Electronic Supplementary Material (ESI) for ChemComm.

Mild Hypervalent Iodine Mediated Oxidative Nitration of *N*-Aryl Sulfonamides

Ulrich Kloeckner and Boris J. Nachtsheim*

Institut für Organische Chemie, Eberhard Karls Universität Tübingen,

Auf der Morgenstelle 18, 72076 Tübingen, Germany

*Corresponding author: Boris.nachtsheim@uni-tuebingen.de

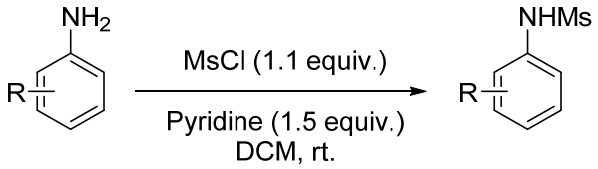
Table of Contents

General Information

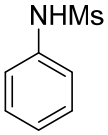
Reagents were either used as received from their commercial supplier or purified according to *Purification of Common Laboratory Chemicals*.[1] Dry solvents were obtained from an MBraun SPS-800 solvent purification system. Thin layer chromatography was performed on fluorescence indicator marked precoated silica gel 60 plates (Macherey-Nagel, ALUGRAM Xtra SIL G/UV254) and visualized by UV light (254 nm/366 nm). Flash column chromatography was performed on silica gel (0.040 – 0.063 mm).

NMR spectra were recorded on an *Avance* 400 MHz instrument. Chemical shifts for 1H NMR were reported as δ (parts per million) relative to the residual signals of CHCl3 at 7.26 ppm (s) or DMSO at 2.50 ppm (qui). Chemical shifts for 13C NMR were reported as δ (parts per million) relative to the CDCl3 triplet at 77.0 ppm or the DMSO-D6 septet at 39.5 ppm. The following abbreviations were used to describe splitting patterns: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sept = septet, m = multiplet. Coupling constants *J* are given in Hertz. Mass spectra were recorded on a Finnigan MAT95 using EI or FAB method. High resolution mass spectra were recorded on an APEX II Bruker Daltonics using ESI method.

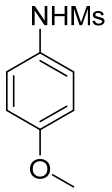
General Procedure for the Preparation of Methanesulfonamides



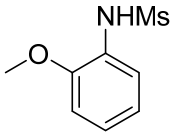
To a solution of the corresponding aniline (2.5 mmol, 1.0 equiv.) and pyridine (3.75 mmol, 303 µL, 1.5 equiv.) in methylene chloride (5 mL) at 0 °C under an argon atmosphere methansulfonyl chloride (2.75 mmol, 213 µL, 1.1 equiv) was added slowly and subsequently the reaction mixture was allowed to warm to room temperature. After complete conversion of the starting material (checked by TLC), the reaction was quenched by addition of water (10 mL). The aqueous layer was extracted three times with methylene chloride, the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (toluene/ethylacetate) affording the desired arylmethanesulfonamides.



***N*-Phenylmethanesulfonamide**[2] (**1a**); yield 91% (12 h); white solid; eluent: toluene/ethyl acetate (30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.26 – 7.24 (m, 2H), 7.20 (br. s, 1H), 7.19 – 7.15 (m, 1H), 3.00(s, 3H); ^{13}C NMR (101 MHz) δ 136.7, 129.6, 125.3, 120.8, 39.1; HRMS (ESI) calculated for $C_7H_9NO_2SNa$ $[M+Na]^+$: 194.024620, found: 194.024774.

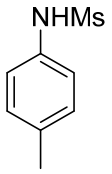


***N*-(4-Methoxyphenyl)methanesulfonamide**[2] (**1b**); yield: 89% (24 h); white solid; eluent: toluene/ethyl acetate (10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.19 (m, 2H), 6.91 – 6.88 (m, 2H), 6.42 (br. s, 1H), 3.80 (s, 3H), 2.95 (s, 3H); ^{13}C NMR (101 MHz) δ 158.2, 128.9, 124.8, 114.8, 55.5, 38.9; HRMS (ESI) calculated for $C_8H_{11}NO_3SNa$ $[M+Na]^+$: 224.035185, found: 224.035246.

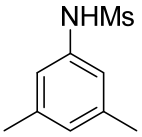


***N*-(2-Methoxyphenyl)methanesulfonamide**[3] (**1c**); yield: 98% (3 h); white solid; eluent: toluene/ethyl acetate (5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.9 and 1.5 Hz, 1H), 7.16 – 7.12 (m, 1H), 6.99 – 6.95 (m, 1H), 6.92 (dd, *J* = 8.2 and 1.4 Hz, 1H), 6.82 (br.s, 1H) 3.88 (s, 3H), 2.95 (s, 3H); ^{13}C NMR (101 MHz) δ 149.4, 126.0, 125.5, 121.3, 120.8, 110.7, 55.7, 39.0; HRMS (ESI) calculated for $C_8H_{11}NO_3SNa$ $[M+Na]^+$: 224.035185, found: 224.035180.

