

Supporting Information

Cathodic N–O Bond Cleavage of *N*-Alkoxy Amide

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1. General Remarks

Nuclear magnetic resonance (NMR) spectra were recorded on JEOL-ECS400 (^1H 400 MHz, ^{13}C 100 MHz), Varian 400-MR (^1H 400 MHz, ^{13}C 100 MHz), Varian NMR System PS600 (^1H 600 MHz, ^{13}C 150 MHz), and JEOL JNM-ECZ600R (^1H 600 MHz, ^{13}C 150 MHz) spectrometers. Chemical shifts for ^1H NMR are expressed in parts per million (ppm) relative to TMS (δ 0.00 ppm) or residual CHCl_3 in CDCl_3 (δ 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, br = broad signal, m = multiplet), coupling constants, and integration. Chemical shifts for ^{13}C NMR are expressed in ppm relative to CDCl_3 (δ 77.16 ppm). Infrared (IR) spectra were recorded on a SHIMAZU IRAffinity-1 spectrometer. Cyclic voltammetry (CV) was recorded on Electrochemical Analyzer CHI-600B. Analytic thin layer chromatography (TLC) was performed on Merck, pre-coated plate silica gel 60 F₂₅₄ (0.25 mm thickness). Column chromatography was performed on KANTO CHEMICAL silica gel 60N (40–50 μm). All electrolysis was performed using PMX350-0.2A purchased from KIKUSUI ELECTRONIC CORPORATION. Unless otherwise noted, all reactions were carried out under argon atmosphere.

Materials

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Acetonitrile (MeCN) was distilled from CaH_2 and dried over molecular sieves 3A. Dichloromethane (CH_2Cl_2) was washed with water, distilled from P_2O_5 , redistilled from dried K_2CO_3 to remove a trace amount of acid, and stored over molecular sieves 4A. *N*-methoxy amide **1a** was commercially available and used without any purification. *N*-Methoxy amides (**1b**, **1g**, **1n**,¹ **1c**, **1d**, **1e**,² **1f**, **1j**,³ **1h**, **1o**,⁴ **1i**,⁵ **1k**, **1m**,⁶ **1l**,⁷ **1p**, **1r**,⁸ and **1q**⁹) were synthesized according to literatures.

2. Synthetic Procedure

General procedure of cathodic reduction

The cathodic reduction was carried out in an H-type divided cell (4G glass filter) equipped with a Pt plate anode ($1.0 \times 1.0 \text{ cm}^2$) and a Pt plate cathode ($1.0 \times 1.0 \text{ cm}^2$). The anodic chamber was placed a solution of Bu_4NBF_4 (0.1 M) in MeCN (5 mL). The cathodic chamber was placed a solution of *N*-methoxy amide **1** (0.50 mmol) and Bu_4NBF_4 (0.1 M) in MeCN (5 mL). The constant current electrolysis (10 mA) was carried out at room temperature with magnetic stirring until 1.0 F/mol of electricity was consumed. After the electrolysis, the reaction mixture was concentrated *in vacuo*. The crude was purified by column chromatography on SiO_2 to give corresponding amide **2**.

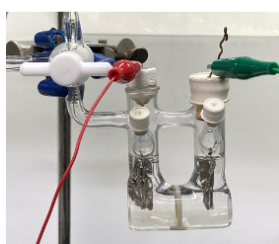
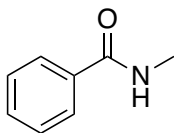


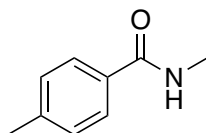
Figure S1. Divided cell equipped with Pt electrodes.

Analytical data for amides **2**



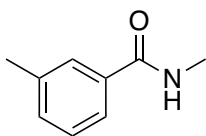
***N*-methylbenzamide (2a)**, 67.3 mg, 0.498 mmol, 98%)¹⁰

^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.3$ Hz, 2H), 7.45 (m, 1H), 7.37 (m, 2H), 6.58 (brs, 1H, NH), 2.97 (d, $J = 5.0$ Hz, 3H); ^{13}C NMR (600 MHz, CDCl_3) δ 168.3, 134.7, 131.4, 128.6, 126.9, 26.9; IR (KBr) 3327, 1730, 1641, 1577, 1409 cm^{-1} ; Rf = 0.28 (hexane/EtOAc = 2:1)



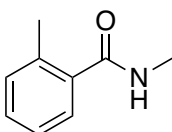
***N*,4-dimethylbenzamide (2b)**, 68.5 mg, 0.459 mmol, 92%)¹¹

^1H NMR (600 MHz, CDCl_3) δ 7.66 (d, $J = 8.2$ Hz, 2H), 7.17 (d, $J = 8.2$ Hz, 2H), 6.61 (brs, 1H, NH), 2.89 (brs, 3H), 2.35 (s, 3H); ^{13}C NMR (600 MHz, CDCl_3) δ 168.3, 141.6, 131.7, 129.1, 126.9, 26.8, 21.4; IR (KBr) 3337, 1635, 1550, 1412, 1303 cm^{-1} ; Rf = 0.22 (hexane/EtOAc = 2:1)



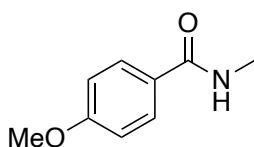
N,3-dimethylbenzamide (2c), 41.9 mg, 0.281 mmol, 56%)¹²

¹H NMR (600 MHz, CDCl₃) δ 7.60 (s, 1H), 7.54 (brd, *J* = 5.2 Hz, 1H), 7.28–7.26 (m, 2H), 6.68 (brs, 1H, NH), 2.98 (d, *J* = 4.8 Hz, 3H), 2.35 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 168.7, 138.4, 134.6, 132.1, 128.4, 127.7, 124.1, 26.9, 21.4; IR (neat) 1771, 1714, 1504, 1462, 738 cm⁻¹; R_f = 0.10 (hexane/EtOAc = 1:4)



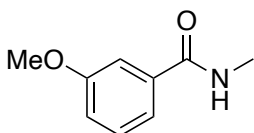
N,2-dimethylbenzamide (2d), 23.5 mg, 0.158 mmol, 32%)¹³

¹H NMR (600 MHz, CDCl₃) δ 7.32–7.27 (m, 2H), 7.20–7.16 (m, 2H), 5.87 (brs, 1H, NH), 2.97 (d, *J* = 4.6 Hz, 3H), 2.42 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 171.0, 136.6, 136.1, 131.1, 129.9, 126.8, 125.8, 26.7, 19.9; IR (KBr) 3291, 1603, 1522, 1458, 783 cm⁻¹; R_f = 0.30 (hexane/EtOAc = 2:1)



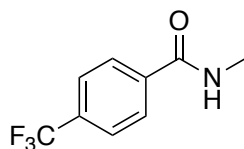
N-methyl-4-methoxybenzamide (2e), 49.7 mg, 0.301 mmol, 60%)¹⁴

¹H NMR (600 MHz, CDCl₃) δ 7.73 (ddd, *J* = 9.0 Hz, 2.1 Hz, 2.1 Hz, 2H), 6.91 (ddd, *J* = 9.0 Hz, 2.1 Hz, 2.1 Hz, 2H), 6.18 (brs, 1H, NH), 3.84 (s, 3H), 3.00 (d, *J* = 4.8 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 168.0, 162.1, 128.8, 127.0, 113.7, 55.4, 26.9; IR (KBr) 1610, 1576, 1447, 1156, 782 cm⁻¹; R_f = 0.25 (hexane/EtOAc = 1:2)



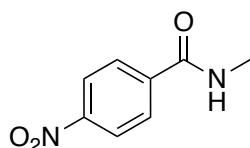
N-methyl-3-methoxybenzamide (2f), 38.5 mg, 0.233 mmol, 46%)¹⁵

¹H NMR (400 MHz, CDCl₃) δ 7.36 (m, 1H), 7.29–7.28 (m, 2H), 7.01 (m, 1H), 6.67 (brs, 1H, NH), 3.80 (s, 3H), 2.97 (d, *J* = 4.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.3, 159.8, 136.1, 129.6, 118.8, 117.6, 112.3, 55.4, 26.9; IR (KBr) 1668, 1564, 1505, 1243, 1047 cm⁻¹; R_f = 0.20 (hexane/EtOAc = 1:1)



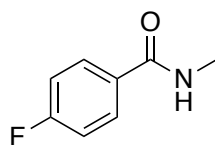
N-methyl-4-trifluoromethylbenzamide (2g), 65.1 mg, 0.320 mmol, 64%)¹²

¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 6.45 (brs, 1H, NH), 3.04 (d, *J* = 4.7 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 167.1, 138.1, 133.3 (q, *J* = 32.4 Hz), 129.4, 127.5, 123.8 (q, *J* = 330.6 Hz), 27.0; IR (KBr) 3302, 1650, 1554, 1324, 1070 cm⁻¹; R_f = 0.24 (hexane/EtOAc = 1:1)



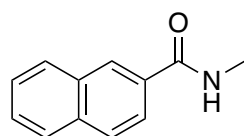
N-methyl-4-nitrobenzamide (2h), 61.3 mg, 0.340 mmol, 68%)¹⁴

¹H NMR (600 MHz, CDCl₃) δ 8.29 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.8 Hz, 2H), 6.22 (brs, 1H, NH), 3.06 (d, *J* = 4.7 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 166.2, 149.6, 140.2, 128.1, 124.0, 27.2; IR (KBr) 3336, 1648, 1512, 1350, 868 cm⁻¹; R_f = 0.24 (hexane/EtOAc = 1:2)



N-methyl-4-fluorobenzamide (2i), 45.7 mg, 0.298 mmol, 59%)¹⁴

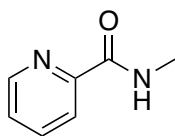
¹H NMR (400 MHz), solvent (CDCl₃) δ 7.79 (dd, *J* = 9.0 Hz, 5.5 Hz, 2H), 7.08 (dd, *J* = 9.0 Hz, 9.0 Hz, 2H), 6.38 (brs, 1H, NH), 2.98 (d, *J* = 4.9 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 167.5, 164.7 (d, *J* = 251.4 Hz), 130.8 (d, *J* = 2.9 Hz), 129.3 (d, *J* = 8.7 Hz), 115.6 (d, *J* = 21.7 Hz), 27.0; IR (KBr) 3350, 1638, 1321, 1292, 766 cm⁻¹; R_f = 0.06 (hexane/EtOAc = 2:1)



N-methylnaphthalene-2-carboxamide (2j), 20.2 mg, 0.109 mmol, 21%)¹¹

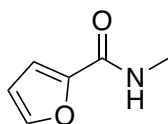
¹H NMR (600 MHz, CDCl₃) δ 8.27 (s, 1H), 7.87–7.81 (m, 4H), 7.56–7.49 (m, 2H), 6.54 (brs, 1H, NH), 3.05 (d, *J* = 4.8 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 168.5, 134.8, 132.7, 131.9, 129.0, 128.5, 127.8, 127.7, 127.4, 126.8, 123.7, 27.1; IR (KBr) 3277, 1644, 1559, 1410, 1324 cm⁻¹; R_f = 0.24

(hexane/EtOAc = 1:3)



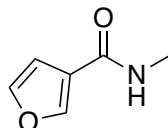
N-methyl-2-picolinamide (2k), 28.5 mg, 0.172 mmol, 34%)¹⁶

¹H NMR (600 MHz, CDCl₃) δ 8.53 (d, *J* = 4.8 Hz, 1H), 8.19 (d, *J* = 7.6 Hz, 1H), 8.03 (brs, 1H, NH), 7.84 (ddd, *J* = 7.6 Hz, 7.6 Hz, 1.7 Hz, 1H), 7.41 (ddd, *J* = 7.6 Hz, 4.8 Hz, 1.7 Hz, 1H), 3.03 (d, *J* = 5.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 165.1, 150.0, 148.2, 137.5, 126.2, 122.2, 26.2; IR (neat) 1655, 1641, 1568, 1464, 1435 cm⁻¹; R_f = 0.55 (chloroform/MeOH = 10:1)



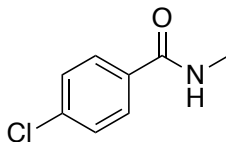
N-methyl-2-furamide (2l), 44.3 mg, 0.354 mmol, 69%)¹⁷

