Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

For

Visible Light-driven highly atom-economic divergent synthesis of substituted fluorenols and cyclopropylcarbaldehydes

Babasaheb S. Gore,[a] Lin-Wei Pan,[a+] Jun-Hao Lin,[a+] Yi-Chi Luo,[a] and Jeh-Jeng Wang*[a,b]

[a] Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, No. 100, Shiquan 1st Rd, Sanmin District, Kaohsiung City, 807, Taiwan.

[b] Department of Medical Research, Kaohsiung Medical University Hospital, No. 100, Tzyou 1st Rd, Sanmin District, Kaohsiung City, 807, Taiwan.

[+]These two authors contributed equally.

E-mail: jjwang@kmu.edu.tw

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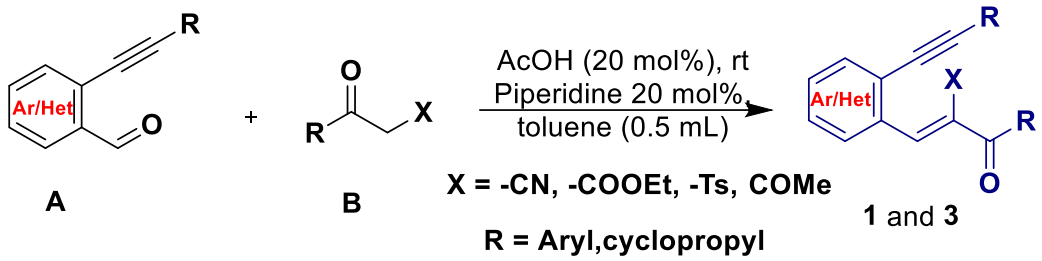
1. General Information

^{1}H, ^{13}C, and DEPT NMR spectra were recorded on a 400 MHz Varian Unity Plus or Varian Mercury plus spectrometer or JEOL ECS-400. The chemical shift (δ) values are reported in parts per million (ppm), and the coupling constants (*J*) are given in Hz. The spectra were recorded using $CDCl_3$ as a solvent. ^{1}H NMR chemical shifts are referenced to tetramethylsilane (TMS) (0 ppm) and 5.3 ppm belongs to CH_2Cl_2. ^{13}C NMR was referenced to $CDCl_3$ (77.0 ppm). The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; ddd, doublet of doublet of doublet; dt, doublet of triplets; td, triplet of doublet; m, multiplet. Mass spectra and High-Resolution Mass spectral (HRMS) data was carried out using an Agilent6890N GC (JEOL JMS-700) TOF instrument, and the ion source is electrospray ionization (ESI), electronic ionization (EI), CI, and FAB as ion source at National Taiwan Normal University, Taipei City, Taiwan and ESI-TOF(FT-MS solariX) at National Sun Yat-Sen University, Kaohsiung, Taiwan, and LTQ Orbitrap XL (Thermo Fischer Scientific) at National Chung Hsing University. Liquid-chromatography mass spectra (LCMS) were measured using the LC-MS/MS-8045 (Shimadzu Corporation, Japan) at Kaohsiung Medical University, Kaohsiung, Taiwan. Melting points were determined on an EZ-Melt (Automated melting point apparatus). Irradiation of photochemical reactions was carried out using 1 x 40 W Kessil Blue LED lamps purchased from Amazon with an output centred at a wavelength of approximately 462 nm. All products reported showed ^{1}H NMR spectra in agreement with the assigned structures. Reaction progress and product mixtures were routinely monitored by TLC using Merck TLC aluminium sheets (silica gel 60 F254). Column chromatography was carried out with 230–400 mesh silica gel 60 (Merck) and a mixture of hexane/ethyl acetate or hexane as eluent.

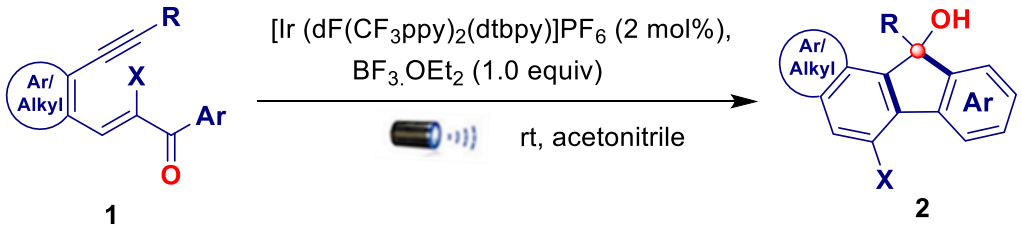
2. Experimental Procedure

a) General Procedure for the Synthesis of (*E*) (ethyl)-2-aroyl-3-(2-(arylalkynyl)aryl)acrylonitrile/carboxylate analogous (1 & 3).



A reaction tube was charged with 2-(phenylalkynyl)benzaldehyde (**A**) (1.0 equiv), 3-oxo-3-aroylacetonitriles/ester/ketone and derivatives (**B**) (1.2 equiv), acetic acid (20 mol%) and pyrrolidine (20 mol%) in 0.5 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×20 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the corresponding (*E*)-2-aroyl-3-(2-(phenylalkynyl)phenyl)aroylacetonitriles/ester/ketone derivatives **1** and **3**.

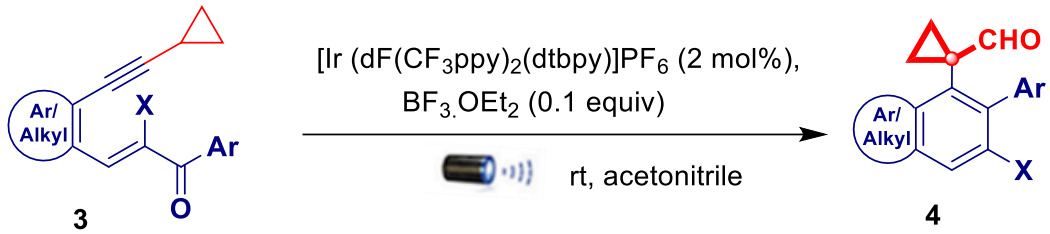
b) General procedure for the synthesis of 11-hydroxy-11-aryl-11*H*-benzo[*a*]fluorene (2) derivatives.



A clean vial (5 mL) equipped with a magnetic stir bar was added to **1** (0.2 mmol), and (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$. Next, acetonitrile (2.0 mL) was added after which, stirred at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room

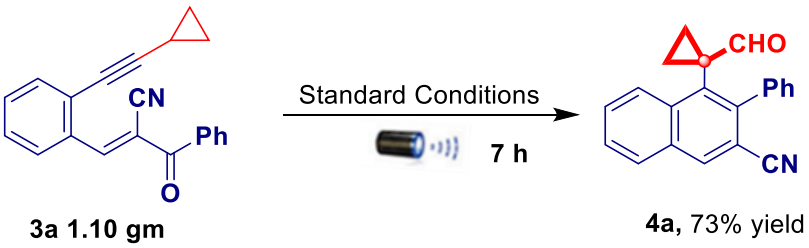
temperature under visible-light irradiation for 24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, water was added to quench the reaction mixture, followed by extraction with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography (Hex/EA = 97/3) on silica gel to afford the corresponding 11-hydroxy-11-aryl-11*H*-benzo[*a*]fluorene (**2**) derivatives.

b) General procedure for the synthesis of 4-(1-formylcyclopropyl)-3-aryl-2-naphthylene (4) derivatives.



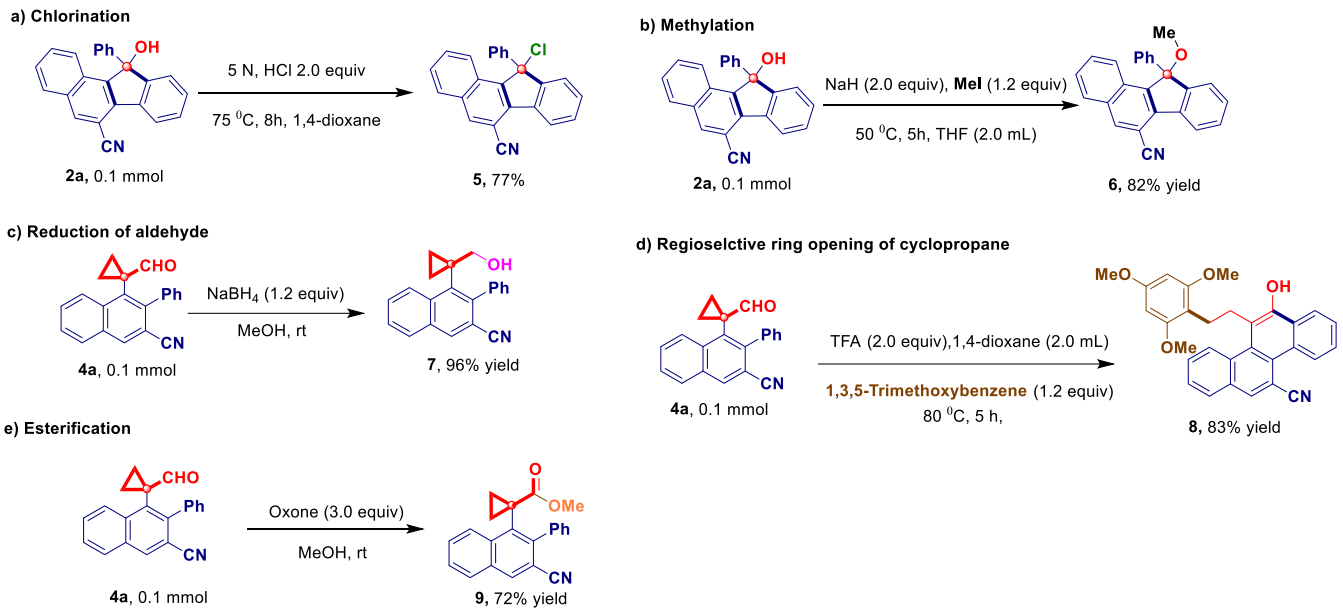
A clean vial (5 mL) equipped with a magnetic stir bar was added to **3** (0.2 mmol), and (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6. Next, acetonitrile (2.0 mL) was added after which, stirred at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 3-7 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, water was added to quench the reaction mixture, followed by extraction with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography (Hex/EA = 95/5) on silica gel to afford the corresponding 4-(1-formylcyclopropyl)-3-aryl-2-naphthylene (**4**) derivatives.

c) General procedure for gram scale synthesis



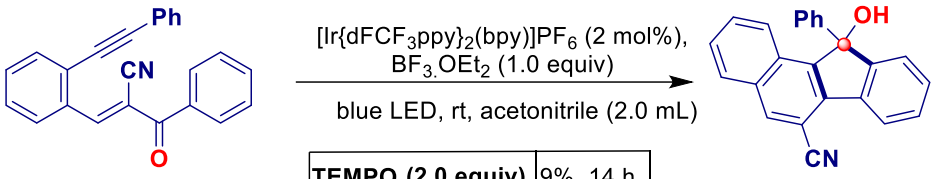
A clean vial (5 mL) equipped with a magnetic stir bar was added to **3** (3.74 mmol), and (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6. Next, acetonitrile (30.0 mL) was added after which, stirred at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 7 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, water was added to quench the reaction mixture, followed by extraction with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography (Hex/EA = 97/3) on silica gel to afford the corresponding 4-(1-formylcyclopropyl)-3-aryl-2-naphthylene (**4a**) derivatives.

3. Synthetic Applications (Scheme S1)



4. Control Studies (Scheme S2)

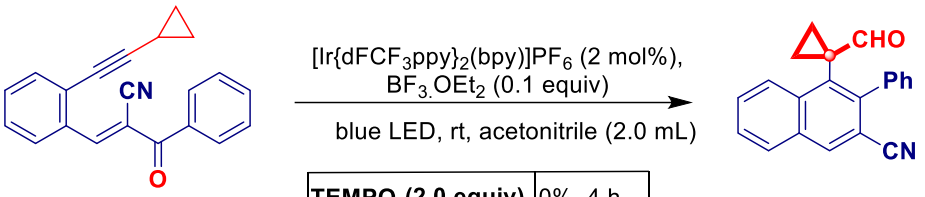
a) Radical control experiment



1a

2a

TEMPO (2.0 equiv)	9%, 14 h
BHT (2.0 equiv)	<5%, 14 h
1,4-CHD (2.0 equiv)	10%, 14 h

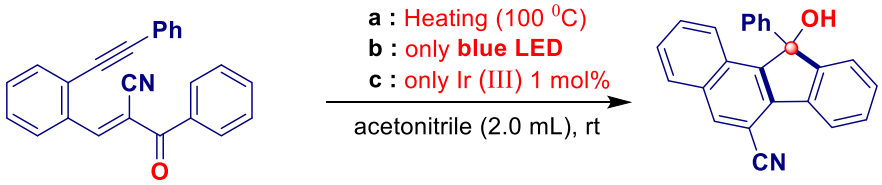


3a

4a

TEMPO (2.0 equiv)	0%, 4 h
BHT (2.0 equiv)	0%, 4 h
1,4-CHD (2.0 equiv)	<5%, 4 h

b) Control studies of temperature, light and catalyst

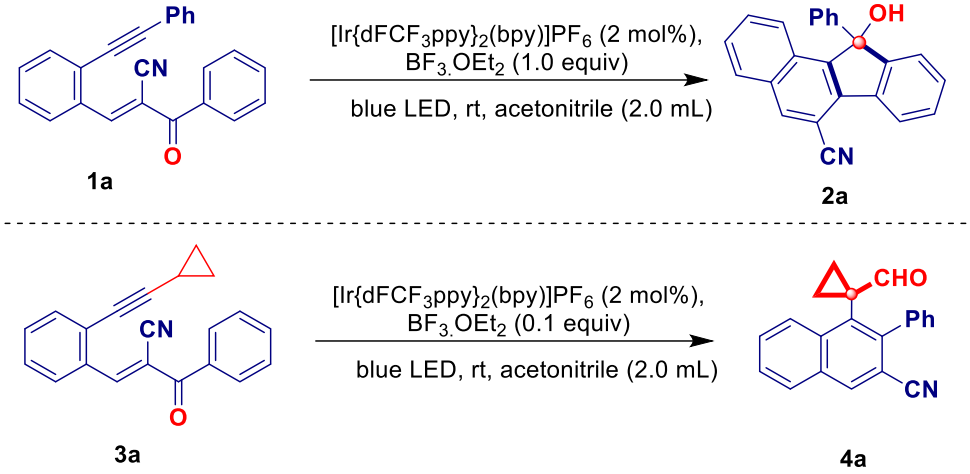


1a, 0.2 mmol

2a

a : Heating (100 ^{0}C): n.d. **b :** only blue LED: n.d. **c :** only Ir (III): n.d.

5. Light On-Off Experiment (Scheme S3)



A light on/off experiment was performed by using the model reaction of **1a** with **3a** irradiated under the standard catalytic system. The reaction proceeded over a period of time under alternating cycles of irradiation and darkness (1-16 h and 30-180 min,), and the progress was monitored by TLC analysis. As shown in Figure S1, cyclization products **2a** and **4a** was only formed under irradiation with blue LED (Scheme S3).

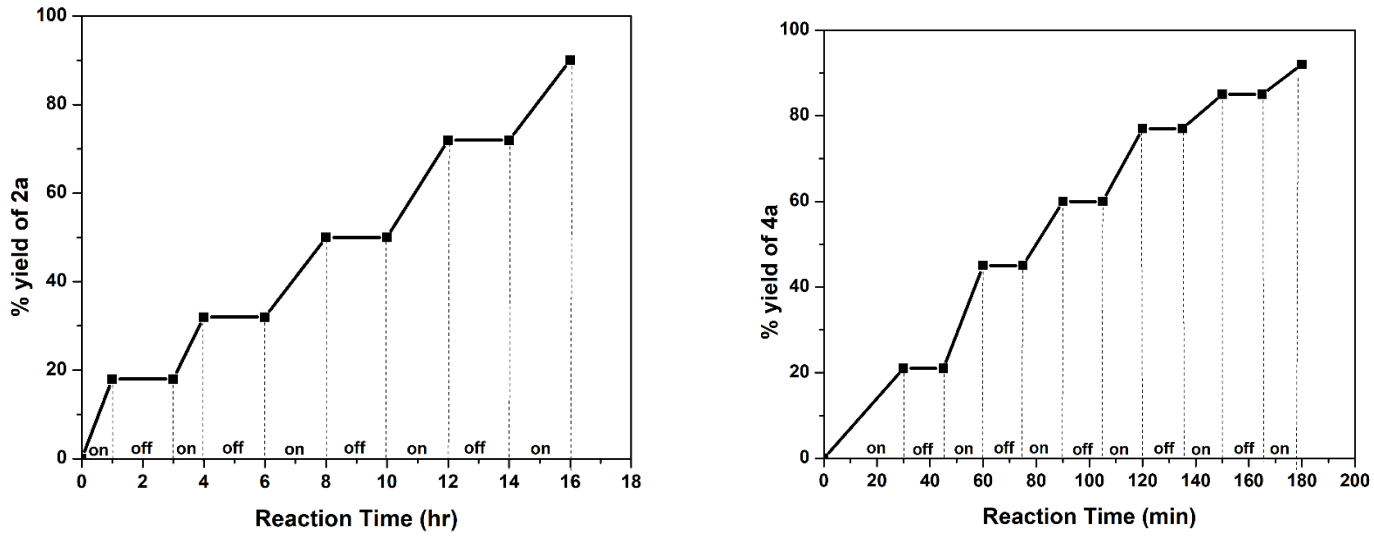
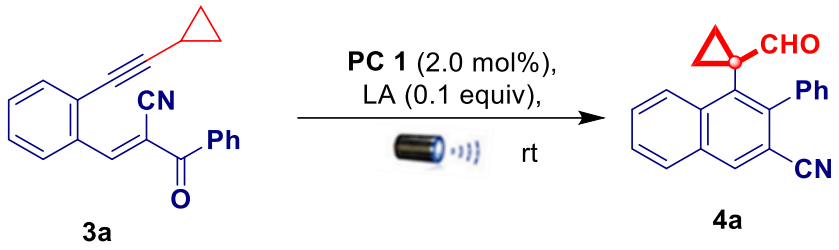


Figure S1. Visible-light Irradiation ON/OFF Experiments

6. Table S1. Optimization of Reaction Conditions[a]



Entry	Catalyst (X mol %)	Deviation from Standard Conditions (Y equiv)	Solvent	Yield (%)[b]
1	None	none	acetonitrile	90
2	**PC 1** (2)	$BF_3.OEt_2$ (1.0)	acetonitrile	21
3	**PC 1** (2)	$BF_3.OEt_2$ (0.5)	acetonitrile	50
4	**PC 1** (2)	$BF_3.OEt_2$ (0.2)	acetonitrile	82
5	**PC 2** instead of **PC 1**	$BF_3.OEt_2$ (0.1)	acetonitrile	41
6	**PC 3** instead of **PC 1**	$BF_3.OEt_2$ (0.1)	acetonitrile	50
7	**PC 1** (2)	-	acetonitrile	0
8	-	$BF_3.OEt_2$ (0.1)	acetonitrile	0

[a] Reaction conditions: **3a** (0.2 mmol), **PC 1** = $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$ = Ir (III), acetonitrile (2.0 mL), 3 h stirred under blue LED at room temperature. [b] Isolated yields by silica gel column. **PC 2** = $[Ru(bpy)_3](PF_6)_2$, **PC 3** = TBADT.

7. Evaluation of Green Metrics of the Process.

Atom economy defined as “how much of the reactants remain in the final desired product"

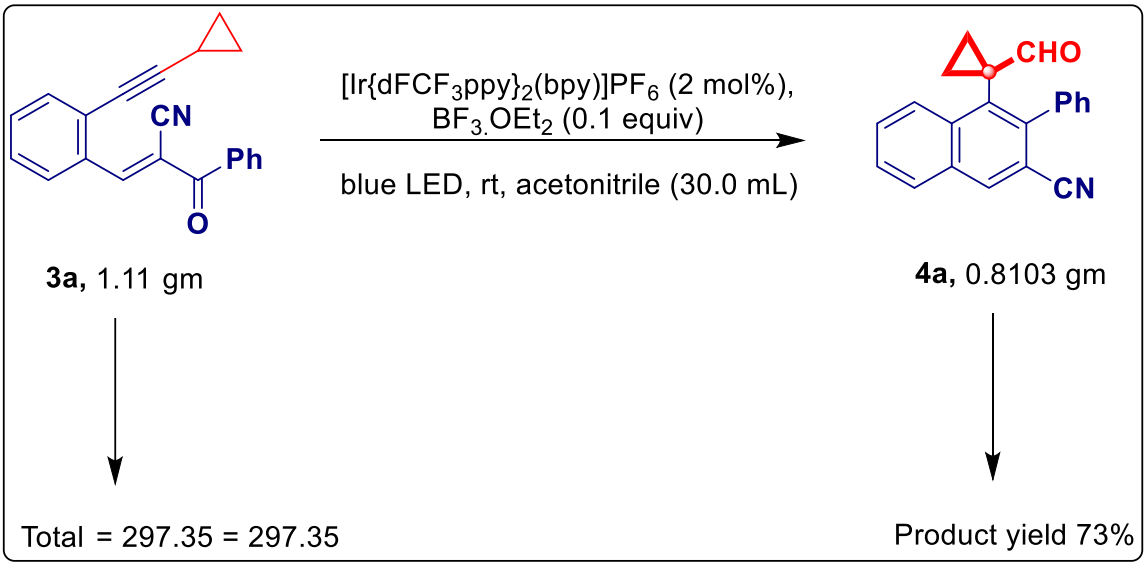
$$\text{Atom economy (AE)} = \frac{\text{Molecular mass of desired product}}{\text{Molecular mass of all reactants}} \times 100$$

Reaction mass efficiency (RME) defined as “the percentage of the mass of the reactants that remain in the product”

$$\text{Reaction mass efficiency (RME)} = \frac{\text{mass of desired product}}{\text{mass of all reactants}} \times 100$$

Evaluation of Green metrics for the current process

Reaction Scheme



Reactant 1	(E)-2-benzoyl-3-(2-(cyclopropylethynyl)phenyl)acrylonitrile (**3a**)	1.11 gm	0.003733 mol	FW 297.35
Auxiliary	Ir(III)	0.0431 gm	0.00003736 mol	1155
Product	4-(1-formylcyclopropyl)-3-phenyl-2-naphthonitrile (**4a**)	0.8103 gm	0.002725 mol	FW 297.35

$$\text{E-factor} = \frac{1.11\ \text{gm} + 0.0431\ \text{gm} - 0.8103\ \text{gm}}{0.8103} = 0.42305\ \text{kg waste / 1 kg product}$$

$$\text{Atom economy} = \frac{297.35}{297.35} \times 100 = 100\%$$

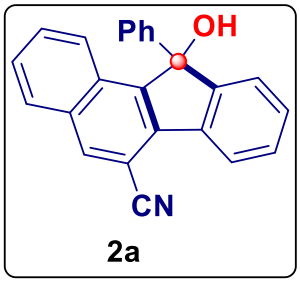
$$\text{Atom efficiency} = \frac{73 \times 100}{100} = 73\%$$

$$\text{Carbon efficiency} = \frac{21}{21} = 100\%$$

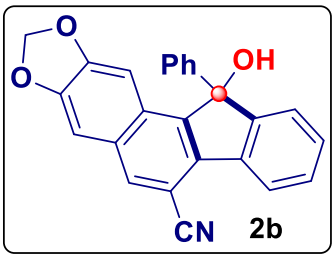
$$\text{Reaction mass efficiency} = \frac{0.8103\ \text{gm}}{1.11\ \text{gm}} \times 100 = 73\%$$

8. Spectral Characterization

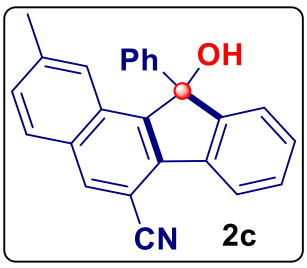
11-hydroxy-11-phenyl-11H-benzo[*a*]fluorene-6-carbonitrile (2a): White solid, (53.95 mg, 81%), m.p. 247-249 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.7 Hz, 1H), 8.31 (s, 1H), 7.96 – 7.86 (m, 2H), 7.49 (ddd, *J* = 6.7, 5.1, 3.4 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.39 – 7.34 (m, 3H), 7.33 – 7.19 (m, 5H), 2.58 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.96, 146.26, 141.76, 137.10, 136.75, 132.66, 130.79, 129.70, 129.52, 129.34, 129.18, 128.56, 127.44, 127.13, 125.17, 124.85, 124.25, 122.01, 118.31, 102.94, 83.67; HRMS (ESI) m/z:[M-H]$^-$ Calcd for: $C_{24}H_{14}NO$ 332.1075;found 332.1078.



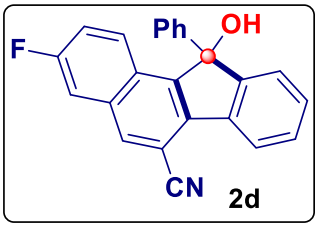
11-hydroxy-11-phenyl-11*H*-indeno[2',1':5,6]naphtho[2,3-*d*][1,3]dioxole-6-carbonitrile (2b): White solid (50.52 mg, 67%), m.p. 260-262 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS)：δ 8.33 (dt, *J* = 7.7, 0.9 Hz, 1H), 8.05 (s, 1H), 7.41 (ddd, *J* = 7.7, 7.2, 1.5 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.33 – 7.29 (m, 1H), 7.29 – 7.18 (m, 6H), 6.01 (dd, *J* = 16.1, 1.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$, TMS)： δ 151.61, 150.39, 148.62, 145.18, 141.66, 136.82, 135.43, 134.83, 130.26, 129.48, 129.11, 129.07, 128.59, 128.42, 127.42, 124.85, 124.15, 121.85, 118.58, 104.69, 101.71, 101.48, 100.97, 83.66; HRMS (ESI) m/z: $[M+H]^+$ $C_{25}H_{16}NO_3$ Calcd for: 378.1130; found 378.1127.



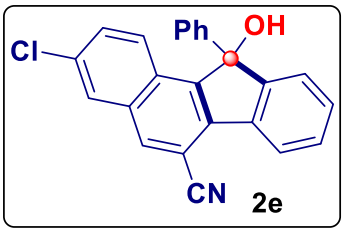
11-hydroxy-2-methyl-11-phenyl-11*H*-benzo[*a*]fluorene-6-carbonitrile (2c): White solid, (52.05 mg, 75%) mp 262-264 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS)：δ 8.34 (d, *J* = 7.7 Hz, 1H), 8.23 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.66 (s, 1H), 7.47 – 7.15 (m, 9H), 2.60 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS)：δ 152.01, 145.32, 141.78, 140.18, 136.79, 136.24, 131.01, 130.97, 129.52, 129.42, 129.20, 128.97, 128.51, 127.35, 124.82, 124.16, 123.97, 121.93, 118.53, 101.83, 83.66, 22.29; HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{25}H_{18}NO$ 348.1388; found 348.1385.



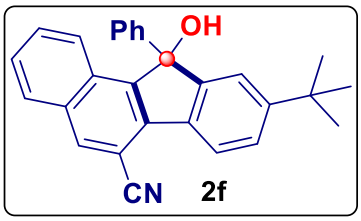
3-fluoro-11-hydroxy-11-phenyl-11H-benzo[*a*]fluorene-6-carbonitrile (2d): White solid, (48.43mg, 69%) mp 256-258 °C. ^{1}H NMR (597 MHz, $CDCl_3$) δ 8.38 – 8.29 (m, 2H), 7.94 – 7.87 (m, 2H), 7.53 – 7.46 (m, 2H), 7.40 – 7.33 (m, 2H), 7.31 – 7.26 (m, 2H), 7.26 – 7.23 (m, 1H), 7.15 – 7.10 (m, 1H), 7.06 (dd, *J* = 8.0, 2.5 Hz, 1H), 2.56 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, TMS) δ 164.48, 162.81 (d, J_{C-F} = 250.5 Hz), 141.12, 137.18, 135.54, 132.43, 130.78, 129.86, 129.23, 128.72 (d, J_{C-F} = 94.5 Hz), 127.74, 127.18, 124.98, 124.78, 123.43, 123.37 (d, J_{C-F} = 9.0 Hz), 118.19, 116.50, 116.35 (d, J_{C-F} = 22.5 Hz), 112.28, 112.12 (d, J_{C-F} = 24.0 Hz), 102.70; HRMS (ESI) m/z: [M-H]$^-$ $C_{24}H_{13}FNO$ Calcd for: 350.0981 found 350.0987.



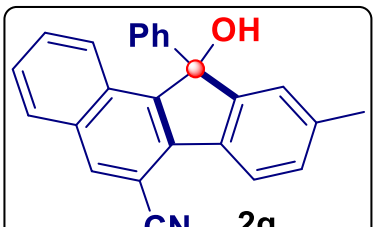
3-chloro-11-hydroxy-11-phenyl-11H-benzo[a]fluorene-6-carbonitrile (2e): White solid (49.51mg, 68%) mp 259-260 °C ^{1}H NMR (597 MHz, $CDCl_3$) δ 8.39 (dt, *J* = 7.7, 0.8 Hz, 1H), 8.23 (s, 1H), 7.89 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.47 – 7.44 (m, 1H), 7.41 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.38 – 7.33 (m, 3H), 7.28 – 7.26 (m, 3H), 7.26 – 7.21 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.80, 146.63, 141.47, 136.52, 136.47, 135.88, 133.30, 133.28, 130.60, 129.70, 129.62, 129.05, 128.66, 127.67, 127.62, 126.81, 124.80, 124.31, 122.13, 117.87, 104.24, 83.78; HRMS (ESI) m/z: $[M+H]^+$ $C_{24}H_{15}ClNO$ Calcd for: 368.0842; found 368.0839.



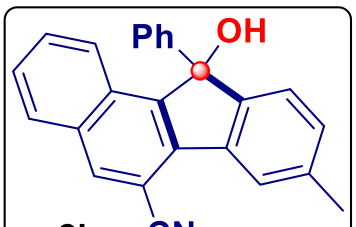
9-(tert-butyl)-11-hydroxy-11-phenyl-11*H*-benzo[*a*]fluorene-6-carbonitrile (2f): White solid (65.35mg, 84%) mp 268-269 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.24 (m, 2H), 7.95 – 7.85 (m, 2H), 7.50 – 7.43 (m, 3H), 7.38 (tt, *J* = 5.0, 2.1 Hz, 3H), 7.29 – 7.20 (m, 4H), 2.54 (s, 1H), 1.29 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.11, 152.00, 146.28, 141.96, 136.90, 136.35, 134.16, 132.44, 130.82, 129.57, 129.17, 128.49, 127.30, 126.86, 126.63, 125.04, 124.92, 121.54, 121.08, 118.35, 102.78, 83.79, 35.11, 31.30; HRMS (ESI) m/z: $[M+H]^+$ $C_{28}H_{24}NO$ Calcd for :390.1858; found 390.1856.



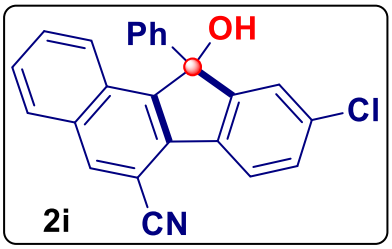
11-hydroxy-9-methyl-11-phenyl-11*H*-benzo[*a*]fluorene-6-carbonitrile (2g): White solid (55.52mg, 80%) mp 227-227 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 11.3, 3.6 Hz, 2H), 8.13 – 8.06 (m, 1H), 7.90 – 7.82 (m, 1H), 7.49 – 7.35 (m, 5H), 7.26 – 7.17 (m, 3H), 7.07 (d, *J* = 7.6 Hz, 1H), 2.45 (s, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 148.98, 146.95, 140.28, 137.43, 137.16, 135.68, 135.55, 132.59, 131.63, 130.46, 129.78, 129.61, 129.14, 128.53, 128.13, 126.93, 125.63, 124.61, 119.42, 118.46, 102.85, 84.65, 17.51; HRMS (ESI) m/z: $[M-H]^-$ $C_{25}H_{16}NO$ Calcd for: 346.1232; found 346.1241.



11-hydroxy-8-methyl-11-phenyl-11*H*-benzo[*a*]fluorene-6-carbonitrile (2h): White solid (53.43mg, 77%) mp 248-250 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.6 Hz, 1H), 8.27 (s, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.67 (s, 1H), 7.43 (dd, *J* = 11.2, 3.8 Hz, 1H), 7.40 – 7.31 (m, 4H), 7.29 – 7.22 (m, 4H), 2.53 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.08, 145.29, 141.79, 140.19, 136.82, 136.26, 131.03, 129.54, 129.47, 129.24, 128.98, 128.53, 127.37, 124.85, 124.19, 124.03, 121.98, 118.52, 102.02, 83.59, 22.30; HRMS (ESI) m/z: $[M+H]^+$ $C_{25}H_{16}NO$ Calcd. for: 346.1232 found 346.1230.

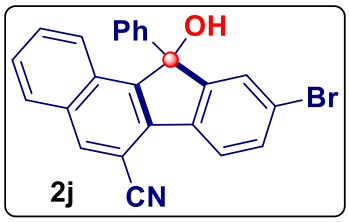


9-chloro-11-hydroxy-11-phenyl-11*H*-benzo[*a*]fluorene-6-carbonitrile (2i): White solid (55.05mg, 75%) mp 296-298 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 – 8.30 (m, 1H), 8.00 (ddd, *J* = 58.1, 9.4, 2.9 Hz, 2H), 7.67 (ddt, *J* = 16.8, 13.5, 7.5 Hz, 1H), 7.56 – 7.38 (m, 5H), 7.32 – 7.16 (m, 5H), 3.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.22, 146.59, 140.02, 139.58, 137.38, 136.32, 134.24, 133.96, 132.88, 131.77, 131.20, 130.75, 130.49, 130.40, 129.99, 129.91, 129.51,



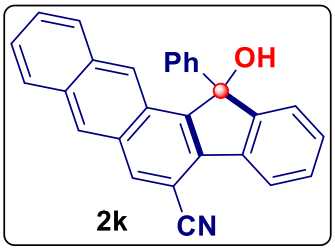
129.36, 129.15, 128.90, 128.70, 128.60, 128.26, 128.18, 127.46, 127.35, 125.91, 125.62, 124.93, 120.45, 118.16, 102.83, 85.04; HRMS (ESI) m/z: $[M+H]^+$ $C_{24}H_{15}ClNO$ Calcd for : 368.0842; found 368.0837.

9-bromo-11-hydroxy-11-phenyl-11*H*-benzo[*a*]fluorene-6-carbonitrile (2j): White solid (58.36mg, 71%)



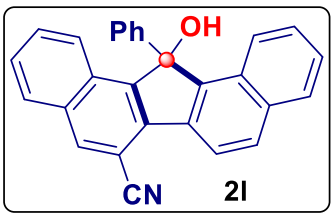
mp 213-21 5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.40 (m, 1H), 8.29 (s, 1H), 8.20 – 8.12 (m, 1H), 7.87 (dd, *J* = 7.0, 2.5 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.45 – 7.29 (m, 4H), 7.27 – 7.19 (m, 3H), 3.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.75, 146.61, 140.49, 139.48, 137.41, 136.31, 133.96, 133.05, 132.88, 131.80, 131.29, 130.50, 130.39, 129.89, 129.35, 129.15, 128.70, 128.61, 128.27, 128.13, 127.45, 127.31, 125.95, 124.94, 120.98, 119.16, 118.18, 102.76, 85.70; HRMS (ESI) m/z: $[M-H]^-$ Calcd for : $C_{24}H_{13}BrNO$ 410.0181; found 410.0192.

13-hydroxy-13-phenyl-13*H*-indeno[2,1-*a*]anthracene-5-carbonitrile (2k): White solid (49.79mg, 65%)



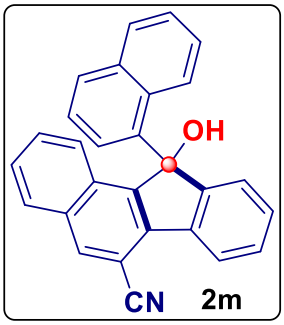
mp 289-291 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.5 Hz, 1H), 8.25 (s, 1H), 8.20 (dd, *J* = 8.1, 1.0 Hz, 1H), 8.16 – 8.09 (m, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.86 (ddd, *J* = 6.0, 3.1, 1.9 Hz, 2H), 7.53 – 7.36 (m, 6H), 7.22 (dd, *J* = 11.6, 4.4 Hz, 2H), 7.17 – 7.09 (m, 1H), 2.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.27, 146.69, 141.16, 136.99, 135.83, 135.00, 134.27, 132.39, 130.94, 130.31, 129.69, 129.17, 128.95, 128.49, 127.09, 127.04, 126.96, 126.24, 125.09, 124.27, 123.93, 119.17, 118.59, 102.75, 85.04; HRMS (ESI) m/z: [M-H]- $C_{28}H_{16}NO$ Calcd for: 382.1232; found 382.1234.

13-hydroxy-13-phenyl-13*H*-dibenzo[a,i]fluorene-6-carbonitrile (2l): White solid (50.55mg, 66%) mp.



243-245 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (d, *J* = 8.7 Hz, 1H), 8.46 (dd, *J* = 23.9, 21.7 Hz, 1H), 8.33 (dd, *J* = 21.7, 5.4 Hz, 1H), 7.88 (dd, *J* = 46.4, 8.6 Hz, 1H), 7.75 (t, *J* = 5.6 Hz, 2H), 7.57 (dd, *J* = 12.3, 7.5 Hz, 1H), 7.49 (dd, *J* = 7.7, 7.0 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.38 – 7.29 (m, 3H), 7.24 (dd, *J* = 7.6, 4.0 Hz, 1H), 7.16 – 7.12 (m, 2H), 2.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.46, 145.91, 141.09, 140.29, 137.64, 137.41, 135.00, 134.92, 134.45, 133.64, 133.15, 132.47, 131.43, 131.16, 130.01, 129.80, 129.51, 129.36, 129.34, 129.26, 128.63, 128.55, 128.41, 128.22, 128.16, 128.07, 127.58, 127.52, 127.48, 127.09, 127.04, 126.25, 126.02, 124.31, 124.17, 122.11, 118.42, 103.10, 85.30; HRMS (ESI) m/z: $[M+H]^+$ $C_{28}H_{18}NO$ Calcd for :384.1388; found 384.1384.

