Supporting Information

Bifunctional Iron-Mediated Multicomponent Markovnikov-Selective Radical Hydrothiolation of Alkenes

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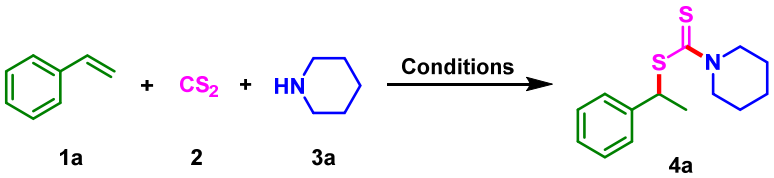
1. General information

All reagents including the starting materials (alkenes, carbon disulfide and amines) and solvents were purchased from commercial vendors and used without further purification. Melting points were determined with an X-4 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer with DMSO-d_6 or $CDCl_3$ as the solvent. Chemical shifts are reported relative to TMS as internal standard. The ^{1}H NMR data are reported as the chemical shift in parts per million, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), coupling constant in hertz, and number of protons. HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource.

2. Optimization details

Table S1. Optimization of the reaction conditions.[a]



Entry	Cat (20 mol%)	$Fe(acac)_3$ (x mol%)	Silane (2 equiv)	Solvent (0.5M)	T (°C)	Time (h)	Yield (%)
1	$FeCl_3$	$Fe(acac)_3$ (10)	$PhSiH_3$	EtOH-DMF (1:1)	r.t.	12	8
2	$FeCl_3$	$Fe(acac)_3$ (50)	$PhSiH_3$	EtOH-DMF (1:1)	r.t.	12	10
3	$FeCl_3$	$Fe(acac)_3$ (100)	$PhSiH_3$	EtOH-DMF (1:1)	r.t.	12	65
4	---	$Fe(acac)_3$ (100)	$PhSiH_3$	EtOH-DMF (1:1)	r.t.	12	---
5	$FeCl_3$	---	$PhSiH_3$	EtOH-DMF (1:1)	r.t.	12	---
6[b]	$FeCl_3$	$Fe(acac)_3$ (100)	---	EtOH-DMF (1:1)	r.t.	12	---
7[c]	$FeCl_3$	$Fe(acac)_3$ (100)	$PhSiH_3$	EtOH-DMF (1:1)	r.t.	12	37
8[d]	$FeCl_3$	$Fe(acac)_3$ (100)	$PhSiH_3$	EtOH-DMF (1:1)	r.t.	12	64
9[e]	$FeCl_3$	$Fe(acac)_3$ (100)	$PhSiH_3$	EtOH-DMF (1:1)	r.t.	12	60
10	$FeCl_3$	$Fe(acac)_3$ (100)	$PhSiH_3$	EtOH-DMF (1:1)	60	1	63
11	$FeCl_3$	$Fe(acac)_3$ (50)	$PhSiH_3$	EtOH-DMF (1:1)	60	1	63
12	$FeCl_3$	$Fe(acac)_3$ (10)	$PhSiH_3$	EtOH-DMF (1:1)	60	1	65
13	$FeCl_3$	$Fe(acac)_3$ (10)	$PhSiH_3$	EtOH	60	1	68
14	$FeCl_3$	$Fe(acac)_3$ (10)	$PhSiH_3$	i-PrOH	60	1	trace
15	$FeCl_3$	$Fe(acac)_3$ (10)	$PhSiH_3$	t-BuOH	60	1	trace
16	$FeCl_3$	$Fe(acac)_3$ (10)	$PhSiH_3$	DMF	60	1	9

17	$FeCl_3$	$Fe(acac)_3$ (10)	$PhSiH_3$	DMSO	60	1	15
18	$FeCl_3$	$Fe(acac)_3$ (10)	$PhSiH_3$	dioxane	60	1	---
19	$FeCl_3$	$Fe(acac)_3$ (10)	$PhSiH_3$	THF	50	1	trace
20	$FeCl_3$	$Fe(acac)_3$ (10)	$PhSiH_3$	EtOH-H_2O (1:1)	60	1	trace
21	$FeCl_3$	$Fe(acac)_3$ (10)	$PhSiH_3$	EtOH	50	4	59
22	$FeCl_3$	$Fe(acac)_3$ (10)	$PhSiH_3$	EtOH	40	4	34
23	$FeBr_3$	$Fe(acac)_3$(10)	$PhSiH_3$	EtOH	60	1	60
24	$Fe_2(SO_4)_3 \cdot xH_2O$	$Fe(acac)_3$(10)	$PhSiH_3$	EtOH	60	1	53
25	$Fe(NO_3)_3 \cdot 9H_2O$	$Fe(acac)_3$(10)	$PhSiH_3$	EtOH	60	1	45
26	$Fe(CF_3SO_3)_3$	$Fe(acac)_3$(10)	$PhSiH_3$	EtOH	60	1	48
27	$FeCl_2 \cdot 4H_2O$	$Fe(acac)_3$(10)	$PhSiH_3$	EtOH	60	1	6
28	$Fe(OAc)_2$	$Fe(acac)_3$(10)	$PhSiH_3$	EtOH	60	1	7
29	$Cu(OAc)_2$ H_2O	$Fe(acac)_3$(10)	$PhSiH_3$	EtOH	60	1	15
30	$FeCl_3$	$Fe(acac)_3$ (10)	$PhSiH_3$	EtOH	60	1	68
31[f]	$FeCl_3$	$Fe(acac)_3$ (10)	$PhSiH_3$	EtOH	60	1	67
32[g]	$FeCl_3$	$Fe(acac)_3$ (10)	$PhSiH_3$	EtOH	60	1	56
33	$FeCl_3$	$Fe(acac)_3$ (10)	Ph_2SiH_2	EtOH	60	1	trace
34	$FeCl_3$	$Fe(acac)_3$ (10)	Ph_3SiH	EtOH	60	1	trace
35	$FeCl_3$	$Fe(acac)_3$ (10)	PhMeSiH	EtOH	60	1	41
36	$FeCl_3$	$Fe(acac)_3$ (10)	Et_3SiH	EtOH	60	1	trace
37	$FeCl_3$	$Fe(acac)_3$ (10)	$HSi(OEt)_3$	EtOH	60	1	trace

[a] Reaction conditions: **1a** (1.0 mmol, 1.0 equiv), **2** (2.5 mmol, 2.5 equiv), **3a** (1.2 mmol, 1.2 equiv), Cat. (20 mol%), silane (2.0 mmol, 2.0 equiv), solvent (2.0 mL), under open air.

[b] Without silane.

[c] $PhSiH_3$ 1 equiv.

[d] $PhSiH_3$ 3 equiv.

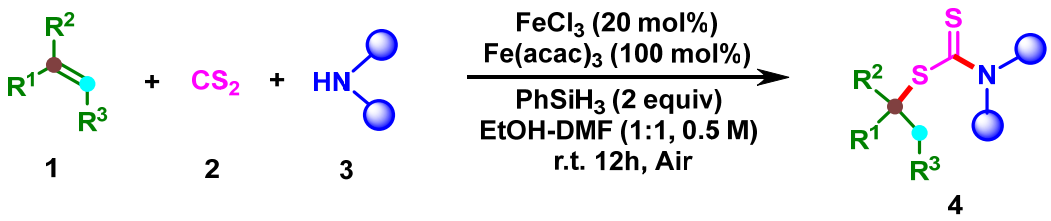
[e] $PhSiH_3$ 5 equiv.

[f] CS_2 3 equiv.

[g] CS_2 2 equiv.

3. General procedure for the synthesis of compound 4

Condition A:

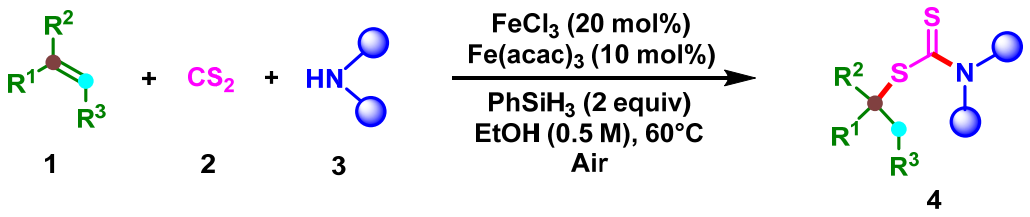


1 2 3 4

In a 10-mL reaction vial, equipped with a magnetic stirring bar, CS_2 (2.5 mmol, 2.5 equiv) and respective amines (1.2 mmol, 1.2 equiv) were added to EtOH-DMF (1:1,

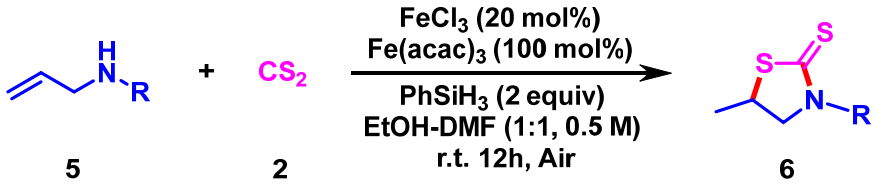
2.0 mL) at room temperature. After 10 min of stirring the resulting solution, alkenes (1.0 mmol, 1.0 equiv), phenylsilane (2.0 mmol, 2.0 equiv), $FeCl_3$ (20 mol%, 0.2 equiv) and $Fe(acac)_3$ (1.0 mmol, 1.0 equiv) were added. Then the mixture was allowed to stir overnight at room temperature. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was quenched with brine (15 mL) and extracted with ethyl acetate (3×10 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (170/1−40/1) as eluent to afford the pure product.

Condition B:



In a 10-mL reaction vial, equipped with a magnetic stirring bar, CS_2 (2.5 mmol, 2.5 equiv) and respective amines (1.2 mmol, 1.2 equiv) were added to ethanol (2.0 mL) at room temperature. After 10 min of stirring the resulting solution, alkenes (1.0 mmol, 1.0 equiv), phenylsilane (2.0 mmol, 2.0 equiv), $FeCl_3$ (20 mol%, 0.2 equiv) and $Fe(acac)_3$ (0.1 mmol, 0.1 equiv) were added. Then the vial was placed in a pre-heated metal block at 60 ºC in the presence of ambient air. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was quenched with brine (15 mL) and cooled to room temperature. Then the mixture was extracted with ethyl acetate (3×10 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (170/1−40/1) as eluent to afford the pure product.

4. General procedure for the synthesis of compound 6



In a 10-mL reaction vial, equipped with a magnetic stirring bar, CS_2 (2.5 mmol, 2.5 equiv) and allylamine (1.0 mmol, 1.0 equiv) were added to EtOH-DMF (1:1, 2.0 mL) at room temperature. After 10 min of stirring the resulting solution, phenylsilane (2.0 mmol, 2.0 equiv), $FeCl_3$ (20 mol%, 0.2 equiv) and $Fe(acac)_3$ (1.0 mmol, 1.0 equiv) were added. Then the mixture was allowed to stir overnight at room temperature. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was quenched with brine (15 mL) and extracted with ethyl acetate (3×10 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (50/1−40/1) as eluent to afford the pure product.

5. Synthetic applications

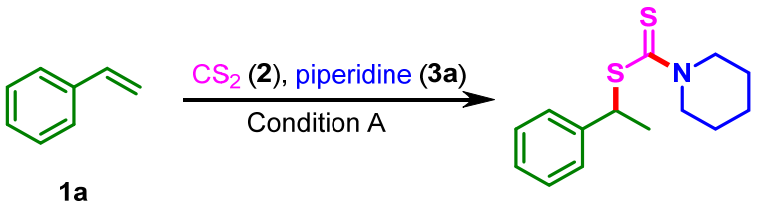
The substrates in Scheme 2 were prepared according the reported literature.[1,2]

5.1 General procedure for the late-stage modification of natural product and drugs

In a 10-mL reaction vial, equipped with a magnetic stirring bar, CS_2 (2.5 mmol, 2.5 equiv) and respective amines (1.2 mmol, 1.2 equiv) were added to EtOH-DMF (1:1, 2.0 mL) at room temperature. After 10 min of stirring the resulting solution, alkene derivatives of complex molecules (1.0 mmol, 1.0 equiv), phenylsilane (2.0 mmol, 2.0 equiv), $FeCl_3$ (20 mol%, 0.2 equiv) and $Fe(acac)_3$ (1.0 mmol, 1.0 equiv) were added. Then the mixture was allowed to stir overnight at room temperature. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was quenched with brine (15 mL) and extracted with ethyl acetate (3×10 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (200–300 mesh) using

petroleum/ethyl acetate (20/1) as eluent to afford the pure product.

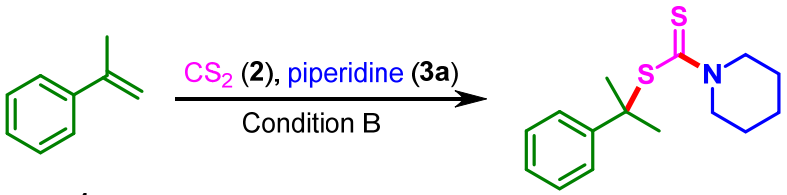
5.2 Gram-scale synthesis of 4a and 4w



1a
(5 mmol)

4a, 65% (0.86g)

In a 50-mL reaction vial, equipped with a magnetic stirring bar, CS_2 (12.5 mmol, 2.5 equiv) and piperidine **3a** (6.0 mmol, 1.2 equiv) were added to EtOH-DMF (1:1, 10.0 mL) at room temperature. After 30 min of stirring the resulting solution, styrene **1a** (5.0 mmol, 1.0 equiv), phenylsilane (10.0 mmol, 2.0 equiv), $FeCl_3$ (20 mol%, 0.2 equiv) and $Fe(acac)_3$ (5.0 mmol, 1.0 equiv) were added. Then the mixture was allowed to stir overnight at room temperature. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was quenched with brine (30 mL) and extracted with ethyl acetate (3×25 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (160/1) as eluent to afford the pure product **4a** in 65% yield (0.86g).



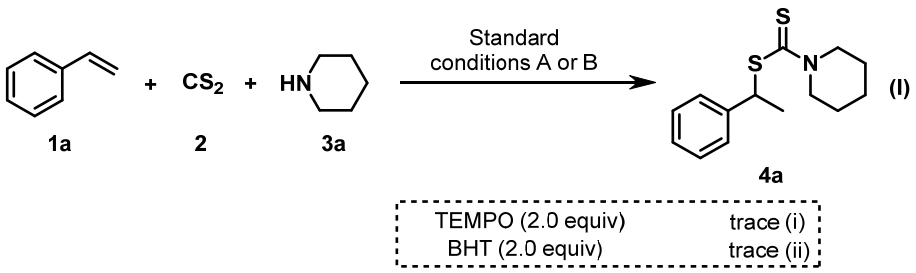
1w
(5 mmol)

4w, 81% (1.13g)

In a 50-mL reaction vial, equipped with a magnetic stirring bar, CS_2 (12.5 mmol, 2.5 equiv) and piperidine **3a** (6.0 mmol, 1.2 equiv) were added to ethanol (10.0 mL) at room temperature. After 30 min of stirring the resulting solution, α-methylstyrene **1w** (5.0 mmol, 1.0 equiv), phenylsilane (10.0 mmol, 2.0 equiv), $FeCl_3$ (20 mol%, 0.2 equiv) and $Fe(acac)_3$ (0.5 mmol, 0.1 equiv) were added. Then the vial was placed in a pre-heated metal block at 60 ºC in the presence of ambient air. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was quenched

with brine (30 mL) and cooled to room temperature. Then the mixture was extracted with ethyl acetate (3×25 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (100/1) as eluent to afford the pure product **4w** in 81% yield (1.13g).

6. Mechanistic studies

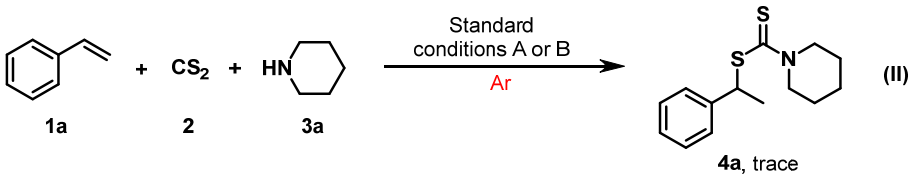


Conditions A:

In a 10-mL reaction vial, equipped with a magnetic stirring bar, CS_2 (2.5 mmol, 2.5 equiv) and piperidine **3a** (1.2 mmol, 1.2 equiv) were added to EtOH-DMF (1:1, 2.0 mL) at room temperature. After 10 min of stirring the resulting solution, styrene **1a** (1.0 mmol, 1.0 equiv), phenylsilane (2.0 mmol, 2.0 equiv), $FeCl_3$ (20 mol%, 0.2 equiv), $Fe(acac)_3$ (1.0 mmol, 1.0 equiv) and TEMPO (2.0 equiv) or BHT (2.0 equiv) were added. Then the mixture was allowed to stir overnight at room temperature. The reactions were monitored by TLC.

Conditions B:

In a 10-mL reaction vial, equipped with a magnetic stirring bar, CS_2 (2.5 mmol, 2.5 equiv) and piperidine **3a** (1.2 mmol, 1.2 equiv) were added to ethanol (2.0 mL) at room temperature. After 10 min of stirring the resulting solution, styrene **1a** (1.0 mmol, 1.0 equiv), phenylsilane (2.0 mmol, 2.0 equiv), $FeCl_3$ (20 mol%, 0.2 equiv) and $Fe(acac)_3$ (0.1 mmol, 0.1 equiv) and TEMPO (2.0 equiv) or BHT (2.0 equiv) were added. Then the vial was placed in a pre-heated metal block at 60 ºC in the presence of ambient air. The formation of the products was monitored by TLC.

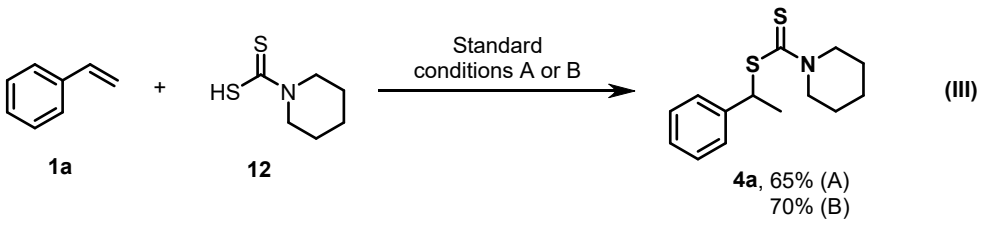


Conditions A:

In a 10-mL reaction vial, equipped with a magnetic stirring bar, CS_2 (2.5 mmol, 2.5 equiv) and piperidine **3a** (1.2 mmol, 1.2 equiv) were added to EtOH-DMF (1:1, 2.0 mL) at room temperature. After 10 min of stirring the resulting solution, styrene **1a** (1.0 mmol, 1.0 equiv), phenylsilane (2.0 mmol, 2.0 equiv), $FeCl_3$ (20 mol%, 0.2 equiv) and $Fe(acac)_3$ (1.0 mmol, 1.0 equiv) were added under an argon atmosphere. Then the mixture was allowed to stir overnight at room temperature. The reactions were monitored by TLC.

Conditions B:

In a 10-mL reaction vial, equipped with a magnetic stirring bar, CS_2 (2.5 mmol, 2.5 equiv) and piperidine **3a** (1.2 mmol, 1.2 equiv) were added to ethanol (2.0 mL) at room temperature. After 10 min of stirring the resulting solution, styrene **1a** (1.0 mmol, 1.0 equiv), phenylsilane (2.0 mmol, 2.0 equiv), $FeCl_3$ (20 mol%, 0.2 equiv) and $Fe(acac)_3$ (0.1 mmol, 0.1 equiv) were added under an argon atmosphere. Then the vial was placed in a pre-heated metal block at 60 ºC. The formation of the products was monitored by TLC.



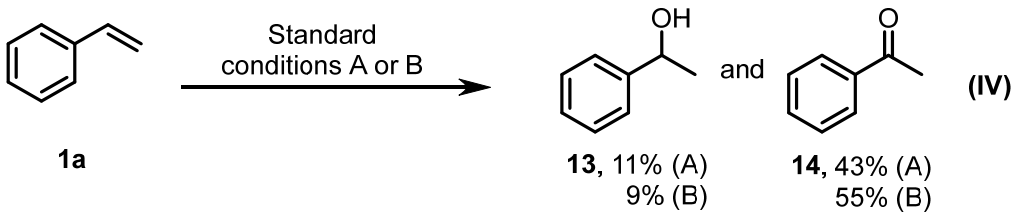
Conditions A:

In a 10-mL reaction vial, equipped with a magnetic stirring bar, styrene **1a** (1.0 mmol, 1.0 equiv), piperidine-1-carbodithioic acid **12** (1.2 mmol, 1.2 equiv), phenylsilane (2.0 mmol, 2.0 equiv), $FeCl_3$ (20 mol%, 0.2 equiv) and $Fe(acac)_3$ (1.0 mmol, 1.0 equiv) were added to EtOH-DMF (1:1, 2.0 mL) at room temperature. Then the mixture was allowed

to stir overnight at room temperature. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was quenched with brine (15 mL) and extracted with ethyl acetate (3×10 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (160/1) as eluent to afford the pure product **4a** in 65% yield (172.1 mg).

Conditions B:

In a 10-mL reaction vial, equipped with a magnetic stirring bar, styrene **1a** (1.0 mmol, 1.0 equiv), piperidine-1-carbodithioic acid **12** (1.2 mmol, 1.2 equiv), phenylsilane (2.0 mmol, 2.0 equiv), $FeCl_3$ (20 mol%, 0.2 equiv) and $Fe(acac)_3$ (0.1 mmol, 0.1 equiv) were added to ethanol (2.0 mL) at room temperature. Then the mixture was placed in a pre-heated metal block at 60 ºC. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was quenched with brine (15 mL) and extracted with ethyl acetate (3×10 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (160/1) as eluent to afford the pure product **4a** in 70% yield (185.3 mg).



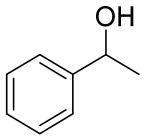
Conditions A:

In a 10-mL reaction vial, equipped with a magnetic stirring bar, styrene **1a** (1.0 mmol, 1.0 equiv), phenylsilane (2.0 mmol, 2.0 equiv), $FeCl_3$ (20 mol%, 0.2 equiv) and $Fe(acac)_3$ (1.0 mmol, 1.0 equiv) were added to EtOH-DMF (1:1, 2.0 mL) at room temperature. Then the mixture was allowed to stir overnight at room temperature. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was quenched with brine (15 mL) and extracted with ethyl acetate (3×10 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced

pressure and the residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (150/1) as eluent to afford the pure product **13** (13.4 mg, 11%) and **14** (51.5 mg, 43%).

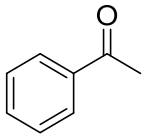
Conditions B:

In a 10-mL reaction vial, equipped with a magnetic stirring bar, styrene **1a** (1.0 mmol, 1.0 equiv), phenylsilane (2.0 mmol, 2.0 equiv), $FeCl_3$ (20 mol%, 0.2 equiv) and $Fe(acac)_3$ (0.1 mmol, 0.1 equiv) were added to ethanol (2.0 mL) at room temperature. Then the mixture was placed in a pre-heated metal block at 60 ºC. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was quenched with brine (15 mL) and extracted with ethyl acetate (3×10 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (150/1) as eluent to afford the pure product **13** (10.9 mg, 9%) and **14** (59.9 mg, 55%).



1-Phenylethanol (13)[3]

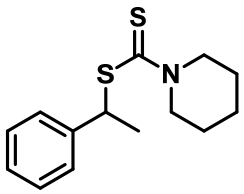
colorless liquid; ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.27 (d, 4H, ArH, *J* = 4.4 Hz), 7.21 (m, 1H, ArH), 4.74 (m, 1H, CH), 3.03 (br s, 1H, OH), 1.38 (d, 3H, CH_3, *J* = 6.4 Hz). ^{13}C NMR (101MHz, $CDCl_3$): δ = 146.0, 128.5, 127.4, 125.5, 70.2, 25.2.



Acetophenone (14)[4]

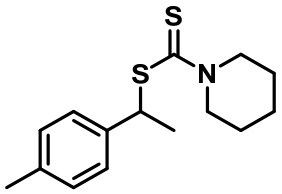
colorless liquid; ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.93 (d, 2H, ArH, *J* = 7.2 Hz), 7.53 (t, 1H, ArH, *J* = 7.2 Hz), 7.43 (t, 2H, ArH, *J* = 8.0 Hz), 2.56 (s, 3H, CH_3). ^{13}C NMR (101MHz, $CDCl_3$): δ = 198.0, 137.1, 133.1, 128.5, 128.2, 26.5.

7. Characterization data for compound 4



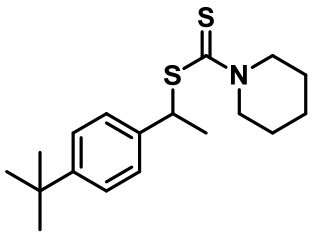
1-Phenylethylpiperidine-1-carbodithioate (4a)[5]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 68% yield (180.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, 2H, ArH, *J* = 7.2 Hz), 7.24 (t, 2H, ArH, *J* = 7.6 Hz), 7.18-7.16 (m, 1H, ArH), 5.24-5.19 (m, 1H, CH), 4.19 (br s, 2H, CH_2), 3.75 (br s, 2H, CH_2), 1.70 (d, 3H, CH_3, *J* = 7.2 Hz), 1.59-1.48 (m, 6H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 142.2, 128.5, 127.9, 127.4, 52.7, 51.3 50.9, 26.0, 25.5, 24.3, 22.2.



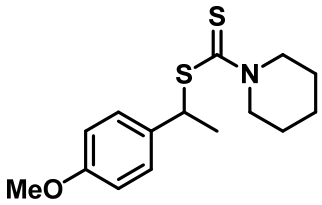
1-(p-Tolyl)ethylpiperidine-1-carbodithioate (4b)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 52% yield (145.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, 2H, ArH, *J* = 8.0 Hz), 7.05 (d, 2H, ArH, *J* = 7.6 Hz), 5.22-5.16 (m, 1H, CH), 4.17 (br s, 2H, CH_2), 3.74 (br s, 2H, CH_2), 2.25 (s, 3H, CH_3), 1.71 (d, 3H, CH_3, *J* = 7.2 Hz), 1.58-1.53 (m, 6H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 139.2, 137.1, 129.3, 127.8, 52.6, 51.3, 50.8, 26.1, 25.6, 24.4, 22.3, 21.2. HRMS (ESI) m/z: calcd for $C_{15}H_{22}NS_2^+$ ($[M+H]^+$), 280.1188; found, 280.1179.



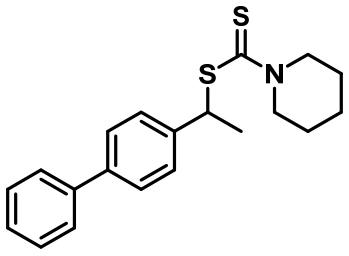
1-(4-(Tert-butyl)phenyl)ethylpiperidine-1-carbodithioate (4c)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 65% yield (209.0 mg). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.36-7.31 (m, 4H, ArH), 5.14-5.09 (m, 1H, CH), 4.20 (br s, 2H, CH_2), 3.82 (br s, 2H, CH_2), 1.68 (d, 3H, CH_3, *J* = 6.8 Hz), 1.64-1.45 (m, 6H, CH_2), 1.26 (s, 9H, CH_3). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 193.2, 150.2, 139.2, 127.8, 125.7, 52.5, 51.3, 50.4, 31.6, 26.3, 25.7, 24.0, 22.5. HRMS (ESI) m/z: calcd for $C_{18}H_{28}NS_2^+$ ([M+H]$^+$), 322.1658; found, 322.1655.



1-(4-Methoxyphenyl)ethylpiperidine-1-carbodithioate (4d)

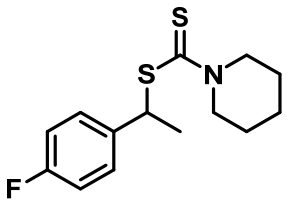
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 70% yield (206.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, 2H, ArH, *J* = 8.4 Hz), 6.85 (d, 2H, ArH, *J* = 8.4 Hz), 5.26-5.21 (m, 1H, CH), 4.25 (br s, 2H, CH_2), 3.83-3.79 (m, 5H, CH_2 and CH_3), 1.77 (d, 3H, CH_3, *J* = 7.2 Hz), 1.67 (br s, 6H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 158.8, 134.1, 129.0, 113.9, 55.3, 52.5, 51.3, 50.5, 26.0, 25.5, 24.3, 22.2. HRMS (ESI) m/z: calcd for $C_{15}H_{22}NOS_2^+$ ([M+H]$^+$), 296.1137; found, 296.1130.



1-([1,1'-Biphenyl]-4-yl)ethylpiperidine-1-carbodithioate (4e)

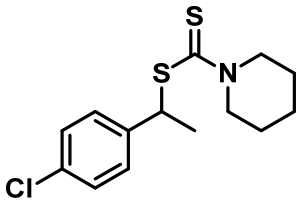
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 41% yield (140.0

mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.48 (m, 6H, ArH), 7.39 (t, 2H, ArH, *J* = 7.6 Hz), 7.30 (t, 1H, ArH, *J* = 7.2 Hz), 5.37-5.32 (m, 1H, CH), 4.26 (br s, 2H, CH_2), 3.81 (br s, 2H, CH_2), 1.80 (d, 3H, CH_3, *J* = 6.8 Hz), 1.64-1.55 (m, 6H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 141.4, 140.8, 140.3, 128.8, 128.4, 127.4, 127.3, 127.1, 52.7, 52.4, 50.7, 26.1, 25.6, 24.4, 22.2. HRMS (ESI) m/z: calcd for $C_{20}H_{24}NS_2^+$ ($[M+H]^+$), 342.1345; found, 342.1340.



1-(4-Fluorophenyl)ethylpiperidine-1-carbodithioate (4f)

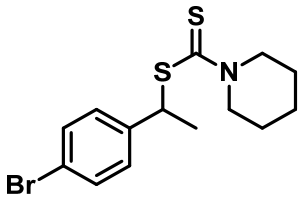
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 75% yield (212.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.31 (m, 2H, ArH), 6.92 (t, 2H, ArH, *J* = 8.8 Hz), 5.23-5.18 (m, 1H, CH), 4.19 (br s, 2H, CH_2), 3.76 (br s, 2H, CH_2), 1.68 (d, 3H, CH_3, *J* = 7.2 Hz), 1.60-1.53 (m, 6H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 163.1, 160.7, 138.2, 129.5, 115.4, 52.6, 51.3, 50.1, 26.0, 25.5, 24.3, 22.3. ^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ 115.1. HRMS (ESI) m/z: calcd for $C_{14}H_{19}FNS_2^+$ ($[M+H]^+$), 284.0937; found, 284.0932.



1-(4-Chlorophenyl)ethylpiperidine-1-carbodithioate (4g)

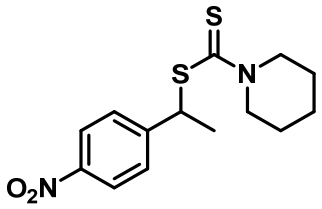
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 62% yield (185.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, 2H, ArH, *J* = 8.4 Hz), 7.27 (d, 2H, ArH, *J* = 8.4 Hz), 5.29-5.24 (m, 1H, CH), 4.25 (br s, 2H, CH_2), 3.82 (br s, 2H, CH_2), 1.74 (d, 3H, CH_3, *J* = 7.2 Hz), 1.67-1.64 (m, 6H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0,

141.1, 133.0, 129.3, 128.6, 52.7, 51.3, 50.1, 26.1, 25.5, 24.3, 22.1. HRMS (ESI) m/z: calcd for $C_{14}H_{19}ClNS_2^+$ ([M+H]$^+$), 300.0642; found, 300.0639.



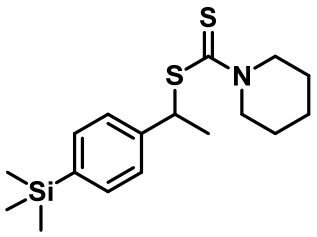
1-(4-Bromophenyl)ethylpiperidine-1-carbodithioate (4h)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 69% yield (237.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, 2H, ArH, *J* = 8.4 Hz), 7.31 (d, 2H, ArH, *J* = 8.8 Hz), 5.28-5.23 (m, 1H, CH), 4.25 (br s, 2H, CH_2), 3.82 (br s, 2H, CH_2), 1.73 (d, 3H, CH_3, *J* = 7.2 Hz), 1.70-1.64 (m, 6H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 141.7, 131.5, 129.6, 121.1, 52.7, 51.3, 50.1, 26.0, 25.5, 24.3, 22.0. HRMS (ESI) m/z: calcd for $C_{14}H_{19}BrNS_2^+$ ([M+H]$^+$), 344.0137; found, 344.0134.



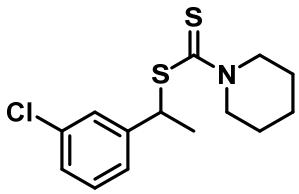
1-(4-Nitrophenyl)ethyl piperidine-1-carbodithioate (4i)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 100/1, v/v) as a light yellow oily liquid in 82% yield (254.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, 2H, ArH, *J* = 8.4 Hz), 7.62 (d, 2H, ArH, *J* = 8.4 Hz), 5.42-5.37 (m, 1H, CH), 4.25 (d, 2H, CH_2, *J* = 36.0 Hz), 3.85 (d, 2H, CH_2, *J* = 18.4 Hz), 1.76 (d, 3H, CH_3, *J* = 7.2 Hz), 1.69 (s, 6H, CH_2). ^{13}C NMR (100 Hz, $CDCl_3$) δ 193.1, 150.8, 146.9, 128.8, 123.7, 52.9, 51.5, 49.9, 26.1, 25.4, 24.2, 21.8. HRMS (ESI) m/z: calcd for $C_{14}H_{19}N_2O_2S_2^+$ ([M+H]$^+$), 311.0882; found, 311.0875.



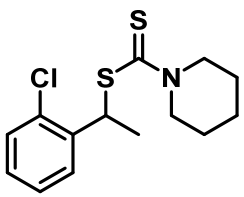
1-(4-(Trimethylsilyl)phenyl)ethyl piperidine-1-carbodithioate (4j)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 100/1, v/v) as a yellow oil liquid in 72% yield (243.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.340 (d, 2H, ArH, J = 8.0 Hz), 7.33 (d, 2H, ArH, J = 8.0 Hz), 5.20 (m, 1H, CH), 4.18 (br s, 2H, CH_2), 3.74 (br s, 2H, CH_2), 1.70 (d, 3H, CH_3, J = 6.8 Hz), 1.59-1.55 (m, 6H, CH_2), 0.17 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 143.7, 140.5, 134.7, 128.3, 53.7, 52.3, 52.0, 27.1, 26.5, 25.4, 23.1, 0.0. HRMS (ESI) m/z: calcd for $C_{17}H_{28}NS_2Si^+$ ($[M+H]^+$), 338.1427; found, 338.1431.



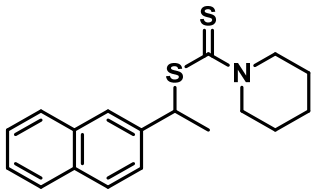
1-(3-Chlorophenyl)ethylpiperidine-1-carbodithioate (4k)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 40% yield (120.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, 1H, ArH, J = 1.6 Hz), 7.32 (td, 1H, ArH, J_1 = 1.6 Hz, J_2 = 7.2 Hz), 7.26-7.19 (m, 2H, ArH), 5.30-5.25 (m, 1H, CH), 4.26 (br s, 2H, CH_2), 3.83 (br s, 2H, CH_2), 1.74 (d, 3H, CH_3, J = 7.2 Hz), 1.68-1.59 (m, 6H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 143.6, 133.1, 128.6, 126.9, 126.4, 125.1, 51.7, 50.3, 49.2, 25.0, 24.4, 23.2, 21.0. HRMS (ESI) m/z: calcd for $C_{14}H_{19}ClNS_2^+$ ($[M+H]^+$), 300.0642; found, 300.0637.



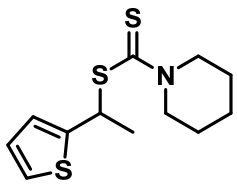
1-(2-Chlorophenyl)ethylpiperidine-1-carbodithioate (4l)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 44% yield (131.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, 1H, ArH, J = 6.4 Hz), 7.37 (d, 1H, ArH, J = 7.6 Hz), 7.25-7.16 (m, 2H, ArH), 5.64-5.59 (m, 1H, CH), 4.24 (br s, 2H, CH_2), 3.84 (br s, 2H, CH_2), 1.77 (d, 3H, CH_3, J = 7.2 Hz), 1.72-1.62 (m, 6H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 139.5, 133.9, 129.9, 128.9, 128.5, 126.9, 52.7, 51.4, 48.0, 26.1, 25.5, 24.3, 21.3. HRMS (ESI) m/z: calcd for $C_{14}H_{19}ClNS_2^+$ ($[M+H]^+$), 300.0642; found, 300.0634.



1-(Naphthalen-2-yl)ethylpiperidine-1-carbodithioate (4m)

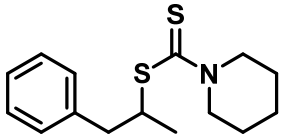
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 53% yield (167.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H, ArH), 7.82-7.79 (m, 3H, ArH), 7.55 (dd, 1H, ArH, J_1 = 1.6 Hz, J_2 = 8.8 Hz), 7.48-7.42 (m, 2H, ArH), 5.50-5.45 (m, 1H, CH), 4.28 (br s, 2H, CH_2), 3.83 (br s, 2H, CH_2), 1.88 (d, 3H, CH_3, J = 7.2 Hz), 1.67-1.62 (m, 6H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 139.6, 133.3, 132.7, 128.3, 128.0, 127.6, 126.4, 126.3, 126.2, 125.9, 52.7, 51.3, 51.1, 26.0, 25.5, 24.3, 22.0. HRMS (ESI) m/z: calcd for $C_{18}H_{22}NS_2^+$ ($[M+H]^+$), 316.1188; found, 316.1186.



1-(Thiophen-2-yl)ethyl piperidine-1-carbodithioate (4n)

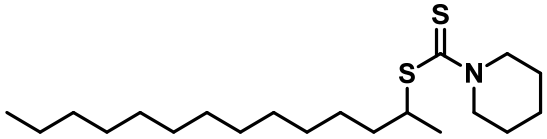
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 100/1, v/v) as a yellow oil liquid in 81% yield (219.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, 1H, ArH, J = 5.2 Hz), 7.06 (d, 1H, ArH, J_1 = 3.6 Hz), 6.92 (dd, 1H, ArH, J_1 = 5.2 Hz, J_2 = 3.6 Hz), 5.61-5.55 (m, 1H, CH_2), 4.26 (br s, 2H, CH_2), 3.81 (br s, 2H, CH_2), 1.85 (d, 3H, CH_3, J = 6.8 Hz), 1.70-1.63 (m, 6H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 145.9, 126.7, 125.2, 124.7, 52.7, 51.3, 46.5, 26.0, 25.5, 24.3, 23.2. HRMS (ESI) m/z: calcd for $C_{12}H_{18}NS_3^+$ ($[M+H]^+$), 272.0596; found, 272.0596.



1-Phenylpropan-2-ylpiperidine-1-carbodithioate (4o)

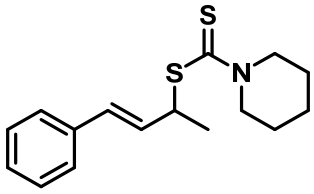
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 79% yield (220.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.19 (m, 4H, ArH), 7.17-7.15 (m, 1H, ArH), 4.24-4.15 (m, 3H, CH and CH_2), 3.81 (br s, 2H, CH_2), 3.30-3.25 (dd, 1H, CH, J_1 = 4.8 Hz, J_2 = 13.6 Hz), 2.64-2.58 (m, 1H, CH), 1.71-1.63 (m, 6H, CH_2), 1.25 (d, 3H, CH_3, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 139.3, 129.4, 128.2, 126.4, 52.5, 51.4, 48.0, 43.0, 26.0, 25.5, 24.4, 19.1. HRMS (ESI) m/z: calcd for $C_{15}H_{22}NS_2^+$ ($[M+H]^+$), 280.1188; found, 280.1181.



Tetradecan-2-yl piperidine-1-carbodithioate (4p)

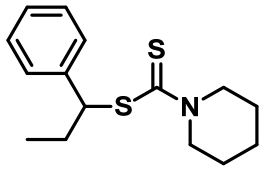
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 67% yield (239.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (br s, 2H, CH_2), 4.00-3.91 (m, 1H, CH), 3.81 (br s, 2H, CH_2), 1.62 (s, 6H, CH_2), 1.33 (d, 5H, CH_2 and CH_3, J = 6.8 Hz), 1.19 (s, 20H, CH_2), .0.81 (t, 3H, CH_3, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 52.4, 51.3, 47.6, 36.3, 31.9, 29.7 (2), 29.6, 29.4, 27.1, 25.9, 25.5, 24.4, 22.7, 21.0, 14.1. HRMS

(ESI) m/z: calcd for $C_{20}H_{40}NS_2^+$ ([M+H]$^+$), 358.2597; found, 358.2589.



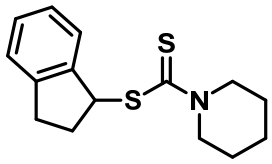
(E)-4-Phenylbut-3-en-2-yl piperidine-1-carbodithioate (4q)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 100/1, v/v) as a yellow oil liquid in 71% yield (206.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, 2H, ArH, *J* = 7.6 Hz), 7.30 (t, 2H, ArH, *J* = 7.2 Hz), 7.21 (t, 1H, ArH, *J* = 7.2 Hz), 6.65 (d, 1H, CH, *J* = 16.0 Hz), 6.39 (dd, 1H, CH, J_1 = 15.6Hz, J_2 = 6.8 Hz), 4.97-4.90 (m, 1H, CH), 4.29 (br s, 2H, CH_2), 3.87 (br s, 2H, CH_2), 1.69-1.67 (s, 6H, CH_2), 1.63 (d, 3H, CH_3, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 136.9, 130.5, 130.1, 128.5, 127.5, 126.4, 52.7, 51.3, 48.7, 26.0, 25.5, 24.3, 19.8. HRMS (ESI) m/z: calcd for $C_{16}H_{22}NS_2^+$ ([M+H]$^+$), 292.1188; found, 292.1188.



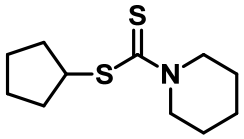
1-phenylpropyl piperidine-1-carbodithioate (4r)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 100/1, v/v) as a yellow oil liquid in 54% yield (150.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, 2H, ArH, *J* = 7.2 Hz), 7.31 (t, 2H, ArH, *J* = 7.6 Hz), 7.24 (d, 1H, ArH, *J* = 7.6 Hz), 5.08 (dd, 1H, CH, J_1 = 9.6 Hz, J_2 = 5.6 Hz), 4.26 (br s, 2H, CH_2), 3.86 (br s, 2H, CH_2), 2.30-2.19 (m, 1H, CH_2), 2.05-1.94 (m, 1H, CH_2), 1.67-1.64 (m, 6H, CH_2), 0.92 (t, 3H, CH_3, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 141.0, 128.4, 127.3, 57.5, 52.7, 51.2, 29.6, 26.0, 25.4, 24.3, 12.3. HRMS (ESI) m/z: calcd for $C_{15}H_{22}NS_2^+$ ([M+H]$^+$), 280.1188; found, 280.1193.



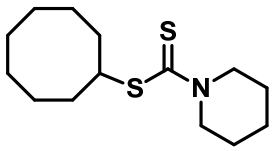
2,3-Dihydro-1H-inden-1-yl piperidine-1-carbodithioate (4s)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 170/1, v/v) as a light yellow oily liquid in 56% yield (155.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, 1H, ArH, *J* = 6.8 Hz), 7.23-7.16 (m, 3H, ArH), 7.59-7.56 (m, 1H, CH), 4.32 (d, 2H, CH_2, *J* = 36.0 Hz), 3.86 (s, 2H, CH_2), 3.09-3.01 (m, 1H, CH_2), 2.96-2.89 (m, 1H, CH_2), 2.82-2.72 (m, 1H, CH_2), 2.35-2.27 (m, 1H, CH_2), 1.71 (s, 6H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 144.5, 141.3, 128.0, 126.7, 125.3, 124.8, 55.8, 52.7, 51.5, 34.4, 30.8, 26.1, 25.5, 24.3. HRMS (ESI) m/z: calcd for $C_{15}H_{20}NS_2^+$ ($[M+H]^+$), 278.1032; found, 278.1028.



Cyclopentyl piperidine-1-carbodithioate (4t)

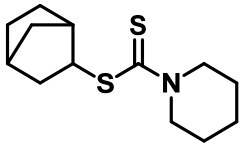
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 32% yield (73.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 (br s, 2H, CH_2), 4.19-4.12 (m, 1H, CH), 3.86 (t, 2H, CH_2, *J* = 6.8 Hz), 2.29-2.20 (m, 2H, CH_2), 1.72-1.63 (m, 12H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 51.3, 50.3, 49.0, 32.0, 24.9, 24.4, 24.0, 23.3. HRMS (ESI) m/z: calcd for $C_{11}H_{19}NNaS_2^+$ ($[M+Na]^+$), 252.0851; found, 252.0855.



Cyclooctyl piperidine-1-carbodithioate (4u)

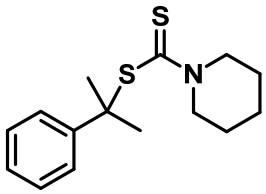
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 170/1, v/v) as a light yellow oily liquid in 52% yield (141.2

mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (s, 2H, CH_2), 4.15-4.09 (m, 1H, CH), 3.81 (s, 2H, CH_2), 2.08-2.00 (m, 2H, CH_2), 1.78-1.69 (m, 2H, CH_2), 1.62-1.47 (m, 16H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 52.4, 51.7, 51.3, 32.4, 27.1, 26.0, 25.6, 24.4. HRMS (ESI) m/z: calcd for $C_{14}H_{26}NS_2^+$ ($[M+H]^+$), 272.1501; found, 272.1493.



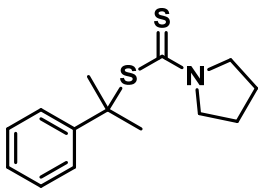
Bicyclo[2.2.1]heptan-2-yl piperidine-1-carbodithioate (4v)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 28% yield (71.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27 (d, 2H, CH_2, J = 47.6 Hz), 3.88-3.77 (m, 3H, CH and CH_2), 2.46 (t, 1H, CH_2, J = 4.4 Hz), 2.31 (t, 1H, CH_2, J = 3.6 Hz), 1.92-1.86 (m, 1H, CH), 1.73-1.59 (m, 7H, CH and CH_2), 1.57-1.44 (m, 4H, CH_2), 1.26-1.19 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 52.6, 52.2, 51.3, 43.6, 37.4, 36.6, 36.3, 28.9, 28.4, 26.0, 25.4, 24.3. HRMS (ESI) m/z: calcd for $C_{13}H_{22}NS_2^+$ ($[M+H]^+$), 256.1188; found, 256.1177.



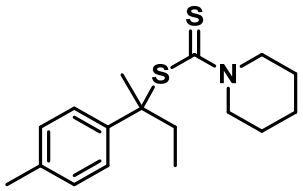
2-Phenylpropan-2-yl piperidine-1-carbodithioate (4w)[6]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 100/1, v/v) as a yellow oil liquid in 85% yield (237.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 2H, ArH, J = 7.6 Hz), 7.30 (t, 2H, ArH, J = 7.6 Hz), 7.19 (t, 1H, ArH, J = 6.8 Hz), 3.99 (br s, 4H, CH_2), 2.01 (s, 6H, CH_3), 1.66-1.56 (m, 6H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 145.8, 127.9, 127.0, 126.5, 55.9, 50.9, 29.5, 25.8, 24.3.



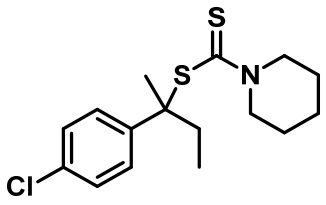
2-Phenylpropan-2-yl pyrrolidine-1-carbodithioate (4x)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 100/1, v/v) as a yellow oil liquid in 62% yield (164.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 2H, ArH, J = 8.0 Hz), 7.32 (t, 2H, ArH, J = 7.6 Hz), 7.21 (t, 1H, ArH, J = 7.6 Hz), 3.79 (t, 2H, CH_2, J = 6.8 Hz), 3.59 (t, 2H, CH_2, J = 6.8 Hz), 2.04 (s, 6H, CH_3), 2.03-1.97 (m, 2H, CH_2), 1.92-1.85 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 145.5, 127.9, 127.0, 126.6, 55.7, 53.6, 50.8, 29.1, 26.3, 24.1. HRMS (ESI) m/z: calcd for $C_{14}H_{19}NNaS_2^+$ ([M+Na]$^+$), 288.0851; found, 288.0853.



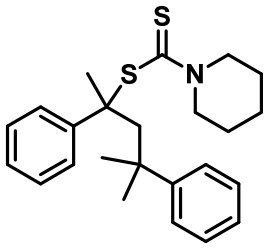
2-(P-tolyl)butan-2-yl piperidine-1-carbodithioate (4y)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 100/1, v/v) as a yellow oil liquid in 71% yield (218.3 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.34 (d, 2H, ArH, J = 8.0 Hz), 7.10 (d, 2H, ArH, J = 8.0 Hz), 3.97 (br s, 4H, CH_2), 2.48-2.41 (m, 1H, CH_2), 2.26 (s, 3H, CH_3), 2.10-2.04 (m, 1H, CH_2), 2.02 (s, 3H, CH_3), 1.64-1.58 (m, 2H, CH_2), 1.52-1.48 (m, 4H, CH_2), 0.72 (t, 3H, CH_3, J = 7.2 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.2, 141.1, 135.7, 128.8, 127.7, 60.2, 50.8, 34.5, 26.1, 24.4, 24.0, 21.0, 9.2. HRMS (ESI) m/z: calcd for $C_{17}H_{25}NNaS_2^+$ ([M+Na]$^+$), 330.1321; found, 330.1329.



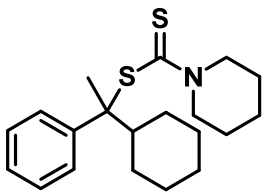
2-(4-Chlorophenyl)butan-2-yl piperidine-1-carbodithioate (4z)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 100/1, v/v) as a white wax in 82% yield (268.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, 2H, ArH, *J* =8.8 Hz), 7.25 (d, 2H, ArH, *J* = 8.4 Hz), 4.00 (br s, 4H, CH_2), 2.39-2.30 (m, 1H, CH_2), 2.08 (s, 3H, CH_3), 2.06-1.97 (m, 1H, CH_2), 1.67-1.61 (m, 6H, CH_2), 0.81 (t, 3H, CH_3, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 142.9, 131.9, 129.1, 127.8, 59.6, 51.0, 35.5, 25.8, 24.3, 8.7. HRMS (ESI) m/z: calcd for $C_{16}H_{22}NNaS_2^+$ ($[M+Na]^+$), 350.0774; found, 350.0777.



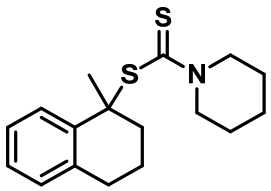
4-Methyl-2,4-diphenylpentan-2-yl piperidine-1-carbodithioate (4aa)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 100/1, v/v) as a yellow oil liquid in 74% yield (294.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, 2H, ArH, *J* = 7.2 Hz), 7.34-7.19 (m, 7H, ArH), 7.14 (t, 1H, ArH, *J* = 7.2 Hz), 3.97 (br s, 4H, CH_2), 3.68 (d, 1H, CH_2, *J* = 14.4 Hz), 2.58 (d, 1H, CH_2, *J* = 14.4 Hz), 1.82 (s, 3H, CH_3), 1.63-1.56 (m, 6H, CH_2), 1.22 (s, 3H, CH_3), 0.90 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 149.1, 144.6, 127.9, 127.8, 127.8, 126.9, 126.3, 125.5, 62.6, 53.1, 50.8, 39.1, 34.0, 28.4, 25.8, 24.4, 23.6. HRMS (ESI) m/z: calcd for $C_{24}H_{31}NNaS_2^+$ ($[M+Na]^+$), 420.1790; found, 420.1791.



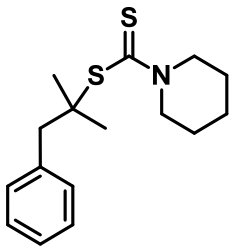
1-Cyclohexyl-1-phenylethyl piperidine-1-carbodithioate (4ab)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 100/1, v/v) as a yellow oil liquid in 83% yield (288.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d 2H, ArH, *J* = 7.2 Hz), 7.27 (t, 2H, ArH, *J* = 8.0 Hz), 7.16 (t, 1H, ArH, *J* = 7.2 Hz), 4.02-3.96 (m, 4H, CH_2), 2.18 (s, 3H, CH_3), 2.05 (d, 1H, CH_2, *J* = 12.8 Hz), 1.95 (t, 1H, CH_2, *J* = 11.6 Hz), 1.81-1.75 (m, 1H, CH_2), 1.65-1.59 (m, 7H, CH_2), 1.33-1.21 (m, 3H, CH_2), 1.16-1.04 (m, 3H, CH_2), 0.99-0.90 (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 144.1, 128.0, 127.4, 125.9, 64.3, 51.1, 50.4, 28.9, 28.0, 26.9, 26.5, 25.8, 24.4, 20.6. HRMS (ESI) m/z: calcd for $C_{20}H_{29}NNaS_2^+$ ($[M+Na]^+$), 370.1634; found, 370.1637.



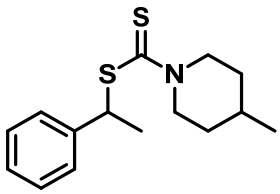
1-Methyl-1,2,3,4-tetrahydronaphthalen-1-yl piperidine-1-carbodithioate (4ac)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 100/1, v/v) as a yellow oil liquid in 70% yield (213.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d 1H, ArH, *J* = 7.6 Hz,), 7.10-7.04 (m, 2H, ArH), 6.98 (d, 1H, ArH, *J* = 7.2 Hz), 3.96 (br s, 4H, CH_2), 3.58-3.51 (m, 1H, CH_2), 2.93-2.82 (m, 1H, CH_2), 2.72-2.66 (m, 1H, CH_2), 1.99-1.93 (m, 1H, CH_2), 1.91 (s, 3H, CH_3), 1.80-1.72 (m, 2H, CH_2), 1.59-1.54 (m, 6H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.0, 140.7, 138.5, 129.0, 128.1, 126.8, 126.0, 57.5, 50.9, 34.7, 30.1, 29.9, 25.9, 24.4, 20.4. HRMS (ESI) m/z: calcd for $C_{17}H_{22}NS_2^+$ (M^+), 304.1188; found, 304.1191.



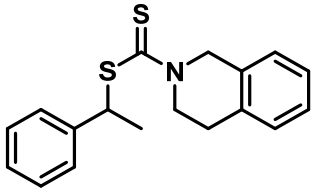
2-Methyl-1-phenylpropan-2-yl piperidine-1-carbodithioate (4ad)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 100/1, v/v) as a yellow oil liquid in 52% yield (152.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.20 (m, 5H, ArH), 4.07 (br s, 4H, CH_2), 3.54 (s, 2H, CH_2), 1.72-1.65 (m, 6H, CH_2), 1.57 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 138.1, 131.1, 127.6, 126.3, 55.3, 51.0, 44.6, 27.8, 25.9, 24.4. HRMS (ESI) m/z: calcd for $C_{16}H_{24}NS_2^+$ ($[M+H]^+$), 294.1345; found, 294.1346.



1-Phenylethyl-4-methylpiperidine-1-carbodithioate (4ae)

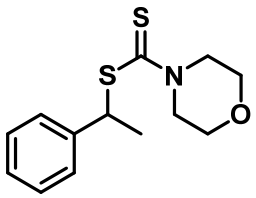
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 60% yield (167.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, 2H, ArH, J = 7.2 Hz), 7.32 (t, 2H, ArH, J = 7.2 Hz), 7.25-7.23 (m, 1H, ArH), 5.52 (br s, 1H, CH_2), 5.31-5.26 (m, 1H, CH), 4.55 (br s, 1H, CH_2), 3.07 (t, 2H, CH_2, J = 10.8 Hz), 1.79-1.65 (m, 6H, CH_3 and CH_2 and CH), 1.33-1.16 (m, 2H, CH_2), 0.96 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 128.5, 127.9, 127.4, 51.9, 51.0, 50.4, 34.0, 33.6, 31.0, 22.2, 21.3. HRMS (ESI) m/z: calcd for $C_{15}H_{22}NS_2^+$ ($[M+H]^+$), 280.1188; found, 280.1184.



1-Phenylethyl-3,4-dihydroisoquinoline-2(1H)-carbodithioate (4af)

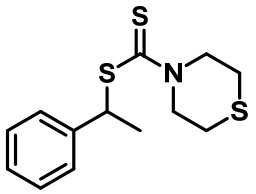
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 81% yield (253.9 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.47 (d, 2H, ArH, J = 7.6 Hz), 7.38 (t, 2H, ArH, J = 7.2 Hz), 7.33-7.26 (m, 5H, ArH), 5.31-5.24 (m, 2H, CH_2), 5.07-4.96 (m, 1H, CH),

4.35 (br s, 1H, CH_2), 4.02 (br s, 1H, CH_2), 2.97 (t, 2H, CH_2, J = 5.6 Hz), 1.77 (d, 3H, CH_3, J = 6.8 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 194.1, 142.2, 135.4, 135.1, 129.0, 128.3, 128.2, 127.9, 127.6, 127.5, 126.9, 53.5, 51.4, 50.5, 50.1, 48.2, 28.7, 28.2, 22.3. HRMS (ESI) m/z: calcd for $C_{18}H_{20}NS_2^+$ ([M+H]$^+$), 314.1032; found, 314.1036.



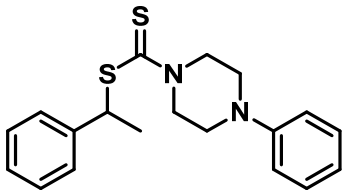
1-Phenylethylmorpholine-4-carbodithioate (4ag)[5]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 40:1, v/v) as a light yellow oil liquid in 72% yield (192.5 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 (d, 2H, ArH, J = 7.6 Hz), 7.35 (t, 2H, ArH, J = 7.2 Hz), 7.28 (t, 1H, ArH, J = 7.2 Hz), 5.21-5.16 (m, 1H, CH), 4.22 (br s, 2H, CH_2), 3.88 (br s, 2H, CH_2), 3.64 (br s, 4H, CH_2), 1.72 (d, 3H, CH_3, J = 7.2 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 194.8, 142.2, 129.0, 128.2, 127.9, 66.0, 51.3, 50.8, 50.6, 22.4.



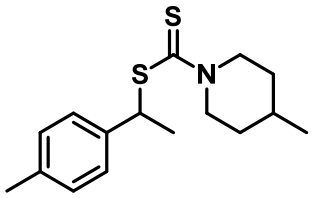
1-Phenylethyl thiomorpholine-4-carbodithioate (4ah)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 170/1, v/v) as a light yellow oily liquid in 71% yield (201.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, 2H, ArH, J = 6.8 Hz), 7.33 (t, 2H, ArH, J = 7.6 Hz), 7.28-7.24 (m, 1H, ArH), 5.30-5.25 (m, 1H, CH), 4.55 (br s, 2H, CH_2), 4.24 (br s, 2H, CH_2), 2.72 (s, 4H, CH_2), 1.79 (d, 3H, CH_3, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 141.9, 128.6, 127.9, 127.5, 51.1, 27.3, 22.0. HRMS (ESI) m/z: calcd for $C_{13}H_{18}NS_3^+$ ([M+H]$^+$), 284.0596; found, 284.0604.



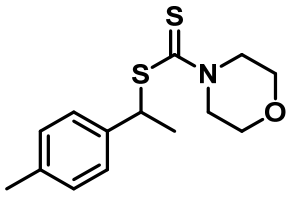
1-Phenylethyl-4-phenylpiperazine-1-carbodithioate (4ai)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 62% yield (212.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, 2H, ArH, *J* = 7.2 Hz), 7.35-7.26 (m, 5H, ArH), 6.93-6.90 (m, 3H, ArH), 5.34-5.28 (m, 1H, CH), 4.48 (br s, 2H, CH_2), 4.07-4.01 (m, 2H, CH_2), 3.27 (br s, 4H, CH_2), 1.80 (d, 3H, CH_3, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 141.9, 134.3, 129.4, 128.6, 127.9, 127.5, 120.7, 116.4, 51.0, 48.8, 22.1. HRMS (ESI) m/z: calcd for $C_{19}H_{22}N_2NaS_2^+$ ($[M+Na]^+$), 365.1117; found, 365.1118.



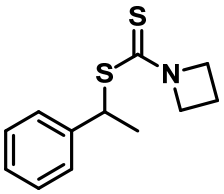
1-(*p*-Tolyl)ethyl 4-methylpiperidine-1-carbodithioate (4aj)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 51% yield (149.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, 2H, ArH, *J* = 8.0 Hz), 7.05 (d, 2H, ArH, *J* = 7.6 Hz), 5.44 (br s, 1H, CH_2), 5.19-5.14 (m, 1H, CH), 4.47 (br s, 1H, CH_2), 2.97 (t, 2H, CH_2, *J* = 10.4 Hz), 2.24 (s, 3H, CH_3), 1.69 (d, 3H, CH_3, *J* = 7.2 Hz), 1.64 (d, 3H, CH and CH_2, *J* = 11.2 Hz), 1.18 (s, 2H, CH_2), 0.87 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 137.1, 129.2, 127.8, 51.9, 50.8, 34.1, 33.5, 31.0, 22.2, 21.3, 21.2. HRMS (ESI) m/z: calcd for $C_{16}H_{24}NS_2^+$ ($[M+H]^+$), 294.1345; found, 294.1347.



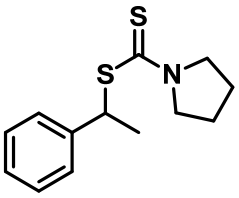
1-(*p*-Tolyl)ethyl morpholine-4-carbodithioate (4ak)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 170/1, v/v) as a light yellow oily liquid in 58% yield (163.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, 2H, ArH, J = 8.0 Hz), 7.13 (d, 2H, ArH, J = 8.0 Hz), 5.29-5.23 (m, 1H, CH), 4.30 (br s, 2H, CH_2), 3.90 (br s, 2H, CH_2), 3.72 (s, 4H, CH_2), 2.32 (s, 3H, CH_3), 1.77 (d, 3H, CH_3, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 138.8, 137.3, 129.3, 127.8, 66.3, 50.7, 22.1, 21.2. HRMS (ESI) m/z: calcd for $C_{14}H_{20}NOS_2^+$ ([M+H]$^+$), 282.0981; found, 282.0975.



1-Phenylethylazetidine-1-carbodithioate (4al)

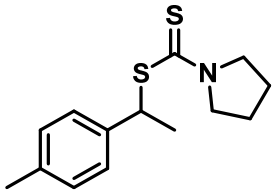
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 54% yield (128.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, 2H, ArH, J = 7.2 Hz), 7.32 (t, 2H, ArH, J = 7.2 Hz), 7.26-7.23 (m, 1H, ArH), 5.20-5.15 (m, 1H, CH), 4.27 (t, 2H, CH_2, J = 8.0 Hz), 4.15-4.08 (m, 2H, CH_2), 2.38-2.30 (m, 2H, CH_2), 1.77 (d, 3H, CH_3, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 142.2, 128.6, 126.9, 127.7, 127.5, 54.5, 53.0, 49.8, 22.4, 15.5. HRMS (ESI) m/z: calcd for $C_{12}H_{16}NS_2^+$ ([M+H]$^+$), 238.0719; found, 238.0719.



