Electronic Supplementary Information (ESI) for

Photoredox-catalyzed coupling of acyl oxime acetates with thiophenols to give arylthioesters in water at room temperature

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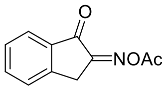
I. General Information and Materials

General Information

Unless otherwise stated, all glassware was oven dried. All reagents were used as received from commercial suppliers unless otherwise indicated. Reactions were monitored using Thin Layer Chromatography (TLC) carried out on Merck silica gel plates (60F-254) using UV light as the visualizing agent and High Performance Liquid Chromatography (HPLC) with UV detection at 254 nm. For HPLC yields, UV response factors relative to an internal standard (diphenyl sulfide). Flash column chromatography was performed using silica gel 60 (200-300 mesh). HRMS data were recorded on Thermo Fisher LTQ OrbitrapXL and micrOTOF-Q III. All ^{1}H NMR, ^{13}C NMR spectra were recorded on Bruker DRX-600 and AMX-400 instruments. Chemical shifts were given in parts per million (ppm, δ), referenced to the solvent peak of $CDCl_3$, defined at δ = 7.26 (^{1}H NMR), defined at δ = 77.16 (^{13}C NMR); or DMSO-d6, defined at δ = 2.5 (^{1}H NMR), defined at δ = 39.52 (^{13}C NMR). Coupling constants were quoted in Hz (J). ^{1}H NMR Spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br).

Materials

Table S1. Oxime acetates used in this study



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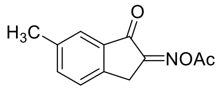

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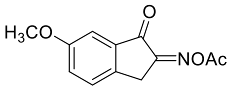

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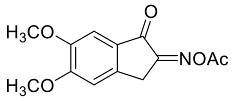

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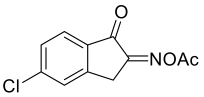

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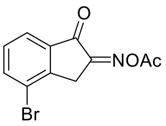

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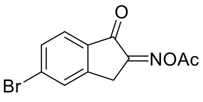

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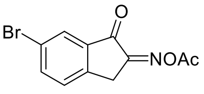

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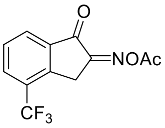

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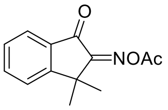

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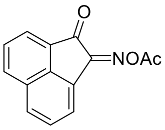
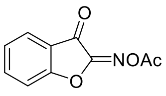
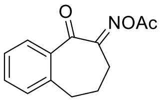


1k



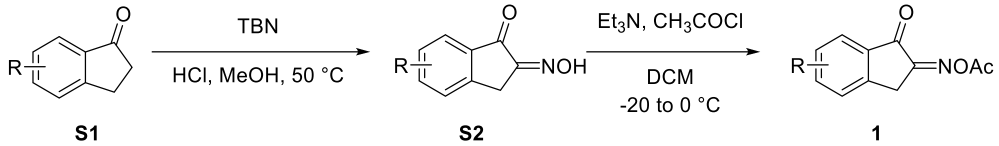
1l



1m

1a-1j、**1m** were synthesized according to Procedure A[1,2], **1k** was synthesized according to Procedure B[3] and **1l** was synthesized according to Procedure C[4].

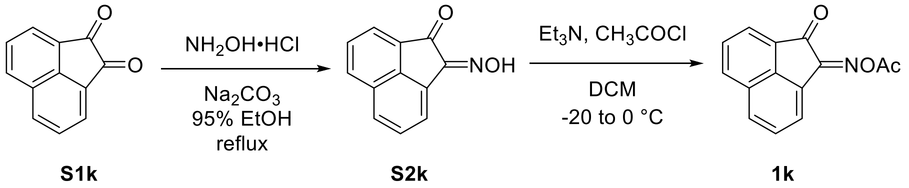
Procedure A[1,2]**:**



Step1 To a solution of 1-indanone **S1** (10 mmol) in methanol (20 mL) was added conc. HCl (480 μL, 5.7 mmol) followed by tert-Butyl nitrite (1.5 mL, 12 mmol) dropwise. The reaction was kept stirring at 50 °C for 2 h. The reaction mixture was cooled to room temperature and a white precipitate formed. Half of MeOH was removed by rotary evaporation before filtration. The crude solid was washed with DCM and filtered to afford the 2-oximino-1-indanon **S2**.

Step2 To a mixture of 2-oximino-1-indanon **S2** (5 mmol), DCM (15mL), Et_3N (1.1mL, 7.5mmol) in a 100 mL flask was added acetyl chloride (544 μL, 7.5mmol) dropwise at -20 °C and the mixture was stirred at 0 °C for 2 h. After then, a saturated solution of aqueous $NaHCO_3$ (30 mL) was added to the above solution, and the mixture was extracted with DCM. The combined organic layers were concentrated in vacuo and the residue was purified by recrystallization with PE and EtOAc to give 1-indanone oxime acetate **1**.

Procedure B[3]:



Step1 A suspension of acenaphthoquinone **S1k** (1.1g, 5 mmol,), hydroxylamine hydrochloride (355 mg, 5mmol) and Na_2CO_3 (535 mg, 5 mmol) in 95% EtOH (25 mL) was heated under reflux condition for 45 min then cooled to rt. The precipitate was filtered, washed with water, and dried under vacuo to afford **S2k**.

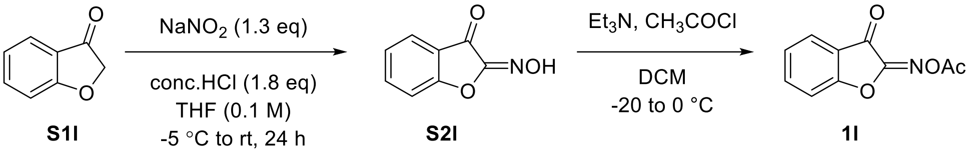
Step2 The preparation of **1k** from **S2k** was the same as Procedure A, Step 2.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (d, J = 7.1 Hz, 1H), 8.15 (d, J = 8.2 Hz, 1H), 8.06 (dd, J = 16.0, 7.7 Hz, 2H), 7.79 - 7.71 (m, 2H), 2.48 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 187.8, 169.5, 153.4, 142.3, 132.6, 131.6, 131.0, 130.3, 129.1, 128.9, 127.4, 125.9, 123.2, 19.4.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{14}H_{11}NO_3$ 240.0655, found 240.0653.

Procedure C[4]:



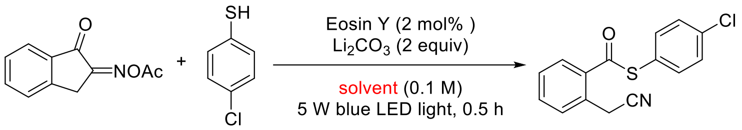
Step1 To a pre-cooled (-5 °C) solution of 3-coumaranone **S1l** (2 mmol) and NaNO$_2$ (182 mg, 2.6 mmol) in THF (20 mL) was slowly added conc. HCl (300 µL, 3.6 mmol). The resulting mixture was kept at -5 °C for 15 min and then warmed up to room temperature with stirring for another 24 h. Subsequently, the mixture was quenched by water and extracted with EtOAc. The combined organic layers were concentrated in vacuo and the residue was purified by recrystallization with PE and EtOAc to give **S2l**. *Step2* The preparation of **1l** from **S2l** was the same as Procedure A, Step 2.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.81 - 7.74 (m, 2H), 7.37 - 7.30 (m, 2H), 2.33 (s, 3H).
^{13}C NMR (150 MHz, CDCl$_3$) δ 179.7, 167.7, 165.3, 149.2, 139.9, 126.0, 125.9, 121.0, 113.6, 19.0.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{10}H_9NO_4$ 206.0448, found 206.0447.
Spectroscopic data matches that reported in the literature.[5]

II. Optimization Tables

All optimization reactions were carried out on 0.1 mmol scale and yields were determined by HPLC analysis with diphenyl sulfide as the internal standard.

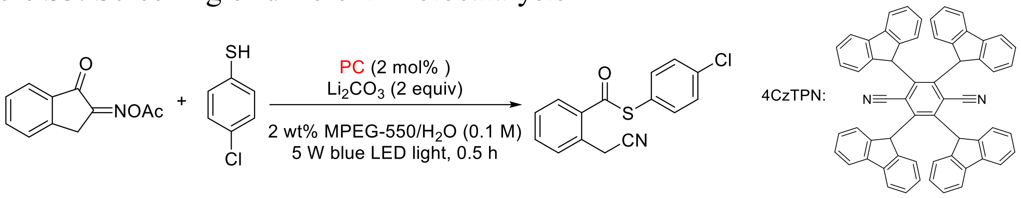
Table S2. Screening of different solvents



Entry	Solvent	Yield	Entry	Solvent	Yield
1	THF	0	11	2 wt% MPEG-750/H_2O	76%
2	CH_3CN	0	12	2 wt% PEG-600/H_2O	81%
3	DCM	0	13	MPEG-550	0
4	Dioxane	0	14	2 wt% THF/H_2O	70%
5	EtOH	0	15	2 wt% 1,4-dioxane/H_2O	70%
6	H_2O	64%	16	2 wt% triethylene glycol dimethyl ether/H_2O	68%
7	2 wt% TWEEN 80[a]	30%	17	0.5 wt% MPEG-550	87%
8	2 wt% DTAB[b]	17%	18	1 wt% MPEG-550	80%
9	2 wt% BrijL23[c]	31%	19	3 wt% MPEG-550	86%
10	**2 wt% MPEG-550[d]/H_2O**	**89%**	20	4 wt% MPEG-550	86%

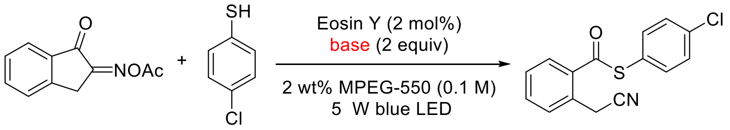
[a]TWEEN = Polysorbate 80. [b]DTAB = Dodecyltrimethylammonium bromide. [c]BrijL23 = Polyoxethyleneglycol-23 lauryl ether. [d]MPEG = Poly(ethylene glycol) methyl ether.

Table S3. Screening of different Photocatalysts



Entry	PC	Yield	Entry	PC	Yield
1	**Eosin Y**	**89%**	6	ErythrosinB	74%
2	Eosin B	83%	7	Rhodamine 6G	15%
3	Eosin Y (2Na$^+$)	76%	8	1 mol% Eosin Y	64%
4	$Ru(bpy)_3Cl_2 \cdot H_2O$	70%	9	3 mol% Eosin Y	67%
5	4CzTPN	18%	10	5 mol% Eosin Y	79%

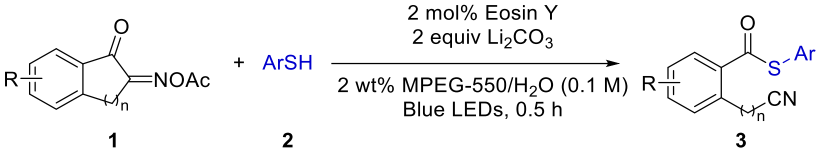
Table S4. Screening of different bases



Entry	Base	Yield	Entry	Base	Yield
1	**Li_2CO_3**	**89%**	7	LiOH	28%
2	Na_2CO_3	84%	8	Et_3N	43%
3	K_2CO_3	85%	9	1 equiv Li_2CO_3	32%
4	Cs_2CO_3	0	10	1 equiv Li_2CO_3	79%
5	LiOAc	8%	11	1 equiv Li_2CO_3	71%
6	^{t}BuOLi	0			

III. Synthesis and Characterization of Product 3-31.

General Procedure D:



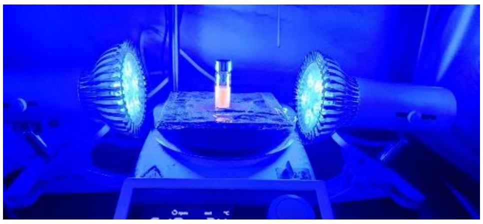
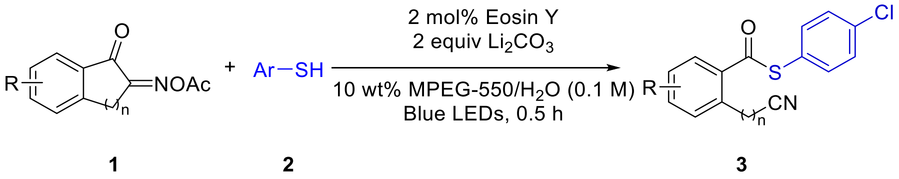


Figure S1 Reaction device

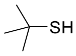
A mixture of 1-indanone oxime acetate **1** (0.1 mmol), thiophenol **2** (0.15 mmol), Eosin Y (1.3 mg, 2 mol%) and Li_2CO_3 (0.2 mmol, 14.9 mg,) in a 4 mL vial was added 2 wt% MPEG-550/H_2O (1 mL). The reaction mixture was stirred under the irradiation of 2×5 W Blue LEDs (λ = 440 - 480nm) at room temperature for 0.5 h. The reaction mixture was quenched by EtOAc and concentrated in vacuo. The crude was purified by flash chromatography (petroleumether/ethyl acetate = 100/1 - 10/1) on silica gel to provide the corresponding products.

Procedure E (preparation of substrates **8, 14, 18, 28** and **31**):



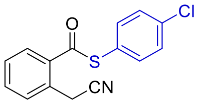
A mixture of 1-indanone oxime acetate **1** (0.1 mmol), thiophenol **2** (0.15 mmol), Eosin Y (1.3 mg, 2 mol%) and Li_2CO_3 (0.2 mmol, 14.9 mg,) in a 4 mL vial was added 10 wt% MPEG-550/H_2O (1 mL). The reaction mixture was stirred under the irradiation of 2×5 W Blue LEDs (λ = 440 - 480nm) at room temperature for 0.5 h. The reaction mixture was quenched by EtOAc and concentrated in vacuo. The crude was purified by flash chromatography (petroleumether/ethyl acetate = 100/1 - 10/1) on silica gel to provide the corresponding products.

Unsuccessful substrates:



$n\text{C}_{12}\text{H}_{25}\text{SH}$

S-(4-chlorophenyl) 2-(cyanomethyl)benzothioate (**3**)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and 4-chlorobenzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.

25.6 mg, 89%. White solid.

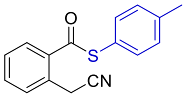
$R_f = 0.39$ (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, J = 7.7 Hz, 1H), 7.64 - 7.60 (m, 2H), 7.53 - 7.49 (m, 1H), 7.45 (s, 4H), 4.04 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 136.8, 136.7, 135.3, 133.9, 130.8, 130.12, 130.09, 129.8, 129.0, 126.0, 117.7, 22.3.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{15}H_{10}ClNOSNa$ 310.0064, found 310.0050.

S-(*p*-tolyl) 2-(cyanomethyl)benzothioate (**4**)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and 4-methylbenzenethiol (19.0 mg, 0.15 mmol) was used to afford the desired product.

17.8 mg, 67%. White solid.

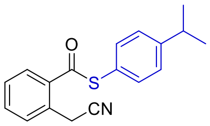
$R_f = 0.32$ (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, J = 7.7 Hz, 1H), 7.64 - 7.58 (m, 2H), 7.53 - 7.47 (m, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 4.06 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 193.3, 140.8, 135.7, 135.4, 133.6, 130.7, 130.7, 130.1, 129.7, 128.9, 124.0, 117.9, 22.3, 21.2.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{14}NOS$ 268.0791, found 268.0782.

S-(4-isopropylphenyl) 2-(cyanomethyl)benzothioate (**5**)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and 4-isopropylbenzenethiol (24.0 mg, 0.15 mmol) was used to afford the desired product.

24.6 mg, 84%. Yellow solid.

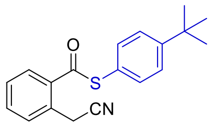
$R_f = 0.40$ (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, J = 7.5 Hz, 1H), 7.65 - 7.59 (m, 2H), 7.54 - 7.48 (m, 1H), 7.46 - 7.41 (m, 2H), 7.35 (d, J = 8.1 Hz, 2H), 4.07 (s, 2H), 3.01 - 2.93 (m, 1H), 1.29 (d, J = 6.9 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 193.3, 151.5, 135.7, 135.4, 133.6, 130.7, 130.2, 129.7, 128.9, 128.1, 124.2, 117.9, 33.9, 23.6, 22.3.

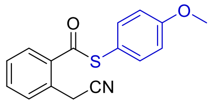
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{18}H_{18}NOS$ 296.1104, found 296.1106.

S-(4-(tert-butyl)phenyl) 2-(cyanomethyl)benzothioate (**6**)



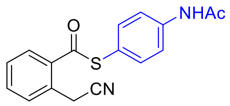
Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and 4-tert-butylbenzenethiol (25.5 mg, 0.15 mmol) was used to afford the desired product.
19.5 mg, 63%. Yellow solid.
$R_f = 0.27$ (10% EA in PE)
^{1}**H NMR** (600 MHz, $CDCl_3$) δ 8.16 (d, J = 7.7 Hz, 1H), 7.65 - 7.59 (m, 2H), 7.50 (dd, J = 12.0, 5.0 Hz, 3H), 7.45 (d, J = 8.4 Hz, 2H), 4.07 (s, 2H), 1.36 (s, 9H).
^{13}**C NMR** (150 MHz, $CDCl_3$) δ 193.3, 153.8, 135.7, 135.1, 133.7, 130.7, 130.2, 129.7, 128.9, 127.0, 124.0, 117.9, 34.7, 31.1, 22.3.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{19}H_{20}NOS$ 310.1260, found 310.1250.

S-(4-methoxyphenyl) 2-(cyanomethyl)benzothioate (**7**)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and 4-methoxybenzenethiol (21.5 mg, 0.15 mmol) was used to afford the desired product.
22.0 mg, 63%. Light yellow solid.
$R_f = 0.43$ (20% EA in PE)
^{1}**H NMR** (600 MHz, $CDCl_3$) δ 8.13 (d, J = 7.7 Hz, 1H), 7.64 - 7.57 (m, 2H), 7.53 - 7.47 (m, 1H), 7.45 - 7.39 (m, 2H), 7.04 - 6.97 (m, 2H), 4.05 (s, 2H), 3.85 (s, 3H).
^{13}**C NMR** (150 MHz, $CDCl_3$) δ 193.8, 161.6, 137.0, 135.6, 133.6, 130.7, 130.1, 129.6, 128.9, 118.0, 117.9, 115.4, 55.4, 22.3.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{14}NO_2S$ 284.0740, found 284.0730.

S-(4-acetamidophenyl) 2-(cyanomethyl)benzothioate (**8**)

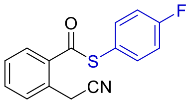


Following Procedure E, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and *N*-(4-mercaptophenyl)acetamide (26.4 mg, 0.15 mmol) was used to afford the desired product.
6.6 mg, 22%. Light yellow solid.
$R_f = 0.41$ (50% EA in PE)
^{1}**H NMR** (600 MHz, DMSO-d6) δ 10.21 (s, 1H), 8.08 (d, J = 7.7 Hz, 1H), 7.74 - 7.70 (m, 3H), 7.63 - 7.58 (m, 2H), 7.46 (d, J = 8.5 Hz, 2H), 4.13 (s, 2H), 2.09 (s, 3H).
^{13}**C NMR** (150 MHz, DMSO-d6) δ 192.4, 169.6, 141.5, 136.2, 135.8, 134.1, 131.7,

130.2, 129.7, 129.4, 120.4, 120.1, 118.9, 24.1, 21.6.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{17}H_{15}N_2O_2S$ 311.0849, found 311.0849.

S-(4-fluorophenyl) 2-(cyanomethyl)benzothioate (**9**)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and 4-fluorobenzenethiol (19.6 mg, 0.15 mmol) was used to afford the desired product.

26.9 mg, 99%. White solid.

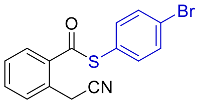
$R_f = 0.50$ (20% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, J = 7.8 Hz, 1H), 7.65 - 7.59 (m, 2H), 7.54 - 7.47 (m, 3H), 7.18 (t, J = 8.6 Hz, 2H), 4.05 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 192.8, 164.4 (d, J = 250.9 Hz), 137.6 (d, J = 8.6 Hz), 135.4, 133.9, 130.8, 130.1, 129.8, 129.0, 122.8 (d, J = 3.4 Hz), 117.7, 117.08 (d, J = 22.2 Hz), 22.3.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{15}H_{10}FNOSNa$ 294.0359, found 294.0345.

S-(4-bromophenyl) 2-(cyanomethyl)benzothioate (**10**)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and 4-bromobenzenethiol (28.9 mg, 0.15 mmol) was used to afford the desired product.

29.4 mg, 88%. White solid.

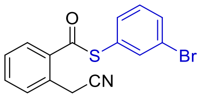
$R_f = 0.36$ (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, J = 7.5 Hz, 1H), 7.63 - 7.57 (m, 4H), 7.53 - 7.49 (m, 1H), 7.40 - 7.35 (m, 2H), 4.04 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 192.1, 136.9, 135.3, 133.9, 133.1, 130.9, 130.1, 129.8, 129.1, 126.6, 125.1, 117.7, 22.3.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{15}H_{10}BrNOSNa$ 353.9559, found 353.9544.

S-(3-bromophenyl) 2-(cyanomethyl)benzothioate (**11**)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and 3-bromobenzenethiol (28.9 mg, 0.15 mmol) was used to afford the desired product.

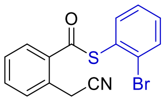
31.9 mg, 96%. White solid.

$R_f = 0.35$ (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, J = 7.7 Hz, 1H), 7.68 (t, J = 1.7 Hz, 1H), 7.65 -

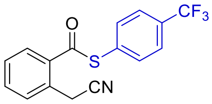
7.59 (m, 3H), 7.54 - 7.49 (m, 1H), 7.48 - 7.45 (m, 1H), 7.36 (t, J = 7.9 Hz, 1H), 4.05 (s, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 191.9, 137.9, 135.3, 134.1, 134.0, 133.4, 131.1, 130.8, 130.2, 129.9, 129.5, 129.1, 123.2, 117.7, 22.3.
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{15}H_{10}BrNOSNa$ 353.9559, found 353.9545.

S-(2-bromophenyl) 2-(cyanomethyl)benzothioate (**12**)



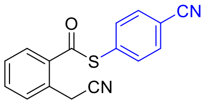
Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and 2-bromobenzenethiol (28.9 mg, 0.15 mmol) was used to afford the desired product.
29.9 mg, 90%. White solid.
$R_f = 0.35$ (10% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, J = 7.5 Hz, 1H), 7.77 (dd, J = 8.0, 1.2 Hz, 1H), 7.67 - 7.60 (m, 3H), 7.55 - 7.49 (m, 1H), 7.42 (td, J = 7.6, 1.3 Hz, 1H), 7.35 (td, J = 7.8, 1.6 Hz, 1H), 4.06 (s, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 191.1, 138.0, 135.4, 134.2, 133.9, 132.1, 130.6, 130.4, 130.1, 129.8, 129.4, 129.0, 128.6, 117.8, 22.2.
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{15}H_{10}BrNOSNa$ 353.9559, found 353.9545.

S-(4-(trifluoromethyl)phenyl) 2-(cyanomethyl)benzothioate (**13**)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and 4-(trifluoromethyl)benzenethiol (27.3 mg, 0.15 mmol) was used to afford the desired product.
26.0 mg, 81%. White solid.
$R_f = 0.20$ (10% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, J = 7.9 Hz, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.63 (t, J = 8.2 Hz, 2H), 7.55 - 7.51 (m, 1H), 4.04 (s, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 191.5, 135.7, 135.2, 134.1, 132.3, 132.2 (q, J = 32.9 Hz),131.0, 130.2, 130.1, 129.1, 126.6 (q, J = 3.6 Hz), 124.1 (q, J = 272.4 Hz), 117.7, 22.4.
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{16}H_{10}F_3NOSNa$ 344.0327, found 344.0314.

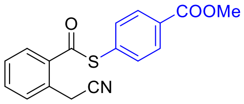
S-(4-cyanophenyl) 2-(cyanomethyl)benzothioate (**14**)



Following Procedure E, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and 4-mercaptobenzonitrile (21.3 mg, 0.15 mmol) was used to afford the desired

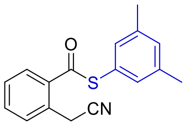
product.
19.2 mg, 69%. White solid.
R_f = 0.41 (20% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 8.1 Hz, 2H), 7.67 - 7.64 (m, 3H), 7.62 (d, J = 7.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 4.04 (s, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 190.8, 135.8, 135.0, 134.3, 134.0, 133.1, 131.1, 130.2, 130.0, 129.2, 118.5, 117.6, 113.8, 22.4.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{11}N_2OS$ 279.0587, found 279.0586.

Methyl 4-((2-(cyanomethyl)benzoyl)thio)benzoate (**15**)



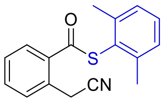
Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and methyl 4-mercaptobenzoate (29.7 mg, 0.15 mmol) was used to afford the desired product.
24.1 mg, 77%. White solid.
R_f = 0.20 (10% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, J = 8.3 Hz, 3H), 7.66 - 7.62 (m, 2H), 7.61 (d, J = 8.1 Hz, 2H), 7.55 - 7.51 (m, 1H), 4.05 (s, 2H), 3.95 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 191.7, 167.0, 135.4, 135.2, 134.1, 133.3, 131.7, 130.9, 130.8, 130.2, 129.9, 129.1, 117.8, 52.4, 22.4.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{17}H_{14}NO_3S$ 312.0689, found 312.0690.

S-(3,5-dimethylphenyl) 2-(cyanomethyl)benzothioate (**16**)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and 3,5-dimethylbenzenethiol (21.2 mg, 0.15 mmol) was used to afford the desired product.
23.8 mg, 85%. Yellow solid.
R_f = 0.36 (10% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, J = 7.7 Hz, 1H), 7.65 - 7.58 (m, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.15 (s, 2H), 7.11 (s, 1H), 4.07 (s, 2H), 2.38 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 193.7, 140.0, 136.2, 134.0, 133.4, 132.7, 131.0, 130.5, 130.0, 129.3, 127.2, 118.3, 22.6, 21.4.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{17}H_{16}NOS$ 282.0947, found 282.0941.

S-(2,6-dimethylphenyl) 2-(cyanomethyl)benzothioate (**17**)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1

mmol) and 2,6-dimethylbenzenethiol (21.4 mg, 0.15 mmol) was used to afford the desired product.

24.3 mg, 87%. White solid.

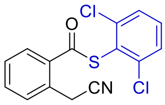
$R_f = 0.37$ (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (d, J = 7.7 Hz, 1H), 7.63 - 7.60 (m, 2H), 7.55 - 7.51 (m, 1H), 7.33 - 7.28 (m, 1H), 7.23 (d, J = 7.6 Hz, 2H), 4.05 (s, 2H), 2.44 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 192.0, 143.6, 136.1, 133.6, 130.7, 130.4, 129.7, 129.0, 128.9, 126.9, 117.9, 22.2, 21.6.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{17}H_{16}NOS$ 282.0947, found 282.0934.

S-(2,6-dichlorophenyl) 2-(cyanomethyl)benzothioate (**18**)



Following Procedure E, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and 2,6-dichlorobenzenethiol (27.4 mg, 0.15 mmol) was used to afford the desired product.

20.0 mg, 62%. White solid.

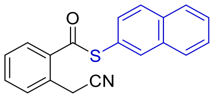
$R_f = 0.23$ (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, J = 7.6 Hz, 1H), 7.67 - 7.62 (m, 2H), 7.54 - 7.48 (m, 3H), 7.38 - 7.34 (m, 1H), 4.05 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 189.2, 141.6, 135.1, 134.0, 132.3, 130.6, 130.2, 129.9, 129.2, 129.0, 127.3, 117.6, 22.0.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{15}H_{10}Cl_2NOS$ 321.9855, found 321.9852.

S-(naphthalen-2-yl) 2-(cyanomethyl)benzothioate (**19**)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (20.9 mg, 0.1 mmol) and 2,6-dimethylbenzenethiol (24.5 mg, 0.15 mmol) was used to afford the desired product.

14.4 mg, 47%. White solid.

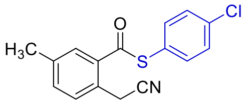
$R_f = 0.19$ (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, J = 8.1 Hz, 1H), 8.06 (s, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.92 - 7.86 (m, 2H), 7.66 - 7.62 (m, 2H), 7.59 - 7.56 (m, 2H), 7.55 - 7.52 (m, 2H), 4.07 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 193.4, 136.1, 135.9, 134.5, 134.4, 134.2, 132.0, 131.1, 130.6, 130.1, 129.9, 129.4, 128.9, 128.7, 128.2, 127.5, 125.2, 118.2, 22.7.

HRMS-ESI (m/z) $[M+K]^+$ calculated for $C_{19}H_{13}NOSK$ 342.0349, found 342.0337.

S-(4-chlorophenyl) 2-(cyanomethyl)-5-methylbenzothioate (**20**)



Following Procedure D, 2-(acetoxyimino)-6-methyl-2,3-dihydro-1*H*-inden-1-one (22.4 mg, 0.1 mmol) and 4-chlorobenzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.

25.1 mg, 83%. White solid.

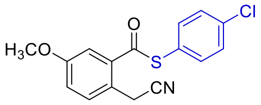
R_f = 0.33 (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.46 - 7.40 (m, 5H), 3.98 (s, 2H), 2.47 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 192.3, 139.3, 136.8, 136.7, 135.2, 134.6, 130.8, 130.7, 130.1, 126.8, 126.1, 117.9, 22.0, 20.8.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{16}H_{12}ClNOSNa$ 324.0220, found 324.0206.

S-(4-chlorophenyl) 2-(cyanomethyl)-5-methoxybenzothioate (**21**)



Following Procedure D, 2-(acetoxyimino)-6-methoxy-2,3-dihydro-1*H*-inden-1-one (24.0 mg, 0.1 mmol) and 4-chlorobenzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.

25.7 mg, 81%. White solid.

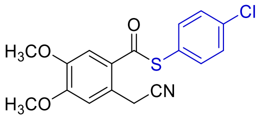
R_f = 0.40 (20% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, J = 2.5 Hz, 1H), 7.49 (d, J = 8.5 Hz, 1H), 7.45 (s, 4H), 7.11 (dd, J = 8.5, 2.5 Hz, 1H), 3.94 (s, 2H), 3.90 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 192.1, 160.0, 136.9, 136.7, 136.4, 132.1, 130.1, 126.0, 121.3, 118.6, 118.1, 115.9, 55.7, 21.5.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{16}H_{12}ClNO_2SNa$ 340.0169, found 340.0158.

S-(4-chlorophenyl) 2-(cyanomethyl)-4,5-dimethoxybenzothioate (**22**)



Following Procedure D, 2-(acetoxyimino)-5,6-dimethoxy-2,3-dihydro-1*H*-inden-1-one (27.1 mg, 0.1 mmol) and 4-chlorobenzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.

29.7 mg, 86%. Yellow solid.

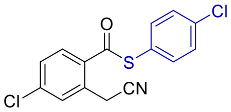
R_f = 0.29 (20% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.46 - 7.41 (m, 4H), 7.05 (s, 1H), 4.03 (s, 2H), 3.99 (d, J = 4.5 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 190.6, 153.6, 148.9, 136.9, 136.8, 130.1, 127.1, 126.2, 124.3, 118.1, 113.1, 112.9, 56.4, 22.2.

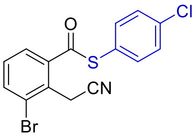
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{17}H_{14}ClNO_3SNa$ 370.0275, found 370.0264.

S-(4-chlorophenyl) 4-chloro-2-(cyanomethyl)benzothioate (**23**)



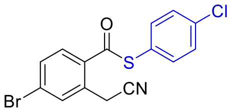
Following Procedure D, 2-(acetoxyimino)-5-chloro-2,3-dihydro-1*H*-inden-1-one (24.5 mg, 0.1 mmol) and 4-chlorobenzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.
23.5 mg, 73%. Yellow solid.
$R_f = 0.50$ (10% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 1.8 Hz, 1H), 7.49 (dd, J = 8.4, 2.0 Hz, 1H), 7.47 – 7.42 (m, 4H), 4.03 (s, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 191.4, 140.4, 137.1, 136.7, 133.6, 131.8, 131.4, 131.0, 130.2, 129.2, 125.5, 117.1, 22.2.
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{15}H_9Cl_2NOSNa$ 343.9674, found 343.9661.

S-(4-chlorophenyl) 3-bromo-2-(cyanomethyl)benzothioate (**24**)



Following Procedure D, 2-(acetoxyimino)-4-bromo-2,3-dihydro-1*H*-inden-1-one (29.1 mg, 0.1 mmol) and 4-chlorobenzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.
28.3 mg, 77%. White solid.
$R_f = 0.30$ (10% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (dd, J = 7.8, 1.1 Hz, 1H), 7.84 (dd, J = 8.1, 1.1 Hz, 1H), 7.49 - 7.44 (m, 4H), 7.38 (t, J = 7.9 Hz, 1H), 4.15 (s, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 192.3, 138.9, 137.7, 137.1, 136.6, 130.4, 130.2, 129.1, 128.8, 127.8, 125.6, 116.4, 21.6.
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{15}H_9BrClNOSNa$ 387.9169, found 387.9155.

S-(4-chlorophenyl) 4-bromo-2-(cyanomethyl)benzothioate (**25**)



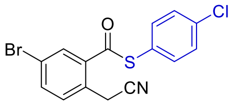
Following Procedure D, 2-(acetoxyimino)-5-bromo-2,3-dihydro-1*H*-inden-1-one (29.1 mg, 0.1 mmol) and 4-chlorobenzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.
29.7 mg, 81%. White solid.
$R_f = 0.37$ (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 1.5 Hz, 1H), 7.66 (dd, J = 8.3, 1.7 Hz, 1H), 7.48 - 7.41 (m, 4H), 4.02 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 191.6, 137.1, 136.7, 134.1, 134.0, 132.3, 131.8, 131.4, 130.2, 128.8, 125.5, 117.1, 22.1.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{15}H_9BrClNOSNa$ 387.9169, found 387.9152.

S-(4-chlorophenyl) 5-bromo-2-(cyanomethyl)benzothioate (**26**)



Following Procedure D, 2-(acetoxyimino)-6-bromo-2,3-dihydro-1*H*-inden-1-one (29.1 mg, 0.1 mmol) and 4-chlorobenzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.

23.0 mg, 77%. White solid.

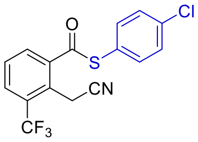
R_f = 0.27 (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, J = 2.0 Hz, 1H), 7.74 (dd, J = 8.2, 2.0 Hz, 1H), 7.49 (d, J = 8.3 Hz, 1H), 7.47 - 7.42 (m, 4H), 3.97 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 191.2, 137.2, 137.1, 136.7, 136.6, 132.8, 132.4, 130.3, 128.6, 125.4, 122.8, 117.2, 21.9.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{15}H_9BrClNOSNa$ 387.9169, found 387.9154.

S-(4-chlorophenyl) 2-(cyanomethyl)-3-(trifluoromethyl)benzothioate (**27**)



Following Procedure D, 2-(acetoxyimino)-4-(trifluoromethyl)-2,3-dihydro-1*H*-inden-1-one (22.9 mg, 0.1 mmol) and 4-chlorobenzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.

20.5 mg, 58%. White solid.

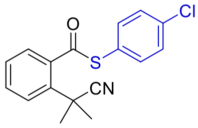
R_f = 0.26 (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, J = 7.7 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.66 (t, J = 7.9 Hz, 1H), 7.52 – 7.45 (m, 4H), 4.10 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 192.6, 139.4, 137.3, 136.7, 132.9, 131.4 (q, J = 30.8 Hz), 130.5 (q, J = 5.6 Hz), 130.3, 129.6, 128.1, 125.3, 123.8 (q, J = 274.7 Hz), 116.4, 17.6, 17.6.

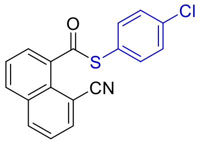
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{16}H_9ClF_3NOSNa$ 377.9938, found 377.9924.

S-(4-chlorophenyl) 2-(2-cyanopropan-2-yl)benzothioate (**28**)



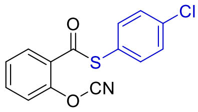
Following Procedure E, 2-(acetoxyimino)-3,3-dimethyl-2,3-dihydro-1*H*-inden-1-one (24.4 mg, 0.1 mmol) and 4-chlorobenzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.
10.9 mg, 35%. White solid.
R_f = 0.62 (20% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, J = 7.6 Hz, 1H), 7.58 – 7.53 (m, 4H), 7.47 – 7.42 (m, 3H), 1.87 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 195.1, 139.2, 138.0, 136.8, 136.7, 132.6, 130.1, 129.8, 128.3, 126.9, 126.5, 124.4, 36.6, 29.5.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{17}H_{15}ClNOS$ 316.0557, found 316.0559

S-(4-chlorophenyl) 8-cyanonaphthalene-1-carbothioate (**29**)



Following Procedure D, (*E*)-2-(acetoxyimino)acenaphthylen-1(2*H*)-one (24.7 mg, 0.1 mmol) and 4-chlorobenzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.
20.5 mg, 63%. Yellow solid.
R_f = 0.41 (20% EA in PE)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.3 Hz, 1H), 8.06 - 8.00 (m, 2H), 7.94 (d, J = 7.1 Hz, 1H), 7.70 (d, J = 7.8 Hz, 2H), 7.61 (dt, J = 15.5, 7.7 Hz, 2H), 7.47 (d, J = 7.9 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 137.5, 137.2, 137.2, 136.9, 134.9, 134.7, 133.4, 130.5, 129.7, 128.1, 127.0, 126.7, 126.6, 118.9, 109.2.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{18}H_{11}ClNOS$ 324.0244, found 324,0246.

