Electronic Supplementary Information

Direct *N*-formylation of Nitroarenes with CO_2

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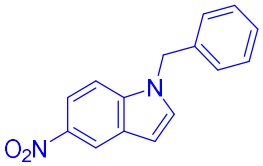
General Considerations

(A) General Analytical Information

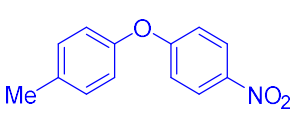
Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 400 MHz at ambient temperature. All ^{1}H NMR spectra were measured in part per million (ppm) relative to the signal of tetramethylsilane (TMS, 0.00 ppm), the signal of residual chloroform in deuterated chloroform ($CDCl_3$, 7.26 ppm), or the signal of residual dimethyl sulfoxide in dimethyl-d_6 sulfoxide (DMSO-d_6, 2.50 ppm).[1] Data for ^{1}H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet), coupling constant (J, in Hz), and integration. All ^{13}C NMR spectra were reported in ppm relative to $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.52 ppm)[1] and were obtained with complete ^{1}H decoupling. High-resolution mass spectrometry (HRMS) images were obtained on a microTOF-QII or Waters Micromass GCT Premier Instrument.

(B) General Reagent Information

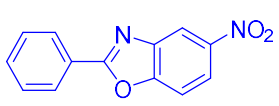
Unless otherwise noted, all chemicals were used as received without further purifications. *N*,*N*-Dimethylformamide (DMF, 99.8% purity) were dried with 4 Å molecular sieve beads prior to use. Carbon dioxide (CO_2), iron nano powder (Fe(0), 50 nm), 1,1,3,3-tetramethyldisiloxane (TMDSO), and potassium iodide (KI) were in 99%, 99.9%, 98%, and 98% purities, respectively. The following known starting materials (nitroarenes) were prepared according to the literature procedures.[2-4]



1-benzyl-5-nitro-1H-indole[2]



1-methyl-4-(4-nitrophenoxy)benzene[3]



5-nitro-2-phenylbenzo[d]oxazole[4]

(C) General Manipulation Considerations

All manipulations for direct *N*-formylation of nitroarenes with CO_2 based on 0.5

mmol of nitroarenes were set up in a 10 mL rubber septum-capped Schlenk tube. Flash column chromatography was performed using silica gel (200-300 mesh). The eluents used for column chromatography were presented as ratios of solvent volumes. Yields reported in the publication are isolated yields unless otherwise noted. All new formamide products were characterized by ^{1}H and ^{13}C NMR spectroscopies and high-resolution mass spectrometry (HRMS). All known formamide products were characterized by ^{1}H and ^{13}C NMR spectroscopies, which were further compared with the reported data when provided.

Experimental Section

General Procedure for the direct *N*-formylation of Nitroarenes with CO_2 (General procedure A).

An oven-dried 10 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with nano Fe powder (Fe, 2 equiv, 1.0 mmol, 56 mg), nitroarene (1 equiv, 0.50 mmol), and potassium iodide (KI, 10 mol%, 0.05 mmol, 8.3 mg). The tube was capped with an airtight rubber septum, and degassed *in vacuo* and then backfilled with carbon dioxide (CO_2) for three times via a CO_2-filled balloon. After being degassed and equipped with a CO_2-filled balloon, *N*,*N*-dimethylformamide solvent (DMF, 1.5 mL) followed by 1,1,3,3-tetramethyldisiloxane (TMDSO, 2 equiv, 1.0 mmol, 178 μL) were then transferred into the reaction mixture via a syringe. The reaction mixture was stirred at 135 °C in a preheated oil bath for 28 h. After the reaction, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate (EtOAc, ~50 mL), and the organic fraction was further acidified with diluted HCl solution (~1 M (aq), ~10 mL), neutralized with diluted NaOH solution (~1 M (aq), ~30 mL), washed with saturated NaCl solution, dried with anhydrous Na_2SO_4, and then concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by flash column chromatography using a mixture of petroleum ether (PE) and ethyl acetate (EtOAc) as eluents to afford the formamide product.

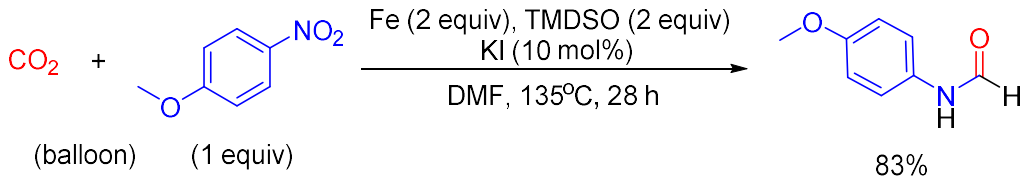
General Procedure for the direct *N*-formylation of electron-deficient nitroarenes with CO_2 (General procedure B).

An oven-dried 10 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with nano Fe powder (Fe, 2 equiv, 1.0 mmol, 56 mg), anhydrous iron(II) chloride ($FeCl_2$, 2 equiv, 1.0 mmol, 127 mg), nitroarene (1 equiv, 0.50 mmol), and potassium iodide (KI, 30 mol%, 0.15 mmol, 25 mg). The tube was capped with an airtight rubber septum, and degassed *in vacuo* and then backfilled with

carbon dioxide (CO_2) for three times via a CO_2-filled balloon. After being degassed and equipped with a CO_2-filled balloon, *N*,*N*-dimethylformamide solvent (DMF, 3 mL) followed by 1,1,3,3-tetramethyldisiloxane (TMDSO, 3 equiv, 1.0 mmol, 265 μL) were then transferred into the reaction mixture via a syringe. The reaction mixture was stirred at 135 °C in a preheated oil bath for 28 h. After the reaction, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate (EtOAc, ~50 mL), and the organic fraction was further acidified with diluted HCl solution (~1 M (aq), ~10 mL), neutralized with diluted NaOH solution (~1 M (aq), ~30 mL), washed with saturated NaCl solution, dried with anhydrous Na_2SO_4, and then concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by flash column chromatography using a mixture of petroleum ether (PE) and ethyl acetate (EtOAc) as eluents to afford the formamide product.

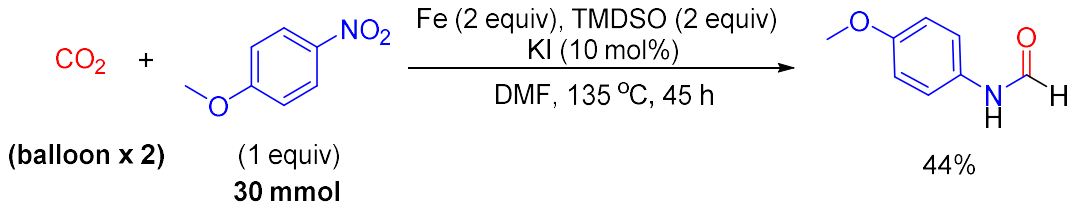
Note: Since the product all existed as two forms of rotamers, the classification of ^1H and ^{13}C signals were made difficult. Thus, all signals were listed in the product characterizations with relative integrations shown in ^1H NMR analysis, without categorizing them to the corresponding rotamers.

***N*-(4-methoxyphenyl)formamide (2a).**[5]



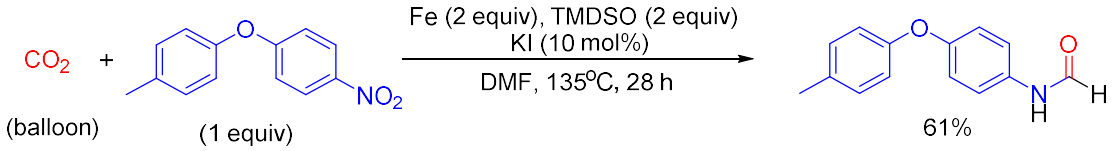
(i) 0.5 mmol scale: Following the general procedure **A**, the title compound was prepared using 1-methoxy-4-nitrobenzene (1.0 equiv, 0.50 mmol, 76 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a white amorphous solid (63 mg, 83%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, J = 11.6 Hz, 0.48H), 8.34 (s, 0.48H), 7.85 (brs, 0.46H), 7.45 (d, J = 8 Hz, 1H), 7.23 (brs, 0.45H), 7.04 (d, J = 8.4 Hz, 1H), 6.88 – 6.86 (m, 2H), 3.80 (d, J = 4.4 Hz, 3H). **^{13}C NMR** (100 MHz, CCl_3) δ 162.98,

158.84, 157.68, 156.76, 129.85, 129.43, 121.80, 121.80, 114.91, 114.25, 55.58, 55.51.



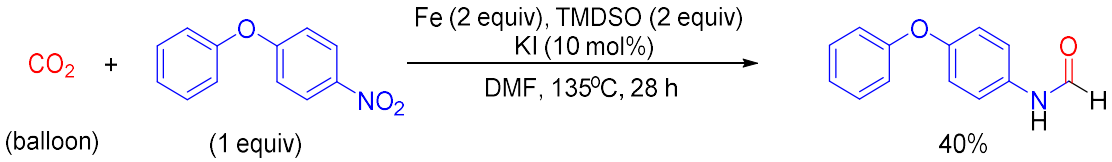
(ii) 5 mmol scale: An oven-dried 500 mL three-neck round bottom flask equipped with an **airtight mechanical stirring setup** was sequentially charged with nano Fe powder (Fe, 2 equiv, 60 mmol, 3.35 g), nitroarene (1 equiv, 30 mmol, 4.59 g), and potassium iodide (KI, 10 mol%, 3 mmol, 498 mg). The flask tube was capped with two airtight rubber septa, and degassed *in vacuo* and then backfilled with carbon dioxide (CO_2) for three times via a CO_2-filled balloon. After being degassed and equipped with two CO_2-filled balloons at both necks of the flask, *N*,*N*-dimethylformamide solvent (DMF, 90 mL) followed by 1,1,3,3-tetramethyldisiloxane (TMDSO, 2 equiv, 60 mmol, 8.06 g) were then transferred into the reaction mixture via a syringe. The reaction mixture was stirred at 135 °C in a preheated **heating mantle** for 45 h. After the reaction, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate (EtOAc, ~300 mL), and the organic fraction was washed with water (300 mL x 3) to remove the majority of DMF solvent. The organic solvent was further acidified with diluted HCl solution (~1 M (aq), ~300 mL), neutralized with diluted NaOH solution (~1 M (aq), ~400 mL), washed with saturated NaCl solution, dried with anhydrous Na_2SO_4, and then concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by flash column chromatography using PE/EtOAc (3:1) as an eluent to afford the title product (2.01 g, 13.2 mmol, 44%). Spectral and analytical data were identical to those reported for the same compound above.

***N*-(4-(p-tolyloxy)phenyl)formamide (2b).**

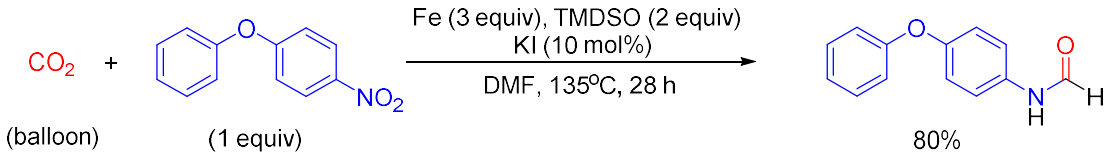


Following the general procedure **A**, the title compound was prepared using 1-methyl-4-(4-nitrophenoxy)benzene (1.0 equiv, 0.50 mmol, 115 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (70 mg, 61%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 11.2 Hz, 0.51H), 8.54 (brs, 0.43H), 8.36 (s, 0.56H), 7.74 (brs, 0.49H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.23 – 7.13 (m, 2H), 7.09 (d, *J* = 8.8 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.95 – 6.88 (m, 2H), 2.36 (d, *J* = 4.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.04, 159.11, 155.57, 154.86, 154.61, 154.54, 133.24, 132.93, 131.97, 131.61, 130.36, 130.28, 121.77, 121.14, 119.53, 119.03, 118.94, 118.78, 20.71, 20.69. **HRMS** (ESI): Calcd for $C_{14}H_{14}NO_2$ [M+H]: 228.1021; Found: 228.1025.

***N*-(4-phenoxyphenyl)formamide (2c).**[6]



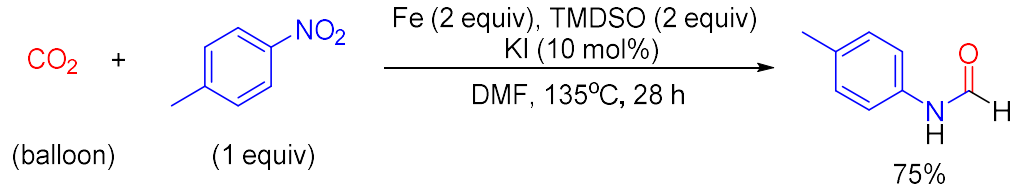
(i) Based on 2 equiv of Fe. Following the general procedure **A**, the title compound was prepared using 1-nitro-4-phenoxybenzene (1.0 equiv, 0.50 mmol, 108 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (43 mg, 40%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 11.2 Hz, 0.45H), 8.35 (s, 0.54H), 8.20 (brs, 0.41H), 7.56-7.49 (m, 1H), 7.49 (brs, 0.56H), 7.38 – 7.28 (m, 2H), 7.17 – 7.04 (m, 2H), 7.03 – 6.93 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.81, 158.93, 157.37, 157.11, 155.02, 153.98, 132.27, 131.91, 129.87, 129.78, 123.54, 123.25, 121.76, 121.18, 120.11, 119.61, 118.75, 118.57. **HRMS** (ESI): Calcd for $C_{13}H_{12}NO_2$ [M+H]: 214.0862; Found: 214.0868.



(ii) Based on 3 equiv of Fe. Following the general procedure **A**, the title compound was prepared using 1-nitro-4-phenoxybenzene (1.0 equiv, 0.50 mmol, 108 mg), Fe (3.0

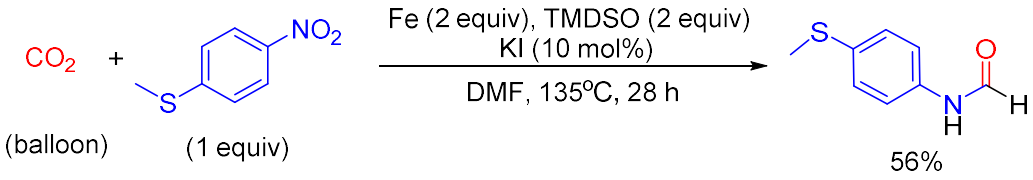
equiv, 1.5 mmol, 84 mg), and PE/EtOAc (3:1) as an eluent to afford the title compound as a white amorphous solid (86 mg, 80%). Spectral and analytical data were identical to those reported for the same compound above.

***N*-p-tolylformamide (2d).**[5]



Following the general procedure **A**, the title compound was prepared using 1-methyl-4-nitrobenzene (1.0 equiv, 0.50 mmol, 68 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (51 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 11.6 Hz, 0.59H), 8.36 (s, 0.49H), 7.96 (brs, 0.55H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.27 (brs, 0.35H), 7.17 – 7.13 (m, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 2.33 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.58, 158.82, 135.22, 134.54, 134.27, 134.01, 130.26, 129.60, 120.02, 119.25, 20.89, 20.80.

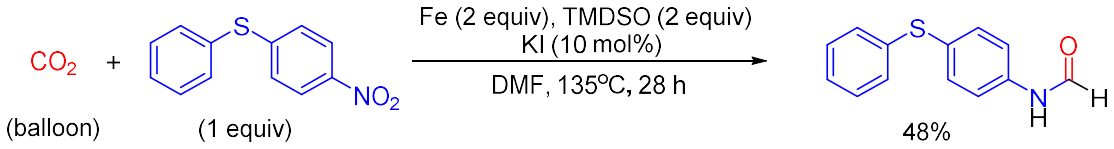
***N*-(4-(methylthio)phenyl)formamide (2e).**[7]



Following the general procedure **A**, the title compound was prepared using 4-nitrothioanisole (1.0 equiv, 0.50 mmol, 75 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (47 mg, 56%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 11.2 Hz, 0.48H), 8.43 (brs, 0.4H), 8.35 (s, 0.66H), 7.58 (brs, 0.59H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.18 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 2.47 (d, *J* = 3.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.52, 158.92, 135.33, 134.47, 134.40, 134.15, 128.49, 127.91, 120.63, 119.69, 16.52, 16.52. **HRMS** (ESI): Calcd for

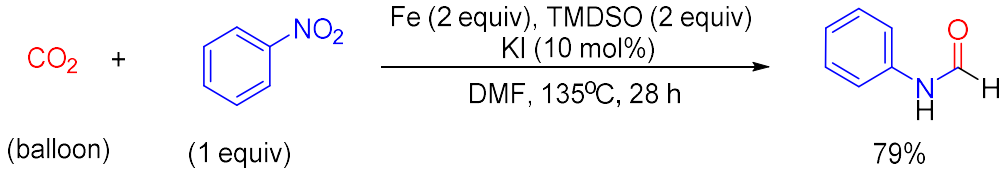
$C_8H_{10}NOS$ [M+H]: 168.0480; Found: 168.0483.

***N*-(4-(phenylthio)phenyl)formamide (2f).**



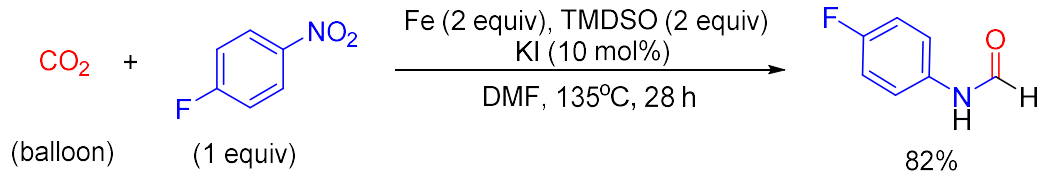
Following the general procedure **A**, the title compound was prepared using (4-nitrophenyl)(phenyl)sulfane (1.0 equiv, 0.50 mmol, 116 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (55 mg, 48%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 11.2 Hz, 0.48H), 8.48 (brs, 0.46H), 8.40 (s, 0.57H), 7.55 (brs, 0.52H), 7.53 – 7.51 (m, 1H), 7.41 – 7.35 (m, 2H), 7.35 – 7.25 (m, 5H), 7.10 – 7.04 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.42, 159.02, 136.37, 136.25, 135.98, 135.92, 133.06, 132.74, 132.18, 131.07, 130.61, 130.25, 129.30, 129.20, 127.13, 126.85, 120.75, 119.44. **HRMS** (ESI): Calcd for $C_{13}H_{12}NOS$ [M+H]: 230.0640; Found: 230.0640.

***N*-phenylformamide (2g).**[6]



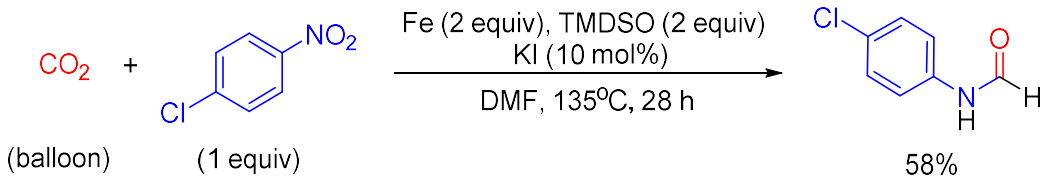
Following the general procedure **A**, the title compound was prepared using nitrobenzene (1.0 equiv, 0.50 mmol, 62 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow oil (48 mg, 79%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 11.2 Hz, 0.53H), 8.44 (brs, 0.49H), 8.30 (s, 0.44H), 7.53 (brs, 0.44H), 7.50 – 7.44 (m, 1H), 7.32 – 7.22 (m, 2H), 7.16 – 6.98 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.75, 158.10, 135.87, 135.71, 128.74, 128.09, 124.27, 123.79, 118.98, 117.78. **HRMS** (ESI): Calcd for C_7H_8NO [M+H]: 122.0602; Found: 122.0606.

***N*-(4-fluorophenyl)formamide (2h).**[5]



Following the general procedure **A**, the title compound was prepared using 1-fluoro-4-nitrobenzene (1.0 equiv, 0.50 mmol, 71 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (59 mg, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 11.6 Hz, 0.45H), 8.36 (s, 0.53H), 8.33 (brs, 0.41H), 7.53 – 7.50 (m, 1H), 7.45 (brs, 0.42H), 7.17 – 6.91 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) 162.91, 162.78, 161.69, 160.85, 159.26, 159.01, 158.81, 158.42, 132.87, 132.85, 132.74, 132.71, 121.89, 121.81, 121.26, 121.18, 116.69, 116.47, 115.91, 115.68 (the multiplicities brought by the fluorine were not demonstrated due to the complexity of the spectra). **HRMS** (ESI): Calcd for C_7H_7FNO [M+H]: 140.0512; Found: 140.0512.