¹H NMR (600 MHz, CDCl₃) δ 7.39 (m, 1H), 7.07 (dd, *J* = 3.4 Hz, 1.7 Hz, 1H), 6.52 (brs, 1H, NH), 6.45 (dd, *J* = 3.4 Hz, 1.7 Hz, 1H), 2.95 (d, *J* = 5.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 159.3, 148.1, 143.9, 113.9, 112.1, 25.9; IR (KBr) 1636, 1541, 1312, 1194, 760 cm⁻¹; R_f = 0.23 (hexane/EtOAc = 1:1)



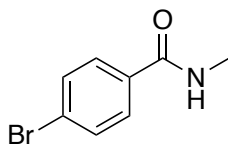
N-methyl-3-furamide (2m), 13.6 mg, 0.109 mmol, 21%)¹⁷

¹H NMR (600 MHz, CDCl₃) δ 7.92 (m, 1H), 7.42 (dd, *J* = 1.4 Hz, 1.4 Hz, 1H), 6.61 (d, *J* = 1.4 Hz, 1H), 6.03 (brs, 1H, NH), 2.94 (d, *J* = 4.8 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 163.5, 144.7, 143.8, 122.7, 108.3, 26.4; IR (KBr) 3268, 1628, 1407, 1214, 876 cm⁻¹; R_f = 0.20 (hexane/EtOAc = 1:1)



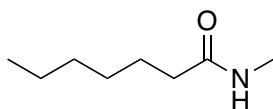
N-methyl-4-chlorobenzamide (2n), 14.0 mg, 0.0825 mmol, 16%)¹²

¹H NMR (600 MHz, CDCl₃) δ 7.70 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 6.18 (brs, 1H, NH), 3.01 (d, *J* = 7.7 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 167.3, 137.7, 133.1, 128.9, 128.4, 27.0; IR (KBr) 3340, 1637, 1490, 1092, 841 cm⁻¹; R_f = 0.08 (hexane/EtOAc = 2:1)



***N*-methyl-4-bromobenzamide (2o)**, 10.8 mg, 0.0599 mmol, 12%)¹²

¹H NMR (600 MHz, CDCl₃) δ 7.62 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 6.18 (brs, 1H, NH), 3.00 (d, *J* = 4.5 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 167.3, 133.5, 131.9, 128.6, 126.1, 27.0; IR (KBr) 3343, 1638, 1595, 1072, 840 cm⁻¹; R_f = 0.13 (hexane/EtOAc = 2:1)



***N*-methylheptanamide (2p)**, 26.2 mg, 0.183 mmol, 35%)¹⁸

¹H NMR (400 MHz, CDCl₃) δ 5.57 (brs, 1H, NH), 2.80 (d, *J* = 4.5 Hz, 3H), 2.16 (t, *J* = 7.7 Hz, 2H), 1.61 (m, 2H), 1.31 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.2, 36.7, 31.6, 29.1, 26.4, 25.8, 22.6, 14.1; IR (KBr) 3291, 2957, 1645, 1549, 1410 cm⁻¹; R_f = 0.10 (hexane/EtOAc = 5:1)

3. Direct NMR Analysis of the Reaction Mixture

The reaction solution in CH₃CN was diluted with CD₃CN after 0.2, 0.4, 0.6, 0.8, and 1.0 F/mol of electrolysis, and the NMR measurements were performed using a WET method which allows to decrease the large solvent signal derived from CH₃CN.

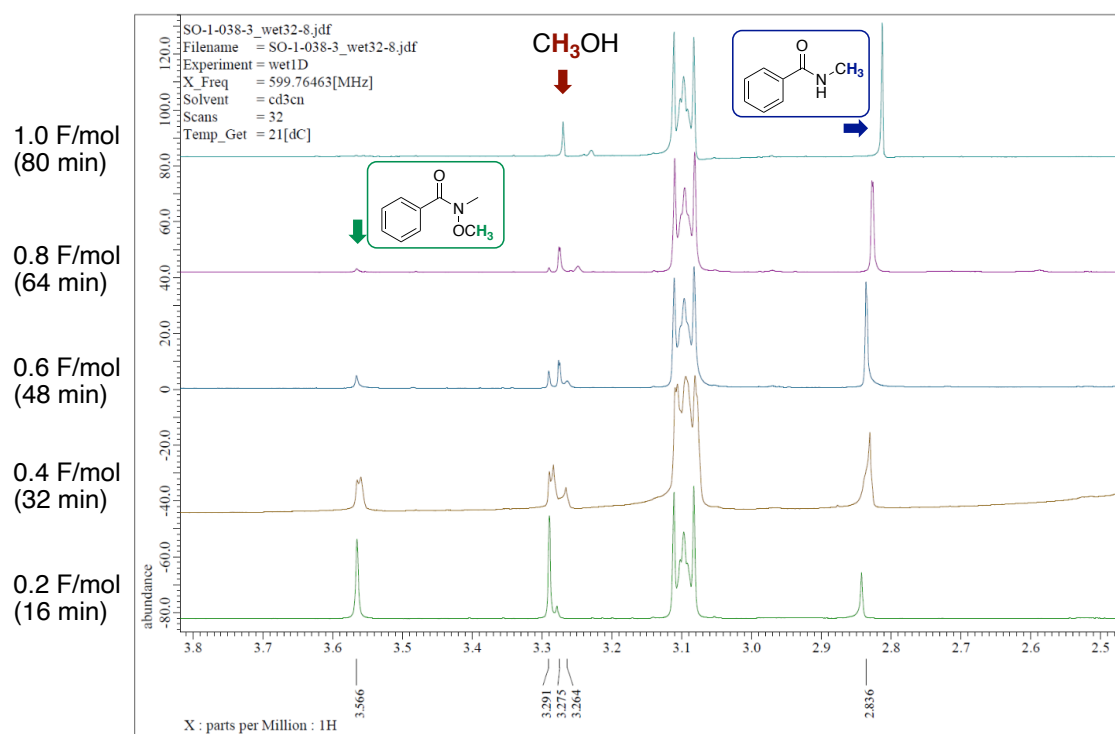


Figure S2. Direct NMR analysis of the reaction mixture.

4. Cyclic Voltammograms

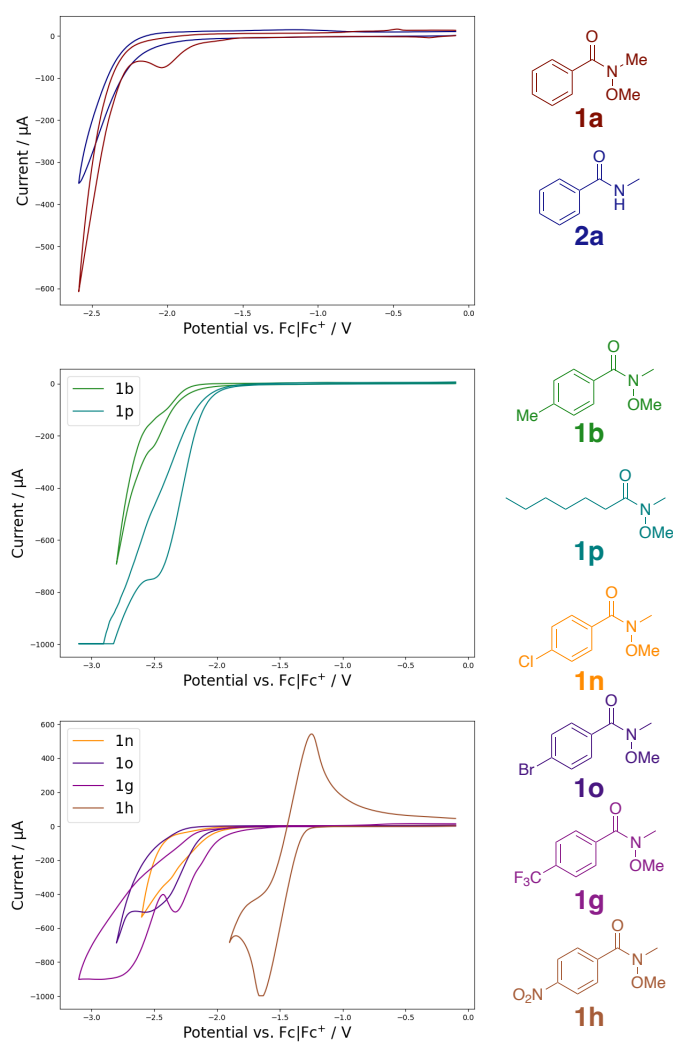


Figure S3. Cyclic voltammograms of various *N*-methoxy-*N*-methyl benzamides. The voltammetry was performed under the following conditions: solvent: CH₃CN, supporting electrolyte: Bu₄NBF₄ (0.1 mol/L), substrate concentration: 50 mM, working electrode: Pt, counter electrode: Pt coil, reference electrode: Ag/Ag⁺ (CH₃CN), standard: Fc/Fc⁺, scan rate: 100 mV/s.

5. DFT Calculations

Density functional theory (DFT) calculations were performed using Gaussian 16 program.¹⁹ Geometries were optimized at the M06-62X/6-31+G(d,p).²⁰ SMD solvation model²¹ in acetonitrile was applied. Thermochemical corrections were obtained from frequency calculations at the same level of theory. The energy profile was illustrated in Figure S2. Calculated structures are illustrated using ChemDraw and CYLView.²²

Underneath the Cartesian coordinates for the optimized geometries are listed the following energies:

Electronic energy (E)

Enthalpy at 298.15 K (H)

Gibbs free energy at 298.15 K and 1 mol/L (G)

Otherwise noted, all energies are given in Hartree.

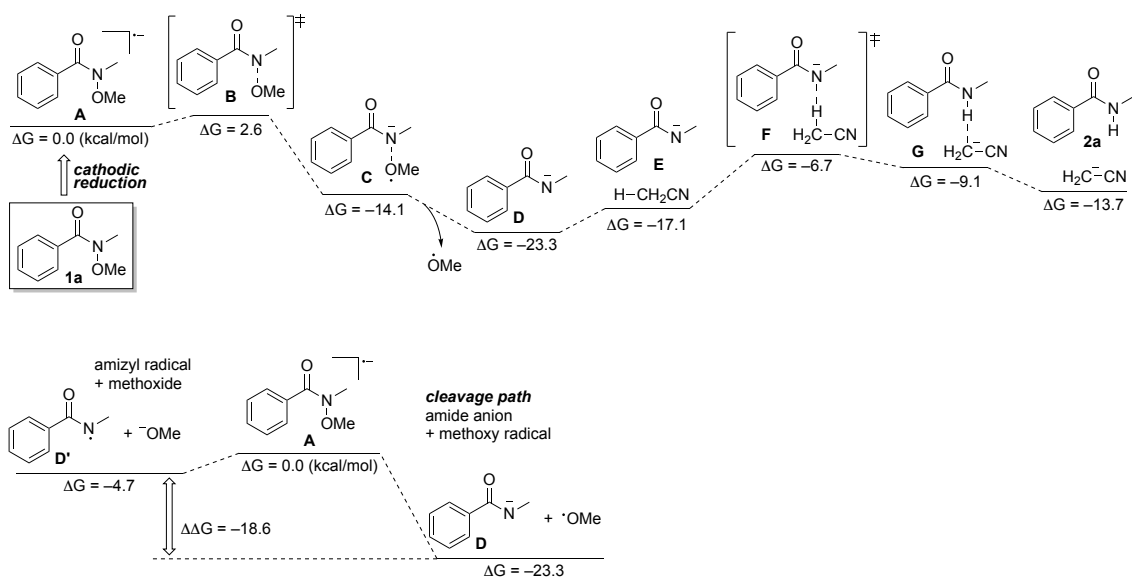
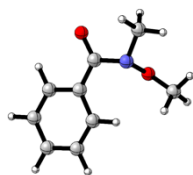


Figure S4. A plausible mechanism from calculations for the cathodic reduction and N–O bond cleavage of *N*-methyl-*N*-methoxybenzamide (**1a**) at the M06-2X/6-31+G(d,p)_{acetonitrile}(SMD) level of theory. Gibbs free energies (ΔG) were shown in parentheses in kcal/mol.



