Supplementary Information

Electrochemical promoted three-component reaction to unsymmetric thiosulfonates

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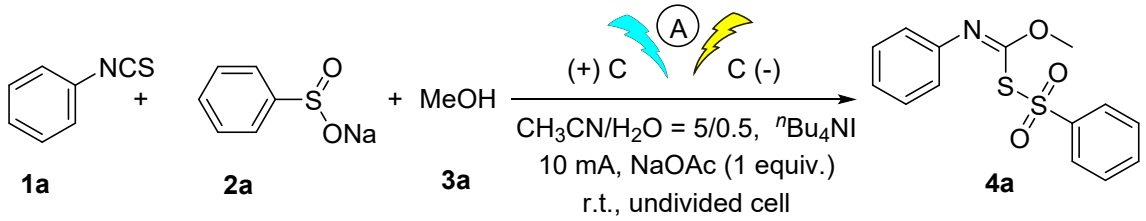
1. General methods

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. Column chromatography on silica gel (300-400 mesh) was carried out using technical grade 60-90 ^{o}C petroleum ether and analytical grade EtOAc (without further purification). ^{1}H and ^{13}C spectra were recorded with Bruker Avance III HD (400 MHz) or Bruker Avance NEO (600 MHz) spectrometer with tetramethylsilane as an internal standard. Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm) or DMSO (2.5 ppm), and ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.0 ppm) or DMSO (39.5 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. LC-MS spectra were recorded on Agilent 6545 Q-TOF LC/MS using electron spray ionization (ESI) source. Cyclic voltammograms were recorded on a CHI 660E potentiostat.

2. Chemical experiment procedure

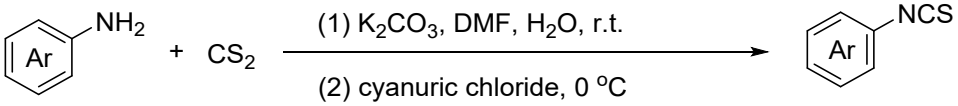
2.1 Synthesis of products



Add phenyl isothiocyanate **1a** (0.3 mmol, 1.0 equiv.), sodium benzenesulfinate **2a** (0.6 mmol, 2.0 equiv.), methanol **3a** (0.6 mmol, 2.0 equiv.), and $^{n}Bu_4NI$ (0.3 mmol, 1.0 equiv.) into a 10 ml three-neck round-bottomed flask. The flask is equipped with a graphite rod (Φ 8 mm) anode and a graphite rod (Φ 8 mm) cathode. Add CH_3CN (5 mL) and H_2O (0.5 mL) as solvents, and add sodium acetate (0.3 mmol, 1.0 equiv.). Pass a current of 10 mA at room temperature for approximately 6 hours until the substrate is completely consumed (monitored by TLC). Concentrate under reduced pressure and purify by silica gel column chromatography to obtain the product **4a**.

Figure S1. Undivided cell for current controlled electrolysis

2.2 Synthesis of Phenyl isothiocyanate derivatives



Add aniline (5 mmol, 1equiv.), DMF (10 mL), H_2O (15 mL), and potassium carbonate

(5.5 mmol) into a dried 100 mL round-bottom flask and stir for 10 minutes at room temperature. Then, add CS_2 (1.5 mL) and stir at room temperature for 24 hours. After cooling the mixture to 0 °C, add cyanuric chloride (5 mmol) and stir the mixture at 0 °C for 2 hours. Adjust the pH of the mixture to 10 by adding an aqueous solution of sodium hydroxide (10% in H_2O) and stir at 0 °C for 30 minutes. Add DCM (30 mL), wash the resulting solution with H_2O (50 mL), and extract with DCM (20 mL×3). Dry the organic layer with Na_2SO_4, concentrate under reduced pressure, and purify by column chromatography.

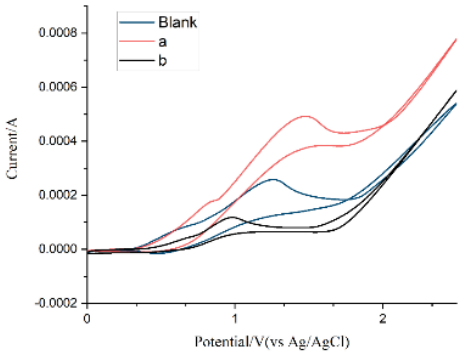
2.3 Optimization of the reaction conditions

Table S2 Optimization study for electrochemical synthesis of unsymmetric thiosulfonates [a]

Entry	Variation from standard conditions	Yield [b]
1	None	82%
2	CH_2Cl_2/H_2O (5/1)	Trace
3	DMSO/H_2O (5/1)	32%
4	DMF/H_2O (5/1)	27%
5	Acetone/H_2O (5/1)	Trace
6	CH_3CN/H_2O (5/1)	78%
7	CH_3CN/H_2O (5/0.2)	74%
8	^{n}Bu$_4$NBF$_4$ instead of ^{n}Bu$_4$NI	N.R.
9	^{n}Bu$_4$NClO$_4$ instead of ^{n}Bu$_4$NI	N.R.
10	^{n}Bu$_4$NOAc instead of ^{n}Bu$_4$NI	N.R.
11	^{n}Bu$_4$NBr instead of ^{n}Bu$_4$NI	Trace
12	Et$_4$NI instead of ^{n}Bu$_4$NI	35%
13	NH_4I instead of ^{n}Bu$_4$NI	40%
14	NaI instead of ^{n}Bu$_4$NI	10%
15	C(+) − Pt(-)	40%
16	C(+) − SS(-)	15%
17	C(+) – Ni(-)	Trace
18	C(+) − Zn(-)	Trace
19	Na_2CO_3 as additive	43%
20	Cs_2CO_3 as additive	27%
21	NaOH as additive	25%
22	DBU as additive	Trace
23	NaOMe as additive	40%
24	^{t}BuONa as additive	Trace

25	LiOAc as additive	44%
26	KOAc as additive	21%
27	0.5 equiv. NaOAc instead of 1equiv.	65%
28	2 equiv. NaOAc instead of 1equiv.	55%
29	5 mA instead of 10 mA	67%
30	15 mA instead of 10 mA	72%
31	Constant potential: 1.5 V vs. Ag/AgCl	73%
32	50 ^{o}C instead of room temperature	76%
33	Reaction under N_2	75%
34	No electricity	N.R.

2.4 Cyclic Voltammetry Experiments



Scheme S1. cyclic voltammetry experiments. Cyclic voltammograms in an electrolyte solution of $^{n}Bu_4NI$ (0.1 M) in CH_3CN/H_2O (v/v = 5/0.5) using a glassy carbon disk working electrode (diameter, 3.0 mm), Pt disk and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate: (Blank) $^{n}Bu_4NI$ (0.1 M) in CH_3CN/H_2O (v/v = 5/0.5); (a) zzThiocarbamate (0.3 mmol); (b) Sodium benzenesulfite (0.3 mmol).

3. the HRMS spectra of Molecules

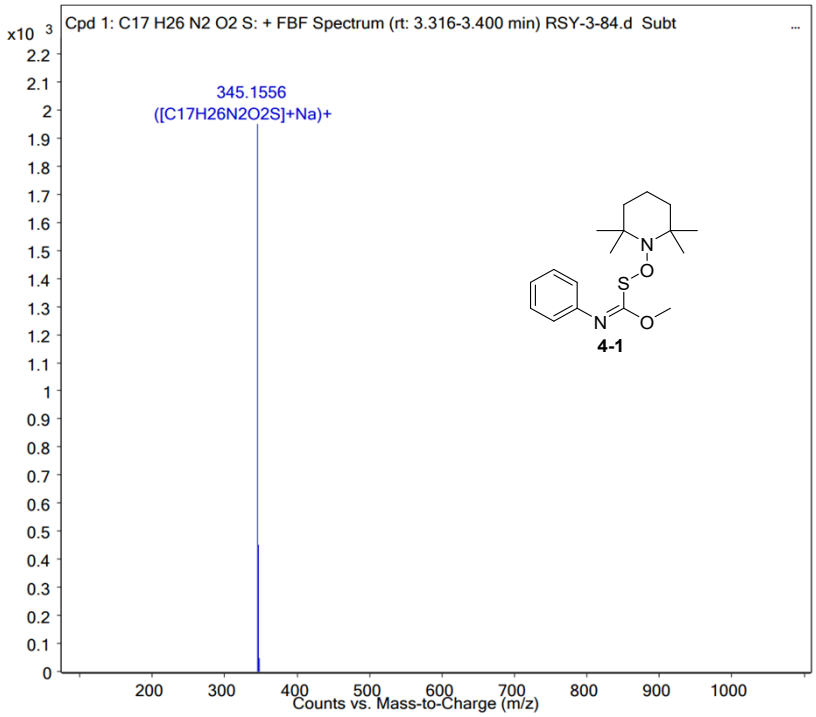


Figure S2. the HRMS spectra of the TEMPO-trapped product (4-1)

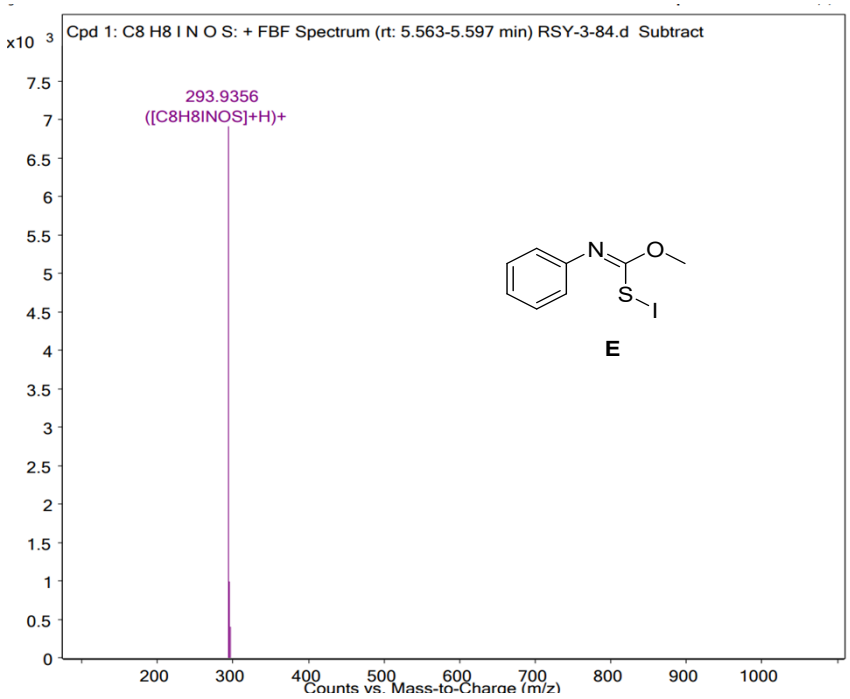


Figure S3. the HRMS spectra of the controls E

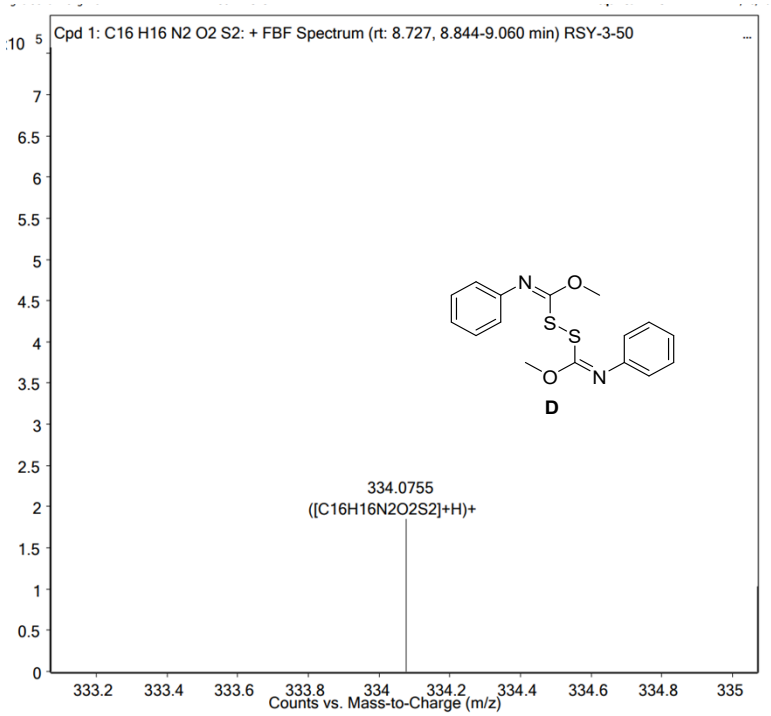


Figure S4. the HRMS spectra of the controls D

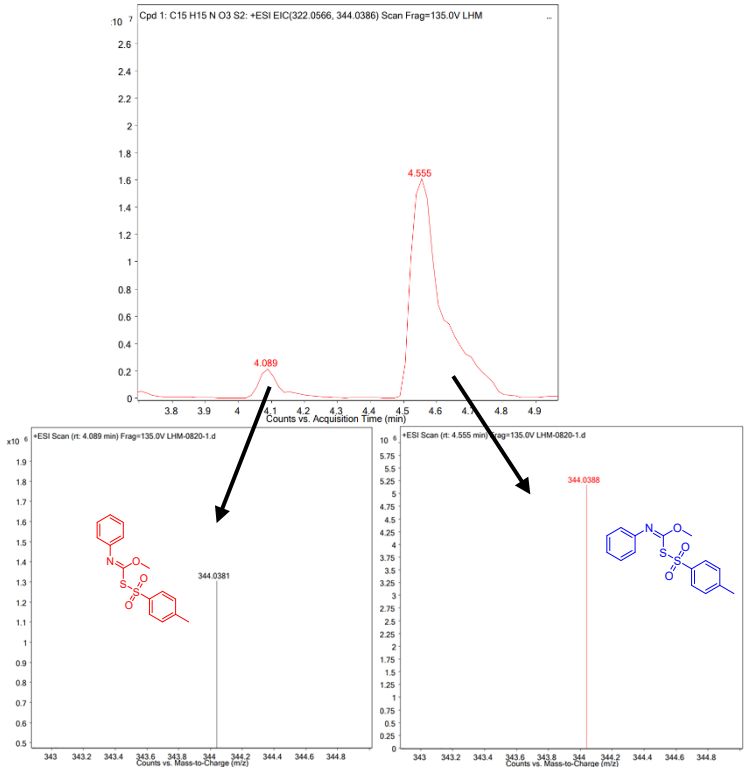
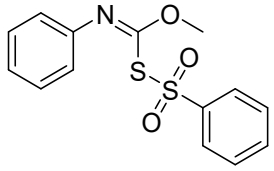
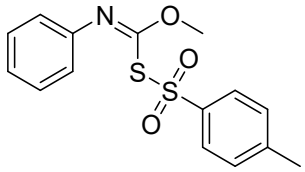


Figure S5. the HRMS spectra of 4b

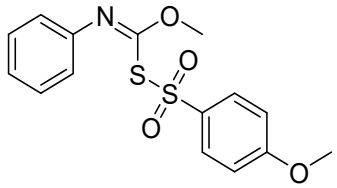
4. ^{1}H, ^{13}C NMR, ^{19}F and MS data of all products



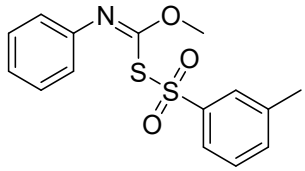
(*Z*)-Benzenesulfonic (methyl (*E*)-phenylcarbonimidic) thioanhydride (**4a**). White solid; Yield = 80%, 73.7 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 – 7.95 (m, 2H), 7.70 – 7.66 (m, 1H), 7.60 – 7.56 (m, 2H), 7.30 – 7.26 (m, 2H), 7.15 – 7.10 (m, 1H), 6.77 – 6.74 (m, 2H), 3.93 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.7, 145.5, 144.9, 134.3, 129.3, 129.2, 127.9, 125.1, 121.4, 57.3; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{14}H_{14}NO_3S_2]^+$ 308.0410, found 308.0411.