1-Phenylethyl pyrrolidine-1-carbodithioate (4am)[5]

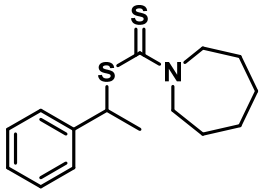
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 170/1, v/v) as a light yellow oily liquid in 55% yield (138.3 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 (d, 2H, ArH, J = 7.2 Hz), 7.34 (t, 2H, ArH,

J = 7.6 Hz), 7.26 (t, 1H, ArH, *J* = 7.2 Hz), 5.19-5.13 (m, 1H, CH), 3.81-3.71 (m, 2H, CH_2), 3.60-3.48 (m, 2H, CH_2), 2.01-1.87 (m, 4H, CH_2), 1.70 (d, 3H, CH_3, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.7, 142.0, 128.5, 127.6, 127.3, 54.8, 50.4, 49.4, 25.5, 23.6, 21.9.



1-(p-Tolyl)ethyl pyrrolidine-1-carbodithioate (4an)

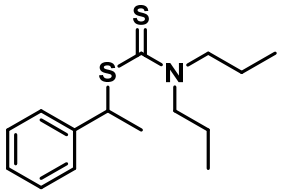
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 54% yield (143.3 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, 2H, ArH, *J* = 8.0 Hz), 7.13 (d, 2H, ArH, *J* = 8.0 Hz), 5.29-5.24 (m, 1H, CH), 3.92 (t, 2H, CH_2, *J* = 6.8 Hz), 3.63-3.51 (m, 2H, CH_2), 2.32 (s, 3H, CH_3), 2.04-1.93 (m, 4H, CH_2), 1.77 (d, 3H, CH_3, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 139.2, 137.1, 129.2, 127.7, 54.8, 50.5, 49.9, 26.1, 24.3, 22.2, 21.2. HRMS (ESI) m/z: calcd for $C_{14}H_{20}NS_2^+$ ($[M+H]^+$), 266.1032; found, 266.1025.



1-Phenylethyl azepane-1-carbodithioate (4ao)

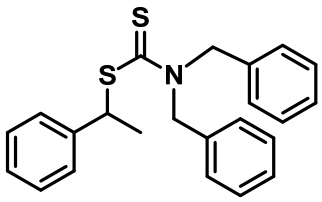
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 170/1, v/v) as a light yellow oily liquid in 52% yield (145.3 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, 2H, ArH, *J* = 7.2 Hz), 7.31 (t, 2H, ArH, *J* = 8.0 Hz), 7.25-7.21 (m, 1H, ArH), 5.31-5.25 (m, 1H, CH), 4.16 (t, 2H, CH_2, *J* = 6.0 Hz), 3.81 (t, 2H, CH_2, *J* = 6.0 Hz), 1.89-1.83 (m, 2H, CH_2), 1.77 (d, 5H, CH_2 and CH_3, *J* = 7.2 Hz), 1.60-1.58 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 142.3, 128.5, 127.9, 127.4, 55.5, 52.8, 50.8, 27.4, 26.7, 26.6, 26.3, 22.2. HRMS (ESI) m/z: calcd for

$C_{15}H_{22}NS_2^+$ ([M+H]$^+$), 280.1188; found, 280.1182.



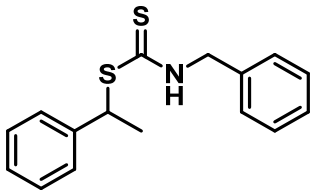
1-Phenylethyl dipropylcarbamodithioate (4ap)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 170/1, v/v) as a light yellow oily liquid in 56% yield (157.6 mg). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.42 (d, 2H, ArH, *J* = 7.6 Hz), 7.35 (t, 2H, ArH, *J* = 7.6 Hz), 7.27 (t, 1H, ArH, *J* = 7.2 Hz), 5.16-5.11 (m, 1H, CH), 3.88-3.84 (m, 2H, CH_2), 3.60 (t, 2H, CH_2, *J* = 8.4 Hz), 1.70 (d, 3H, CH_3, *J* = 6.8 Hz), 1.66-1.60 (m, 4H, CH_2), 0.86 (t, 6H, CH_3, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 193.4, 141.9, 128.5, 127.7, 127.3, 55.9, 53.7, 50.3, 21.9, 20.3, 19.1, 11.0, 10.9. HRMS (ESI) m/z: calcd for $C_{15}H_{24}NS_2^+$ ([M+H]$^+$), 282.1345; found, 282.1336.



1-Phenylethyldibenzylcarbamodithioate (4aq)[5]

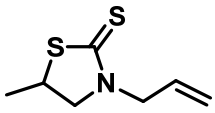
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 160:1, v/v) as a light yellow oil liquid in 85% yield (320.9 mg). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.41-7.24 (m, 13H, ArH), 7.17 (d, 2H, ArH, *J* = 7.2 Hz), 5.32-5.22 (m, 2H, CH_2), 5.19-5.14 (m, 1H, CH), 4.94 (t, 2H, CH_2, *J* = 18.0 Hz), 1.71 (d, 3H, CH_3, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 197.0, 141.5, 135.5, 134.9, 128.7, 128.5, 127.7, 127.6, 127.4, 126.7, 56.2, 54.3, 51.3, 21.8.



1-Phenylethyl benzylcarbamodithioate (4ar)

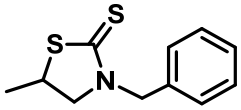
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 40/1, v/v) as a yellow oil liquid in 72% yield (207.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.30 (m, 2H, ArH), 7.25-7.22 (m, 4H, ArH), 7.21-7.16 (m, 2H, ArH), 7.14-7.12 (m, 2H,ArH), 6.91 (br s, 1H, NH), 5.04-4.99 (m, 1H, CH), 4.79-4.68 (m, 2H, CH_2), 1.64 (d, 3H, CH_3, J = 7.2 Hz).^{13}C NMR (100 MHz, CDCl) δ 196.9, 142.0, 136.0, 128.9, 128.8, 128.3, 128.1, 127.7, 127.5, 51.0, 49.4, 22.3. HRMS (ESI) m/z: calcd for $C_{16}H_{18}NS_2^+$ ($[M+H]^+$), 288.0875; found, 288.0867.

8. Characterization data for compound 6



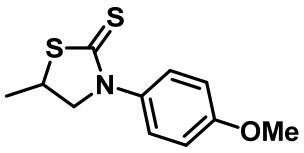
3-Allyl-5-methylthiazolidine-2-thione (6a)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 50/1, v/v) as a light yellow oily liquid in 60% yield (104.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88-5.78 (m, 1H, CH), 5.31 (s, 1H, CH_2), 5.28 (d, 1H, CH_2, J = 6.8 Hz), 4.46 (dd, 1H, CH_2, J_1 = 6.0 Hz, J_2 = 15.2 Hz), 4.35 (dd, 1H, CH_2, J_1 = 6.4 Hz, J_2 = 14.8 Hz), 4.12-4.07 (m, 1H, CH_2), 3.81-3.73 (m, 1H, CH), 3.66-3.62 (m, 1H, CH_2), 1.46 (d, 3H, CH_3, J = 6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 130.7, 119.5, 62.9, 51.6, 38.2, 20.6. HRMS (ESI) m/z: calcd for $C_7H_{12}NS_2^+$ ($[M+H]^+$), 174.0406; found, 174.0404.



3-Benzyl-5-methylthiazolidine-2-thione (6b)

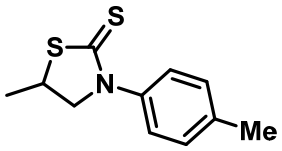
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 50/1, v/v) as a light yellow oily liquid in 56% yield (125.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (m, 5H, ArH), 5.07 (d, 1H, CH_2, J = 14.8 Hz), 4.92 (d, 1H, CH_2, J = 14.4 Hz), 4.02-3.98 (m, 1H, CH_2), 3.75-3.67 (m, 1H, CH), 3.55-3.50 (m, 1H, CH_2), 1.37 (d, 3H, CH_3, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 135.1, 129.0, 128.2 (2), 62.6, 52.6, 38.2, 20.6. HRMS (ESI) m/z: calcd for $C_{11}H_{14}NS_2^+$ ($[M+H]^+$), 224.0562; found, 224.0553.



3-(4-Methoxyphenyl)-5-methylthiazolidine-2-thione (6c)

The title compound was isolated by silica-gel column chromatography (eluent:

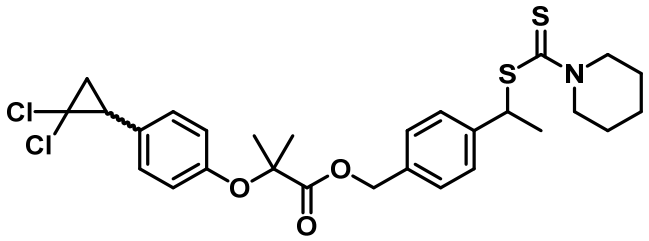
petroleum ether /EtOAc = 40/1, v/v) as a light yellow oily liquid in 71% yield (169.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, 2H, ArH, *J* = 8.8 Hz), 6.95 (d, 2H, ArH, *J* = 8.8 Hz), 4.453-4.48 (m, 1H, CH_2), 4.04-3.99 (m, 1H, CH_2), 3.95-3.86 (m, 1H, CH), 3.782 (s, 3H, CH_3), 1.455 (d, 3H, CH_3, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 158.9, 133.3, 114.6, 67.5, 55.5, 39.2, 20.4. HRMS (ESI) m/z: calcd for $C_{11}H_{14}NOS_2^+$ ($[M+H]^+$), 240.0511; found, 240.0511.



5-Methyl-3-(p-tolyl)thiazolidine-2-thione (6d)[7]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 40/1, v/v) as a light yellow oily liquid in 45% yield (100.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 4H, ArH), 4.55-4.50 (m, 1H, CH_2), 4.06-4.02 (m, 1H, CH_2), 3.95-3.87 (m, 1H, CH), 2.37 (s, 3H, CH_3), 1.56 (d, 3H, CH_3, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 138.1, 138.0, 130.0, 125.6, 67.4, 39.4, 21.2, 20.4.

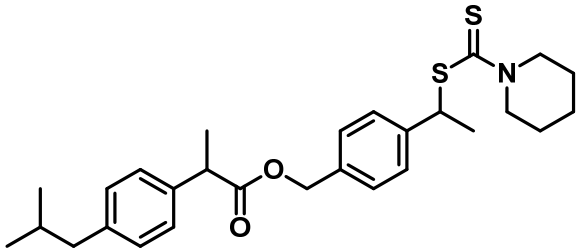
9. Characterization data for compound 7-11



4-(1-((Piperidine-1-carbonothioyl)thio)ethyl)benzyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (7):

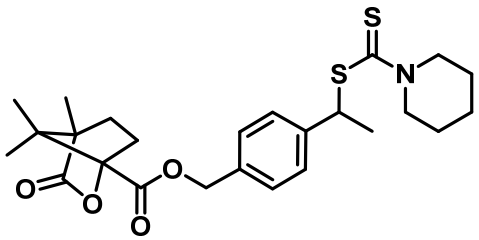
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 20/1, v/v) as a yellow oily liquid in 75% yield (425.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, 2H, ArH, *J* = 8.0 Hz), 7.18 (d, 2H, ArH, *J* = 8.0 Hz), 7.04 (d, 2H, ArH, *J* = 8.0 Hz), 6.74 (d, 2H, ArH, *J* = 8.4 Hz), 5.31-5.26 (m, 1H, CH), 5.15 (s, 2H, CH_2), 4.26 (br s, 2H, CH_2), 3.83 (br s, 2H, CH_2), 2.82 (dd, 1H, CH,

J_1 = 10.8 Hz, J_2 = 8.4 Hz), 1.95-1.90 (m, 1H, CH), 1.78 (d, 1H, CH_2, J = 8.4 Hz), 1.76 (d, 3H, CH_3, J = 6.8 Hz), 1.67-1.63 (m, 6H, CH_2), 1.60 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 174.0, 154.9, 142.6, 134.3, 129.6, 128.5, 128.5, 128.1, 128.1, 128.0, 118.6, 79.2, 66.9, 60.9, 52.7, 51.3, 50.5, 34.8, 25.8, 25.8, 25.5, 25.5, 25.4, 25.4, 24.3, 22.2. HRMS (ESI) m/z: calcd for $C_{28}H_{34}Cl_2NO_3S_2^+$ ([M+H]$^+$), 566.1352; found, 566.1345.



4-(1-((Piperidine-1-carbonothioyl)thio)ethyl)benzyl 2-(4-isobutylphenyl)propanoate (8):

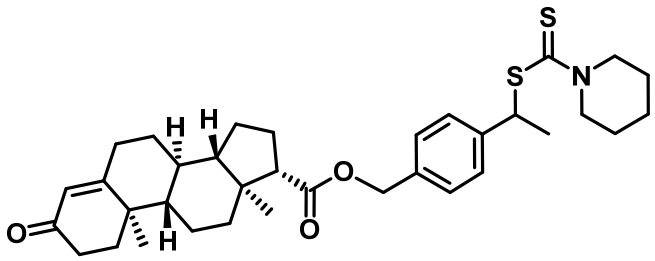
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 20/1, v/v) as a yellow oily liquid in 46% yield (222.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, 2H, ArH, J = 8.0 Hz), 7.21-7.14 (m, 4H, ArH), 7.08 (d, 2H, ArH, J = 8.0 Hz), 5.30-5.25 (m, 1H, CH), 5.10-5.02 (m, 2H, CH_2), 4.25 (br s, 2H, CH_2), 3.78 (br s, 2H, CH_2), 3.76-3.71 (m, 1H, CH), 2.45 (d, 2H, CH_2, J = 7.2 Hz), 1.88-1.81 (m, 1H, CH), 1.74 (d, 3H, CH_3, J = 7.2 Hz), 1.65-1.62 (m, 6H, CH_2), 1.49 (d, CH_3, 3H, J = 7.2 Hz), 0.90 (d, 6H, CH_3, J = 6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 174.5, 142.2, 140.6, 137.6, 135.2, 129.4, 128.0, 127.9, 127.2, 66.0, 52.8, 51.3, 50.6, 45.2, 45.1, 30.2, 26.0, 25.5, 24.3, 22.5, 22.1, 18.5. HRMS (ESI) m/z: calcd for $C_{28}H_{38}NO_2S_2^+$ ([M+H]$^+$), 484.2338; found, 484.2341.



4-(1-((Piperidine-1-carbonothioyl)thio)ethyl)benzyl (1S,4S)-4,7,7-trimethyl-3-

oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (9):

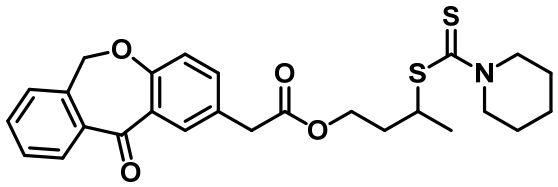
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 20/1, v/v) as a yellow oily liquid in 51% yield (242.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, 2H, ArH, *J* = 8.0 Hz), 7.32 (d, 2H, ArH, *J* = 8.0 Hz), 5.32-5.27 (m, 1H, CH), 5.23 (s, 2H, CH_2), 4.26 (br s, 2H, CH_2), 3.84 (br s, 2H, CH_2), 2.47-2.40 (m, 1H, CH_2), 2.07-2.00 (m, 1H, CH_2), 1.96-1.89 (m, 1H, CH_2), 1.76 (d, 3H, CH_3, *J* = 7.2 Hz), 1.68-1.66 (m, 7H, CH_2), 1.10 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 0.92 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 178.1, 167.4, 142.9, 134.1, 128.5, 128.2, 91.1, 66.9, 54.8, 54.3, 52.7, 51.3, 50.5, 30.7, 28.9, 26.0, 25.5, 24.3, 22.1, 16.8, 16.7, 9.7. HRMS (ESI) m/z: calcd for $C_{25}H_{34}NO_4S_2^+$ ($[M+H]^+$), 476.1924; found, 476.1924.



4-(1-((Piperidine-1-carbonothioyl)thio)ethyl)benzyl (8S,9S,10R,13S,14S,17S)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene-17-carboxylate (10):

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 20/1, v/v) as a yellow oily liquid in 41% yield (243.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, 2H, ArH, *J* = 8.0 Hz), 7.31 (d, 2H, ArH, *J* = 8.0 Hz), 5.73 (s, 1H, CH), 5.33-5.28 (m, 1H, CH), 5.09 (s, 2H, CH_2), 4.27 (br s, 2H, CH_2), 3.84 (br s, 2H, CH_2), 2.47-2.36 (m, 4H, CH_2), 2.31-2.25 (m, 1H, CH), 2.22-2.13 (m, 1H, CH), 2.04-2.02 (m, 2H, CH_2), 1.87-1.82 (m, 2H, CH_2), 1.77 (d, 3H, CH_3, *J* = 7.2 Hz), 1.73-1.51 (m, 10H, CH_2), 1.42-1.39 (m, 1H, CH), 1.33-1.26 (m, 2H, CH_2), 1.18 (s, 3H, CH_3), 1.15-1.02 (m, 2H, CH_2), 0.99-0.93 (m, 1H, CH), 0.69 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 194.3, 173.7, 171.1, 142.3, 135.3, 128.3, 128.3, 128.0, 123.9, 65.7, 55.4, 55.1, 53.7, 52.7, 51.3, 50.5, 44.1, 38.6, 38.1, 35.7, 35.7, 34.0, 32.8,

31.9, 26.0, 25.4, 24.4, 24.3, 23.6, 22.1, 22.1, 20.9, 17.4, 13.5. HRMS (ESI) m/z: calcd for $C_{35}H_{48}NO_3S_2^+$ ([M+H]$^+$), 594.3070; found, 594.3068.



3-((Piperidine-1-carbonothioyl)thio)butyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (11):

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc = 20/1, v/v) as a yellow oily liquid in 67% yield (324.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, 1H, ArH, *J* = 2.4 Hz), 7.89 (d, 1H, ArH, *J* = 7.6 Hz), 7.55 (td, ArH, J_1 = 7.2 Hz, J_2 = 1.2 Hz), 7.50-7.43 (m, 2H, ArH), 7.36 (d, 1H, ArH, *J* = 7.6 Hz), 7.03 (d, 1H, ArH, *J* = 8.4 Hz), 5.18 (s, 2H, CH_2), 4.31-4.13 (m, 5H, CH_2 and CH), 3.86 (br s, 2H, CH_2), 3.66 (s, 2H, CH_2), 2.16-2.08 (m, 1H, CH_2), 2.02-1.94 (m, 1H, CH_2), 1.68-1.66 (m, 6H, CH_2), 1.42 (d, 3H, CH_3, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 190.8, 171.4, 160.4, 140.5, 136.5, 135.6, 132.7, 132.5, 129.5, 129.2, 127.8, 127.8, 125.1, 121.1, 73.6, 62.7, 52.6, 51.3, 44.3, 40.3, 35.1, 25.9, 25.5, 24.3, 21.0. HRMS (ESI) m/z: calcd for $C_{26}H_{30}NO_4S_2^+$ ([M+H]$^+$), 484.1611; found, 484.1614.

10. References

[1] S. KC, R. K. Dhungana, B. Shrestha, S. Thapa, N. Khanal, P. Basnet, R. W. Lebrun, R. Giri, J. Am. Chem. Soc. 2018, 140, 31, 9801.

[2] Z. Wang, Z. Jin, B. Zhou, Org. Chem. Front. 2024, 11, 1382

[3] J. Y. Kim, W. K. Shin, A. K. Jaladi, D. K. An, *Tetrahedron* **2018**, *74*, 4236.

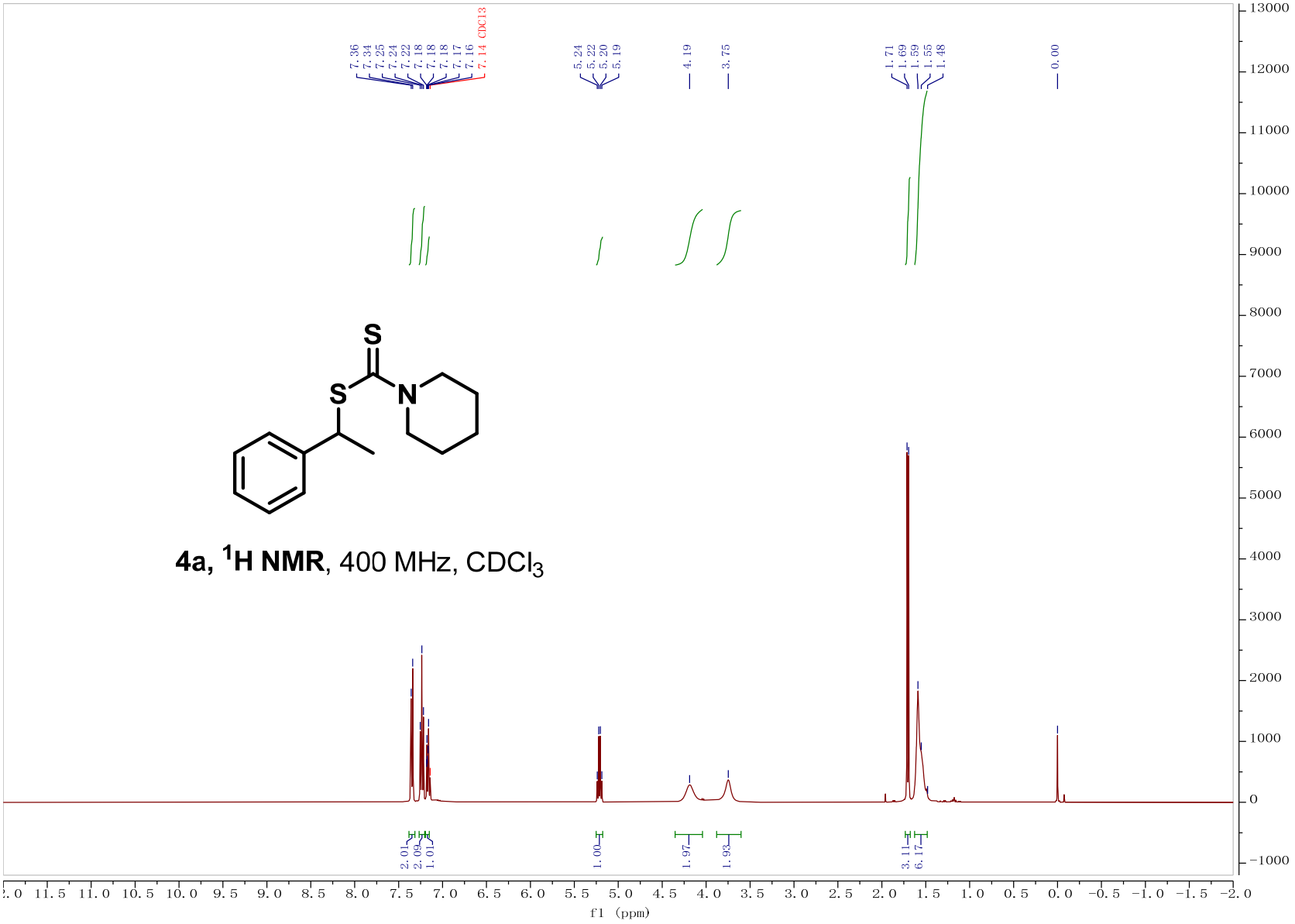
[4] Y. Jing, C. G. Daniliuc, A. Studer, *Org. Lett.*, **2014**, *16*, 4932.

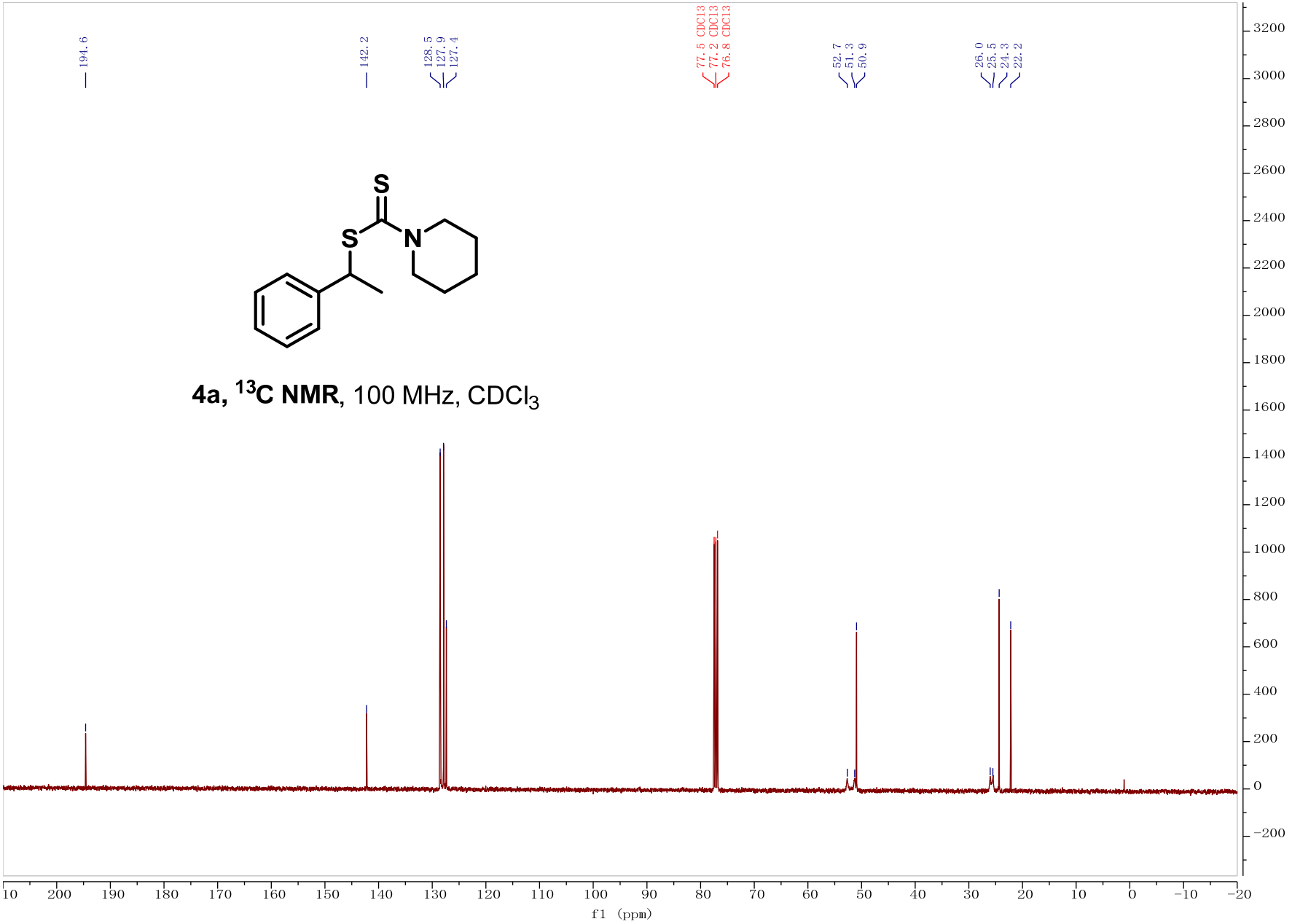
[5] Q. Sha, Y.-Y. Wei, *Org. Biomol. Chem.*, **2013**, *11*, 5615.

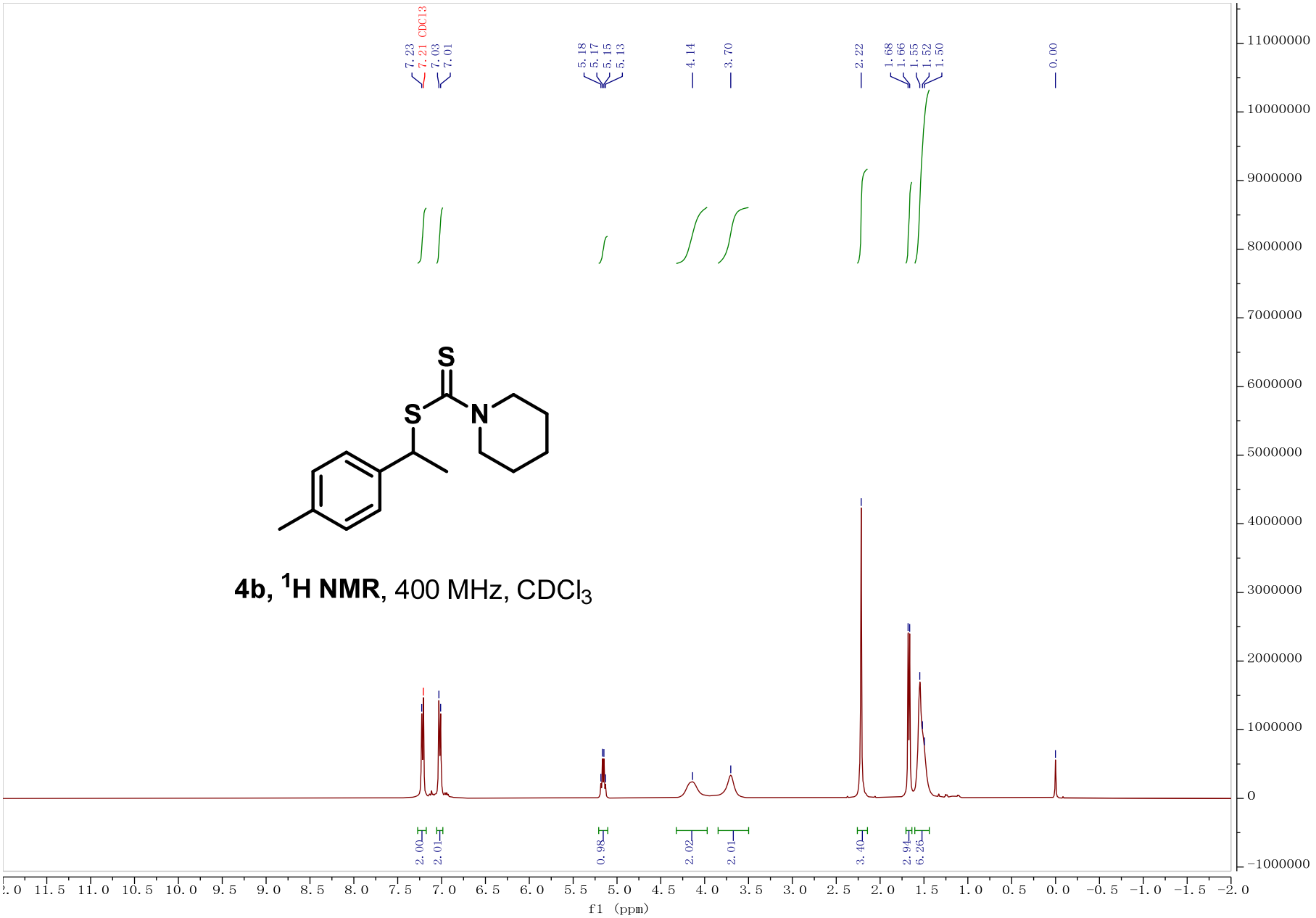
[6] Nihon Bayer Agrochem K.K. *European Patent Organization*, EP578090A2.

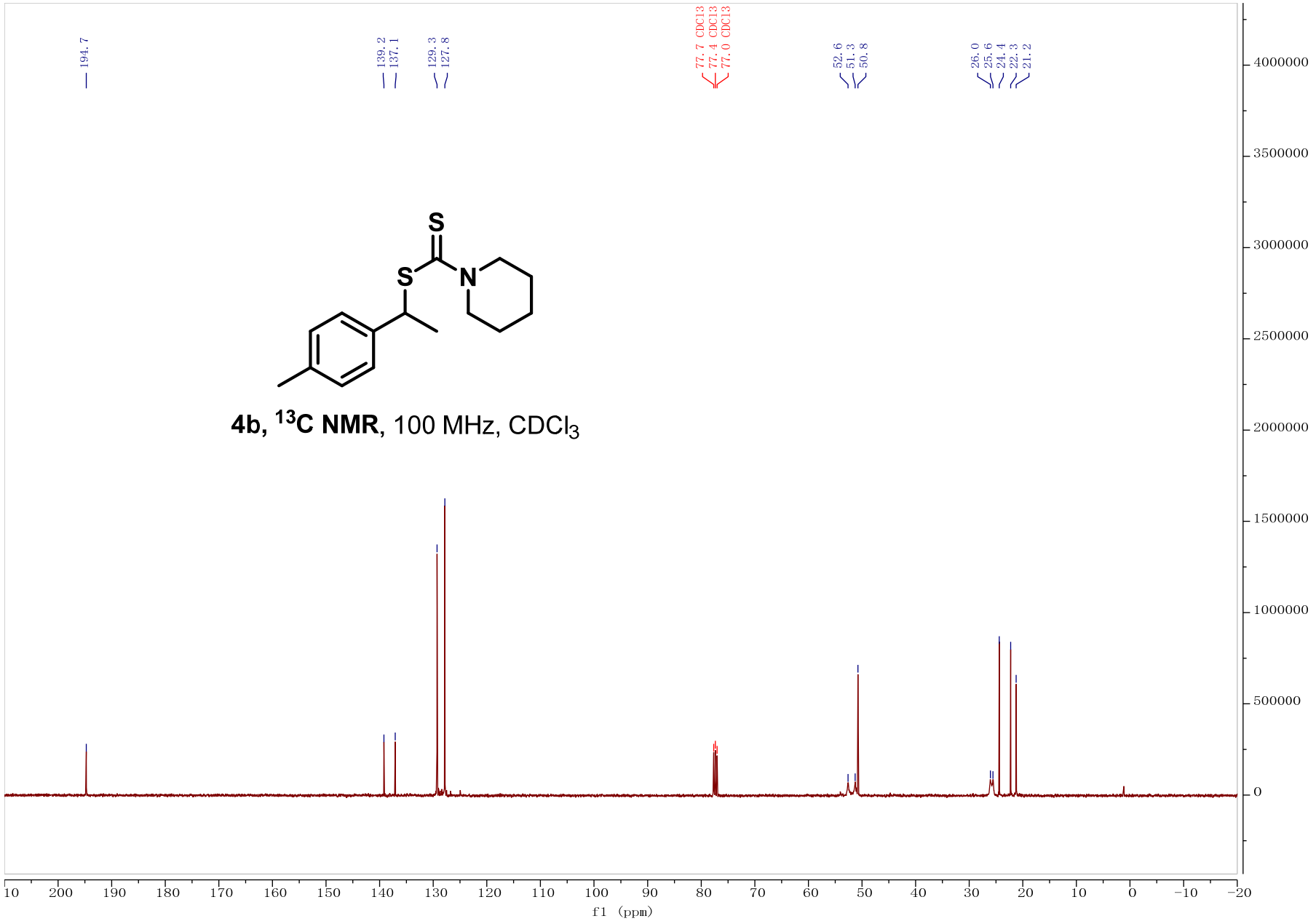
[7] Hercules Inc. United States, US3474045A.

11. Spectroscopic data for compound 4

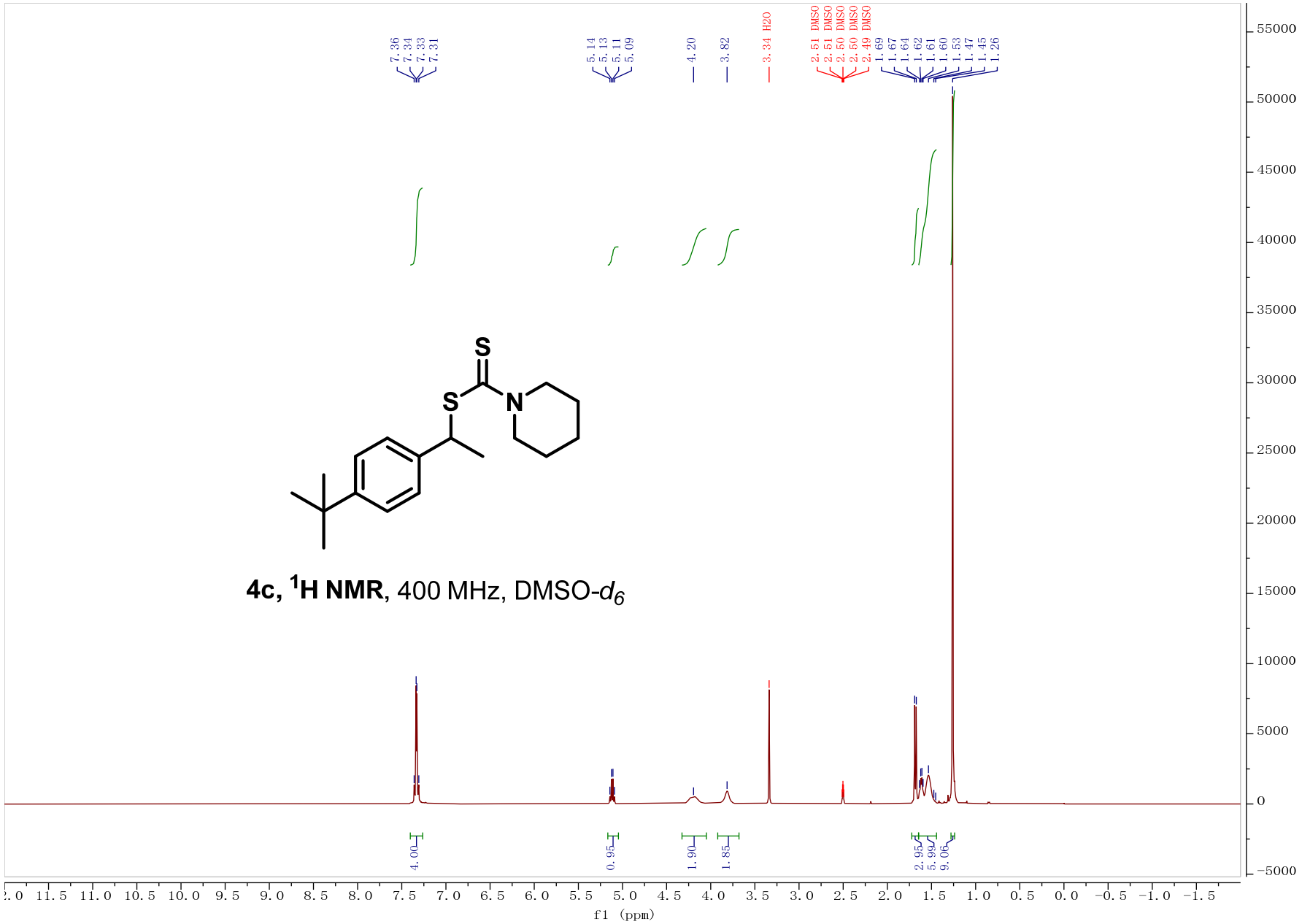


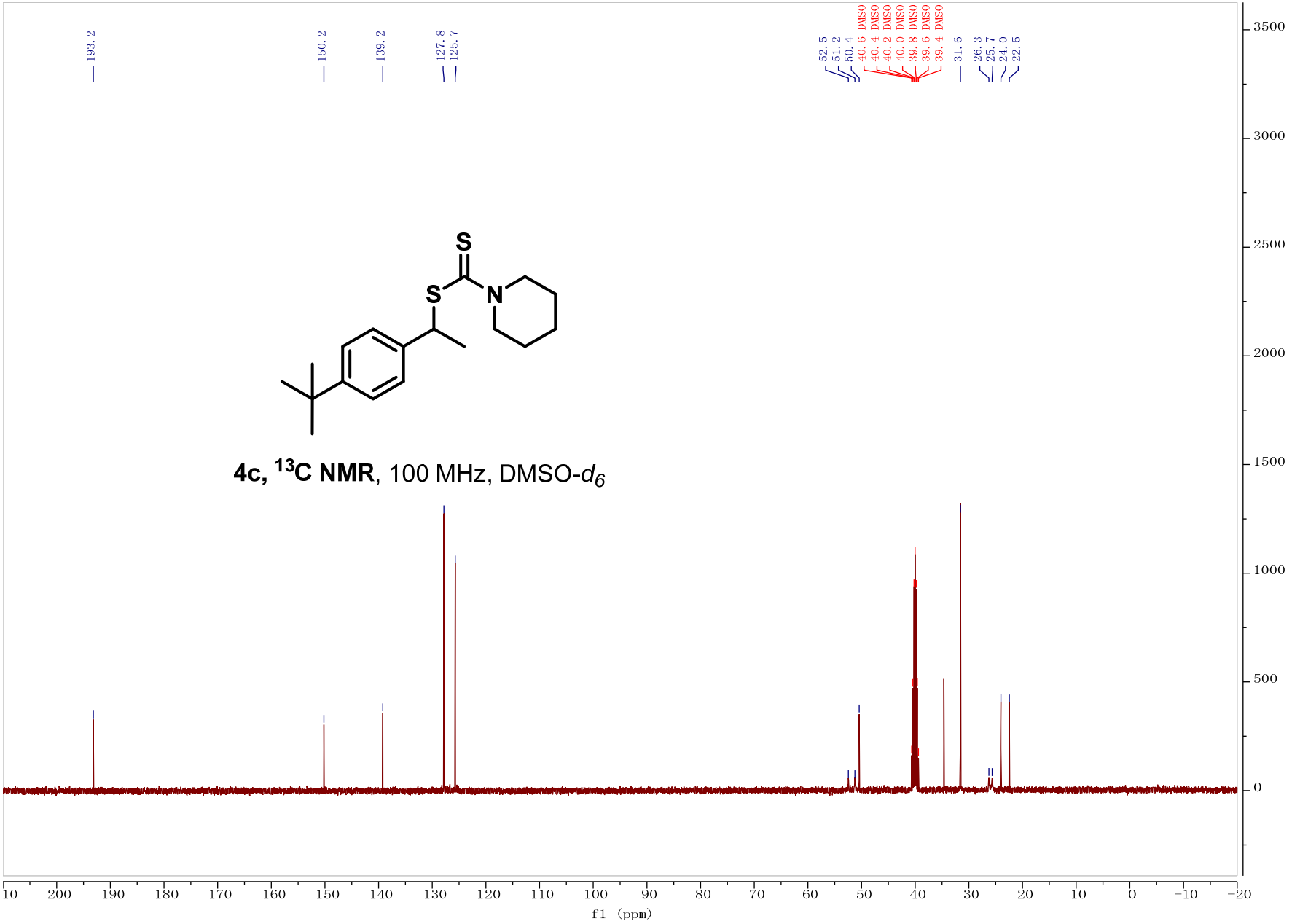

194.6
142.2
128.5
127.9
127.4
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
52.7
51.3
50.9
26.0
25.5
24.3
22.2
S
S
N
4a, 13C NMR, 100 MHz, CDCl3
f1 (ppm)

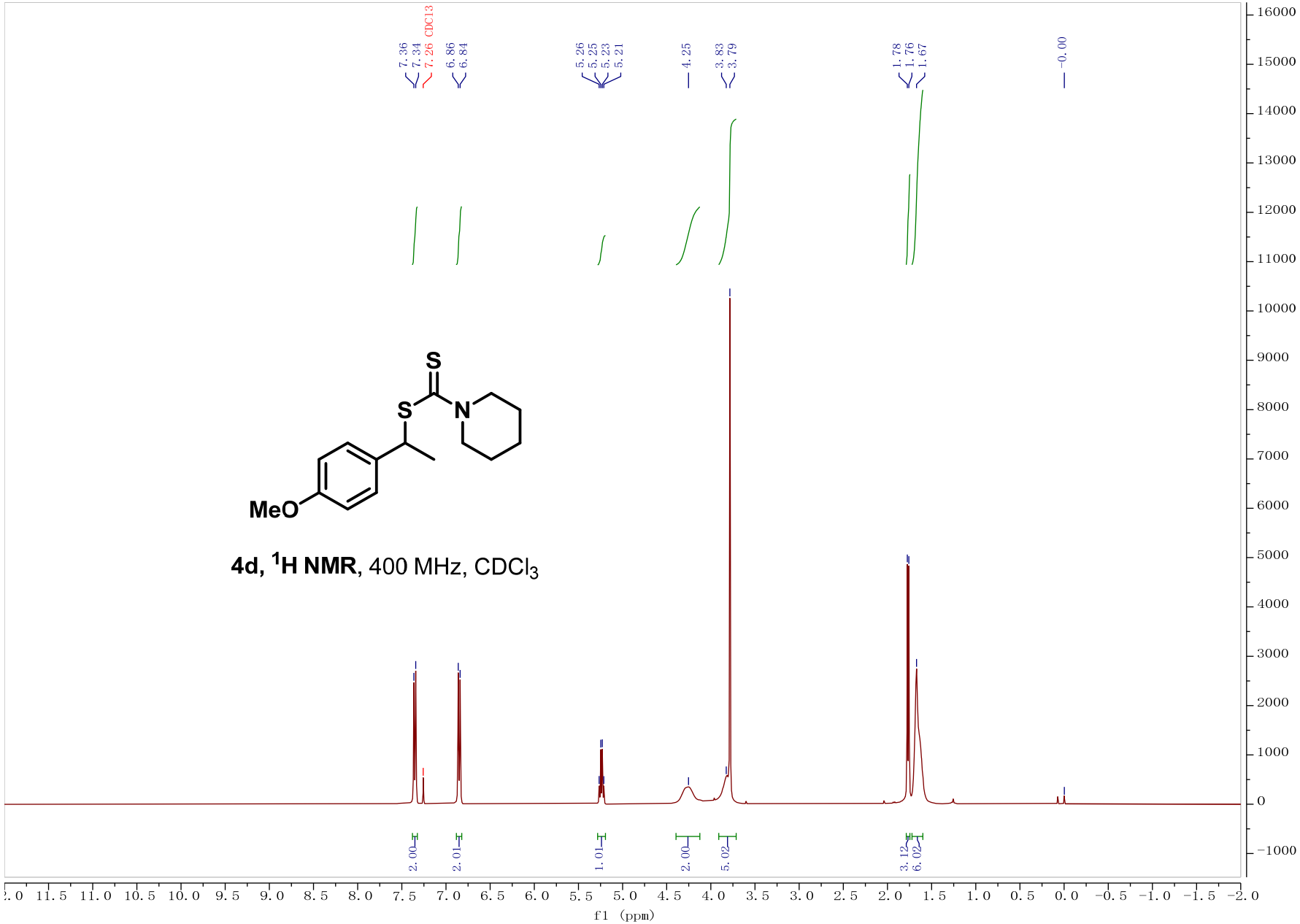

7.23
7.21
CDCl3
7.03
7.01
5.18
5.17
5.15
5.13
4.14
3.70
2.22
1.68
1.66
1.55
1.52
1.50
0.00
S
S
N
4b, 1H NMR, 400 MHz, CDCl3
2.00
2.01
0.98
2.02
2.01
3.40
2.94
6.26
f1 (ppm)

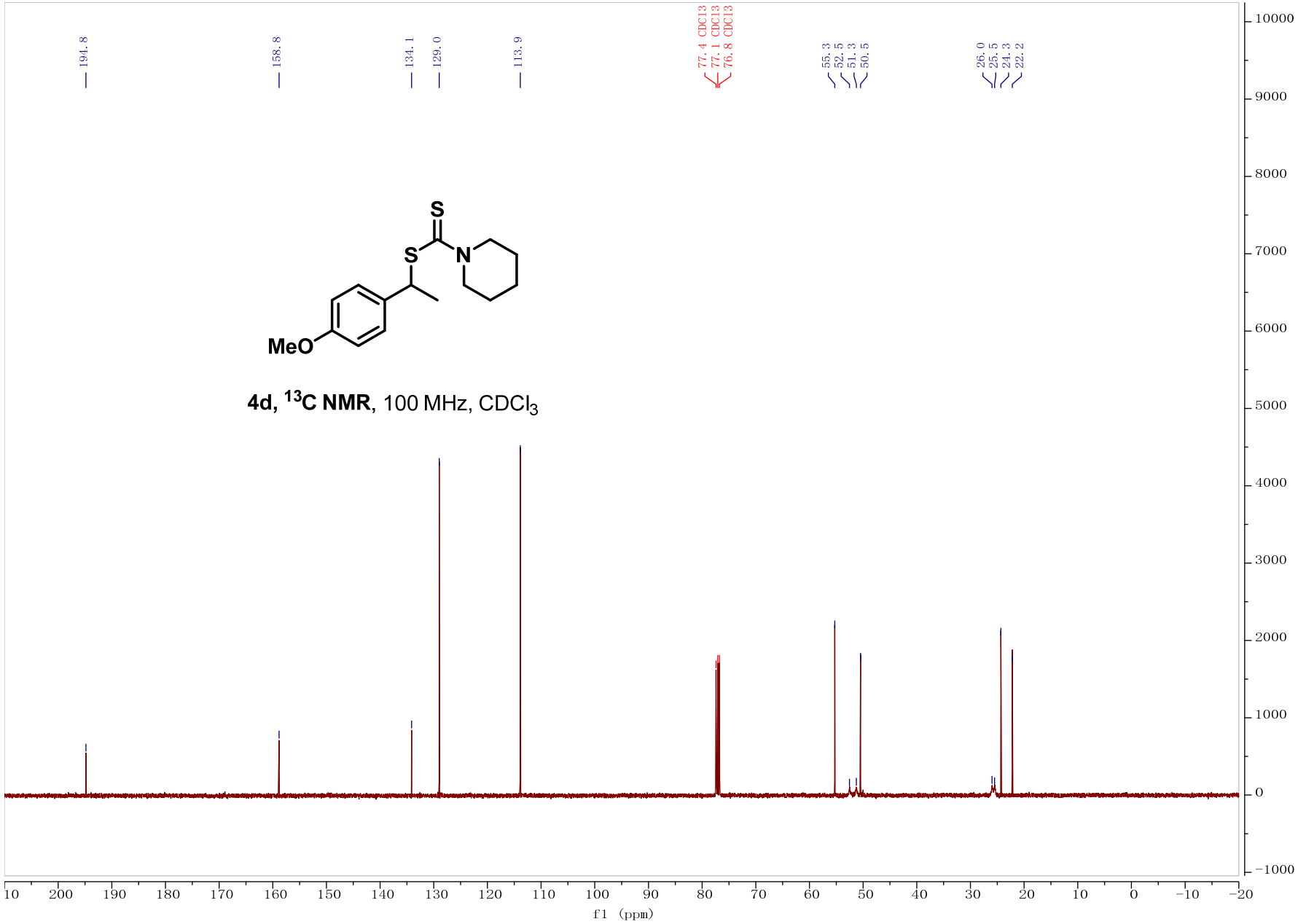


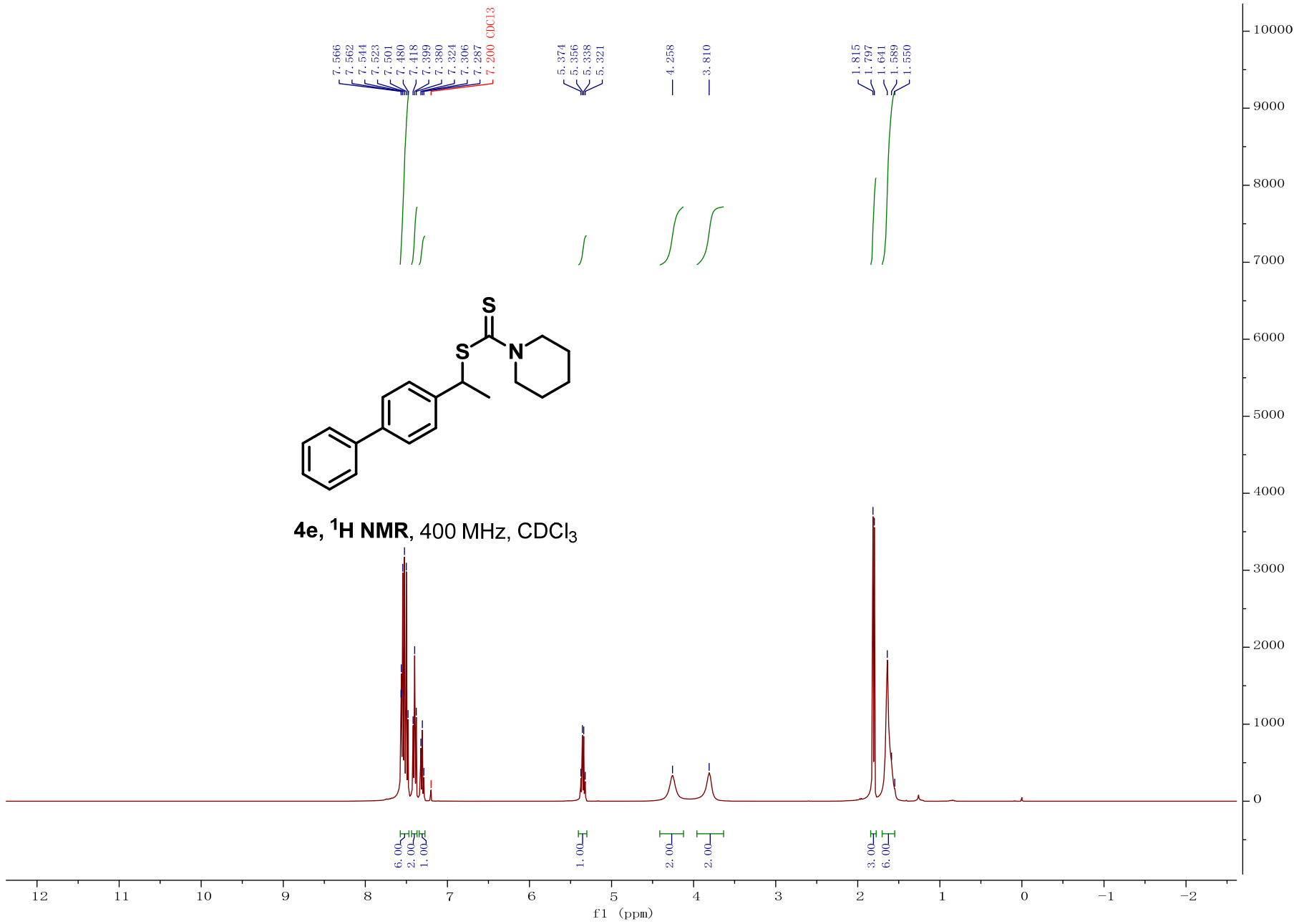
4b, ^{13}C NMR, 100 MHz, $CDCl_3$

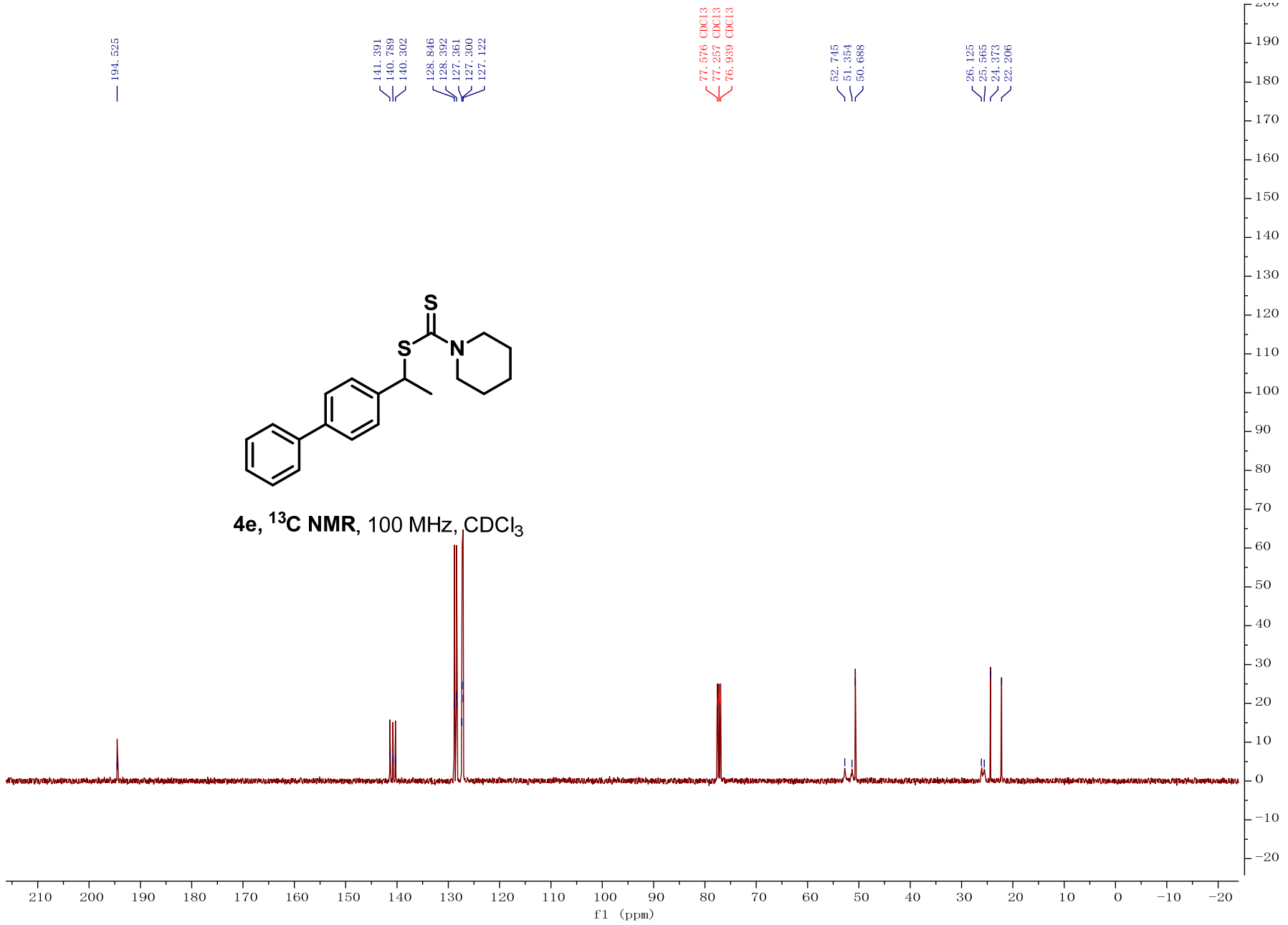

7.36
7.34
7.33
7.31
5.14
5.13
5.11
5.09
4.20
3.82
3.34 H2O
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
1.69
1.67
1.64
1.62
1.61
1.60
1.53
1.47
1.45
1.26
S
S
N
4c, 1H NMR, 400 MHz, DMSO-d6
4.00
0.95
1.90
1.85
2.95
5.99
9.06
f1 (ppm)


193.2
150.2
139.2
127.8
125.7
52.5
51.2
50.4
40.6 DMSO
40.4 DMSO
40.2 DMSO
40.0 DMSO
39.8 DMSO
39.6 DMSO
39.4 DMSO
31.6
26.3
25.7
24.0
22.5
S
S
N
4c, 13C NMR, 100 MHz, DMSO-d6
f1 (ppm)

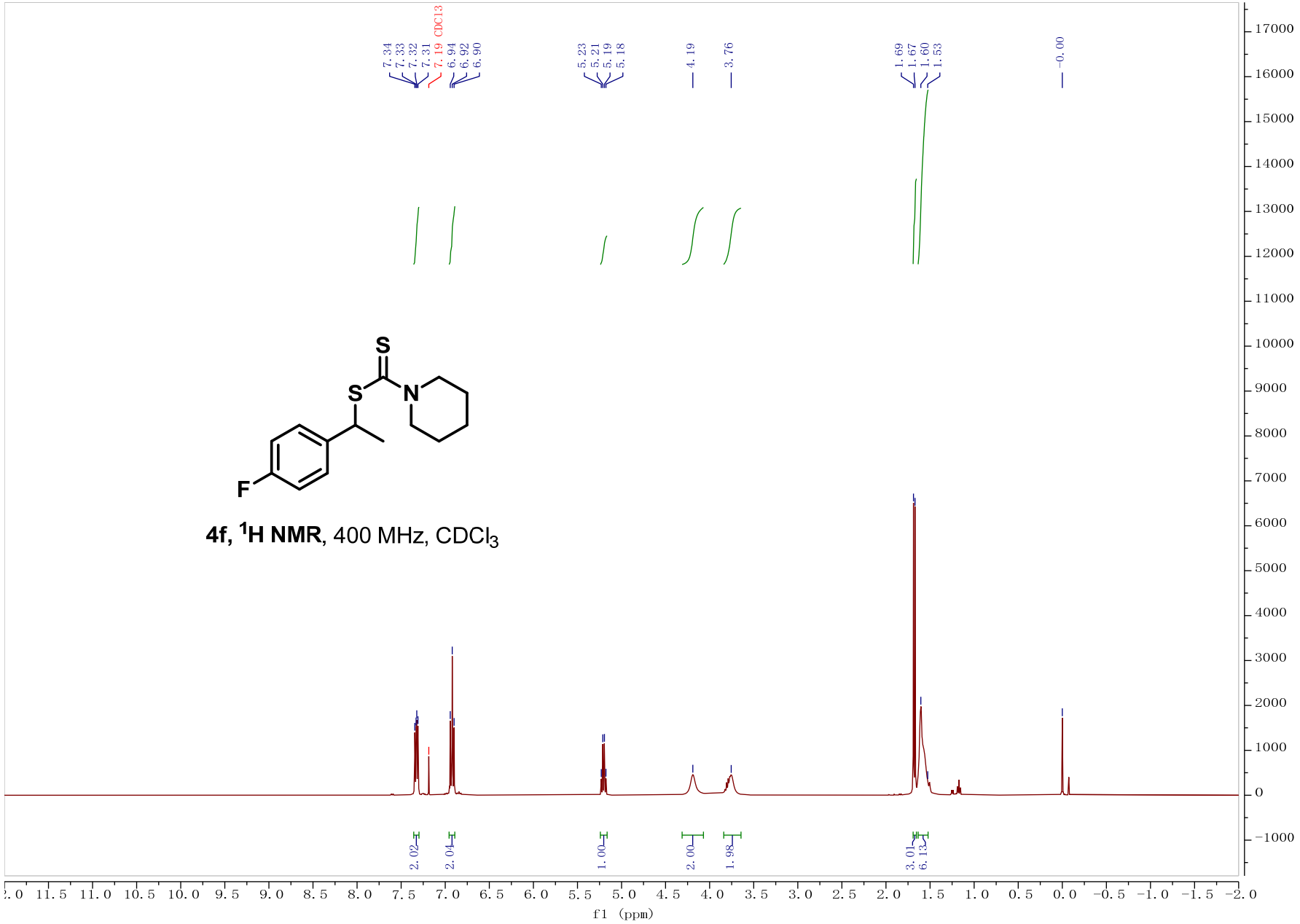

7.36
7.34
7.26 CDCl3
6.86
6.84
5.26
5.25
5.23
5.21
4.25
3.83
3.79
1.78
1.76
1.67
0.00
S
S
N
MeO
4d, 1H NMR, 400 MHz, CDCl3
2.00
2.01
1.01
2.00
5.02
3.12
6.02
f1 (ppm)


194.8
158.8
134.1
129.0
113.9
77.4 CDCl3
77.1 CDCl3
76.8 CDCl3
55.3
52.5
51.3
50.5
26.0
25.5
24.3
22.2
S
S
N
MeO
4d, 13C NMR, 100 MHz, CDCl3
f1 (ppm)

