Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

For

Photocatalyst- and transition-metal-free syntheses of furan-fused dihydroazepines by visible light

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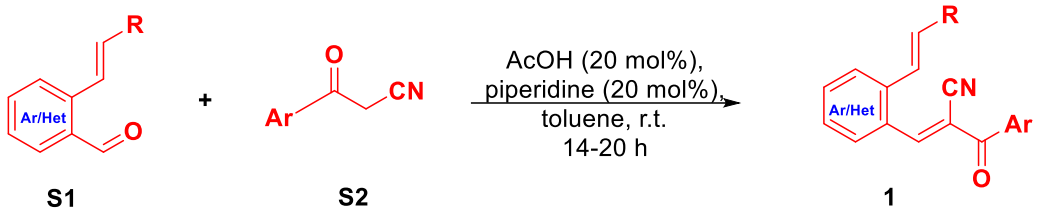
1. General Information

^{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). ^{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[1] 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.

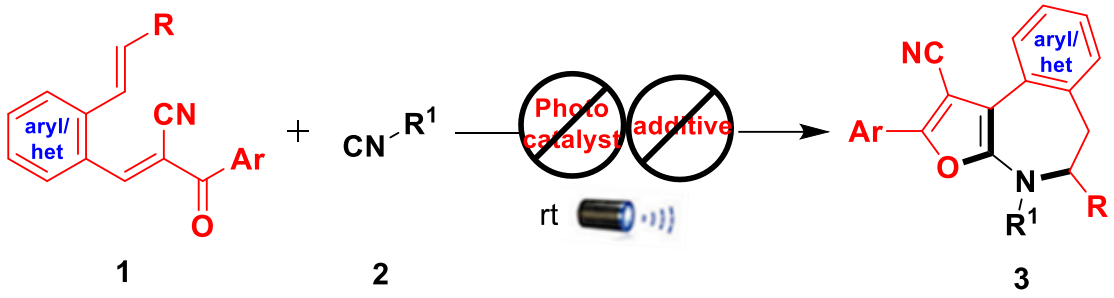
2. Experimental Procedure

a) General Procedure for the Synthesis of (*E*)-2-aroyl-3-(2-((*E*)-styryl)aryl/alkyl)acrylonitrile (1)[2]

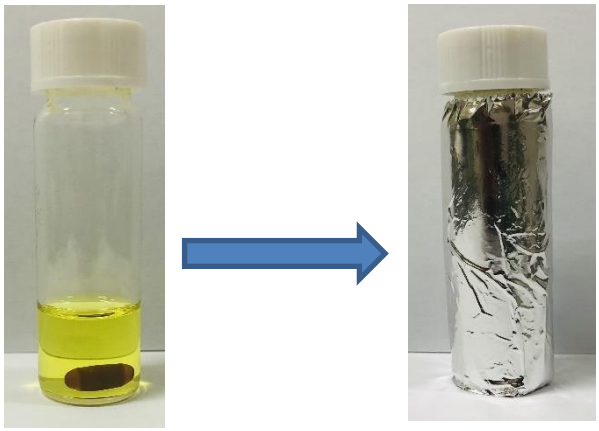


A reaction tube was charged with (*E*)-2-styrylbenzaldehyde (**S1**) (1.0 equiv), 3-oxo-3-aroylacetonitriles and derivatives (**S2**) (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 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-((*E*)-styryl)aryl/alkyl)acrylonitrile derivatives **1**.

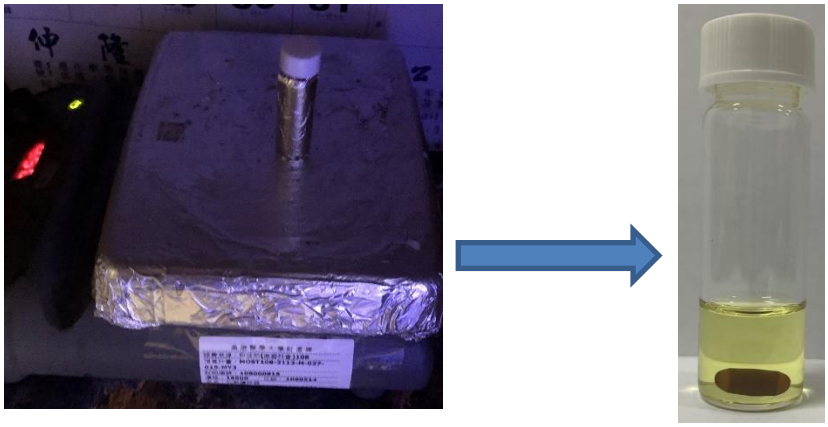
b) General procedure for the synthesis of dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile derivatives



A clean vial (5 mL) equipped with a magnetic stir bar was added to **1** (0.2 mmol). Next, EtOAc (2.0 mL) was added after which, **2** (0.2 mmol) were added at room temperature, and then solution was stirred at room temperature under dark for 20-30 h and placed at a distance of approx. 3.0 cm from a 40 W blue LED, and the visible-light irradiation for 1-10 h. The progress of the reaction was monitored by TLC. 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 = 99/1) on silica gel to afford the corresponding dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile derivatives **3**.



Before reaction 1a + 2a in ethyl acetate

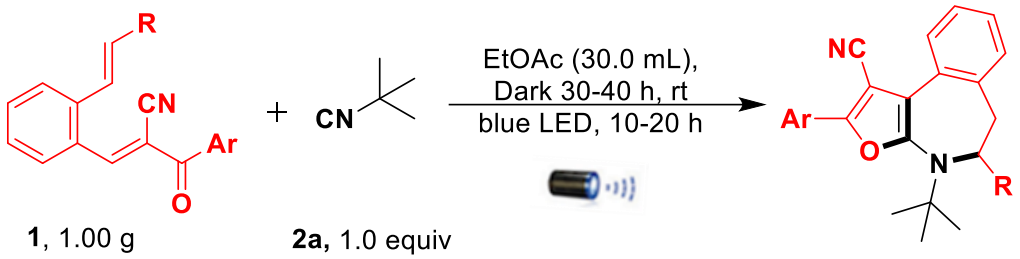


After 20 h (intermediate)

After reaction

Figure S1: Reaction setup

c) General procedure for gram scale synthesis



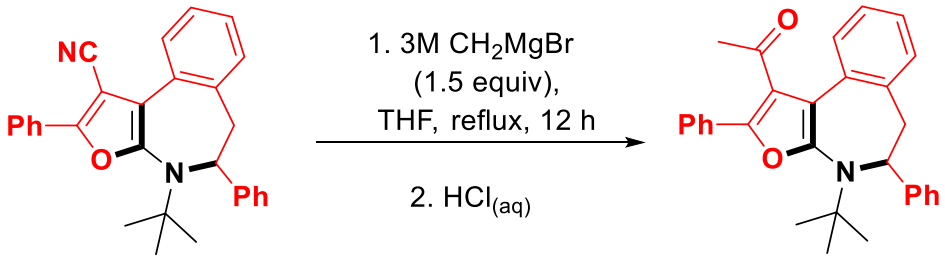
1, 1.00 g **2a,** 1.0 equiv

1 =	**1a, R = Ph Ar = Ph**	**1k, R = Ph, Ar = Ph-*m*Br**	**1l, R = Ph, Ar = Ph-*o*-Br**
Yield	**3aa**, 72 %	**3ka**, 60 %	**3la**, 58 %

A clean round-bottomed flask (50 mL) equipped with a magnetic stir bar was added to **1** (1.00 g). Next, EtOAc (0.1 M) was added after which, **2** (1.0 equiv) were added at room temperature, and then solution was stirred at room temperature under dark for 30-40 h and placed at a distance of approx. 3.0 cm from a 40 W blue LED, and the visible-light irradiation for 10-20 h. The progress of the reaction was monitored by TLC. When the reaction was complete, water was added to quench the reaction mixture, followed by extraction with ethyl acetate (3×30 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 = 99/1) on silica gel to afford the corresponding dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile derivatives.

3. Synthetic Applications (Scheme S1)

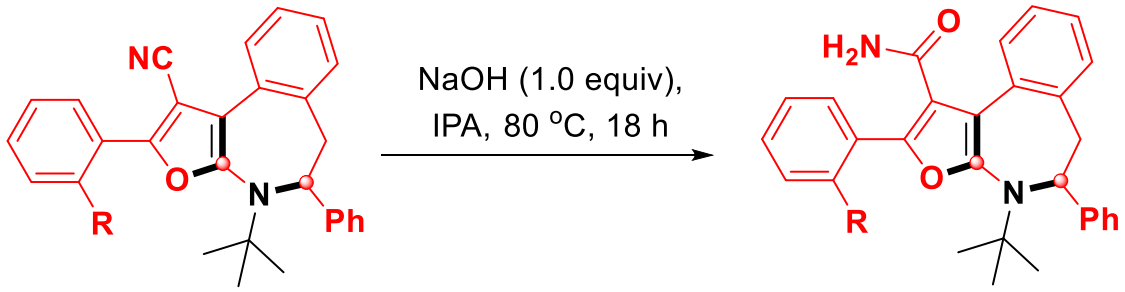
(a) General procedure for the synthesis of 1-(4-(*tert*-butyl)-2,5-diphenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepin-1-yl)ethan-1-one (3ya) :



3aa **3ya**, 68 % yield

Prepare a clean 15 mL sealed tube with a magnetic stir bar **3aa** (0.2 mmol) was added to the bottle, followed by the solvent anhydrous THF (3.0 mL), and then the tube was filled with nitrogen. Then 3 M CH_3MgBr (1.5 equiv) was slowly added dropwise, then heated to about 100 °C to reflux in the tube, and the reaction was monitored by TLC. After the reaction was completed, it was cooled to room temperature and then 1 M aqueous $HCl_{(aq)}$ was added, then heating the reaction to reflux for about 1 hour. After reaction finished, cooled the reaction to room temperature, and then extracted with ethyl acetate (3 x 15 mL) and water. Finally, all organic layers were combined and removed with anhydrous sodium sulfate, filtered and concentrated in vacuo. After concentration, the residue was purified by column chromatography (Hex/EA = 99/1) to obtain the product **3ya**.

b) General procedure for the synthesis of 5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carboxamide (5 and 8:



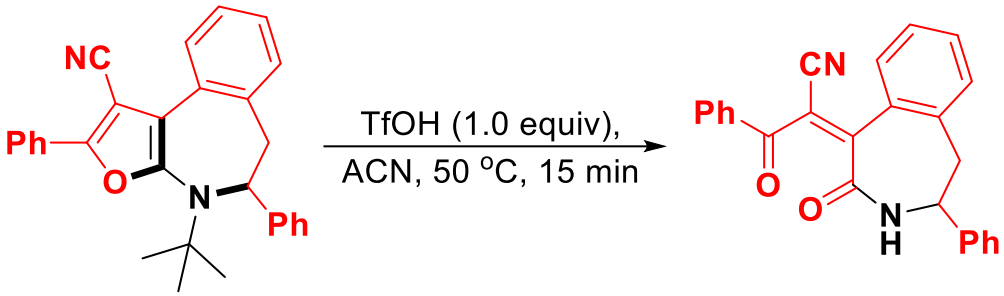
3aa,
3la

R=H **5**, 77 % yield
R=Br **8**, 67%, yield

Prepare a clean 15 mL sealed tube with a magnetic stir bar. **3aa/3la** (0.2 mmol) was added to the bottle, followed by the solvent EtOH (3.0 mL). Finally, NaOH (1.0 equiv) was added and the mixture was heated to 80 °C and the reaction was monitored by TLC. After completion of the reaction, water was added to stop the reaction and the reaction was neutralized to about pH=7 by 1 M $HCl_{(aq)}$, then extracted with ethyl acetate (3 x 15 mL) and water. Finally, all organic layers were combined and removed with anhydrous sodium sulfate,

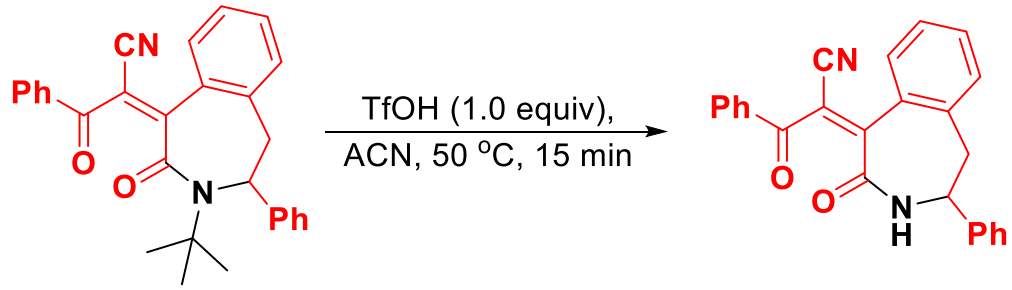
filtered and concentrated in vacuo. After concentration, the residue was purified by column chromatography (Hex/EA = 5/1) to obtain the product.

(c) General procedure for the synthesis of (*Z*)-3-oxo-2-(2-oxo-4-phenyl-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepin-1-ylidene)-3-phenylpropanenitrile (6):



3aa **6**, 83 % yield

Synthesis route 1: Prepare a clean 15 mL sealed tube with a magnetic stir bar. **3aa** (0.1 mmol) and ACN (3.0 mL) were added to the bottle. TfOH (1.0 equiv) was then added slowly, followed by heating to about 50 °C and the reaction monitored by TLC. After the reaction was completed, cooled to room temperature and then added $Na_2CO_{3(aq)}$ solution to neutralize the reaction to about pH=7. It was then extracted with ethyl acetate (3 x 15 mL) and water. Finally, all organic layers were combined and removed with anhydrous sodium sulfate, filtered and concentrated in vacuo. After concentration, the residue was purified by column chromatography (Hex/EA = 5/1) to obtain the product **6**.

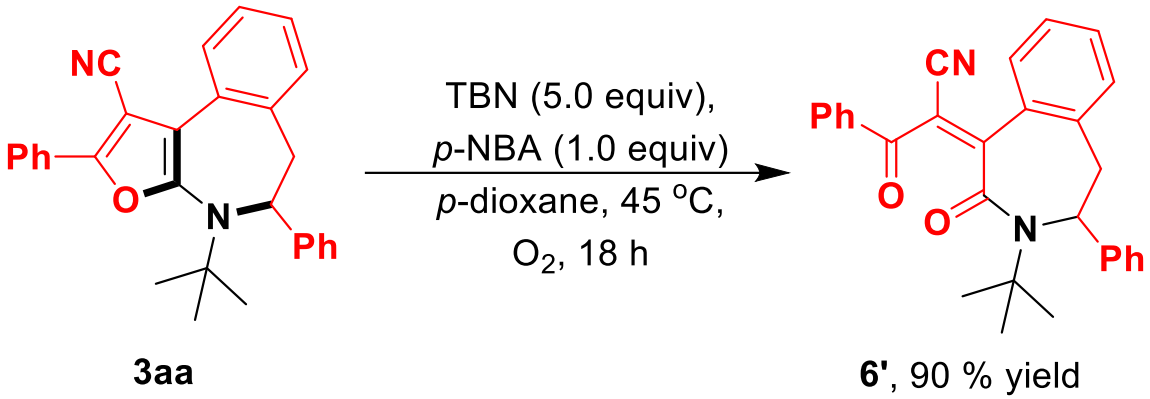


6', 83 % yield **6,** 92 % yield

Synthesis route 2: Prepare a clean 15 mL sealed tube with a magnetic stir bar. **6'** (0.1 mmol) and ACN (3.0 mL) were added to the bottle. TfOH (1.0 equiv) was then added slowly, followed by heating to about 50 °C and the reaction monitored by TLC. After the reaction was completed, cooled to room temperature and then added $Na_2CO_{3(aq)}$ solution to neutralize the reaction to about pH=7. It was then extracted with ethyl acetate (3 x 15 mL) and water. Finally, all organic layers were combined and removed with anhydrous sodium sulfate, filtered and

concentrated in vacuo. After concentration, the residue was purified by column chromatography (Hex/EA = 5/1) to obtain the product **6**.

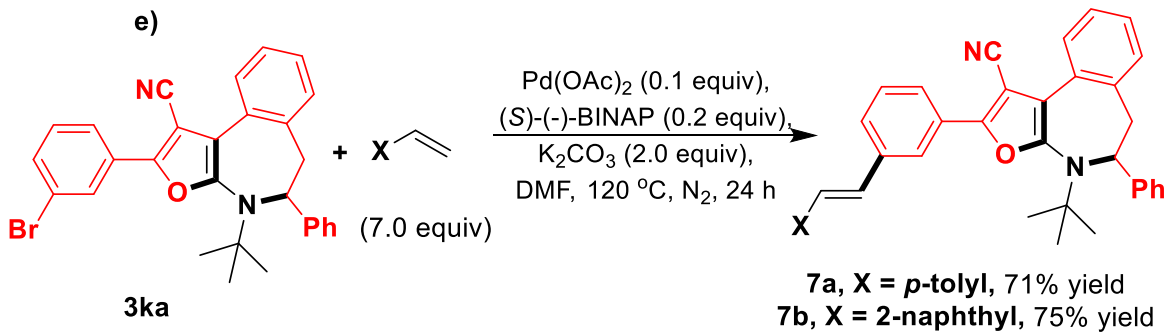
General procedure for the synthesis of (*Z*)-2-(3-(*tert*-butyl)-2-oxo-4-phenyl-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepin-1-ylidene)-3-oxo-3-phenylpropanenitrile (6'):



3aa **6'**, 90 % yield

Prepare a clean 15 mL sealed tube with a magnetic stir bar. **3aa** (0.2 mmol), TBN (5.0 equiv), *p*-NBA (1.0 equiv), and *p*-dioxane (3.0 mL) were added to the bottle in sequence. The tube was then filled with oxygen and then heated to about 45 °C and the reaction was monitored by TLC. After the reaction was completed, cooled to room temperature and then added $Na_2CO_{3(aq)}$ solution to neutralize the reaction to about pH=7. It was then extracted with ethyl acetate (3 x 15 mL) and ater. Finally, all organic layers were combined and removed with anhydrous sodium sulfate, filtered and concentrated in vacuo. After concentration, the residue was purified by column chromatography (Hex/EA = 9/1) to obtain the product **6'**.

(f) General procedure for the synthesis of (*E*)-4-(*tert*-butyl)-2-(3-(styryl/vinyl)phenyl)-5-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (7a and 7b):



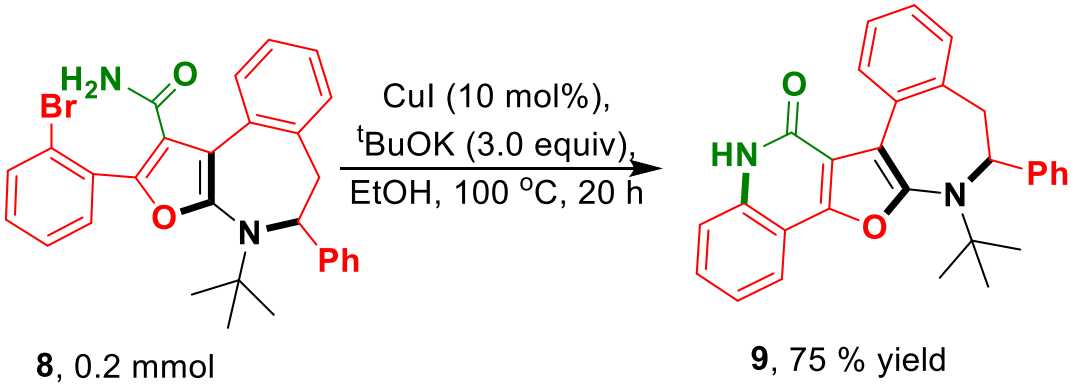
3ka

7a, X = *p*-tolyl, 71% yield
7b, X = 2-naphthyl, 75% yield

First, **3ka** (1.0 equiv, 0.1 mmol), $Pd(OAc)_2$ (0.1 equiv), and (*S*)-(-)-BINAP (0.2 equiv) were added to a 25 mL round-bottomed flask, respectively, followed by nitrogen The round bottom flask was filled with nitrogen. Next,

5 mL of DMF was added as a solvent, then K_2CO_3 (2.0 equiv) was added. After waiting for the reaction to react at room temperature for 10 minutes, then respective alkenes (7.0 equiv) was slowly added. Heating to 120 °C and was monitored by TLC. After the reaction was completed, the reaction was cooled to room temperature, and secondary water was added, followed by extraction with ethyl acetate and water. After 2~3 times in total, all organic layers were combined and removed with anhydrous sodium sulfate. The water was concentrated by a vacuum concentrator to obtain the crude product, and then further purified by column chromatography (Hex/EA = 50/1) to obtain the compound**7a/7b**.

(e) General procedure for the synthesis of 13-(*tert*-butyl)-12-phenyl-5,11,12,13-tetrahydro-6*H*-benzo[4',5']azepino[3',2':4,5]furo[3,2-c]quinolin-6-one (9)

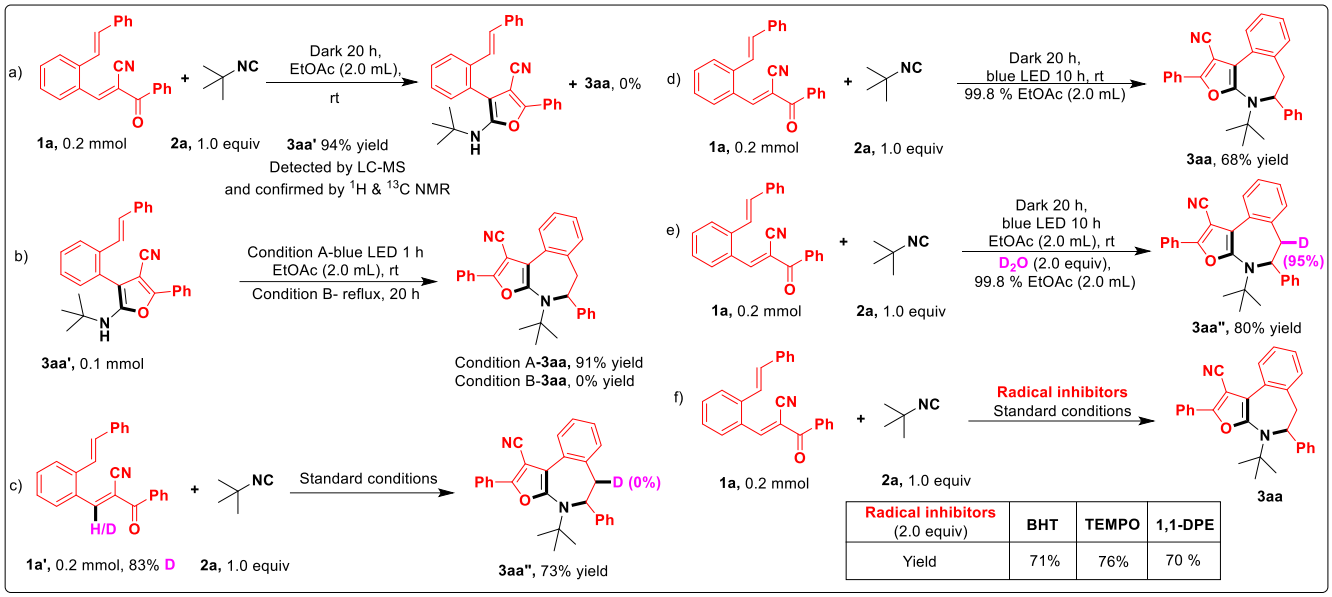


8, 0.2 mmol

9, 75 % yield

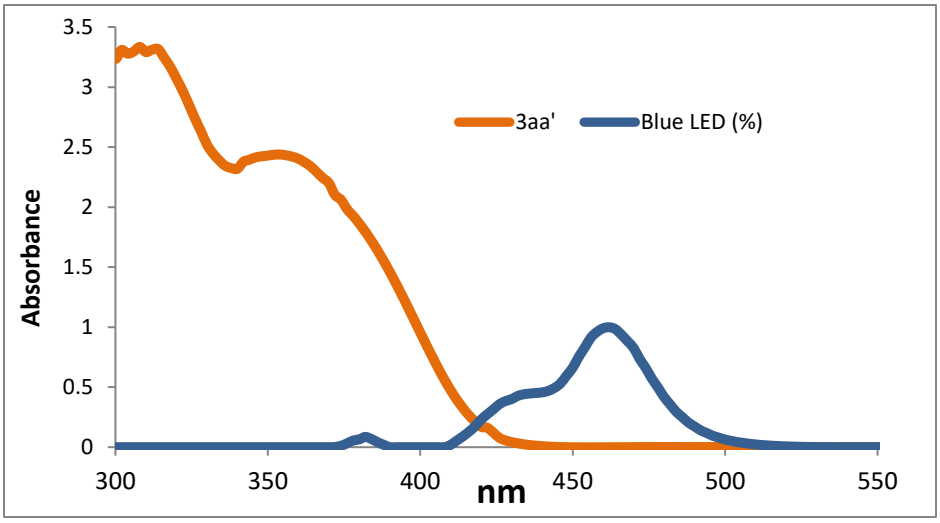
Prepare a clean 15 mL sealed tube with a magnetic stir bar. To the bottle was added **8** (0.1 mmol), *t*-BuOK (3.0 equiv), and the solvent ethanol (2.0 mL). Later, CuI (10 mol%) was added and heated to 100 °C, and the reaction was monitored by TLC. After the reaction was completed, water was added to stop the reaction, followed by extraction with ethyl acetate (3×15 mL) and water. Finally, all organic layers were combined and removed with anhydrous sodium sulfate, filtered and concentrated in vacuo. After concentration, the residue was purified by column chromatography (Hex/EA = 19/1) to obtain the product **9**.

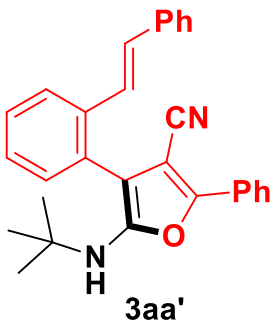
4. Control Studies (Scheme S2)



Radical inhibitors (2.0 equiv)	BHT	TEMPO	1,1-DPE
Yield	71%	76%	70 %

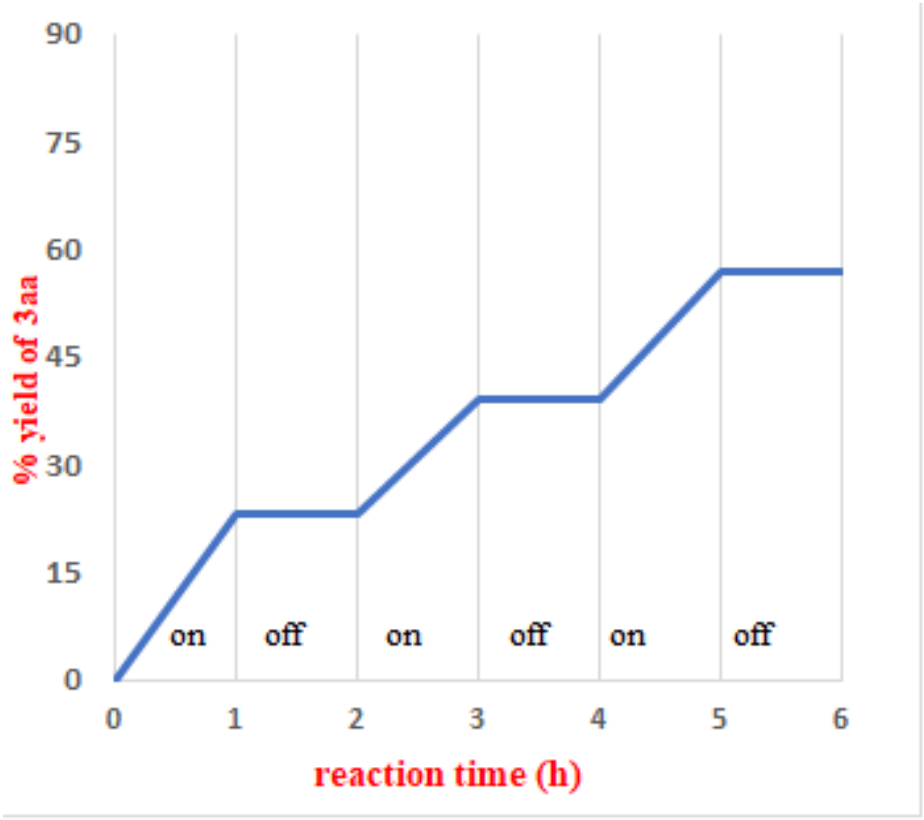
5. Fluorescence Quenching Study





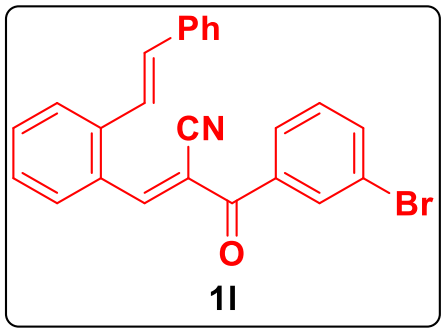
3aa'

6. Light on-off study



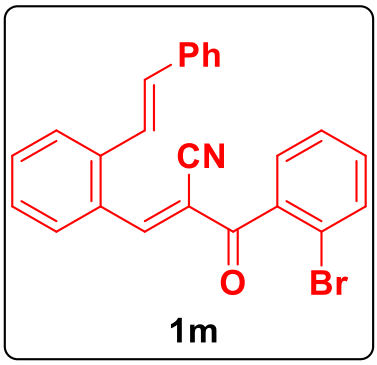
7. Spectral Characterization

(*E*)-2-(3-bromobenzoyl)-3-(2-((*E*)-styryl)phenyl)acrylonitrile (1l): A reaction tube was charged with **S1a** (1.0 equiv), **S2c** (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 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 (3×15 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 **1l**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 2.2 Hz, 1H), 8.20 (t, *J* = 5.5 Hz, 1H), 8.02 (d, *J* = 1.8 Hz, 1H), 7.81 (ddd, *J* = 9.0, 5.0, 3.5 Hz, 1H), 7.75 – 7.69 (m, 1H), 7.65 (t, *J* = 5.5 Hz, 1H), 7.55 (dd, *J* = 15.0, 7.3 Hz, 1H), 7.52 – 7.36 (m, 5H), 7.35 – 7.28 (m, 2H), 7.28 – 7.20 (m, 1H), 6.90 (dd, *J* = 16.0, 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 187.55, 154.93, 139.91, 137.57, 136.35, 136.22, 135.65, 132.91, 132.03, 130.10, 129.71, 129.02, 128.85, 128.69, 127.98, 127.77, 127.64, 126.90, 124.56, 123.03, 116.25, 111.57; Yield: 73 % (301.5 mg), yellow solid, m.p. 112 – 114 °C. HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{24}H_{17}BrNO$ 414.0494; found 414.0498.



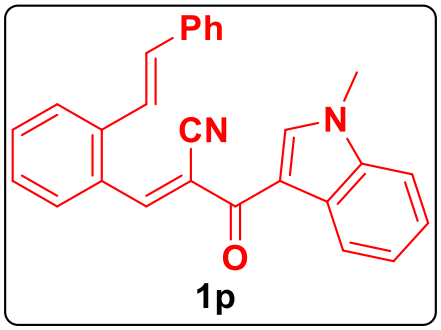
1l

(*E*)-2-(2-bromobenzoyl)-3-(2-((*E*)-styryl)phenyl)acrylonitrile (1m): A reaction tube was charged with **S1a** (1.0 equiv), **S2b** (1.5 equiv),AcOH (20 mol%) and piperidine (20 mol%) in 5.0 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 (3×15 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 **1m**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 – 8.21 (m, 2H), 7.64 – 7.51 (m, 1H), 7.59 – 7.50 (m, 2H), 7.47 – 7.38 (m, 5H), 7.46 – 7.26 (m, 1H), 7.37 – 7.25 (m, 4H), 7.15 (dd, *J* = 16.0, 2.1 Hz, 1H), 7.15 (dd, *J* = 16.0, 2.1 Hz, 1H), 6.78 (dd, *J* = 16.0, 2.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.35, 155.23, 140.22, 138.69, 136.35, 136.03, 133.25, 133.09, 132.01, 129.45, 129.09, 128.75, 128.67, 128.01, 127.95, 127.62, 126.85, 124.65, 119.16, 115.21, 112.85; Yield: 72 % (297.4 mg), yellow solid, m.p. 132 – 134 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{24}H_{17}BrNO$ 414.0494; found 414.0491.

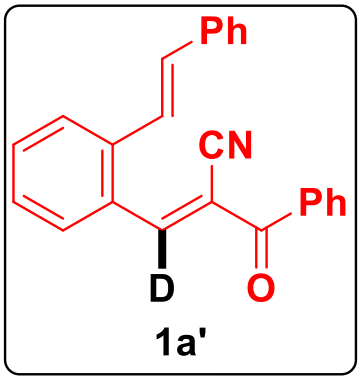


1m

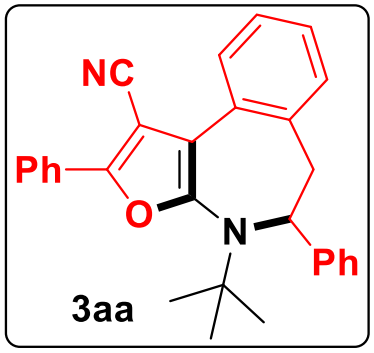
(*E*)-2-(1-methyl-1*H*-indole-3-carbonyl)-3-(2-((*E*)-styryl)phenyl)acrylonitrile (1p): A reaction tube was charged with **S1a** (1.0 equiv), **S2g** (1.5 equiv),AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 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-((*E*)-styryl)aryl/alkyl)acrylonitrile derivatives **1p**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 8.49 – 8.43 (m, 1H), 8.34 (s, 1H), 8.12 – 8.06 (m, 1H), 7.69 – 7.65 (m, 1H), 7.56 – 7.46 (m, 3H), 7.42 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38 – 7.35 (m, 4H), 7.33 (s, 1H), 7.31 – 7.24 (m, 2H), 6.98 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$)**:** δ 178.77, 152.76, 139.02, 137.22, 137.01, 136.62, 134.39, 131.79, 130.72, 128.88, 128.76, 128.40, 127.77, 127.44, 127.24, 126.91, 124.97, 124.11, 123.37, 122.95, 118.58, 114.16, 112.71, 109.87, 33.79; Yield: 68 % (263.9 mg), yellow solid, m.p. 150 – 152 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{27}H_{21}N_2O$ 389.1654; found 389.1651.



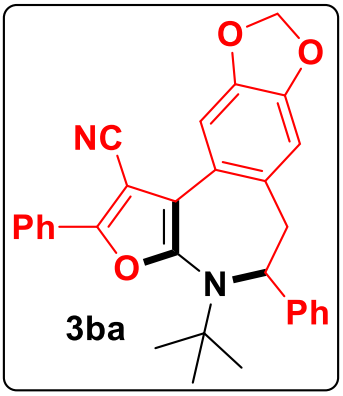
(*E*)-2-benzoyl-3-(2-((*E*)-styryl)phenyl)acrylonitrile-*d* (1a'): A reaction tube was charged with **S1a'** (1.0 equiv), **S2a** (1.5 equiv),AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 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 **1a'**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.21 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.93 – 7.88 (m, 2H), 7.95 – 7.87 (m, 2H), 7.69 – 7.64 (m, 1H), 7.68 – 7.53 (m, 4H), 7.63 – 7.58 (m, 1H), 7.55 (td, *J* = 7.6, 1.3 Hz, 1H), 7.51 – 7.44 (m, 6H), 7.43 – 7.30 (m, 3H), 7.25 (t, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$):δ 189.01, 154.55, 139.67, 136.46, 135.81, 135.38, 133.39, 132.62, 132.59, 129.88, 129.27, 129.00, 128.83, 128.69, 128.63, 127.97, 127.65, 126.87, 124.74, 124.72, 116.46, 112.20; Yield: 76% (255.5 mg), yellow solid, m.p. 131 – 133 °C: HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{24}H_{17}DNO$ 337.1451; found 337.1454.



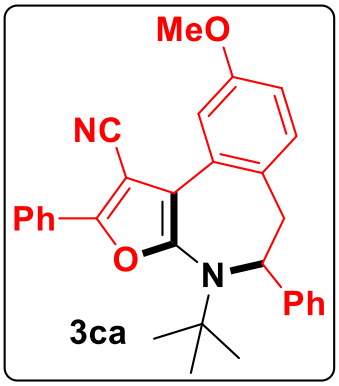
4-(*tert*-butyl)-2,5-diphenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (3aa): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.7 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.49 – 7.39 (m, 4H), 7.32 – 7.21 (m, 1H), 5.02 (d, *J* = 12.1 Hz, 1H), 3.00 (dd, *J* = 14.3, 12.3 Hz, 1H), 2.78 (dd, *J* = 14.3, 3.9 Hz, 1H), 0.97 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.70, 154.53, 146.97, 138.37, 131.13, 129.50, 129.29, 129.05, 128.80, 128.49, 127.70, 127.59, 126.80, 126.32, 125.83, 125.11, 116.18, 115.09, 91.02, 71.03, 58.96, 44.31, 28.93; Yield: 90% (75.2 mg), white solid, m.p. 171-173 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{29}H_{27}N_2O$ 419.2123; found 419.2119.



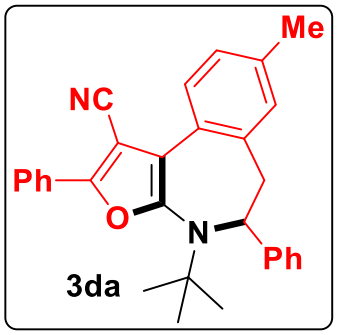
4-(*tert*-butyl)-2,5-diphenyl-5,6-dihydro-4*H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-*d*]furo[2,3-*b*]azepine-1-carbonitrile (3ba): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 – 8.03 (m, 1H), 7.52 (ddd, *J* = 8.4, 5.6, 2.0 Hz, 2H), 7.46 – 7.40 (m, 3H), 7.38 – 7.32 (m, 2H), 7.24 (d, *J* = 1.9 Hz, 1H), 7.11 (s, 1H), 6.81 (s, 1H), 6.00 (dd, *J* = 17.8, 1.4 Hz, 1H), 4.97 (dd, *J* = 12.2, 3.7 Hz, 1H), 2.90 (dd, *J* = 14.4, 12.3 Hz, 1H), 2.65 (dd, *J* = 14.5, 3.8 Hz, 1H), 0.98 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.64, 154.50, 147.06, 146.82, 132.36, 129.50, 129.04, 129.01, 128.49, 126.81, 125.82, 125.10, 124.34, 116.50, 115.06, 109.77, 106.91, 101.21, 90.94, 71.43, 58.81, 44.16, 28.97; Yield: 81% (75.0 mg), pale yellow solid, m.p. 263-265 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{30}H_{27}N_2O_3$ 463.2022; found 463.2016.



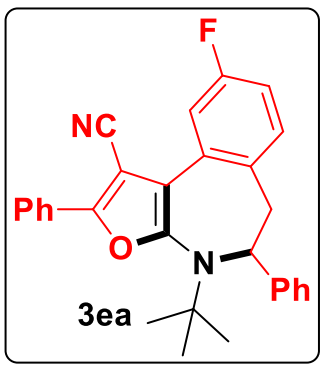
4-(*tert*-butyl)-9-methoxy-2,5-diphenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (3ca): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (597 MHz, $CDCl_3$): δ 8.11 – 8.04 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.47 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.45 – 7.41 (m, 1H), 7.38 – 7.32 (m, 2H), 7.23 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.93 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.88 (d, *J* = 2.6 Hz, 1H), 4.99 (dd, *J* = 12.4, 3.9 Hz, 1H), 3.86 (s, 3H), 2.96 (dd, *J* = 14.4, 12.4 Hz, 1H), 2.72 (dd, *J* = 14.4, 3.9 Hz, 1H), 0.96 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.14, 154.55, 154.15, 147.05, 139.99, 129.42, 129.04, 128.91, 128.49, 127.47, 126.79, 125.85, 125.09, 123.52, 116.40, 115.47, 115.20, 112.41, 91.09, 70.62, 58.90, 55.34, 44.51, 28.91; Yield: 82% (73.5 mg), white solid, m.p. 226-228 °C. HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{30}H_{28}N_2O_2$ 448.2151; found 448.2152.



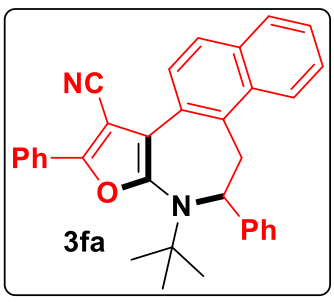
4-(*tert*-butyl)-8-methyl-2,5-diphenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (3da): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (597 MHz, $CDCl_3$): δ 8.13 – 8.04 (m, 2H), 7.55 – 7.49 (m, 2H), 7.48 (dd, *J* = 5.2, 3.1 Hz, 2H), 7.45 – 7.43 (m, 1H), 7.36 (dd, *J* = 9.2, 6.3 Hz, 2H), 7.27 – 7.22 (m, 1H), 7.20 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.14 (d, *J* = 1.8 Hz, 1H), 4.99 (dd, *J* = 12.4, 3.9 Hz, 1H), 2.96 (dd, *J* = 14.4, 12.5 Hz, 1H), 2.72 (dd, *J* = 14.4, 3.9 Hz, 1H), 2.39 (s, 2H), 2.39 (s, 3H), 0.97 (s, 10H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.59, 154.43, 147.15, 138.32, 137.55, 130.11, 129.42, 129.04, 128.91, 128.49, 128.26, 126.91, 126.77, 126.17, 125.85, 125.10, 116.45, 115.14, 91.11, 58.95, 44.35, 28.95, 21.34; Yield: 84% (72.7 mg), white solid, m.p. 176 – 178 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{30}H_{28}N_2O$ 432.2202; found 432.2207.



4-(*tert*-butyl)-9-fluoro-2,5-diphenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (3ea): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel to get R/S = 52:48 isomer mixture. ^{1}H NMR (597 MHz, $CDCl_3$): δ 8.11 – 8.04 (m, 2H), 7.59 (dd, *J* = 8.4, 5.5 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.47 – 7.41 (m, 3H), 7.37 – 7.33 (m, 2H), 7.28 – 7.22 (m, 1H), 7.09 (td, *J* = 8.5, 2.6 Hz, 1H), 7.05 (s, 1H), 6.96 (td, J = 8.4, 2.6 Hz, 1H), 5.01 (ddd, *J* = 12.4, 8.9, 3.9 Hz, 1H), 2.98 (dd, *J* = 12.1, 10.3 Hz, 1H), 2.81 – 2.76 (m, 1H), 2.76 – 2.71 (m, 1H), 0.98 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 162.17 (d, $J_{C\text{-}F}$ = 245.6 Hz), 161.99 (d, $J_{C\text{-}F}$ = 247.2 Hz), 154.80, 154.36, 146.60, 146.56, 140.74, 140.69, 134.03 (d, $J_{C\text{-}F}$ = 3.0 Hz), 133.00, 132.94, 130.69 (d, $J_{C\text{-}F}$ = 8.6 Hz), 129.63 (d, $J_{C\text{-}F}$ = 7.1 Hz), 129.10, 129.09, 128.71, 128.61, 128.57, 128.54, 127.90 (d, $J_{C\text{-}F}$ = 8.6 Hz), 127.18 (d, $J_{C\text{-}F}$ = 2.9 Hz), 126.95 (d, $J_{C\text{-}F}$ =7.4 Hz), 125.79, 125.78, 125.12, 125.11, 116.38 (d, $J_{C\text{-}F}$ = 21.6 Hz), 115.39, 115.02, 115.00, 114.95, 114.70, 114.35 (d, $J_{C\text{-}F}$ = 24.8 Hz), 114.49 (d, $J_{C\text{-}F}$ = 25.1 Hz), 113.25 (d, $J_{C\text{-}F}$ = 22.7 Hz), 90.94, 90.83, 71.00, 70.68, 59.07, 58.98, 44.17, 43.50, 28.99, 28.94; Yield: 77% (67.2 mg), white solid, m.p. 203 – 205 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{29}H_{25}FN_2O$ 436.1951; found 436.1953.

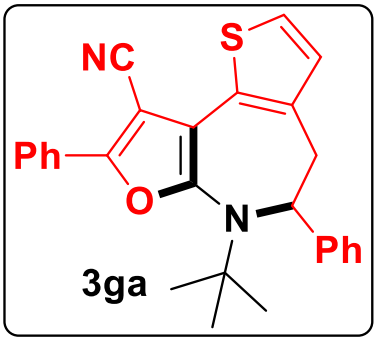


3-(*tert*-butyl)-2,5-diphenyl-2,3-dihydro-1*H*-furo[2,3-*b*]naphtho[2,1-*d*]azepine-6-carbonitrile (3fa): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 – 8.08 (m, 2H), 7.93 – 7.79 (m, 4H), 7.69 – 7.59 (m, 2H), 7.58 – 7.38 (m, 6H), 7.37 – 7.26 (m, 2H), 5.19 (dd, *J* = 11.7, 3.6 Hz, 1H), 3.09 (dd, *J* = 14.3, 12.3 Hz, 1H), 2.85 (dd, *J* = 14.4, 3.9 Hz, 1H), 0.99 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.76, 154.56, 144.44, 138.34, 133.44, 132.64, 131.14, 129.53, 129.34, 129.10, 128.84, 128.39, 127.85, 127.75, 127.72, 127.65,

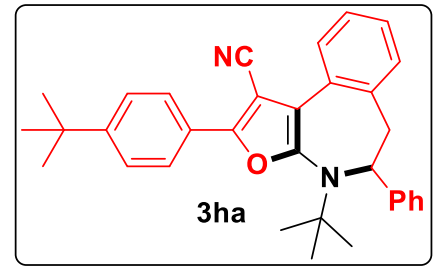


126.37, 126.10, 125.60, 125.12, 124.48, 124.16, 116.23, 115.08, 91.09, 71.21, 59.09, 44.22, 28.99; Yield: 74% (69.3 mg), pale yellow solid, m.p. 195 – 197 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{33}H_{28}N_2O$ 468.2202; found 468.2203.

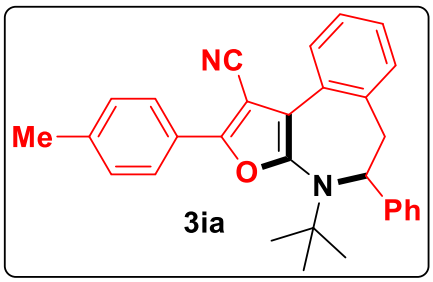
6-(*tert*-butyl)-5,8-diphenyl-5,6-dihydro-4*H*-furo[2,3-*b*]thieno[2,3-*d*]azepine-9-carbonitrile (3ga): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.50 – 7.44 (m, 1H), 7.39 (s, 1H), 7.27 (s, 1H), 7.23 – 7.16 (m, 1H), 7.12 (dd, *J* = 8.5, 5.8 Hz, 1H), 6.98 (dd, *J* = 5.1, 1.4 Hz, 1H), 5.20 – 5.11 (m, 1H), 3.56 (ddd, *J* = 16.4, 6.6, 1.7 Hz, 1H), 3.21 – 3.12 (m, 1H), 1.37 (d, *J* = 1.3 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.64, 152.46, 142.63, 135.56, 129.30, 129.24, 128.98, 128.53, 128.18, 127.96, 126.67, 126.30, 124.87, 122.98, 115.46, 59.61, 58.61, 36.51, 29.60; Yield: 78% (66.3 mg), dark brown solid, m.p. 132 – 134 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{27}H_{25}N_2OS$ 425.1688; found 425.1683.



4-(*tert*-butyl)-2-(4-(*tert*-butyl)phenyl)-5-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-b]azepine-1-carbonitrile (3ha): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.7 Hz, 2H), 7.62 (d, *J* = 0.9 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.36 (dd, *J* = 13.8, 6.6 Hz, 3H), 7.27 (ddd, *J* = 12.1, 7.9, 2.8 Hz, 3H), 5.01 (dd, *J* = 12.3, 3.9 Hz, 1H), 2.99 (dd, *J* = 14.2, 12.5 Hz, 1H), 2.77 (dd, *J* = 14.3, 3.9 Hz, 1H), 1.38 (s, 9H), 0.96 (s, 9H); δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.08, 154.23, 152.95, 147.03, 138.37, 131.26, 129.81, 129.27, 128.47, 127.61, 127.56, 126.77, 126.32, 126.09, 125.99, 125.83, 124.97, 116.09, 115.23, 90.34, 71.04, 58.91, 44.35, 34.91, 31.17, 29.69, 29.65, 28.90; Yield: 86% (81.52 mg), pale yellow solid, m.p. 42 – 44 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{33}H_{35}N_2OS$ 475.6480; found 475.6484.

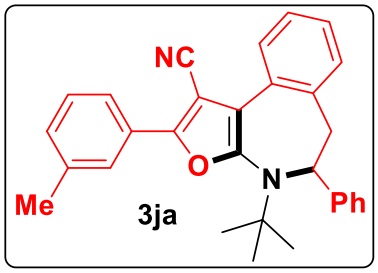


4-(*tert*-butyl)-5-phenyl-2-(*p*-tolyl)-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (3ia): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.42 – 7.21 (m, 8H), 5.01 (dd, *J* = 12.3, 3.8 Hz, 1H), 2.99 (dd, *J* = 14.3, 12.3 Hz, 1H), 2.77 (dd, *J* = 14.3, 3.9 Hz, 1H), 2.44 (s, 3H), 0.95 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.16, 154.21, 147.06, 139.84, 138.40, 131.26, 129.72, 129.28, 128.48, 127.64,



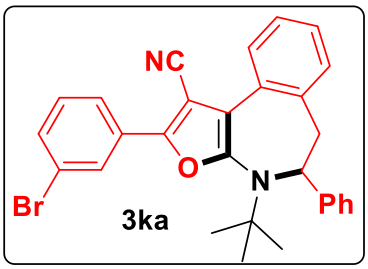
127.58, 126.78, 126.32, 126.15, 125.85, 125.12, 116.14, 115.25, 90.23, 71.04, 58.94, 44.34, 28.89, 21.52; Yield: 85% (73.4 mg), white solid, m.p. 183 – 185 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{30}H_{28}N_2O$ 432.2202; found 432.2201.