S-(4-chlorophenyl) 2-cyanatobenzothioate (**30**)

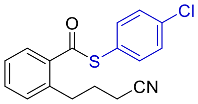


Following Procedure D, *S*-(4-chlorophenyl) 2-cyanatobenzothioate (21.6 mg, 0.1 mmol) and 4-chlorobenzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.
2.9 mg, 14%. Yhite solid.
R_f = 0.50 (10% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.8 Hz, 1H), 7.73 - 7.69 (m, 1H), 7.56 (d, J = 8.5 Hz, 2H), 7.40 - 7.36 (m, 2H), 7.30 - 7.26 (m, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 176.8, 163.9, 146.7, 139.0, 135.6, 134.0, 129.7, 127.5,

125.7, 125.2, 121.6, 113.4.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{14}H_9ClNO_2S$ 290.0037, found 290.0036.

S-(4-chlorophenyl) 2-(3-cyanopropyl)benzothioate (**31**)



Following Procedure E, (*E*)-6-(acetoxyimino)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (24.4 mg, 0.1 mmol) and 4-chlorobenzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.

20.9 mg, 66%. Yellow solid.

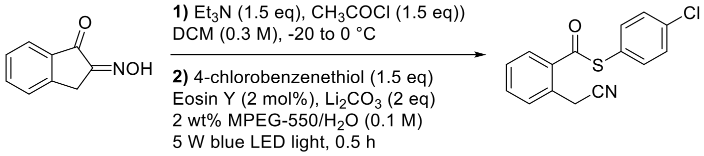
R_f = 0.58 (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (dd, J = 7.8, 1.1 Hz, 1H), 7.51 (td, J = 7.6, 1.3 Hz, 1H), 7.47 – 7.42 (m, 4H), 7.38 (td, J = 7.7, 1.1 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 2.93 (t, 2H), 2.33 (t, J = 7.2 Hz, 2H), 2.00 - 1.94 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 192.7, 139.8, 136.9, 136.6, 136.6, 133.1, 131.7, 130.1, 129.6, 127.3, 126.8, 119.9, 32.5, 27.0, 16.5.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{17}H_{15}ClNOS$ 316.0557, found 316.0558.

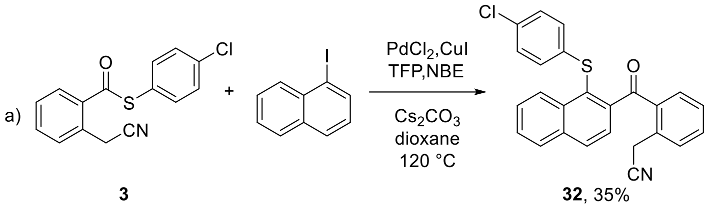
IV . One-pot Protocol



To a mixture of 2-(hydroxyimino)-2,3-dihydro-1*H*-inden-1-one (0.2 mmol, 33.2 mg), DCM (0.6 mL), Et_3N (42.2 µL, 0.3 mmol) in a 5 mL tube was added acetyl chloride (21.8 µL, 0.3mmol) dropwise at -20 °C and the mixture was stirred at 0 °C for 2 h. The solvent was then removed in vacuo to give the crude oxime, which was directly used in the next step without further purification.

A mixture of the crude oxime acetate 1 (0.2 mmol), 4-chlorobenzenethiol (0.3 mmol, 44.2 mg), Eosin Y (2.6 mg, 2 mol%) and Li_2CO_3 (0.3 mmol, 29.9 mg,) in a 5 mL tube was added 2 wt% MPEG-550/H_2O (2 mL). The reaction mixture was stirred under the irradiation of 2×5 W Blue LEDs (λ = 440 - 480nm) at room temperature for 0.5 h. The reaction mixture was quenched by EtOAc and concentrated in vacuo. The crude was purified by flash chromatography (petroleumether/ethyl acetate = 100/1 - 10/1) on silica gel to provide the corresponding products (48.0 mg, 84%).

V . Derivatization of compound 3

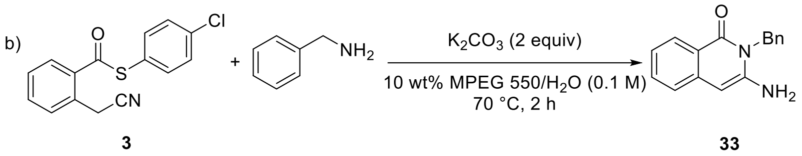


According to literature 6, to a 10 mL Schlenk tube was sequentially added 1-iodonaphthalene (30 μL, 0.20 mmol), thioester **3** (87.2 mg, 0.30 mmol), $PdCl_2$ (3.6 mg, 0.02 mmol), TFP (11.9 mg, 0.05 mmol), CuI (7.8 mg, 0.04 mmol), norbornene (57.1 mg, 0.60 mmol), Cs_2CO_3 (197.5 mg, 0.60 mmol) and 1,4-dioxane (3.0 mL). The mixture was stirred at 120 °C for 12 h afforded **32** (29.3 mg, 35%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 7.9 Hz, 1H), 8.10 (d, J = 8.3 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.68 - 7.55 (m, 4H), 7.46 (t, J = 7.5 Hz, 1H), 7.22 (d, J = 7.7 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 6.76 (d, J = 8.0 Hz, 2H), 4.27 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 146.0, 136.9, 136.4, 135.6, 135.4, 133.8, 133.3, 132.5, 132.3, 131.9, 130.9, 129.9, 129.8, 129.5, 128.80, 128.75, 128.6, 127.0, 126.7, 125.4, 118.8, 23.0.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{25}H_{16}ClNOSNa$ 436.0533, found 436.0516.



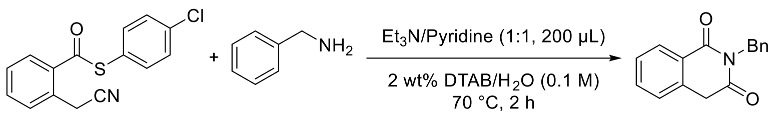
To a 4 mL vial, thioester **3** (29.1 mg, 0.1 mmol), benzylamine (22.3 μL, 0.2 mmol), K_2CO_3 (27.9 mg, 0.2 mmol) and 10 wt%MPEG-550/H_2O (1 mL) were added with a stir bar. The resulting mixture was allowed to stir at 70 ℃ for 2 h. Then, the reaction was cooled to rt, the reaction mixture was extracted with EtOAc. The organic phase was dried over Na_2SO_4, evaporated in vacuo and subjected to flash column chromatography on silica gel to obtain compound **33** (23.5 mg, 94%).

^{1}H NMR (600 MHz, DMSO-d6) δ 7.97 (d, J = 7.8 Hz, 1H), 7.45 - 7.41 (m, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.25 - 7.22 (m, 2H), 7.19 (d, J = 7.4 Hz, 2H), 7.02 (t, J = 7.5 Hz, 1H), 5.98 (s, 2H), 5.69 (s, 1H), 5.34 (s, 2H).

^{13}C NMR (150 MHz, DMSO-d6) δ 162.7, 147.8, 140.2, 137.8, 132.8, 128.9, 128.0, 127.4, 127.2, 123.7, 121.4, 118.5, 82.8, 43.8.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{15}N_2O$ 251.1179, found 251.1178.
Spectroscopic data matches that reported in the literature.[7]

c)



3

34, 69%

To a 4 mL vial, thioester **3** (29.1 mg, 0.1 mmol), benzylamine (22.3 μL, 0.2 mmol) , Et_3N/pyridine (1:1, 200 μL) and 2 wt% DTAB/H_2O (1 mL) (DTAB = dodecyltrimethylammonium bromide) were added with a stir bar. The resulting mixture was allowed to stir at 70 °C for 2 h. Then, the reaction was cooled to rt, 1 M HCl was added to the reaction mixture and extracted with EtOAc. The organic phase was dried over Na_2SO_4, evaporated in vacuo and subjected to flash column chromatography on silica gel to obtain compound **34** (17.3 mg, 69%).

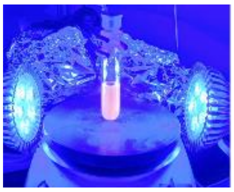
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, J = 7.9 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.46 (d, J = 7.5 Hz, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.29 (t, J = 7.5 Hz, 2H), 7.24 (dd, J = 12.8, 7.1 Hz, 2H), 5.19 (s, 2H), 4.06 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 165.5, 137.5, 134.5, 134.2, 129.7, 129.4, 128.9, 128.2, 128.0, 127.5, 125.8, 43.2, 36.4.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{14}NO_2$ 252.1019, found 252.1017.

Spectroscopic data matches that reported in the literature.[8]

VI． Recycle Study and E Factor Calculation



A mixture of 1-indanone oxime acetate **1a** (0.5 mmol, 104.8 mg), 4-chlorobenzenethiol **2a** (0.75 mmol, 110.8 mg), Eosin Y (6.6 mg, 2 mol%) and Li_2CO_3 (0.2 mmol, 74.6 mg) in a 10 mL tube was added 2 wt% MPEG-550/H_2O (5 mL). The reaction mixture was stirred under the irradiation of 2×5 W Blue LEDs (λ = 440 - 480nm) at room temperature for 0.5 h. Then the reaction mixture was extracted by EtOAc (1 mL) for two times. The combined organic layer was concentrated under reduced pressure and purified by flash chromatography on silica gel to provide the corresponding products **3**. Reuse of the solvent: 1-indanone oxime acetate **1a** (0.5 mmol, 104.8 mg), 4-chlorobenzenethiol **2a** (0.5 mmol, 1.0 equiv) and Li_2CO_3 (0.5 mmol, 37.4 mg,) were added to the solvent, while no additional Eosin Y was required.

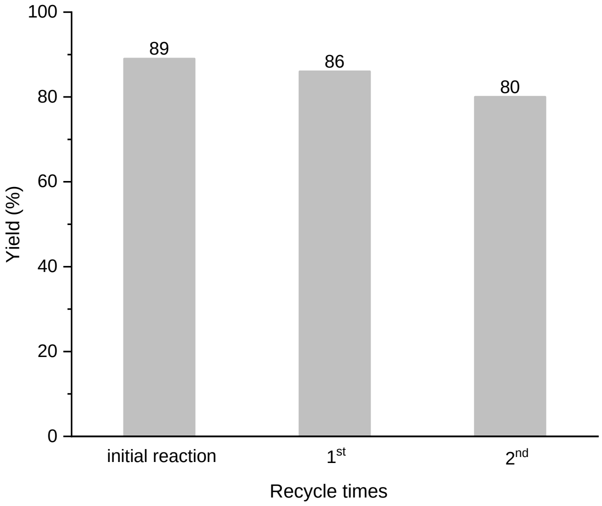


Figure S2 The yield of each run for recycle experiment

Note: Density of each liquid at 25 °C; ethyl acetate = 0.897 g/mL;
Mol. Wt.; 4-chlorobenzenethiol **2a** = 144.62 mg/mmol; *S*-(4-chlorophenyl) 2-(cyanomethyl)benzothioate (**3**) = 287.76 mg/mmol

Total organic wastes:
4 mL EtOAc (3588.0 mg)
0.54 mmol 4-chlorobenzenethiol **2a** (78.1 mg)

Product (**3**): 128.3 + 123.4 + 115.7 = 367.4 mg

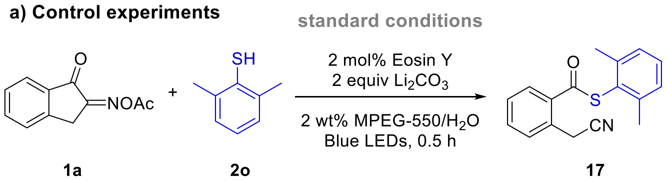
$$\textbf{E Factor} = \frac{\text{total organic wastes (Kg)}}{\text{Product (Kg)}}$$

$$= \frac{3588 + 78.1 \text{ (mg)}}{367.4 \text{ (mg)}}$$

$$= 10.0$$

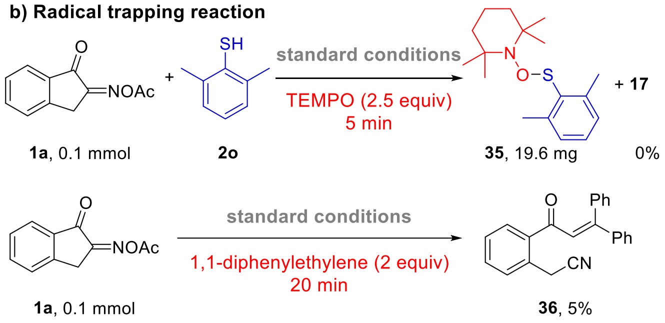
VII． Mechanistic Studies

a) Control experiments

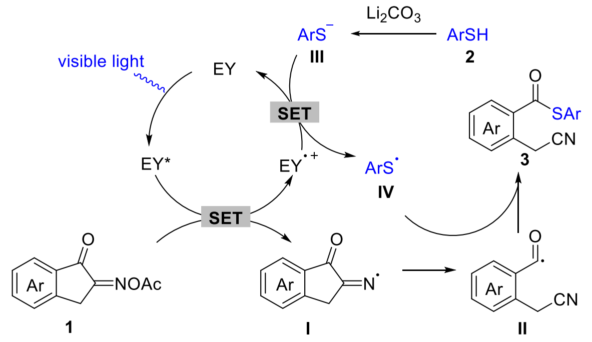


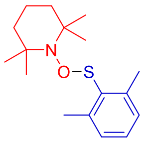
Entry	Variation from the above	Yield
1	none	87%
2	no light	0%
3	no Eosin Y	0%
4	no Li_2CO_3	0%

b) Radical trapping reaction



c) Proposed reaction mechanism.



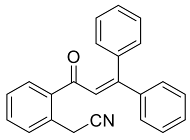


35

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (t, J = 7.5 Hz, 1H), 6.94 (d, J = 7.5 Hz, 2H), 2.62 (s, 6H), 1.70 (s, 6H), 1.13 (s, 6H), 1.05 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 142.6, 138.5, 131.4, 130.0, 62.4, 42.7, 38.8, 31.8, 31.3, 30.3, 21.9, 20.2, 16.8, 16.7.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{17}H_{28}NOS$ 316.0557, found 316.0558.



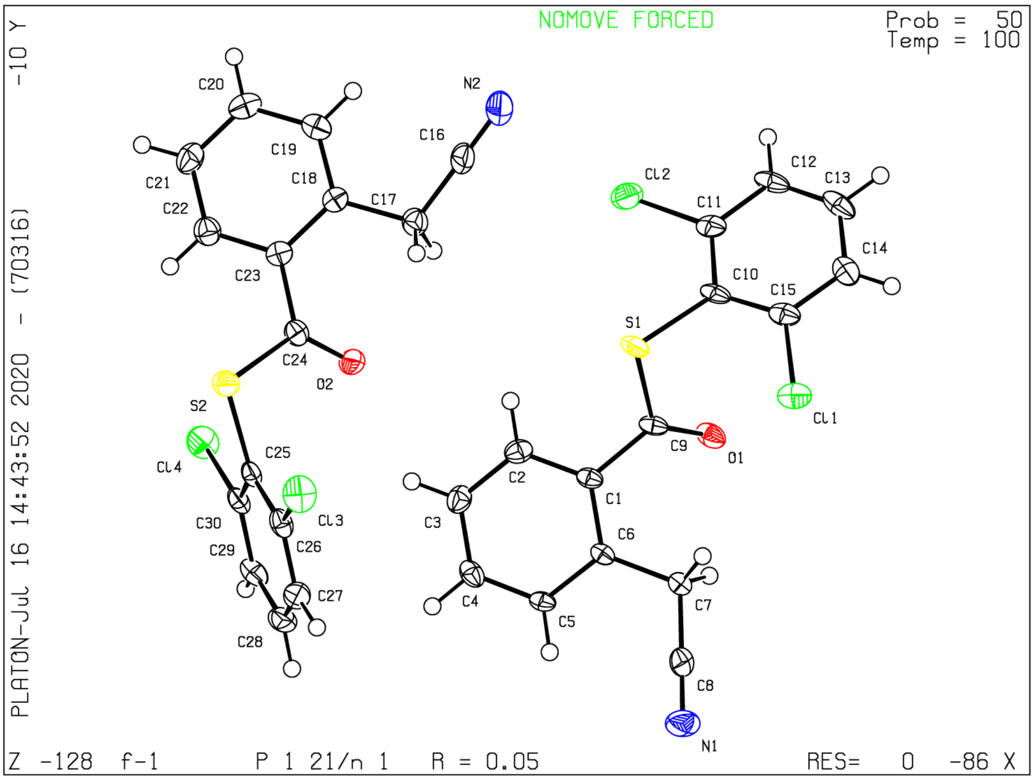
36

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.7, 0.7 Hz, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.42 - 7.36 (m, 6H), 7.28 - 7.22 (m, 4H), 7.14 - 7.10 (m, 2H), 6.95 (s, 1H), 4.05 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 196.3, 156.4, 141.1, 139.2, 137.5, 132.5, 131.0, 130.6, 130.2, 130.2, 130.1, 129.2, 129.04, 128.97, 128.6, 128.1, 126.2, 118.4, 21.9. Spectroscopic data matches that reported in the literature.[9]

VIII． Crystal Data for 18 and 33

Crystal Data for 18

A suitable crystal was selected and then tested on a SuperNova, Dual, Mo at zero, AtlasS2 diffractometer. The crystal was kept at 100.0(2) K during data collection.



CCDC 2175261

X-ray structure and CCDC number of **18**

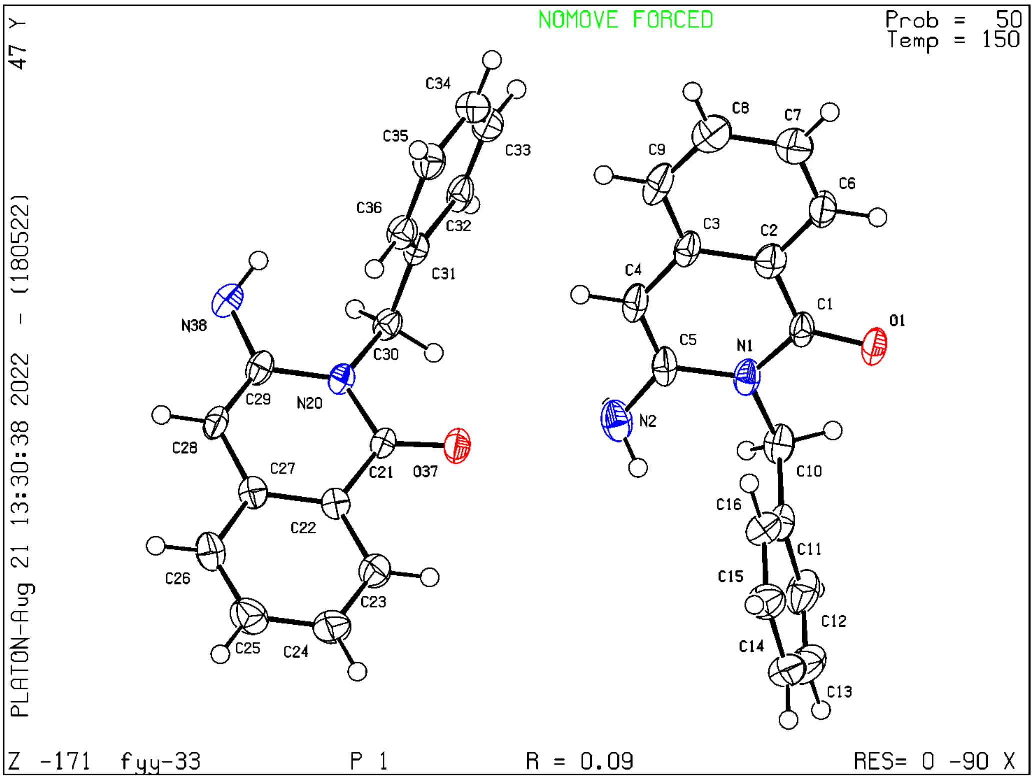
Crystal data and structure refinement for **18**

Identification code	F-1
Empirical formula	$C_{15}H_9Cl_2NOS$
Formula weight	322.19
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	16.3755(11)
b/Å	7.2951(4)
c/Å	23.9248(14)
α/°	90
β/°	103.152(7)
γ/°	90

Volume/Å^3	2783.1(3)
Z	8
ρ_{calc}g/cm^3	1.538
μ/mm^{-1}	0.609
F(000)	1312.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.11 to 50
Index ranges	$-17 \leq h \leq 19$, $-8 \leq k \leq 8$, $-23 \leq l \leq 28$
Reflections collected	11896
Independent reflections	4906 [R_{int} = 0.0597, R_{sigma} = 0.0718]
Data/restraints/parameters	4906/0/361
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0470, wR_2 = 0.1070
Final R indexes [all data]	R_1 = 0.0609, wR_2 = 0.1170
Largest diff. peak/hole / e Å^{-3}	0.34/-0.35

Crystal Data for 33

A suitable crystal was selected and then tested on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 150.01(10) K during data collection.



CCDC 2202642

X-ray structure and CCDC number of **33**

Crystal data and structure refinement for **33**.

Identification code	fyy-33
Empirical formula	$C_{16}H_{14}N_2O$
Formula weight	250.29
Temperature/K	150.01(10)
Crystal system	triclinic
Space group	P1
a/Å	5.7192(2)
b/Å	10.2210(7)
c/Å	11.4399(8)
α/°	79.456(6)
β/°	89.714(5)
γ/°	76.365(5)
Volume/Å^3	638.40(7)
Z	2

ρ_{calc}g/cm^3	1.302
μ/mm^{-1}	0.657
F(000)	264.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.868 to 143.1
Index ranges	$-6 \leqslant h \leqslant 6, -8 \leqslant k \leqslant 12, -13 \leqslant l \leqslant 14$
Reflections collected	5417
Independent reflections	3054 [Rint = 0.0367, Rsigma = 0.0538]
Data/restraints/parameters	3054/3/345
Goodness-of-fit on F^2	1.308
Final R indexes [I>=2σ (I)]	R_1 = 0.0868, wR_2 = 0.2769
Final R indexes [all data]	R_1 = 0.0883, wR_2 = 0.2790
Largest diff. peak/hole / e Å^{-3}	0.73/-0.39
Flack parameter	-0.2(4)

IX． References

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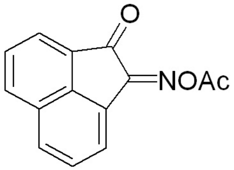
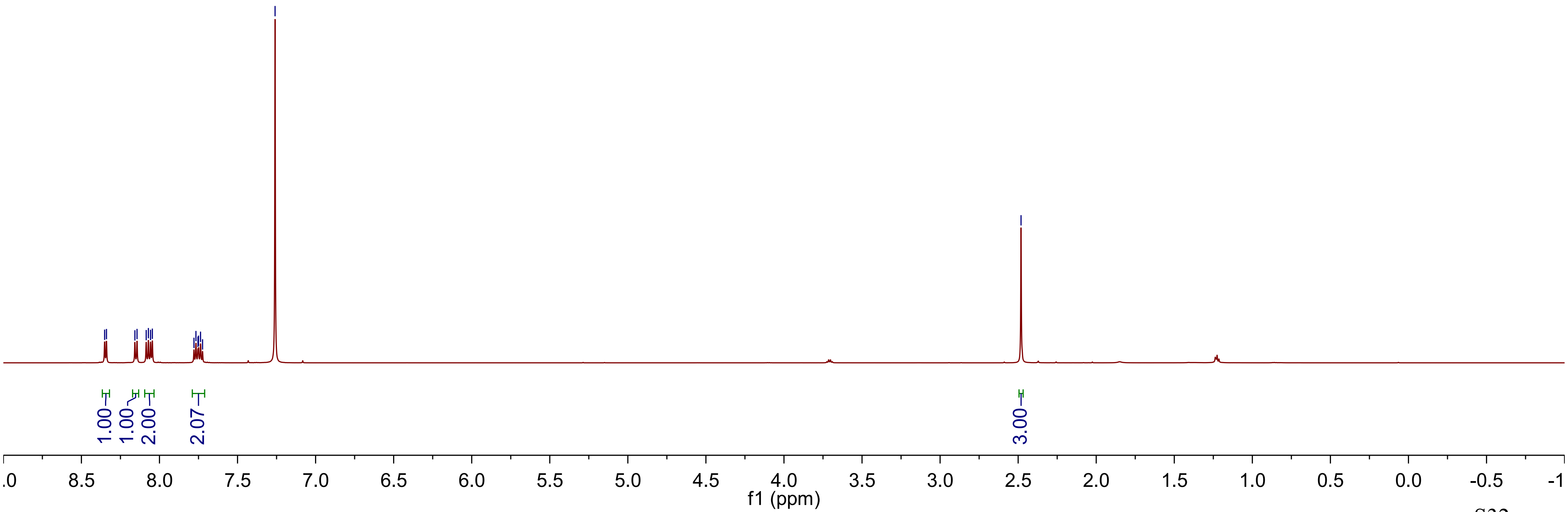
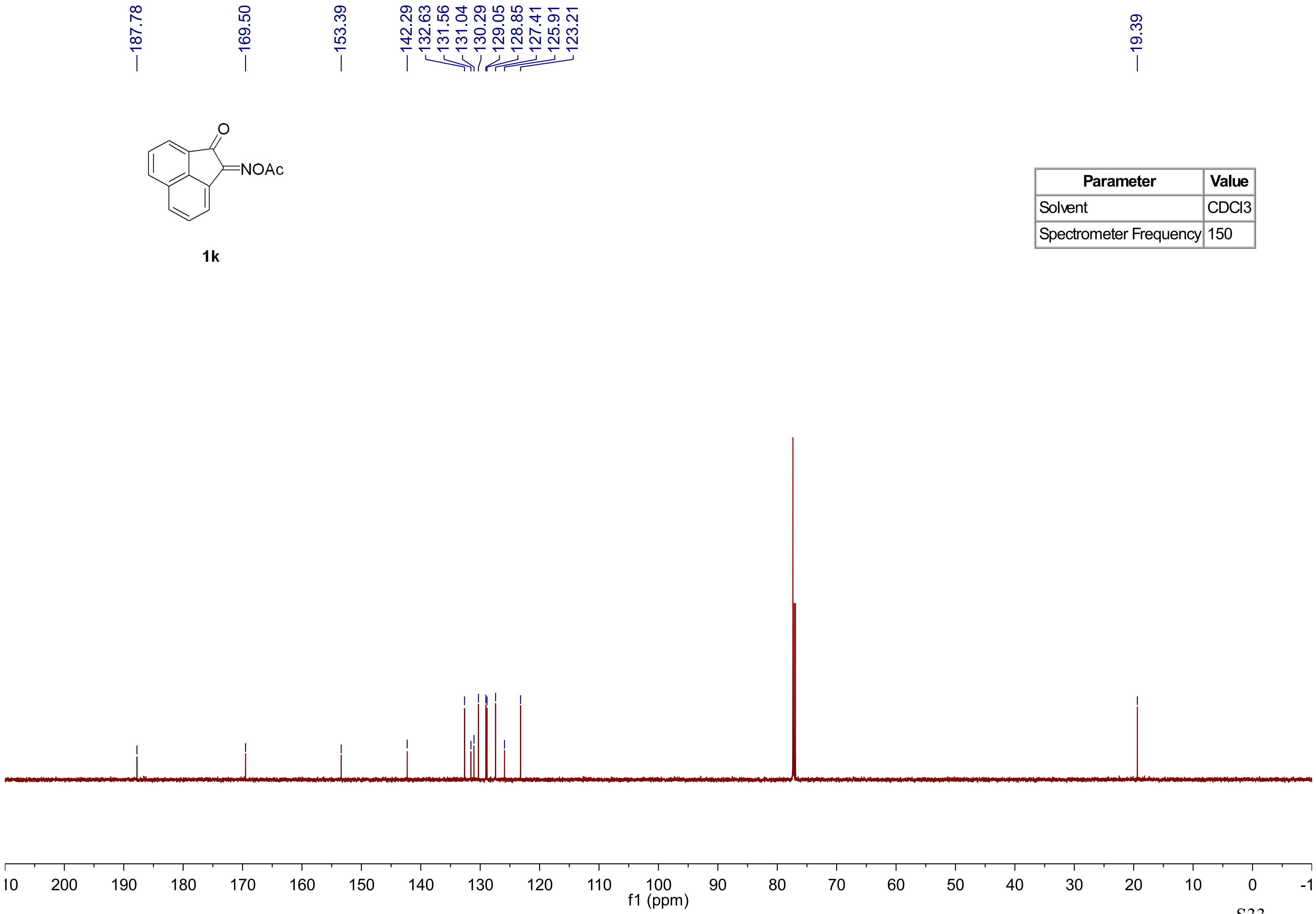
X . NMR Spectra



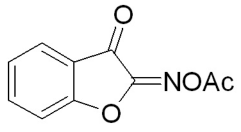
1k

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



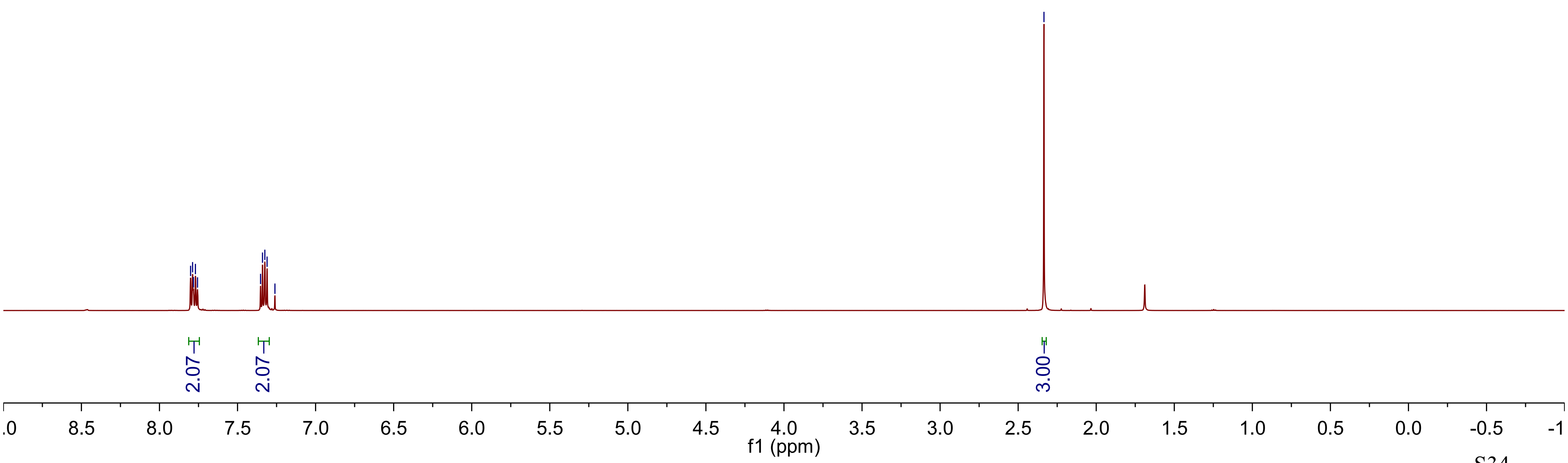


Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150



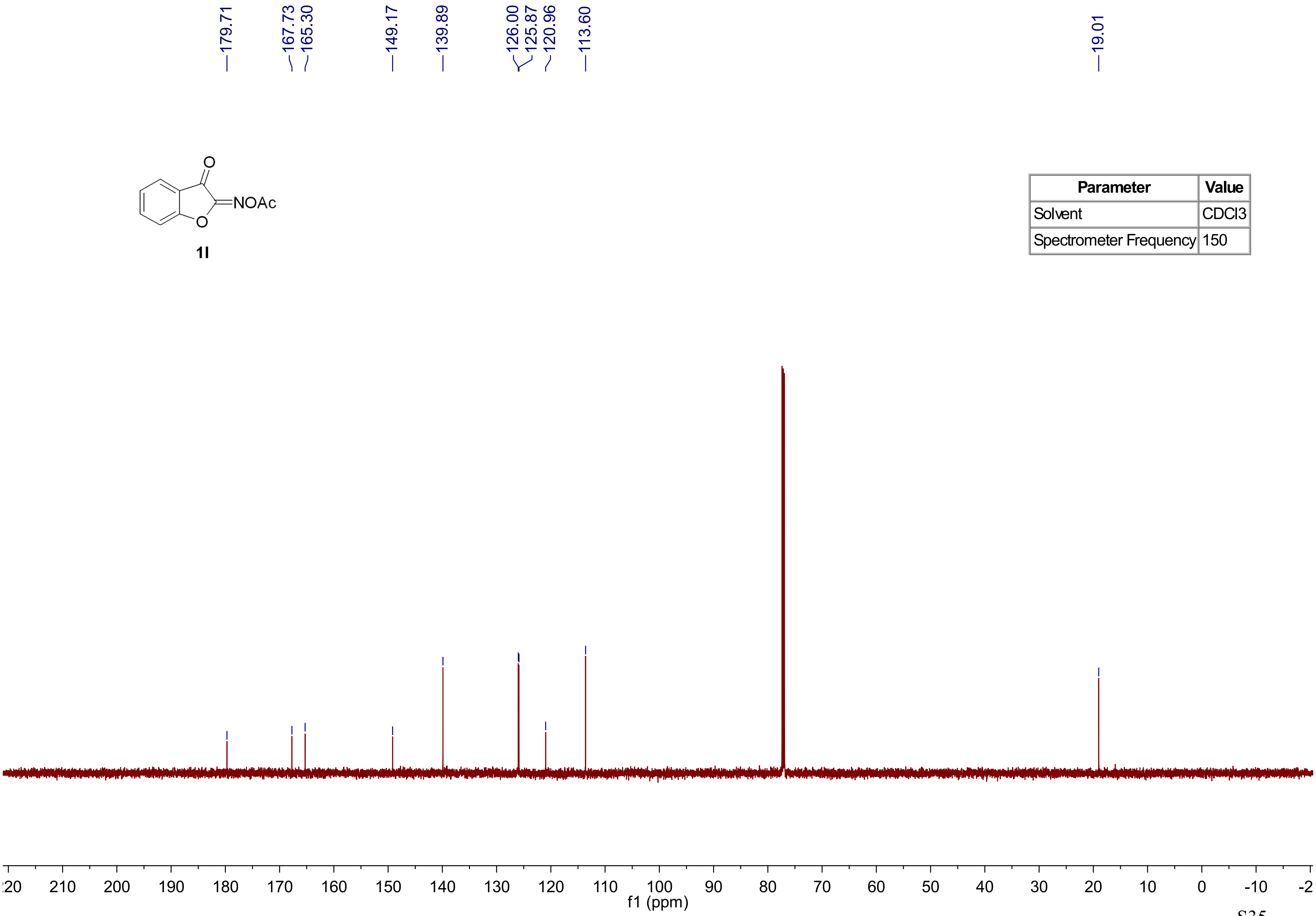
1l

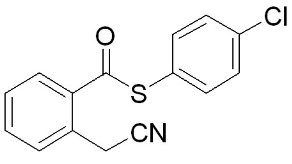
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



