Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Divergent Upgrading Pathways of Sulfones with Primary Alcohols: Nickel-catalyzed α-Alkylation under N_2 and Metal Free Promoted β-Olefination in Open Air

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1. General Information

All NMR spectra were acquired on Bruker AV 400 MHz NMR spectrometers. ^{1}H NMR chemical shifts were recorded relative to $SiMe_4$ (δ 0.00). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a *J* value in Hz. ^{13}C NMR chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ 77.16). High resolution mass spectral analyses (HRMS) were recorded on a Bruck micro-TOF mass spectrometer using electrospray ionization (ESI), positive ion mode.

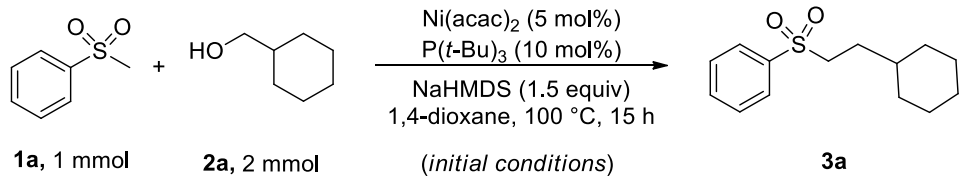
All air-sensitive compounds were handled under an atmosphere of argon or in a nitrogen-filled glovebox. Glassware was dried at 120 ^{o}C for at least 3 h before use. Extra dry solvents 1,4-dioxane, THF, toluene, DME were purchased from BidePharm. Co. Ltd. and stored in a glove box. Unless noted otherwise, commercially available chemicals were used as received without purification. All reaction were heated by metal sand bath (WATTCAS, LAB-500, https://www.wattcas.com). Flash column chromatographies were performed using the indicated solvent system on silica gel (200–300 mesh).

2. α-Alkylation of sulfones with alcohols.

(1) Condition optimization.

A general procedure for condition optimization: In a nitrogen-filled glove box, Ni salt (0.05 mmol), Ligand (0.1 mmol) and dry solvent (1 mL) were charged into a 10-mL Schlenk tube. After stirring for 30 min, cyclohexyl methanol **2a** (250.1 μL, 2.0 mmol), phenyl methyl sulfone **1a** (156.2 mg, 1.0 mmol) and base (1.5 mmol) were added. The Schlenk tube was sealed and the reaction mixture was stirred in a metal sand bath maintained at 100 ℃ for 15 h. After cooled to room temperature, the reaction mixture was subjected to silica gel column chromatography directly using EA/Hexanes (1:10) as eluent to give the **3a**.

Table S1. Condition optimization of α-alkylation of sulfone **1a** with alcohol **2a**:



Entry	Change from initial conditions	Yield(%)
1	None	65
2	$P(Cy)_3$ as a ligand	48
3	Dcype as a ligand	24
4	1,10-phenanthroline as a ligand	0
5	Tetrahydrofuran as a solvent	63
6	Toluene as a solvent	53

7	Dimethoxyethane as a solvent	52
8	*t*-BuOK as a base	0
9	KOH as a base	0
10	**1a** : **2a** = 1 : 1.5	59
11	**1a** : **2a** = 1 : 1	52
12	**1a** : **2a** = 2 : 1	17
13	4% $Ni(acac)_2$, 8% P(*t*-Bu)$_3$	49
14	2% $Ni(acac)_2$, 4% P(*t*-Bu)$_3$	26
15	$Ni(OAc)_2$ as a catalyst	54
16	$NiCl_2$(DME) as a catalyst, optimal condition	85
17	$Ni(OTf)_2$ as a catalyst	52
18	$NiCl_2$(DME), NaHMDs (1.0 mmol)	40
19	$NiCl_2$(DME), 90 ℃	35
20	No catalyst	NR

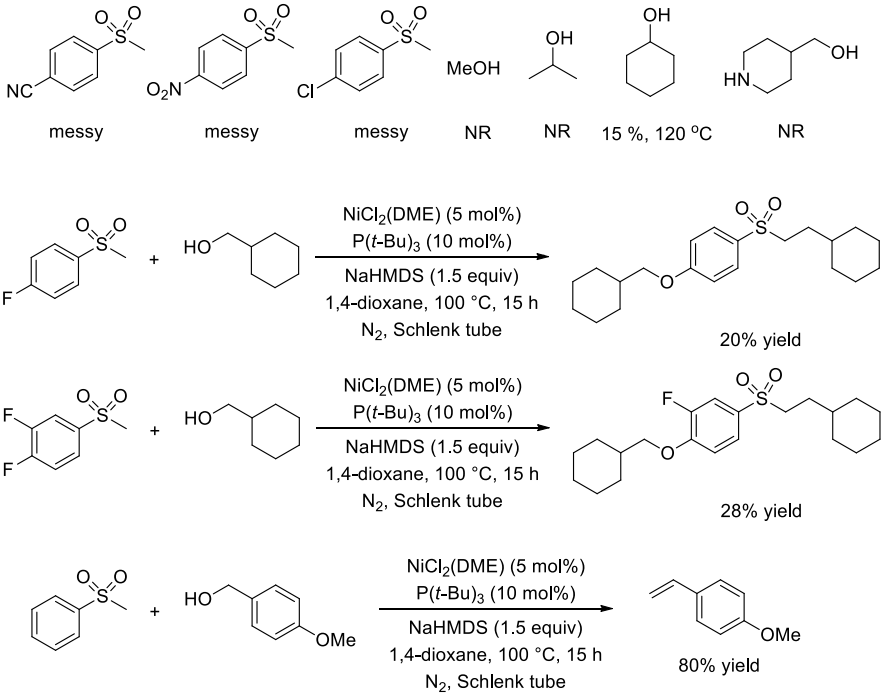
Figure S1. Typical experimental setup with 10 mL Schlenk tubes.

(2) A general procedure for the α-alkylation of sulfone 1a with alcohol 2a:

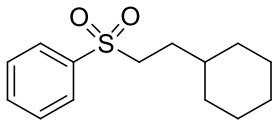
In an nitrogen-filled glove box, $NiCl_2$(DME) (11.0 mg, 0.05 mmol), P(*t*-Bu)$_3$ (202.5 μL, 10%w/v in toluene, 0.1 mmol) and dry 1,4-dioxane (1 mL) were charged into a 10-mL Schlenk tube. After stirring for 30 min, cyclohexyl methanol **2a** (250.1 μL, 2.0 mmol), phenyl methyl sulfone **1a** (156.2 mg, 1.0 mmol) and NaHMDS (0.75 mL 2.0 mol/L in THF, 1.5 mmol) were added. The Schlenk tube was sealed and the reaction mixture was stirred in a metal sand bath maintained at 100 ℃ for 15 h. After cooled to room temperature, the reaction was quenched by 2 mL of dilute HCl (1.0 M). The reaction mixture was extracted 3 times by DCM and dried by anhydrous Na_2SO_4. Solvent was removed and the

residue was purified by silica gel column chromatography using EA/Hexanes as eluent to give the alkylation product.

(3) Figure S2. Failed sulfone and alcohol substrates.



(4) Analytical data for alkylation products:



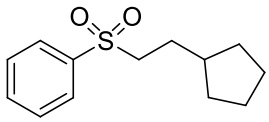
((2-Cyclohexylethyl)sulfonyl)benzene (3a) [126002-58-2]

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow oily liquid. Yield: 85%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 3.15-3.05 (m, 2H), 1.72-1.56 (m, 7H), 1.27-1.02 (m, 4H), 0.93-0.79 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.3, 133.7, 129.3, 128.1, 54.4, 36.7, 32.8, 29.7, 26.3, 26.0.

HRMS (ESI): calculated for $C_{14}H_{20}O_2S$ $[M+Na]^+$ 275.1082, found 275.1065.



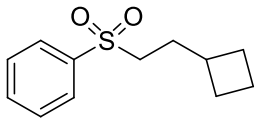
((2- Cyclopentenyl)sulfonyl)benzene (3b) [97764-00-6]

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow oily liquid. Yield: 65%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.72 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 3.10-2.93 (m, 2H), 1.73-1.59 (m, 5H), 1.57-1.38 (m, 4H), 1.05-0.89 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.3, 133.7, 129.4, 128.1, 55.8, 38.9, 32.4, 28.6, 25.1.

HRMS (ESI): calculated for $C_{13}H_{18}O_2S$ $[M+Na]^+$ 261.0926, found 261.0942.



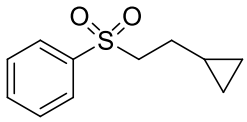
((2-Cyclobutylethyl)sulfonyl)benzene (3c) [152954-14-8]

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow solid. Yield: 69%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 2.97-2.82 (m, 2H), 2.19 (m, 1H), 1.99-1.89 (m, 2H), 1.82-1.65 (m, 4H), 1.57-1.41 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.5, 133.7, 129.4, 128.2, 54.5, 34.5, 29.5, 27.8, 18.3.

HRMS (ESI): calculated for $C_{12}H_{16}O_2S$ $[M+Na]^+$ 247.0769, found 247.0761.



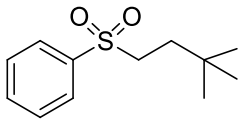
((2-Cyclopropylethyl)sulfonyl)benzene (3d)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow solid. Yield: 75%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.80 (m, 2H), 7.59 (m, 1H), 7.51 (m, 2H), 3.18-3.09 (m, 2H), 1.58-1.51 (m, 2H), 0.65-0.62 (m, 1H), 0.40-0.38 (m, 2H), 0.01 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.5, 133.7, 129.4, 128.2, 56.5, 28.0, 9.8, 4.8.

HRMS (ESI): calculated for $C_{11}H_{14}O_2S$ $[M+Na]^+$ 233.0613, found 233.0605.



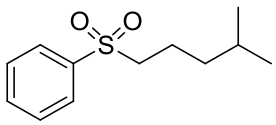
((3,3-Dimethylbutyl)sulfonyl)benzene (3e) [81536-20-1]

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as white solid. Yield: 72%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.3 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 3.12-3.01 (m, 2H), 1.65-1.55 (m, 2H), 0.87 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.4, 133.7, 129.4, 128.2, 53.1, 35.8, 30.2, 29.1.

HRMS (ESI): calculated for $C_{12}H_{18}O_2S$ $[M+Na]^+$ 249.0926, found 249.0919.



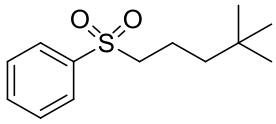
((4-Methylpentyl)sulfonyl)benzene (3f) [1268636-30-1]

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as white solid. Yield: 81%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.3 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 3.14-3.02 (m, 2H), 1.80-1.64 (m, 2H), 1.51 (m, 1H), 1.24 (m, 2H), 0.84 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.4, 133.7, 129.3, 128.1, 56.6, 37.4, 27.7, 22.3, 20.6.

HRMS (ESI): calculated for $C_{12}H_{18}O_2S$ $[M+Na]^+$ 249.0926, found 249.0918.



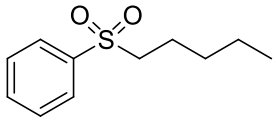
((4,4-dimethylpentyl)sulfonyl)benzene (3g) [1361197-91-2]

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow liquid. Yield: 70%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.88 (m, 2H), 7.69-7.63 (m, 1H), 7.58 (t, *J* = 7.5 Hz, 2H), 3.06 (t, *J* = 8.0 Hz, 2H), 1.79-1.65 (m, 2H), 1.27-1.18 (m, 2H), 0.85 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.4, 133.7, 129.4, 128.1, 57.1, 42.6, 30.5, 29.2, 18.1.

HRMS (ESI): calculated for $C_{13}H_{20}O_2S$ $[M+Na]^+$ 263.1082, found 263.1067.



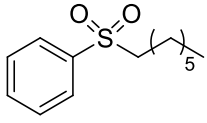
(Pentylsulfonyl)benzene (3h) [34009-04-6]

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow liquid. Yield: 68%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 3.09-2.83 (m, 2H), 1.64 (m, 2H), 1.28-1.18 (m, 4H), 0.78 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.3, 133.7, 129.3, 128.1, 56.4, 30.4, 22.4, 22.2, 13.7.

HRMS (ESI): calculated for $C_{12}H_{18}O_2S$ $[M+Na]^+$ 235.0769, found 235.0758.



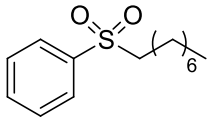
(Heptylsulfonyl)benzene (3i) [52075-21-5]

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow liquid. Yield: 71%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 2H), 3.05-2.94 (m, 2H), 1.64 (m, 2H), 1.17 (m, 8H), 0.78 (t, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.5, 133.7, 129.4, 128.2, 56.5, 31.56, 28.8, 28.4, 22.8, 22.6, 14.1.

HRMS (ESI): calculated for $C_{13}H_{20}O_2S$ $[M+Na]^+$ 263.1082, found 263.1070.



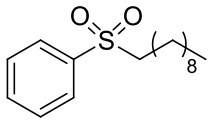
(Octylsulfonyl)benzene (3j) [34009-05-7]

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow liquid. Yield: 70%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (m, 2H), 7.66 (m, 1H), 7.57 (m, 2H), 3.15-2.99 (m, 2H), 1.76-1.64 (m, 2H), 1.29-1.20 (m, 10H), 0.86 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.4, 133.6, 129.3, 128.1, 56.4, 31.7, 29.0, 28.9, 28.3, 22.7, 22.6 14.1.

HRMS (ESI): calculated for $C_{14}H_{22}O_2S$ $[M+Na]^+$ 277.1239, found 277.1221.



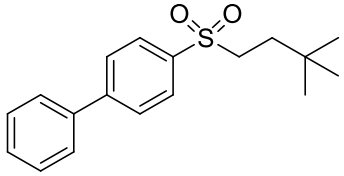
(Decylsulfonyl)benzene (3k) [96550-93-5]

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow liquid. Yield: 80%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 3.16-2.99 (m, 2H), 1.70 (m, 2H), 1.28 (m, 14H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.3, 133.7, 129.3, 128.1, 56.4, 31.9, 29.4, 29.3, 29.1, 28.3, 22.73, 22.72, 14.2.

HRMS (ESI): calculated for $C_{16}H_{26}O_2S$ $[M+Na]^+$ 305.1552, found 305.1540.



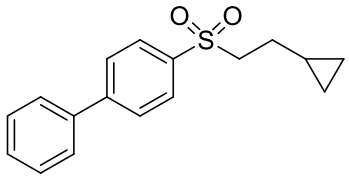
4-((3,3-dimethylbutyl)sulfonyl)-1,1'-biphenyl (3l)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as white solid. Yield: 79%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.96 (m, 2H), 7.79 (m, 2H), 7.64 (m, 2H), 7.54-7.43 (m, 3H), 3.18-3.05 (m, 2H), 1.70-1.62 (m, 2H), 0.90 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.7, 139.3, 137.9, 129.3, 128.8, 128.7, 128.0, 127.5, 53.2, 35.8, 30.2, 29.1, 28.0.

HRMS (ESI): calculated for $C_{18}H_{22}O_2S$ $[M+Na]^+$ 325.1239, found 325.1234.



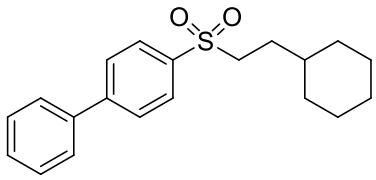
4-((2-cyclopropylethyl)sulfonyl)-1,1'-biphenyl (3m)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as white solid. Yield: 63%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.65-7.59 (m, 2H), 7.54-7.41 (m, 3H), 3.30-3.19 (m, 2H), 1.67-1.62 (m, 2H), 0.78-0.68 (m, 1H), 0.51-0.43 (m, 2H), 0.08 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.7, 139.3, 137.9, 129.2, 128.8, 128.7, 128.0, 127.5, 56.6, 28.0, 9.8, 4.8.

HRMS (ESI): calculated for $C_{17}H_{18}O_2S$ $[M+Na]^+$ 309.0926, found 309.0896.



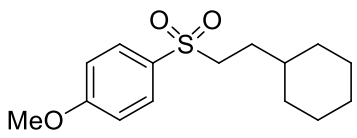
4-((2-Cyclohexylethyl)sulfonyl)-1,1'-biphenyl (3n)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow solid. Yield: 73%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 7.0 Hz, 2H), 7.40 (m, 3H), 3.12-2.99 (m, 2H), 1.62-1.51 (m, 7H), 1.19-0.99 (m, 4H), 0.86-0.75 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.7, 139.3, 137.9, 129.2, 128.8, 128.7, 128.0, 127.5, 54.6, 36.8, 32.9, 29.8, 26.4, 26.1.

HRMS (ESI): calculated for $C_{20}H_{24}O_2S$ $[M+Na]^+$ 351.1395, found 351.1371.



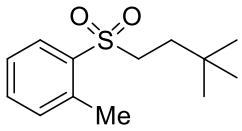
1-((2-cyclohexylethyl)sulfonyl)-4-methoxybenzene (3o)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as white liquid. Yield: 65%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.9 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 3.10-3.03 (m, 2H), 1.64-1.54 (m, 7H), 1.15 (m, 4H), 0.91-0.83 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.8, 131.0, 130.3, 114.5, 55.8, 54.8, 36.8, 32.9, 30.0, 26.4, 26.1.

HRMS (ESI): calculated for $C_{15}H_{22}O_3S$ $[M+Na]^+$ 305.1188, found 305.1198.



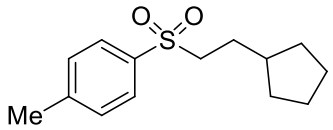
1-((3,3-dimethylbutyl)sulfonyl)-2-methylbenzene (3p)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow liquid. Yield: 62%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.52 (td, *J* = 7.5, 1.3 Hz, 1H), 7.37 (m, 2H), 3.14-3.06 (m, 2H), 2.70 (s, 3H), 1.63-1.54 (m, 2H), 0.88 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 137.8, 137.3, 133.7, 132.8, 130.3, 126.7, 52.0, 35.5, 30.1, 29.0, 20.5.

HRMS (ESI): calculated for $C_{13}H_{20}O_2S$ $[M+Na]^+$ 263.1082, found 263.1097.



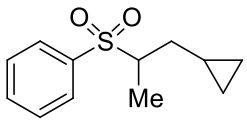
1-((2-cyclopentylethyl)sulfonyl)-4-methylbenzene (3q)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as white liquid. Yield: 66%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 3.13-3.02 (m, 2H), 2.46 (s, 3H), 1.79-1.65 (m, 5H), 1.59-1.42 (m, 4H), 1.09-1.01 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.7, 136.4, 130.0, 128.2, 56.0, 39.0, 32.4, 28.8, 25.2, 21.8.

HRMS (ESI): calculated for $C_{14}H_{20}O_2S$ $[M+Na]^+$ 275.1082, found 275.1069.



((1-Cyclopropylpropan-2-yl)sulfonyl)benzene (3r)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow liquid. Yield: 73%.

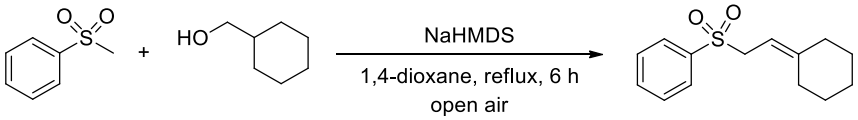
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.78 (m, 2H), 7.61-7.55 (m, 1H), 7.52-7.45 (m, 2H), 3.08 (m, 1H), 1.65 (m, 1H), 1.38 (m, 1H), 1.27 (d, *J* = 6.9 Hz, 3H), 0.69-0.57 (m, 1H), 0.50-0.40 (m, 1H), 0.39-0.31 (m, 1H), 0.04 (m, 1H), -0.05 – -0.12 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 137.3, 133.6, 129.1, 129.0, 60.8, 34.1, 13.4, 8.4, 5.8, 3.8.

HRMS (ESI): calculated for $C_{12}H_{16}O_2S$ $[M+Na]^+$ 247.0769, found 247.0778.

3. β-Olefination of sulfones with alcohols.

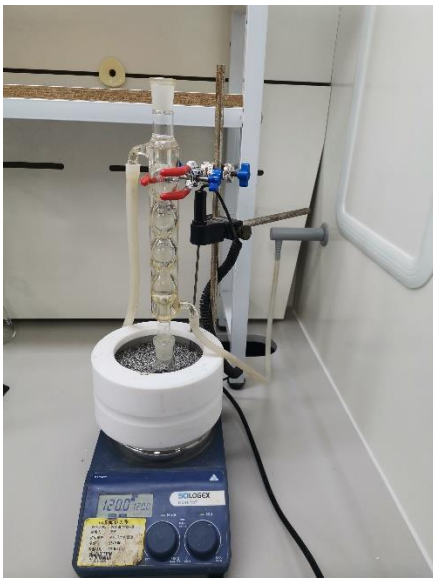
(1) General procedure of β-alkenylation of sulfones with primary alcohols in open air



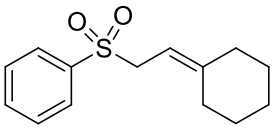
1a **2a** **5a**

A 10-mL round-bottom flask with a ball condenser were charged with alcohols (2.0 mmol), sulfones (1.0 mmol), NaHMDS (0.75 mL 2.0 mol/L in THF, 1.5 mmol) and dry 1,4-dioxane (1 mL). The reaction mixture was kept at reflux for 6 h with vigorous stirring. After cooled to room temperature, the reaction was quenched by 2 mL of dilute HCl (1.0 M). The reaction mixture was extracted 3 times by DCM and dried by anhydrous Na_2SO_4. Solvent was removed and the residue was purified by silica gel column chromatography using EA/Hexanes as eluent to give the alkenylation product.

Figure S3. Typical experimental setup with 10 mL round-bottom flask.



(2) Analytical data for products:



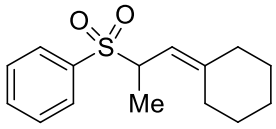
((2-cyclohexylideneethyl)sulfonyl)benzene (5a) [21378-28-9]

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as white solid. Yield: 48% (based on the conversion of sulfone).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.77 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.07 (t, *J* = 8.0 Hz, 1H), 3.75 (d, *J* = 8.0 Hz, 2H), 2.02-1.99 (m, 2H), 1.73-1.67 (m, 2H), 1.41-1.32 (m, 4H), 1.10-1.04 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.5, 138.8, 133.6, 129.1, 128.8, 107.3, 55.4, 37.3, 28.9, 28.2, 27.1, 26.4.

HRMS (ESI): calculated for $C_{14}H_{20}O_2S$ $[M+Na]^+$ 273.0925, found 273.0914.



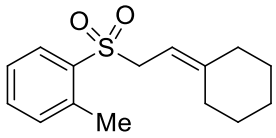
((1-cyclohexylidenepropan-2-yl)sulfonyl)benzene (5b)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow liquid. Yield: 48% (based on the conversion of sulfone).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.72 (m, 2H), 7.54 (t, *J* = 6.8 Hz, 1H), 7.45 (t, *J* = 7.0 Hz, 2H), 4.87 (d, *J* = 10.1 Hz, 1H), 3.88 (m, 1H), 1.96 (m, 2H), 1.76-1.70 (m, 1H), 1.60-1.56 (m, 1H), 1.44-1.17 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.0, 138.1, 133.5, 129.4, 128.8, 115.3, 59.0, 37.2, 29.3, 28.1, 27.1, 26.4, 14.2.

HRMS (ESI): calculated for $C_{15}H_{20}O_2S$ $[M+Na]^+$ 287.1082, found 287.1084.



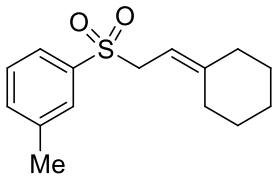
1-((2-cyclohexylideneethyl)sulfonyl)-2-methylbenzene (5c)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow liquid. Yield: 51% (based on the conversion of sulfone).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.42 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29-7.23 (m, 2H), 5.05 (t, *J* = 8.0 Hz, 1H), 3.78 (d, *J* = 8.0 Hz, 2H), 2.64 (s, 3H), 1.97 (m, 2H), 1.77-1.71 (m, 2H), 1.36-1.30 (m, 4H), 1.09-1.08 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.3, 138.4, 136.9, 133.6, 132.7, 131.2, 126.4, 107.1, 54.7, 37.3, 29.0, 28.1, 27.2, 26.4, 20.7.

HRMS (ESI): calculated for $C_{15}H_{20}O_2S$ $[M+Na]^+$ 287.1082, found 287.1066.



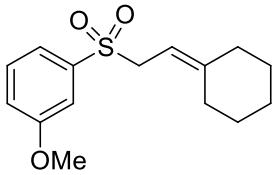
1-((2-cyclohexylideneethyl)sulfonyl)-3-methylbenzene (5d)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow solid. Yield: 50% (based on the conversion of sulfone).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.59 (m, 2H), 7.36-7.37 (m, 2H), 5.08 (t, *J* = 8.0 Hz, 1H), 3.73 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 2.02 (t, *J* = 5.3 Hz, 2H), 1.76-1.70 (m, 2H), 1.42-1.34 (m, 4H), 1.08 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.3, 139.2, 138.6, 134.4, 129.0(d, *J* = 18.4 Hz), 125.9, 107.4, 77.5, 77.2, 76.8, 55.4, 37.3, 28.9, 28.2, 27.1, 26.4, 21.4.

HRMS (ESI): calculated for $C_{15}H_{20}O_2S$ $[M+Na]^+$ 287.1082, found 287.1075.



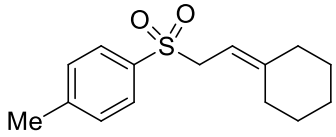
1-((2-cyclohexylideneethyl)sulfonyl)-3-methoxybenzene (5e)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow solid. Yield: 52% (based on the conversion of sulfone).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.34 (m, 2H), 7.31 – 7.26 (m, 1H), 7.12 – 7.05 (m, 1H), 5.07 (t, *J* = 8.0 Hz, 1H), 3.80 (d, *J* = 5.9 Hz, 3H), 3.74 (d, *J* = 8.0 Hz, 2H), 2.02-1.98 (m, 2H), 1.78-1.72 (m, 2H), 1.42-1.35 (m, 4H), 1.13-1.12 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.0, 150.5, 140.0, 130.2, 120.9, 120.3, 113.1, 107.3, 55.9, 55.4, 37.3, 28.9, 28.3, 27.2, 26.4.

HRMS (ESI): calculated for $C_{15}H_{20}O_3S$ $[M+Na]^+$ 303.1031, found 303.1014.



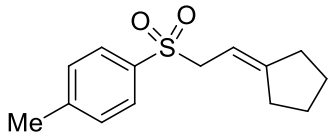
1-((2-cyclohexylideneethyl)sulfonyl)-4-methylbenzene (5f) [54646-50-3]

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow solid. Yield: 47% (based on the conversion of sulfone).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 5.05 (t, *J* = 8.0 Hz, 1H), 3.72 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H), 2.00 (m, 2H), 1.75-1.70 (m, 2H), 1.42-1.34 (m, 4H), 1.11 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.2, 144.5, 135.9, 129.6, 128.7, 107.3, 55.4, 37.2, 28.9, 28.1, 27.1, 26.4, 21.7.

HRMS (ESI): calculated for $C_{15}H_{20}O_2S$ $[M+Na]^+$ 287.1082, found 287.1088.



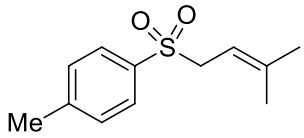
1-((2-cyclopentylideneethyl)sulfonyl)-4-methylbenzene (5g)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow liquid. Yield: 50% (based on the conversion of sulfone).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.24-5.19 (m, 1H), 3.68 (d, *J* = 7.9 Hz, 2H), 2.37 (s, 3H), 2.18 (t, *J* = 6.5 Hz, 2H), 1.76 (t, *J* = 6.7 Hz, 2H), 1.49-1.40 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.1, 144.5, 136.1, 129.6, 128.7, 106.3, 58.0, 34.2, 28.9, 26.1, 26.0, 21.8.

HRMS (ESI): calculated for $C_{14}H_{18}O_2S$ $[M+Na]^+$ 273.0926, found 273.0913.



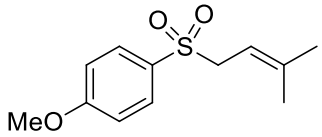
1-methyl-4-((3-methylbut-2-en-1-yl)sulfonyl)benzene (5h) [15543-64-3]

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow liquid. Yield: 49% (based on the conversion of sulfone).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 5.11 (t, *J* = 7.9 Hz, 1H), 3.69 (d, *J* = 7.9 Hz, 2H), 2.38 (s, 3H), 1.65 (s, 3H), 1.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.6, 142.9, 136.0, 129.7, 128.6, 110.7, 56.4, 26.0, 21.8, 17.9.

HRMS (ESI): calculated for $C_{12}H_{16}O_2S$ $[M+Na]^+$ 247.0769, found 247.0753.



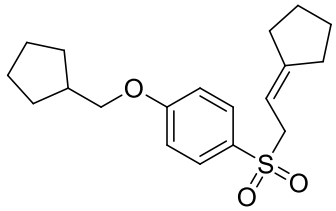
1-methoxy-4-((3-methylbut-2-en-1-yl)sulfonyl)benzene (5i)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as white solid. Yield: 52% (based on the conversion of sulfone).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 5.16-5.08 (m, 1H), 3.82 (s, 3H), 3.69 (d, *J* = 8.0 Hz, 2H), 1.65 (s, 3H), 1.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ162.6, 141.6, 129.6, 129.3, 113.1, 109.7, 55.4, 54.6, 24.8, 16.8.

HRMS (ESI): calculated for $C_{12}H_{16}O_3S$ $[M+Na]^+$ 263.0718, found 263.0705.



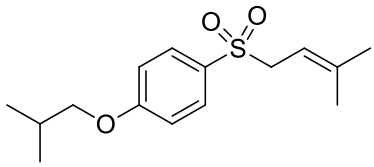
1-(2-cyclopentylethoxy)-4-((2-cyclopentylideneethyl)sulfonyl)benzene (5j)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as white solid. Yield: 48% (based on the conversion of sulfone).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 5.26-5.17 (m, 1H), 3.82 (d, *J* = 7.0 Hz, 2H), 3.67 (d, *J* = 7.8 Hz, 2H), 2.35-2.27 (m, 1H), 2.18 (m, 2H), 1.78 (m, 4H), 1.58-1.42 (m, 8H), 1.31-1.25 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.5, 154.9, 130.7, 130.3, 114.7, 106.6, 72.8, 58.2, 39.0, 34.2, 29.6, 28.9, 26.2, 26.1, 25.5.

HRMS (ESI): calculated for $C_{20}H_{28}O_3S$ $[M+Na]^+$ 357.1501, found 357.1486.



1-(isobutoxy)-4-((3-methylbut-2-en-1-yl)sulfonyl)benzene (5k)

The product was isolated by flash chromatography (EA/hexanes 1/20-1/10) as yellow liquid. Yield: 49% (based on the conversion of sulfone).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.12 (t, *J* = 7.9 Hz, 1H), 3.72 (d, *J* = 6.5 Hz, 2H), 3.68 (d, *J* = 8.0 Hz, 2H), 2.04 (m, 1H), 1.65 (s, 3H), 1.28 (s, 3H), 0.97 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.5, 142.7, 130.7, 130.1, 114.7, 110.9, 74.9, 56.5, 28.3, 26.0, 19.3, 17.9.

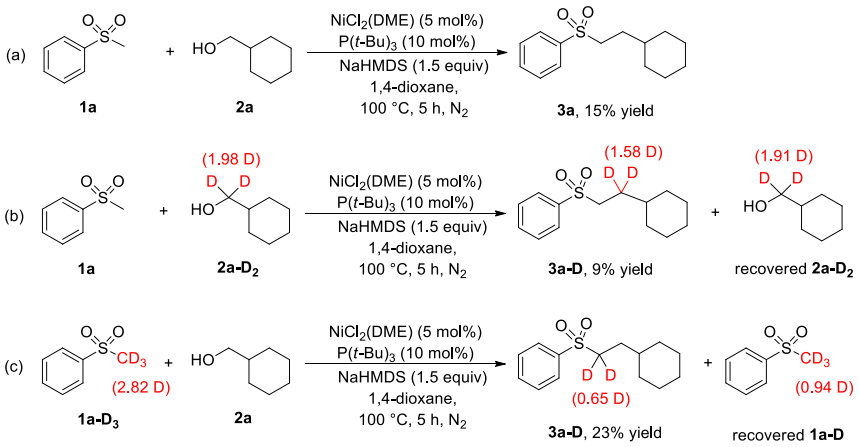
HRMS (ESI): calculated for $C_{16}H_{24}O_3S$ $[M+Na]^+$ 305.1188, found 305.1211.

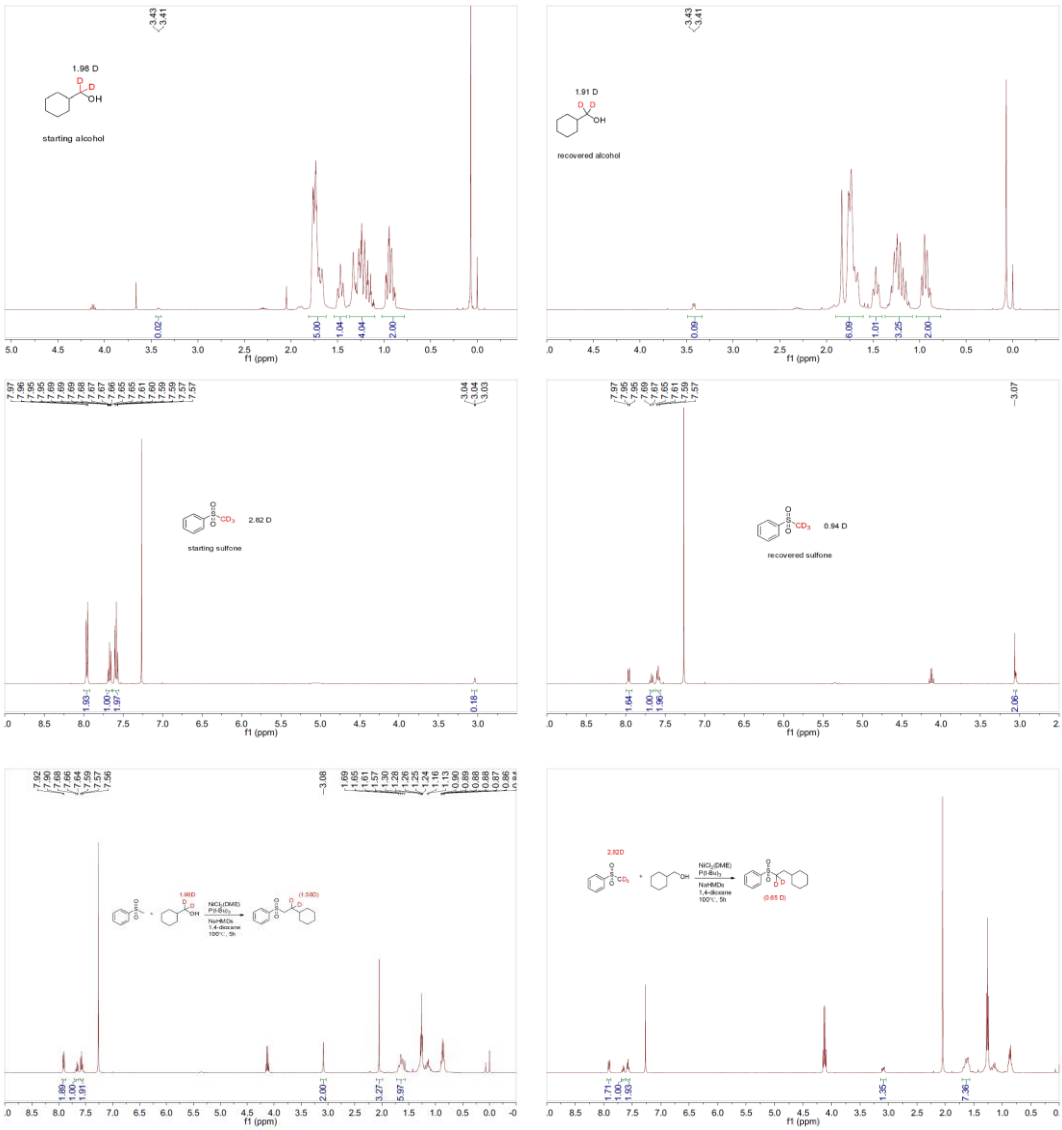
4. Mechanism studies.