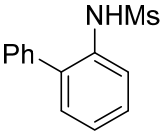
***N*-(*p*-tolyl)methanesulfonamide**[4] (**1d**); yield: 90% (3 h); white solid; eluent: toluene/ethyl acetate (5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 4H), 7.02 (br. s, 1H), 2.98 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz) δ 135.5, 134.0, 130.1, 121.5, 38.9, 20.8; HRMS (ESI) calculated for $C_8H_{11}NO_2SNa$ [M+Na]$^+$: 208.040270, found: 208.040232.



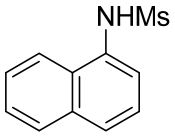
***N*-(3,5-Dimethylphenyl)methanesulfonamide**[2] (**1e**); yield 91% (5 h); white solid; eluent: toluene/ethyl acetate (10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 2H), 6.83 (s, 1H), 6.79 (br.s, 1H), 3.01 (s, 3H), 2.30 (s, 6H); ^{13}C NMR (101 MHz) δ 139.5, 136.5, 127.1, 118.3, 39.1, 21.3; HRMS (ESI) calculated for $C_9H_{13}NO_2SNa$ [M+Na]$^+$: 222.055920, found: 222.055945.



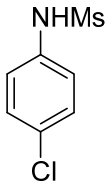
***N*-([1,1'-biphenyl]-2-yl)methanesulfonamide**[5] (**1f**); yield: 96% (8 h); white solid; eluent: toluene/ethyl acetate (5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.66 (m, 1H), 7.52 – 7.48 (m, 2H), 746 – 7.37 (m, 2H), 7.34 – 7.32 (m, 2H), 7.28 (dd, *J* = 7.6 and 1.8 Hz, 1H), 7.25 – 7.21 (m, 1H), 6.51 (br. s, 1H), 2.87 (s, 3H); ^{13}C NMR (101 MHz) δ 137.3, 133.9, 133.2, 130.7, 129.4, 129.0, 128.4, 124.9, 120.0 (2*), 39.6; HRMS (ESI) calculated for $C_{13}H_{13}NO_2SNa$ [M+Na]$^+$: 270.055920, found: 270.055773.



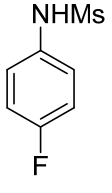
***N*-(Naphtalen-1-yl)-methanesulfonamide**[6] (**1g**); yield: 98% (3 h); white solid; eluent: toluene/ethyl acetate (10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 1H), 7.92 – 7.90 (m, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.58 – 7.54 (m, 1H), 7.51 – 7.47 (m, 1H), 7.07 (br. s, 1H), 3.02 (s, 3H); ^{13}C NMR (101 MHz) δ 134.4, 131.3, 128.8, 128.6, 127.5, 127.1, 126.5, 125.7, 122.6, 121.1, 39.8; HRMS (ESI) calculated for $C_{11}H_{11}NO_2SNa$ [M+Na]$^+$: 244.040270, found: 244.040220.



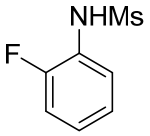
***N*-(4-Chlorophenyl)methanesulfonamide**[3] (**1h**); yield 83% (5 h); white solid; eluent: toluene/ethyl acetate (10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.20 – 7.16 (m, 2H), 6.72 (br. s , 1H), 3.02 (s, 3H); ^{13}C NMR (101 MHz) δ 135.2, 131.1, 129.8, 122.1, 39.4; HRMS (ESI) calculated for $C_7H_8ClNO_2SNa$ [M+Na]$^+$: 227.985648, found: 227.985644.



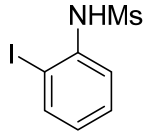
***N*-(4-Fluorophenyl)methanesulfonamide** (**1i**); yield: 89% (4 h); white solid; eluent: toluene/ethyl acetate (5:1); ^{1}H NMR (400 MHz, DMSO) δ 9.69 (br. s, 1H), 7.26 – 7.16 (m, 4H), 2.95 (s, 3H); ^{13}C NMR (101 MHz) δ 159.0 (d, *J* = 240.5 Hz), 134.5 (d, *J* = 2.6 Hz), 122.5 (d, *J* = 8.3 Hz), 115.9 (d, *J* = 22.6 Hz), 38.9; HRMS (ESI) calculated for $C_7H_8FNO_2SNa$ [M+Na]$^+$: 212.015198, found: 212.015073.



