Supporting Information

A One-Step Strategy for Synthesizing *N*-Formanilide via Benzamide Activation and Oxalic Acid-Driven Reduction

Heewon Lee,[a] Nithin Pootheri,[a] Chang Woo Kim* [a] and Sunwoo Lee*[a]

[a] Department of Chemistry, Chonnam National University, Gwangju 61186, Republic of Korea

Contents

1. General Information

All reagents were purchased and used without further purification. 1H spectra were recorded in DMSO-d_6 on 500 MHz NMR spectrometers and data's are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, m = multiplet), coupling constants (Hz), and integration. ^{13}C spectra were recorded in DMSO-d_6 on 126 MHz NMR spectrometers and resonances (δ) are given in ppm. High resolution mass spectra were recorded on a time of flight (TOF) mass spectrometer. 500MHz ^1H NMR and ^{13}C NMR were recorded on Agilent-ProPulse NMR spectrometer. The product exists as a mixture of rotamers, and therefore, the proton integration values are presented as decimal numbers to reflect the ratio of these rotamers. The FT-IR spectra were obtained via ATR as a solid on a ZnSe crystal (Pike MIRacle) in the region of 650–4000 cm^{-1} on a Nicolet iS50R (Thermo Fisher Scientific Inc.). *N*-phenyl-*N*-tosylbenzamide derivatives were synthesized by following the reported method.[37]

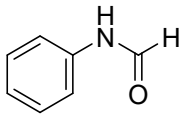
2. General Procedure for the synthesis of *N*-phenyl-*N*-tosylbenzamide derivatives

An oven-dried round-bottomed flask (100 mL) equipped with a stir bar was charged with 4-methyl-*N*-phenylbenzenesulfonamide (1.24 g, 5 mmol, 1.0 equiv), triethylamine (1.4 mL, 10 mmol, 2.0 equiv), 4-dimethylaminopyridine (153 mg, 1.25 mmol, 0.25 equiv) and dichloromethane (50 mL). Acyl chloride (5.5 mmol, 1.1 equiv) was added dropwise to the reaction mixture with vigorous stirring at 0 °C, and the reaction mixture was stirred at 25 °C for 16 h. The reaction mixture was diluted with dichloromethane (20 mL). The organic mixture was washed with aqueous 1 N HCl (20 mL), saturated $NaHCO_3$ (20 mL), and brine (20 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude was purified by column chromatography on silica gel to provide the corresponding *N*-phenyl-*N*-tosylbenzamide derivatives (**1a**-**1w**).

3. General procedure for the synthesis of *N*-Arylformamides

To an oven dried 20 mL seal tube was charged with *N*-phenyl-*N*-tosylbenzamide derivatives (1.0 mmol, 1.0 equiv), sodium azide (130 mg, 2.0 mmol, 2.0 equiv), oxalic acid (540 mg, 6.0 mmol, 6.0 equiv), and NMP (5.0 mL, 0.2 M) was added. The resulting solution was stirred for 16 h at 130 °C. After completion of reaction, the reaction mixture was diluted with water (20 mL) and extracted with ethyl acetate (20 mL × 2). The organic layers were combined, washed with brine solution (20 mL), dried over anhydrous magnesium sulfate and concentrated under reduced pressure to get the crude mass. The crude obtained was purified by silica gel column chromatography with ethyl acetate/hexane (v/v) as eluent to afford the desired products. The rotamer ratio of the product was determined by NMR analysis.

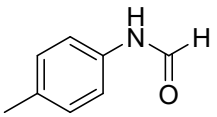
4. Characterization data for the products



***N*-Phenylformamide (2a)**[1]

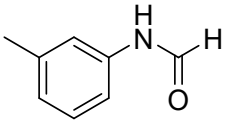
According to the general procedure, the reaction of *N*-[(4-methylphenyl)sulfonyl]-*N*-phenylbenzamide (351 mg, 1.0 mmol) afforded *N*-phenylformamide) (**2a**) (108 mg, 0.89 mmol, 89 %) as a yellow solid after column chromatography (eluent = Hex/EtOAc (60:40, v/v)); mp 66-68 °C; [The ratio of rotamer = 7:3], ^1H NMR (500 MHz, DMSO-d_6) δ 10.16 (s, 0.70H), 10.12 (d, *J* = 11.4 Hz, 0.31H), 8.78 (d, *J* = 11.1 Hz, 0.27H), 8.27 (d, *J* = 2.0 Hz, 0.77H), 7.60-7.57 (m, 1.52H), 7.33-7.29 (m, 2.11H), 7.20-7.18 (m, 0.55H), 7.07 (qt, *J* = 7.4, 1.3 Hz, 1.05H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.5, 159.6, 138.3, 138.2,

129.4, 128.9, 123.61, 123.57, 119.1, 117.5; IR (ATR, cm^{-1}): = 2830, 2724, 1704. MS (EI) m/z = 121.05 $[M]^+$. HRMS (FD-TOF) m/z: [M]+ calcd for C7H7NO 121.0528; Found 121.0522.



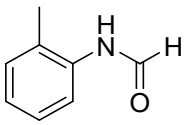
***N*-*p*-Tolylformamide (2b)**[1]

According to the general procedure, the reaction of 4-methyl-*N*-[(4-methylphenyl)sulfonyl]-*N*-phenylbenzamide (365 mg, 1.0 mmol) afforded *N*-*p*-tolylformamide (**2b**) (95 mg, 0.70 mmol, 70%) as a brown oil after column chromatography (eluent = Hex/EtOAc (70:30, v/v)); [The ratio of rotamer = 7:3], ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.07 (s, 0.67H), 10.03 (d, *J* = 10.9 Hz, 0.27H), 8.70 (d, *J* = 11.1 Hz, 0.25H), 8.23 (d, *J* = 2.0 Hz, 0.74H), 7.47 (td, *J* = 8.5, 2.3 Hz, 1.50H), 7.12-7.09 (m, 2.00H), 7.07 (td, *J* = 8.6, 2.3 Hz, 0.51H), 2.24 (s, 3.00H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.5, 159.3, 135.77, 135.76, 132.7, 132.5, 129.8, 129.2, 119.1, 117.7, 20.4, 20.3; IR (ATR, cm^{-1}): = 2839, 2737, 1678. MS (EI) m/z = 135.07 $[M]^+$. HRMS (FD-TOF) m/z: [M]+ calcd for C8H9NO 135.0684; Found 135.0679.



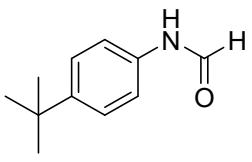
***N*-*m*-Tolylformamide (2c)** [1]

According to the general procedure, the reaction of 3-methyl-*N*-[(4-methylphenyl)sulfonyl]-*N*-phenylbenzamide (365 mg, 1.0 mmol) afforded *N*-*m*-tolylformamide (**2b**) (93 mg, 0.69 mmol, 69%) as a brown oil after column chromatography (eluent = Hex/EtOAc (70:30, v/v)); [The ratio of rotamer = 7:3], ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.08 (s, 0.76H), 10.05 (s, 0.20H), 8.76 (d, *J* = 11.0 Hz, 0.27H), 8.24 (d, *J* = 2.0 Hz, 0.70H), 7.42-7.41 (m, 0.73H), 7.38-7.36 (m, 0.73H), 7.18 (t, *J* = 7.8 Hz, 1.03H), 7.01-7.00 (m, 0.27H), 6.99-6.97 (m, 0.28H), 6.90-6.87 (m, 1.00H), 2.27 (s, 3.00H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.5, 159.5, 138.8, 138.3, 138.2, 138.1, 129.2, 128.7, 124.33, 124.28, 119.6, 118.0, 116.3, 114.6, 21.1, 21.0; IR (ATR, cm^{-1}): = 2825, 2730, 1672. MS (EI) m/z = 135.07 $[M]^+$



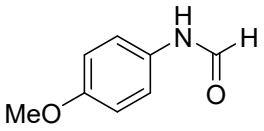
***N*-*o*-Tolylformamide (2d)** [1]

According to the general procedure, the reaction of 2-methyl-*N*-[(4-methylphenyl)sulfonyl]-*N*-phenylbenzamide (365 mg, 1.0 mmol) afforded *N*-*o*-tolylformamide (**2d**) (51 mg, 0.38 mmol, 38%) as a brown oil after column chromatography (eluent = Hex/EtOAc (70:30, v/v)); [The ratio of rotamer = 7:3], ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.71 (d, *J* = 10.9 Hz, 0.28H), 9.54 (s, 0.67H), 8.41 (d, *J* = 10.9 Hz, 0.28H), 8.29 (d, *J* = 2.0 Hz, 0.68H), 7.73 (dd, *J* = 8.0, 1.3 Hz, 0.70H), 7.23-7.14 (m, 2.31H), 7.12-7.09 (m, 0.30H), 7.05 (td, *J* = 7.5, 1.4Hz, 0.73H), 2.23 (d, *J* = 9.8 Hz, 3.00H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.6, 159.8, 136.2, 135.6, 130.8, 130.4, 130.3, 129.3, 126.7, 126.1, 125.3, 124.6, 122.8, 121.9, 17.8, 17.7; IR (ATR, cm^{-1}): = 2813, 2723, 1666. MS (EI) m/z = 135.07 $[M]^+$.



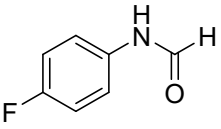
***N*-[4-(1,1-Dimethylethyl)phenyl]formamide (2e)** [2]

According to the general procedure, the reaction of 4-(tert-butyl)-*N*-[(4-methylphenyl)sulfonyl]-*N*-phenylbenzamide (408 mg, 1.0 mmol) afforded *N*-(4-chlorophenyl)formamide (**2e**) (161 mg, 0.91 mmol, 91%) as a yellow oil after column chromatography (eluent = Hex/EtOAc (60:40, v/v)); [The ratio of rotamer = 7:3], ^{1}H NMR (500 MHz, DMSO-d^{6}) δ 10.08 (s, 0.67H), 10.04 (d, *J* =11.1 Hz, 0.28H), 8.71 (d, *J* = 11.1 Hz, 0.26H), 8.23 (d, *J* = 1.9 Hz, 0.73H), 7.49 (td, *J* = 8.7, 2.5 Hz, 1.50H), 7.32 (td, *J* = 8.8, 2.4 Hz, 2.05H), 7.10 (td, *J* = 8.7, 2.5 Hz, 0.54H), 1.244-1.237 (m, 9.00H); ^{13}C NMR (126 MHz, DMSO-d^{6}) δ 162.5, 159.3, 146.1, 146.0, 135.70, 135.68, 126.0, 125.4, 119.0, 117.5, 34.01, 33.96, 31.16, 31.14; IR (ATR, cm^{-1}): = 2820, 2721, 1694. MS (EI) m/z = 177.24 [M]$^{+}$.



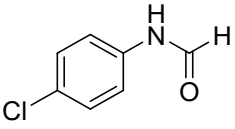
***N*-(4-Methoxyphenyl)formamide (2f)** [1]

According to the general procedure, the reaction of 4-methoxy-*N*-[(4-methylphenyl)sulfonyl]-*N*-phenylbenzamide (381 mg, 1.0 mmol) afforded *N*-(4-methoxyphenyl)formamide (**2f**) (97 mg, 0.64 mmol, 64%) as a yellow solid after column chromatography (eluent = Hex/EtOAc (60:40, v/v)); mp 67-69 °C; [The ratio of rotamer = 8:2], ^{1}H NMR (500 MHz, DMSO-d$_{6}$) δ 10.00 (s, 0.78H), 9.93 (d, *J* = 11.2 Hz, 0.22H), 8.59 (d, *J* = 11.2 Hz, 0.23H), 8.20 (d, *J* = 2.0 Hz, 0.78H), 7.50 (td, *J* = 9.0, 2.9 Hz, 1.67H), 7.11 (td, *J* = 9.0, 2.9 Hz, 0.45H), 6.91-6.87 (m, 2.16H), 3.72 (s, 3.00H); ^{13}C NMR (126 MHz, DMSO-d$_{6}$) δ 162.6, 159.0, 156.0, 155.4, 131.4, 131.3, 120.6, 120.0, 114.6, 114.0, 55.24, 55.15; IR (ATR, cm^{-1}): = 2828, 2732, 1688. MS (EI) m/z = 151.06 [M]$^{+}$.



***N*-(4-Fluorophenyl)formamide (2g)** [1]

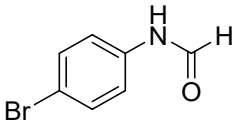
According to the general procedure, the reaction of 4-fluoro-*N*-[(4-methylphenyl)sulfonyl]-*N*-phenylbenzamide (369 mg, 1.0 mmol) afforded *N*-(4-fluorophenyl)formamide) (**2g**) (132 mg, 0.95 mmol, 95%) as a yellow solid after column chromatography (eluent = Hex/EtOAc (60:40, v/v)); mp 66-68 °C; [The ratio of rotamer = 8:2], ^{1}H NMR (500 MHz, DMSO-d$_{6}$) δ 10.22 (s, 0.78H), 10.12 (d, *J* = 10.9 Hz, 0.22H), 8.69 (d, *J* = 11.0 Hz, 0.21H), 8.25 (d, *J* = 1.9 Hz, 0.80H), 7.63-7.58 (m, 1.61H), 7.23-7.19 (m, 0.42H), 7.18-7.12 (m, 2.03H); ^{13}C NMR (126 MHz, DMSO-d$_{6}$) δ 162.7, 159.5, 158.7 (d, $J_{C\text{-}F}$ = 240.1 Hz), 158.1 (d, $J_{C\text{-}F}$ = 240.6 Hz), 134.8 (d, $J_{C\text{-}F}$ = 2.6 Hz), 134.7 (d, $J_{C\text{-}F}$ = 2.5 Hz), 120.9 (d, $J_{C\text{-}F}$ = 7.9 Hz), 119.5 (d, $J_{C\text{-}F}$ = 8.1 Hz), 116.0 (d, $J_{C\text{-}F}$ = 22.6 Hz), 115.4 (d, $J_{C\text{-}F}$ = 22.4 Hz); IR (ATR, cm^{-1}): = 2823, 2717, 1698. MS (EI) m/z = 139.04 [M]$^{+}$.



***N*-(4-Chlorophenyl)formamide (2h)** [1]

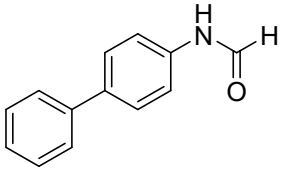
According to the general procedure, the reaction of 4-chloro-*N*-[(4-methylphenyl)sulfonyl]-*N*-phenylbenzamide (386 mg, 1.0 mmol) afforded *N*-(4-chlorophenyl)formamide (**2h**) (115 mg, 0.74 mmol, 74%) as a yellow solid after column chromatography (eluent = Hex/EtOAc (60:40, v/v)); mp 102-104 °C; [The ratio of rotamer = 8:2], ^{1}H NMR (500 MHz, DMSO-d^{6}) δ 10.31 (s, 0.80H), 10.21 (d, *J* = 10.9 Hz, 0.23H), 8.78 (d, *J* = 10.9 Hz, 0.21H), 8.28 (d, *J* = 1.9 Hz, 0.80H), 7.61 (td, *J* = 8.9, 2.6 Hz, 1.63H), 7.38-7.34 (m, 2.01H), 7.22 (td, *J* = 8.9, 2.7 Hz, 0.44H); ^{13}C NMR (126 MHz, DMSO-d^{6}) δ 162.5, 160.0, 137.4, 137.2, 129.2, 129.0, 127.4, 127.2, 120.7, 119.0; IR (ATR, cm^{-1}): = 2824, 2719, 1693. MS (EI)

m/z = 155.01 $[M]^+$.



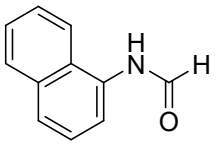
***N*-(4-Bromophenyl)formamide (2i)** [1]

According to the general procedure, the reaction of 4-bromo-*N*-[(4-methylphenyl)sulfonyl]-*N*-phenylbenzamide (430 mg, 1.0 mmol) afforded *N*-(4-bromophenyl)formamide (**2i**) (156 mg, 0.78 mmol, 78%) as a yellow solid after column chromatography (eluent = Hex/EtOAc (60:40, v/v)); mp 117-119 ºC; [The ratio of rotamer = 8:2], ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.31 (s, 0.73H), 10.20 (d, *J* = 11.1 Hz, 0.25H), 8.79 (d, *J* = 10.9 Hz, 0.28H), 8.29 (d, *J* = 1.9 Hz, 0.75H), 7.57-7.54 (m, 1.56H), 7.51-7.48 (m, 1.97H), 7.17-7.16 (m, 0.46H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.5, 160.0, 137.84, 137.56, 132.1, 131.7, 121.1, 119.3, 115.4, 115.2; IR (ATR, cm^{-1}): = 2822, 2718, 1690. MS (EI) m/z = 200.03 $[M]^+$. HRMS (FD-TOF) m/z: [M]+ calcd for C7H6BrNO 198.9633; Found 198.9626.



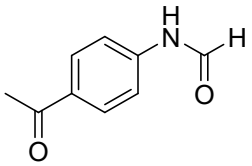
***N*-([1,1'-Biphenyl]-4-yl)formamide (2j)** [1]

According to the general procedure, the reaction of *N*-[(4-methylphenyl)sulfonyl]-*N*-phenyl[1,1′-biphenyl]-4-carboxamide (428 mg, 1.0 mmol) afforded *N*-([1,1'-biphenyl]-4-yl)formamide (**2j**) (150 mg, 0.76 mmol, 76%) as a yellow solid after column chromatography (eluent = Hex/EtOAc (60:40, v/v)); mp 118-120 ºC; [The ratio of rotamer = 7:3], ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.28 (s, 0.72H), 10.22 (d, *J* = 11.0 Hz, 0.26H), 8.85 (d, *J* = 11.0 Hz, 0.24H), 8.31 (d, *J* = 1.9 Hz, 0.75H), 7.69 (td, *J* = 8.7, 2.3 Hz, 1.50H), 7.65-7.61 (m, 4.00H), 7.46-7.42 (m, 2.06H), 7.34-7.28 (m, 1.54H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.5, 159.62, 159.58, 159.3, 139.62, 139.5, 137.79, 137.67, 135.4, 135.3, 129.0, 128.0, 127.1, 126.3, 126.2, 120.0, 117.92, 117.80; IR (ATR, cm^{-1}): = 2830, 2724, 1665. MS (EI) m/z = 197.08 $[M]^+$.