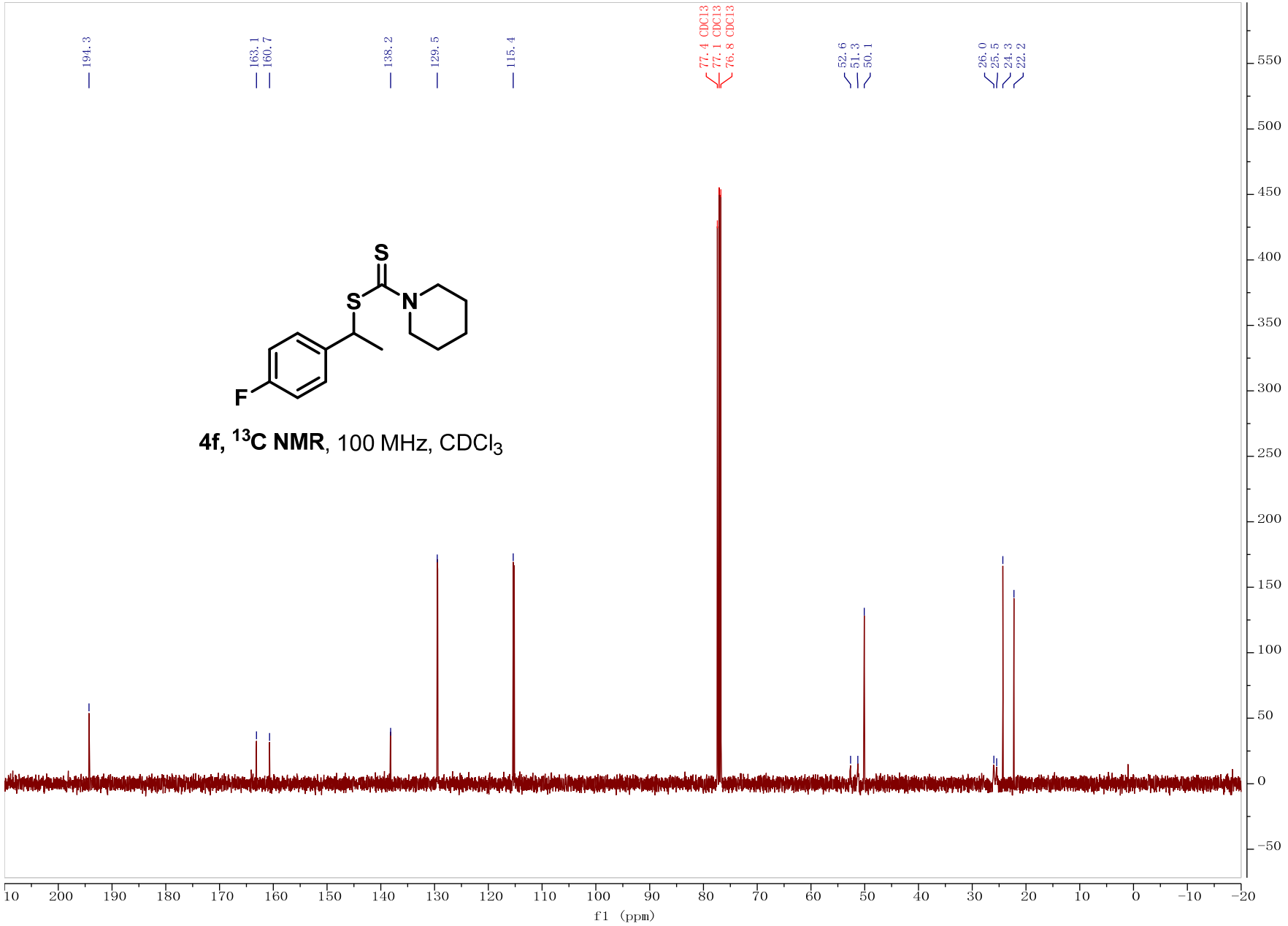

7.566
7.562
7.544
7.523
7.501
7.480
7.418
7.399
7.380
7.324
7.306
7.287
7.200 CDCl3
5.374
5.356
5.338
5.321
4.258
3.810
1.815
1.797
1.641
1.589
1.550
S
S
N
4e, 1H NMR, 400 MHz, CDCl3
6.00
2.00
1.00
1.00
2.00
2.00
3.00
6.00
f1 (ppm)



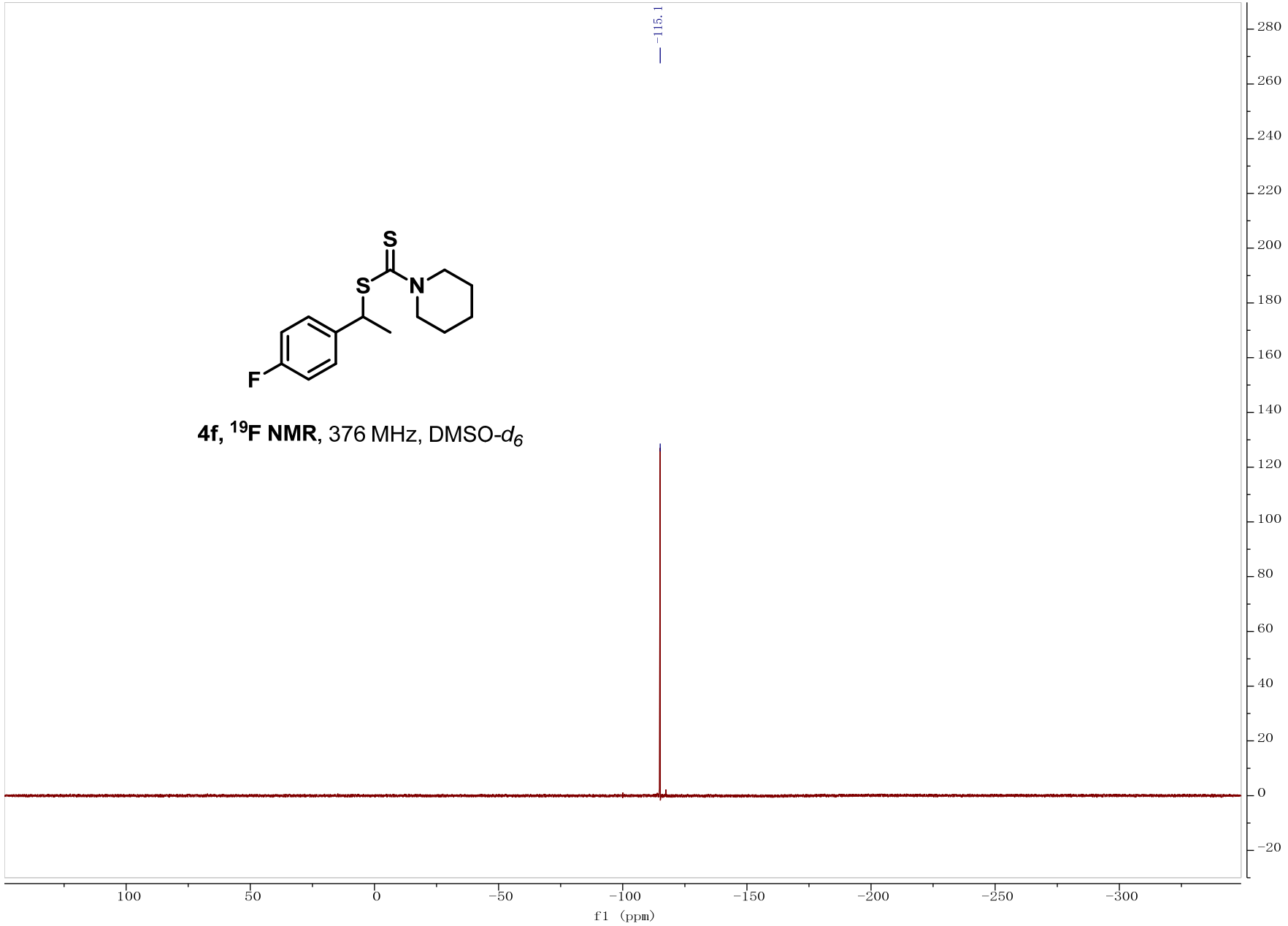
4e, ^{13}C NMR, 100 MHz, $CDCl_3$



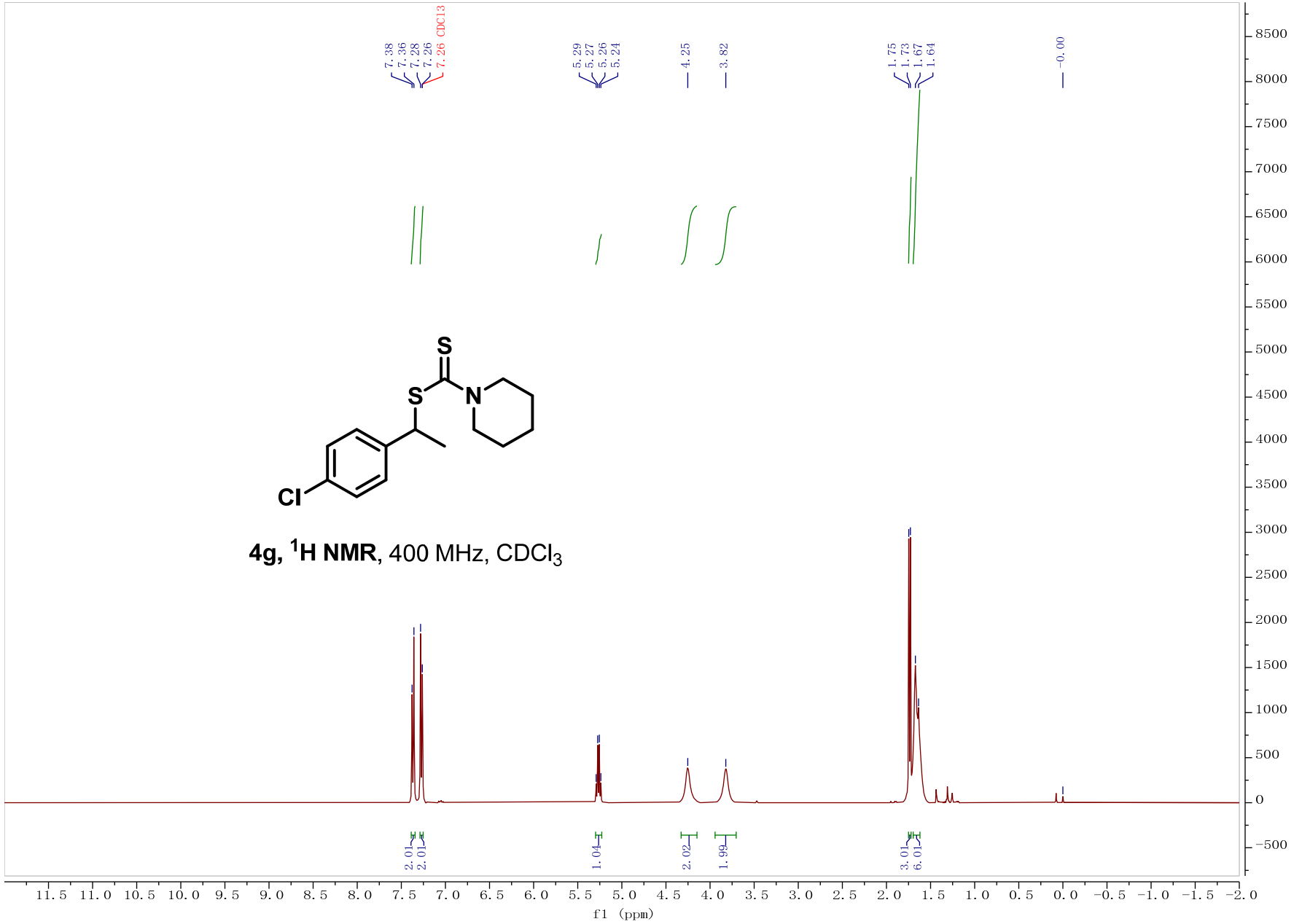
4f, ^{1}H NMR, 400 MHz, $CDCl_3$



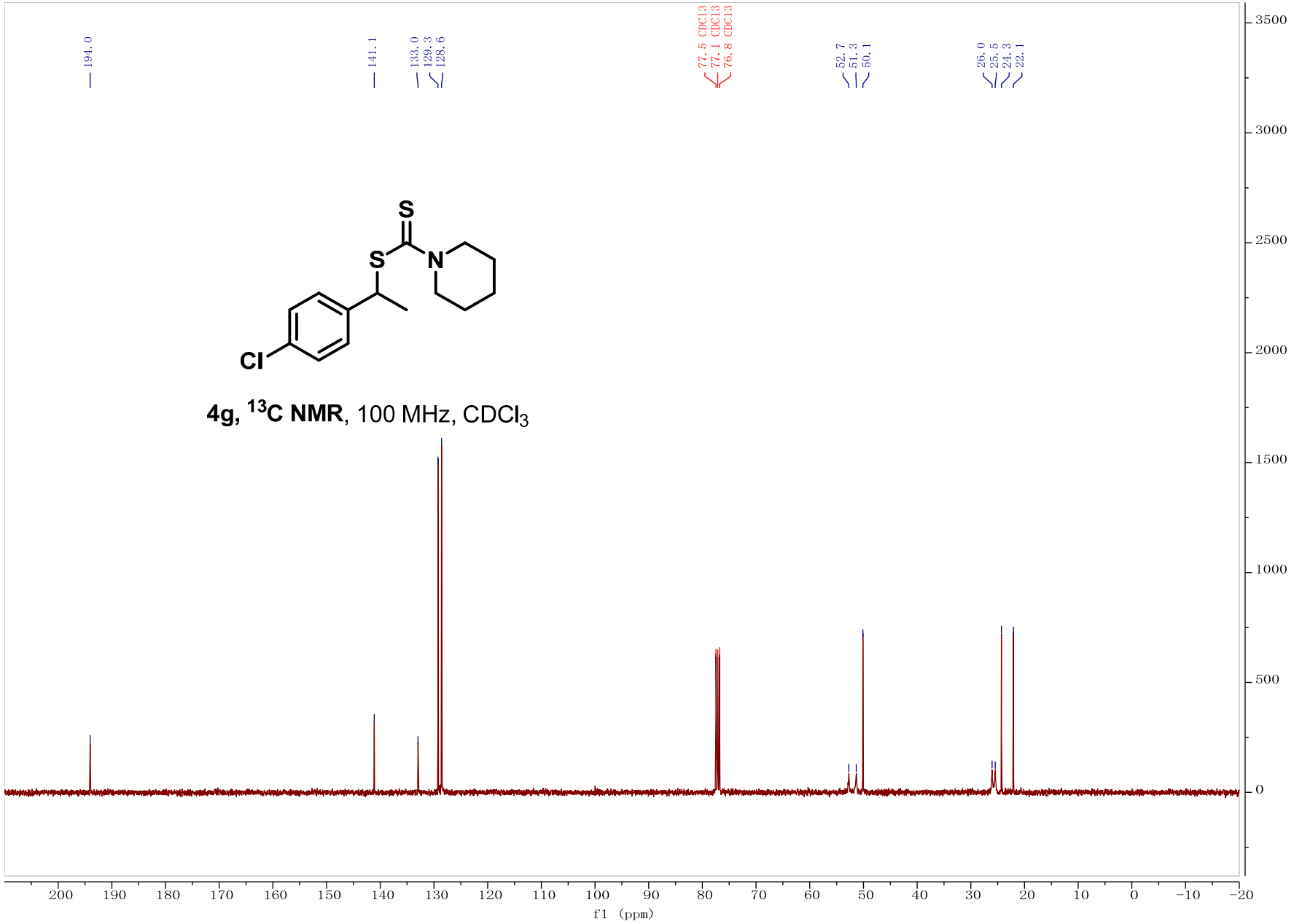
4f, ^{13}C NMR, 100 MHz, $CDCl_3$

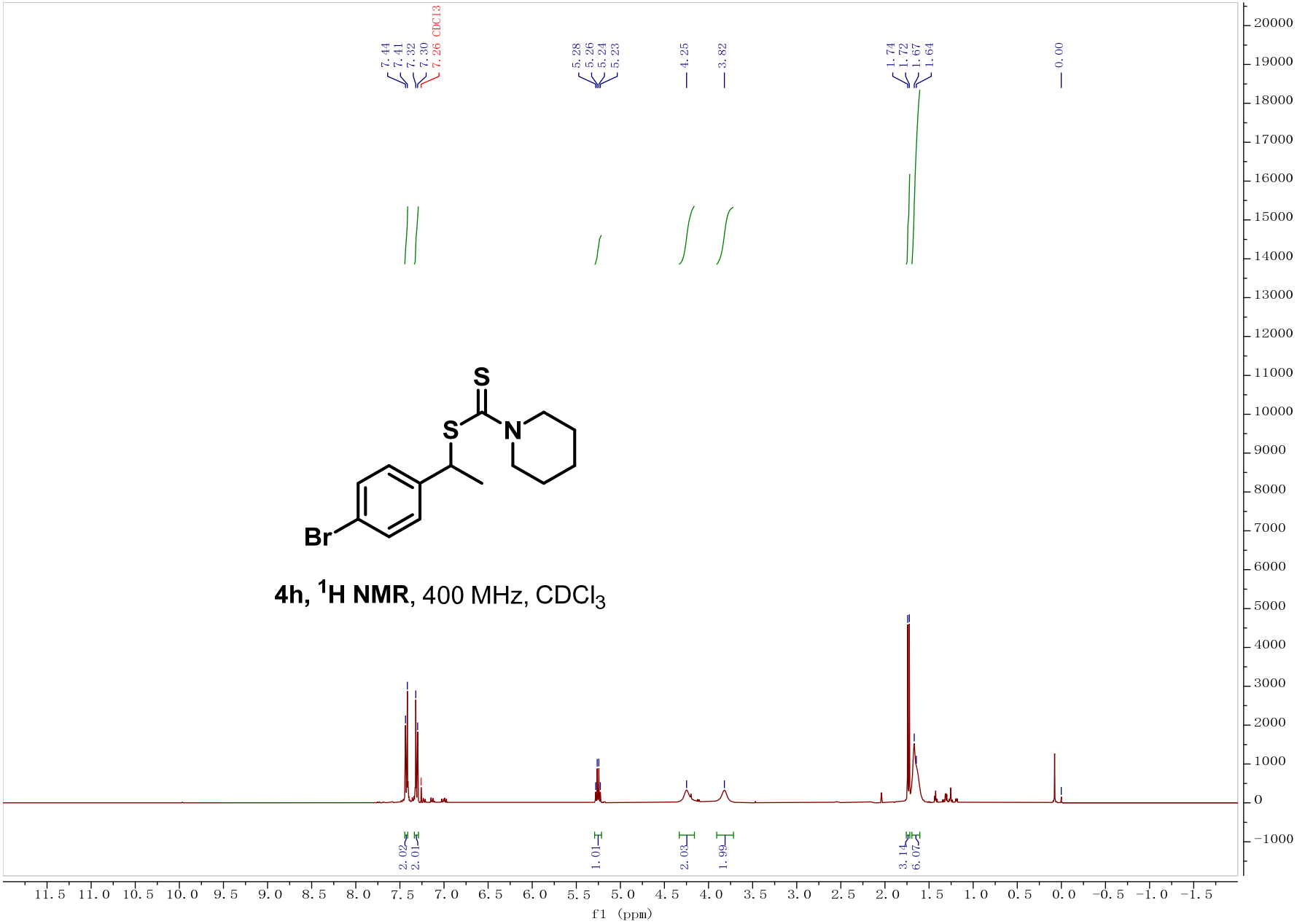


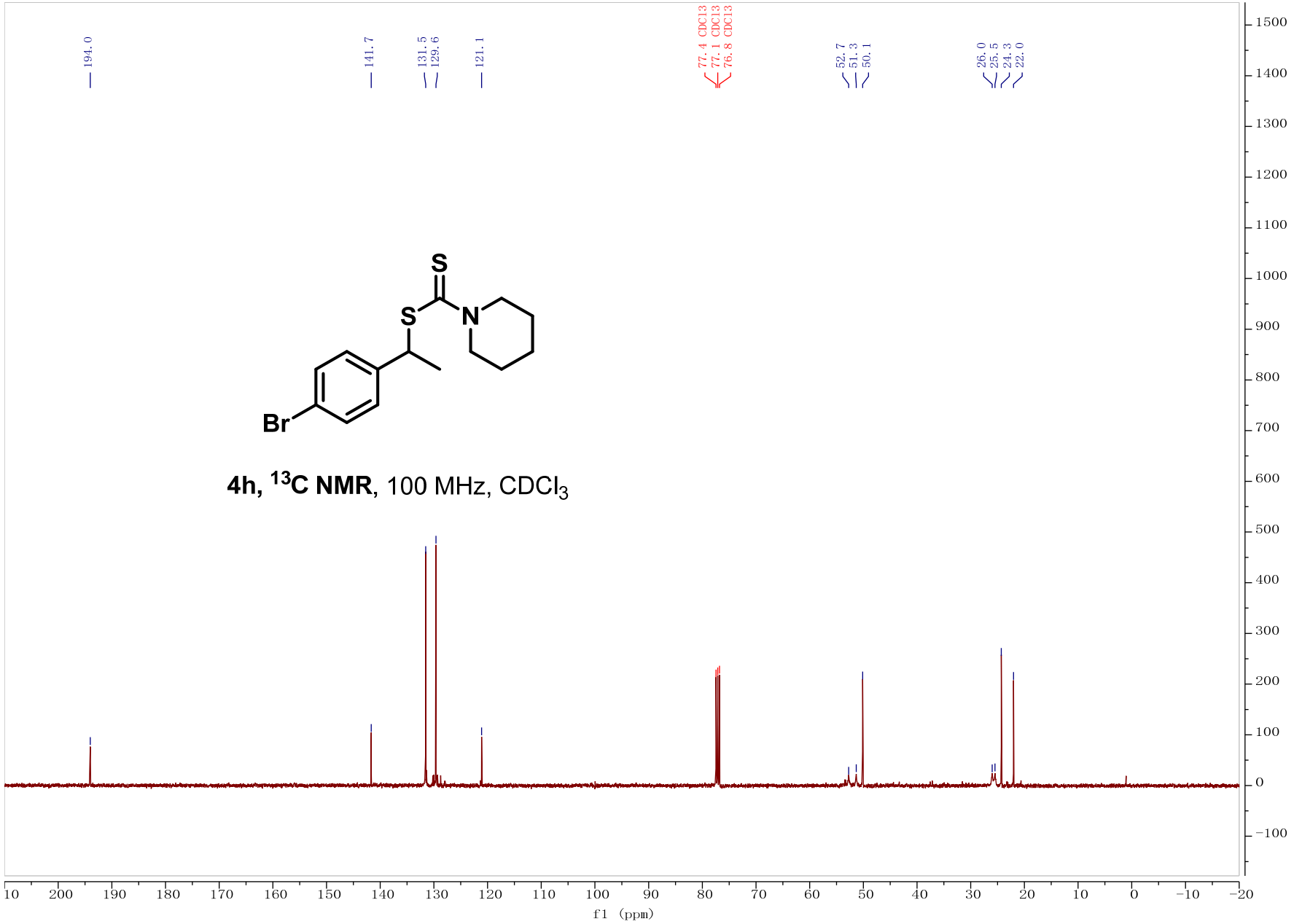
4f, ^{19}F NMR, 376 MHz, DMSO-d_6

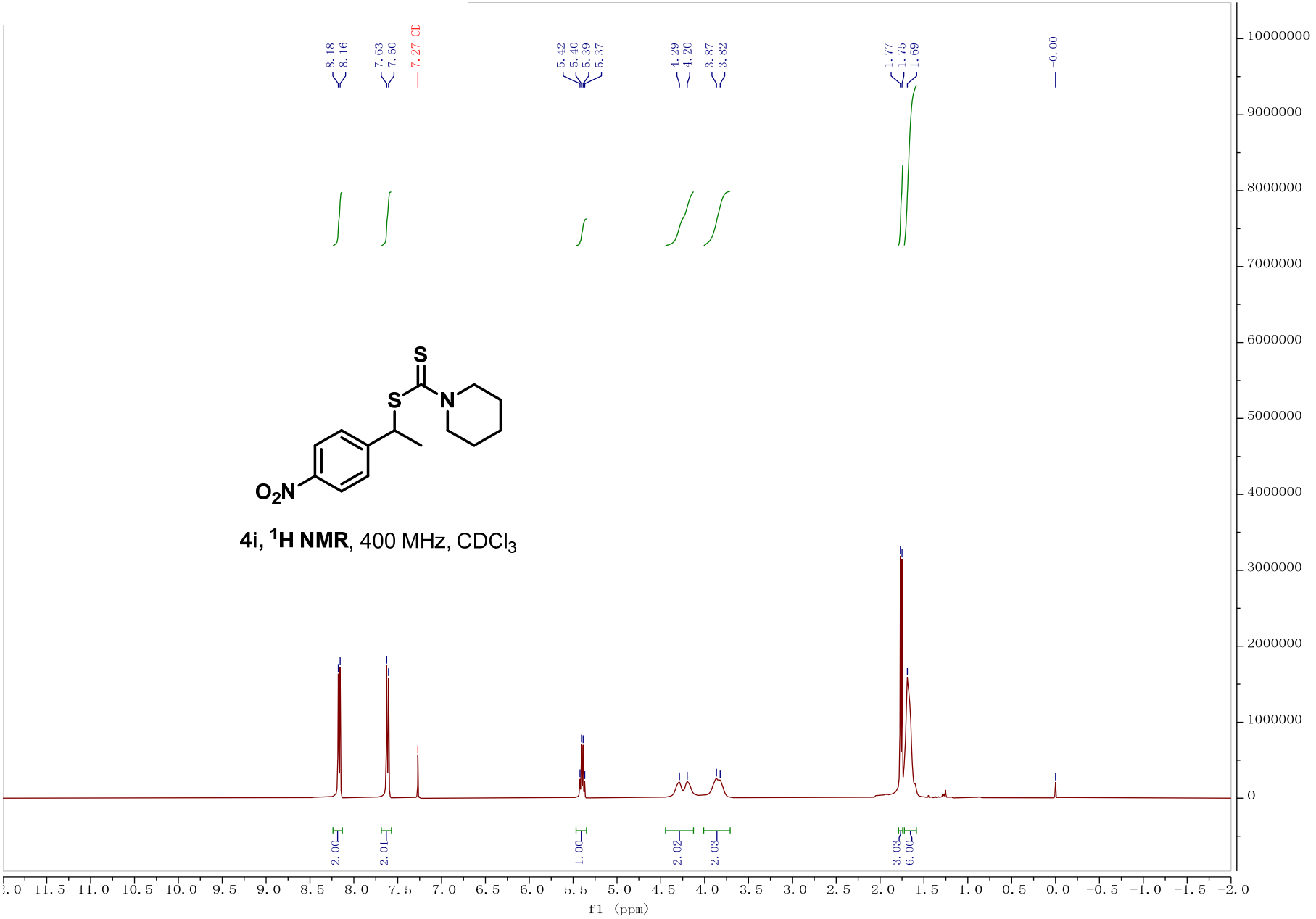


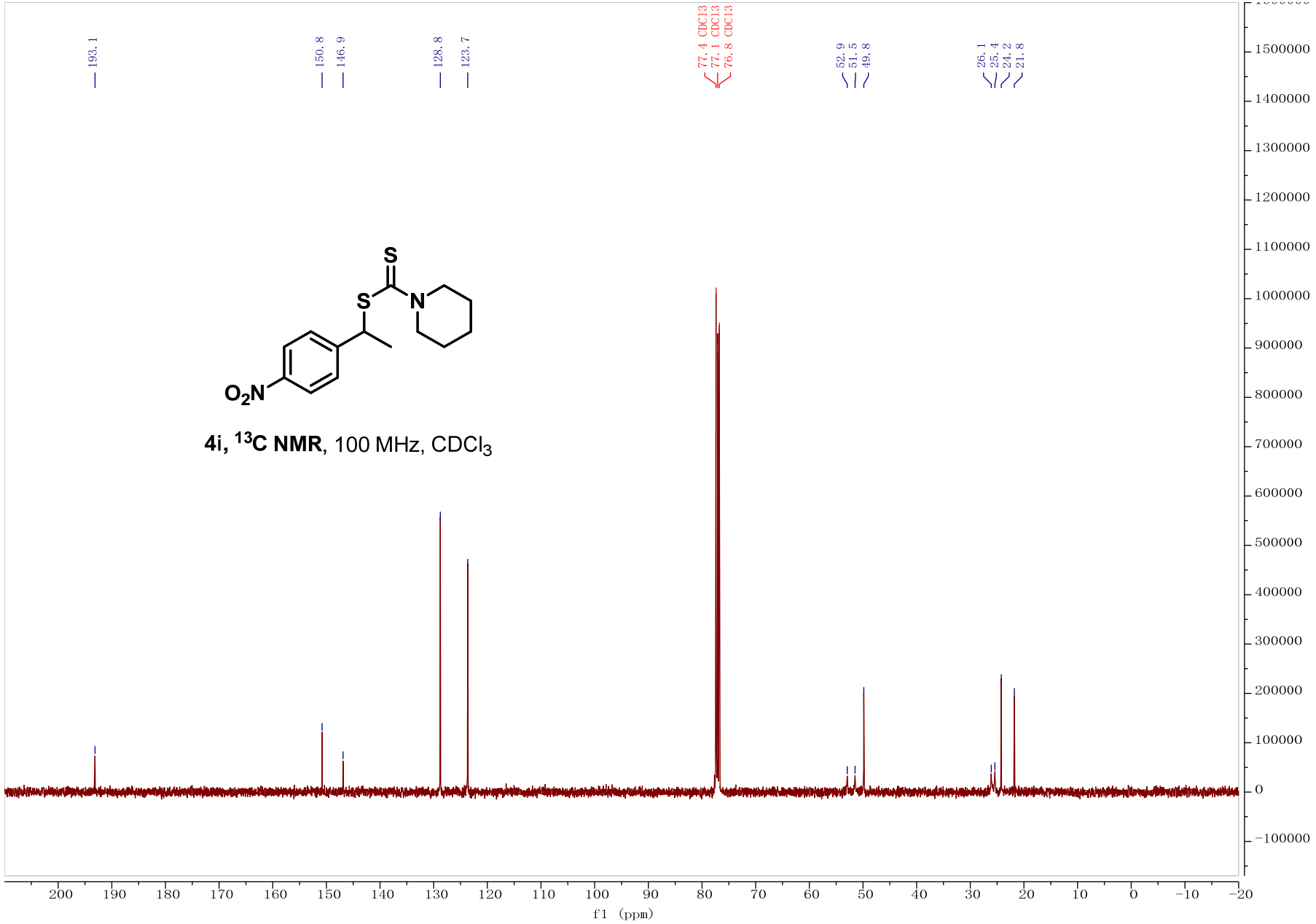
4g, ^{1}H NMR, 400 MHz, $CDCl_3$

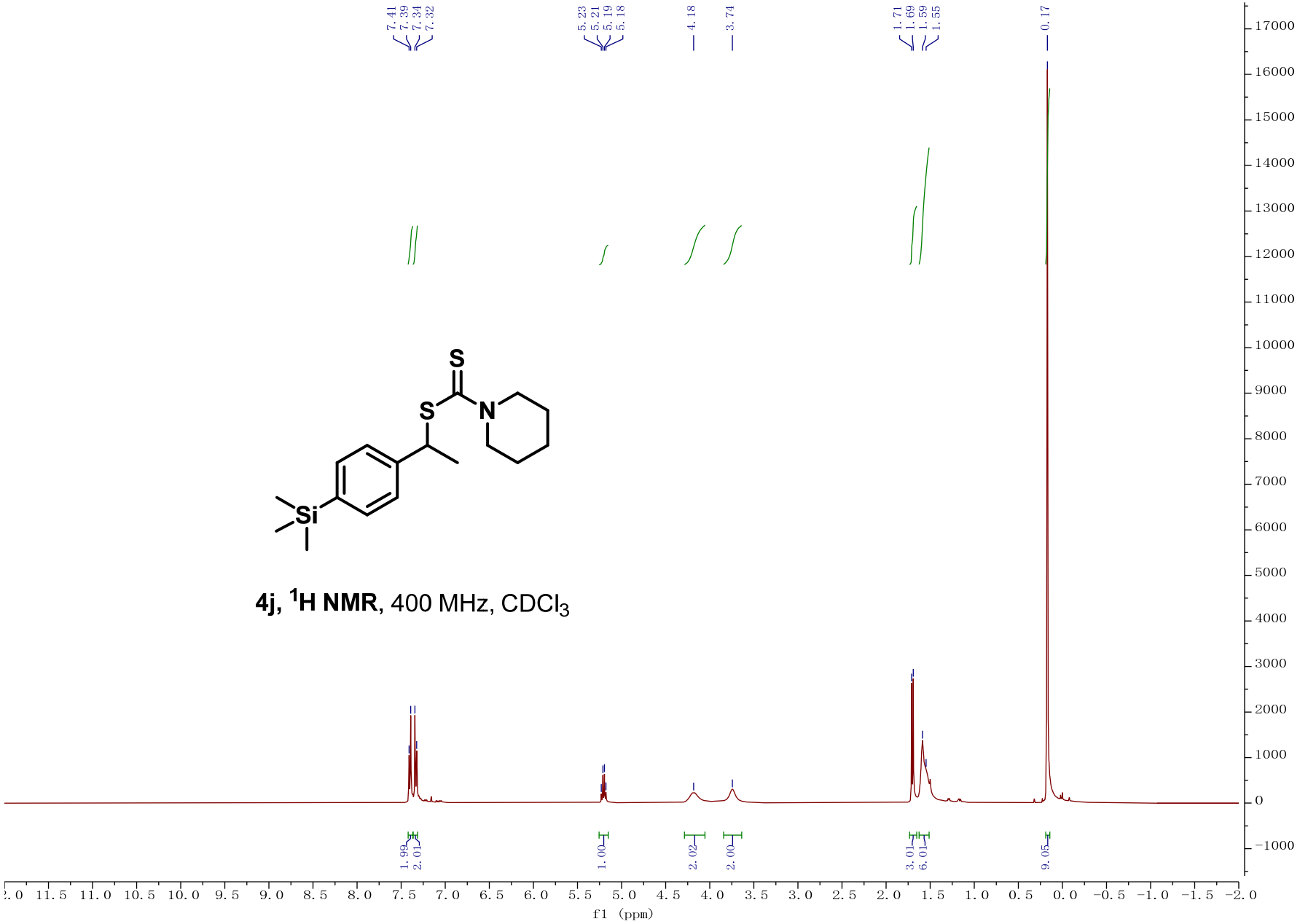

194.0
141.1
133.0
129.3
128.6
77.5 CDCl3
77.1 CDCl3
76.8 CDCl3
52.7
51.3
50.1
26.0
25.5
24.3
22.1
S
S
N
Cl
4g, 13C NMR, 100 MHz, CDCl3
f1 (ppm)


7.44
7.41
7.32
7.30
7.26 CDCl3
5.28
5.26
5.24
5.23
4.25
3.82
1.74
1.72
1.67
1.64
0.00
S
S
N
Br
4h, 1H NMR, 400 MHz, CDCl3
2.02
2.01
1.01
2.03
1.99
3.14
6.07
f1 (ppm)

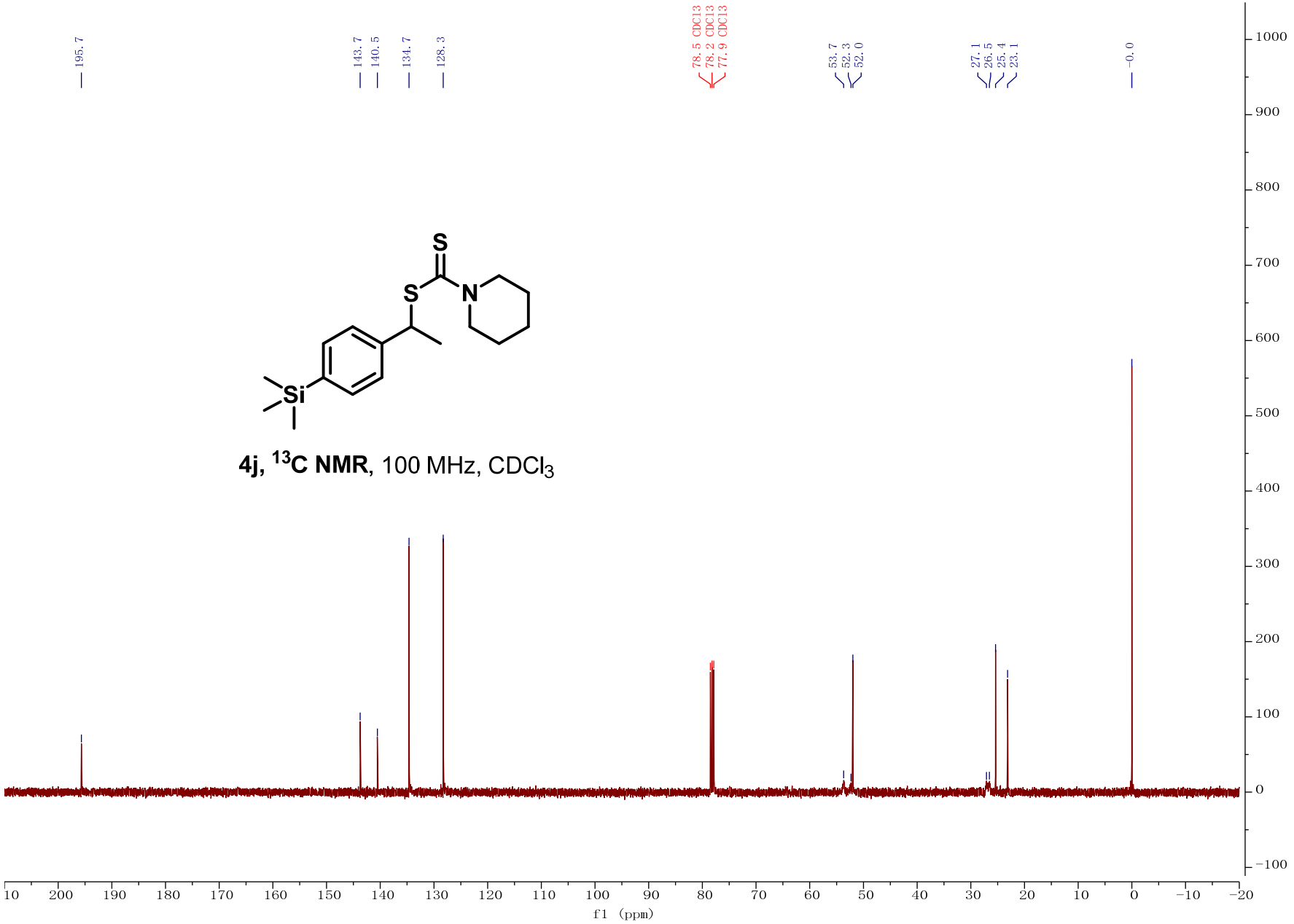

194.0
141.7
131.5
129.6
121.1
77.4 CDCl3
77.1 CDCl3
76.8 CDCl3
52.7
51.3
50.1
26.0
25.5
24.3
22.0
S
S
N
Br
4h, 13C NMR, 100 MHz, CDCl3
f1 (ppm)


8.18
8.16
7.63
7.60
7.27 CD
5.42
5.40
5.39
5.37
4.29
4.20
3.87
3.82
1.77
1.75
1.69
-0.00
S
S
N
O2N
4i, 1H NMR, 400 MHz, CDCl3
2.00
2.01
1.00
2.02
2.03
3.03
6.00
f1 (ppm)

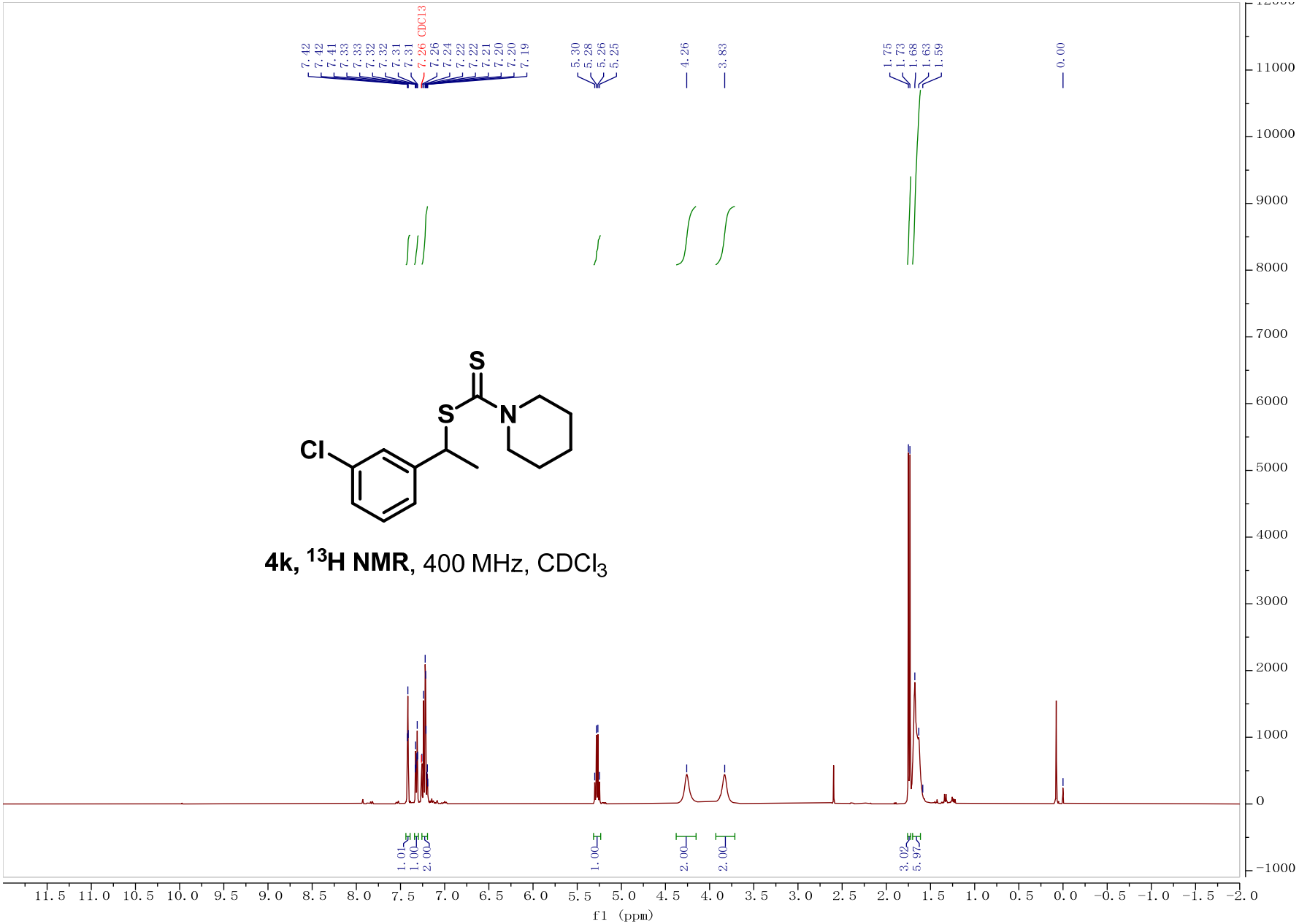

193.1
150.8
146.9
128.8
123.7
77.4 CDCl3
77.1 CDCl3
76.8 CDCl3
52.9
51.5
49.8
26.1
25.4
24.2
21.8
S
S
N
O2N
4i, 13C NMR, 100 MHz, CDCl3
f1 (ppm)



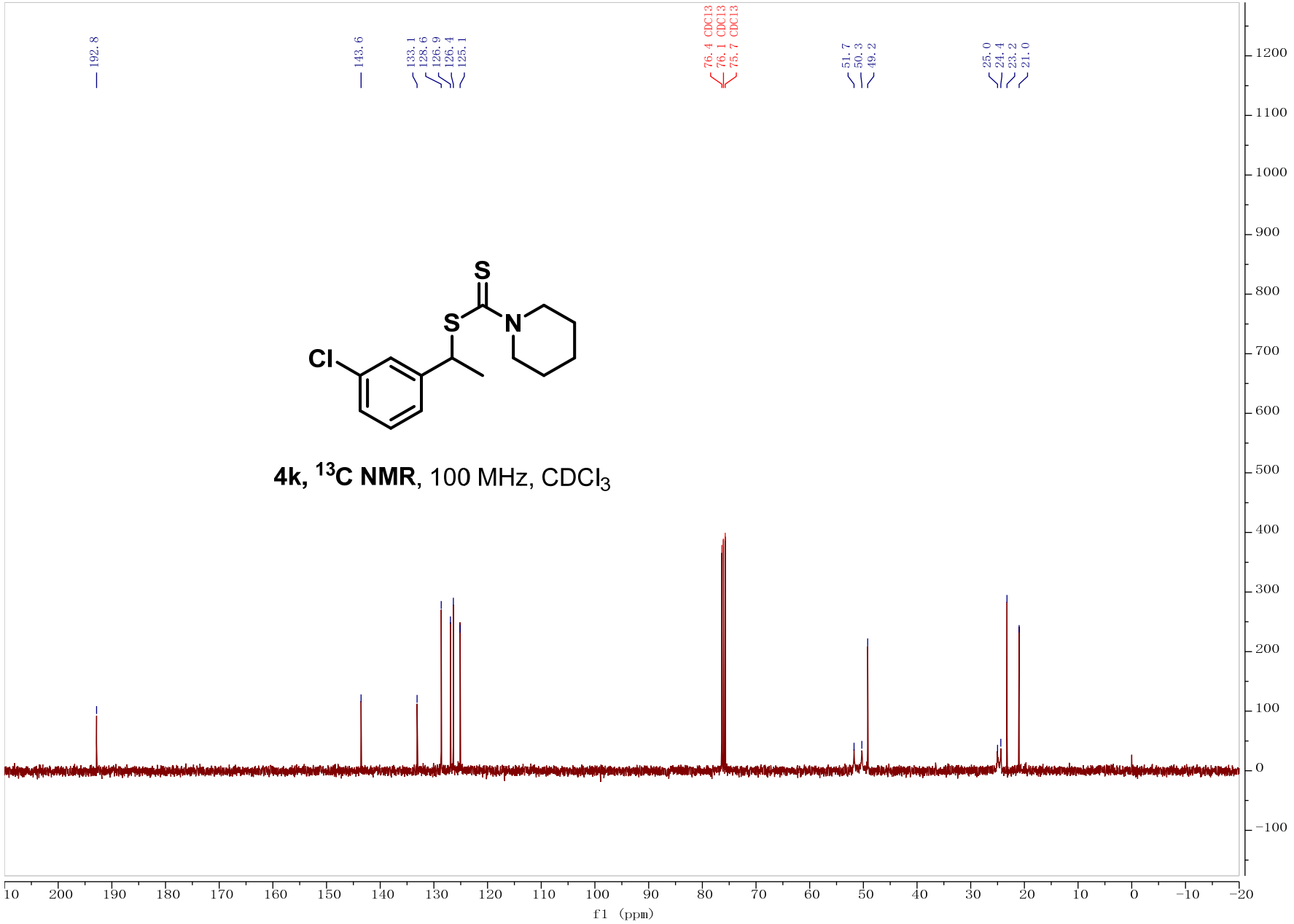
4j, ^{1}H NMR, 400 MHz, $CDCl_3$



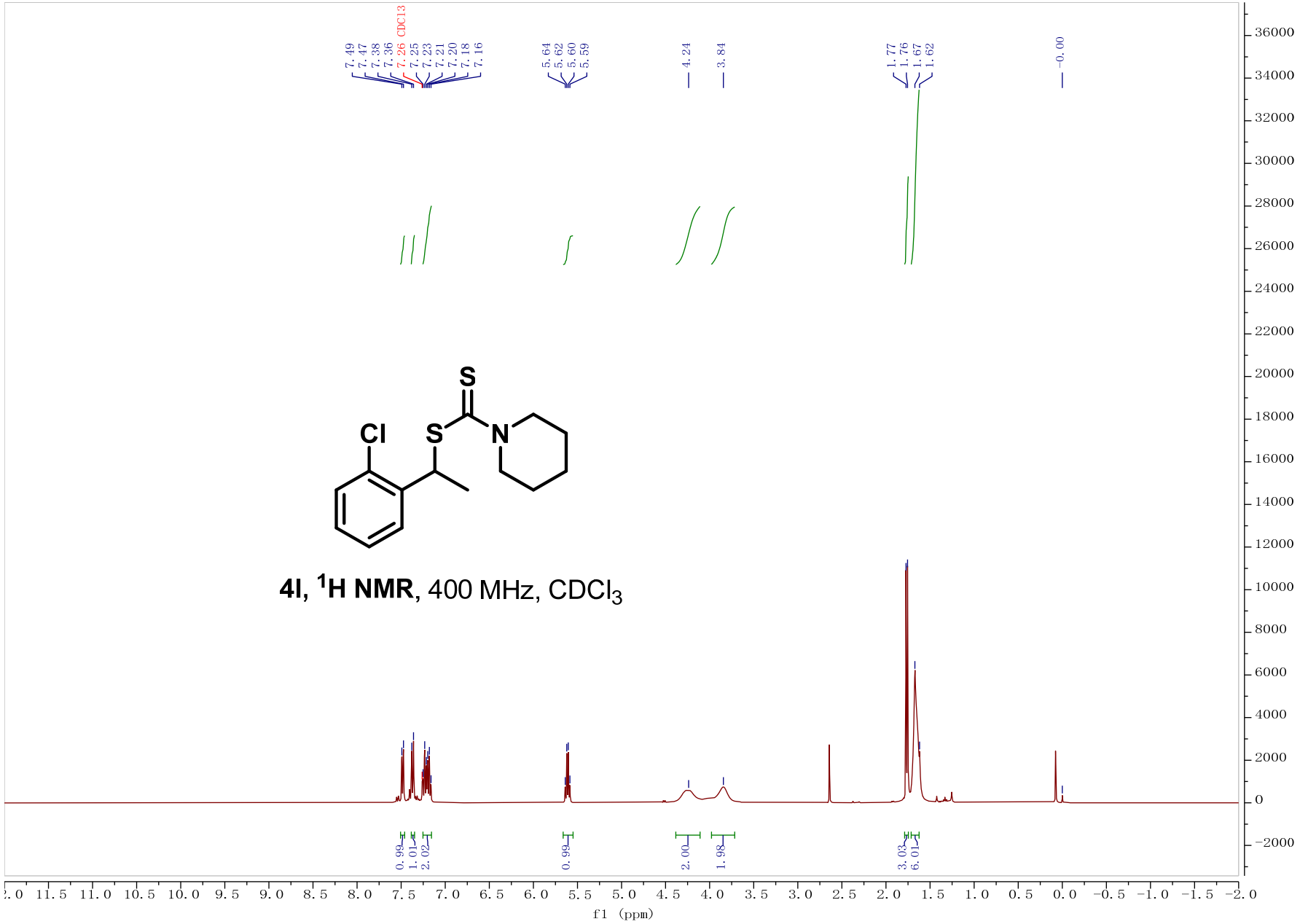
4j, ^{13}C NMR, 100 MHz, $CDCl_3$

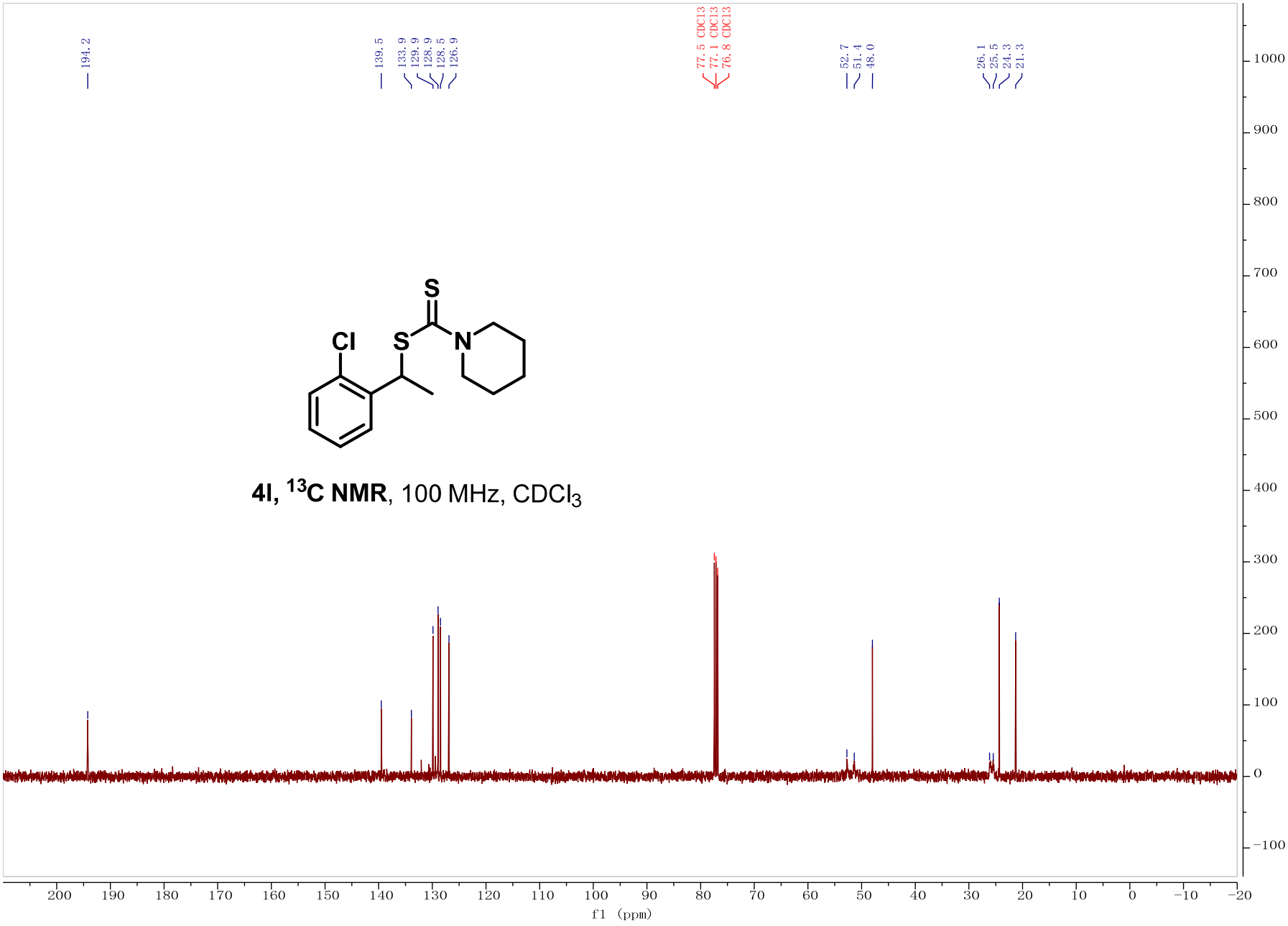


4k, ^{13}H NMR, 400 MHz, $CDCl_3$

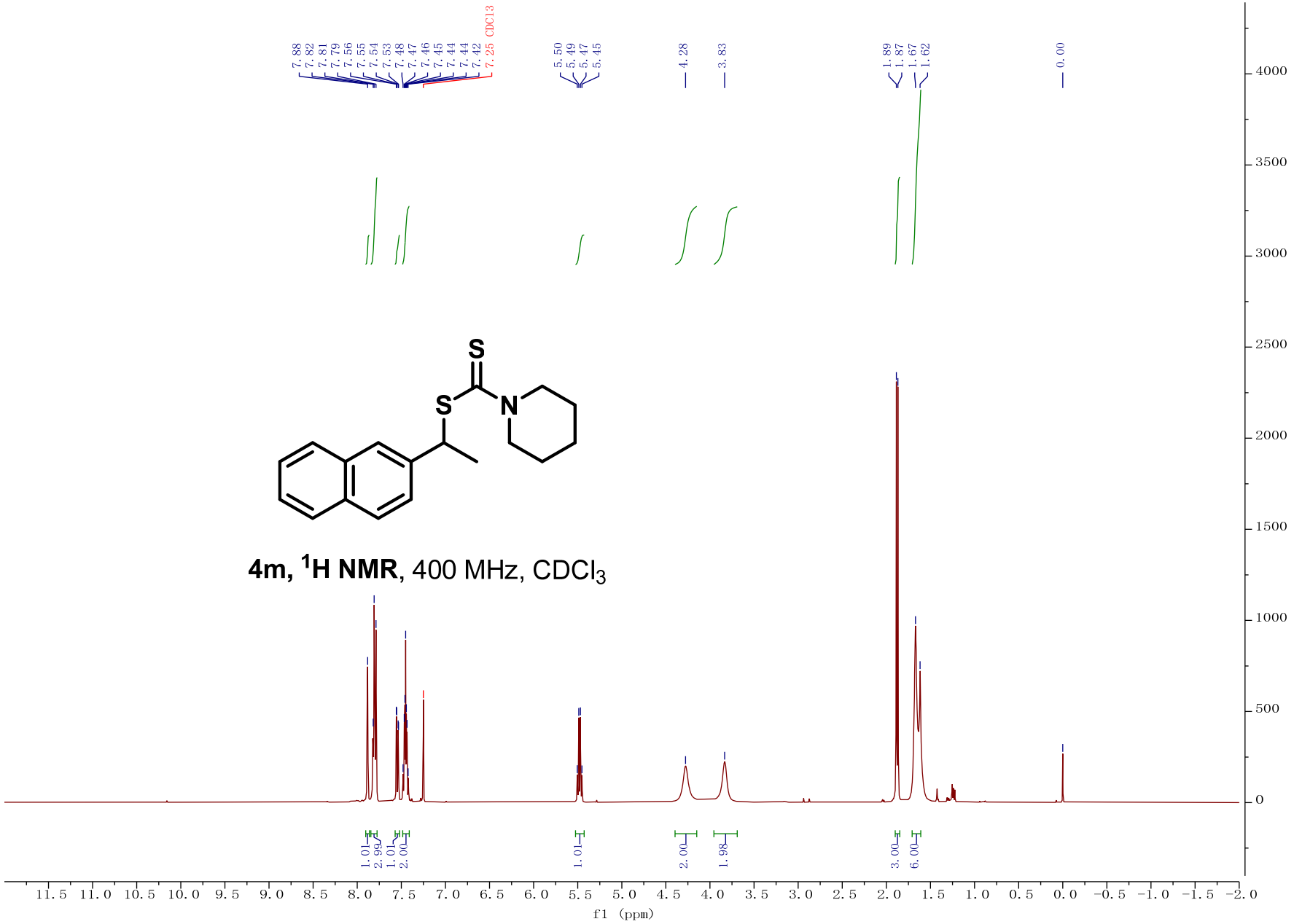


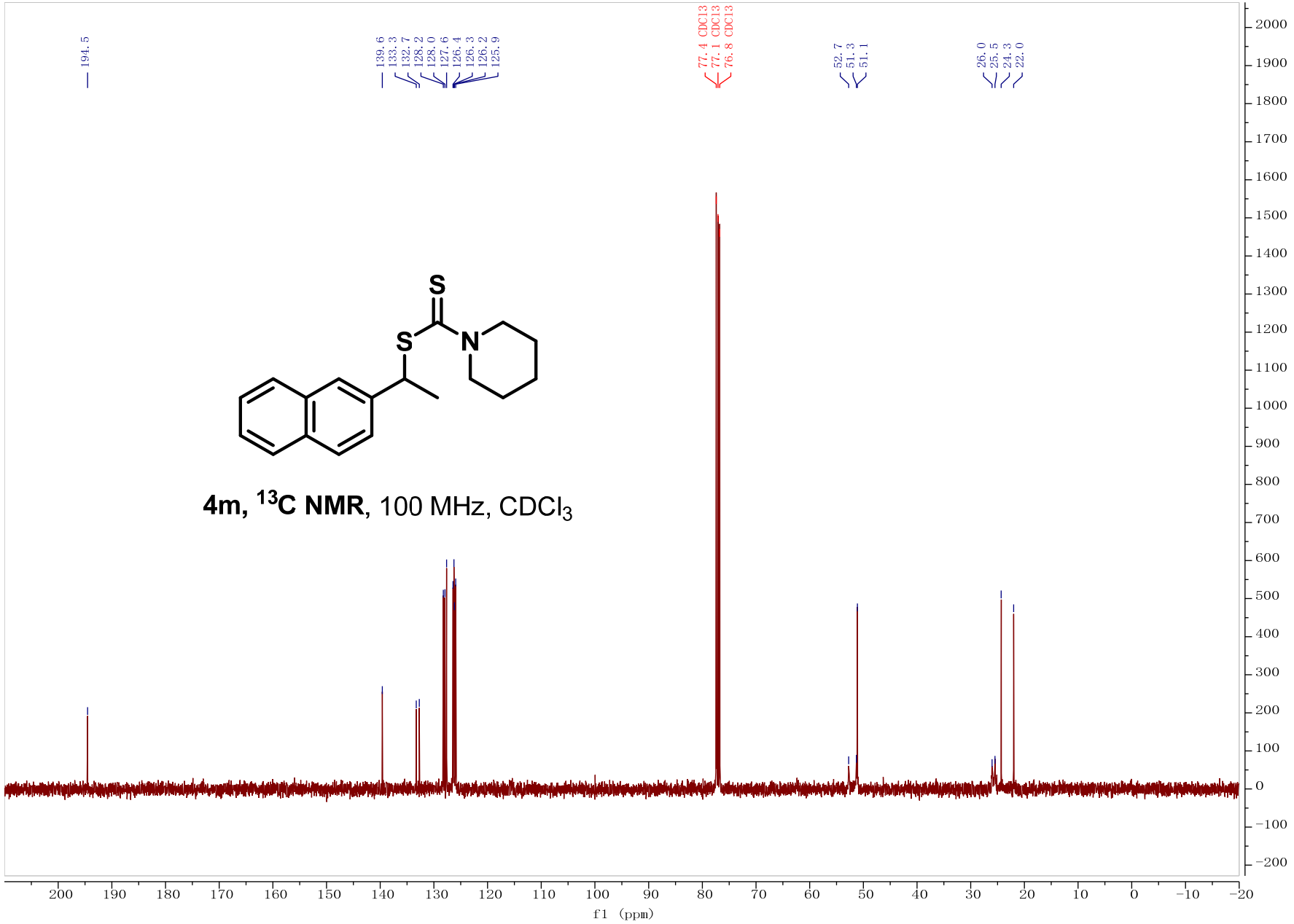
4k, ^{13}C NMR, 100 MHz, $CDCl_3$

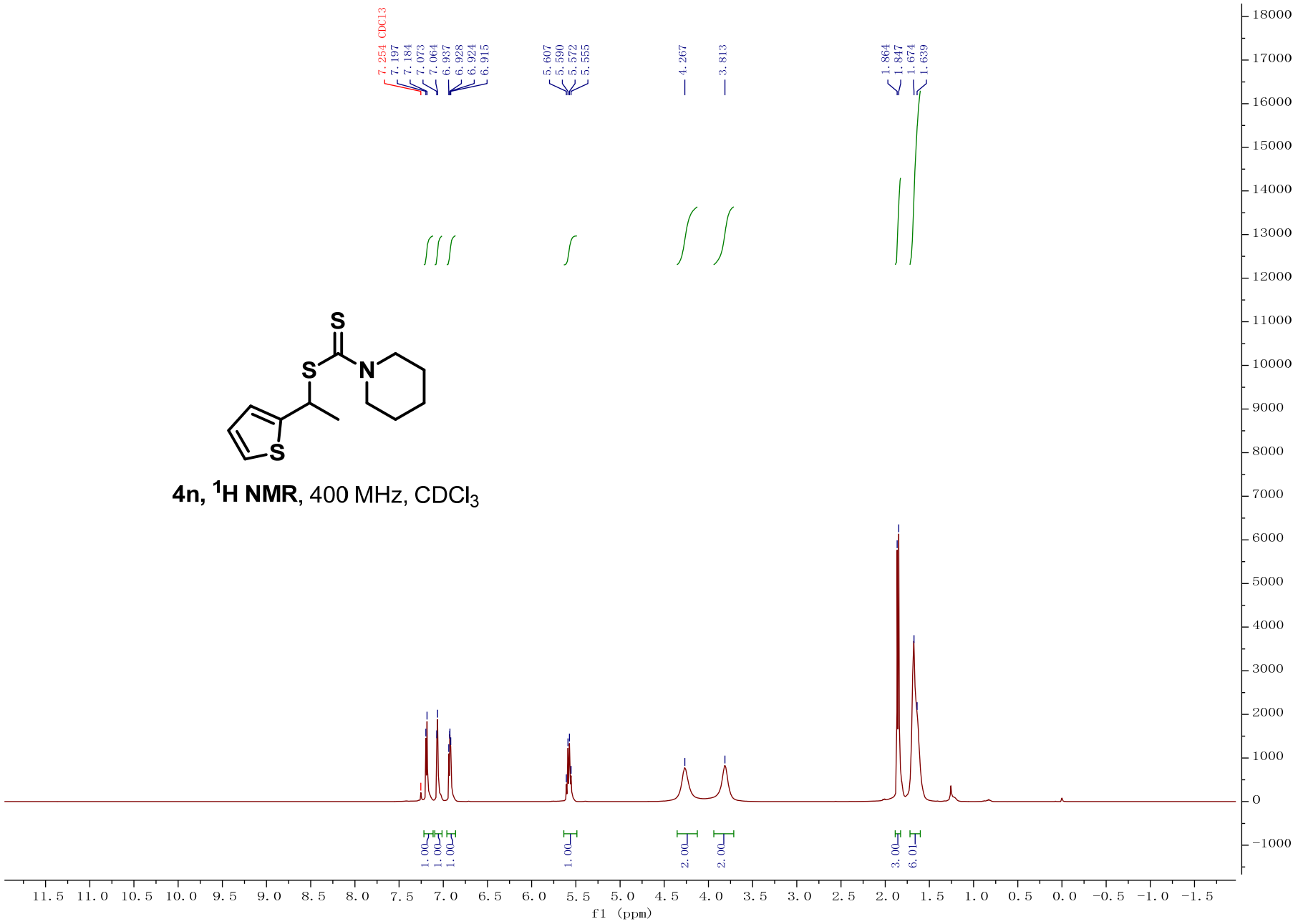

7.49
7.47
7.38
7.36
7.26 CDCl3
7.25
7.23
7.21
7.20
7.18
7.16
5.64
5.62
5.60
5.59
4.24
3.84
1.77
1.76
1.67
1.62
0.00
Cl
S
S
N
4I, 1H NMR, 400 MHz, CDCl3
0.99
1.01
2.02
0.99
2.00
1.98
3.03
6.01
f1 (ppm)

