Supporting Information

Thioxanthone-Photocatalyzed Aerobic Oxidation of *N,N*-Dimethylanilines to *N*-Formyl Anilines under Visible Light

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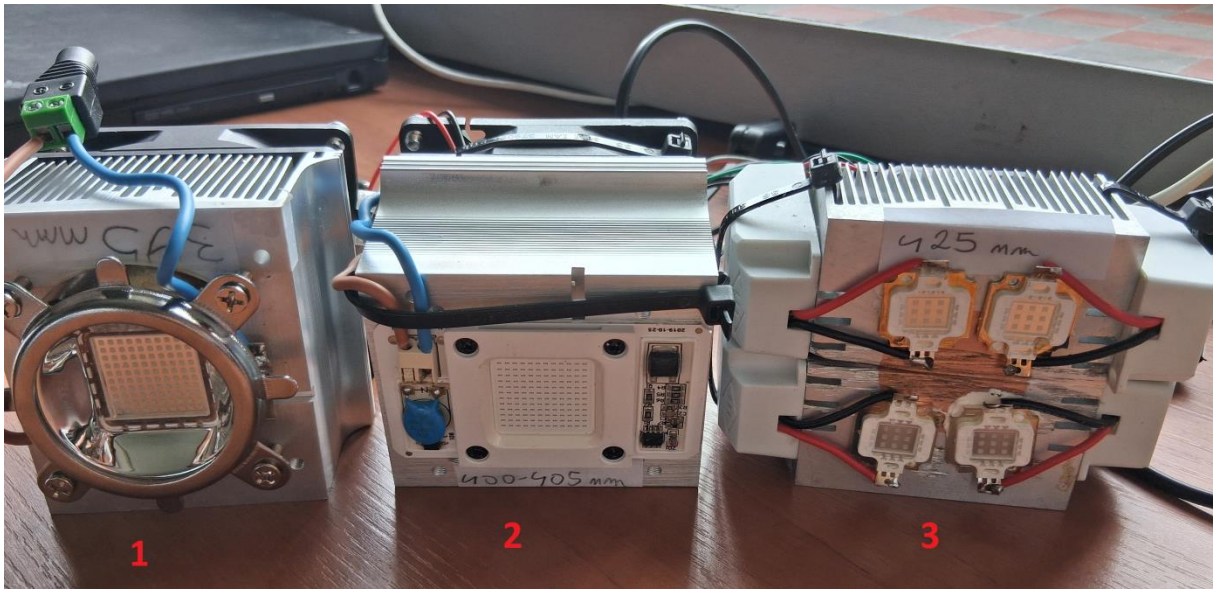
Table of Context:

1. General Information:

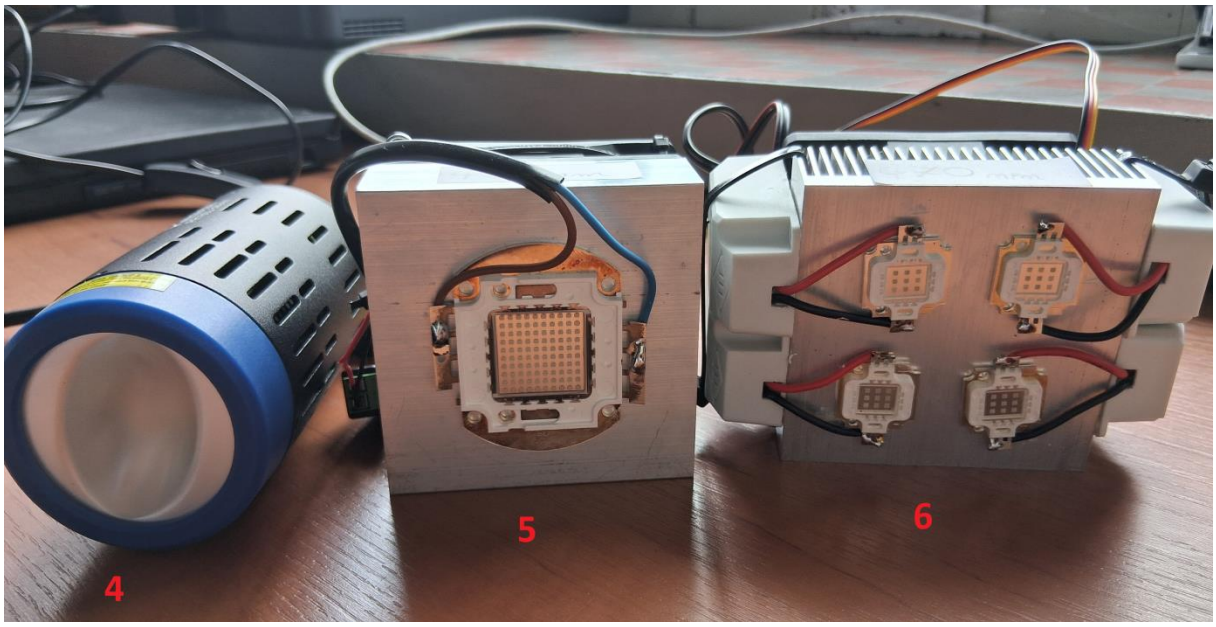
^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker 400 and Varian VNMRS 600 spectrometers. ^{1}H NMR spectra were referenced to: chloroform-*d* (δ = 7.26 ppm), ^{13}C NMR spectra were referenced to: chloroform-*d* (δ = 77.16 ppm). Chemical shifts (δ) were given in ppm and coupling constants (*J*) were given in Hertz (Hz). Multiplicity was indicated as follows: s (singlet), bs (brought singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet). HRMS spectra were recorded on Synapt G2S HDMS (Waters) spectrometer for ESI ionization technique. UV–Vis absorption spectra were recorded on a JASCO V-670 UV–Vis–NIR spectrophotometer. Steady-state emission (fluorescence) spectra were recorded on an Edinburgh Instruments FS5 fluorimeter equipped with a Hamamatsu R13456 photomultiplier tube. Thin layer chromatography was performed on Merck aluminum sheet Silica Gel 60 F254. Flash column chromatography was carried out using Merck silica gel (230-400 mesh). All starting materials **1a–o**, **1r-t**, **3a-j** *Padimate O Mifepristone, Thioflavin T, Tropinone* and thioxanthones **TX-III-VI** were purchased from commercial suppliers (TCI, Sigma-Aldrich, Alfa Aesar, and Ambeed) and used as received without further purification. 4-(Benzyloxy)-*N*,*N*-dimethylaniline (**1p**) was prepared according to a literature procedure.[1]

2. Information about the Light Sources used in the Study

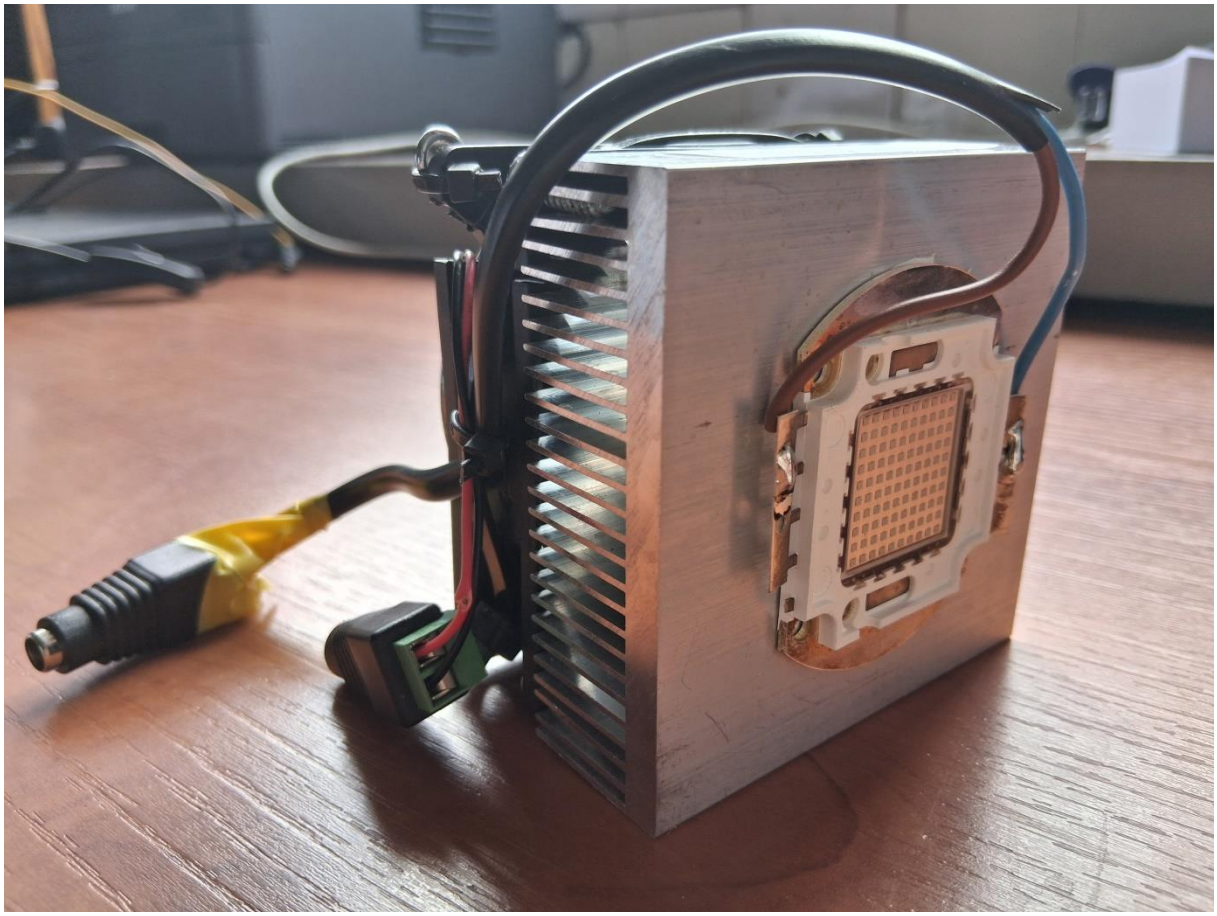
In the optimization studies, custom-built light sources were used, assembled from commercially available components: an LED lamp, a power supply, and a lamp cooling system (heat sink and computer fan).



Picture 1. **1** 395 nm**,** 100 W, **2** 400-405 nm 50 W, **3** 425 nm 4x10W



Picture 2. **4** Kessil lamp 440 nm 40 W, **5** 450 nm 100 W, **6** 475 nm 4x10W



Picture 3. Self-Made 450 nm 100 W Lamp

Picture 4. Self-Made 450 nm 100 W Lamp

3. General Procedure for the Formylation of *N,N*-Dimethylanilines

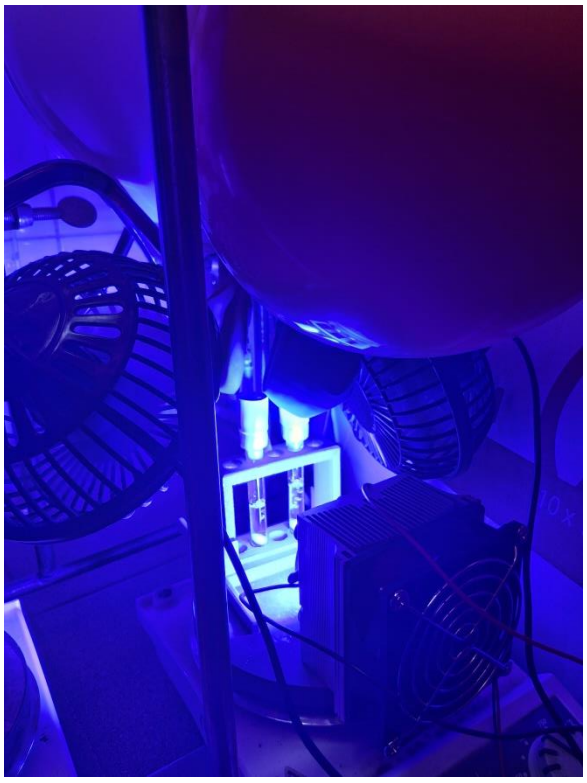
General Remarks for Photochemical Reaction:

The formylation reaction was carried out using a self-made 100 W LED lamp with a wavelength of 450 nm. The reaction was conducted at a temperature of 30–35°C. Two desktop fans were used to cool the lamp and the reaction vessel. The distance between the light source and the reaction vessel was 5 cm. The reactions were performed in a glass vial with dimensions of 1 cm diameter and 8 cm height. A 0.01 M solution of thioxanthone **TX-III** in MeCN was used for the reaction. This solution can be stored at room temperature for extended periods. At higher concentrations, thioxanthone **TX-III** does not dissolve completely.

General Procedure:

A glass vial was charged with *N,N*-dimethylaniline (0.4 mmol), then 4 mL of a pre-prepared solution of thioxanthone **TX-III** (10 mol%) in MeCN was added. The vial was sealed with a septum, and an oxygen balloon (1 atm) was inserted to ensure a continuous flow of gas. The reaction mixture was irradiated with a 100 W LED lamp at a wavelength of 450 nm at room temperature overnight. Afterwards, the solvent was evaporated under reduced pressure

using a rotary evaporator, the residue was adsorbed onto silica gel, and purified by flash chromatography.

Picture 5 and **6** Formylation Reaction in Bath

4. Formylation of DMAP in 10 mmol Scale

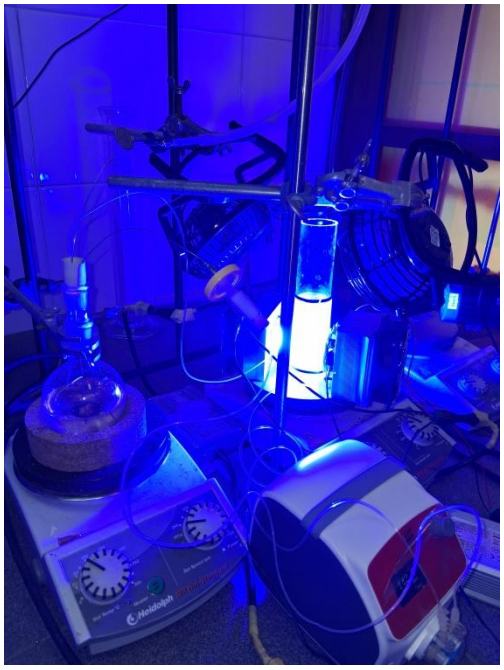
General Remarks for Photochemical Formylation Reaction in 10 mmol Scale Performed in Continues Flow:

Photochemical formylation reaction in continues flow was performed in a closed system under an oxygen in self-made flow set consisting of: two Blue-LED lamp (100 W, 450 nm), UV-transparent FEP tubing of dimensions 0.7 mm i.d. × 1.1 mm o.d, wound on a quartz tube of dimensions 18 cm in length and 4 cm in diameter (*loop length 14 m, capacity 7 mL, number of coils 111*), peristaltic pump (*model LLG-uniPERIPUMP 1*), magnetic stirrer (Picture 7 and 8). The distance between the UV-transparent FEP tubing and the light source was 0.5 cm)

Flow reactor parameters. The FEP loop (0.7 mm i.d. × 1.1 mm o.d., 14 m length) has a volume of 7.0 mL**.** The solution was pumped at 5.0 mL·min^{-1}, giving a residence time τ = 7.0/5.0 = 1.4 min (84 s)**.** The reaction was run in a closed (recirculating) system until complete substrate consumption after 22 h**.** Over 22 h 6.6 L of solution were processed, corresponding to ≈943 reactor volumes**.** Starting substrate: 10 mmol (0.10 M, 100 mL); yield of **5** = 91% (determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard).

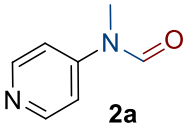
Procedure:

To a 250 mL round-bottom flask were added 4-(dimethylamino)pyridine **1a** (10 mmol, 1.222 g), thioxanthone **TX-III** (10 mol%, 212 mg), and MeCN (100 mL). The flask was sealed with a septum, and an oxygen balloon (1 atm) was attached to ensure a continuous supply of O_2. The flask was connected to a flow system equipped with a filter placed between the reaction vessel and the pump. The solution was pumped at a flow rate of 5 mL/min. After a 5 min equilibration period to stabilize the flow, two LED lamp (450 nm, 100 W) and two desktop cooling fans were switched on. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. After complete consumption of substrate **1a** (22 h), the reaction mixture was collected in a flask, and the flow system was rinsed with MeCN (50 mL). The combined solutions were concentrated under reduced pressure, and the crude product **5** (1.57 g) was used directly in the next step without purification. The yield of **5** (91%) was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.



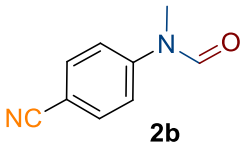
Picture 7 and **8** Formylation Reaction in Flow

5. Characterization Data:



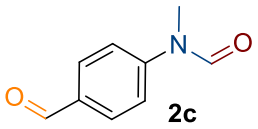
2a

***N*-Methyl-*N*-(pyridin-4-yl)formamide**; 84% (46 mg obtained from 49 mg of DMAP); white solid; m.p. 75-76°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 (s, 1H), 8.61 – 8.56 (m, 2H), 7.12 – 7.06 (m, 2H), 3.32 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 161.2, 151.2, 148.8, 113.7, 30.2; Flash column chromatography (5-10% MeOH in DCM); The spectroscopic data are in agreement with literature data.[2]



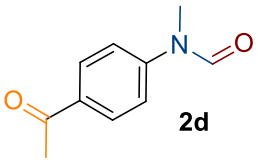
2b

***N*-(4-Cyanophenyl)-*N*-methylformamide**; 70% (45 mg obtained from 58 mg of 4-(dimethylamino)benzonitrile); white solid; m.p. 97-98°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (s, 1H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 3.33 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 161.6, 145.9, 133.8, 121.1, 118.2, 109.3, 31.3; The spectroscopic data are in agreement with literature data.[2]



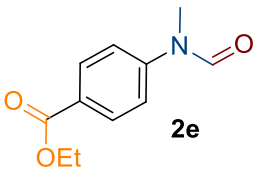
2c

***N*-(4-Formylphenyl)-*N*-methylformamide**; 52% (34 mg obtained from 60 mg of 4-(dimethylamino)benzaldehyde); brown waxy solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 8.69 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 3.37 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 190.7, 161.8, 147.2, 133.7, 131.3, 120.8, 31.4; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[3]



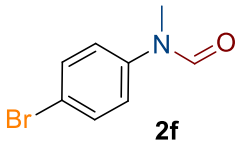
2d

***N*-(4-Acetylphenyl)-*N*-methylformamide;** 78% (55 mg obtained from 65 mg of 1-(4-(dimethylamino)phenyl)ethanone); yellow solid; m.p. 79-80°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (s, 1H), 8.01 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 3.35 (s, 3H), 2.60 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 196.7, 161.8, 146.1, 134.5, 130.0, 120.6, 31.4, 26.5; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[2]



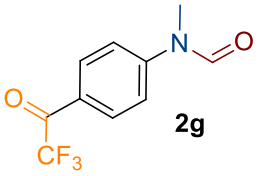
2e

Ethyl 4-(*N*-methylformamido)benzoate; 63% (52 mg obtained from 77 mg of ethyl 4-(dimethylamino)benzoate); white solid; m.p. 57-58°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 8.06 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.33 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 165.7, 161.9, 145.9, 131.1, 127.9, 120.6, 61.1, 31.5, 14.3; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[2]



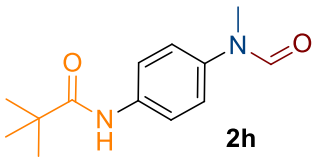
2f

***N*-(4-Bromophenyl)-*N*-methylformamide**; 73% (63 mg obtained from 80 mg of 4-bromo-N,N-dimethylaniline); brown solid; m.p. 70-71°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 7.54 – 7.49 (m, 2H), 7.11 – 7.02 (m, 2H), 3.29 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 161.9, 141.2, 132.7, 123.8, 119.7, 32.0; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[2]



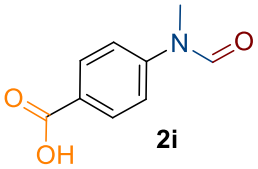
2g

***N*-Methyl-*N*-(4-(2,2,2-trifluoroacetyl)phenyl)formamide**; 71% (66 mg obtained from 87 mg of 1-(4-(dimethylamino)phenyl)-2,2,2-trifluoroethanone); white solid; m.p. 64-65°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 (s, 1H), 8.13 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 3.38 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 178.9, 161.5, 148.1, 132.05, 132.02, 126.8, 120.1, 116.6 (q, *J* = 290.6 Hz), 31.12; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -71.4; HRMS (ESI-TOF) m/z calc for $C_{10}H_9F_3NO_2$ [M+H$^+$] 232.0585. Found 232.0581; Flash column chromatography (0-50% AcOEt in hexanes).



2h

***N*-(4-(*N*-Methylformamido)phenyl)pivalamide;** 62% (62 mg obtained from 88 mg of N-(4-(dimethylamino)phenyl)pivalamide); brown solid; m.p. 144-145°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.60 – 7.56 (m, 2H), 7.52 (bs, 1H), 7.10 (d, *J* = 8.8 Hz, 2H), 3.27 (s, 3H), 1.30 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 176.8, 162.2, 138.1, 136.7, 123.2, 121.2, 39.6, 32.3, 27.6; HRMS (ESI-TOF) m/z calc for $C_{13}H_{18}N_2O_2Na$ [M+Na$^+$] 257.1266. Found 257.1265; Flash column chromatography (0-50% AcOEt in hexanes).

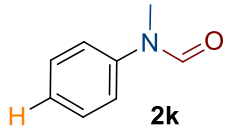


2i

4-(*N*-Methylformamido)benzoic acid; 59% (42 mg obtained from 66 mg of 4-(dimethylamino)benzoic acid); waxy solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.94 (s, 1H), 8.72

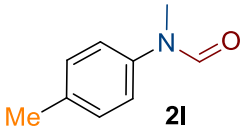
(s, 1H), 7.94 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 3.23 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6) δ 167.2, 162.6, 146.2, 131.1, 127.7, 120.5, 30.9; HRMS (ESI-TOF) m/z calc for $C_9H_8NO_3$ [M-H^+] 178.0504. Found 178.0506; Flash column chromatography (0-10% MeOH in DCM + 1% NH_3 aq.).

**4-(Dimethylamino)benzoic acid is not soluble in MeCN; a few drops of DMSO were added to achieve complete dissolution of the substrate.*



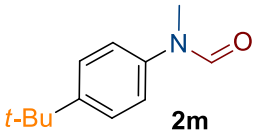
2k

***N*-Methyl-*N*-phenylformamide**; 68% (37 mg obtained from 48 mg of *N*-methyl-*N*-phenylformamide); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 7.43 – 7.34 (m, 2H), 7.31 – 7.20 (m, 1H), 7.20 – 7.09 (m, 2H), 3.30 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 162.3, 142.2, 129.6, 126.4, 122.3, 32.0; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[2]



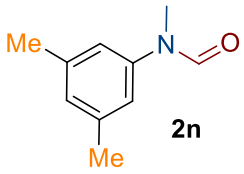
2l

***N*-Methyl-*N*-(p-tolyl)formamide;** 50% (30 mg obtained from 54 mg of *N,N,*4-trimethylaniline); waxy solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 3.29 (s, 3H), 2.36 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 162.4, 139.7, 136.4, 130.2, 122.6, 32.2, 20.9; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[2]



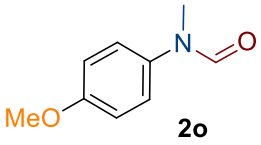
2m

***N*-(4-(*Tert*-butyl)phenyl)-*N*-methylformamide;** 48% (37 mg obtained from 71 mg of 4-(*tert*-butyl)-*N,N*-dimethylaniline); waxy solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 7.44 – 7.39 (m, 2H), 7.12 – 7.07 (m, 2H), 3.30 (s, 3H), 1.32 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 162.4, 149.6, 139.6, 126.5, 122.3, 34.5, 32.1, 31.3; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[2]



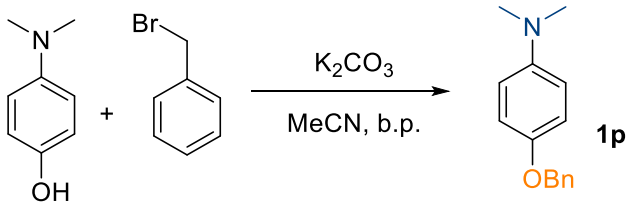
2n

***N*-(3,5-Dimethylphenyl)-*N*-methylformamide**; 45% (29 mg obtained from 60 mg of *N,N*,3,5-tetramethylaniline); waxy solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 6.91 (s, 1H), 6.78 (s, 2H), 3.28 (s, 3H), 2.33 (s, 6H); two rotamers ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 162.4, 162.4, 142.1, 139.4, 128.1, 128.0, 120.3, 120.2, 32.1, 21.3, 21.3; The spectroscopic data are in agreement with literature data.[3]



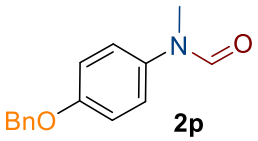
2o

***N*-(4-Methoxyphenyl)-*N*-methylformamide**; 20% (13 mg obtained from 60 mg of 4-methoxy-*N,N*-dimethylaniline); waxy solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8. 33 (s, 1H), 7.09 (d, *J* = 9.2 Hz, 2H), 6.92 (d, *J* = 9.1 Hz, 2H), 3.81 (s, 3H), 3.26 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 162.4, 158.3, 135.3, 124.7, 114.8, 55.5, 32.7; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[2]



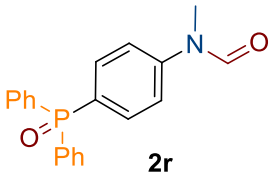
1p

4-(Benzyloxy)-*N,N*-dimethylaniline. The compound was prepared according to a literature procedure with slight modification. To a reaction ampule were added 4-(dimethylamino)phenol (200 mg, 1.458 mmol) and K_2CO_3 (201 mg, 1.458 mmol), followed by MeCN (3 mL). Benzyl bromide (1.325 mmol, 150 µL) was then added, and the reaction mixture was heated to reflux and stirred overnight. After completion, the reaction was quenched by addition of 10% aqueous NaOH. The aqueous phase was extracted with Et_2O (3 ×). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography (EtOAc/hexanes, 3:7) to afford the product (123 mg, 41%) as a brown waxy solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.41 – 7.36 (m, 2H), 7.36 – 7.28 (m, 1H), 6.93 (d, *J* = 9.1 Hz, 2H), 6.75 (d, *J* = 9.1 Hz, 2H), 5.02 (s, 2H), 2.88 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 146.0, 137.7, 128.5, 127.8, 127.5, 115.9, 114.7, 70.8, 41.7; The spectroscopic data are in agreement with literature data.[1]



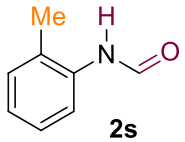
2p

***N*-(4-(Benzyloxy)phenyl)-*N*-methylformamide**; 17% (13 mg obtained from 74 mg of 4-(benzyloxy)-*N*,*N*-dimethylaniline); white solid; m.p. 88-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (bs, 1H), 7.54 – 7.46 (m, 5H), 7.14 – 7.07 (m, 2H), 7.05 – 6.95 (m, 2H), 5.08 (s, 2H), 3.27 (s, 3H); Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[4]



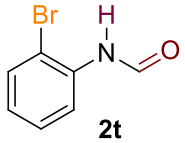
2r

***N*-(4-(Diphenylphosphoryl)phenyl)-*N*-methylformamide**; 62% (83 mg obtained from 122 mg of 4-(diphenylphosphino)-*N*,*N*-dimethylaniline); waxy solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.61 (bs, 1H), 7.72 – 7.64 (m, 6H), 7.58 – 7.53 (m, 2H), 7.51 – 7.45 (m, 4H), 7.29 – 7.21 (m, 2H), 3.33 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, Chloroform-*d*) δ 161.9, 145.21, 133.7, 133.6, 132.17, 132.15, 132.04, 132.02, 131.96, 128.7, 128.6, 121.0, 120.9, 31.5; ^{31}P NMR (202 MHz, Chloroform-*d*) δ 28.37; HRMS (ESI-TOF) m/z calc for $C_{20}H_{19}NO_2P$ [M+H$^+$] 336.1153. Found 336.1161.



