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Supporting Information

Graphitic Carbon Nitride as Photocatalyst for the Direct Formylation of Anilines

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Summary

General information

All the chemicals involved in material synthesis and organic reactions have been purchased from vendors (Merck, TCI, Apollo Scientific) and used without further purification.

The UV-Vis characterization has been performed through an Agilent Cary 5000 equipped with an integrating sphere for the analysis of reflectance on solid samples. TEM images were collected with a Philips EM 208 microscope. The NMR spectra were recorded on a Varian 400 instrument (^{1}H: 400 MHz; ^{13}C: 101.0 MHz; ^{19}F: 376.0 MHz). The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvents ($CHCl_3$ @ 7.26 ppm for ^{1}H NMR, and @ 77.16 ppm for ^{13}C NMR; $CFCl_3$ @ 0.0 ppm for ^{19}F NMR spectra). The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High-Resolution Mass Spectra (HRMS) were obtained using Bruker micrOTOF-Q (ESI-TOF). Absorption spectroscopy studies have been performed on a Varian Cary 50 UV-Vis double beam spectrophotometer also equipped with an integrating sphere for reflectance analysis. All the spectra were recorded at room temperature using 10-mm path length Hellma Analytics quartz cuvettes. The Kessil lamps PR160L 50W (427 nm, 440 nm, 456 nm, 525 nm) were purchased from Kessil webpage (link: https://kessil.com/products/science_PR160L.php). The photochemical reactions were carried out in borosilicate glass Schlenk tubes.

g-CN synthesis

The material has been synthetized by following a reported procedure.[48] Briefly, 5 g of melamine are placed in a alumina crucible and heated at 550°C for 5 h (ramp: 5°C/min). Then, the resulting agglomerate is milled in a mortar up to get a uniform fine yellow powder.

UV-Visible characterization and studies

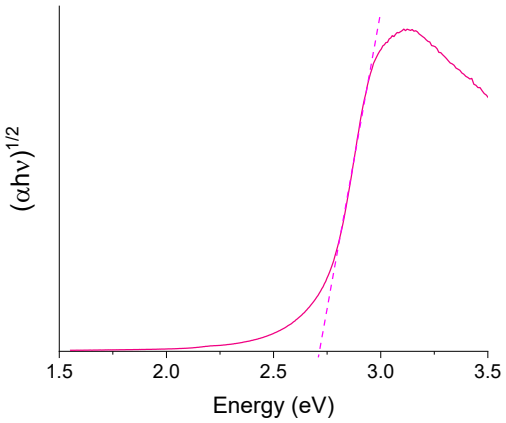


Figure S1. Tauc plot for the g-CN exploited for these reactions. Accordingly, the semiconductor exhibits a direct band gap equal to 2.72eV.

Photocatalyst, namely g-CN, is the only species that can absorb light at 440 nm. We did not observe any ground-state association between the starting materials, because their combination did not lead to relevant change of the absorption spectra (Figure S2). Moreover, we confirmed that product **2a** does not absorb photons at 440 nm. This suggests that this compound does not undergo photoinduced degradation under the reaction conditions.

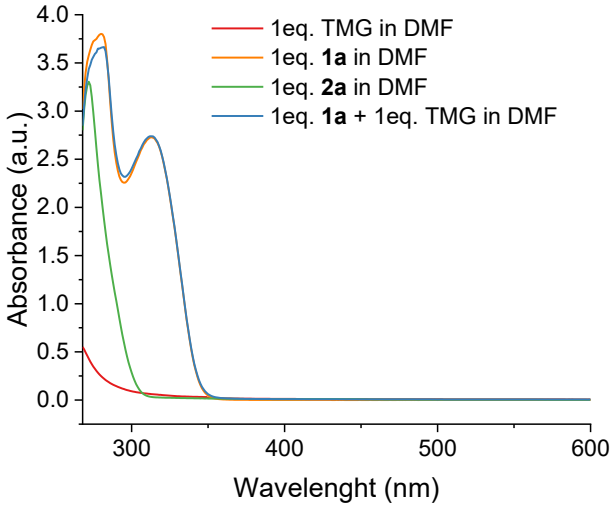


Figure S2. UV-Vis spectra of 1,1,3,3-tetramethylguanidine (TMG), 4-bromo-*N,N*-dimethylaniline (**1a**), *N*-(4-bromophenyl)-*N*-methylformamide (**2a**) in DMF and the combination of TMG and **1a** as at the initial reaction.

General procedure for the formylation of 1

A 10 mL Schlenk tube was charged with the aniline **1** (0.1 mmol, 1equiv.), *N*,*N*-dimethylformamide (DMF, 1 mL), 1,1,3,3-tetramethylguanidine (TMG, 12.5 µL, 1 equiv.) and 10 mg of g-CN. A balloon filled with air was connected to the Schlenk tube to ensure an abundant reservoir of air. The reaction vessel was then placed at 1.5 cm from a Kessil lamp (λ = 440 nm). The temperature was kept at around 30°C by using a fan. Stirring was maintained for 16 hours.

After the due time, the reaction crude was filtrated on a celite plug to remove the heterogeneous catalyst. The filtered crude was purified by column chromatography.

For the recyclability tests, instead, the crude mixture has been centrifuged and the settled solid was washed several times with ethyl acetate. After drying under vacuum at room temperature, the catalyst was reused additional four times. The presented yields are the average results of at least three repeats.

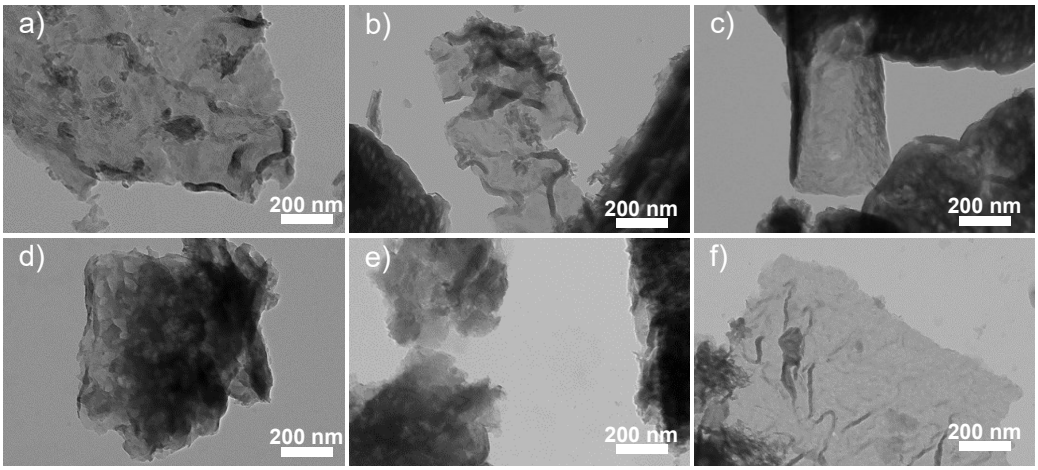


Figure S3. TEM images (20k magnification) of the g-CN before use (**a-c**) and after the 5th cycle (**d-f**).

Electrochemical measurements

Impedance electrochemical measurements (EIS) have been performed in a 0.1 M tert-butyl ammonium phosphate (TBAP) electrolyte solution in DMF with the addition of 5.0×10^{-3} M of the anilines 4-bromo-*N,N*-dimethylaniline (**1a**), 4-(dimethylamino)benzonitrile (**1d**), *N,N*-dimethylaniline (**1j**) and 4,*N,N*-trimethylaniline (**1k**) to investigate polarization (Rp) and charge transfer resistance (Rct) at Open Circuit Potential (OCP) condition.

EIS measurements were performed using a frequency response analyzer (FRA, AutoLab 302 N, Metrohm) at room temperature. EIS spectra were recorded in a three-electrode thin film rotating disc electrode (TF-RDE) configuration under dark condition and with a light source (Kessil lamp at 440nm): a platinum wire was used as the counter electrode; a catalyst-coated glassy-carbon (GC, 16 mL of catalysts ink) rotating disk electrode (Autolab RDE, Metrohm) with surface area of 0.196 cm^2 was used as working electrode; a saturated calomel electrode (SCE) was used as reference electrode, that was separated from the solution by a bridge equipped with a Vycor frit. EIS spectra (single sine measurements) were acquired at OCP under pure Ar atmosphere with a 10-mV amplitude voltage perturbation in the frequency range from 100 kHz to 0.1 Hz, at a rotation speed of 1200 rpm.

Regarding the ink preparation, 2.5 mg of finely grounded g-CN have been dispersed into 0.5 mL of DMF containing 20 µL of Nafion. After sonicating for 1 h, 16 µL of as-prepared ink has been used to cover the GC and left drying under vacuum.

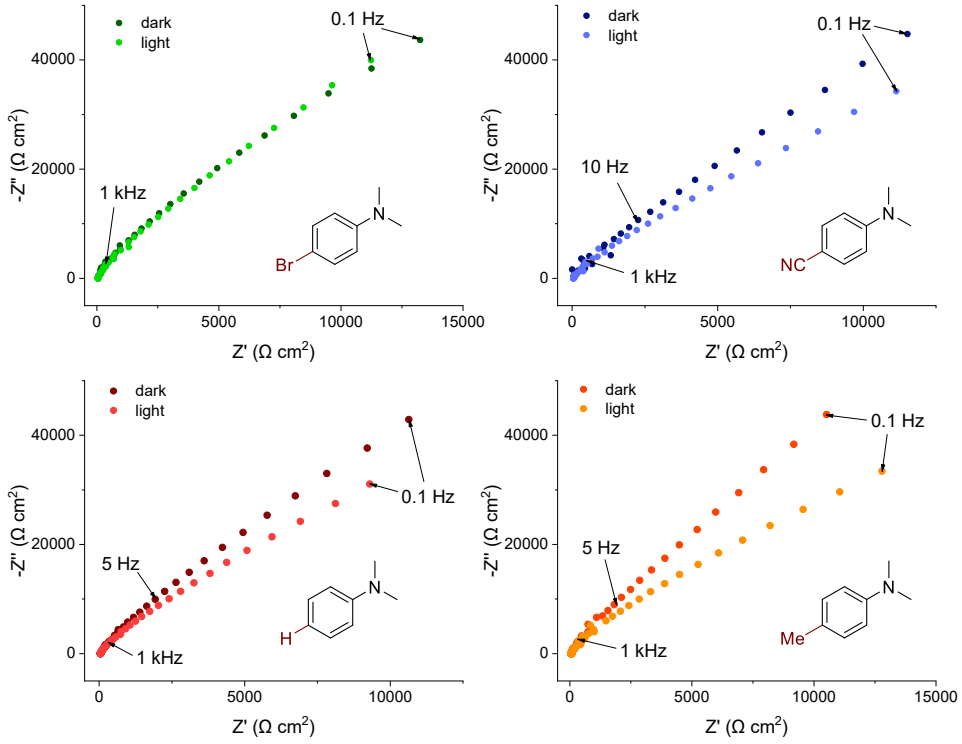


Figure S4. Nyquist plot for the anilines **1a**, **1d**, **1j** and **1k**

Cyclic Voltammetry (CV) measurements were performed in a 0.1 M TBAP electrolyte solution in DMF with the addition of 5.0×10^{-3} M of the anilines **1a**, **1d**, **1j** and **1k** to determine the oxidation potential of the four different probe molecules.

CVs were performed in the same three-electrode TF-RDE cell previously described under pure Ar atmosphere, by using the Potentiostat AutoLab 302 N (Metrohm) in the potential range from 0 to 1.5 V with a scan rate of 50 mV/s. A polished GC disk electrode (Autolab RDE, Metrohm) with surface area of 0.196 cm^2 was used as working electrode in static condition.

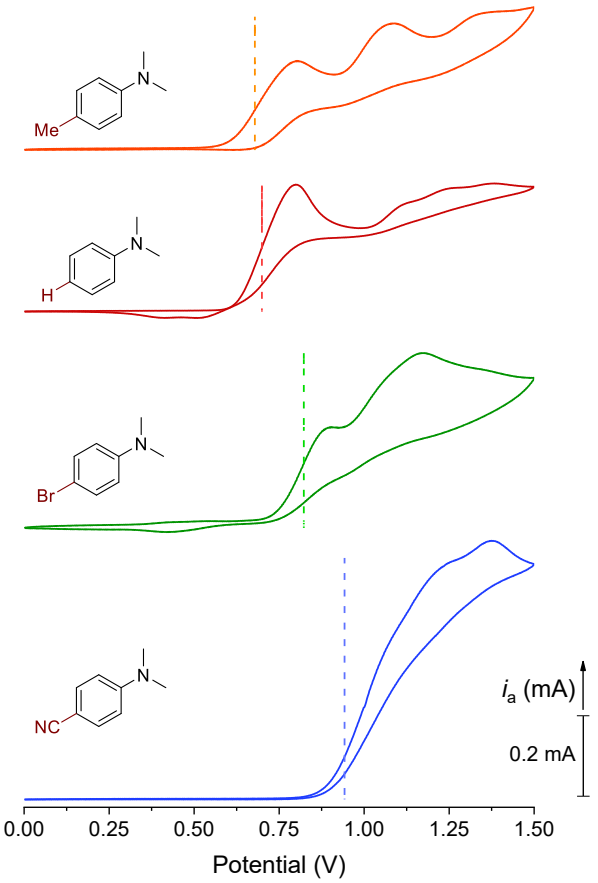
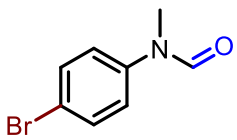


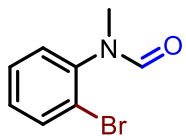
Figure S5. Cyclovoltammetry profiles for the amines (from the bottom) **1d**, **1a**, **1j** and **1k**

Observations obtained through cyclic voltammetry measurements are in good agreement with the features already known from previous reports. The formation of radical cations can be associated to the first oxidation peak[65-68], whose corresponding values upshift passing from electron-donating groups to electron withdrawing ones[69]. In particular, we obtained the following $E_{1/2}$ values: 0.82 V (**1a**), 0.94 V (**1d**), 0.70 V (**1j**), and 0.68 V (**1k**).

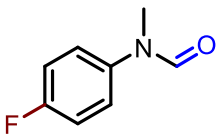
Characterization data of the reaction products



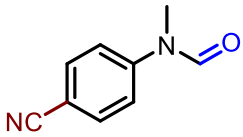
***N*-(4-bromophenyl)-*N*-methylformamide (2a).** Prepared according to the general procedure using 4-bromo-*N,N*-dimethylaniline **1a** (0.1 mmol, 20.0 mg). Product **2a** was purified by purified by silica gel flash chromatography (eluent: cyclohexane/ethyl acetate 7:3), recrystallized in hexane and obtained as white solid (17.22 mg, 80% yield). The characterization of the compound matches with the data reported in the literature.[43] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 7.55 – 7.51 (m, 2H), 7.08 – 7.03 (m, 2H), 3.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.91, 132.73, 123.77, 119.72, 31.98. HRMS (ESI): *m/z* calculated for $C_8H_8BrNO+Na^+$: 235.9681 $[M+Na]^+$; found: 235.9681.



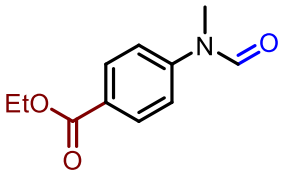
***N*-(2-bromophenyl)-*N*-methylformamide (2b).** Prepared according to the general procedure using *2*-bromo-*N,N*-dimethylaniline **1b** (0.1 mmol, 14.40 µL). Product **2b** was purified by silica gel flash chromatography (eluent: cyclohexane/ethyl acetate 4:1) and obtained as yellow oil (5.24 mg, 24% yield). The characterization of the compound matches with the data reported in the literature.[70] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.70 – 7.68 (m, 1H), 7.41 – 7.38 (m, 1H), 7.27 – 7.25 (m, 2H), 3.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.88, 133.95, 129.86, 129.55, 128.72, 122.39, 33.05. HRMS (ESI): *m/z* calculated for $C_8H_8BrNO+Na^+$: 235.9681 $[M+Na]^+$; found: 235.9681.