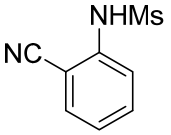
***N*-(2-Fluorophenyl)methanesulfonamide** (**1j**); yield: 98% (2 h); white solid; eluent: toluene/ethyl acetate (5:1); ^{1}H NMR (400 MHz, DMSO) δ 9.61 (br. s, 1H), 7.42 – 7.38 (m, 1H), 7.31 – 7.17 (m, 3H), 3.02 (s, 3H); ^{13}C NMR (101 MHz) δ 155.6 (d, *J* = 246.2 Hz), 127.1 (d, *J* = 7.6 Hz), 126.7, 124.9 (d, *J* = 12.8 Hz), 124.7 (d, *J* = 3.8 Hz), 116.0 (d, *J* = 19.9 Hz), 40.2 (d, *J* = 1.4 Hz); HRMS (ESI) calculated for $C_7H_8FNO_2SNa$ [M+Na]$^+$: 212.015198, found: 212.015252.



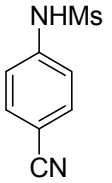
***N*-(2-Iodophenyl)methanesulfonamide**[7] (**1k**); yield 83% (5 h); white solid; eluent: toluene/ethyl acetate (100:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0 and 1.4 Hz, 1H), 7.65 (dd, *J* = 8.2 and 1.5 Hz, 1H), 7.40 – 7.36 (m, 1H), 6.96 – 6.92 (m, 1H), 6.64 (br. s, 1H), 3.01 (s, 3H); ^{13}C NMR (101 MHz) δ 139.4, 137.6, 129.9, 127.2, 122.4, 92.1, 40.1; HRMS (ESI) calculated for $C_7H_8INO_2SNa$ [M+Na]$^+$: 319.921264, found: 319.921483.



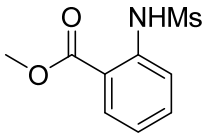
***N*-(2-Cyanophenyl)methanesulfonamide**[8] (**1m**); yield: 49% (24 h); white solid; eluent: toluene/ethyl acetate (5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.28 (dd, *J* = 7.6 and 1.1 Hz, 1H), 7.11 (br. s, 1H), 3.14 (s, 3H); ^{13}C NMR (101 MHz) δ 139.3, 134.5, 133.1, 125.4, 121.7, 116.0, 104.4, 40.6; HRMS (ESI) calculated for $C_8H_8N_2O_2SNa$ [M+Na]$^+$: 219.019869, found: 219.019825.



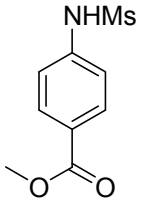
***N*-(4-Cyanophenyl)methanesulfonamide**[3] (**1n**); yield: 35% (6 h); white solid; eluent: toluene/ethyl acetate (5:1); ^{1}H NMR (400 MHz, DMSO) δ 10.50 (br. s, 1H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 3.14 (s, 3H); ^{13}C NMR (101 MHz) δ 142.9, 133.7, 118.8, 118.0, 104.8, 40.0; HRMS (ESI) calculated for $C_8H_8N_2O_2SNa$ [M+Na]$^+$: 219.019869, found: 219.019778.



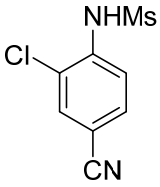
Methyl 2-(methylsulfonamido)benzoate (**1o**); yield: 85% (24 h); white solid; eluent: toluene/ethyl acetate (100:1); ^{1}H NMR (400 MHz, DMSO) δ 10.1 (br. s, 1H), 7.96 (dd, *J* = 7.9 and 1.2 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.59 (d, 1H), 7.24 – 7.20 (m, 1H), 3.88 (s, 3H), 3.19 (s, 3H); ^{13}C NMR (101 MHz) δ 167.6, 139.5, 134.6, 131.0, 123.1, 118.9, 116.7, 52.6, 39.9; HRMS (ESI) calculated for $C_9H_{11}NO_4SNa$ [M+Na]$^+$: 252.030100, found: 252.030006.



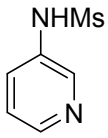
Methyl 4-(methylsulfonamido)benzoate (**1p**); yield: 91% (1 h); white solid; eluent: toluene/ethyl acetate (30:1); ^{1}H NMR (400 MHz, DMSO) δ 10.35 (br. s, 1H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.98 (d, *J* = 8.7, 2H), 3.82 (s, 3H), 3.11 (s, 3H); ^{13}C NMR (101 MHz) δ 165.7, 143.0, 130.7, 123.8, 117.5, 51.9, 39.8; HRMS (ESI) calculated for $C_9H_{11}NO_4SNa$ [M+Na]$^+$: 252.030100, found: 252.030052.



***N*-(2-Chloro-4-cyanophenyl)methanesulfonamide** (**1q**); yield: 54% (24 h); white solid; eluent: toluene/ethyl acetate (5:1); ^{1}H NMR (400 MHz, DMSO) δ 9.90 (br. s, 1H), 8.11 (d, *J* = 1.7 Hz, 1H), 7.82 (dd, *J* = 8.5 and 1.8 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 3.19 (s, 3H); ^{13}C NMR (101 MHz) δ 139.1, 133.6, 132.0, 126.3, 124.1, 117.4, 108.0, 41.1; HRMS (ESI) calculated for $C_8H_7ClN_2O_2SNa$ [M+Na]$^+$: 252.980897, found: 252.980889.