2s

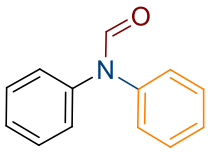
***N*-o-Tolylformamide**; 22% (12 mg obtained from 55 mg of *N,N,*2-trimethylaniline); colorless oil; mixture of two rotamers; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 – 8.52 (m, 1H), 8.44 (s, 0.5H), 7.90 – 7.88 (m, 0.7H), 7.82 (bs, 1.0H), 7.26 – 7.08 (m, 6.6H), 2.30 – 2.20 (m, 4.6H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 163.2, 159.1, 135.0, 134.6, 131.3, 130.6, 129.6, 128.5, 127.2, 126.9, 126.1, 125.5, 123.0, 120.6, 17.74, 17.70; HRMS (ESI-TOF) m/z calc for $C_8H_{10}NO$ [M+H$^+$] 136.0762. Found 136.0765; Flash column chromatography (0-30% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[5]



2t

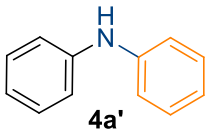
***N*-(2-Bromophenyl)formamide**; 22% (18 mg obtained from 80 mg of 2-bromo-*N,N*-dimethylaniline); red waxy solid; mixture of two rotamers; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 – 8.69 (m, 0.5H), 8.50 (s, 1H), 8.40 (d, *J* = 7.6 Hz, 1H), 7.70 – 7.59 (m, 1.0H), 7.56 (d, *J* =

7.9 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.29 – 7.26 (m, 0.6H), 7.12 – 7.05 (m, 0.5H), 7.01 (t, *J* = 7.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 161.4, 158.7, 133.5, 132.4, 128.7, 128.5, 126.4, 125.7, 123.1, 122.2, 118.8, 114.4, 112.9; Flash column chromatography (0-30% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[5]



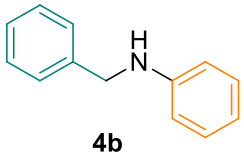
4a

***N,N*-Diphenylformamide**; 40% (32 mg obtained from 73 mg of *N*-methyl-*N*-phenylaniline); yellow solid; m.p. 70-71°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (s, 1H), 7.45 – 7.37 (m, 4H), 7.35 – 7.26 (m, 4H), 7.20 – 7.15 (m, 2H); two rotamers $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 161.8, 141.8, 139.6, 129.7, 129.2, 127.1, 126.9, 126.1, 125.1; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[2]



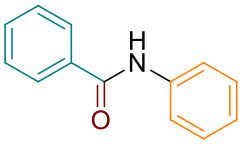
4a'

***N,N*-Diphenylformamide**; 25% (17 mg obtained from 73 mg of *N*-methyl-*N*-phenylaniline); white solid; m.p. 50-51°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (dd, *J* = 8.3, 7.6 Hz, 5H), 7.09 (d, *J* = 7.6 Hz, 4H), 6.94 (t, *J* = 7.3 Hz, 2H), 5.70 (bs, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 143.1, 129.3, 121.0, 117.8; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[3]



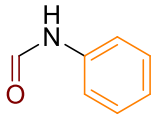
4b

***N*-Benzylaniline**; 6% (4 mg obtained from 79 mg of *N*-benzyl-*N*-methylaniline); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.34 (m, 4H), 7.35 – 7.28 (m, 1H), 7.24 – 7.17 (m, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 4.35 (s, 2H), 4.04 (s, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 148.2, 139.5, 129.3, 128.7, 127.5, 127.3, 117.6, 112.9, 48.3; Flash column chromatography (0-15% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[6]



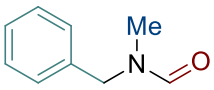
4b'

***N*-Phenylbenzamide**; 6% (5 mg obtained from 79 mg of *N*-benzyl-*N*-methylaniline); white solid; m.p.162-163°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.80 (m, 3H), 7.71 – 7.61 (m, 2H), 7.61 – 7.53 (m, 1H), 7.53 – 7.45 (m, 2H), 7.42 – 7.33 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 165.8, 137.9, 135.0, 131.8, 129.1, 128.8, 127.0, 124.6, 120.2; Flash column chromatography (15-30% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[7]



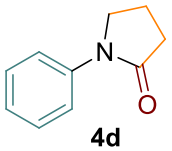
4b''

N-Phenylformamide; 28% (14 mg obtained from 79 mg of *N*-benzyl-*N*-methylaniline); yellow oil; mixture of rotamers; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.71 – 8.65 (m, 1H), 8.42 – 8.36 (m, 2H), 7.55 – 7.51 (m, 2H), 7.40 – 7.29 (m, 4H), 7.23 – 7.16 (m, 1H), 7.16 – 7.08 (m, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.7, 159.1, 136.9, 136.7, 129.8, 129.1, 125.3, 124.8, 120.0, 118.8; Flash column chromatography (30-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[5]



4c

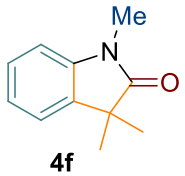
***N*-Benzyl-*N*-methylformamide**; 54% (32 mg obtained from 54 mg of *N,N*-dimethyl-1-phenylmethanamine); colorless oil; mixture or rotamers in ratio 1:0.75; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (s, 1H), 8.15 (s, 0.75H), 7.41 – 7.16 (m, 9H), 4.51 (s, 1.6H), 4.38 (s, 2H), 2.84 (s, 2.3H), 2.77 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 162.8, 162.6, 135.8, 128.9, 128.7, 128.3, 128.1, 127.7, 127.4, 53.5, 47.8, 34.1, 29.5; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[8]



4d

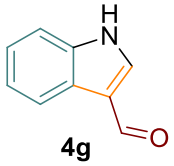
1-Phenylpyrrolidin-2-one; 39% (25 mg obtained from 59 mg of 1-phenylpyrrolidine); white solid; m.p. 67-68°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.52 (m, 2H), 7.41 – 7.32 (m, 2H), 7.19 – 7.10 (m, 1H), 3.85 (t, *J* = 7.0 Hz, 2H), 2.60 (t, *J* = 8.1 Hz, 2H), 2.21 – 2.09 (m, 2H);

$^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 174.2, 139.4, 128.8, 124.5, 120.0, 48.8, 32.8, 18.0; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[2]



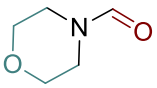
4f

1,3,3-Trimethylindolin-2-one; 35% (25 mg obtained from 69 mg of 1,3,3-trimethyl-2-methyleneindoline); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.21 (m, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.21 (s, 3H), 1.37 (s, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 181.4, 142.6, 135.9, 127.6, 122.5, 122.2, 108.0, 44.2, 26.2, 24.4; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[3]



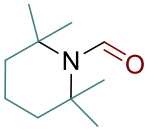
4g

1H-Indole-3-carbaldehyde; 41% (24 mg obtained from 70 mg of gramine); yellow solid; 196-197°C ; 1:1 EtOAc/hexane,^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.08 (s, 1H), 8.74 (bs, 1H), 8.36 – 8.28 (m, 1H), 7.85 (d, *J* = 3.1 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.38 – 7.30 (m, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-*d*) δ 185.5, 138.9, 137.5, 124.6, 123.9, 122.6, 121.3, 118.6, 112.9; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[9]



4h

Morpholine-4-carbaldehyde; 59% (27 mg obtained from 40 mg of 4-methylmorpholine); colorless oil; 27 mg; flash chromatography 10% MeOH:DCM; mixture of rotamers: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 3.70 – 3.60 (m, 4H), 3.58 – 3.51 (m, 2H), 3.40 – 3.35 (m, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 160.9, 67.2, 66.4, 45.8, 40.6; Flash column chromatography (0-10% MeOH:DCM); The spectroscopic data are in agreement with literature data.[8]



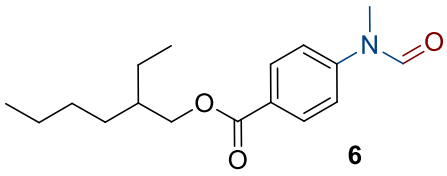
4i

2,2,6,6-Tetramethylpiperidine-1-carbaldehyde; 64%*; waxy solid; crude reaction mixture; mixture of rotamers: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.68 (s, 1H), 1.70 – 1.64 (m, 2H), 1.63 – 1.56 (m, 4H), 1.41 – 1.34 (m, 12H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 168.0, 54.9, 35.4, 27.9, 16.7; The spectroscopic data are in agreement with literature data.[10]

* the product **4i** could not be separated from Thioxanthone **TX-III**; the reaction yield was determined by ^{1}H NMR using 1,3,5- trimethoxybenzene as internal standard.

6. Formylation of *Padimate O*

The reaction was performed according to the general procedure (see S4).

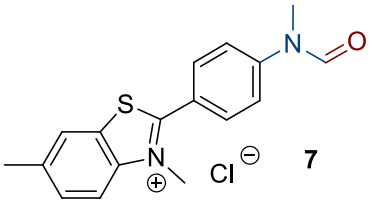


6

2-Ethylhexyl 4-(*N*-methylformamido)benzoate; 75%; (87 mg obtained from 111 mg of Padimate O); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 8.09 – 8.04 (m, 2H), 7.25 – 7.20 (m, 2H), 4.23 (dt, *J* = 8.5, 4.2 Hz, 2H), 3.34 (s, 3H), 1.71 (p, *J* = 6.1 Hz, 1H), 1.50 – 1.22 (m, 8H), 0.93 (t, *J* = 7.5 Hz, 3H), 0.91 – 0.86 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 165.8, 161.9, 145.9, 131.1, 128.0, 120.6, 67.5, 38.9, 31.5, 30.6, 29.0, 24.0, 23.0, 14.0, 11.1; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[11]

7. Formylation of *Thioflavin T*

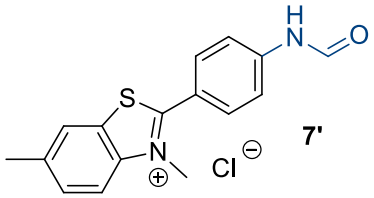
The reaction was performed according to the general procedure (see S4), with a minor modification: irradiation was carried out using a 440 nm Kessil lamp (40 W) in a MeCN:DMSO mixture, as Thioflavin T is insoluble in MeCN.



7

3,6-Dimethyl-2-(4-(*N*-methylformamido)phenyl)benzo[d]thiazol-3-ium chloride; 36% (48 mg obtained from 113 mg of Thioflavin T); yellow solid; m.p. 197-198°C; ^{1}H NMR (400 MHz, Methanol-d_4) δ 8.85 (s, 1H), 8.20 (d, *J* = 9.3 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 7.83 (d, *J* = 8.2 Hz,

1H), 7.73 (d, *J* = 8.7 Hz, 2H), 4.34 (s, 3H), 3.41 (s, 3H), 2.64 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Methanol-d_4) δ 172.8, 162.6, 147.1, 140.9, 140.3, 131.7, 131.6, 130.0, 123.2, 122.0, 121.2, 116.7, 37.2, 30.0, 20.2; HRMS (ESI-TOF) m/z calc for $C_{17}H_{17}N_2OS$ [M^+] 297.1062. Found 297.1064; Flash column chromatography (0-20% AcOEt in hexanes).

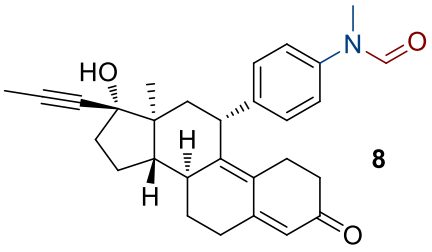


7'

2-(4-formamidophenyl)-3,6-dimethylbenzo[d]thiazol-3-ium chloride; 7% (determined by ^{1}H-NMR using 1,3,5- trimethoxybenzene as internal standard); not isolated in pure form, mixture of **2t** and **2t'** in ratio 1:0.4; HRMS (ESI-TOF) m/z calc for $C_{16}H_{15}N_2OS$ [M^+] 283.0905. Found 283.0907; Flash column chromatography (0-20% AcOEt in hexanes).

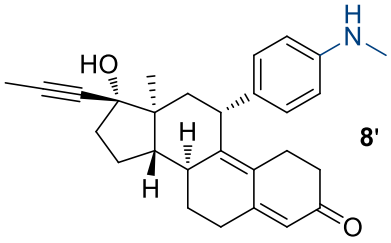
8. Formylation of *Mifepristone*

The reaction was performed according to the general procedure (see S4), with a minor modification: the reaction was stopped after 8 h, as prolonged reaction time led to product decomposition.



8

N-(4-((8S,11R,13S,14S,17S)-17-hydroxy-13-methyl-3-oxo-17-(prop-1-yn-1-yl)-2,3,6,7,8,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-11-yl)phenyl)-N-methylformamide; 40% (71 mg obtained from 172 mg of Mefipristone); yellow solid m.p. 149-150 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.45 (d, *J* = 13.9 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 5.77 (s, 1H), 4.41 (d, *J* = 7.4 Hz, 1H), 3.28 (s, 2H), 2.77 – 2.72 (m, 1H), 2.59 – 2.56 (m, 2H), 2.47 – 2.39 (m, 3H), 2.37 – 2.32 (m, 1H), 2.30 – 2.25 (m, 2H), 2.23 – 2.20 (m, 1H), 2.04 – 2.00 (m, 1H), 1.96 – 1.90 (m, 2H), 1.88 (s, 3H), 1.75 – 1.69 (m, 2H), 1.50 – 1.43 (m, 1H), 1.36 – 1.31 (m, 1H), 0.49 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 199.2, 162.2, 156.4, 145.1, 142.9, 139.9, 129.8, 128.1, 123.2, 122.2, 82.7, 82.2, 80.0, 49.7, 46.8, 40.0, 39.14, 39.10, 38.9, 36.8, 32.0, 31.1, 27.3, 25.9, 23.3, 13.9, 3.8; HRMS (ESI-TOF) m/z calc for $C_{29}H_{33}NO_3Na$ [M^++Na] 466.2358. Found 466.2360; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[12]

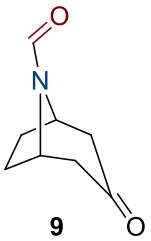


8'

(8S,11R,13S,14S,17S)-17-hydroxy-13-methyl-11-(4-(methylamino)phenyl)-17-(prop-1-yn-1-yl)-6,7,8,11,12,13,14,15,16,17-decahydro-1H-cyclopenta[a]phenanthren-3(2H)-one; 18% (30 mg obtained from 172 mg of Mefipristone); yellow solid m.p 230-231°C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.96 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 7.9 Hz, 2H), 5.74 (s, 1H), 4.33 (d, *J* = 7.0 Hz, 1H), 3.66 (bs, 1H), 2.80 (s, 3H), 2.78 – 2.73 (m, 1H), 2.57 – 2.55 (m, 2H), 2.45 – 2.41 (m, 2H), 2.35 – 2.30 (m, 3H), 2.24 – 2.21 (m, 2H), 2.01 – 1.98 (m, 1H), 1.95 – 1.90 (m, 1H), 1.88 (s, 3H), 1.72 – 1.68 (m, 2H), 1.49 – 1.42 (m, 1H), 1.33 (dd, *J* = 11.1, 4.7 Hz, 1H), 0.54 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 199.6, 156.9, 147.1, 146.7, 132.8, 129.1, 127.6, 122.7, 112.5, 82.5, 82.3, 80.2, 49.8, 46.8, 39.6, 39.1, 38.90, 38.85, 36.9, 31.1, 30.8, 27.4, 25.8, 23.3, 13.7, 3.8; HRMS (ESI-TOF) m/z calc for $C_{28}H_{33}NNaO_2$ [M^++Na] 438.2409. Found 438.2403; Flash column chromatography (0-50% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[12]

9. Formylation of *Tropinone*

The reaction was performed according to the general procedure (see S4).



9

3-oxo-8-Azabicyclo[3.2.1]octane-8-carbaldehyde; 67% (41 mg obtained from 56 mg of Tropinone); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 4.90 – 4.81 (m, 1H), 4.41 – 4.33 (m, 1H), 2.66 (dd, *J* = 16.1, 4.7 Hz, 1H), 2.56 (dd, *J* = 16.0, 4.7 Hz, 1H), 2.49 – 2.44 (m, 1H), 2.42 – 2.36 (m, 1H), 2.10 – 2.01 (m, 2H), 1.78 – 1.67 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 206.7, 158.1, 53.5, 50.7, 49.0, 48.8, 29.3, 28.4; Flash column chromatography (0-100% AcOEt in hexanes); The spectroscopic data are in agreement with literature data.[13]

10. Deformylation of *N*-Methyl-*N*-Phenylformamide 2a *via* Base Hydrolysis

Crude *N*-Methyl-*N*-phenylformamide **2a** (87 mg, 0.635 mmol) was dissolved in EtOH (5 mL). Then, H_2O (1 mL) and NaOH (101 mg, 2.54 mmol, 4.0 equiv) were added. The reaction mixture was stirred at room temperature overnight. After completion, the mixture was

concentrated under reduced pressure using a rotary evaporator. The reaction yield (84%) was determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as an internal standard.

11. Deformylation of *N*-Methyl-*N*-Phenylformamide 2a *via* Acid Hydrolysis

Crude *N*-Methyl-*N*-phenylformamide **2a** (72 mg, 0.53 mmol) was dissolved in MeOH (5 mL). Then, 3M aqueous H_2SO_4 (1.75 mL, 5.3 mmol, 10.0 equiv) was added. The reaction mixture was stirred at room temperature overnight. After completion, the mixture was neutralized to pH 7–8 by the addition of saturated aqueous $NaHCO_3$ solution. MeOH was removed under reduced pressure using a rotary evaporator. The residue was extracted multiple times with AcOEt (*Caution:* N-*Methylpyridin-4-amine* ***3a*** *remains in the aqueous phase for an extended period*). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The yield (78%) was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

12. Deformylation of *N*-Methyl-*N*-Phenylformamide 2a *via* Irradiation by UV-C Light

General Remarks for Photochemical Deformylation Reaction:

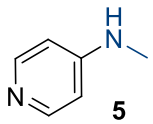
The photochemical deformylation reaction was performed in a Rayonet-type, self-made photoreactor consisting of eight UV-C lamps (Osram, Puritec, HNS, S 9W, λmax 254 nm). (The distance between the reaction vessel and the light source was 1.5 cm) For the detailed plan for the construction of the photoreactor, see ref.[14]

Rayonet-type, self-made photoreactor consisting of the following elements:

cooling system ,temperature control, mixing system
test tube racks, quartz vial, 8 x UV-C lamps
(*Osram, Puritec, HNS, S 9W*)

Picture 9. Rayonet-type, self-made photoreactor.

The quartz vial containing crude *N*-Methyl-*N*-phenylformamide **2a** (36 mg, 0.26 mmol) was placed in a glove box, and degassed MeCN (4 mL) was added. The vial was sealed with a septum wrapped in aluminum foil and transferred to a self-made Rayonet-type photoreactor (Picture 9). The reaction mixture was irradiated with eight UV-C lamps (9W, 254 nm) at an internal temperature of 25-35°C for 6 hours (The distance between the reaction vessel and the light source was 1.5 cm. After evaporation of the solvent, the residue was dissolved in DCM and purified on column chromatography (1:9) (MeOH:DCM+ 1% (25% aq. solution of NH_3)) to afford 21 mg (73% yield) of *N*-methylpyridin-4-amine **5** as a white solid.



5

m.p. 124-125°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 4.6 Hz, 2H), 6.41 (d, *J* = 5.7 Hz, 2H), 4.41 (s, 1H), 2.84 (d, *J* = 4.9 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 154.3, 149.8, 107.2, 29.4; The spectroscopic data are in agreement with literature data.[15]

13. Literature:

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14. UV–Visible Characterization and Photophysical Studies

To further elucidate the photophysical features of the photocatalytic system, UV–Vis absorption and emission studies were performed for thioxanthone (**TH-III**), the model substrate DMAP (**1a**), and their combinations under conditions relevant to the reaction.

The UV–Vis absorption spectrum of **TH-III** in MeCN exhibits a strong absorption band in the near-UV region with a tail extending into the visible range up to ca. 400–410 nm (Figure 3). Increasing the concentration of **TH-III** from 3×10^{-4} M to 1×10^{-2} M, corresponding to the reaction conditions, does not result in any bathochromic shift or spectral broadening (Figure 4), indicating the absence of aggregation-induced effects. Similarly, oxygenation of the **TH-III** solution does not influence its absorption profile (Figure 5), suggesting that molecular oxygen does not perturb the ground-state electronic structure of the photocatalyst.

To investigate the possibility of donor–acceptor complex formation, UV–Vis spectra of **TH-III** and DMAP (**1a**) were recorded in a 1:1 ratio at room temperature and at 40 °C (reaction temperature). No new absorption bands or shifts were observed relative to the individual components (Figures 6 and 7), ruling out the formation of an electron donor–acceptor (EDA) complex that could account for visible-light absorption at longer wavelengths.

The emission spectrum of **TH-III** in oxygenated MeCN shows very weak fluorescence, with a quantum yield of 0.27%, which is comparable to that measured in degassed MeCN (0.28%, Figure 8). This behavior is consistent with efficient intersystem crossing and the population of the triplet excited state, in agreement with the known photosensitizing properties of thioxanthone.

The 450 nm LED light source used in this study displays a broad emission profile spanning approximately 400–500 nm (Figures 9 and 10). Overlaying the absorption spectrum of **TH-III** with the emission spectrum of the LED lamp reveals a narrow but significant spectral overlap in the 400–410 nm region (Figure 11), which enables effective excitation of the photocatalyst despite the absorption maximum of **TH-III** being located at shorter wavelengths.

Key conclusions from photophysical studies

- The absorption profile of thioxanthone is unaffected by concentration, oxygenation, or the presence of tertiary amines.
- No donor–acceptor complex formation between **TH-III** and DMAP is observed under reaction conditions.
- Thioxanthone exhibits negligible fluorescence, consistent with a triplet excited state responsible for energy transfer to molecular oxygen.
- The broad-band emission of the 450 nm LED lamp provides sufficient spectral overlap to enable photocatalyst excitation under mild and selective reaction conditions.

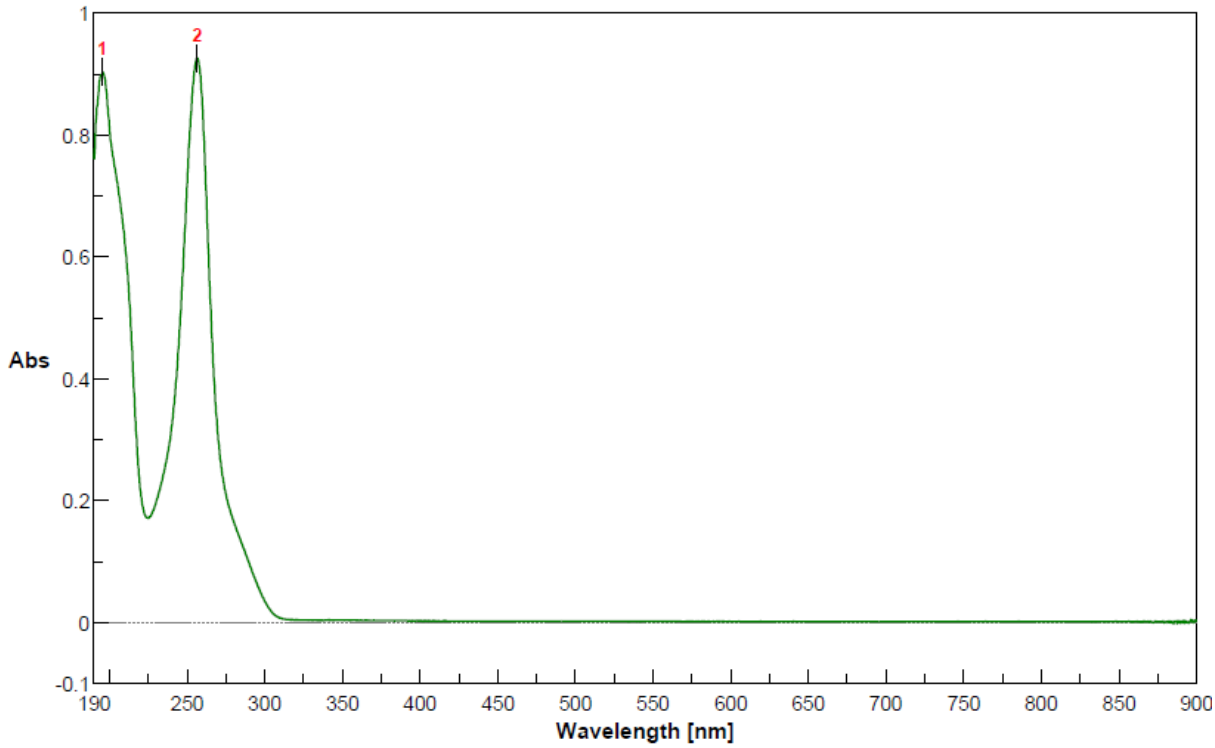


Figure 1. UV-Vis spectra of 4-(dimethylamino)pyridine (DMAP) **1a** in MeCN.

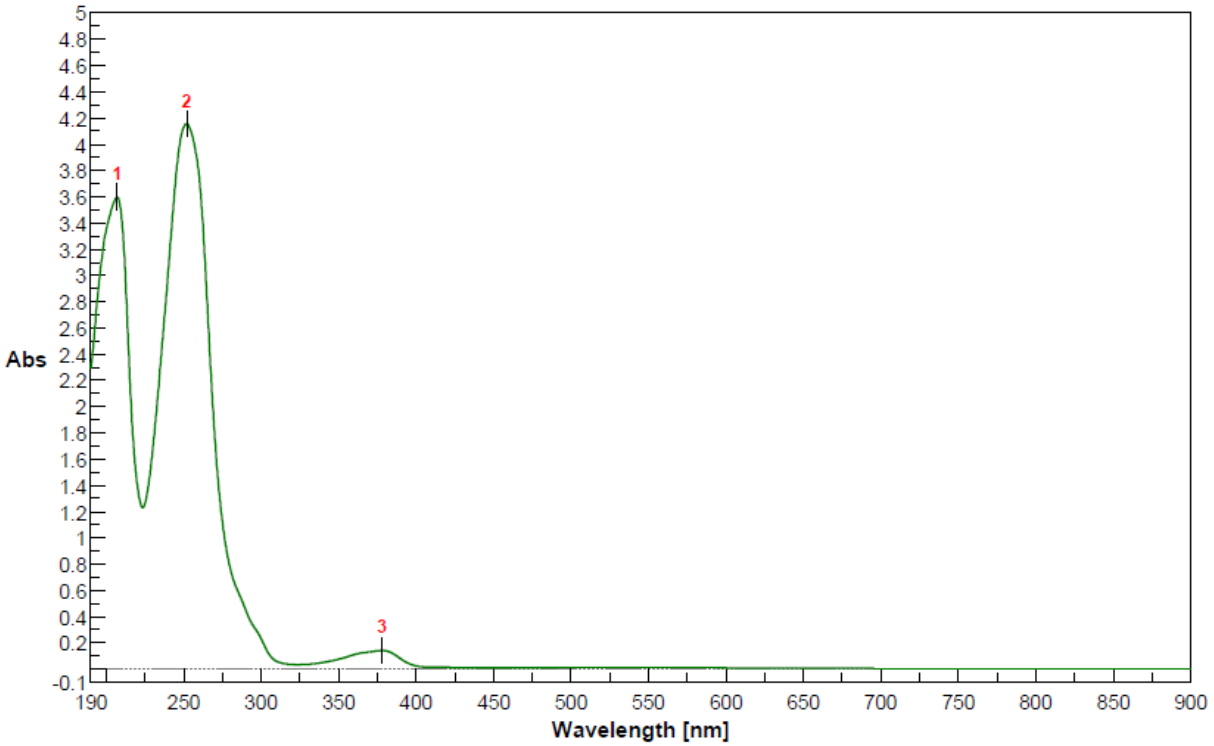


Figure 2. UV-Vis spectra of the crude reaction mixture: **2a** and thioxanthone **TH-III** in MeCN.

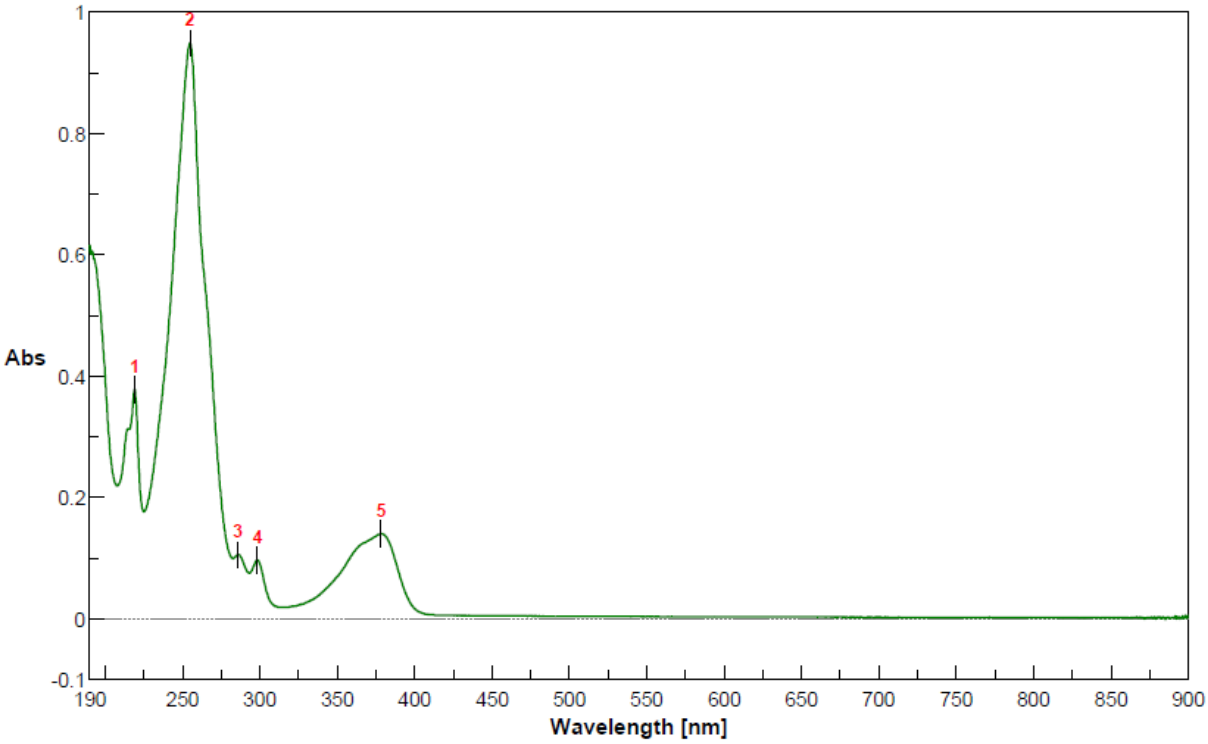


Figure 3. UV–Vis spectra of thioxanthone **TH-III** in MeCN (C = 3 × 10^{-4} M) at room temperature.