(1) Kinetic isotope experiments (KIE).

Three parallel experiments using $PhSO_2CH_3$ with Cy-CH_2OH (a), $PhSO_2CH_3$ with Cy-CD_2OH (b), and $PhSO_2CD_3$ with Cy-CH_2OH (c) respectively were carried out simultaneously and stopped at 5 h. Yields were determined by GC. Each reaction was conducted two times and the average GC yield was

used to calculate KIE effect. The deuterimu contents of product and recoverd starting material were estimated by ^{1}H NMR integration.

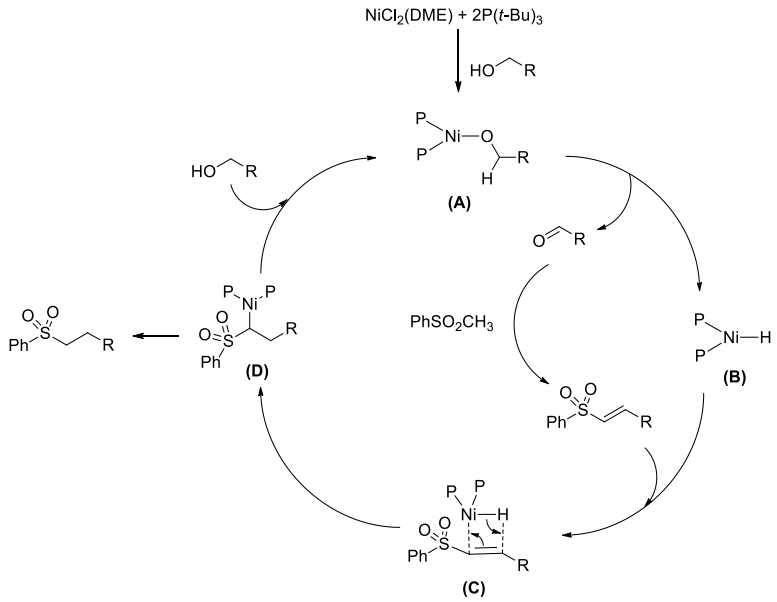




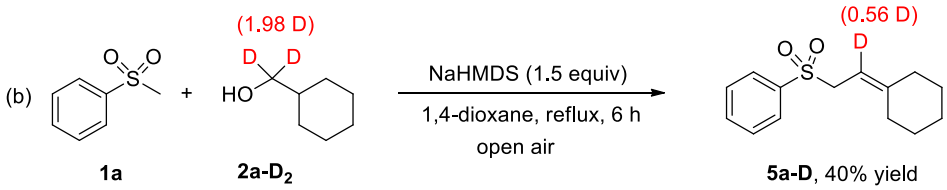
^{1}H NMR spectra of deuterated compounds.

(2) **Figure S4**: A plausible mechanism for nickel-catalyzed α-alkylation of sulfones with alcohols.

The alkylation reaction of sulfone takes place via a borrowing hydrogen pathway. Nickel catalyst takes the hydrogen atom from the α-C-H of alcohol to form nickel hydride (**B**) and aldehyde. The latter condensed with sulfone to form α,β-unsaturated sulfone. Finally hydrogenation of α,β-unsaturated sulfone by Ni-H afford the alkylation product.

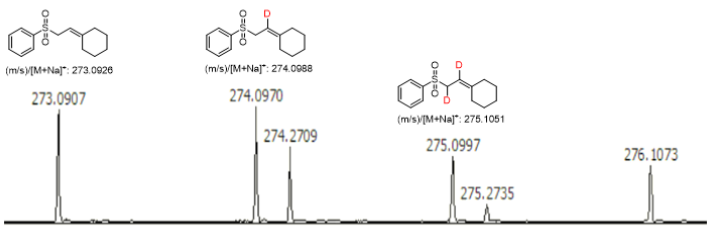


(2) β-alkenylation of sulfone **1a** with cyclohexyl methanol **2a-D$_2$**.

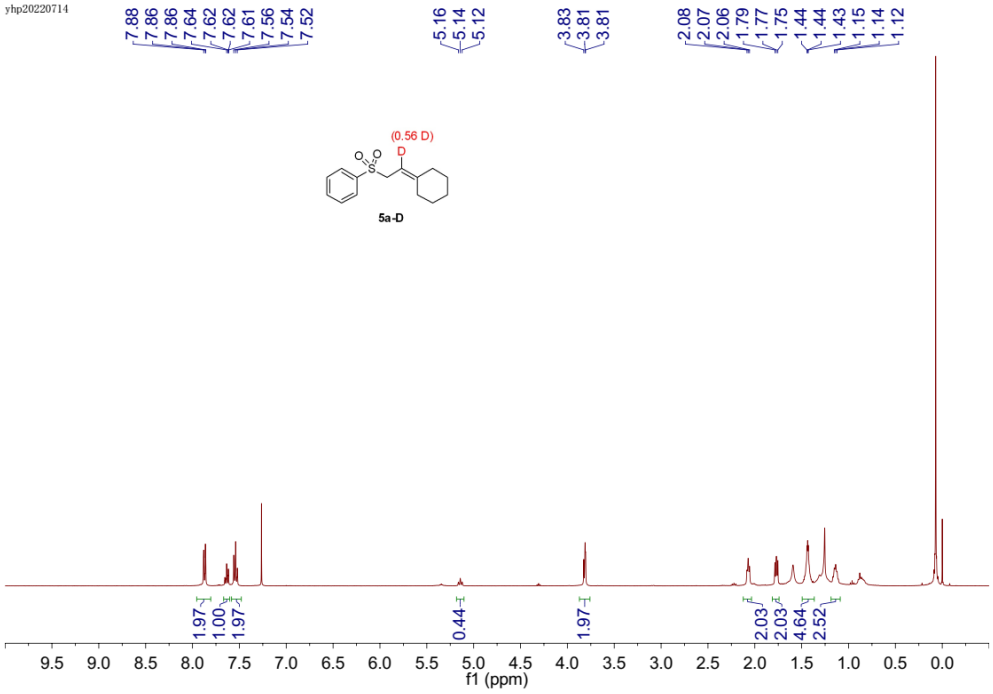


A 10-mL round-bottom flask with a ball condenser were charged with alcohols (2.0 mmol), sulfones (1.0 mmol), NaHMDS (0.75 mL 2.0 mol/L in THF, 1.5 mmol) and dry 1,4-dioxane (1 mL). The reaction mixture was kept at reflux for 6 h with vigorous stirring. After cooled to room temperature, the reaction mixture was subjected to silica gel column chromatography directly using EA/hexanes (1:20) as eluent to give the **5a-D** product in 40% yield. The ^{1}H NMR integration of β-C-H was 0.44, indicating that the deuterium content was 0.56. HRMS give samilar ratio of **5a-D1** but there was also 23% **5a-D2** product.

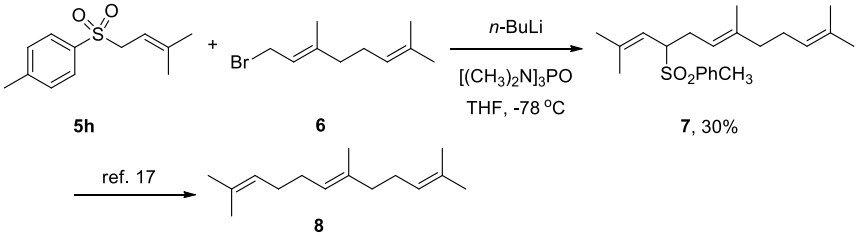
HRMS (ESI) of **5a-D**



^{1}H NMR ($CDCl_3$) of **5a-D**



5. Synthetic applications



A solution of **5h** (53 mg, 0.238 mmol), dissolved in 5 mL of the mixed solvent of THF and $[(CH_3)_2N]_3PO$ (4:1), was cooled at -20 °C and then 1.0 mL of n-BuLi (1.60 M in n-hexane) was added, the color changing to orange, and stirred for 20 min. The temperature was further lowered to -78 °C. To the cooled solution, geranyl bromide (18 μL, 0.089 mmol) in THF (2.5 mL) was added and stirred for 1 h. The reaction mixture was poured into ice-water, extracted with hexane, and dried over anhydrous Na_2SO_4. The concentrated reaction mixture was subjected to silica gel column chromatography using EA/Hexanes (1:9) as eluent to give the **6** as yellow liquid. Yield: 69%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.05-4.92 (m, 2H), 4.65 (m, 1H), 3.69 (m, 1H), 2.89-2.74 (m, 1H), 2.44 (s, 3H), 2.37-2.28 (m, 1H), 2.03-1.86 (m, 4H), 1.67 (d, *J* = 10.2 Hz, 6H), 1.58 (d, *J* = 5.5 Hz, 6H), 1.20 (d, *J* = 4.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.2, 140.6, 137.4, 134.0, 130.5, 128.3, 128.1, 122.9, 117.7, 116.2, 63.9, 38.6, 38.1, 36.0, 25.5, 24.8, 24.7, 20.6, 17.1, 16.6, 15.3, 15.1.

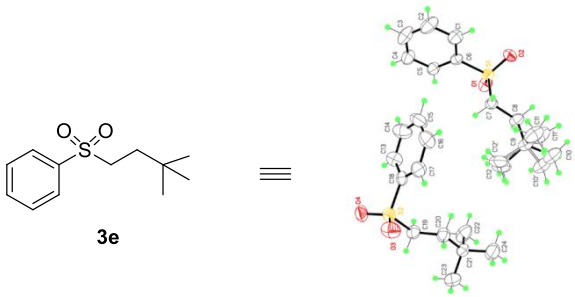
MS (ESI): calculated for $C_{22}H_{32}O_2S$ $[M+Na]^+$ 383.20, found 383.20.

6. X-ray crystallographic analysis of compound 3e, 5b and 5j.

(1) General method for crystal growth

In a 10-mL glass vial, 20 mg of pure compound was dissolved in 5 mL solvent (DCM/hexane 5:1). The vial was sealed with filter paper and fixed in a quiet, well ventilated place. Solvent was evaporated very slowly from the solution at room temperature until saturation was reached and crystals formed.

(2) X-ray crystallographic analysis of **3e**



3e

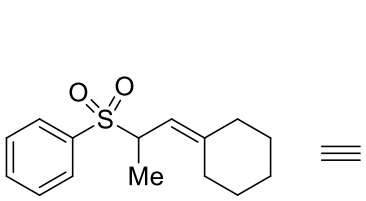
(Displacement ellipsoids are drawn at the 30% probability level) (CCDC 2208308)

exp_983

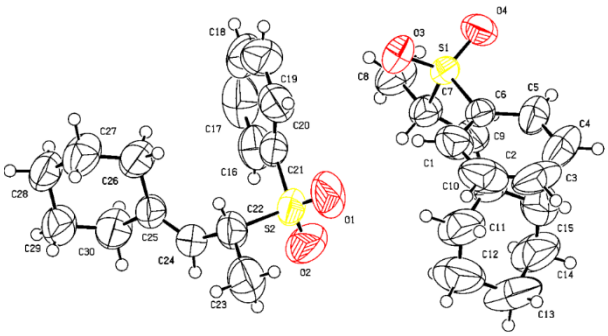
Table 1 Crystal data and structure refinement for exp_983

Identification code	exp_983
Empirical formula	$C_{12}H_{18}O_2S$
Formula weight	226.32
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	19.9158(17)
b/Å	12.0713(9)
c/Å	10.9676(7)
α/°	90.00
β/°	91.873(7)
γ/°	90.00
Volume/Å^3	2635.3(3)
Z	8
ρ_{calc}mg/mm^3	1.141
m/mm^{-1}	2.024
F(000)	976.0
Crystal size/mm^3	0.27 × 0.24 × 0.02
2Θ range for data collection	8.56 to 134.12°
Index ranges	-21 ≤ h ≤ 23, -14 ≤ k ≤ 10, -12 ≤ l ≤ 13
Reflections collected	11609
Independent reflections	4705[R(int) = 0.0474]
Data/restraints/parameters	4705/24/302
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0613, wR_2 = 0.1627
Final R indexes [all data]	R_1 = 0.1043, wR_2 = 0.1929
Largest diff. peak/hole / e Å^{-3}	0.44/-0.39

(4) X-ray crystallographic analysis of **5b**



5b



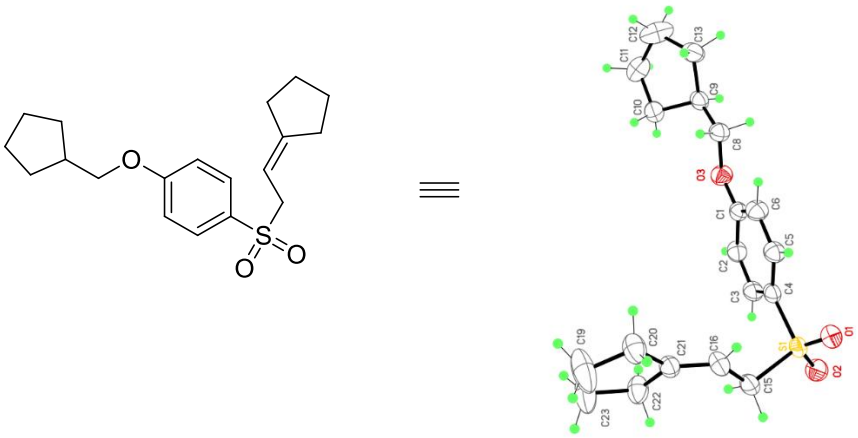
(Displacement ellipsoids are drawn at the 50% probability level) (CCDC 2208307)

exp_964

Table 1 Crystal data and structure refinement for exp_964

Identification code	exp_964
Empirical formula	$C_{15}H_{20}O_2S$
Formula weight	264.37
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.5020(4)
b/Å	13.0247(10)
c/Å	13.5023(7)
α/°	92.066(5)
β/°	95.165(4)
γ/°	99.518(5)
Volume/Å^3	1466.64(15)
Z	4
ρ_{calc}mg/mm^3	1.197
m/mm^{-1}	1.893
F(000)	568.0
Crystal size/mm^3	0.7 × 0.5 × 0.3
2Θ range for data collection	9.28 to 134.14°
Index ranges	-6 ≤ h ≤ 10, -15 ≤ k ≤ 15, -15 ≤ l ≤ 16
Reflections collected	10229
Independent reflections	5224[R(int) = 0.0176]
Data/restraints/parameters	5224/1/327
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0830, wR_2 = 0.2398
Final R indexes [all data]	R_1 = 0.0961, wR_2 = 0.2572
Largest diff. peak/hole / e Å^{-3}	0.65/-0.44

(5) X-ray crystallographic analysis of **5j**



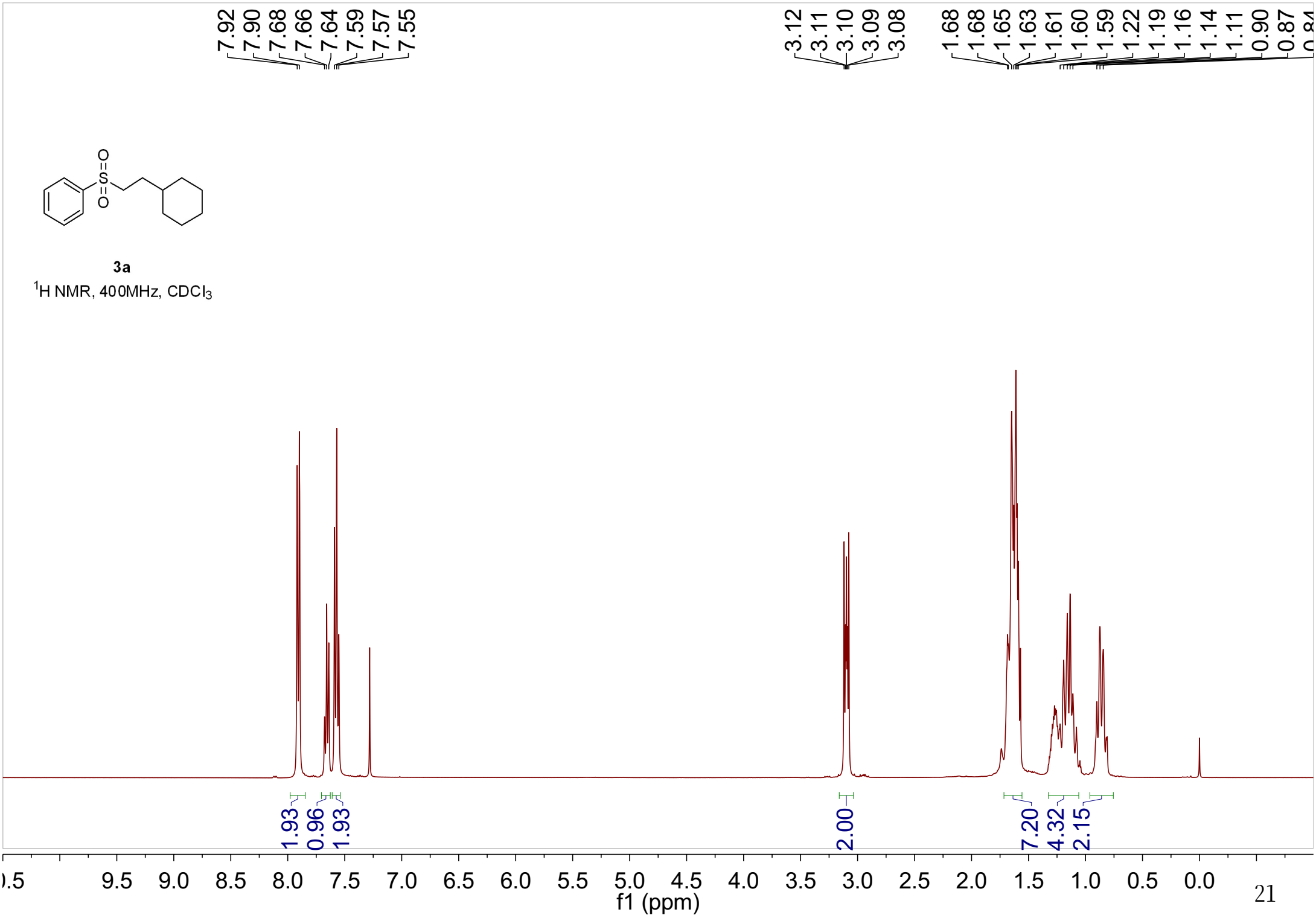
(Displacement ellipsoids are drawn at the 50% probability level) (CCDC 2208305)

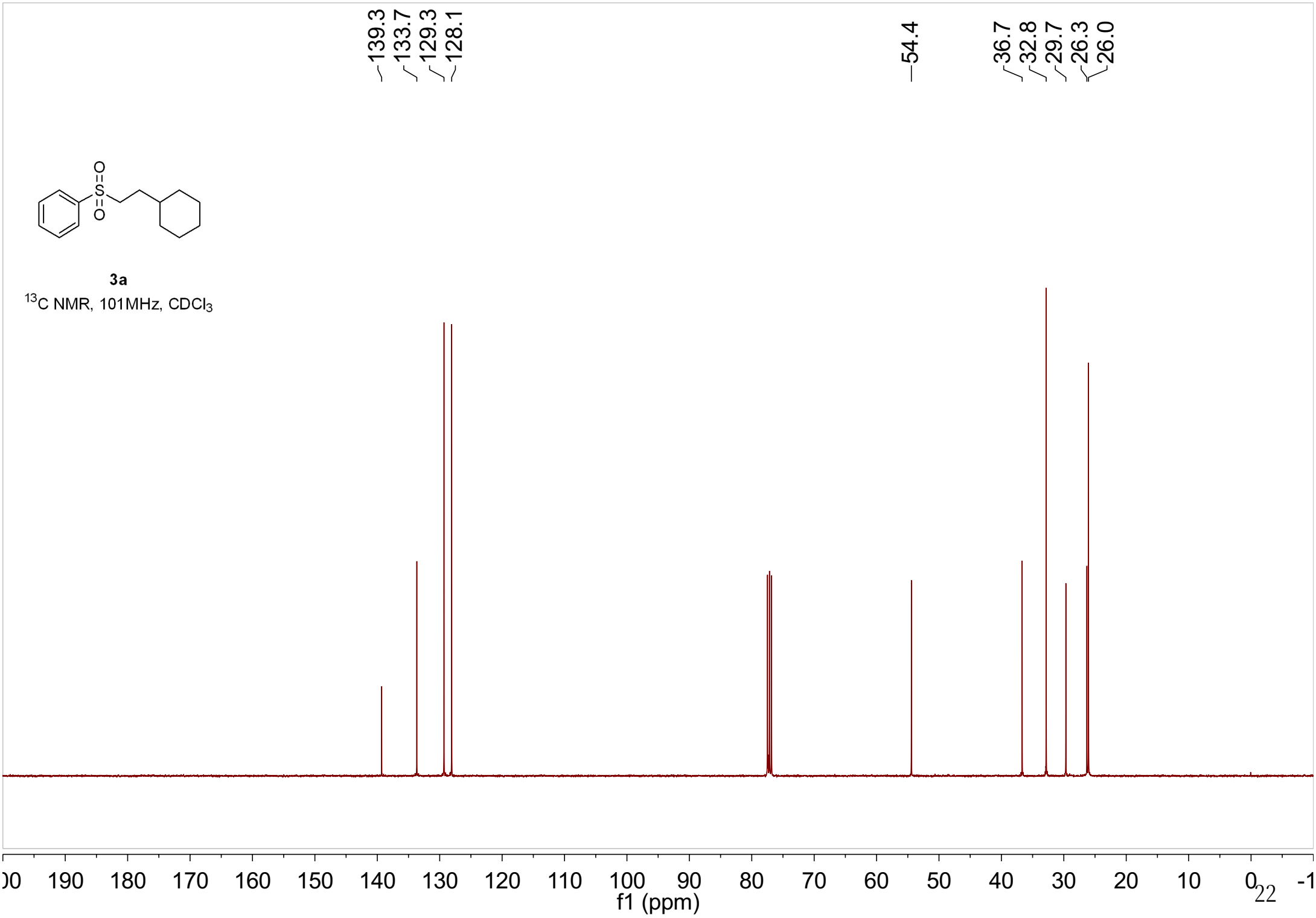
exp_949

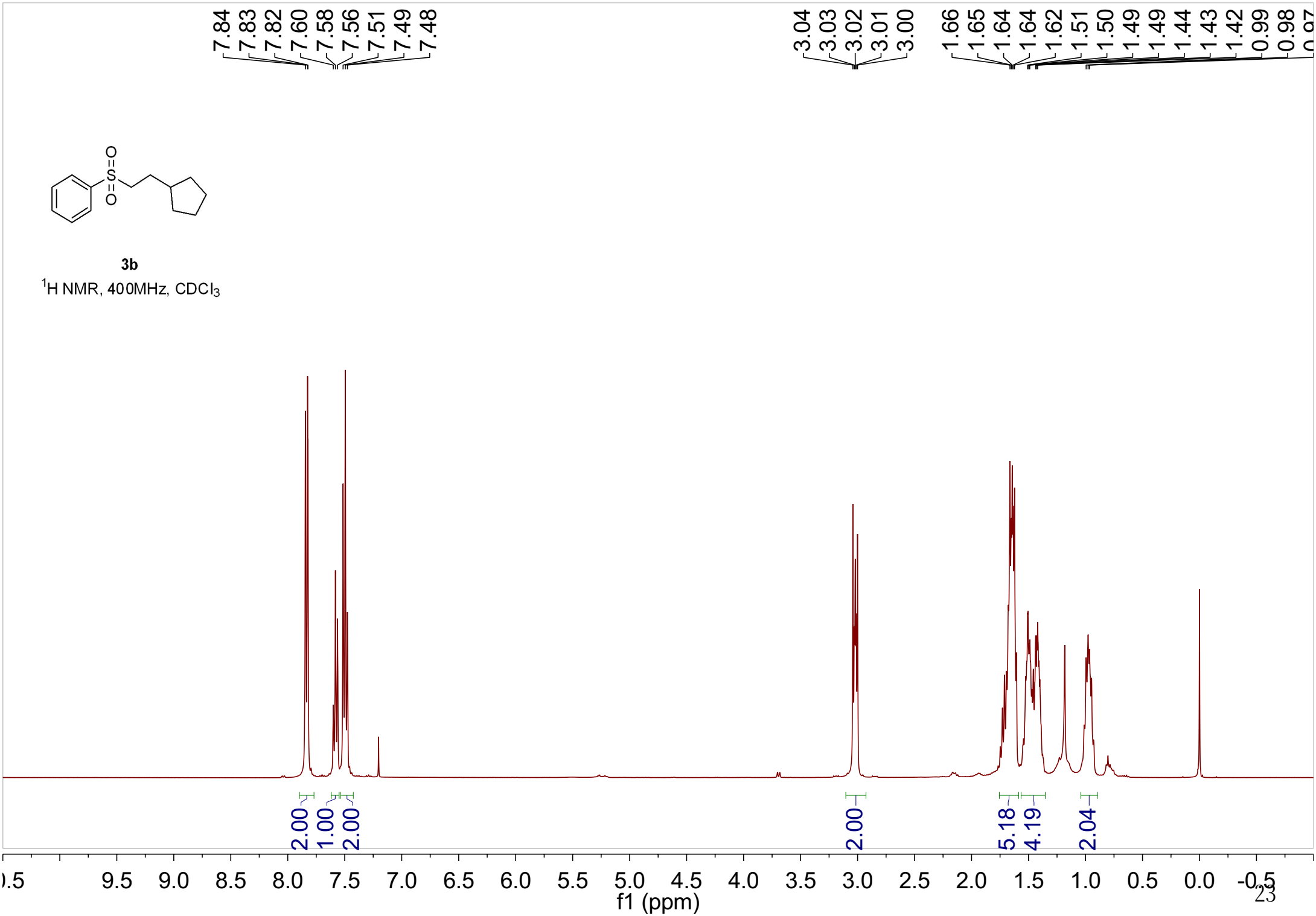
Table 1 Crystal data and structure refinement for exp_949

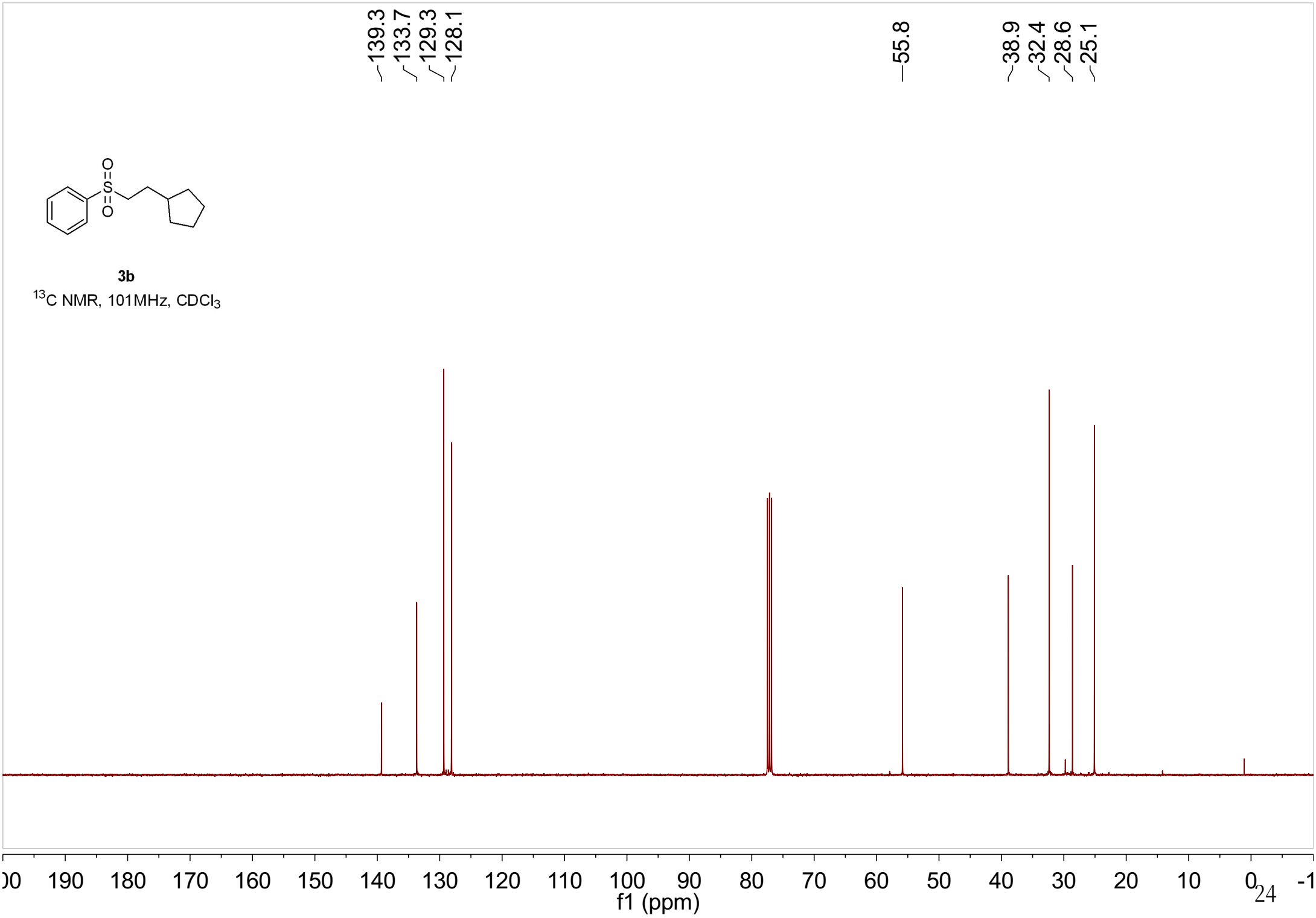
Identification code	exp_949
Empirical formula	$C_{19}H_{26}O_3S$
Formula weight	334.46
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.1676(5)
b/Å	11.8368(9)
c/Å	13.6151(10)
α/°	112.511(7)
β/°	96.462(6)
γ/°	97.113(6)
Volume/Å^3	897.20(12)
Z	2
ρ_{calc}mg/mm^3	1.238
m/mm^{-1}	1.696
F(000)	360.0
Crystal size/mm^3	0.36 × 0.19 × 0.01
2Θ range for data collection	7.14 to 134.12°
Index ranges	-7 ≤ h ≤ 6, -14 ≤ k ≤ 12, -11 ≤ l ≤ 16
Reflections collected	6248
Independent reflections	3198[R(int) = 0.0327]
Data/restraints/parameters	3198/0/208
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0613, wR_2 = 0.1682
Final R indexes [all data]	R_1 = 0.0742, wR_2 = 0.1884
Largest diff. peak/hole / e Å^{-3}	0.24/-0.39

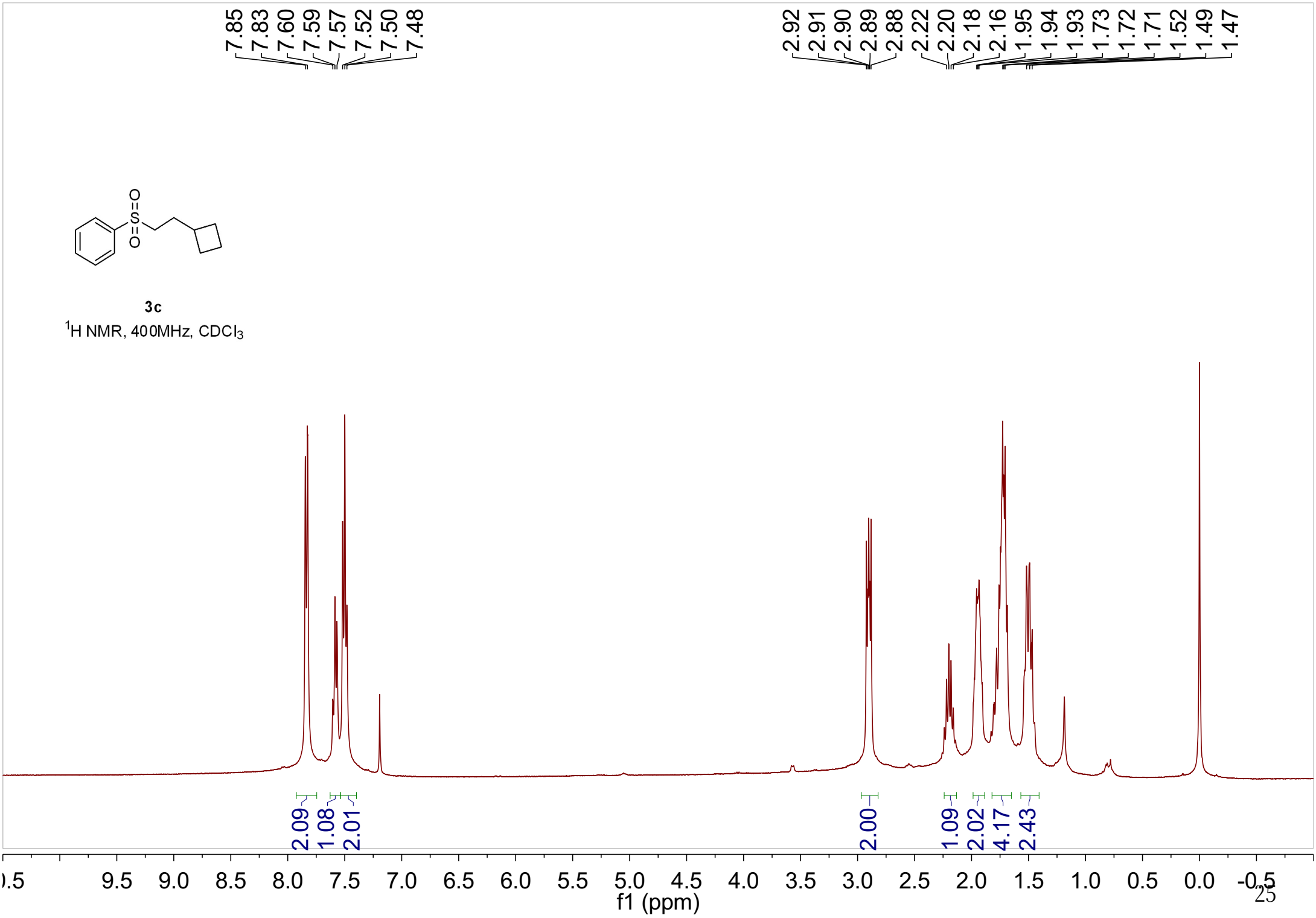
7. NMR spectra

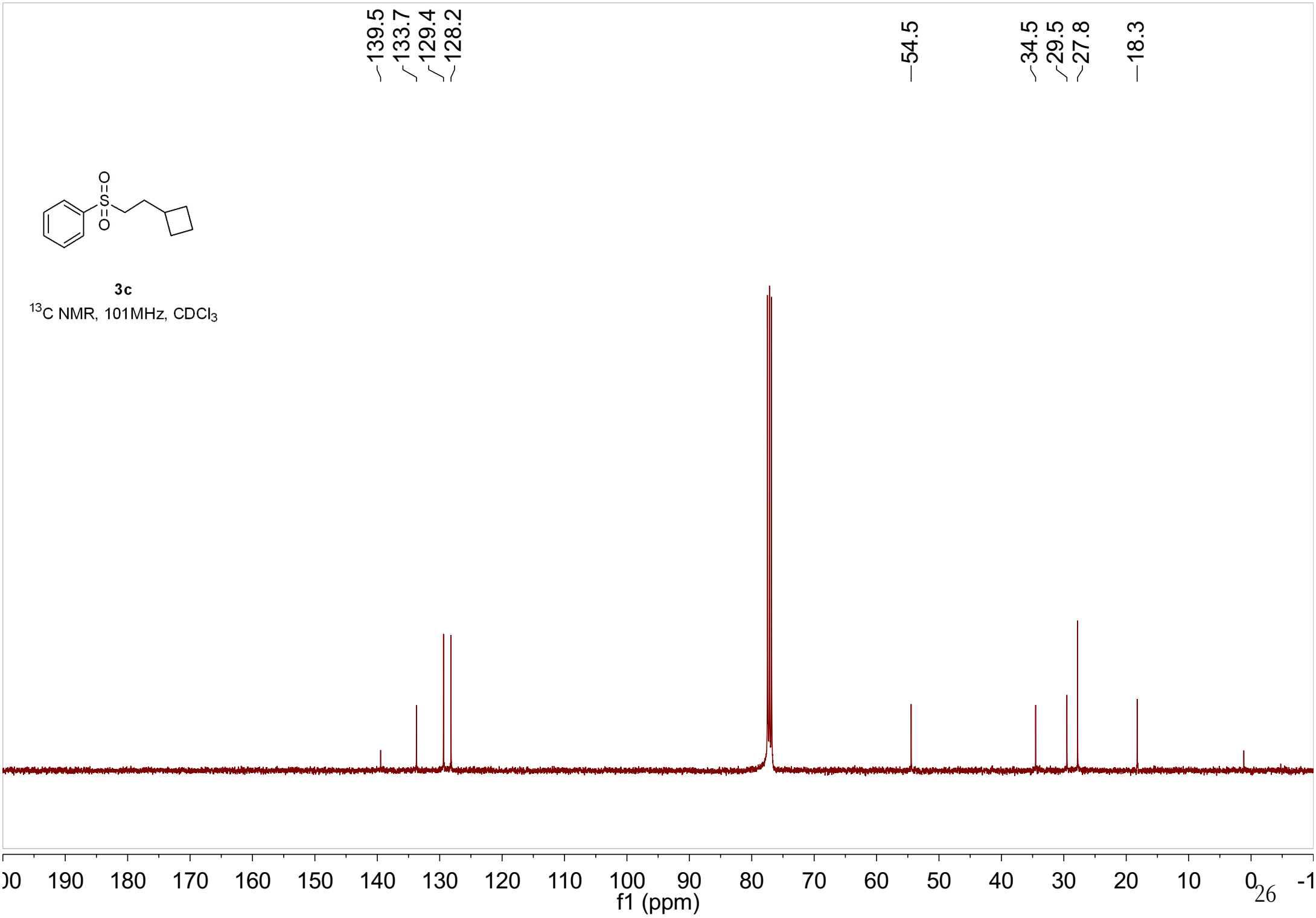

7.92
7.90
7.68
7.66
7.64
7.59
7.57
7.55
3.12
3.11
3.10
3.09
3.08
1.68
1.68
1.65
1.63
1.61
1.60
1.59
1.22
1.19
1.16
1.14
1.11
0.90
0.87
O
S
O
O
3a
1H NMR, 400MHz, CDCl3
1.93
0.96
1.93
2.00
7.20
4.32
2.15
f1 (ppm)