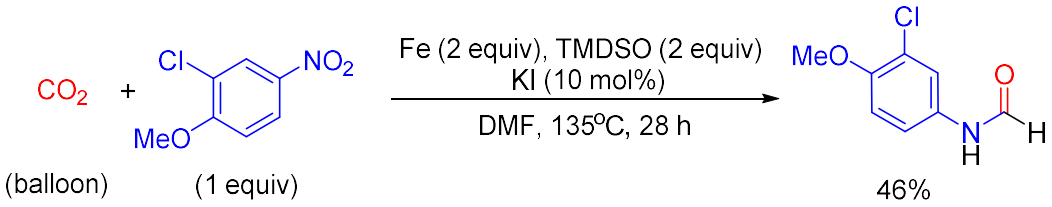
***N*-(4-chlorophenyl)formamide (2i).**[5]



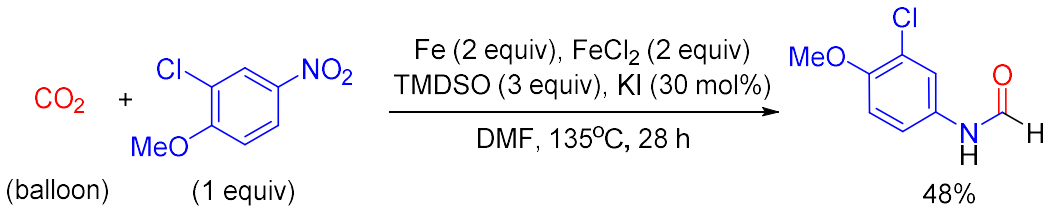
Following the general procedure **A**, the title compound was prepared using 1-chloro-4-nitrobenzene (1.0 equiv, 0.50 mmol, 78 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (45 mg, 58%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 10.8 Hz, 0.47H), 8.39 (brs, 0.38H), 8.36 (s, 0.63H), 7.50 (d, *J* = 8.0Hz, 1H), 7.45 (brs, 0.52H), 7.36 – 7.19 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.53, 159.01, 135.38, 135.28, 130.78, 129.87, 129.17, 121.22,

120.10. (9 carbon signals were observed out of expected 10 carbon signals). **HRMS** (ESI): Calcd for C_7H_7ClNO [M+H]: 156.0219; Found: 156.0216.

***N*-(3-chloro-4-methoxyphenyl)formamide (2j).**



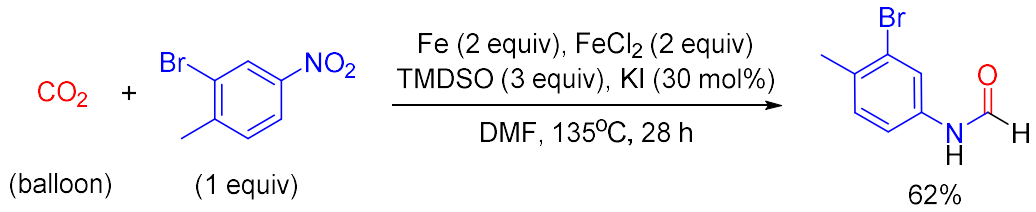
(i) General procedure A: Following the general procedure **A**, the title compound was prepared using 2-chloro-1-methoxy-4-nitrobenzene (1.0 equiv, 0.50 mmol, 94 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (43 mg, 46%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 11.2 Hz, 0.43H), 8.36 (s, 0.60H), 7.70 (brs, 0.38H), 7.65 – 7.56 (m, 0.58H), 7.45 (s, 0.23H), 7.40 (brs, 0.37H), 7.18 (s, 0.75H), 7.05 – 6.97 (m, 0.43H), 6.96 – 6.88 (m, 1H), 3.92 (d, *J* = 5.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.46, 158.69, 153.20, 152.30, 130.24, 129.89, 123.51, 122.68, 122.49, 122.49, 119.68, 119.55, 112.84, 112.28, 56.47, 56.40. **HRMS** (ESI): Calcd for C_8H_9ClNO [M+H]: 186.0327; Found: 186.0322.



(ii) General procedure B: Following the general procedure **B**, the title compound was prepared using 2-chloro-1-methoxy-4-nitrobenzene (1.0 equiv, 0.50 mmol, 94 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (45 mg, 48%). Spectral and analytical data were identical to those reported for the same compound above.

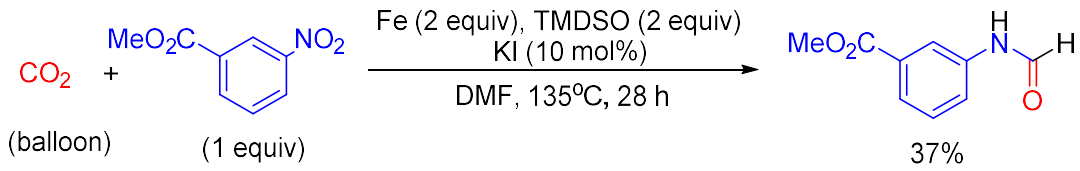
***N*-(3-bromo-4-methylphenyl)formamide (2k).**

(i) General procedure A: Following the general procedure **A**, the title compound was prepared using 2-bromo-1-methyl-4-nitrobenzene (1.0 equiv, 0.50 mmol, 108 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (52 mg, 49%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (d, J = 9.6 Hz, 0.46H), 8.48 (brs, 0.42H), 8.36 (s, 0.58H), 7.81 (s, 0.60H), 7.68 (brs, 0.49H), 7.44 - 7.36 (m, 0.60H), 7.33 (s, 0.46H), 7.25 - 7.15 (m, 1.H), 7.02 - 6.94 (m, 0.44H), 2.38 (d, J = 8.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.56, 159.09, 135.65, 135.55, 134.98, 134.33, 131.55, 130.88, 125.47, 124.80, 123.72, 122.76, 118.97, 117.93, 22.31, 22.24. **HRMS** (ESI): Calcd for C_8H_9BrNO [M+H]: 213.9863; Found: 213.9868.

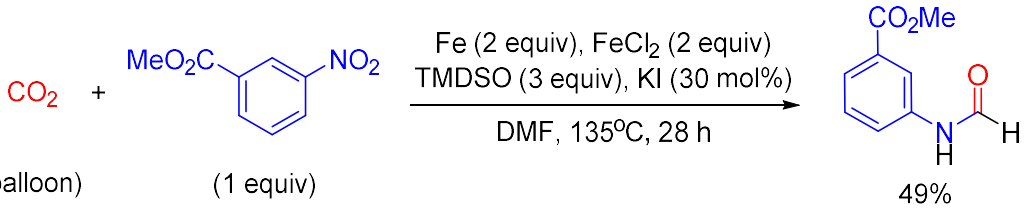


(ii) General procedure B: Following the general procedure **B**, the title compound was prepared using 2-bromo-1-methyl-4-nitrobenzene (1.0 equiv, 0.50 mmol, 108 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (67 mg, 62%). Spectral and analytical data were identical to those reported for the same compound above.

Methyl 3-formamidobenzoate (2l).[8]



(i) General procedure A. Following the general procedure **A**, the title compound was prepared using methyl 3-nitrobenzoate (1.0 equiv, 0.50 mmol, 91 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (35 mg, 37%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 11.2 Hz, 0.45H), 8.61 (brs, 0.41H), 8.45 (s, 0.59H), 8.15 – 8.09 (m, 0.62H), 8.02 – 7.95 (m, 0.69H), 7.93 (brs, 0.50H), 7.90 – 7.85 (m, 0.58H), 7.85 – 7.78 (m, 1H), 7.49 – 7.39 (m, 1H), 7.34 – 7.30 (m, 0.45H), 3.95 (d, *J* = 10.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.72, 166.31, 162.43, 159.27, 137.23, 137.14, 131.78, 130.95, 129.92, 129.33, 126.22, 125.77, 124.56, 122.95, 120.72, 119.40, 52.47, 52.35. **HRMS** (ESI): Calcd for $C_9H_{10}NO_3$ [M+H]: 180.0659; Found: 180.0661.

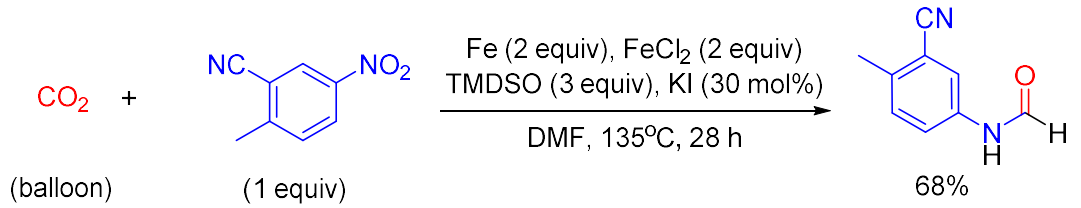


(ii) General procedure B. Following the general procedure **B**, the title compound was prepared using methyl 3-nitrobenzoate (1.0 equiv, 0.50 mmol, 91 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (47 mg, 49%). Spectral and analytical data were identical to those reported for the same compound above.

***N*-(3-cyano-4-methylphenyl)formamide (2m).**

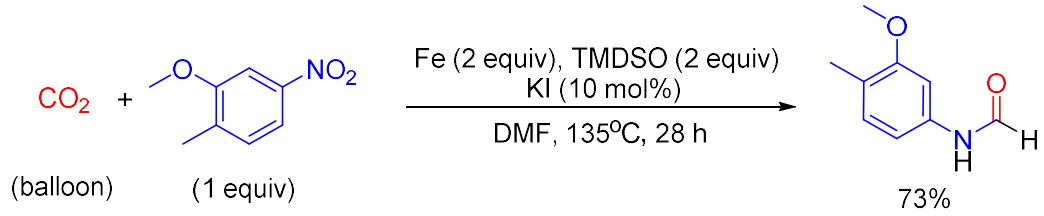
(i) General procedure A: Following the general procedure **A**, the title compound was prepared using 2-methyl-5-nitrobenzonitrile (1.0 equiv, 0.50 mmol, 81 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (35 mg, 44%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 10.8 Hz, 0.29H), 8.40 (s, 0.71H), 7.97 (brs, 0.34H), 7.87 (s, 0.75H), 7.71 – 7.58 (m, 0.81H), 7.38 (brs, 0.57H),

7.35 (s, 0.23H), 7.33 – 7.27 (m, 1H), 7.25 – 7.20 (m, 0.31H), 2.53 (d, J = 8.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.78, 158.88, 138.97, 138.27, 135.08, 135.01, 131.83, 131.02, 124.10, 123.31, 123.25, 122.16, 117.56, 117.16, 114.09, 113.30, 19.95, 19.90. **HRMS** (ESI): Calcd for $C_9H_9N_2O$ [M+H]: 161.0714; Found: 161.0715.



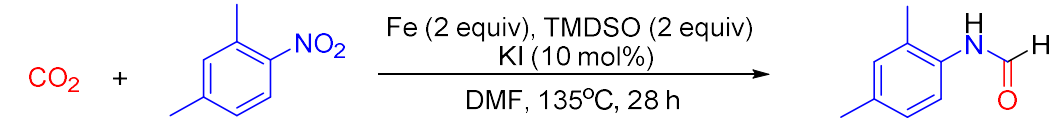
(ii) General procedure B. Following the general procedure **B**, the title compound was prepared using 2-methyl-5-nitrobenzonitrile (1.0 equiv, 0.50 mmol, 81 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (55 mg, 68%). Spectral and analytical data were identical to those reported for the same compound above.

***N*-(3-methoxy-4-methylphenyl)formamide (2n).**



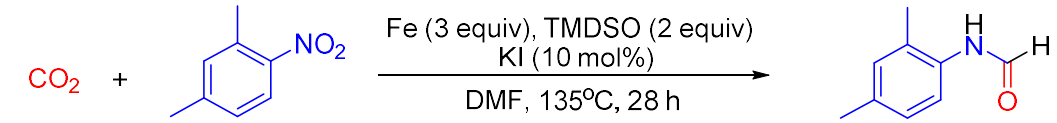
Following the general procedure **A**, the title compound was prepared using 2-methoxy-1-methyl-4-nitrobenzene (1.0 equiv, 0.50 mmol, 84 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (60 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (brs, 0.53H), 8.67 (d, J = 10.4 Hz, 0.52H), 8.35 (s, 0.50H), 7.80 (brs, 0.48H), 7.35 (s, 0.50H), 7.18 – 6.98 (m, 1H), 6.93 – 6.79 (m, 0.51H), 6.69 – 6.59 (m, 0.54H), 6.55 (s, 0.54H), 3.83 (d, J = 4.0 Hz, 3H), 2.19 (d, J = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.11, 159.27, 158.53, 157.93, 135.93, 135.60, 131.21, 130.46, 123.91, 123.11, 111.36, 110.61, 102.99, 101.98, 55.41, 55.36, 15.79, 15.69. **HRMS** (ESI): Calcd for $C_9H_{12}NO_2$ [M+H]: 166.0869; Found: 166.0868.

***N*-(2,4-dimethylphenyl)formamide (2o).**[9]



(balloon) (1 equiv) 48%

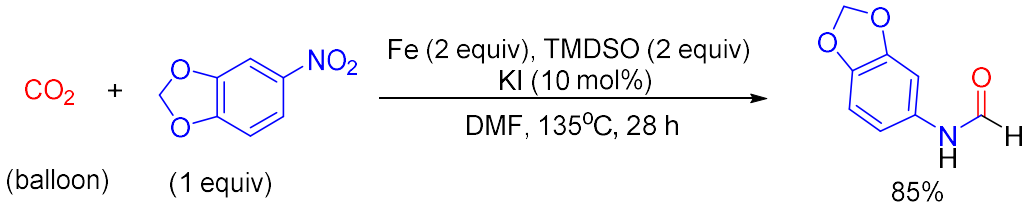
(i) Based on 2 equiv of Fe. Following the general procedure **A**, the title compound was prepared using 2,4-dimethyl-1-nitrobenzene (1.0 equiv, 0.50 mmol, 76 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (36 mg, 48%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 11.6 Hz, 0.64H), 8.43 (s, 0.34H), 7.94 (brs, 0.56H), 7.76 – 7.66 (m, 0.37H), 7.19 (brs, 0.32H), 7.10 – 7.06 (m, 0.63H), 7.06 – 7.00 (m, 2H), 2.33 (d, *J* = 9.2 Hz, 3H), 2.28 (d, *J* = 10.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.50, 159.18, 135.98, 135.35, 132.39, 131.94, 131.88, 131.22, 130.00, 128.99, 127.57, 127.32, 123.35, 121.28, 20.87, 20.80, 17.70, 17.67. **HRMS** (ESI): Calcd for $C_9H_{12}NO$ [M+H]: 150.0918; Found: 150.0919.



(balloon) (1 equiv) 60%

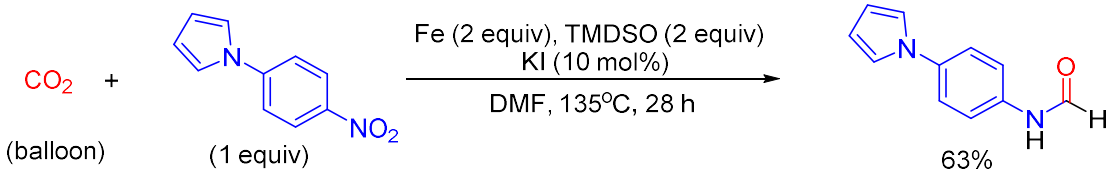
(ii) Based on 3 equiv of Fe. Following the general procedure **A**, the title compound was prepared using 2,4-dimethyl-1-nitrobenzene (1.0 equiv, 0.50 mmol, 76 mg), Fe (3.0 equiv, 1.5 mmol, 84 mg), and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (45 mg, 60%). Spectral and analytical data were identical to those reported for the same compound above.

***N*-(benzo[d][1,3]dioxol-5-yl)formamide (2p).**[10]



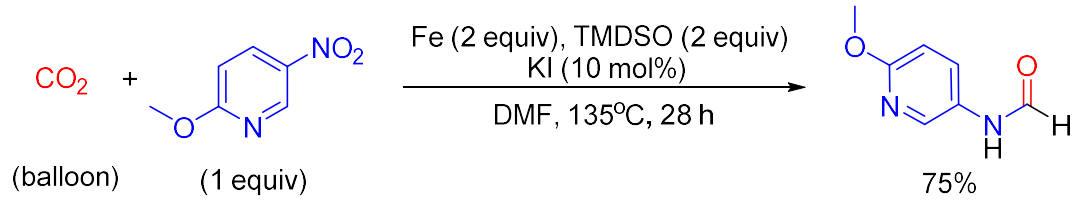
Following the general procedure **A**, the title compound was prepared using 5-methylbenzo[d][1,3]dioxole (1.0 equiv, 0.50 mmol, 91 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (70 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 11.2 Hz, 0.48H), 8.40 (brs, 0.42H), 8.31 (s, 0.55H), 7.65 (brs, 0.46H), 7.25 (d, *J* = 2.0 Hz, 0.51H), 6.87 (dd, *J* = 8.4, 2.0 Hz, 0.53H), 6.81 - 6.74 (m, 1H), 6.65 (d, *J* = 2.0 Hz, 0.44H), 6.65 (dd, *J* = 8.4, 2.0 Hz, 0.48H), 5.98 (d, *J* = 13.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.12, 159.04, 148.57, 147.84, 145.63, 144.63, 131.05, 130.81, 113.23, 113.15, 108.69, 108.13, 102.87, 102.08, 101.65, 101.35. **HRMS** (ESI): Calcd for $C_8H_8NO_3$ [M+H]: 166.0504; Found: 166.0504.

***N*-(4-(1H-pyrrol-1-yl)phenyl)formamide (2q).**



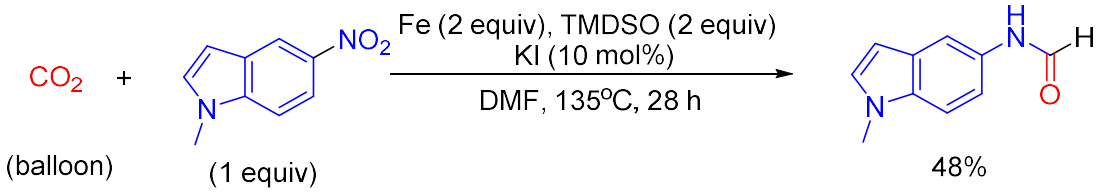
Following the general procedure **A**, the title compound was prepared using 1-(4-nitrophenyl)-1H-pyrrole (1.0 equiv, 0.50 mmol, 94 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (58 mg, 63%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 11.2 Hz, 0.47H), 8.40 (s, 0.66H), 8.01 (brs, 0.5H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.31 (brs, 0.55H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.05 (s, 2H), 6.36 (d, *J* = 5.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.32, 158.83, 138.32, 137.56, 134.40, 134.12, 121.79, 121.12, 121.10, 120.27, 119.32, 119.30, 110.73, 110.48. **HRMS** (ESI): Calcd for $C_{11}H_{11}N_2O$ [M+H]: 187.0868; Found: 187.0871.

***N*-(6-methoxypyridin-3-yl)formamide (2r).**



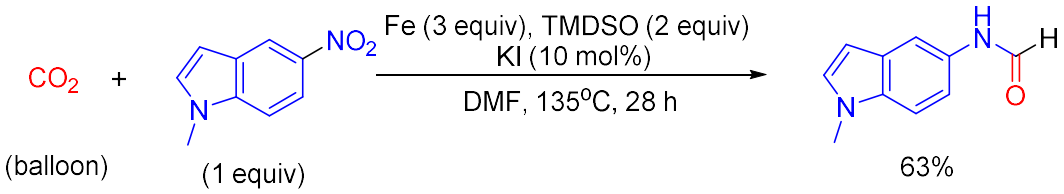
Following the general procedure **A**, the title compound was prepared using 2-methoxy-5-nitropyridine (1.0 equiv, 0.50 mmol, 77 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (57 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 11.2 Hz, 0.38H), 8.39 (brs, 0.64H), 8.22 (s, 0.66H), 8.03 (s, 0.36H), 7.96 (d, *J* = 8.8 Hz, 0.67H), 7.75 (brs, 0.35H), 7.40 (d, *J* = 9.2 Hz, 0.43H), 7.35 (s, 0.49H), 6.83 – 6.72 (m, 1H), 3.94 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.78, 162.48, 161.39, 159.06, 139.45, 138.52, 132.58, 132.27, 127.47, 126.78, 111.65, 110.84, 53.81, 53.66. **HRMS** (ESI): Calcd for $C_7H_9N_2O_2$ [M+H]: 153.0666; Found: 153.0664.

***N*-(1-methyl-1H-indol-5-yl)formamide (2s).**[11]



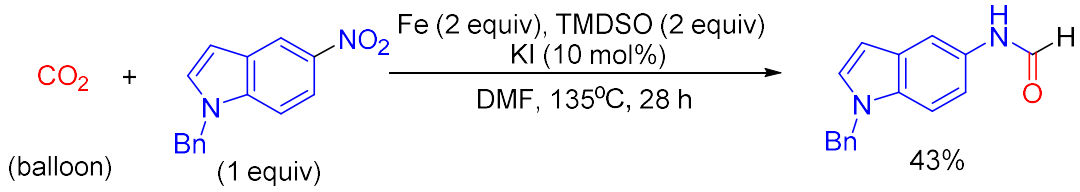
(i) Based on 2 equiv of Fe. Following the general procedure **A**, the title compound was prepared using 1-methyl-5-nitro-1H-indole (1.0 equiv, 0.50 mmol, 88 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (42 mg, 48%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 11.2 Hz, 0.61H), 8.38 (s, 0.39H), 8.28 (brs, 0.54H), 7.89 (d, *J* = 1.6 Hz, 0.39H), 7.55 (brs, 0.37H), 7.38 (d, *J* = 1.6 Hz, 0.60H), 7.34 – 7.29 (m, 1H), 7.29 – 7.25 (m, 0.54H), 7.12 (d, *J* = 3.2 Hz, 0.60H), 7.07 (d, *J* = 2.8 Hz, 0.39H), 7.03 – 6.98 (m, 0.60H), 6.49 (d, *J* = 2.8 Hz, 0.58H), 6.47 (d, *J* = 3.2 Hz, 0.38H), 3.80 (d, *J* = 12.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.74, 159.13, 134.98, 134.39, 130.39, 129.87, 129.20, 128.89, 128.84, 128.50, 115.68,

115.60, 112.82, 112.53, 110.14, 109.40, 101.12, 100.93, 33.03, 32.93. **HRMS** (ESI): Calcd for $C_{10}H_{11}N_2O$ [M+H]: 175.0870; Found: 175.0871.