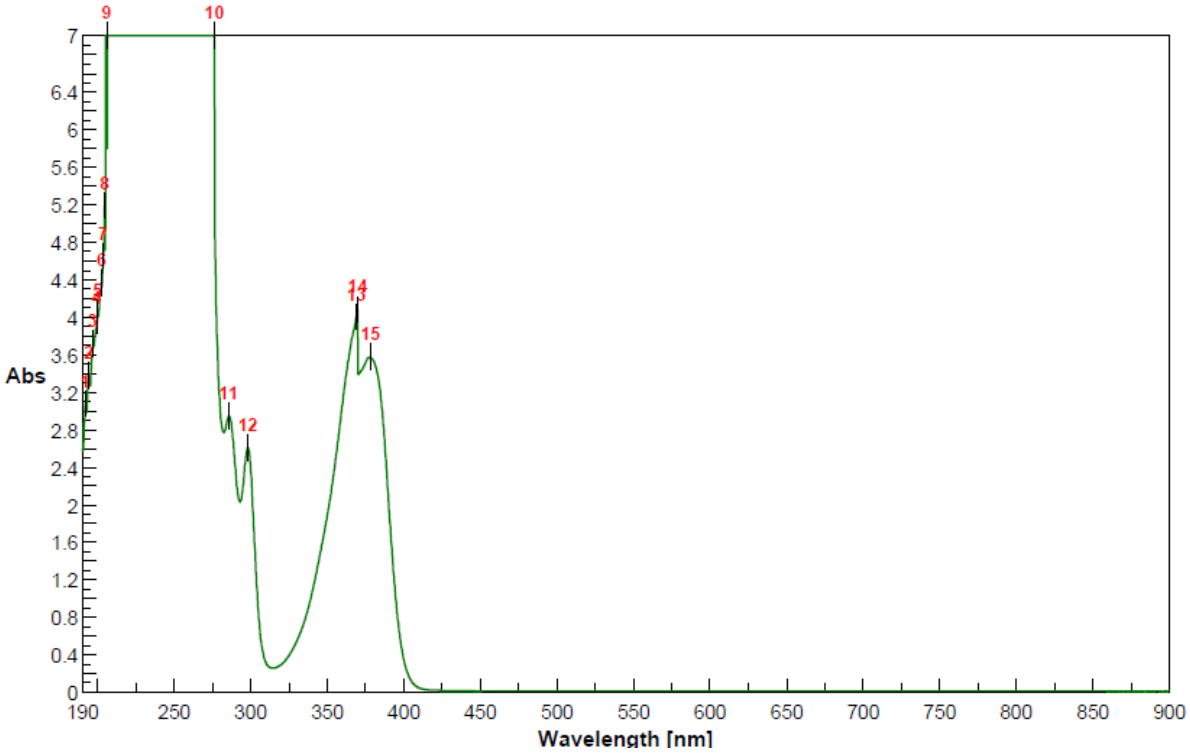


Figure 4. UV–Vis spectra of thioxanthone **TH-III** in MeCN (C = 1 × 10^{-2} M) under conditions analogous to the reaction, at room temperature.

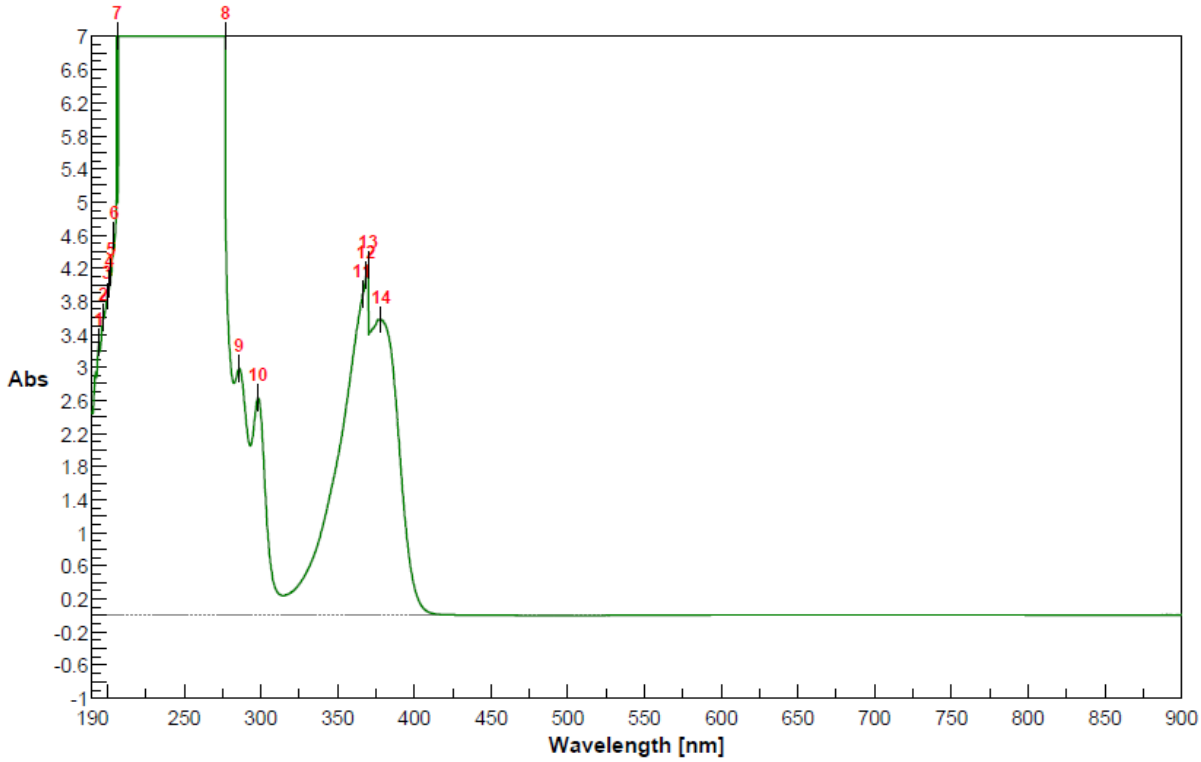


Figure 5. UV–Vis spectra of thioxanthone **TH-III** in oxygenated MeCN (C = 1 × 10^{-2} M) at room temperature.

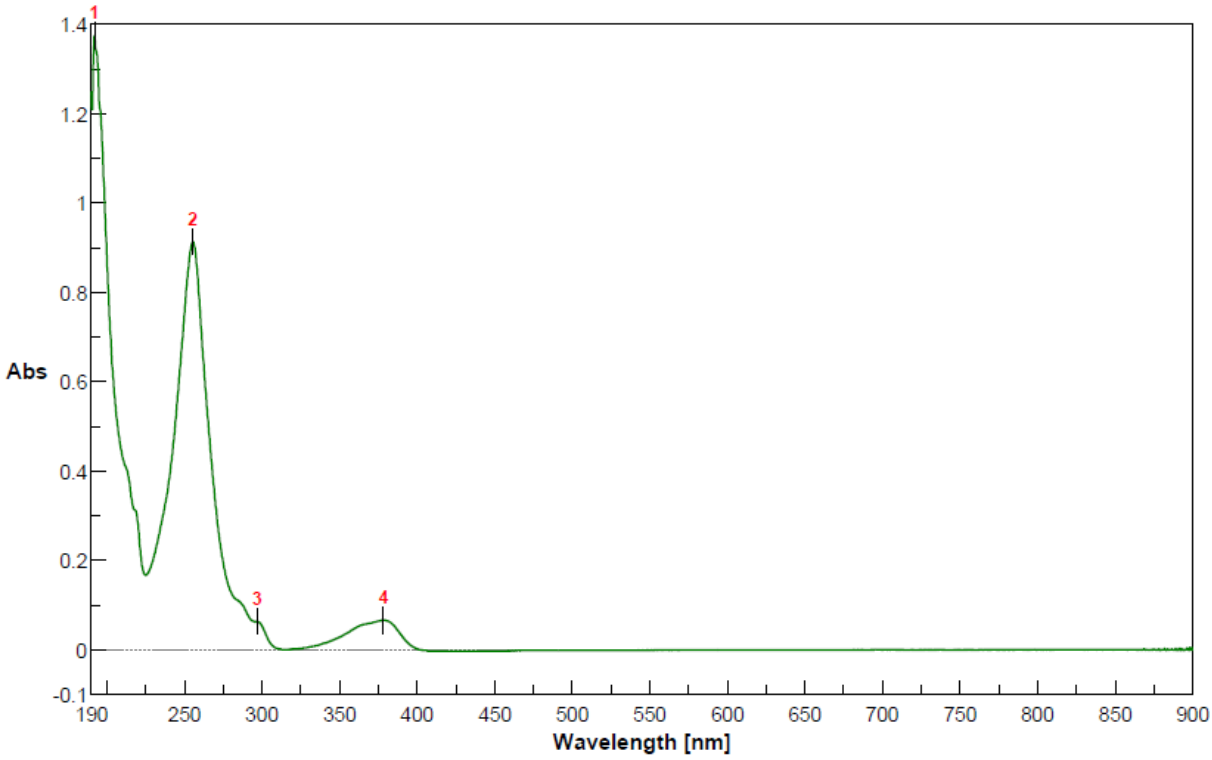


Figure 6. UV–Vis spectra of thioxanthone **TH-III** and DMAP (**1a**) in a 1:1 ratio (C = 1 × 10^{-4} M) at room temperature.

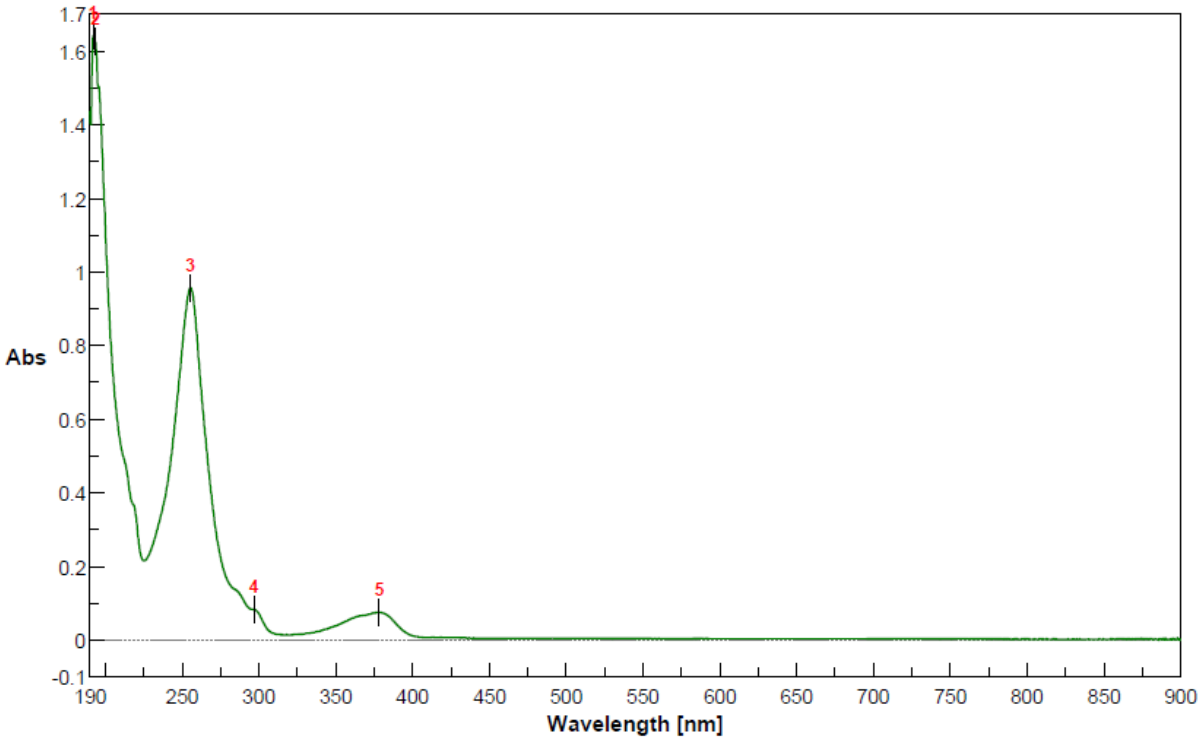


Figure 7. UV–Vis spectra of thioxanthone **TH-III** and DMAP (**1a**) in a 1:1 ratio (C = 1 × 10^{-4} M) at 40 °C (reaction conditions).

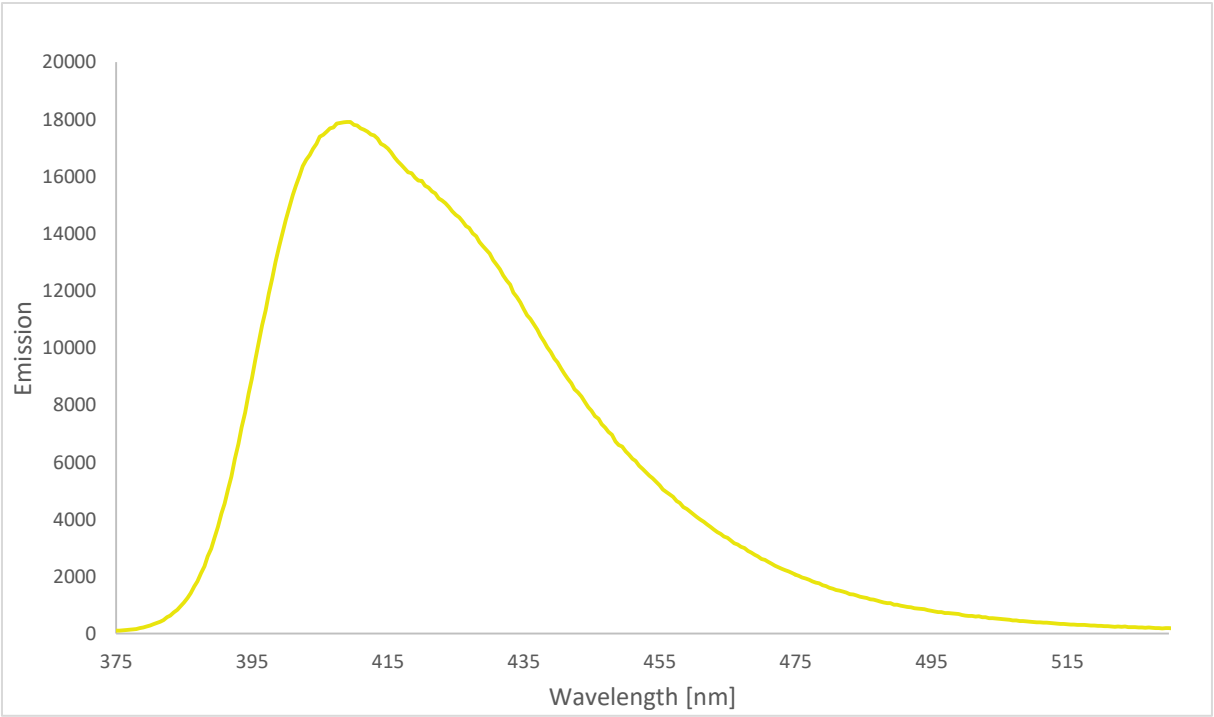


Figure 8. Emission spectrum of thioxanthone **TH-III** in oxygenated MeCN.

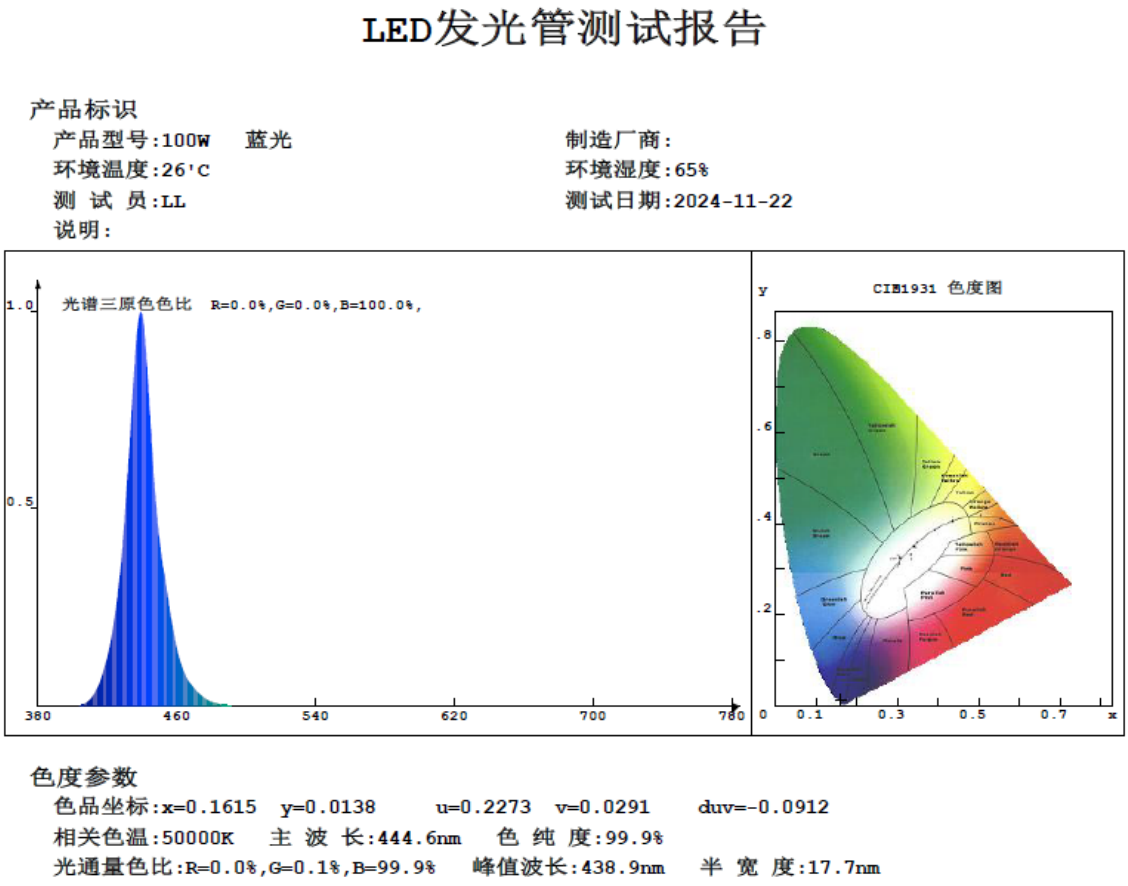


Figure 9. Specifications and manufacturer-declared emission spectrum of the 450 nm, 100 W LED lamp used in the study.

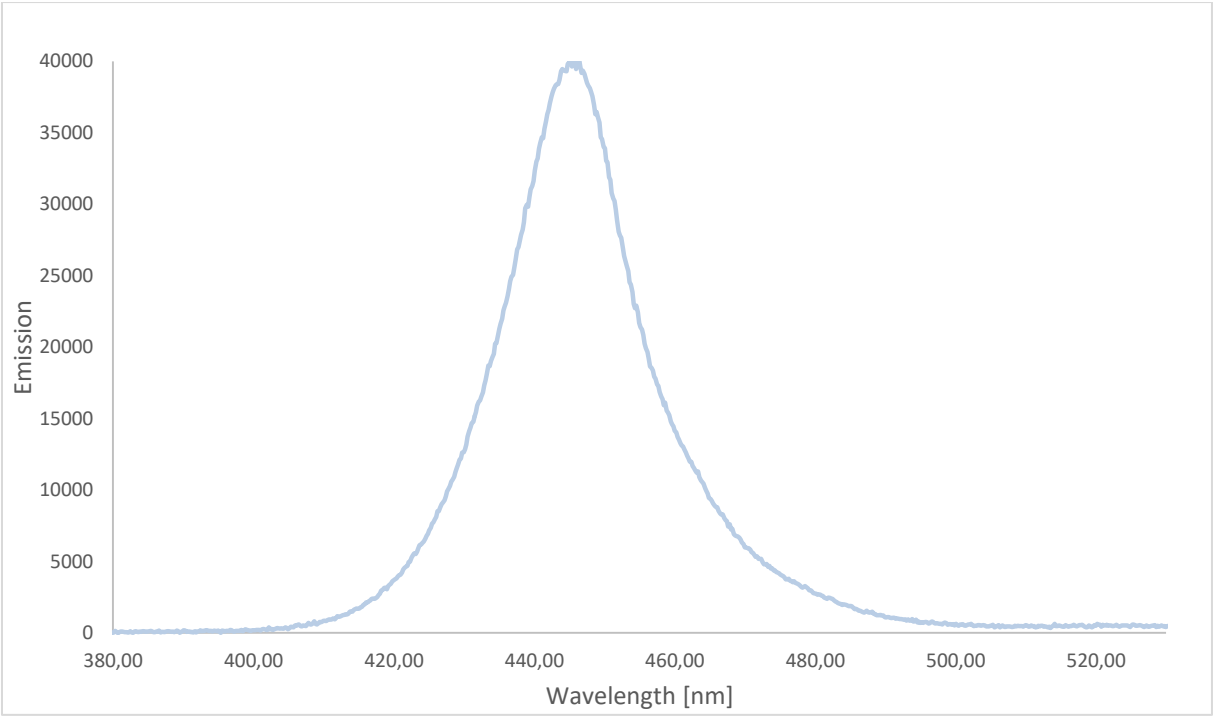
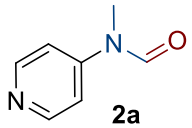


Figure 10. Emission spectrum of the 450 nm, 100 W LED lamp, measured by our team.

^{1}H NMR (400 MHz, Chloroform-*d*)



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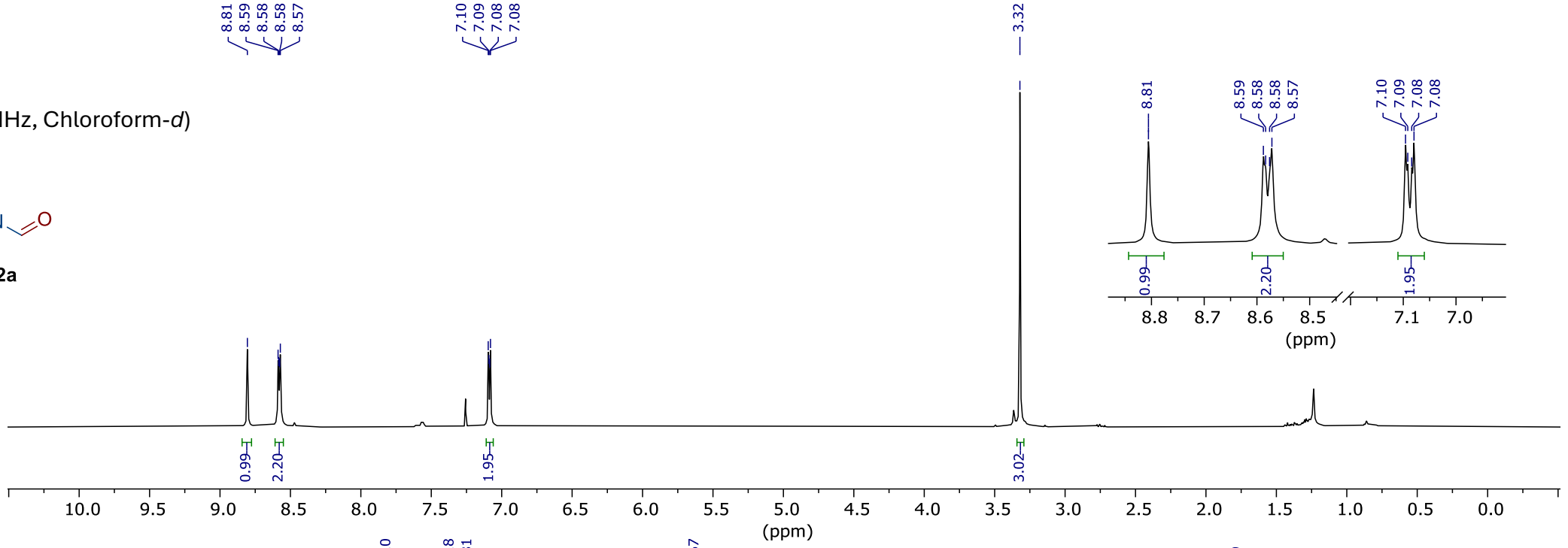
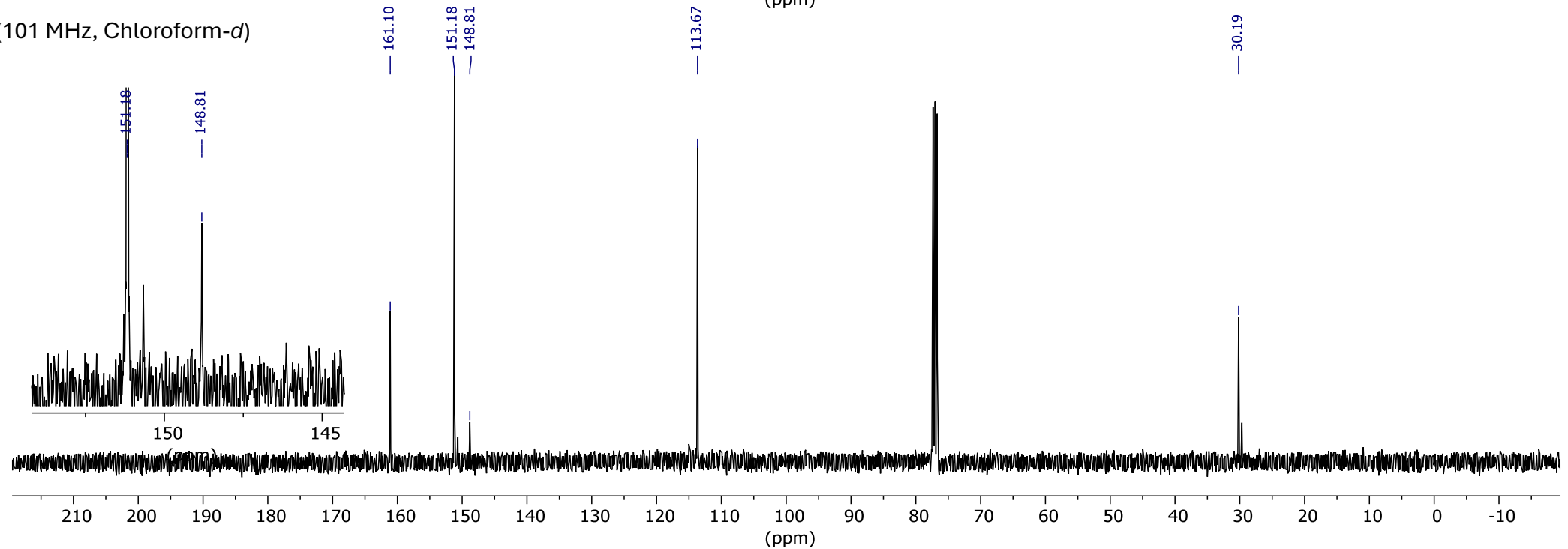
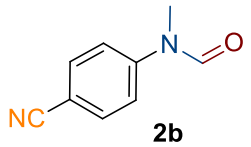


^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



^{1}H NMR (400 MHz, Chloroform-*d*)



