

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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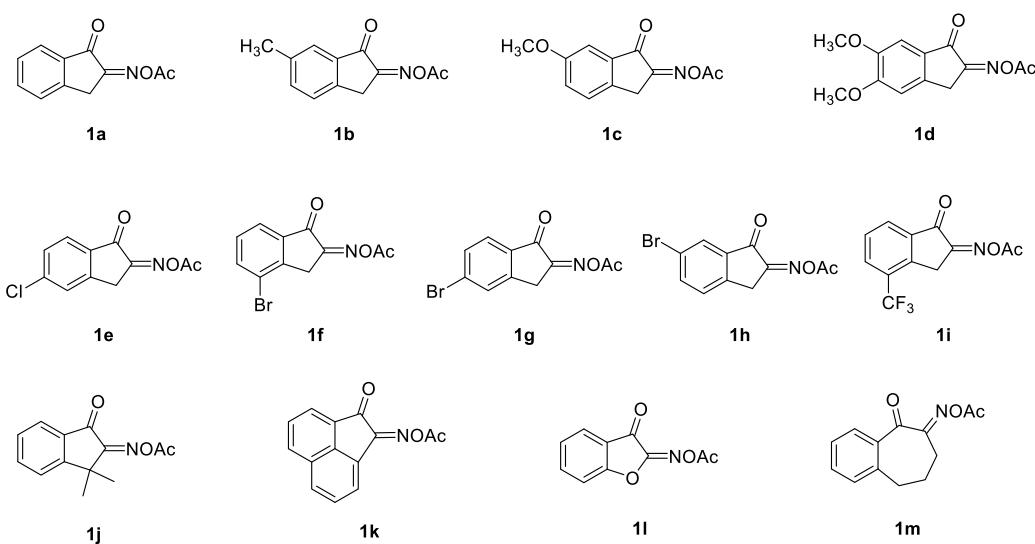
I. General Information and Materials

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 ¹H NMR, ¹³C 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 CDCl₃, defined at δ = 7.26 (¹H NMR), defined at δ = 77.16 (¹³C NMR); or DMSO-d6, defined at δ = 2.5 (¹H NMR), defined at δ = 39.52 (¹³C NMR). Coupling constants were quoted in Hz (J). ¹H 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).

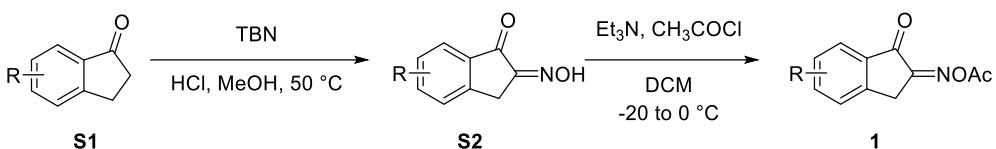
Materials

Table S1. Oxime acetates used in this study



1a-1j, 1m were synthesized according to Procedure A^{1,2}, **1k** was synthesized according to Procedure B³ and **1l** was synthesized according to Procedure C⁴.

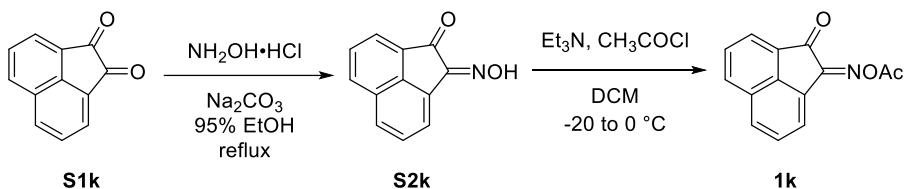
Procedure A^{1,2}:



Step 1 To a solution of 1-indanone **S1** (10 mmol) in methanol (20 mL) was added conc. HCl (480 μ L, 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**.

Step 2 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 acetyl chloride (544 μ L, 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 acetate **1**.

Procedure B³:



Step 1 A suspension of acenaphthoquinone **S1k** (1.1g, 5 mmol), hydroxylamine hydrochloride (355 mg, 5mmol) and Na₂CO₃ (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**.

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

¹H NMR (600 MHz, CDCl₃) 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).

¹³C NMR (150 MHz, CDCl₃) 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 C₁₄H₁₁NO₃ 240.0655, found 240.0653.

Procedure C⁴:



Step 1 To a pre-cooled (-5 °C) solution of 3-coumaranone **S1I** (2 mmol) and NaNO₂ (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 **S2I**.

Step 2 The preparation of **1I** from **S2I** was the same as Procedure A, Step 2.

¹H NMR (600 MHz, CDCl₃) δ 7.81 - 7.74 (m, 2H), 7.37 - 7.30 (m, 2H), 2.33 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) 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 C₁₀H₉NO₄ 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.

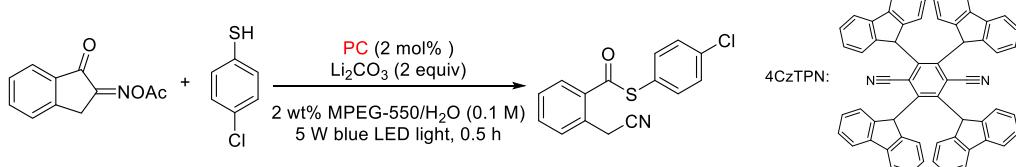
Table S2. Screening of different solvents



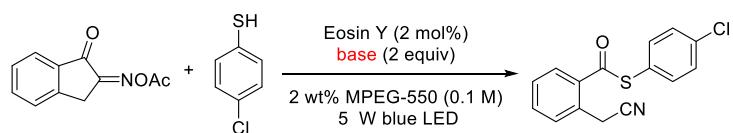
Entry	Solvent	Yield	Entry	Solvent	Yield
1	THF	0	11	2 wt% MPEG-750/H ₂ O	76%
2	CH ₃ CN	0	12	2 wt% PEG-600/H ₂ O	81%
3	DCM	0	13	MPEG-550	0
4	Dioxane	0	14	2 wt% THF/H ₂ O	70%
5	EtOH	0	15	2 wt% 1,4-dioxane/H ₂ O	70%
6	H ₂ O	64%	16	2 wt% triethylene glycol dimethyl ether/H ₂ O	68%
7	2 wt% TWEEN 80 ^a	30%	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/H₂O	89%	20	4 wt% MPEG-550	86%

^aTWEEN = Polysorbate 80. ^bDTAB = Dodecyltrimethylammonium bromide. ^cBrijL23 = Polyoxethyleneglycol-23 lauryl ether. ^dMPEG = 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) ₃ Cl ₂ ·H ₂ O	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	Li₂CO₃	89%	7	LiOH	28%
2	Na ₂ CO ₃	84%	8	Et ₃ N	43%
3	K ₂ CO ₃	85%	9	1 equiv Li ₂ CO ₃	32%
4	Cs ₂ CO ₃	0	10	1 equiv Li ₂ CO ₃	79%
5	LiOAc	8%	11	1 equiv Li ₂ CO ₃	71%
6	<i>t</i> BuOLi	0			

III. Synthesis and Characterization of Product 3-31.

General Procedure D:

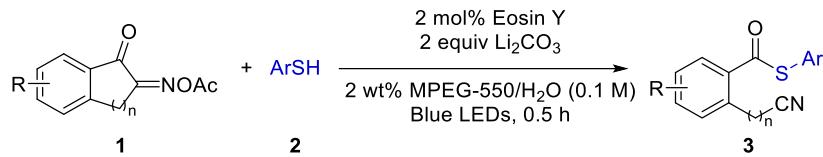
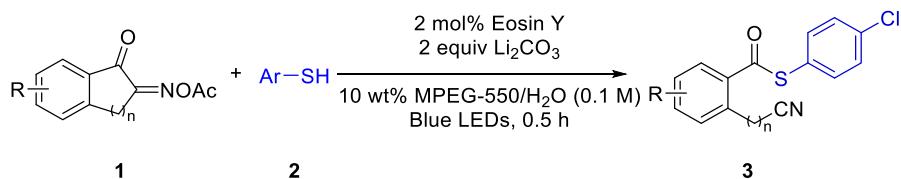


Figure S1 Reaction device

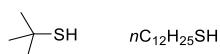
A mixture of 1-indanone oxime acetate **1** (0.1 mmol), thiophenol **2** (0.15 mmol), Eosin Y (1.3 mg, 2 mol%) and Li_2CO_3 (0.2 mmol, 14.9 mg,) in a 4 mL vial was added 2 wt% MPEG-550/ H_2O (1 mL). The reaction mixture was stirred under the irradiation of 2×5 W Blue LEDs ($\lambda = 440 - 480\text{nm}$) 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 ($\lambda = 440 - 480\text{nm}$) 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:



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-chlorobzenethiol (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)

1H NMR (600 MHz, CDCl₃) 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, CDCl₃) 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 C₁₅H₁₀ClNOSNa 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)

1H NMR (600 MHz, CDCl₃) 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, CDCl₃) 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 C₁₆H₁₄NOS 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.

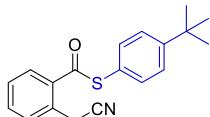
R_f = 0.40 (10% EA in PE)

1H NMR (600 MHz, CDCl₃) 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, CDCl₃) 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 C₁₈H₁₈NOS 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.

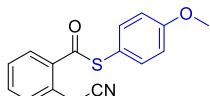
R_f = 0.27 (10% EA in PE)

¹H NMR (600 MHz, CDCl₃) 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).

¹³C NMR (150 MHz, CDCl₃) 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 C₁₉H₂₀NOS 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)

¹H NMR (600 MHz, CDCl₃) 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).

¹³C NMR (150 MHz, CDCl₃) 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 C₁₆H₁₄NO₂S 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)

¹H 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).

¹³C 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 C₁₇H₁₅N₂O₂S 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)

¹H NMR (600 MHz, CDCl₃) 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).

¹³C NMR (150 MHz, CDCl₃) 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 C₁₅H₁₀FNOSNa 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)

¹H NMR (600 MHz, CDCl₃) 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).

¹³C NMR (150 MHz, CDCl₃) 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 C₁₅H₁₀BrNOSNa 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)

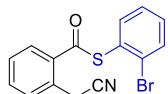
¹H NMR (600 MHz, CDCl₃) δ 8.11 (d, J = 7.7 Hz, 1H), 7.68 (t, J = 1.7 Hz, 1H), 7.65 -

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 $\text{C}_{15}\text{H}_{10}\text{BrNOSNa}$ 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-bromobzenethiol (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)

^1H 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 $\text{C}_{15}\text{H}_{10}\text{BrNOSNa}$ 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.

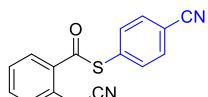
R_f = 0.20 (10% EA in PE)

^1H 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 $\text{C}_{16}\text{H}_{10}\text{F}_3\text{NOSNa}$ 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-mercaptopbenzonitrile (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)

$^1\text{H NMR}$ (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).

$^{13}\text{C NMR}$ (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 $\text{C}_{16}\text{H}_{11}\text{N}_2\text{OS}$ 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-mercaptopbenzoate (29.7 mg, 0.15 mmol) was used to afford the desired product.

24.1 mg, 77%. White solid.

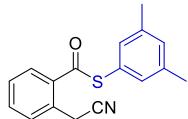
$R_f = 0.20$ (10% EA in PE)

$^1\text{H NMR}$ (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).

$^{13}\text{C NMR}$ (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 $\text{C}_{17}\text{H}_{14}\text{NO}_3\text{S}$ 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.

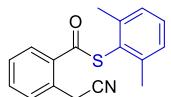
$R_f = 0.36$ (10% EA in PE)

$^1\text{H NMR}$ (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).

$^{13}\text{C NMR}$ (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 $\text{C}_{17}\text{H}_{16}\text{NOS}$ 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.

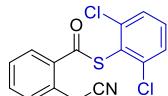
$R_f = 0.37$ (10% EA in PE)

1H NMR (600 MHz, CDCl₃) 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, CDCl₃) 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 C₁₇H₁₆NOS 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.

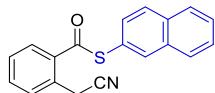
$R_f = 0.23$ (10% EA in PE)

1H NMR (600 MHz, CDCl₃) 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, CDCl₃) 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 C₁₅H₁₀Cl₂NOS 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.

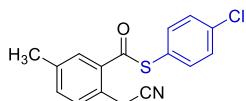
$R_f = 0.19$ (10% EA in PE)

1H NMR (600 MHz, CDCl₃) 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, CDCl₃) 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 C₁₉H₁₃NOSK 342.0349, found 342.0337.

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



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

25.1 mg, 83%. White solid.

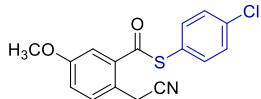
R_f = 0.33 (10% EA in PE)

$^1\text{H NMR}$ (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).

$^{13}\text{C NMR}$ (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) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{12}\text{ClNOOSNa}$ 324.0220, found 324.0206.

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



Following Procedure D, 2-(acetoxymino)-6-methoxy-2,3-dihydro-1*H*-inden-1-one (24.0 mg, 0.1 mmol) and 4-chlorobzenethiol (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)

$^1\text{H NMR}$ (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).

$^{13}\text{C NMR}$ (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) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{12}\text{ClNO}_2\text{SNa}$ 340.0169, found 340.0158.

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



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

29.7 mg, 86%. Yellow solid.

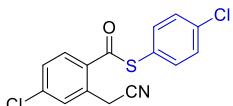
R_f = 0.29 (20% EA in PE)

$^1\text{H NMR}$ (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).

$^{13}\text{C NMR}$ (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 C₁₇H₁₄ClNO₃SNa 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.

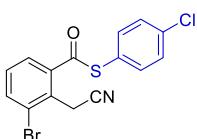
R_f = 0.50 (10% EA in PE)

¹H NMR (600 MHz, CDCl₃) 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).

¹³C NMR (150 MHz, CDCl₃) 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 C₁₅H₉Cl₂NOSNa 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.

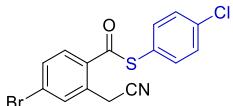
R_f = 0.30 (10% EA in PE)

¹H NMR (600 MHz, CDCl₃) 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).

¹³C NMR (150 MHz, CDCl₃) 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 C₁₅H₉BrClNOSNa 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.

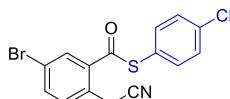
R_f = 0.37 (10% EA in PE)

¹H NMR (600 MHz, CDCl₃) 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).

¹³C NMR (150 MHz, CDCl₃) 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 C₁₅H₉BrClNOSNa 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-chlorobzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.

23.0 mg, 77%. White solid.

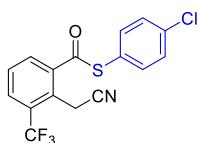
R_f = 0.27 (10% EA in PE)

¹H NMR (600 MHz, CDCl₃) 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).

¹³C NMR (150 MHz, CDCl₃) 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 C₁₅H₉BrClNOSNa 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-chlorobzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.

20.5 mg, 58%. White solid.

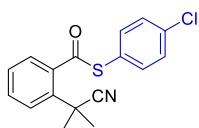
R_f = 0.26 (10% EA in PE)

¹H NMR (600 MHz, CDCl₃) 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).

¹³C NMR (150 MHz, CDCl₃) 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 C₁₆H₉ClF₃NOSNa 377.9938, found 377.9924.

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



Following Procedure E, 2-(acetoxymino)-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.

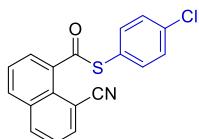
$R_f = 0.62$ (20% EA in PE)

1H NMR (600 MHz, CDCl₃) 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, CDCl₃) 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 C₁₇H₁₅ClNOS 316.0557, found 316.0559

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



Following Procedure D, (E)-2-(acetoxymino)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)

1H NMR (400 MHz, CDCl₃) 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, CDCl₃) 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 C₁₈H₁₁ClNOS 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%. White solid.

$R_f = 0.50$ (10% EA in PE)

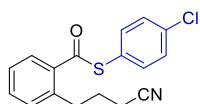
1H NMR (600 MHz, CDCl₃) δ 7.76 (d, J = 7.8 Hz, 1H), 7.73 - 7.69 (m, 1H), 7.56 (d, J = 8.5 Hz, 2H), 7.40 - 7.36 (m, 2H), 7.30 - 7.26 (m, 2H).

^{13}C NMR (150 MHz, CDCl₃) 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 C₁₄H₉ClNO₂S 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-chlorobzenethiol (22.1 mg, 0.15 mmol) was used to afford the desired product.

20.9 mg, 66%. Yellow solid.

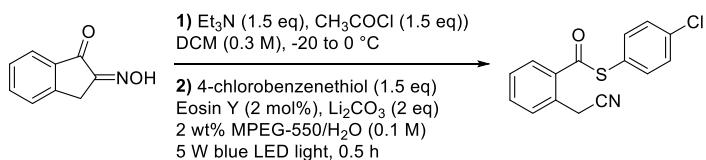
R_f = 0.58 (10% EA in PE)

¹H NMR (600 MHz, CDCl₃) 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).

¹³C NMR (150 MHz, CDCl₃) 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 C₁₇H₁₅ClNOS 316.0557, found 316.0558.

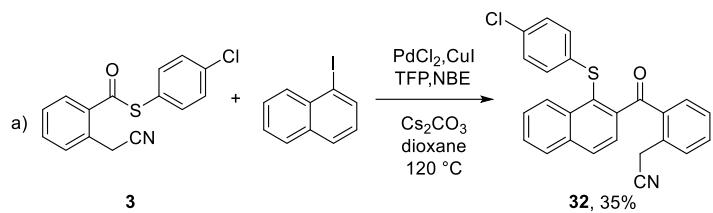
IV . One-pot Protocol



To a mixture of 2-(hydroxyimino)-2,3-dihydro-1*H*-inden-1-one (0.2 mmol, 33.2 mg), DCM (0.6 mL), Et₃N (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 Li₂CO₃ (0.3 mmol, 29.9 mg,) in a 5 mL tube was added 2 wt% MPEG-550/H₂O (2 mL). The reaction mixture was stirred under the irradiation of 2×5 W Blue LEDs ($\lambda = 440 - 480\text{nm}$) 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

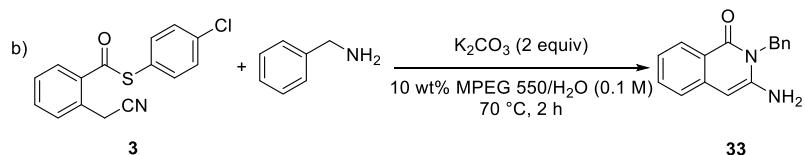


According to literature 6, to a 10 mL Schlenk tube was sequentially added 1-iodonaphthalene (30 μ L, 0.20 mmol), thioester **3** (87.2 mg, 0.30 mmol), PdCl_2 (3.6 mg, 0.02 mmol), TFP (11.9 mg, 0.05 mmol), CuI (7.8 mg, 0.04 mmol), norbornene (57.1 mg, 0.60 mmol), Cs_2CO_3 (197.5 mg, 0.60 mmol) and 1,4-dioxane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

$^1\text{H NMR}$ (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).

$^{13}\text{C NMR}$ (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 $\text{C}_{25}\text{H}_{16}\text{ClNO}_2\text{Na}$ 436.0533, found 436.0516.



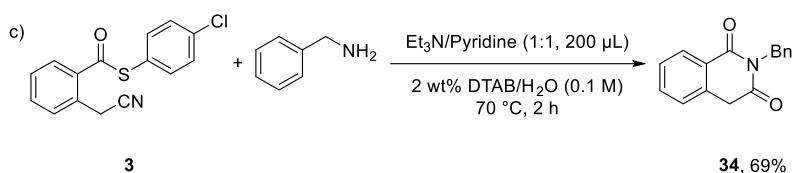
To a 4 mL vial, thioester **3** (29.1 mg, 0.1 mmol), benzylamine (22.3 μ L, 0.2 mmol), K_2CO_3 (27.9 mg, 0.2 mmol) and 10 wt%MPEG-550/ H_2O (1 mL) were added with a stir bar. The resulting mixture was allowed to stir at 70 °C for 2 h. Then, the reaction was cooled to rt, the reaction mixture was extracted 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%).

$^1\text{H NMR}$ (600 MHz, DMSO-d_6) 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).

$^{13}\text{C NMR}$ (150 MHz, DMSO-d_6) 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 $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}$ 251.1179, found 251.1178.

Spectroscopic data matches that reported in the literature.⁷



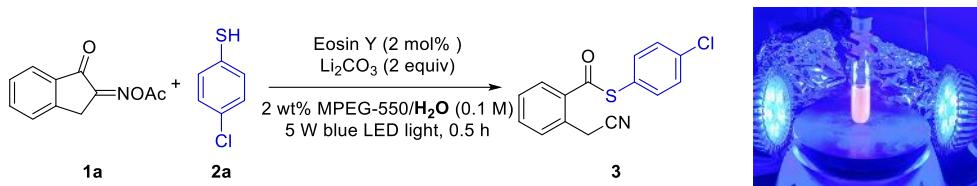
To a 4 mL vial, thioester **3** (29.1 mg, 0.1 mmol), benzylamine (22.3 μ L, 0.2 mmol), Et₃N/pyridine (1:1, 200 μ L) and 2 wt% DTAB/H₂O (1 mL) (DTAB = dodecyltrimethylammonium bromide) were added with a stir bar. The resulting mixture was allowed to stir at 70 °C for 2 h. Then, the reaction was cooled to rt, 1 M HCl was added to the reaction mixture and extracted with EtOAc. The organic phase was dried over Na₂SO₄, evaporated in vacuo and subjected to flash column chromatography on silica gel to obtain compound **34** (17.3 mg, 69%).

¹H NMR (600 MHz, CDCl₃) 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).

¹³C NMR (150 MHz, CDCl₃) 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 C₁₆H₁₄NO₂ 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-chlorobzenethiol **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 ($\lambda = 440 - 480\text{nm}$) 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-chlorobzenethiol **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.

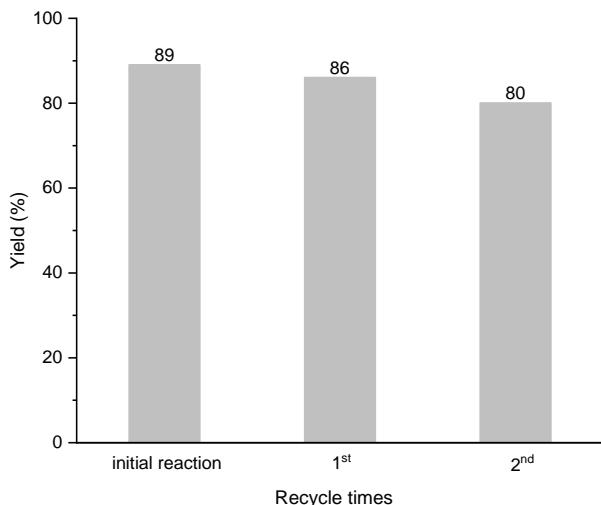


Figure S2 The yield of each run for recycle experiment

Note: Density of each liquid at 25 °C; ethyl acetate = 0.897 g/mL;
Mol. Wt.; 4-chlorobzenethiol **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-chlorobzenethiol **2a** (78.1 mg)

Product (**3**): $128.3 + 123.4 + 115.7 = 367.4 \text{ mg}$

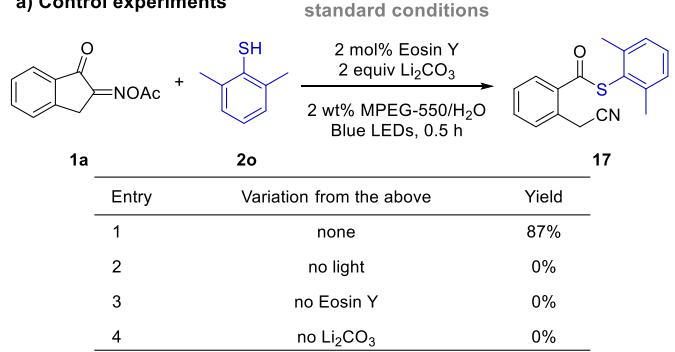
$$\text{E Factor} = \frac{\text{total organic wastes (Kg)}}{\text{Product (Kg)}}$$

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

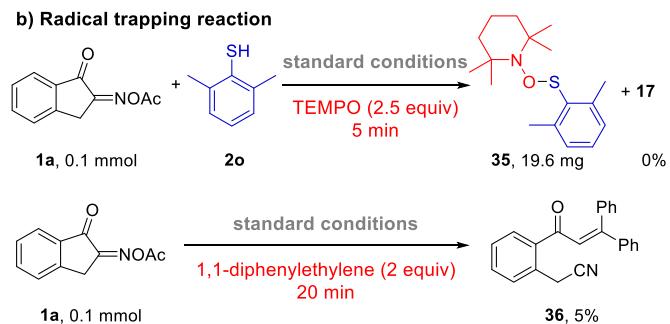
$$= 10.0$$

VII . Mechanistic Studies

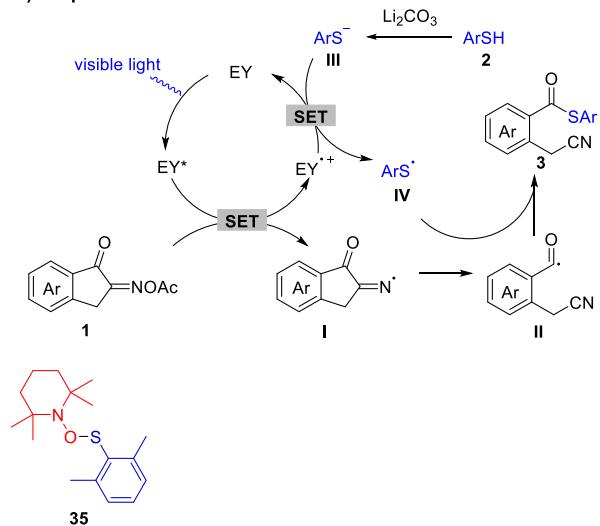
a) Control experiments



b) Radical trapping reaction



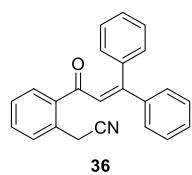
c) Proposed reaction mechanism.



¹H 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).

¹³C 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 $\text{C}_{17}\text{H}_{28}\text{NOS}$ 316.0557, found 316.0558.



¹H NMR (600 MHz, CDCl₃) 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).

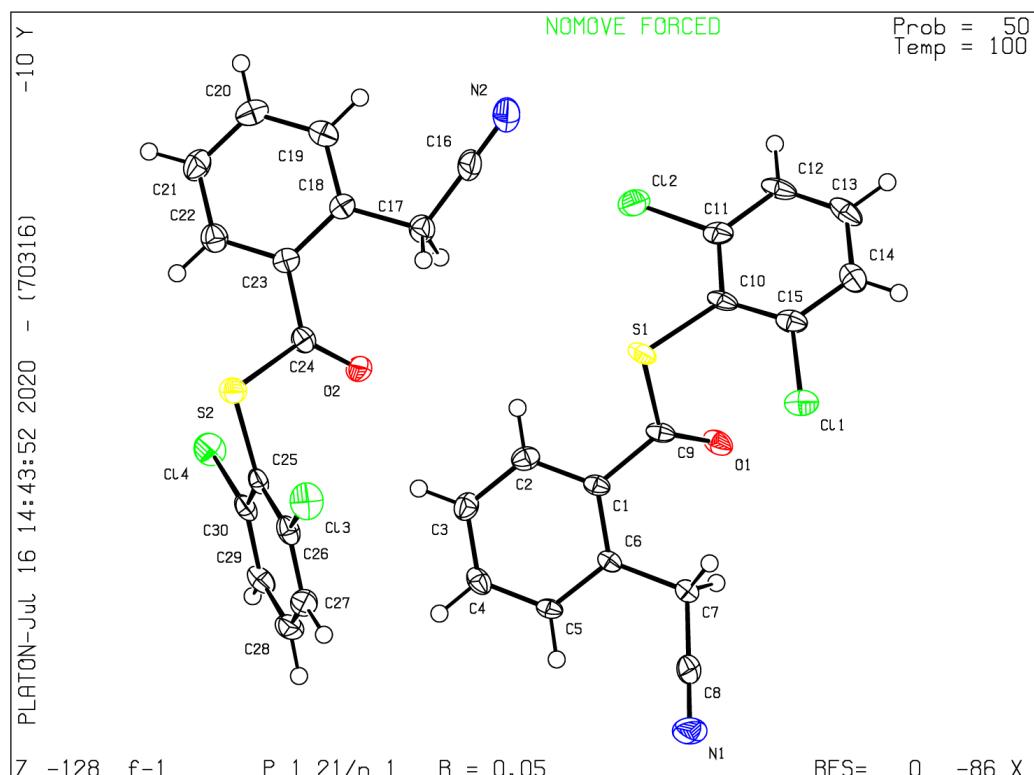
¹³C NMR (150 MHz, CDCl₃) δ 196.3, 156.4, 141.1, 139.2, 137.5, 132.5, 131.0, 130.6, 130.2, 130.2, 130.1, 129.2, 129.04, 128.97, 128.6, 128.1, 126.2, 118.4, 21.9.