4-(*tert*-butyl)-5-phenyl-2-(*m*-tolyl)-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (3ja): The



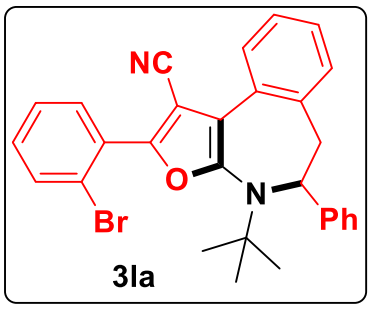
residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.85 (m, 2H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 7.3 Hz, 2H), 7.44 – 7.34 (m, 4H), 7.33 – 7.23 (m, 4H), 5.01 (dd, *J* = 12.3, 3.8 Hz, 1H), 3.07 – 2.94 (m, 1H), 2.78 (dd, *J* = 14.4, 3.9 Hz, 1H), 2.47 (s, 3H), 0.96 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.94, 154.42, 147.01, 138.82, 138.36, 131.17, 130.37, 129.27, 128.95, 128.73, 128.47, 127.66, 127.58, 126.78, 126.32, 125.83, 125.57, 122.38, 116.24, 115.12, 90.84, 77.31, 76.99, 76.68, 71.03, 58.98, 44.32, 28.90, 21.59; ; Yield: 82% (70.80 mg), white solid, m.p. 174 – 176 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{30}H_{28}N_2O$ 432.2202; found 432.2201.

2-(3-bromophenyl)-4-(tert-butyl)-5-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile



(3ka): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 1.9 Hz, 1H), 7.62 (t, *J* = 4.1 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.45 (ddd, *J* = 6.1, 1.5, 0.6 Hz, 1H), 7.39 (tt, *J* = 13.2, 4.3 Hz, 1H), 7.33 – 7.21 (m, 3H), 5.02 (dd, *J* = 12.3, 3.8 Hz, 1H), 2.99 (dd, *J* = 14.4, 12.4 Hz, 1H), 2.79 (dd, *J* = 14.4, 3.9 Hz, 1H), 0.97 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$)：δ 155.08, 152.67, 146.78, 138.30, 132.32, 130.79, 130.62, 130.58, 129.33, 128.54, 127.88, 127.80, 127.75, 127.66, 126.89, 126.31, 125.79, 123.54, 123.21, 116.37, 114.59, 92.16, 71.03, 59.14, 44.23, 28.95; Yield: 72% (71.5 mg), white solid, m.p. 202-204 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{29}H_{26}BrN_2O$ 497.1229; found 497.1226.

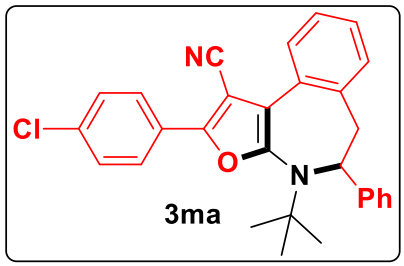
2-(2-bromophenyl)-4-(*tert*-butyl)-5-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile



(3la): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.72 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.62 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.42 – 7.35 (m, 2H), 7.35 – 7.20 (m, 4H), 5.05 (dd, *J* = 12.4, 4.0 Hz, 1H), 3.00 (dd, *J* = 14.3, 12.4 Hz, 1H), 2.79 (dd, *J* = 14.4, 4.1 Hz, 1H), 0.97 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.54, 154.69, 146.83, 138.45, 134.13, 131.70, 131.35, 131.17, 129.75, 129.32, 128.45, 127.78, 127.65, 127.61, 126.81, 126.42, 125.93, 122.10, 115.94, 114.02, 95.40, 71.27,

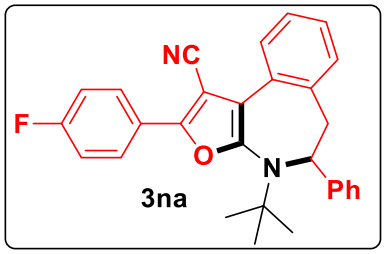
58.90, 44.27, 29.04; Yield: 68% (67.5 mg), white solid, m.p. 144-146 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{29}H_{25}BrN_2O$ 496.1150; found 496.1146.

4-(*tert*-butyl)-2-(4-chlorophenyl)-5-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile



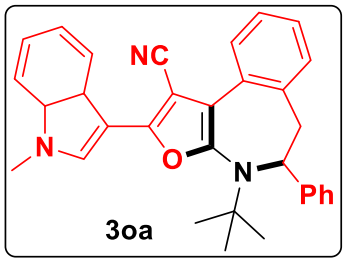
(3ma): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 – 7.97 (m, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.41 – 7.33 (m, 2H), 7.31 – 7.23 (m, 1H), 5.02 (dd, J = 12.3, 3.9 Hz, 1H), 2.99 (dd, *J* = 14.3, 12.3 Hz, 1H), 2.78 (dd, *J* = 14.4, 3.9 Hz, 1H), 0.96 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.79, 153.48, 146.84, 138.31, 135.35, 130.90, 129.34, 128.51, 127.83, 127.65, 127.24, 126.87, 126.28, 125.80, 116.23, 114.86, 91.45, 71.02, 59.06, 44.24, 28.93; Yield: 79% (71.6 mg), white solid, m.p. 204-206 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{29}H_{26}ClN_2O$ 453.1734; found 453.1727.

4-(*tert*-butyl)-2-(4-fluorophenyl)-5-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile

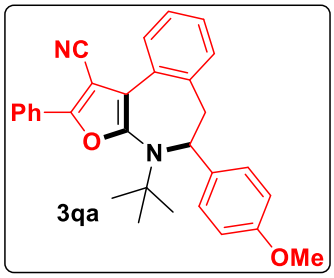


(3na): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 – 8.04 (m, 2H), 7.62 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.42 – 7.33 (m, 4H), 7.30 (qd, *J* = 7.1, 1.2 Hz, 3H), 5.01 (dd, *J* = 12.3, 3.8 Hz, 1H), 2.99 (dd, *J* = 14.3, 12.4 Hz, 1H), 2.78 (dd, *J* = 14.3, 3.9 Hz, 1H), 0.96 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.24 (d, $J_{C\text{-}F}$ = 251.9 Hz), 154.56, 153.92, 146.94, 138.37, 131.02, 129.33, 128.51, 127.79, 127.64, 127.20 (d, $J_{C\text{-}F}$ = 8.4 Hz), 126.84, 126.30, 125.81, 125.20 (d, $J_{C\text{-}F}$ = 3.4 Hz), 116.27 (d, $J_{C\text{-}F}$ = 22.1 Hz), 116.22, 115.03, 90.78, 71.05, 59.03, 44.29, 28.91; Yield: 73% (63.9 mg), white solid, m.p. 209-211 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{29}H_{26}FN_2O$ 437.2029; found 437.2026.

4-(*tert*-butyl)-2-(1-methyl-1*H*-indol-3-yl)-5-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (3oa): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (597 MHz, $CDCl_3$): 8.32 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.01 (s, 1H), 7.63 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.30 – 7.22 (m, 3H), 5.02 (dd, *J* = 12.5, 4.0 Hz, 1H), 3.91 (s, 3H), 3.02 (dd, *J* = 14.4, 12.5 Hz, 1H), 2.78 (dd, *J* = 14.4, 4.0 Hz, 1H), 0.97 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 155.17, 152.92, 147.37, 138.63, 136.80, 131.76, 129.30, 128.74, 128.49, 127.55, 127.51, 126.67, 126.34, 125.89, 125.13, 123.05, 121.43, 121.38, 116.17, 115.69, 109.83, 105.61, 86.51, 71.24, 59.19, 44.49, 33.38, 28.82; Yield: 78% (73.5 mg), white solid, m.p. 175-177 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{32}H_{29}N_3O$ 471.2311; found 471.2311.

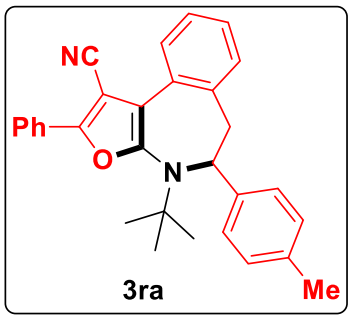


4-(*tert*-butyl)-5-(4-methoxyphenyl)-2-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile

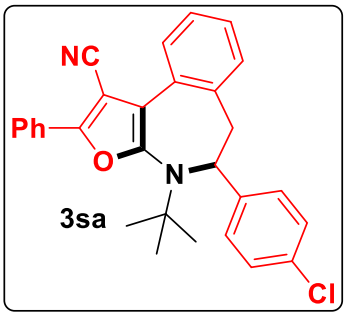


(3qa): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.46 – 7.35 (m, 5H), 7.33 – 7.26 (m, 2H), 6.96 – 6.85 (m, 2H), 4.99 (dd, *J* = 12.3, 3.9 Hz, 1H), 3.81 (s, 3H), 2.97 (dd, *J* = 14.3, 12.4 Hz, 1H), 2.75 (dd, *J* = 14.3, 3.9 Hz, 1H), 0.97 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.40, 154.61, 154.55, 139.26, 138.41, 131.13, 129.46, 129.27, 129.05, 128.82, 127.65, 127.53, 126.87, 126.28, 125.08, 116.02, 115.11, 113.79, 91.00, 70.51, 58.85, 55.25, 44.51, 28.96; Yield: 84% (75.3 mg), pale yellow solid, m.p. 222-224 °C; HRMS (ESI) m/z: $(M+Na)^+$ Calcd. for $C_{30}H_{28}N_2NaO_2$ 471.2048; found 471.2046.

4-(*tert*-butyl)-2-phenyl-5-(*p*-tolyl)-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (3ra): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 2H), 7.64 (s, 1H), 7.53 (s, 2H), 7.47 – 7.26 (m, 1H), 7.48 – 7.23 (m, 6H), 7.17 (dd, *J* = 8.0, 5.4 Hz, 1H), 4.99 (dt, *J* = 12.3, 3.2 Hz, 1H), 3.08 – 2.91 (m, 1H), 2.80 – 2.71 (m, 1H), 0.97 (d, *J* = 1.6 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.62, 154.59, 144.08, 138.44, 136.36, 131.16, 129.45, 129.29, 129.15, 129.05, 128.83, 127.65, 127.54, 126.28, 125.74, 125.08, 116.08, 115.12, 90.99, 70.86, 58.89, 44.41, 28.95, 21.08; Yield: 85% (73.6 mg), pale yellow solid, m.p. 196-198 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{30}H_{29}N_2O$ 433.2280; found 433.2272.

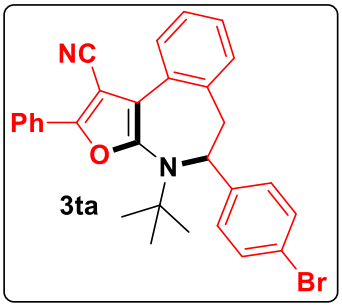


4-(*tert*-butyl)-5-(4-chlorophenyl)-2-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile



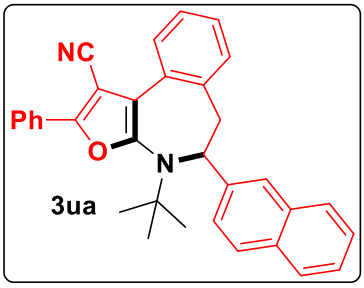
(3sa): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 7.2 Hz, 2H), 7.67 – 7.60 (m, 1H), 7.54 (d, *J* = 1.7 Hz, 1H), 7.44 (dd, *J* = 13.2, 8.8 Hz, 4H), 7.35 (d, *J* = 2.1 Hz, 4H), 7.34 (s, 1H), 5.03 – 4.94 (m, 1H), 2.96 (s, 1H), 2.81 – 2.68 (m, 1H), 0.95 (d, *J* = 1.4 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.88, 154.21, 145.52, 137.97, 132.39, 130.98, 129.61, 129.30, 129.08, 128.68, 128.66, 127.82, 127.75, 127.24, 126.39, 125.12, 116.45, 114.97, 91.06, 70.24, 59.14, 44.12, 28.84; Yield: 70% (63.3 mg), pale yellow solid, m.p. 210-212 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{29}H_{26}ClN_2O$ 453.1734; found 453.1730.

5-(4-bromophenyl)-4-(*tert*-butyl)-2-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (3ta)



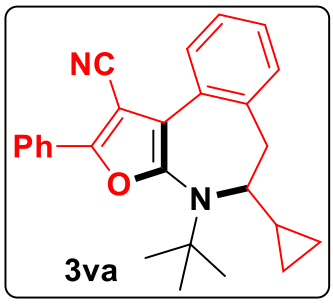
The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 – 8.04 (m, 2H), 7.64 (d, *J* = 7.6 Hz, 1H),7.52 (ddd, *J* = 13.6, 7.2, 1.8 Hz, 3H), 7.55 – 7.44 (m, 5H), 7.42 – 7.35 (m, 3H), 7.29 (dd, *J* = 6.3, 1.6 Hz, 2H), 4.97 (dd, *J* = 12.2, 3.8 Hz, 1H), 2.95 (dd, *J* = 14.3, 12.3 Hz, 1H), 2.95 (dd, *J* = 14.3, 12.3 Hz, 1H), 2.75 (dd, *J* = 14.3, 3.9 Hz, 1H), 0.95 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.90, 154.18, 146.06, 137.95, 131.62, 130.97, 129.63, 129.30, 129.08, 129.05, 128.67, 127.84, 127.76, 127.64, 126.40, 125.13, 120.47, 116.48, 114.97, 91.06, 70.28, 59.15, 44.05, 28.84; Yield: 69% (68.5 mg), pale yellow solid, m.p. 227-229 °C; HRMS (EI) m/z; $(M)^+$ Calcd. for $C_{29}H_{25}BrN_2O$ 496.1150; found 496.1148.

4-(*tert*-butyl)-5-(naphthalen-2-yl)-2-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile



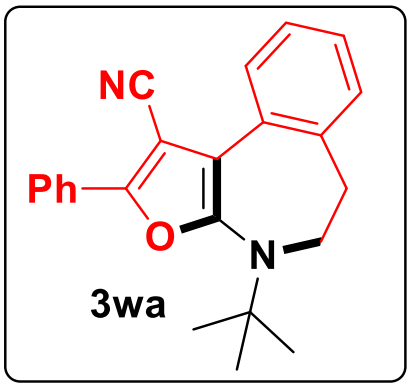
(3ua): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (dd, *J* = 7.2, 1.5 Hz, 2H), 8.12 (dd, *J* = 7.2, 1.5 Hz, 2H), 7.91 – 7.82 (m, 3H), 7.66 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.63 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.43 – 7.37 (m, 1H), 7.36 – 7.33 (m, 1H), 7.32 – 7.27 (m, 1H), 5.19 (dd, *J* = 11.7, 3.6 Hz, 1H), 3.09 (dd, *J* = 14.3, 12.3 Hz, 1H), 2.85 (dd, *J* = 14.4, 3.9 Hz, 1H), 0.99 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.76, 154.56, 144.44, 138.34, 133.44, 132.64, 131.14, 129.53, 129.34, 129.10, 128.84, 128.39, 127.85, 127.75, 127.72, 127.65, 126.37, 126.10, 125.60, 125.12, 124.48, 124.16, 116.23, 115.08, 91.09, 71.21, 59.09, 44.22, 28.99; Yield: 75% (70.2 mg), white solid, m.p. 196-198 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{33}H_{28}N_2O$ 468.2202; found 468.2205.

4-(*tert*-butyl)-5-cyclopropyl-2-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (3va):

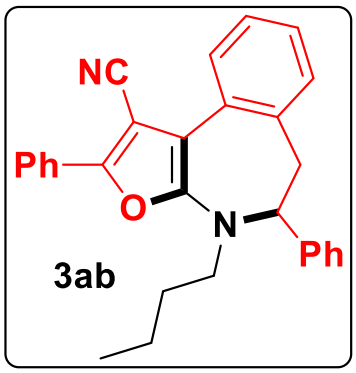


The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (597 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.48 (dd, J = 10.6, 4.8 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.33 (td, *J* = 7.5, 1.5 Hz, 1H), 7.33 (td, *J* = 7.5, 1.5 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.28 – 7.19 (m, 2H), 3.78 – 3.72 (m, 1H), 2.93 (dd, J = 14.3, 11.7 Hz, 1H), 2.74 (dd, *J* = 14.4, 4.6 Hz, 1H), 0.98 (s, 9H), 0.96 – 0.91 (m, 1H), 0.97 – 0.85 (m, 1H), 0.53 (ddd, *J* = 10.7, 6.6, 2.4 Hz, 1H), 0.55 – 0.44 (m, 3H), 0.37 (ddd, *J* = 10.9, 6.7, 4.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.83, 154.40, 138.51, 131.54, 129.56, 129.41, 128.97, 128.81, 127.31, 127.15, 126.17, 125.13, 116.69, 115.27, 90.72, 67.05, 58.14, 40.72, 29.27, 18.75, 3.27, 3.21; Yield: 55% (42.1 mg), white solid, m.p. 133-135 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{26}H_{26}N_2O$ 382.2045; found 382.2042.

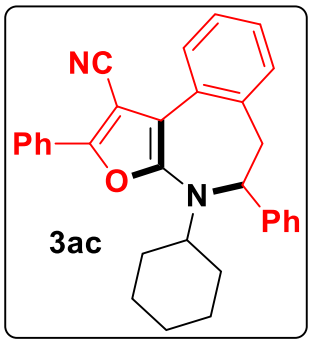
4-(*tert*-butyl)-2-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (3wa): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.64 (dd, *J* = 7.7, 2.9 Hz, 1H), 7.48 (s, 1H), 7.38 (s, 1H), 7.38 (s, 2H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 2H), 3.80 (s, 2H), 2.89 (s, 2H), 1.32 (d, *J* = 1.1 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$)：δ 154.01, 152.43, 139.90, 131.26, 128.98, 128.80, 128.65, 127.17, 126.84, 126.41, 124.41, 115.57, 107.73, 91.84, 57.32, 55.01, 33.73, 29.67, 28.53; Yield: 76% (52.0 mg), pale yellow solid, m.p. 154-156 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{23}H_{22}N_2O$ 342.1732; found 342.1732.



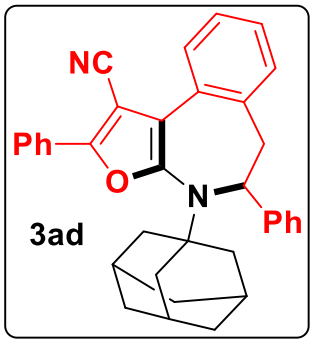
4-butyl-2,5-diphenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (3ab): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel; ^{1}H NMR (400 MHz, $CDCl_3$); δ 8.00 – 7.93 (m, 2H), 7.76 (d, *J* = 7.0 Hz, 1H), 7.48 (dd, *J* = 10.6, 4.9 Hz, 2H), 7.40 – 7.32 (m, 1H), 7.29 – 7.13 (m, 4H), 7.21 (dd, J = 10.9, 4.3 Hz, 1H), 7.07 – 7.00 (m, 2H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.72 (d, J = 7.1 Hz, 1H), 5.08 (dd, *J* = 5.9, 3.1 Hz, 1H), 3.62 – 3.45 (m, 1H), 3.19 – 3.11 (m, 1H), 1.69 – 1.58 (m, 3H), 1.34 – 1.25 (m, 3H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$)： δ 153.68, 150.84, 141.88, 135.10, 131.20, 130.17, 129.00, 128.63, 128.53, 128.29, 127.28, 127.09, 126.35, 125.51, 125.40, 124.14, 116.12, 92.53, 68.54, 49.89, 41.97, 29.85, 20.12, 13.86; Yield: 69% (57.7 mg), pale yellow solid, m.p. 134-136 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{29}H_{26}N_2O$ 418.2045; found 418.2045.



4-cyclohexyl-2,5-diphenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (3ac): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 – 7.95 (m, 2H), 7.73 (dd, *J* = 7.8, 2.6 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.41 – 7.33 (m, 1H), 7.28 – 7.21 (m, 1H), 7.20 (s, 1H), 7.06 (t, J = 5.7 Hz, 2H), 6.98 – 6.89 (m, 1H), 6.71 (t, *J* = 5.5 Hz, 1H), 5.16 (t, *J* = 6.1 Hz, 1H), 3.54 – 3.40 (m, 1H), 3.23 – 3.13 (m, 1H), 3.11 – 3.02 (m, 1H), 3.11 – 3.03 (m, 1H), 1.84 (s, 5H), 1.61 (d, *J* = 14.2 Hz, 1H), 1.49 – 1.35 (m, 1H), 1.31 – 0.79 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.57, 150.98, 143.61, 135.59, 130.97, 129.90, 129.04, 128.70, 128.56, 128.06, 126.99, 126.90, 126.15, 125.66, 125.54, 124.22, 116.06, 92.55, 67.81, 61.23, 42.28, 31.27, 31.03, 26.30, 26.17, 25.64; Yield: 77% (68.4 mg), pale yellow solid, m.p. 112-114 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{31}H_{28}N_2O$ 444.2202; found 444.2202.

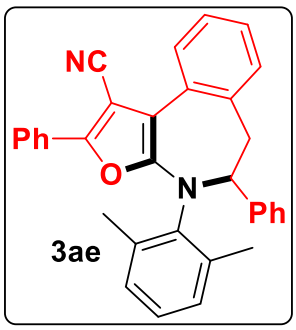


4-(adamantan-1-yl)-2,5-diphenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (3ad): The



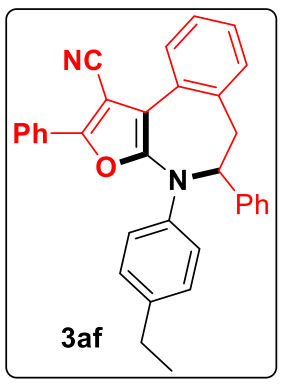
residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 2H), 7.66 – 7.61 (m, 1H), 7.55 (s, 4H), 7.47 – 7.41 (m, 1H), 7.41 – 7.29 (m, 5H), 7.28 – 7.21 (m, 1H), 5.16 – 5.04 (m, 1H), 3.02 – 2.91 (m, 1H), 2.82 – 2.73 (m, 1H), 1.90 (d, J = 11.5 Hz, 3H), 1.55 (s, 1H), 1.42 (t, J = 10.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.83, 153.99, 147.40, 138.51, 131.19, 129.51, 129.29, 129.06, 128.87, 128.42, 127.71, 127.62, 126.69, 126.40, 125.86, 125.17, 117.49, 115.09, 90.96, 68.95, 59.47, 44.27, 41.46, 36.07, 29.67; Yield: 71% (70.5 mg), white solid, m.p. 297 – 299 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{35}H_{33}N_2O$ 497.2593; found 497.2585.

4-(2,6-dimethylphenyl)-2,5-diphenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (3ae): The



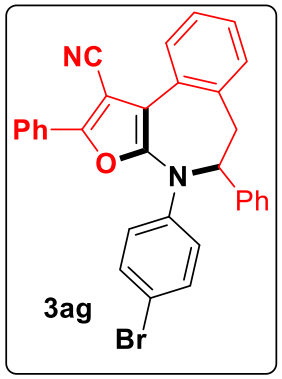
residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (597 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.63 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.37 (td, *J* = 7.7, 1.3 Hz, 1H), 7.40 – 7.31 (m, 4H), 7.29 – 7.23 (m, 1H), 7.16 – 7.09 (m, 3H), 7.03 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.92 (d, J = 7.3 Hz, 1H), 6.84 (d, *J* = 7.3 Hz, 2H), 6.82 (dd, *J* = 28.1, 7.4 Hz, 2H), 6.79 (d, J = 7.5 Hz, 1H), 5.07 (dd, J = 6.7, 1.9 Hz, 1H), 5.07 (dd, *J* = 6.7, 1.9 Hz, 1H), 3.55 (d, J = 12.7 Hz, 1H), 3.41 (d, *J* = 6.5 Hz, 1H), 22.33 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.05, 151.47, 141.30, 140.96, 138.35, 135.97, 135.10, 131.17, 130.72, 129.30, 128.84, 128.82, 128.55, 128.31, 127.94, 127.66, 127.64, 127.49, 127.38, 125.82, 125.66, 124.11, 116.17, 92.50, 70.23, 41.50, 29.69, 18.95, 18.82; Yield: 62% (60.5 mg), white solid, m.p. 226 – 227 °C. HRMS (ESI) m/z: $(M+Na)^+$ Calcd. for $C_{33}H_{26}N_2NaO$ 489.1943; found 489.1939.

4-(4-ethylphenyl)-2,5-diphenyl-5,6-dihydro-4H-benzo[d]furo[2,3-b]azepine-1-carbonitrile (3af): The

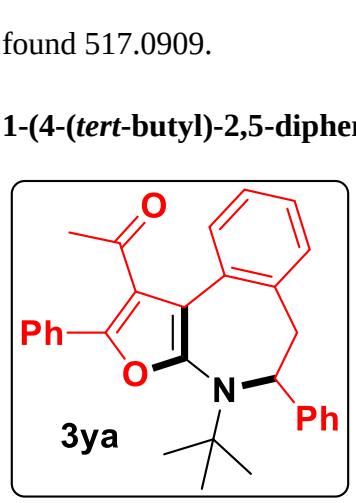


residue was purified by column chromatography (Hex/EA = 99/1) to obtain the product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.53 – 7.43 (m, 6H), 7.39 – 7.35 (m, 1H), 7.33 – 7.26 (m, 4H), 7.19 (d, J = 7.3 Hz, 1H), 7.05 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 8.3 Hz, 2H), 4.25 – 4.06 (m, 2H), 3.25 (dd, J = 14.4, 6.7 Hz, 1H), 2.58 (q, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.56, 155.63, 143.71, 141.93, 141.67, 140.77, 136.38, 132.33, 128.94, 128.68, 128.28, 127.88, 127.75, 127.41, 127.07, 126.15, 125.46, 123.70, 122.53, 114.99, 89.32, 67.08, 56.26, 34.73, 28.31, 15.51; Yield: 64% (59.65 mg), white solid; m.p. 207 – 209 °C; HRMS (EI) m/z: $(M+H)^+$ Calcd. for $C_{33}H_{26}N_2O$ 466.2045; found 467.2116.

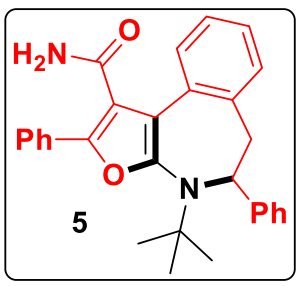
4-(4-bromophenyl)-2,5-diphenyl-5,6-dihydro-4H-benzo[d]furo[2,3-b]azepine-1-carbonitrile (3ag): The residue was purified by column chromatography (Hex/EA = 99/1) to obtain the product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.97 (m, 2H), 7.75 (d, *J* = 7.1 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.44 – 7.34 (m, 5H), 7.31 – 7.24 (m, 2H), 7.23 – 7.18 (m, 3H), 6.61 – 6.53 (m, 2H), 5.42 (dd, *J* = 9.9, 4.4 Hz, 1H), 3.26 – 3.10 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.48, 148.83, 144.61, 142.38, 136.98, 131.79, 131.56, 130.01, 129.95, 129.92, 129.12, 129.02, 128.34, 128.00, 127.96, 127.88, 127.66, 126.99, 126.50, 125.54, 125.10, 118.99, 114.66, 114.01, 91.70, 74.69, 43.27; Yield: 51% (52.63 mg), white solid; m.p. 241 – 243 °C; HRMS (EI) m/z: $(M+H)^+$ Calcd. for $C_{31}H_{21}BrN_2O$ 516.0837; found 517.0909.



1-(4-(*tert*-butyl)-2,5-diphenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepin-1-yl)ethan-1-one (3ya): The residue was purified by column chromatography (Hex/EA = 99/1) to obtain the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.76 (m, 2H), 7.52 (dd, J = 8.3, 1.3 Hz, 2H), 7.46 (ddd, J = 6.6, 4.3, 0.9 Hz, 2H), 7.40 – 7.31 (m, 4H), 7.30 – 7.21 (m, 4H), 4.97 (dd, J = 12.4, 4.1 Hz, 1H), 3.10 (dd, J = 14.0, 12.4 Hz, 1H), 2.80 (dd, J = 14.1, 4.1 Hz, 1H), 2.25 (s, 3H), 0.92 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$)：δ 198.76, 153.96, 148.42, 147.34, 138.62, 133.11, 130.43, 129.00, 128.60, 128.51, 128.38, 127.59, 127.28, 126.98, 126.88, 126.61, 125.90, 122.58, 115.42, 70.77, 58.65, 44.39, 31.50, 28.88; Yield: 73% (63.6 mg), yellow liquid; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{30}H_{29}NO_2$ 435.2198; found 435.2196.

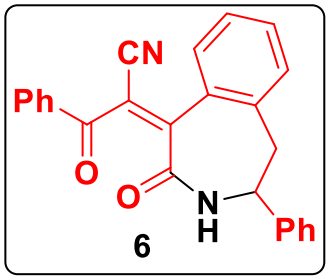


4-(*tert*-butyl)-2,5-diphenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carboxamide (5): Prepare a clean 15 mL sealed tube with a magnetic stir bar. **3aa** (0.2 mmol) was added to the bottle, followed by the solvent EtOH (3.0 mL). Finally, NaOH (1.0 equiv) was added and the mixture was heated to 80 °C and the reaction was monitored by TLC. After completion of the reaction, water was added to stop the reaction and the reaction was neutralized to about pH=7 by 1 M $HCl_{(aq)}$, then extracted with ethyl acetate (3 x 15 mL) and water. Finally, all organic layers were combined and removed with anhydrous sodium sulfate, filtered and concentrated in vacuo. After concentration, the residue was purified by column chromatography (Hex/EA = 5/1) to obtain the product. ^{1}H NMR (597 MHz, $CDCl_3$): δ 7.98 – 7.78 (m, 2H), 7.56 – 7.40 (m, 3H), 7.32 (d, J = 29.1 Hz, 9H), 7.23 (dd, J = 14.6, 7.3 Hz, 1H), 5.86 (s, 1H), 5.58 (s, 1H), 4.96 (s, 1H), 3.06 (s, 1H), 2.78 (dd, J = 14.1, 3.9 Hz, 1H), 2.40 – 2.03 (m, 1H), 0.93 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$)：δ 166.87, 153.99, 147.44, 138.80, 132.51, 130.12, 129.04, 128.40, 127.12, 127.06, 126.80,



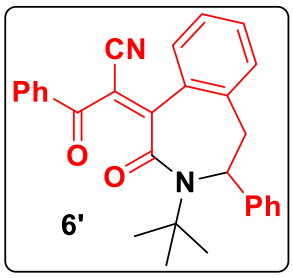
126.64, 125.89, 125.10, 115.47, 115.00, 70.80, 58.71, 44.47, 28.92, 22.30, 14.02; Yield: 84% (73.3 mg), white solid, m.p. 185 – 186 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{29}H_{28}N_2O_2$ 436.2151; found 436.2150.

(*Z*)-3-oxo-2-(2-oxo-4-phenyl-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepin-1-ylidene)-3-phenylpropanenitrile (6):

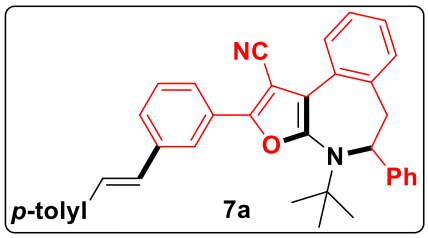


Prepare a clean 15 mL sealed tube with a magnetic stir bar. **3aa** (0.1 mmol) and ACN (3.0 mL) were added to the bottle. TfOH (1.0 equiv) was then added slowly, followed by heating to about 50 °C and the reaction monitored by TLC. After the reaction was completed, cooled to room temperature and then added $Na_2CO_{3(aq)}$ solution to neutralize the reaction to about pH=7. It was then extracted with ethyl acetate (3 x 15 mL) and water. Finally, all organic layers were combined and removed with anhydrous sodium sulfate, filtered and concentrated in vacuo. After concentration, the residue was purified by column chromatography (Hex/EA = 5/1) to obtain the product. ^{1}H NMR (597 MHz, $CDCl_3$): δ 1H NMR (597 MHz, cdcl3) δ 8.09 – 8.06 (m, 2H), 7.76 – 7.72 (m, 1H), 7.69 – 7.64 (m, 1H), 7.57 – 7.53 (m, 2H), 7.45 – 7.41 (m, 2H), 7.39 – 7.33 (m, 5H), 7.22 (dd, J = 6.2, 2.6 Hz, 1H), 6.14 (s, 1H), 4.94 (d, J = 9.6 Hz, 1H), 3.45 (dd, J = 16.2, 11.3 Hz, 1H), 3.34 (d, J = 16.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$)：δ 187.75, 166.01, 159.69, 139.84, 135.93, 134.74, 134.46, 131.24, 130.92, 130.29, 129.70, 129.14, 129.06, 128.93, 128.62, 127.60, 126.36, 117.93, 114.97, 57.14, 40.44; Yield: 92 % and 83 % (34.8 mg and 31.4 mg), white solid, m.p. 198 – 199 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{25}H_{19}N_2O_2$ 379.1447； found 379.1442.

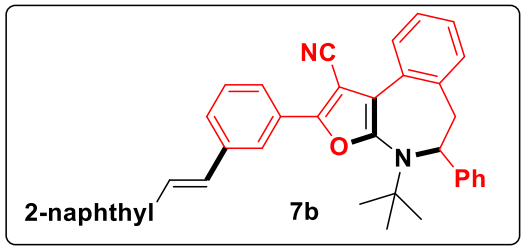
(*Z*)-2-(3-(*tert*-butyl)-2-oxo-4-phenyl-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepin-1-ylidene)-3-oxo-3-phenylpropanenitrile (6'):



Prepare a clean 15 mL sealed tube with a magnetic stir bar. **3aa** (0.2 mmol), TBN (5.0 equiv), *p*-NBA (1.0 equiv), and *p*-dioxane (3.0 mL) were added to the bottle in sequence. The tube was then filled with oxygen and then heated to about 45 °C and the reaction was monitored by TLC. After the reaction was completed, cooled to room temperature and then added $Na_2CO_{3(aq)}$ solution to neutralize the reaction to about pH=7. It was then extracted with ethyl acetate (3 x 15 mL) and ater. Finally, all organic layers were combined and removed with anhydrous sodium sulfate, filtered and concentrated in vacuo. After concentration, the residue was purified by column chromatography (Hex/EA = 9/1) to obtain the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.75 (m, 2H), 7.72 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.50 – 7.47 (m, 1H), 7.46 – 7.36 (m, 2H), 7.34 – 7.29 (m, 2H), 7.25 (ddd, *J* = 8.7, 4.8, 1.2 Hz, 2H), 7.25 (ddd, *J* = 8.7, 4.8, 1.2 Hz, 1H), 7.17 (dd, *J* = 7.3, 1.5 Hz, 1H), 5.37 (t, *J* = 4.5 Hz, 1H), 3.83 (dd, *J* = 18.2, 4.3 Hz, 1H), 3.52 (dd, *J* = 18.2, 4.6 Hz, 1H), 1.64 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$)：δ 186.04, 166.53, 165.07, 138.84, 136.19, 136.03, 133.24, 131.78, 130.48, 130.38, 130.26, 128.96, 128.32, 128.30, 127.44, 127.33, 127.17, 116.72, 110.71, 59.61, 54.74, 36.71, 29.09; Yield: 90 % (78.1 mg), white solid, m.p. 197 – 198 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{29}H_{27}N_2O_2$ 435.2073; found 435.2068.

(*E*)-4-(*tert*-butyl)-2-(3-(4-methylstyryl)phenyl)-5-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (7a)： 

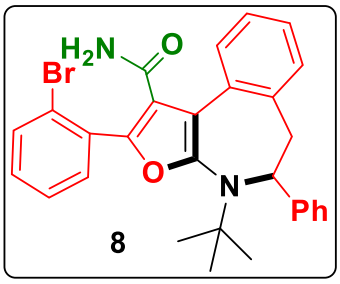
First, **3ja** (1.0 equiv, 0.1 mmol), $Pd(OAc)_2$ (0.1 equiv), and (*S*)-(-)-BINAP (0.2 equiv) were added to a 25 mL round-bottomed flask, respectively, followed by nitrogen The round bottom flask was filled with nitrogen. Next, 5 mL of DMF was added as a solvent, then K_2CO_3 (2.0 equiv) was added. After waiting for the reaction to react at room temperature for 10 minutes, 4-methyl styrene (7.0 equiv) was slowly added. Heating to 120°C and was monitored by TLC. After the reaction was completed, the reaction was cooled to room temperature, and secondary water was added, followed by extraction with ethyl acetate and water. After 2~3 times in total, all organic layers were combined and removed with anhydrous sodium sulfate. The water was concentrated by a vacuum concentrator to obtain the crude product, and then further purified by column chromatography (Hex/EA = 50/1) to obtain the compound. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.63 (dd, *J* = 15.7, 7.6 Hz, 2H), 7.55 – 7.45 (m, 5H), 7.39 (dt, *J* = 15.1, 4.9 Hz, 3H), 7.44 – 7.26 (m, 6H), 7.26 – 7.14 (m, 5H), 5.03 (dd, *J* = 12.3, 3.7 Hz, 1H), 3.07 – 2.96 (m, 1H), 2.79 (dd, *J* = 14.4, 3.8 Hz, 1H), 2.38 (s, 3H), 0.98 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.58, 146.98, 138.41, 137.92, 134.17, 131.12, 129.92, 129.44, 129.38, 129.30, 129.20, 128.51, 127.73, 127.63, 126.88, 126.83, 126.65, 126.61, 126.35, 126.31, 125.85, 123.97, 123.28, 116.27, 115.09, 91.23, 71.06, 59.06, 44.32, 28.95, 21.30; Yield: 71% (38.0 mg), pale yellow solid, m.p. 178 – 179 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{38}H_{34}N_2O$ 534.2671; found 534.2671.

(*E*)-4-(*tert*-butyl)-2-(3-(2-(naphthalen-2-yl)vinyl)phenyl)-5-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile (7b)： 

First, **3ja** (1.0 equiv, 0.1 mmol), $Pd(OAc)_2$ (0.1 equiv), and (*S*)-(-)-BINAP (0.2 equiv) were added to a 25 mL round-bottomed flask, respectively, followed by nitrogen The round bottom flask was filled with nitrogen. Next, 5 mL of DMF was added as a solvent, then K_2CO_3 (2.0 equiv) was added. After waiting for the reaction to react at room temperature for 10 minutes, 2-naphthylstyrene (7.0 equiv) was slowly added. Heating to 120°C and was monitored by TLC. After the reaction was completed, the reaction was cooled to room temperature, and secondary water was added, followed by extraction with ethyl acetate and water. After 2~3 times in total, all organic layers were combined and removed with anhydrous sodium sulfate. The water was concentrated by a vacuum concentrator to obtain the crude product, and then further purified by column chromatography (Hex/EA = 50/1) to obtain the compound. ^{1}H NMR (597 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.99 (d, *J* = 7.0 Hz, 1H), 7.93 (s, 1H), 7.86 (dd, *J* = 8.2, 3.4 Hz, 2H), 7.87 – 7.79 (m, 4H), 7.66 (d, *J* = 5.0 Hz, 2H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.48 (ddt, *J* = 7.6, 2.4, 1.5 Hz, 4H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 9.4 Hz, 1H), 7.31 (dd, *J* = 16.6, 6.1 Hz, 2H), 7.27 – 7.24 (m, 2H), 5.04 (d, *J* = 11.4 Hz, 1H), 3.02 (dd, *J* = 14.3, 12.6 Hz, 1H), 2.80 (dd, J = 14.4, 3.7 Hz, 1H), 1.00 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$); δ 154.67, 154.52, 146.98, 138.39, 138.29,

134.47, 133.69, 133.21, 131.12, 130.09, 129.46, 129.31, 128.53, 128.38, 128.35, 128.22, 128.08, 127.77, 127.76, 127.71, 127.64, 127.03, 126.84, 126.39, 126.06, 125.86, 124.22, 123.57, 123.38, 116.31, 115.09, 91.33, 71.09, 59.08, 44.33, 28.99; Yield: 75% (42.8 mg), pale yellow solid, m.p. 223 – 224 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{41}H_{34}N_2O$ 570.2671; found 570.2670.

2-(2-bromophenyl)-4-(*tert*-butyl)-5-phenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carboxamide (8):



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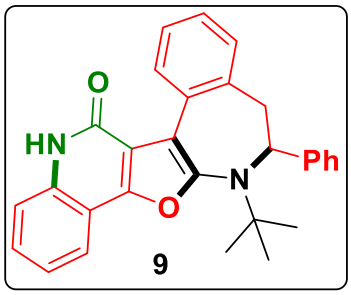
Prepare a clean 15 mL sealed tube with a magnetic stir bar. **3ka** (0.2 mmol) was added to the bottle, followed by the solvent EtOH (3.0 mL). Finally, NaOH (1.0 equiv) was added and the mixture was heated to 80 °C and the reaction was monitored by TLC. After completion of the reaction, water was added to stop the reaction and the reaction was neutralized to about pH=7 by 1 M $HCl_{(aq)}$, then extracted with ethyl acetate (3 x 15 mL) and water. Finally, all organic layers were combined and removed with anhydrous sodium sulfate, filtered and concentrated in vacuo. After concentration, the residue was purified by column chromatography (Hex/EA = 5/1) to obtain the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.60 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.55 – 7.49 (m, 3H), 7.44 – 7.40 (m, 1H), 7.33 (dd, *J* = 7.4, 1.5 Hz, 5H), 7.25 – 7.18 (m, 1H), 5.47 (s, 1H), 4.95 (dd, *J* = 12.5, 4.1 Hz, 1H), 3.07 (dd, *J* = 14.0, 12.5 Hz, 1H), 2.78 (dd, *J* = 14.0, 4.1 Hz, 1H), 1.78 (d, *J* = 46.4 Hz, 2H), 0.90 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$)：δ 160.43, 156.65, 152.76, 147.20, 138.64, 136.18, 131.98, 130.03, 128.84, 128.63, 128.46, 127.17, 126.71, 125.94, 122.64, 120.63, 116.16, 113.64, 112.43, 71.71, 58.90, 44.52, 29.02, 22.32, 14.05; Yield: 67% (68.9 mg), pale yellow solid, m.p. 177 – 178 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{29}H_{27}BrN_2O_2$ 514.1256; found 514.1260.

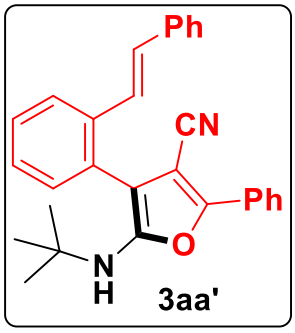
13-(*tert*-butyl)-12-phenyl-5,11,12,13-tetrahydro-6*H*-benzo[4',5']azepino[3',2':4,5]furo[3,2-c]quinolin-6-one (9):



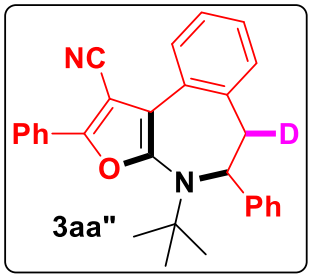
9

Prepare a clean 15 mL sealed tube with a magnetic stir bar. To the bottle was added **8** (0.1 mmol), *t*-BuOK (3.0 equiv), and the solvent ethanol (2.0 mL). Later, CuI (10 mol%) was added and heated to 100 °C, and the reaction was monitored by TLC. After the reaction was completed, water was added to stop the reaction, followed by extraction with ethyl acetate (3×15 mL) and water. Finally, all organic layers were combined and removed with anhydrous sodium sulfate, filtered and concentrated in vacuo. After concentration, the residue was purified by column chromatography (Hex/EA = 19/1) to obtain the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.16 (s, 1H), 8.09 (dd, *J* = 7.9, 1.0 Hz, 1H), 8.02 (d, *J* = 7.4 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.51 – 7.42 (m, 3H), 7.39 – 7.18 (m, 7H), 5.08 (dd, *J* = 12.5, 4.0 Hz, 1H), 3.12 – 3.01 (m, 1H), 2.80 (dd, *J* = 14.2, 4.1 Hz, 1H), 0.98 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.42, 156.64, 152.75, 147.19, 138.63, 136.18, 131.97, 130.03, 128.83, 128.62, 128.45, 127.17, 126.71, 125.93, 122.64, 120.63, 116.15, 113.64, 112.42, 71.70, 58.90, 44.52, 29.03, 22.33, 14.05; Yield: 75% (32.6 mg), white solid, m.p. 286 – 287 °C; HRMS (EI) m/z: $(M)^+$ Calcd. for $C_{29}H_{26}N_2O_2$ 434.1994; found 434.1994.

(*E*)-5-(*tert*-butylamino)-2-phenyl-4-(2-styrylphenyl)furan-3-carbonitrile (3aa'): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.78 – 7.72 (m, 1H), 7.47 (tt, J = 9.7, 1.6 Hz, 4H), 7.42 – 7.31 (m, 6H), 7.28 – 7.23 (m, 2H), 7.16 (d, J = 16.3 Hz, 1H), 7.04 (d, J = 16.2 Hz, 1H), 2.67 (s, 1H), 1.19 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$)：δ 152.44, 151.86, 137.17, 136.00, 131.00, 130.80, 129.02, 128.98, 128.69, 128.59, 128.21, 128.08, 127.96, 127.08, 126.66, 126.23, 124.20, 115.27, 102.71, 94.37, 53.27, 29.98; Yield: 94% (78.9 mg), yellow solid, m.p. 160 – 161 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{29}H_{27}N_2O$ 419.2123; found 419.2126.



4-(*tert*-butyl)-2,5-diphenyl-5,6-dihydro-4*H*-benzo[*d*]furo[2,3-*b*]azepine-1-carbonitrile-6-*D* (3aa''): The residue was purified by column chromatography (Hex/EA = 99/1) on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 7.6 Hz, 2H), 7.63 (d, J = 7.6 Hz, 1H), 7.57 – 7.39 (m, 6H), 7.38 – 7.22 (m, 5H), 5.02 (s, 1H), 3.04 – 2.94 (m, 1H), 2.77 (d, J = 3.7 Hz, 1H), 0.97 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.70, 154.51, 146.96, 138.32, 131.13, 129.50, 129.30, 129.05, 128.79, 128.49, 127.70, 127.59, 126.80, 126.32, 125.83, 125.11, 116.16, 115.09, 91.01, 70.97, 58.96, 44.31, 44.14, 43.95, 43.75, 28.94; Yield: 80% (67.0 mg), white solid, m.p. 171 – 172 °C; HRMS (ESI) m/z: $(M+H)^+$ Calcd. for $C_{29}H_{26}DN_2O$ 420.2186; found 420.2184.



8. References

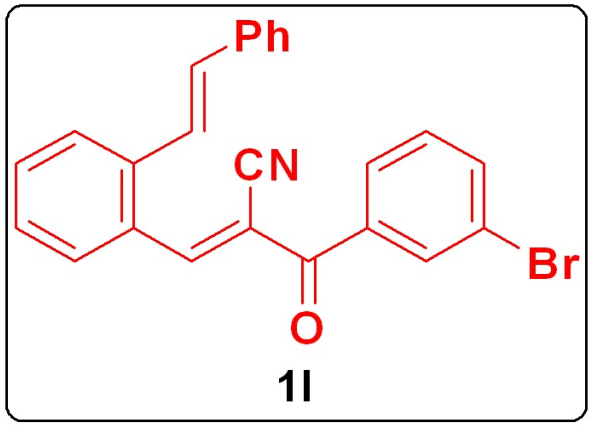
1. M. R. Mutra and J.-J. Wang, *Nat. Commun*., 2022, **13**, 2345.

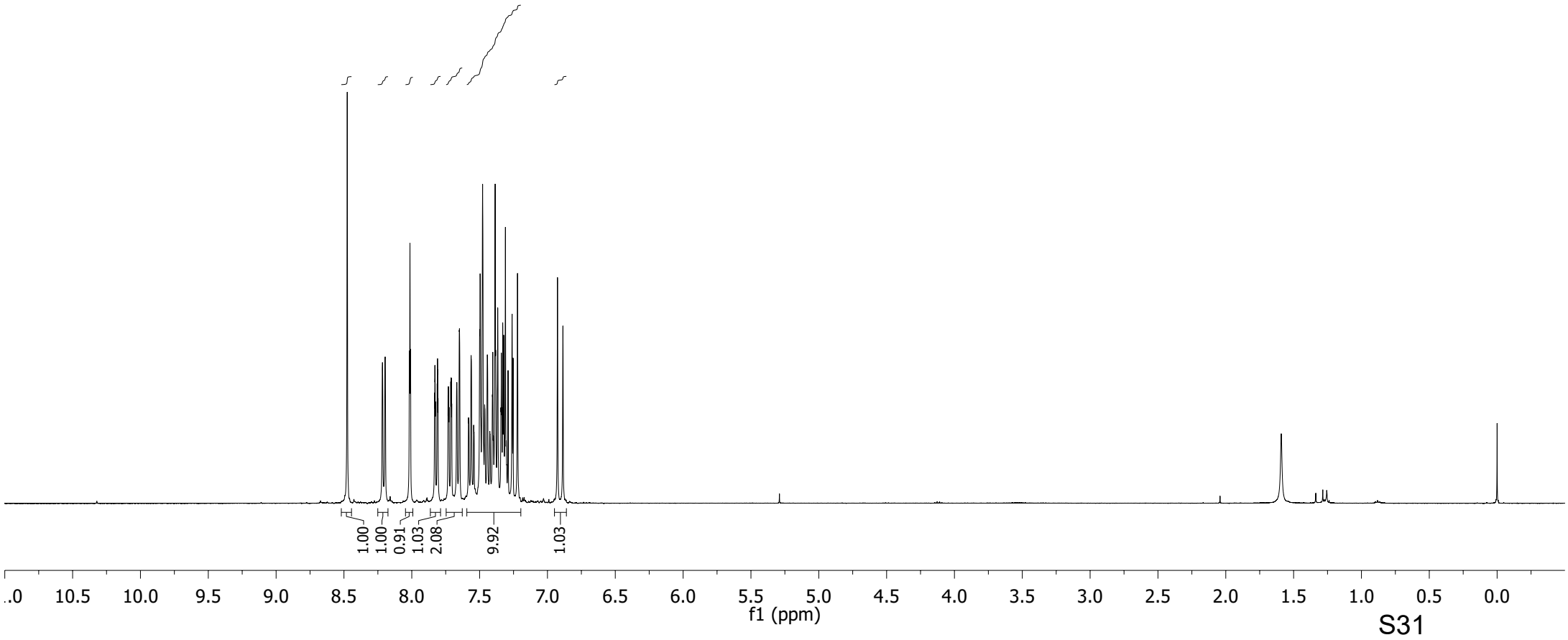
2. B. S. Gore, C.-H. Chiang, C. C. Lee, Y.-L. Shih, J.-J. Wang, *Org. Lett*. 2020, **22**, 7848-7852.