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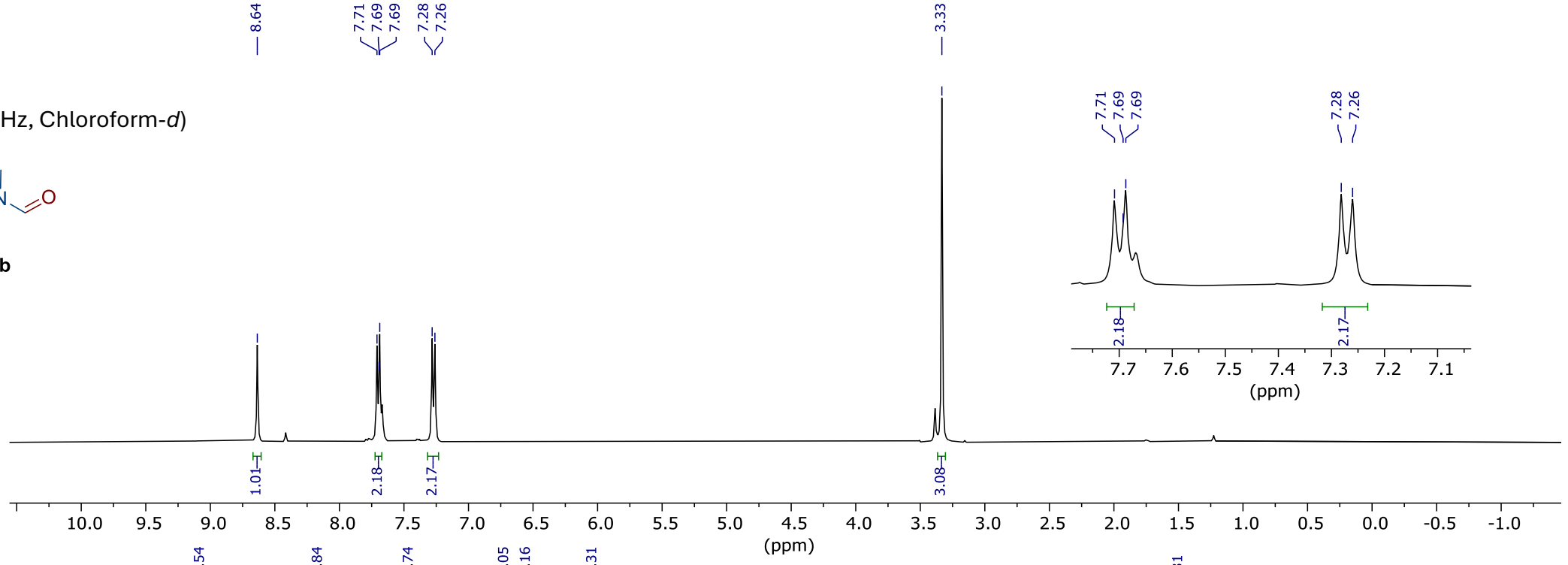
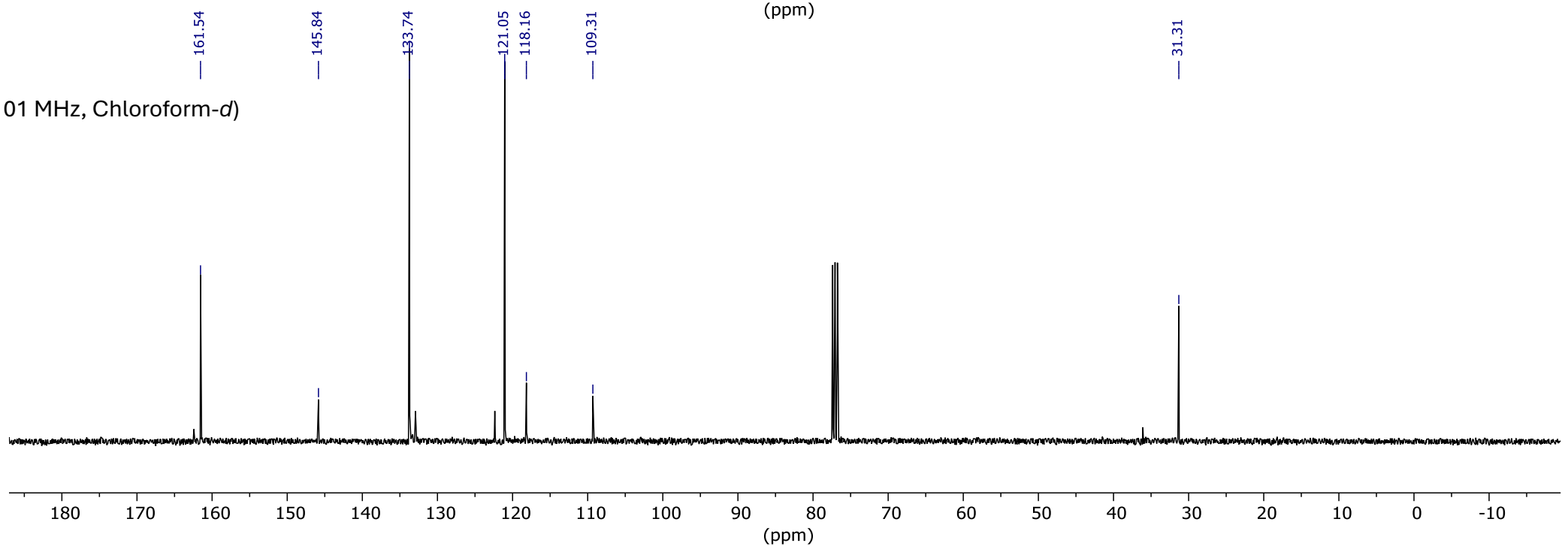


^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



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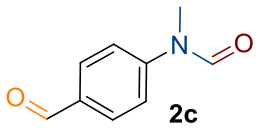

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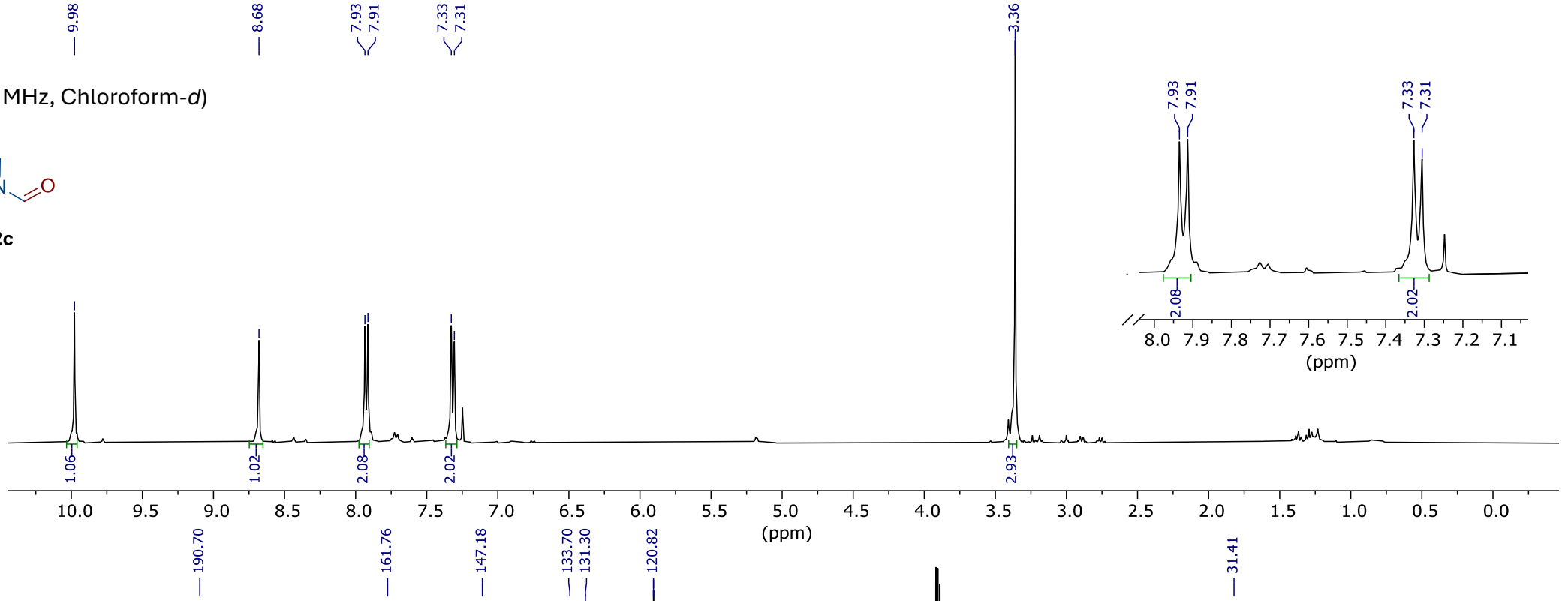
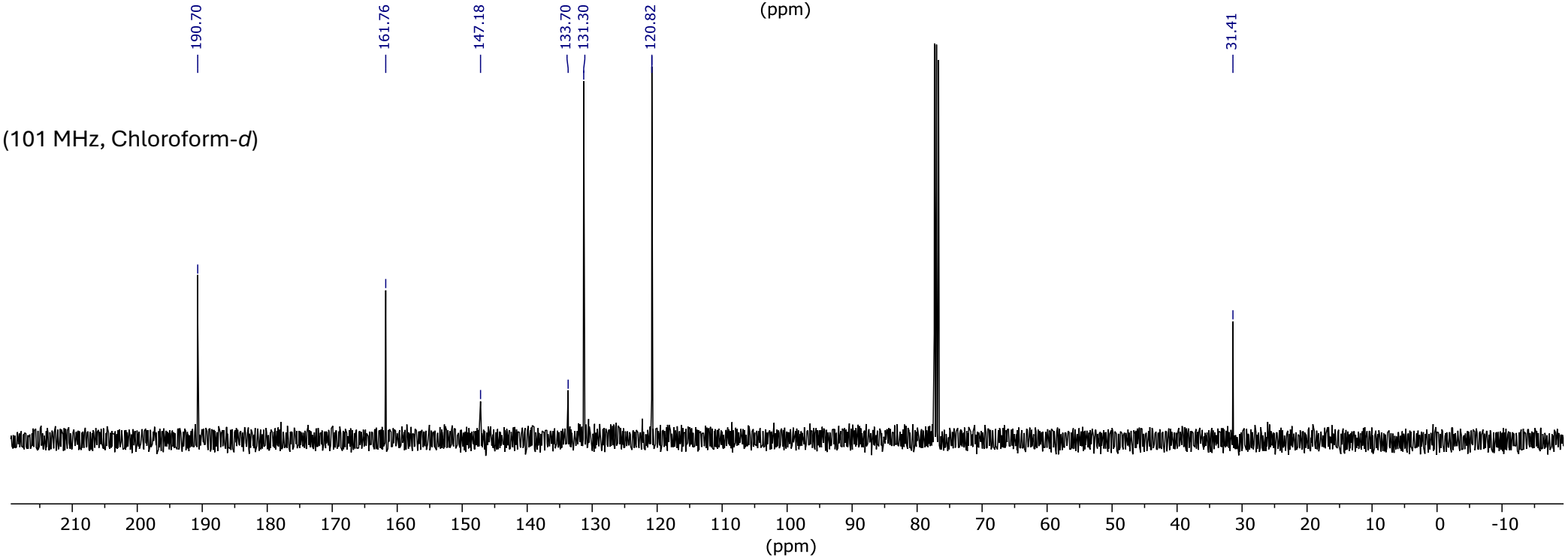


^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



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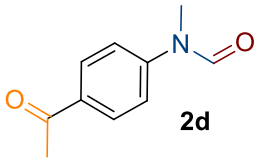

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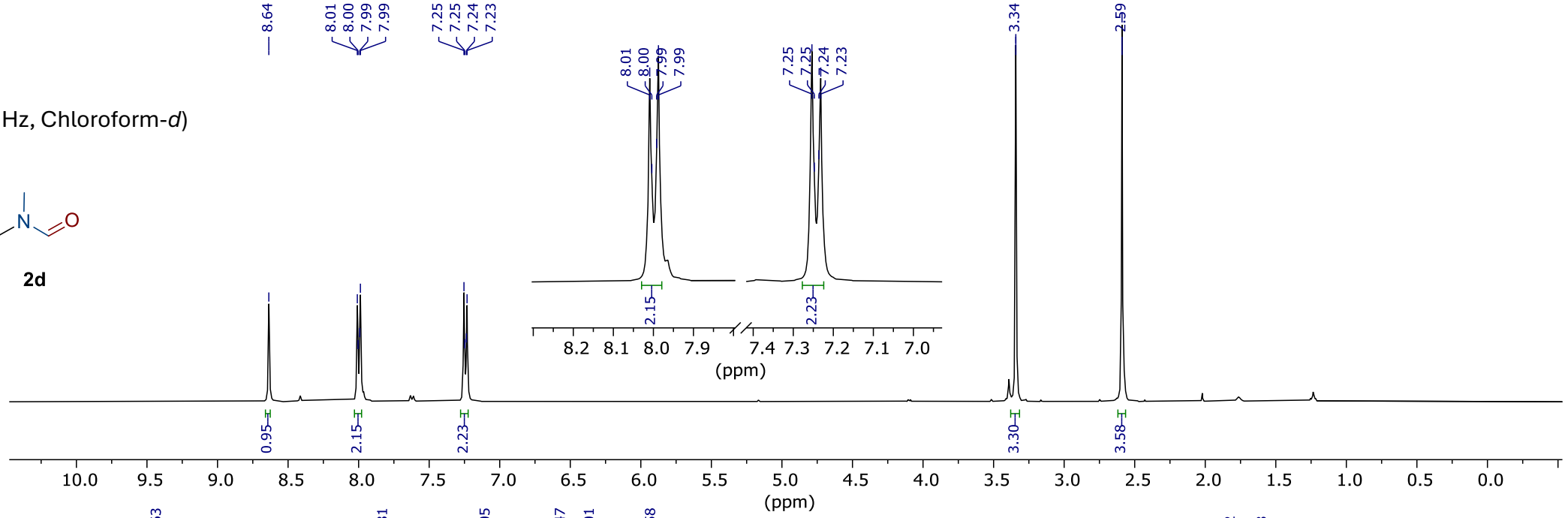
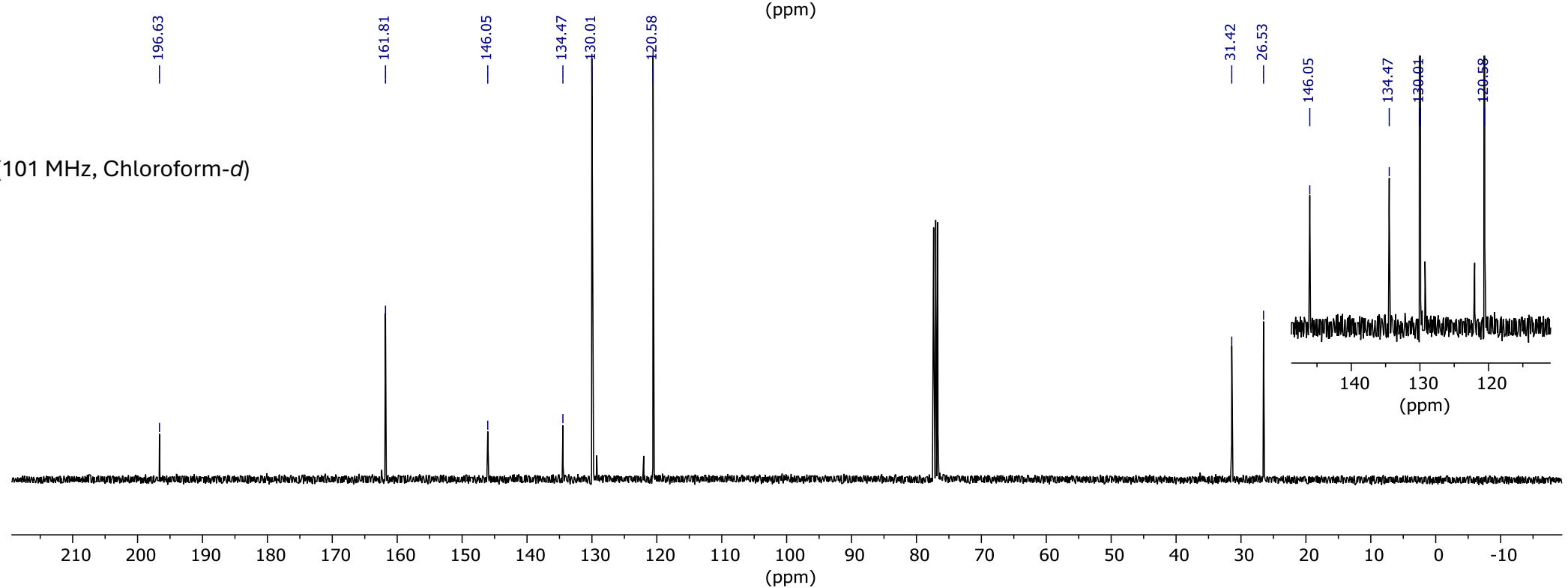
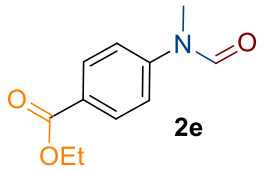


^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



^{1}H NMR (400 MHz, Chloroform-*d*)



2e

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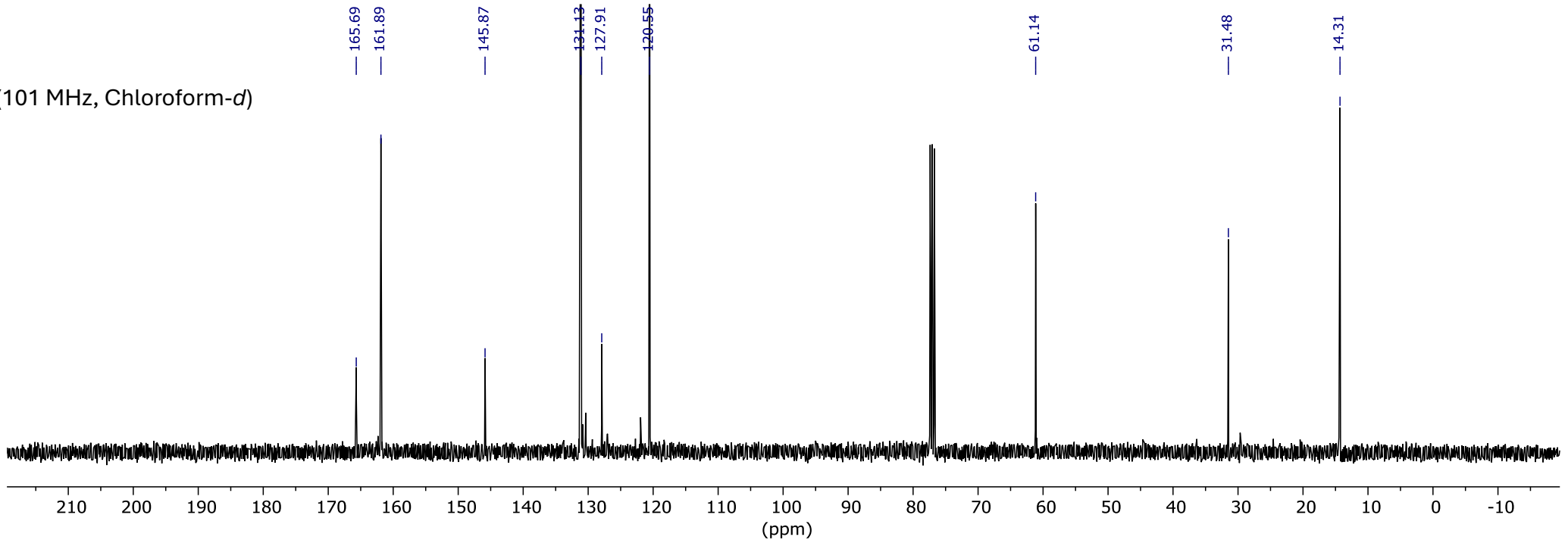
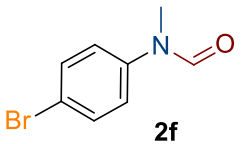


^{1}H NMR (400 MHz, Chloroform-*d*)



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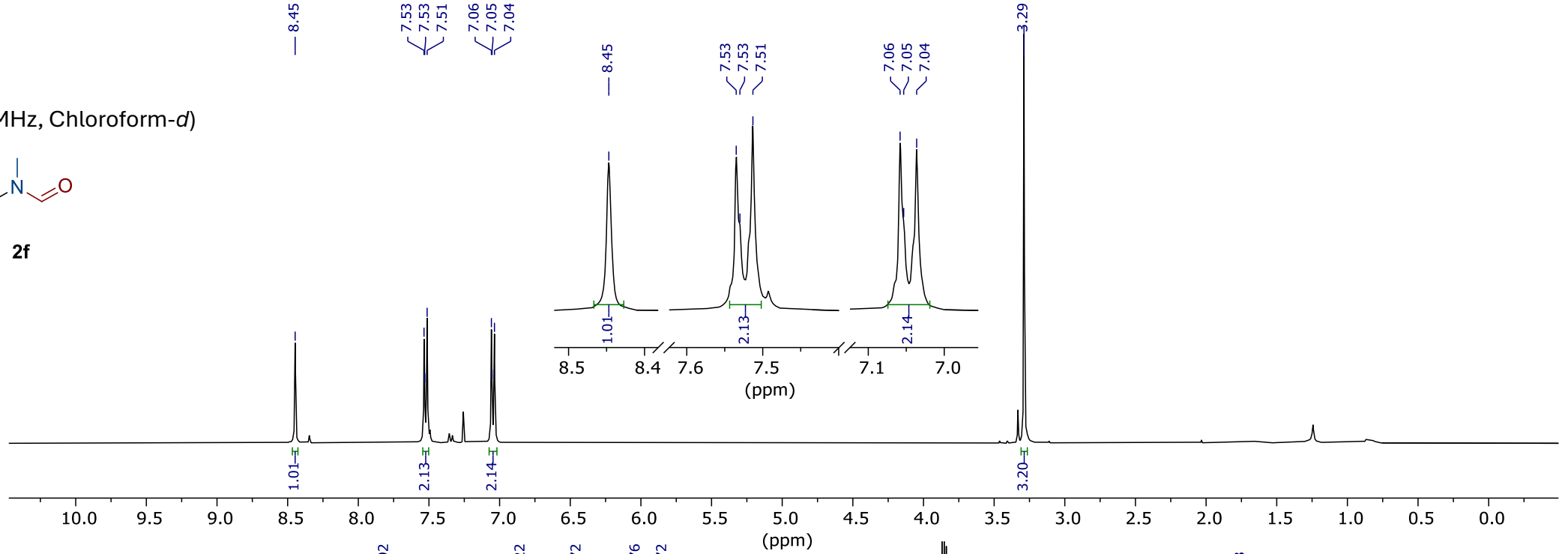
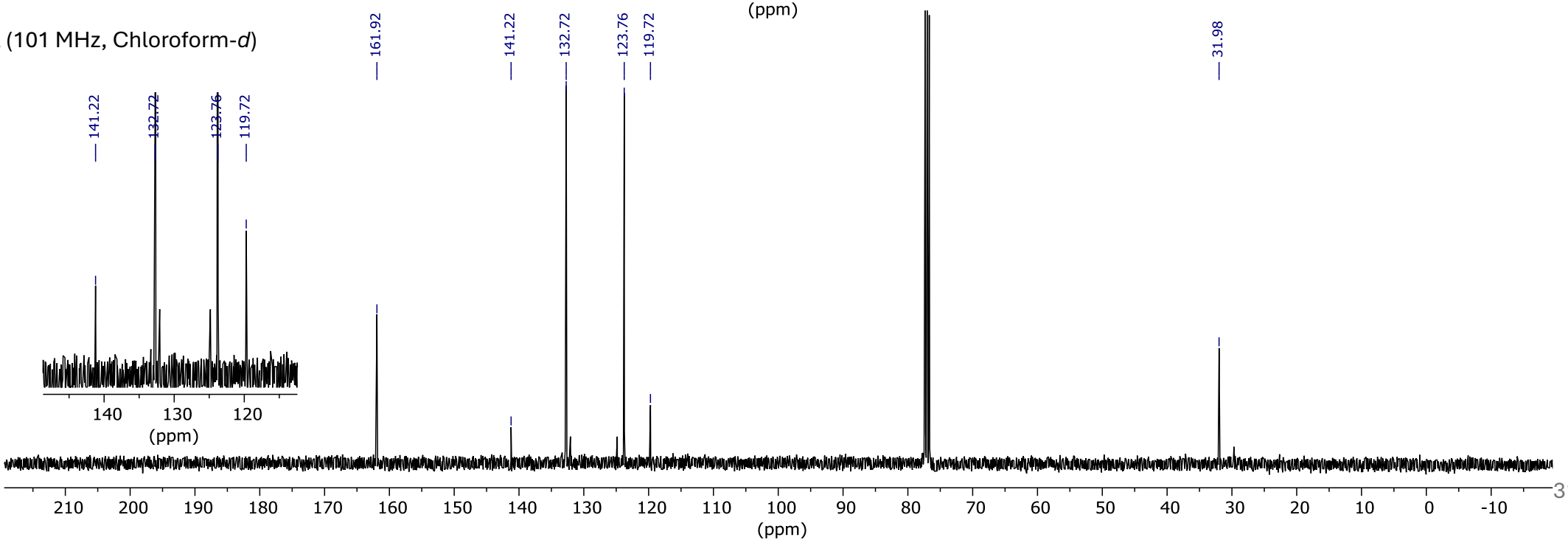
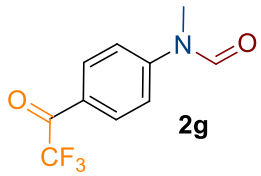


^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)

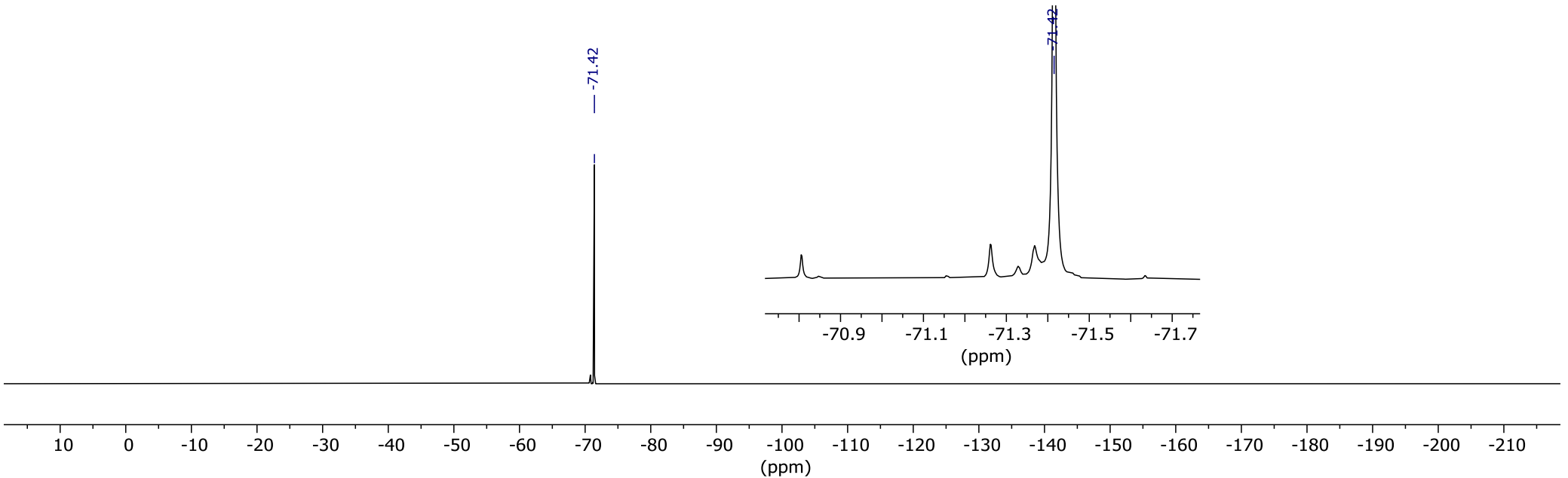


^{1}H NMR (400 MHz, Chloroform-*d*)

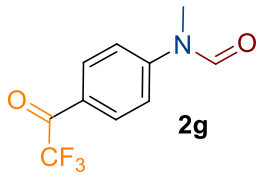


2g

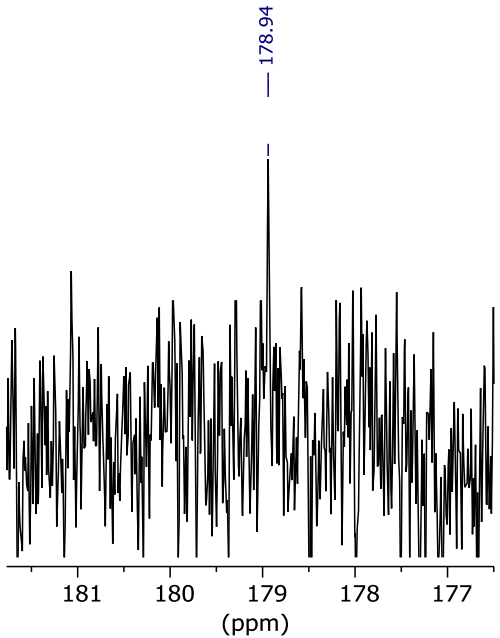
^{19}F NMR (376 MHz, Chloroform-*d*)