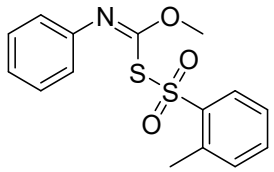
(*Z*)-(Methyl (*E*)-phenylcarbonimidic) 4-methylbenzenesulfonic thioanhydride (**4b**). White solid; Yield = 82%, 78.9 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 – 7.84 (m, 2H), 7.37 – 7.35 (m, 2H), 7.30 – 7.27 (m, 2H), 7.13 – 7.09 (m, 1H), 6.76 – 6.74 (m, 2H), 3.94 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.9, 145.6, 144.9, 142.6, 129.7, 129.2, 129.1, 128.0, 125.0, 121.4, 57.22, 21.89; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{15}H_{16}NO_3S_2]^+$ 322.0566, found 322.0565.



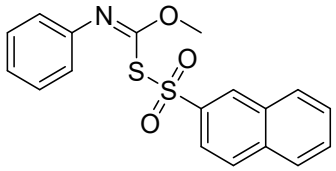
(*Z*)-4-Methoxybenzenesulfonic (methyl (*E*)-phenylcarbonimidic) thioanhydride (**4c**). White solid; Yield = 80%, 80.9 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 – 7.88 (m, 2H), 7.30 – 7.26 (m, 2H), 7.14 – 7.09 (m, 1H), 7.03 – 6.99 (m, 2H), 6.77 – 6.75 (m, 2H), 3.96 (s, 3H), 3.91 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 164.2, 151.1, 145.0, 137.1, 130.4, 129.3, 125.0, 121.4, 114.2, 57.2, 56.0; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{15}H_{16}NO_4S_2]^+$ 338.0515, found 338.0510.



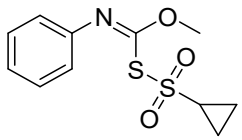
(*Z*)-(Methyl (*E*)-phenylcarbonimidic) 3-methylbenzenesulfonic thioanhydride (**4d**). White solid; Yield = 76%, 73.2 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*)*δ* 7.86 – 7.84 (m, 2H), 7.37 – 7.35 (m, 2H), 7.31 – 7.28 (m, 2H), 7.12 – 7.05(m, 1H), 6.76 – 6.74 (m, 2H), 3.94 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 151.0, 145.6, 145.0, 142.7, 129.7, 129.3, 129.2, 128.0, 125.0, 121.4, 57.2, 21.9; **HRMS** (ESI-TOF) *m/z*: [M + H]$^+$ Calcd. for $[C_{15}H_{16}NO_3S_2]^+$ 322.0566, found 322.0559.



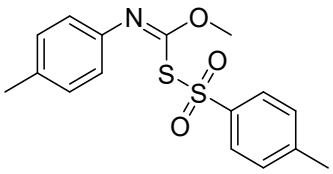
(*Z*)-(Methyl (*E*)-phenylcarbonimidic) 2-methylbenzenesulfonic thioanhydride (**4e**). White solid; Yield = 75%, 72.2 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.98 (m , 2H), 7.67 (m, 1H), 7.58 (m, 2H), 7.16 (m, 1H), 7.10 (m, 1H), 7.04 (m, 1H), 6.60 (m, 1H), 3.96 (s, 3H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) *δ* 150.3, 145.5, 143.5, 134.3, 130.8, 129.5, 129.2, 127.9, 126.6, 125.2, 120.9, 57.2, 17.7; **HRMS** (ESI-TOF) *m/z*: [M + H]$^+$ Calcd. for $[C_{15}H_{16}NO_3S_2]^+$ 322.0566, found 322.0563.



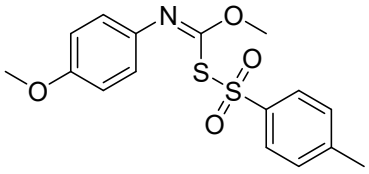
(*Z*)-(Methyl (*E*)-phenylcarbonimidic) naphthalene-2-sulfonic thioanhydride (**4f**). White solid; Yield = 71%, 76.1 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 8.49 – 8.48 (m, 1H), 7.96 – 7.93 (m, 2H), 7.90 – 7.86 (m, 2H), 7.67 – 7.57 (m, 2H), 7.23 – 7.19 (m, 2H), 7.07 – 7.03 (m, 1H), 6.70 – 6.67 (m, 2H), 3.86 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) *δ* 144.9, 142.2, 135.5, 131.9, 129.9, 129.8, 129.7, 129.4, 129.3, 129.1, 128.2, 128.1, 125.0, 122.5, 121.4, 57.3; **HRMS** (ESI-TOF) *m/z*: [M + H]$^+$ Calcd. for $[C_{18}H_{16}NO_3S_2]^+$ 358.0566, found 358.0570.



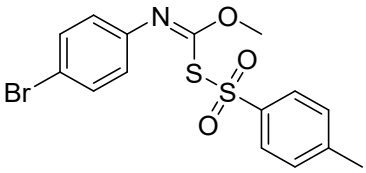
(*Z*)-Cyclopropanesulfonic (methyl (*E*)-phenylcarbonimidic) thioanhydride (**4g**). Yellow oil; Yield =73%, 59.3 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 – 7.30(m, 2H), 7.16 – 7.12 (m, 1H), 6.85 – 6.82 (m, 2H), 4.11 (s, 3H), 1.48 – 1.44 (m, 2H), 1.23 – 1.19 (m, 2H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.9, 145.3, 129.3, 125.1, 121.5, 57.5, 42.1, 8.4; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{11}H_{14}NO_3S_2]^+$ 272.0410, found 272.0416.



(*Z*)-(Methyl (*E*)-p-tolylcarbonimidic) 4-methylbenzenesulfonic thioanhydride (**4h**). Yellow oil; Yield = 76%, 76.4 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 – 7.84 (m, 2H), 7.37 – 7.34 (m, 2H), 7.12 – 7.07 (m, 3H), 6.66 – 6.64 (m, 2H), 3.93 (s, 3H), 2.47 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.8, 145.5, 142.7, 142.4, 134.6, 129.9, 129.7, 128.0, 121.2, 57.2, 21.9, 21.0; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{16}H_{18}NO_3S_2]^+$ 336.0723, found 336.0720.

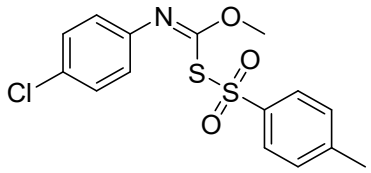


(*Z*)-(Methyl (*E*)-(4-methoxyphenyl)carbonimidic) 4-methylbenzenesulfonic thioanhydride (**4i**). Yellow oil; Yield = 75%, 78.9 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 – 7.83 (d, J = 8.4 Hz, 2H), 7.36 – 7.34 (m, 2H), 6.83 – 6.79 (m, 2H), 6.71 – 6.67 (m, 2H), 3.92 (s, 3H), 3.77 (s, 3H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 157.1, 150.9, 145.5, 142.7, 138.1, 129.7, 128.0, 122.5, 114.5, 57.2, 55.5, 21.9; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{16}H_{18}NO_4S_2]^+$ 352.0672, found 352.0674.

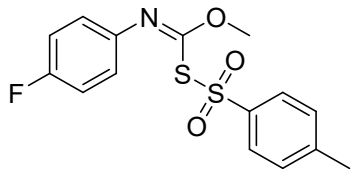


(*Z*)-(Methyl (*E*)-(4-bromophenyl)carbonimidic) 4-methylbenzenesulfonic thioanhydride (**4j**). Yellow oil; Yield = 71%, 84.8 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 – 7.82 (m, 2H), 7.39 – 7.37 (m, 3H), 7.36 – 7.34 (m, 1H), 6.65 – 6.62 (m, 2H), 3.93 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 151.5, 145.8, 144.1, 142.6,

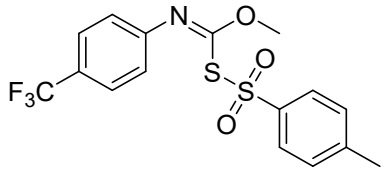
132.3, 129.8, 128.0, 123.2, 118.2, 57.4, 21.9; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{15}H_{15}BrNO_3S_2]^+$ 399.9671, found 399.9665.



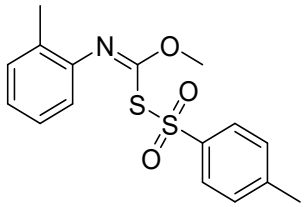
(*Z*)-(Methyl (*E*)-(4-chlorophenyl)carbonimidic) 4-methylbenzenesulfonic thioanhydride (**4k**). Yellow oil; Yield = 76%, 80.9 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 – 7.82 (m, 2H), 7.37 – 7.35 (m, 2H), 7.25 – 7.22 (m, 2H), 6.71 – 6.67 (m, 2H), 3.93 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 151.5, 145.7, 143.5, 142.5, 130.3, 129.7, 129.3, 127.9, 122.7, 57.3, 21.8; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{15}H_{15}ClNO_3S_2]^+$ 356.0176, found 356.0169.



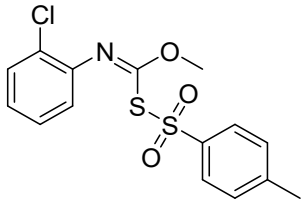
(*Z*)-(Methyl (*E*)-(4-fluorophenyl)carbonimidic) 4-methylbenzenesulfonic thioanhydride (**4l**). Yellow oil; Yield = 71%, 72.2 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 – 7.83 (m, 2H), 7.37 – 7.35 (m, 2H), 6.99 – 6.94 (m, 2H), 6.73 – 6.69 (m, 2H), 3.93 (s, 3H), 2.47(s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 160.3 (d, J = 242), 151.5, 145.7, 142.6, 141.10, 141.07, 129.9, 128.0, 123.0, 122.8, 115.5 (d, J = 21.0), 57.3, 21.9; **^{19}F NMR** (376 MHz, DPBP) δ -116.05; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{15}H_{15}FNO_3S_2]^+$ 340.0472, found 340.0473.



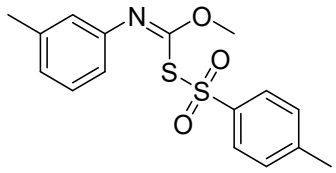
(*Z*)-(Methyl (*E*)-(4-(trifluoromethyl)phenyl)carbonimidic) 4-methylbenzenesulfonic thioanhydride (**4m**). Yellow oil; Yield = 72%, 84.0 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 – 7.83 (m, 2H), 7.54 –7.52 (m, 2H), 7.38 – 7.36 (m, 2H), 6.86 – 6.84 (m, 2H), 3.96 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 151.8, 148.3, 145.9, 142.5, 129.9, 128.0, 126.5 (d, J = 4), 121.8, 57.5, 21.9; **^{19}F NMR** (376 MHz, DPBP) δ -61.90; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{16}H_{15}F_3NO_3S_2]^+$ 390.0440, found 390.0440.



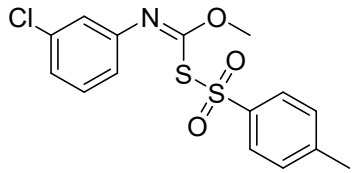
(*Z*)-(Methyl (*E*)-o-tolylcarbonimidic) 4-methylbenzenesulfonic thioanhydride (**4n**). Yellow oil; Yield = 74%, 74.4 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 – 7.85 (m, 2H), 7.37 – 7.35 (m, 2H), 7.17 – 7.15 (m, 1H), 7.12 – 7.08 (m, 1H), 7.07 – 7.02 (m, 1H), 6.63 – 6.60 (m, 1H), 3.98 (s, 3H), 2.47 (s, 3H), 2.08 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.5, 145.6, 143.5, 142.6, 130.7, 129.7, 129.4, 127.9, 126.6, 125.1, 120.8, 57.2, 21.8, 17.8.; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{16}H_{18}NO_3S_2]^+$ 336.0723, found 336.0715.



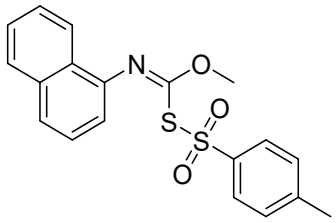
(*Z*)-(Methyl (*E*)-(2-chlorophenyl)carbonimidic) 4-methylbenzenesulfonic thioanhydride (**4o**). Yellow oil; Yield = 76%, 80.9 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 – 7.84 (m, 2H), 7.37 – 7.34 (m, 3H), 7.20 – 7.15 (m, 1H), 7.07 – 7.03 (m, 1H), 6.79 – 6.77 (m, 1H), 3.99 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 152.7, 145.7, 142.5, 142.2, 130.1, 129.8, 128.0, 127.5, 126.1, 125.9, 122.7, 57.6, 21.9; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{15}H_{15}ClNO_3S_2]^+$ 356.0176, found 356.0179.



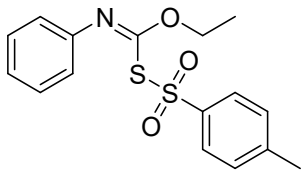
(*Z*)-(Methyl (*E*)-m-tolylcarbonimidic) 4-methylbenzenesulfonic thioanhydride(**4p**). Yellow oil; Yield = 72%, 72.4 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 – 7.84 (m, 2H), 7.37 – 7.35 (m, 2H), 7.17 – 7.14 (m, 1H), 6.94 – 6.92 (m, 1H), 6.57 – 6.53 (m, 2H), 3.93 (s, 3H), 2.48 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.7, 145.5, 144.8, 142.6, 139.2, 129.6, 129.0, 127.9, 125.7, 121.9, 118.3, 57.1, 21.8, 21.4; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{16}H_{18}NO_3S_2]^+$ 336.0723, found 336.0717.



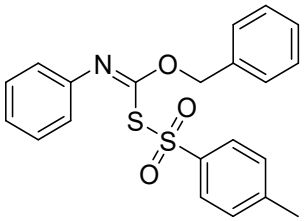
(*Z*)-(Methyl (*E*)-(3-chlorophenyl)carbonimidic) 4-methylbenzenesulfonic thioanhydride (**4q**). Yellow oil; Yield = 77%, 82.0 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 – 7.84 (m, 2H), 7.37 – 7.33 (m, 3H), 7.20 – 7.16 (m, 1H), 7.07 – 7.03 (m, 1H), 6.79 – 6.77 (m, 1H), 3.99 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 152.7, 145.7, 142.5, 142.2, 130.0, 129.7, 128.0, 127.5, 126.1, 125.8, 122.7, 57.6, 21.8.; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{15}H_{15}ClNO_3S_2]^+$ 356.0176, found 356.0174.



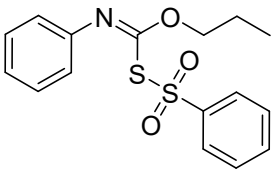
(*Z*)-(Methyl (*E*)-naphthalen-1-ylcarbonimidic) 4-methylbenzenesulfonic thioanhydride (**4r**). Yellow oil; Yield = 73%, 81.2 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.84 – 7.81 (m, 3H), 7.77 – 7.75 (m, 1H), 7.65 – 7.63 (m, 1H), 7.53 – 7.48 (m, 1H), 7.47 – 7.43 (m, 1H), 7.38 – 7.31 (m, 3H), 6.81 – 6.78 (m, 1H), 4.12 (s, 3H), 2.46 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 145.5, 142.5, 141.3, 134.2, 129.7, 128.1, 127.9, 127.0, 126.6, 126.0, 125.6, 125.3, 123.3, 116.6, 57.5, 21. 9; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{19}H_{18}NO_3S_2]^+$ 372.0723, found 372.0724.