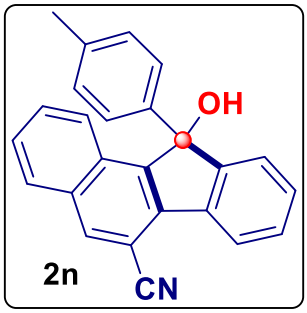
11-hydroxy-11-(naphthalen-1-yl)-11*H*-benzo[*a*]fluorene-6-carbonitrile (2m): White solid (52.08mg, 68%)



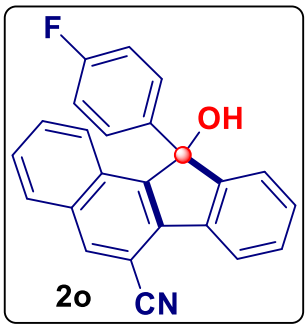
mp 234-235 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 6.4 Hz, 1H), 8.54 (d, J = 7.7 Hz, 1H), 8.34 (s, 1H), 7.87 (dd, J = 16.5, 8.3 Hz, 2H), 7.78 – 7.70 (m, 3H), 7.49 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.2 Hz, 1H), 7.31 (t, J = 7.7 Hz, 1H), 7.25 (s, 1H), 7.21 – 7.14 (m, 2H), 6.90 – 6.81 (m, 2H), 2.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.39, 147.19, 137.38, 137.08, 136.72, 135.86, 134.09, 132.65, 131.13, 129.93, 129.76, 129.65, 129.39, 129.16, 128.77, 127.22, 125.98, 125.36, 125.15, 124.96, 124.06, 123.52, 122.59, 118.43, 110.07, 103.39, 82.65; HRMS (ESI) m/z: $[M-H]^-$

$C_{28}H_{16}NO$ Calcd for: 382.1232;found 382.1233.

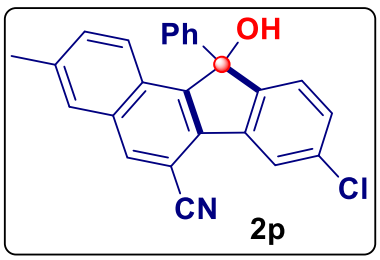
11-hydroxy-11-(*p*-tolyl)-11H-benzo[*a*]fluorene-6-carbonitrile (2n): White solid (55.52mg, 80%) mp 224-226 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.7 Hz, 1H), 8.32 (s, 1H), 7.96 – 7.89 (m, 2H), 7.54 – 7.41 (m, 3H), 7.39 – 7.29 (m, 2H), 7.21 – 7.12 (m, 3H), 7.07 – 7.01 (m, 1H), 2.41 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.03, 146.32, 141.60, 138.21, 137.06, 136.75, 136.32, 132.65, 130.83, 129.69, 129.47, 129.33, 129.17, 128.43, 128.28, 127.11, 125.36, 125.23, 124.22, 121.99, 121.91, 118.35, 102.95, 83.56, 21.59; HRMS (ESI) m/z: [M H] $C_{25}H_{16}NO$ Calcd for: 346.1232 found, 346.1241



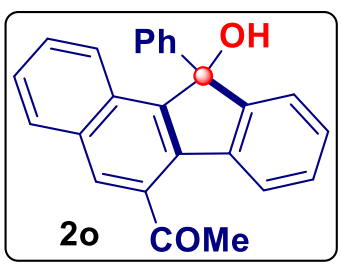
11-(4-fluorophenyl)-11-hydroxy-11*H*-benzo[*a*]fluorene-6-carbonitrile (2n): White solid (53.35mg, 76%) mp 200-202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.39 (m, 1H), 8.34 (s, 1H), 7.95 – 7.88 (m, 2H), 7.55 – 7.45 (m, 3H), 7.39 – 7.31 (m, 2H), 7.25 – 7.22 (m, 1H), 7.18 (td, *J* = 8.0, 5.9 Hz, 1H), 7.01 (dd, *J* = 6.6, 1.3 Hz, 1H), 6.91 (tdd, *J* = 8.4, 2.6, 0.9 Hz, 1H), 2.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.12, 162.32 (d, $J_{C\text{-}F}$ = 254.0 Hz), 151.39, 145.72, 144.52, 137.31, 136.77, 136.25, 132.72, 130.71, 130.19, 130.13 (d, $J_{C\text{-}F}$ = 9.0 Hz), 129.87, 129.81 13 (d, $J_{C\text{-}F}$ = 8.5 Hz), 129.45, 129.27 13 (d, $J_{C\text{-}F}$ = 27.0 Hz), 127.28, 125.00, 124.19, 122.16, 120.58, 120.56, 118.18, 114.49, 114.35 (d, $J_{C\text{-}F}$ = 21 Hz), 112.35, 112.20(d, $J_{C\text{-}F}$ = 22.5 Hz), 103.04, 83.18; HRMS (ESI) m/z: [M-H]- $C_{24}H_{13}FNO$ Calcd for: 350.0981;found 350.0983.



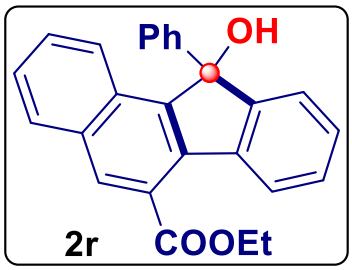
8-chloro-11-hydroxy-3-methyl-11-phenyl-11*H*-benzo[*a*]fluorene-6-carbonitrile (2p): White solid (53.34mg, 70%) mp 225-226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.7 Hz, 1H), 8.15 (s, 1H), 8.05 (d, *J* = 9.1 Hz, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.46 – 7.32 (m, 4H), 7.25 – 7.14 (m, 3H), 7.08 (d, *J* = 7.6 Hz, 1H), 2.47 (d, *J* = 21.4 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.75, 147.36, 139.98, 137.11, 137.07, 135.93, 135.79, 133.17, 133.07, 131.89, 130.48, 129.92, 128.71, 128.68, 128.25, 127.60, 127.11, 126.25, 125.53, 119.51, 118.04, 104.00, 84.47, 17.49; HRMS (ESI) m/z: $[M\text{-}H]^-$ $C_{25}H_{15}ClNO$ Calcd for : 380.0842; found 380.0845.



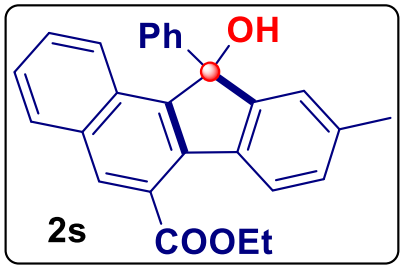
(11-hydroxy-11-phenyl-11*H*-benzo[*a*]fluoren-6-yl)ethan-1-one (2q): White solid (54.60mg, 78%) mp 225-227 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.70 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.44 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.38 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.25 – 7.18 (m, 4H), 7.14 – 7.07 (m, 2H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.72, 149.48, 145.13, 141.48, 139.39, 135.87, 134.45, 131.88, 131.26, 129.38, 129.27, 128.97, 128.13, 127.99, 127.30, 127.16, 126.88, 126.23, 124.80, 124.71, 123.59, 53.75, 30.26; HRMS (ESI) m/z: $[M+H]^+$ $C_{25}H_{19}O_2$ Calcd for : 351.1307; found 351.1310.



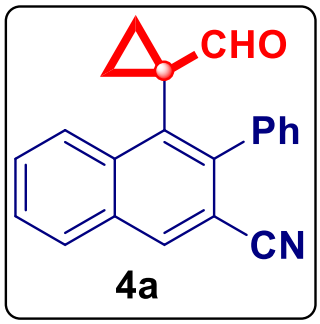
11-phenyl-6-tosyl-11*H*-benzo[*a*]fluoren-11-ol (2r): White solid (66.88mg, 88%) mp 240-242 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.29 – 8.22 (m, 1H), 7.97 – 7.90 (m, 1H), 7.74 – 7.68 (m, 1H), 7.45 – 7.31 (m, 4H), 7.25 – 7.20 (m, 3H), 7.12 – 7.08 (m, 2H), 4.60 (q, *J* = 7.1 Hz, 2H), 1.53 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.45, 149.47, 144.82, 141.60, 139.44, 131.90, 131.48, 131.38, 129.51, 128.96, 128.14, 127.98, 127.25, 127.10, 126.85, 126.08, 125.54, 124.73, 124.63, 124.02, 61.53, 53.74, 14.41; HRMS (ESI) m/z: $[M+H]^+$ $C_{26}H_{20}O_3$ Calcd for : 380.4430; found 380.4430.



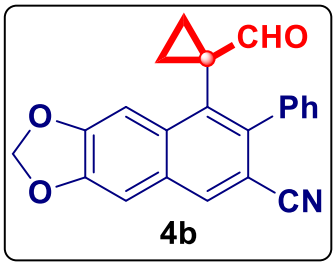
ethyl-11-hydroxy-9-methyl-11-phenyl-11*H*-benzo[*a*]fluorene-6-carboxylate (2s): White solid (67.77mg, 86%) mp 210-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.48 (dd, *J* = 18.4, 17.2 Hz, 1H), 8.36 (s, 1H), 8.22 – 8.16 (m, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.84 – 7.79 (m, 1H), 7.72 – 7.66 (m, 2H), 7.41 (ddd, *J* = 7.7, 4.5, 1.2 Hz, 3H), 7.36 – 7.29 (m, 2H), 7.22 (ddd, *J* = 11.7, 5.1, 3.2 Hz, 3H), 7.11 (s, 1H), 4.57 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.52 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.17, 152.46, 145.66, 142.67, 141.07, 138.61, 137.98, 135.64, 134.57, 132.90, 131.32, 131.20, 131.01, 130.68, 130.57, 130.28, 130.20, 129.68, 129.23, 128.86, 128.82, 128.37, 128.27, 127.02, 126.31, 124.96, 124.86, 124.57, 124.32, 124.05, 123.84, 120.52, 118.16, 83.50, 61.51, 22.56, 22.24, 14.40; HRMS (ESI) m/z: $[M+H]^+$ $C_{26}H_{20}O_3$ Calcd for : 380.4430; found 380.4430.



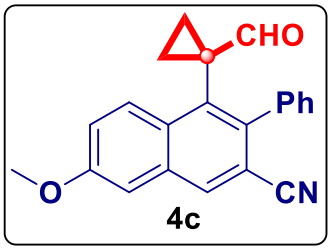
4-(1-formylcyclopropyl)-3-phenyl-2-naphthonitrile (4a): Off-White solid (51.68mg, 87%) mp 207-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.35 (s, 1H), 8.08 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.70 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.57 – 7.49 (m, 1H), 7.49 – 7.38 (m, 3H), 7.20 (d, *J* = 7.4 Hz, 1H), 1.89 (ddd, *J* = 9.9, 7.5, 4.7 Hz, 1H), 1.35 (ddd, *J* = 8.9, 7.6, 4.7 Hz, 1H), 1.18 (ddd, *J* = 9.9, 7.6, 5.8 Hz, 1H), 0.91 (ddd, *J* = 9.0, 7.5, 5.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.08, 141.92, 137.75, 135.76, 135.19, 132.73, 131.86, 129.82, 129.58, 129.32, 129.24, 128.53, 128.37, 127.29, 125.29, 118.37, 111.58, 34.21, 19.27, 17.41; HRMS (ESI) m/z: $[M+H]^+$ $C_{21}H_{15}NO$ Calcd for : 298.1154; found 298.1157.



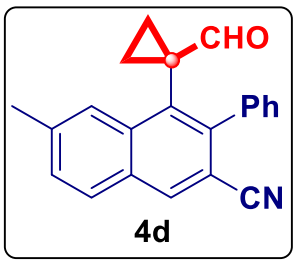
8-(1-formylcyclopropyl)-7-phenylnaphtho[2,3-d][1,3]dioxole-6-carbonitrile (4b): Light brown solid (54.56mg, 80%) mp 268-270 °C; ^{1}H NMR (400 MHz, DMSO-d_6 + $CDCl_3$) δ 8.85 (s, 1H), 8.12 (s, 1H), 7.57 – 7.36 (m, 5H), 7.34 (s, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.15 (d, *J* = 3.3 Hz, 2H), 1.93 – 1.83 (m, 1H), 1.32 – 1.27 (m, 1H), 1.20 – 1.10 (m, 1H), 0.92 – 0.85 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.68, 150.46, 148.04, 140.30, 137.42, 133.23, 132.99, 131.01, 128.87, 128.78, 127.82, 127.78, 127.73, 118.18, 108.86, 104.04, 101.51, 101.31, 34.13, 18.40, 16.93; HRMS (ESI) m/z: $[M+H]^+$ $C_{22}H_{16}NO_3$ Calcd for : 342.3660; found 342.3662.



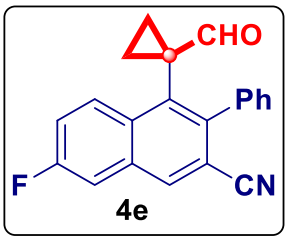
4-(1-formylcyclopropyl)-7-methoxy-3-phenyl-2-naphthonitrile (4c):): Light brown solid (53.62mg, 82%) mp 228-230 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.22 (s, 1H), 7.98 (d, *J* = 9.3 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.48 – 7.38 (m, 3H), 7.34 (dd, *J* = 9.3, 2.7 Hz, 1H), 7.19 (dd, *J* = 12.6, 5.0 Hz, 2H), 3.96 (s, 3H), 1.86 (ddd, *J* = 9.9, 7.4, 4.6 Hz, 1H), 1.33 (ddd, *J* = 9.0, 7.6, 4.7 Hz, 1H), 1.16 (ddd, *J* = 9.9, 7.5, 5.7 Hz, 1H), 0.90 (ddd, *J* = 9.0, 7.4, 5.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.13, 158.44, 139.88, 137.83, 134.23, 133.37, 132.64, 130.71, 129.70, 129.43, 128.47, 128.36, 128.33, 126.85, 122.63, 118.54, 112.00, 106.62, 55.56, 34.26, 19.34, 17.42; HRMS (ESI) m/z: $[M+H]^+$ $C_{22}H_{18}NO_2$ Calcd for : 328.3830; found 327.3830.



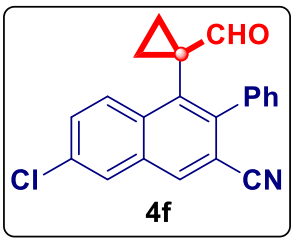
4-(1-formylcyclopropyl)-6-methyl-3-phenyl-2-naphthonitrile (4d):): Off-white solid (52.25mg, 84%) mp 248-250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.28 (s, 1H), 7.89 – 7.77 (m, 2H), 7.58 – 7.35 (m, 5H), 7.19 (d, *J* = 7.4 Hz, 1H), 2.57 (s, 3H), 1.88 (ddd, *J* = 9.9, 7.5, 4.7 Hz, 1H), 1.33 (ddd, *J* = 8.9, 7.7, 4.7 Hz, 1H), 1.16 (ddd, *J* = 9.9, 7.6, 5.7 Hz, 1H), 0.90 (ddd, *J* = 8.9, 7.5, 5.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.33, 142.01, 140.25, 137.91, 135.44, 135.39, 131.89, 130.14, 129.56, 129.53, 129.32, 129.05, 128.45, 128.42, 128.30, 124.27, 118.58, 110.49, 34.14, 22.60, 19.39, 17.61; HRMS (ESI) m/z: $[M+H]^+$ $C_{22}H_{17}NO$ Calcd for : 312.3840; found 312.3842.



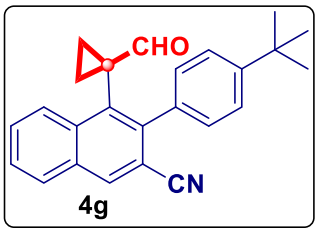
7-fluoro-4-(1-formylcyclopropyl)-3-phenyl-2-naphthonitrile (4e):): Light brown solid (45.68mg, 73%) mp 226-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.27 (s, 1H), 8.09 (dd, *J* = 9.4, 5.3 Hz, 1H), 7.61 – 7.38 (m, 6H), 7.18 (d, *J* = 7.5 Hz, 1H), 1.89 (ddd, *J* = 9.9, 7.5, 4.7 Hz, 1H), 1.34 (ddd, *J* = 8.9, 7.6, 4.7 Hz, 1H), 1.18 (ddd, *J* = 9.9, 7.5, 5.9 Hz, 1H), 0.93 (ddd, *J* = 8.9, 7.4, 5.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.75, 162.29, 159.80 (d, J_{C-F} = 249.0 Hz), 137.44, 134.77, 134.71 (d, J_{C-F} = 6.0 Hz), 132.92, 132.83, 132.24, 129.51, 129.30 (d, J_{C-F} = 21.0 Hz), 128.65, 128.59, 128.43, 128.15, 128.06, 120.16, 119.92 (d, J_{C-F} = 24.0 Hz), 117.99, 112.95, 112.33, 112.12 (d, J_{C-F} = 21.0 Hz), 34.38, 19.04, 17.21; HRMS (ESI) m/z: $[M+H]^+$ $C_{21}H_{15}FNO$ Calcd for : 316.3474; found 316.3476.



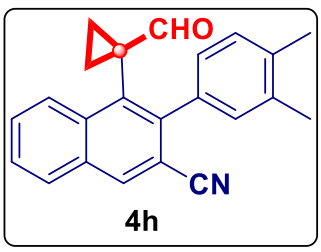
7-chloro-4-(1-formylcyclopropyl)-3-phenyl-2-naphthonitrile (4f): Light brown solid (50.31mg, 76%) mp 211-214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.24 (s, 1H), 8.02 (d, *J* = 9.1 Hz, 1H), 7.93 (d, *J* = 2.1 Hz, 1H), 7.62 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.57 – 7.35 (m, 4H), 7.18 (d, *J* = 7.5 Hz, 1H), 1.88 (ddd, *J* = 9.9, 7.4, 4.7 Hz, 1H), 1.33 (ddd, *J* = 8.9, 7.6, 4.7 Hz, 1H), 1.18 (ddd, *J* = 9.9, 7.5, 5.9 Hz, 1H), 0.92 (ddd, *J* = 8.9, 7.4, 5.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.65, 142.19, 137.34, 134.56, 133.49, 133.40, 133.01, 132.52, 130.57, 129.43, 129.21, 128.71, 128.59, 128.43, 127.63, 127.03, 117.91, 112.91, 34.24, 18.95, 17.07; HRMS (ESI) m/z: $[M+H]^+$ $C_{21}H_{15}ClNO$ Calcd for : 332.7990; found 332.7993.



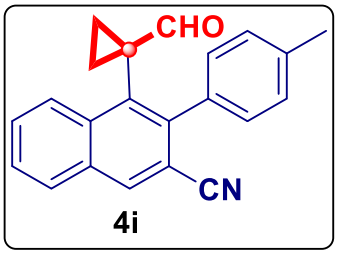
3-(4-(tert-butyl)phenyl)-4-(1-formylcyclopropyl)-2-naphthonitrile (4g): Off-white solid (67.07mg, 95%) mp 265-267 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 – 8.97 (m, 1H), 8.33 (s, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.69 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.65 – 7.57 (m, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 9.0 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 1H), 1.88 (ddd, *J* = 9.9, 7.5, 4.7 Hz, 1H), 1.39 (d, *J* = 12.4 Hz, 9H), 1.34 – 1.29 (m, 1H), 1.16 (ddd, *J* = 9.9, 7.6, 5.8 Hz, 1H), 0.88 (ddd, *J* = 8.9, 7.5, 5.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.30, 151.48, 141.99, 135.78, 135.25, 134.62, 132.77, 131.77, 129.73, 129.33, 129.20, 128.96, 127.14, 125.28, 125.19, 118.53, 111.67, 34.69, 34.19, 31.33, 19.55, 17.54; HRMS (ESI) m/z: $[M+H]^+$ $C_{25}H_{24}NO$ Calcd for : 354.1780; found 354.1778.



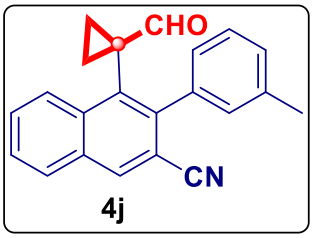
3-(3,4-dimethylphenyl)-4-(1-formylcyclopropyl)-2-naphthonitrile (4h): White solid (59.80mg, 92%) mp 258-260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, *J* = 8.5 Hz, 1H), 8.32 (s, 1H), 8.07 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.65 (dt, *J* = 14.8, 7.2 Hz, 2H), 7.26 – 7.11 (m, 2H), 6.97 – 6.87 (m, 1H), 2.31 (t, *J* = 22.3 Hz, 6H), 1.88 (ddd, *J* = 9.8, 7.5, 4.6 Hz, 1H), 1.33 (td, *J* = 8.3, 4.7 Hz, 1H), 1.25 – 1.14 (m, 1H), 1.01 – 0.89 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.25, 200.18, 142.26, 136.89, 136.66, 136.47, 135.68, 135.61, 135.28, 135.20, 132.64, 131.77, 130.71, 130.38, 129.74, 129.69, 129.58, 129.20, 127.10, 126.69, 125.29, 118.53, 111.89, 34.16, 19.88, 19.72, 19.64, 19.58, 17.71; HRMS (ESI) m/z: $[M+H]^+$ $C_{23}H_{20}NO$ Calcd for : 326.1467; found 326.1465.



4-(1-formylcyclopropyl)-3-(p-tolyl)-2-naphthonitrile (4i): White solid (55.98mg, 90%) mp 253-255 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.33 (s, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.73 – 7.58 (m, 2H), 7.33 (s, 2H), 7.14 (dd, *J* = 52.0, 7.8 Hz, 2H), 2.43 (s, 3H), 1.89 (ddd, *J* = 9.8, 7.5, 4.6 Hz, 1H), 1.37 – 1.31 (m, 1H), 1.21 (ddd, *J* = 9.8, 7.5, 5.7 Hz, 1H), 0.93 (ddd, *J* = 8.9, 7.5, 5.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.21, 142.02, 138.30, 135.70, 135.23, 134.77, 132.69, 131.79, 129.75, 129.45, 129.22, 129.15, 129.08, 127.17, 125.27, 118.52, 111.91, 34.20, 21.36, 19.45, 17.60; HRMS (ESI) m/z: $[M+H]^+$ $C_{22}H_{17}NO$ Calcd for : 312.3840; found 312.3842.

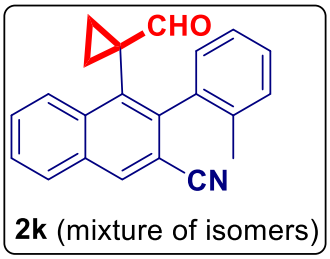


4-(1-formylcyclopropyl)-3-(m-tolyl)-2-naphthonitrile (4j): Off-white solid (53.49mg, 86%) mp 236-238 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.29 (s, 1H), 7.87 – 7.79 (m, 2H), 7.55 – 7.49 (m, 1H), 7.48 – 7.38 (m, 4H), 7.19 (d, *J* = 7.5 Hz, 1H), 2.57 (s, 3H), 1.88 (ddd, *J* = 9.9, 7.5, 4.7 Hz, 1H), 1.33 (ddd, *J* = 8.9, 7.7, 4.7 Hz, 1H), 1.17 (ddd, *J* = 9.9, 7.6, 5.7 Hz, 1H), 0.90 (ddd, *J* = 8.9, 7.5, 5.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.35, 142.02, 140.26, 137.91, 135.45, 135.40, 131.88, 130.14, 129.57, 129.54, 129.32, 129.06, 128.46, 128.43, 128.31, 124.27, 118.58, 110.50, 34.15, 22.61, 19.40, 17.63; HRMS (ESI) m/z: $[M+H]^+$ $C_{22}H_{17}NO$ Calcd for : 312.3840; found

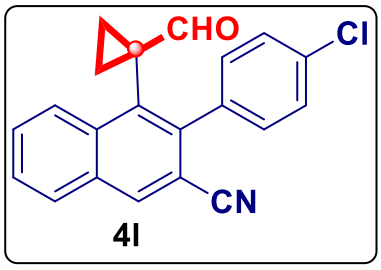


312.3842.

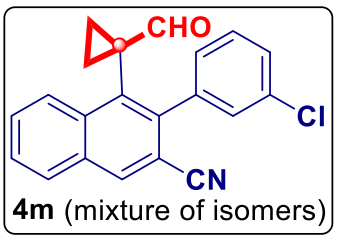
4-(1-formylcyclopropyl)-3-(o-tolyl)-2-naphthonitrile (2k mixture of isomers): Off white solid (54.11mg, 87%) mp 194-196 °C; ^{1}H NMR (597 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.90 (s, 1H), 8.35 (s, 1H), 8.32 (s, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.66 – 7.60 (m, 1H), 7.39 – 7.33 (m, 2H), 7.32 (s, 1H), 7.24 – 7.19 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 2.17 (d, *J* = 11.1 Hz, 3H), 2.00 (s, 1H), 1.88 (ddd, *J* = 9.9, 7.4, 4.7 Hz, 1H), 1.83 – 1.75 (m, 1H), 1.40 (ddd, *J* = 8.9, 7.7, 4.7 Hz, 1H), 1.30 (tdd, *J* = 16.2, 13.9, 8.4 Hz, 1H), 1.11 (ddd, *J* = 9.9, 7.6, 5.8 Hz, 1H), 0.88 (ddd, *J* = 8.9, 7.4, 5.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.69, 199.51, 141.71, 137.49, 135.57, 135.42, 135.36, 135.20, 132.68, 132.01, 131.91, 130.71, 130.33, 129.91, 129.79, 129.72, 129.59, 129.30, 128.87, 128.70, 127.31, 127.26, 126.14, 125.44, 125.35, 125.21, 118.04, 112.06, 33.97, 19.87, 19.81, 19.74, 18.62, 17.80, 16.08; HRMS (ESI) m/z: $[M+H]^+$ $C_{22}H_{17}NO$ Calcd for : 312.3840; found 312.3842.



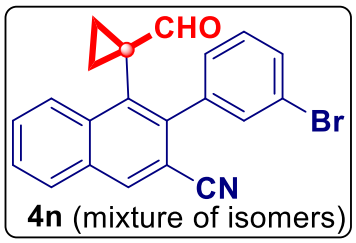
3-(4-chlorophenyl)-4-(1-formylcyclopropyl)-2-naphthonitrile (4l): Light brown solid (50.97mg, 77%) mp 253-255 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.34 (s, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.71 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1H), 7.67 – 7.61 (m, 1H), 7.52 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.40 (ddd, *J* = 8.1, 5.9, 2.1 Hz, 2H), 7.15 (dd, *J* = 8.2, 2.1 Hz, 1H), 1.92 (ddd, *J* = 9.9, 7.4, 4.8 Hz, 1H), 1.41 – 1.34 (m, 1H), 1.24 (ddd, *J* = 9.9, 7.5, 5.8 Hz, 1H), 0.90 (ddd, *J* = 8.9, 7.4, 5.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.82, 140.52, 136.20, 135.87, 135.07, 134.77, 132.90, 131.92, 131.19, 130.93, 130.64, 129.99, 129.26, 129.16, 128.98, 128.82, 128.68, 127.51, 125.26, 118.18, 111.20, 67.05, 34.25, 19.02, 17.29; HRMS (ESI) m/z: $[M+H]^+$ $C_{21}H_{15}ClNO$ Calcd for : 332.7990; found 332.7993.



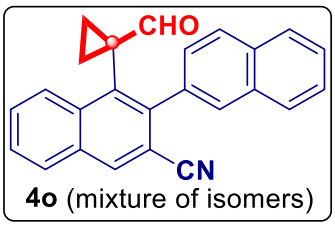
3-(3-chlorophenyl)-4-(1-formylcyclopropyl)-2-naphthonitrile (4m isomers): Light brown solid (52.30mg, 79%) mp 209-211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 10.7 Hz, 1H), 8.35 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.74 – 7.62 (m, 2H), 7.51 – 7.31 (m, 3H), 7.17 (dd, *J* = 49.4, 4.7 Hz, 1H), 1.96 – 1.88 (m, 1H), 1.38 (ddd, *J* = 10.9, 8.9, 6.8 Hz, 1H), 1.29 – 1.20 (m, 1H), 0.93 (dddd, *J* = 24.0, 8.9, 7.5, 5.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.78, 199.55, 139.49, 135.90, 135.06, 134.53, 134.26, 132.94, 131.98, 130.02, 129.85, 129.65, 129.56, 129.35, 129.30, 129.27, 128.80, 128.77, 127.84, 127.62, 127.59, 125.35, 125.28, 118.11, 117.97, 111.11, 34.20, 19.00, 18.84, 17.32, 17.03; HRMS (ESI) m/z: $[M+H]^+$ $C_{21}H_{15}ClNO$ Calcd for : 332.7990; found 332.7993.



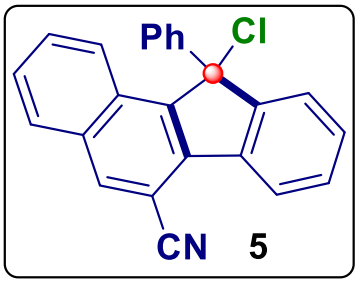
3-(3-bromophenyl)-4-(1-formylcyclopropyl)-2-naphthonitrile (4n): Light brown solid (60.75mg, 81%) mp 238-240 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 13.7 Hz, 1H), 8.35 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.2 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.40 (dd, *J* = 6.9, 3.9 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 1.97 – 1.88 (m, 1H), 1.42 – 1.33 (m, 1H), 1.25 (ddd, *J* = 9.9, 8.4, 4.1 Hz, 1H), 0.93 (ddd, *J* = 29.3, 14.5, 7.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.76, 199.50, 139.76, 139.68, 135.90, 135.07, 132.45, 132.19, 132.01, 131.69, 130.08, 130.02, 129.88, 129.30, 129.26, 128.28, 128.05, 127.60, 125.36, 125.28, 122.59, 122.31, 118.11, 117.95, 111.06, 34.21, 19.00, 18.87, 17.34, 17.05; HRMS (ESI) m/z: $[M+H]^+$ $C_{21}H_{15}BrNO$ Calcd for : 377.2530; found 377.2533.



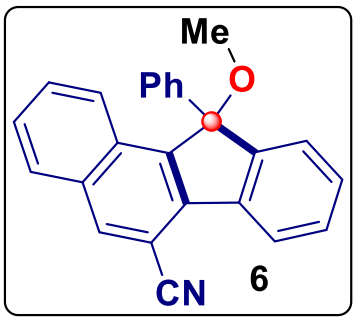
1-(1-formylcyclopropyl)-[2,2'-binaphthalene]-3-carbonitrile (4o): White solid (55.52mg, 80%) mp 223-224 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.93 (s, 1H), 8.38 (d, *J* = 11.4 Hz, 2H), 8.15 – 8.06 (m, 2H), 8.03 – 7.86 (m, 8H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.75 – 7.68 (m, 3H), 7.64 (t, *J* = 7.5 Hz, 2H), 7.54 (ddd, *J* = 19.3, 9.6, 5.1 Hz, 5H), 7.32 (dd, *J* = 8.4, 1.6 Hz, 1H), 1.87 (dt, *J* = 10.6, 6.8 Hz, 2H), 1.36 (ddd, *J* = 16.4, 7.6, 4.8 Hz, 2H), 1.15 – 1.00 (m, 2H), 0.91 (ddd, *J* = 22.2, 14.1, 7.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.13, 199.95, 141.92, 135.94, 135.71, 135.23, 135.19, 133.31, 133.03, 132.97, 132.89, 132.77, 131.94, 131.86, 129.88, 129.27, 128.82, 128.78, 128.38, 128.17, 127.83, 127.79, 127.35, 126.87, 126.73, 126.67, 126.56, 126.54, 125.38, 125.27, 118.47, 118.34, 111.63, 34.34, 19.43, 19.01, 17.47, 17.24; HRMS (ESI) m/z: $[M+H]^+$ $C_{25}H_{18}NO$ Calcd for : 348.4170; found 348.4171.



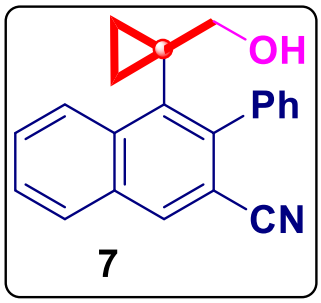
11-chloro-11-phenyl-11*H*-benzo[*a*]fluorene-6-carbonitrile (5): White solid (27.03mg, 77%) mp 257-259 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.6 Hz, 1H), 8.31 (s, 1H), 7.95 – 7.87 (m, 2H), 7.52 – 7.41 (m, 3H), 7.41 – 7.34 (m, 3H), 7.31 (td, *J* = 7.4, 0.9 Hz, 1H), 7.27 – 7.22 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.94, 146.23, 141.74, 137.10, 136.74, 136.18, 132.64, 130.78, 129.70, 129.52, 129.34, 129.18, 128.56, 127.44, 127.13, 125.16, 124.84, 124.25, 122.00, 118.31, 102.92, 83.65;HRMS (ESI) m/z: $[M+H]^+$ $C_{24}H_{15}ClN$ Calcd for : 352.8330; found 352.8332.



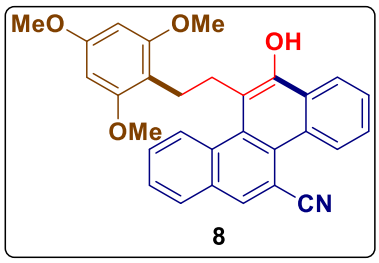
11-methoxy-11-phenyl-11*H*-benzo[*a*]fluorene-6-carbonitrile (6): White solid (28.45mg, 82%) mp 170-172 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.42 (dt, *J* = 7.7, 0.9 Hz, 1H), 8.34 (s, 1H), 7.95 (dddd, *J* = 18.2, 7.0, 2.6, 1.1 Hz, 2H), 7.54 – 7.42 (m, 3H), 7.36 – 7.27 (m, 4H), 7.24 – 7.14 (m, 3H), 2.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.62, 143.26, 142.09, 137.95, 137.63, 137.14, 132.17, 131.25, 129.81, 129.35, 129.08, 128.36, 127.28, 127.18, 125.07, 124.79, 124.65, 121.83, 118.41, 102.96, 89.28, 51.47; HRMS (ESI) m/z: $[M+H]^+$ $C_{25}H_{18}NO$ Calcd for : 348.1310; found 348.1310.



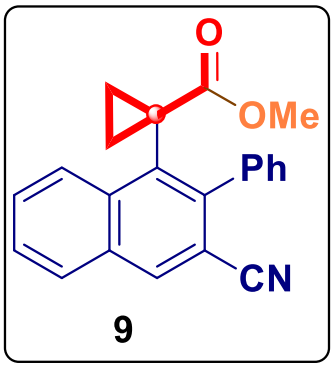
4-(1-(hydroxymethyl)cyclopropyl)-3-phenyl-2-naphthonitrile (7): White solid (28.74mg, 96%) mp 208-210 °C;[1]H NMR (597 MHz, $CDCl_3$) δ 8.66 (dd, J = 8.6, 0.7 Hz, 1H), 8.23 (s, 1H), 7.94 – 7.87 (m, 1H), 7.71 (ddd, J = 8.5, 6.9, 1.4 Hz, 1H), 7.61 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 7.55 – 7.38 (m, 4H), 7.34 (d, J = 7.4 Hz, 1H), 3.92 (d, J = 11.4 Hz, 1H), 3.75 (d, J = 11.4 Hz, 1H), 1.47 (s, 1H), 1.28 – 1.21 (m, 1H), 0.85 – 0.78 (m, 1H), 0.51 (dt, J = 9.5, 5.9 Hz, 1H), 0.49 – 0.42 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.64, 138.61, 137.62, 135.36, 134.42, 132.11, 129.91, 129.47, 129.07, 129.04, 128.16, 128.10, 128.02, 127.04, 126.46, 118.38, 112.30, 70.26, 23.41, 14.04, 12.82; HRMS (ESI) m/z: $[M+H]^+$ $C_{21}H_{18}NO$ Calcd for : 300.3730; found 300.3730.



12-hydroxy-11-(2,4,6-trimethoxyphenethyl)chrysene-5-carbonitrile (8): Brown solid (38.47mg, 83%) mp 165-167 °C; [1]H NMR (400 MHz, $CDCl_3$) δ 9.52 – 9.40 (m, 1H), 8.87 (d, *J* = 8.4 Hz, 1H), 8.40 (s, 1H), 8.02 – 7.92 (m, 3H), 7.74 – 7.62 (m, 4H), 6.10 (s, 2H), 3.81 (s, 3H), 3.76 (s, 6H), 3.51 (dd, *J* = 9.5, 6.7 Hz, 2H), 3.19 (dd, *J* = 9.5, 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.49, 158.72, 138.03, 137.47, 132.17, 132.03, 131.29, 131.09, 130.51, 128.54, 128.25, 128.02, 127.73, 127.51, 127.22, 126.74, 126.01, 125.04, 121.84, 110.03, 106.53, 90.30, 55.62, 55.32, 36.59, 25.40; HRMS (ESI) m/z: $[M+H]^+$ $C_{30}H_{26}O_4$ Calcd for : 464.5330; found 464.5333.

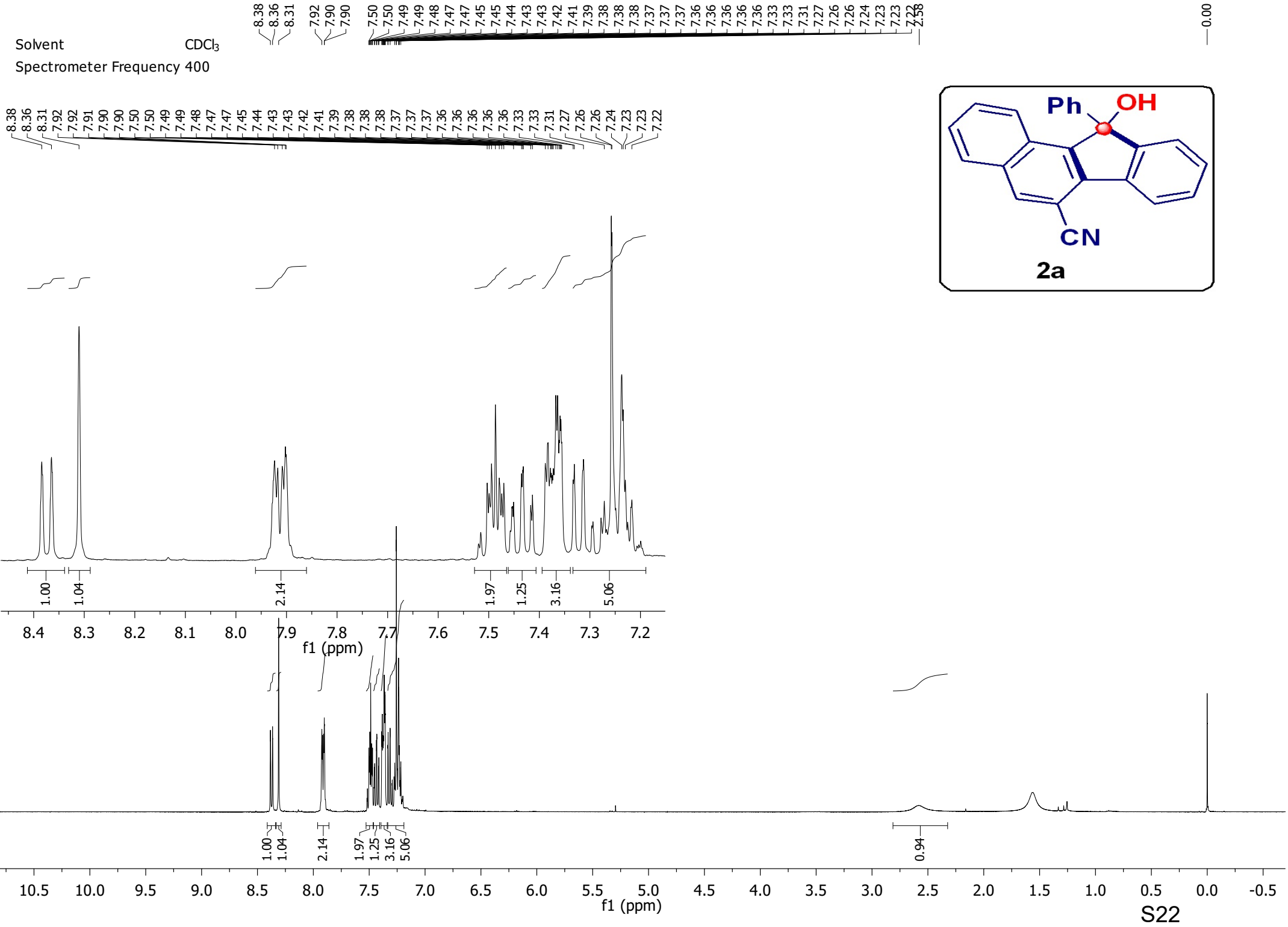


methyl 1-(3-cyano-2-phenylnaphthalen-1-yl)cyclopropane-1-carboxylate (9): [1]H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.25 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.71 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.56 – 7.50 (m, 1H), 7.49 – 7.38 (m, 3H), 7.31 (d, *J* = 6.8 Hz, 1H), 3.67 (s, 3H), 1.94 (ddd, *J* = 9.9, 7.5, 3.8 Hz, 1H), 1.23 (ddd, *J* = 9.9, 7.6, 4.9 Hz, 1H), 1.08 (ddd, *J* = 9.5, 7.6, 3.8 Hz, 1H), 0.69 (ddd, *J* = 9.5, 7.5, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.01, 140.81, 138.10, 135.41, 134.82, 131.80, 129.58, 129.53, 129.04, 128.49, 128.37, 127.04, 125.62, 118.56, 111.58, 52.55, 25.38, 22.32, 20.39; HRMS (ESI) m/z: $[M+H]^+$ $C_{22}H_{17}O_2$ Calcd for : 327.3830; found 327.3834.