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**

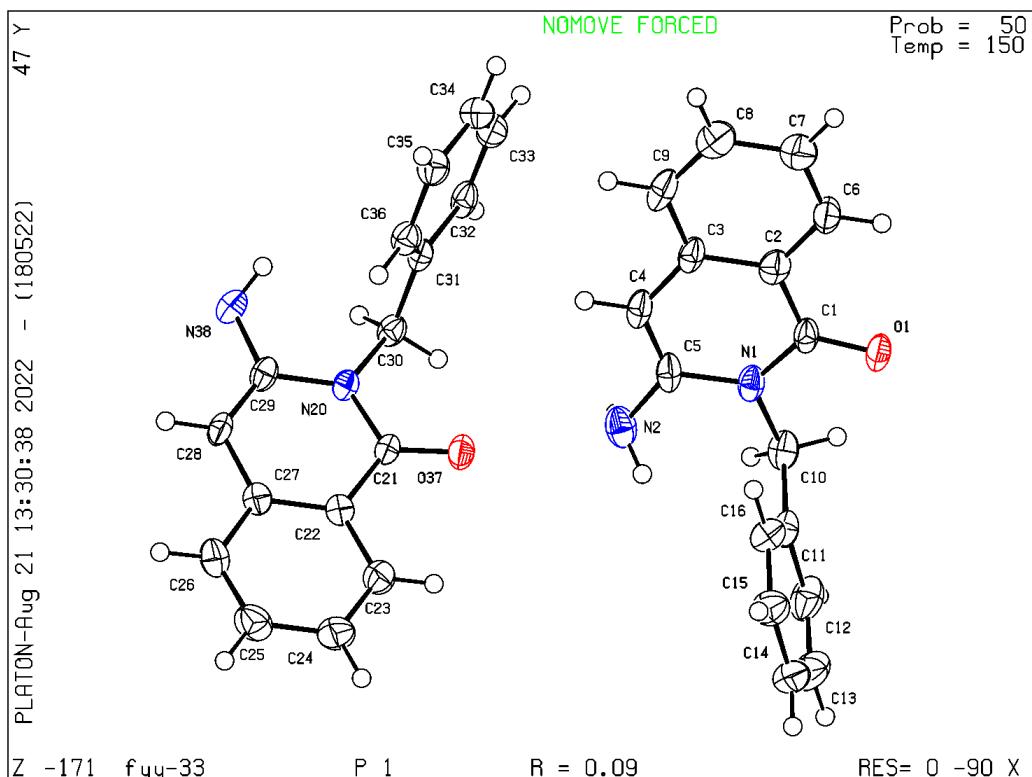
Crystal data and structure refinement for **18**

Identification code	F-1
Empirical formula	C ₁₅ H ₉ Cl ₂ NOS
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/ \AA^3	2783.1(3)
Z	8
$\rho_{\text{calcg}}/\text{cm}^3$	1.538
μ/mm^{-1}	0.609
F(000)	1312.0
Crystal size/ mm^3	$0.14 \times 0.13 \times 0.12$
Radiation	Mo K α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	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 [$R_{\text{int}} = 0.0597, R_{\text{sigma}} = 0.0718$]
Data/restraints/parameters	4906/0/361
Goodness-of-fit on F^2	1.035
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0470, wR_2 = 0.1070$
Final R indexes [all data]	$R_1 = 0.0609, wR_2 = 0.1170$
Largest diff. peak/hole / e \AA^{-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 C₁₆H₁₄N₂O

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)

$\alpha/^\circ$ 79.456(6)

$\beta/^\circ$ 89.714(5)

$\gamma/^\circ$ 76.365(5)

Volume/Å³ 638.40(7)

Z 2

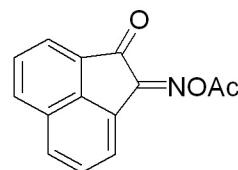
ρ_{calc} g/cm³ 1.302
 μ/mm^{-1} 0.657
F(000) 264.0
Crystal size/mm³ 0.14 × 0.12 × 0.11
Radiation Cu K α ($\lambda = 1.54184$)
2 Θ range for data collection/° 7.868 to 143.1
Index ranges -6 ≤ h ≤ 6, -8 ≤ k ≤ 12, -13 ≤ l ≤ 14
Reflections collected 5417
Independent reflections 3054 [Rint = 0.0367, Rsigma = 0.0538]
Data/restraints/parameters 3054/3/345
Goodness-of-fit on F² 1.308
Final R indexes [$I \geq 2\sigma(I)$] R₁ = 0.0868, wR₂ = 0.2769
Final R indexes [all data] R₁ = 0.0883, wR₂ = 0.2790
Largest diff. peak/hole / e Å⁻³ 0.73/-0.39
Flack parameter -0.2(4)

IX . References

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6. F. Sun, M. Li, C. He, B. Wang, B. Li, X. Sui and Z. Gu. *J. Am. Chem. Soc.* 2016, **138**, 7456.
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8. S. H. Kennedy, M. N. Schaeff and D. A. Klumpp. *J. Org. Chem.* 2019, **84**, 14133.
9. B.-Q. He, Y. Gao, P.-Z. Wang, H. Wu, H.-B. Zhou, X-P. Liu and J.-R. Chen. *Synlett.* 2021; **32**, 373.

8.35
8.34
8.16
8.14
8.09
8.07
8.06
8.05
7.77
7.75
7.74
7.26

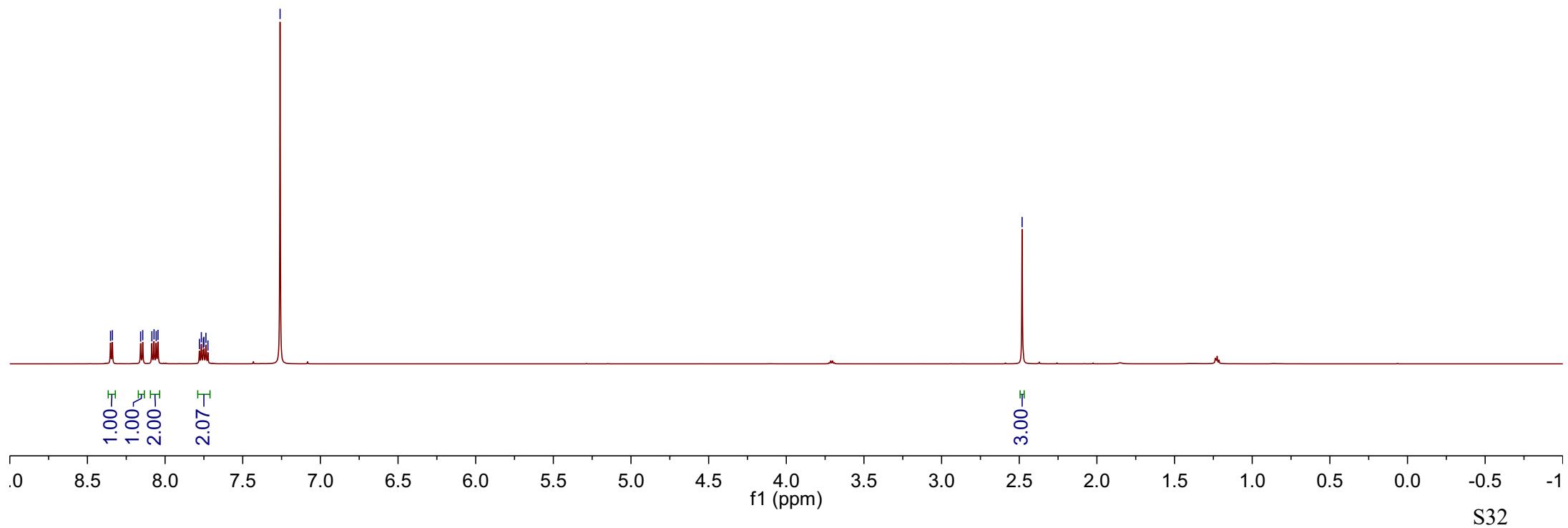
X . NMR Spectra

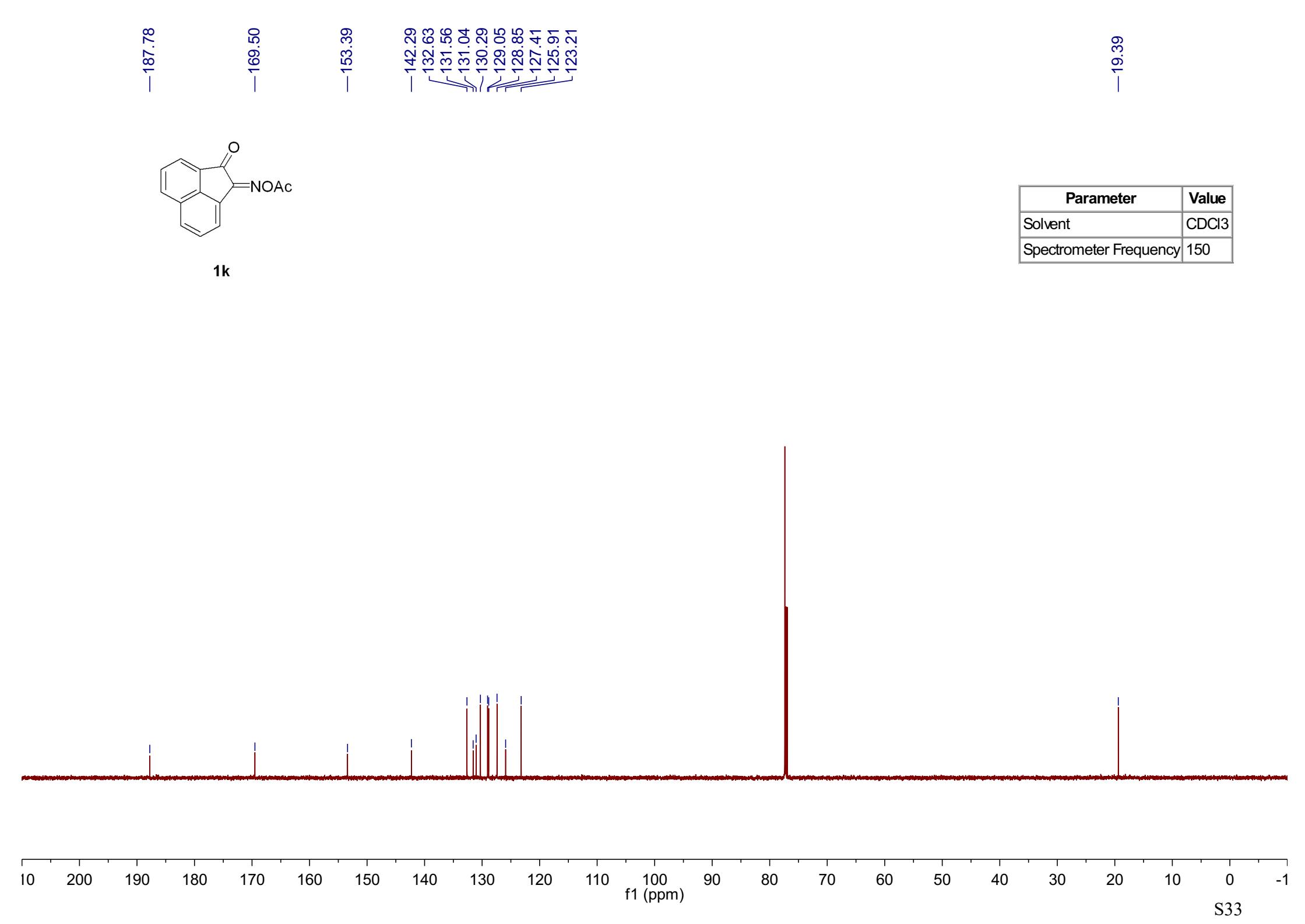


1k

-2.48

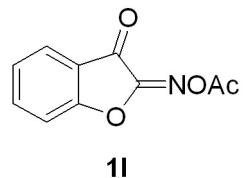
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Spectrometer Frequency	600



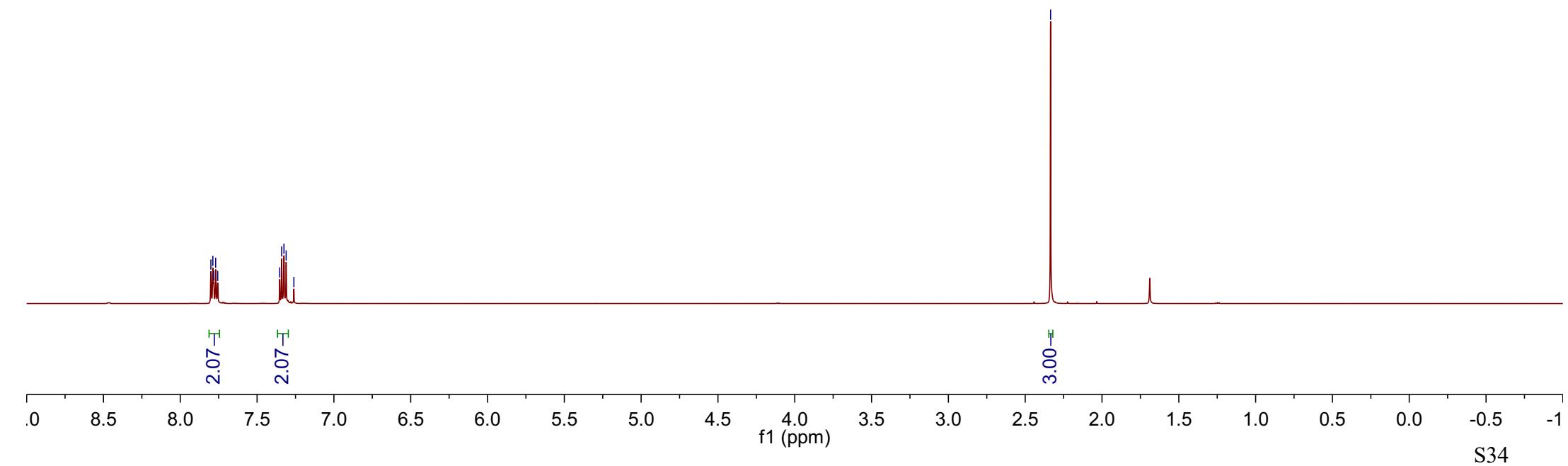


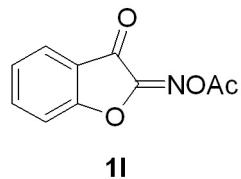
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7.35
7.34
7.33
7.31
7.26

-2.33



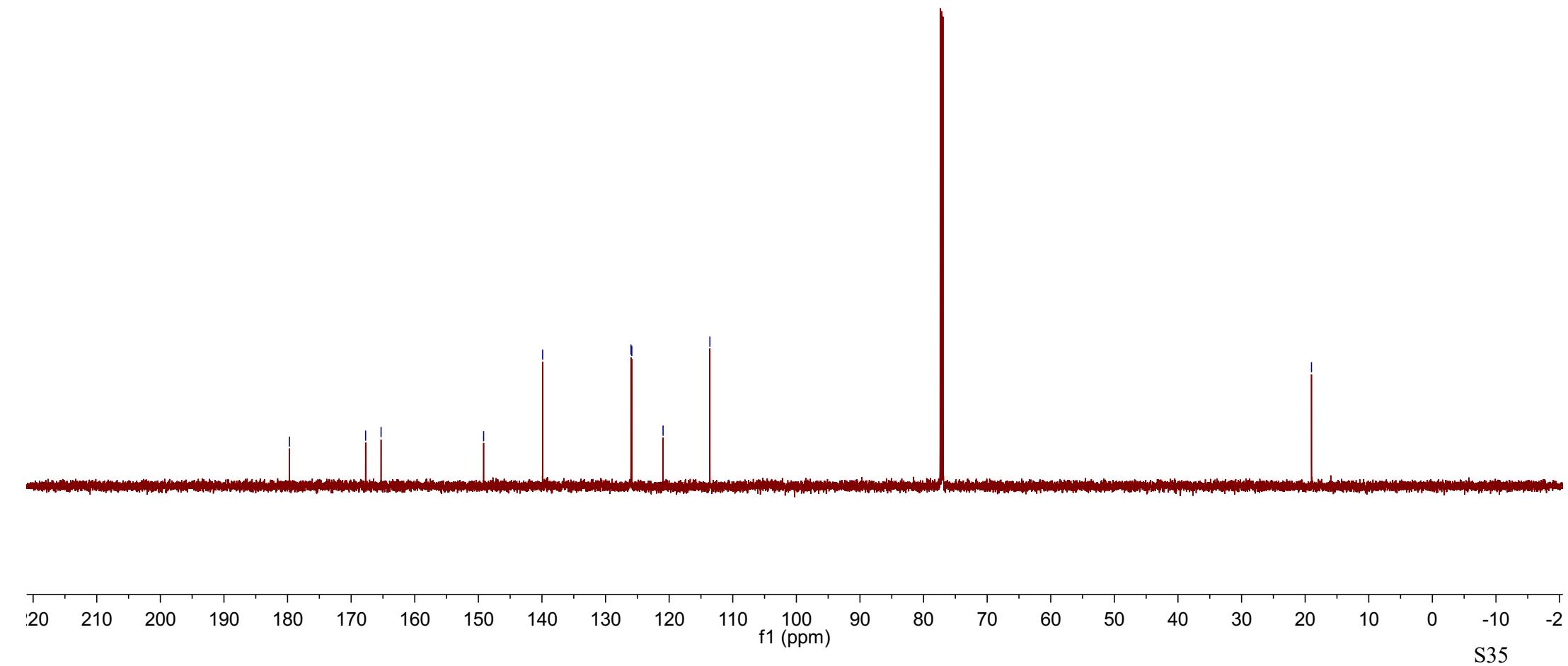
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600





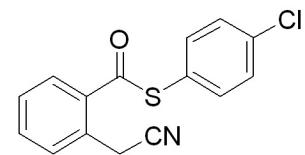
—179.71
—167.73
~165.30
—149.17
—139.89
—126.00
—125.87
~120.96
—113.60
—19.01

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150



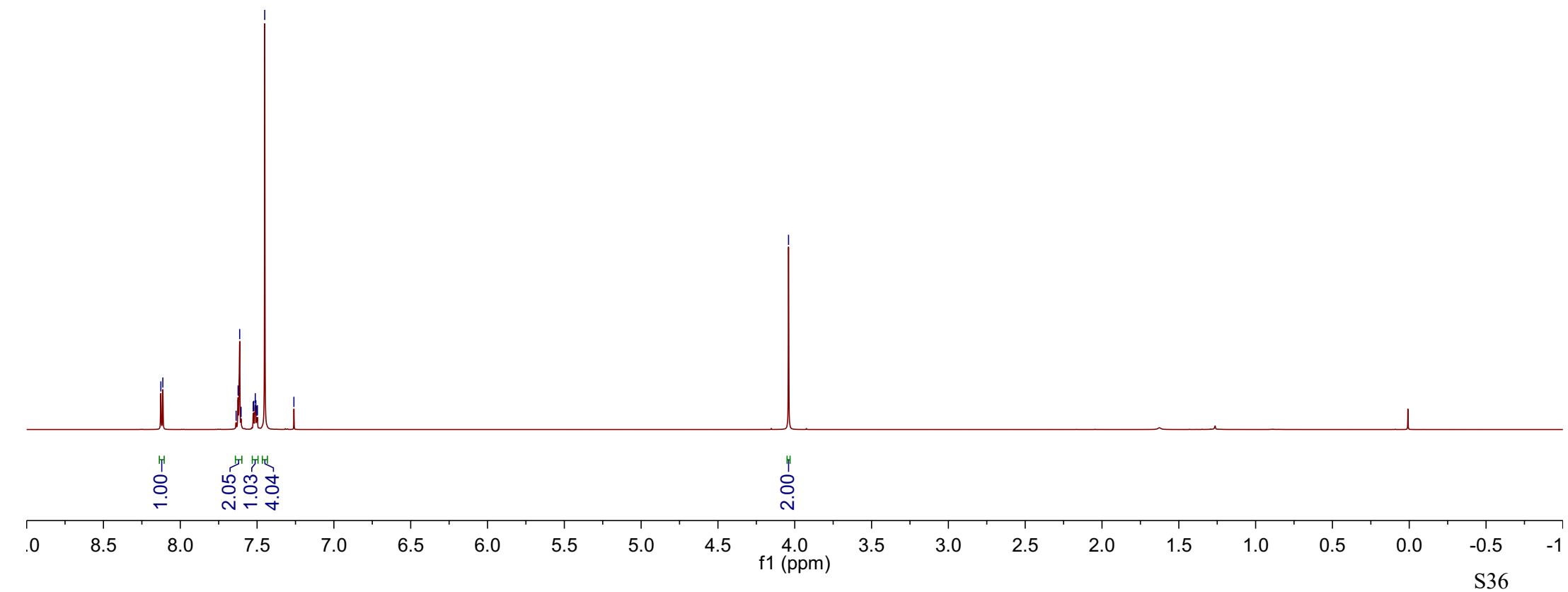
8.13
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7.64
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7.60
7.53
7.52
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7.51
7.50
7.45
7.26

-4.04



3

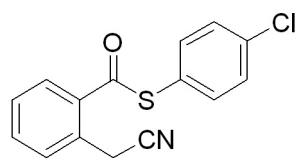
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



-192.22

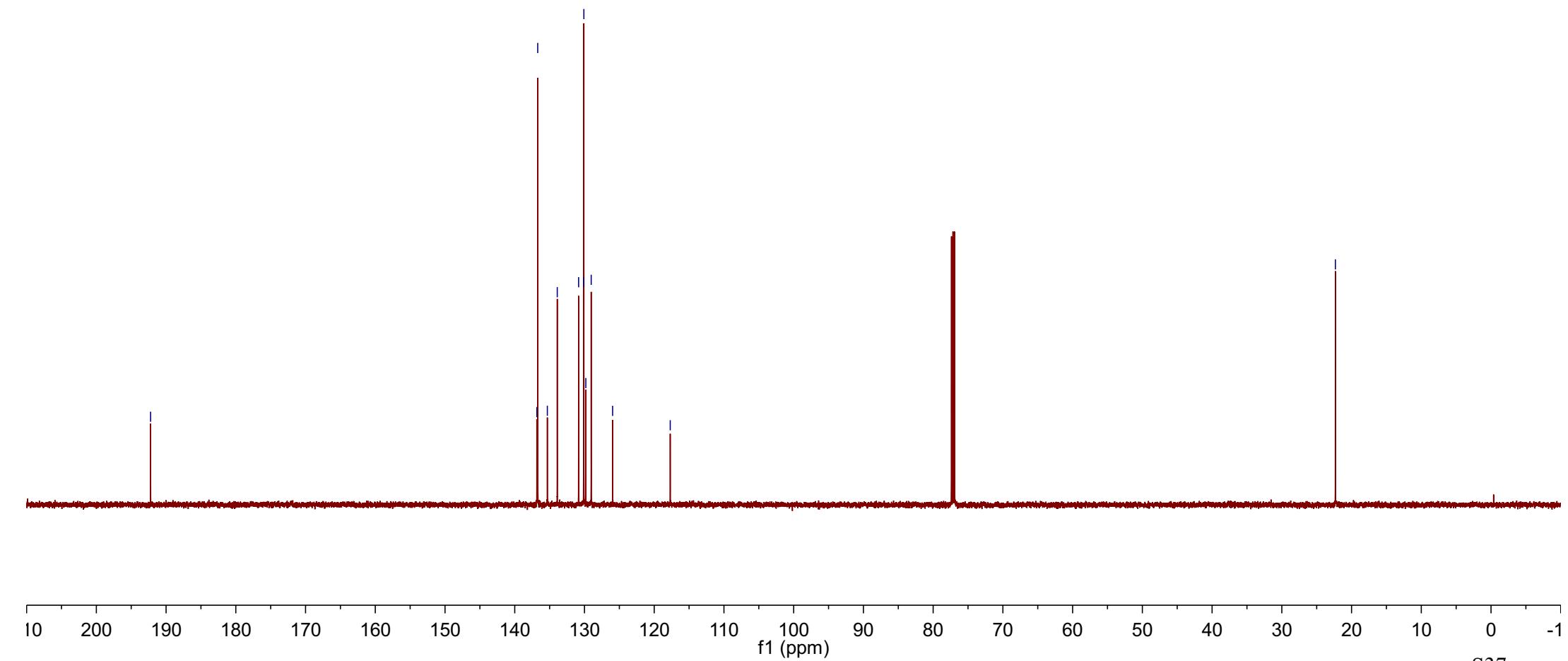
-22.32

136.83
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135.33
133.90
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130.09
129.81
129.04
125.96
117.70



3

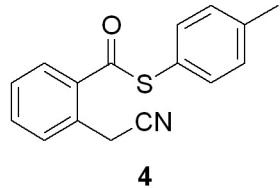
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150



8.15
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7.62
7.62
7.61
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7.51
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7.49
7.49
7.41
7.40
7.31
7.29
7.26

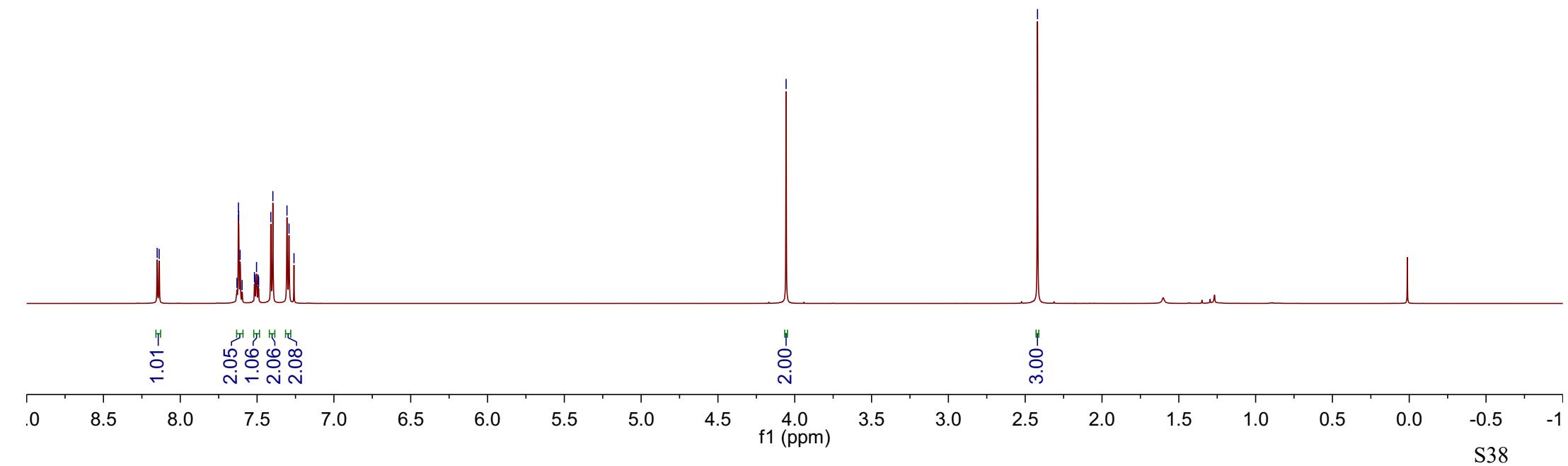
-4.06

-2.42



4

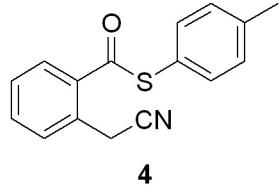
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



-193.31

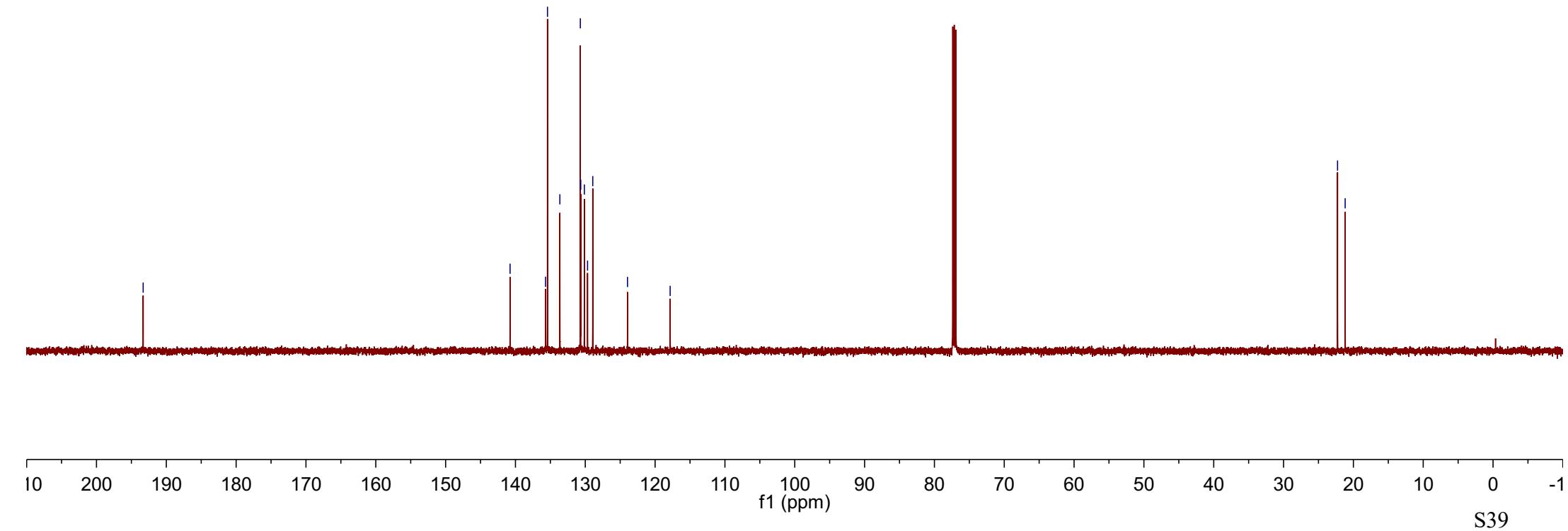
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135.69
135.41
133.64
130.71
130.65
130.13
129.67
128.93
123.95
117.85

22.27
21.18



4

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

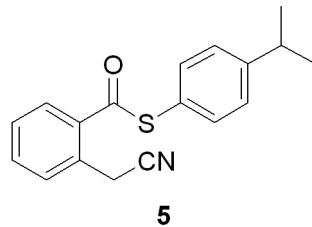


S39

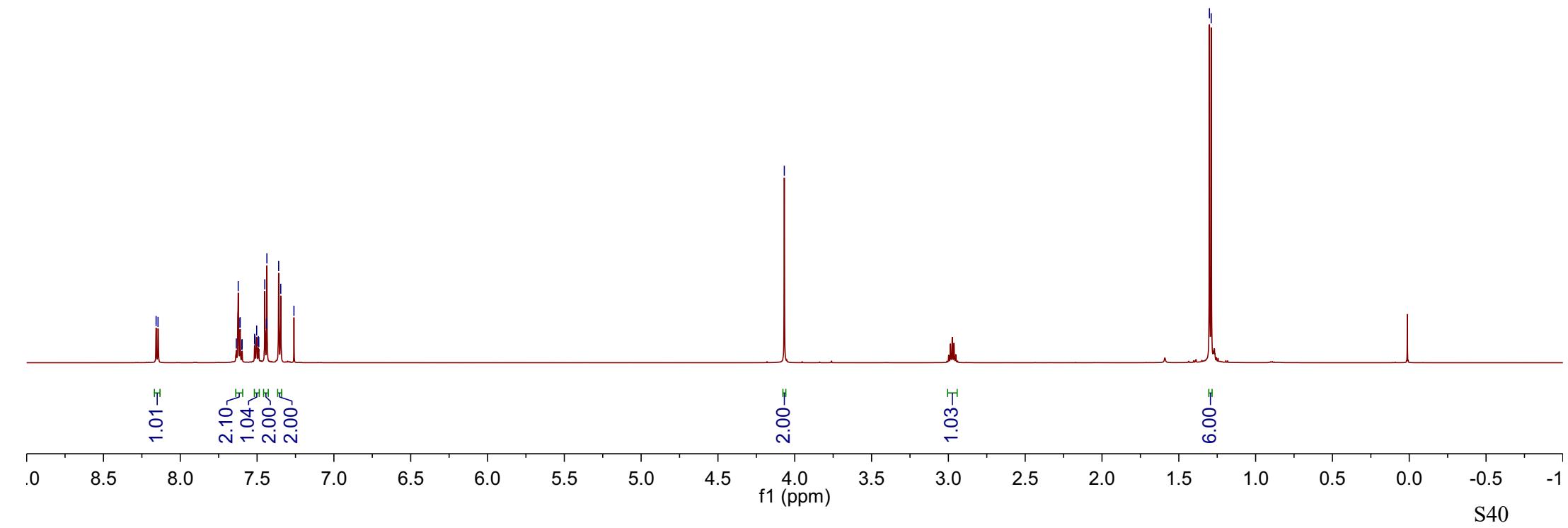
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7.35
7.26