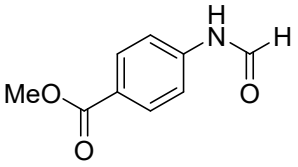
***N*-(Naphthalen-1-yl)formamide (2k)** [1]

According to the general procedure, the reaction of *N*-[(4-methylphenyl)sulfonyl]-N-phenyl[1,1′-biphenyl]-4-carboxamide (401 mg, 1.0 mmol) afforded *N*-(naphthalen-2-yl)formamide (**2j**) (109 mg, 0.64 mmol, 64%) as a yellow solid after column chromatography (eluent = Hex/EtOAc (60:40, v/v)); mp 134-136 ºC; [The ratio of rotamer = 7:3], ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.50 (d, *J* = 10.5 Hz, 0.32H), 10.32 (s, 0.66H), 8.59 (d, *J* = 10.5 Hz, 0.32H), 8.50 (d, *J* = 1.9 Hz, 0.66H), 8.16-8.13 (m, 1.02H), 8.02 (dd, *J* = 7.6, 1.2 Hz, 0.69H), 7.96-7.93 (m, 1.02H), 7.79 (d, *J* = 8.2 Hz, 0.32H), 7.74 (d, *J* = 8.2 Hz, 0.69H), 7.60-7.53 (m, 2.08H), 7.51-7.47 (m, 1.06H), 7.41 (d, *J* = 7.3 Hz, 0.35H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 164.0, 160.3, 133.8, 133.65, 133.63, 132.6, 128.3, 128.1, 127.1, 126.5, 126.2, 126.10, 126.09, 126.0, 125.9, 125.6, 125.5, 125.0, 122.5, 121.8, 119.3, 118.2; IR (ATR, cm^{-1}): = 2822, 2718, 1687. MS (EI) m/z = 171.07 $[M]^+$.



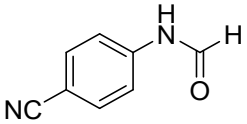
***N*-(4-Acetylphenyl)formamide (2l)** [1]

According to the general procedure, the reaction of 4-acetyl-*N*-[(4-methylphenyl)sulfonyl]-*N*-phenylbenzamide (393 mg, 1.0 mmol) afforded *N*-(4-acetylphenyl)formamide (**2l**) (57 mg, 0.35 mmol, 35%) as a yellow solid after column chromatography (eluent = Hex/EtOAc (60:40, v/v)); mp 104-106 ºC; [The ratio of rotamer = 7:3], ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.53 (s, 0.70H), 10.45 (d, *J* = 10.7 Hz, 0.26H), 8.98 (d, *J* = 10.7 Hz, 0.26H), 8.35 (d, 1.8 Hz, 0.76H), 7.95-7.90 (m, 2.10H), 7.71 (td, *J* = 8.8, 2.2 Hz, 1.56H), 7.31 (d, *J* = 8.6 Hz, 0.54H), 2.523 (s, 1.97H), 2.520 (s, 0.93H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 196.5, 196.4, 162.6, 160.1, 142.9, 142.4, 132.1, 132.0, 130.0, 129.6, 118.5, 116.3, 26.4; IR (ATR, cm^{-1}): = 2823, 2718, 1735, 1677. MS (EI) m/z = 163.06 [M]$^{+}$.



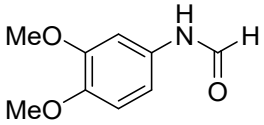
Methyl 4-formamidobenzoate (2m) [1]

According to the general procedure, the reaction of metyl 4-[[[(4-methylphenyl)sulfonyl]phenylamino]carbonyl]benzoate (98 mg, 0.55 mmol, 55%) afforded methyl 4-formamidobenzoate (**2m**) (98 mg, 0.55 mmol, 55%) as a yellow solid after column chromatography (eluent = Hex/EtOAc (60:40, v/v)); mp 123-125 ºC; [The ratio of rotamer = 7:3], ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.54 (s, 0.77H), 10.46 (d, 0.25H), 8.97 (d, *J* = 10.7 Hz, 0.24H), 8.35 (d, *J* = 1.8 Hz, 0.78H), 7.93 (td, *J* = 4.1, 2.1 Hz, 1.53H), 7.91-7.88 (m, 0.56H), 7.72 (td, *J* = 8.8, 2.2 Hz, 1.56H), 7.32 (d, *J* = 8.7 Hz, 0.57H), 3.82 (s, 3.00H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.7, 162.6, 160.2, 143.0, 142.5, 130.8, 130.4, 128.8, 124.4, 124.3, 118.6, 116.4, 51.9, 51.8; IR (ATR, cm^{-1}): = 2830, 2720, 1720, 1688. MS (EI) m/z = 179.06 [M]$^{+}$. HRMS (FD-TOF) m/z: [M]+ calcd for C9H9NO3 179.0582; Found 179.0576.



***N*-(4-Cyanophenyl)formamide (2n)** [1]

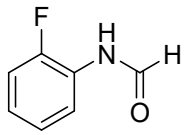
According to the general procedure, the reaction of 4-cyano-*N*-[(4-methylphenyl)sulfonyl]-*N*-phenylbenzamide (376 mg, 1.0 mmol) afforded N-(4-cyanophenyl)formamide (**2n**) (85 mg, 0.58 mmol, 58%) as a white solid after column chromatography (eluent = Hex/EtOAc (70:30, v/v)); mp 189-191 ºC; [The ratio of rotamer = 7:3], ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.63 (s, 0.73H), 10.52 (d, *J* = 10.7 Hz, 0.24H), 8.99 (d, *J* = 10.6 Hz, 0.25H), 8.37 (d, *J* = 1.8 Hz, 0.76H), 7.80-7.75 (m, 3.59H), 7.37 (d, *J* = 8.3 Hz, 0.46H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.7, 160.4, 142.9, 142.3, 133.8, 133.4, 119.3, 119.0, 117.1, 105.4, 105.2; IR (ATR, cm^{-1}): = 2825, 2719, 2225, 1708. MS (EI) m/z = 146.05 [M]$^{+}$.



***N*-(3,4-Dimethoxyphenyl)formamide (2o)** [1]

According to the general procedure, the reaction of 3,4-dimethoxy-*N*-[(4-methylphenyl)sulfonyl]-*N*-phenylbenzamide (411 mg, 1.0 mmol) afforded *N*-(3,4-Dimethoxyphenyl)formamide (**2n**) (114 mg, 0.63mmol, 63%) as a white solid after column chromatography (eluent = Hex/EtOAc (70:30, v/v)); mp 74-76 °C; [The ratio of rotamer = 7:3], ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.00 (s, 0.72H), 9.93-9.90 (m, 0.27H), 8.65 (d, *J* = 11.1 Hz, 0.24H), 8.20 (d, *J* = 2.0 Hz, 0.73H), 7.29-7.28 (m, 0.74H), 7.08 (dd, *J* = 8.7, 2.4 Hz, 0.77H), 6.88 (dd, *J* = 8.6, 1.5 Hz, 0.98H), 6.83 (d, *J* = 2.5 Hz, 0.25H), 6.67 (dd, *J* = 8.5, 2.5Hz, 0.25H), 3.74-3.71 (m, 6.18H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.7, 159.1, 149.4, 148.6, 145.6, 145.1, 131.9, 131.7, 112.7, 112.1, 111.1, 110.0, 104.3, 103.4, 55.8, 55.7, 55.6, 55.4; IR (ATR, cm^{-1}): = 2823, 2719, 1692. MS (EI) m/z = 181.07 $[M]^+$. HRMS (FD-TOF) m/z: [M]+ calcd for C9H11NO3 181.0739; Found 181.0735.

***N*-(2-Fluorophenyl)formamide (2p)** [3]



According to the general procedure, the reaction of 2-fluoro-*N*-[(4-methylphenyl)sulfonyl]-*N*-phenylbenzamide (369 mg, 1.0 mmol) afforded *N*-(2-Fluorophenyl)formamide (**2p**) (47 mg, 0.34 mmol, 34%) as a brown oil after column chromatography (eluent = Hex/EtOAc (70:30, v/v)); [The ratio of rotamer = 7:3], ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.11 (s, 1.00H), 8.56 (d, *J* = 1.9 Hz, 0.18H), 8.31 (s, 0.77H), 8.09 (td, *J* = 8.0, 2.2 Hz, 0.82H), 7.39-7.24 (m, 1.01H), 7.19-7.11(m, 2.04H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.41, 163.39, 160.03, 153.6 (d, $J_{C\text{-}F}$ = 245.7 Hz), 152.6 (d, $J_{C\text{-}F}$ = 245.7 Hz), 125.8 (d, $J_{C\text{-}F}$ = 7.6 Hz), 125.5 (d, $J_{C\text{-}F}$ = 11.3 Hz), 125.0 (d, $J_{C\text{-}F}$ = 7.6 Hz), 124.5 (d, $J_{C\text{-}F}$ = 2.5 Hz), 122.7 (d, $J_{C\text{-}F}$ = 1.3 Hz), 122.4 (d, $J_{C\text{-}F}$ = 1.3 Hz), 116.3 (d, $J_{C\text{-}F}$ = 20.2 Hz), 115.4 (d, $J_{C\text{-}F}$ = 18.9 Hz); IR (ATR, cm^{-1}): = 2815, 2710, 1692. MS (EI) m/z = 139.13 $[M]^+$.

5. References

1. N. Pootheri, S. Lee, Palladium-Catalyzed One-Pot Synthesis of *N*-Formylaniline Derivatives Using Oxalic Acid as a Dual Carbon Monoxide and Hydrogen Donor, *Org. Lett.,* **2024**, *26*, 9407−9412.

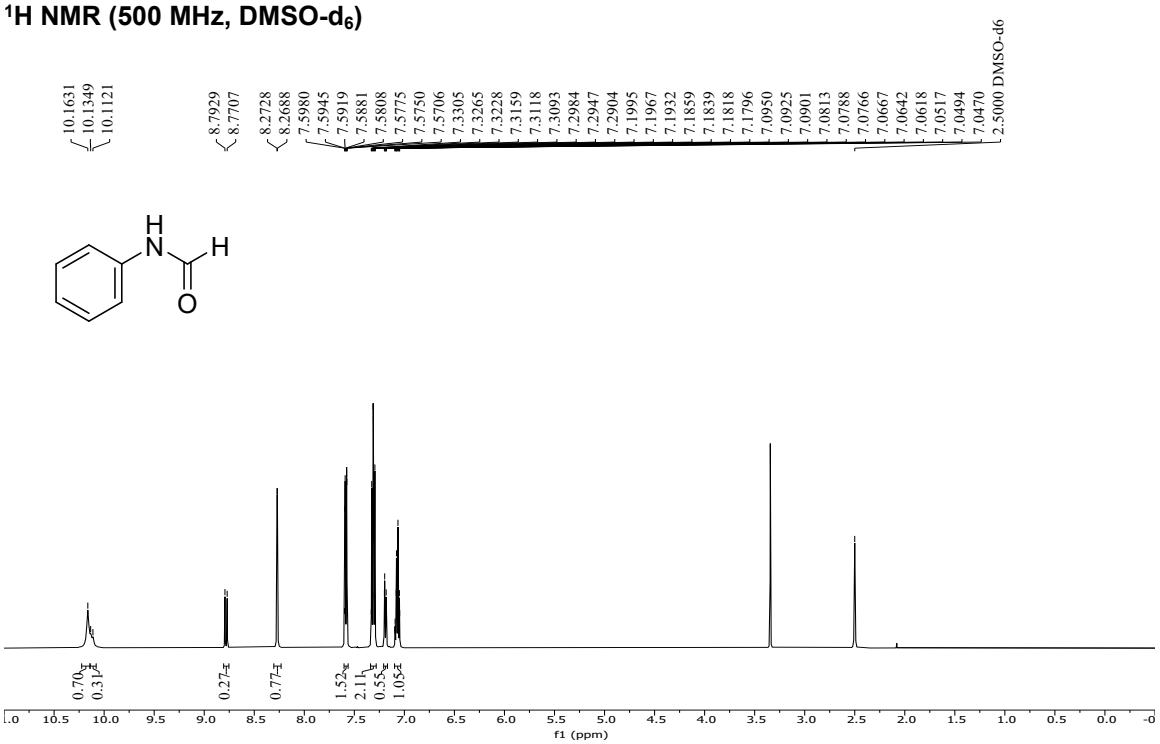
2. Y.-X. Wang, F.-P. Zhang, Y.-X. Luan, M. Ye, Ligand-Enabled Ni–Al Bimetallic Catalysis for Nonchelated Dual C–H Annulation of Arylformamides and Alkynes, *Org. Lett.*, **2020**, *22*, 2230-2234.

3. R. B. Sonawane, N. K. Rasal, S. V. Jagtap, Nickel-(II)-Catalyzed *N*-Formylation and *N*-Acylation of Amines, *Org. Lett.*, **2017**, *19*, 2078-2081.

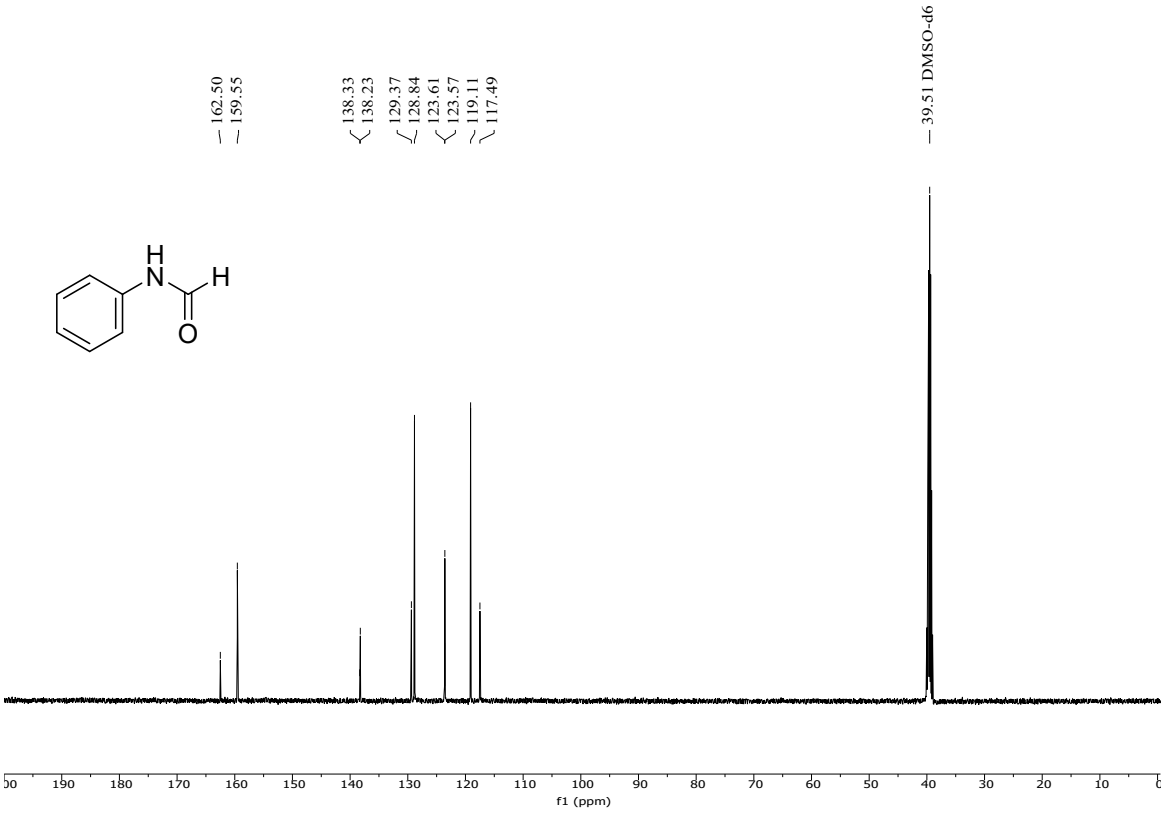
6. Copy of NMR Spectra

N-Phenylformamide (2a)

^{1}H NMR (500 MHz, DMSO-d_6)

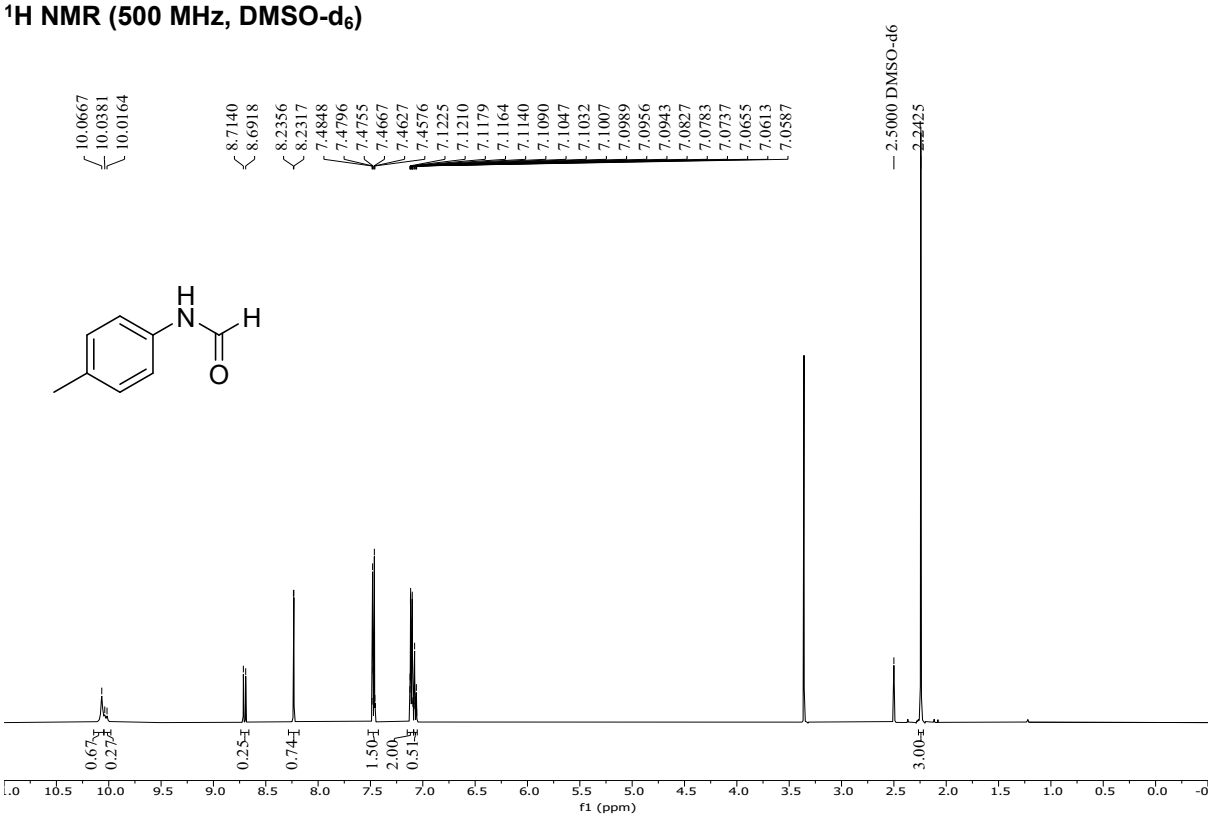


^{13}C NMR (126 MHz, DMSO-d_6)