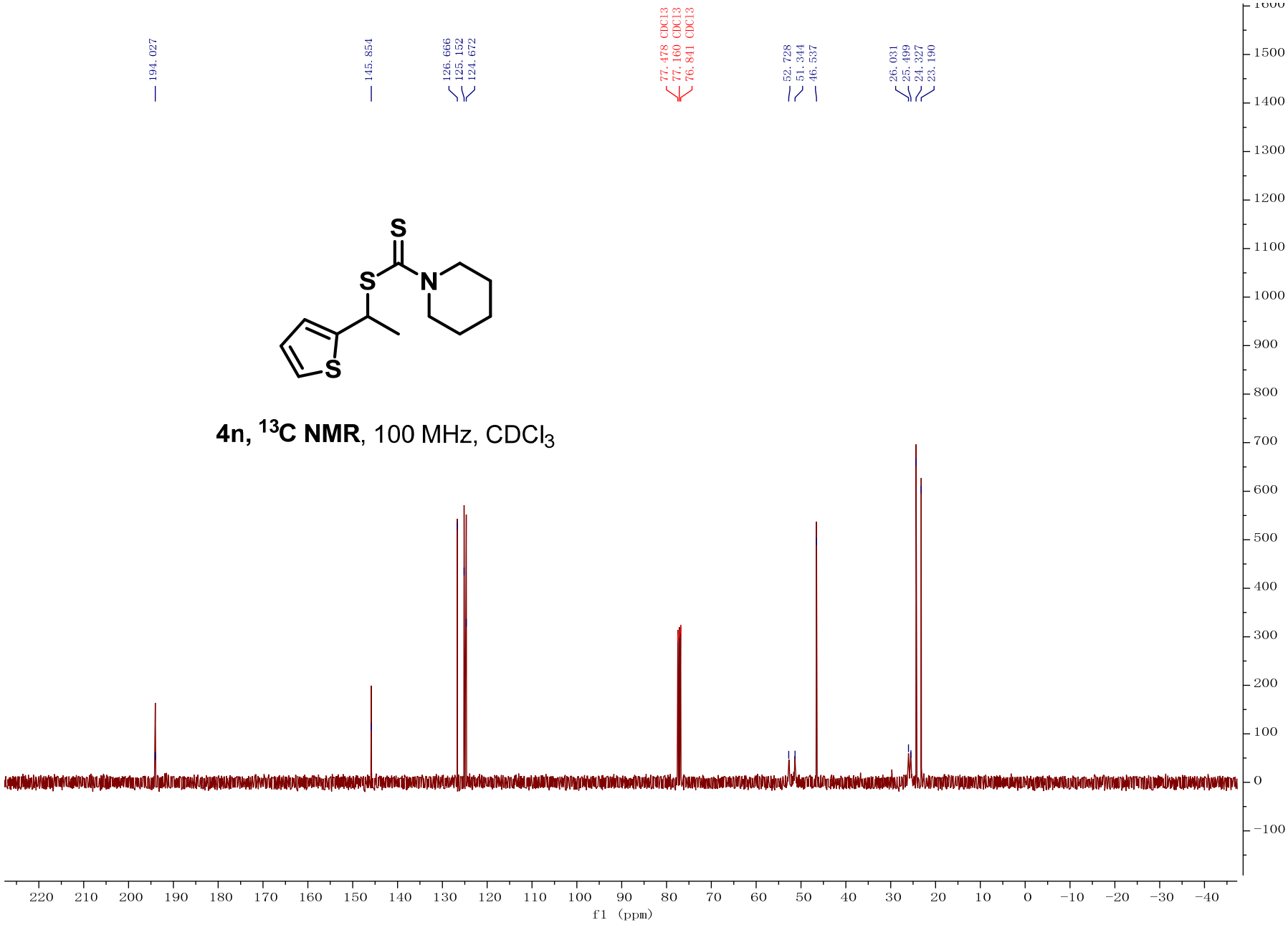


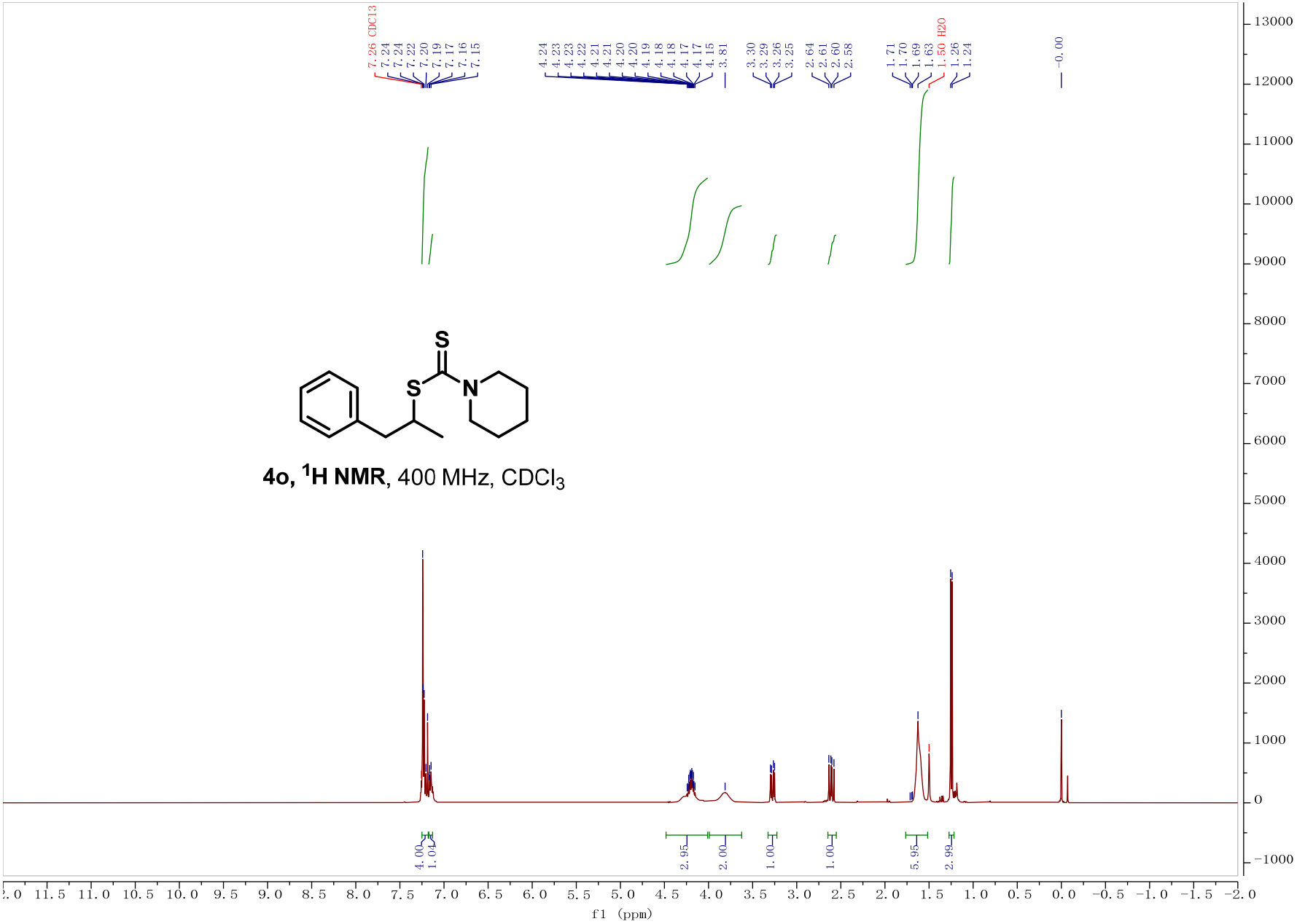
4l, ^{13}C NMR, 100 MHz, $CDCl_3$


7.88
7.82
7.81
7.79
7.56
7.55
7.54
7.53
7.48
7.47
7.46
7.45
7.44
7.44
7.42
7.25
CDCl3
5.50
5.49
5.47
5.45
4.28
3.83
1.89
1.87
1.67
1.62
0.00
S
S
N
4m, 1H NMR, 400 MHz, CDCl3
1.01
2.99
1.01
2.00
1.01
2.00
1.98
3.00
6.00
f1 (ppm)

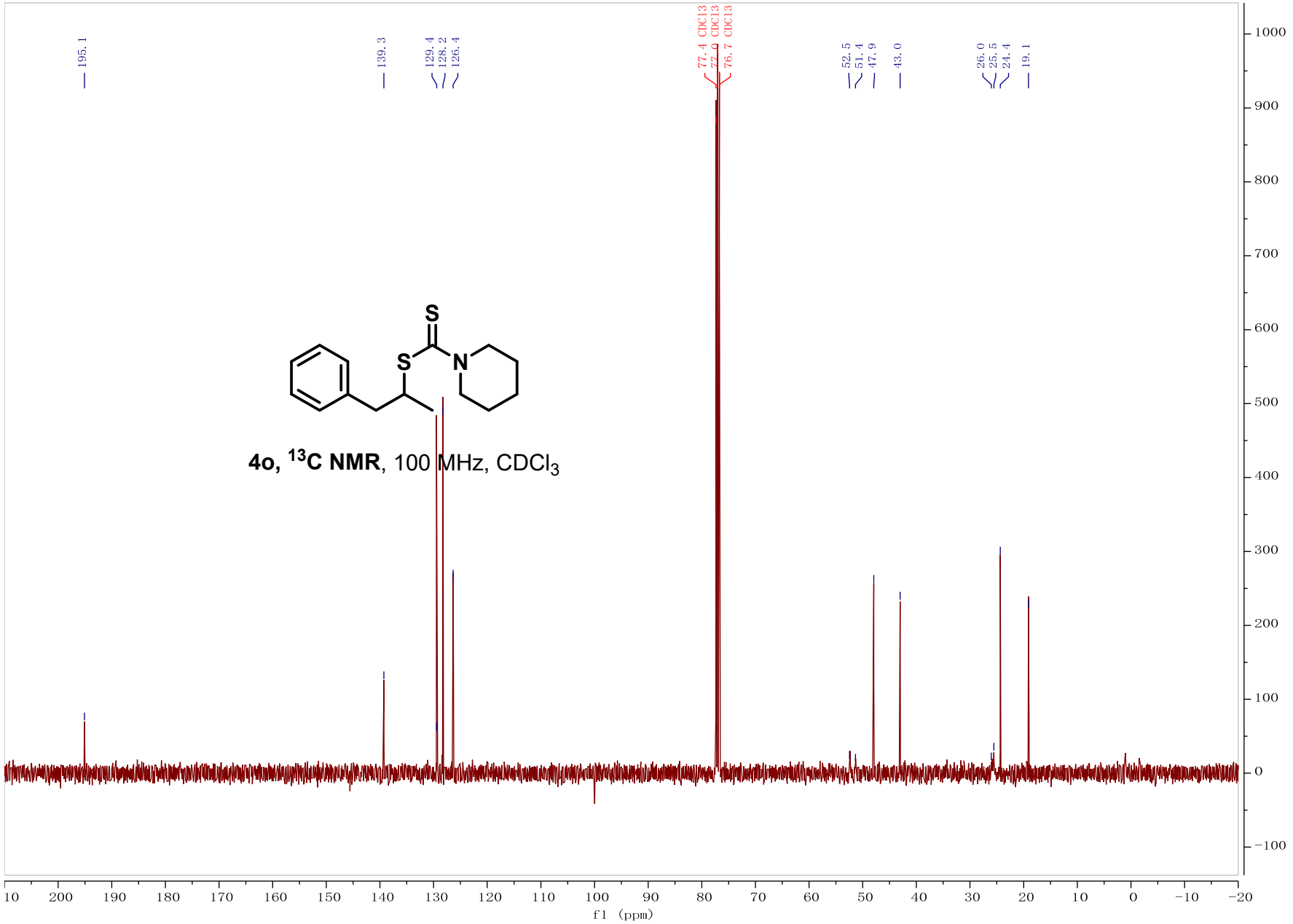

194.5
139.6
133.3
132.7
128.2
128.0
127.6
126.4
126.3
126.2
125.9
77.4 CDCl3
77.1 CDCl3
76.8 CDCl3
52.7
51.3
51.1
26.0
25.5
24.3
22.0
S
S
N
4m, 13C NMR, 100 MHz, CDCl3
f1 (ppm)


7.254 CDCl3
7.197
7.184
7.073
7.064
6.937
6.928
6.924
6.915
5.607
5.590
5.572
5.555
4.267
3.813
1.864
1.847
1.674
1.639
S
S
N
S
4n, 1H NMR, 400 MHz, CDCl3
1.00
1.00
1.00
1.00
2.00
2.00
3.00
6.01
f1 (ppm)

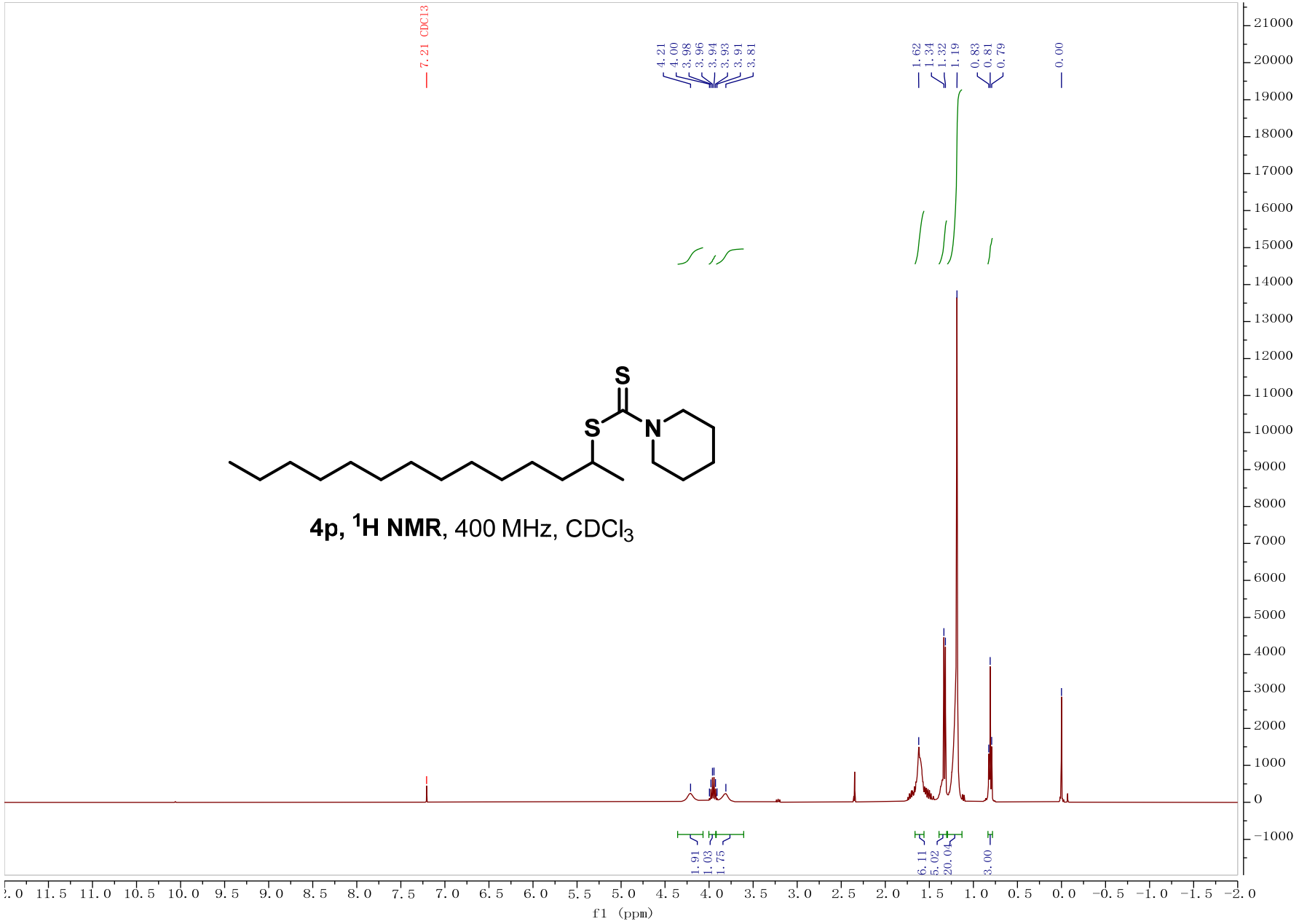

194.027
145.854
126.666
125.152
124.672
77.478 CDCl3
77.160 CDCl3
76.841 CDCl3
52.728
51.344
46.537
26.031
25.499
24.327
23.190
S
S
N
S
4n, 13C NMR, 100 MHz, CDCl3
f1 (ppm)



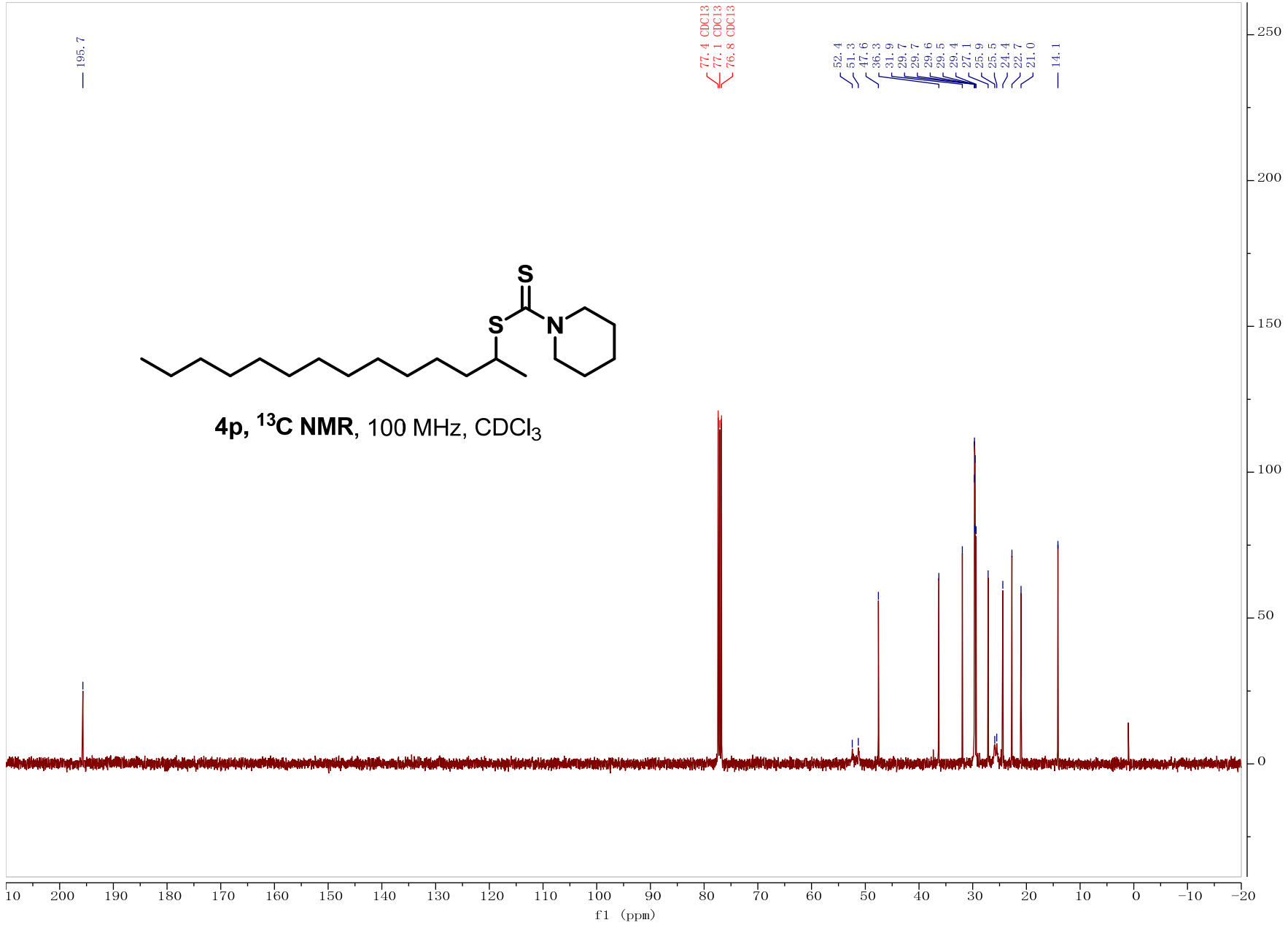
4o, ^{1}H NMR, 400 MHz, $CDCl_3$

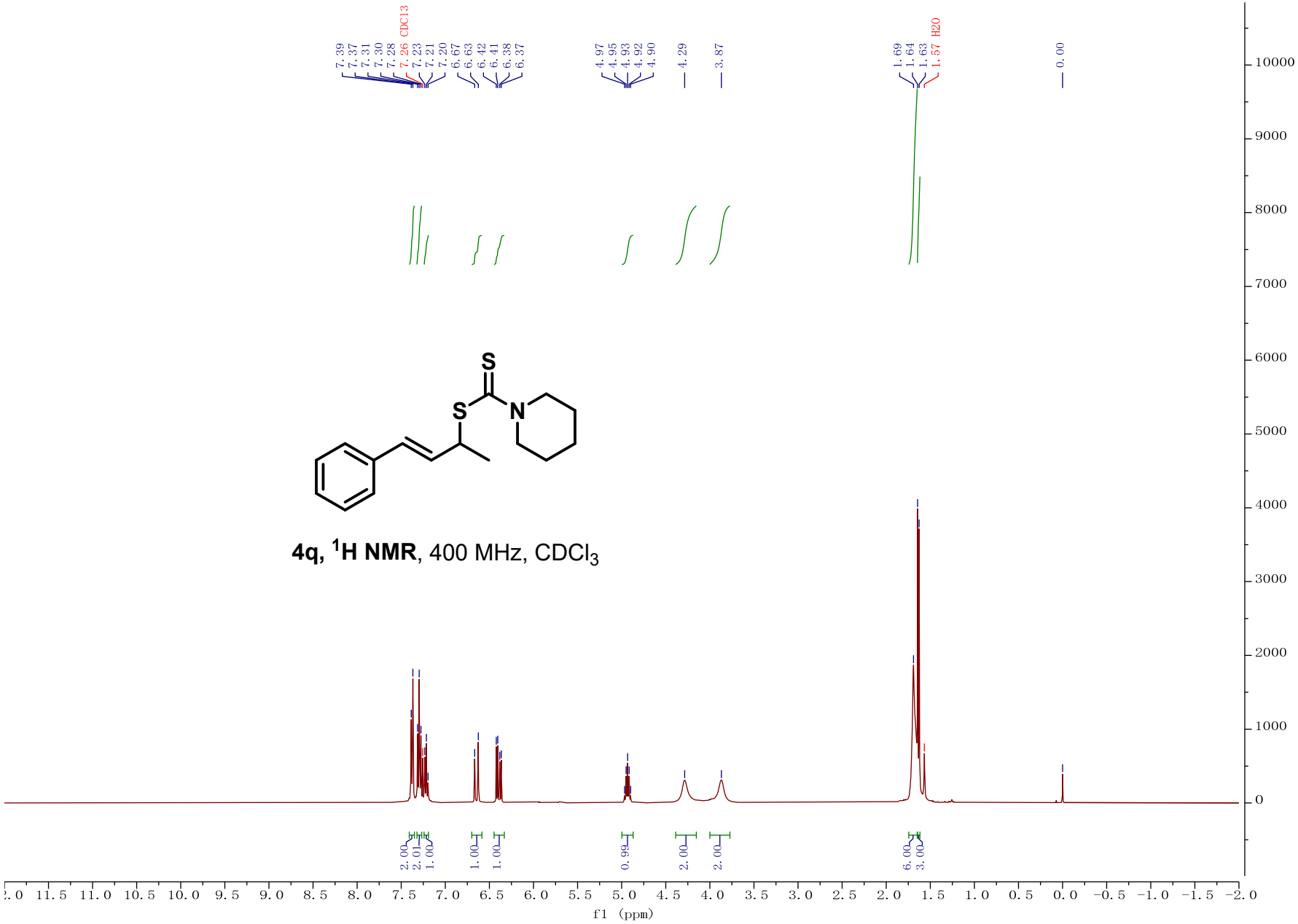


4o, ^{13}C NMR, 100 MHz, $CDCl_3$

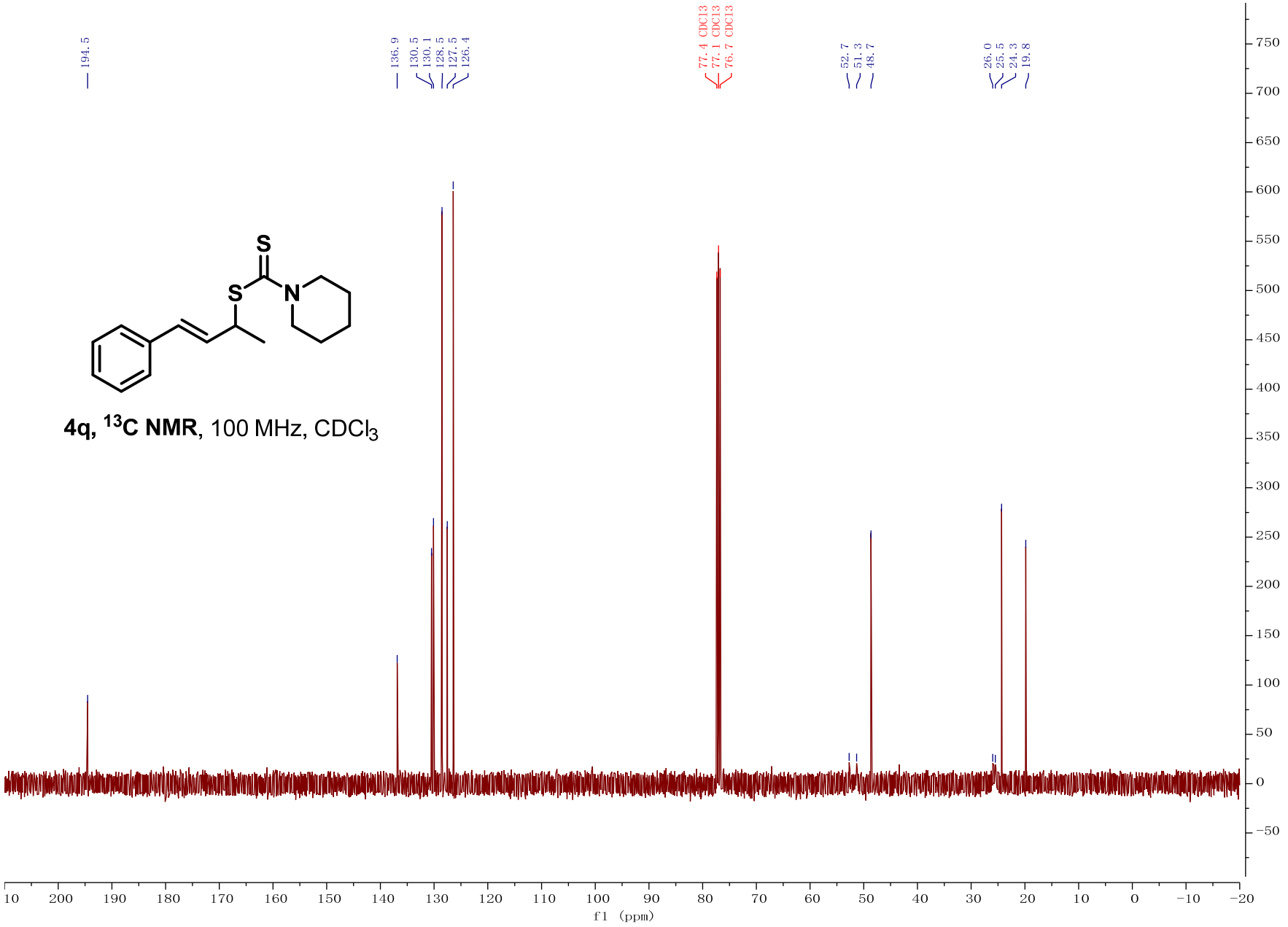


4p, ^{1}H NMR, 400 MHz, $CDCl_3$

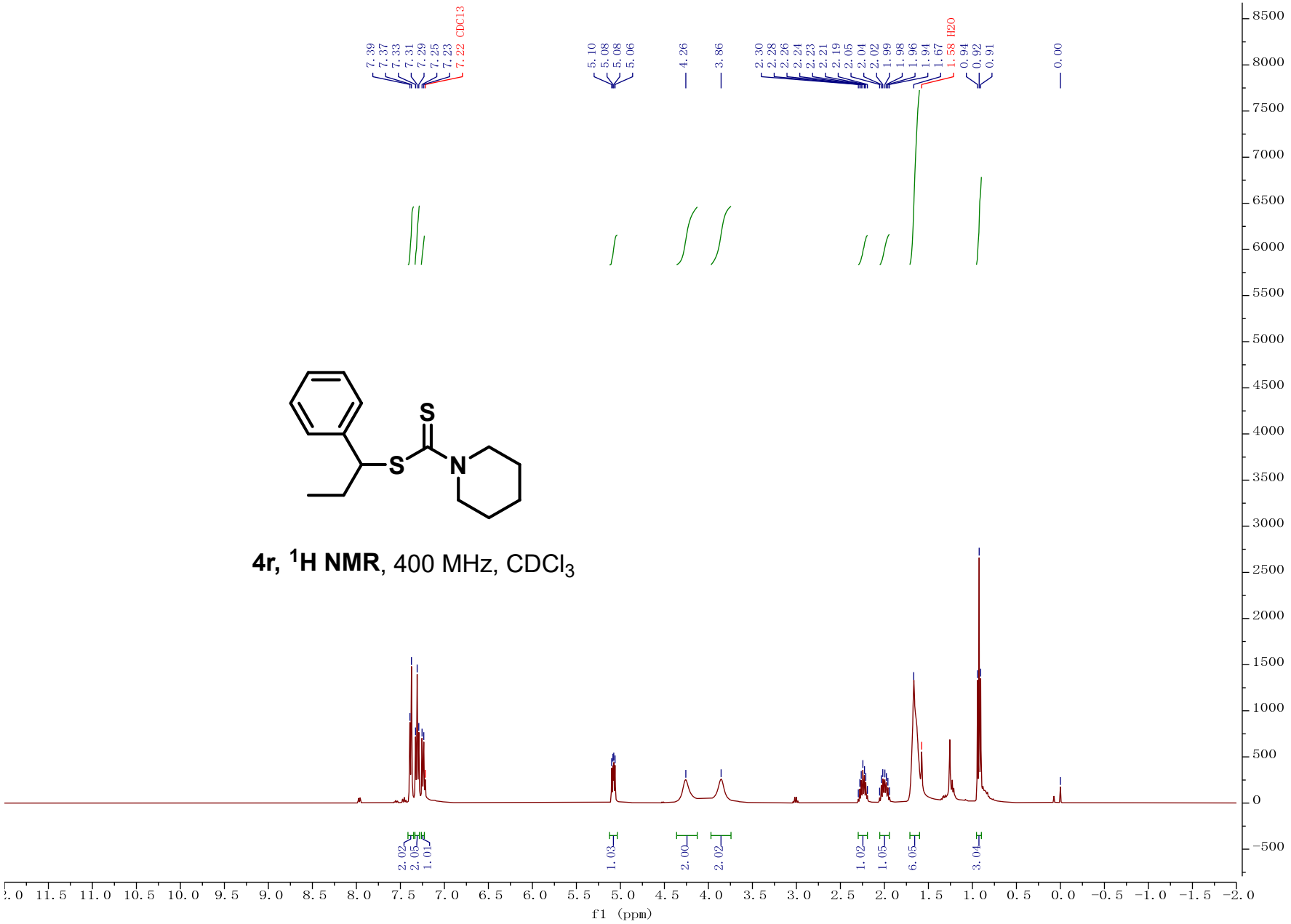

195.7
77.4 CDCl3
77.1 CDCl3
76.8 CDCl3
52.4
51.3
47.6
36.3
31.9
29.7
29.7
29.6
29.5
29.4
27.1
25.9
25.5
24.4
22.7
21.0
14.1
S
S
N
4p, 13C NMR, 100 MHz, CDCl3
250
200
150
100
50
0
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)



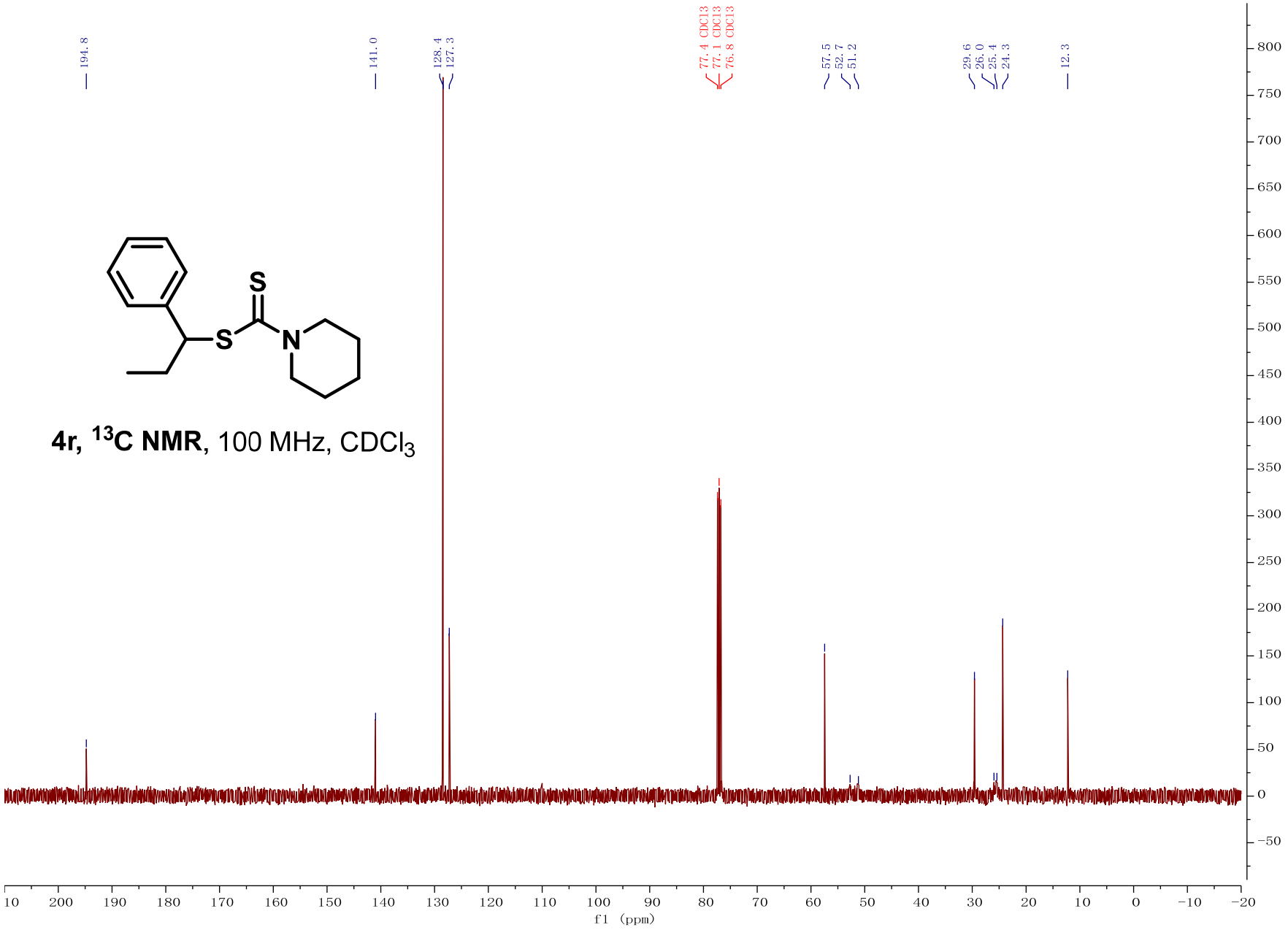
4q, ^{1}H NMR, 400 MHz, $CDCl_3$



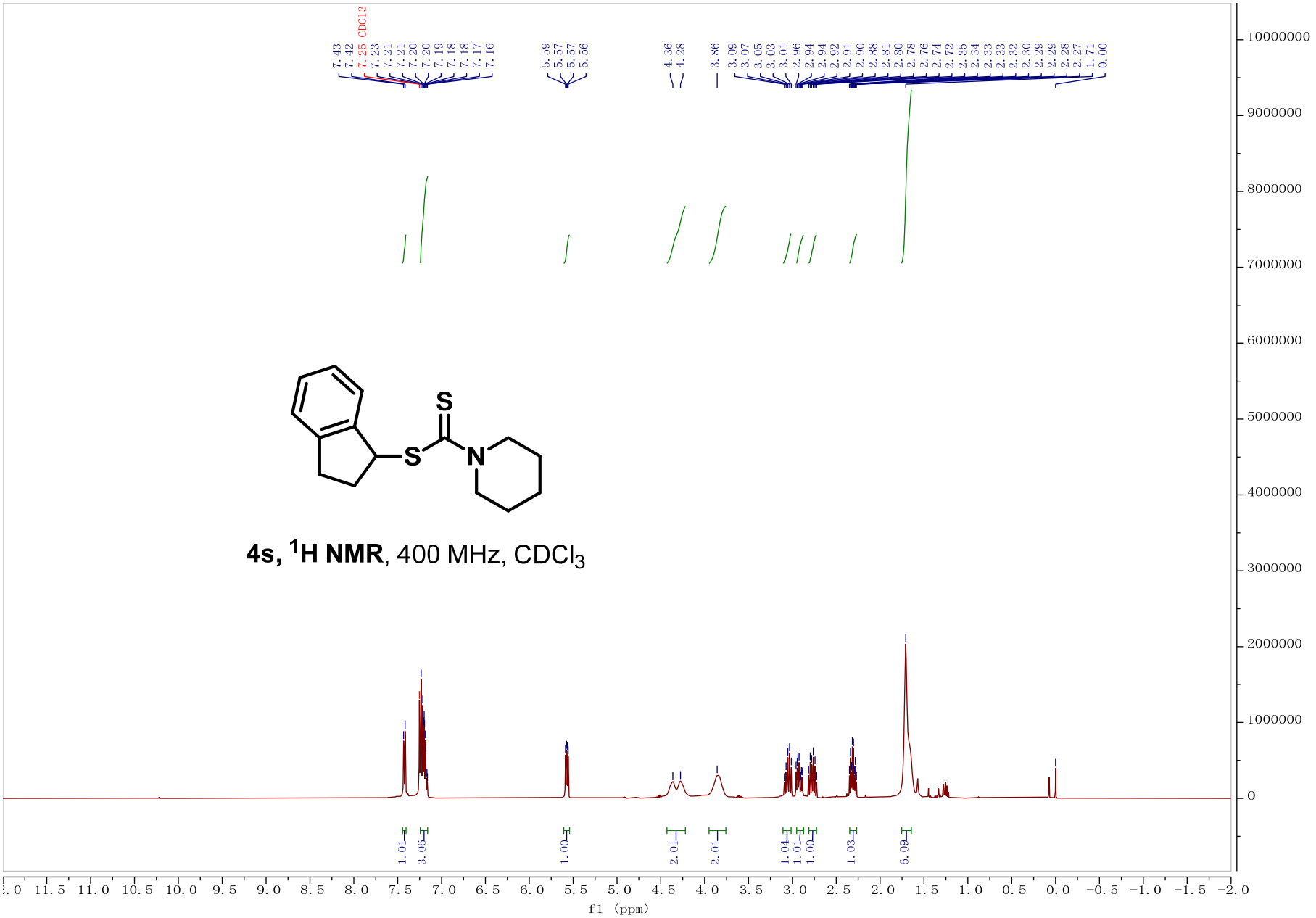
4q, ^{13}C NMR, 100 MHz, $CDCl_3$



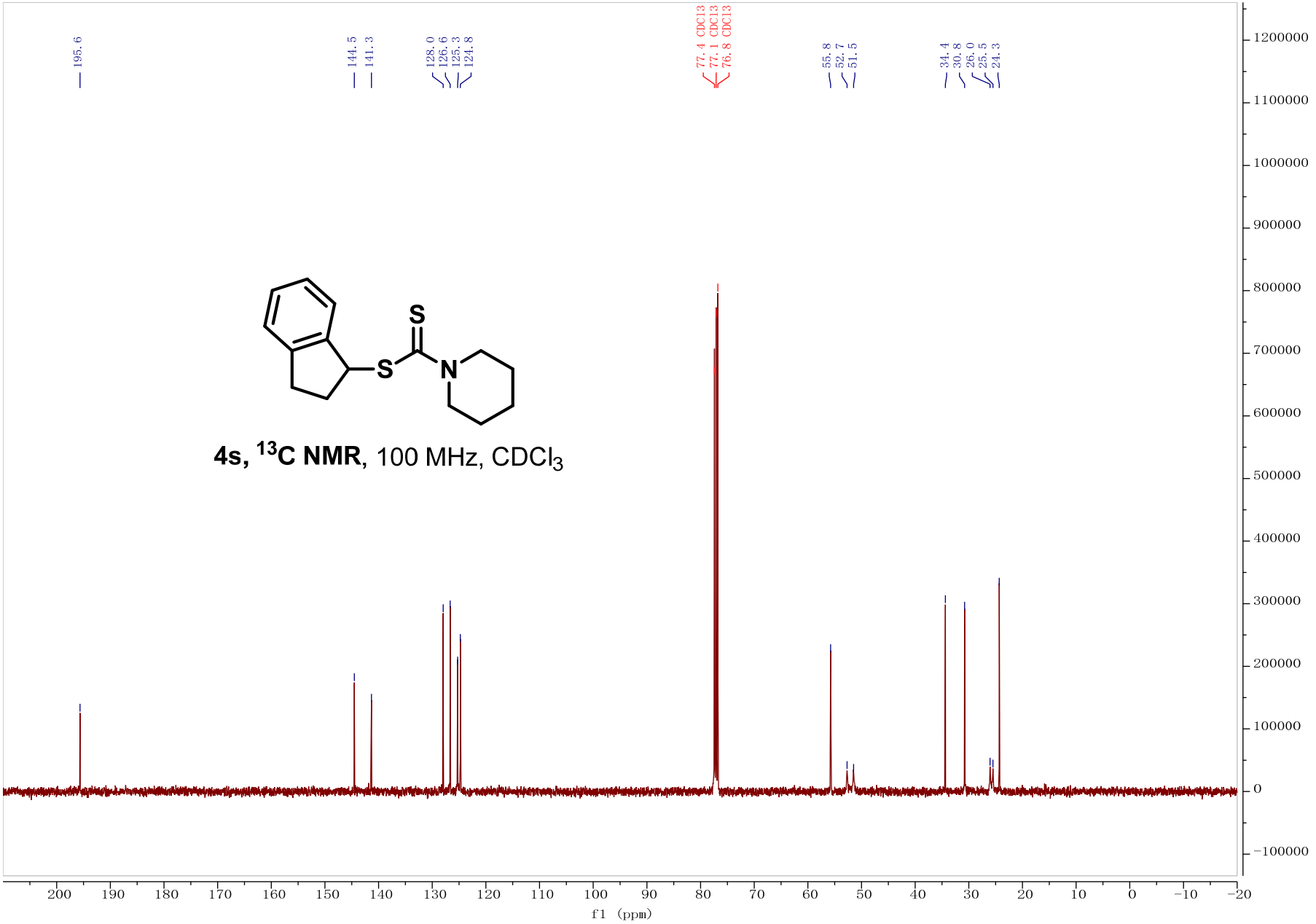
4r, ^{1}H NMR, 400 MHz, $CDCl_3$

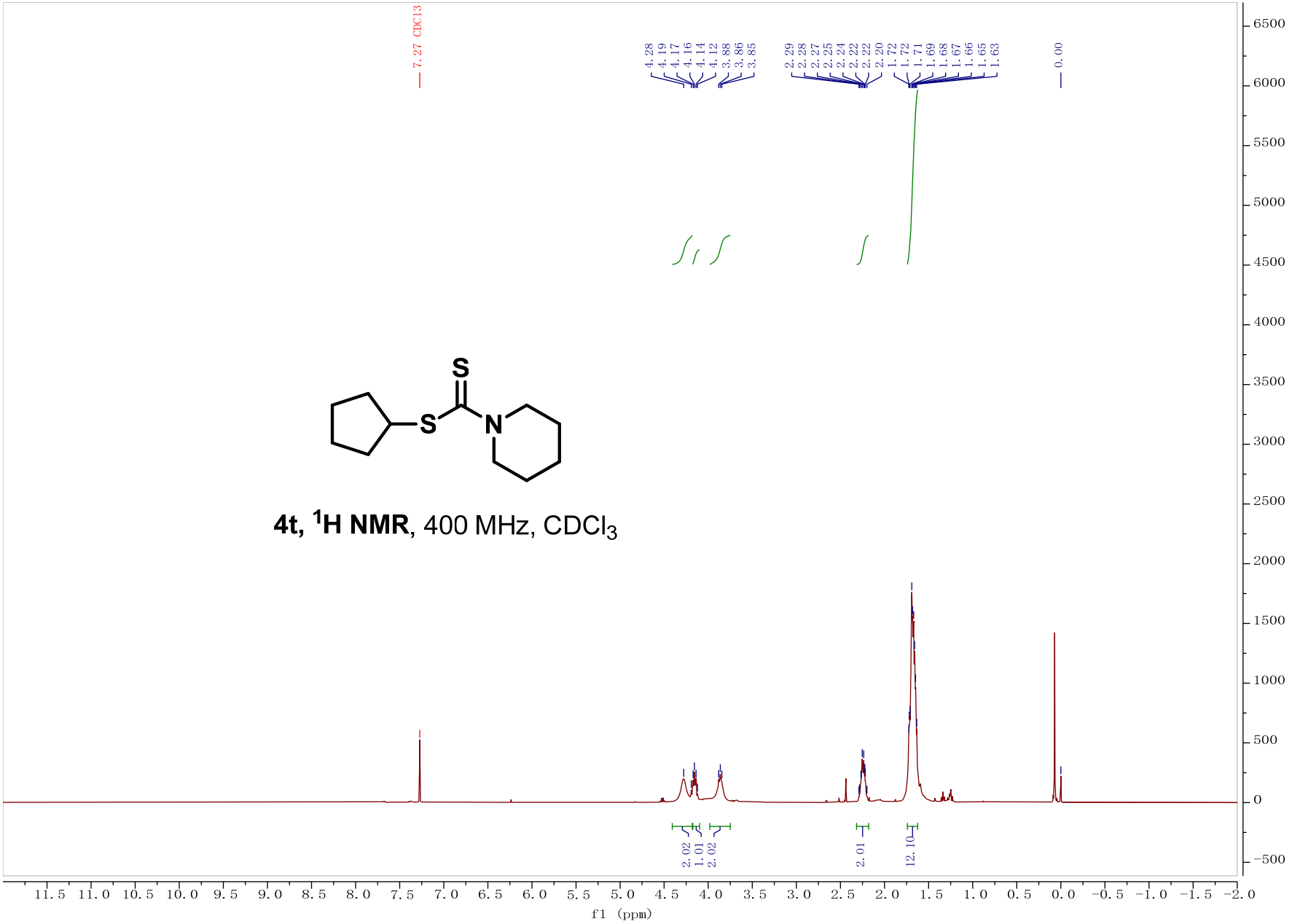


4r, ^{13}C NMR, 100 MHz, $CDCl_3$

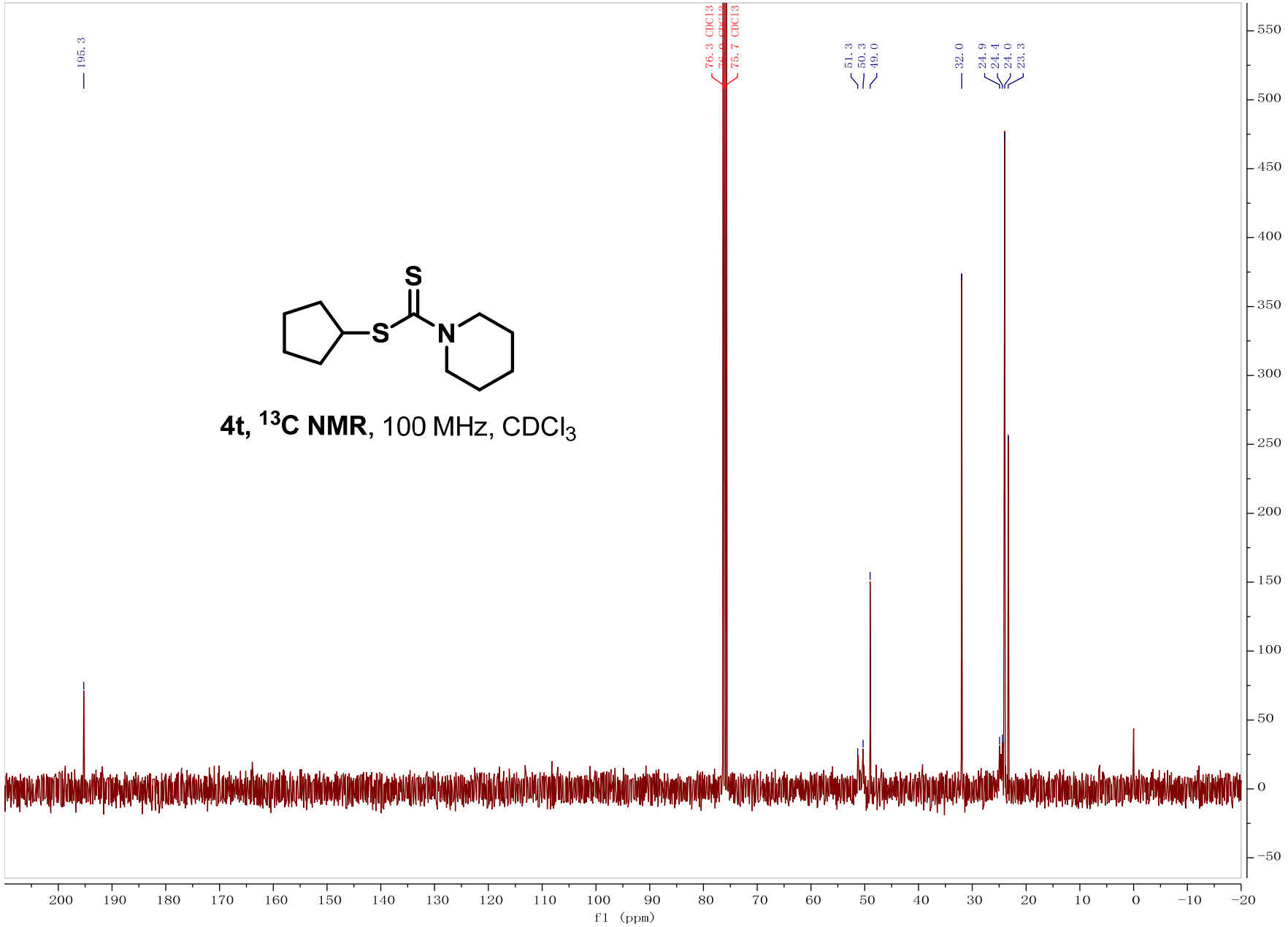


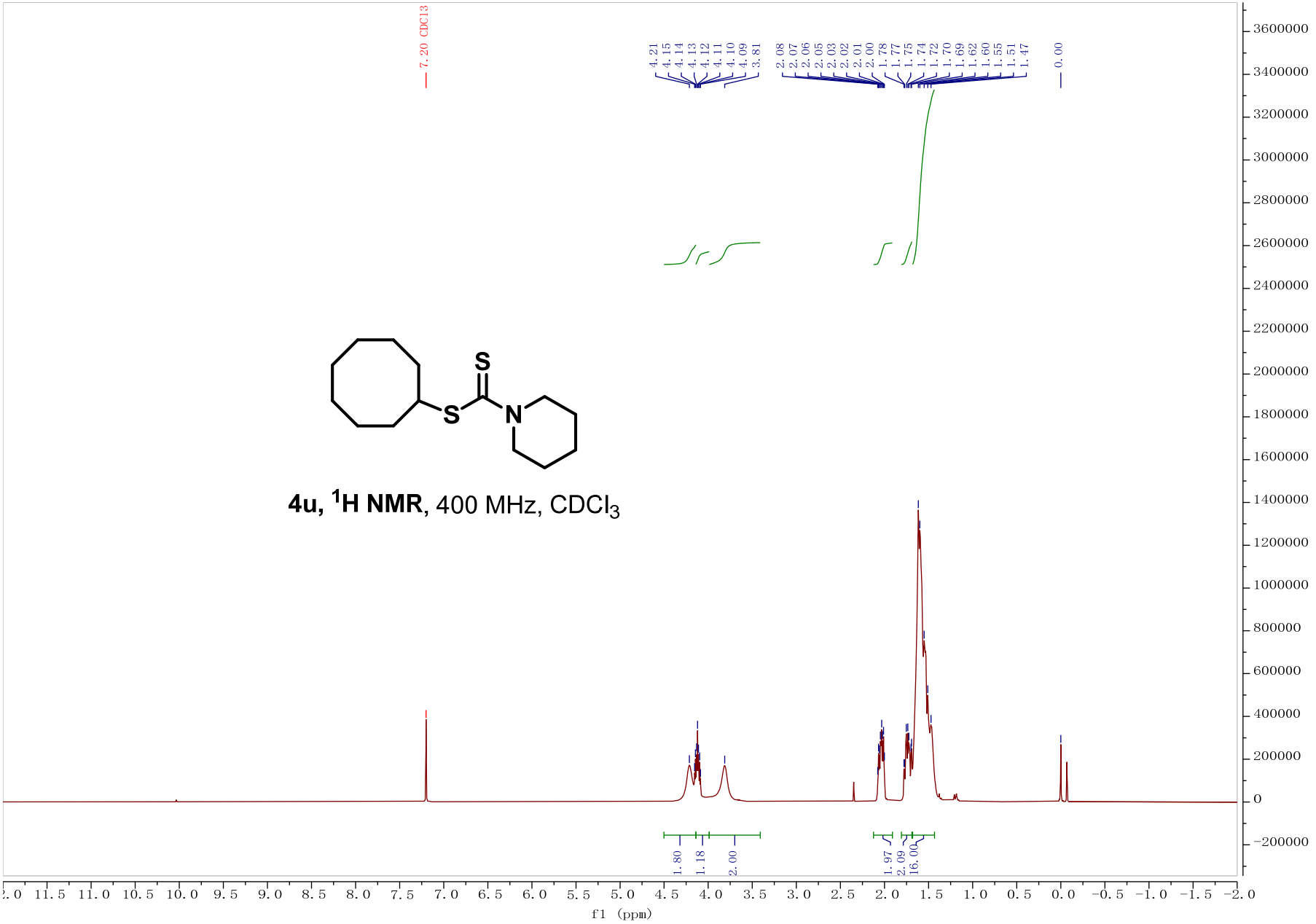
4s, ^{1}H NMR, 400 MHz, $CDCl_3$

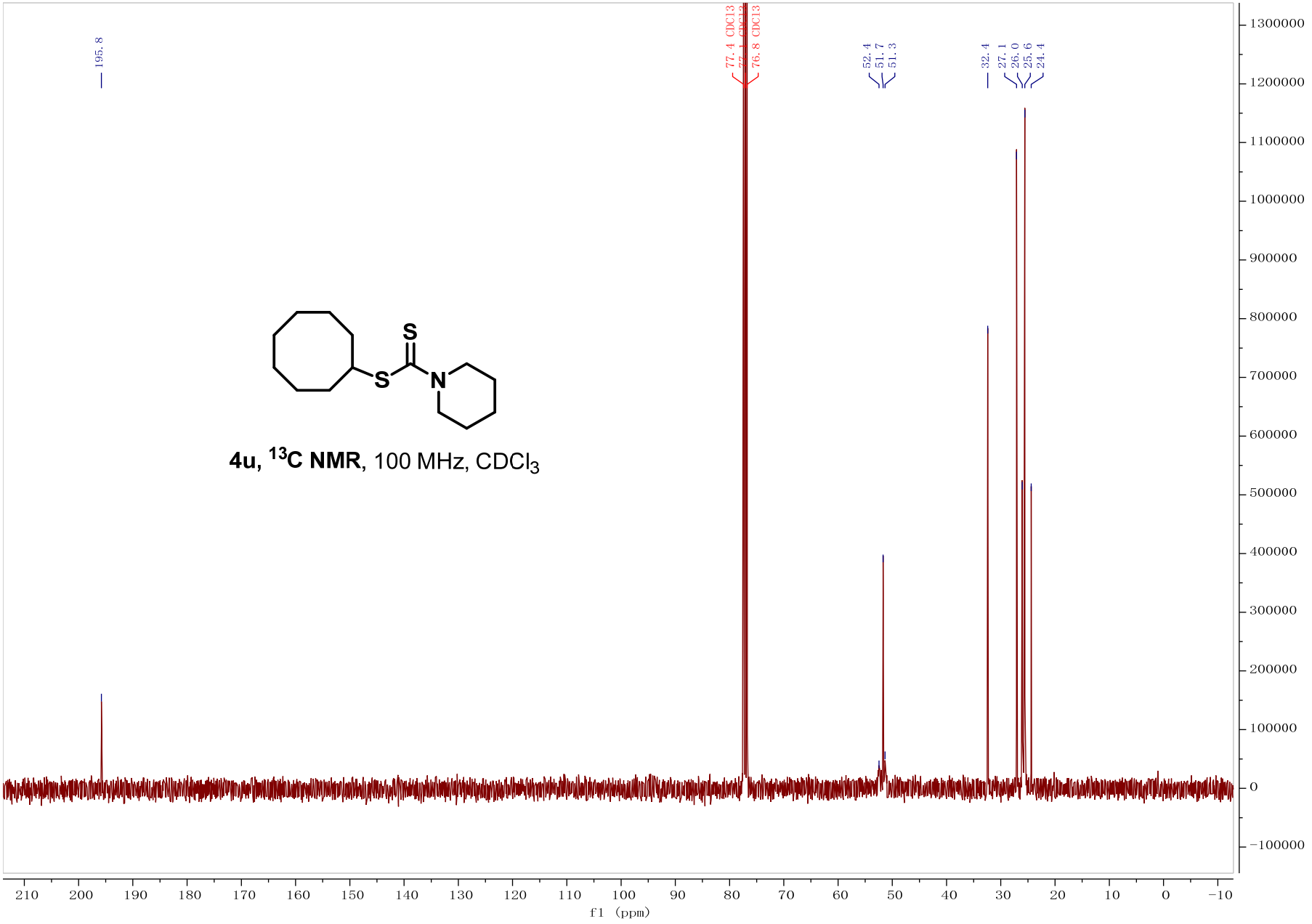

195.6
144.5
141.3
128.0
126.6
125.3
124.8
77.4 CDCl3
77.1 CDCl3
76.8 CDCl3
55.8
52.7
51.5
34.4
30.8
26.0
25.5
24.3
S
S
N
4s, 13C NMR, 100 MHz, CDCl3
f1 (ppm)