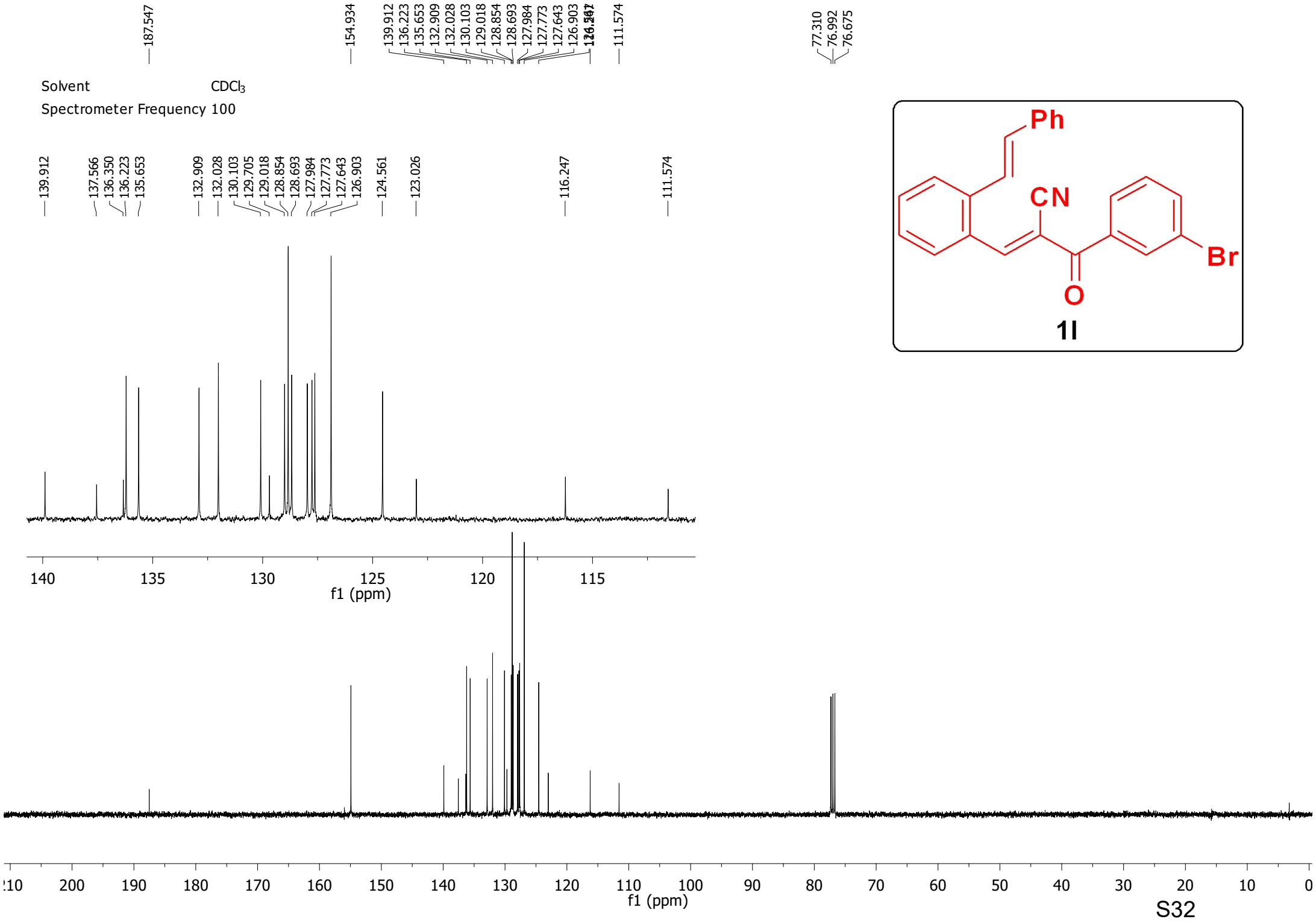
8.476 8.216 8.196 8.018 8.013 8.009 7.830 7.810 7.809 7.710 7.650 7.648 7.563 7.500 7.496 7.478 7.443 7.403 7.385 7.382 7.366 7.340 7.330 7.322 7.310 7.290 7.261 7.253 7.221 6.926 6.886

Solvent $CDCl_3$

Spectrometer Frequency 400



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132.028
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127.643
126.903
111.574
77.310
76.992
76.675
Solvent CDCl3
Spectrometer Frequency 100
Ph
CN
Br
O
1l
139.912
137.566
136.350
136.223
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132.909
132.028
130.103
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126.903
124.561
123.026
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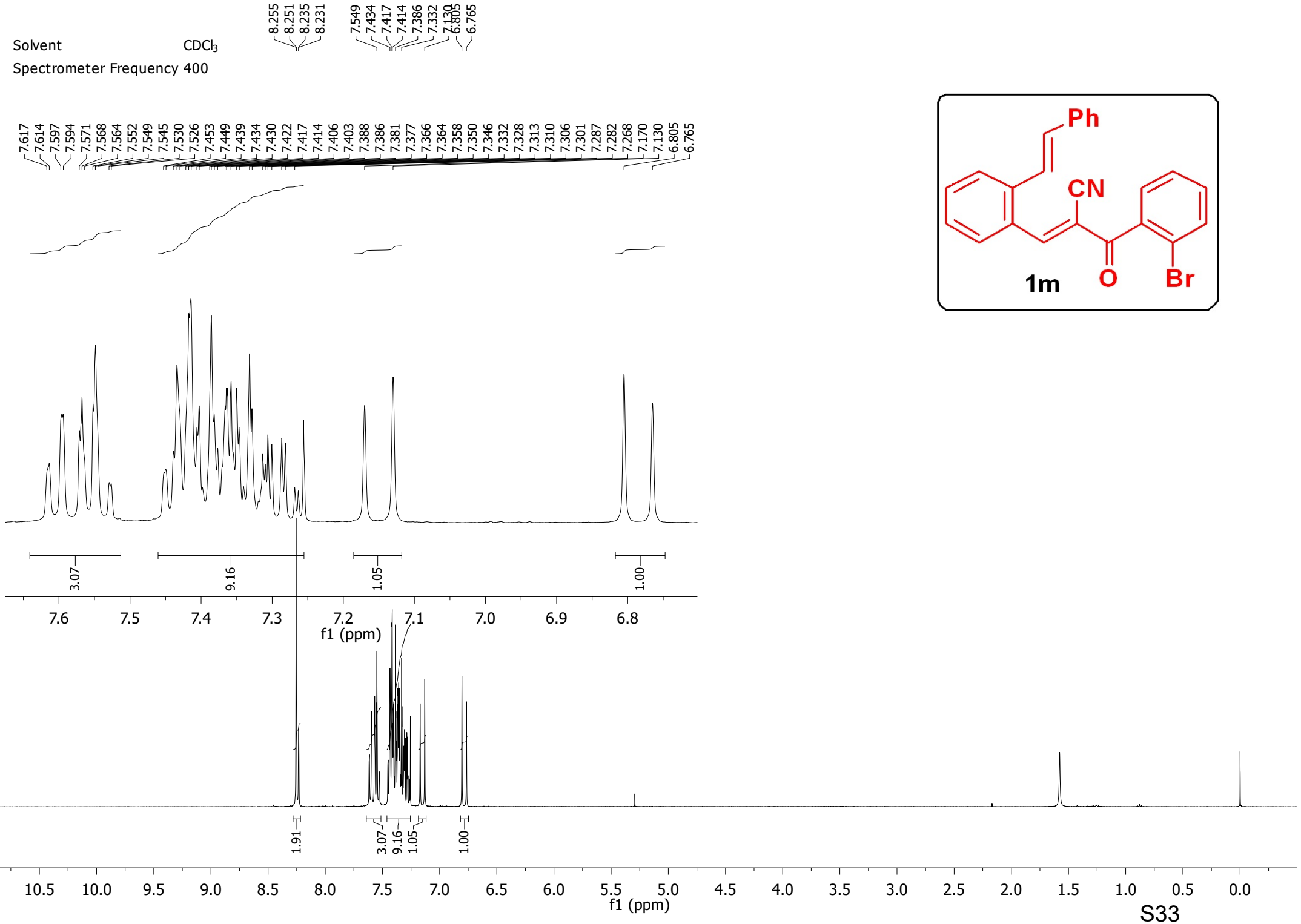
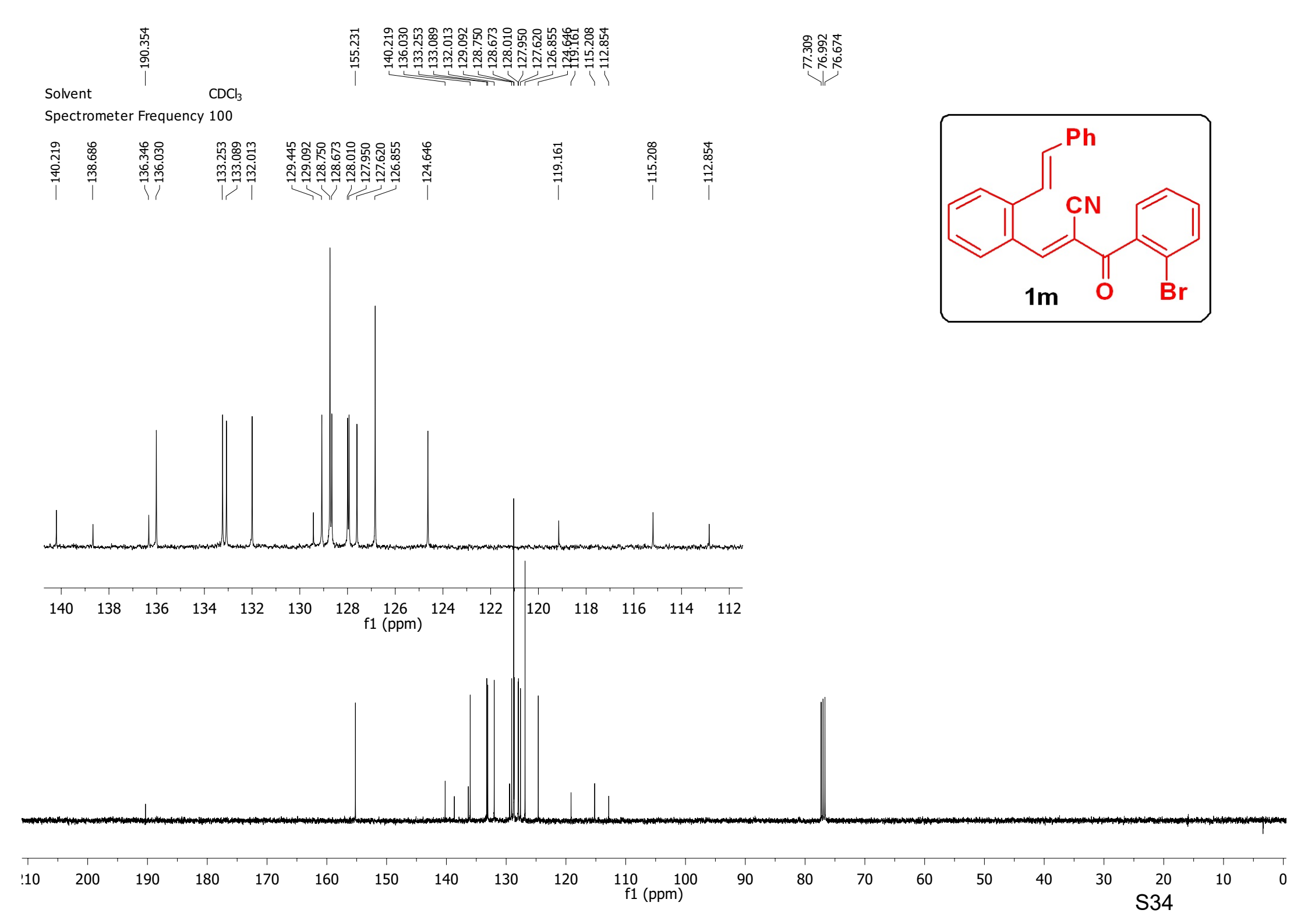
140
135
130
125
120
115
f1 (ppm)
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400

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124.646
119.161
115.208
112.854
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Solvent CDCl3
Spectrometer Frequency 100
Ph
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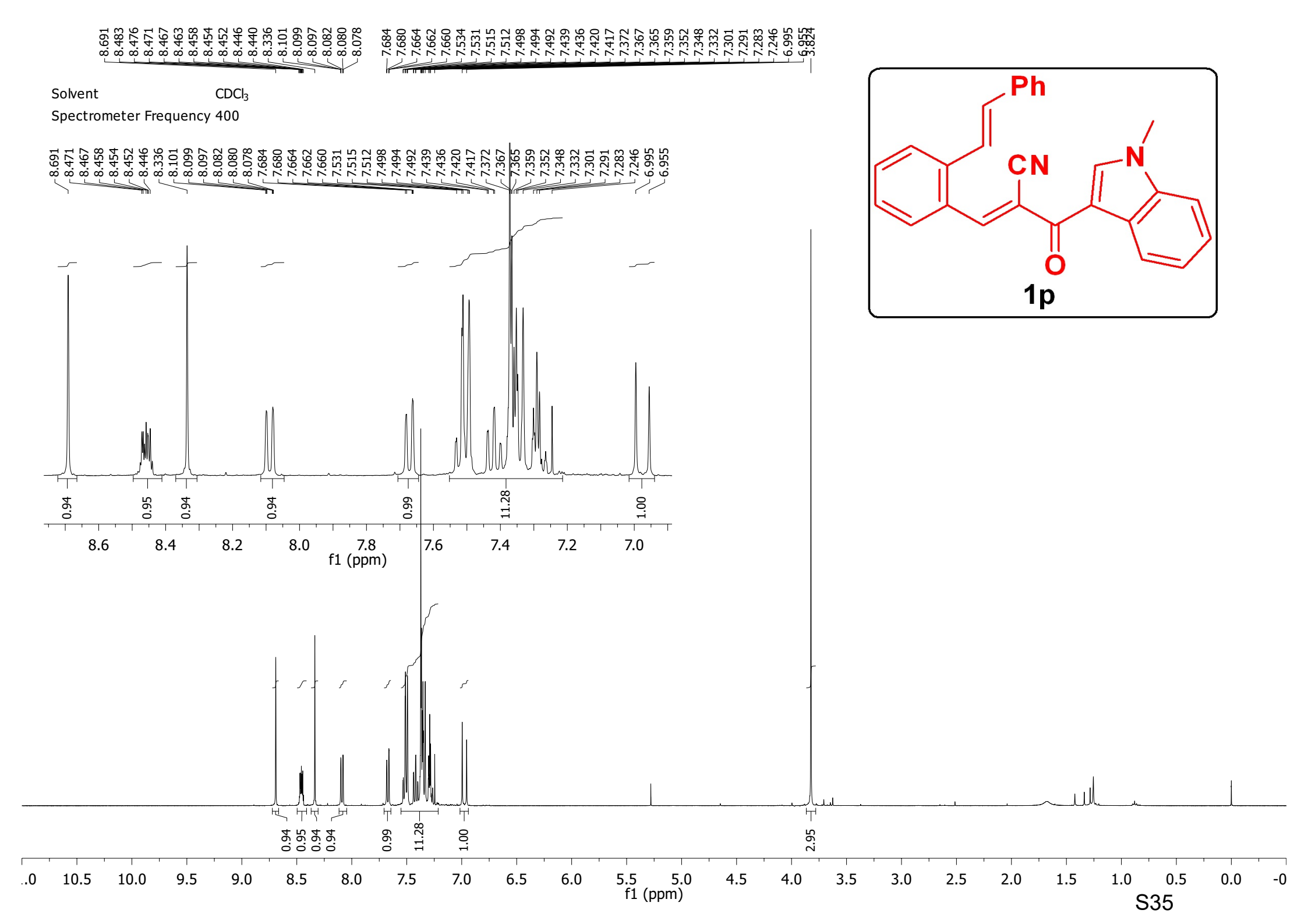
O
Br
1m
f1 (ppm)
f1 (ppm)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N
O
1p
f1 (ppm)
f1 (ppm)

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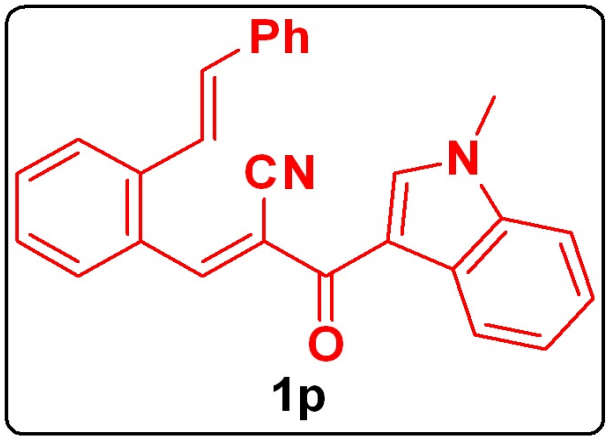
3.793

Solvent $CDCl_3$

Spectrometer Frequency 100

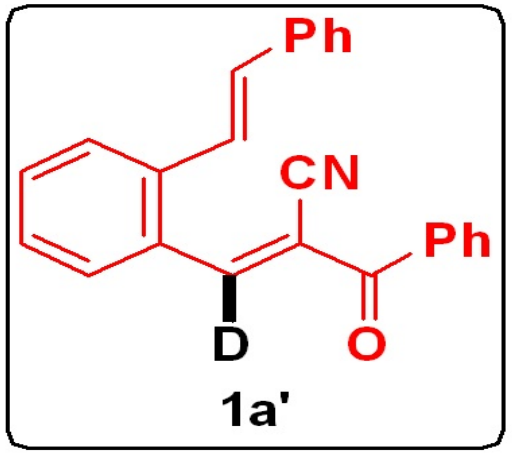


1p

f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400



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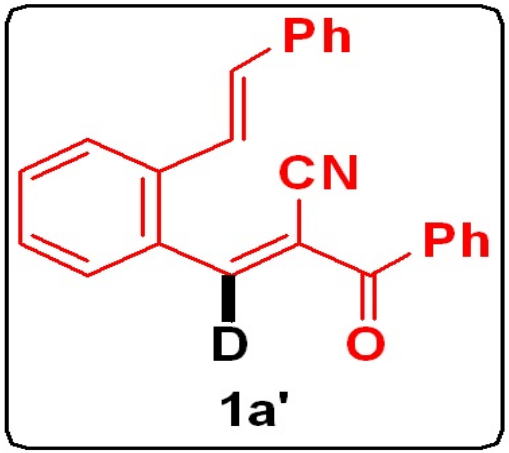
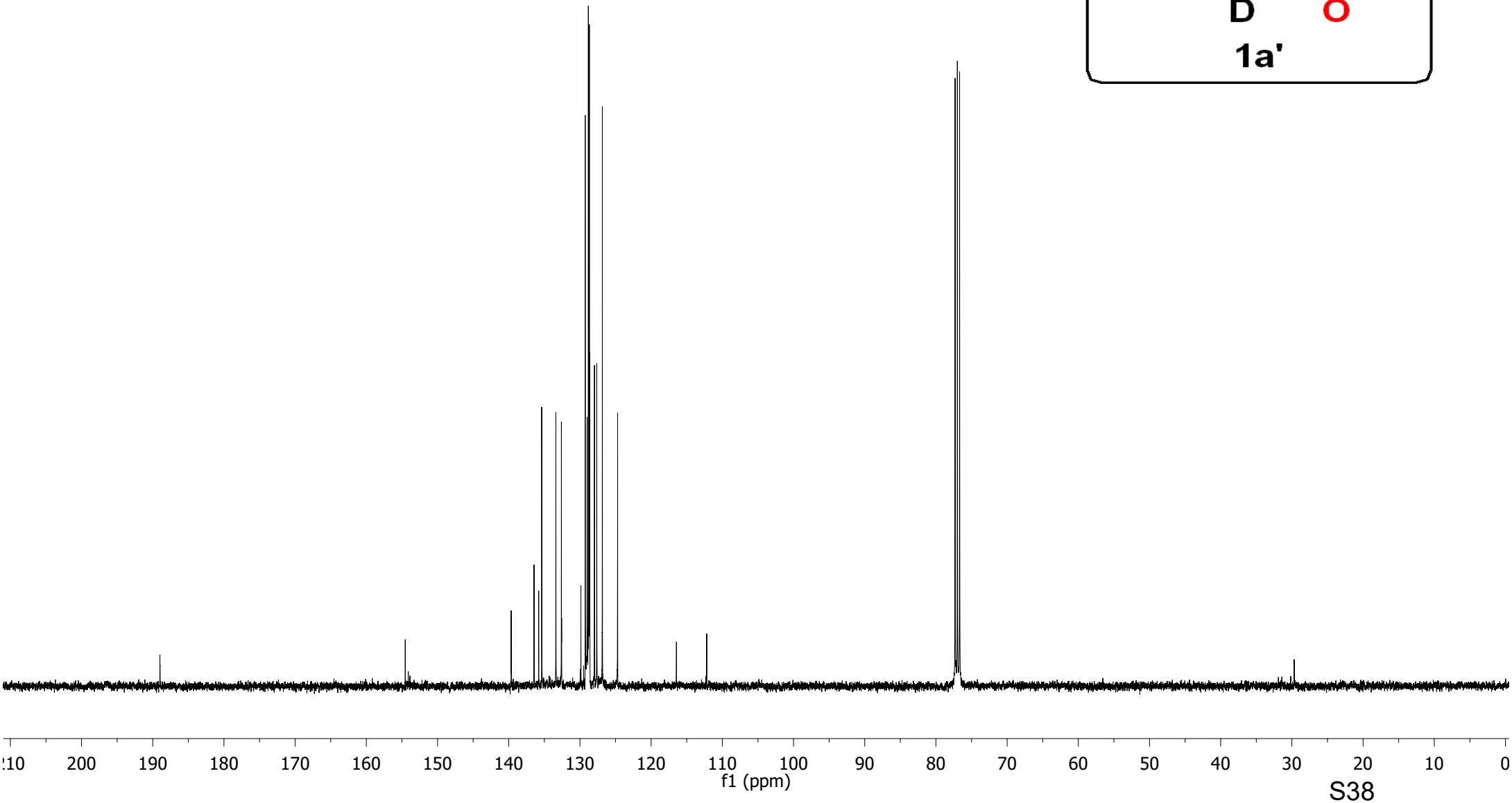
76.673

Solvent $CDCl_3$

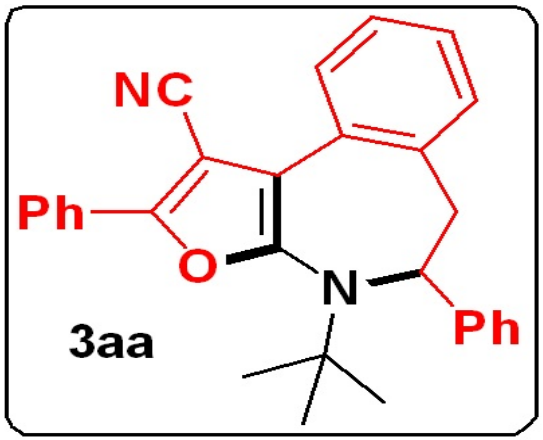
Spectrometer Frequency 100

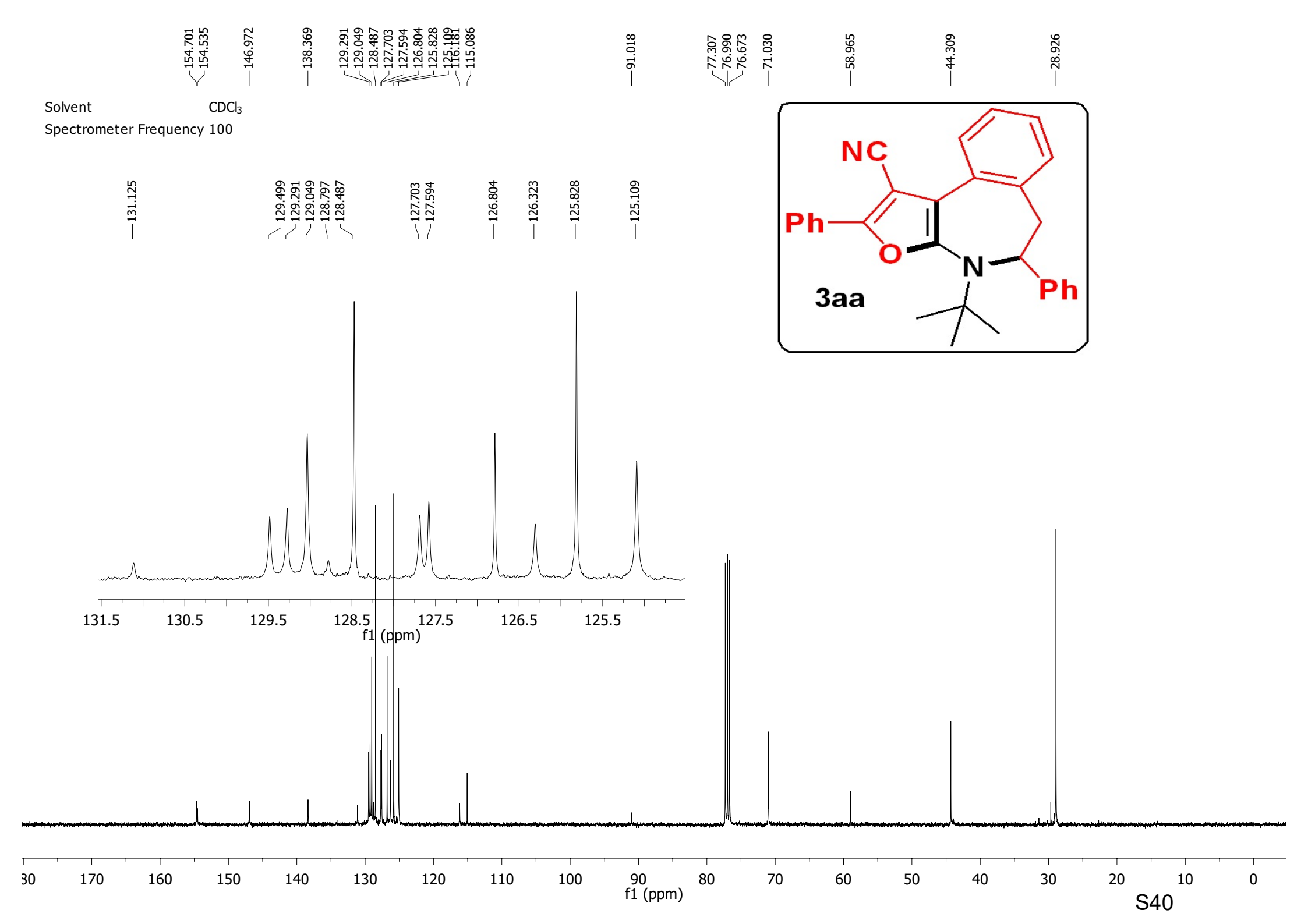




Solvent $CDCl_3$

Spectrometer Frequency 400

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115.086
91.018
77.307
76.990
76.673
71.030
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44.309
28.926
Solvent CDCl3
Spectrometer Frequency 100
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126.323
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125.109
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N
Ph
3aa
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127.5
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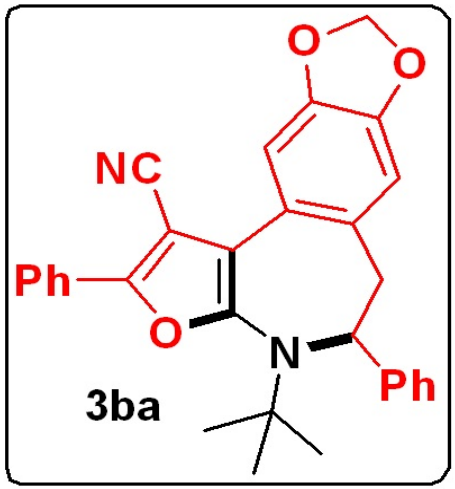
125.5
f1 (ppm)
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400



Solvent $CDCl_3$

Spectrometer Frequency 100

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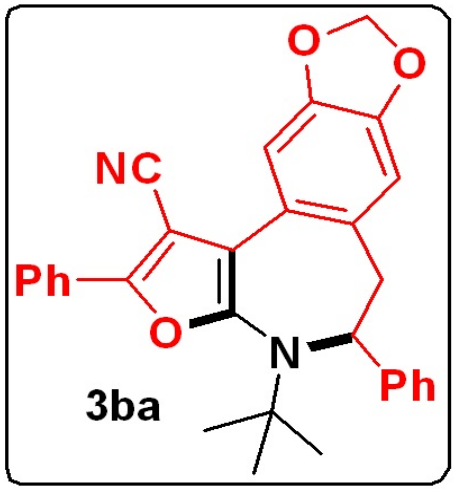
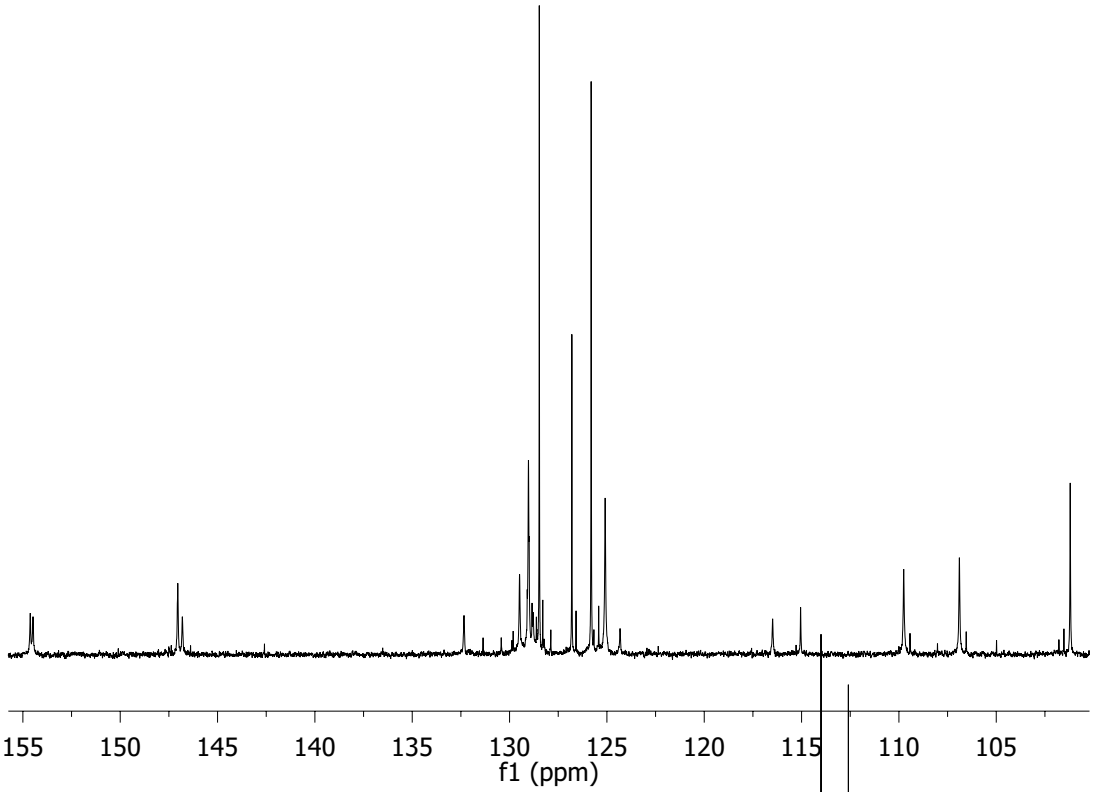
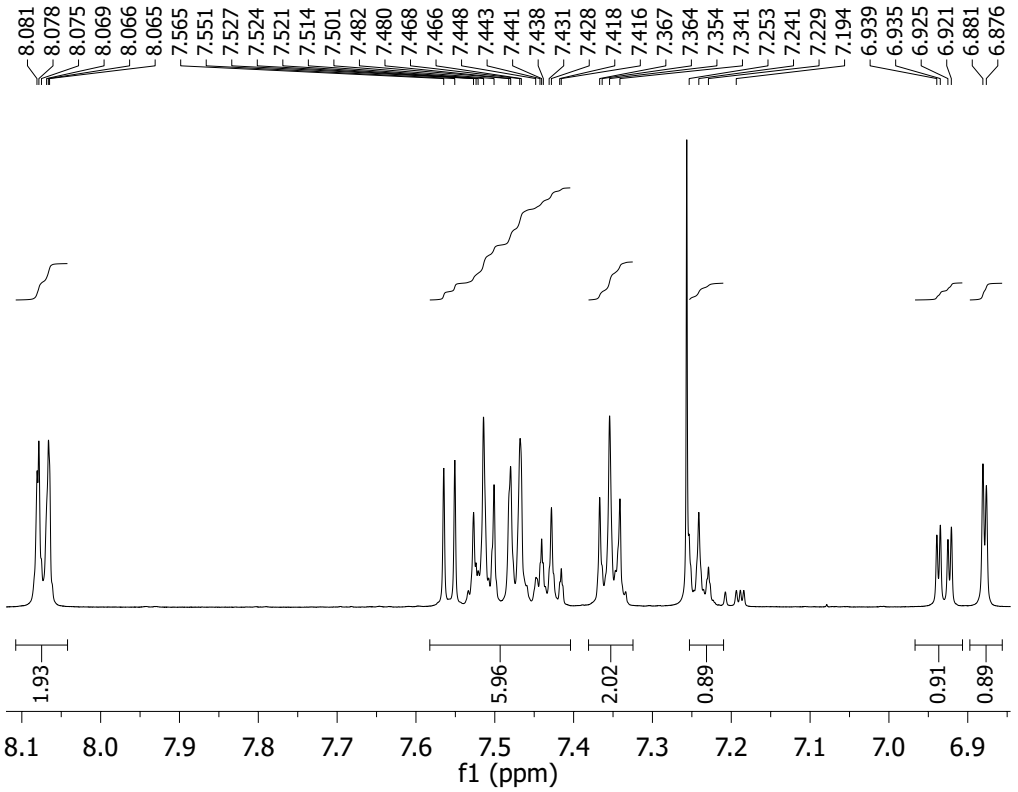
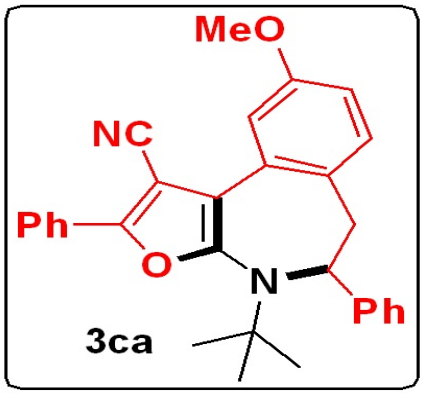


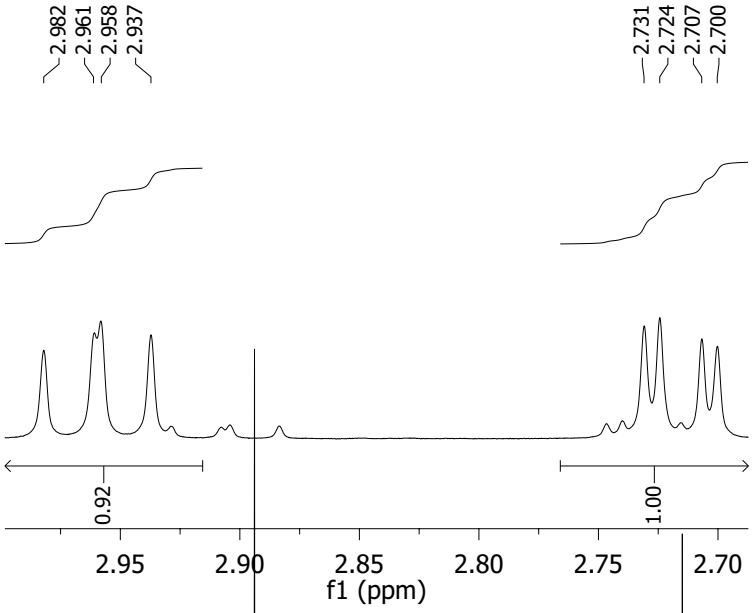


Solvent $CDCl_3$

Spectrometer Frequency 597







Solvent $CDCl_3$

Spectrometer Frequency 150

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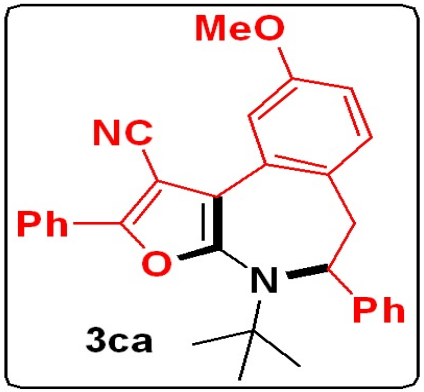

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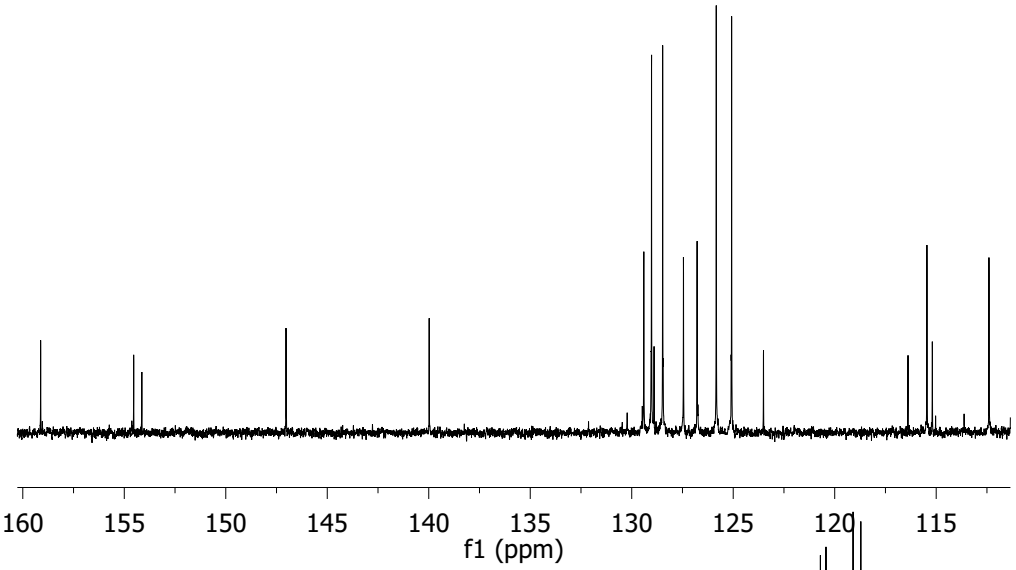
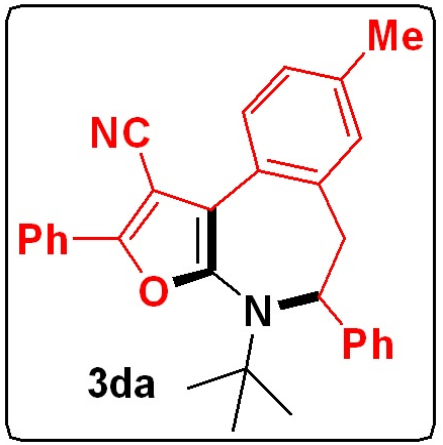


Solvent $CDCl_3$

Spectrometer Frequency 597



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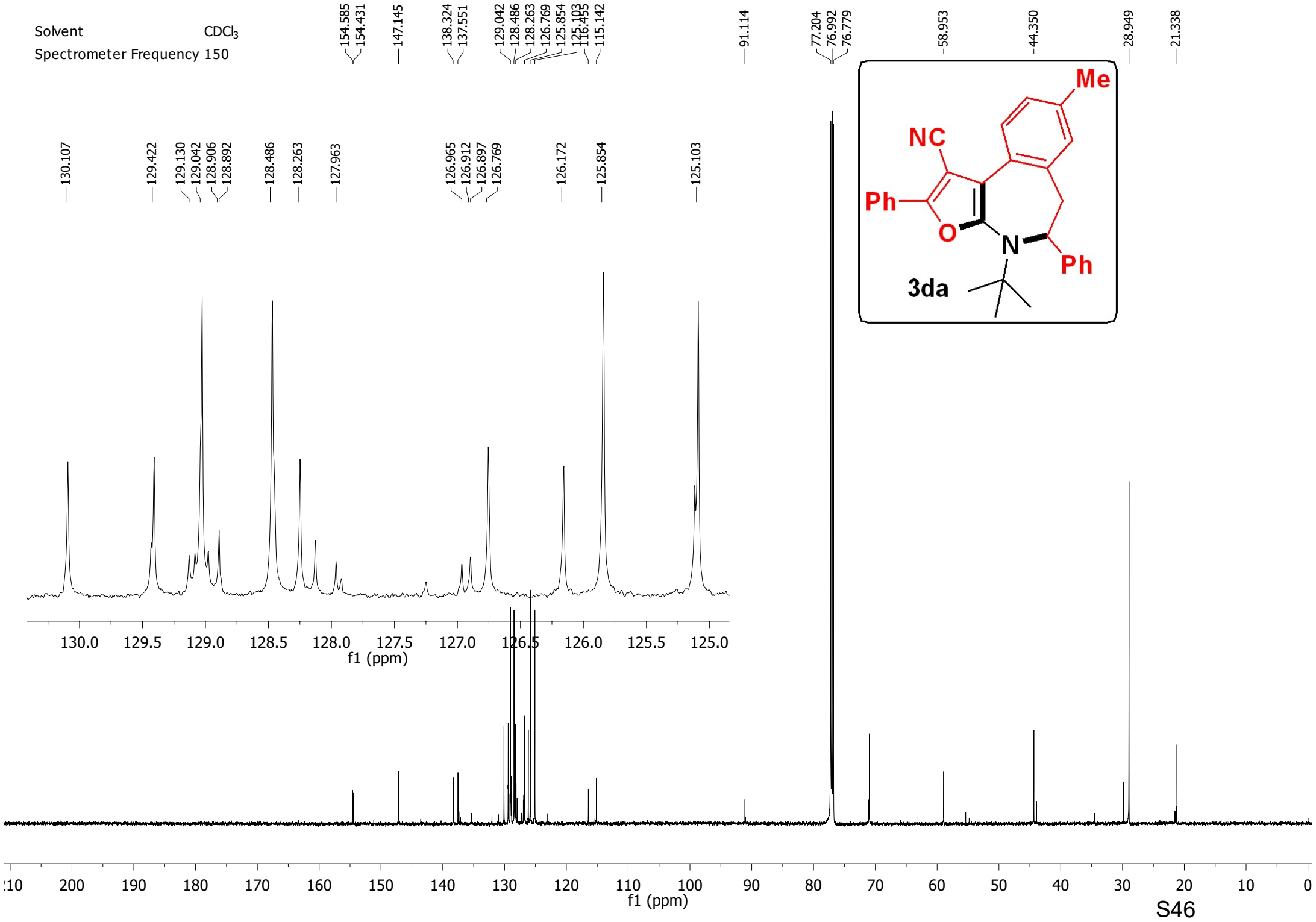
f1 (ppm)

f1 (ppm)


Solvent CDCl3
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Ph
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Ph
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125.0
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200
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180
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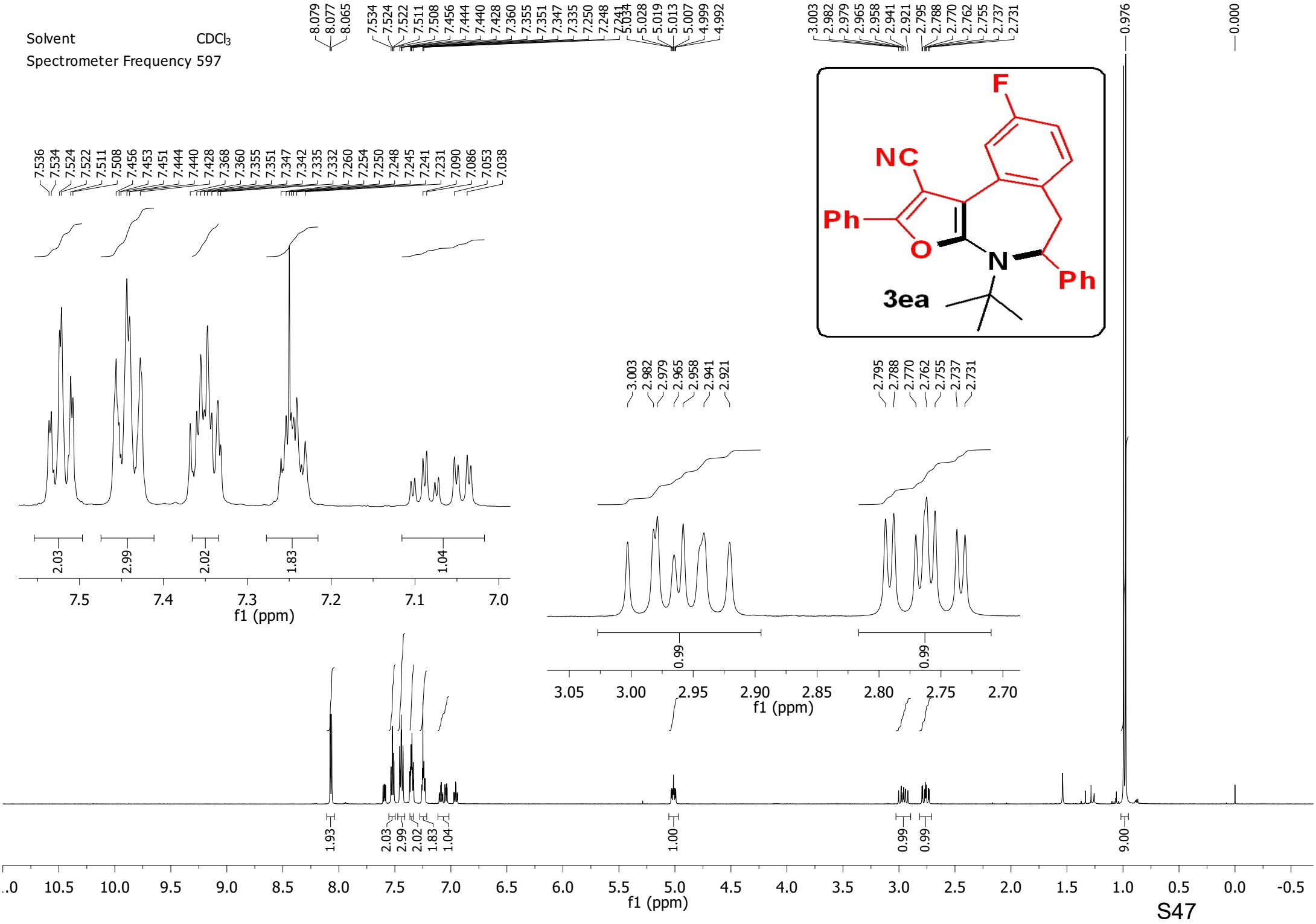
f1 (ppm)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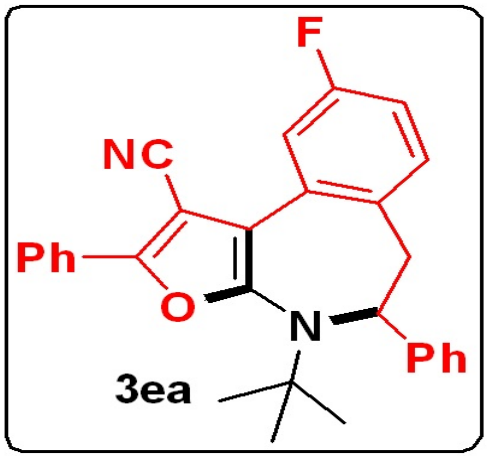
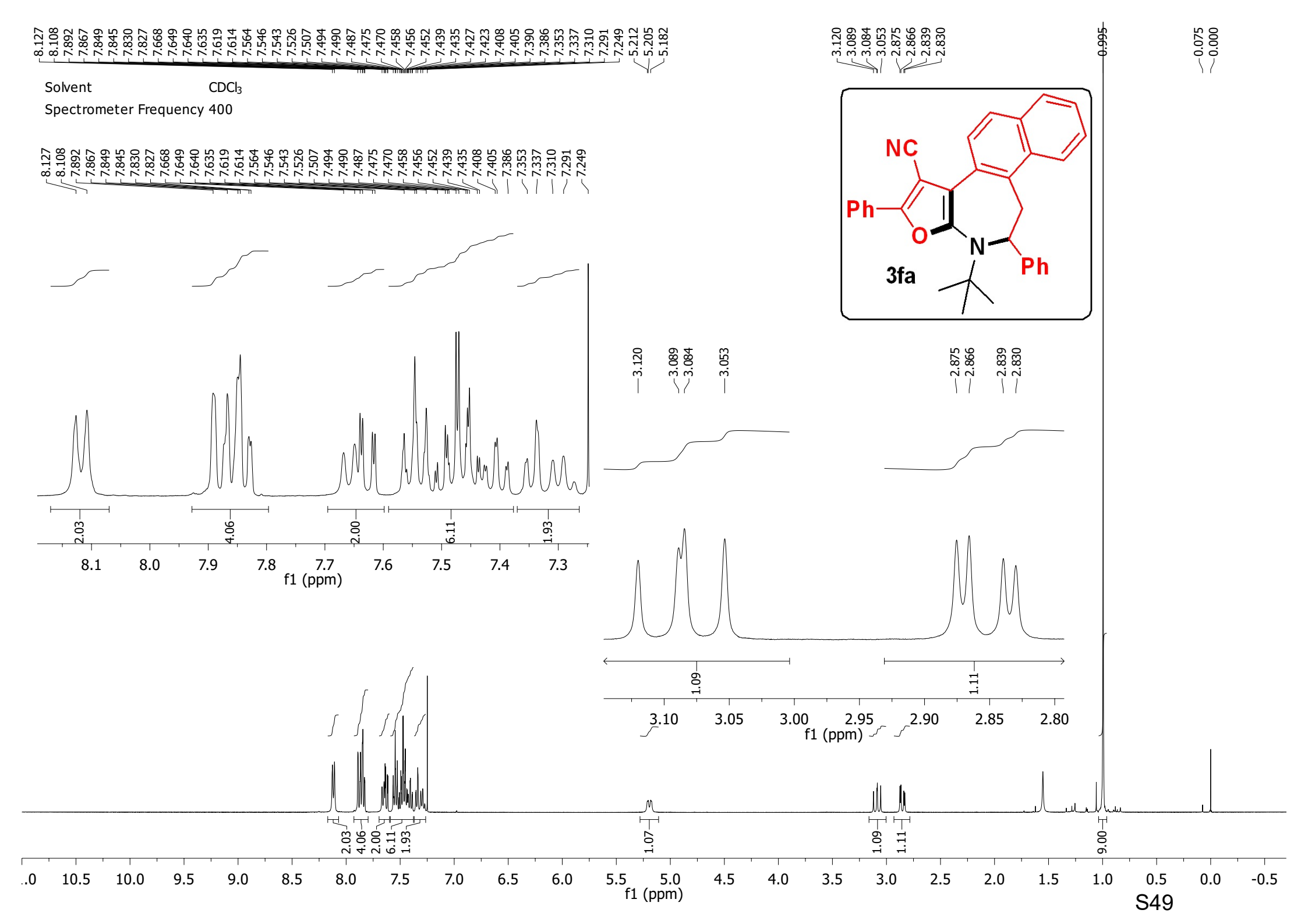
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 150



f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400
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N
Ph
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f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 100