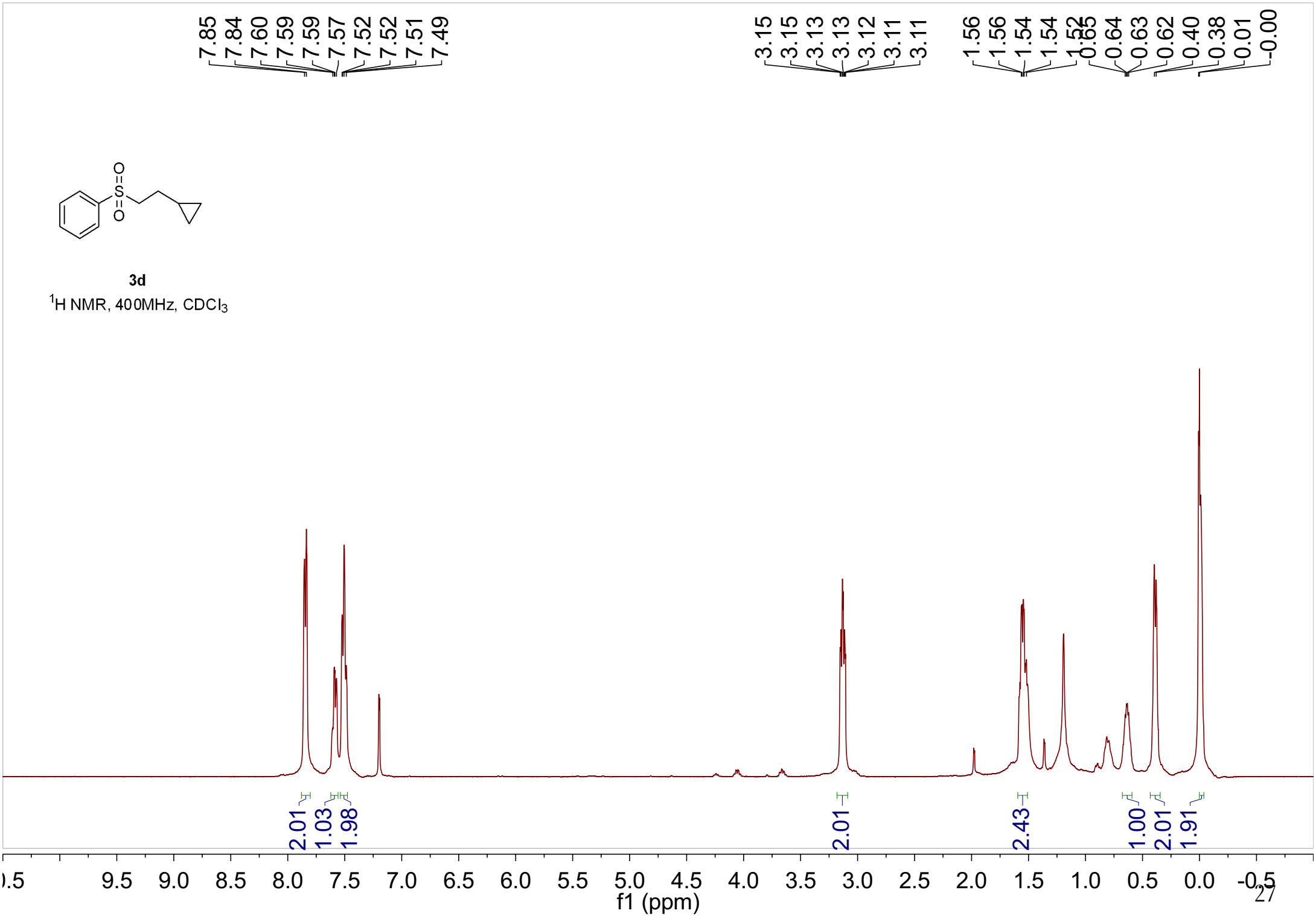

139.3
133.7
129.3
128.1
54.4
36.7
32.8
29.7
26.3
26.0
O
S
O
O
3a
^{13}C NMR, 101MHz, $CDCl_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

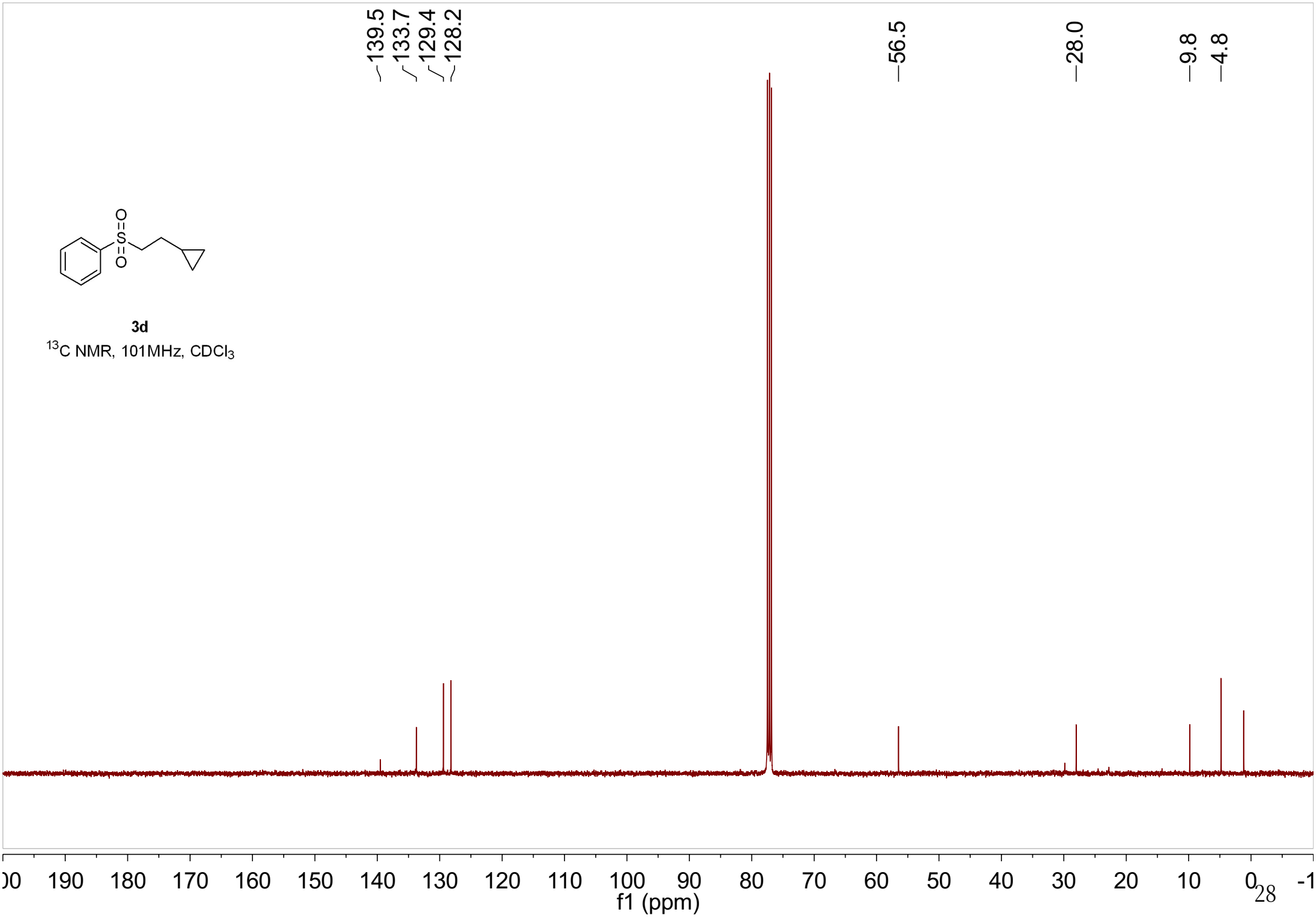

7.84
7.83
7.82
7.60
7.58
7.56
7.51
7.49
7.48
3.04
3.03
3.02
3.01
3.00
1.66
1.65
1.64
1.64
1.62
1.51
1.50
1.49
1.49
1.44
1.43
1.42
0.99
0.98
O
S
O
O
3b
1H NMR, 400MHz, CDCl3
2.00
1.00
2.00
2.00
5.18
4.19
2.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

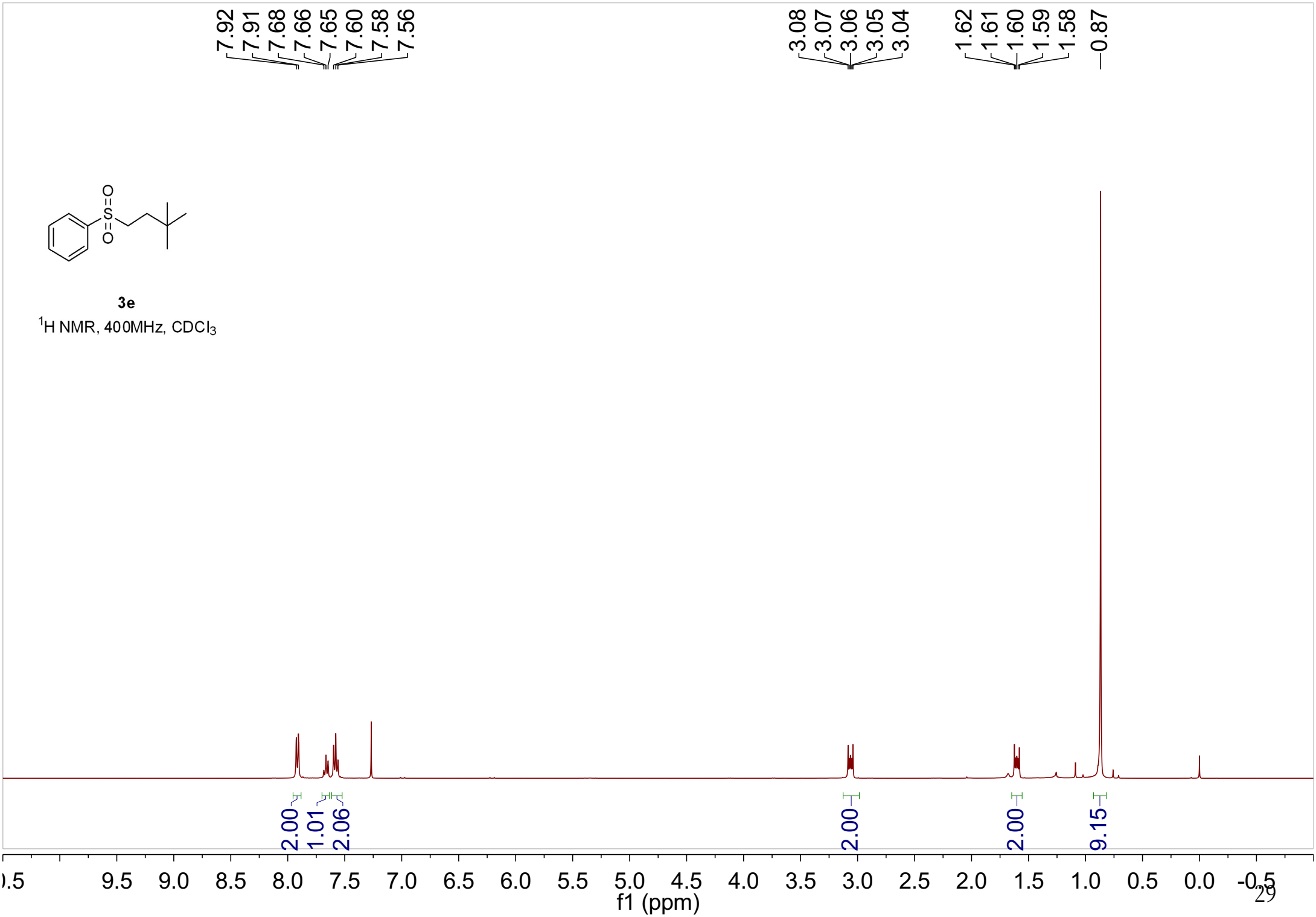

139.3
133.7
129.3
128.1
55.8
38.9
32.4
28.6
25.1
O
S
O
3b
13C NMR, 101MHz, CDCl3
f1 (ppm)


7.85
7.83
7.60
7.59
7.57
7.52
7.50
7.48
2.92
2.91
2.90
2.89
2.88
2.22
2.20
2.18
2.16
1.95
1.94
1.93
1.73
1.72
1.71
1.52
1.49
1.47
3c
1H NMR, 400MHz, CDCl3
2.09
1.08
2.01
2.00
1.09
2.02
4.17
2.43
f1 (ppm)


139.5
133.7
129.4
128.2
54.5
34.5
29.5
27.8
18.3
O
S
O
O
3c
13C NMR, 101MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

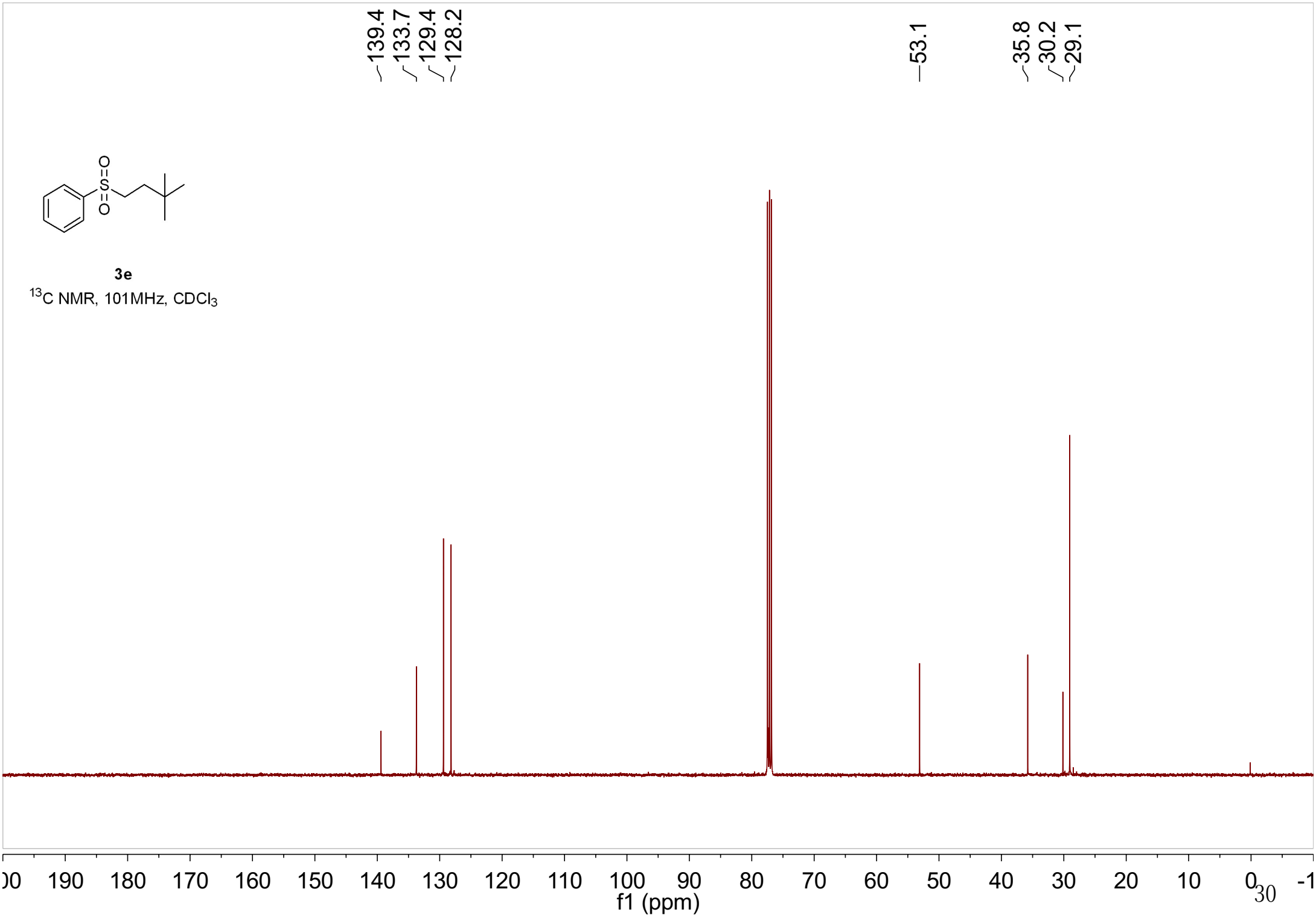

7.85
7.84
7.60
7.59
7.59
7.57
7.52
7.52
7.51
7.49
3.15
3.15
3.13
3.13
3.12
3.11
3.11
1.56
1.56
1.54
1.54
1.52
0.65
0.64
0.63
0.62
0.40
0.38
0.01
-0.00
O
S
O
O
3d
1H NMR, 400MHz, CDCl3
2.01
1.03
1.98
2.01
2.43
1.00
2.01
1.91
f1 (ppm)

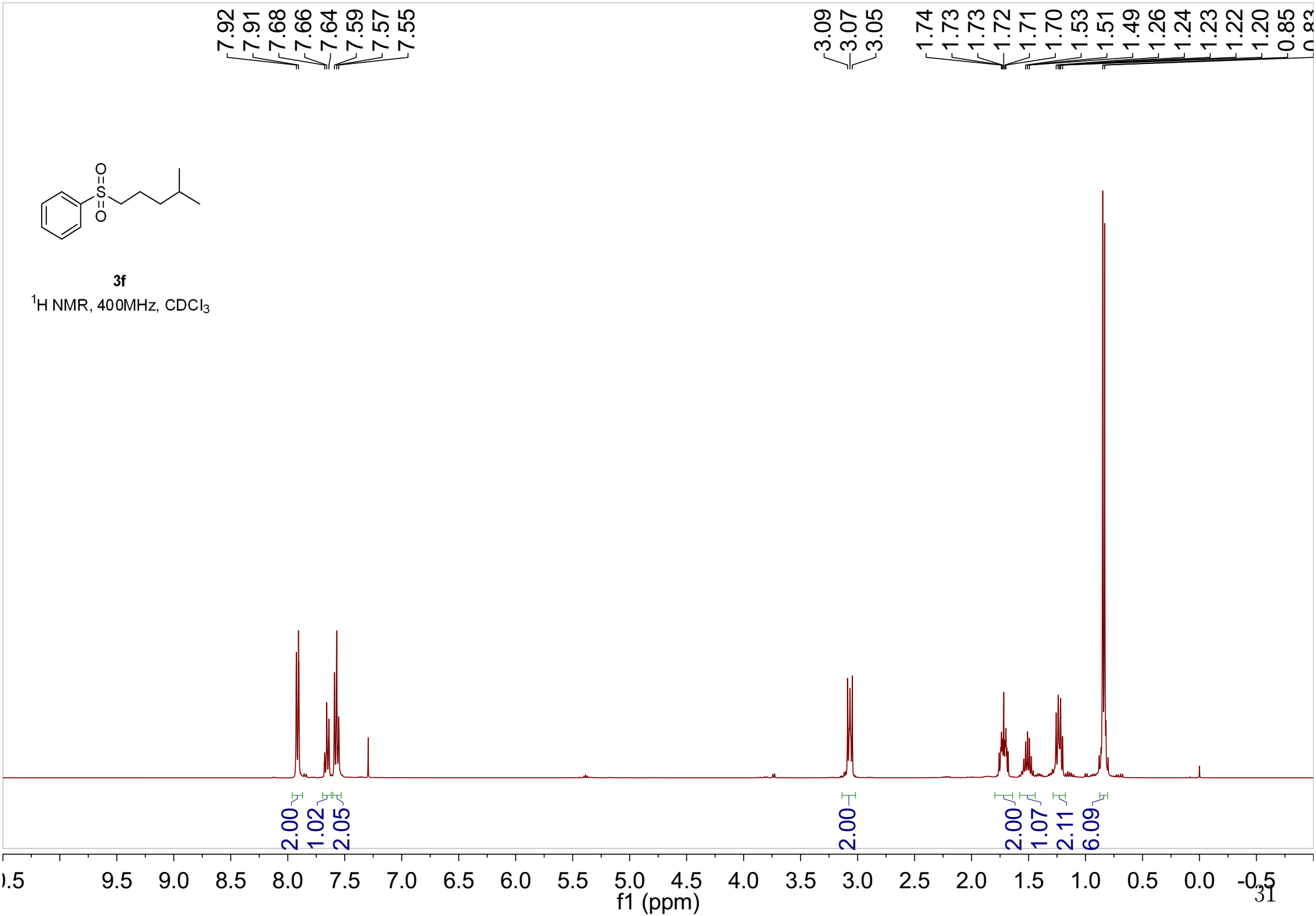

139.5
133.7
129.4
128.2
56.5
28.0
9.8
4.8
3d
13C NMR, 101MHz, CDCl3
f1 (ppm)

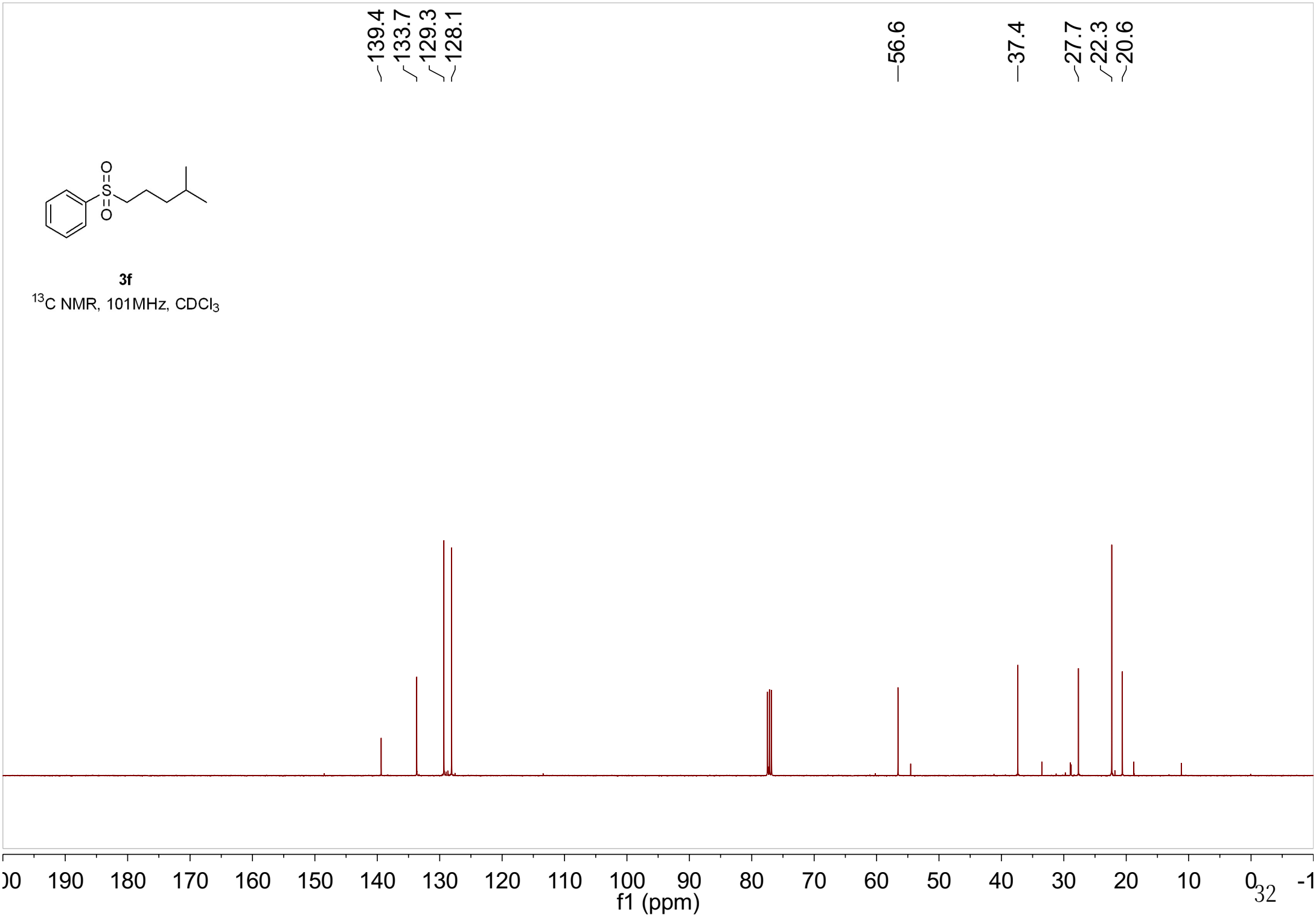


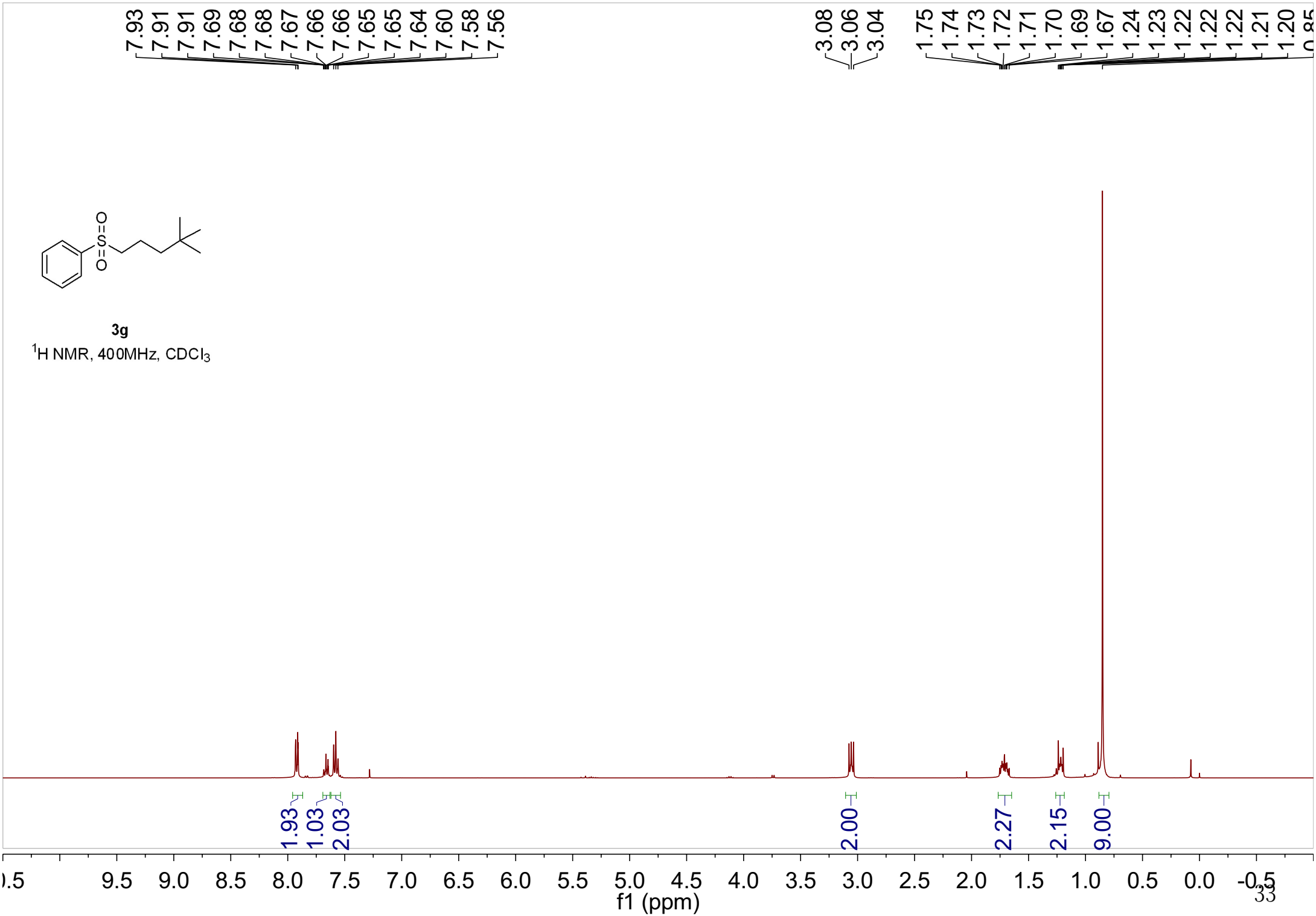
3e

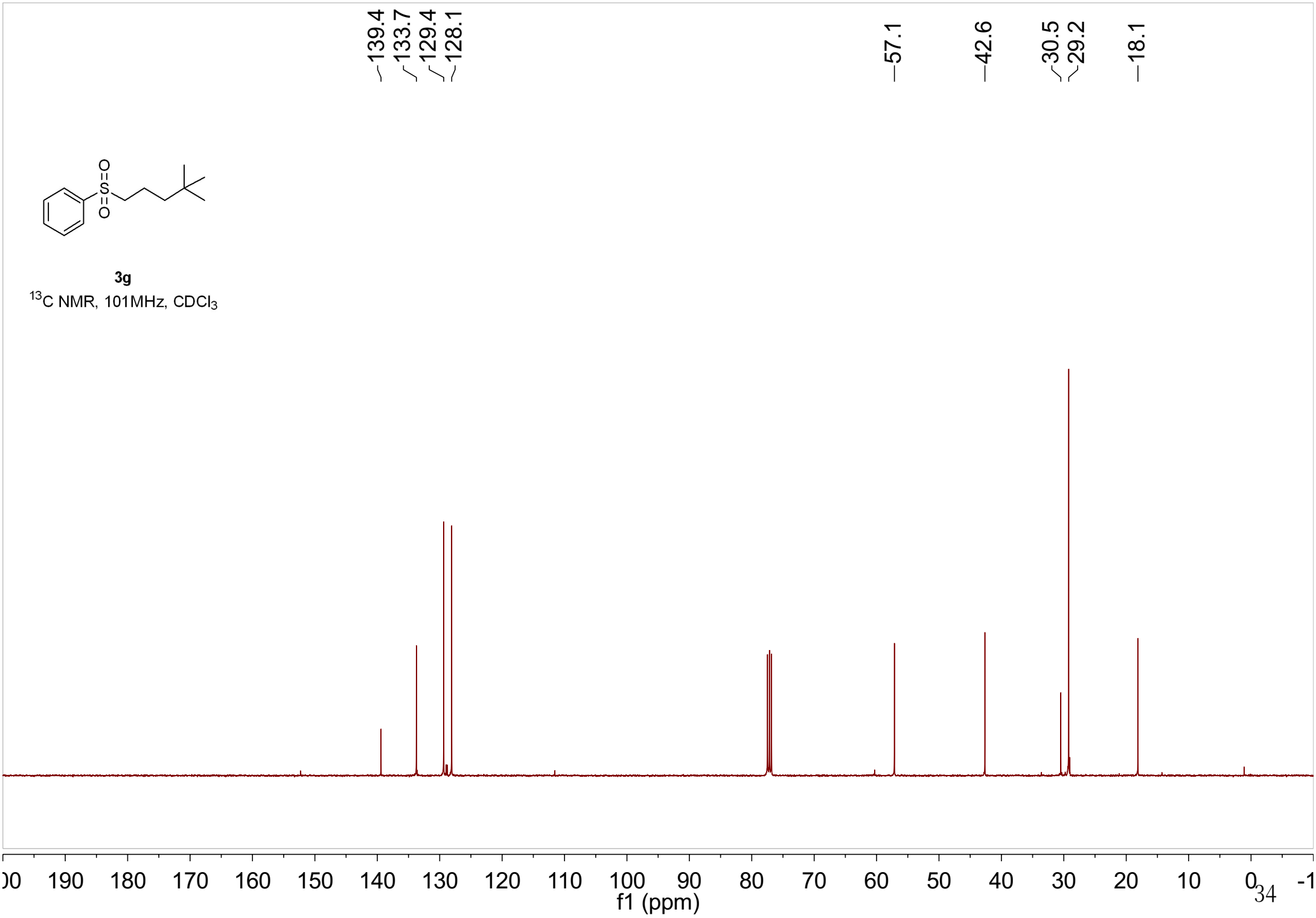
^{1}H NMR, 400MHz, $CDCl_3$

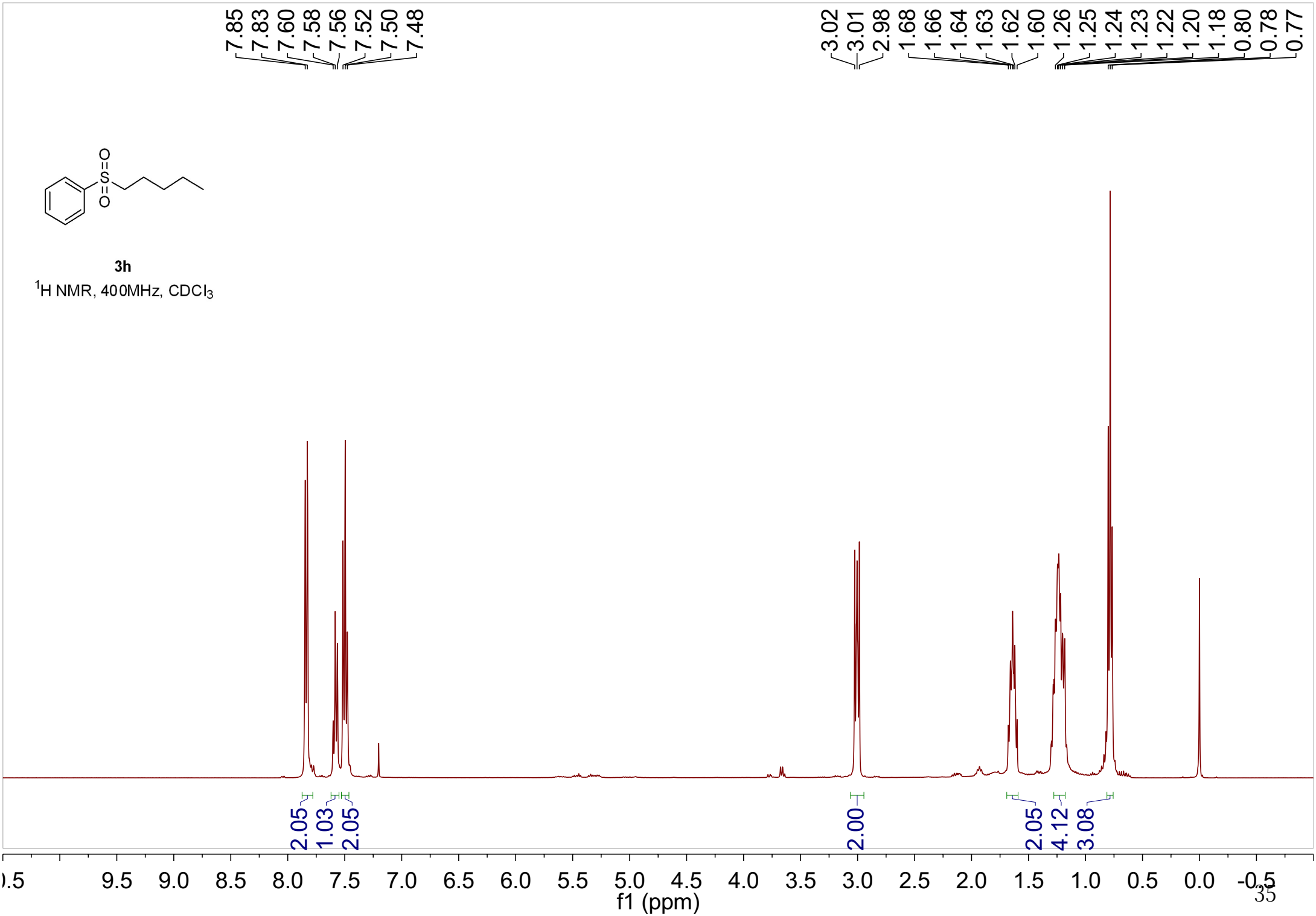

139.4
133.7
129.4
128.2
53.1
35.8
30.2
29.1
O
S
O
3e
13C NMR, 101MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