1l

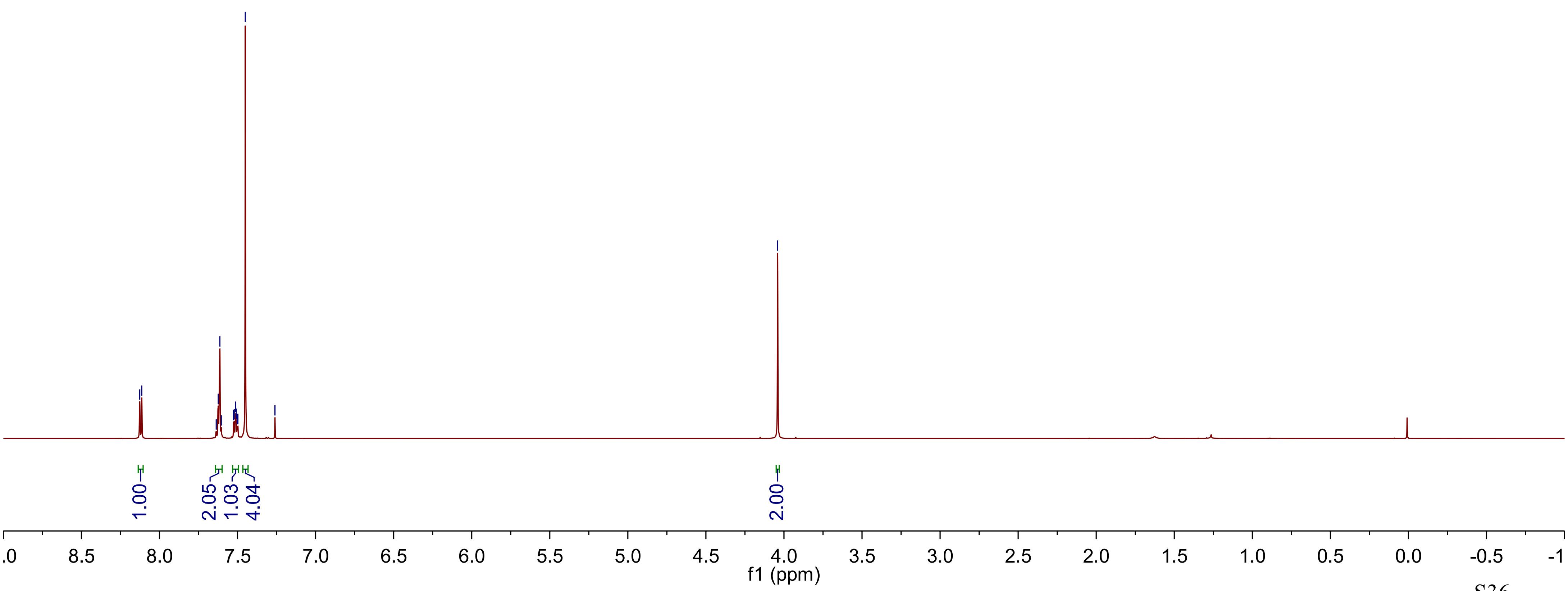
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

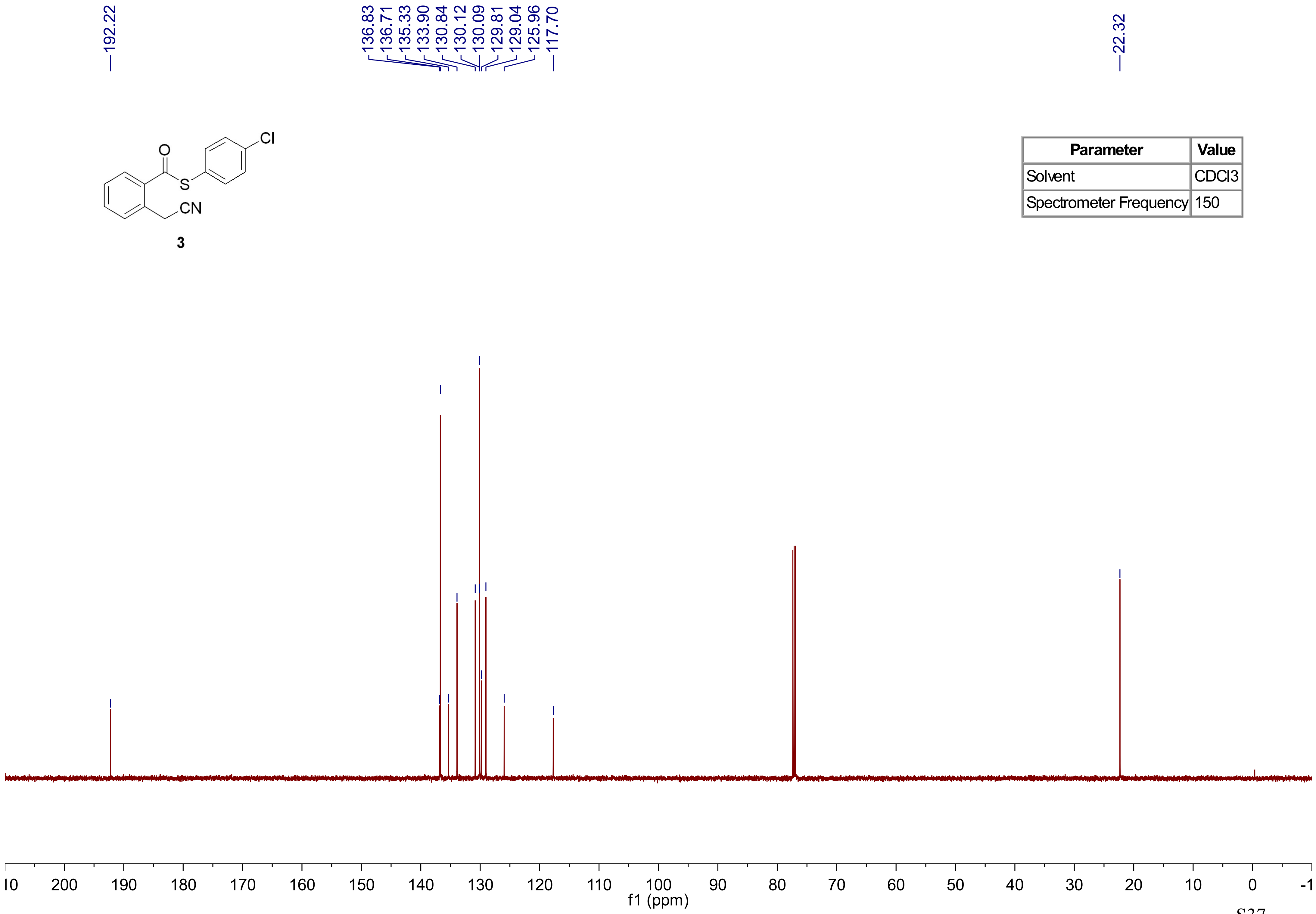




3

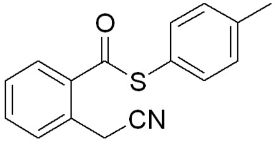
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600





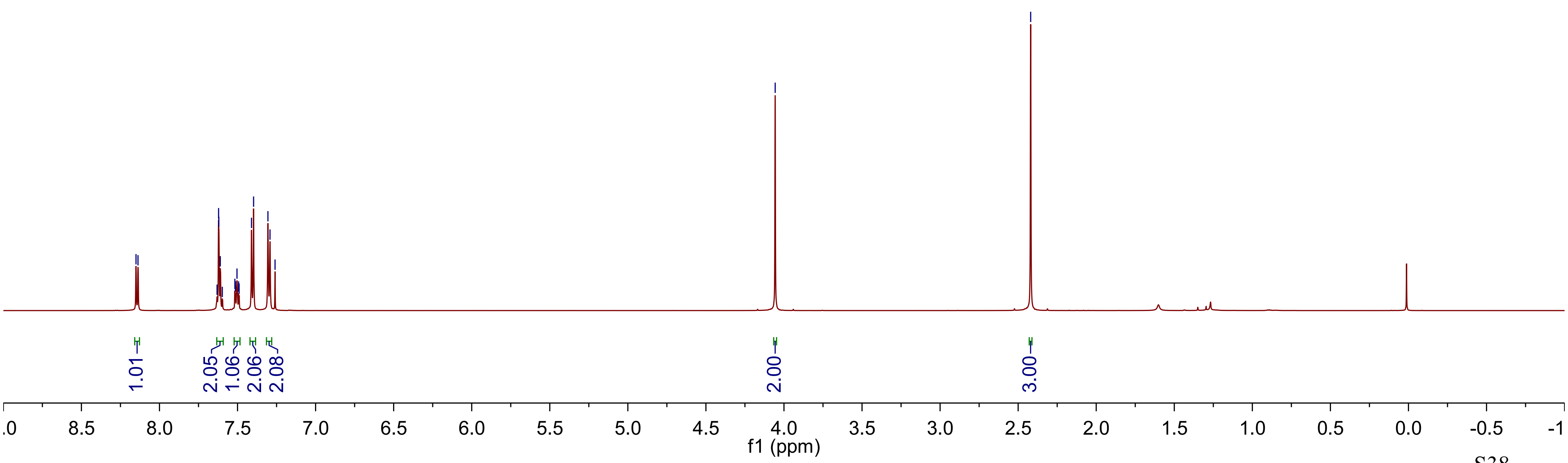
3

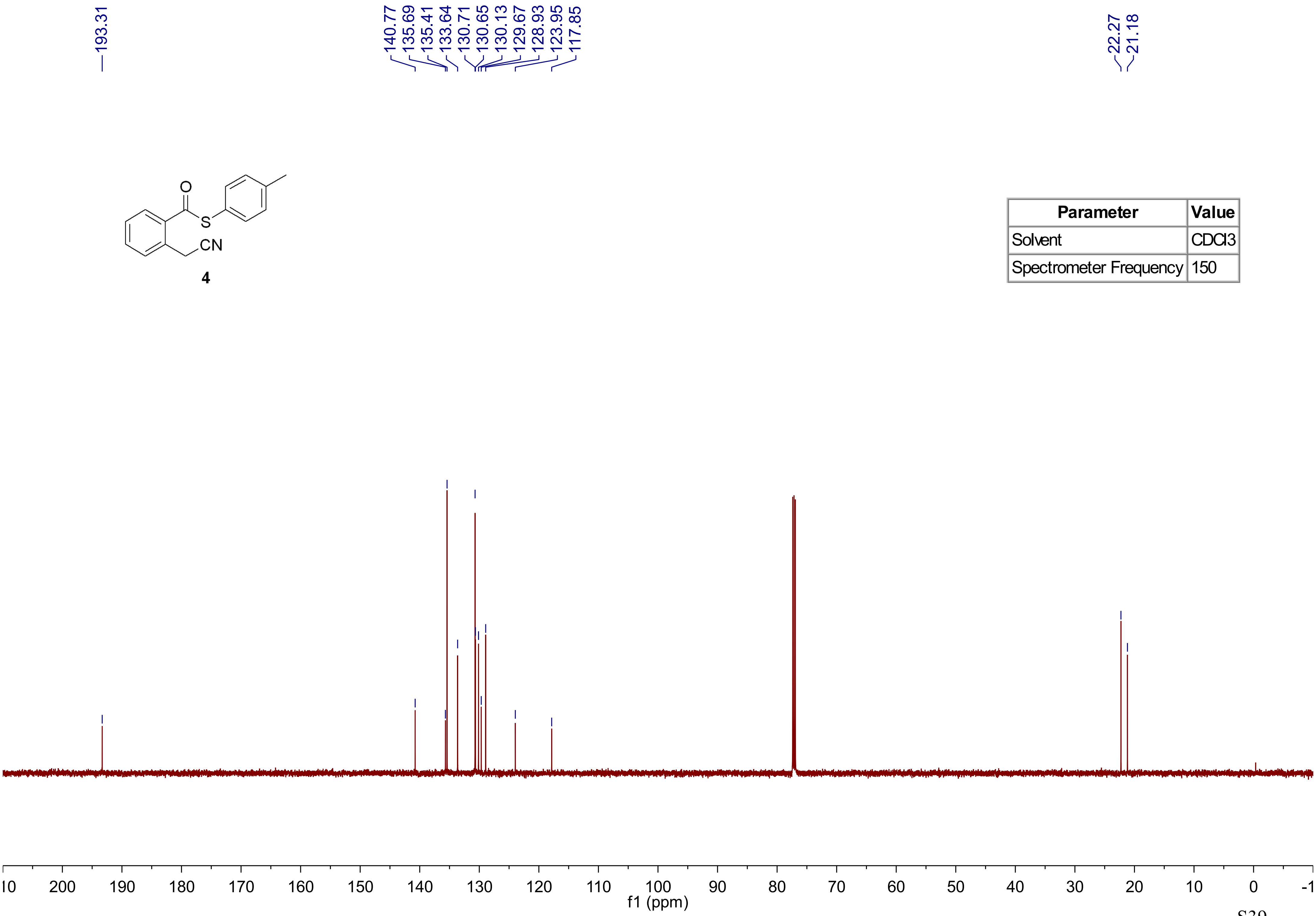
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150



4

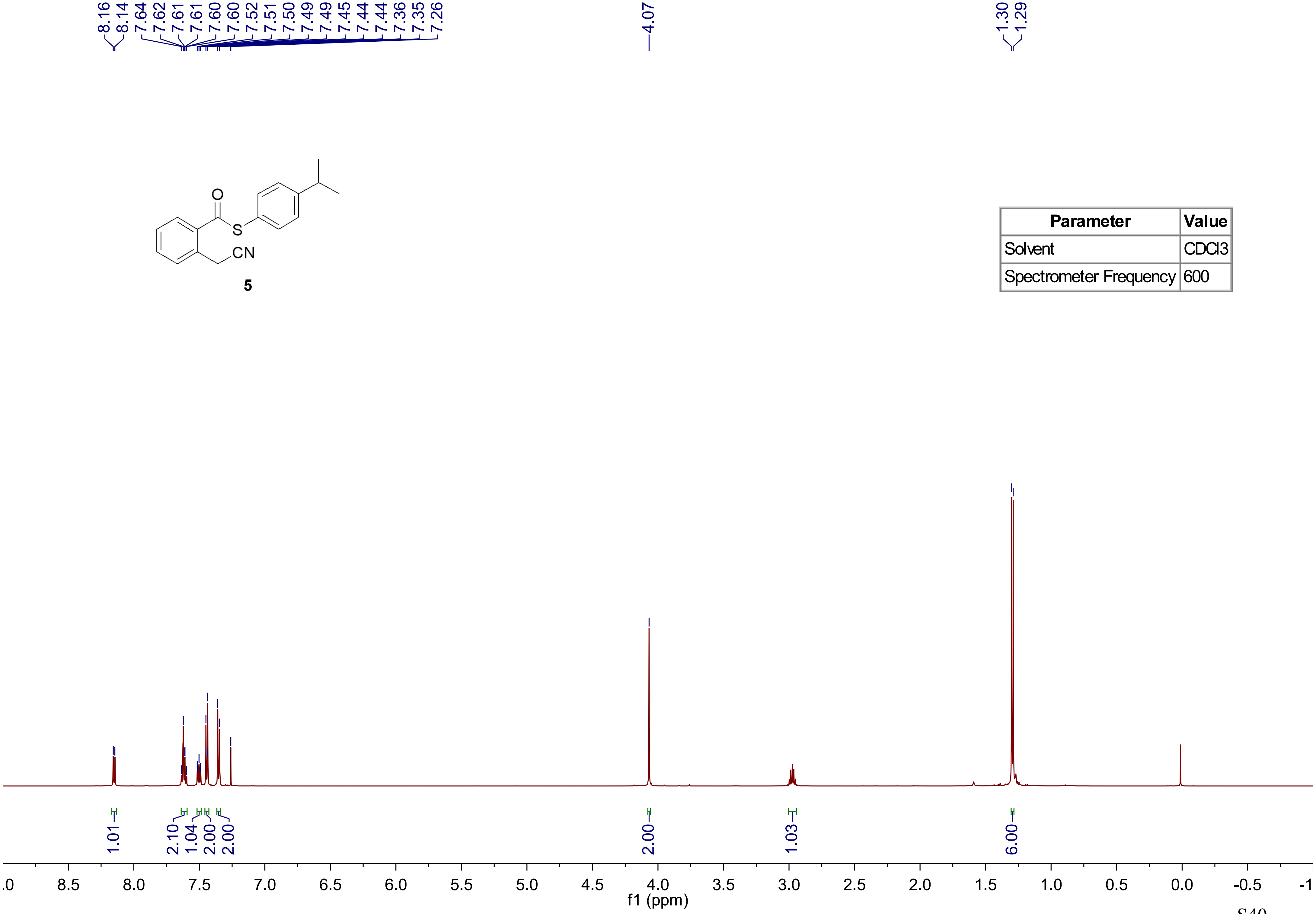
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600





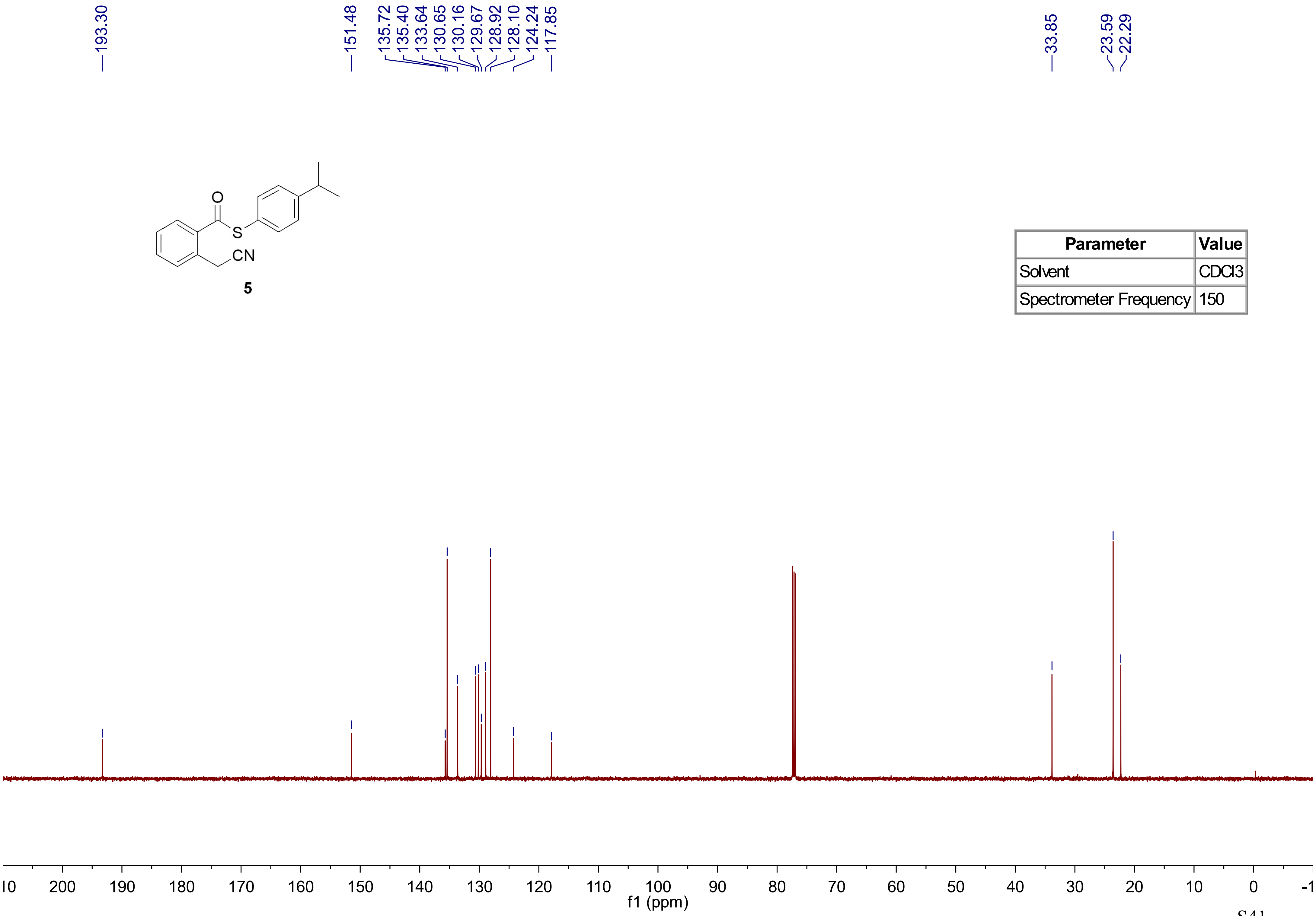
4

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150



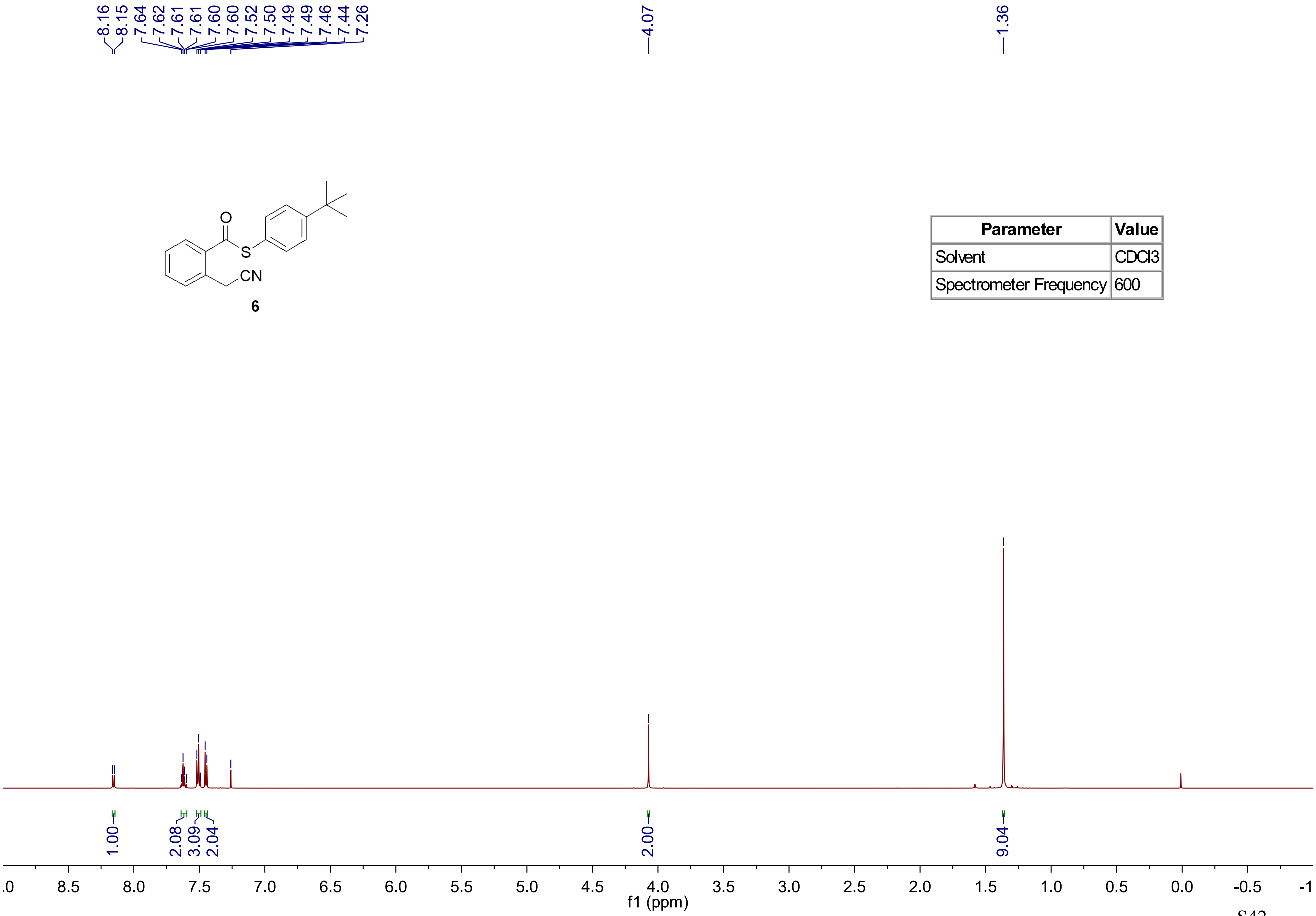
5

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



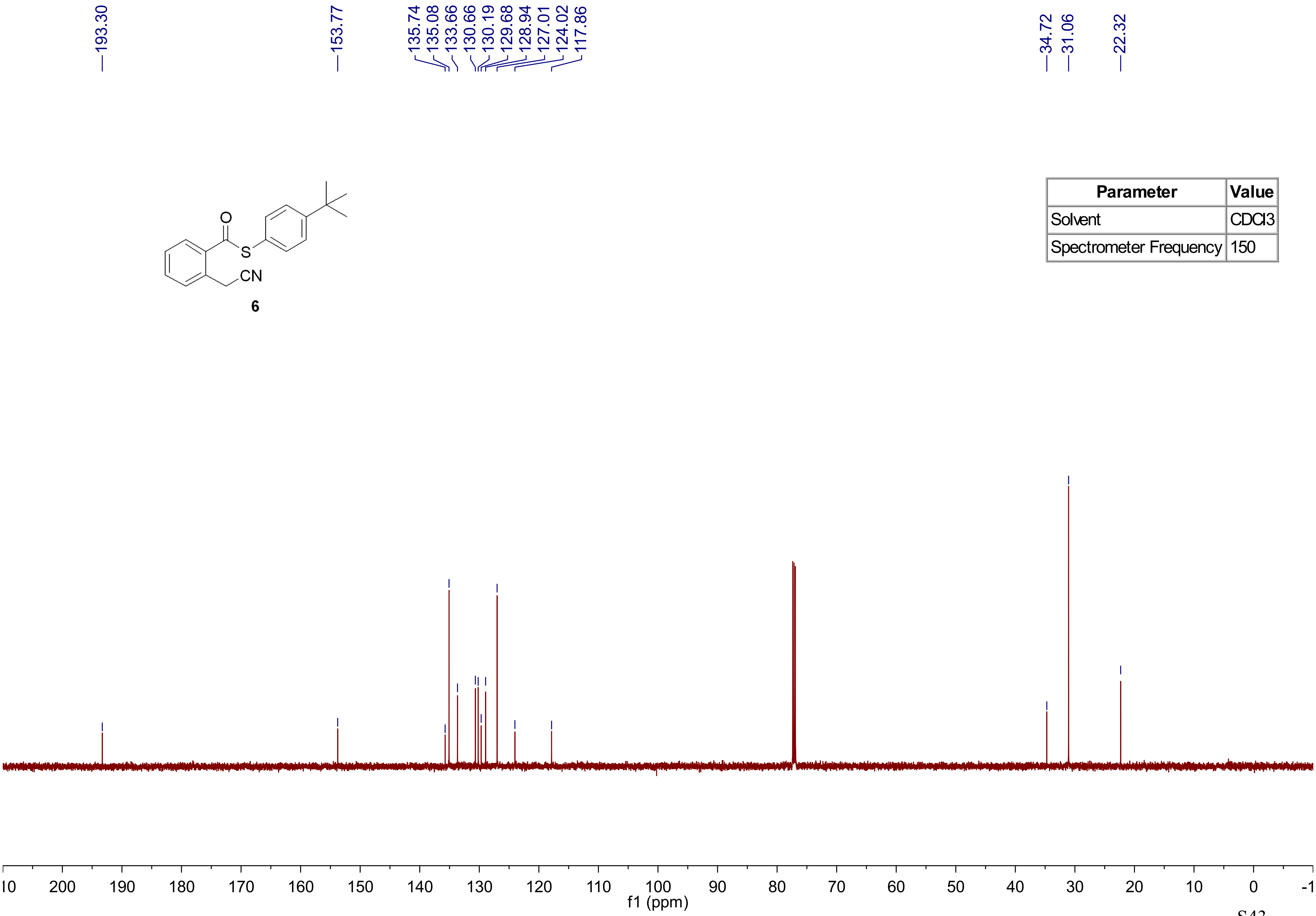
5

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150



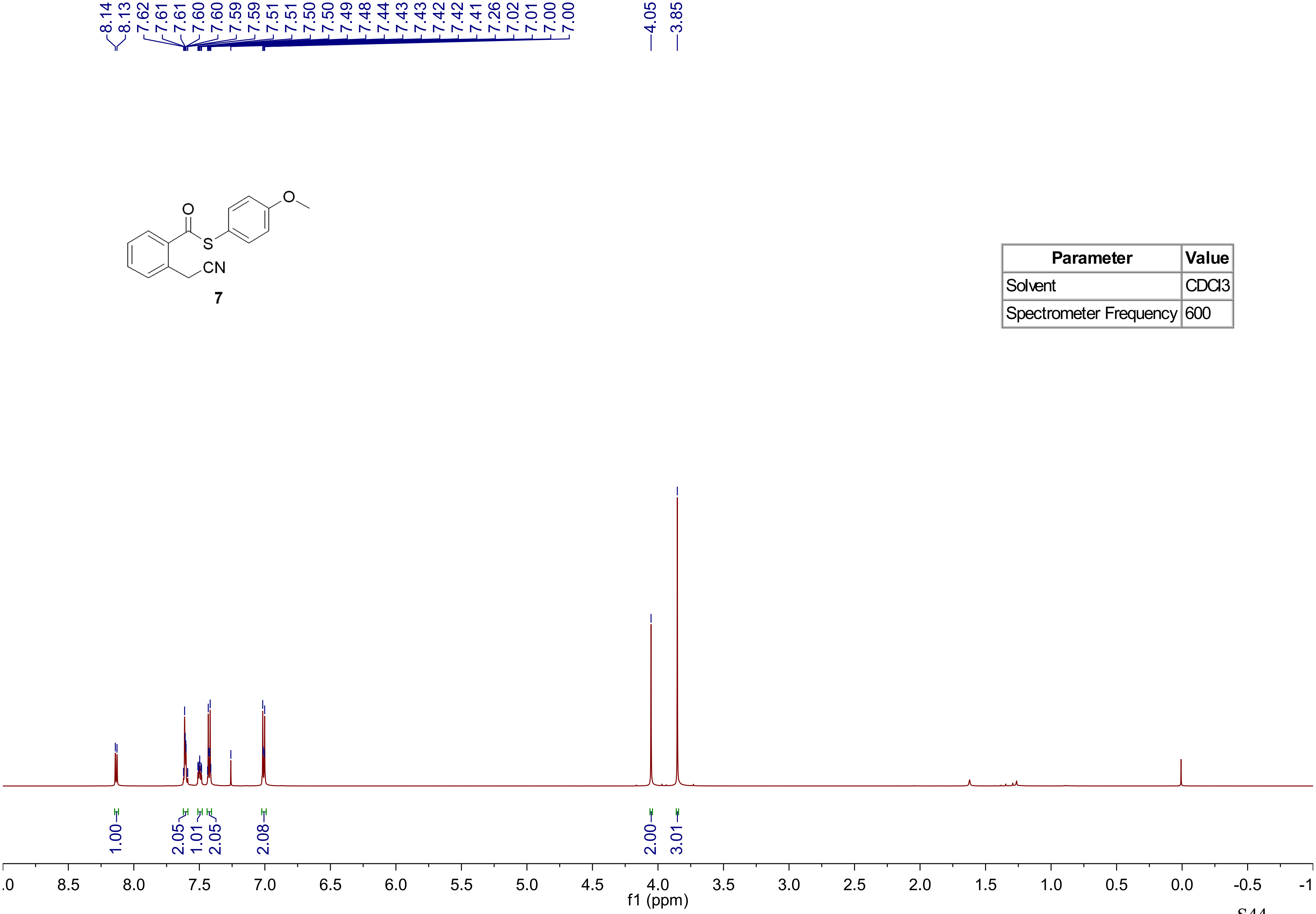
6

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

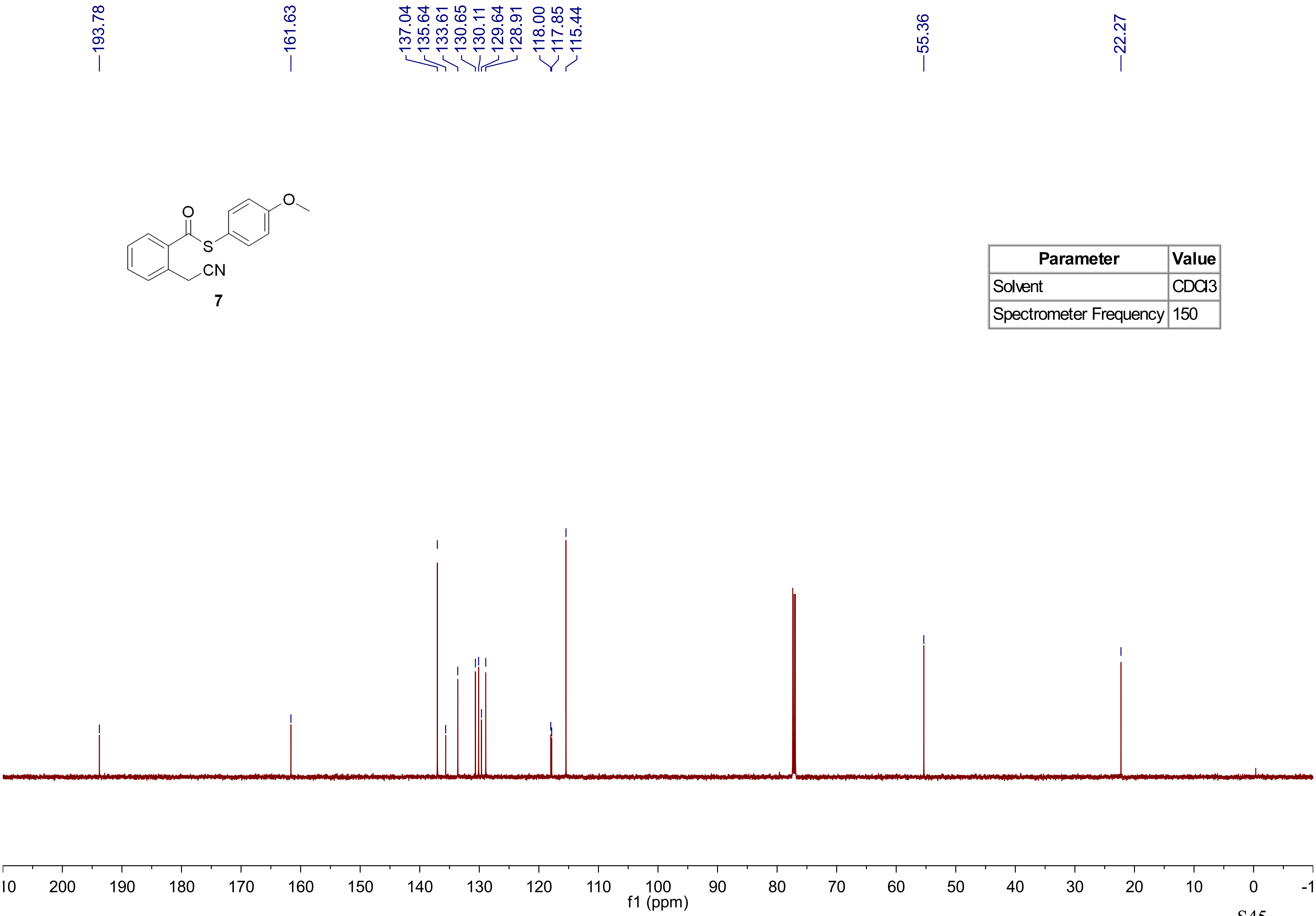


6

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

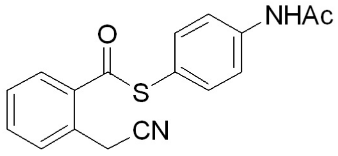


Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



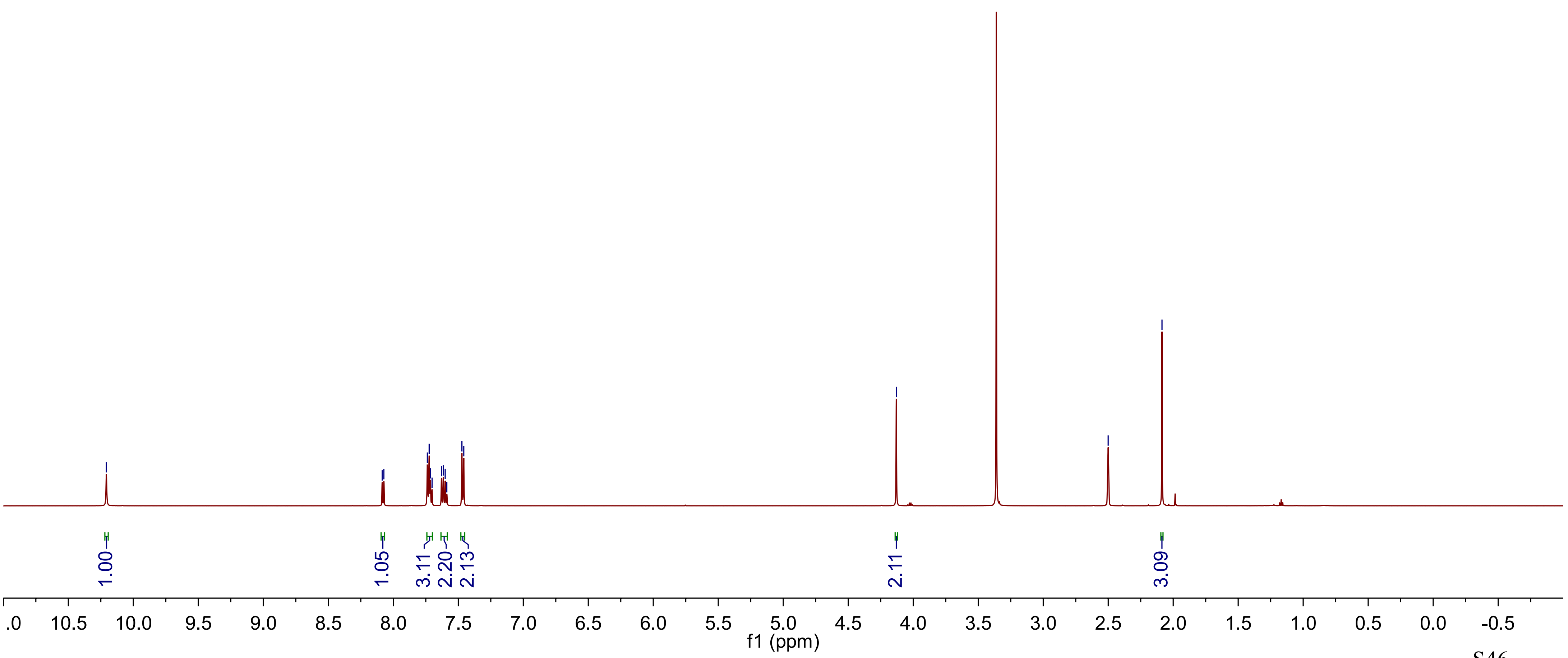
7

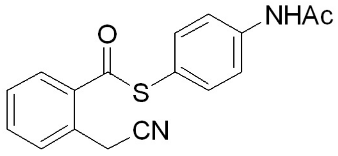
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150