Solvent $CDCl_3$

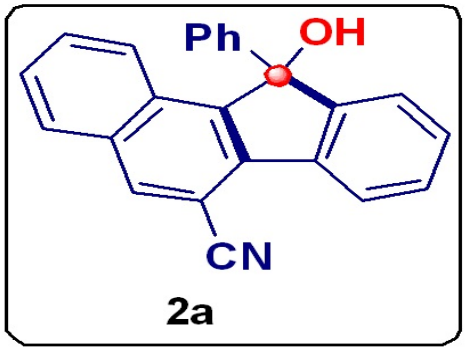
Spectrometer Frequency 400



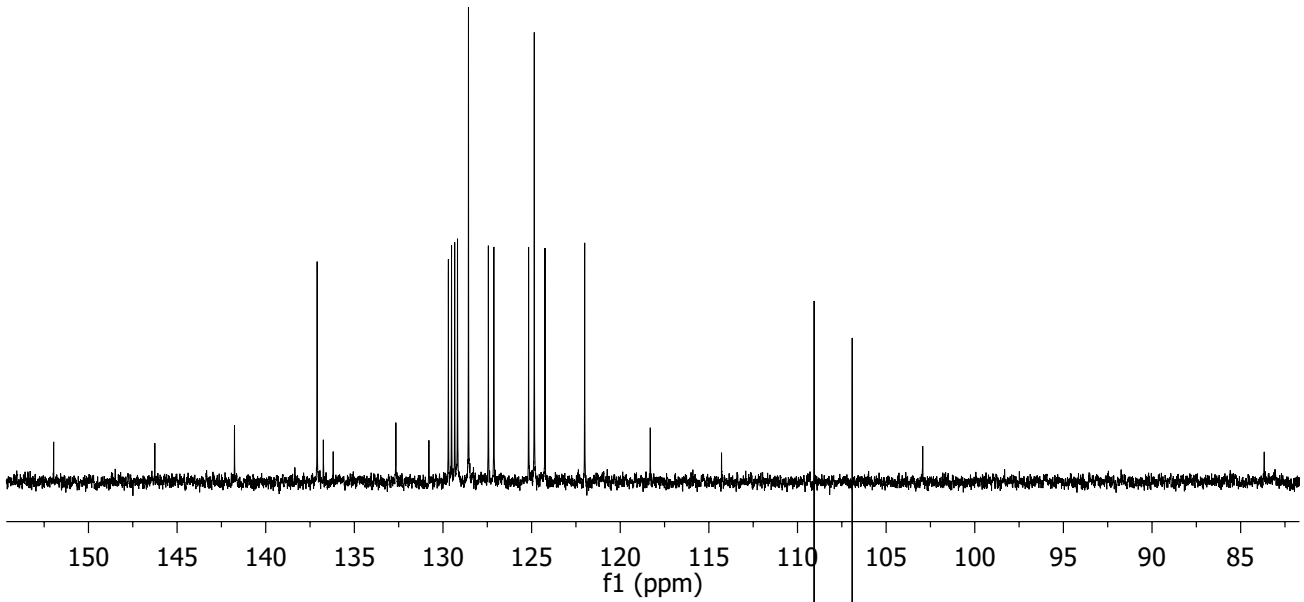
Solvent $CDCl_3$

Spectrometer Frequency 100

151.96 146.26 141.76 137.10 136.75 132.66 130.79 129.70 129.52 129.34 129.18 128.56 127.44 127.13 125.17 124.85 124.25 122.01 118.31 102.94 83.67 77.31 76.99 76.68

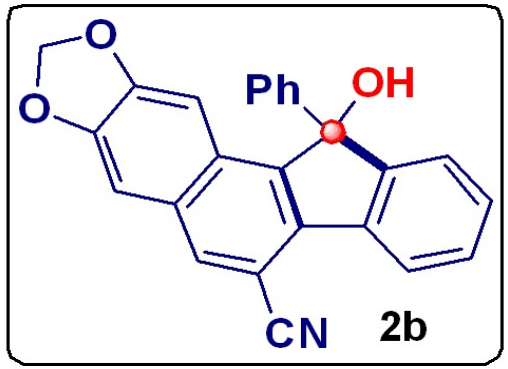


2a



Solvent $CDCl_3$

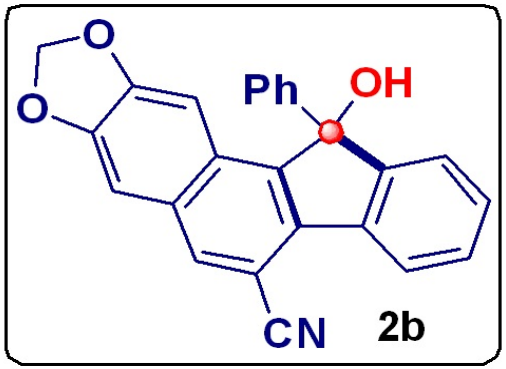
Spectrometer Frequency 400



Solvent $CDCl_3$

Spectrometer Frequency 100

151.61 150.39 148.62 145.18 141.66 136.82 135.43 134.83 130.26 129.48 129.11 129.07 128.59 128.42 127.42 124.85 124.15 121.85 118.58 104.69 101.71 101.48 100.97 83.66 77.31 77.19 76.99 76.67

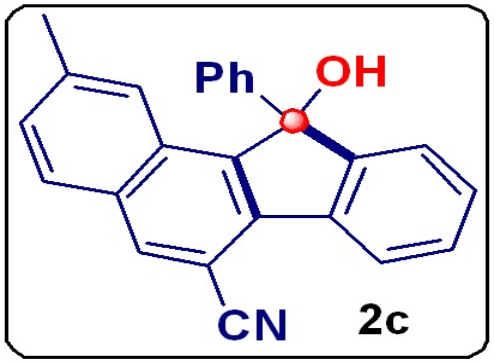


f1 (ppm)

f1 (ppm)

Solvent $CDCl_3$

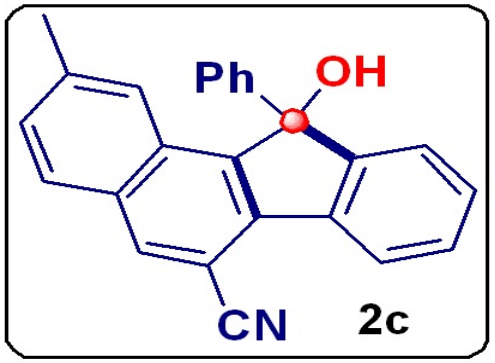
Spectrometer Frequency 400



Solvent $CDCl_3$

Spectrometer Frequency 100

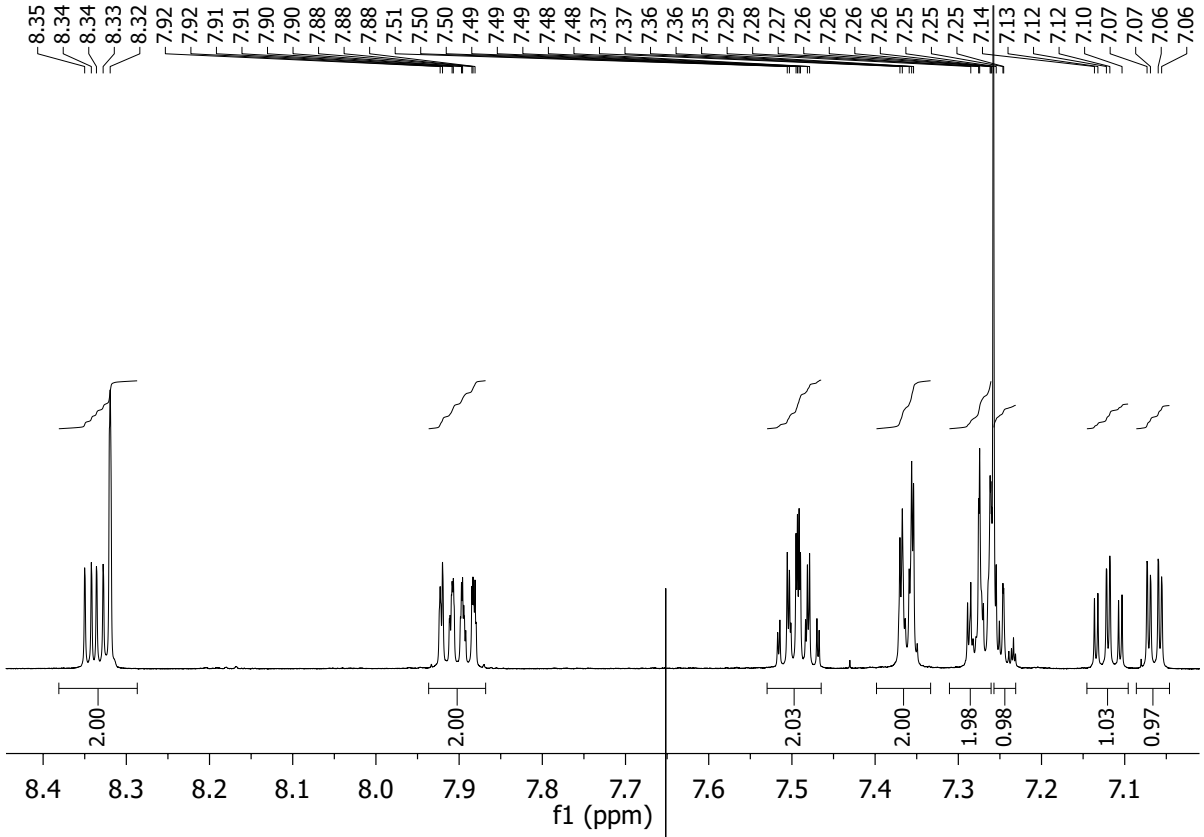
152.01
145.32
141.78
140.18
136.79
136.24
131.01
130.97
129.52
129.42
129.20
128.97
128.51
127.35
124.82
124.16
123.97
121.93
121.83
83.66
77.31
76.99
76.67
22.29

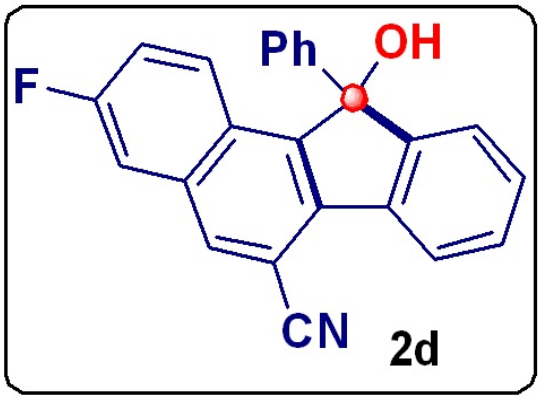


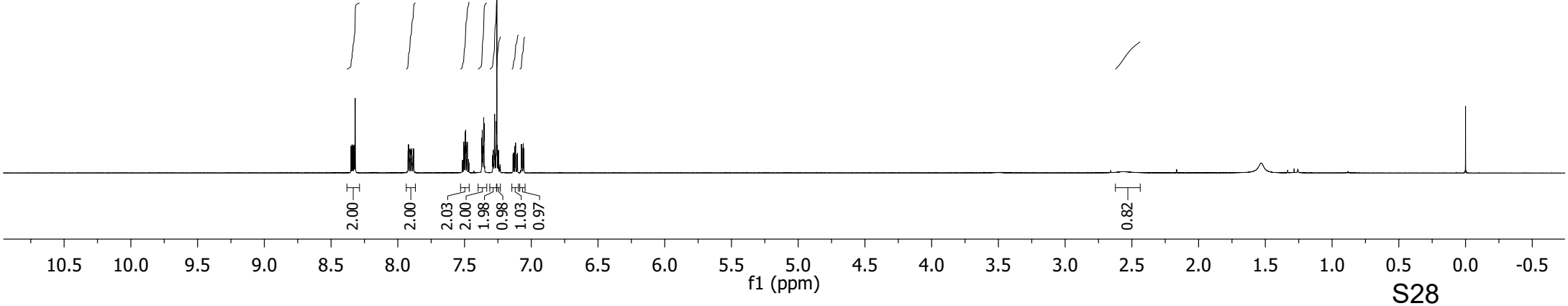
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 597



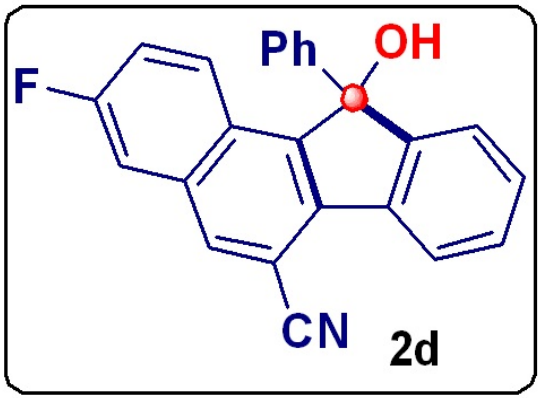




Solvent $CDCl_3$

Spectrometer Frequency 150

164.48 162.81 141.12 137.18 135.54 132.43 130.78 129.86 129.23 128.72 127.74 127.18 124.98 124.78 123.43 123.37 118.19 116.50 116.35 112.28 112.12 102.70 77.20 76.99 76.78



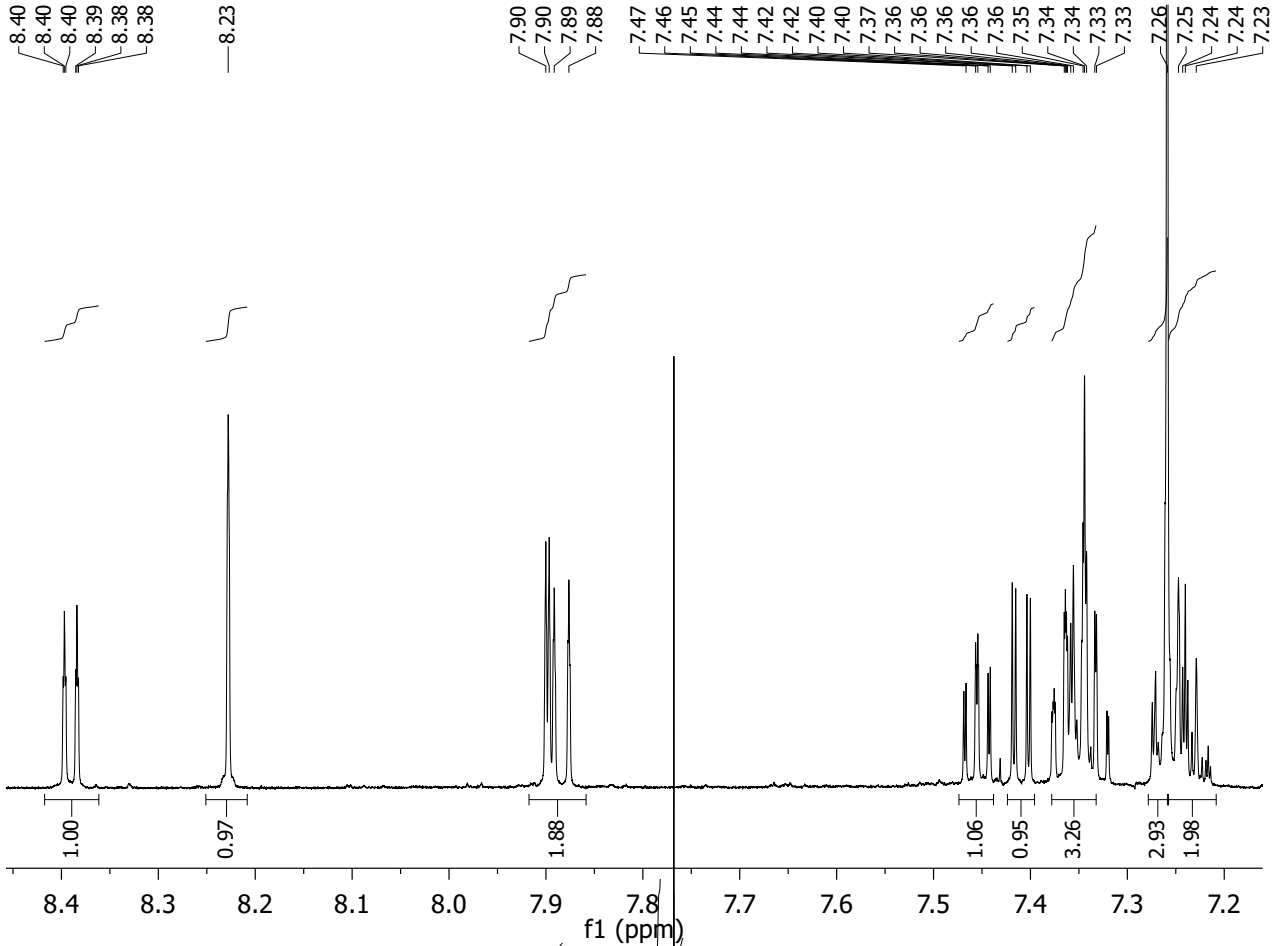
2d

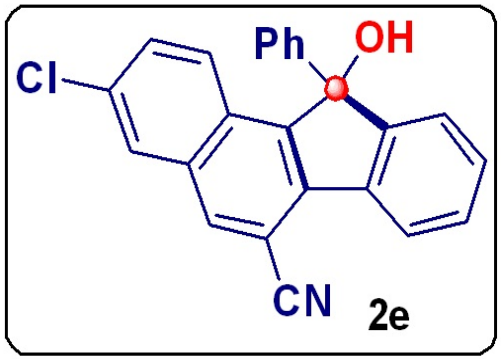
f1 (ppm)

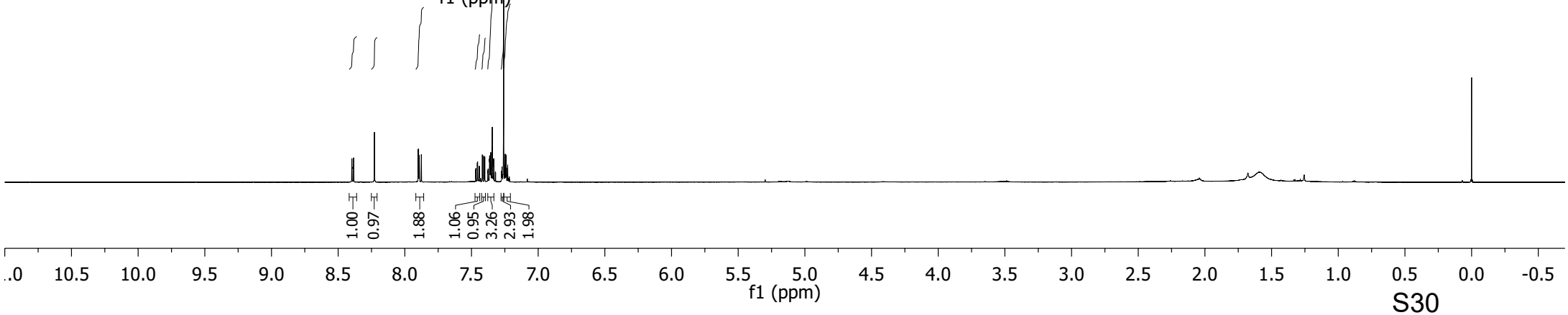
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 597



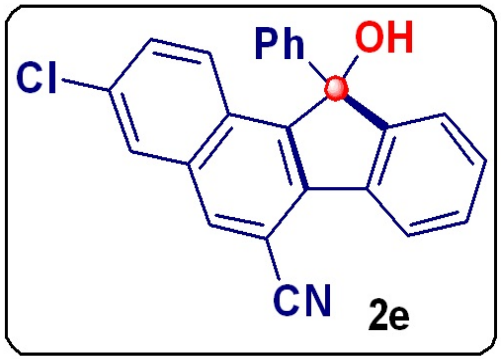


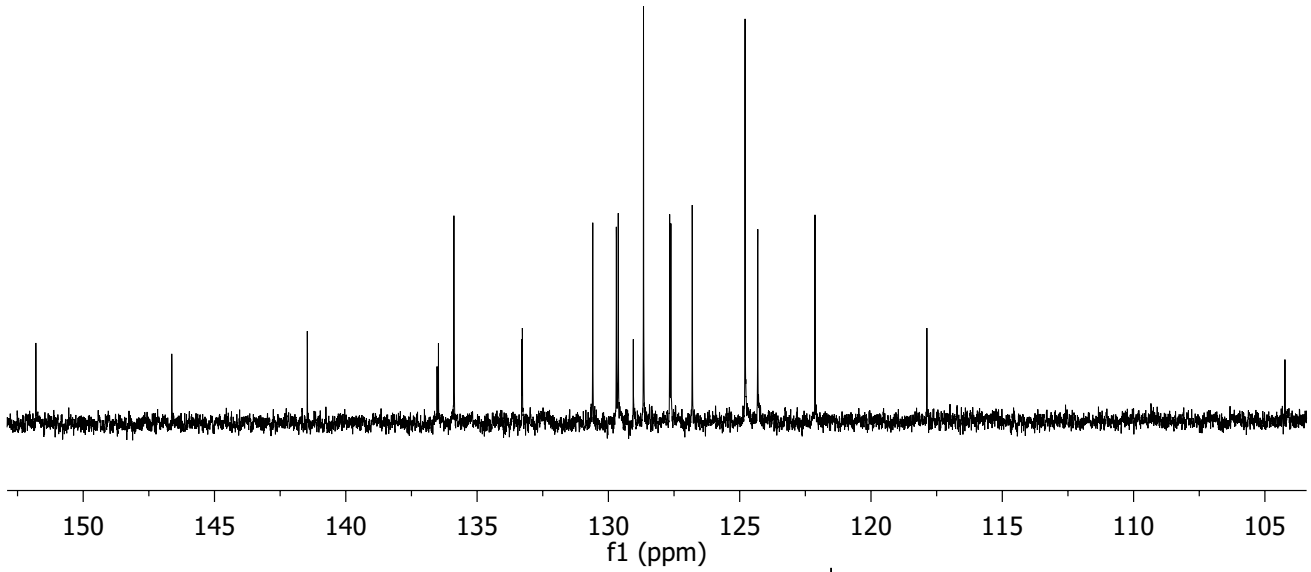


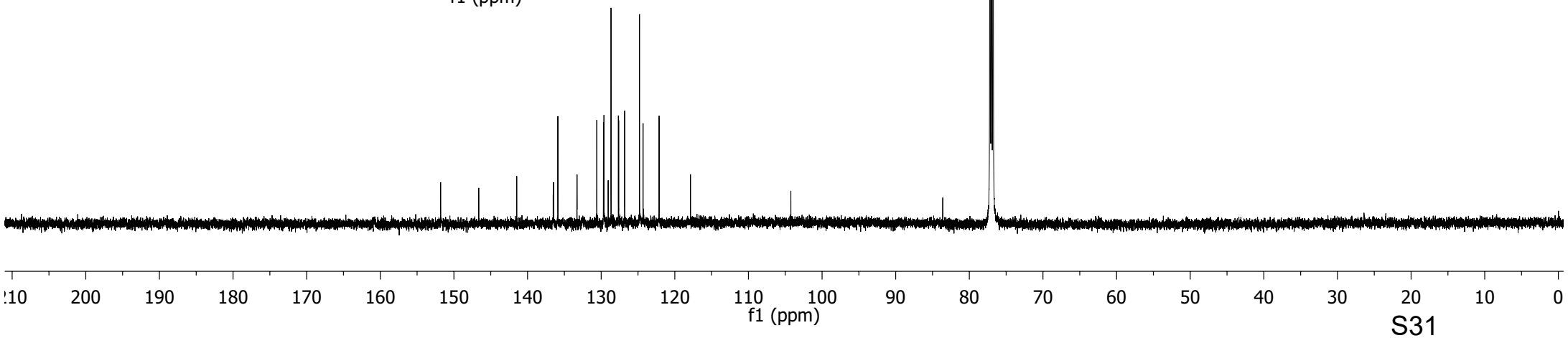
Solvent $CDCl_3$

Spectrometer Frequency 150

151.80 146.63 141.47 135.88 133.30 133.28 130.60 129.70 129.62 129.05 128.66 127.67 127.62 126.81 124.80 124.31 122.13 117.87 104.24 83.78 77.20 76.99 76.78

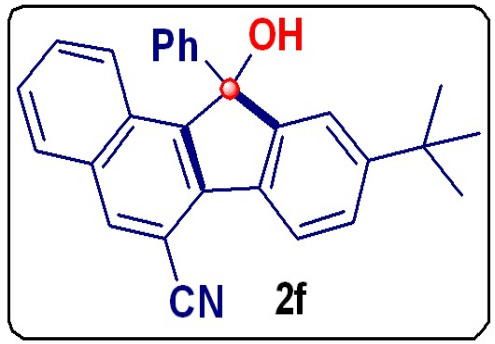






Solvent $CDCl_3$

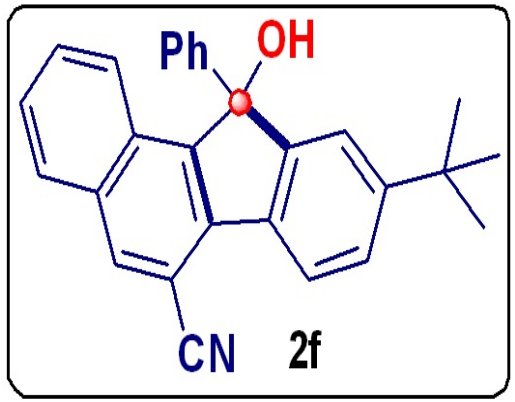
Spectrometer Frequency 400

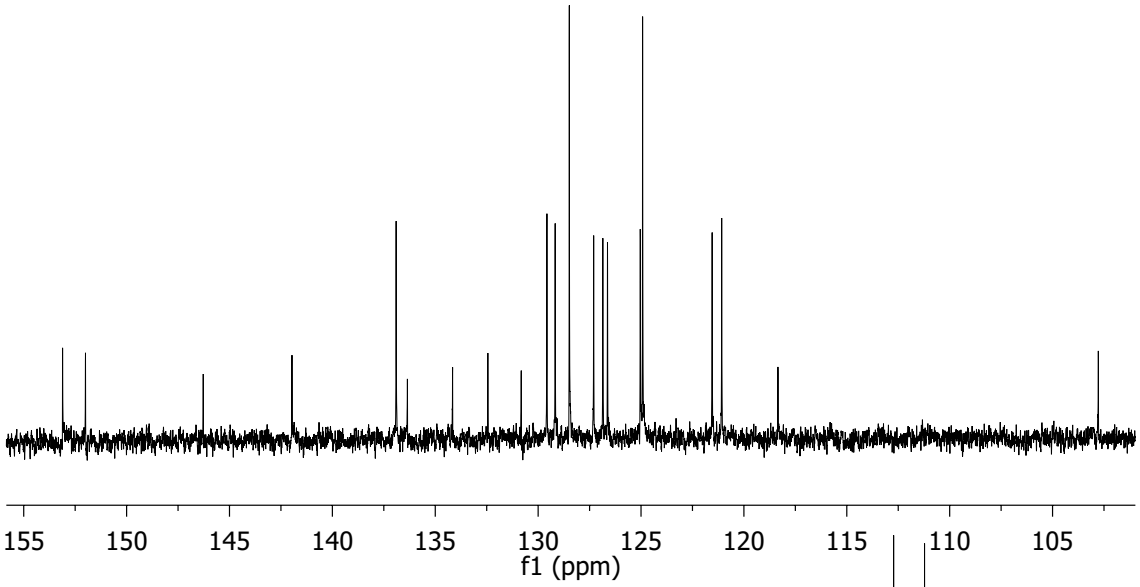


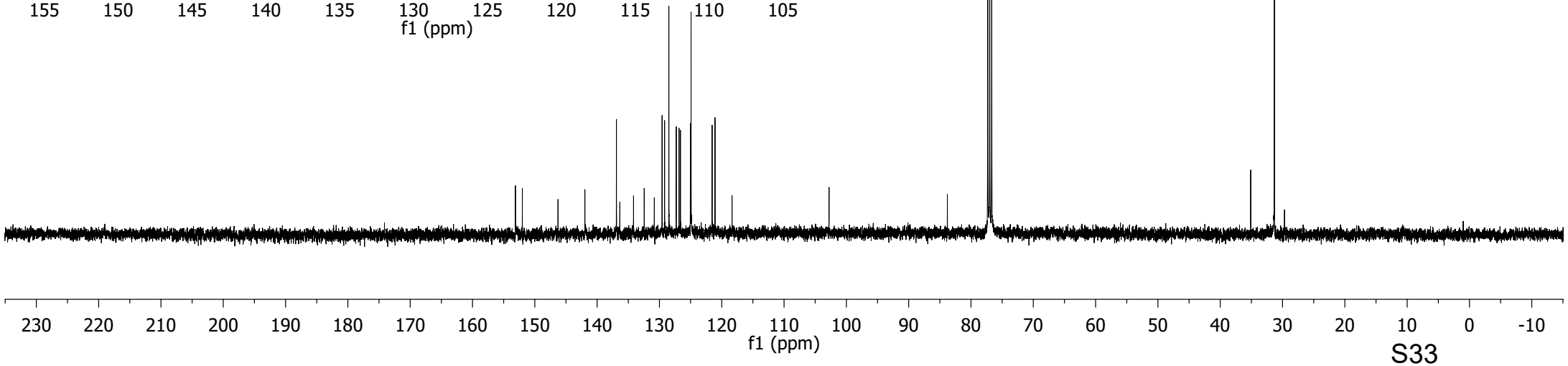
Solvent $CDCl_3$

Spectrometer Frequency 100

153.11 152.00 146.28 141.96 136.90 136.35 134.16 132.44 130.82 129.57 129.17 128.49 127.30 126.86 126.63 125.04 124.92 121.54 121.08 118.35 102.78 83.79 77.31 76.99 76.67 35.11 31.30

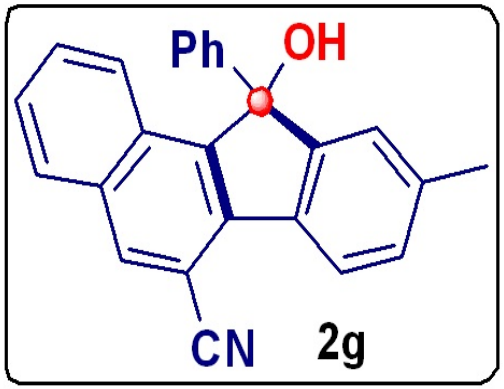






Solvent $CDCl_3$

Spectrometer Frequency 400

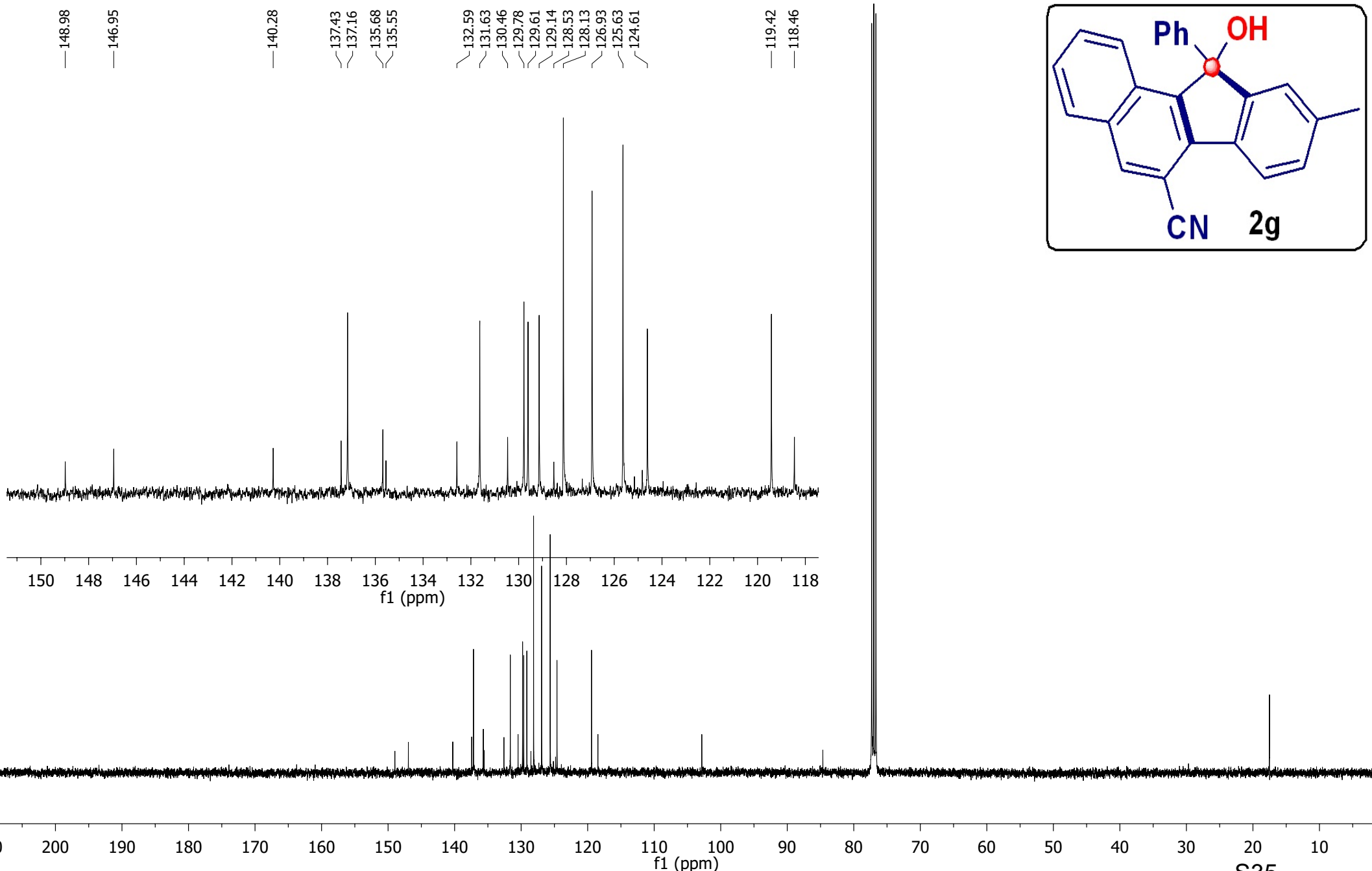


Solvent $CDCl_3$

Spectrometer Frequency 100

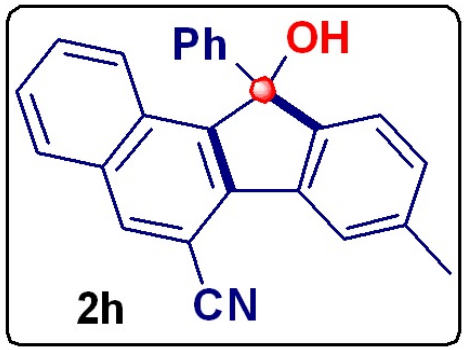
148.98 146.95 137.16 131.63 129.78 129.61 129.14 128.13 126.93 125.63 124.61 119.42 118.46 102.85 84.65 77.31 76.99 76.67 17.51

148.98 146.95 140.28 137.43 137.16 135.68 135.55 132.59 131.63 130.46 129.78 129.61 129.14 128.53 128.13 126.93 125.63 124.61 119.42 118.46