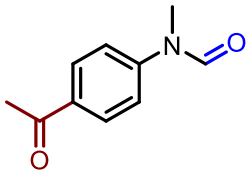
***N*-(4-Fluorophenyl)-*N*-methylformamide (2c)** Prepared according to the general procedure using 4-fluoro-*N,N*-dimethylaniline **1c** (0.1 mmol, 13.92 mg). Product **2c** was purified by silica gel flash chromatography (eluent: dichloromethane) and obtained as clear oil (7.15 mg, 47% yield). The characterization of the compound matches with the data reported in the literature.[43] ^{1}H NMR (400 MHz, CD_3CN): δ 8.40 (s, 1H), 7.32 – 7.29 (m, 2H), 7.21 – 7.18 (m, 2H), 3.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.21, 160.08, 138.32, 124.65, 116.40, 32.49. ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.32. HRMS (ESI): *m/z* calculated for $C_8H_8FNO+H^+$: 154.0663 $[M+H]^+$; found: 154.0663.



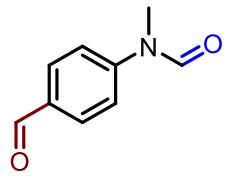
***N*-(4-Cyanophenyl)-*N*-methylformamide (2d)** Prepared according to the general procedure using 4-(dimethylamino)benzonitrile **1d** (0.1 mmol, 14.62 mg). Product **2d** was purified by silica gel flash chromatography (eluent: cyclohexane/ethyl acetate 1:1) and obtained as white solid (14.23 mg, 89% yield). The characterization of the compound matches with the data reported in the literature.[43] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 7.72 – 7.70 (m, 2H), 7.29 – 7.27 (m, 2H), 3.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.54, 145.85, 133.75, 121.06, 118.18, 109.37, 31.32. HRMS (ESI): *m/z* calculated for $C_9H_8N_2O+Na^+$: 183.0529 $[M+Na]^+$; found: 183.0529.



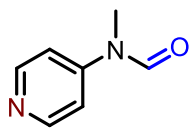
Ethyl 4-(*N*-methylformamido)benzoate (2e) Prepared according to the general procedure using ethyl 4-(dimethylamino)benzoate **1e** (0.1 mmol, 19.32 mg). Product **2e** was purified by silica gel flash chromatography (eluent: cyclohexane/ethyl acetate 3:2) and obtained as white solid (17.50 mg, 84% yield). The characterization of the compound matches with the data reported in the literature.[43] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 1H), 8.10 – 8.07 (m, 2H), 7.24 – 7.21 (m, 2H), 4.40-3.36 (q, 2H) 3.35 (s, 3H), 1.41-1.38 (t, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.71, 161.90, 145.89, 131.16, 127.95, 120.58, 61.16, 31.50, 14.31. HRMS (ESI): *m/z* calculated for $C_{11}H_{13}NO_3+Na^+$: 230.0788 $[M+Na]^+$; found: 230.0788.



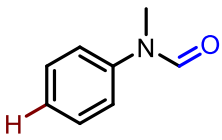
***N*-(4-Acetylphenyl)-*N*-methylformamide (2f)** Prepared according to the general procedure using 4-dimethylaminoacetophenone **1f** (0.1 mmol, 16.32 mg). Product **2f** was purified by silica gel flash chromatography (eluent: cyclohexane/ethyl acetate 1:1) and obtained as white solid (13.57 mg, 77% yield). The characterization of the compound matches with the data reported in the literature.[70] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.02 – 8.00 (m, 2H), 7.26 – 7.24 (m, 2H), 3.36 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.71, 161.90, 145.89, 131.16, 127.95,120.58, 61.16, 31.50, 14.31. HRMS (ESI): *m/z* calculated for $C_{10}H_{11}NO_2+Na^+$: 200.0682 $[M+Na]^+$; found: 200.0682.



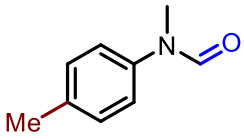
***N*-(4-Formylphenyl)-*N*-methylformamide (2g)** Prepared according to the general procedure using 4-(dimethylamino)benzaldehyde **1g** (0.1 mmol, 14.92 mg). Product **2g** was purified by silica gel flash chromatography (eluent: cyclohexane/ethyl acetate 7:3) and obtained as white solid (12.12 mg, 74% yield). The characterization of the compound matches with the data reported in the literature.[33] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 8.69 (s, 1H), 7.95 – 7.93 (m, 2H), 7.35 – 7.32 (m, 2H), 3.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.70, 161.75, 147.20, 133.71, 131.31, 120.82, 31.40.



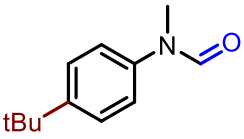
***N*-methyl-*N*-(pyridin-4-yl)formamide (2i)** Prepared according to the general procedure using 4-(dimethylamino)pyridine **1i** (0.1 mmol, 12.21 mg). Product **2i** was purified by silica gel flash chromatography (eluent: dichloromethane/methanol 95:5) and obtained as white solid (11.69 mg, 86% yield). The characterization of the compound matches with the data reported in the literature.[72] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.60 – 8.58 (m, 2H), 7.11 – 7.09 (m, 2H), 3.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.11, 151.20, 148.82, 113.68, 30.19.



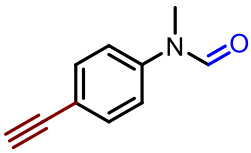
***N*-methyl-*N*-phenylformamide (2j)** Prepared according to the general procedure using *N,N*-dimethylaniline **1j** (0.1 mmol, 12.67 µL). Product **2j** was purified by silica gel flash chromatography (eluent: cyclohexane/ethyl acetate 3:1) and obtained as white solid (8.55 mg, 63% yield). The characterization of the compound matches with the data reported in the literature.[71] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 7.44 – 7.39 (m, 2H), 7.30 – 7.26 (m, 1H), 7.19 – 7.17 (m, 2H), 3.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.35, 142.20, 129.62, 122.39, 32.06. HRMS (ESI): *m/z* calculated for $C_8H_9NO+Na^+$: 158.0576 [*M*+Na]$^+$; found: 158.0576.



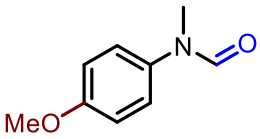
***N*-(4-Methylphenyl)-*N*-methylformamide (2k)** Prepared according to the general procedure using 4,*N,N*-trimethylaniline **1k** (0.1 mmol, 14.43 µL). Product **2k** was purified by silica gel flash chromatography (eluent: cyclohexane/ethyl acetate 3:1) and obtained as white solid (9.77 mg, 65% yield). The characterization of the compound matches with the data reported in the literature.[43] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.22 – 7.19 (m, 2H), 7.07 – 7.05 (m, 2H), 3.39 (s, 3H) 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.37, 139.70, 136.38, 130.15, 32.23, 20.86. HRMS (ESI): *m/z* calculated for $C_9H_{11}NO+Na^+$: 172.0733 [*M*+Na]$^+$; found: 172.0733.



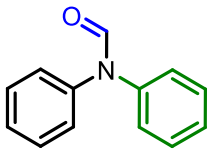
***N*-(4-(*tert*-Butyl)phenyl)-*N*-methylformamide (2l)** Prepared according to the general procedure using 4-(*tert*-butyl)-*N,N*-dimethylaniline **1l** (0.1 mmol, 19.57 µL). Product **2l** was purified by silica gel flash chromatography (eluent: cyclohexane/ethyl acetate 3:1) and obtained as orange solid (15.32 mg, 80% yield). The characterization of the compound matches with the data reported in the literature.[43] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.43 – 7.41 (m, 2H), 7.11 – 7.09 (m, 2H), 3.30 (s, 3H), 1.66 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.38, 149.59, 139.57,126.47, 122.16, 34.50, 32.11, 31.29. HRMS (ESI): *m/z* calculated for $C_{12}H_{17}NO+Na^+$: 214.1202 [*M*+Na]$^+$; found: 214.1202.



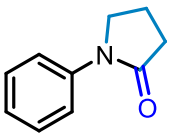
***N*-(4-Ethynylphenyl)-*N*-methylformamide (2m)** Prepared according to the general procedure using 4-ethynyl-*N,N*-dimethylaniline **1k** (0.1 mmol, 14.42 mg). Product **2m** was purified by silica gel flash chromatography (eluent: cyclohexane/ethyl acetate 3:1) and obtained as clear solid (11.68 mg, 73% yield). The characterization of the compound resulted as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 7.54 – 7.52 (m, 2H), 7.14 – 7.12 (m, 2H), 3.31 (s, 3H), 3.11(s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.97, 142.36, 133.44, 120.02, 82.55, 78.02, 31.71. HRMS (ESI): *m/z* calculated for $C_{10}H_9NO+Na^+$: 182.0576 [*M*+Na]$^+$; found: 182.0576.



4'-Methoxy-*N*-methylformanilide (2n) Prepared according to the general procedure using 4-methoxy-*N,N*-dimethylaniline **1n** (0.1 mmol, 15.12 mg). Product **2n** was purified by silica gel flash chromatography (eluent: cyclohexane/ethyl acetate 7:3) and obtained as orange oil (9.52 mg, 58% yield). The characterization of the compound matches with the data reported in the literature.[33] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.11 – 7.08 (m, 2H), 6.93 – 6.92 (m, 2H), 3.82 (s, 3H), 3.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.46, 158.29, 135.25, 124.66, 114.75, 55.54, 32.69.



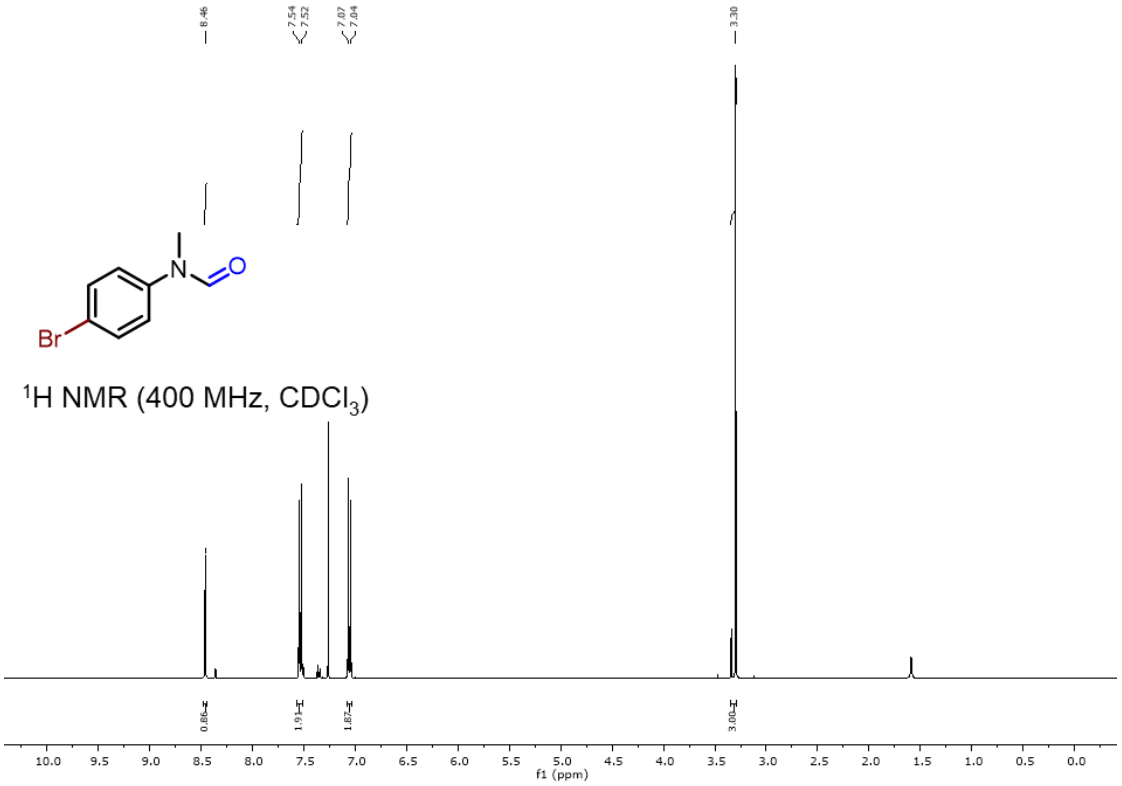
***N,N*-diphenylformamide (2o)** Prepared according to the general procedure using *N*-methyldiphenylamine **1o** (0.1 mmol, 17.45 mg). Product **2o** was purified by silica gel flash chromatography (eluent: cyclohexane/ethyl acetate 3:1) and obtained as yellow solid (12.21 mg, 62% yield). The characterization of the compound matches with the data reported in the literature.[43] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.41 – 7.39 (m, 4H), 7.30 – 7.19 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.75, 141.79, 139.62, 129.70, 129.19, 127.05, 126.88, 126.12, 125.09. HRMS (ESI): *m/z* calculated for $C_{13}H_{11}NO+Na^+$: 220.0733 [*M*+Na]$^+$; found: 220.0733.



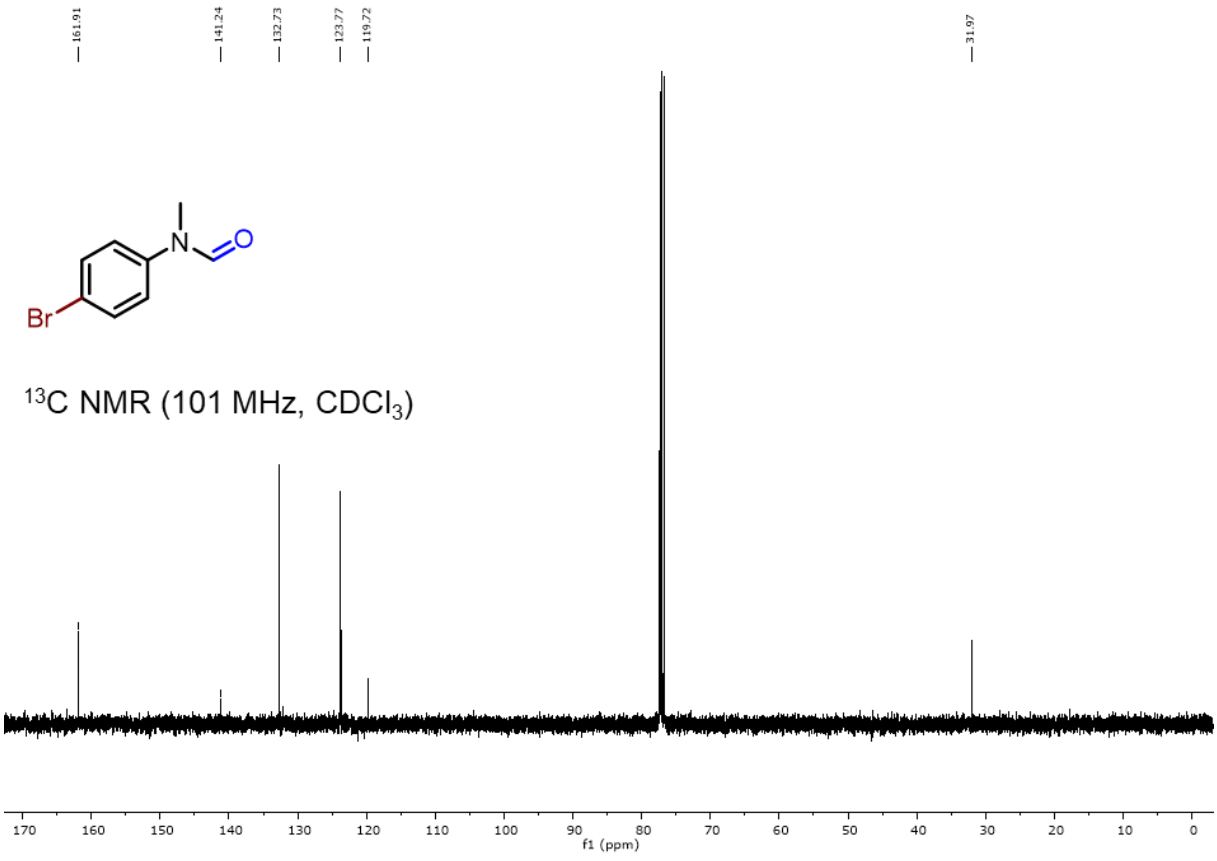
1-Phenylpyrrolidin-2-one (2p) Prepared according to the general procedure using 1-phenylpyrrolidine **1p** (0.1 mmol, 14.72 µL). Product **2p** was purified by silica gel flash chromatography (eluent: cyclohexane/ethyl acetate 7:3) and obtained as orange solid (6.33 mg, 39% yield). The characterization of the compound matches with the data reported in the literature.[73] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.60 (m, 2H), 7.38 – 7.35 (m, 2H), 7.16 – 7.14 (m, 1H), 3.88 – 3.86 (t, 2H), 2.63 – 2.60 (t, 2H), 2.20 – 2.13 (q, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.19.11, 139.41, 128.81, 124.49, 119.95, 48.78, 32.75, 18.04.