8

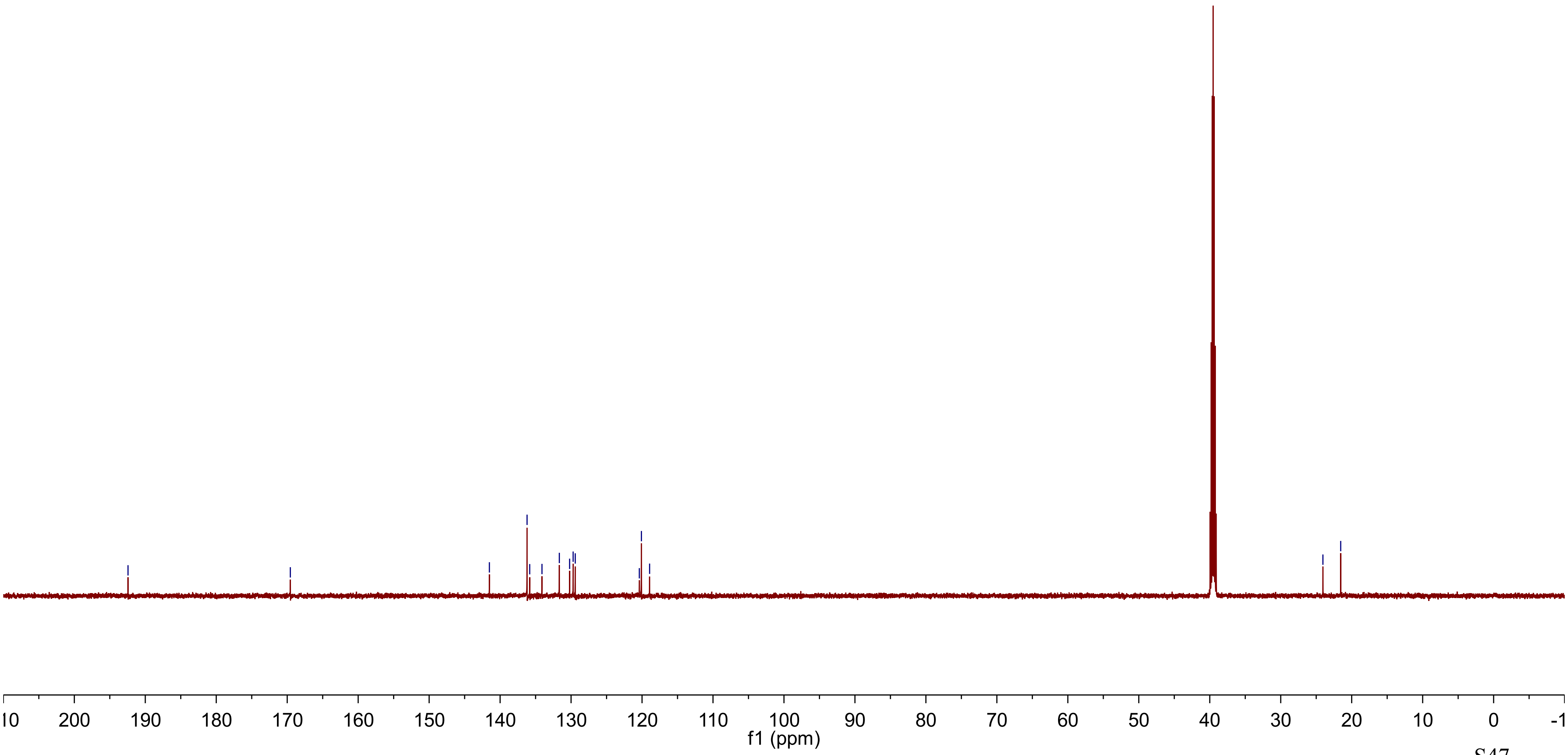
Parameter	Value
Solvent	DMSO
Spectrometer Frequency	600

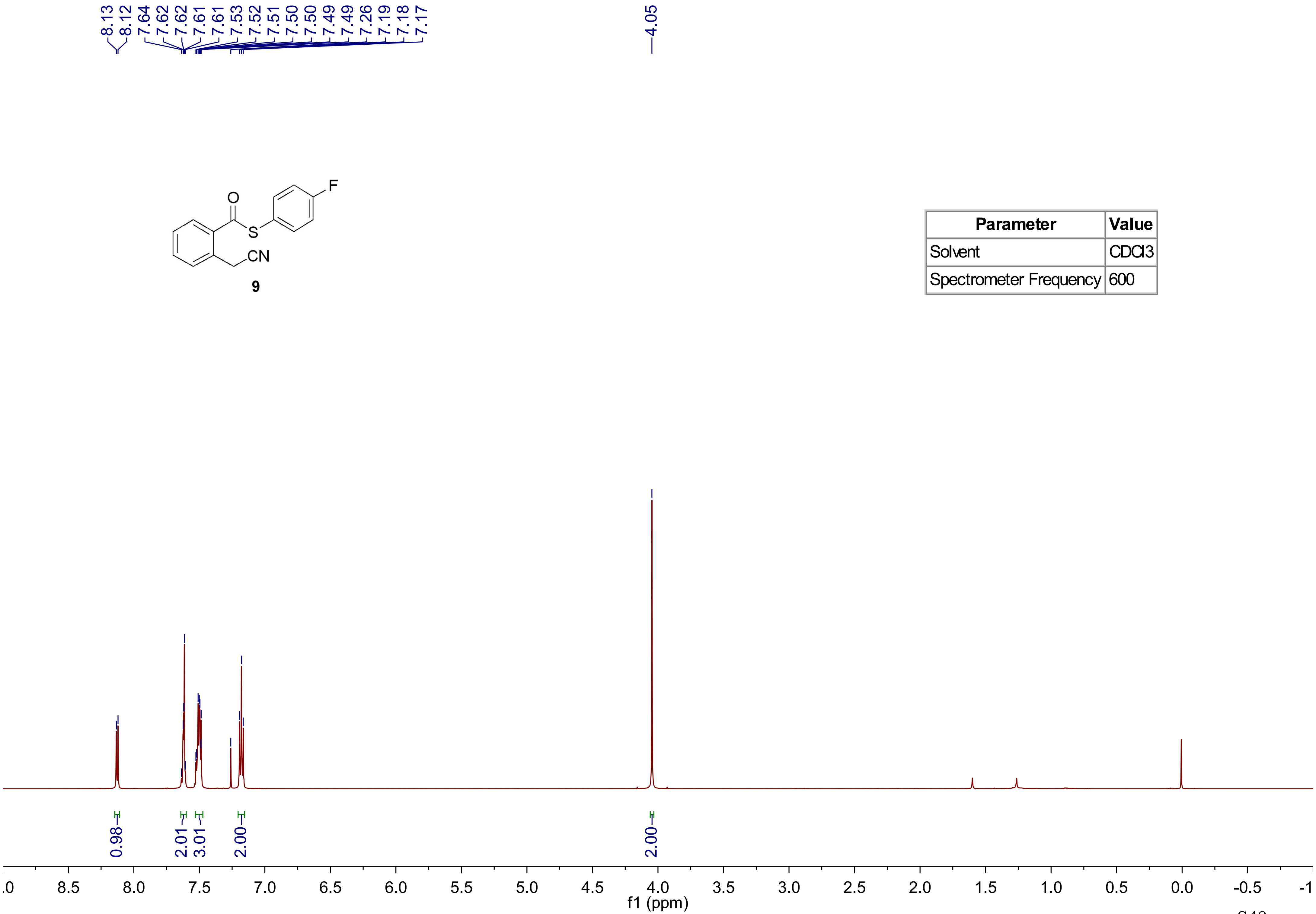




8

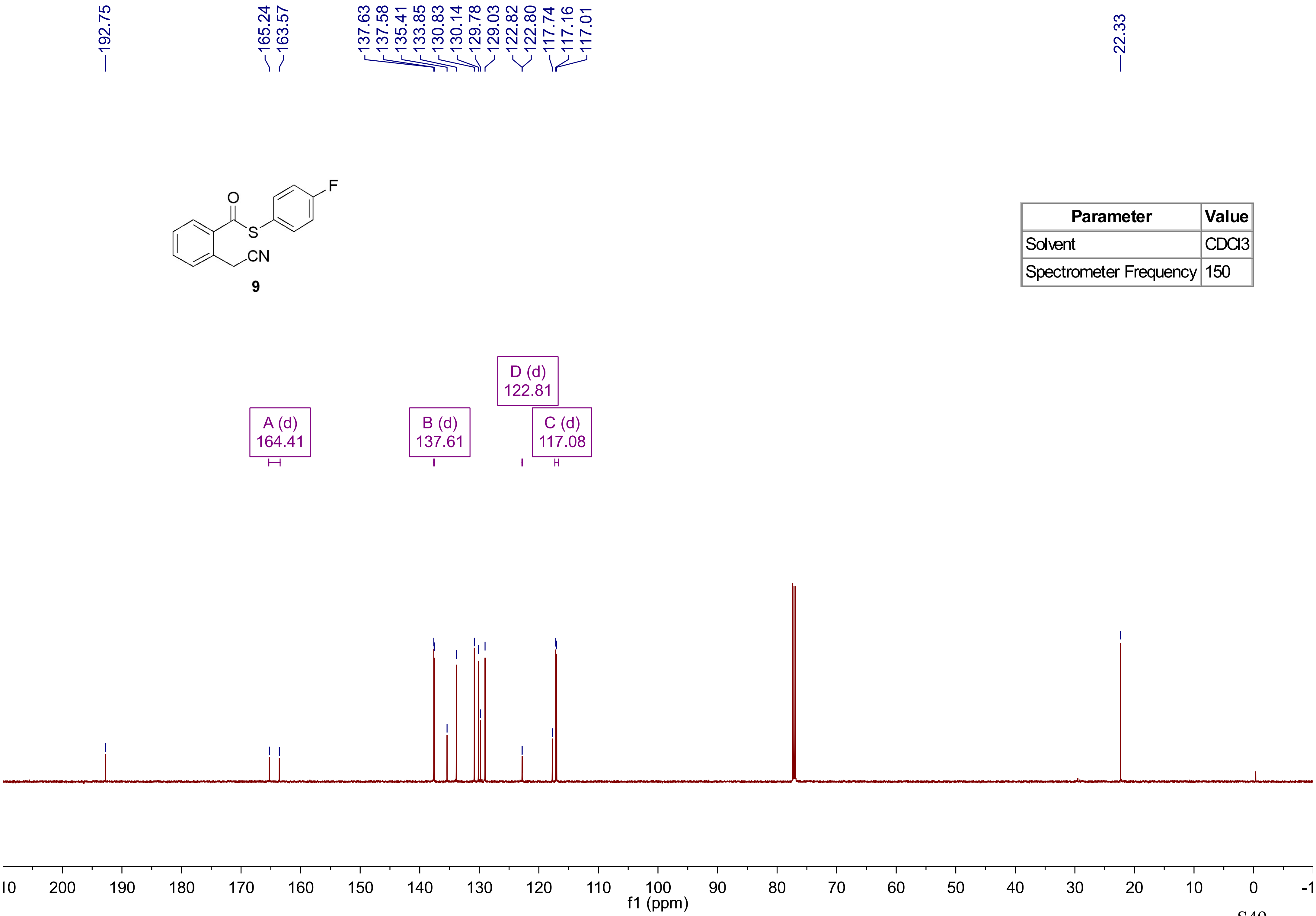
Parameter	Value
Solvent	DMSO
Spectrometer Frequency	150





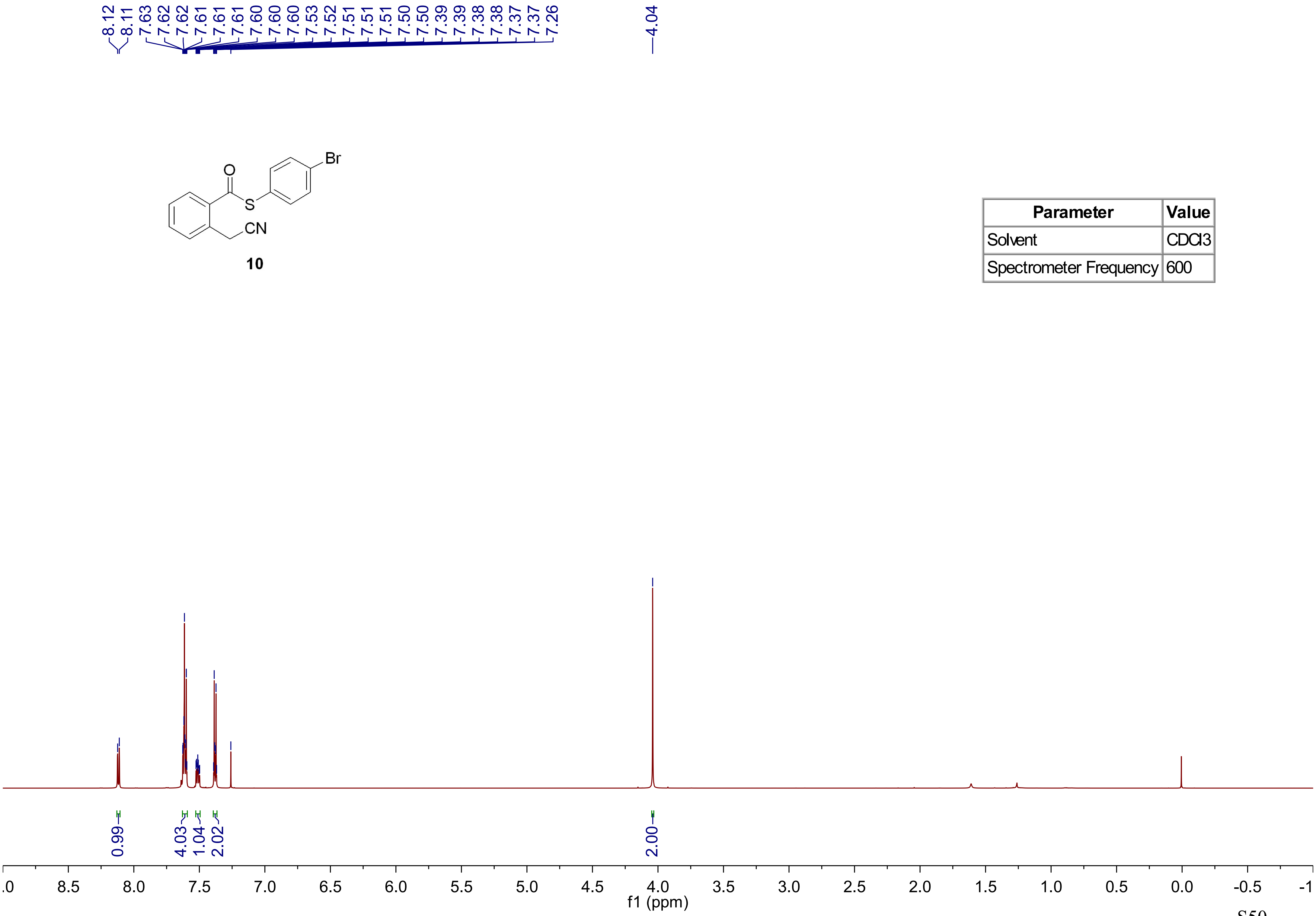
9

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



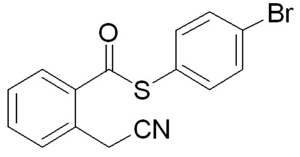
9

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150



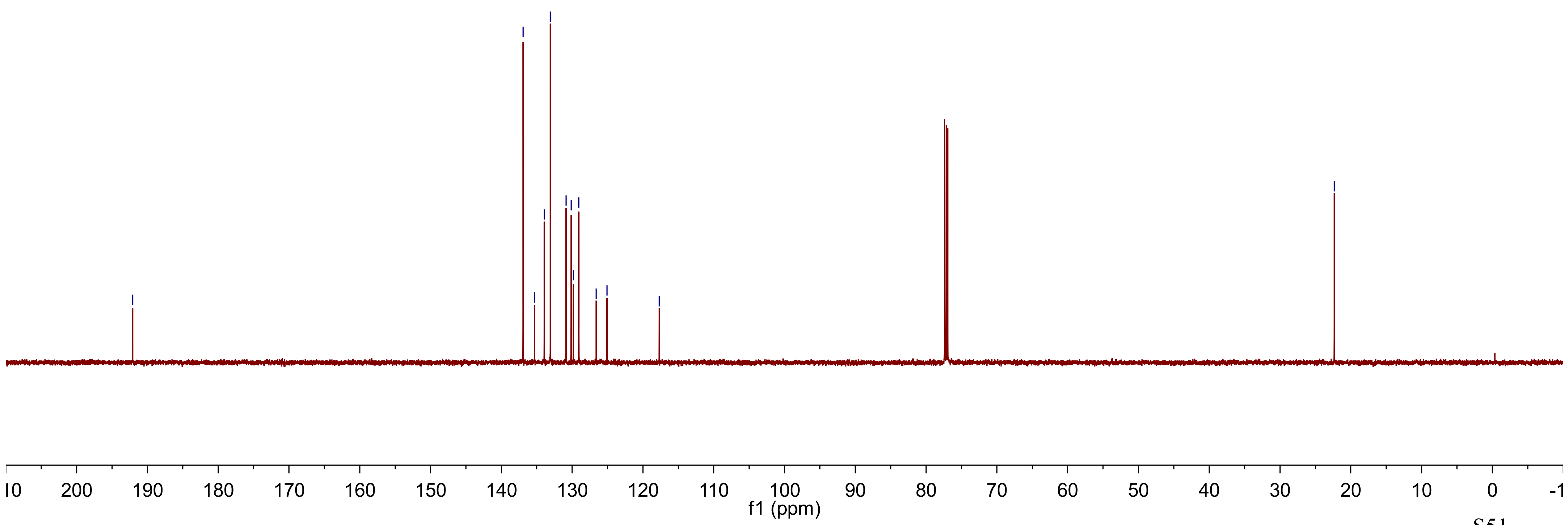
10

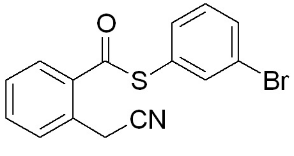
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



10

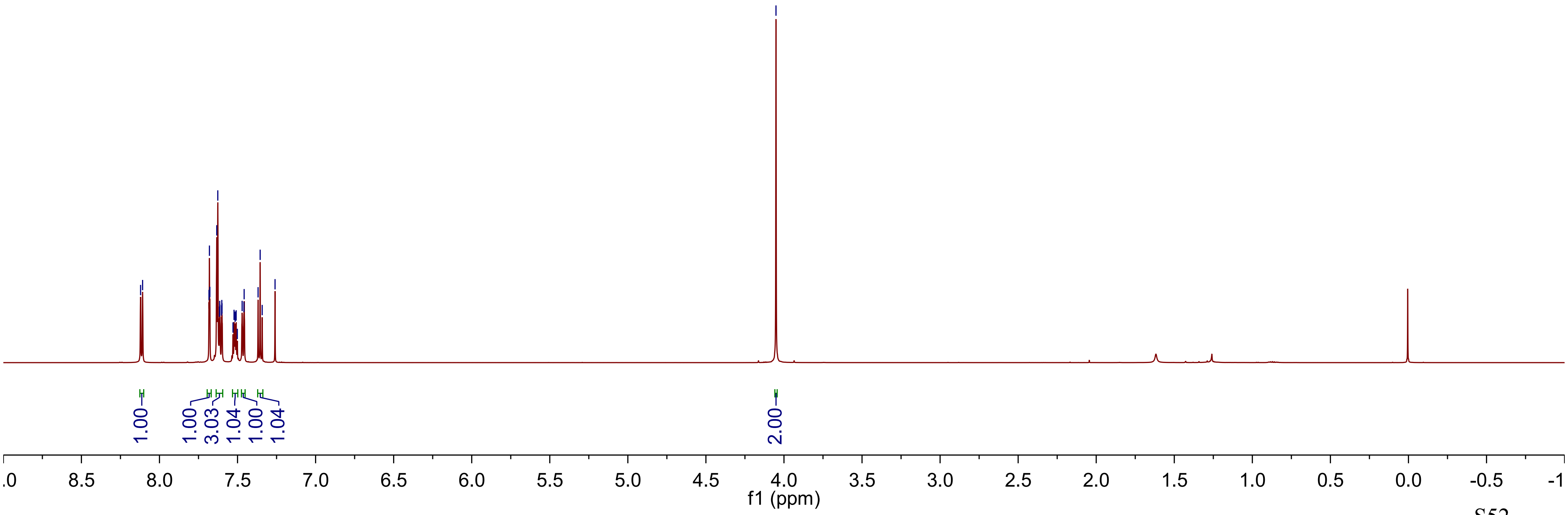
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

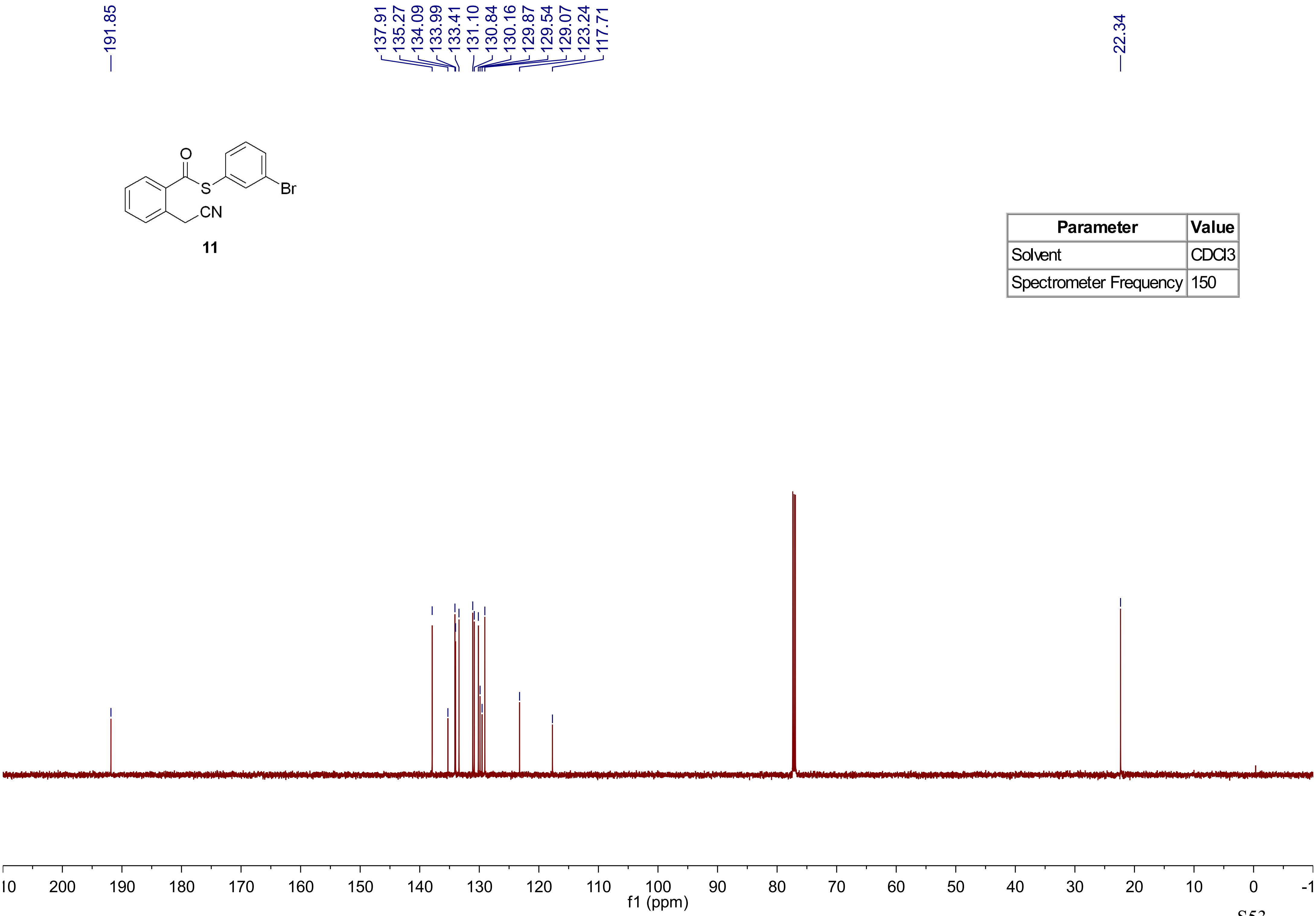




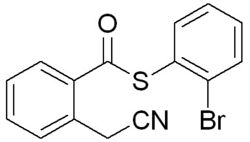
11

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



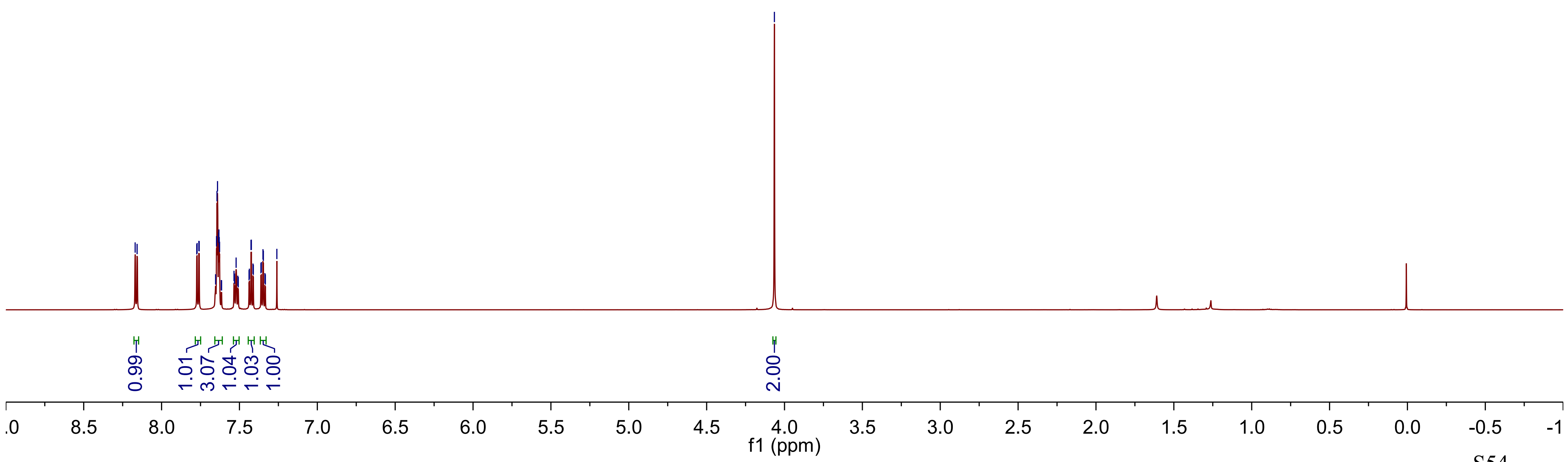


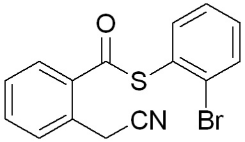
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150



12

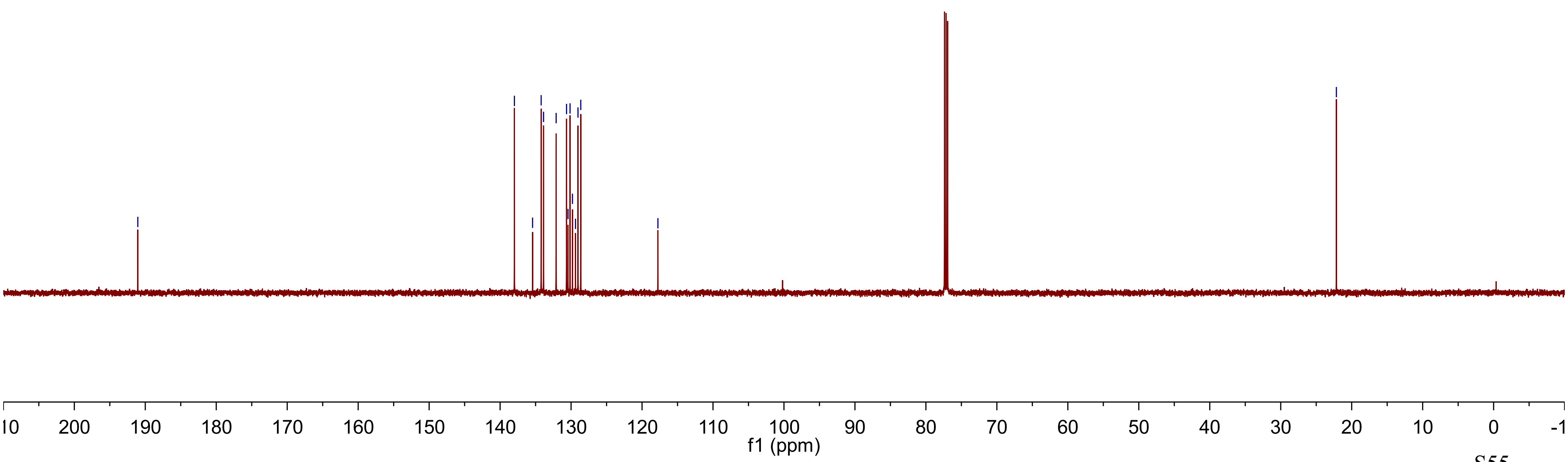
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

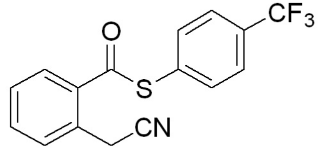




12

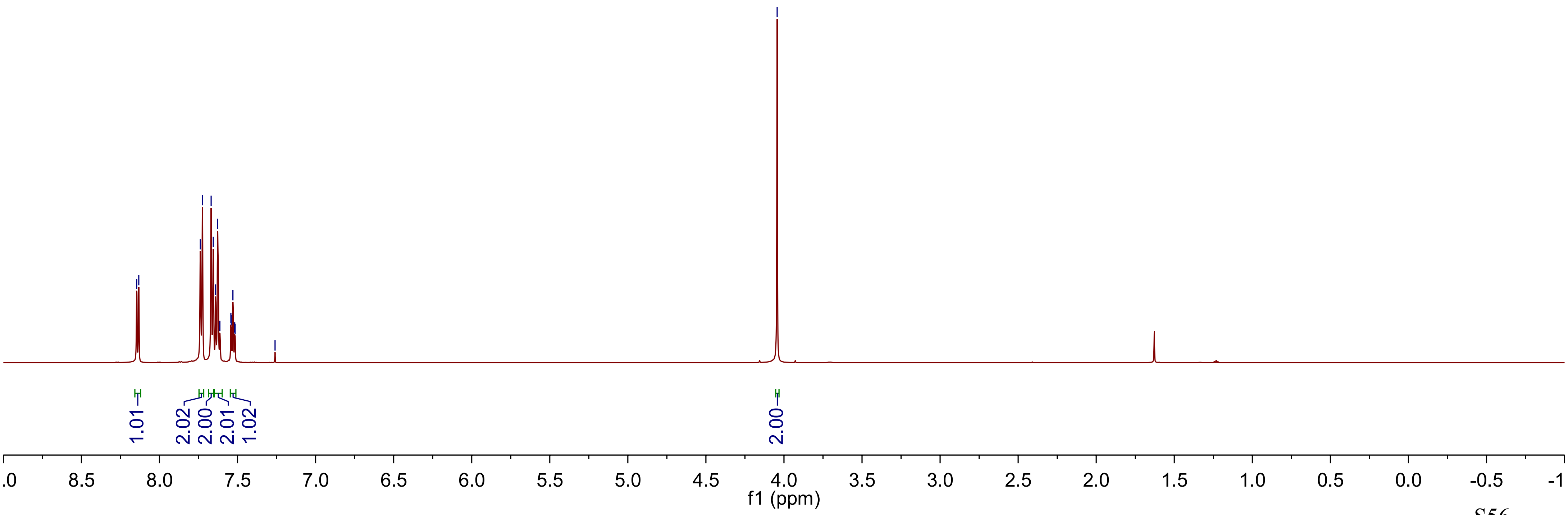
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

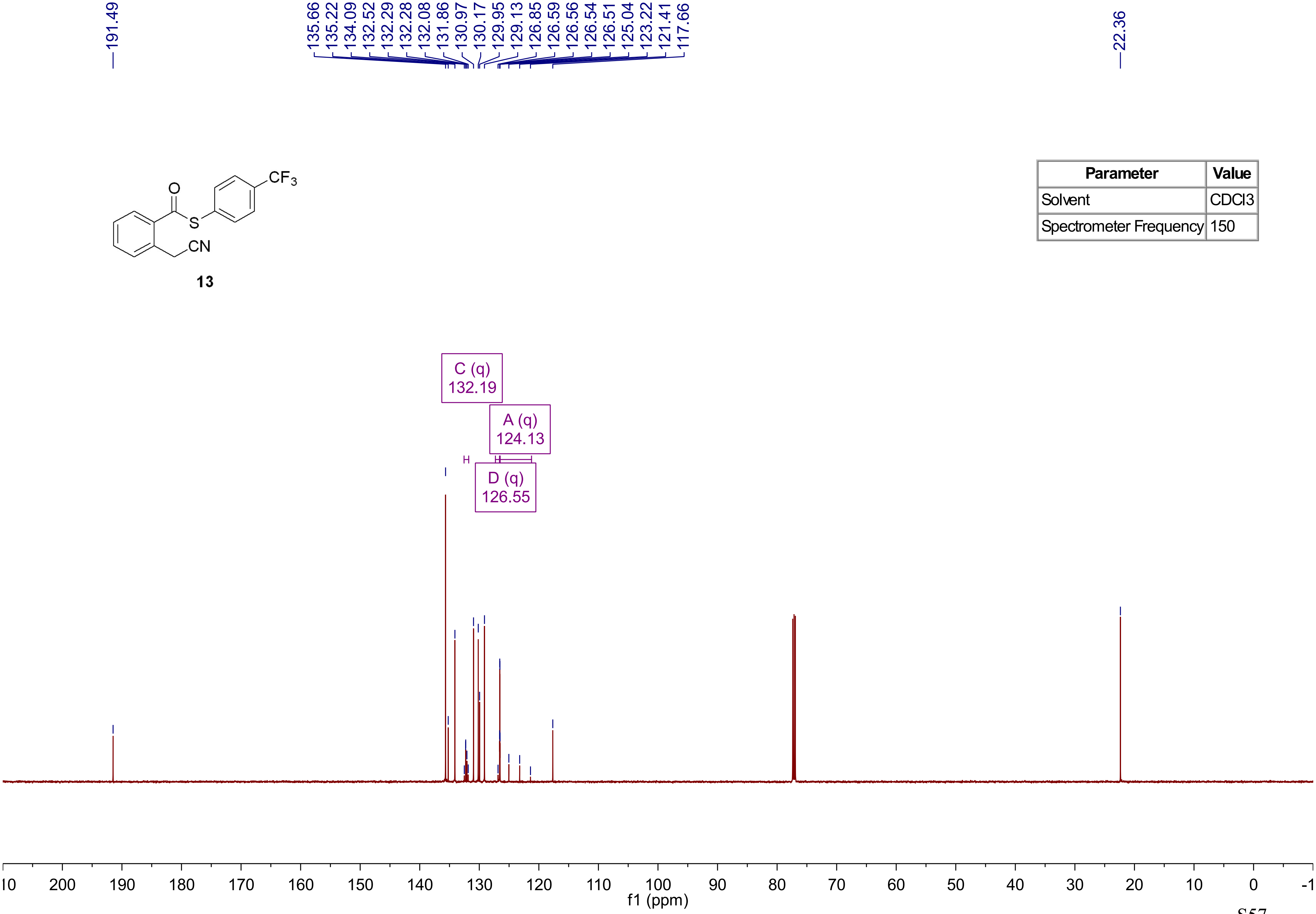




13

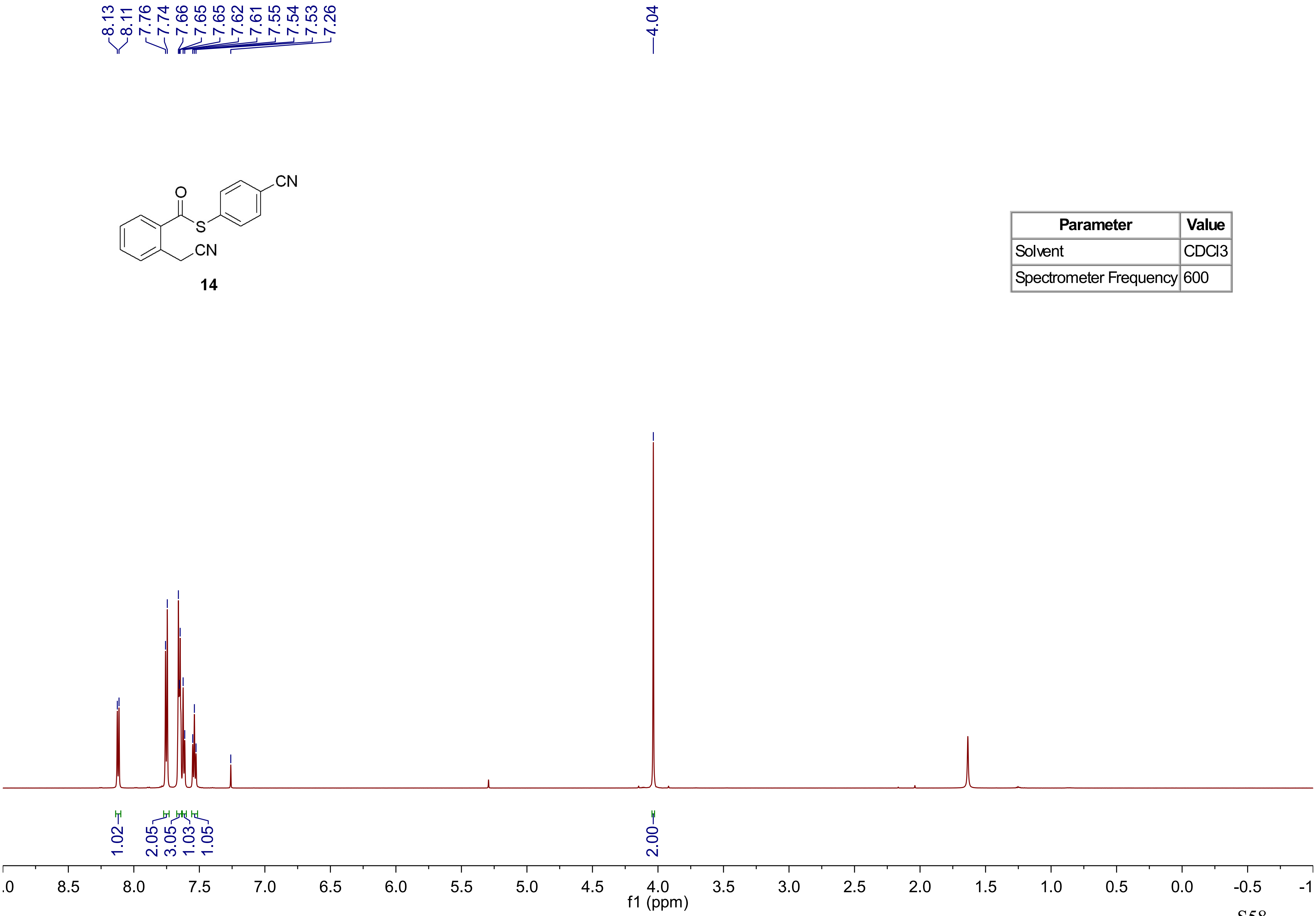
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600