-4.07

1.30
1.29



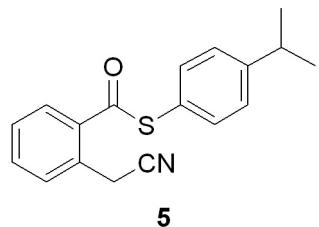
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



-193.30

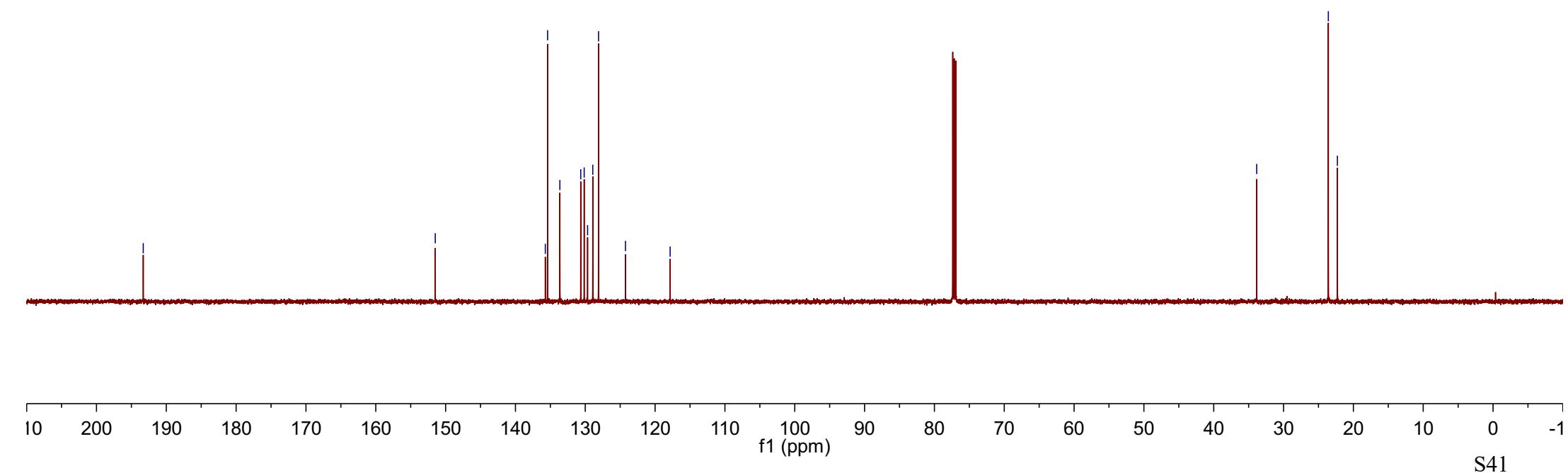
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130.65
130.16
129.67
128.92
128.10
124.24
117.85

-33.85
23.59
22.29



5

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

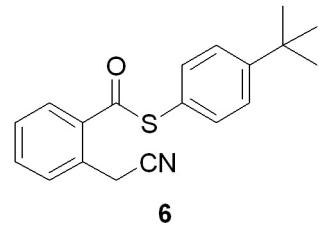


S41

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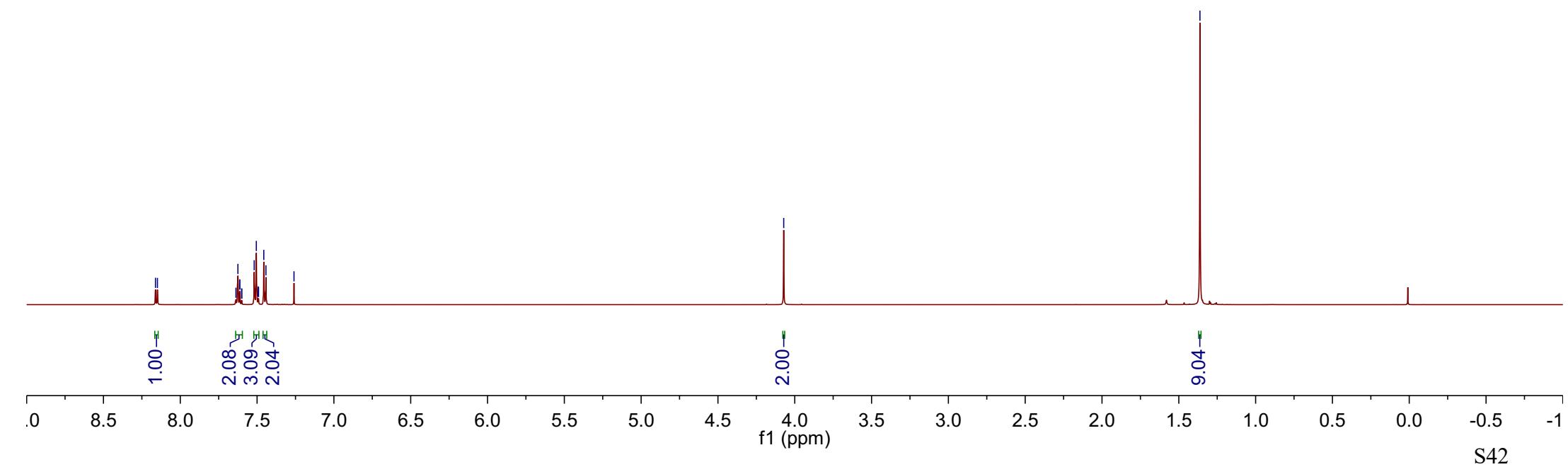
-4.07

-1.36



6

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



f1 (ppm)

S42

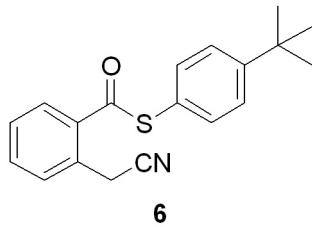
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-153.77

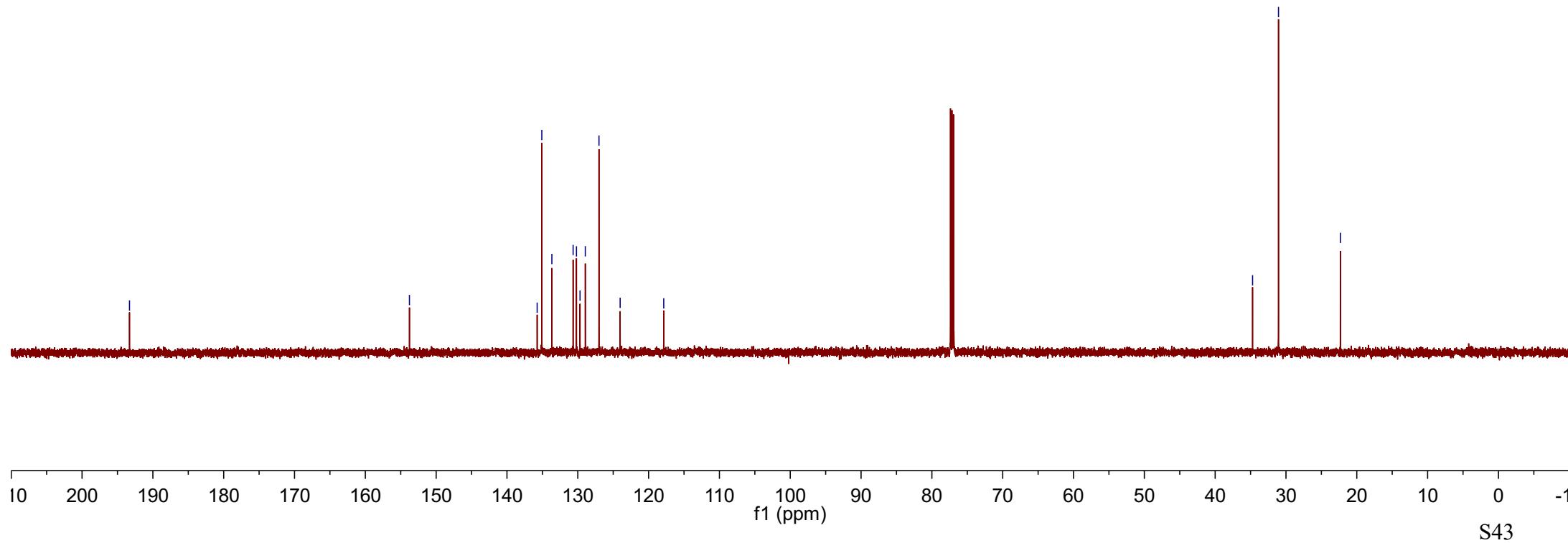
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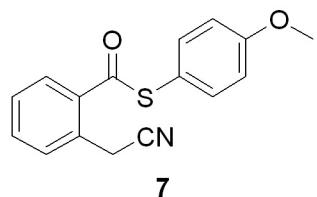
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-22.32

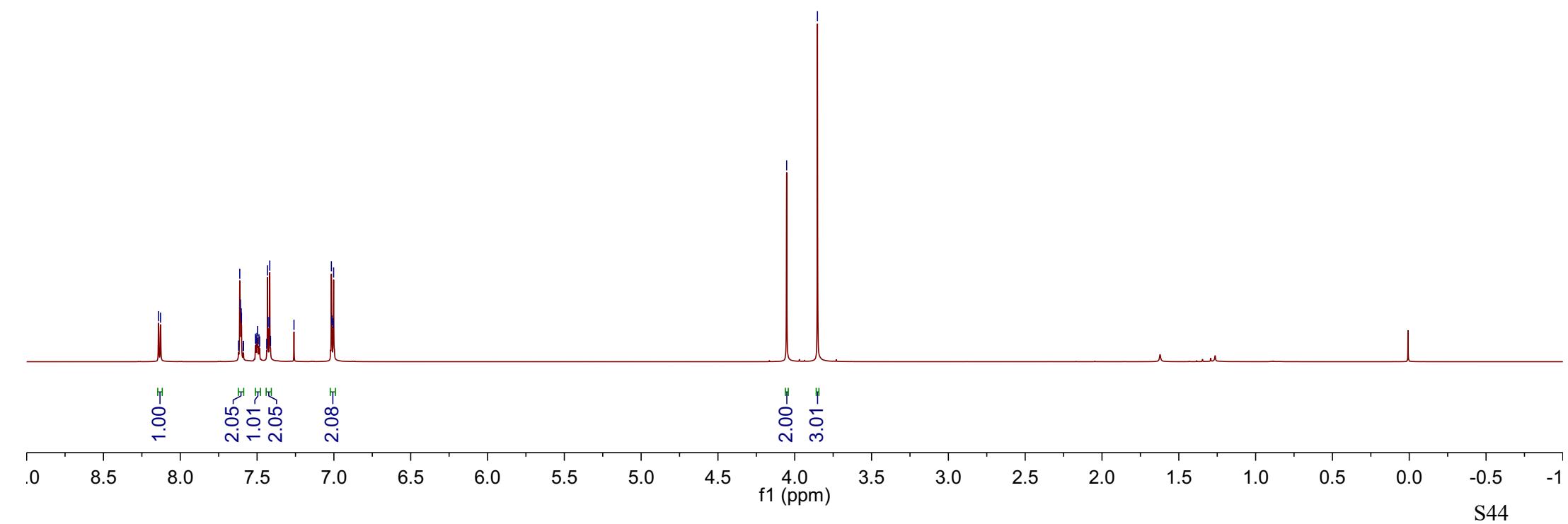


Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150





Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



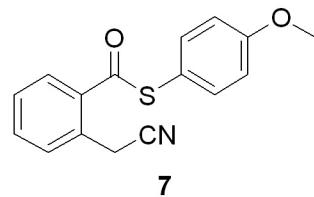
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—161.63

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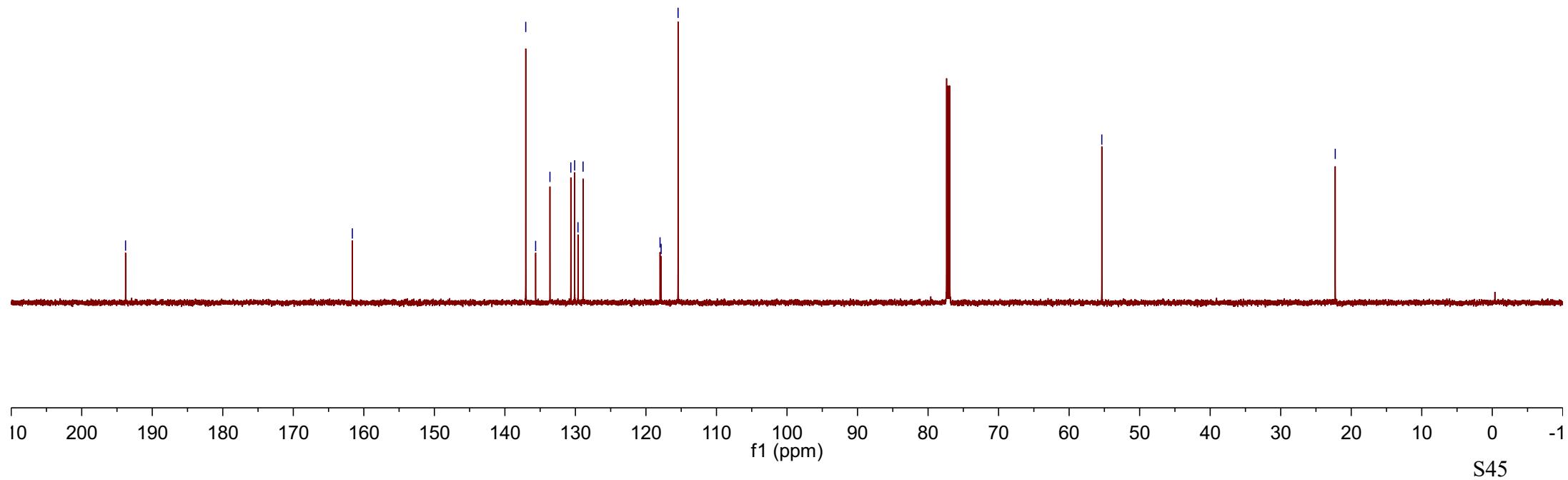
—55.36

—22.27



7

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

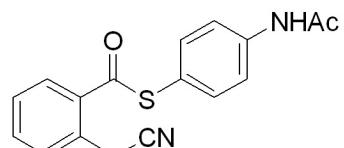


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7.46

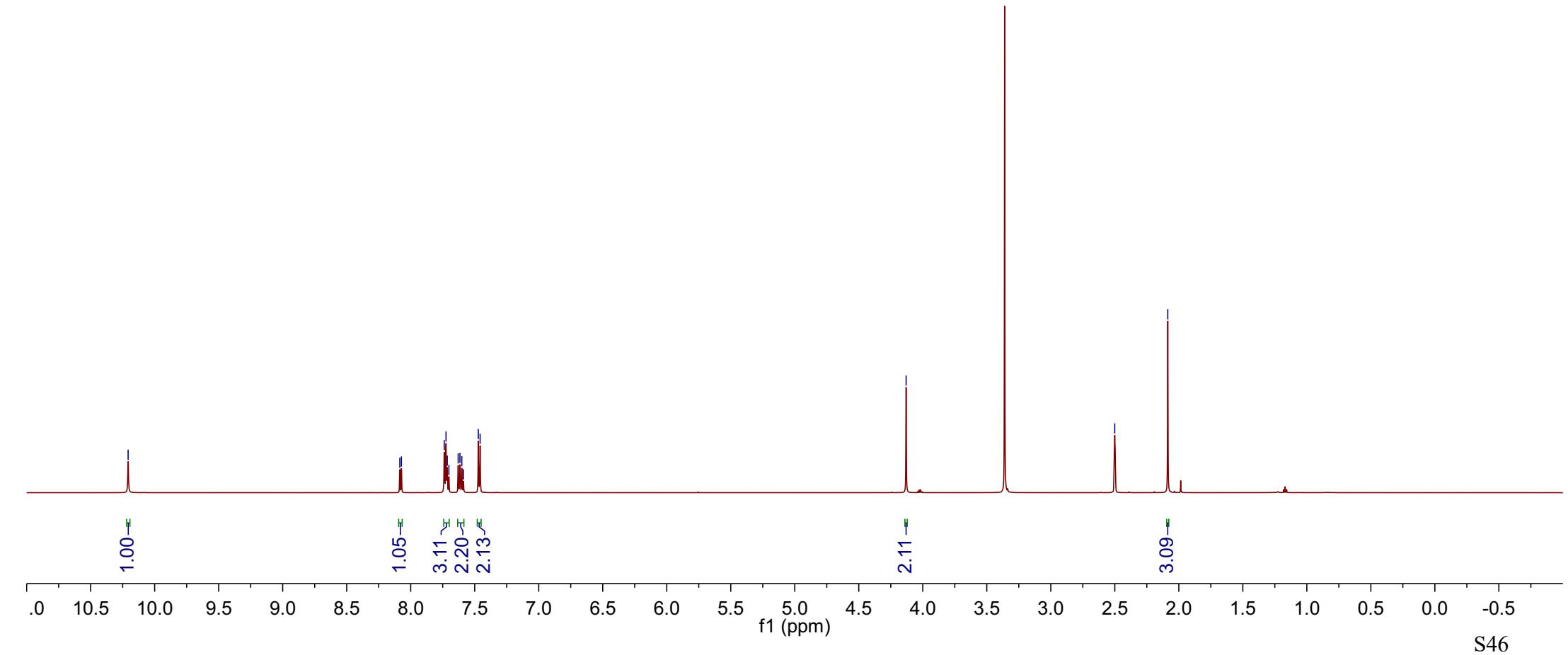
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-2.50
-2.09



8

Parameter	Value
Solvent	DMSO
Spectrometer Frequency	600

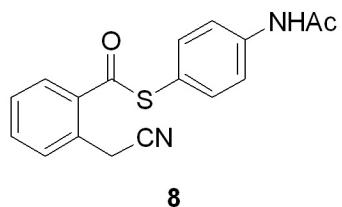


-192.43

-169.56

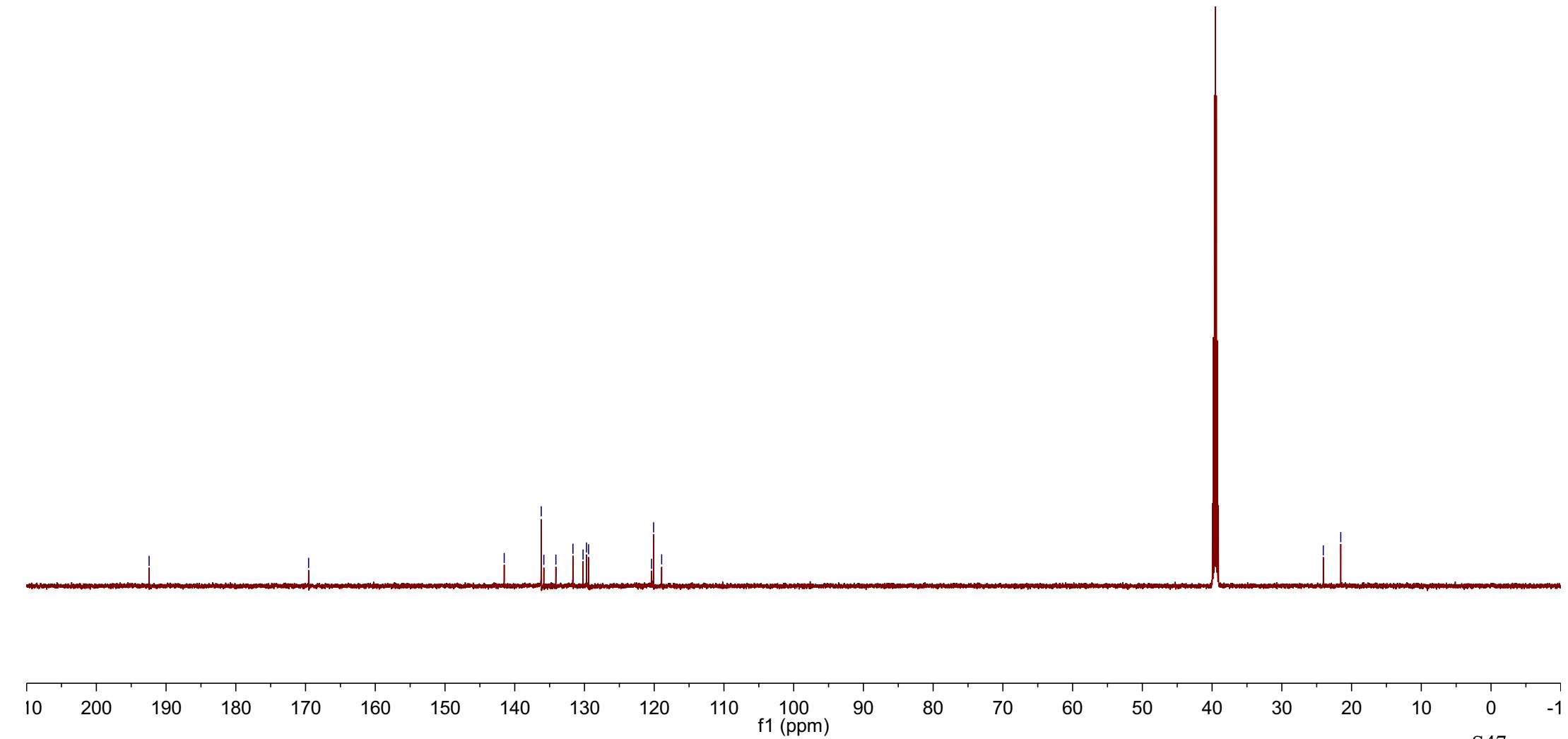
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120.09
118.93

-24.05
-21.55



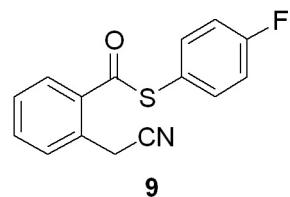
8

Parameter	Value
Solvent	DMSO
Spectrometer Frequency	150

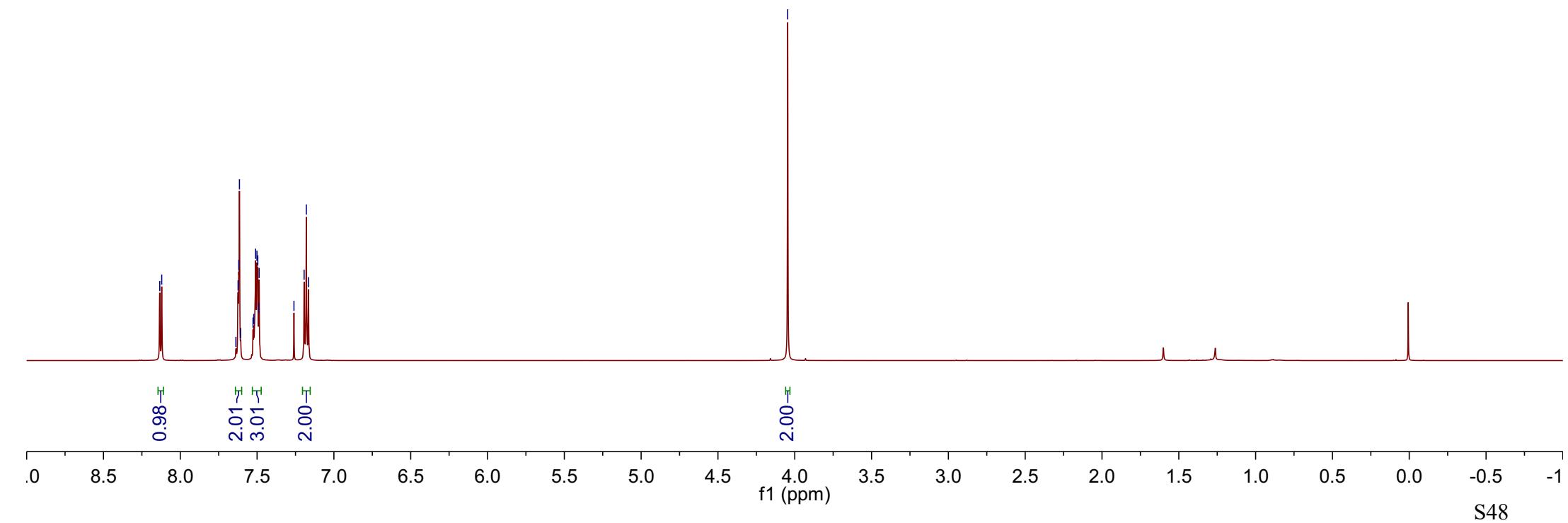


8.13
8.12
7.64
7.62
7.62
7.61
7.61
7.53
7.52
7.51
7.50
7.50
7.49
7.49
7.26
7.19
7.18
7.17

-4.05



Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600

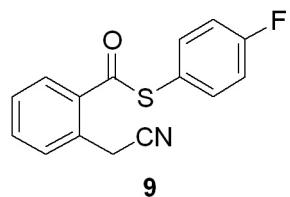


-192.75

-165.24
~163.57

137.63
137.58
135.41
133.85
130.83
130.14
129.78
129.03
122.82
122.80
117.74
117.16
117.01

-22.33



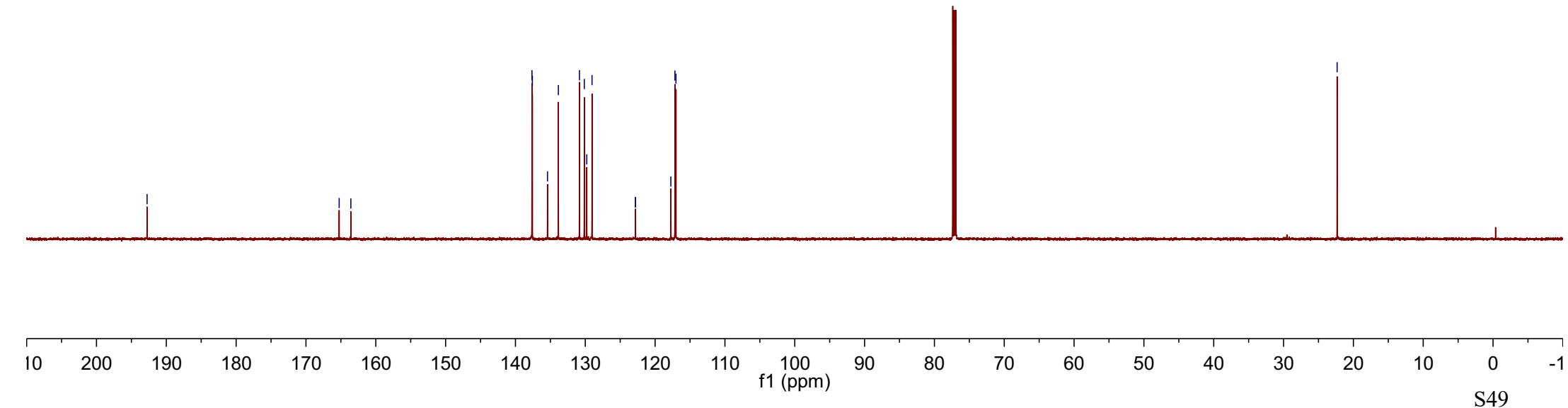
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

A (d)
164.41

B (d)
137.61

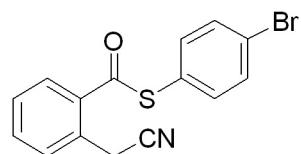
C (d)
117.08

D (d)
122.81



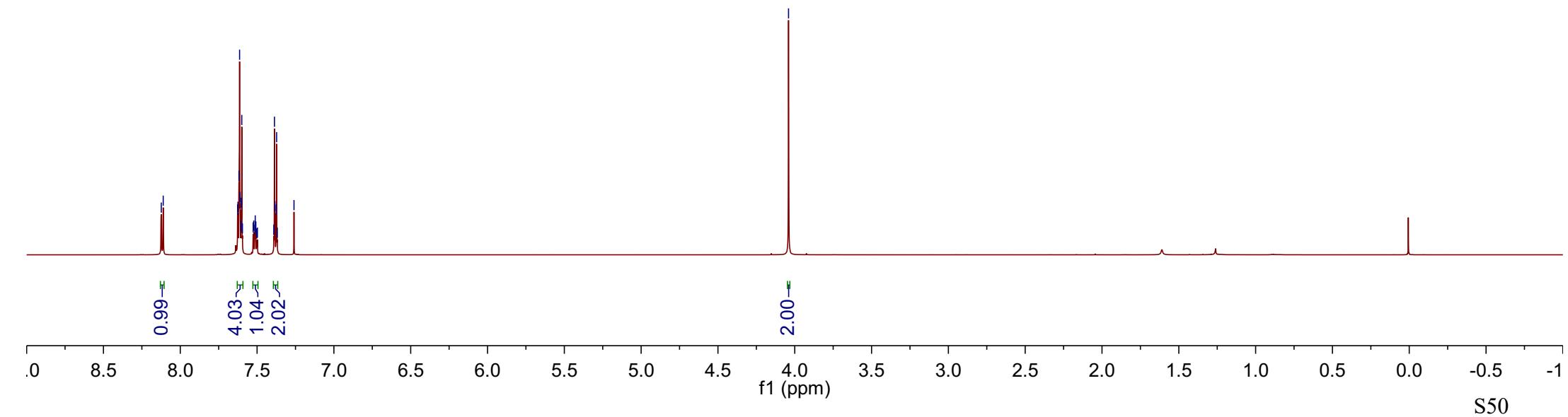
8.12
8.11
7.63
7.62
7.62
7.61
7.61
7.61
7.60
7.60
7.60
7.53
7.52
7.51
7.51
7.51
7.50
7.50
7.39
7.39
7.38
7.38
7.37
7.37
7.26

4.04



10

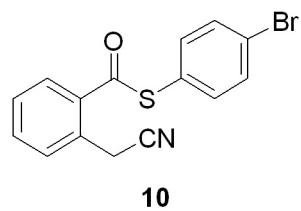
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