Radical anion of **1a** (**A**)

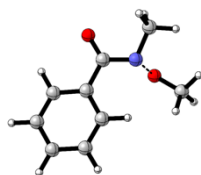
C	-2.1696740	-2.6093870	0.3575430
C	-0.7946290	-2.5247990	0.6534870
C	-0.1026560	-1.3309070	0.5400900
C	-0.7598050	-0.1273540	0.1238010
C	-2.1609140	-0.2318370	-0.1640110
C	-2.8333890	-1.4369950	-0.0511350
H	-2.7019520	-3.5513170	0.4442120
H	-0.2601350	-3.4147980	0.9797390
H	0.9548270	-1.3024860	0.7798760
H	-2.6879630	0.6644870	-0.4775430
H	-3.8962950	-1.4743000	-0.2819790
C	-0.1127350	1.1389120	-0.0055490
O	-0.7168510	2.2215620	-0.2662210
C	1.8694590	2.5166660	0.2147940
H	1.6897290	3.0256960	-0.7398070
H	1.3994720	3.0920770	1.0144220
H	2.9432550	2.4624550	0.4089930
O	1.9569100	0.4304460	-0.8323430
C	3.1422180	-0.1828620	-0.3626290
H	3.5051670	-0.8060530	-1.1840130
H	3.9132140	0.5561690	-0.1109220
H	2.9476750	-0.8089680	0.5158090
N	1.3204470	1.1669810	0.2348050

Imaginary frequency = 0

E = -554.604154

H = -554.406135

G = -554.456522



Transition state of N–O cleavage (**B**)

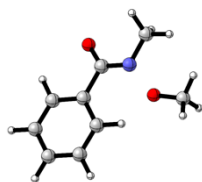
C	-1.0274140	0.3364730	0.2373370
C	0.3329630	0.4198750	0.5633430
C	1.0262050	1.6168420	0.4242010
C	0.3786910	2.7852950	-0.0409390
C	-0.9929260	2.6839950	-0.3693210
C	-1.6801680	1.4814490	-0.2311390
H	-1.5641950	-0.6014240	0.3440700
H	0.8566340	-0.4611330	0.9263460
H	2.0806350	1.6650640	0.6747030
H	-1.5007140	3.5721210	-0.7326280
H	-2.7350000	1.4343710	-0.4908470
C	1.0614340	4.0705480	-0.2031700
O	0.4480380	5.0971770	-0.6439270
C	2.9868540	5.4160160	0.1481840
H	2.7838670	5.9818850	-0.7671160
H	2.5511600	5.9603050	0.9930500
H	4.0653320	5.3400380	0.3073480
O	3.2136740	3.4075300	-1.1768210
C	4.3380650	2.7442540	-0.6739650
H	4.8743270	2.3089050	-1.5272570
H	5.0311420	3.4237370	-0.1533740
H	4.0735310	1.9300330	0.0165490
N	2.4157450	4.0787510	0.1172310

Imaginary frequency = 1

E = -554.597345

H = -554.401469

G = -554.452418



Intermediate C

C	-2.255639315723	-2.570064824640	0.393609642382
C	-0.965750713290	-2.480868119451	0.924332035924
C	-0.253059303840	-1.285463367083	0.840536510675
C	-0.813303173042	-0.158636231261	0.224441993638
C	-2.103244358838	-0.260463851199	-0.306448476063
C	-2.822654956340	-1.454327740391	-0.222440968094
H	-2.810924097807	-3.501528782406	0.458753698612
H	-0.514820033472	-3.346704743635	1.401810901977
H	0.750065220426	-1.213706159786	1.248255576088
H	-2.530072016333	0.613592632772	-0.788820596955
H	-3.824595420476	-1.513660788930	-0.638995255287
C	-0.065397762773	1.161247027322	0.105956457215
O	-0.606704581434	2.073462038303	-0.586685237460
C	1.770713085728	2.485399367688	0.584288650056
H	2.002399843655	2.696211035637	-0.472564384652
H	1.182107576670	3.344918276727	0.944531628125
H	2.714024501364	2.471103299801	1.142054099760
O	2.125080725551	-0.032368440587	-1.448946449282
C	3.337078315783	-0.173907488547	-0.812068898340
H	4.023111383149	-0.583267344625	-1.577547747287
H	3.757042139266	0.785362084204	-0.481348107073
H	3.302753485715	-0.893788753175	0.016273969335
N	1.080776506229	1.223803010590	0.755519882465

Imaginary frequency = 0

E = -554.619142

H = -554.422688

G = -554.47892



Methoxy radical

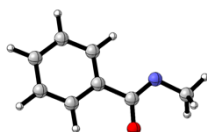
O	1.8548330	1.2526490	1.2265200
C	2.6873150	2.0379700	0.4722670
H	3.0815300	2.8005210	1.1734250
H	3.5531930	1.4860450	0.0837450
H	2.1551060	2.5801450	-0.3202640

Imaginary frequency = 0

E = -115.004039

H = -114.96327

G = -114.990201



Amide D

C	-3.338912895043	0.684822548913	-0.023162327565
C	-2.253290366739	1.500112724160	-0.353101558221
C	-0.963708998801	0.971192128326	-0.392697346466
C	-0.734059221008	-0.380727423002	-0.103808389627
C	-1.828849056206	-1.187280314468	0.225241957622
C	-3.121748892914	-0.662521744067	0.266239412246
H	-4.343416559705	1.097302694386	0.007566770746
H	-2.412852636540	2.550764473083	-0.580019072295
H	-0.121511100631	1.605573150007	-0.649103721289
H	-1.645724777411	-2.233803609410	0.448189952947
H	-3.959233031699	-1.305203708013	0.523998845445
C	0.657390535884	-1.002071935465	-0.134616728086
O	0.744589739780	-2.235727006822	0.144564245313
C	2.940611097426	-0.831123307271	-0.465291351089

H	3.209604040745	-1.262331912798	0.512370786572
H	2.993438000062	-1.662158627396	-1.186893967806
H	3.712365014369	-0.102311000325	-0.734951405905
N	1.641267108431	-0.185173129840	-0.451989102542

Imaginary frequency = 0

E = -439.612283

H = -439.459608

G = -439.503477



Acetonitrile

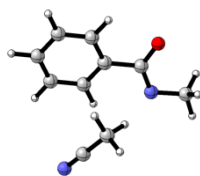
C	-0.5825290	0.3962850	-0.0233730
H	-0.2182050	-0.6326990	-0.0243360
H	-0.2182040	0.9115590	0.8673930
H	-1.6742160	0.3967880	-0.0242430
C	-0.0964840	1.0836730	-1.2141420
N	0.2892260	1.6290650	-2.1586520

Imaginary frequency = 0

E = -132.711334

H = -132.661152

G = -132.689655



Intermediate E

C	-2.4921960	1.6640890	-0.2315600
C	-2.0200870	0.6136370	-1.0226680
C	-0.6721660	0.2588000	-0.9864210
C	0.2276850	0.9440570	-0.1597890

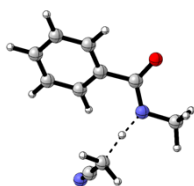
C	-0.2546320	1.9982600	0.6231690
C	-1.6033940	2.3568490	0.5914670
H	-3.5428250	1.9389530	-0.2576210
H	-2.7048810	0.0667210	-1.6654560
H	-0.3063830	-0.5629270	-1.5944260
H	0.4474830	2.5268550	1.2605900
H	-1.9611140	3.1753030	1.2103610
C	1.6989650	0.5635530	-0.0623710
O	2.4459720	1.3133530	0.6355840
C	3.4539000	-0.8572930	-0.5689600
H	4.1139870	-0.0564910	-0.9390120
H	3.7464730	-1.0286160	0.4796990
H	3.6796250	-1.7679420	-1.1339060
N	2.0467490	-0.5312340	-0.7082240
C	-0.4331130	-2.1414960	1.3554370
H	-0.1438240	-2.9222230	2.0621390
H	0.4471790	-1.7827500	0.8105050
H	-0.8900180	-1.3089160	1.8957880
C	-1.3954000	-2.6826060	0.4032670
N	-2.1568780	-3.1096730	-0.3566320

Imaginary frequency = 0

E = -572.327675

H = -572.123043

G = -572.183184



Transition state F

C	2.4244780	2.1903830	0.0824390
C	1.1448860	2.1394000	-0.4725970
C	0.4734300	0.9206350	-0.5732820
C	1.0759000	-0.2592880	-0.1218790
C	2.3651280	-0.2026980	0.4176090

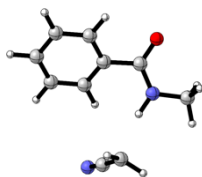
C	3.0342810	1.0154000	0.5270130
H	2.9462140	3.1396350	0.1632590
H	0.6700450	3.0477150	-0.8327090
H	-0.5163970	0.8829970	-1.0182550
H	2.8320570	-1.1244170	0.7518710
H	4.0312430	1.0492420	0.9569780
C	0.3790580	-1.5977210	-0.2071540
O	1.0671650	-2.6413200	-0.2625510
C	-1.6595040	-2.8093130	-0.2503280
H	-1.4900570	-3.3394580	-1.1958020
H	-1.3591560	-3.4856090	0.5613370
H	-2.7322540	-2.6094950	-0.1566190
N	-0.9513970	-1.5467140	-0.2072040
C	-2.4759130	0.3362320	0.9947820
H	-3.2907720	-0.2173820	1.4686720
H	-1.6316960	-0.5956290	0.3266100
H	-1.8735040	0.8534760	1.7465170
C	-2.9756320	1.2523810	0.0271820
N	-3.3276050	1.9587210	-0.8354500

Imaginary frequency = 1

E = -572.309894

H = -572.110857

G = -572.166664



Intermediate G

C	2.3793270	2.2139480	0.1410590
C	1.0770580	2.1449770	-0.3551510
C	0.4316560	0.9128730	-0.4594000
C	1.0898800	-0.2578160	-0.0682170
C	2.4013900	-0.1871190	0.4112730
C	3.0417270	1.0452710	0.5231550

H	2.8792400	3.1744710	0.2251310
H	0.5617900	3.0489220	-0.6670840
H	-0.5766930	0.8700950	-0.8613600
H	2.9074970	-1.1037350	0.6991600
H	4.0563490	1.0953140	0.9070060
C	0.4375050	-1.6096090	-0.1643060
O	1.1139600	-2.6298640	-0.3494930
C	-1.6199980	-2.8883680	-0.0979800
H	-1.4668340	-3.3788880	-1.0636580
H	-1.2960870	-3.5762970	0.6906640
H	-2.6833740	-2.6767840	0.0286890
N	-0.8995380	-1.6326970	-0.0381740
C	-2.7495330	0.5141910	1.1408010
H	-3.6040090	-0.1314580	1.3303320
H	-1.4252020	-0.8035410	0.3068300
H	-2.2230120	0.8698630	2.0237690
C	-2.8973320	1.4365770	0.1130410
N	-2.9561130	2.1799350	-0.8037510

Imaginary frequency = 0

E = -572.316119

H = -572.112346

G = -572.170541



Cyanomethanide

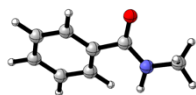
C	2.5665160	-1.2575060	1.1832560
H	3.5065010	-0.7399100	1.3363440
H	1.8908540	-1.3678910	2.0236200
C	2.4488110	-2.1211570	0.1174560
N	2.3297060	-2.8396870	-0.8190380

Imaginary frequency = 0

E = -132.192732

H = -132.15738

G = -132.186175



***N*-Methylbenzamide (2a)**

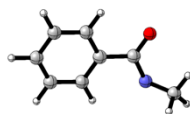
C	-2.8629940	-1.5482130	0.0705320
C	-1.5662240	-1.8194150	-0.3667830
C	-0.6226920	-0.7952720	-0.4391780
C	-0.9761770	0.5093620	-0.0778840
C	-2.2810410	0.7795570	0.3459220
C	-3.2196010	-0.2463800	0.4268330
H	-3.5949190	-2.3483130	0.1284670
H	-1.2886770	-2.8277760	-0.6582130
H	0.3764490	-1.0195370	-0.8020740
H	-2.5470490	1.7977140	0.6126640
H	-4.2283380	-0.0311370	0.7660200
C	-0.0114060	1.6607610	-0.1457810
O	-0.4096430	2.8210360	-0.2788590
C	2.3079420	2.4064710	-0.0968270
H	2.2219990	2.9796170	-1.0235760
H	2.2002740	3.0950050	0.7473230
H	3.2908240	1.9378860	-0.0548480
N	1.2999090	1.3633860	-0.0529180
H	1.5874620	0.4219780	0.1761280

Imaginary frequency = 0

E = -440.114239

H = -439.947139

G = -439.991599



Amizyl radical (**D'**)