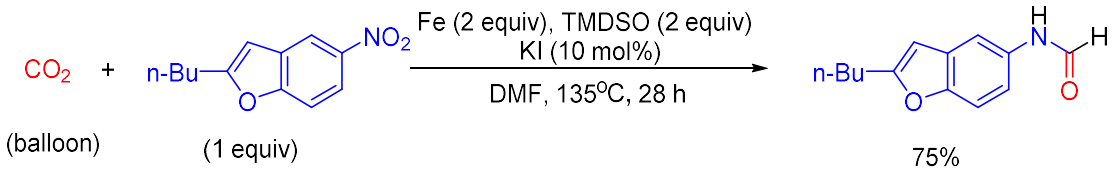
(ii) Based on 3 equiv of Fe. Following the general procedure **A**, the title compound was prepared using 1-methyl-5-nitro-1H-indole (1.0 equiv, 0.50 mmol, 88 mg), Fe (3.0 equiv, 1.5 mmol, 84 mg), and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (55 mg, 63%). Spectral and analytical data were identical to those reported for the same compound above.

***N*-(1-benzyl-1H-indol-5-yl)formamide (2t).**



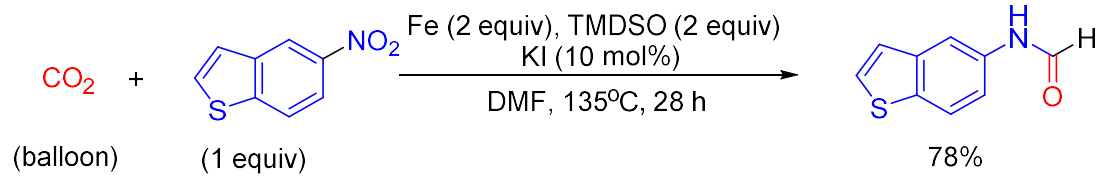
Following the general procedure **A**, the title compound was prepared using 1-benzyl-5-nitro-1H-indole (1.0 equiv, 0.50 mmol, 126 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (54 mg, 43%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 11.6 Hz, 0.60H), 8.37 (s, 0.40H), 7.89 (s, 0.39H), 7.70 (s, 0.60H), 7.37 (s, 0.63H), 7.34 – 7.23 (m, 4H), 7.21 – 7.12 (m, 2H), 7.12 – 7.02 (m, 2H), 6.93 – 6.85 (m, 0.62H), 6.52 (s, 1H), 5.31 (d, *J* = 7.2 Hz, 2H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.42, 158.94, 137.32, 137.08, 134.56, 133.99, 129.95, 129.95, 129.42, 129.41, 129.23, 129.21, 128.87, 128.80, 127.82, 127.69, 126.74, 126.70, 115.98, 115.77, 113.04, 112.85, 110.70, 109.99, 101.91, 101.68, 50.40, 50.27. **HRMS** (ESI): Calcd for $C_{16}H_{15}N_2O$ [M+H]: 251.1188; Found: 251.1184.

***N*-(2-butylbenzofuran-5-yl)formamide (2u).**



Following the general procedure **A**, the title compound was prepared using 2-butyl-5-nitrobenzofuran (1.0 equiv, 0.50 mmol, 110 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (81 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 11.2 Hz, 0.54H), 8.51 (brs, 0.41H), 8.39 (s, 0.46H), 7.87 – 7.79 (m, 0.48H), 7.72 (brs, 0.44H), 7.42 – 7.31 (m, 1H), 7.26 – 7.17 (m, 1H), 7.06 – 6.87 (m, 0.54H), 6.36 (d, *J* = 11.2 Hz, 1H), 2.96 – 2.55 (m, 2H), 1.91 – 1.63 (m, 2H), 1.44 (tq, *J* = 14.4, 7.2 Hz, 2H), 1.06 – 0.82 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.59, 161.67, 161.04, 159.20, 152.57, 151.84, 131.76, 131.60, 130.08, 129.52, 116.11, 115.99, 112.33, 111.51, 111.48, 110.78, 102.03, 101.80, 29.69, 29.67, 28.19, 28.18, 22.28, 22.28, 13.80. (25 carbon signals were observed out of expected 26 carbon signals) **HRMS** (ESI): Calcd for $C_{13}H_{16}NO_2$ [M+H]: 218.1179; Found: 218.1181.

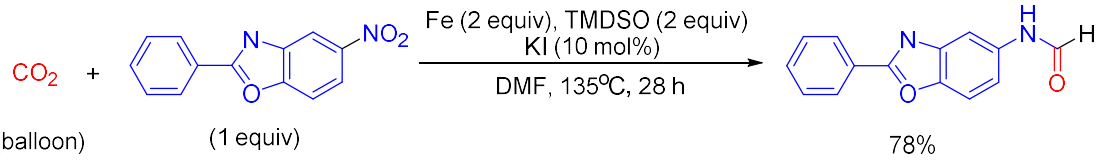
***N*-(benzo[b]thiophen-5-yl)formamide (2v).**[11]



Following the general procedure **A**, the title compound was prepared using 5-nitrobenzo[b]thiophene (1.0 equiv, 0.50 mmol, 90 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (69 mg, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 11.2 Hz, 0.53H), 8.69 (brs, 0.45H), 8.44 (s, 0.52H), 8.23 (d, *J* = 1.6 Hz, 0.51H), 7.93 – 7.78 (m, 1H), 7.73 (brs, 0.46H), 7.57 (d, *J* = 1.6 Hz, 0.49H), 7.54 (d, *J* = 5.2Hz, 0.50H),7.49 (d, *J* = 5.2 Hz, 0.50H), 7.38 (dd, *J* = 8.4, 1.6 Hz, 0.52H), 7.33 – 7.26 (m, 1H), 7.13 (dd, *J* = 8.4, 1.6 Hz, 0.50H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.20, 159.26, 140.50, 140.16, 136.76, 136.02, 133.66, 133.56, 128.61,

127.84, 123.91, 123.69, 123.53, 122.86, 117.43, 116.92, 114.89, 113.58. **HRMS** (ESI): Calcd for C_9H_8NOS [M+H]: 178.0322; Found: 178.0327.

***N*-(2-Phenylbenzo[d]oxazol-5-yl)benzamide (2w).**



Following the general procedure **A**, the title compound was prepared using 5-nitro-2-phenylbenzo-[d]oxazole (1.0 equiv., 0.50 mmol, 120.1 mg) and PE/EtOAc (3:1) as an eluent to afford the title compound as a yellow amorphous solid (93 mg, 78%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.39 (s, 0.83H), 10.27 (d, J = 10.8 Hz, 0.26H), 8.83 (d, J = 10.8 Hz, 0.28H), 8.34 (d, J = 1.6 Hz, 0.87H), 8.22 – 8.18 (m, 2H), 8.15 (d, J = 2.0 Hz, 0.77H), 7.75 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 2.0 Hz, 0.31H), 7.66 – 7.60 (m, 3H), 7.54 (dd, J = 8.8, 2.0 Hz, 0.87H), 7.23 (dd, J = 8.8, 2.0 Hz, 0.28H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 163.52, 163.46, 162.07, 160.11, 153.80, 150.77, 146.98, 142.75, 142.18, 140.82, 136.21, 135.98, 132.53, 132.47, 129.80, 127.73, 126.83, 119.91, 117.86, 116.95, 111.89, 111.41, 110.49, 108.72. **HRMS** (ESI): Calcd for $C_{14}H_{11}N_2O_2$ [M+H]: 239.0818; Found: 239.0821.

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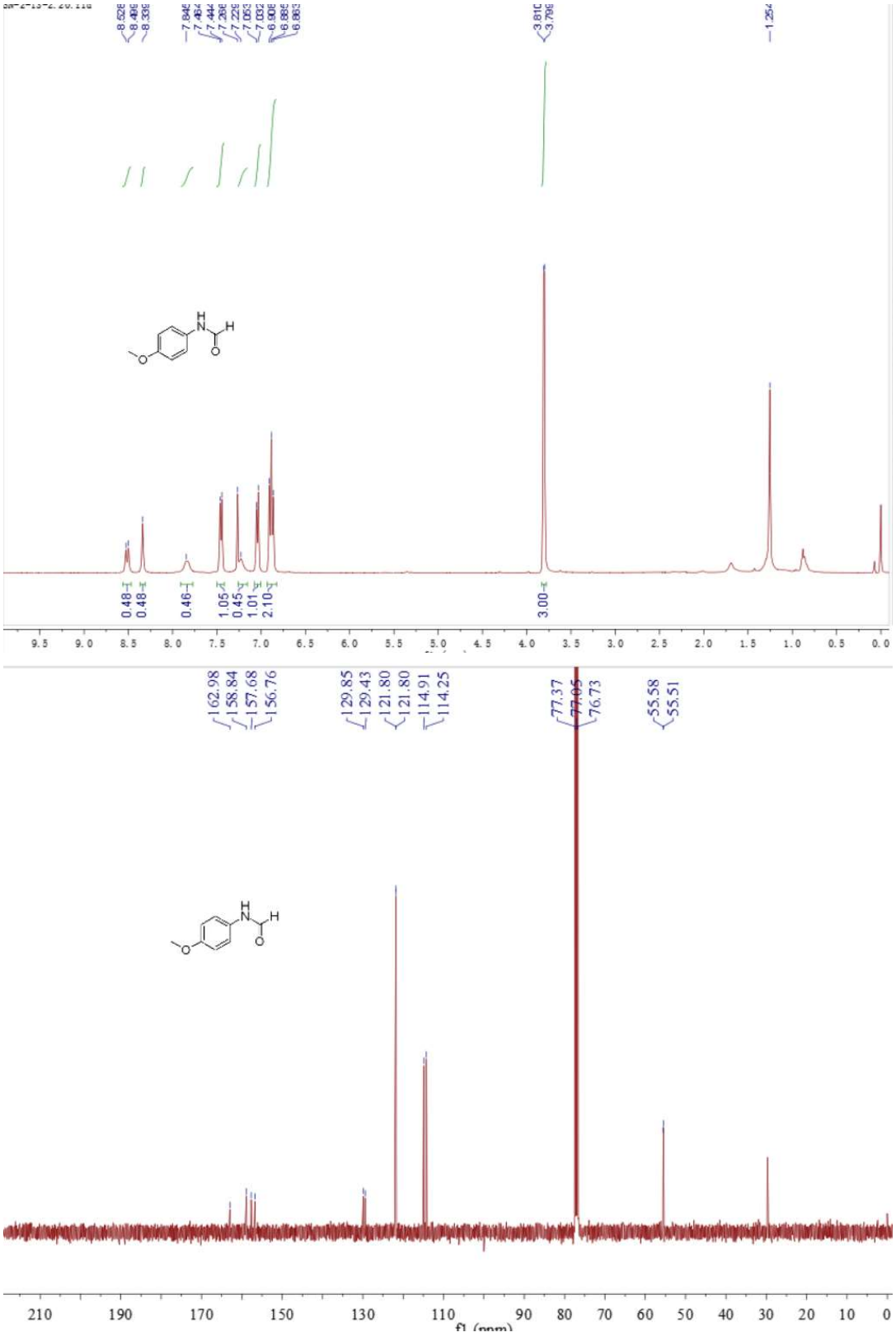
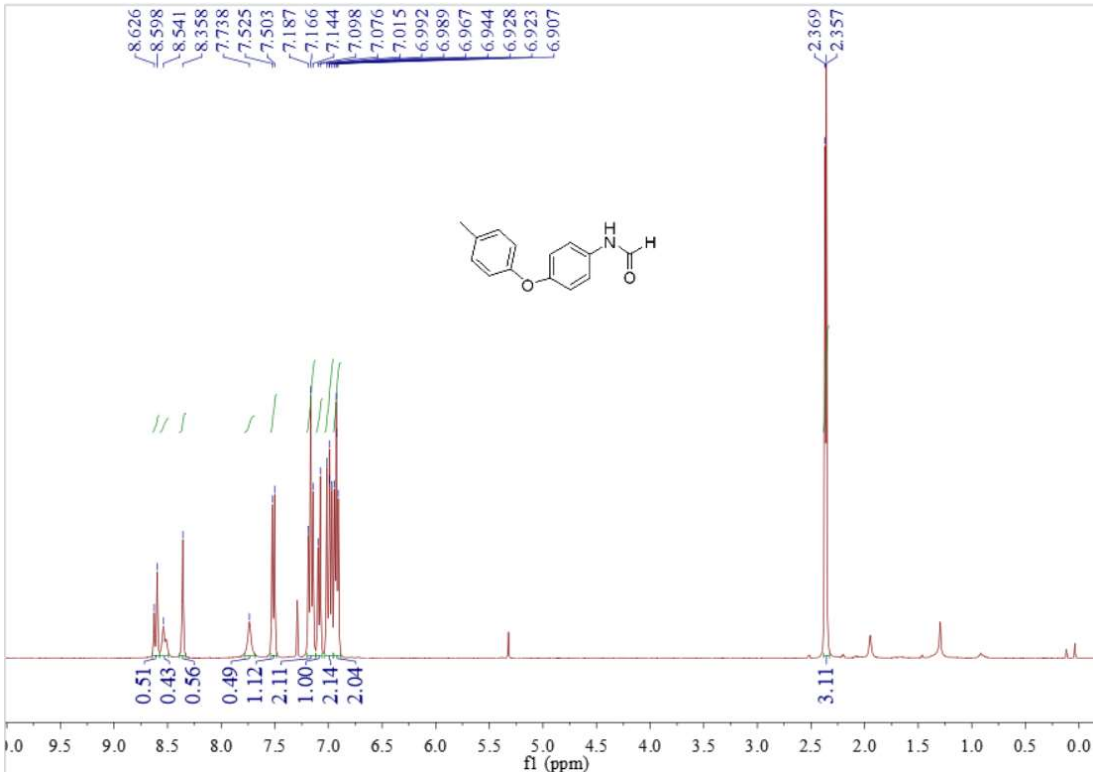
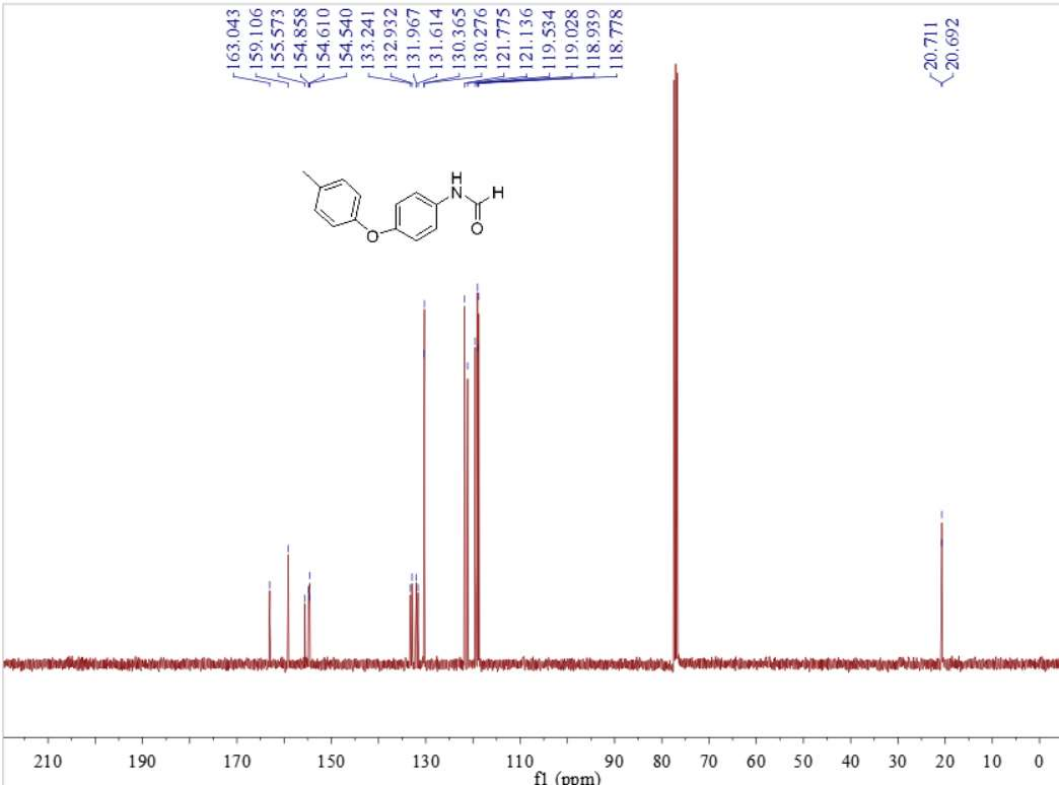
NMR Spectra

N-(4-methoxyphenyl)formamide (2a)

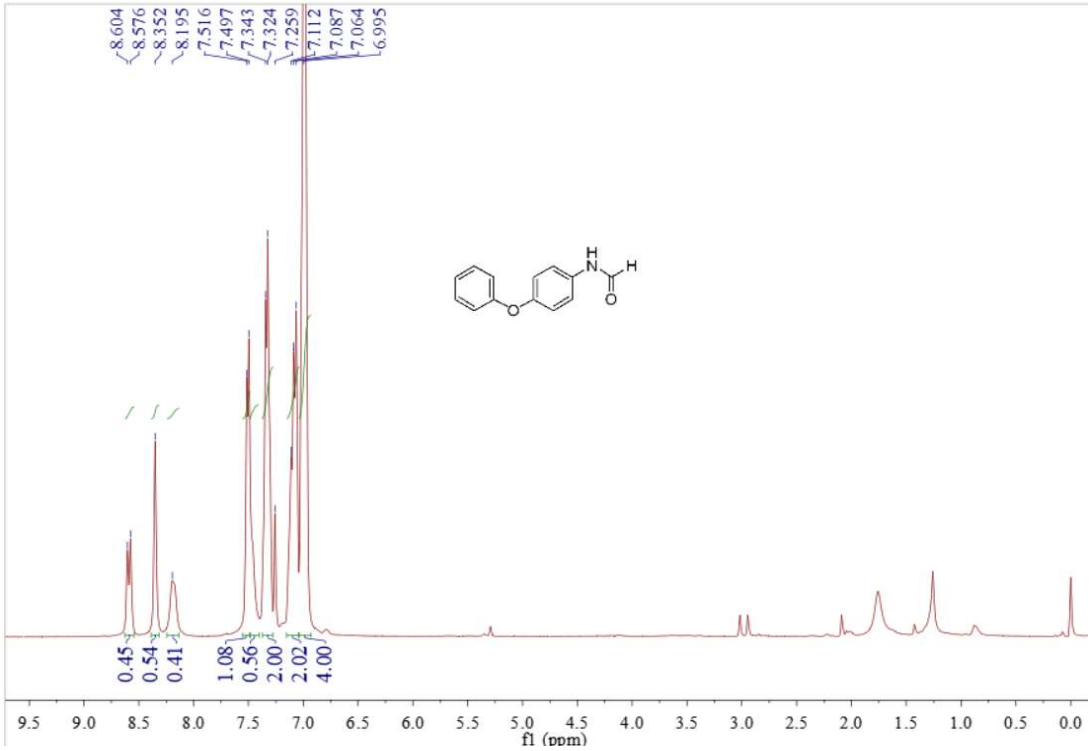


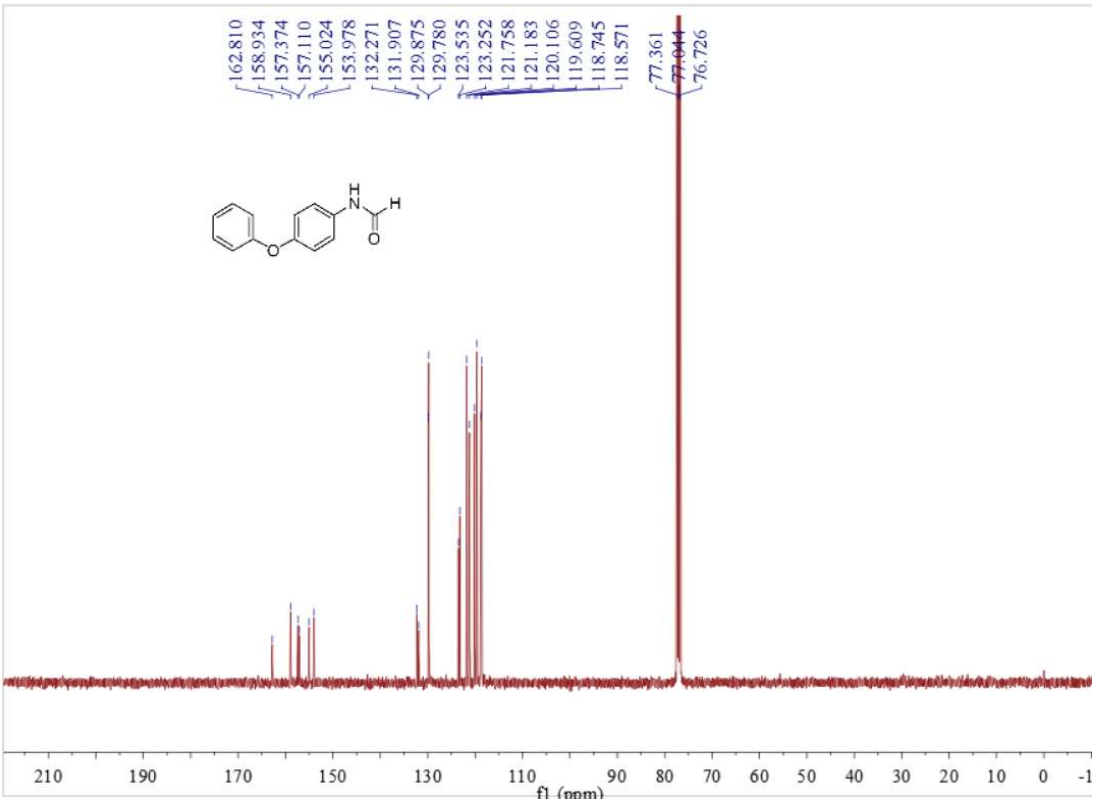
N-(4-(p-tolyloxy)phenyl)formamide (2b)



