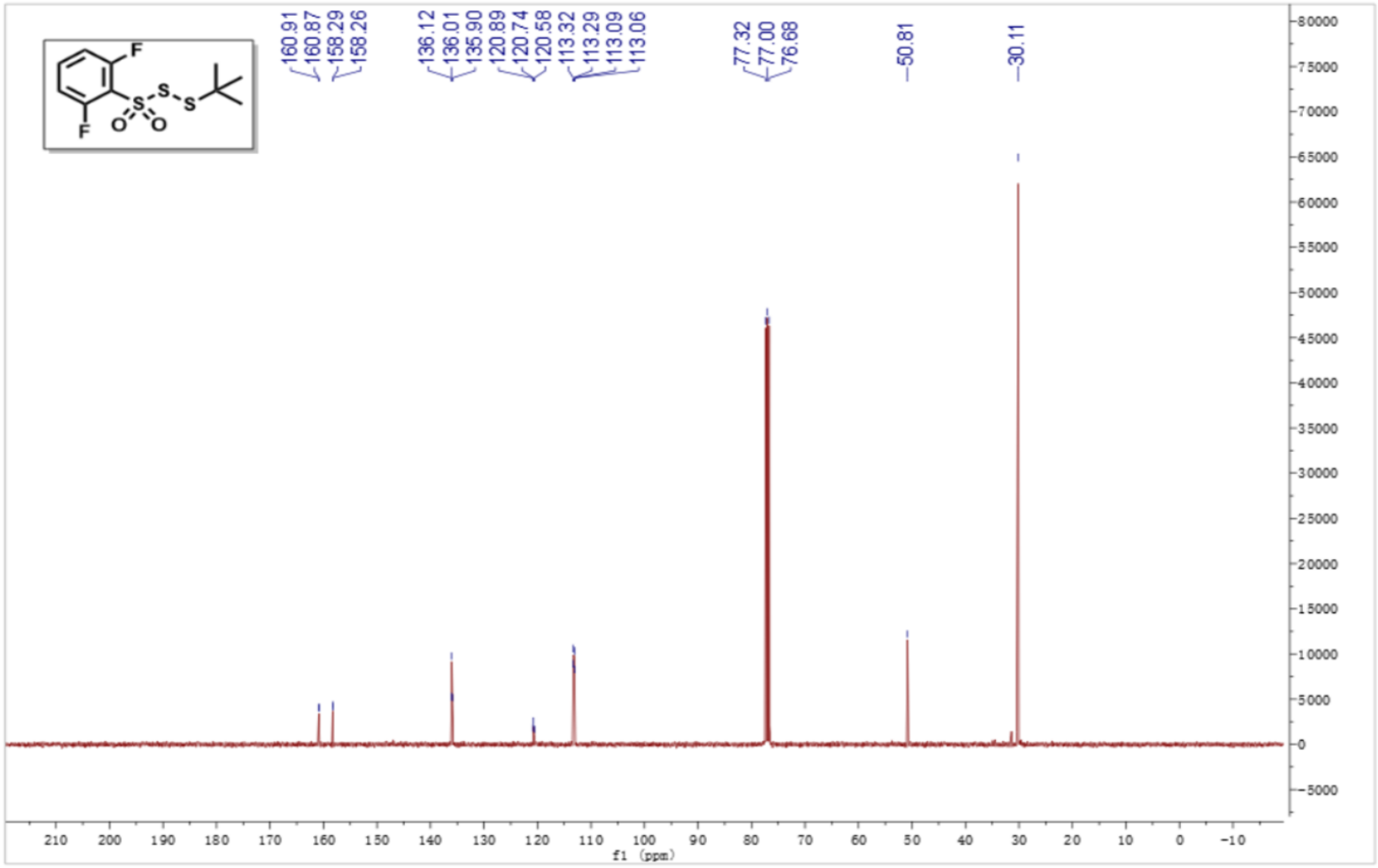
^{19}F NMR of 3h


-63.20
F3C
S
S
S
O
O
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

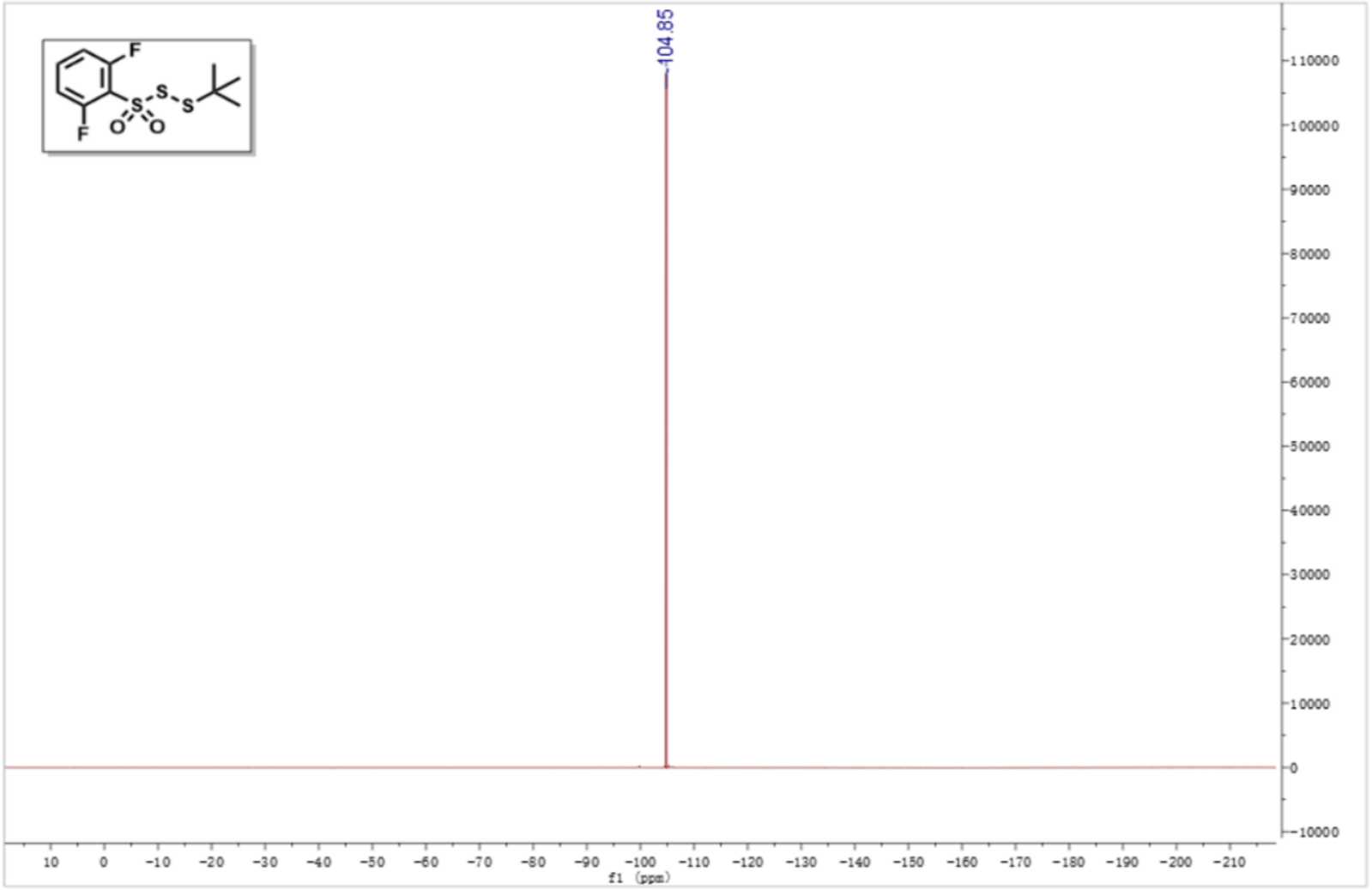
^{1}H NMR of 3i


7.61
7.60
7.58
7.57
7.56
7.26
7.07
7.05
7.05
7.03
1.39
F
S
S
S
O
O
F
1.00
2.01
9.18
f1 (ppm)

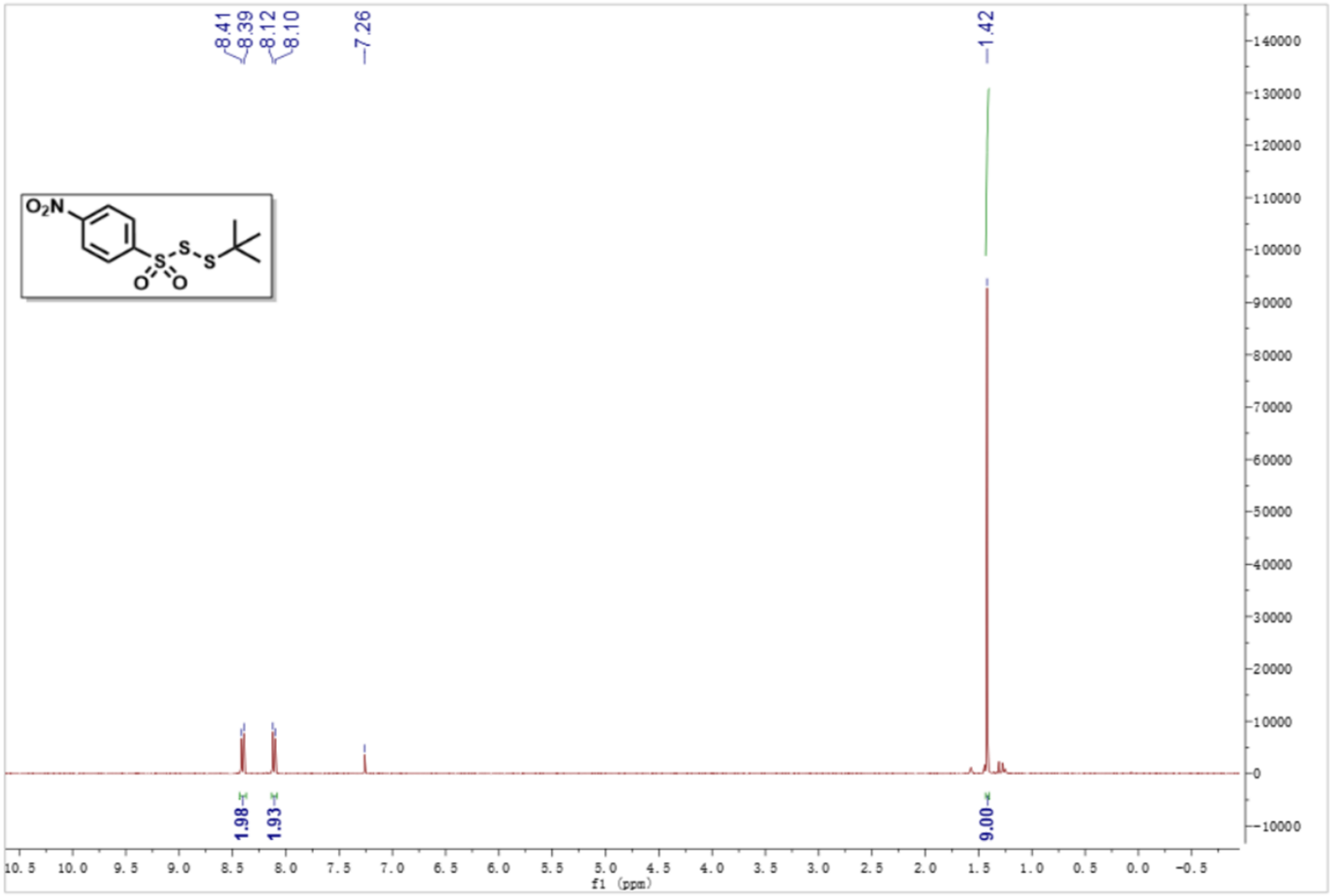
^{13}C NMR of 3i


160.91
160.87
158.29
158.26
136.12
136.01
135.90
120.89
120.74
120.58
113.32
113.29
113.09
113.06
77.32
77.00
76.68
50.81
30.11
f1 (ppm)