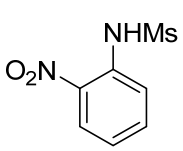
***N*-(Pyridin-3-yl)methanesulfonamide** (**1r**); yield: 44% (4 h); white solid; eluent: toluene/ethyl acetate (5:1); ^{1}H NMR (400 MHz, DMSO) δ 10.00 (br. s, 1H), 8.43 (d, *J* = 2.5 Hz, 1H), 8.32 (dd, *J* = 4.7 and 1.4 Hz, 1H), 7.62 (ddd, *J* = 8.3 and 2.7 and 1.5 Hz, 1H), 7.37 (ddd, *J* = 8.3 and 4.7 and 0.6 Hz, 1H), 3.05 (s, 3H); ^{13}C NMR (101 MHz) δ 144.9, 141.5, 134.9, 126.9, 124.0, 39.6; HRMS (ESI) calculated for $C_6H_8N_2O_2SMNa$ [M+H]$^+$: 173.037925, found: 173.037977.



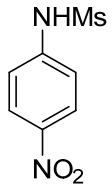
General Procedure for Nitration of Arylmethanesulfonamids

To a solution of the corresponding arylmethanesulfonamide (0.2 mmol, 1.0 equiv.) and sodium nitrite (0.24 mmol, 16.6 mg, 1.2 equiv.) in acetonitrile (1 mL) was added PIFA (0.24 mmol, 103.2 mg, 1.2 equiv.) at room temperature. After complete conversion of the starting material, the reaction was quenched by the addition 2 mL water. The aqueous layer was extracted with ethyl acetate (3*5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (toluene/ethylacetate) affording the desired nitrated arylmethanesulfonamides.

***N*-(2-Nitrophenyl)methanesulfonamide 2a** (ortho) and ***N*-(4-Nitrophenyl)methanesulfonamide 2a** (para)



2a (ortho)



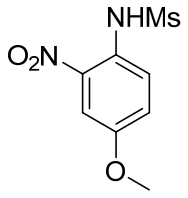
2a (para)

2a (ortho): yield: 41%, yellow solid; **2a** (para): yield: 46%, yellow solid; reaction time: 4 h; eluent: toluene/ethyl acetate (30:1);

2a (ortho): ^{1}H NMR (400 MHz, DMSO) δ 9.79 (br. s, 1H), 8.03 (dd, *J* = 8.2 and 1.5 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.64 (dd, *J* = 8.2 and 1.3 Hz, 1H), 7.43 – 7.39 (m, 1H), 3.15 (s, 3H); ^{13}C NMR (101 MHz) δ 141.9, 134.6, 131.2, 125.5, 124.7, 119.0, 40.4; HRMS (ESI) calculated for $C_7H_8N_2O_4SNa$ $[M+Na]^+$: 239.009699 found: 239.009762.

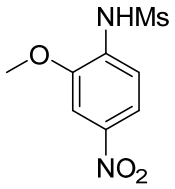
2a (para): ^{1}H NMR (400 MHz, DMSO) δ 10.74 (br. s, 1H), 8.23 (d, *J* = 9.2 Hz, 1H), 7.37 (d, *J* = 9.2 Hz, 1H), 3.19 (s, 3H); ^{13}C NMR (101 MHz) δ 144.9, 142.1, 125.4, 117.4, 40.1; HRMS (ESI) calculated for $C_7H_8N_2O_4SNa$ $[M+Na]^+$: 239.009699 found: 239.009720.

***N*-(4-Methoxy-2-nitrophenyl)methanesulfonamide 2b**



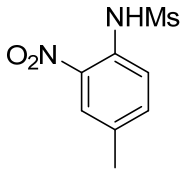
yield: 62%, reaction time: 2 h; yellow solid; eluent: toluene/ethyl acetate (100:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (br. s, 1H), 7.82 (d, *J* = 9.2 Hz, 1H), 7.71 (d, *J* = 3.0 Hz, 1H), 7.27 (dd, *J* = 9.2 and 3.0 Hz, 1H), 3.88 (s, 3H), 3.05 (s, 3H); ^{13}C NMR (101 MHz) δ 156.0, 127.0, 123.8, 123.0, 109.3, 56.1, 40.4; HRMS (ESI) calculated for $C_8H_{10}N_2O_5SNa$ $[M+Na]^+$: 269.020263, found: 269.020247.

***N*-(2-Methoxy-4-nitrophenyl)methanesulfonamide 2c**



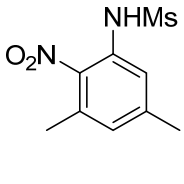
yield: 48%, reaction time: 3.5 h; yellow solid; eluent: toluene/ethyl acetate (30:1); ^{1}H NMR (400 MHz, DMSO) δ 9.60 (br. s, 1H), 7.88 (dd, *J* = 8.9 and 2.5 Hz, 1H), 7.81 (d, *J* = 2.5 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 1H), 3.95 (s, 3H), 3.16 (s, 3H); ^{13}C NMR (101 MHz) δ 149.6, 143.3, 133.7, 119.5, 116.8, 106.5, 56.4, 40.6; HRMS (ESI) calculated for $C_8H_{10}N_2O_5SNa$ [M+Na]$^+$: 269.020263, found: 269.020016.