C	-3.2668290	0.5974640	-0.2583090
C	-2.1564060	1.4049800	-0.5067130
C	-0.8715750	0.9078850	-0.2966310
C	-0.7003310	-0.4027360	0.1641080
C	-1.8152290	-1.2124810	0.4100220
C	-3.0959740	-0.7114910	0.2001100
H	-4.2671120	0.9875090	-0.4215980
H	-2.2903890	2.4222120	-0.8610500
H	-0.0054110	1.5356240	-0.4807410
H	-1.6663470	-2.2287690	0.7615820
H	-3.9613140	-1.3385120	0.3910050
C	0.6574150	-0.9805590	0.3734750
O	0.8437310	-2.0911790	0.8548090
C	2.8092000	-0.7390330	-0.6721050
H	2.8833900	-1.8170370	-0.4879250
H	2.6033470	-0.5953230	-1.7449090
H	3.7466750	-0.2329770	-0.4380480
N	1.7291180	-0.1462420	0.0654550

Imaginary frequency = 0

E = -439.43194

H = -439.279696

G = -439.326261



Methoxide

O	0.0000000	0.0000000	-0.8602930
C	0.0000000	0.0000000	0.4989650
H	0.0000000	1.0197310	0.9679160
H	-0.8831130	-0.5098650	0.9679160

H 0.8831130 -0.5098650 0.9679160

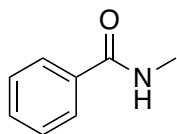
Imaginary frequency = 0

E = -115.153481

H = -155.112699

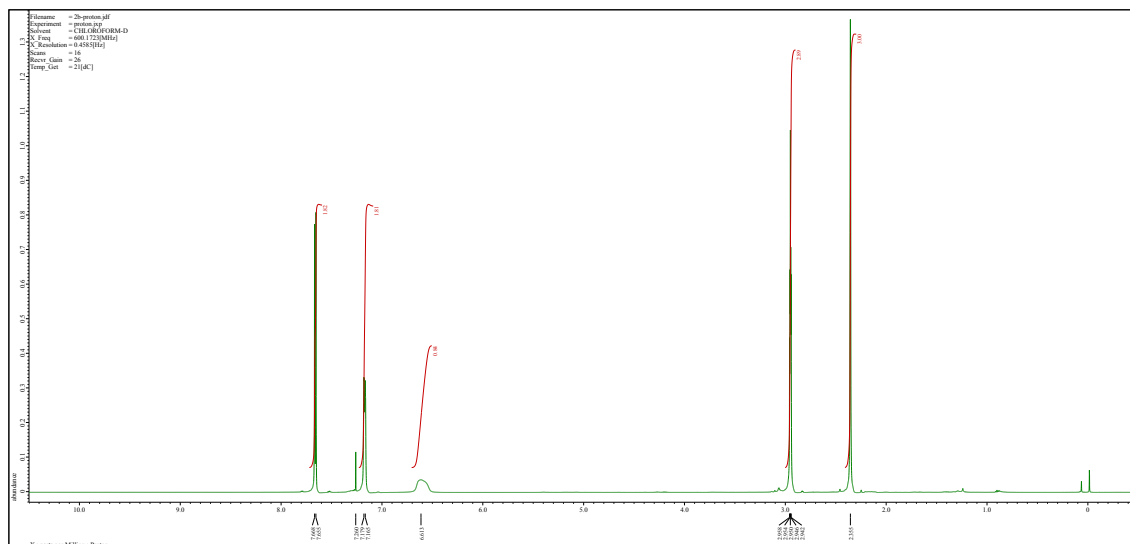
G = -115.137763

6. Copies of NMR Spectra

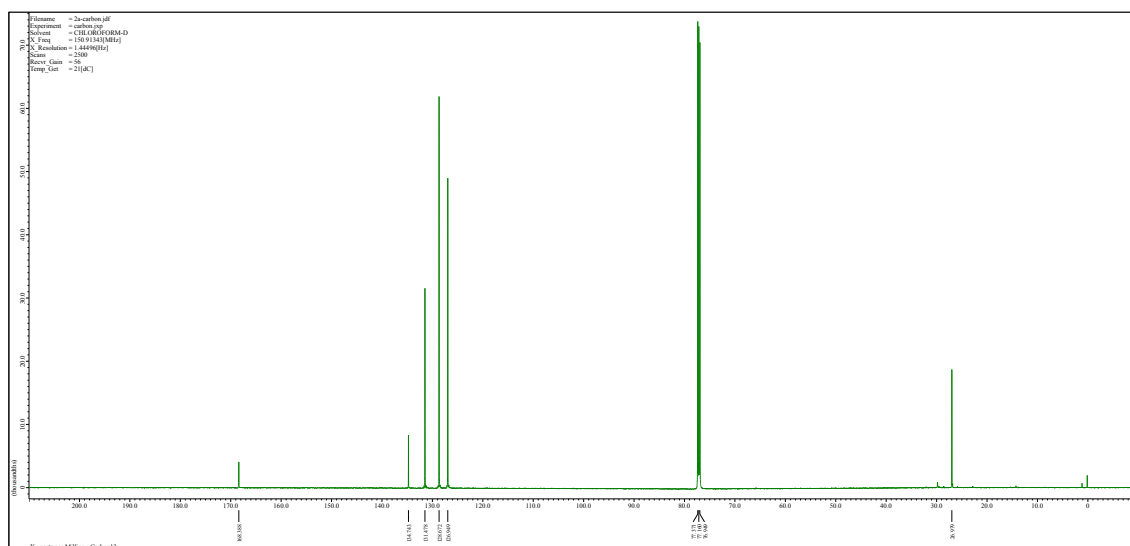


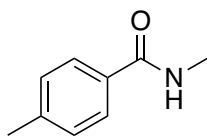
N-methylbenzamide (**1a**)

^1H NMR (600 MHz, CDCl_3)



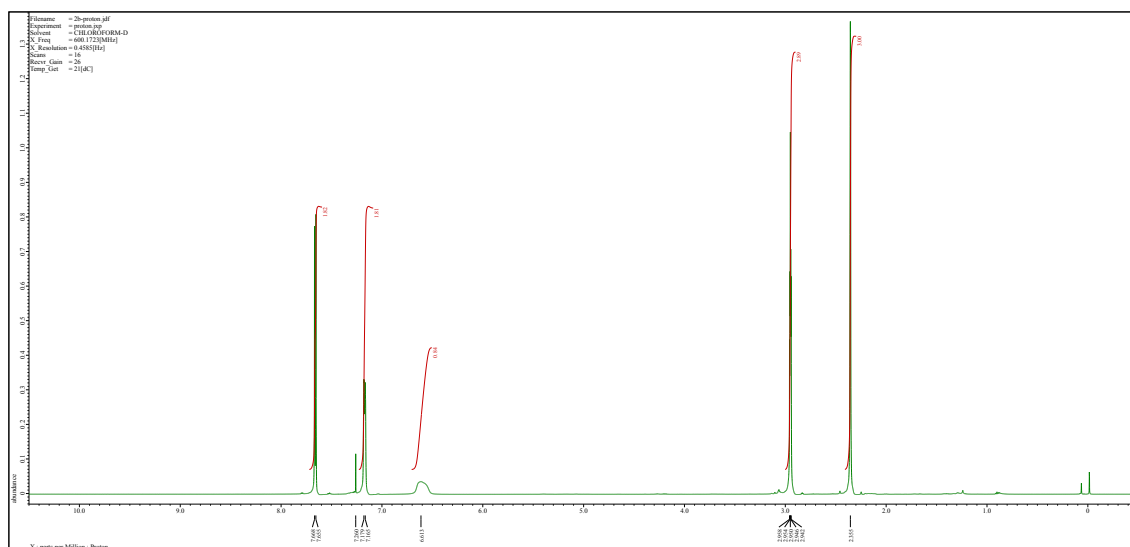
^{13}C NMR (150 MHz, CDCl_3)



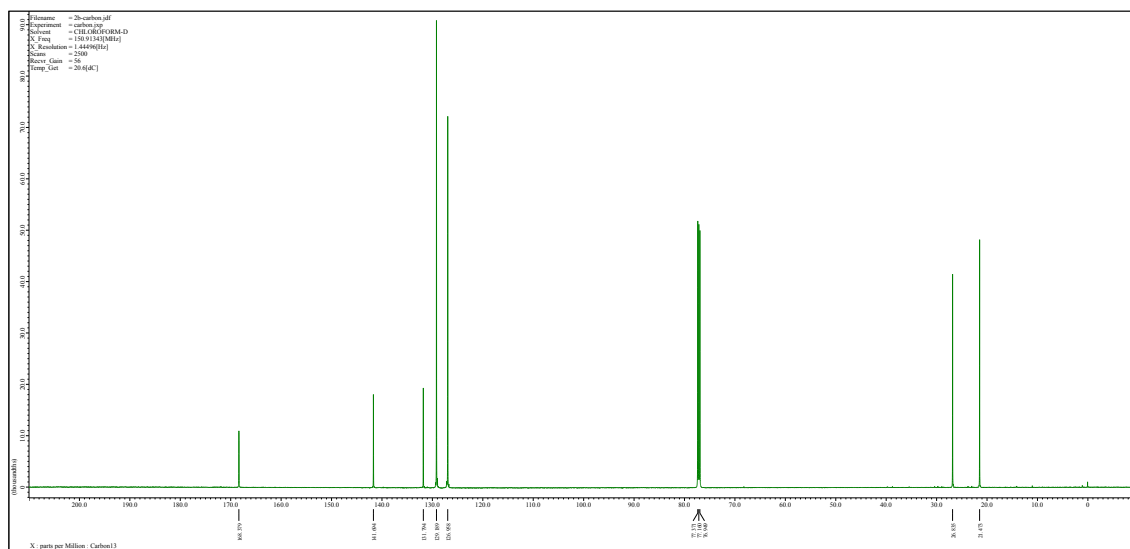


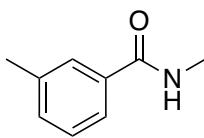
N,4-dimethylbenzamide (**2b**)

^1H NMR (600 MHz, CDCl_3)



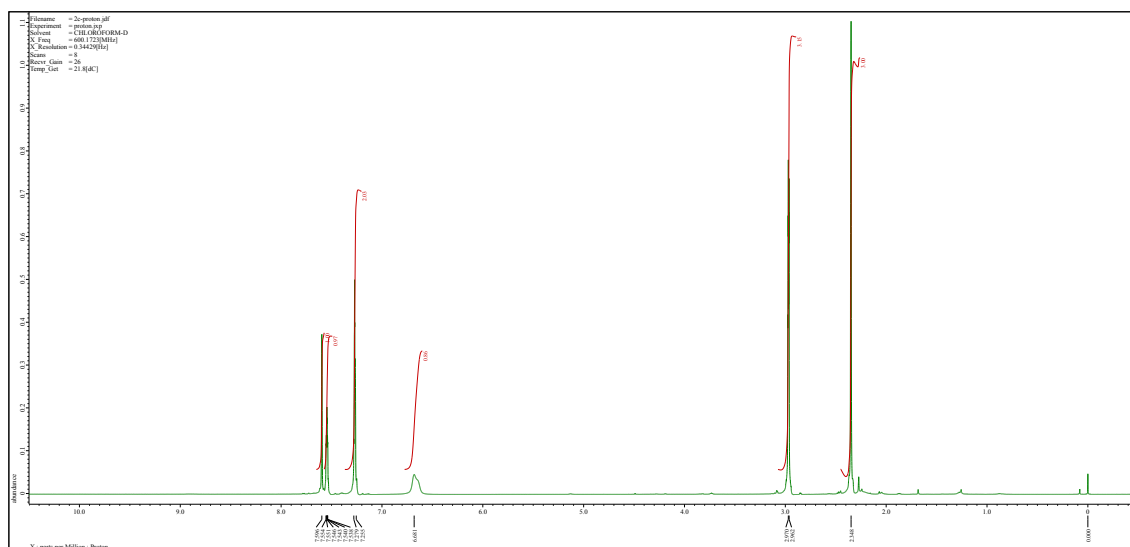
^{13}C NMR (150 MHz, CDCl_3)