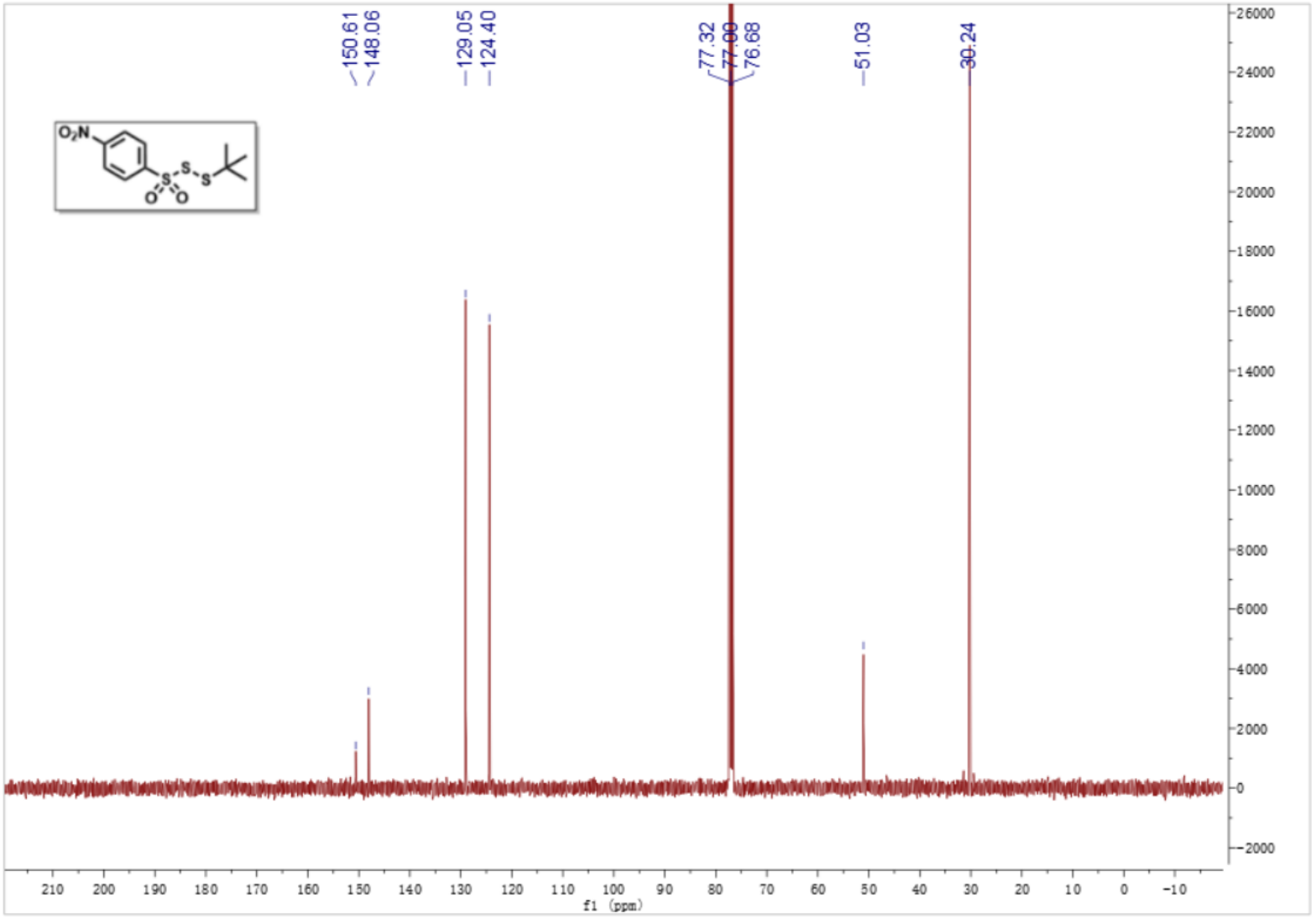
^{19}F NMR of 3i


104.85
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

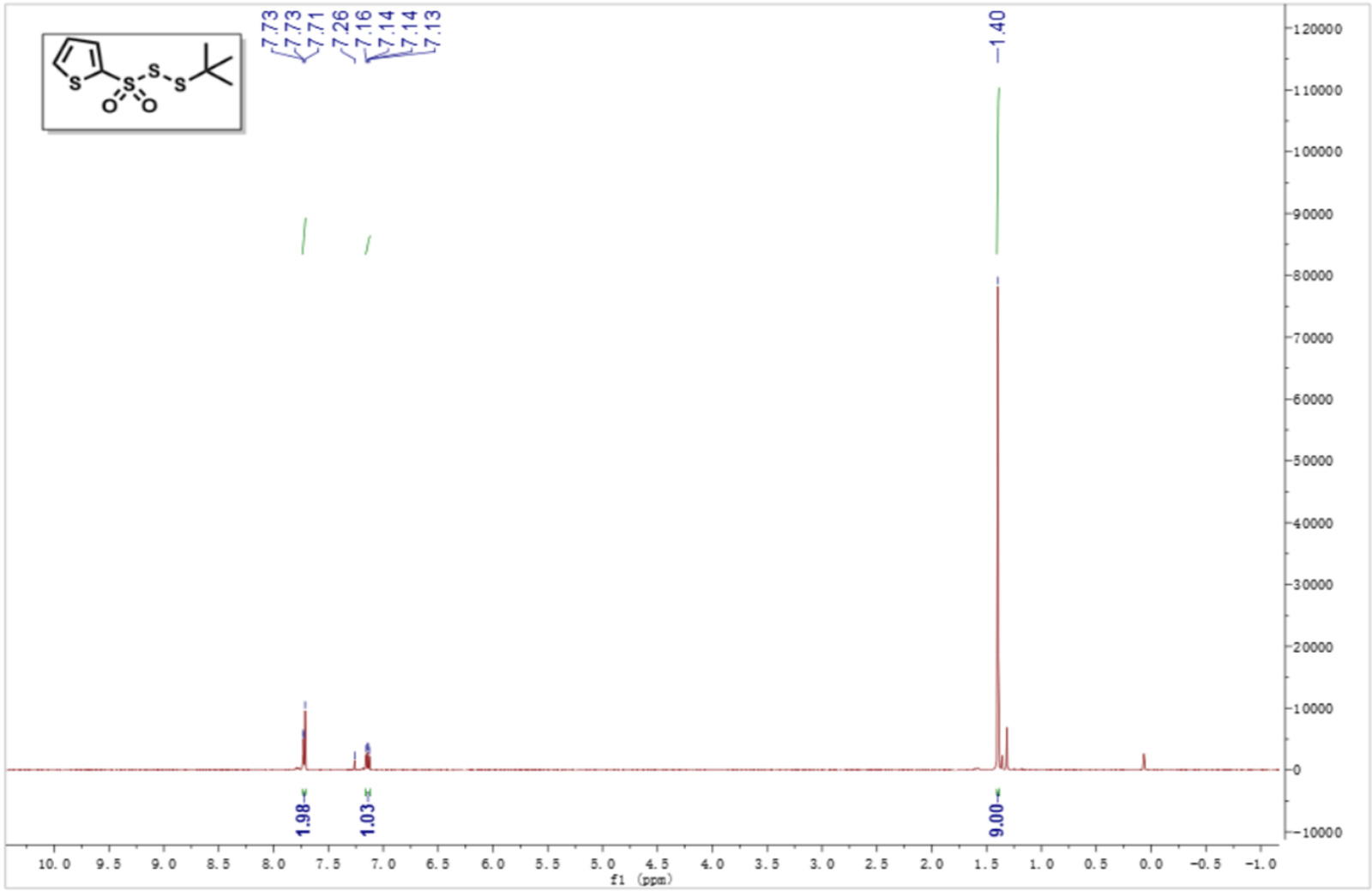
^{1}H NMR of 3j



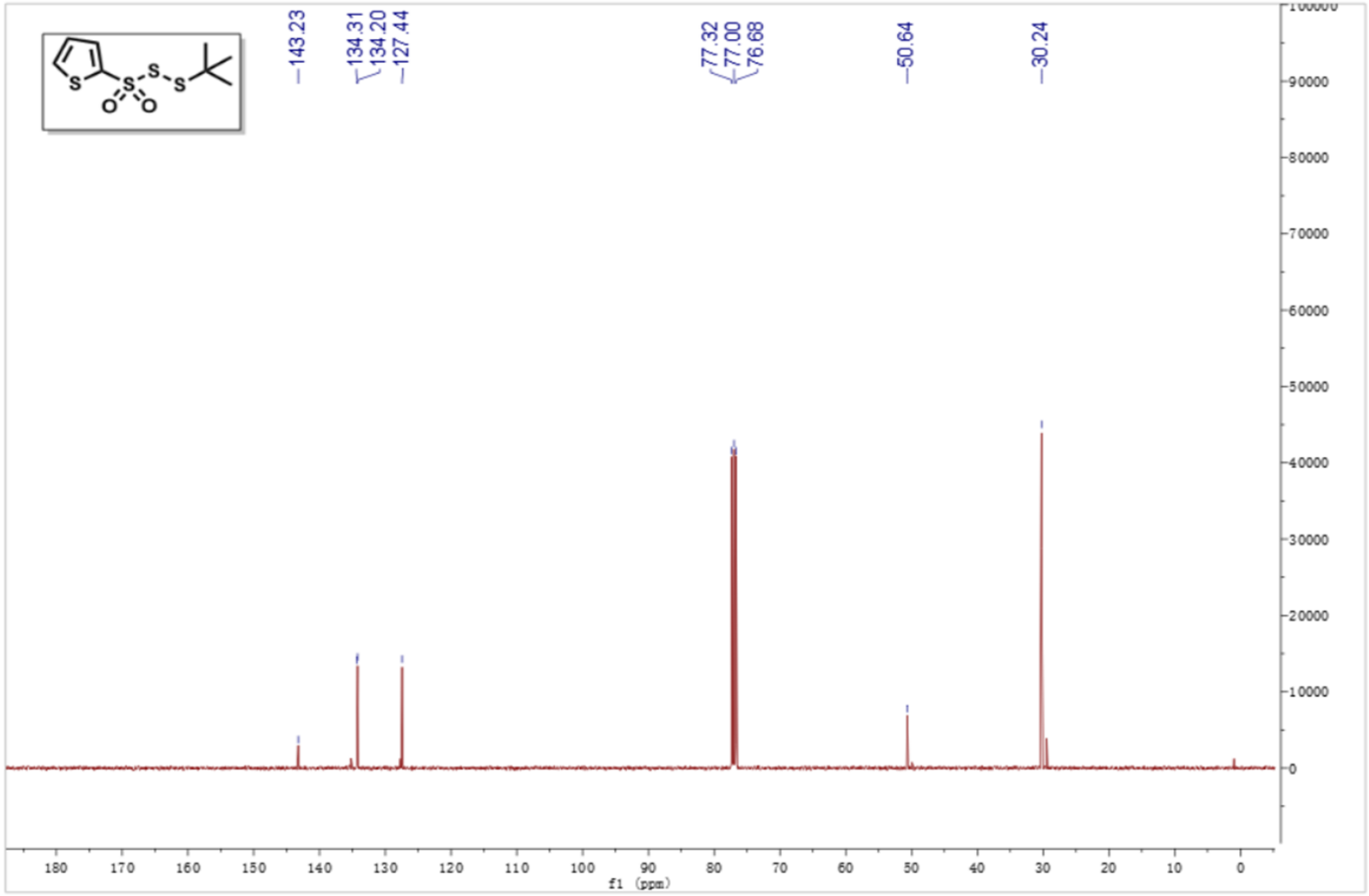
^{13}C NMR of 3j



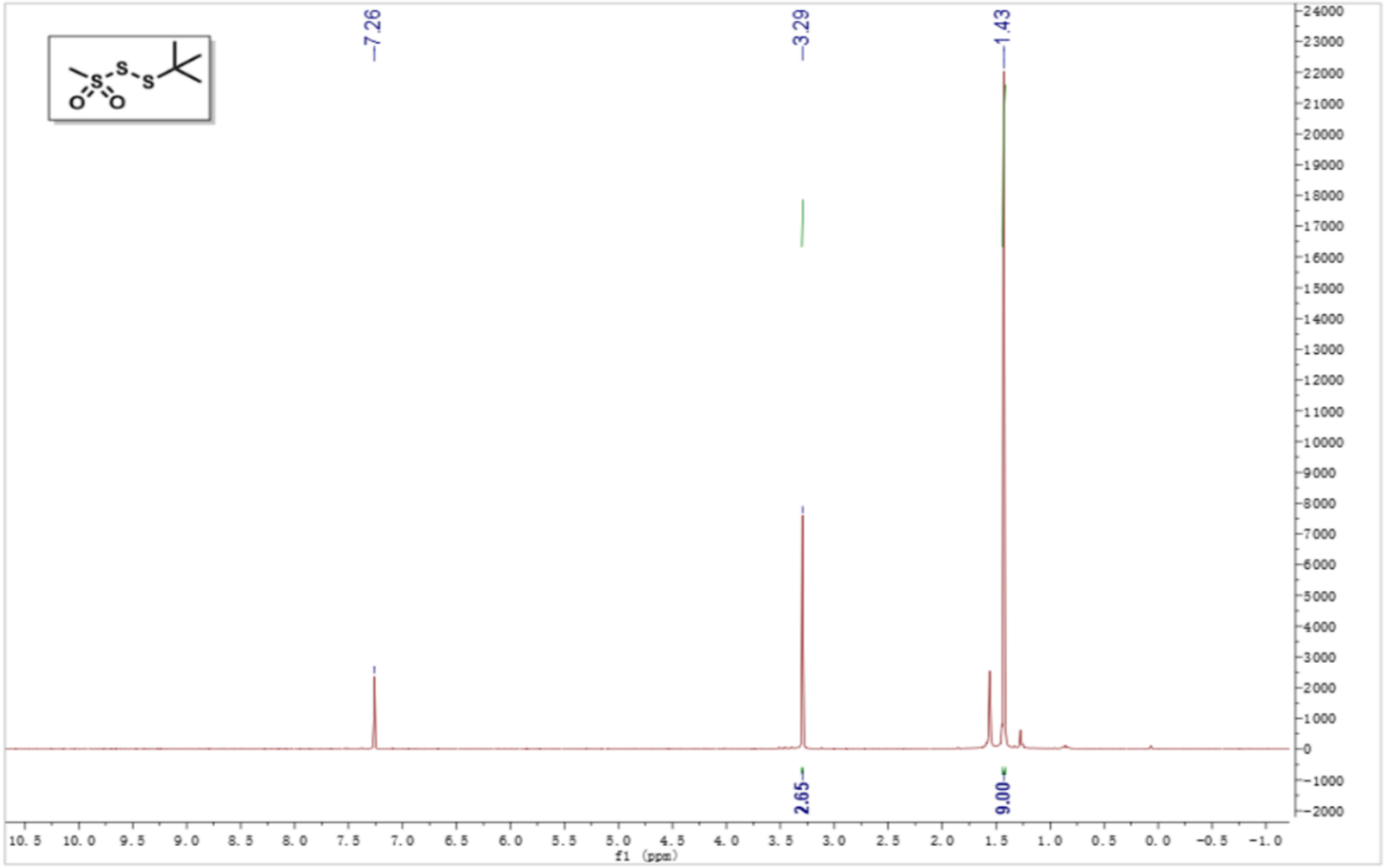
^{1}H NMR of 3k



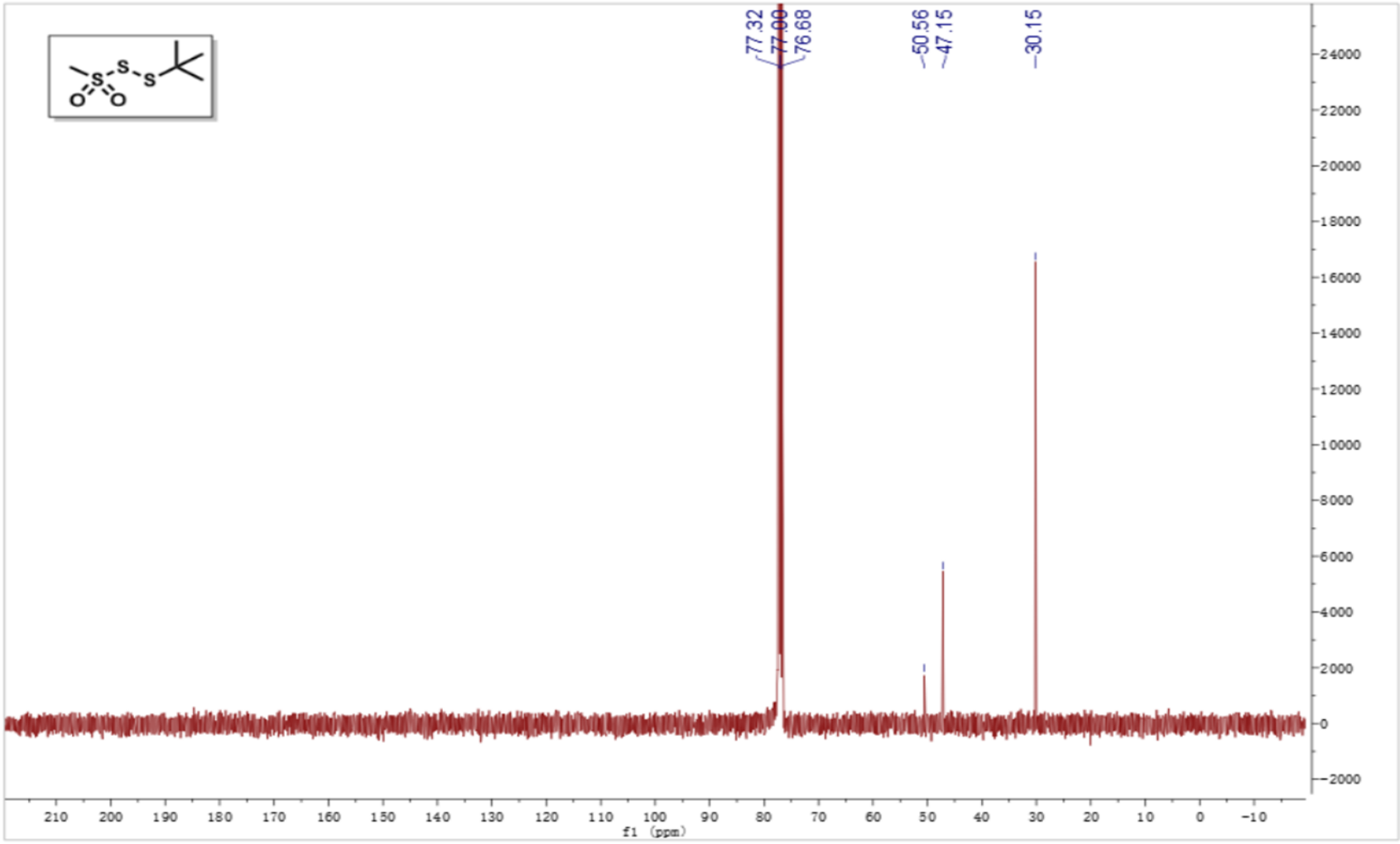
^{13}C NMR of 3k



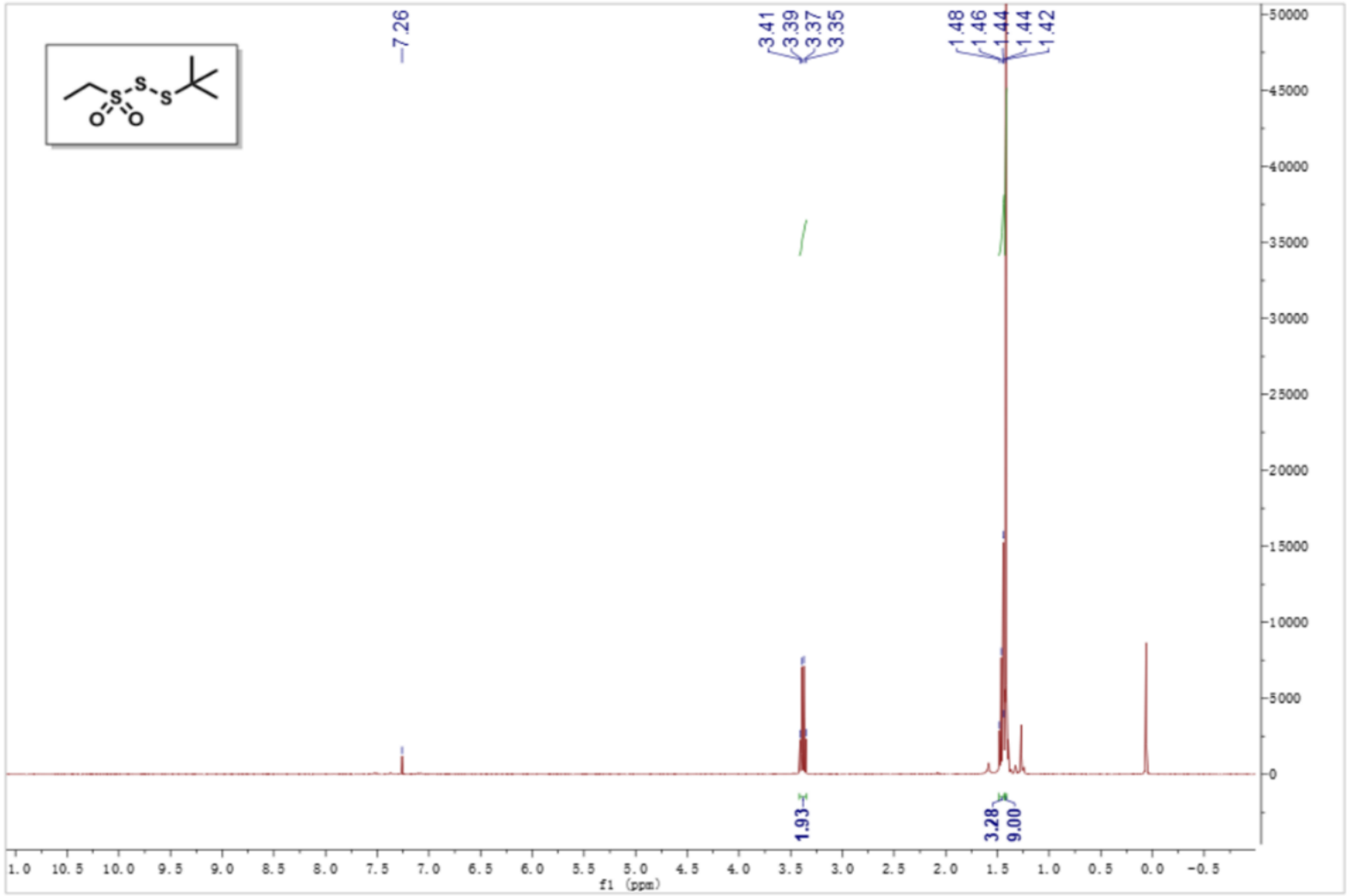
^{1}H NMR of 3l



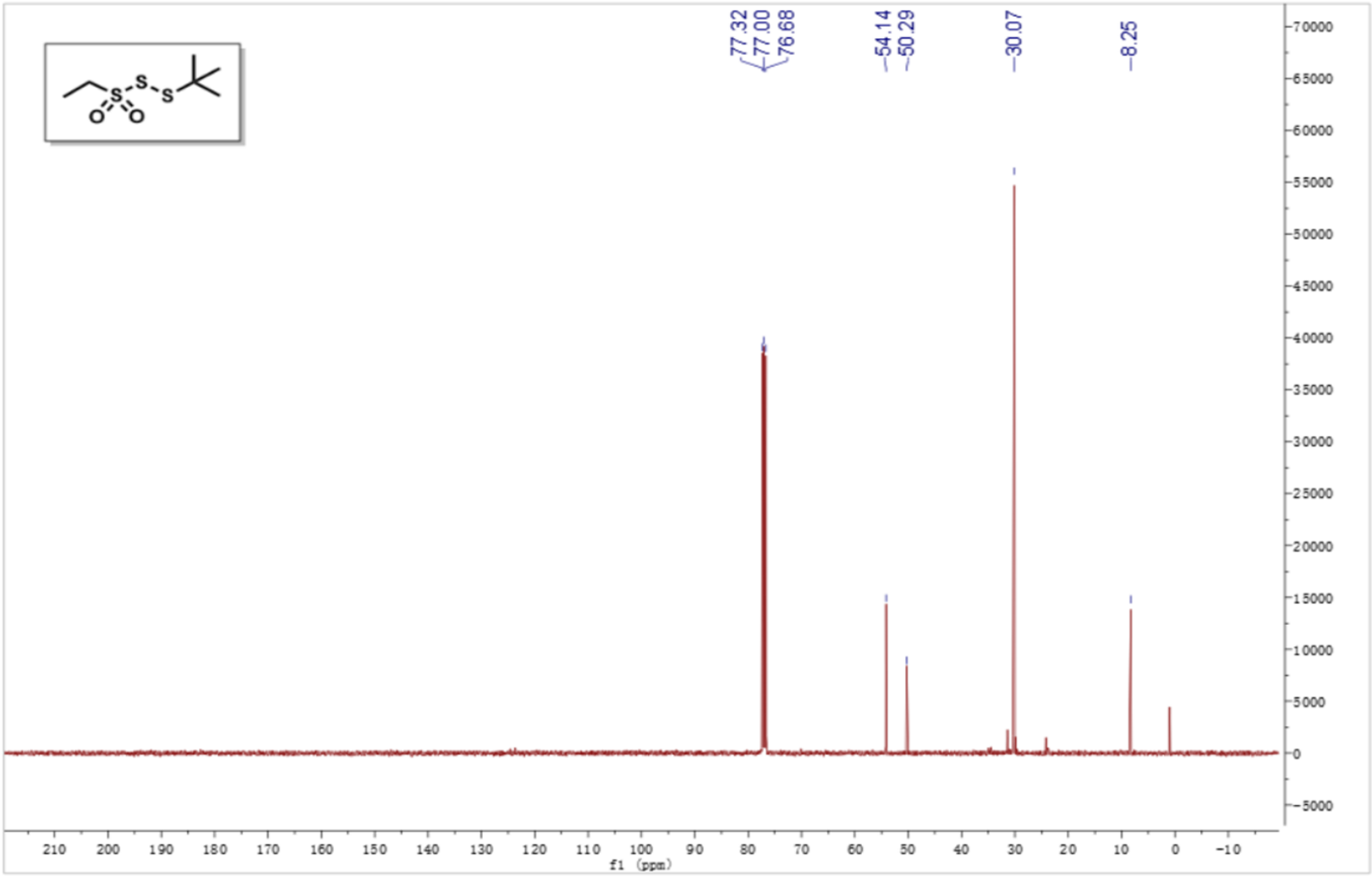
^{13}C NMR of 3l


77.32
77.00
76.68
50.56
47.15
30.15
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

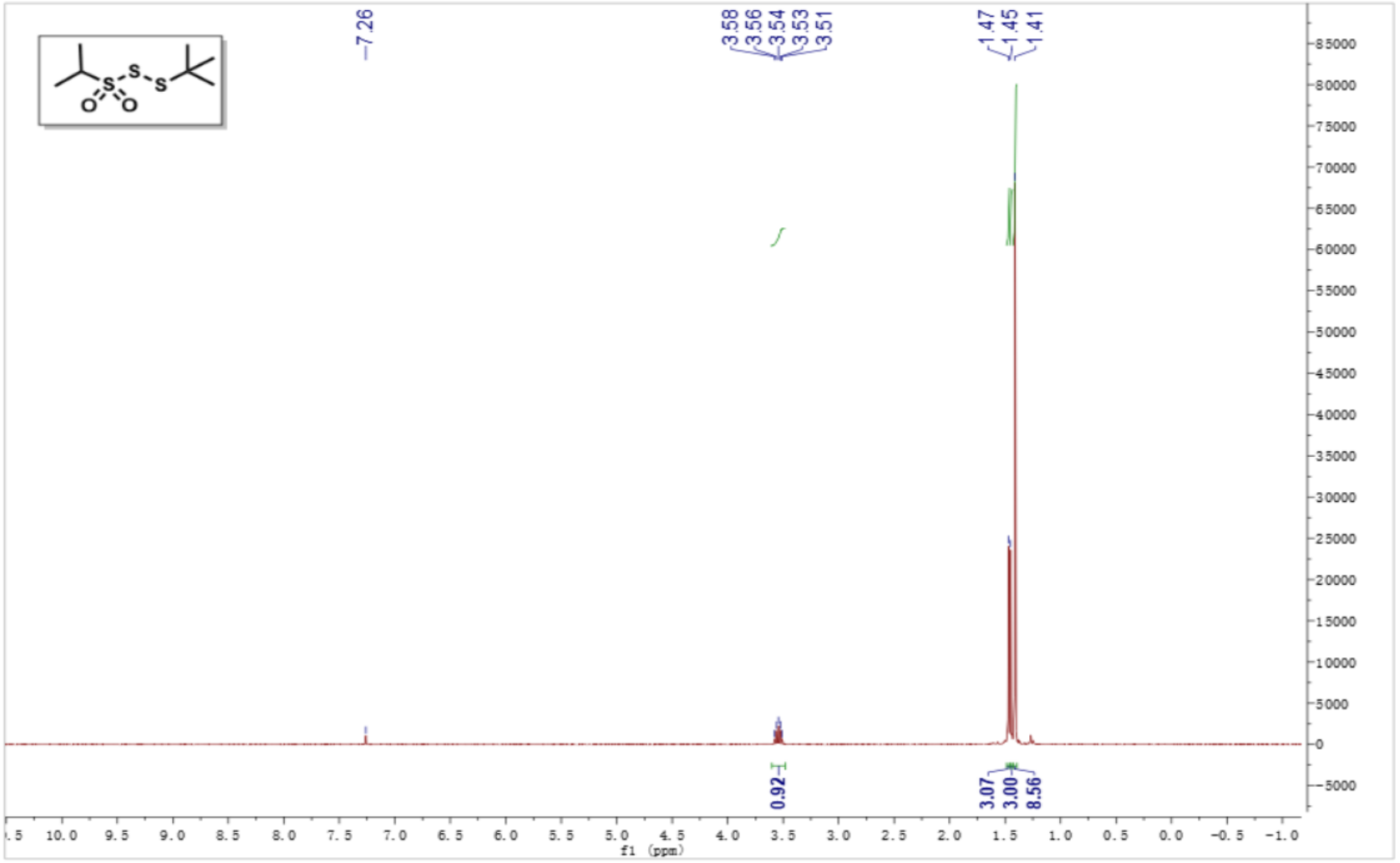
^{1}H NMR of 3m



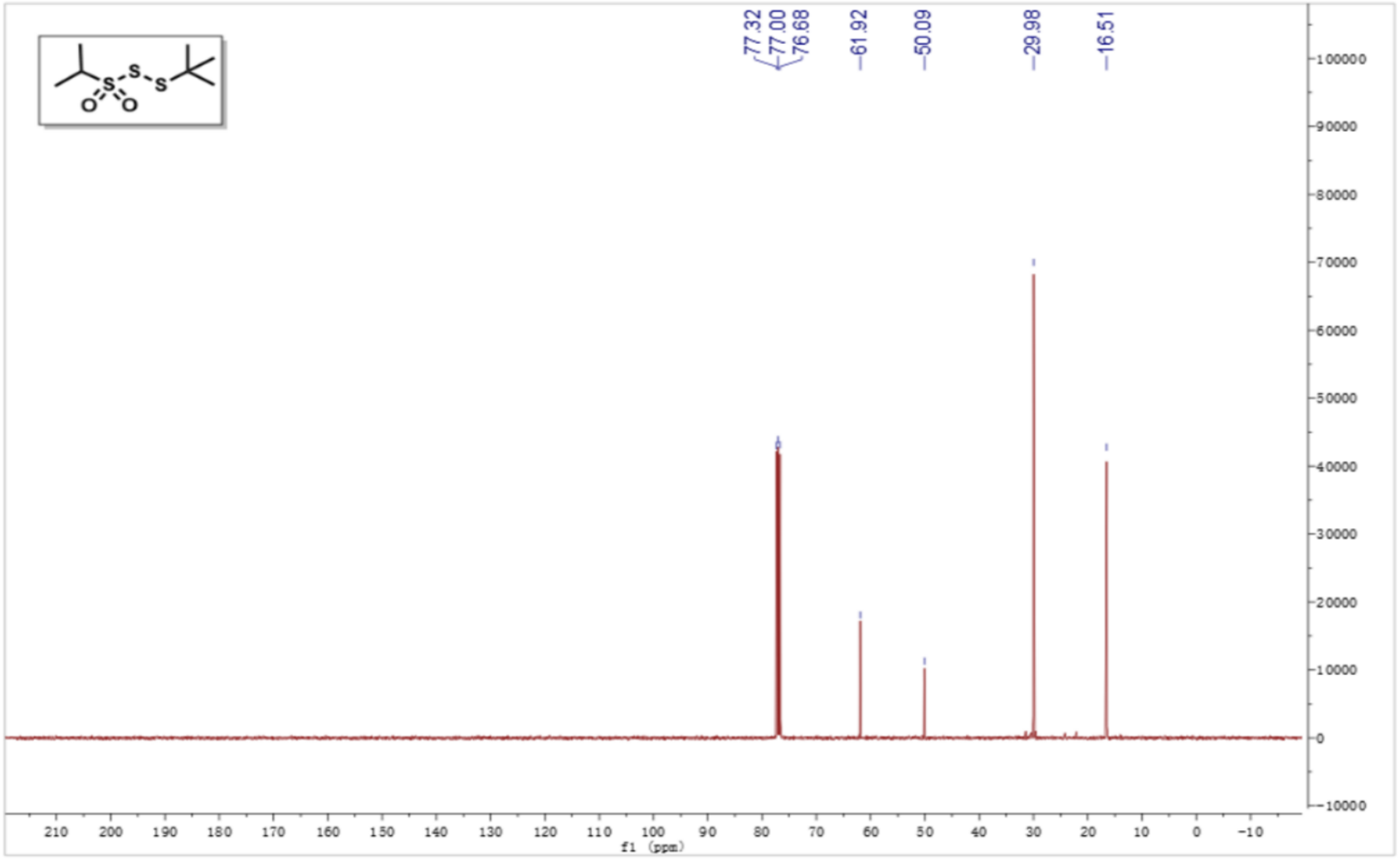
^{13}C NMR of 3m



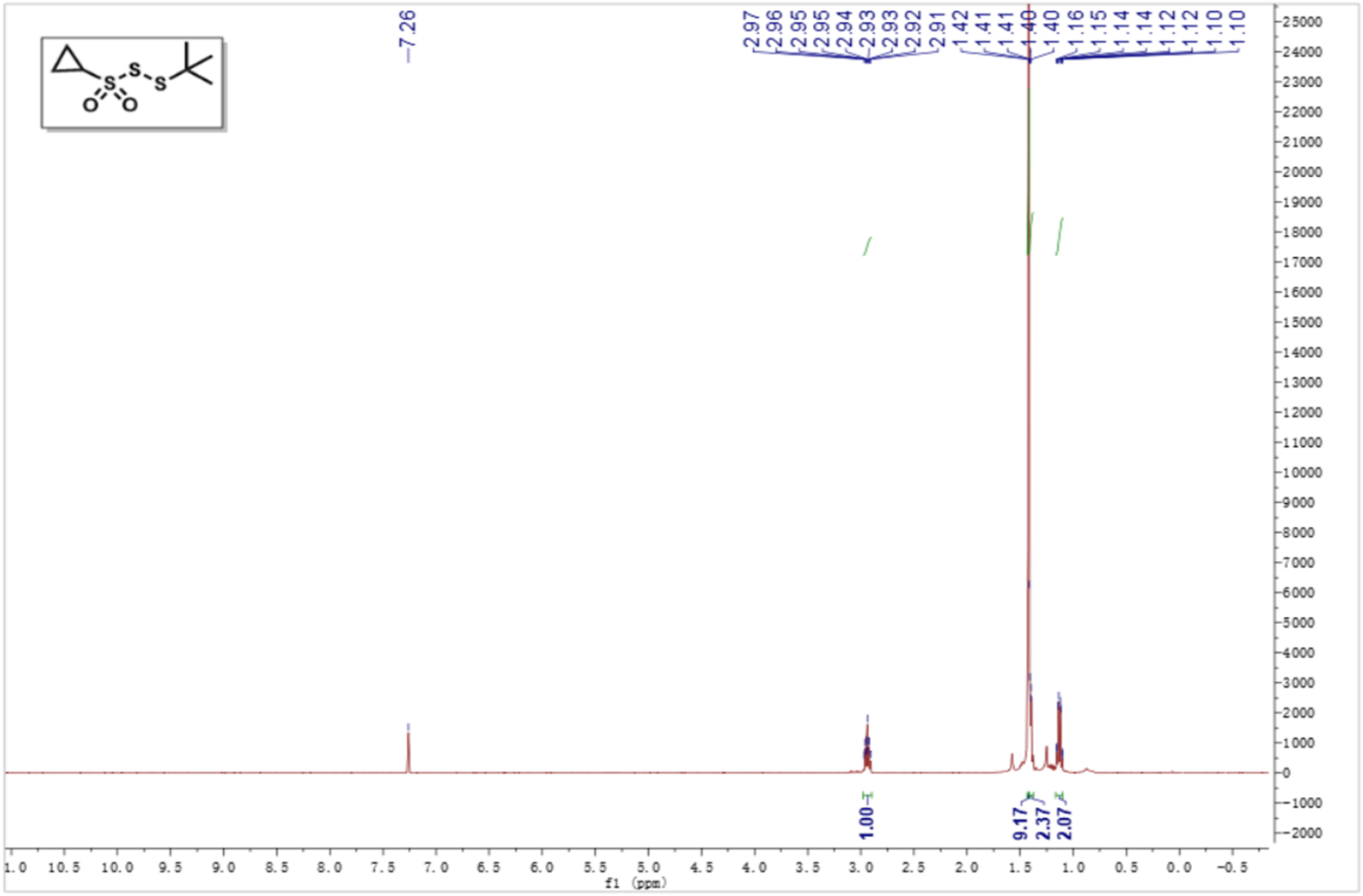
^{1}H NMR of 3n



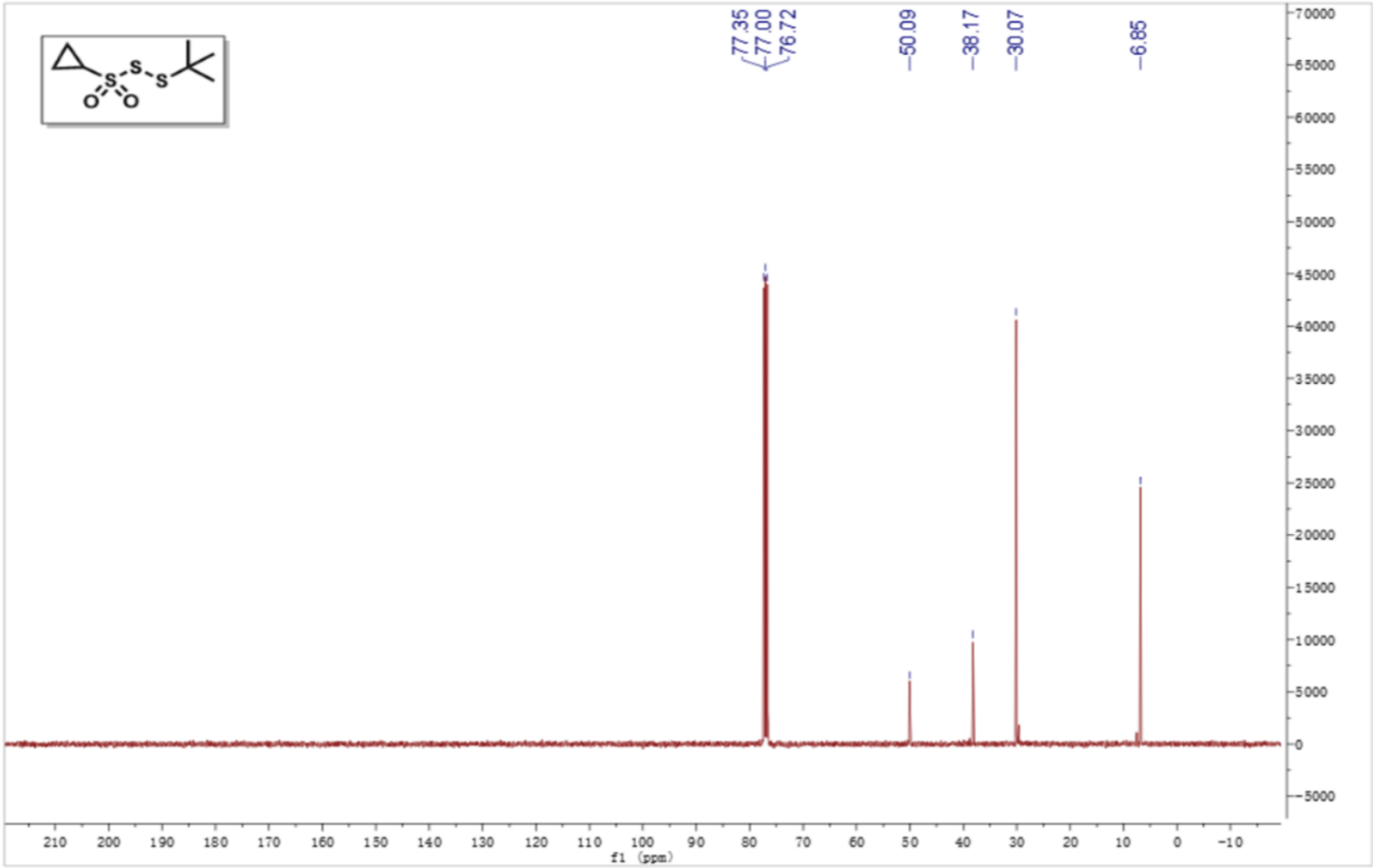
^{13}C NMR of 3n


77.32
77.00
76.68
61.92
50.09
29.98
16.51
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