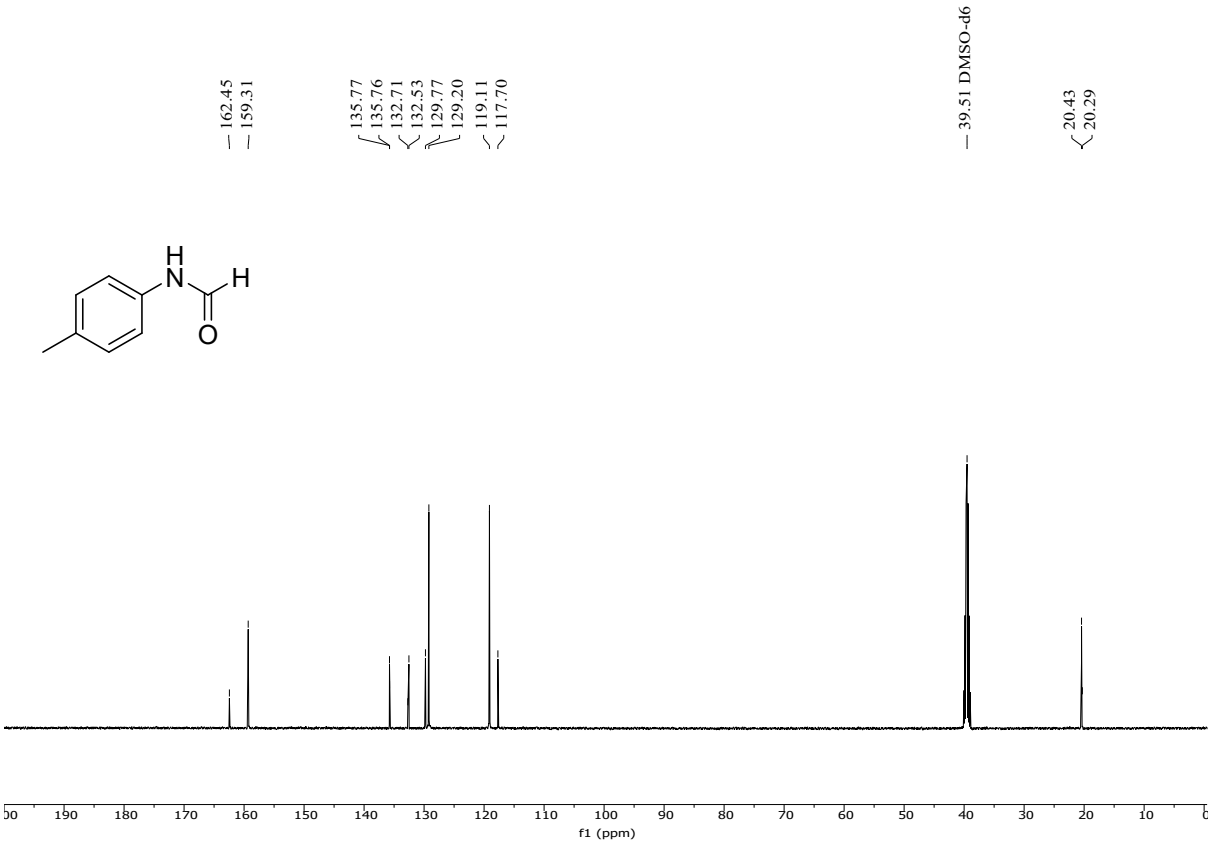


***N-p*-Tolylformamide (2b)**

^{1}H NMR (500 MHz, DMSO-d_6)

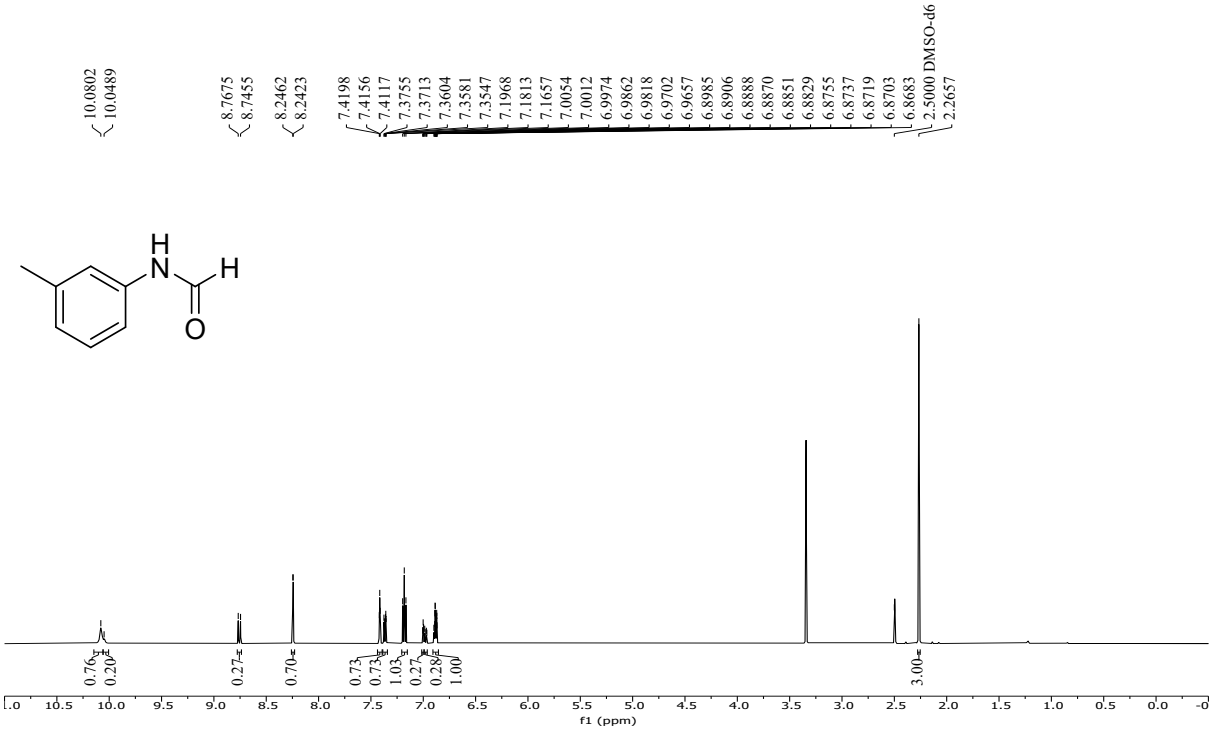


^{13}C NMR (126 MHz, DMSO-d_6)

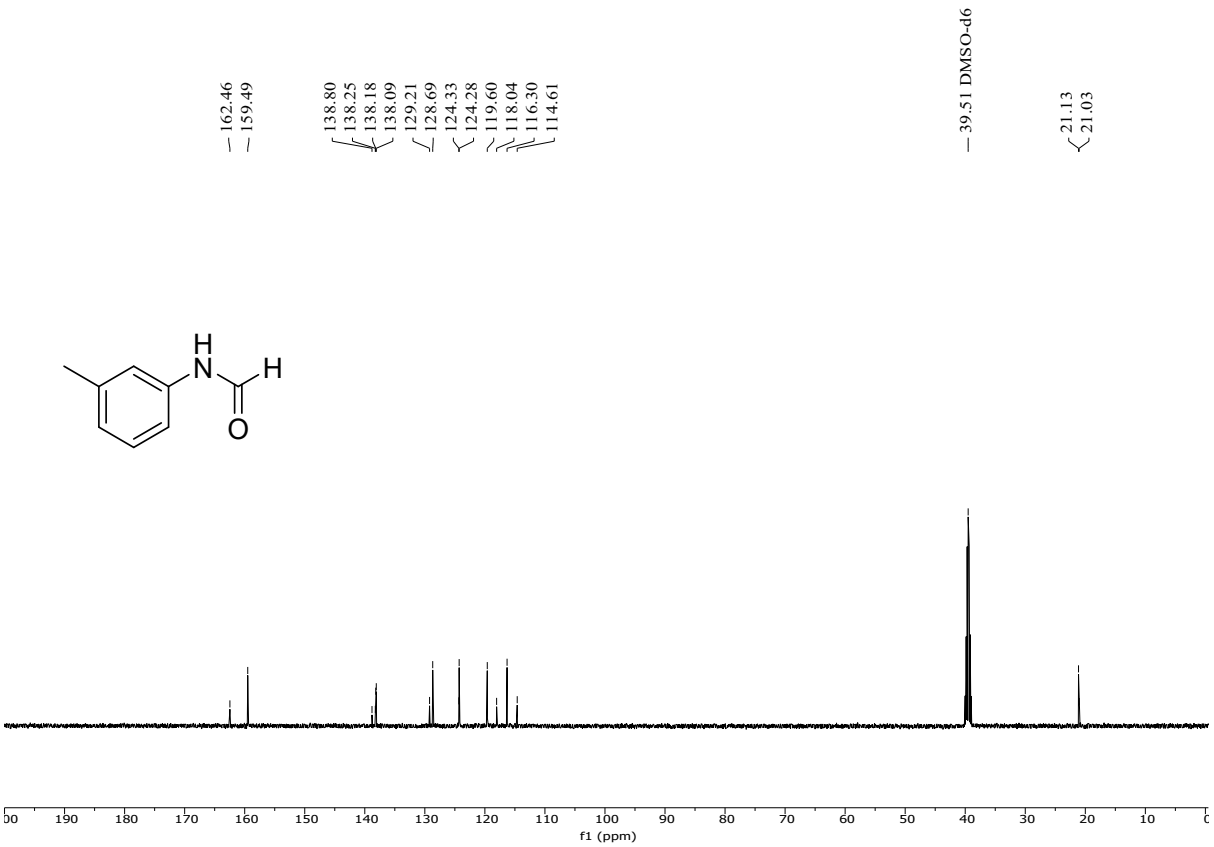


***N*-*m*-Tolylformamide (2c)**

^{1}H NMR (500 MHz, DMSO-d_6)

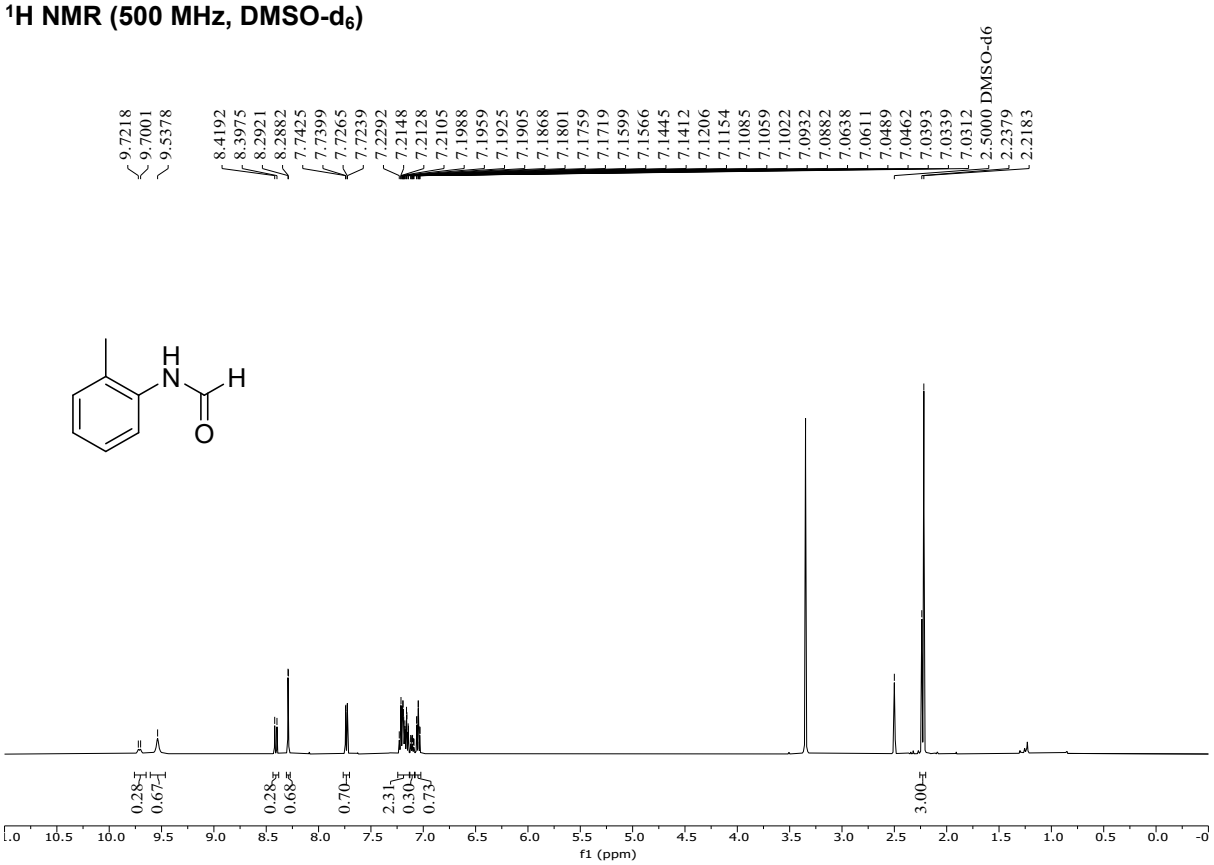


^{13}C NMR (126 MHz, DMSO-d_6)

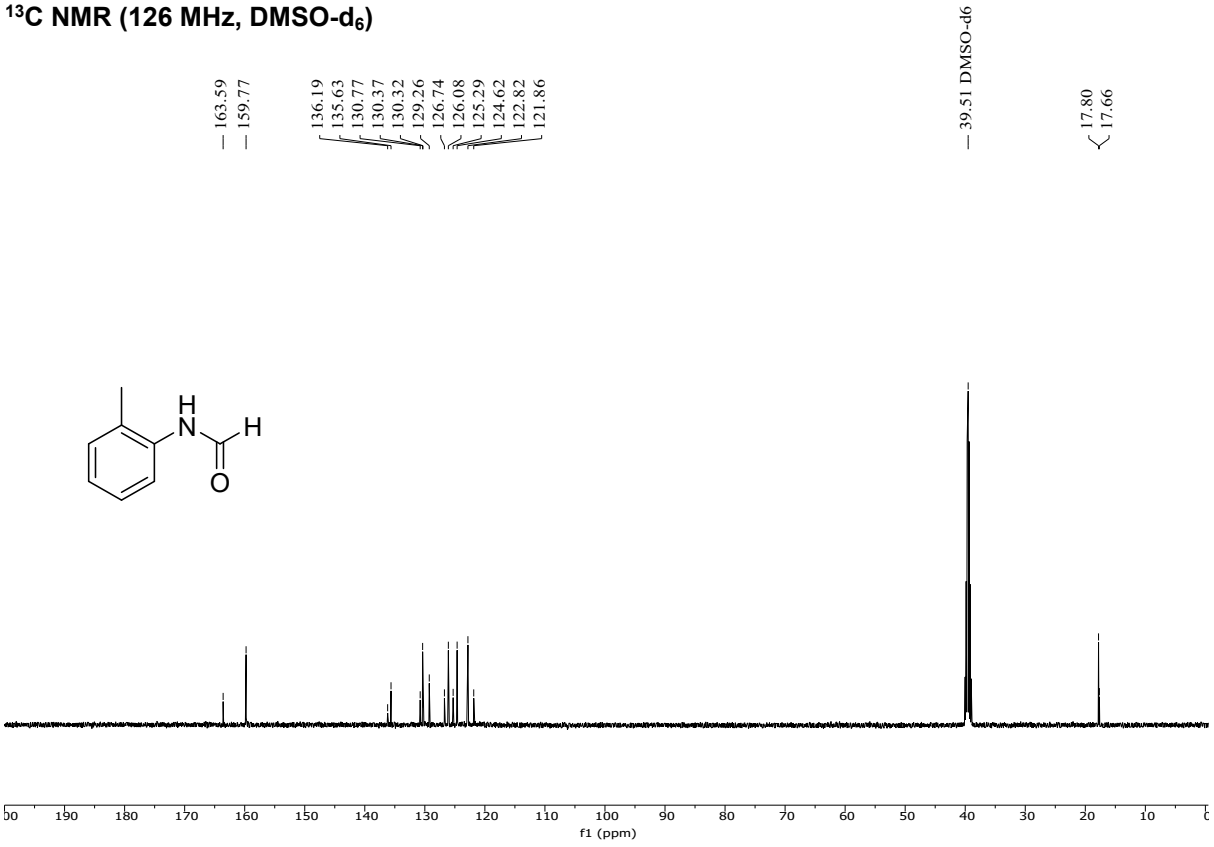


***N*-*o*-Tolylformamide (2d)**

^{1}H NMR (500 MHz, DMSO-d_6)

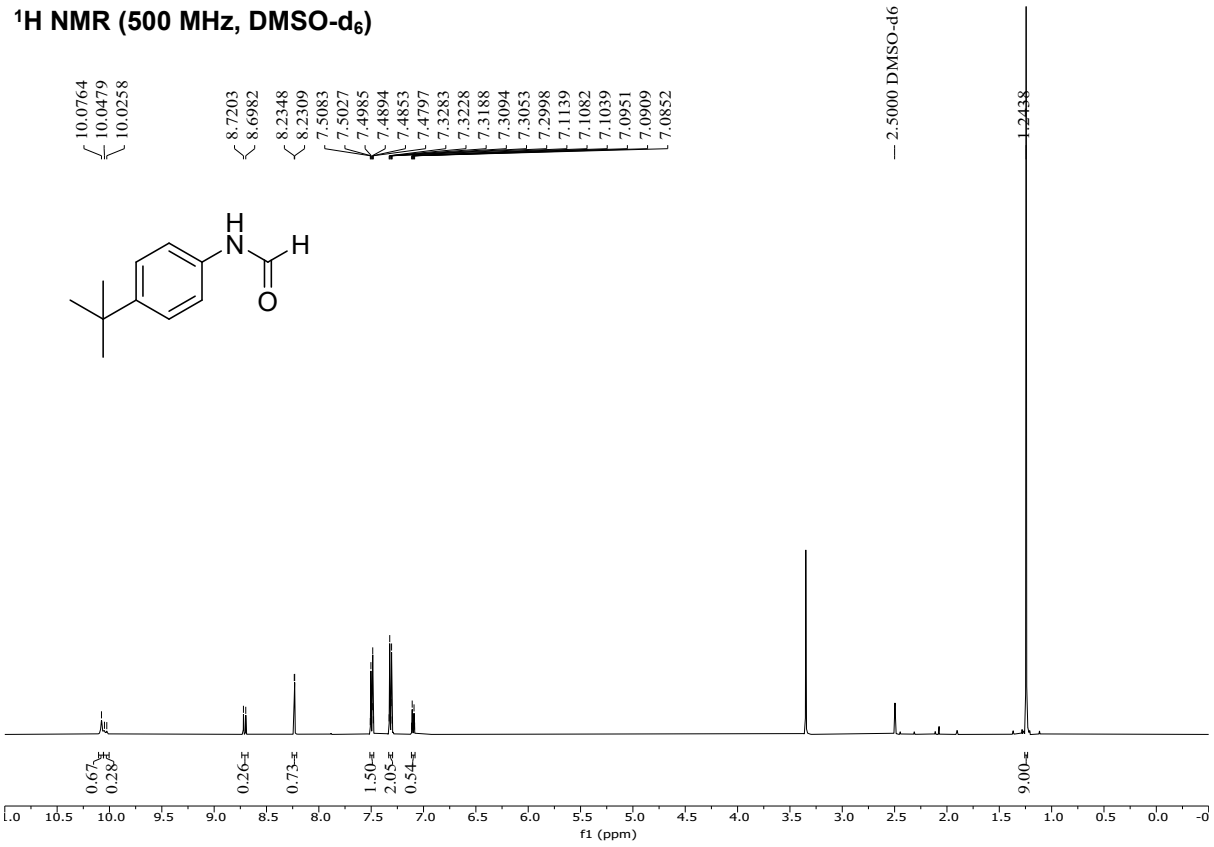


^{13}C NMR (126 MHz, DMSO-d_6)