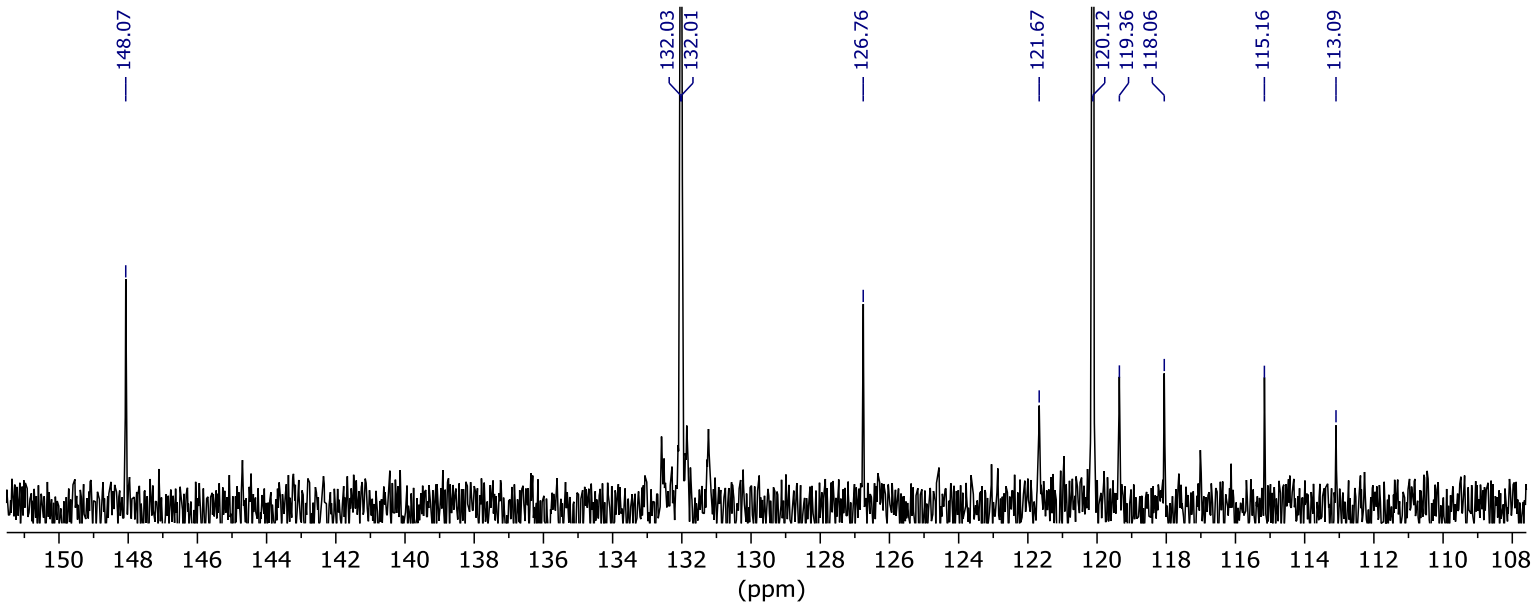


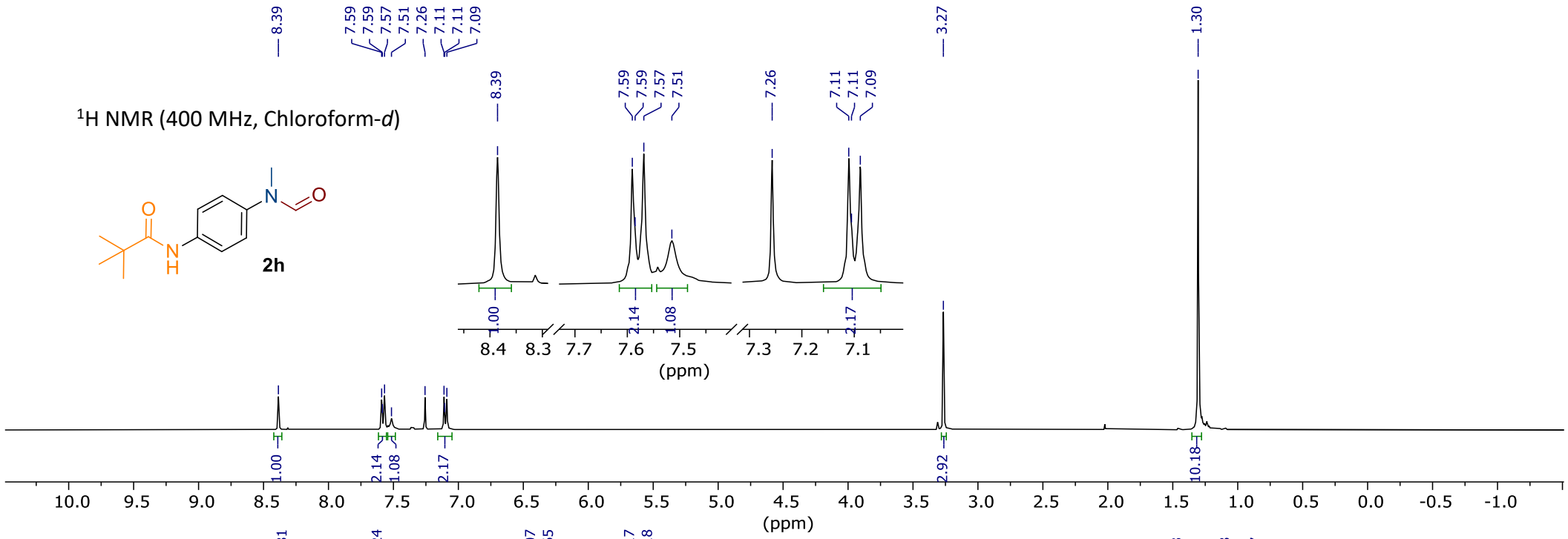
$^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*)



2g



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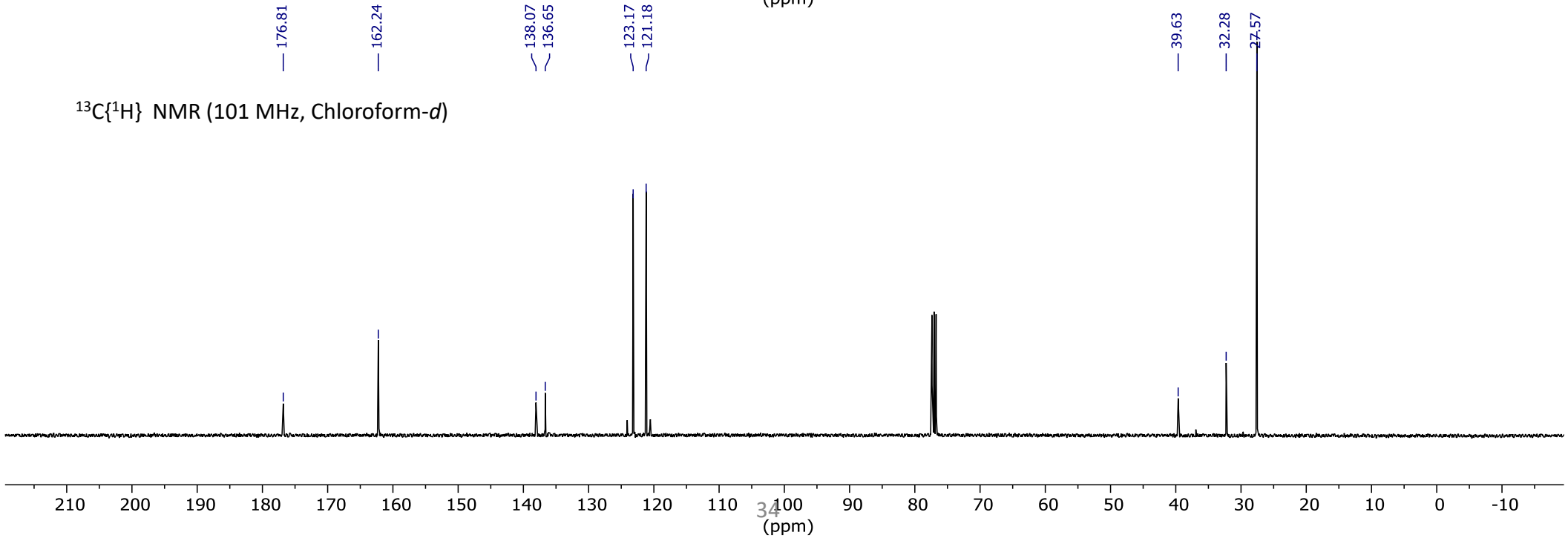
7.59
7.59
7.57
7.51
7.26
7.11
7.11
7.09
3.27
1.30
^{1}H NMR (400 MHz, Chloroform-*d*)
2h
1.00
2.14
1.08
2.17
2.92
10.18
(ppm)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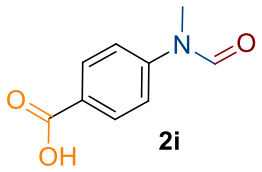
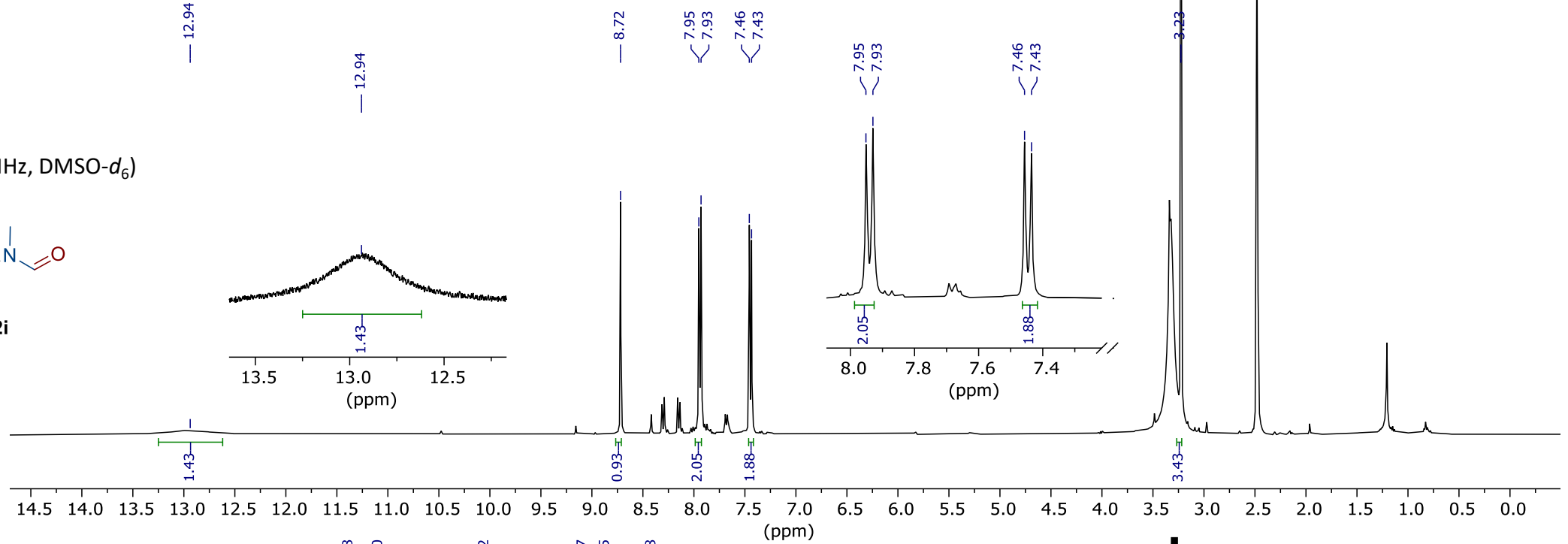
162.24
138.07
136.65
123.17
121.18
39.63
32.28
27.57
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)
(ppm)

34

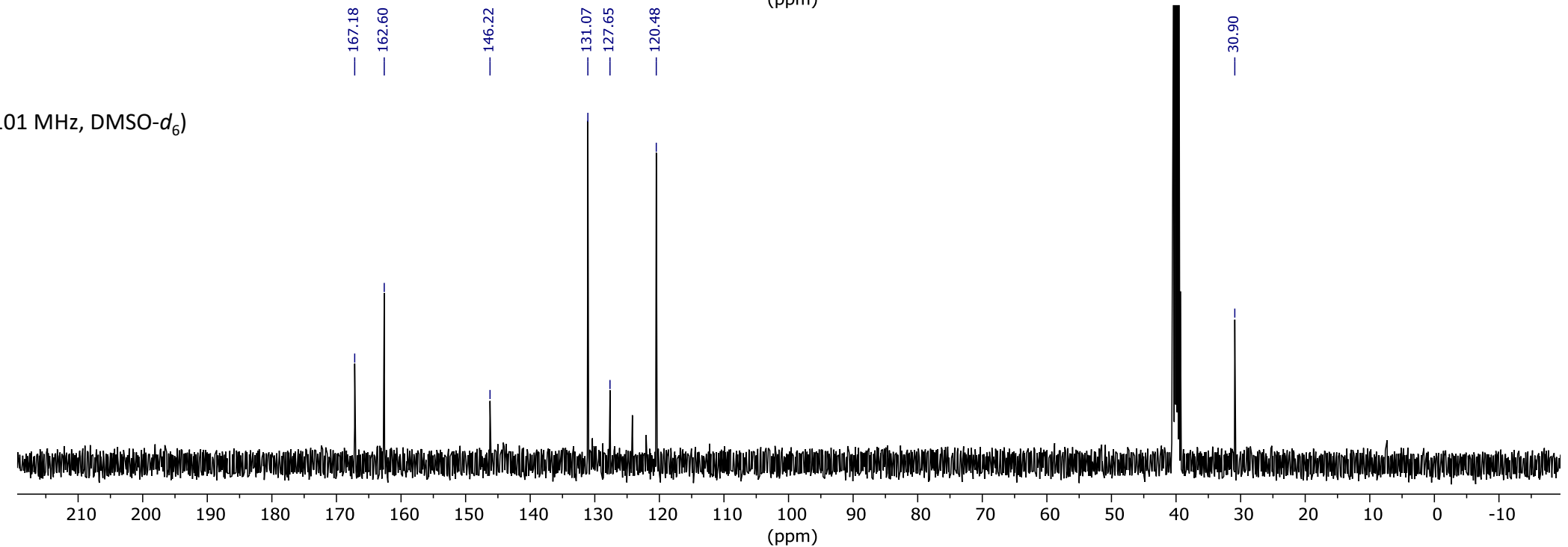
^{1}H NMR (400 MHz, DMSO-d_6)



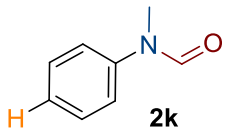
2i



^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)

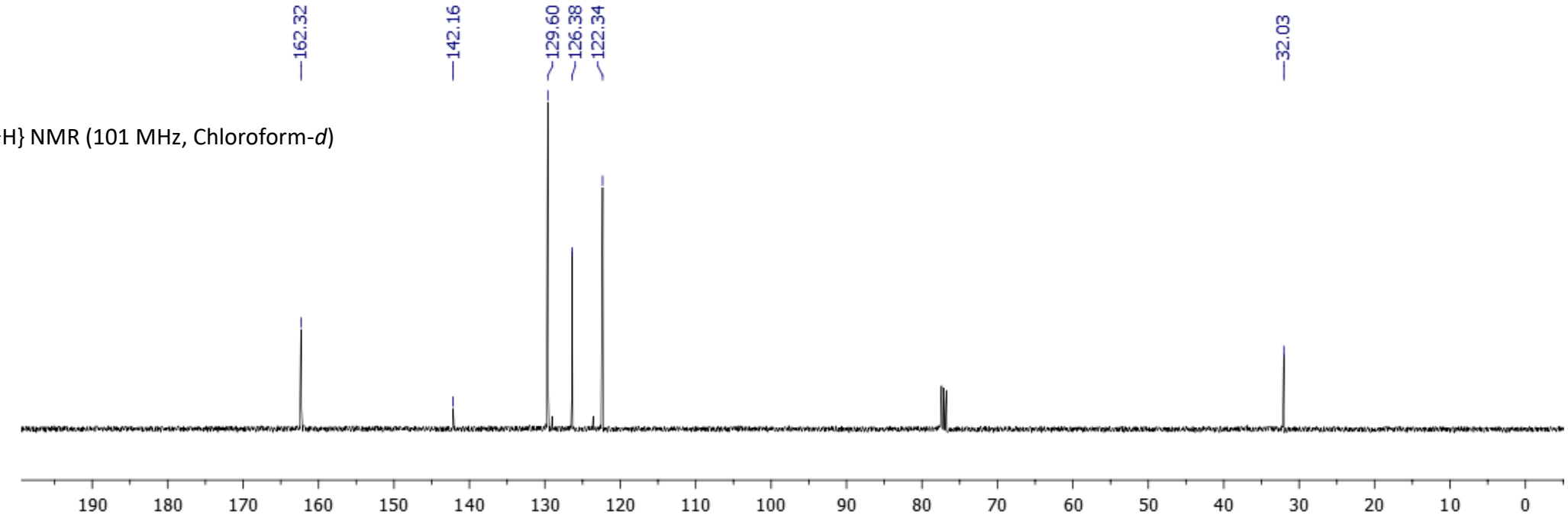


^{1}H NMR (400 MHz, Chloroform-*d*)

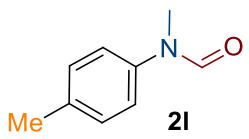


2k

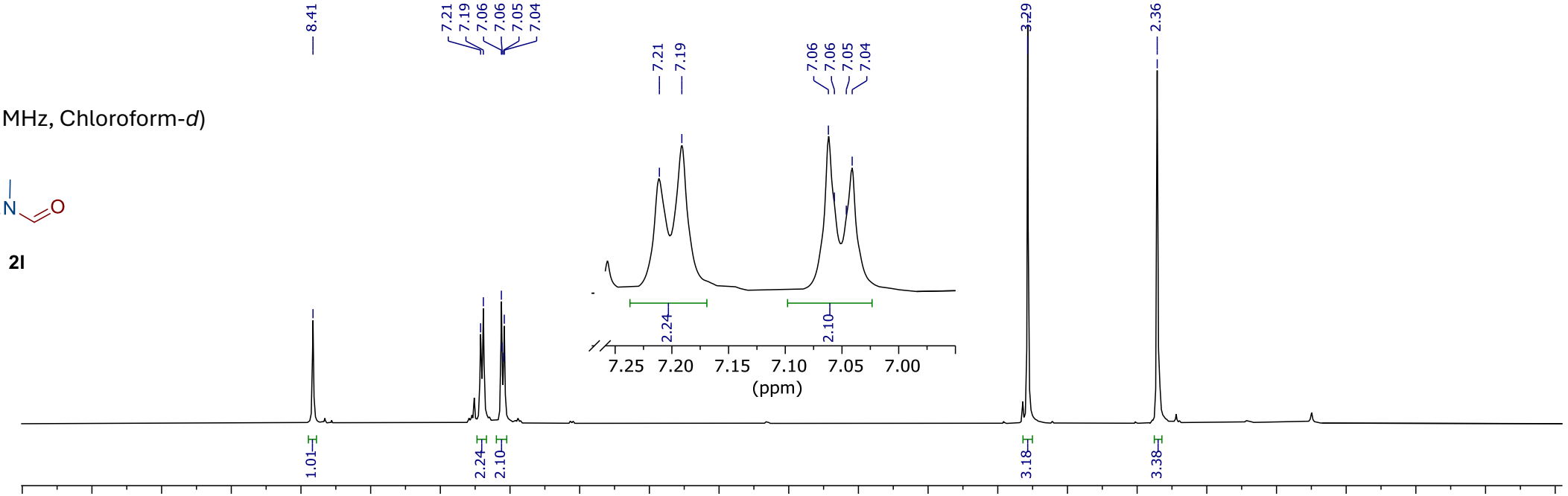
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



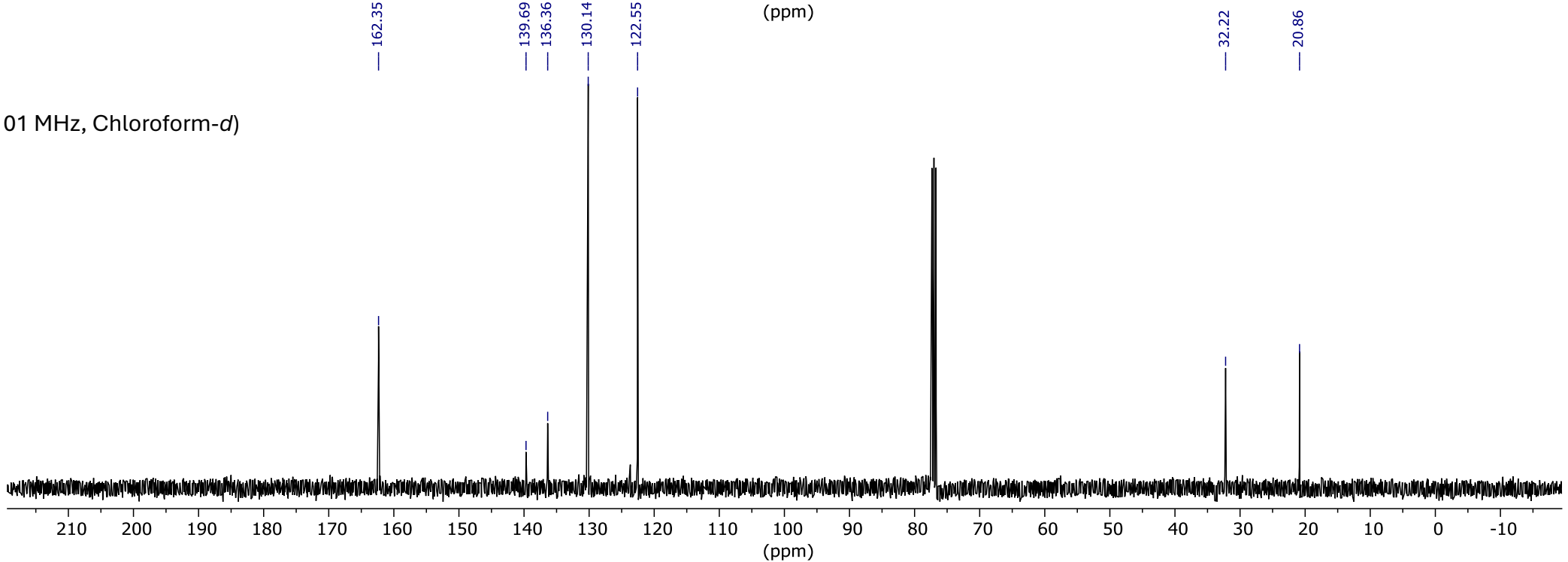
^{1}H NMR (400 MHz, Chloroform-*d*)



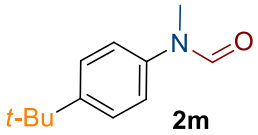
2l



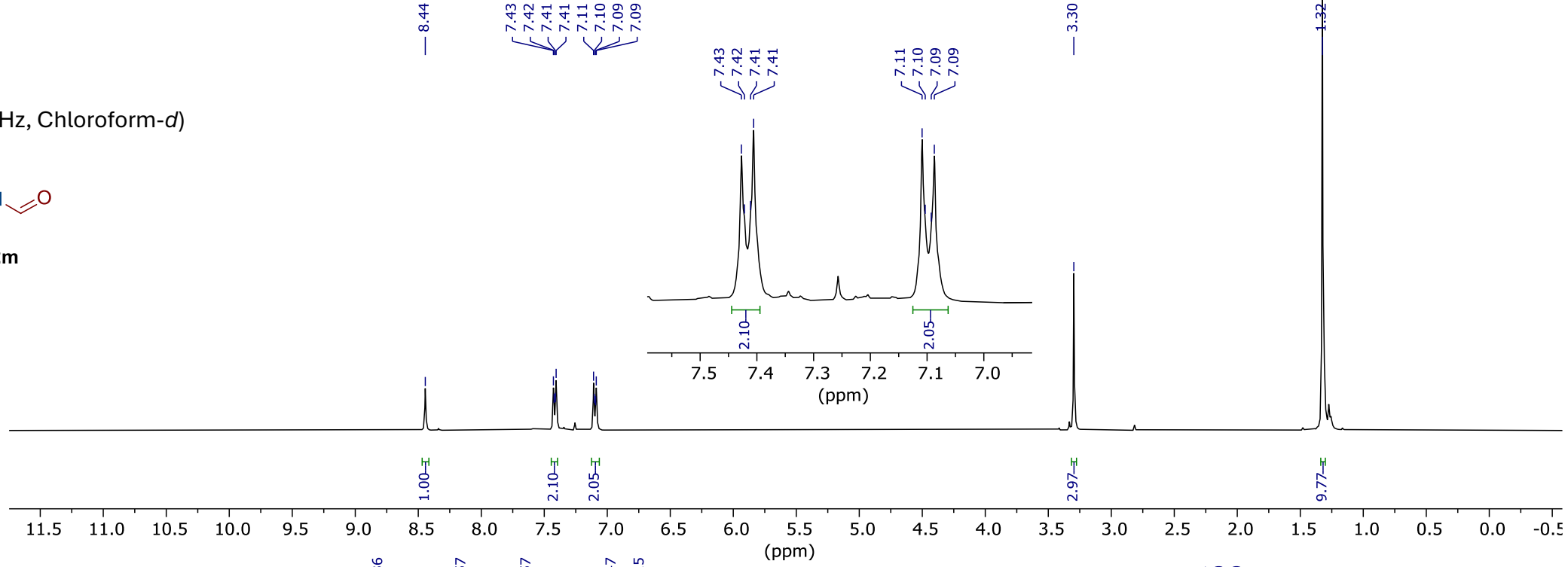
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



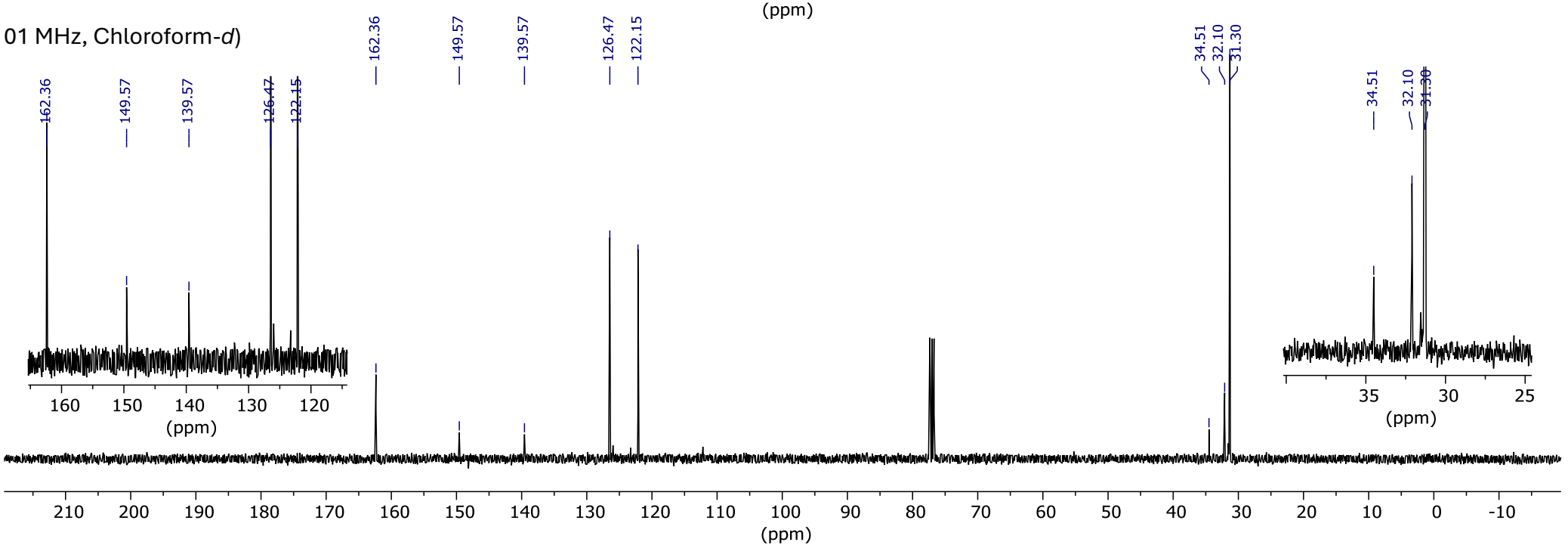
^{1}H NMR (400 MHz, Chloroform-*d*)



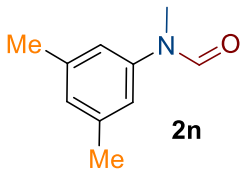
2m



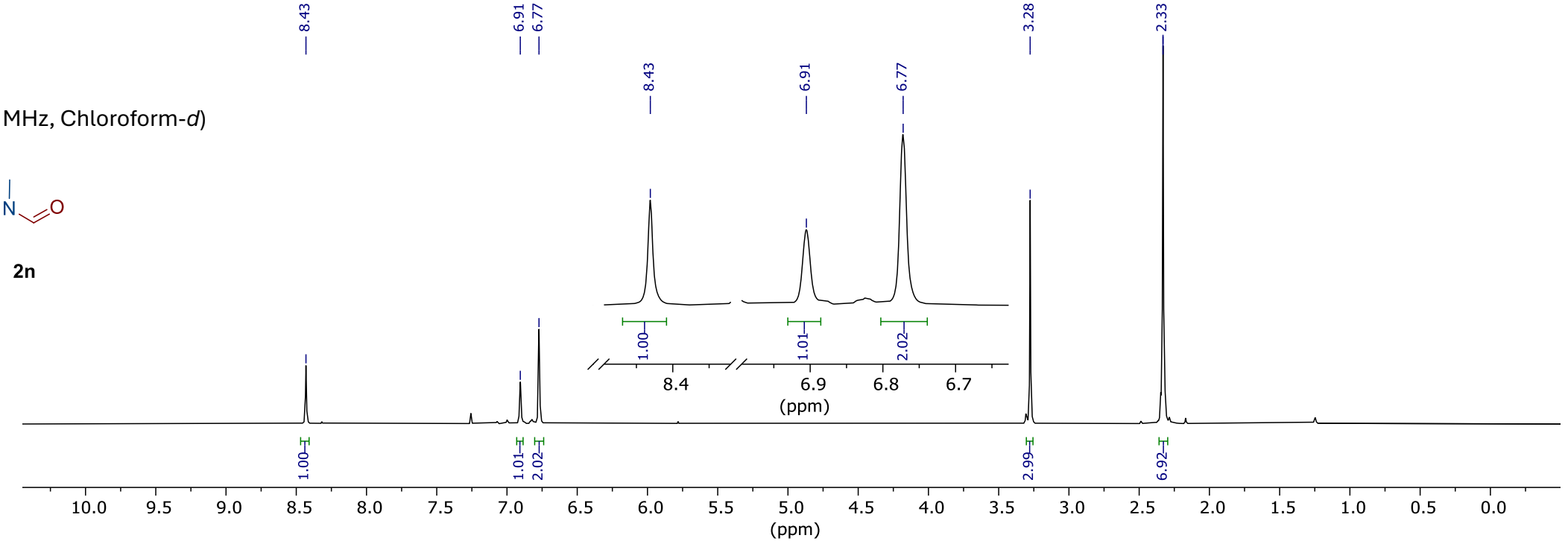
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