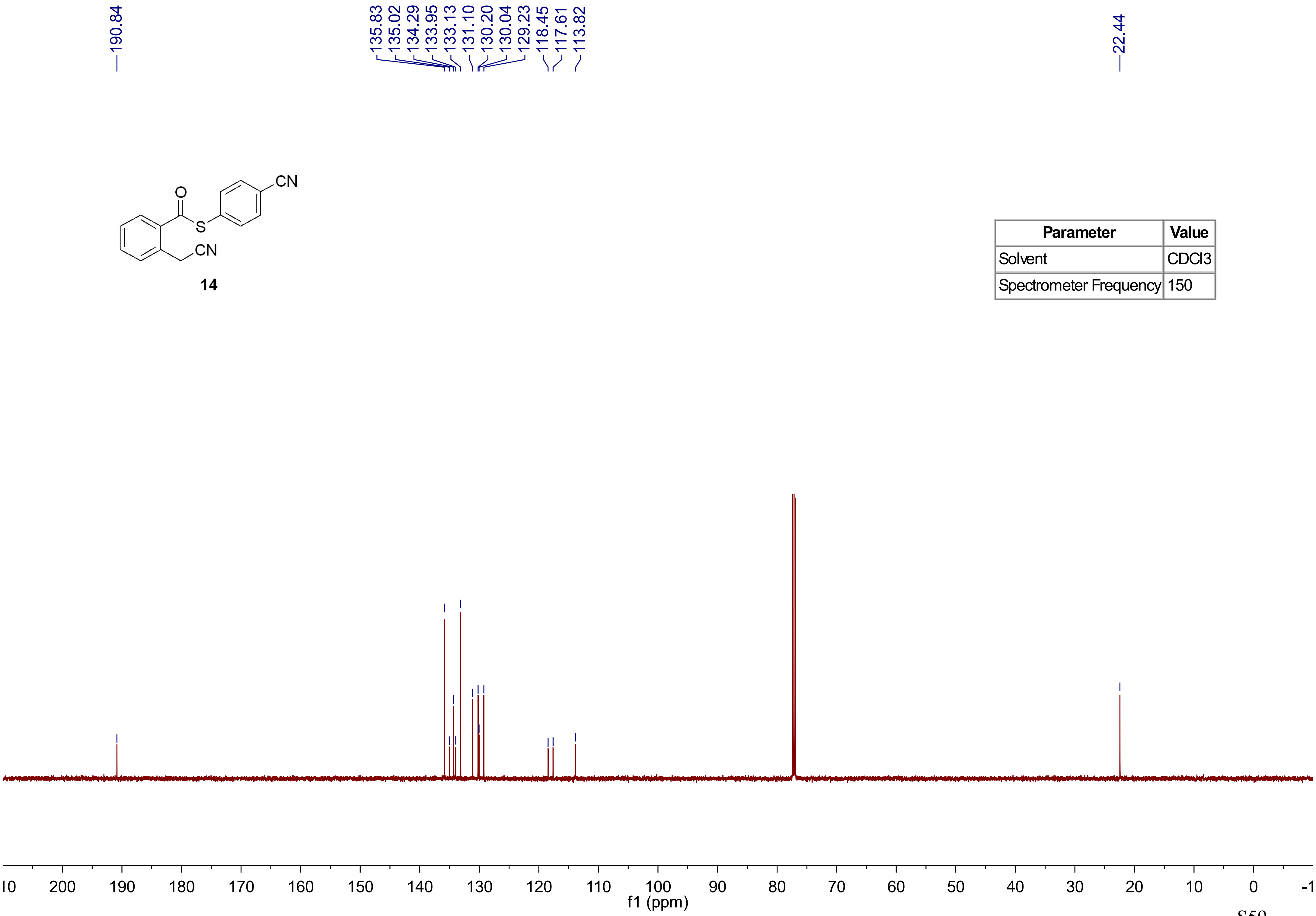
13

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150



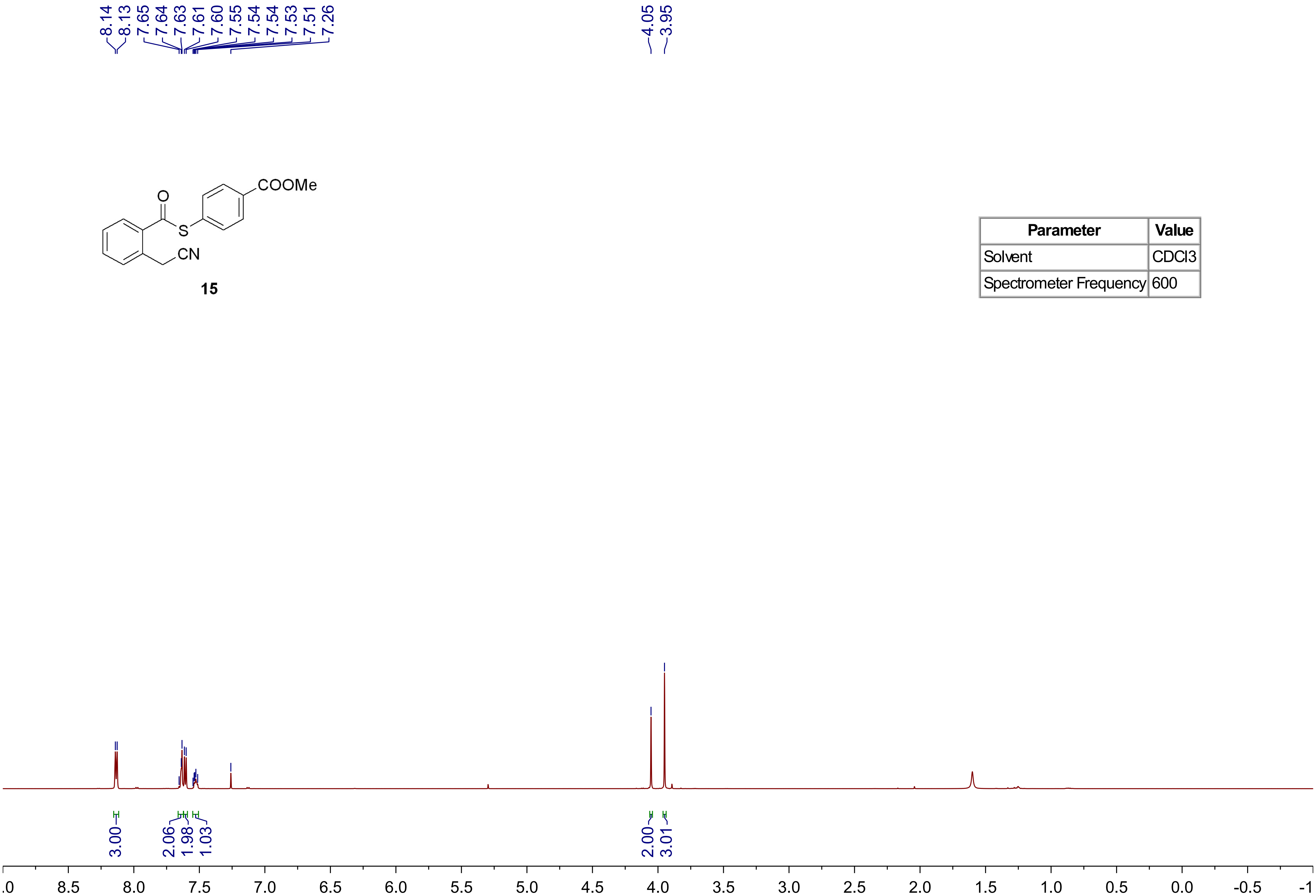
14

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

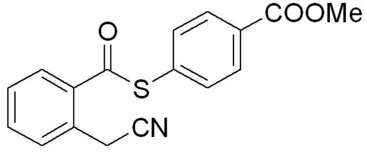


14

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

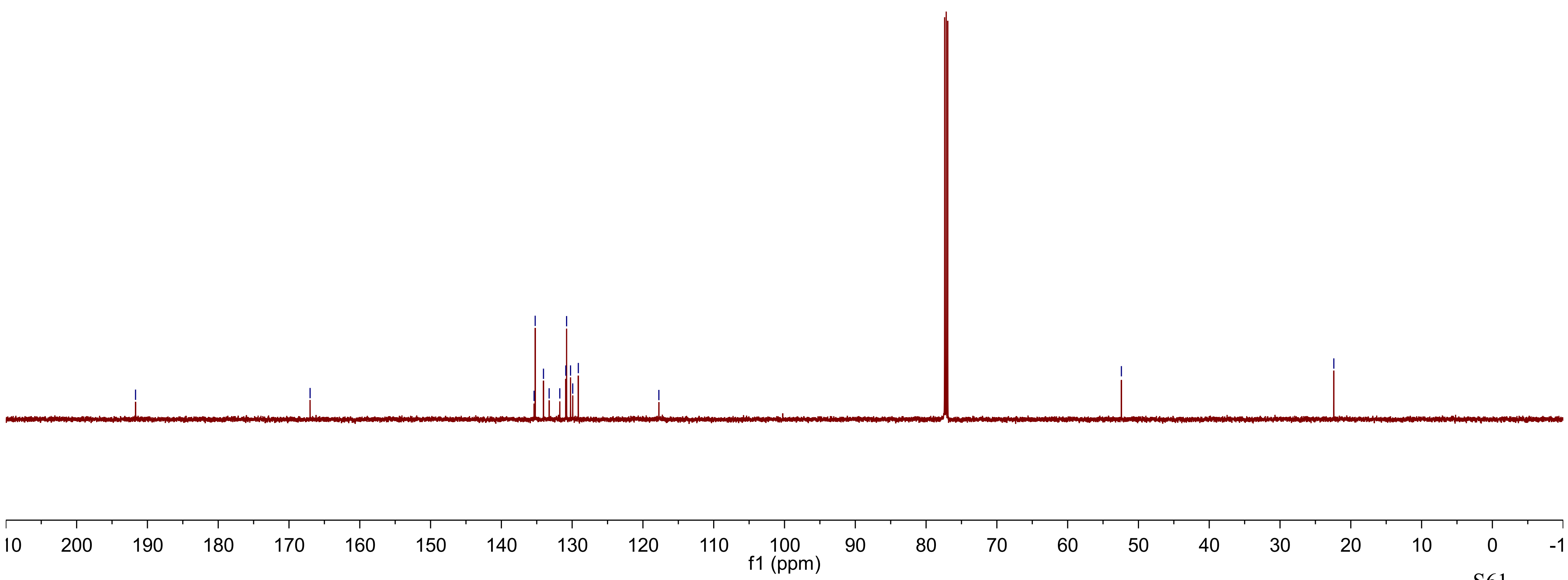


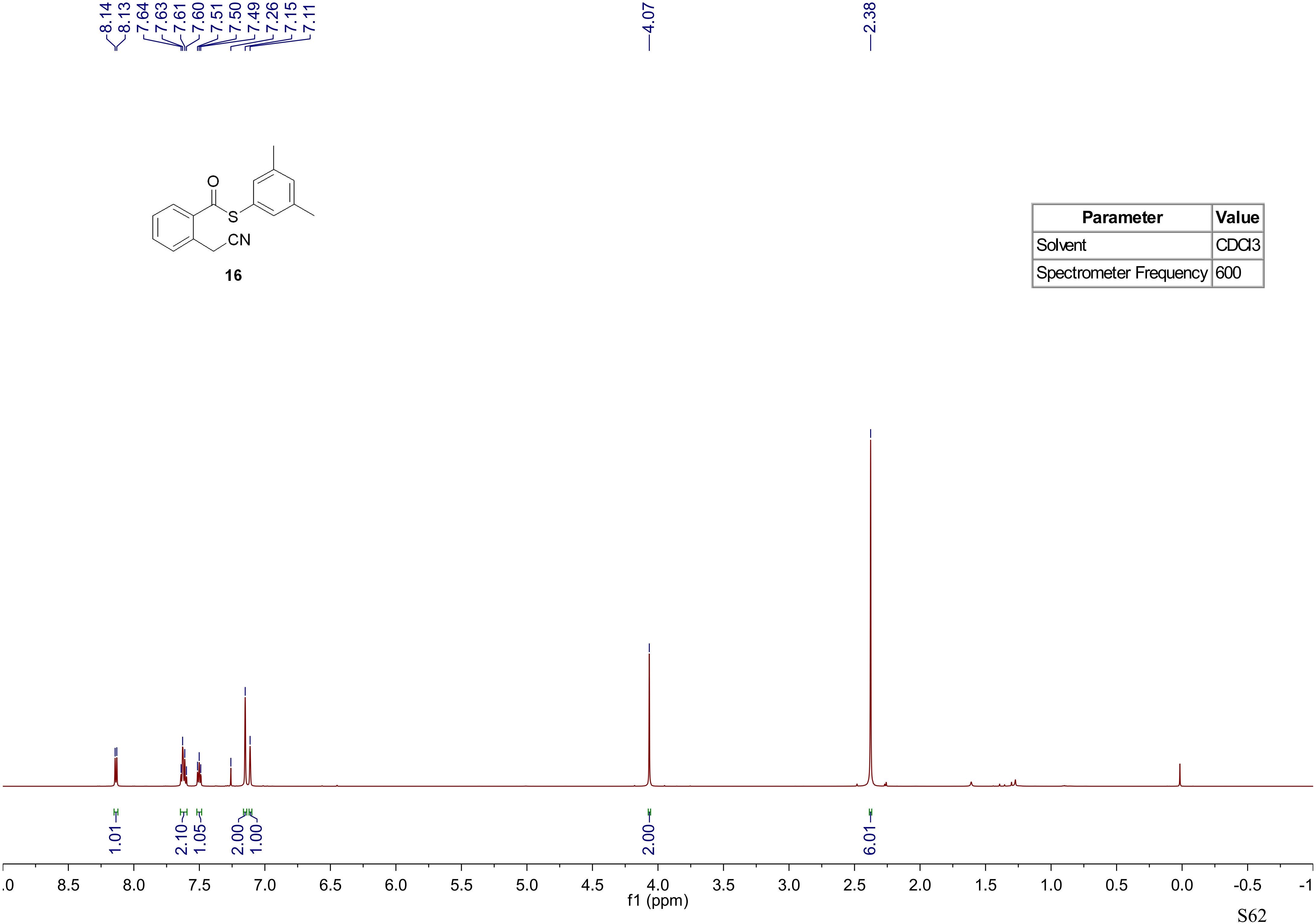
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



15

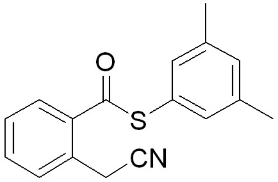
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150





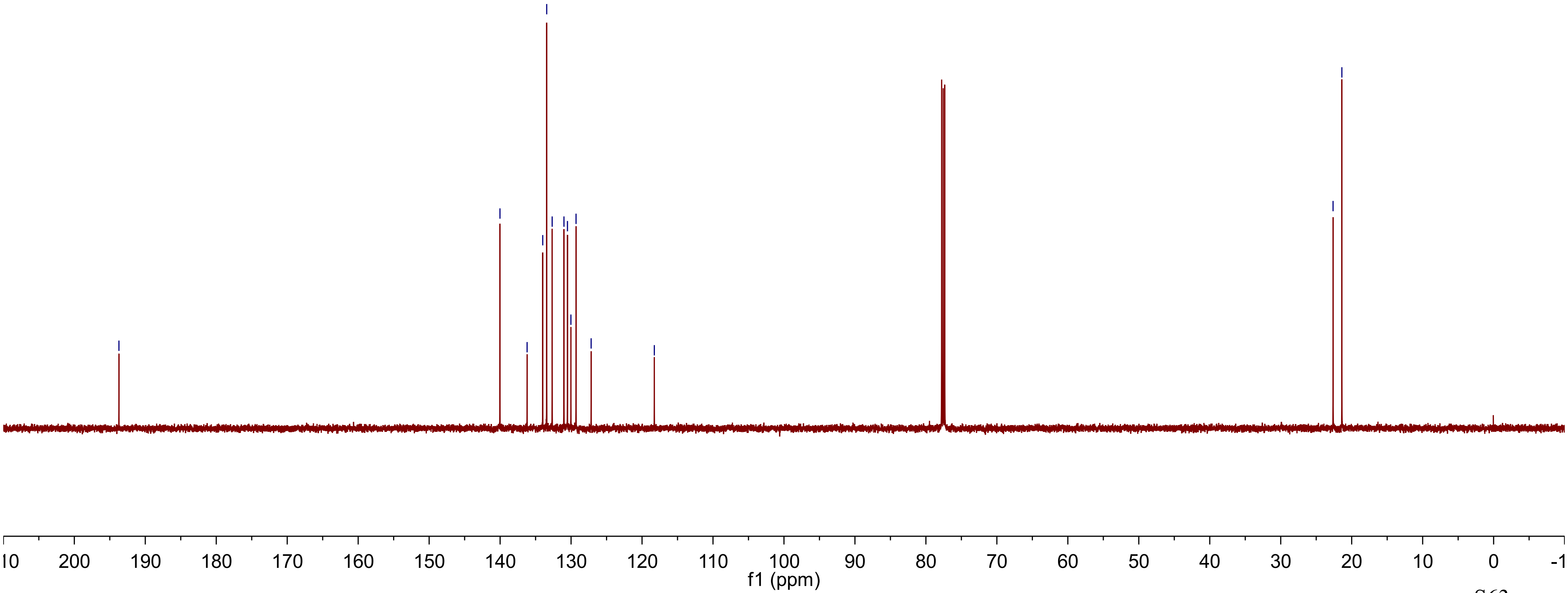
16

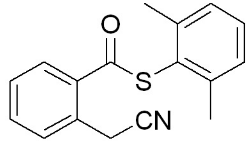
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



16

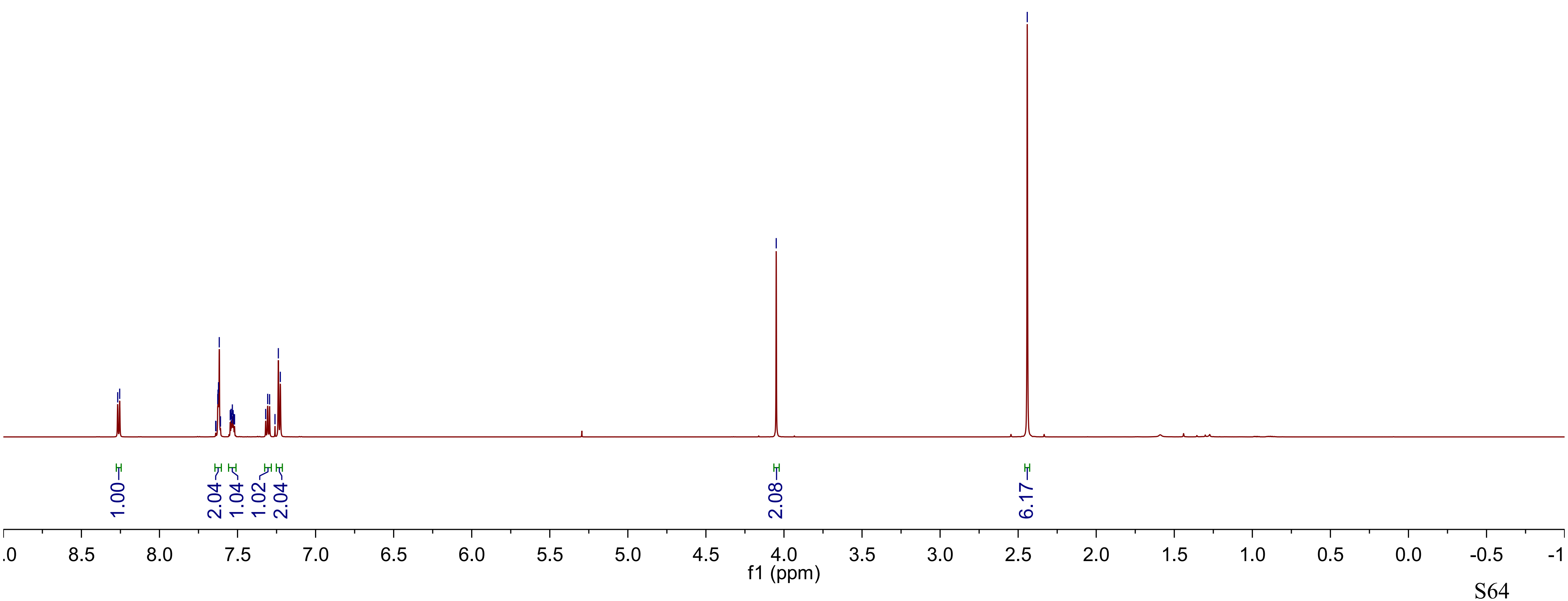
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

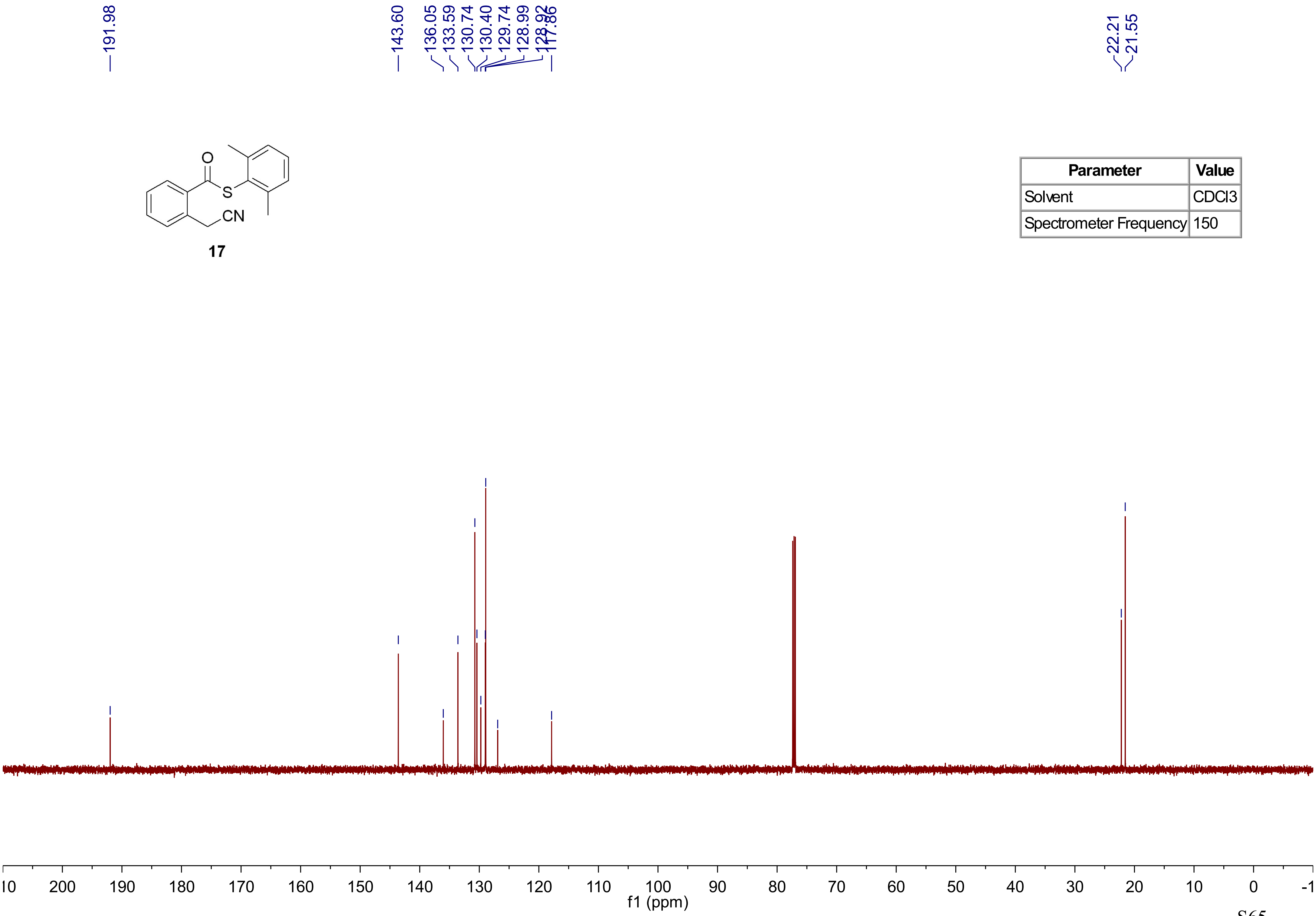




17

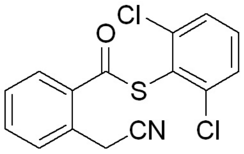
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600





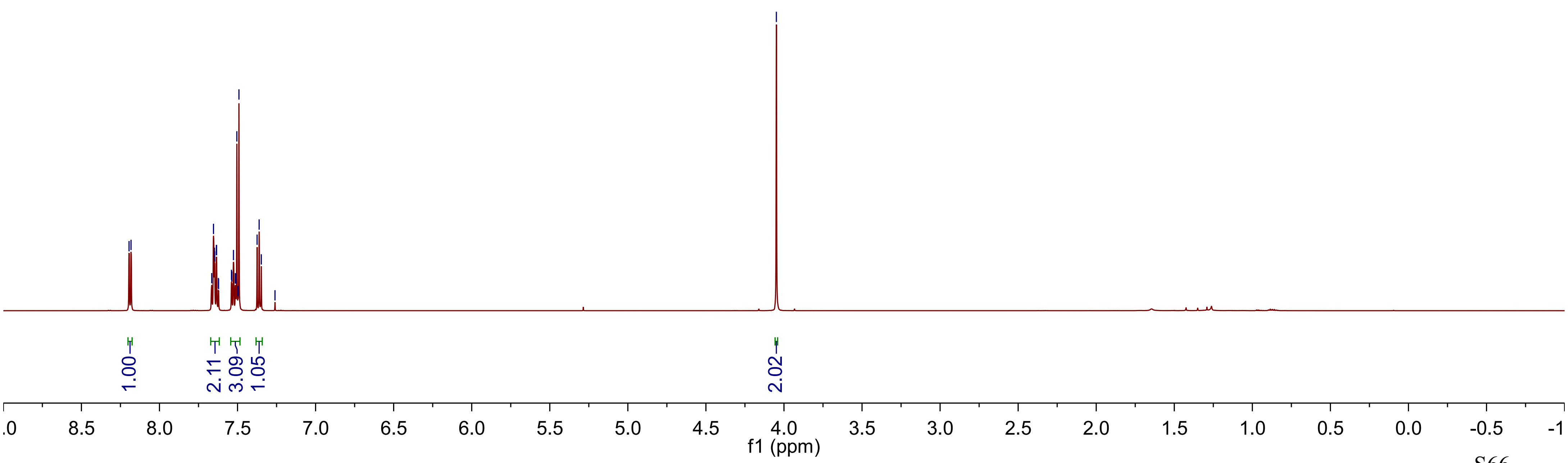
17

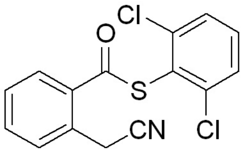
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150



18

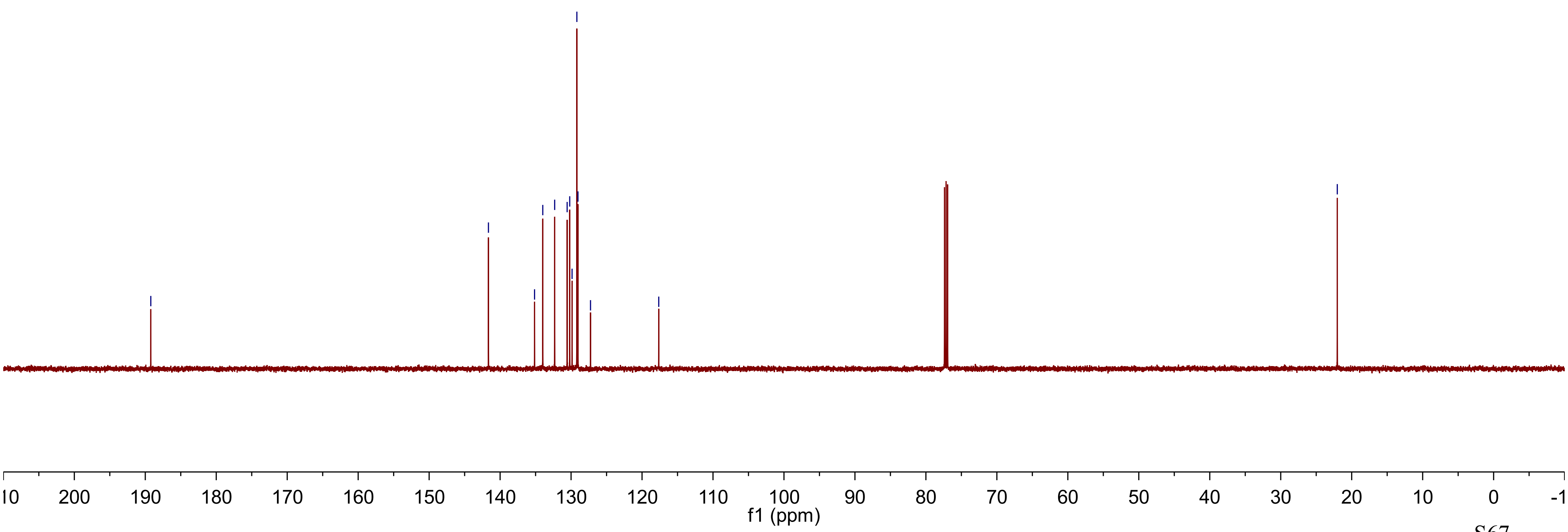
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

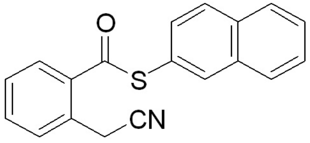




18

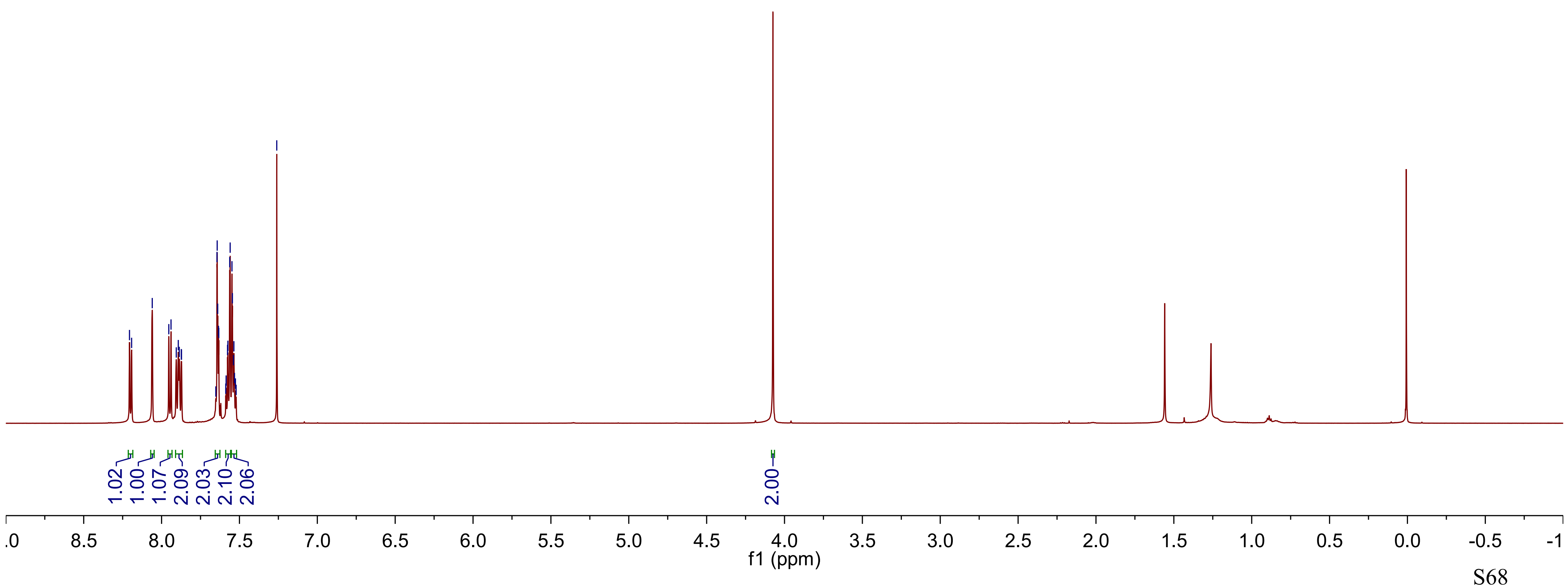
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