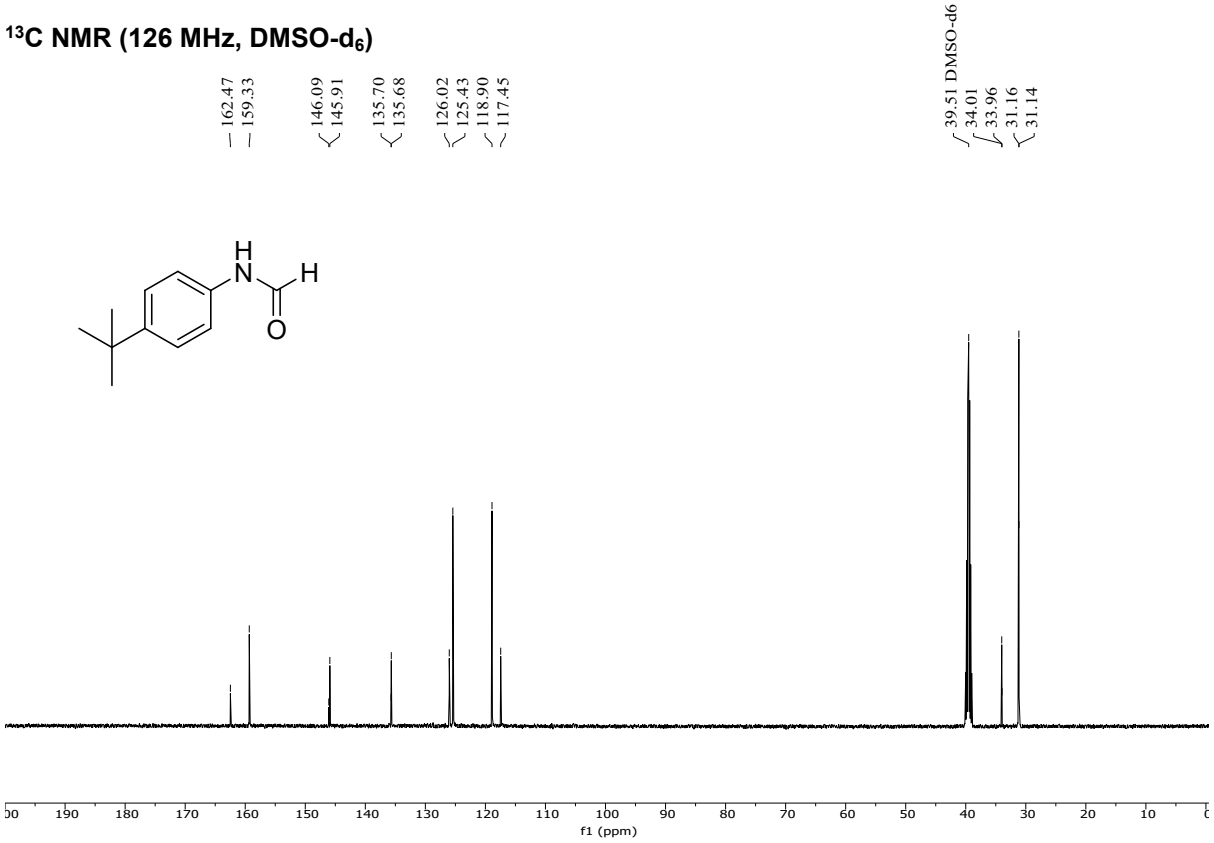


***N*-[4-(1,1-Dimethylethyl)phenyl]formamide (2e)**

^{1}H NMR (500 MHz, DMSO-d_6)

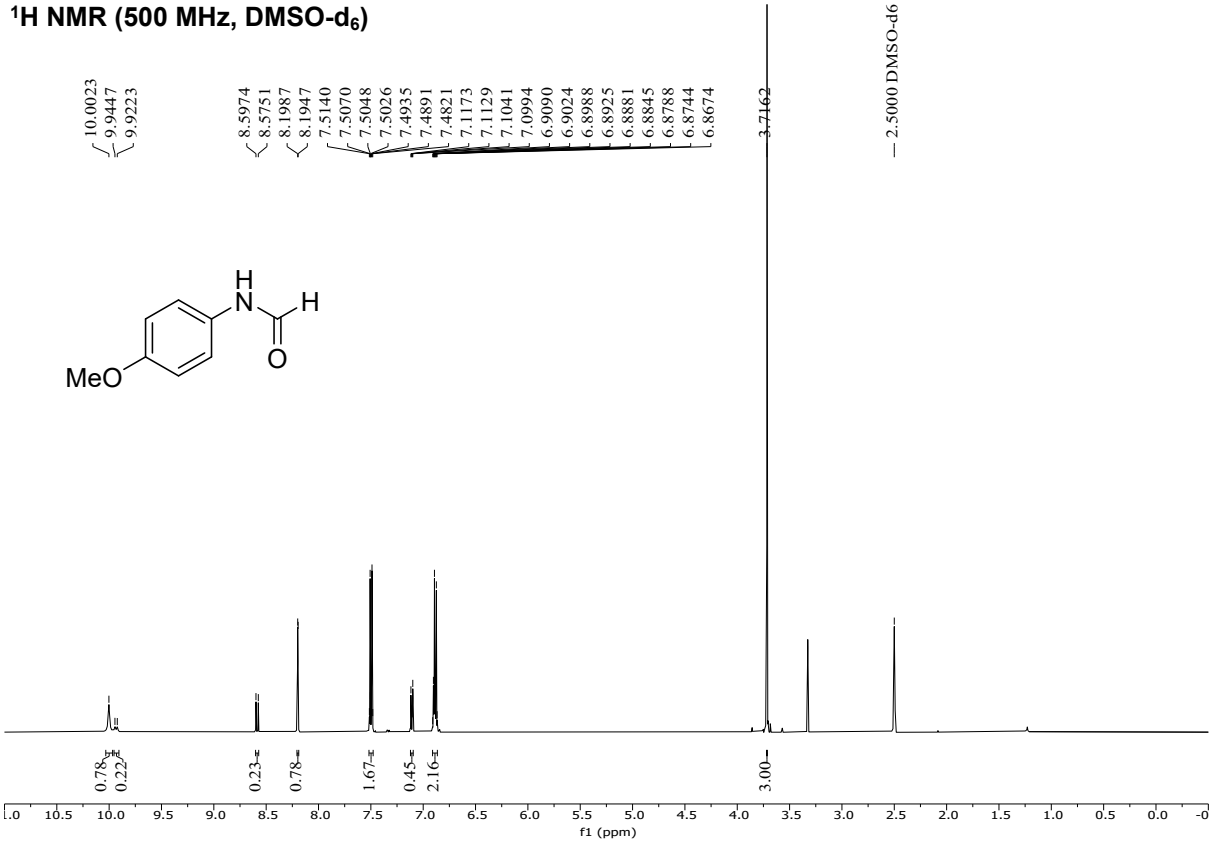


^{13}C NMR (126 MHz, DMSO-d_6)

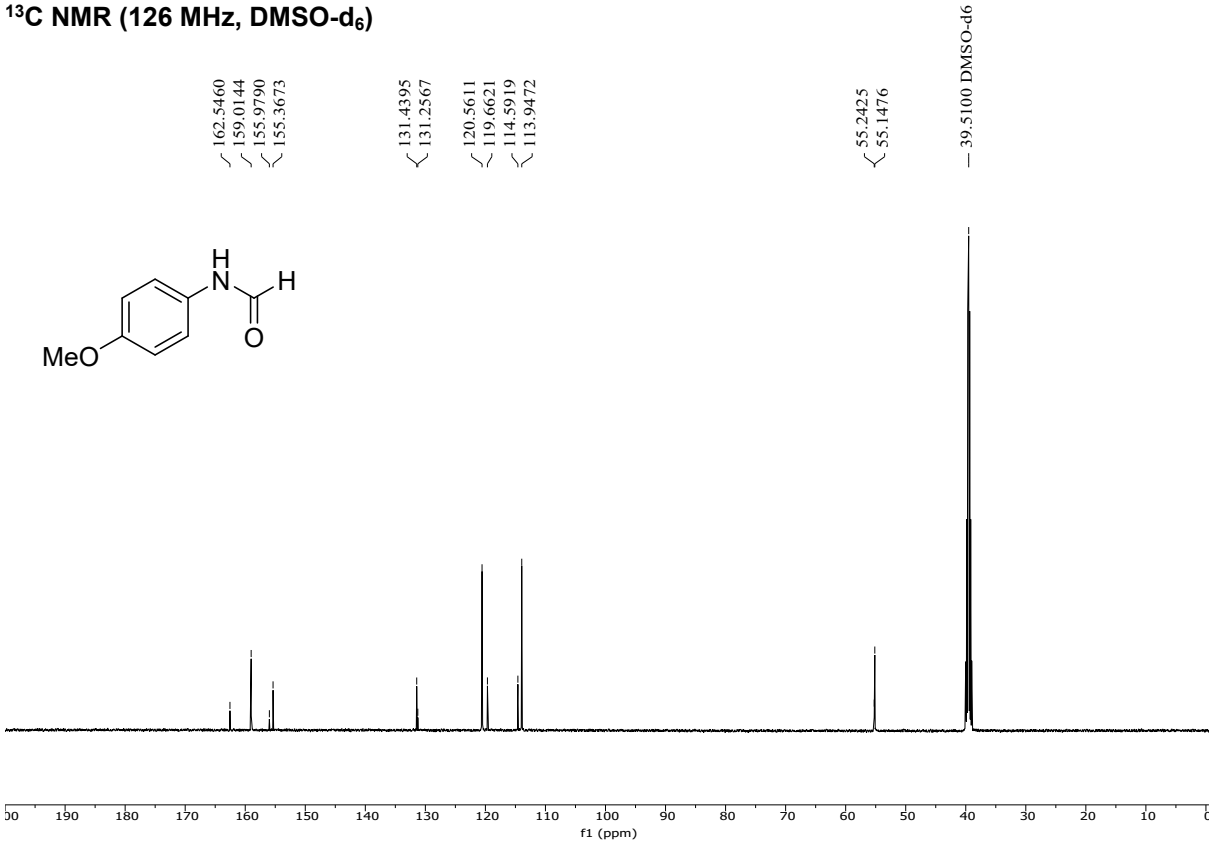


***N*-(4-Methoxyphenyl)formamide (2f)**

^{1}H NMR (500 MHz, DMSO-d$_6$)

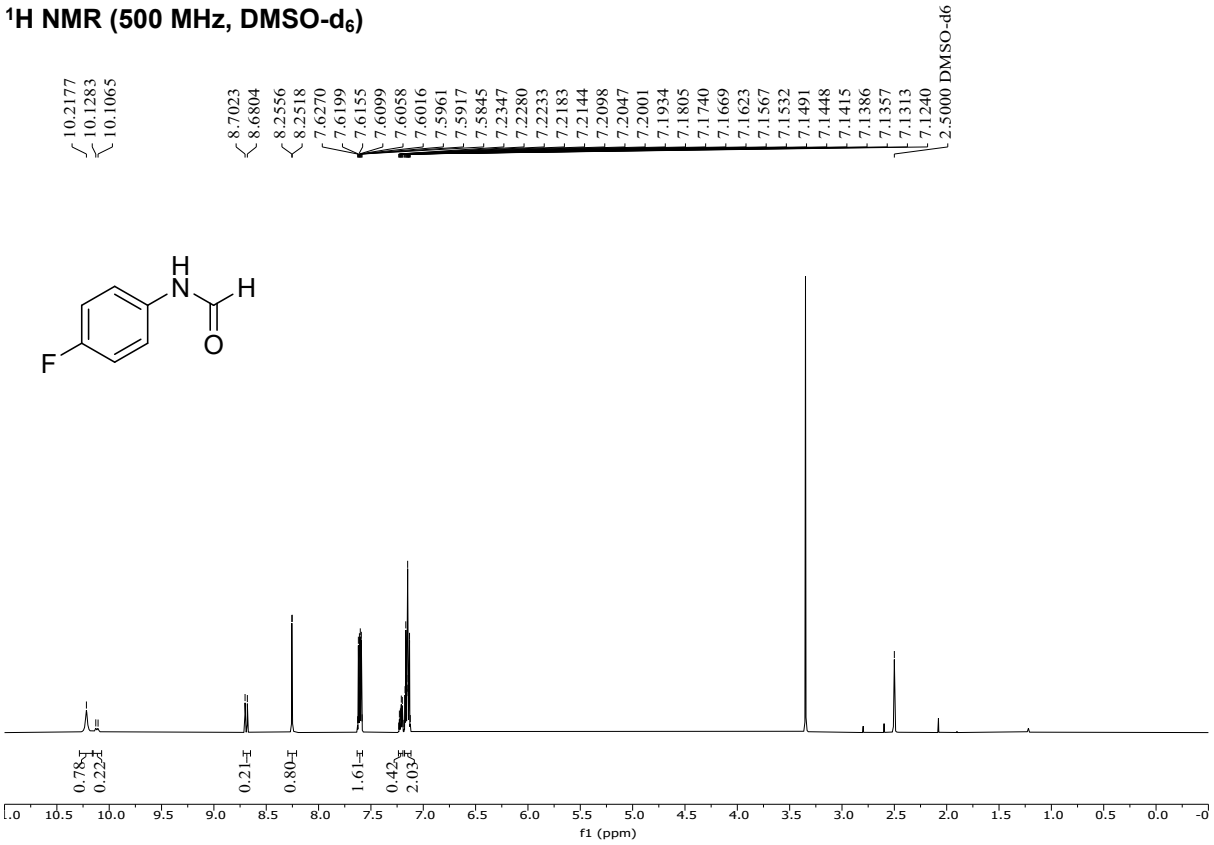


^{13}C NMR (126 MHz, DMSO-d$_6$)

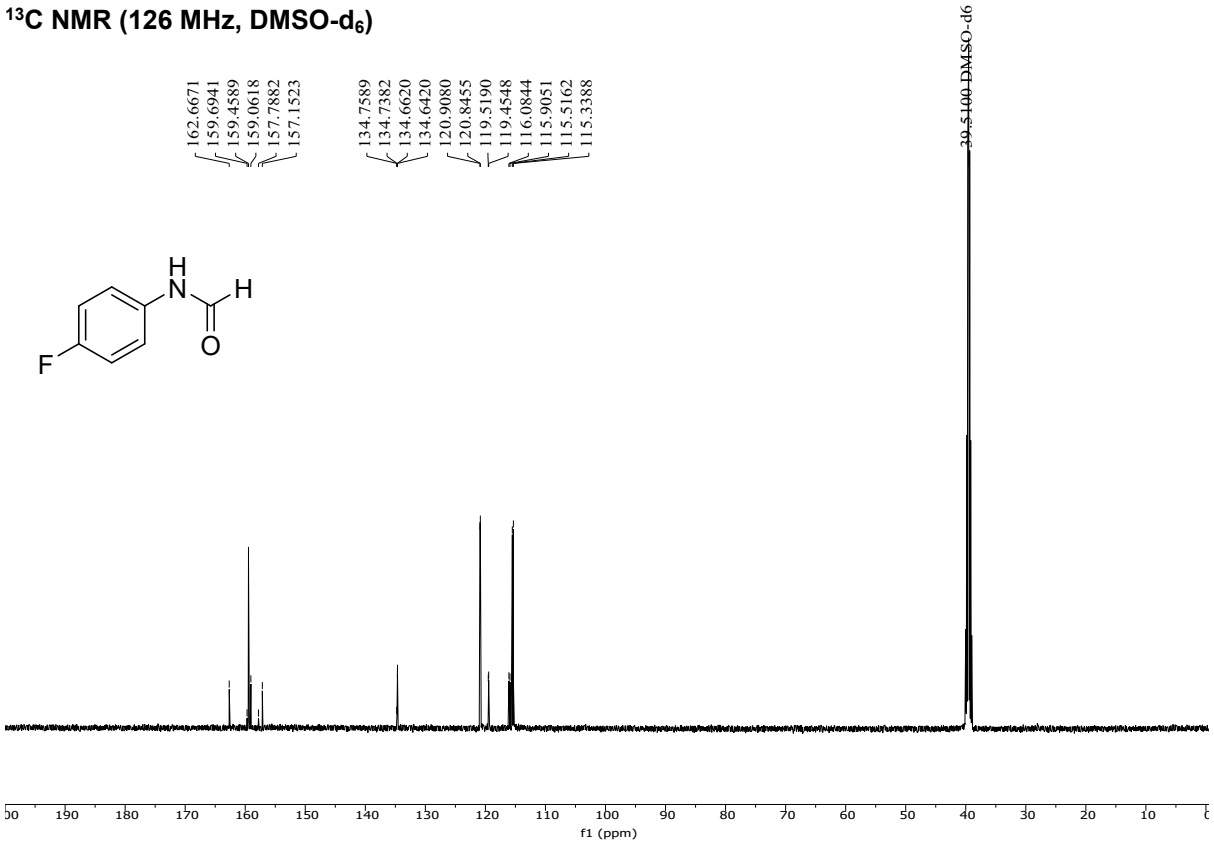


N-(4-Fluorophenyl)formamide (2g)

^{1}H NMR (500 MHz, DMSO-d_6)

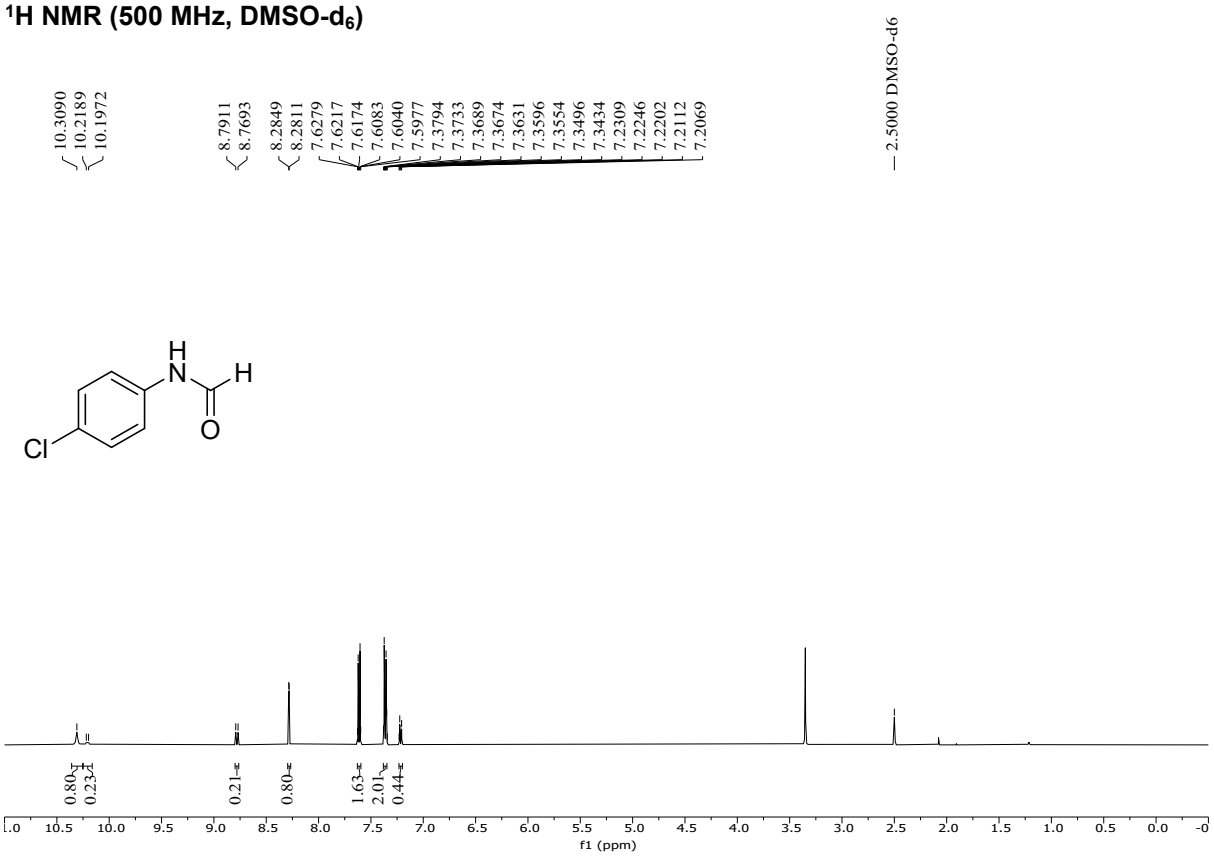


^{13}C NMR (126 MHz, DMSO-d_6)