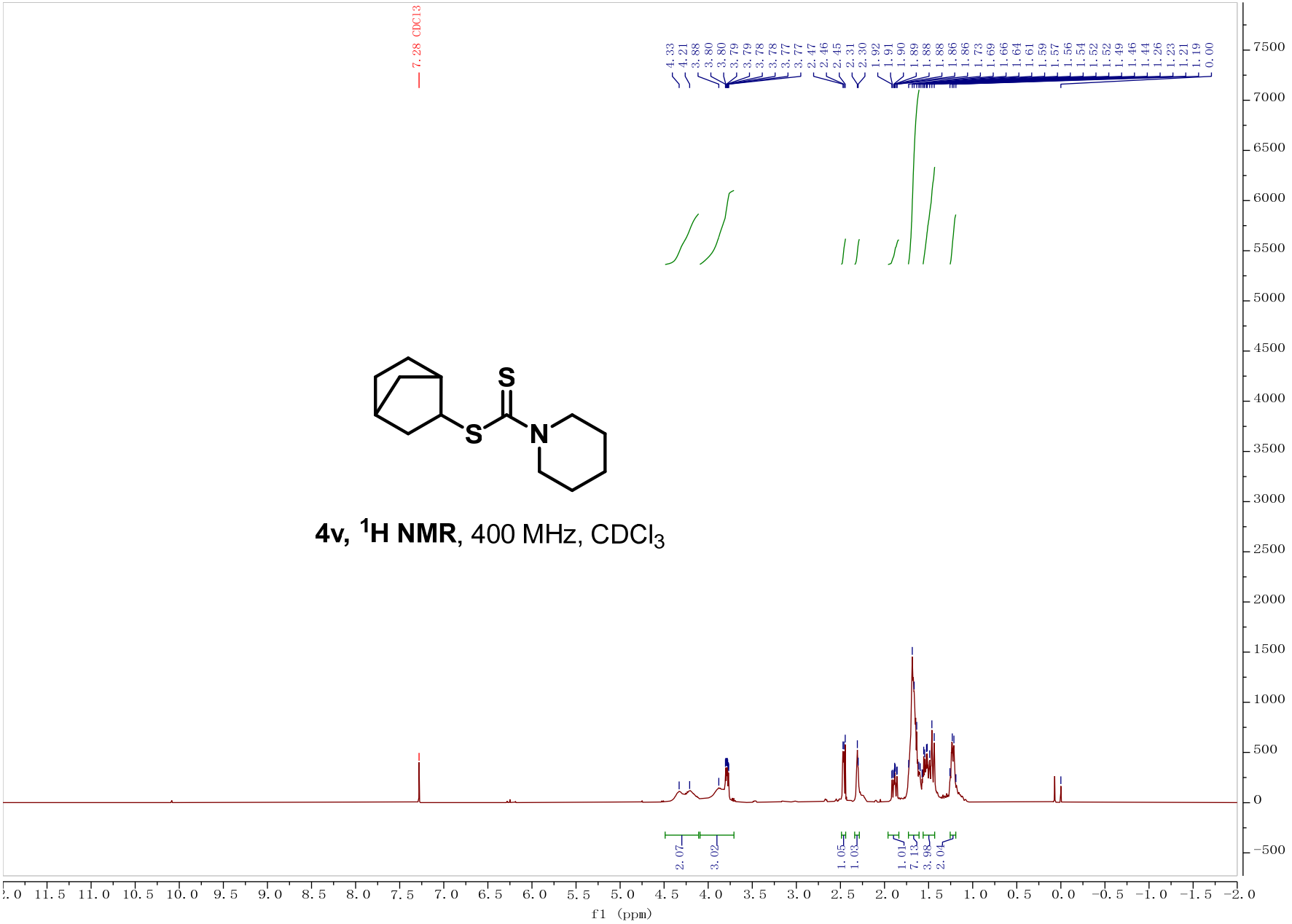


4t, ^{1}H NMR, 400 MHz, $CDCl_3$

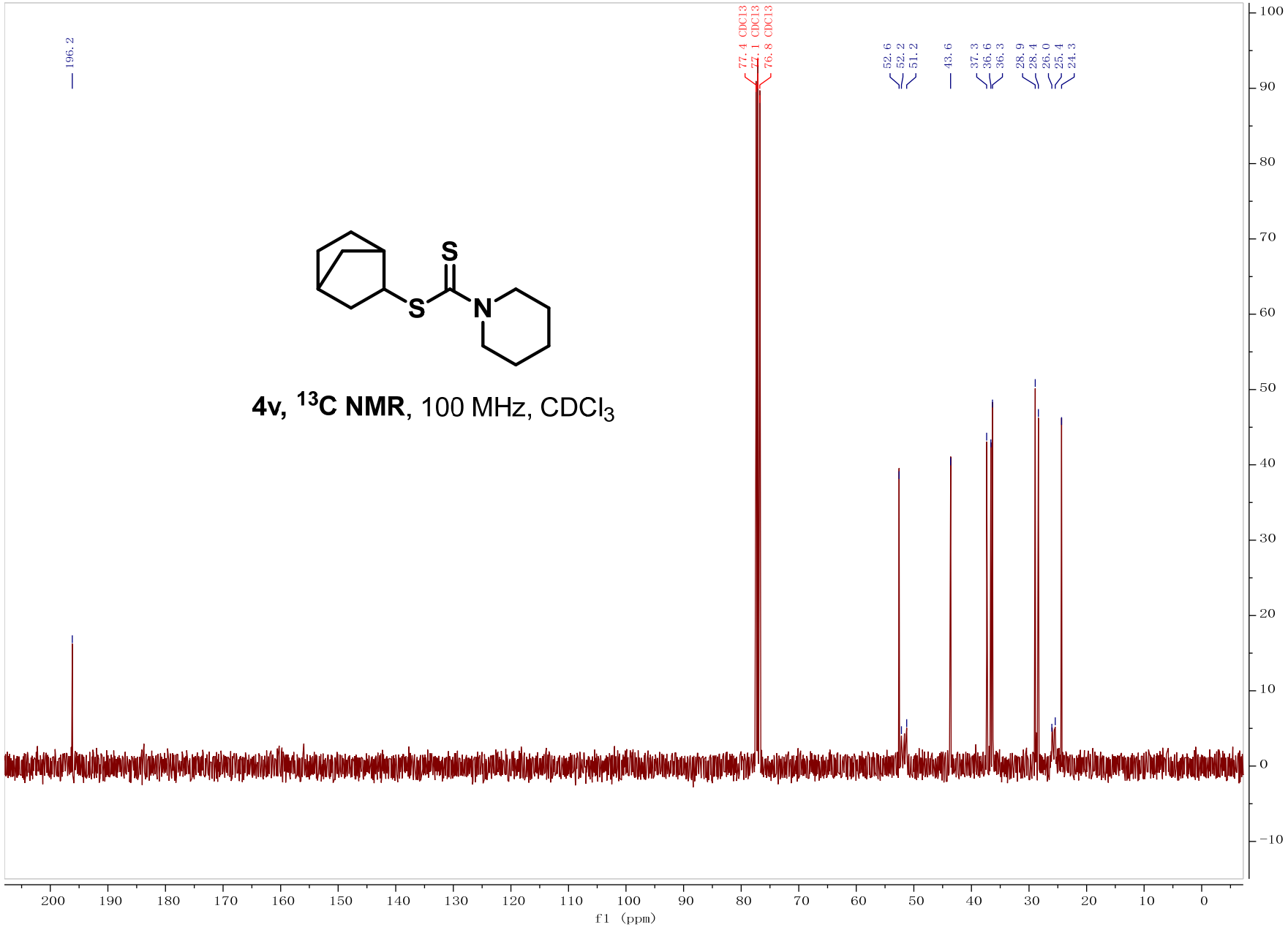

195.3
76.3 CDCl3
76.0 CDCl3
75.7 CDCl3
51.3
50.3
49.0
32.0
24.9
24.4
24.0
23.3
S
S
N
4t, 13C NMR, 100 MHz, CDCl3
f1 (ppm)

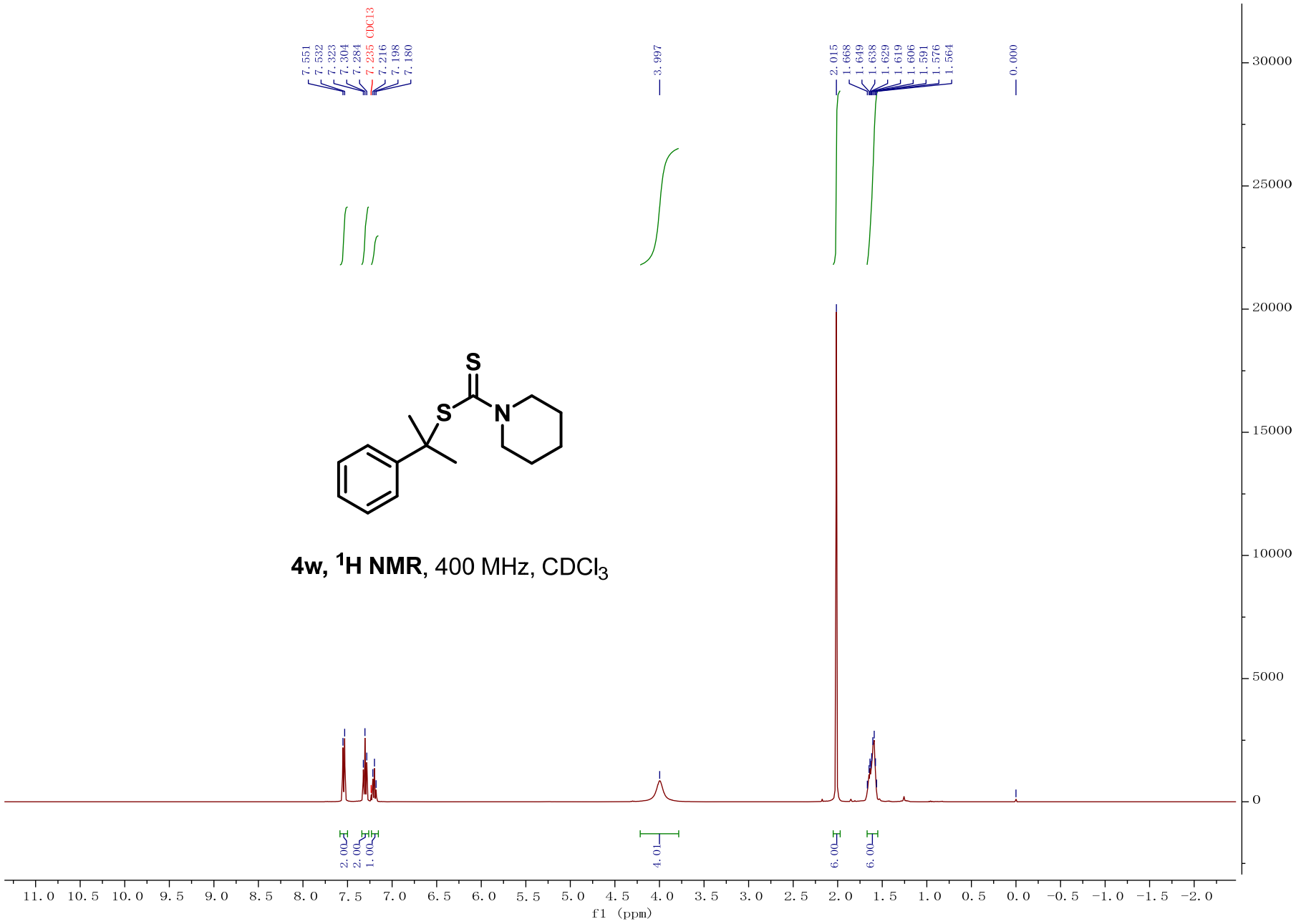

7.20 CDCl3
4.21
4.15
4.14
4.13
4.12
4.11
4.10
4.09
3.81
2.08
2.07
2.06
2.05
2.03
2.02
2.01
2.00
1.78
1.77
1.75
1.74
1.72
1.70
1.69
1.62
1.60
1.55
1.51
1.47
0.00
S
S
N
4u, 1H NMR, 400 MHz, CDCl3
1.80
1.18
2.00
1.97
2.09
16.00
f1 (ppm)


195.8
77.4 CDCl3
77.1 CDCl3
76.8 CDCl3
52.4
51.7
51.3
32.4
27.1
26.0
25.6
24.4
S
S
N
4u, 13C NMR, 100 MHz, CDCl3
f1 (ppm)

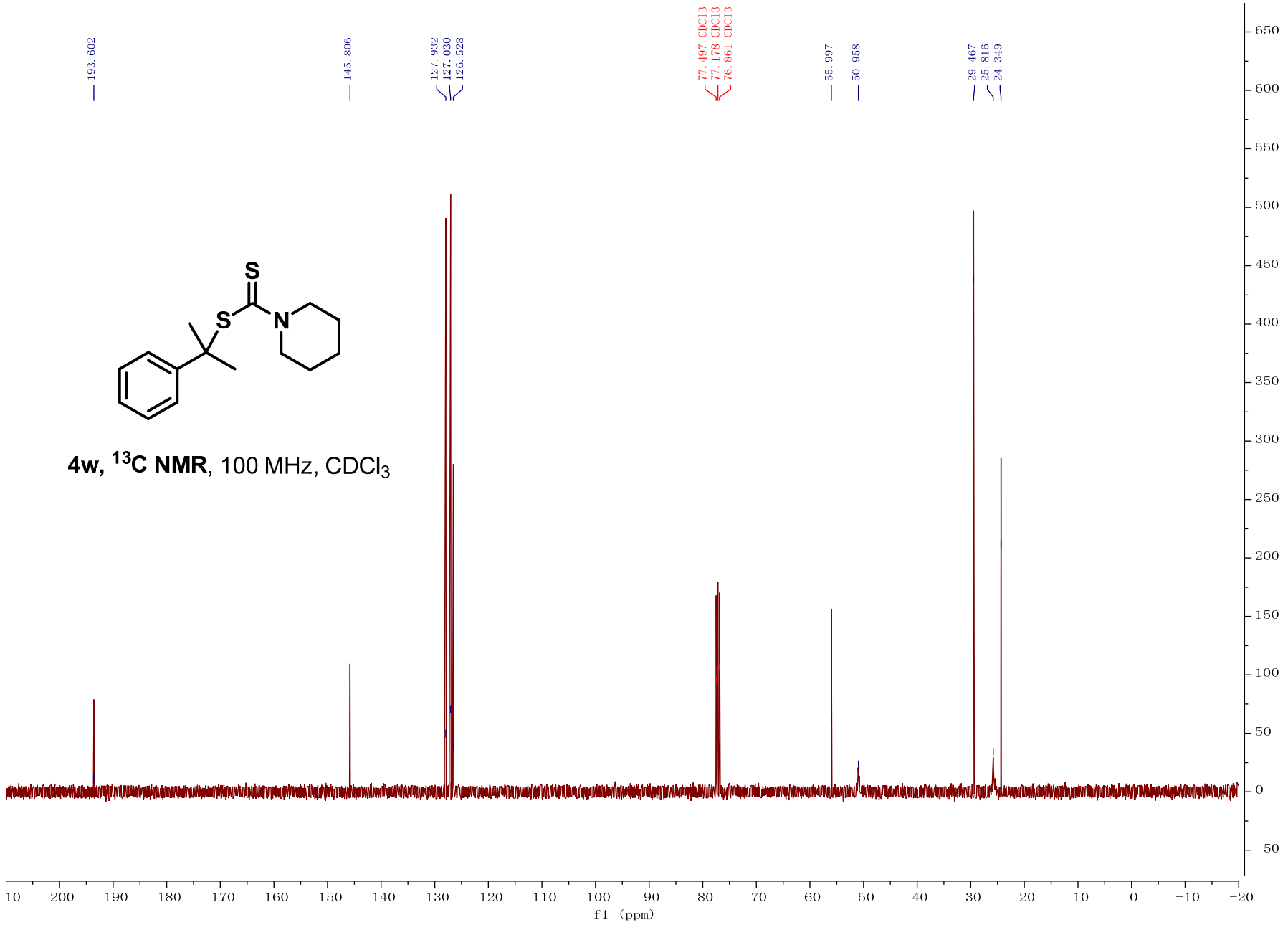


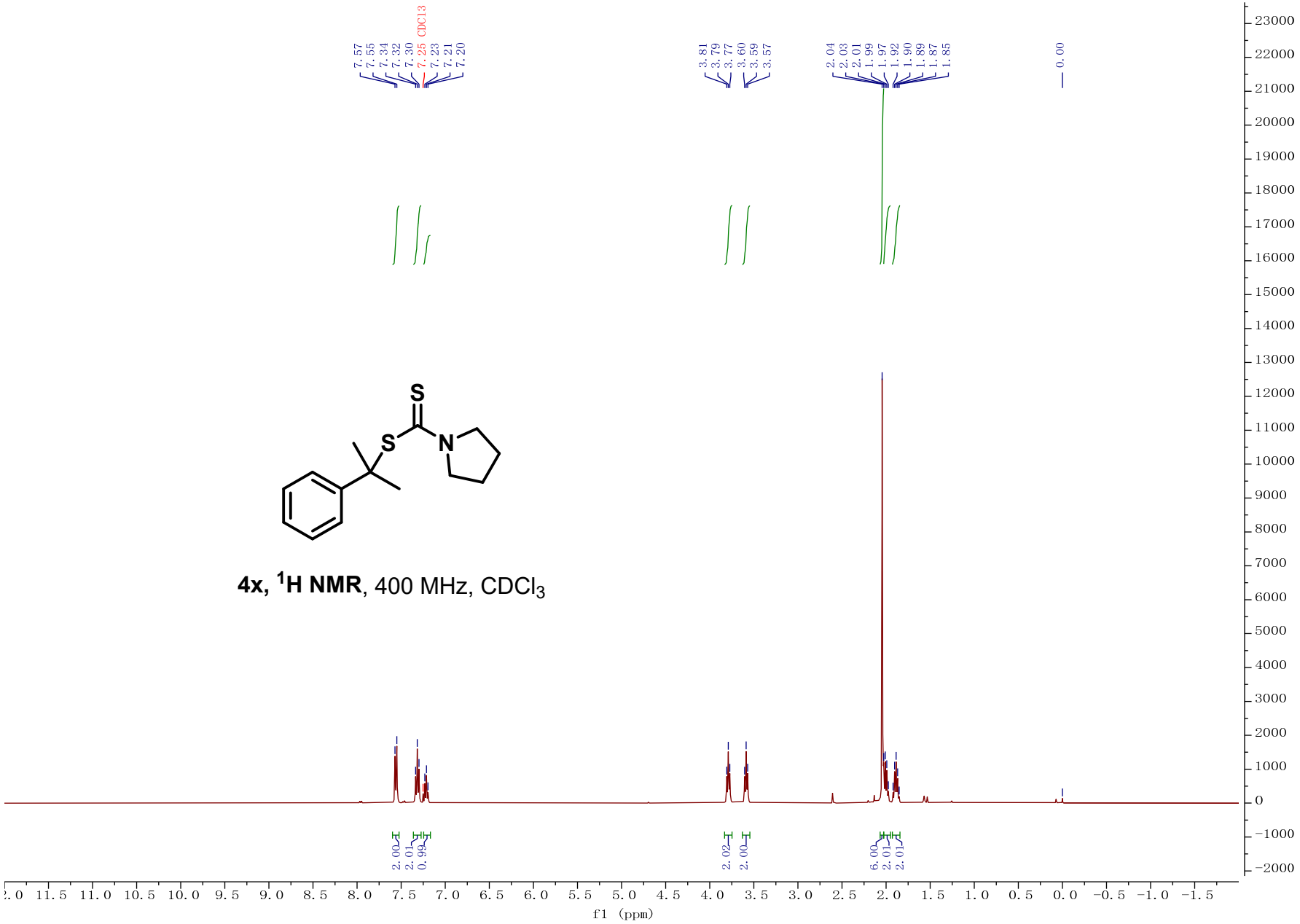
4v, ^{1}H NMR, 400 MHz, $CDCl_3$


196.2
77.4 CDCl3
77.1 CDCl3
76.8 CDCl3
52.6
52.2
51.2
43.6
37.3
36.6
36.3
28.9
28.4
26.0
25.4
24.3
S
S
N
4v, 13C NMR, 100 MHz, CDCl3
f1 (ppm)

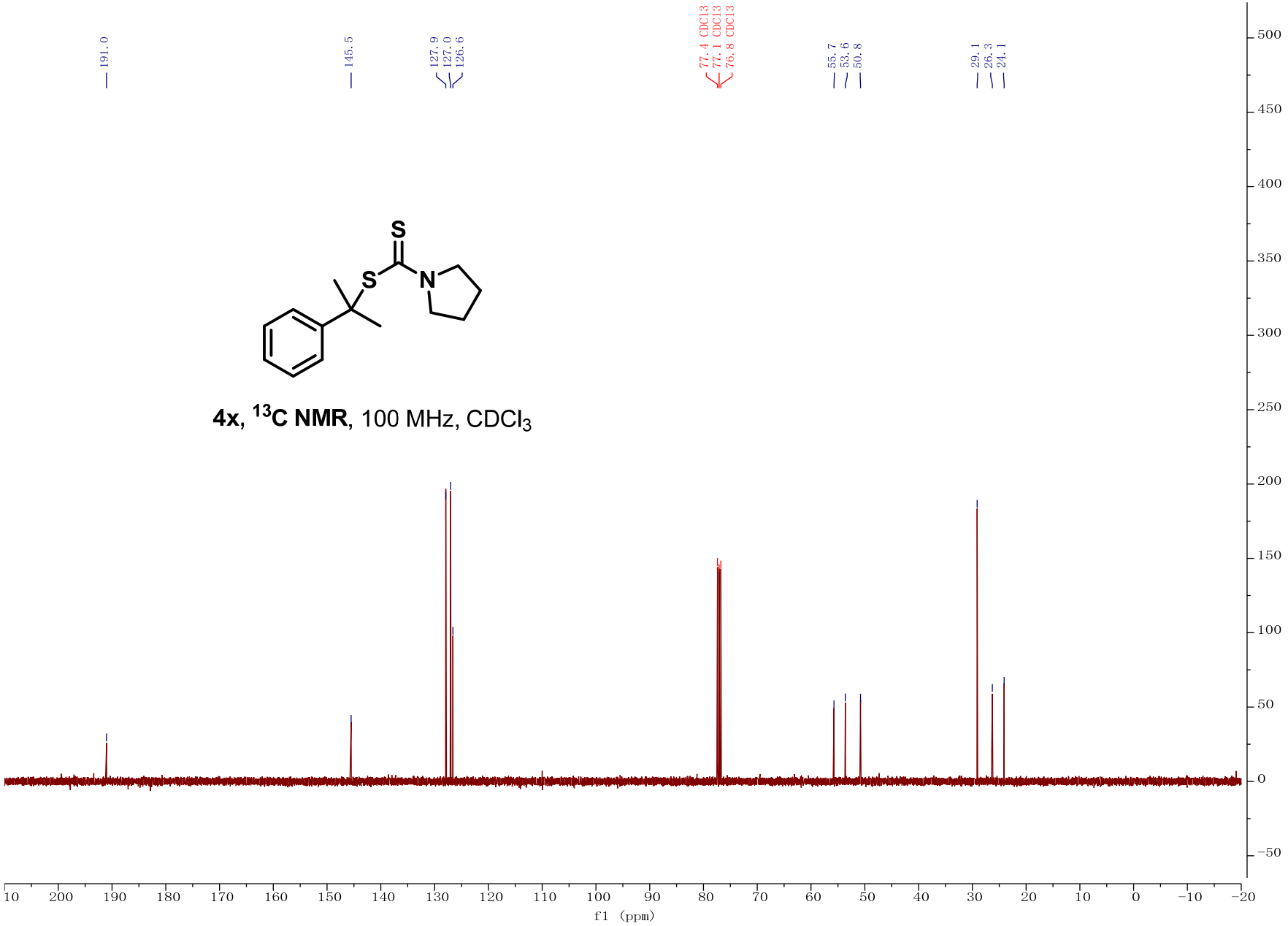


4w, ^{1}H NMR, 400 MHz, $CDCl_3$

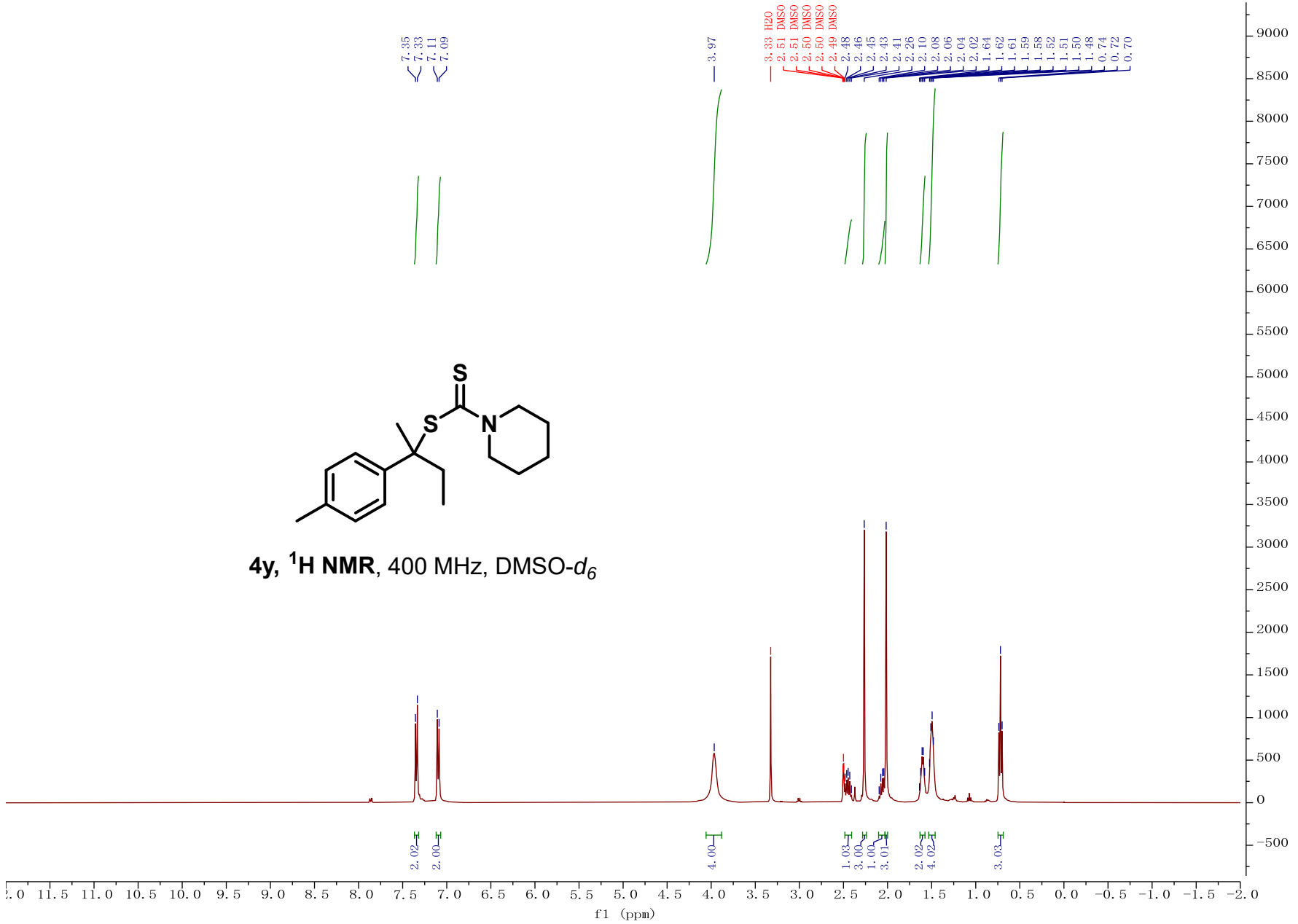

193.602
145.806
127.932
127.030
126.528
77.497 CDCl3
77.178 CDCl3
76.861 CDCl3
55.997
50.958
29.467
25.816
24.349
S
S
N
4w, 13C NMR, 100 MHz, CDCl3
f1 (ppm)



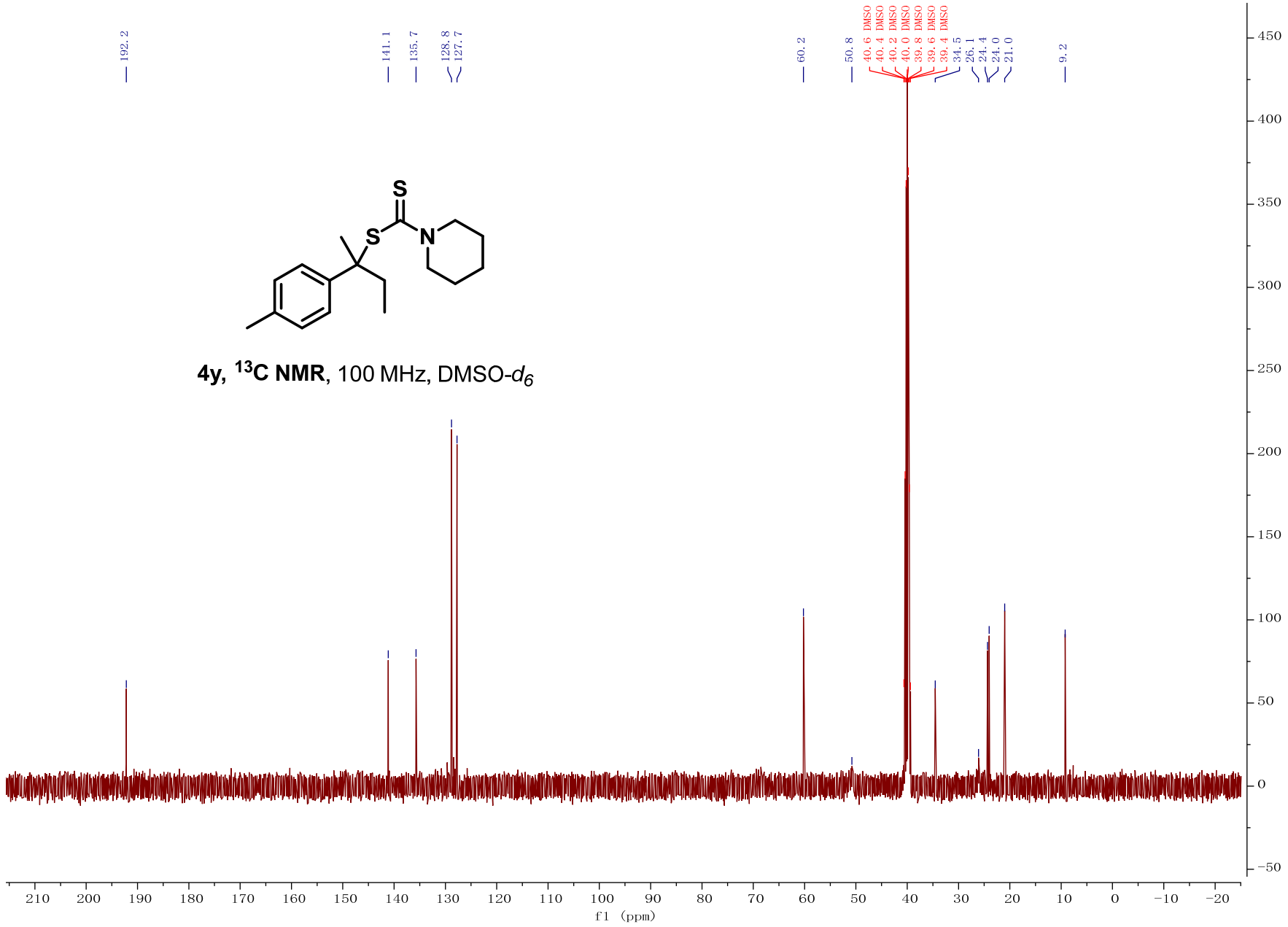
4x, ^{1}H NMR, 400 MHz, $CDCl_3$

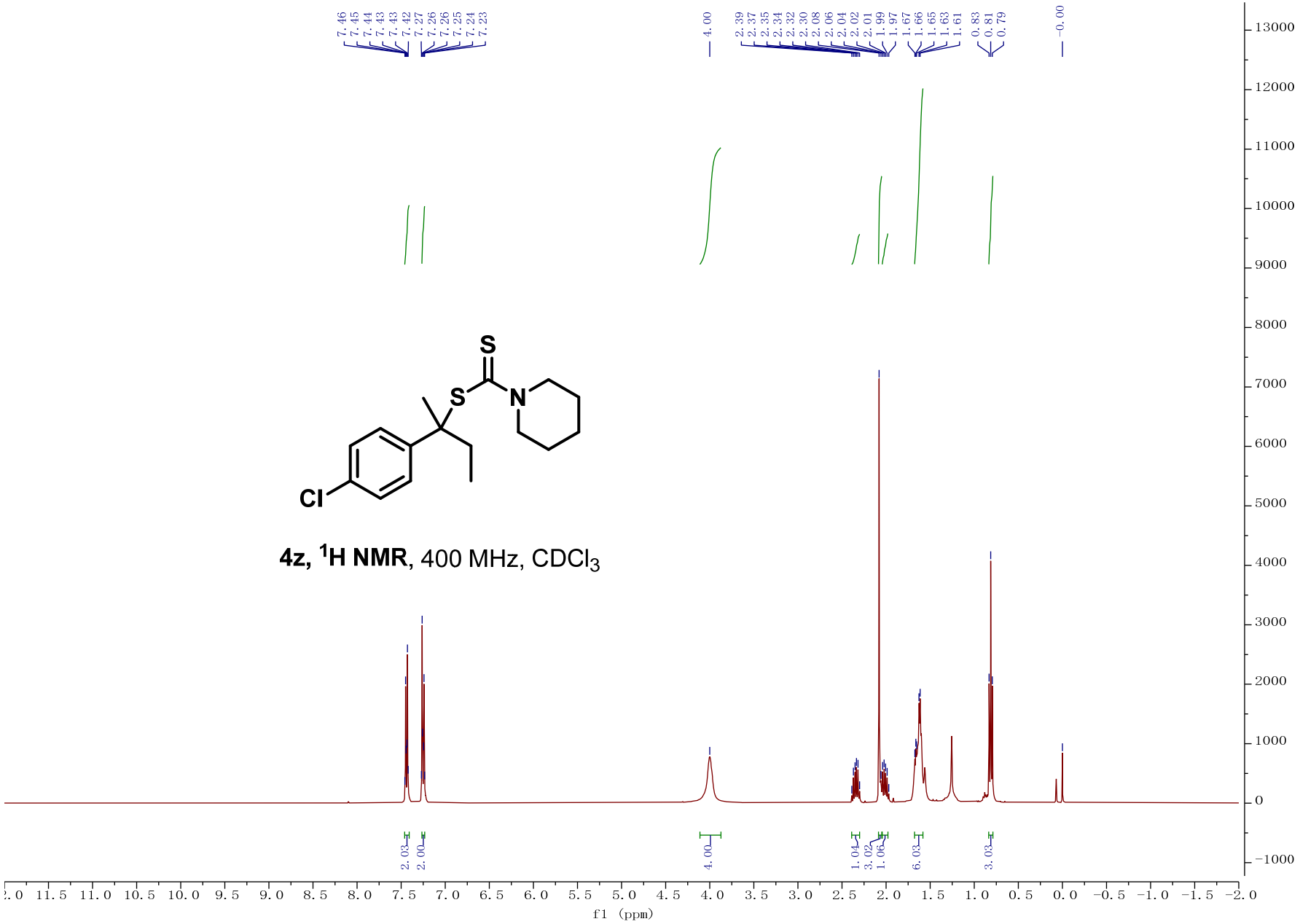


4x, **^{13}C NMR**, 100 MHz, $CDCl_3$

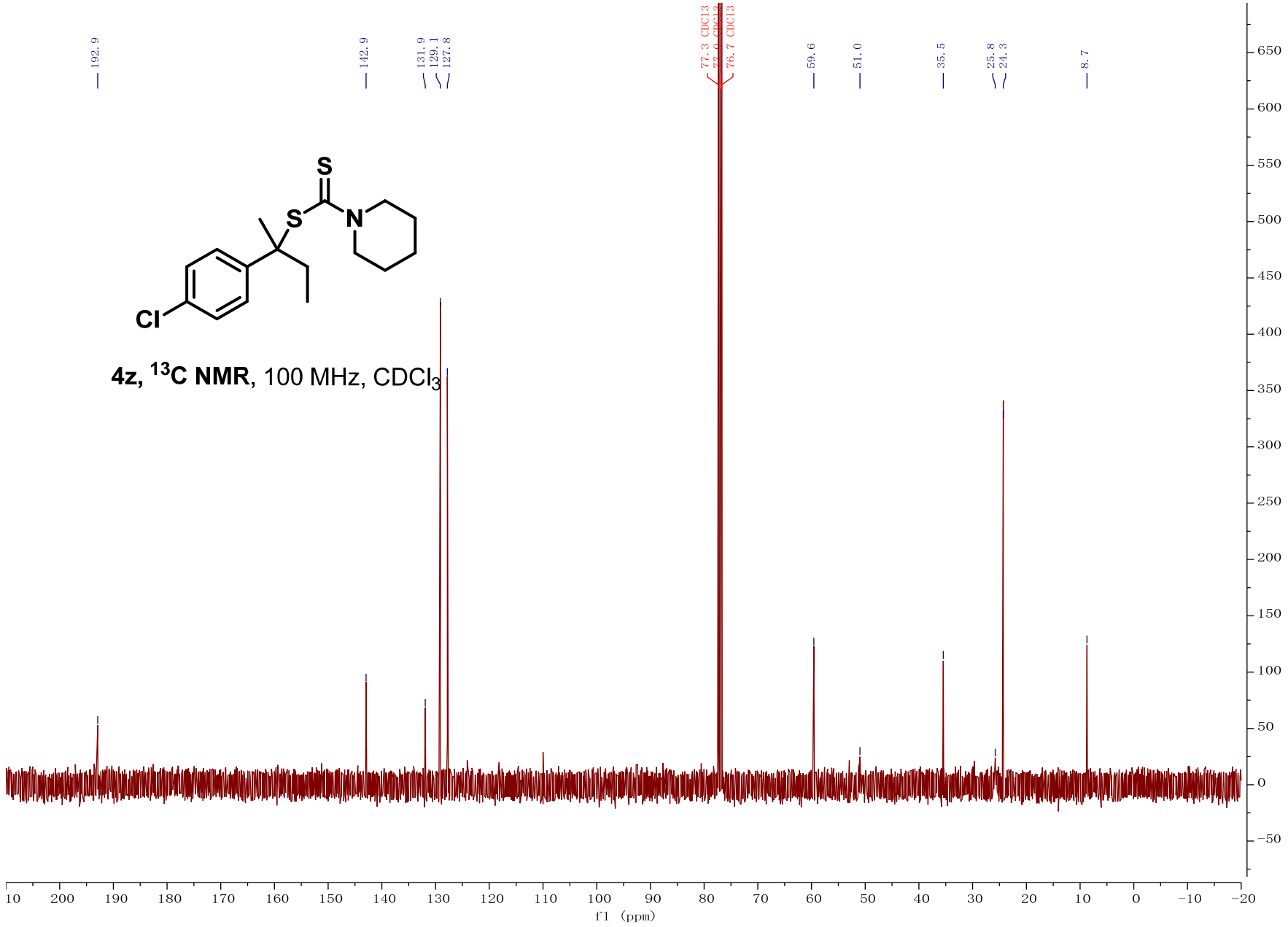


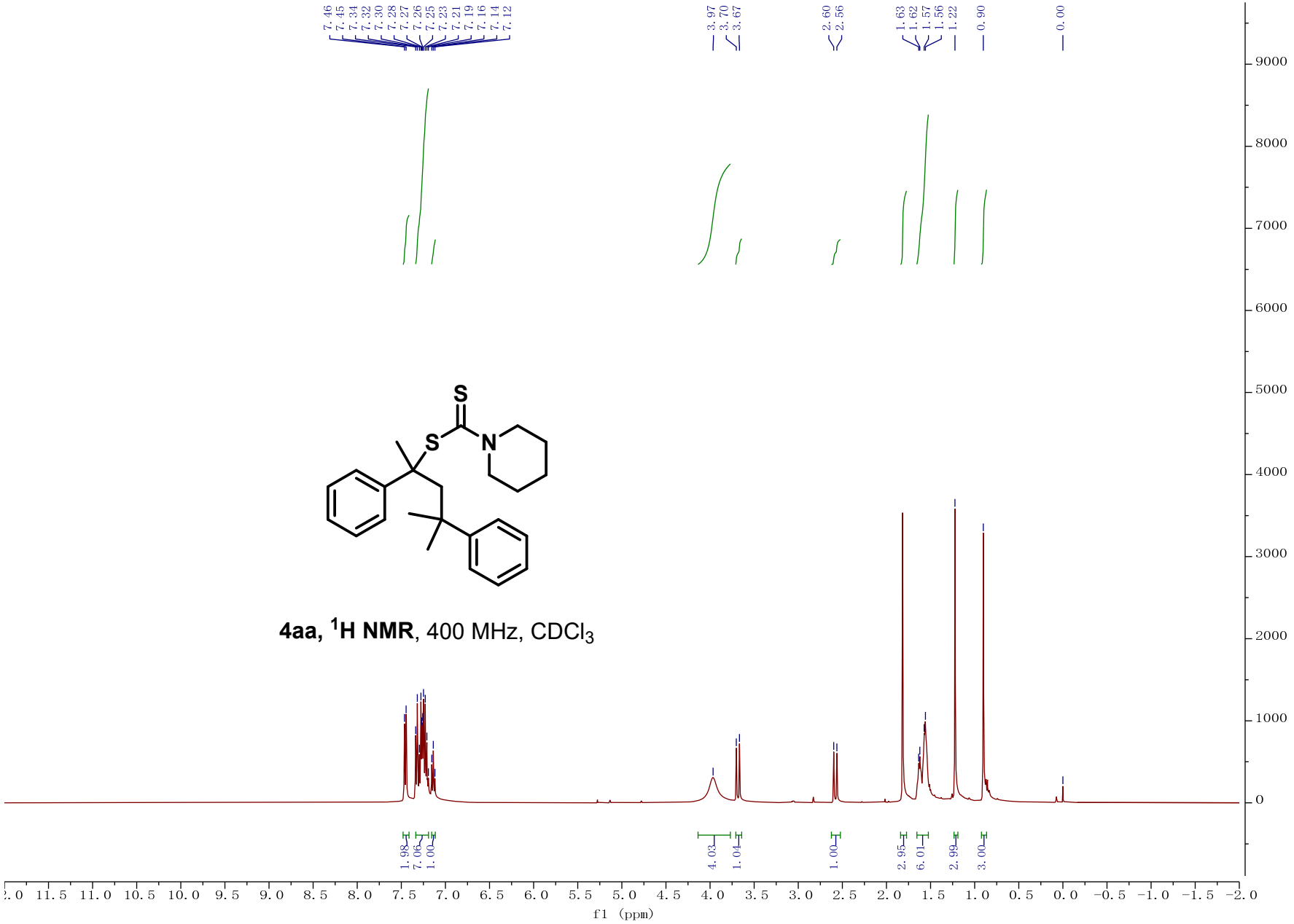
4y, ^{1}H NMR, 400 MHz, DMSO-d_6


192.2
141.1
135.7
128.8
127.7
60.2
50.8
40.6 DMSO
40.4 DMSO
40.2 DMSO
40.0 DMSO
39.8 DMSO
39.6 DMSO
39.4 DMSO
34.5
26.1
24.4
24.0
21.0
9.2
S
S
N
4y, 13C NMR, 100 MHz, DMSO-d6
f1 (ppm)

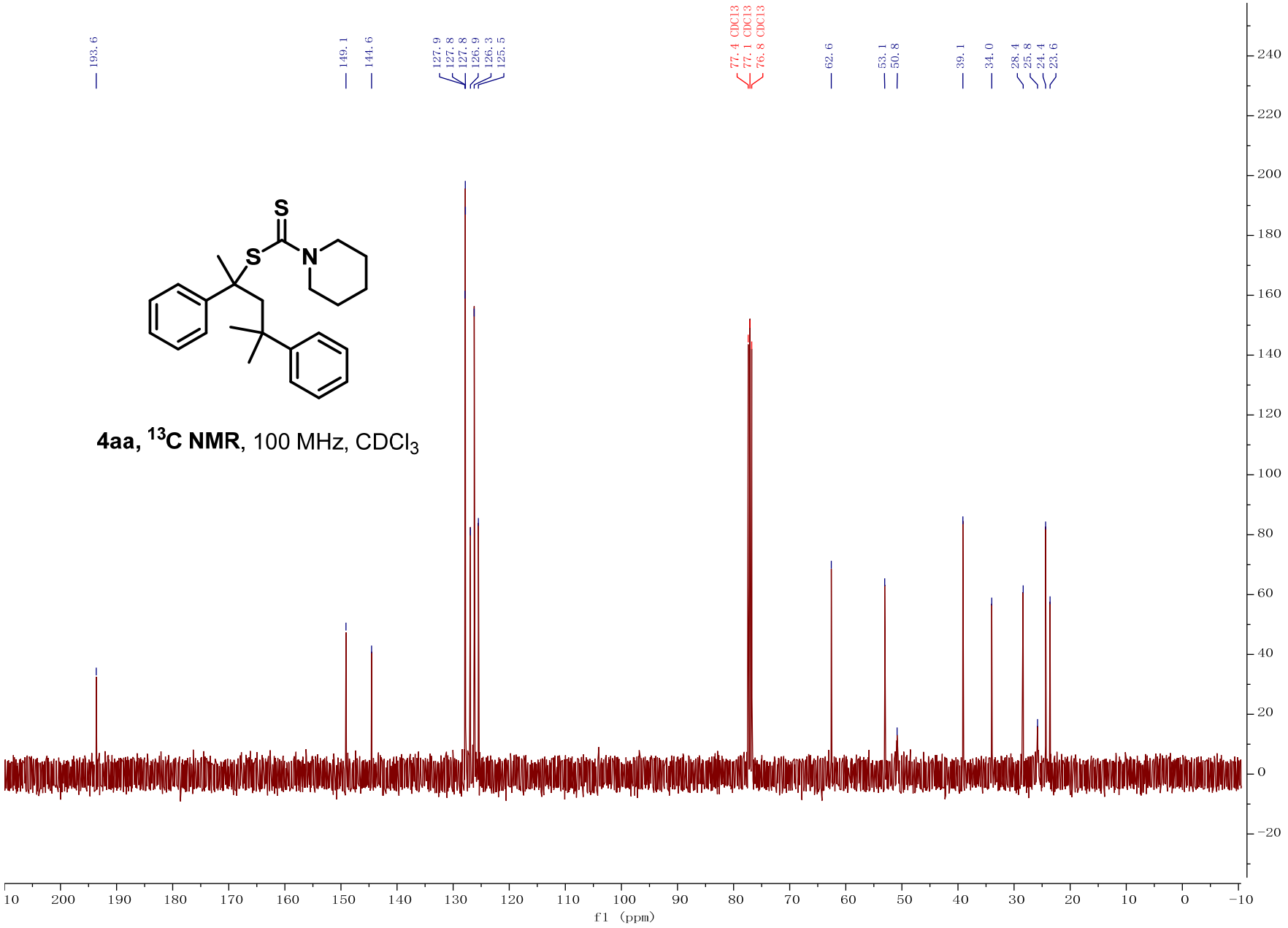


4z, ^{1}H NMR, 400 MHz, $CDCl_3$

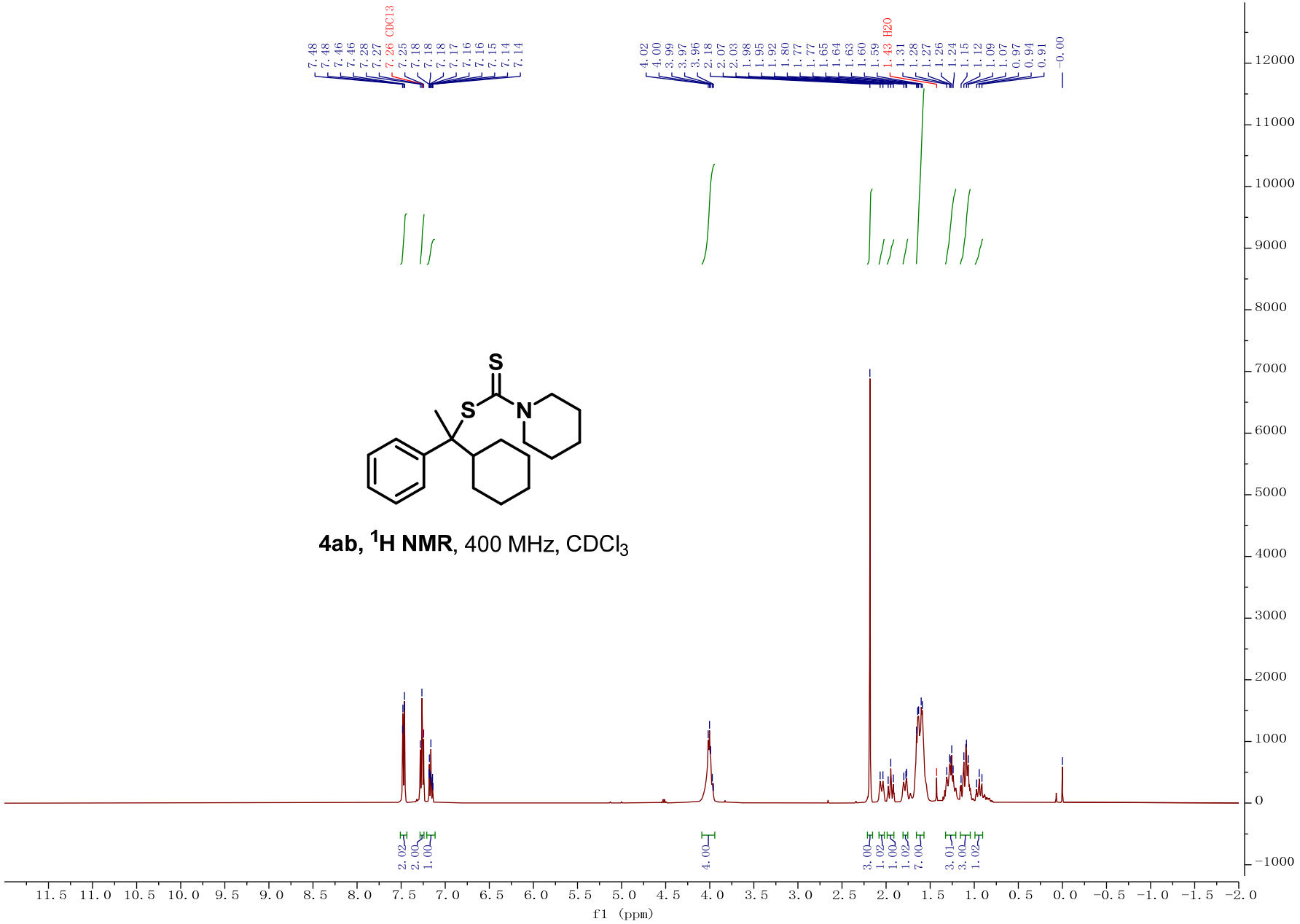

192.9
142.9
131.9
129.1
127.8
77.3 CDCl3
76.7 CDCl3
59.6
51.0
35.5
25.8
24.3
8.7
S
S
N
Cl
4z, 13C NMR, 100 MHz, CDCl3
f1 (ppm)

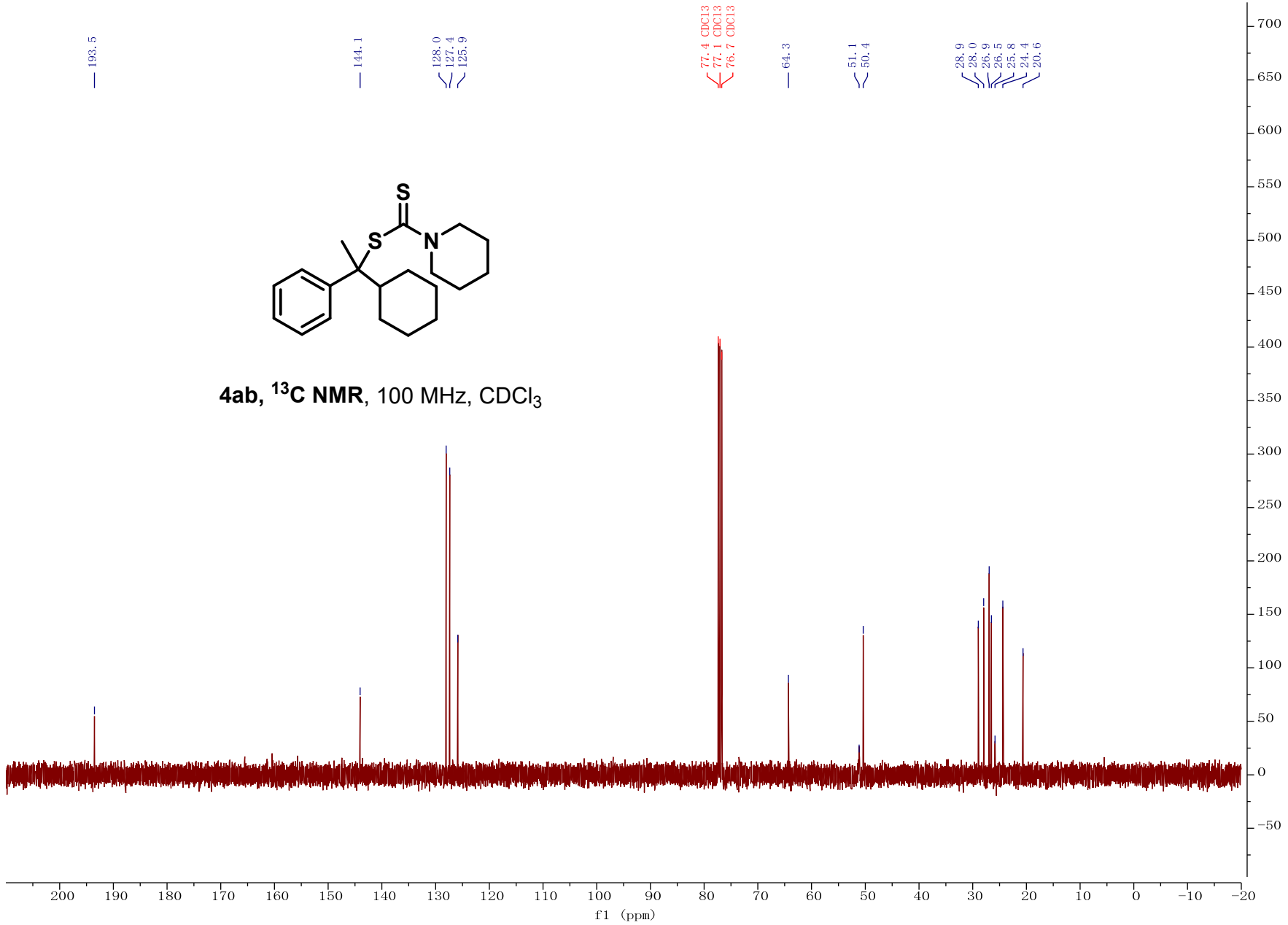


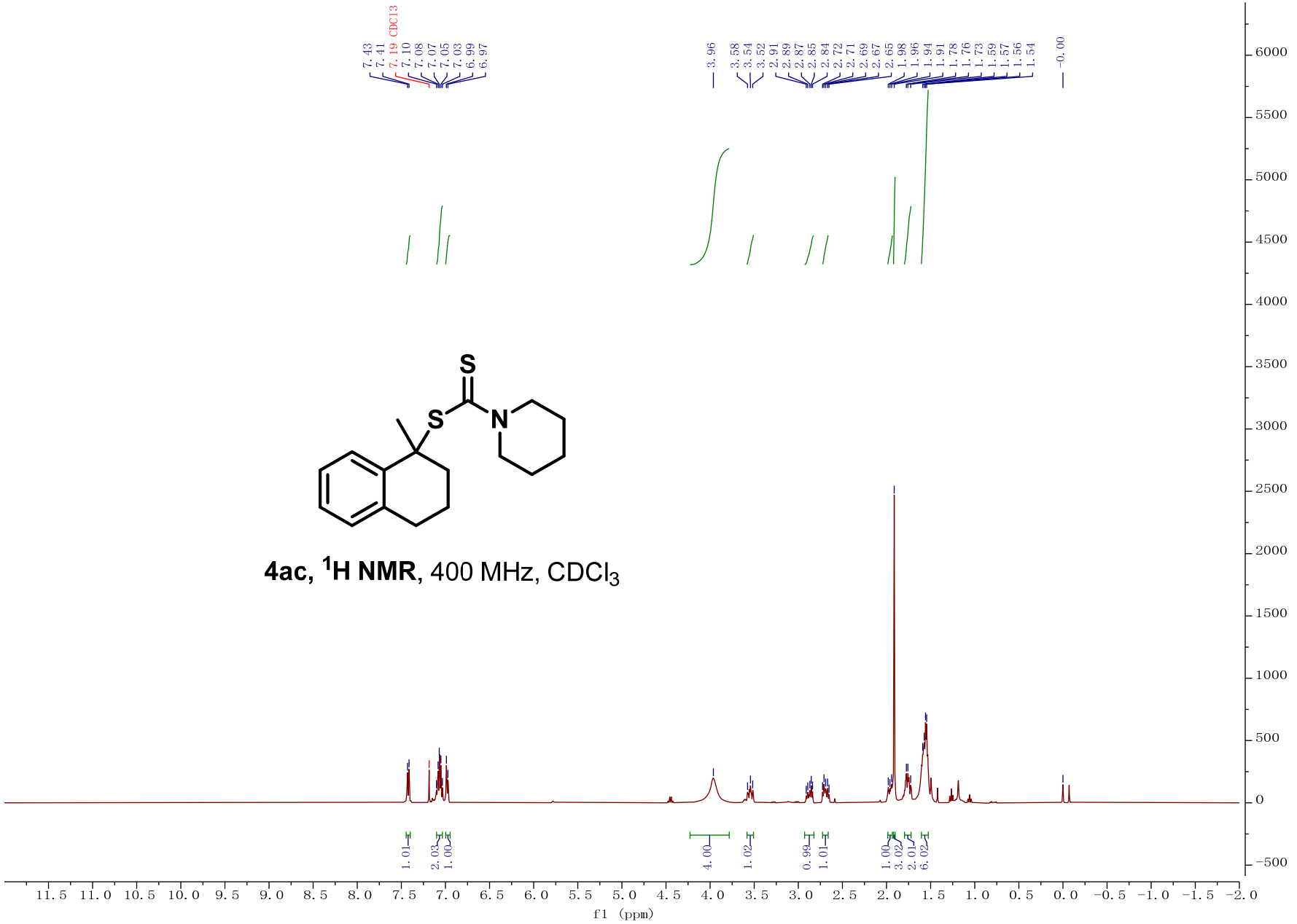
4aa, ^{1}H NMR, 400 MHz, $CDCl_3$



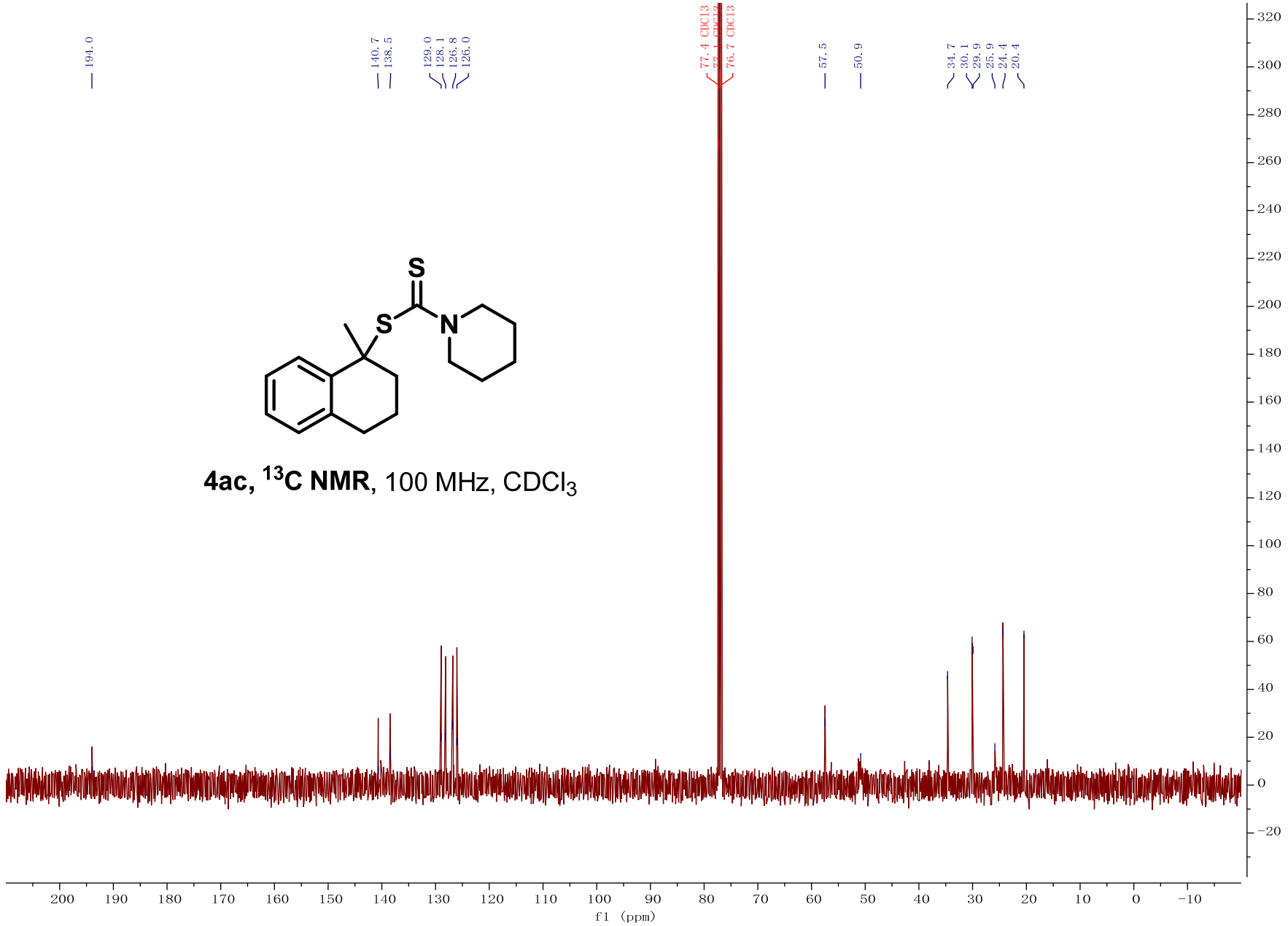
4aa, ^{13}C NMR, 100 MHz, $CDCl_3$


7.48
7.48
7.46
7.46
7.28
7.27
7.26 CDCl3
7.25
7.18
7.18
7.18
7.17
7.16
7.16
7.15
7.14
7.14
4.02
4.00
3.99
3.97
3.96
2.18
2.07
2.03
1.98
1.95
1.92
1.80
1.77
1.77
1.65
1.64
1.63
1.60
1.59
1.43 H2O
1.31
1.28
1.27
1.26
1.24
1.15
1.12
1.09
1.07
0.97
0.94
0.91
-0.00
S
S
N
4ab, 1H NMR, 400 MHz, CDCl3
2.02
2.00
1.00
4.00
3.00
1.02
1.00
1.02
7.00
3.01
3.00
1.02
f1 (ppm)