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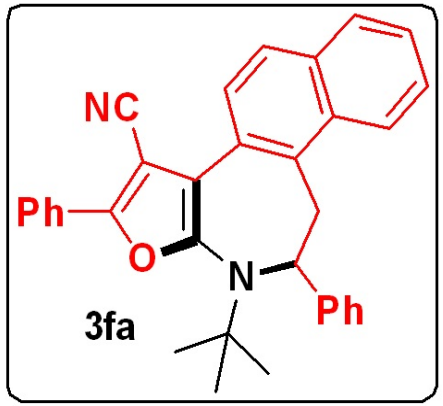
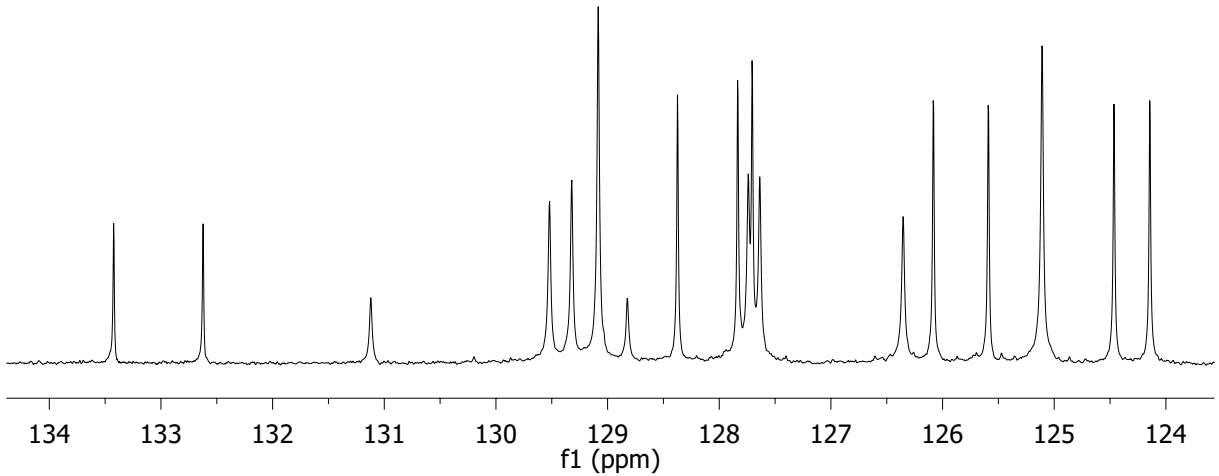
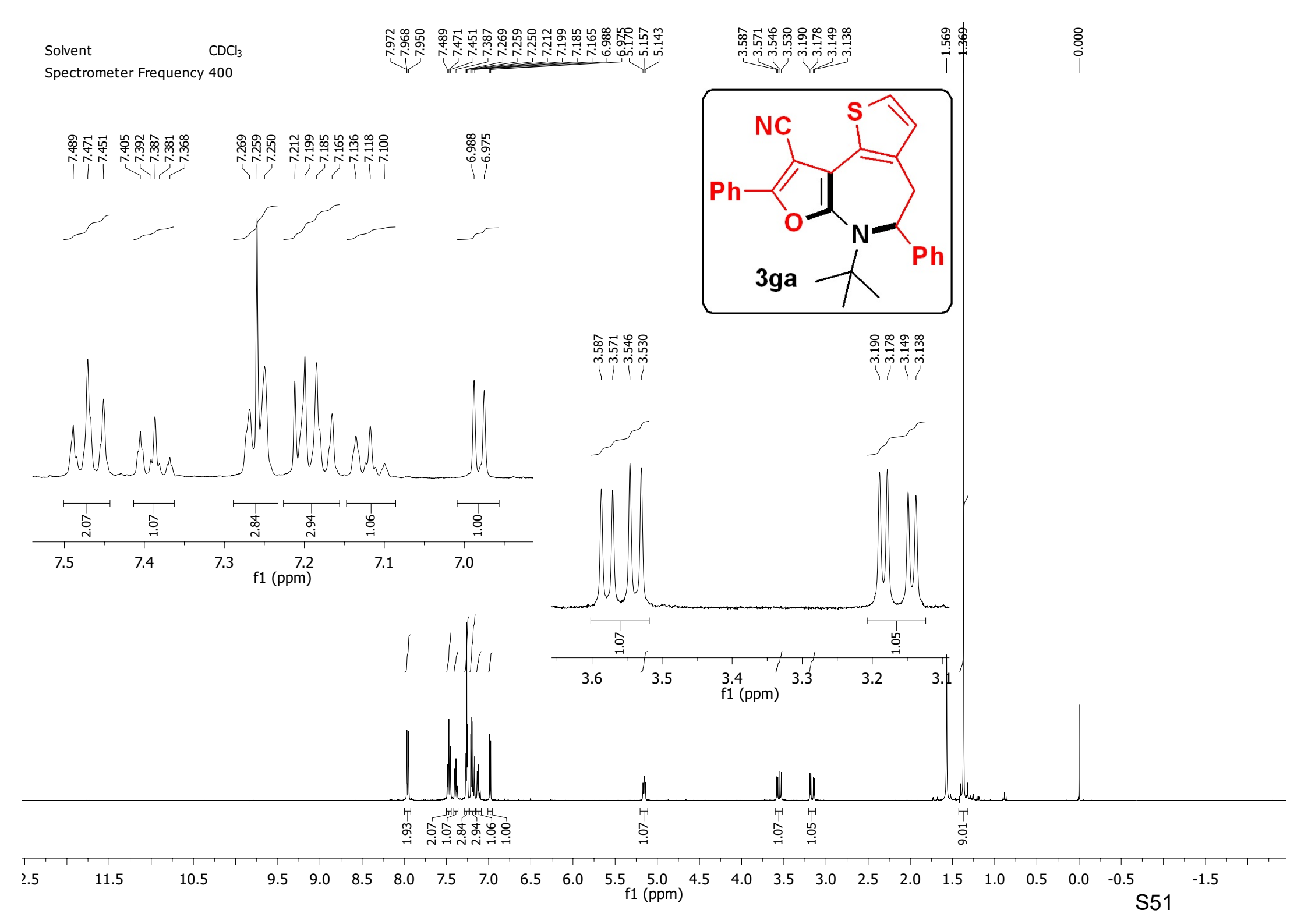
133.439, 132.638, 131.136, 129.535, 129.336, 129.098, 128.838, 128.388, 127.849, 127.754, 127.719, 127.651, 126.367, 126.097, 125.604, 125.123, 124.479, 124.158






Solvent CDCl3
Spectrometer Frequency 400
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S
Ph
O
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f1 (ppm)
f1 (ppm)
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 100

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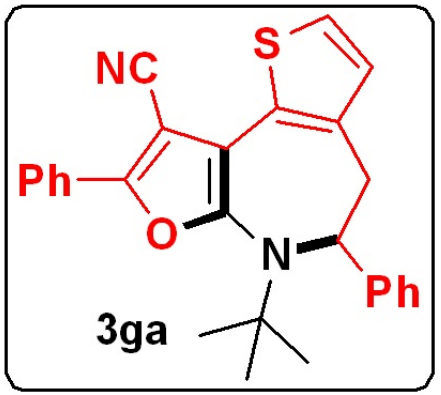
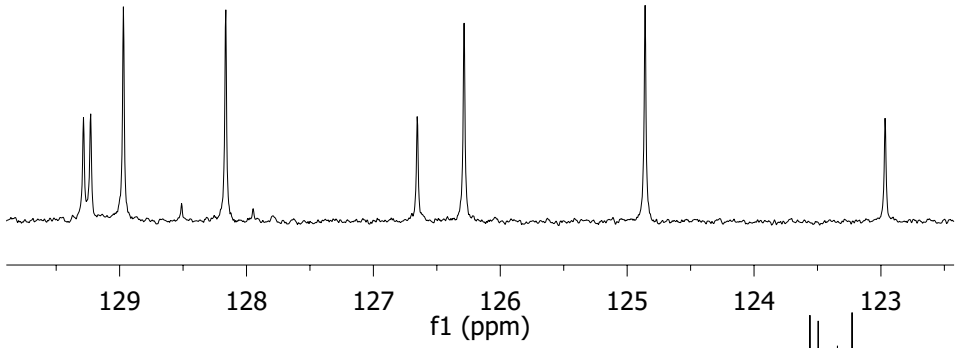
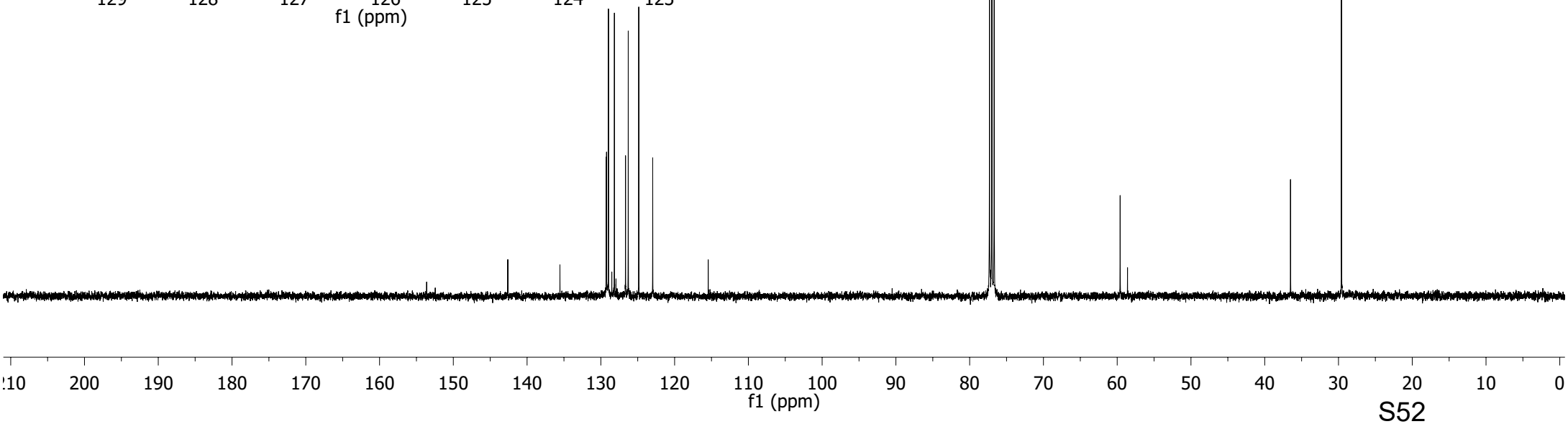


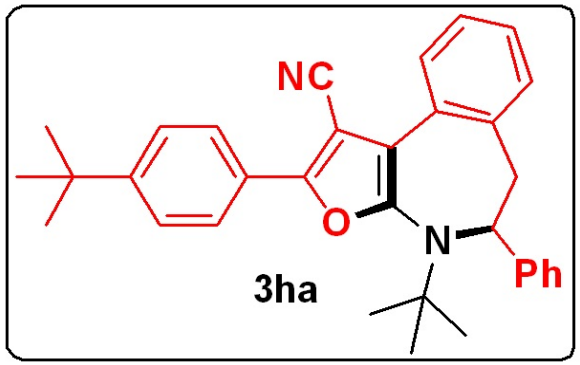
129.300 129.244 128.985 128.526 128.179 127.963 126.669 126.300 124.873 122.981





Solvent $CDCl_3$

Spectrometer Frequency 400

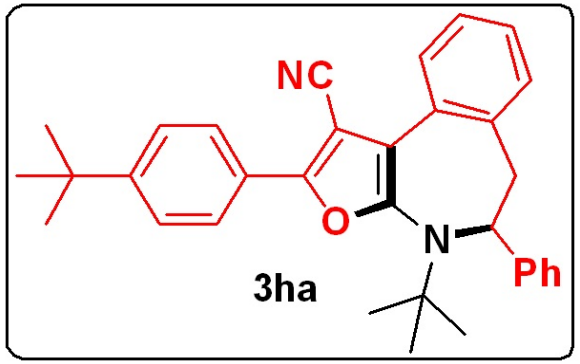


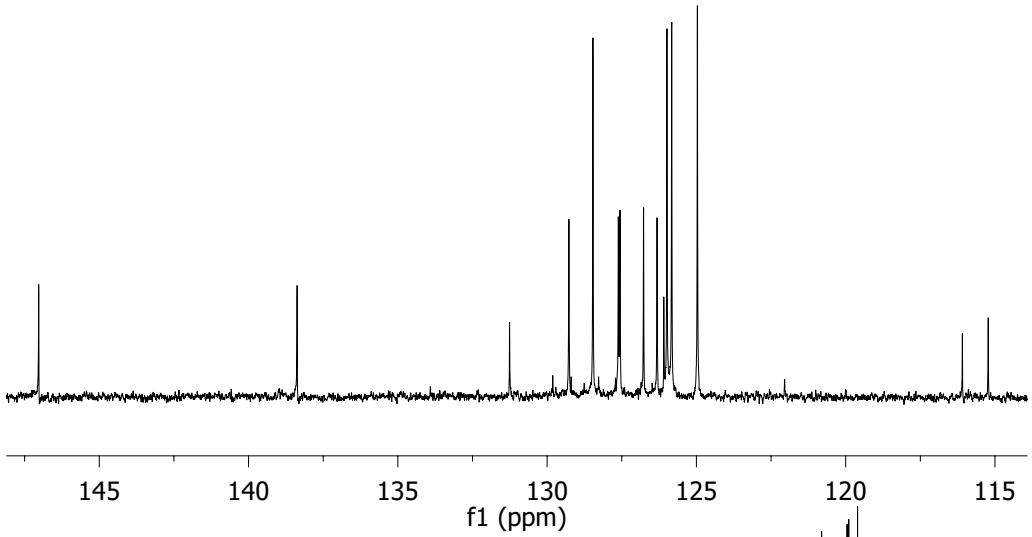
Solvent $CDCl_3$

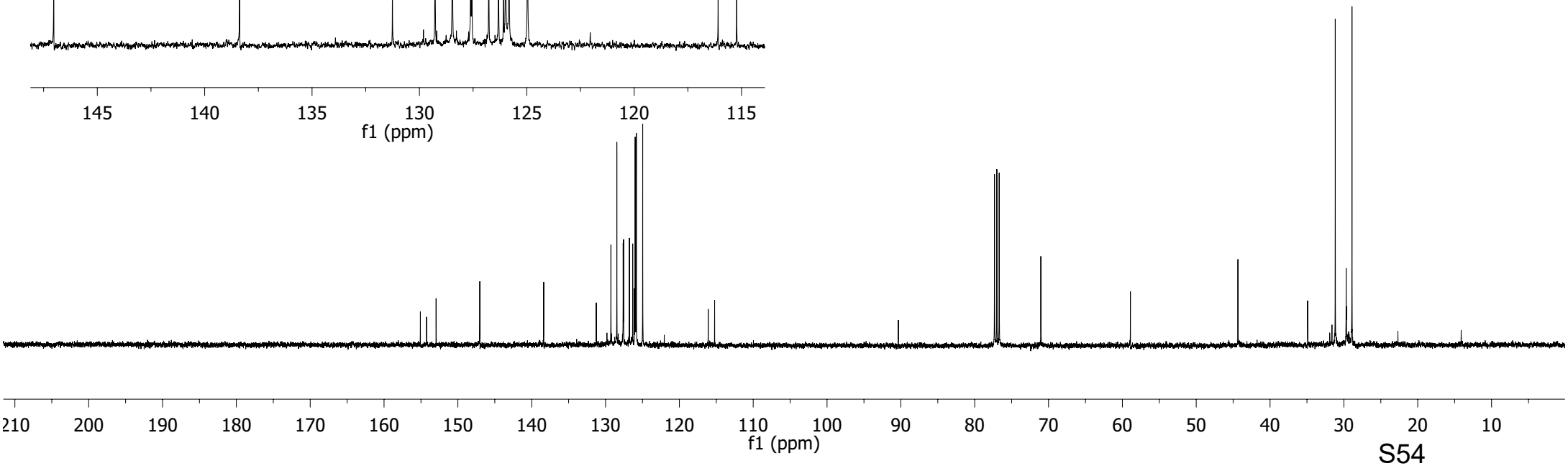
Spectrometer Frequency 100

155.081 154.233 152.951 147.029 138.373 128.466 127.614 127.559 126.770 125.987 125.827 124.967 116.091 115.225 90.345 77.319 77.001 76.684 71.044 58.911 44.352 34.907 31.169 29.689 29.652 28.901

147.029 138.373 131.257 129.811 129.270 128.466 127.614 127.559 126.770 126.317 126.092 125.987 125.827 124.967 116.091 115.225

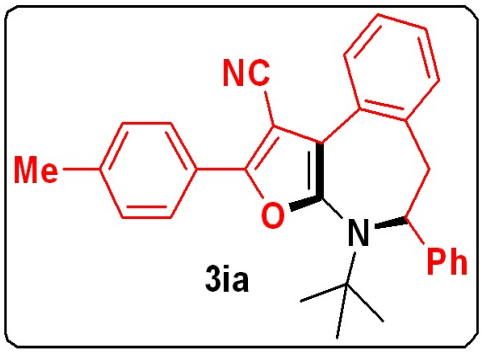






Solvent $CDCl_3$

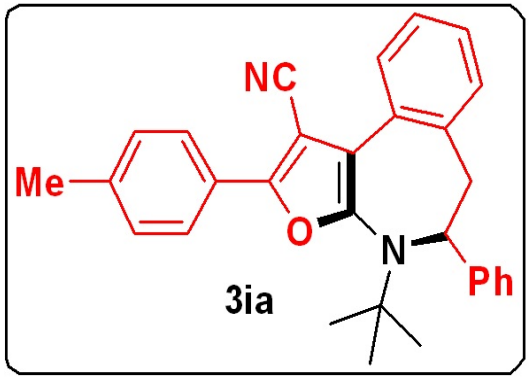
Spectrometer Frequency 400



Solvent $CDCl_3$

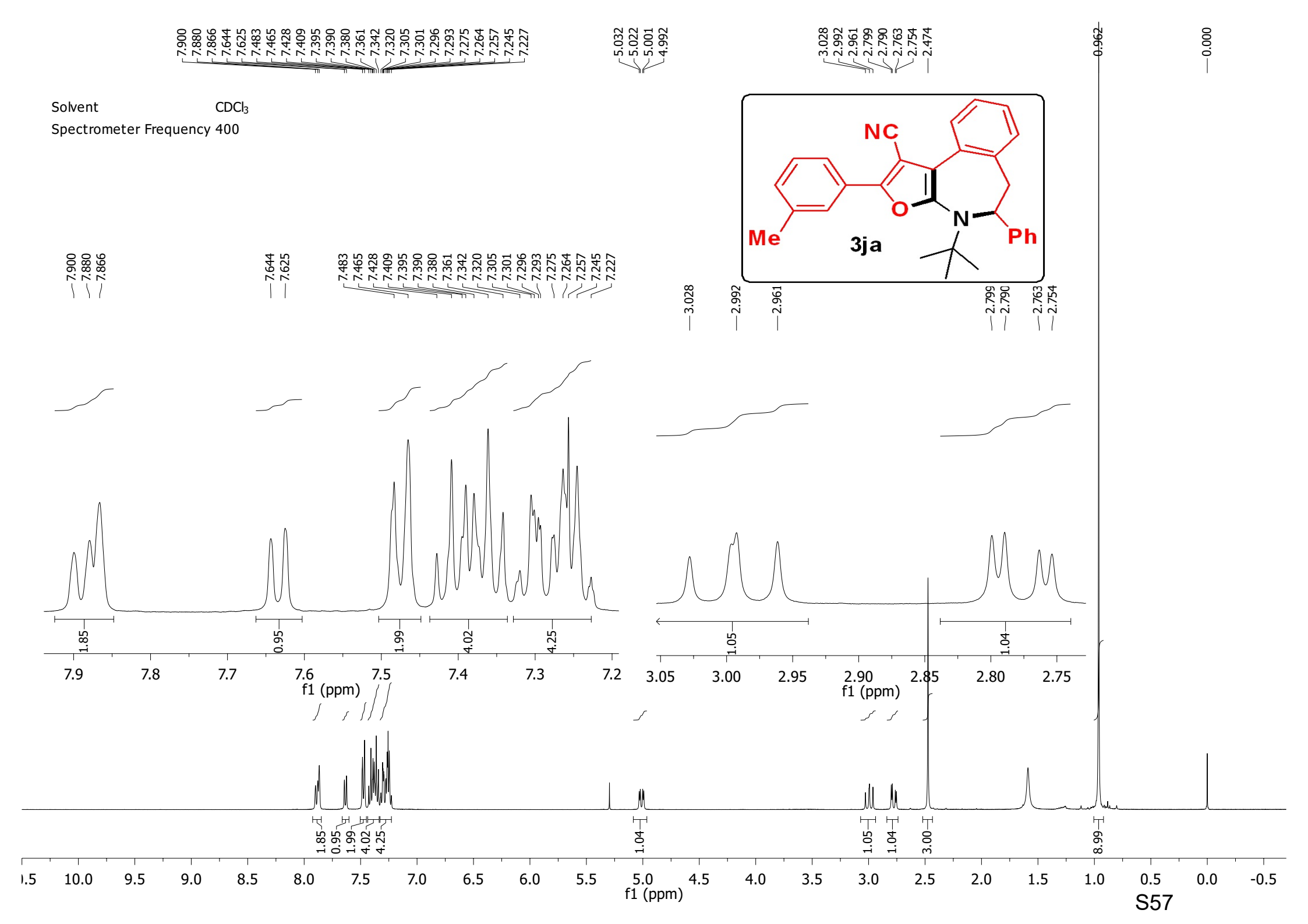
Spectrometer Frequency 100

155.164
154.206
147.058
139.844
138.399
129.720
129.281
128.476
127.581
126.775
125.849
125.116
116.138
115.253
90.228
77.310
76.993
76.676
71.037
58.939
44.341
28.895
21.516



3ia

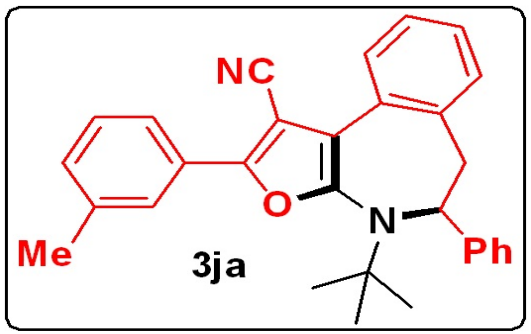
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400
NC
O
N
Me
Ph
3ja
f1 (ppm)
S57

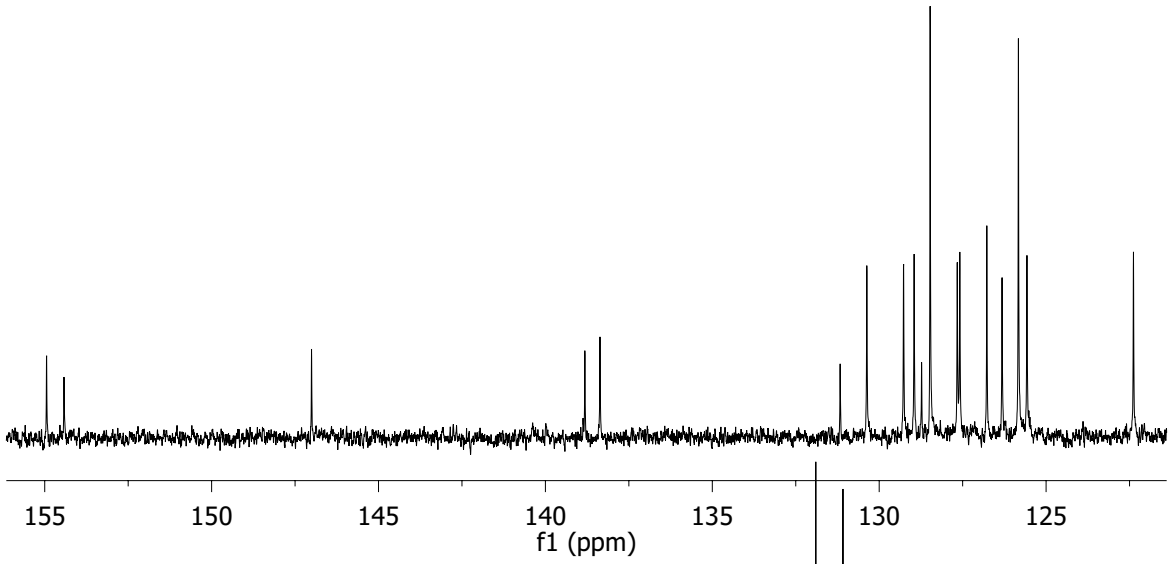
Solvent $CDCl_3$

Spectrometer Frequency 100

154.945 154.422 147.006 138.818 138.365 128.954 128.473 127.585 126.776 125.829 125.574 122.383 116.240 115.118 90.840 77.310 76.993 76.675 71.025 58.977 44.323 28.898 21.593

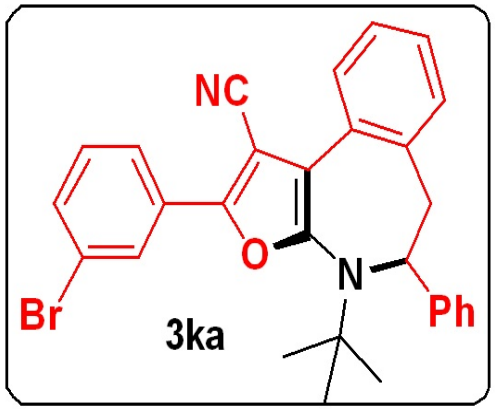


154.945 154.422 147.006 138.818 138.365 131.170 130.370 129.270 128.954 128.729 128.473 127.662 127.585 126.776 126.319 125.829 125.574 122.383



Solvent $CDCl_3$

Spectrometer Frequency 400

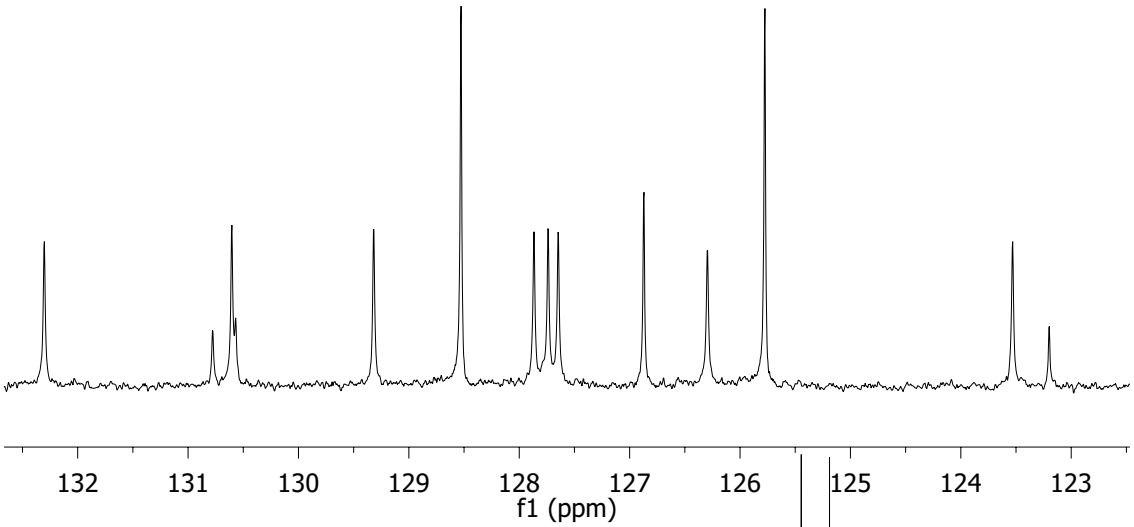


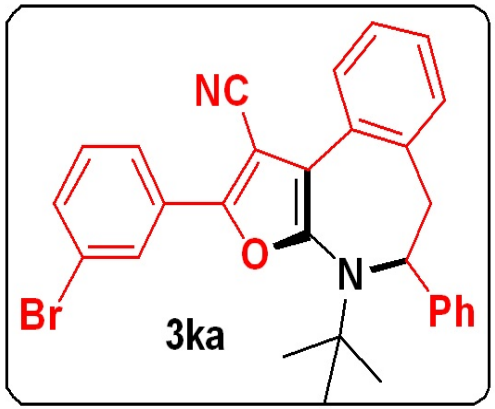
Solvent $CDCl_3$

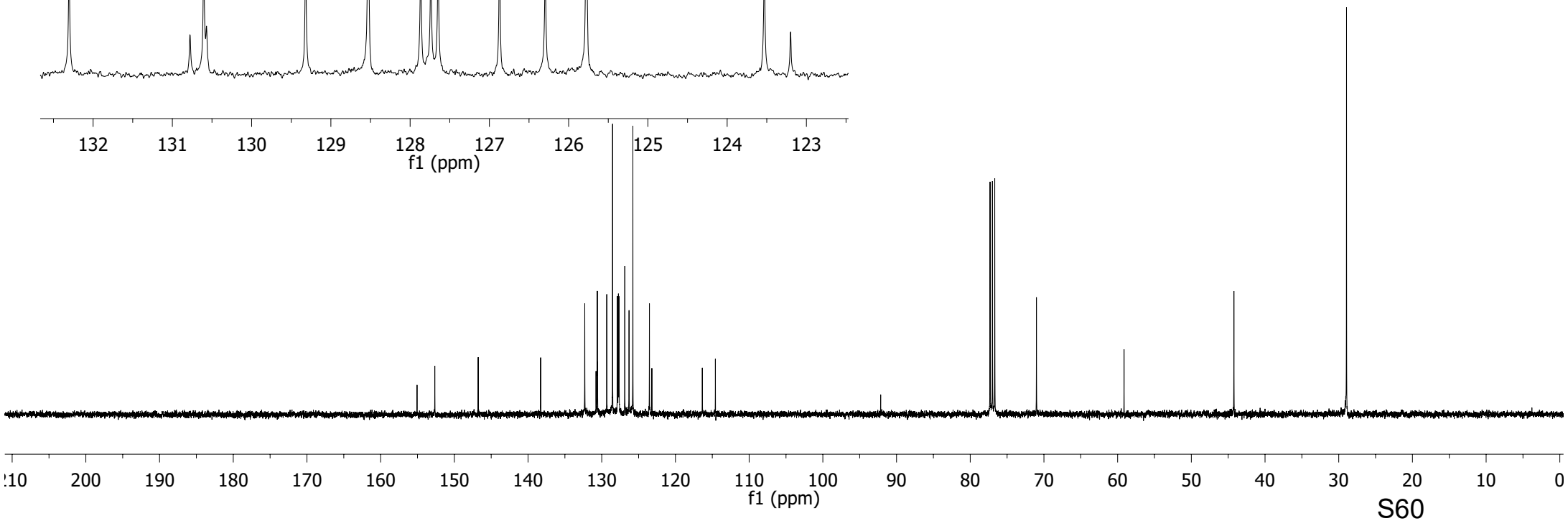
Spectrometer Frequency 100

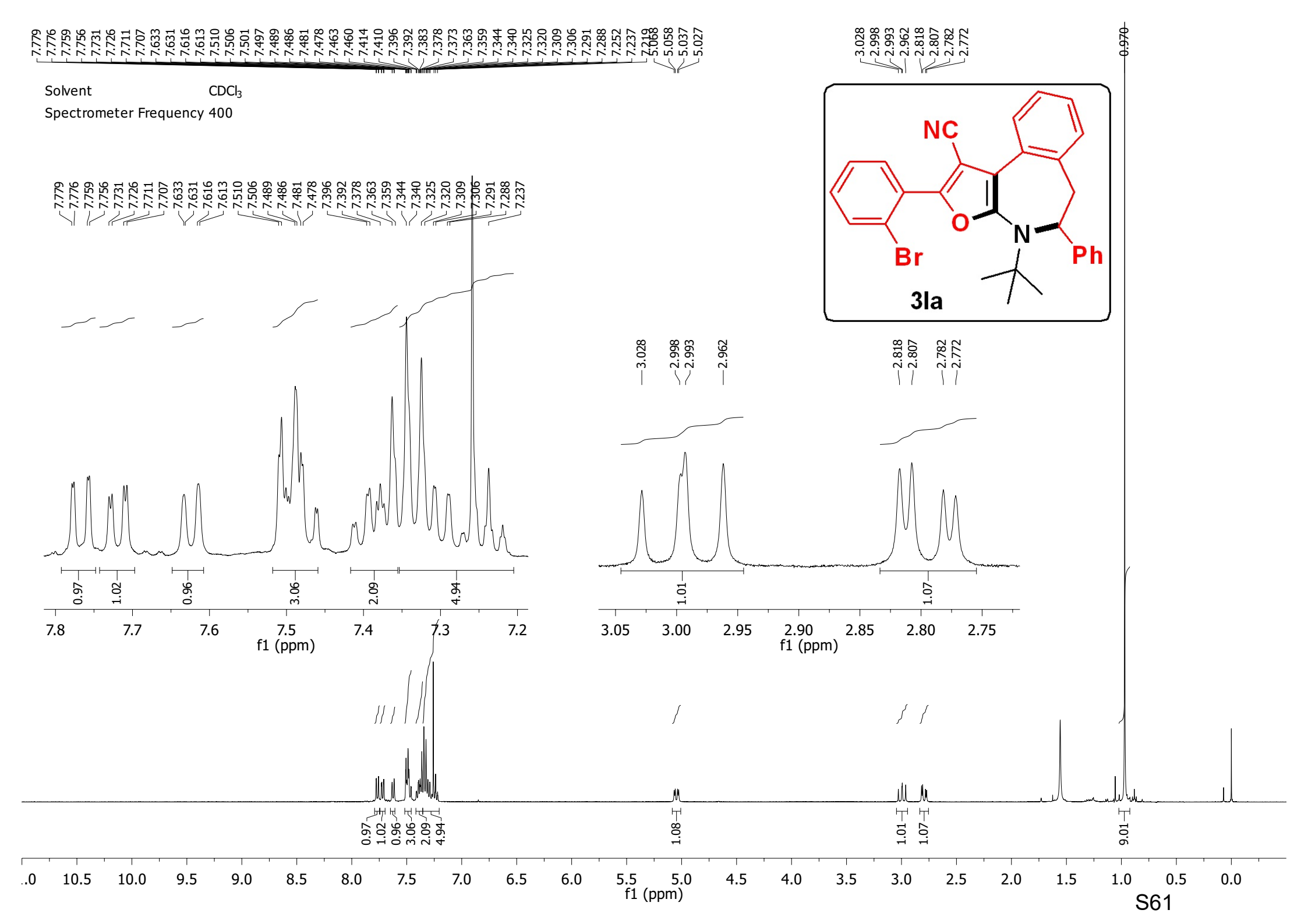
155.078 152.667 146.782 138.303 130.619 129.334 128.542 127.881 127.662 126.886 125.790 116.366 114.595 92.163 77.309 76.991 76.674 71.025 59.137 44.226 28.948

132.318 130.792 130.619 130.583 129.334 128.542 127.881 127.802 127.753 127.662 126.886 126.310 125.790 123.545 123.213





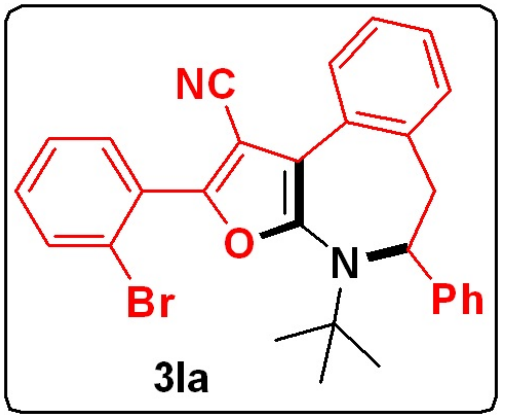



Solvent CDCl3
Spectrometer Frequency 400
NC
O
N
Br
Ph
3la
f1 (ppm)
S61

Solvent $CDCl_3$

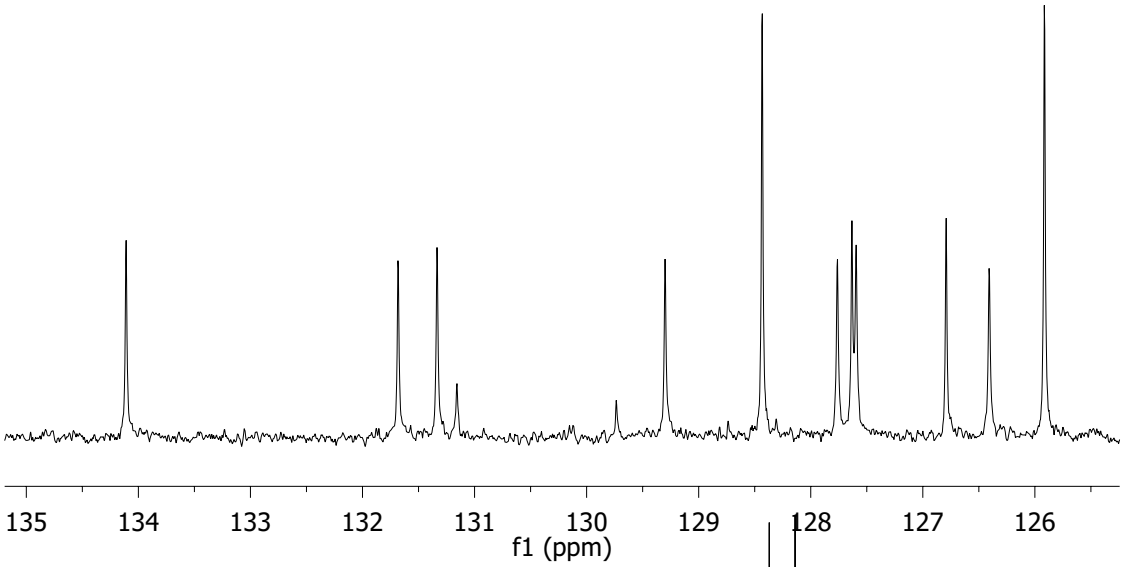
Spectrometer Frequency 100

155.535 154.686 146.826 134.125 131.697 131.349 129.315 128.448 127.777 127.647 127.610 126.806 126.422 125.929 125.944 114.019 95.396 77.309 76.991 76.674 71.274 58.901 44.269 29.045



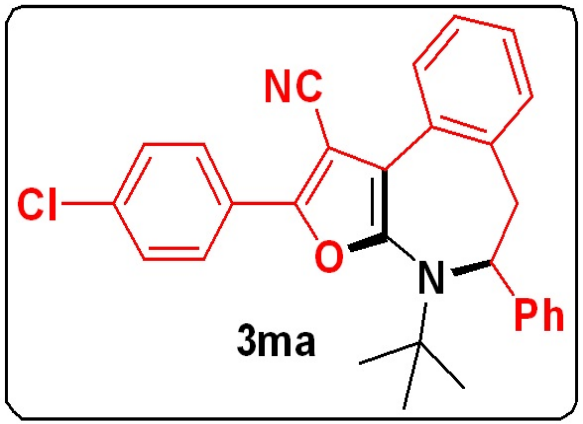
3la

134.125 131.697 131.349 131.172 129.749 129.315 128.448 127.777 127.647 127.610 126.806 126.422 125.929



Solvent $CDCl_3$

Spectrometer Frequency 400



f1 (ppm)

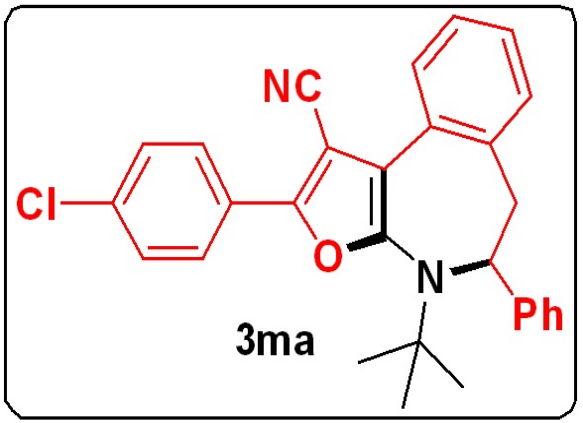
f1 (ppm)

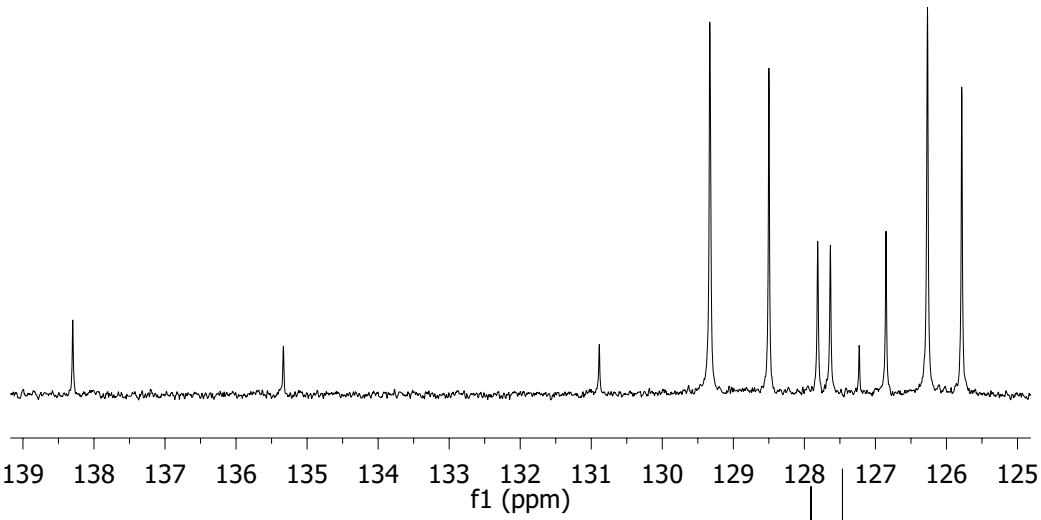
f1 (ppm)

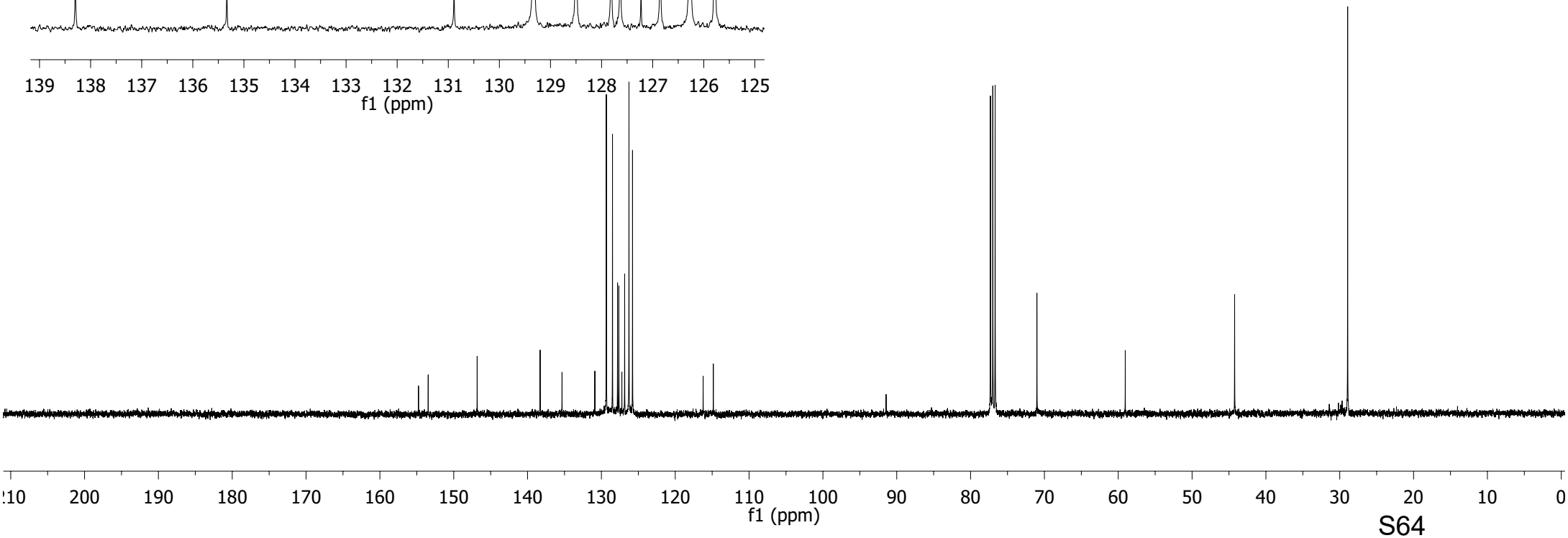
Solvent $CDCl_3$

Spectrometer Frequency 100

154.789 153.480 146.844 138.314 135.349 130.902 129.345 128.514 127.827 127.648 127.242 126.865 126.281 125.799 116.234 114.858 91.452 77.310 76.992 76.675 71.022 59.057 44.245 28.932

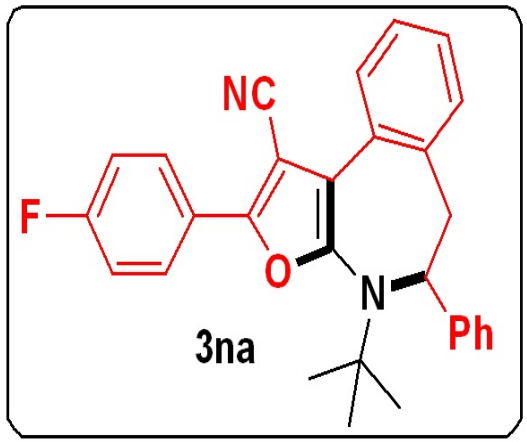


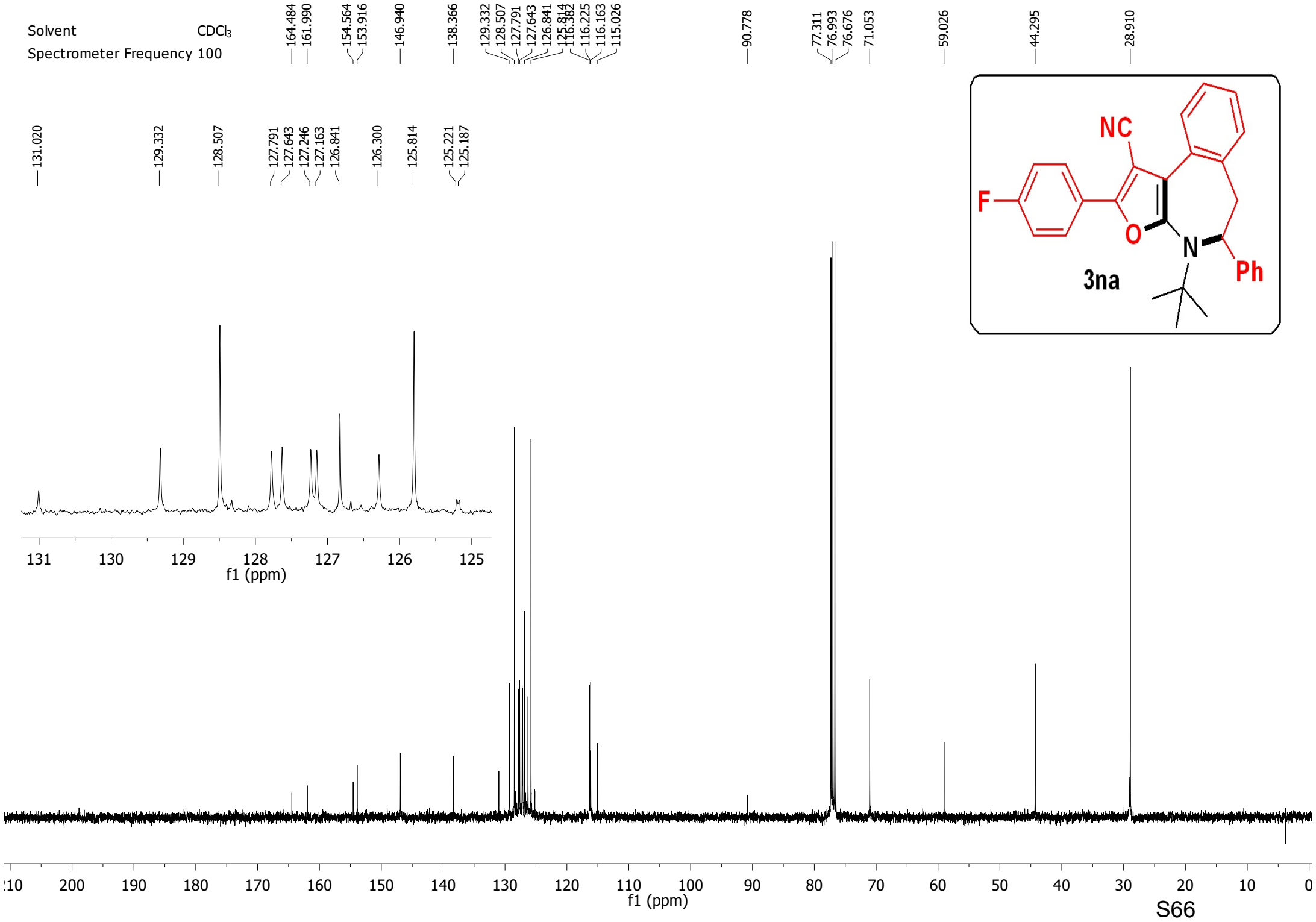




Solvent $CDCl_3$

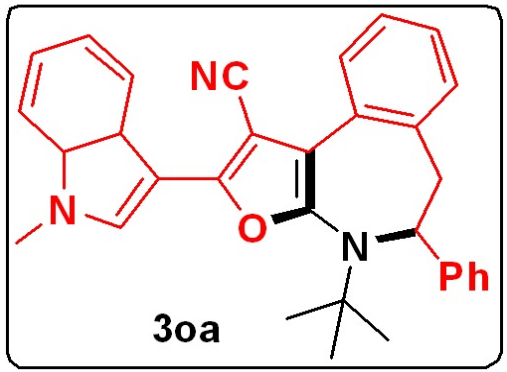
Spectrometer Frequency 400




Solvent CDCl3
Spectrometer Frequency 100
164.484
161.990
154.564
153.916
146.940
138.366
129.332
128.507
127.791
127.643
126.841
125.814
125.382
116.225
116.163
115.026
90.778
77.311
76.993
76.676
71.053
59.026
44.295
28.910
131.020
129.332
128.507
127.791
127.643
127.246
127.163
126.841
126.300
125.814
125.221
125.187
NC
F
O
N
Ph
3na
131
130
129
128
127
126
125
f1 (ppm)
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 597