Solvent $CDCl_3$

Spectrometer Frequency 400



f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 100

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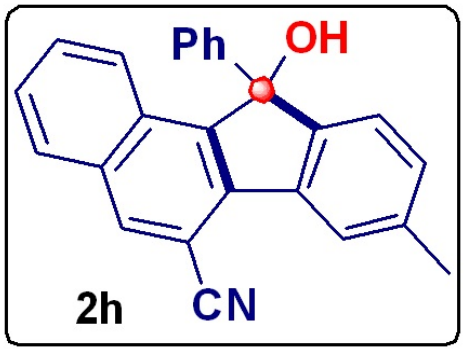
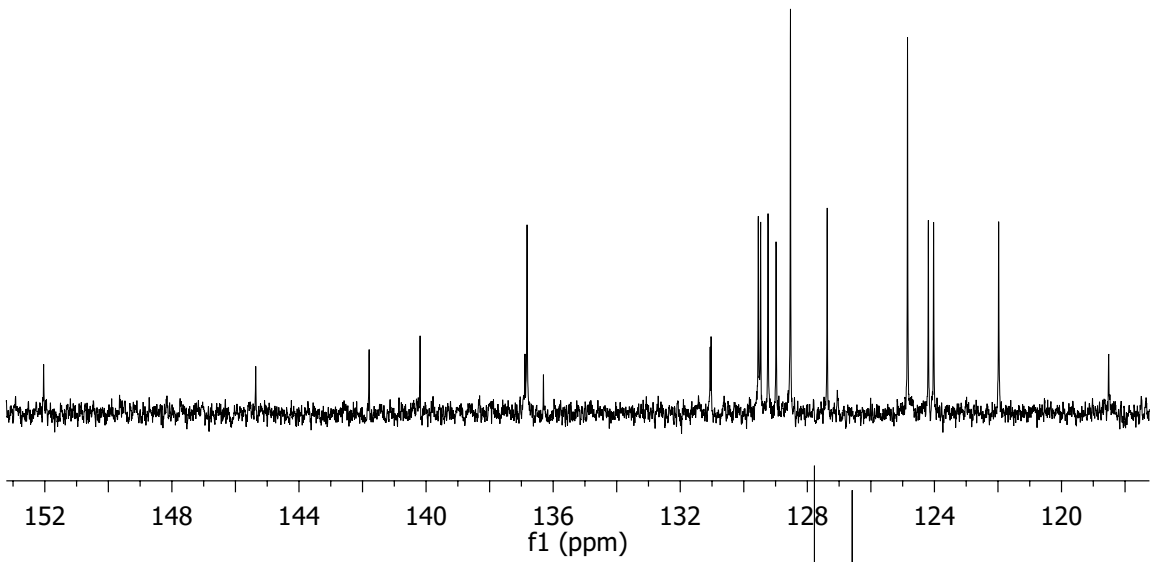
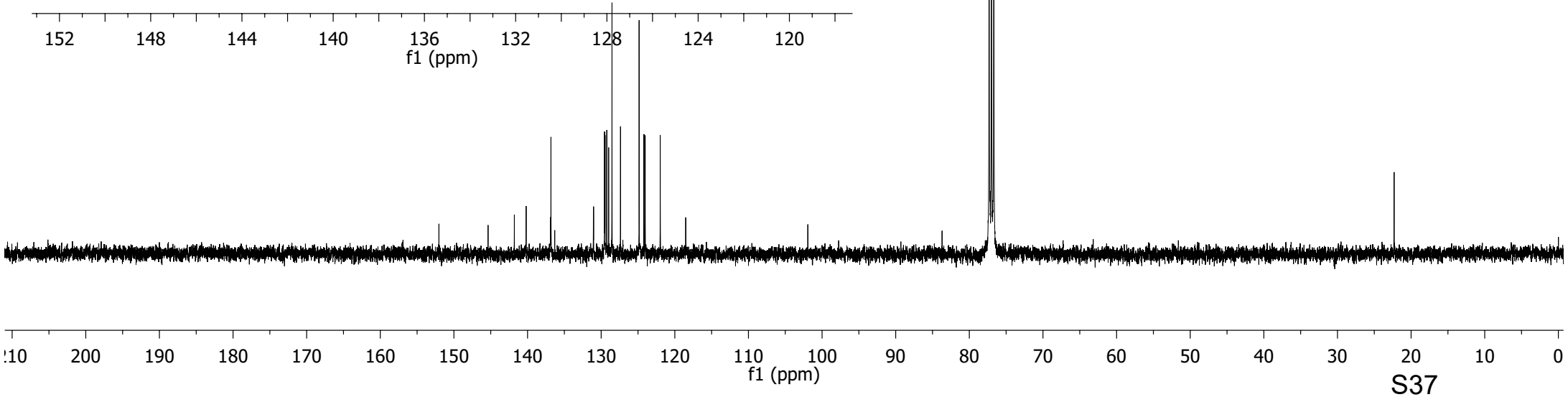
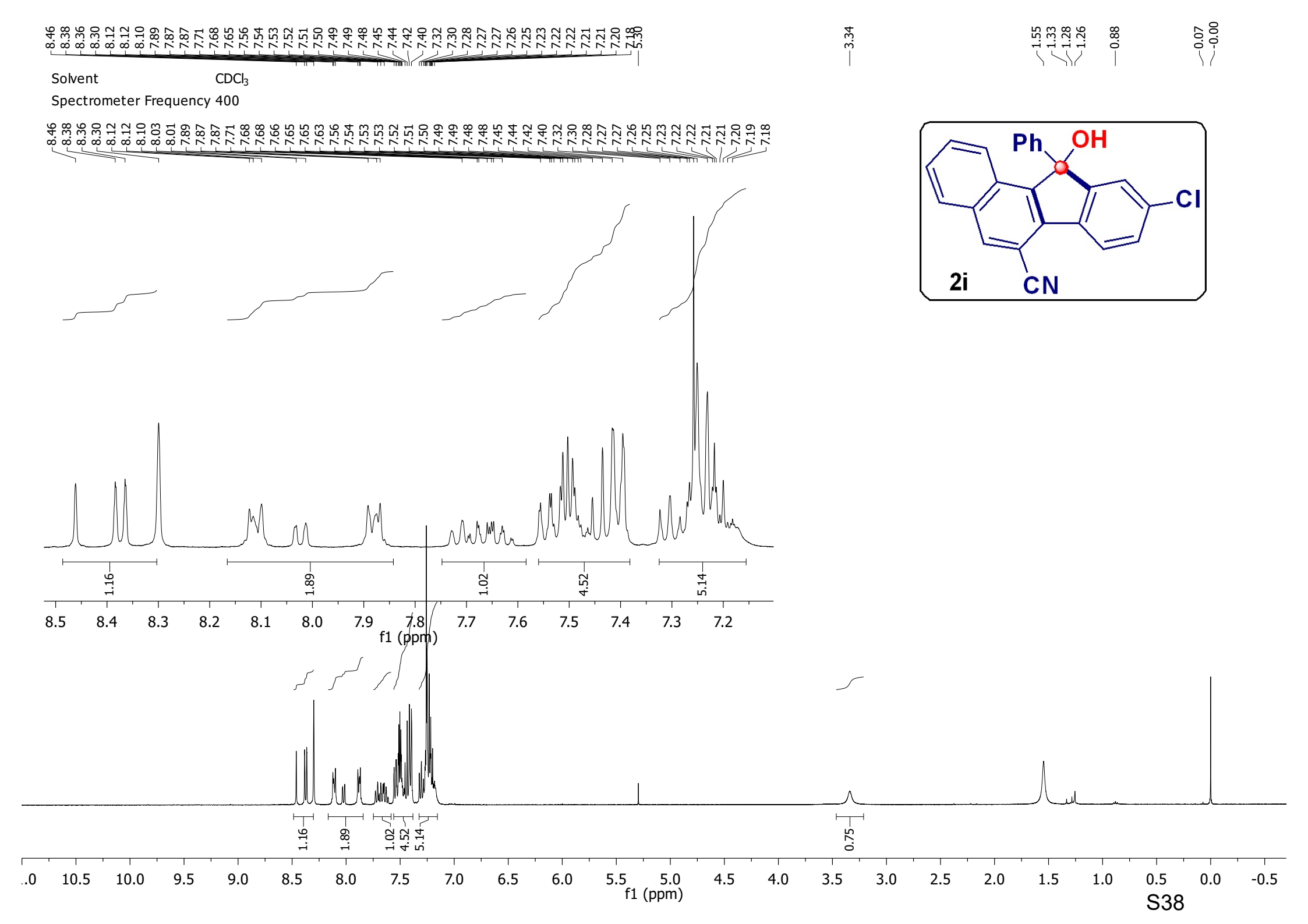






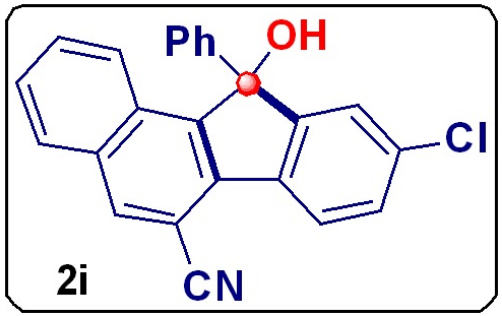

Solvent CDCl3
Spectrometer Frequency 400
Ph
OH
Cl
CN
2i
f1 (ppm)
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 100

147.22 146.59 137.38 136.32 131.20 129.99 129.91 129.36 129.15 128.90 128.60 128.26 128.18 127.46 127.35 125.62 124.93 120.45 102.83 85.04 77.31 76.99 76.68

147.22 146.59 140.02 139.58 137.38 136.32 133.96 132.88 131.20 130.75 130.49 130.40 129.99 129.91 129.51 129.36 129.15 128.90 128.70 128.60 128.26 128.18 127.46 127.35 125.91 125.62 124.93 120.45 118.16



148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118

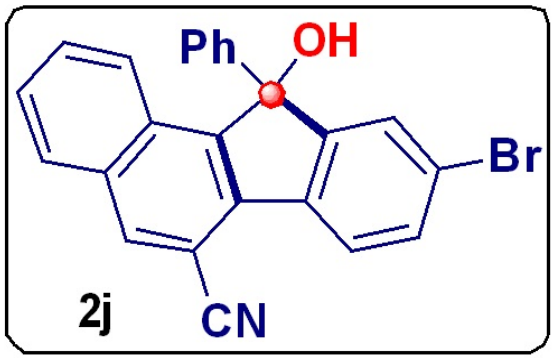
f1 (ppm)

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400



Solvent $CDCl_3$

Spectrometer Frequency 100

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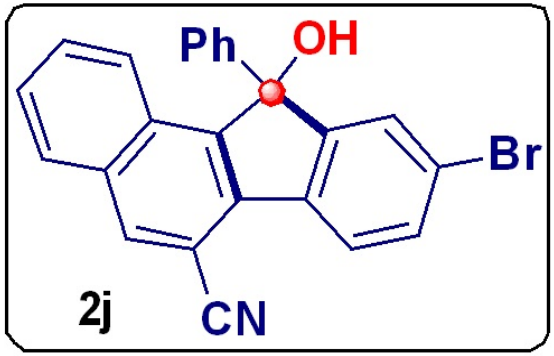
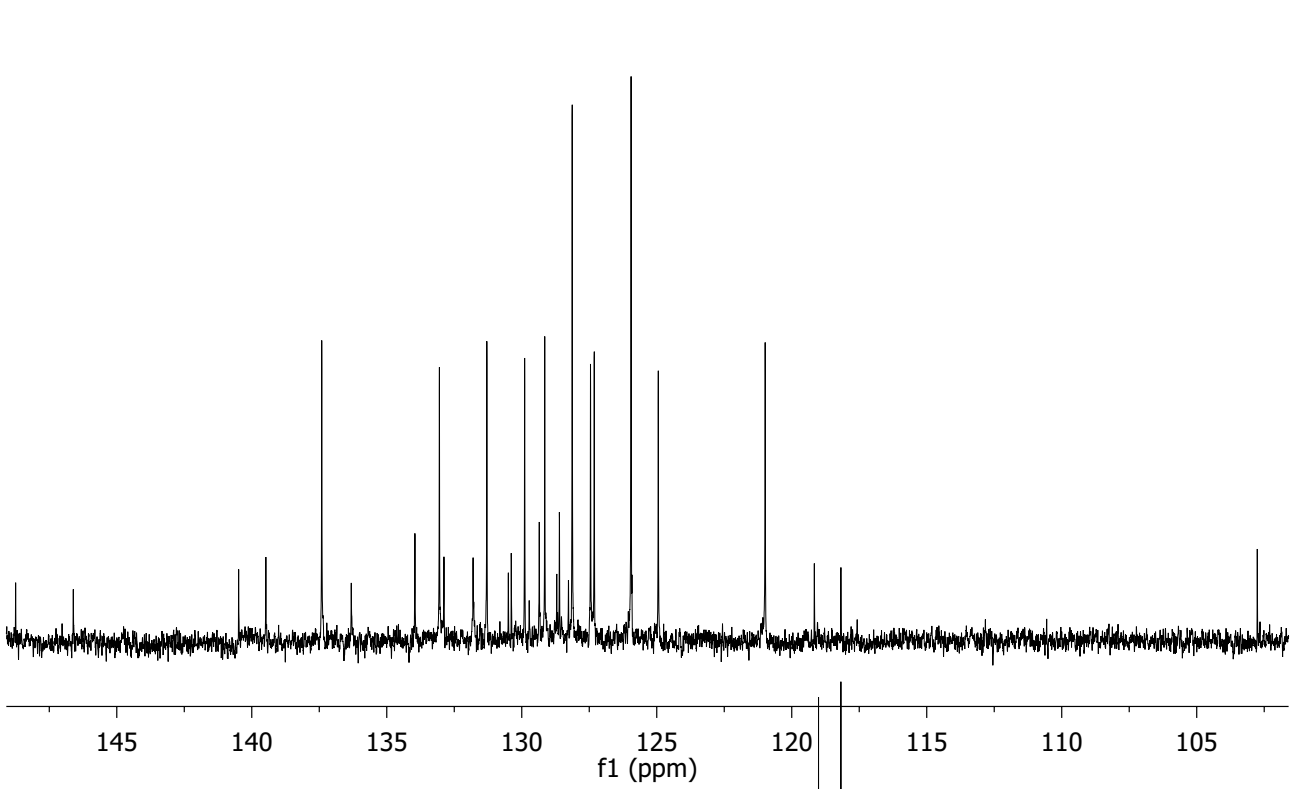
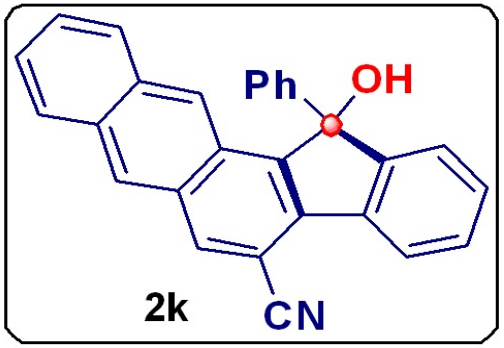
148.75 146.61 140.49 139.48 137.41 136.31 133.96 133.05 132.88 131.80 131.29 130.39 129.89 129.35 129.15 128.61 128.13 127.45 127.31 125.95 124.94 120.98 119.16 118.18 102.76





Solvent $CDCl_3$

Spectrometer Frequency 400



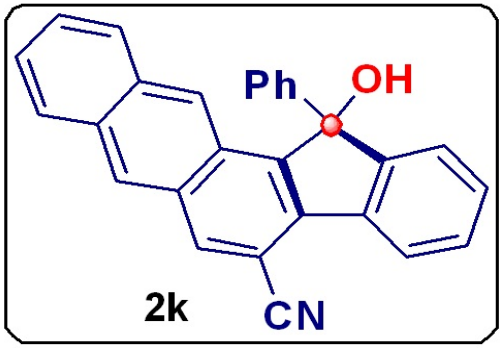
f1 (ppm)

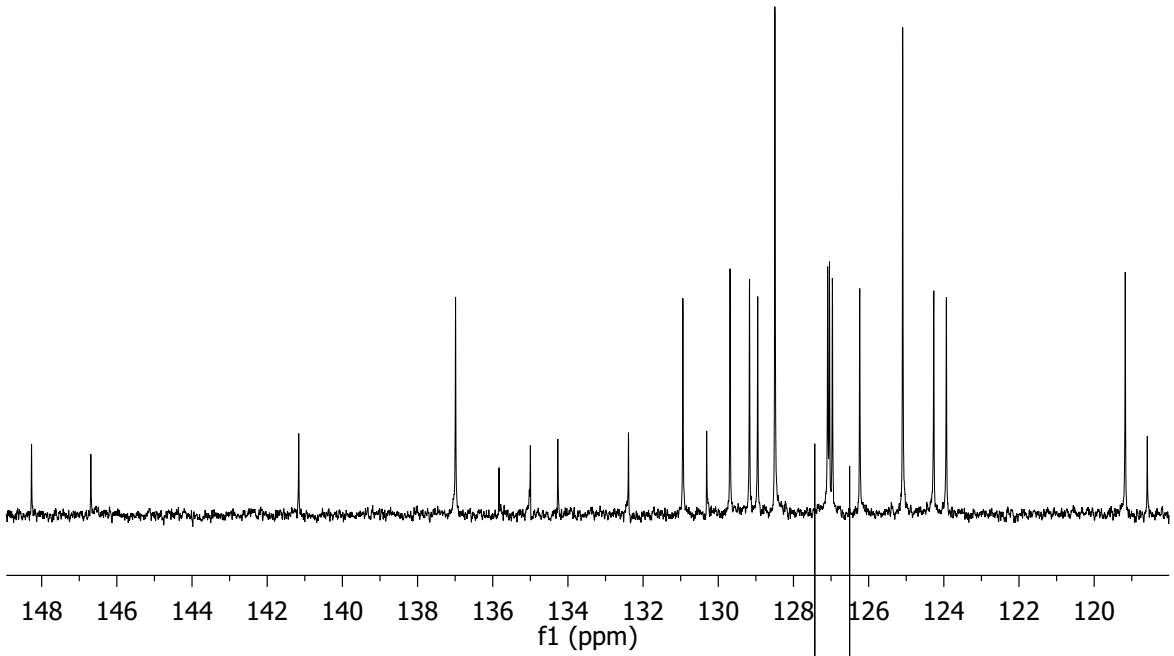
Solvent $CDCl_3$

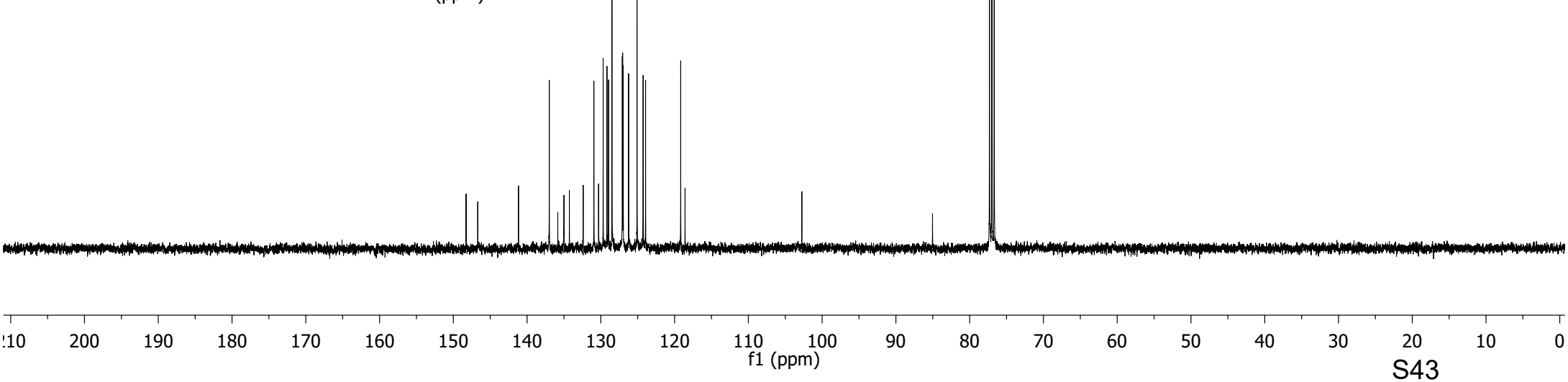
Spectrometer Frequency 100

148.27 146.69 136.99 132.39 130.94 130.31 129.69 129.17 128.95 128.49 127.09 127.04 126.96 126.24 125.09 124.27 123.93 119.17 102.75 85.04 77.31 76.99 76.68

148.27 146.69 141.16 136.99 135.83 135.00 134.27 132.39 130.94 130.31 129.69 129.17 128.95 128.49 127.09 127.04 126.96 126.24 125.09 124.27 123.93 119.17 118.59

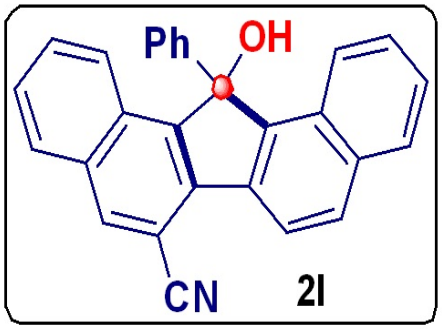






Solvent $CDCl_3$

Spectrometer Frequency 597



f1 (ppm)

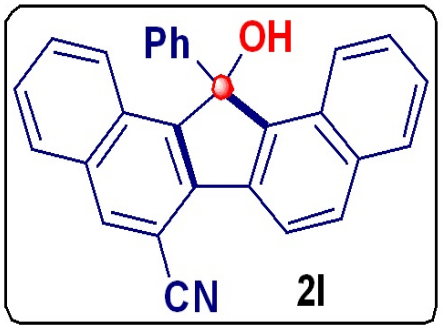
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 100

151.46 137.41 131.43 129.80 129.36 129.34 129.26 128.63 128.55 128.41 128.22 128.16 128.07 127.48 127.04 126.02 124.31 124.17 122.11 103.10 85.30 77.31 76.99 76.67

151.46 145.91 141.09 140.29 137.64 137.41 131.43 129.80 129.36 129.34 129.26 128.63 128.55 128.41 128.22 128.16 128.07 127.52 127.48 127.04 126.92 124.31 124.17 122.11 118.42



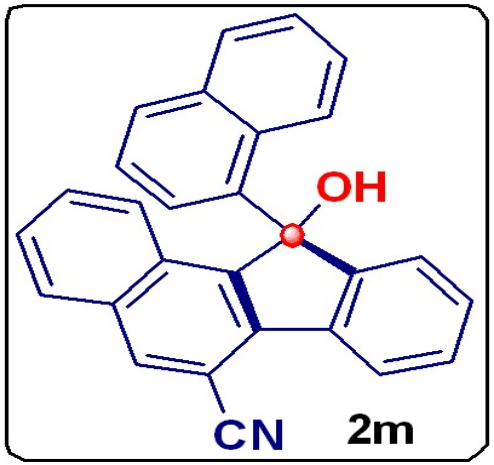
2l

150 145 140 135 130 125 120
f1 (ppm)

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 597



f1 (ppm)

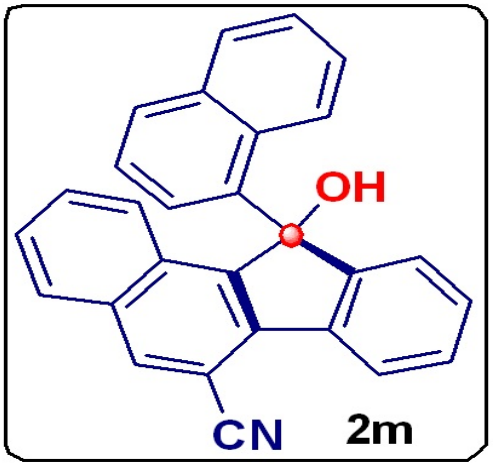
f1 (ppm)

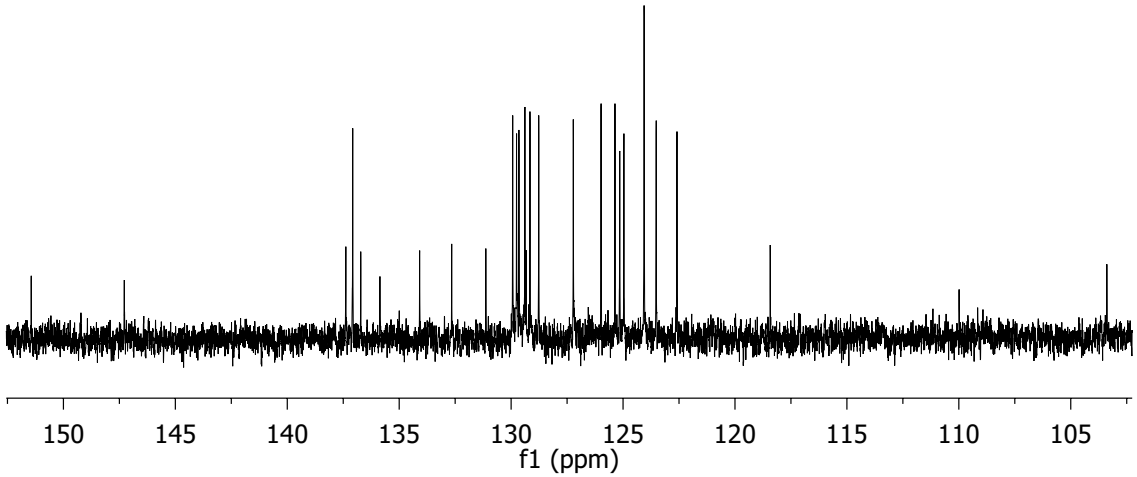
Solvent $CDCl_3$

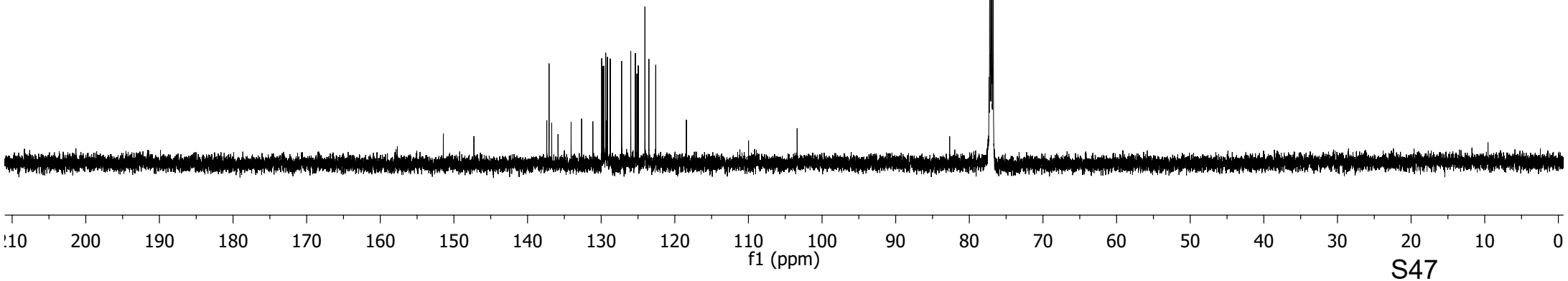
Spectrometer Frequency 150

151.39 147.19 137.08 129.93 129.76 129.65 129.39 129.16 128.77 127.22 125.98 125.36 124.96 124.06 123.52 122.59 110.07 103.39 82.65 77.20 76.99 76.78

151.39 147.19 137.38 137.08 136.72 135.86 134.09 132.65 131.13 129.93 129.76 129.65 129.39 129.16 128.77 127.22 125.98 125.36 125.15 124.96 124.06 123.52 122.59 118.43 110.07 103.39

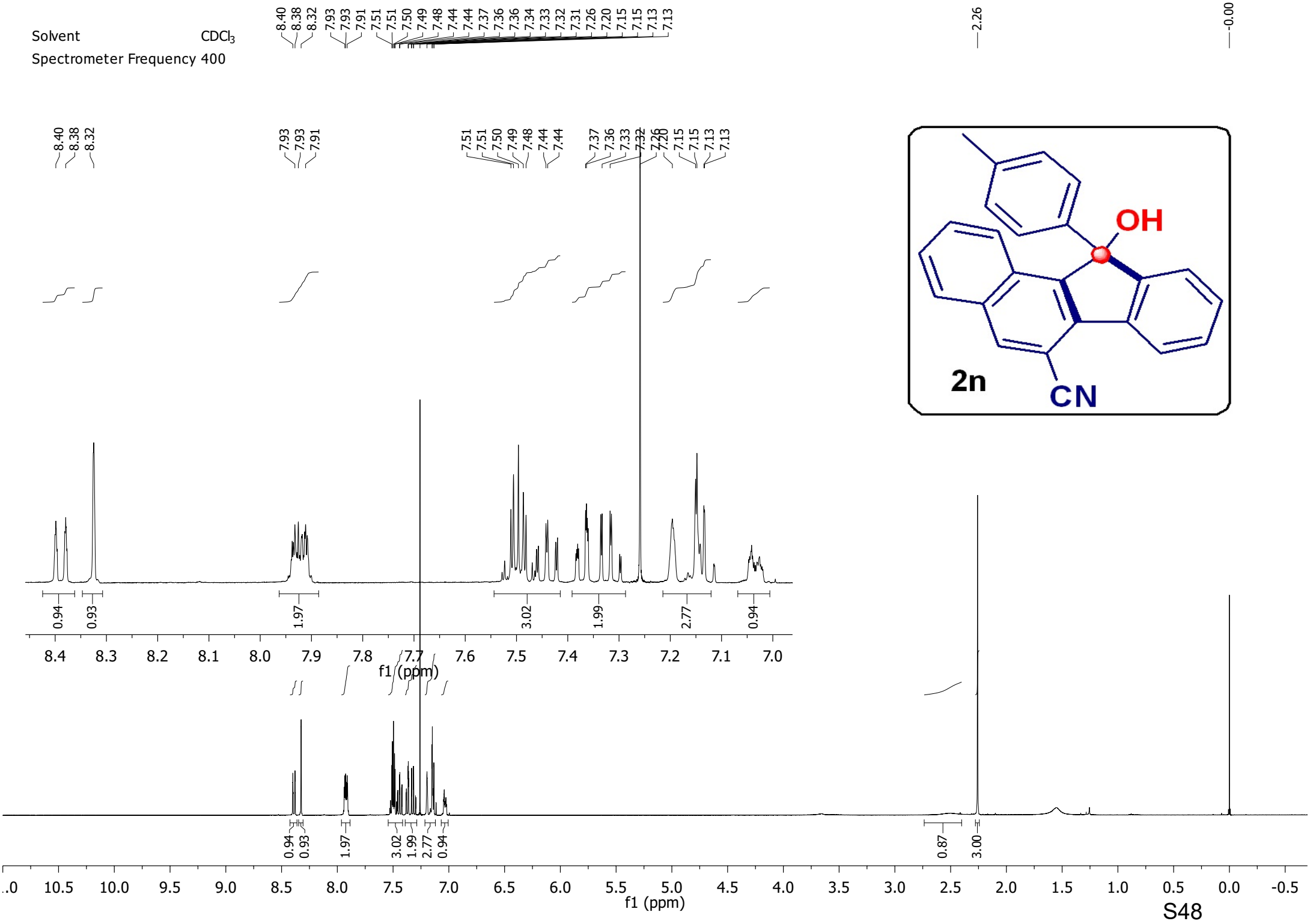






Solvent $CDCl_3$

Spectrometer Frequency 400

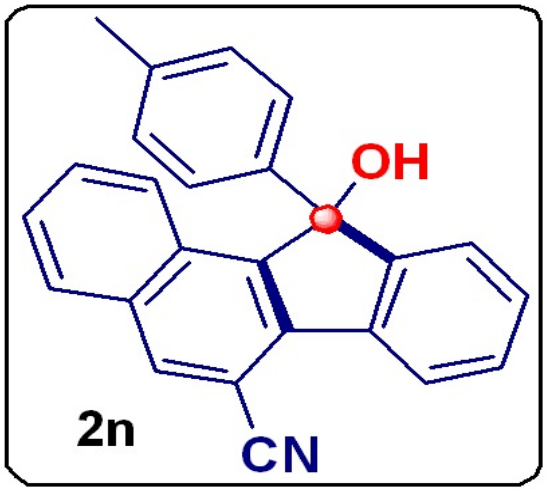


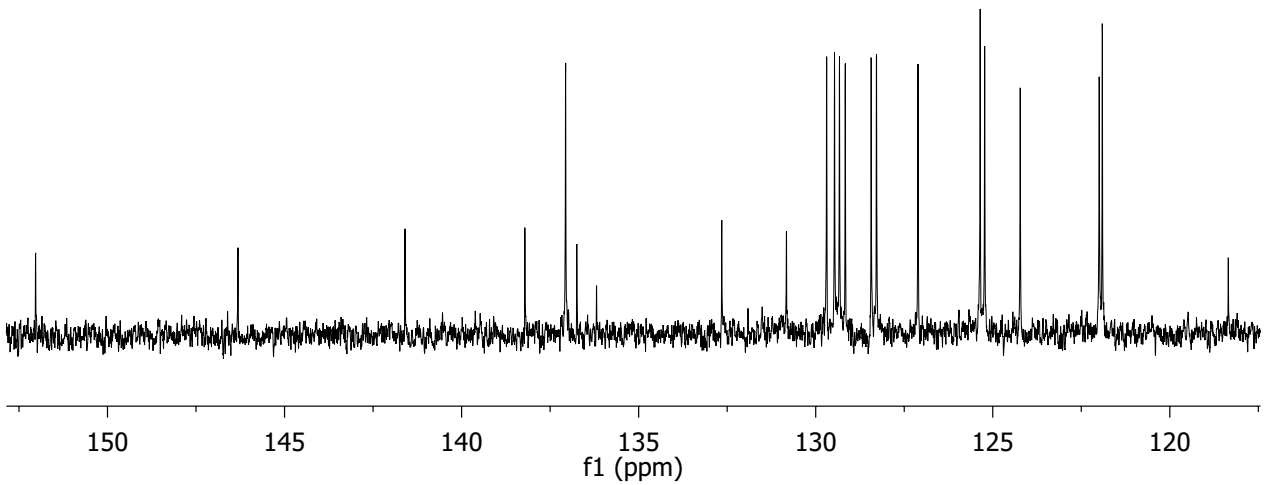
Solvent $CDCl_3$

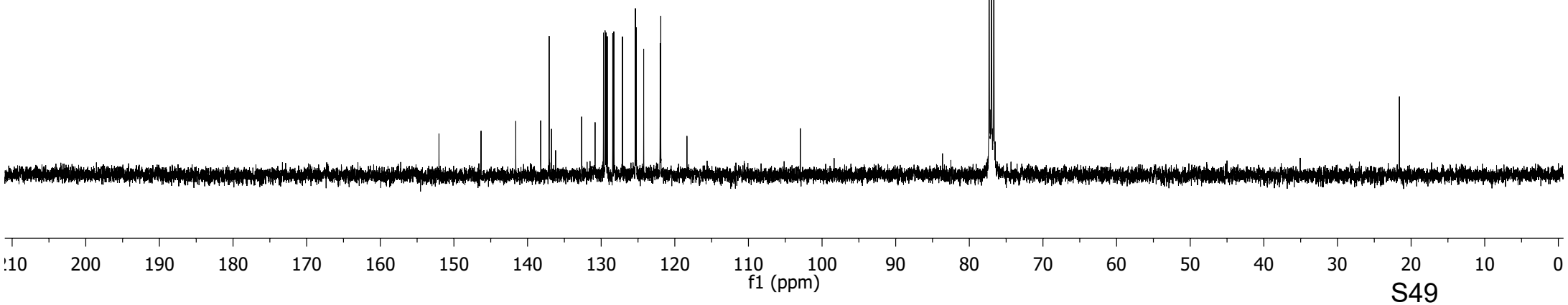
Spectrometer Frequency 100

152.03 141.60 138.21 137.06 136.75 132.65 130.83 129.69 129.47 129.33 129.17 128.43 128.28 127.11 125.36 125.23 124.22 121.99 121.91 102.95 83.56 77.31 76.99 76.67 21.59

152.03 146.32 141.60 138.21 137.06 136.75 136.32 132.65 130.83 129.69 129.47 129.33 129.17 128.43 128.28 127.11 125.36 125.23 124.22 121.99 121.91 118.35

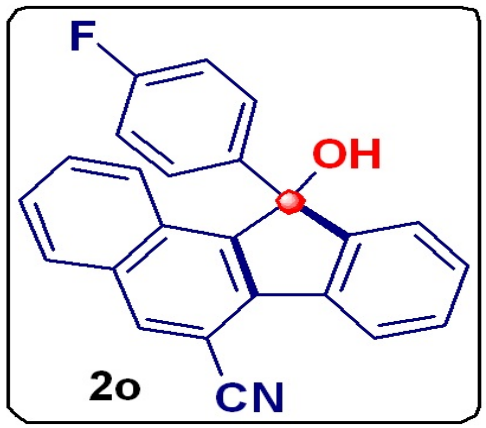






Solvent $CDCl_3$

Spectrometer Frequency 597

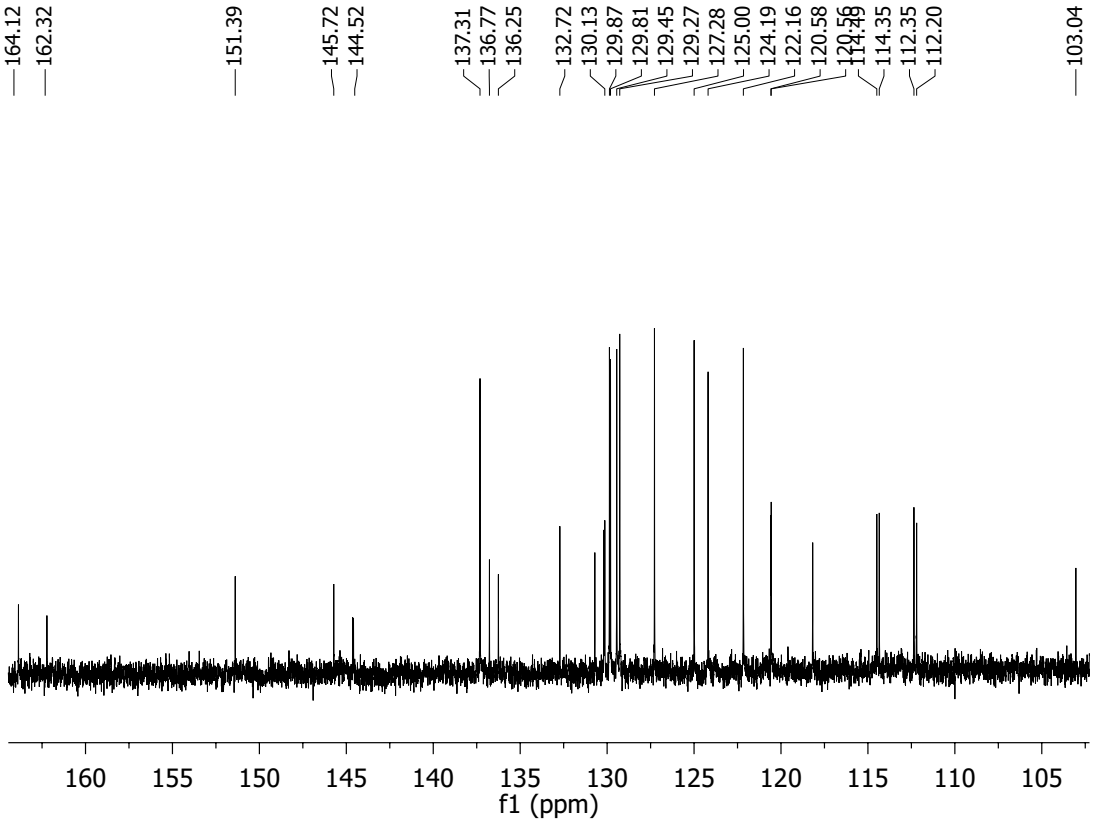


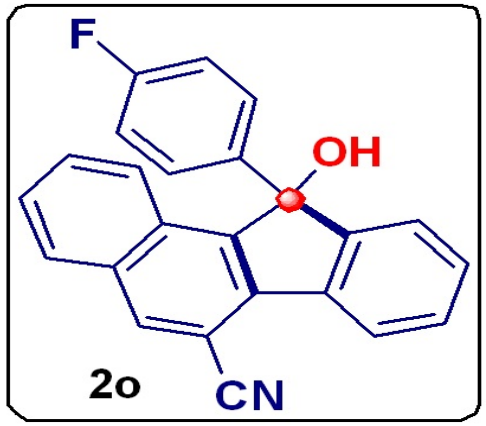
f1 (ppm)

