Electronic Supplementary Information (ESI) for

Cu-catalyzed coupling of indanone oxime acetates with thiols to 2,3-difunctionalized indenones

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I. General Information and Materials

General Information

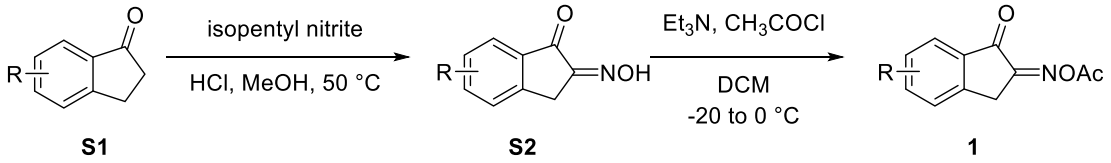
Unless otherwise stated, all glassware was oven dried. All reagents were used as received from commercial suppliers unless otherwise indicated. Reactions were monitored using Thin Layer Chromatography (TLC) carried out on Merck silica gel plates (60F-254) using UV light as the visualizing agent and High 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 Agilent 6500 QTOFMS-ESI, ABSCIEX TripleTOF 5600+ QTOFMS and a Thermo Fisher LTQ OrbitrapXl. 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-d_6, 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

All reagents asused as dimethyl sulfoxide (DMSO), N,N-dimethylformamide(DMF), N,N-dimethylacetamide(DMA), superdry dichloromethane(DCM), superdry tetrahydrofuran (THF), superdry acetonitrile(CH_3CN), superdry 1,4-dioxane and ethyl acetate(EA) used as received from commercial sources and used without further purification. Flash column chromatography was performed using 200-300 mesh silica gel as the stationary phase. The 1-indanone-derived oxime acetates were synthesized according to the reported literatures.[1,2]

Preparation of 1-indanone-derived oxime esters

General Procedure A:



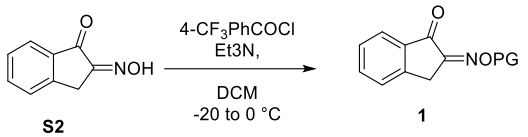
S1 S2 1

To a solution of 1-indanone **S1** (10 mmol) in methanol (20 mL) was added conc. HCl (480 μL, 5.7 mmol) followed by isoamyl nitrite (1.7 mL, 12 mmol) dropwise. The reaction was kept stirring at 40 °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**.

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**.

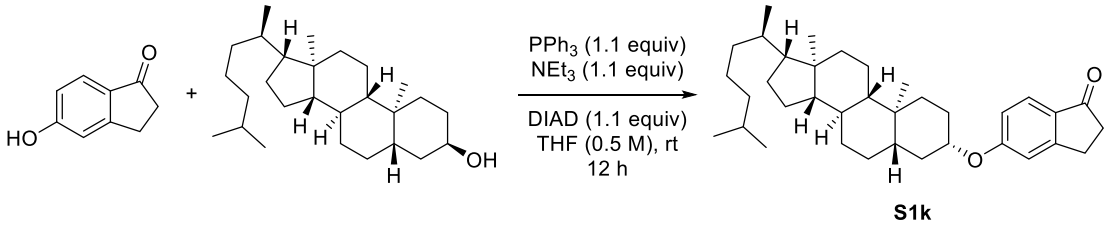
General Procedure B



PG = 4-(trifluoromethyl)benzoyl.

To a mixture of 2-oximino-1-indanon **S2** (5 mmol), DCM (15mL), Et3N (1.1mL, 7.5mmol) in a 100 mL flask was added (trifluoromethyl)benzoyl chloride (1.14 mL, 7.5mmol) dropwise at -20 °C and the mixture was stirred at 0 °C for 2 h. After then, a saturated solution of aqueous NaHCO3 (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 ester.

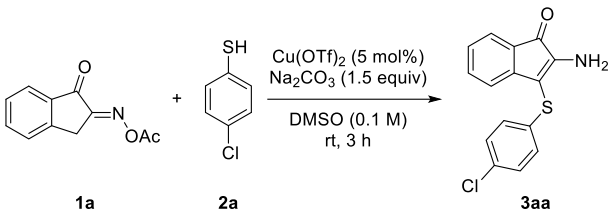
Procedure C for the synthesis of Cholestanol derivative:



To a 100 mL flask with a stir bar was added 5-hydroxy-2,3-dihydro-1H-inden-1-one (755.9 mg, 5 mmol), dihydrocholesterol (2.18 g, 5.5 mmol), PPh_3 (1.47 g, 5.5 mmol) and THF (5 mL). The solution was then added NEt_3 (772 µL, 5.5 mmol) and DIAD (1.1 mL, 5.5 mmol). After being stirred at room temperature for 12 h, the reaction mixture was concentrated under reduced pressure, and then purified by flash column chromatography to silica gel chromatography (20% EtOAc in PE) to afford **S1k** as a white solid in 83% yield (2.45 g).

R_f = 0.37 (20% EA in PE)

II. Optimization of the Reaction Conditions



1a 2a 3aa

Table S1. Optimization of the reaction conditions[a]

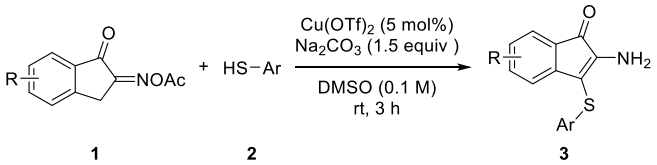
Entry	Catalyst (mol %)	Base	Solvent	T (℃)	Yield[b] (%)
1	$Cu(OTf)_2$ (5)	Na_2CO_3	DMSO	25	99%
2	$Cu(OTf)_2$ (5)	Na_2CO_3	DMF	25	78%
3	$Cu(OTf)_2$ (5)	Na_2CO_3	DMA	25	90%
4	$Cu(OTf)_2$ (5)	Na_2CO_3	DCM	25	2%
5	$Cu(OTf)_2$ (5)	Na_2CO_3	EtOAc	25	9%
6	$Cu(OTf)_2$ (5)	Na_2CO_3	THF	25	13%
7	$Cu(OTf)_2$ (5)	Na_2CO_3	CH_3CN	25	8%
8	$Cu(OTf)_2$ (5)	Na_2CO_3	1,4-Dioxane	25	23%
9	$Cu(OAc)_2$ (5)	Na_2CO_3	DMSO	25	56%
10	CuI (5)	Na_2CO_3	DMSO	25	25%
11	CuBr (5)	Na_2CO_3	DMSO	25	51%
12	CuCl (5)	Na_2CO_3	DMSO	25	87%
13	$Cu(OTf)_2$ (10)	Na_2CO_3	DMSO	25	74%
14	$Cu(OTf)_2$ (15)	Na_2CO_3	DMSO	25	76%
15	$Cu(OTf)_2$ (5)	K_2CO_3	DMSO	25	80%
16	$Cu(OTf)_2$ (5)	NaOH	DMSO	25	87%
17	$Cu(OTf)_2$ (5)	Et_3N	DMSO	25	72%
18	$Cu(OTf)_2$ (5)	KO*t*-Bu	DMSO	25	66%
19	$Cu(OTf)_2$ (5)	none	DMSO	25	NR
20	$Cu(OTf)_2$ (5)	Na_2CO_3	DMSO	60	99%
21	$Cu(OTf)_2$ (5)	Na_2CO_3	DMSO	70	66%
22[c]	$Cu(OTf)_2$ (5)	Na_2CO_3	DMSO	25	33%

23[d]	$Cu(OTf)_2$ (5)	Na_2CO_3	DMSO	25	75%
24[e]	$Cu(OTf)_2$ (5)	Na_2CO_3	DMSO	25	89%

[a]Standard conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), $Cu(OTf)_2$ (0.005 mmol, 5 mol%), DMSO (1 mL) , rt, 3 h, N_2. [b]Yields were determined by HPLC analysis with diphenyl sulfide as the internal standard. [c]Under air atmosphere. [d]DMSO (0.05 M). [e]DMSO(1 M)

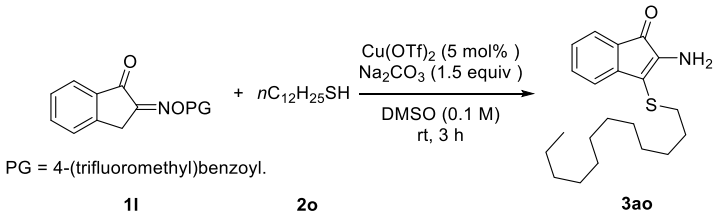
III. Synthesis and Characterization of Product 3.

General Procedure D:



1-Indanone oxime acetate **1** (0.2 mmol, 1 equiv), thiophenol **2** (0.3 mmol, 1.5 equiv), $Cu(OTf)_2$ (3.7 mg, 0.01 mmol, 5 mol%), and Na_2CO_3 (32.1 mg, 0.3mmol, 1.5 equiv) was added to a 25 mL flask with a stir bar. Then DMSO (2 mL) was added to the flask through the rubber septum using syringes. Subsequently, the reaction mixture was stirred at room temperature. After the completion of the reaction indicated by TLC (≈ 3 h), the reaction mixture was quenched by water and was extracted by EtOAc for three times. The combined organic layer was dried over anhydrous sodium sulfate, filtered, concentrated, and then purified by flash chromatography on silica gel to provide the corresponding products.

Procedure E for the synthesis of product 3ao:



2-(((4-(trifluoromethyl)benzoyl)oxy)imino)-2,3-dihydro-1*H*-inden-1-one **1l** (0.2 mmol, 1 equiv), 1-dodecanethiol **2o** (0.42 mmol, 2.1 equiv), $Cu(OTf)_2$ (3.7 mg, 0.01 mmol, 5 mol%), and Na_2CO_3 (32.1 mg, 0.3mmol, 1.5 equiv) was added to a 25 mL flask with a stir bar. Then dimethyl sulfoxide (2 mL) was added to the flask through the rubber septum using syringes. Subsequently, the reaction mixture was stirred at room temperature. After the completion of the reaction indicated by TLC (≈ 3 h), the reaction mixture was quenched by water and was extracted by EtOAc for three times. The combined organic layer was dried over anhydrous sodium sulfate, filtered, concentrated, and then purified by flash chromatography on silica gel to provide the corresponding product **3ao**.

10.5 mg, 15%. Black solid.

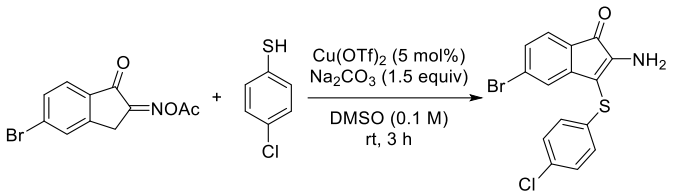
R_f = 0.48 (3% EA in PE)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, J = 7.4 Hz, 2H), 6.92 - 6.86 (m, 2H), 4.27 (s, 2H), 2.81 - 2.63 (m, 2H), 1.60 (dt, J = 14.9, 7.3 Hz, 3H), 1.44 - 1.33 (m, 2H), 1.27 - 1.21 (m, 15H), 0.88 (t, J = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 148.9, 144.3, 135.8, 128.8, 125.4, 122.7, 118.0, 114.8, 32.8, 31.8, 30.5, 29.5, 29.42, 29.35, 29.2, 29.0, 28.5, 22.5, 21.2, 13.9.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{21}H_{32}NOS$ 346.2199, found 346.2196.

Procedure F for the synthesis of product 3ga:



1g 2a 3ga

2-(acetoxyimino)-5-bromo-2,3-dihydro-1H-inden-1-one **1g** (0.22 mmol, 1.1 equiv), 4-chlorothiophenol **2a** (0.2 mmol, 1 equiv), $Cu(OTf)_2$ (3.7 mg, 0.01 mmol, 5 mol%), and Na_2CO_3 (32.1 mg, 0.3mmol, 1.5 equiv) was added to a 25 mL flask with a stir bar. Then dimethyl sulfoxide (2 mL) was added to the flask through the rubber septum using syringes. Subsequently, the reaction mixture was stirred at room temperature. After the completion of the reaction indicated by TLC (≈ 3 h), the reaction mixture was quenched by water and was extracted by EtOAc for three times. The combined organic layer was dried over anhydrous sodium sulfate, filtered, concentrated, and then purified by flash chromatography on silica gel to provide the corresponding product **3ga**.

73.0 mg, 99%. Black solid.

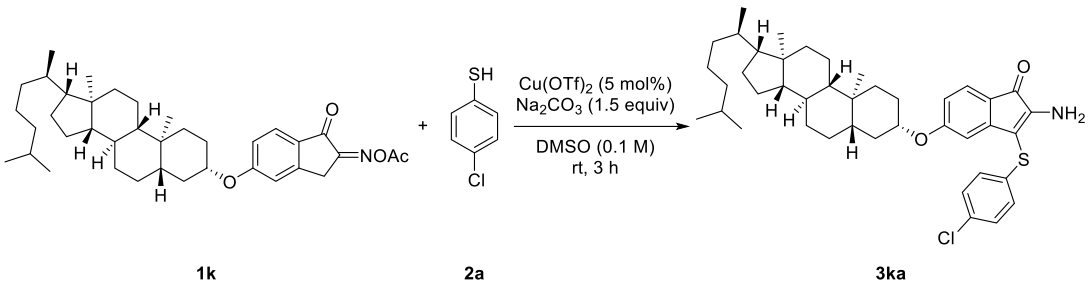
R_f = 0.53 (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 - 7.23 (m, 2H), 7.22 - 7.18 (m, 2H), 7.11 (d, J = 7.6 Hz, 1H), 7.06 (dd, J = 7.6, 1.5 Hz, 1H), 6.82 (d, J = 1.5 Hz, 1H), 4.57 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 190.8, 150.7, 145.9, 132.7, 132.4, 131.4, 129.9, 129.1, 128.2, 127.0, 124.3, 121.8, 107.0.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{15}H_{10}BrClNOS$ 365.9350, found 365.9387.

Procedure G for the synthesis of product 3ka:



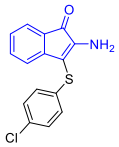
1k 2a 3ka

1-Indanone oxime acetate **1k** (0.2 mmol, 1 equiv), 4-chlorothiophenol **2a** (0.3 mmol, 1.5 equiv), $Cu(OTf)_2$ (3.7 mg, 0.01 mmol, 5 mol%), and Na_2CO_3 (32.1 mg, 0.3mmol, 1.5 equiv) was added to a 25 mL flask with a stir bar. Then dimethyl sulfoxide (1 mL) and EtOAc (1 mL) was added to the flask through the rubber septum using syringes.

Subsequently, the reaction mixture was stirred at room temperature for 3 h. After the completion of the reaction indicated by TLC, the reaction mixture was quenched by water and was extracted by EtOAc for three times. The combined organic layer was dried over anhydrous sodium sulfate, filtered, concentrated, and then purified by flash chromatography on silica gel to provide the corresponding product **3ka**.
38.0 mg, 56%. Black solid.
R_f = 0.50 (60% EA in PE)

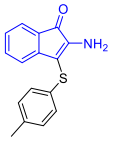
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 - 7.20 (m, 5H), 6.29 (d, J = 2.0 Hz, 1H), 6.27 (dd, J = 8.1, 2.0 Hz, 1H), 4.54 (s, 2H), 4.49 (s, 1H), 1.99 - 1.92 (m, 1H), 1.85 - 1.76 (m, 2H), 1.57 - 1.40 (m, 8H), 1.36 - 1.29 (m, 4H), 1.28 - 1.19 (m, 4H), 1.18 - 1.05 (m, 8H), 1.02 - 0.95 (m, 3H), 0.90 (d, J = 6.5 Hz, 4H), 0.86 (dd, J = 6.6, 2.8 Hz, 6H), 0.79 (s, 3H), 0.64 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 190.1, 165.8, 152.2, 147.1, 133.8, 132.1, 129.7, 128.7, 125.9, 120.2, 108.9, 108.3, 104.3, 72.8, 56.5, 56.3, 54.0, 42.5, 39.9, 39.4, 36.1, 35.7, 35.6, 35.4, 32.44, 32.40, 31.8, 28.3, 28.1, 27.9, 25.5, 24.0, 23.7, 22.6, 22.4, 20.6, 18.5, 11.8, 11.1.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{42}H_{57}ClNO_2S$ 674.3793, found 674.3775.

2-Amino-3-((4-chlorophenyl)thio)-1*H*-inden-1-one (3aa)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (41.9 mg, 0.2 mmol) and 4-chlorobenzenethiol (44.3 mg, 0.3 mmol) was used to afford the desired product.
57.4 mg, 99%. Black solid.
R_f = 0.37 (10% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, J = 7.2 Hz, 1H), 7.23 (s, 4H), 7.16 (t, J = 7.5 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.65 (d, J = 7.3 Hz, 1H), 4.45 (s, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 192.1, 148.3, 144.9, 136.0, 132.8, 132.5, 129.8, 129.3, 128.5, 125.5, 123.2, 118.5, 108.7.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{15}H_{11}ClNOS$ 288.0244, found 288.0251.

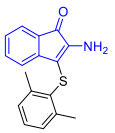
2-Amino-3-(*p*-tolylthio)-1*H*-inden-1-one (3ab)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (41.9 mg, 0.2 mmol) and 4-methylbenzenethiol (38.1 mg, 0.3 mmol) was used to afford the desired product.
54.2 mg, 99%. Black solid.

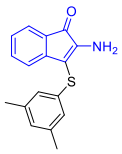
R_f = 0.32 (10% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 - 7.22 (m, 3H), 7.15 (td, J = 7.6, 1.1 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 6.90 - 6.86 (m, 1H), 6.68 (d, J = 7.3 Hz, 1H), 4.27 (s, 2H), 2.31 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 192.3, 148.5, 143.8, 137.0, 135.8, 130.5, 129.9, 129.0, 128.7, 125.4, 122.8, 118.5, 111.5, 20.8.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{14}NOS$ 268.0791, found 268.0793.

2-Amino-3-((2,6-dimethylphenyl)thio)-1*H*-inden-1-one (3ac)



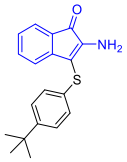
Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (41.9 mg, 0.2 mmol) and 2,6-dimethylbenzenethiol (42.3 mg, 0.3 mmol) was used to afford the desired product.
43.7 mg, 78%. Black solid.
R_f = 0.31 (10% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 - 7.18 (m, 1H), 7.18 - 7.16 (d, J = 7.0 Hz, 1H), 7.15 - 7.11 (m, 3H), 6.90 - 6.86 (m, 1H), 6.60 (d, J = 7.2 Hz, 1H), 3.48 (s, 2H), 2.52 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 192.1, 147.8, 144.0, 139.0, 135.6, 130.1, 129.7, 129.4, 128.8, 126.3, 122.4, 118.3, 117.6, 22.4.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{17}H_{16}NOS$ 282.0947, found 282.0952.

2-Amino-3-((3,5-dimethylphenyl)thio)-1*H*-inden-1-one (3ad)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (41.9 mg, 0.2 mmol) and 3,5-dimethylbenzenethiol (46.1 mg, 0.3 mmol) was used to afford the desired product.
48.4 mg, 86%. Black solid.
R_f = 0.43 (10% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, J = 6.9 Hz, 1H), 7.16 (td, J = 7.7, 1.2 Hz, 1H), 6.94 (s, 2H), 6.91 - 6.87 (m, 1H), 6.82 (s, 1H), 6.71 (d, J = 7.3 Hz, 1H), 4.29 (s, 2H), 2.29 - 2.23 (m, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 192.4, 148.6, 143.9, 139.4, 135.8, 133.1, 128.8, 128.7, 126.2, 125.4, 122.8, 118.5, 111.0, 21.1.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{17}H_{16}NOS$ 282.0947, found 282.0942.

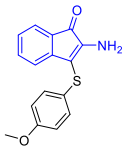
2-Amino-3-((4-isopropylphenyl)thio)-1*H*-inden-1-one (3ae)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (41.9 mg, 0.2 mmol) and 4-tert-butylbenzenethiol (51.4 mg, 0.3 mmol) was used to afford the desired product.
57.1 mg, 93%. Purple solid.
R_f = 0.50 (10% EA in PE)

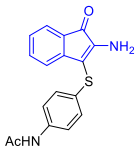
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 - 7.29 (m, 2H), 7.28 - 7.26 (m, 2H), 7.26 - 7.25 (m, 1H), 7.20 - 7.13 (m, 1H), 6.89 (t, J = 7.4 Hz, 1H), 6.72 (d, J = 7.3 Hz, 1H), 4.32 (s, 2H), 1.30 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 192.3, 150.1, 148.6, 144.1, 135.8, 130.2, 128.7, 128.3, 126.7, 125.4, 122.9, 118.5, 110.9, 34.3, 31.1.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{19}H_{20}NOS$ 310.1260, found 310.1249.

2-Amino-3-((4-methoxyphenyl)thio)-1*H*-inden-1-one (3af)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (41.9 mg, 0.2 mmol) and 4-methoxybenzenethiol (46.0 mg, 0.3 mmol) was used to afford the desired product.
46.0 mg, 82%. Black solid.
R_f = 0.43 (20% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 - 7.30 (m, 2H), 7.23 (d, J = 7.1 Hz, 1H), 7.14 (td, J = 7.7, 1.1 Hz, 1H), 6.90 - 6.86 (m, 1H), 6.85 - 6.82 (m, 2H), 6.67 (d, J = 7.3 Hz, 1H), 4.19 (s, 2H), 3.78 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 159.6, 148.3, 142.9, 135.6, 131.6, 128.9, 125.5, 123.4, 122.7, 118.5, 115.3, 113.1, 55.4.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{14}NO_2S$ 284.0740, found 284.0743.

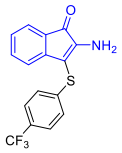
***N*-(4-((2-Amino-1-oxo-1*H*-inden-3-yl)thio)phenyl)acetamide (3ag)**



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (41.9 mg, 0.2 mmol) and N-(4-mercaptophenyl)acetamide (55.7 mg, 0.3 mmol) was used to afford the desired product.
55.1 mg, 89%. Black solid.
R_f = 0.48 (50% EA in PE)

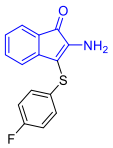
^{1}H NMR (600 MHz, DMSO-d_6) δ 9.94 (s, 1H), 7.51 (d, J = 8.7 Hz, 2H), 7.26 - 7.20 (m, 2H), 7.16 (m, 2H), 6.86 - 6.79 (m, 1H), 6.48 (m, 1H), 6.31 (s, 2H), 2.01 (s, 3H).
^{13}C NMR (150 MHz, DMSO-d_6) δ 193.0, 169.4, 150.4, 147.3, 138.5, 136.6, 129.0, 128.6, 128.5, 124.7, 123.0, 120.8, 117.6, 104.1, 24.1.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{17}H_{15}N_2O_2S$ 311.0849, found 311.0853.

2-Amino-3-((4-(trifluoromethyl)phenyl)thio)-1*H*-inden-1-one (3ah)



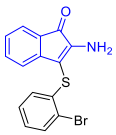
Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (41.9 mg, 0.2 mmol) and 4-(trifluoromethyl)benzenethiol (54.5 mg, 0.3 mmol) was used to afford the desired product.
65.5 mg, 99%. Black solid.
R_f = 0.31 (10% EA in PE)
1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 7.1 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 6.92 (t, J = 7.4 Hz, 1H), 6.68 (d, J = 7.3 Hz, 1H), 4.54 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 148.4, 145.8, 140.0, 136.3, δ 128.4 (q, J = 32.7 Hz), 128.3, 127.2, 126.5 (q, J = 3.7 Hz), 125.6, δ 124.5 (q, J = 272.0 Hz). 123.6, 118.5, 106.5.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{11}F_3NOS$ 322.0508, found 322.0513.

2-Amino-3-((4-fluorophenyl)thio)-1*H*-inden-1-one (3ai)



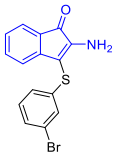
Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (41.9 mg, 0.2 mmol) and 4-fluorobenzenethiol (39.2 mg, 0.3 mmol) was used to afford the desired product.
53.6 mg, 99%. Black solid.
R_f = 0.34 (10% EA in PE)
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.33 - 7.30 (m, 2H), 7.19 - 7.12 (m, 4H), 6.83 (t, J = 7.3 Hz, 1H), 6.52 (d, J = 7.5 Hz, 1H), 6.45 (s, 2H).
^{13}C NMR (150 MHz, DMSO-d_6) δ 192.8, 161.5 (d, J = 242.7 Hz), 150.2, 147.7, 136.6, 131.0 (d, J = 2.9 Hz), 129.7 (d, J = 8.1 Hz), 128.0, 124.6, 123.0, 117.2, 116.9 (d, J = 22.1 Hz), 102.3.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{15}H_{11}FNOS$ 272.0540, found 272.0545.

2-Amino-3-((2-bromophenyl)thio)-1*H*-inden-1-one (3aj)



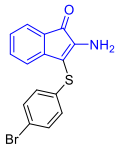
Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (41.9 mg, 0.2 mmol) and 2-bromobenzenethiol (57.9 mg, 0.3 mmol) was used to afford the desired product.
62.5 mg, 95%. Black solid.
R_f = 0.38 (10% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, J = 7.7 Hz, 1H), 7.68 (t, J = 1.7 Hz, 1H), 7.63 (d, J = 4.0 Hz, 2H), 7.62 - 7.59 (m, 1H), 7.52 (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 192.0, 138.0, 135.4, 134.2, 134.1, 133.5, 131.2, 130.9, 130.3, 130.0, 129.6, 129.2, 123.3, 117.8, 22.4.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{15}H_{11}BrNOS$ 331.9739, found 331.9742.

2-Amino-3-((3-bromophenyl)thio)-1*H*-inden-1-one (3ak)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (41.9 mg, 0.2 mmol) and 3-bromobenzenethiol (57.9 mg, 0.3 mmol) was used to afford the desired product.
49.9 mg, 76%. Black solid.
R_f = 0.38 (10% EA in PE)
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.40 (s, 1H), 7.35 - 7.30 (m, 1H), 7.28 - 7.22 (m, 2H), 7.22 - 7.18 (m, 2H), 6.84 (t, J = 7.3 Hz, 1H), 6.59 (s, 2H), 6.51 (d, J = 7.4 Hz, 1H).
^{13}C NMR (150 MHz, DMSO-d_6) δ 192.5, 150.2, 148.4, 138.8, 136.7, 131.7, 128.8, 128.8, 127.8, 125.9, 124.4, 123.2, 122.8, 117.1, 99.8.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{15}H_{11}BrNOS$ 331.9739, found 331.9742.

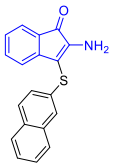
2-Amino-3-((4-bromophenyl)thio)-1*H*-inden-1-one (3al)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (41.9 mg, 0.2 mmol) and 4-bromobenzenethiol (57.9 mg, 0.3 mmol) was used to afford the desired product.
65.9 mg, 99%. Black solid.
R_f = 0.38 (10% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 - 7.36 (m, 2H), 7.28 (d, J = 7.1 Hz, 1H), 7.19 - 7.14

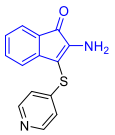
(m, 3H), 6.93 - 6.88 (m, 1H), 6.65 (d, J = 7.3 Hz, 1H), 4.45 (s, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 148.4, 145.1, 136.2, 133.6, 132.8, 129.6, 128.5, 125.6, 123.4, 120.3, 118.6, 108.5
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{15}H_{11}BrNOS$ 331.9739, found 331.9741.