-192.09

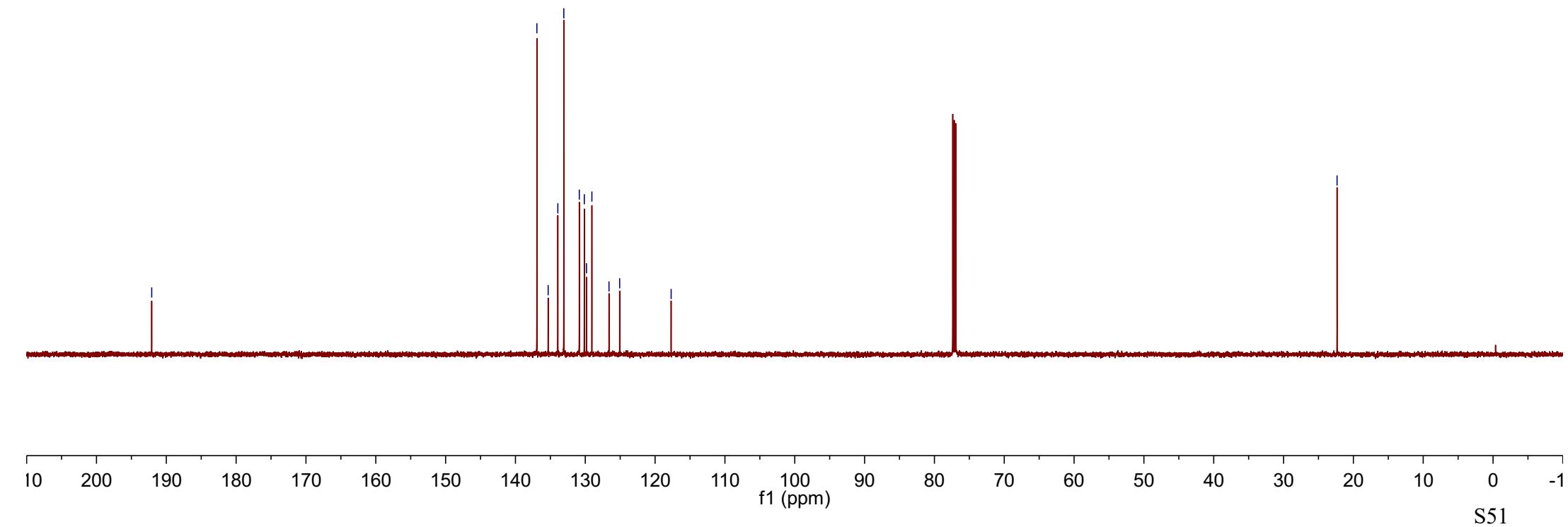
136.93
135.32
133.93
133.07
130.85
130.14
129.82
129.05
126.60
125.08
117.70

-22.34



10

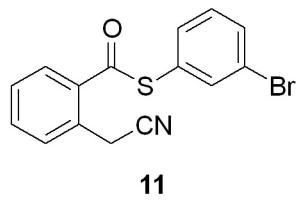
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150



S51

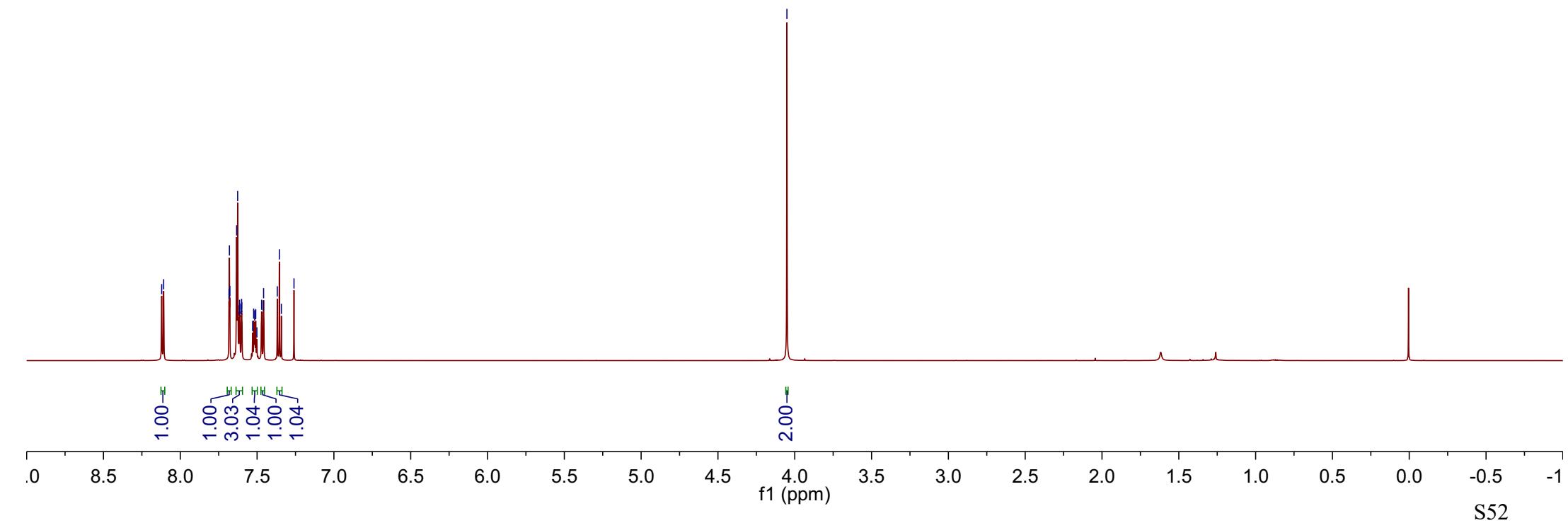
8.12
7.68
7.68
7.63
7.63
7.62
7.61
7.61
7.60
7.60
7.60
7.60
7.53
7.52
7.52
7.51
7.50
7.47
7.46
7.46
7.37
7.36
7.34
7.26

-4.05



11

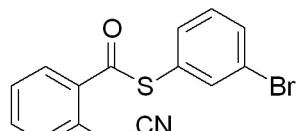
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



-191.85

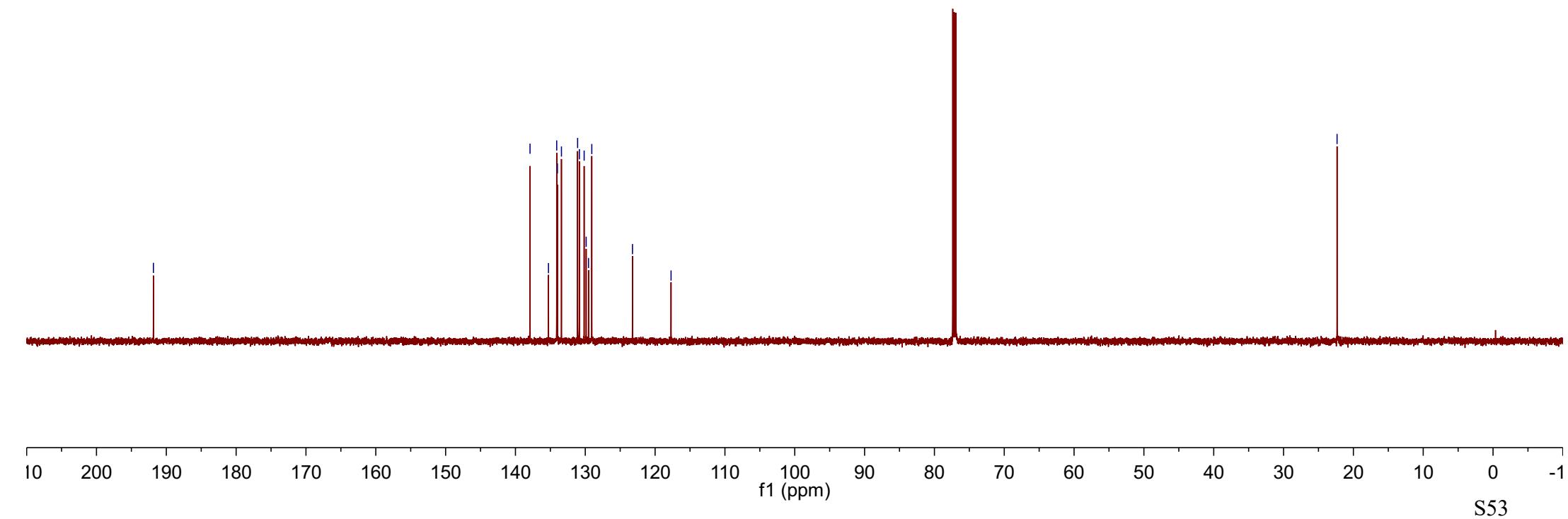
137.91
135.27
134.09
133.99
133.41
131.10
130.84
130.16
129.87
129.54
129.07
123.24
117.71

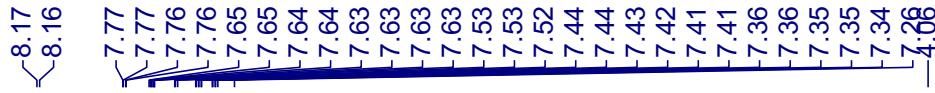
-22.34



11

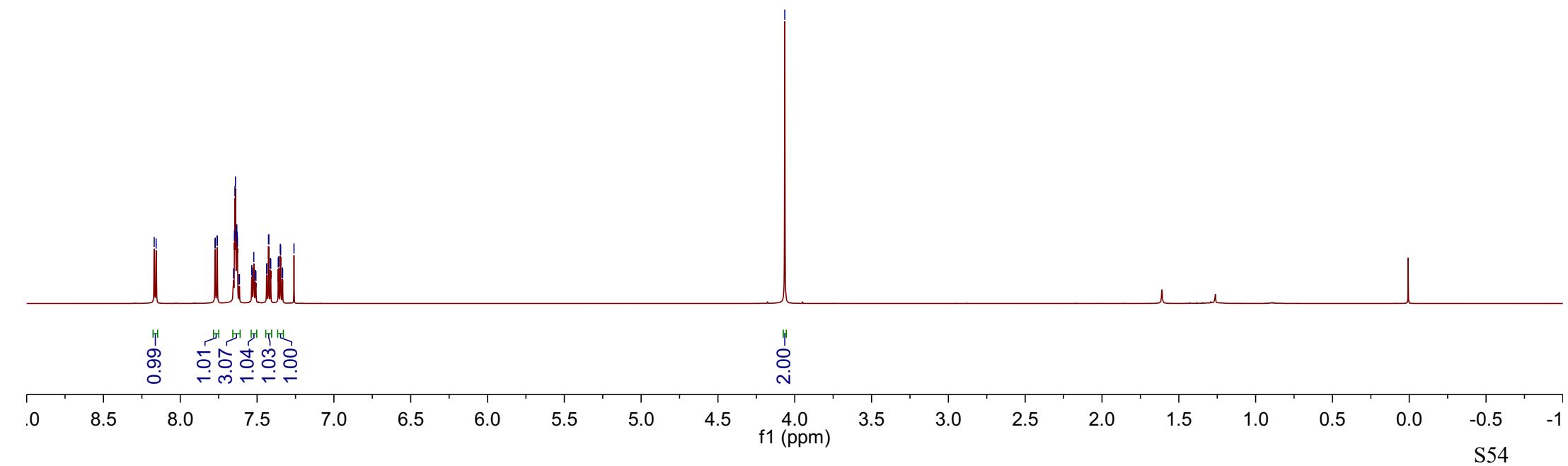
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150





12

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



-191.05

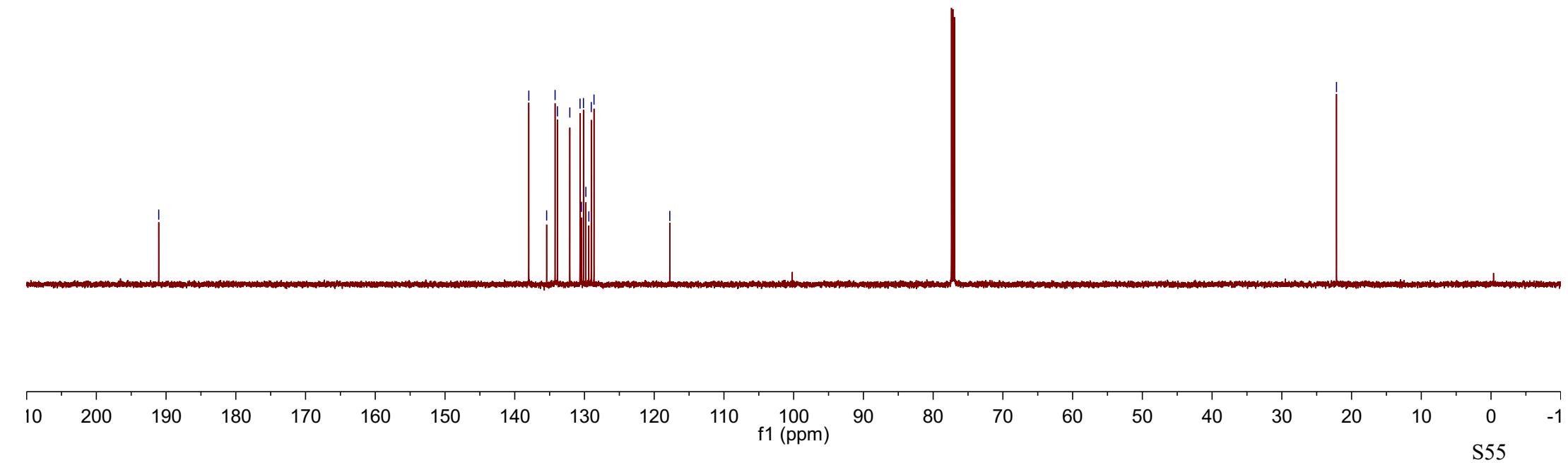
137.98
135.42
134.21
133.88
132.10
130.64
130.43
130.14
129.80
129.38
129.03
128.63
117.76

-22.16



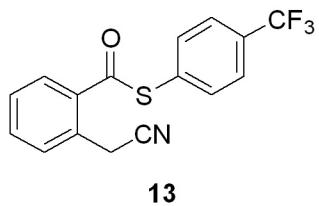
12

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

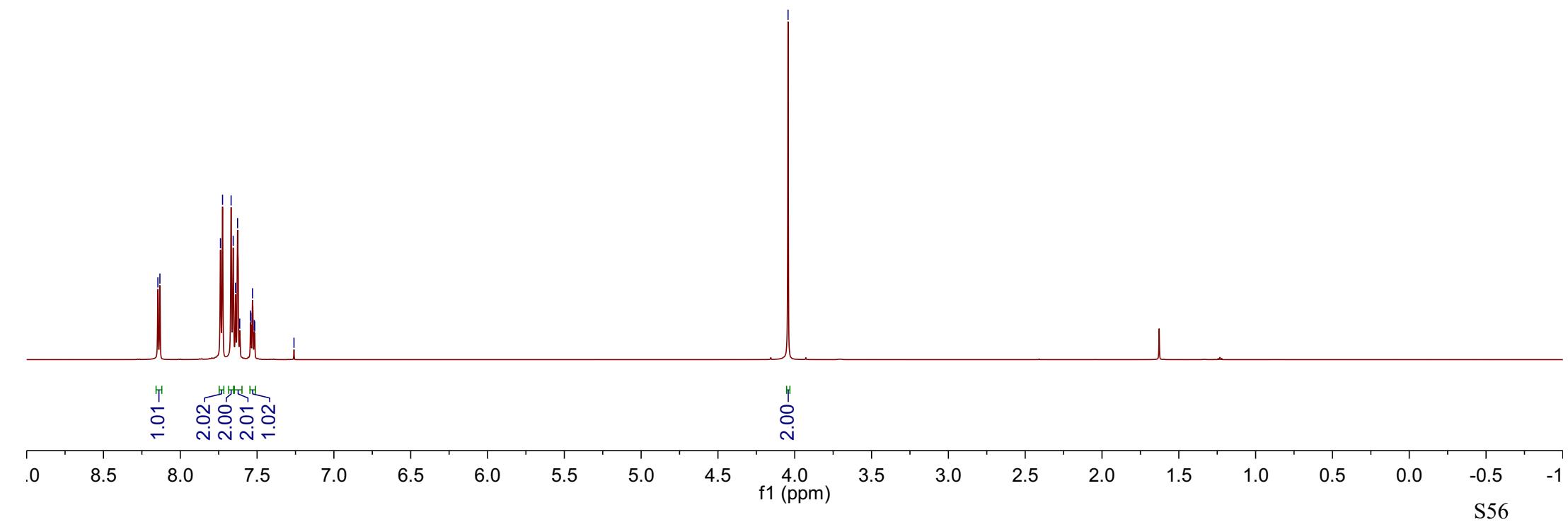


8.13
7.74
7.72
7.67
7.66
7.64
7.63
7.61
7.54
7.54
7.53
7.52
7.52
7.26

-4.04



Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



-191.49

135.66
135.22
134.09
132.52
132.29
132.28
132.08
131.86
130.97
130.17
129.95
129.13
128.85
126.59
126.56
126.54
126.51
125.04
123.22
121.41
117.66

-22.36



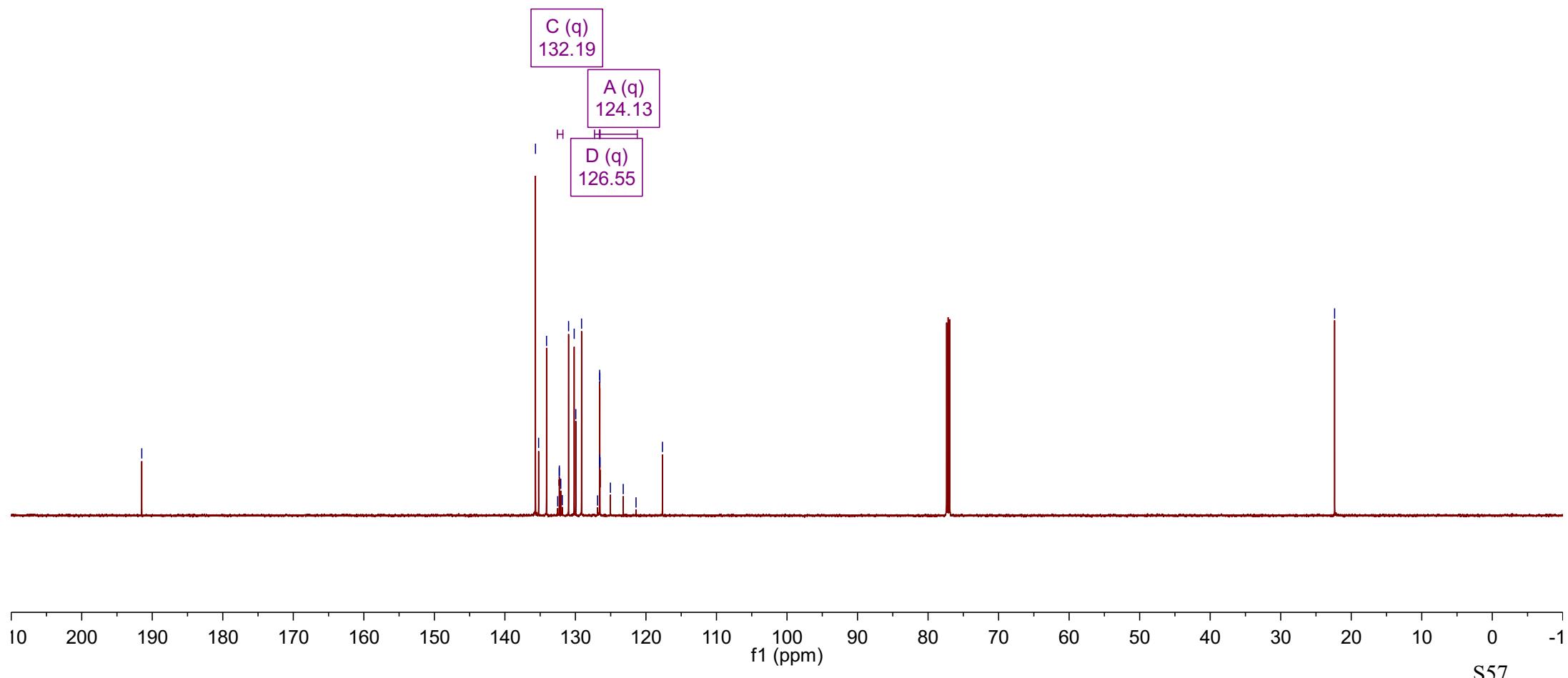
13

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

C (q)
132.19

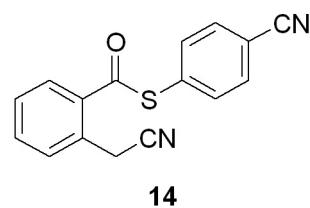
A (q)
124.13

D (q)
126.55

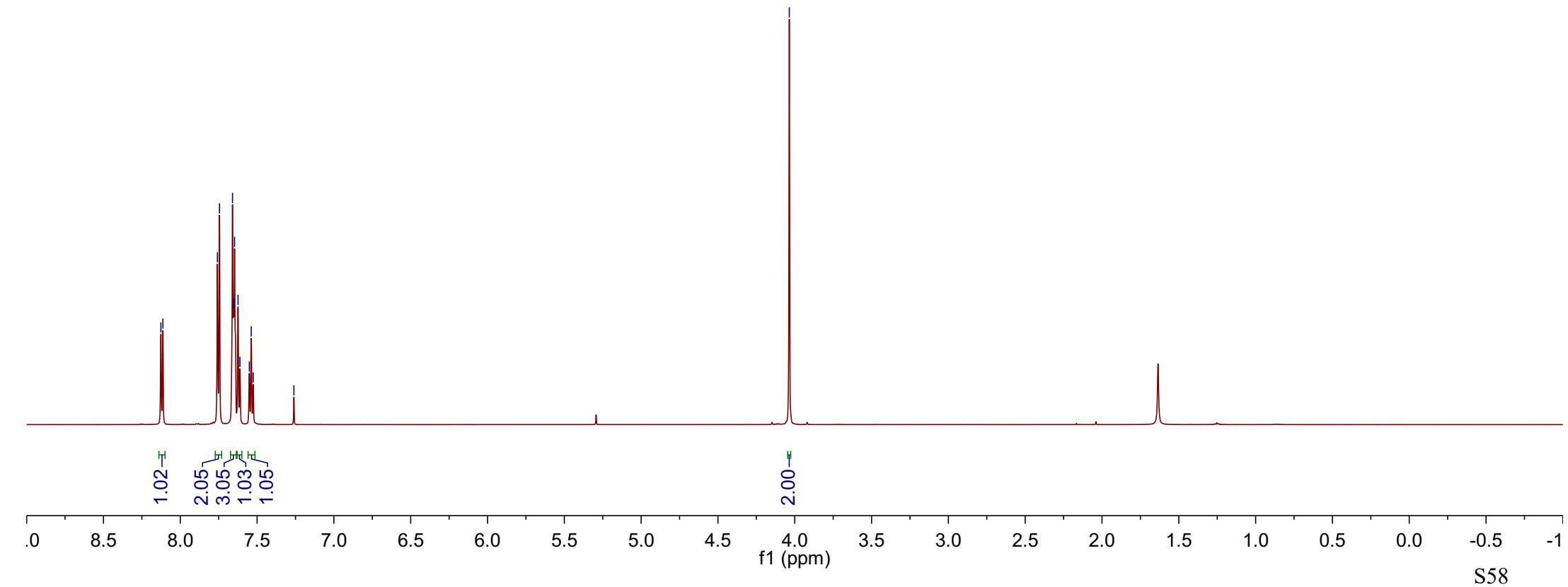


8.13
8.11
7.76
7.74
7.66
7.65
7.65
7.62
7.61
7.55
7.54
7.53
7.26

—4.04



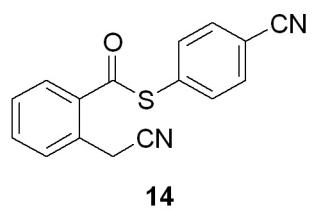
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



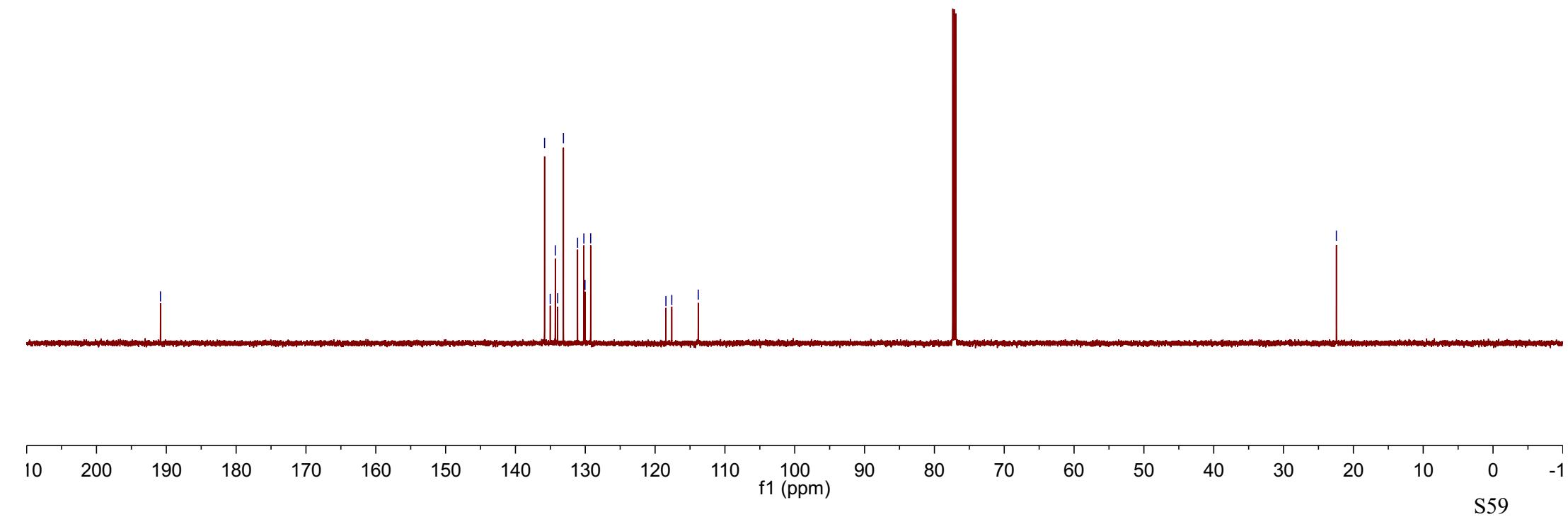
-190.84

135.83
135.02
134.29
133.95
133.13
131.10
130.20
130.04
129.23
118.45
117.61
113.82

-22.44

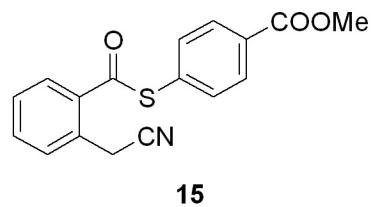


Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

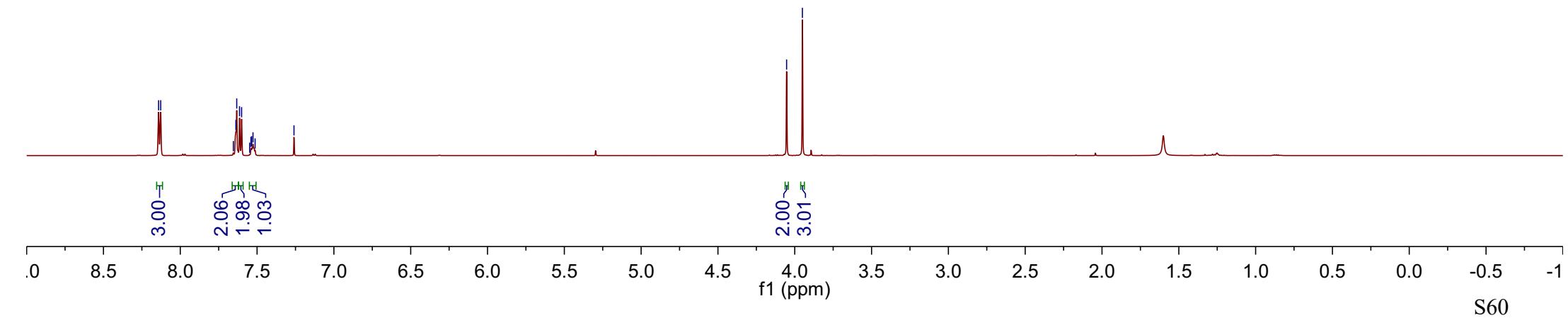


8.14
7.65
7.64
7.63
7.61
7.60
7.55
7.54
7.54
7.53
7.51
7.26

~4.05
~3.95



Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



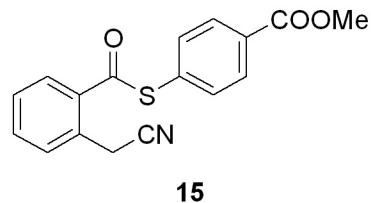
—191.68

—167.02

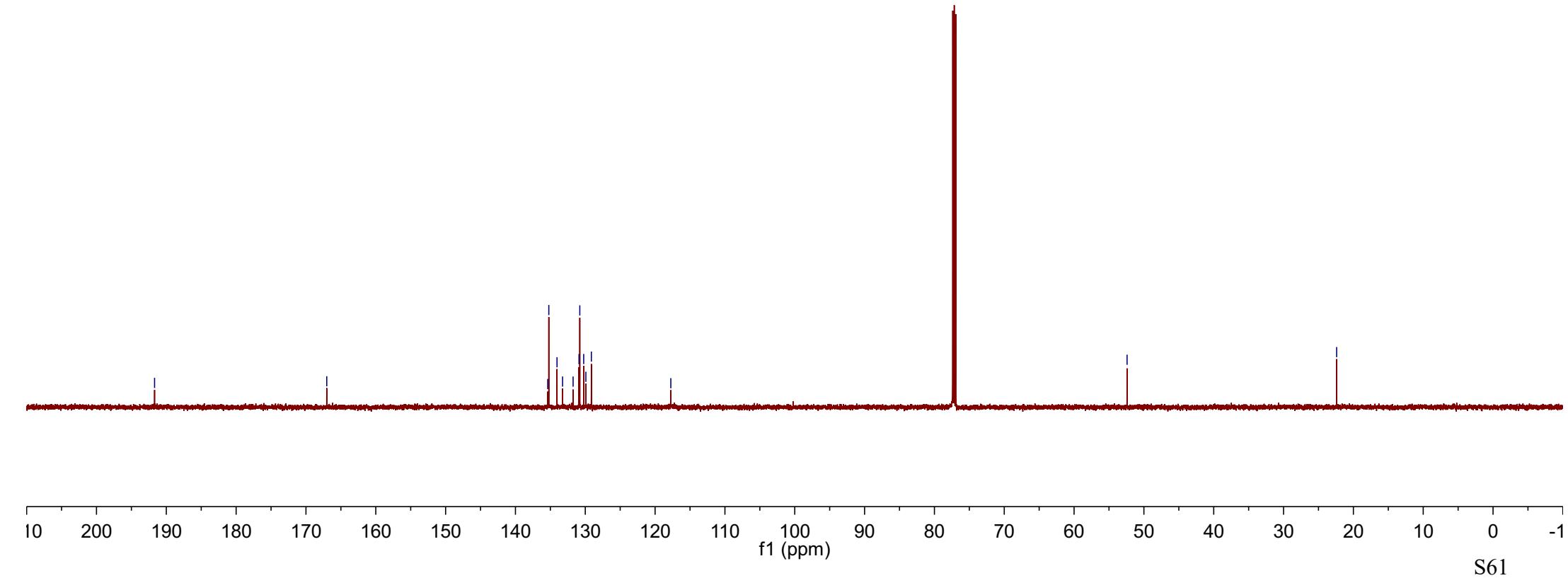
135.38
135.22
134.05
133.25
131.74
130.90
130.78
130.23
129.92
129.13
—117.75