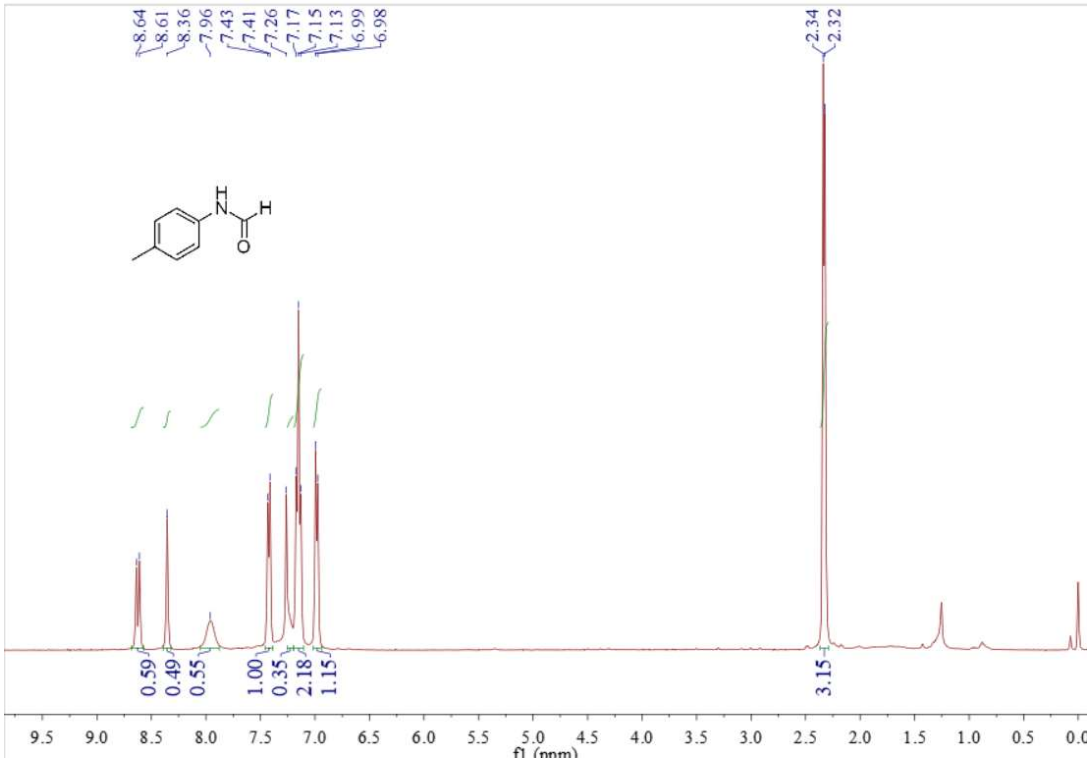


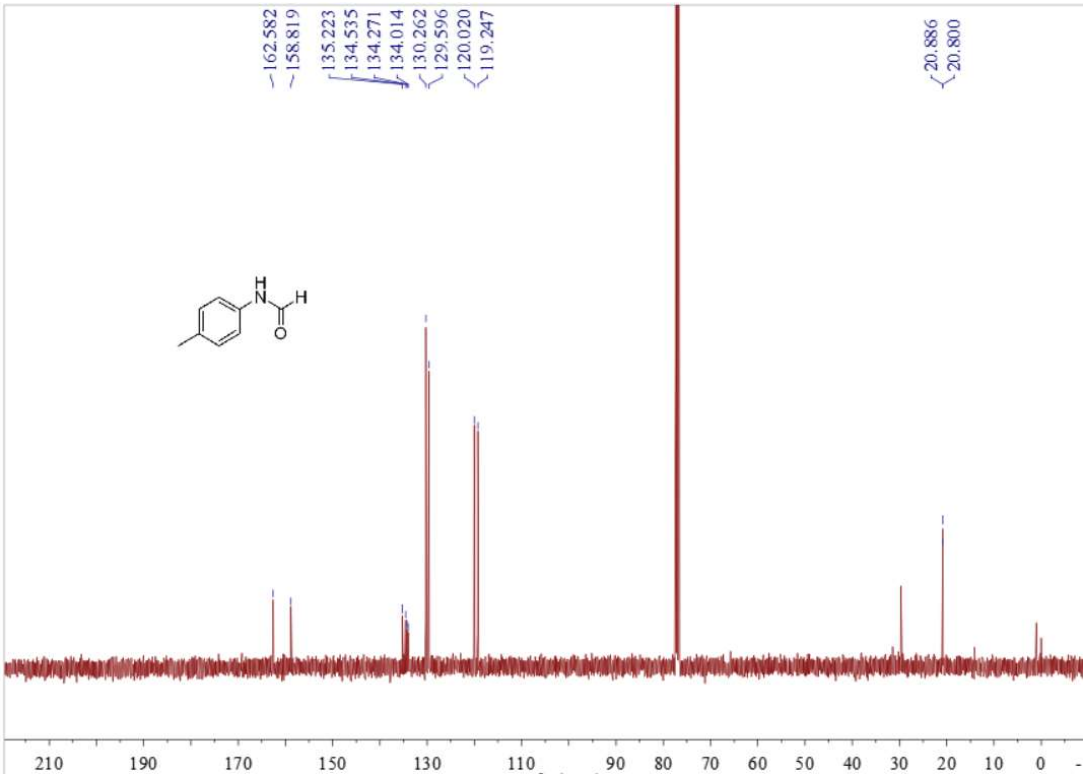
N-(4-phenoxyphenyl)formamide (2c)



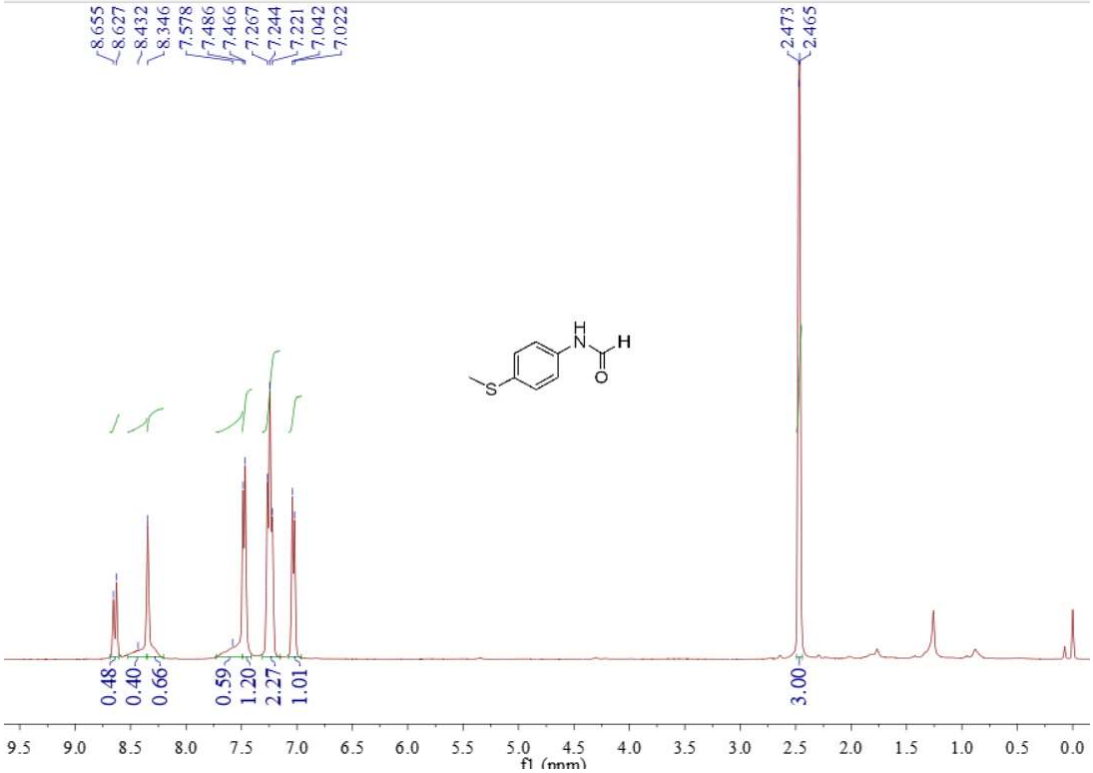


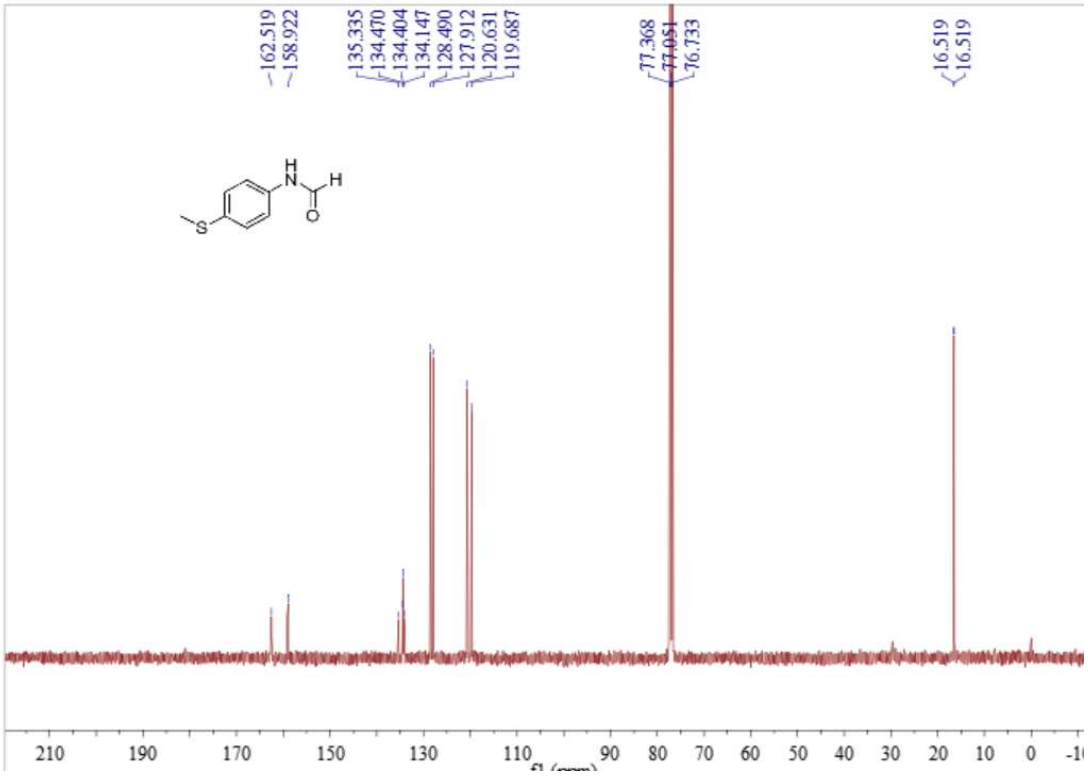
N-p-tolylformamide (2d)





N-(4-(methylthio)phenyl)formamide (2e)





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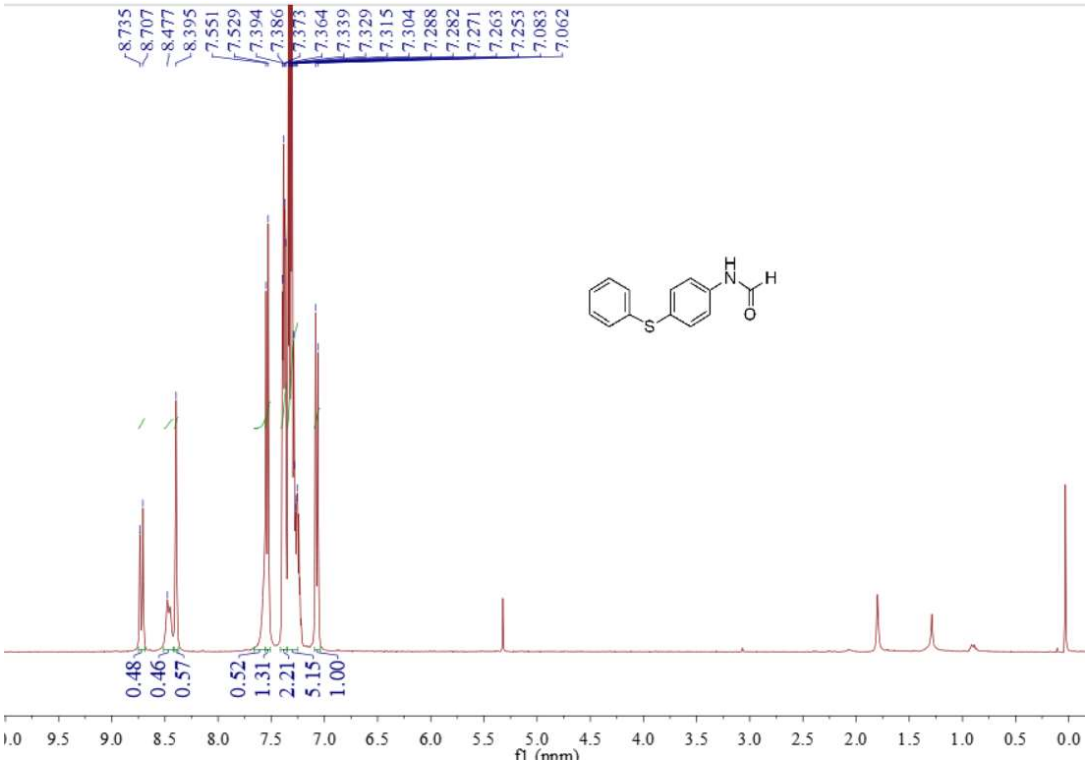
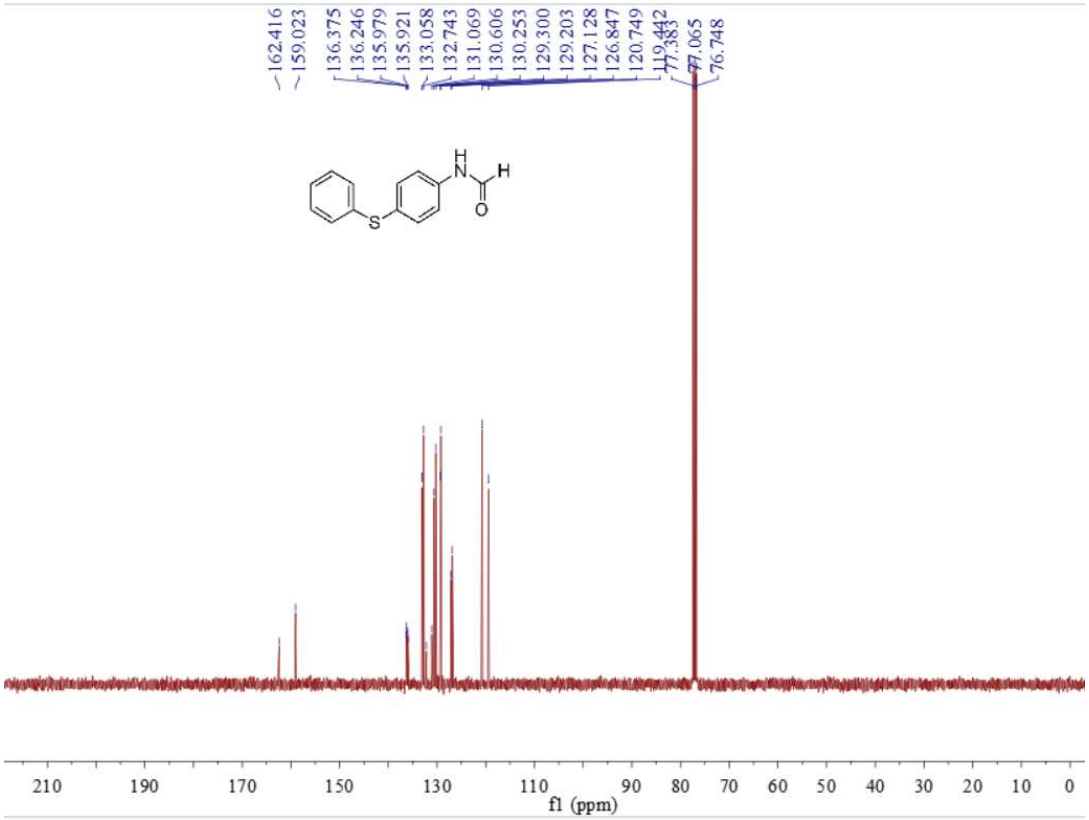
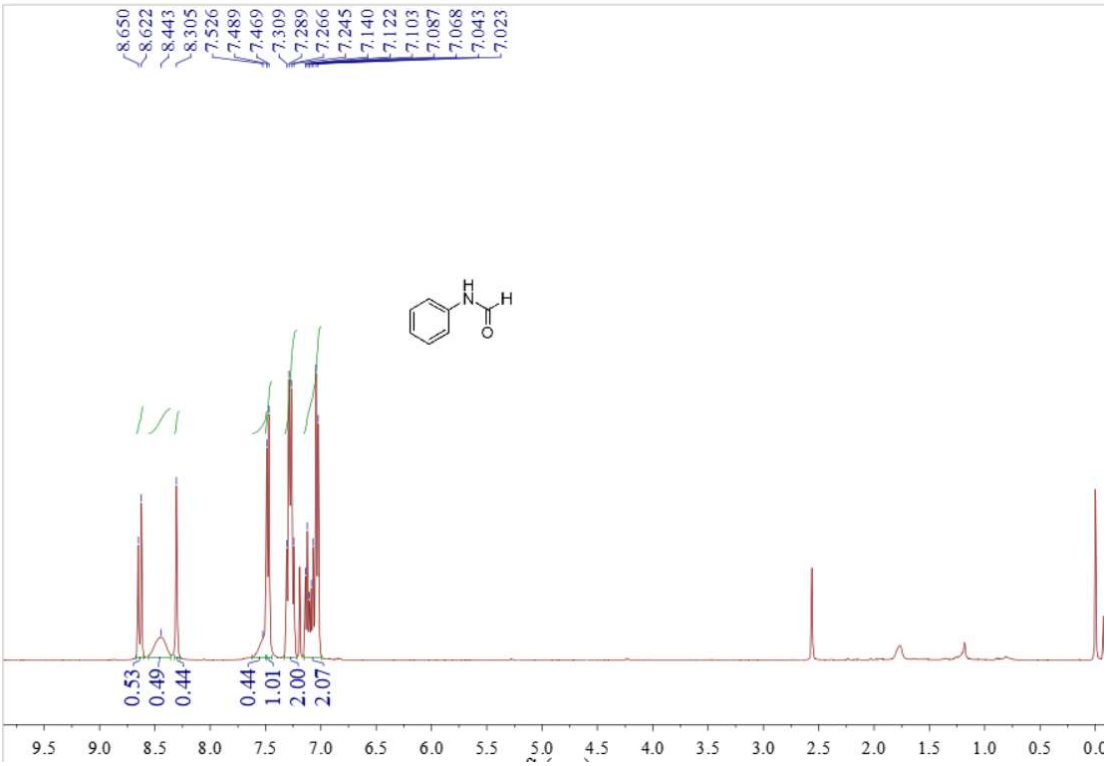
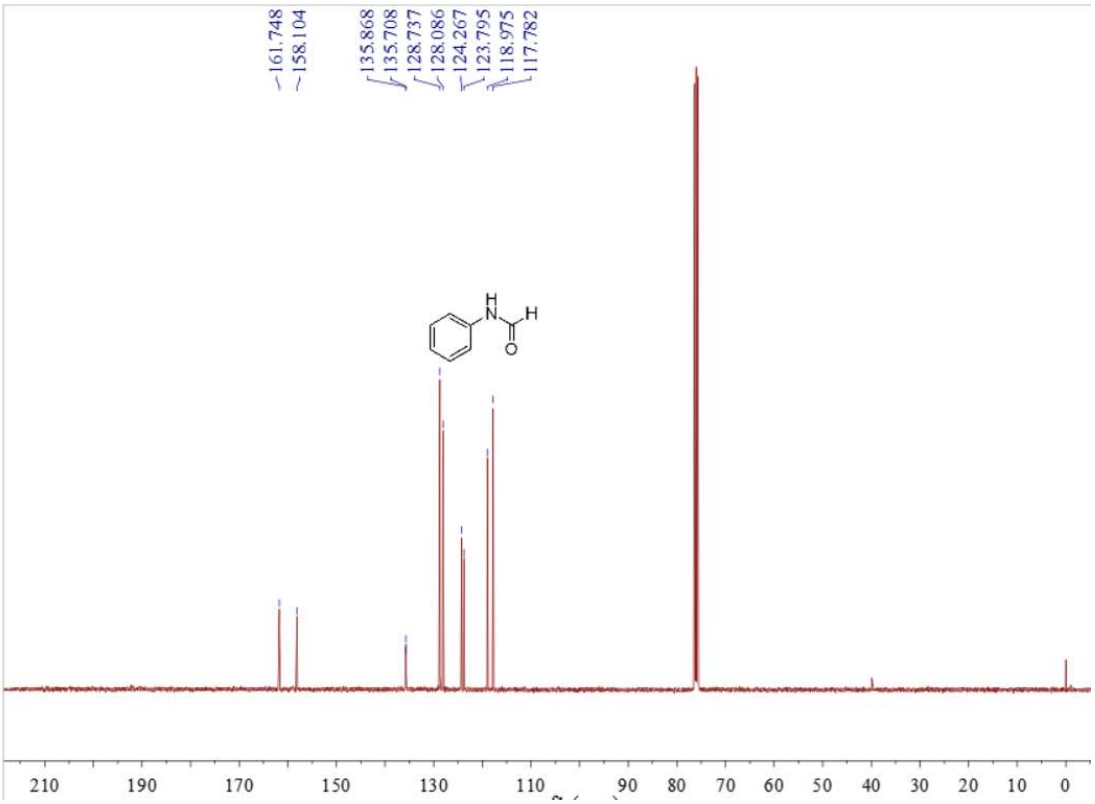