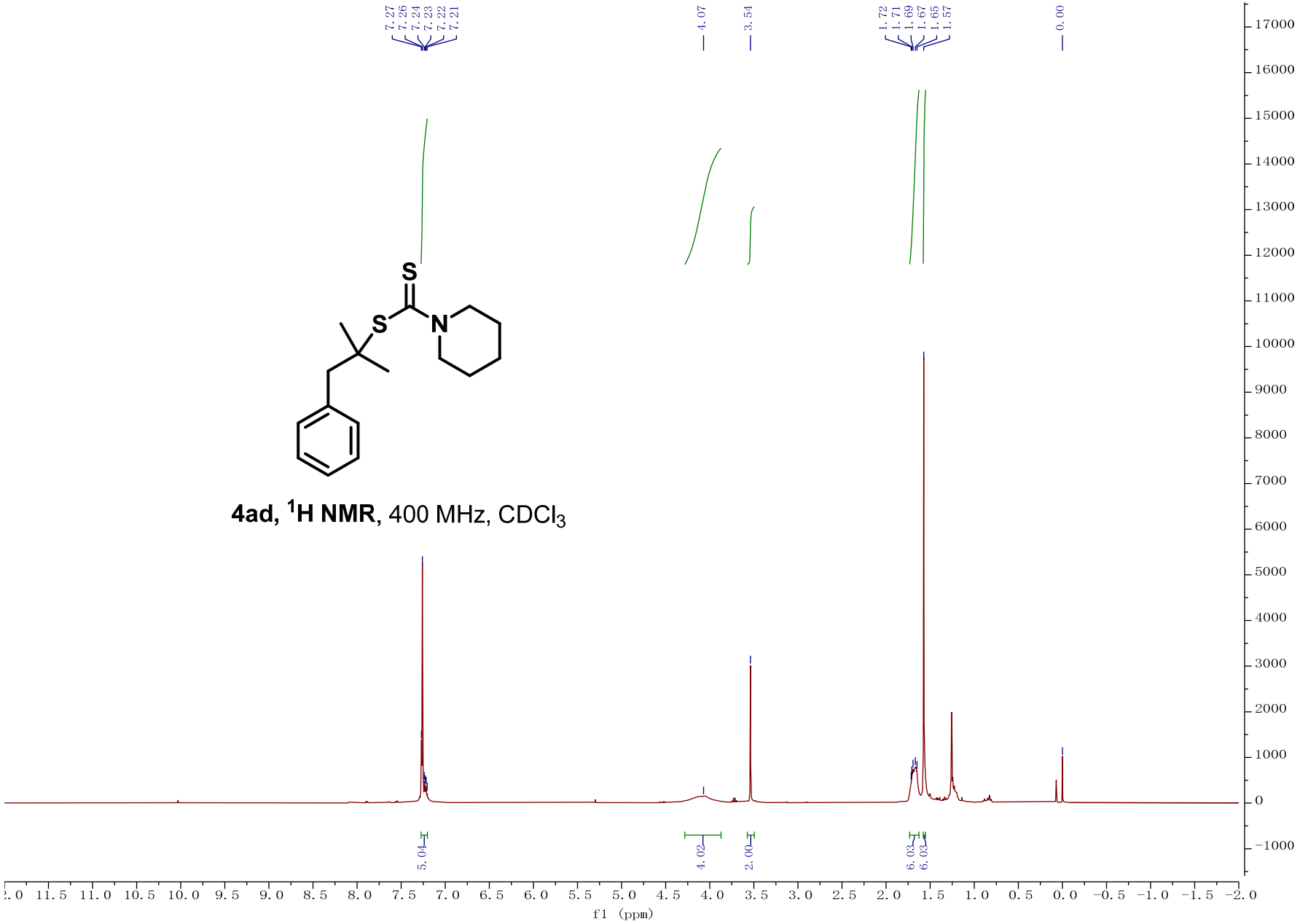

193.5
144.1
128.0
127.4
125.9
77.4 CDCl3
77.1 CDCl3
76.7 CDCl3
64.3
51.1
50.4
28.9
28.0
26.9
26.5
25.8
24.4
20.6
S
S
N
4ab, 13C NMR, 100 MHz, CDCl3
f1 (ppm)



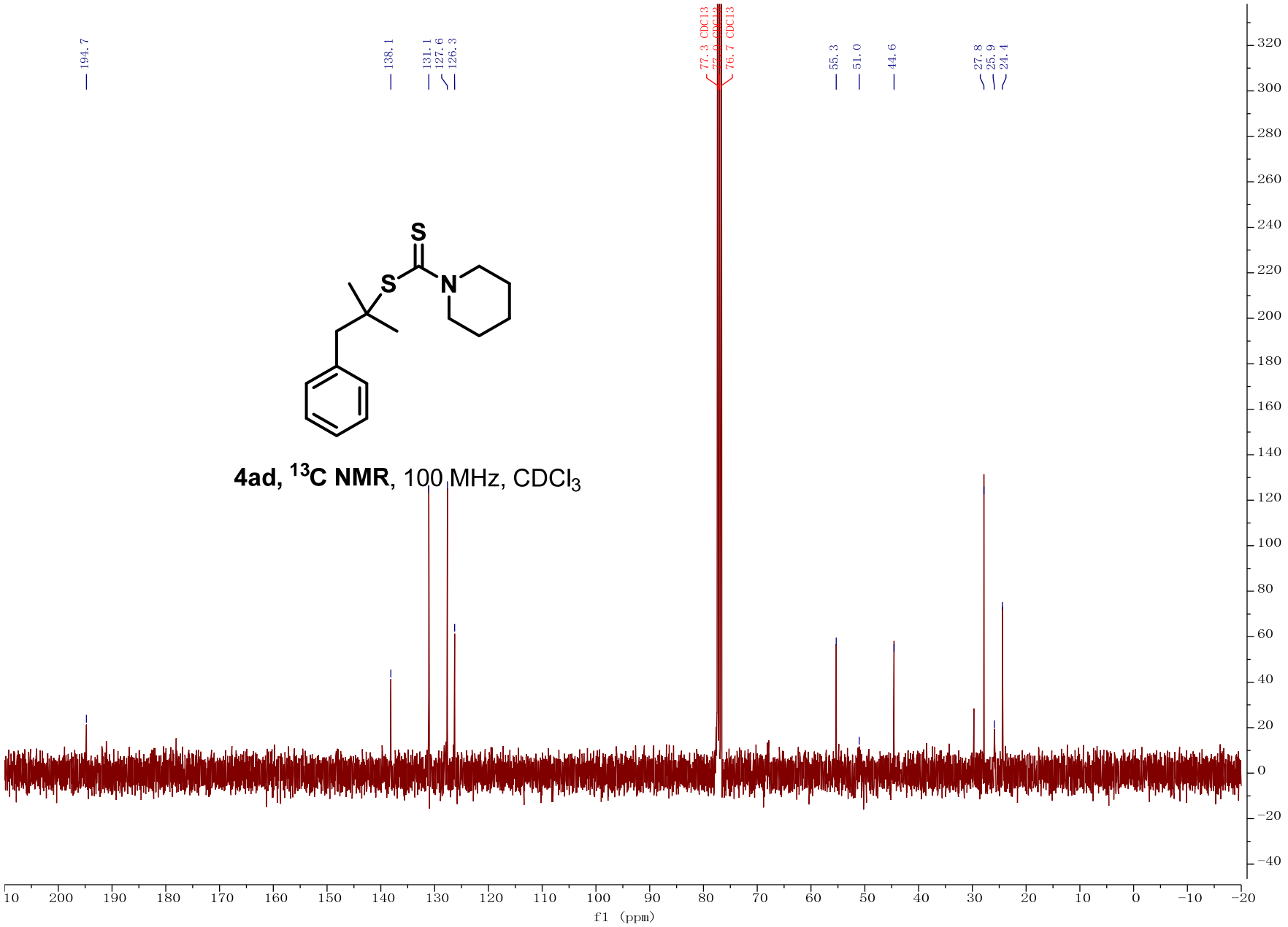
4ac, ^{1}H NMR, 400 MHz, $CDCl_3$



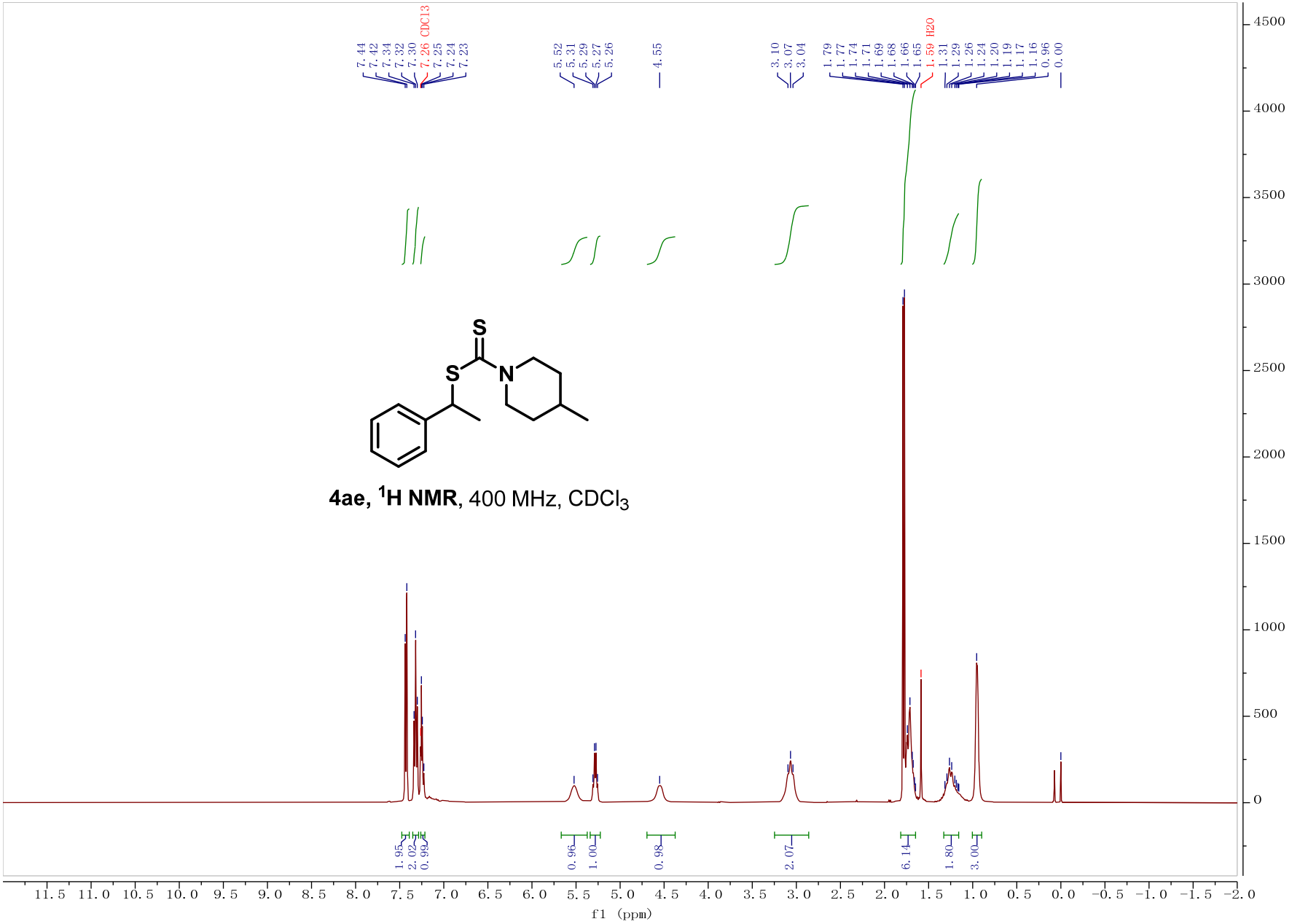
4ac, ^{13}C NMR, 100 MHz, $CDCl_3$



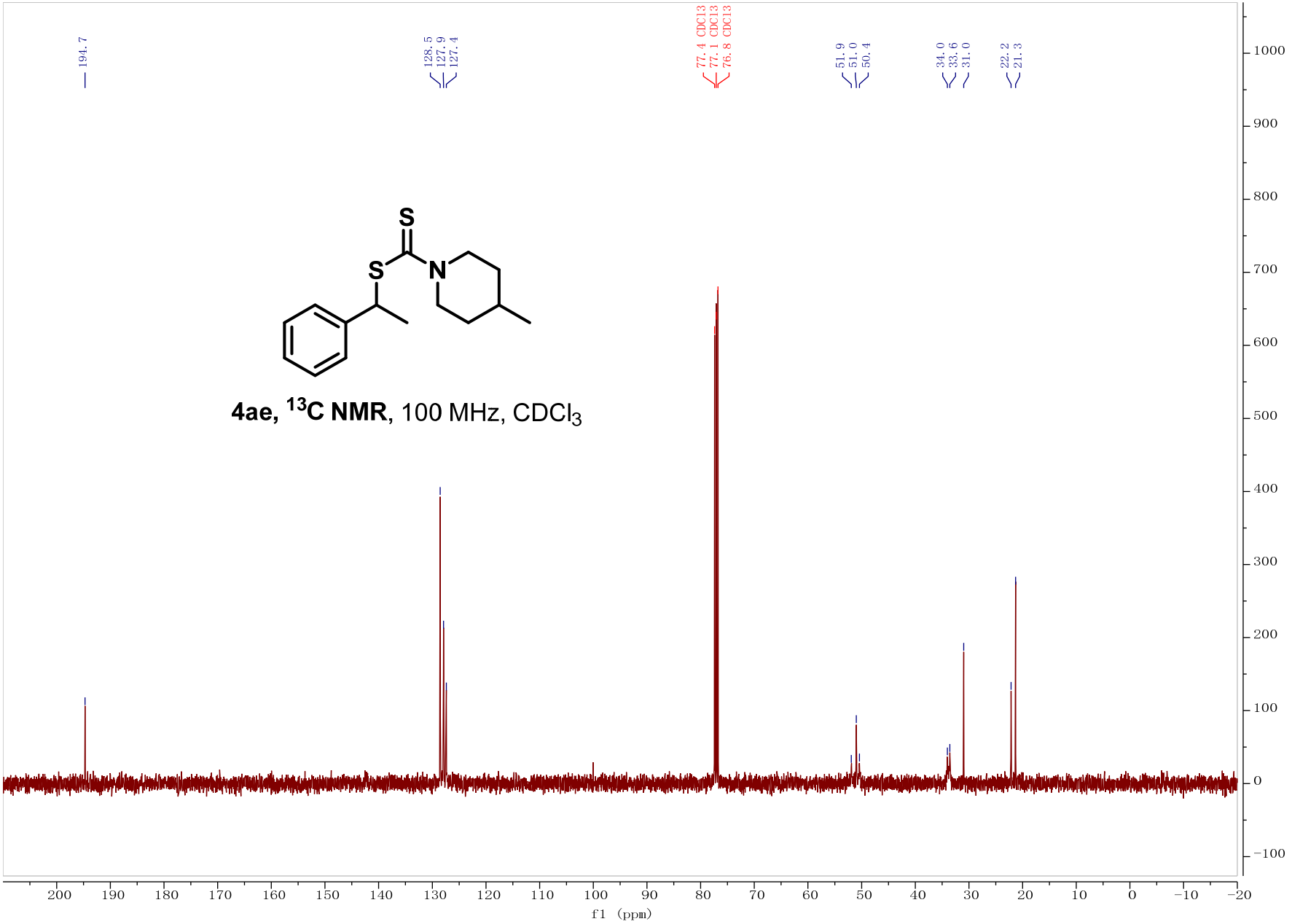
4ad, ^{1}H NMR, 400 MHz, $CDCl_3$

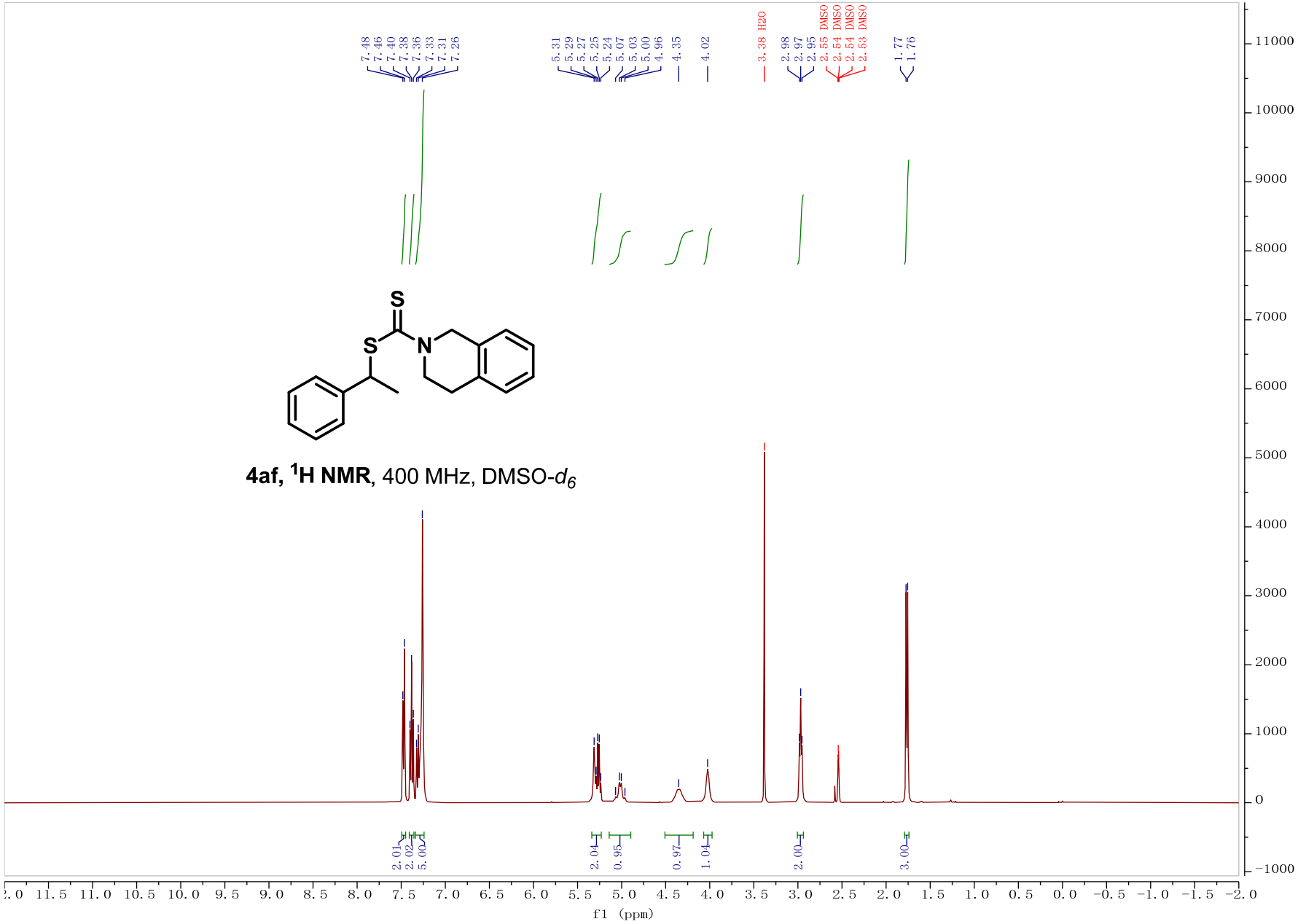


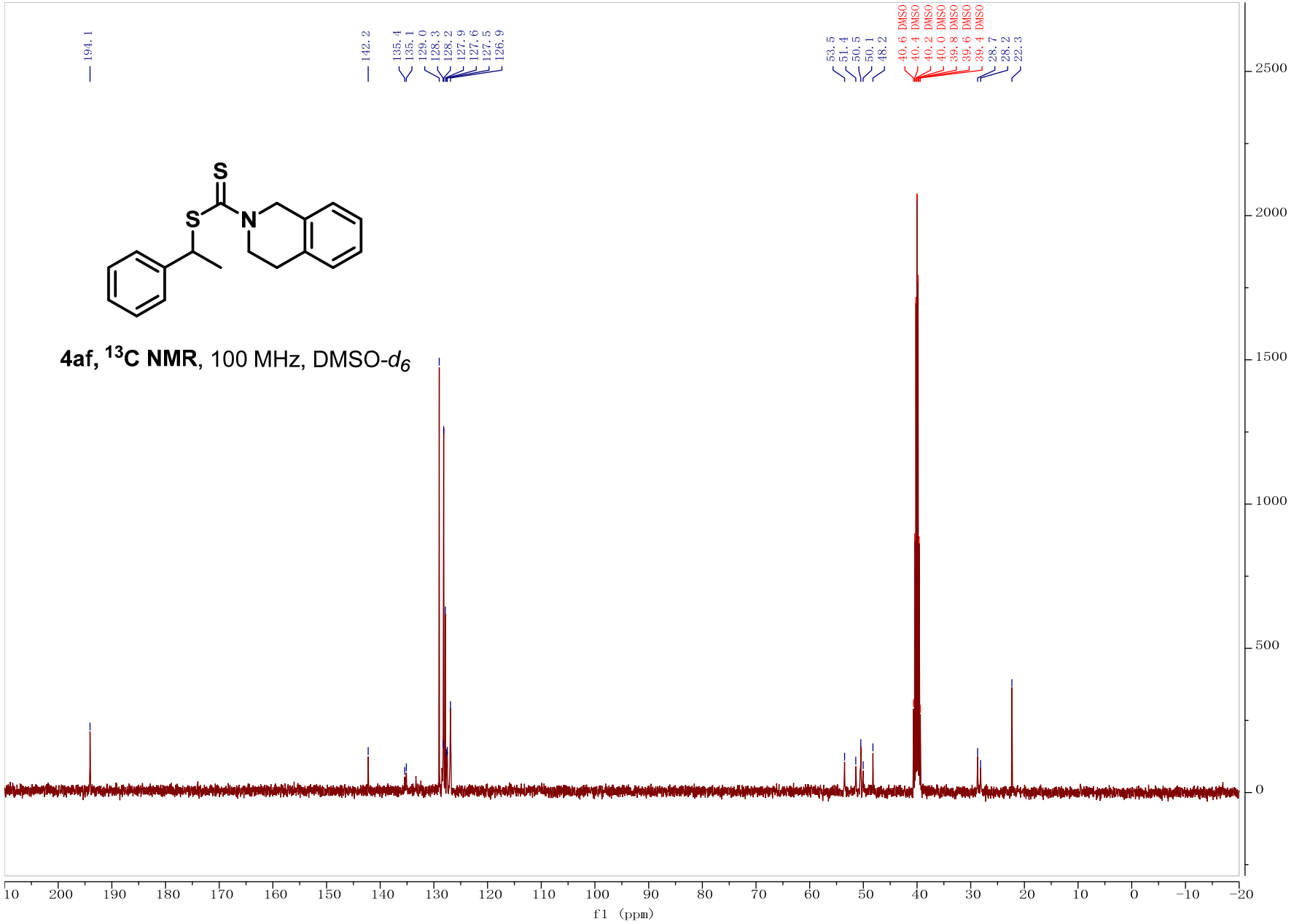
4ad, ^{13}C NMR, 100 MHz, $CDCl_3$

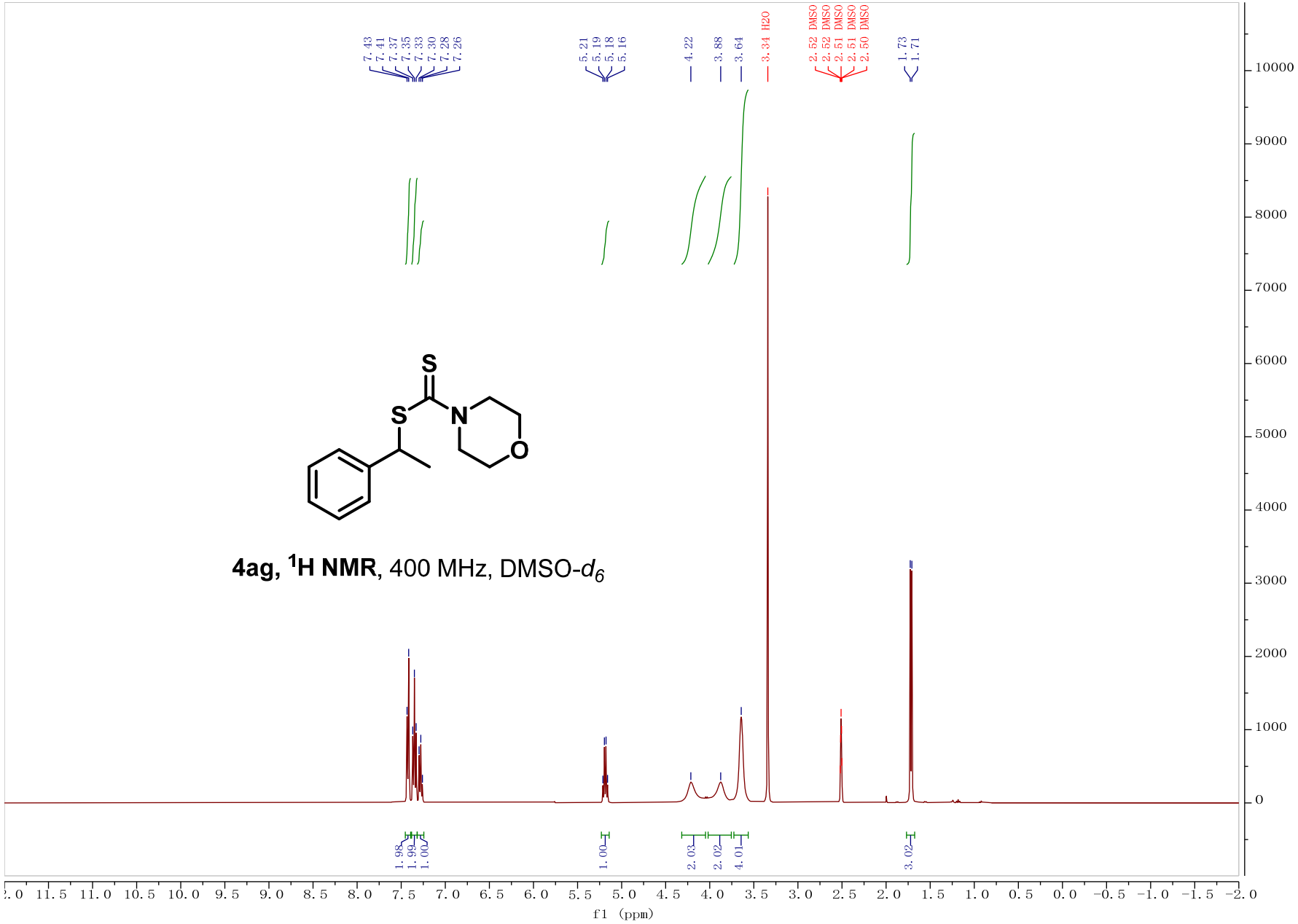


4ae, ^{1}H NMR, 400 MHz, $CDCl_3$

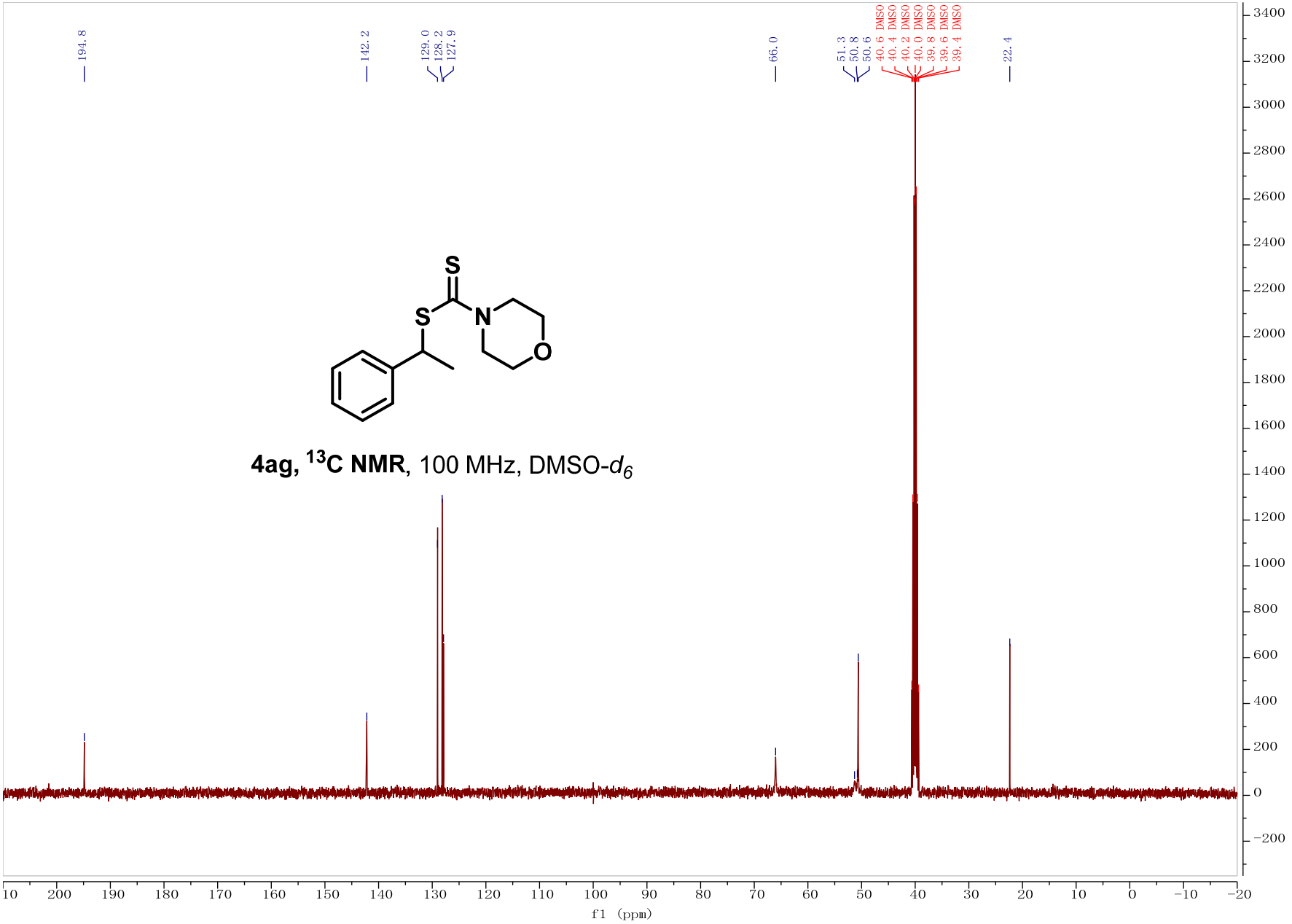

194.7
128.5
127.9
127.4
77.4 CDCl3
77.1 CDCl3
76.8 CDCl3
51.9
51.0
50.4
34.0
33.6
31.0
22.2
21.3
S
S
N
4ae, 13C NMR, 100 MHz, CDCl3
f1 (ppm)

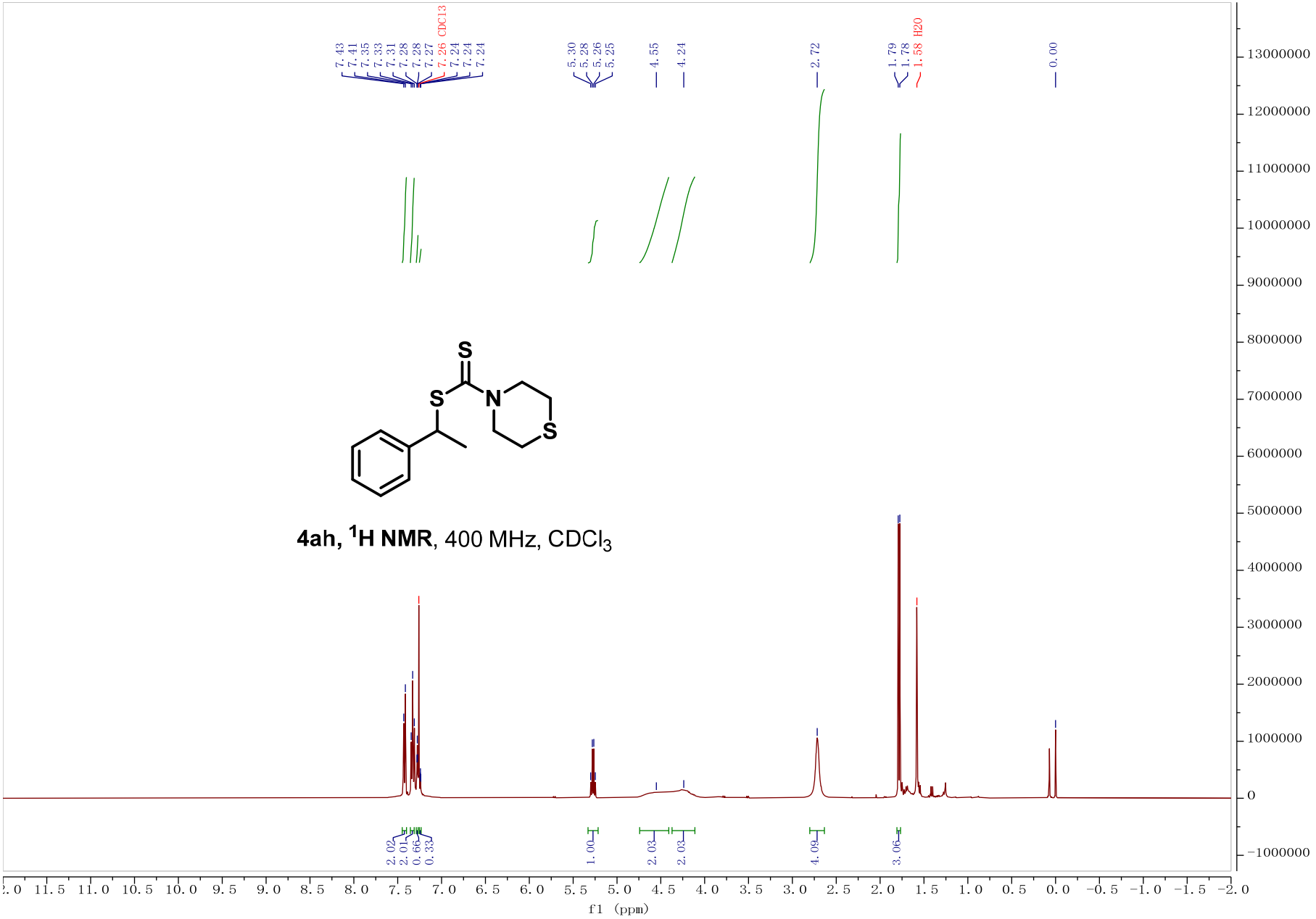

7.48
7.46
7.40
7.38
7.36
7.33
7.31
7.26
5.31
5.29
5.27
5.25
5.24
5.07
5.03
5.00
4.96
4.35
4.02
3.38 H2O
2.98
2.97
2.95
2.55 DMSO
2.54 DMSO
2.54 DMSO
2.53 DMSO
1.77
1.76
S
S
N
4af, 1H NMR, 400 MHz, DMSO-d6
2.01
2.02
5.00
2.04
0.95
0.97
1.04
2.00
3.00
f1 (ppm)

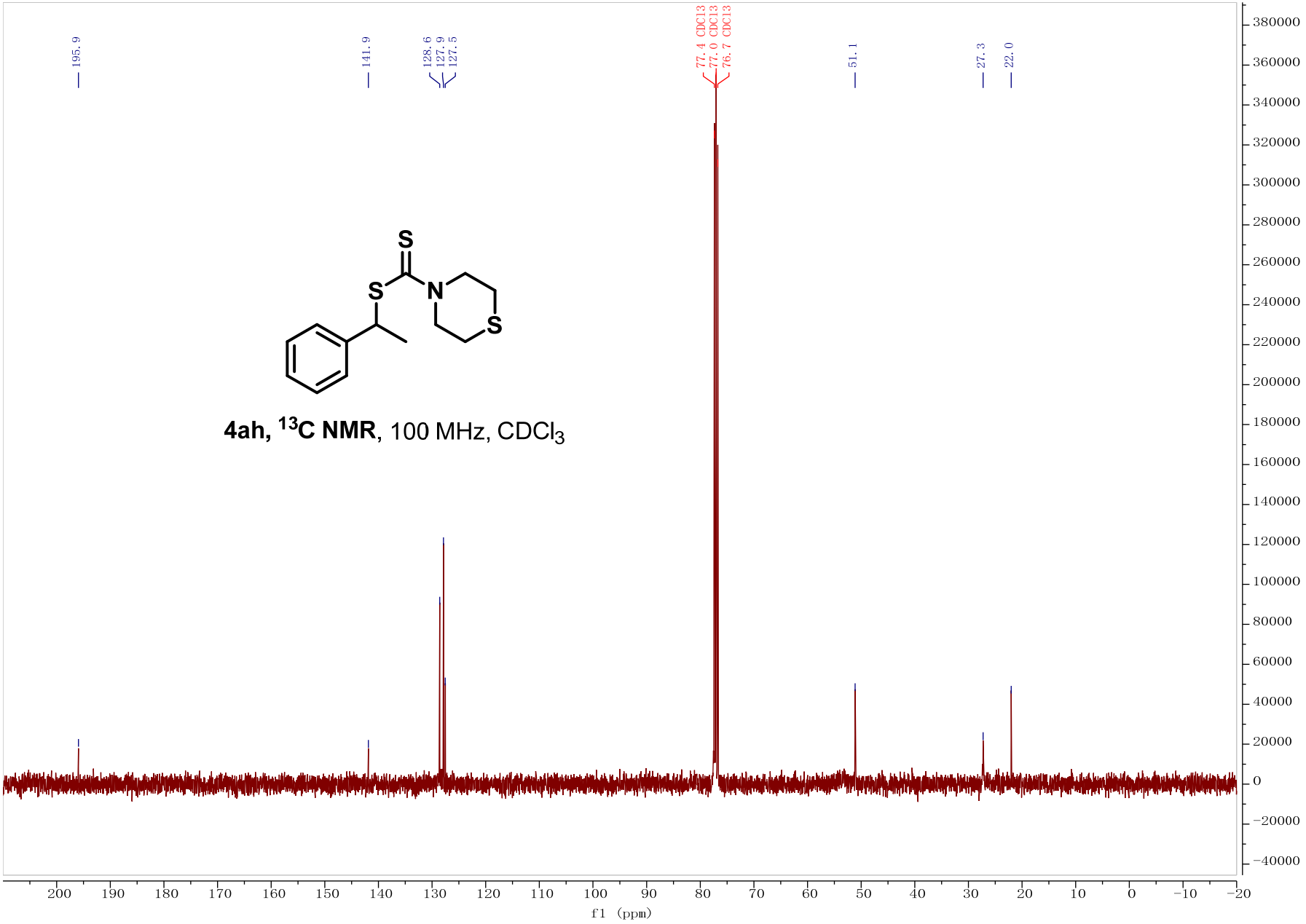

194.1
142.2
135.4
135.1
129.0
128.3
128.2
127.9
127.6
127.5
126.9
53.5
51.4
50.5
50.1
48.2
40.6 DMSO
40.4 DMSO
40.2 DMSO
40.0 DMSO
39.8 DMSO
39.6 DMSO
39.4 DMSO
28.7
28.2
22.3
S
S
N
4af, 13C NMR, 100 MHz, DMSO-d6
2500
2000
1500
1000
500
0
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

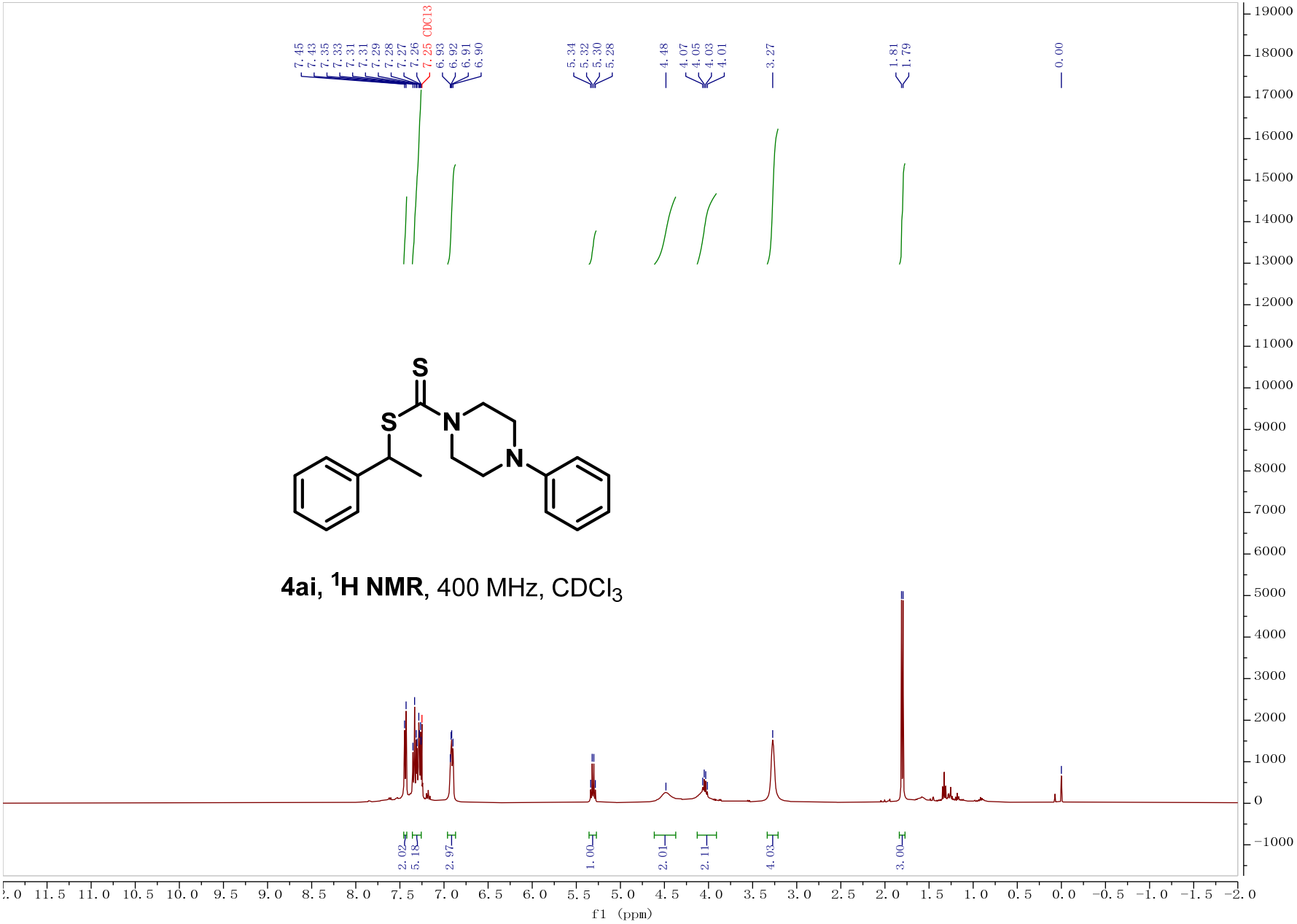


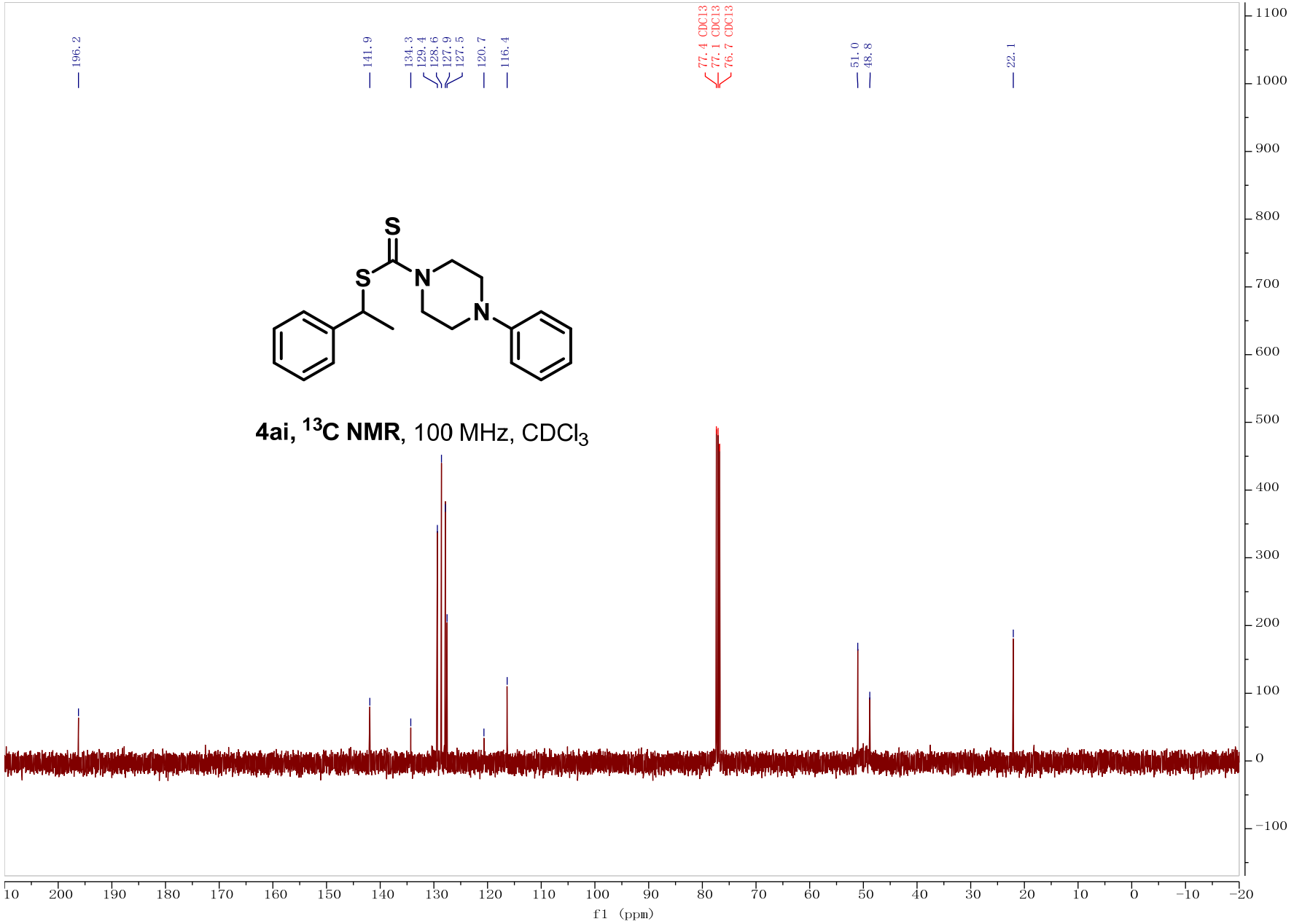
4ag, ^{1}H NMR, 400 MHz, DMSO-d_6

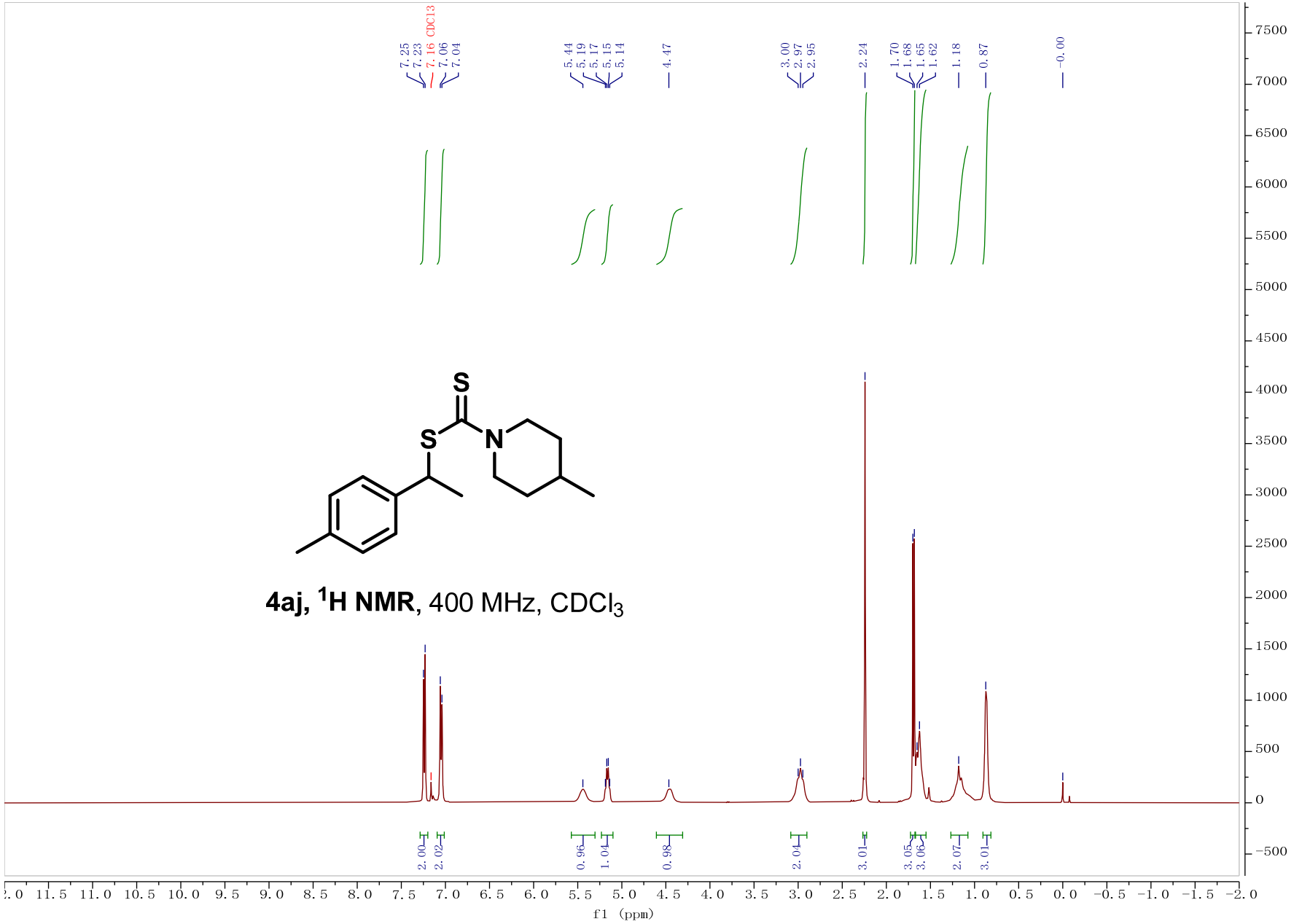

194.8
142.2
129.0
128.2
127.9
66.0
51.3
50.8
50.6
40.6 DMSO
40.4 DMSO
40.2 DMSO
40.0 DMSO
39.8 DMSO
39.6 DMSO
39.4 DMSO
22.4
S
S
N
O
4ag, 13C NMR, 100 MHz, DMSO-d6
f1 (ppm)

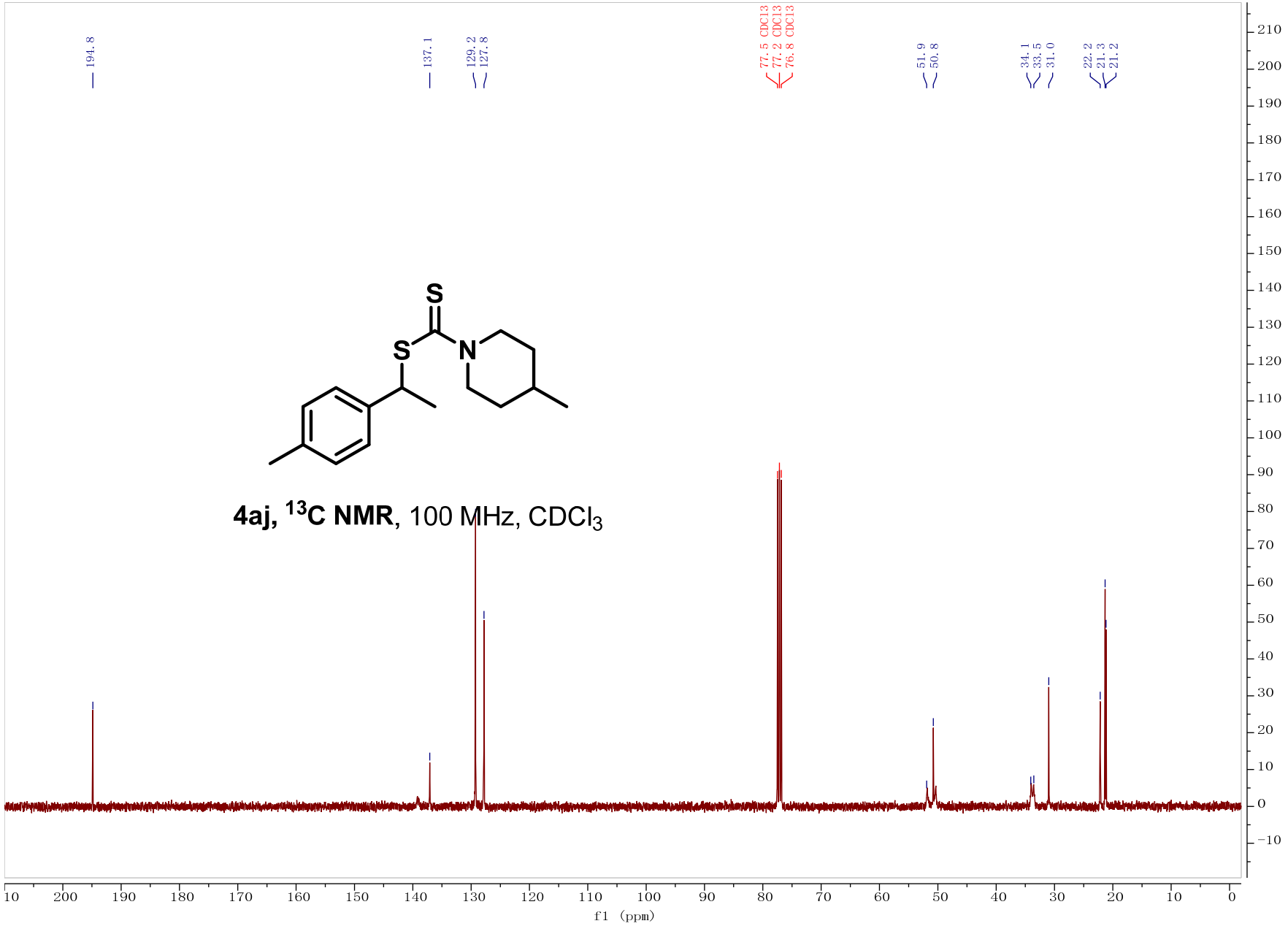

7.43
7.41
7.35
7.33
7.31
7.28
7.28
7.27
7.26 CDCl3
7.24
7.24
7.24
5.30
5.28
5.26
5.25
4.55
4.24
2.72
1.79
1.78
1.58 H2O
0.00
S
S
N
S
4ah, 1H NMR, 400 MHz, CDCl3
2.02
2.01
0.66
0.33
1.00
2.03
2.03
4.09
3.06
f1 (ppm)


195.9
141.9
128.6
127.9
127.5
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
51.1
27.3
22.0
S
S
N
S
4ah, 13C NMR, 100 MHz, CDCl3
f1 (ppm)

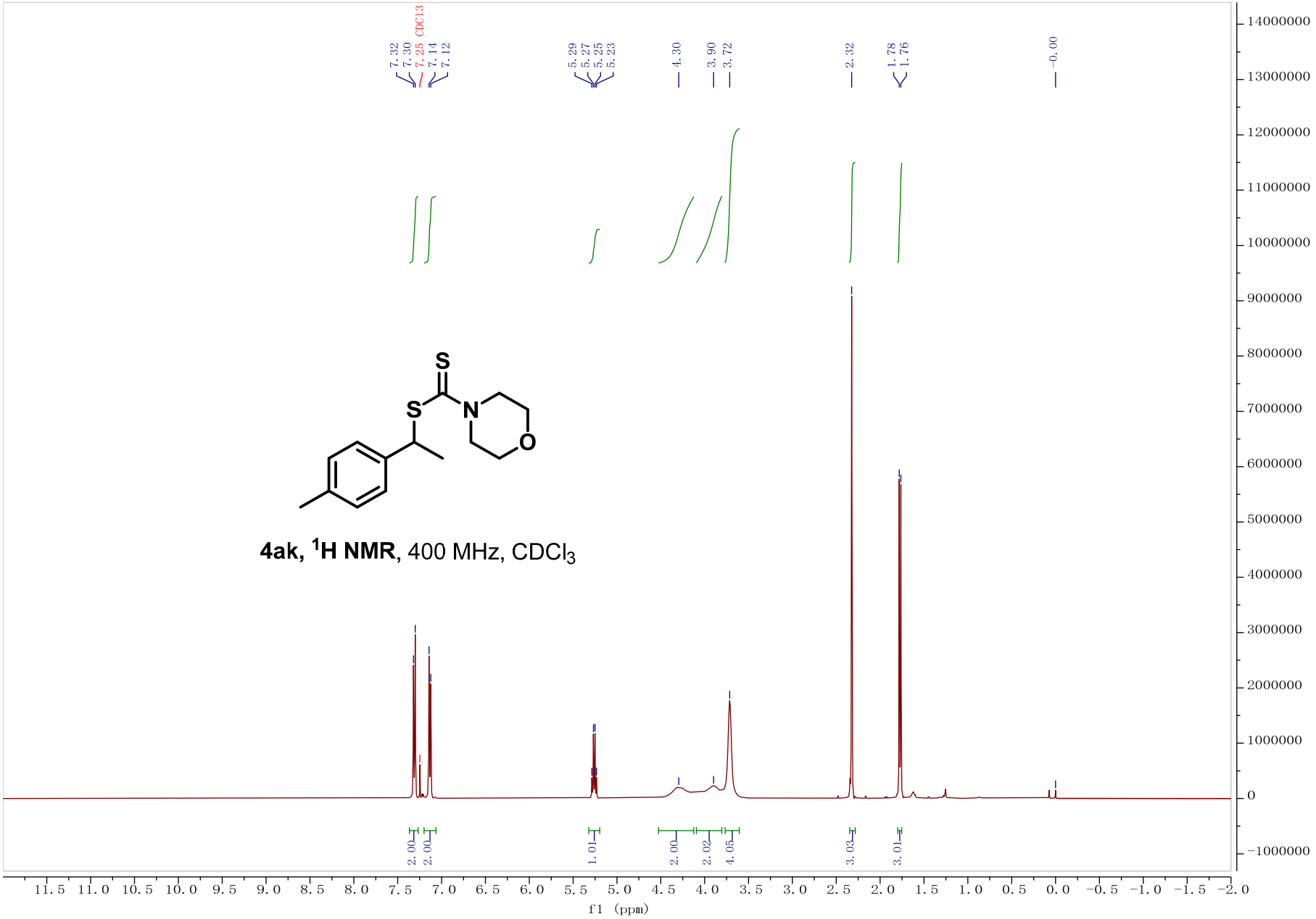

7.45
7.43
7.35
7.33
7.31
7.31
7.29
7.28
7.27
7.26
7.25
CDCl3
6.93
6.92
6.91
6.90
5.34
5.32
5.30
5.28
4.48
4.07
4.05
4.03
4.01
3.27
1.81
1.79
0.00
S
S
N
N
4ai, 1H NMR, 400 MHz, CDCl3
2.02
5.18
2.97
1.00
2.01
2.11
4.03
3.00
f1 (ppm)

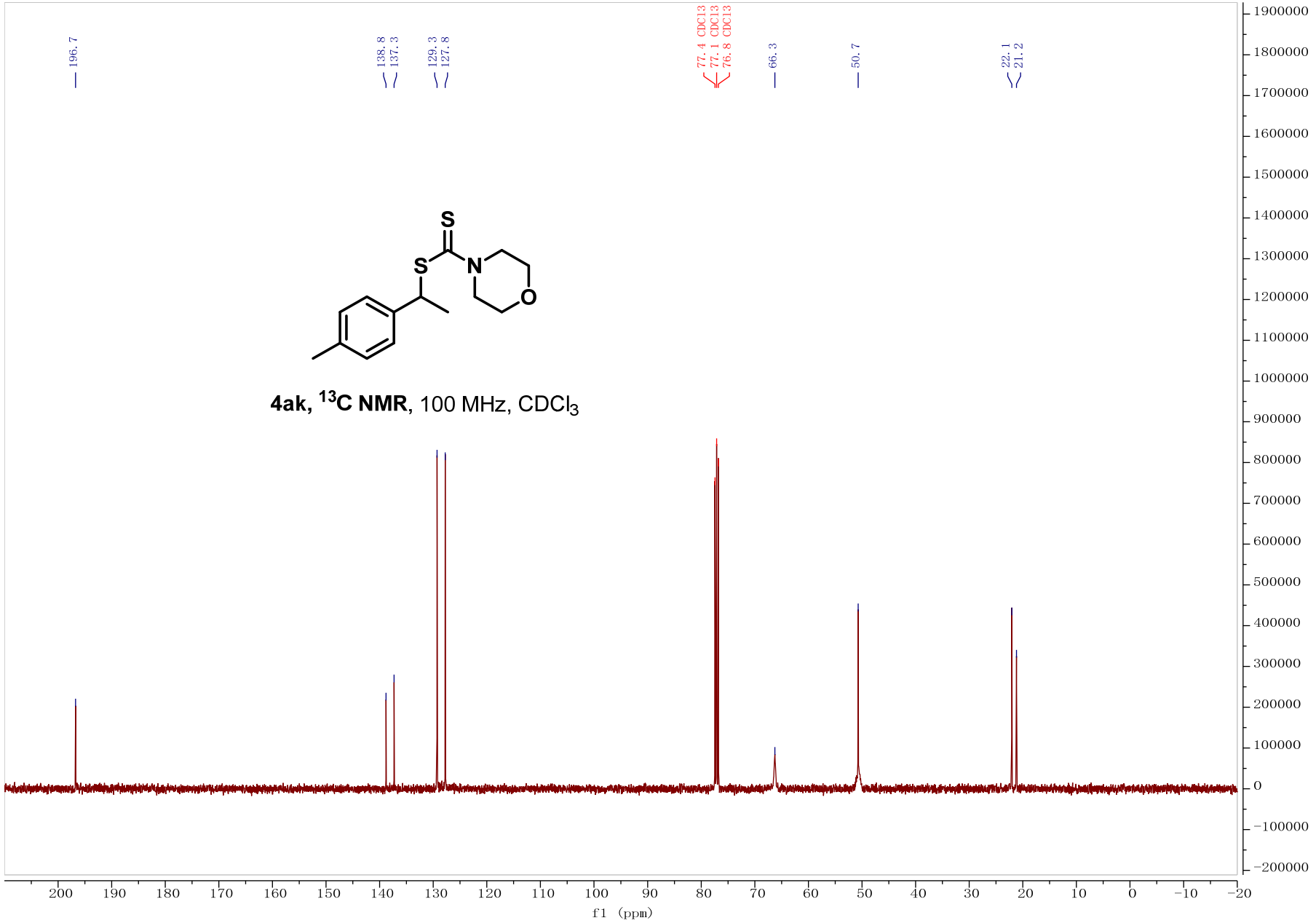

196.2
141.9
134.3
129.4
128.6
127.9
127.5
120.7
116.4
77.4 CDCl3
77.1 CDCl3
76.7 CDCl3
51.0
48.8
22.1
S
S
N
N
4ai, 13C NMR, 100 MHz, CDCl3
f1 (ppm)