***N*-(4-Methyl-2-nitrophenyl)methanesulfonamide 2d**

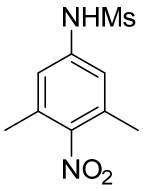


yield: 67%, reaction time: 4 h; yellow solid; eluent: toluene/ethyl acetate (50:1); ^{1}H NMR (400 MHz, DMSO) δ 9.67 (br. s, 1H), 7.84 (m, 1H), 7.55 (dd, *J* = 8.4 and 1.8 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 3.09 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz) δ 142.4, 136.0, 135.0, 128.4, 125.5, 125.3, 40.2, 19.9; HRMS (ESI) calculated for $C_9H_{10}N_2O_6SNa$ [M+Na]$^+$: 253.025349, found: 253.025159.

***N*-(3,5-Dimethyl-2-nitrophenyl)methanesulfonamide 2e** (ortho) and ***N*-(3,5-Dimethyl-4-nitrophenyl)methanesulfonamide 2e** (para)



2e (ortho)



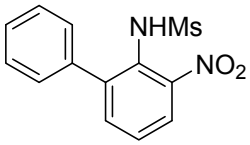
2e (para)

2e (ortho): yield: 19%; **2e** (para): yield: 41%; yellow solid; reaction time: 5 h; eluent: toluene/ethyl acetate (30:1);

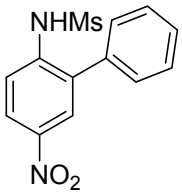
2e (ortho): ^{1}H NMR (400 MHz, DMSO) δ 9.73 (br. s, 1H), 7.21 (s, 1H), 7.17 (s, 1H), 3.04 (s, 3H), 2.34 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (101 MHz) δ 145.0, 141.4, 130.6, 129.6, 128.6, 125.4, 40.5, 20.6, 17.3; HRMS (ESI) calculated for $C_9H_{12}N_2O_4SNa$ [M+Na]$^+$: 267.040999, found: 267.040919.

2e (para): ^{1}H NMR (400 MHz, DMSO) δ 10.20 (br. s, 1H), 7.03 (s, 2H), 3.11 (s, 3H), 2.24 (s, 6H); ^{13}C NMR (101 MHz) δ 146.6, 140.1, 131.1, 118.1, 39.8, 17.4; HRMS (ESI) calculated for $C_9H_{12}N_2O_4SNa$ $[M+Na]^+$: 267.040999, found: 267.040938.

***N*-(3-nitro-[1,1'-biphenyl]-2-yl)methanesulfonamide 2f** (ortho) and ***N*-(5-nitro-[1,1'-biphenyl]-2-yl)methanesulfonamide 2f** (para)



2f (ortho)



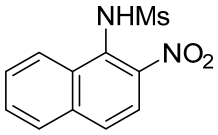
2f (para)

2f (ortho): yield: 23%; white solid; **2f** (para): yield: 51%; yellow solid; reaction time: 3 h; eluent: toluene/ethyl acetate (50:1);

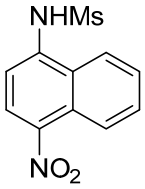
2f (ortho): ^{1}H NMR (400 MHz, DMSO) δ 9.70 (br. s, 1H), 7.96 (dd, *J* = 7.9 and 1.7 Hz, 1H), 7.73 (dd, *J* = 7.9 and 1.7 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.56 – 7.43 (m, 5H), 2.15 (s, 3H); ^{13}C NMR (101 MHz) δ 150.4, 143.7, 137.2, 134.8, 129.7, 129.0, 128.3, 128.1, 125.6, 123.9, 41.2; HRMS (ESI) calculated for $C_{13}H_{12}N_2O_4SNa$ $[M+Na]^+$: 315.040999, found: 315.041027.

2f (para): ^{1}H NMR (400 MHz, DMSO) δ 9.42 (br. s, 1H), 8.25 (dd, *J* = 9.0 and 2.8 Hz, 1H), 8.04 (d, *J* = 2.8 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.55 – 7.45 (m, 5H), 3.07 (s, 3H); ^{13}C NMR (101 MHz) δ 143.5, 141.0, 136.5, 135.0, 129.2, 128.7, 128.2, 125.9, 123.6, 122.6, 41.0; HRMS (ESI) calculated for $C_{13}H_{12}N_2O_4SNa$ $[M+Na]^+$: 315.040999, found: 315.040975.