—52.41

—22.40



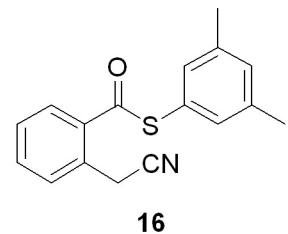
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150



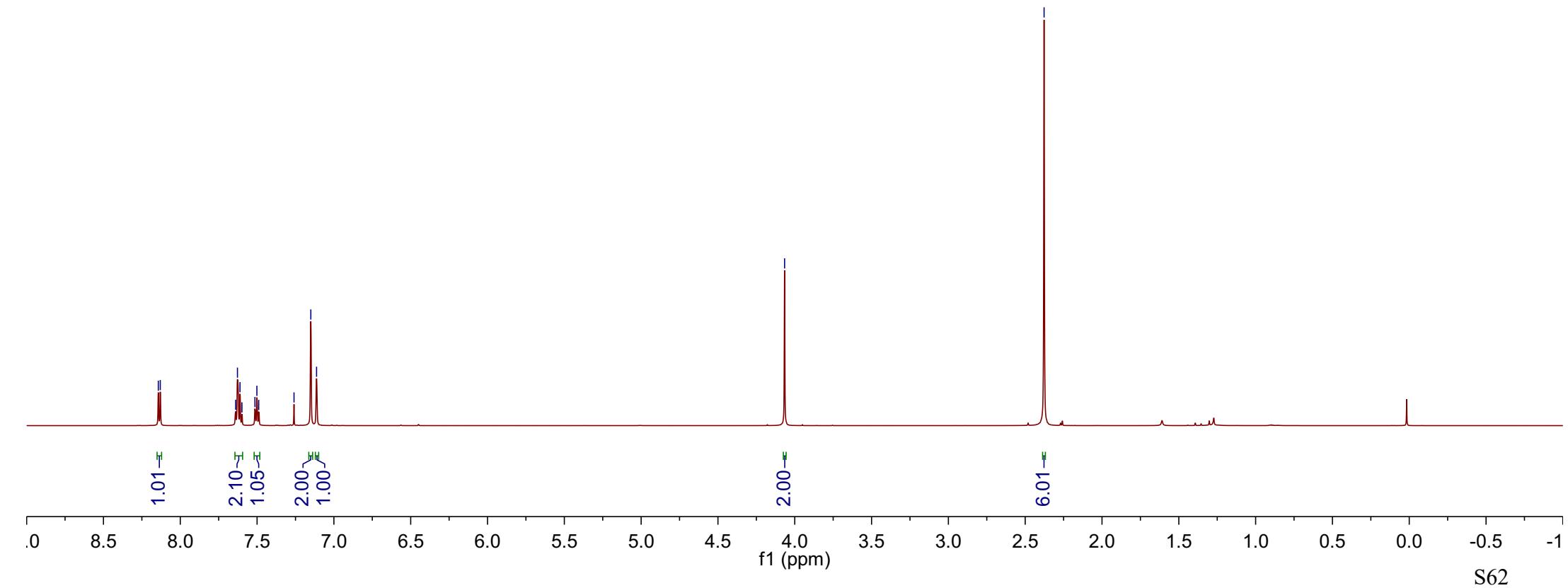
8.14
7.64
7.63
7.61
7.60
7.51
7.50
7.49
7.26
7.15
7.11

-4.07

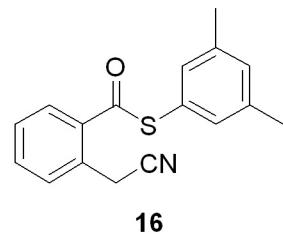
-2.38



Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



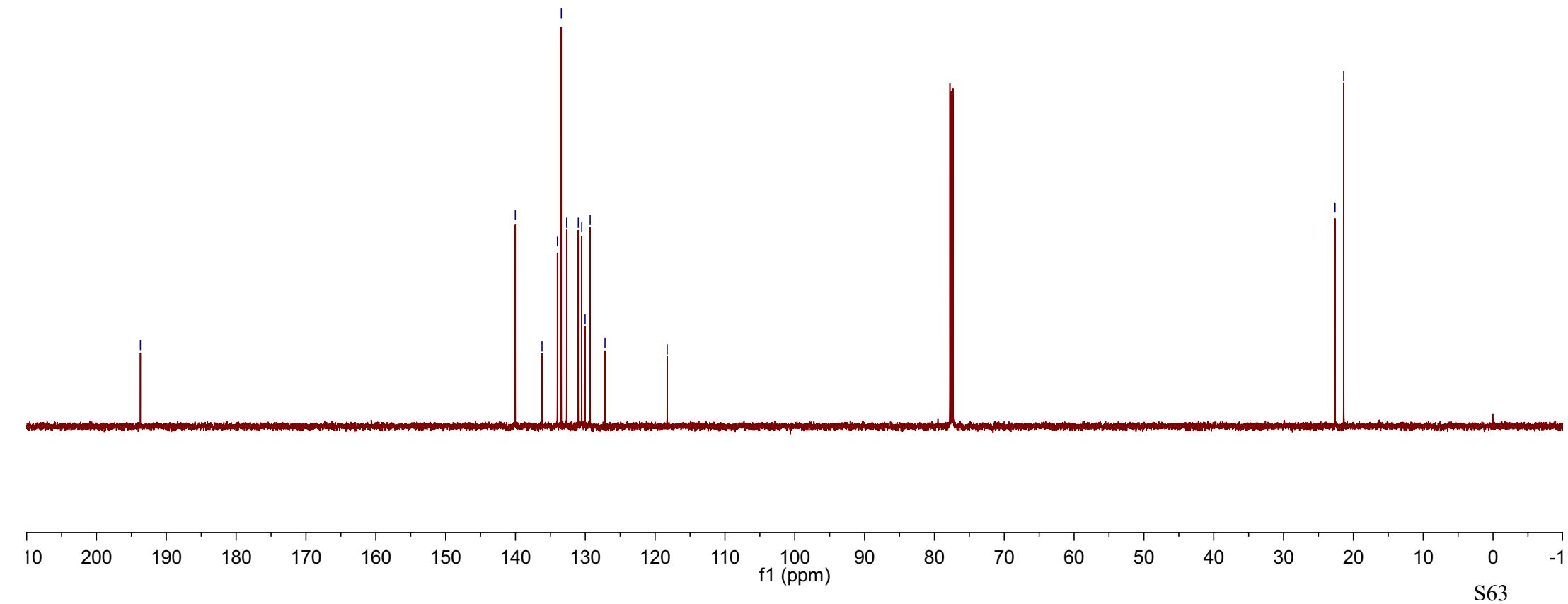
— 193.71



140.02
136.20
133.99
133.43
132.66
131.00
130.51
130.02
129.30
127.17
118.27

~22.63
~21.39

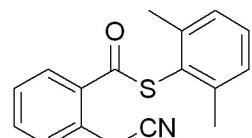
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150



8.27
8.25
7.64
7.64
7.63
7.63
7.62
7.62
7.61
7.55
7.53
7.52
7.52
7.54
7.54
7.53
7.52
7.52
7.51
7.50
7.49
7.48
7.47
7.46
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.23

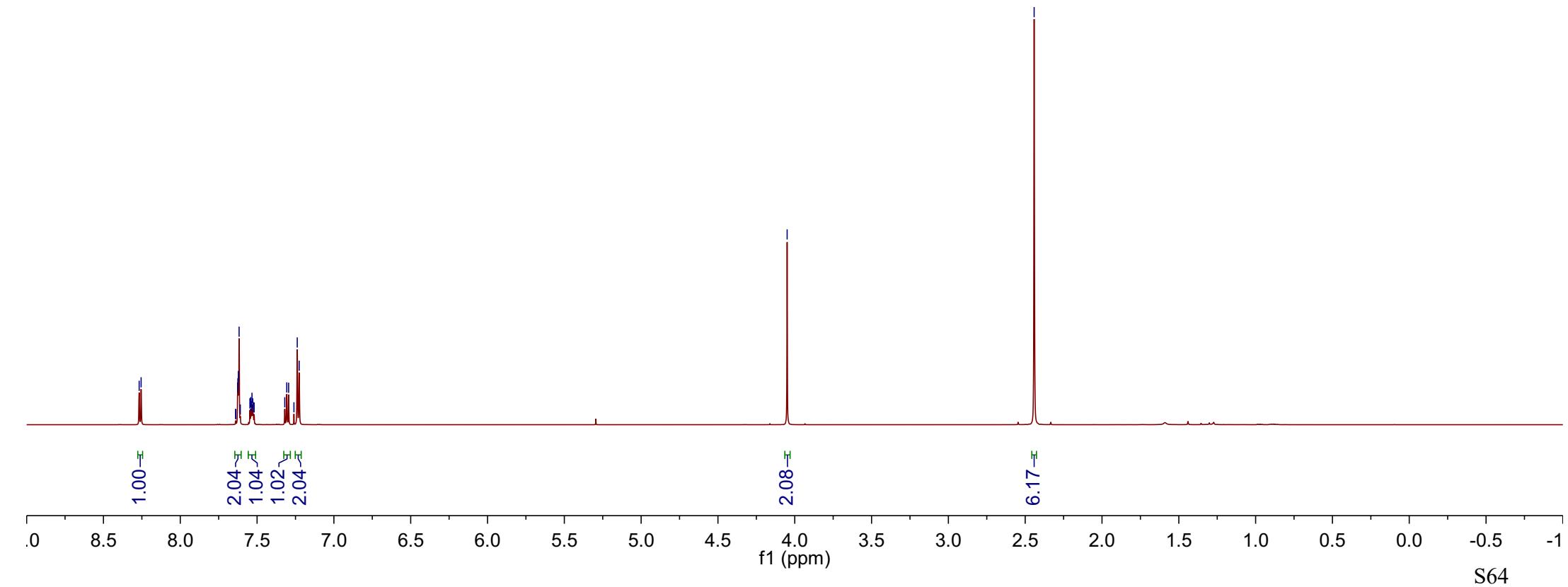
-4.05

-2.44



17

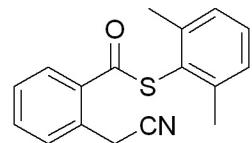
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



-191.98

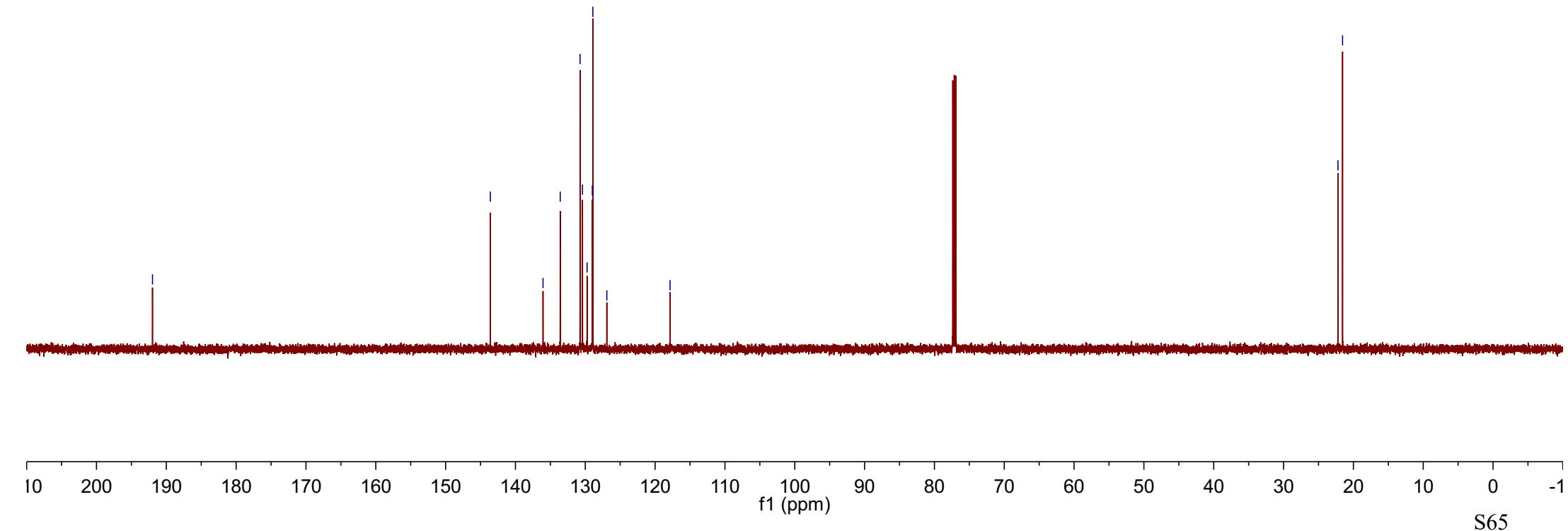
-143.60
136.05
133.59
130.74
130.40
129.74
128.99
128.86

22.21
21.55



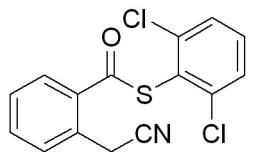
17

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150



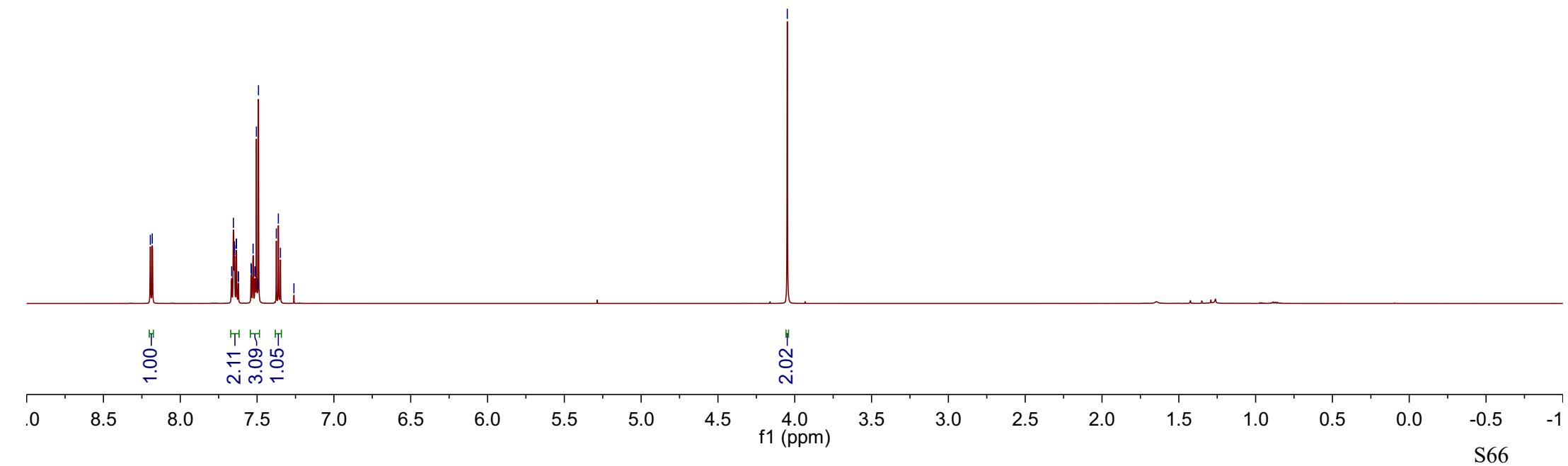
8.19
8.18
7.67
7.65
7.65
7.64
7.63
7.62
7.62
7.54
7.54
7.53
7.51
7.51
7.50
7.50
7.49
7.49
7.37
7.36
7.35
7.26

—4.05



18

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600

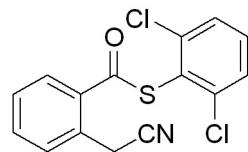


-189.22

-141.64

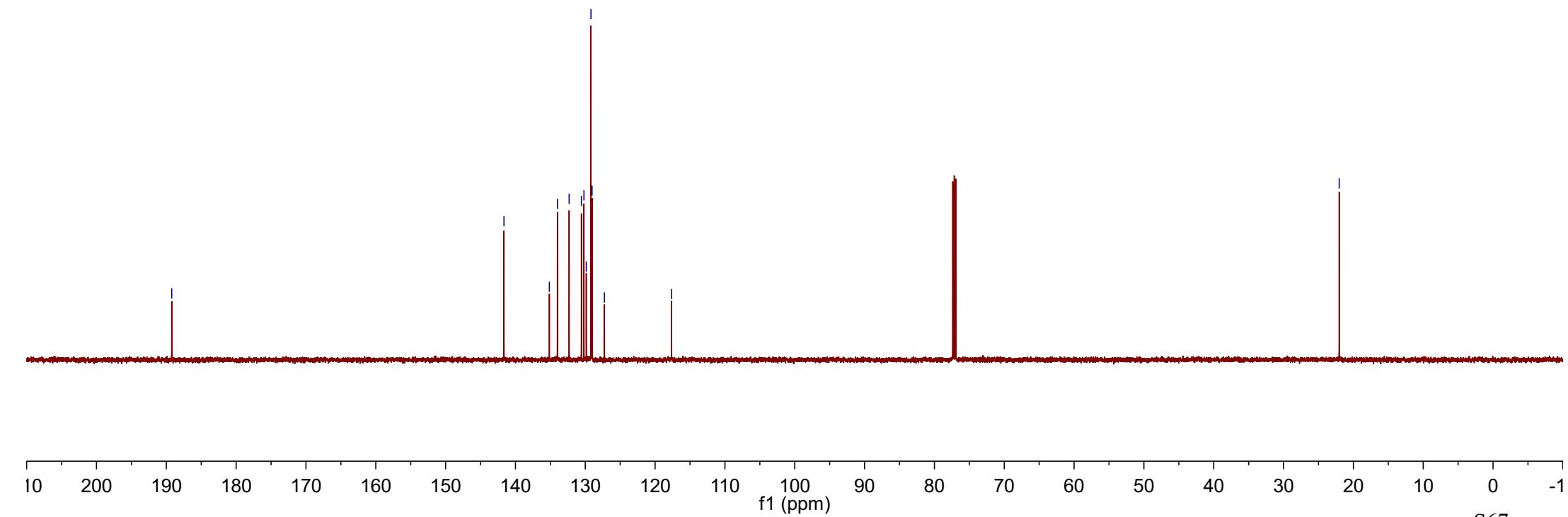
~133.99
~132.31
130.55
130.19
129.18
129.03

-22.03



18

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

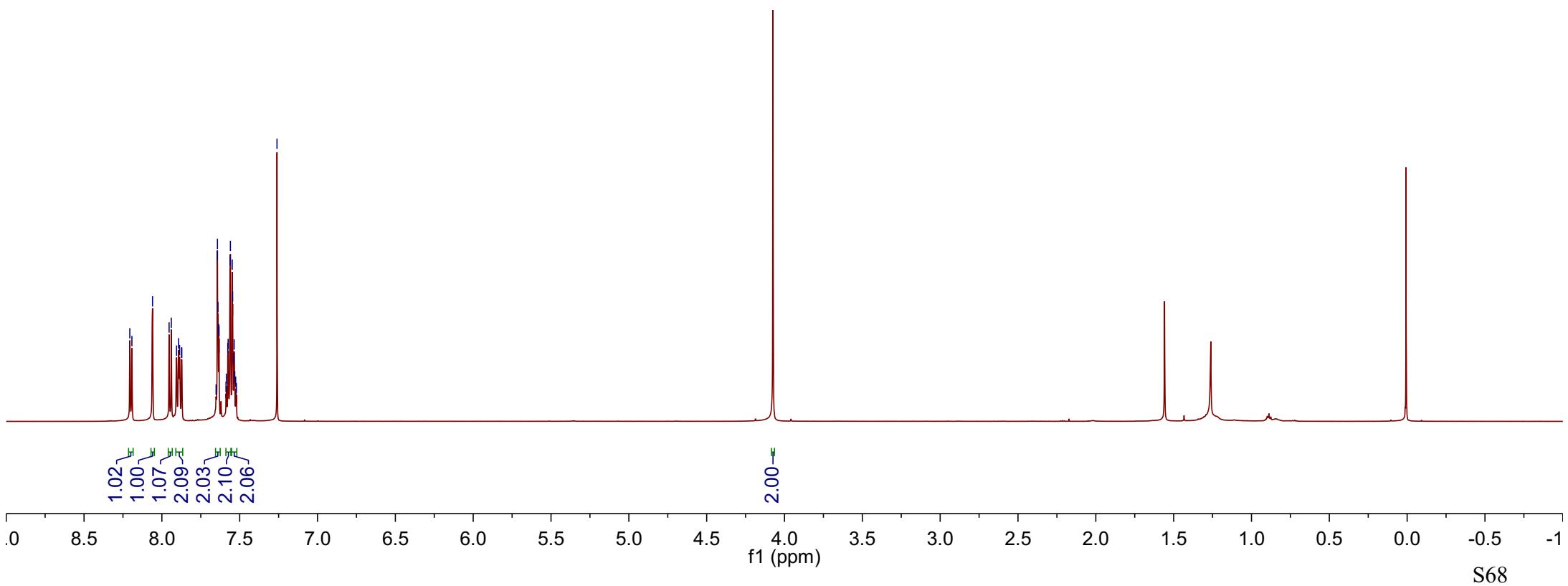


8.21
8.19
8.06
7.95
7.94
7.91
7.89
7.89
7.87
7.87
7.65
7.64
7.64
7.64
7.63
7.63
7.59
7.58
7.57
7.56
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.26



19

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



-193.44

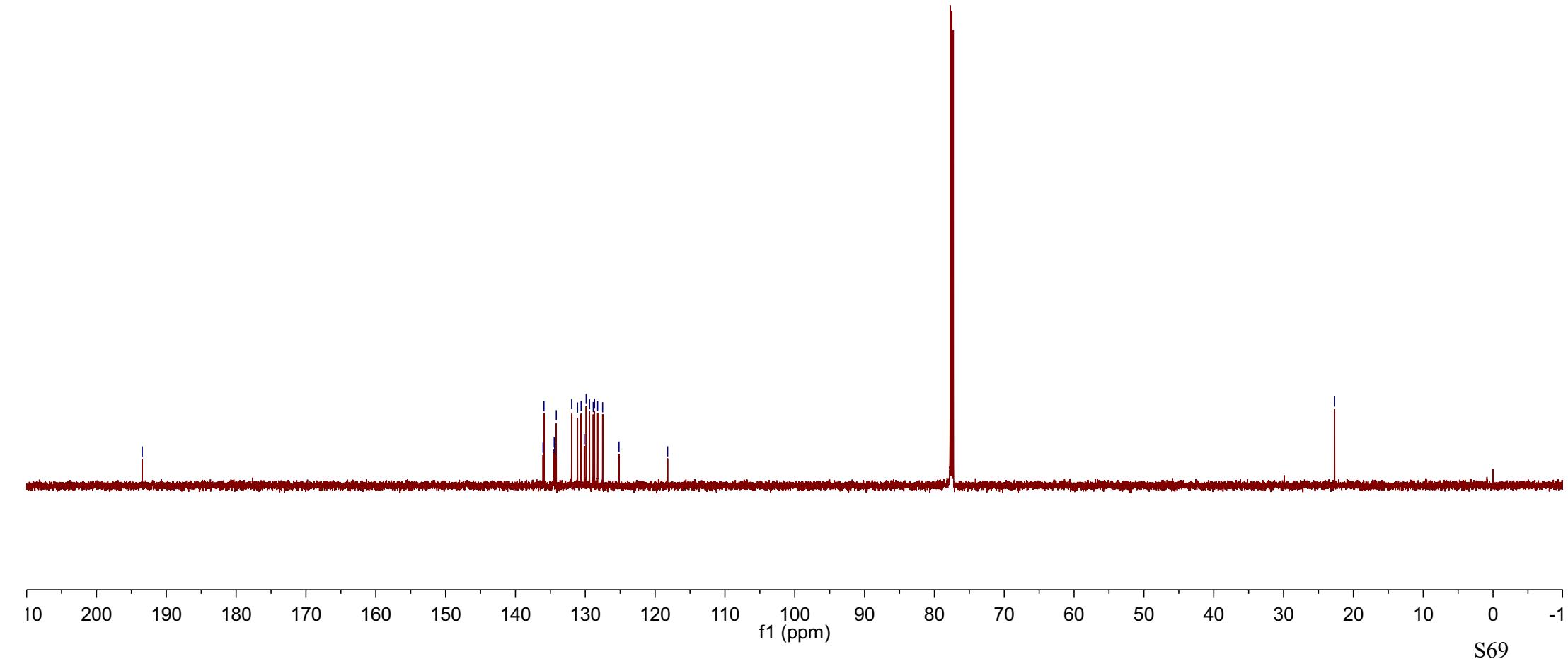
136.05
135.91
134.45
134.39
134.15
131.95
131.11
130.60
130.14
129.87
129.38
128.86
128.67
128.23
127.51
125.17
118.20

-22.69



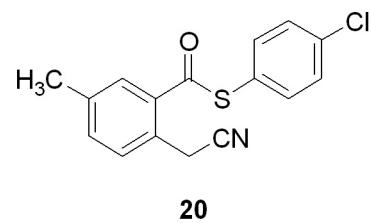
19

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150



S69

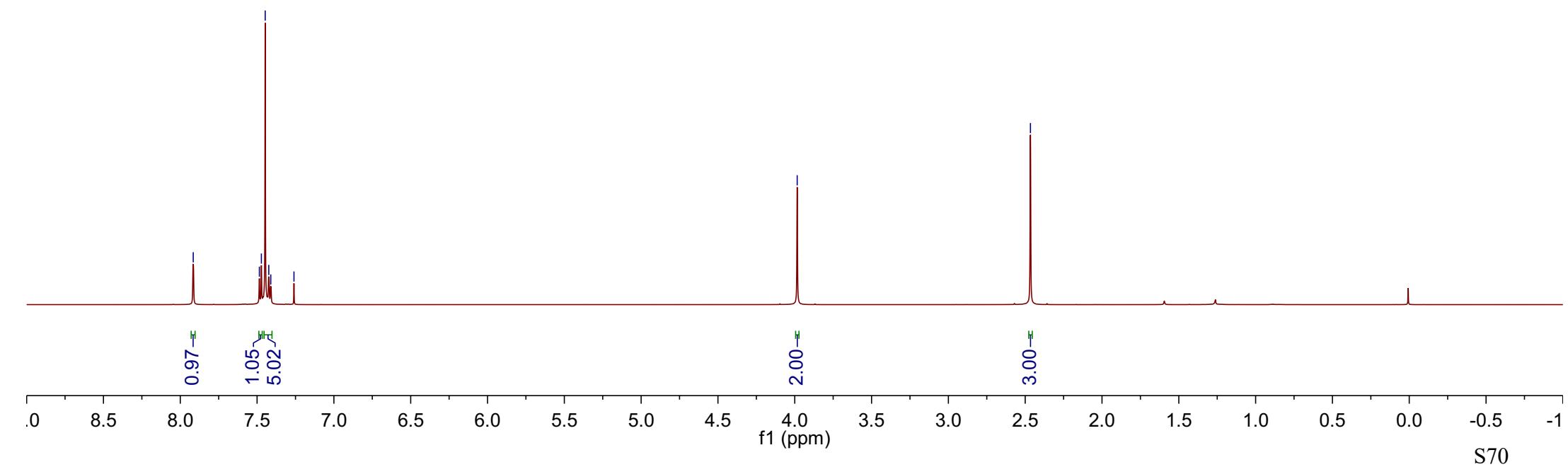
-7.92
7.49
7.47
7.45
7.42
7.41
7.26



-3.98

-2.47

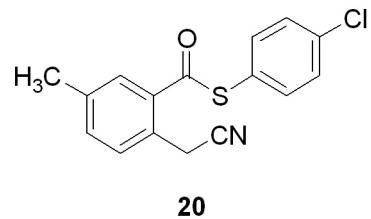
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