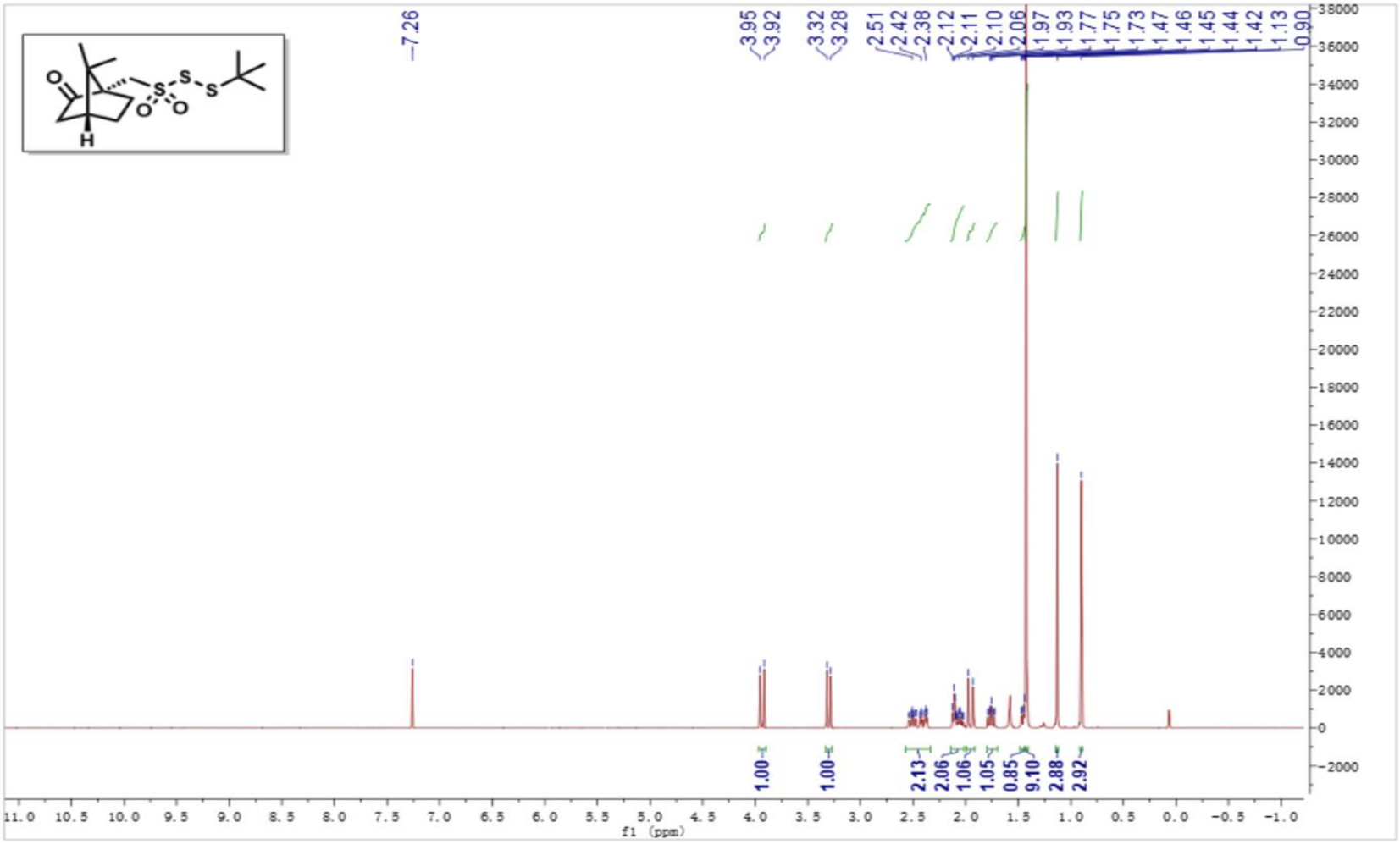
^{1}H NMR of 3o


7.26
2.97
2.96
2.95
2.95
2.94
2.93
2.93
2.92
2.91
1.42
1.41
1.41
1.40
1.40
1.16
1.15
1.14
1.14
1.12
1.12
1.10
1.10
1.00
9.17
2.37
2.07
f1 (ppm)

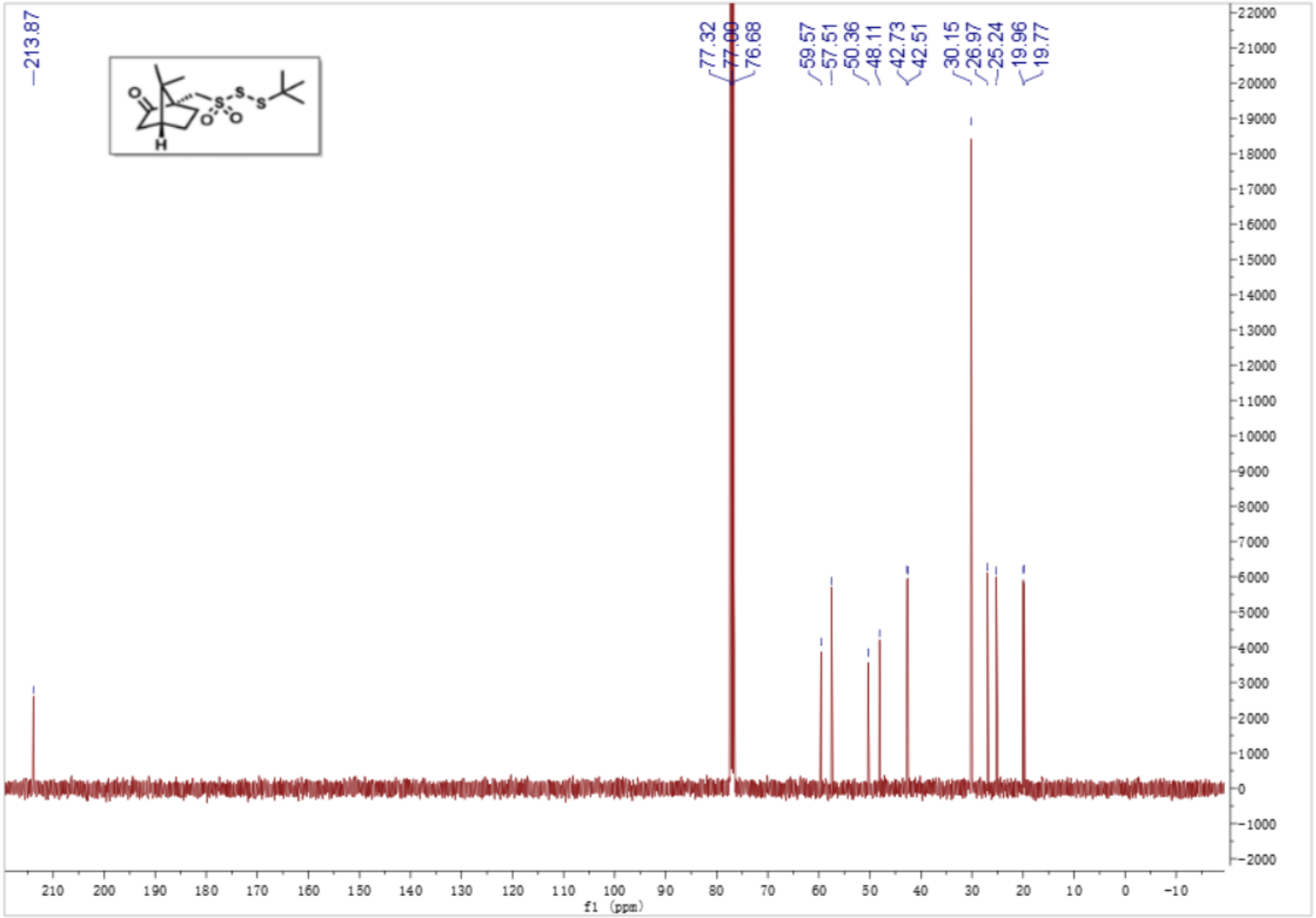
^{13}C NMR of 3o



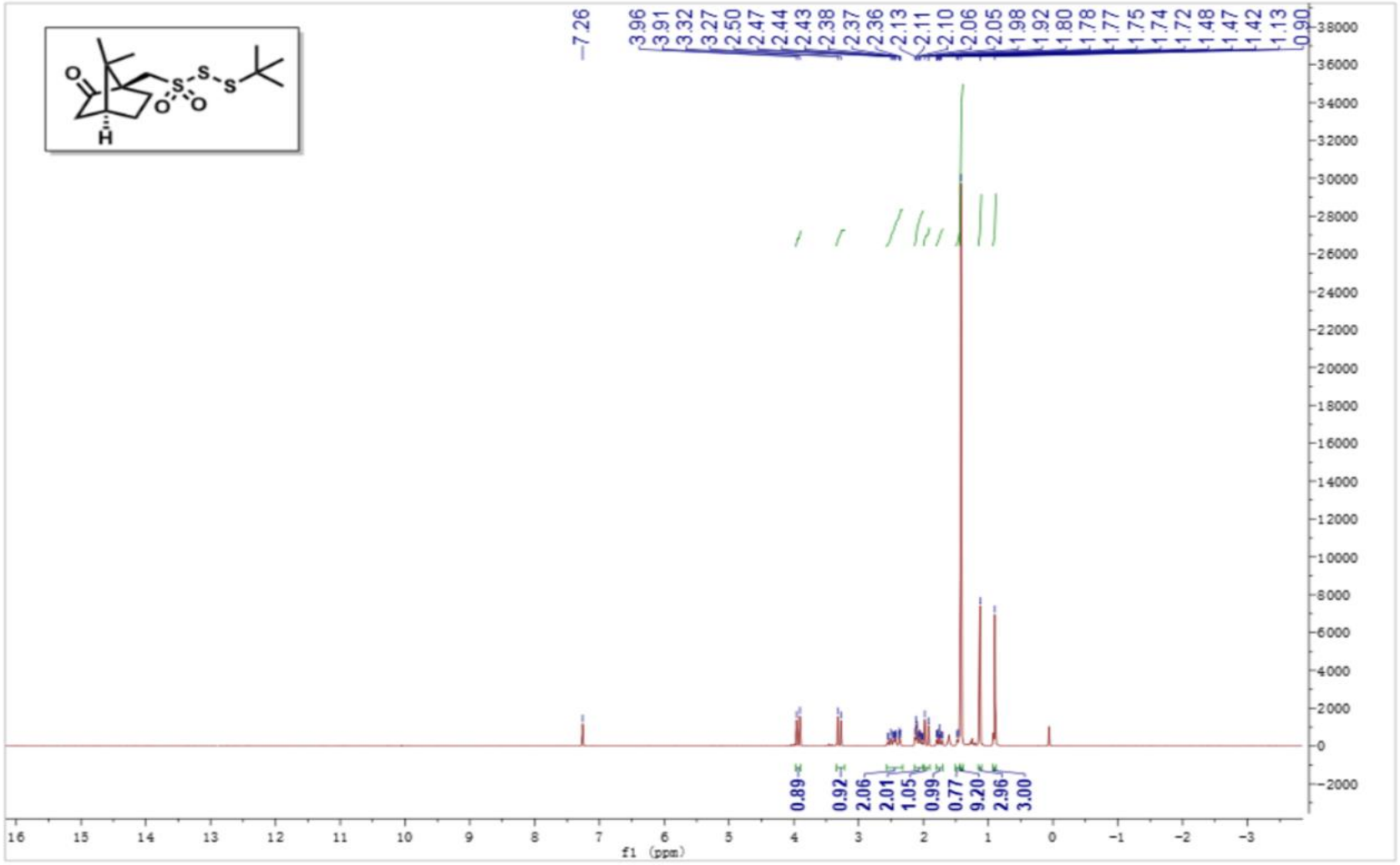
^{1}H NMR of 3p


7.26
3.95
3.92
3.32
3.28
2.51
2.42
2.38
2.12
2.11
2.10
2.06
1.97
1.93
1.77
1.75
1.73
1.47
1.46
1.45
1.44
1.42
1.13
0.90
1.00
1.00
2.13
2.06
1.06
1.05
0.85
9.10
2.88
2.92
f1 (ppm)

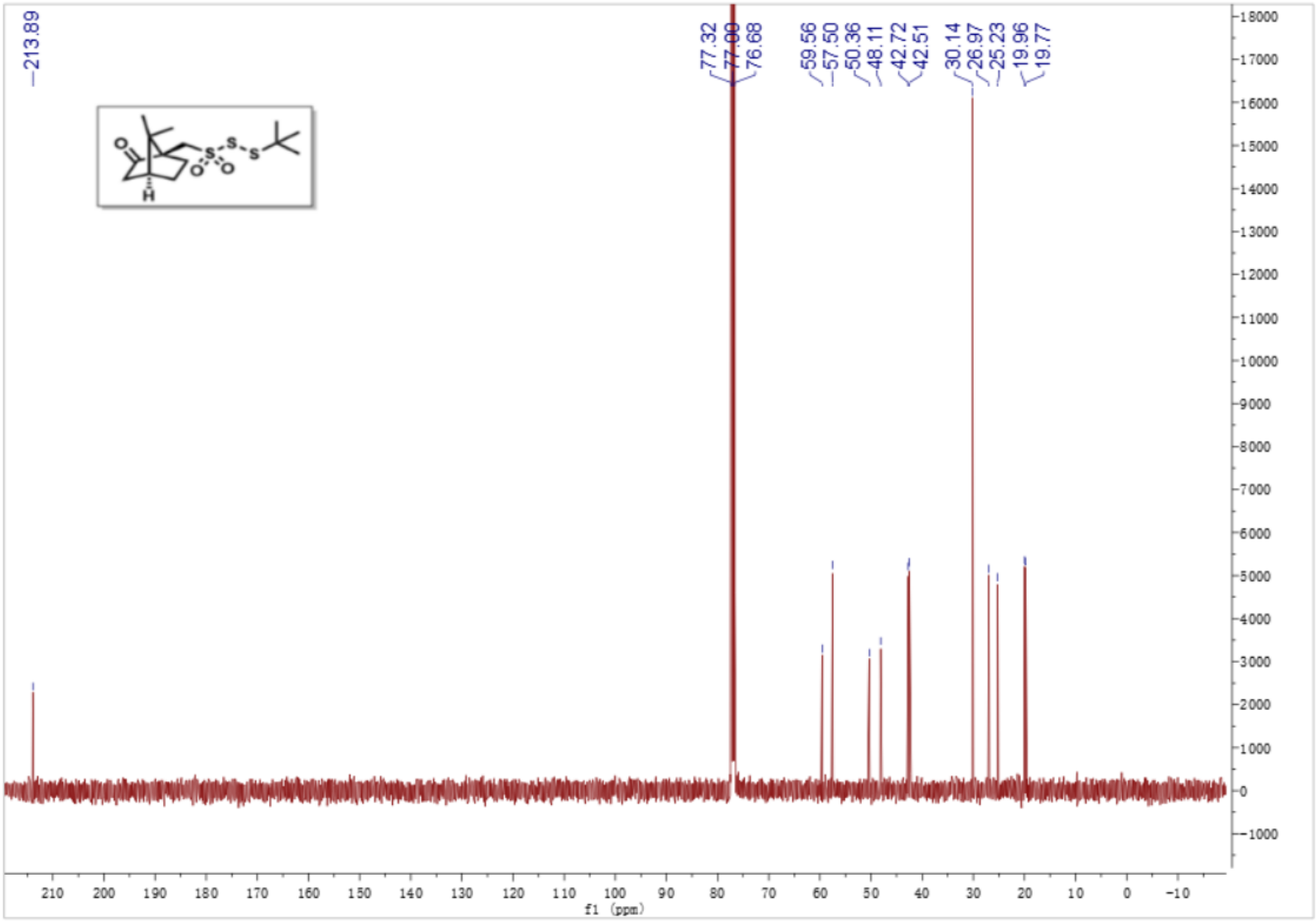
^{13}C NMR of 3p


213.87
77.32
77.00
76.68
59.57
57.51
50.36
48.11
42.73
42.51
30.15
26.97
25.24
19.96
19.77
f1 (ppm)

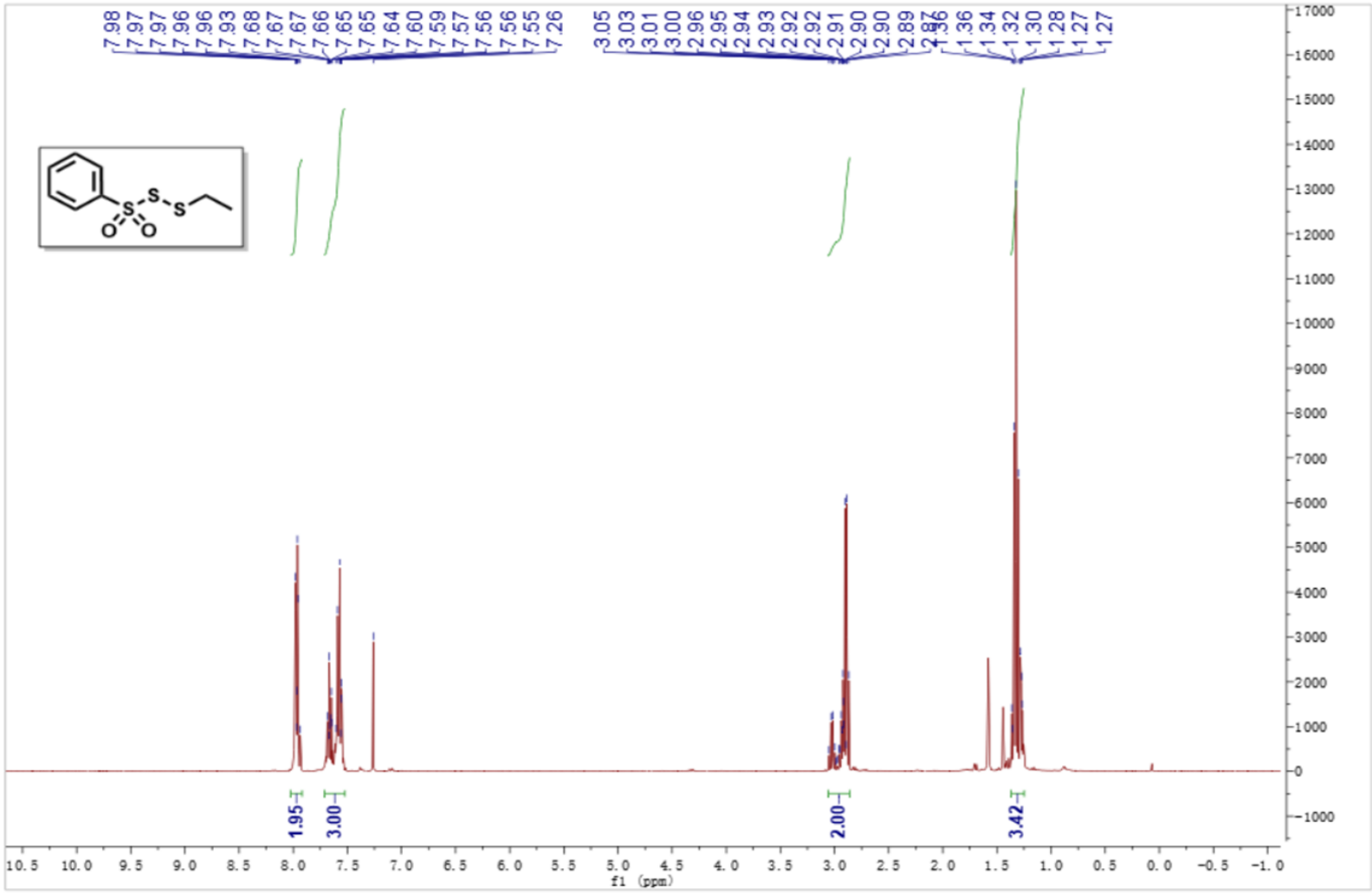
^{1}H NMR of 3q


7.26
3.96
3.91
3.32
3.27
2.50
2.47
2.44
2.43
2.38
2.37
2.36
2.13
2.11
2.10
2.06
2.05
1.98
1.92
1.80
1.78
1.77
1.75
1.74
1.72
1.48
1.47
1.42
1.13
0.90
0.89
0.92
2.06
2.01
1.05
0.99
0.77
9.20
2.96
3.00
f1 (ppm)

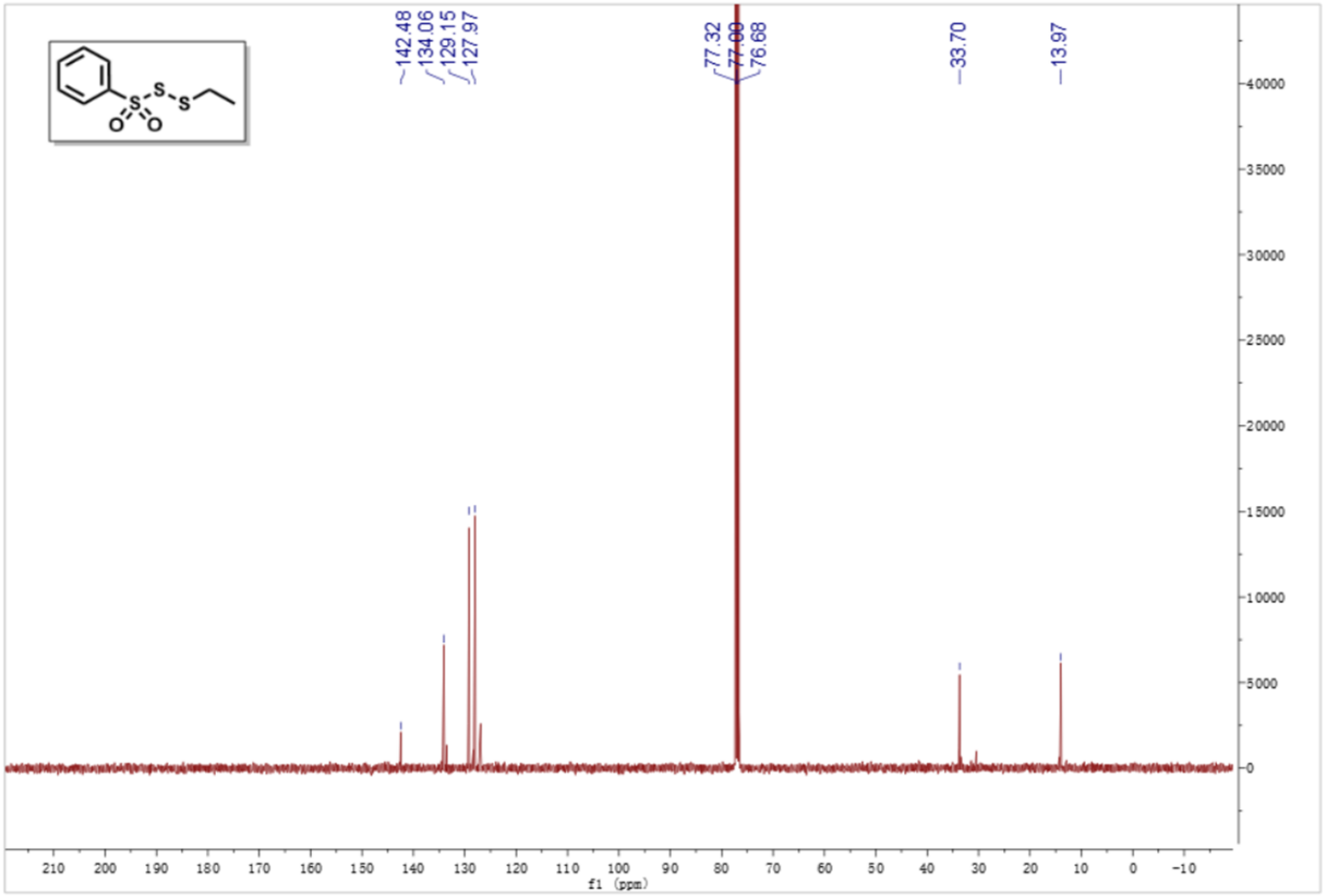
^{13}C NMR of 3q


213.89
77.32
77.00
76.68
59.56
57.50
50.36
48.11
42.72
42.51
30.14
26.97
25.23
19.96
19.77
f1 (ppm)

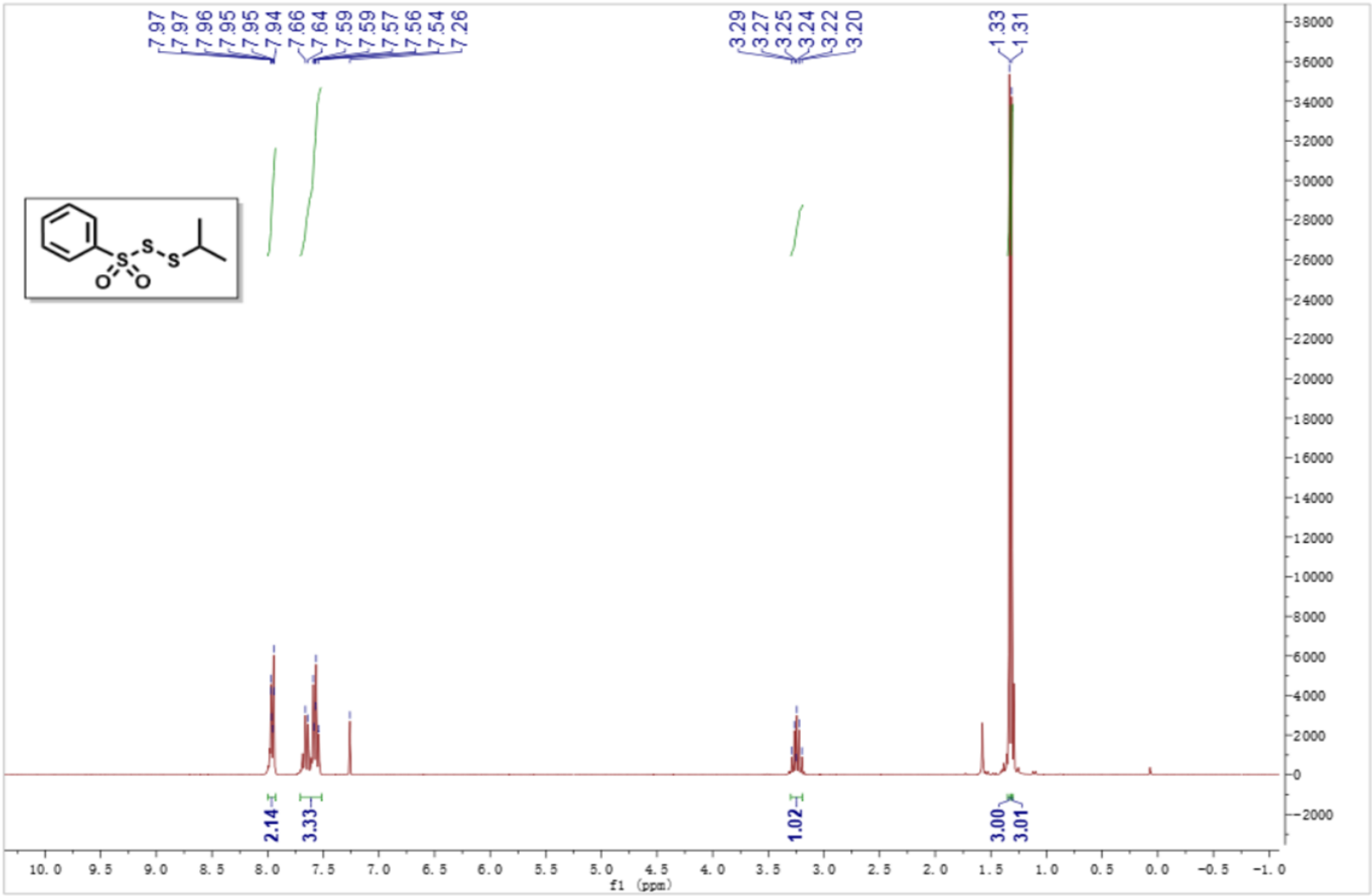
^{1}H NMR of 3r


7.98
7.97
7.97
7.96
7.96
7.93
7.68
7.67
7.67
7.66
7.65
7.65
7.64
7.60
7.59
7.57
7.56
7.56
7.55
7.26
3.05
3.03
3.01
3.00
2.96
2.95
2.94
2.93
2.92
2.92
2.91
2.90
2.90
2.89
1.36
1.34
1.32
1.30
1.28
1.27
1.27
S
S
S
O
O
1.95
3.00
2.00
3.42
f1 (ppm)