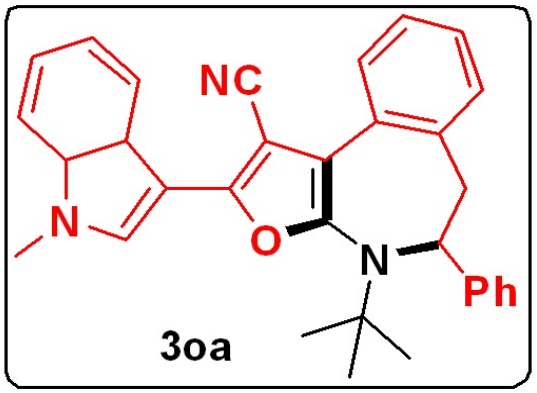


3oa

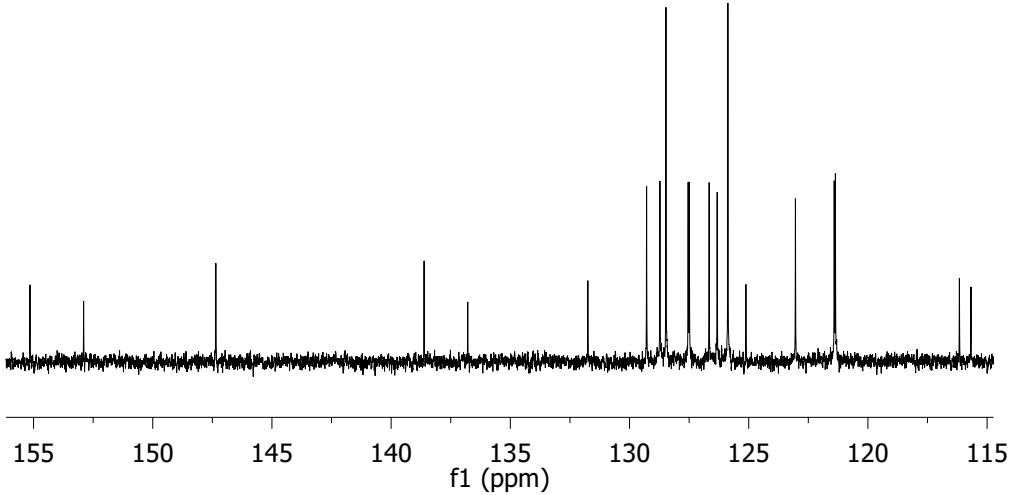
Solvent $CDCl_3$

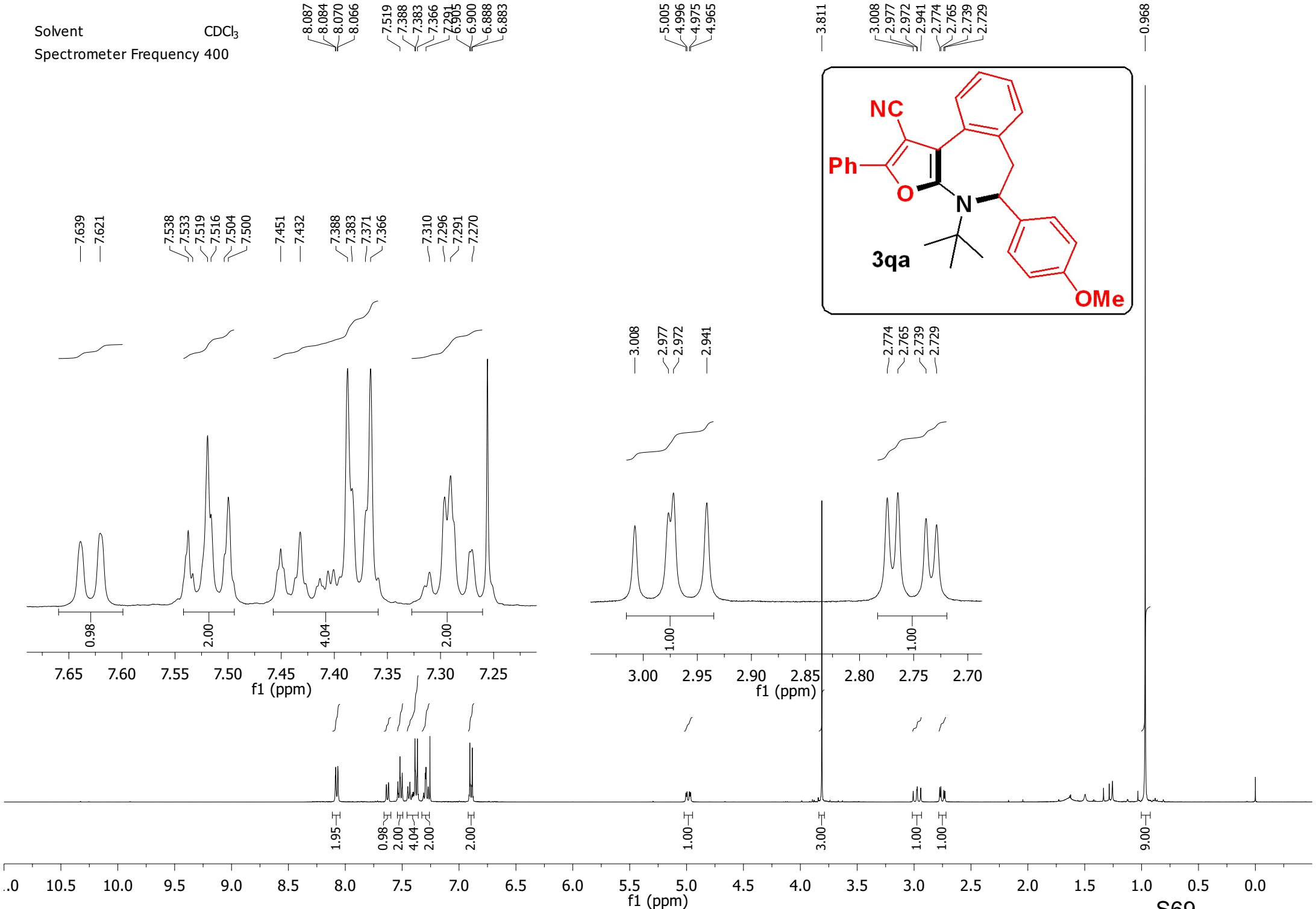
Spectrometer Frequency 150

155.167 152.916 147.370 138.633 136.801 128.739 128.486 127.505 126.336 125.888 121.427 116.175 115.689 109.834 105.608 86.514 77.204 76.991 76.779 71.241 59.187 44.485 33.377 28.822



155.167 152.916 147.370 138.633 136.801 131.762 129.298 128.739 128.486 127.555 127.505 126.674 126.336 125.888 125.131 123.054 121.427 121.377 116.175 115.689



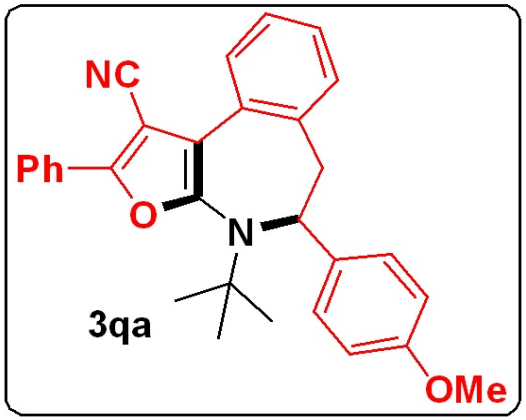

Solvent CDCl3
Spectrometer Frequency 400
8.087 8.084 8.070 8.066 7.519 7.388 7.383 7.366 7.291 6.905 6.900 6.888 6.883
5.005 4.996 4.975 4.965 3.811 3.008 2.977 2.972 2.941 2.774 2.765 2.739 2.729 0.968
NC
Ph
O
N
3qa
OMe
7.639 7.621 7.538 7.533 7.519 7.516 7.504 7.500 7.451 7.432 7.388 7.383 7.371 7.366 7.310 7.296 7.291 7.270
0.98 2.00 4.04 2.00
7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25
f1 (ppm)
3.008 2.977 2.972 2.941 2.774 2.765 2.739 2.729
1.00 1.00
3.00 2.95 2.90 2.85 2.80 2.75 2.70
f1 (ppm)
1.95 0.98 2.00 4.04 2.00 2.00 1.00 3.00 1.00 1.00 9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

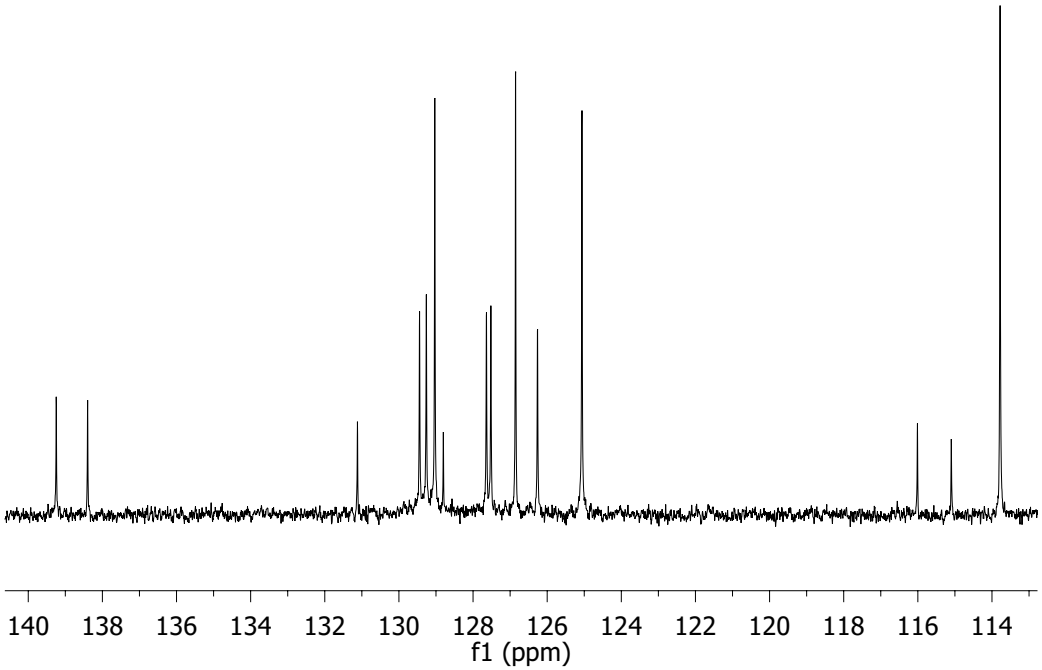
Solvent $CDCl_3$

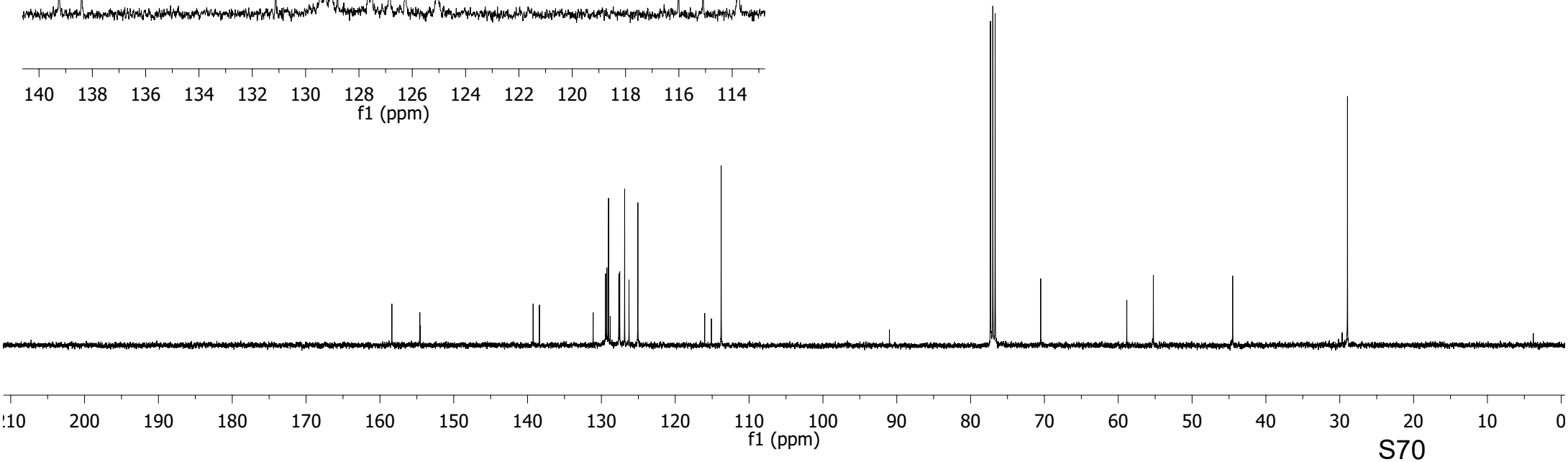
Spectrometer Frequency 100

158.397 154.607 154.552 139.260 138.414 129.458 129.275 129.047 127.654 127.533 126.867 125.076 116.024 115.110 113.794 90.999 77.309 76.991 76.674 70.514 58.848 55.254 44.507 28.956

139.260 138.414 131.133 129.458 129.275 129.047 128.816 127.654 127.533 126.867 126.275 125.076 116.024 115.110 113.794

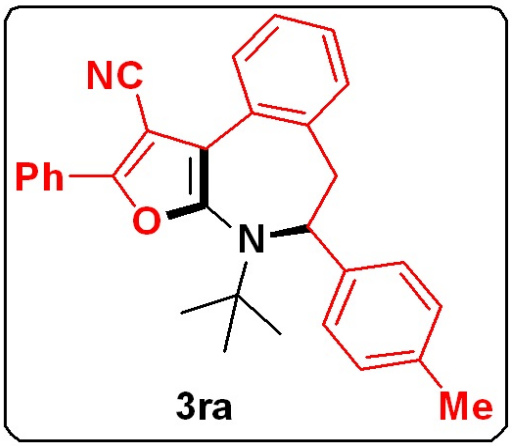






Solvent $CDCl_3$

Spectrometer Frequency 400



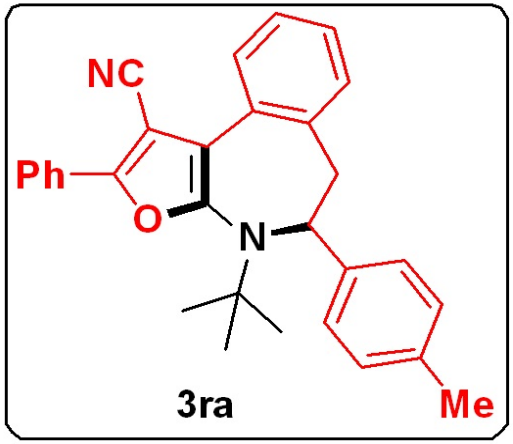
f1 (ppm)

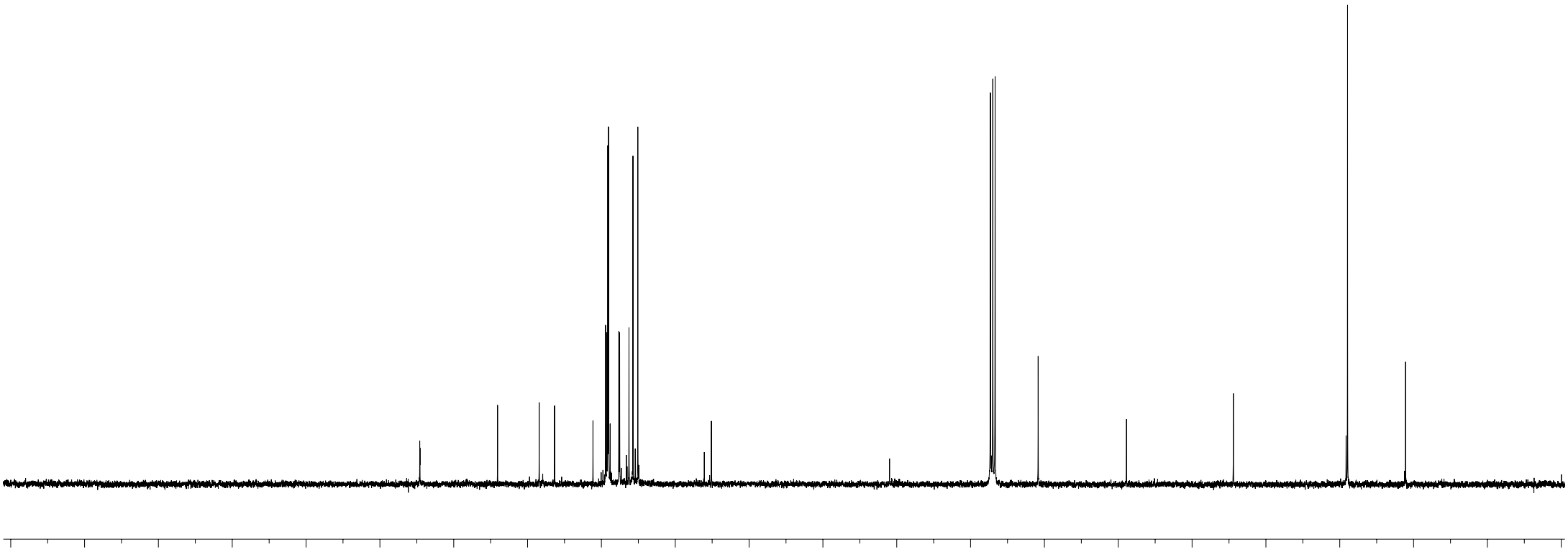
S71

Solvent $CDCl_3$

Spectrometer Frequency 100

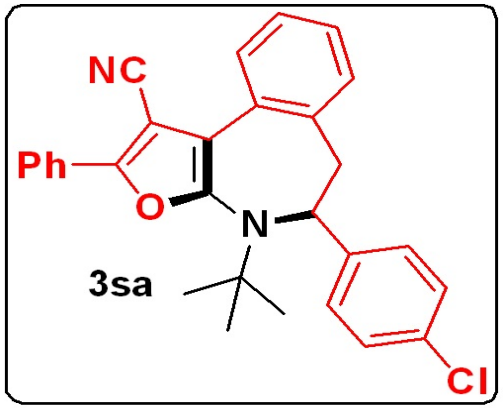
154.622
154.592
144.080
138.441
136.358
129.455
129.148
129.046
126.279
125.742
125.081
116.076
115.117
90.985
77.307
76.990
76.673
70.856
58.887
44.413
28.949
21.085





Solvent $CDCl_3$

Spectrometer Frequency 400

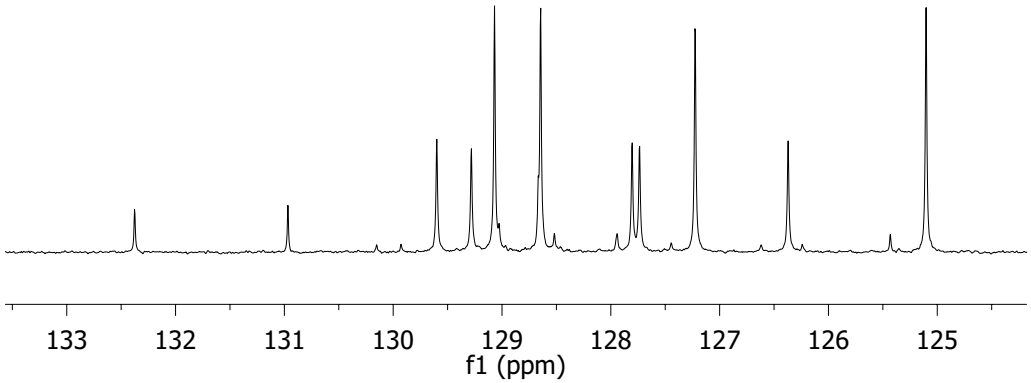


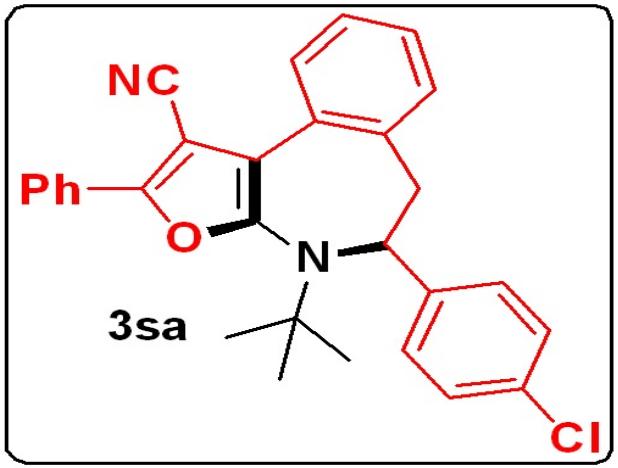
Solvent $CDCl_3$

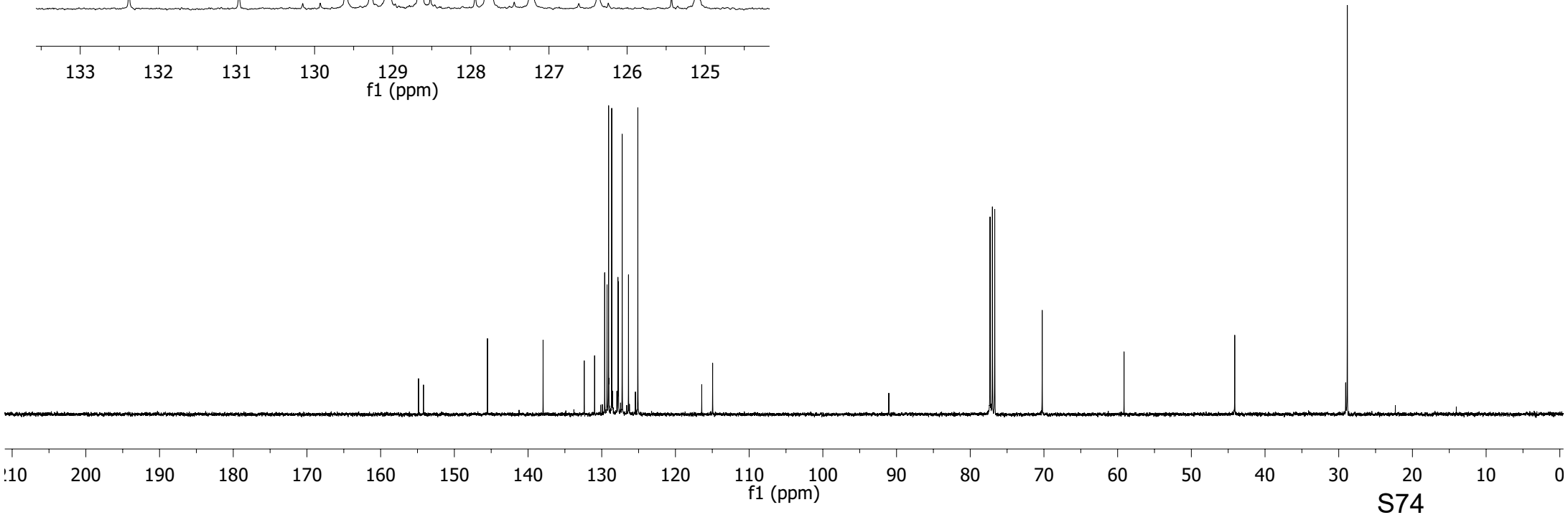
Spectrometer Frequency 100

154.880, 154.206, 145.525, 137.974, 129.614, 129.084, 128.660, 127.819, 127.240, 126.385, 125.117, 116.446, 114.968, 91.059, 77.308, 76.991, 76.673, 70.242, 59.137, 44.116, 28.837

132.392, 130.982, 129.614, 129.296, 129.084, 128.682, 128.660, 127.819, 127.751, 127.240, 126.385, 125.117

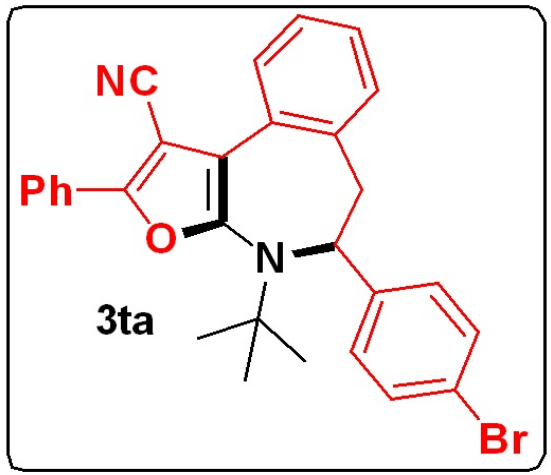


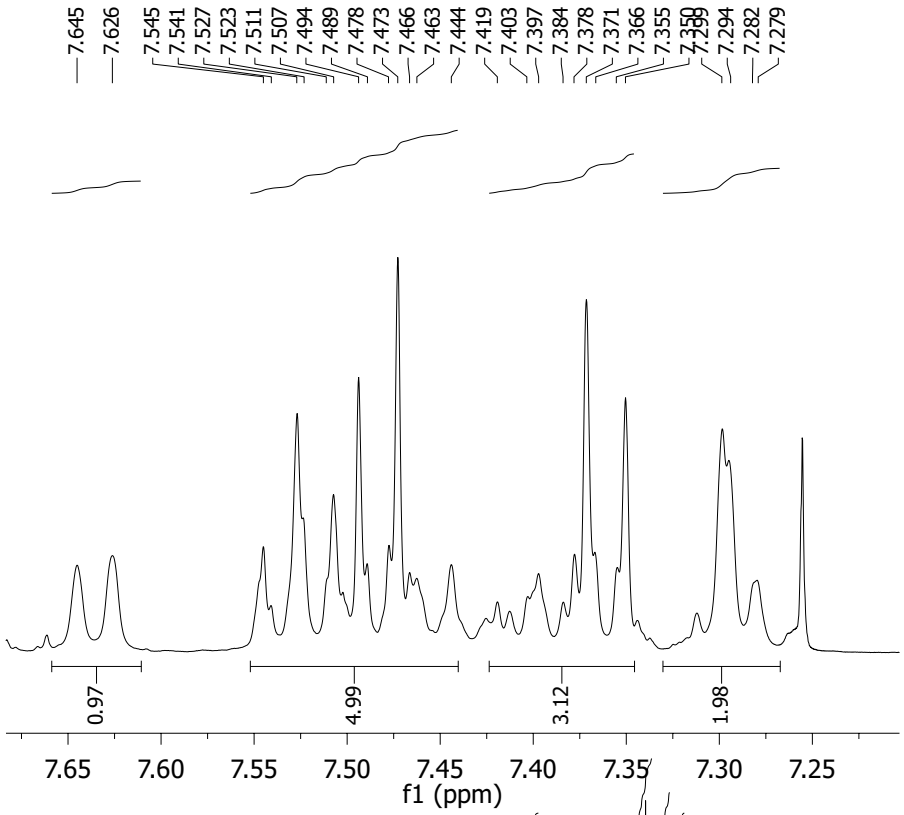


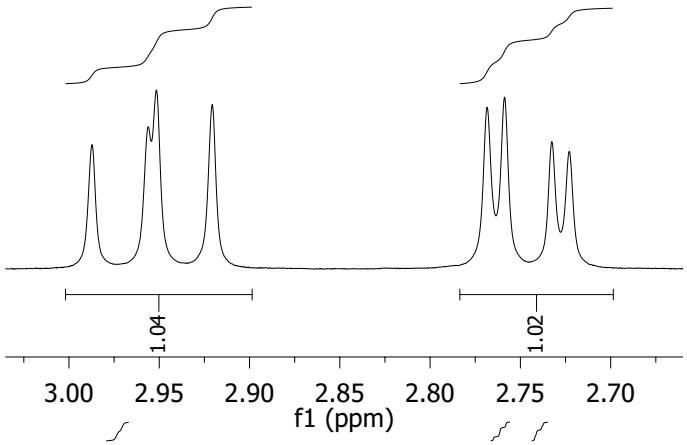


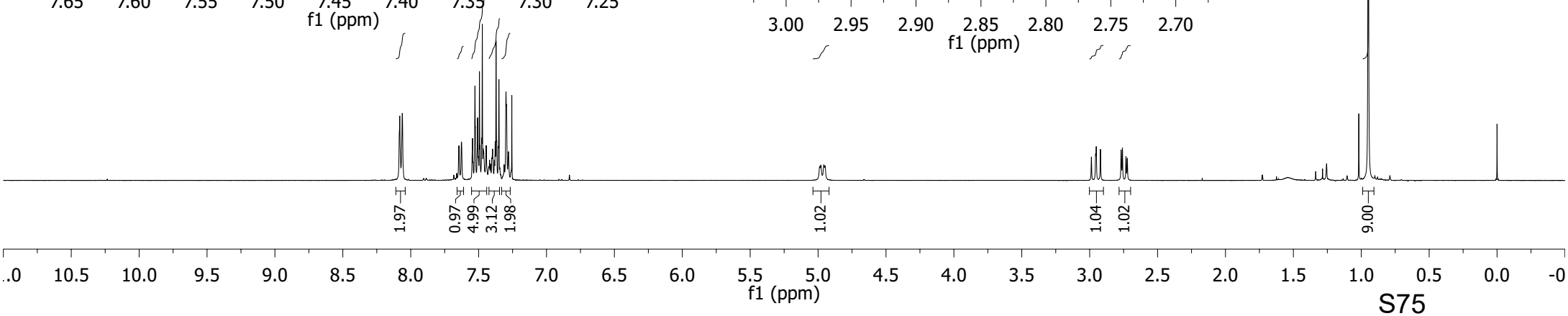
Solvent $CDCl_3$

Spectrometer Frequency 400





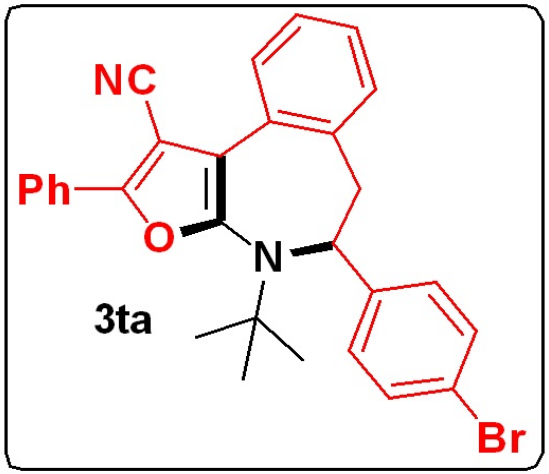


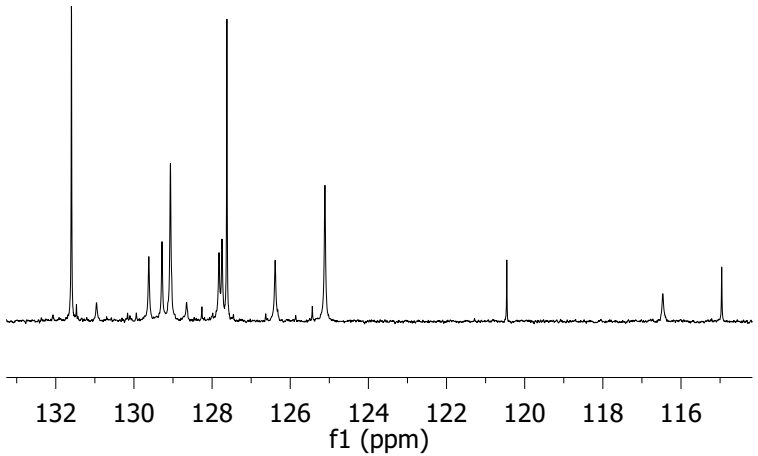


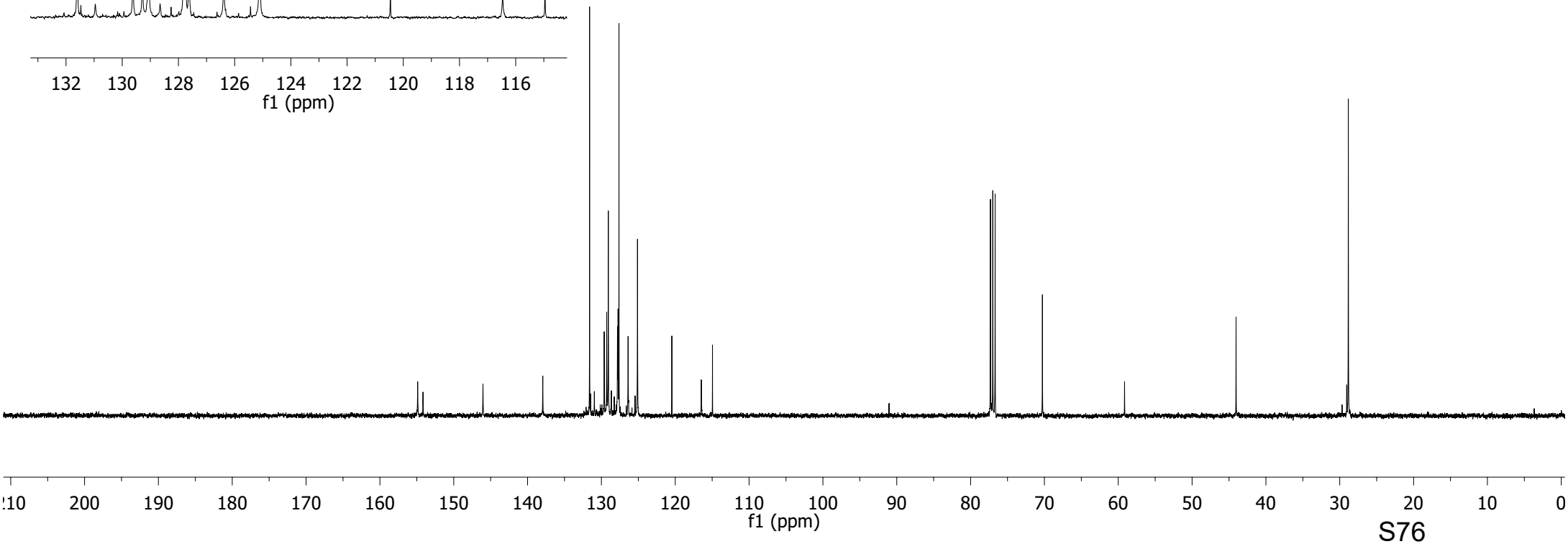
Solvent $CDCl_3$

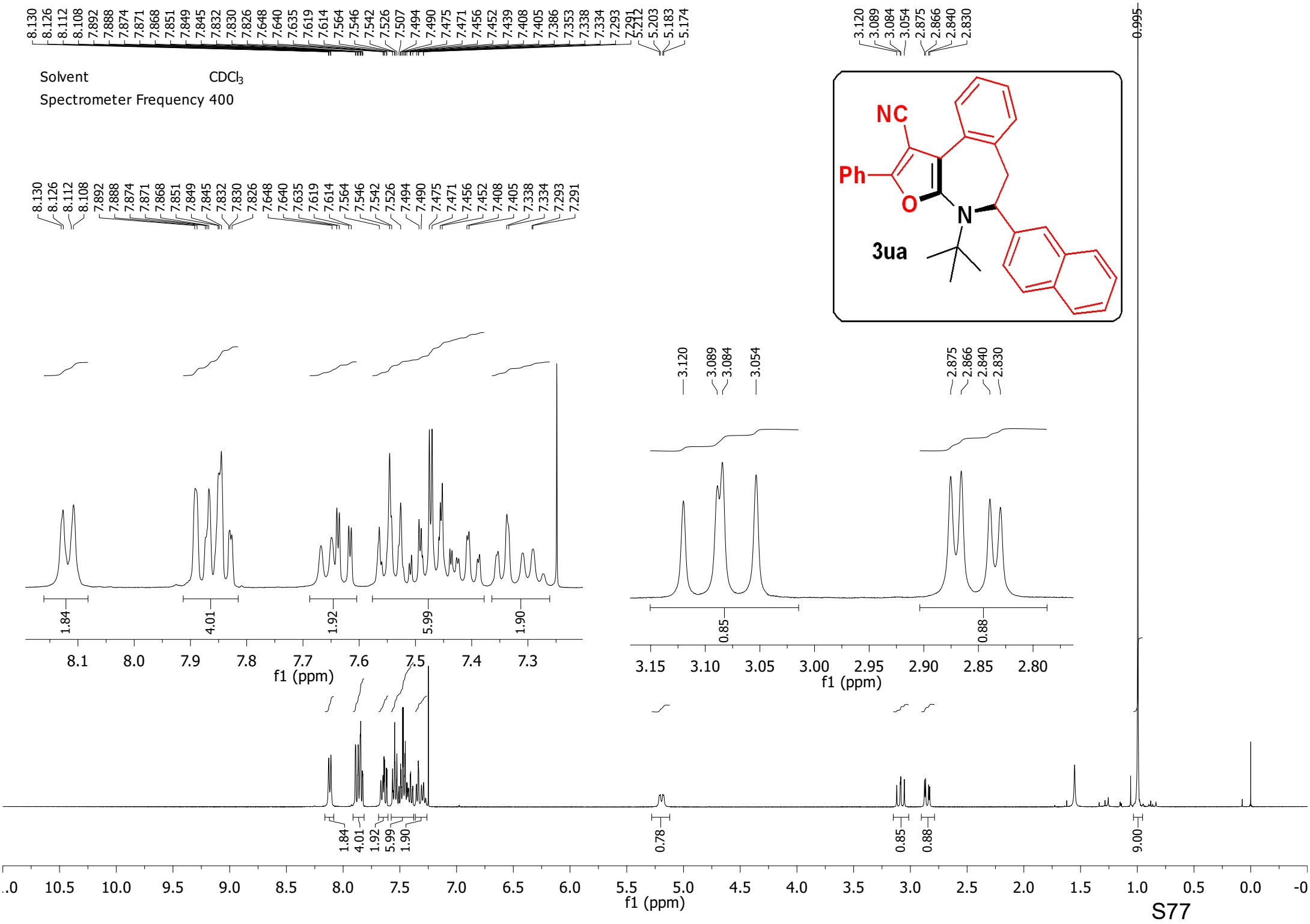
Spectrometer Frequency 100

154.902, 154.182, 146.056, 137.954, 131.615, 130.971, 129.634, 129.296, 129.081, 129.046, 128.667, 127.838, 127.760, 127.636, 126.400, 125.127, 120.472, 116.480, 114.972, 91.056, 77.309, 76.992, 76.674, 70.280, 59.152, 44.049, 28.842







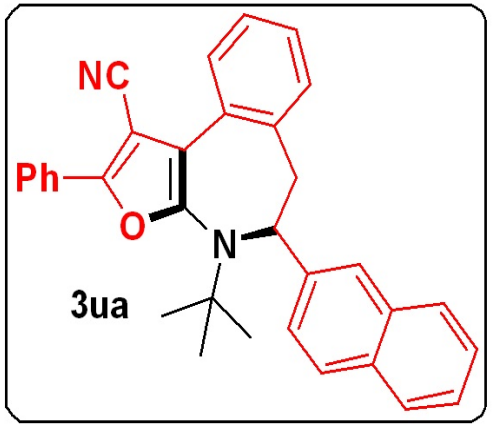

Solvent CDCl3
Spectrometer Frequency 400
NC
Ph
O
N
3ua
f1 (ppm)

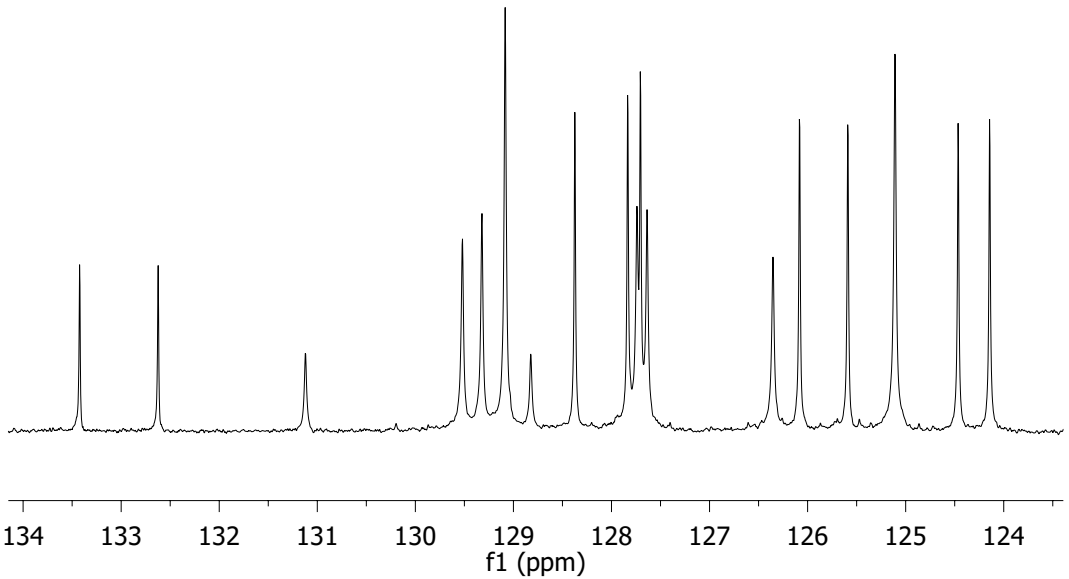
Solvent $CDCl_3$

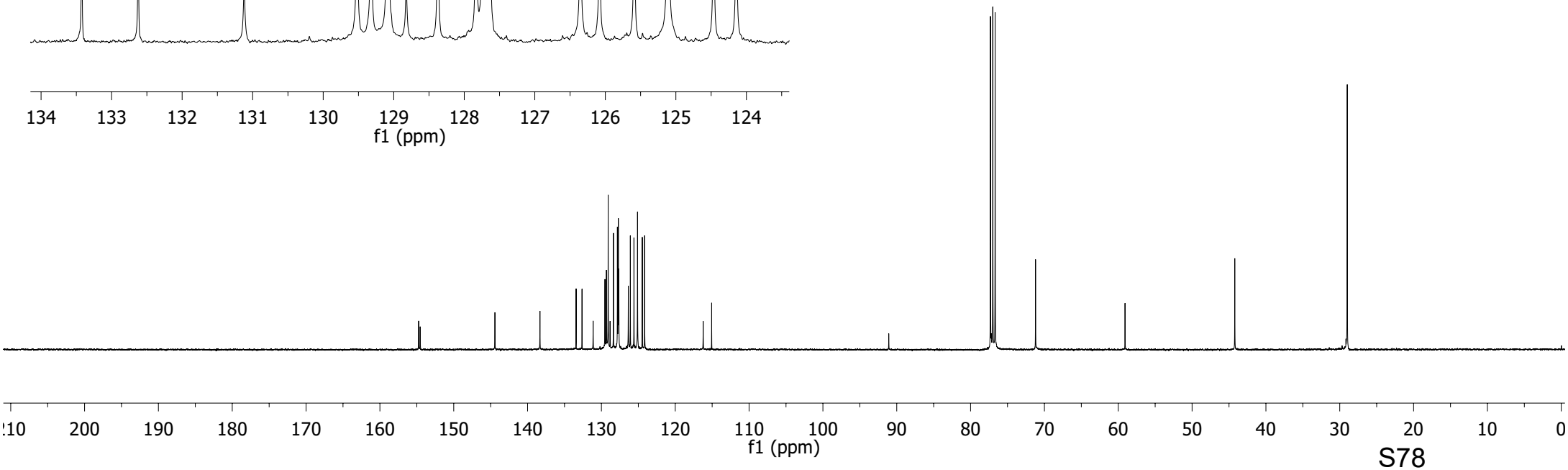
Spectrometer Frequency 100

154.765, 154.561, 144.437, 129.336, 129.098, 128.388, 127.849, 127.719, 126.097, 125.604, 125.123, 124.479, 124.158, 116.227, 115.081, 91.089, 77.308, 76.991, 76.673, 71.207, 59.087, 44.222, 28.987

133.439, 132.638, 131.136, 129.535, 129.336, 129.098, 128.838, 128.388, 127.849, 127.754, 127.719, 127.651, 126.367, 126.097, 125.604, 125.123, 124.479, 124.158

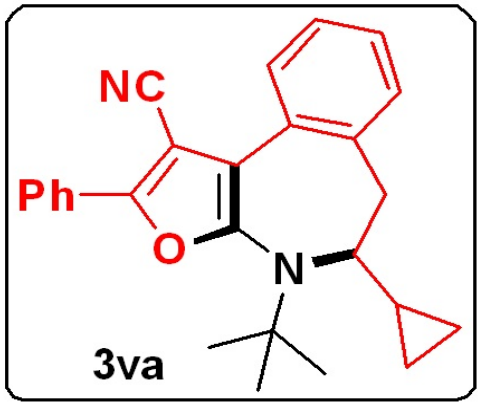






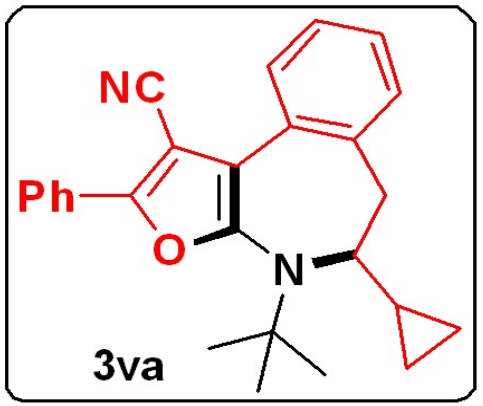
Solvent $CDCl_3$

Spectrometer Frequency 597



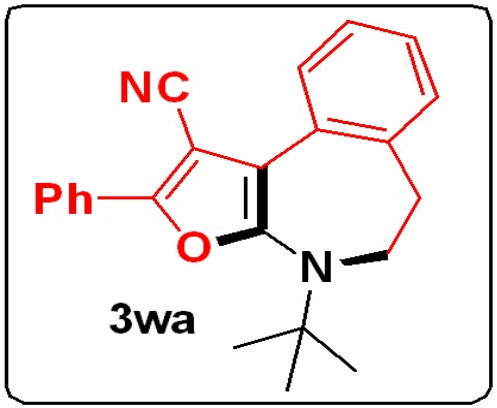
Solvent $CDCl_3$

Spectrometer Frequency 150



Solvent $CDCl_3$

Spectrometer Frequency 400



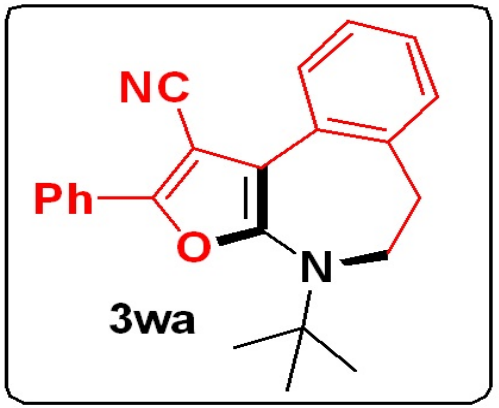
f1 (ppm)

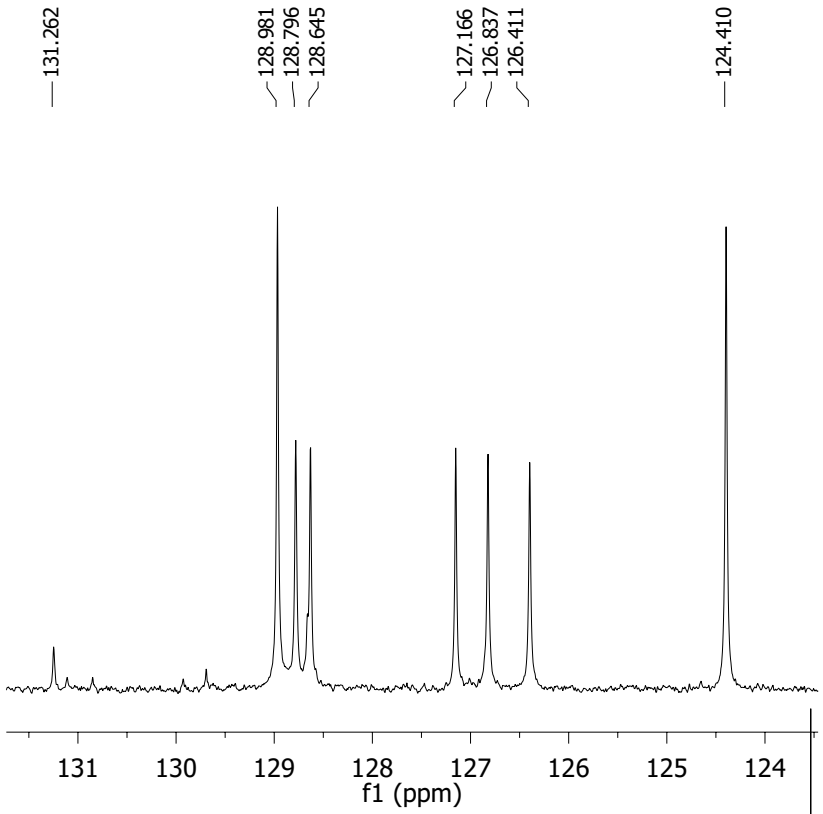
f1 (ppm)