2-Amino-3-(naphthalen-2-ylthio)-1*H*-inden-1-one (3am)



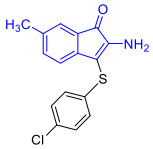
Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (41.9 mg, 0.2 mmol) and naphthalene-2-thiol (49.1 mg, 0.3 mmol) was used to afford the desired product.
60.0 mg, 99%. Black solid.
R_f = 0.47 (10% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J = 7.9 Hz, 1H), 7.77 - 7.74 (m, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.49 - 7.44 (m, 2H), 7.42 (dd, J = 8.6, 1.8 Hz, 1H), 7.30 (d, J = 7.1 Hz, 1H), 7.16 - 7.09 (m, 1H), 6.89 (t, J = 7.4 Hz, 1H), 6.71 (d, J = 7.3 Hz, 1H), 4.42 (s, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 148.5, 144.5, 135.9, 134.2, 132.3, 131.3, 129.3, 128.6, 128.2, 127.5, 127.2, 126.5, 126.34, 126.25, 125.4, 123.0, 118.5, 109.8.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{19}H_{14}NOS$ 304.0791, found 304.0790.

2-Amino-3-(pyridin-4-ylthio)-1*H*-inden-1-one (3an)



Following Procedure D, 2-(acetoxyimino)-2,3-dihydro-1*H*-inden-1-one (41.9 mg, 0.2 mmol) and pyridine-4-thiol (34.7 mg, 0.3 mmol) was used to afford the desired product.
49.5 mg, 97%. Black solid.
R_f = 0.28 (50% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, J = 6.0 Hz, 2H), 7.31 (d, J = 7.1 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 6.1 Hz, 2H), 6.92 (t, J = 7.4 Hz, 1H), 6.68 (d, J = 7.3 Hz, 1H), 4.70 (s, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 191.8, 150.1, 148.4, 146.9, 146.5, 136.4, 128.0, 125.6, 123.8, 121.3, 118.3, 103.7.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{14}H_{11}N_2OS$ 255.0587, found 255.0586.

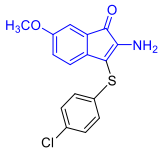
2-Amino-3-((4-chlorophenyl)thio)-6-methyl-1*H*-inden-1-one (3ba)



Following Procedure D, 2-(acetoxyimino)-6-methyl-2,3-dihydro-1*H*-inden-1-one (44.8

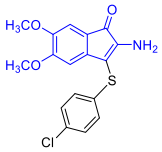
mg, 0.2 mmol) and 4-chlorobenzenethiol (44.3 mg, 0.3 mmol) was used to afford the desired product.
62.6 mg, 99%. Black solid.
R_f = 0.34 (10% EA in PE)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (s, 4H), 7.11 (s, 1H), 6.95 (d, J = 7.3 Hz, 1H), 6.52 (d, J = 7.4 Hz, 1H), 4.35 (s, 2H), 2.22 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 192.3, 145.2, 144.4, 135.8, 135.4, 132.8, 132.5, 129.7, 129.4, 128.8, 124.4, 118.3, 109.4, 20.7.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{13}ClNOS$ 302.0401, found 302.0400.

2-Amino-3-((4-chlorophenyl)thio)-6-methoxy-1*H*-inden-1-one (3ca)



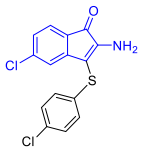
Following Procedure D, 2-(acetoxyimino)-6-methoxy-2,3-dihydro-1*H*-inden-1-one (48.1 mg, 0.2 mmol) and 4-chlorobenzenethiol (44.3 mg, 0.3 mmol) was used to afford the desired product.
57.3 mg, 90%. Black solid.
R_f = 0.44 (10% EA in PE)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 4H), 6.92 (s, 1H), 6.60 (dd, J = 7.9, 1.9 Hz, 1H), 6.49 (d, J = 8.0 Hz, 1H), 4.25 (s, 2H), 3.74 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 158.9, 143.9, 139.4, 132.6, 132.5, 130.2, 129.8, 129.6, 119.0, 118.0, 111.6, 110.9, 55.7.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{13}ClNO_2S$ 318.0350, found 318.0344.

2-Amino-3-((4-chlorophenyl)thio)-5,6-dimethoxy-1*H*-inden-1-one (3da)



Following Procedure D, 2-(acetoxyimino)-5,6-dimethoxy-2,3-dihydro-1*H*-inden-1-one (54.3 mg, 0.2 mmol) and 4-chlorobenzenethiol (44.3 mg, 0.3 mmol) was used to afford the desired product.
40.4 mg, 58%. Brown solid.
R_f = 0.50 (20% EA in PE)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 4H), 6.94 (s, 1H), 6.30 (s, 1H), 4.43 (s, 2H), 3.81 (s, 3H), 3.78 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 155.8, 146.6, 145.4, 145.0, 133.6, 132.3, 129.7, 128.8, 119.3, 108.9, 104.3, 103.4, 56.5, 56.2.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{17}H_{15}ClNO_3S$ 348.0456, found 348.0460.

2-Amino-5-chloro-3-((4-chlorophenyl)thio)-1*H*-inden-1-one (3ea)



Following Procedure D, 2-(acetoxyimino)-5-chloro-2,3-dihydro-1*H*-inden-1-one (49.0 mg, 0.2 mmol) and 4-chlorobenzenethiol (44.3 mg, 0.3 mmol) was used to afford the desired product.

67.4 mg, 99%. Black solid.

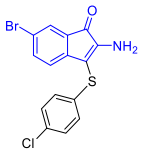
R_f = 0.44 (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (dd, J = 8.2, 1.0 Hz, 1H), 7.25 - 7.23 (m, 3H), 7.21 - 7.18 (m, 2H), 6.77 (dd, J = 8.2, 7.0 Hz, 1H), 4.63 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 190.7, 147.4, 144.7, 141.83, 134.9, 132.2, 131.0, 129.8, 128.5, 126.8, 122.5, 113.4, 109.1.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{15}H_{10}Cl_2NOS$ 321.9855, found 321.9851.

2-Amino-6-bromo-3-((4-chlorophenyl)thio)-1*H*-inden-1-one (3fa)



Following Procedure D, 2-(acetoxyimino)-6-bromo-2,3-dihydro-1*H*-inden-1-one (58.3 mg, 0.2 mmol) and 4-chlorobenzenethiol (44.3 mg, 0.3 mmol) was used to afford the desired product.

73.1 mg, 99%. Black solid.

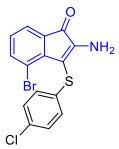
R_f = 0.53 (10% EA in PE)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, J = 1.7 Hz, 1H), 7.28 (dd, J = 7.8, 1.7 Hz, 1H), 7.25 - 7.23 (m, 2H), 7.22 - 7.19 (m, 2H), 6.50 (d, J = 7.8 Hz, 1H), 4.46 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 190.7, 146.9, 144.6, 138.0, 132.9, 132.1, 130.1, 129.9, 129.5, 126.3, 119.8, 118.7, 109.2.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{15}H_{10}BrClNOS$ 365.9350, found 365.9349.

2-Amino-4-bromo-3-((4-chlorophenyl)thio)-1*H*-inden-1-one (3ha)



Following Procedure D, 2-(acetoxyimino)-4-bromo-2,3-dihydro-1*H*-inden-1-one (58.3 mg, 0.2 mmol) and 4-chlorobenzenethiol (44.3 mg, 0.3 mmol) was used to afford the desired product.

48.7 mg, 67%. Black solid.

R_f = 0.53 (10% EA in PE)

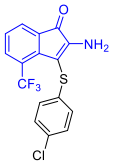
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (dd, J = 8.2, 0.9 Hz, 1H), 7.25 - 7.23 (m, 3H), 7.21 - 7.18 (m, 2H), 6.77 (dd, J = 8.2, 7.0 Hz, 1H), 4.64 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 190.7, 147.4, 144.7, 141.8, 134.9, 132.2, 131.0, 129.8, 128.5, 126.8, 122.5, 113.4, 109.1.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{15}H_{10}BrClNOS$ 365.9350, found 365.9352.

2-Amino-3-((4-chlorophenyl)thio)-1-oxo-1*H*-indene-4-carbonitrile (3ia)

Following Procedure D, 2-(acetoxyimino)-1-oxo-2,3-dihydro-1*H*-indene-4-carbonitrile (47.1 mg, 0.2 mmol) and 4-chlorobenzenethiol (44.3 mg, 0.3 mmol) was used to afford the desired product.
35.2 mg, 56%. Black solid.
R_f = 0.37 (20% EA in PE)
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.39 (dd, J = 16.2, 7.5 Hz, 2H), 7.34 (d, J = 8.6 Hz, 2H), 7.31 - 7.24 (m, 4H), 6.92 (t, J = 7.6 Hz, 1H).
^{13}C NMR (150 MHz, DMSO-d_6) δ 190.1, 153.8, 152.1, 139.8, 136.3, 130.6, 129.7, 129.0, 128.2, 126.4, 124.7, 117.5, 99.8, 98.5.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{10}ClN_2OS$ 313.0197, found 313.0180.

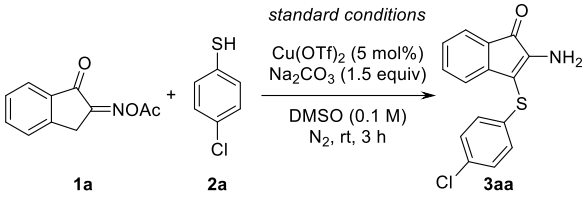
2-Amino-3-((4-chlorophenyl)thio)-4-(trifluoromethyl)-1*H*-inden-1-one (3ja)



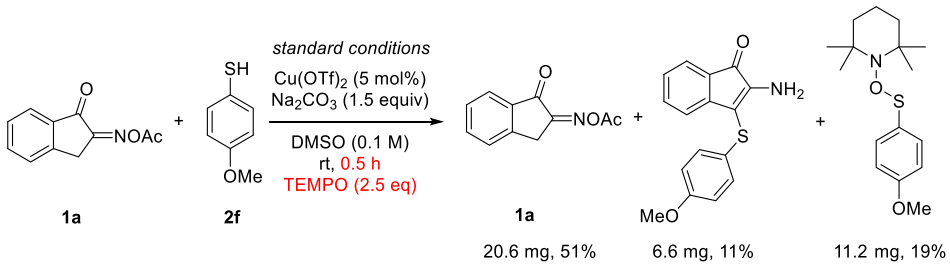
Following Procedure D, 2-(acetoxyimino)-4-(trifluoromethyl)-2,3-dihydro-1*H*-inden-1-one (55.9 mg, 0.2 mmol) and 4-chlorobenzenethiol (44.3 mg, 0.3 mmol) was used to afford the desired product.
60.7 mg, 90%. Black solid.
R_f = 0.27 (10% EA in PE)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.2 Hz, 1H), 7.42 (d, J = 7.0 Hz, 1H), 7.25 - 7.17 (m, 4H), 7.00 (t, J = 7.6 Hz, 1H), 4.78 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 148.4, 147.6, 133.8, δ 133.1 (q, J = 5.8 Hz), 132.1, 130.1, 129.7, 128.2, 125.9, 125.3, 123.5 (q, J = 273.2 Hz), 121.7 (q, J = 33.4 Hz), 107.2.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{10}ClF_3NOS$ 356.0118, found 356.0116.

IV. Mechanistic Studies

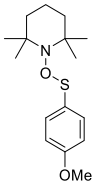
Control experiments



entry	devation from standard conditions	yield
1	none	99%
2	TEMPO (2.5 equiv)	4%
3	no base	0%
4	4-Cl-C_6H_4SNa instead of **2a**, no base	81%
5	no $Cu(OTf)_2$	82%



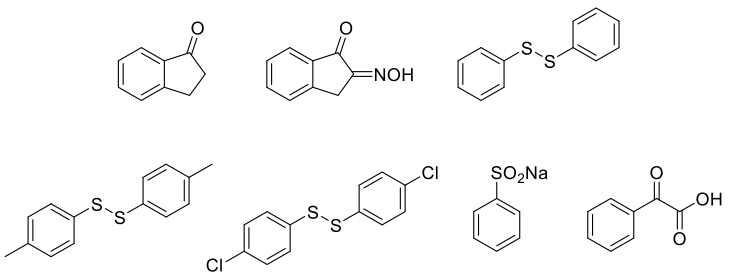
Scheme S1 control experiments



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 - 7.56 (m, 2H), 6.97 - 6.95 (m, 2H), 3.84 (s, 3H), 1.65 (s, 6H), 1.58 - 1.22 (m, 12H).

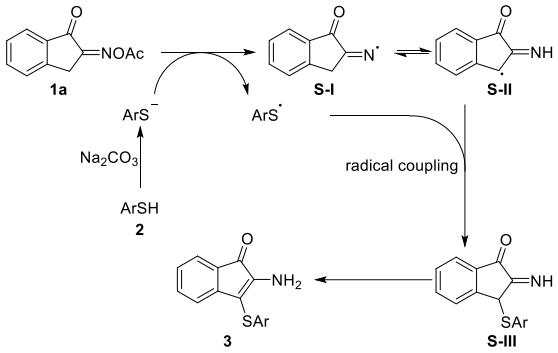
Spectroscopic data matches that reported in the literature.[3]

Unsuccessful substrate:



Scheme S2

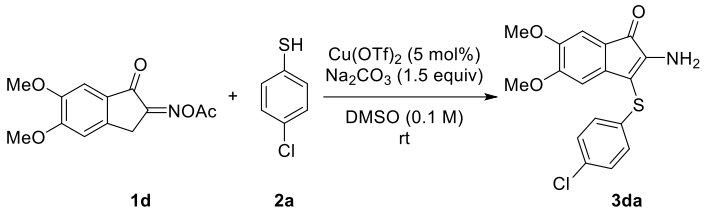
Proposed reaction mechanism without $Cu(OTf)_2$



Scheme S3 Proposed reaction mechanism without $Cu(OTf)_2$

Kinetic experiments

Reaction conditions: 2-(acetoxyimino)-5,6-dimethoxy-2,3-dihydro-1H-inden-1-one **1d** (0.6 mmol, 1 equiv) and 4-chlorobenzenethiol **1a** (0.9 mmol, 1,5 equiv), $Cu(OTf)_2$ (5 mol%), Na_2CO_3 (0.9 mmol, 1.5 equiv), and internal standard 4-nitrotoluene (0.6 mmol) was added to a 25 mL flask with a stir bar. Then DMSO (6 mL) was added to the flask through the rubber septum using syringes. At regular intervals, an aliquot of sample was taken out from the reaction vessel, quenched by water and was extracted by EtOAc, then concentrated. The yields were monitored by ^1H NMR analysis.



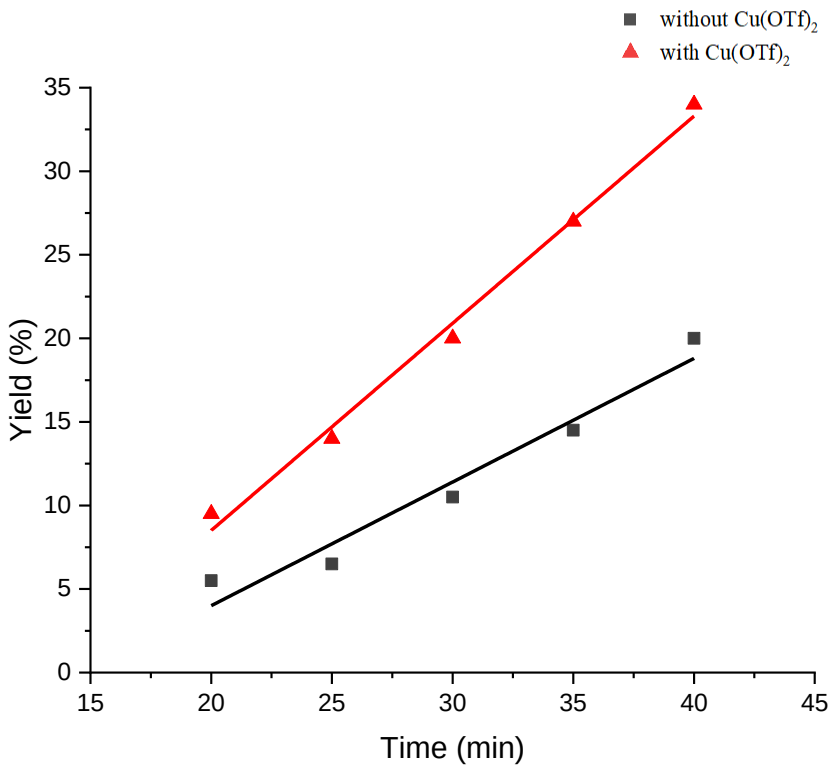
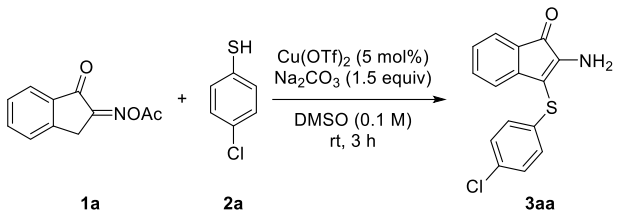


Figure S1 Reaction condition with or without copper

To gain more insight into the reaction, we compared the reactions with and without the copper catalyst. It further proved that copper significantly promoted the reaction rate.

V. Scale-Up Reaction

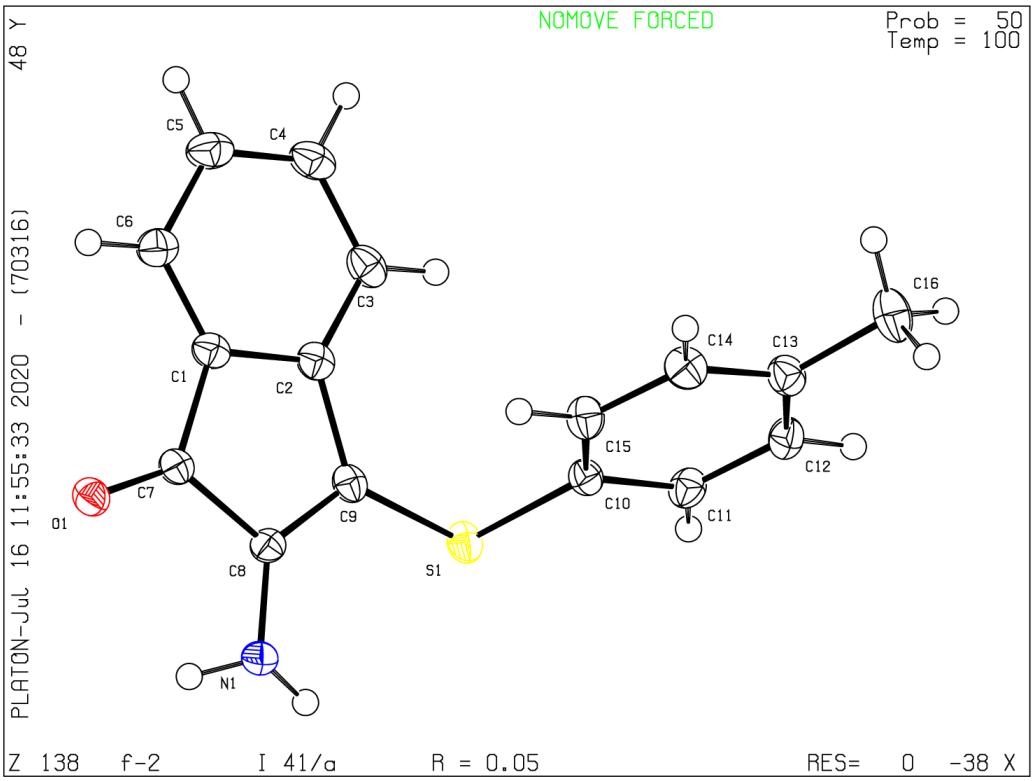


1a 838 mg, 4 mmol | **2a** | **3aa** 1.12g, 3.9 mmol

For scale-up reaction, 1-indanone oxime acetate **1a** (838 mg, 4 mmol, 1 equiv), 4-chlorothiophenol **2a** (885 mg, 6 mmol, 1.5 equiv), $Cu(OTf)_2$ (73.8 mg, 0.2 mmol, 5 mol%), and Na_2CO_3 (642 mg, 6 mmol, 1.5 equiv) were added to a solution of DMSO (40 mL). Then, the reaction mixture was stirred at room temperature for 3 h. After the completion of the reaction indicated by TLC, the reaction mixture was quenched by water and was extracted by EtOAc for three times. The combined organic layer was dried over anhydrous sodium sulfate, filtered, concentrated, and then purified by flash chromatography on silica gel to provide the corresponding product **3aa** in 82% yield.

VI． Crystal Data for 3aa

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



CCDC 2090352

X-ray structure and CCDC number of compound **3ab**

Crystal data and structure refinement for 3ab.

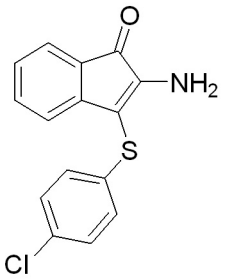
Identification code	3ab
Empirical formula	$C_{16}H_{13}NOS$
Formula weight	267.33
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.9615(2)
b/Å	5.21490(10)
c/Å	20.9115(7)
α/°	90
β/°	98.104(3)
γ/°	90

Volume/Å^3	643.62(3)
Z	2
ρ_{calc}g/cm^3	1.379
μ/mm^{-1}	2.142
F(000)	280.0
Crystal size/mm^3	0.13 × 0.11 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.268 to 147.52
Index ranges	$-7 \leq h \leq 7$, $-4 \leq k \leq 6$, $-26 \leq l \leq 25$
Reflections collected	4464
Independent reflections	1890 [R_{int} = 0.1130, R_{sigma} = 0.0738]
Data/restraints/parameters	1890/1/182
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0578, wR_2 = 0.1488
Final R indexes [all data]	R_1 = 0.0589, wR_2 = 0.1512
Largest diff. peak/hole / e Å^{-3}	0.76/-0.49
Flack parameter	0.01(4)

VII. Reference

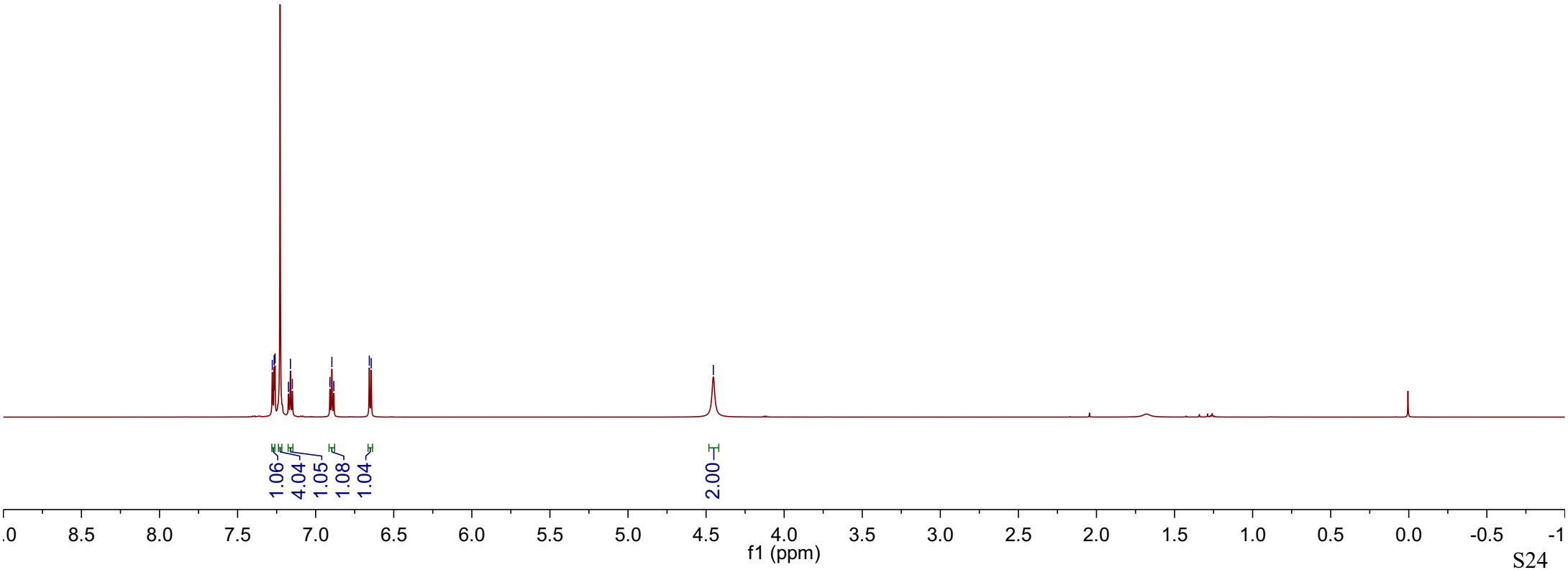
1. X. Meng, D. Chen, R. Liu, P. Jiang and S. Huang. *J. Org. Chem.*, 2021, **86**, 10852.
2. Y. Xia, S. Ochi and G. Dong. *J. Am. Chem. Soc*., 2019, **141**, 13038.
3. M. Jiang, H. Li, H. Yang, H. Fu. *Angew. Chem. Int. Ed*., 2017, **56**, 874.