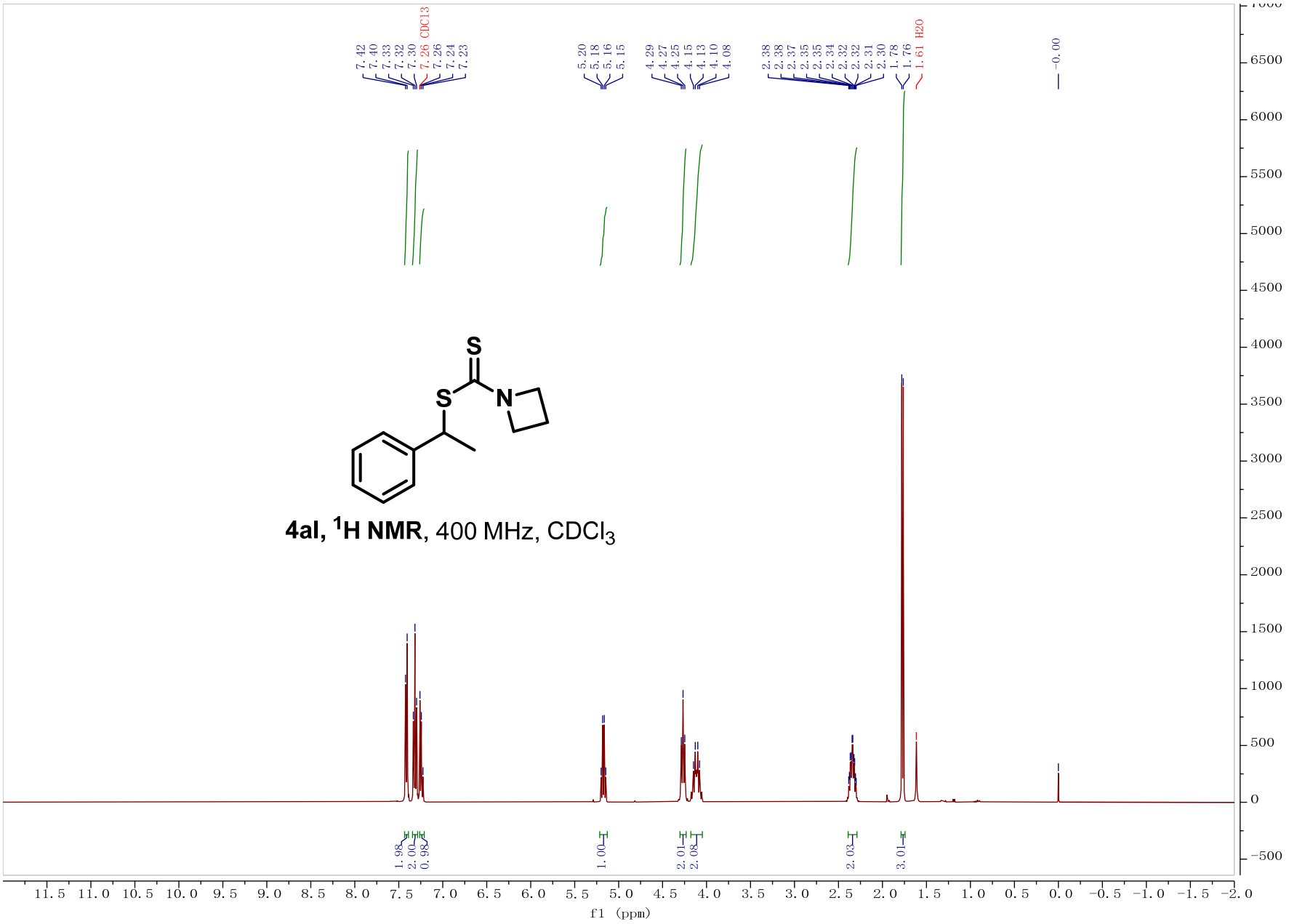

7.25
7.23
7.16 CDCl3
7.06
7.04
5.44
5.19
5.17
5.15
5.14
4.47
3.00
2.97
2.95
2.24
1.70
1.68
1.65
1.62
1.18
0.87
-0.00
S
S
N
4aj, 1H NMR, 400 MHz, CDCl3
2.00
2.02
0.96
1.04
0.98
2.04
3.01
3.05
3.06
2.07
3.01
f1 (ppm)

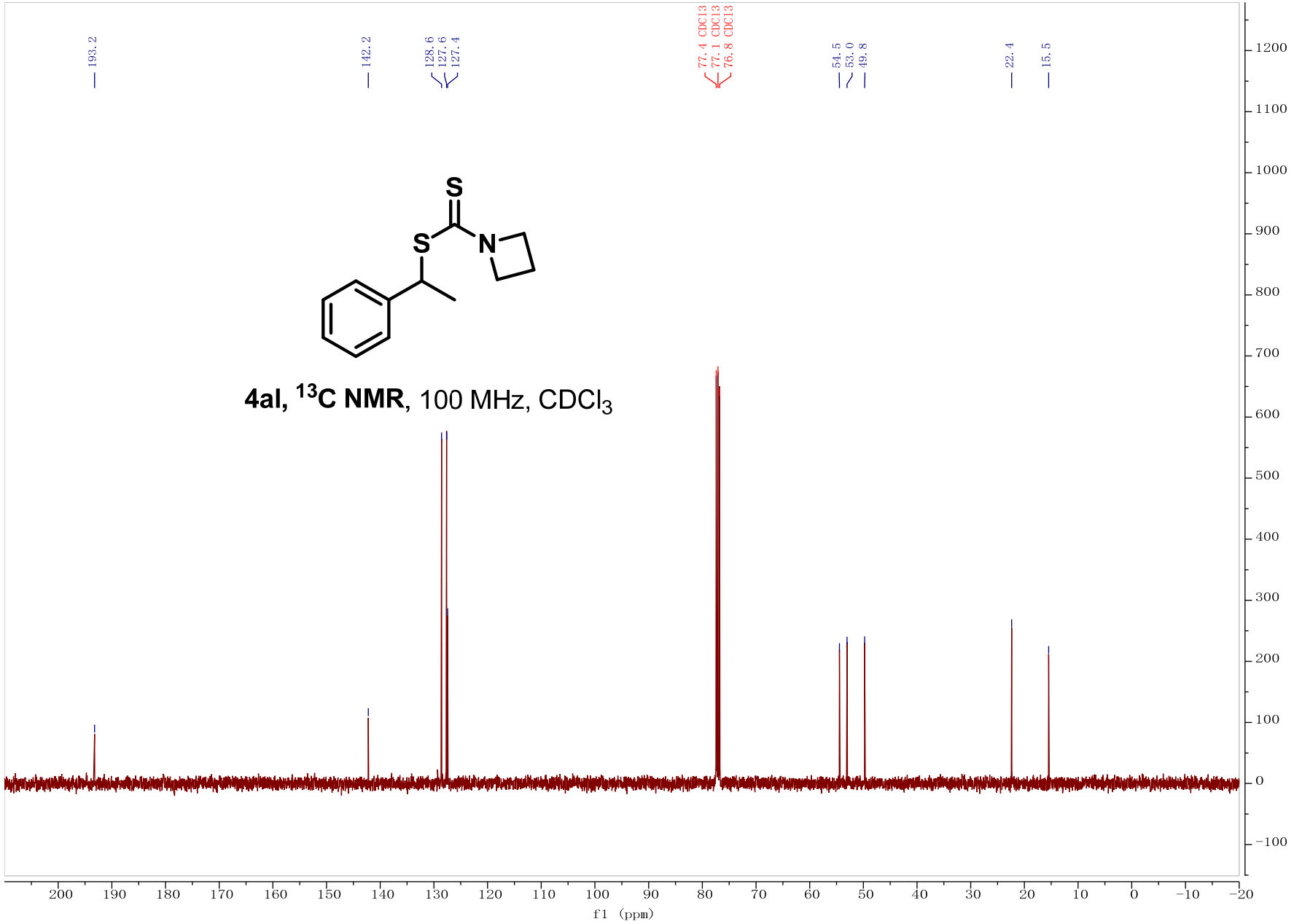


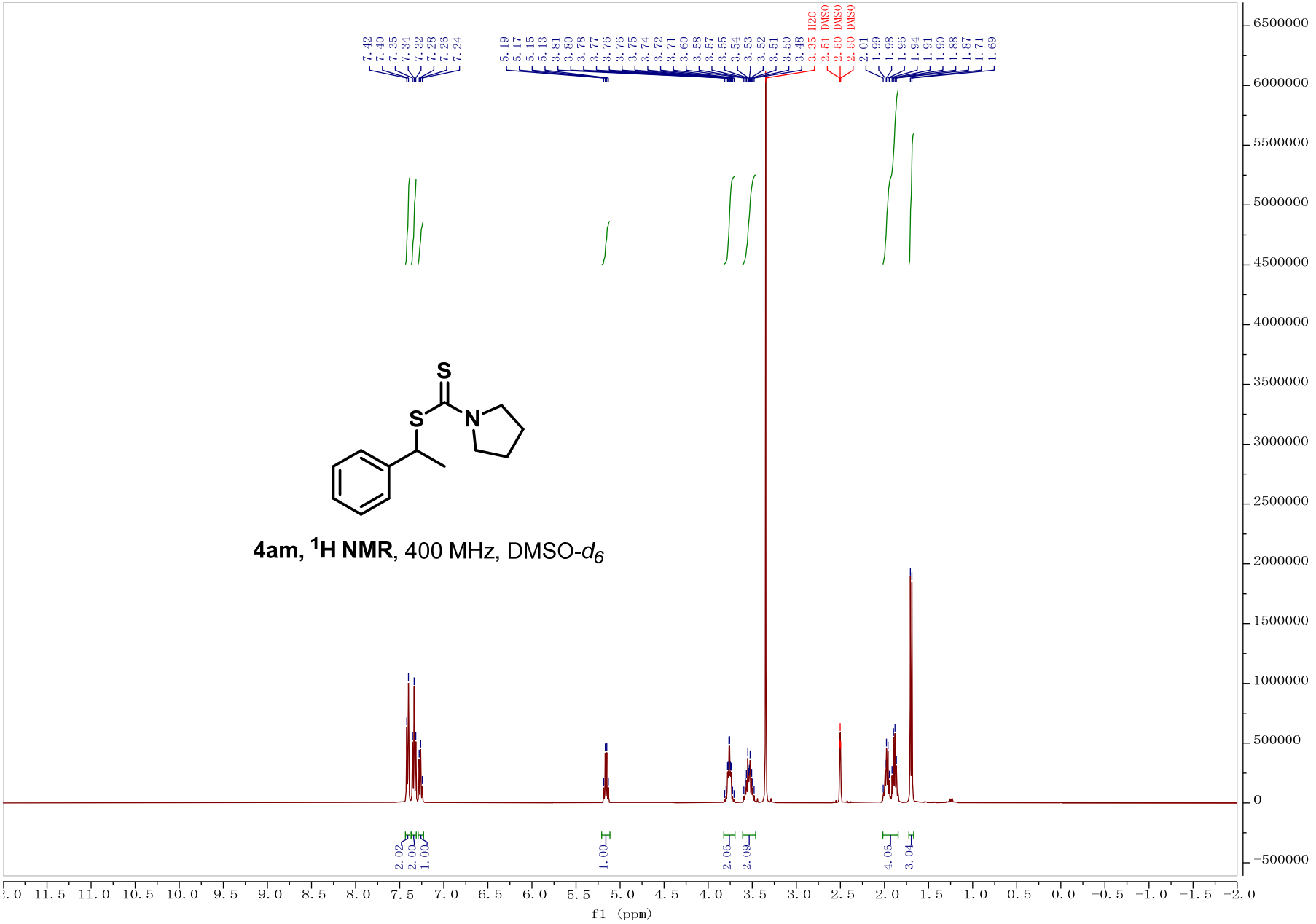
4aj, ^{13}C NMR, 100 MHz, $CDCl_3$

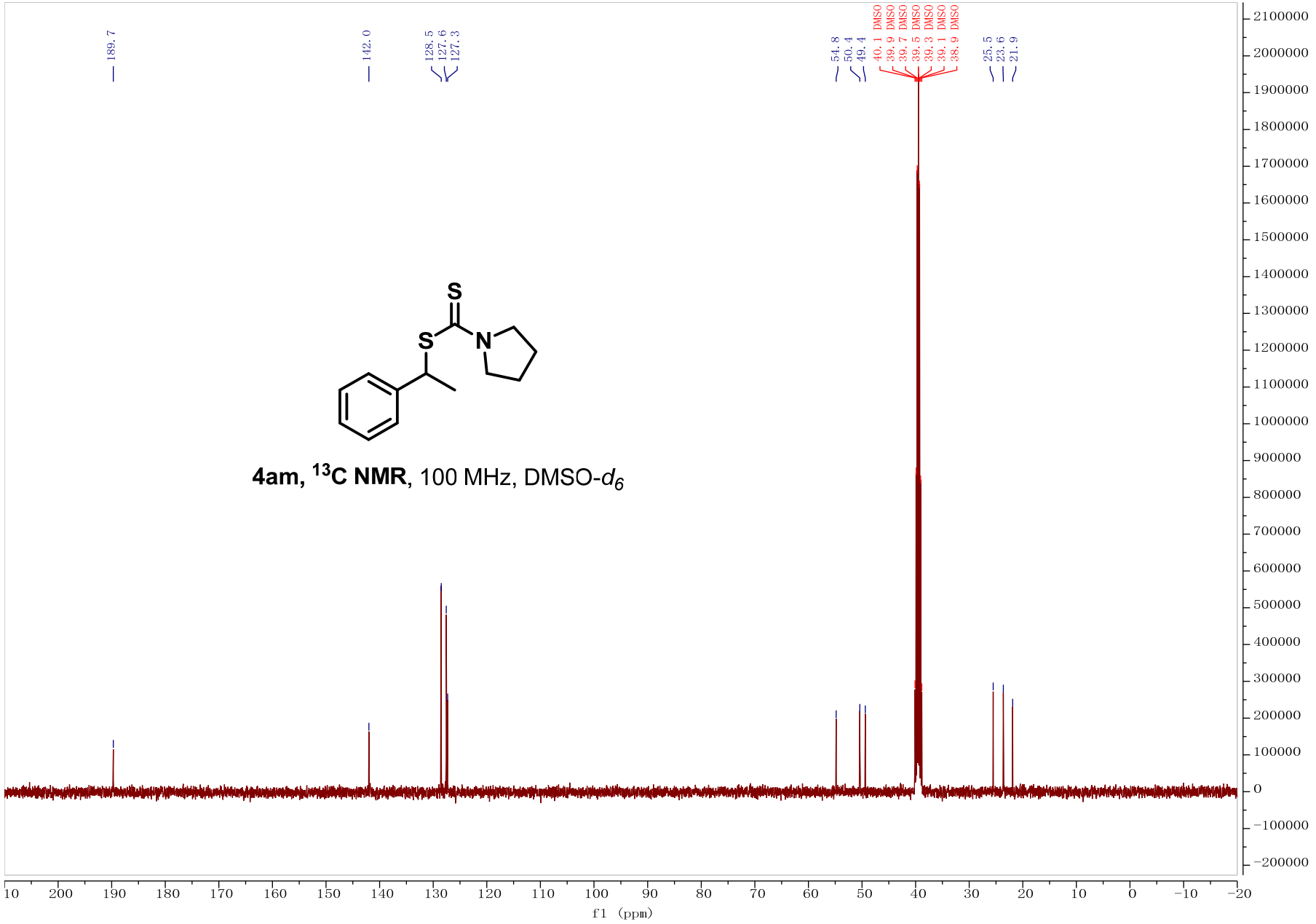

7.32
7.30
7.25 CDCl3
7.14
7.12
5.29
5.27
5.25
5.23
4.30
3.90
3.72
2.32
1.78
1.76
-0.00
S
S
N
O
4ak, 1H NMR, 400 MHz, CDCl3
2.00
2.00
1.01
2.00
2.02
4.05
3.03
3.01
f1 (ppm)

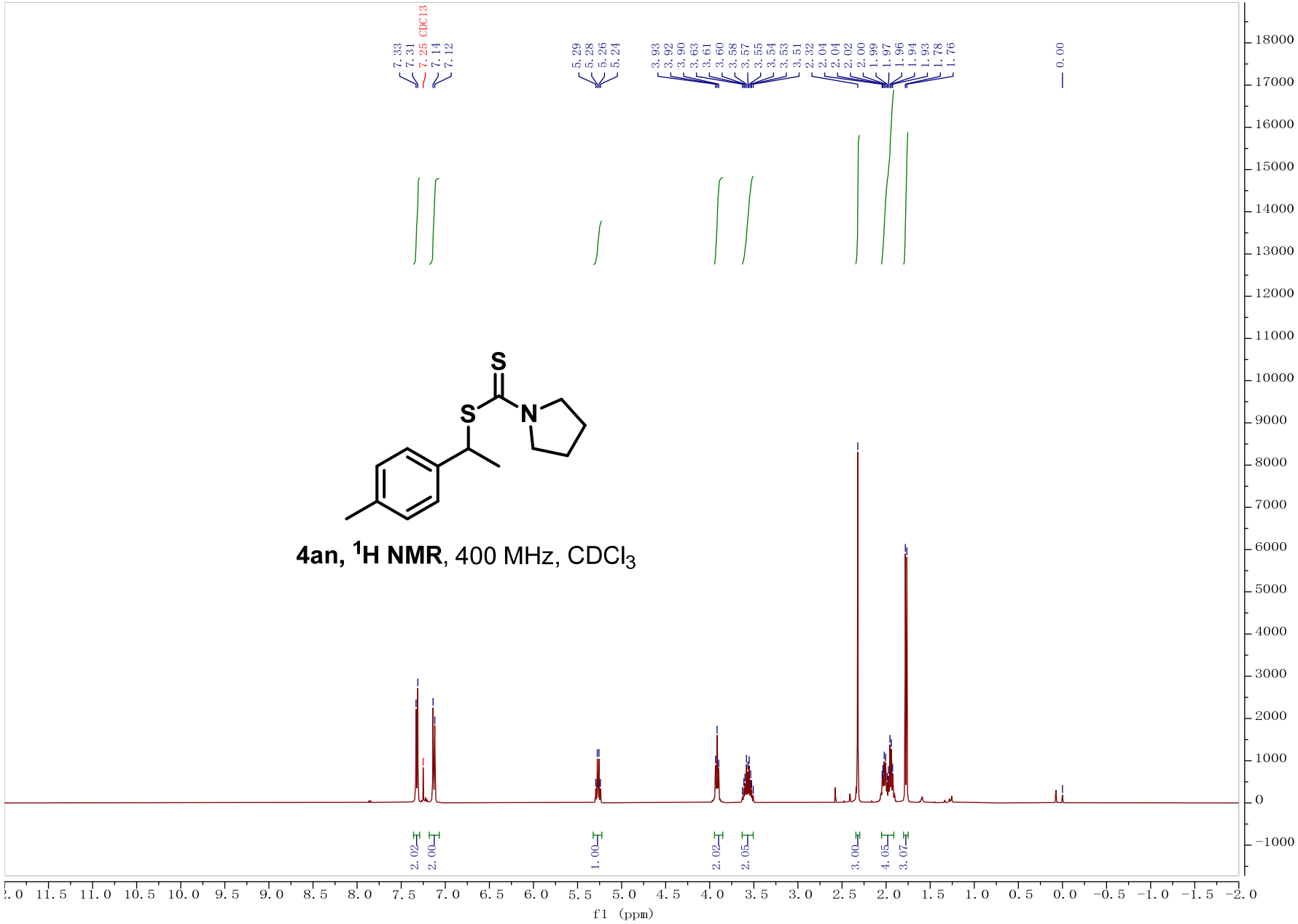

196.7
138.8
137.3
129.3
127.8
77.4 CDCl3
77.1 CDCl3
76.8 CDCl3
66.3
50.7
22.1
21.2
S
S
N
O
4ak, 13C NMR, 100 MHz, CDCl3
f1 (ppm)

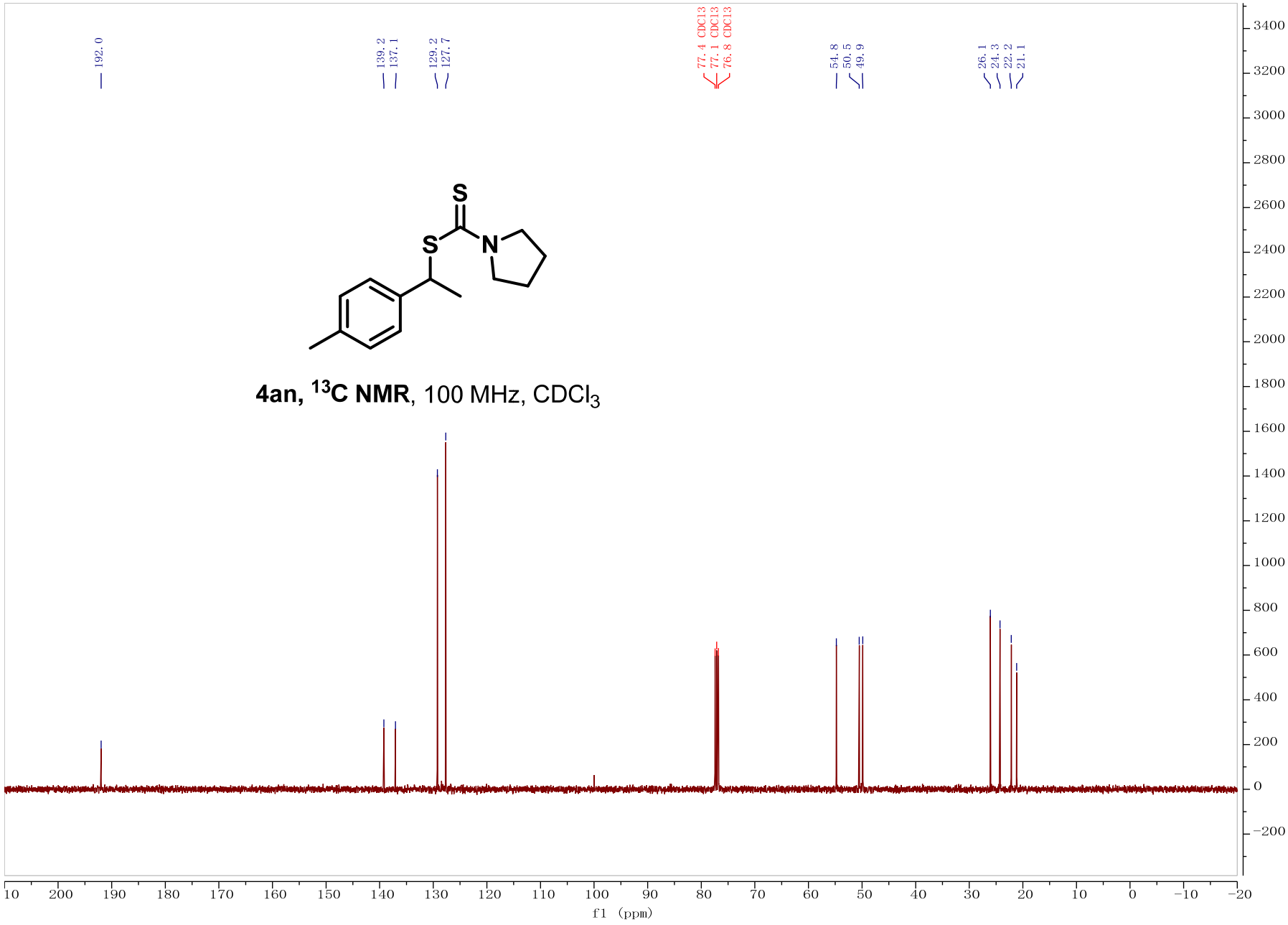

7.42
7.40
7.33
7.32
7.30
7.26 CDCl3
7.26
7.24
7.23
5.20
5.18
5.16
5.15
4.29
4.27
4.25
4.15
4.13
4.10
4.08
2.38
2.38
2.37
2.35
2.35
2.34
2.32
2.32
2.31
2.30
1.78
1.76
1.61 H2O
0.00
S
S
N
4al, 1H NMR, 400 MHz, CDCl3
1.98
2.00
0.98
1.00
2.01
2.08
2.03
3.01
f1 (ppm)


193.2
142.2
128.6
127.6
127.4
77.4 CDCl3
77.1 CDCl3
76.8 CDCl3
54.5
53.0
49.8
22.4
15.5
S
S
N
4aI, 13C NMR, 100 MHz, CDCl3
f1 (ppm)

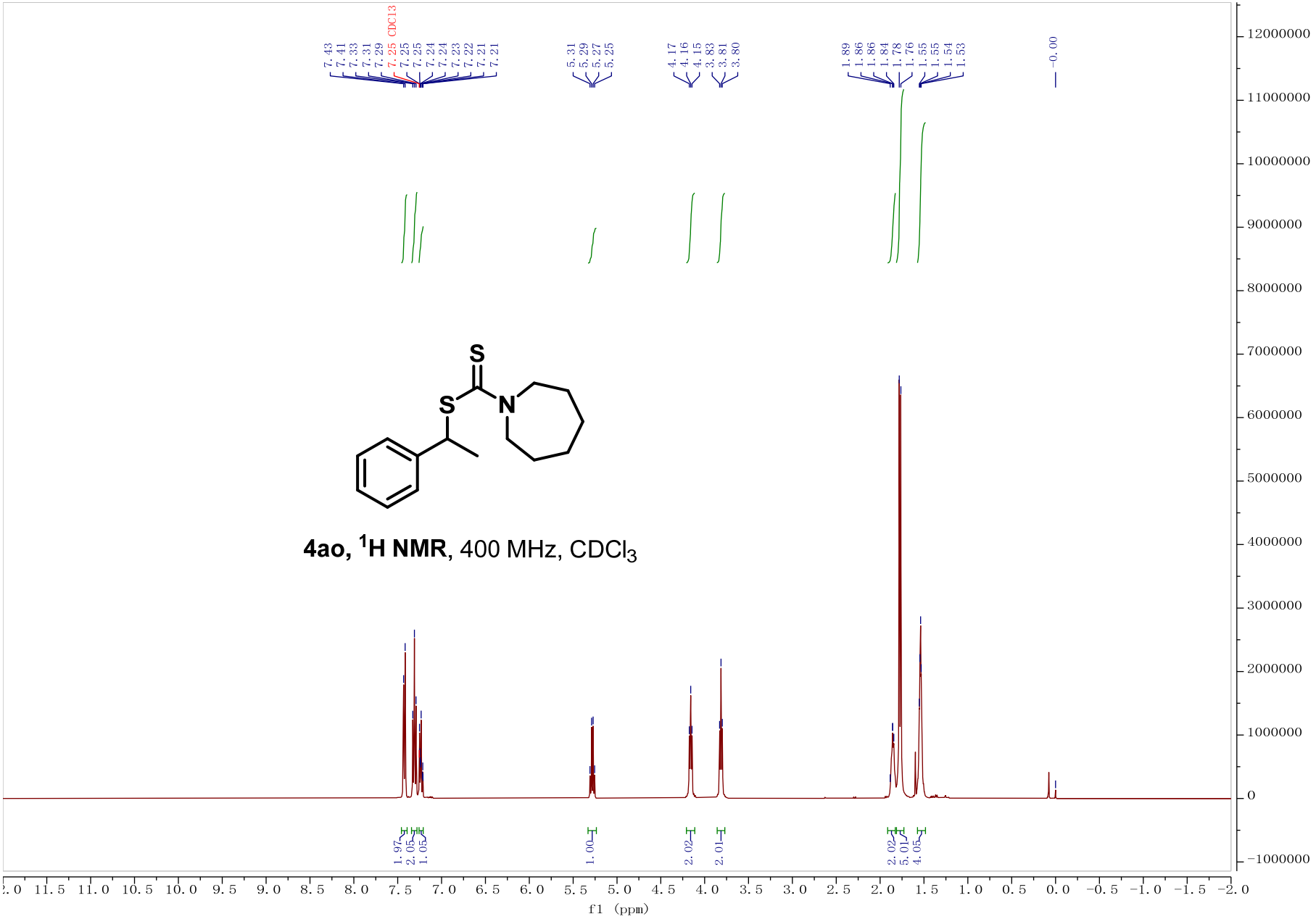

7.42
7.40
7.35
7.34
7.32
7.28
7.26
7.24
5.19
5.17
5.15
5.13
3.81
3.80
3.78
3.77
3.76
3.76
3.75
3.74
3.72
3.71
3.60
3.58
3.57
3.55
3.54
3.53
3.52
3.51
3.50
3.48
3.35
H2O
2.51
DMSO
2.50
DMSO
2.50
DMSO
2.01
1.99
1.98
1.96
1.94
1.91
1.90
1.88
1.87
1.71
1.69
S
S
N
4am, 1H NMR, 400 MHz, DMSO-d6
2.02
2.00
1.00
1.00
2.06
2.09
4.06
3.04
f1 (ppm)

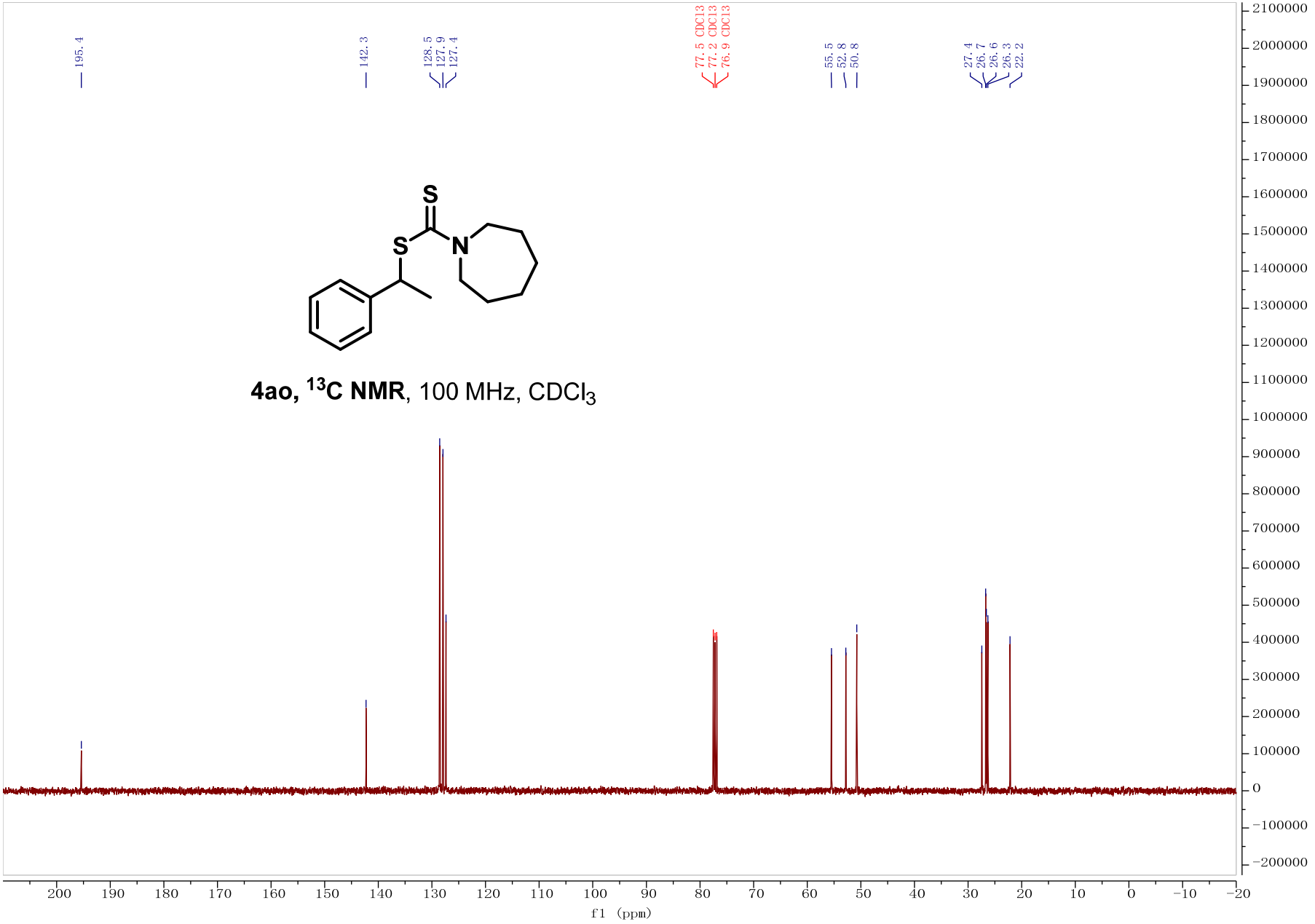

189.7
142.0
128.5
127.6
127.3
54.8
50.4
49.4
40.1 DMSO
39.9 DMSO
39.7 DMSO
39.5 DMSO
39.3 DMSO
39.1 DMSO
38.9 DMSO
25.5
23.6
21.9
S
S
N
4am, 13C NMR, 100 MHz, DMSO-d6
f1 (ppm)

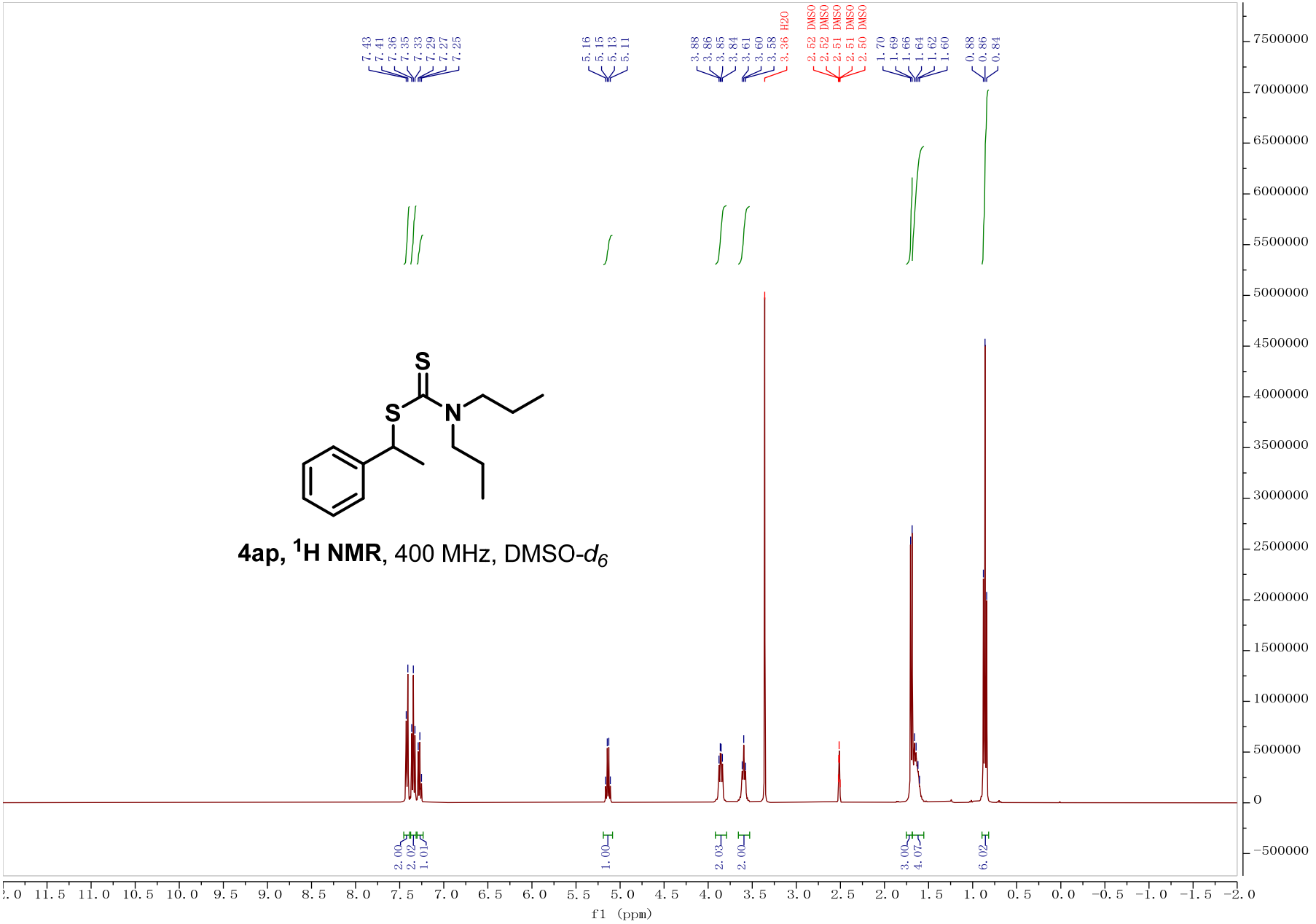

7.33
7.31
CDCl3
7.25
7.14
7.12
5.29
5.28
5.26
5.24
3.93
3.92
3.90
3.63
3.61
3.60
3.58
3.57
3.55
3.54
3.53
3.51
2.32
2.04
2.04
2.02
2.00
1.99
1.97
1.96
1.94
1.93
1.78
1.76
0.00
S
S
N
4an, 1H NMR, 400 MHz, CDCl3
2.02
2.00
1.00
2.02
2.05
3.00
4.05
3.07
f1 (ppm)



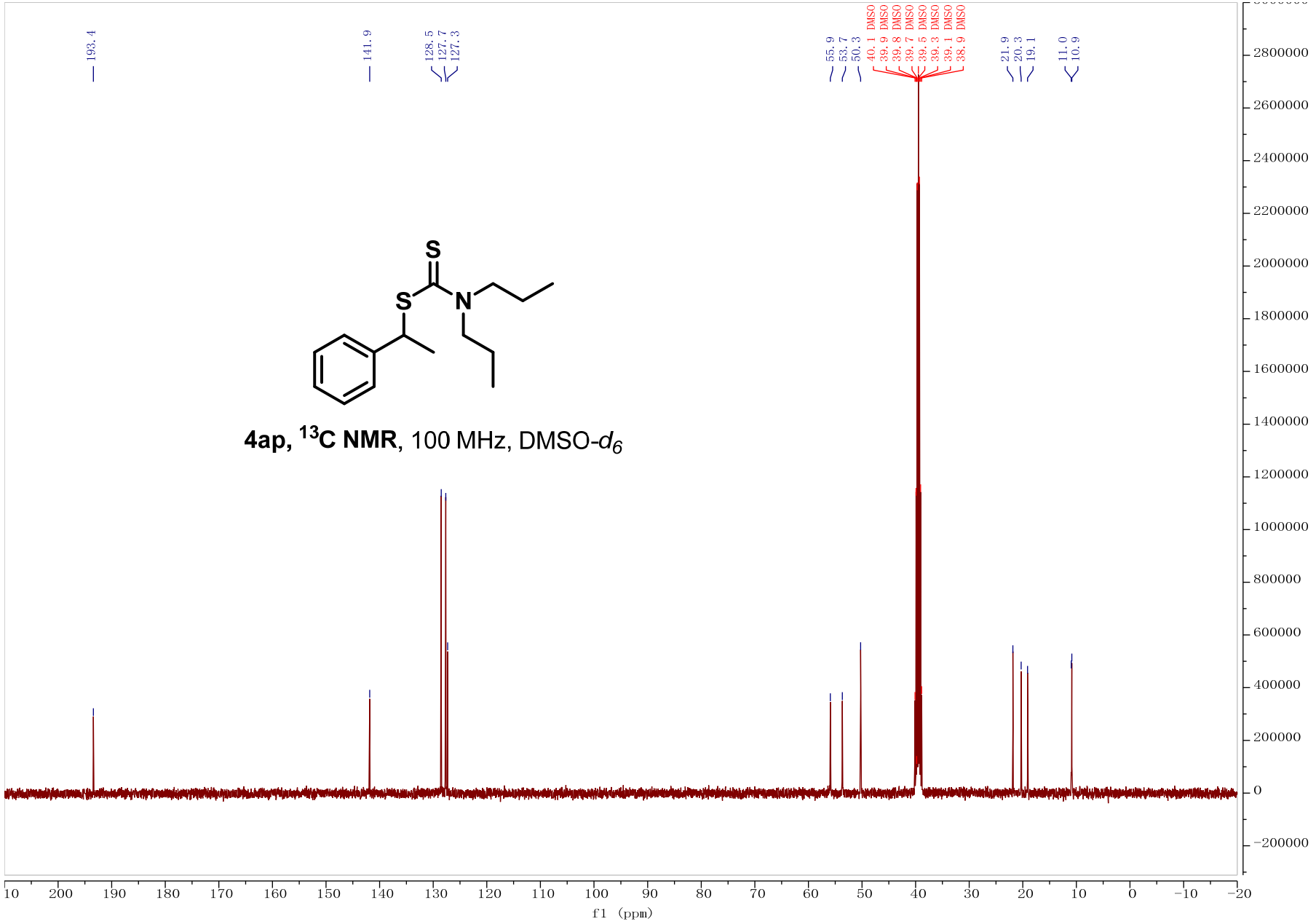
4an, ^{13}C NMR, 100 MHz, $CDCl_3$

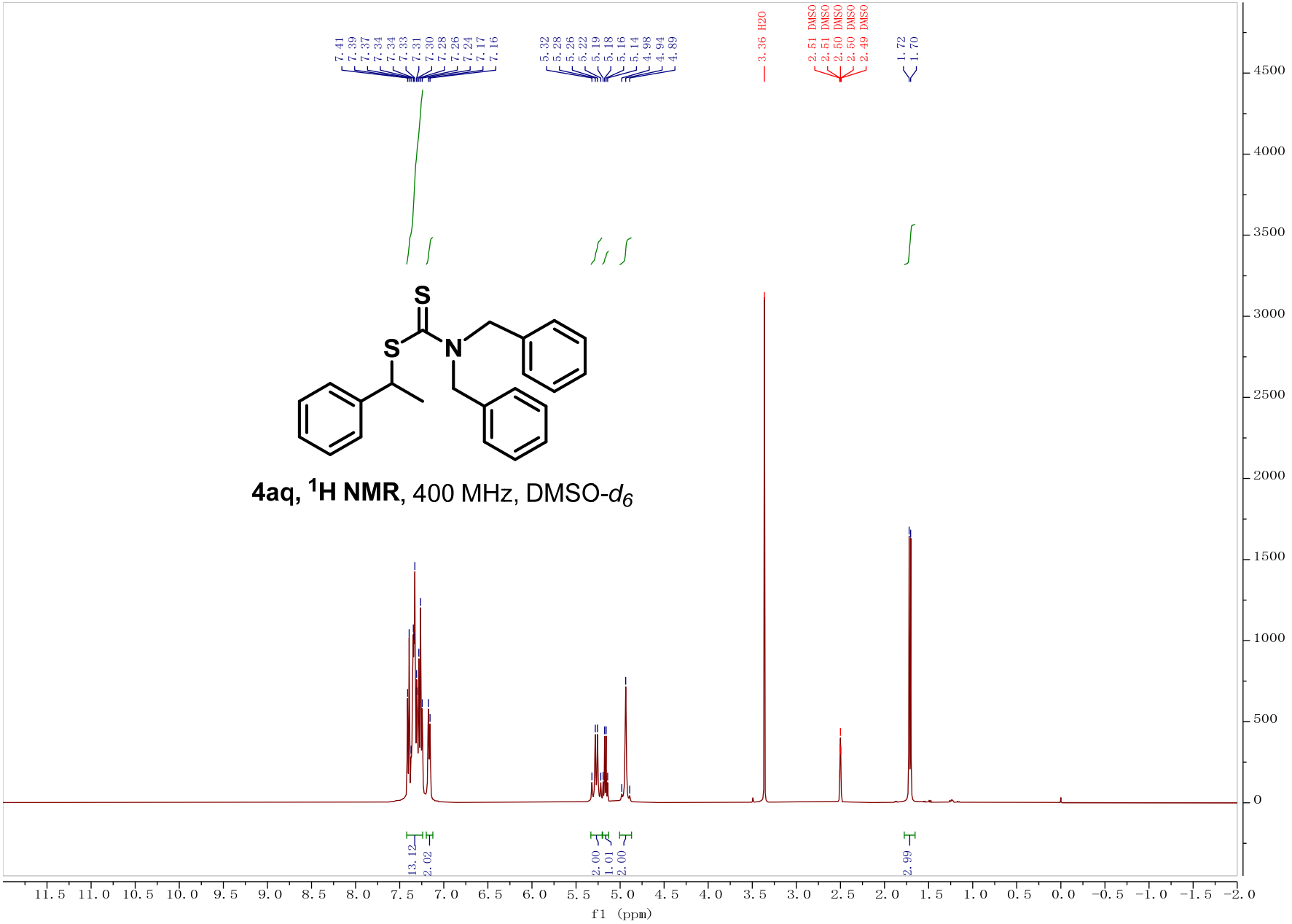

7.43
7.41
7.33
7.31
7.29
7.25 CDCl3
7.25
7.25
7.24
7.24
7.23
7.22
7.21
7.21
5.31
5.29
5.27
5.25
4.17
4.16
4.15
3.83
3.81
3.80
1.89
1.86
1.86
1.84
1.78
1.76
1.55
1.55
1.54
1.53
0.00
S
S
N
4ao, 1H NMR, 400 MHz, CDCl3
1.97
2.05
1.05
1.00
2.02
2.01
2.02
5.01
4.05
f1 (ppm)

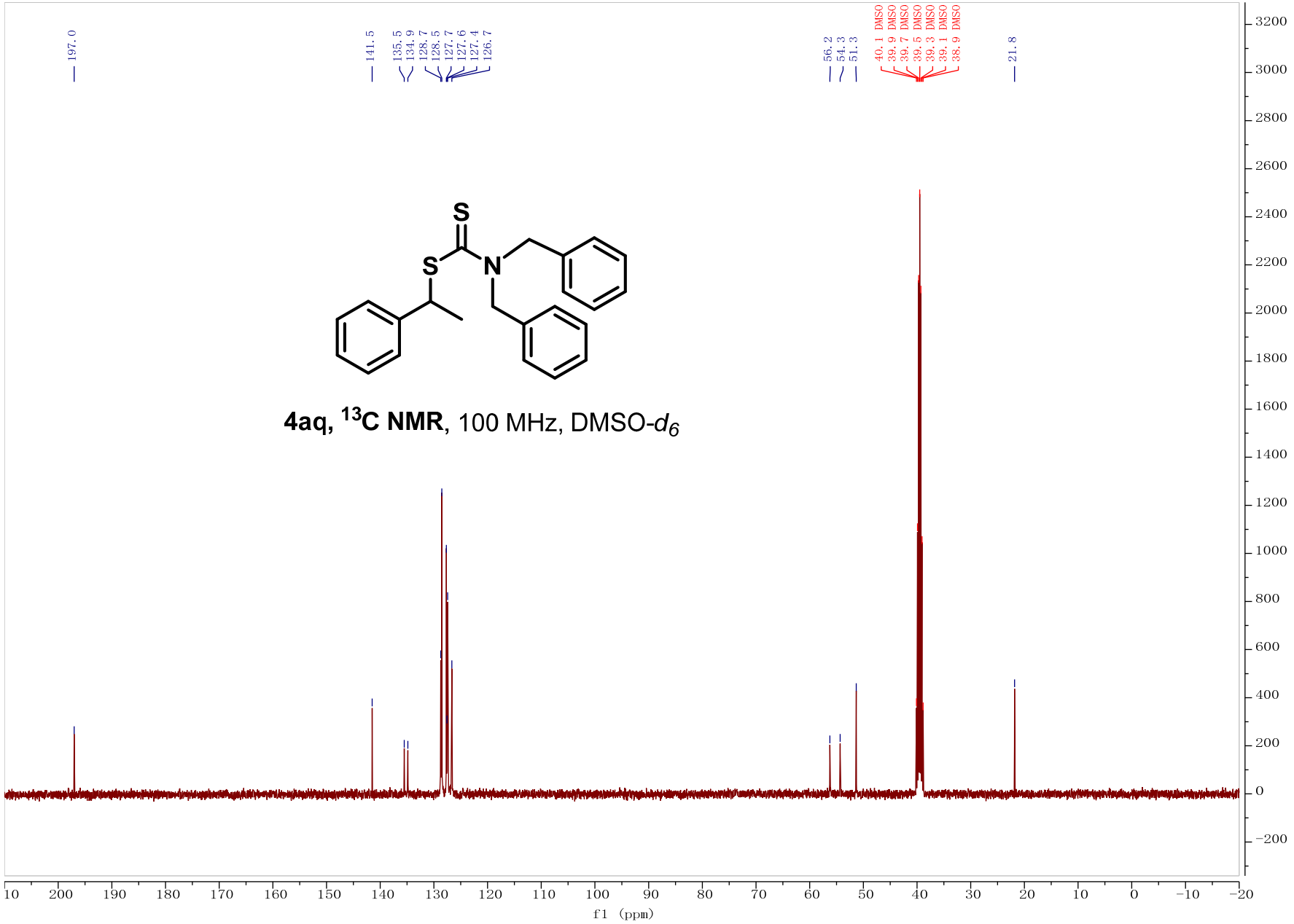

195.4
142.3
128.5
127.9
127.4
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
55.5
52.8
50.8
27.4
26.7
26.6
26.3
22.2
S
S
N
4ao, 13C NMR, 100 MHz, CDCl3
f1 (ppm)

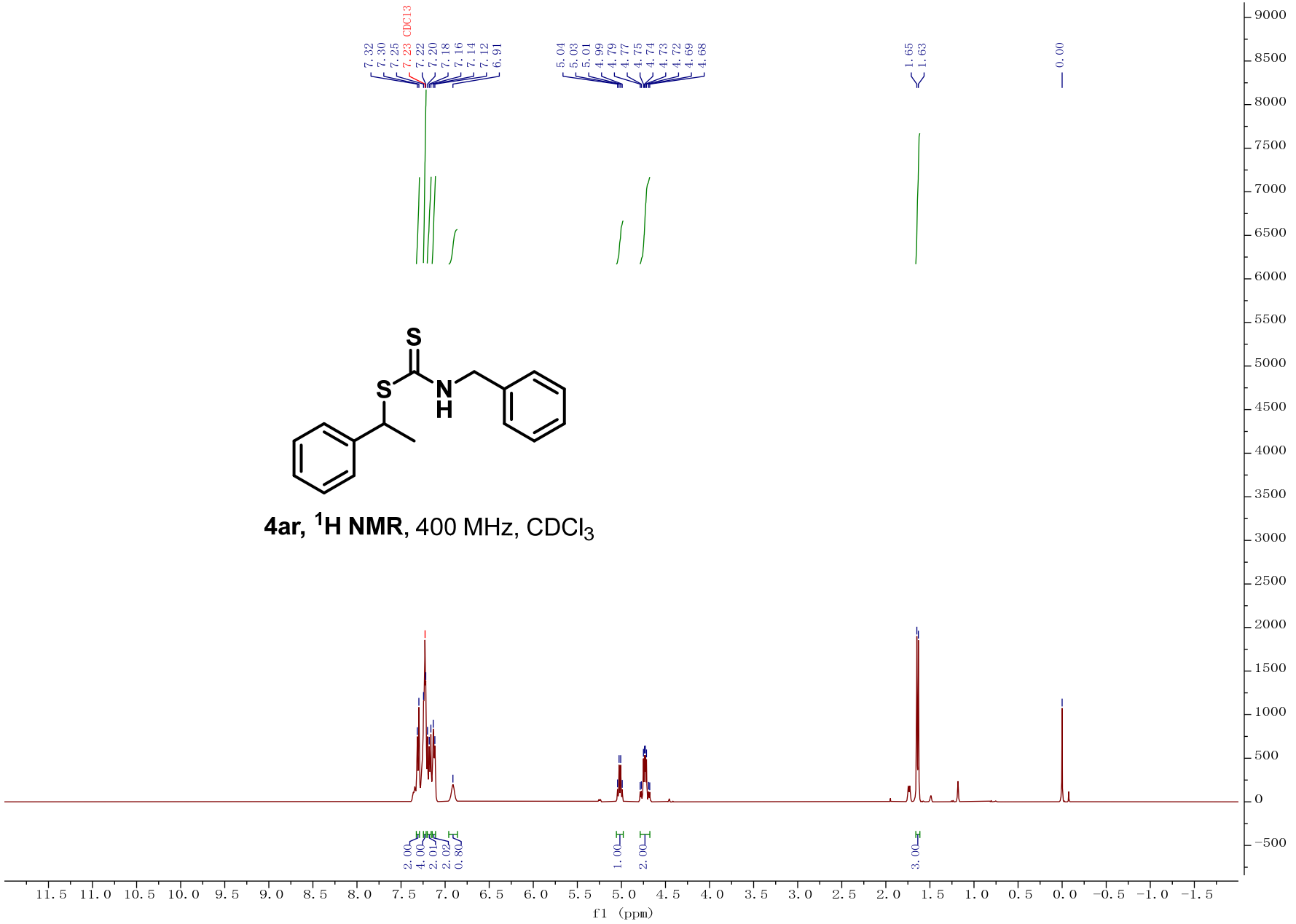


4ap, ^{1}H NMR, 400 MHz, DMSO-d_6

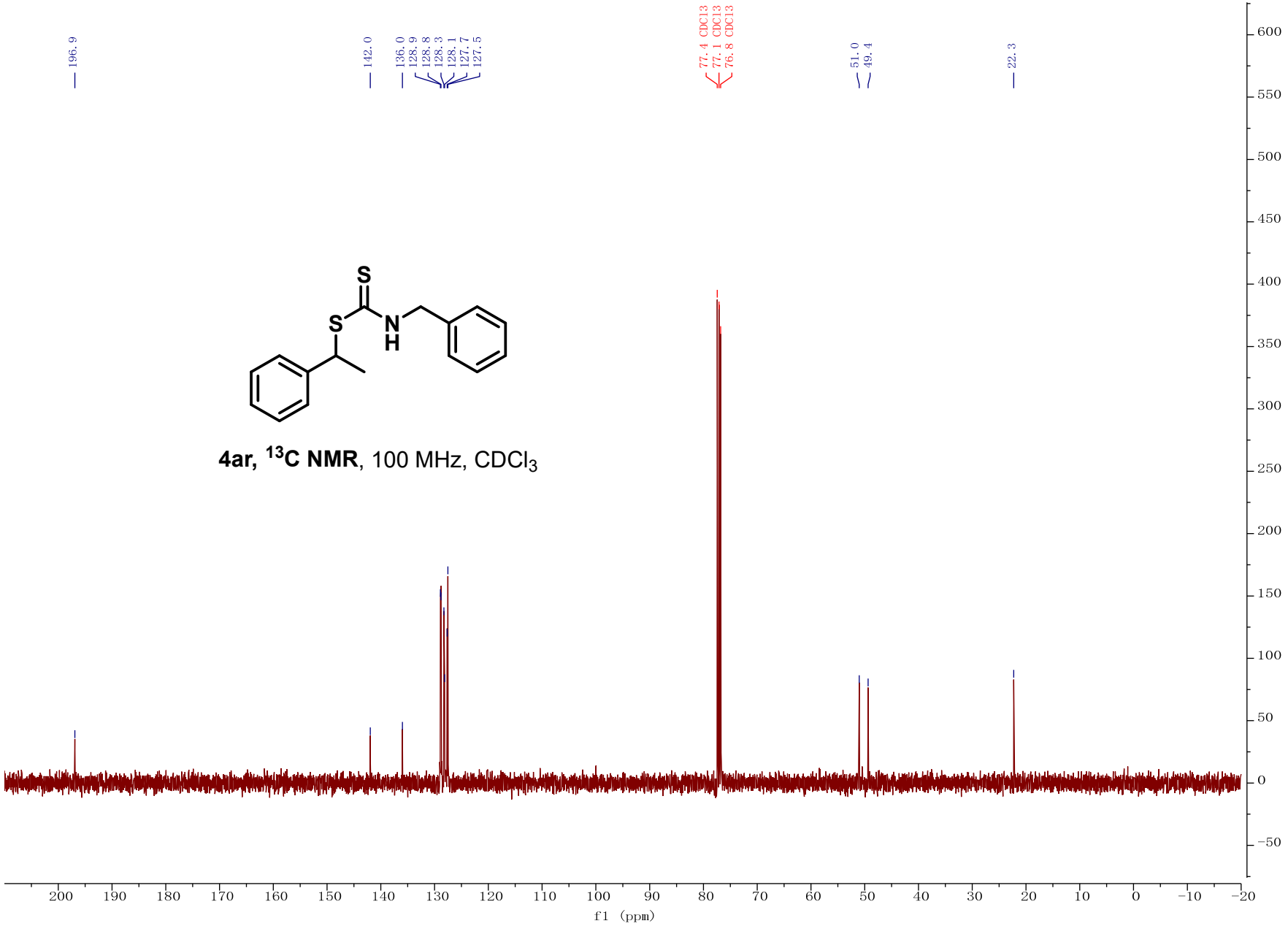

193.4
141.9
128.5
127.7
127.3
55.9
53.7
50.3
40.1 DMSO
39.9 DMSO
39.8 DMSO
39.7 DMSO
39.5 DMSO
39.3 DMSO
39.1 DMSO
38.9 DMSO
21.9
20.3
19.1
11.0
10.9
S
S
N
4ap, 13C NMR, 100 MHz, DMSO-d6
f1 (ppm)


7.41
7.39
7.37
7.34
7.34
7.33
7.31
7.30
7.28
7.26
7.24
7.17
7.16
5.32
5.28
5.26
5.22
5.19
5.18
5.16
5.14
4.98
4.94
4.89
3.36 H2O
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
1.72
1.70
S
S
N
4aq, 1H NMR, 400 MHz, DMSO-d6
13.12
2.02
2.00
1.01
2.00
2.99
f1 (ppm)


197.0
141.5
135.5
134.9
128.7
128.5
127.7
127.6
127.4
126.7
56.2
54.3
51.3
40.1 DMSO
39.9 DMSO
39.7 DMSO
39.5 DMSO
39.3 DMSO
39.1 DMSO
38.9 DMSO
21.8
S
S
N
4aq, ^{13}C NMR, 100 MHz, DMSO-d_6
f1 (ppm)