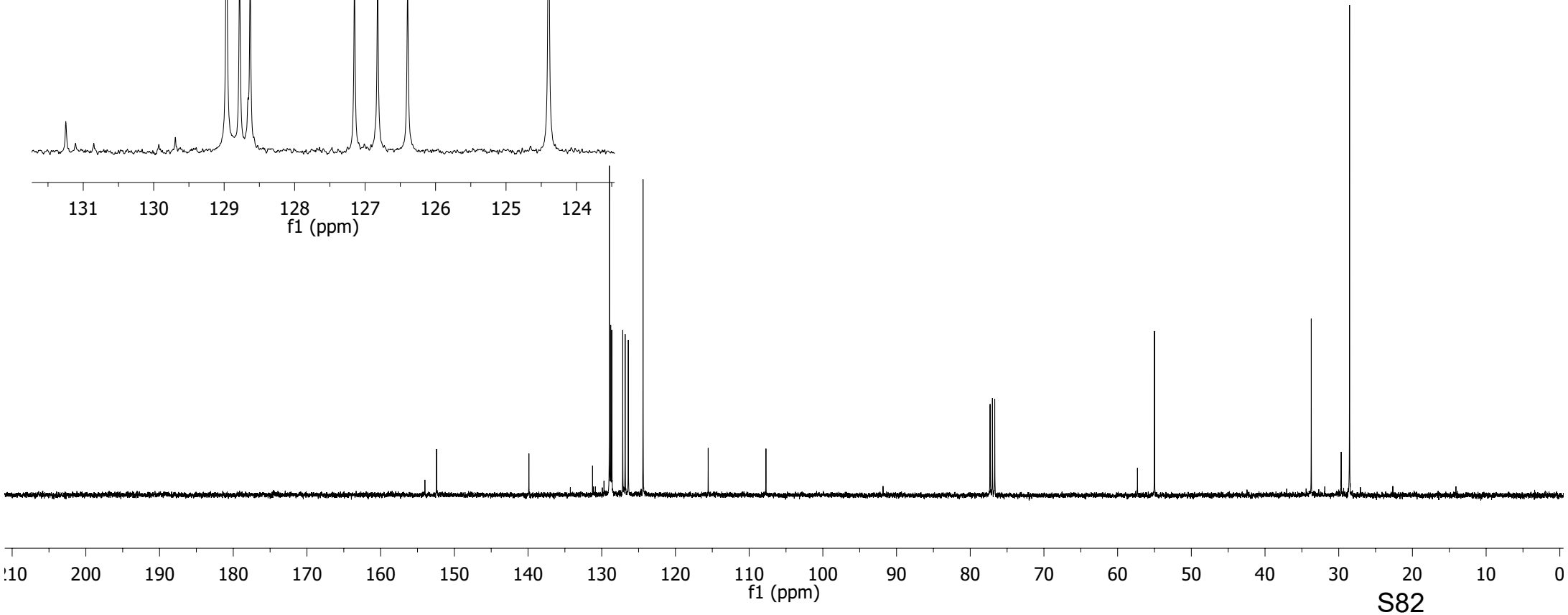
Solvent $CDCl_3$

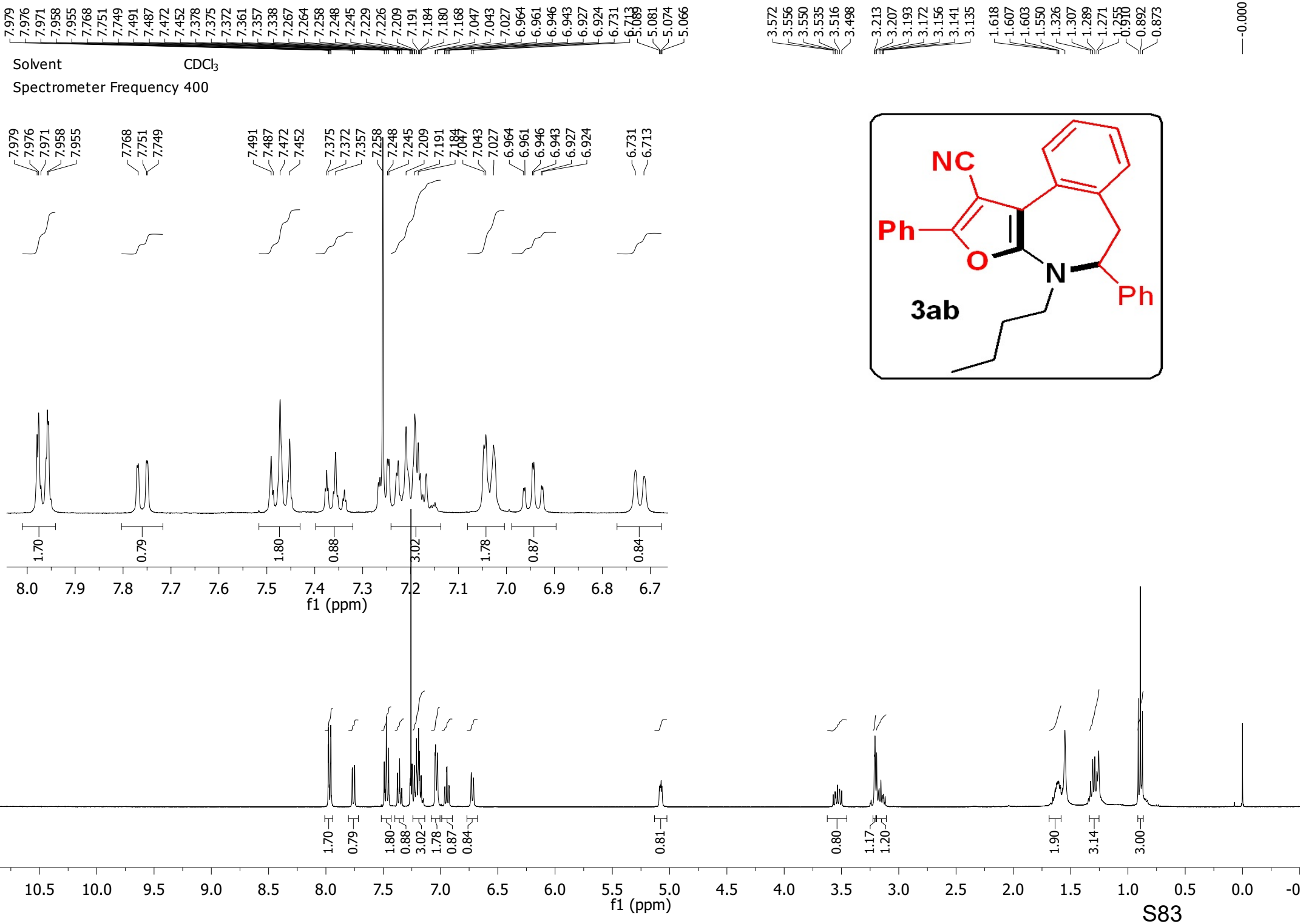
Spectrometer Frequency 100

154.011, 152.428, 139.897, 131.262, 128.981, 128.796, 128.645, 127.166, 126.837, 126.411, 124.410, 115.571, 107.731, 91.842, 77.307, 76.990, 76.673, 57.317, 55.005, 33.732, 29.669, 28.533







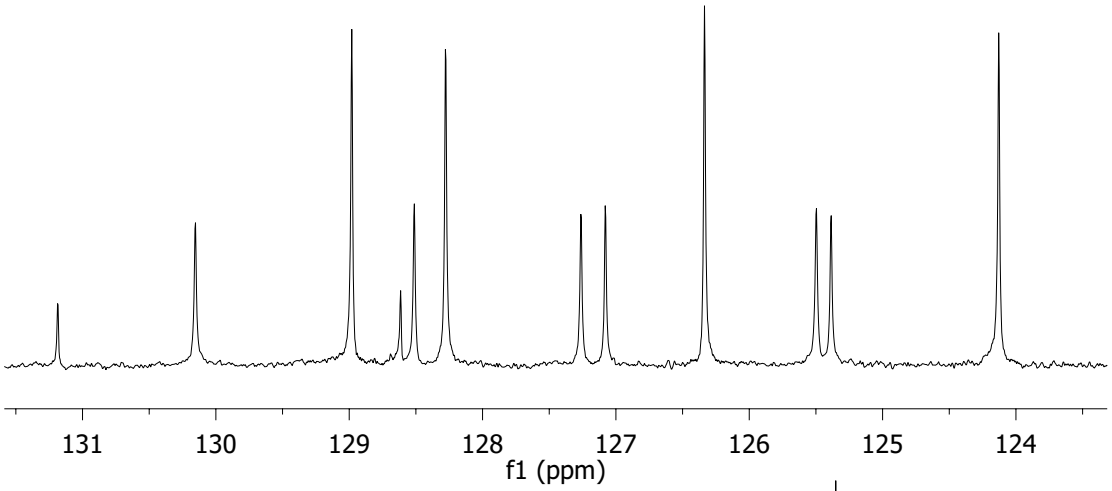

Solvent CDCl3
Spectrometer Frequency 400
NC
Ph
O
N
Ph
3ab
f1 (ppm)
f1 (ppm)

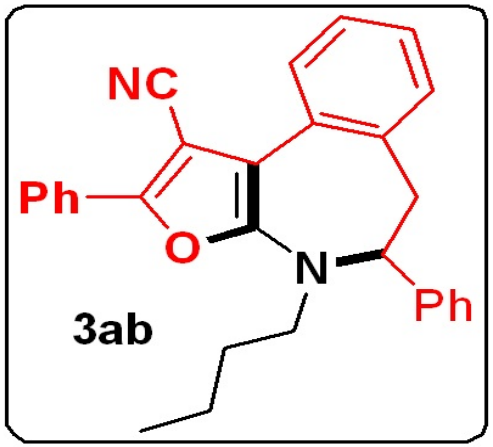
Solvent $CDCl_3$

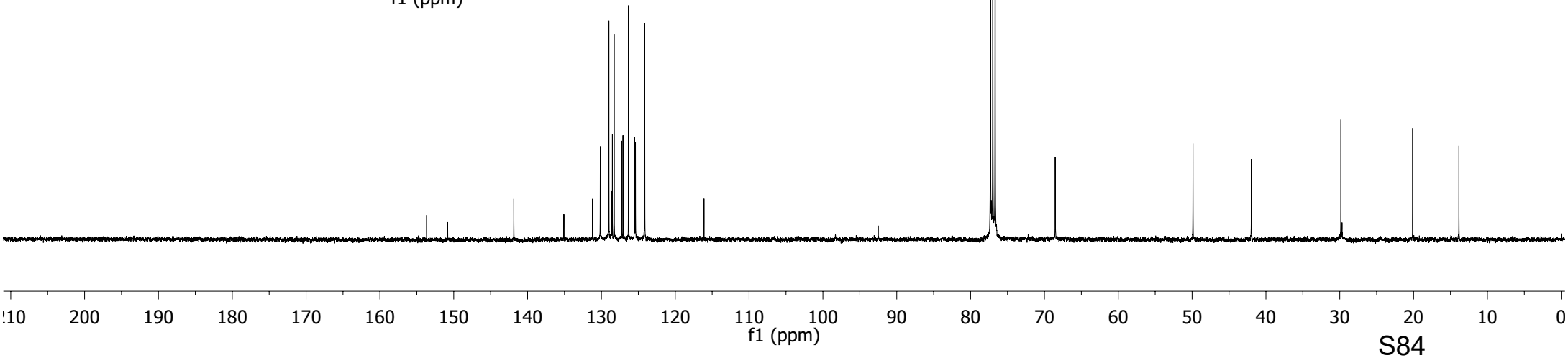
Spectrometer Frequency 100

153.683 150.839 141.875 128.995 128.527 128.292 127.276 127.093 126.349 125.511 125.400 124.143 116.118 92.529 77.311 76.993 76.676 68.543 49.887 41.970 29.847 20.119 13.858

131.201 130.168 128.995 128.629 128.527 128.292 127.276 127.093 126.349 125.511 125.400 124.143

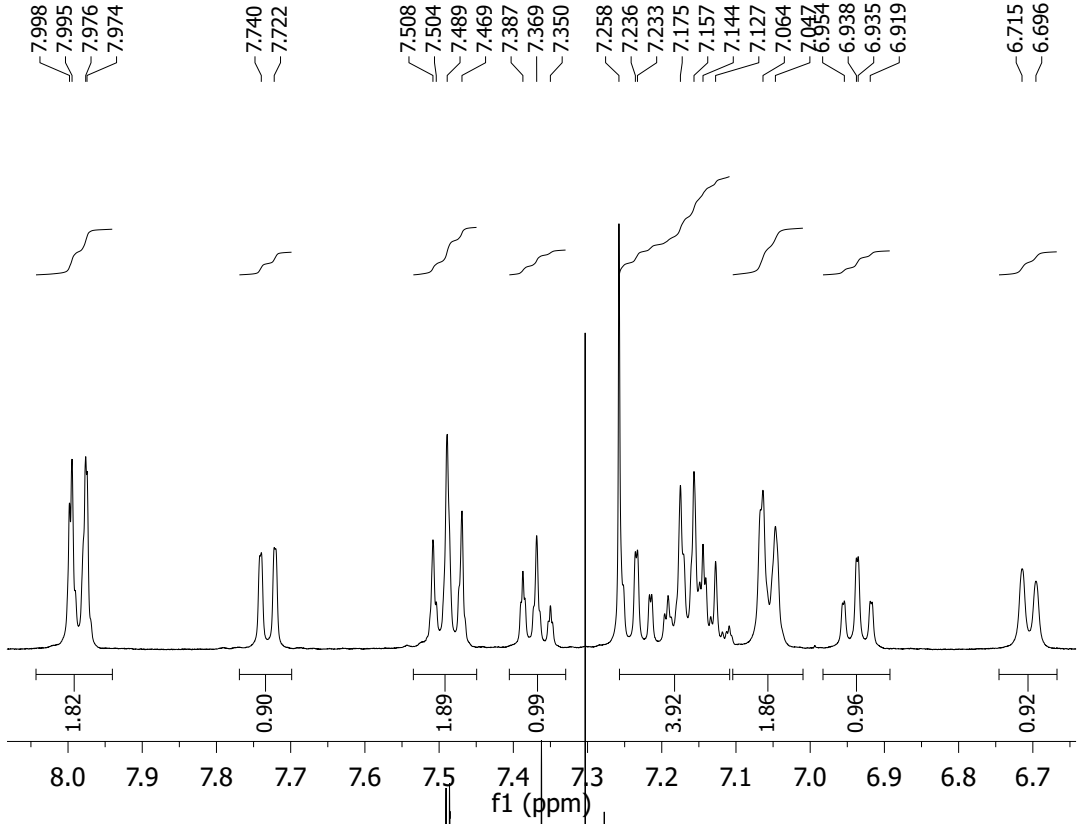


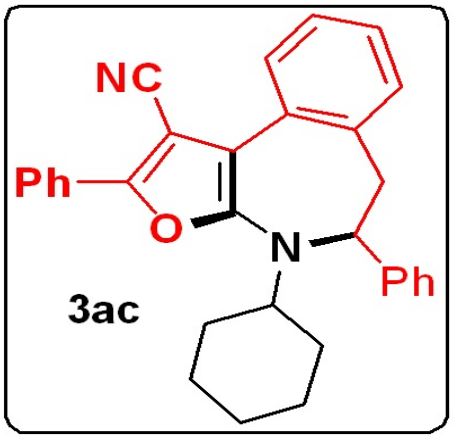




Solvent $CDCl_3$

Spectrometer Frequency 400



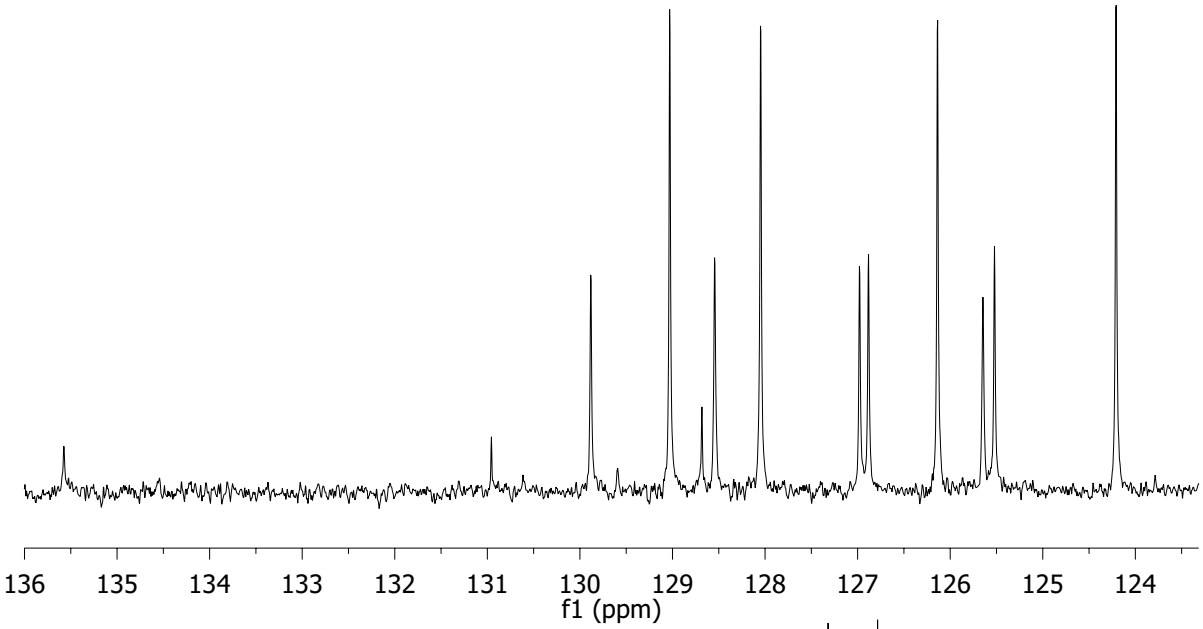


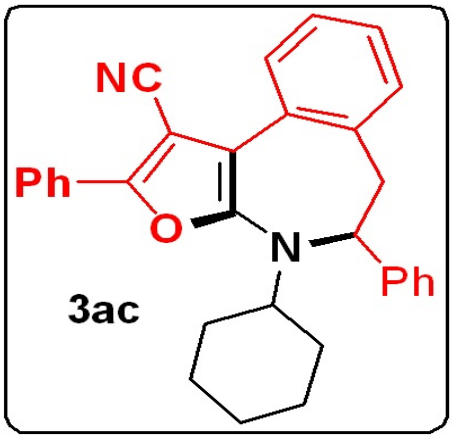
Solvent $CDCl_3$

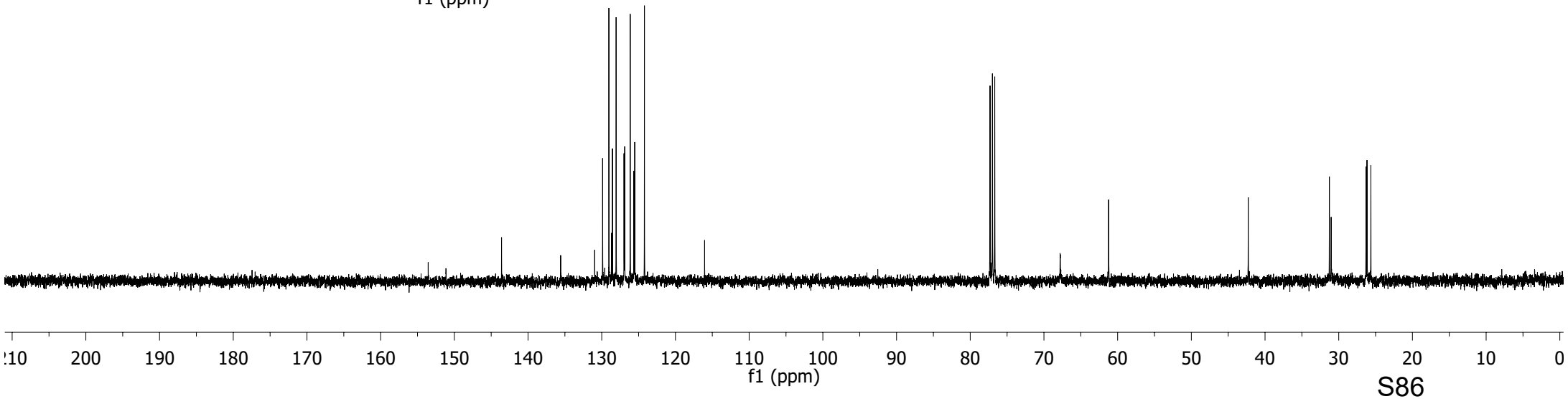
Spectrometer Frequency 100

153.568 150.979 143.611 129.897 129.045 128.559 128.063 126.994 126.897 126.151 125.661 125.536 124.223 116.057 92.555 77.309 76.991 76.674 67.810 61.230 42.283 31.273 31.028 26.302 26.169 25.640

135.591 130.971 129.897 129.045 128.697 128.559 128.063 126.994 126.897 126.151 125.661 125.536 124.223

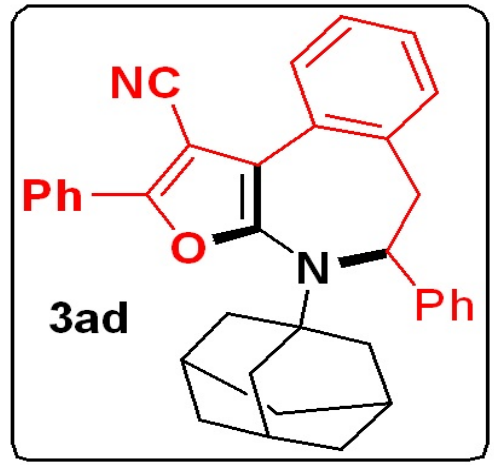






Solvent $CDCl_3$

Spectrometer Frequency 400

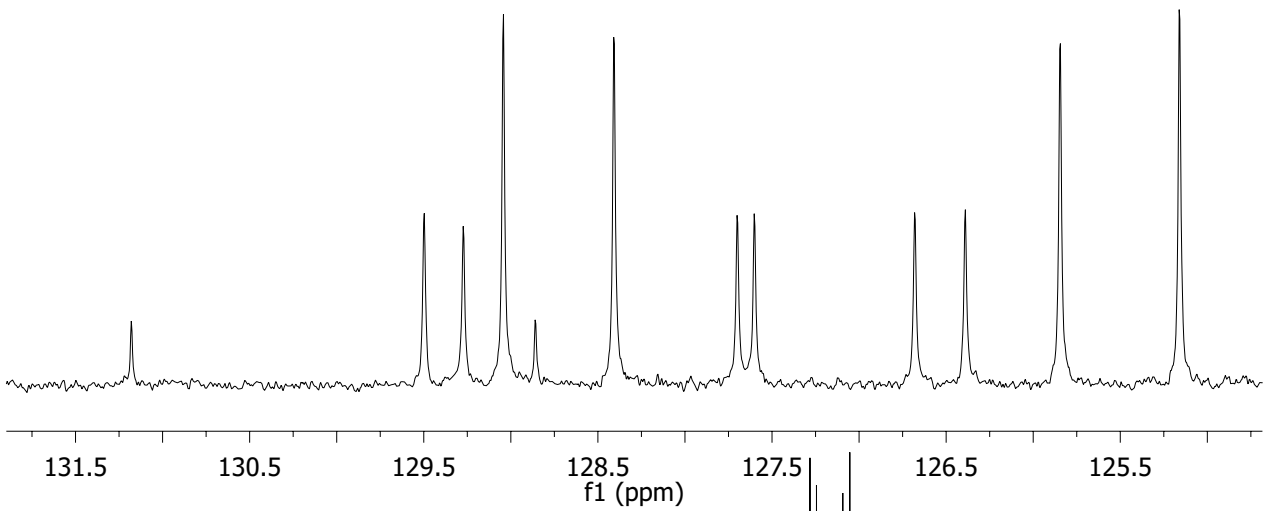


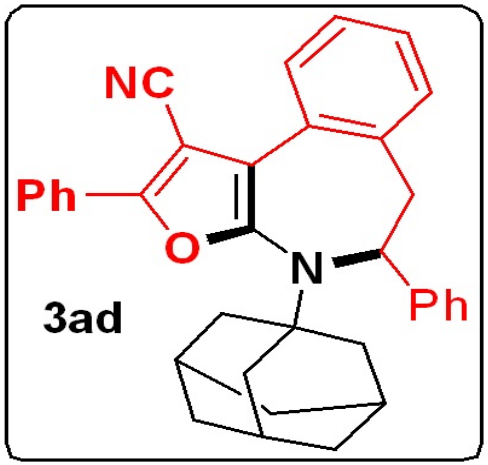
Solvent $CDCl_3$

Spectrometer Frequency 100

154.833 153.988 147.396 138.505 129.512 129.057 128.423 127.714 126.405 125.859 125.175 117.494 115.091 90.955 77.308 76.991 76.673 68.951 59.467 44.266 41.460 36.066 29.666

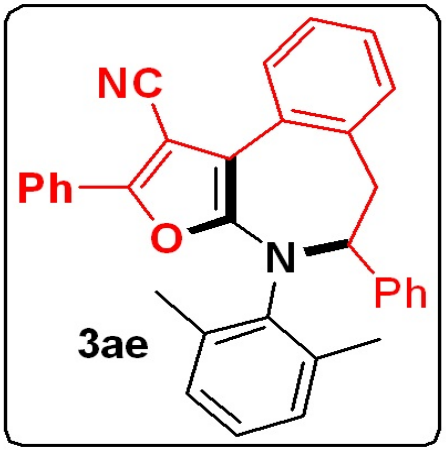
131.194 129.512 129.288 129.057 128.874 128.423 127.714 127.616 126.695 126.405 125.859 125.175

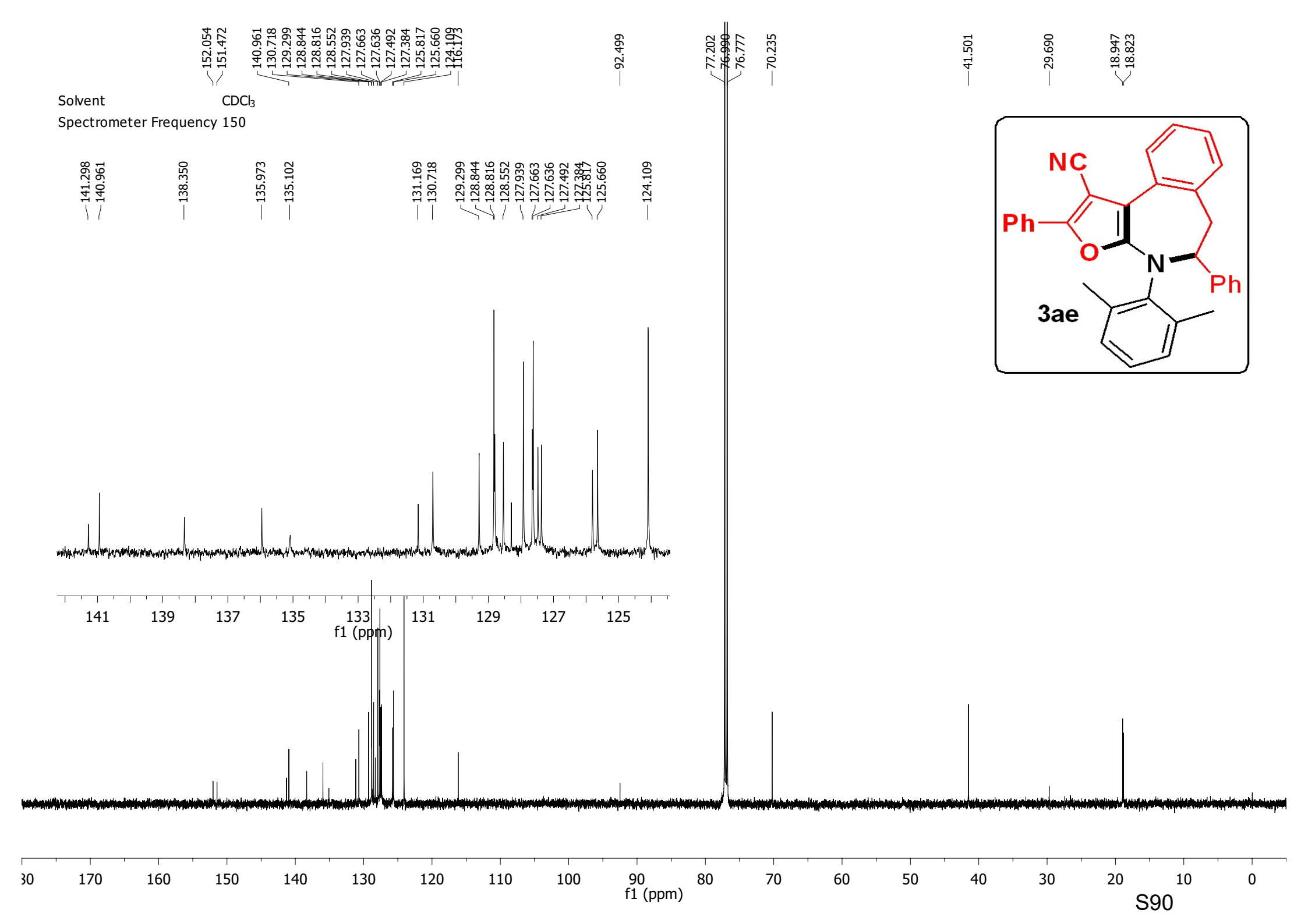




Solvent $CDCl_3$

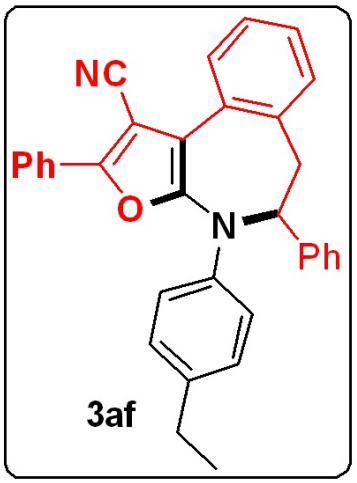
Spectrometer Frequency 597




152.054
151.472
140.961
130.718
129.299
128.844
128.816
128.552
127.939
127.663
127.636
127.492
127.384
125.817
125.660
124.109
116.173
92.499
77.202
76.990
76.777
70.235
41.501
29.690
18.947
18.823
Solvent CDCl3
Spectrometer Frequency 150
141.298
140.961
138.350
135.973
135.102
131.169
130.718
129.299
128.844
128.816
128.552
127.939
127.663
127.636
127.492
127.384
125.817
125.660
124.109
NC
Ph
O
N
Ph
3ae
f1 (ppm)
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400

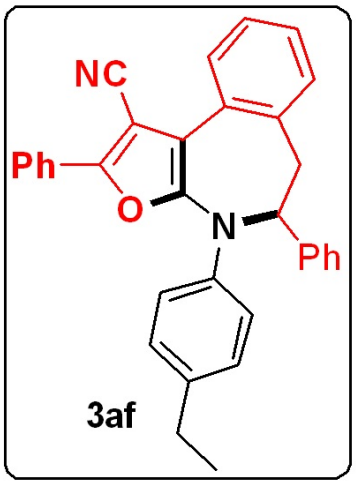


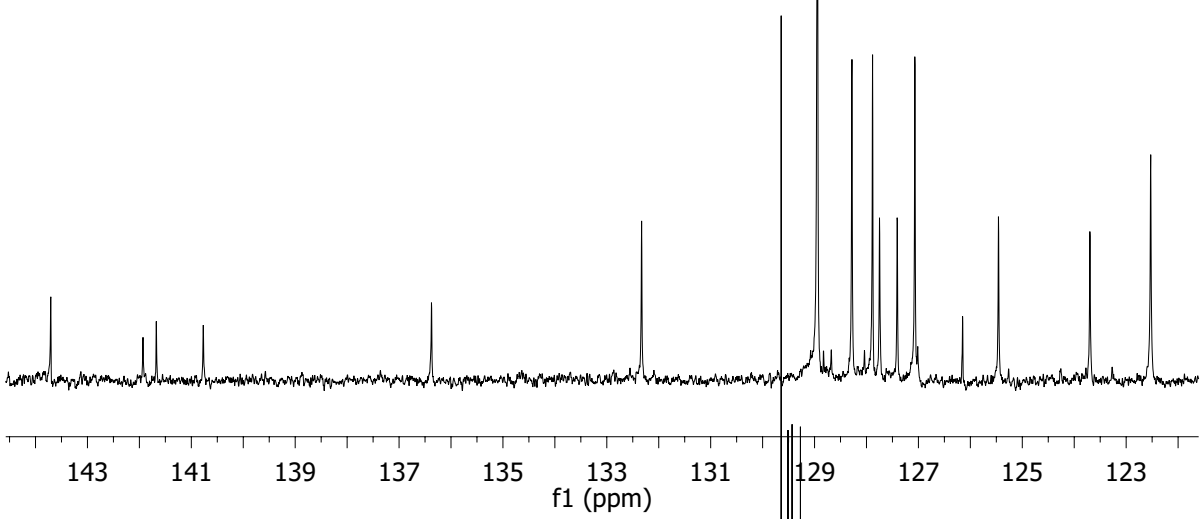
Solvent $CDCl_3$

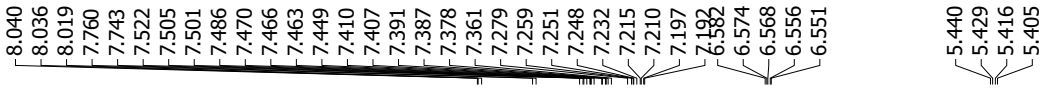
Spectrometer Frequency 100

163.561 155.631 143.707 141.674 140.770 136.375 132.330 128.944 128.281 127.883 127.748 127.408 127.068 126.149 125.458 123.698 122.528 114.993 89.319 77.307 76.990 76.673 67.077 56.260 34.726 28.314 15.507

143.707 141.931 141.674 140.770 136.375 132.330 128.944 128.678 128.281 127.883 127.748 127.408 127.068 126.149 125.458 123.698 122.528

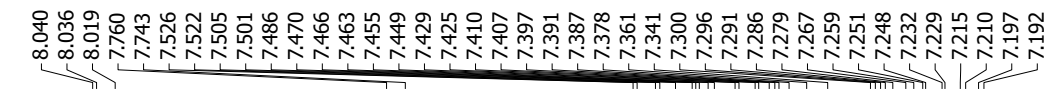


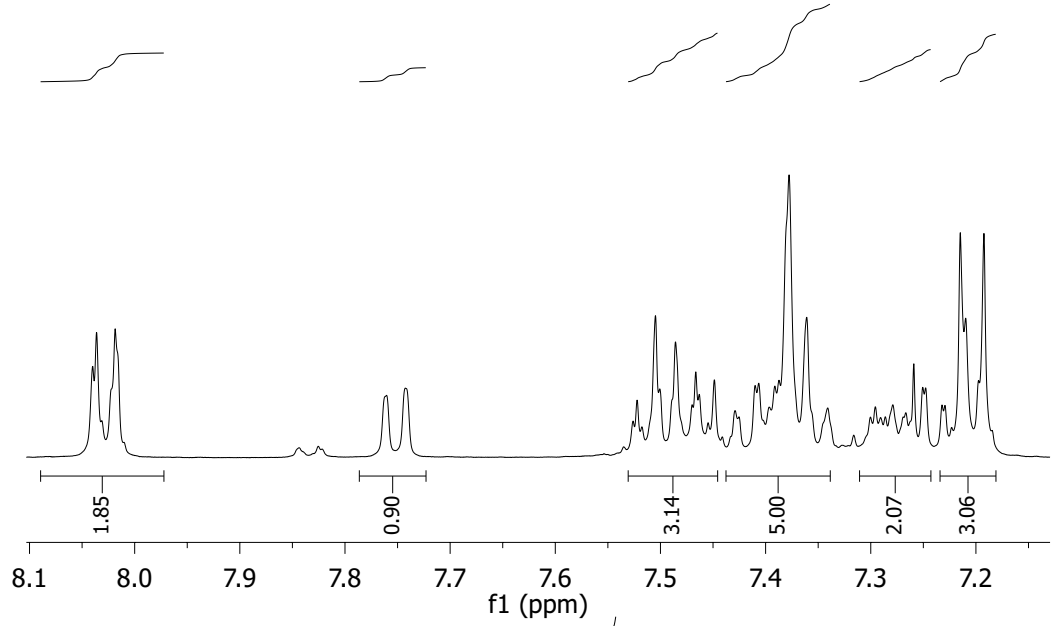


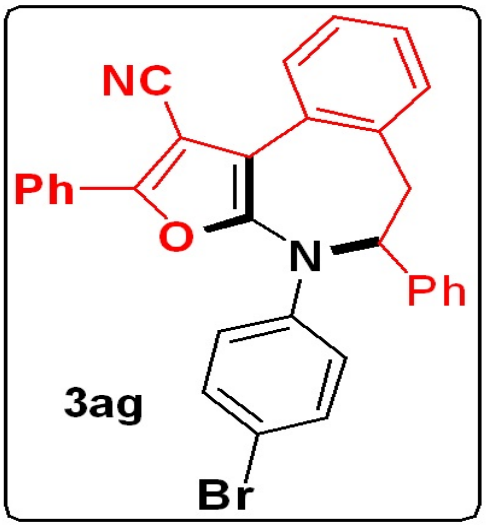


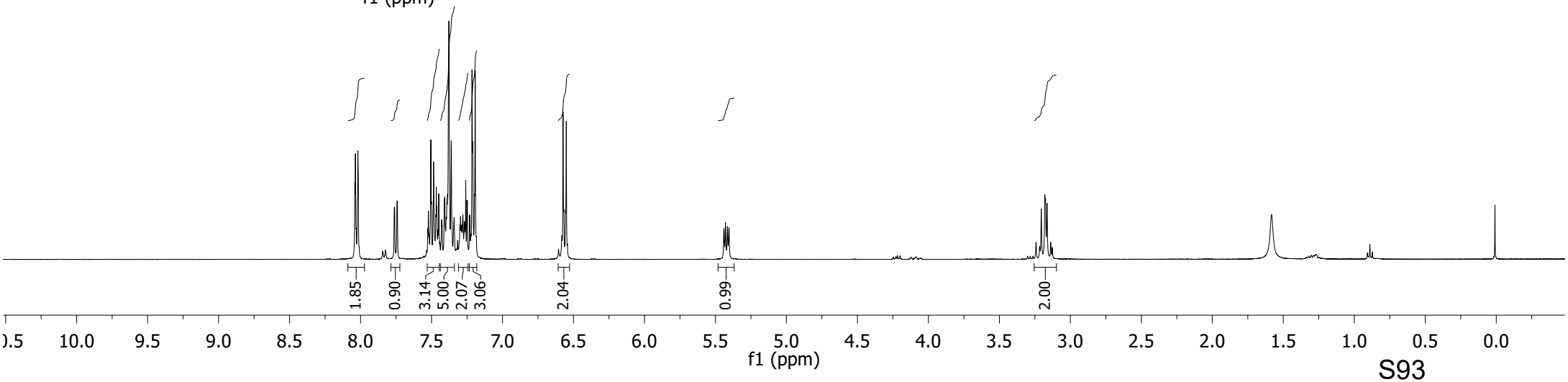
Solvent $CDCl_3$

Spectrometer Frequency 400





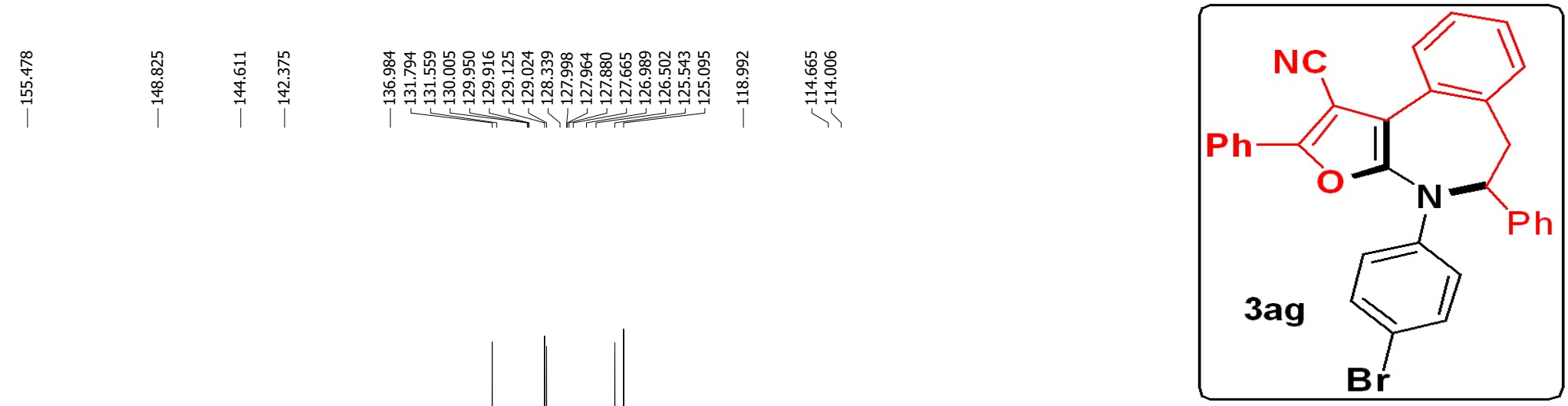




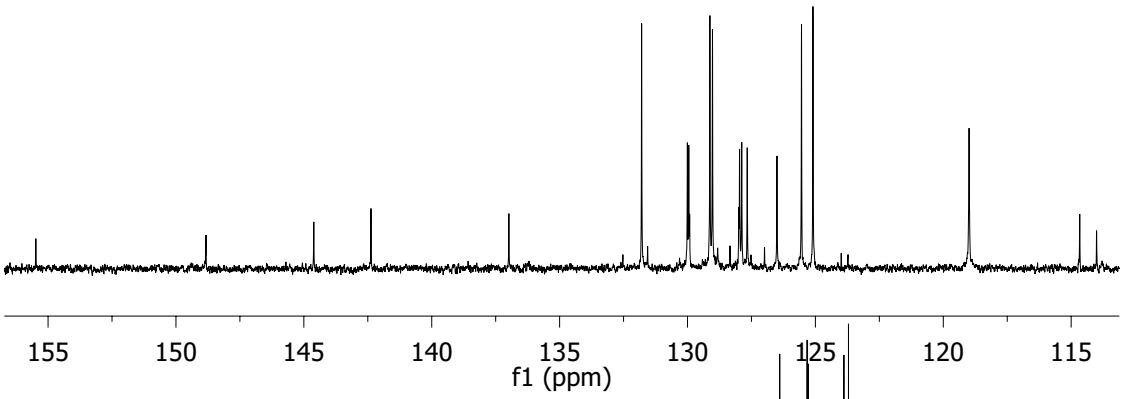
Solvent $CDCl_3$

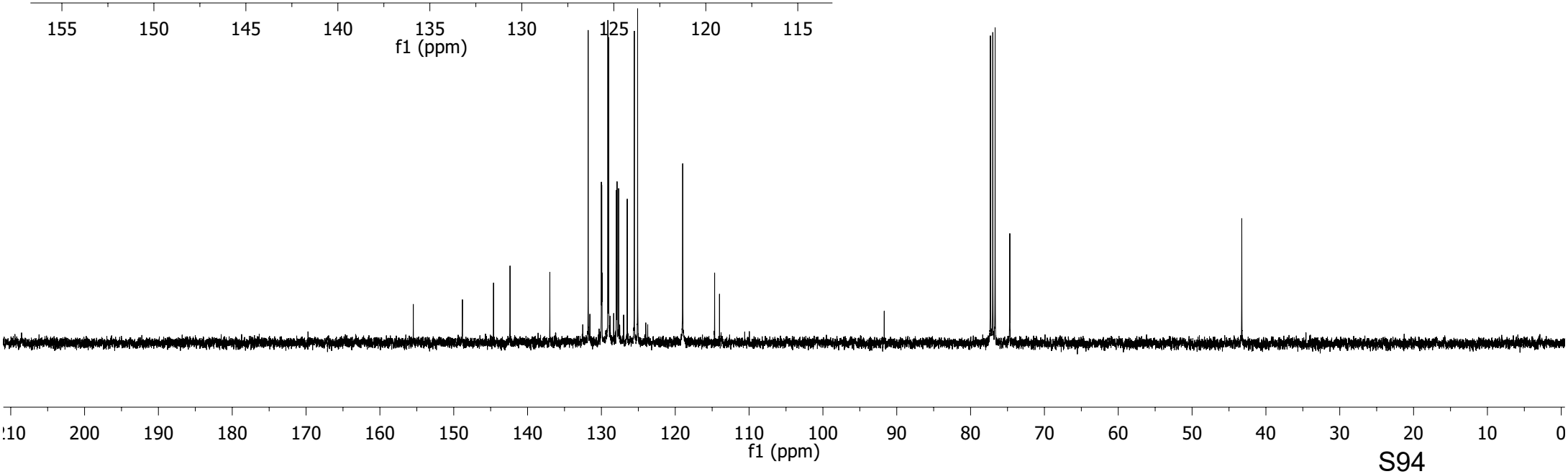
Spectrometer Frequency 100

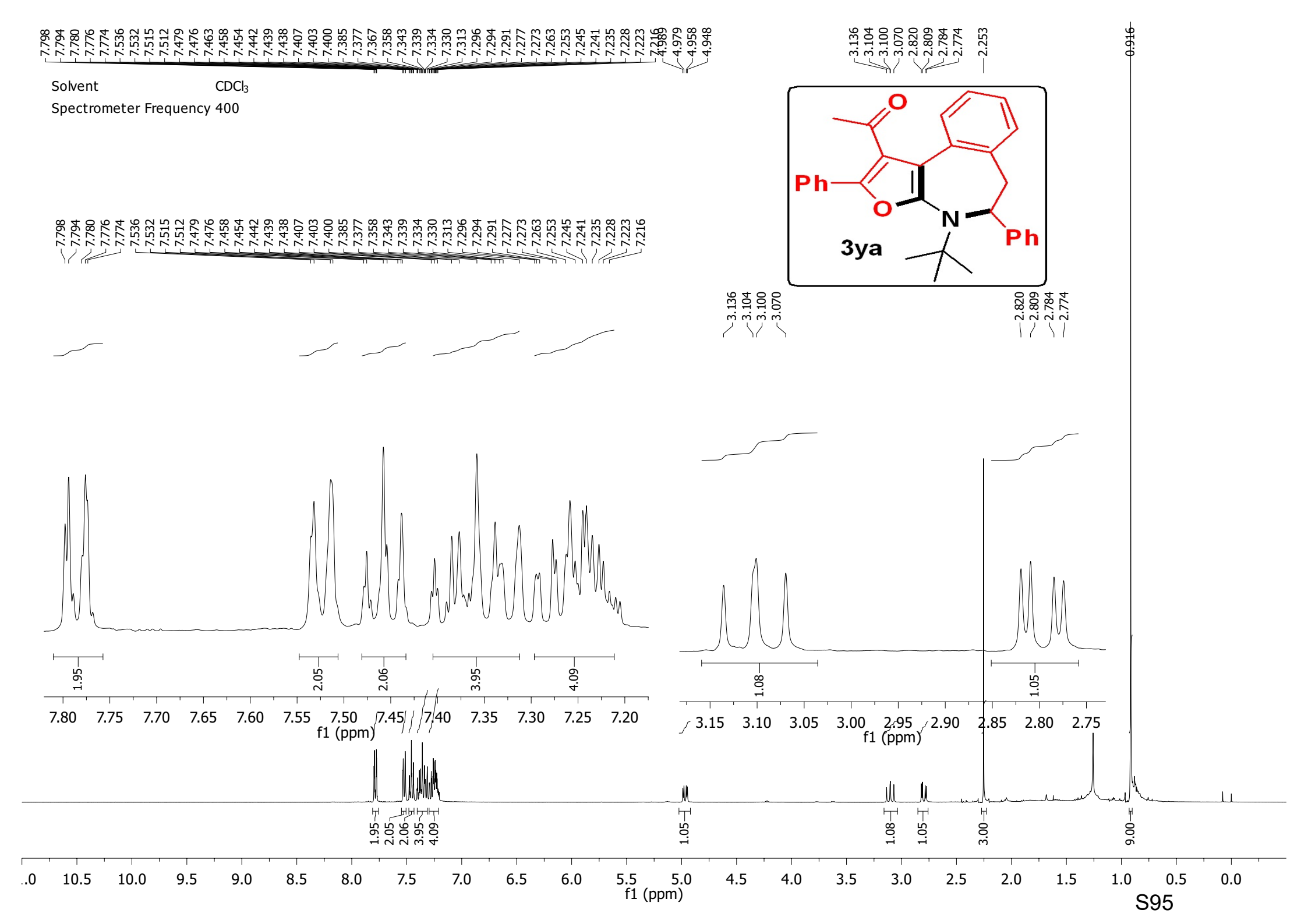
155.478 148.825 144.611 142.375 136.984 131.794 129.125 129.024 127.880 125.543 125.095 118.992 114.665 114.006 91.697 77.311 76.993 76.676 74.686 43.268



155.478 148.825 144.611 142.375 136.984 131.794 131.559 130.005 129.950 129.916 129.125 129.024 128.339 127.998 127.964 127.880 127.665 126.989 126.502 125.543 125.095 118.992 114.665 114.006