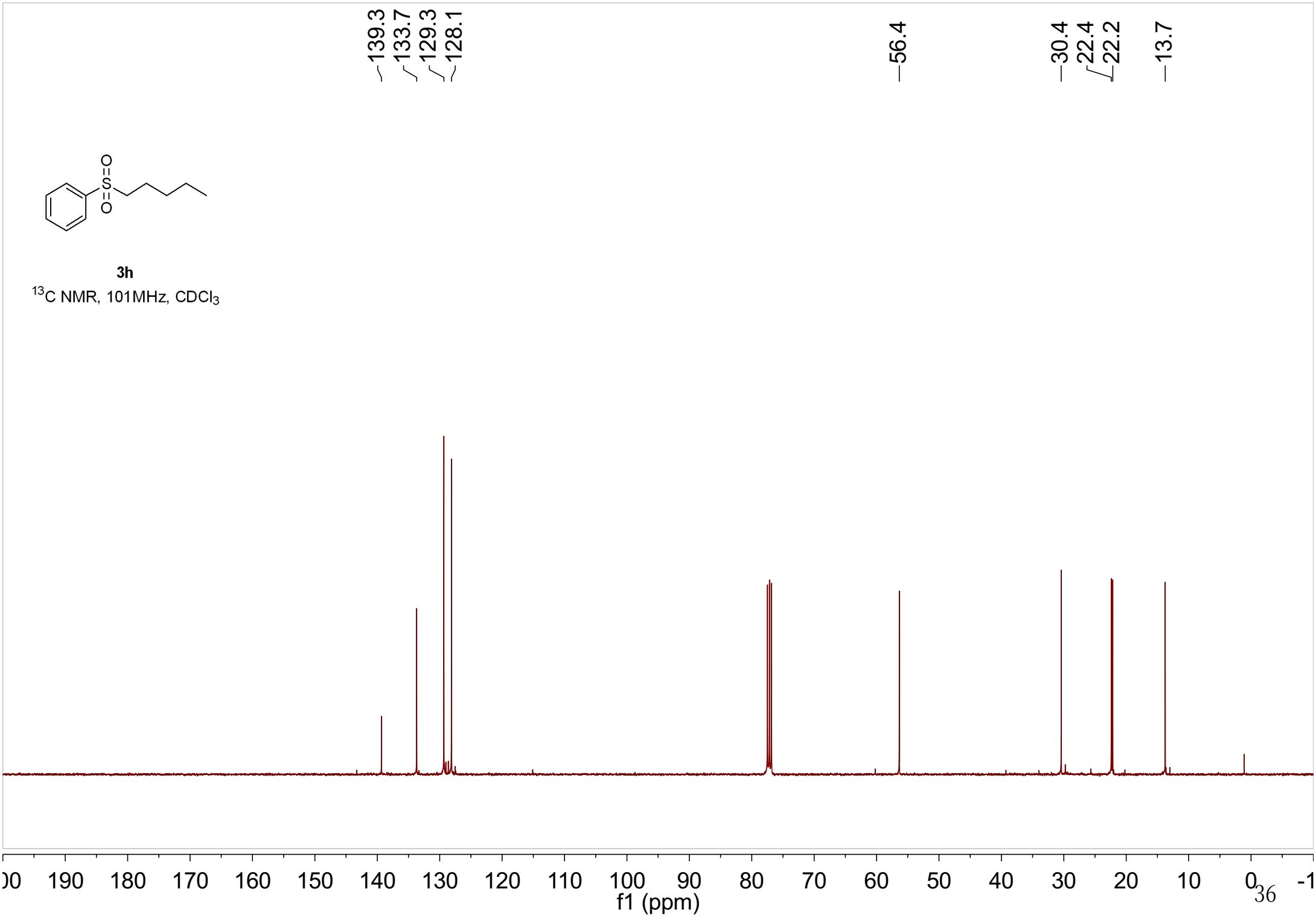

7.92
7.91
7.68
7.66
7.64
7.59
7.57
7.55
3.09
3.07
3.05
1.74
1.73
1.73
1.72
1.71
1.70
1.53
1.51
1.49
1.26
1.24
1.23
1.22
1.20
0.85
O
S
O
3f
1H NMR, 400MHz, CDCl3
2.00
1.02
2.05
2.00
2.00
1.07
2.11
6.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

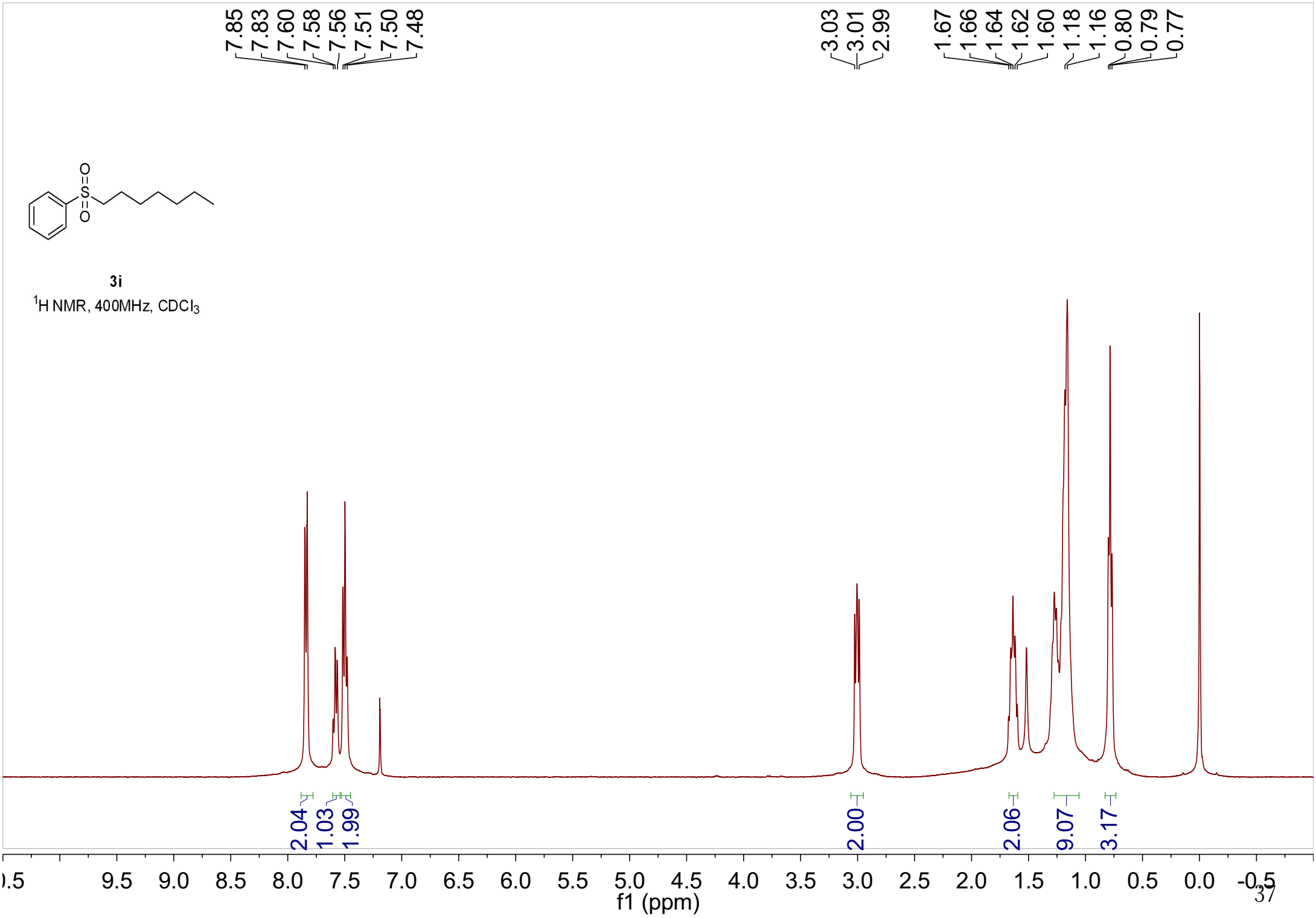

139.4
133.7
129.3
128.1
56.6
37.4
27.7
22.3
20.6
O
S
O
O
3f
13C NMR, 101MHz, CDCl3
f1 (ppm)

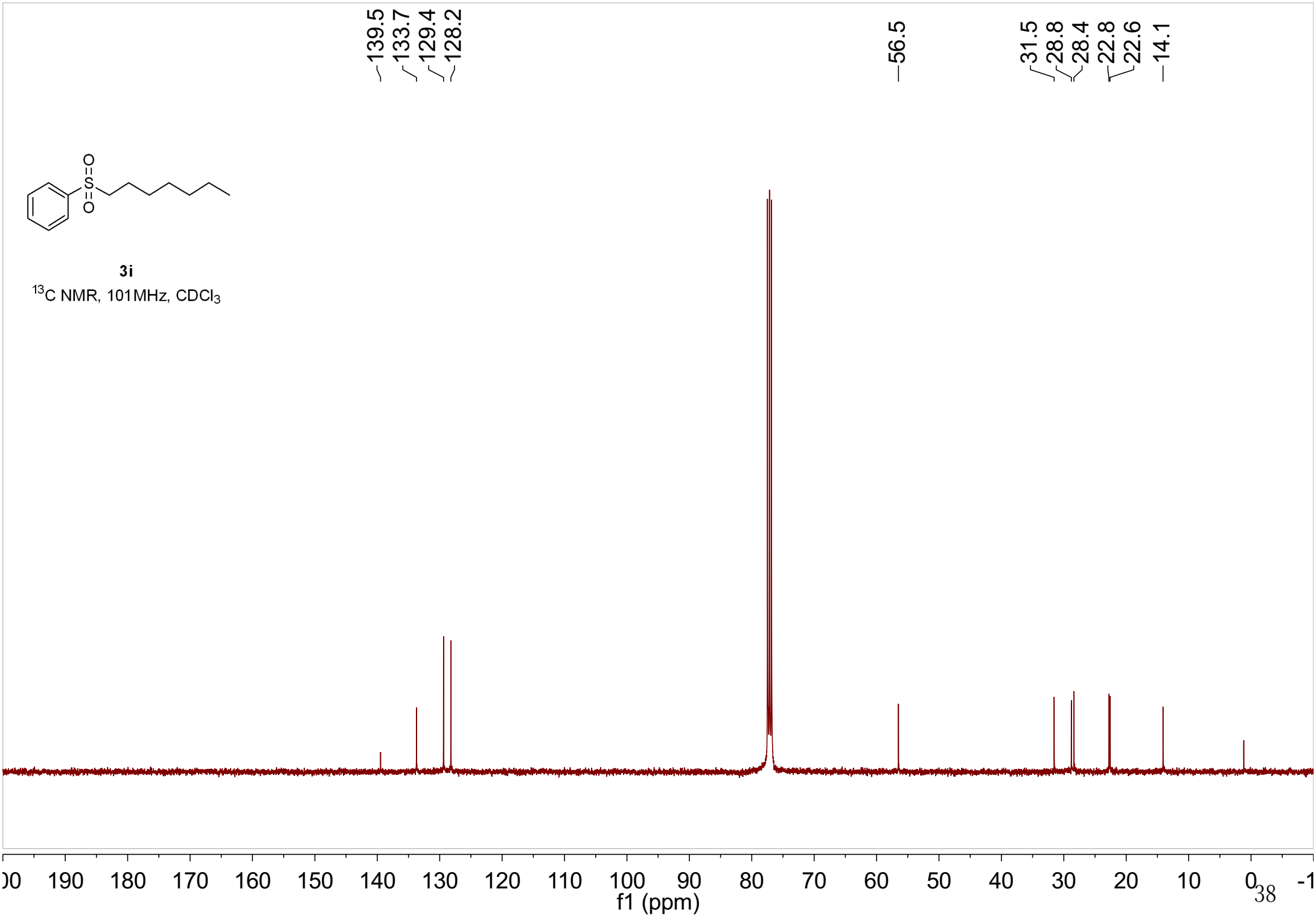

7.93
7.91
7.91
7.69
7.68
7.68
7.67
7.66
7.66
7.65
7.65
7.64
7.60
7.58
7.56
3.08
3.06
3.04
1.75
1.74
1.73
1.72
1.71
1.70
1.69
1.67
1.24
1.23
1.22
1.22
1.22
1.21
1.20
O
S
O
O
3g
1H NMR, 400MHz, CDCl3
1.93
1.03
2.03
2.00
2.27
2.15
9.00
f1 (ppm)

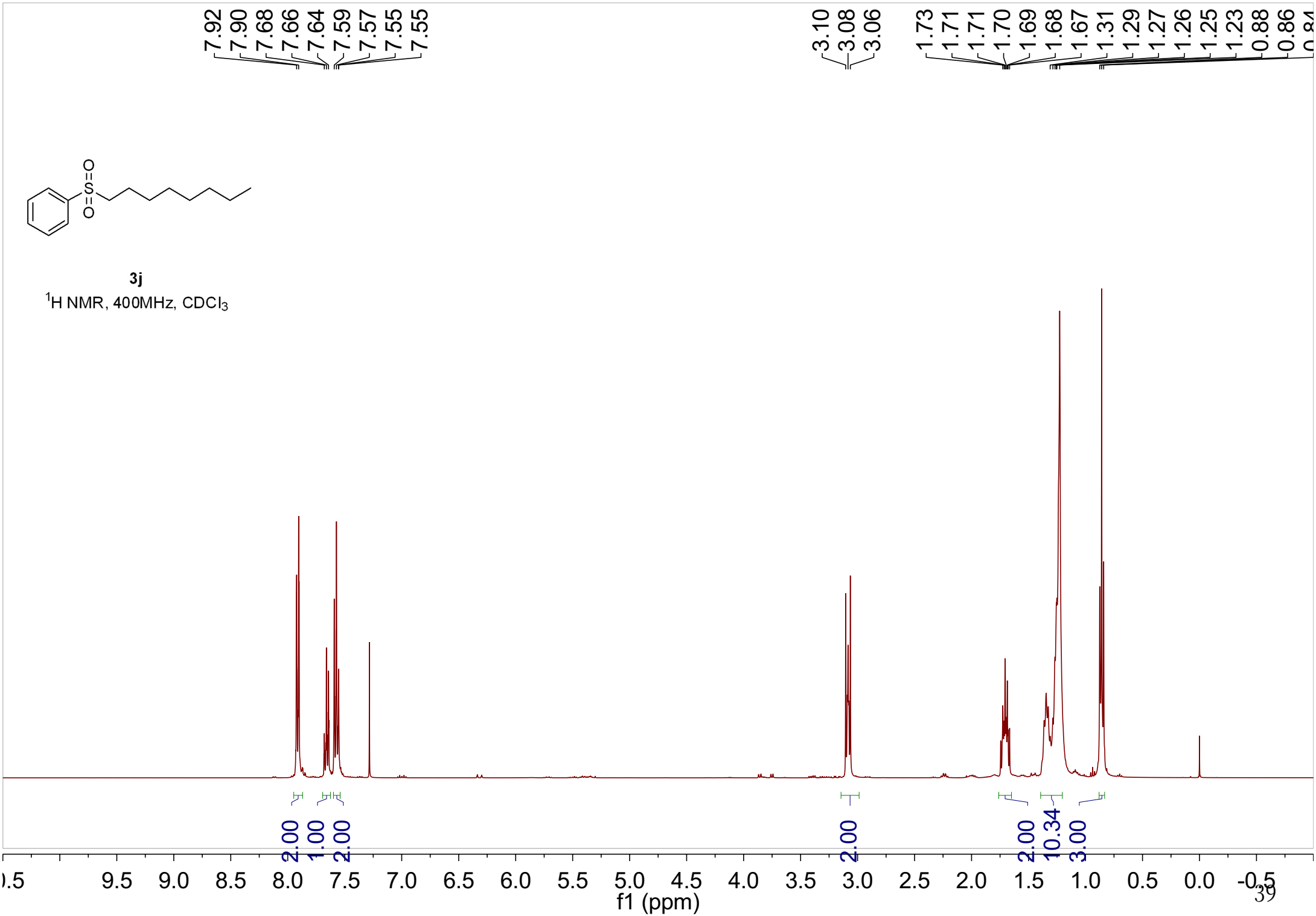

139.4
133.7
129.4
128.1
57.1
42.6
30.5
29.2
18.1
O=S=O
3g
13C NMR, 101MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.85
7.83
7.60
7.58
7.56
7.52
7.50
7.48
3.02
3.01
2.98
1.68
1.66
1.64
1.63
1.62
1.60
1.26
1.25
1.24
1.23
1.22
1.20
1.18
0.80
0.78
0.77
O
S
O
O
3h
1H NMR, 400MHz, CDCl3
2.05
1.03
2.05
2.00
2.05
4.12
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


139.3
133.7
129.3
128.1
56.4
30.4
22.4
22.2
13.7
O
S
O
O
3h
13C NMR, 101MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.85
7.83
7.60
7.58
7.56
7.51
7.50
7.48
3.03
3.01
2.99
1.67
1.66
1.64
1.62
1.60
1.18
1.16
0.80
0.79
0.77
3i
1H NMR, 400MHz, CDCl3
2.04
1.03
1.99
2.00
2.06
9.07
3.17
f1 (ppm)


139.5
133.7
129.4
128.2
56.5
31.5
28.8
28.4
22.8
22.6
14.1
O
S
O
3i
13C NMR, 101MHz, CDCl3
f1 (ppm)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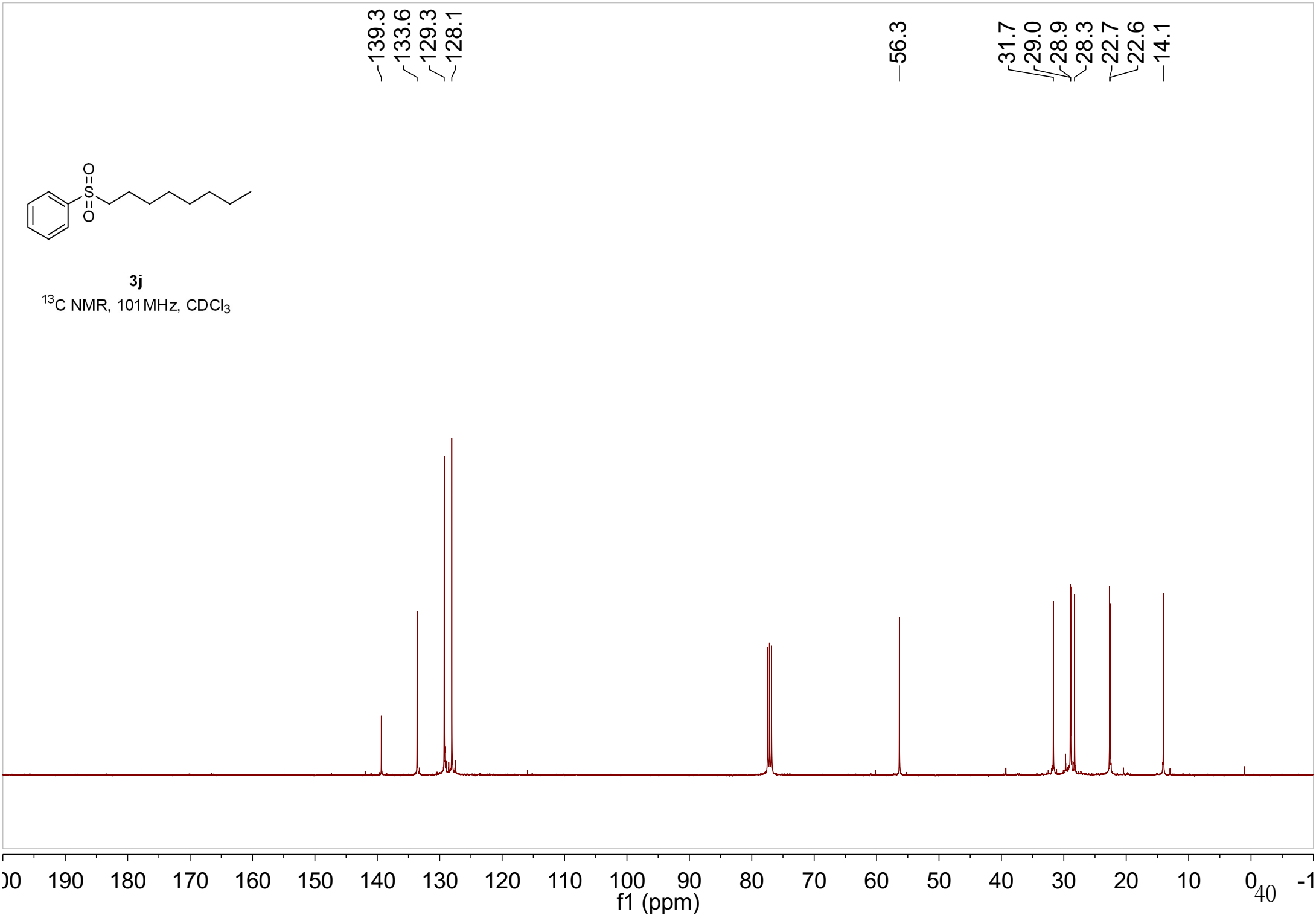
7.90
7.68
7.66
7.64
7.59
7.57
7.55
7.55
3.10
3.08
3.06
1.73
1.71
1.71
1.70
1.69
1.68
1.67
1.31
1.29
1.27
1.26
1.25
1.23
0.88
0.86
3j
1H NMR, 400MHz, CDCl3
2.00
1.00
2.00
2.00
2.00
10.34
3.00
f1 (ppm)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133.6
129.3
128.1
56.3
31.7
29.0
28.9
28.3
22.7
22.6
14.1
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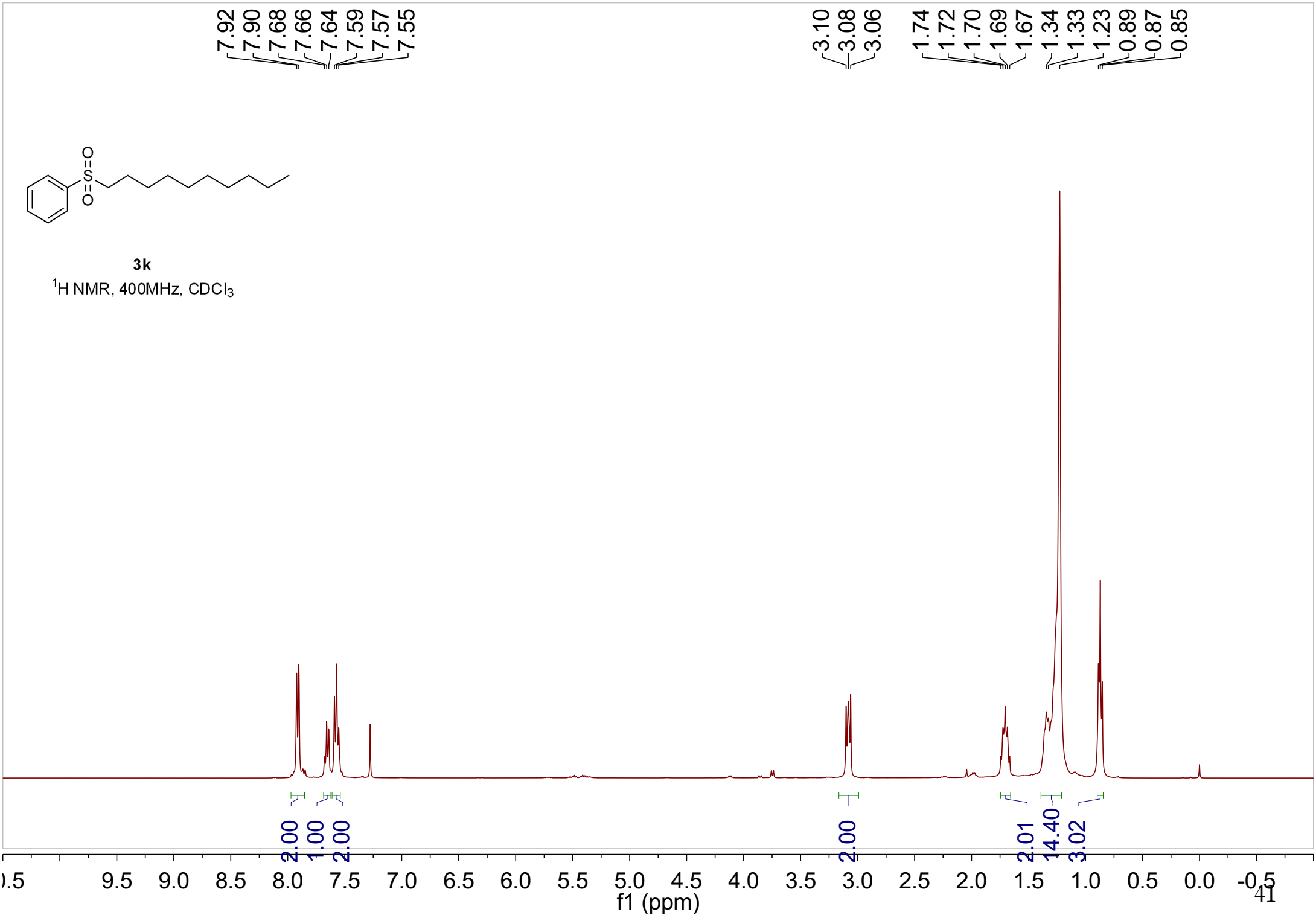
S
O
O
3j
13C NMR, 101MHz, CDCl3
f1 (ppm)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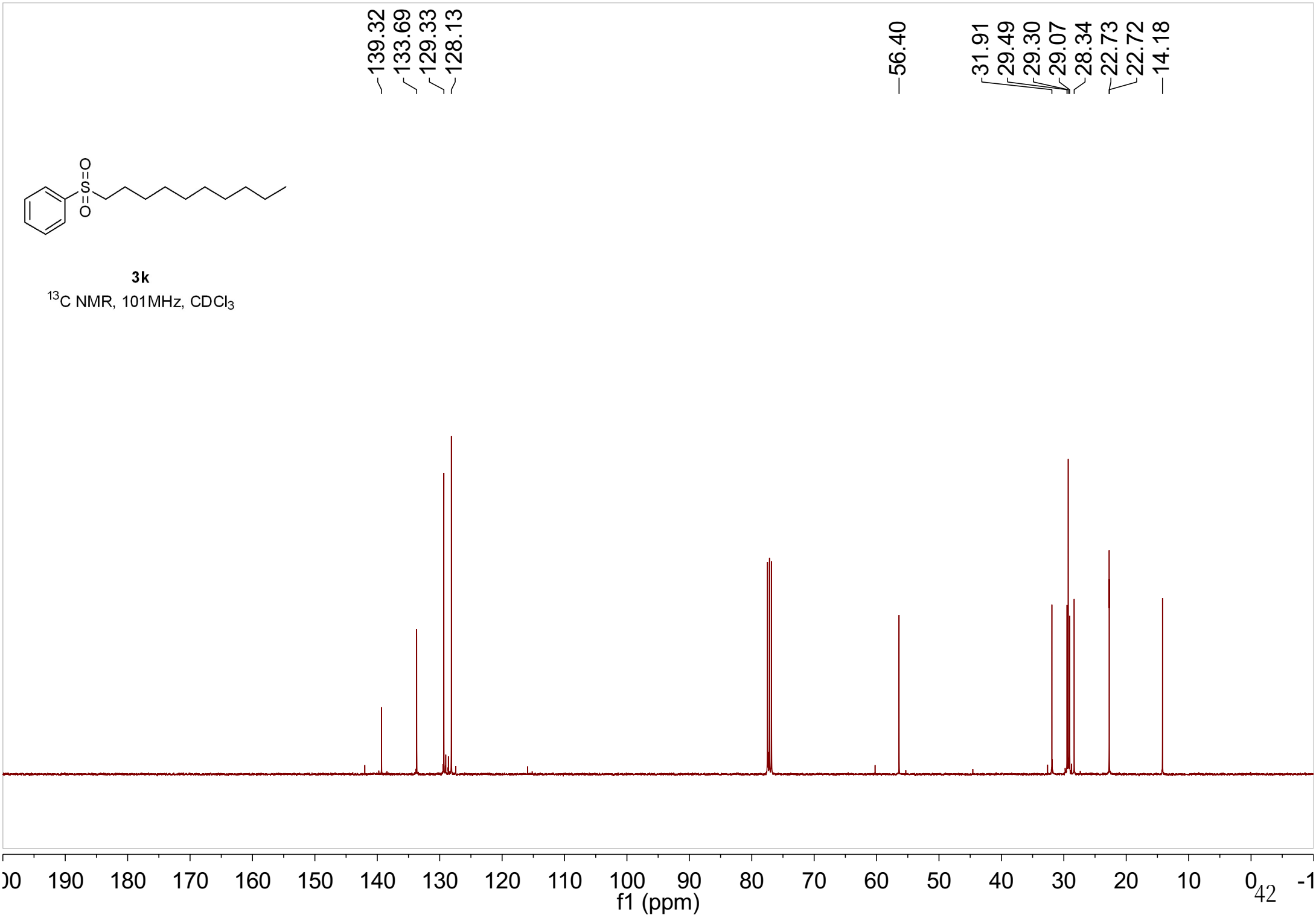
7.90
7.68
7.66
7.64
7.59
7.57
7.55
3.10
3.08
3.06
1.74
1.72
1.70
1.69
1.67
1.34
1.33
1.23
0.89
0.87
0.85
3k
1H NMR, 400MHz, CDCl3
2.00
1.00
2.00
2.00
2.01
14.40
3.02
f1 (ppm)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133.69
129.33
128.13
56.40
31.91
29.49
29.30
29.07
28.34
22.73
22.72
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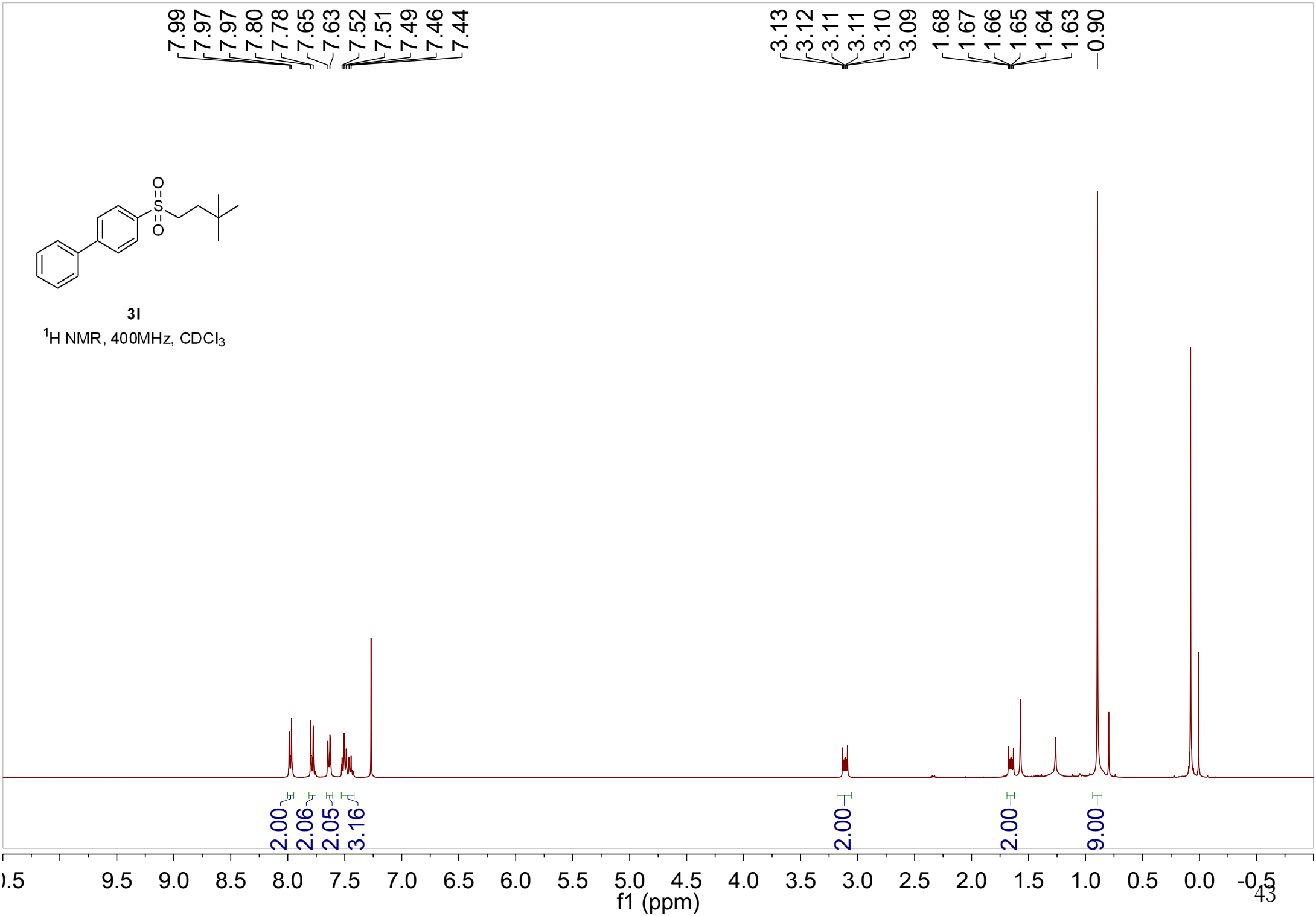
O
O
3k
13C NMR, 101MHz, CDCl3
f1 (ppm)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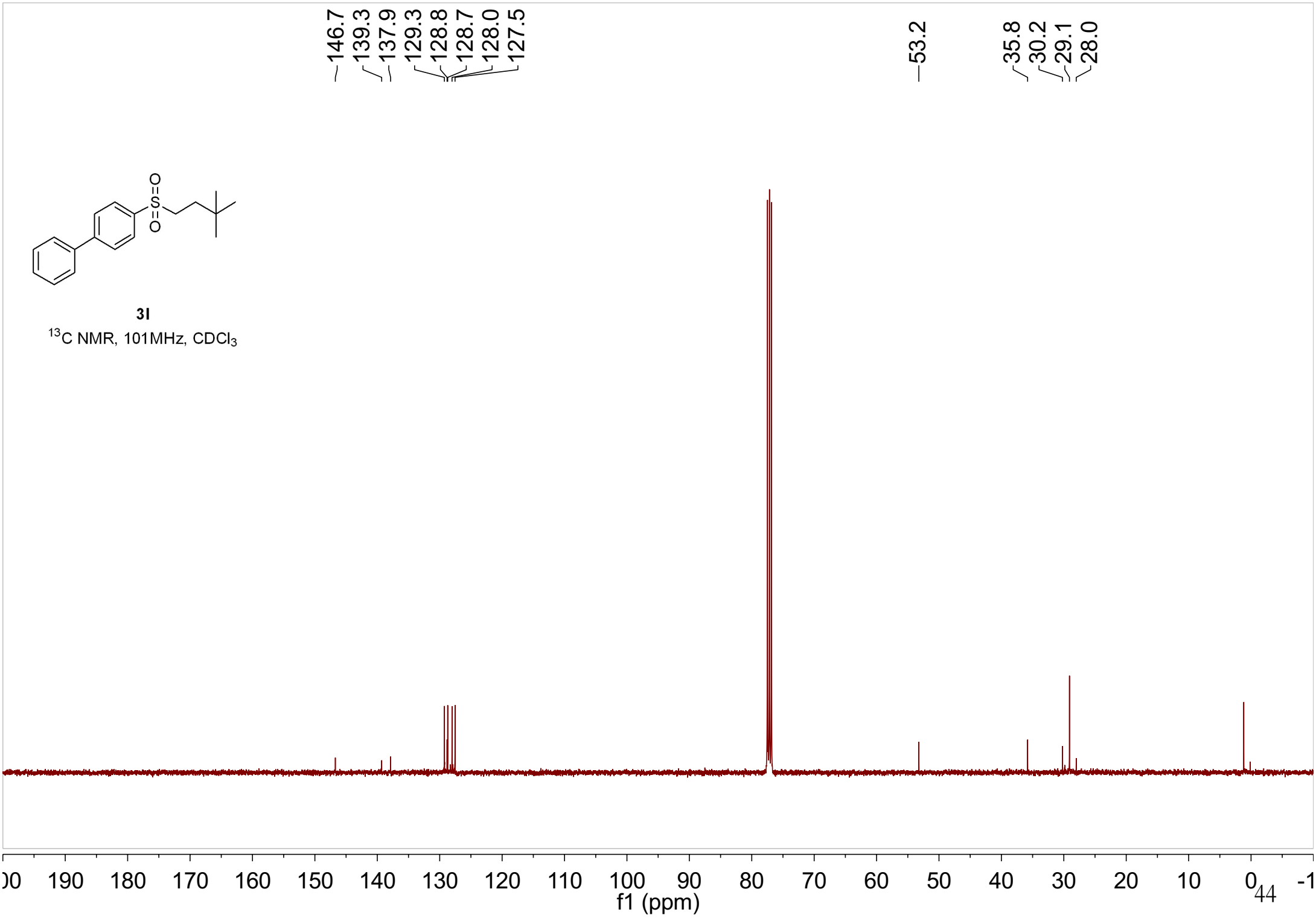
7.97
7.97
7.80
7.78
7.65
7.63
7.52
7.51
7.49
7.46
7.44
3.13
3.12
3.11
3.11
3.10
3.09
1.68
1.67
1.66
1.65
1.64
1.63
0.90
3l
1H NMR, 400MHz, CDCl3
2.00
2.06
2.05
3.16
2.00
2.00
9.00
f1 (ppm)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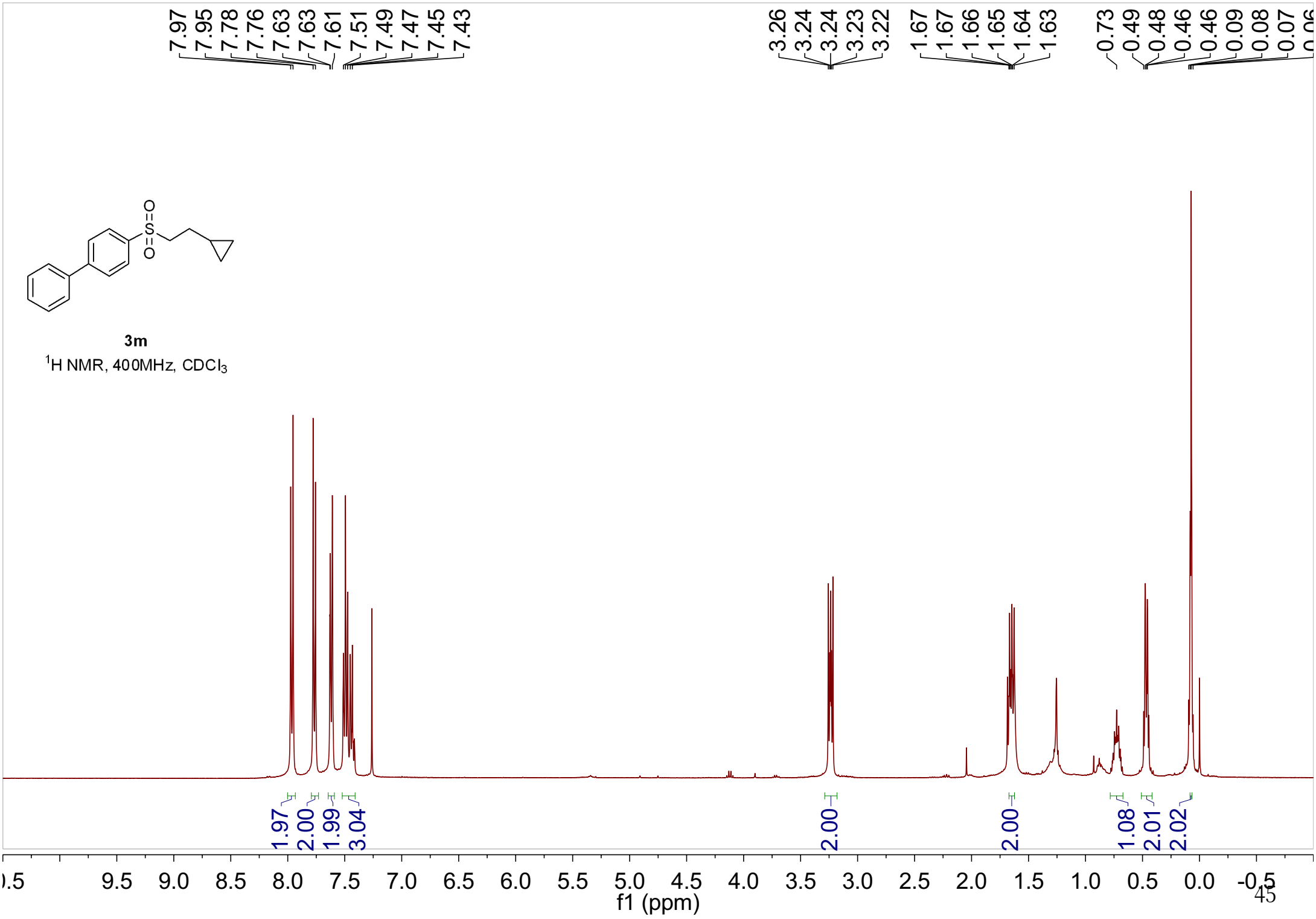
139.3
137.9
129.3
128.8
128.7
128.0
127.5
53.2
35.8
30.2
29.1
28.0
O
S
O
3l
13C NMR, 101MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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7.76
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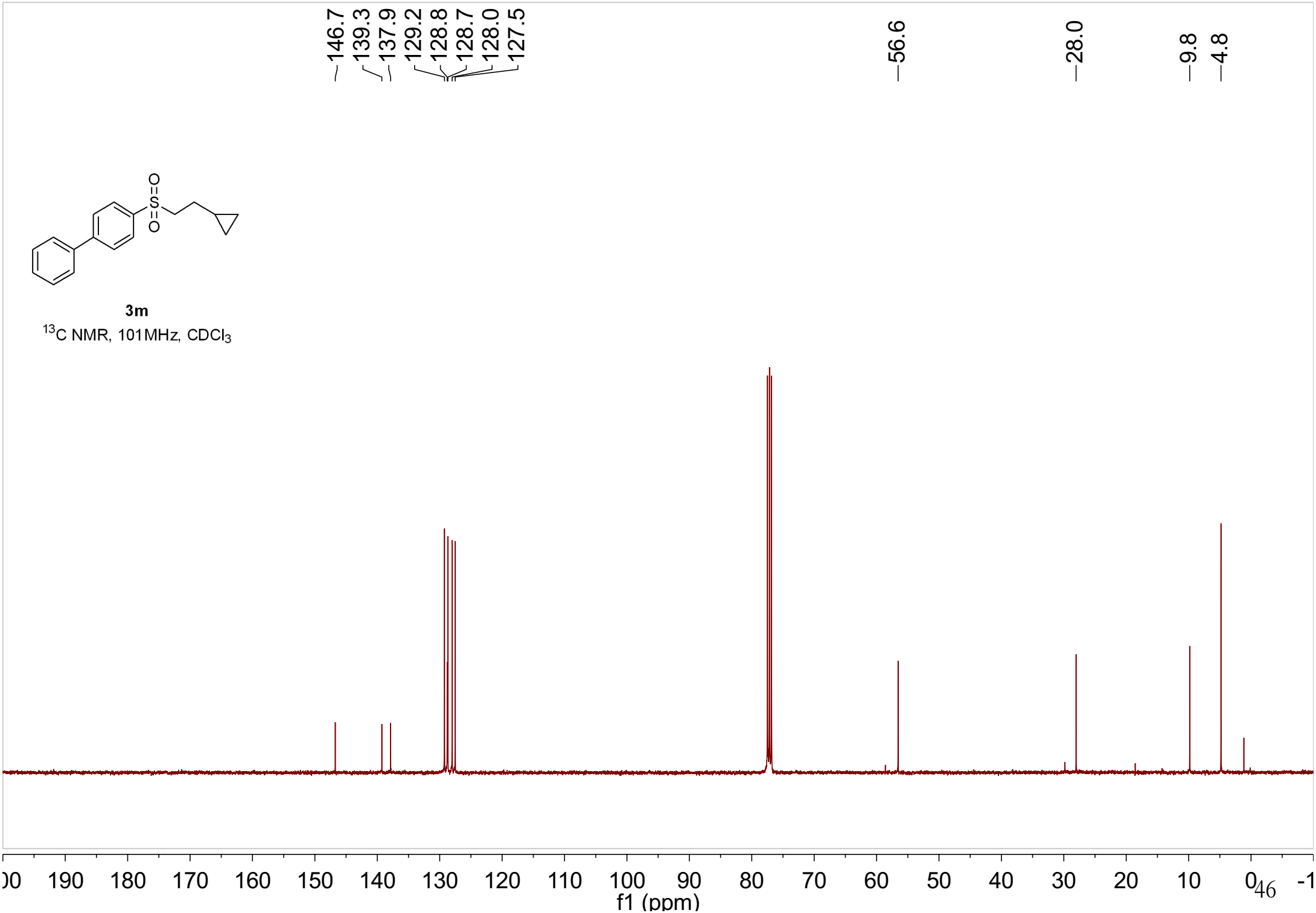
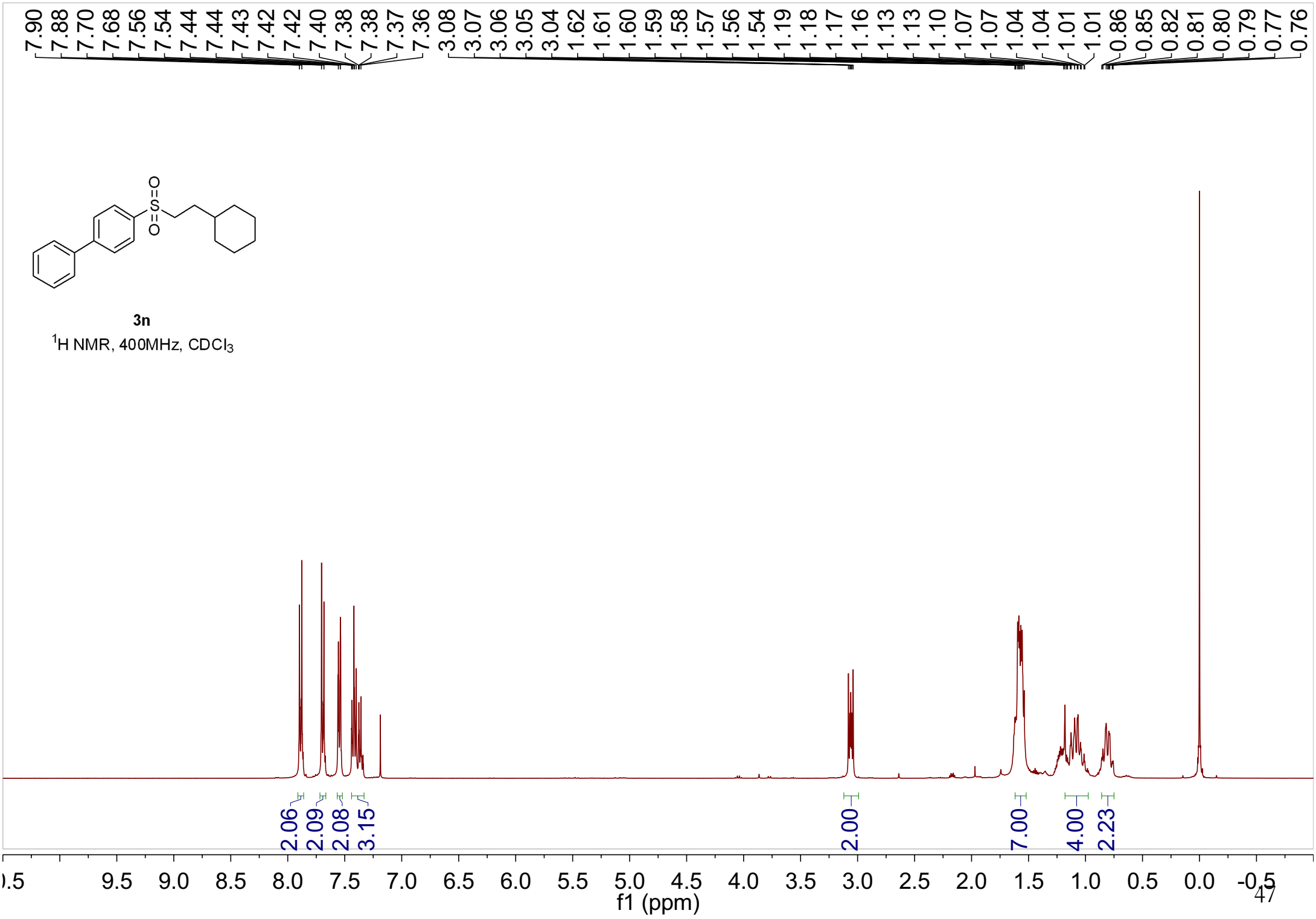
7.63
7.61
7.51
7.49
7.47
7.45
7.43
3.26
3.24
3.24
3.23
3.22
1.67
1.67
1.66
1.65
1.64
1.63
0.73
0.49
0.48
0.46
0.46
0.09
0.08
0.07
O
S
O
O
3m
1H NMR, 400MHz, CDCl3
1.97
2.00
1.99
3.04
2.00
2.00
1.08
2.01
2.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