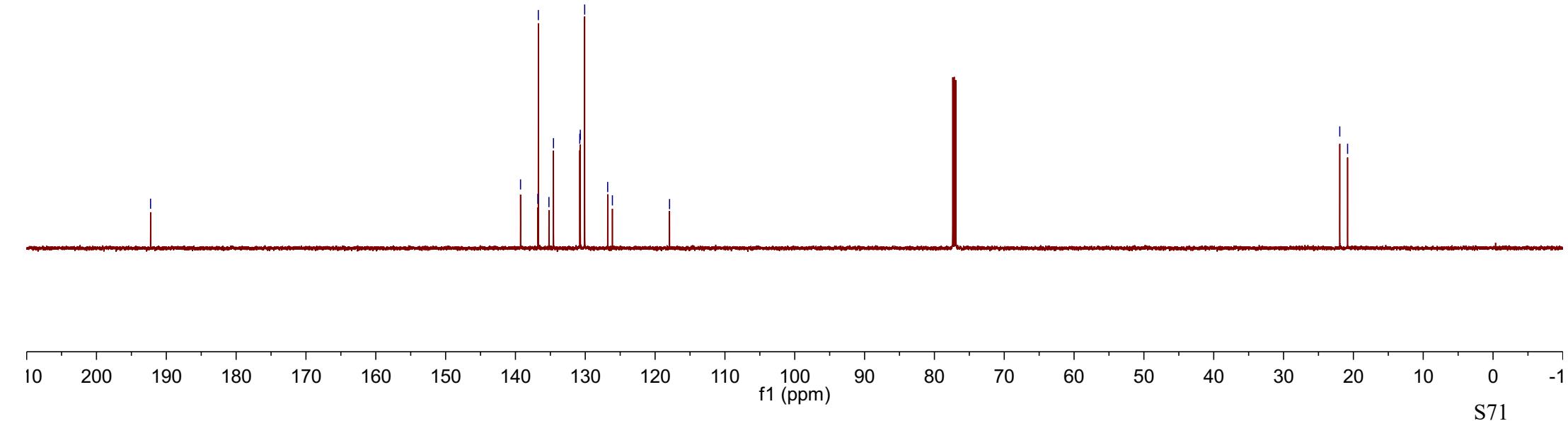
-192.26

139.27
136.80
136.72
135.20
134.55
130.79
130.71
130.09
126.79
126.12
117.93

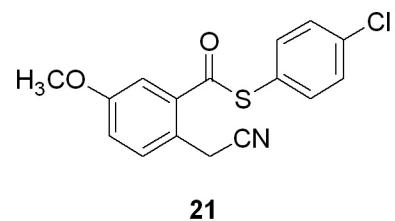
21.95
20.83



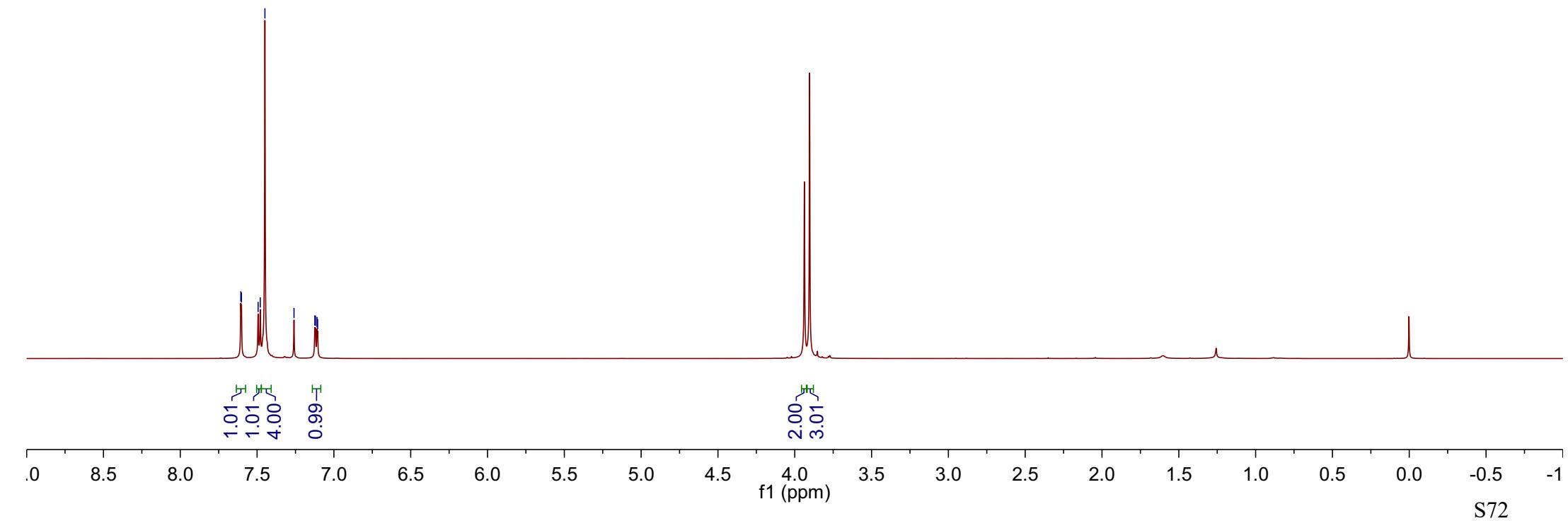
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150



7.61
7.60
7.49
7.48
7.45
7.26
7.26
7.12
7.11
7.11



Parameter	Value
Solvent	CDCl_3
Spectrometer Frequency	600



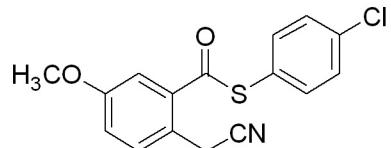
-192.13

-160.03

136.90
136.70
136.41
132.14
130.14
125.97
121.33
118.63
118.07
115.87

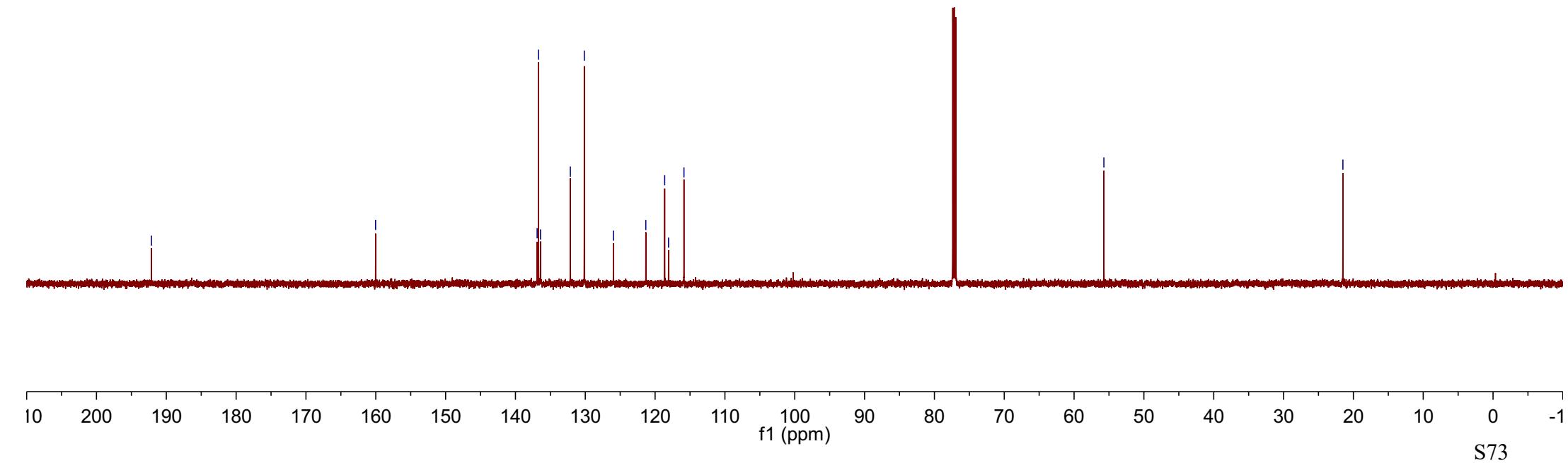
-55.73

-21.50



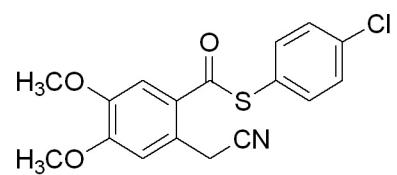
21

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150



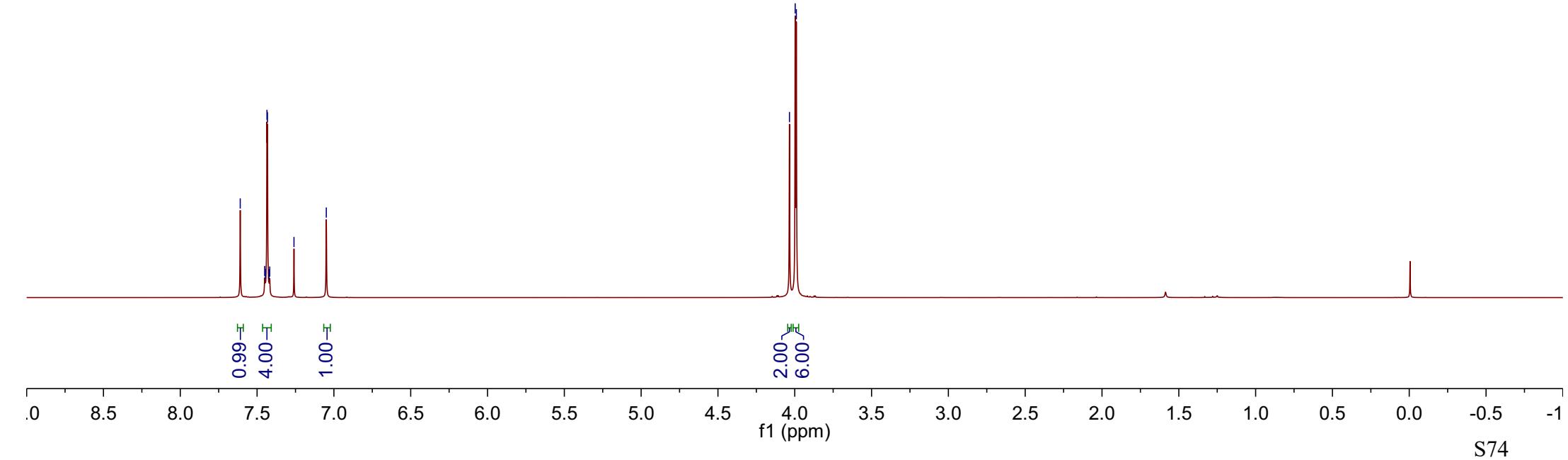
7.61
7.45
7.45
7.44
7.43
7.42
7.42
7.26
7.05

4.03
4.00
3.99



22

Parameter	Value
Solvent	CDCl3
Spectrometer Frequency	600



-190.56

-153.64

-148.88

<136.86

<136.83

~130.12

~127.12

~126.22

~124.26

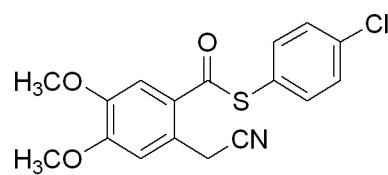
-118.13

<113.11

<112.87

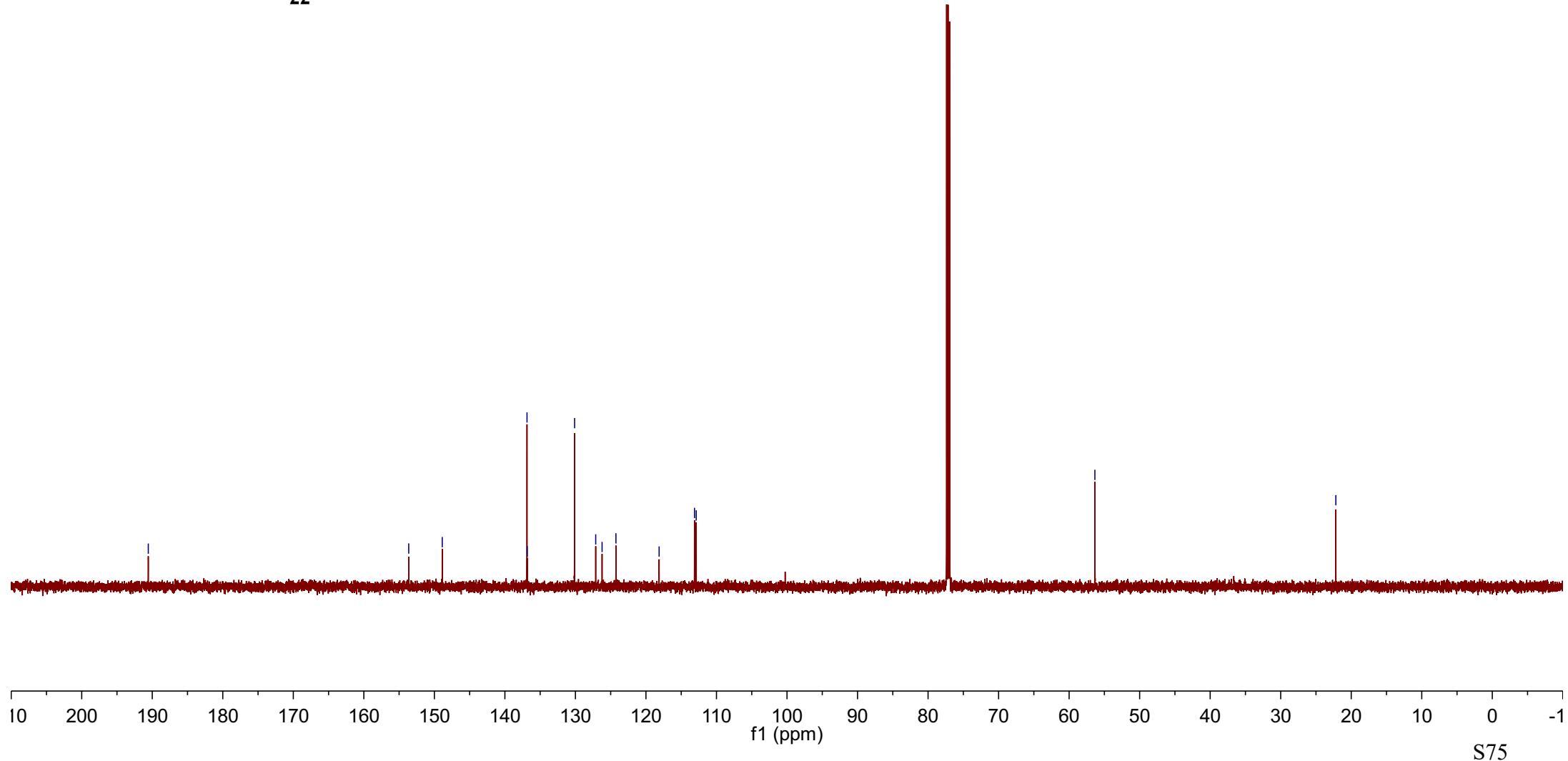
-56.35

-22.18



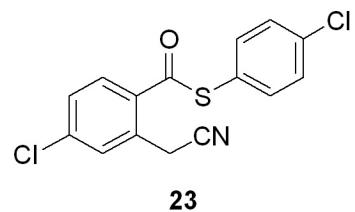
22

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

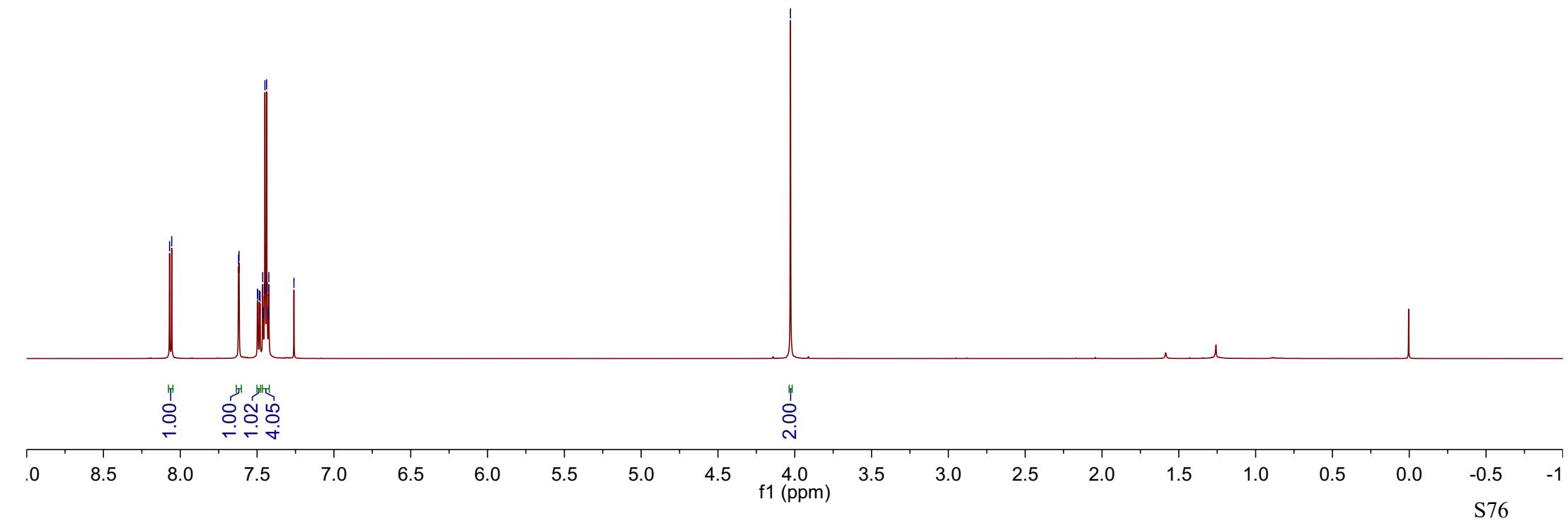


8.07
8.06
7.62
7.62
7.50
7.49
7.48
7.48
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.26

—4.03



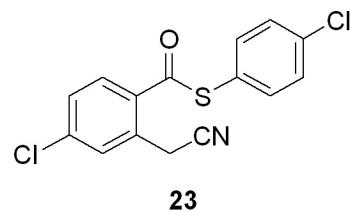
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



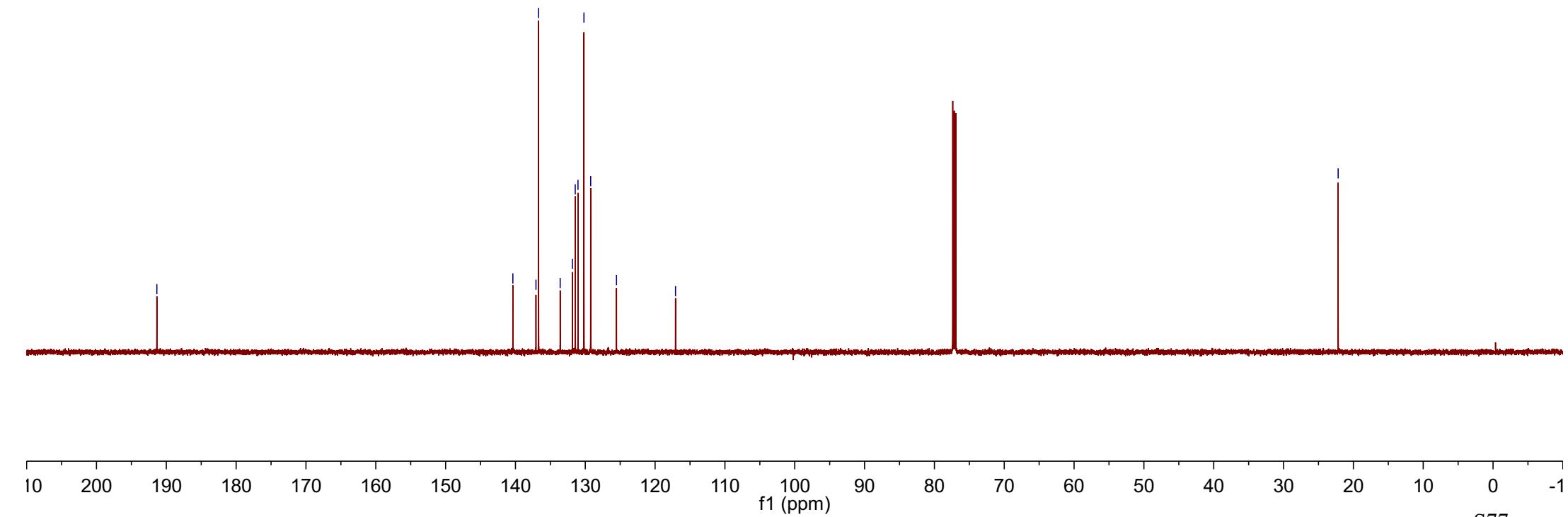
-191.35

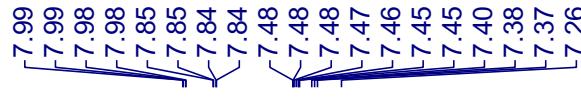
140.37
137.06
136.69
133.59
131.84
131.44
131.04
130.19
129.23
125.53
-117.08

-22.18

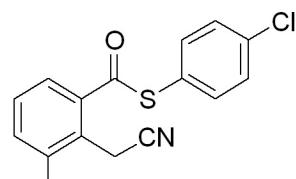


Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

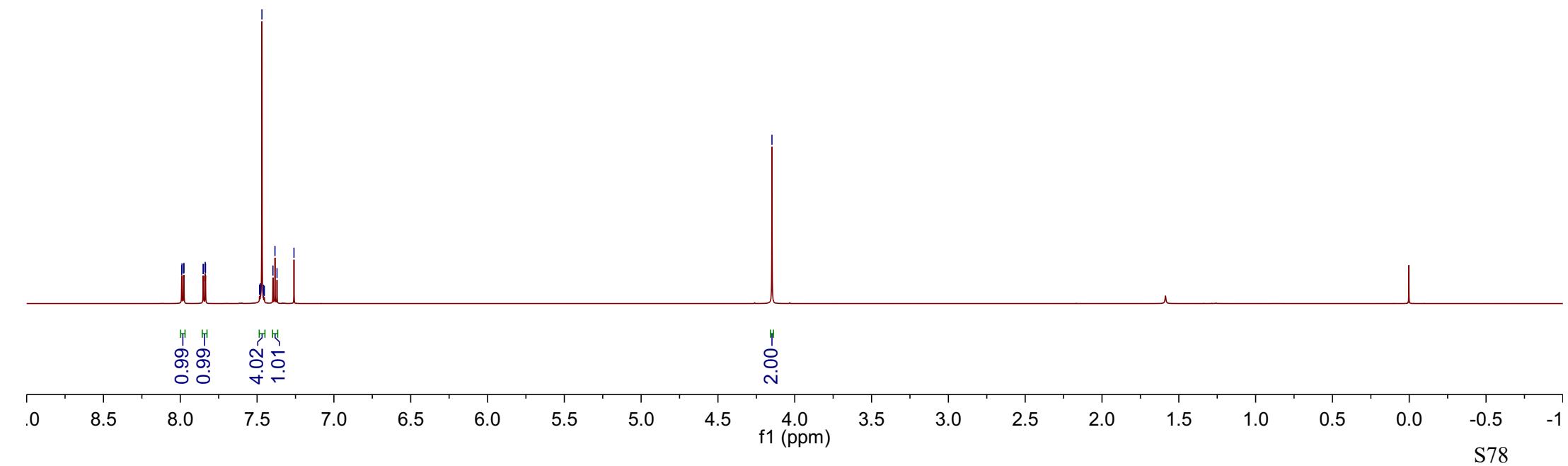




-4.15



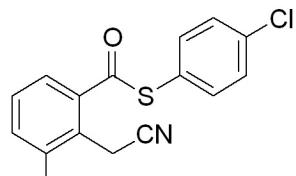
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



-192.29

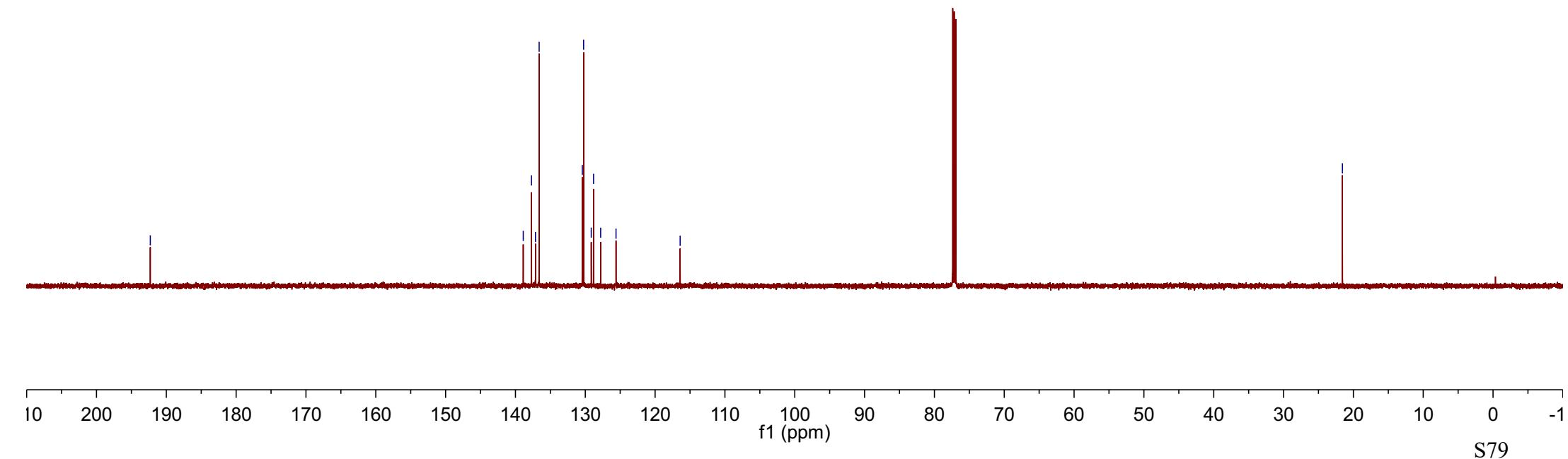
138.88
137.70
137.13
136.61
130.42
130.24
129.14
128.81
127.80
125.60
116.41

-21.57



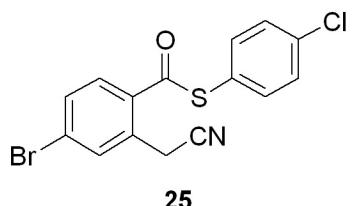
24

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

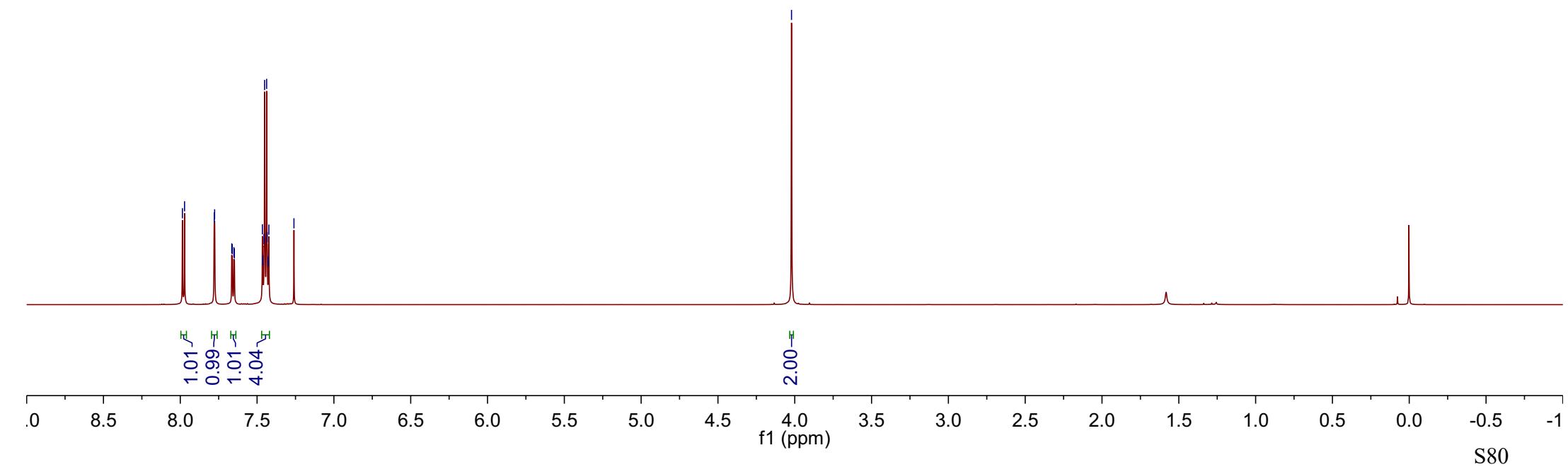


7.99
7.97
7.78
7.78
7.66
7.66
7.65
7.65
7.65
7.65
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.42
7.26

-4.02



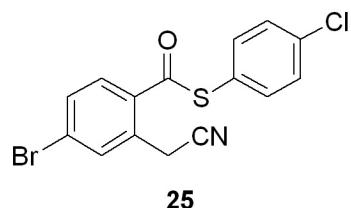
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



-191.57

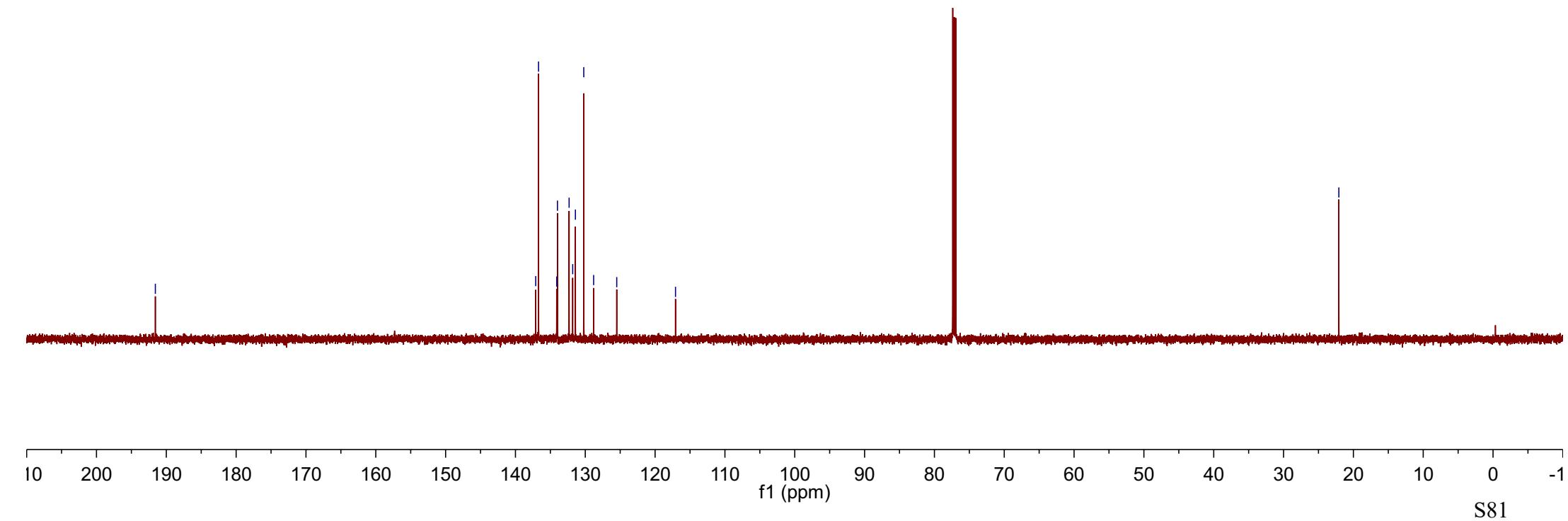
137.10
136.69
134.09
133.98
132.31
131.80
131.41
130.22
128.80
125.49
117.08