***N*-(2-Nitronaphtalen-1-yl)-methanesulfonamide 2g** (ortho) and ***N*-(4-Nitronaphtalen-1-yl)-methanesulfonamide 2g** (para)



2g (ortho)



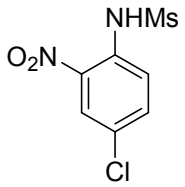
2g (para)

2g (ortho): yield: 34%; yellow solid; **2g** (para): yield: 32%; yellow solid; reaction time: 1 h; eluent: toluene/ethyl acetate (30:1);

2g (ortho): ^{1}H NMR (400 MHz, DMSO) δ 10.30 (br. s, 1H), 8.41 (d, *J* = 8.9 Hz, 1H), 8.15 – 8.13 (m, 2H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.83 – 7.76 (m, 2H), 3.04 (s, 3H); ^{13}C NMR (101 MHz) δ 145.3, 134.9, 130.8, 129.1, 128.8, 128.5, 128.3, 126.0, 125.3, 120.7, 41.7; HRMS (ESI) calculated for $C_{11}H_{10}N_2O_4SNa$ $[M+Na]^+$: 289.025349, found: 289.025220.

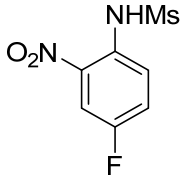
2g (para): ^{1}H NMR (400 MHz, DMSO) δ 10.43 (br. s, 1H), 8.48 – 8.44 (m, 2H), 8.37 (d, *J* = 8.5 Hz, 1H), 7.87 – 7.85 (m, 1H), 7.83 – 7.75 (s, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 3.19 (s, 3H); ^{13}C NMR (101 MHz) δ 142.6, 139.5, 129.8, 127.6, 127.4, 125.3, 125.0, 123.9, 122.6, 117.5, 40.4; HRMS (ESI) calculated for $C_{11}H_{10}N_2O_4SNa$ $[M+Na]^+$: 289.025349, found: 289.025394.

***N*-(4-Chloro-2-nitrophenyl)methanesulfonamide 2h**;



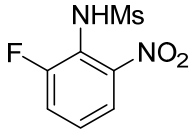
yield: 79%, reaction time: 5 h; yellow solid; eluent: toluene/ethyl acetate (100:1); ^{1}H NMR (400 MHz, DMSO) δ 9.89 (br. s, 1H), 8.13 (d, *J* = 2.5 Hz, 1H), 7.83 (dd, *J* = 8.8 and 2.5 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 3.15 (s, 3H); ^{13}C NMR (101 MHz) δ 142.6, 134.2, 130.0,129.3, 126.8, 125.1, 40.4; HRMS (ESI) calculated for $C_7H_7ClN_2O_4SNa$ $[M+Na]^+$: 272.970726, found: 272.970707.

***N*-(4-Fluoro-2-nitrophenyl)methanesulfonamide 2i**

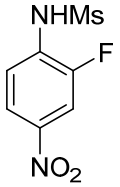


yield: 68%, reaction time: 3.5 h; yellow solid; eluent: toluene/ethyl acetate (100:1); ^{1}H NMR (400 MHz, DMSO) δ 9.81 (br. s, 1H), 7.99 – 7.96 (m, 1H), 7.67 – 7.64 (m, 2H), 3.09 (s, 3H); ^{13}C NMR (101 MHz) δ 158.5 (d, *J* = 246.8 Hz), 143.6 (d, *J* = 9.1 Hz), 128.5 (d, *J* = 8.5 Hz), 127.2 (d, *J* =3.3 Hz), 121.4 (d, *J* =22.5 Hz), 112.7 (d, *J* = 27.9 Hz), 40.3; HRMS (ESI) calculated for $C_7H_7FN_2O_4SNa$ $[M+Na]^+$: 257.000277, found: 257.000114.

***N*-(2-Fluoro-6-nitrophenyl)methanesulfonamide 2j** (ortho) and ***N*-(2-Fluoro-4-nitrophenyl)methanesulfonamide 2j** (para)



2j (ortho)

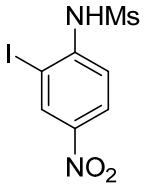


2j (para)

2j (ortho): yield: 52%; white solid; **2j** (para): yield: 14%; yellow solid; reaction time: 4 h; eluent: toluene/ethyl acetate (50:1);