146.7
139.3
137.9
129.2
128.8
128.7
128.0
127.5
56.6
28.0
9.8
4.8
O
S
O
O
3m
13C NMR, 101MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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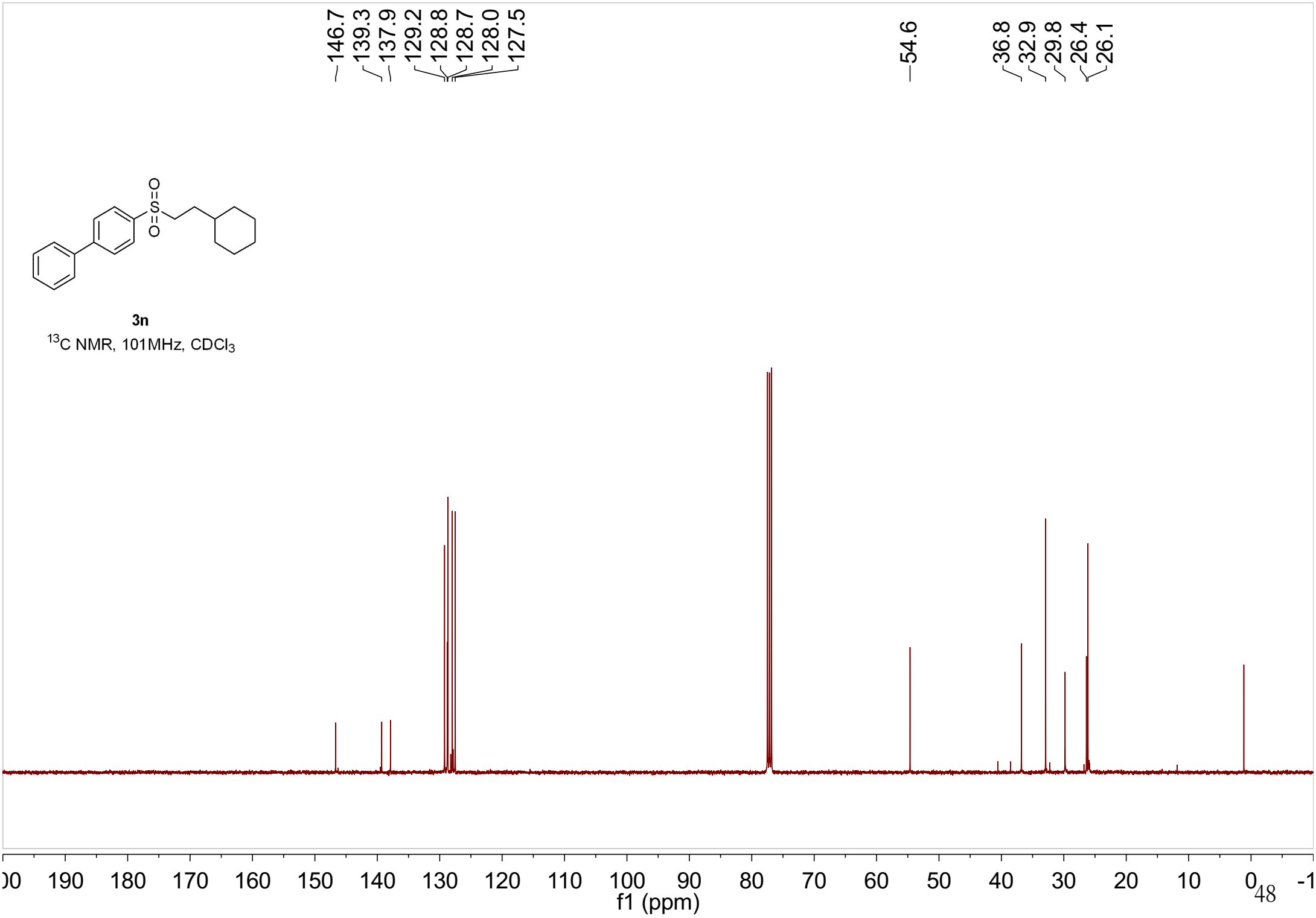
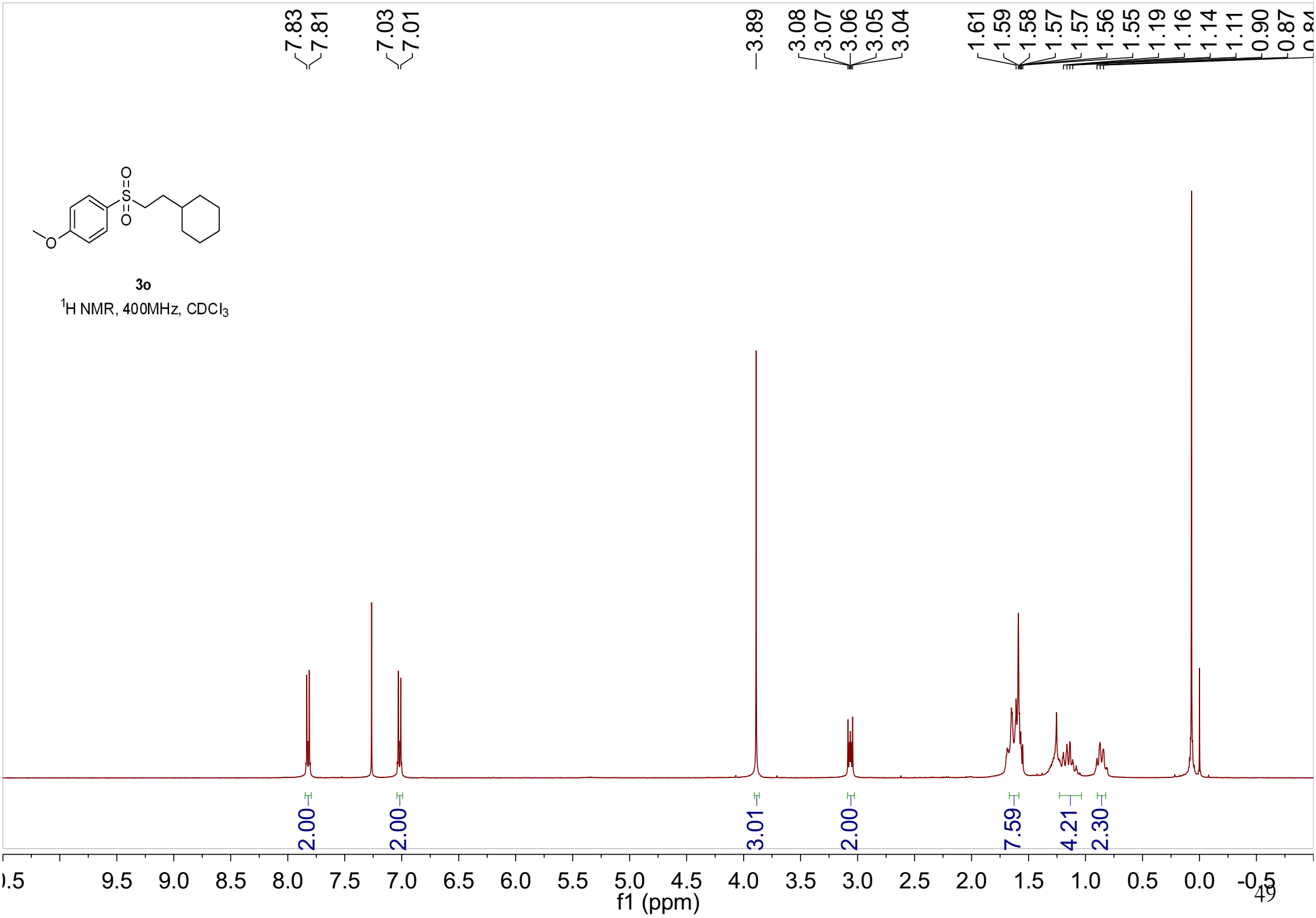
3.08 3.07 3.06 3.05 3.04 1.62 1.61 1.60 1.59 1.58 1.57 1.56 1.54 1.19 1.18 1.17 1.16 1.13 1.13 1.10 1.07 1.07 1.04 1.04 1.01 1.01 0.86 0.85 0.82 0.81 0.80 0.79 0.77 0.76
O
S
O
O
3n
1H NMR, 400MHz, CDCl3
2.06
2.09
2.08
3.15
2.00
7.00
4.00
2.23
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


146.7
139.3
137.9
129.2
128.8
128.7
128.0
127.5
54.6
36.8
32.9
29.8
26.4
26.1
O
S
O
O
3n
13C NMR, 101MHz, CDCl3
f1 (ppm)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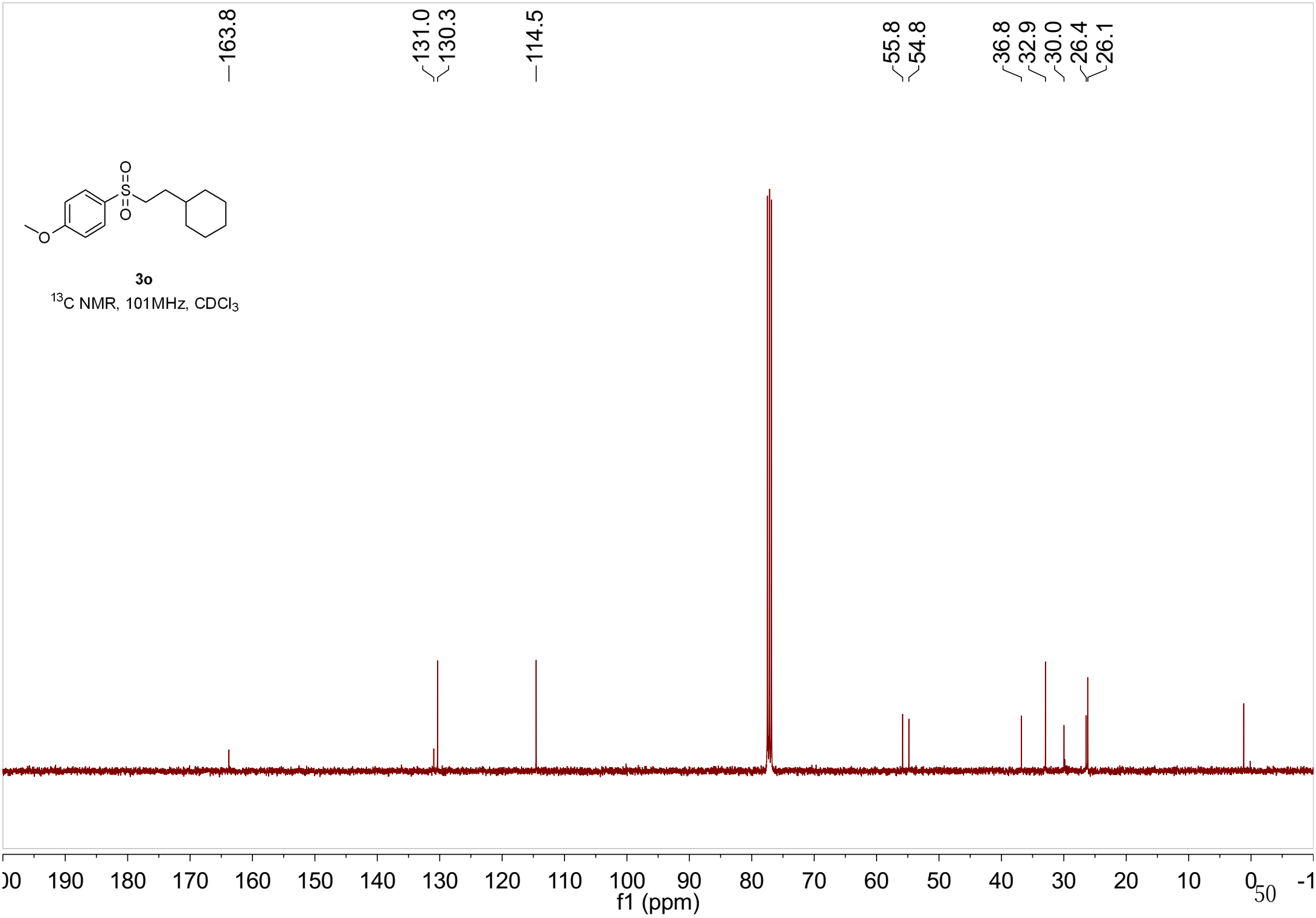
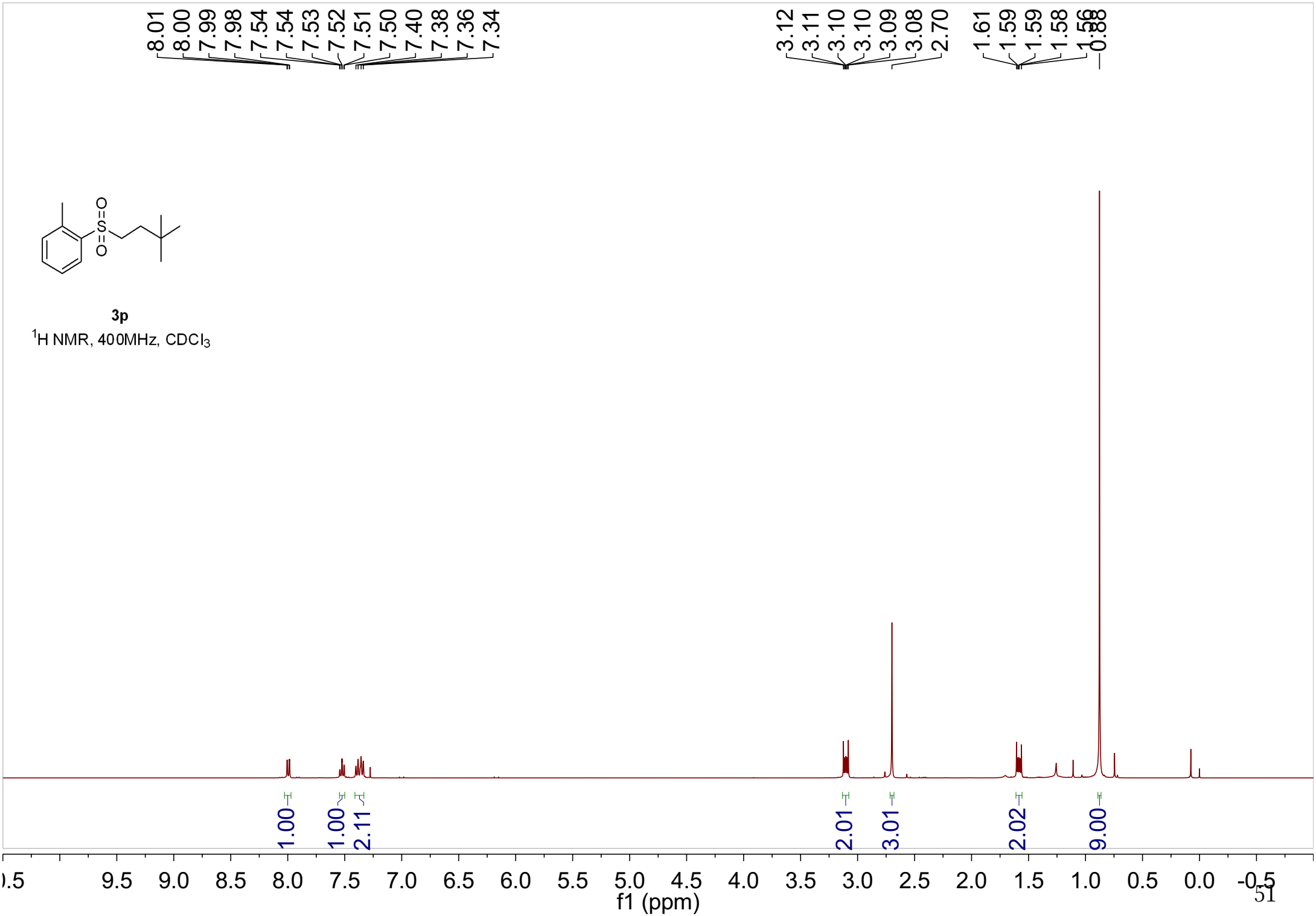
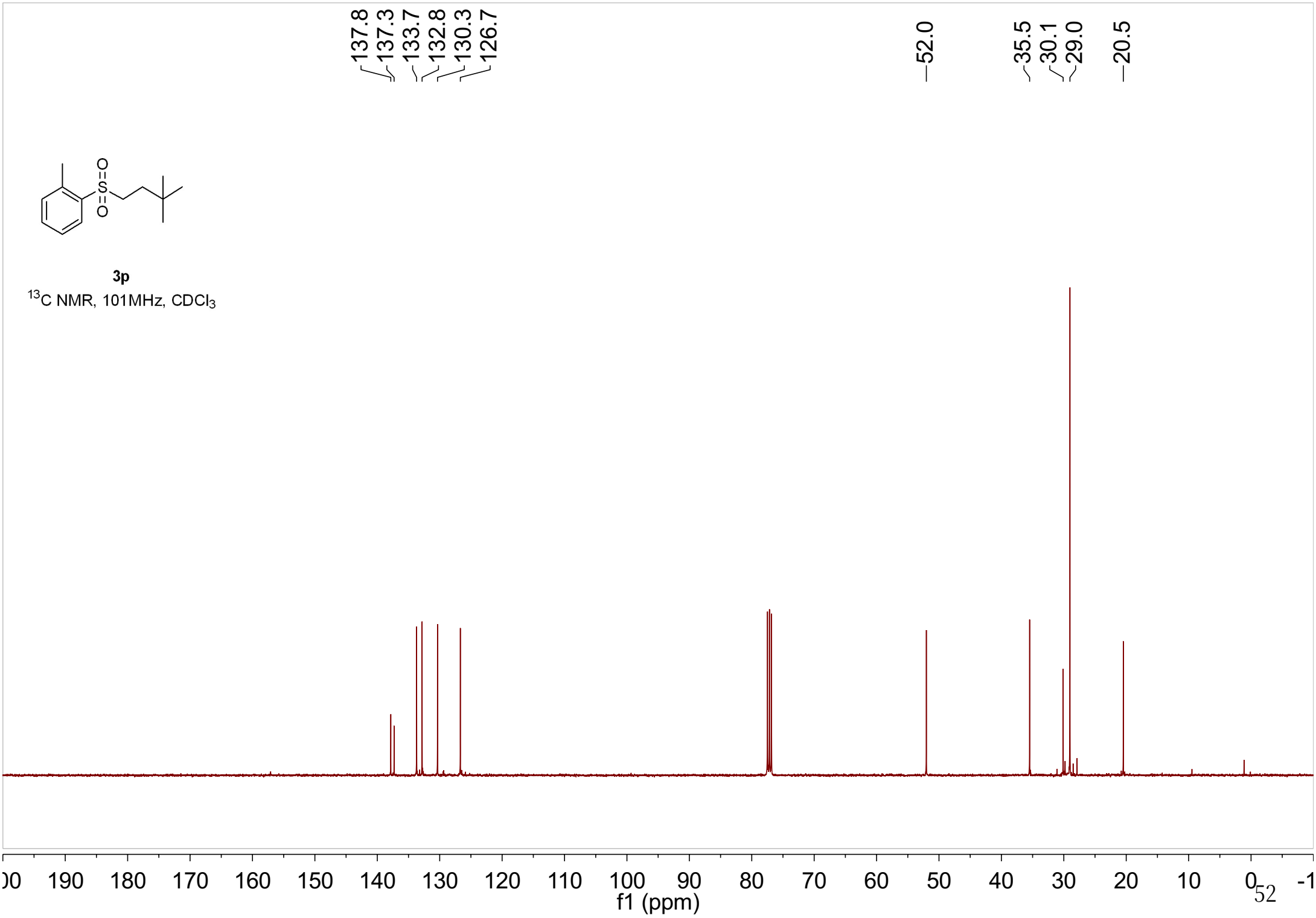
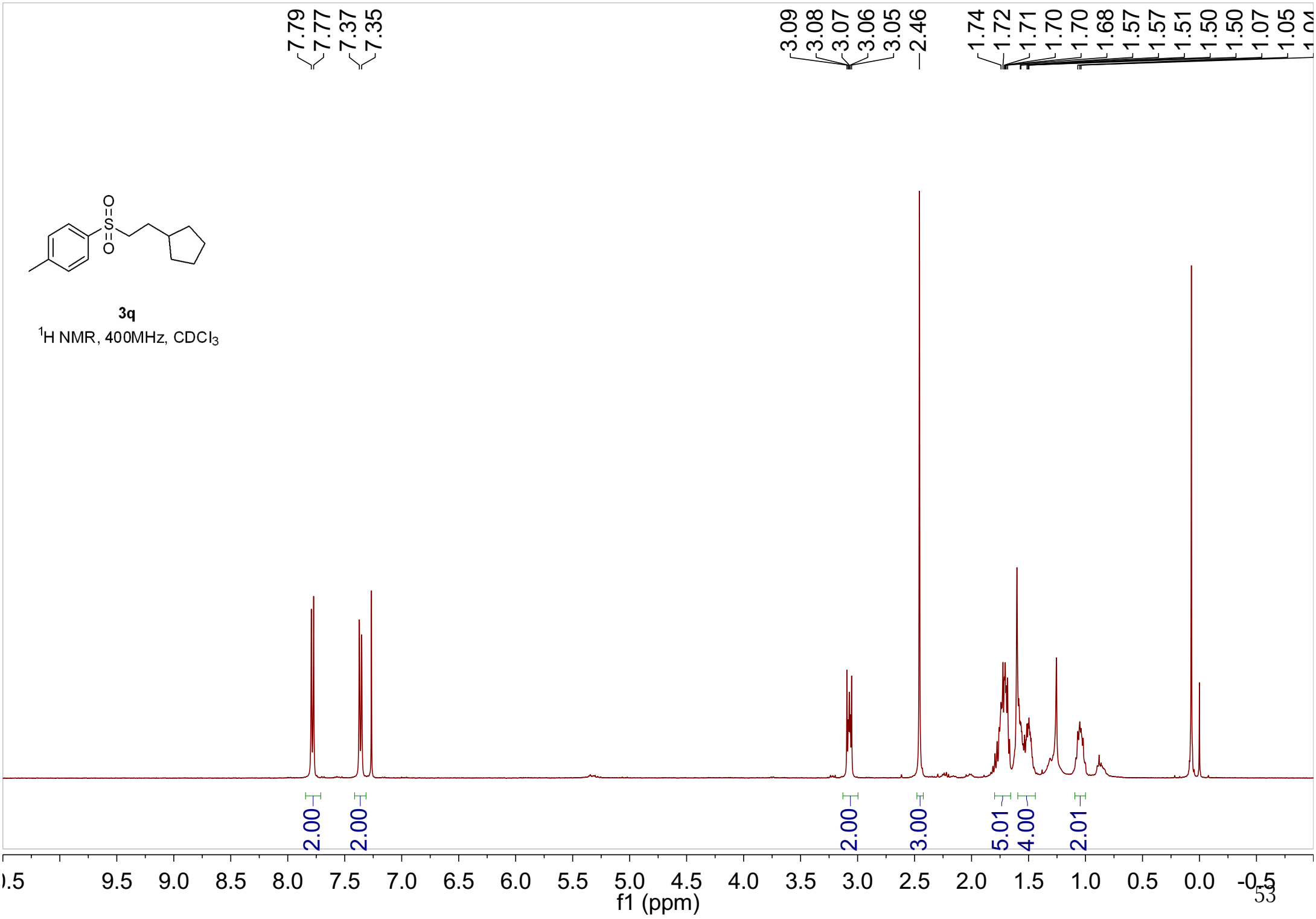
7.81
7.03
7.01
3.89
3.08
3.07
3.06
3.05
3.04
1.61
1.59
1.58
1.57
1.57
1.56
1.55
1.19
1.16
1.14
1.11
0.90
0.87
O
S
O
O
O
3o
1H NMR, 400MHz, CDCl3
2.00
2.00
3.01
2.00
7.59
4.21
2.30
f1 (ppm)