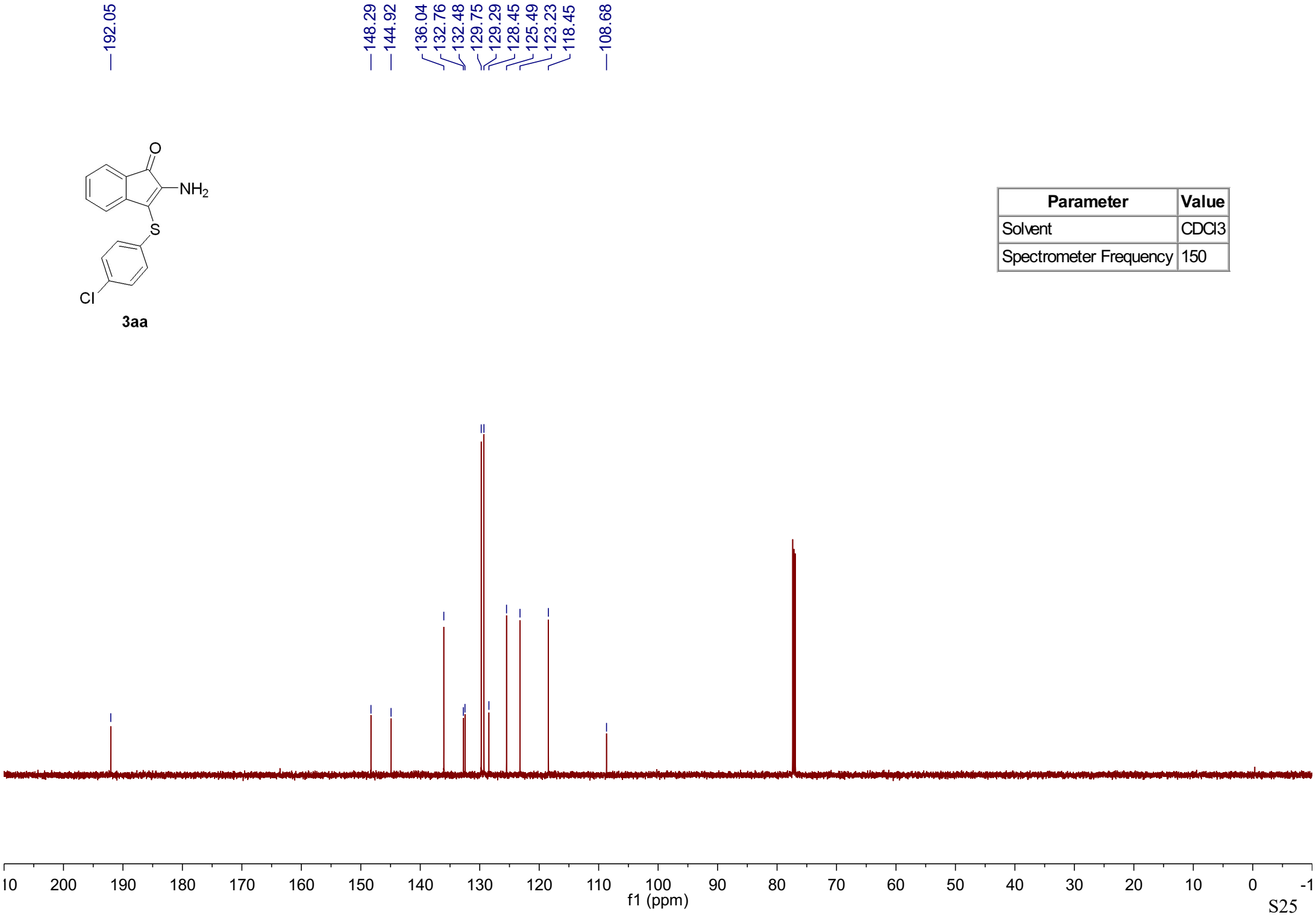
VIII . NMR Spectra

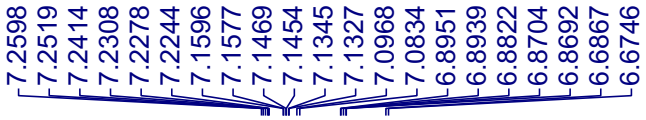


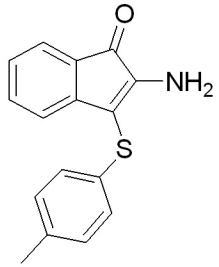
3aa

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



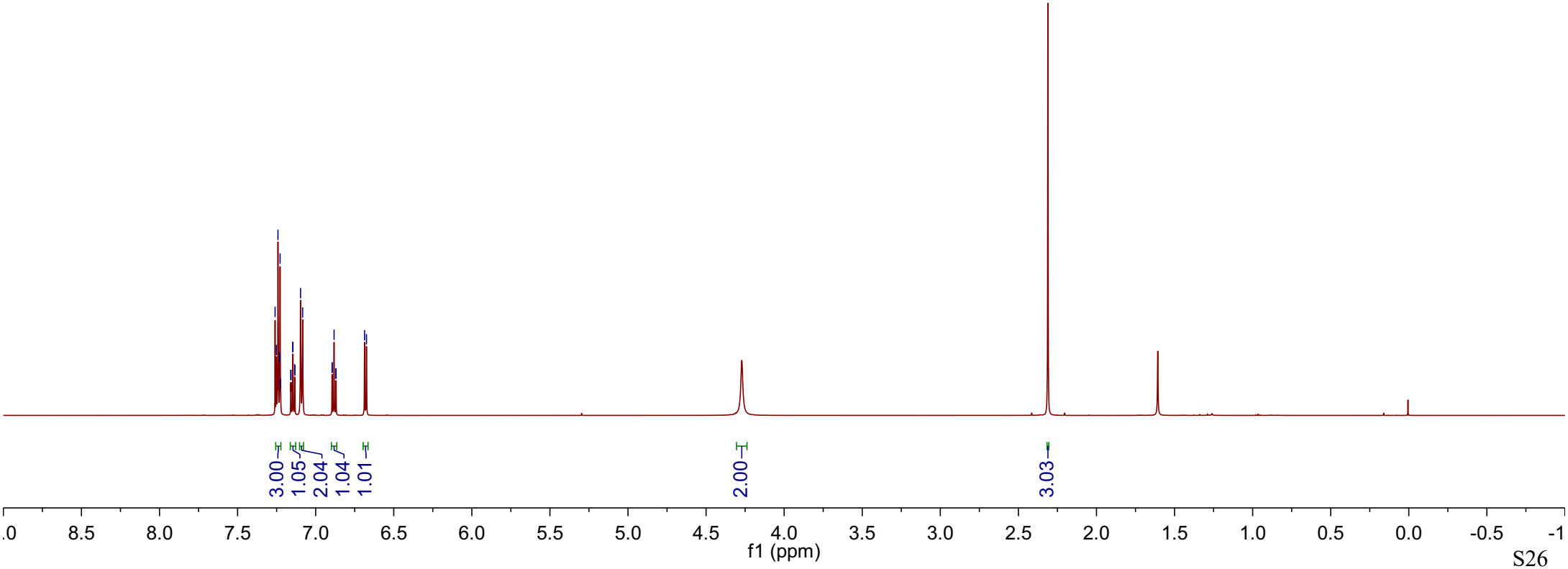

192.05
148.29
144.92
136.04
132.76
132.48
129.75
129.29
128.45
125.49
123.23
118.45
108.68
O
NH2
S
Cl
3aa
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
150
f1 (ppm)

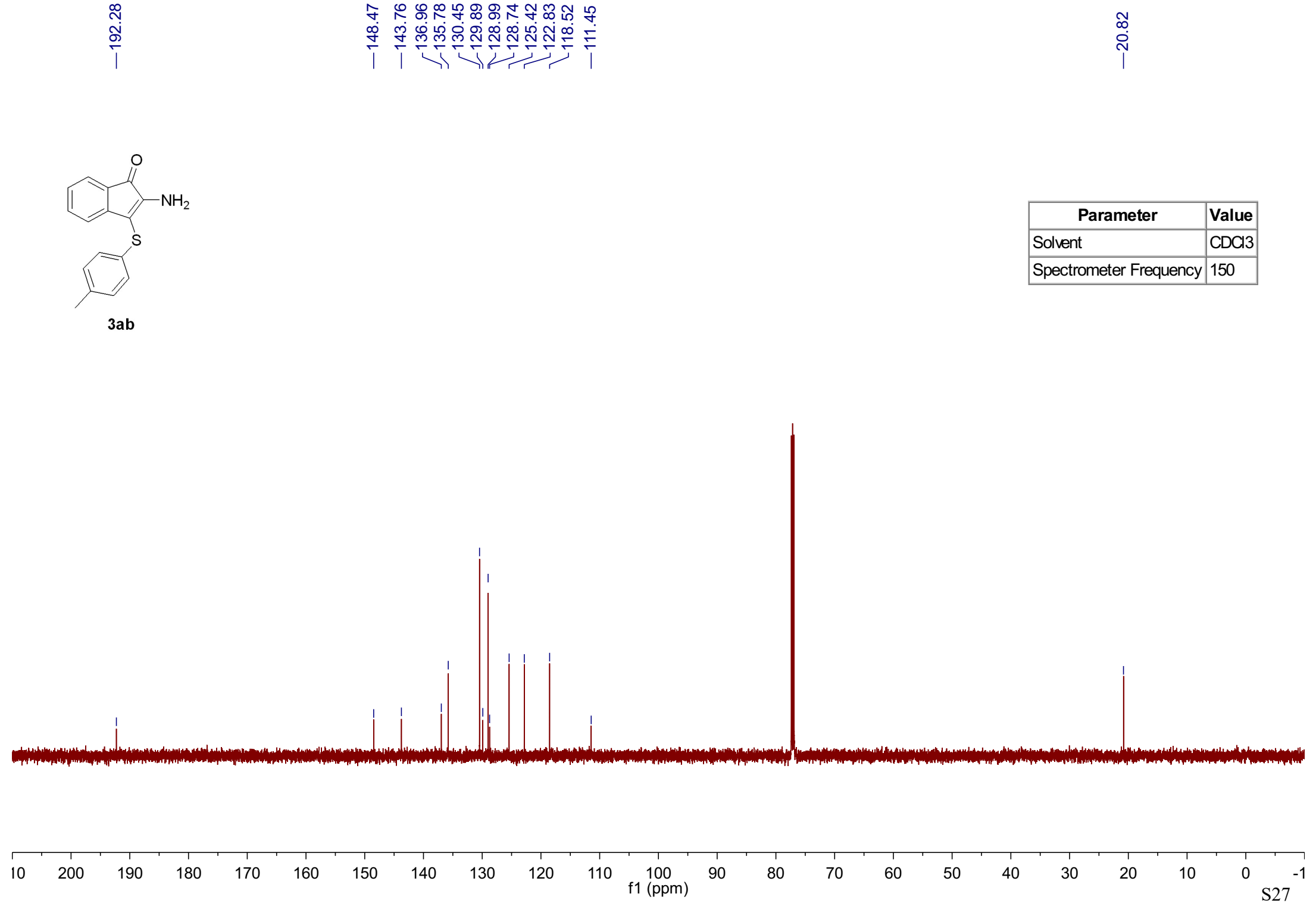




3ab

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

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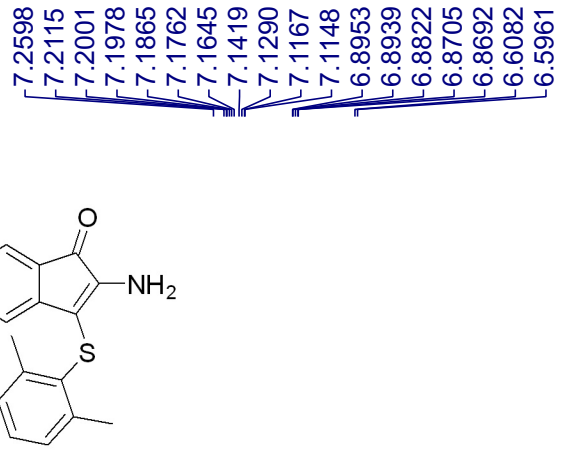
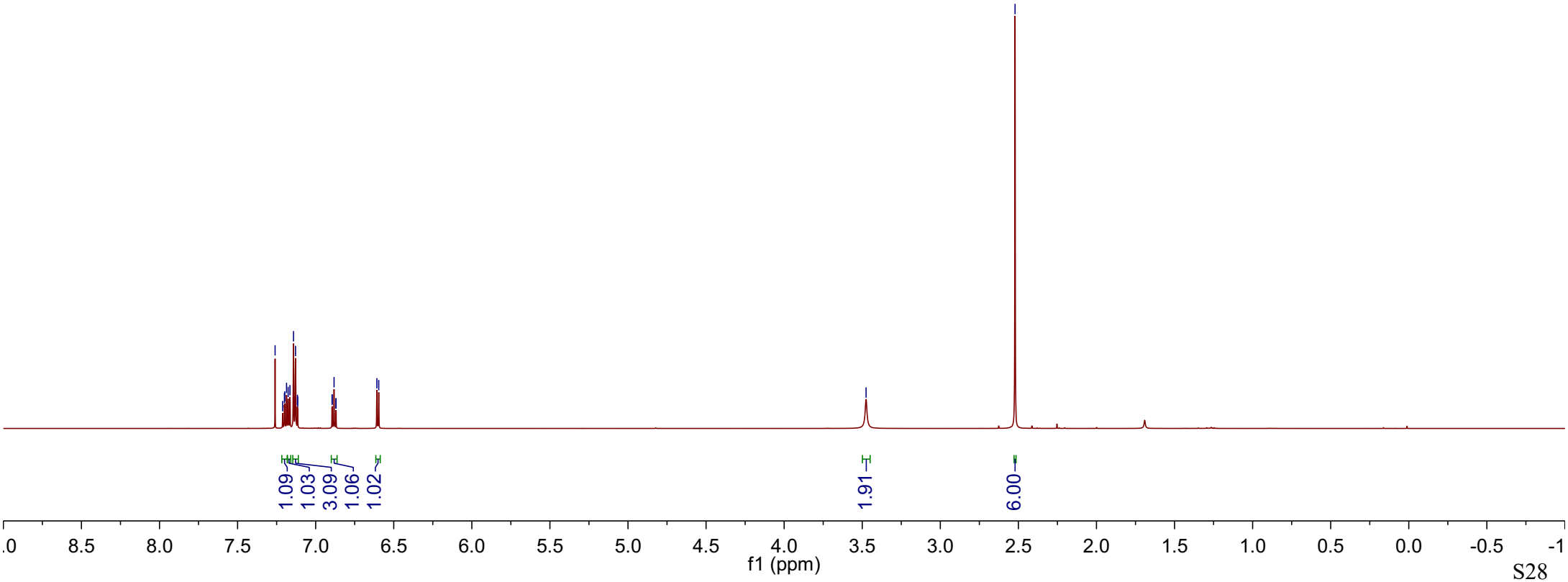
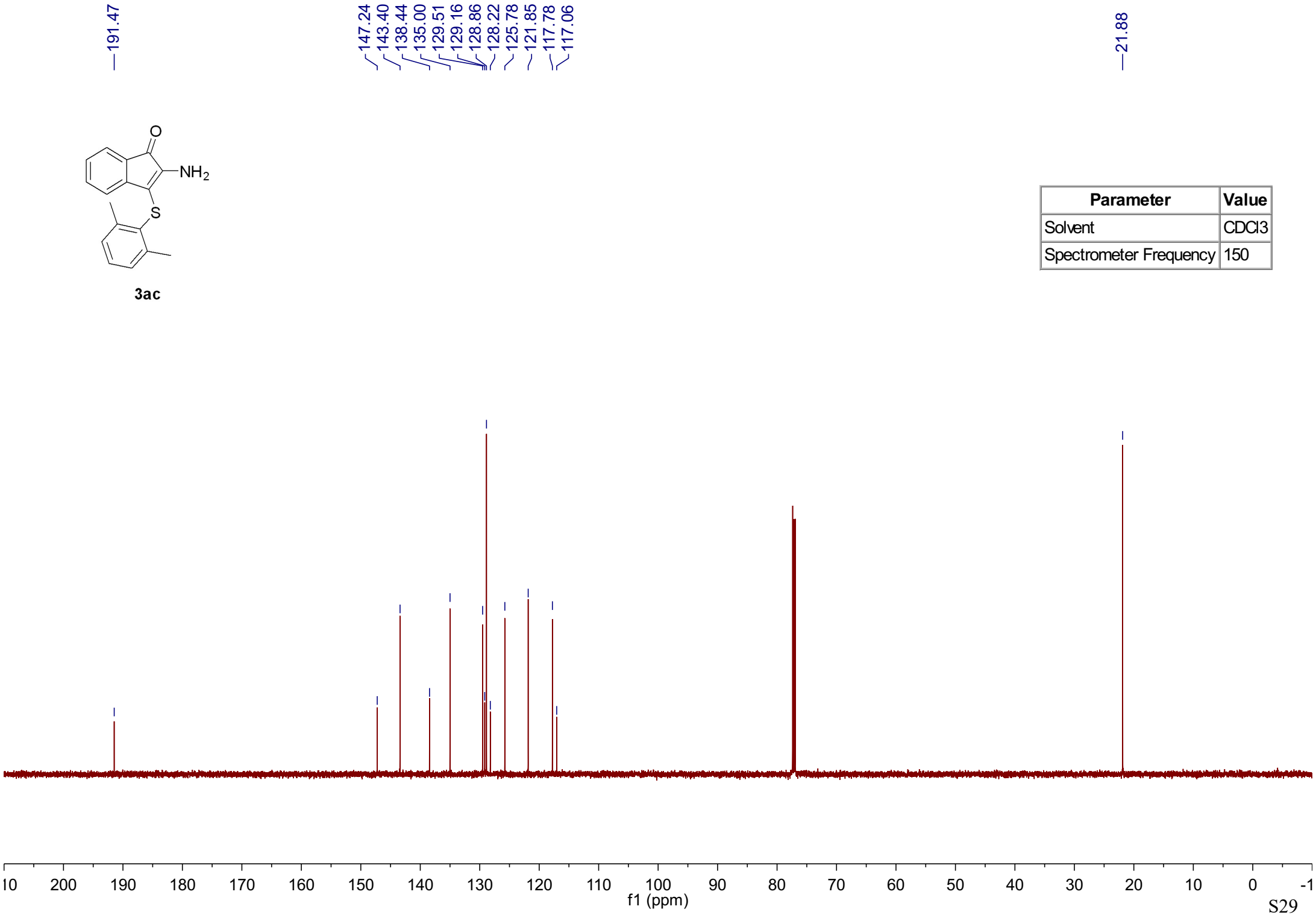
148.47
143.76
136.96
135.78
130.45
129.89
128.99
128.74
125.42
122.83
118.52
111.45
20.82
O
NH2
S
3ab
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
150
f1 (ppm)