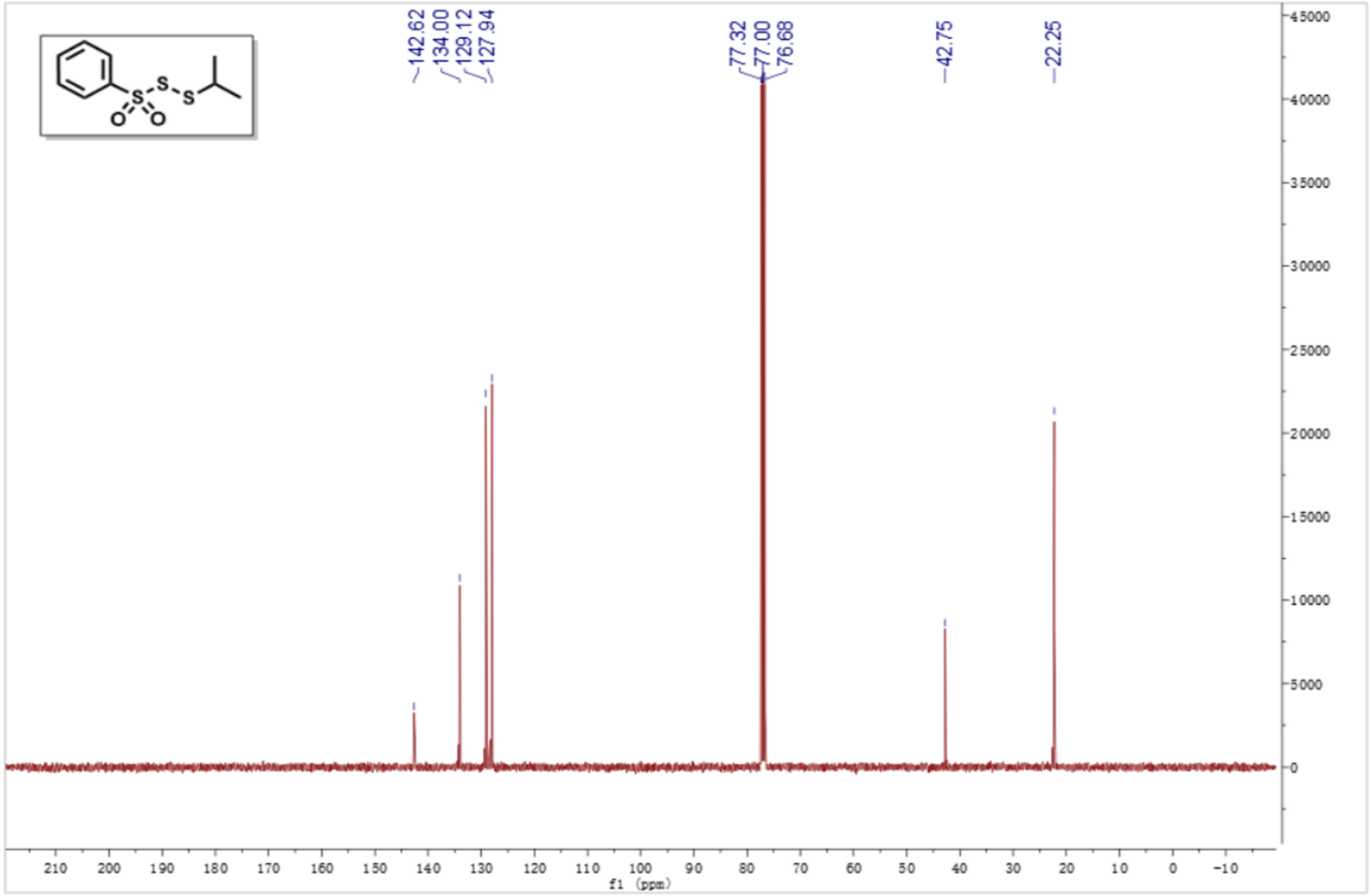
^{13}C NMR of 3r


142.48
134.06
129.15
127.97
77.32
77.00
76.68
33.70
13.97
40000
35000
30000
25000
20000
15000
10000
5000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

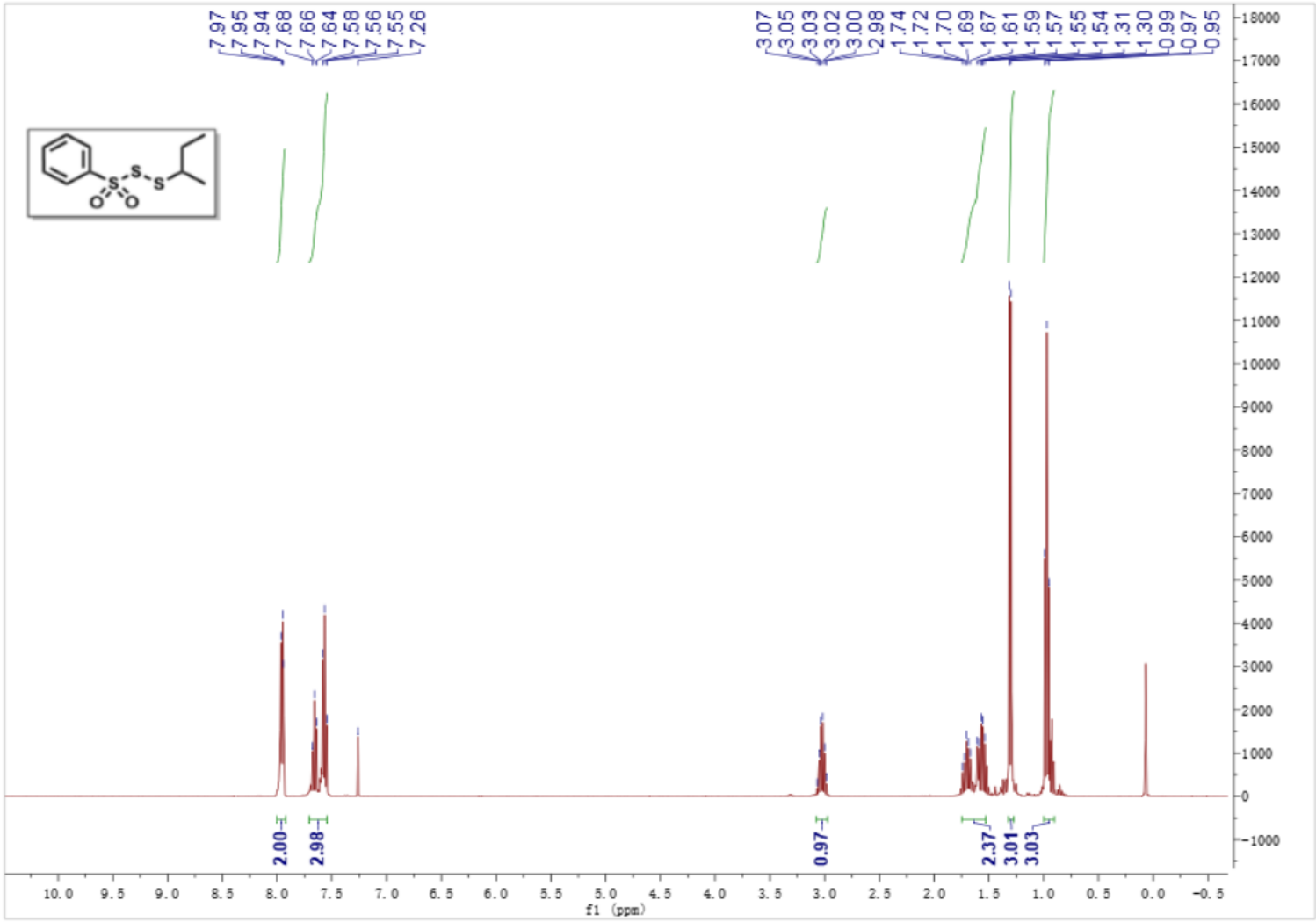
^{1}H NMR of 3s


7.97
7.97
7.96
7.95
7.95
7.94
7.66
7.64
7.59
7.59
7.57
7.56
7.54
7.26
3.29
3.27
3.25
3.24
3.22
3.20
1.33
1.31
2.14
3.33
1.02
3.00
3.01
f1 (ppm)

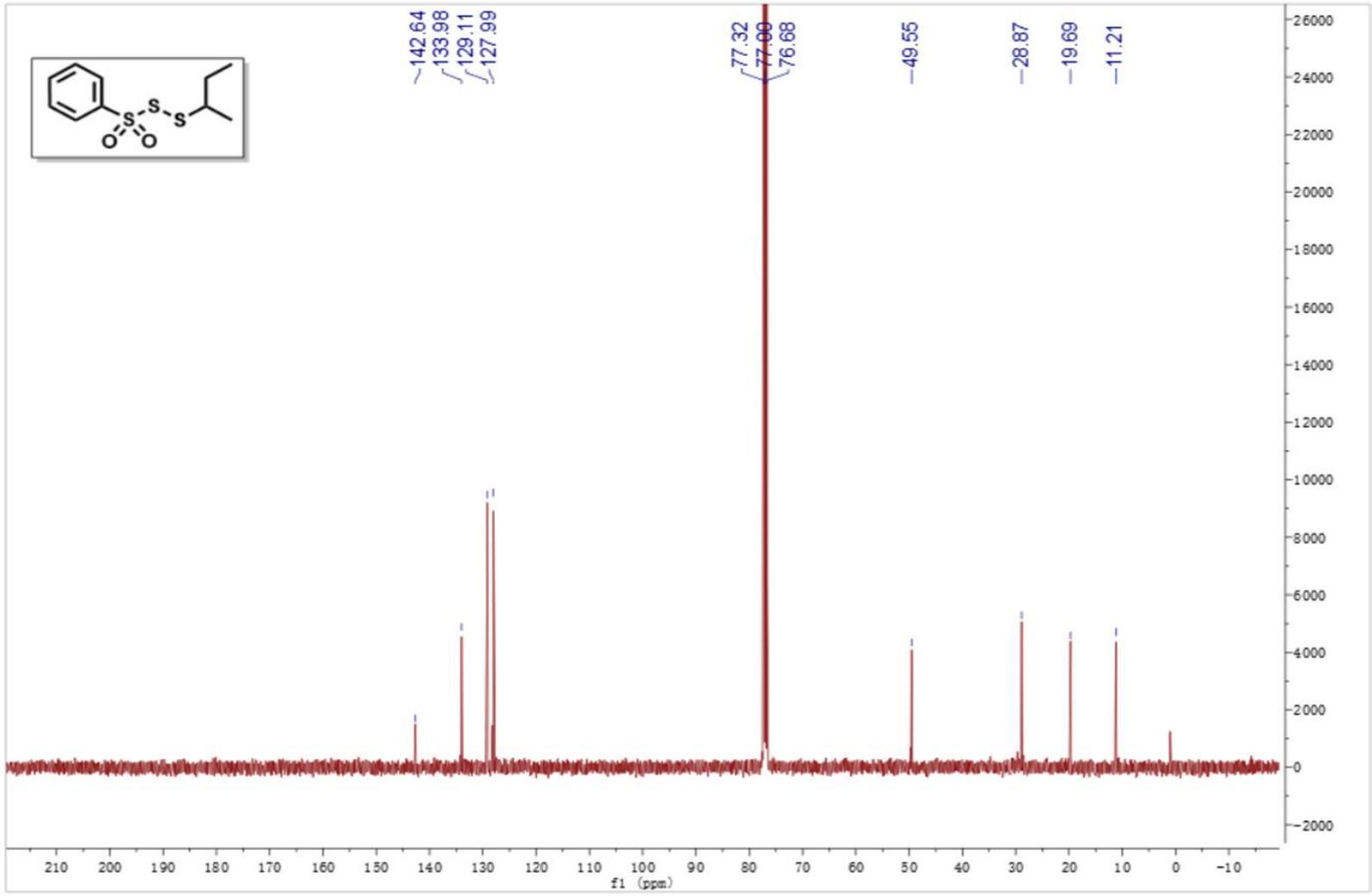
^{13}C NMR of 3s


142.62
134.00
129.12
127.94
77.32
77.00
76.68
42.75
22.25
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

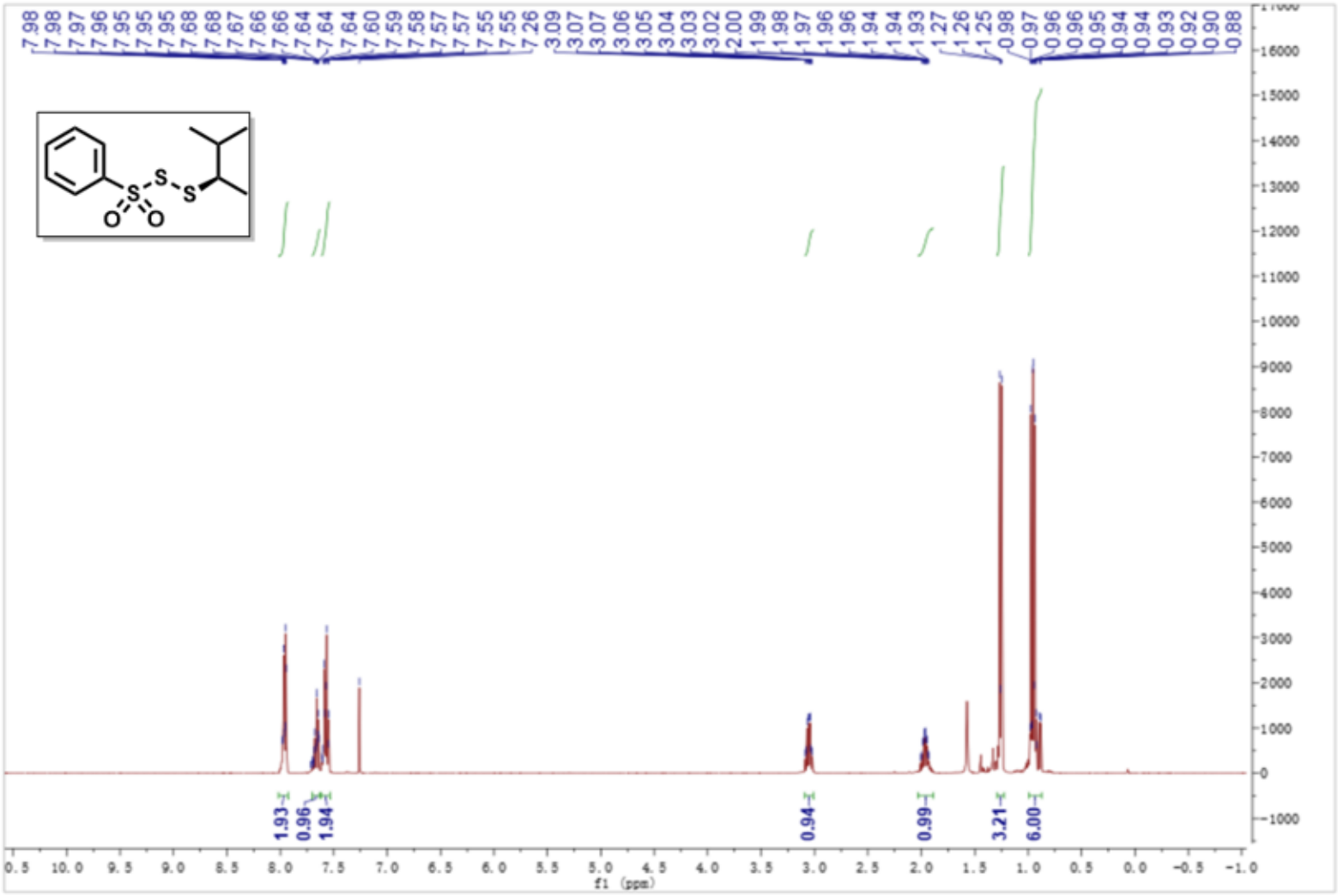
^{1}H NMR of 3t


7.97
7.95
7.94
7.68
7.66
7.64
7.58
7.56
7.55
7.26
3.07
3.05
3.03
3.02
3.00
2.98
1.74
1.72
1.70
1.69
1.67
1.61
1.59
1.57
1.55
1.54
1.31
1.30
0.99
0.97
0.95
2.00
2.98
0.97
2.37
3.01
3.03
f1 (ppm)

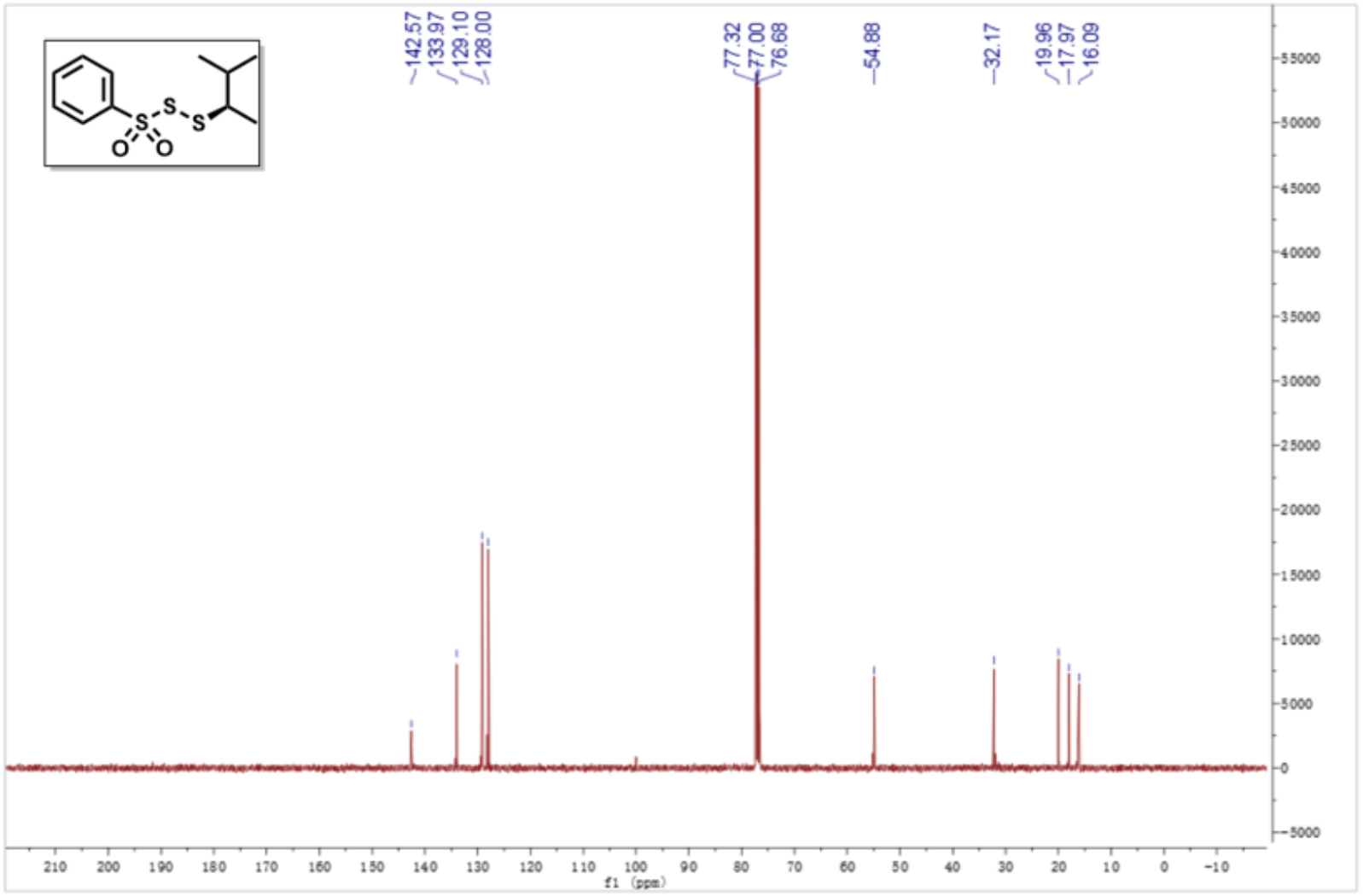
^{13}C NMR of 3t


142.64
133.98
129.11
127.99
77.32
77.00
76.68
49.55
28.87
19.69
11.21
f1 (ppm)

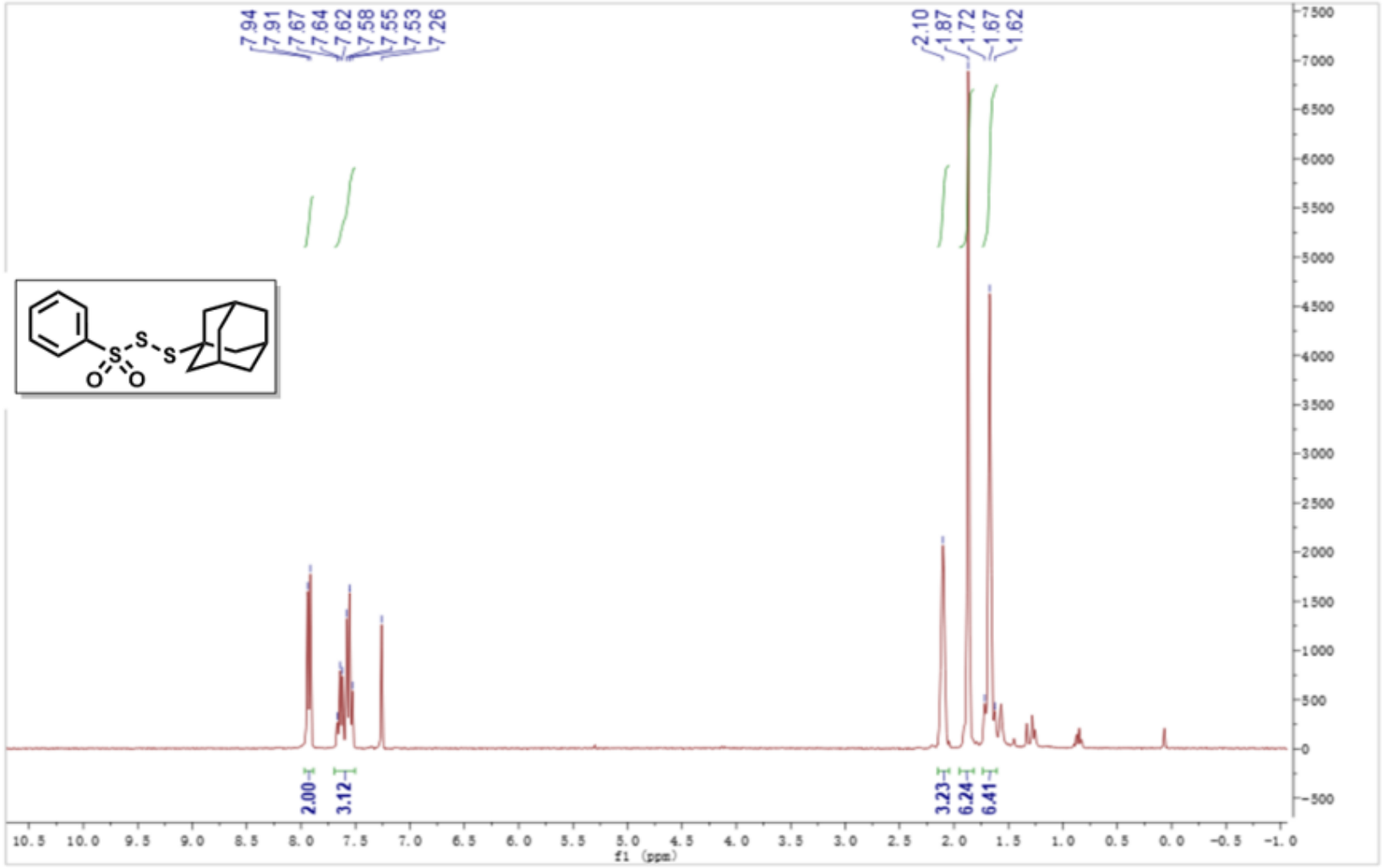
^{1}H NMR of 3u


7.98 7.98 7.97 7.96 7.95 7.95 7.95 7.68 7.68 7.67 7.66 7.66 7.64 7.64 7.64 7.60 7.59 7.58 7.57 7.57 7.55 7.55 7.26 3.09 3.07 3.07 3.06 3.05 3.04 3.03 3.02 2.00 1.99 1.98 1.97 1.96 1.96 1.94 1.94 1.93 1.27 1.26 1.25 0.98 0.97 0.96 0.96 0.95 0.94 0.94 0.93 0.92 0.90 0.88
1.93 0.96 1.94 0.94 0.99 3.21 6.00
f1 (ppm)