^{1}H, ^{13}C and ^{19}F NMR spectra of the isolated products

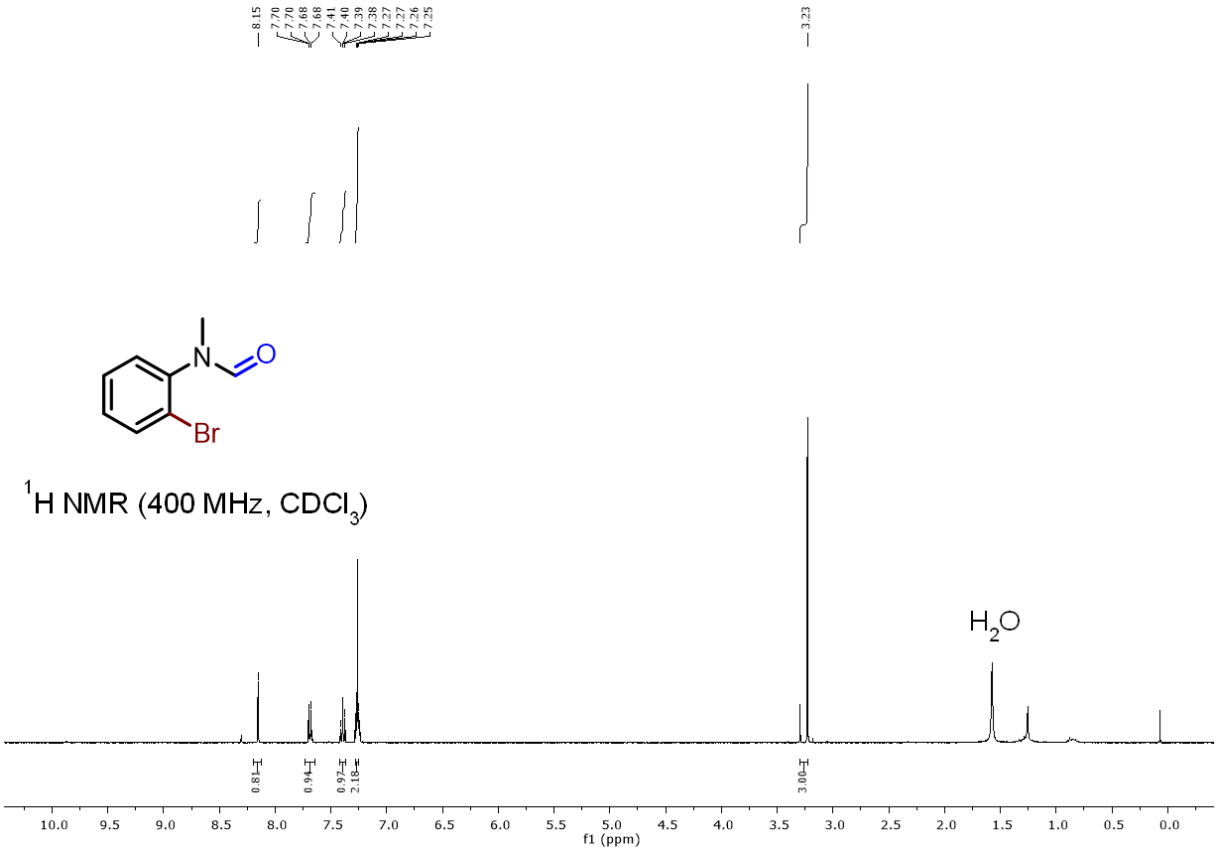
2a-^{1}H NMR



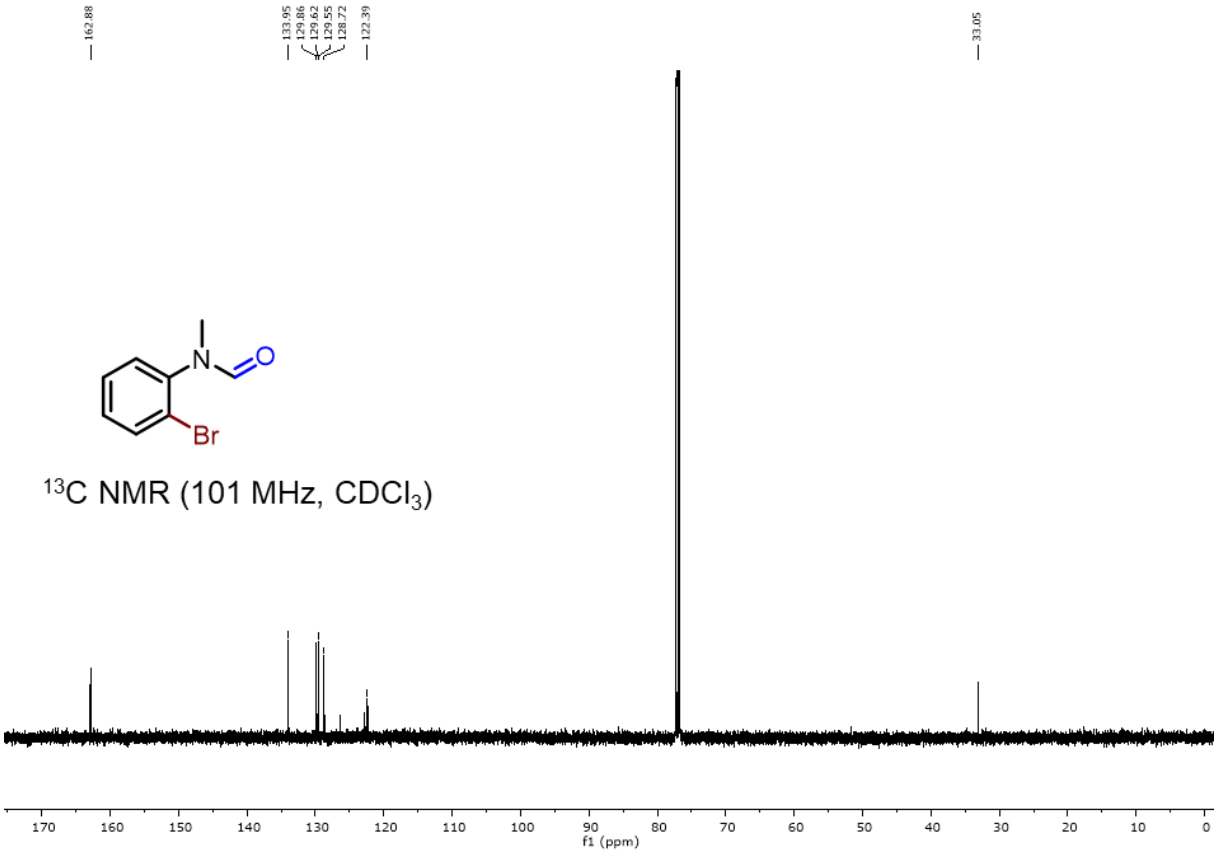
2a-^{13}C NMR



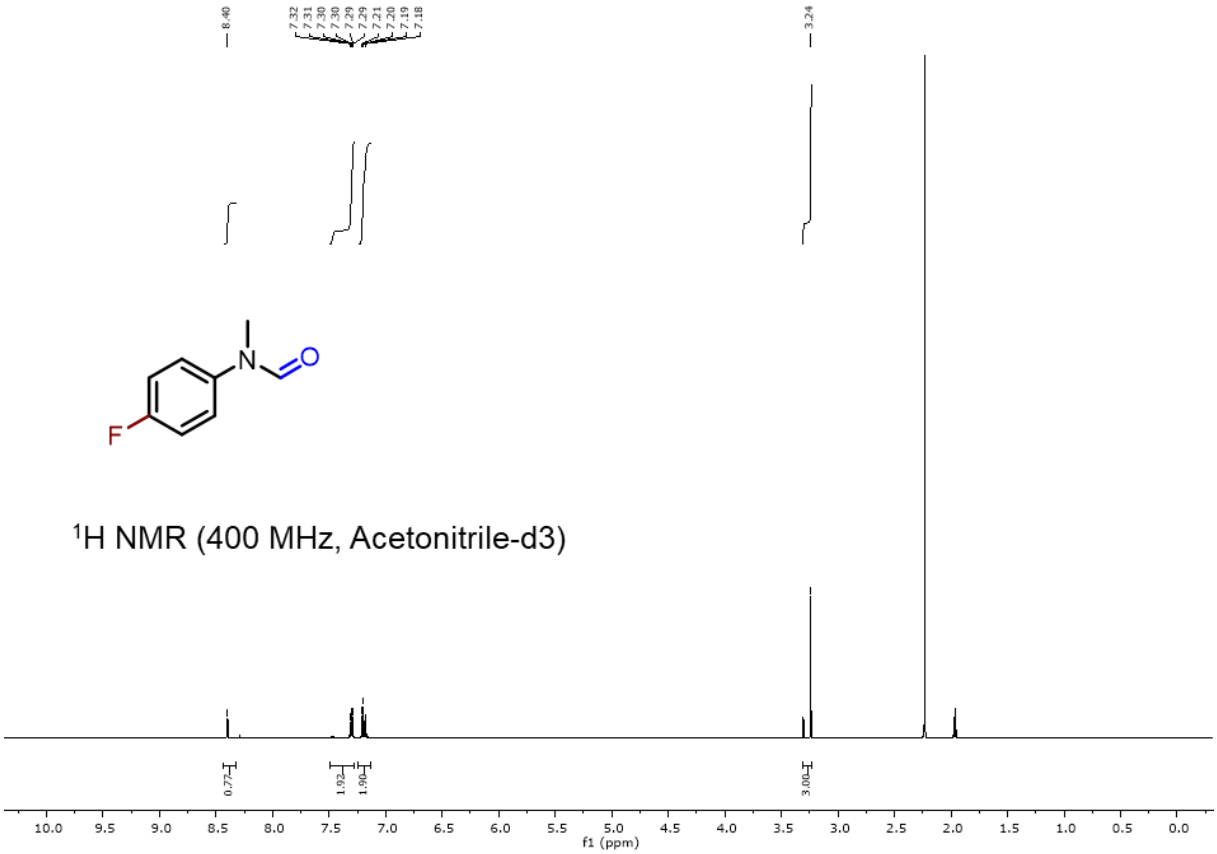
2b-^{1}H NMR



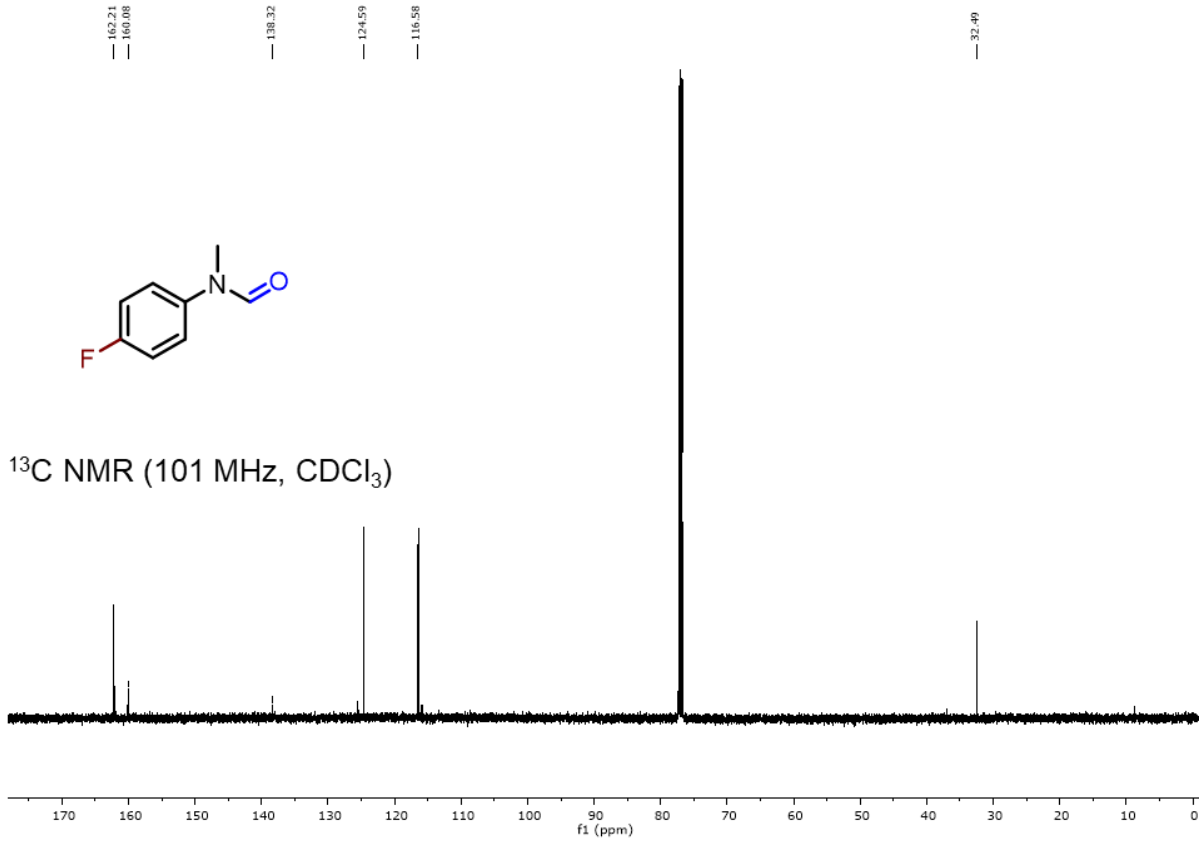
2b-^{13}C NMR



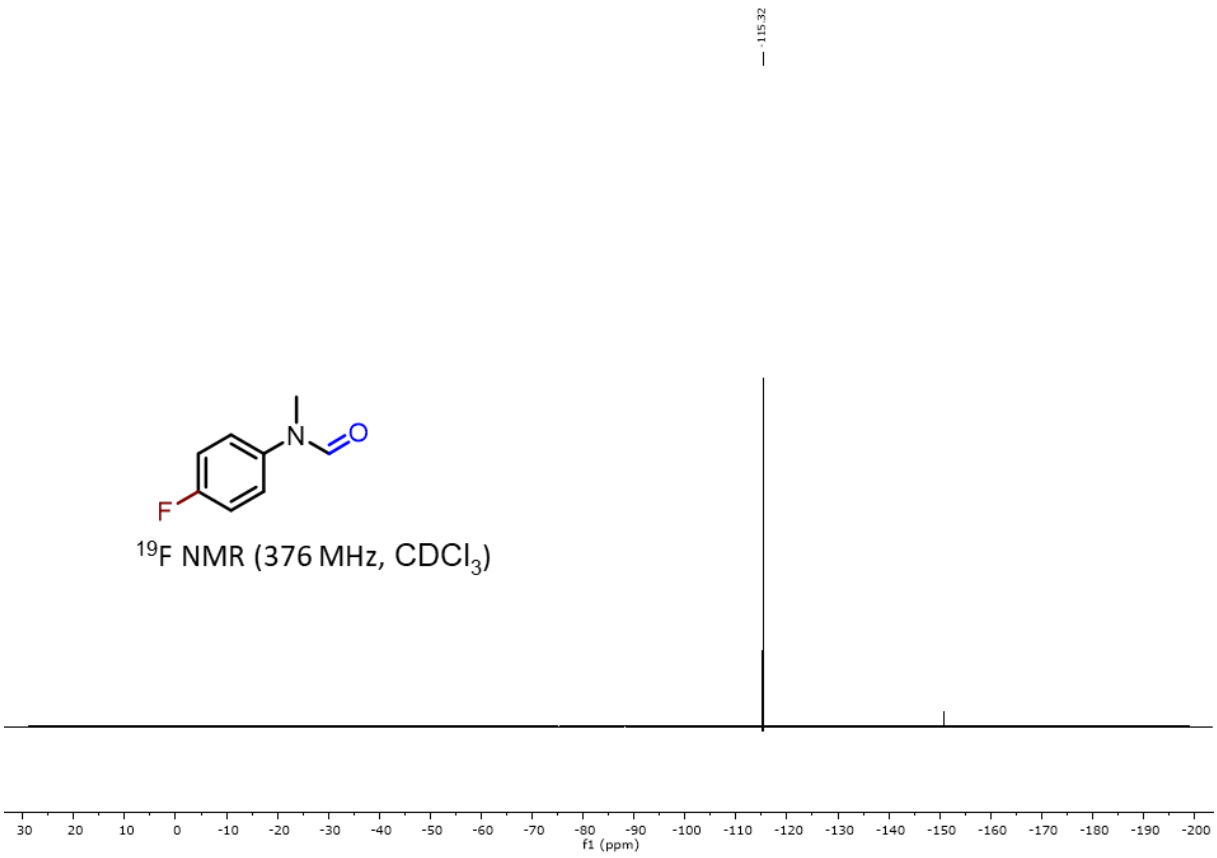