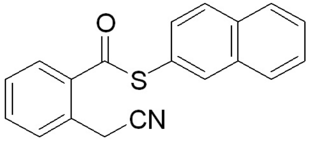




19

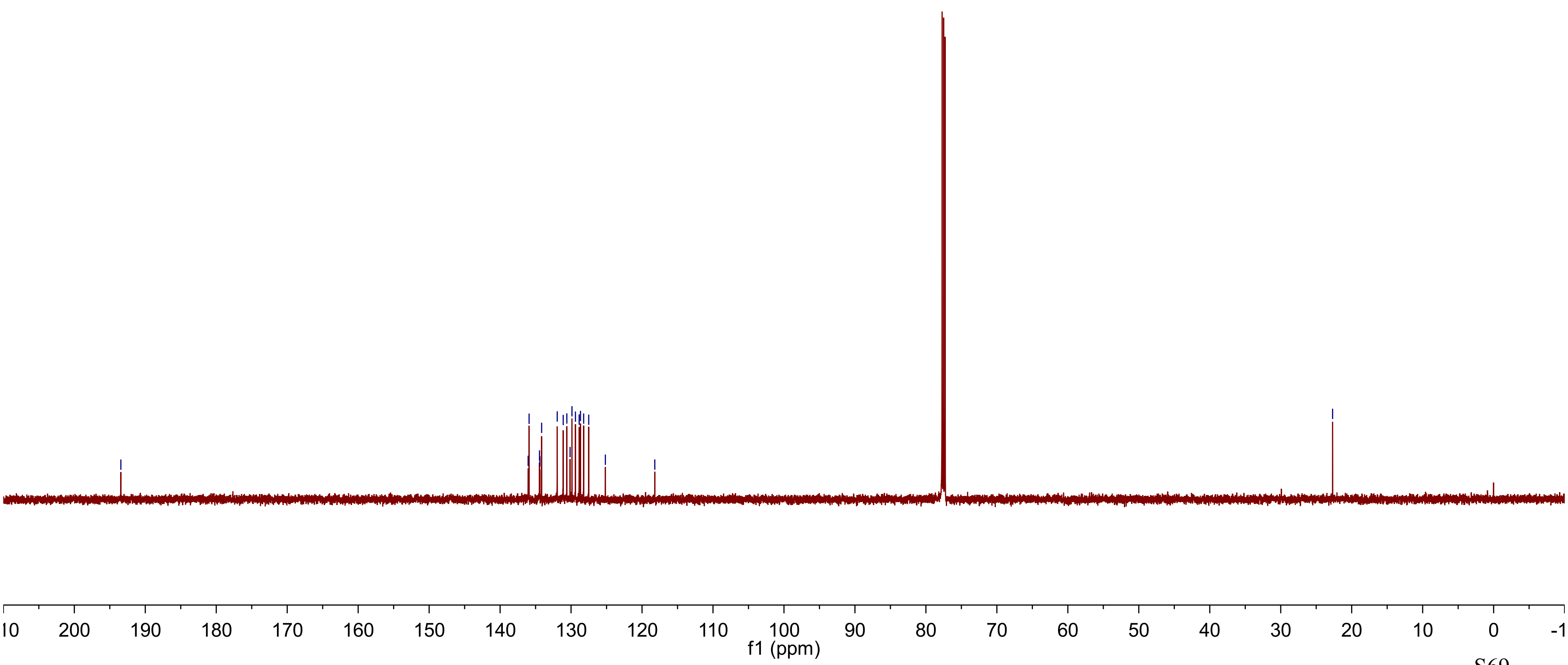
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

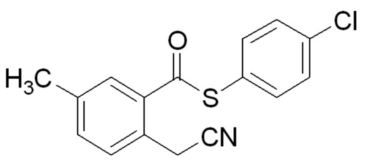




19

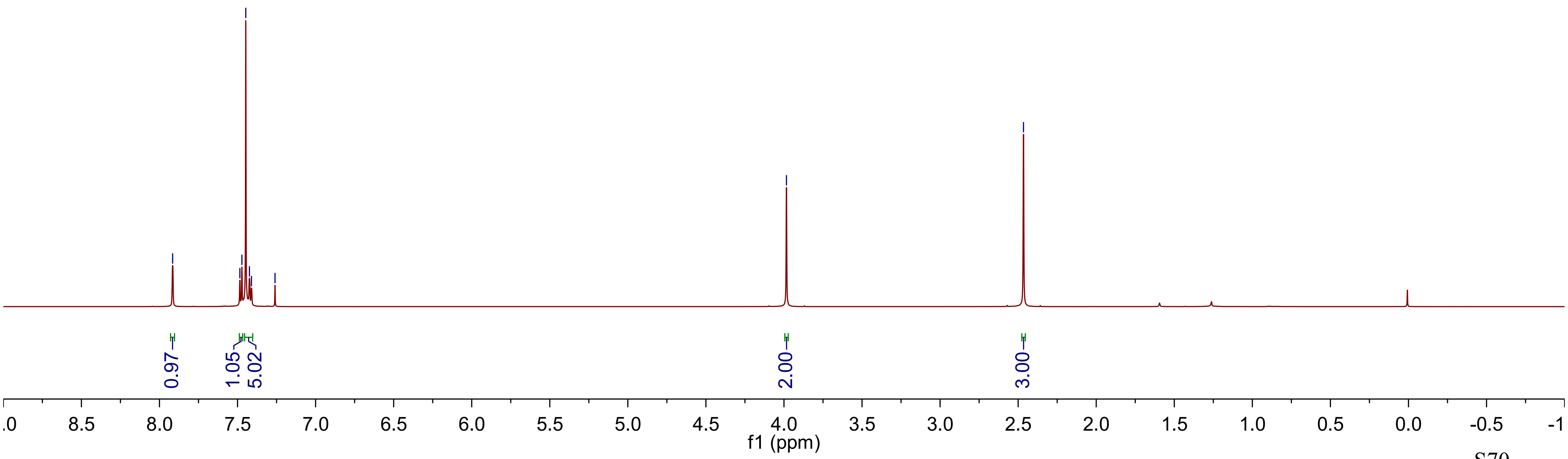
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

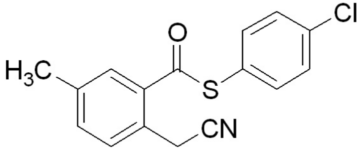




20

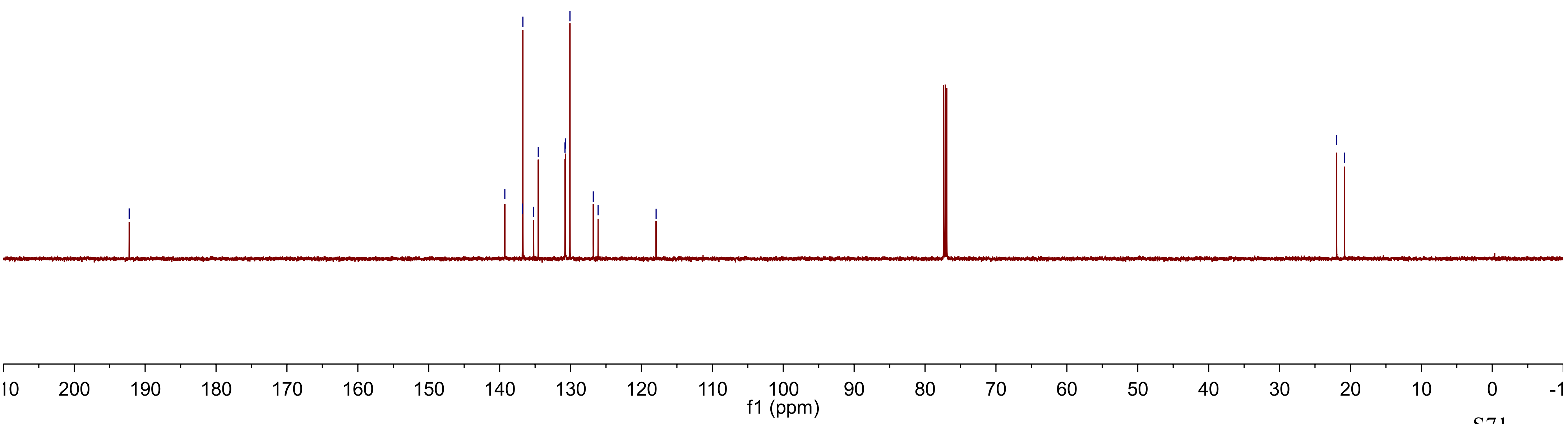
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

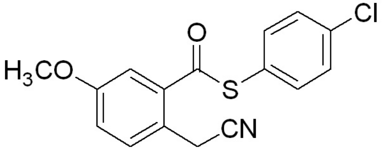




20

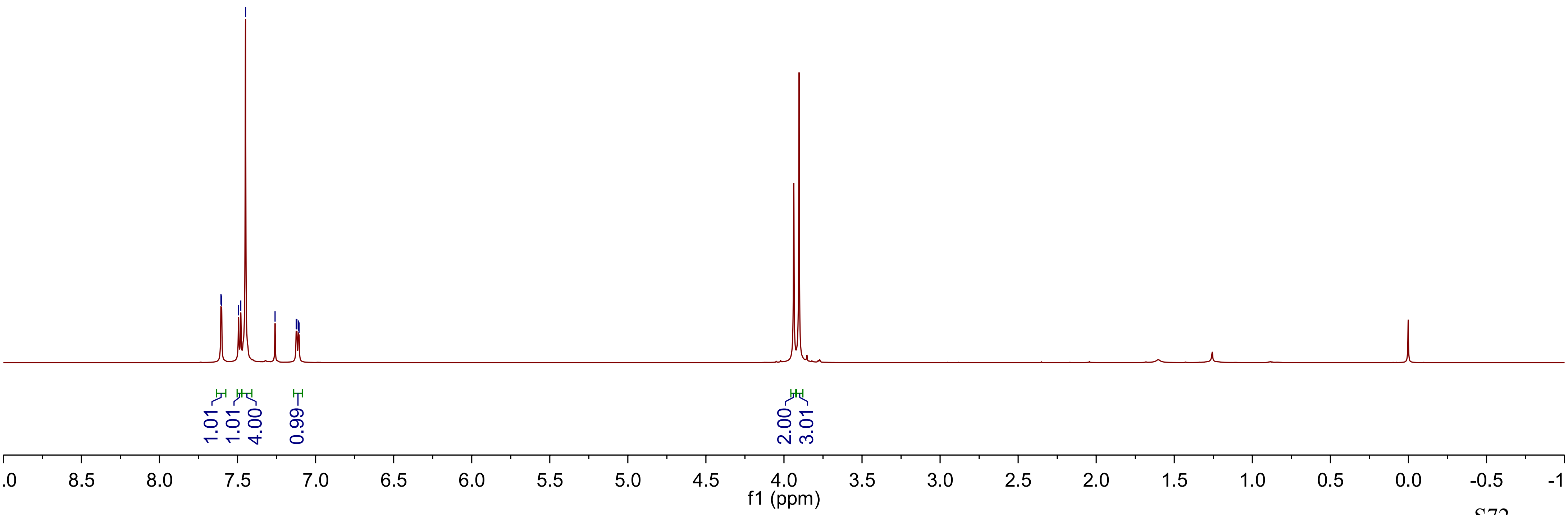
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

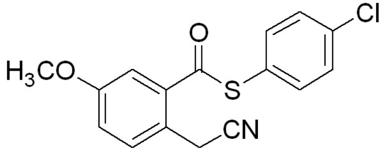




21

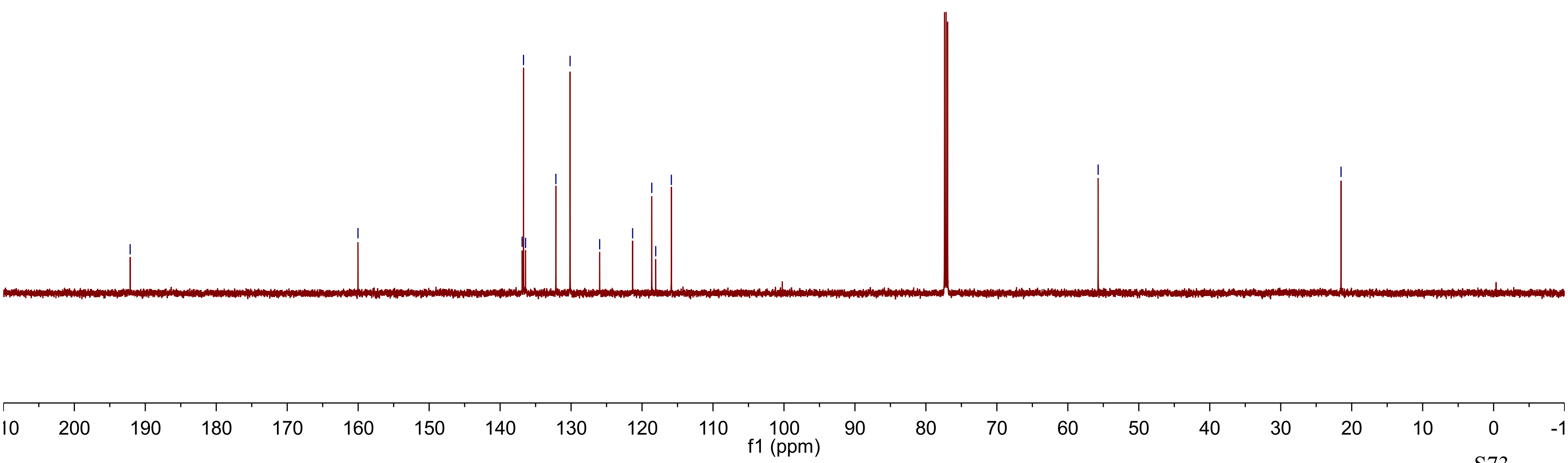
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

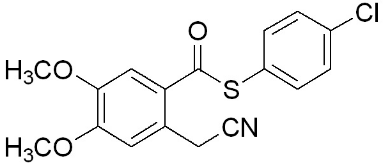




21

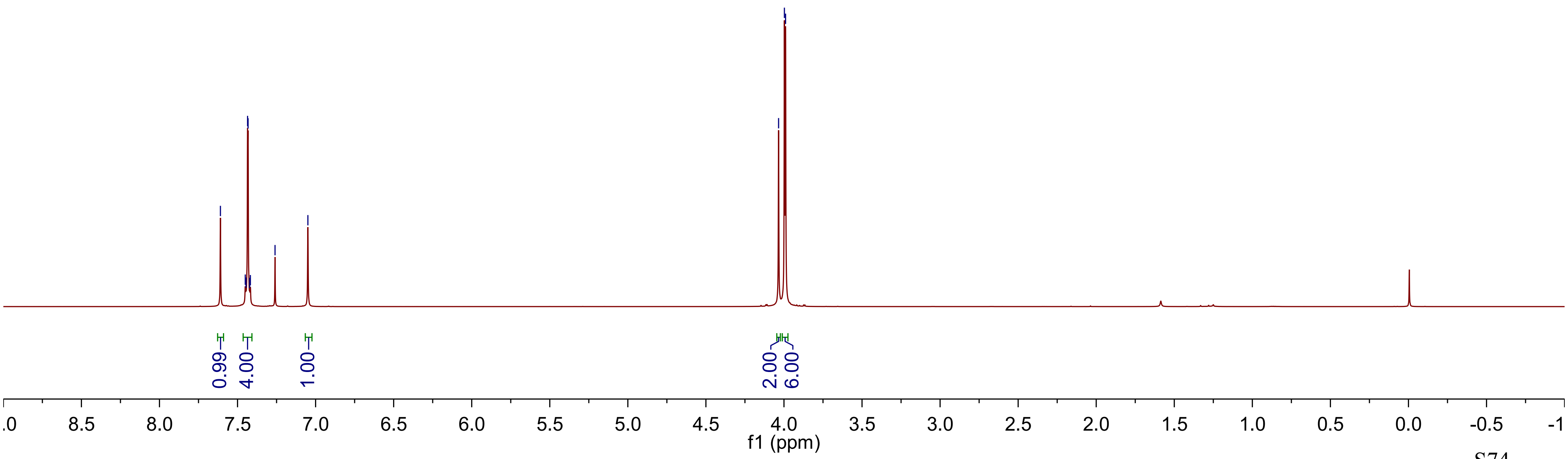
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

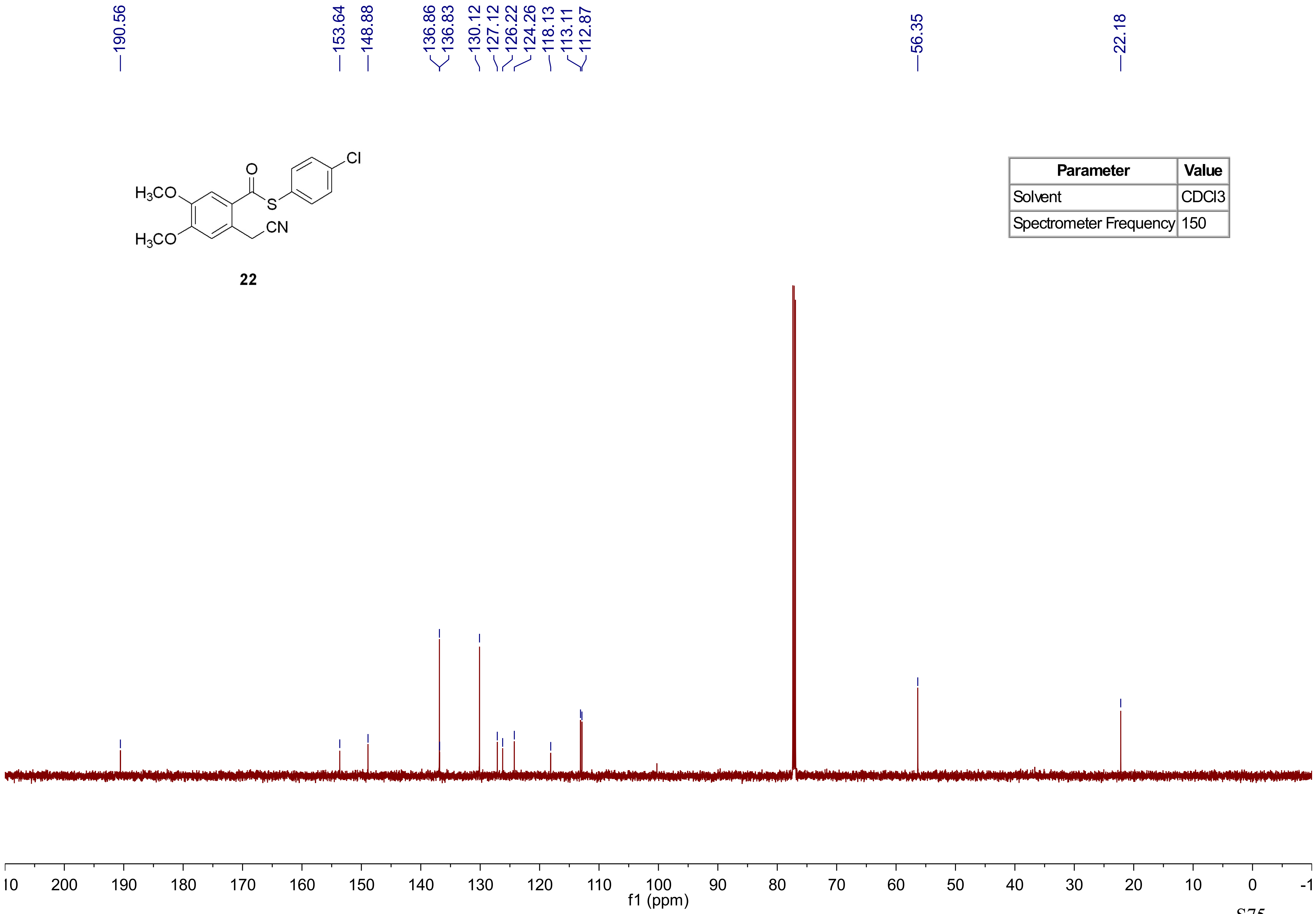




22

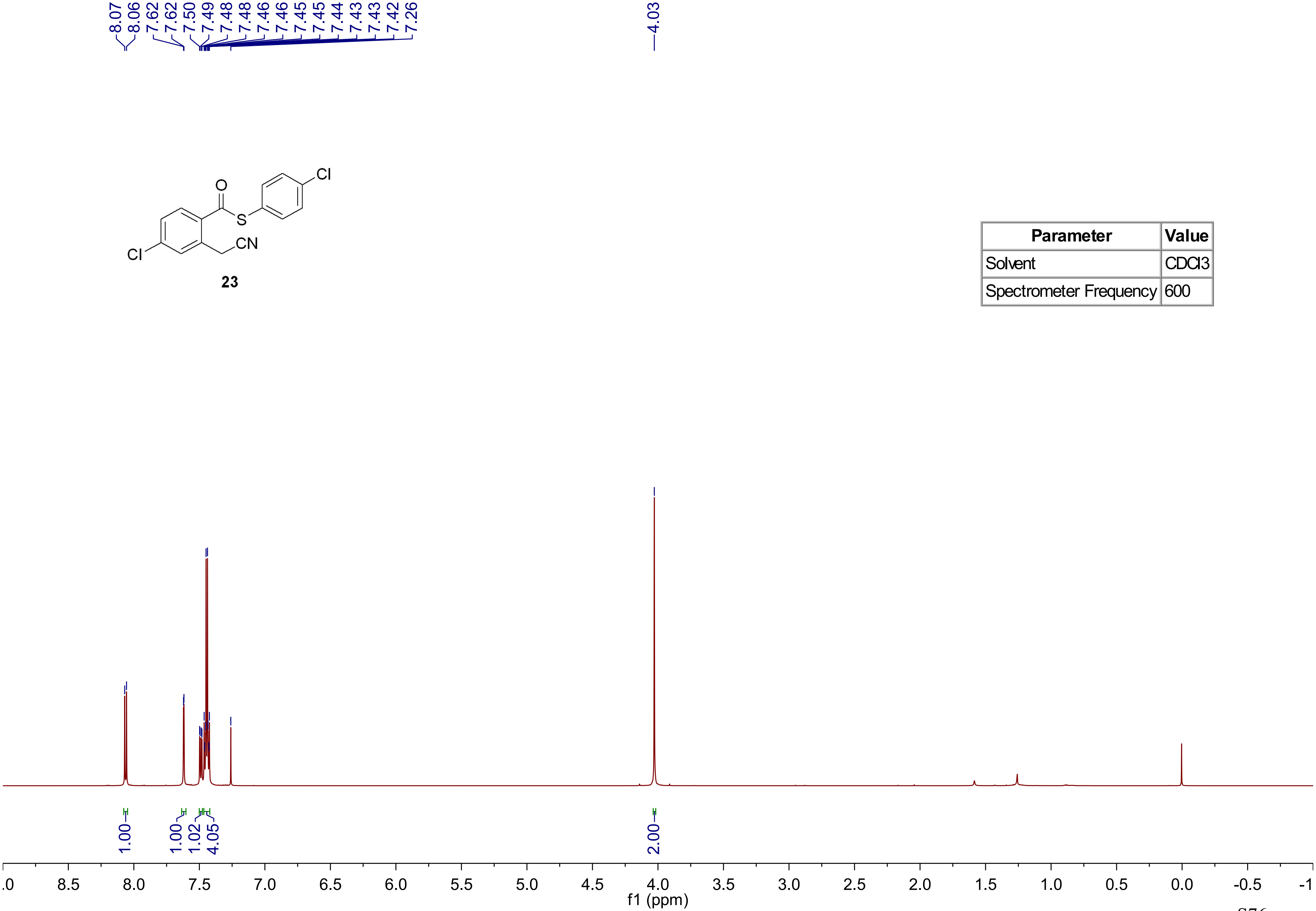
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600





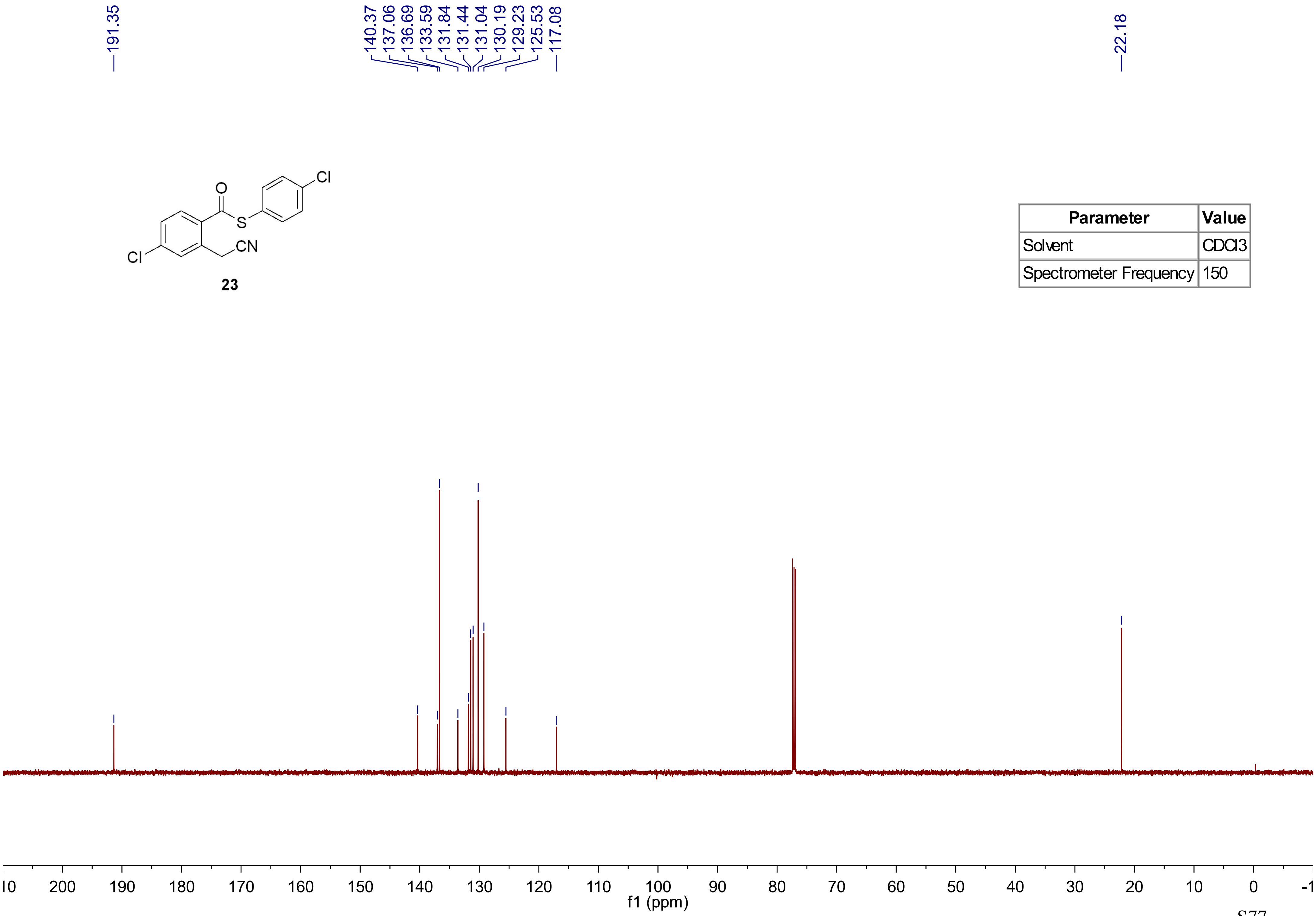
22

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150



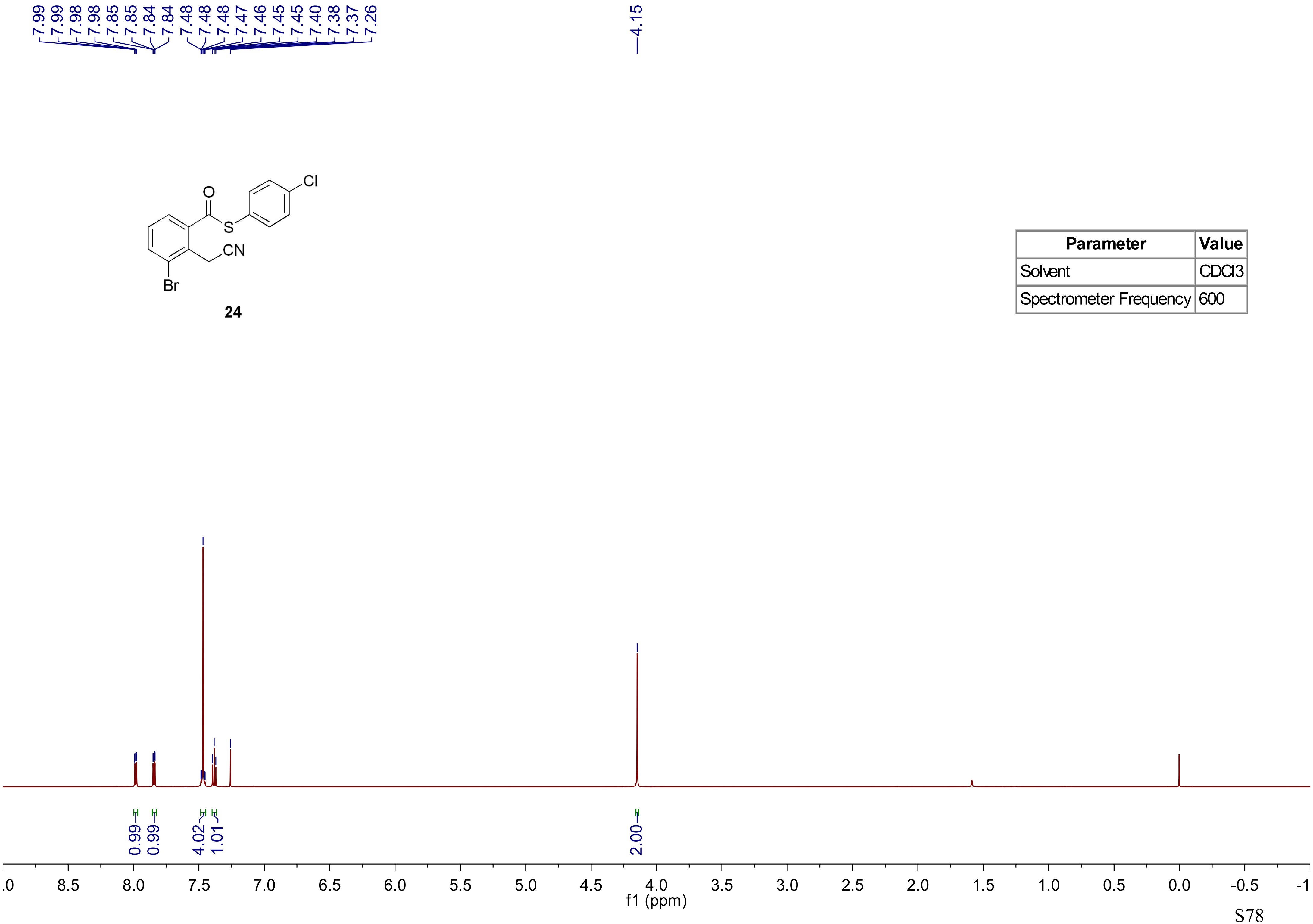
23

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



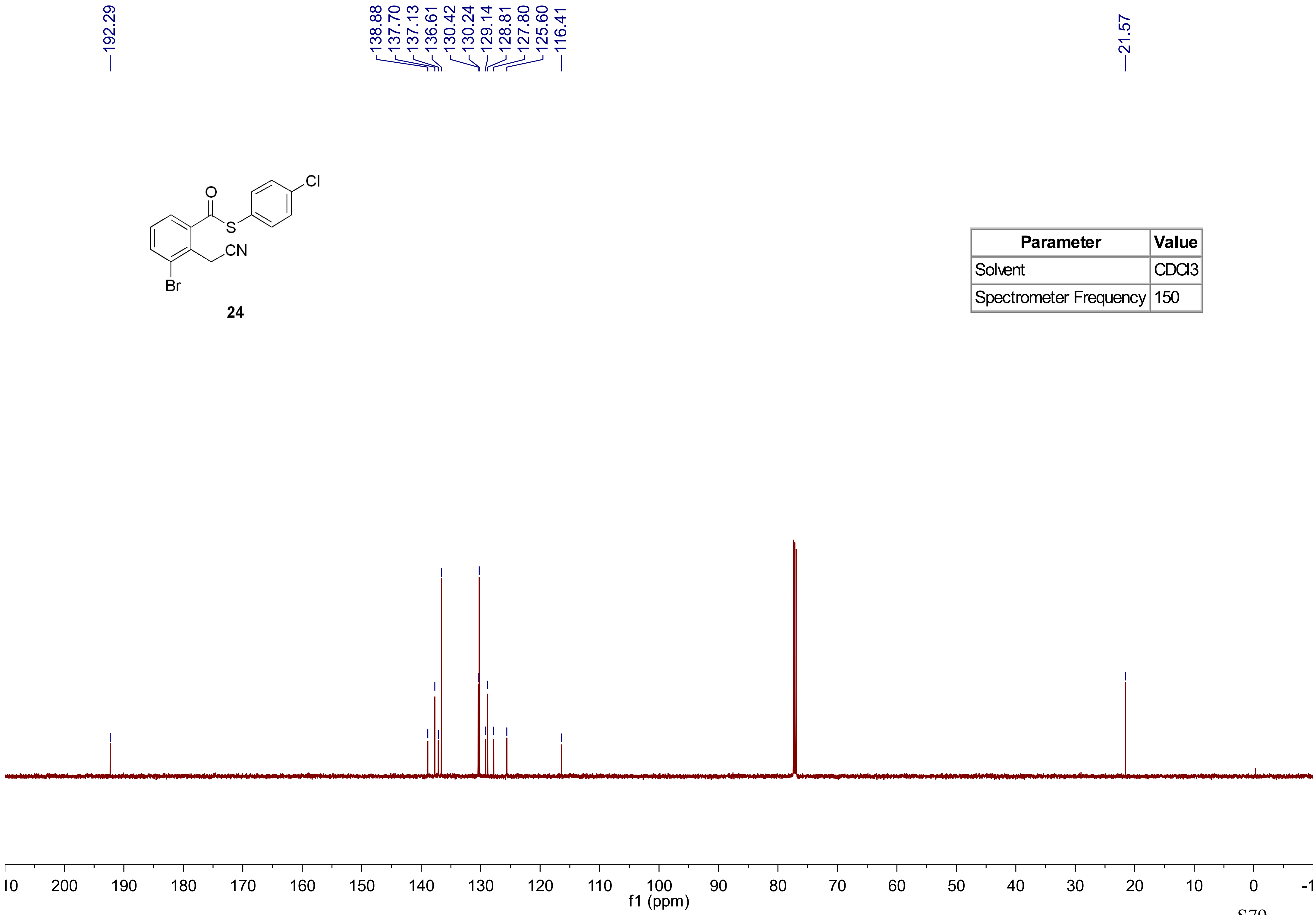
23

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150



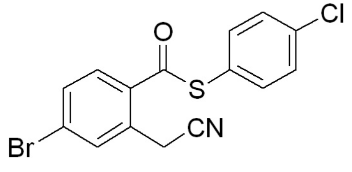
24

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



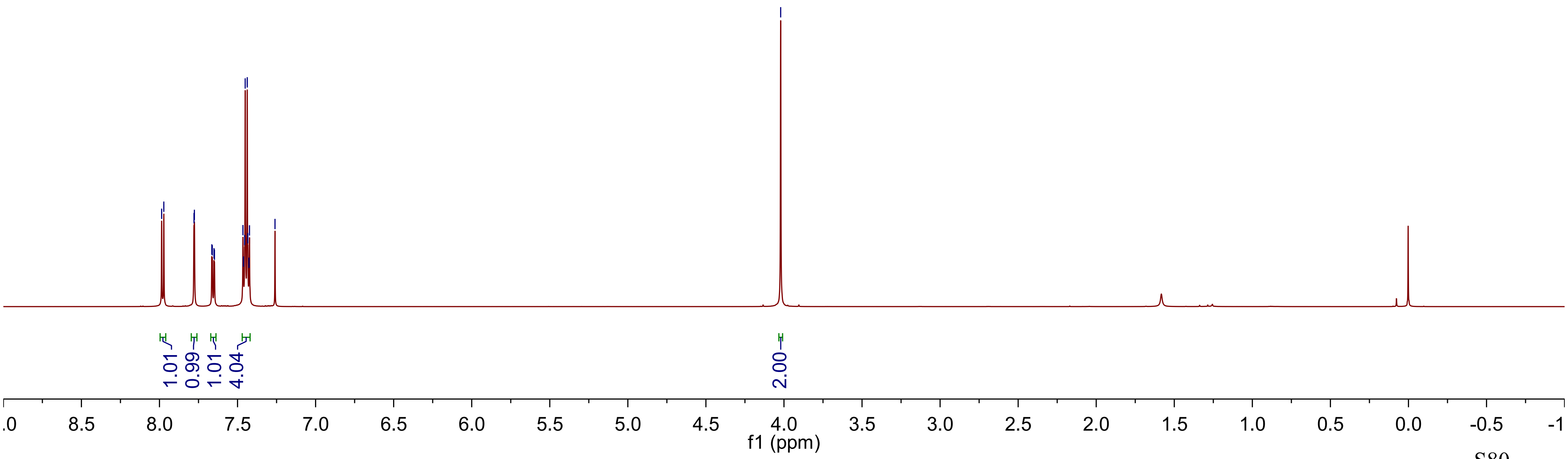
24

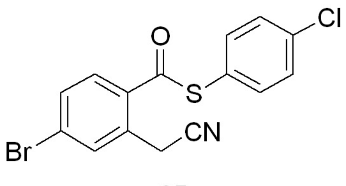
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150