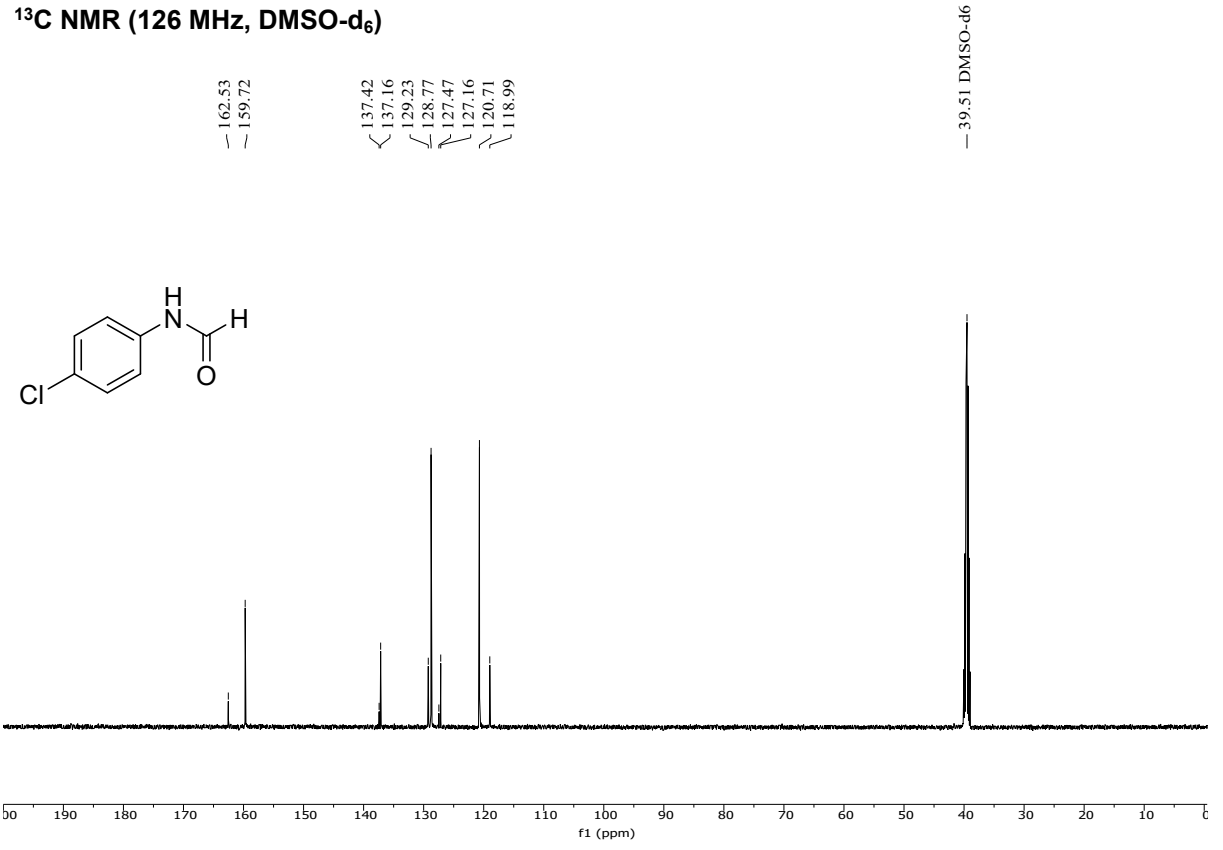


***N*-(4-Chlorophenyl)formamide (2h)**

^{1}H NMR (500 MHz, DMSO-d_6)

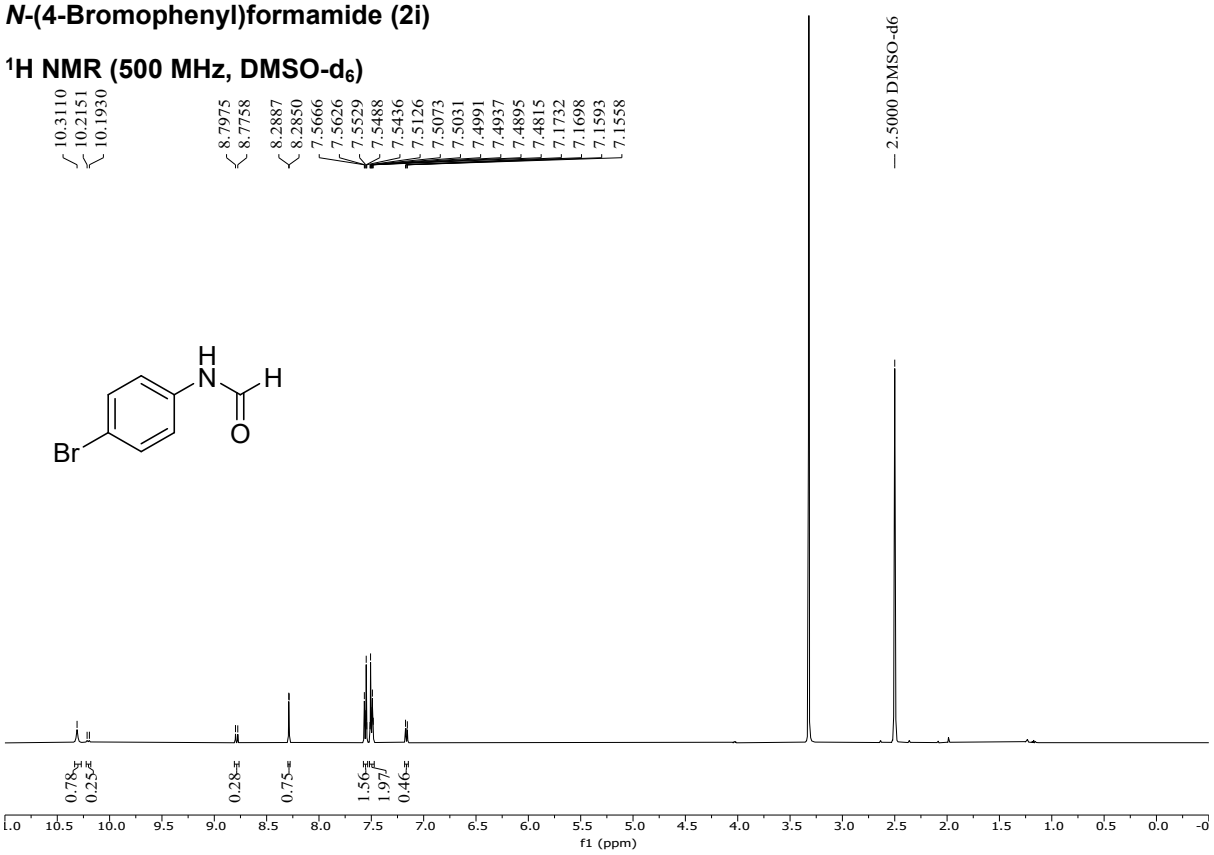


^{13}C NMR (126 MHz, DMSO-d_6)

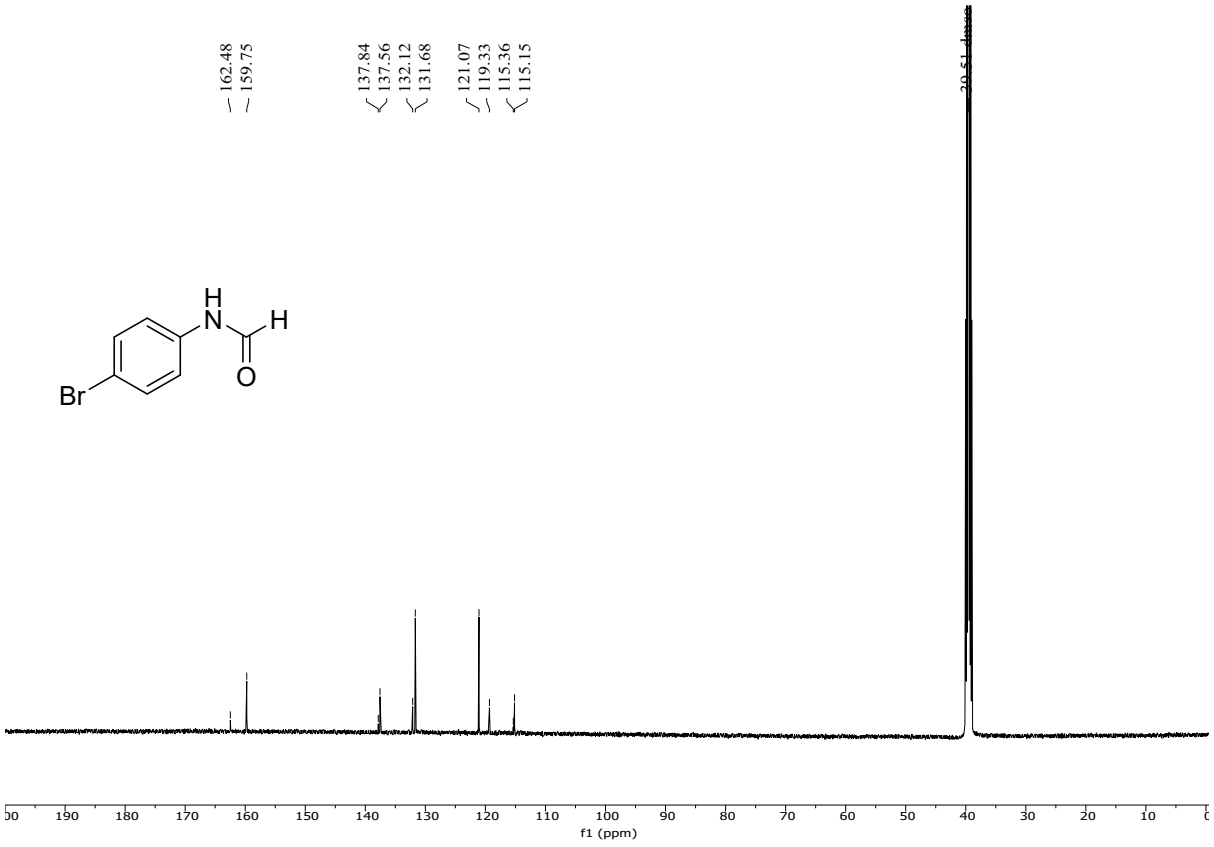


***N*-(4-Bromophenyl)formamide (2i)**

^{1}H NMR (500 MHz, DMSO-d_6)

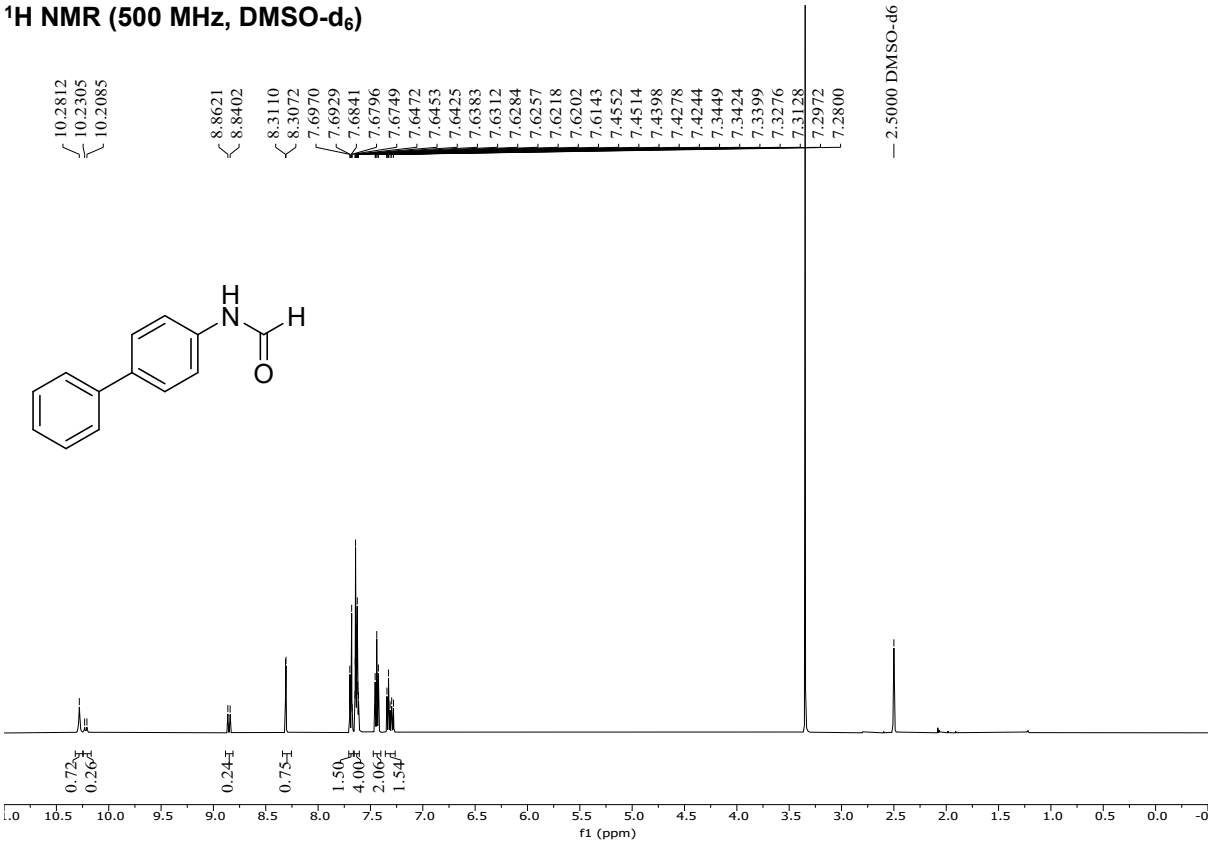


^{13}C NMR (126 MHz, DMSO-d_6)

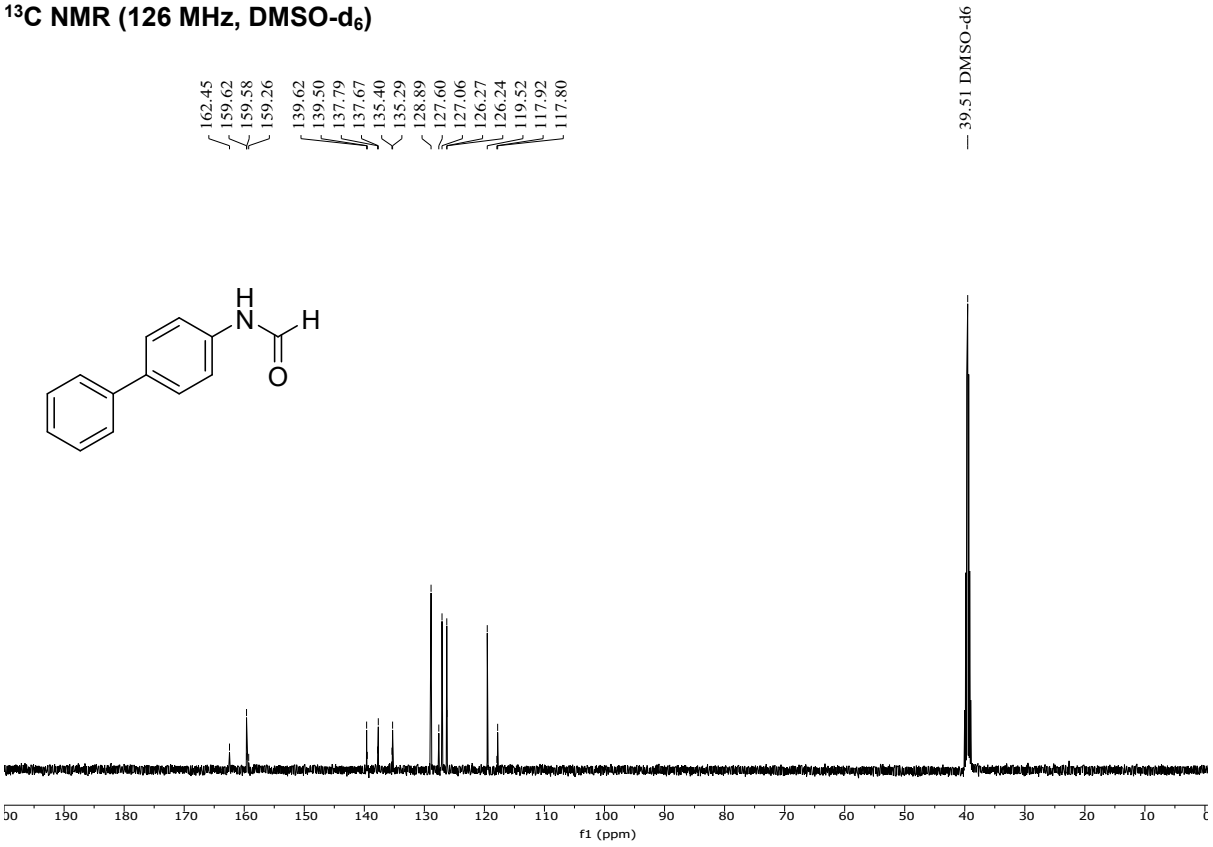


***N*-([1,1'-Biphenyl]-4-yl)formamide (2j)**

^{1}H NMR (500 MHz, DMSO-d_6)