163.8
131.0
130.3
114.5
55.8
54.8
36.8
32.9
30.0
26.4
26.1
O
S
O
O
3o
13C NMR, 101MHz, CDCl3
f1 (ppm)


8.01
8.00
7.99
7.98
7.54
7.54
7.53
7.52
7.51
7.50
7.40
7.38
7.36
7.34
3.12
3.11
3.10
3.10
3.09
3.08
2.70
1.61
1.59
1.59
1.58
1.56
0.88
O
S
O
3p
1H NMR, 400MHz, CDCl3
1.00
1.00
2.11
2.01
3.01
2.02
9.00
f1 (ppm)


137.8
137.3
133.7
132.8
130.3
126.7
52.0
35.5
30.1
29.0
20.5
O
S
O
O
3p
13C NMR, 101MHz, CDCl3
f1 (ppm)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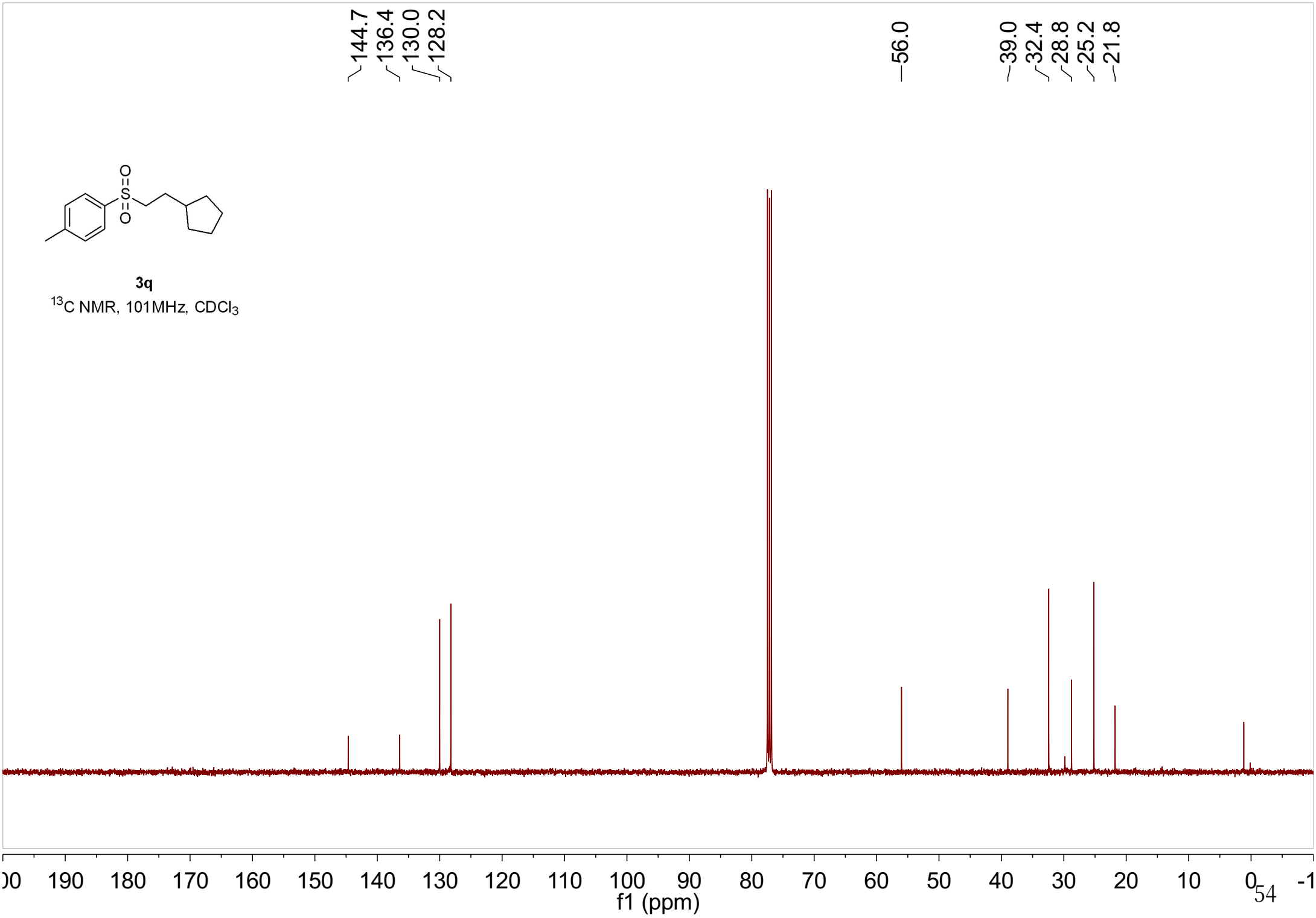
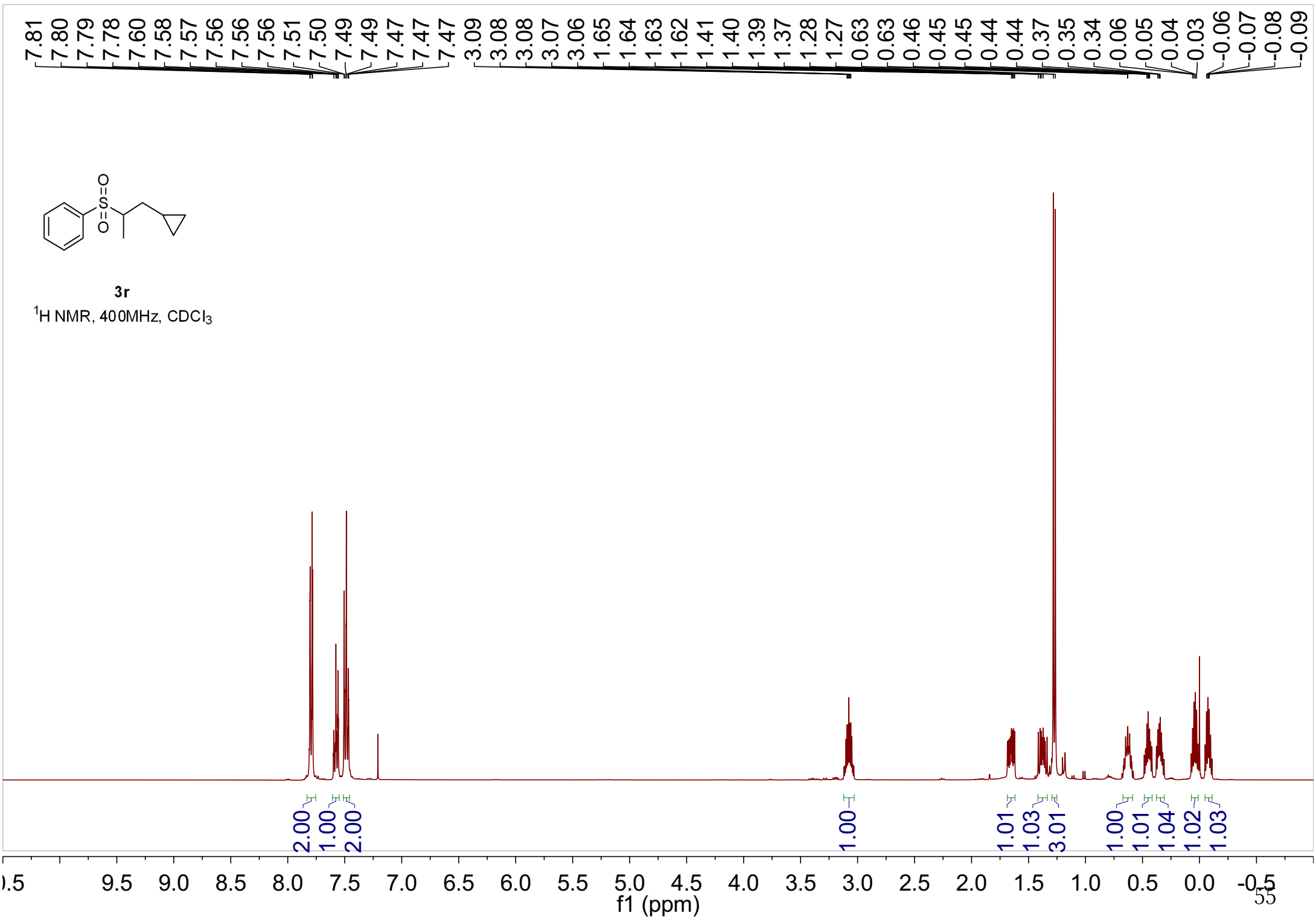
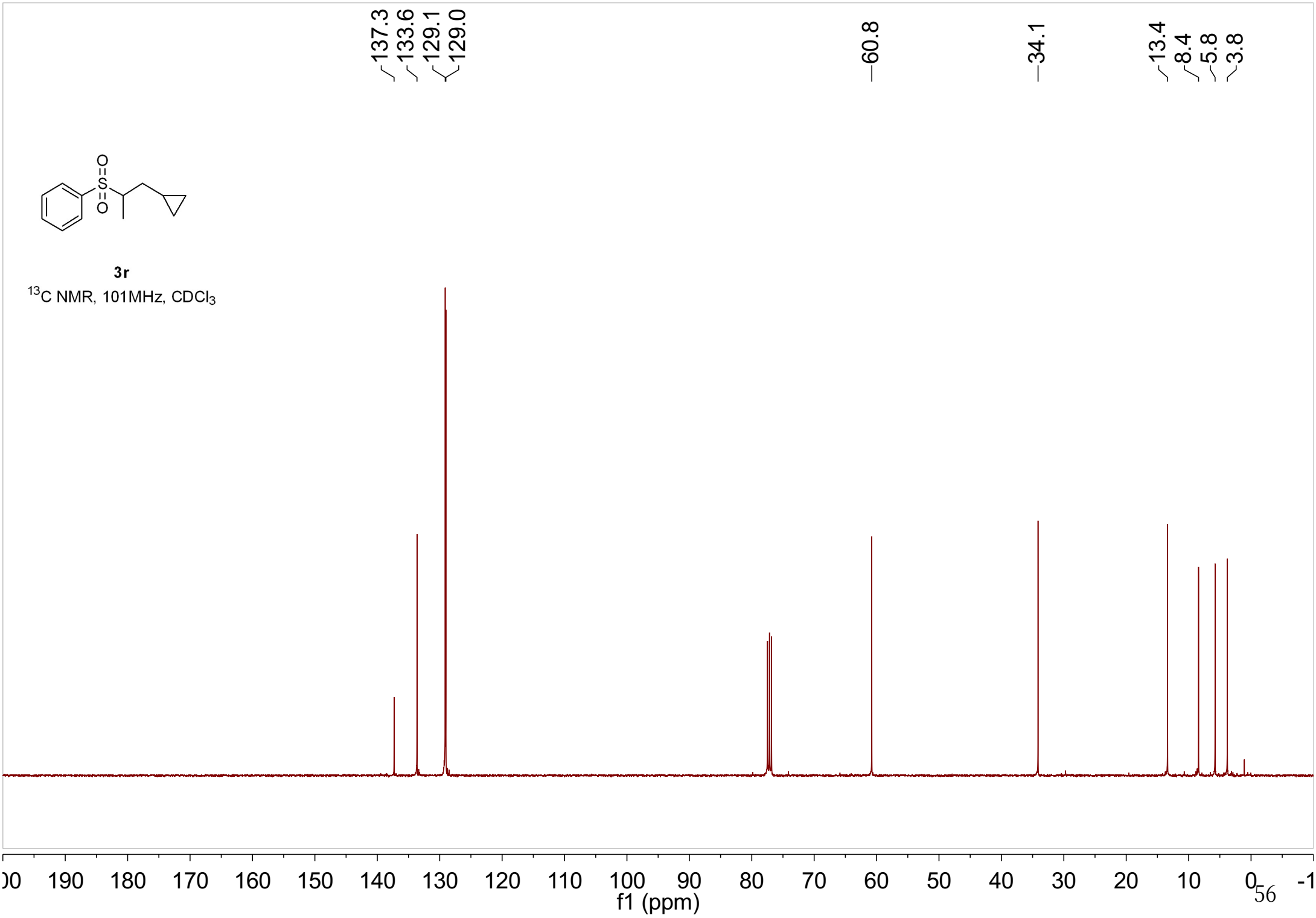
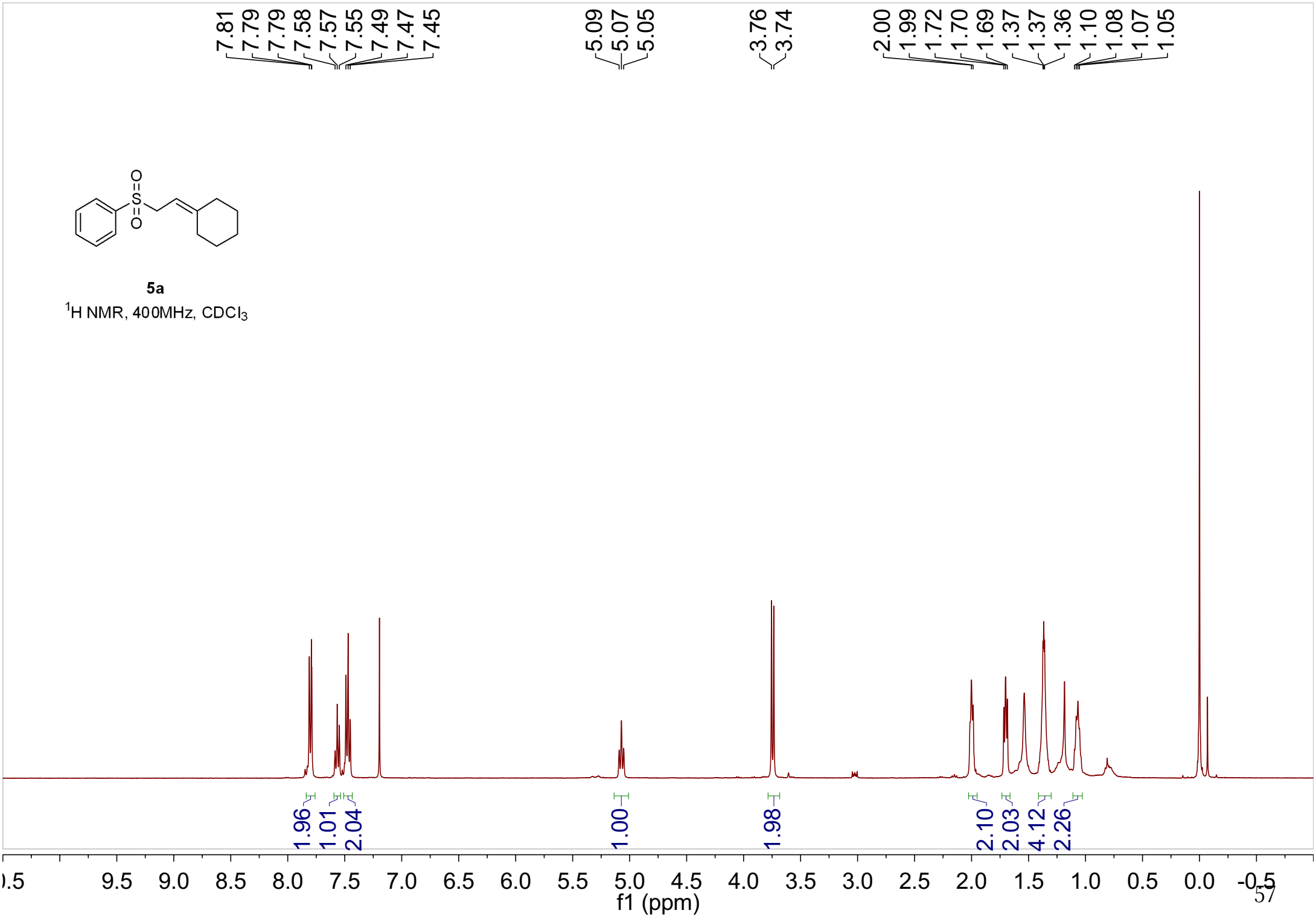
7.77
7.37
7.35
3.09
3.08
3.07
3.06
3.05
2.46
1.74
1.72
1.71
1.70
1.70
1.68
1.57
1.57
1.51
1.50
1.50
1.07
1.05
O
S
O
3q
1H NMR, 400MHz, CDCl3
2.00
2.00
2.00
3.00
5.01
4.00
2.01
f1 (ppm)


144.7
136.4
130.0
128.2
56.0
39.0
32.4
28.8
25.2
21.8
O
S
O
3q
13C NMR, 101MHz, CDCl3
f1 (ppm)


7.81 7.80 7.79 7.78 7.60 7.58 7.57 7.56 7.56 7.56 7.51 7.50 7.49 7.49 7.47 7.47 7.47
3.09 3.08 3.08 3.07 3.06 1.65 1.64 1.63 1.62 1.41 1.40 1.39 1.37 1.28 1.27 0.63 0.63 0.46 0.45 0.45 0.44 0.44 0.37 0.35 0.34 0.06 0.05 0.04 0.03 -0.06 -0.07 -0.08 -0.09
O
S
O
3r
1H NMR, 400MHz, CDCl3
2.00 1.00 2.00 1.00 1.01 1.03 3.01 1.00 1.01 1.04 1.02 1.03
f1 (ppm)


137.3
133.6
129.1
129.0
60.8
34.1
13.4
8.4
5.8
3.8
3r
^{13}C NMR, 101MHz, $CDCl_3$
f1 (ppm)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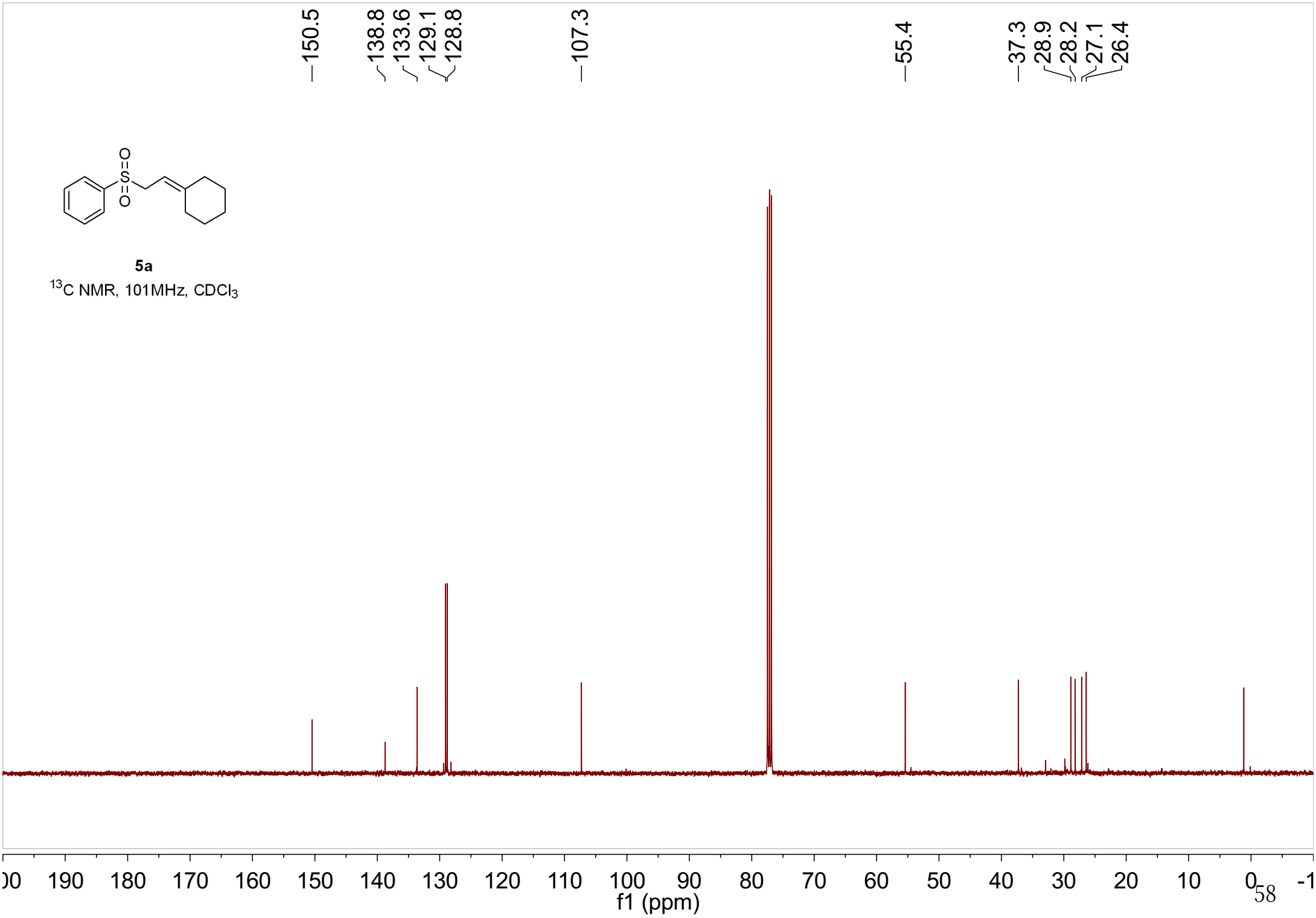
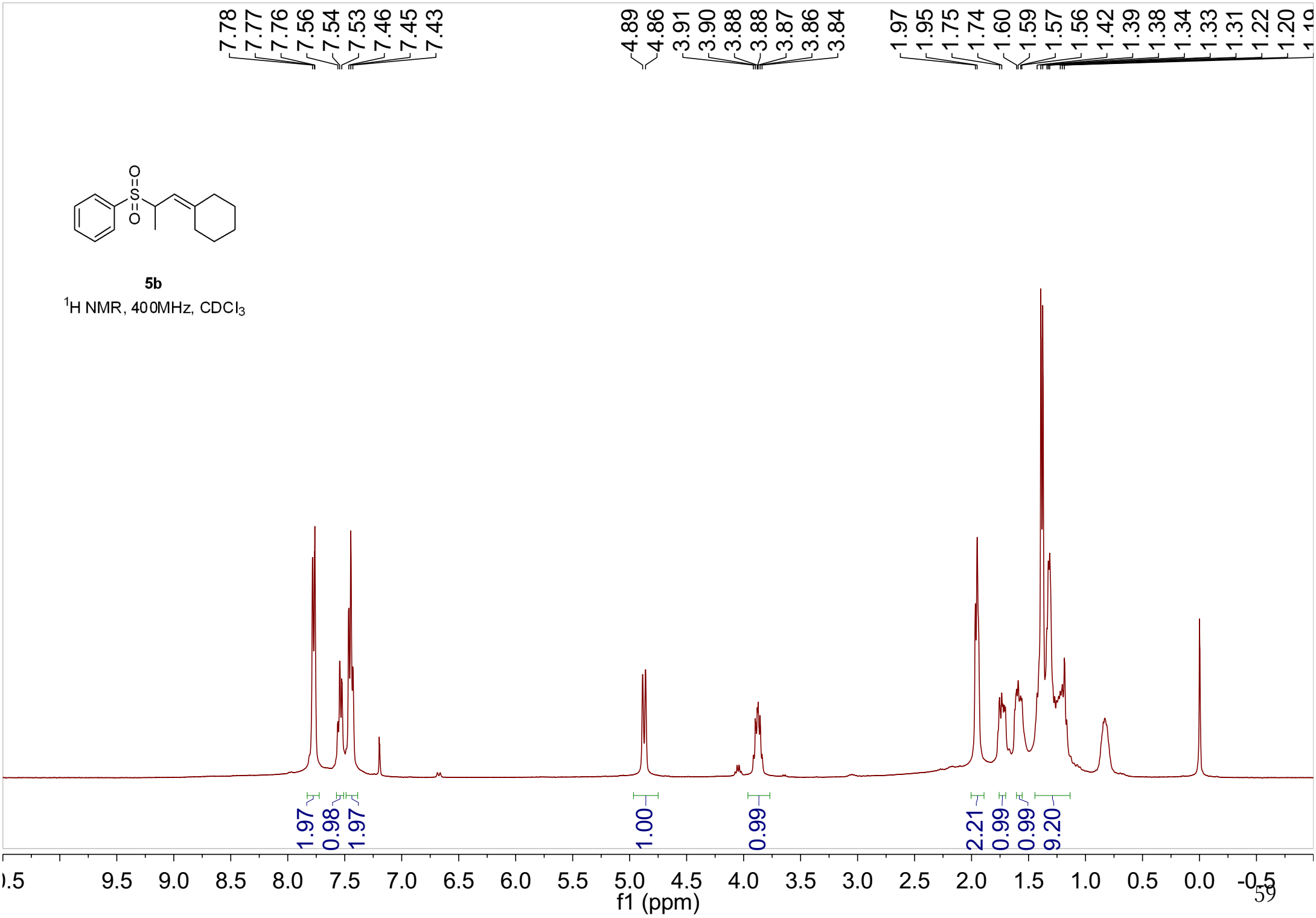
7.79
7.79
7.58
7.57
7.55
7.49
7.47
7.45
5.09
5.07
5.05
3.76
3.74
2.00
1.99
1.72
1.70
1.69
1.37
1.37
1.36
1.10
1.08
1.07
1.05
5a
1H NMR, 400MHz, CDCl3
1.96
1.01
2.04
1.00
1.98
2.10
2.03
4.12
2.26
f1 (ppm)


150.5
138.8
133.6
129.1
128.8
107.3
55.4
37.3
28.9
28.2
27.1
26.4
O
S
O
5a
13C NMR, 101MHz, CDCl3
f1 (ppm)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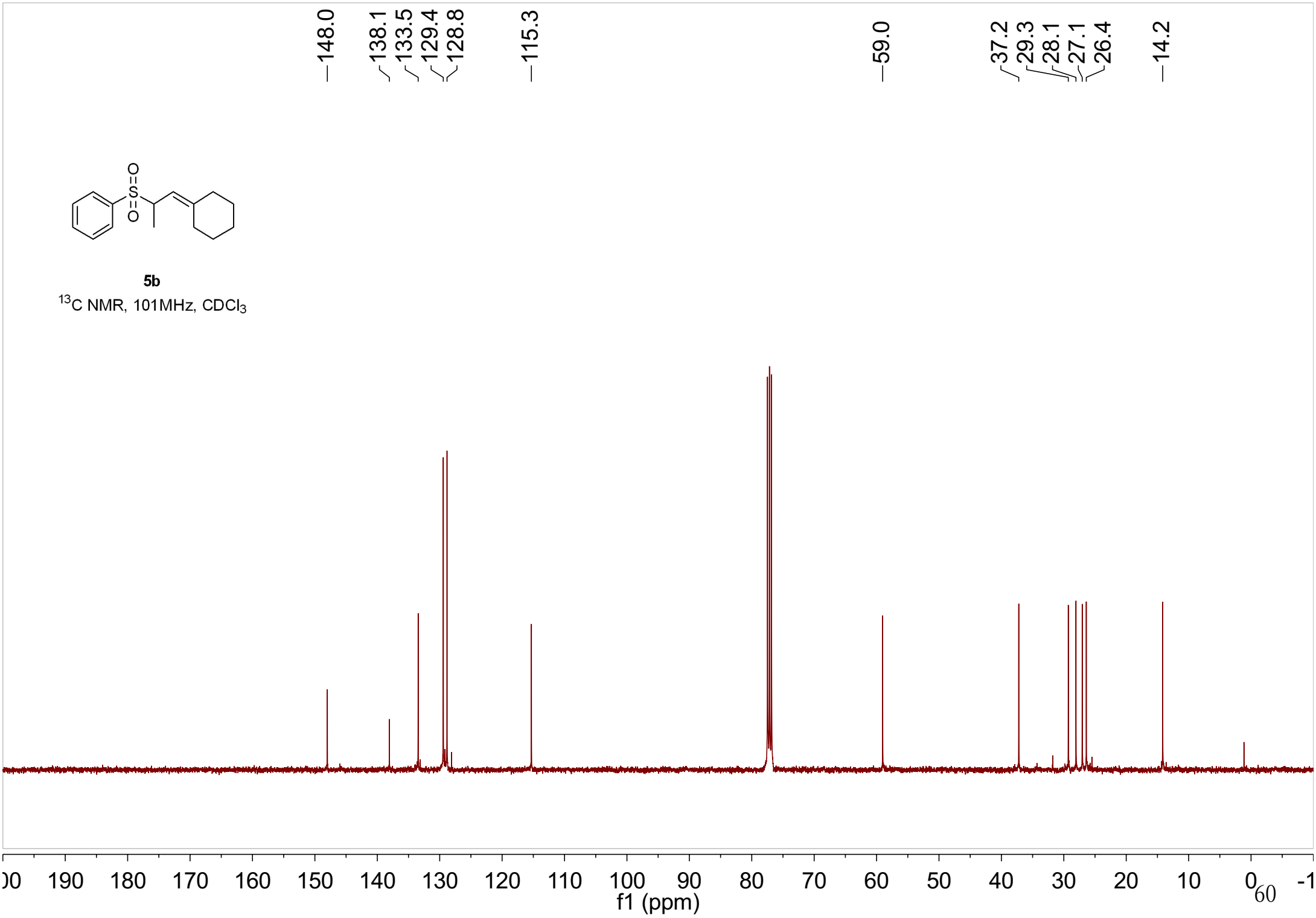
7.77
7.76
7.56
7.54
7.53
7.46
7.45
7.43
4.89
4.86
3.91
3.90
3.88
3.88
3.87
3.86
3.84
1.97
1.95
1.75
1.74
1.60
1.59
1.57
1.56
1.42
1.39
1.38
1.34
1.33
1.31
1.22
1.20
O
S
O
O
5b
1H NMR, 400MHz, CDCl3
1.97
0.98
1.97
1.00
0.99
2.21
0.99
0.99
9.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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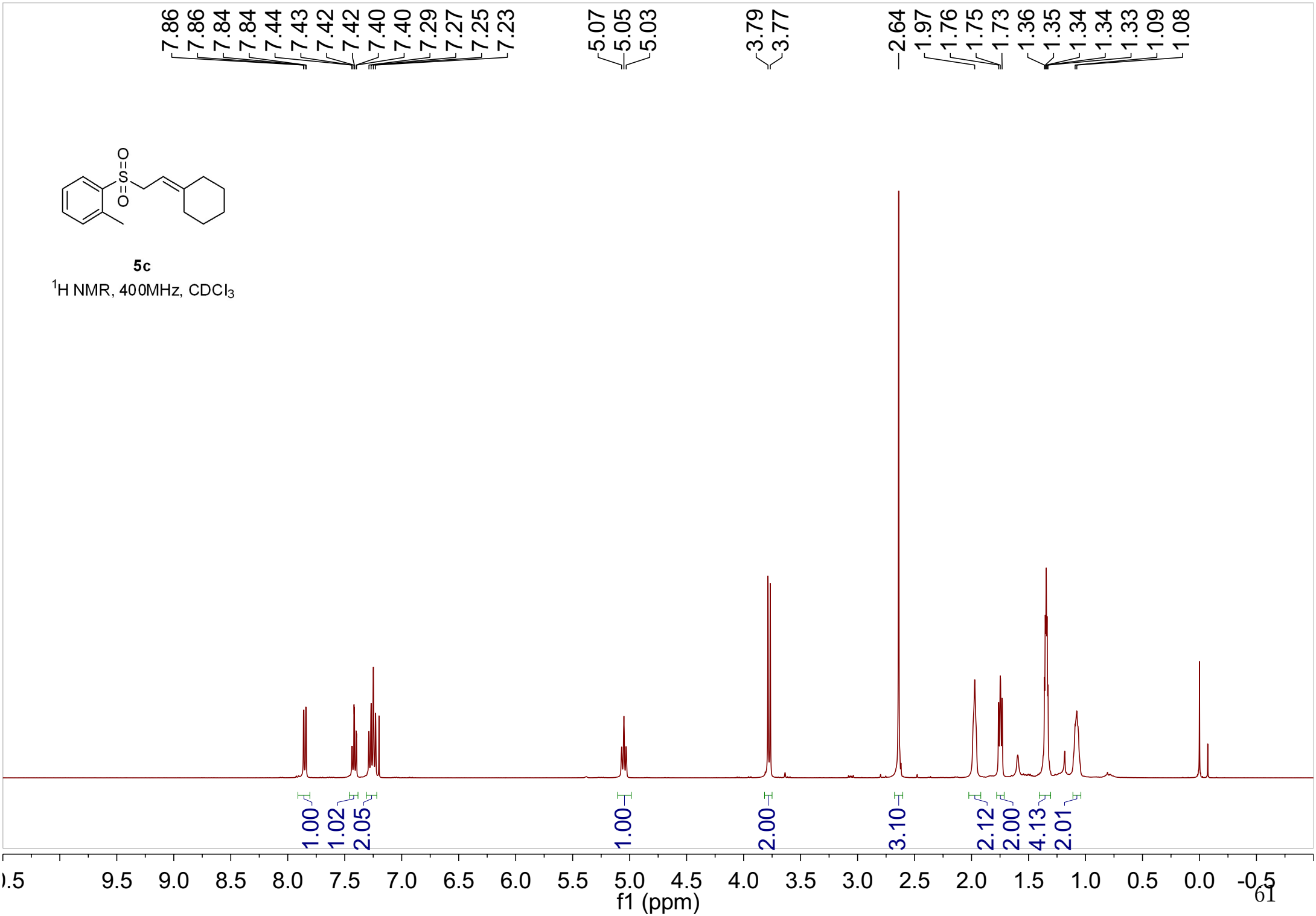
138.1
133.5
129.4
128.8
115.3
59.0
37.2
29.3
28.1
27.1
26.4
14.2
5b
13C NMR, 101MHz, CDCl3
f1 (ppm)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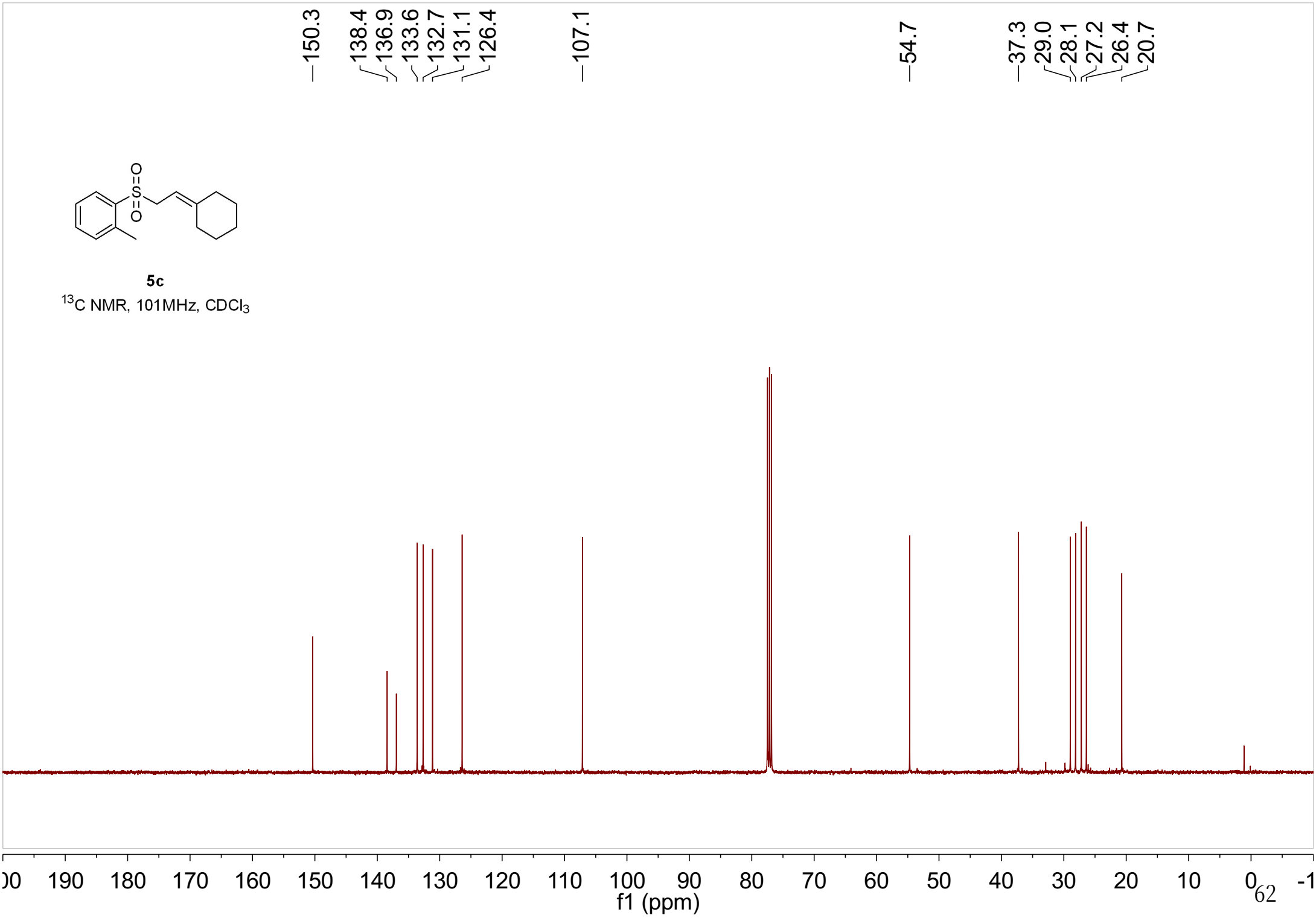
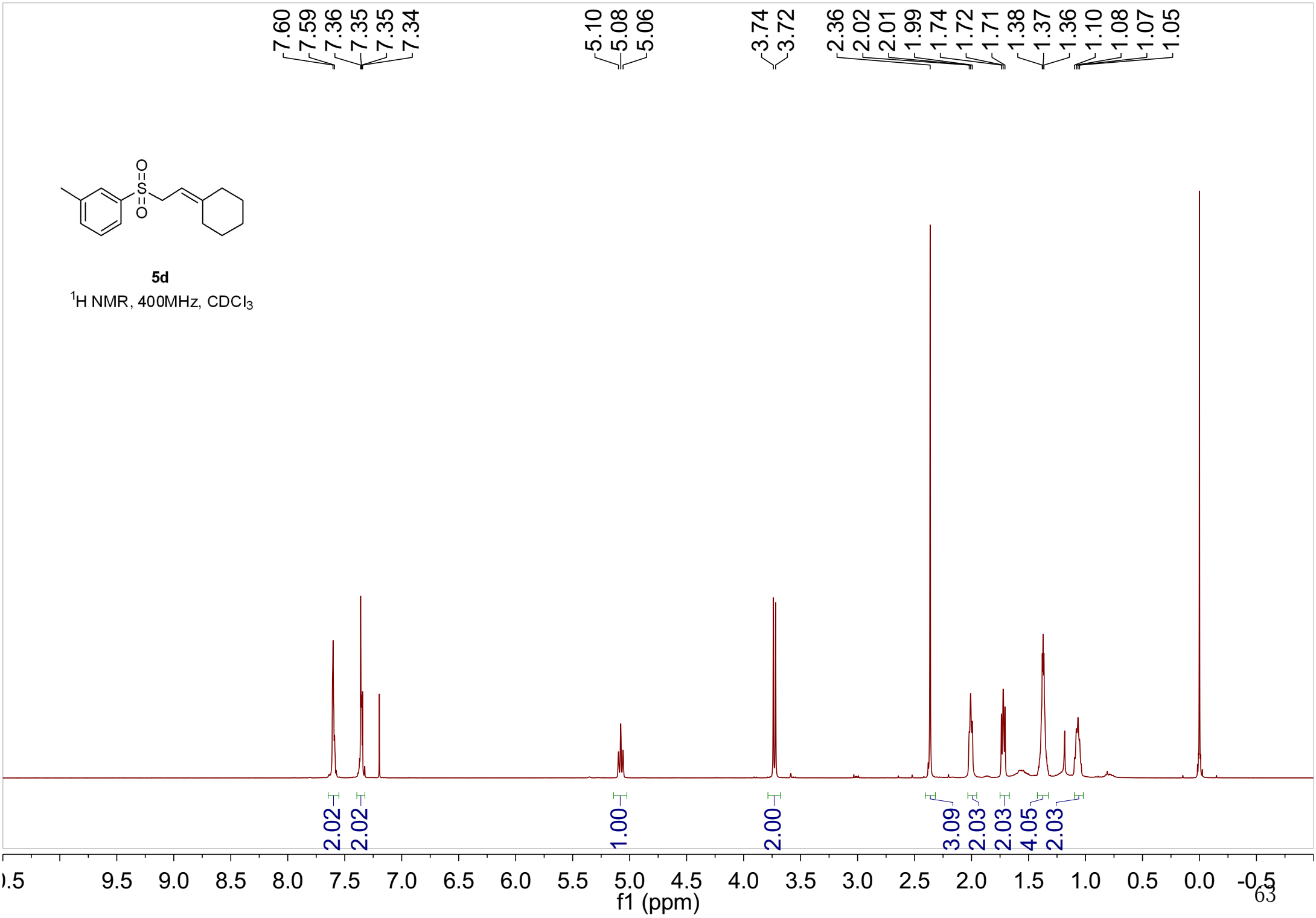
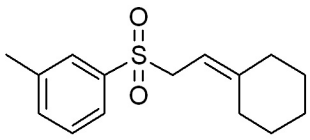
7.86
7.84
7.84
7.44
7.43
7.42
7.42
7.40
7.40
7.29
7.27
7.25
7.23
5.07
5.05
5.03
3.79
3.77
2.64
1.97
1.76
1.75
1.73
1.36
1.35
1.34
1.34
1.33
1.09
1.08
O
S
O
5c
1H NMR, 400MHz, CDCl3
1.00
1.02
2.05
1.00
2.00
3.10
2.12
2.00
4.13
2.01
f1 (ppm)