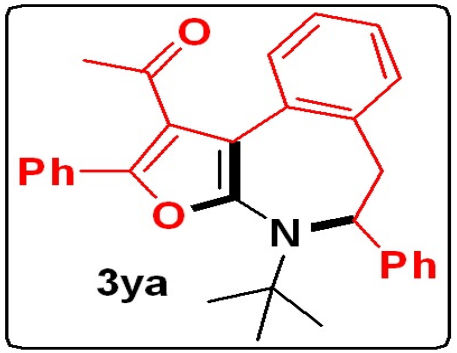

Solvent CDCl3
Spectrometer Frequency 400
3ya
Ph
O
N
Ph
f1 (ppm)
S95

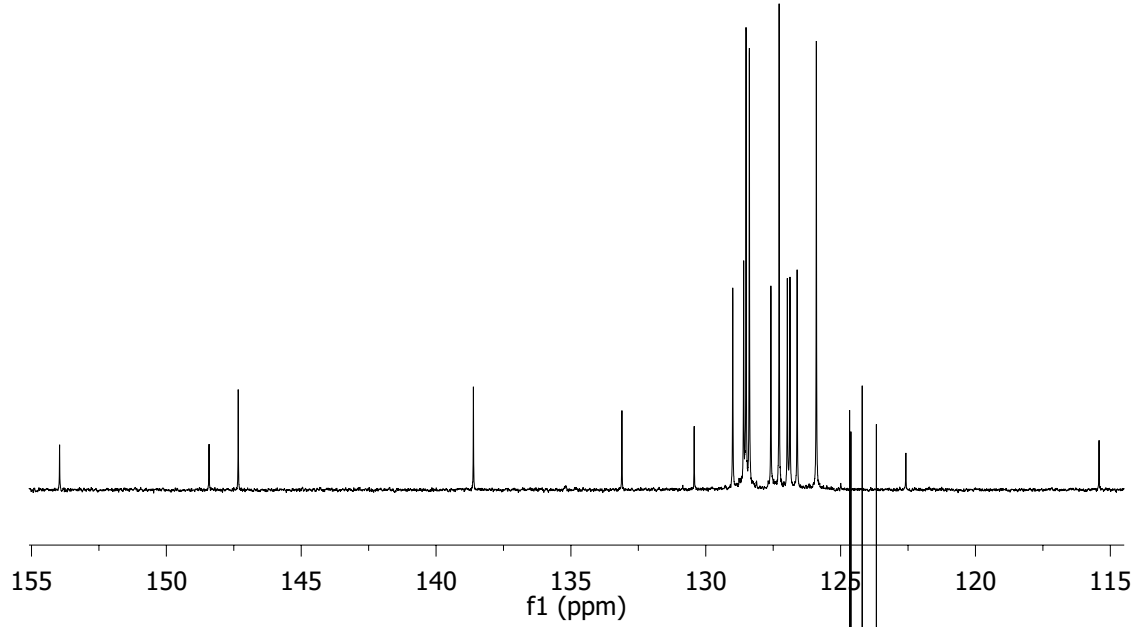
198.758
153.959
148.418
147.335
138.616
128.595
128.506
128.384
127.586
127.279
126.976
126.612
125.900
115.418
77.308
76.991
76.673
70.771
58.648
44.391
31.500
28.881

Solvent $CDCl_3$

Spectrometer Frequency 100

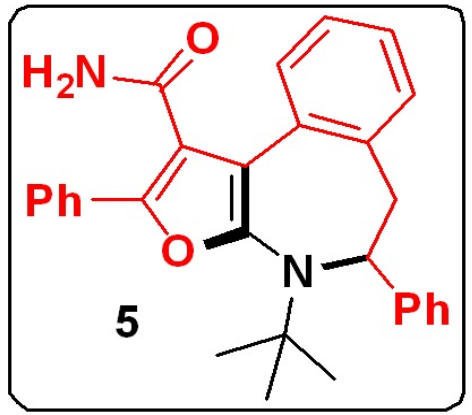
153.959
148.418
147.335
138.616
133.109
129.000
128.595
128.506
128.384
127.586
127.279
126.976
126.878
126.612
125.900
122.581
115.418

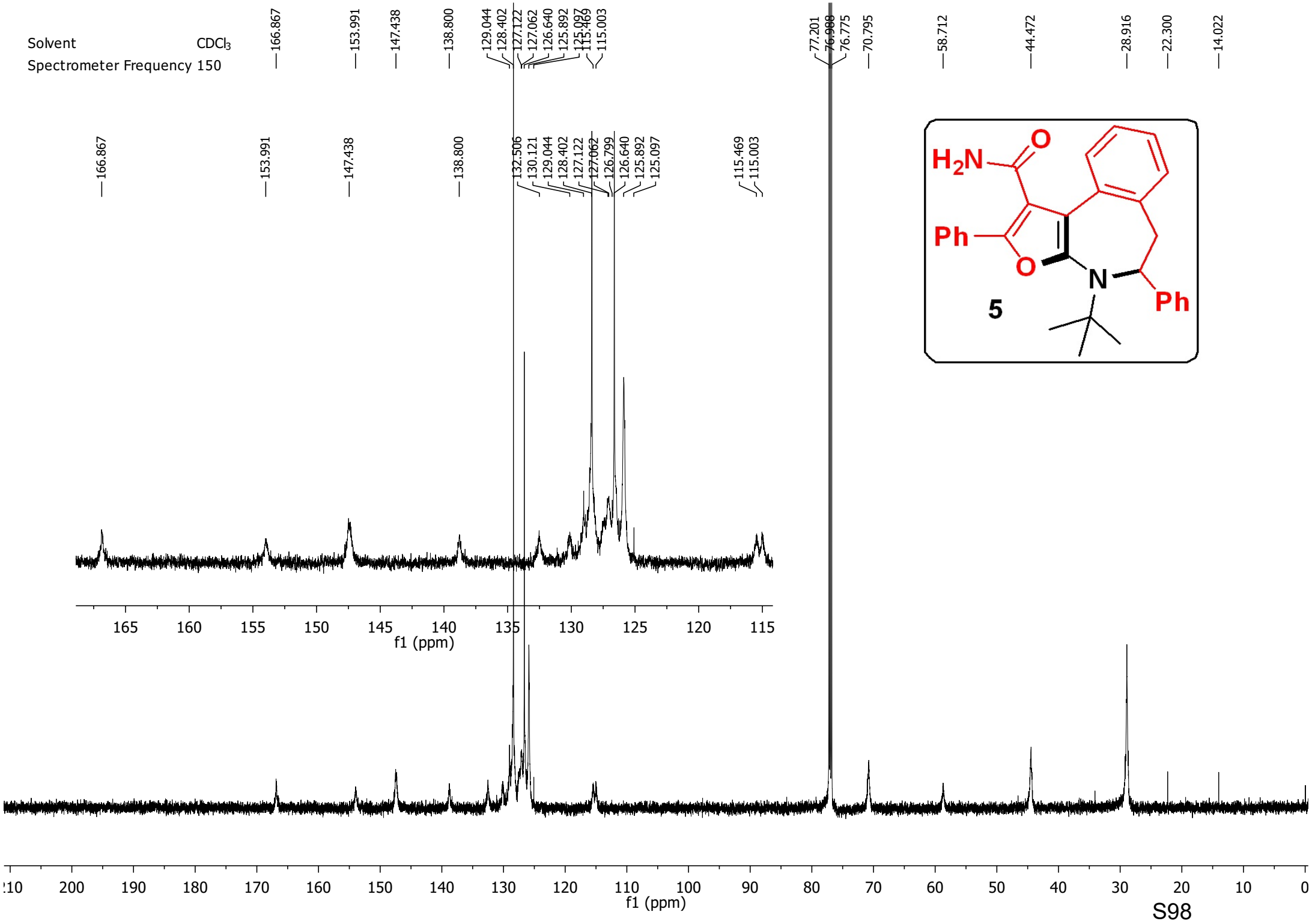




Solvent $CDCl_3$

Spectrometer Frequency 597



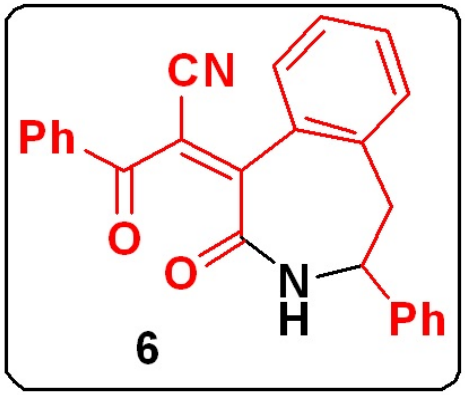

Solvent CDCl3
Spectrometer Frequency 150
166.867
153.991
147.438
138.800
129.044
128.402
127.122
127.062
126.640
125.892
125.097
115.469
115.003
77.201
76.988
76.775
70.795
58.712
44.472
28.916
22.300
14.022
132.506
130.121
126.799
f1 (ppm)
H2N
O
Ph
O
N
Ph
5

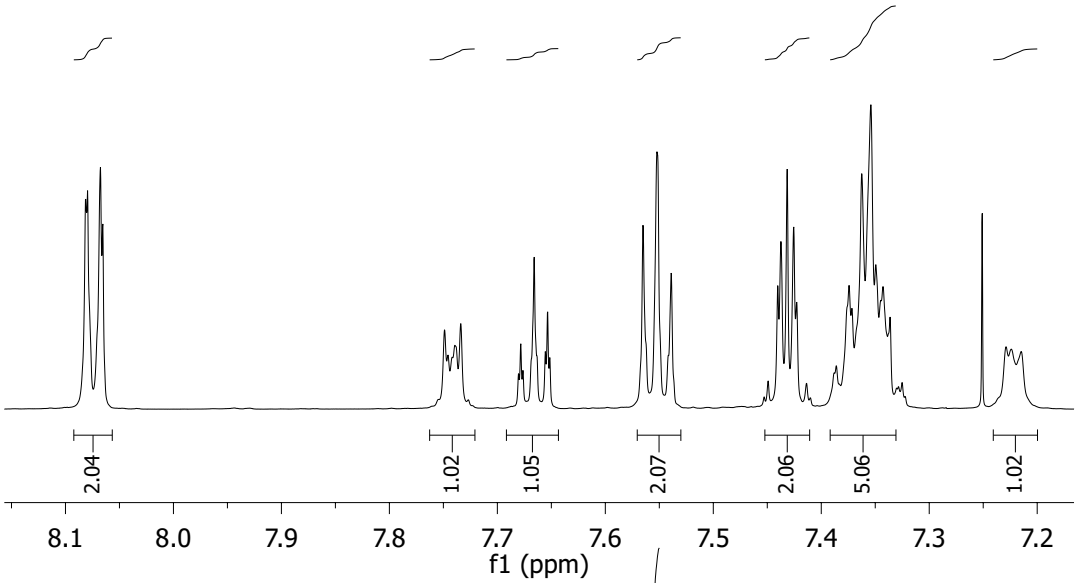
Solvent $CDCl_3$

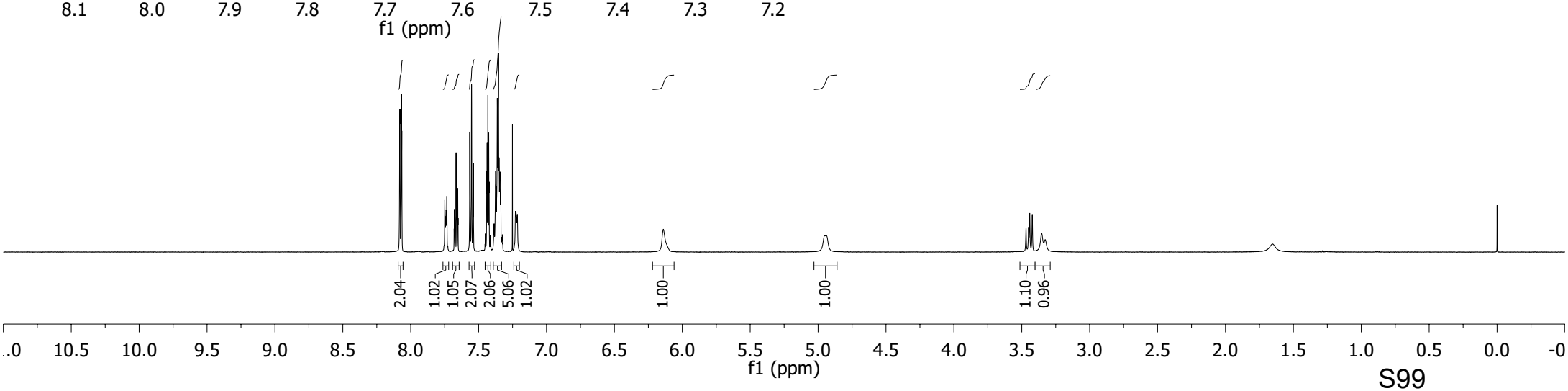
Spectrometer Frequency 597

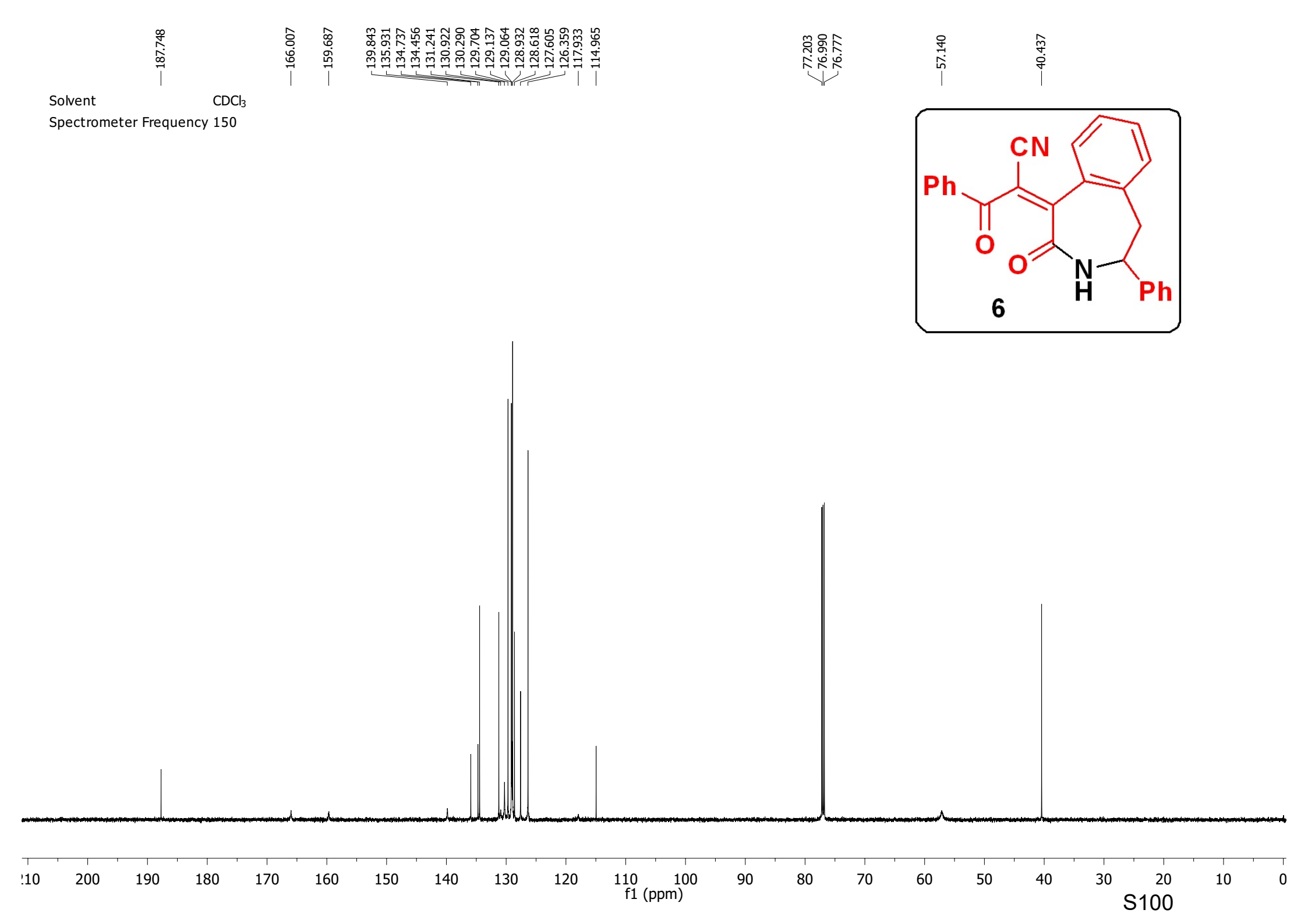
8.082 8.080 8.077 8.071 8.068 8.065 7.666 7.654 7.565 7.552 7.539 7.440 7.437 7.432 7.426 7.363 7.354 7.343 6.139 4.953 4.937 3.469 3.450 3.441 3.423 3.354 3.326

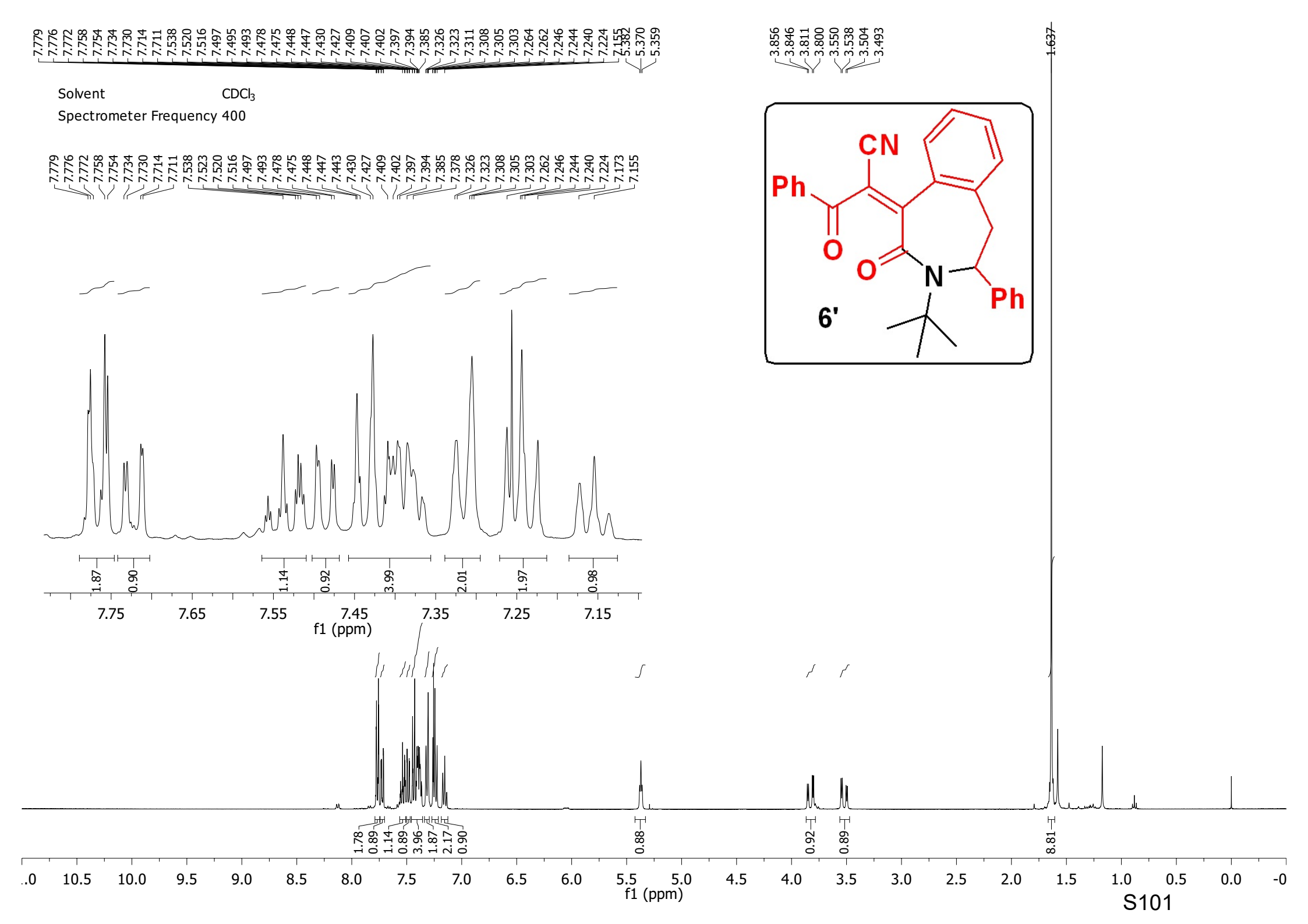
8.082 8.080 8.077 8.071 8.068 8.065 7.749 7.746 7.742 7.740 7.738 7.734 7.681 7.678 7.676 7.666 7.656 7.654 7.651 7.565 7.563 7.552 7.542 7.539 7.440 7.437 7.432 7.426 7.423 7.386 7.377 7.374 7.371 7.363 7.354 7.349 7.343 7.336 7.229 7.224 7.214

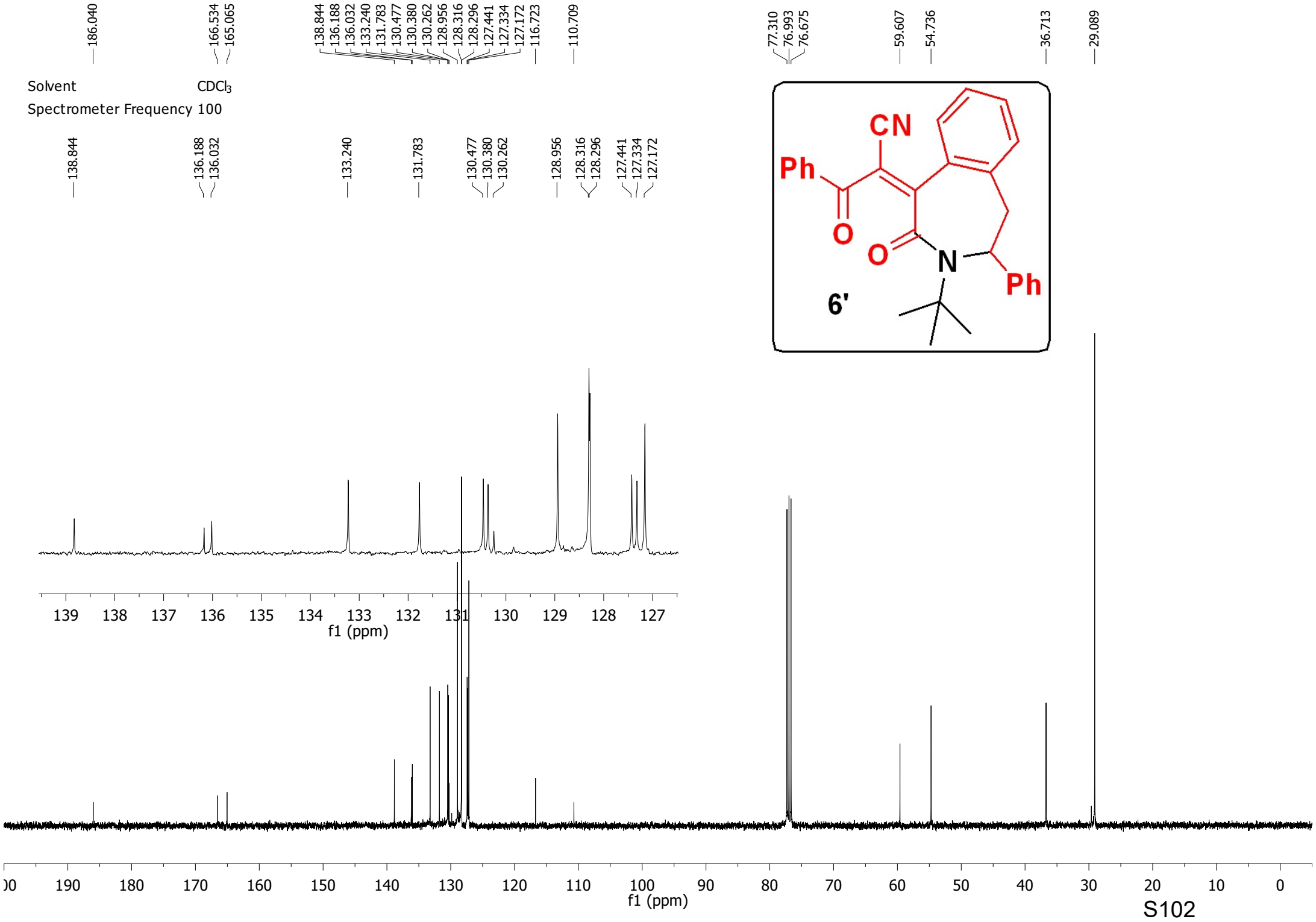






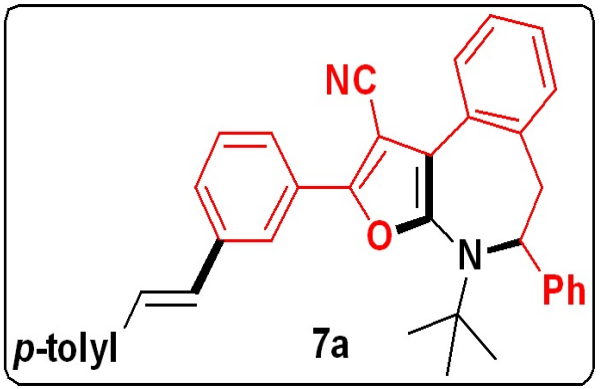

187.748
166.007
159.687
139.843
135.931
134.737
134.456
131.241
130.922
130.290
129.704
129.137
129.064
128.932
128.618
127.605
126.359
117.933
114.965
77.203
76.990
76.777
57.140
40.437
Solvent CDCl3
Spectrometer Frequency 150
CN
Ph
O
O
N
H
Ph
6
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400
CN
Ph
O
O
N
Ph
6'
f1 (ppm)
f1 (ppm)

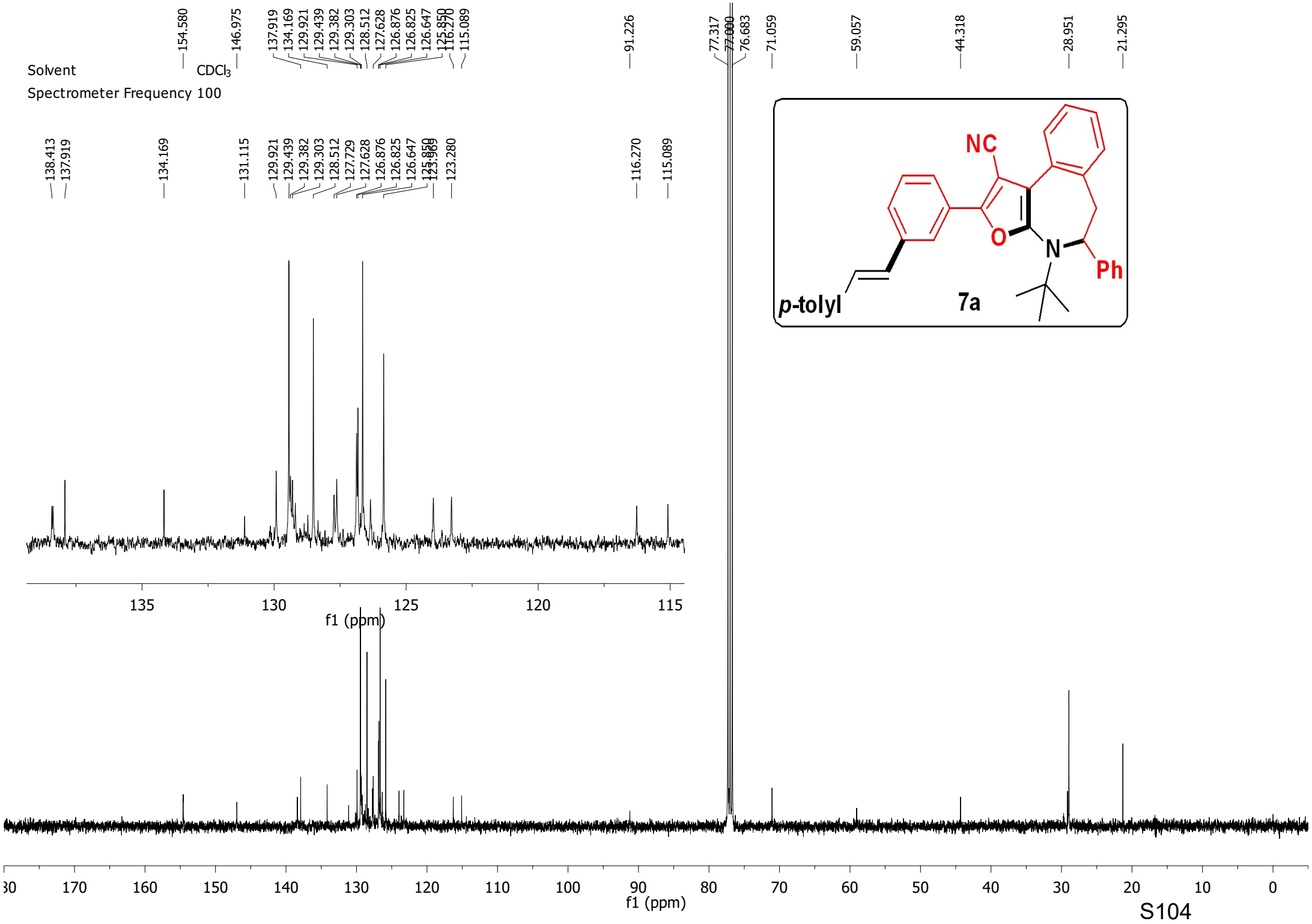

186.040
166.534
165.065
138.844
136.188
136.032
133.240
131.783
130.477
130.380
130.262
128.956
128.316
128.296
127.441
127.334
127.172
116.723
110.709
77.310
76.993
76.675
59.607
54.736
36.713
29.089
Solvent CDCl3
Spectrometer Frequency 100
CN
Ph
O
O
N
Ph
6'
f1 (ppm)
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400

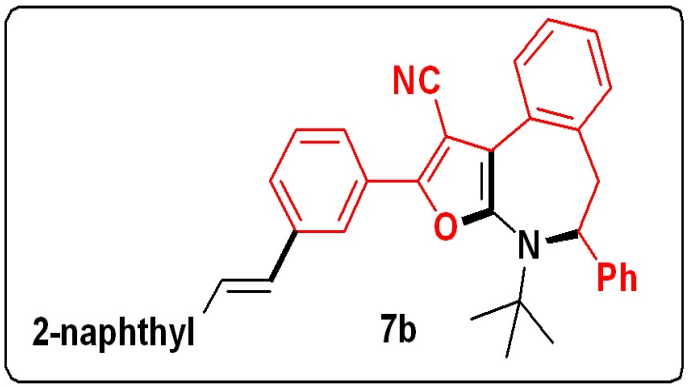


f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 100
154.580
146.975
137.919
134.169
129.921
129.439
129.382
129.303
128.512
127.628
126.876
126.825
126.647
125.850
116.270
115.089
91.226
77.317
77.000
76.683
71.059
59.057
44.318
28.951
21.295
138.413
137.919
134.169
131.115
129.921
129.439
129.382
129.303
128.512
127.729
127.628
126.876
126.825
126.647
123.280
116.270
115.089
NC
O
N
Ph
p-tolyl
7a
135
130
125
120
115
f1 (ppm)
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



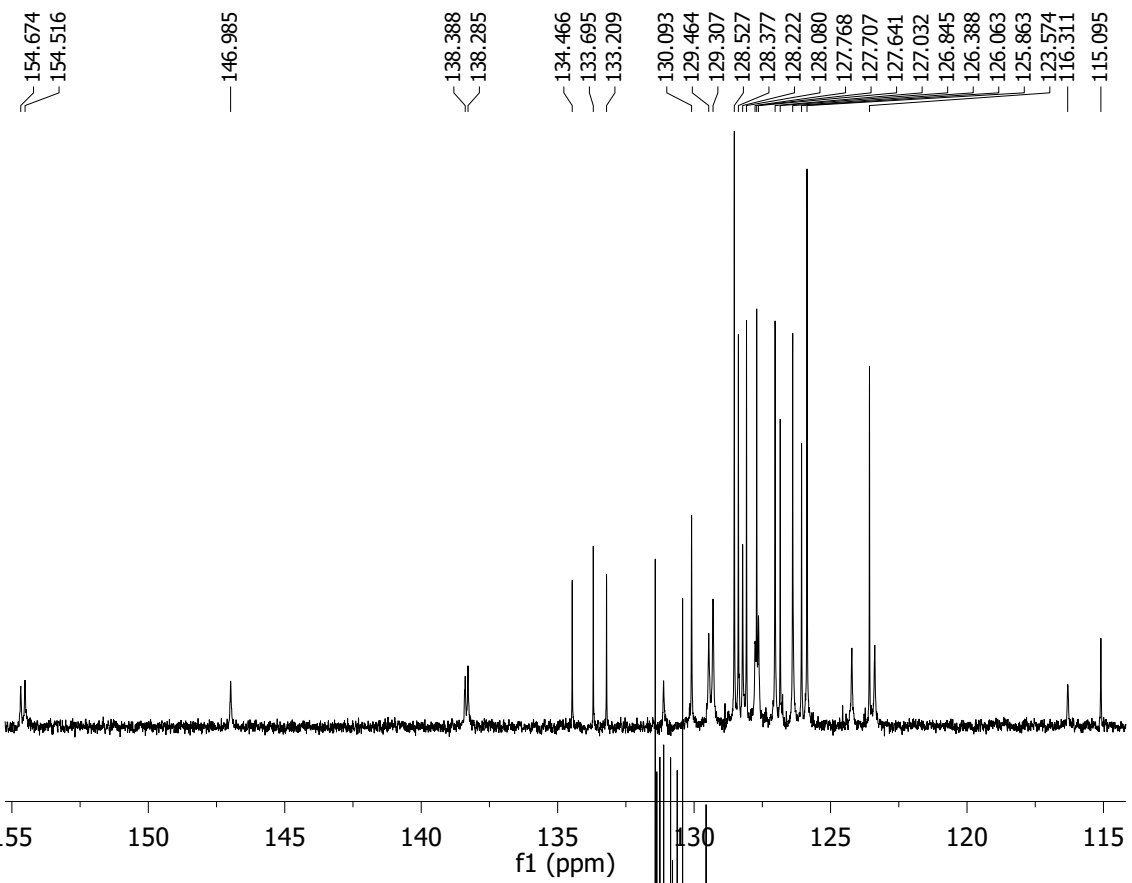
f1 (ppm)

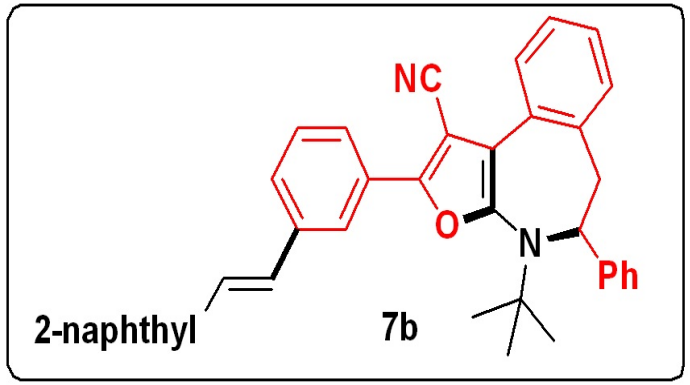
f1 (ppm)

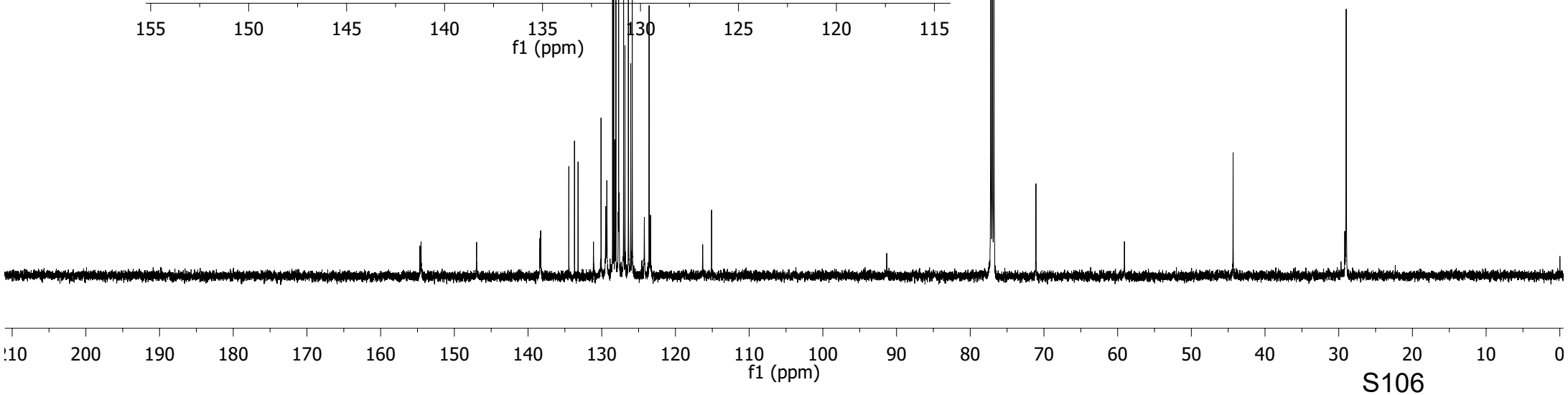
Solvent $CDCl_3$

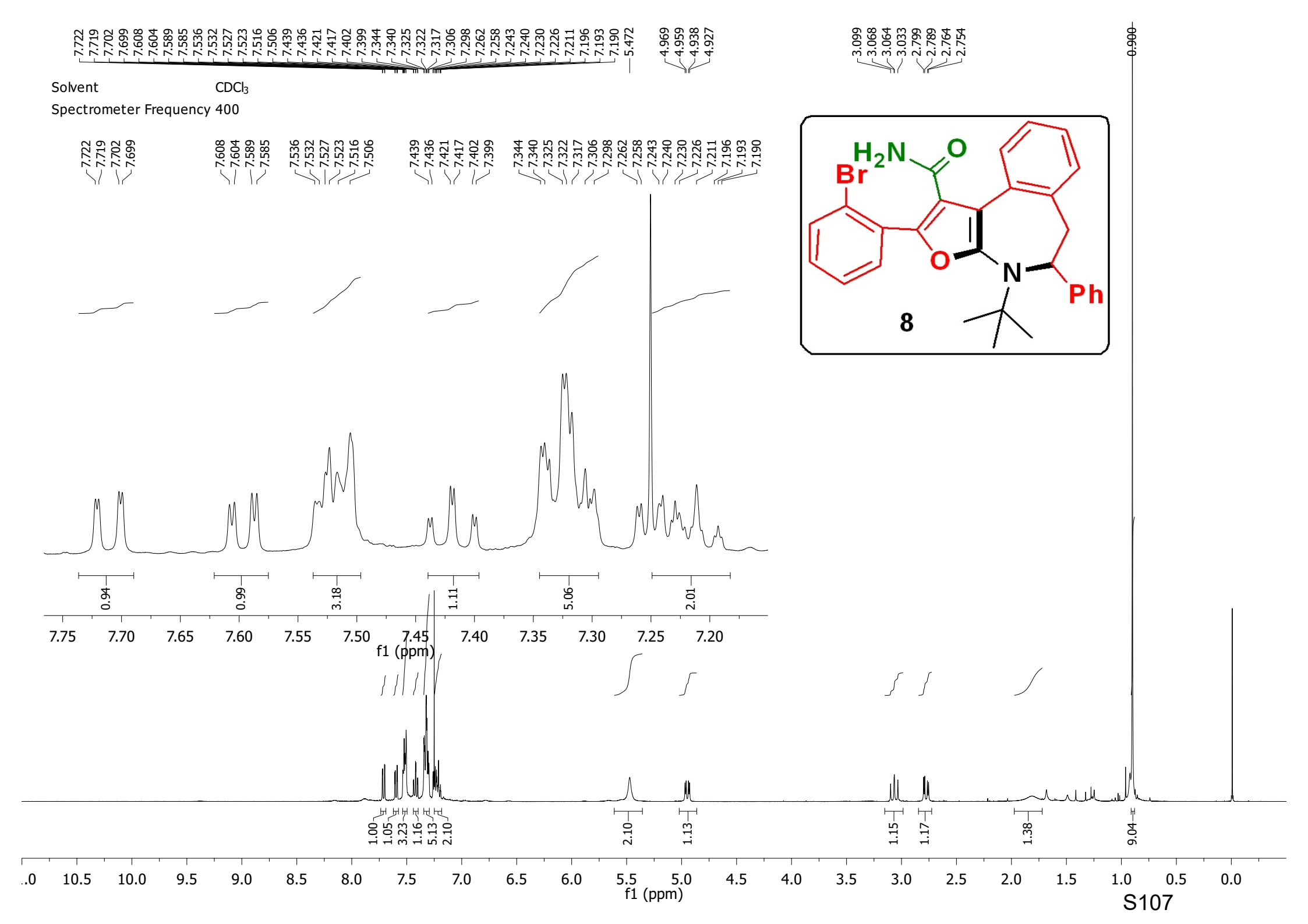
Spectrometer Frequency 150

154.674 154.516 146.985 130.093 128.527 128.377 128.080 127.707 127.032 126.845 126.388 126.063 125.863 123.574 116.311 115.095 91.327 77.213 77.000 76.788 71.088 59.078 44.333 28.987







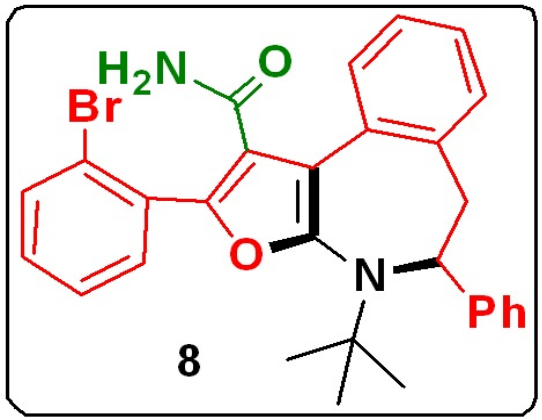

Solvent CDCl3
Spectrometer Frequency 400
8
f1 (ppm)
f1 (ppm)

Solvent $CDCl_3$

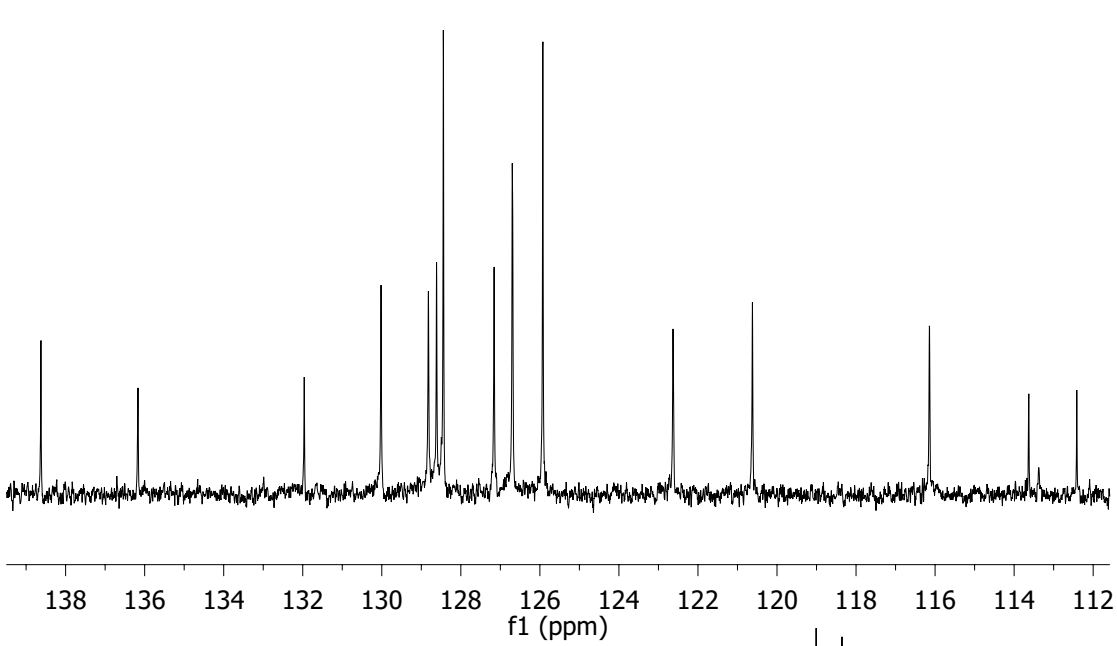
Spectrometer Frequency 100

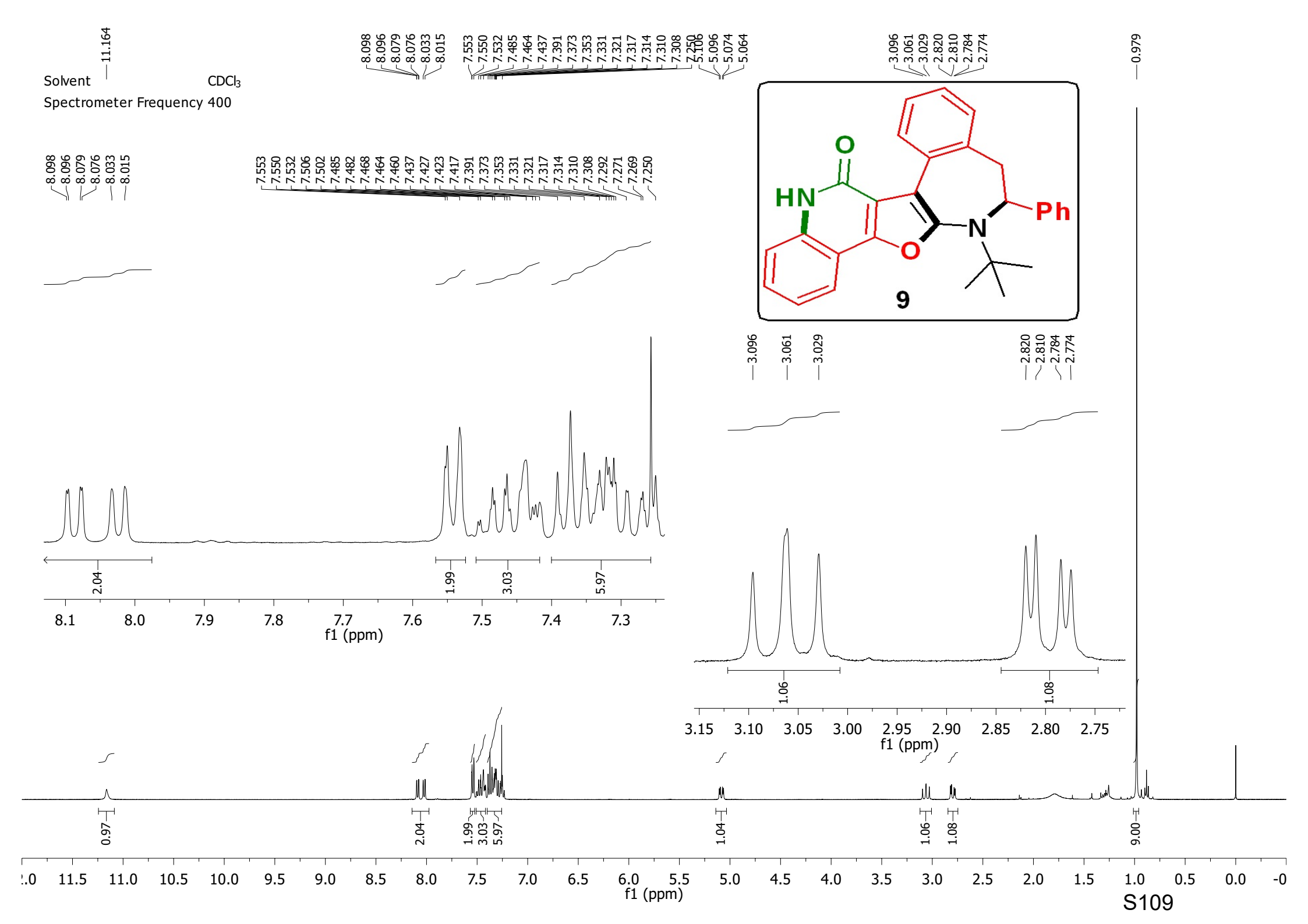
160.433 156.654 152.762 147.197 138.641 136.185 131.977 130.033 128.835 128.628 128.457 127.173 126.711 125.940 122.645 120.635 116.157 113.643 112.427

77.311 76.993 76.676 71.705 58.900 44.520 29.023 22.325 14.048



8



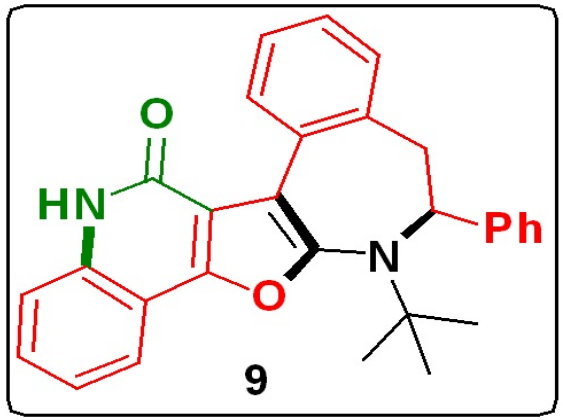

Solvent CDCl3
Spectrometer Frequency 400
11.164
8.098 8.096 8.079 8.076 8.033 8.015
7.553 7.550 7.532 7.485 7.464 7.437 7.391 7.373 7.353 7.331 7.321 7.317 7.314 7.310 7.308 7.250 5.106 5.096 5.074 5.064
3.096 3.061 3.029 2.820 2.810 2.784 2.774
0.979
O
HN
Ph
N
O
9
2.04
1.99
3.03
5.97
1.06
1.08
0.97
2.04
1.99
3.03
5.97
1.04
1.06
1.08
9.00
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 100