3ac

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

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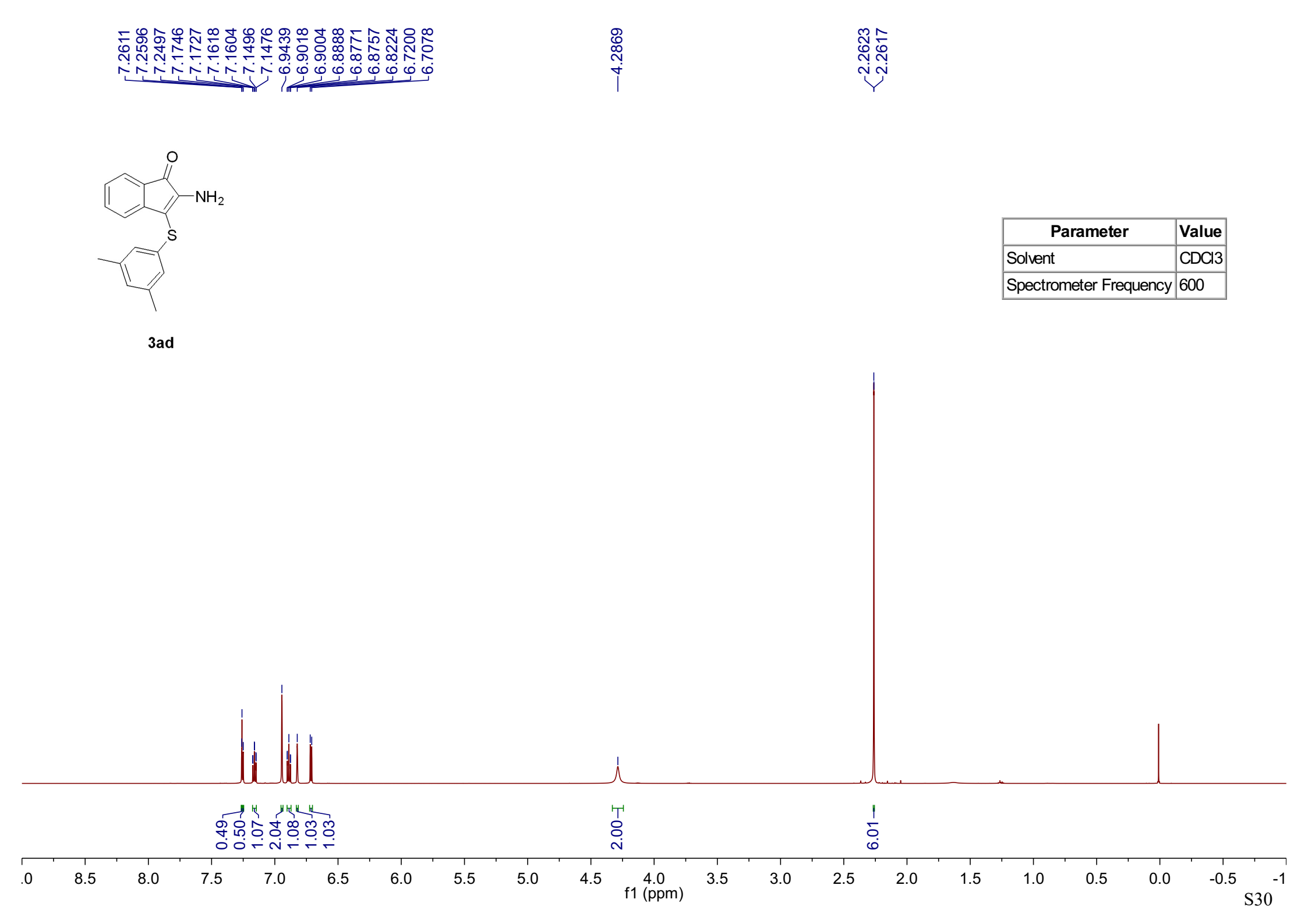
147.24
143.40
138.44
135.00
129.51
129.16
128.86
128.22
125.78
121.85
117.78
117.06
21.88
O
NH2
S
3ac
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
150
f1 (ppm)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7.2596
7.2497
7.1746
7.1727
7.1618
7.1604
7.1496
7.1476
6.9439
6.9018
6.9004
6.8888
6.8771
6.8757
6.8224
6.7200
6.7078
4.2869
2.2623
2.2617
O
NH2
S
3ad
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
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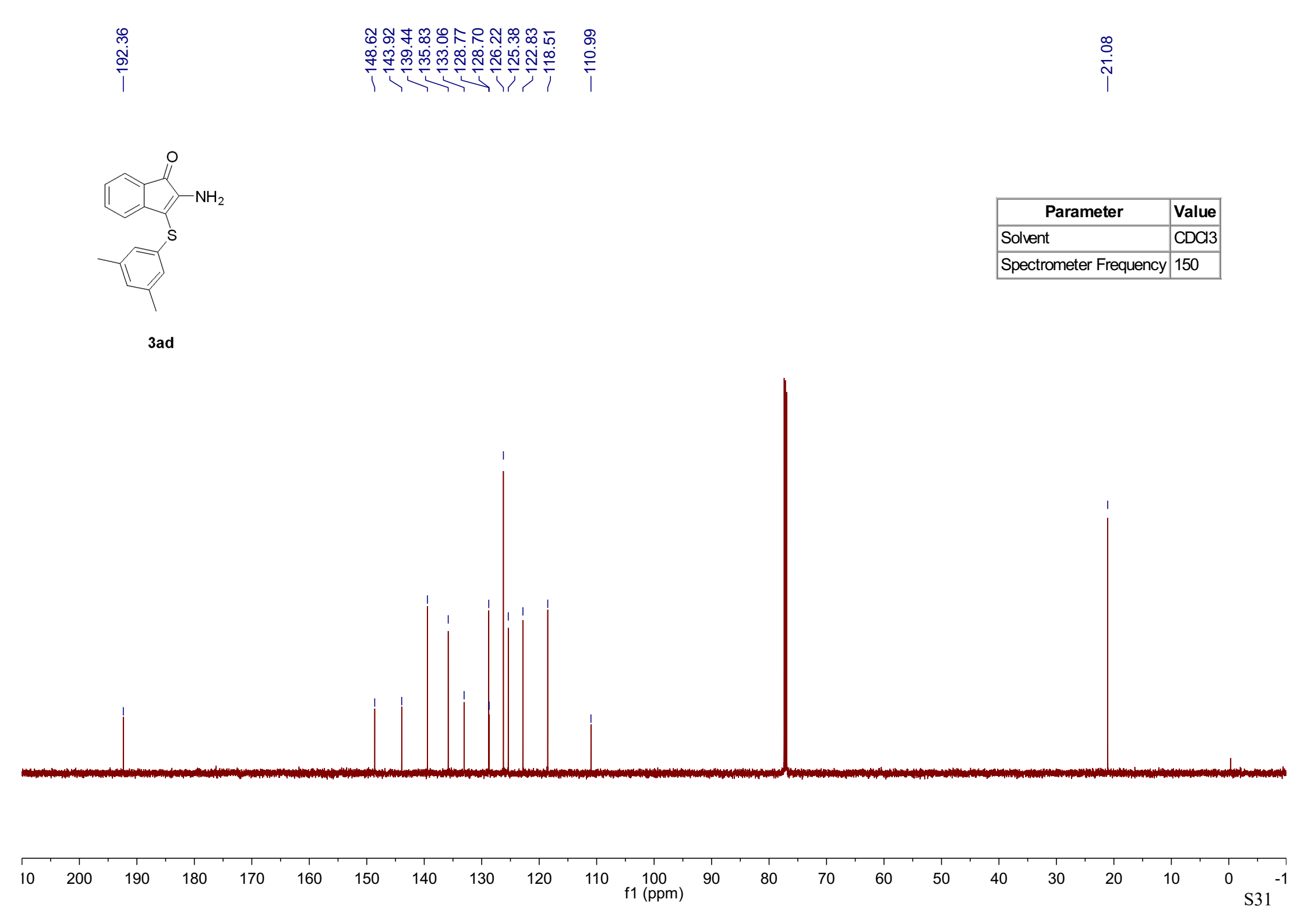
0.50
1.07
2.04
1.08
1.03
1.03
2.00
6.01
f1 (ppm)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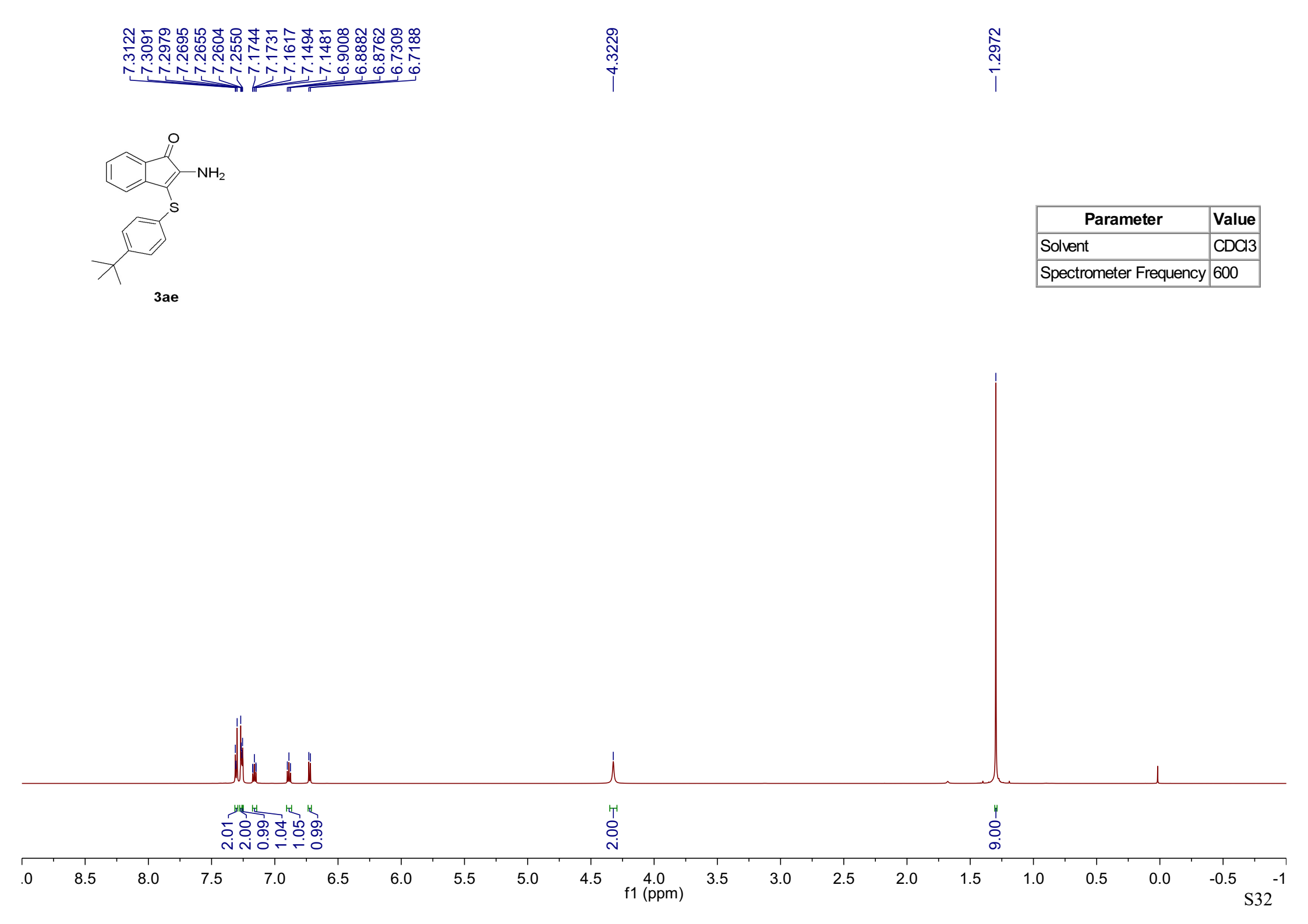
148.62
143.92
139.44
135.83
133.06
128.77
128.70
126.22
125.38
122.83
118.51
110.99
21.08
O
NH2
S
3ad
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
150
f1 (ppm)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7.3091
7.2979
7.2695
7.2655
7.2604
7.2550
7.1744
7.1731
7.1617
7.1494
7.1481
6.9008
6.8882
6.8762
6.7309
6.7188
4.3229
1.2972
O
NH2
S
3ae
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
600
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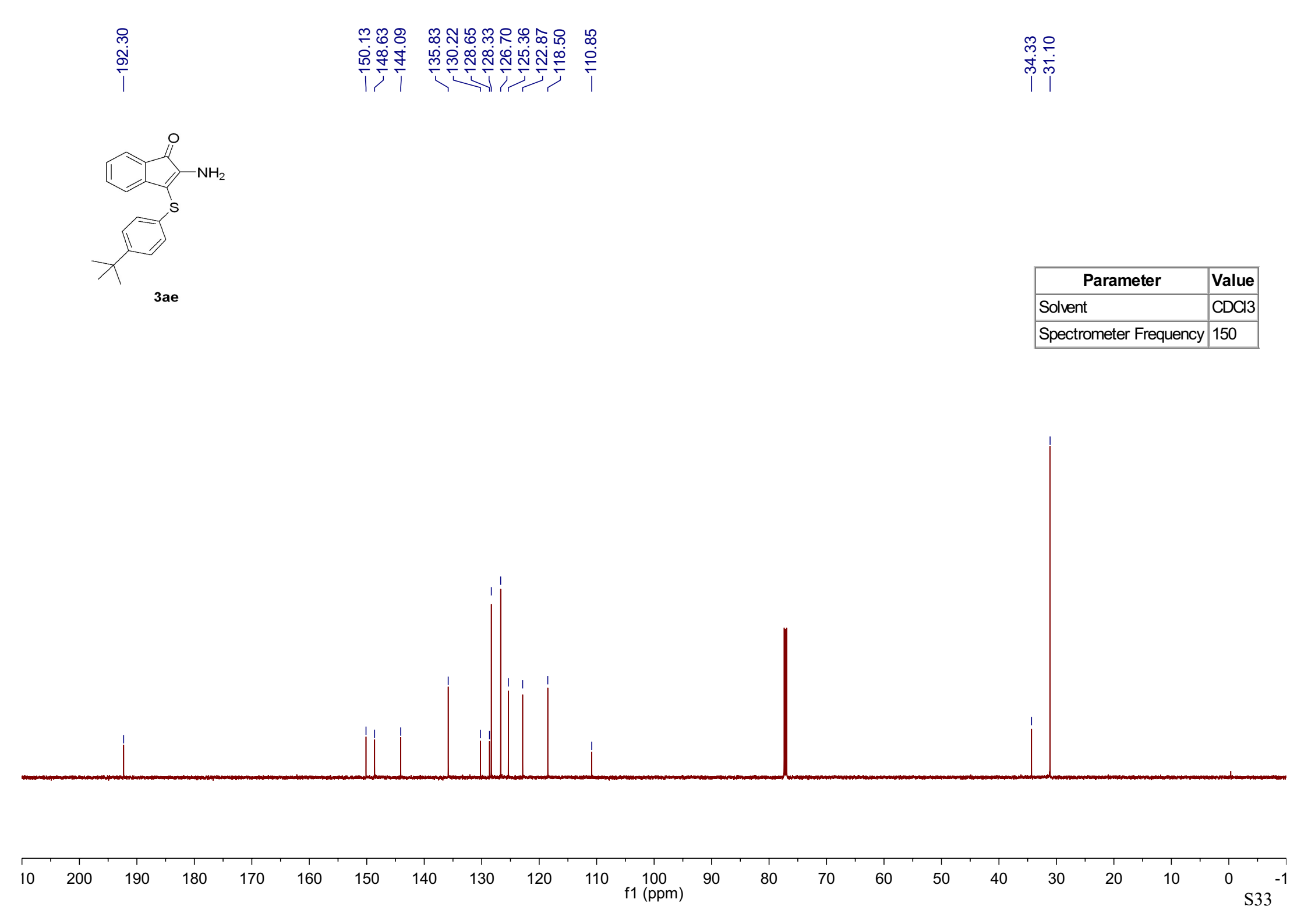
2.00
0.99
1.04
1.05
0.99
2.00
9.00
f1 (ppm)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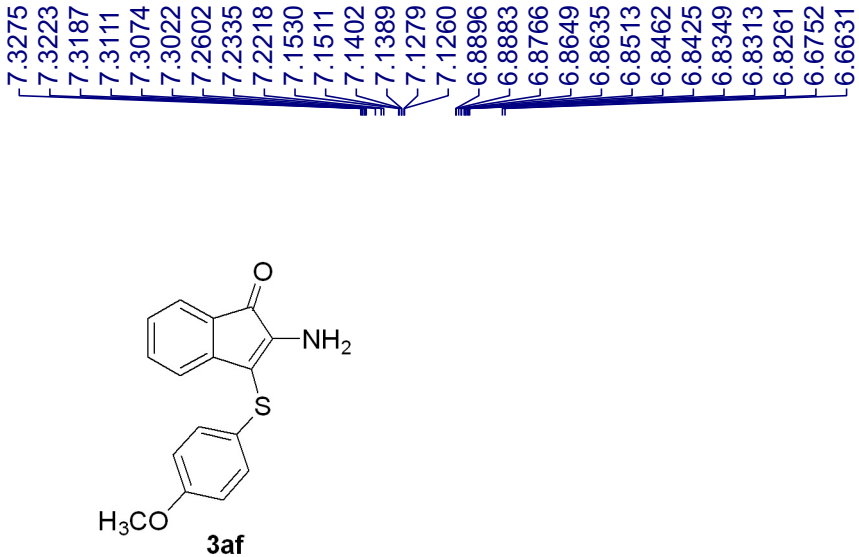
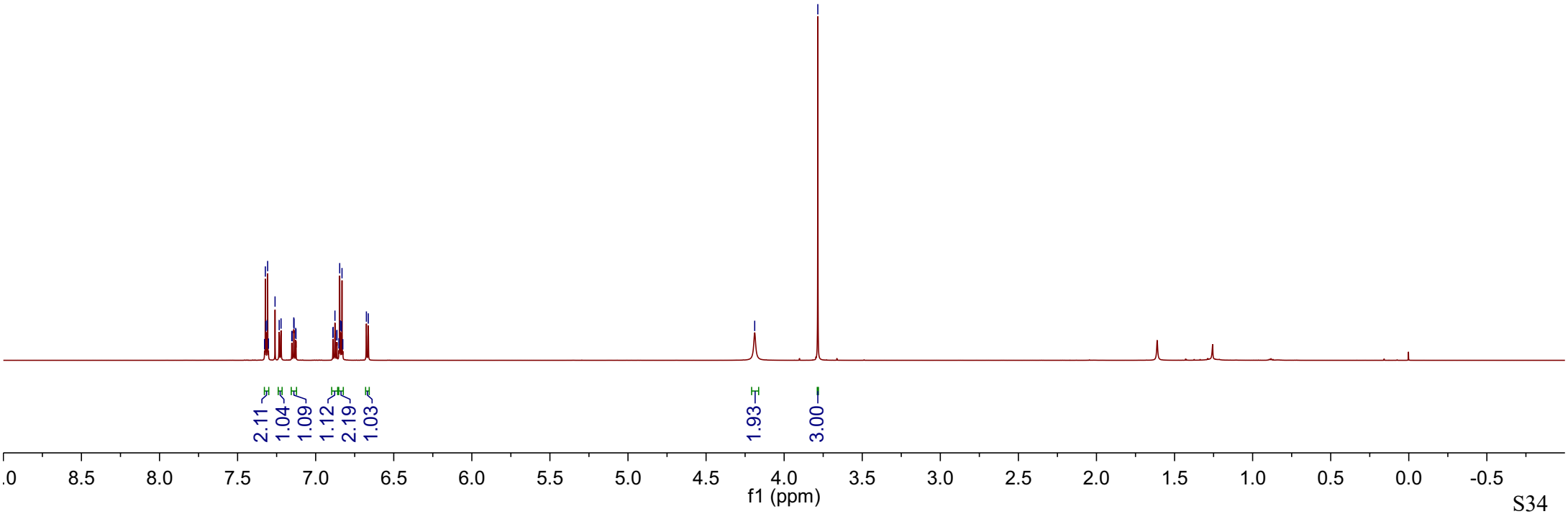
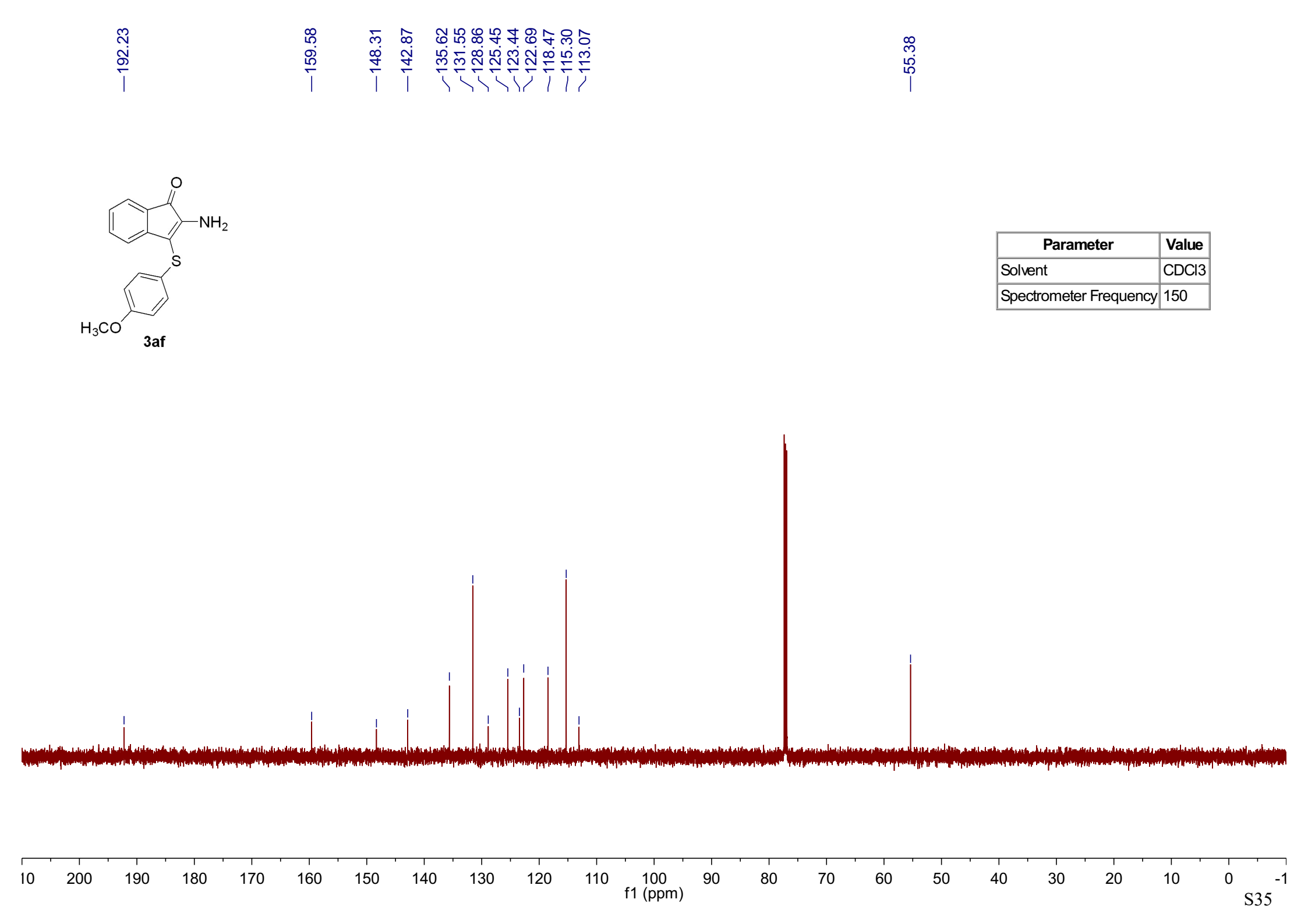
135.83
130.22
128.65
128.33
126.70
125.36
122.87
118.50
110.85
34.33
31.10
O
NH2
S
3ae
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
150
f1 (ppm)



Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

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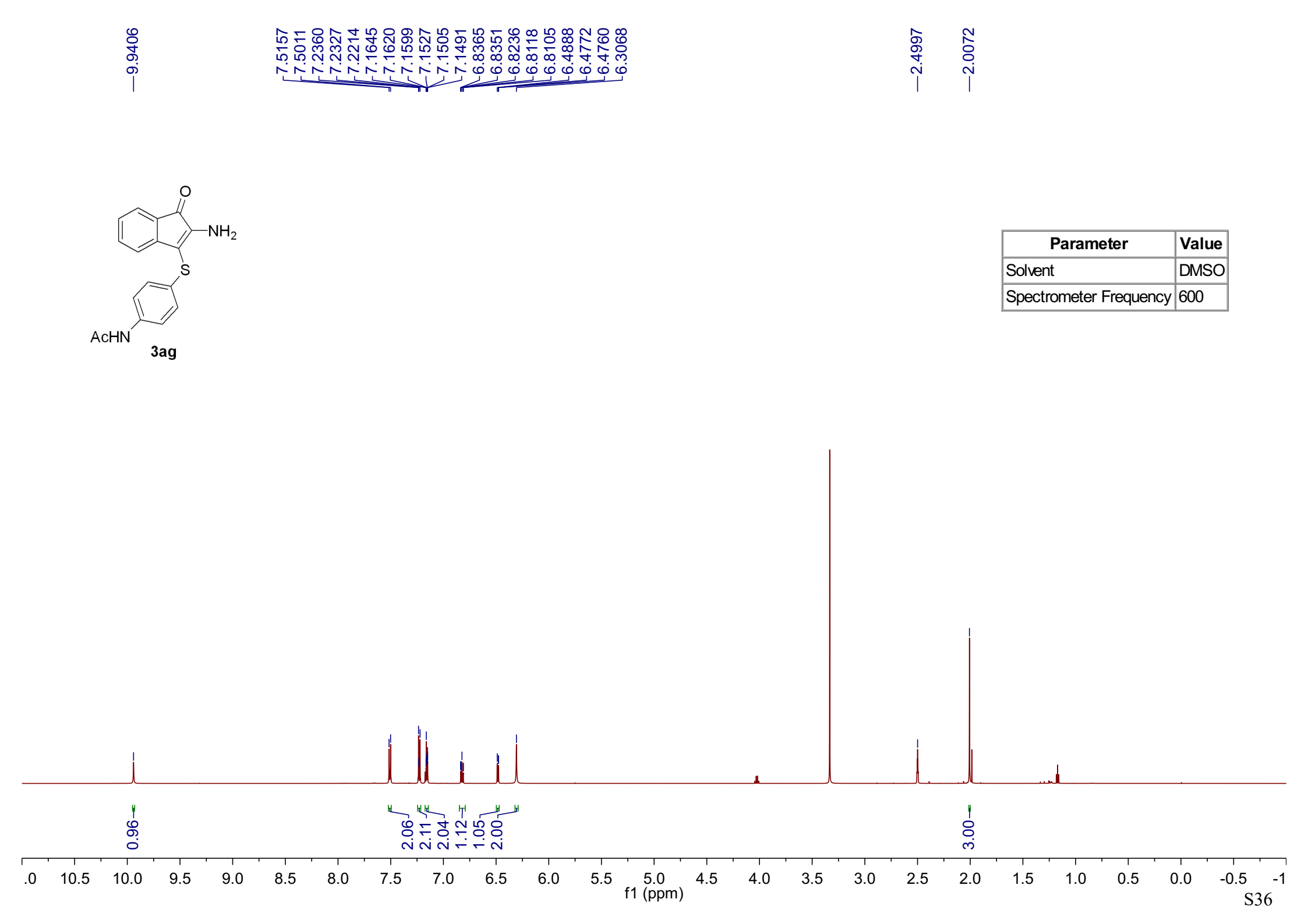
135.62
131.55
128.86
125.45
123.44
122.69
118.47
115.30
113.07
55.38
O
NH2
S
H3CO
3af
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
150
f1 (ppm)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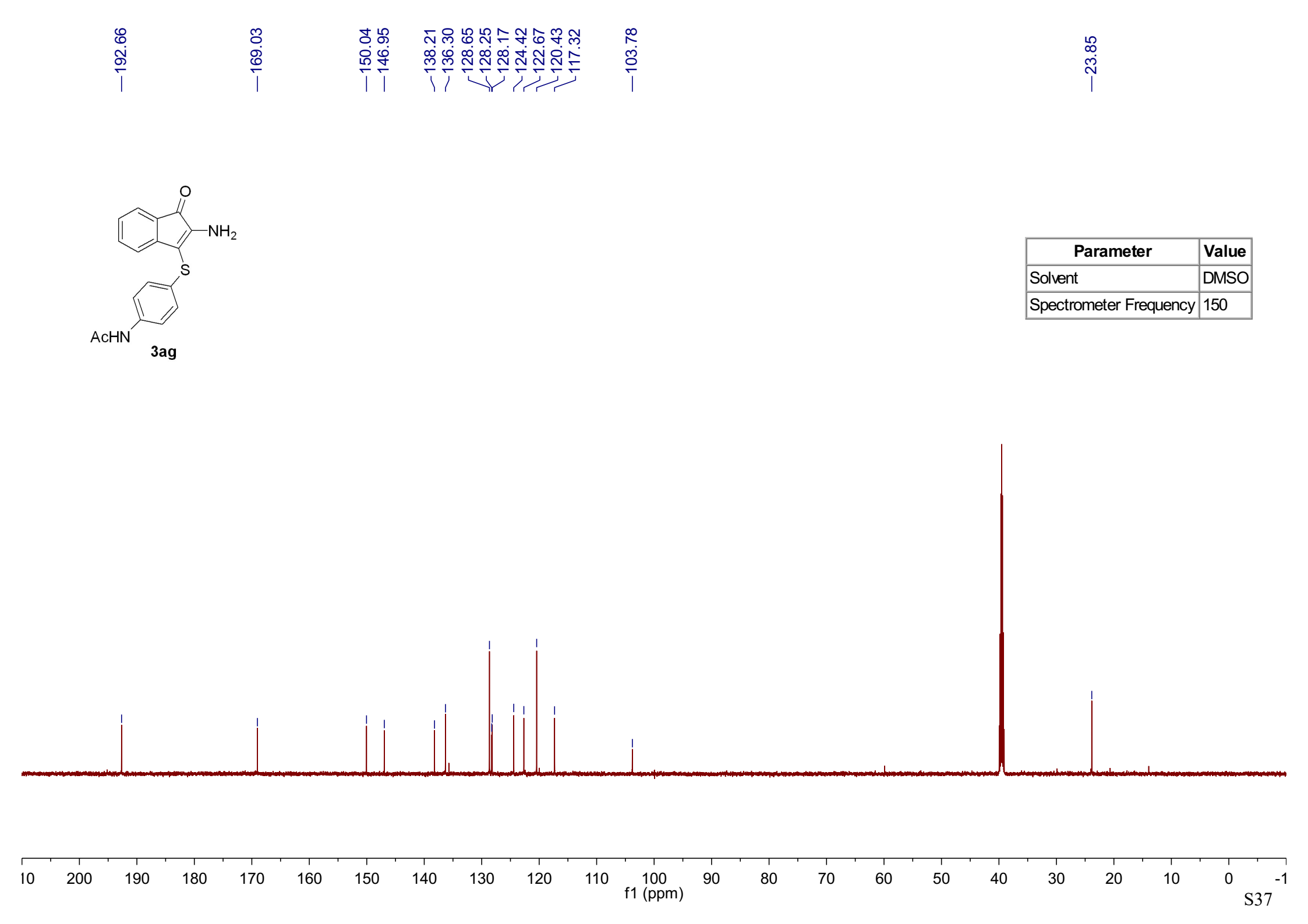
7.5157
7.5011
7.2360
7.2327
7.2214
7.1645
7.1620
7.1599
7.1527
7.1505
7.1491
6.8365
6.8351
6.8236
6.8118
6.8105
6.4888
6.4772
6.4760
6.3068
2.4997
2.0072
O
NH2
S
AcHN
3ag
Parameter
Value
Solvent
DMSO
Spectrometer Frequency
600
0.96
2.06
2.11
2.04
1.12
1.05
2.00
3.00
f1 (ppm)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128.25
128.17
124.42
122.67
120.43
117.32
103.78
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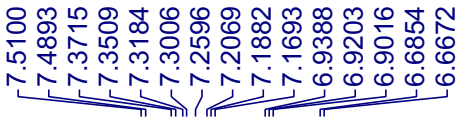
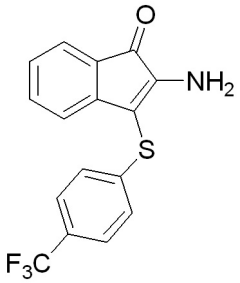
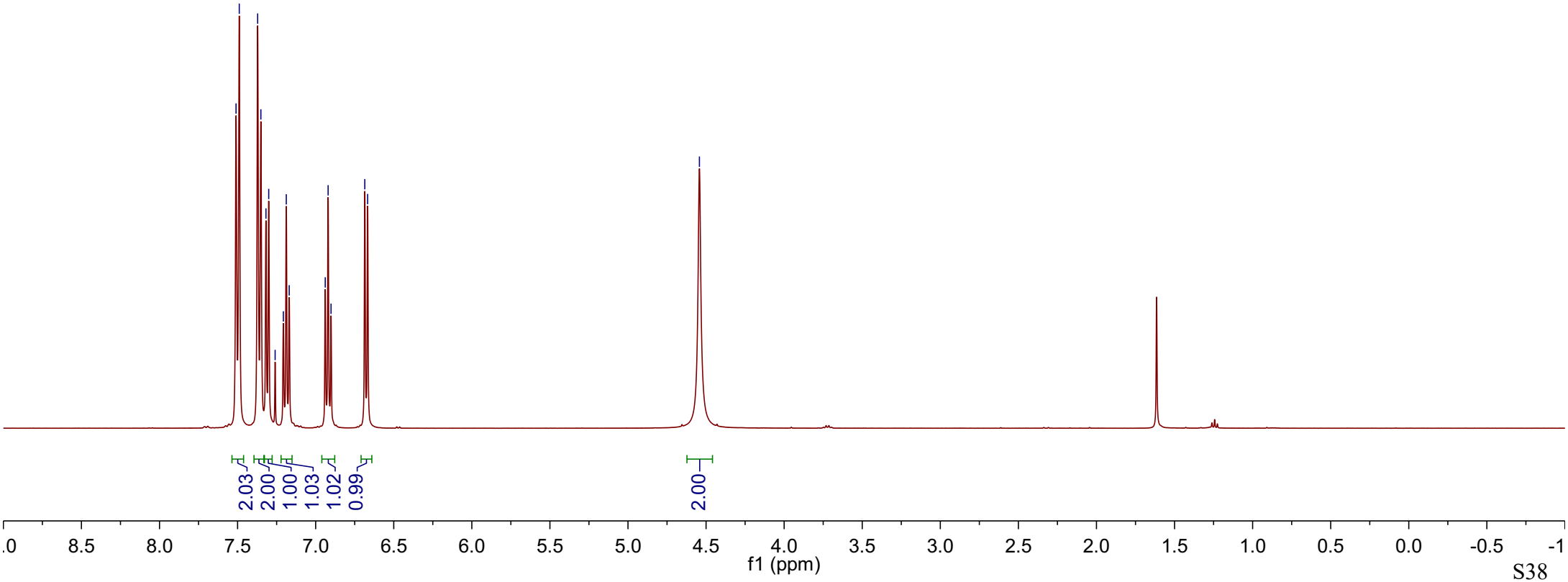
NH2
S
AcHN
3ag
Parameter
Value
Solvent
DMSO
Spectrometer Frequency
150
f1 (ppm)





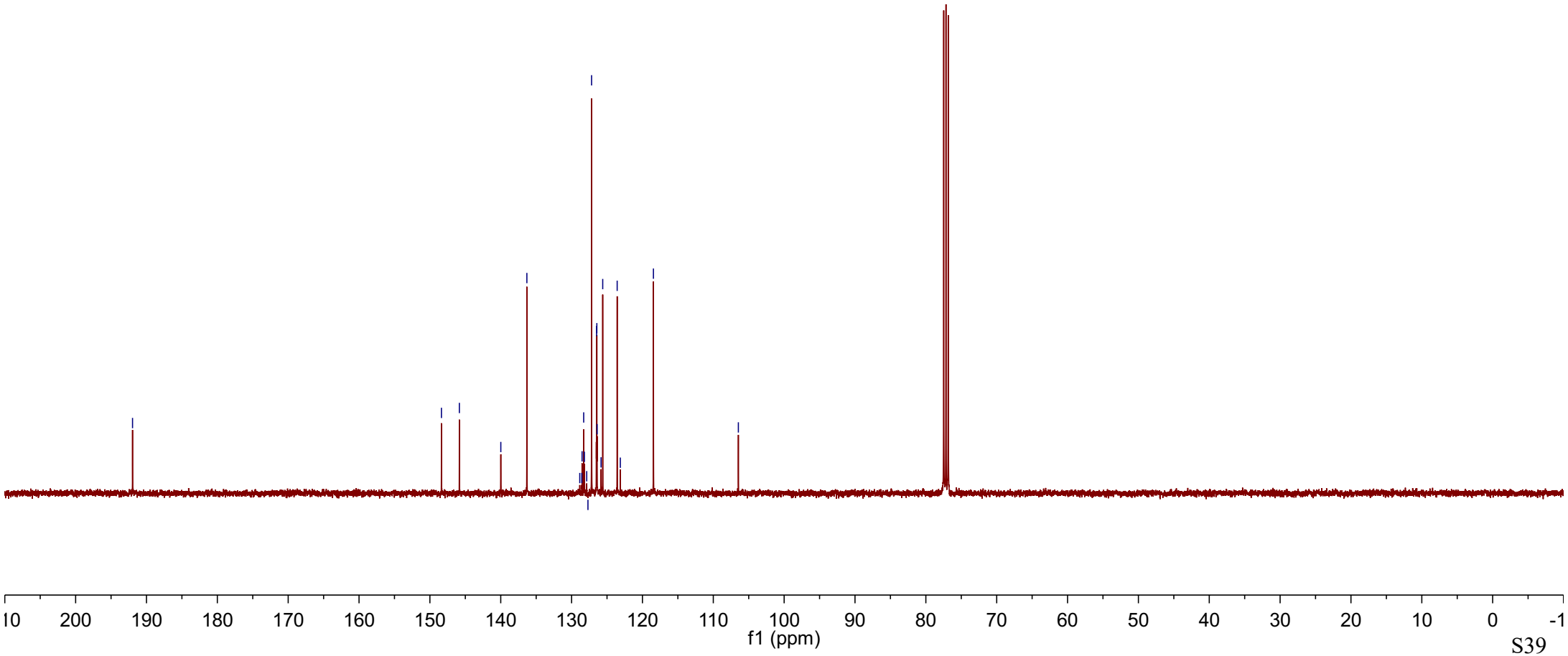
3ah

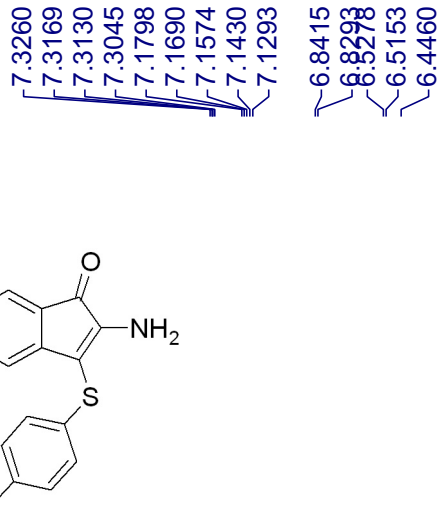
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	400