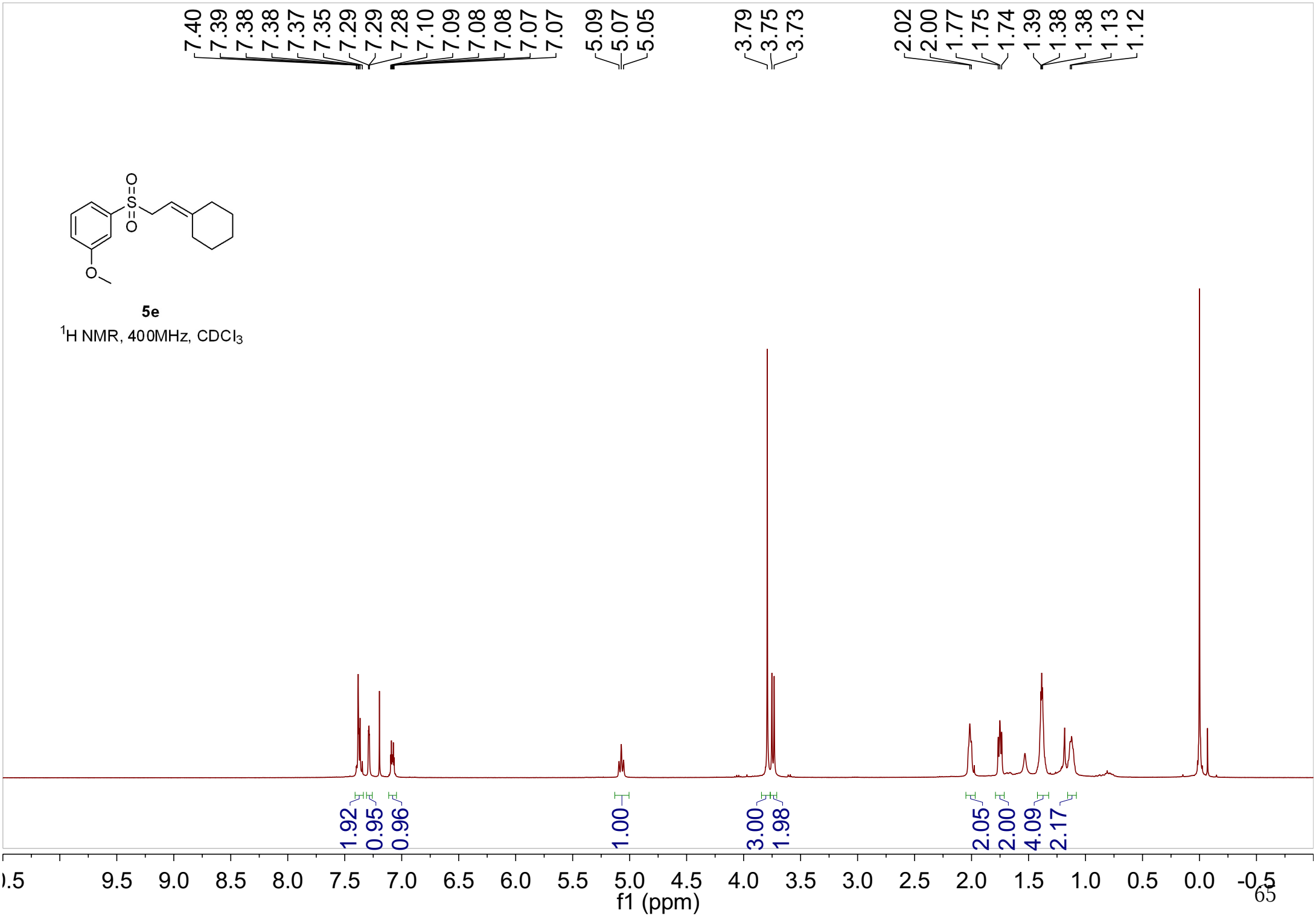

150.3
138.4
136.9
133.6
132.7
131.1
126.4
107.1
54.7
37.3
29.0
28.1
27.2
26.4
20.7
O
S
O
5c
13C NMR, 101MHz, CDCl3
f1 (ppm)


7.60
7.59
7.36
7.35
7.35
7.34
5.10
5.08
5.06
3.74
3.72
2.36
2.02
2.01
1.99
1.74
1.72
1.71
1.38
1.37
1.36
1.10
1.08
1.07
1.05
O
S
O
5d
1H NMR, 400MHz, CDCl3
2.02
2.02
1.00
2.00
3.09
2.03
2.03
4.05
2.03
f1 (ppm)



5d

^{13}C NMR, 101MHz, $CDCl_3$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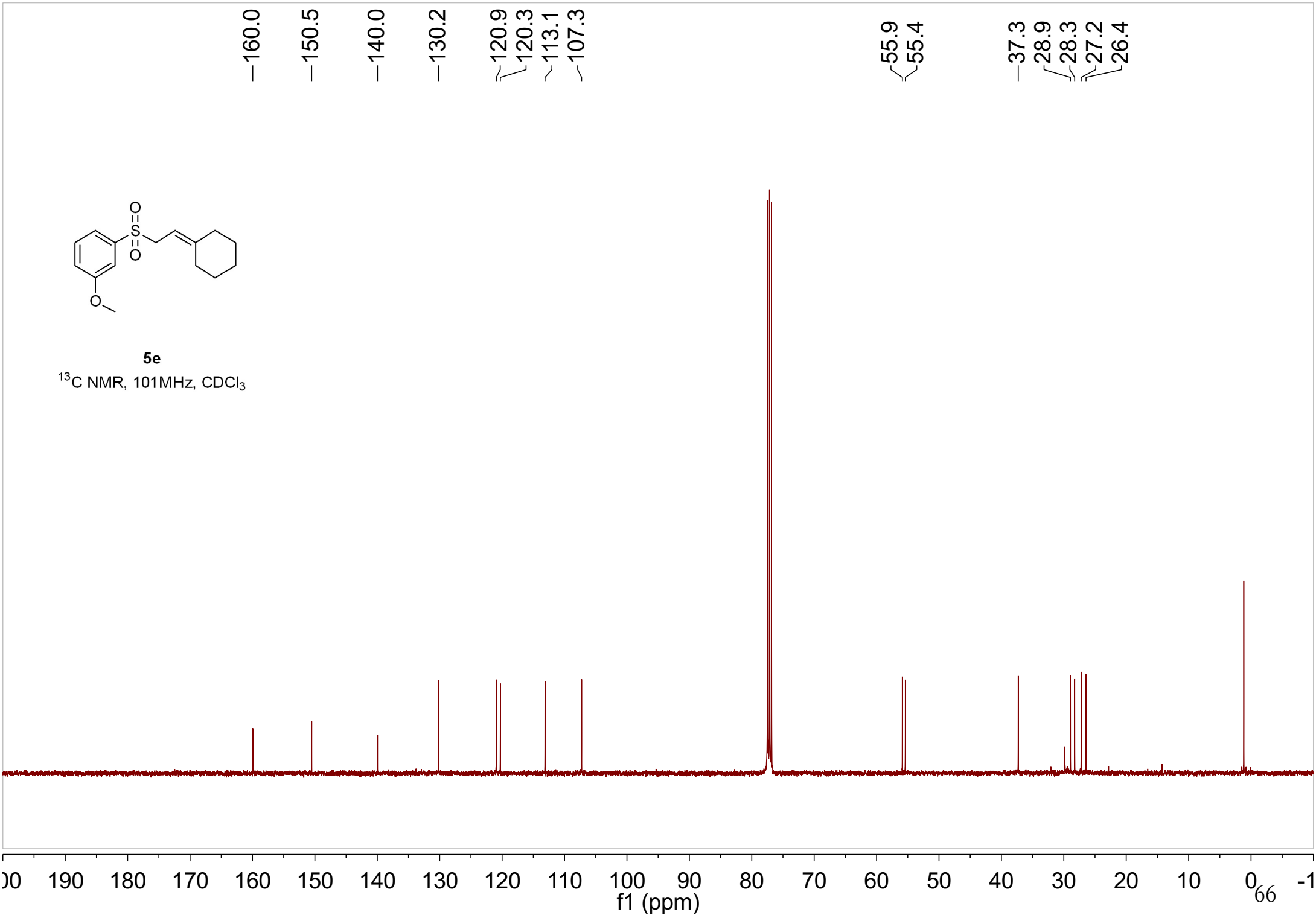
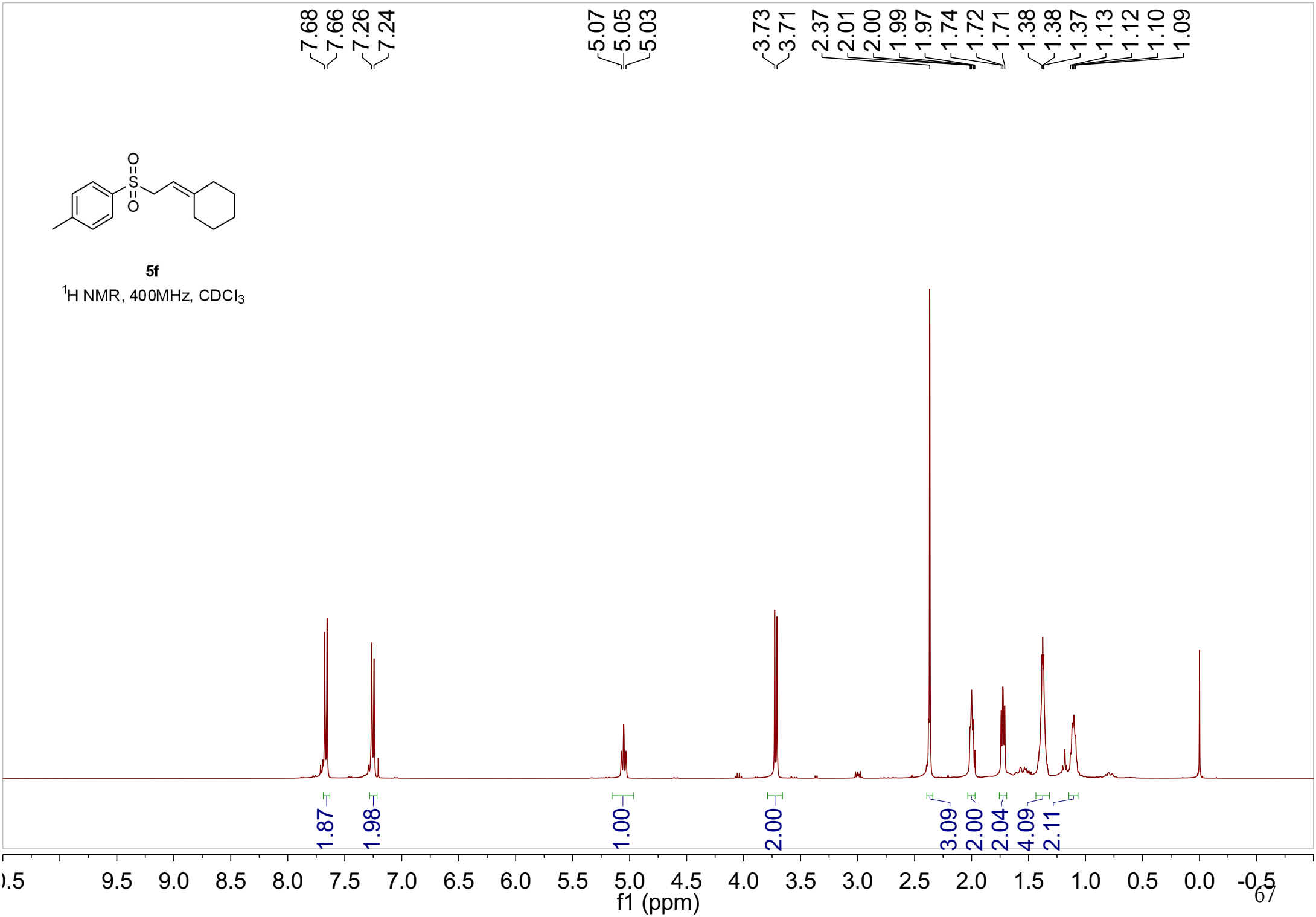
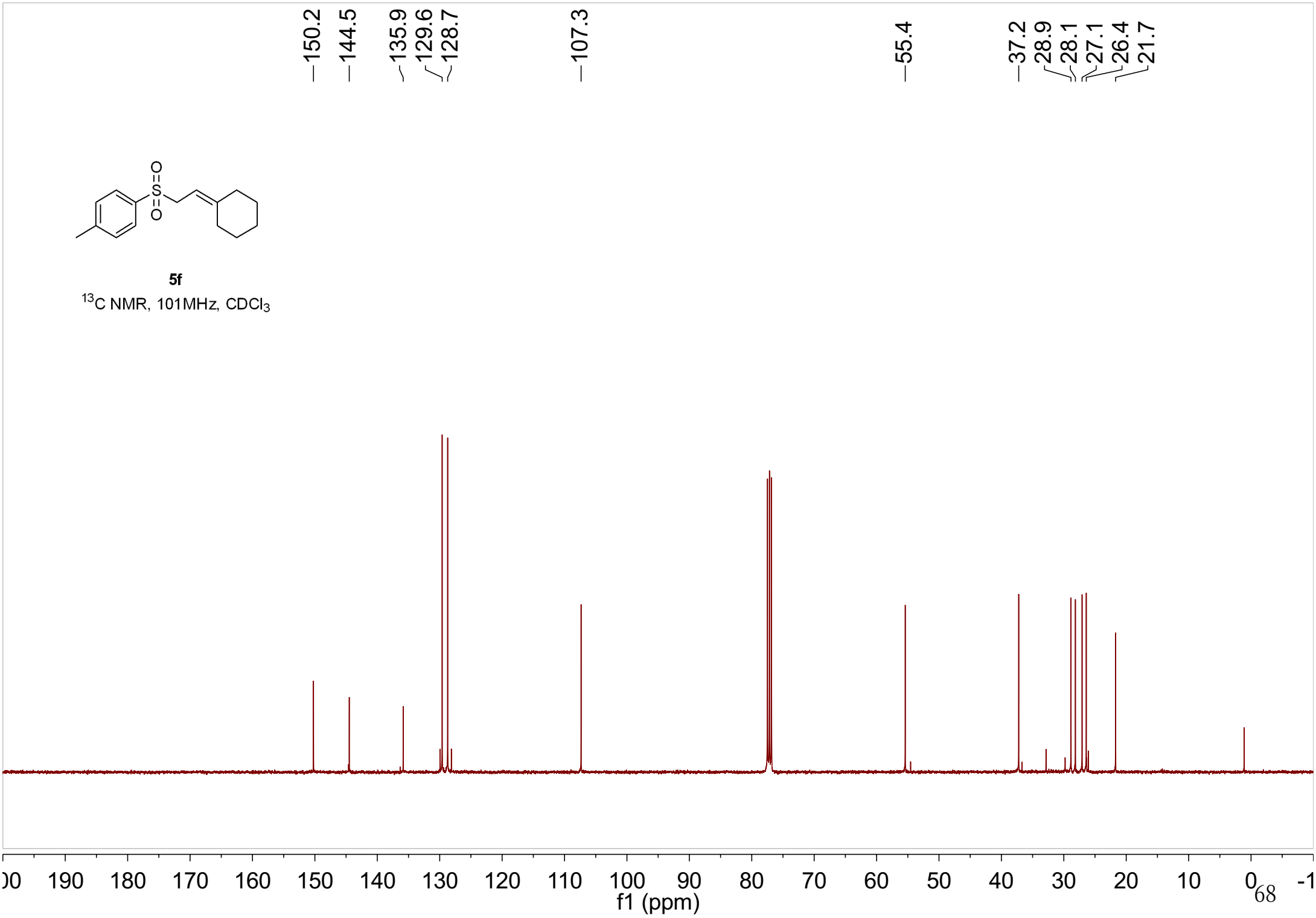
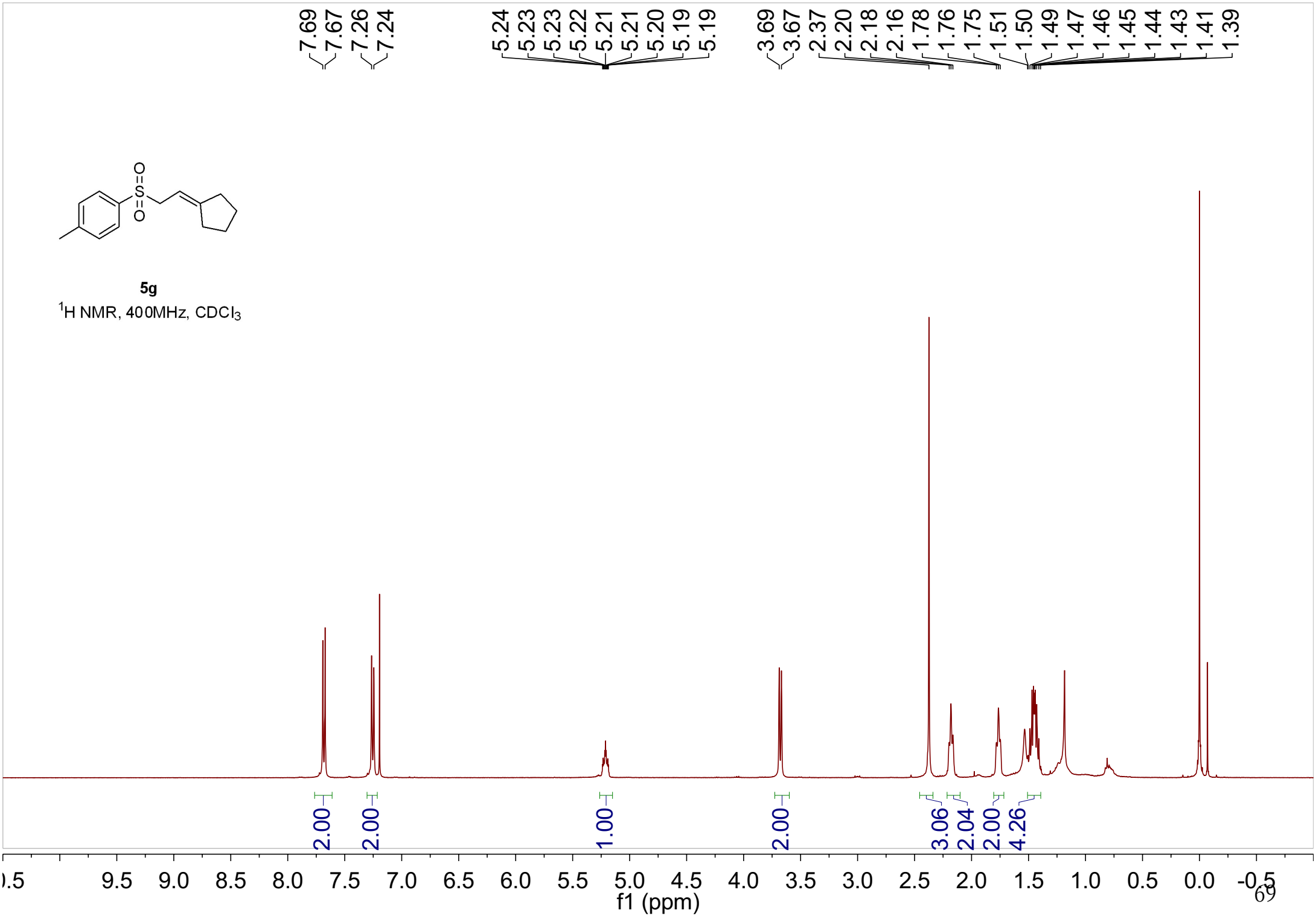
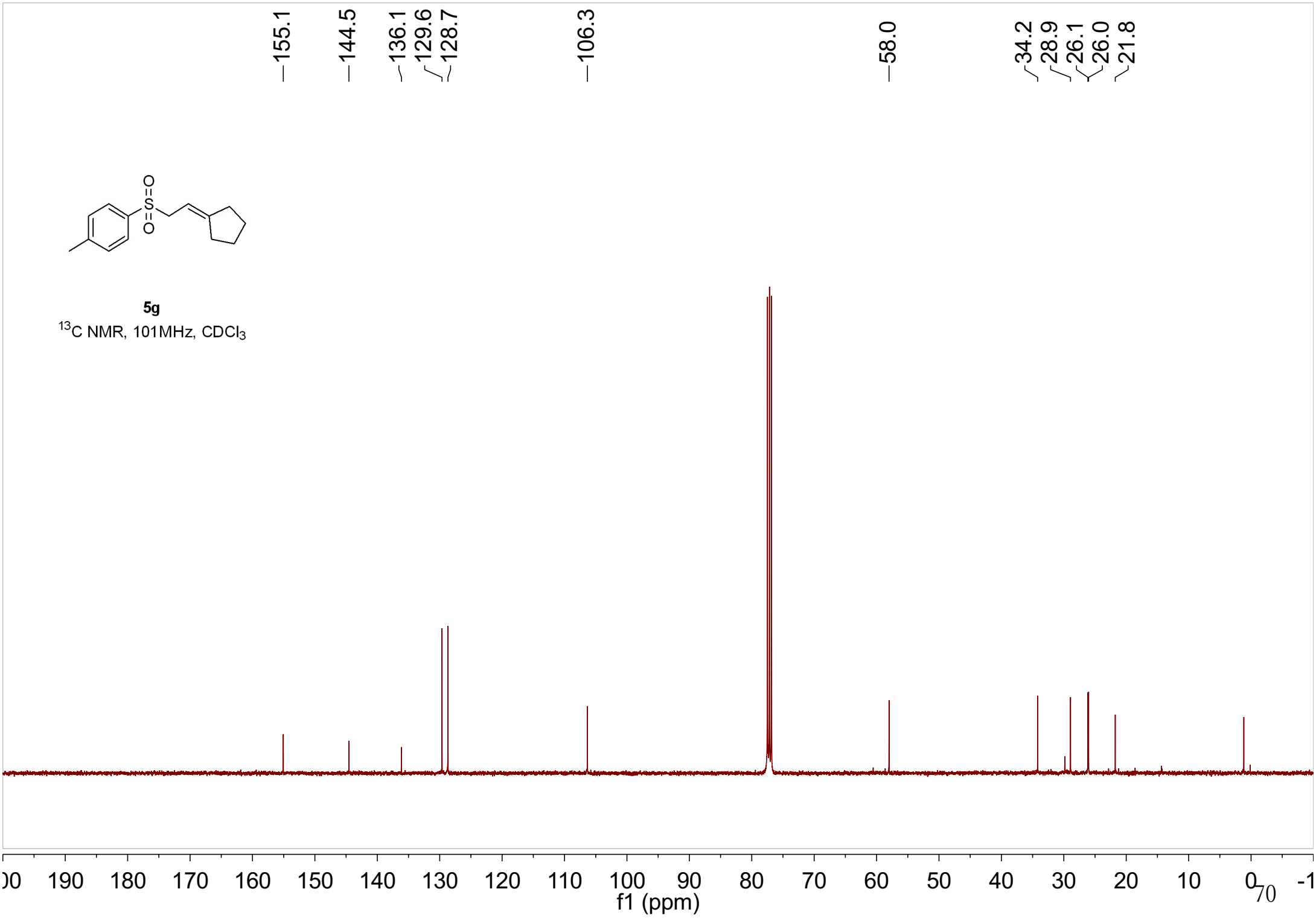
7.39
7.38
7.38
7.37
7.35
7.29
7.29
7.28
7.10
7.09
7.08
7.08
7.07
7.07
5.09
5.07
5.05
3.79
3.75
3.73
2.02
2.00
1.77
1.75
1.74
1.39
1.38
1.38
1.13
1.12
5e
1H NMR, 400MHz, CDCl3
1.92
0.95
0.96
1.00
3.00
1.98
2.05
2.00
4.09
2.17
f1 (ppm)

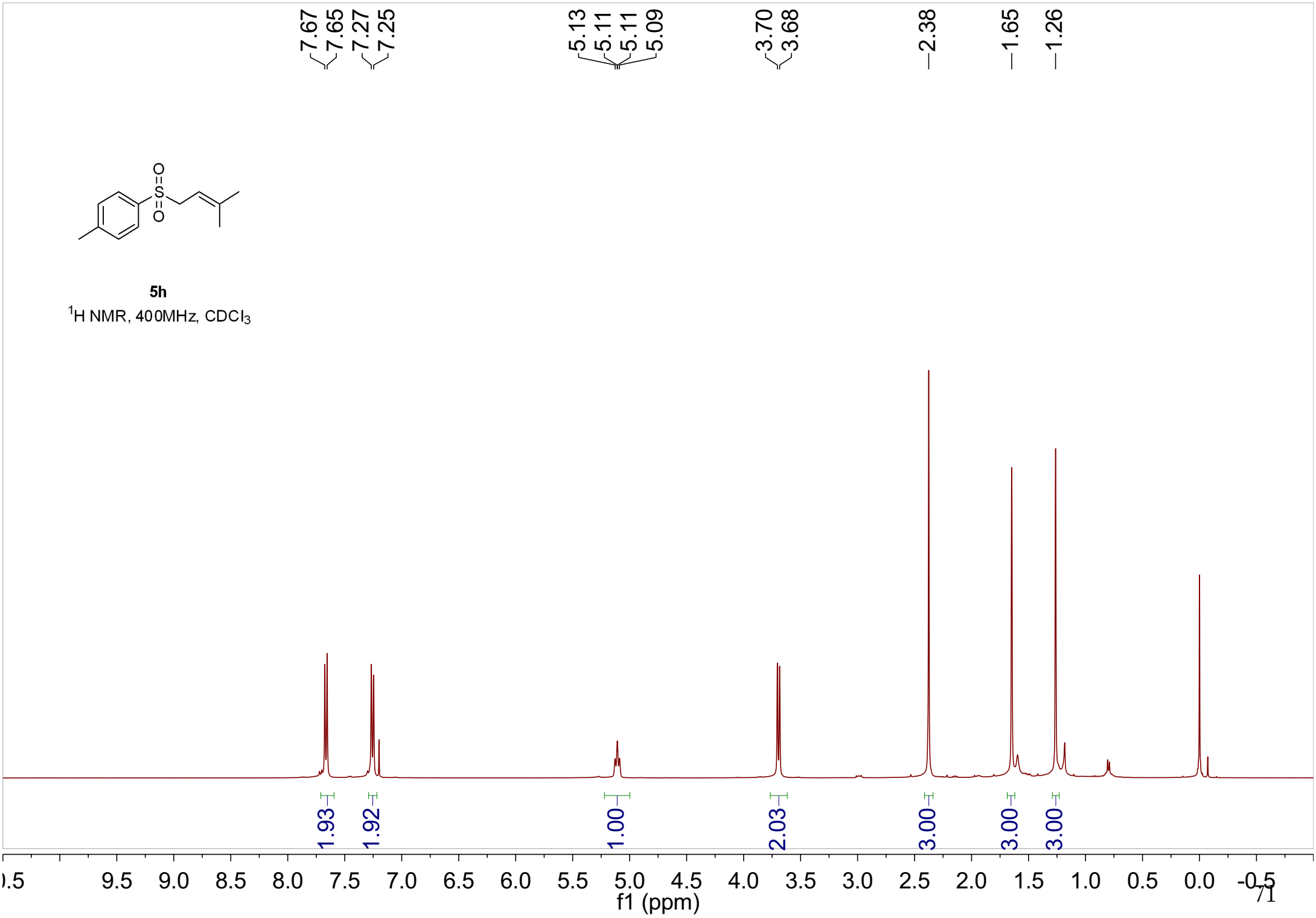

160.0
150.5
140.0
130.2
120.9
120.3
113.1
107.3
55.9
55.4
37.3
28.9
28.3
27.2
26.4
O
S
O
O
5e
13C NMR, 101MHz, CDCl3
f1 (ppm)


7.68
7.66
7.26
7.24
5.07
5.05
5.03
3.73
3.71
2.37
2.01
2.00
1.99
1.97
1.74
1.72
1.71
1.38
1.38
1.37
1.13
1.12
1.10
1.09
O
S
O
O
5f
1H NMR, 400MHz, CDCl3
1.87
1.98
1.00
2.00
3.09
2.00
2.04
4.09
2.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


150.2
144.5
135.9
129.6
128.7
107.3
55.4
37.2
28.9
28.1
27.1
26.4
21.7
O
S
O
O
5f
13C NMR, 101MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