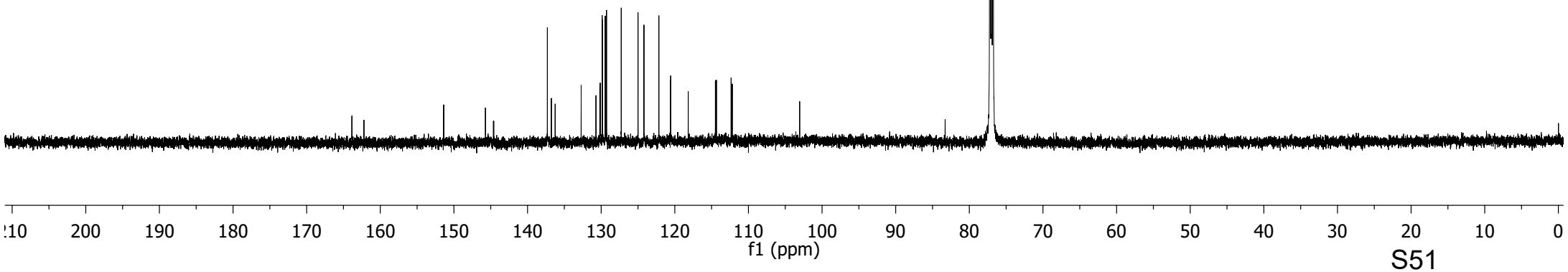
Solvent $CDCl_3$

Spectrometer Frequency 150

164.12 162.32 151.39 145.72 144.52 137.31 130.13 129.87 129.81 129.45 129.27 127.28 125.00 124.19 122.16 120.58 120.56 114.49 114.35 112.35 103.04 83.18 77.20 76.99 76.78

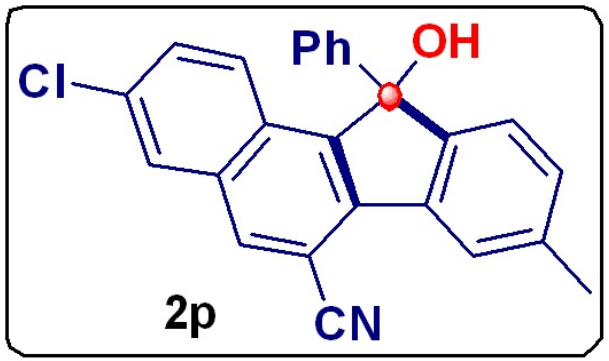






Solvent $CDCl_3$

Spectrometer Frequency 400



f1 (ppm)

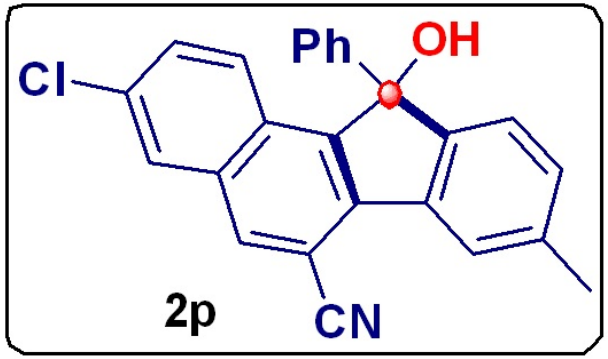
f1 (ppm)

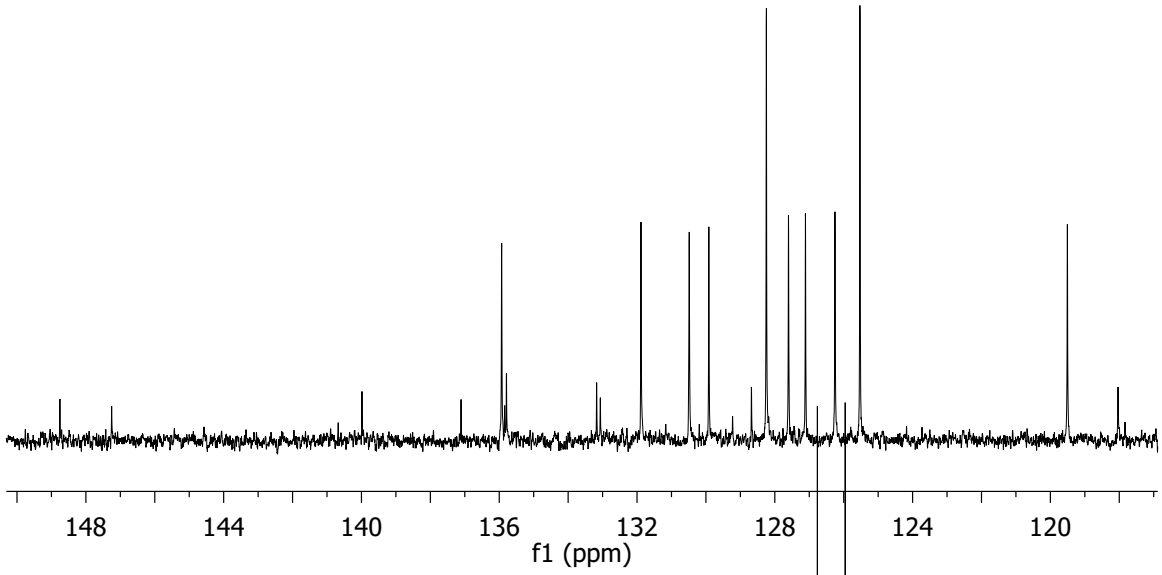
Solvent $CDCl_3$

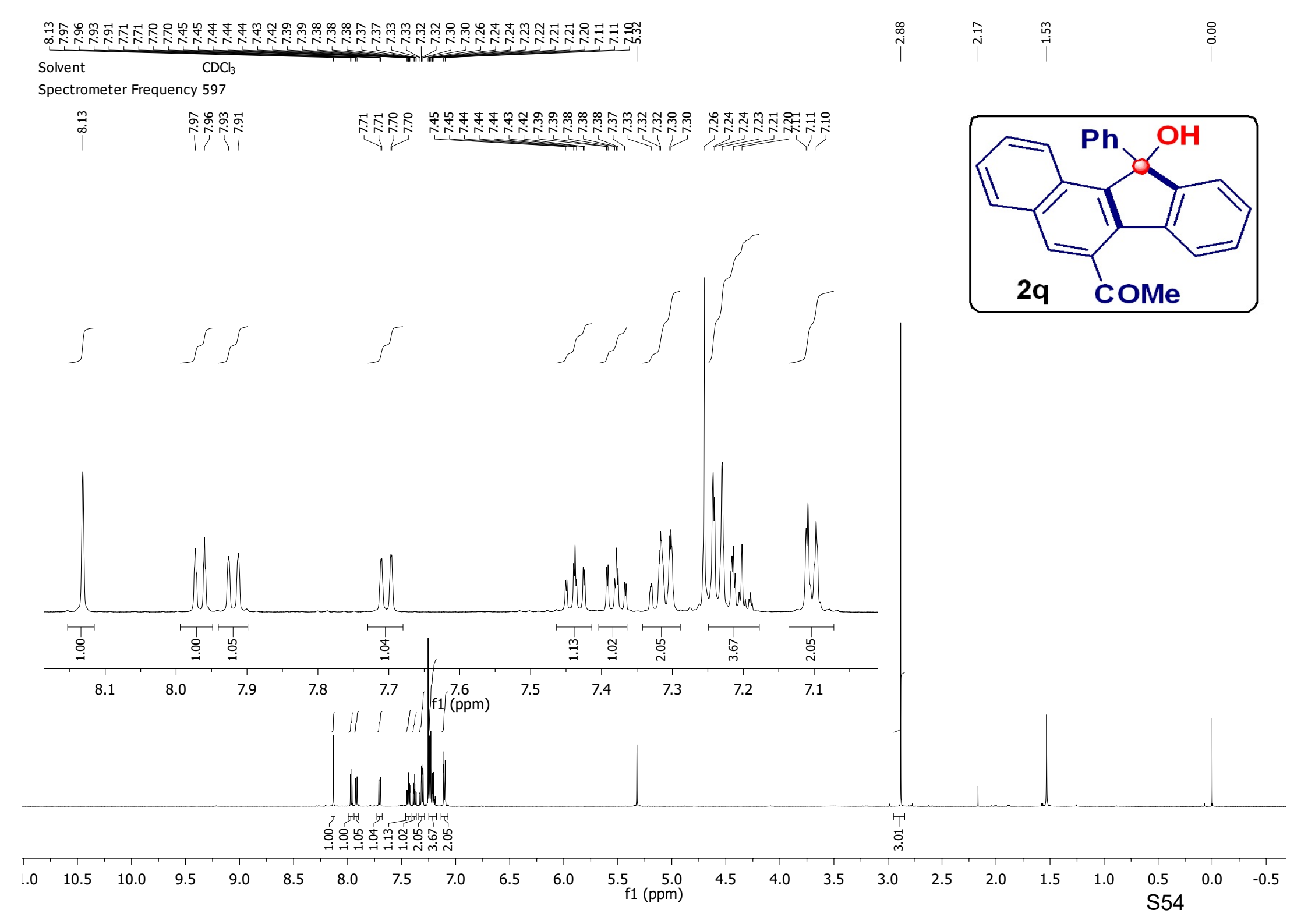
Spectrometer Frequency 100

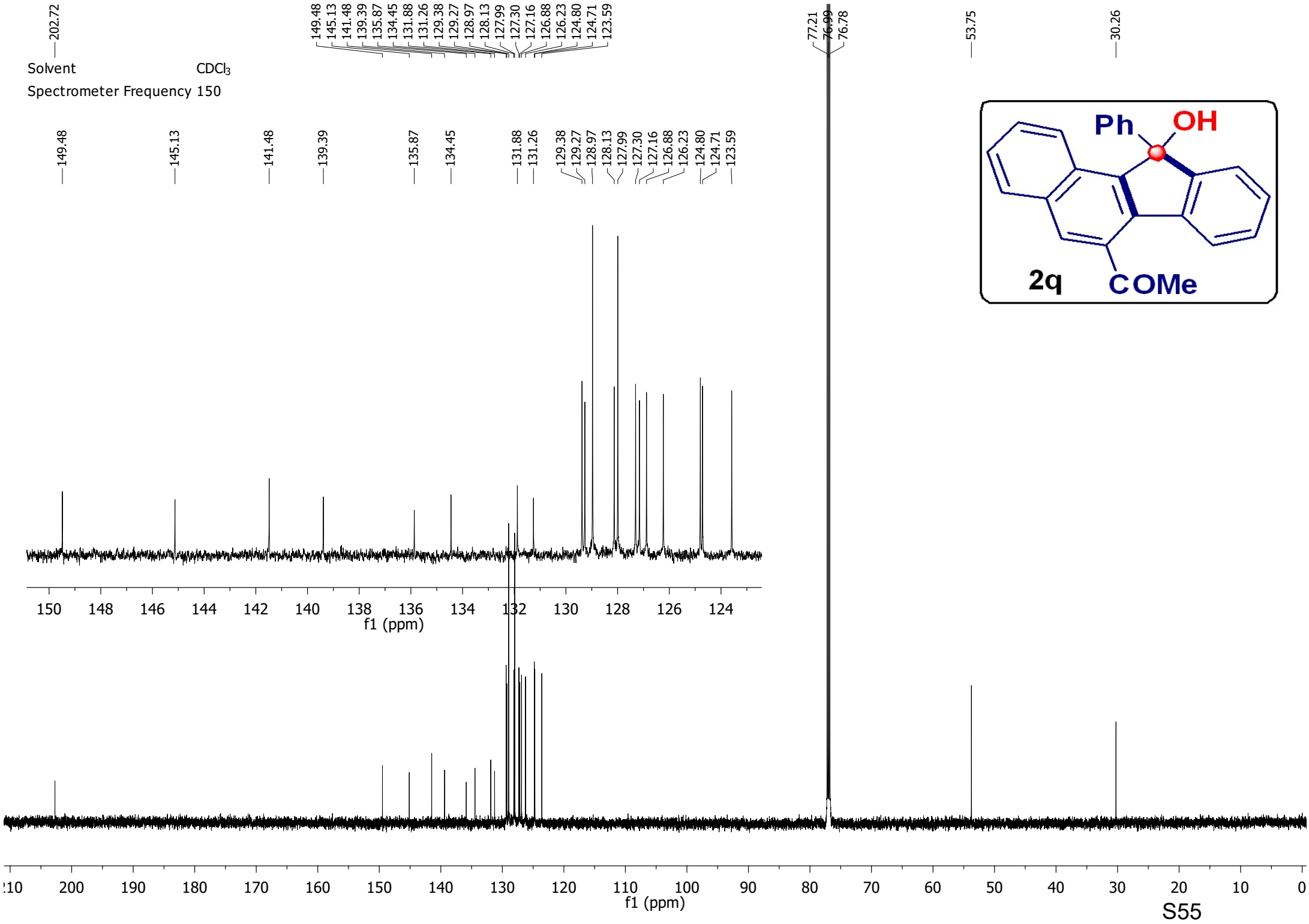
148.75 147.36 135.93 131.89 130.48 129.92 128.25 127.60 127.11 126.25 125.53 119.51 118.04 104.00 84.47 77.32 77.00 76.68 17.49

148.75 147.36 139.98 137.11 137.07 135.93 135.79 133.17 133.07 131.89 130.48 129.92 128.71 128.68 128.25 127.60 127.11 126.25 125.53 119.51 118.04



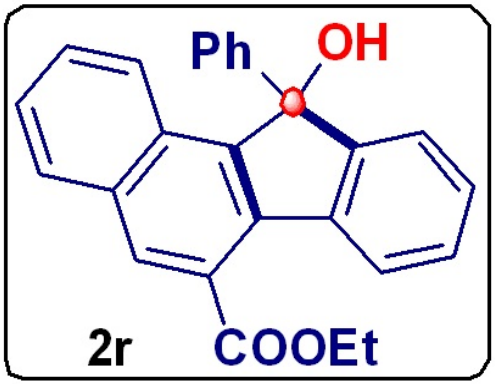



Solvent CDCl3
Spectrometer Frequency 597
Ph
OH
2q
COMe
f1 (ppm)


202.72
149.48
145.13
141.48
139.39
135.87
134.45
131.88
131.26
129.38
129.27
128.97
128.13
127.99
127.30
127.16
126.88
126.23
124.80
124.71
123.59
77.21
76.99
76.78
53.75
30.26
Solvent CDCl3
Spectrometer Frequency 150
Ph
OH
2q
COMe
f1 (ppm)
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400



Solvent $CDCl_3$

Spectrometer Frequency 100

168.45

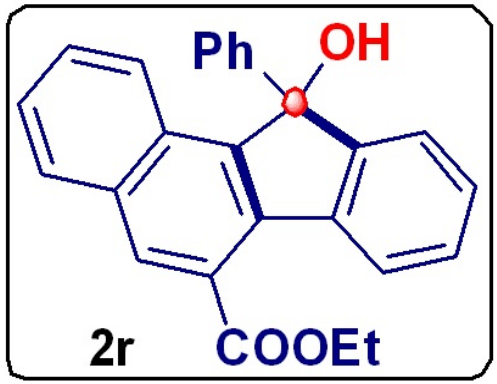
149.47 144.82 141.60 139.44 131.90 131.48 131.38 129.51 128.96 128.14 127.98 127.25 127.10 126.85 126.08 125.54 124.73 124.63 124.02

77.31 76.99 76.68

61.53

53.74

14.41

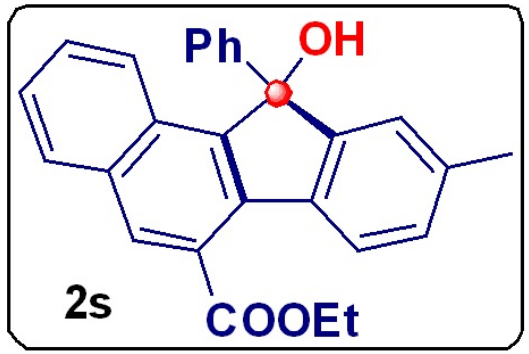


f1 (ppm)

f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400

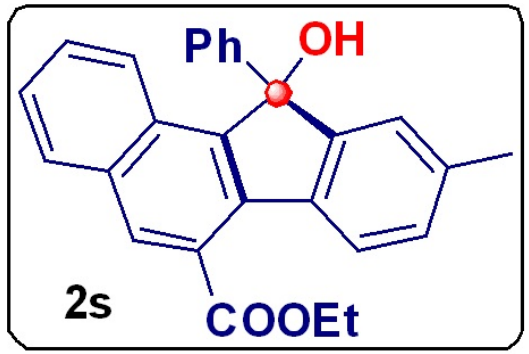


f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 100

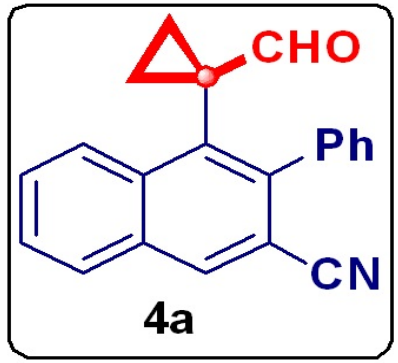
168.17
152.46
142.67
138.61
137.98
134.57
132.90
131.20
131.01
130.68
130.57
130.28
130.20
129.68
129.23
128.86
128.82
128.37
128.27
127.02
126.31
124.96
124.86
124.57
124.05
123.84
120.52
118.16
83.50
77.31
77.19
76.99
76.68
61.51
22.56
22.24
14.40



f1 (ppm)

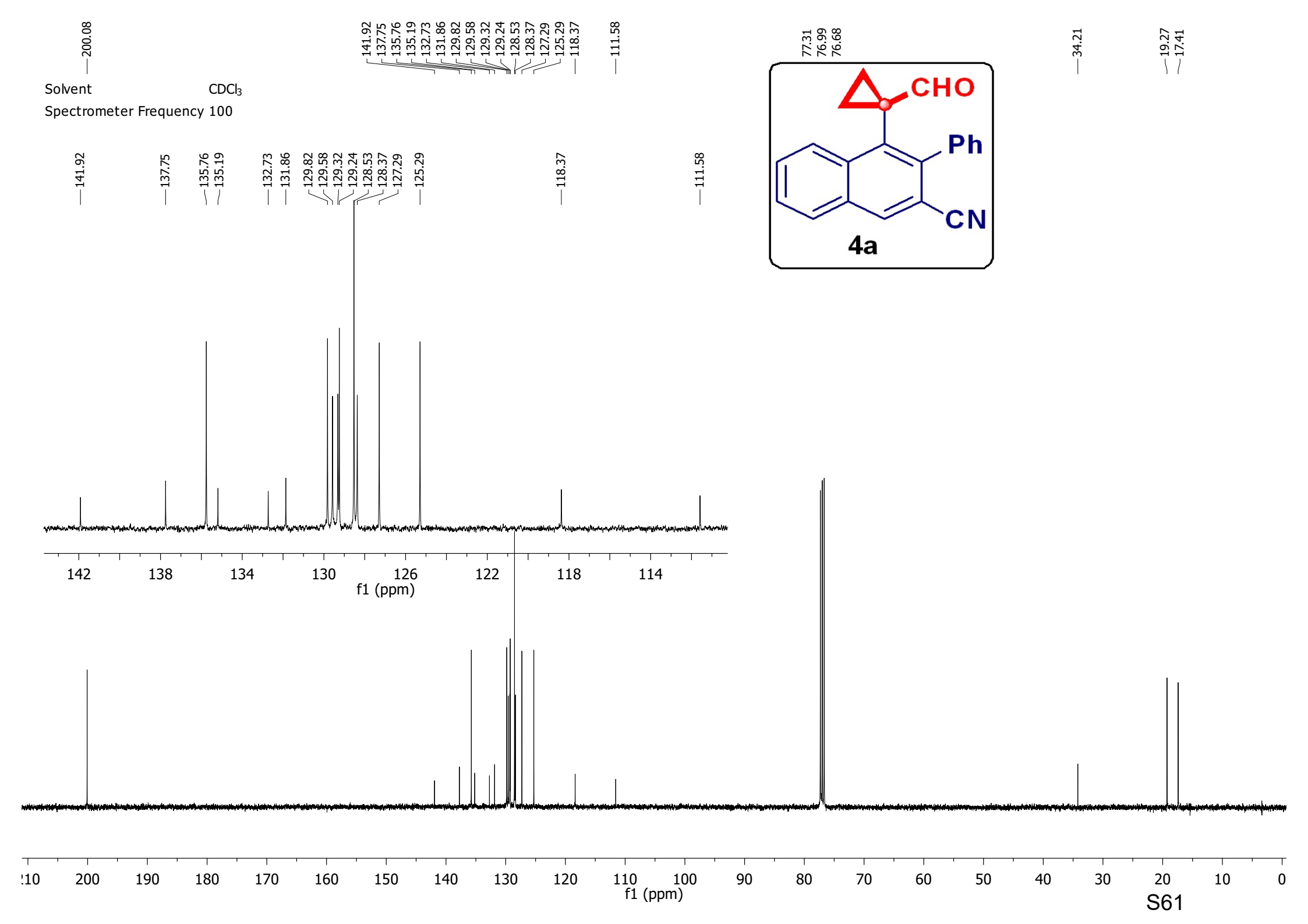
Solvent $CDCl_3$

Spectrometer Frequency 400



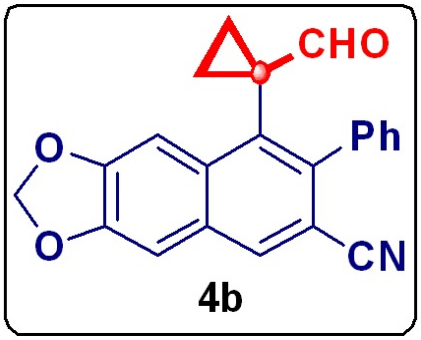
4a

f1 (ppm)


200.08
141.92
137.75
135.76
135.19
132.73
131.86
129.82
129.58
129.32
129.24
128.53
128.37
127.29
125.29
118.37
111.58
77.31
76.99
76.68
34.21
19.27
17.41
Solvent CDCl3
Spectrometer Frequency 100
CHO
Ph
CN
4a
f1 (ppm)
f1 (ppm)

Solvent DMSO-d_6 + $CDCl_3$

Spectrometer Frequency 400



4b

199.68

150.46 148.04 140.30 137.42 133.23 132.99 131.01 128.87 128.78 127.82 127.78 127.73 118.18 108.86 104.04 101.51 101.31

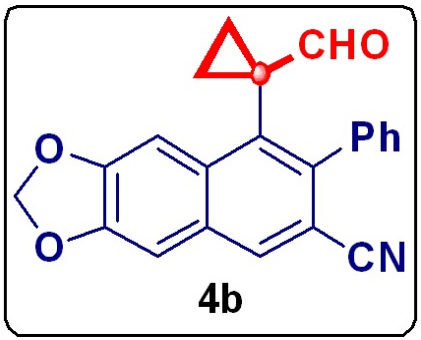
77.32 77.00 76.67

39.84 39.63 39.42 39.21 39.00 34.13

18.40 16.93

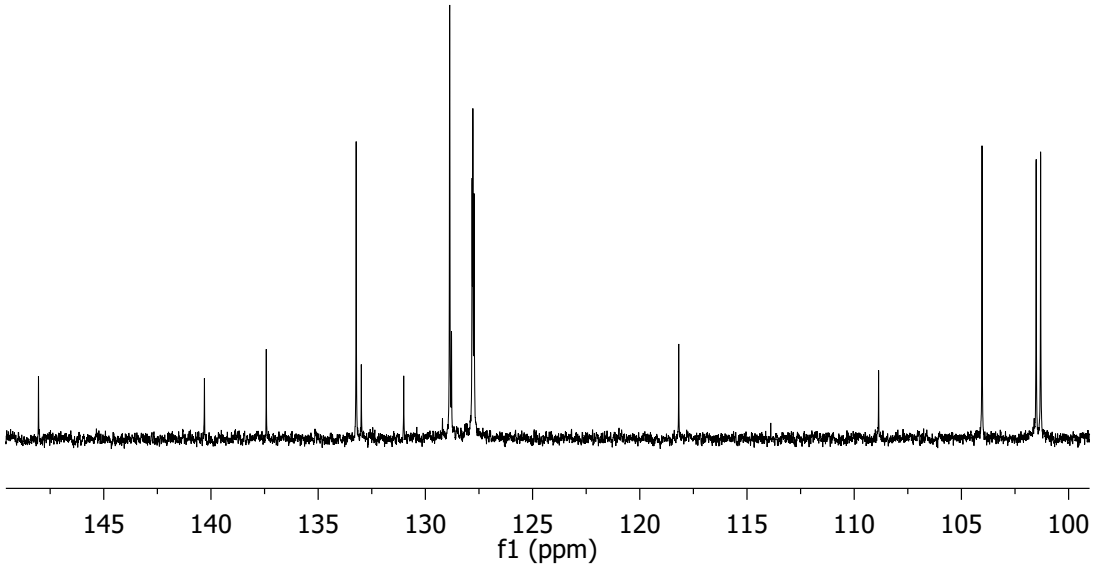
Solvent DMSO-d_6 + $CDCl_3$

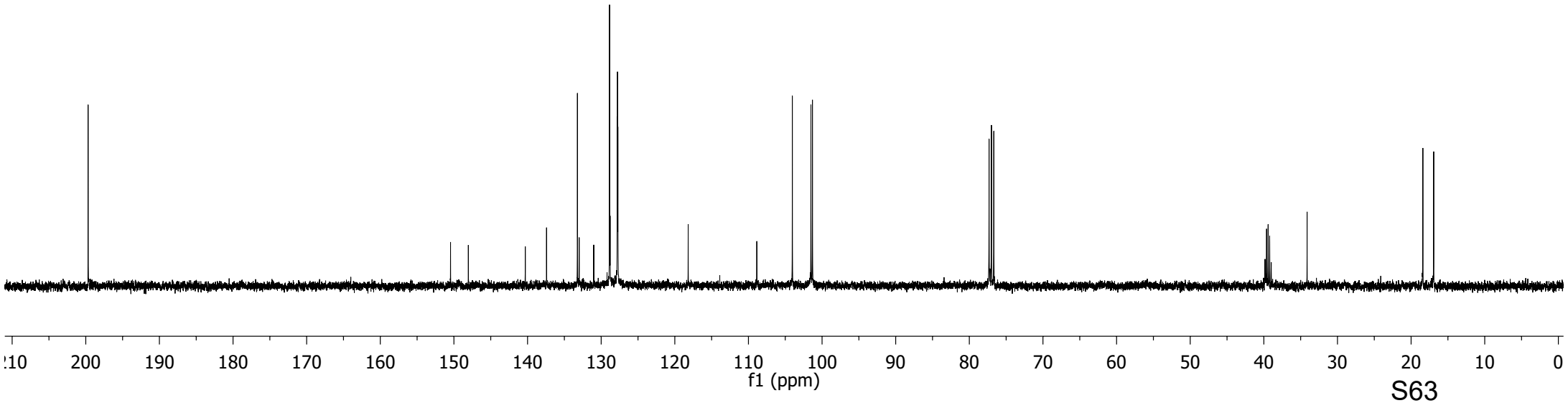
Spectrometer Frequency 100



4b

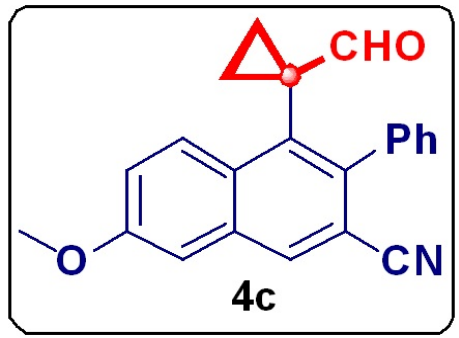
148.04 140.30 137.42 133.23 132.99 131.01 128.87 128.78 127.82 127.78 127.73 118.18 108.86 104.04 101.51 101.31



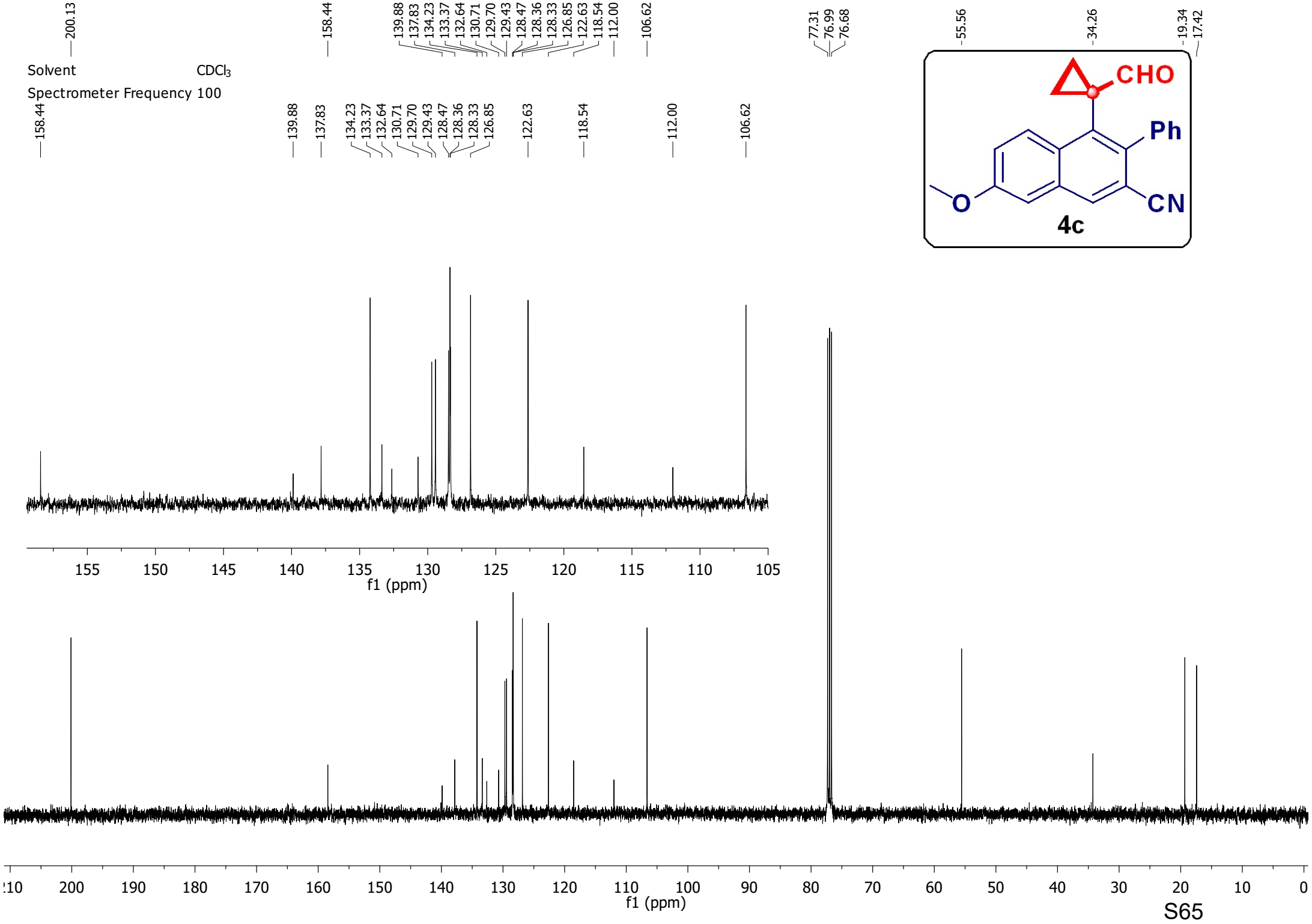


Solvent $CDCl_3$

Spectrometer Frequency 400

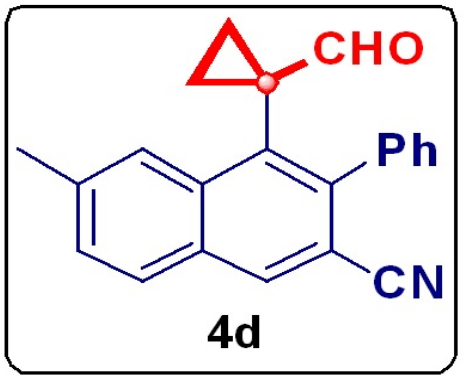


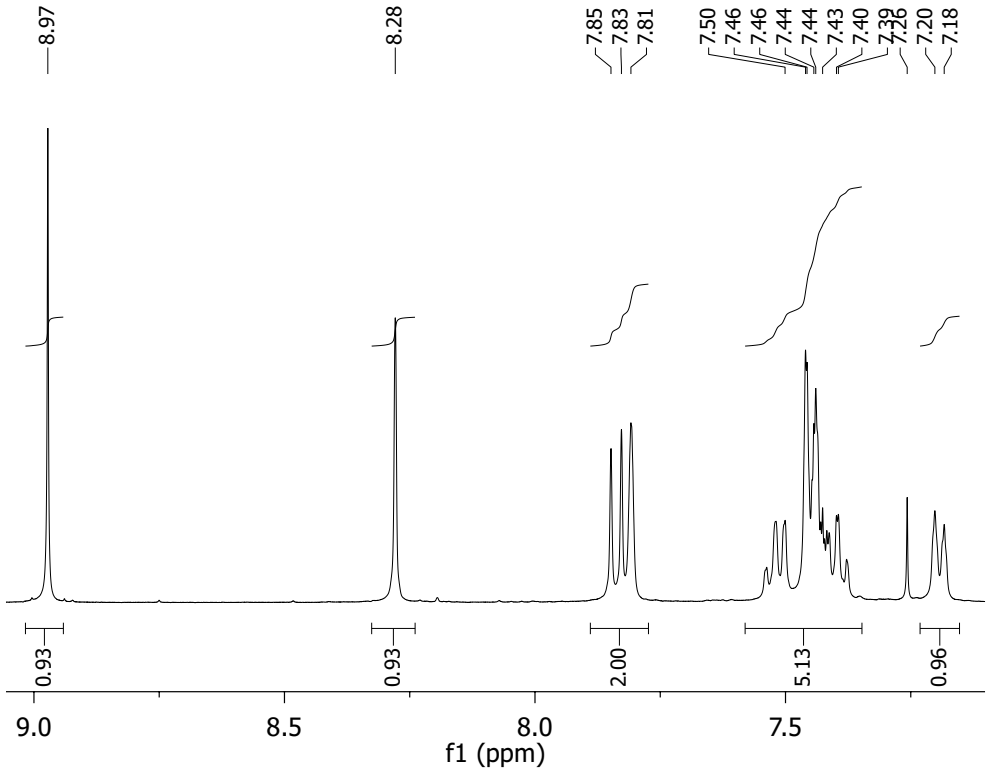
f1 (ppm)

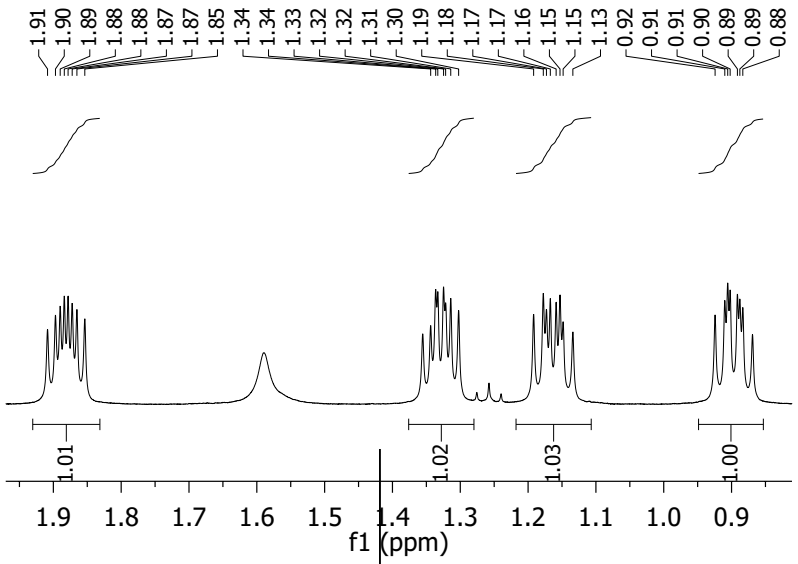

200.13
158.44
139.88
137.83
134.23
133.37
132.64
130.71
129.70
129.43
128.47
128.36
128.33
126.85
122.63
118.54
112.00
106.62
77.31
76.99
76.68
55.56
34.26
19.34
17.42
Solvent CDCl3
Spectrometer Frequency 100
CHO
Ph
CN
O
4c
f1 (ppm)
f1 (ppm)