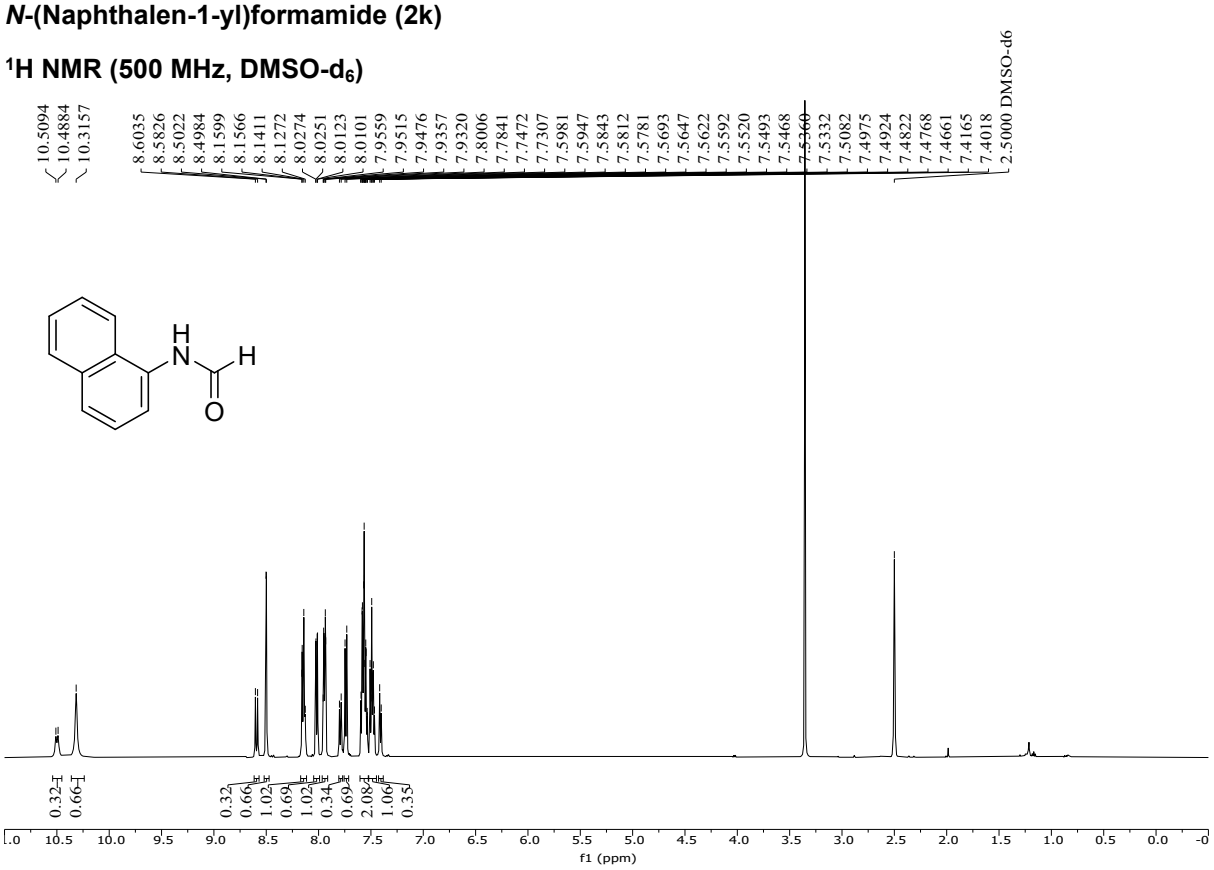


^{13}C NMR (126 MHz, DMSO-d_6)

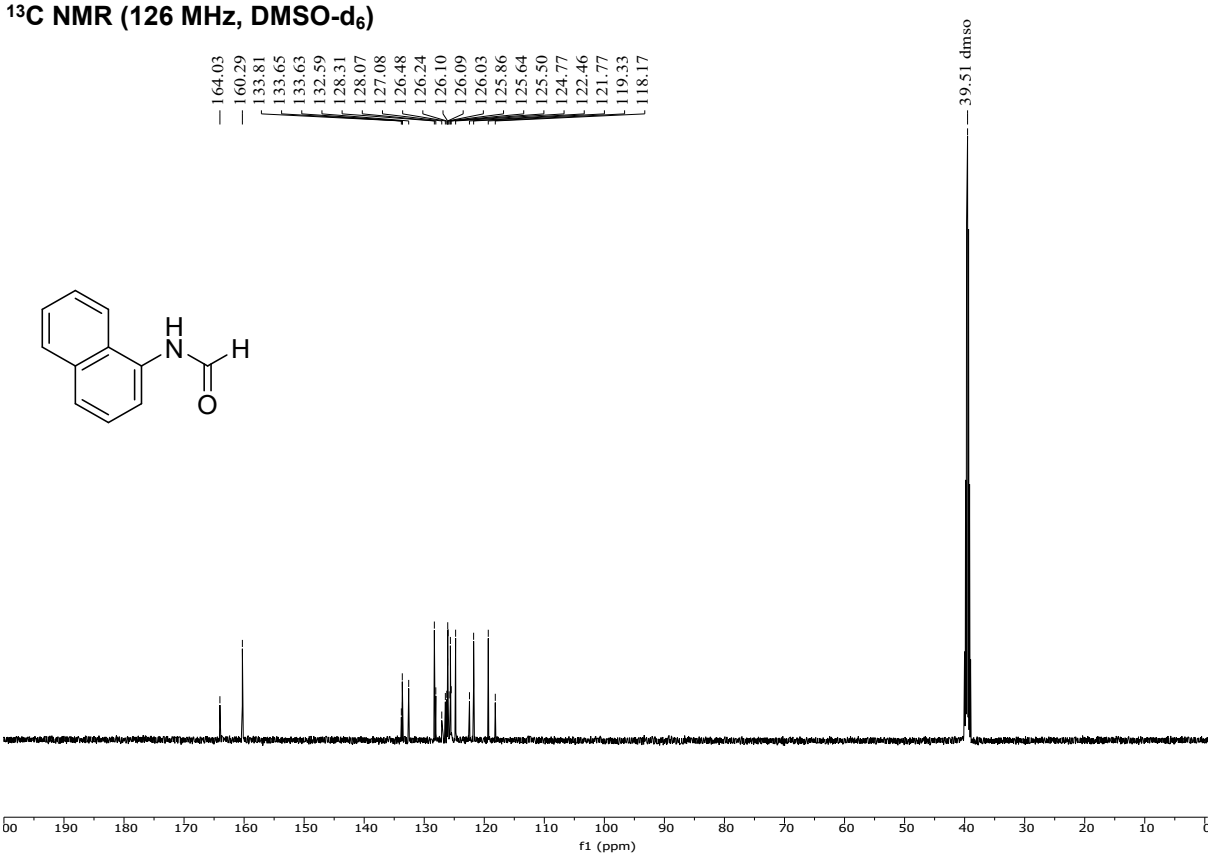


***N*-(Naphthalen-1-yl)formamide (2k)**

^{1}H NMR (500 MHz, DMSO-d_6)

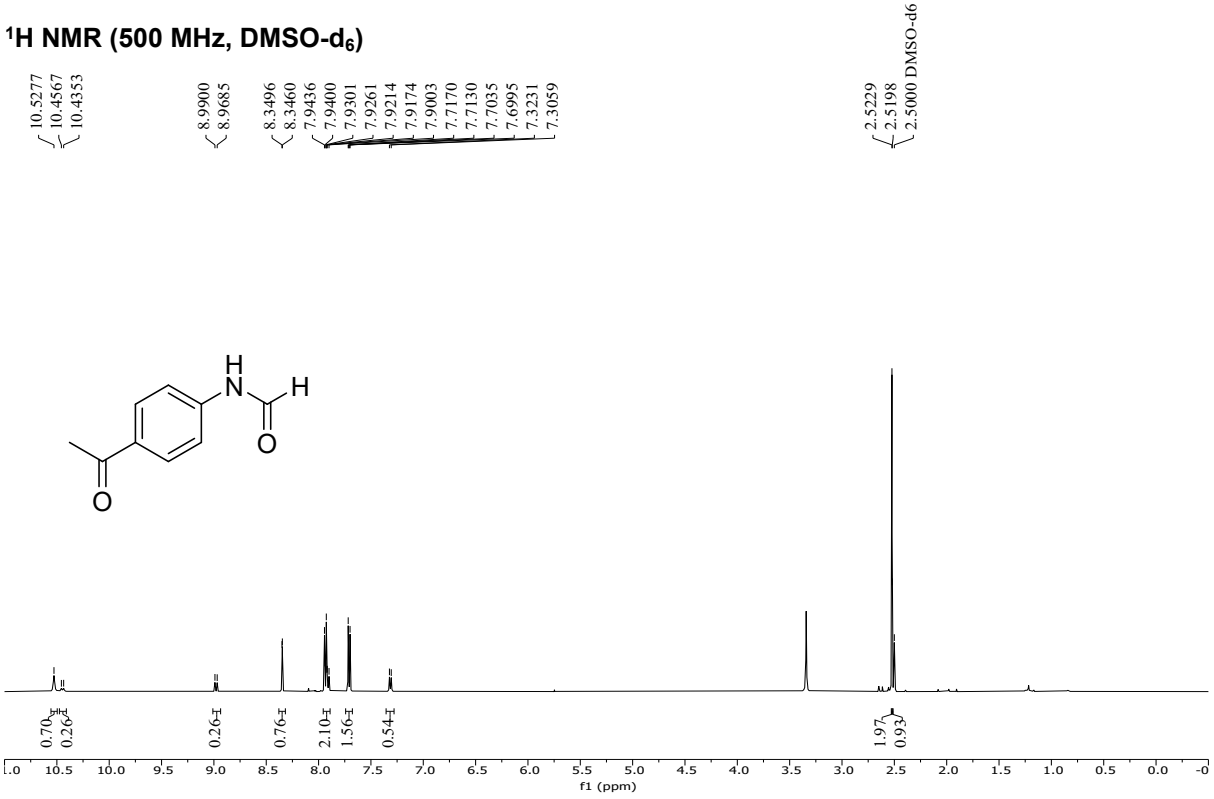


^{13}C NMR (126 MHz, DMSO-d_6)

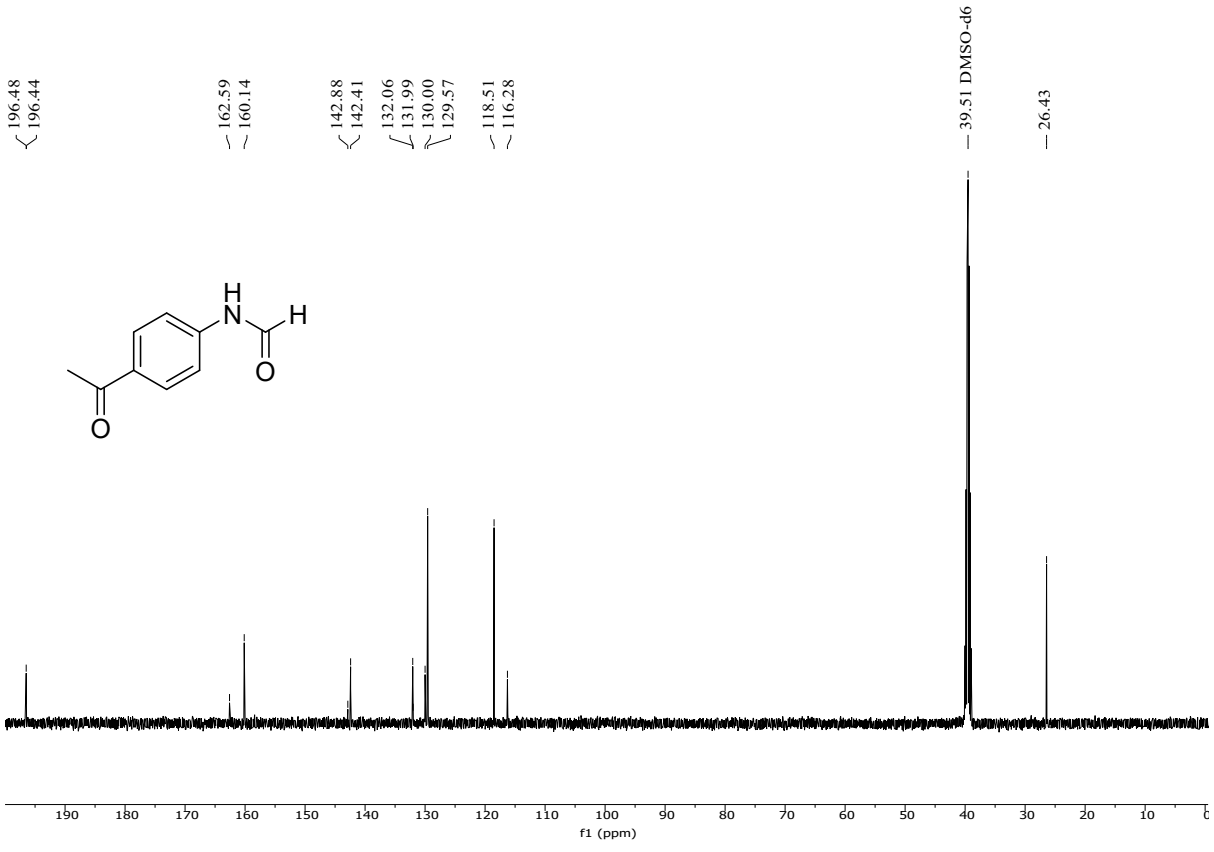


N-(4-Acetylphenyl)formamide (2l)

^{1}H NMR (500 MHz, DMSO-d_6)

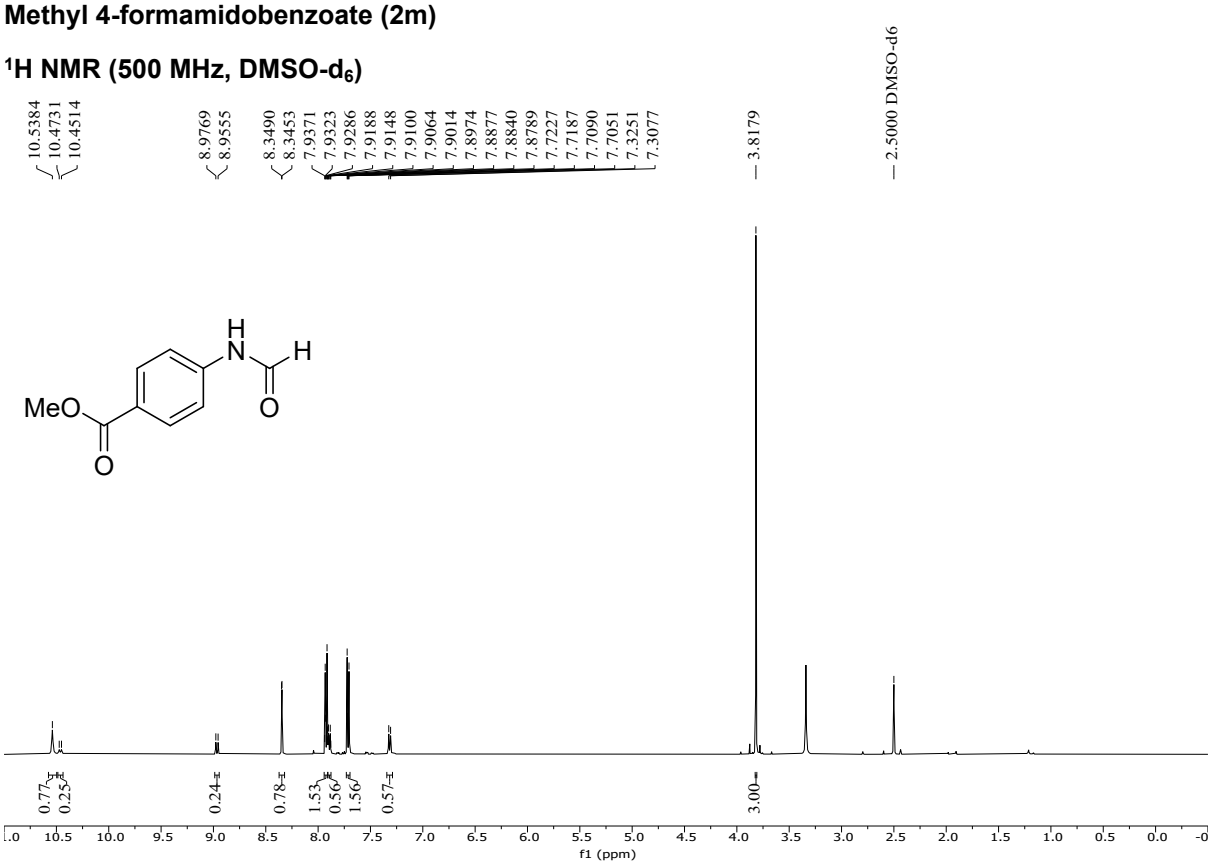


^{13}C NMR (126 MHz, DMSO-d_6)

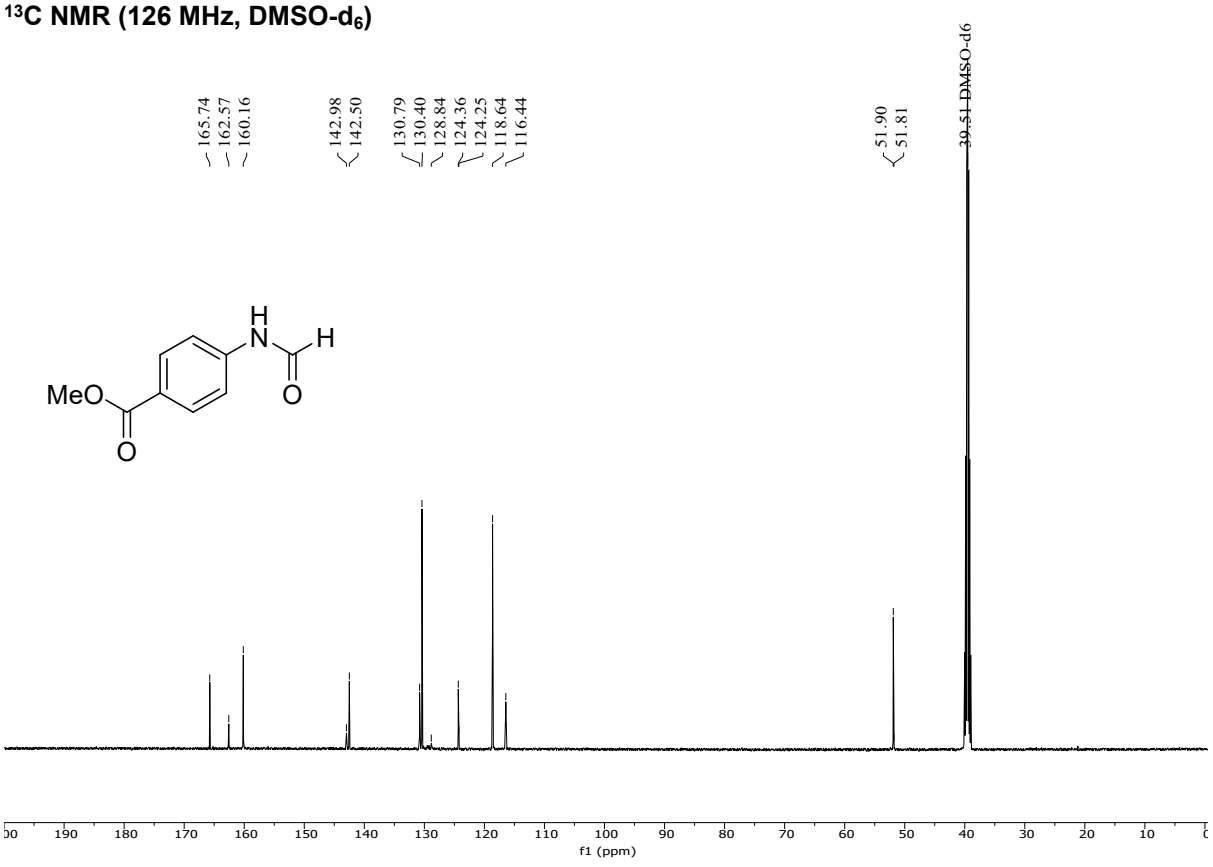


Methyl 4-formamidobenzoate (2m)