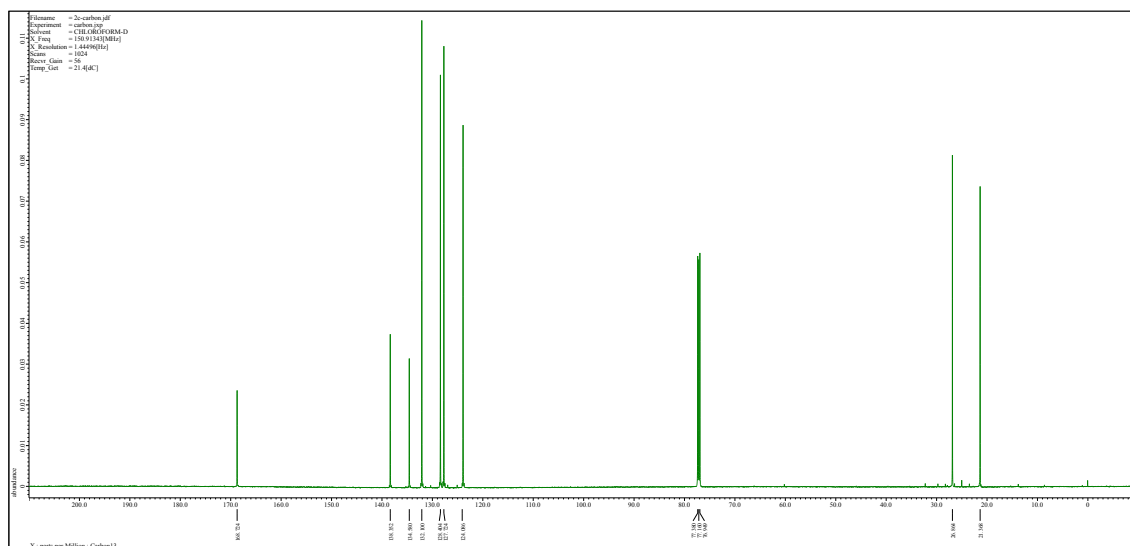


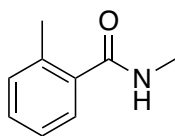
N,3-dimethylbenzamide (**2c**)

^1H NMR (600 MHz, CDCl_3)



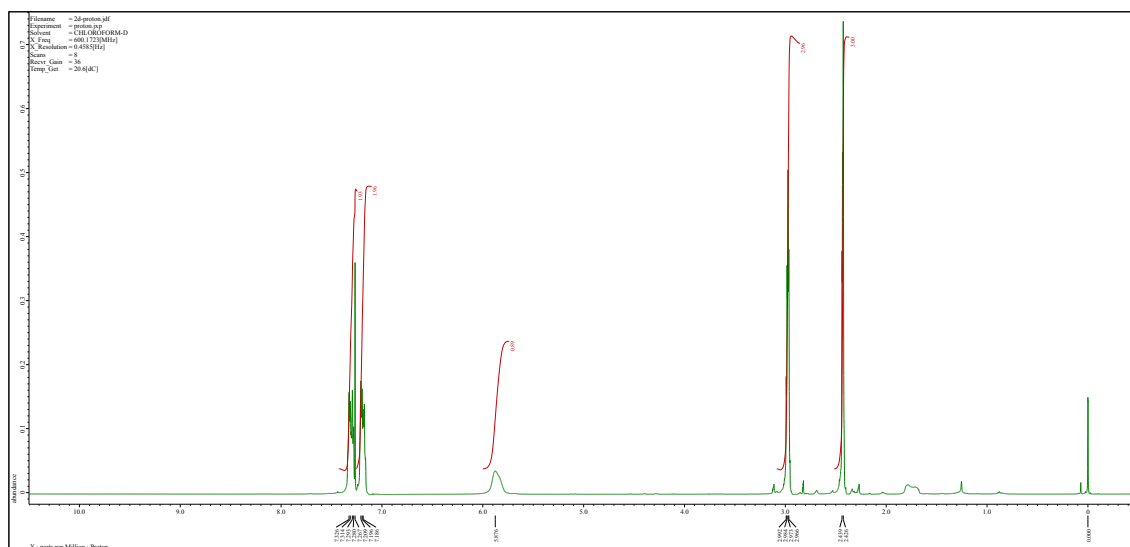
^{13}C NMR (150 MHz, CDCl_3)



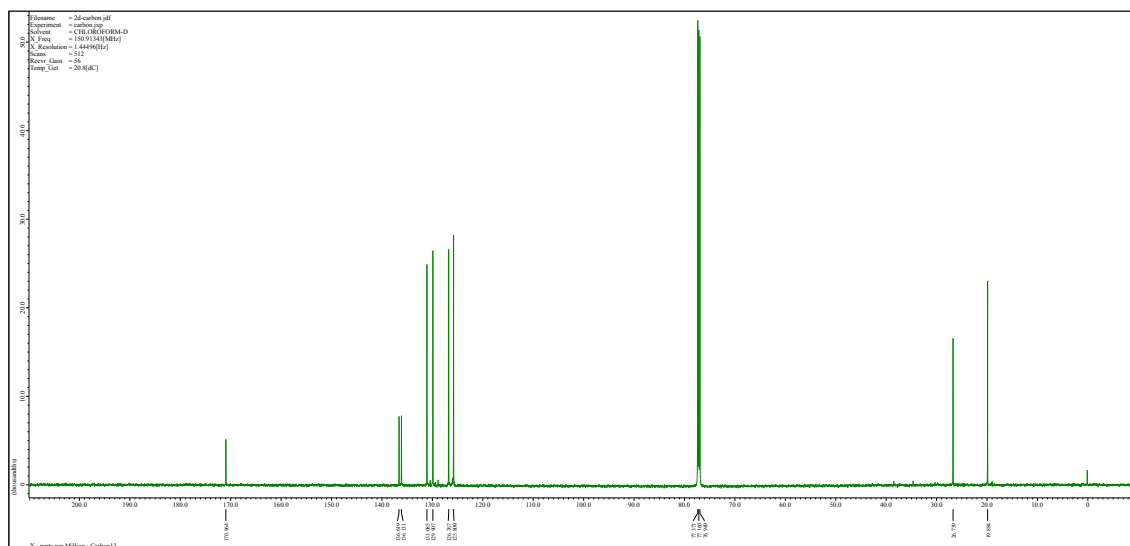


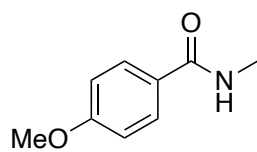
N,2-dimethylbenzamide (**2d**)

^1H NMR (600 MHz, CDCl_3)



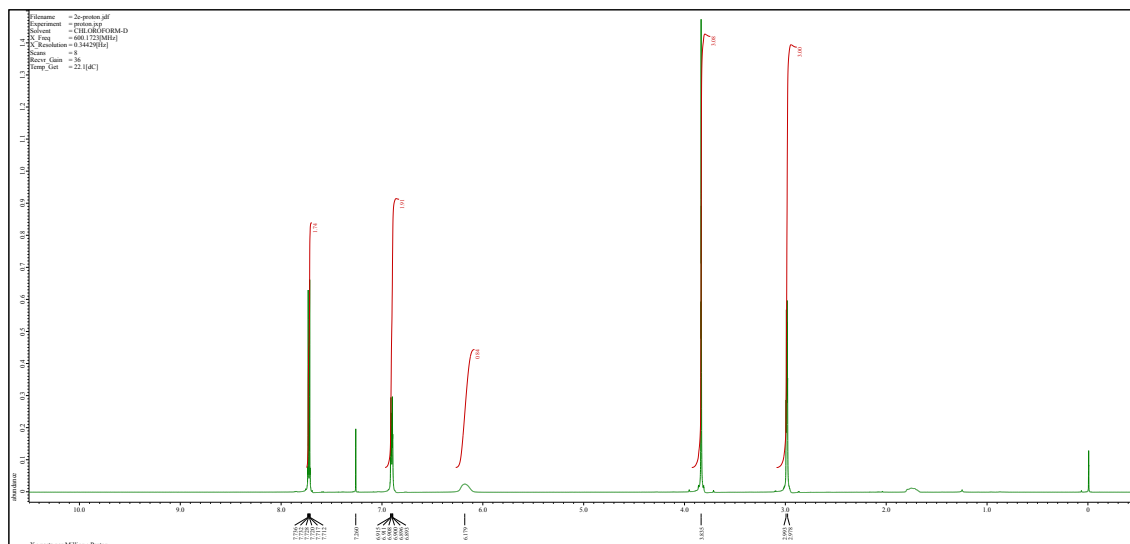
^{13}C NMR (150 MHz, CDCl_3)



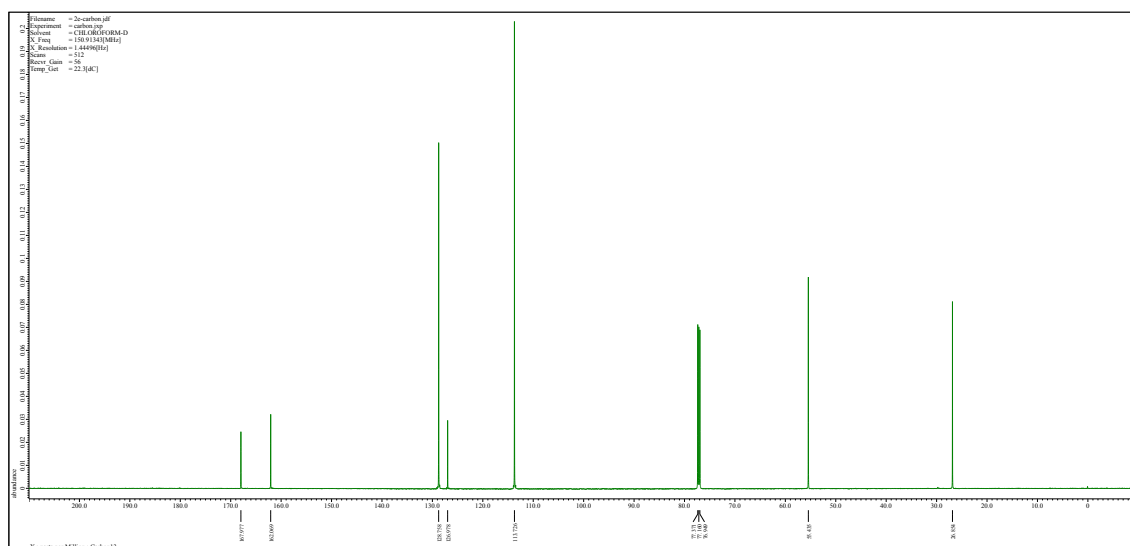


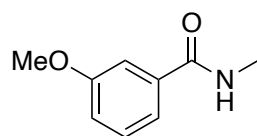
N-methyl-4-methoxybenzamide (**2e**)

^1H NMR (600 MHz, CDCl_3)



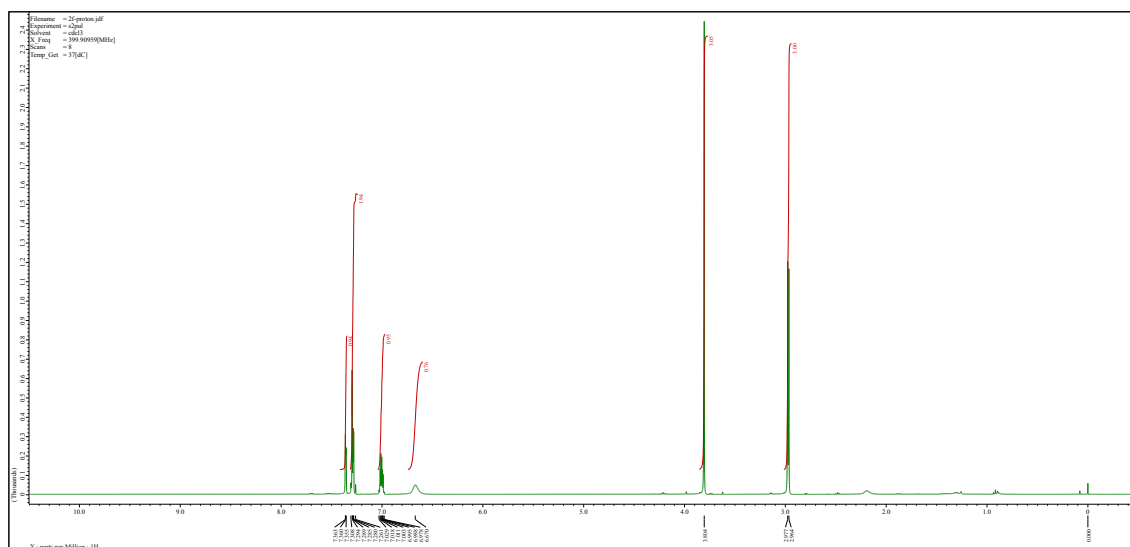
^{13}C NMR (150 MHz, CDCl_3)