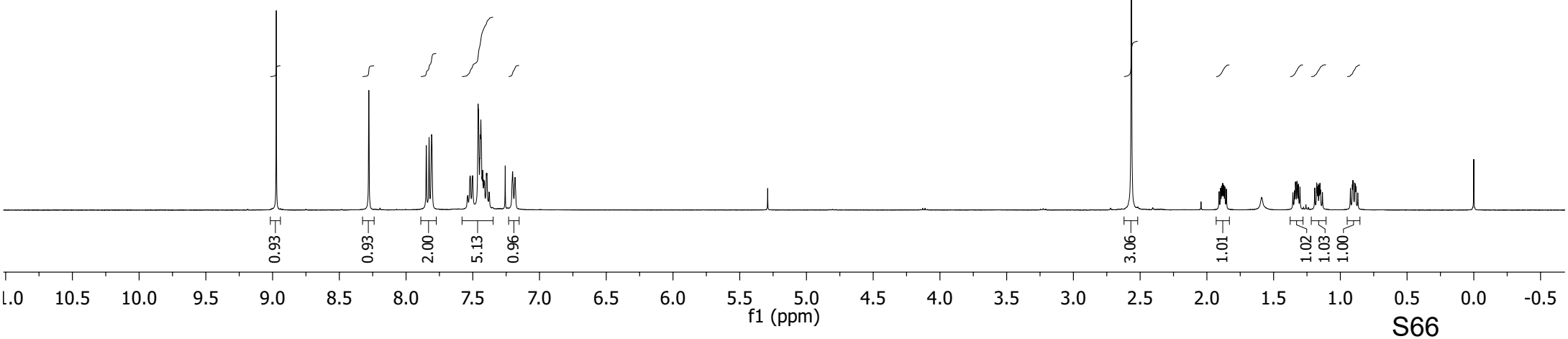
Solvent $CDCl_3$

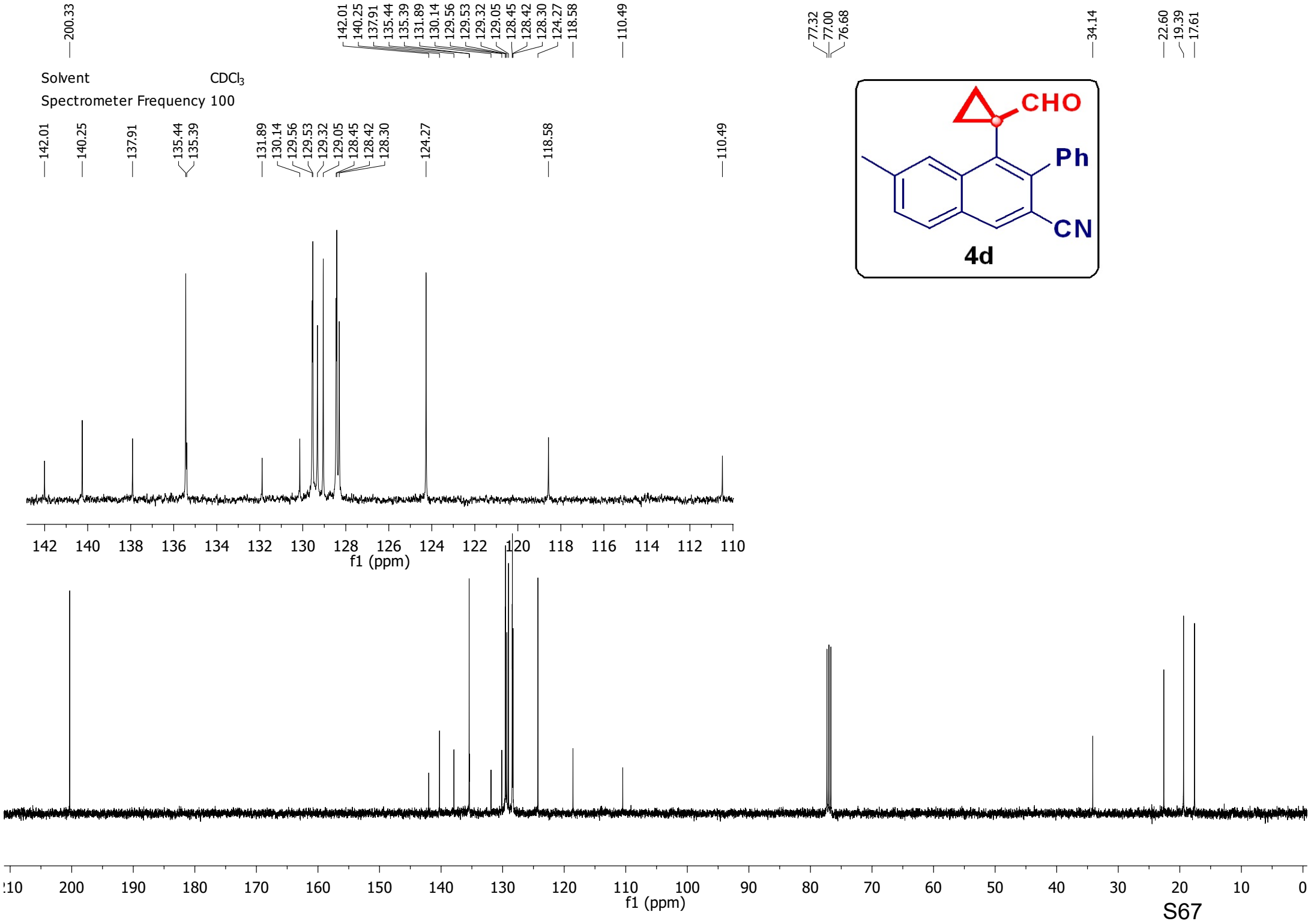
Spectrometer Frequency 400





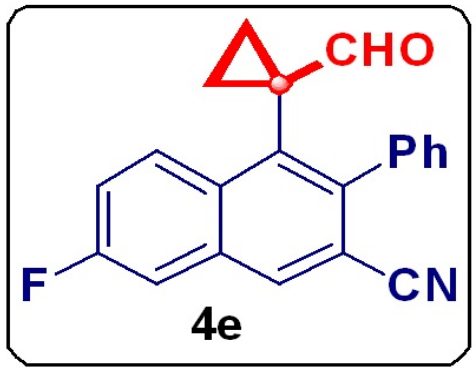





200.33
142.01
140.25
137.91
135.44
135.39
131.89
130.14
129.56
129.53
129.32
129.05
128.45
128.42
128.30
124.27
118.58
110.49
77.32
77.00
76.68
34.14
22.60
19.39
17.61
Solvent CDCl3
Spectrometer Frequency 100
CHO
Ph
CN
4d
f1 (ppm)
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400

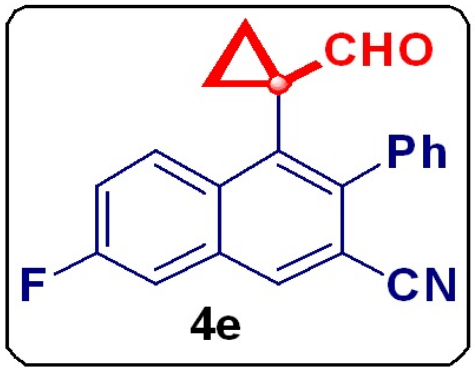


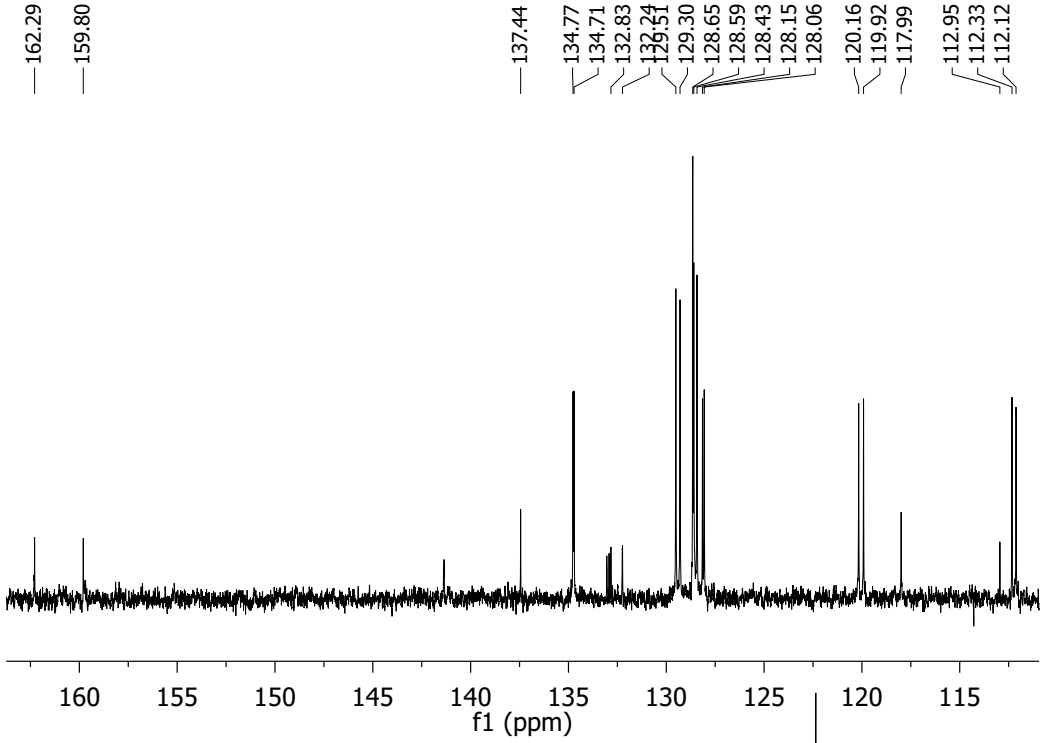
f1 (ppm)

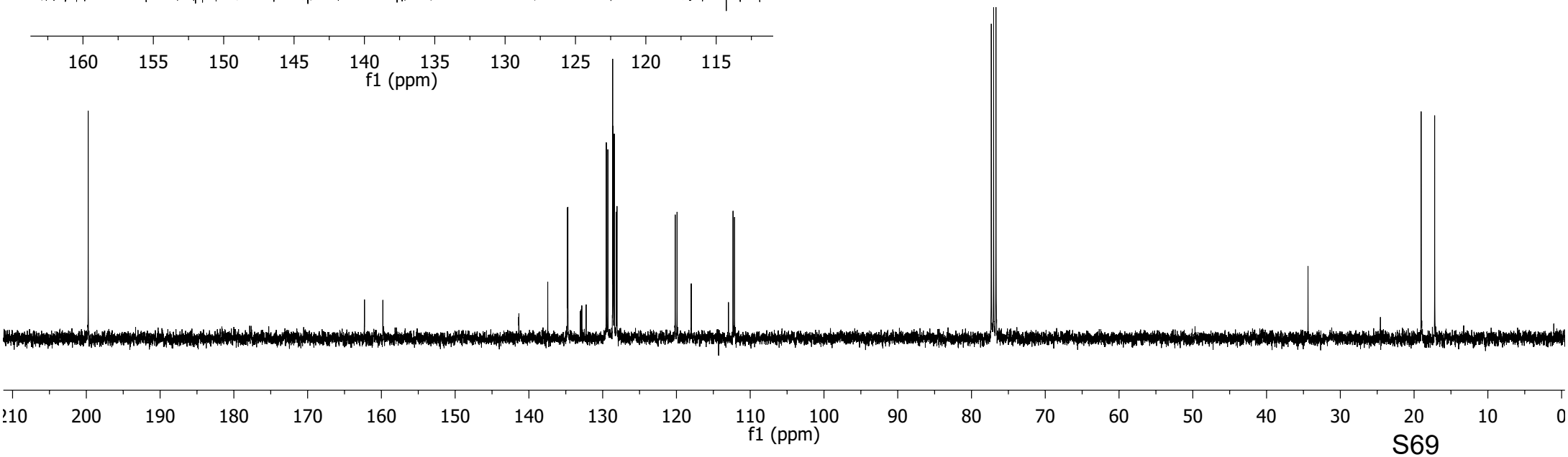
199.75
162.29
159.80
137.44
134.77
134.71
132.92
132.83
132.24
129.51
129.30
128.65
128.59
128.43
128.15
128.06
120.16
119.92
117.99
112.95
112.33
112.12
77.32
77.00
76.68
34.38
19.04
17.21

Solvent $CDCl_3$

Spectrometer Frequency 100

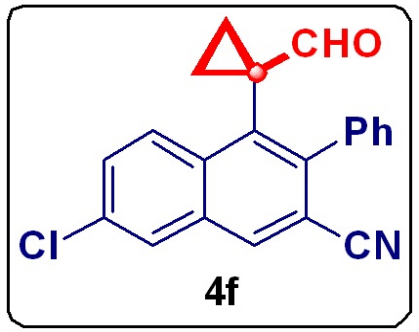






Solvent $CDCl_3$

Spectrometer Frequency 400

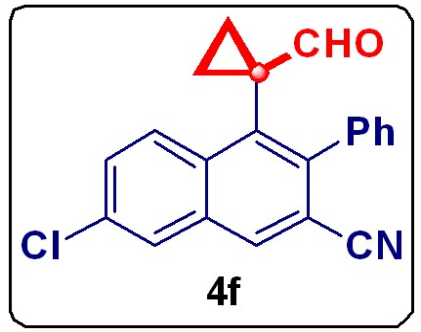


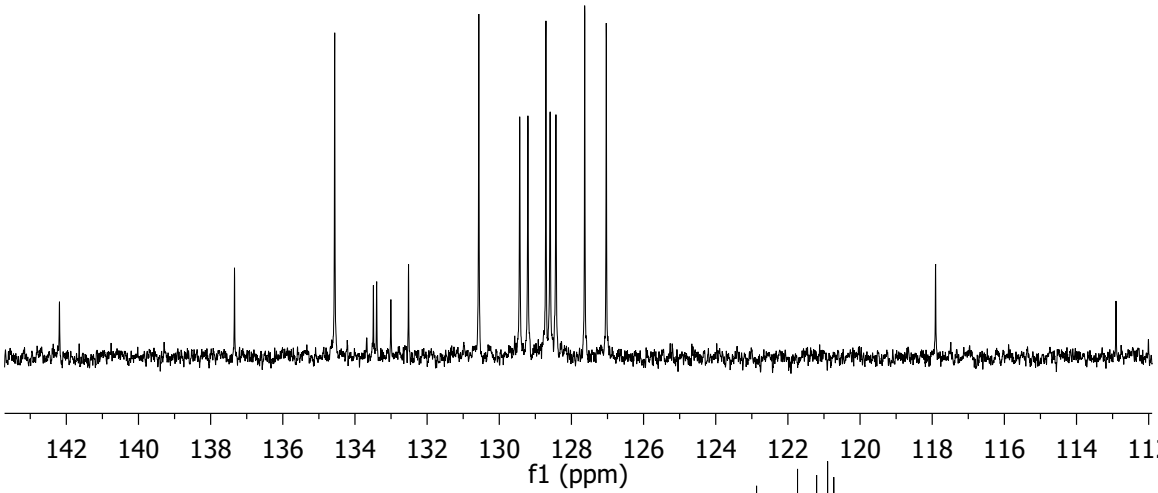
4f

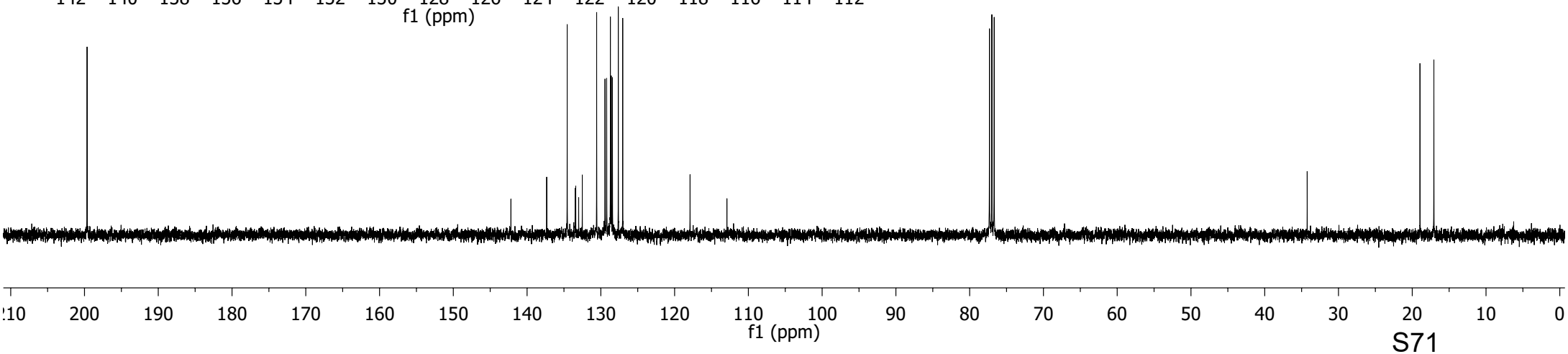
f1 (ppm)

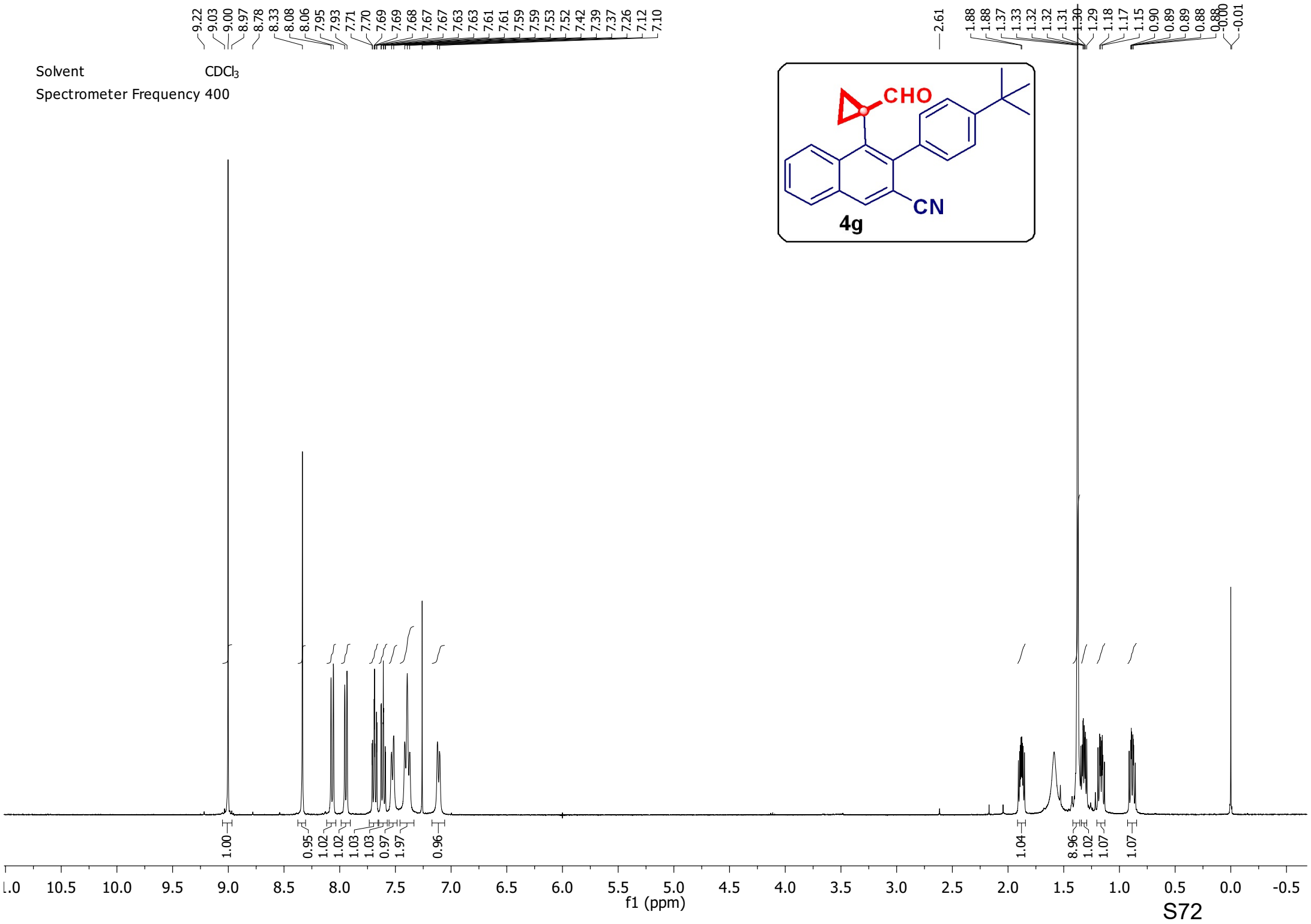
Solvent $CDCl_3$

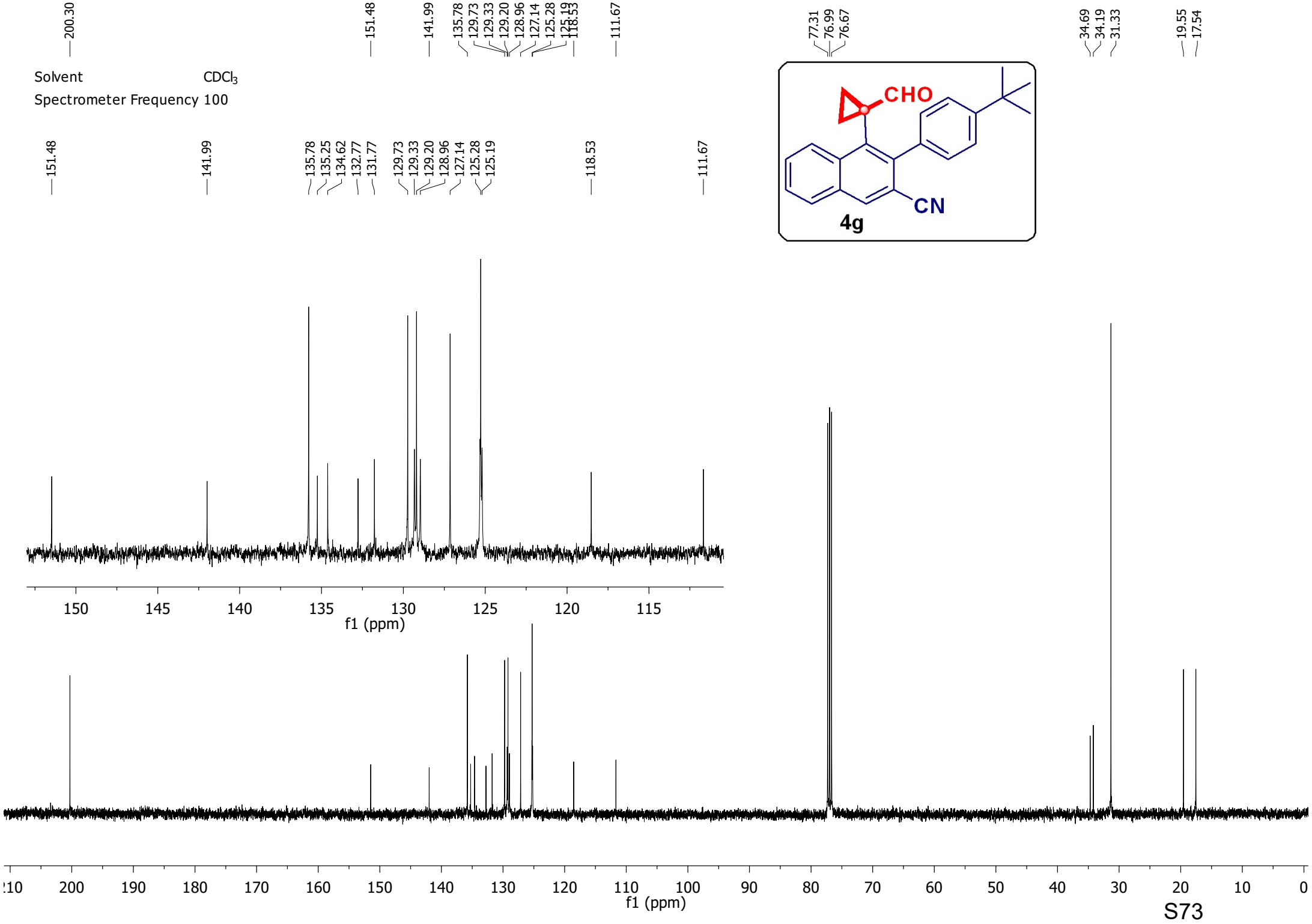
Spectrometer Frequency 100

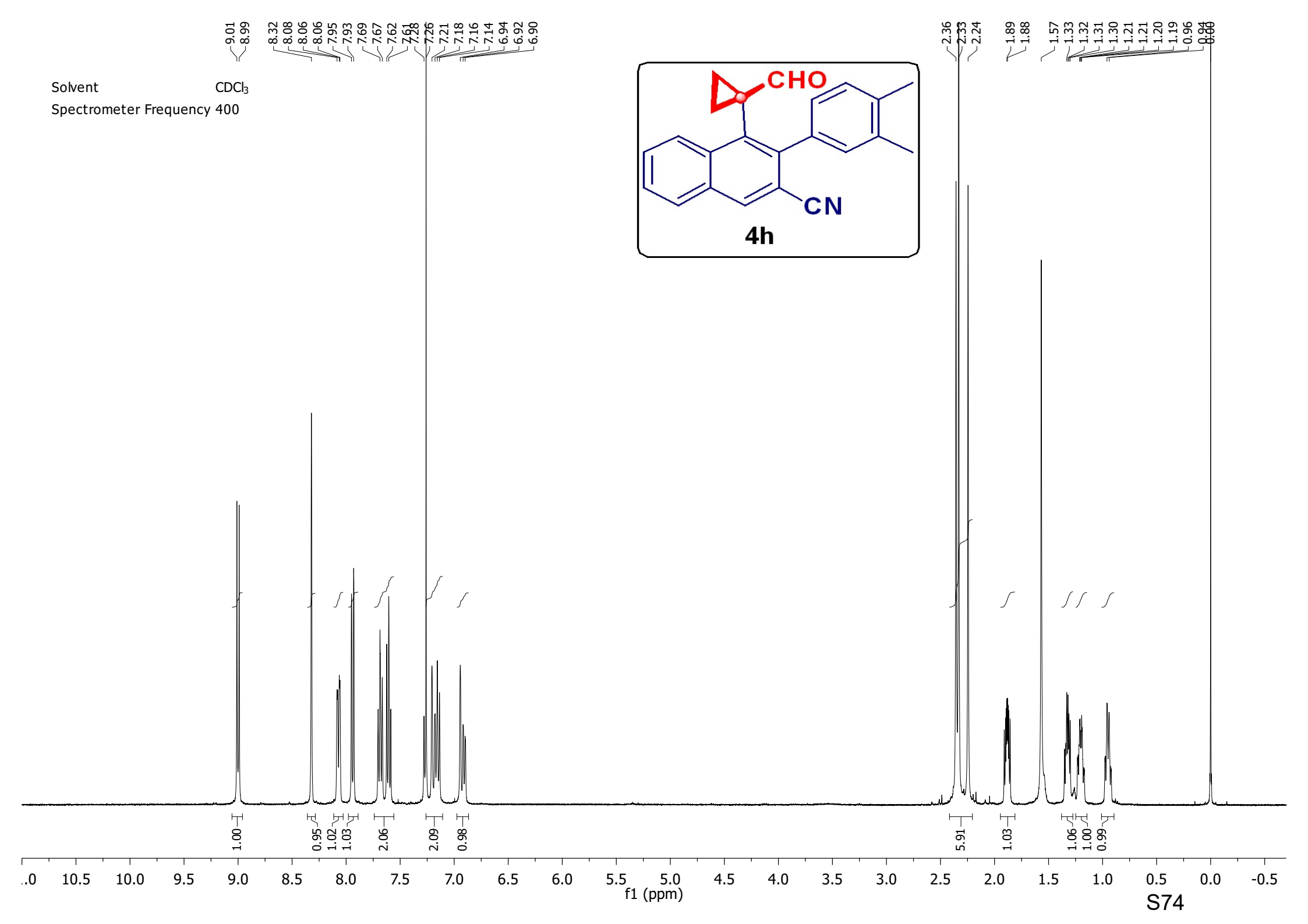


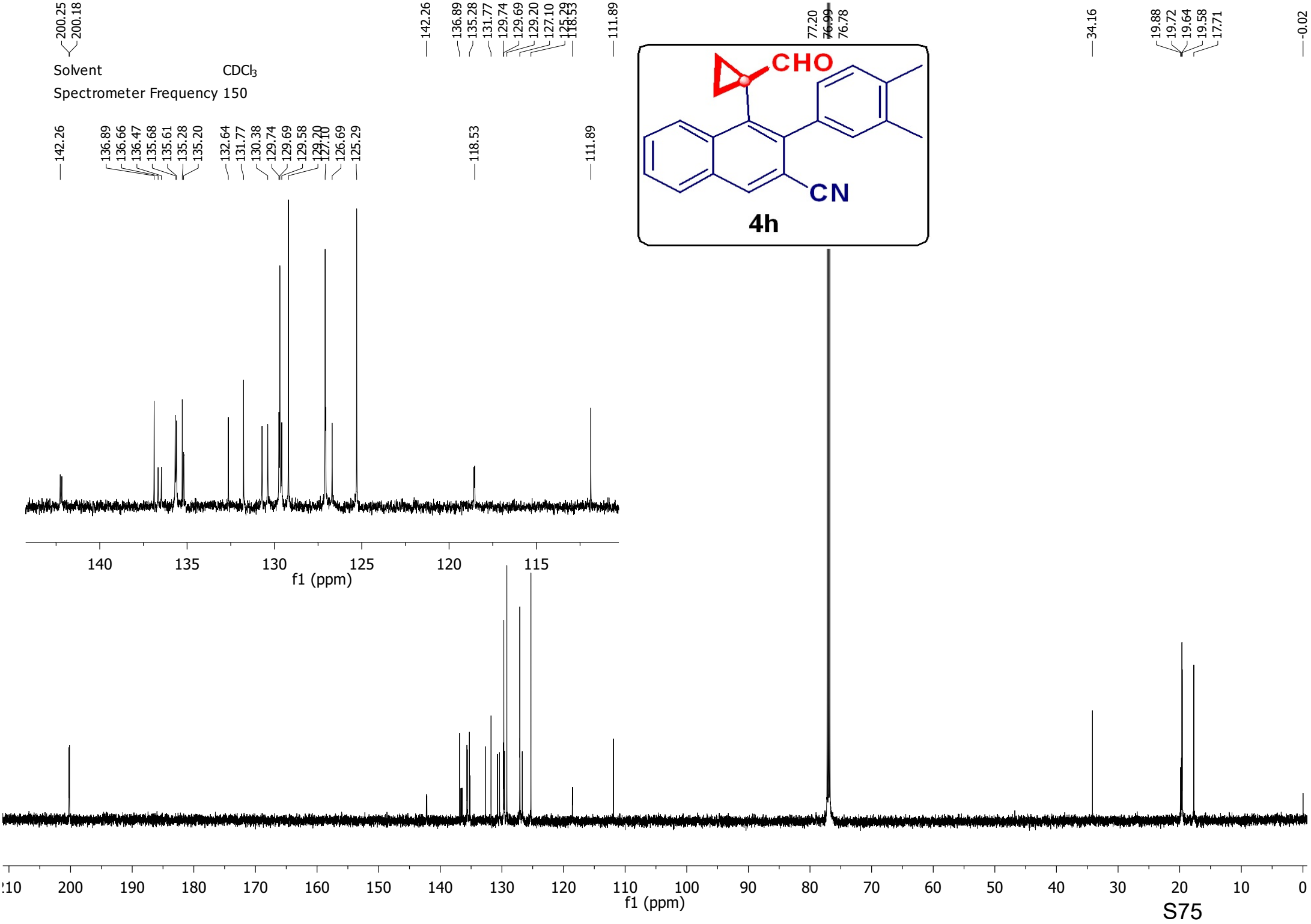


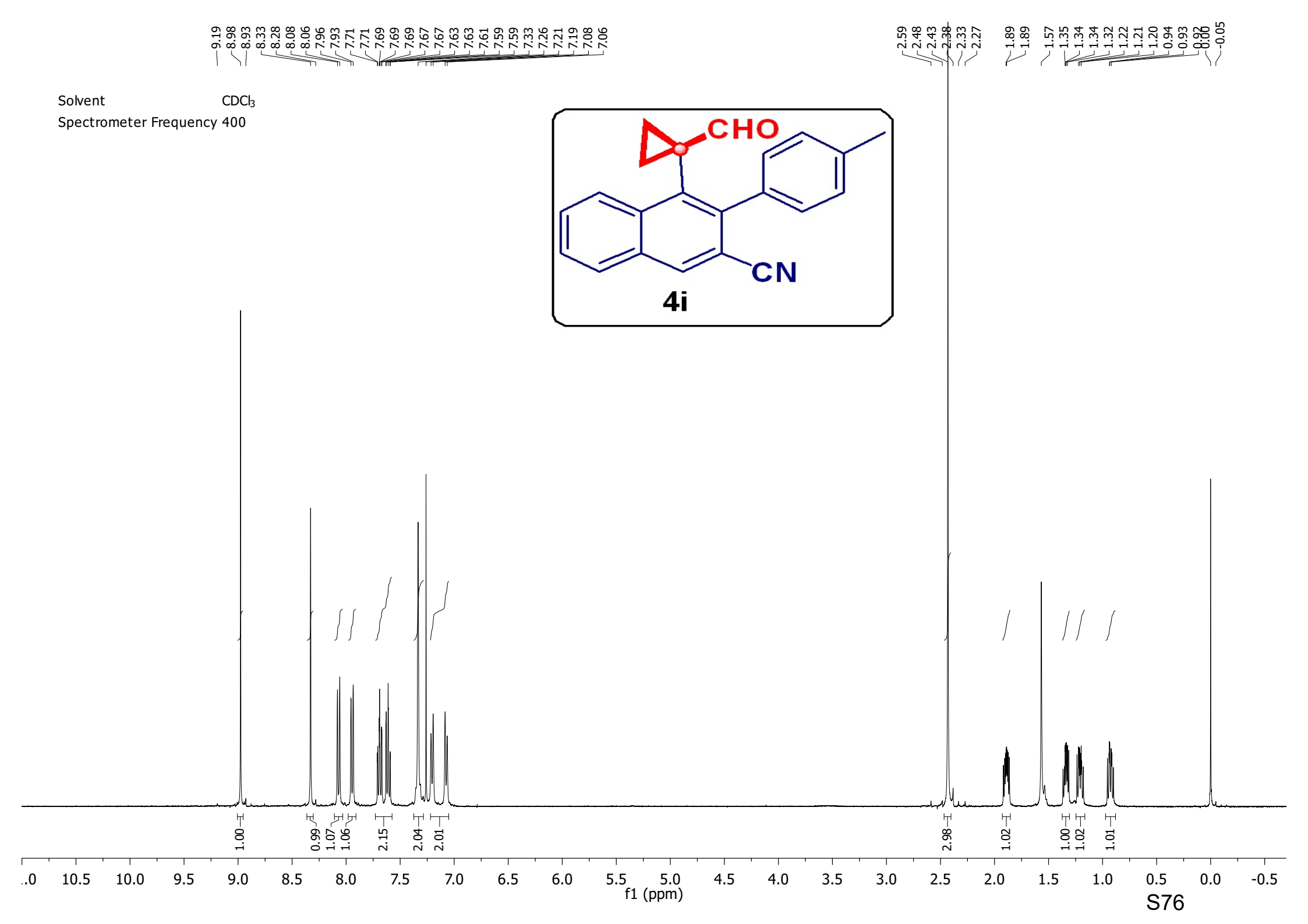


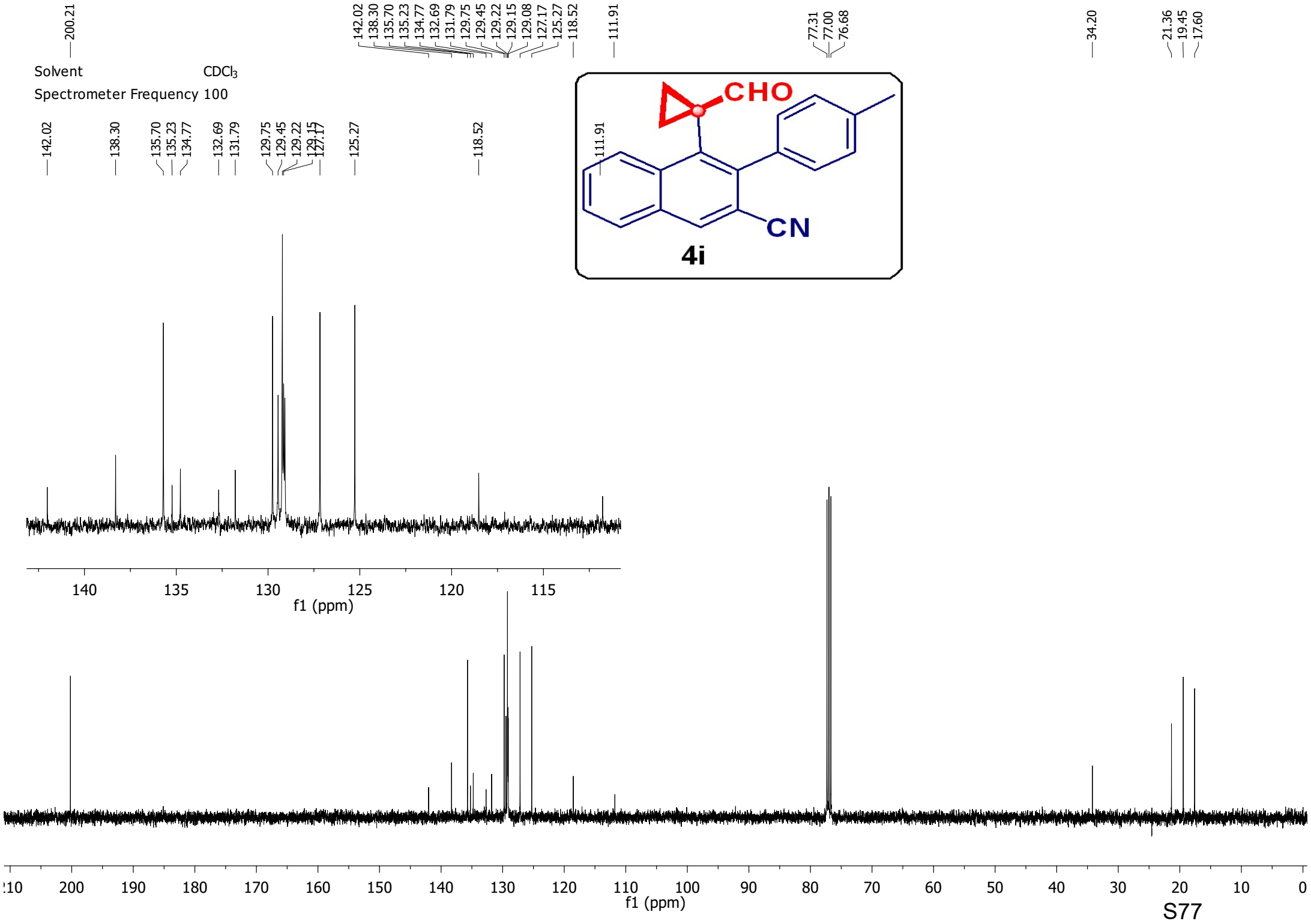

9.22
9.03
9.00
8.97
8.78
8.33
8.08
8.06
7.95
7.93
7.71
7.70
7.69
7.69
7.68
7.67
7.67
7.63
7.63
7.61
7.61
7.59
7.59
7.53
7.52
7.42
7.39
7.37
7.26
7.12
7.10
2.61
1.88
1.88
1.37
1.33
1.32
1.32
1.31
1.30
1.29
1.18
1.17
1.15
0.90
0.89
0.89
0.88
0.88
0.00
-0.01
Solvent CDCl3
Spectrometer Frequency 400
CHO
CN
4g
1.00
0.95
1.02
1.02
1.03
1.03
0.97
1.97
0.96
1.04
8.96
1.02
1.07
1.07
f1 (ppm)


200.30
151.48
141.99
135.78
129.73
129.33
129.20
128.96
127.14
125.28
125.19
118.53
111.67
77.31
76.99
76.67
34.69
34.19
31.33
19.55
17.54
Solvent CDCl3
Spectrometer Frequency 100
CHO
CN
4g
f1 (ppm)
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400
CHO
CN
4h
f1 (ppm)

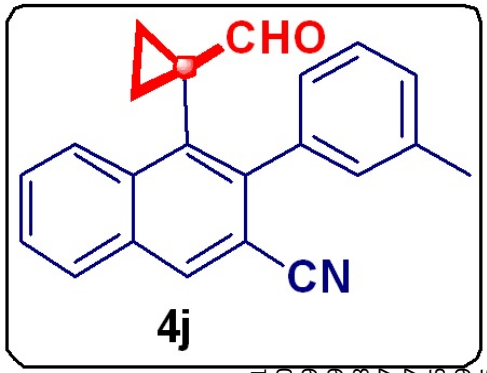

200.25
200.18
Solvent
CDCl3
Spectrometer Frequency 150
142.26
136.89
135.28
131.77
129.74
129.69
129.20
127.10
125.29
118.53
111.89
77.20
76.99
76.78
34.16
19.88
19.72
19.64
19.58
17.71
-0.02
CHO
CN
4h
142.26
136.89
136.66
136.47
135.68
135.61
135.28
135.20
132.64
131.77
130.38
129.74
129.69
129.58
129.20
127.10
126.69
125.29
118.53
111.89
140
135
130
125
120
115
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.19
8.98
8.93
8.33
8.28
8.08
8.06
7.96
7.93
7.71
7.71
7.69
7.69
7.69
7.67
7.67
7.63
7.63
7.61
7.59
7.59
7.33
7.26
7.21
7.19
7.08
7.06
2.59
2.48
2.43
2.38
2.33
2.27
1.89
1.89
1.57
1.35
1.34
1.34
1.32
1.22
1.21
1.20
0.94
0.93
0.92
0.00
-0.05
Solvent CDCl3
Spectrometer Frequency 400
CHO
CN
4i
1.00
0.99
1.07
1.06
2.15
2.04
2.01
2.98
1.02
1.00
1.02
1.01
f1 (ppm)