2c-^{1}H NMR



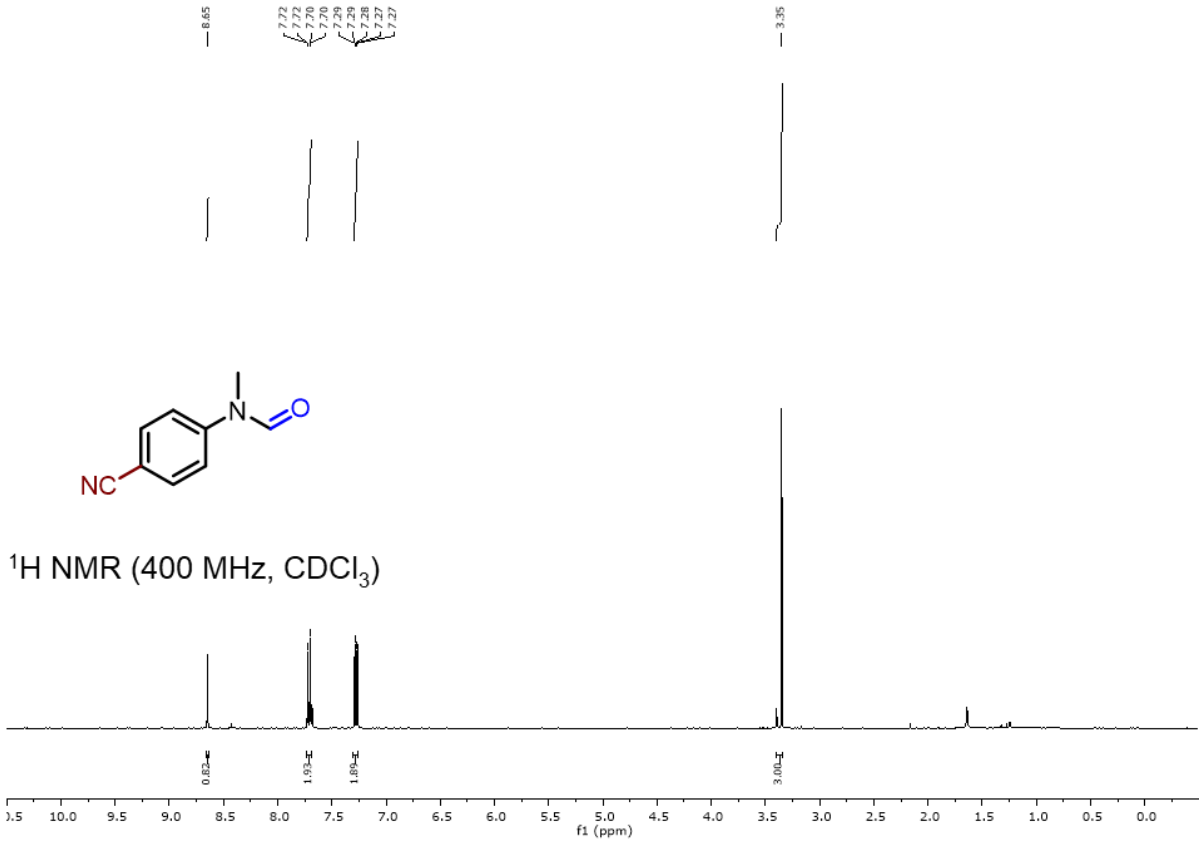
2c-^{13}C NMR



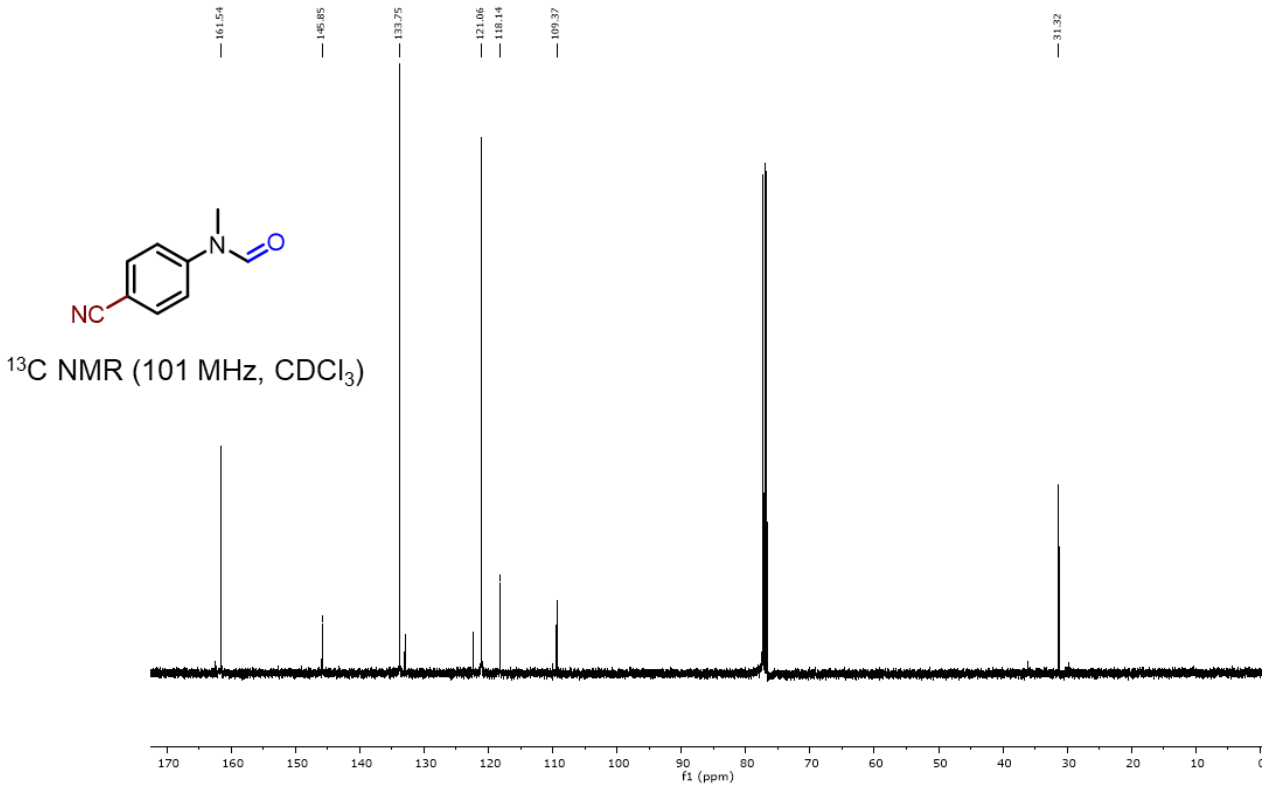
2c-^{19}F NMR



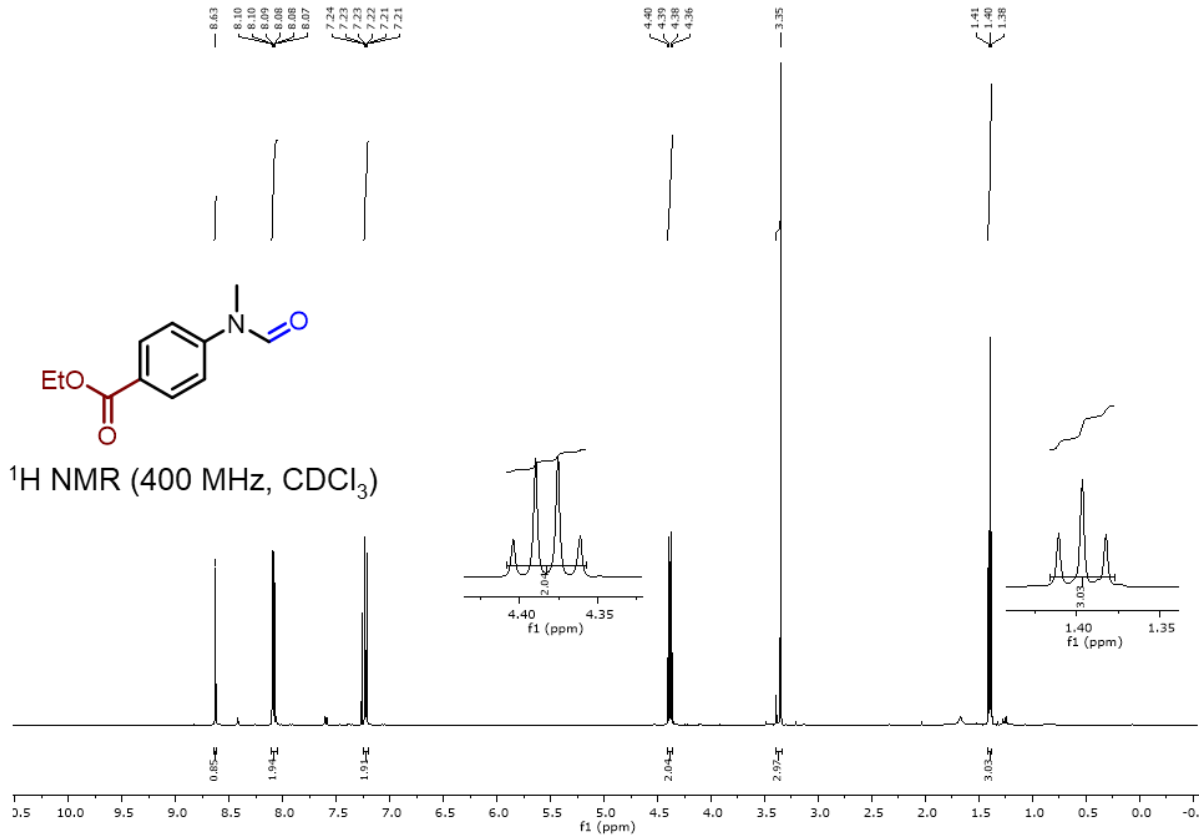
2d-^{1}H NMR



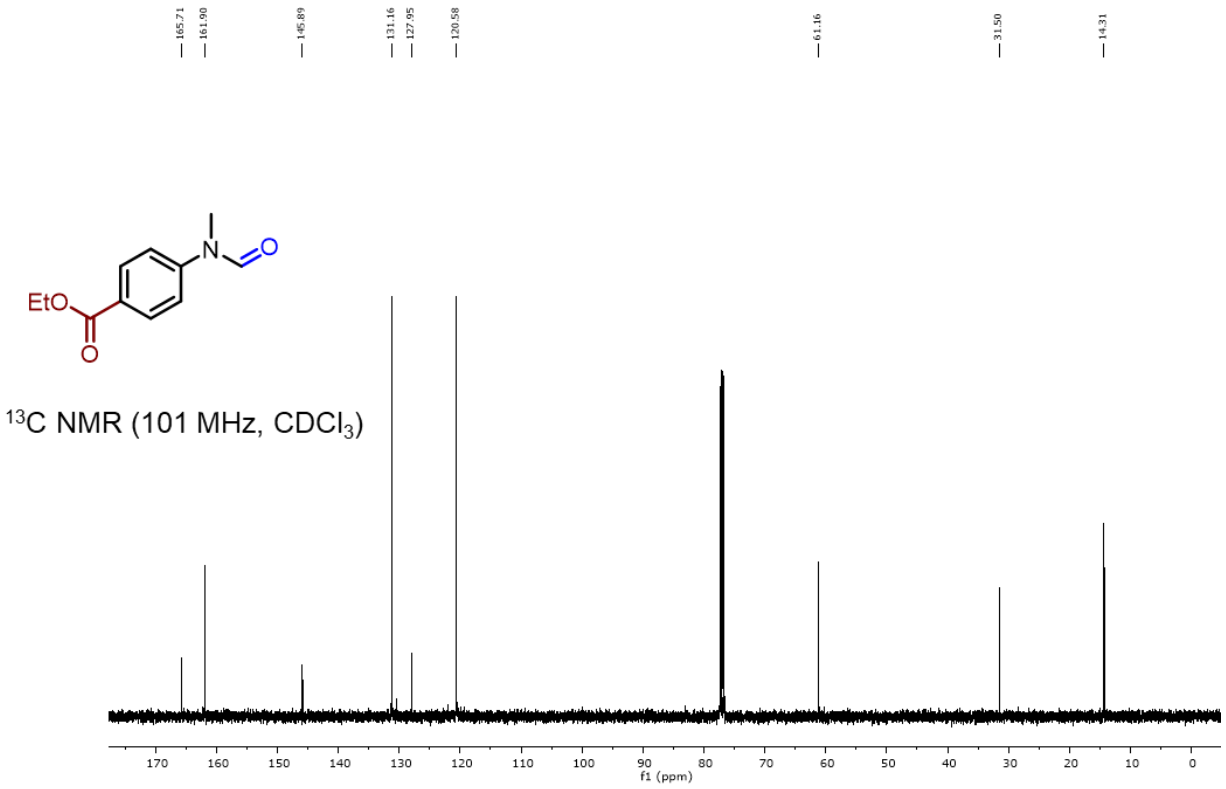
2d-^{13}C NMR



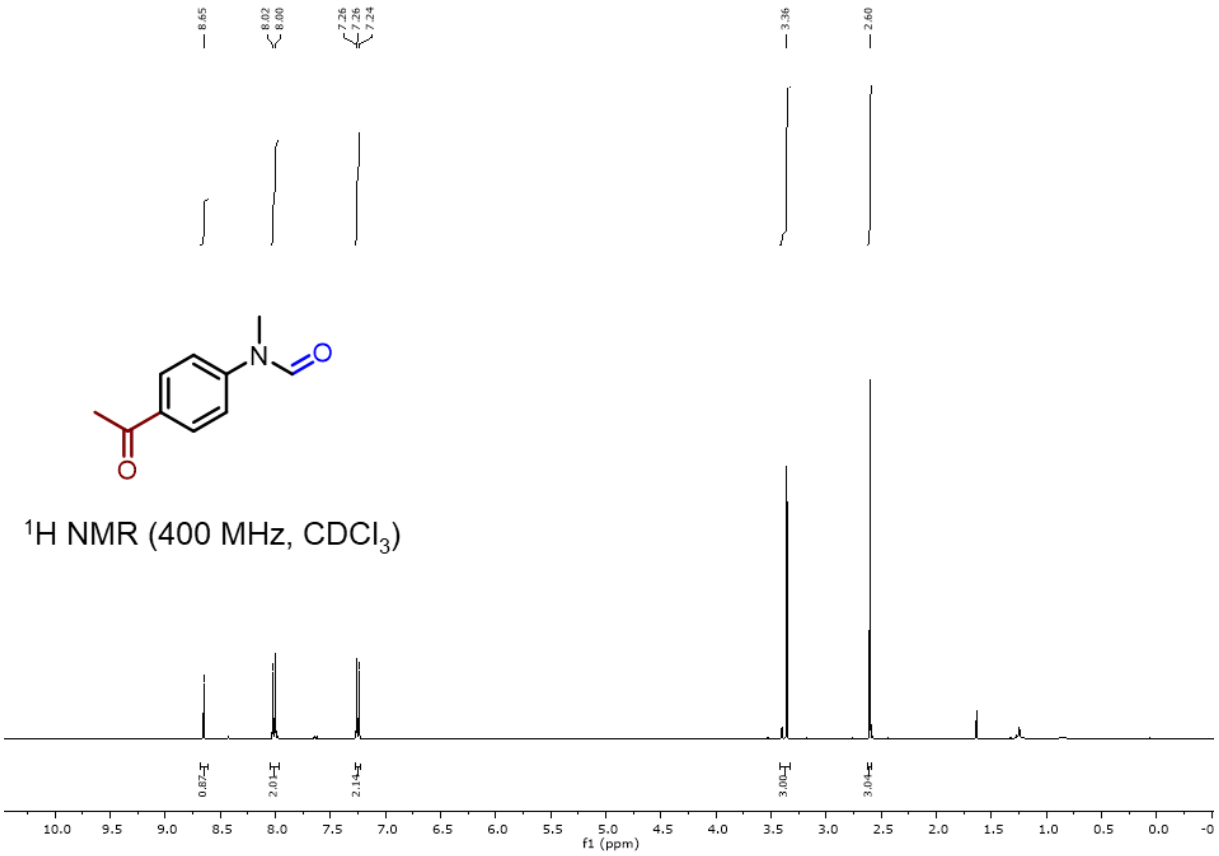
2e-^{1}H NMR