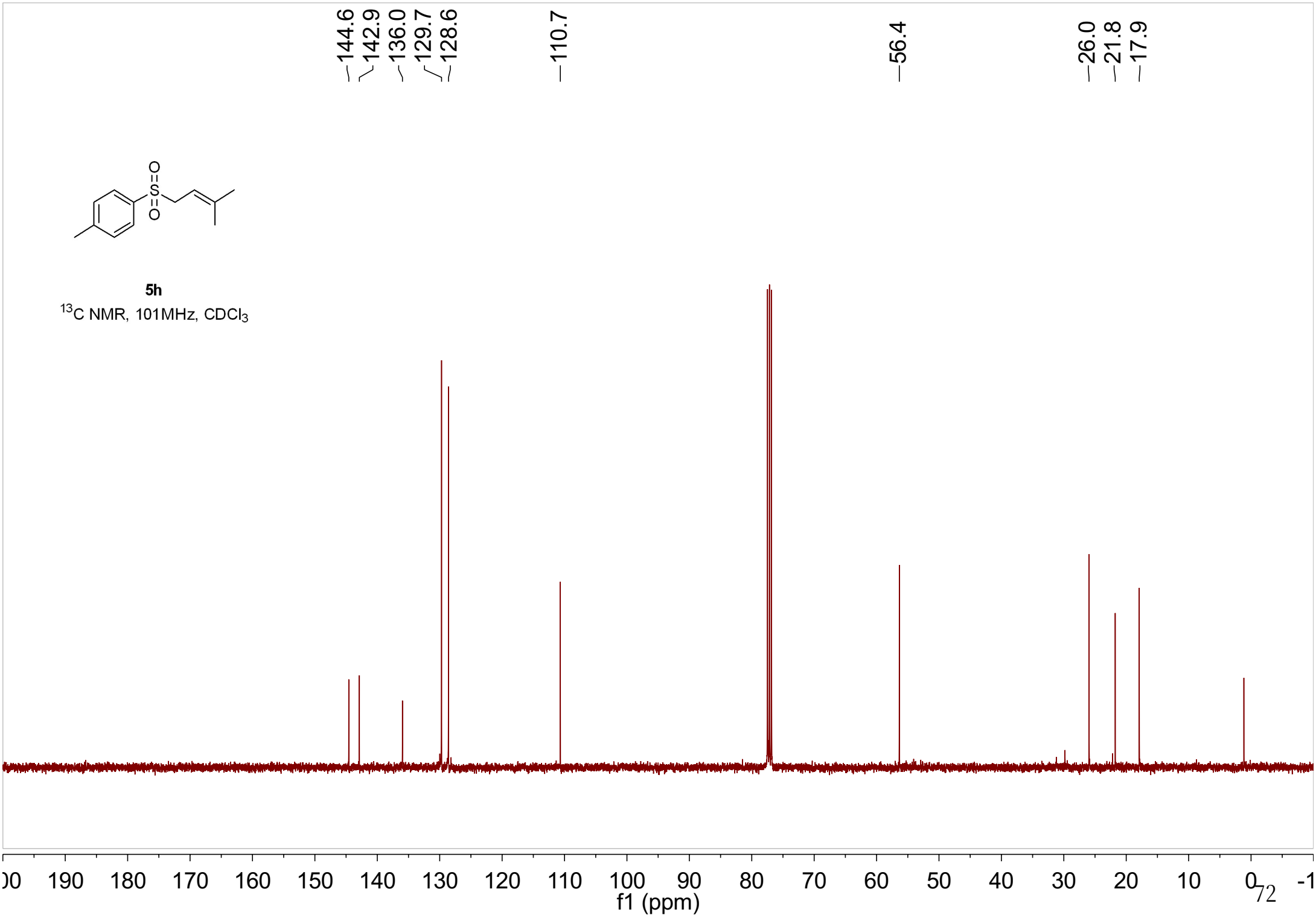

7.69
7.67
7.26
7.24
5.24
5.23
5.23
5.22
5.21
5.21
5.20
5.19
5.19
3.69
3.67
2.37
2.20
2.18
2.16
1.78
1.76
1.75
1.51
1.50
1.49
1.47
1.46
1.45
1.44
1.43
1.41
1.39
O
S
O
O
5g
1H NMR, 400MHz, CDCl3
2.00
2.00
1.00
2.00
3.06
2.04
2.00
4.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

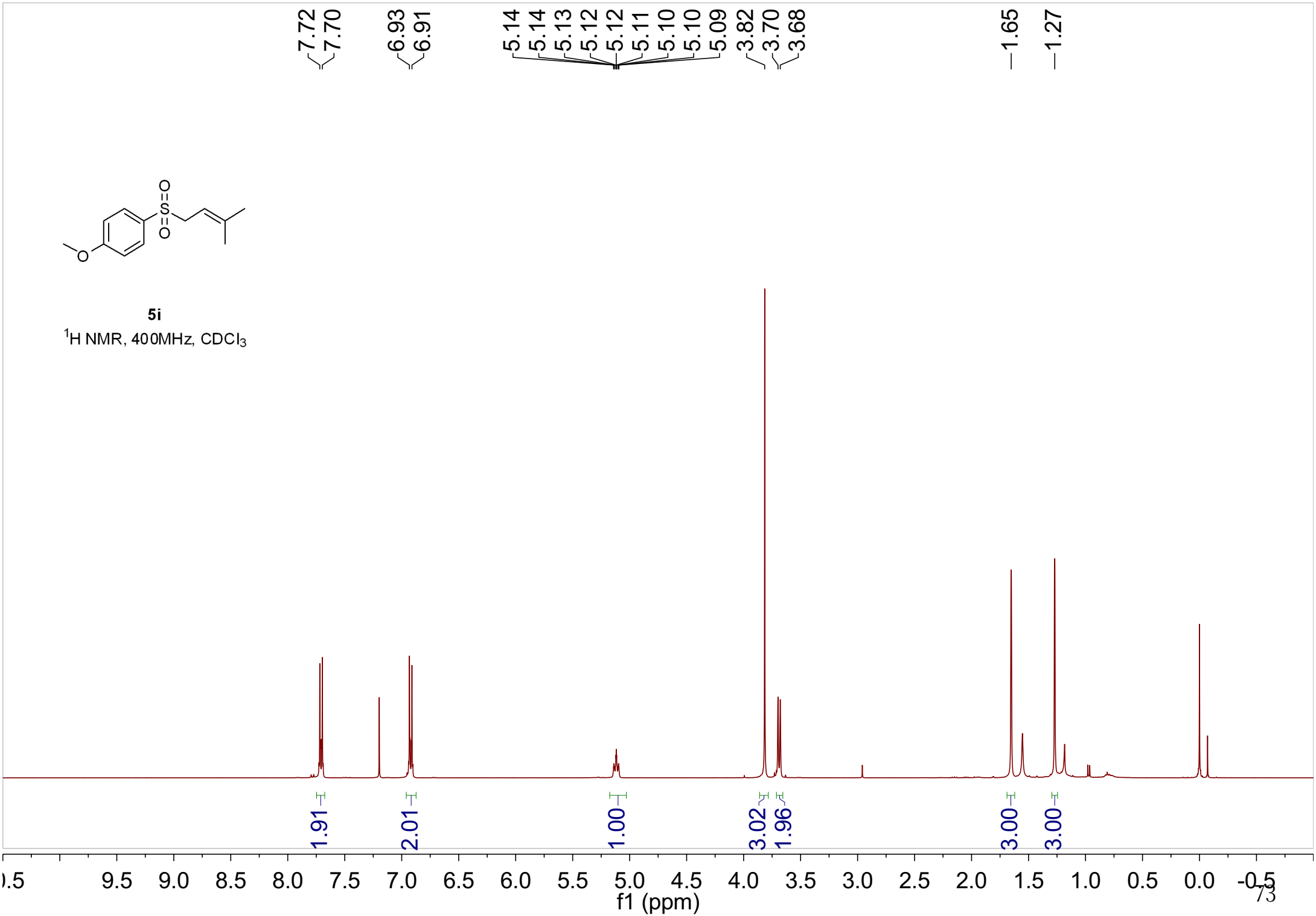

155.1
144.5
136.1
129.6
128.7
106.3
58.0
34.2
28.9
26.1
26.0
21.8
O
S
O
5g
13C NMR, 101MHz, CDCl3
f1 (ppm)



5h

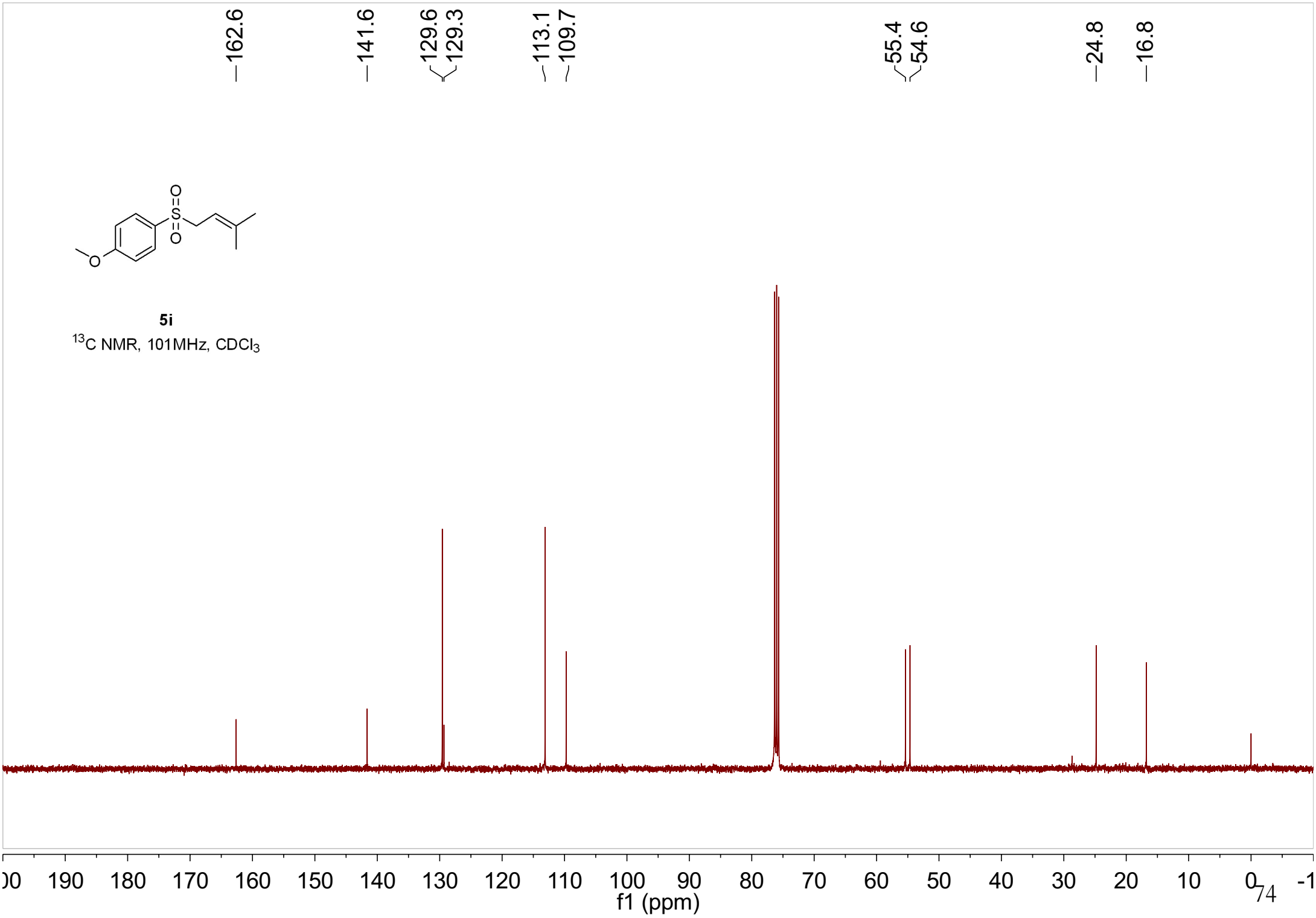
^{1}H NMR, 400MHz, $CDCl_3$

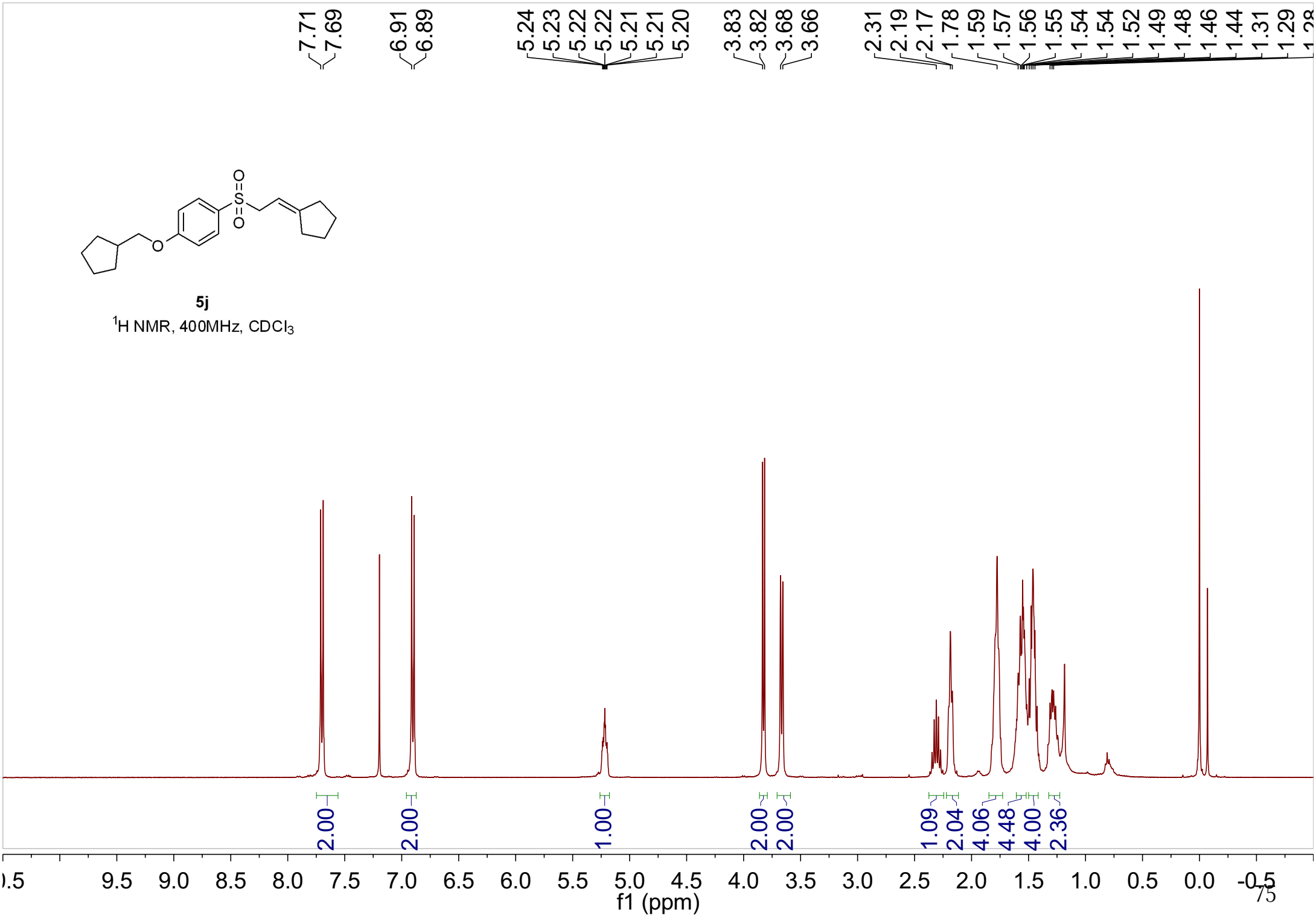

144.6
142.9
136.0
129.7
128.6
110.7
56.4
26.0
21.8
17.9
O
S
O
5h
13C NMR, 101MHz, CDCl3
f1 (ppm)

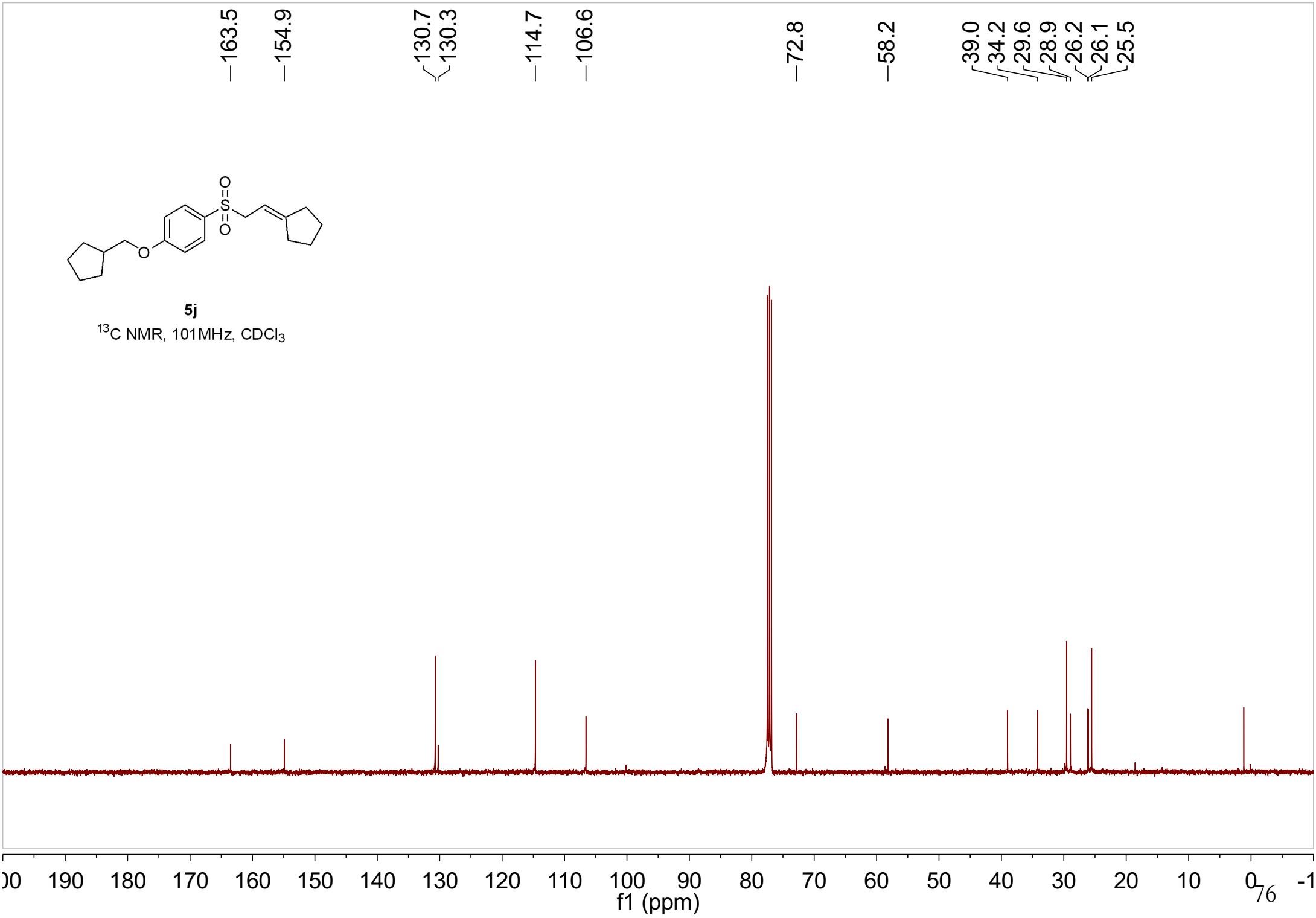


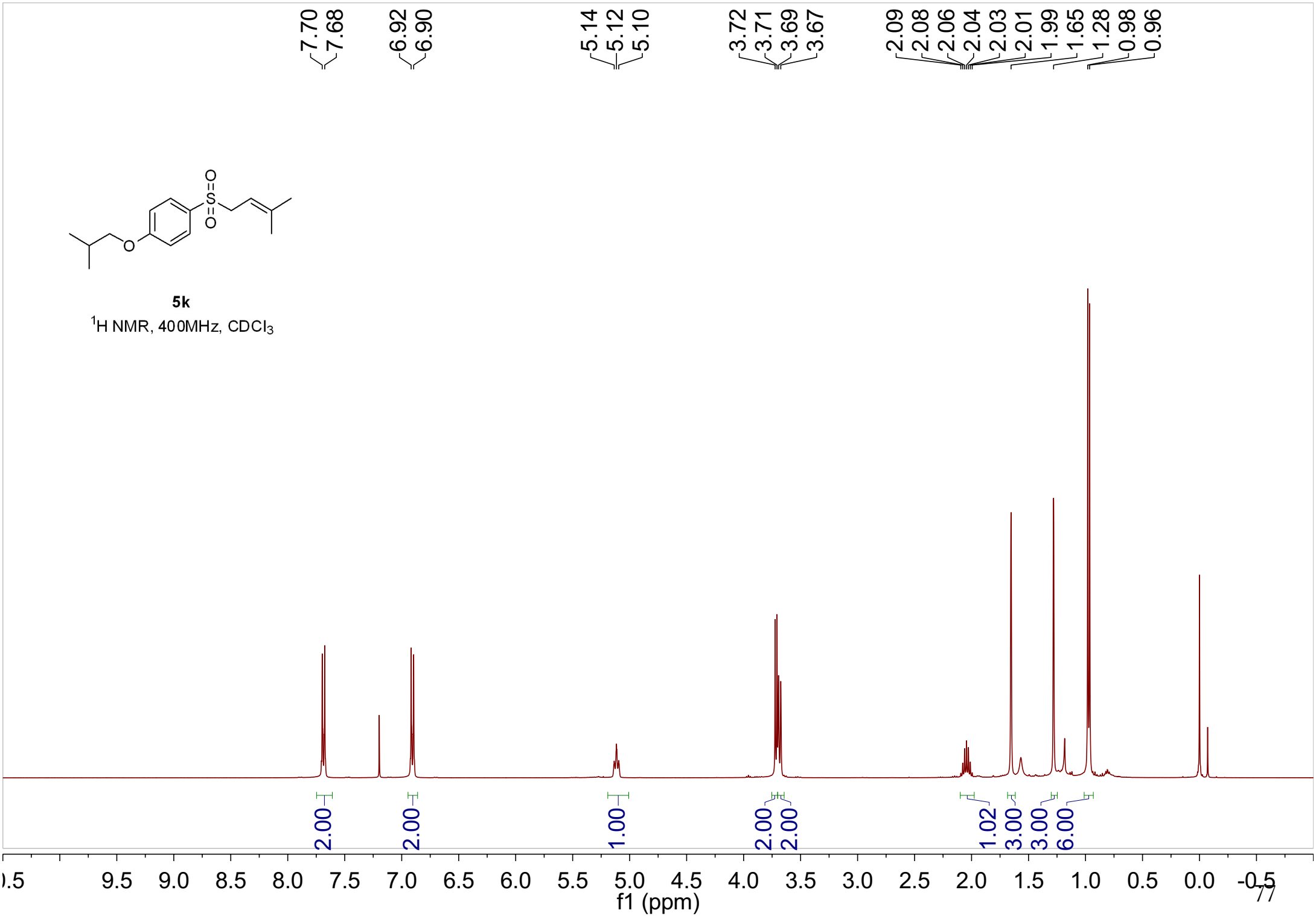
5i

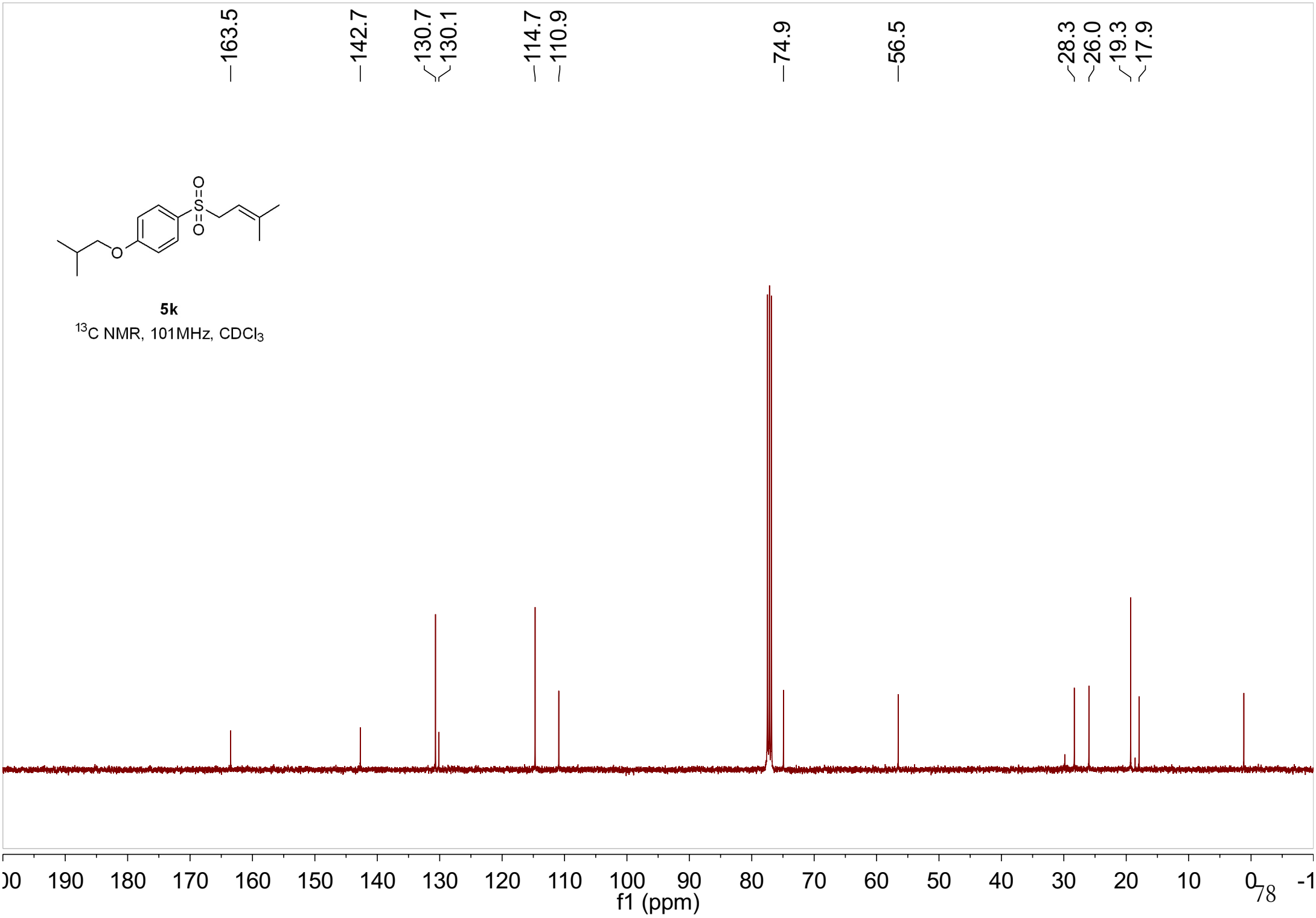
^{1}H NMR, 400MHz, $CDCl_3$

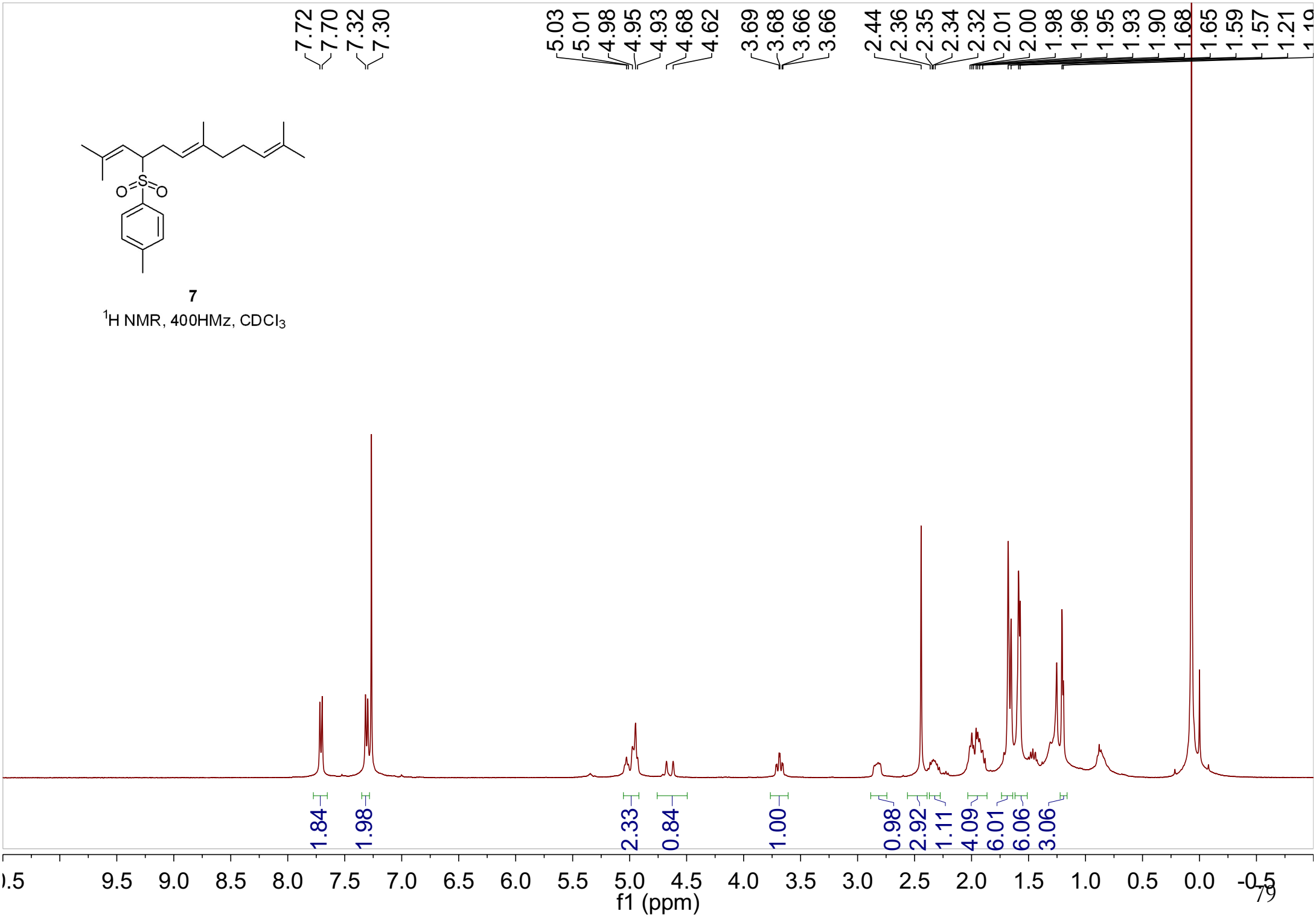

162.6
141.6
129.6
129.3
113.1
109.7
55.4
54.6
24.8
16.8
O
S
O
O
5i
13C NMR, 101MHz, CDCl3
f1 (ppm)

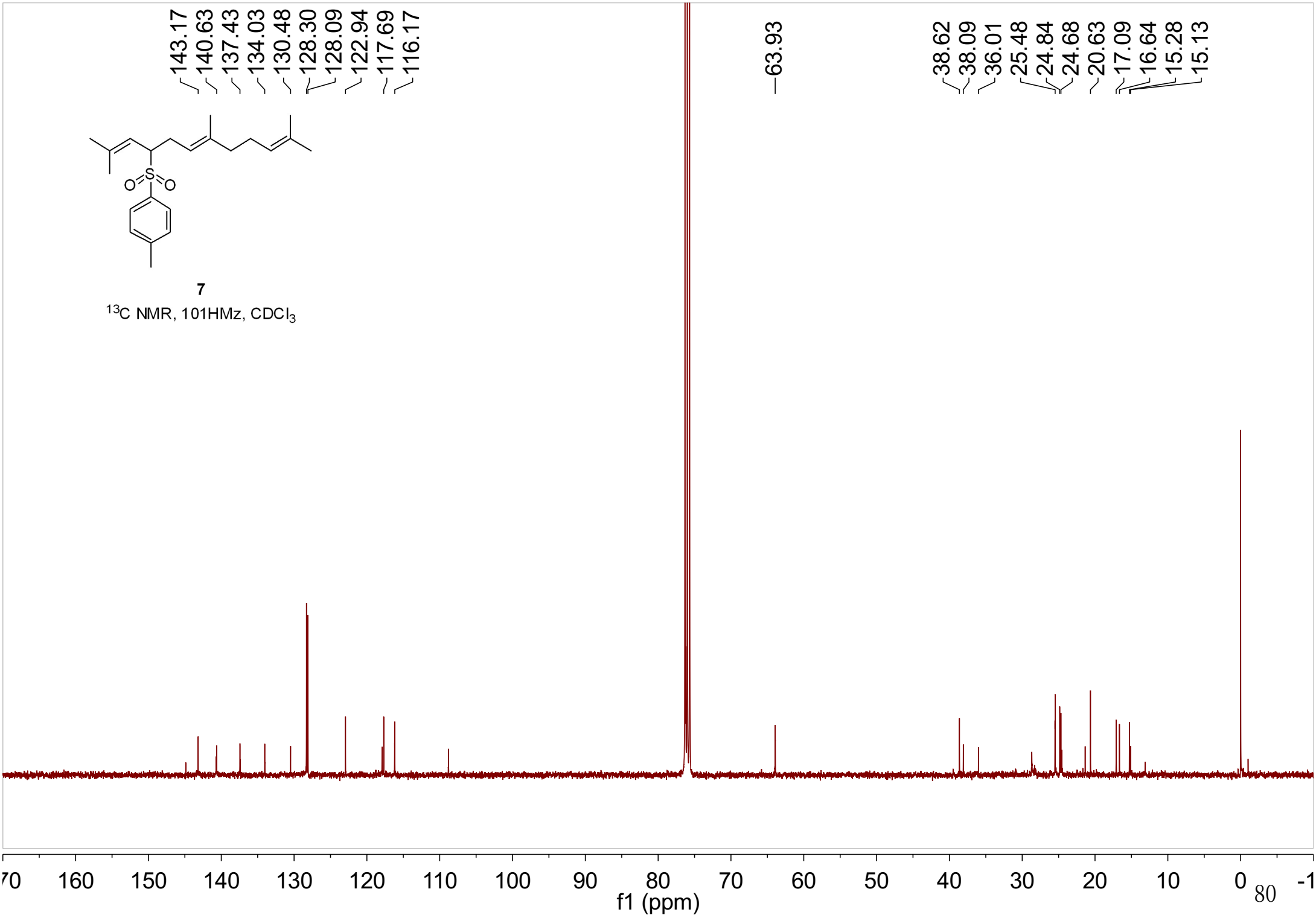

7.71
7.69
6.91
6.89
5.24
5.23
5.22
5.22
5.21
5.21
5.20
3.83
3.82
3.68
3.66
2.31
2.19
2.17
1.78
1.59
1.57
1.56
1.55
1.54
1.54
1.52
1.49
1.48
1.46
1.44
1.31
1.29
O
S
O
O
5j
1H NMR, 400MHz, CDCl3
2.00
2.00
1.00
2.00
2.00
1.09
2.04
4.06
4.48
4.00
2.36
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


163.5
154.9
130.7
130.3
114.7
106.6
72.8
58.2
39.0
34.2
29.6
28.9
26.2
26.1
25.5
O
S
O
O
5j
13C NMR, 101MHz, CDCl3
f1 (ppm)


7.70
7.68
6.92
6.90
5.14
5.12
5.10
3.72
3.71
3.69
3.67
2.09
2.08
2.06
2.04
2.03
2.01
1.99
1.65
1.28
0.98
0.96
O
S
O
O
5k
1H NMR, 400MHz, CDCl3
2.00
2.00
1.00
2.00
2.00
1.02
3.00
3.00
6.00
f1 (ppm)


163.5
142.7
130.7
130.1
114.7
110.9
74.9
56.5
28.3
26.0
19.3
17.9
O
S
O
O
5k
13C NMR, 101MHz, CDCl3
f1 (ppm)


7.72
7.70
7.32
7.30
5.03
5.01
4.98
4.95
4.93
4.68
4.62
3.69
3.68
3.66
3.66
2.44
2.36
2.35
2.34
2.32
2.01
2.00
1.98
1.96
1.95
1.93
1.90
1.68
1.65
1.59
1.57
1.21
O
S
O
7
1H NMR, 400HMz, CDCl3
1.84
1.98
2.33
0.84
1.00
0.98
2.92
1.11
4.09
6.01
6.06
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


143.17
140.63
137.43
134.03
130.48
128.30
128.09
122.94
117.69
116.17
63.93
38.62
38.09
36.01
25.48
24.84
24.68
20.63
17.09
16.64
15.28
15.13
O
S
O
7
13C NMR, 101HMz, CDCl3
f1 (ppm)