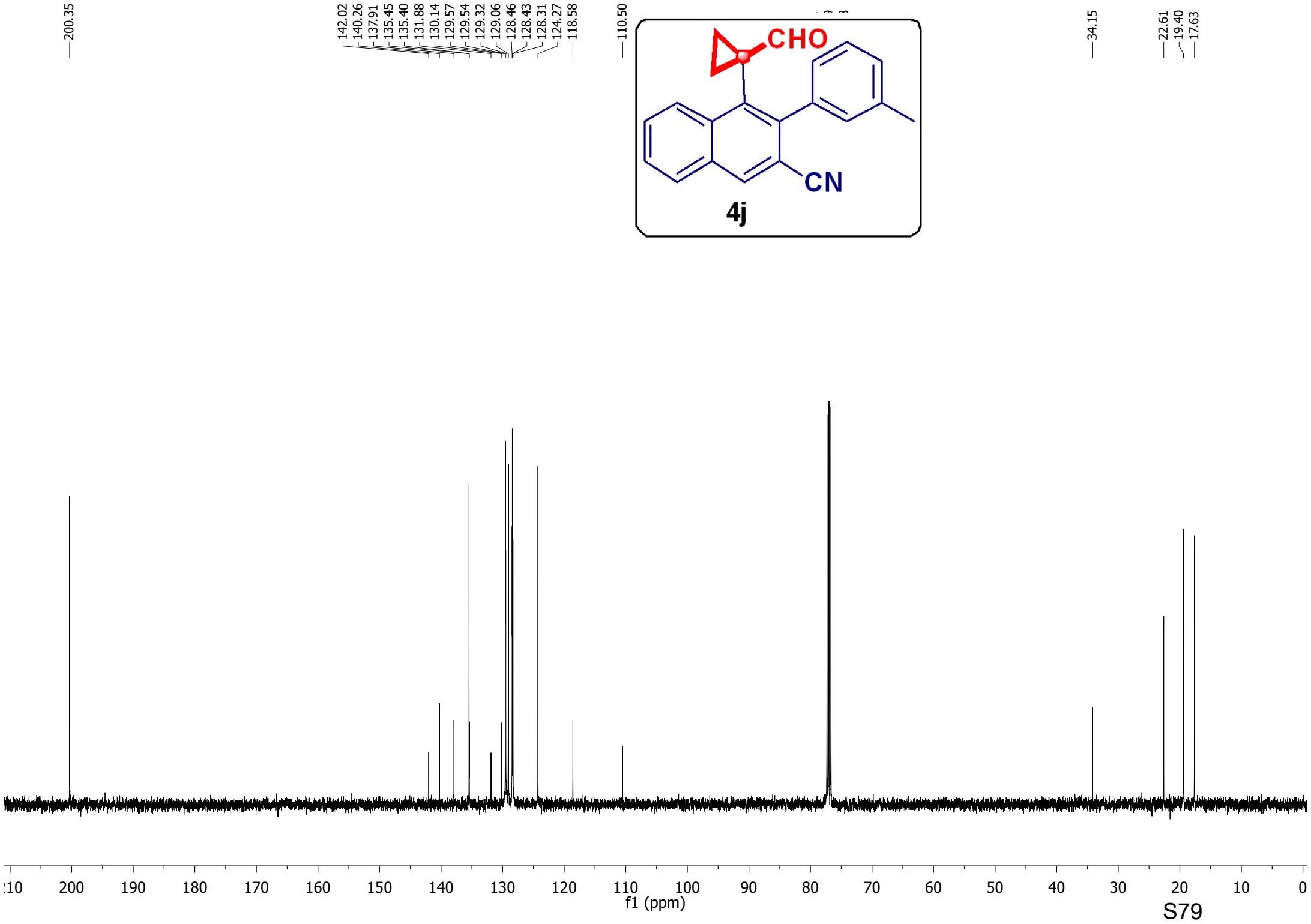

200.21
142.02
138.30
135.70
135.23
134.77
132.69
131.79
129.75
129.45
129.22
129.15
129.08
127.17
125.27
118.52
111.91
77.31
77.00
76.68
34.20
21.36
19.45
17.60
Solvent CDCl3
Spectrometer Frequency 100
CHO
CN
4i
f1 (ppm)
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400

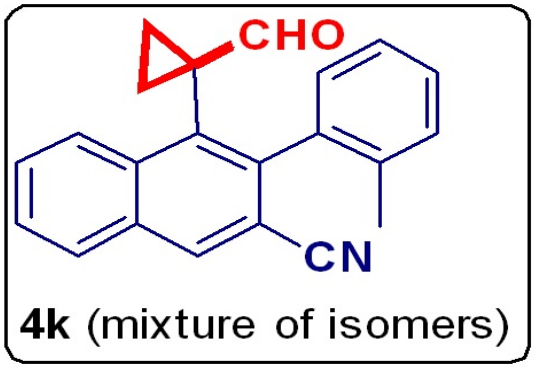


4j


200.35
142.02
140.26
137.91
135.45
135.40
131.88
130.14
129.57
129.54
129.32
129.06
128.46
128.43
128.31
124.27
118.58
110.50
34.15
22.61
19.40
17.63
CHO
CN
4j
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400



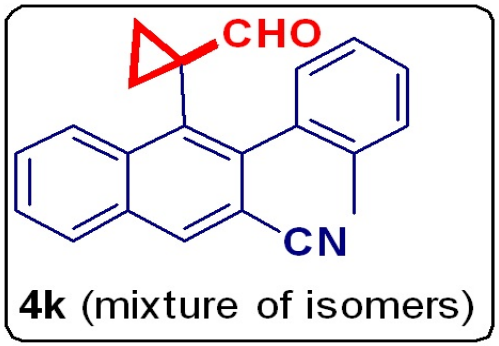
4k (mixture of isomers)

f1 (ppm)

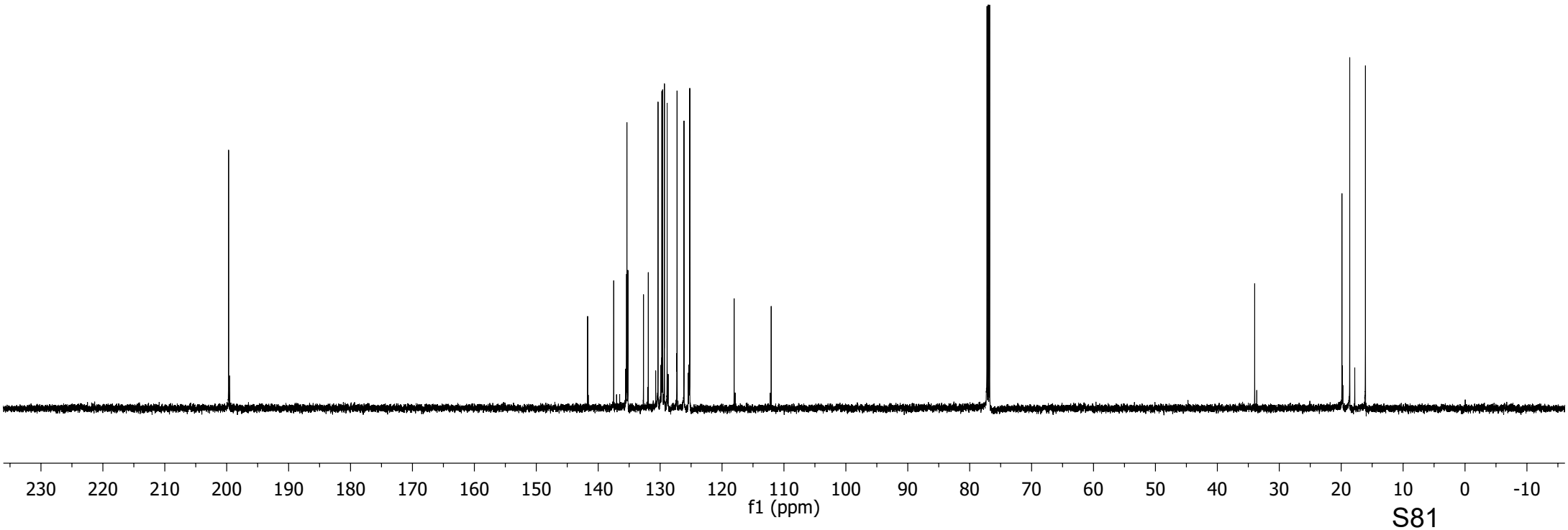
199.69
199.51
141.71
137.49
135.57
135.42
135.36
135.20
132.68
132.01
131.91
130.71
130.33
129.91
129.79
129.72
129.59
129.30
128.87
128.70
127.31
127.26
126.14
125.44
125.35
125.21
118.04
112.06
77.21
76.99
76.78
33.97
19.87
19.81
19.74
18.62
17.80
16.08

Solvent $CDCl_3$

Spectrometer Frequency 150

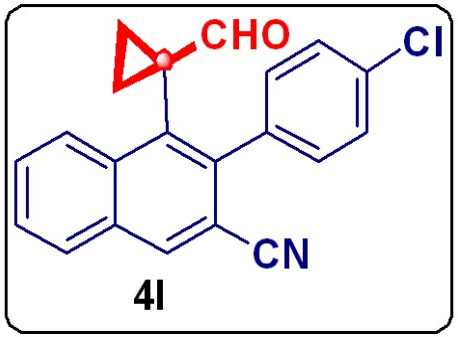


4k (mixture of isomers)



Solvent $CDCl_3$

Spectrometer Frequency 400



4l

f1 (ppm)

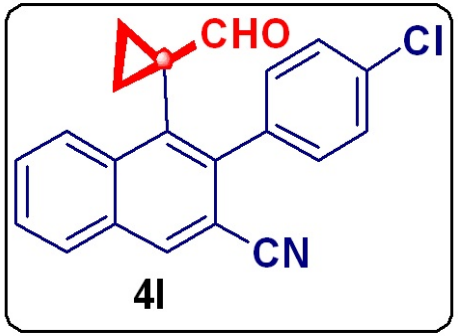
f1 (ppm)

f1 (ppm)

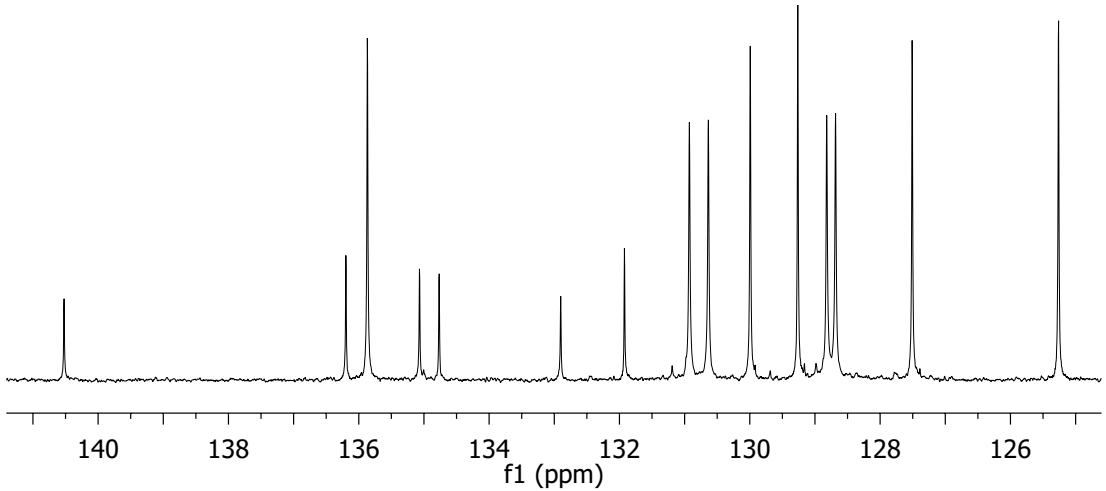
199.82
140.52 136.20 135.87 135.07 134.77 132.90 131.92 131.19 130.93 130.64 129.99 129.26 129.16 128.98 128.82 128.68 127.51 125.26 118.18
111.20
77.31 77.20 77.00 76.68
67.05
34.25
19.02 17.29
-0.03

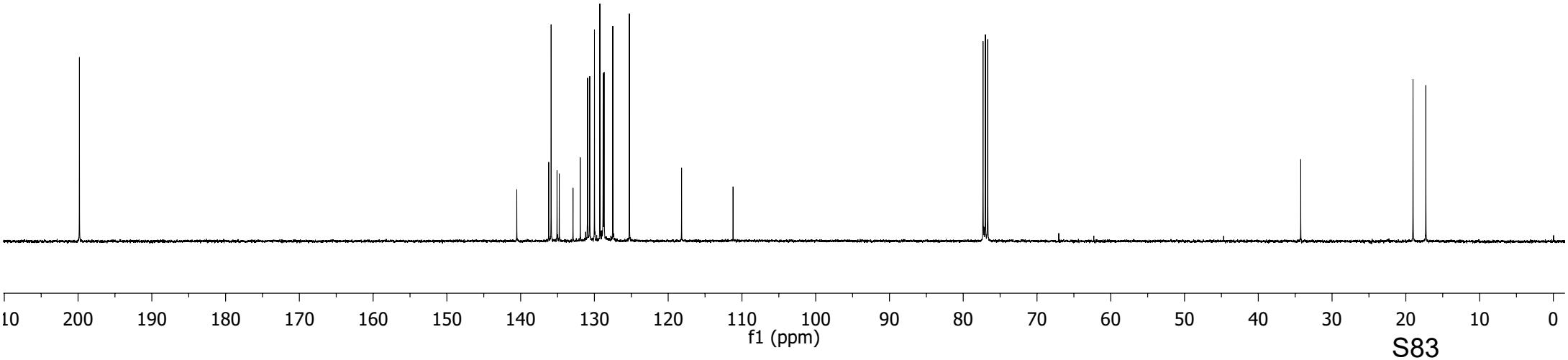
Solvent $CDCl_3$

Spectrometer Frequency 100



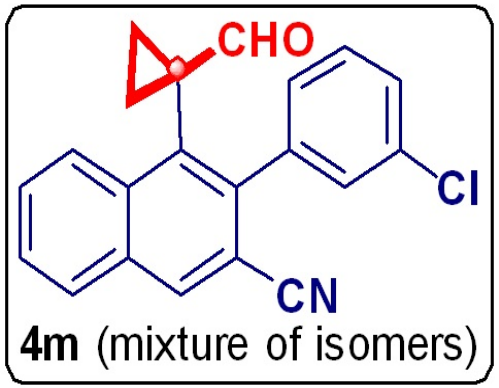
140.52 136.20 135.87 135.07 134.77 132.90 131.92 131.19 130.93 130.64 129.99 129.26 129.16 128.98 128.82 128.68 127.51 125.26



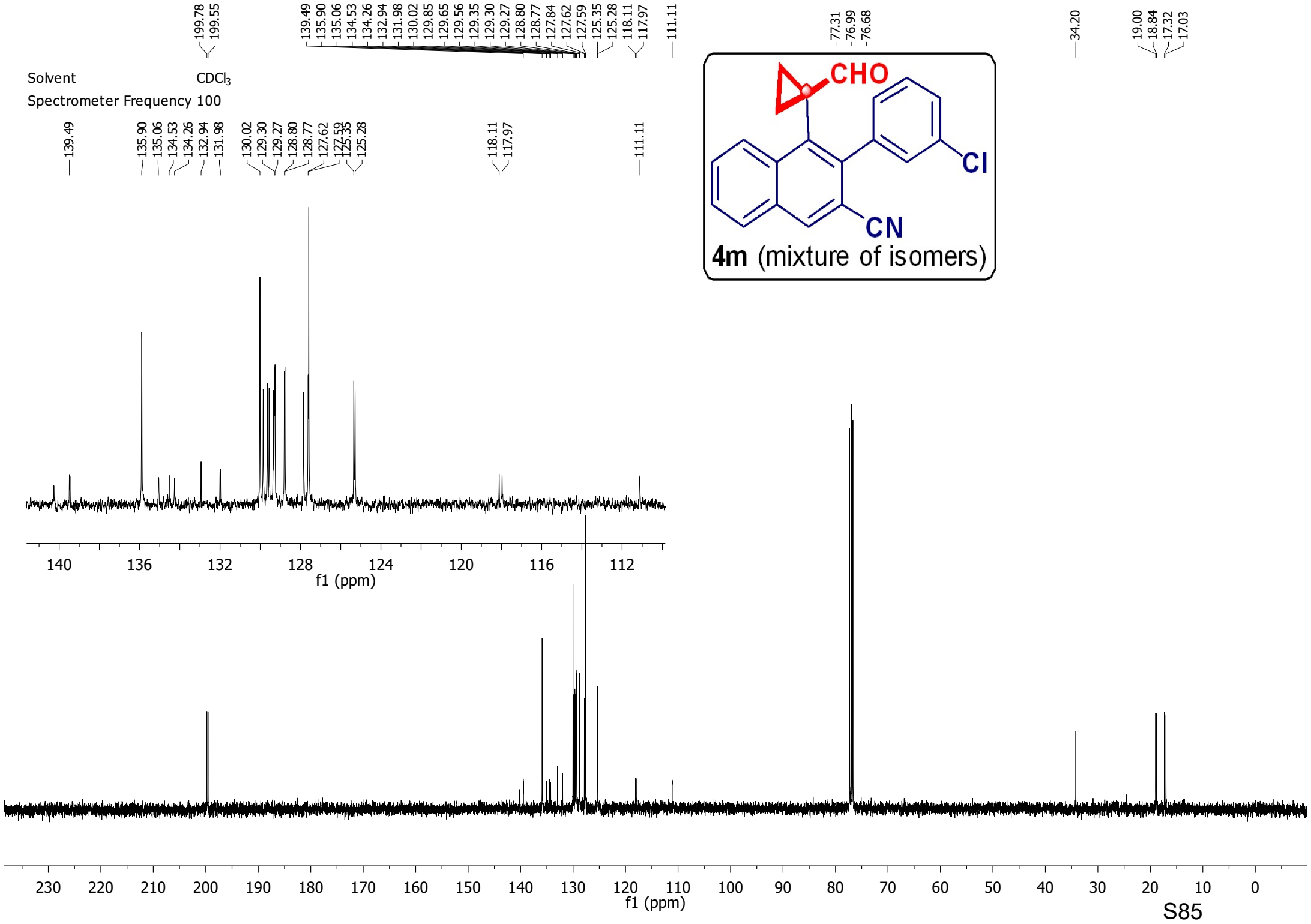


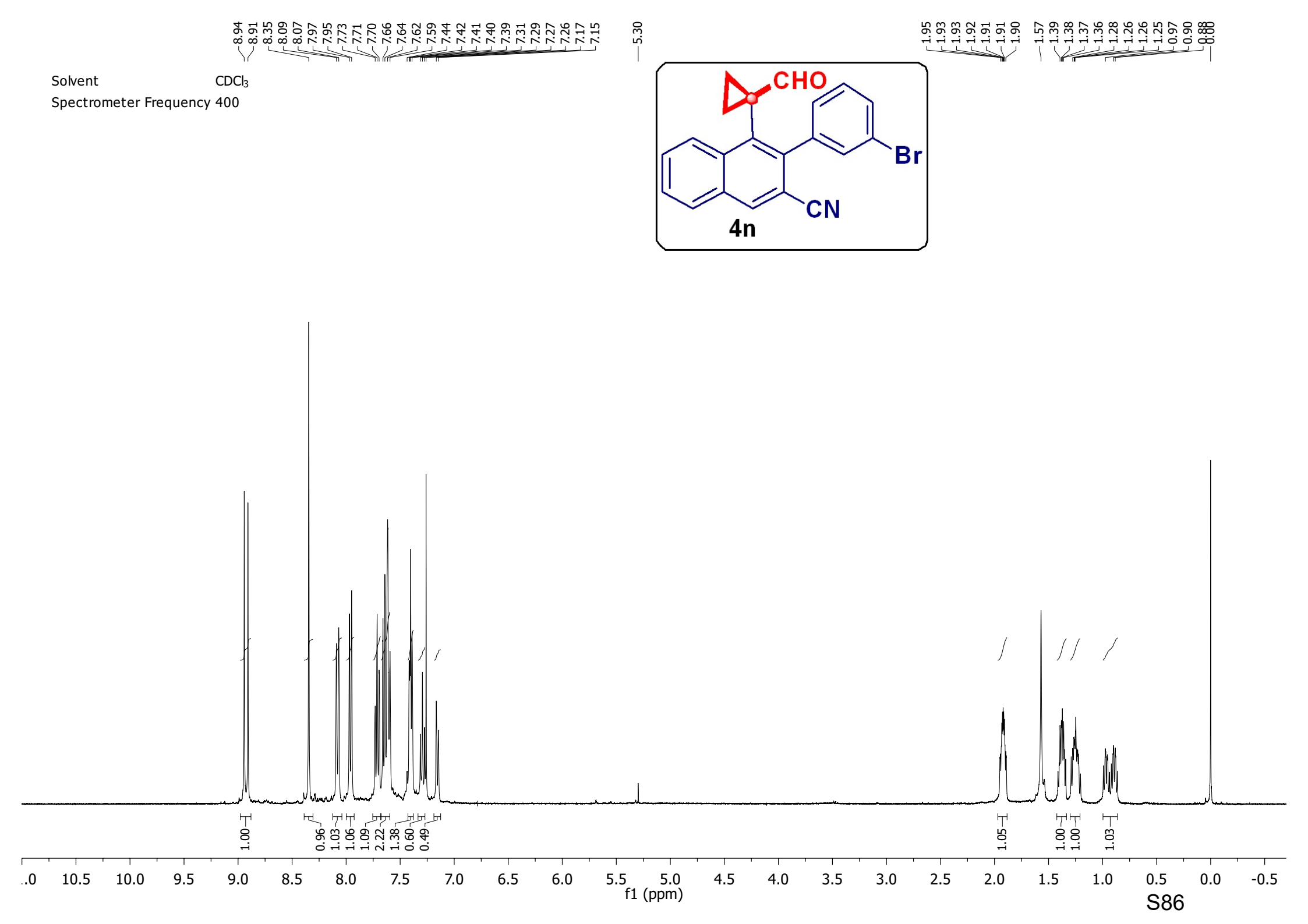
Solvent $CDCl_3$

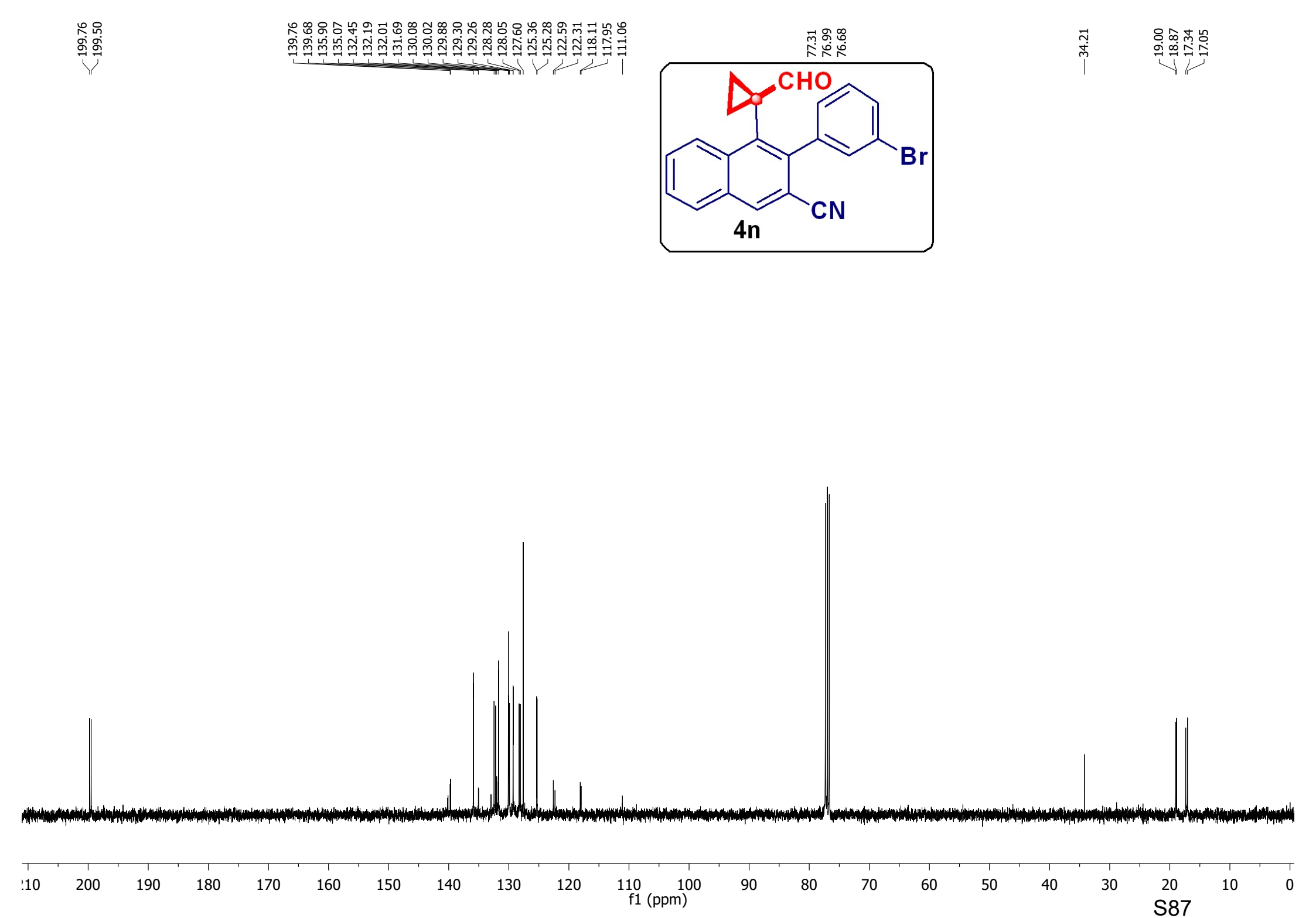
Spectrometer Frequency 400



4m (mixture of isomers)

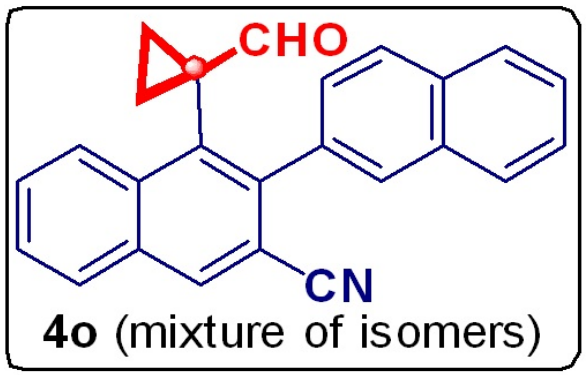

199.78
199.55
139.49
135.90
135.06
134.53
134.26
132.94
131.98
130.02
129.85
129.65
129.56
129.35
129.30
129.27
128.80
128.77
127.84
127.62
127.59
125.35
125.28
118.11
117.97
111.11
77.31
76.99
76.68
34.20
19.00
18.84
17.32
17.03
Solvent CDCl3
Spectrometer Frequency 100
CHO
Cl
CN
4m (mixture of isomers)
f1 (ppm)
f1 (ppm)


8.94
8.91
8.35
8.09
8.07
7.97
7.95
7.73
7.71
7.70
7.66
7.64
7.62
7.59
7.44
7.42
7.41
7.40
7.39
7.31
7.29
7.27
7.26
7.17
7.15
5.30
1.95
1.93
1.93
1.92
1.91
1.91
1.90
1.57
1.39
1.38
1.37
1.36
1.28
1.26
1.26
1.25
0.97
0.90
0.88
0.88
Solvent CDCl3
Spectrometer Frequency 400
CHO
Br
CN
4n
1.00
0.96
1.03
1.06
1.09
2.22
1.38
0.60
0.49
1.05
1.00
1.00
1.03
f1 (ppm)


199.76
199.50
139.76
139.68
135.90
135.07
132.45
132.19
132.01
131.69
130.08
130.02
129.88
129.30
129.26
128.28
128.05
127.60
125.36
125.28
122.59
122.31
118.11
117.95
111.06
77.31
76.99
76.68
34.21
19.00
18.87
17.34
17.05
CHO
Br
CN
4n
f1 (ppm)

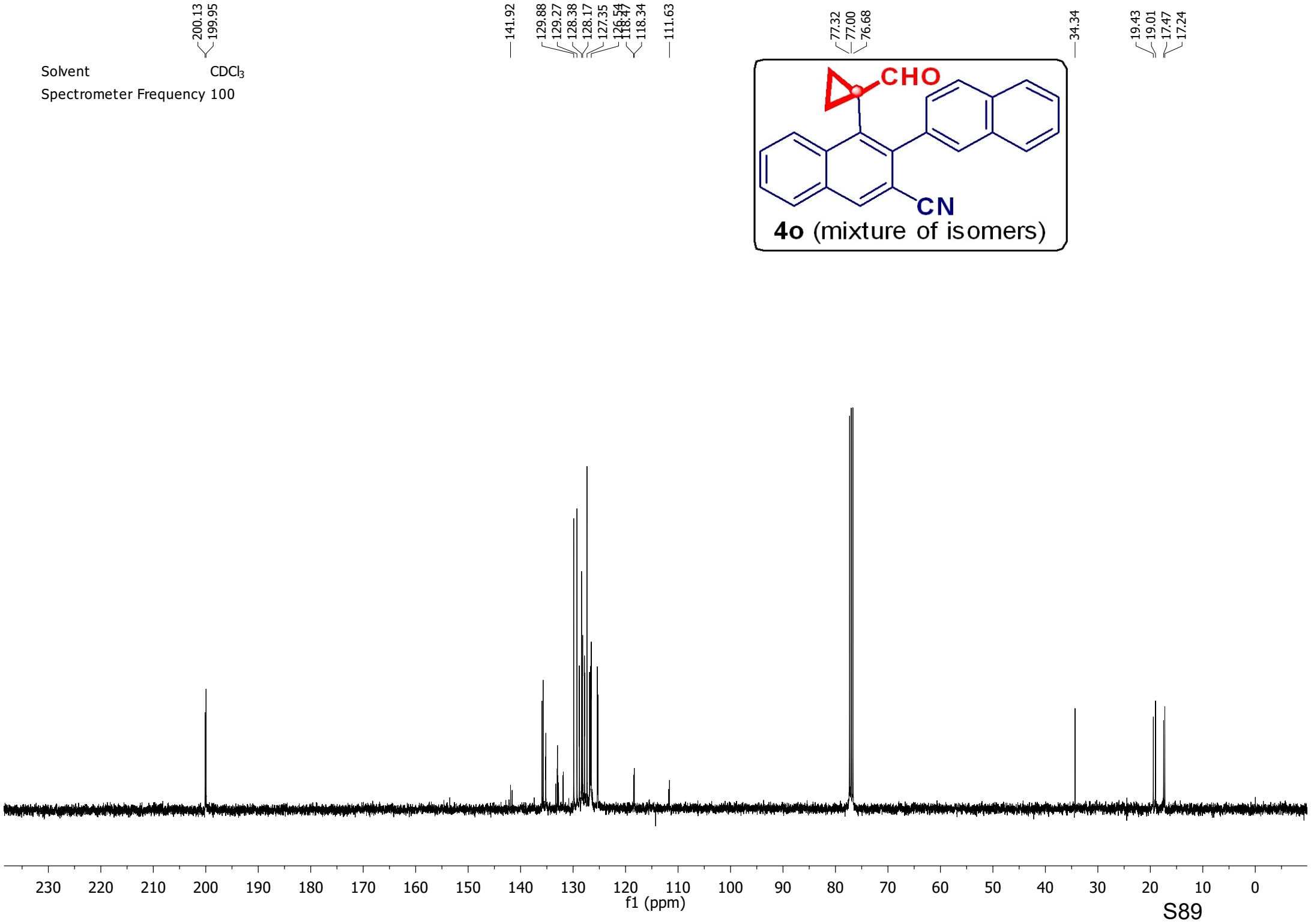
Solvent $CDCl_3$

Spectrometer Frequency 400



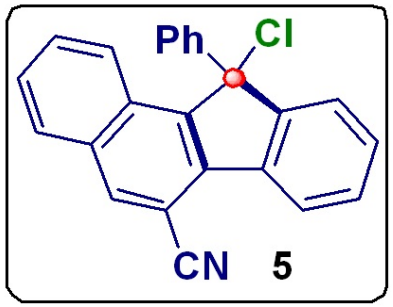
4o (mixture of isomers)

f1 (ppm)


200.13
199.95
141.92
129.88
129.27
128.38
128.17
127.35
126.54
118.34
111.63
77.32
77.00
76.68
34.34
19.43
19.01
17.47
17.24
Solvent CDCl3
Spectrometer Frequency 100
CHO
CN
4o (mixture of isomers)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400



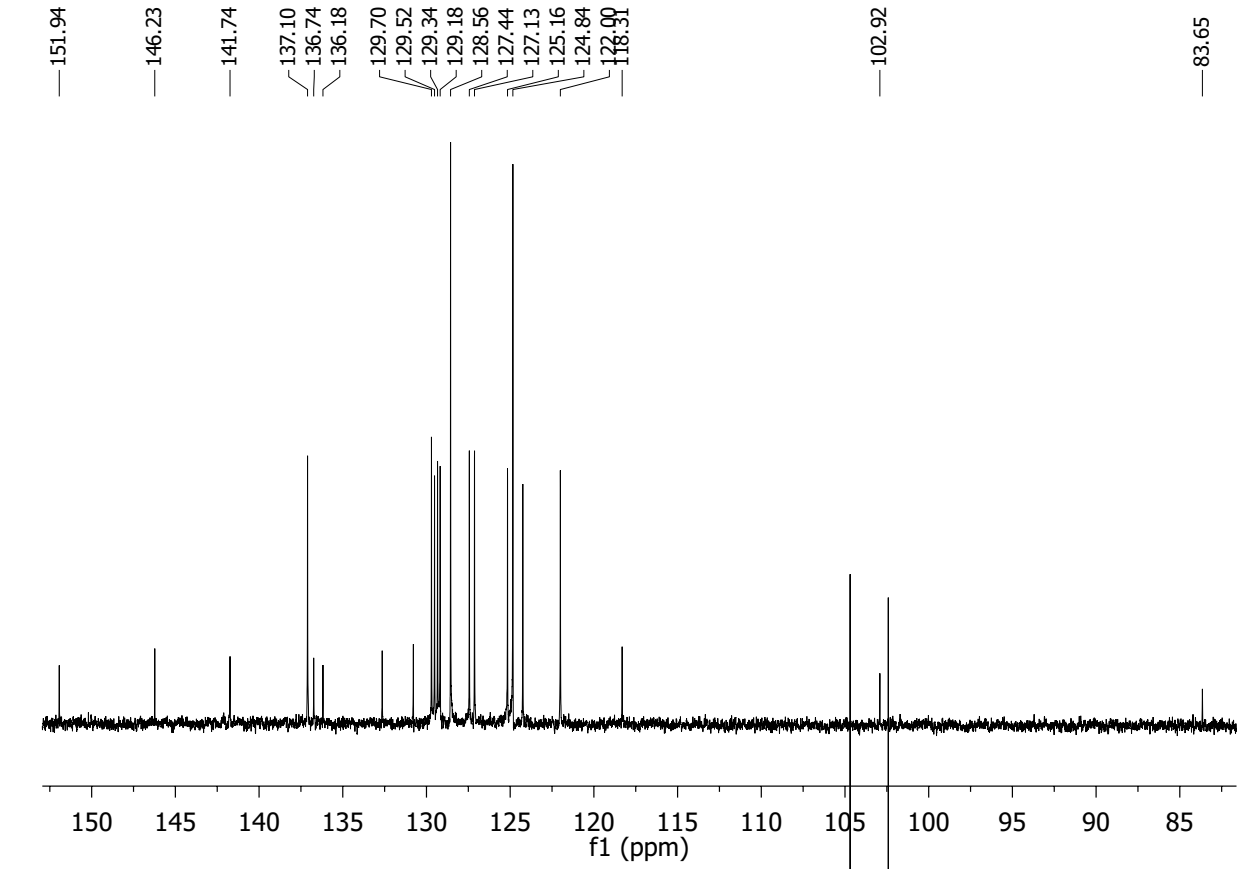
f1 (ppm)

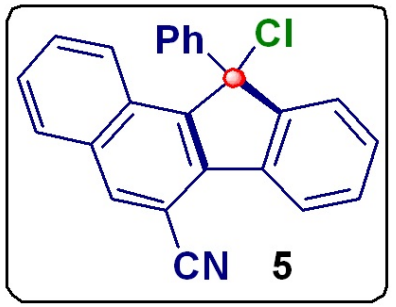
f1 (ppm)

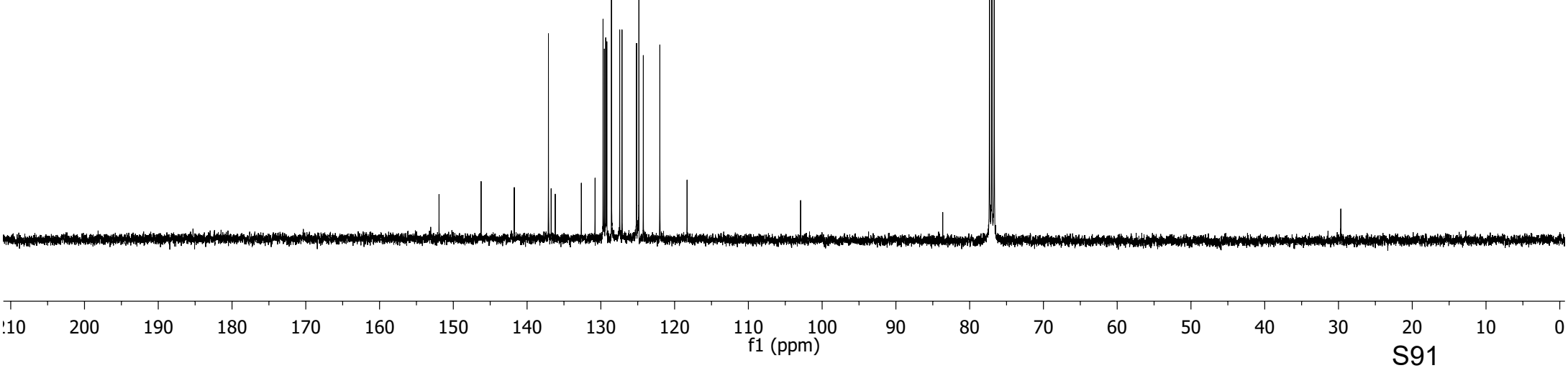
Solvent $CDCl_3$

Spectrometer Frequency 100

151.94 146.23 141.74 137.10 136.74 132.64 130.78 129.70 129.52 129.34 129.18 128.56 127.44 127.13 125.16 124.84 124.25 122.00 118.31 102.92 83.65 77.31 76.99 76.67