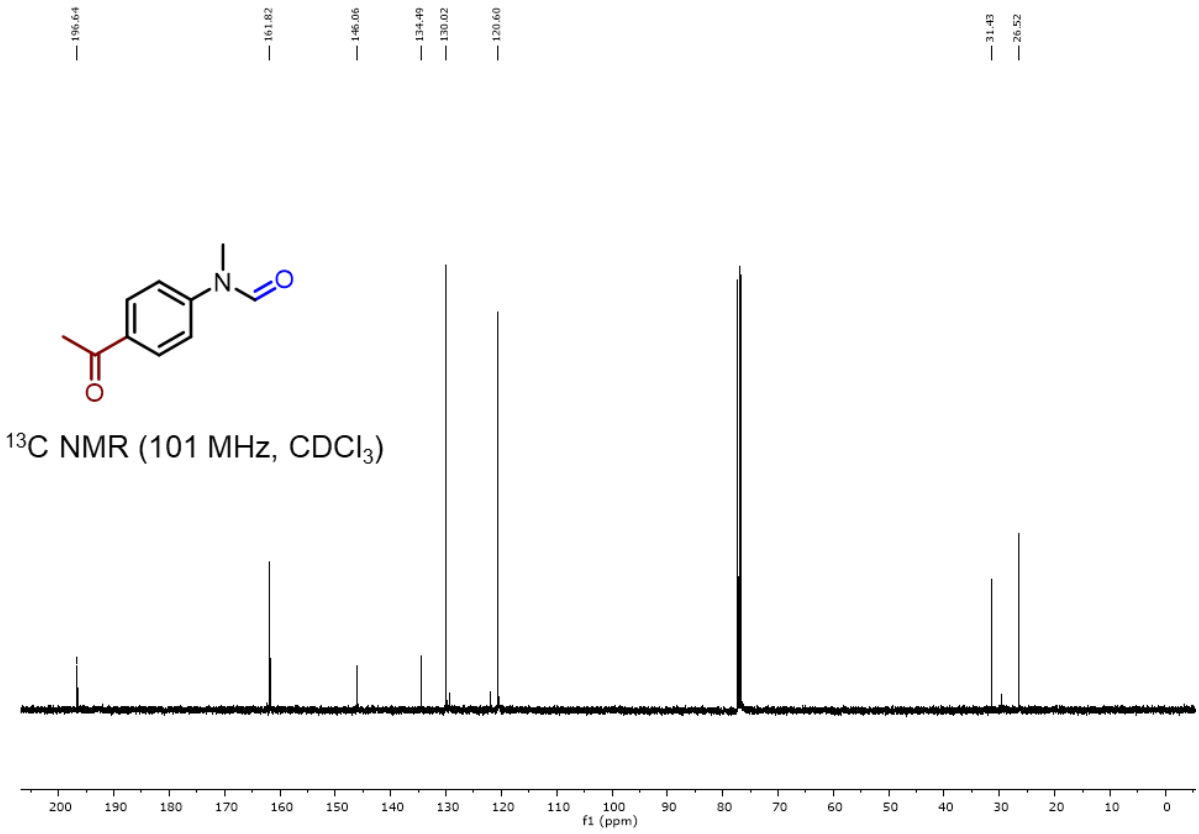
2e-^{13}C NMR



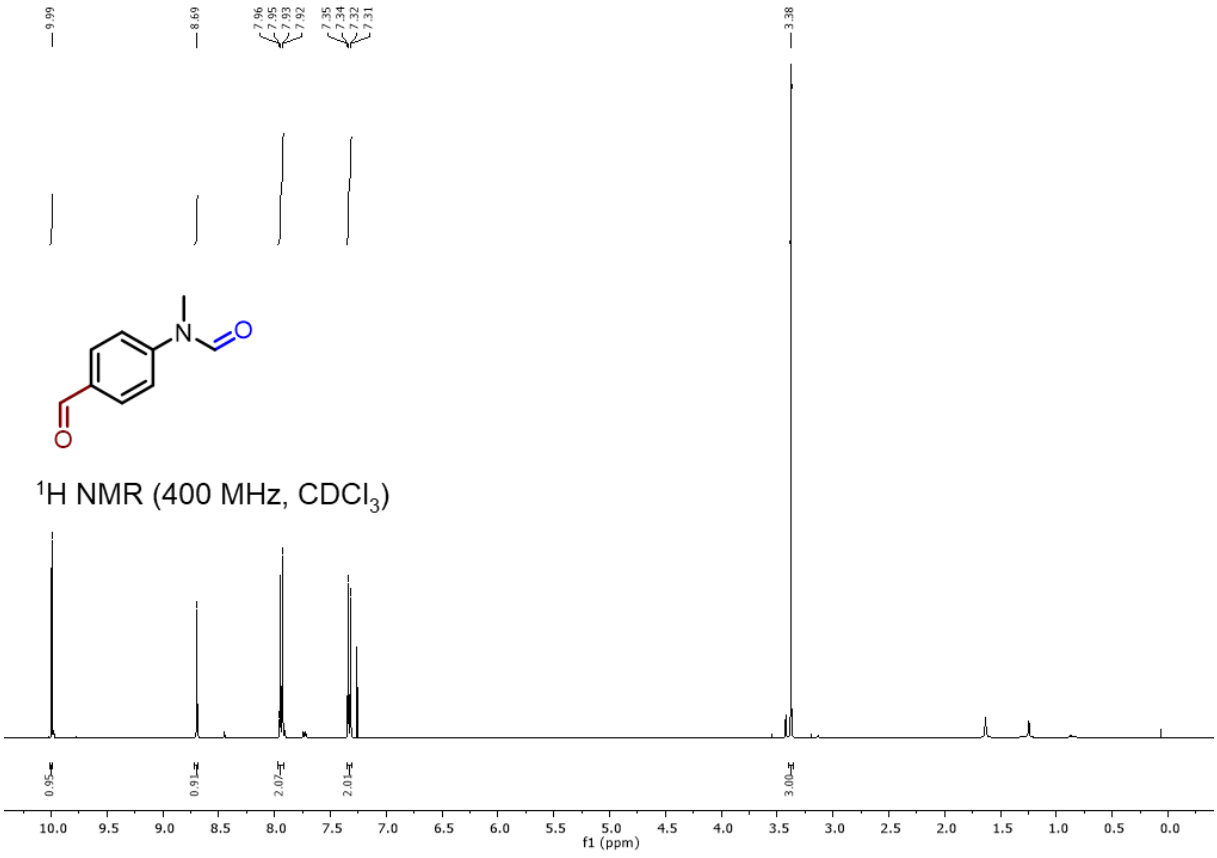
2f-^{1}H NMR



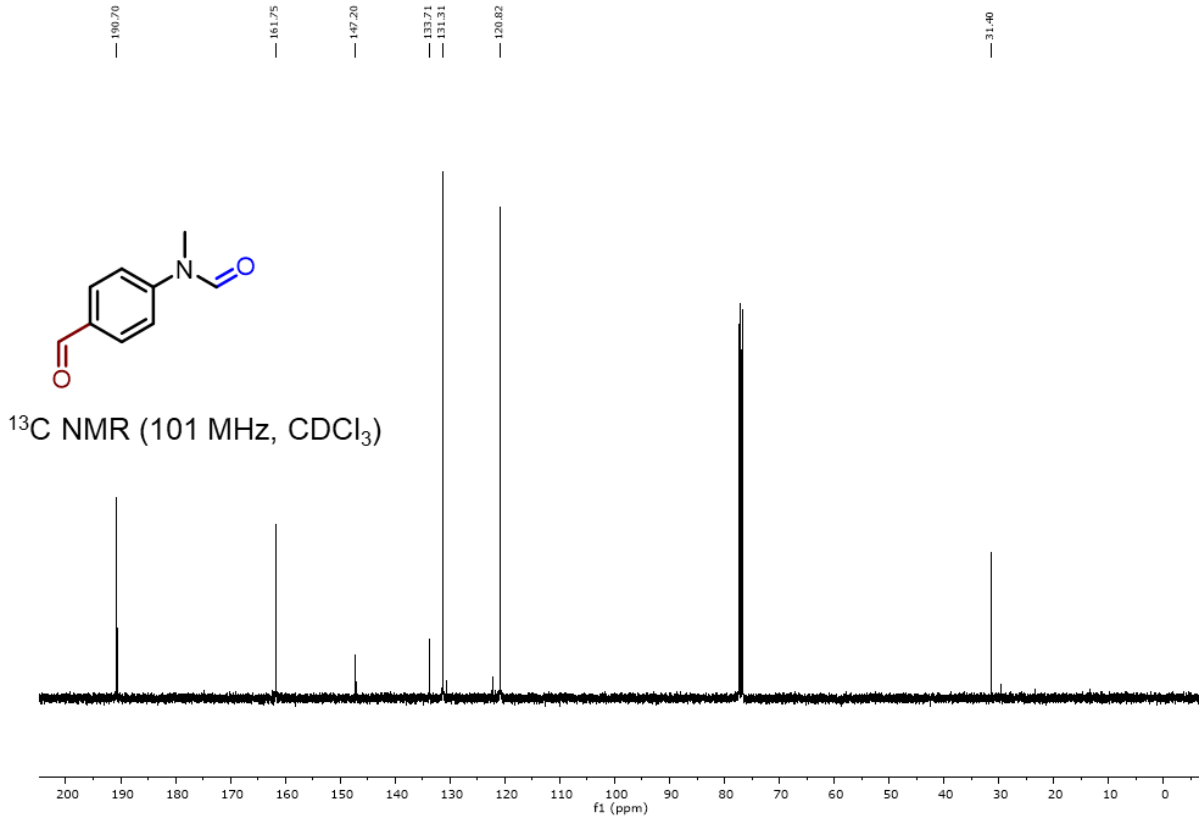
2f-^{13}C NMR



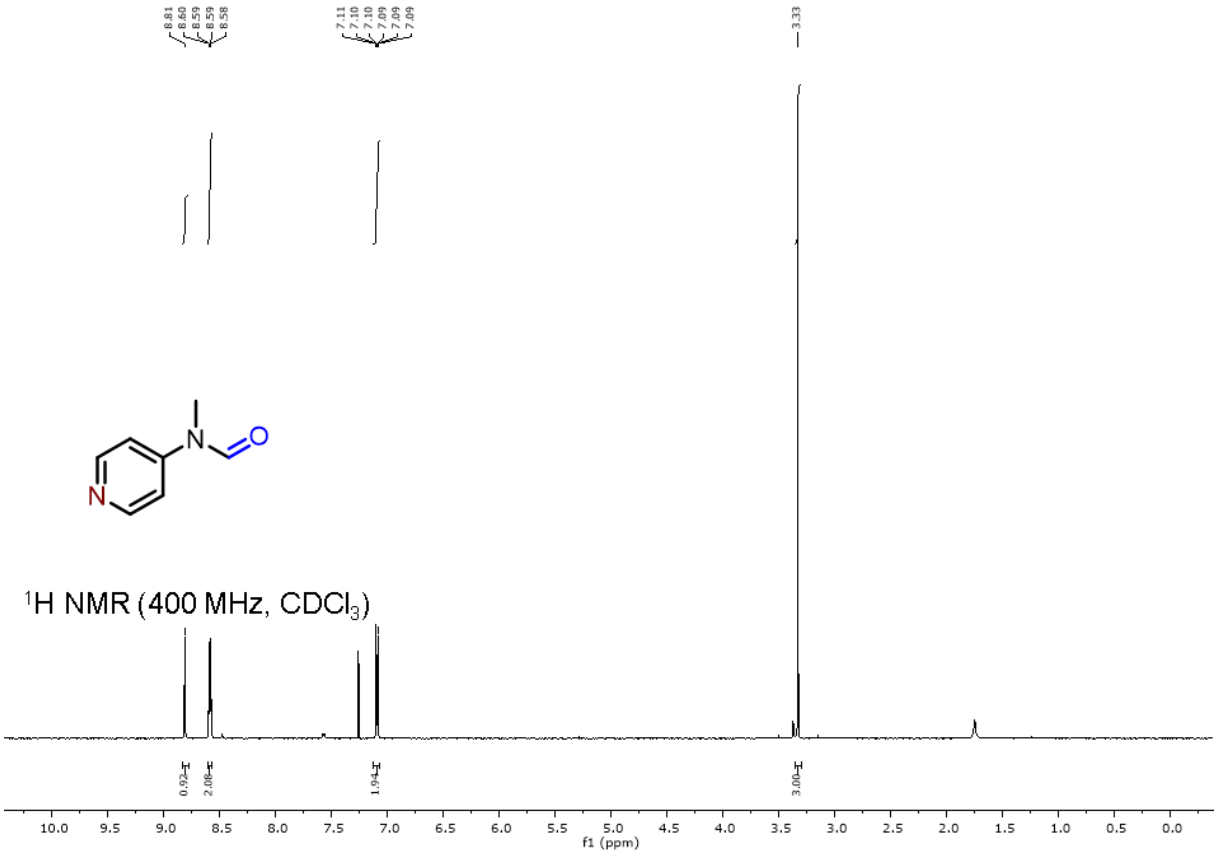
2g-^{1}H NMR



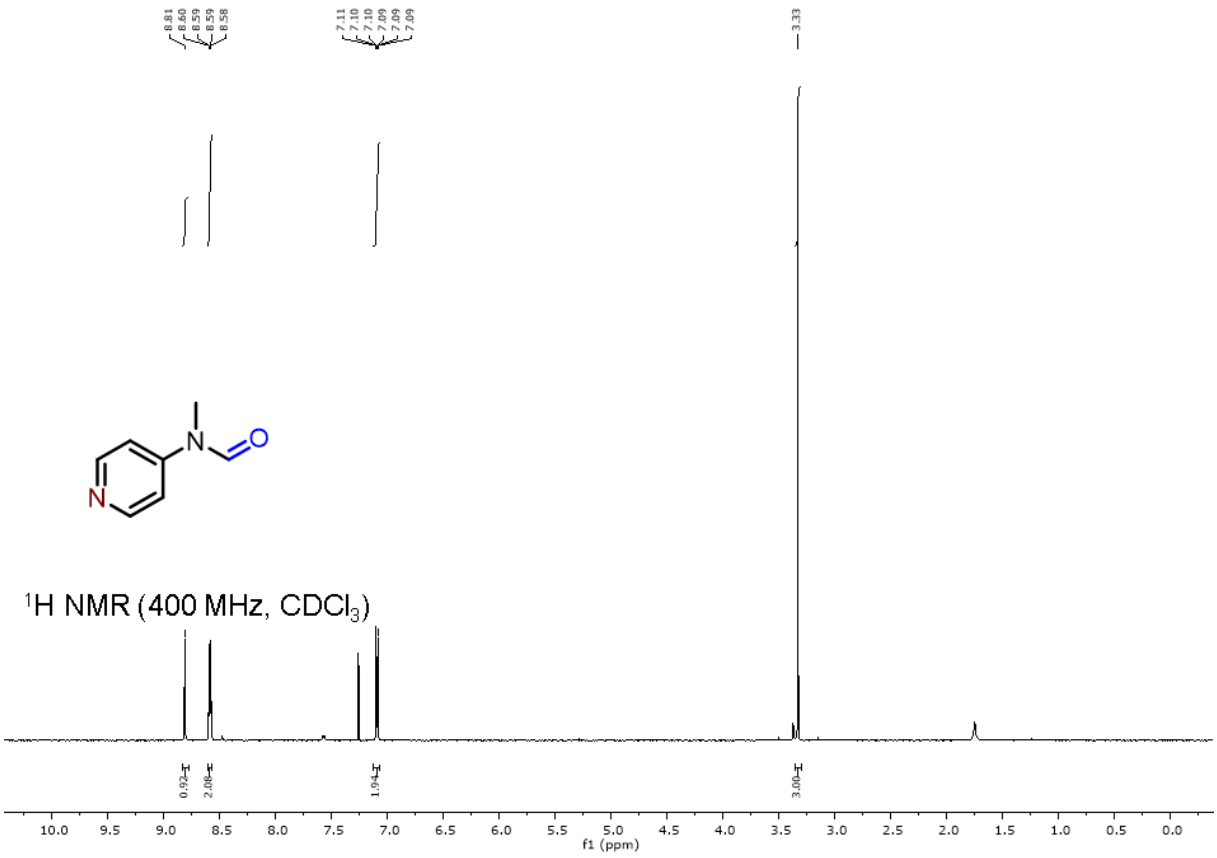
2g-^{13}C NMR



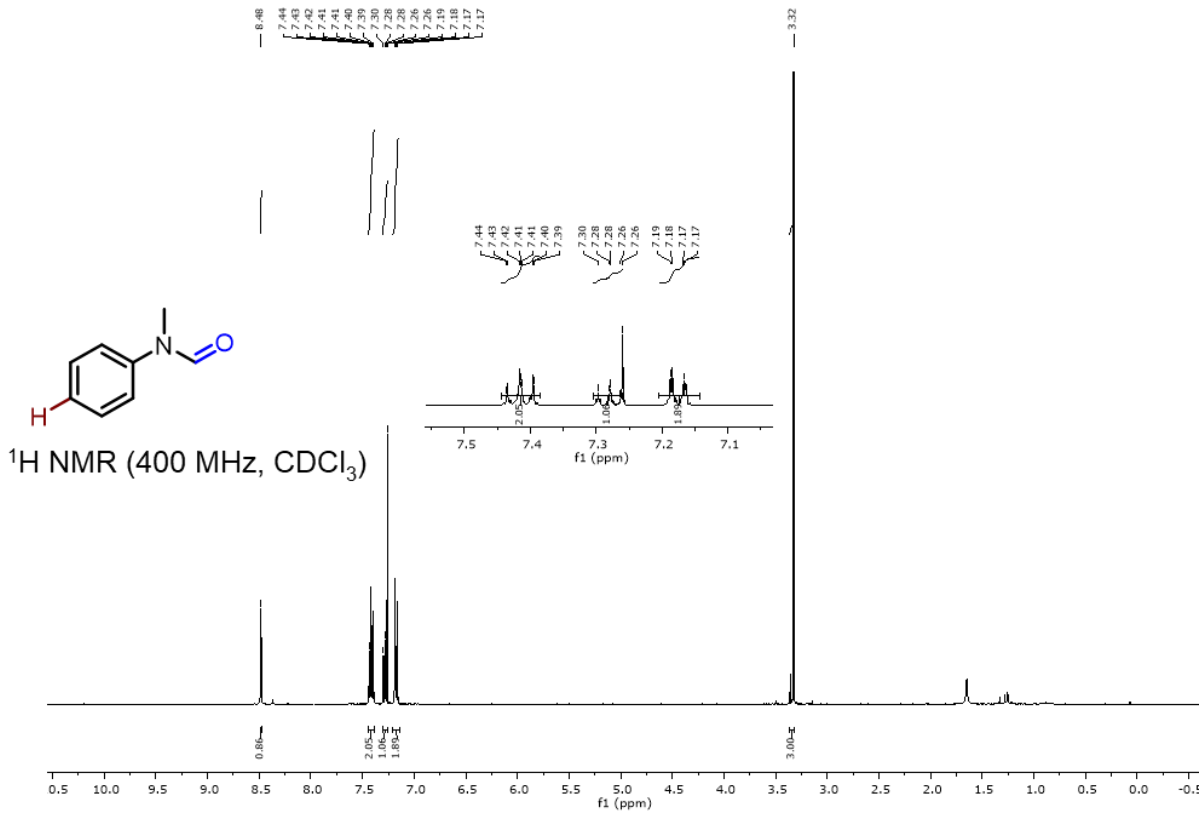