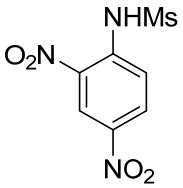
2j (ortho): ^{1}H NMR (400 MHz, DMSO) δ 10.51 (br. s, 1H), 8.19 (dd, *J* = 10.6 and 2.5 Hz, 1H), 8.12 – 8.09 (m, 1H), 7.72 – 7.68 (m, 1H), 3.22 (s, 3H); ^{13}C NMR (101 MHz) δ 151.8 (d, *J* = 249.4), 142.9 (d, *J* = 8.2 Hz), 132.8 (d, *J* = 12.6 Hz), 121.3 (d, *J* = 1.7 Hz), 120.7 (d, *J* = 3.2 Hz), 112.0 (d, *J* = 24.7 Hz), 40.8; HRMS (ESI) calculated for $C_7H_7FN_2O_4SNa$ $[M+Na]^+$: 257.000277, found: 257.000097.
2j (para): ^{1}H NMR (400 MHz, DMSO) δ 9.98 (br. s, 1H), 7.82 (dd, *J* = 8.2 and 1.3 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.61 – 7.6 (m, 1H), 3.07 (s, 3H); ^{13}C NMR (101 MHz) δ 157.8 (d, *J* = 249.9), 148.0, 129.0 (d, *J* = 9.1 Hz), 120.9 (d, *J* = 25.1 Hz), 120.8 , 118.4 (d, *J* = 17.9 Hz), 41.4 (d, *J* = 2.8 Hz); HRMS (ESI) calculated for $C_7H_7FN_2O_4SNa$ $[M+Na]^+$: 257.000277, found: 257.000234.

***N*-(2-Iodo-4-nitrophenyl)methanesulfonamide 2k**



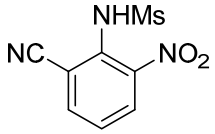
yield: 42%, reaction time: 4.5 h; yellow solid; eluent: toluene/ethyl acetate (50:1); ^{1}H NMR (400 MHz, DMSO) δ 9.64 (br. s, 1H), 8.68 (d, *J* = 2.7 Hz, 1H), 8.30 (dd, *J* = 9.0 and 2.7 Hz, 1H), 7.68 (d, *J* = 9.0 Hz, 1H), 3.28 (s, 3H); ^{13}C NMR (101 MHz) δ 145.1, 144.1, 134.3, 124.3, 123.2, 94.0, 41.5; HRMS (ESI) calculated for $C_7H_7IN_2O_4SNa$ $[M+Na]^+$: 364.906342, found: 364.906080.

***N*-(2,4-Dinitrophenyl)methanesulfonamide 2l**

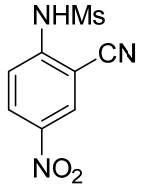


yield: 66%, reaction time: 24 h; yellow solid; eluent: toluene/ethyl acetate (50:1); ^{1}H NMR (400 MHz, DMSO) δ 8.77 (d, *J* = 2.7 Hz, 1H), 8.52 (dd, *J* = 9.2 and 2.7 Hz, 1H), 7.90 (d, *J* = 9.2 Hz, 1H), 3.32 (s, 3H); ^{13}C NMR (101) MHz) δ 141.9, 138.6, 137.7, 129.1, 122.4, 121.8, 40.9; HRMS (ESI) calculated for $C_7H_7N_3O_6SNa$ $[M+Na]^+$: 283.994777, found: 283.994660.

***N*-(2-Cyano-6-nitrophenyl)methanesulfonamide 2m** (ortho) and ***N*-(2-Cyano-4-nitrophenyl)methanesulfonamide 2m** (para)



2m (ortho)



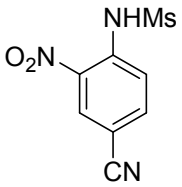
2m (para)

2m (ortho): yield: 22%; white solid; **2m** (para): yield: 53%; yellow solid; reaction time: 6.5 h, eluent: toluene/ethyl acetate (30:1);

2m (ortho): ^{1}H NMR (400 MHz, DMSO) δ 10.56 (br. s, 1H), 8.30 (dd, *J* = 8.2 and 1.5 Hz, 1H), 8.26 (dd, *J* = 7.8 and 1.5 Hz, 1H), 7.76 – 7.72 (m, 1H), 3.16 (s, 3H); ^{13}C NMR (101 MHz) δ 147.4, 138.1, 131.7, 129.8, 129.2, 115.7, 114.9, 42.4; HRMS (ESI) calculated for $C_8H_7N_3O_4SNa$ $[M+Na]^+$: 264.004948, found: 264.004908.

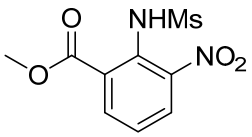
2m (para): ^{1}H NMR (400 MHz, DMSO) δ 8.71 (d, *J* = 2.7 Hz, 1H), 8.46 (dd, *J* = 9.2 and 2.8 Hz, 1H), 7.73 (d, *J* = 9.2 Hz, 1H), 3.24 (s, 3H); ^{13}C NMR (101 MHz) δ 177.2, 142.6, 129.9, 129.2, 122.5, 115.3, 105.5, 41.1; HRMS (ESI) calculated for $C_8H_7N_3O_4SNa$ $[M+Na]^+$: 264.004948, found: 264.004924.