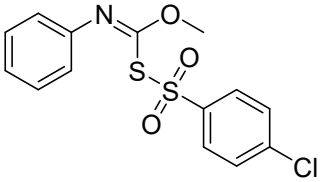
(*Z*)-(Ethyl (*E*)-phenylcarbonimidic) 4-methylbenzenesulfonic thioanhydride (**4s**). Yellow oil; Yield = 78%, 78.4 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 – 7.86 (m, 2H), 7.36 – 7.34 (m, 2H), 7.29 – 7.26 (m, 2H), 7.13 – 7.10 (m, 1H), 6.79 – 6.75 (m, 2H), 4.41 – 4.37 (m, 2H), 2.47 (s, 3H), 1.37 – 1.34 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.2, 145.5, 145.1, 142.6, 129.6, 129.2, 128.0, 124.9, 121.4, 66.8, 21.9, 14.0; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{16}H_{18}NO_3S_2]^+$ 336.0723, found 336.0720.



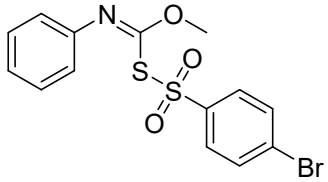
(*Z*)-(Benzyl (*E*)-phenylcarbonimidic) 4-methylbenzenesulfonic thioanhydride (**4t**). Yellow oil; Yield = 72%, 85.8 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.55 – 7.53(m, 2H), 7.45 – 7.42 (m, 5H), 7.32 – 7.29 (m, 2H), 7.16 – 7.12 (m, 1H), 7.03 – 7.01 (m, 2H), 6.81 – 6.80 (m, 2H), 5.33 (s, 2H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.2, 145.1, 144.9, 142.4, 134.7, 129.6, 129.4, 129.3, 128.9, 128.7, 127.9, 125.05, 121.44, 77.41, 76.91, 72.55, 21.81; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{21}H_{20}NO_3S_2]^+$ 398.0879, found 398.0880.



(*Z*)-benzenesulfonic (propyl (*E*)-phenylcarbonimidic) thioanhydride (**4u**). Yellow oil; Yield = 74%, 74.4 mg (PE/EA = 10:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 – 7.97 (m, 2H), 7.70 – 7.62 (m, 1H), 7.56 (dd, 2H), 7.31 – 7.26 (m, 2H), 7.16 – 7.08 (m, 1H), 6.82 – 6.72 (m, 2H), 4.28 (t, 2H), 1.72 (q, 2H), 0.94 (t, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.1, 145.5, 145.1, 134.2, 129.3, 129.2, 127.8, 125.0, 121.5, 72.6, 21.8, 10.5. **HRMS** (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd. for $[C_{16}H_{17}NO_3S_2Na]^+$ 358.0542, found 358.0524.



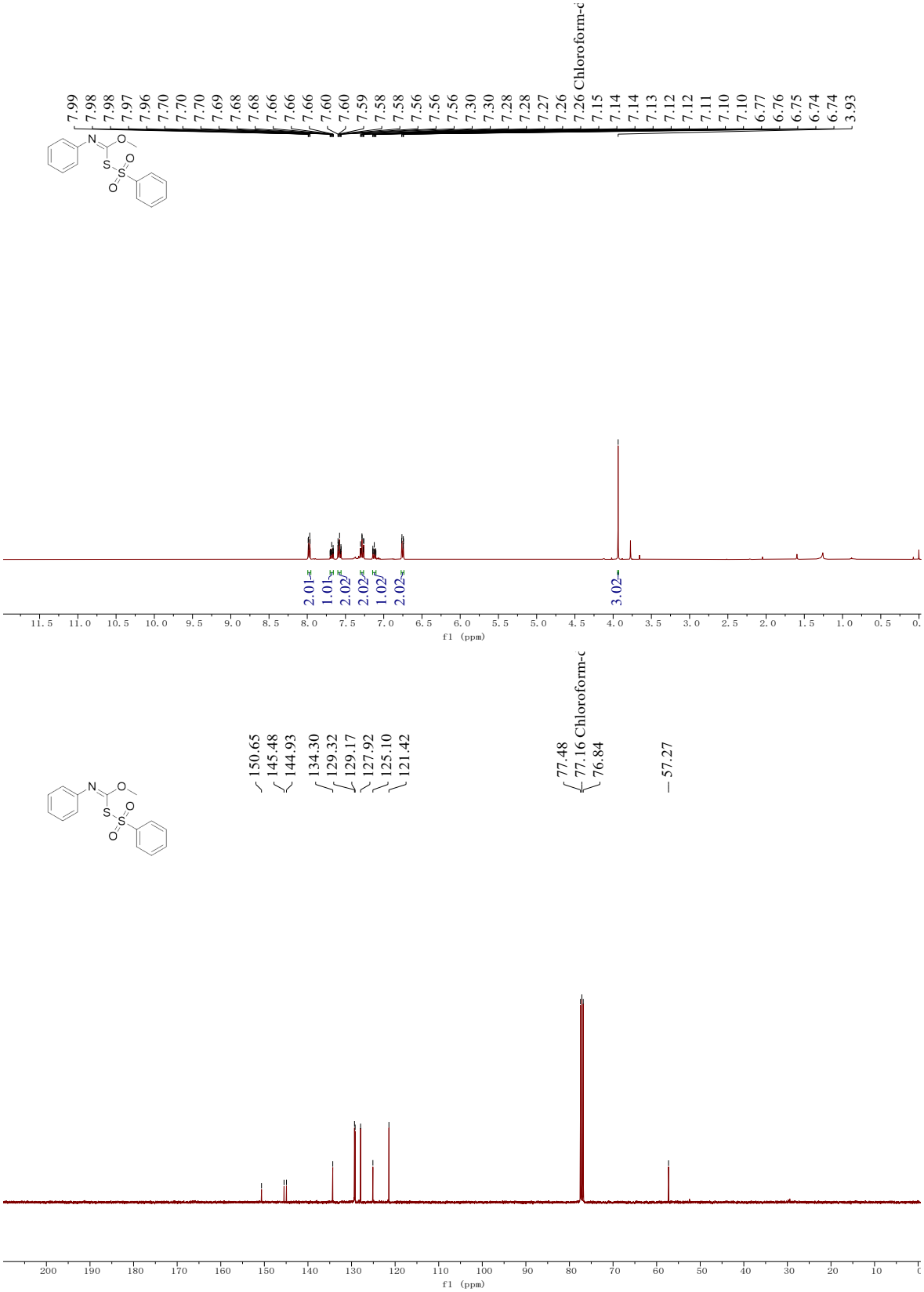
(*Z*)-4-chlorobenzenesulfonic (methyl (*E*)-phenylcarbonimidic) thioanhydride. Yellow oil; Yield = 68%, 69.6 mg (PE/EA = 10:1);**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 – 7.95 (m, 2H), 7.70 – 7.65 (m, 1H), 7.58 (m, *m* 2H), 7.35 (m, 1H), 7.18 (m, 1H), 7.08 – 7.03 (m, 1H), 6.77 (m, 1H), 3.98 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 152.4, 145.3, 142.2, 134.4, 130.05, 129.2, 127.9, 127.6, 126.1, 125.9, 122.7, 57.6. **HRMS** (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd. for $[C_{14}H_{12}ClNO_3S_2Na]^+$ 363.9839, found 363.9831.



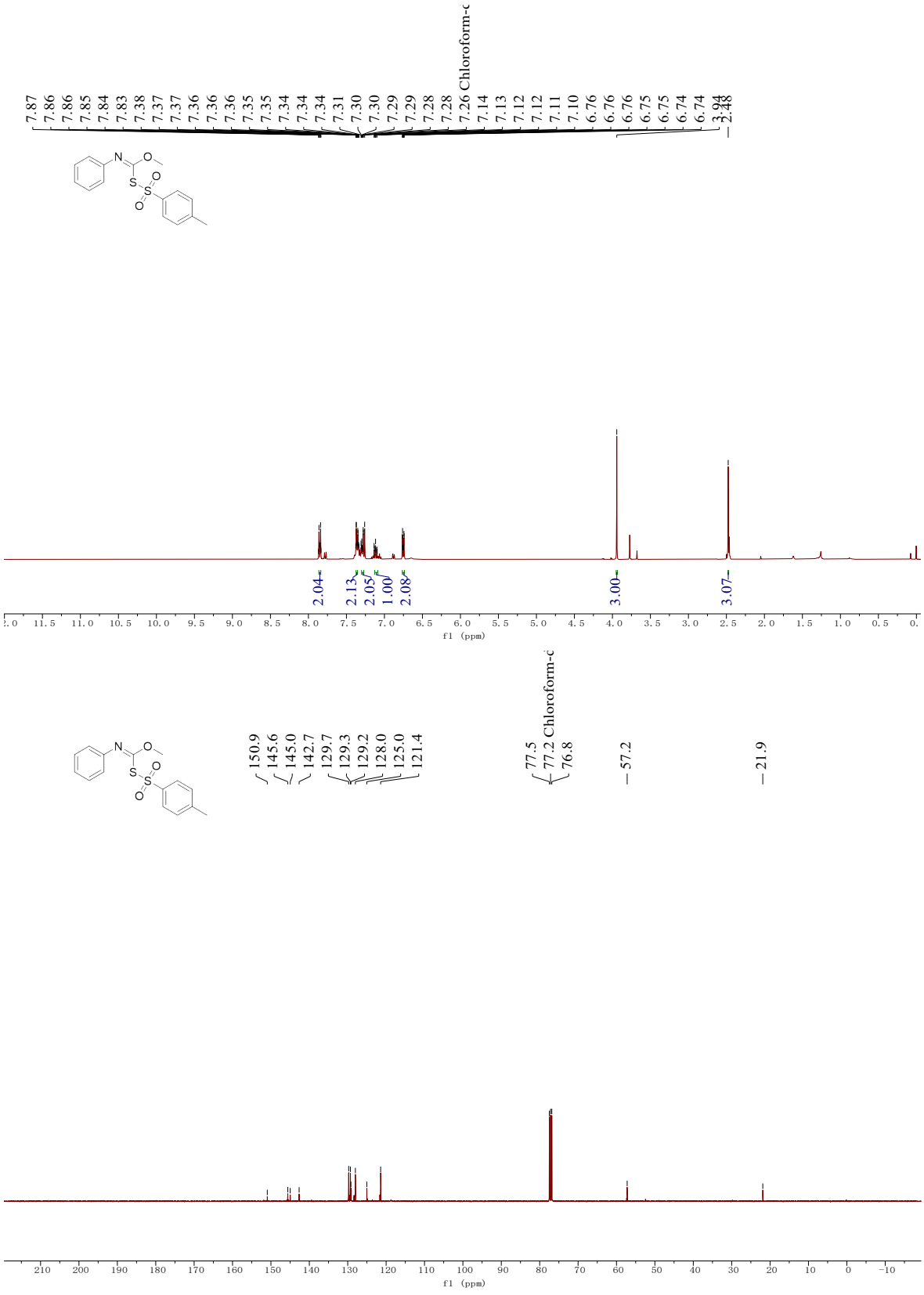
(*Z*)-4-bromobenzenesulfonic (methyl (*E*)-phenylcarbonimidic) thioanhydride. Yellow oil; Yield = 68%, 75.1 mg (PE/EA = 10:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.95 (m, 2H), 7.70-7.66 (m, 1H), 7.60-7.56 (m, 2H), 7.36-7.34 (m, 1H), 7.20-7.16 (m, 1H), 7.07-7.03 (m, 1H), 6.78-6.76 (m, 1H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 152.4, 145.3, 142.15, 134.4, 130.0, 129.2, 127.9, 127.5, 126.1, 125.9, 122.7, 57.6. **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $[C_{14}H_{12}BrNO_3S_2]^+$ 385.9442, found 385.9440.

4.Copies of ^{13}C and ^{1}H NMR spectra for all product

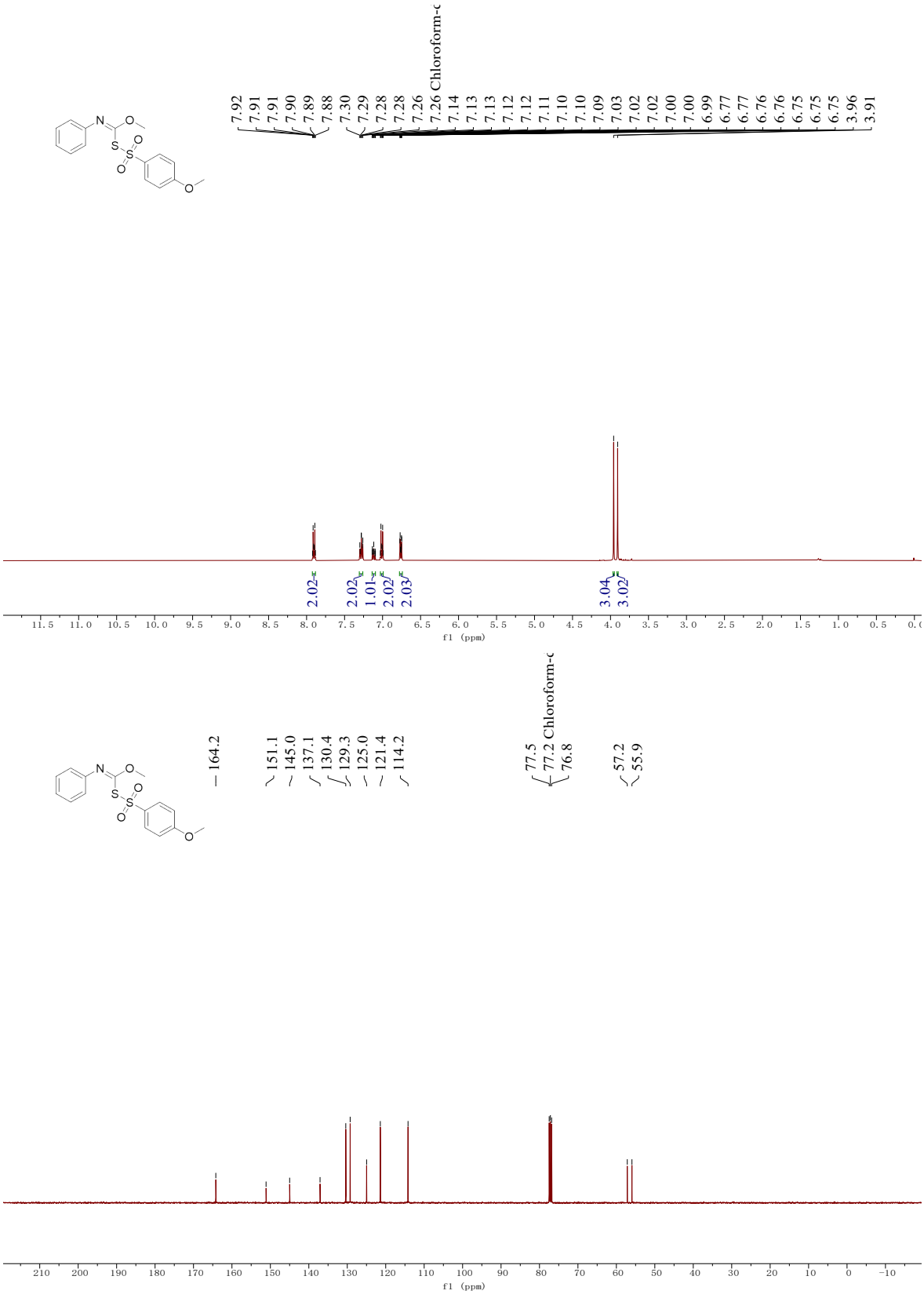
^{1}H and ^{13}C NMR Spectrum of **4a** (400 MHz, Chloroform-*d*).