2i-^{1}H NMR



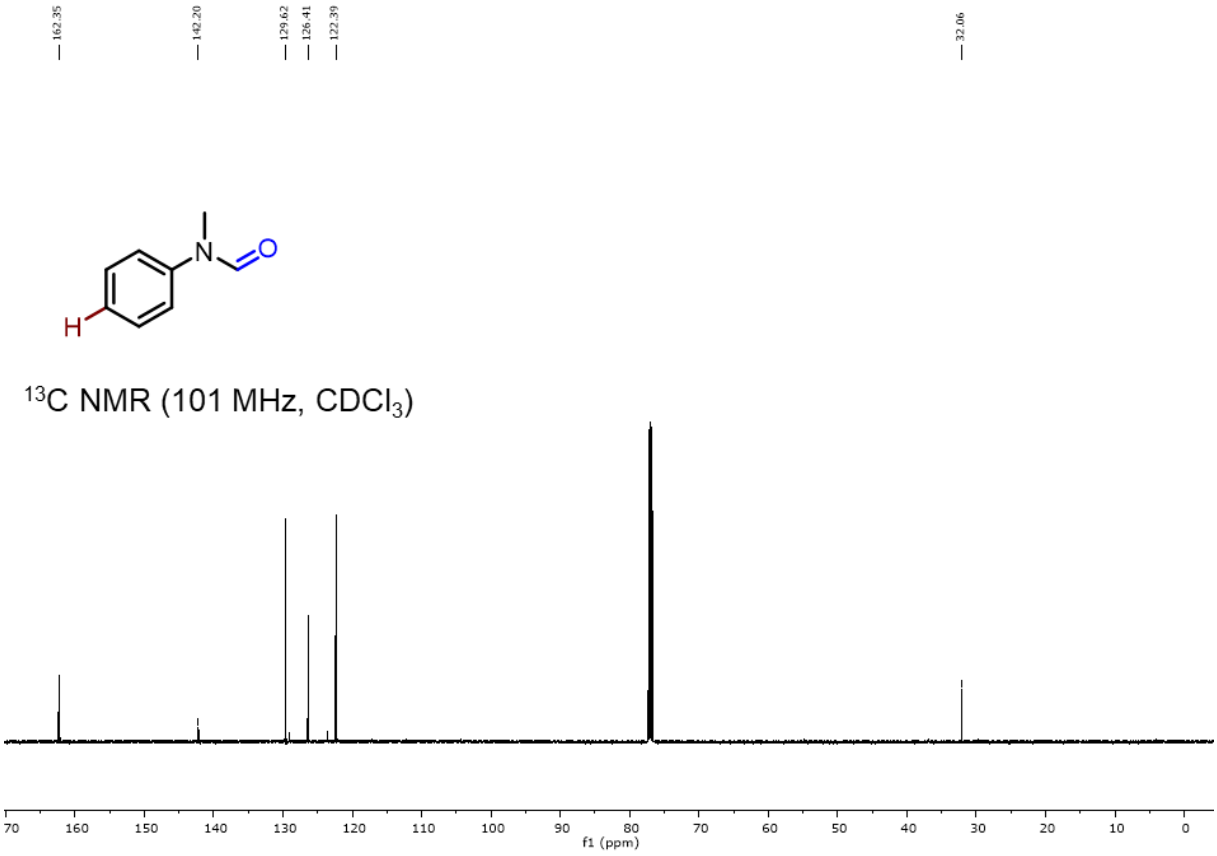
2i-^{13}C NMR



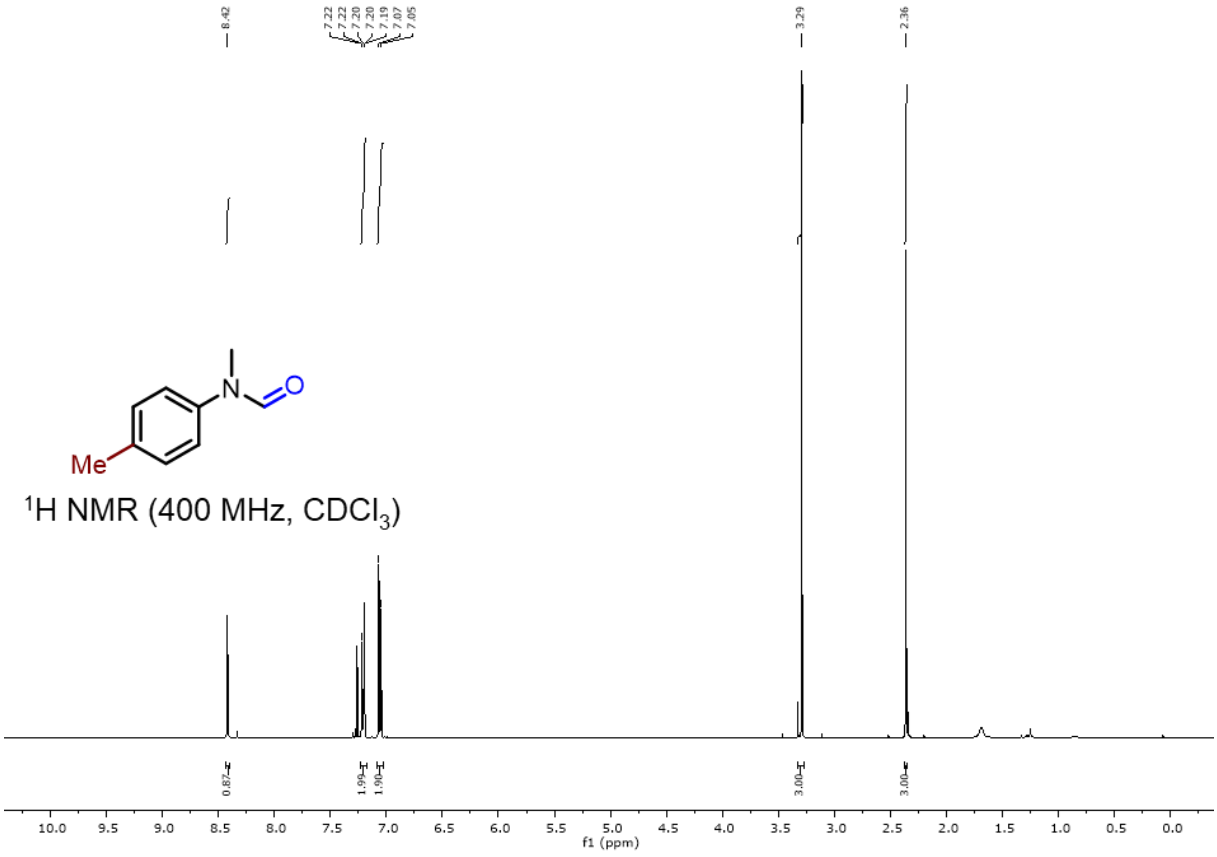
2j-^{1}H NMR



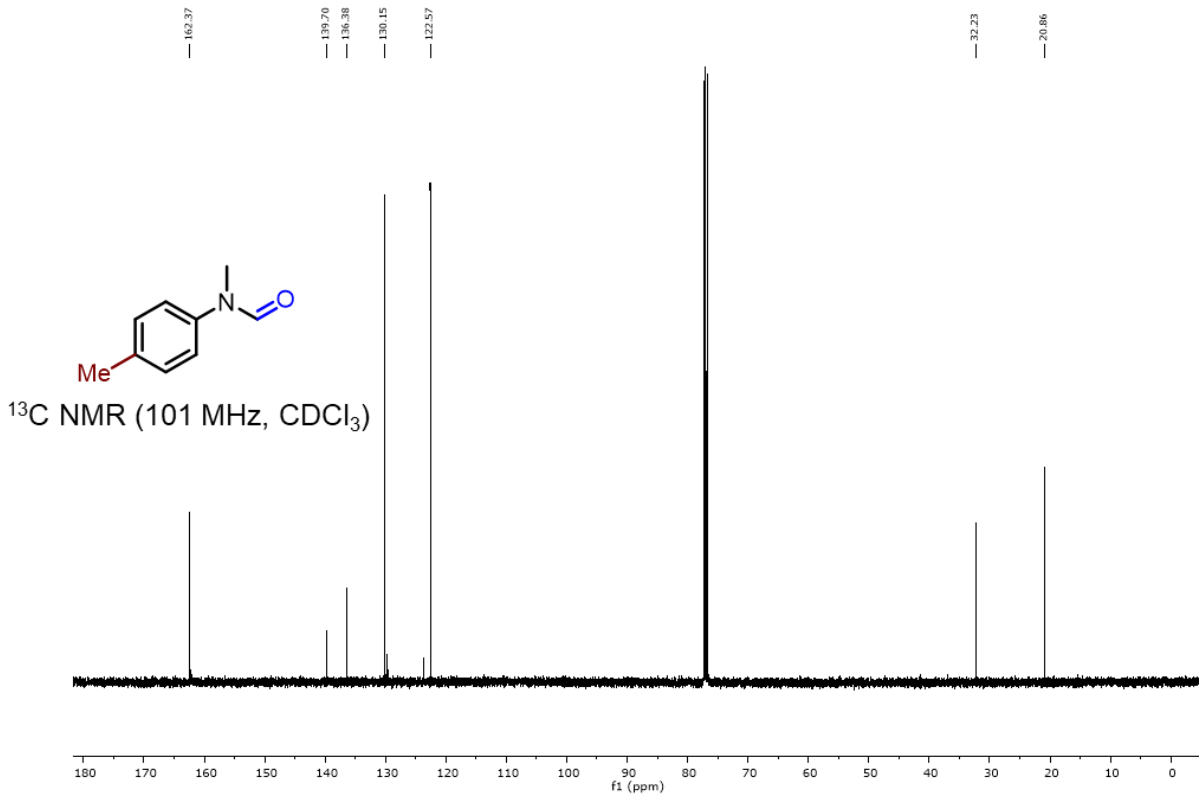
2j-^{13}C NMR



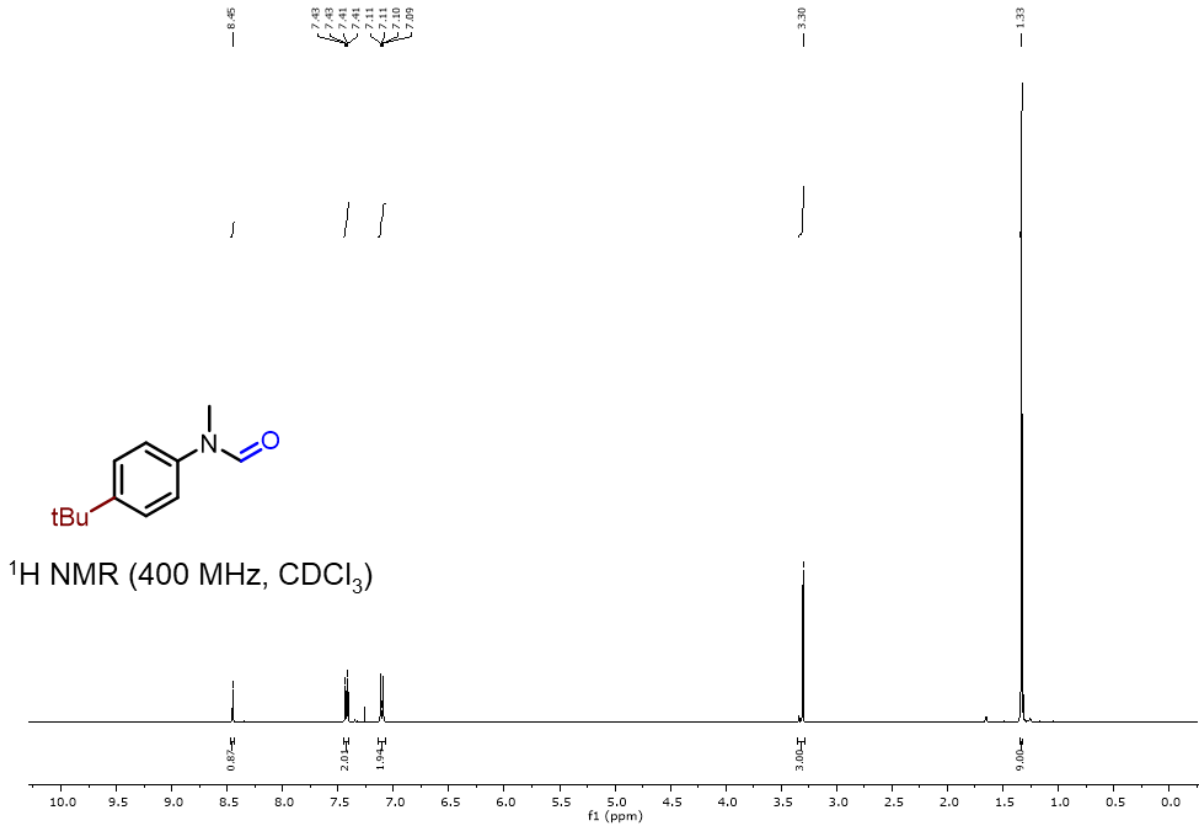
2k-^{1}H NMR



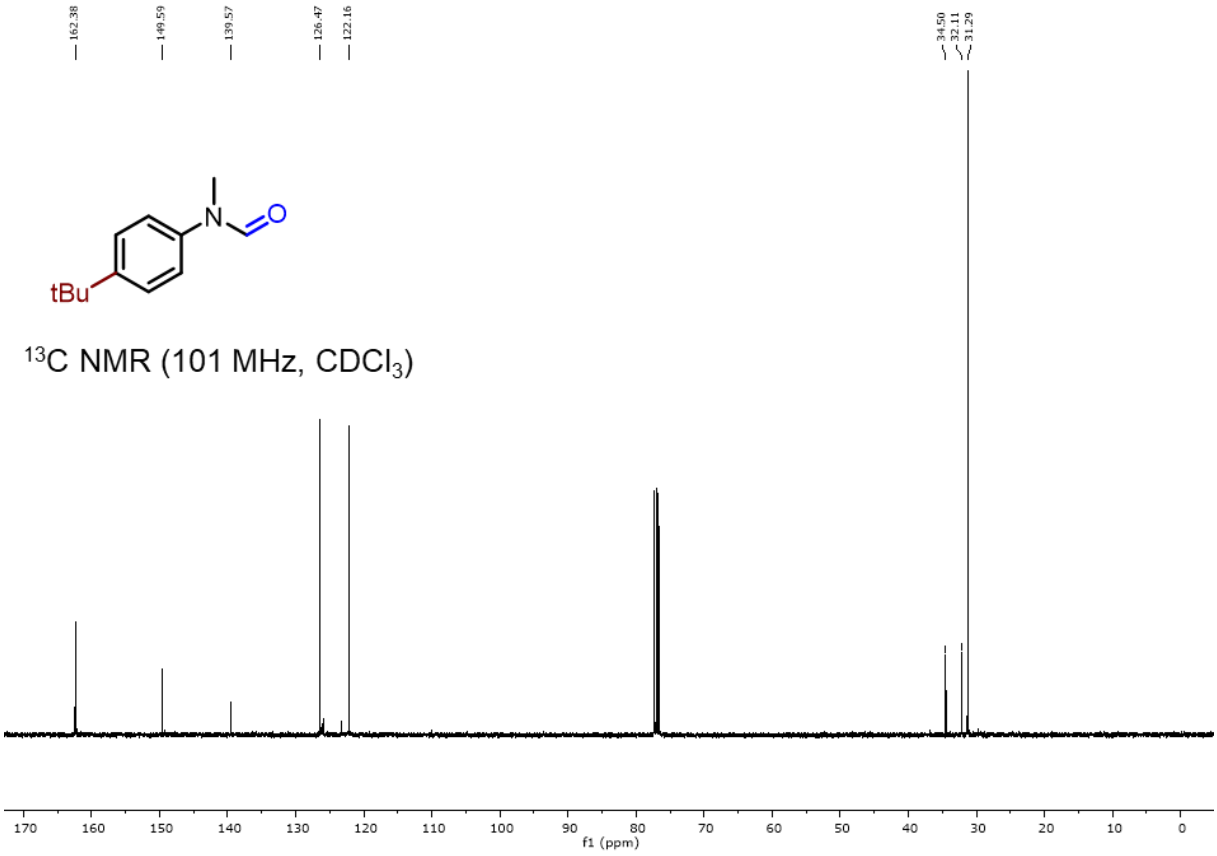
2k-^{13}C NMR