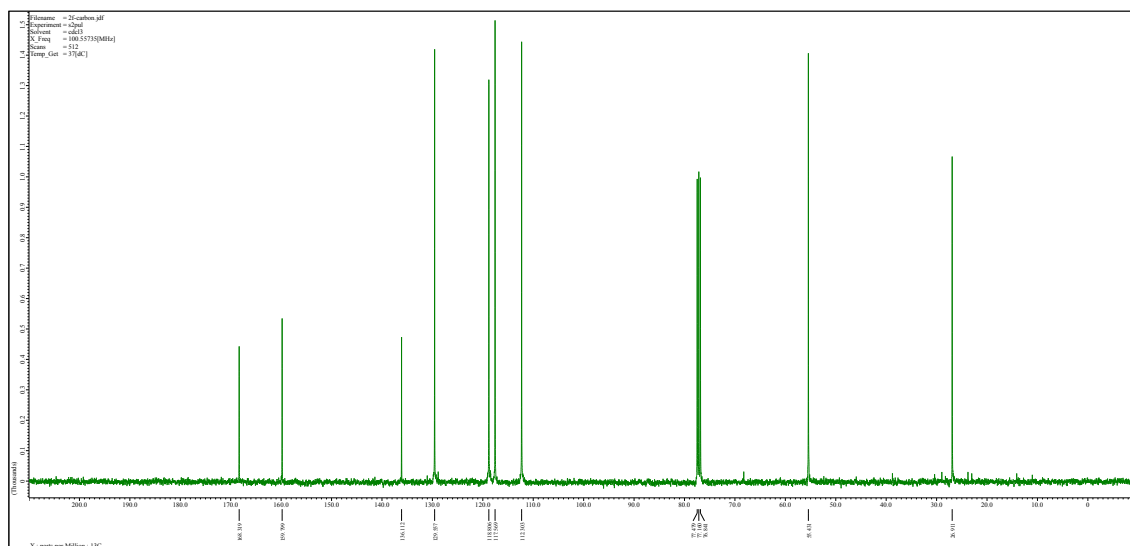


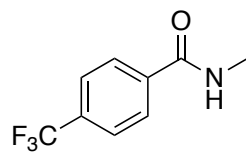
N-methyl-3-methoxybenzamide (**2f**)

^1H NMR (400 MHz, CDCl_3)



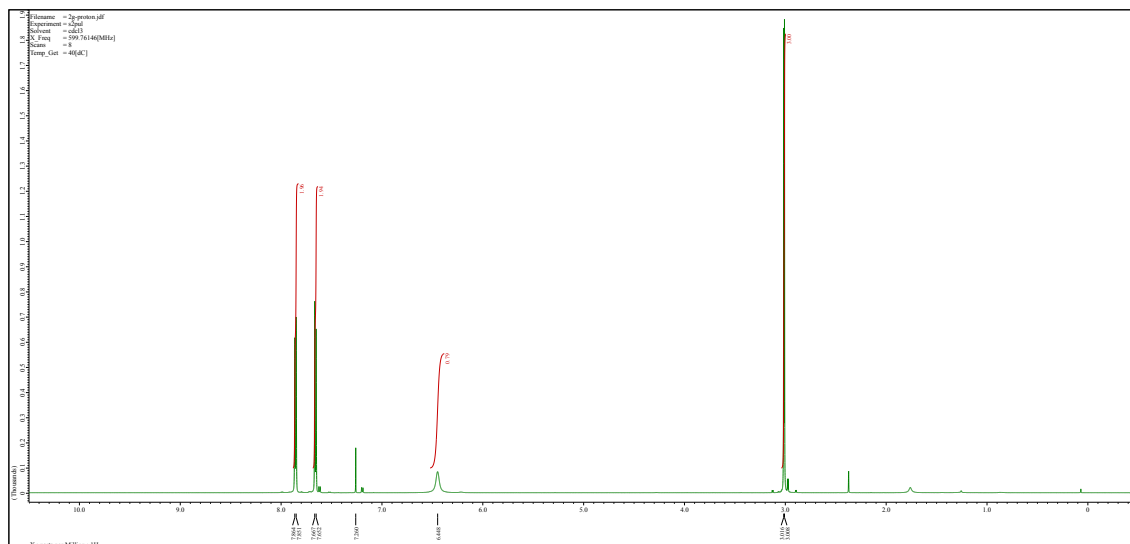
^{13}C NMR (100 MHz, CDCl_3)



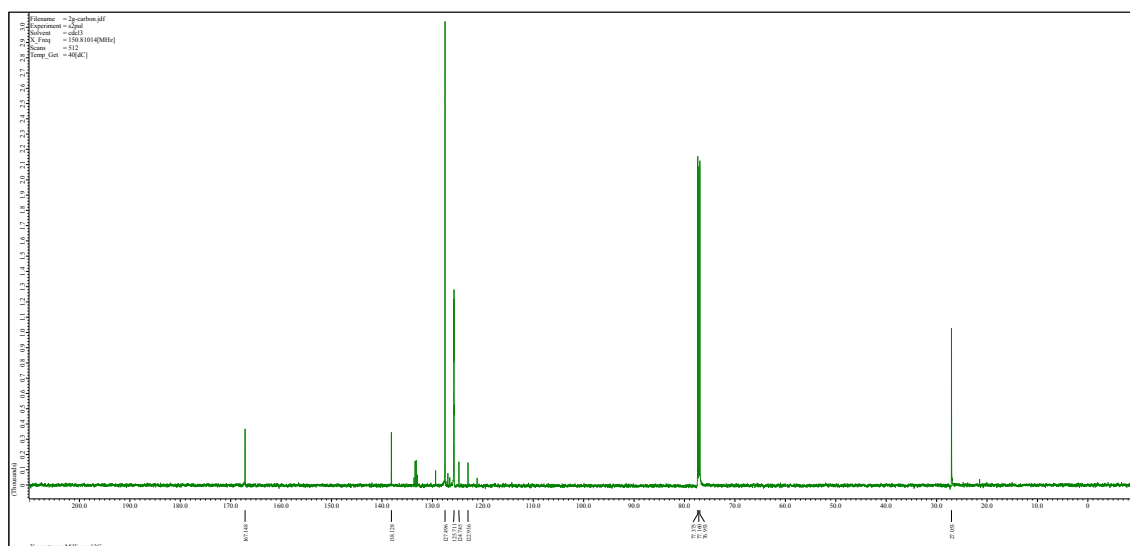


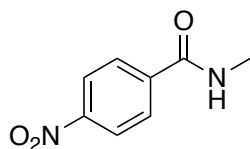
N-methyl-4-trifluoromethylbenzamide (**2g**)

^1H NMR (600 MHz, CDCl_3)



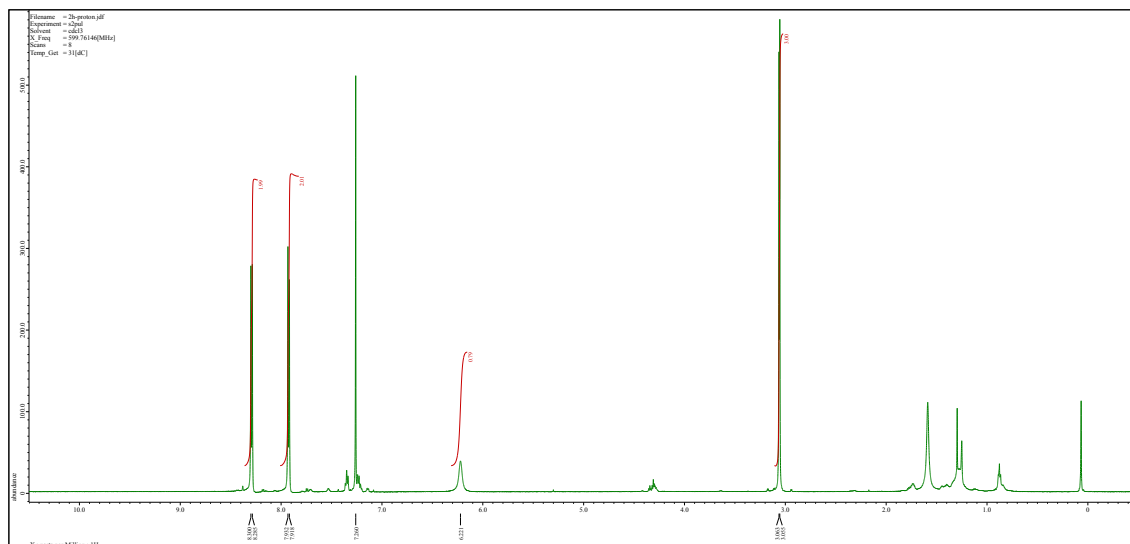
^{13}C NMR (150 MHz, CDCl_3)



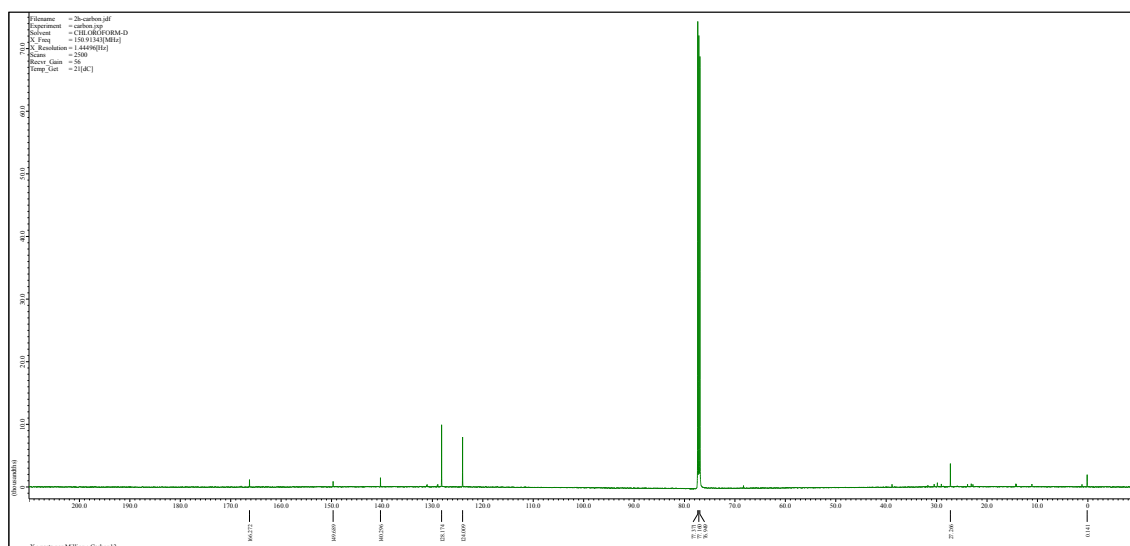


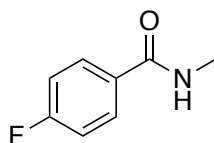
N-methyl-4-nitrobenzamide (**2h**)

^1H NMR (600 MHz, CDCl_3)



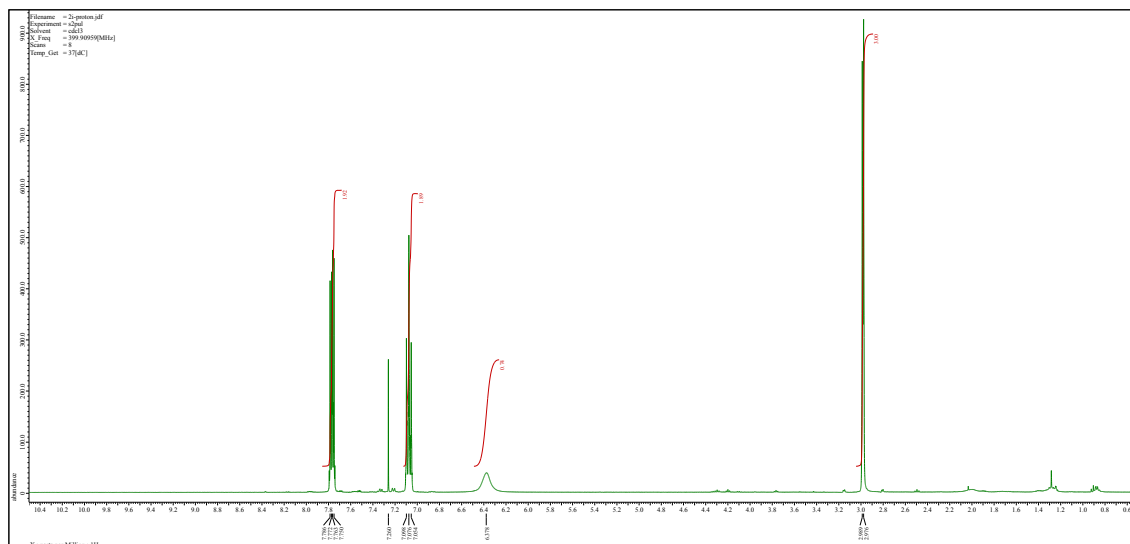
^{13}C NMR (150 MHz, CDCl_3)