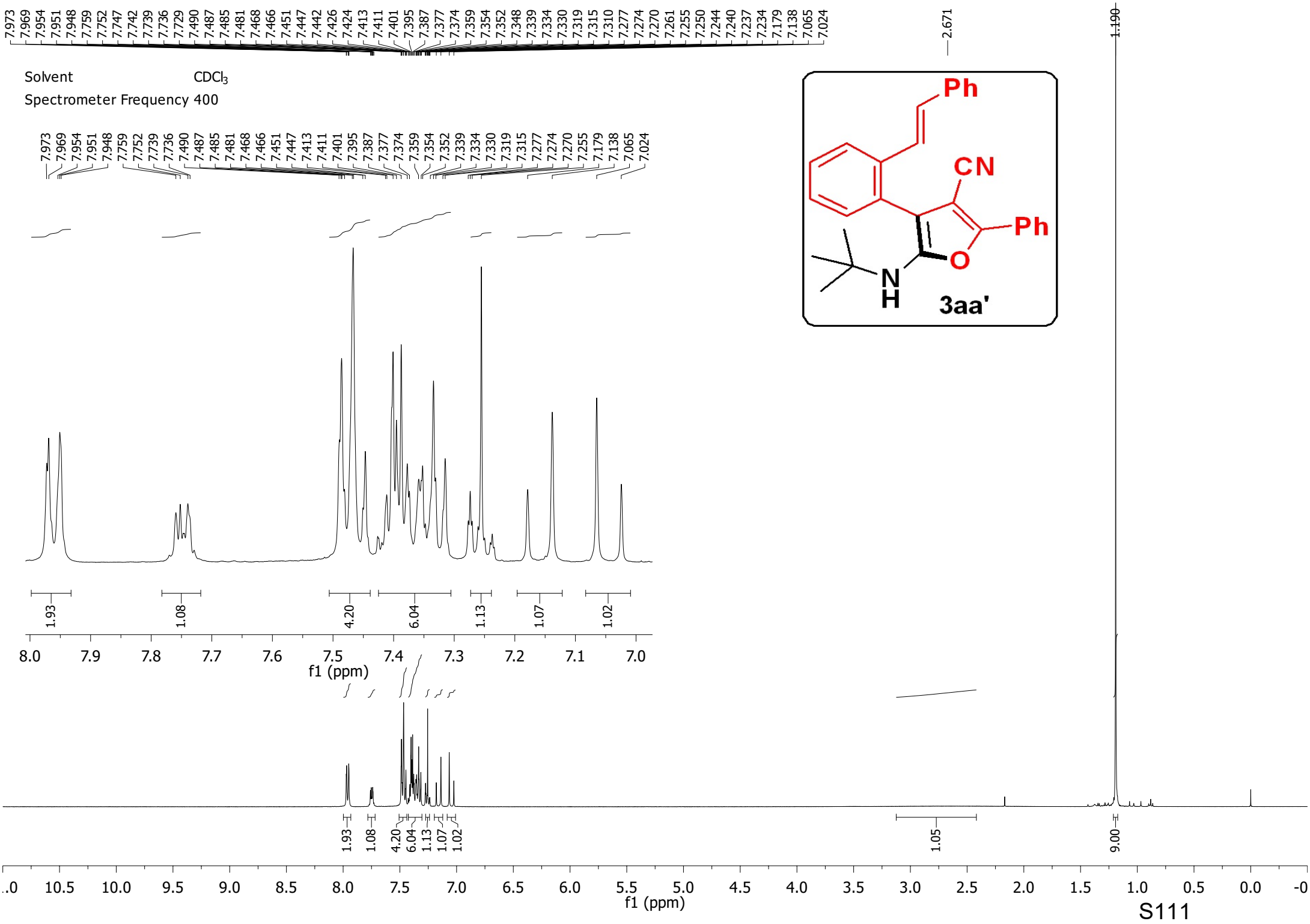
160.422 156.644 152.754 147.188 138.632 136.176 131.970 130.026 128.828 128.621 128.449 127.165 126.705 125.932 122.638 120.629 116.150 113.637 112.422

77.317 77.000 76.683 71.704 58.900 44.520 29.026 22.328 14.053



9

f1 (ppm)

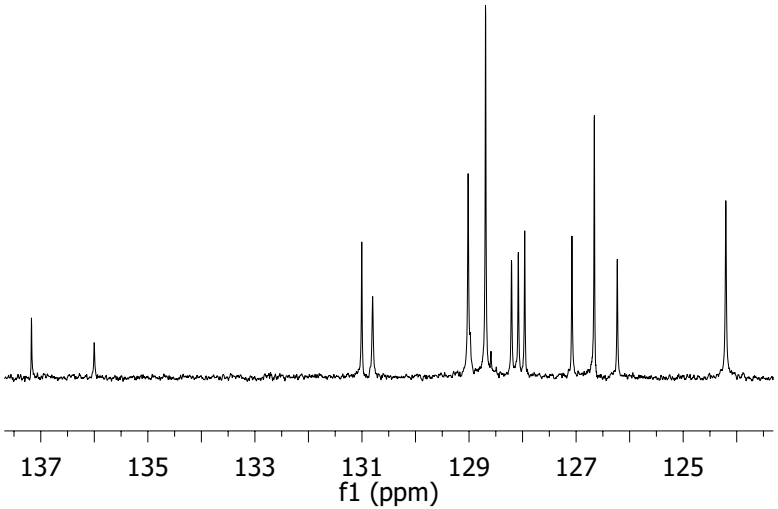

Solvent CDCl3
Spectrometer Frequency 400
Ph
CN
Ph
O
N
H
3aa'
f1 (ppm)
f1 (ppm)

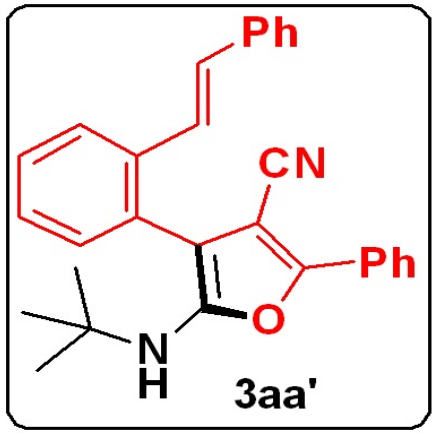
Solvent $CDCl_3$

Spectrometer Frequency 100

152.445 151.864 137.174 136.002 131.004 129.017 128.691 127.960 127.078 126.660 124.204 115.275 102.711 94.375 77.317 77.000 76.683 53.268 29.981

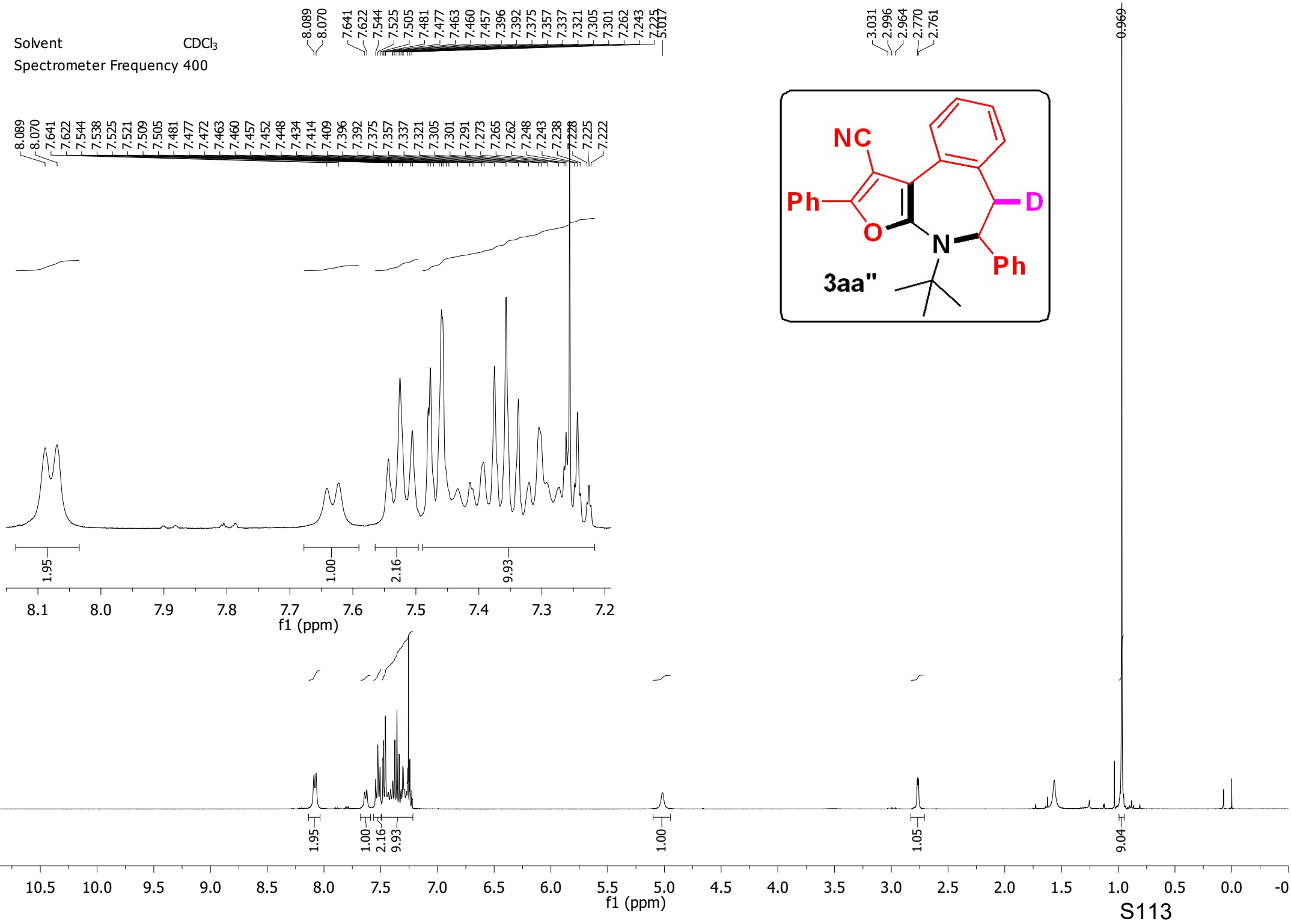
137.174 136.002 131.004 130.801 129.017 128.976 128.691 128.590 128.207 128.080 127.960 127.078 126.660 126.231 124.204





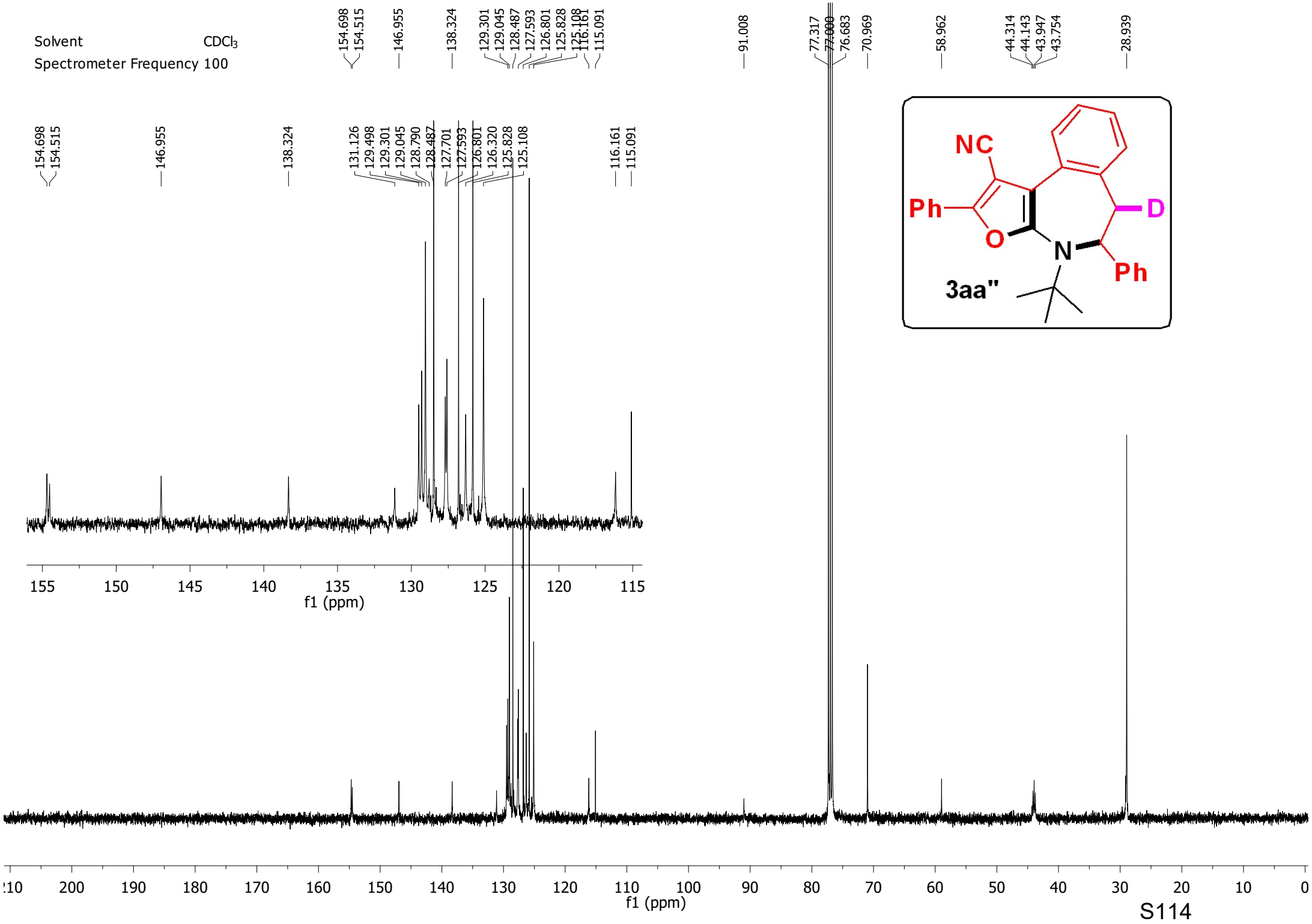
Solvent $CDCl_3$

Spectrometer Frequency 400



Solvent $CDCl_3$

Spectrometer Frequency 100



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) I

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 = 0.0036 A          Wavelength=0.71073

Cell:            a=24.6112(4)    b=10.2554(2)       c=36.0411(5)
                 alpha=90        beta=99.385(2)     gamma=90
Temperature:     113 K

                 Calculated                Reported
Volume           8974.9(3)                 8974.9(3)
Space group      C 2/c                     C 1 2/c 1
Hall group       -C 2yc                    -C 2yc
Moiety formula   C29 H26 N2 O [+ solvent]  2(C29 H26 N2 O)
Sum formula      C29 H26 N2 O [+ solvent]  C58 H52 N4 O2
Mr               418.52                    837.03
Dx,g cm-3        1.239                     1.239
Z                16                        8
Mu (mm-1)        0.075                     0.075
F000             3552.0                    3552.0
F000'            3553.32
h,k,lmax         29,12,42                  29,12,42
Nref             7906                      7887
Tmin,Tmax        0.985,0.996               0.203,1.000
Tmin'            0.985

Correction method= # Reported T Limits: Tmin=0.203 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 24.999

R(reflections)= 0.0689( 6445)     wR2(reflections)= 0.1844( 7887)

S = 1.088                 Npar= 584
```

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

```
DIFMX02_ALERT_1_C  The maximum difference density is > 0.1*ZMAX*0.75
           The relevant atom site should be identified.
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       2.60 Report
PLAT097_ALERT_2_C Large Reported Max.  (Positive) Residual Density       0.64 eA-3
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      5.393 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.595         19 Report
```

Alert level G

```
PLAT042_ALERT_1_G Calc. and Reported Moiety Formula Strings Differ     Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...       2.00 Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large      18.70 Why ?
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O1             107.6 Degree
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O2             107.3 Degree
PLAT605_ALERT_4_G Largest Solvent Accessible VOID in the Structure          0 A**3
PLAT793_ALERT_4_G Model has Chirality at C19         (Centro SPGR)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C48         (Centro SPGR)          R Verify
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        61% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         19 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          0 Info
```

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

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   7 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
   3 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.
```

```
   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.

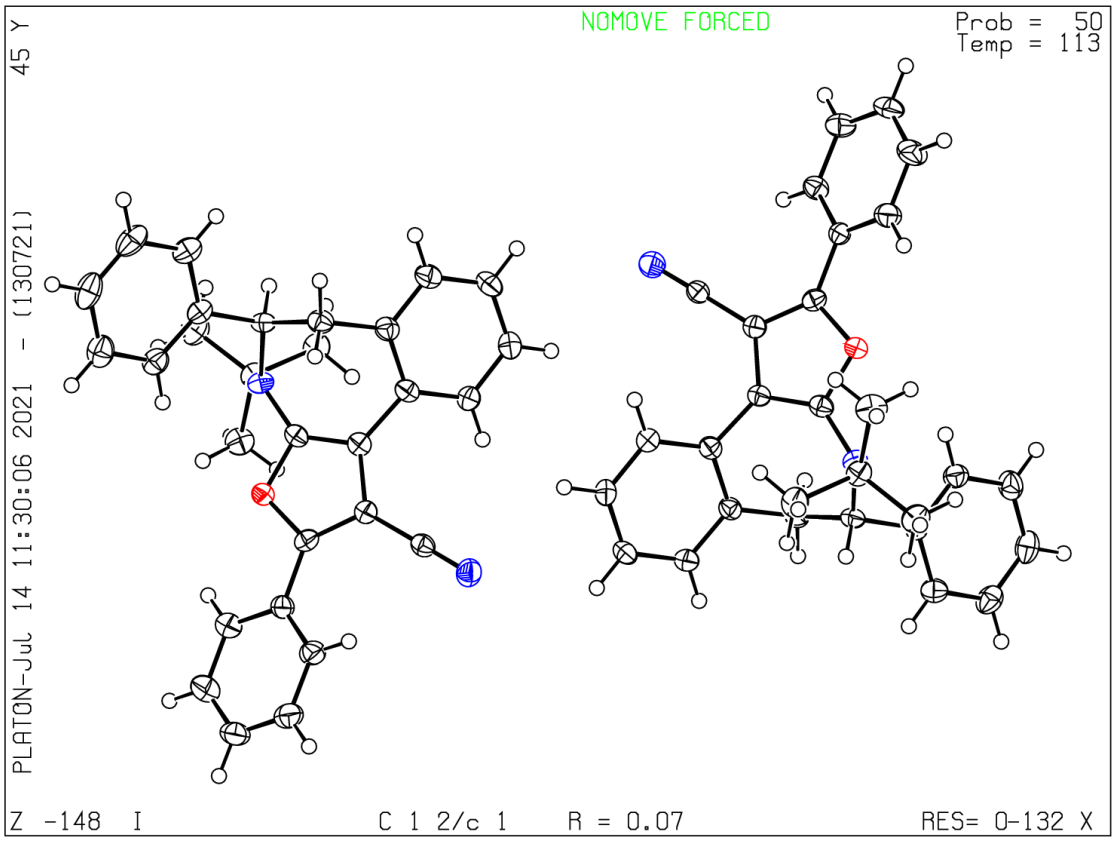
```
# start Validation Reply Form
_vrf_PUBL004_GLOBAL
;
PROBLEM: The contact author’s name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
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 = 0.0030 A          Wavelength=0.71073

Cell:            a=10.2545(3)    b=11.7840(4)       c=18.9397(6)
                 alpha=90        beta=91.018(3)     gamma=90
Temperature:     113 K

                Calculated                Reported
Volume          2288.29(13)               2288.29(13)
Space group     P 21/n                    P 1 21/n 1
Hall group      -P 2yn                    -P 2yn
Moiety formula  C30 H26 N2 O3             C30 H26 N2 O3
Sum formula     C30 H26 N2 O3             C30 H26 N2 O3
Mr              462.53                    462.53
Dx,g cm-3       1.343                     1.343
Z               4                         4
Mu (mm-1)       0.087                     0.087
F000            976.0                     976.0
F000'           976.42
h,k,lmax        13,15,24                  13,15,24
Nref            5030                      4785
Tmin,Tmax       0.979,0.991               0.712,1.000
Tmin'           0.978

Correction method= # Reported T Limits: Tmin=0.712 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.951          Theta(max)= 27.078

R(reflections)= 0.0523( 3902)     wR2(reflections)= 0.1457( 4785)

S = 1.054                 Npar= 319
```

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

```
DIFMX02_ALERT_1_C  The maximum difference density is > 0.1*ZMAX*0.75
           The relevant atom site should be identified.
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       2.27 Report
PLAT097_ALERT_2_C Large Reported Max.  (Positive) Residual Density       0.62 eA-3
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.908 Check
```

Alert level G

```
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O1            107.7 Degree
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O2            104.8 Degree
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O3            105.7 Degree
PLAT793_ALERT_4_G Model has Chirality at C11         (Centro SPGR)         R Verify
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        243 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          6 Info
```

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4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
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1 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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Validation response form

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

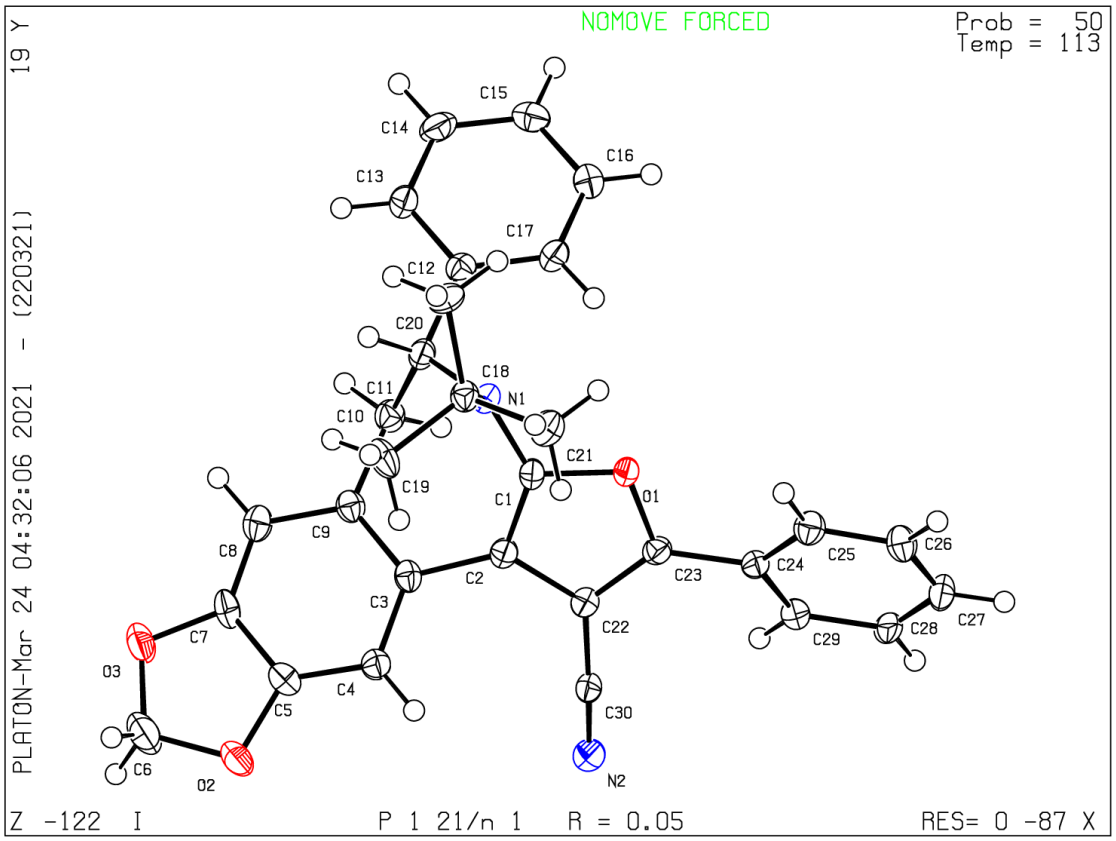
```
# start Validation Reply Form
_vrf_PUBL004_GLOBAL
;
PROBLEM: The contact author’s name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
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 22/03/2021; check.def file version of 19/03/2021

Datablock I - 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 = 0.0019 A          Wavelength=0.71073

Cell:             a=16.0365(3)     b=8.1410(2)         c=19.0830(5)
                  alpha=90         beta=93.993(2)      gamma=90
Temperature:      113 K

                 Calculated                Reported
Volume           2485.30(10)               2485.30(10)
Space group      P 21/c                    P 1 21/c 1
Hall group       -P 2ybc                   -P 2ybc
Moiety formula   C33 H28 N2 O              C33 H28 N2 O
Sum formula      C33 H28 N2 O              C33 H28 N2 O
Mr               468.57                    468.57
Dx,g cm-3        1.252                     1.252
Z                4                         4
Mu (mm-1)        0.075                     0.075
F000             992.0                     992.0
F000'            992.37
h,k,lmax         19,9,22                   19,9,22
Nref             4378                      4377
Tmin,Tmax        0.978,0.989               0.397,1.000
Tmin'            0.978

Correction method= # Reported T Limits: Tmin=0.397 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000           Theta(max)= 24.994

R(reflections)= 0.0392( 3919)                wR2(reflections)=
                                             0.1049( 4377)
S = 1.069                Npar= 328
```

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 ...        36 Report
PLAT005_ALERT_5_G No Embedded Refinement Details Found  in the CIF    Please Do !
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C25      --C33      .       6.1 s.u.
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O1            107.4 Degree
PLAT793_ALERT_4_G Model has Chirality at C10         (Centro SPGR)         S Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............      1056 Note
```

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

0 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
1 ALERT type 3 Indicator that the structure quality may be low
1 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.

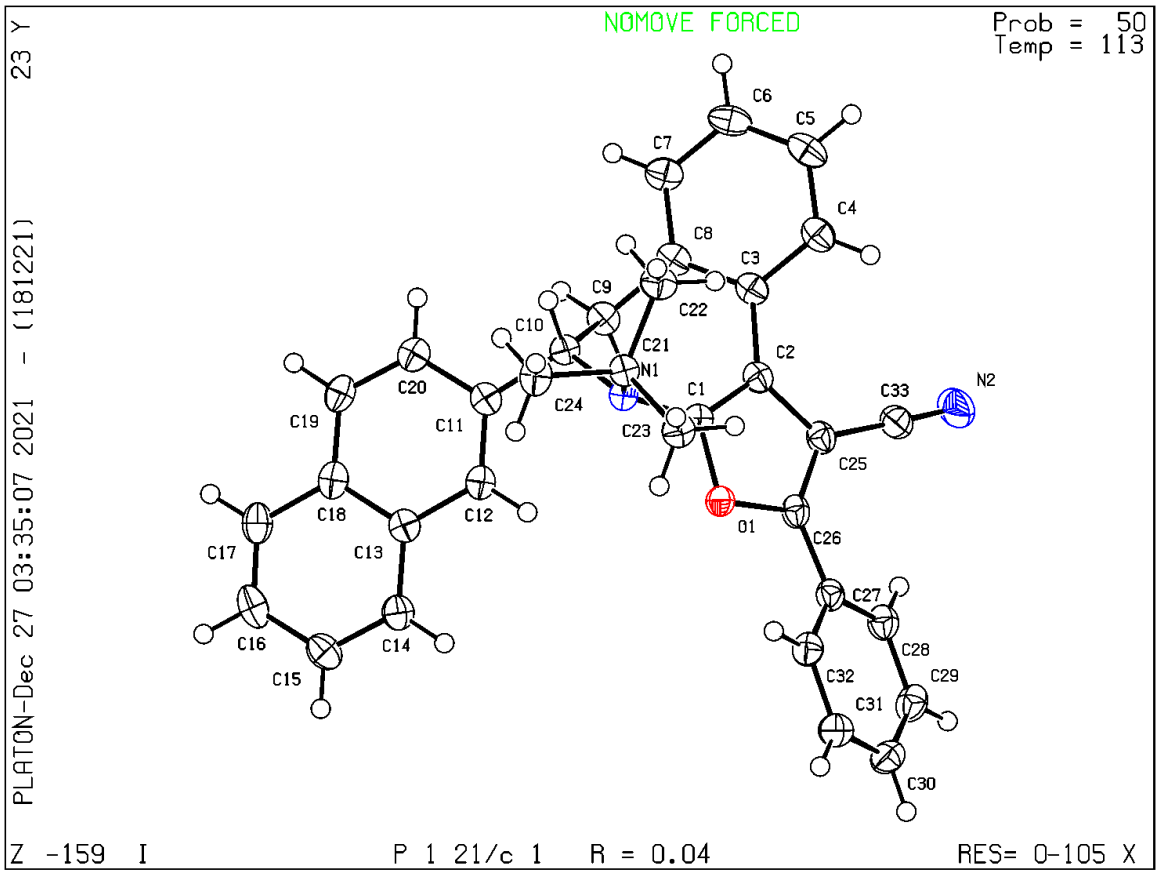
```
# start Validation Reply Form
_vrf_PUBL004_GLOBAL
;
PROBLEM: The contact author’s name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
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 18/12/2021; check.def file version of 18/12/2021

Datablock I - 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 = 0.0032 A          Wavelength=0.71073

Cell:             a=11.9969(6)    b=12.1767(6)        c=18.3724(11)
                  alpha=90        beta=103.405(6)     gamma=90
Temperature:      113 K

                 Calculated                Reported
Volume           2610.8(2)                 2610.8(2)
Space group      P 21/n                    P 1 21/n 1
Hall group       -P 2yn                    -P 2yn
Moiety formula   C35 H32 N2 O              C35 H32 N2 O
Sum formula      C35 H32 N2 O              C35 H32 N2 O
Mr               496.63                    496.62
Dx,g cm-3        1.263                     1.263
Z                4                         4
Mu (mm-1)        0.076                     0.076
F000             1056.0                    1056.0
F000'            1056.39
h,k,lmax         14,14,21                  14,14,21
Nref             4595                      4594
Tmin,Tmax        0.985,0.992               0.423,1.000
Tmin'            0.985

Correction method= # Reported T Limits: Tmin=0.423 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000           Theta(max)= 24.995

R(reflections)= 0.0590( 3329)                wR2(reflections)=
                                             0.1723( 4594)
S = 1.068                Npar= 343
```

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

PLAT761_ALERT_1_C CIF Contains no X-H Bonds ..... Please Check
PLAT762_ALERT_1_C CIF Contains no X-Y-H or H-Y-H Angles ..... Please Check

Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 3 Report
PLAT005_ALERT_5_G No Embedded Refinement Details Found in the CIF Please Do !
PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O1 . 107.7 Degree
PLAT793_ALERT_4_G Model has Chirality at C19 (Centro SPGR) R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 6 Note

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

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
1 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.

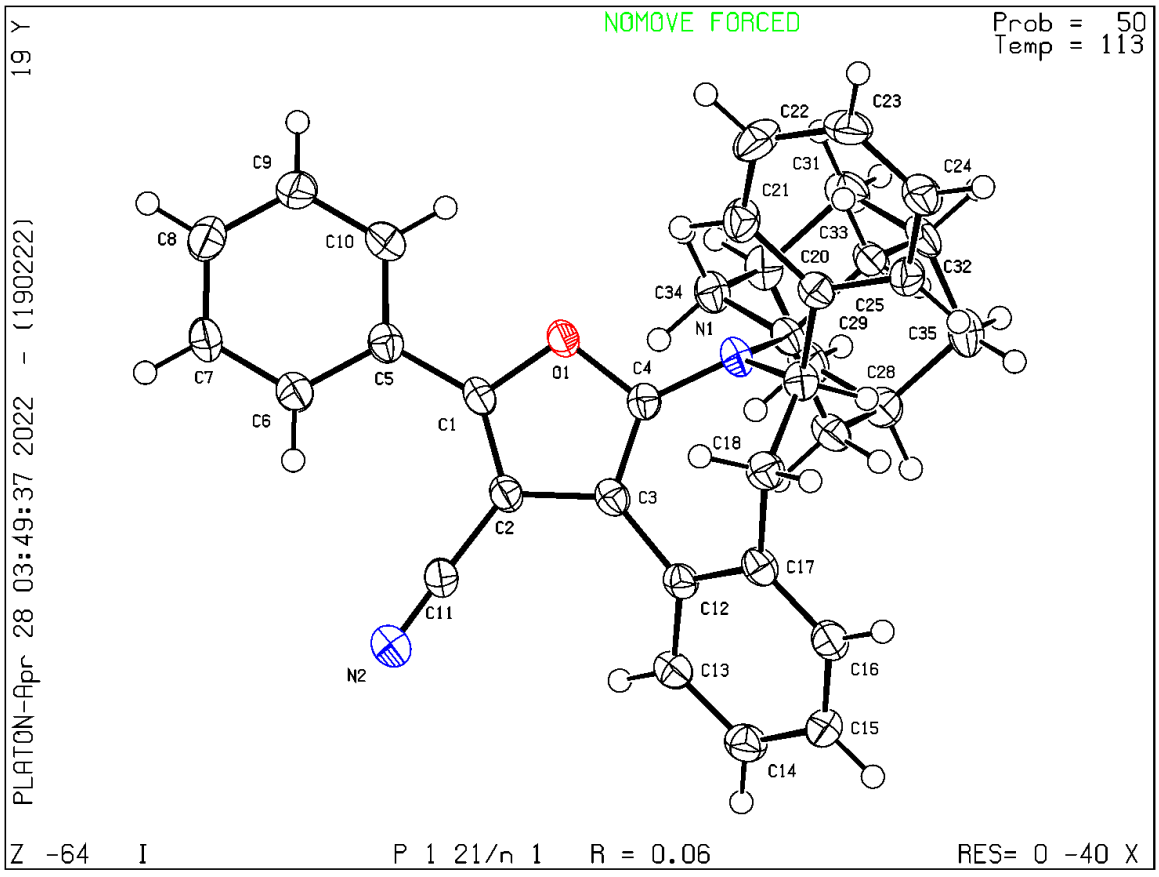
```
# start Validation Reply Form
_vrf_PUBL004_GLOBAL
;
PROBLEM: The contact author’s name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
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 19/02/2022; check.def file version of 19/01/2022

Datablock I - 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 = 0.0024 A          Wavelength=0.71073

Cell:           a=18.5654(4)    b=11.0141(2)        c=23.2460(5)
                alpha=90        beta=104.797(2)     gamma=90
Temperature:    113 K

                Calculated                Reported
Volume          4595.73(17)               4595.73(17)
Space group     I 2/a                     I 1 2/a 1
Hall group      -I 2ya                    -I 2ya
Moiety formula  C29 H26 N2 O2             2(C29 H26 N2 O2)
Sum formula     C29 H26 N2 O2             C58 H52 N4 O4
Mr              434.52                    869.03
Dx,g cm-3       1.256                     1.256
Z               8                         4
Mu (mm-1)       0.079                     0.079
F000            1840.0                    1840.0
F000'           1840.74
h,k,lmax        22,13,27                  22,13,27
Nref            4044                      4039
Tmin,Tmax                                 0.617,1.000
Tmin'

Correction method= # Reported T Limits: Tmin=0.617 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max)= 24.999

R(reflections)= 0.0453( 3661)     wR2(reflections)= 0.1097( 4039)

S = 1.046                 Npar= 301
```

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

```
PLAT053_ALERT_1_C Minimum Crystal Dimension Missing (or Error) ...     Please Check
PLAT054_ALERT_1_C Medium  Crystal Dimension Missing (or Error) ...     Please Check
```

Alert level G

```
PLAT005_ALERT_5_G No Embedded Refinement Details Found  in the CIF     Please Do !
PLAT042_ALERT_1_G Calc. and Reported Moiety Formula Strings Differ     Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...       2.00 Check
PLAT793_ALERT_4_G Model has Chirality at C18         (Centro SPGR)          S Verify
```

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

4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
1 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.

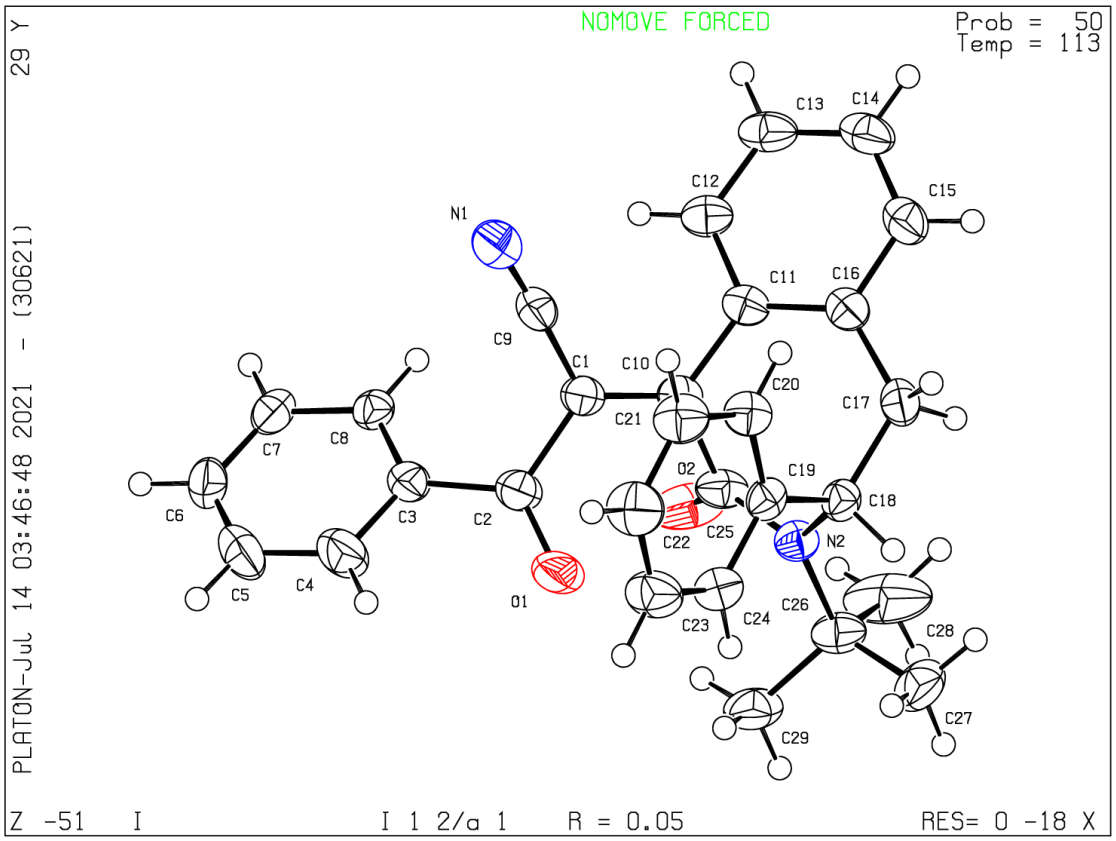
```
# start Validation Reply Form
_vrf_PUBL004_GLOBAL
;
PROBLEM: The contact author’s name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
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 03/06/2021; check.def file version of 02/06/2021

Datablock I - 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 = 0.0051 A          Wavelength=0.71073

Cell:            a=9.1385(2)     b=17.3865(3)     c=23.9664(4)
                 alpha=90        beta=90          gamma=90
Temperature:     113 K
```

	Calculated	Reported
Volume	3807.94(12)	3807.94(12)
Space group	P c a 21	P c a 21
Hall group	P 2c -2ac	P 2c -2ac
Moiety formula	C25 H18 N2 O2	2(C25 H18 N2 O2)
Sum formula	C25 H18 N2 O2	C50 H36 N4 O4
Mr	378.41	756.83
Dx,g cm-3	1.320	1.320
Z	8	4
Mu (mm-1)	0.085	0.085
F000	1584.0	1584.0
F000’	1584.66	
h,k,lmax	10,20,28	10,20,28
Nref	6707[3446]	6705
Tmin,Tmax	0.975,0.983	0.544,1.000
Tmin’	0.975	

```
Correction method= # Reported T Limits: Tmin=0.544 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.95/1.00      Theta(max)= 24.996

R(reflections)= 0.0572( 6222)     wR2(reflections)= 0.1457( 6705)

S = 1.046                 Npar= 524
```

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

```
STRVA01_ALERT_2_C           Chirality of atom sites is inverted?
          From the CIF: _refine_ls_abs_structure_Flack    1.200
          From the CIF: _refine_ls_abs_structure_Flack_su    1.700
PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ........       6.58 Note
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       2.08 Report
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00511 Ang.
PLAT369_ALERT_2_C Long   C(sp2)-C(sp2) Bond  C1       - C2       .       1.53 Ang.
PLAT369_ALERT_2_C Long   C(sp2)-C(sp2) Bond  C17      - C19      .       1.53 Ang.
PLAT761_ALERT_1_C CIF Contains no X-H Bonds ......................     Please Check
PLAT762_ALERT_1_C CIF Contains no X-Y-H or H-Y-H Angles ..........     Please Check
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #          1 Note
             C25 H18 N2 O2
PLAT907_ALERT_2_C Flack x > 0.5, Structure Needs to be Inverted? .       1.20 Check
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         58 Report
PLAT005_ALERT_5_G No Embedded Refinement Details Found  in the CIF     Please Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............         2 Report
PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High .     1.700 Report
PLAT042_ALERT_1_G Calc. and Reported Moiety Formula Strings Differ     Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...       2.00 Check
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.12 Report
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          2 Note
             C25 H18 N2 O2
PLAT792_ALERT_1_G Model has Chirality at C10         (Polar  SPGR)          S Verify
PLAT792_ALERT_1_G Model has Chirality at C35         (Polar  SPGR)          R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       1657 Note
```

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

   6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   7 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   2 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.

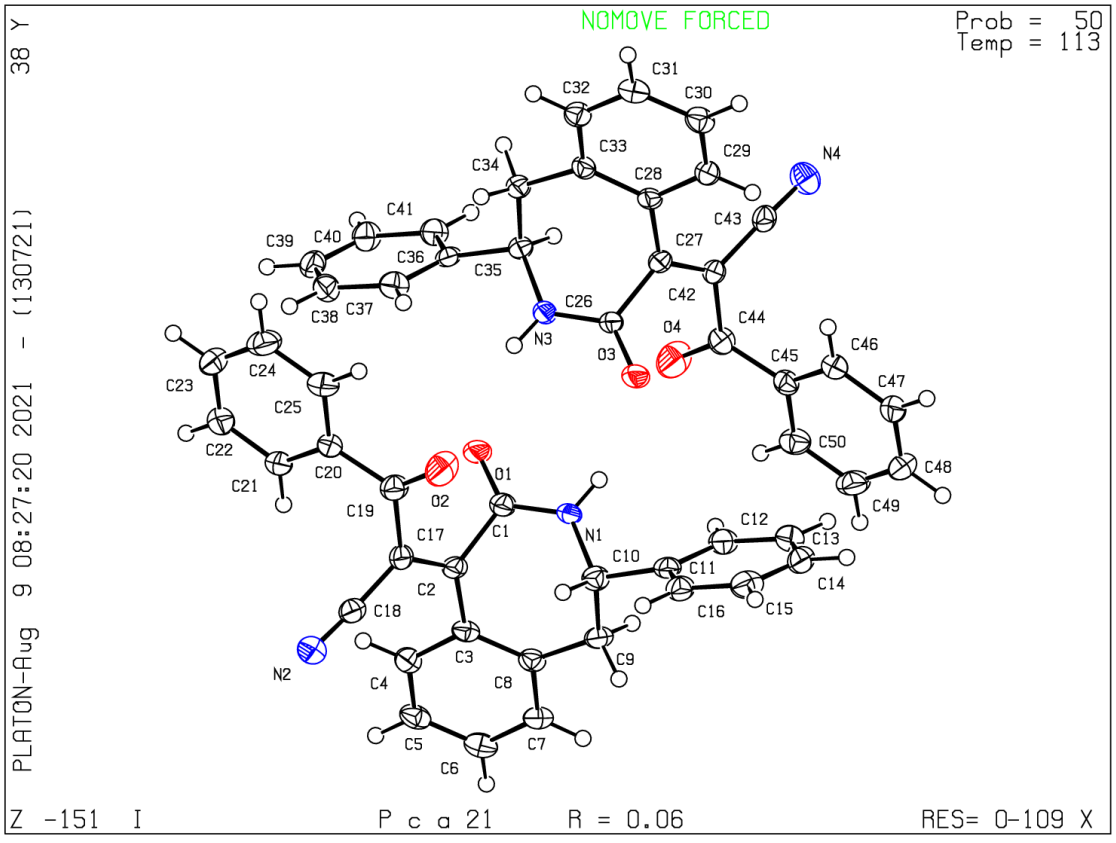
```
# start Validation Reply Form
_vrf_PUBL004_GLOBAL
;
PROBLEM: The contact author’s name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
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

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 = 0.0032 A          Wavelength=0.71073

Cell:             a=18.9264(3)    b=10.15909(17)        c=12.9510(2)
                  alpha=90        beta=100.3841(15)     gamma=90
Temperature:      113 K

                  Calculated                Reported
Volume            2449.37(7)                2449.37(7)
Space group       P 21/c                    P 1 21/c 1
Hall group        -P 2ybc                   -P 2ybc
Moiety formula    C29 H27 Br N2 O2          C29 H27 Br N2 O2
Sum formula       C29 H27 Br N2 O2          C29 H27 Br N2 O2
Mr                515.43                    515.43
Dx,g cm-3         1.398                     1.398
Z                 4                         4
Mu (mm-1)         1.707                     1.707
F000              1064.0                    1064.0
F000'             1063.23
h,k,lmax          22,12,15                  22,12,15
Nref              4314                      4314
Tmin,Tmax         0.815,0.918               0.872,1.000
Tmin'             0.815

Correction method= # Reported T Limits: Tmin=0.872 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000          Theta(max)= 24.994

R(reflections)= 0.0302( 3797)                wR2(reflections)=
                                             0.0692( 4314)
S = 1.036                 Npar= 311
```

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

```
PLAT005_ALERT_5_G No Embedded Refinement Details Found  in the CIF     Please Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............          2 Report
PLAT398_ALERT_2_G Deviating  C-O-C   Angle From 120 for O1       .      106.6 Degree
PLAT432_ALERT_2_G Short Inter X...Y Contact  Br1      ..C7       .       3.30 Ang.
                                                  x,1+y,z  =      1_565 Check
PLAT793_ALERT_4_G Model has Chirality at C10         (Centro SPGR)          S Verify
```

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

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

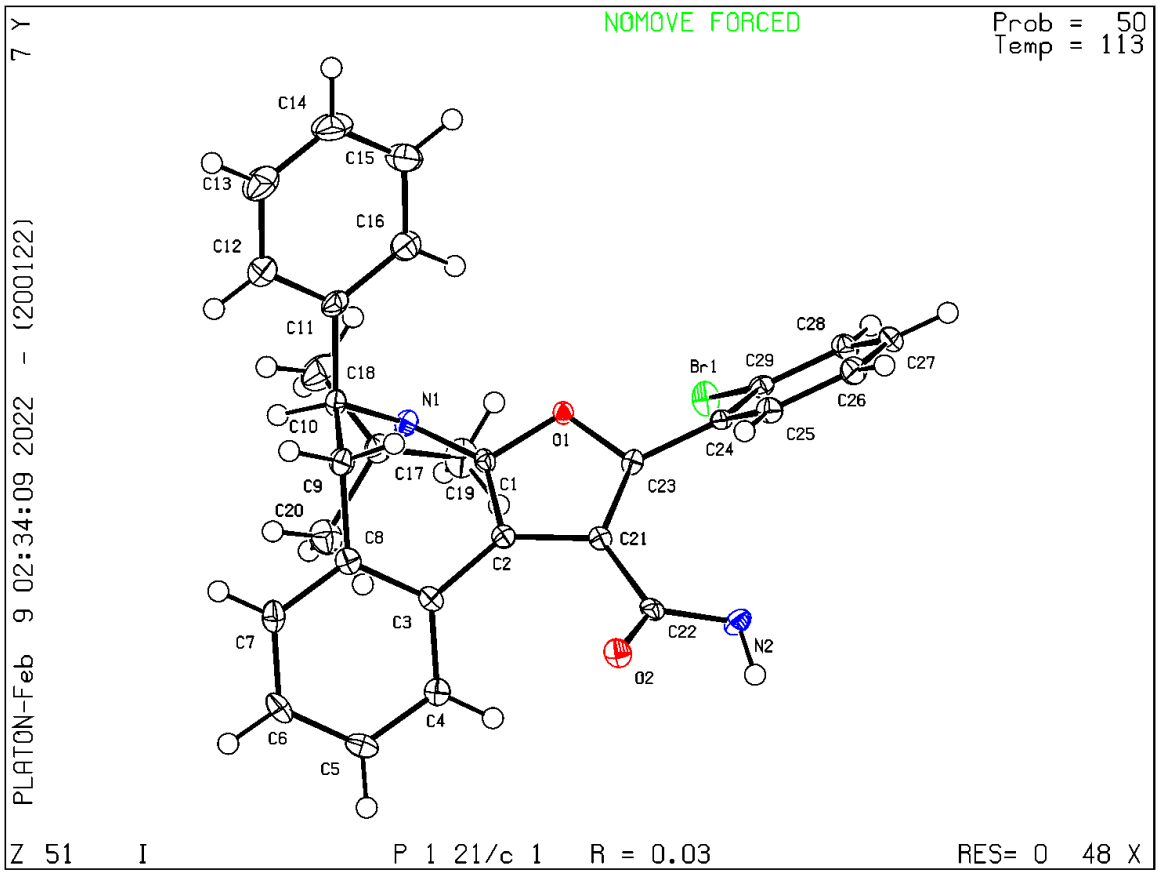
```
# start Validation Reply Form
_vrf_PUBL004_GLOBAL
;
PROBLEM: The contact author’s name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
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 20/01/2022; check.def file version of 19/01/2022

Datablock I - ellipsoid plot



checkCIF/PLATON report

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

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

```
Bond precision:   C-C = 0.0020 A          Wavelength=0.71073

Cell:             a=10.6050(3)     b=11.8204(3)       c=17.9554(5)
                  alpha=90         beta=92.512(3)     gamma=90
Temperature:      113 K
```

	Calculated	Reported
Volume	2248.64(11)	2248.64(11)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C29 H26 N2 O2	C29 H26 N2 O2
Sum formula	C29 H26 N2 O2	C29 H26 N2 O2
Mr	434.52	434.52
Dx,g cm-3	1.283	1.283
Z	4	4
Mu (mm-1)	0.081	0.081
F000	920.0	920.0
F000'	920.37	
h,k,lmax	12,14,21	12,14,21
Nref	3954	3954
Tmin,Tmax	0.990,0.992	0.464,1.000
Tmin'	0.984	

```
Correction method= # Reported T Limits: Tmin=0.464 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000           Theta(max)= 24.997

R(reflections)= 0.0400( 3257)                    wR2(reflections)=
                                                 0.1057( 3954)
S = 1.082                 Npar= 301
```

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

```
PLAT005_ALERT_5_G No Embedded Refinement Details Found  in the CIF     Please Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............          1 Report
PLAT398_ALERT_2_G Deviating  C-O-C   Angle From 120 for O1       .      105.7 Degree
PLAT793_ALERT_4_G Model has Chirality at C10         (Centro SPGR)          R Verify
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
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1 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
2 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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_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
```

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PLATON version of 19/02/2022; check.def file version of 19/01/2022

Datablock I - ellipsoid plot