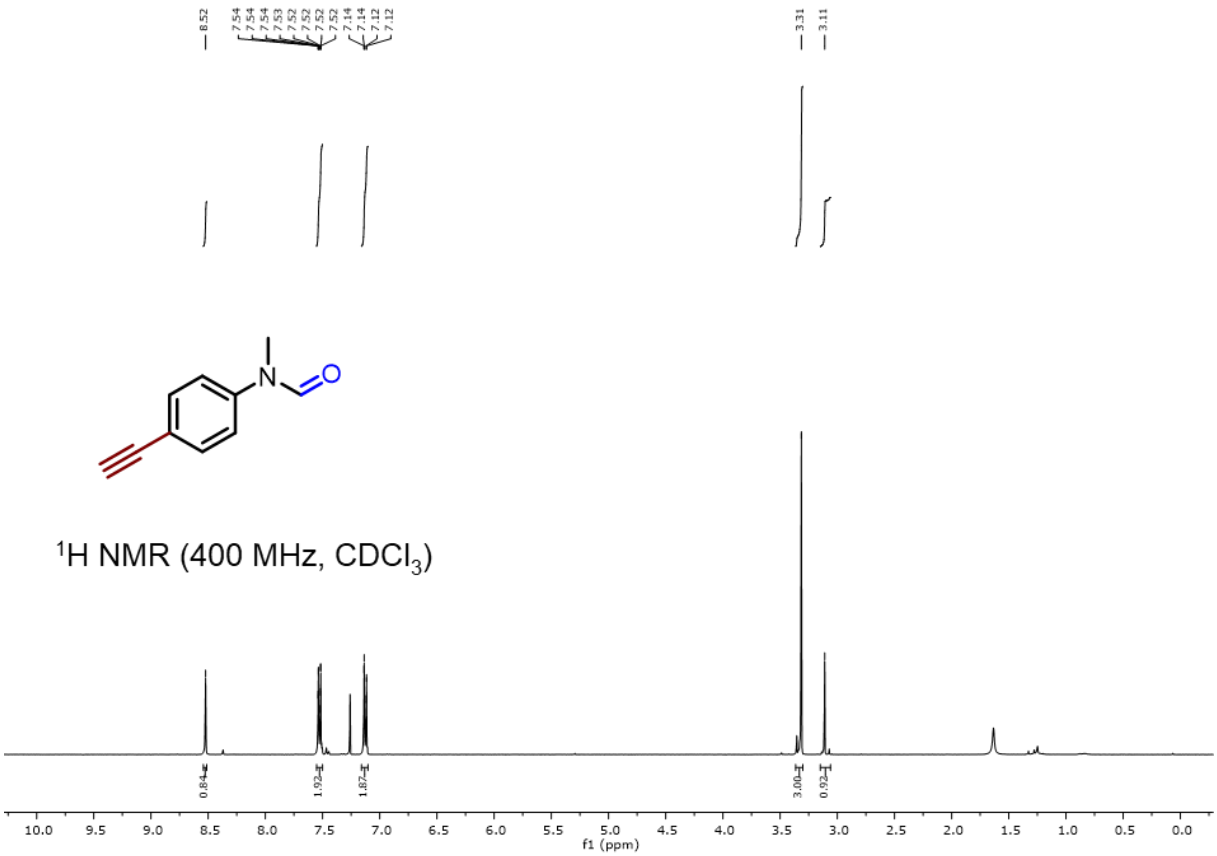
2l-^{1}H NMR



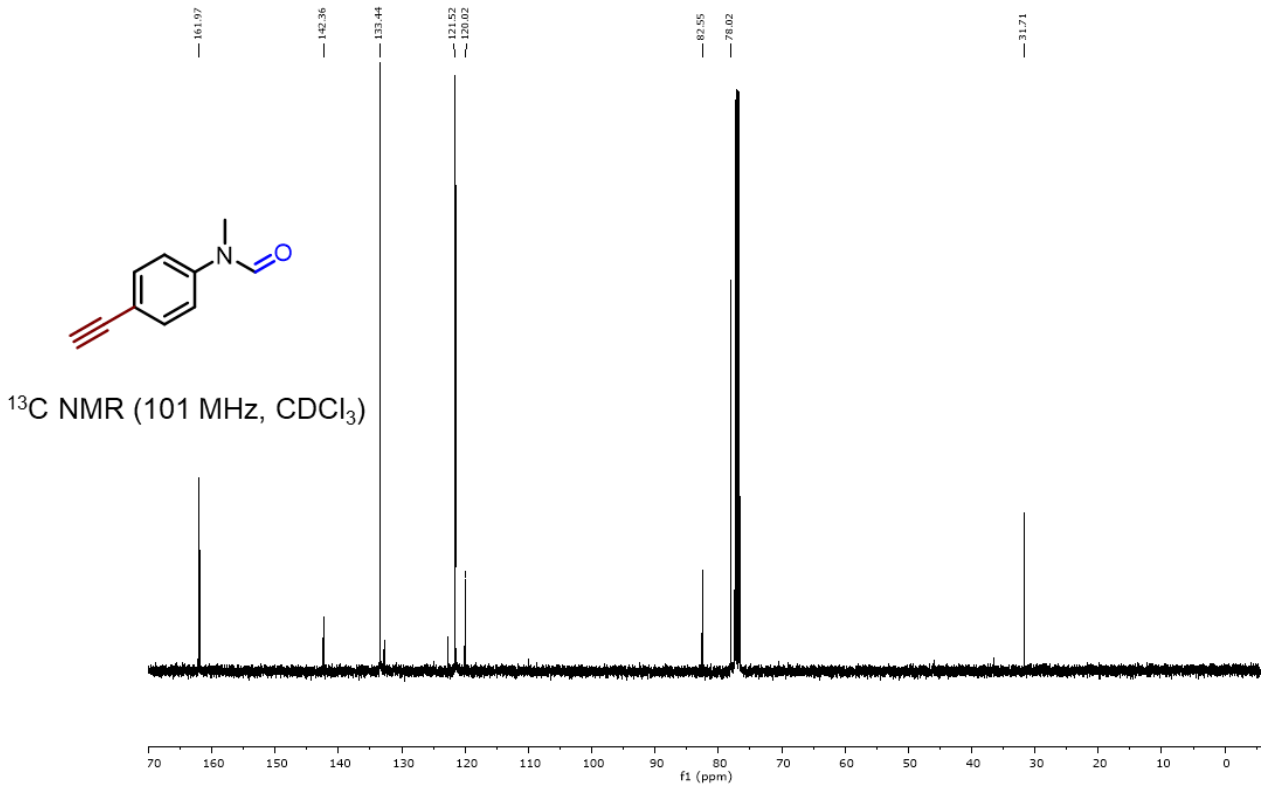
2l-^{13}C NMR



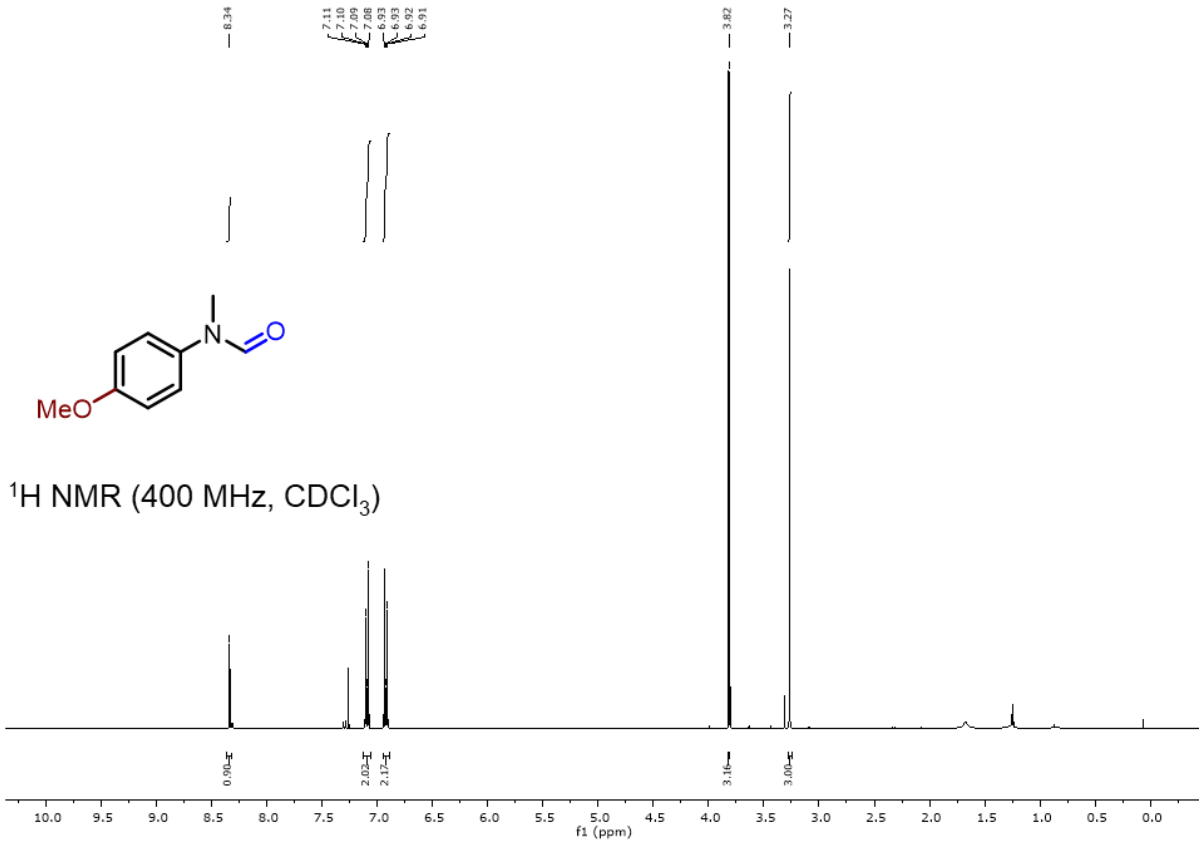
2m-^{1}H NMR



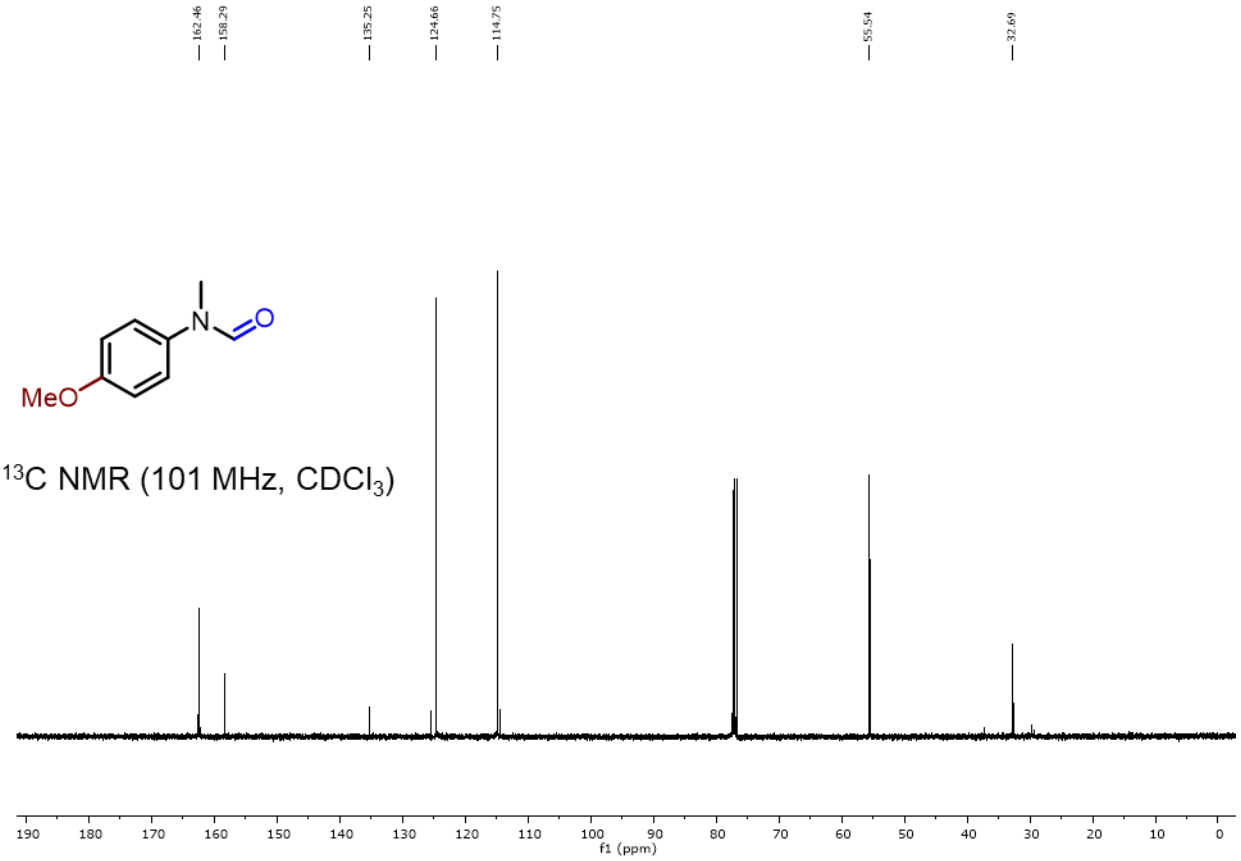
2m-^{13}C NMR



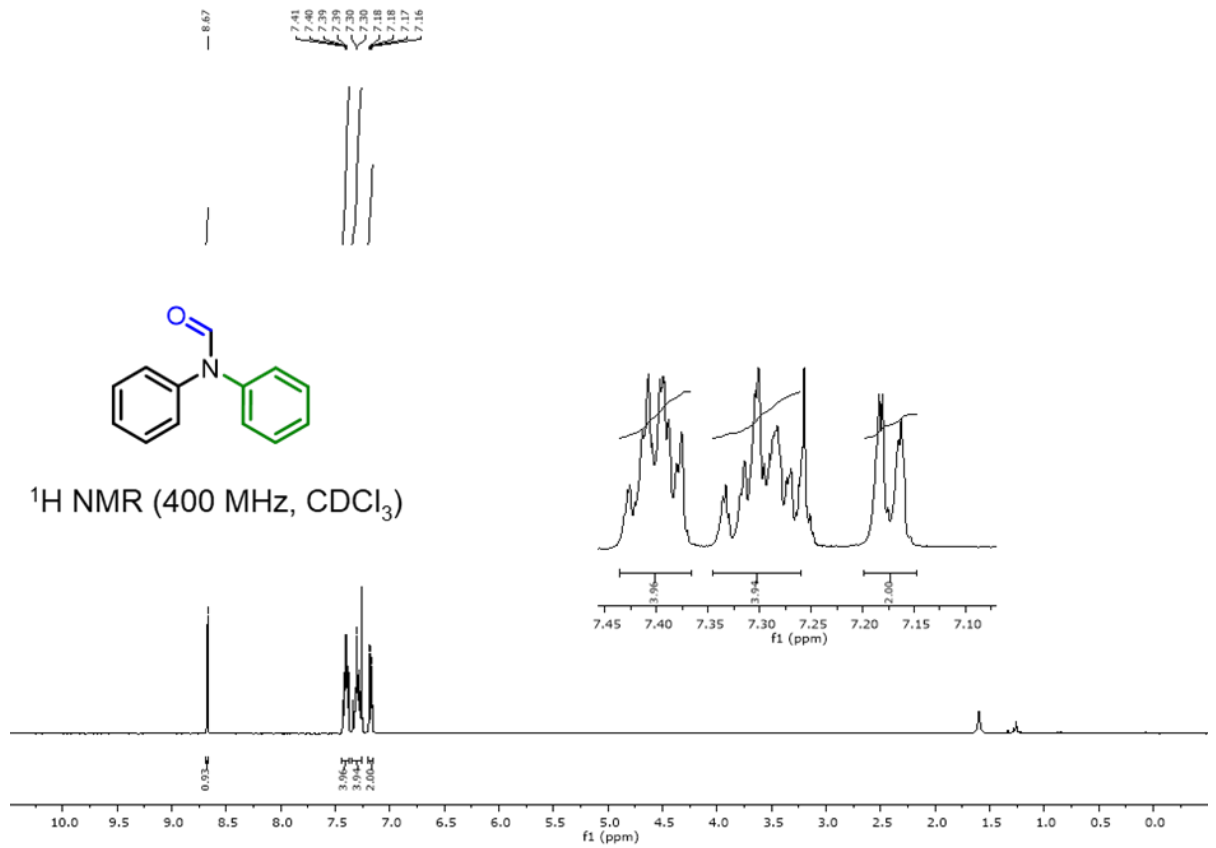
2n-^{1}H NMR



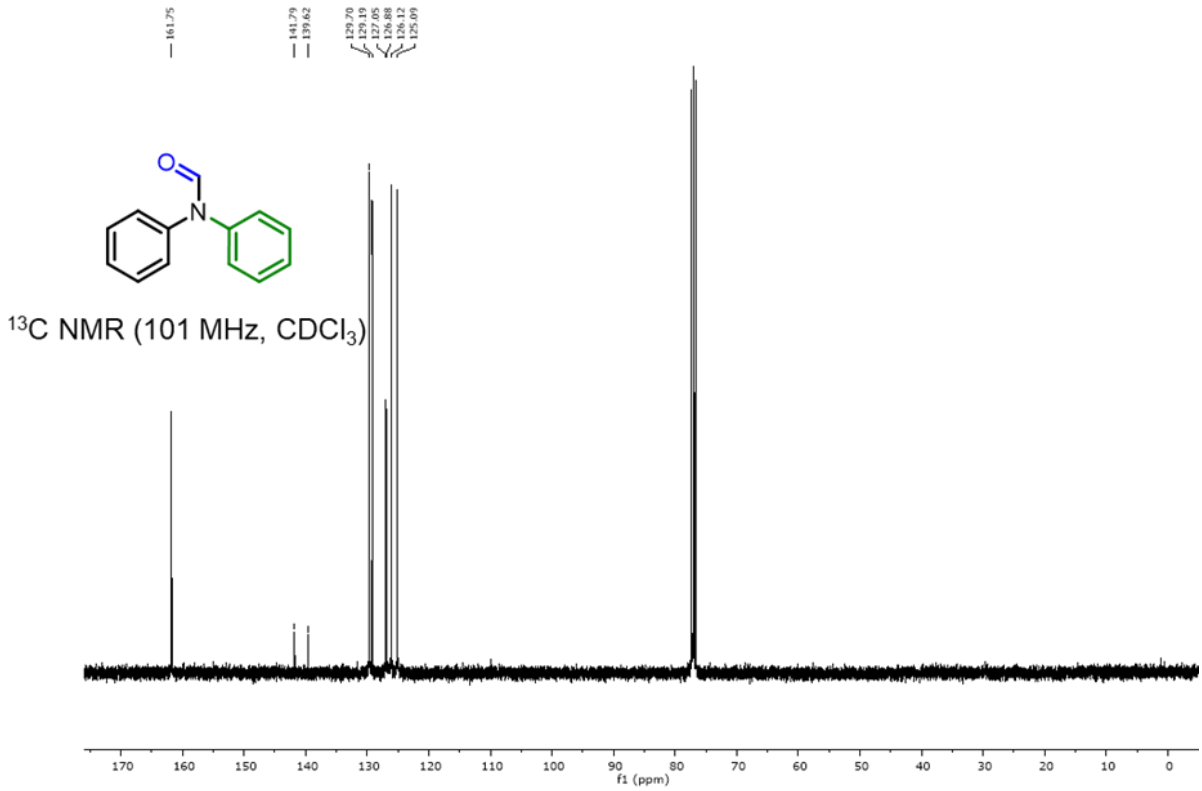