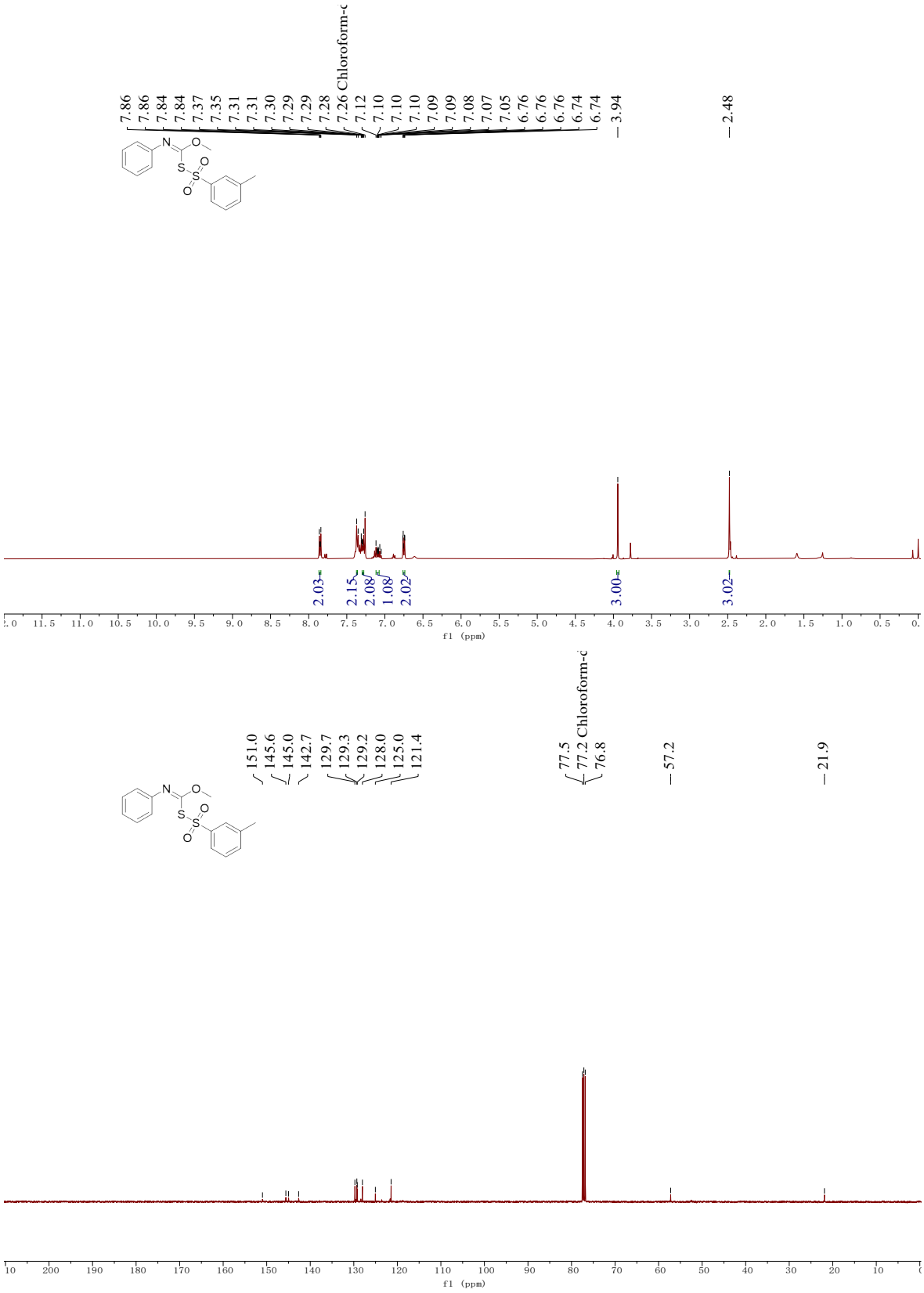
^{1}H and ^{13}C NMR Spectrum of **4b** (400 MHz, Chloroform-*d*).



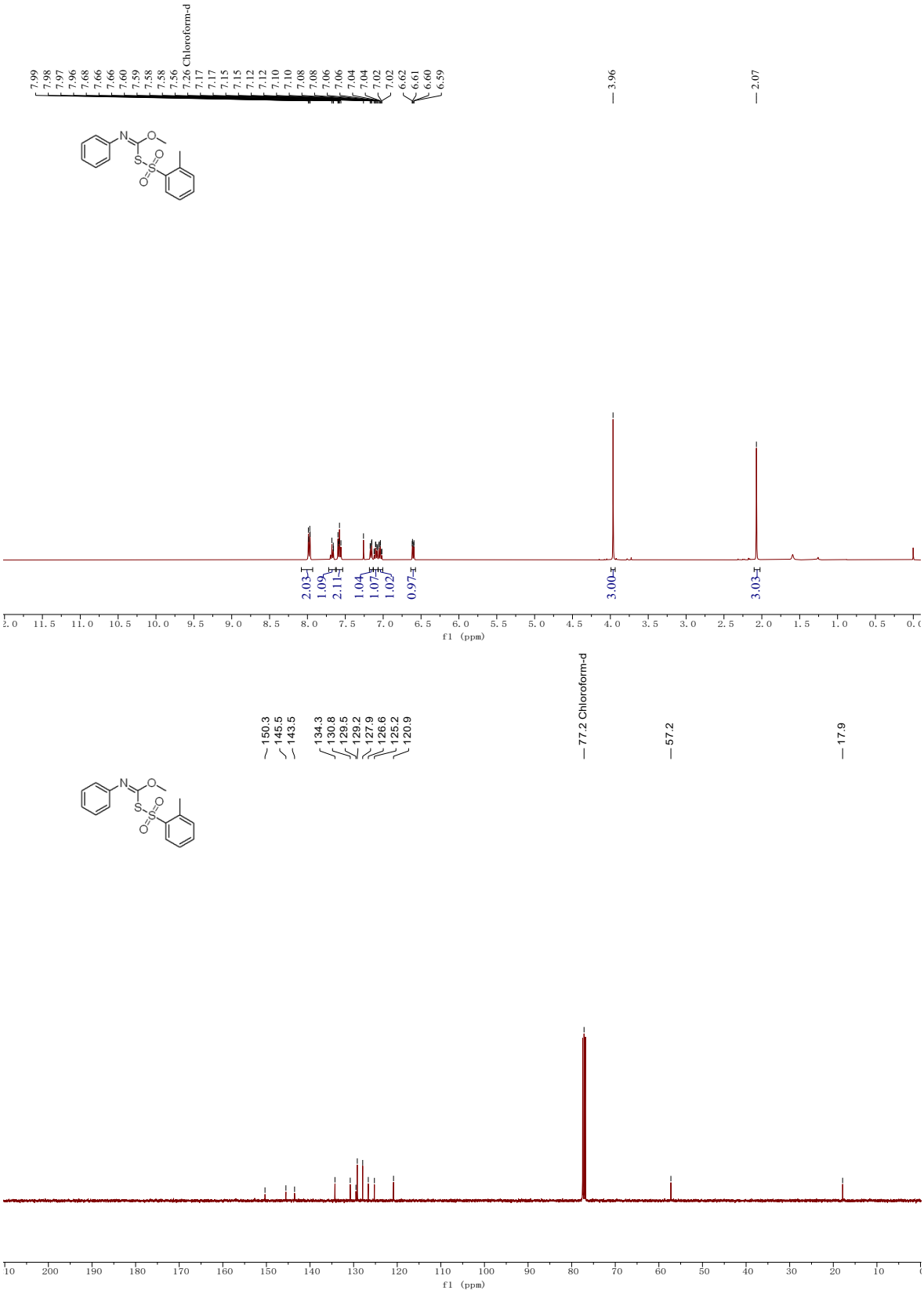
^{1}H and ^{13}C NMR Spectrum of **4c** (400 MHz, Chloroform-*d*).



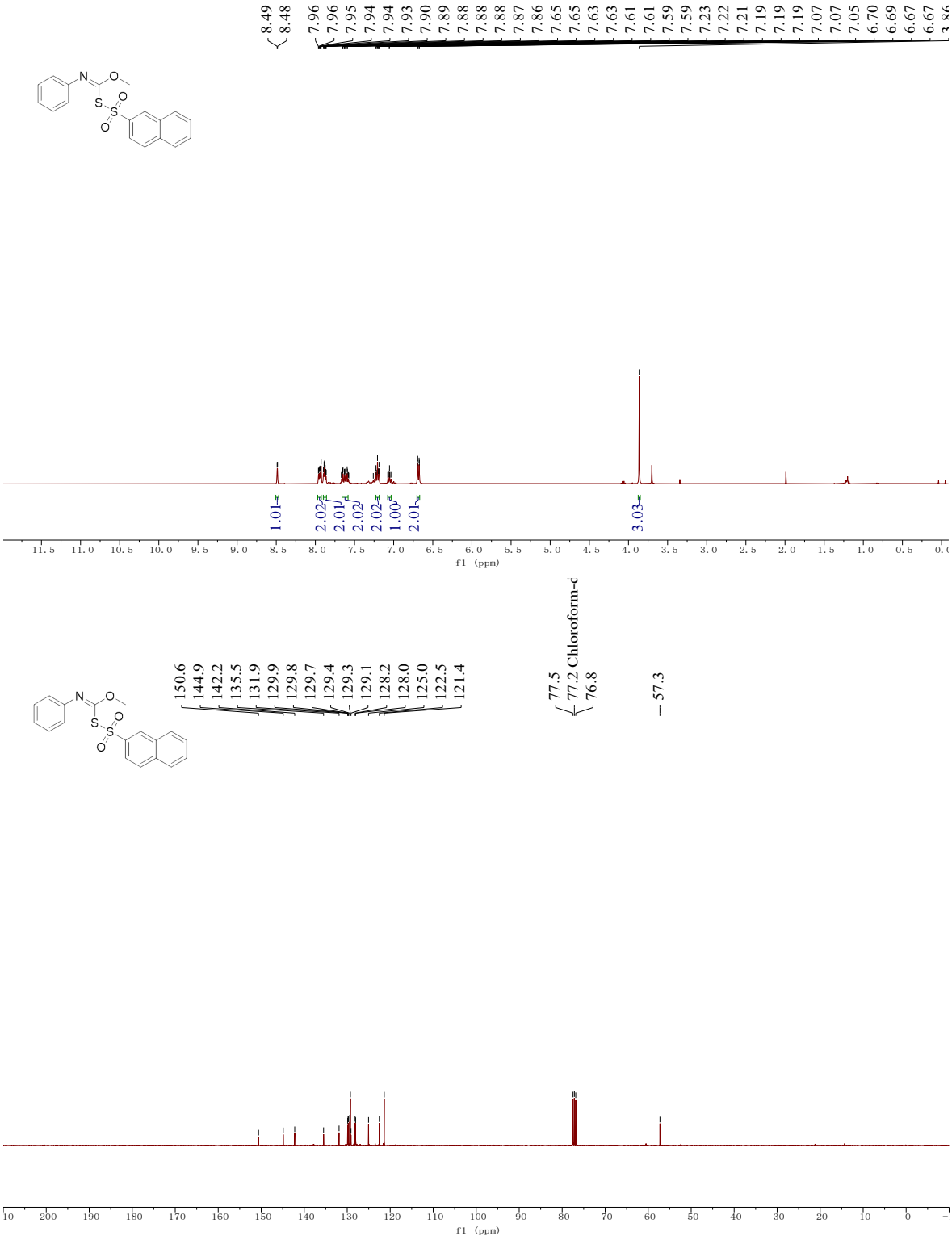
^{1}H and ^{13}C NMR Spectrum of **4d** (400 MHz, Chloroform-*d*).



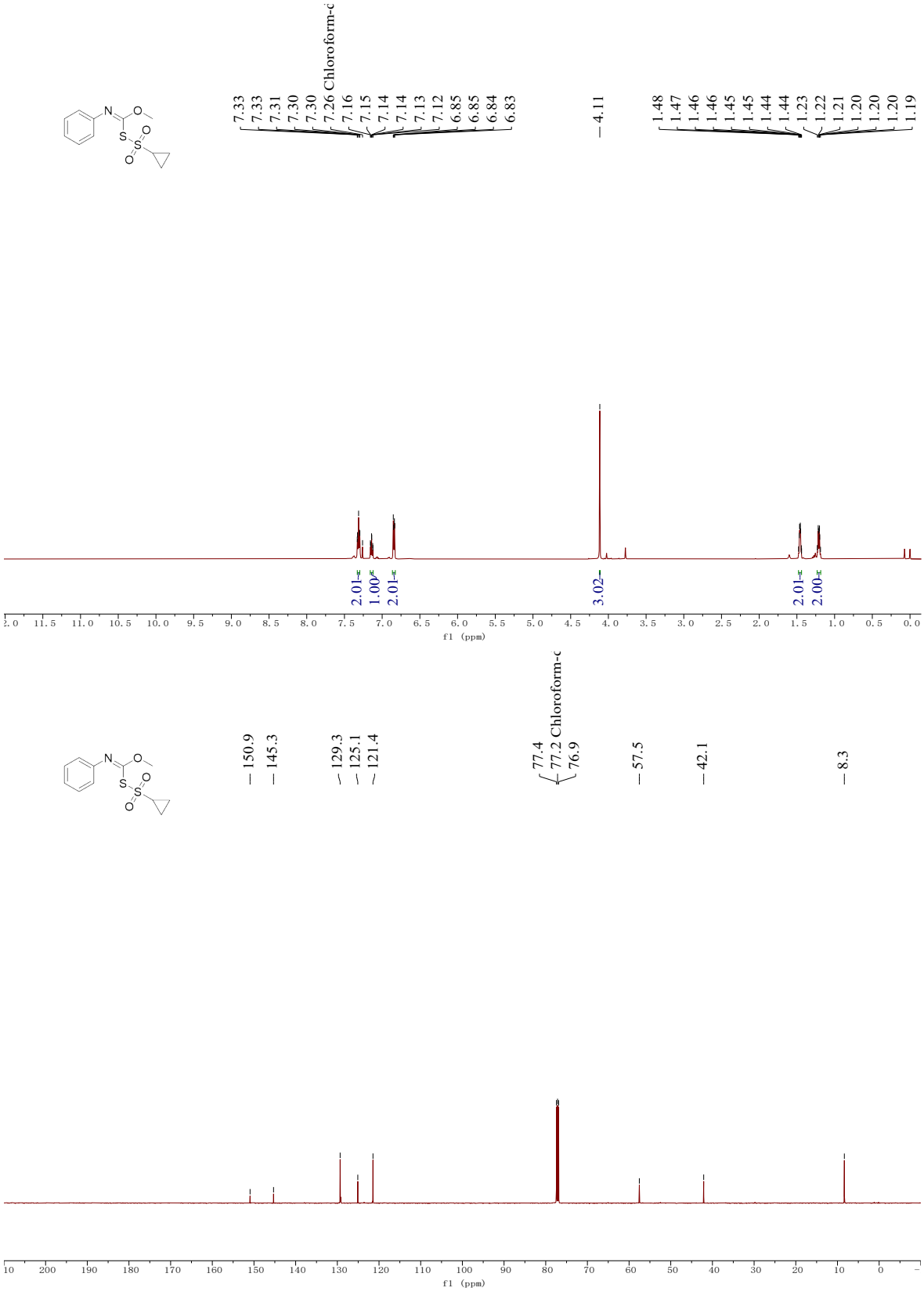
^{1}H and ^{13}C NMR Spectrum of **4e** (400 MHz, Chloroform-*d*).