25

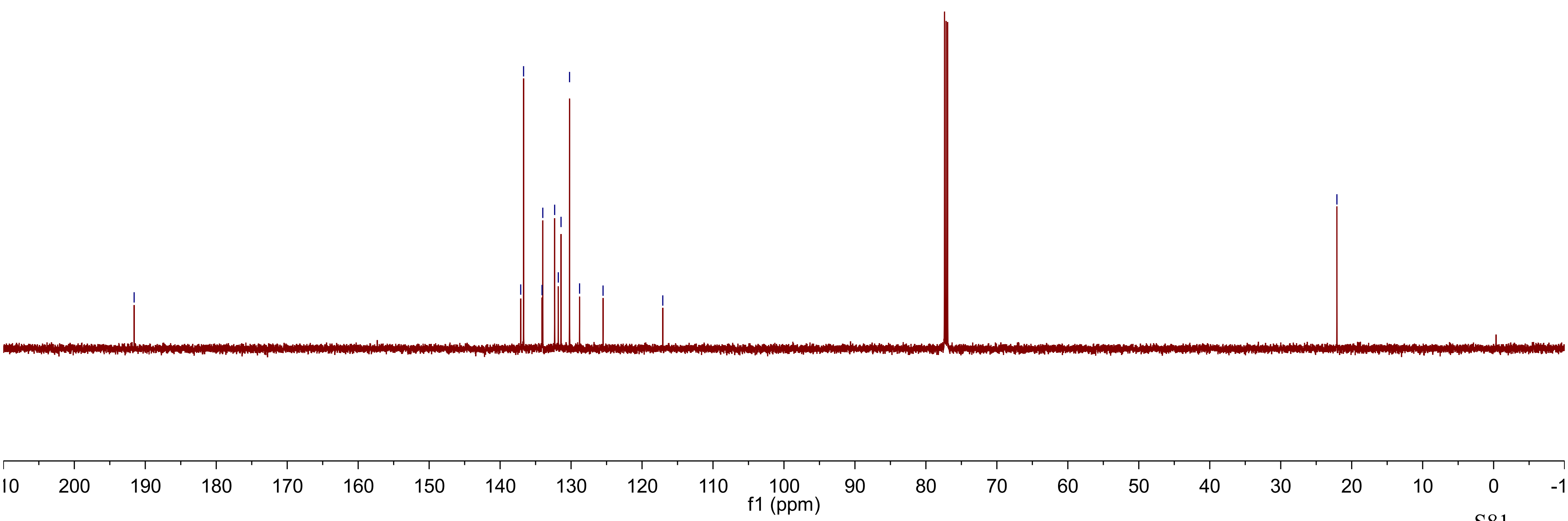
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

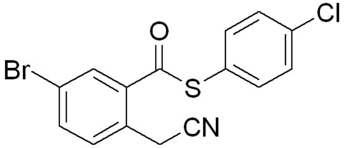




25

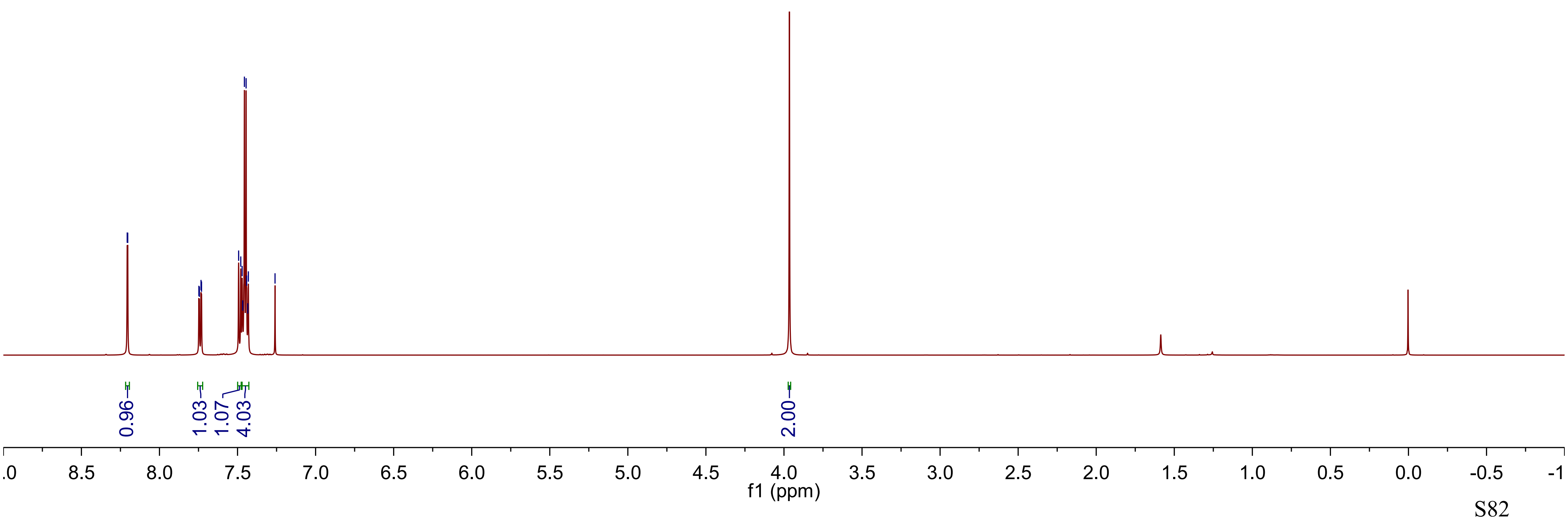
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

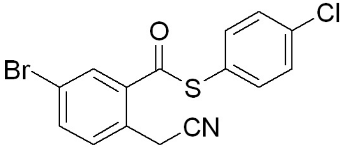




26

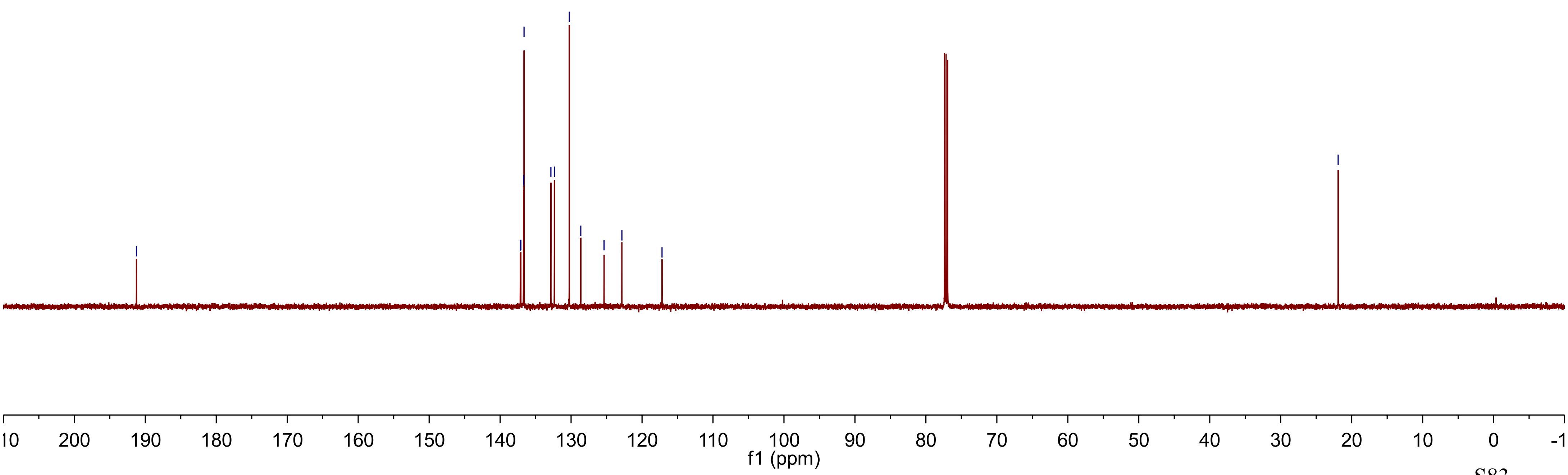
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

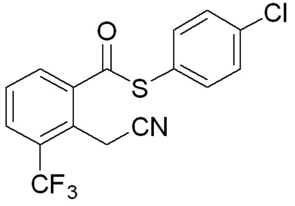




26

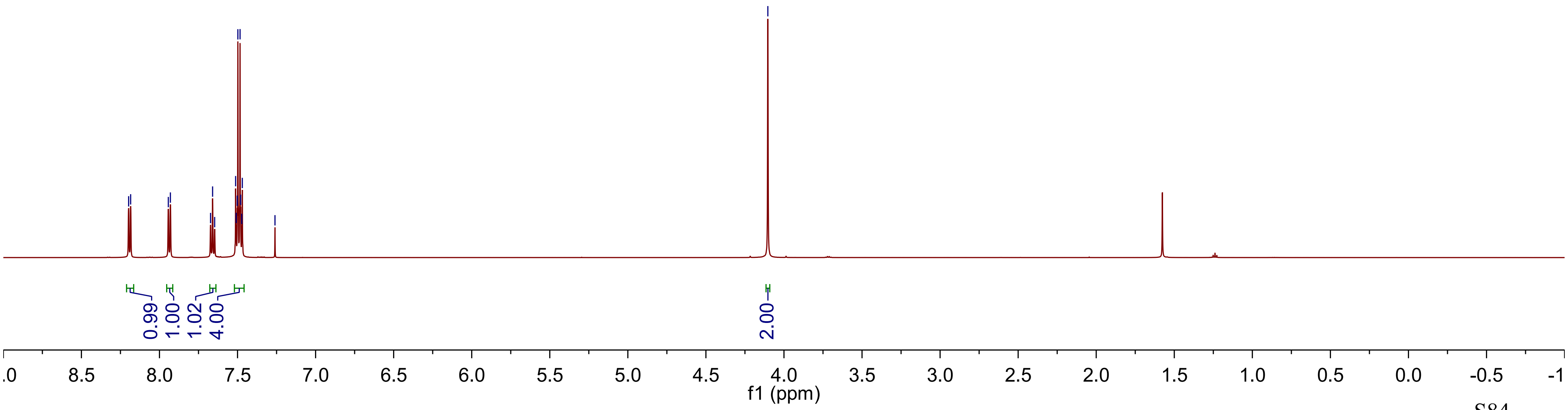
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

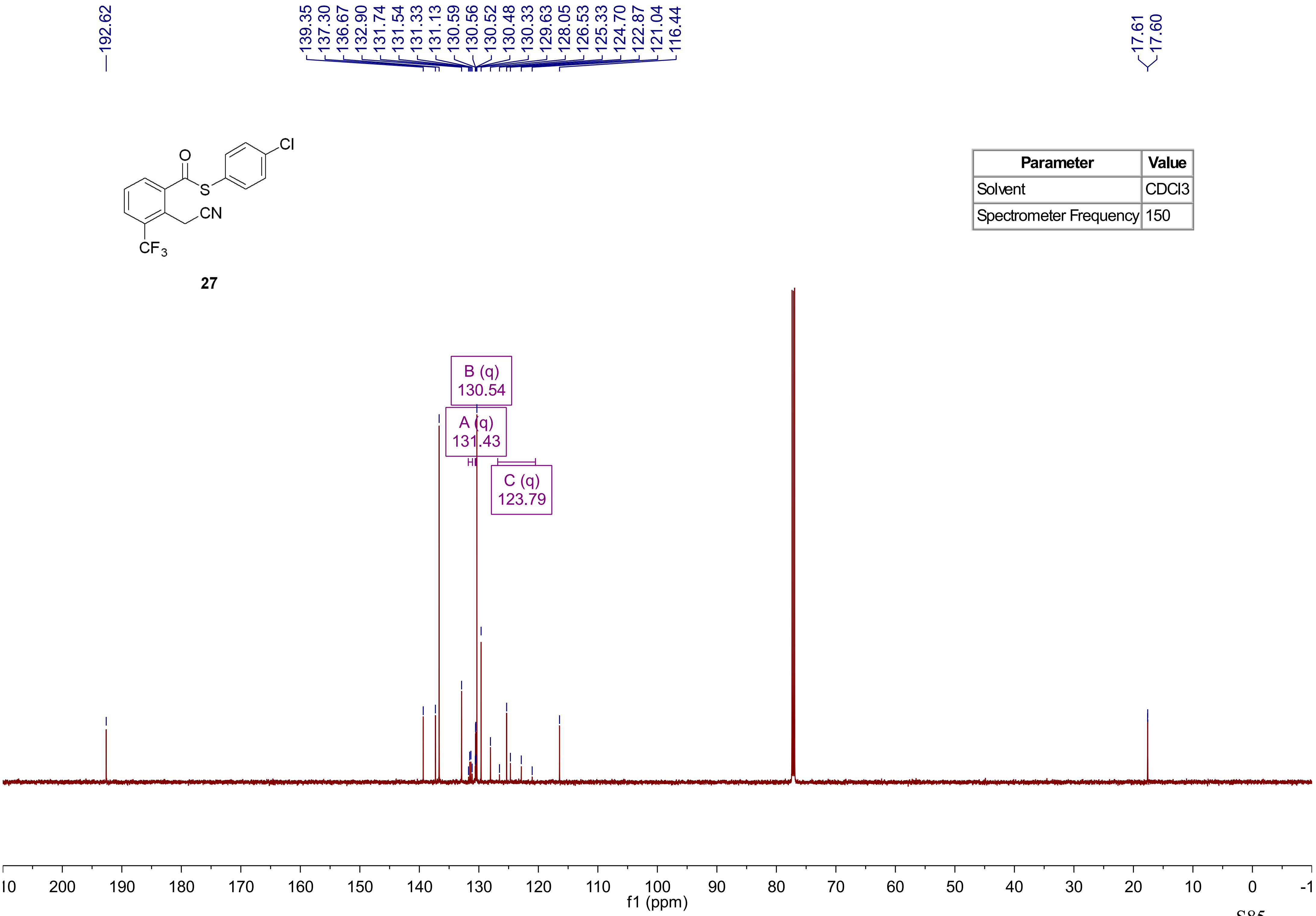




27

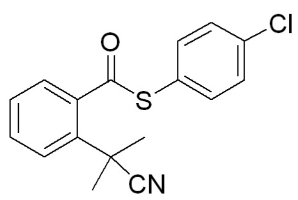
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600





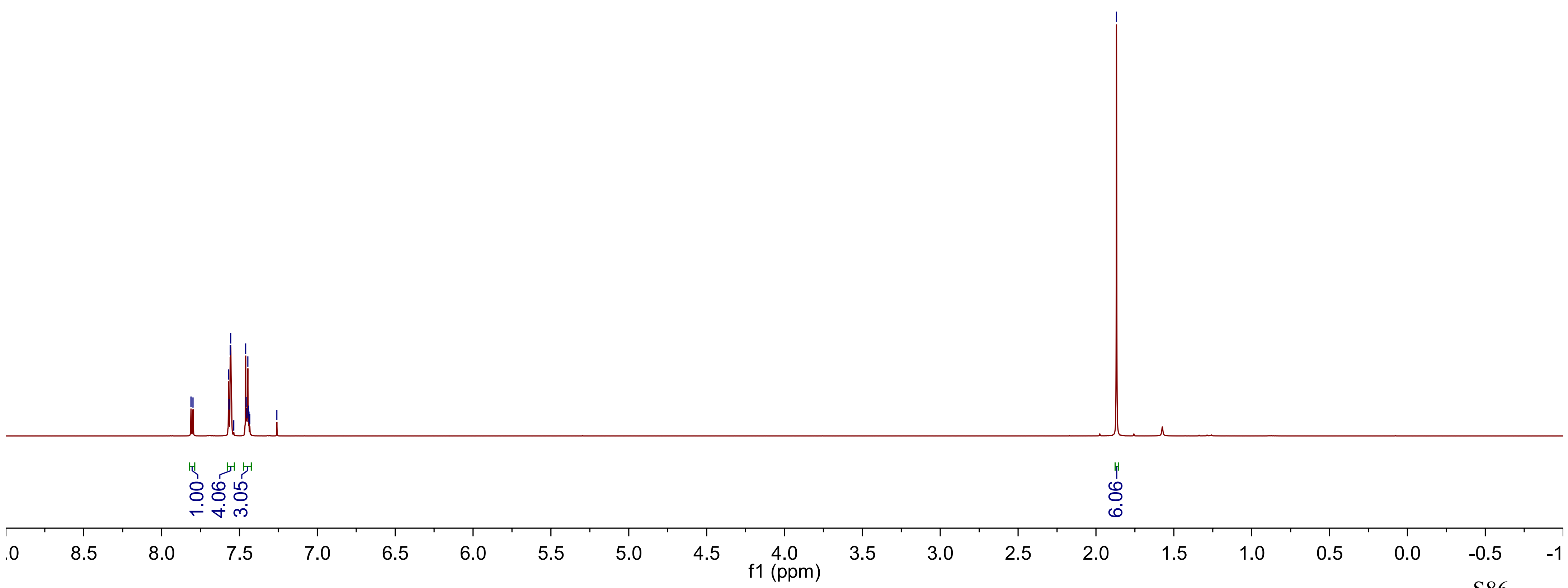
27

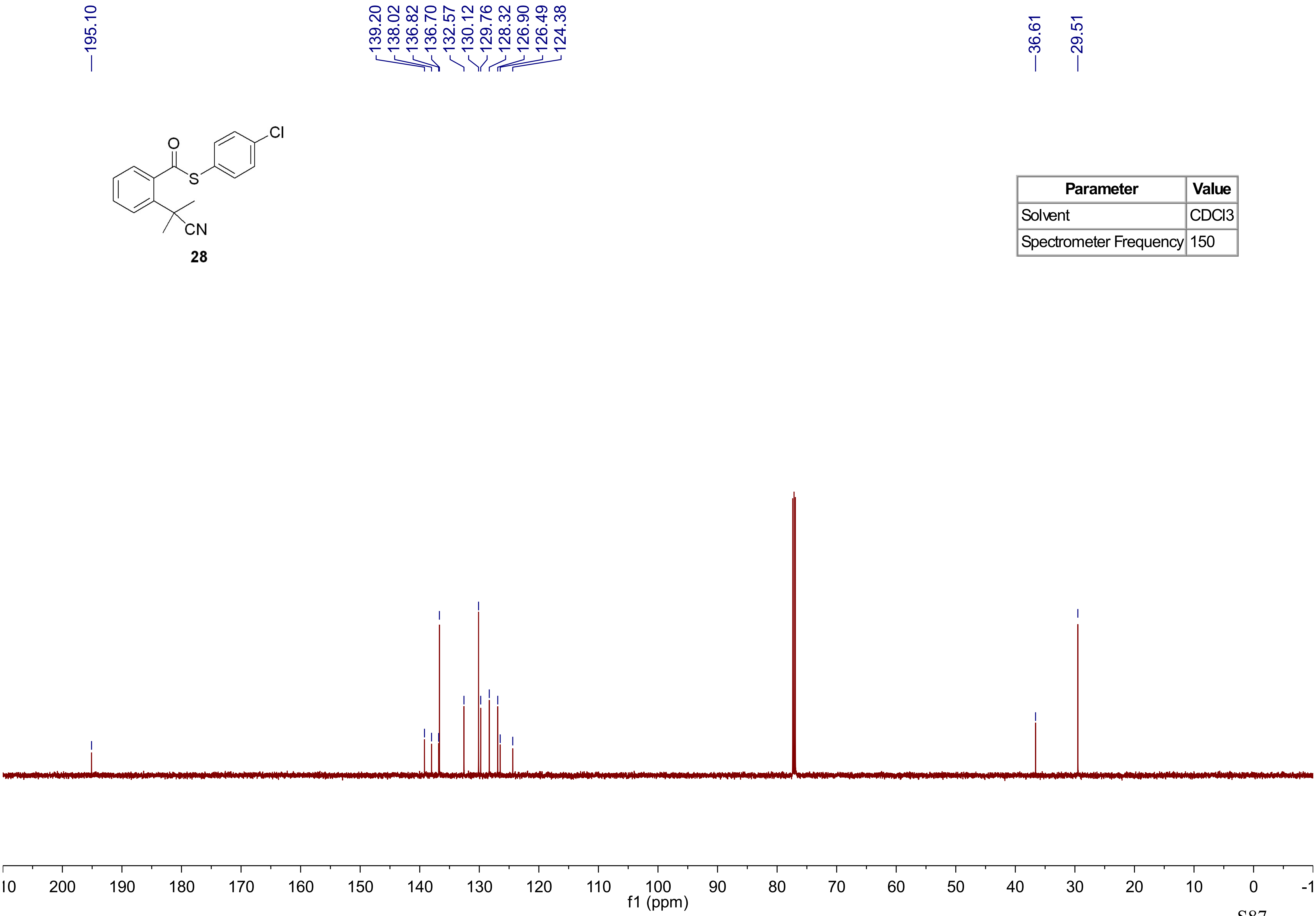
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150



28

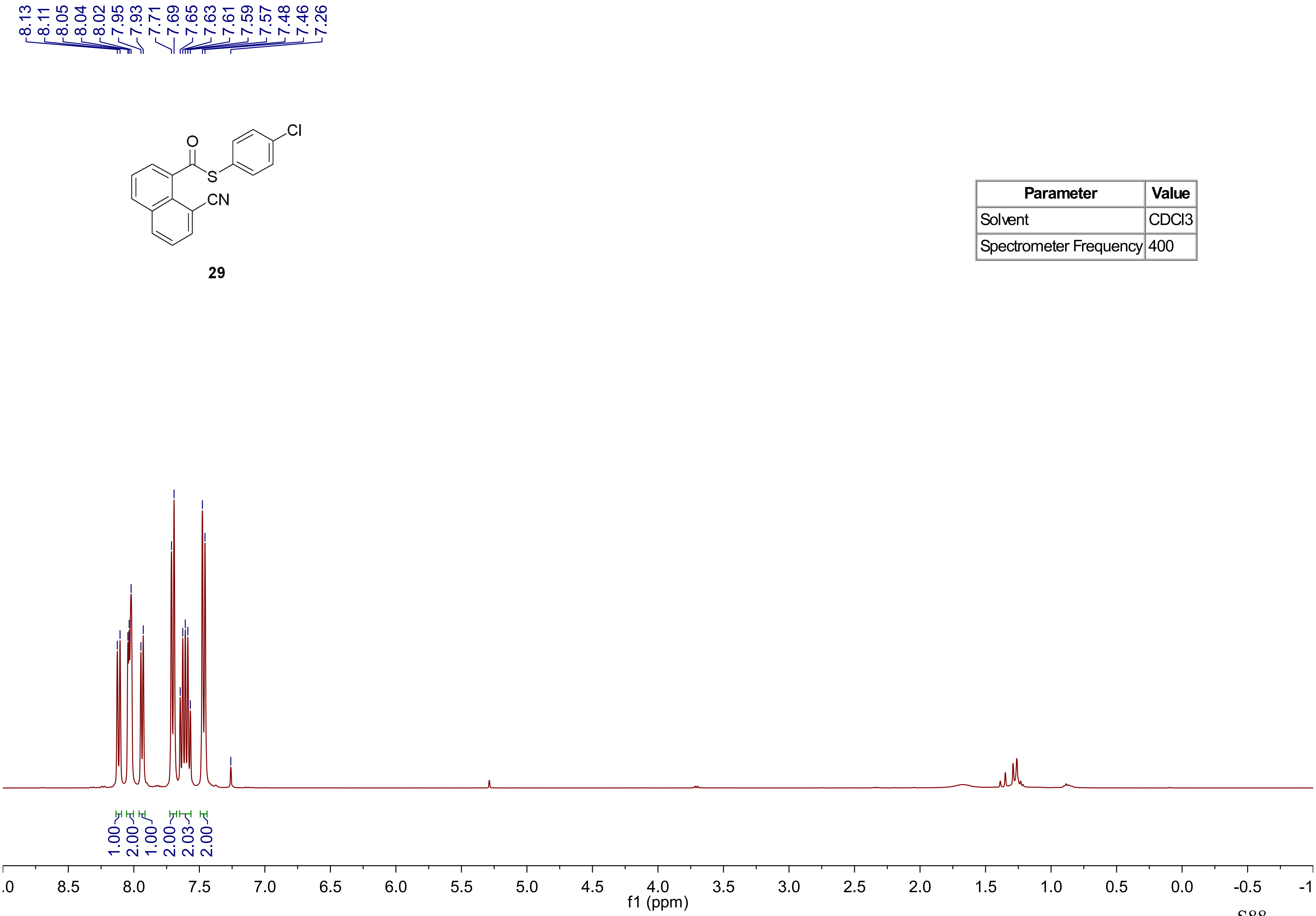
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600





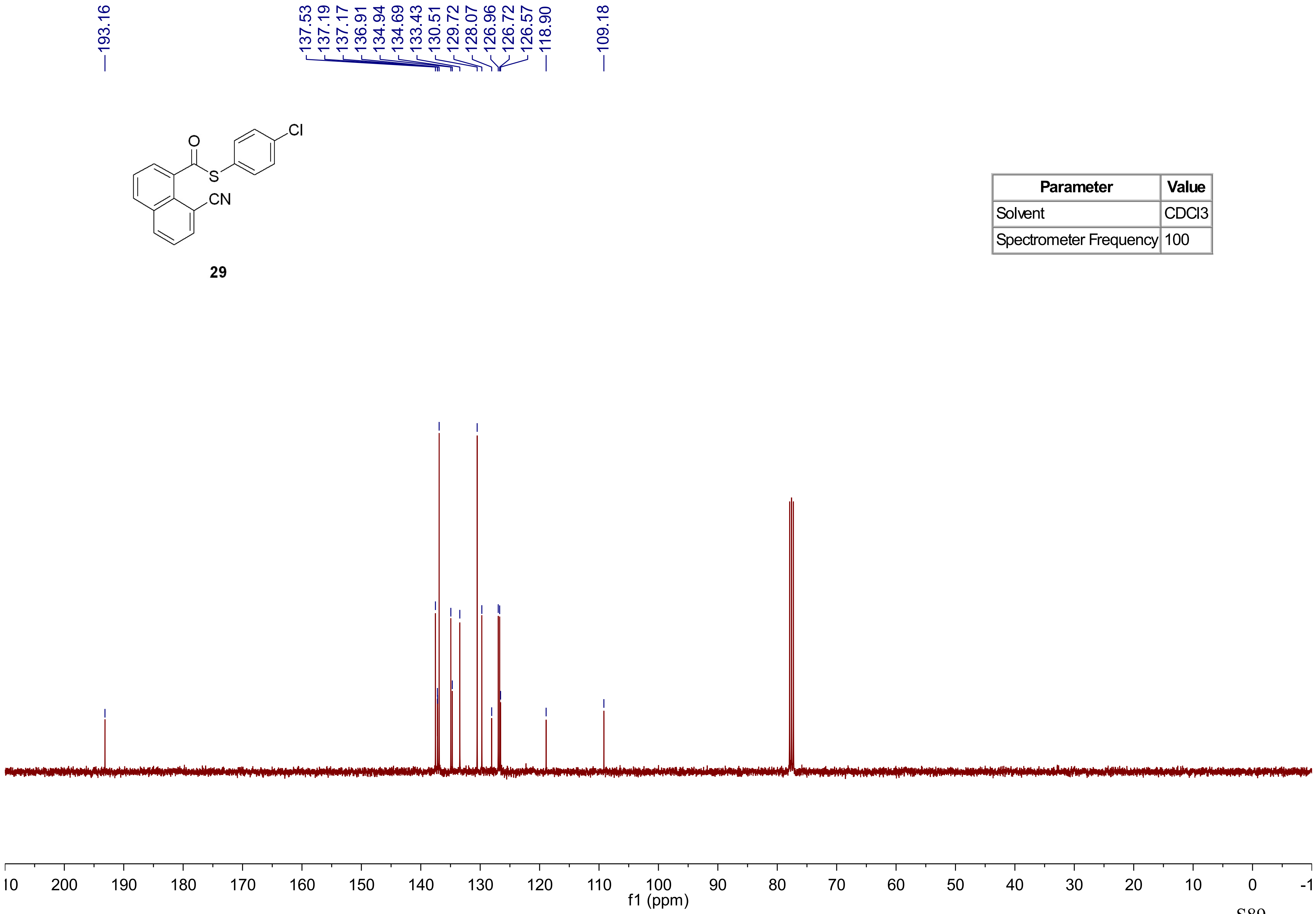
28

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150



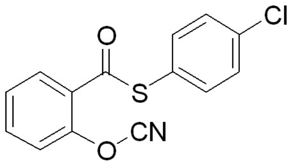
29

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	400



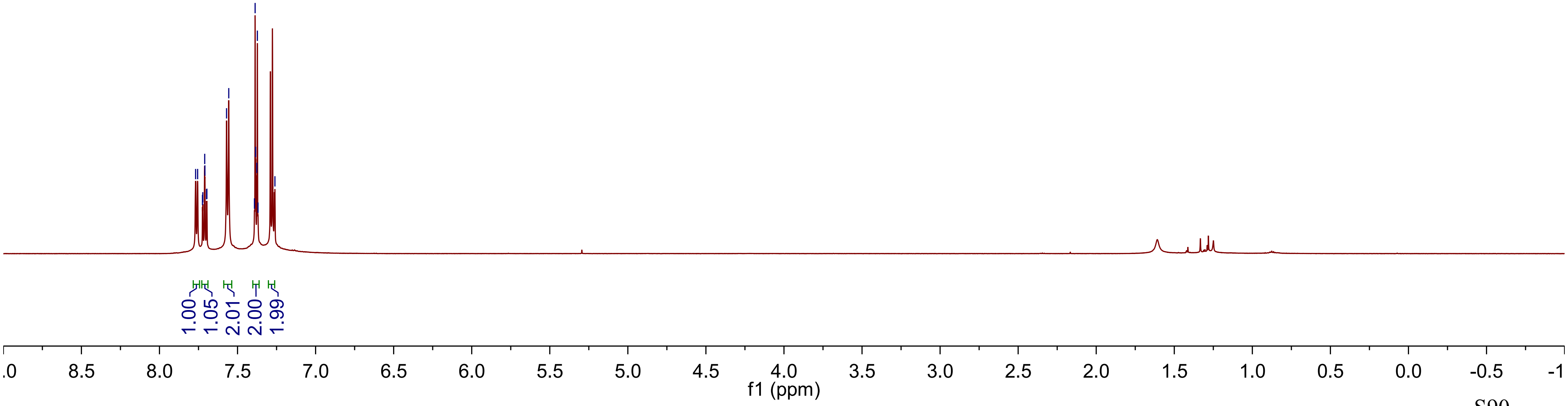
29

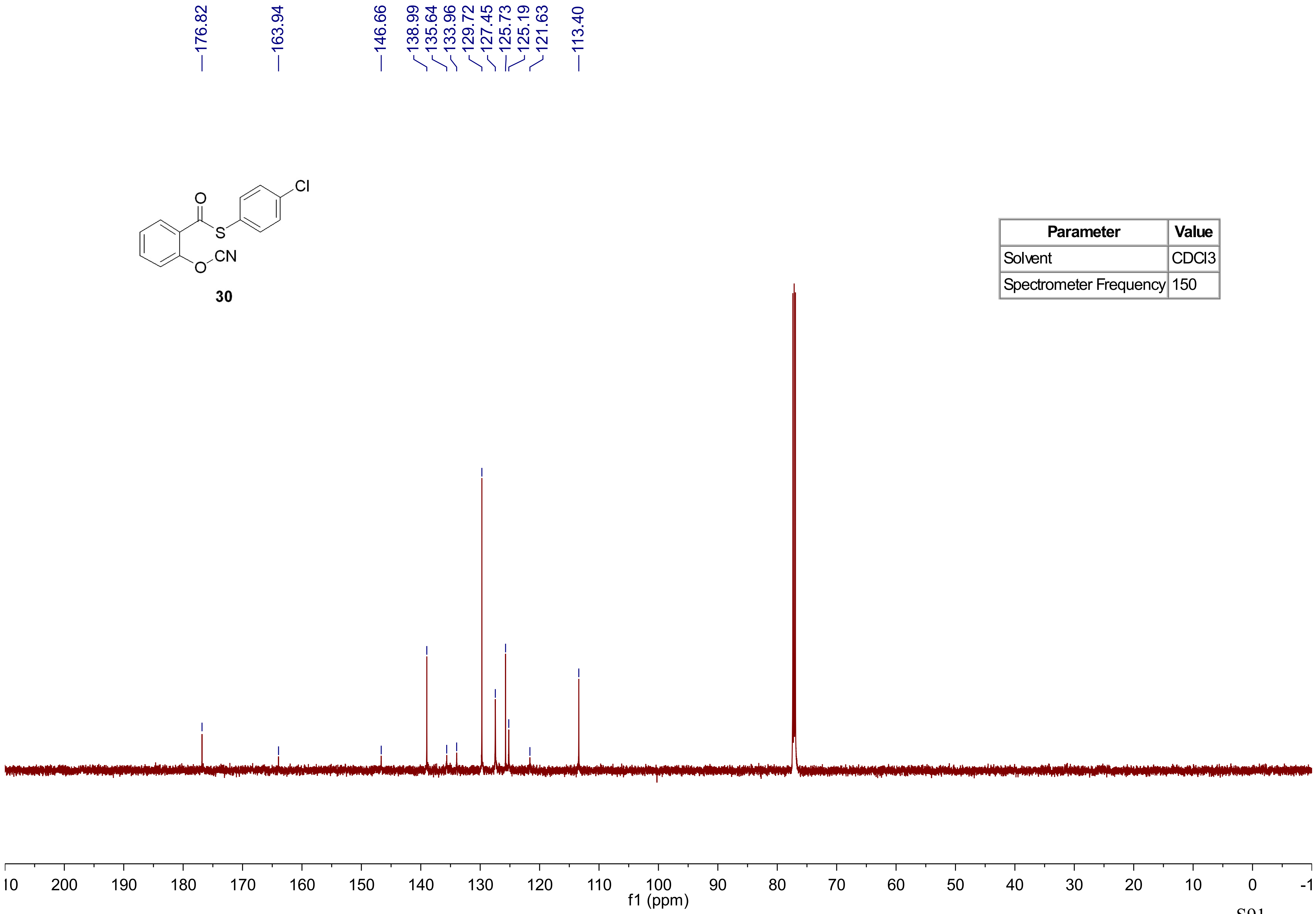
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	100



30

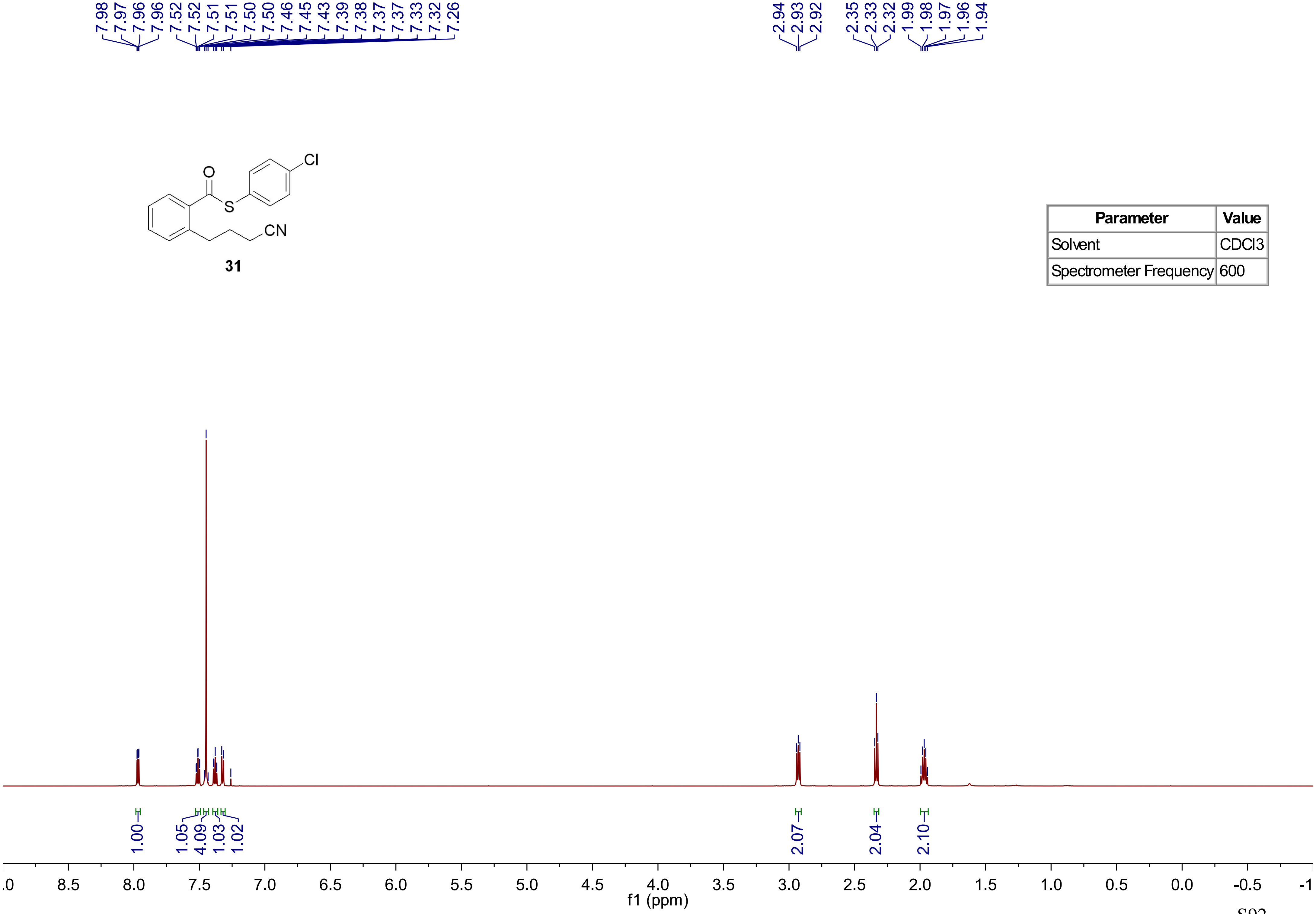
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