3ah

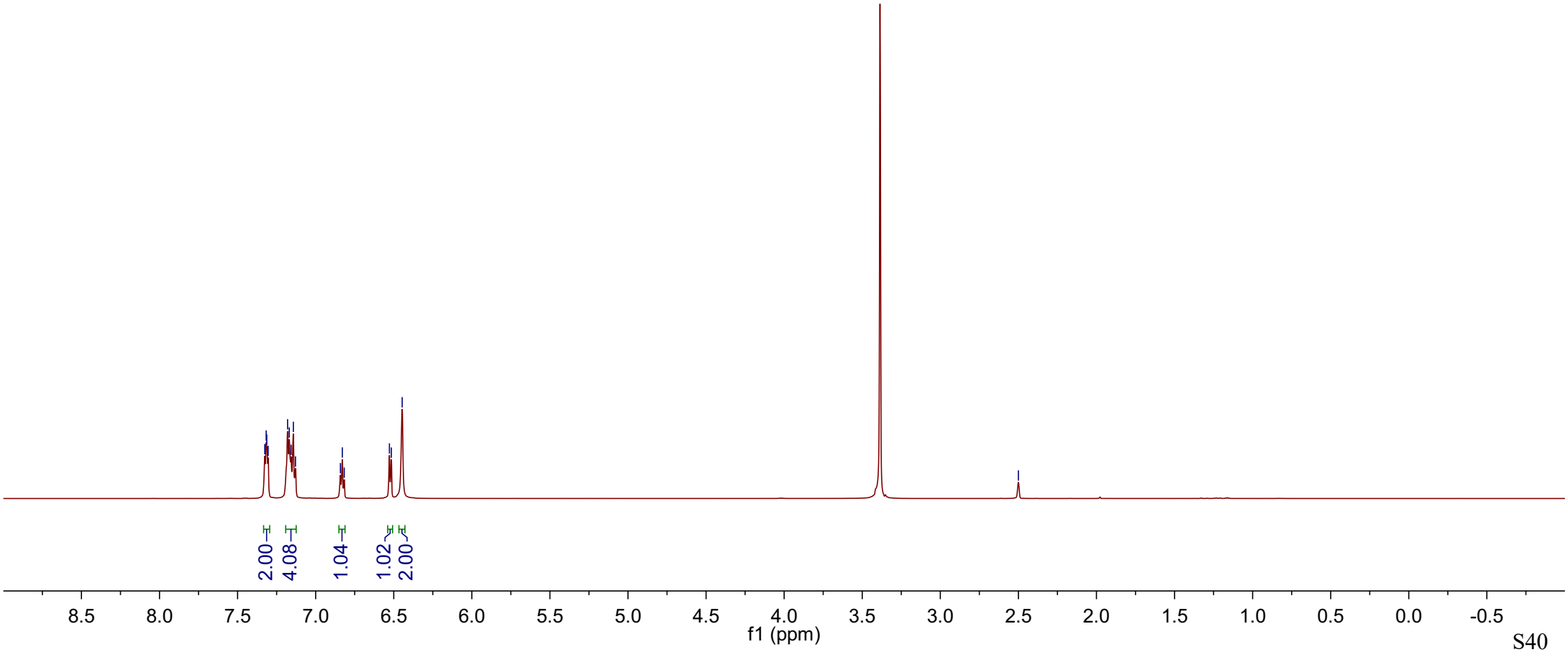
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	100

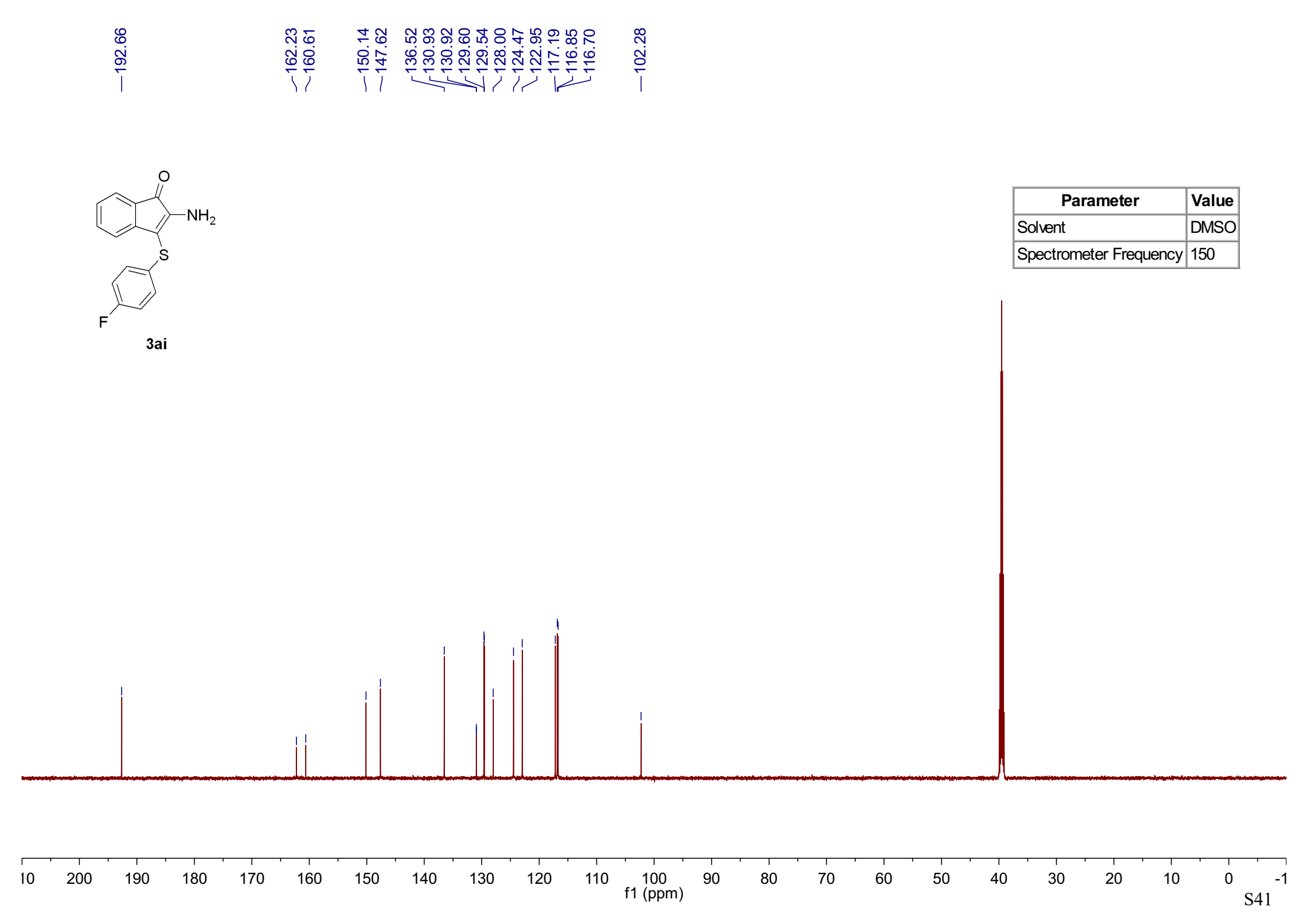




3ai

Parameter	Value
Solvent	DMSO
Spectrometer Frequency	600

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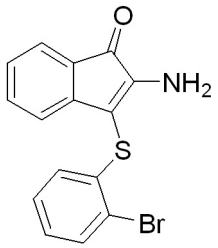
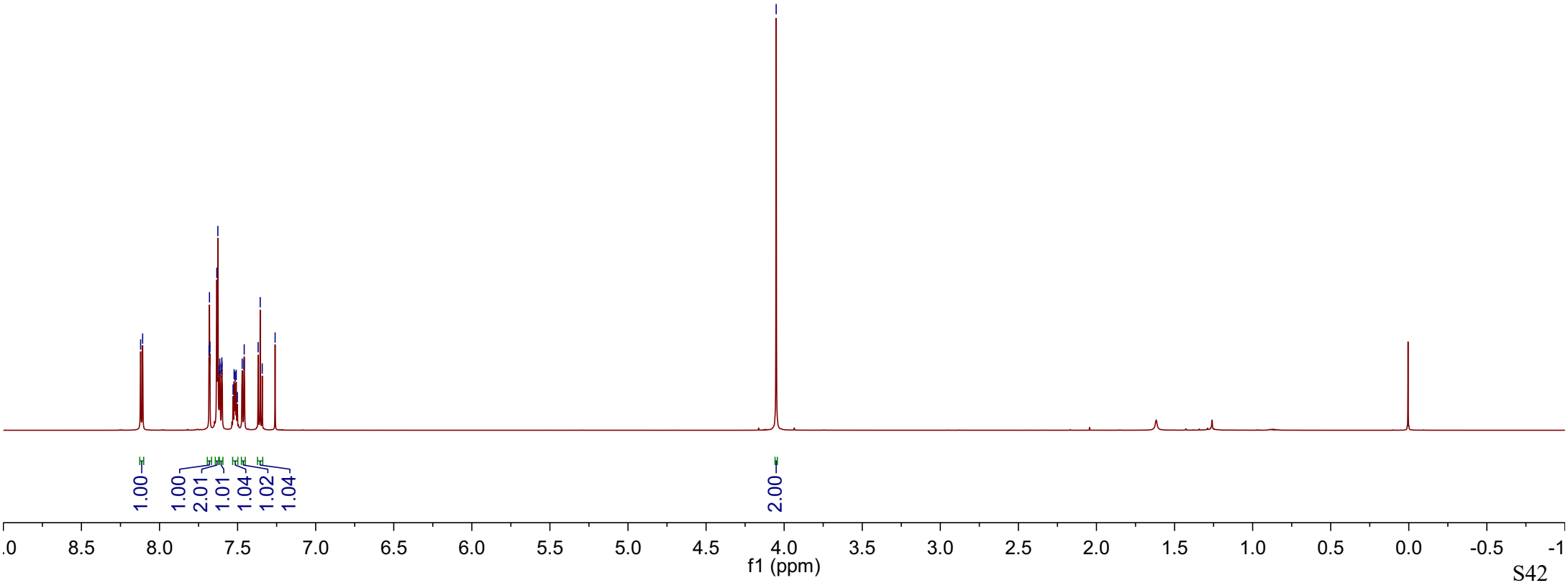
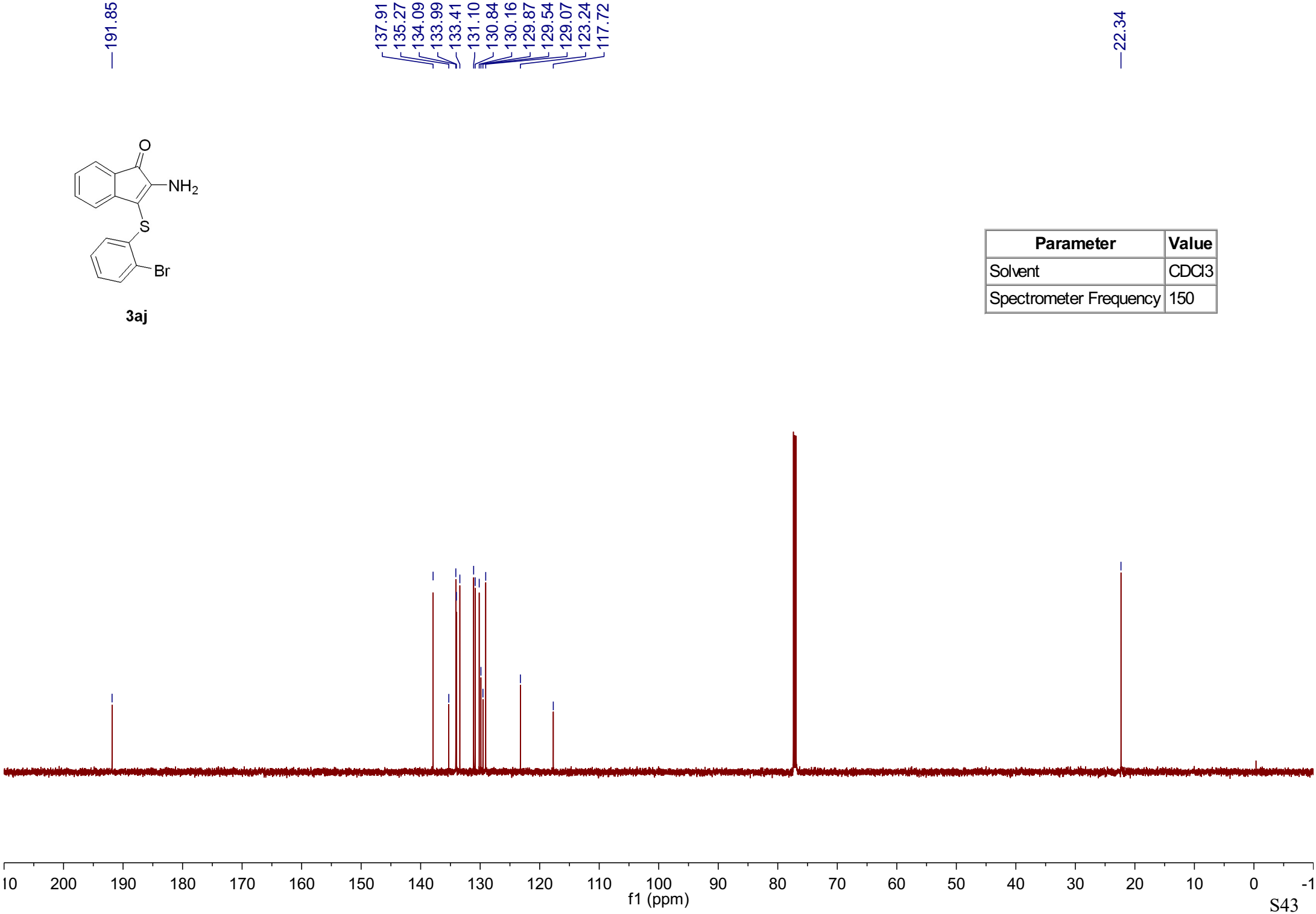
162.23
160.61
150.14
147.62
136.52
130.93
130.92
129.60
129.54
128.00
124.47
122.95
117.19
116.85
116.70
102.28
O
NH2
S
F
3ai
Parameter
Value
Solvent
DMSO
Spectrometer Frequency
150
f1 (ppm)

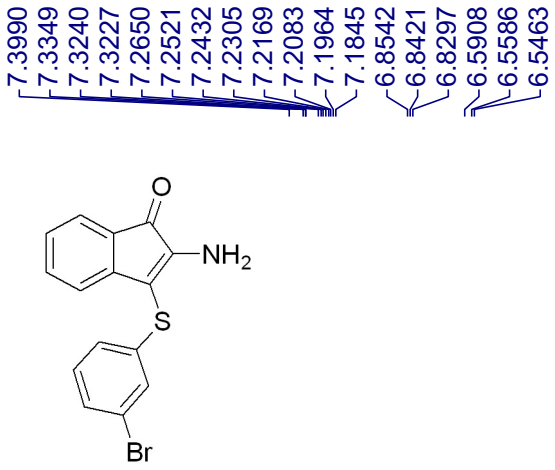


3aj

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

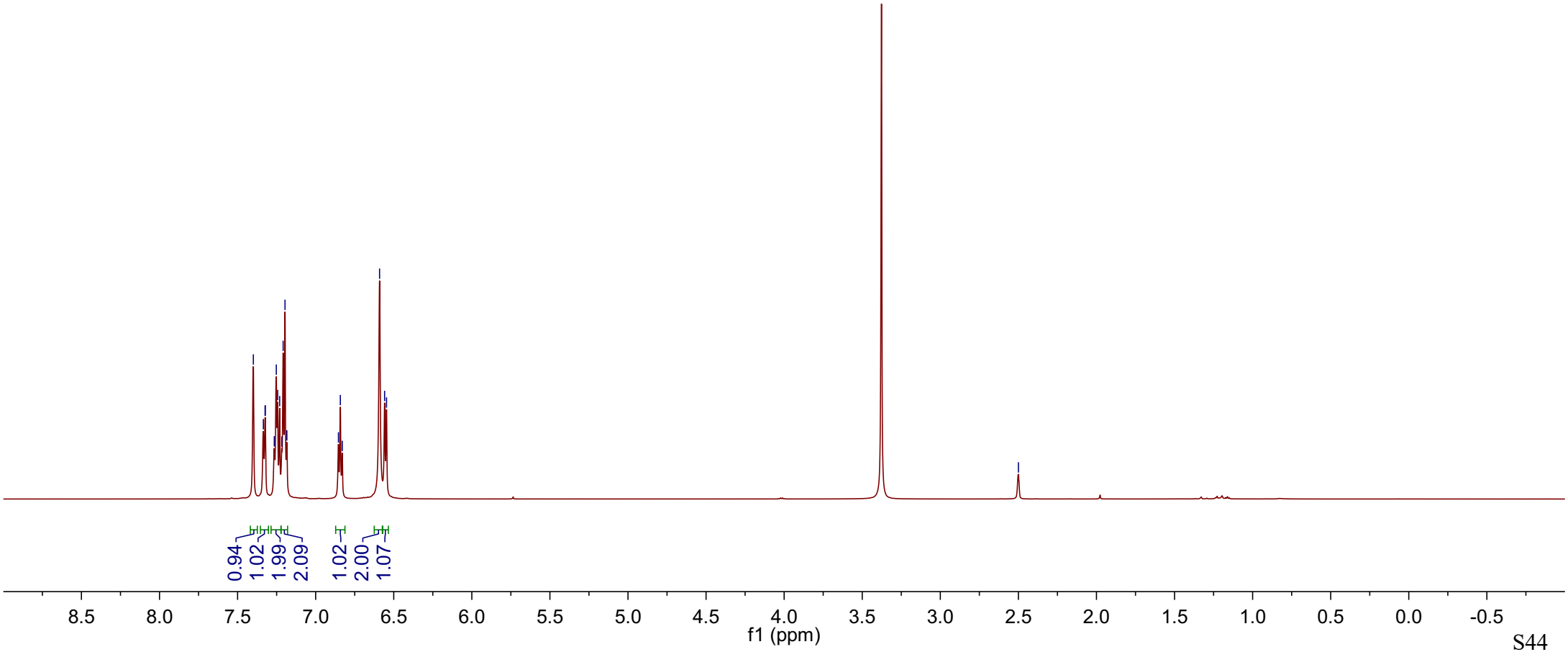


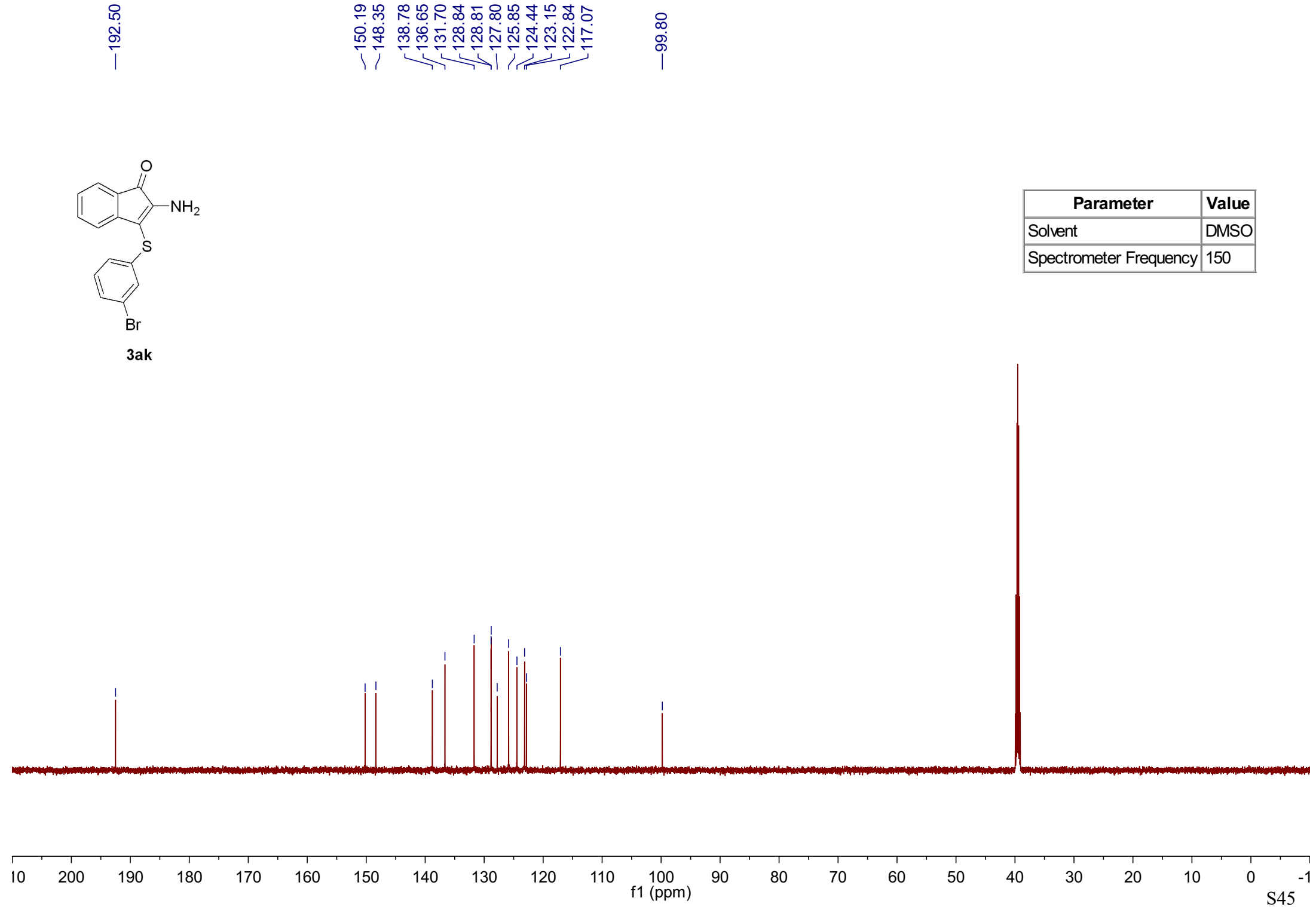

191.85
137.91
135.27
134.09
133.99
133.41
131.10
130.84
130.16
129.87
129.54
129.07
123.24
117.72
22.34
O
NH2
S
Br
3aj
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
150
f1 (ppm)

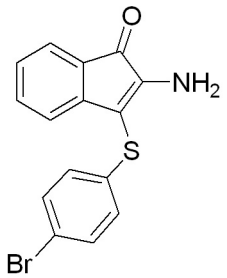


3ak

Parameter	Value
Solvent	DMSO
Spectrometer Frequency	600

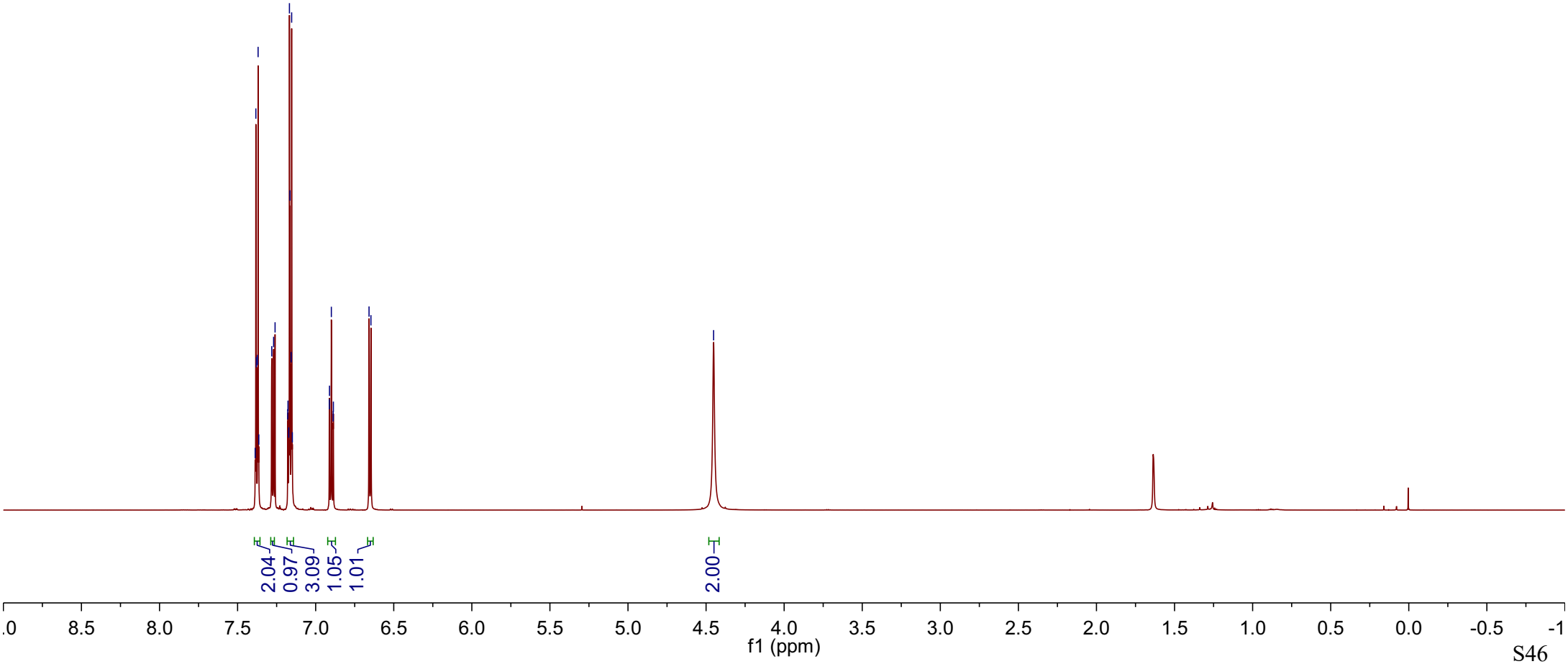


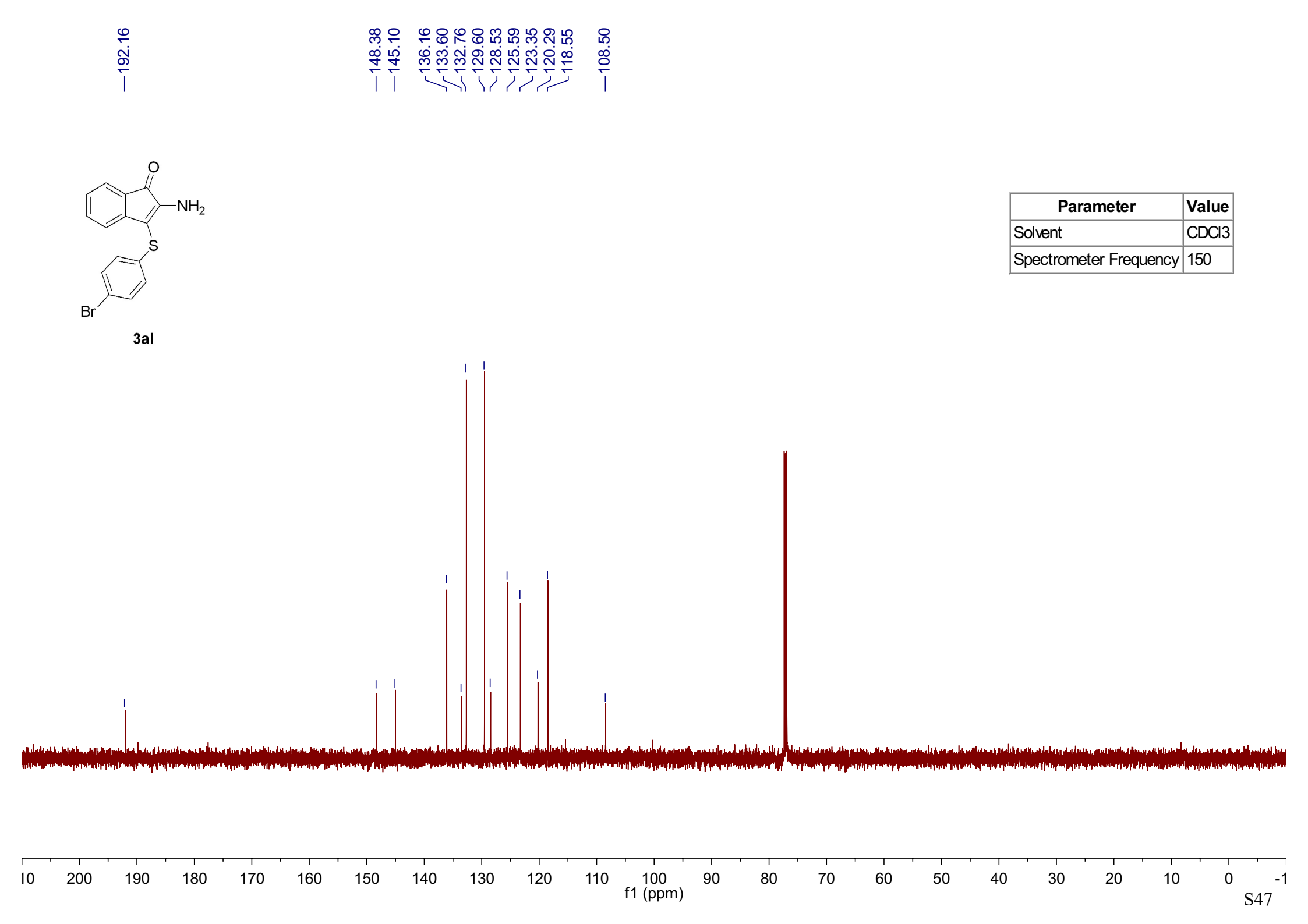

192.50
150.19
148.35
138.78
136.65
131.70
128.84
128.81
127.80
125.85
124.44
123.15
122.84
117.07
99.80
O
NH2
S
Br
3ak
Parameter
Value
Solvent
DMSO
Spectrometer Frequency
150
f1 (ppm)