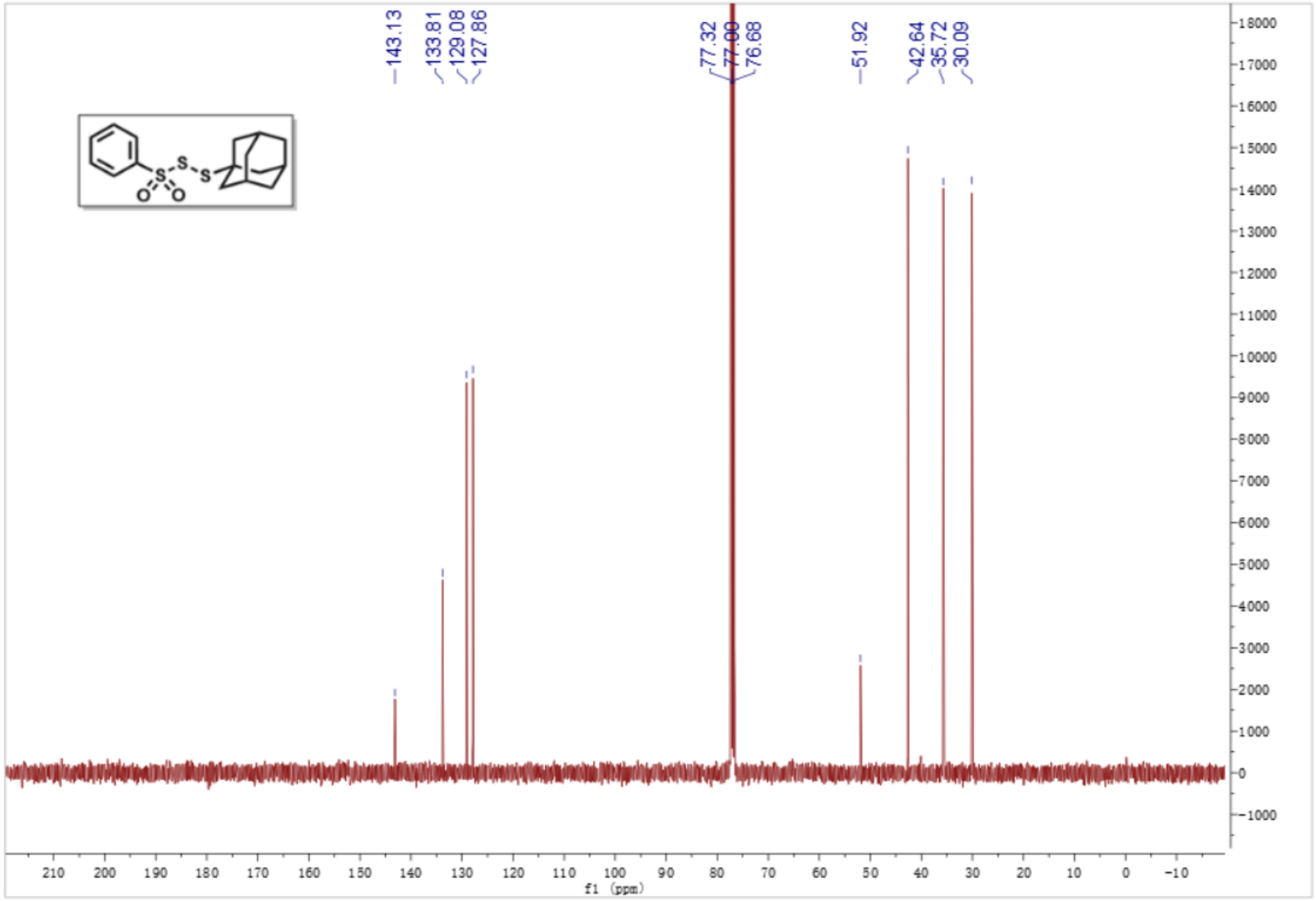
^{13}C NMR of 3u


142.57
133.97
129.10
128.00
77.32
77.00
76.68
54.88
32.17
19.96
17.97
16.09
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

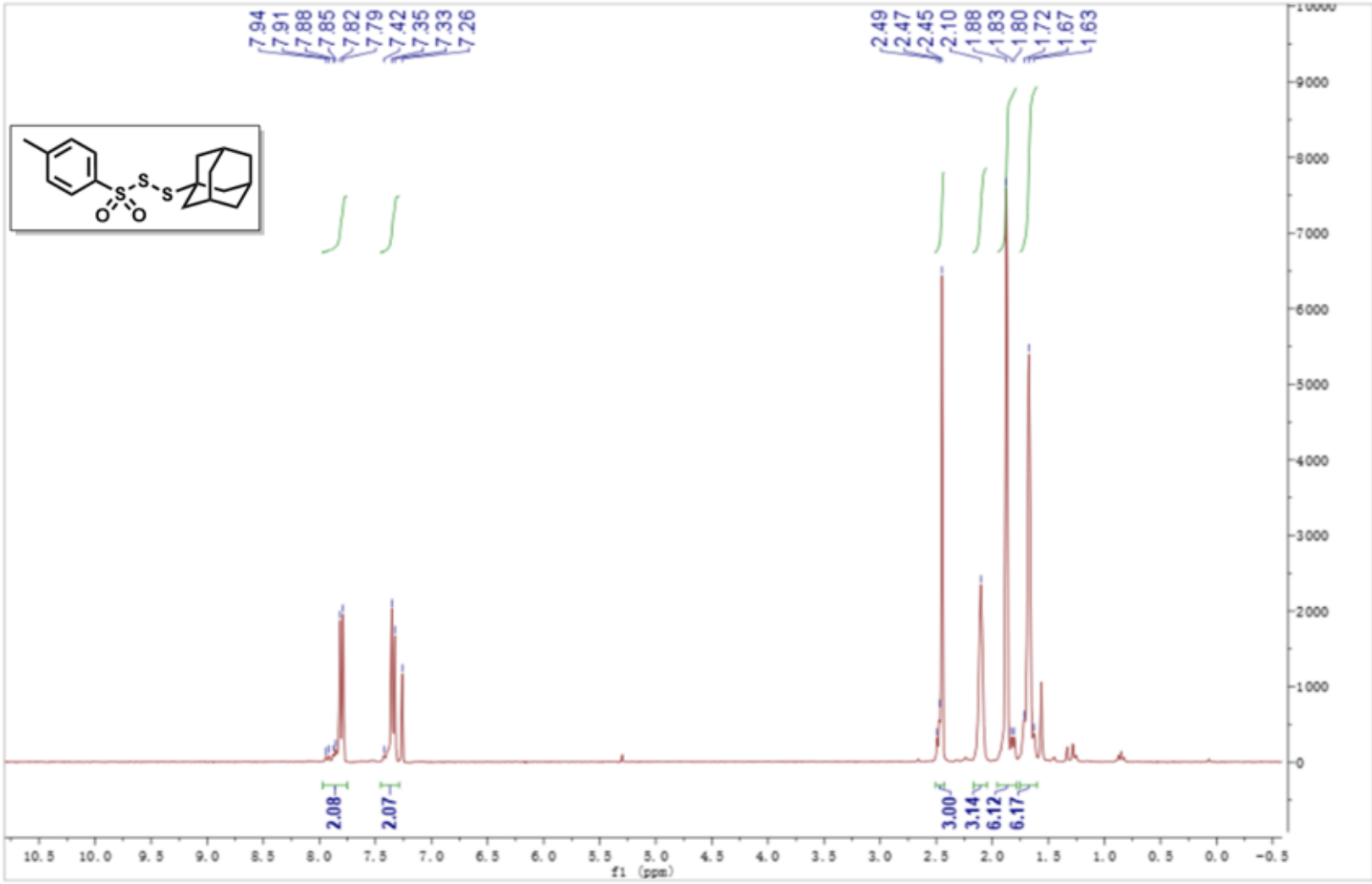
^{1}H NMR of 3v


7.94
7.91
7.67
7.64
7.62
7.58
7.55
7.53
7.26
2.10
1.87
1.72
1.67
1.62
2.00
3.12
3.23
6.24
6.41
f1 (ppm)

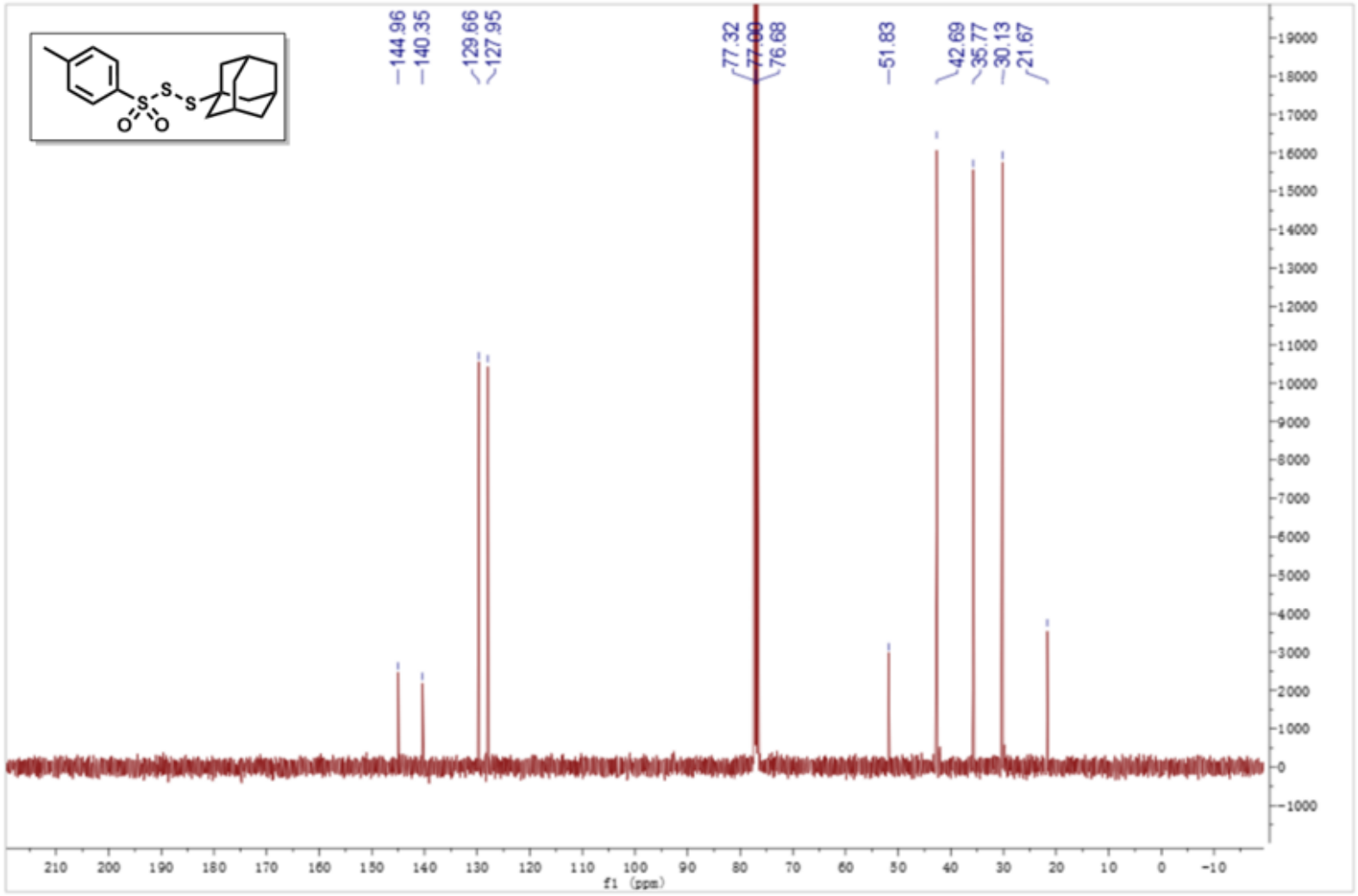
^{13}C NMR of 3v


143.13
133.81
129.08
127.86
77.32
77.00
76.68
51.92
42.64
35.72
30.09
f1 (ppm)

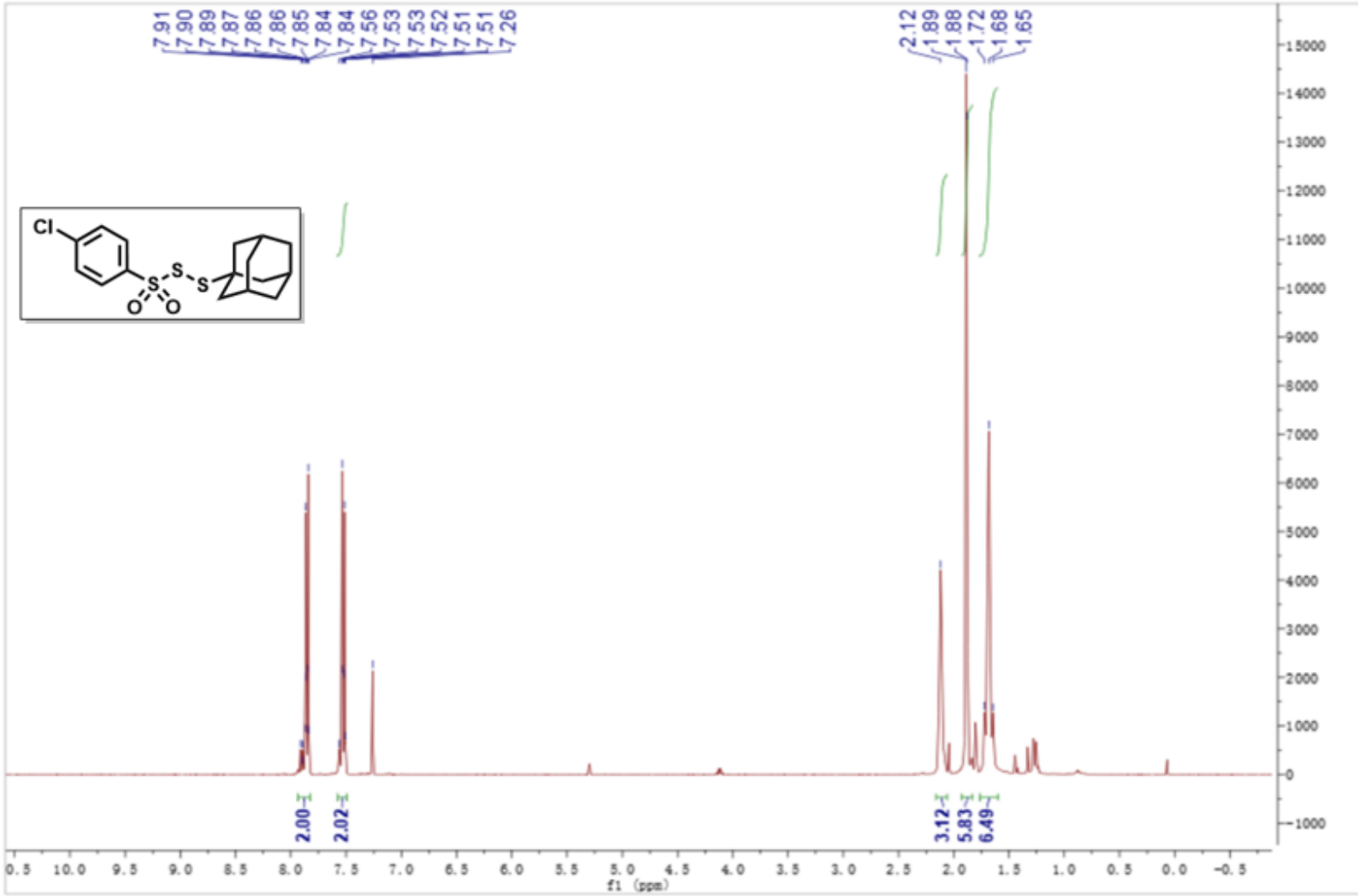
^{1}H NMR of 3w


7.94
7.91
7.88
7.85
7.82
7.79
7.42
7.35
7.33
7.26
2.49
2.47
2.45
2.10
1.88
1.83
1.80
1.72
1.67
1.63
2.08
2.07
3.00
3.14
6.12
6.17
f1 (ppm)

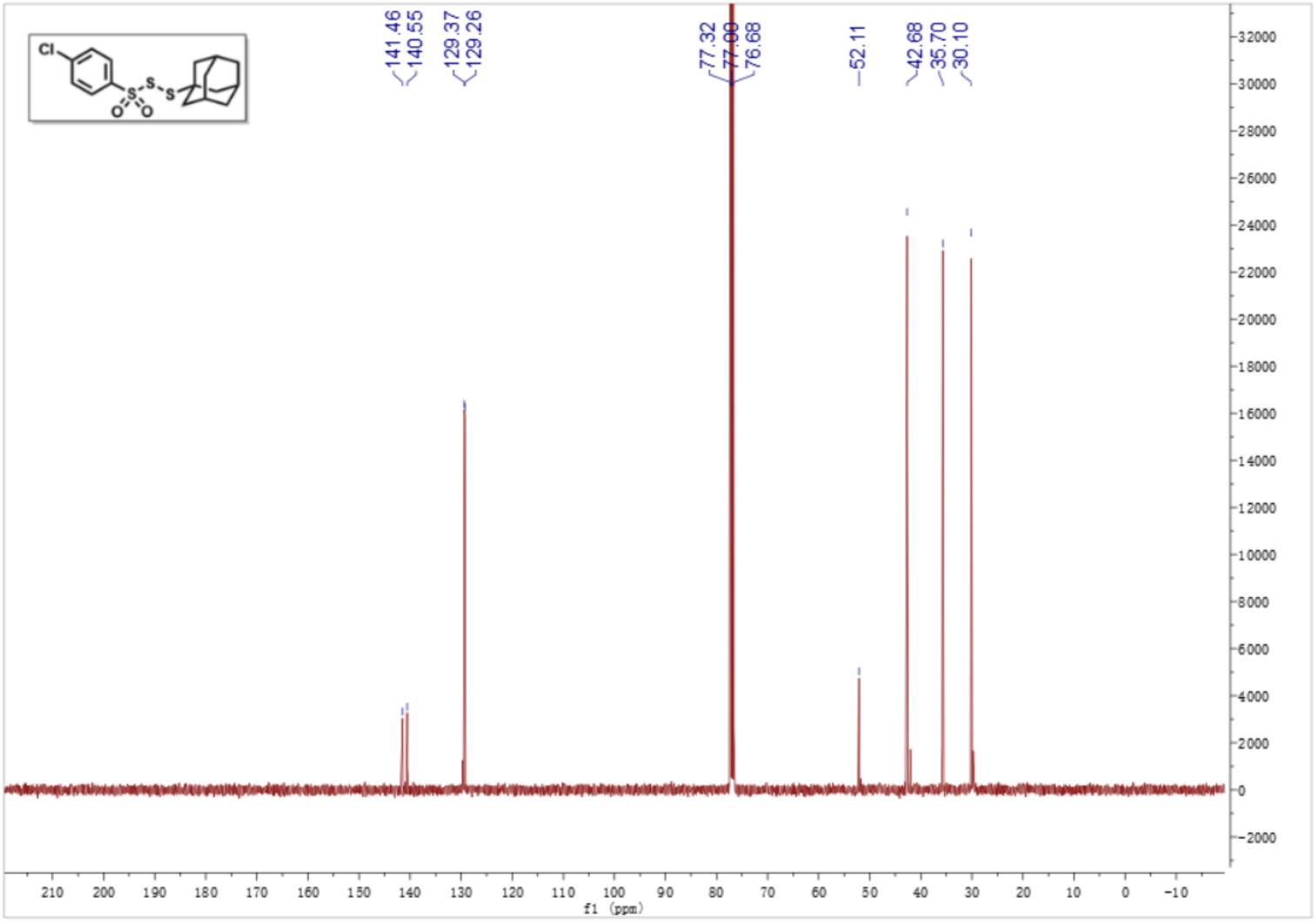
^{13}C NMR of 3w


144.96
140.35
129.66
127.95
77.32
77.00
76.68
51.83
42.69
35.77
30.13
21.67
f1 (ppm)

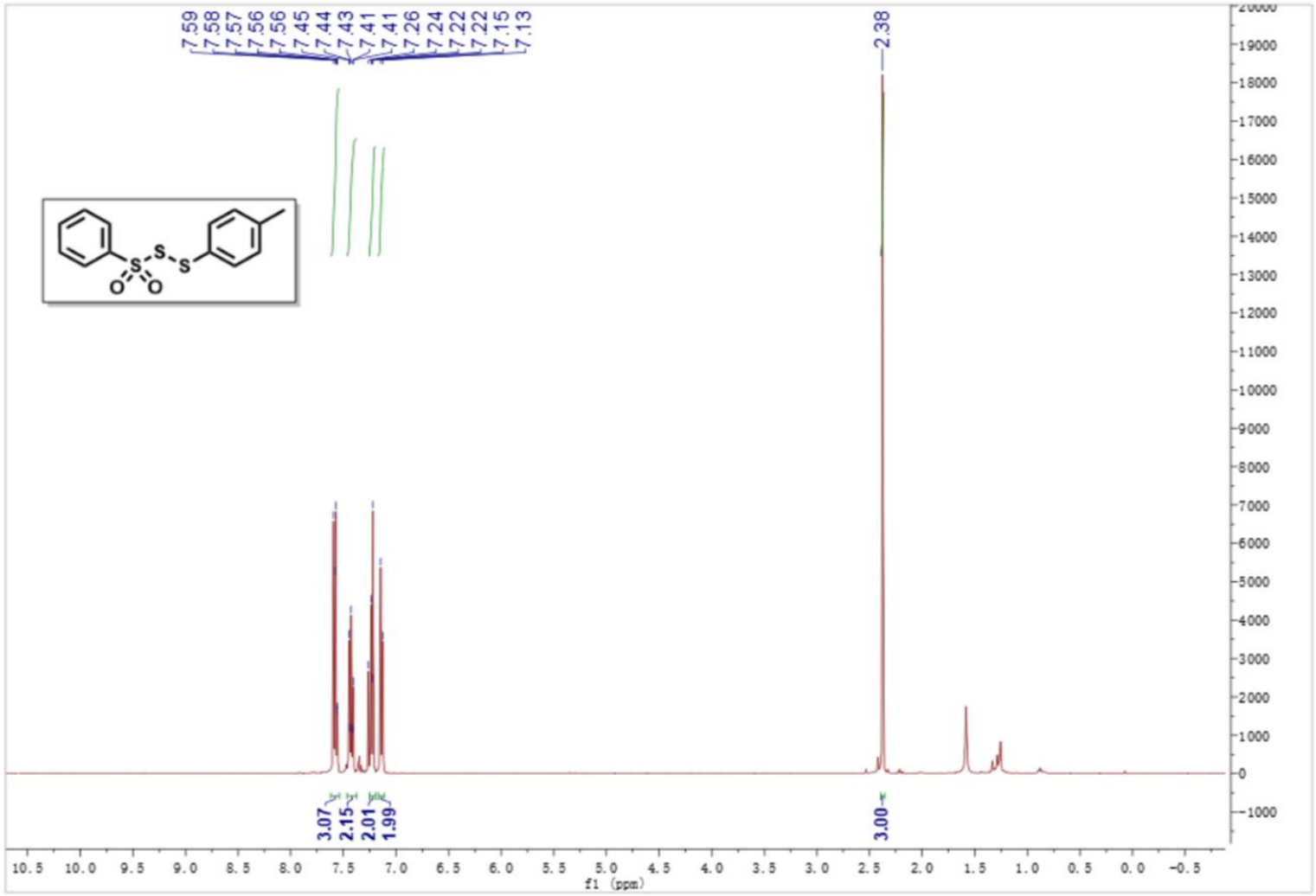
^{1}H NMR of 3x


7.91
7.90
7.89
7.87
7.86
7.86
7.85
7.84
7.84
7.56
7.53
7.53
7.52
7.51
7.51
7.26
2.12
1.89
1.88
1.72
1.68
1.65
Cl
S
S
S
O
O
2.00
2.02
3.12
5.83
6.49
f1 (ppm)

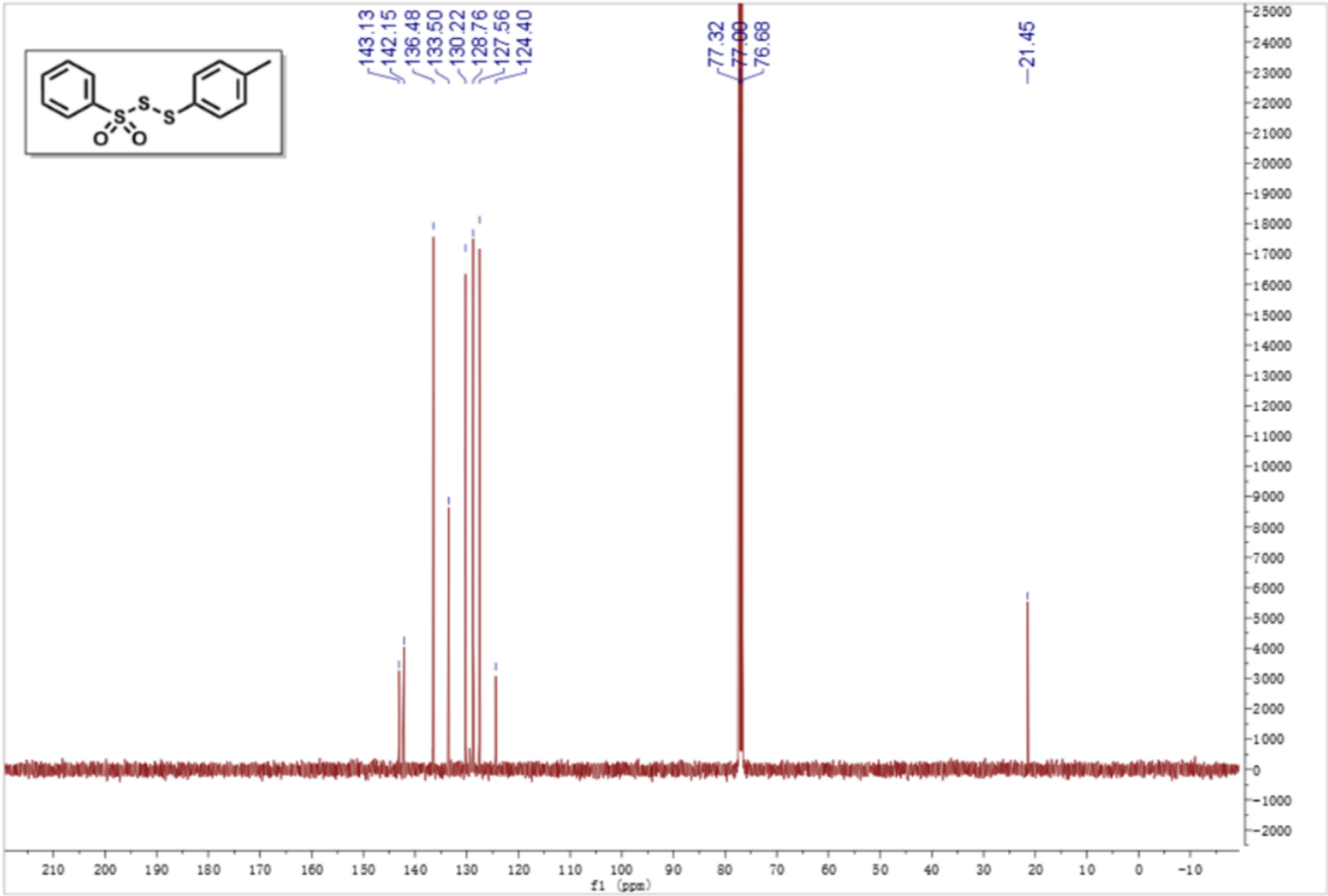
^{13}C NMR of 3x


141.46
140.55
129.37
129.26
77.32
77.00
76.68
52.11
42.68
35.70
30.10
f1 (ppm)