-22.08



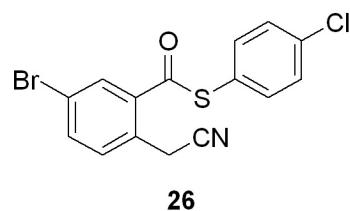
25

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

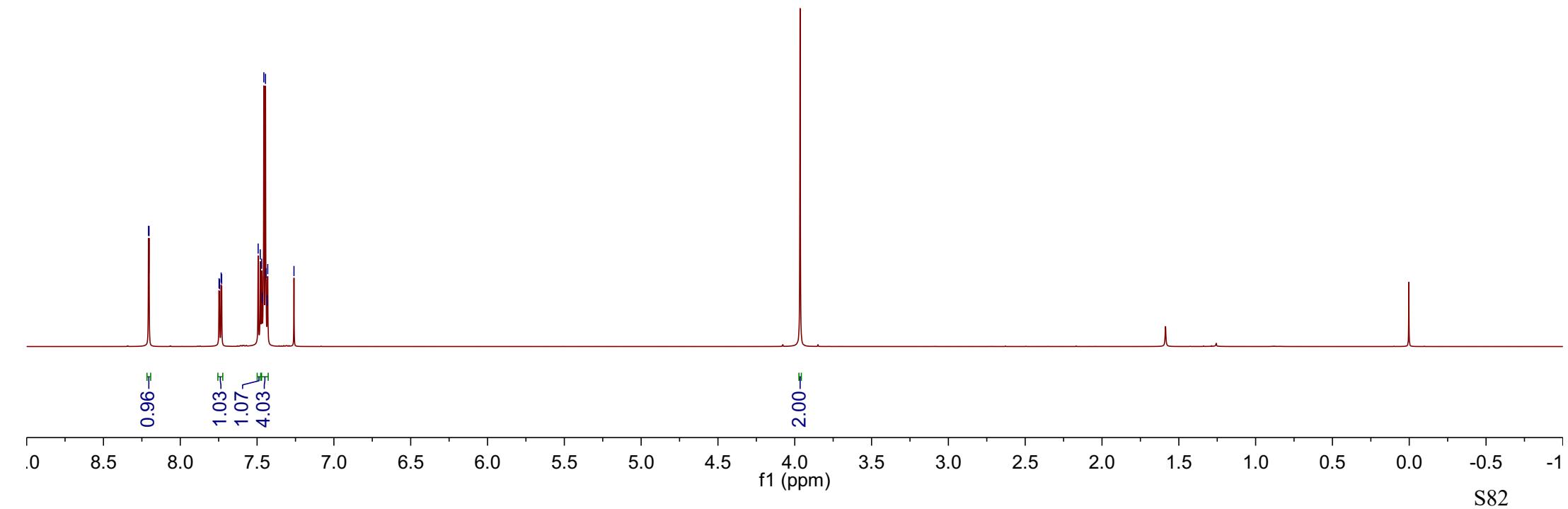


S81

8.21
8.20
7.75
7.74
7.73
7.73
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.43
7.26



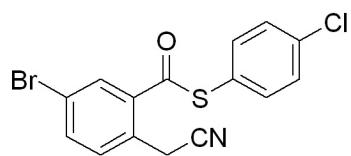
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



-191.24

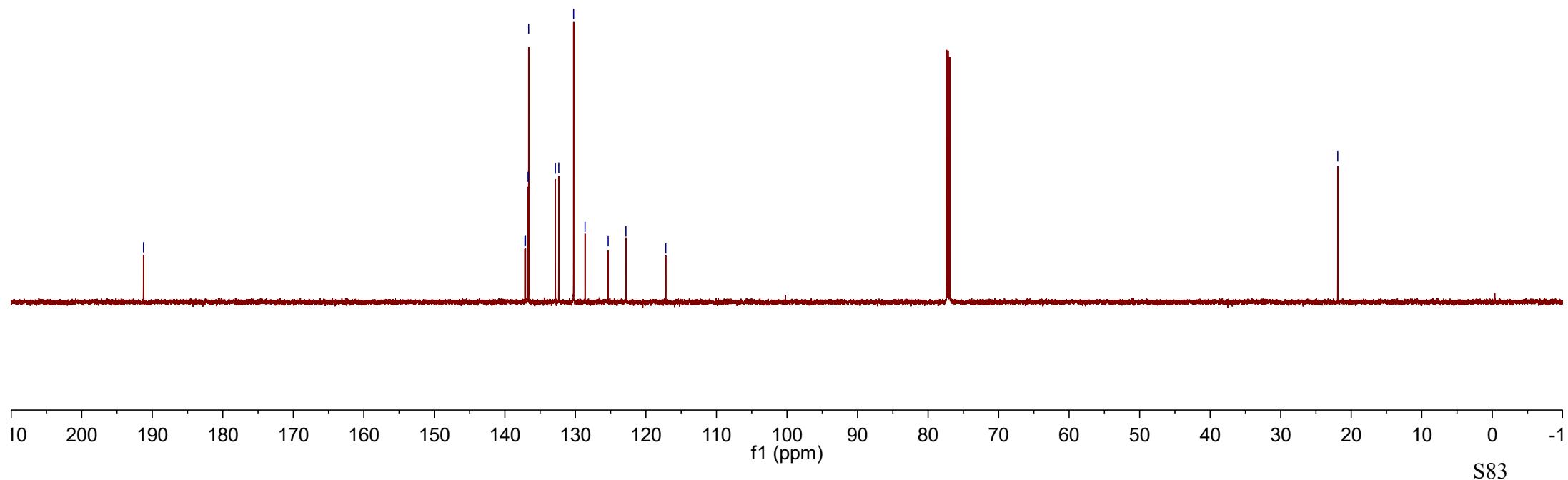
137.16
137.08
136.70
136.63
132.84
132.35
130.25
128.63
125.35
122.84
117.18

-21.91



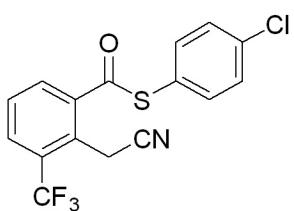
26

Parameter	Value
Solvent	CDCl_3
Spectrometer Frequency	150



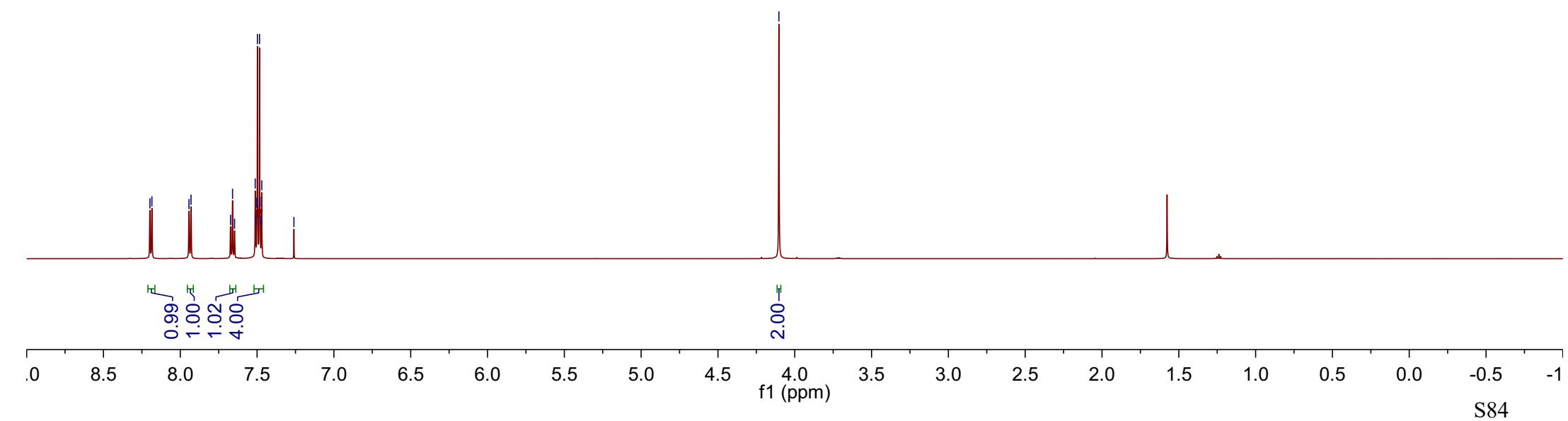
8.20
8.18
7.94
7.93
7.67
7.66
7.65
7.51
7.51
7.50
7.50
7.48
7.48
7.47
7.47
7.26

—4.10



27

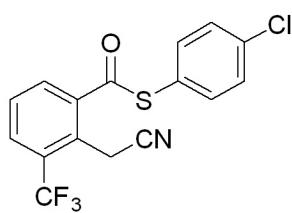
Parameter	Value
Solvent	CDCl_3
Spectrometer Frequency	600



-192.62

139.35
137.30
136.67
132.90
131.74
131.54
131.33
131.13
130.59
130.56
130.48
130.33
129.63
128.05
126.53
125.33
124.70
122.87
121.04
116.44

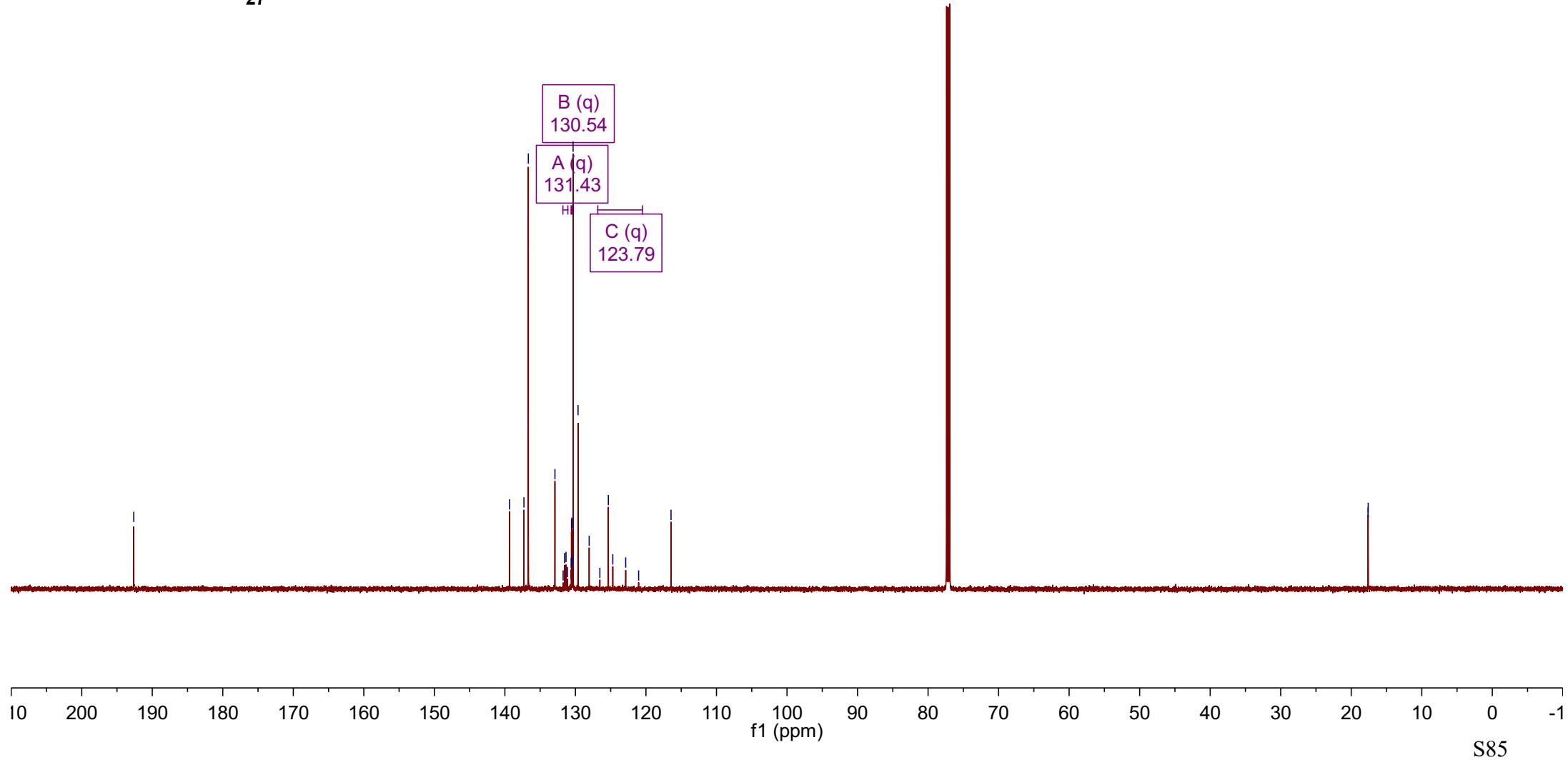
17.61
17.60



27

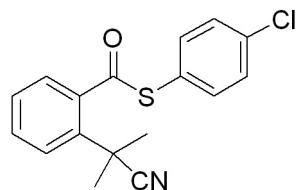
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

B (q)
130.54
A (q)
131.43
C (q)
123.79



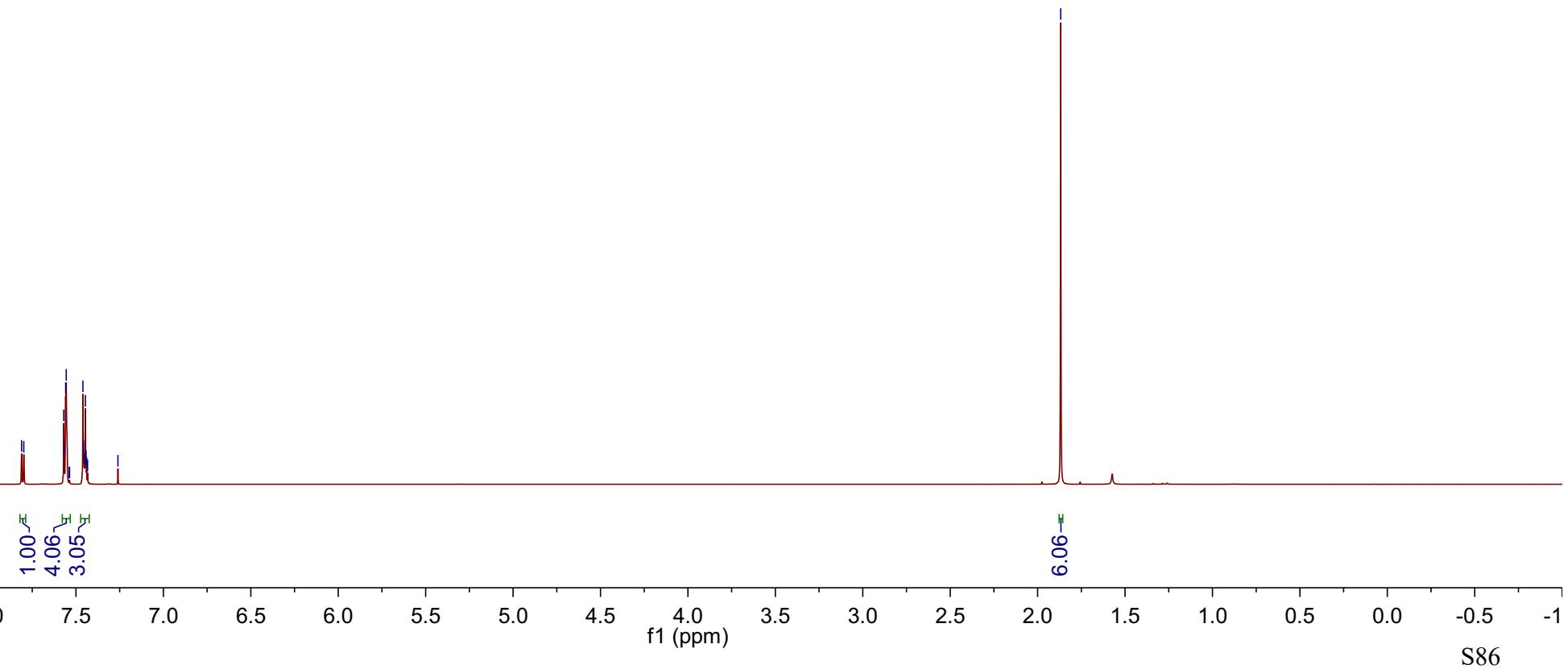
7.81
7.80
7.57
7.57
7.56
7.56
7.54
7.54
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.26

-1.87

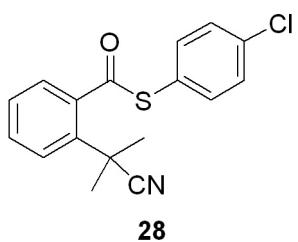


28

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



-195.10

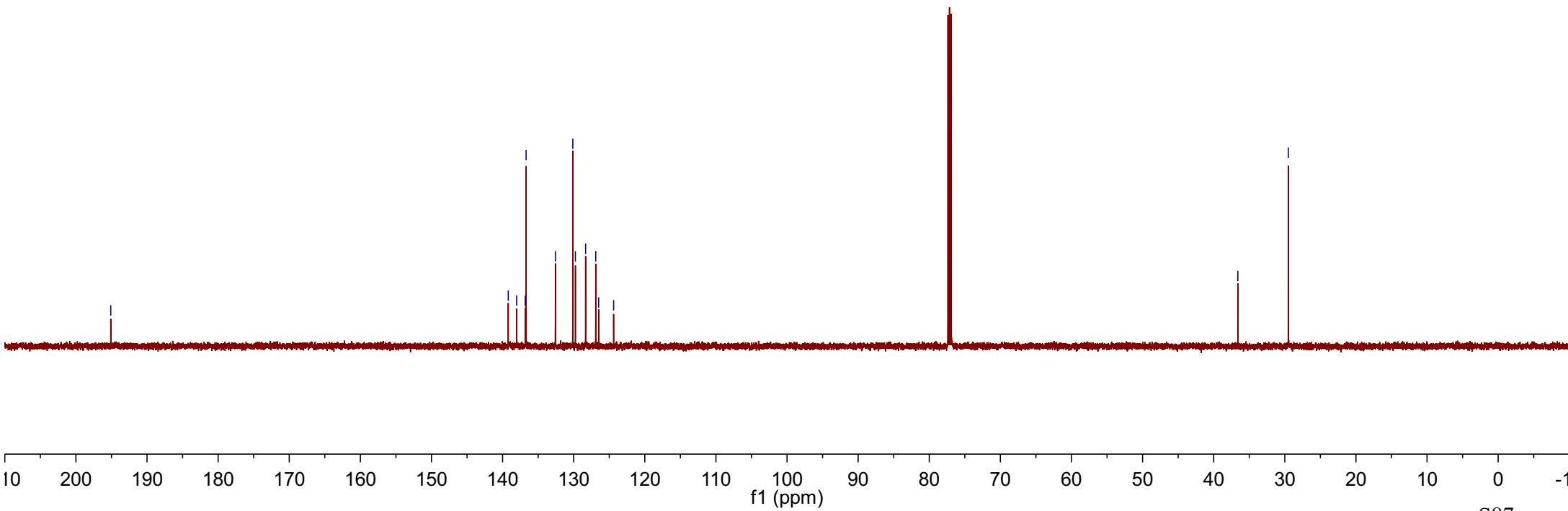


139.20
138.02
136.82
136.70
132.57
130.12
129.76
128.32
126.90
126.49
124.38

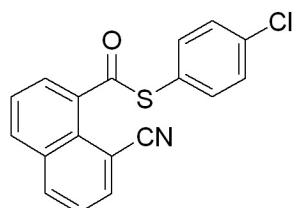
-36.61

-29.51

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

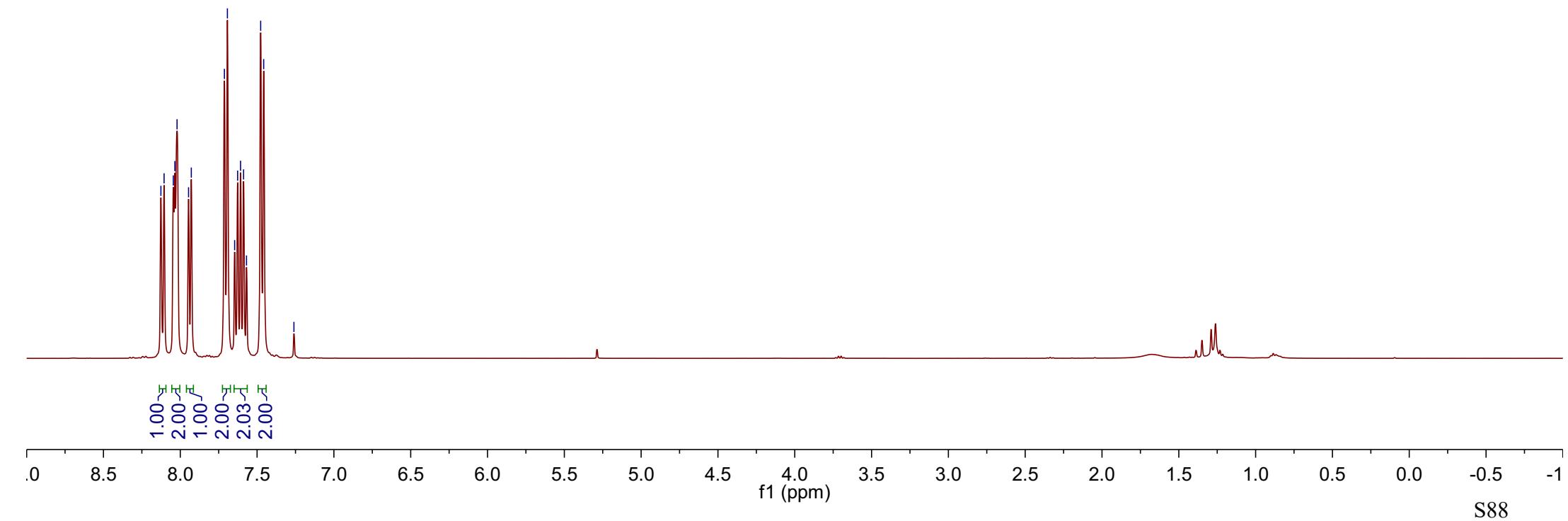


8.13
8.11
8.05
8.04
8.02
7.95
7.93
7.71
7.69
7.65
7.63
7.61
7.59
7.57
7.48
7.46
7.26



29

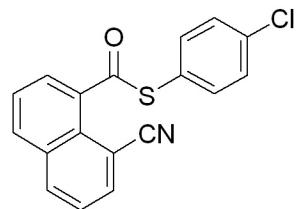
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	400



-193.16

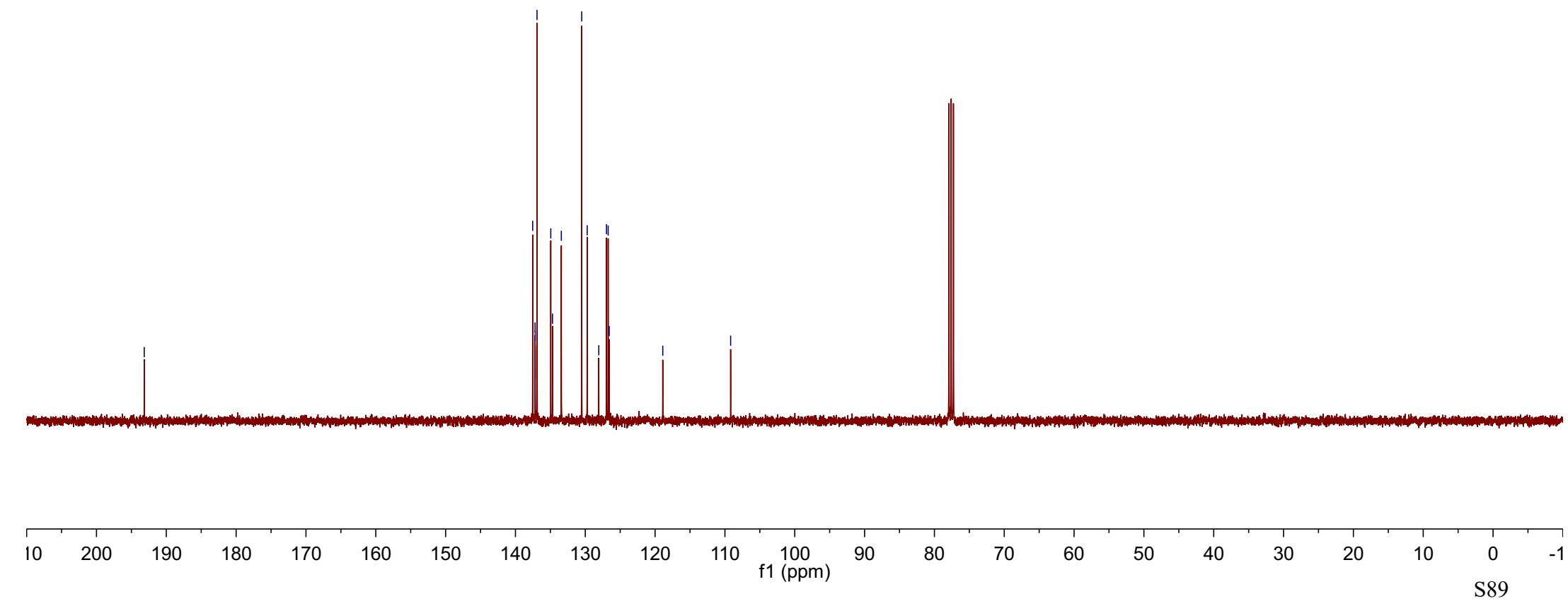
137.53
137.19
137.17
136.91
134.94
134.69
133.43
130.51
129.72
128.07
126.96
126.72
126.57
118.90

-109.18



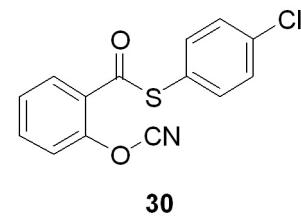
29

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	100



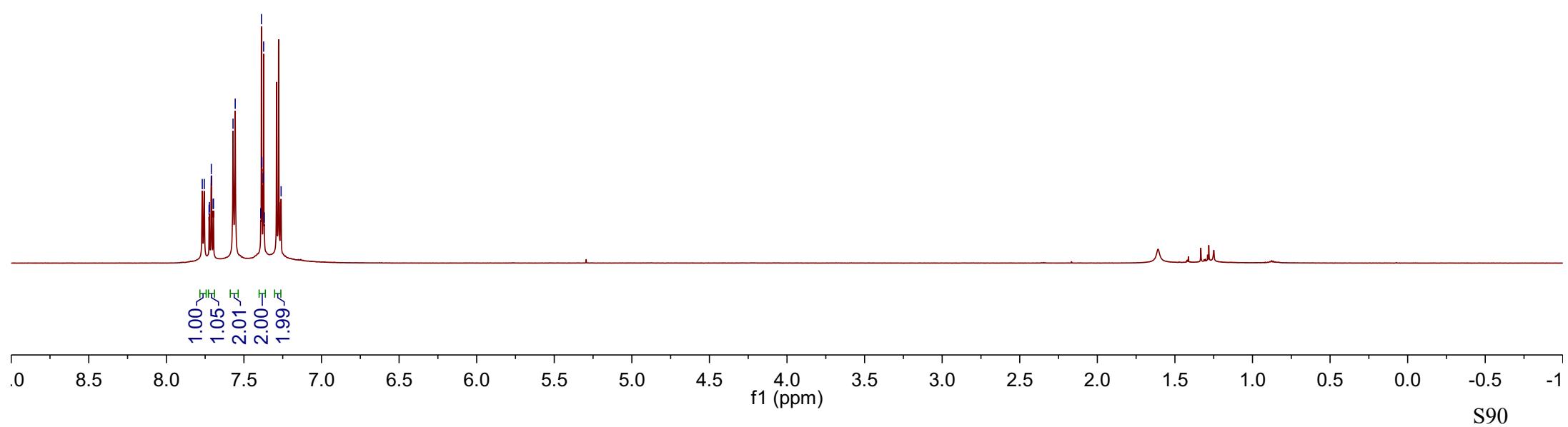
S89

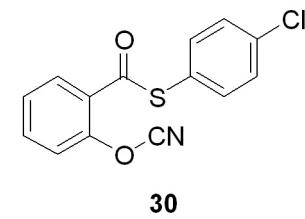
7.77
7.76
7.72
7.71
7.71
7.70
7.57
7.56
7.39
7.39
7.38
7.38
7.37
7.37
7.26



Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600

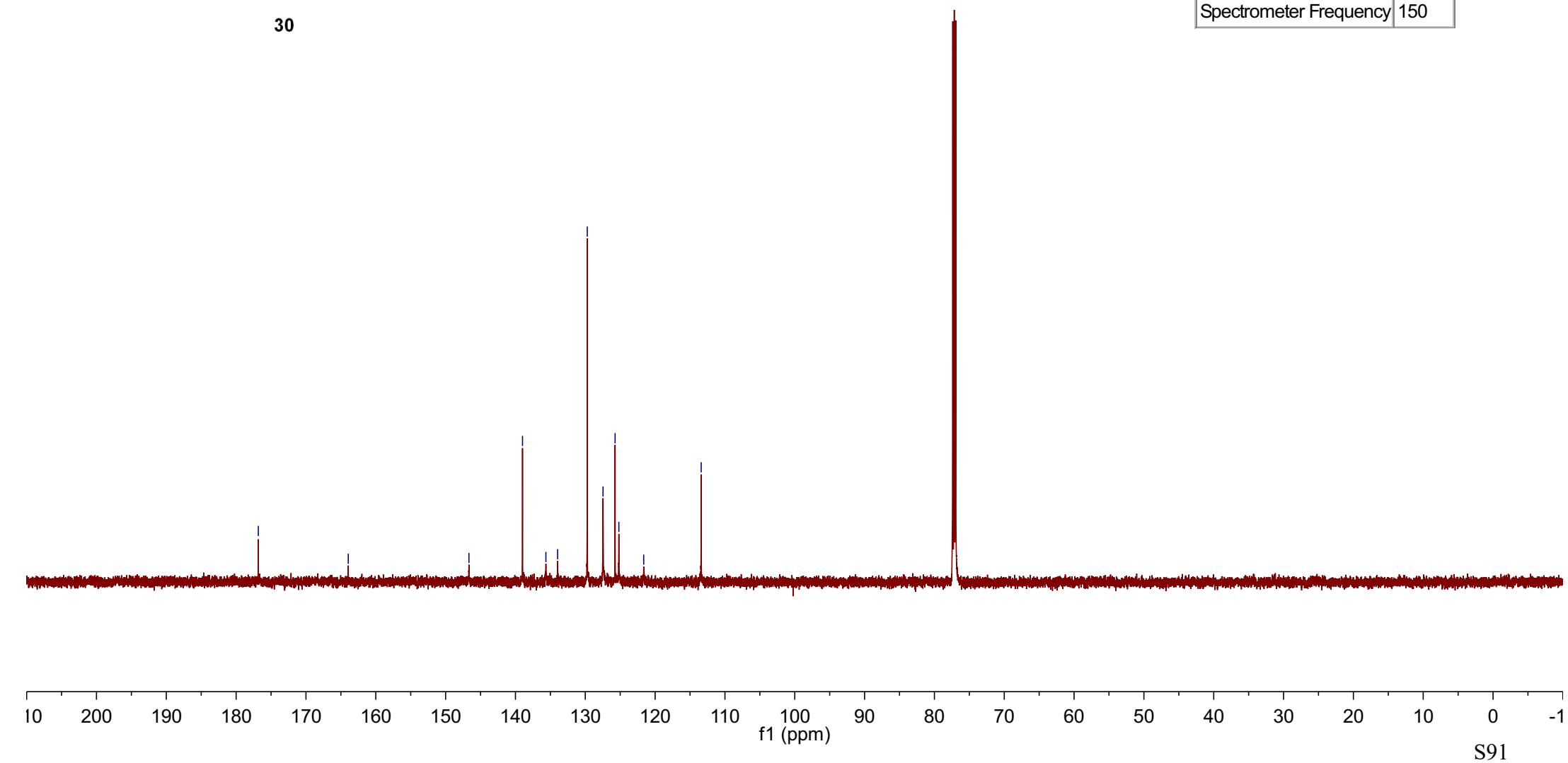
1.00
1.05
2.01
2.00
1.99





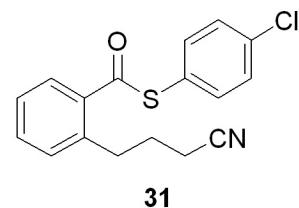
-176.82
-163.94
-146.66
138.99
135.64
133.96
129.72
127.45
125.73
125.19
121.63
-113.40