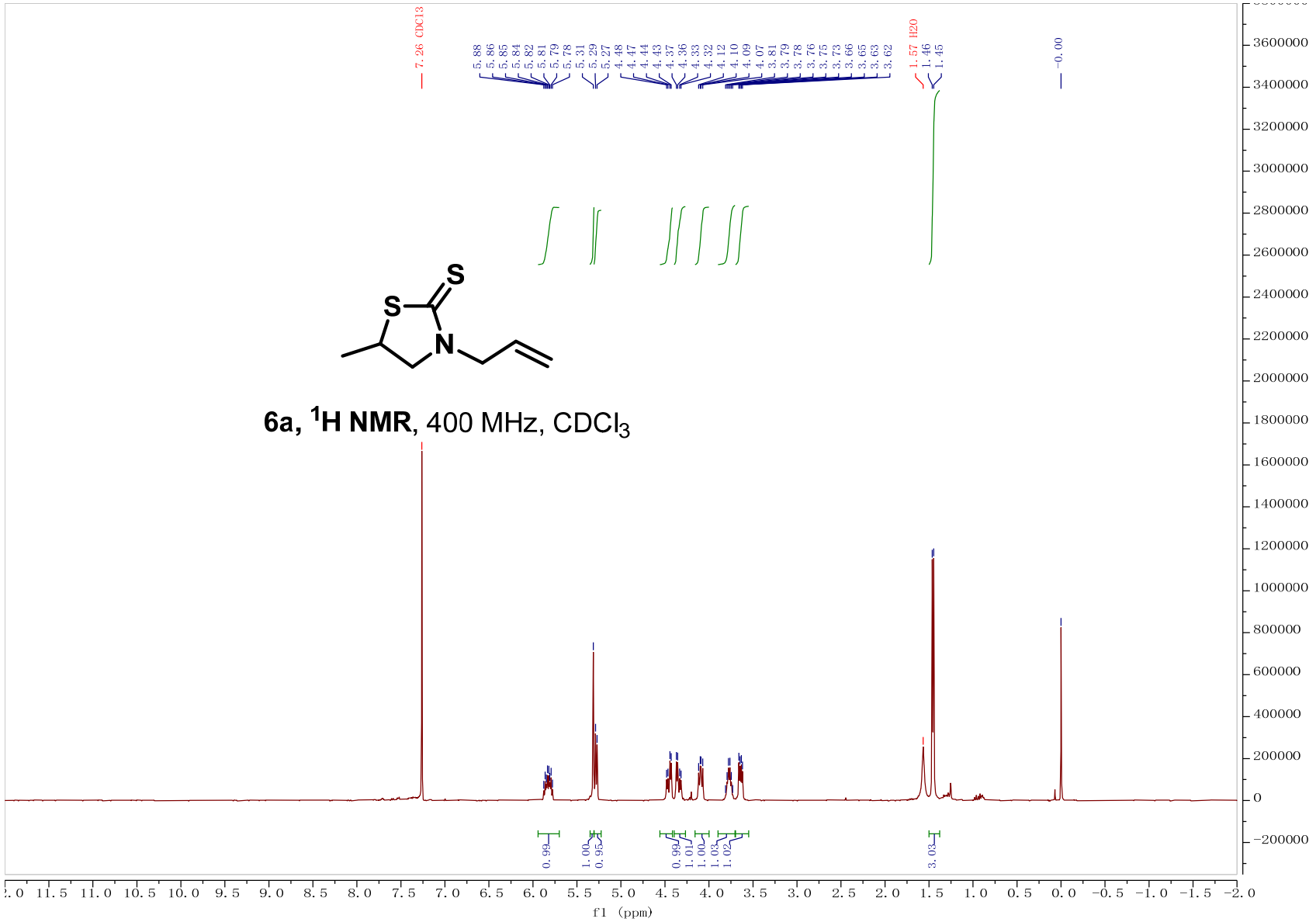


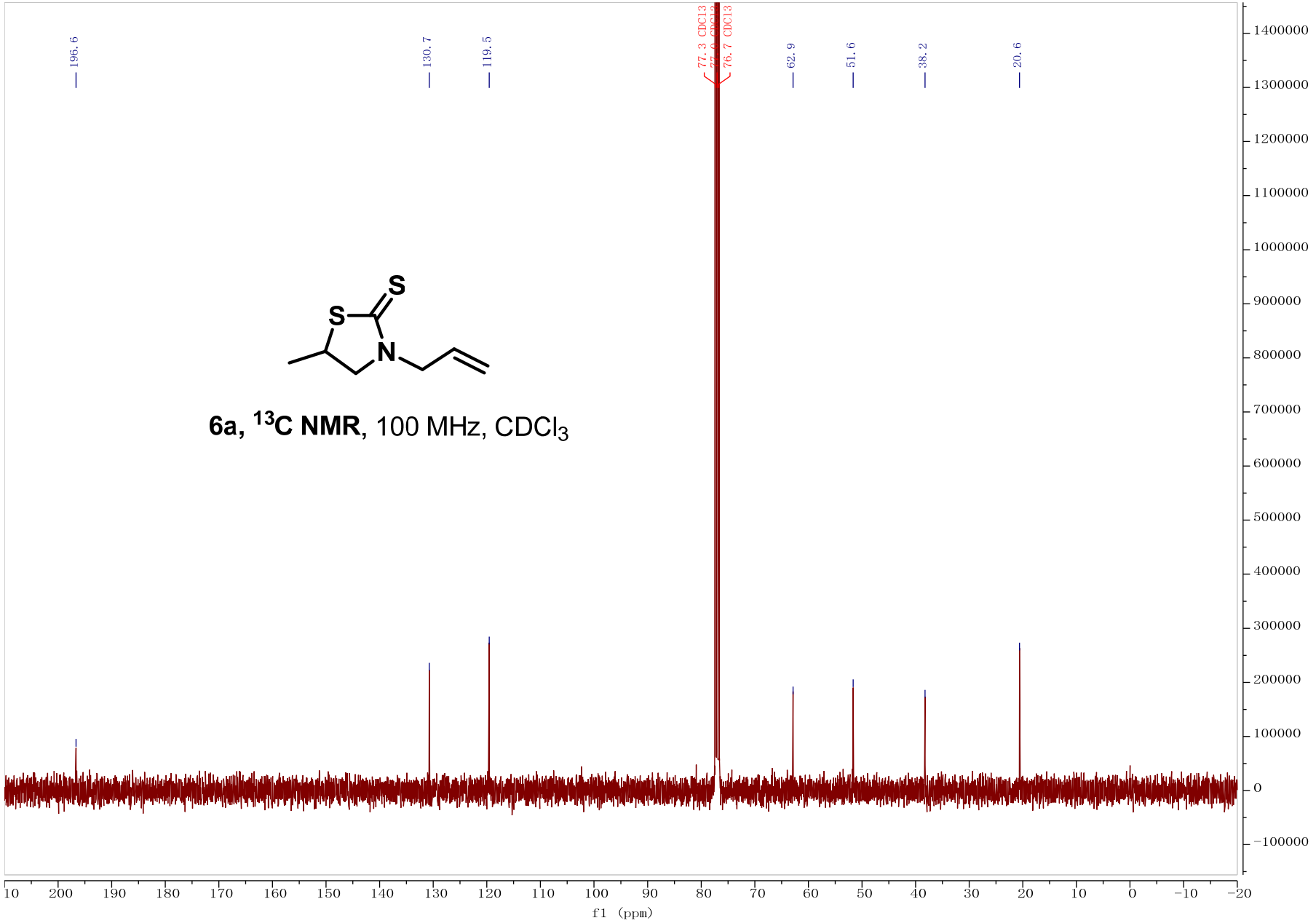
4ar, ^{1}H NMR, 400 MHz, $CDCl_3$

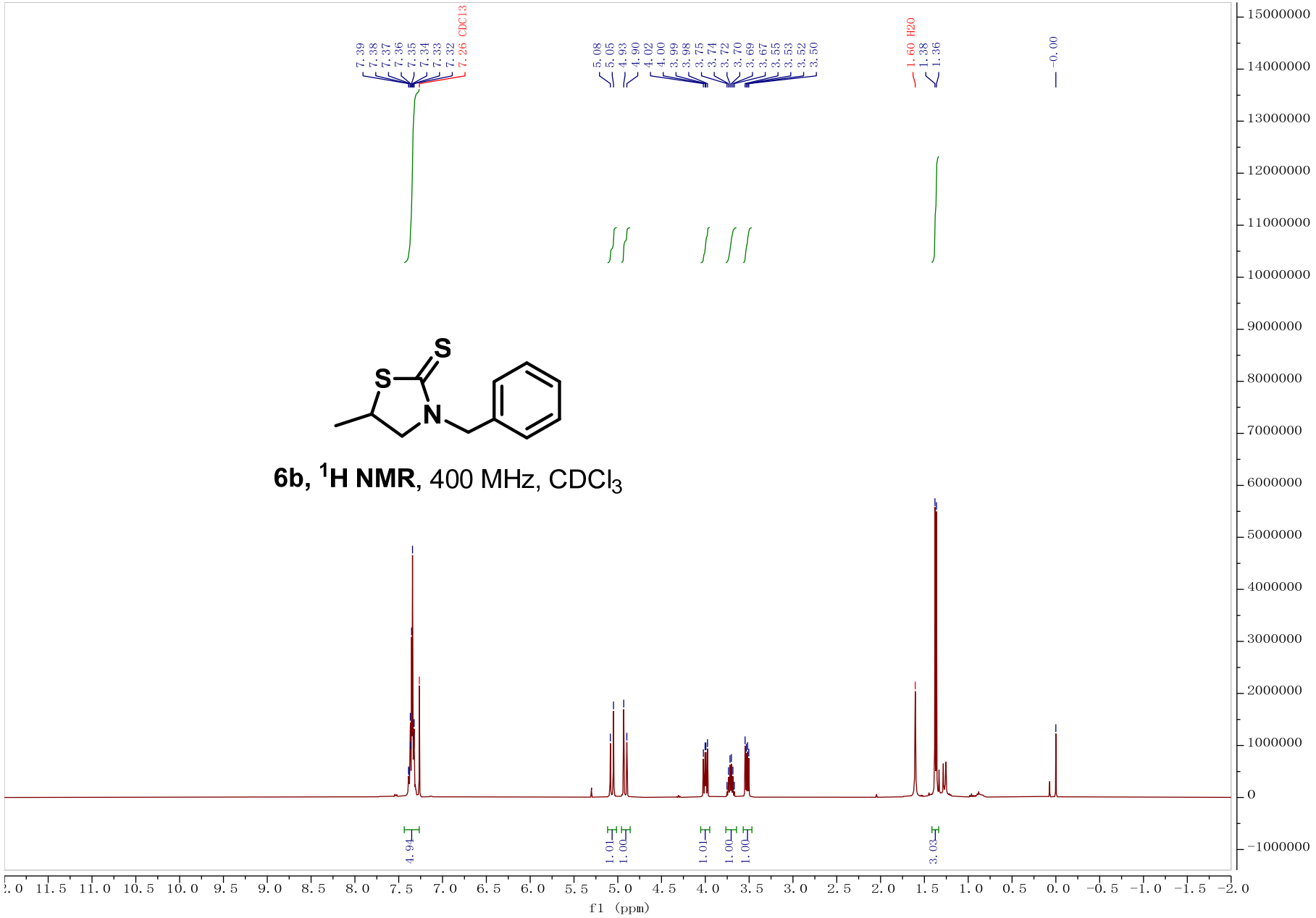


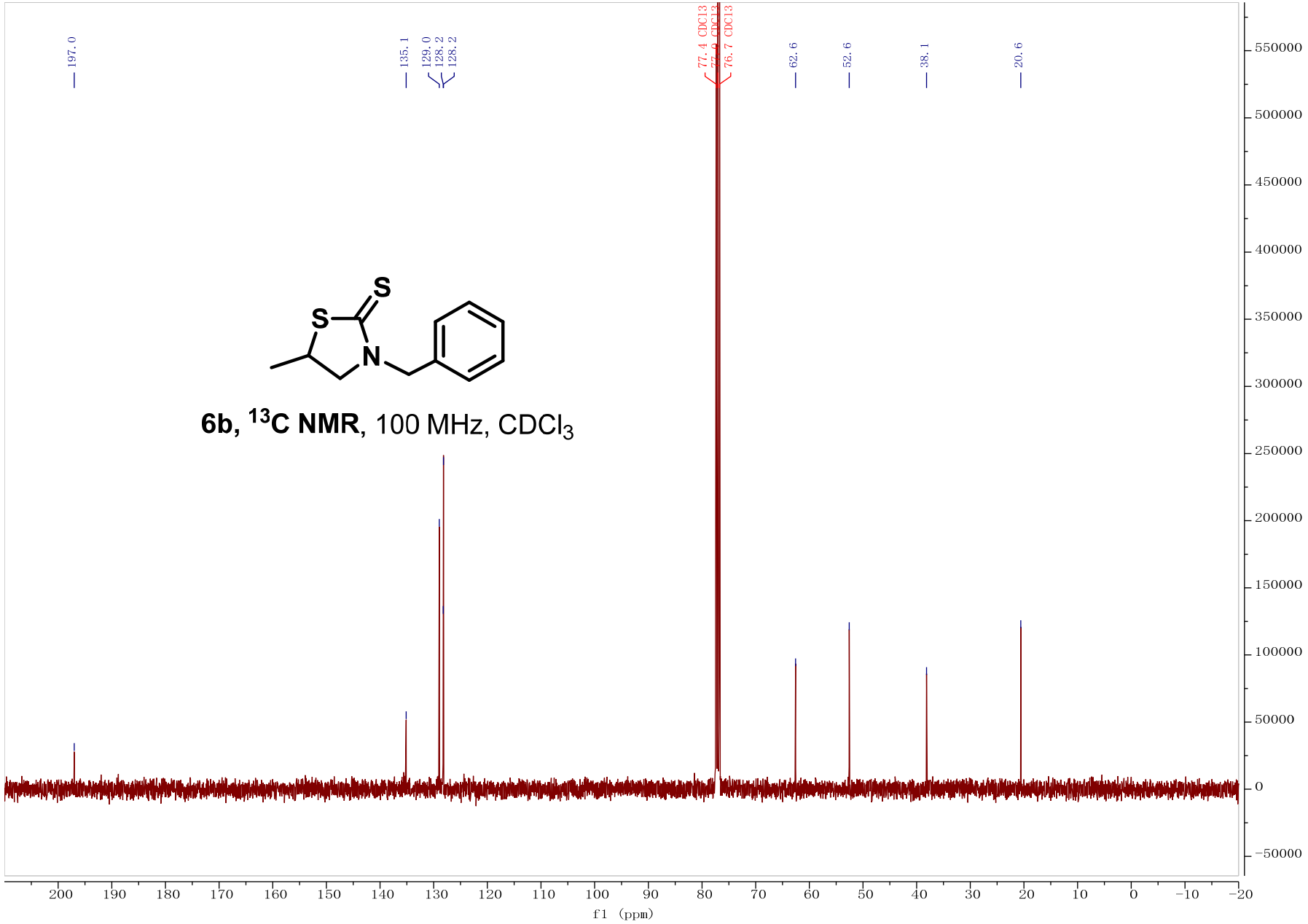
4ar, ^{13}C NMR, 100 MHz, $CDCl_3$

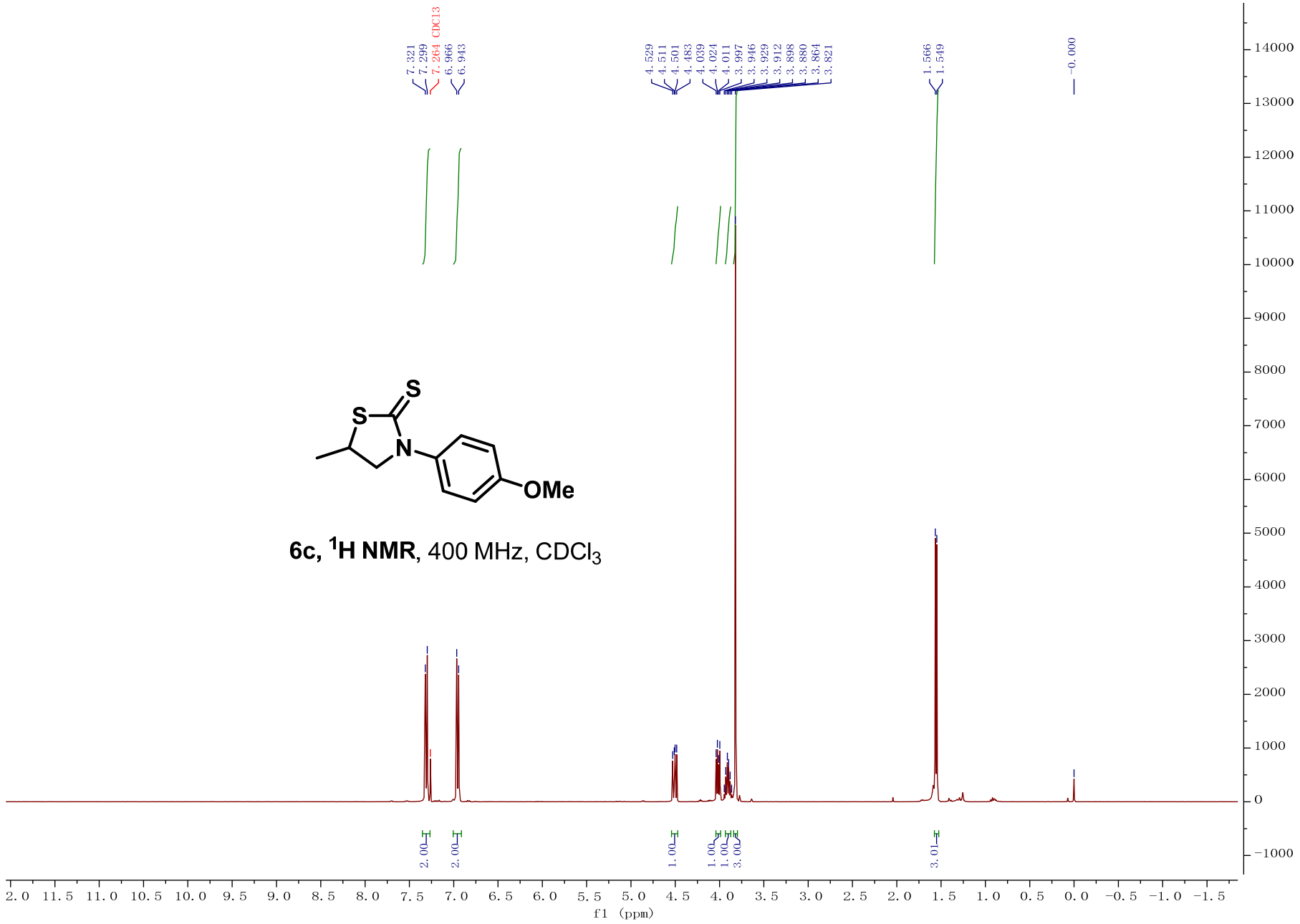
12. Spectroscopic data for compounds compound 6



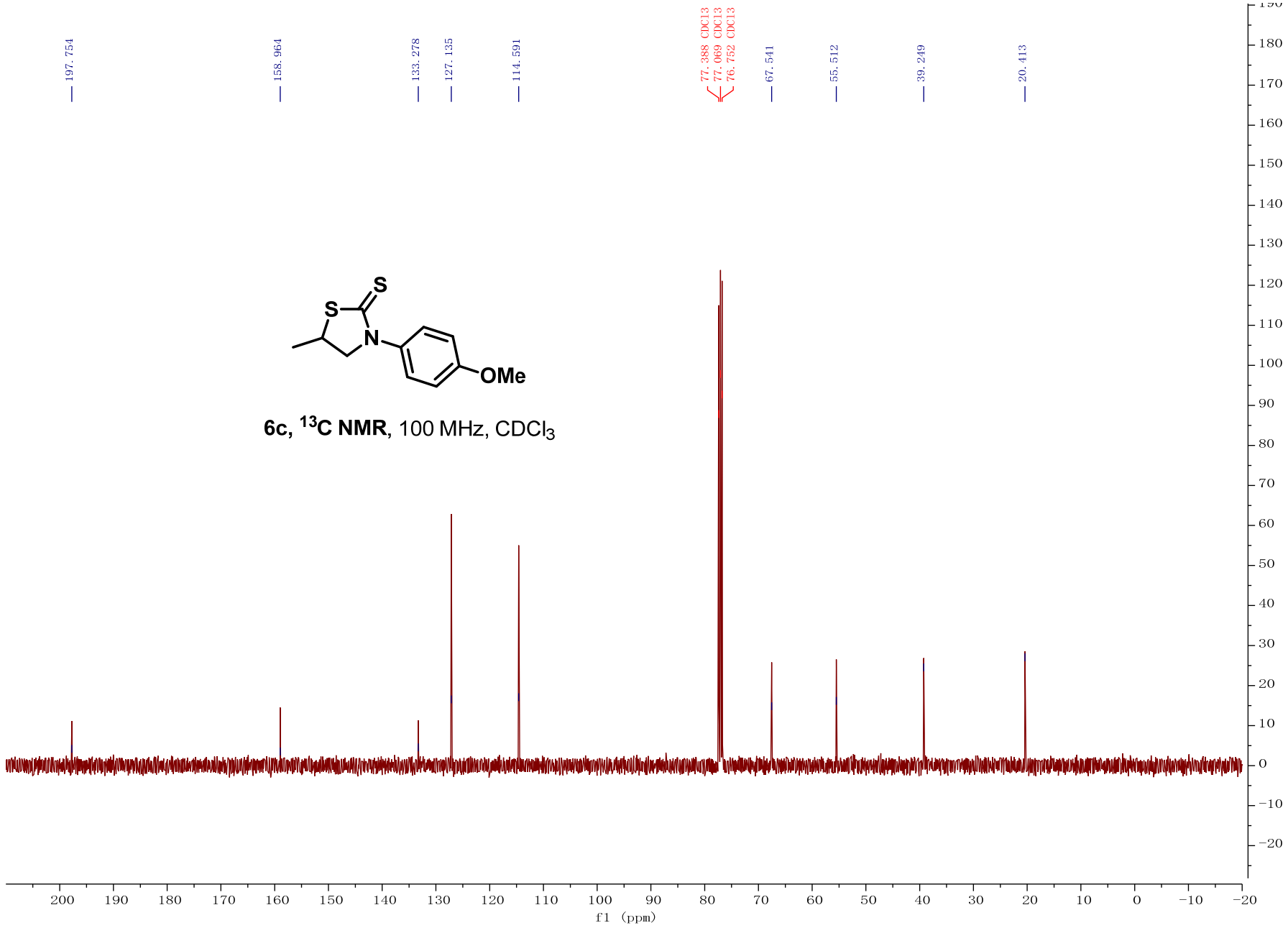

196.6
130.7
119.5
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
62.9
51.6
38.2
20.6
S
S
N
6a, 13C NMR, 100 MHz, CDCl3
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)


7.39
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.26 CDCl3
5.08
5.05
4.93
4.90
4.02
4.00
3.99
3.98
3.75
3.74
3.72
3.70
3.69
3.67
3.55
3.53
3.52
3.50
1.60 H2O
1.38
1.36
0.00
S
S
N
6b, 1H NMR, 400 MHz, CDCl3
4.94
1.01
1.00
1.01
1.00
1.00
3.03
f1 (ppm)

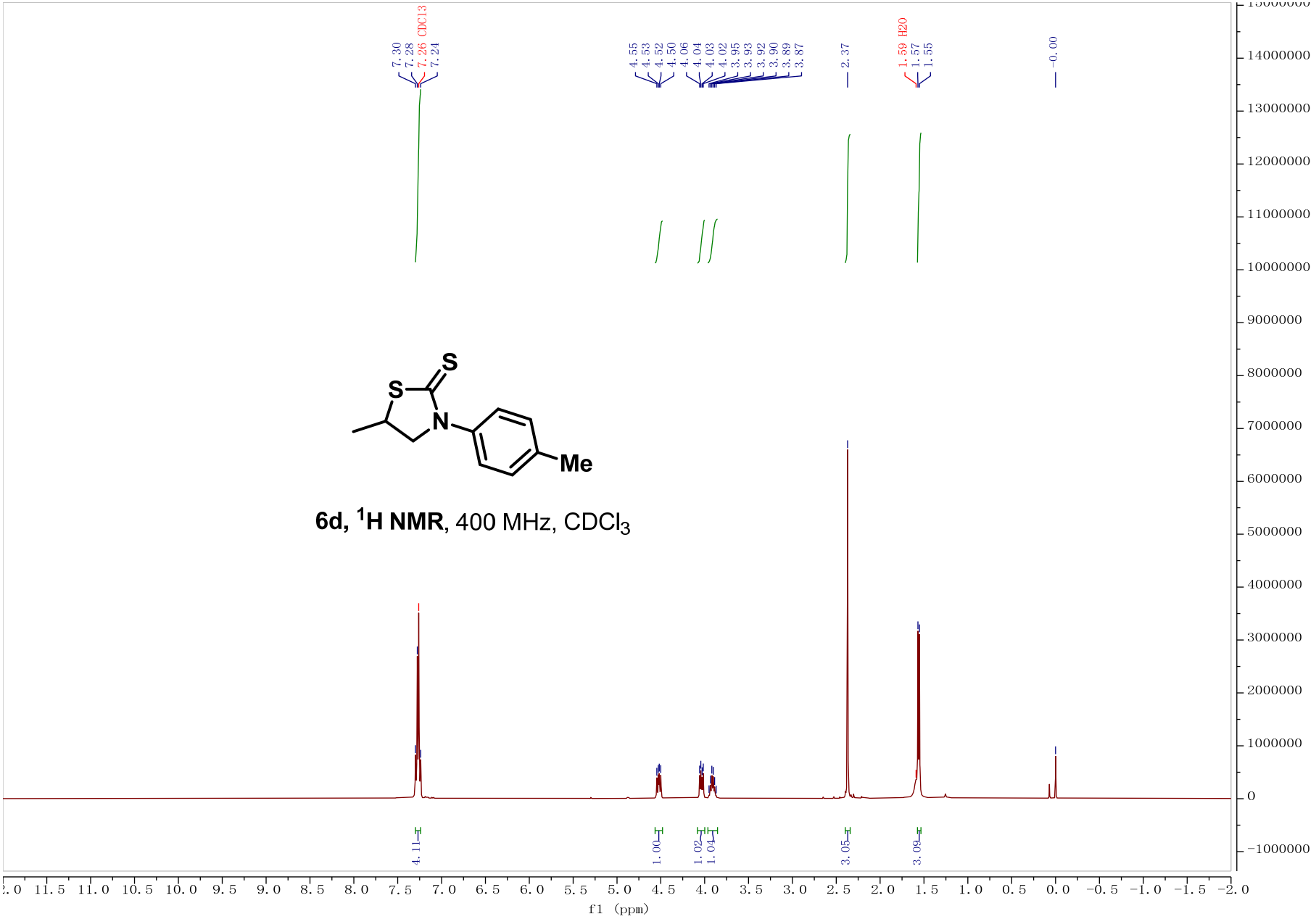

197.0
135.1
129.0
128.2
128.2
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
62.6
52.6
38.1
20.6
S
S
N
6b, 13C NMR, 100 MHz, CDCl3
f1 (ppm)



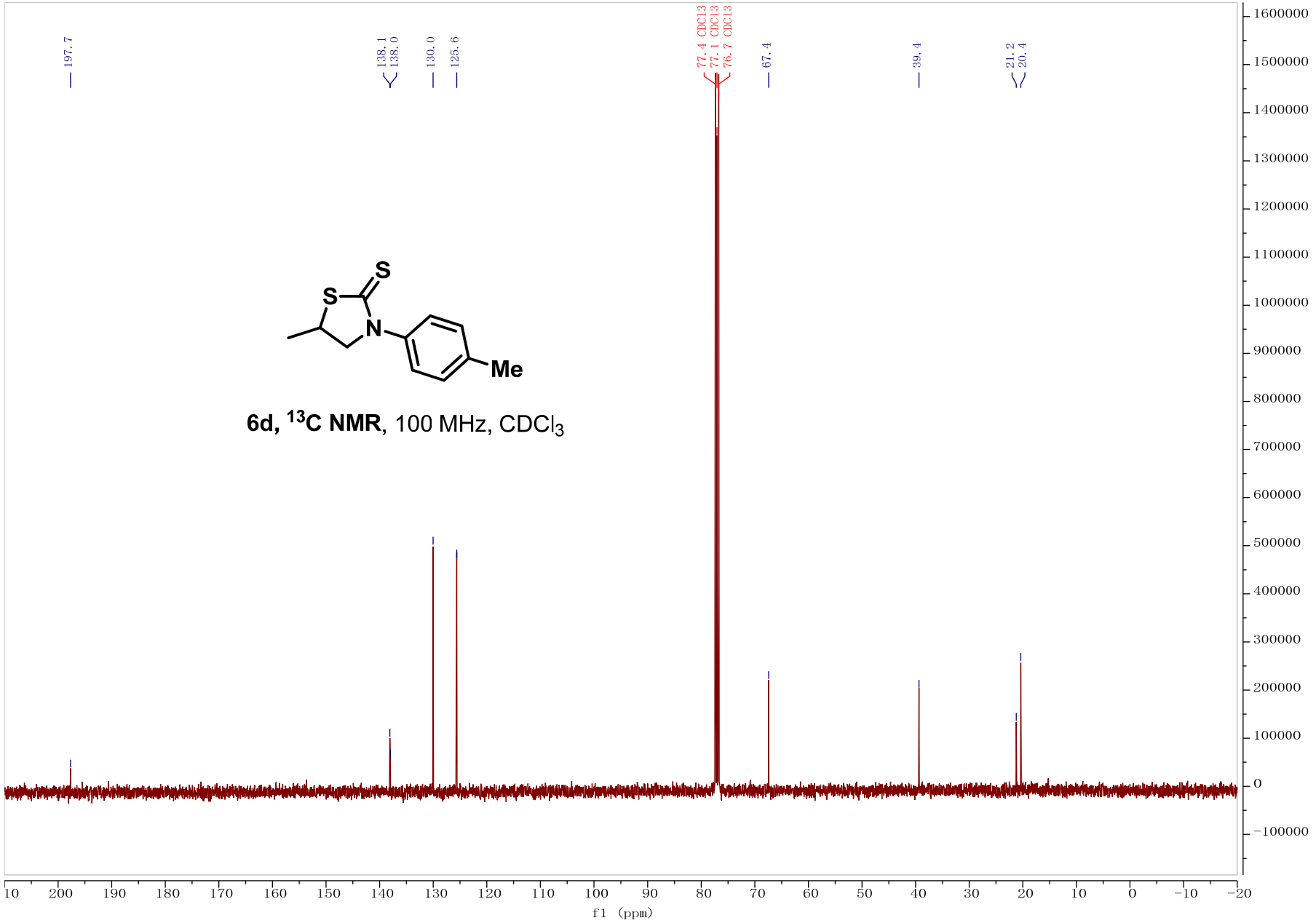
6c, ^{1}H NMR, 400 MHz, $CDCl_3$



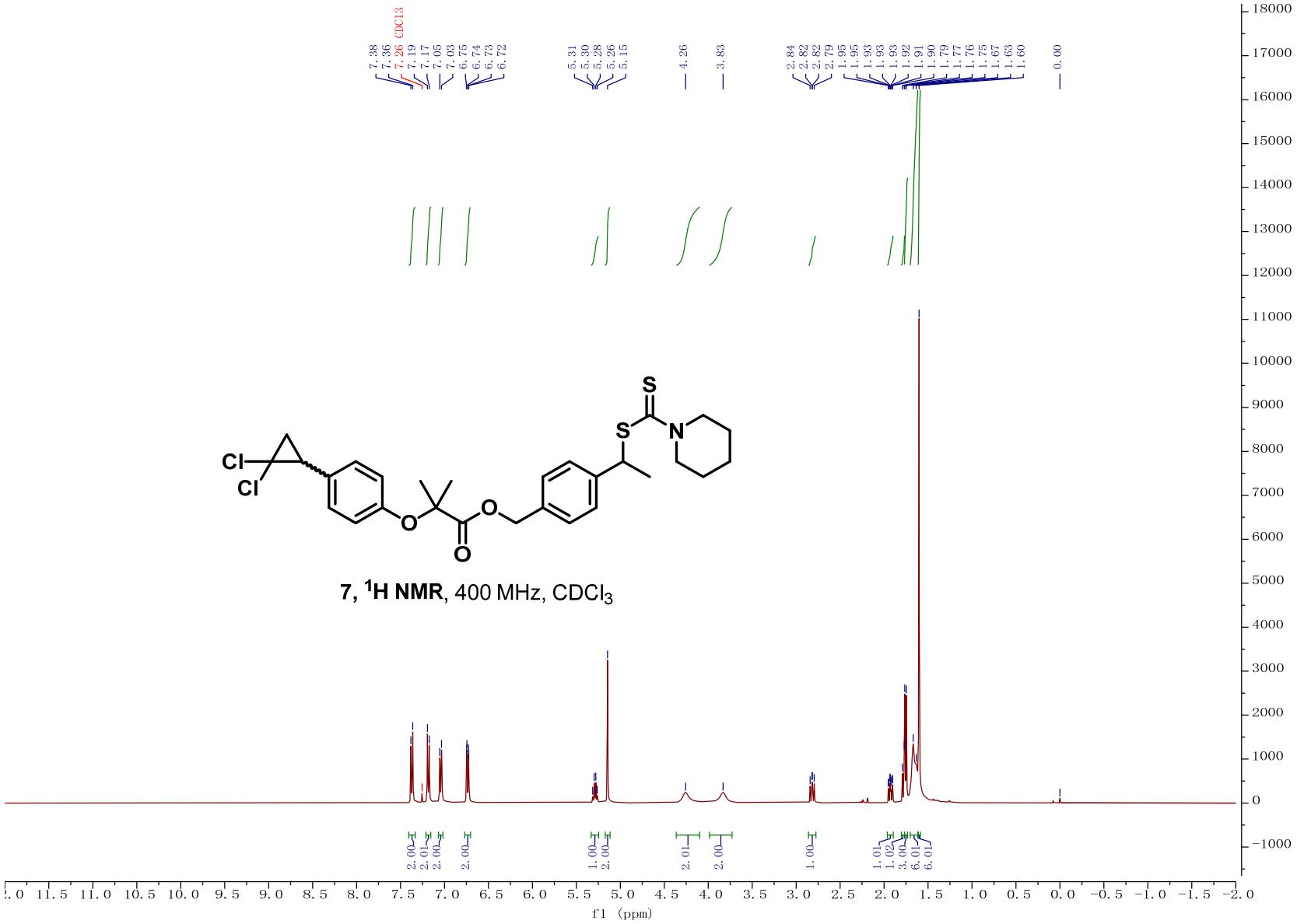
6c, ^{13}C NMR, 100 MHz, $CDCl_3$



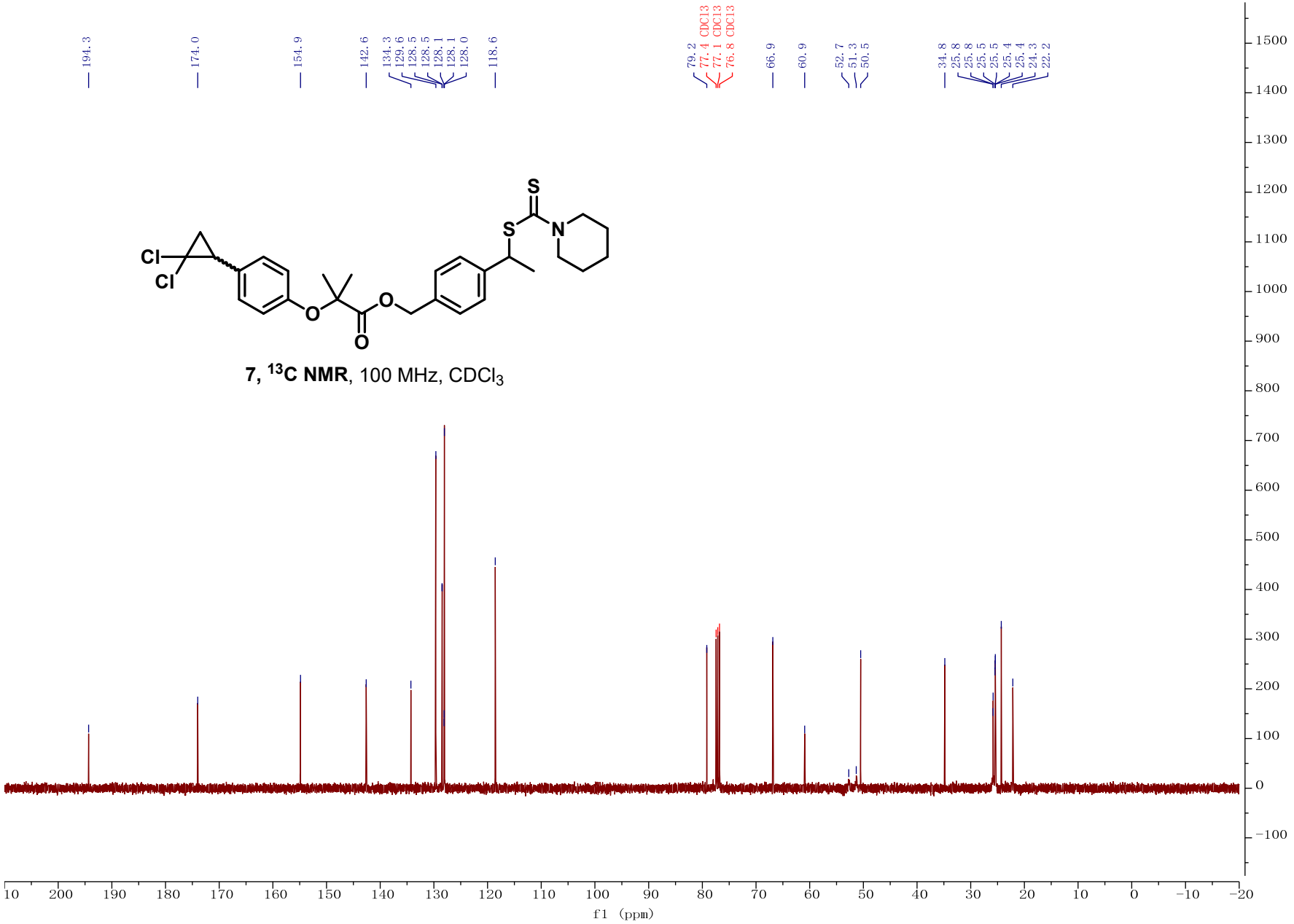
6d, ^{1}H NMR, 400 MHz, $CDCl_3$


197.7
138.1
138.0
130.0
125.6
77.4 CDCl3
77.1 CDCl3
76.7 CDCl3
67.4
39.4
21.2
20.4
S
S
N
Me
6d, 13C NMR, 100 MHz, CDCl3
f1 (ppm)

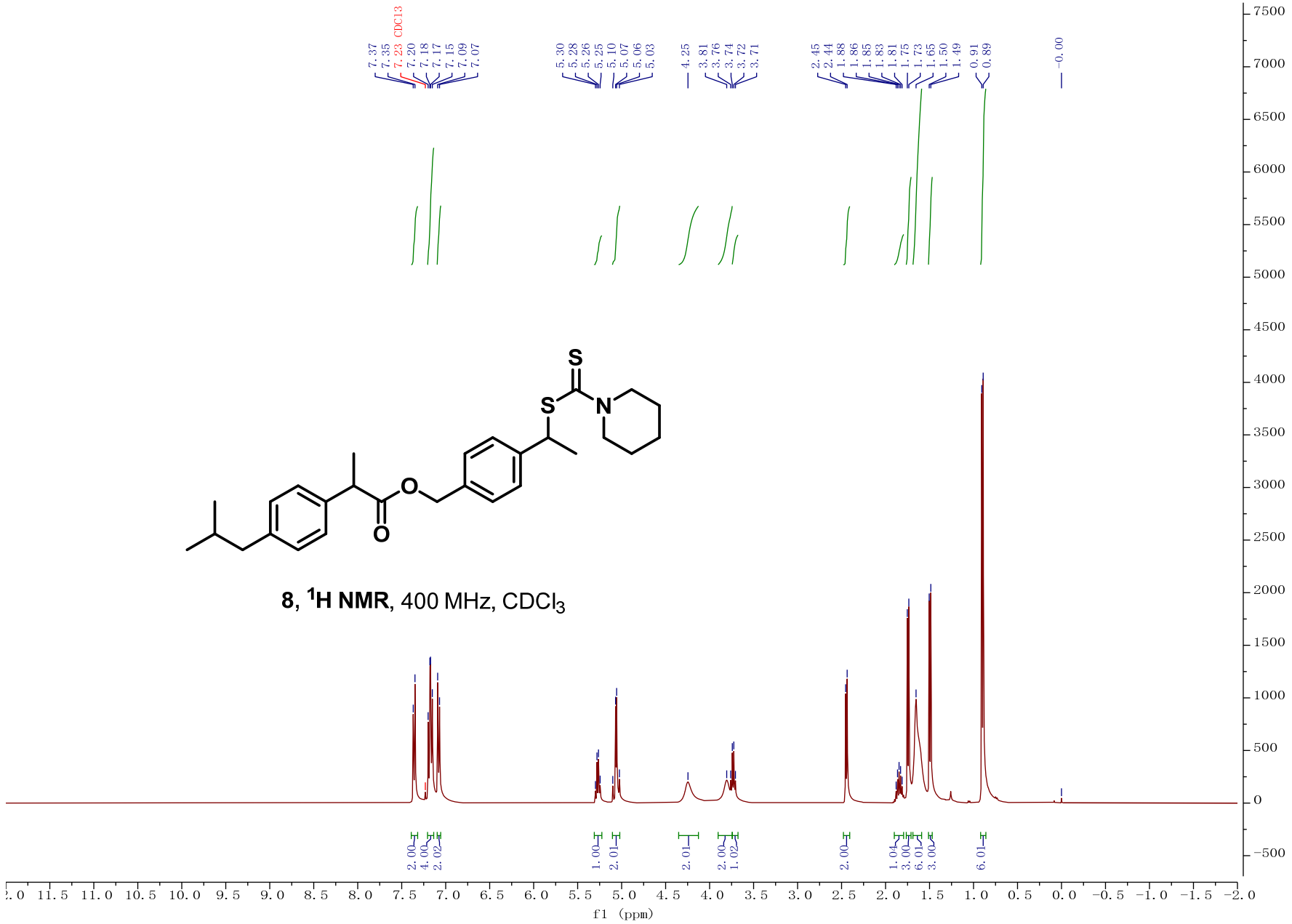
13. Spectroscopic data for compounds compound 7-11

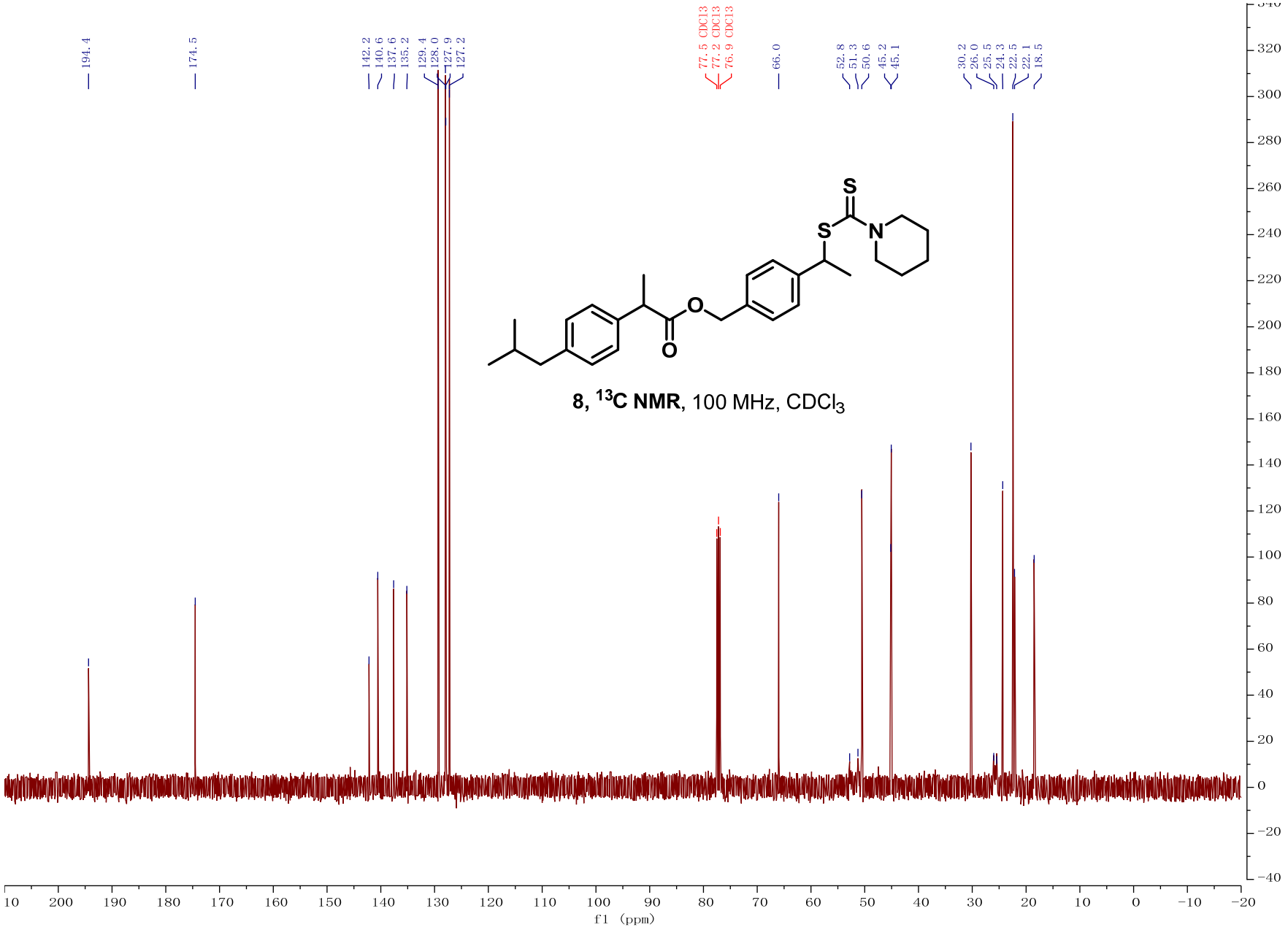


7, ^{1}H NMR, 400 MHz, $CDCl_3$

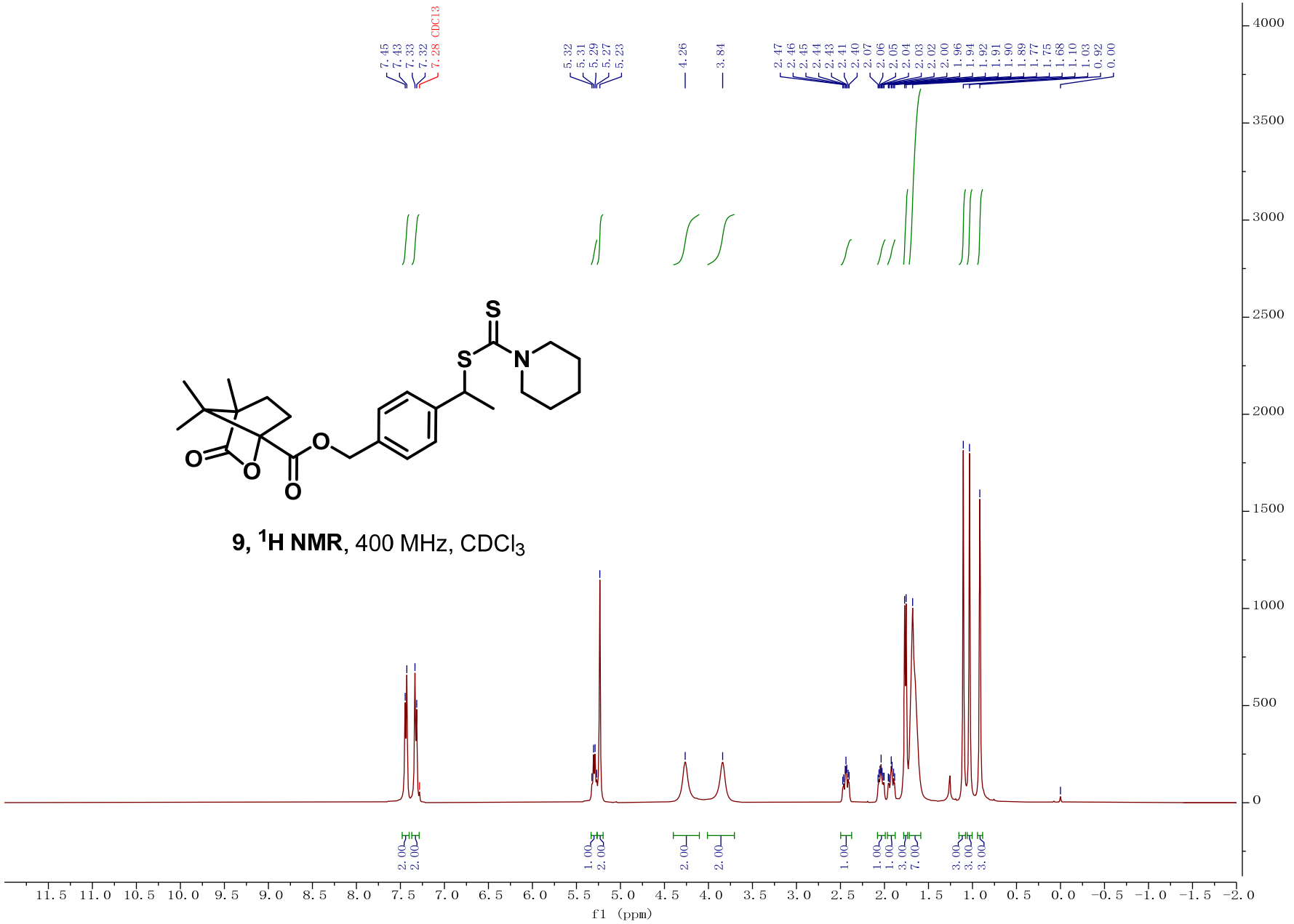


7, ^{13}C NMR, 100 MHz, $CDCl_3$

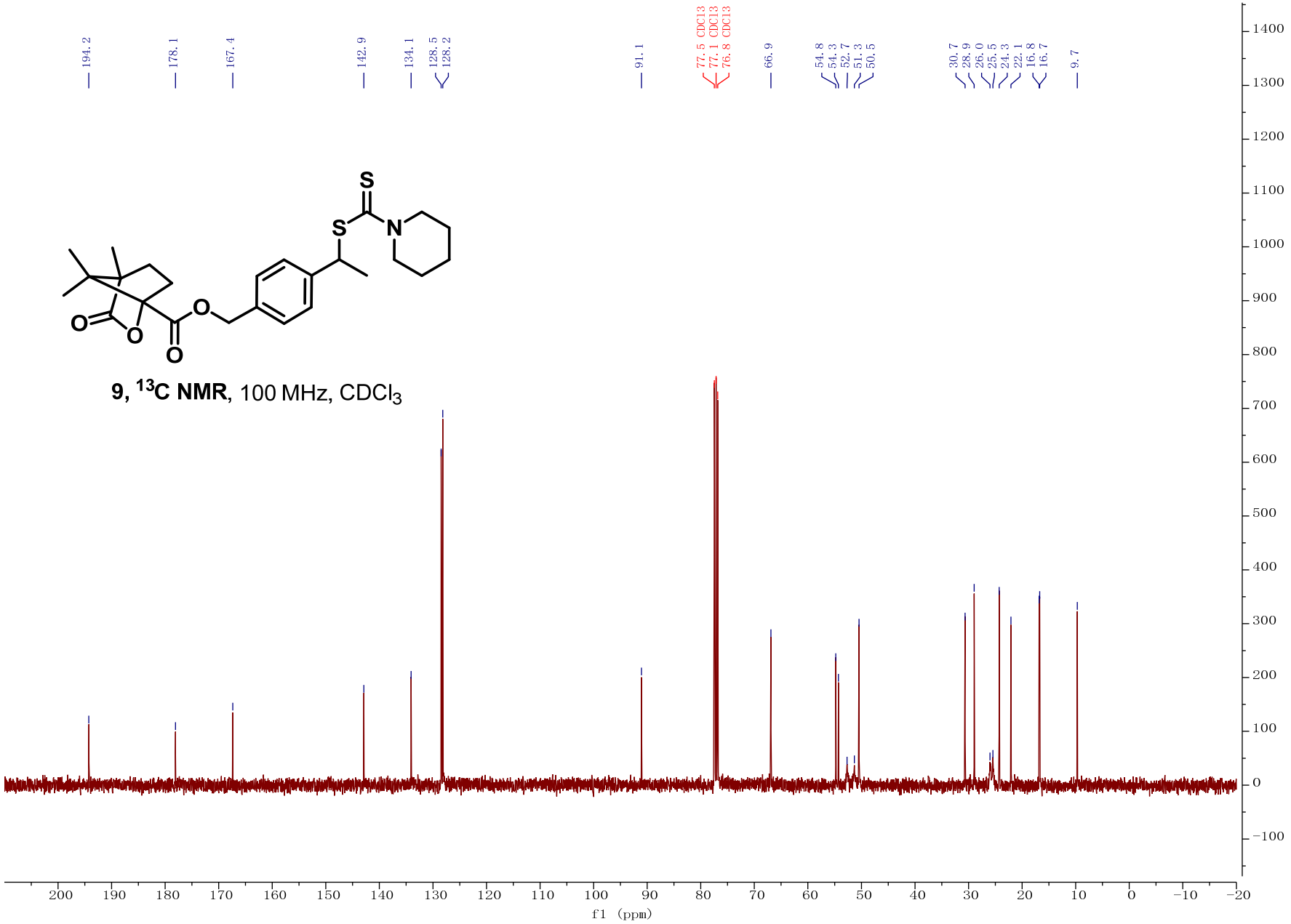

7.37
7.35
7.23
CDCl3
7.20
7.18
7.17
7.15
7.09
7.07
5.30
5.28
5.26
5.25
5.10
5.07
5.06
5.03
4.25
3.81
3.76
3.74
3.72
3.71
2.45
2.44
1.88
1.86
1.85
1.83
1.81
1.75
1.73
1.65
1.50
1.49
0.91
0.89
0.00
S
S
N
O
O
8, 1H NMR, 400 MHz, CDCl3
f1 (ppm)

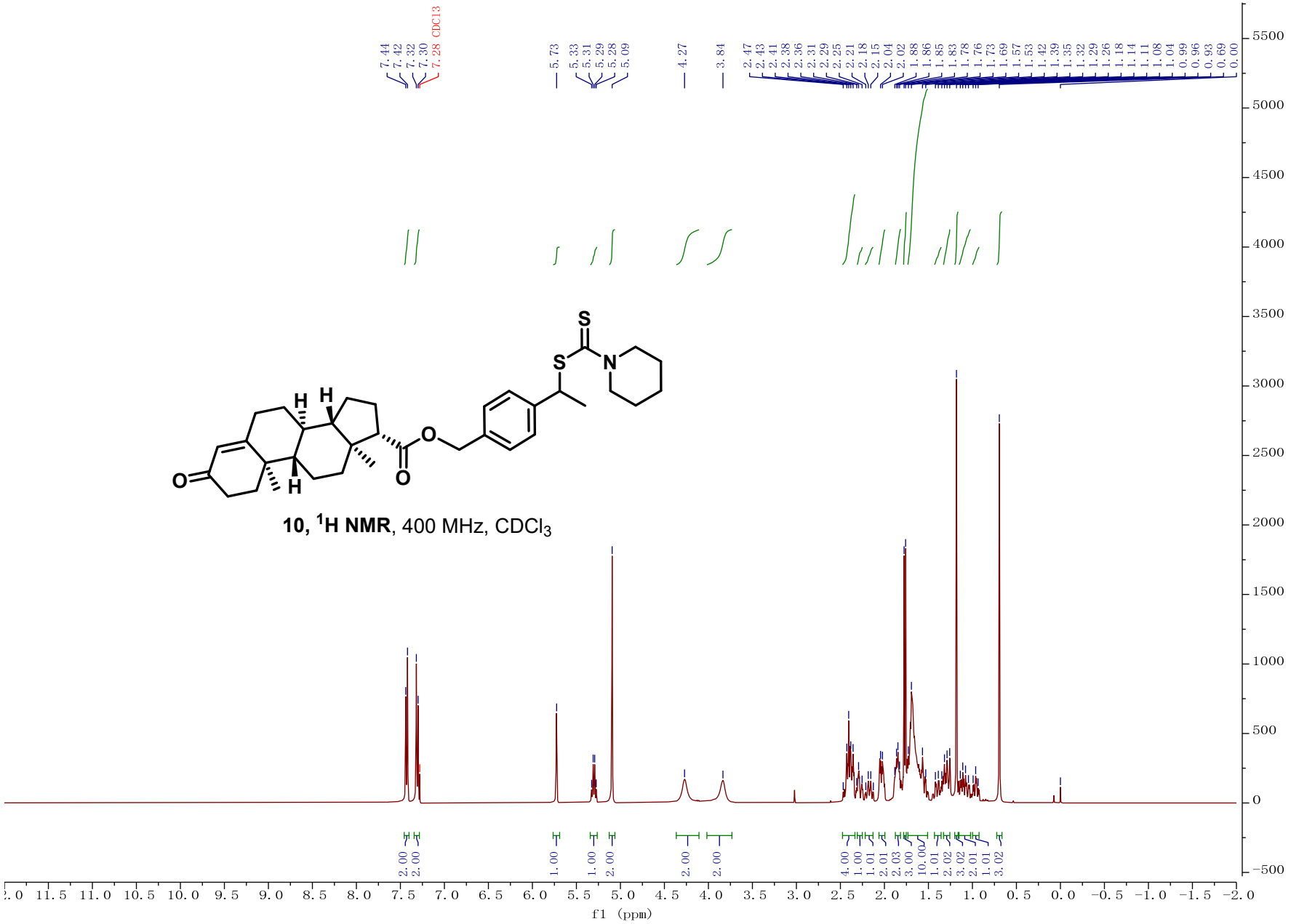


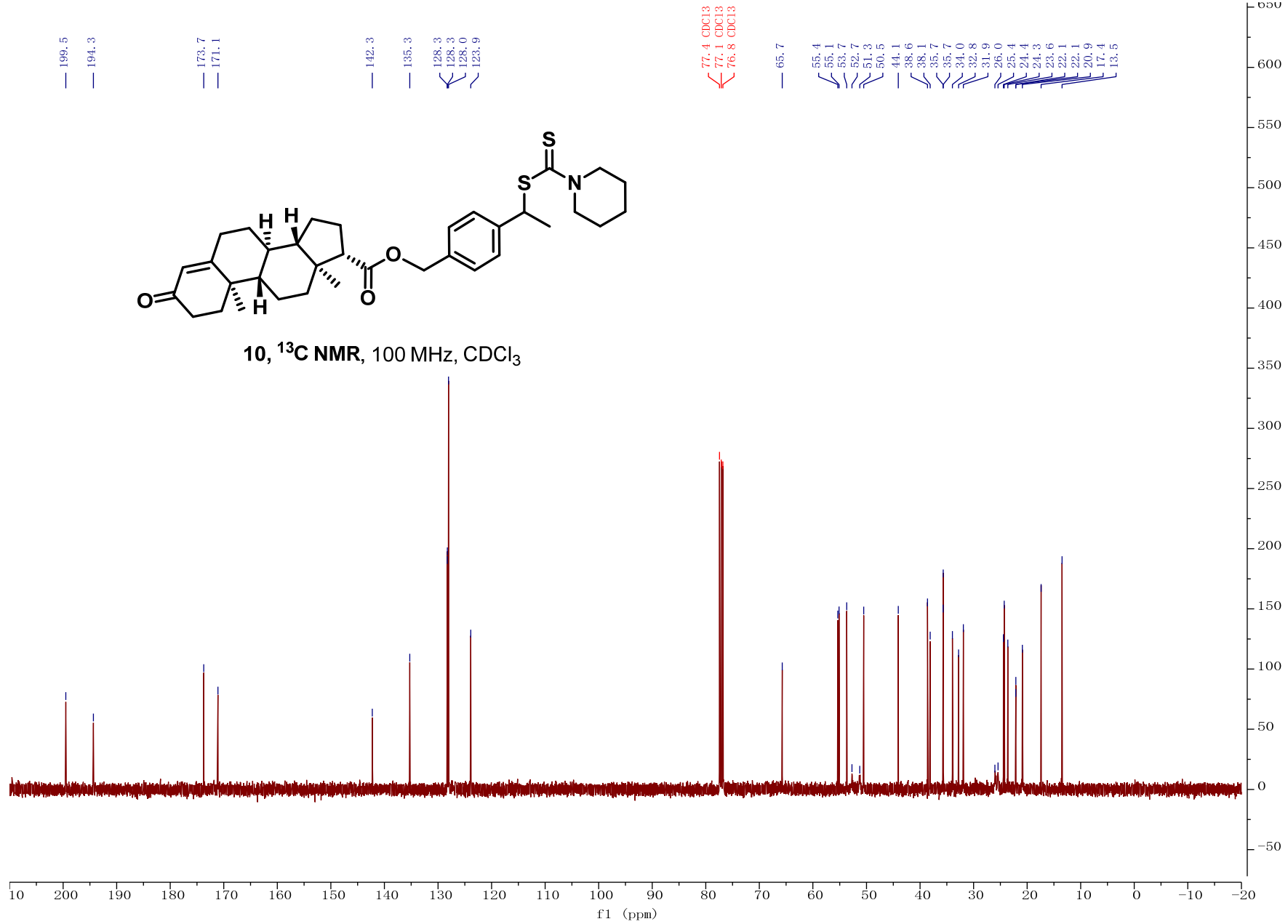
8, ^{13}C NMR, 100 MHz, $CDCl_3$



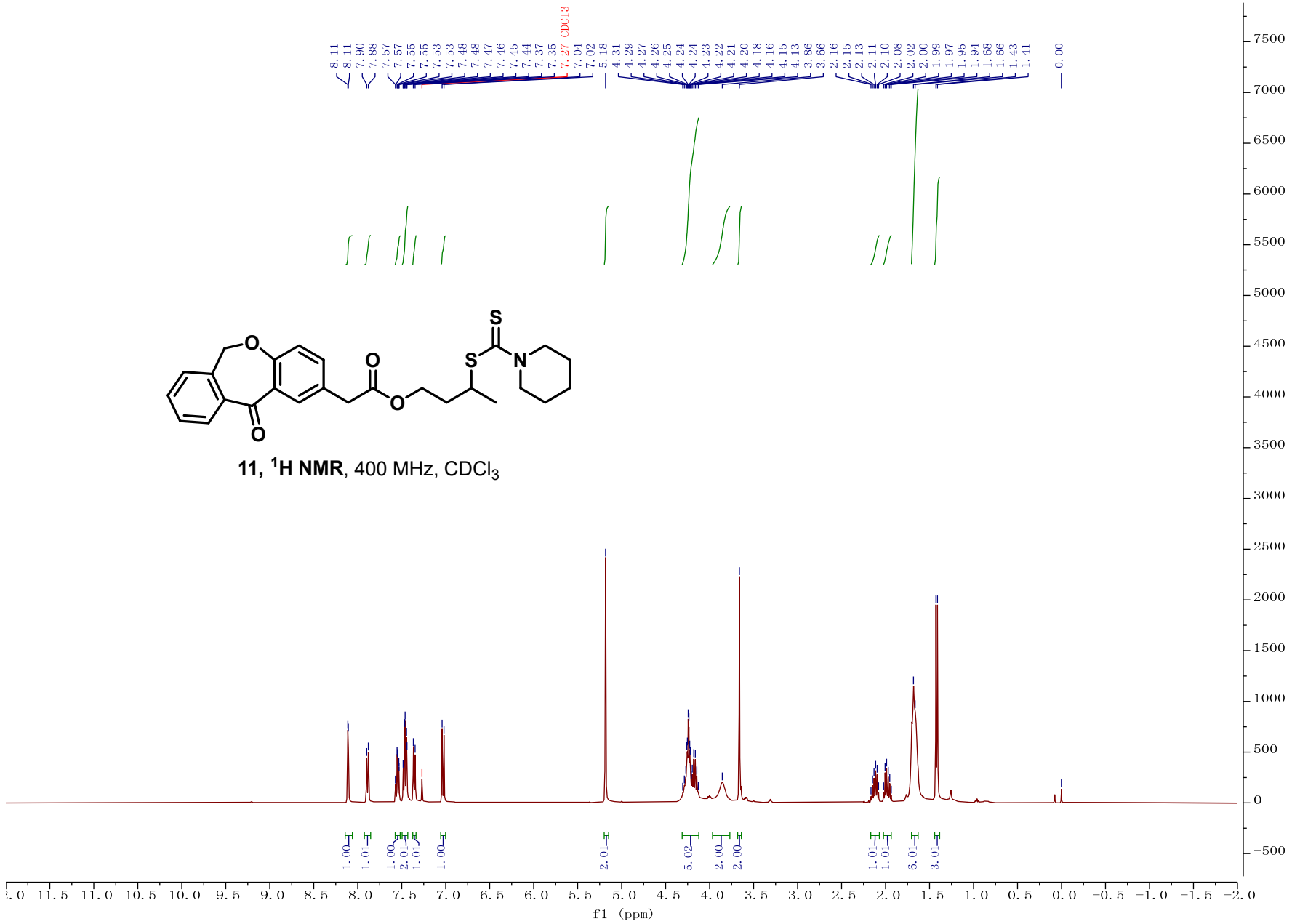
9, ^{1}H NMR, 400 MHz, $CDCl_3$


194.2
178.1
167.4
142.9
134.1
128.5
128.2
91.1
77.5 CDCl3
77.1 CDCl3
76.8 CDCl3
66.9
54.8
54.3
52.7
51.3
50.5
30.7
28.9
26.0
25.5
24.3
22.1
16.8
16.7
9.7
S
S
N
O
O
O
O
9, 13C NMR, 100 MHz, CDCl3
f1 (ppm)

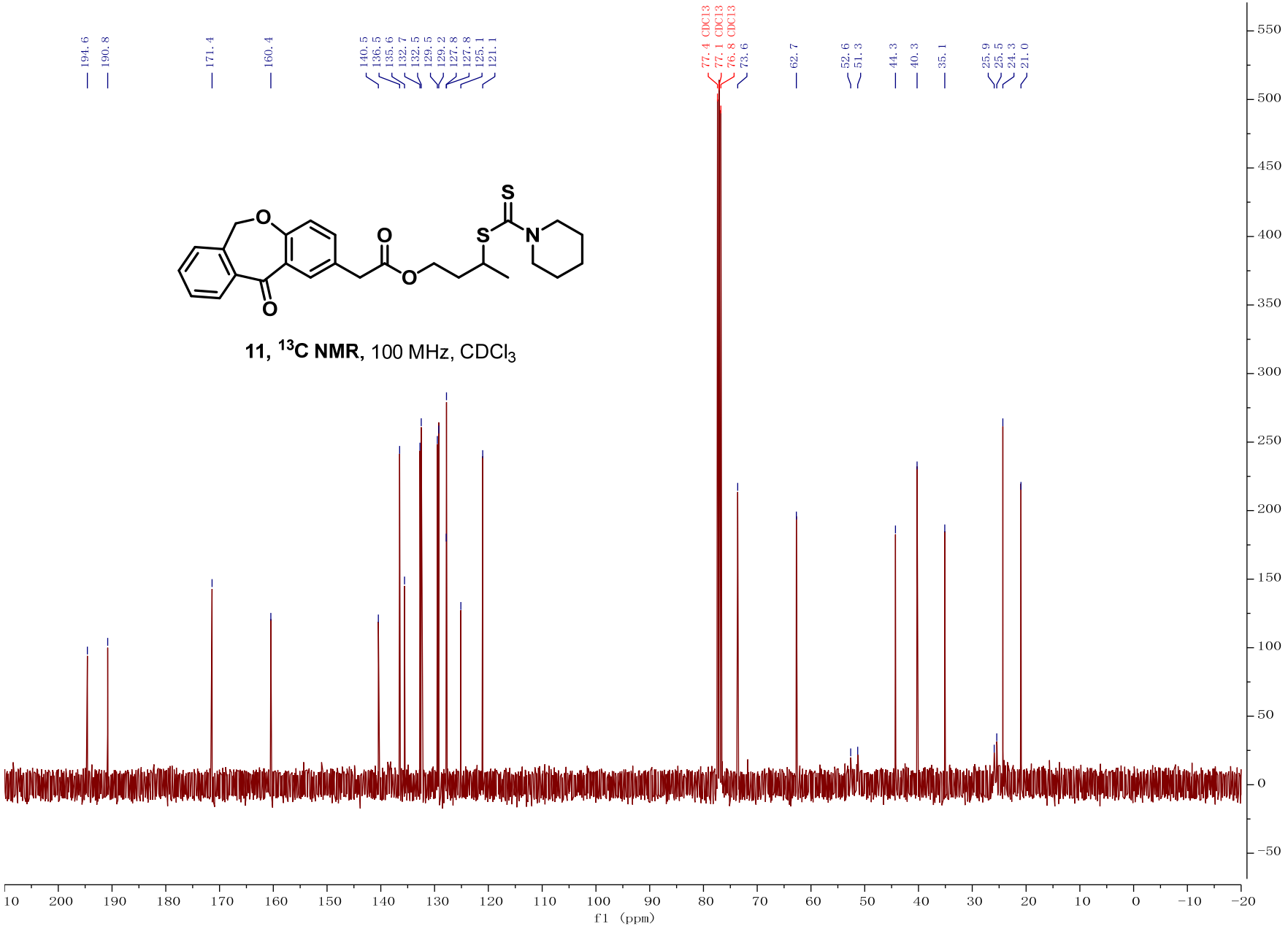

7.44
7.42
7.32
7.30
7.28 CDCl3
5.73
5.33
5.31
5.29
5.28
5.09
4.27
3.84
2.47
2.43
2.41
2.38
2.36
2.31
2.29
2.25
2.21
2.18
2.15
2.04
2.02
1.88
1.86
1.85
1.83
1.78
1.76
1.73
1.69
1.57
1.53
1.42
1.39
1.35
1.32
1.29
1.26
1.18
1.14
1.11
1.08
1.04
0.99
0.96
0.93
0.69
0.00
S
S
N
H
H
O
O
O
H
10, 1H NMR, 400 MHz, CDCl3
2.00
2.00
1.00
1.00
2.00
2.00
2.00
4.00
1.00
1.01
2.01
2.03
3.00
10.00
1.01
2.02
3.02
2.01
1.01
3.02
f1 (ppm)



10, ^{13}C NMR, 100 MHz, $CDCl_3$



11, ^{1}H NMR, 400 MHz, $CDCl_3$



11, ^{13}C NMR, 100 MHz, $CDCl_3$