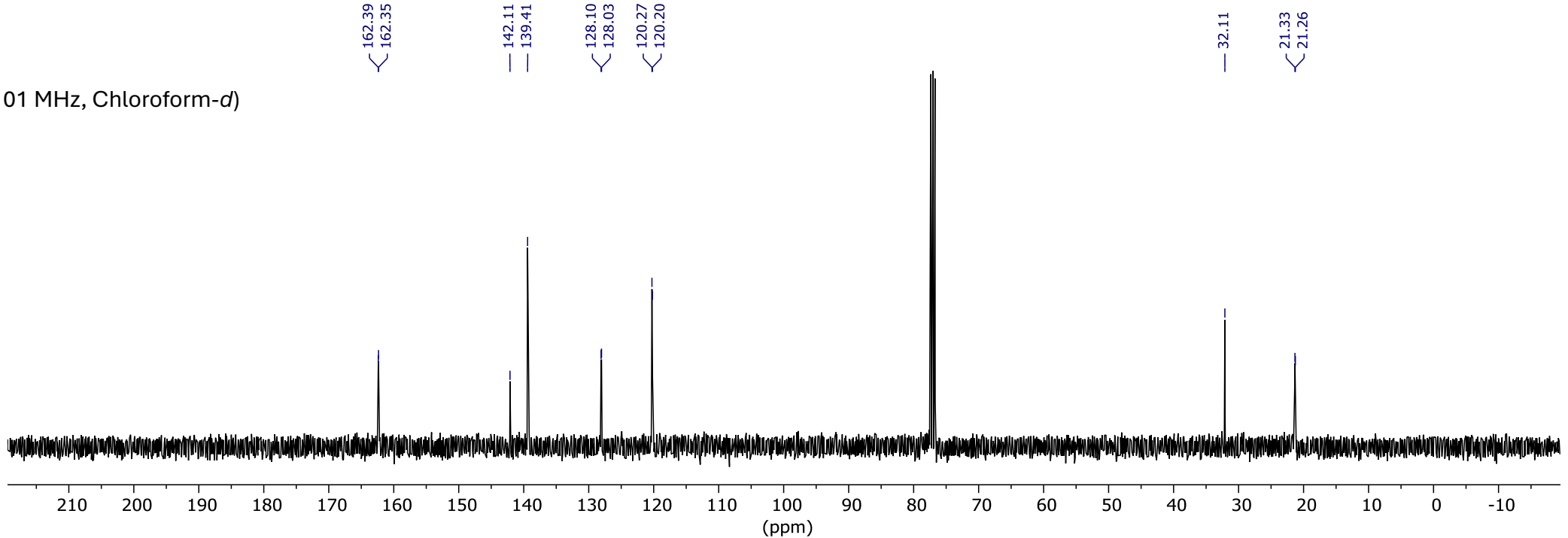
^{1}H NMR (400 MHz, Chloroform-*d*)



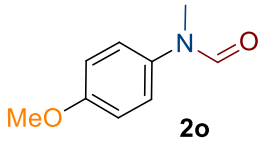
2n



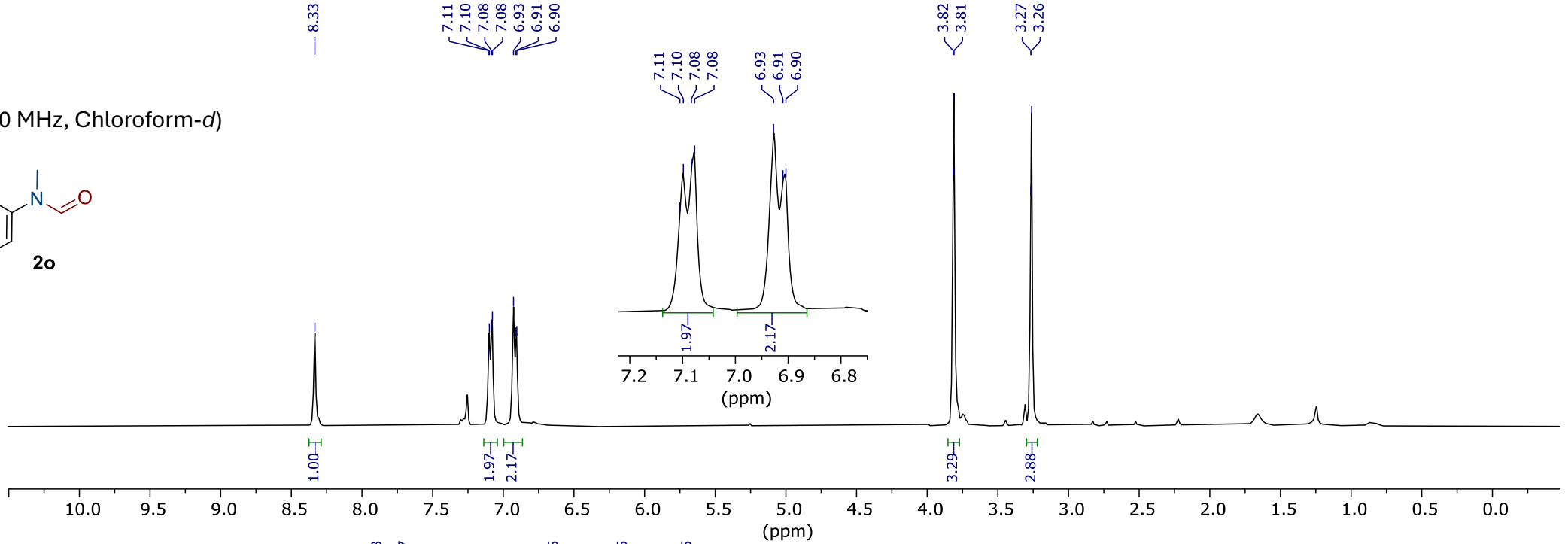
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



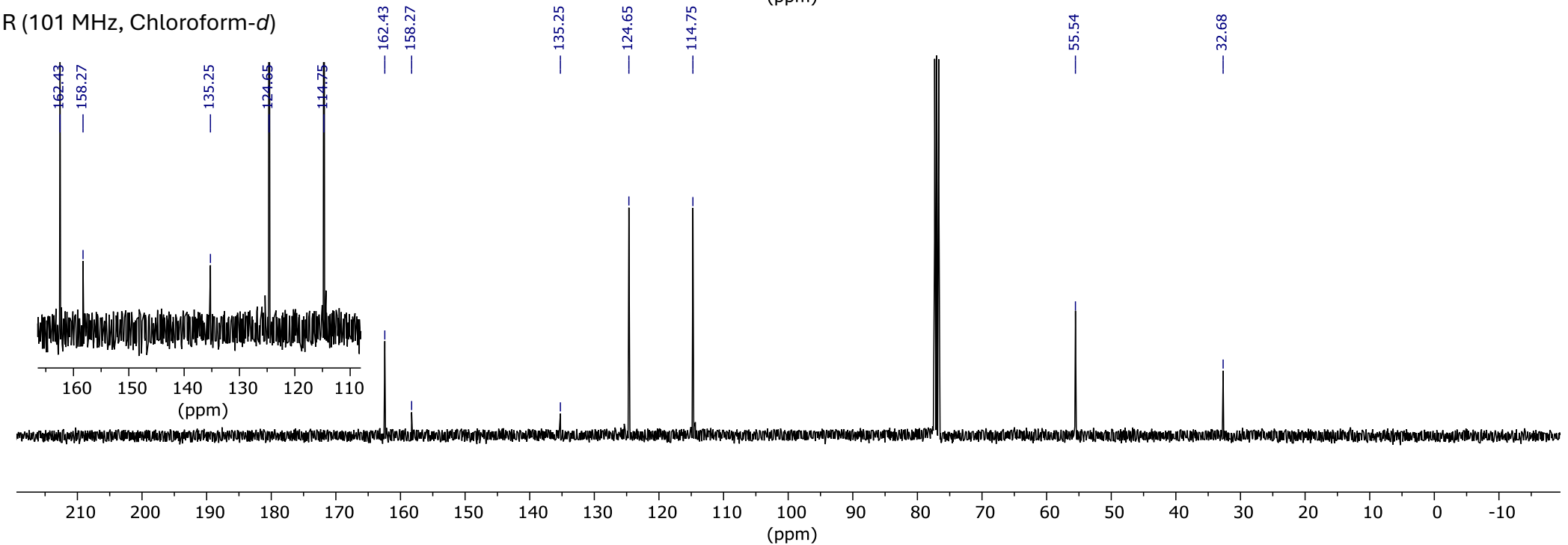
^{1}H NMR (400 MHz, Chloroform-*d*)



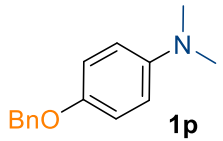
2o



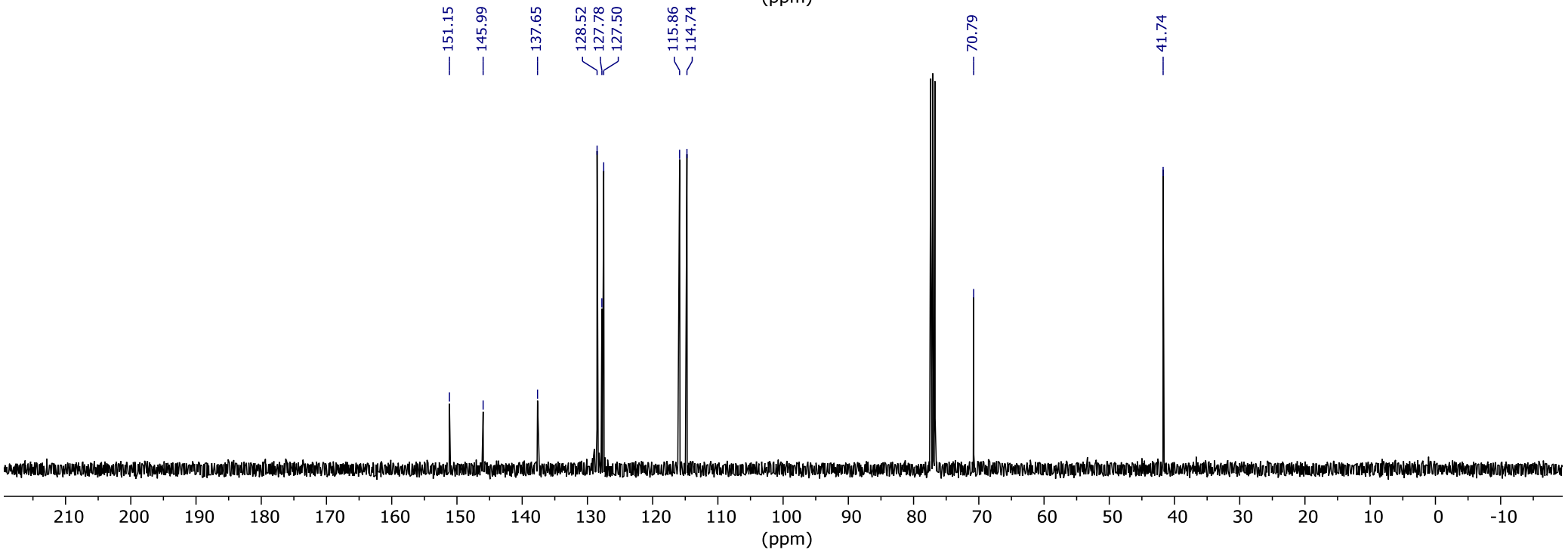
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



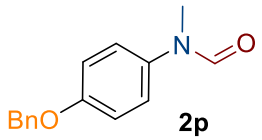
^{1}H NMR (400 MHz, Chloroform-*d*)



1p

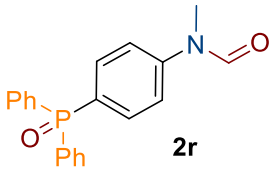


^{1}H NMR (400 MHz, Chloroform-*d*)



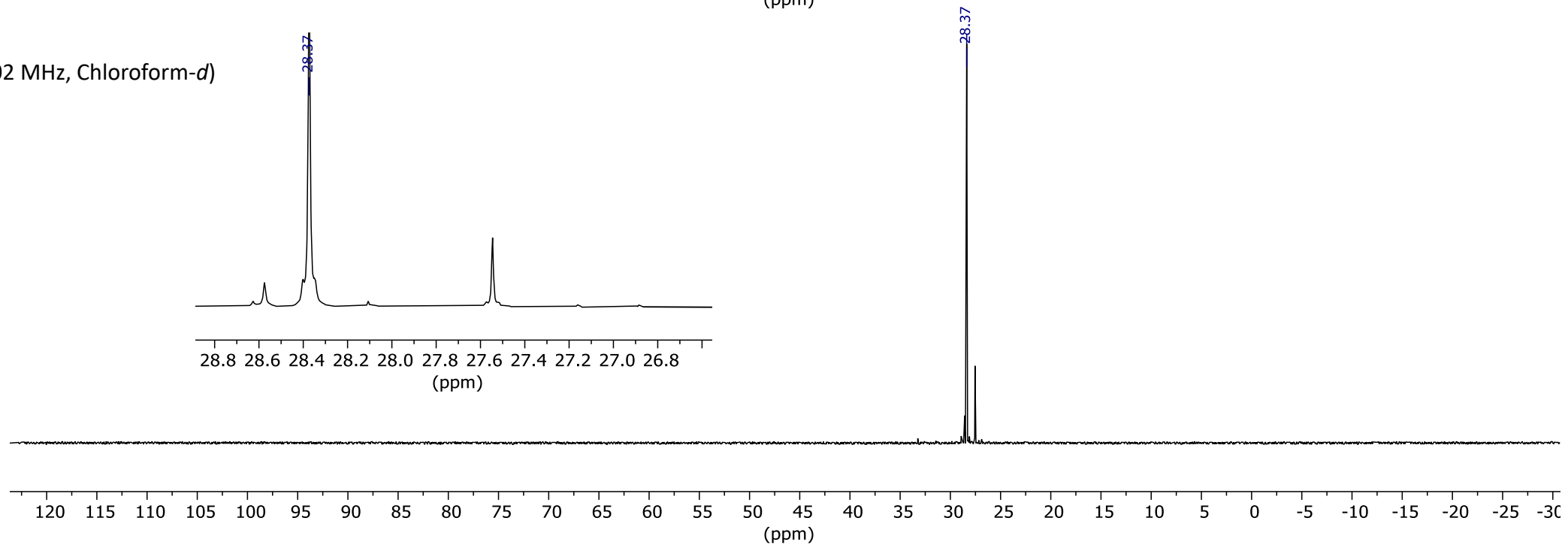
2p

^{1}H NMR (500 MHz, Chloroform-*d*)

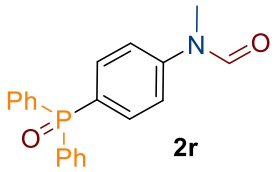


2r

^{31}P NMR (202 MHz, Chloroform-*d*)

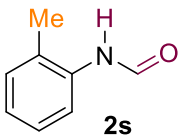


$^{13}C\{^{1}H\}$ NMR (126 MHz, Chloroform-*d*)



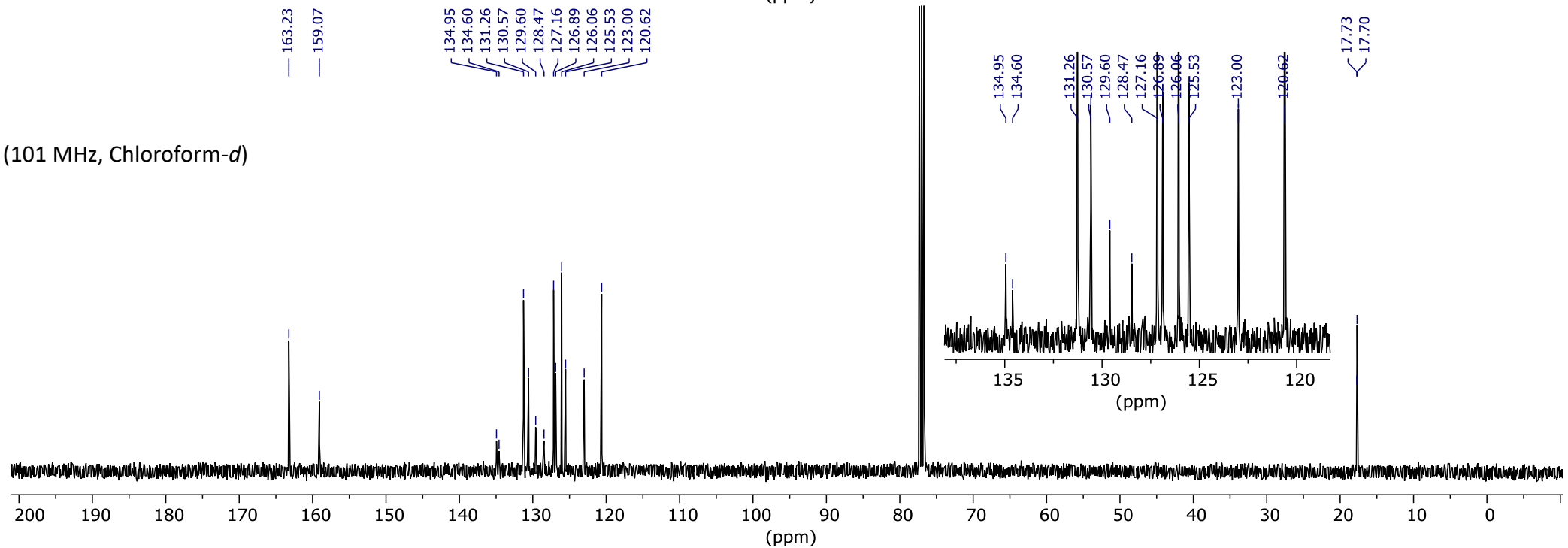
2r

^{1}H NMR (400 MHz, Chloroform-*d*)

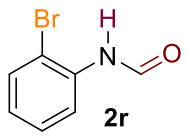


2s

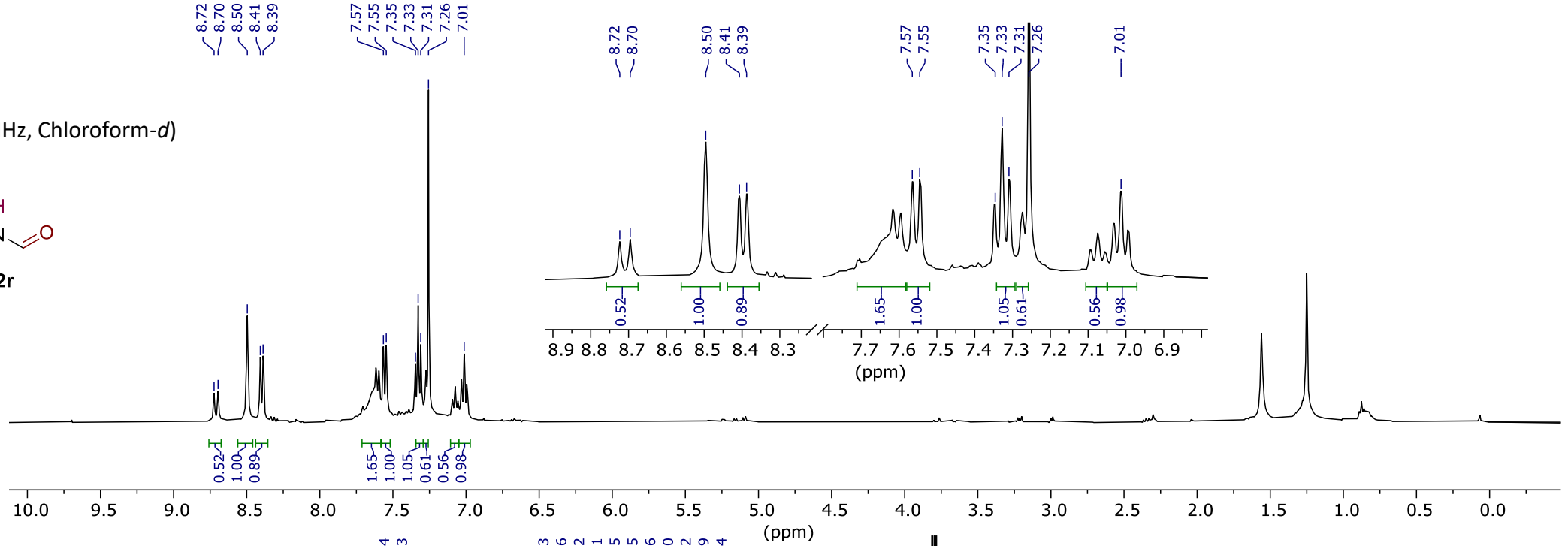
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



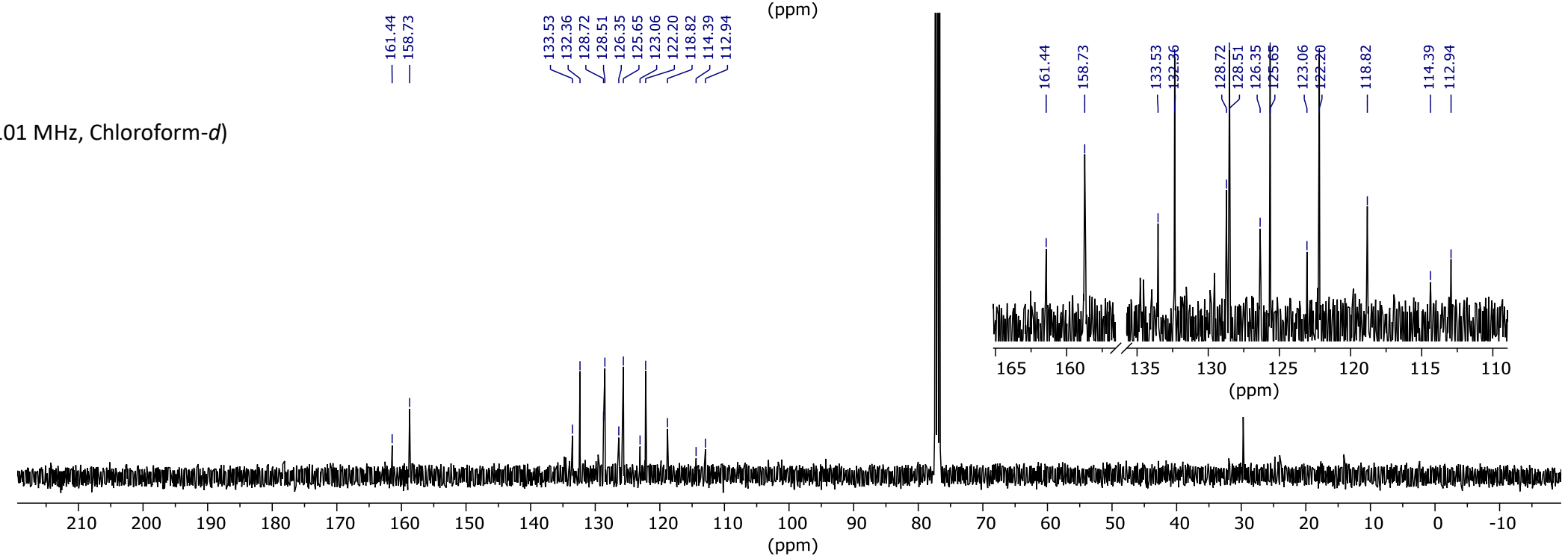
^{1}H NMR (400 MHz, Chloroform-*d*)



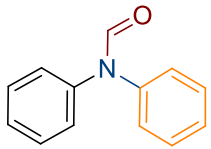
2r



^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)

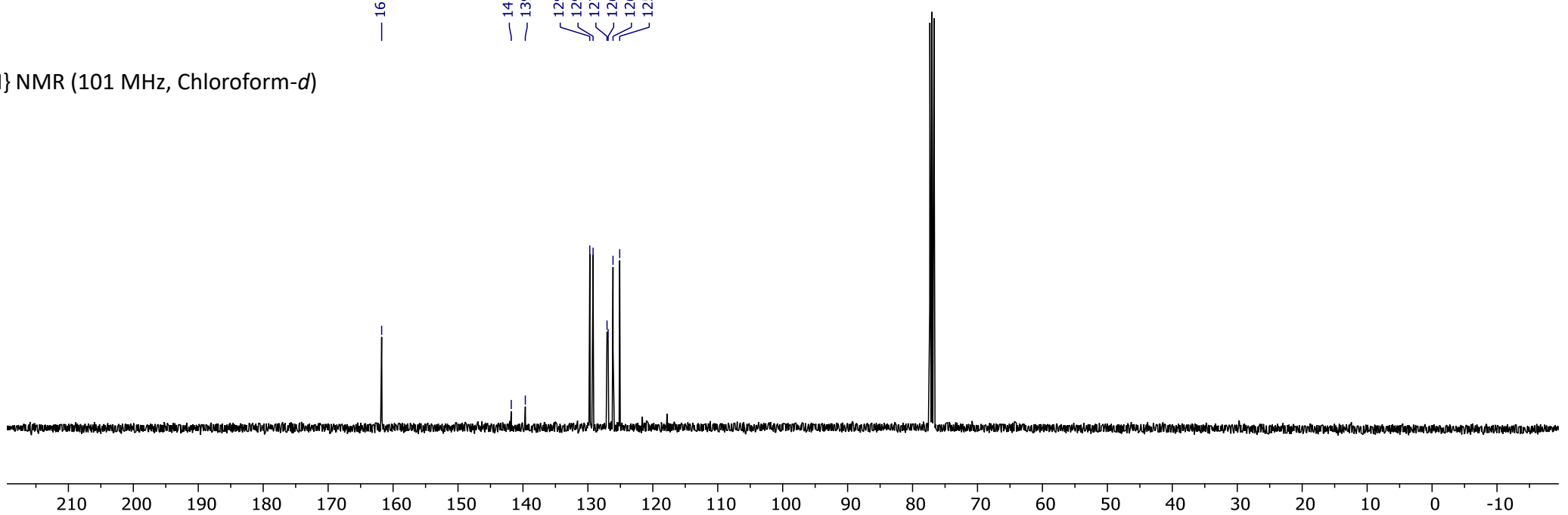


^{1}H NMR (400 MHz, Chloroform-*d*)

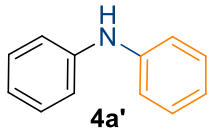


4a

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)

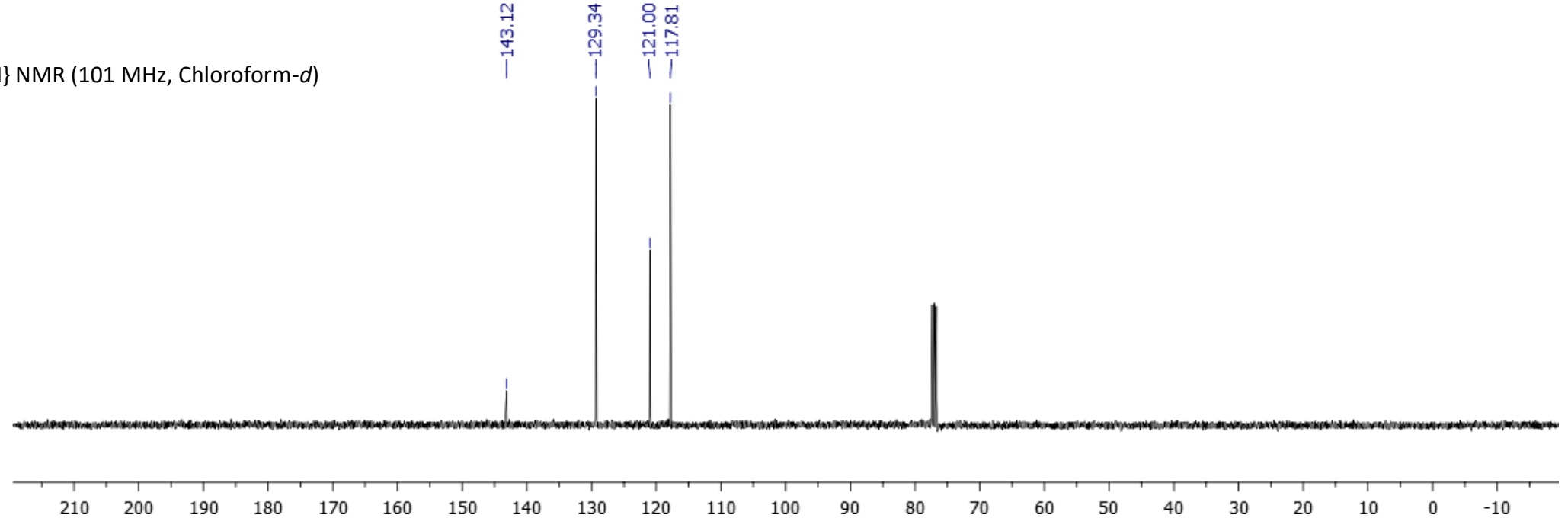


^{1}H NMR (400 MHz, Chloroform-*d*)

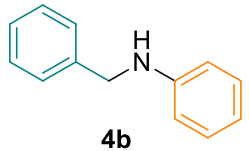


4a'

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)