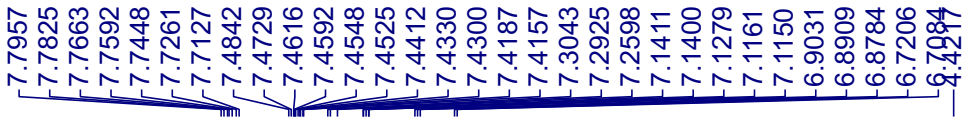


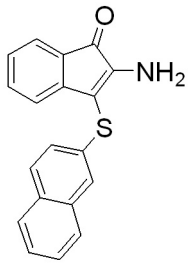
3al

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



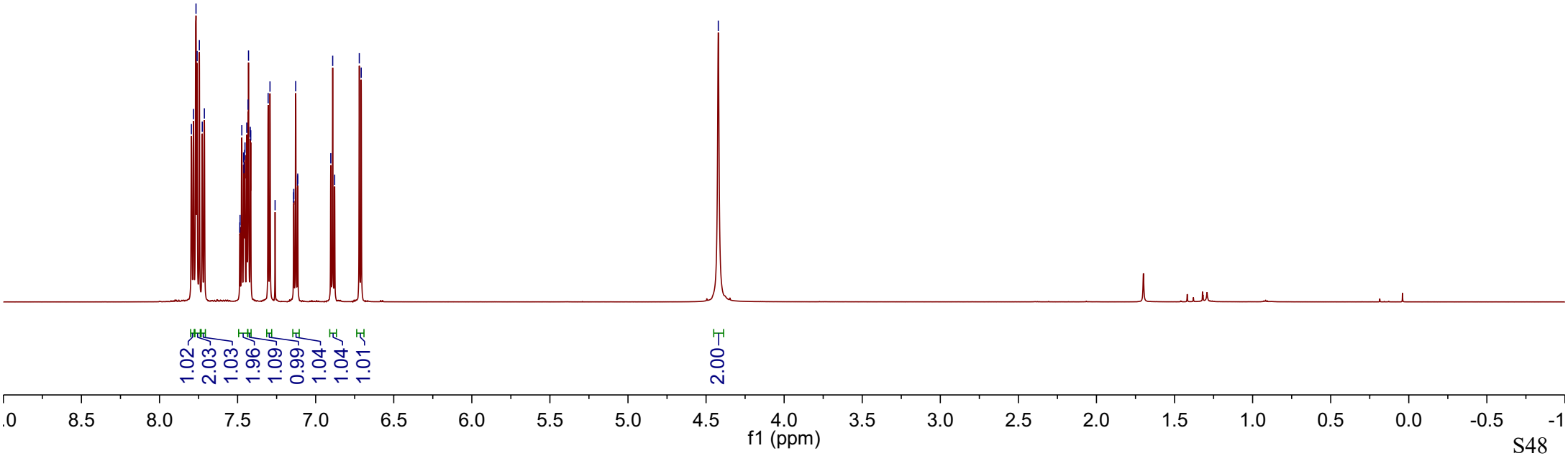

192.16
148.38
145.10
136.16
133.60
132.76
129.60
128.53
125.59
123.35
120.29
118.55
108.50
O
NH2
S
Br
3al
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
150
f1 (ppm)

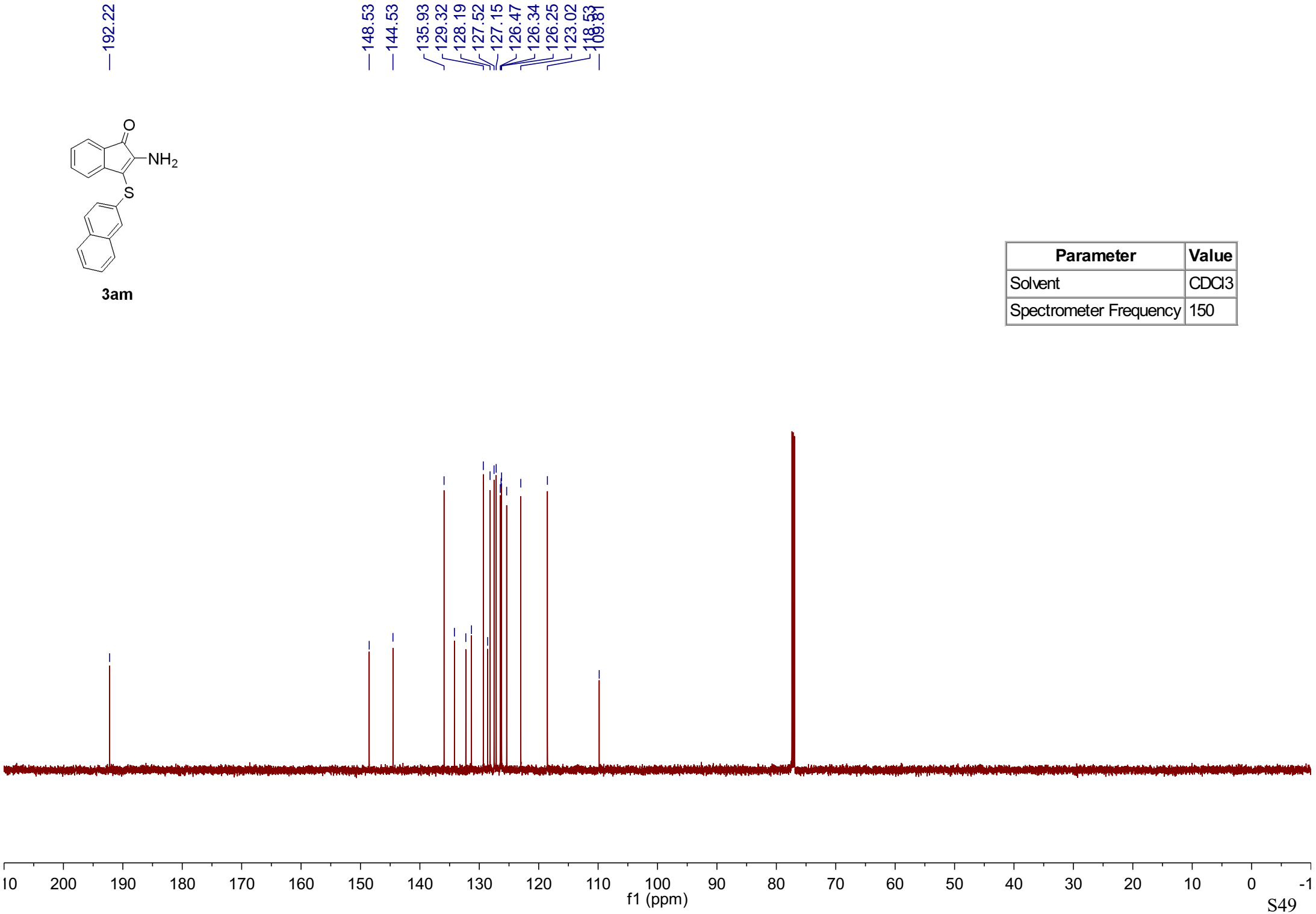


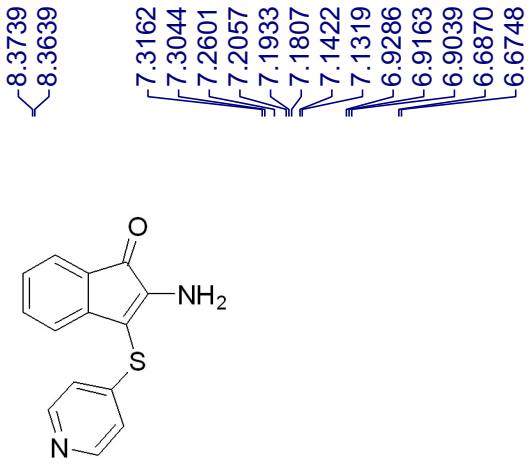


3am

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

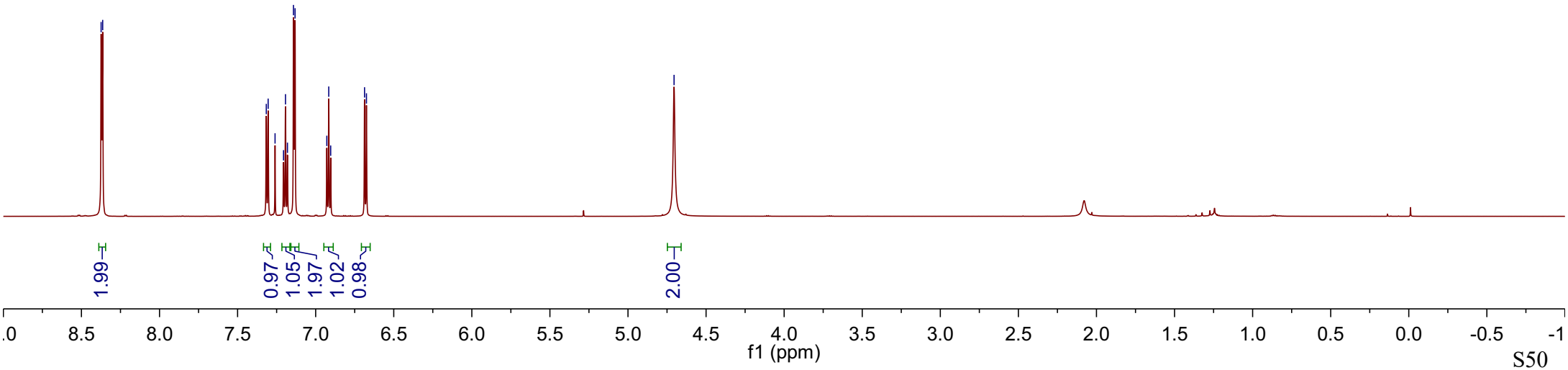


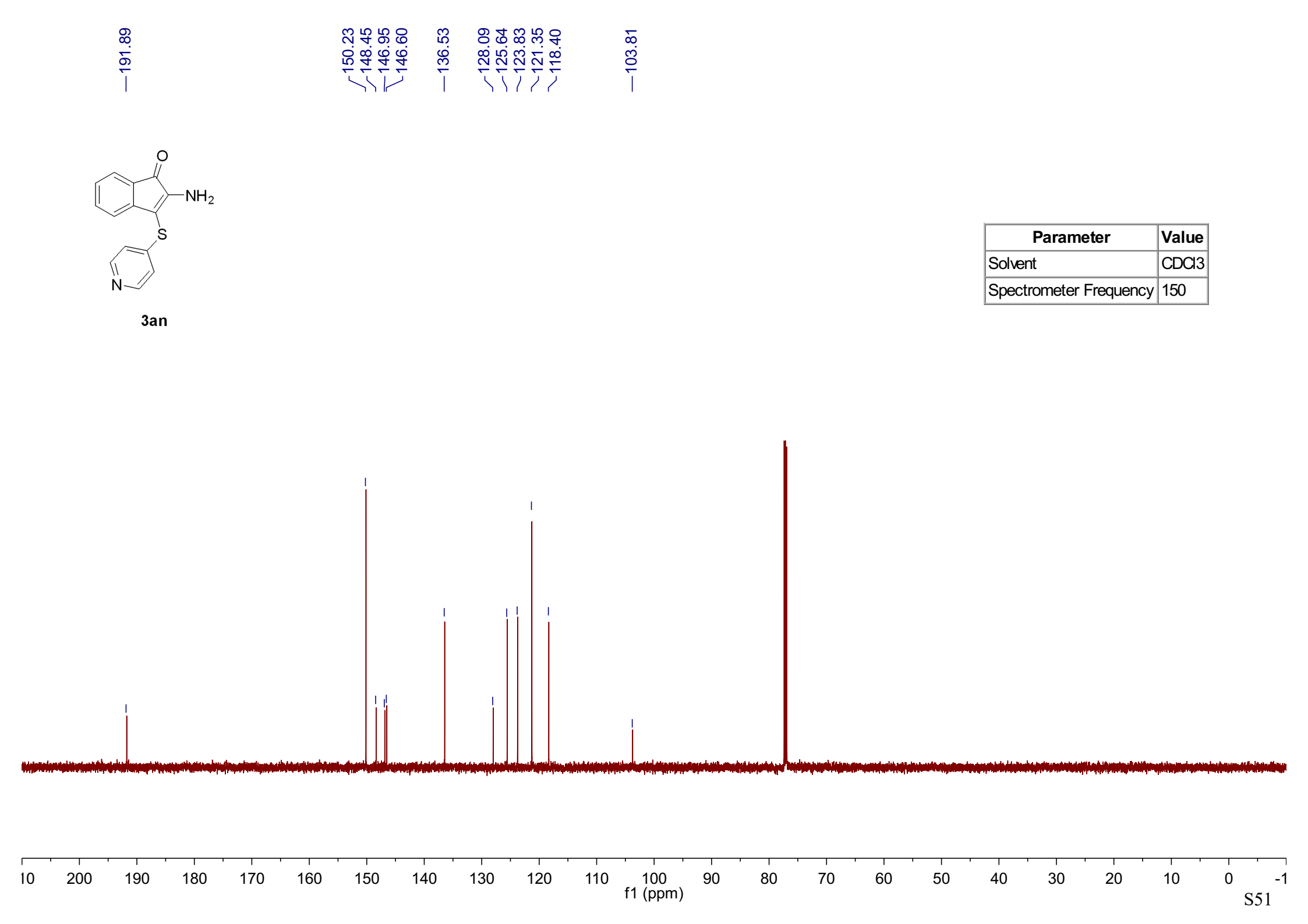

192.22
148.53
144.53
135.93
129.32
128.19
127.52
127.15
126.47
126.34
126.25
123.02
118.53
109.81
O
NH2
S
3am
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
150
f1 (ppm)

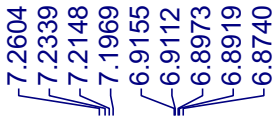


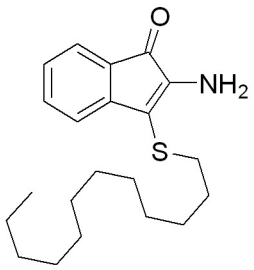
3an

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



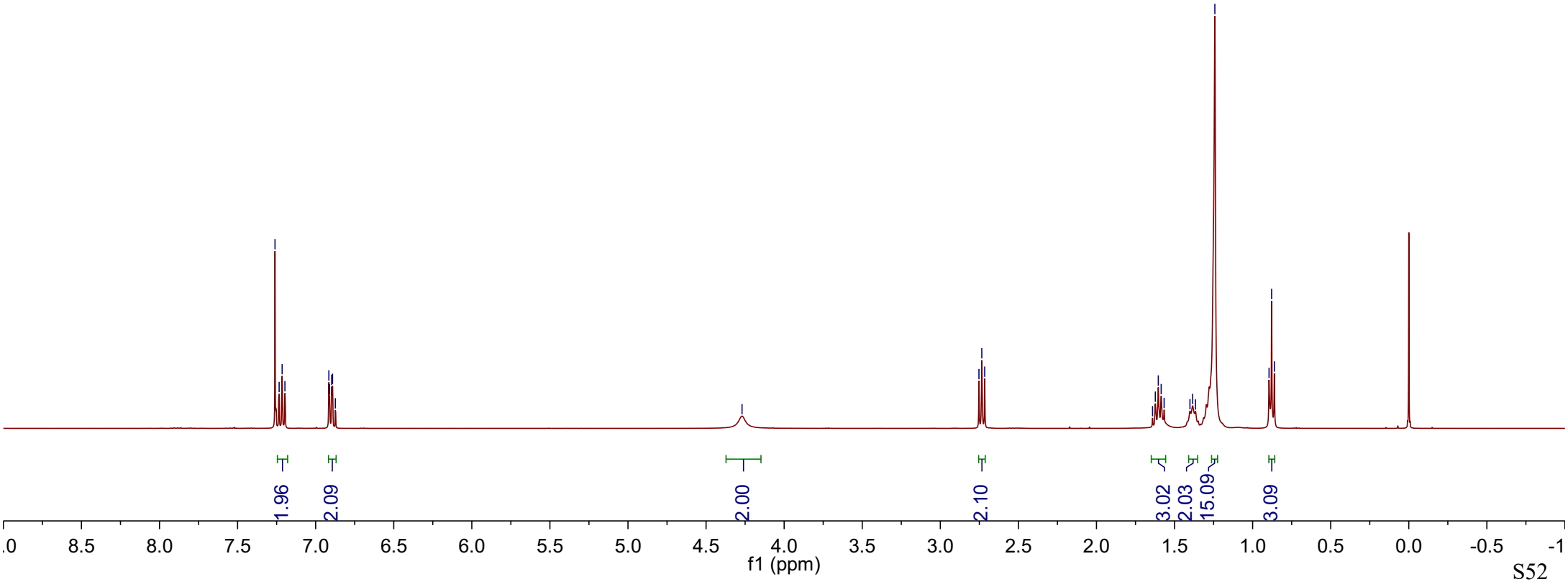

191.89
150.23
148.45
146.95
146.60
136.53
128.09
125.64
123.83
121.35
118.40
103.81
O
NH2
S
N
3an
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
150
f1 (ppm)

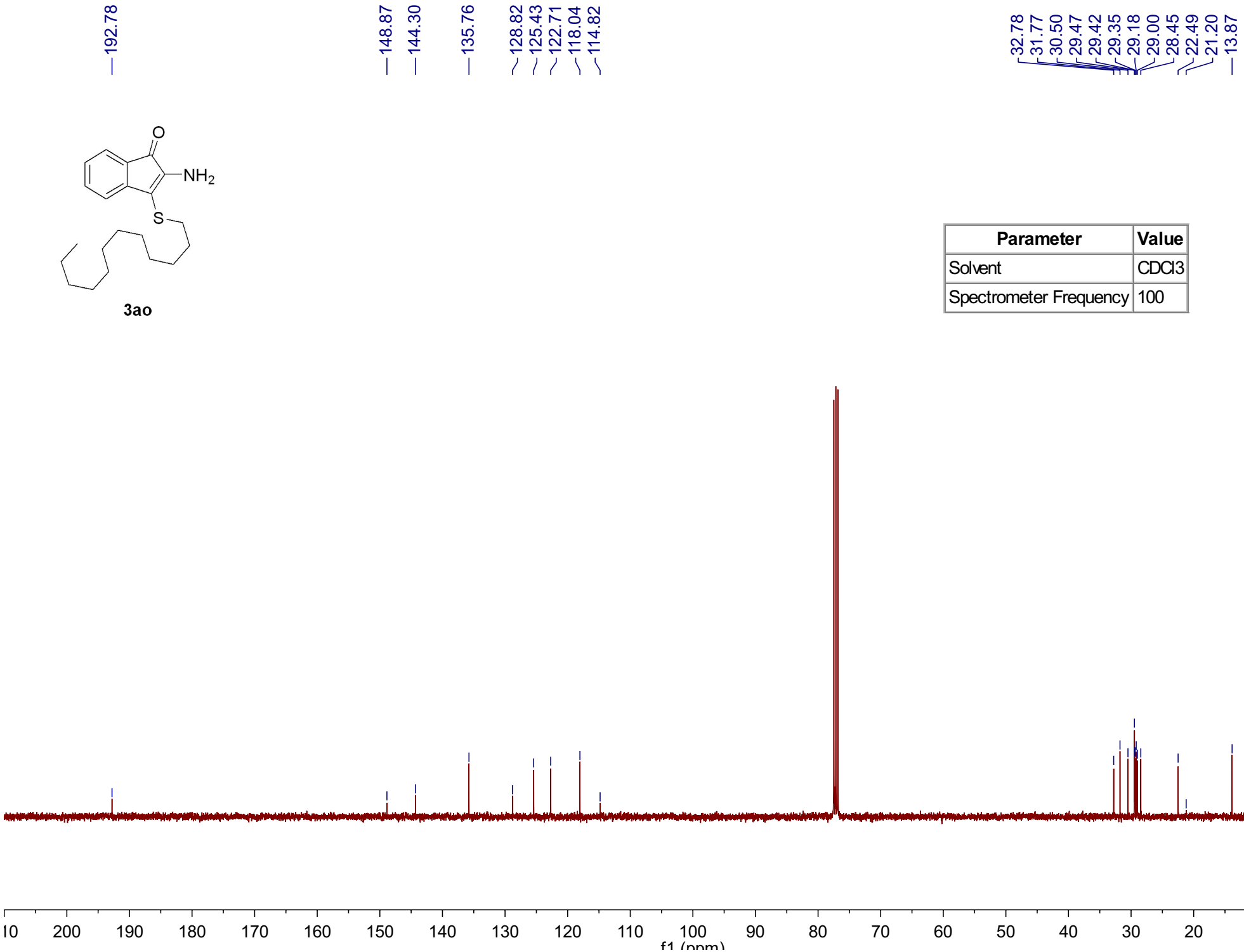


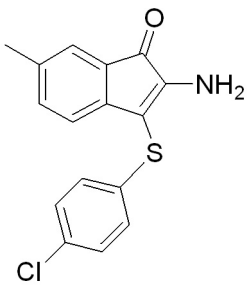


3ao

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	400

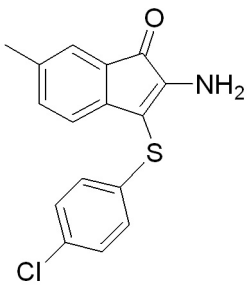



192.78
148.87
144.30
135.76
128.82
125.43
122.71
118.04
114.82
32.78
31.77
30.50
29.47
29.42
29.35
29.18
29.00
28.45
22.49
21.20
13.87
O
NH2
S
3ao
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
100
f1 (ppm)



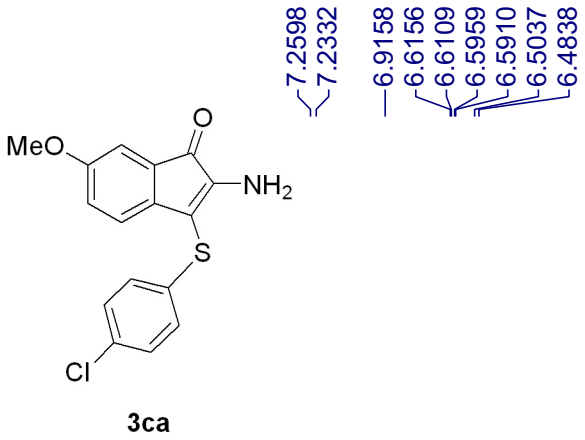
3ba

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



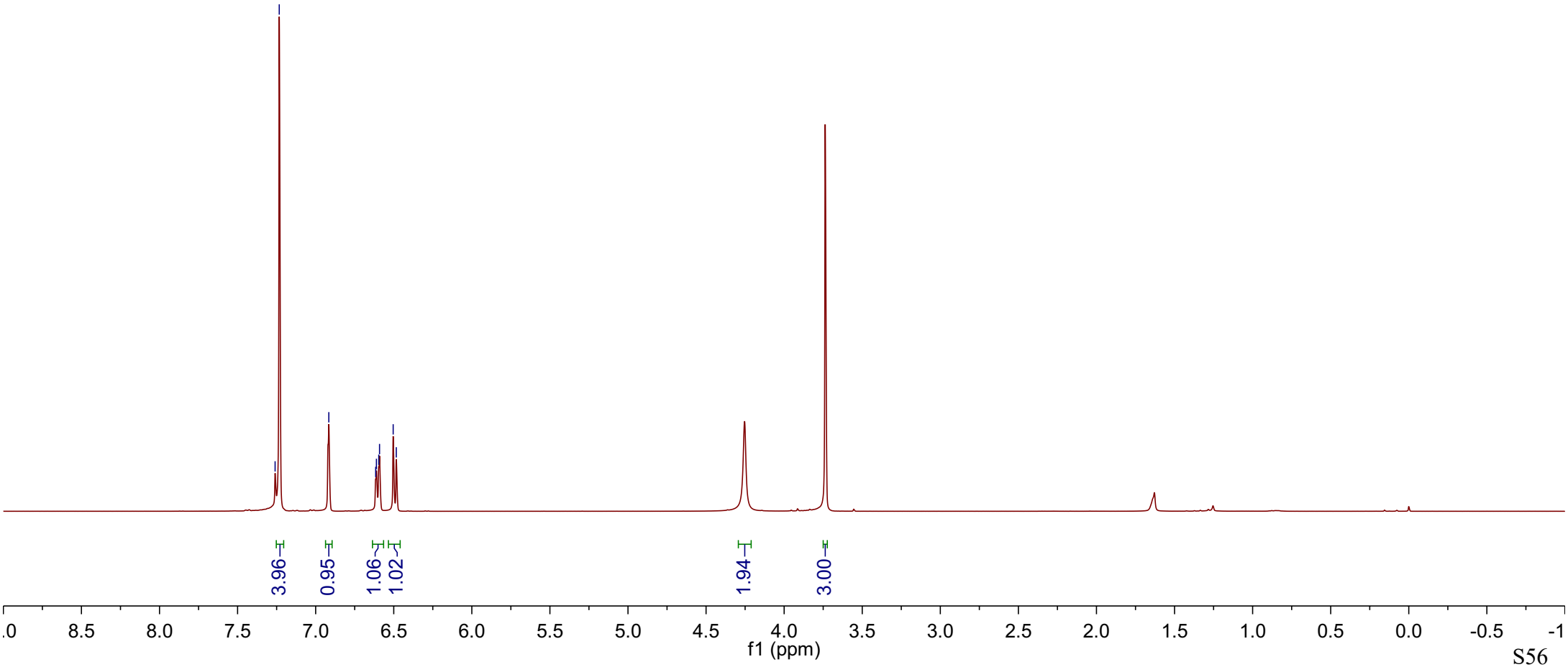
3ba

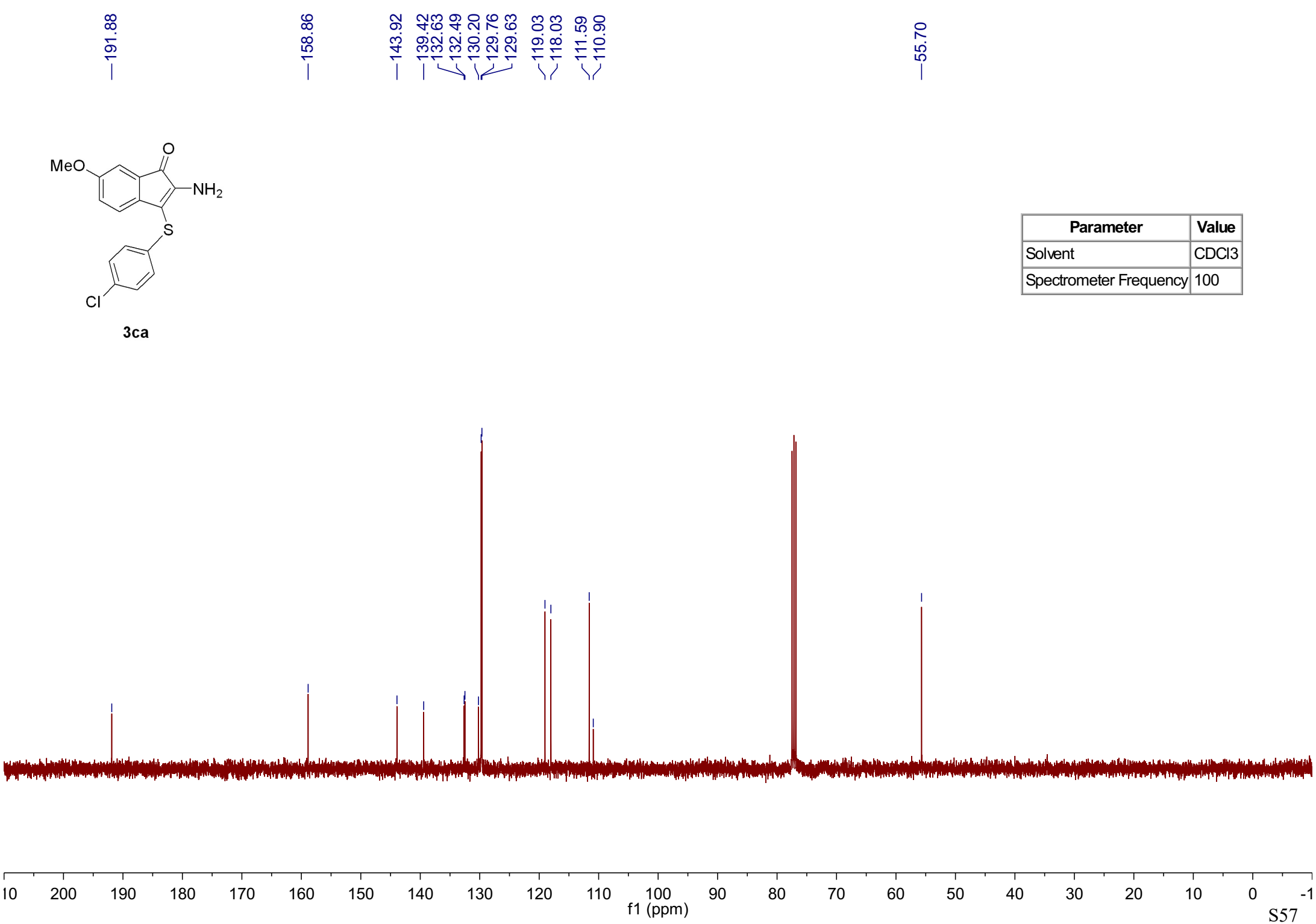
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