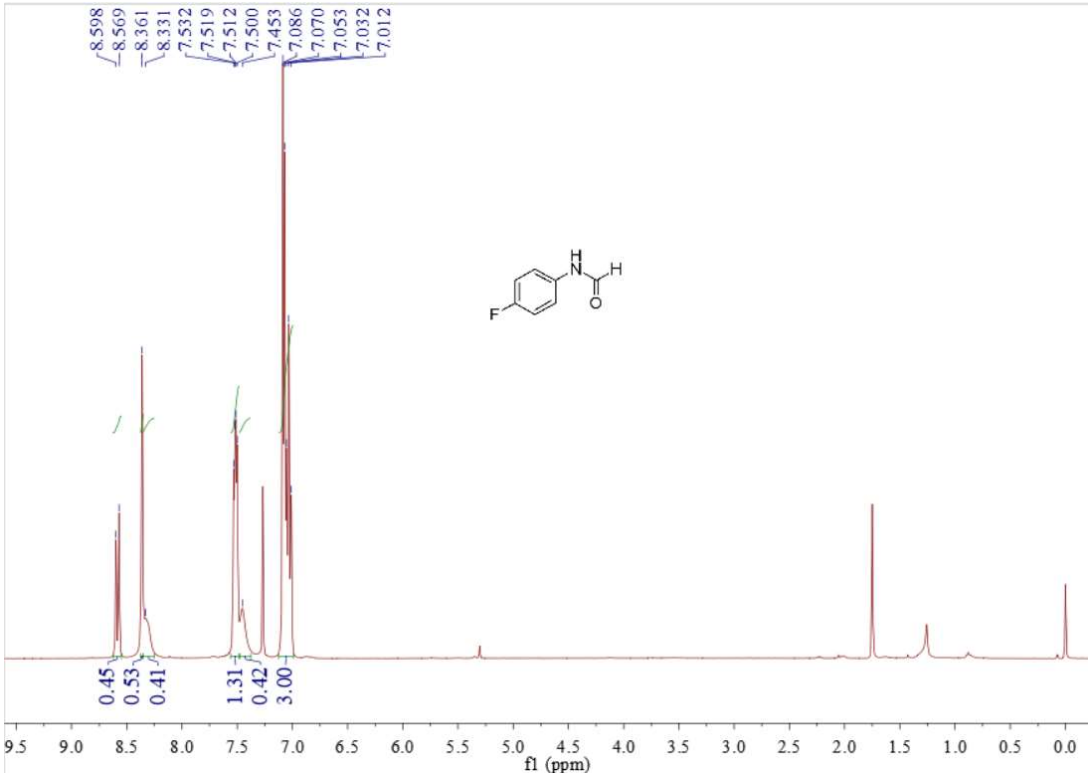


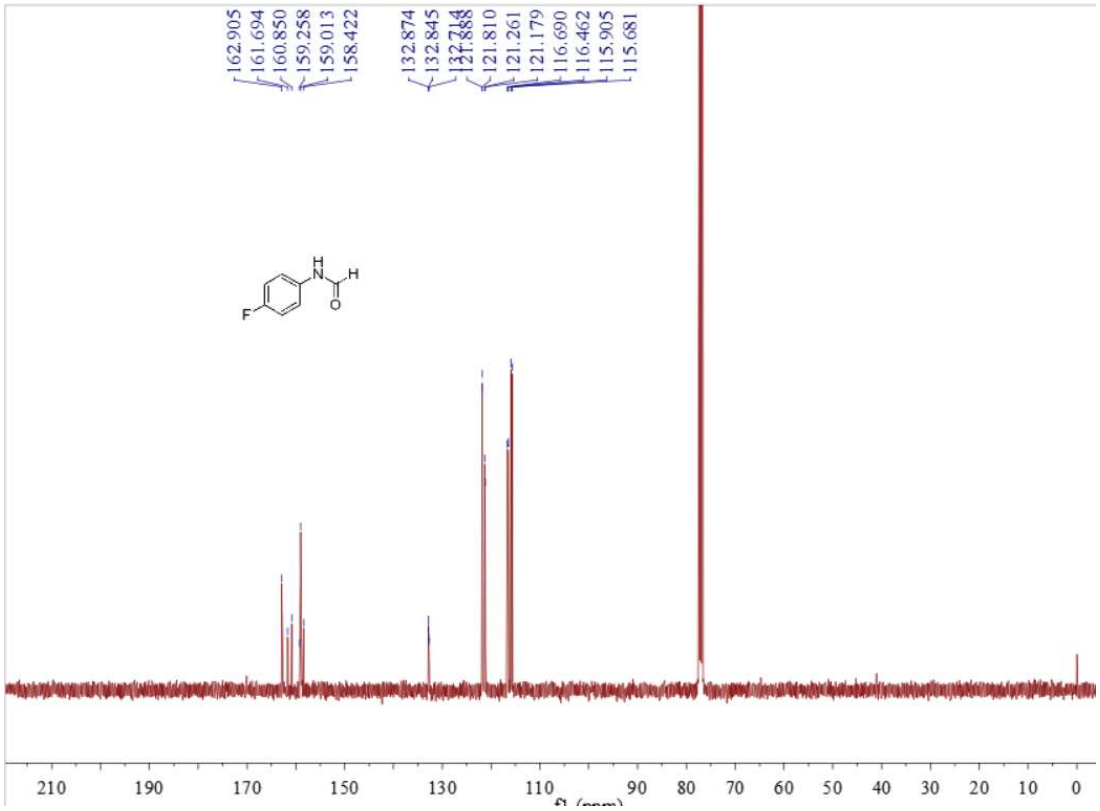
N-phenylformamide (2g)



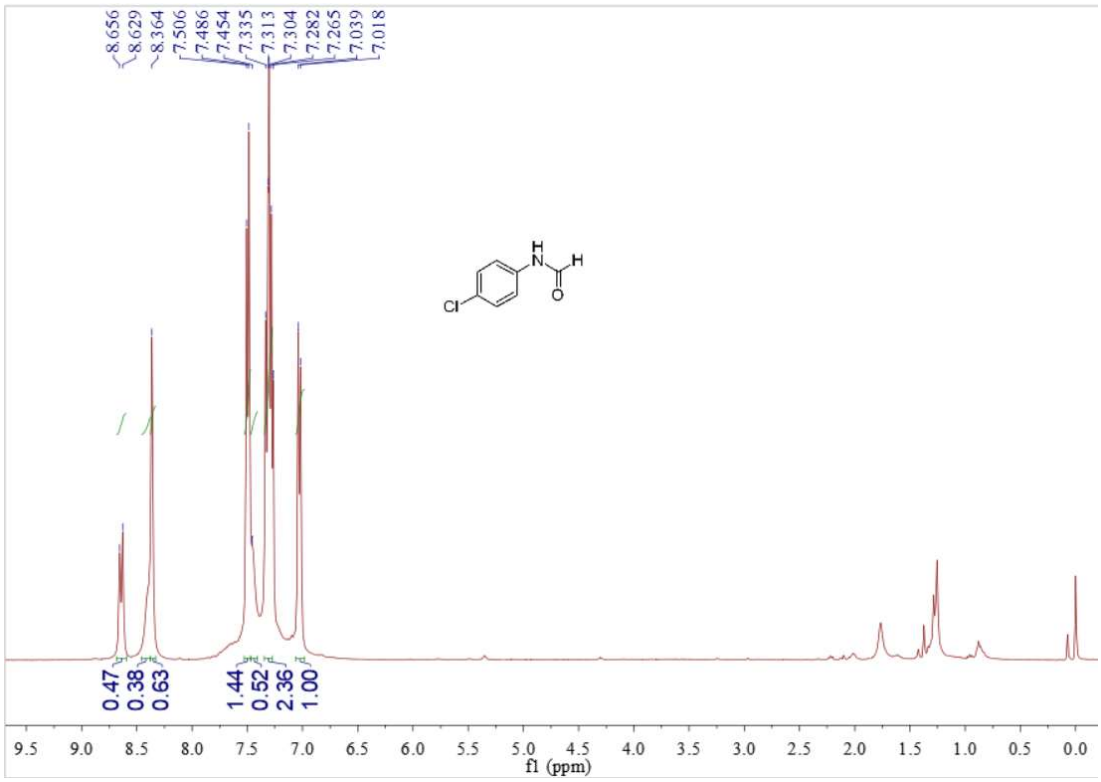


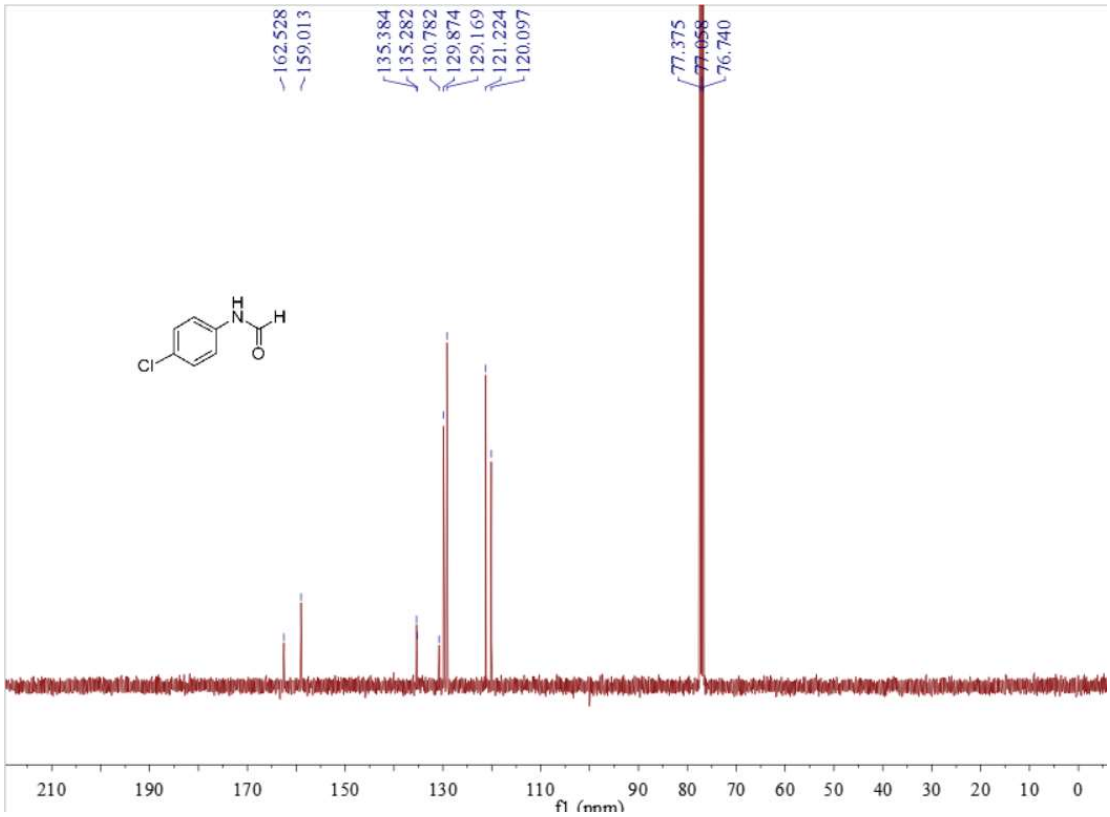
N-(4-fluorophenyl)formamide (2h)



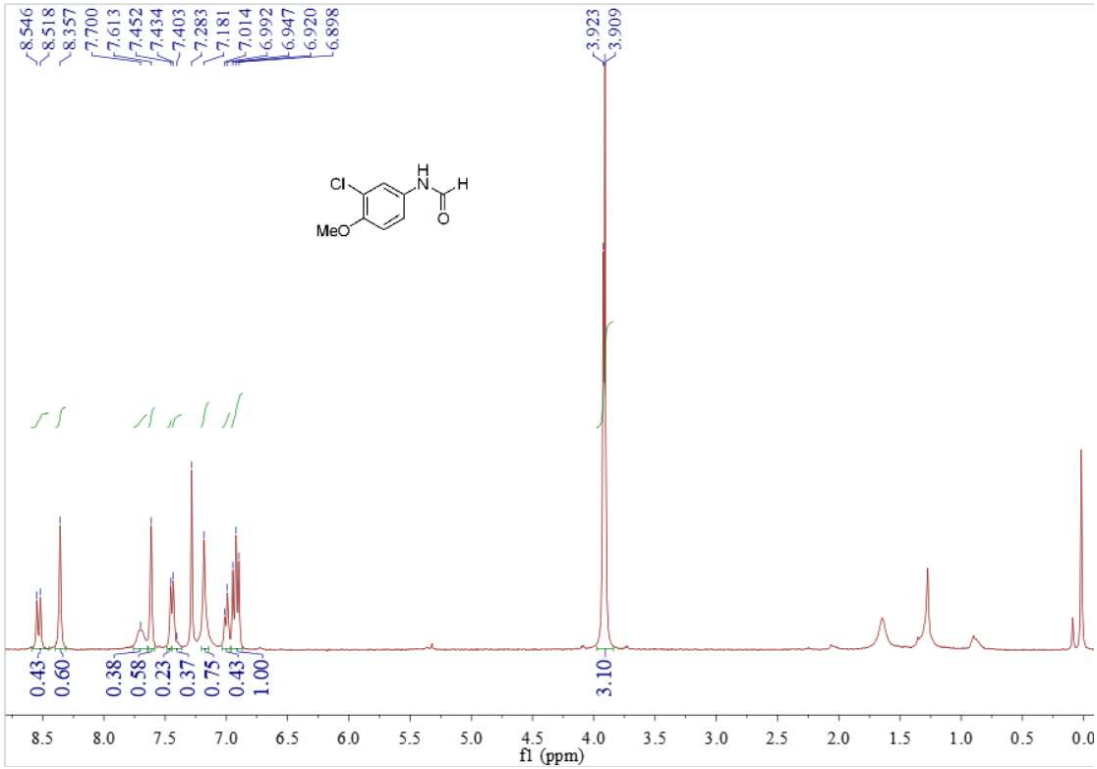


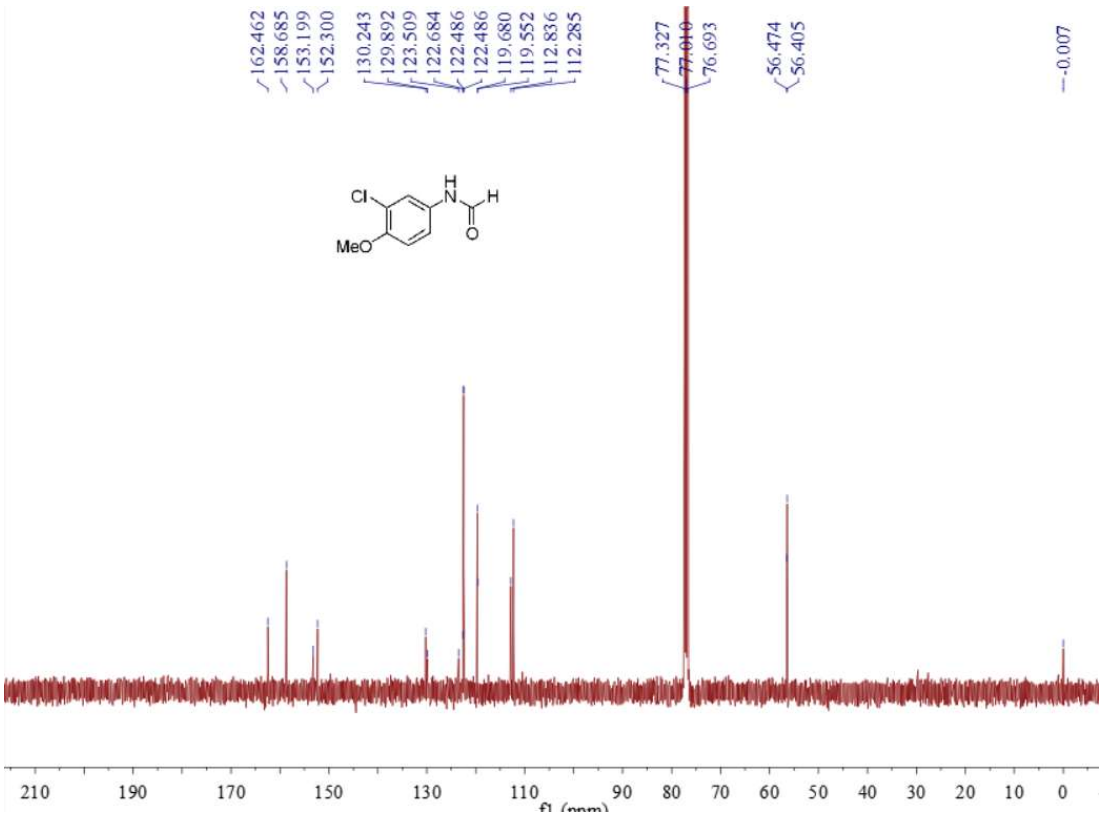
N-(4-chlorophenyl)formamide (2i)



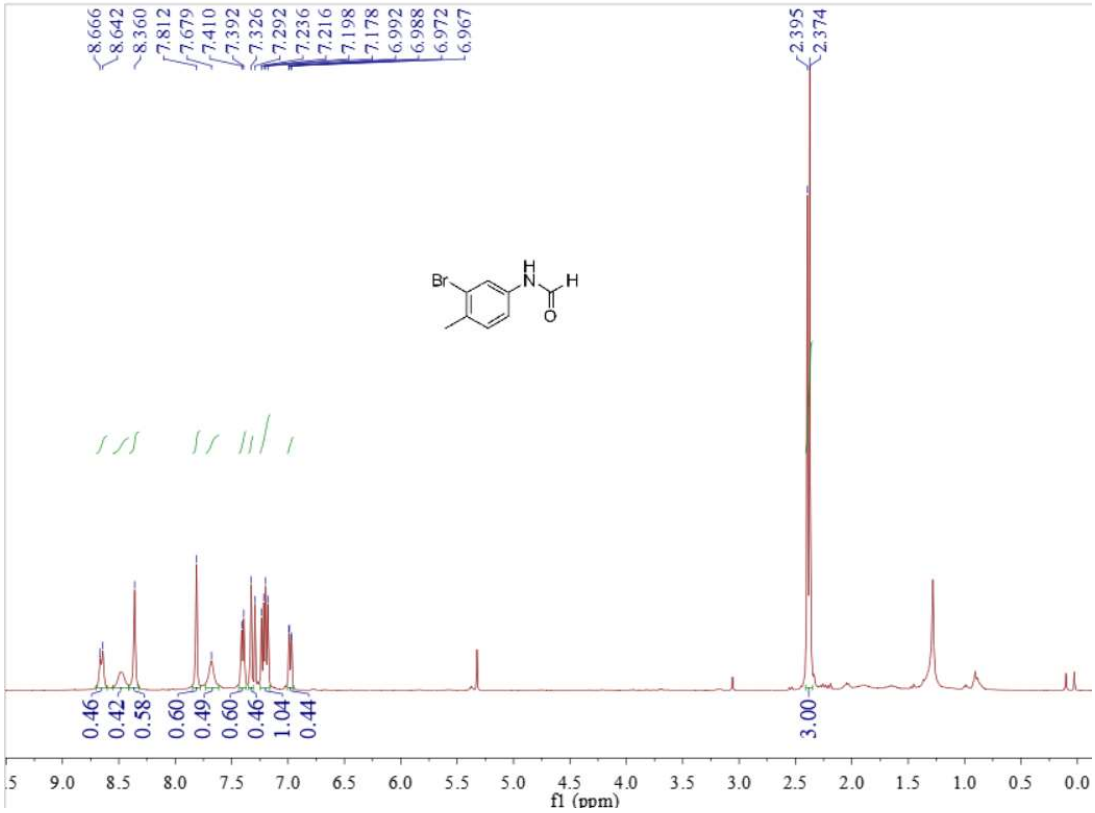


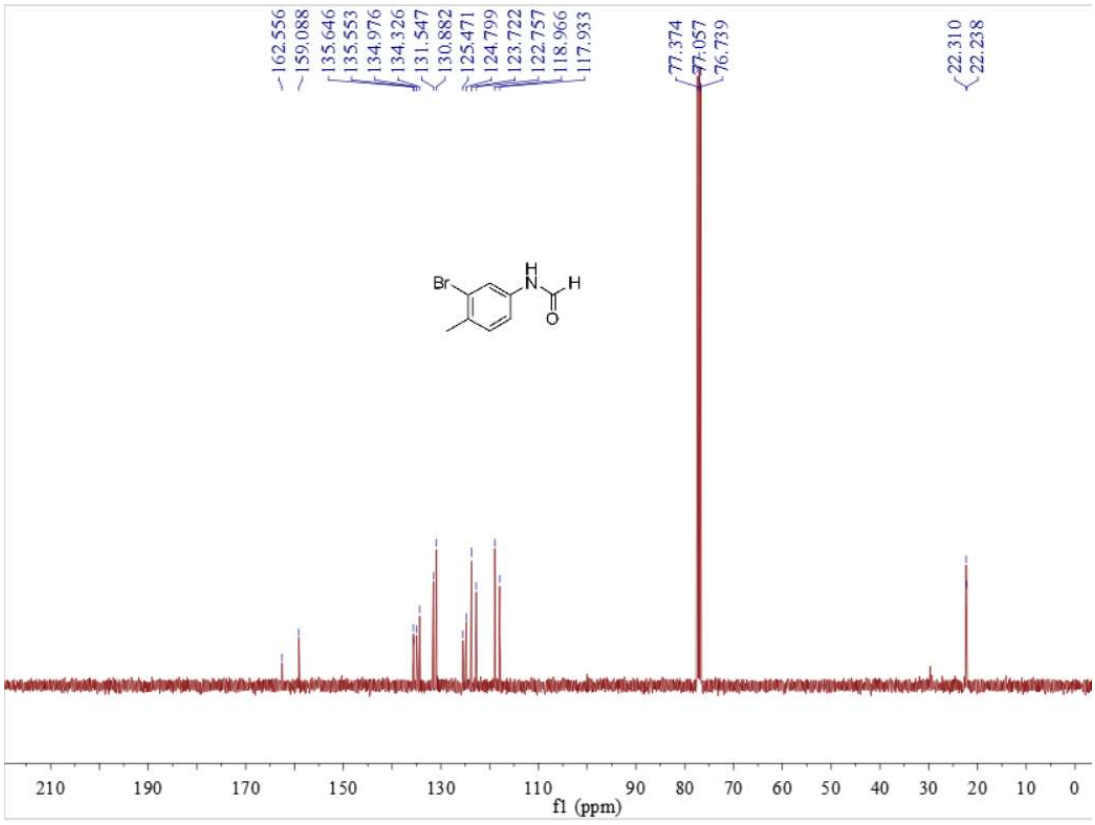
N-(3-chloro-4-methoxyphenyl)formamide (2j)