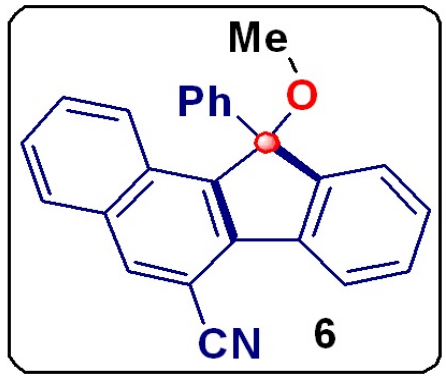


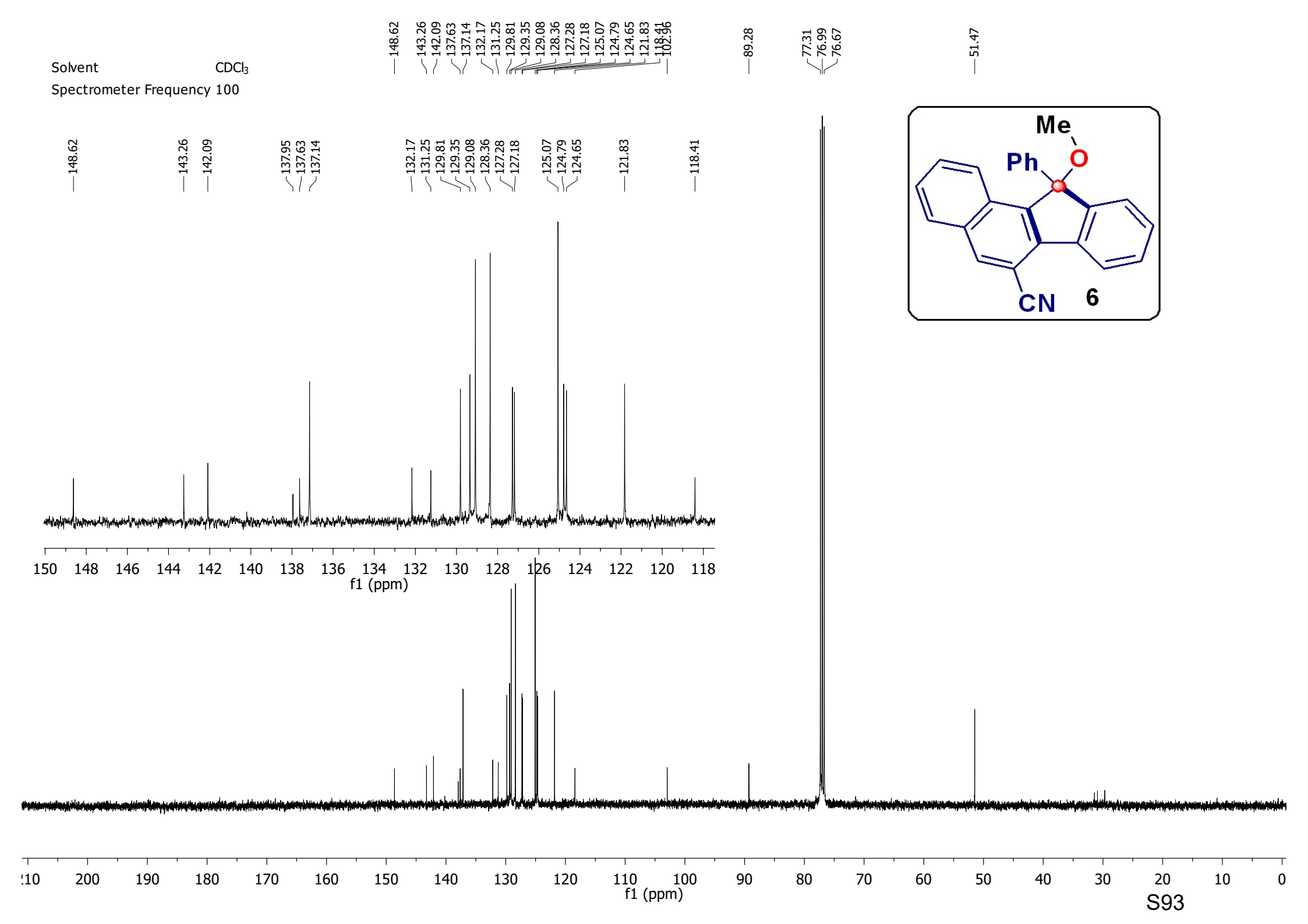




Solvent $CDCl_3$

Spectrometer Frequency 400

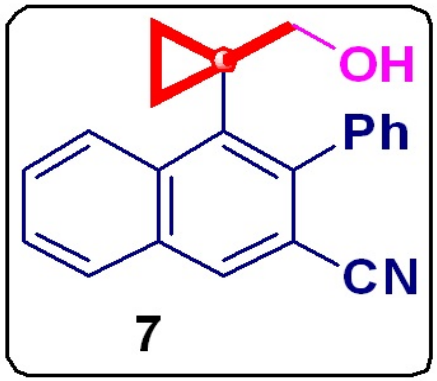


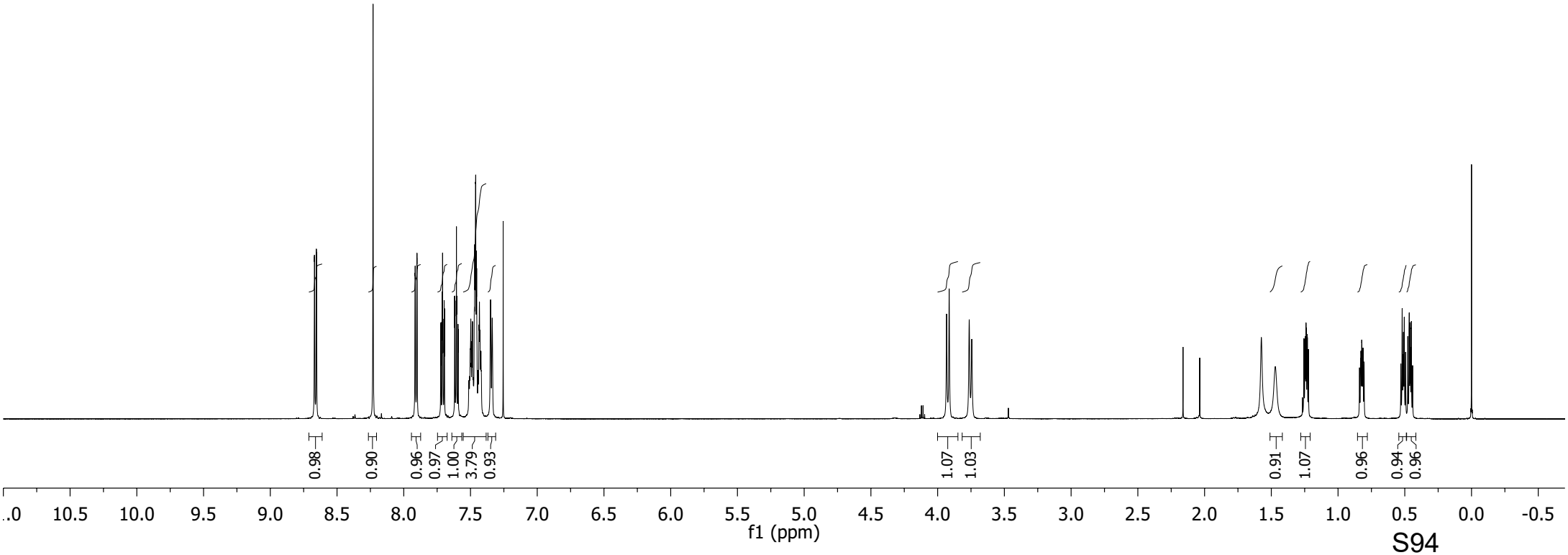

148.62
143.26
142.09
137.63
137.14
132.17
131.25
129.81
129.35
129.08
128.36
127.28
127.18
125.07
124.79
124.65
121.83
118.41
102.96
89.28
77.31
76.99
76.67
51.47
Solvent CDCl3
Spectrometer Frequency 100
Me
Ph
O
CN
6
f1 (ppm)
f1 (ppm)

8.67 8.67 8.65 8.65 8.23 7.92 7.91 7.91 7.90 7.90 7.90 7.72 7.72 7.71 7.71 7.71 7.70 7.69 7.62 7.62 7.61 7.61 7.60 7.59 7.59 7.51 7.50 7.49 7.49 7.49 7.48 7.47 7.47 7.47 7.46 7.46 7.46 7.45 7.44 7.44 7.44 7.43 7.43 7.42 7.42 7.35 7.34 7.26 3.93 3.91 3.76 3.74 2.16 2.04 1.57 1.47 1.26 1.25 1.25 1.24 1.24 1.24 1.23 1.22 0.84 0.83 0.83 0.82 0.82 0.81 0.81 0.53 0.52 0.51 0.51 0.50 0.49 0.48 0.47 0.46 0.46 0.45 0.44 -0.00

Solvent $CDCl_3$

Spectrometer Frequency 597





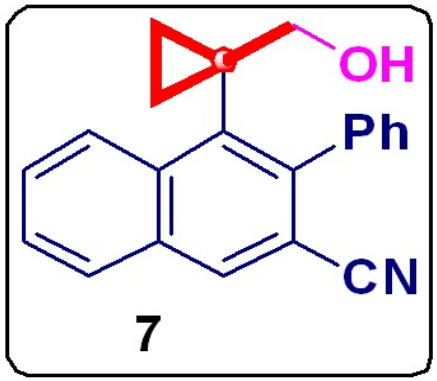
Solvent $CDCl_3$

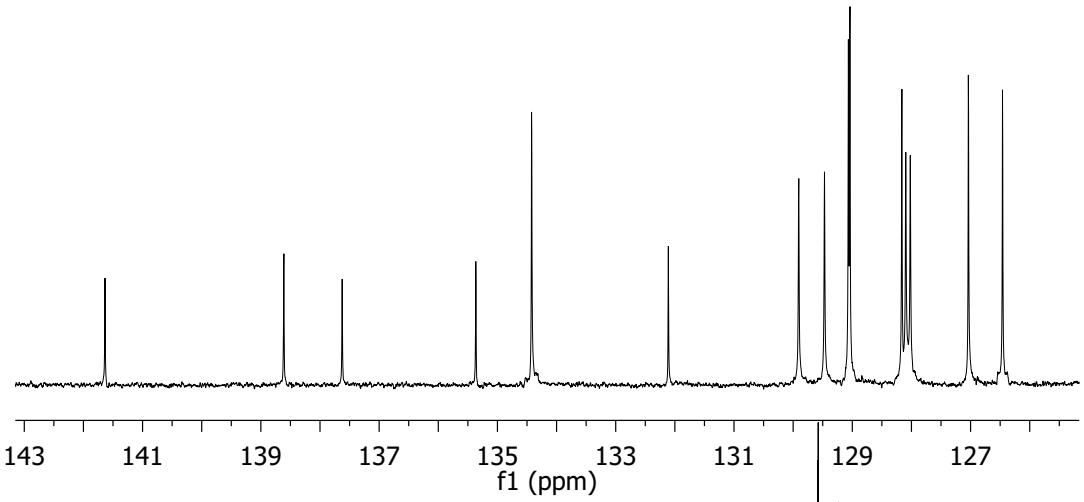
Spectrometer Frequency 150

141.64 138.61 137.62 135.36 134.42 132.11 129.91 129.47 129.07 129.04 128.16 128.10 128.02 127.04 126.46 118.38 112.30

77.20 76.99 76.78 70.26

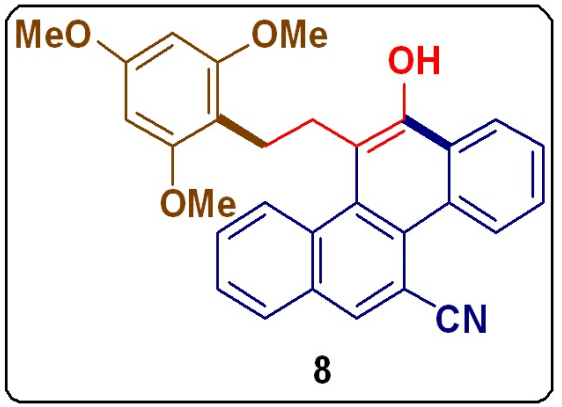
23.41 14.04 12.82





Solvent $CDCl_3$

Spectrometer Frequency 400



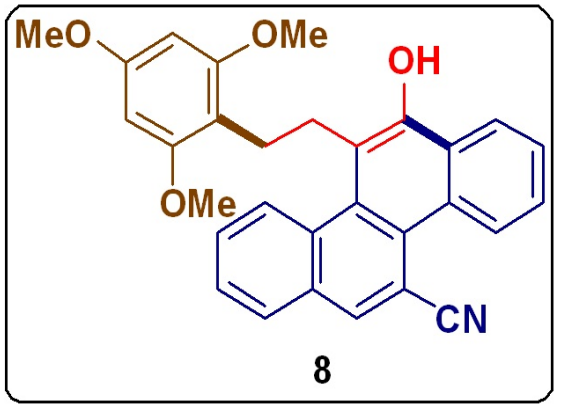
8

159.49
158.72
138.03
137.47
131.29
128.54
128.25
128.02
127.51
127.22
126.74
126.01
106.53
90.30
77.32
77.00
76.68
55.62
55.32
36.59
25.40

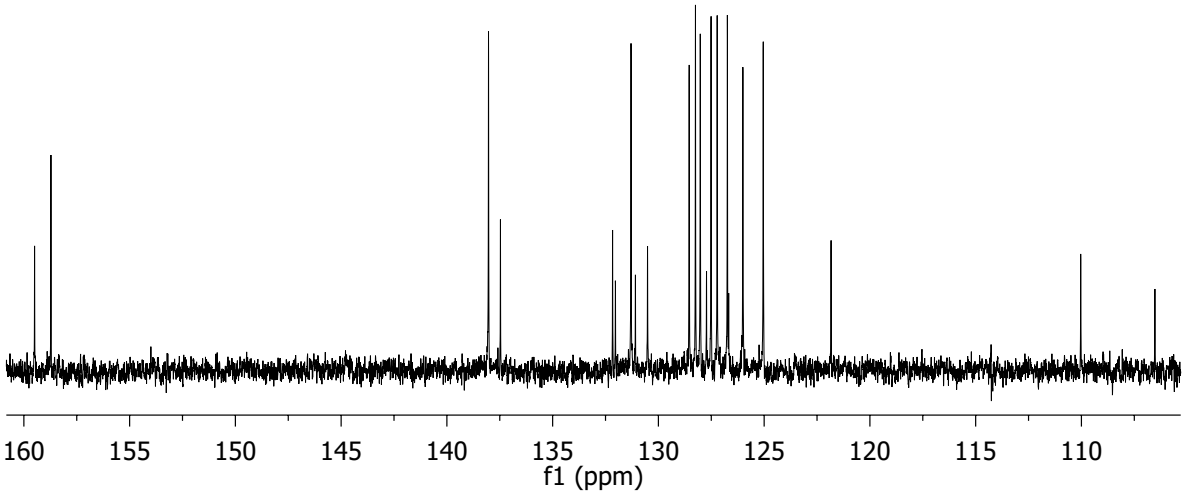
Solvent $CDCl_3$

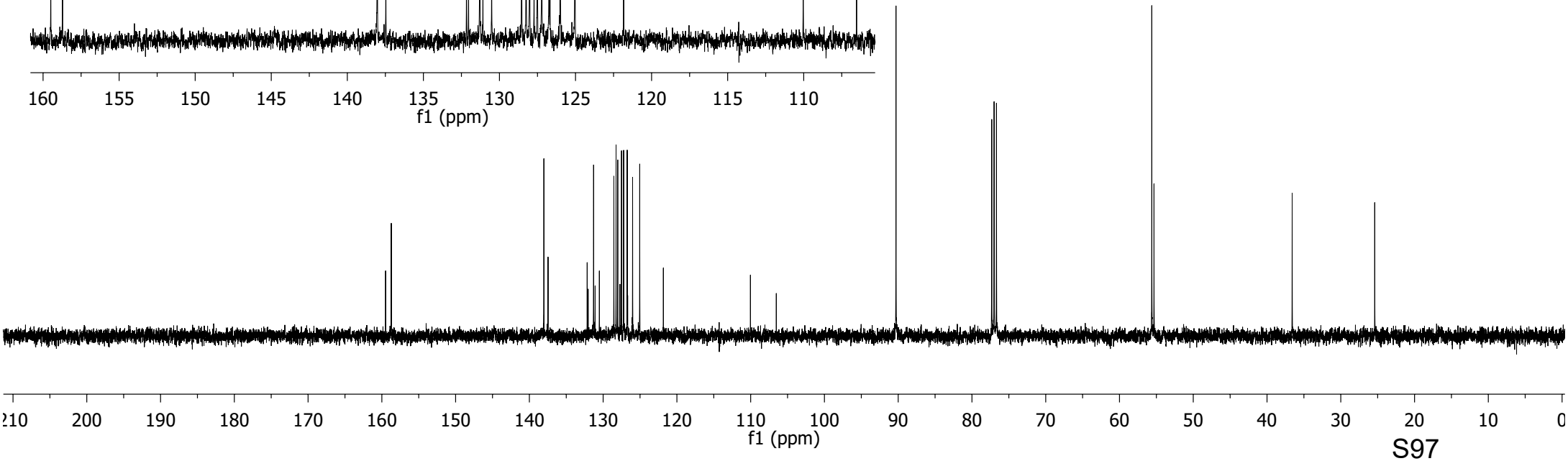
Spectrometer Frequency 100

159.49
158.72
138.03
137.47
132.17
131.29
130.51
128.54
128.25
128.02
127.51
127.22
126.74
126.01
110.03
106.53



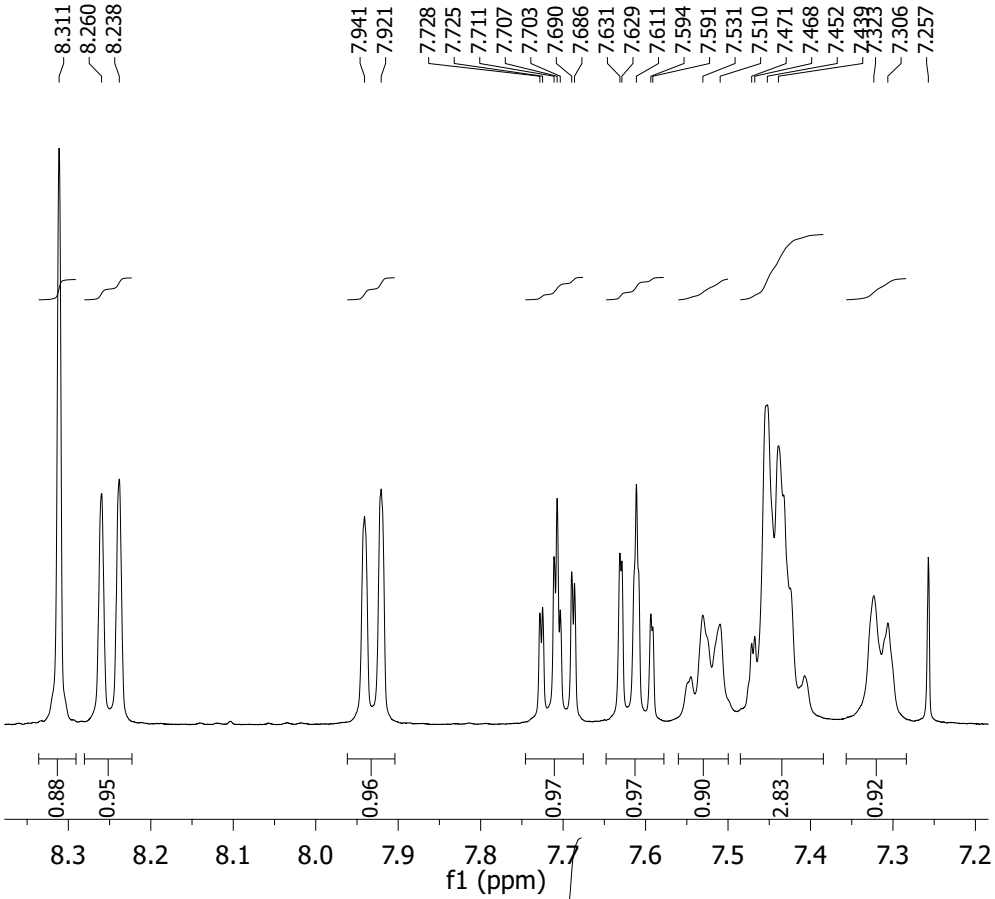
8

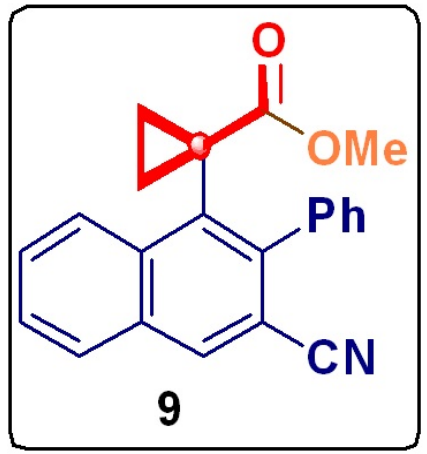


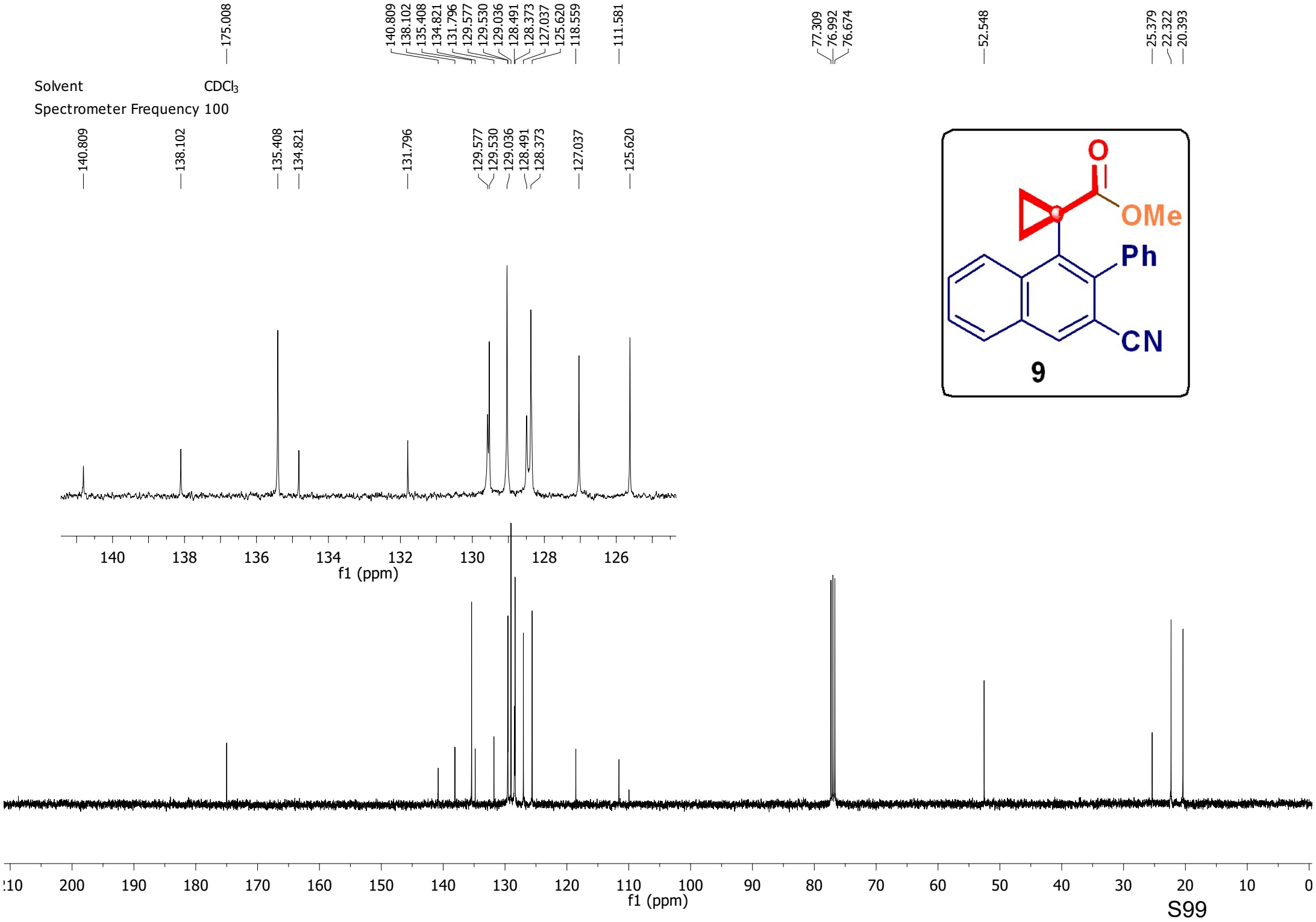


Solvent $CDCl_3$

Spectrometer Frequency 400






175.008
140.809
138.102
135.408
134.821
131.796
129.577
129.530
129.036
128.491
128.373
127.037
125.620
118.559
111.581
77.309
76.992
76.674
52.548
25.379
22.322
20.393
Solvent CDCl3
Spectrometer Frequency 100
O
OMe
Ph
CN
9
f1 (ppm)
f1 (ppm)

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) eggpr2104

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: eggpr2104

```
Bond precision:   C-C = 0.0028 A          Wavelength=0.71073

Cell:             a=12.2536(11)     b=7.8538(6)        c=17.2655(15)
                  alpha=90          beta=92.428(4)     gamma=90
Temperature:      150 K

                 Calculated                Reported
Volume           1660.1(2)                 1660.1(2)
Space group      P 21/c                    P 21/c
Hall group       -P 2ybc                   -P 2ybc
Moiety formula   C24 H15 N O               C24 H15 N O
Sum formula      C24 H15 N O               C24 H15 N O
Mr               333.37                    333.37
Dx,g cm-3        1.334                     1.334
Z                4                         4
Mu (mm-1)        0.081                     0.081
F000             696.0                     696.0
F000'            696.28
h,k,lmax         15,9,21                   15,9,21
Nref             3425                      3399
Tmin,Tmax        0.982,0.995               0.789,0.928
Tmin'            0.977

Correction method= # Reported T Limits: Tmin=0.789 Tmax=0.928
AbsCorr = MULTI-SCAN

Data completeness= 0.992           Theta(max)= 26.453

R(reflections)= 0.0517( 2495)                wR2(reflections)=
                                             0.1668( 3399)
S = 1.048                  Npar= 239
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT905_ALERT_3_C Negative K value in the Analysis of Variance ...     -0.336 Report
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min).          5 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         12 Report
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF ....         10 Note
```

Alert level G

```
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          1 Note
PLAT793_ALERT_4_G Model has Chirality at C17         (Centro SPGR)          S Verify
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT898_ALERT_4_G Second Reported H-M Symbol in CIF Ignored ......          ! Check
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          9 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          3 Note
PLAT965_ALERT_2_G The SHELXL WEIGHT Optimisation has not Converged     Please Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          6 Info
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
8 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

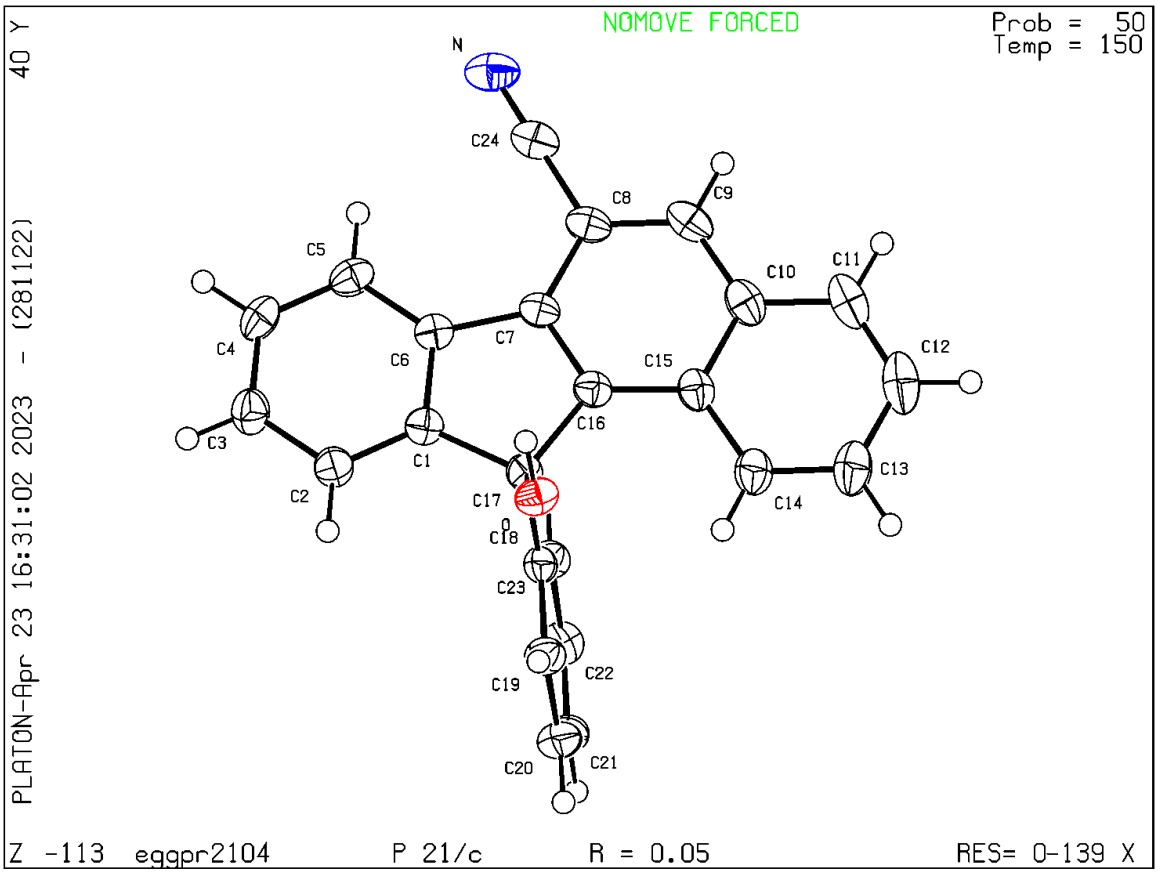
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 28/11/2022; check.def file version of 28/11/2022

Datablock eggpr2104 - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

```
Bond precision:   C-C = 0.0018 A          Wavelength=0.71073

Cell:           a=8.7518(2)         b=9.3697(2)      c=10.0504(2)
                alpha=107.912(2)    beta=94.173(2)   gamma=100.409(2)
Temperature:    113 K

                 Calculated                Reported
Volume           764.01(3)                 764.01(3)
Space group      P -1                      P -1
Hall group       -P 1                      -P 1
Moiety formula   C21 H15 N O               C21 H15 N O
Sum formula      C21 H15 N O               C21 H15 N O
Mr               297.34                    297.34
Dx,g cm-3        1.293                     1.293
Z                2                         2
Mu (mm-1)        0.079                     0.079
F000             312.0                     312.0
F000'            312.12
h,k,lmax         10,11,11                  10,11,11
Nref             2685                      2683
Tmin,Tmax        0.984,0.984               0.406,1.000
Tmin'            0.984

Correction method= # Reported T Limits: Tmin=0.406 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.999           Theta(max)= 25.000

R(reflections)= 0.0344( 2484)                    wR2(reflections)=
                                                 0.0945( 2683)
S = 1.064                  Npar= 208
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...        23 Report
PLAT005_ALERT_5_G No Embedded Refinement Details Found  in the CIF    Please Do !
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)     0.002 Degree
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C13      --C14      .       5.8 s.u.
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       684 Note
```

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0 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
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1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
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1 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

checkCIF publication errors

Alert level A

```
PUBL004_ALERT_1_A  The contact author's name and address are missing,
           _publ_contact_author_name and _publ_contact_author_address.
PUBL005_ALERT_1_A  _publ_contact_author_email, _publ_contact_author_fax and
           _publ_contact_author_phone are all missing.
           At least one of these should be present.
PUBL006_ALERT_1_A  _publ_requested_journal is missing
           e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A  _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A  _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A  _publ_author_address is missing. Author(s) address(es).
PUBL012_ALERT_1_A  _publ_section_abstract is missing.
           Abstract of paper in English.
```

7 **ALERT level A** = Data missing that is essential or data in wrong format
0 **ALERT level G** = General alerts. Data that may be required is missing

Publication of your CIF

You should attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the nature of your study may justify the reported deviations from journal submission requirements and the more serious of these should be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. *checkCIF* was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

If level A alerts remain, which you believe to be justified deviations, and you intend to submit this CIF for publication in a journal, you should additionally insert an explanation in your CIF using the Validation Reply Form (VRF) below. This will allow your explanation to be considered as part of the review process.

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

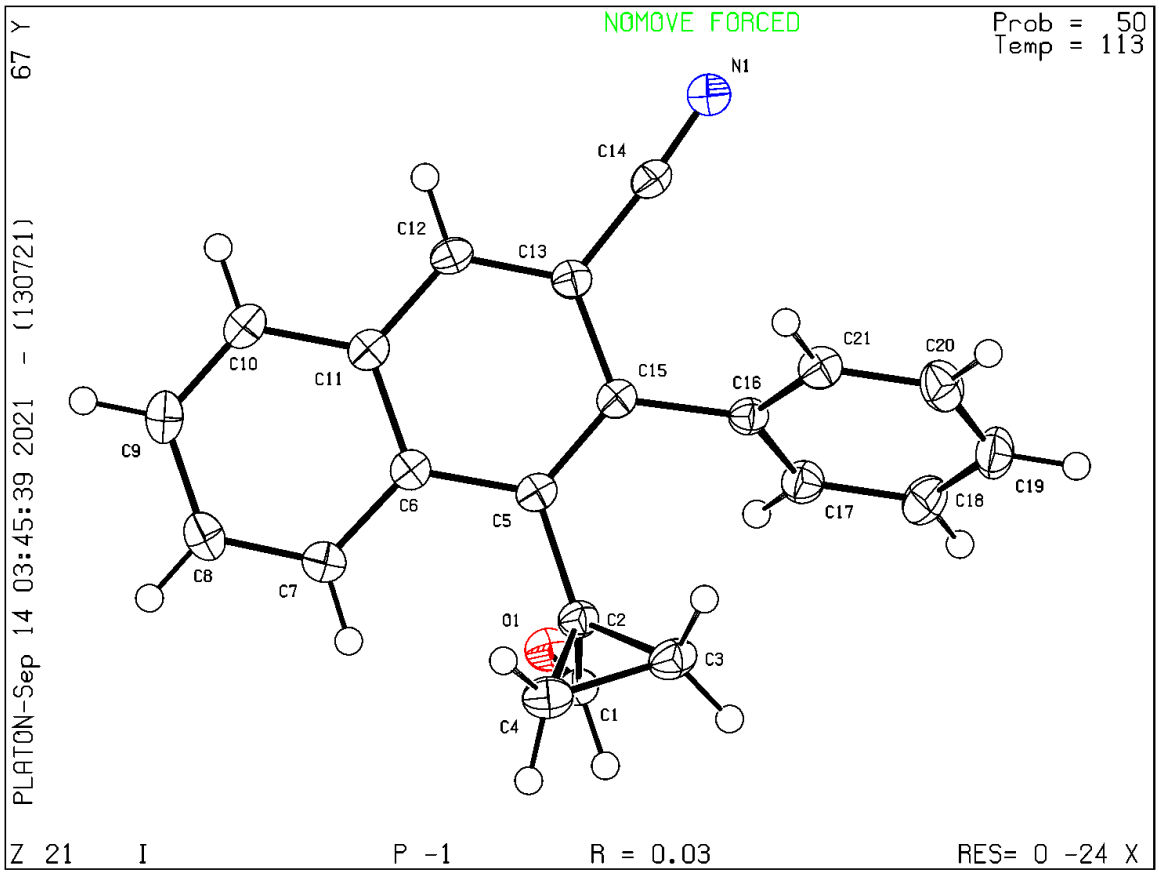
```
# start Validation Reply Form
_vrf_PUBL004_GLOBAL
;
PROBLEM: The contact author’s name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
```

```
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```

If you wish to submit your CIF for publication in Acta Crystallographica Section C or E, you should upload your CIF via the web. If you wish to submit your CIF for publication in IUCrData you should upload your CIF via the web. If your CIF is to form part of a submission to another IUCr journal, you will be asked, either during electronic submission or by the Co-editor handling your paper, to upload your CIF via our web site.

PLATON version of 13/07/2021; check.def file version of 13/07/2021

Datablock I - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) I

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

```
Bond precision:  C-C = 0.0018 A          Wavelength=0.71073

Cell:            a=11.5468(2)     b=16.9648(2)       c=8.6098(2)
                 alpha=90         beta=91.476(1)     gamma=90
Temperature:     113 K

                Calculated                Reported
Volume          1686.01(5)                1686.01(5)
Space group     P 21/c                    P 1 21/c 1
Hall group      -P 2ybc                   -P 2ybc
Moiety formula  C24 H14 Cl N              C24 H14 Cl N
Sum formula     C24 H14 Cl N              C24 H14 Cl N
Mr              351.81                    351.81
Dx,g cm-3       1.386                     1.386
Z               4                         4
Mu (mm-1)       0.233                     0.233
F000            728.0                     728.0
F000'           728.84
h,k,lmax        14,21,11                  14,21,10
Nref            3711                      3598
Tmin,Tmax       0.920,0.954               0.349,1.000
Tmin'           0.920

Correction method= # Reported T Limits: Tmin=0.349 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.970          Theta(max)= 27.092

R(reflections)= 0.0318( 3298)     wR2(reflections)= 0.0851( 3598)

S = 1.055                 Npar= 235
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .          1 Check
PLAT939_ALERT_3_C Large Value of Not (SHELXL) Weight Optimized S .      20.74 Check
```

Alert level G

```
PLAT153_ALERT_1_G The s.u.'s on the Cell Axes   are Equal ..(Note)     0.0002 Ang.
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C15      --C24      .        6.1 s.u.
PLAT793_ALERT_4_G Model has Chirality at C1          (Centro SPGR)          S Verify
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        111 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         20 Info
```

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2 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

checkCIF publication errors

Alert level A

```
PUBL004_ALERT_1_A  The contact author's name and address are missing,
           _publ_contact_author_name and _publ_contact_author_address.
PUBL005_ALERT_1_A  _publ_contact_author_email, _publ_contact_author_fax and
           _publ_contact_author_phone are all missing.
           At least one of these should be present.
PUBL006_ALERT_1_A  _publ_requested_journal is missing
           e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A  _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A  _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A  _publ_author_address is missing. Author(s) address(es).
PUBL012_ALERT_1_A  _publ_section_abstract is missing.
           Abstract of paper in English.
```

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Publication of your CIF

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Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PUBL004_GLOBAL
;
PROBLEM: The contact author’s name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
```

```
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```

If you wish to submit your CIF for publication in Acta Crystallographica Section C or E, you should upload your CIF via the web. If you wish to submit your CIF for publication in IUCrData you should upload your CIF via the web. If your CIF is to form part of a submission to another IUCr journal, you will be asked, either during electronic submission or by the Co-editor handling your paper, to upload your CIF via our web site.

PLATON version of 05/12/2020; check.def file version of 05/12/2020

Datablock I - ellipsoid plot