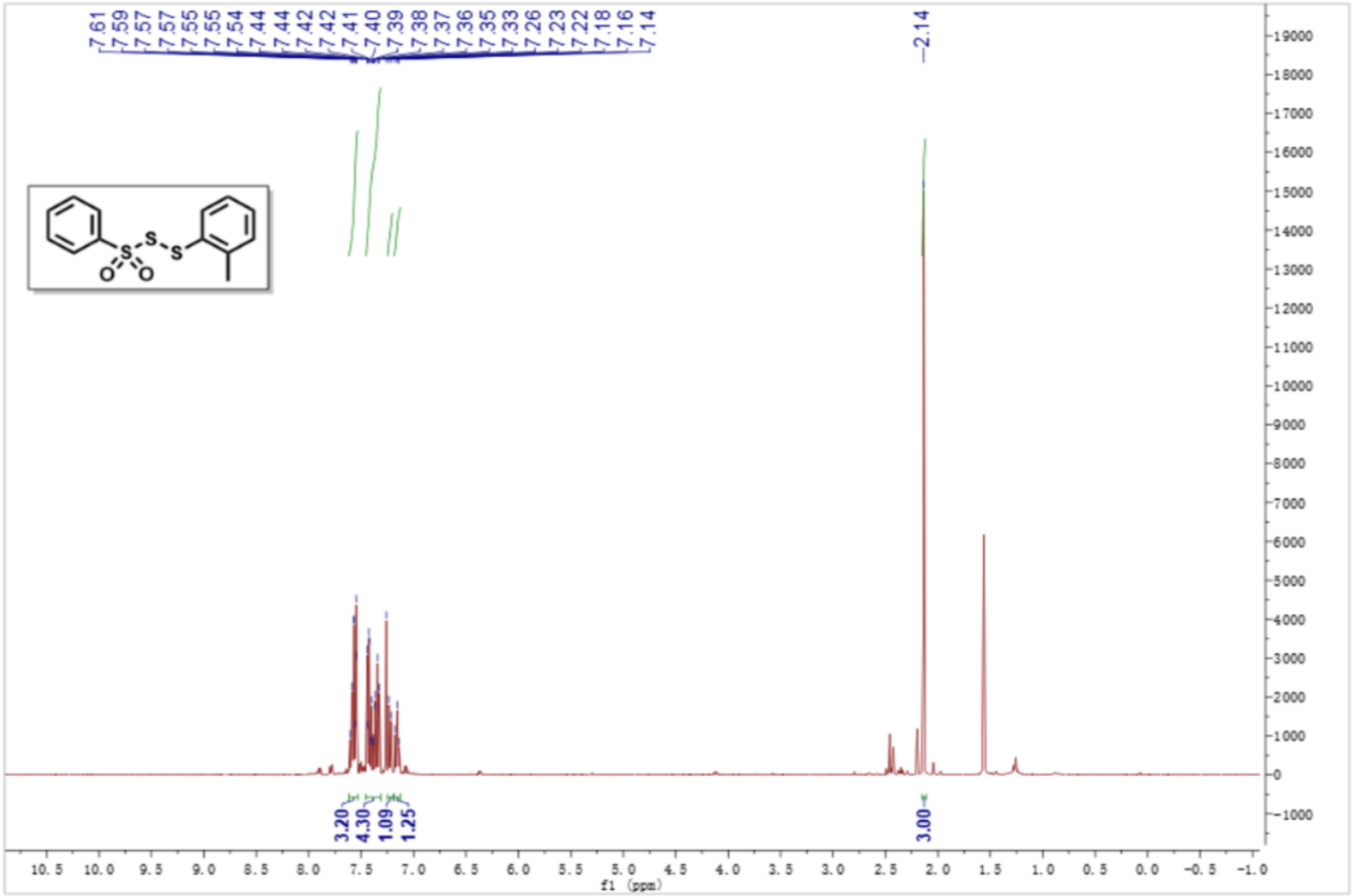
^{1}H NMR of 3y


7.59
7.58
7.57
7.56
7.56
7.45
7.44
7.43
7.41
7.41
7.26
7.24
7.22
7.22
7.15
7.13
2.38
3.07
2.15
2.01
1.99
3.00
f1 (ppm)

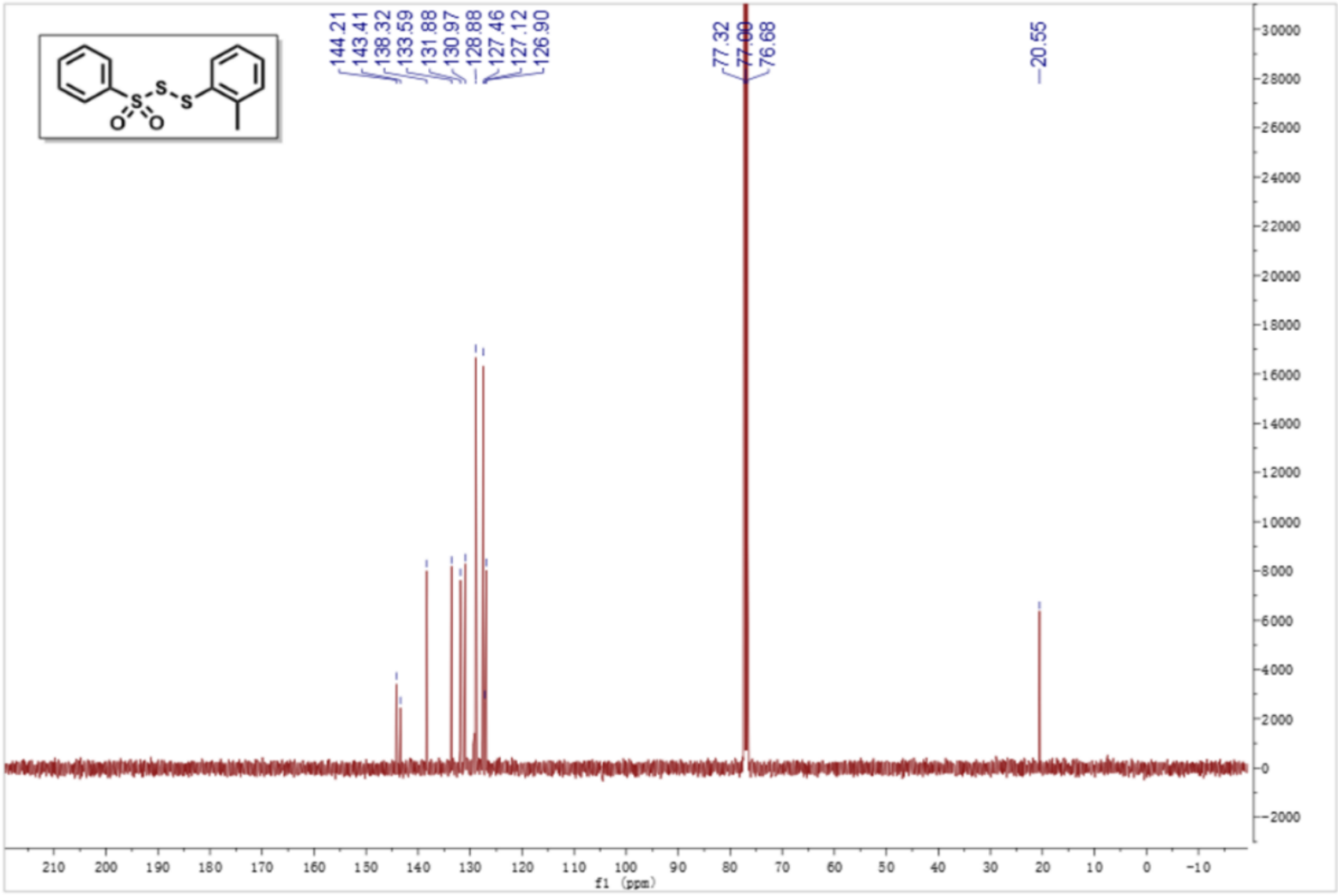
^{13}C NMR of 3y


143.13
142.15
136.48
133.50
130.22
128.76
127.56
124.40
77.32
77.00
76.68
21.45
f1 (ppm)

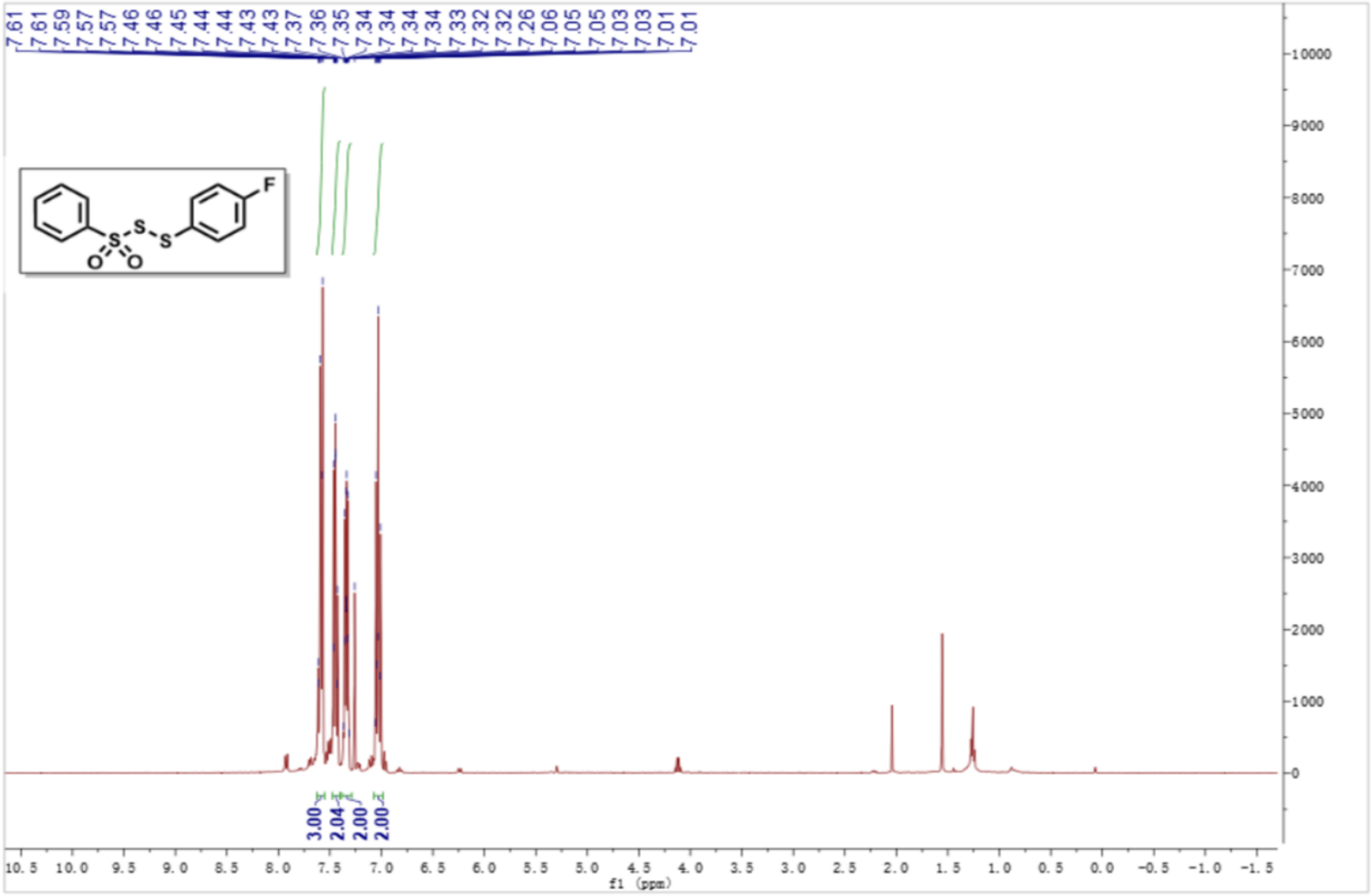
^{1}H NMR of 3z


7.61
7.59
7.57
7.57
7.55
7.55
7.54
7.44
7.44
7.42
7.42
7.41
7.40
7.39
7.38
7.37
7.36
7.35
7.33
7.26
7.23
7.22
7.18
7.16
7.14
2.14
3.20
4.30
1.09
1.25
3.00
f1 (ppm)

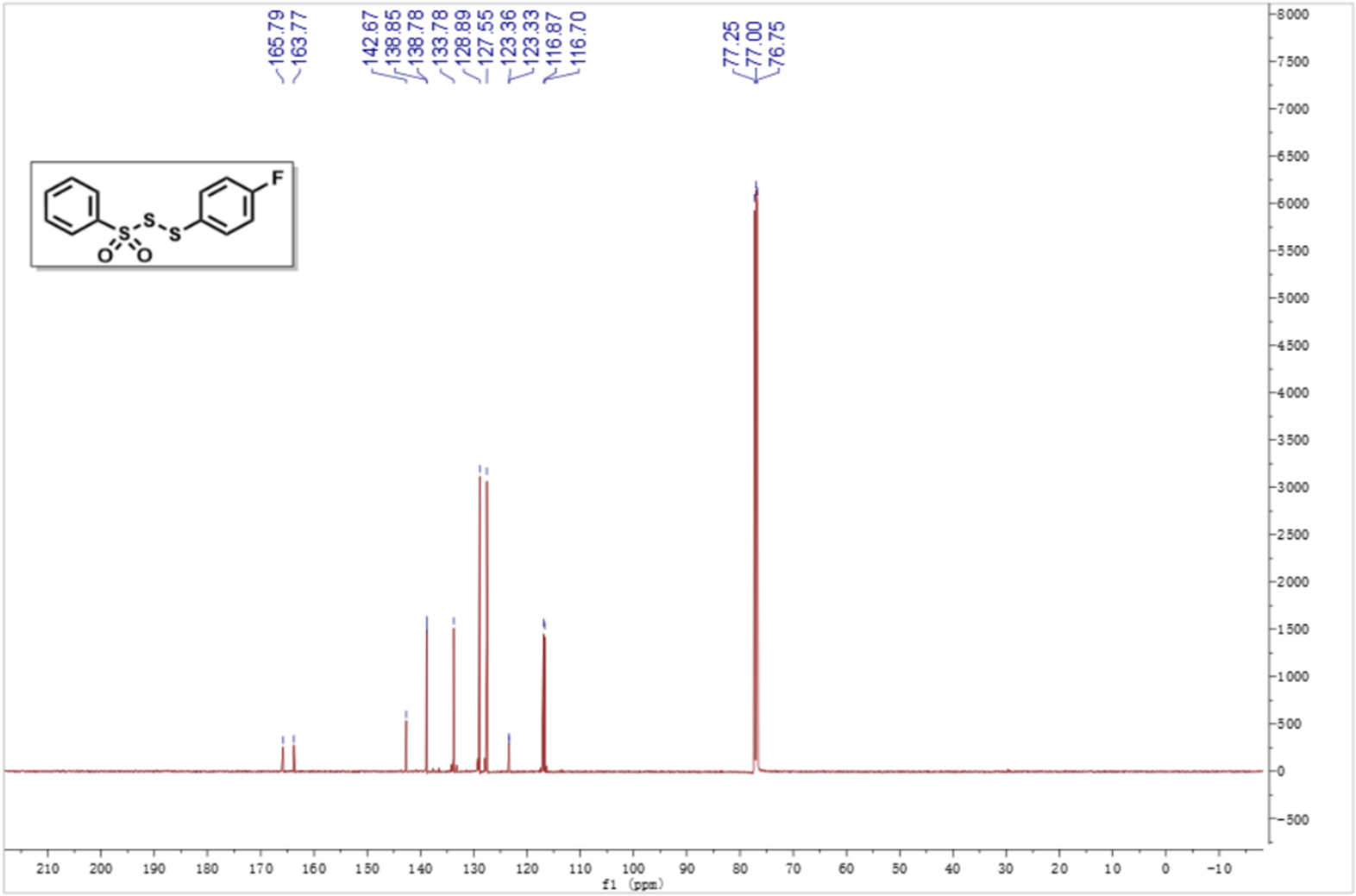
^{13}C NMR of 3z


144.21
143.41
138.32
133.59
131.88
130.97
128.88
127.46
127.12
126.90
77.32
77.00
76.68
20.55
f1 (ppm)

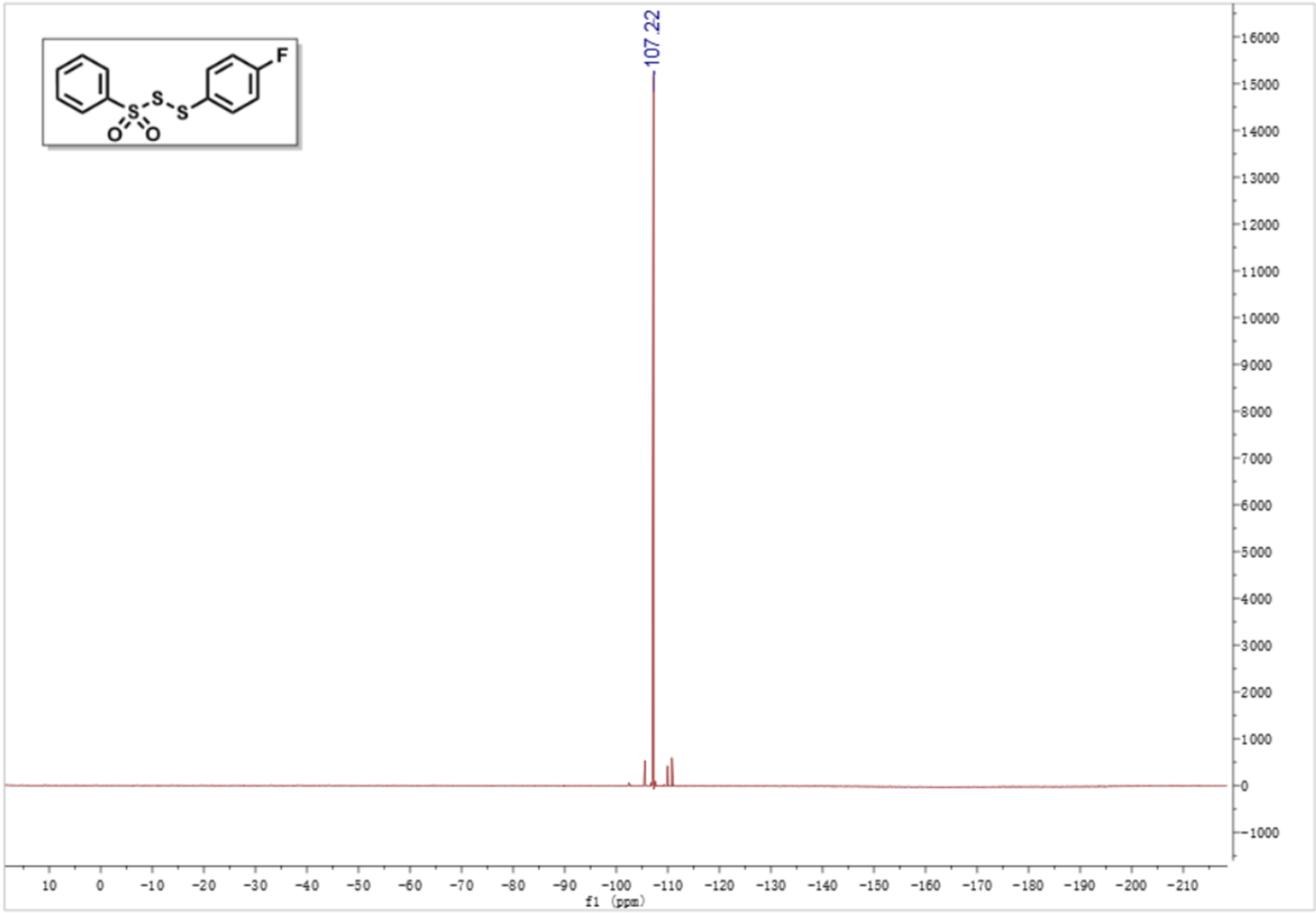
^{1}H NMR of 3aa


7.61
7.61
7.59
7.57
7.57
7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.37
7.36
7.35
7.34
7.34
7.34
7.34
7.33
7.32
7.32
7.26
7.06
7.05
7.05
7.03
7.03
7.01
7.01
F
S
S
S
O
O
3.00
2.04
2.00
2.00
f1 (ppm)