^{1}H NMR (500 MHz, DMSO-d_6)

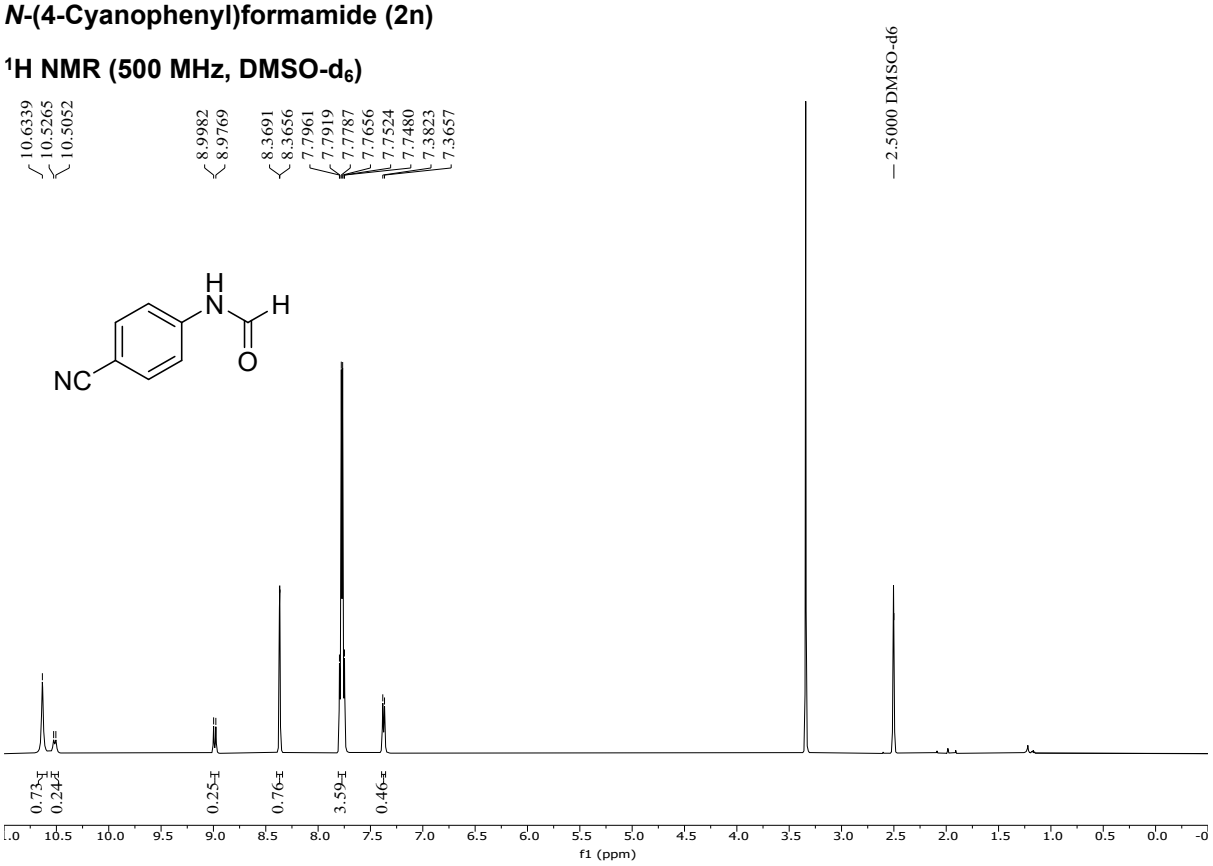


^{13}C NMR (126 MHz, DMSO-d_6)

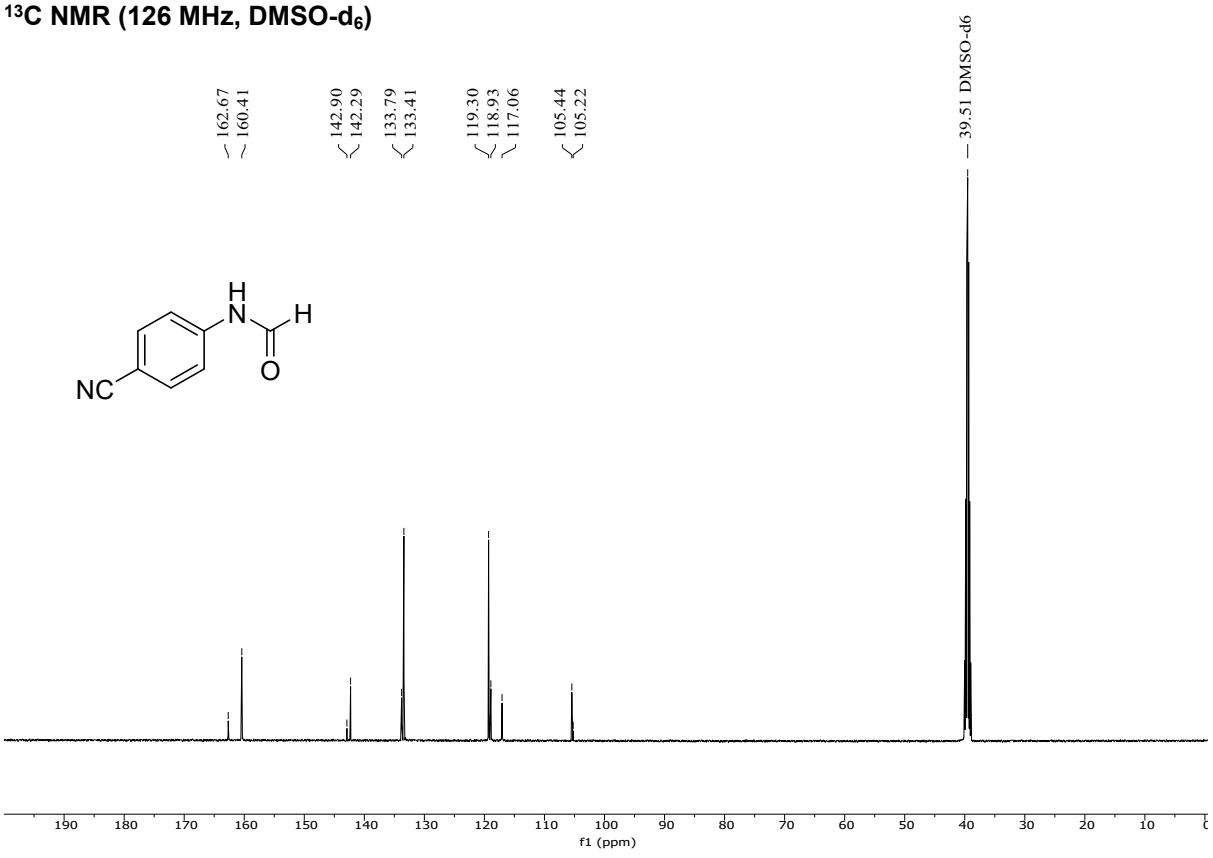


***N*-(4-Cyanophenyl)formamide (2n)**

^{1}H NMR (500 MHz, DMSO-d_6)

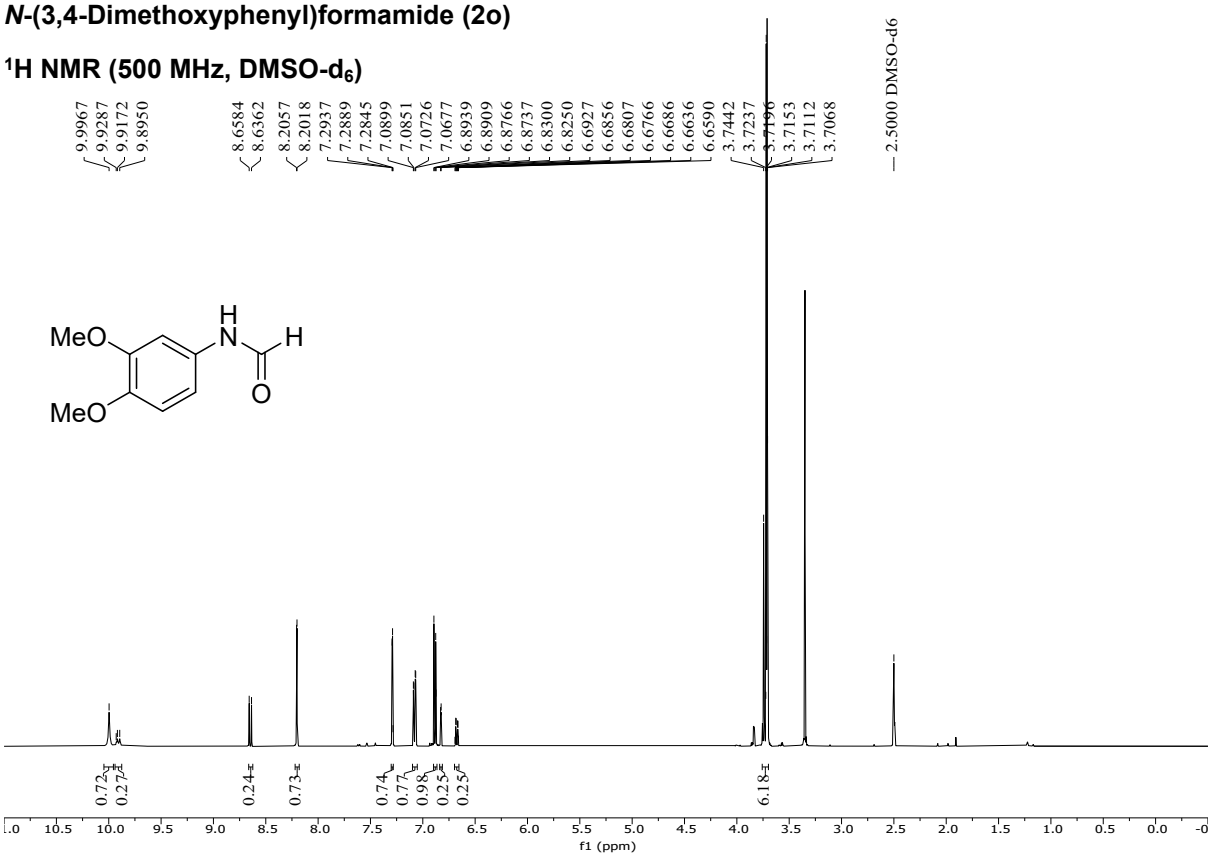


^{13}C NMR (126 MHz, DMSO-d_6)

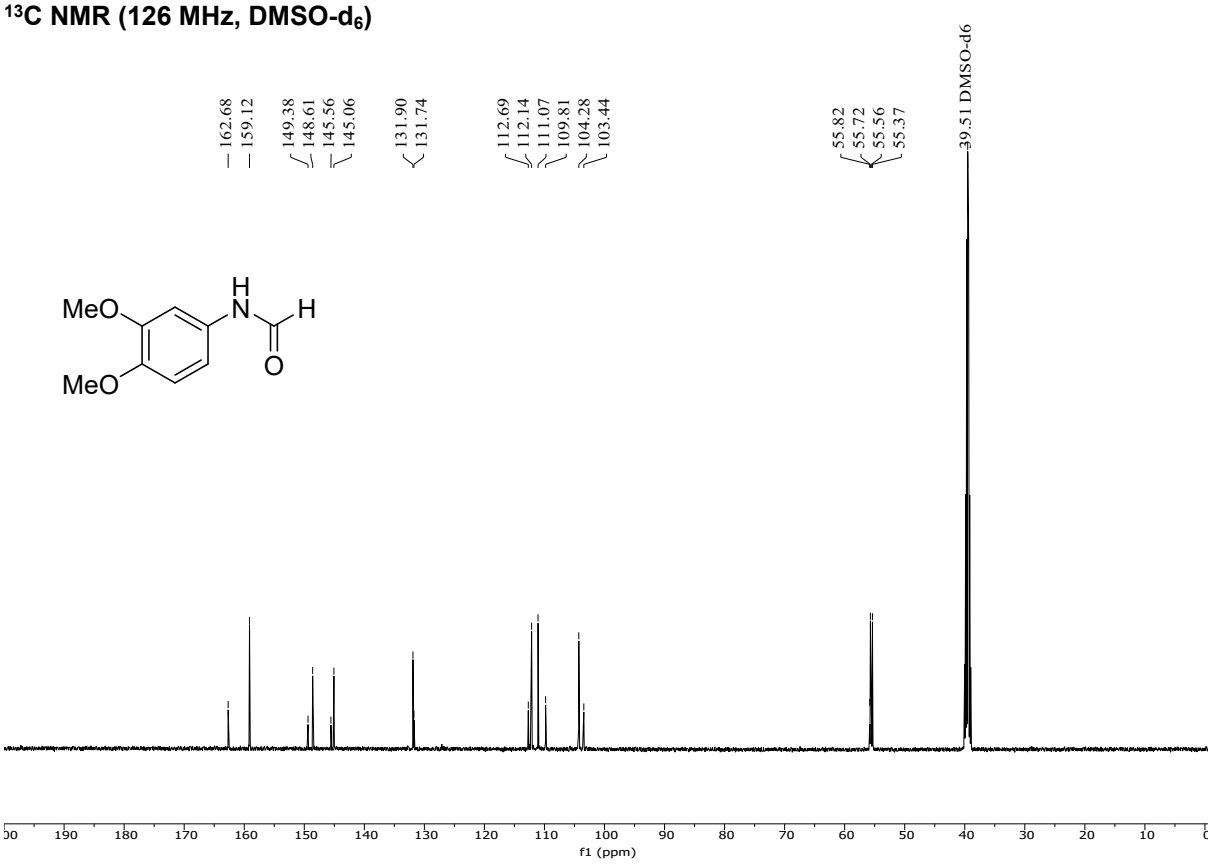


***N*-(3,4-Dimethoxyphenyl)formamide (2o)**

^{1}H NMR (500 MHz, DMSO-d_6)

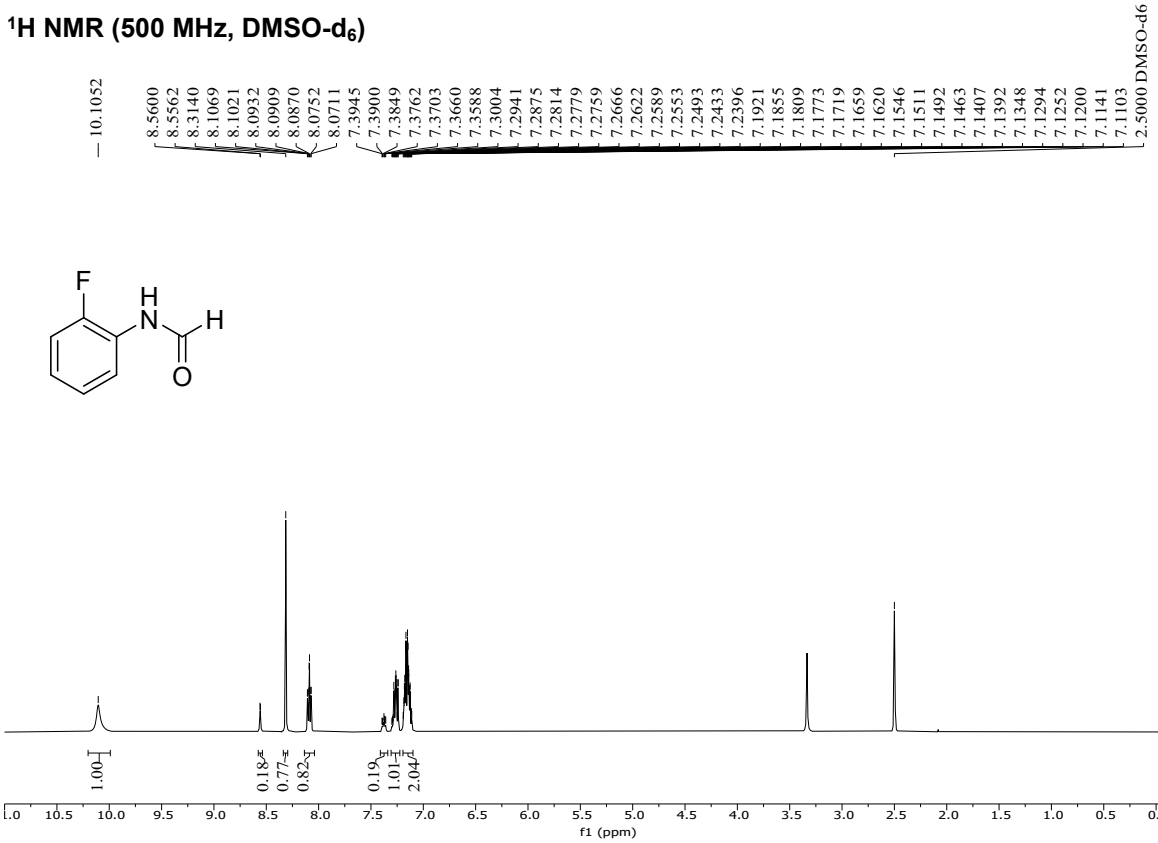


^{13}C NMR (126 MHz, DMSO-d_6)