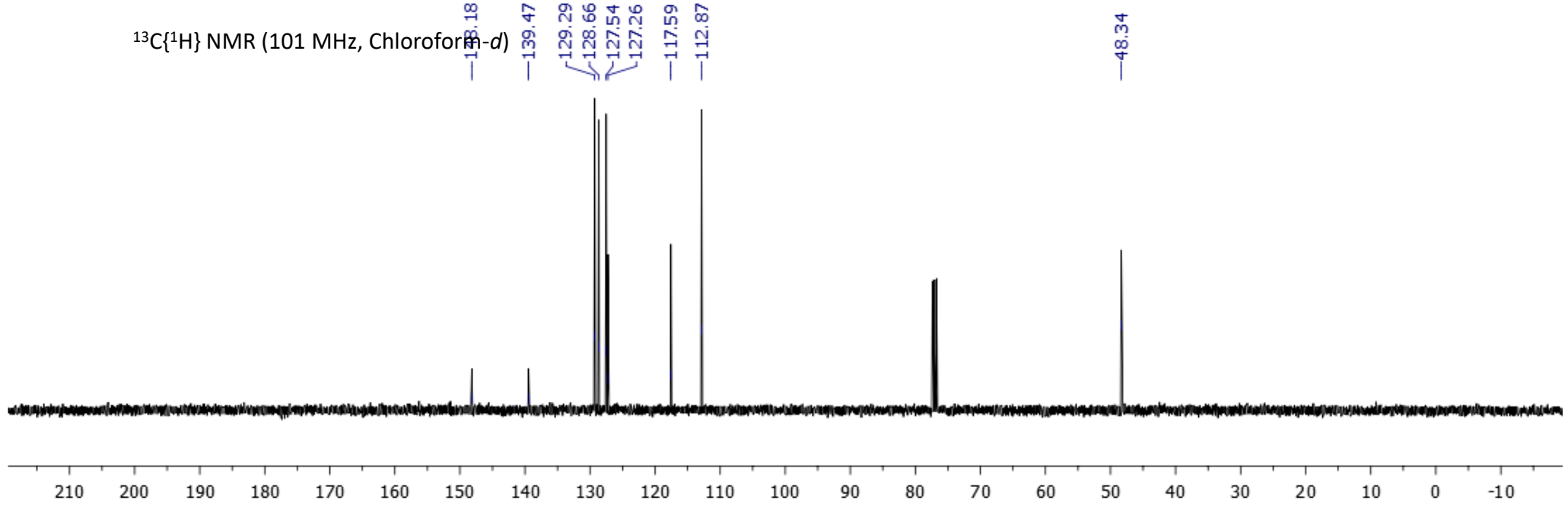


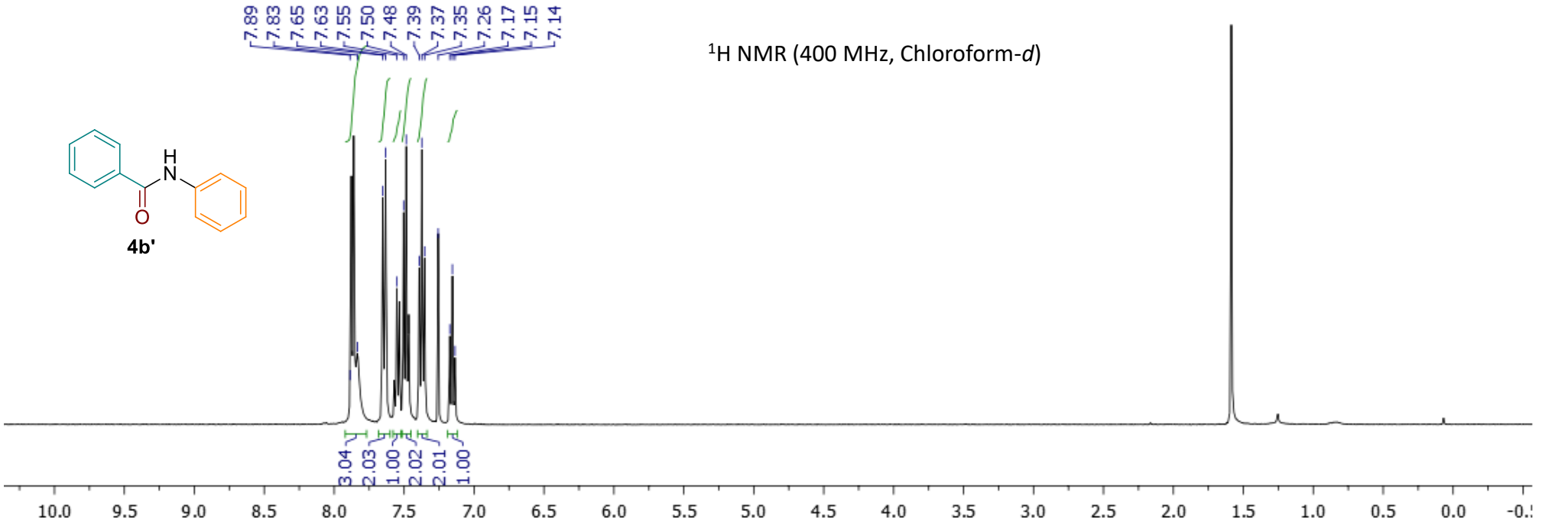
^{1}H NMR (400 MHz, Chloroform-*d*)



4b

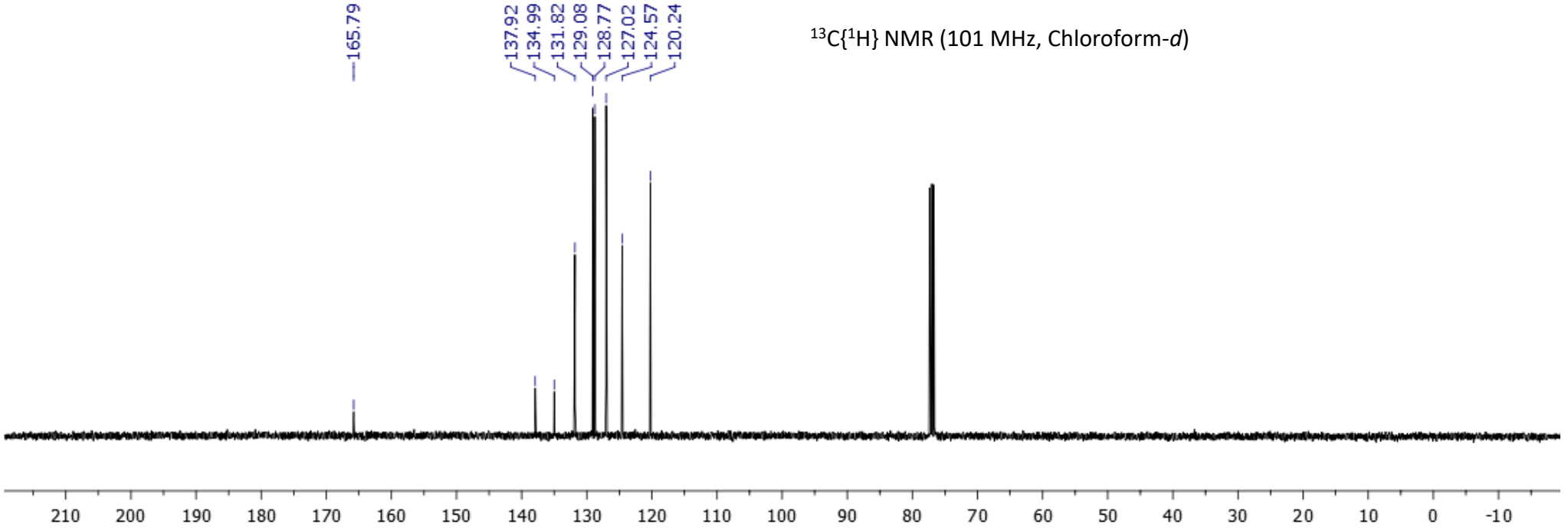
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)





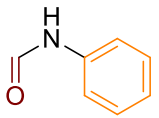
^{1}H NMR (400 MHz, Chloroform-*d*)

4b'

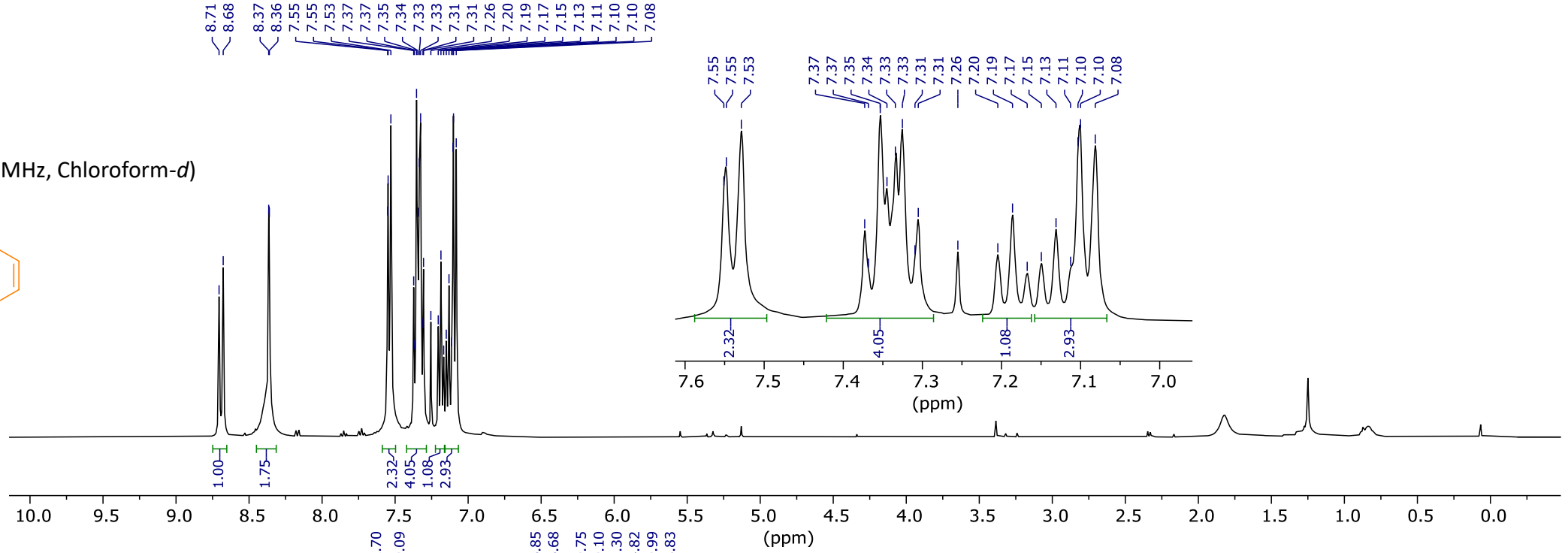


^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)

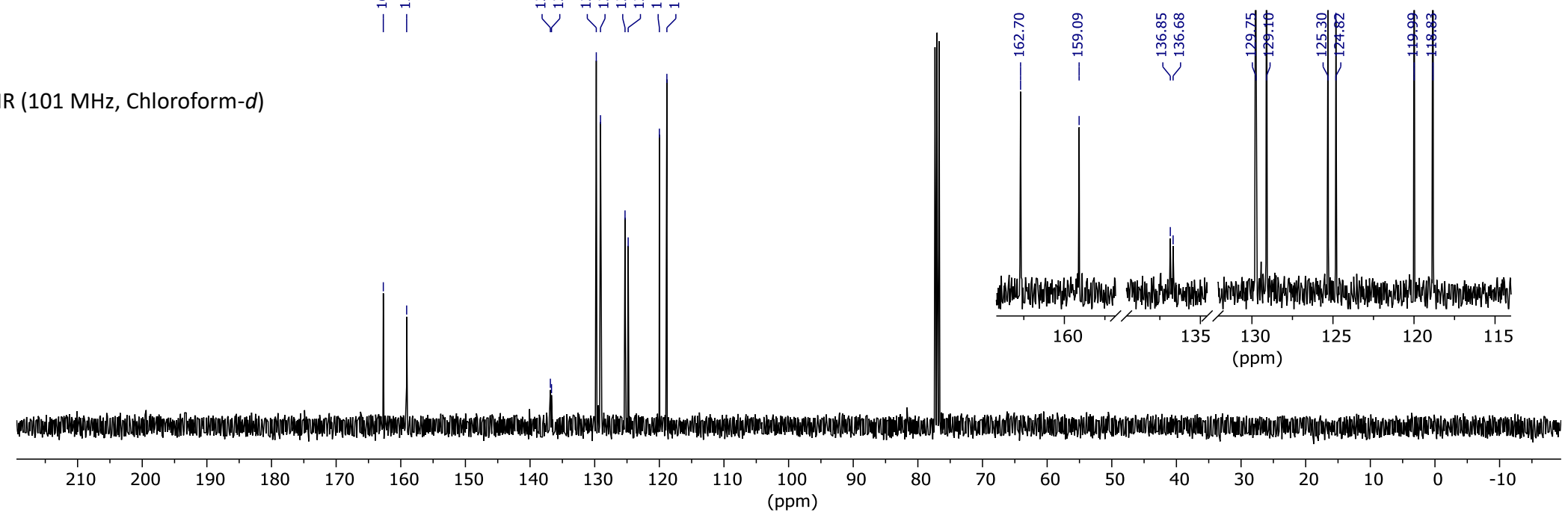
^{1}H NMR (400 MHz, Chloroform-*d*)



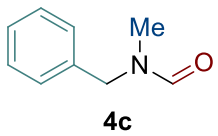
4b"



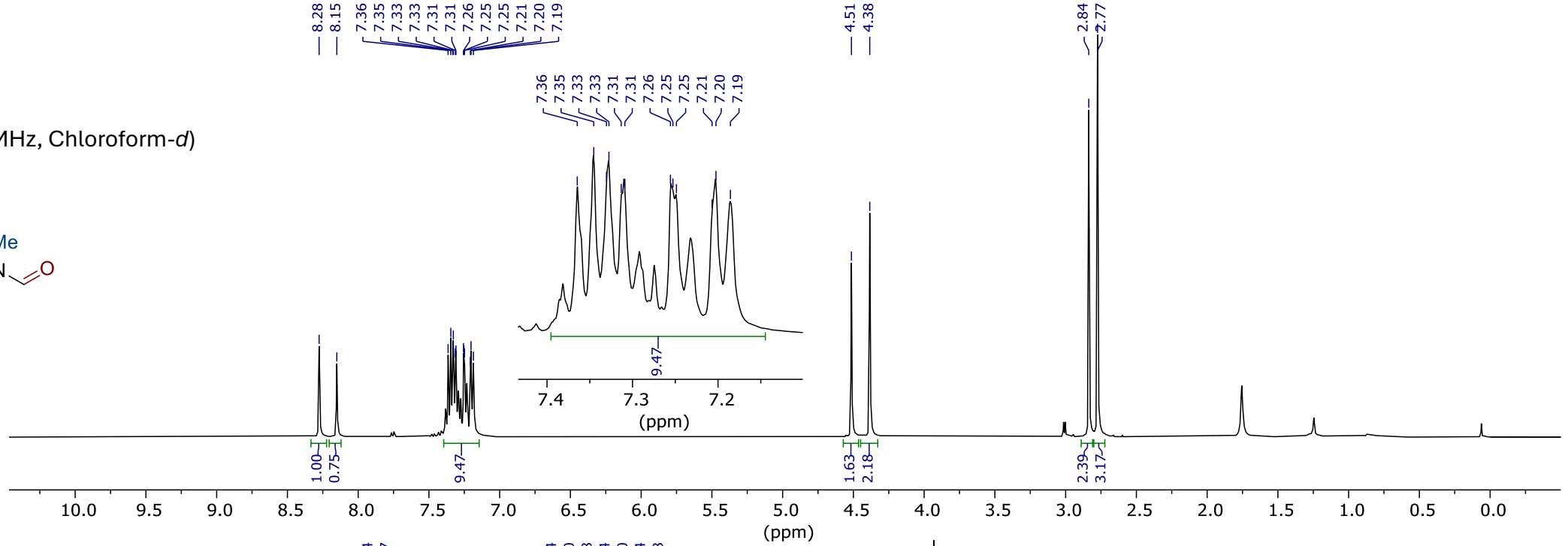
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



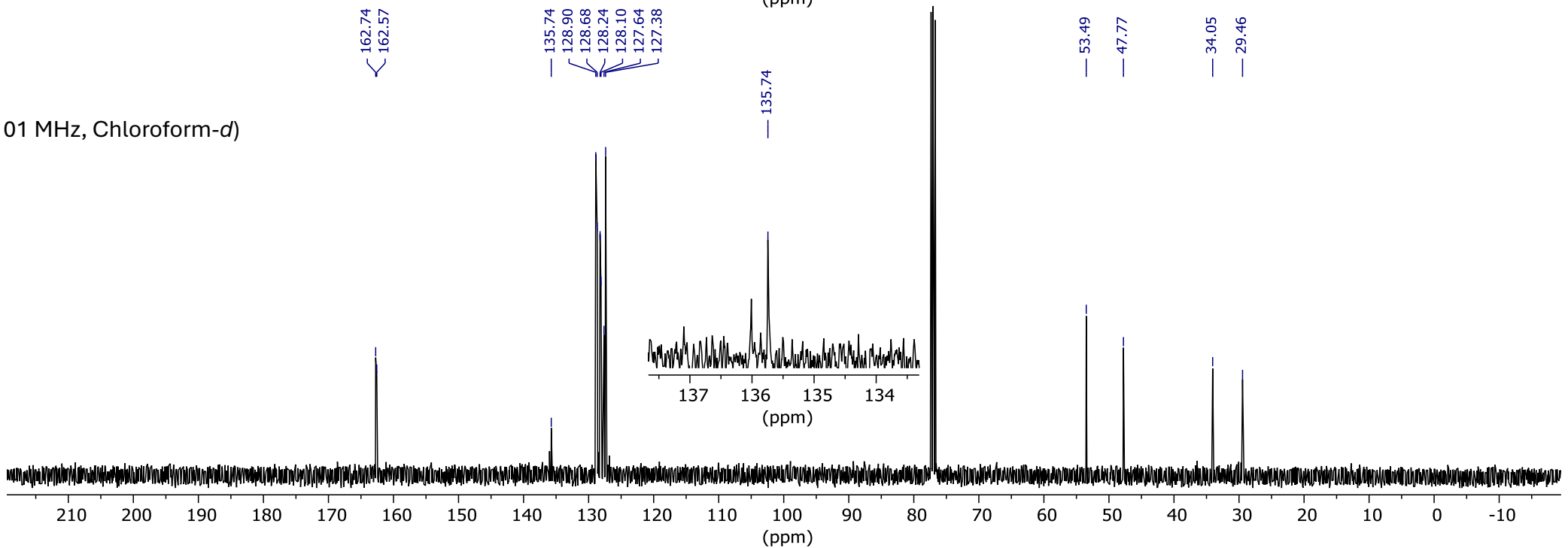
^{1}H NMR (400 MHz, Chloroform-*d*)



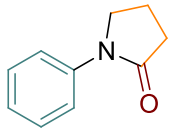
4c



^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)

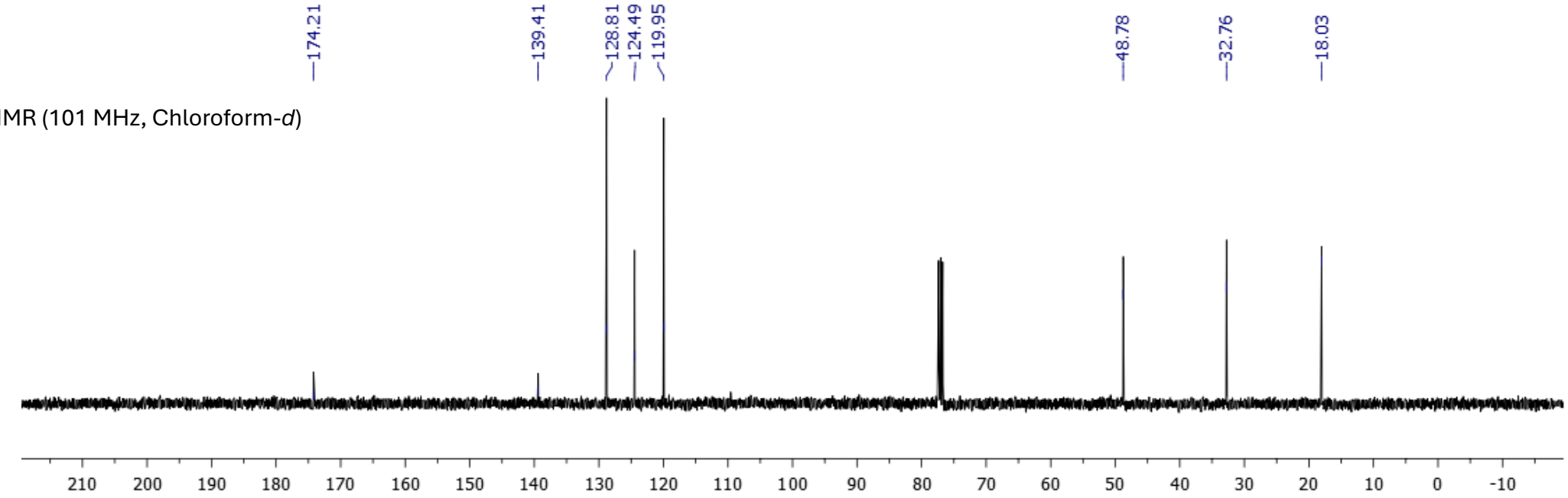


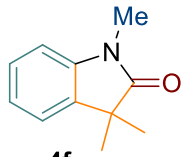
^{1}H NMR (400 MHz, Chloroform-*d*)



4d

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)

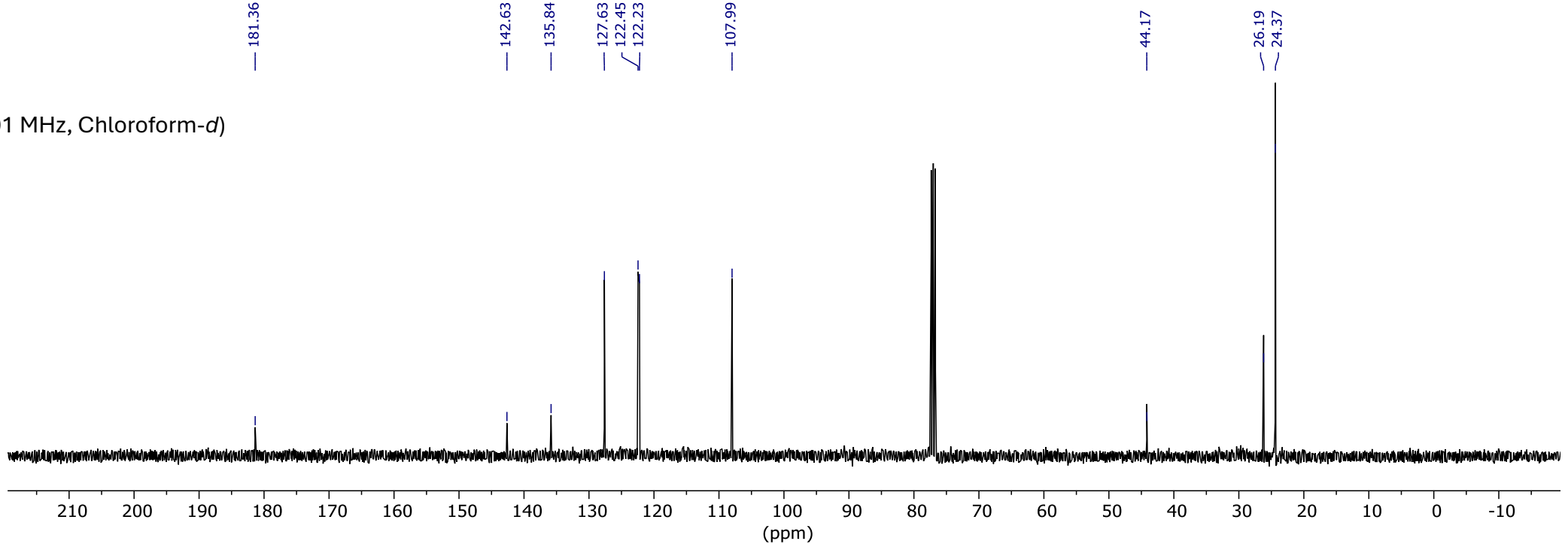




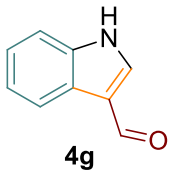
4f

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)

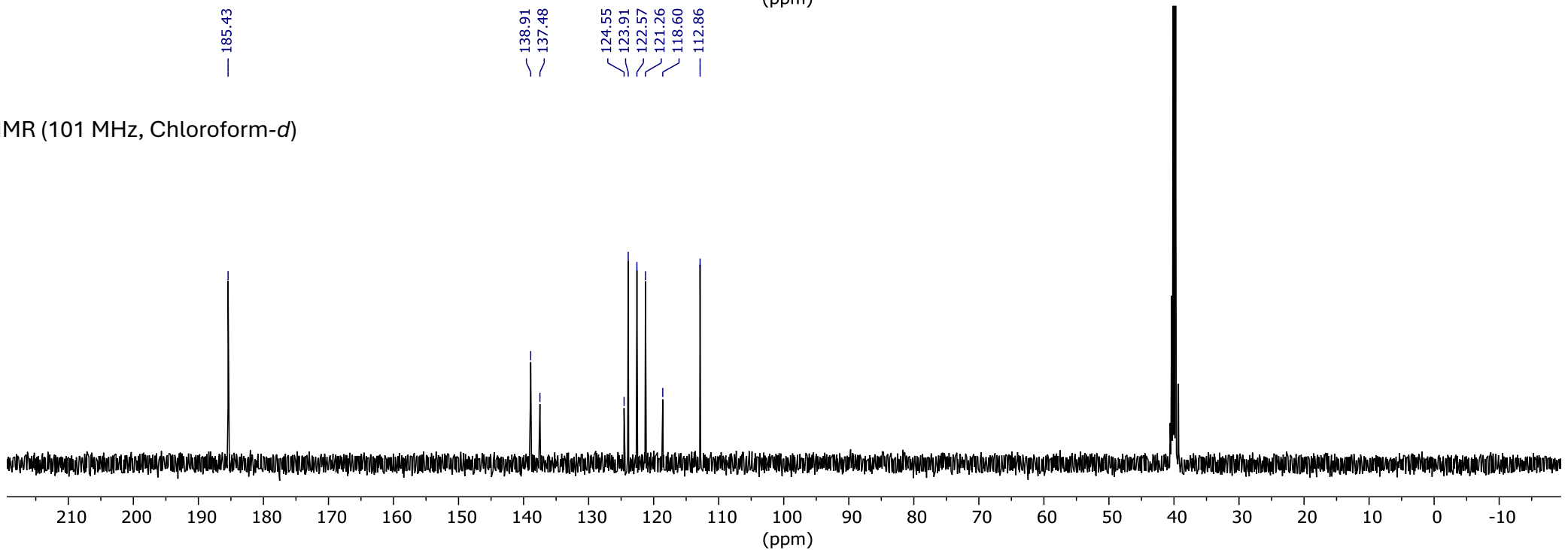


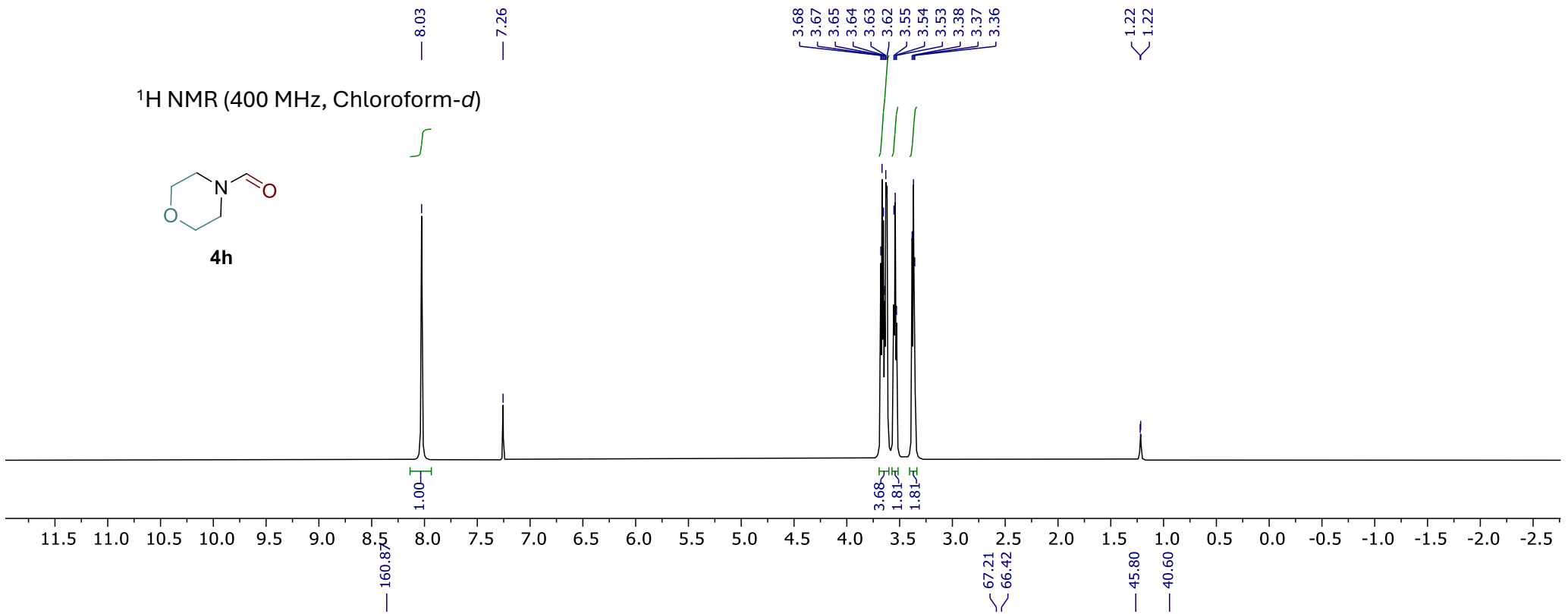
^{1}H NMR (400 MHz, Chloroform-*d*)