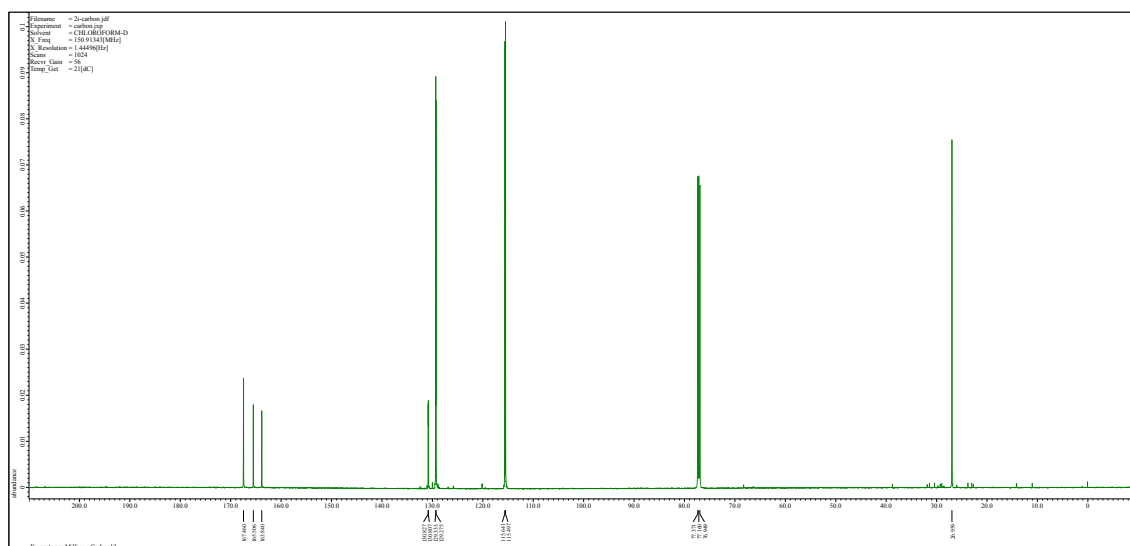


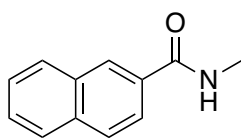
N-methyl-4-fluorobenzamide (**2i**)

^1H NMR (400 MHz, CDCl_3)



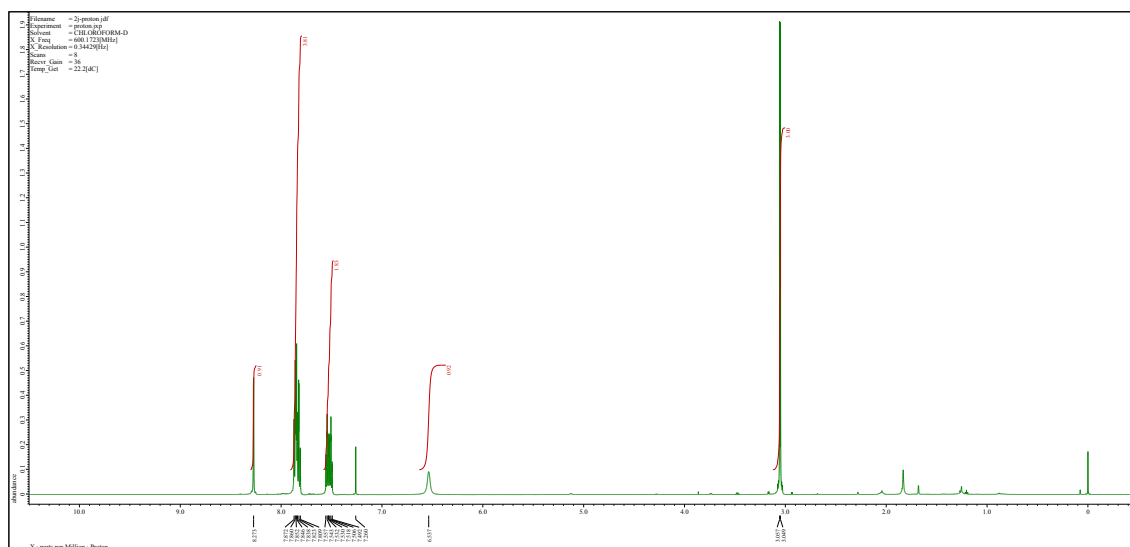
^{13}C NMR (150 MHz, CDCl_3)



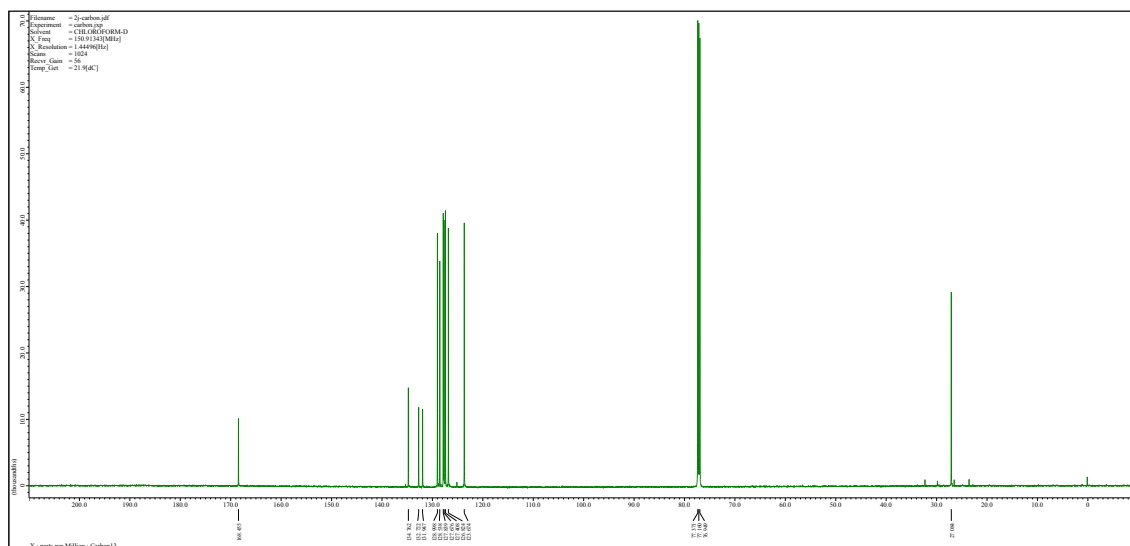


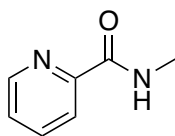
N-methylnaphthalene-2-carboxamide (**2j**)

^1H NMR (600 MHz, CDCl_3)



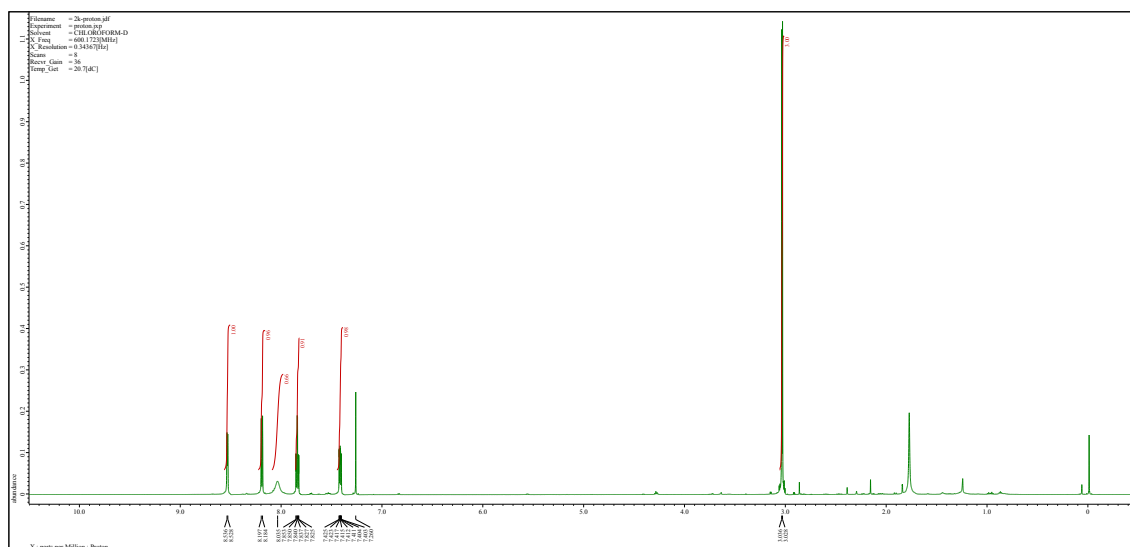
^{13}C NMR (150 MHz, CDCl_3)



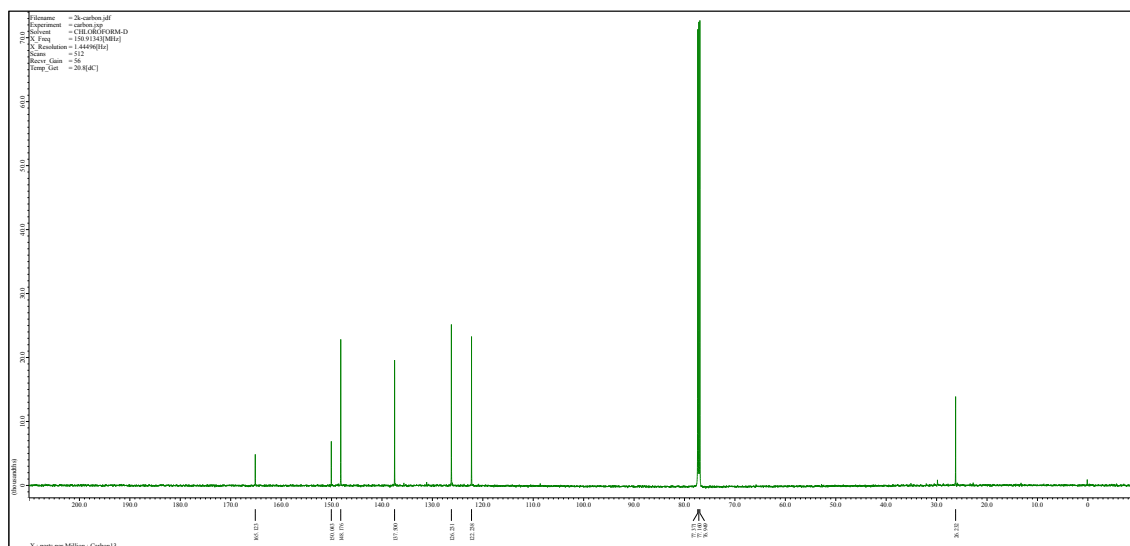


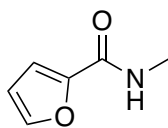
N-methyl-2-picolinamide (**2k**)

^1H NMR (600 MHz, CDCl_3)