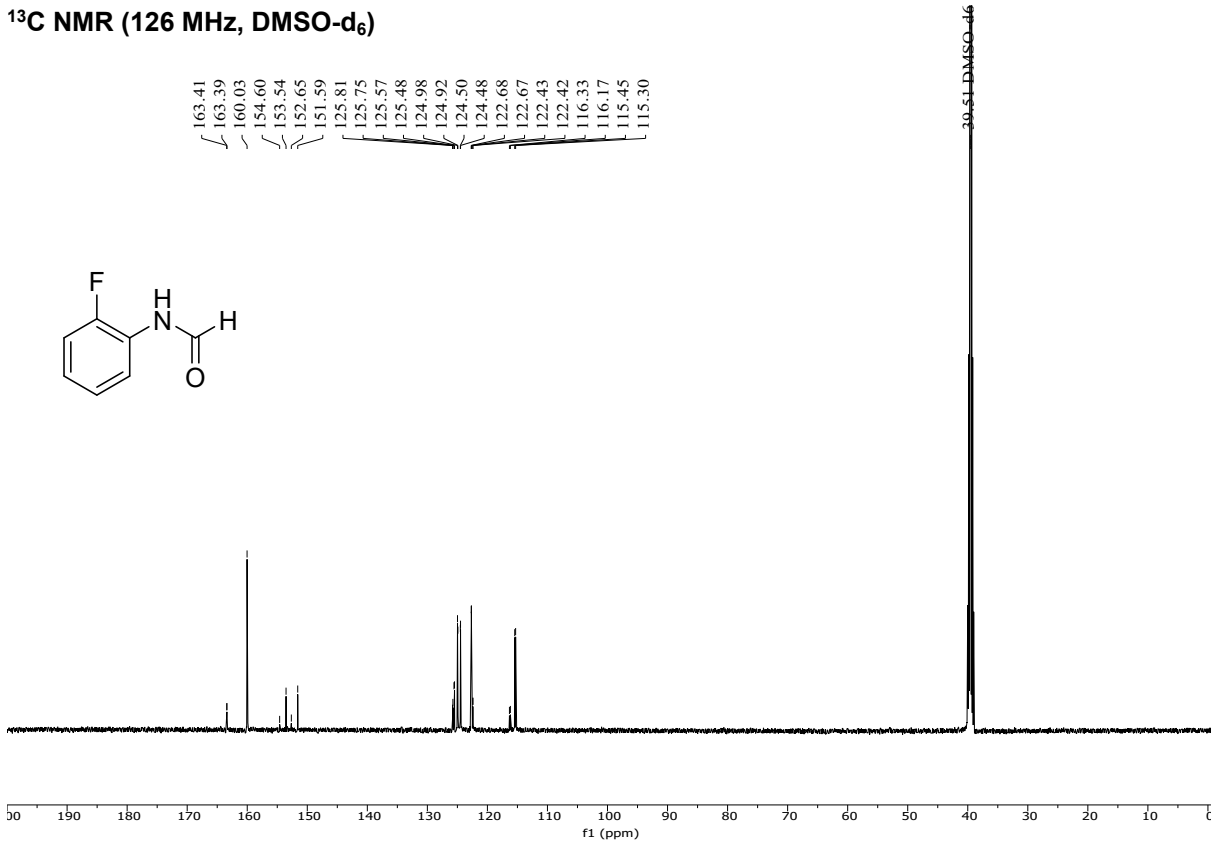


***N*-(2-Fluorophenyl)formamide (2p)**

^{1}H NMR (500 MHz, DMSO-d_6)



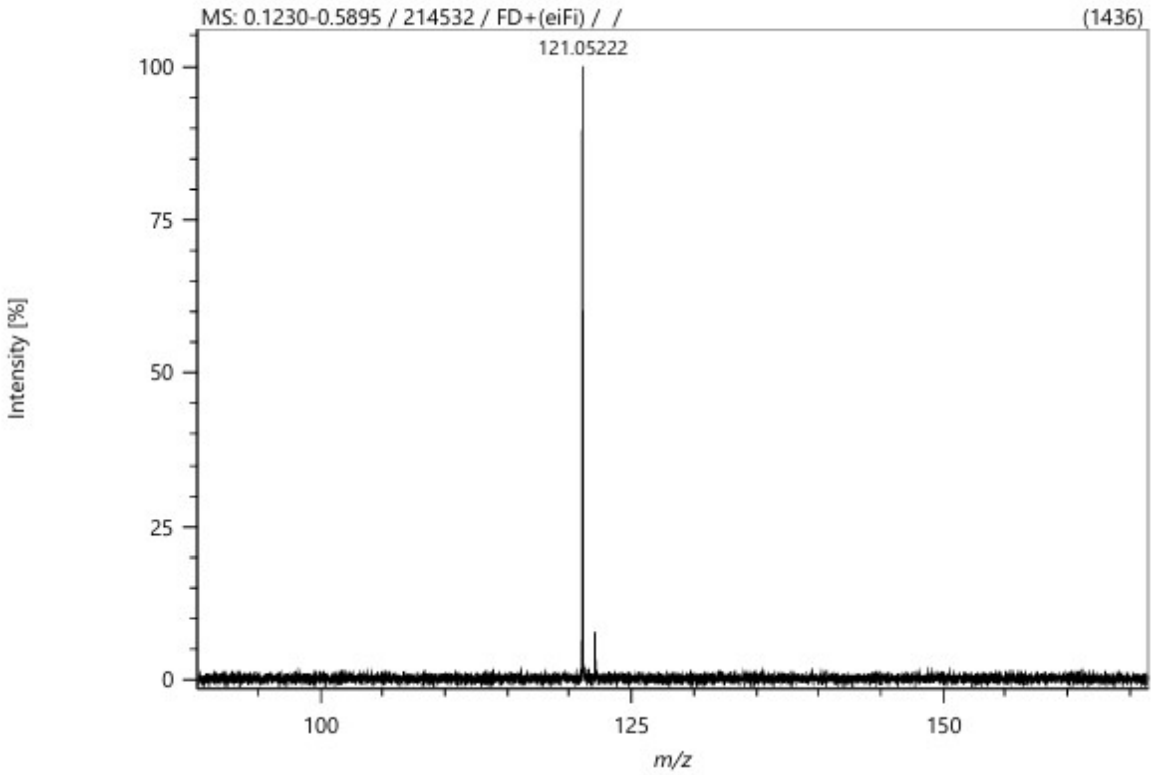
^{13}C NMR (126 MHz, DMSO-d_6)



7. Copy of HRMS Spectra

N-Phenylformamide (2a)

Spectrum



Elemental Composition

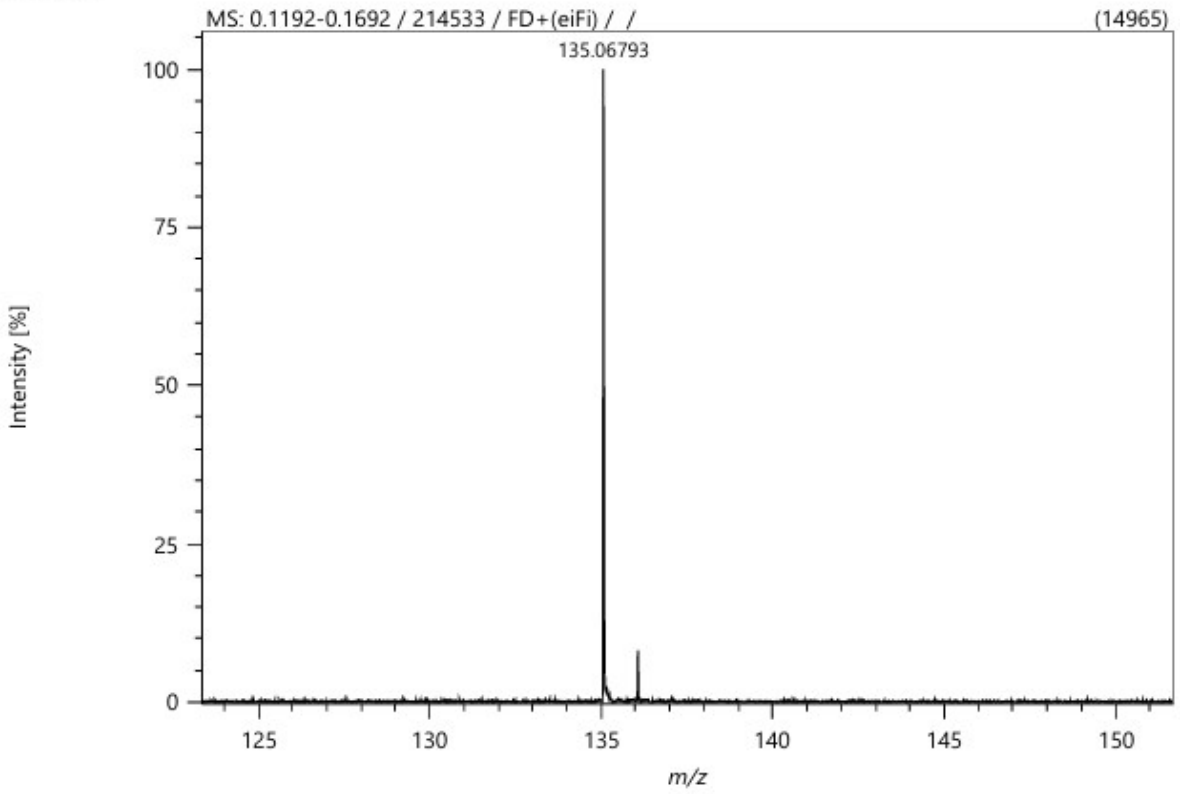
Parameters		Elements Set 1:				
Tolerance:	30.00 mDa	Symbol	C	H	O	N
Electron:	Odd/Even	Min	7	7	1	1
Charge:	+1	Max	7	7	1	1
DBE:	-90.0 - 90.0					

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
121.05222	1436.35	C7 H7 N O	121.05222	0.01	0.06	5.0

***N*-*p*-Tolylformamide (2b)**

Spectrum



Elemental Composition

Parameters	
Tolerance:	30.00 mDa
Electron:	Odd/Even
Charge:	+1
DBE:	-90.0 - 90.0

Elements Set 1:

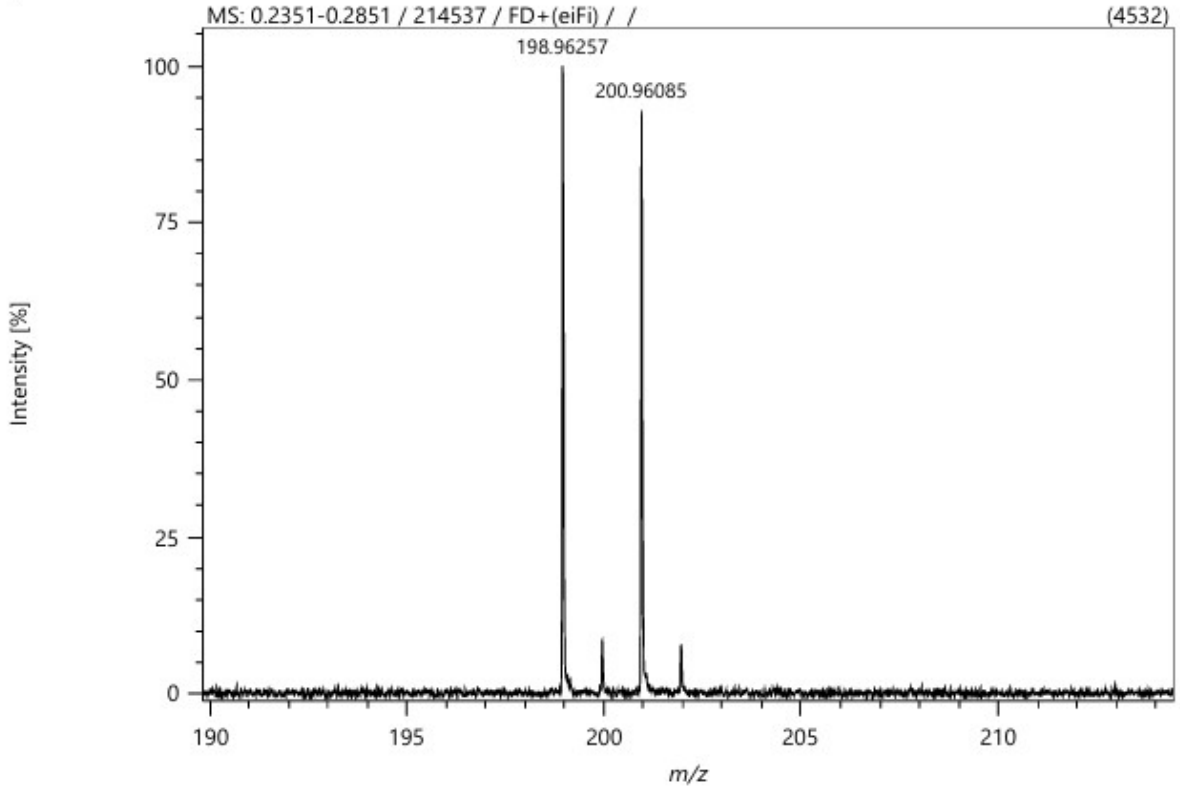
Symbol	C	H	O	N
Min	7	7	1	1
Max	8	9	1	1

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
135.06793	14964.92	C8 H9 N O	135.06787	0.06	0.47	5.0

***N*-(4-Bromophenyl)formamide (2i)**

Spectrum



Elemental Composition

Parameters	
Tolerance:	30.00 mDa
Electron:	Odd/Even
Charge:	+1
DBE:	-90.0 - 90.0

Elements Set 1:

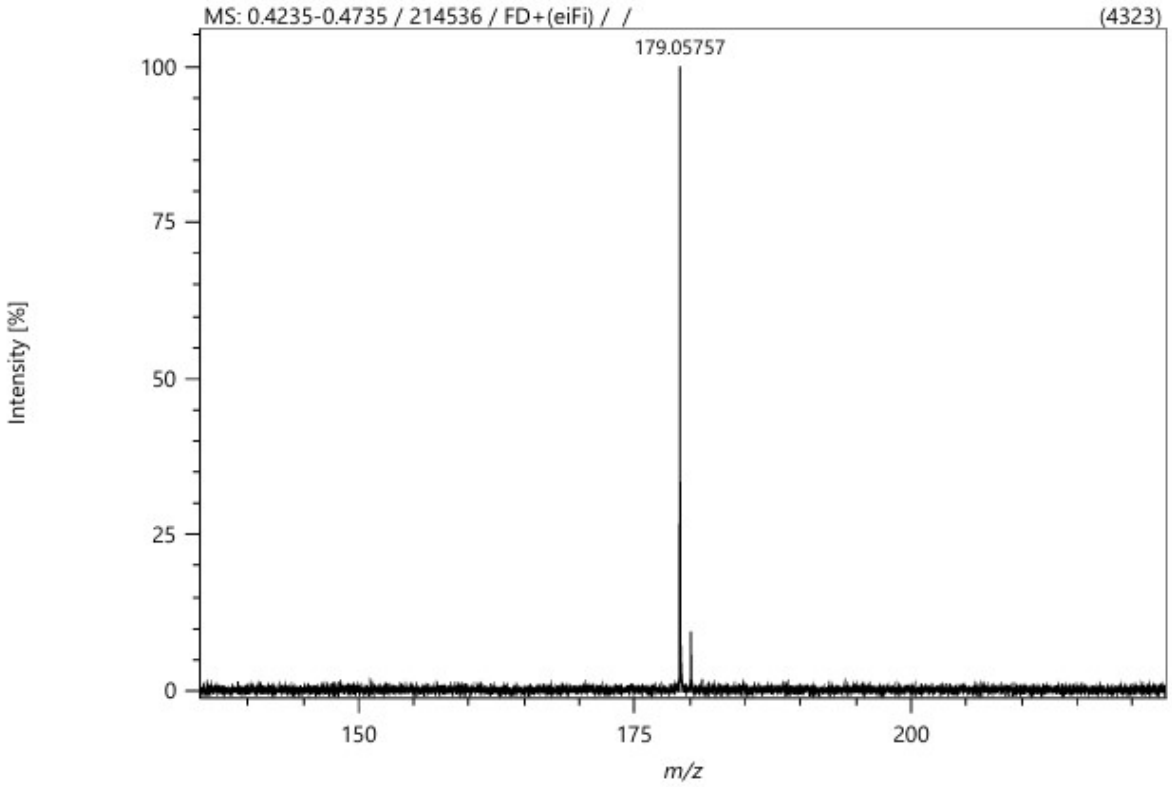
Symbol	C	H	O	N	Br
Min	7	6	1	1	1
Max	7	6	1	1	1

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
198.96257	4532.40	C7 H6 N O Br	198.96273	-0.15	-0.77	5.0

Methyl 4-formamidobenzoate (2m)

Spectrum



Elemental Composition

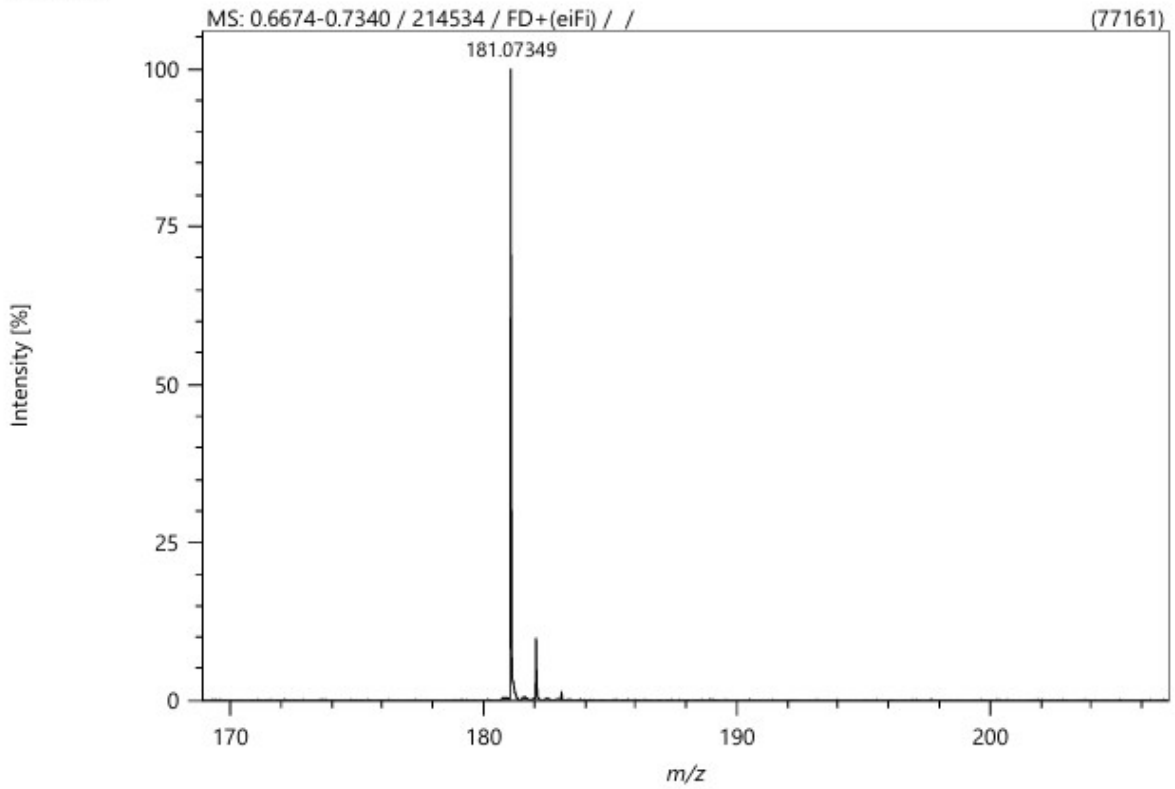
Parameters		Elements Set 1:				
Tolerance:	30.00 mDa	Symbol	C	H	O	N
Electron:	Odd/Even	Min	7	6	1	1
Charge:	+1	Max	9	9	3	1
DBE:	-90.0 - 90.0					

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
179.05757	4322.69	C9 H9 N O3	179.05769	-0.13	-0.72	6.0

***N*-(3,4-Dimethoxyphenyl)formamide (2o)**

Spectrum



Elemental Composition

Parameters	
Tolerance:	30.00 mDa
Electron:	Odd/Even
Charge:	+1
DBE:	-90.0 - 90.0

Elements Set 1:

Symbol	C	H	O	N
Min	7	7	1	1
Max	9	11	3	1

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
181.07349	77160.97	C9 H11 N O3	181.07334	0.14	0.79	5.0