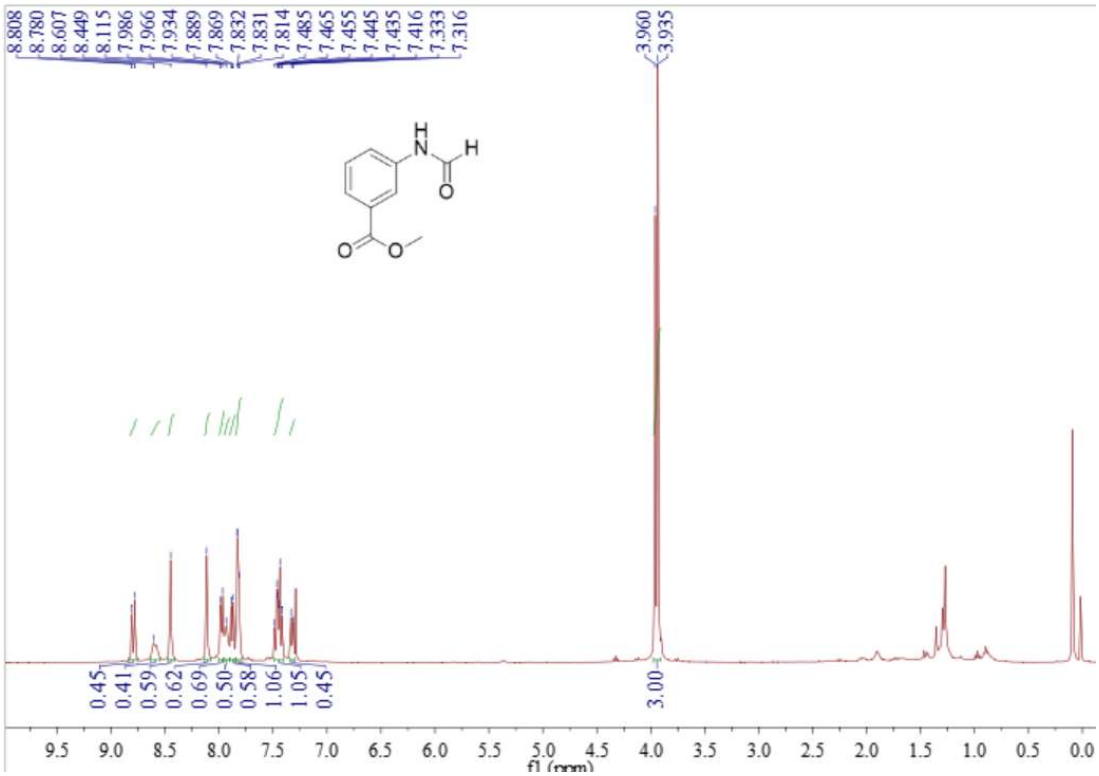


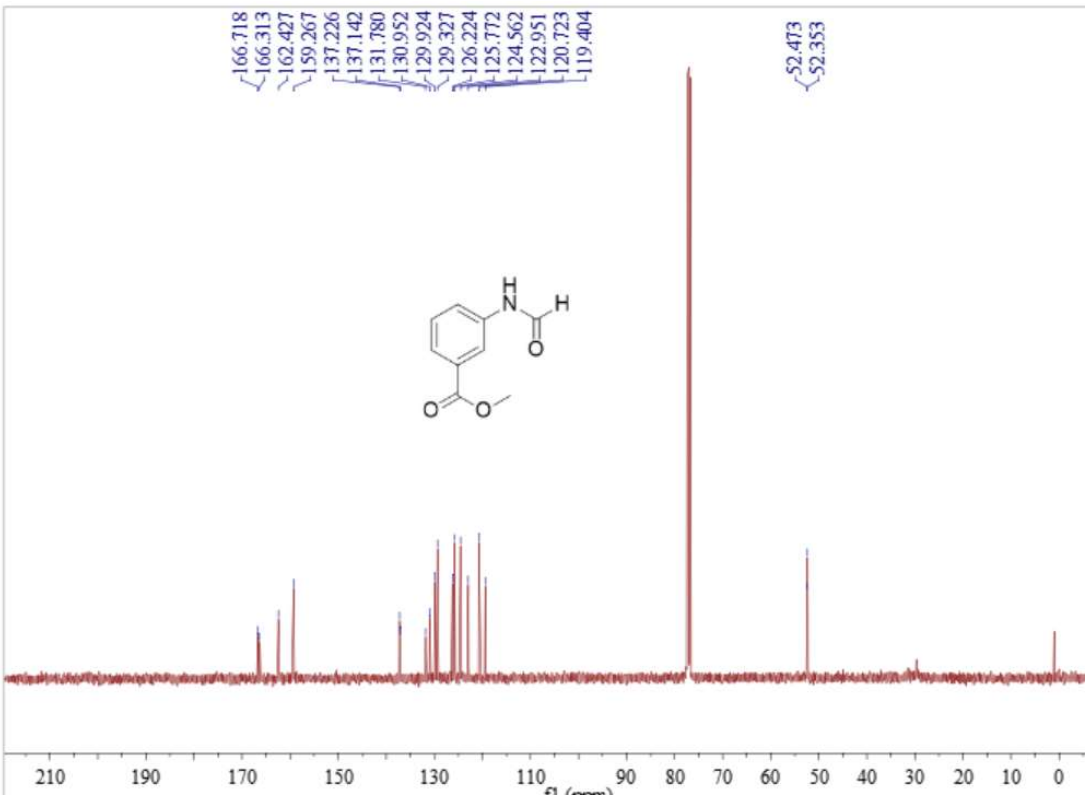
N-(3-bromo-4-methylphenyl)formamide (2k)



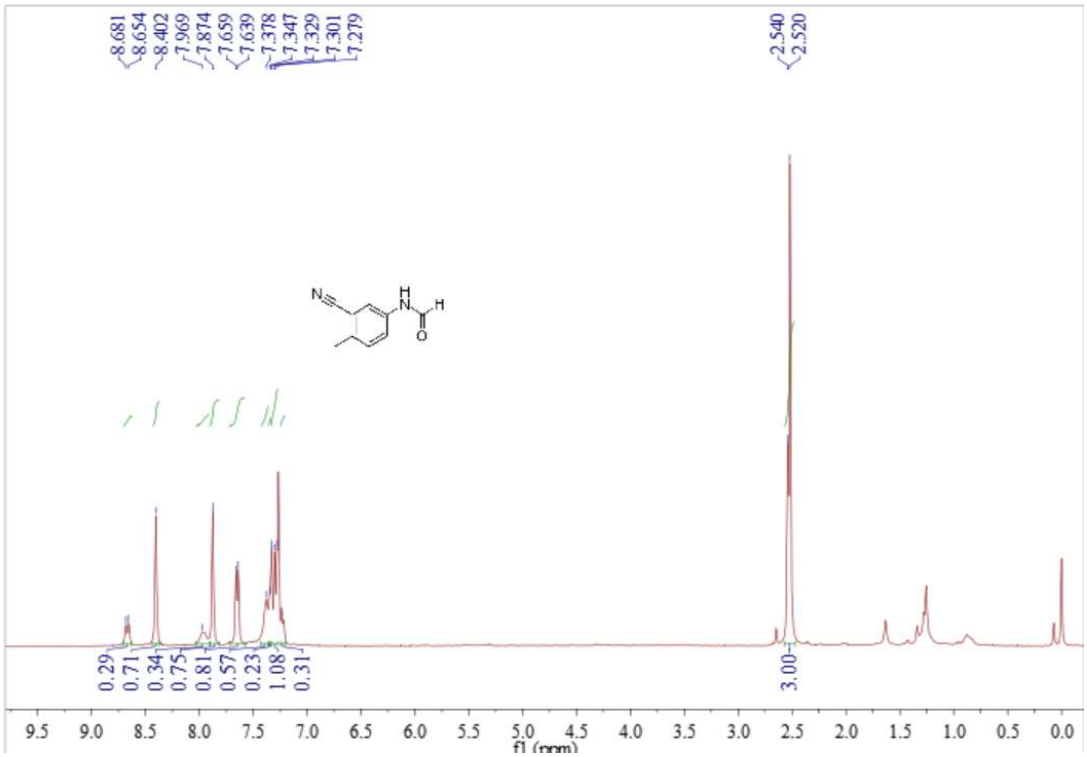


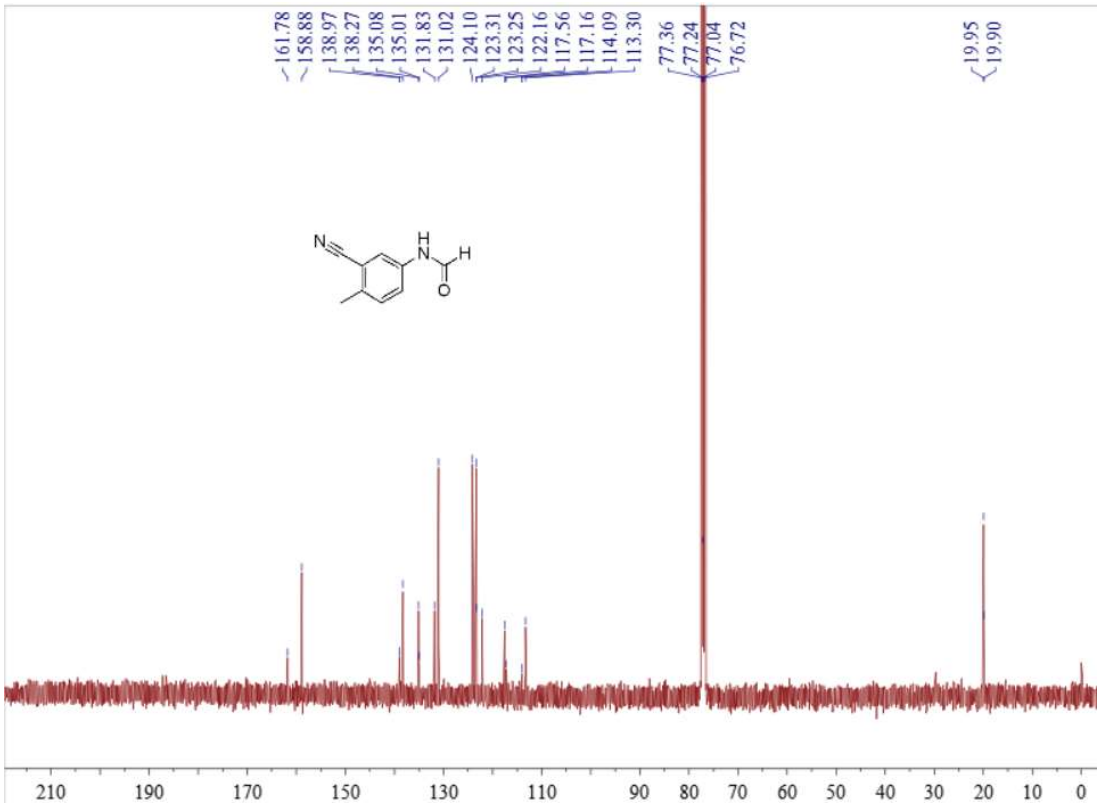
methyl 3-formamidobenzoate (2l)



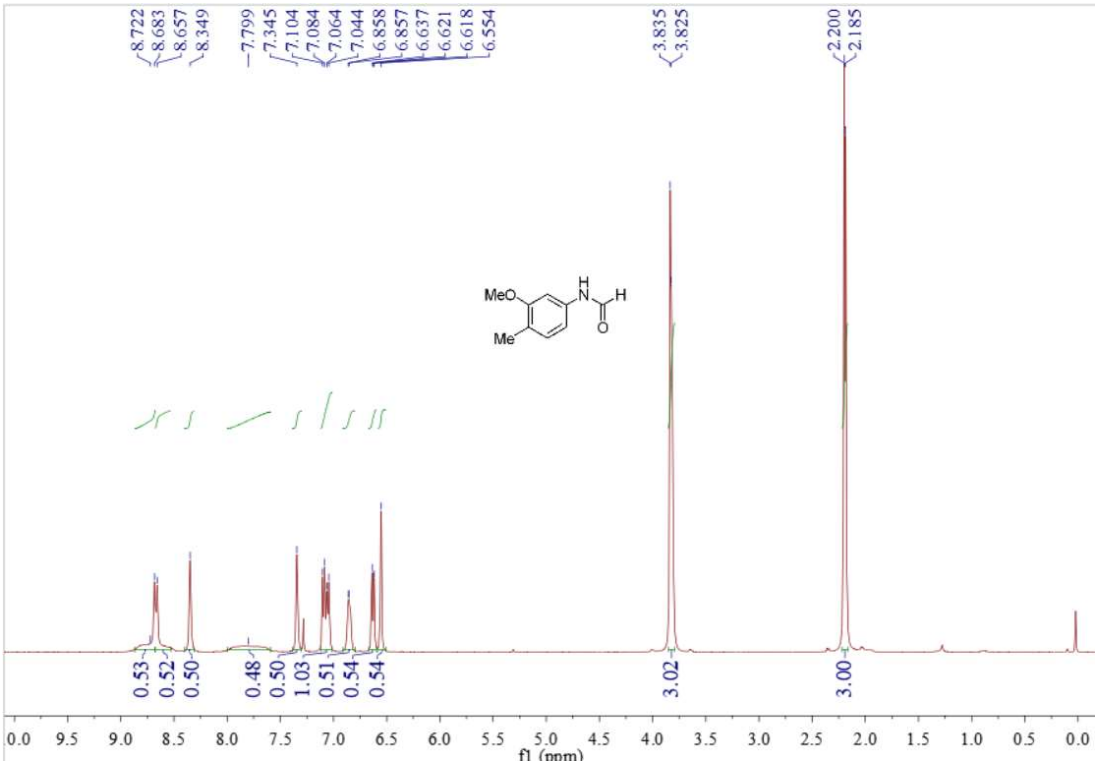


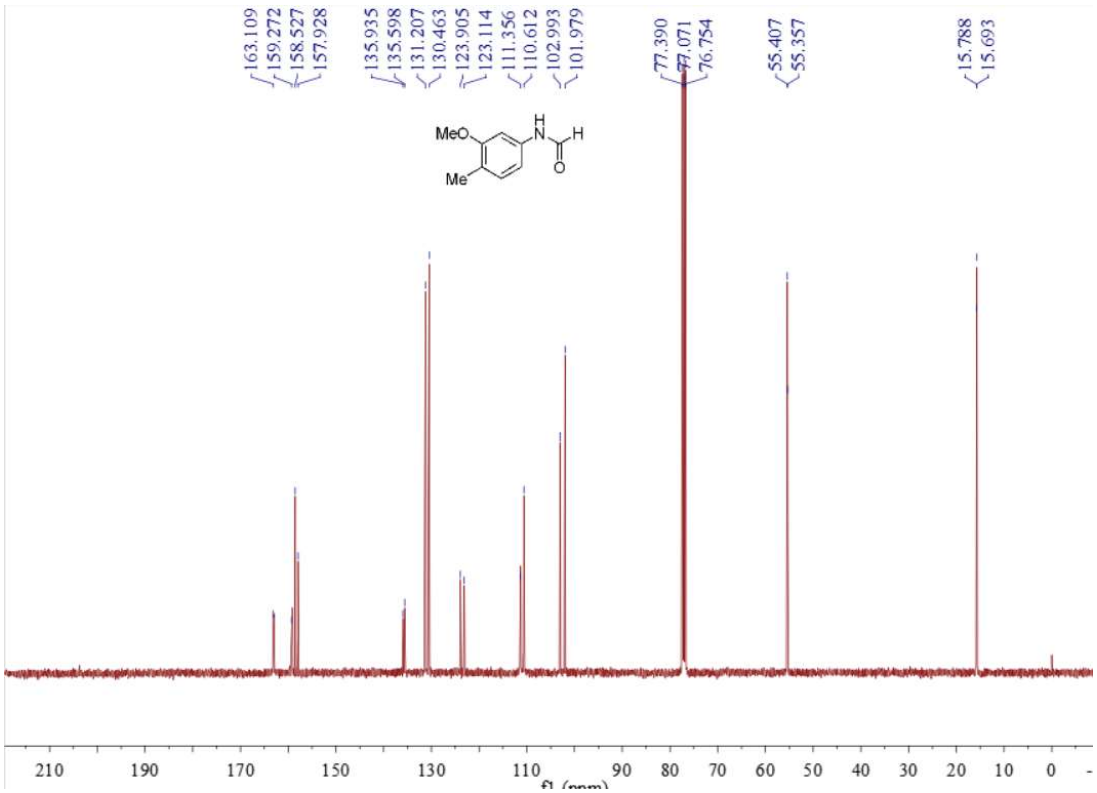
N-(3-cyano-4-methylphenyl)formamide (2m)