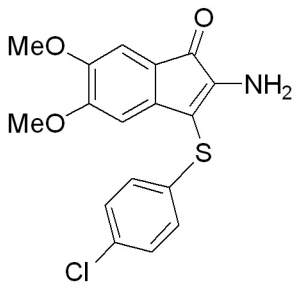


3ca

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	400

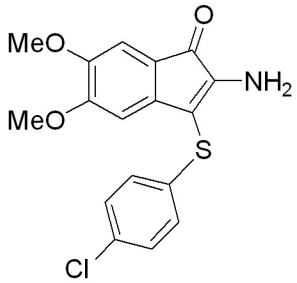



191.88
158.86
143.92
139.42
132.63
132.49
130.20
129.76
129.63
119.03
118.03
111.59
110.90
55.70
MeO
O
NH2
S
Cl
3ca
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
100
f1 (ppm)



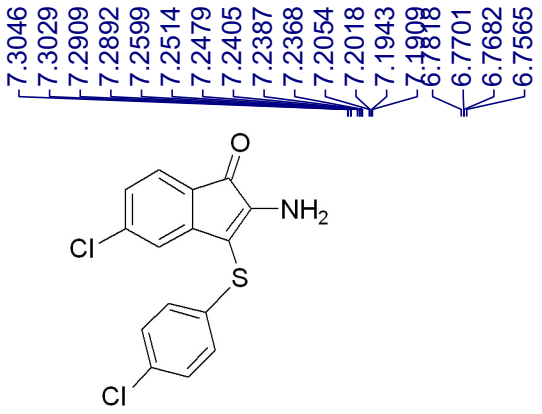
3da

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	400



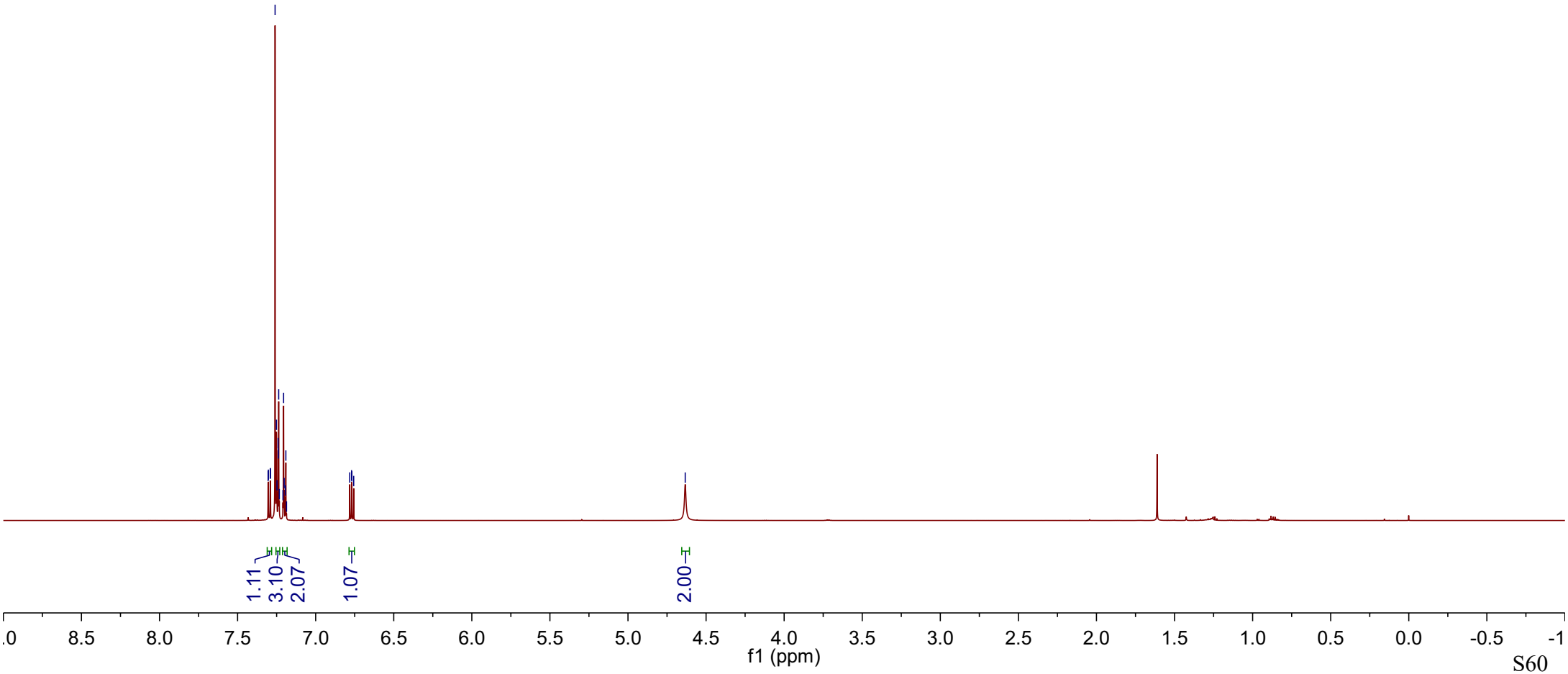
3da

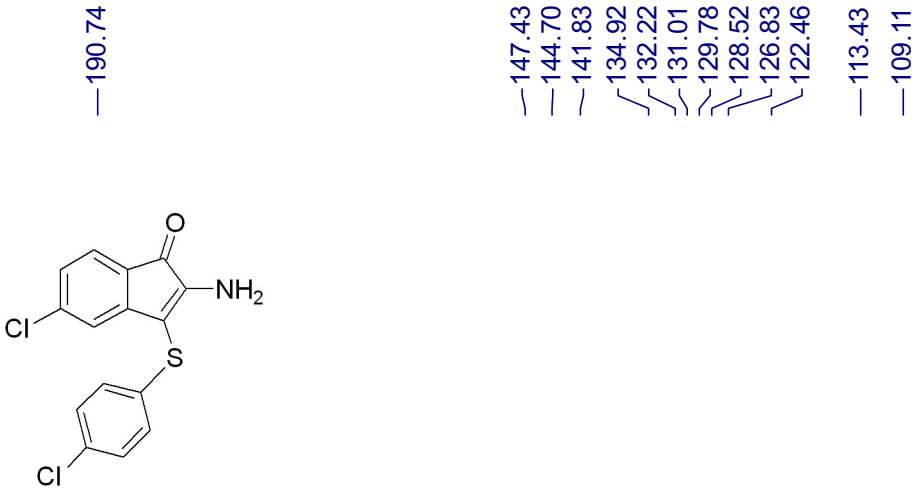
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	100



3ea

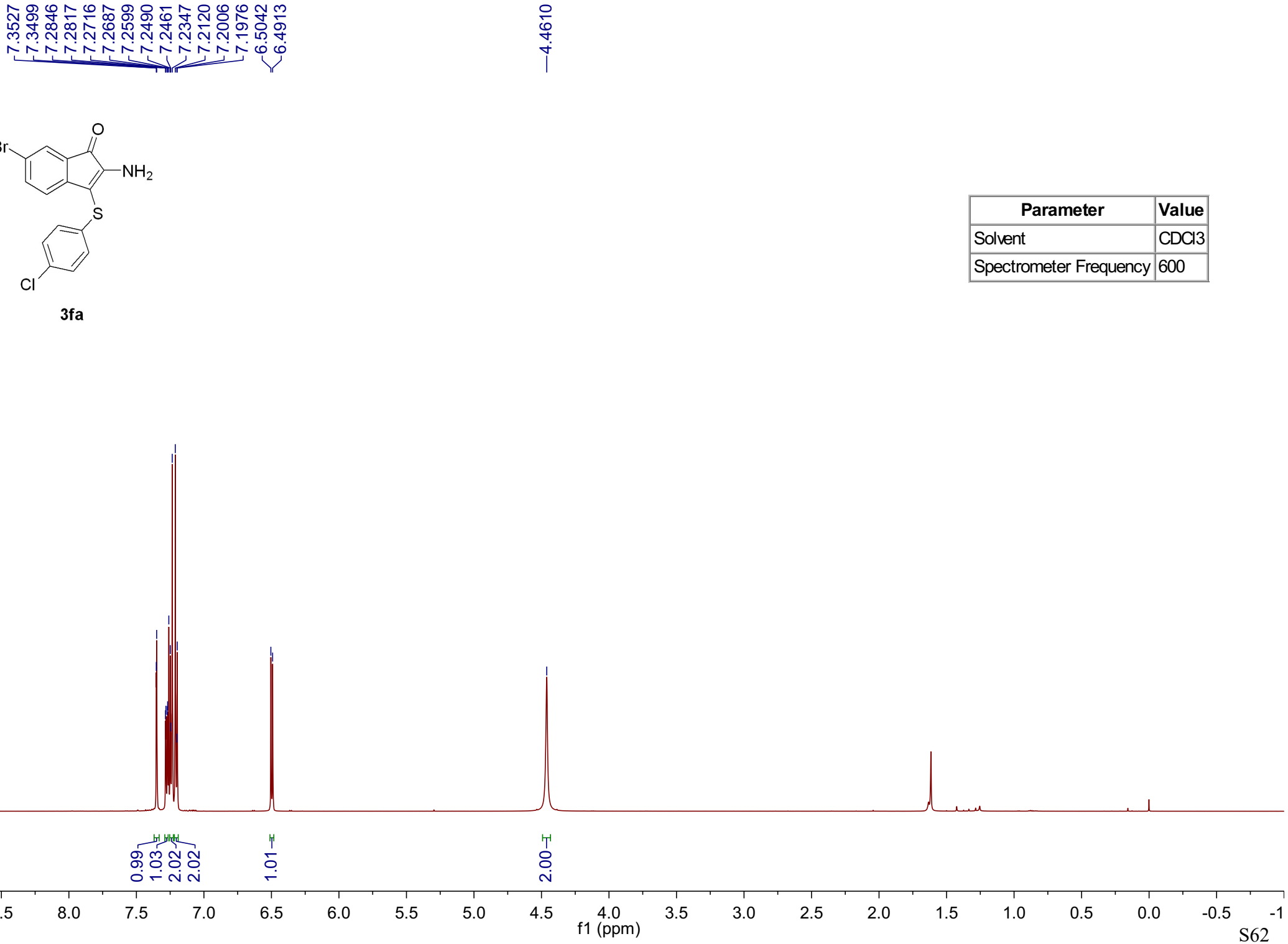
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

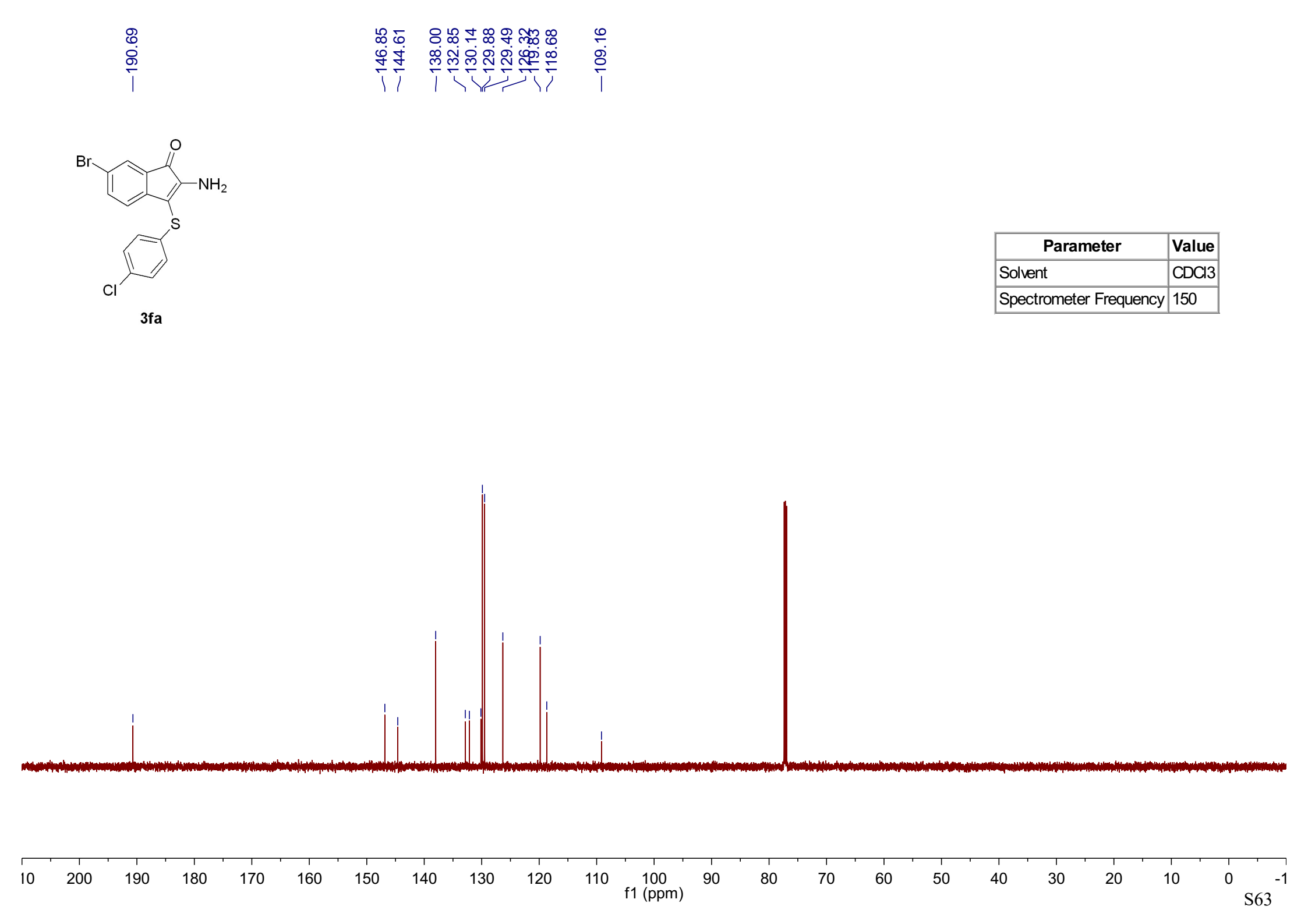


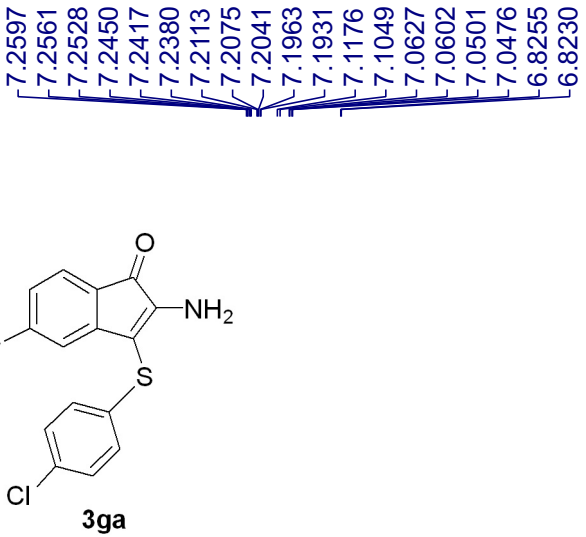


3ea

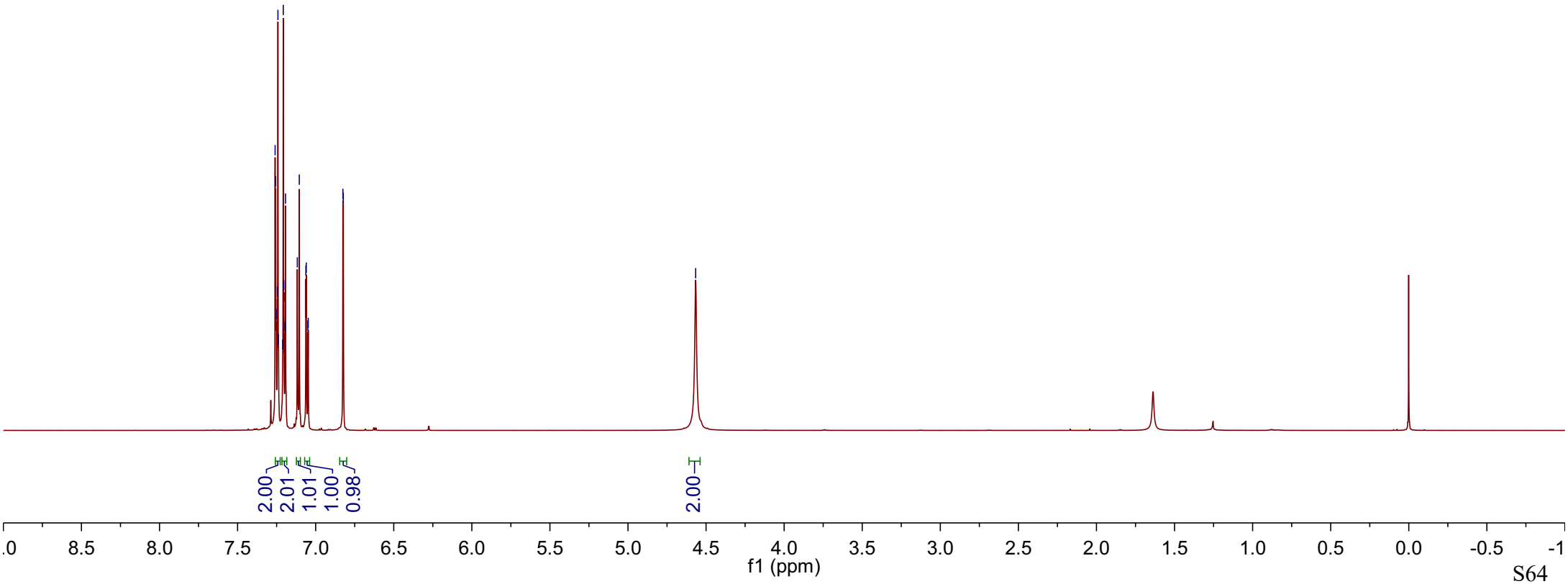
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150

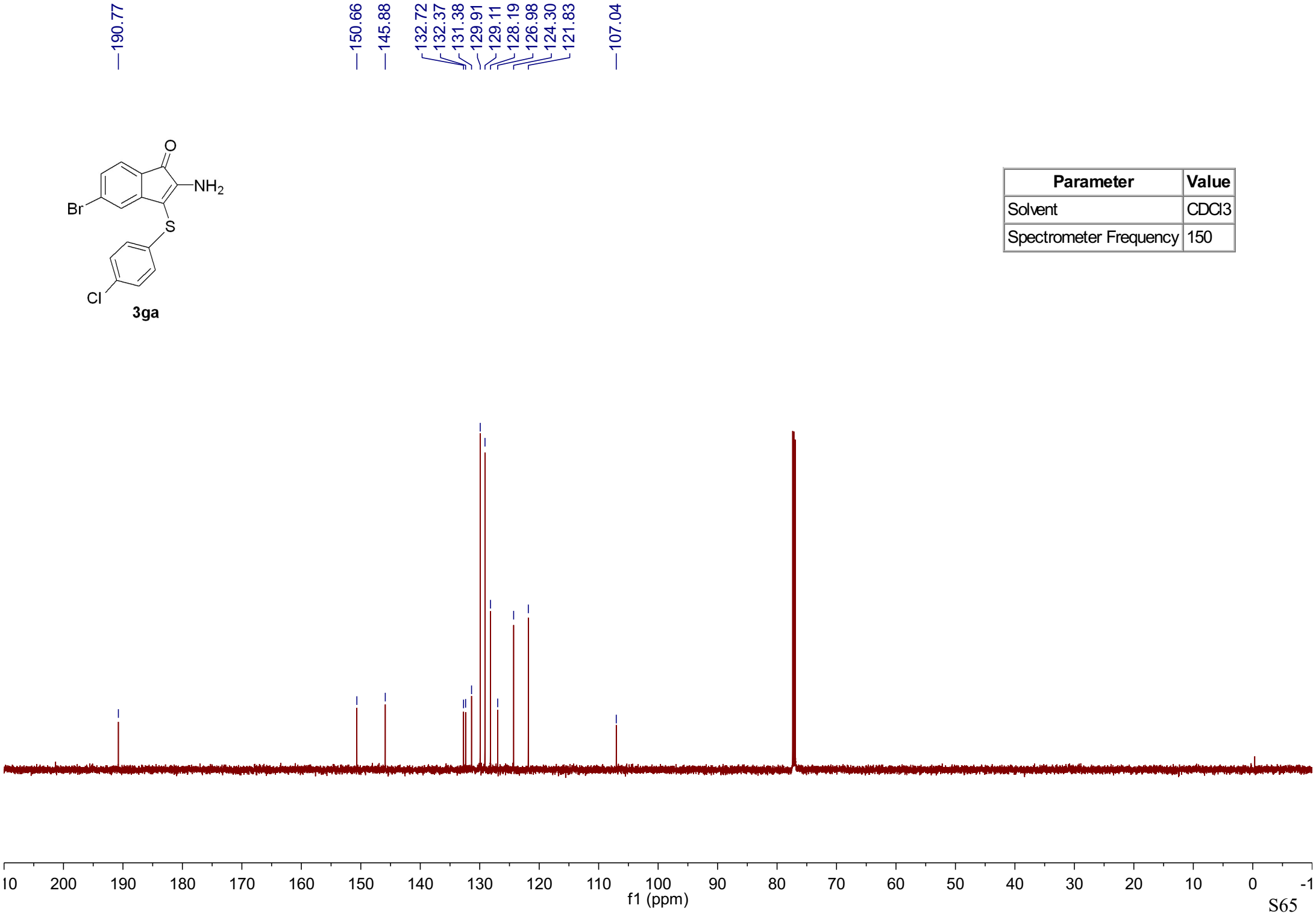

7.3527
7.3499
7.2846
7.2817
7.2716
7.2687
7.2599
7.2490
7.2461
7.2347
7.2120
7.2006
7.1976
6.5042
6.4913
4.4610
Br
O
NH2
S
Cl
3fa
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
600
0.99
1.03
2.02
2.02
1.01
2.00
f1 (ppm)

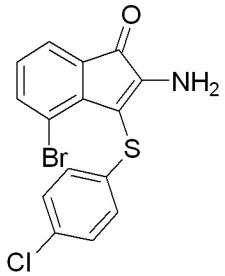

190.69
146.85
144.61
138.00
132.85
130.14
129.88
129.49
126.32
119.83
118.68
109.16
Br
O
NH2
S
Cl
3fa
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
150
f1 (ppm)



Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

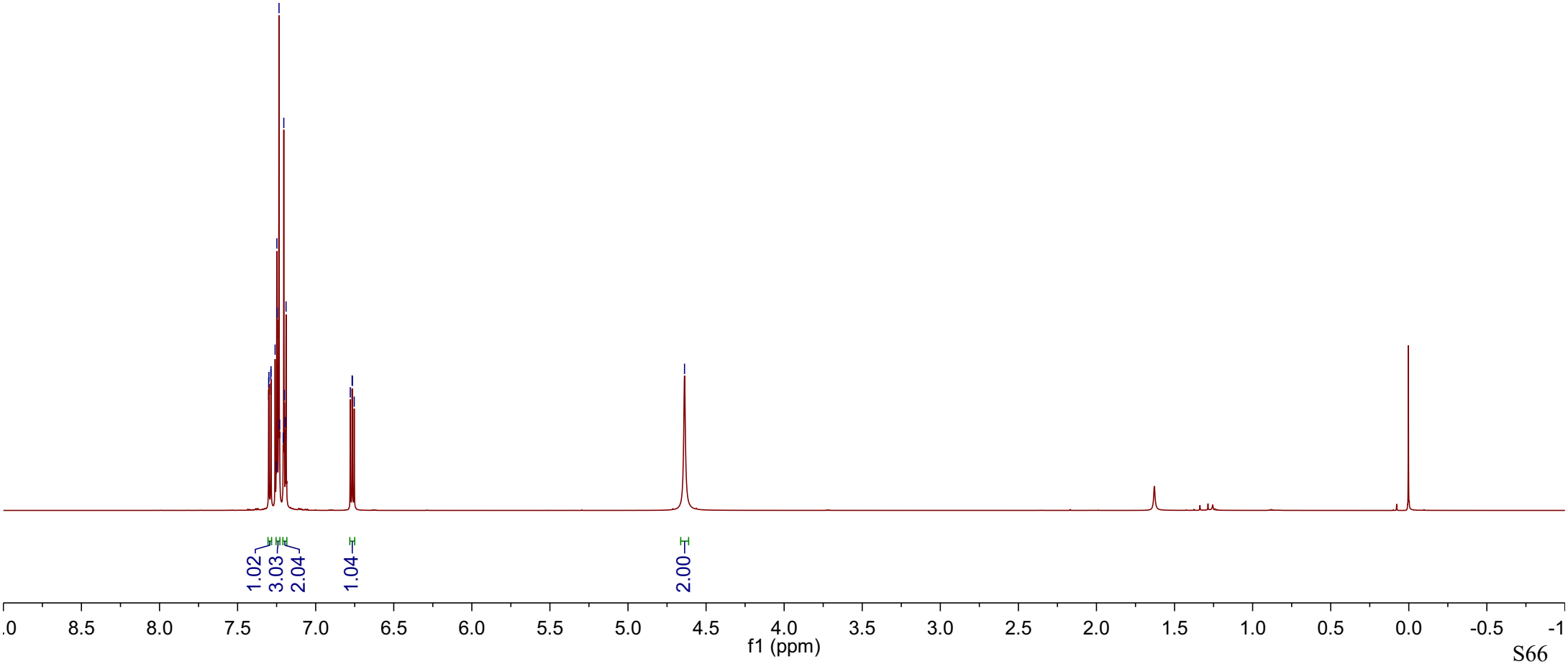


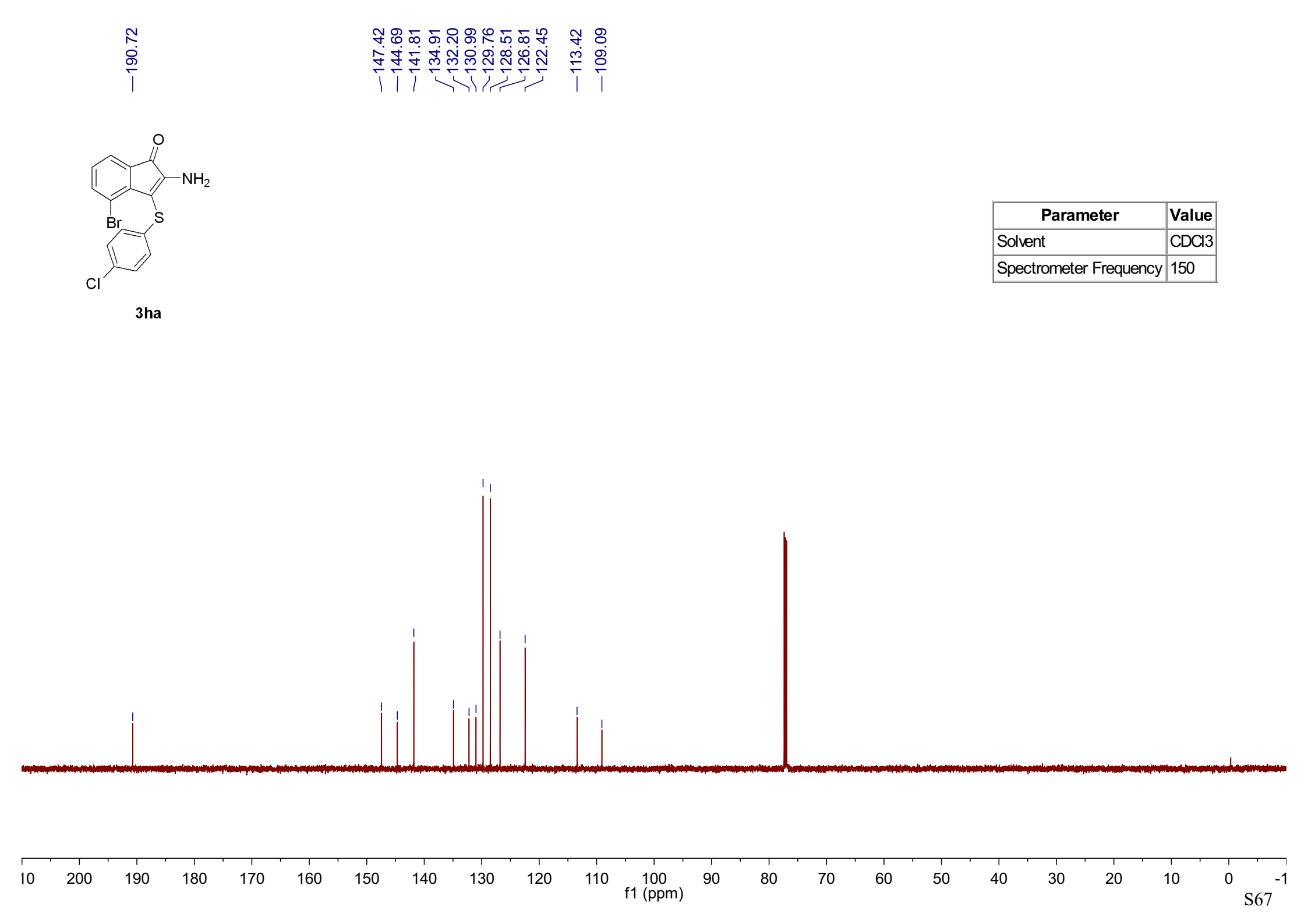

190.77
150.66
145.88
132.72
132.37
131.38
129.91
129.11
128.19
126.98
124.30
121.83
107.04
O
NH2
Br
S
Cl
3ga
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
150
f1 (ppm)

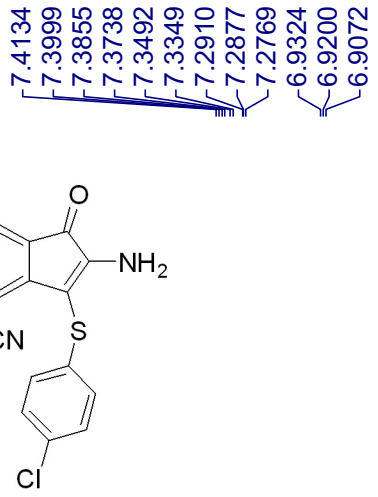


3ha

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600

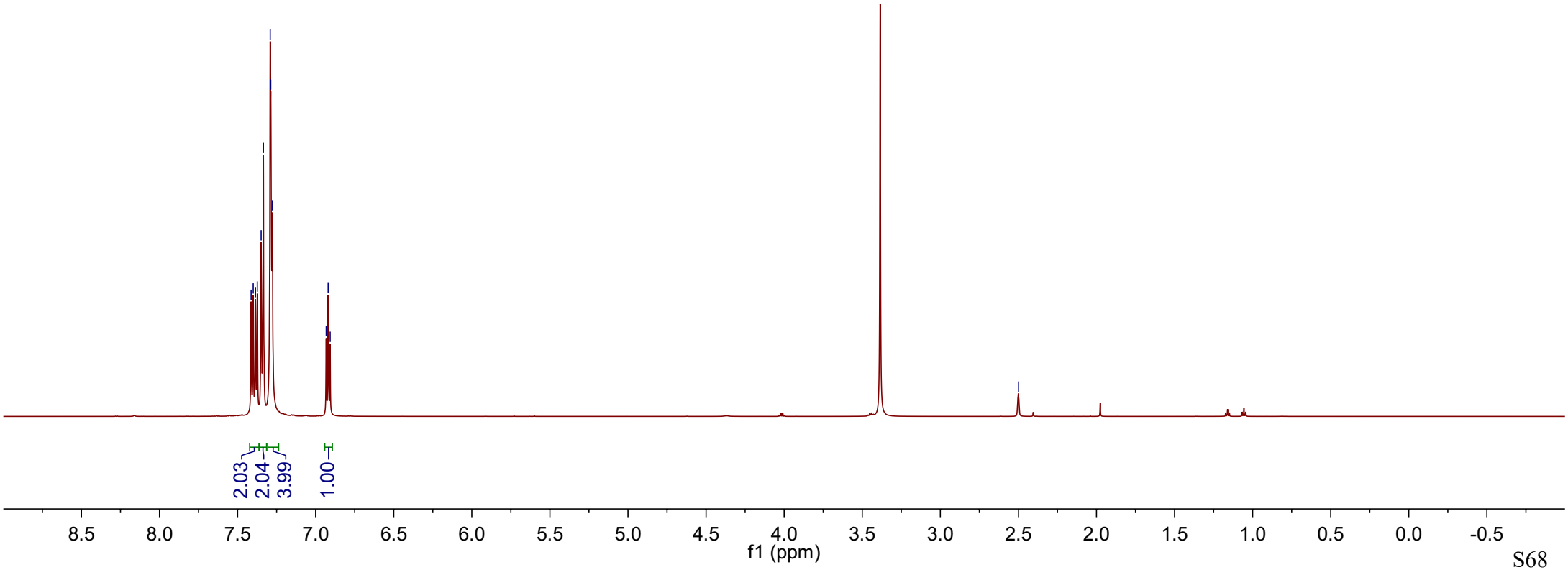


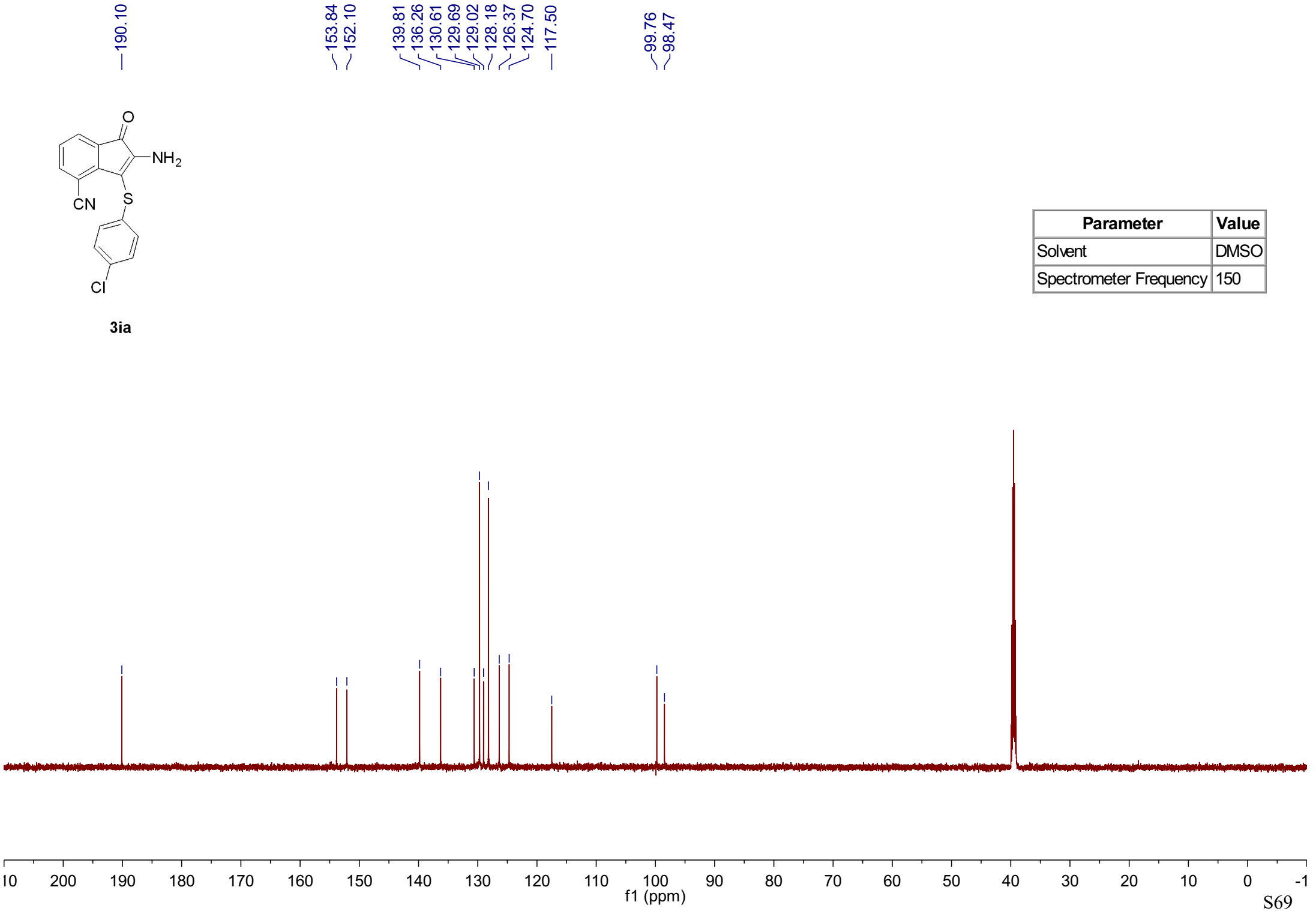

190.72
147.42
144.69
141.81
134.91
132.20
130.99
129.76
128.51
126.81
122.45
113.42
109.09
O
NH2
Br
S
Cl
3ha
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
150
f1 (ppm)

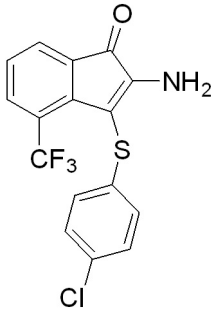


3ia

Parameter	Value
Solvent	DMSO
Spectrometer Frequency	600

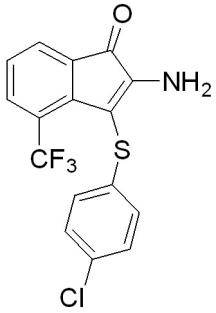



190.10
153.84
152.10
139.81
136.26
130.61
129.69
129.02
128.18
126.37
124.70
117.50
99.76
98.47
O
NH2
CN
S
Cl
3ia
Parameter
Value
Solvent
DMSO
Spectrometer Frequency
150
f1 (ppm)



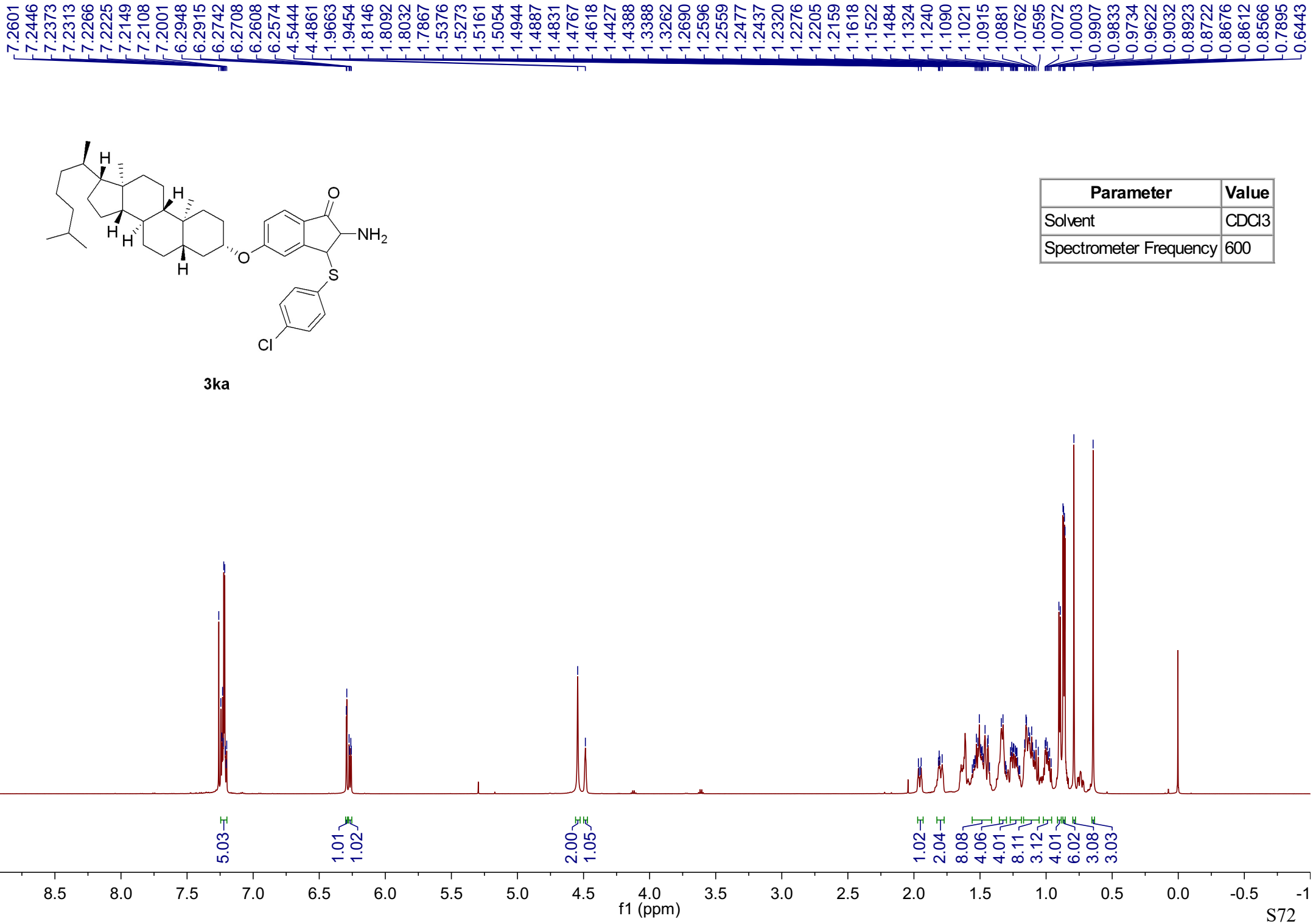
3ja

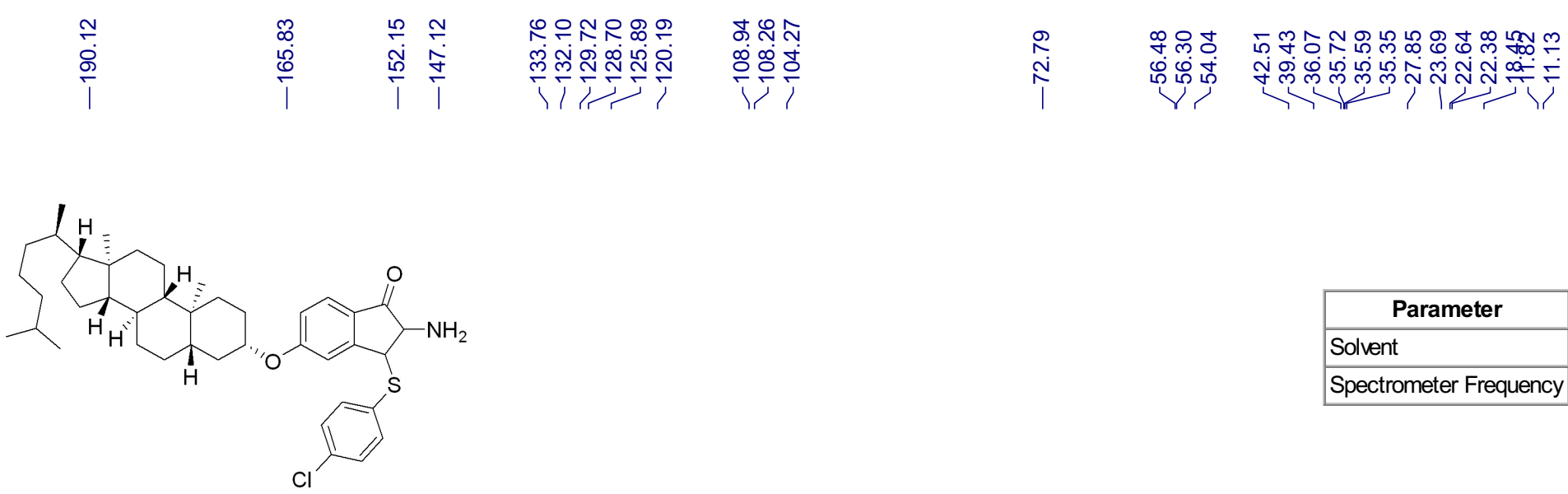
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	400



3ja

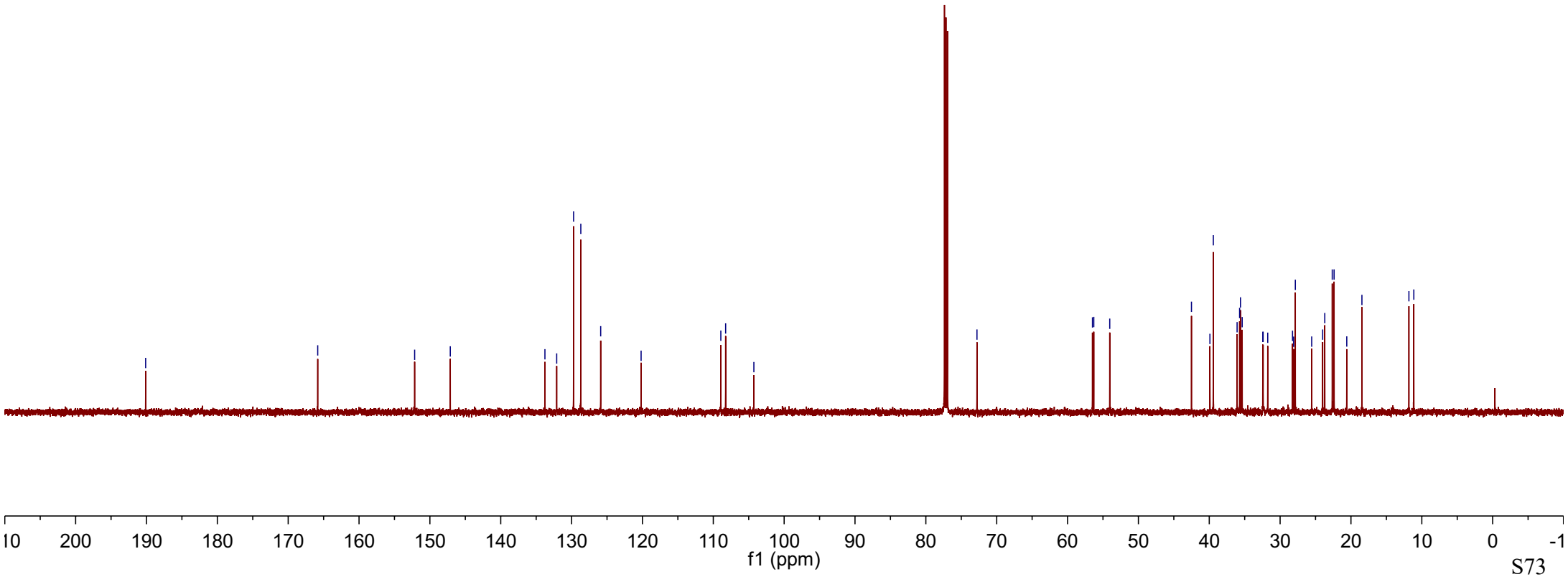
Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	100

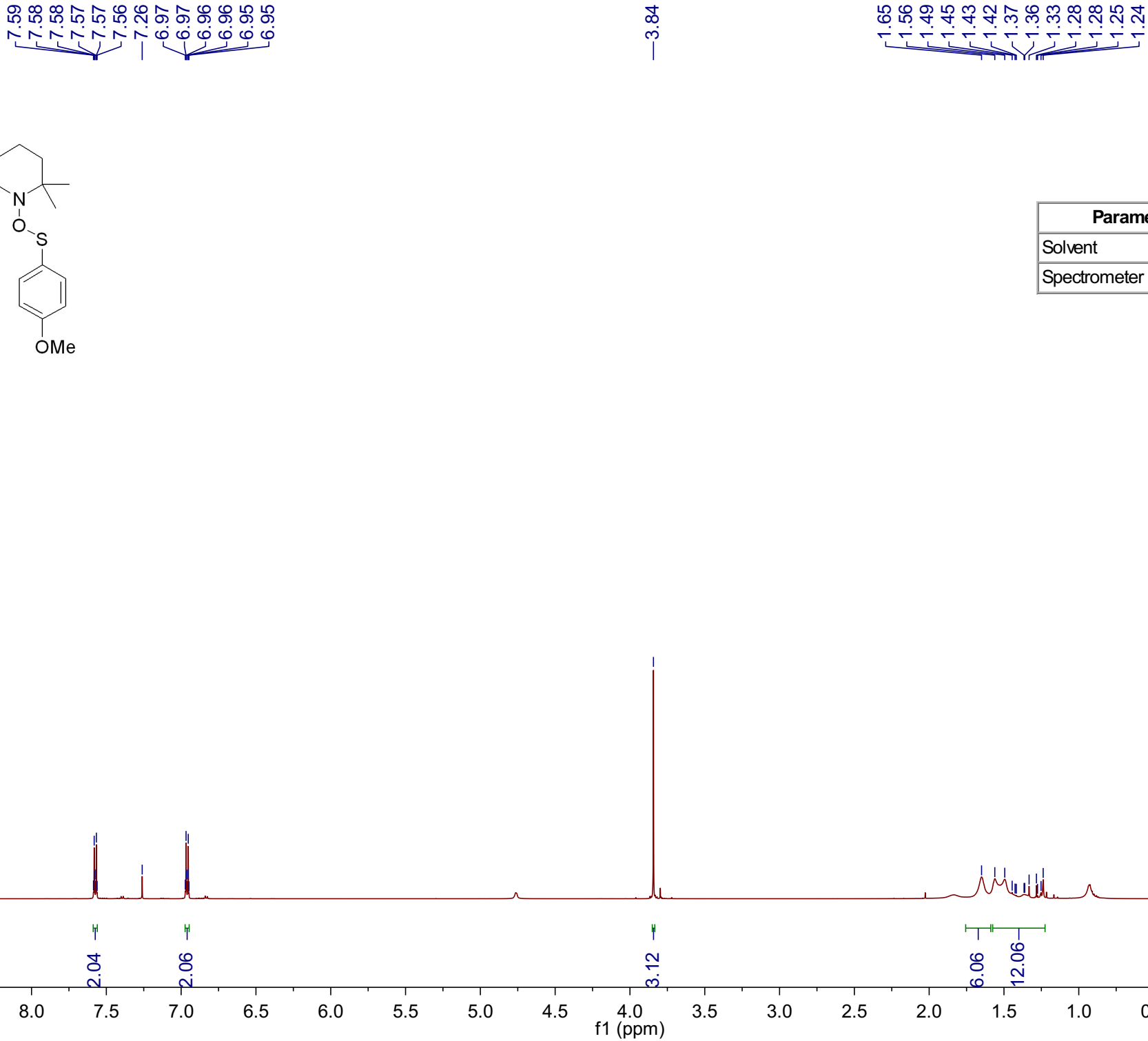

7.2601
7.2446
7.2373
7.2313
7.2266
7.2225
7.2149
7.2108
7.2001
6.2948
6.2915
6.2742
6.2708
6.2608
6.2574
4.5444
4.4861
1.9663
1.9454
1.8146
1.8092
1.8032
1.7867
1.5376
1.5273
1.5161
1.5054
1.4944
1.4887
1.4831
1.4767
1.4618
1.4427
1.4388
1.3388
1.3262
1.2690
1.2596
1.2559
1.2477
1.2437
1.2320
1.2276
1.2205
1.2159
1.1618
1.1522
1.1484
1.1324
1.1240
1.1090
1.1021
1.0915
1.0881
1.0762
1.0595
1.0072
1.0003
0.9907
0.9833
0.9734
0.9622
0.9032
0.8923
0.8722
0.8676
0.8612
0.8566
0.7895
0.6443
H
H
H
H
O
NH2
O
S
Cl
3ka
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
600
5.03
1.01
1.02
2.00
1.05
1.02
2.04
8.08
4.06
4.01
8.11
3.12
4.01
6.02
3.08
3.03
f1 (ppm)



3ka

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	150




7.59
7.58
7.58
7.57
7.57
7.56
7.26
6.97
6.97
6.96
6.96
6.95
6.95
3.84
1.65
1.56
1.49
1.45
1.43
1.42
1.37
1.36
1.33
1.28
1.28
1.25
1.24
N
O
S
OMe
Parameter
Value
Solvent
CDCl3
Spectrometer Frequency
600
2.04
2.06
3.12
6.06
12.06
f1 (ppm)