2n-^{13}C NMR



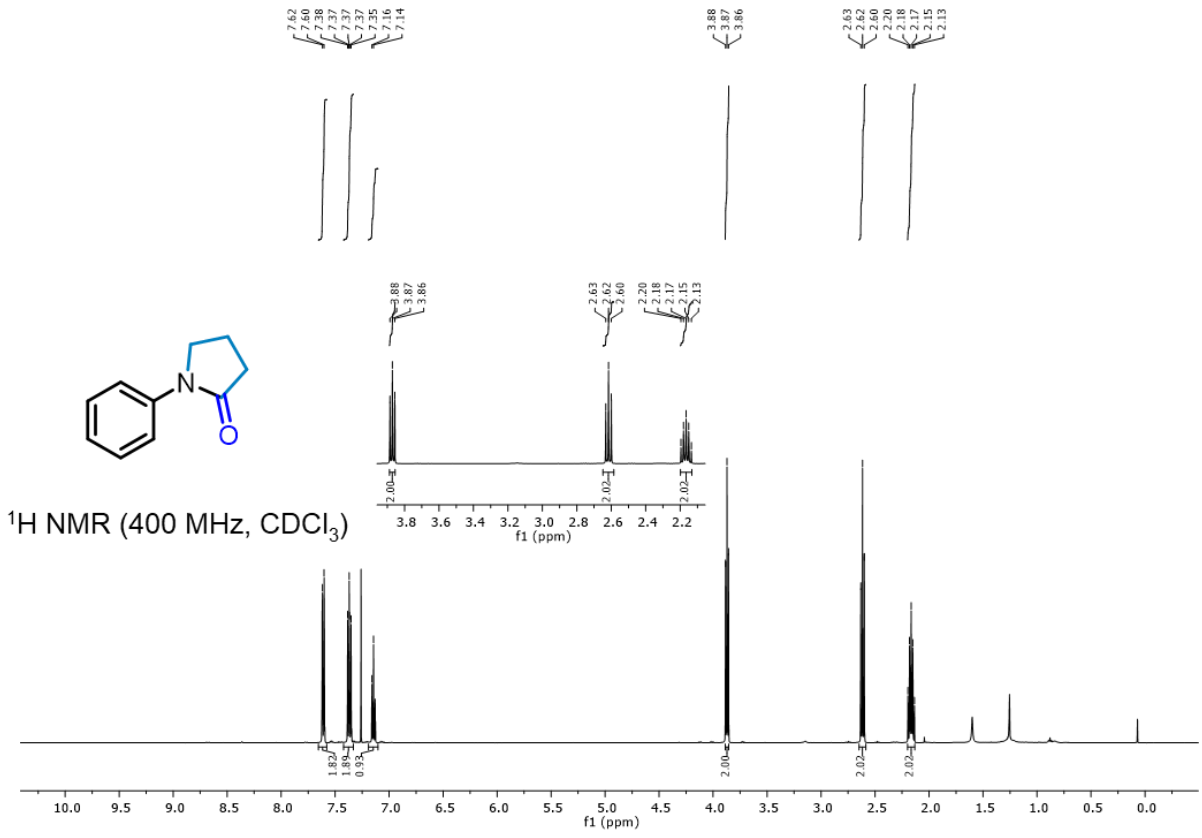
2o-^{1}H NMR



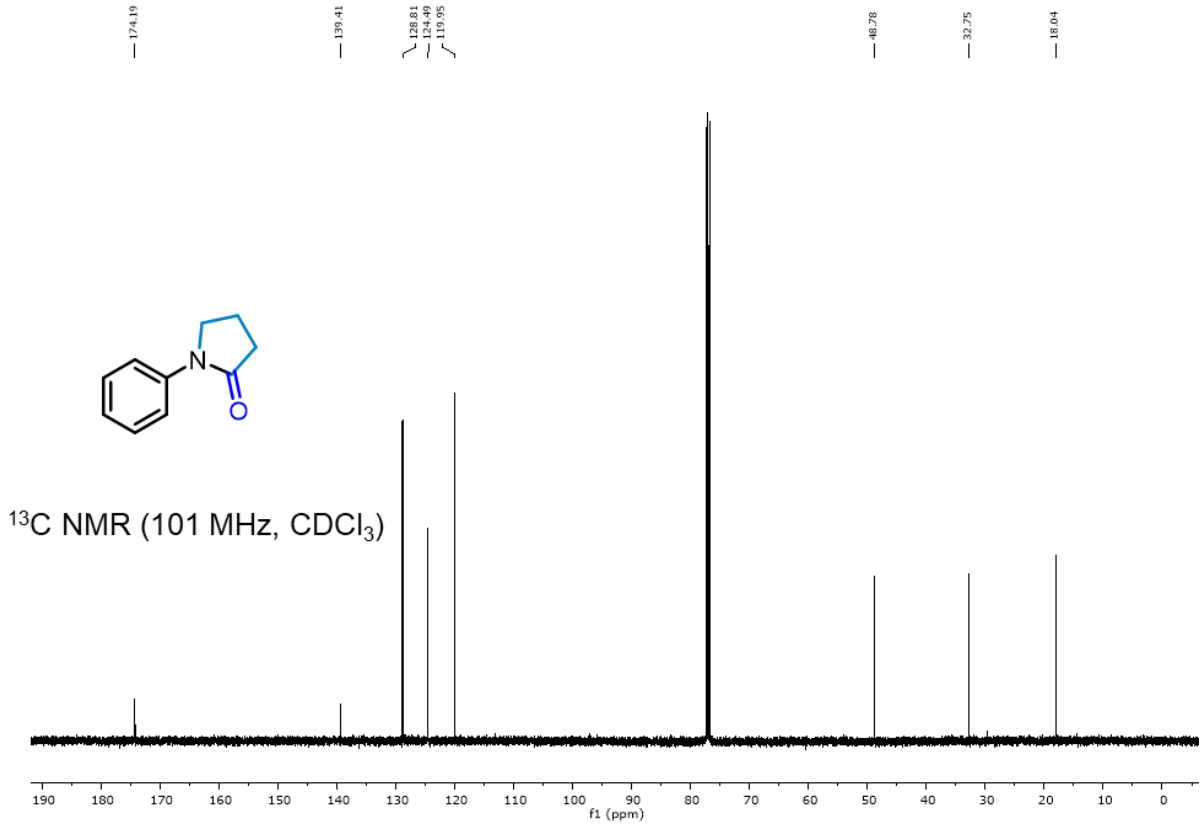
2o-^{13}C NMR



2p-^{1}H NMR



2p-^{13}C NMR


174.19
139.41
128.81
124.49
119.95
48.78
32.75
18.04
^{13}C NMR (101 MHz, $CDCl_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)