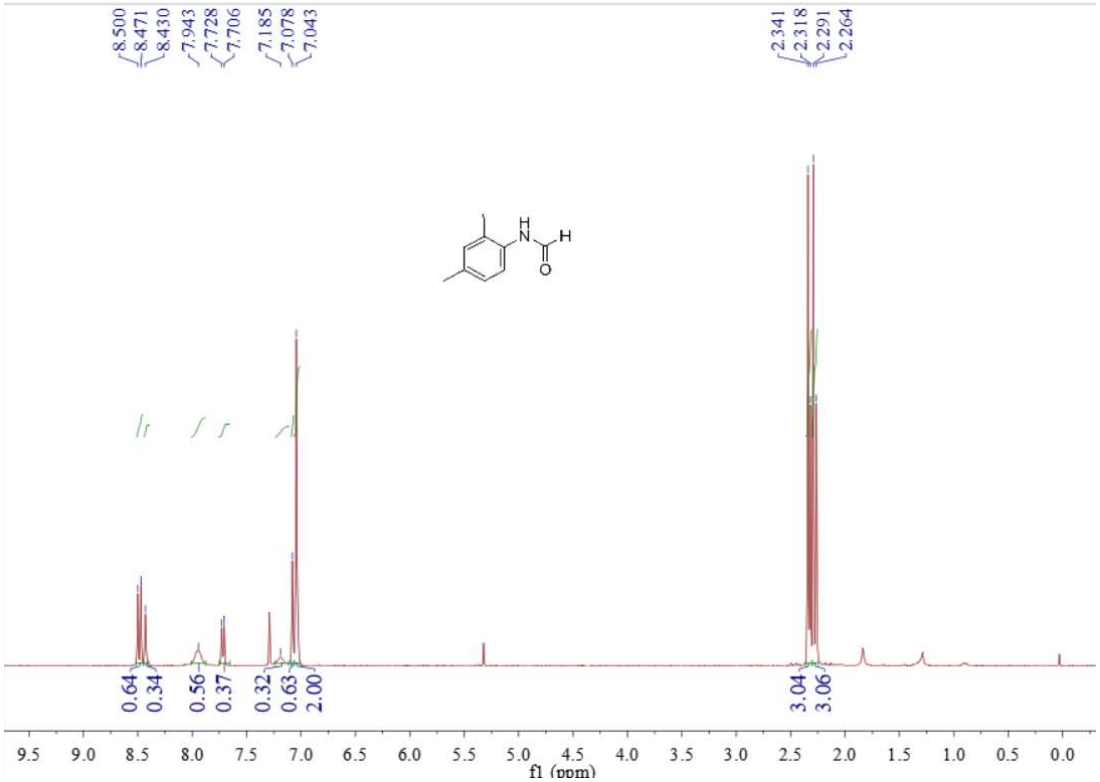


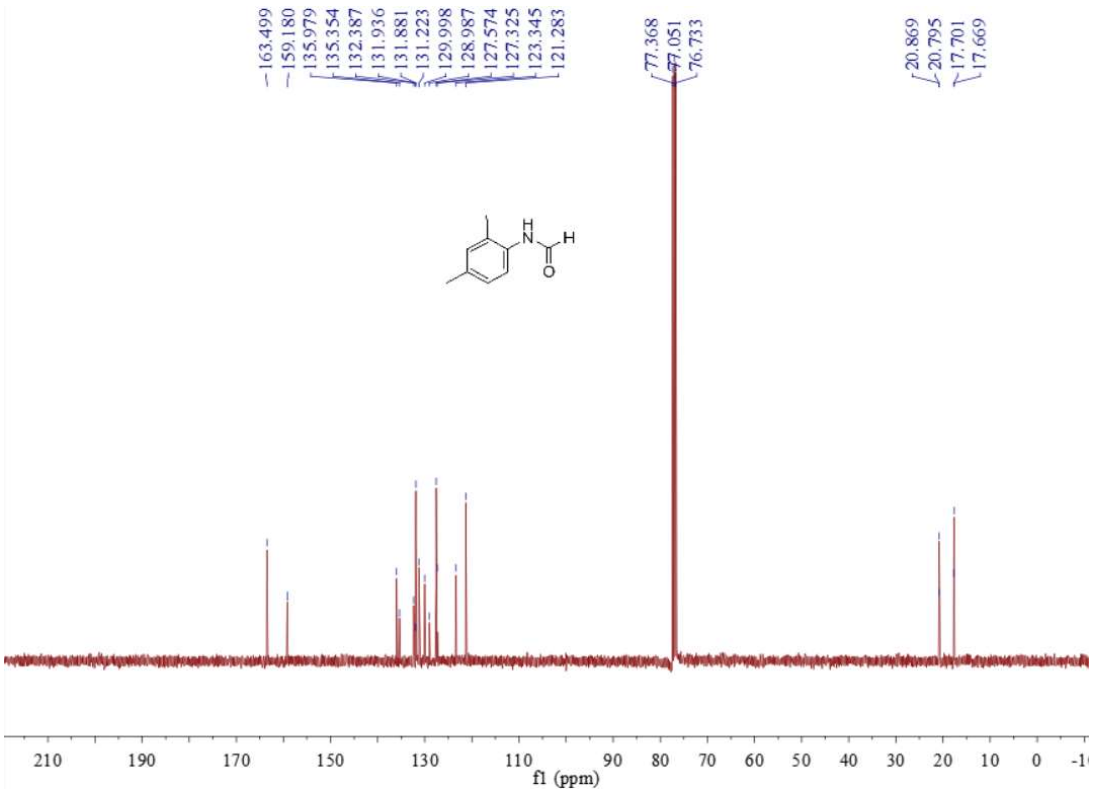
N-(3-methoxy-4-methylphenyl)formamide (2n)



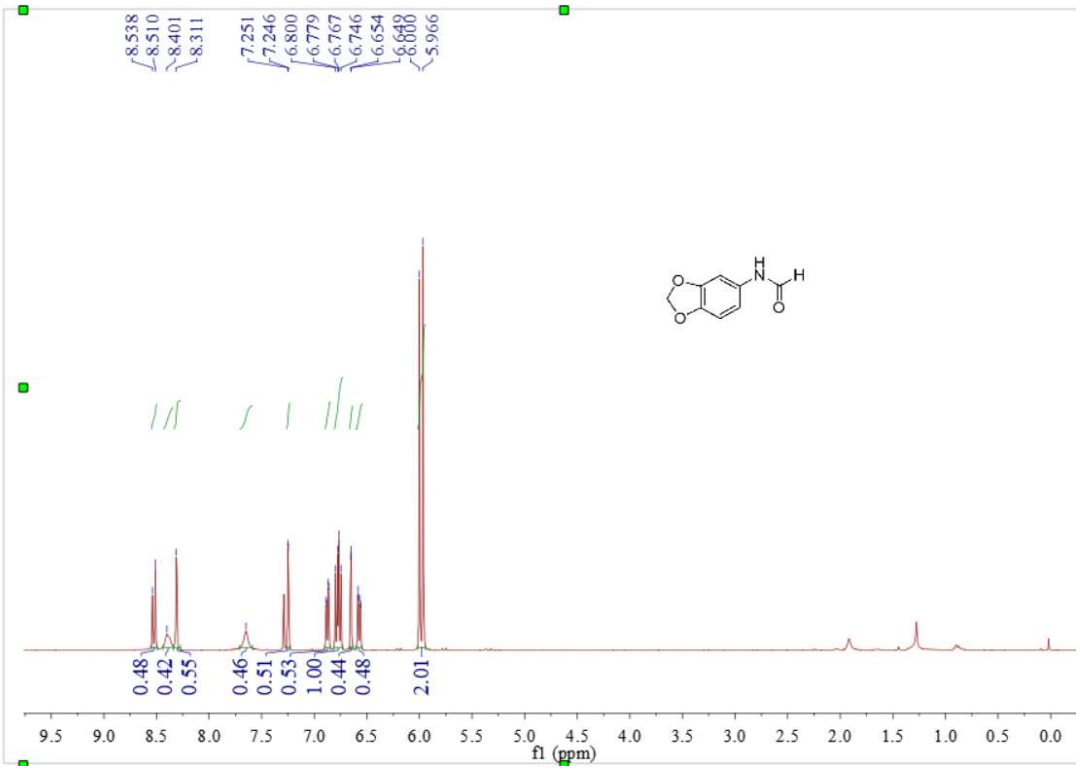


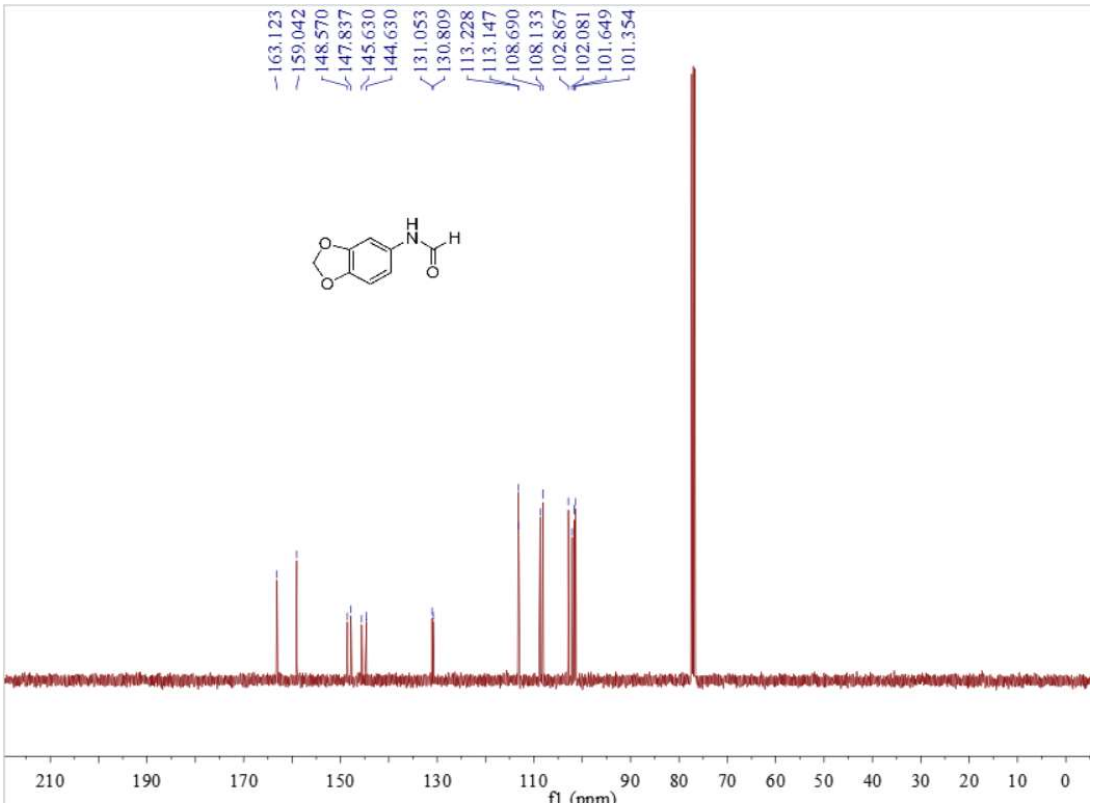
N-(2,4-dimethylphenyl)formamide (2o)



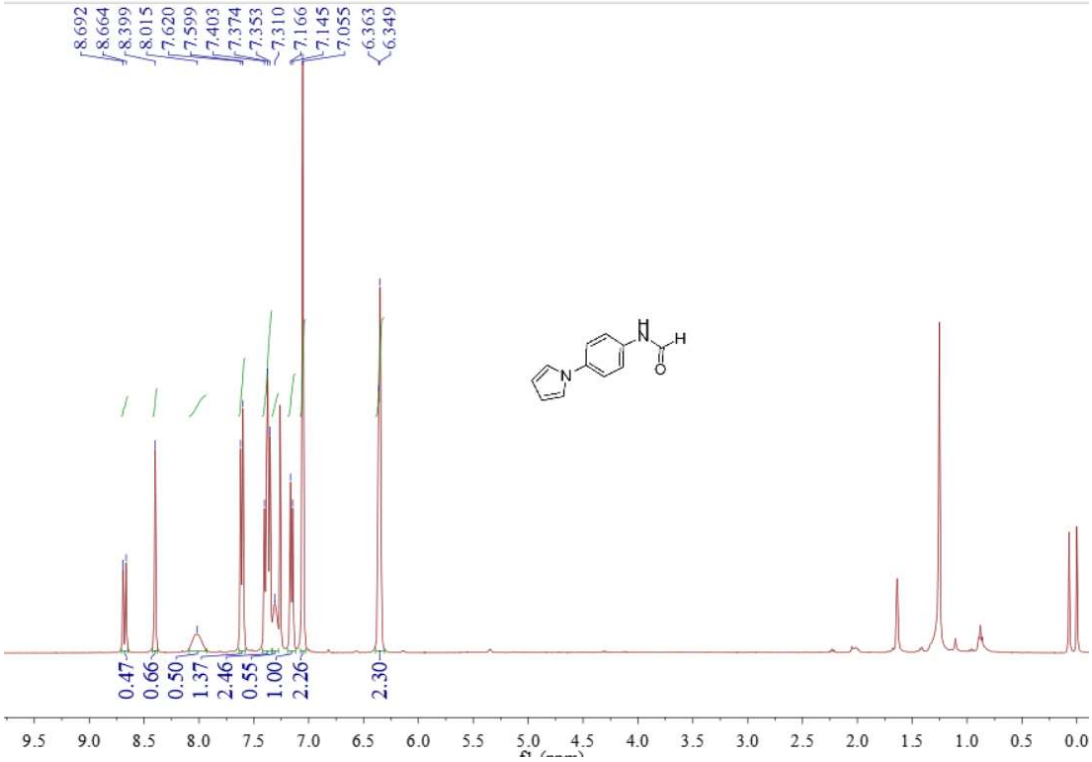


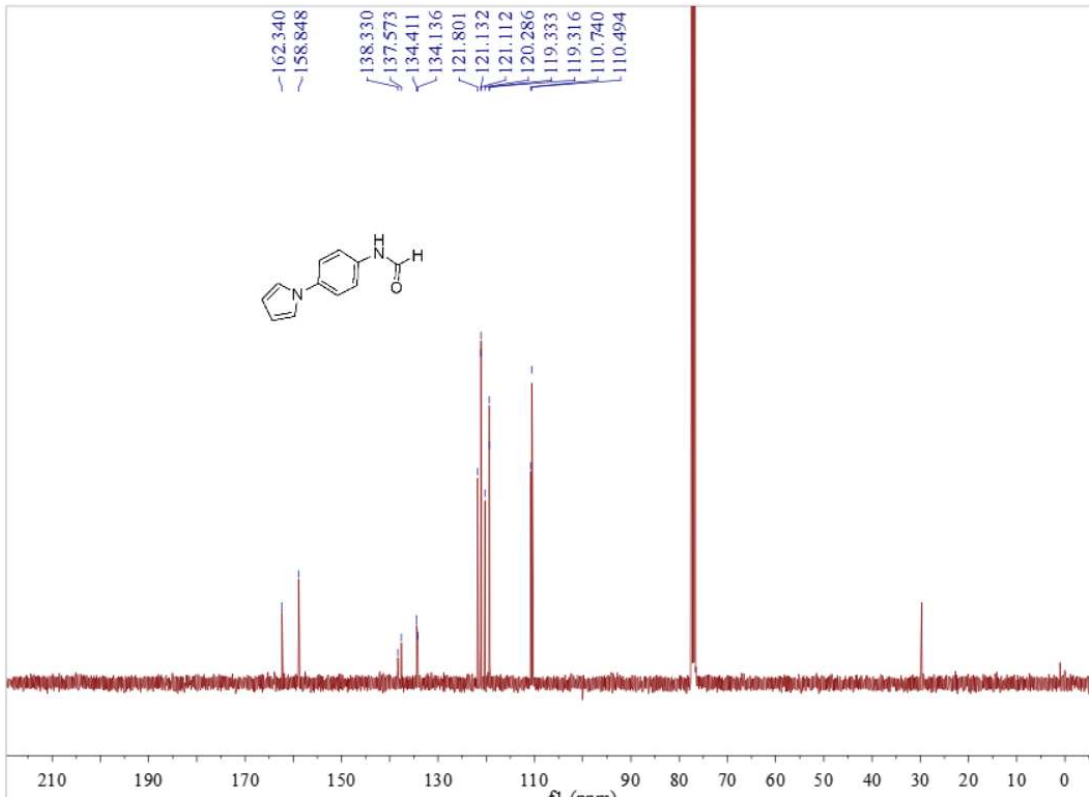
N-(benzo[d][1,3]dioxol-5-yl)formamide(2p)



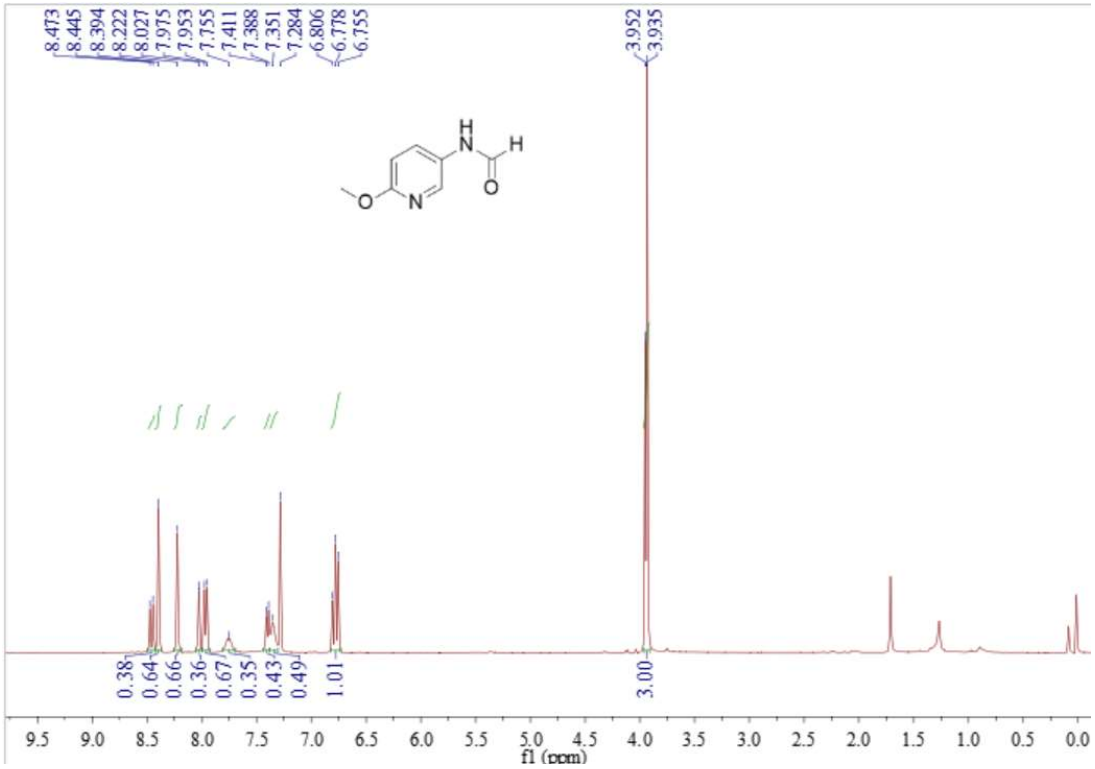


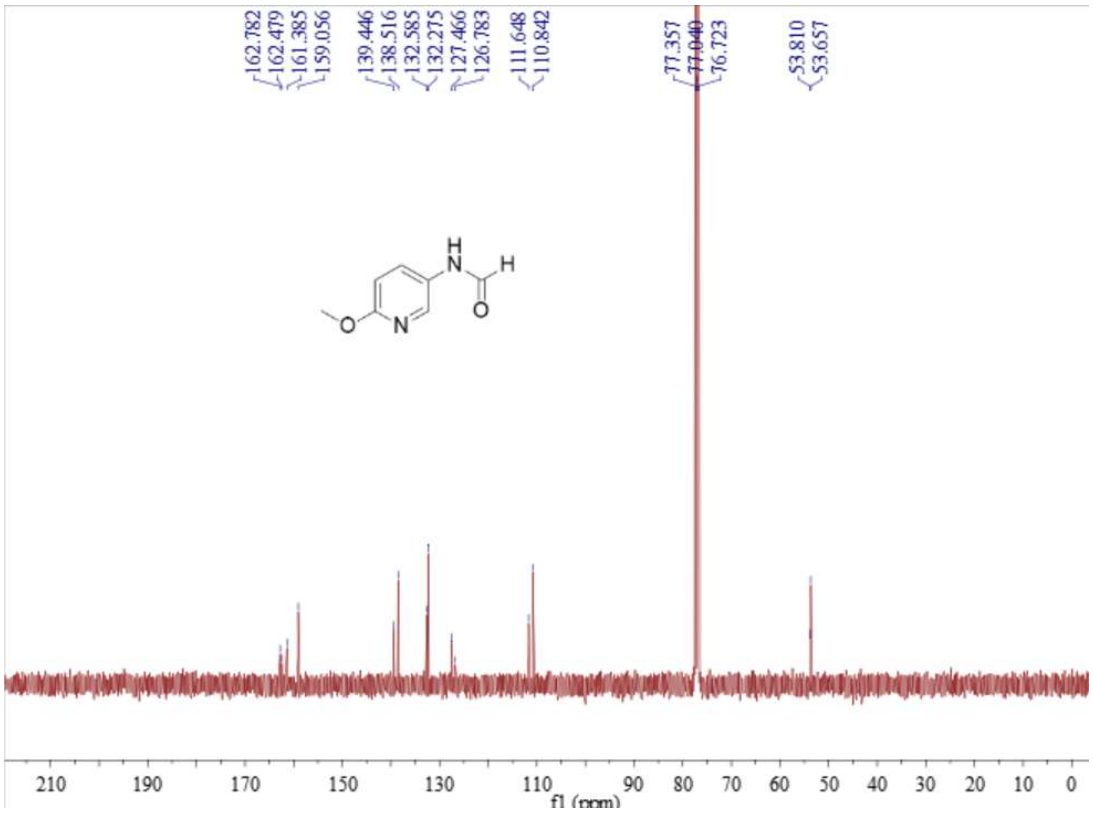
N-(4-(1H-pyrrol-1-yl)phenyl)formamide (2q)