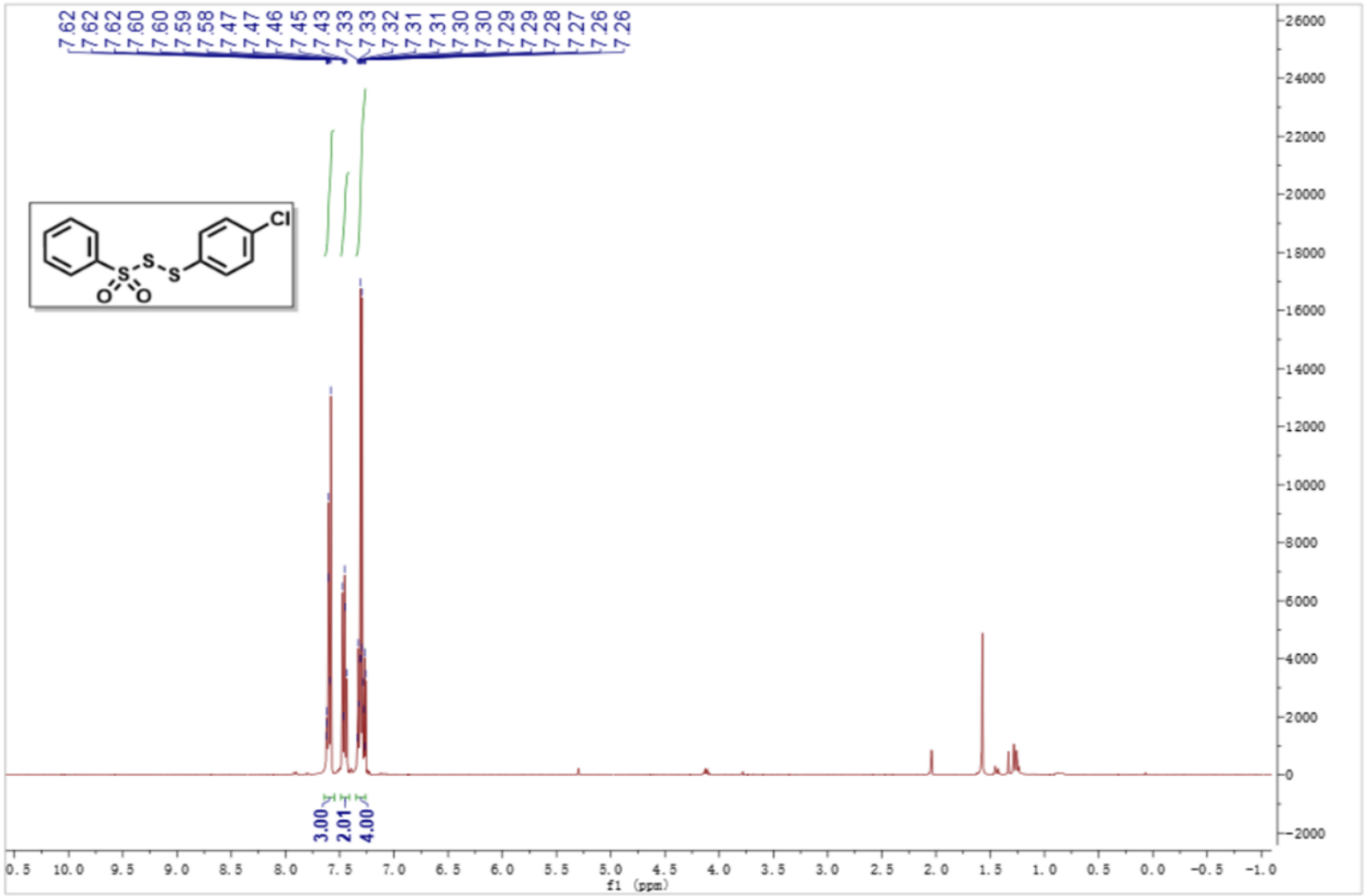
^{13}C NMR of 3aa



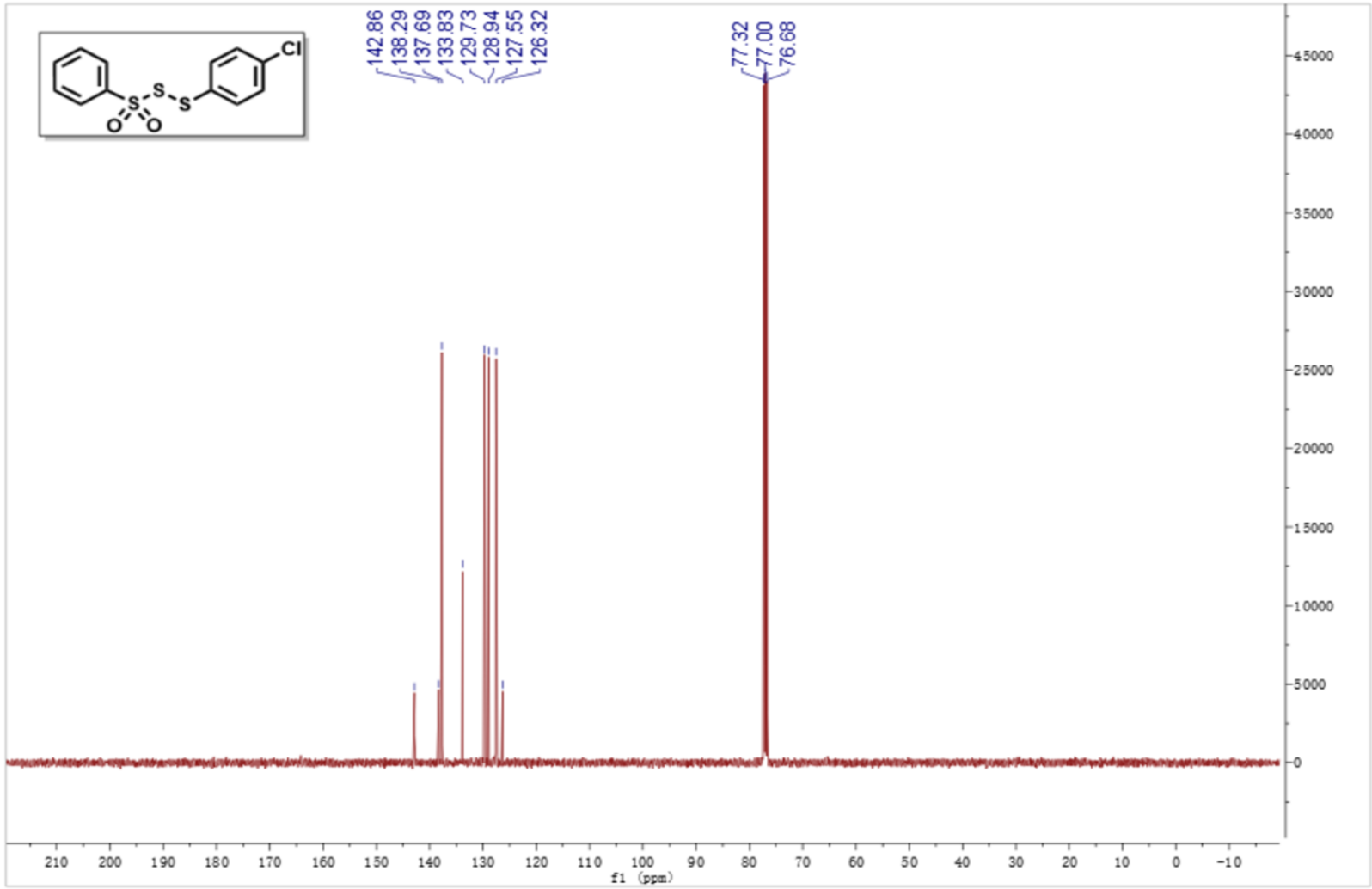
^{19}F NMR of 3aa



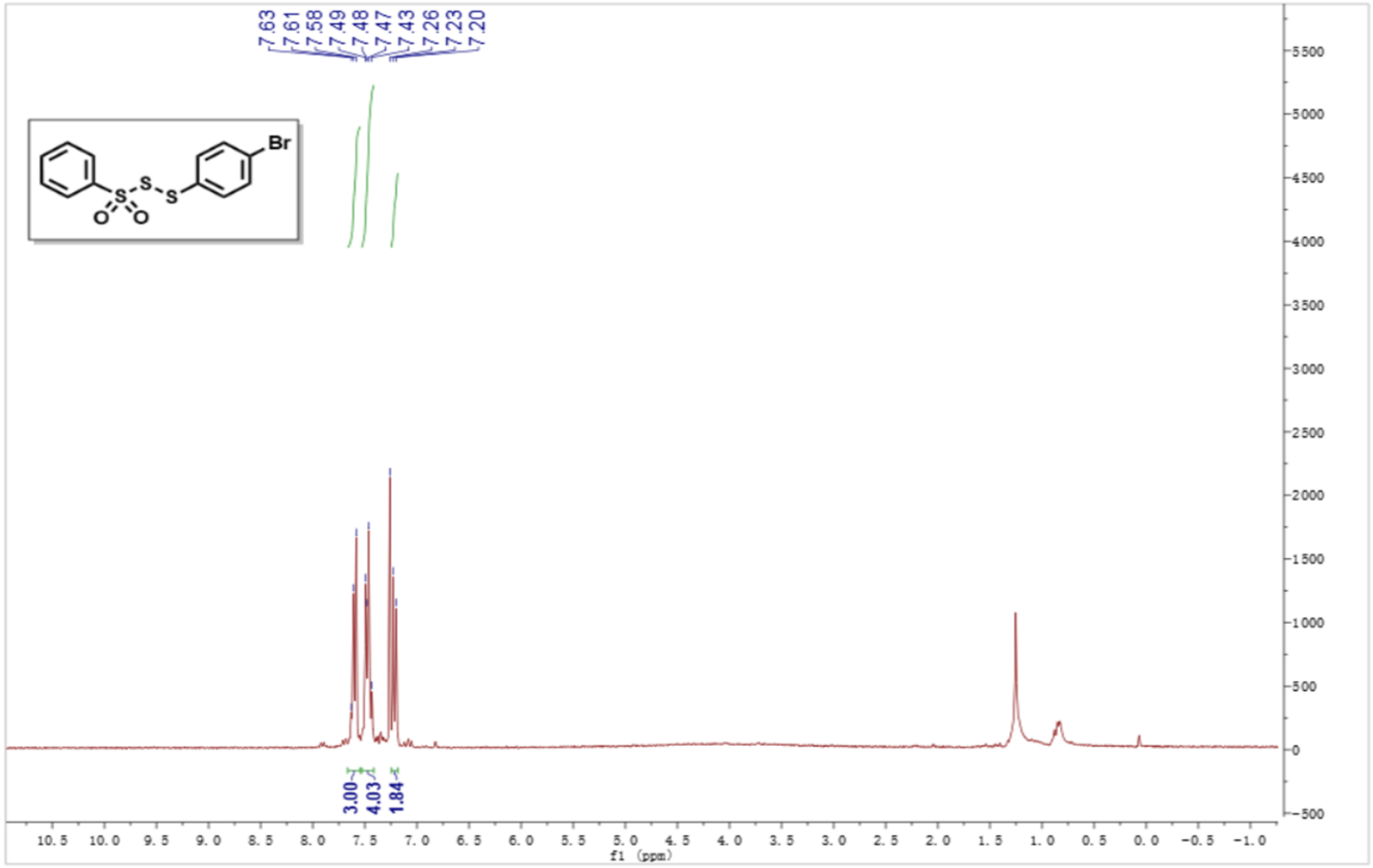
^{1}H NMR of 3ab


7.62
7.62
7.62
7.60
7.60
7.59
7.58
7.47
7.47
7.46
7.45
7.43
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.27
7.26
7.26
Cl
S
S
S
O
O
3.00
2.01
4.00
f1 (ppm)

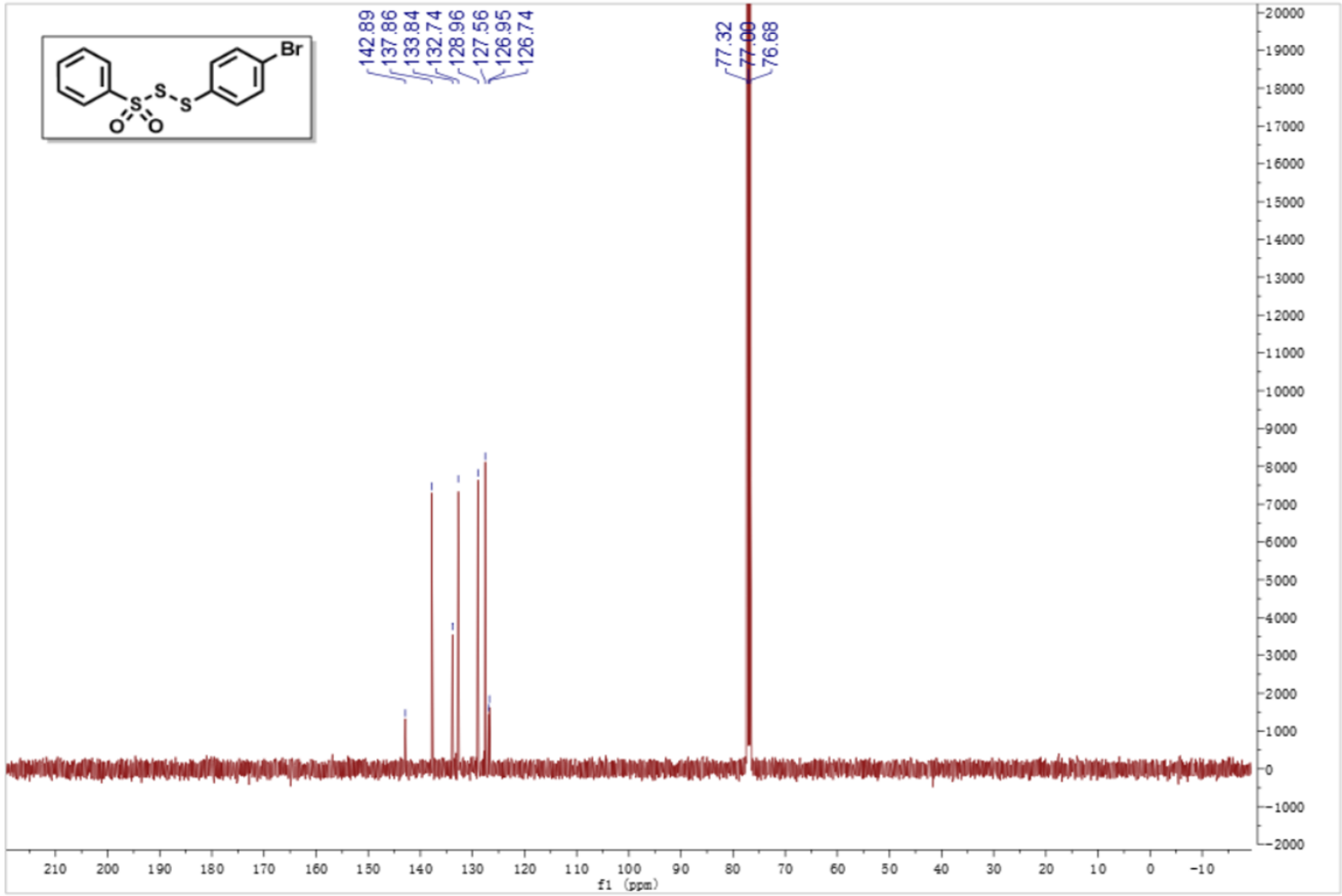
^{13}C NMR of 3ab



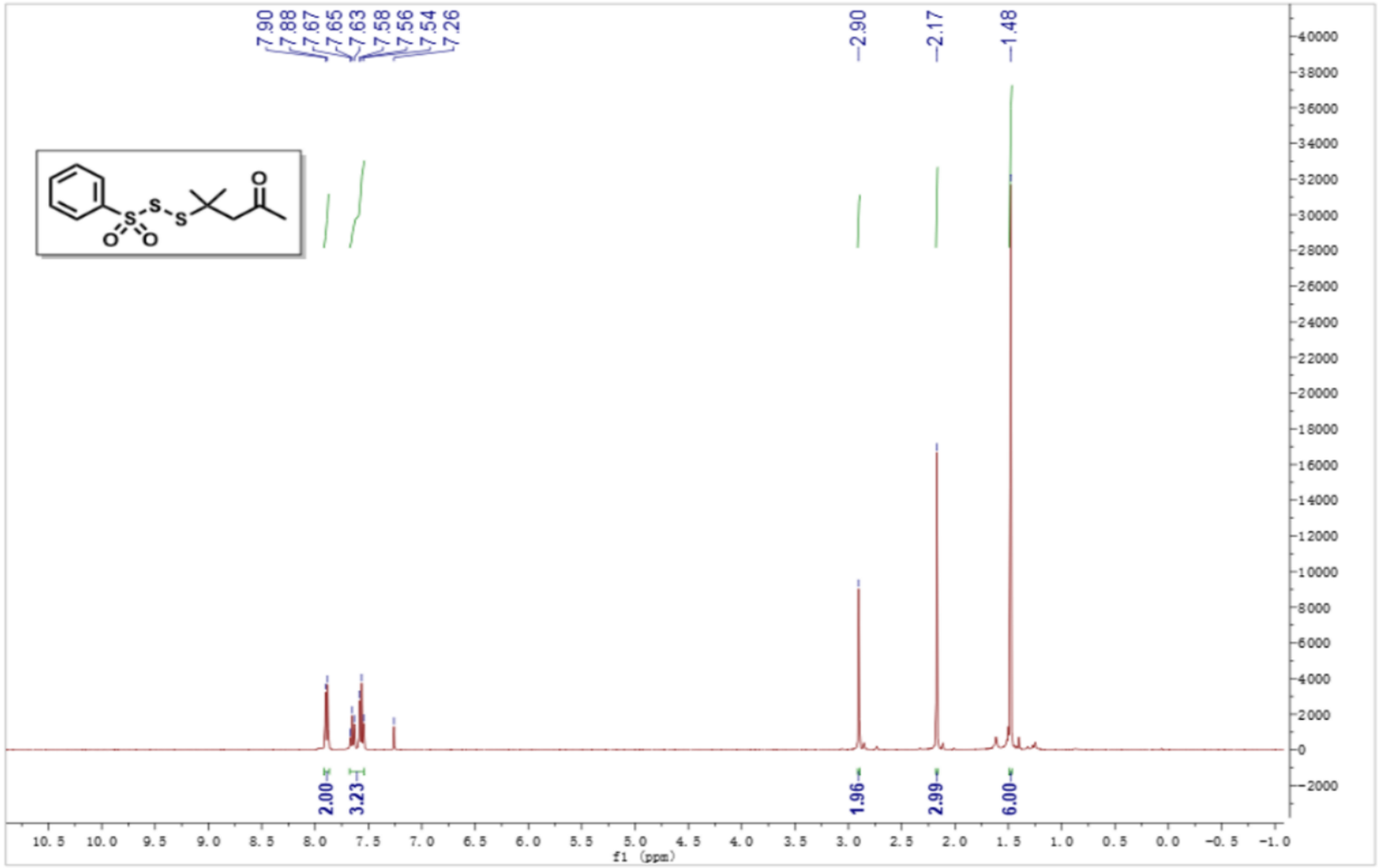
^{1}H NMR of 3ac



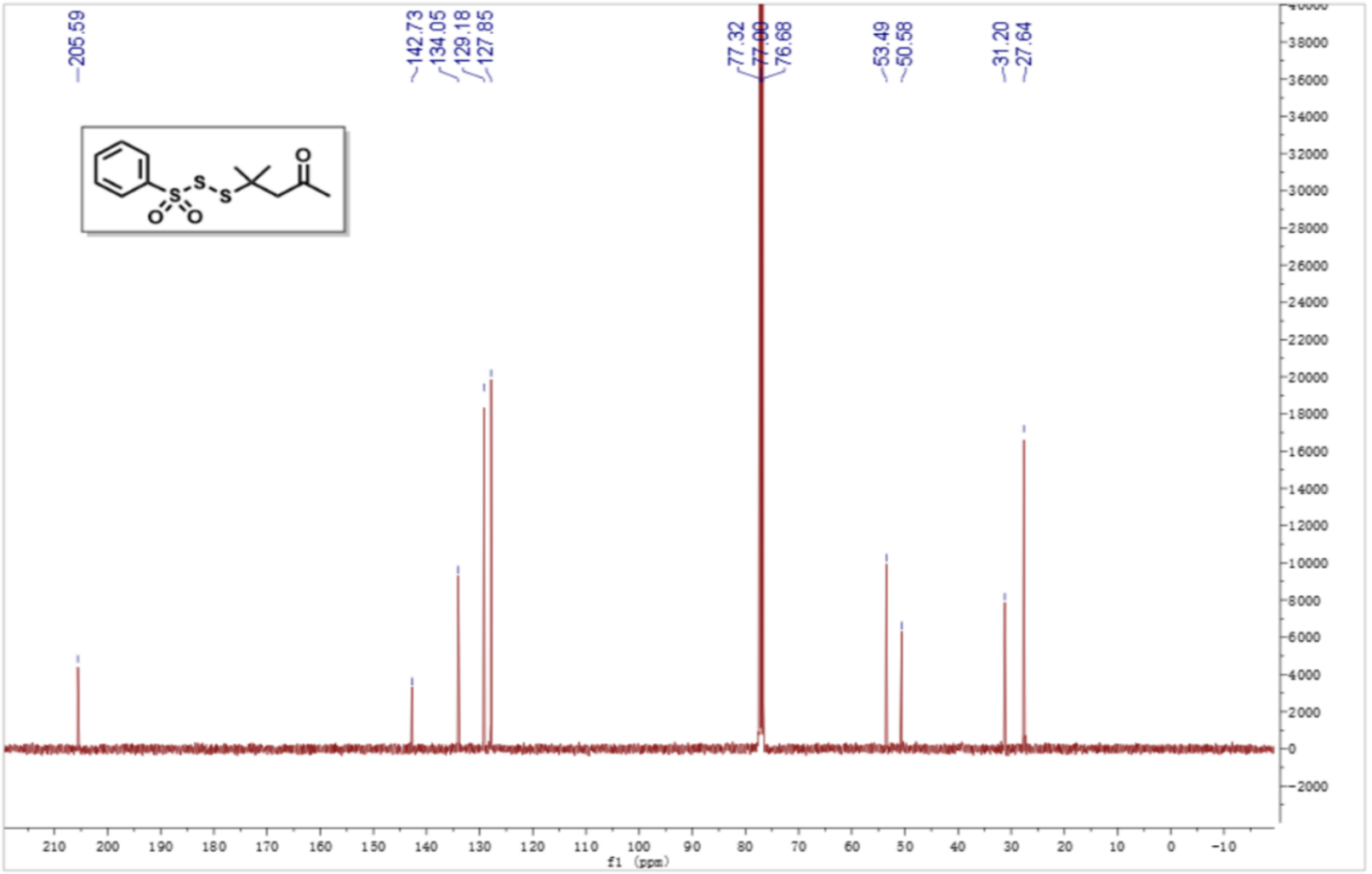
^{13}C NMR of 3ac



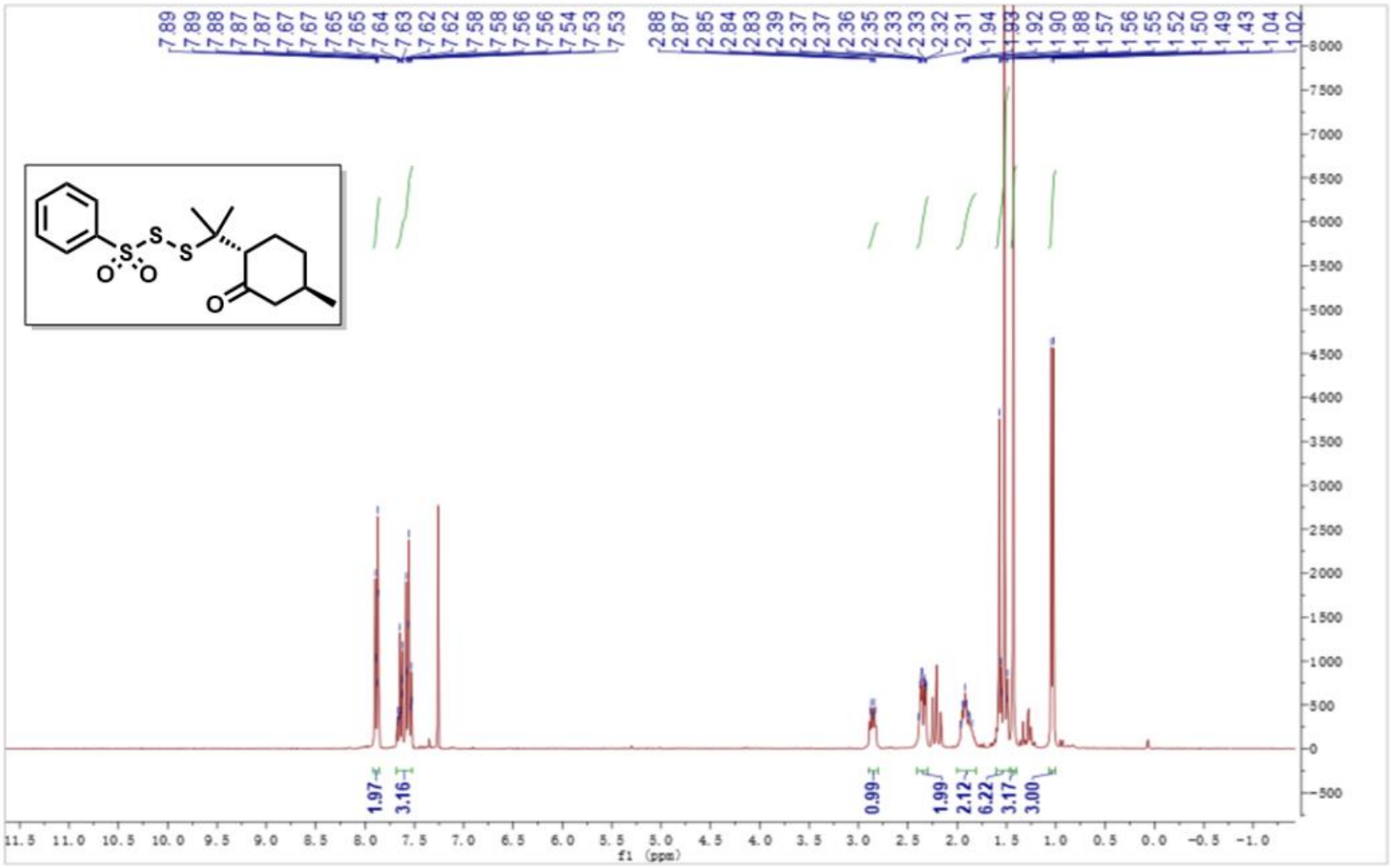
^{1}H NMR of 3ad


7.90
7.88
7.67
7.65
7.63
7.58
7.56
7.54
7.26
2.90
2.17
1.48
2.00
3.23
1.96
2.99
6.00
f1 (ppm)

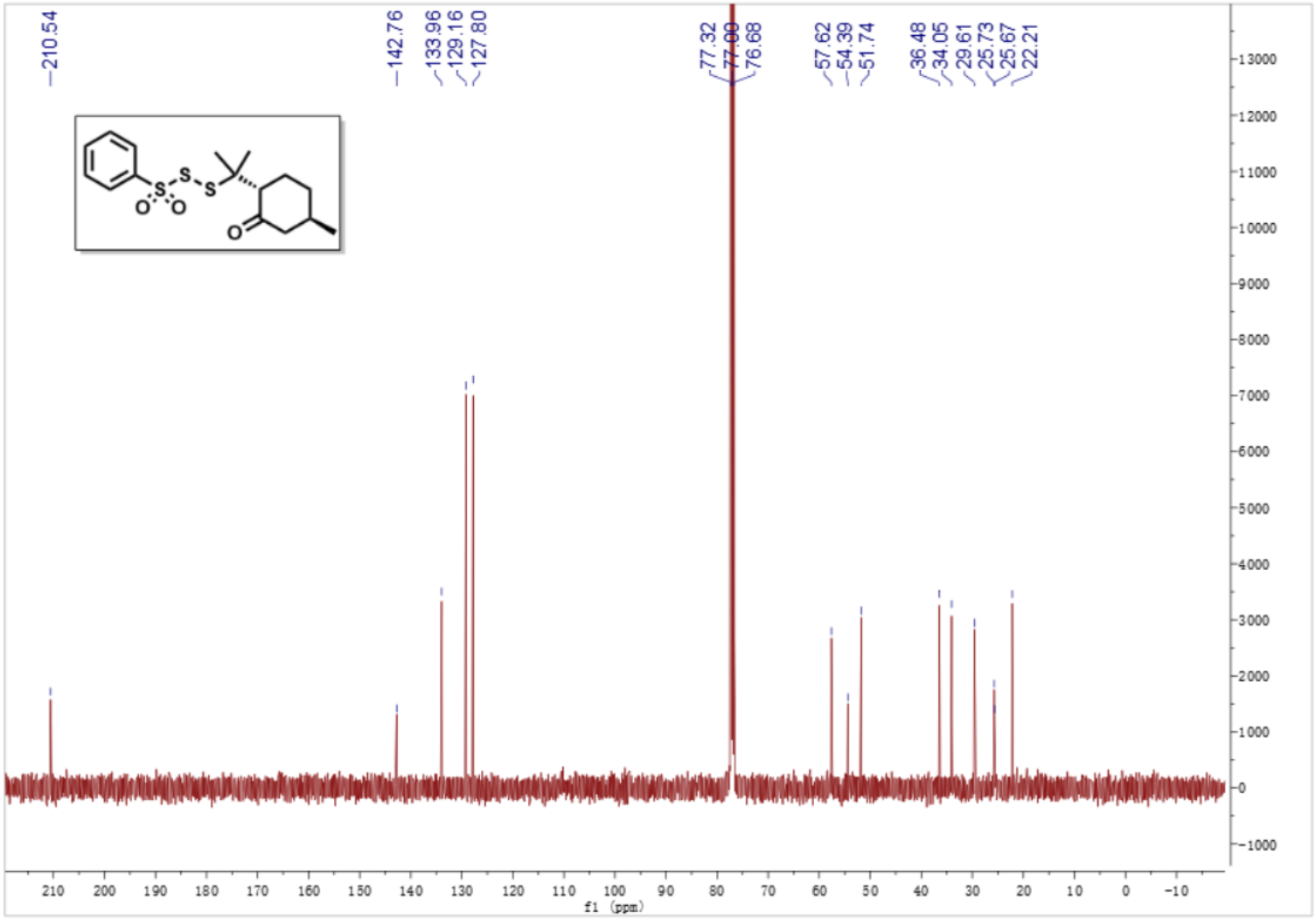
^{13}C NMR of 3ad



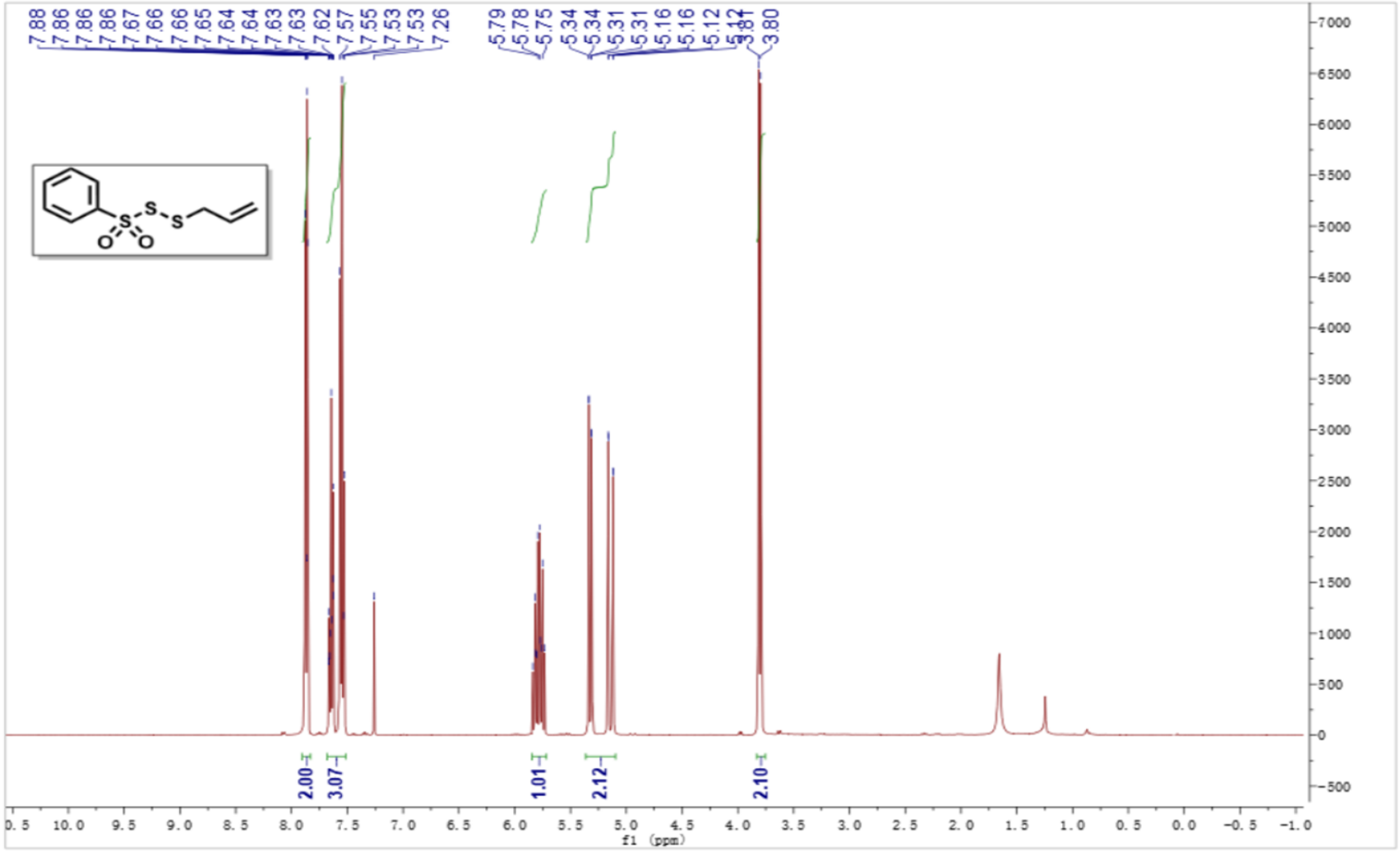
^{1}H NMR of 3ae


7.89 7.89 7.88 7.87 7.87 7.67 7.67 7.65 7.65 7.64 7.63 7.62 7.62 7.58 7.58 7.56 7.56 7.54 7.53 7.53
2.88 2.87 2.85 2.84 2.83 2.39 2.37 2.37 2.36 2.35 2.33 2.33 2.32 2.31 1.94 1.93 1.92 1.90 1.88 1.57 1.56 1.55 1.52 1.50 1.49 1.43 1.04 1.02
1.97 3.16 0.99 1.99 2.12 6.22 3.17 3.00
f1 (ppm)