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

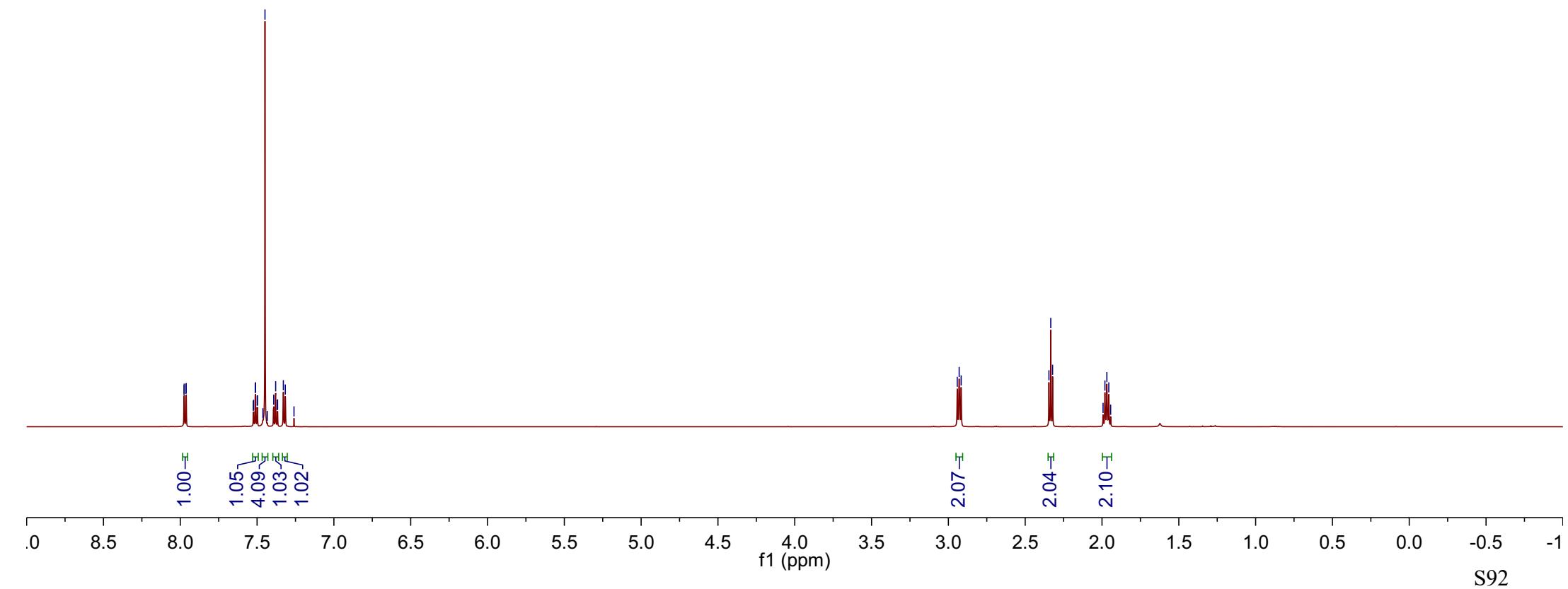


7.98
7.97
7.96
7.96
7.52
7.52
7.51
7.51
7.50
7.50
7.46
7.45
7.43
7.39
7.38
7.37
7.37
7.37
7.33
7.32
7.26

2.94
2.93
2.92
2.35
2.33
2.32
1.99
1.98
1.97
1.96
1.94
1.94



Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



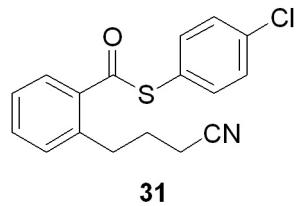
-192.64

139.79
136.83
136.59
136.56
133.03
131.71
130.04
129.58
127.30
126.74
119.88

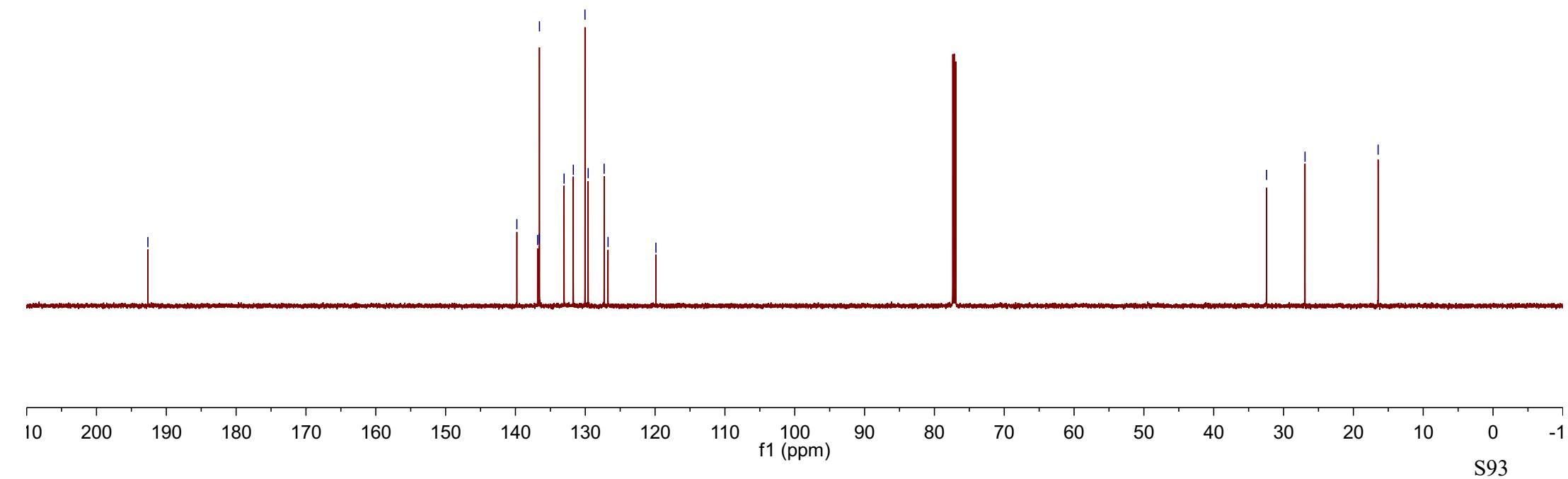
-32.44

-26.93

-16.46

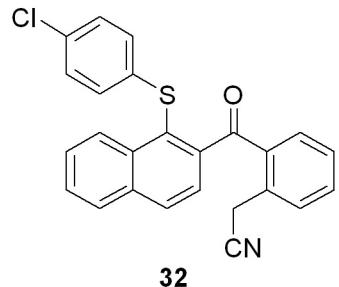


Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

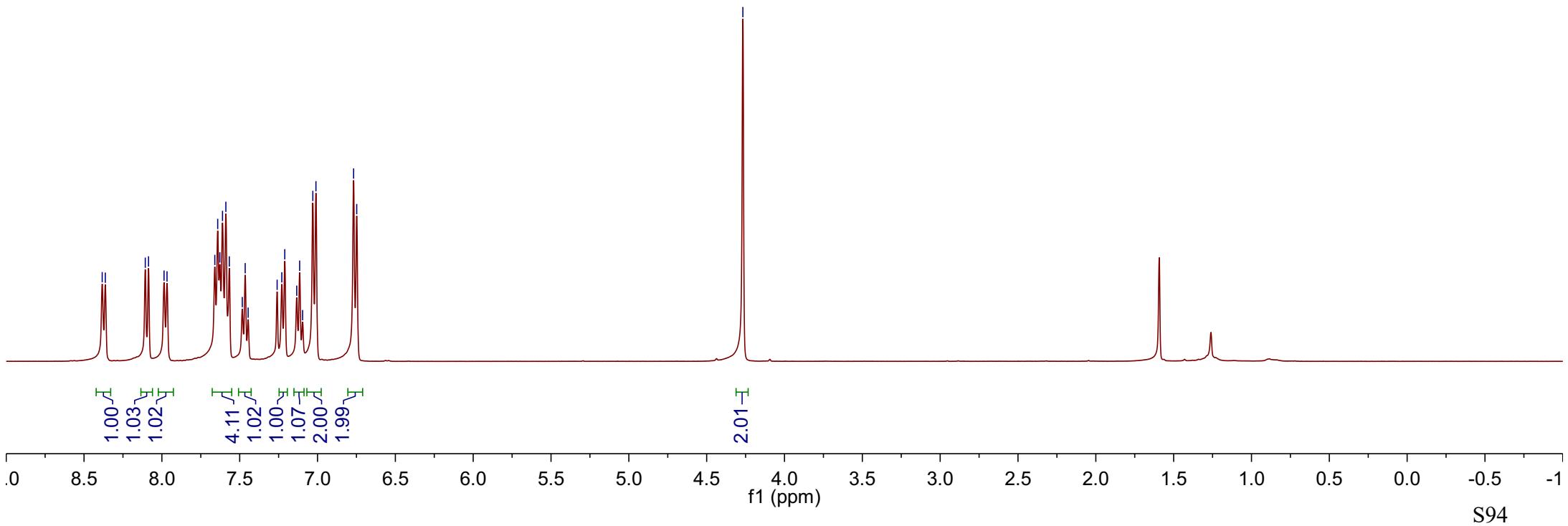


8.38
8.36
8.11
8.09
7.99
7.97
7.66
7.64
7.63
7.61
7.59
7.57
7.48
7.46
7.45
7.26
7.23
7.21
7.13
7.11
7.10
7.03
7.01
6.77
6.75

-4.27



Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	400

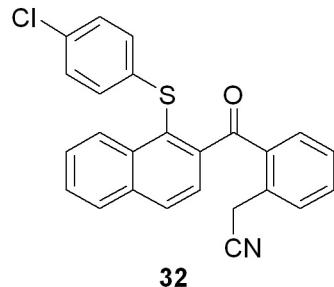


-199.92

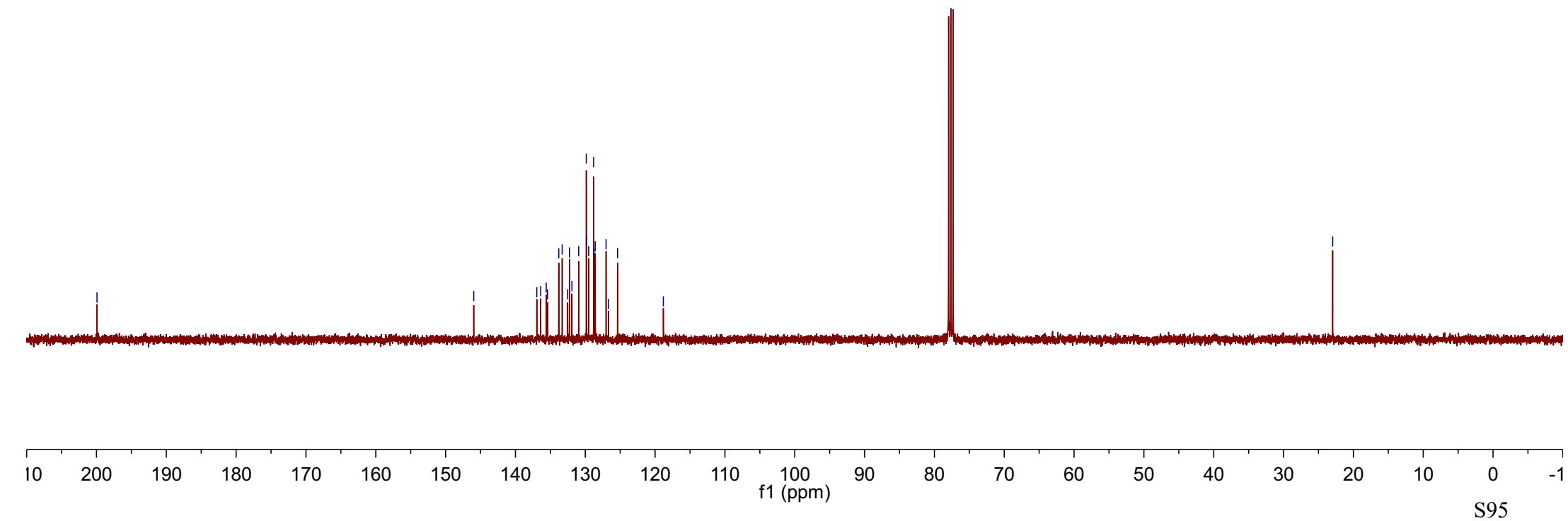
-145.97

133.30
129.85
129.81
129.51
128.80
128.57
128.82

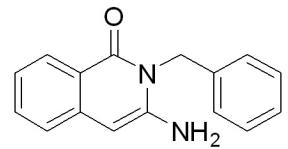
-22.97



Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	100

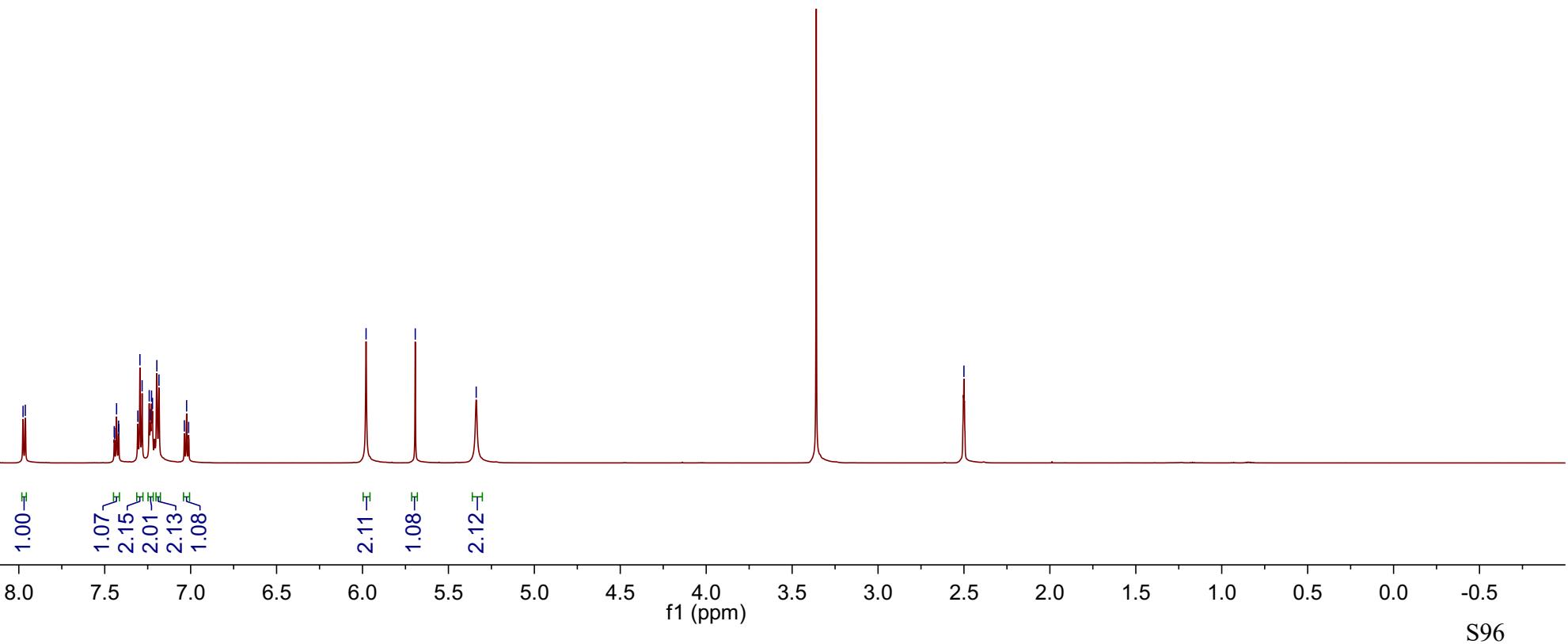


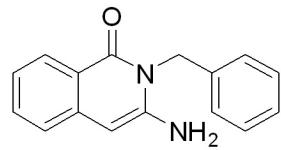
7.98
7.96
7.43
7.31
7.30
7.28
7.24
7.23
7.23
7.22
7.20
7.18
7.04
7.98
5.69
5.34
-2.50



33

Parameter	Value
Solvent	DMSO
Spectrometer Frequency	600





33

-162.69

-147.78
140.15
137.81
132.83
128.87
128.03
127.39
127.20
123.71
121.43
118.46

-82.84

-43.82

Parameter	Value
Solvent	DMSO
Spectrometer Frequency	150

10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

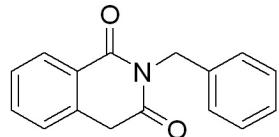
f1 (ppm)

S97

8.22
8.21
7.58
7.57
7.56
7.47
7.46
7.44
7.43
7.42
7.31
7.29
7.28
7.26
7.25
7.24
7.23

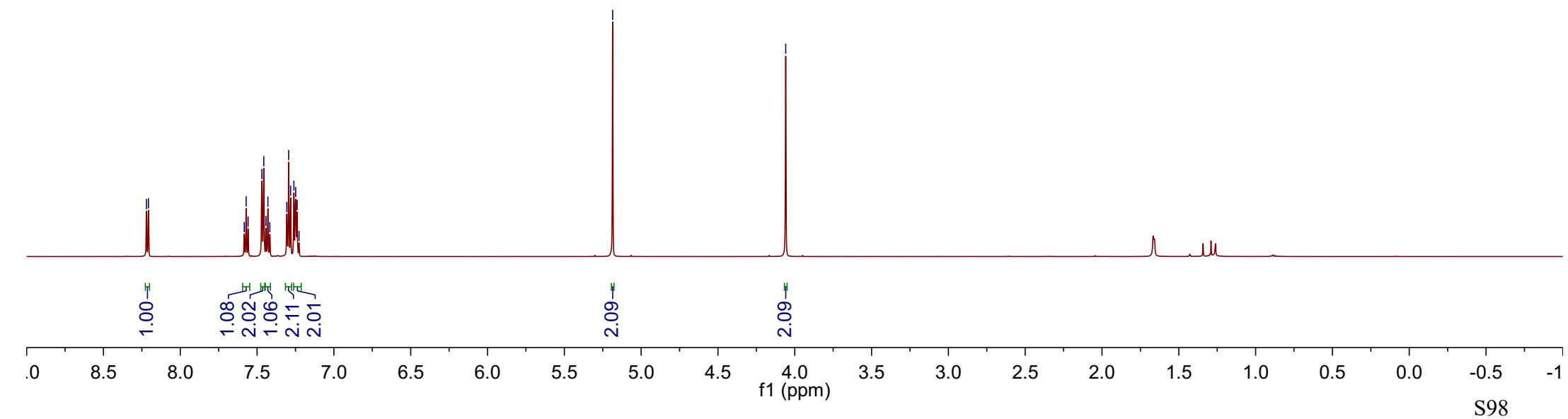
—5.19

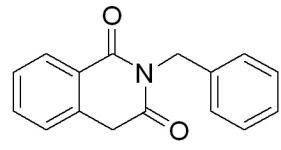
—4.06



34

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



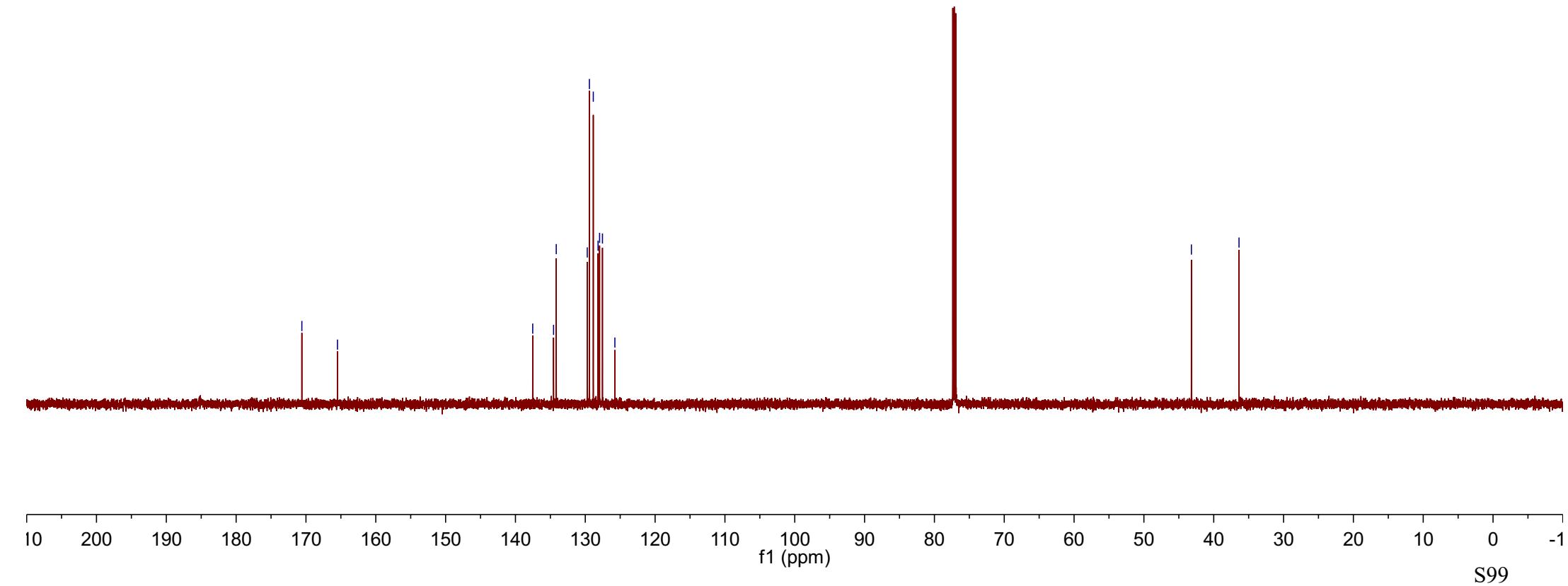


34

—170.59
—165.49

137.53
134.54
134.16
129.71
129.41
128.85
128.17
127.95
127.54
125.76

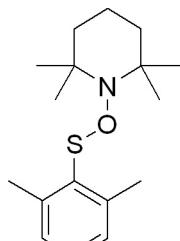
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150



7.26
7.14
7.12
7.11
6.95
6.94

-2.62

-1.70
-1.13
-1.05



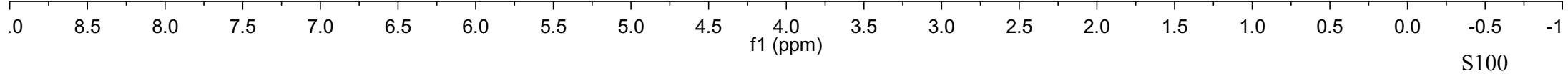
35

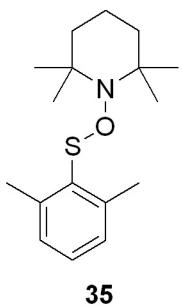
Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600

1.00
2.01

6.09

6.11
6.04
6.05

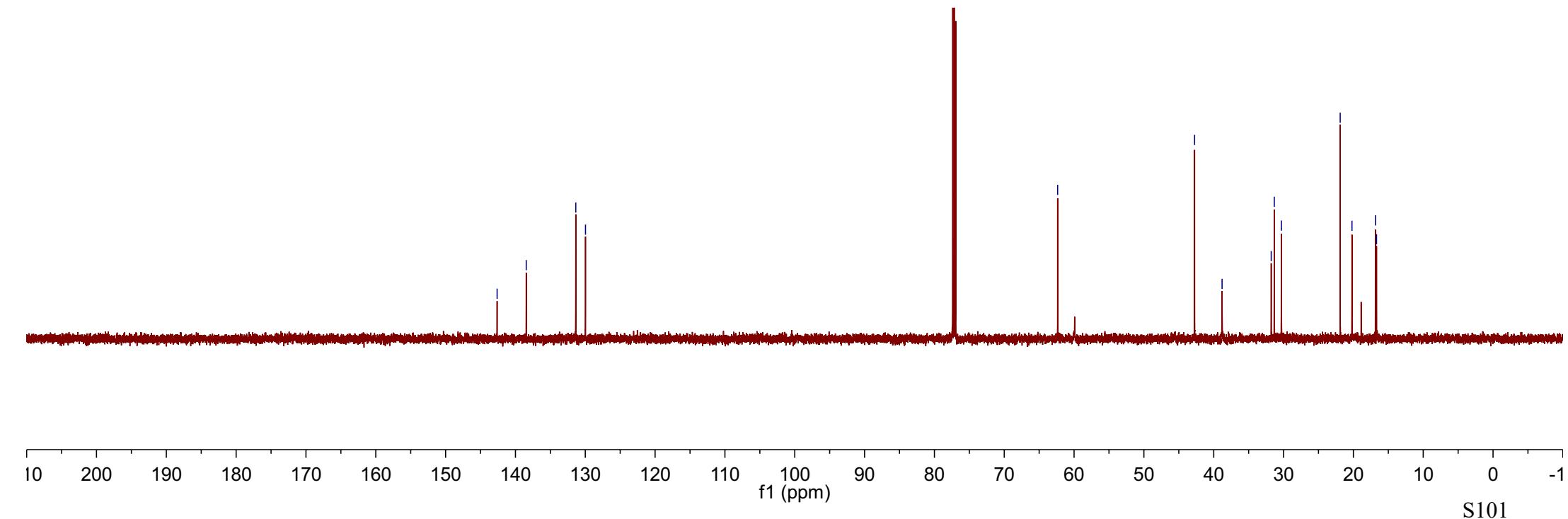


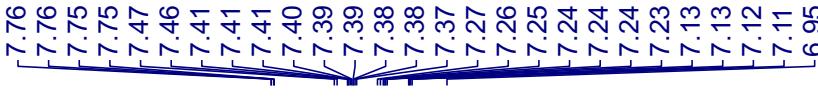


-142.63
-138.45
-131.36
-129.97

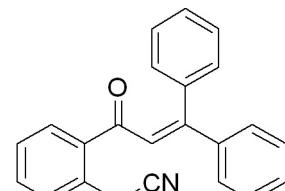
-62.35
-42.74
-38.80
-31.77
-31.33
-30.31
-21.89
-20.20
-16.84
-16.68

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150



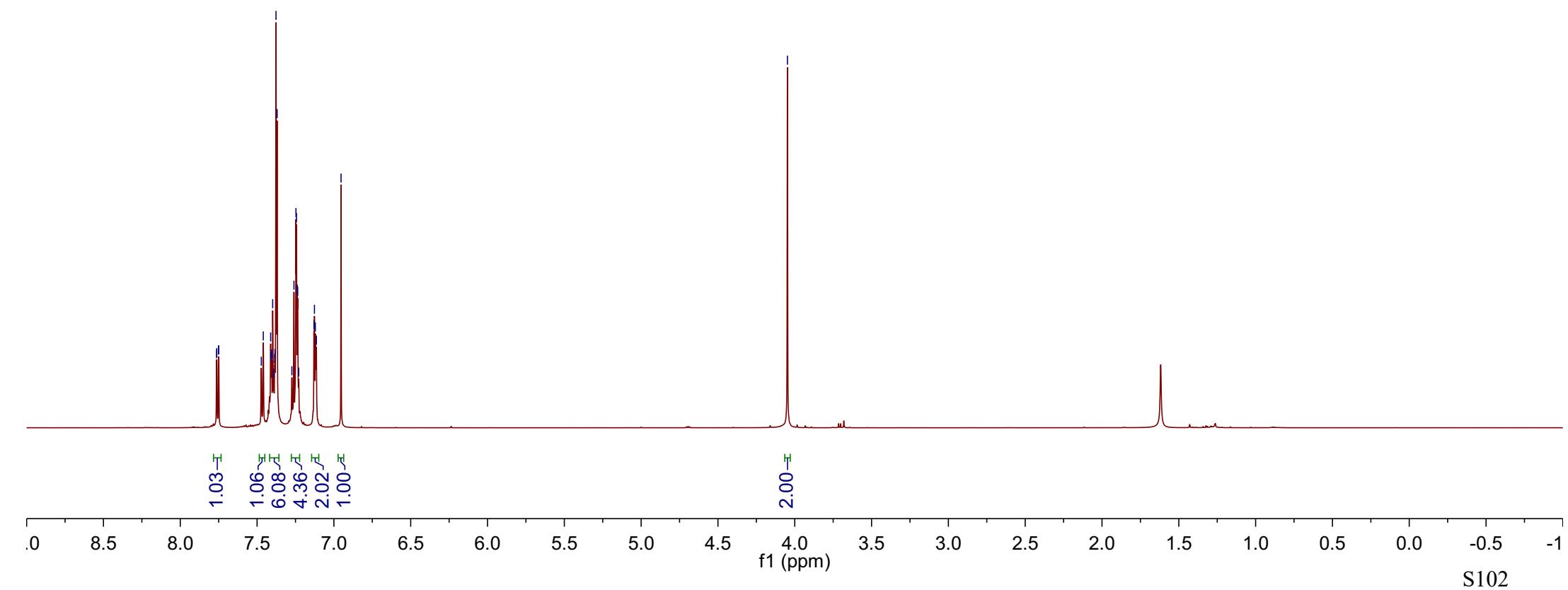


-4.05



36

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	600



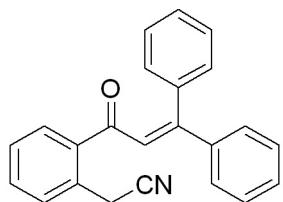
f1 (ppm)

S102

-196.26

-156.41
-156.51
-130.97
-130.22
-130.18
-130.09
-129.18
-129.04
-128.97
-128.58
-128.13
-126.37

-21.92



36

Parameter	Value
Solvent	CDCl ₃
Spectrometer Frequency	150