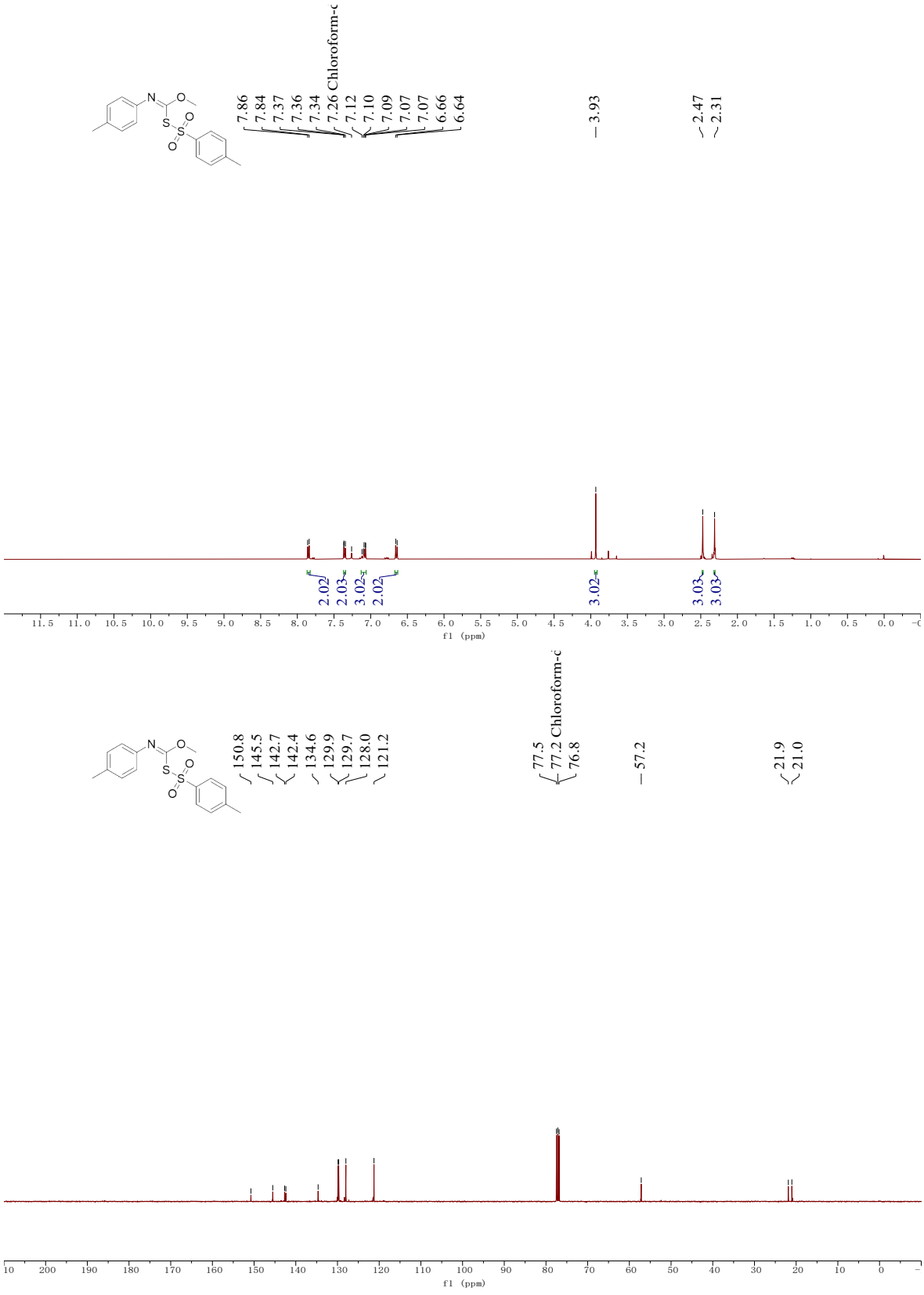
^{1}H and ^{13}C NMR Spectrum of **4f** (400 MHz, Chloroform-*d*).



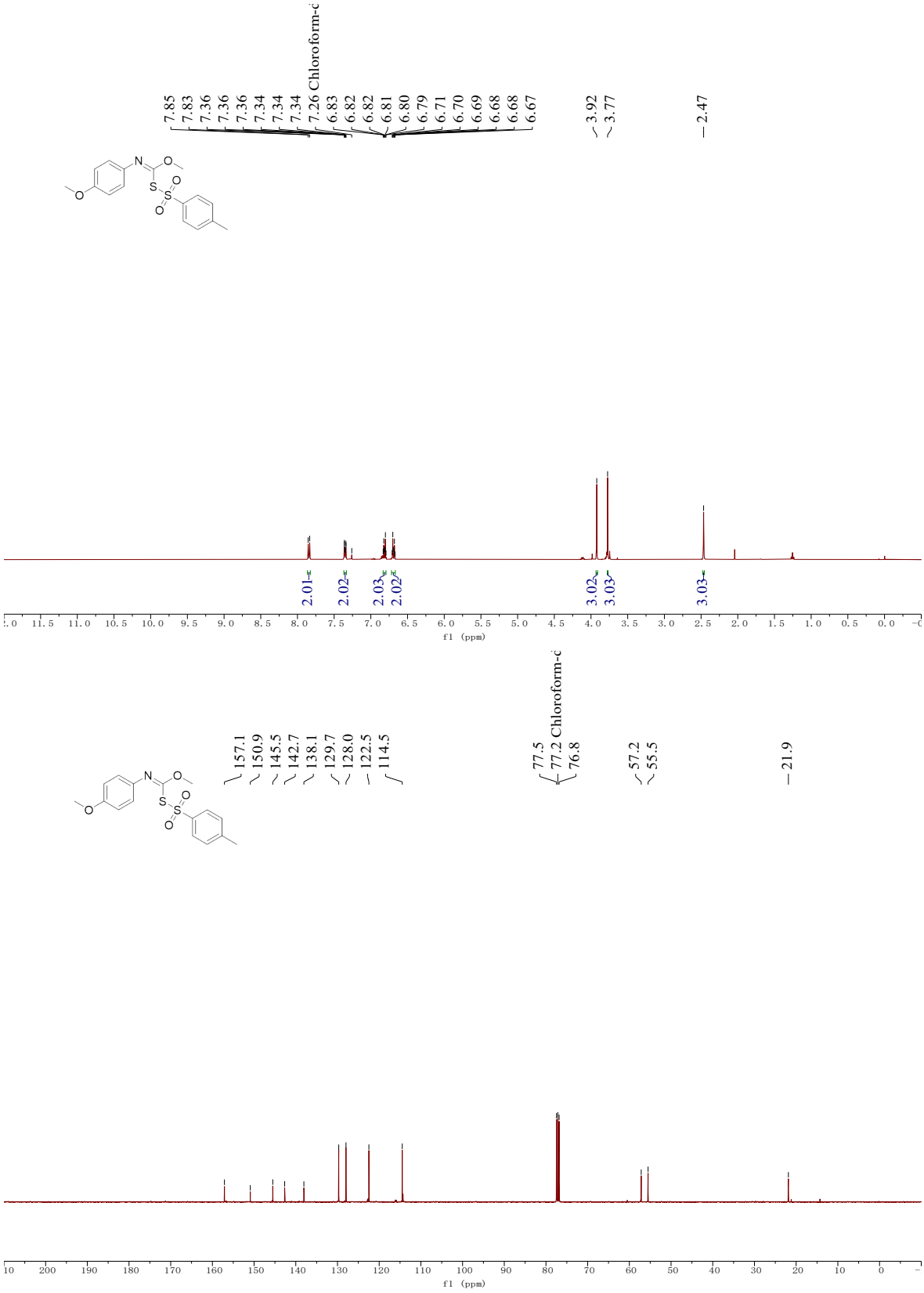
^{1}H and ^{13}C NMR Spectrum of **4g** (400 MHz, Chloroform-*d*).



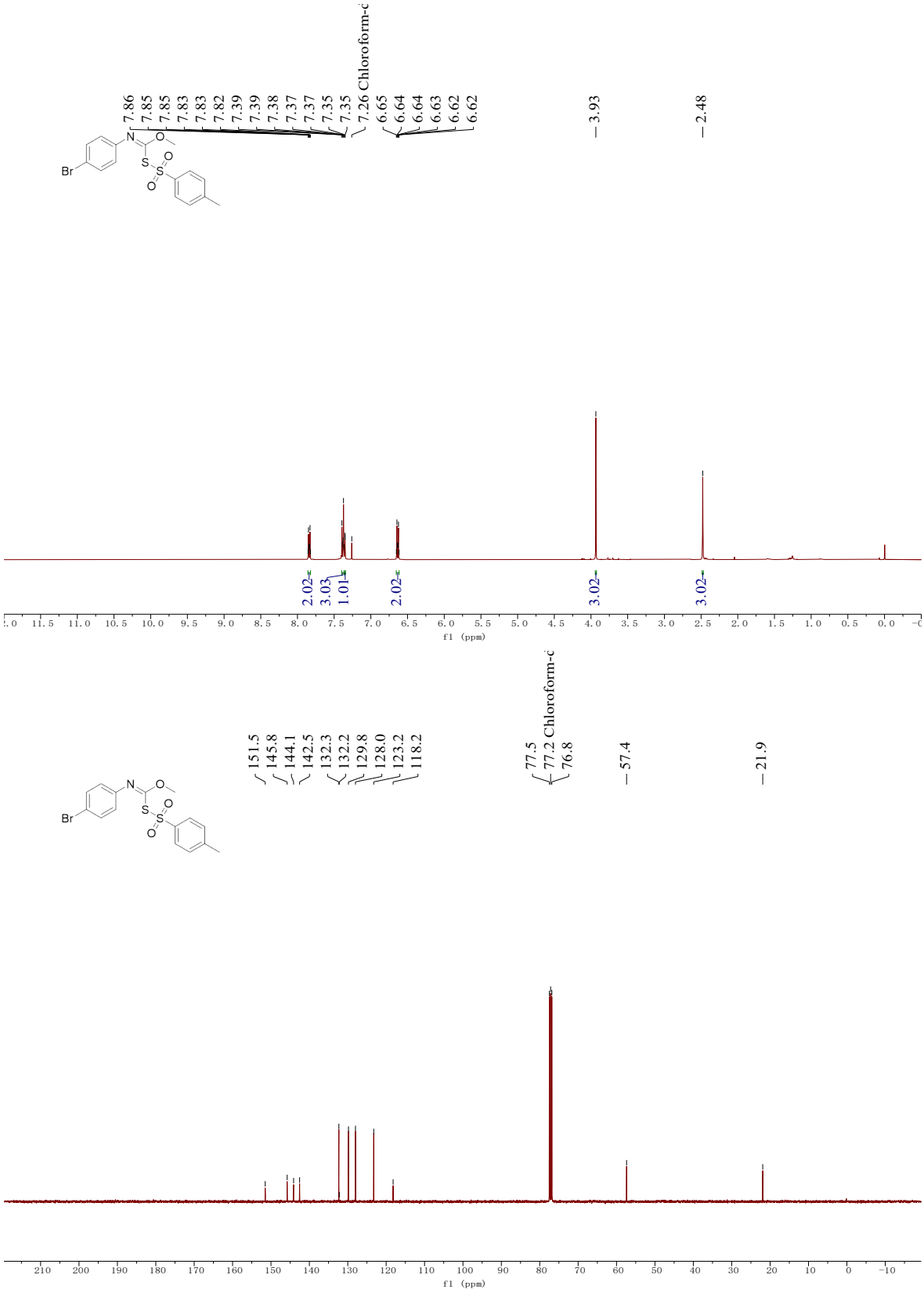
^{1}H and ^{13}C NMR Spectrum of **4h** (400 MHz, Chloroform-*d*).



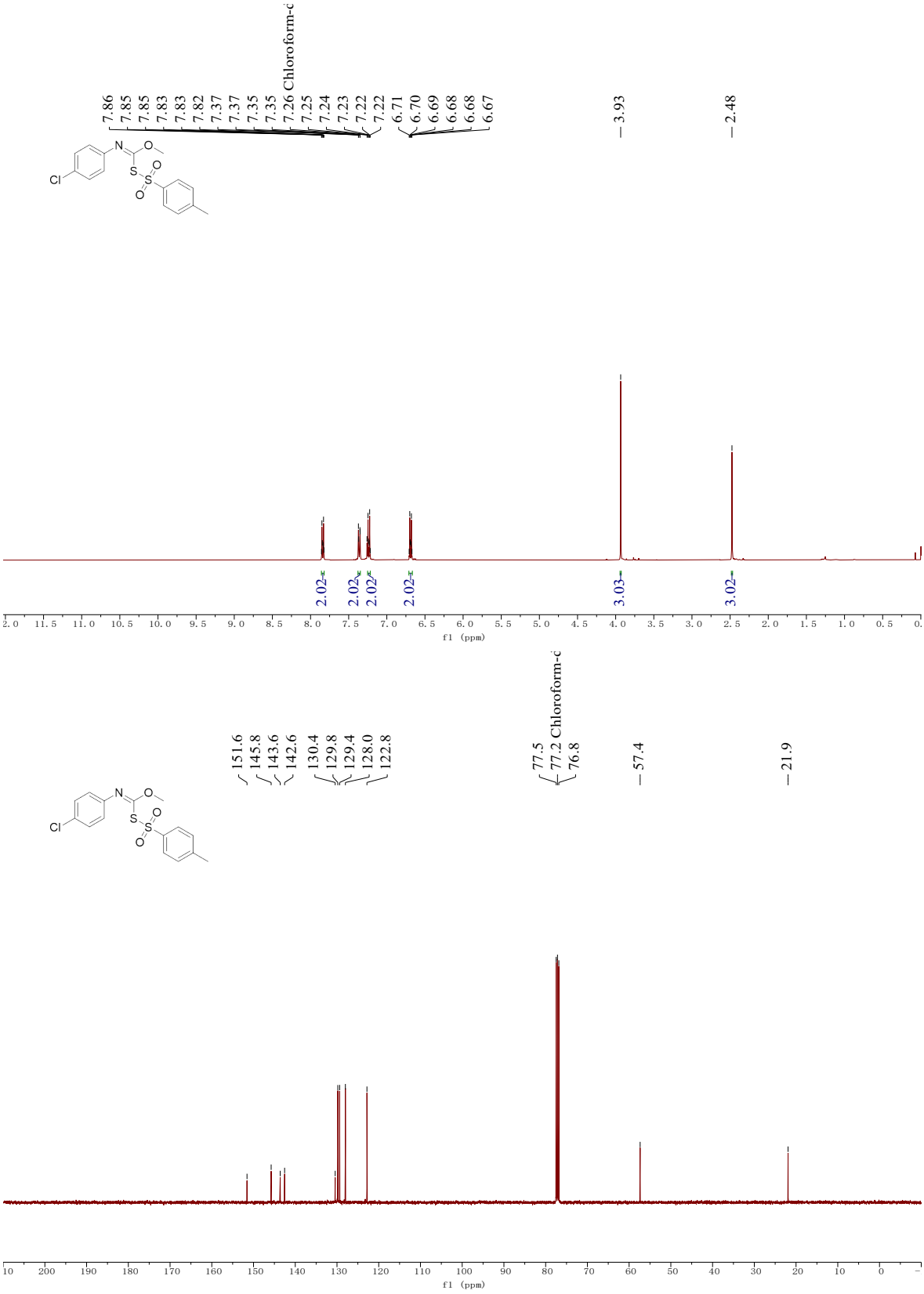
^{1}H and ^{13}C NMR Spectrum of **4i** (400 MHz, Chloroform-*d*.