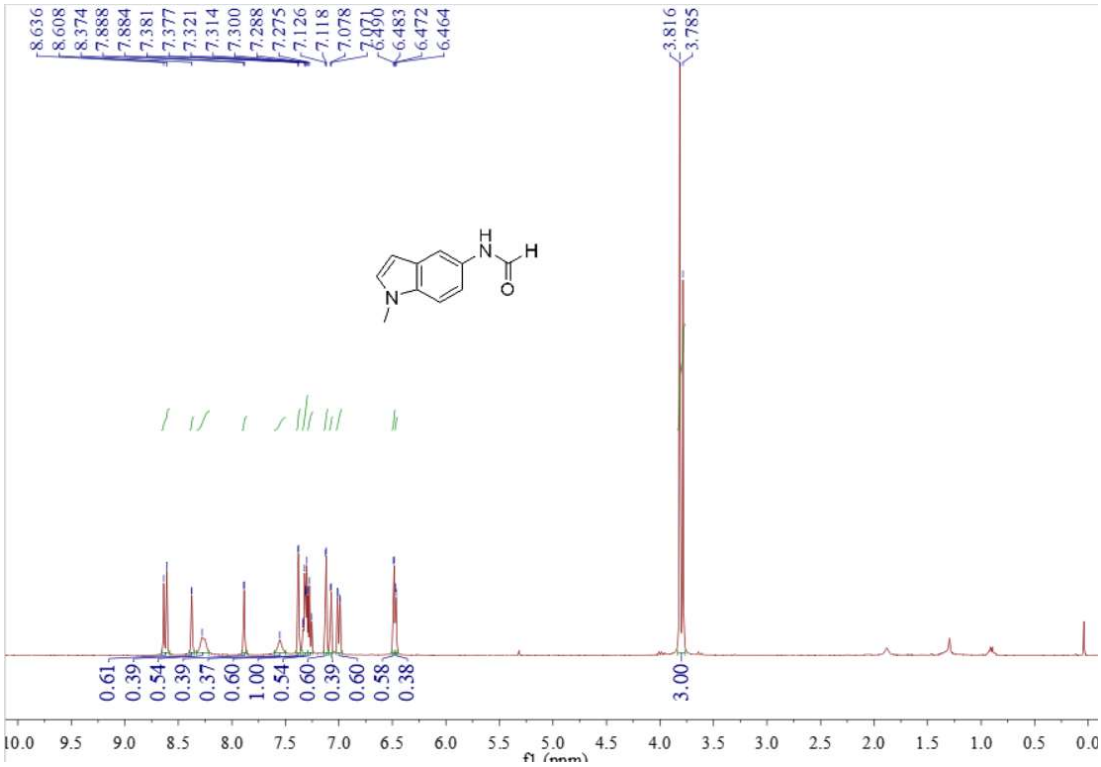


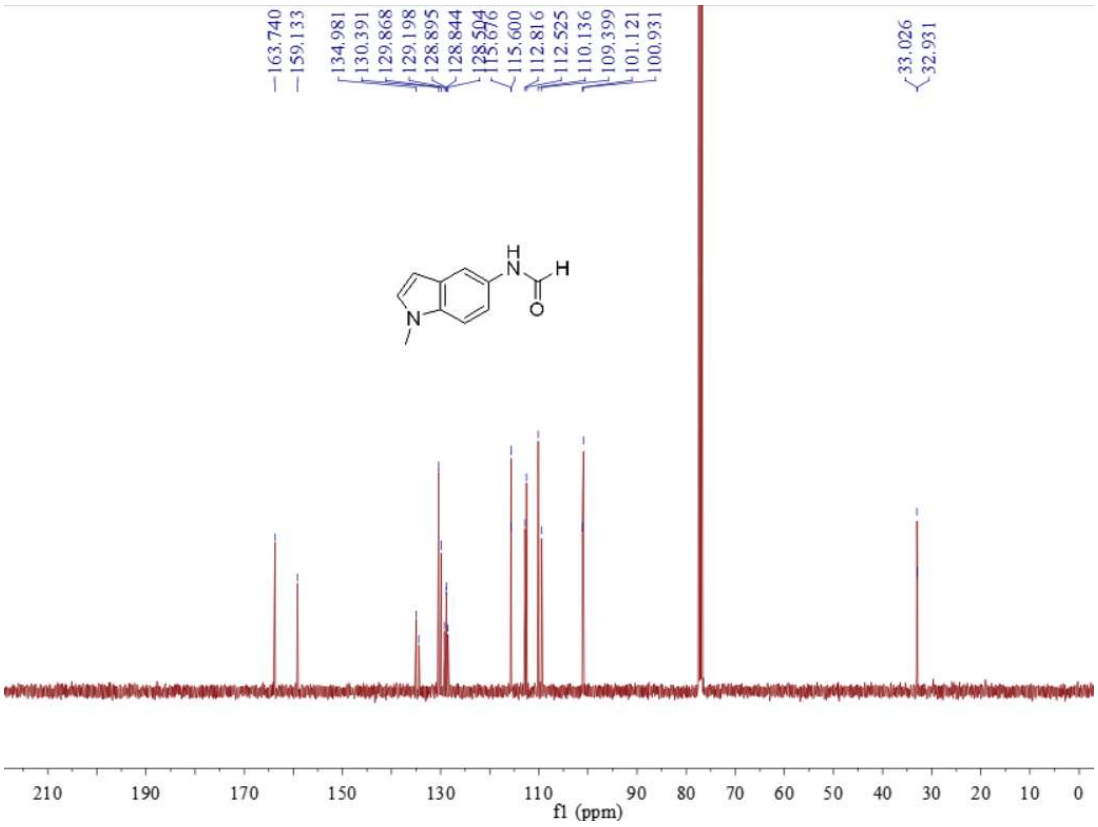
N-(6-methoxypyridin-3-yl)formamide (2r)



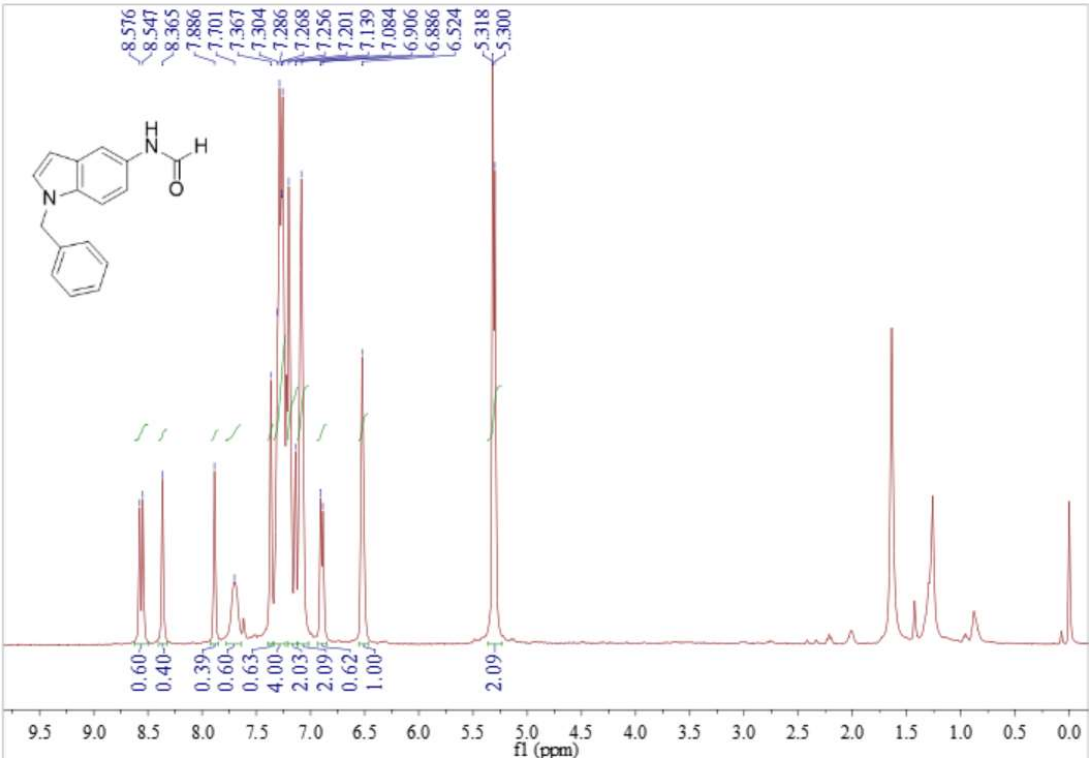


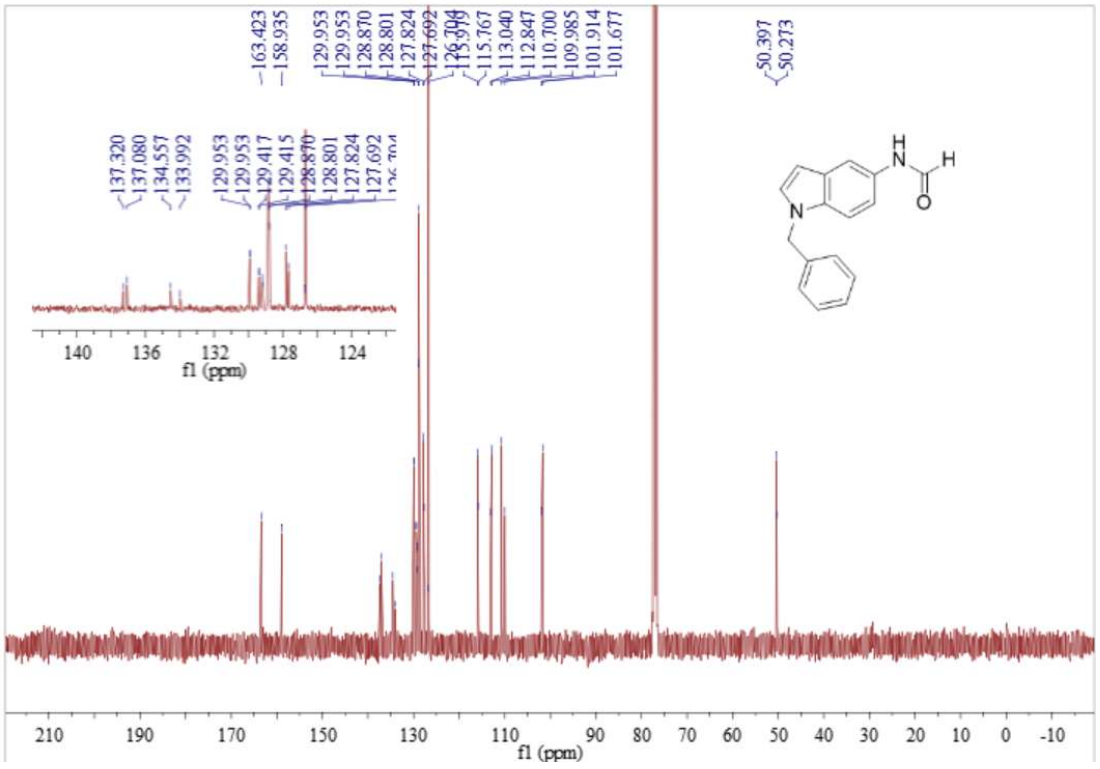
N-(1-methyl-1H-indol-5-yl)formamide (2s)



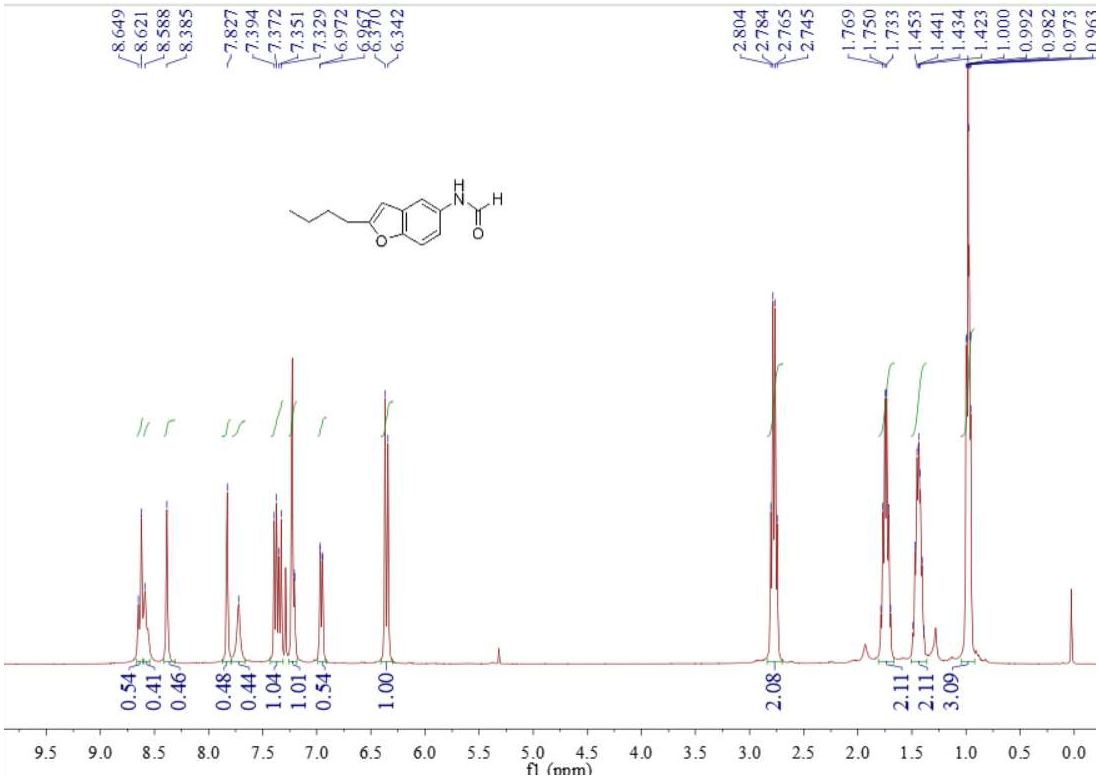


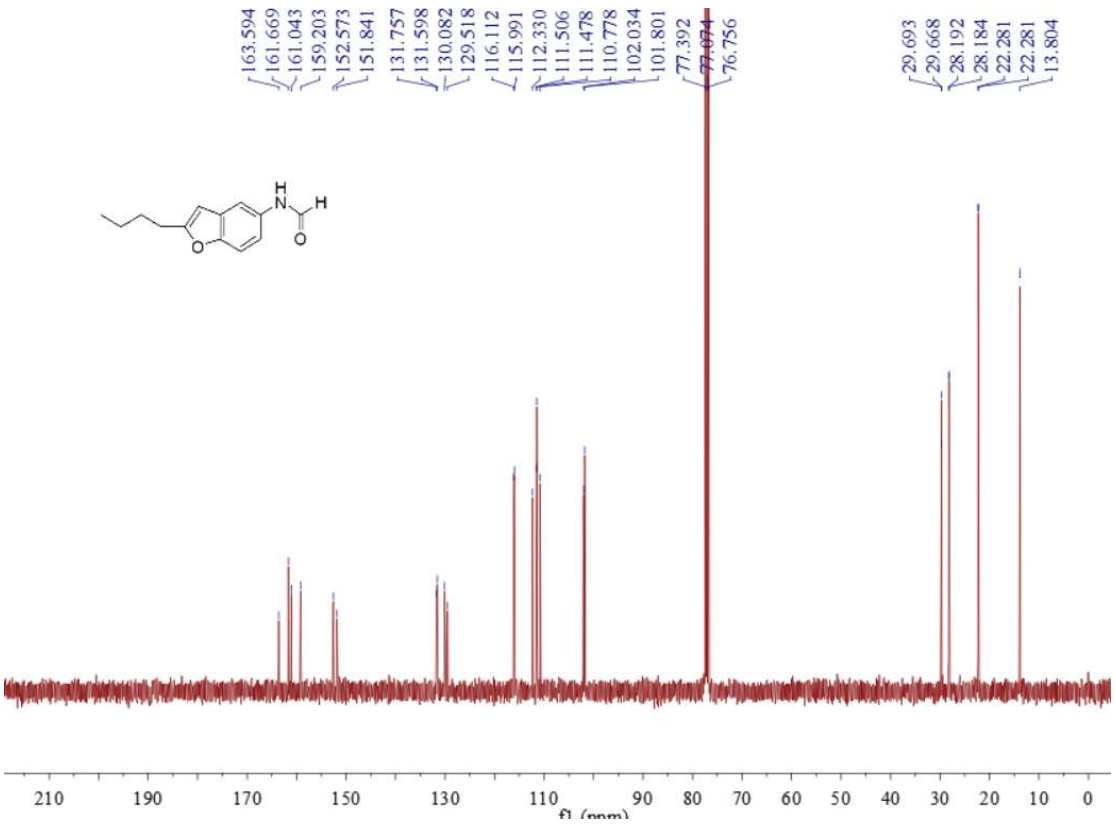
N-(1-benzyl-1H-indol-5-yl)formamide (2t)



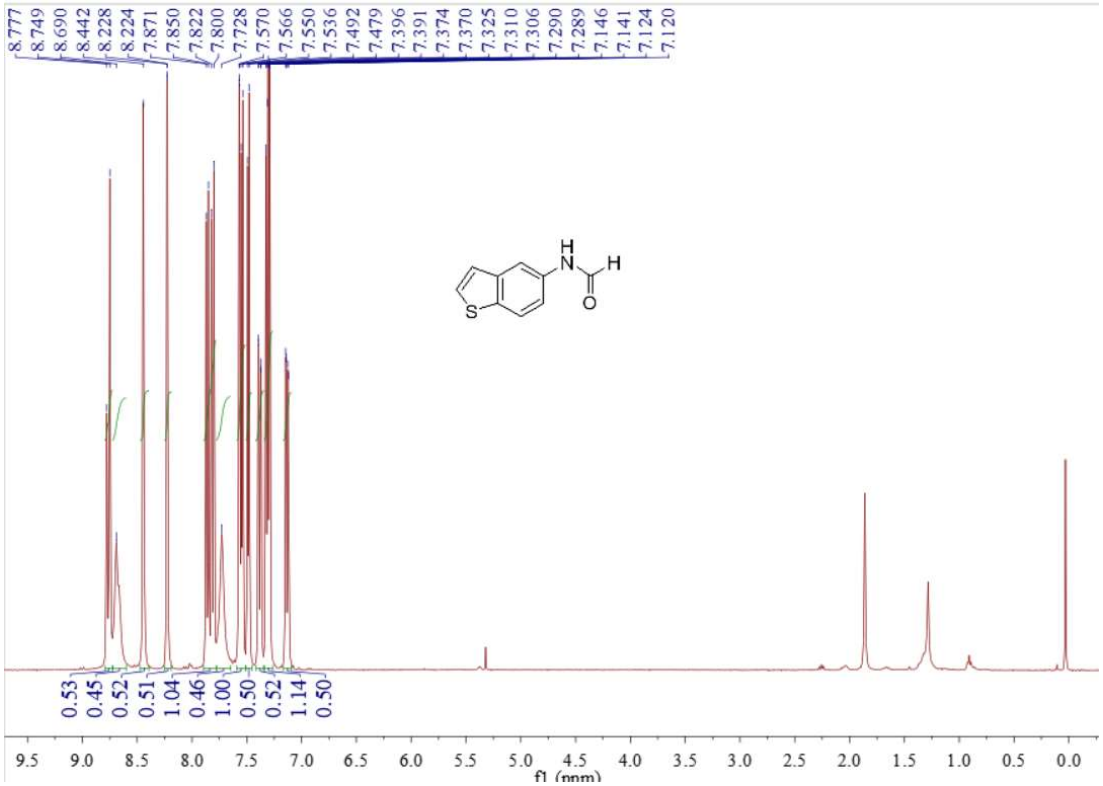


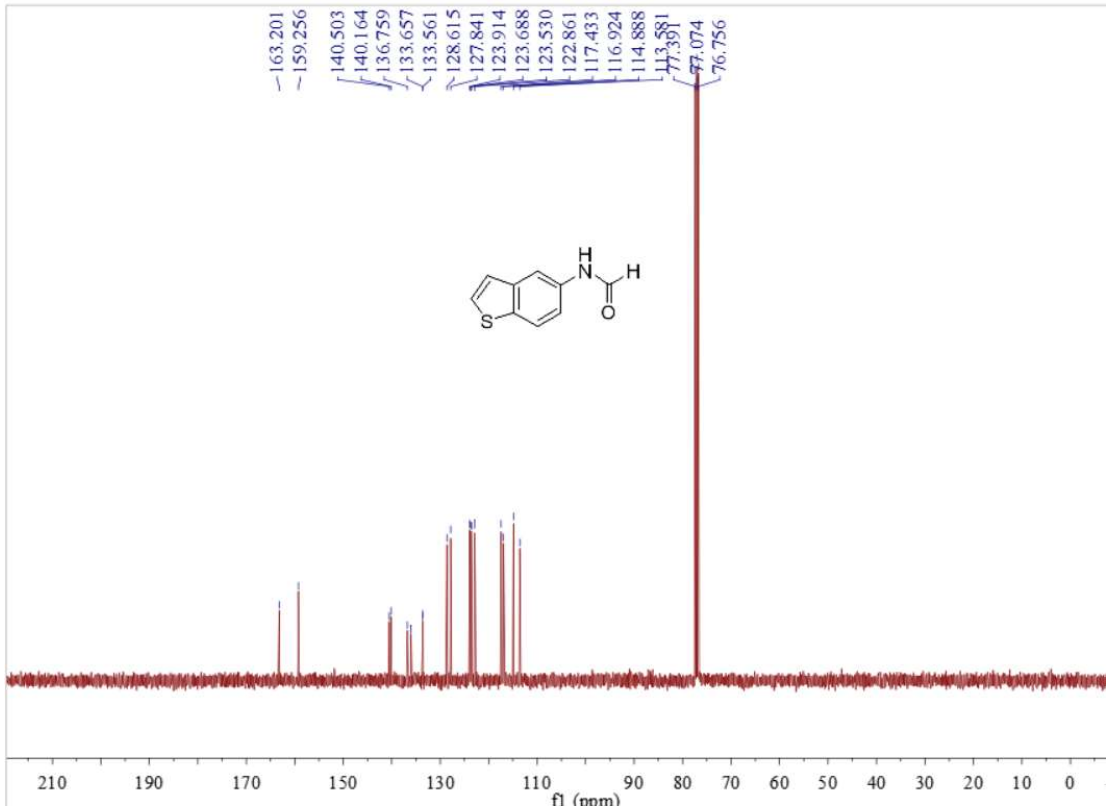
N-(2-butylbenzofuran-5-yl)formamide (2u)





N-(benzo[b]thiophen-5-yl)formamide (2v)





N-(2-Phenylbenzo[d]oxazol-5-yl)benzamide (2w)