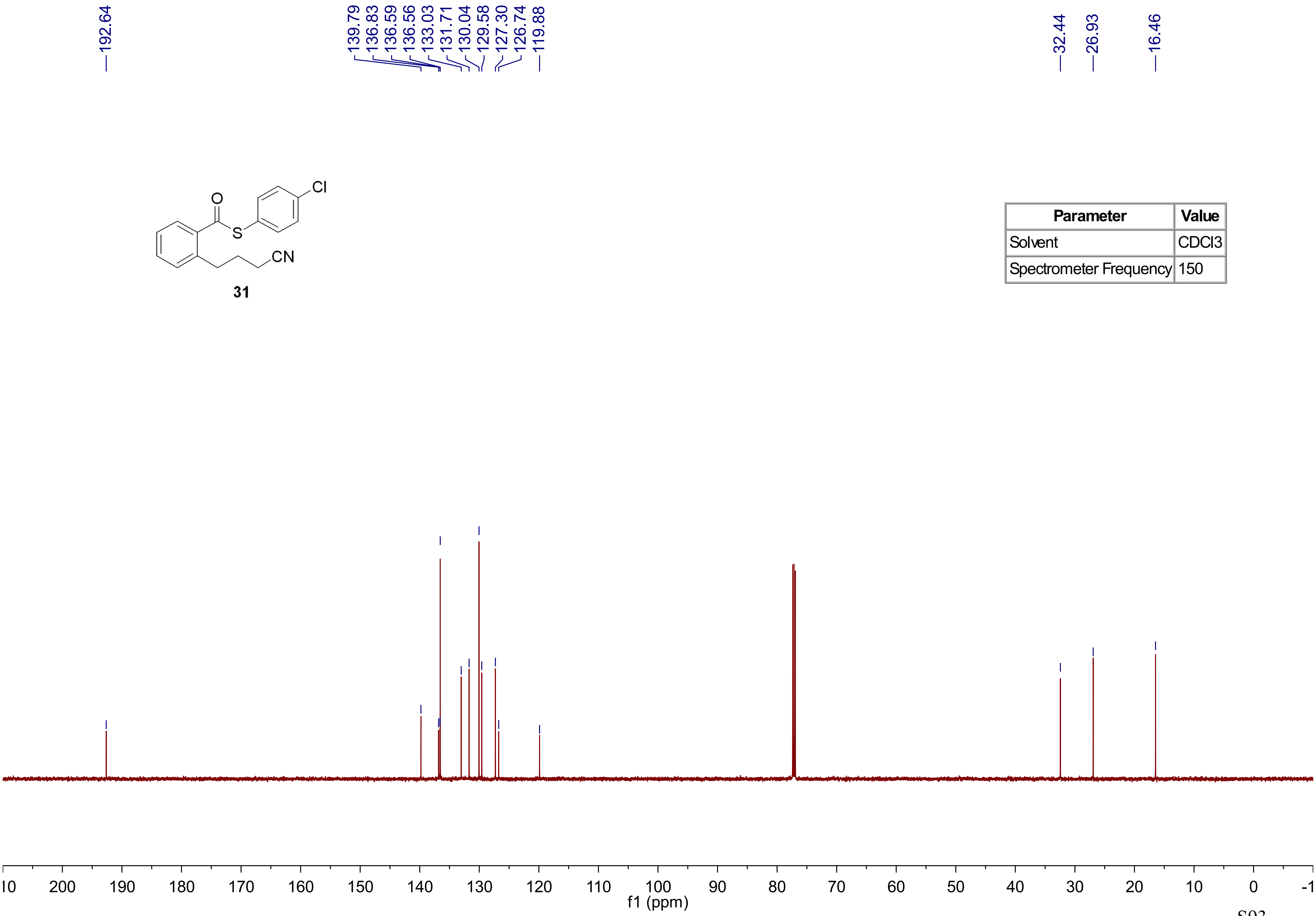


30

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

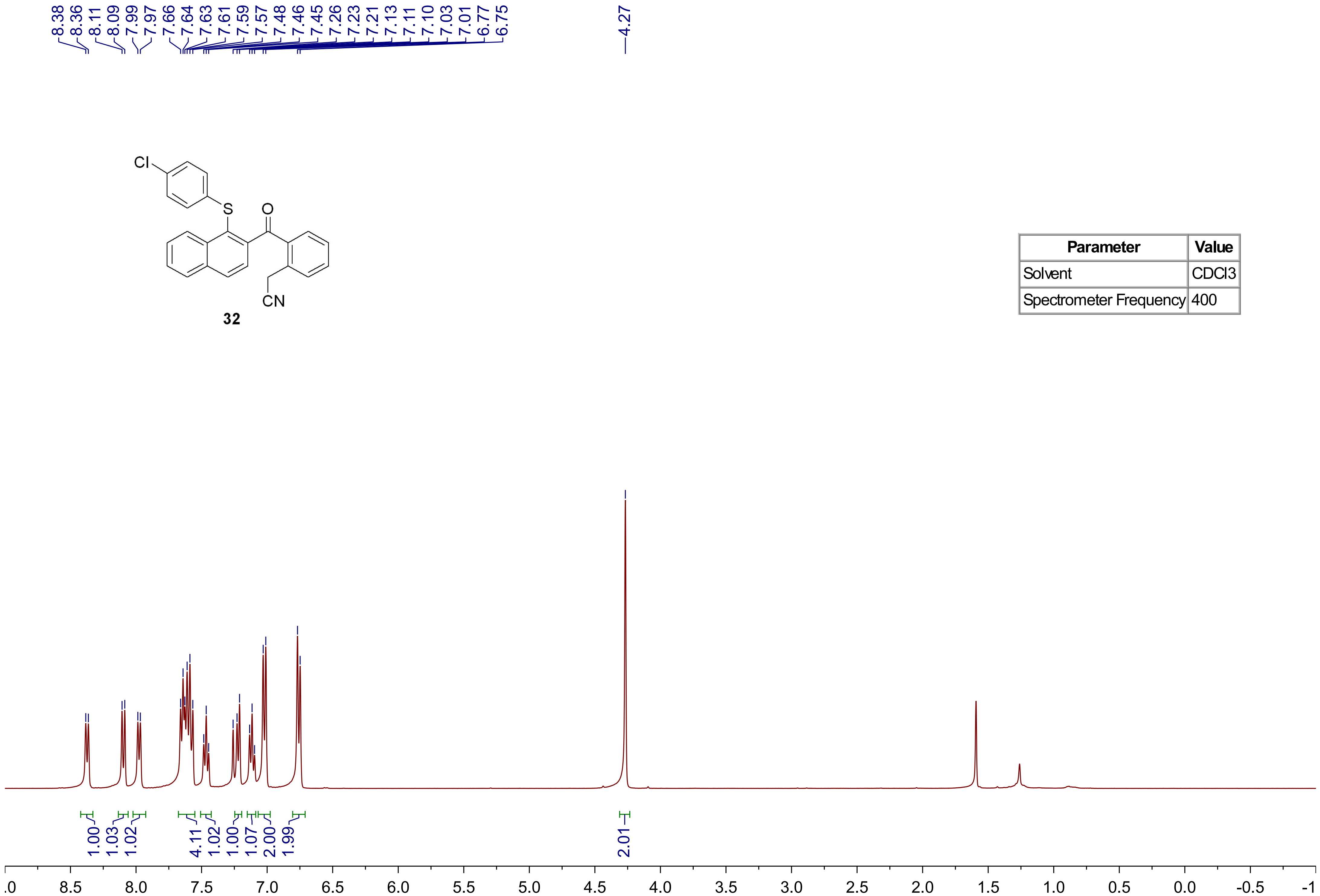


Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



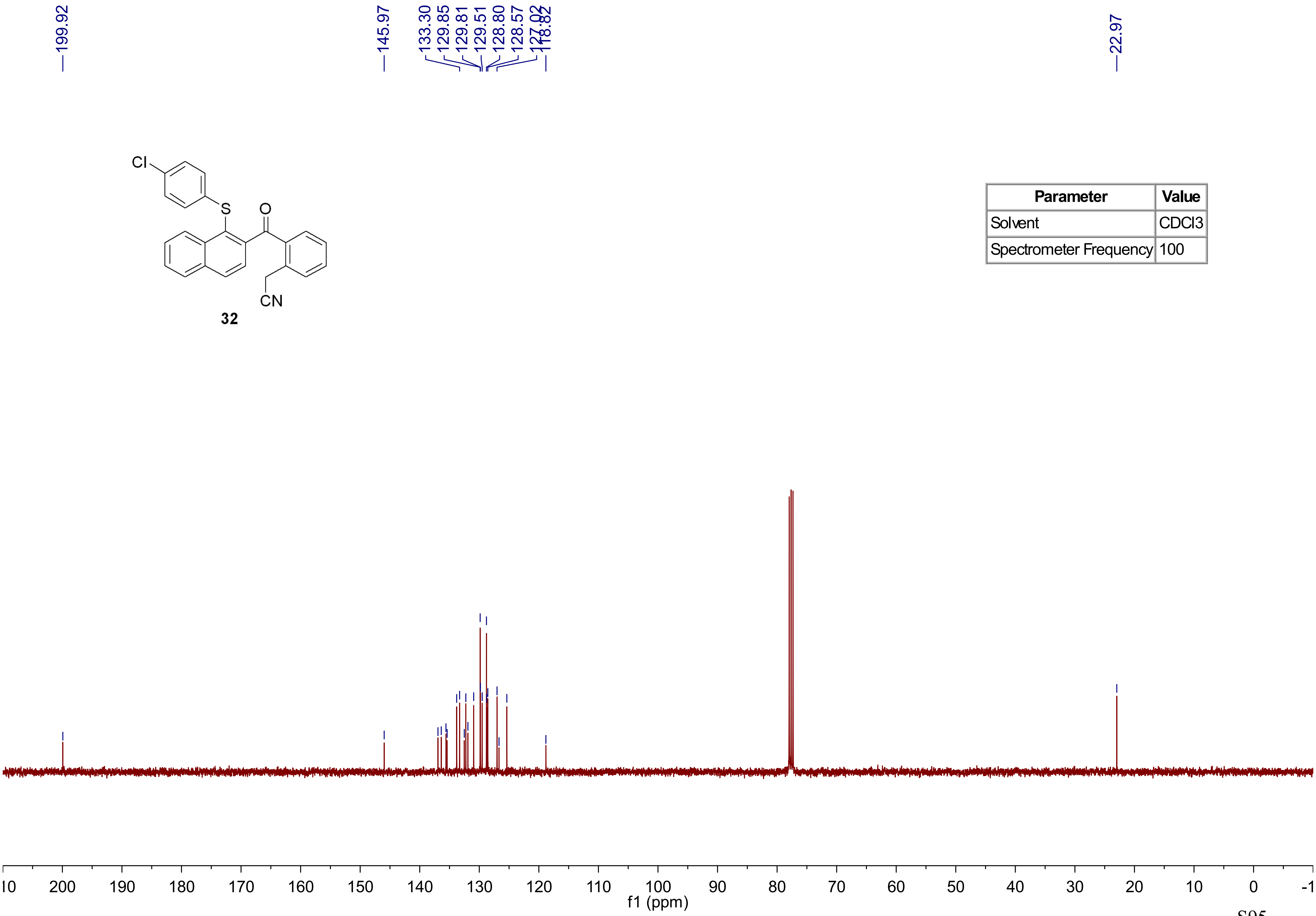
31

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

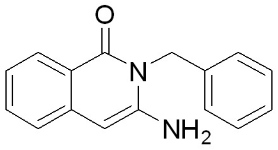


32

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	400

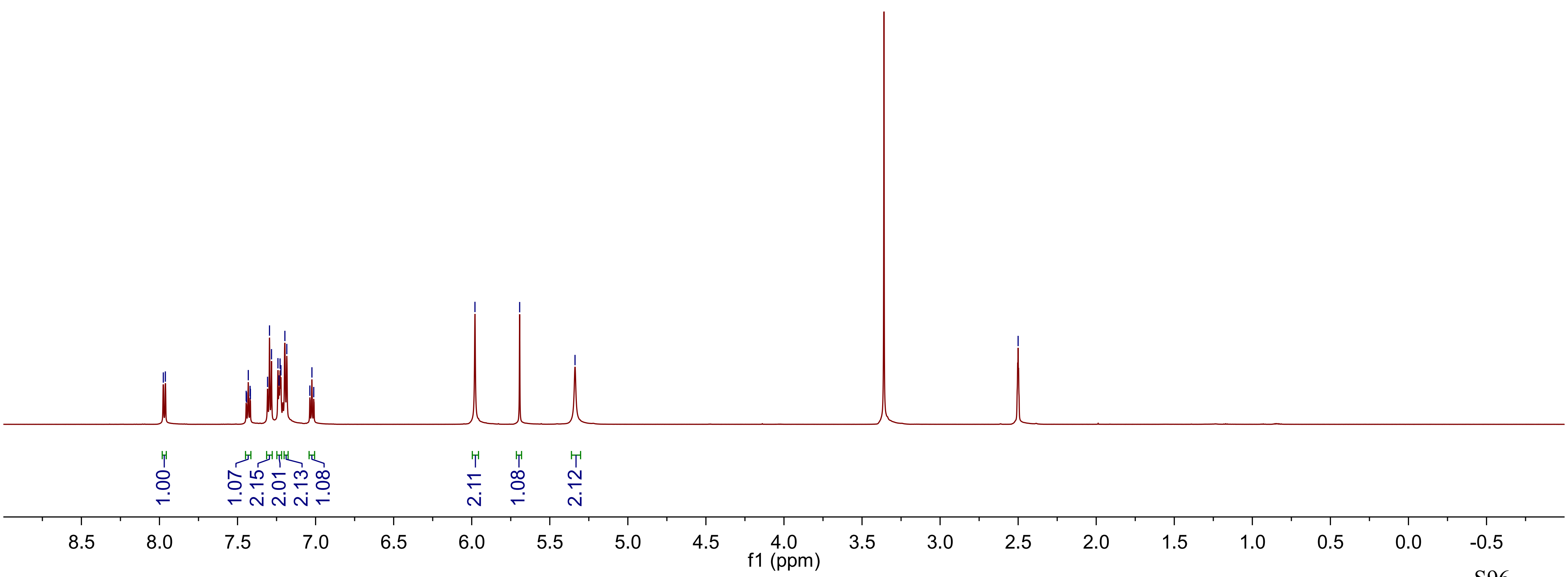


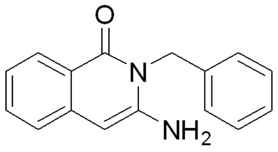
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	100



33

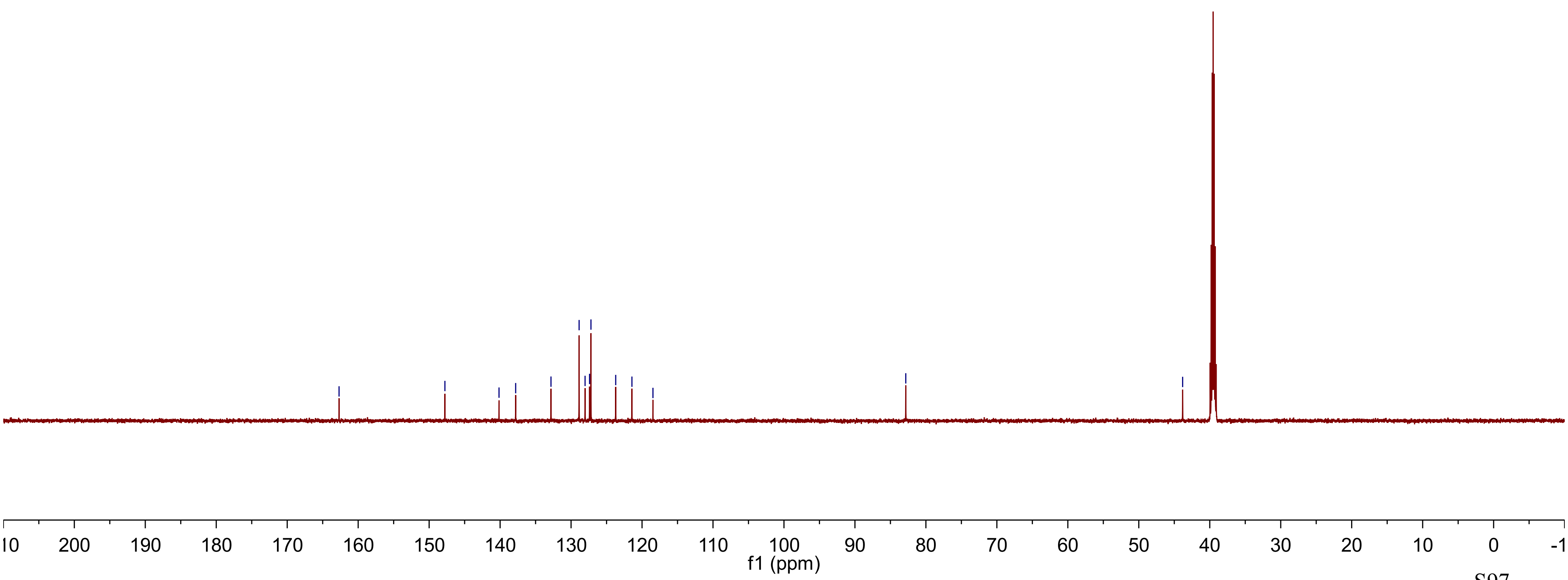
Parameter	Value
Solvent	DMSO
Spectrometer Frequency	600

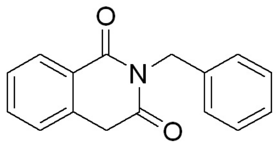




33

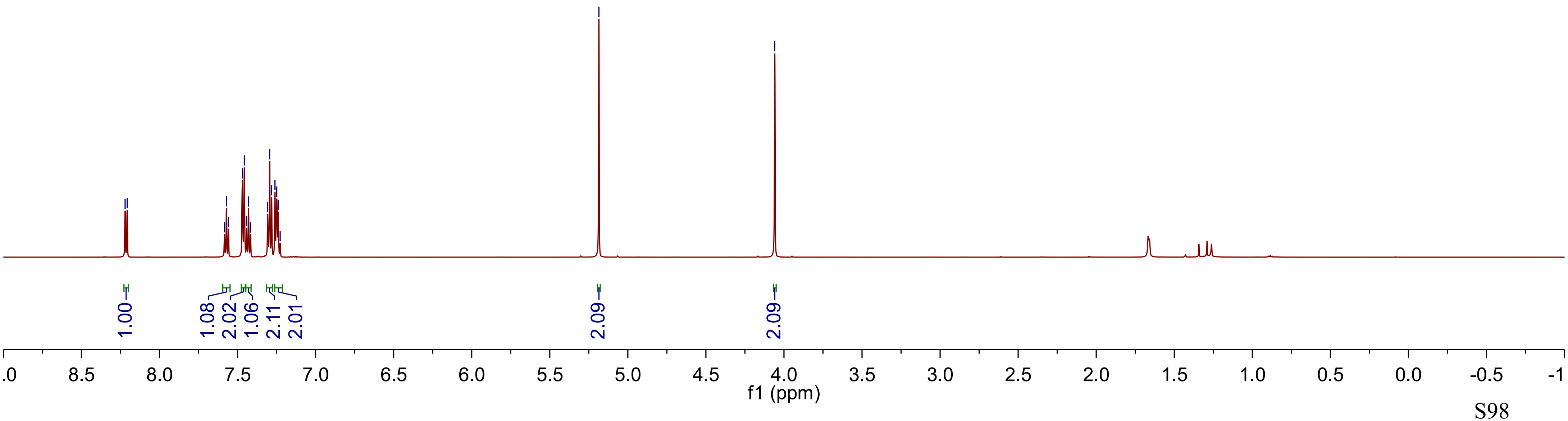
Parameter	Value
Solvent	DMSO
Spectrometer Frequency	150

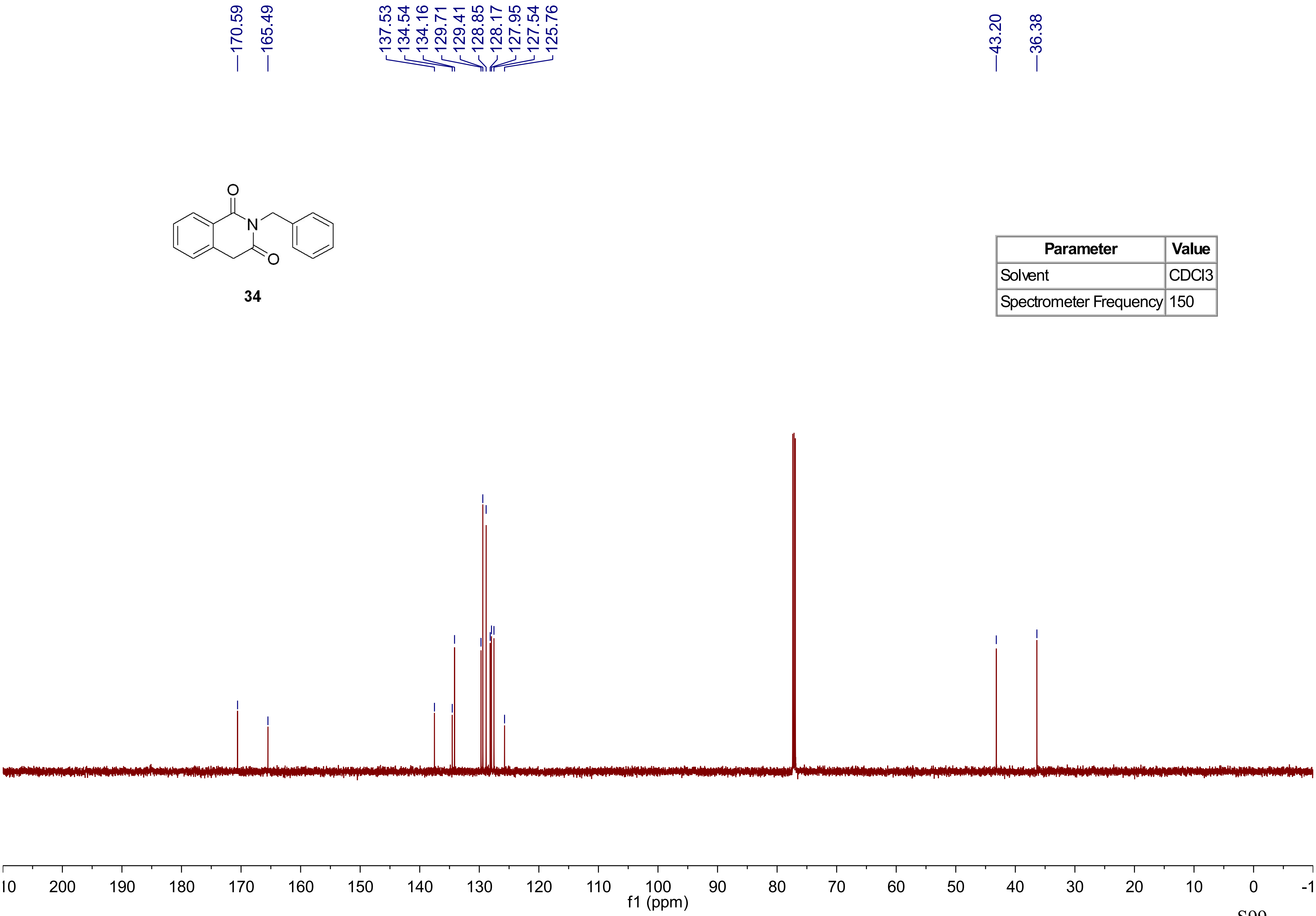




34

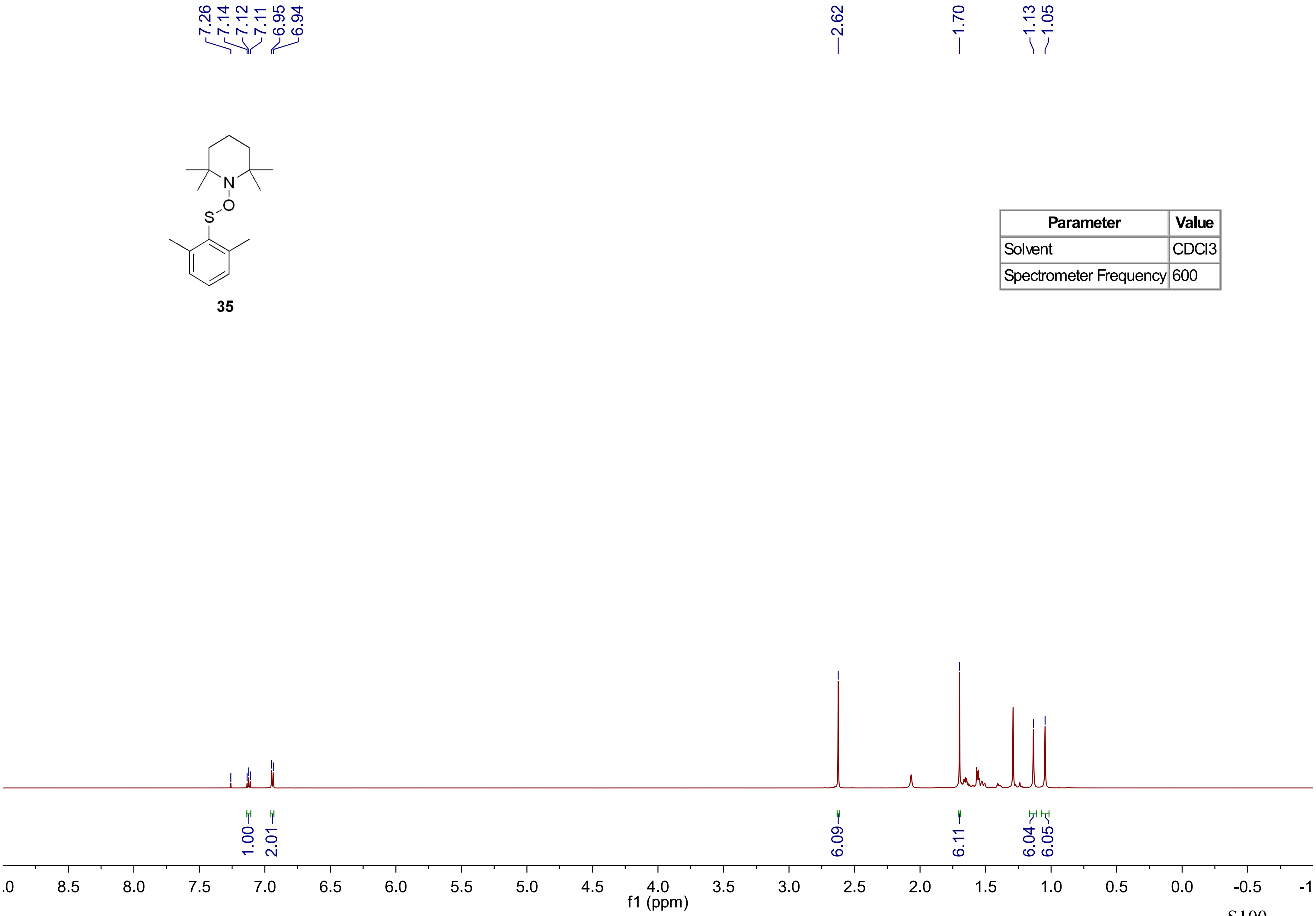
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600





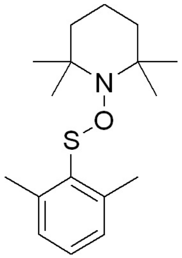
34

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150



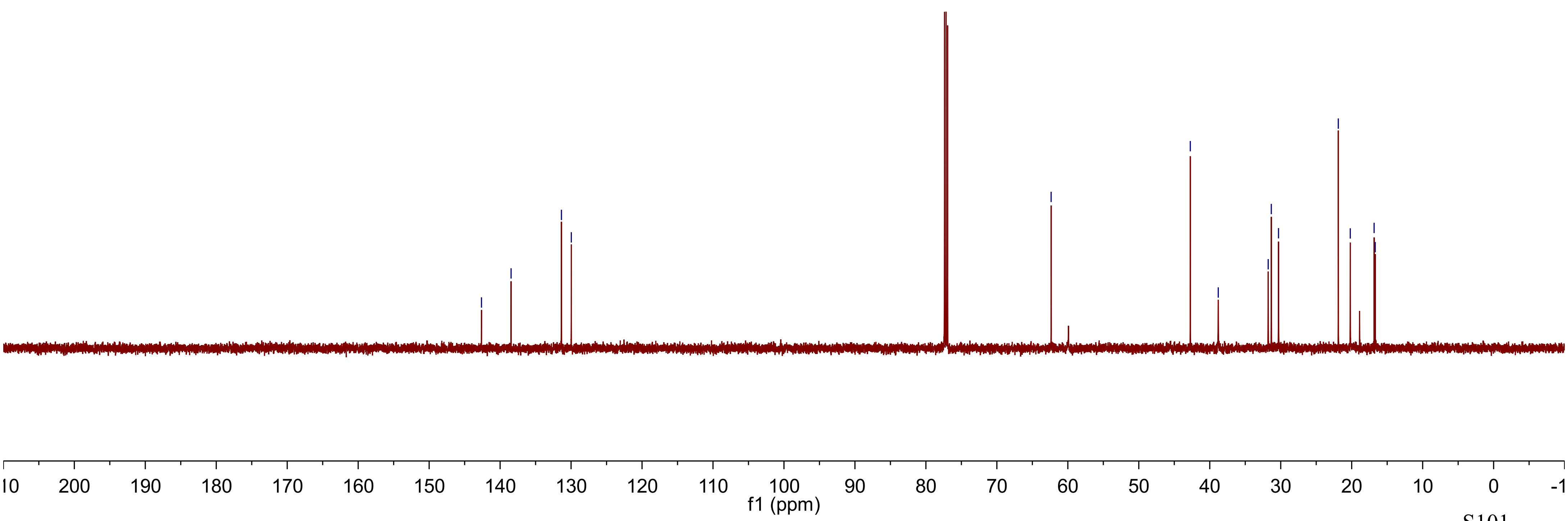
35

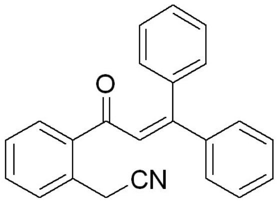
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



35

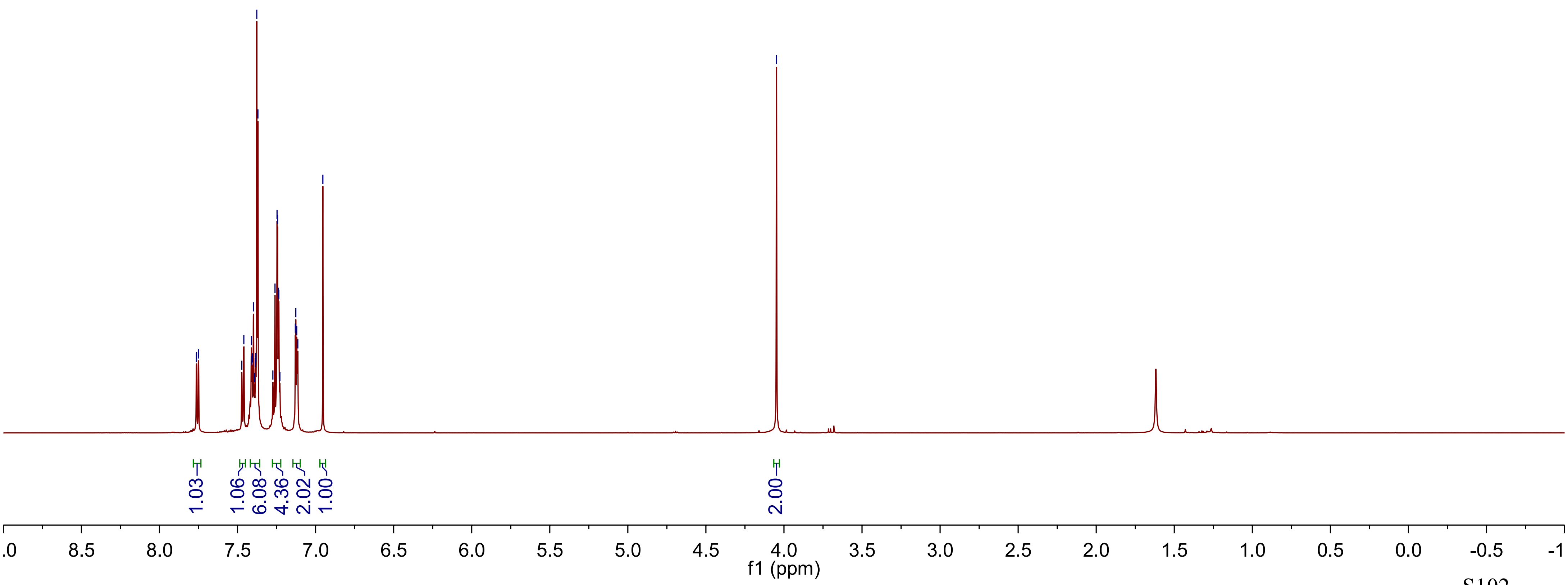
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

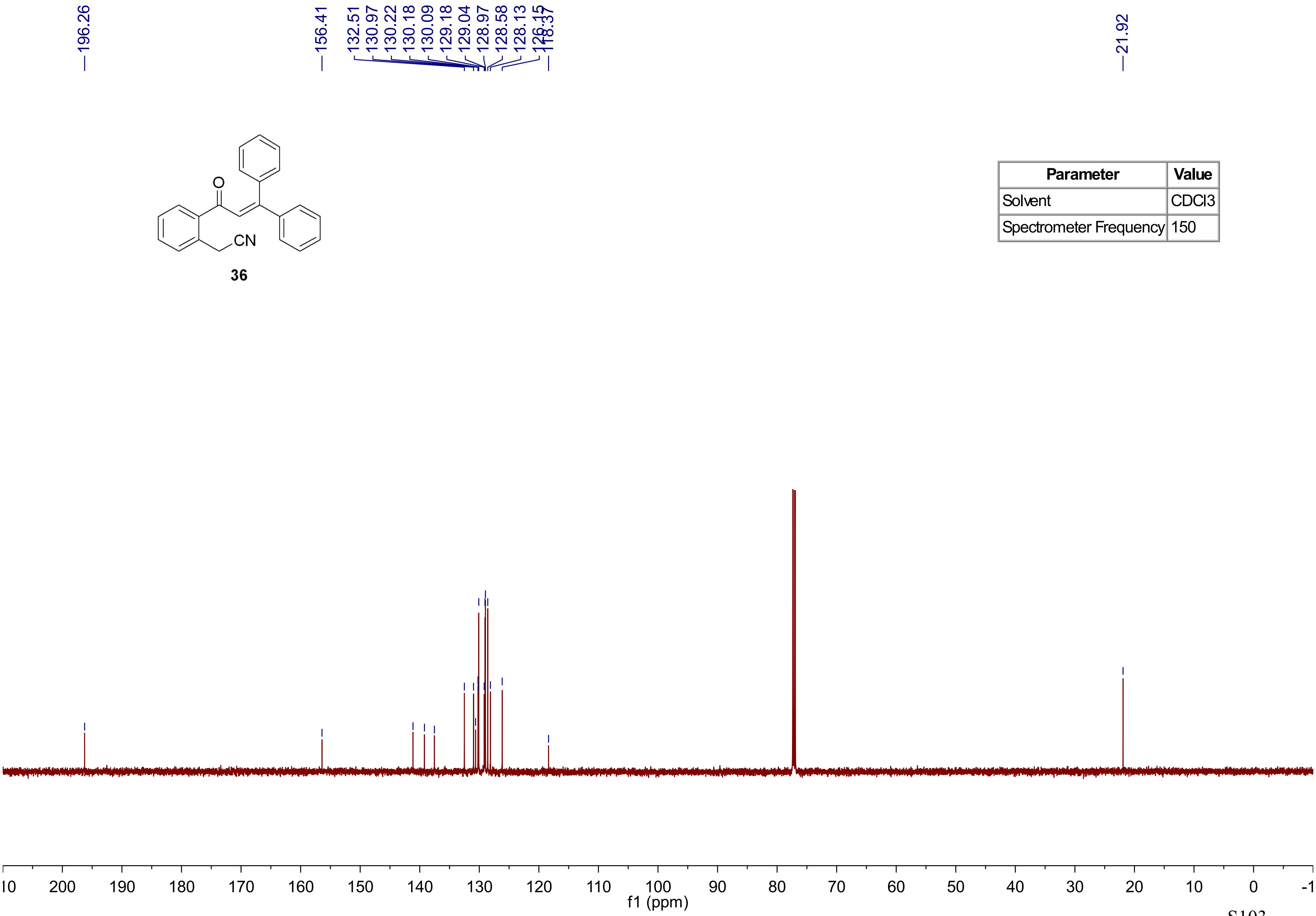




36

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600





36

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150