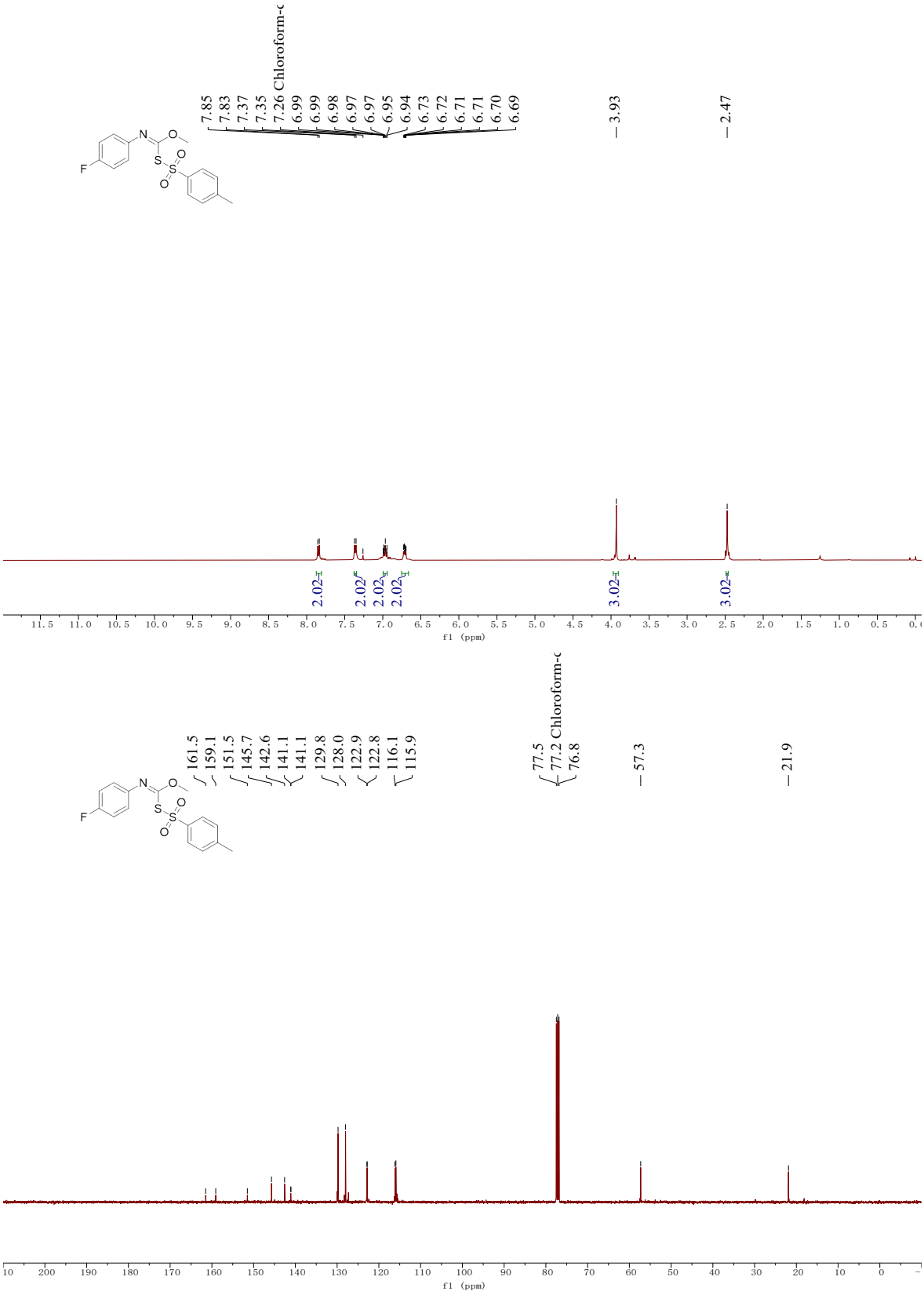
^{1}H and ^{13}C NMR Spectrum of **4j** (500 MHz, Chloroform-*d*).

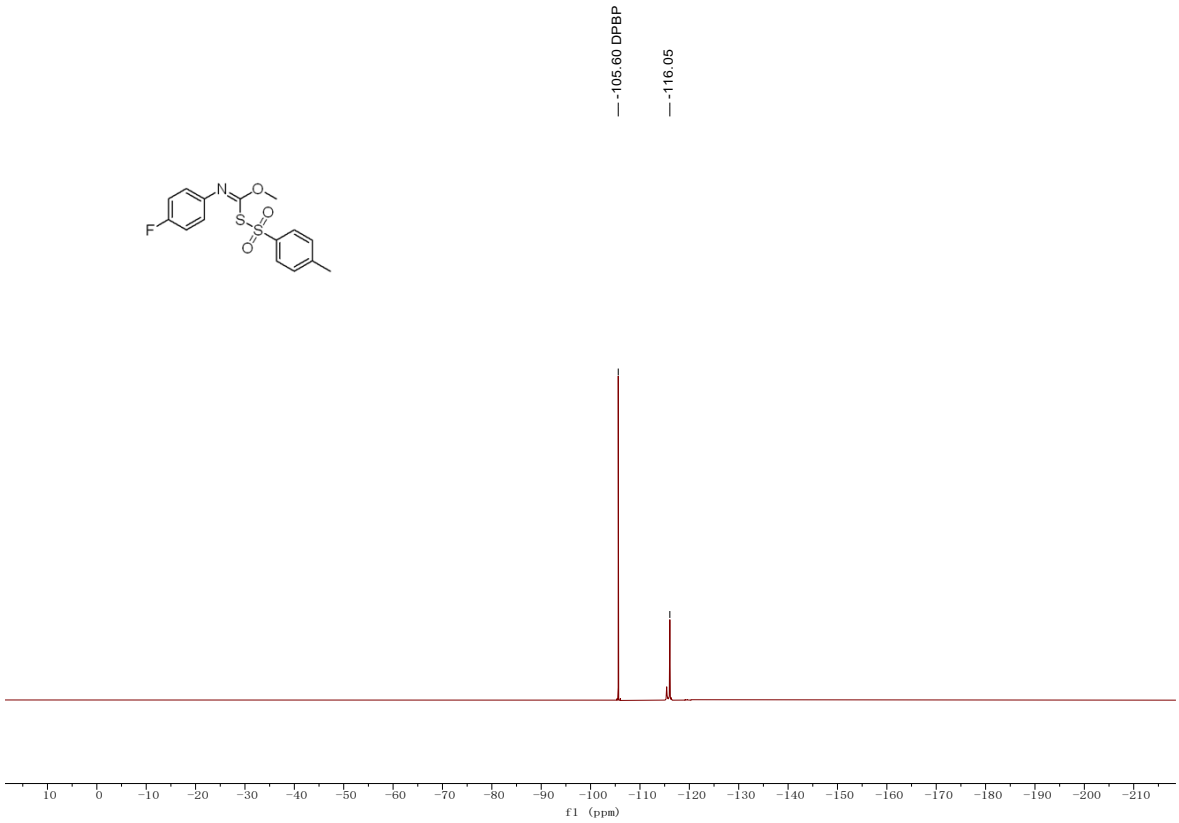


^{1}H and ^{13}C NMR Spectrum of **4k** (500 MHz, Chloroform-*d*).

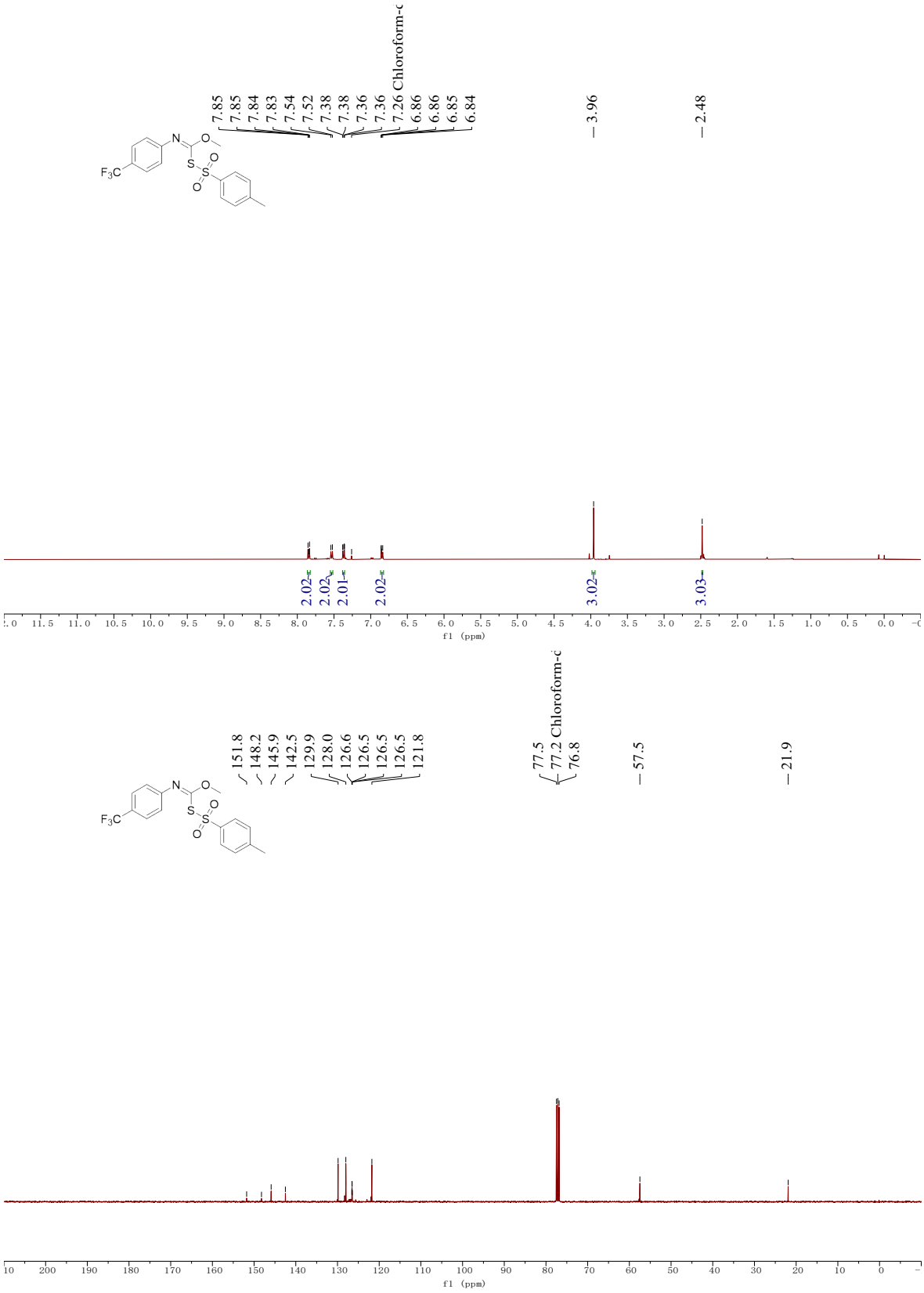


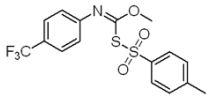
^{1}H, ^{13}C and ^{19}F NMR Spectrum of **4l** (500 MHz, Chloroform-*d*).




-105.60 DPBP
-116.05
F
N
O
S
S
O
O
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, ^{13}C and ^{19}F NMR Spectrum of **4m** (500 MHz, Chloroform-*d*).





-61.90
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-20
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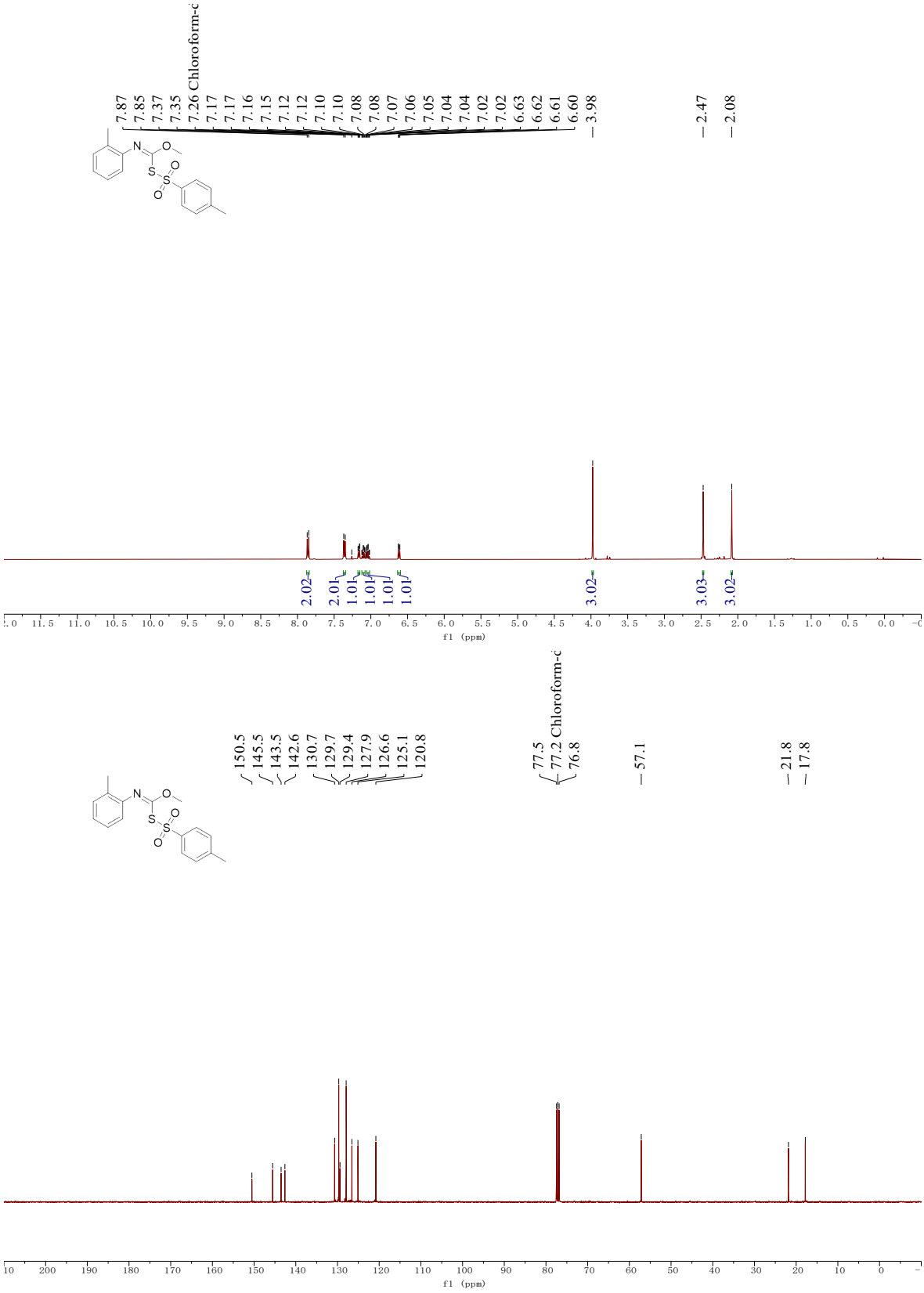
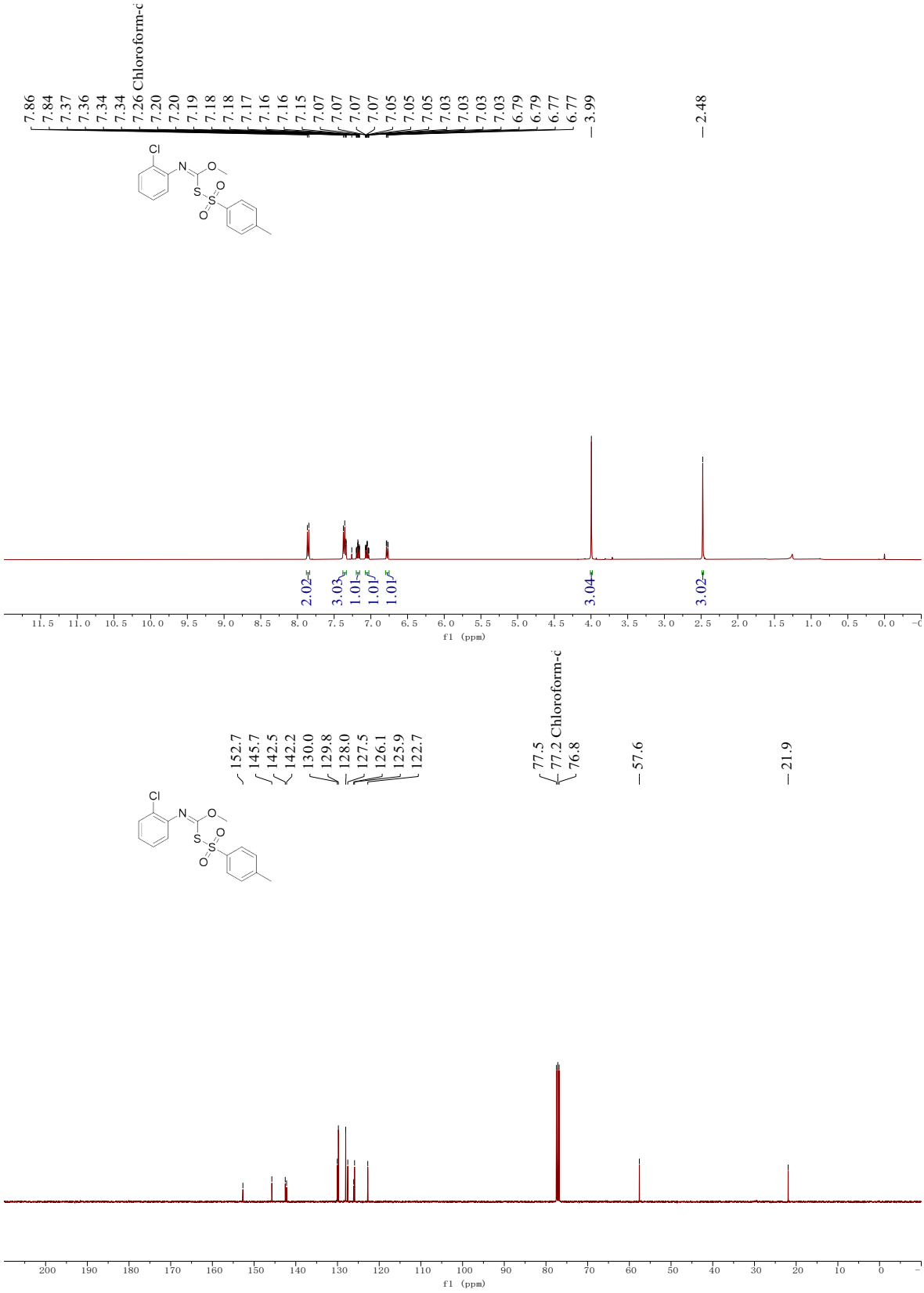
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