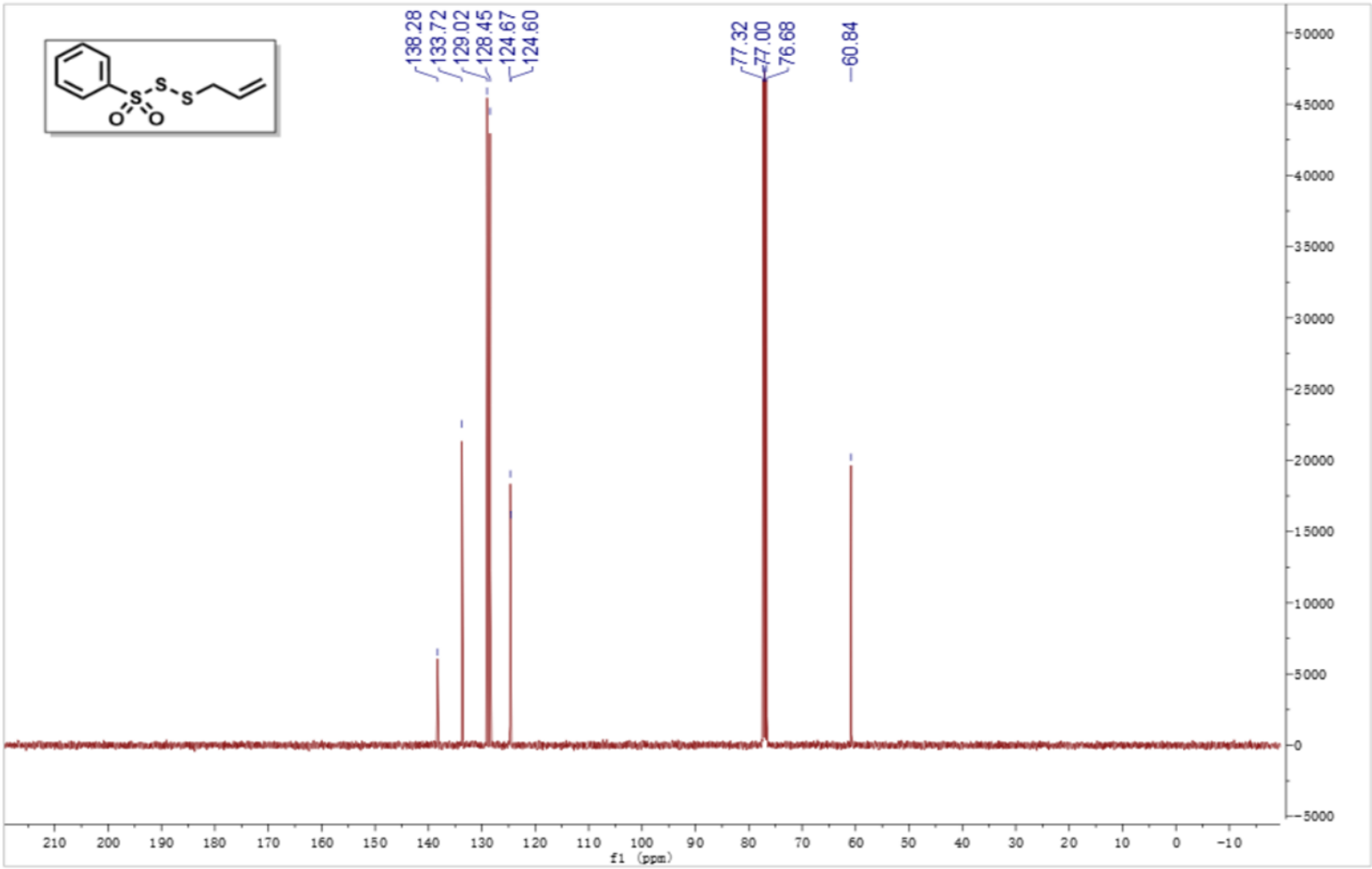
^{13}C NMR of 3ae



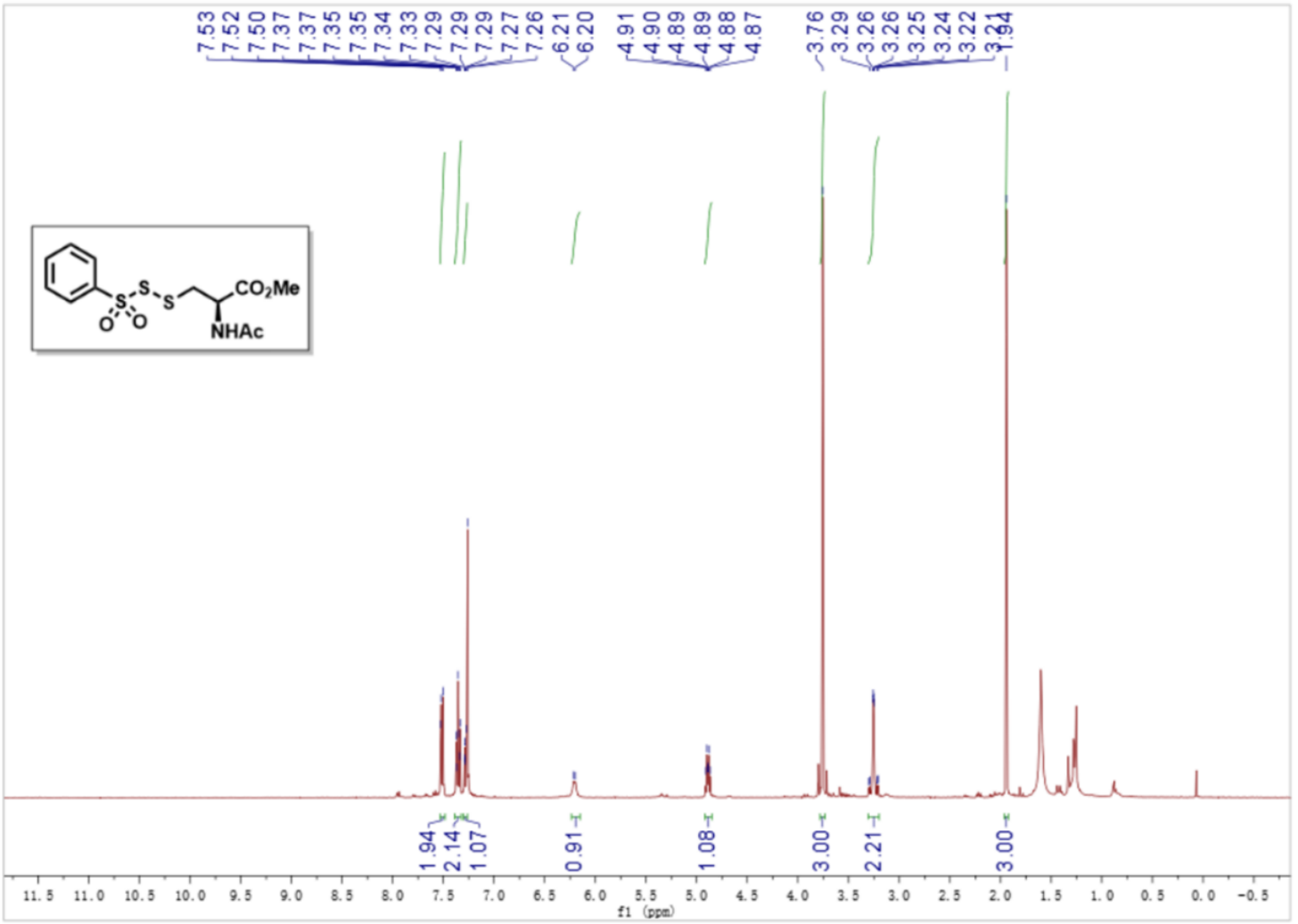
^{1}H NMR of 3af


7.88
7.86
7.86
7.86
7.67
7.66
7.66
7.65
7.64
7.64
7.63
7.63
7.62
7.57
7.55
7.53
7.53
7.26
5.79
5.78
5.75
5.34
5.34
5.31
5.31
5.16
5.16
5.12
3.81
3.80
2.00
3.07
1.01
2.12
2.10
f1 (ppm)

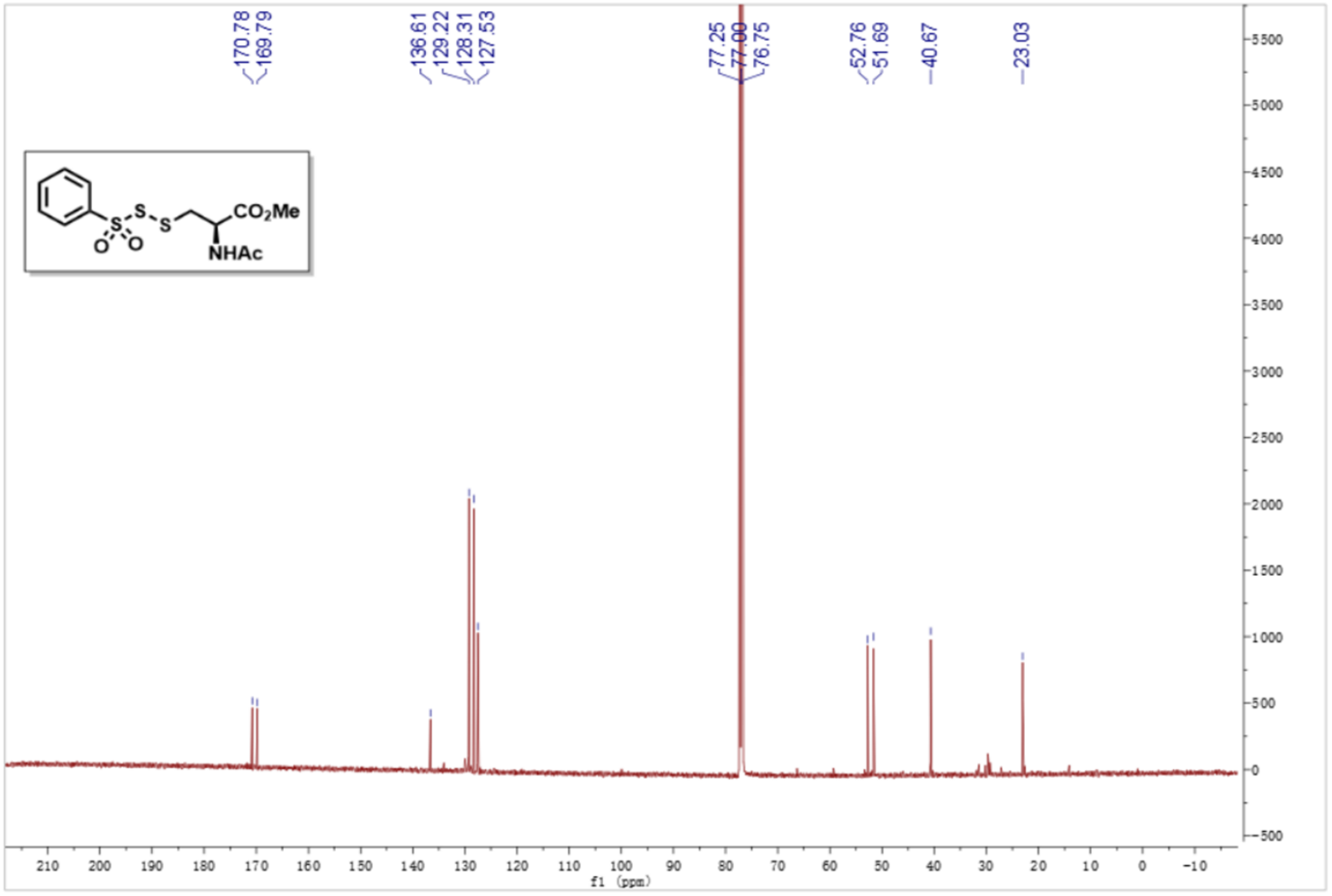
^{13}C NMR of 3af



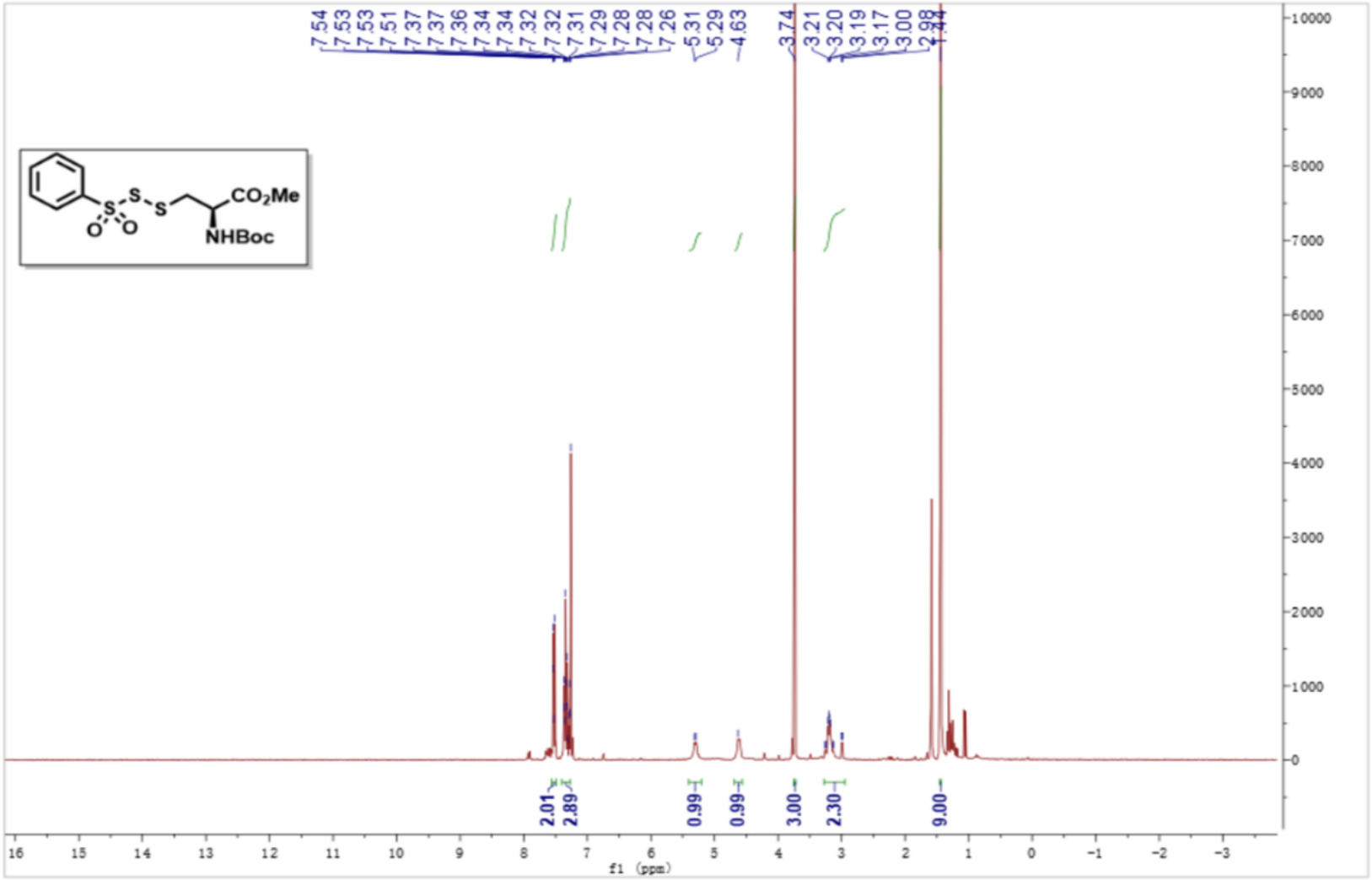
^{1}H NMR of 3ag


7.53
7.52
7.50
7.37
7.37
7.35
7.35
7.34
7.33
7.29
7.29
7.29
7.27
7.26
6.21
6.20
4.91
4.90
4.89
4.89
4.88
4.87
3.76
3.29
3.26
3.26
3.25
3.24
3.22
3.21
1.94
CO2Me
NHAc
1.94
2.14
1.07
0.91
1.08
3.00
2.21
3.00
f1 (ppm)

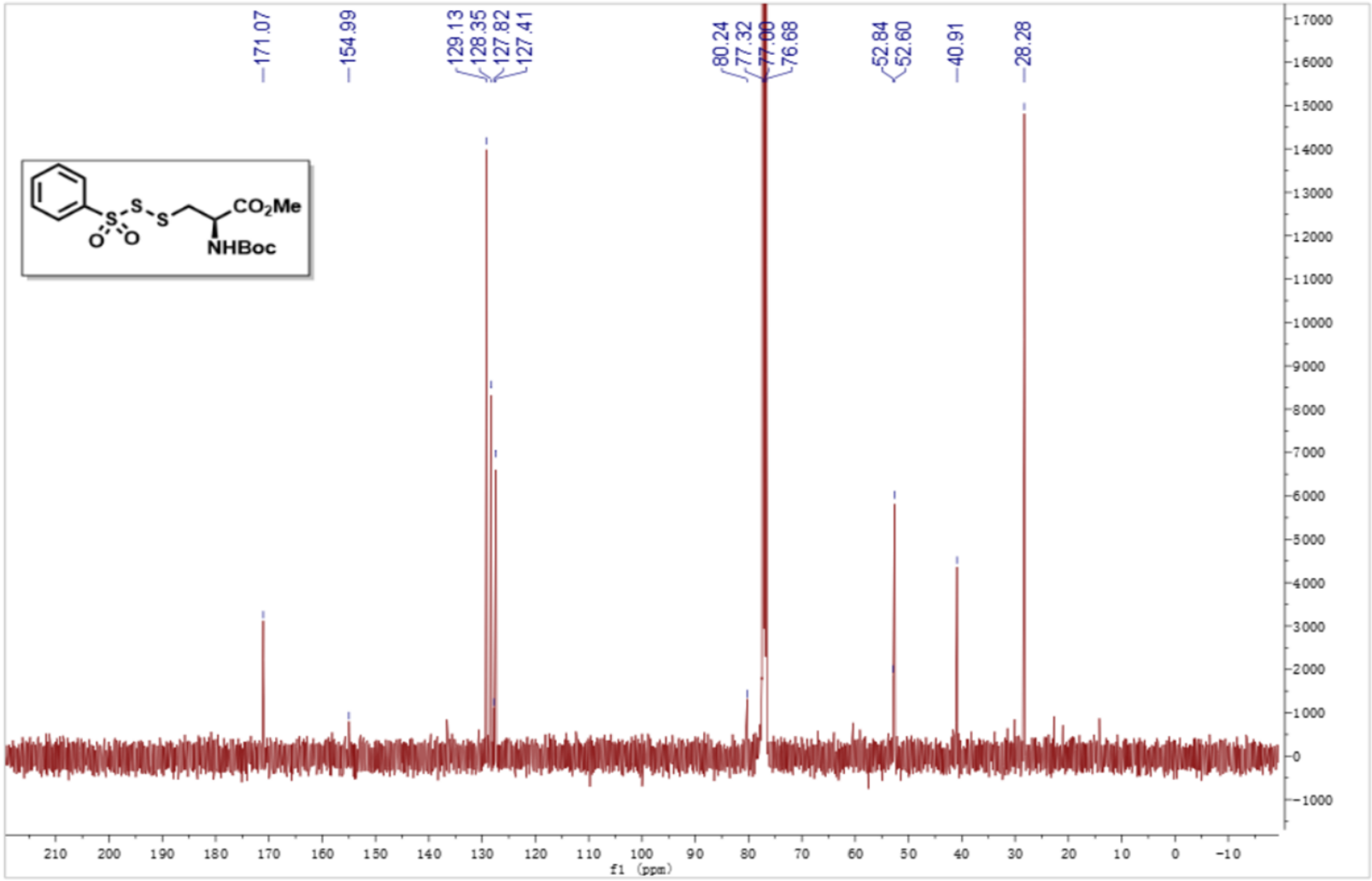
^{13}C NMR of 3ag



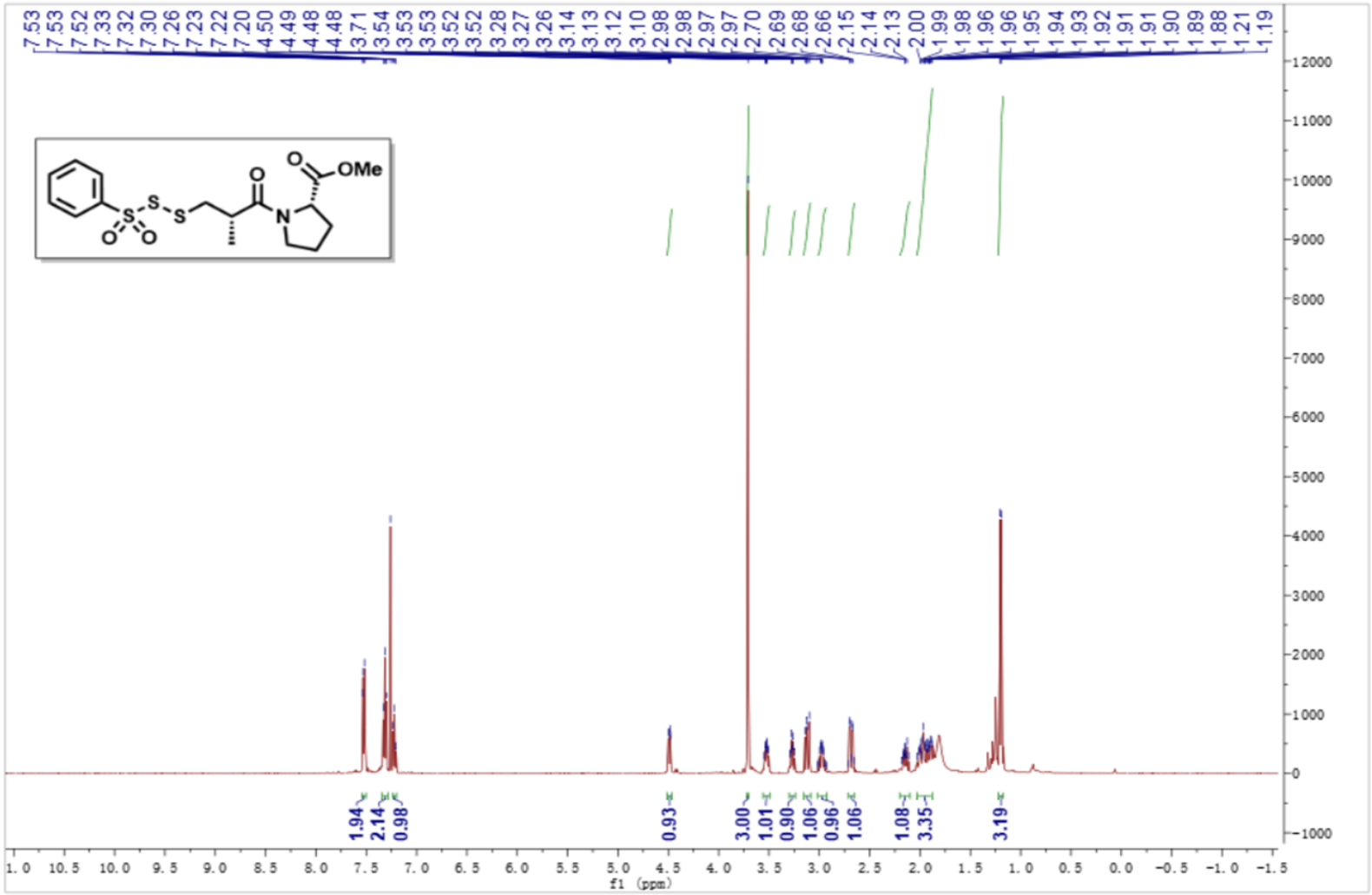
^{1}H NMR of 3ah


7.54
7.53
7.53
7.51
7.37
7.37
7.36
7.34
7.34
7.32
7.32
7.31
7.29
7.28
7.28
7.26
5.31
5.29
4.63
3.74
3.21
3.20
3.19
3.17
3.00
2.98
1.44
CO2Me
NHBoc
2.01
2.89
0.99
0.99
3.00
2.30
9.00
f1 (ppm)

^{13}C NMR of 3ah



^{1}H NMR of 3ai


7.53 7.53 7.52 7.33 7.32 7.30 7.26 7.23 7.22 7.20 4.50 4.49 4.48 4.48 3.71 3.54 3.53 3.53 3.52 3.52 3.28 3.27 3.26 3.14 3.13 3.12 3.10 2.98 2.98 2.97 2.97 2.70 2.69 2.68 2.66 2.15 2.14 2.13 2.00 1.99 1.98 1.96 1.96 1.95 1.94 1.93 1.92 1.91 1.91 1.90 1.89 1.88 1.21 1.19
OMe
1.94 2.14 0.98 0.93 3.00 1.01 0.90 1.06 0.96 1.06 1.08 3.35 3.19
f1 (ppm)

^{13}C NMR of 3ai