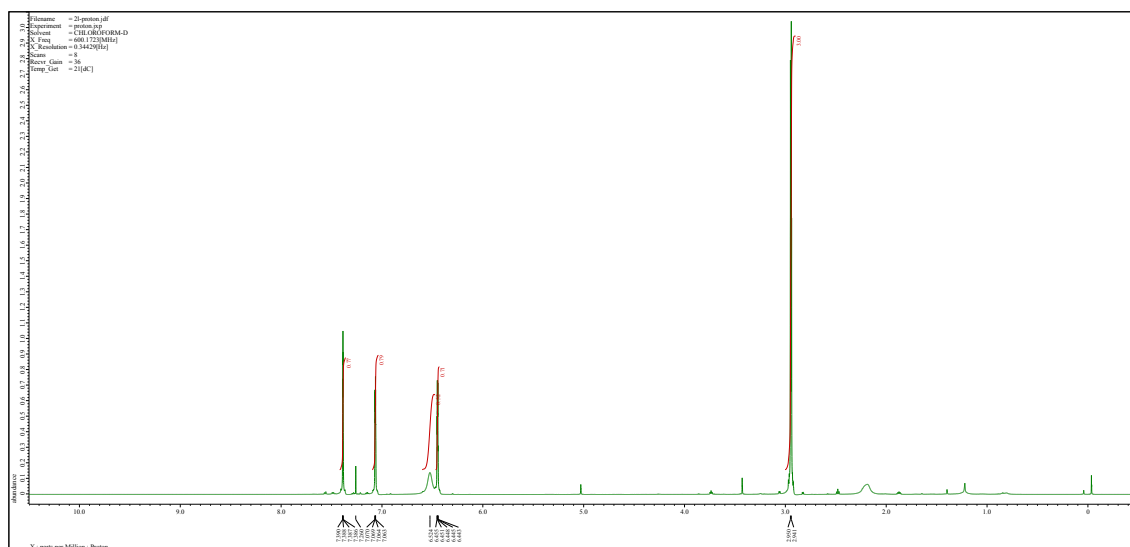
^{13}C NMR (150 MHz, CDCl_3)



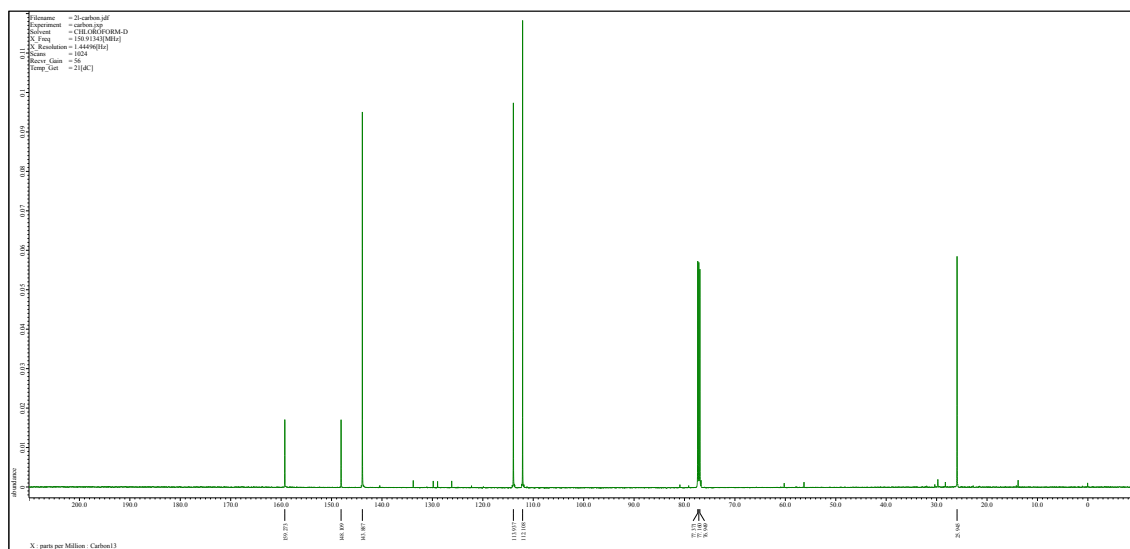


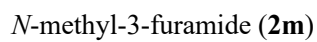
N-methyl-2-furamide (**2l**)

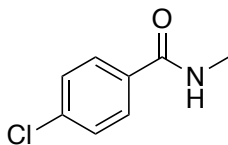
^1H NMR (600 MHz, CDCl_3)



^{13}C NMR (150 MHz, CDCl_3)

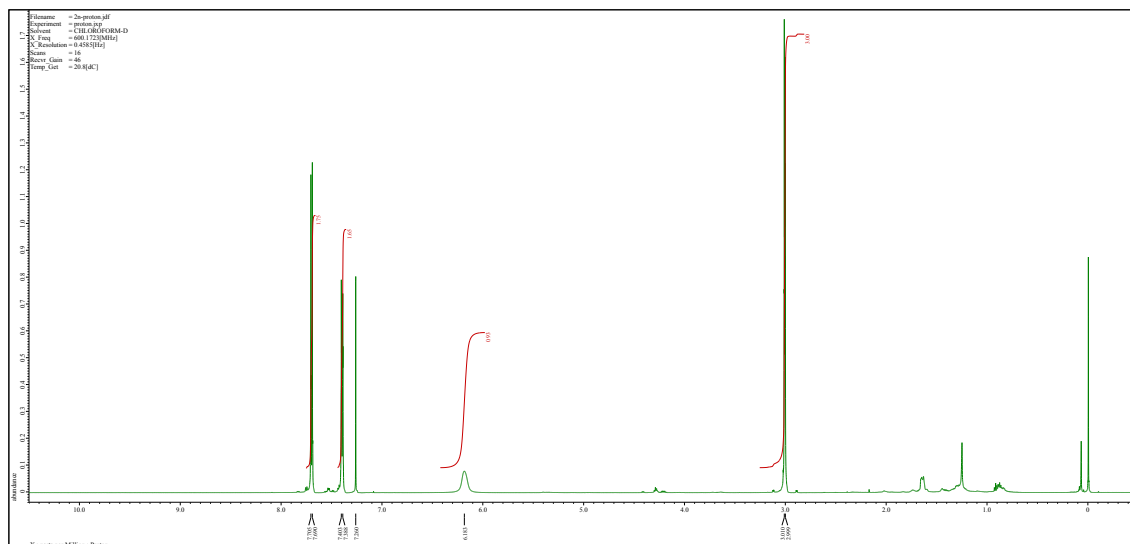


¹H NMR (600 MHz, CDCl₃)

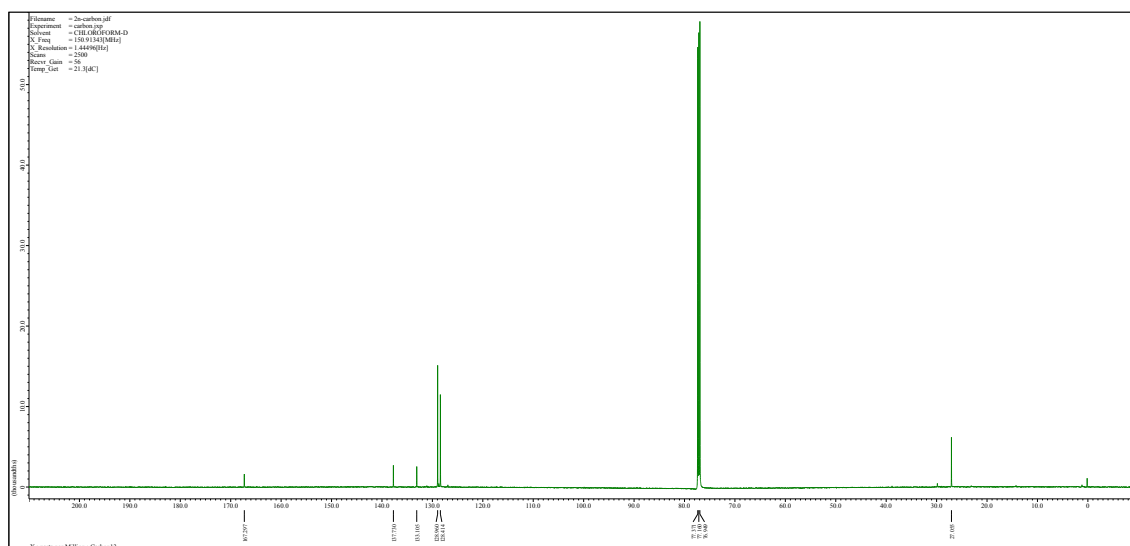


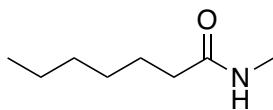
N-methyl-4-chlorobenzamide (**2n**)

^1H NMR (600 MHz, CDCl_3)



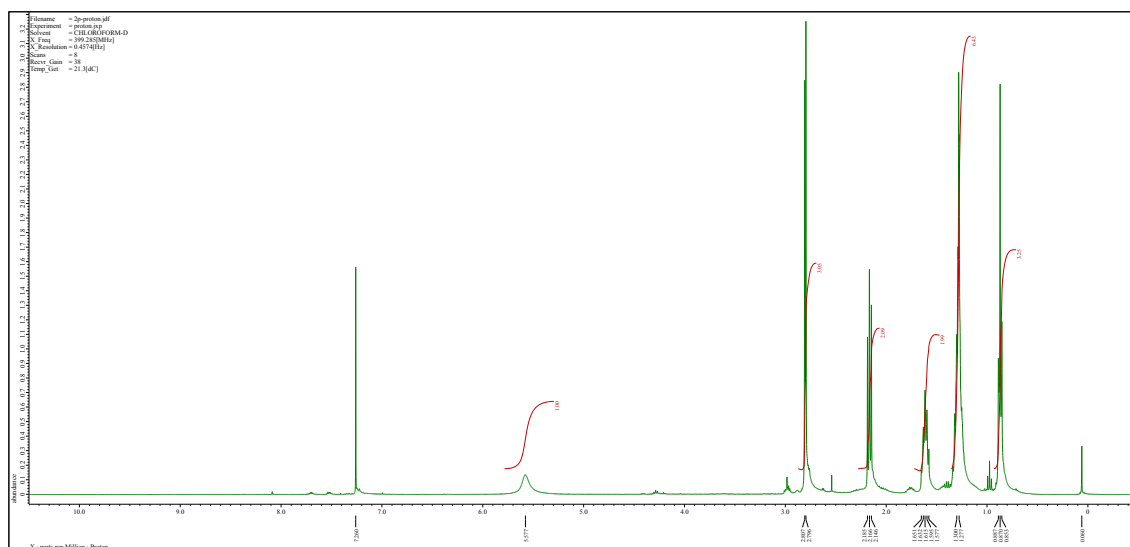
^{13}C NMR (150 MHz, CDCl_3)



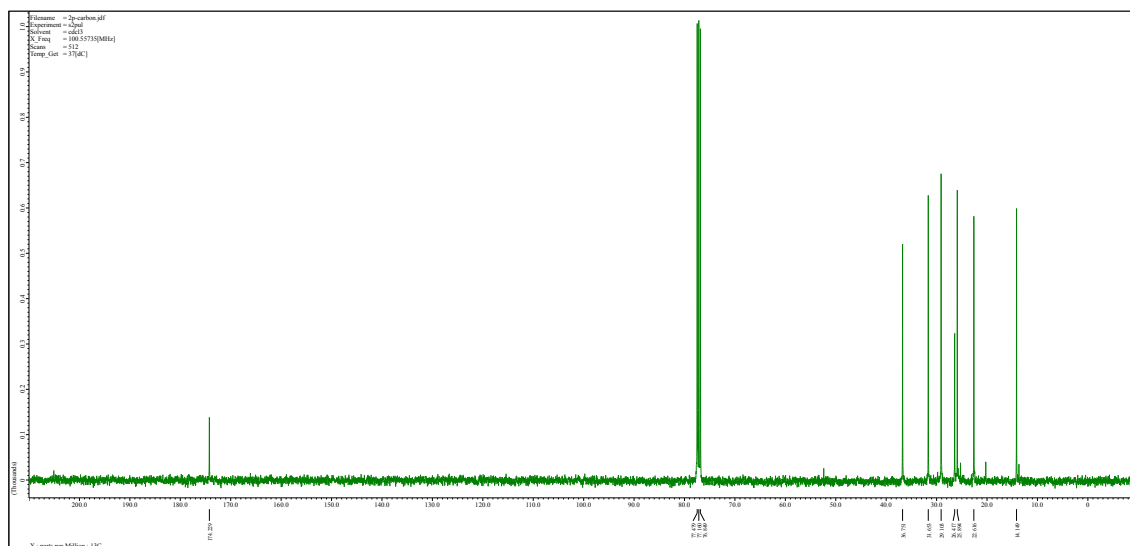


N-methylheptanamide (**2p**)

^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (150 MHz, CDCl_3)



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