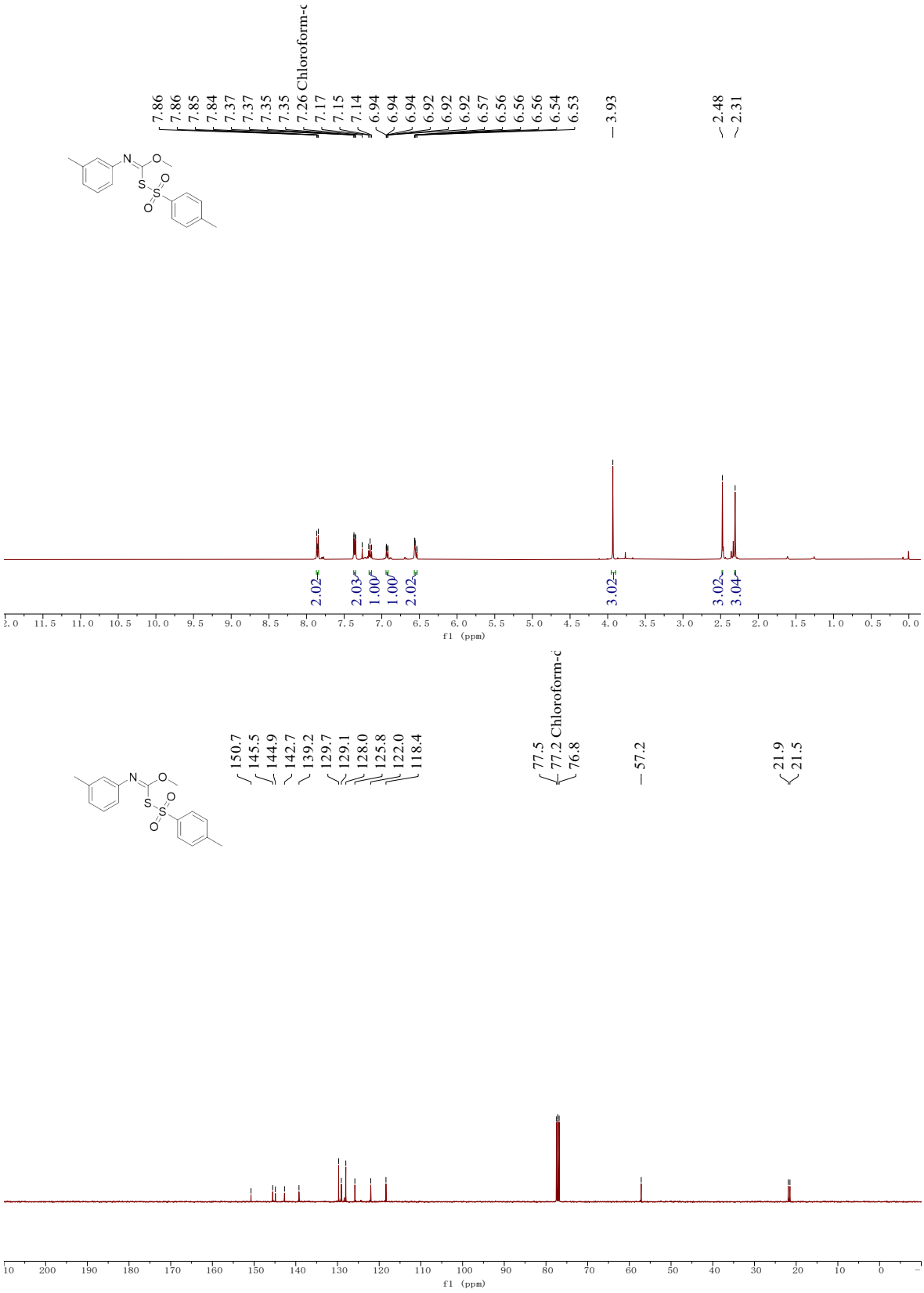
^{1}H and ^{13}C NMR Spectrum of **4n** (400 MHz, Chloroform-*d*).



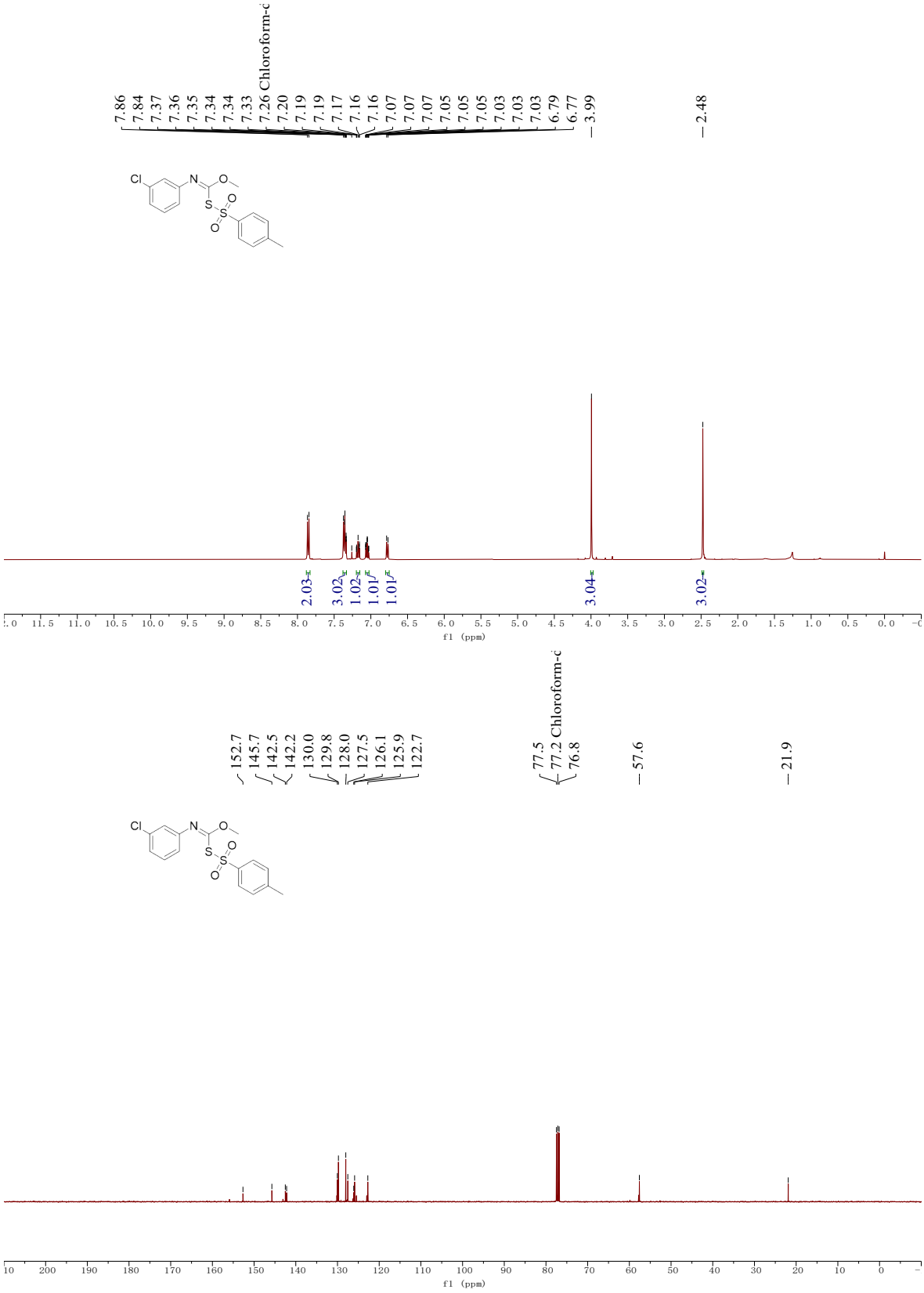
^{1}H and ^{13}C NMR Spectrum of **4o** (400 MHz, Chloroform-*d*).



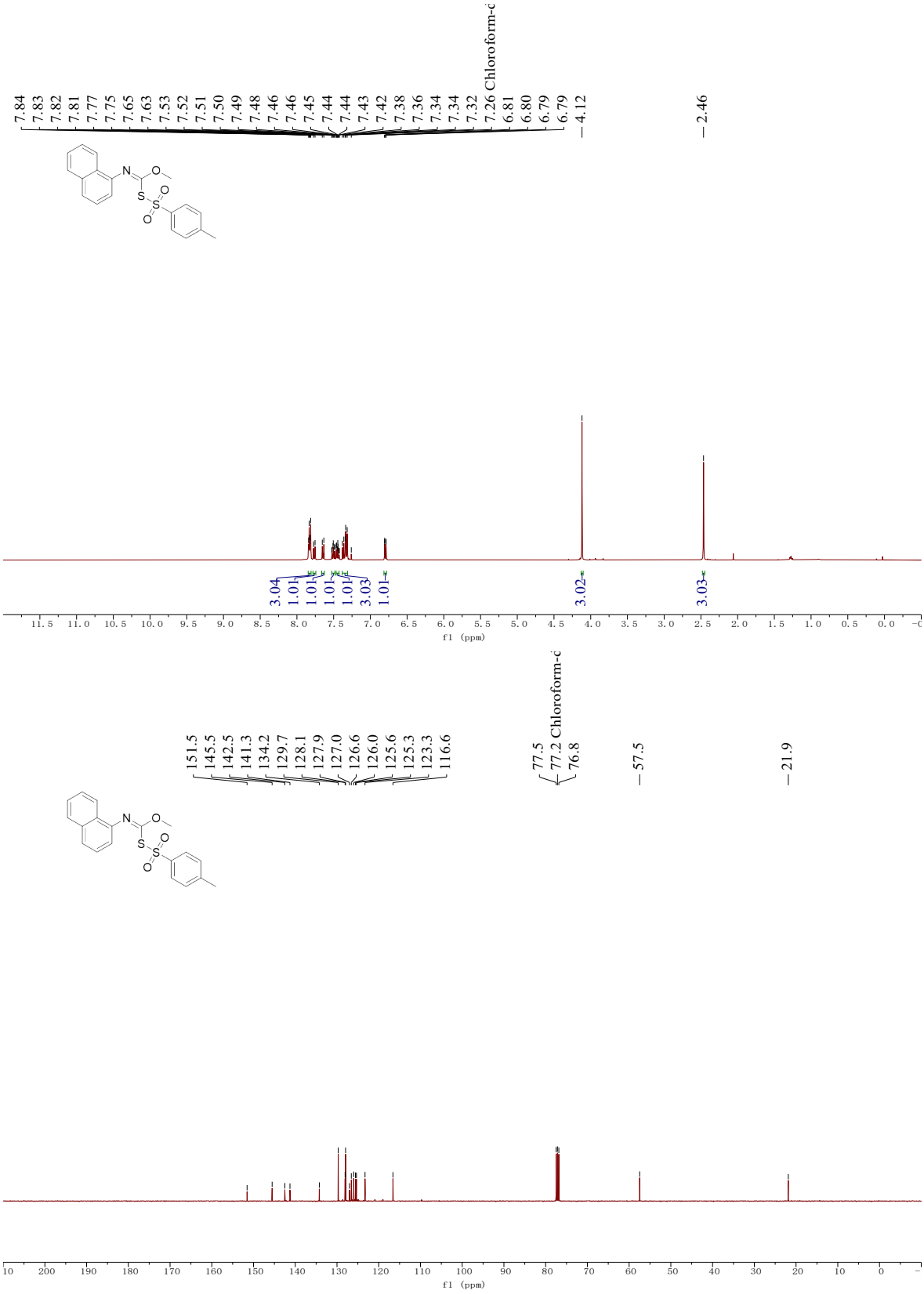
^{1}H and ^{13}C NMR Spectrum of **4p** (400 MHz, Chloroform-*d*).