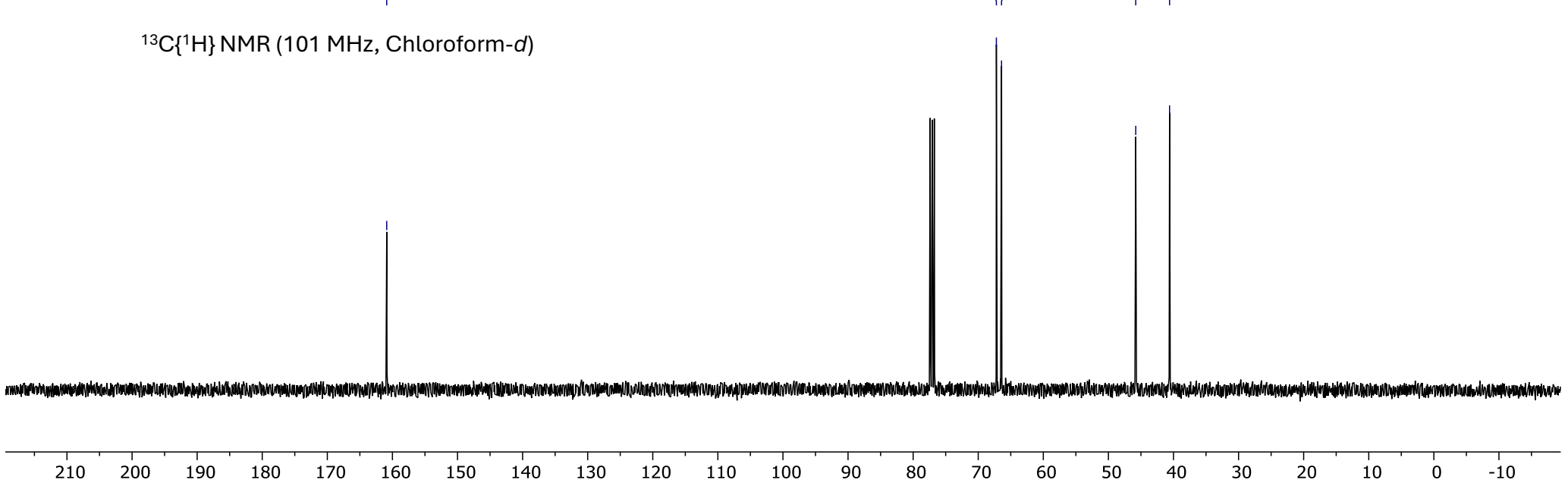


4g

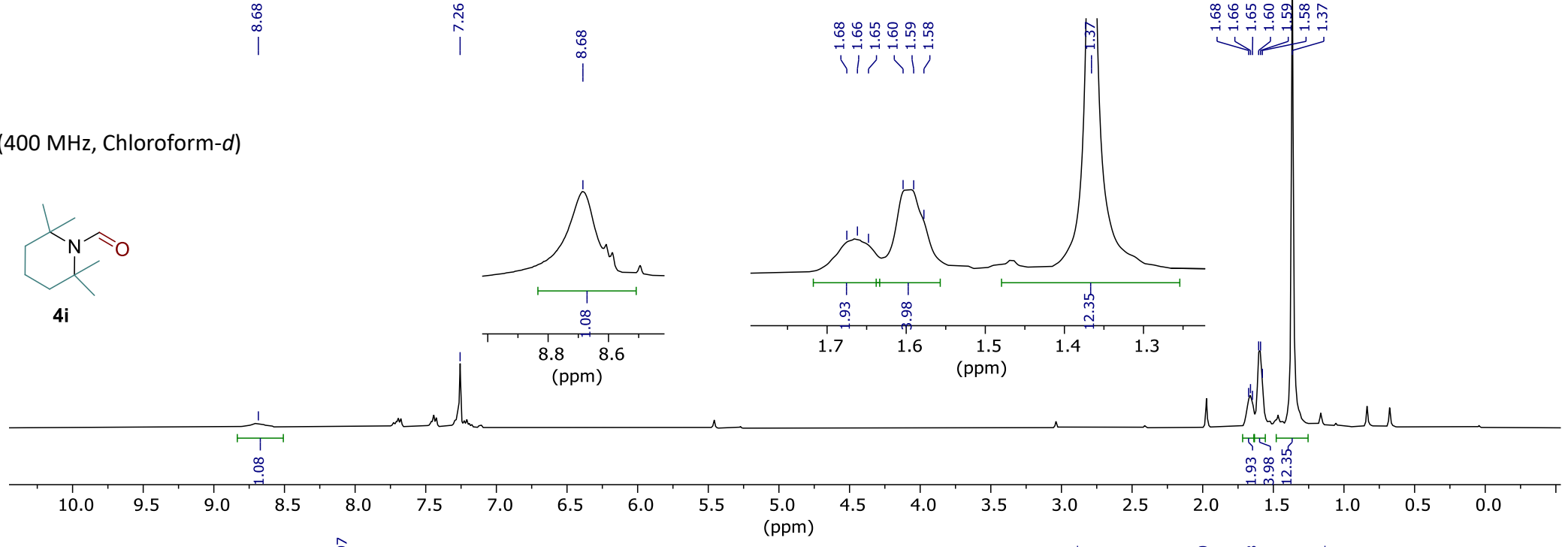
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)




8.03
7.26
3.68
3.67
3.65
3.64
3.63
3.62
3.55
3.54
3.53
3.38
3.37
3.36
1.22
1.22
1H NMR (400 MHz, Chloroform-d)
4h
1.00
3.68
1.81
1.81
11.5 11.0 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 -0.5 -1.0 -1.5 -2.0 -2.5

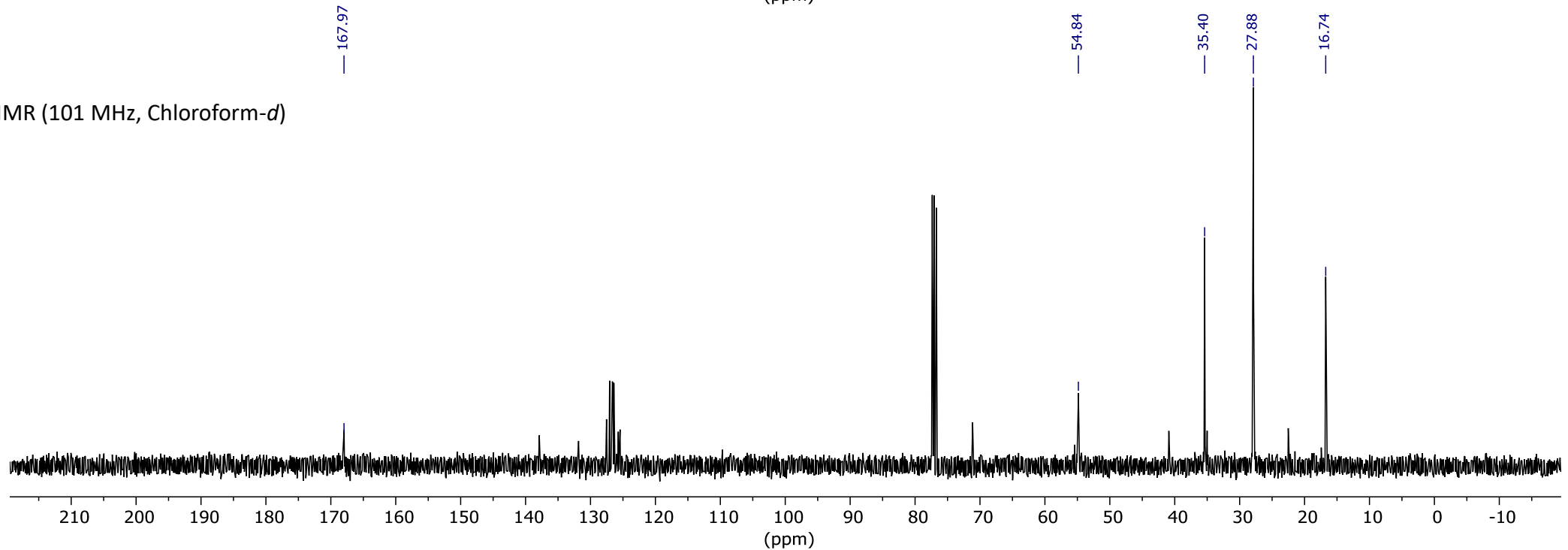

160.87
67.21
66.42
45.80
40.60
13C{1H} NMR (101 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

^{1}H NMR (400 MHz, Chloroform-*d*)

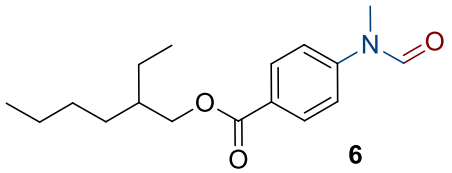


4i

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)

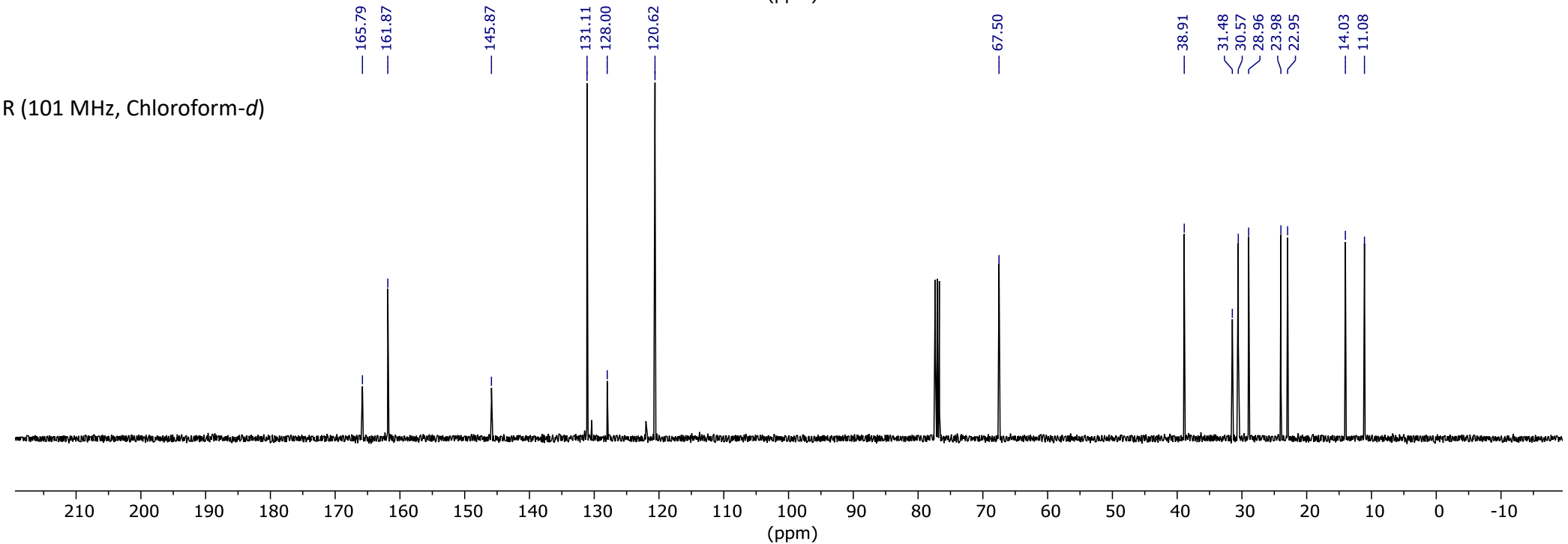


^{1}H NMR (400 MHz, Chloroform-*d*)

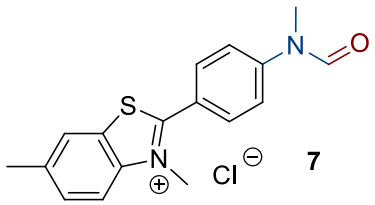


6

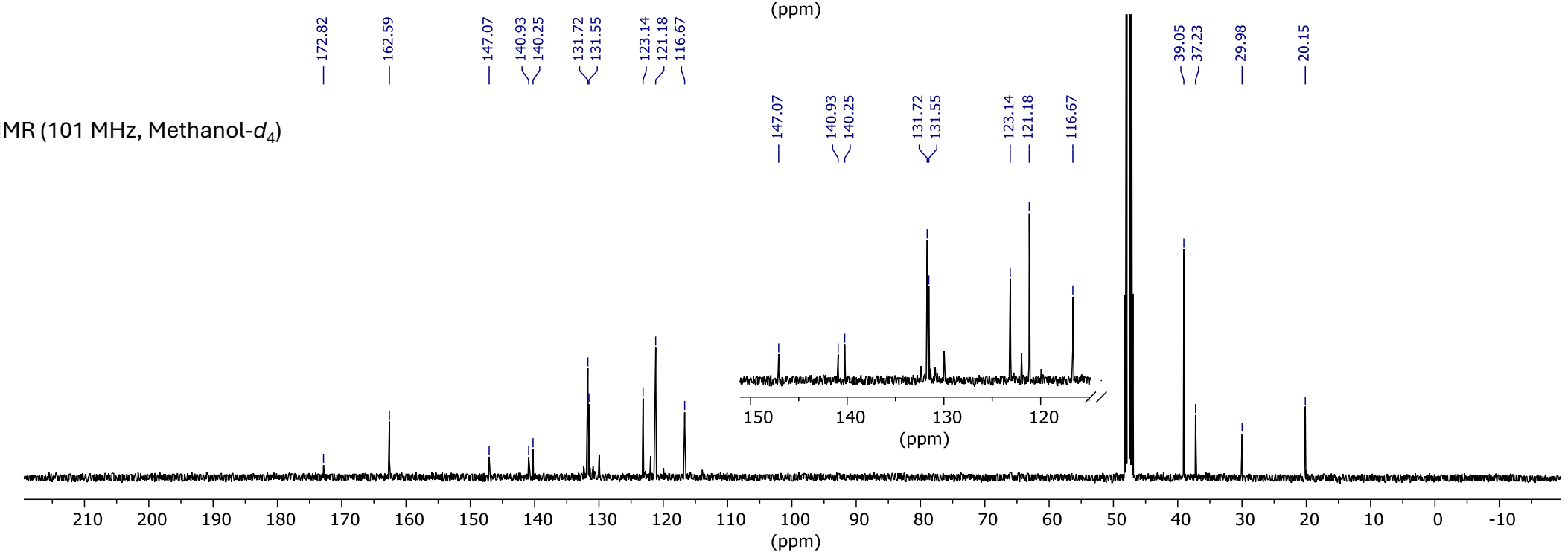
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



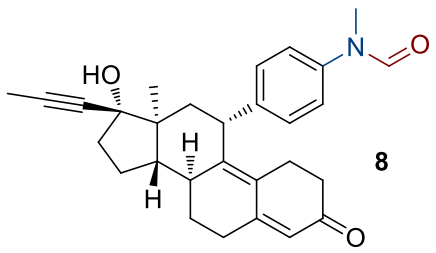
^{1}H NMR (400 MHz, Methanol-d_4)



^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4)

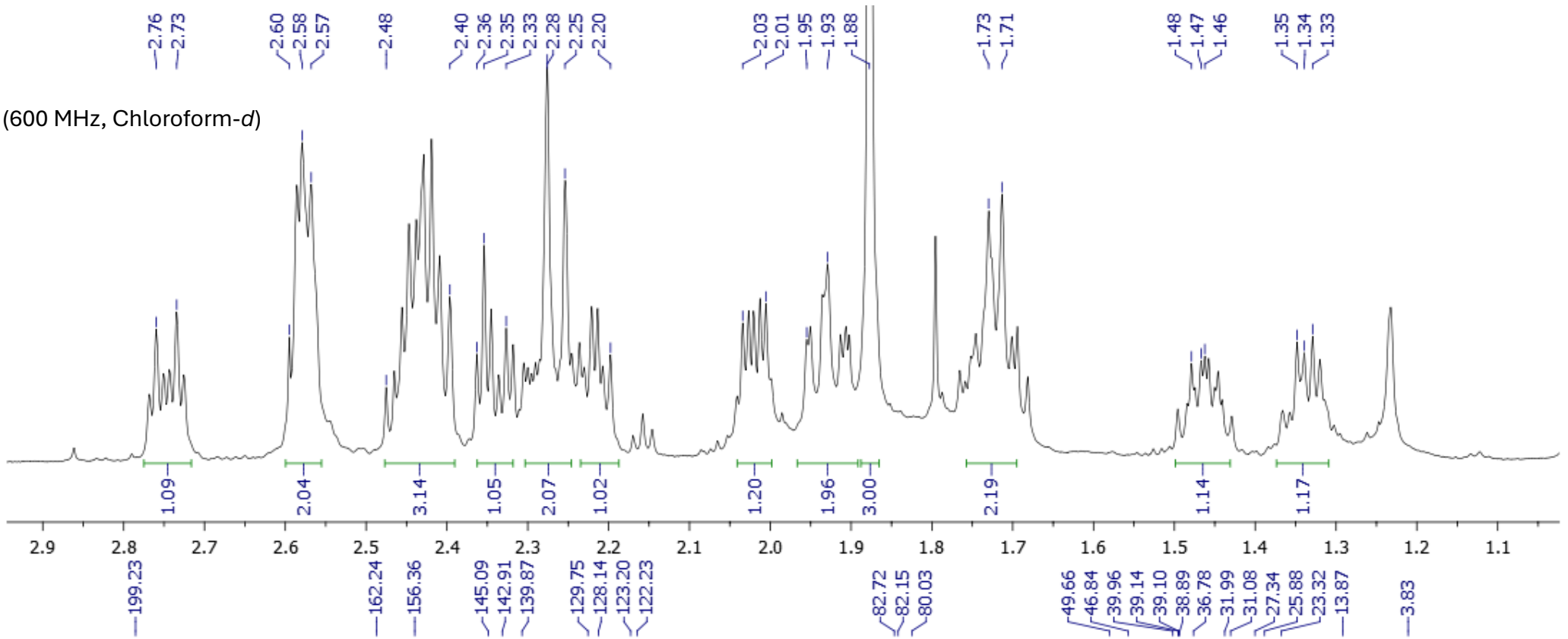


^{1}H NMR (600 MHz, Chloroform-*d*)

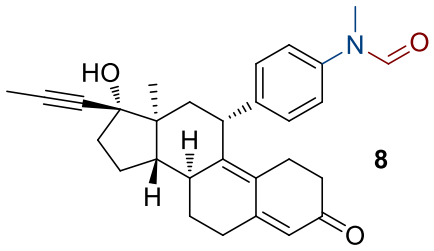


8

^{1}H NMR (600 MHz, Chloroform-*d*)

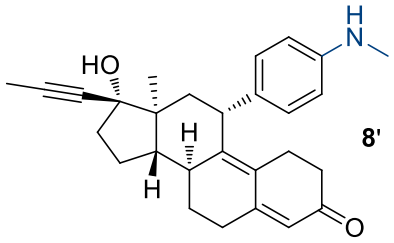


^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



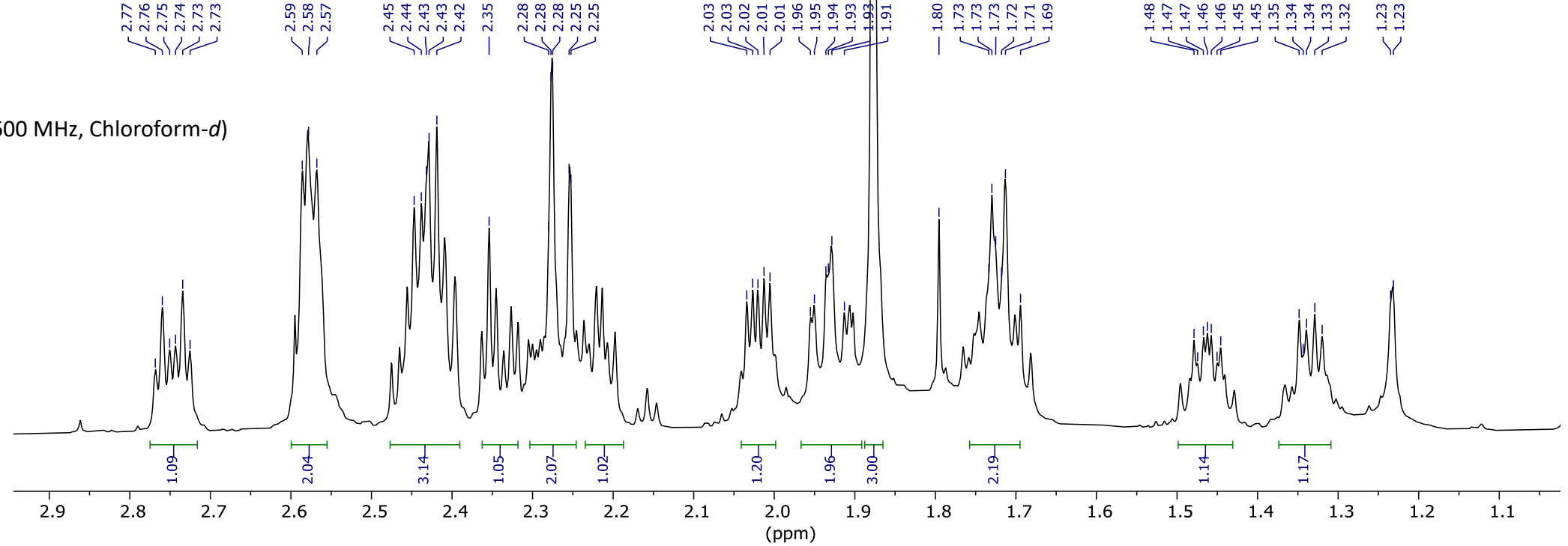
8

^{1}H NMR (600 MHz, Chloroform-*d*)

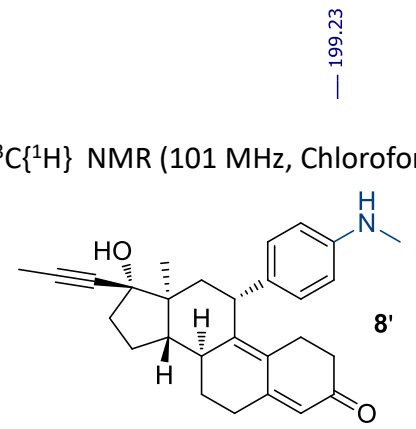


8'

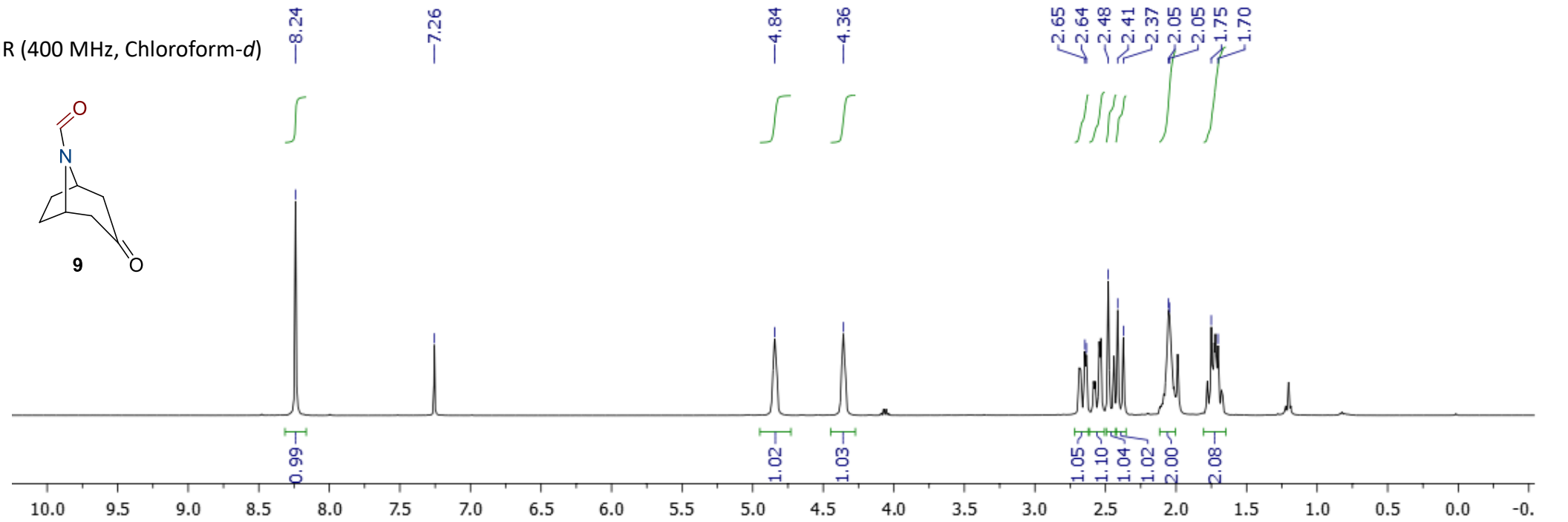
^{1}H NMR (600 MHz, Chloroform-*d*)



^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)

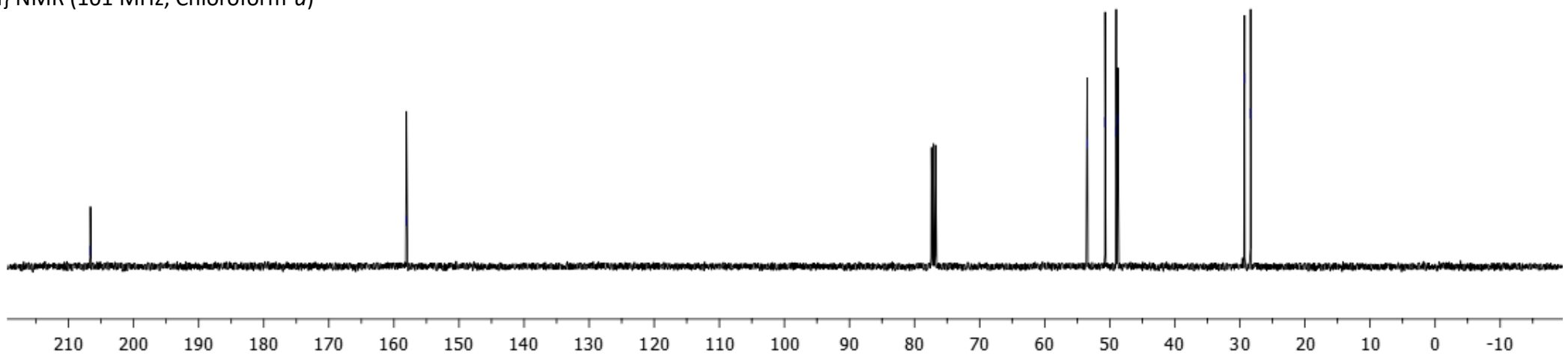


^{1}H NMR (400 MHz, Chloroform-*d*)

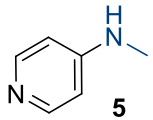


9

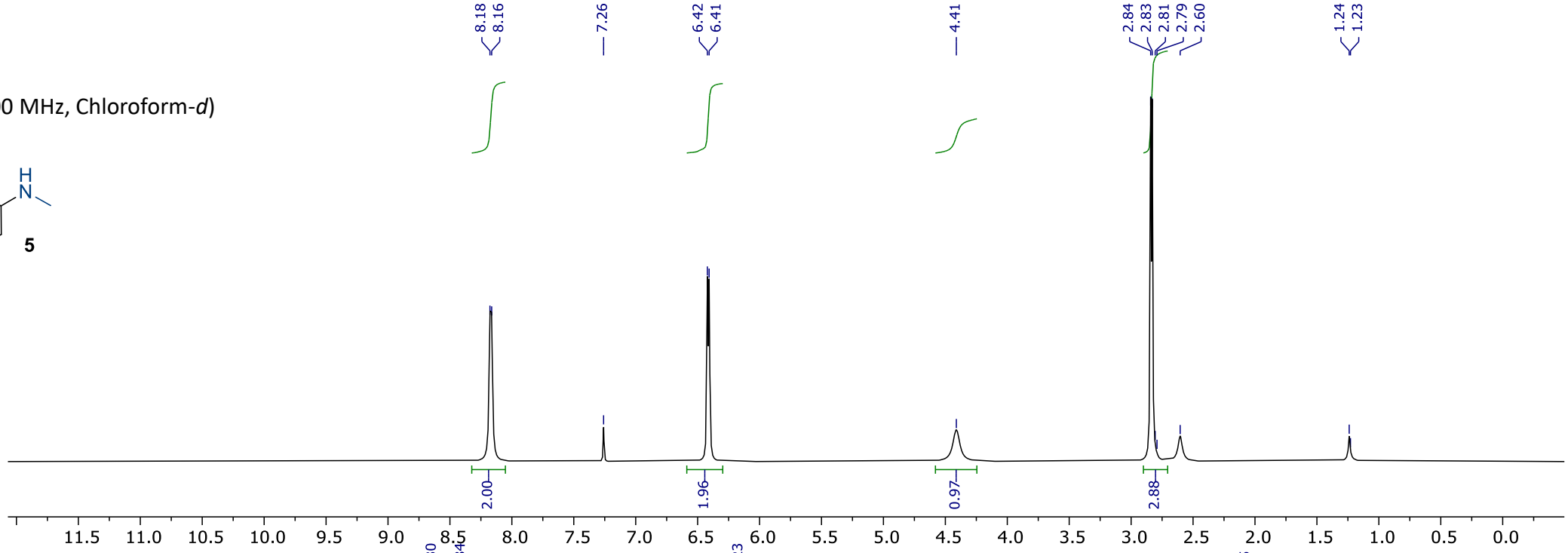
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)



^{1}H NMR (400 MHz, Chloroform-*d*)



5



^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)