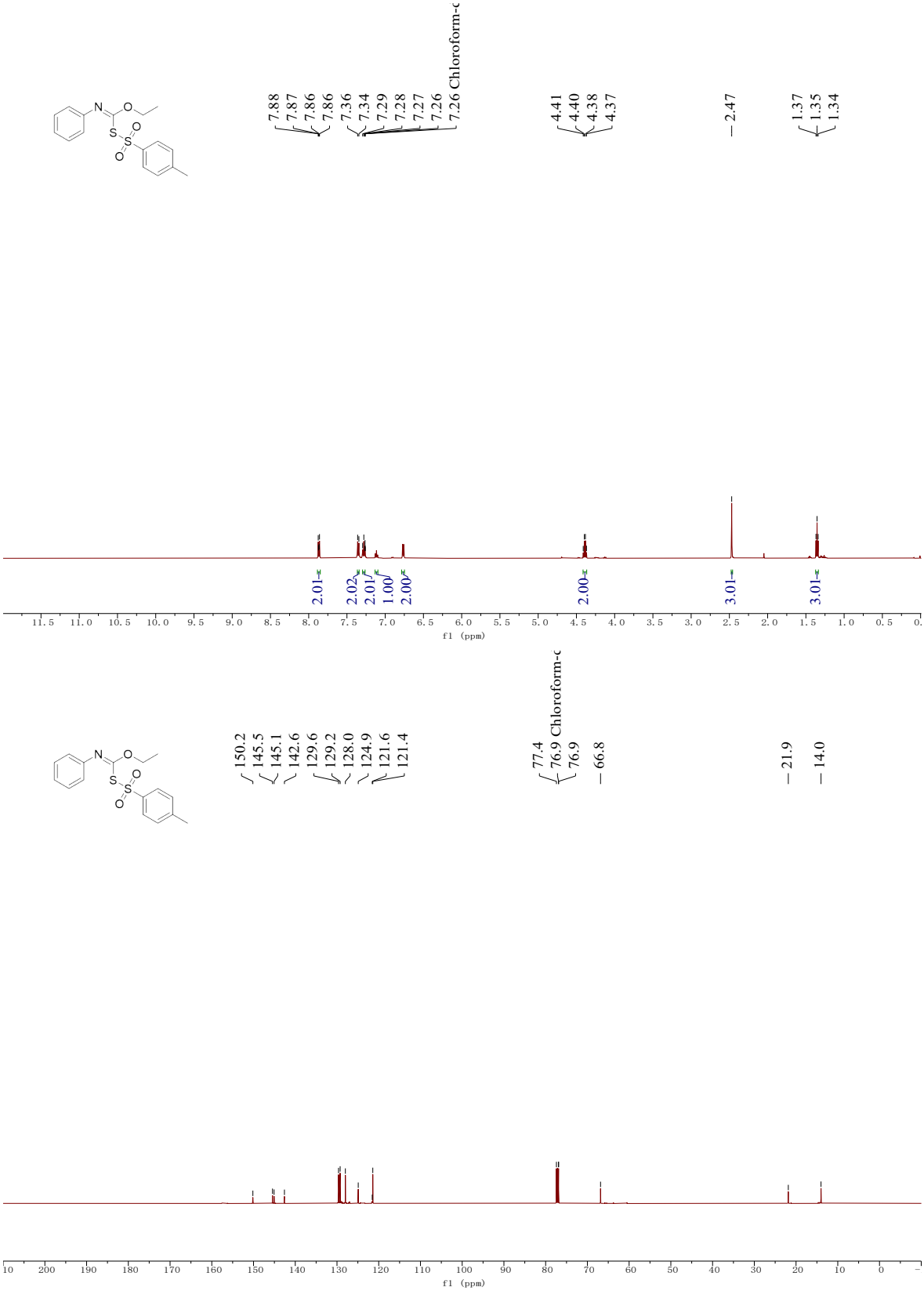
^{1}H and ^{13}C NMR Spectrum of **4q** (400 MHz, Chloroform-*d*).



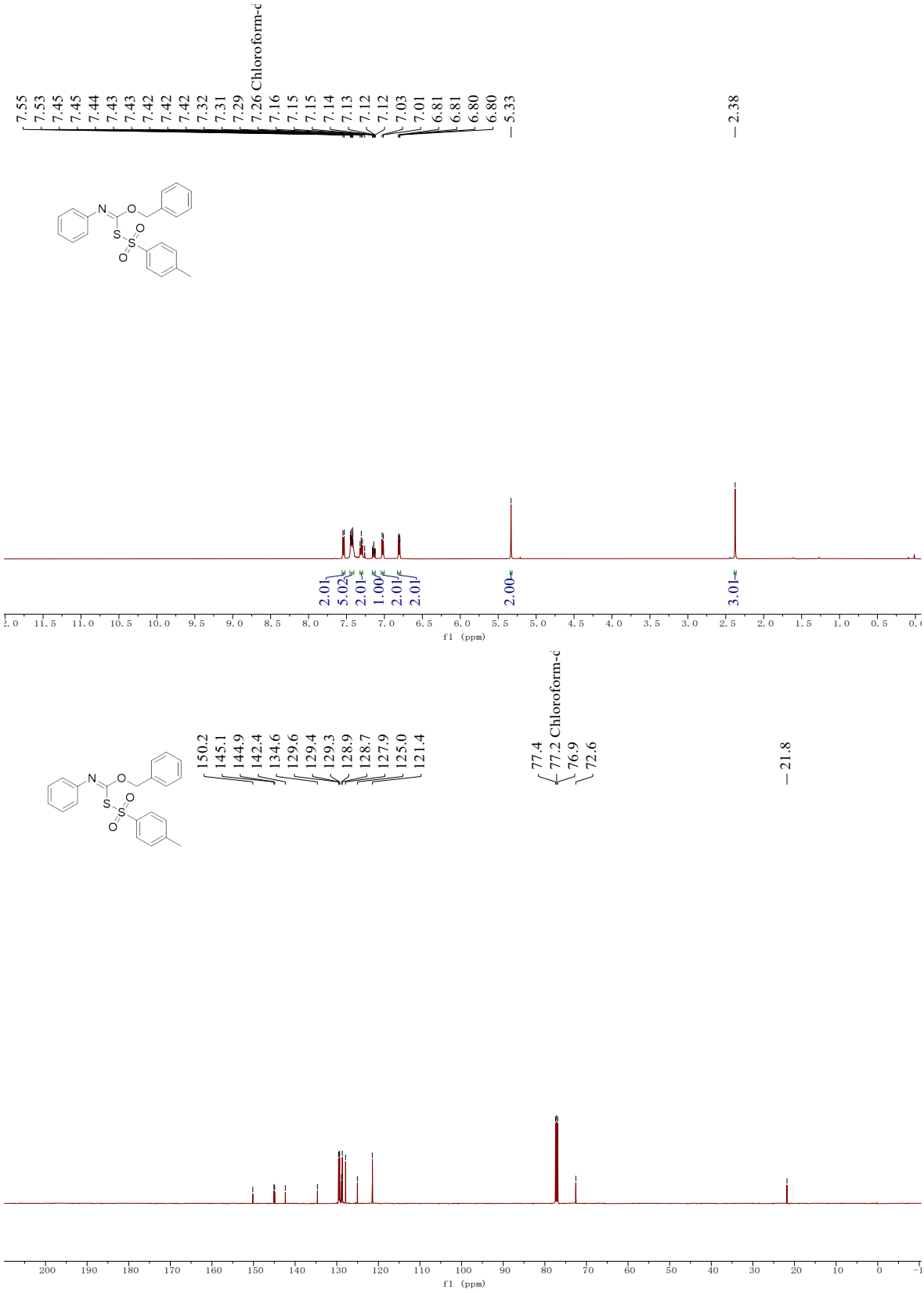
^{1}H and ^{13}C NMR Spectrum of **4r** (400 MHz, Chloroform-*d*).



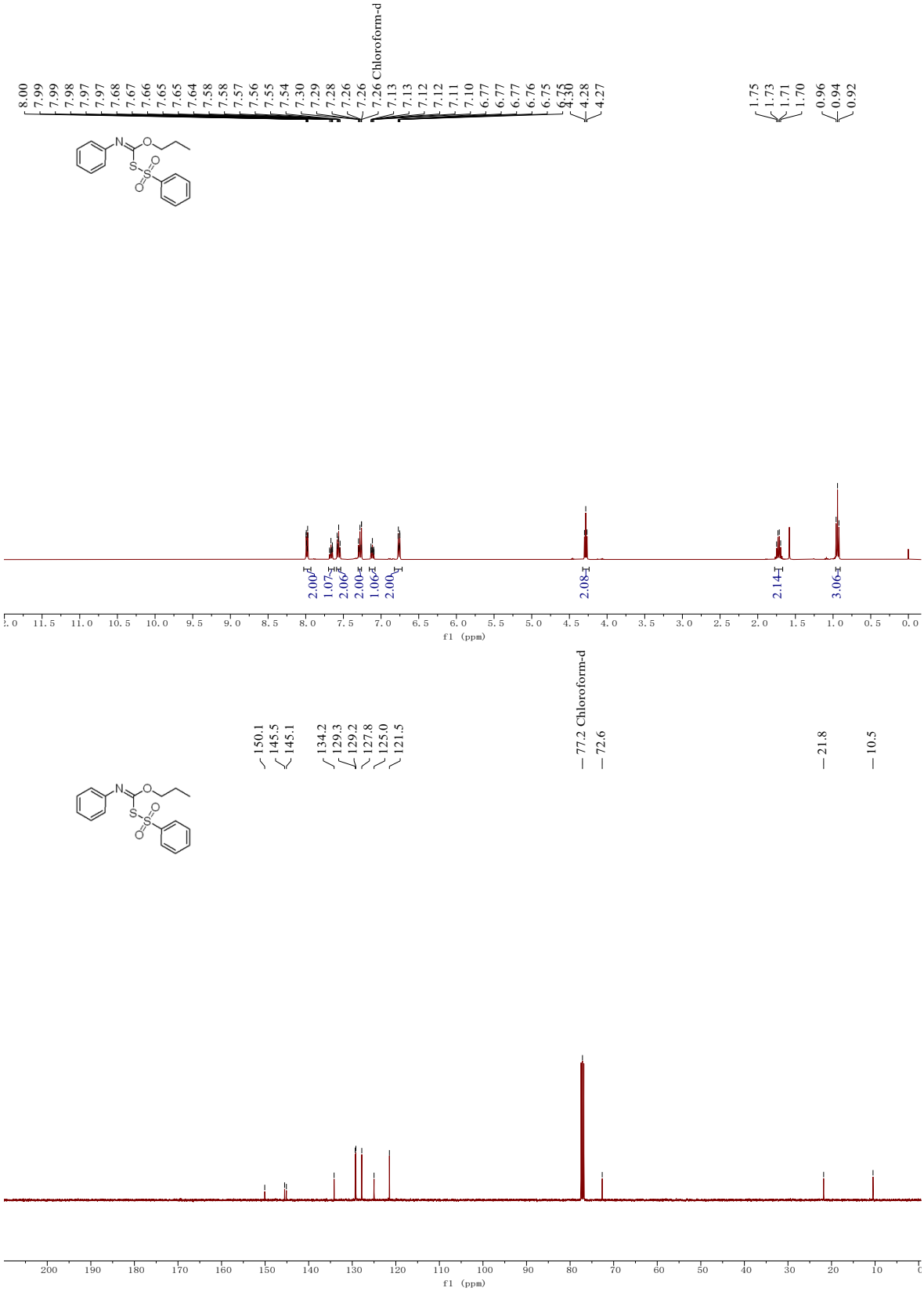
^{1}H and ^{13}C NMR Spectrum of **4s** (400 MHz, Chloroform-*d*).



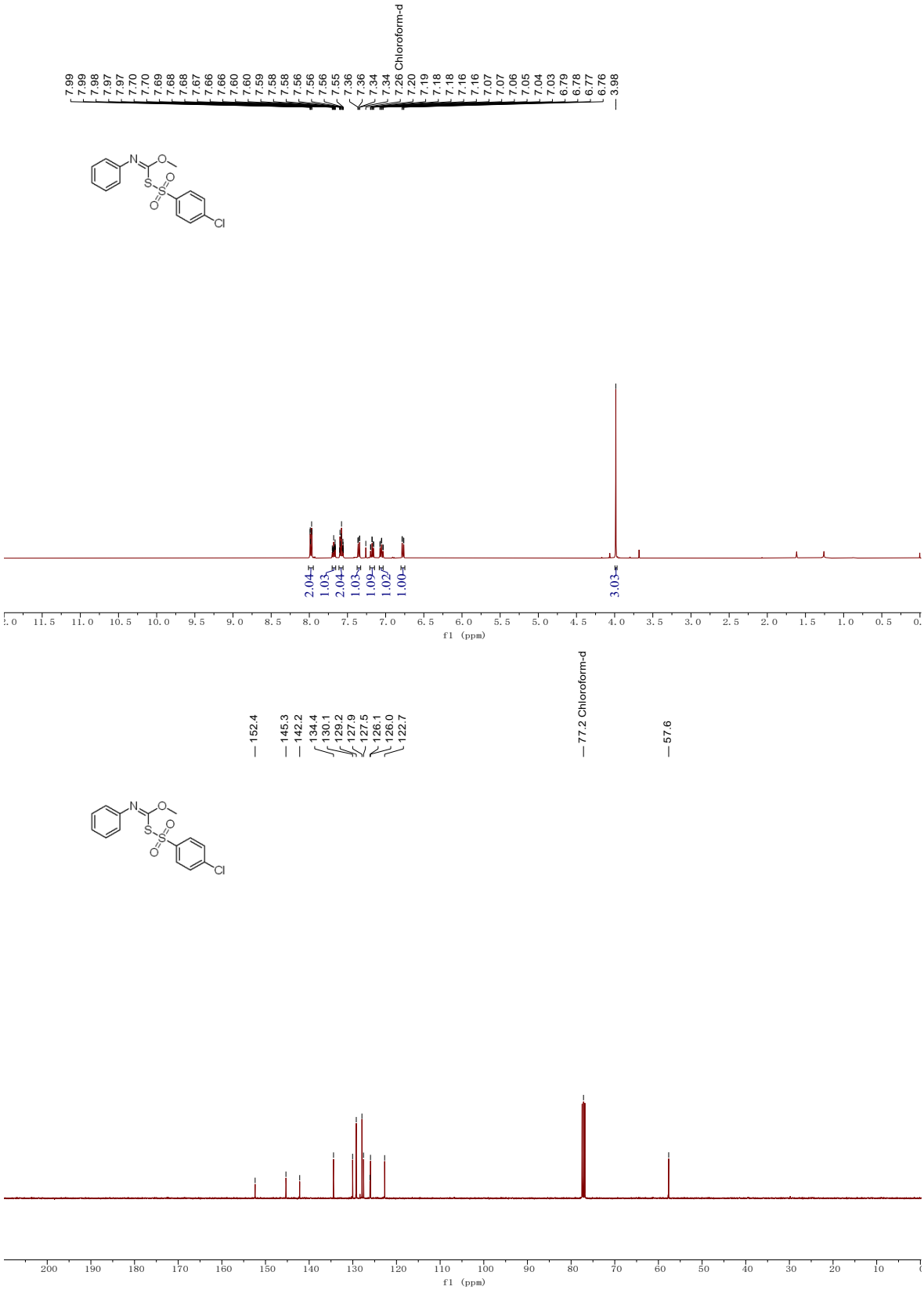
^{1}H and ^{13}C NMR Spectrum of **4t** (400 MHz, Chloroform-*d*).



^{1}H and ^{13}C NMR Spectrum of **4u** (400 MHz, Chloroform-*d*).



^{1}H and ^{13}C NMR Spectrum of **4v** (400 MHz, Chloroform-*d*).



^{1}H and ^{13}C NMR Spectrum of **4w** (400 MHz, Chloroform-*d*).