***N*-(4-Cyano-2-nitrophenyl)methanesulfonamide**[9] **2n**

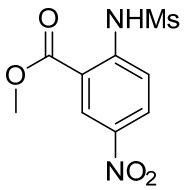


yield: 71%, reaction time: 28 h; white solid; eluent: toluene/ethyl acetate (10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (br. s, 1H), 8.61 (d, *J* = 1.9 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.91 (dd, *J* = 8.9 and 1.9 Hz, 1H), 3.26 (s, 3H); ^{13}C NMR (101 MHz) 138.6, 138.1, 131.1, 119.3, 116.1, 107.0, 77.2, 41.6; HRMS (ESI) calculated for $C_8H_7N_3O_4SNa$ $[M+Na]^+$: 264.004948, found: 264.004942.

Methyl-2-(methylsulfonamido)-3-nitrobenzoate 2o (ortho) and **Methyl-2-(methylsulfonamido)-5-nitrobenzoate 2o** (para)



2o (ortho)

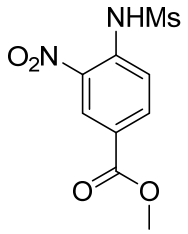


2o (para)

2o (ortho): yield: 15%; white solid; **2o** (para): yield: 55%; white solid; reaction time: 48 h; eluent: toluene/ethyl acetate (50:1);

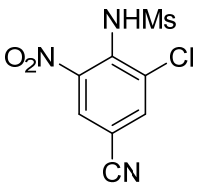
2oa: ^{1}H NMR (400 MHz, DMSO) δ 9.96 (br. s, 1H), 8.14 (dd, *J* = 8.1 and 1.6 Hz, 1H), 8.07 (dd, *J* = 7.9 and 1.6 Hz, 1H), 7.63 – 7.59 (m, 1H), 3.86 (s, 3H), 3.02 (s, 3H); ^{13}C NMR (101 MHz δ) 165.4, 147.3, 134.4, 130.0, 128.5, 128.3, 127.4, 52.7, 41.5; HRMS (ESI) calculated for $C_9H_{10}N_2O_6SNa$ [M+Na]$^+$: 297.015178, found: 297.015019.
2ob: ^{1}H NMR (400 MHz, DMSO) δ 10.57 (br. s, 1H), 8.70 (d, *J* = 2.8 Hz, 1H), 8.48 (dd, *J* = 9.3 and 2.8 Hz, 1H), 7.82 (d, *J* = 9.3 Hz, 1H), 3.95 (s, 3H), 3.36 (s, 3H); ^{13}C NMR (101 MHz) δ 166.1, 145.0, 141.4, 129.4, 126.6, 118.2, 115.8, 53.2, 40.4; HRMS (ESI) calculated for $C_9H_{10}N_2O_6SNa$ [M+Na]$^+$: 297.015178, found: 297.015033.

Methyl 4-(methylsulfonamido)-3-nitrobenzoate 2p



yield: 82%, reaction time: 48 h; white solid; eluent: toluene/ethyl acetate (50:1); ^{1}H NMR (400 MHz, DMSO) δ 10.11 (br. s, 1H), 8.49 (d, *J* = 2.0 Hz, 1H), 8.24 (dd, *J* = 8.7 and 2.1 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 3.89 (s, 3H), 3.28 (s, 3H); ^{13}C NMR (101 MHz) δ 164.1, 139.3, 136.0, 134.9, 126.6, 125.0, 122.4, 52.6, 40.6; HRMS (ESI) calculated for $C_9H_{10}N_2O_6SNa$ [M+Na]$^+$: 297.015178, found: 297.014992.

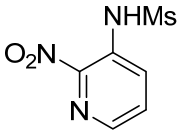
***N*-(2-Chloro-4-cyano-6-nitrophenyl)methanesulfonamide 2q**



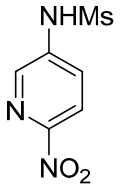
yield: 24%, reaction time: 48 h; brown solid; eluent: toluene/ethyl acetate (50:1); ^{1}H NMR (400 MHz, DMSO) δ 10.52 (br. s, 1H), 8.57 (d, *J* = 1.9 Hz, 1H), 8.54 (d, *J* = 1.9 Hz, 1H), 3.12 (s, 3H); ^{13}C NMR (101

MHz) δ 148.3, 137.5, 134.2, 131.4, 128.2, 115.7, 111.0, 42.4; HRMS (ESI) calculated for $C_8H_6N_3O_4SNa$ $[M+Na]^+$: 297.965975, found: 297.965981.

***N*-(2-nitropyridin-3-yl)methanesulfonamide**[10] **2r** (ortho) and ***N*-(6-nitropyridin-3-yl)methanesulfonamide** [10] **2r** (para)



2r (ortho)



2r (para)

2r (ortho): yield: 28%; white solid; **2r** (para): yield: 28%; yellow solid; reaction time: 4.5 h; eluent: toluene/ethyl acetate (5:1);

2r (ortho): ^{1}H NMR (400 MHz, DMSO) δ 10.10 (br. s, 1H), 8.40 (dd, *J* = 4.5 and 1.4 Hz, 1H), 8.17 (dd, *J* = 8.2 and 1.4 Hz, 1H), 7.84 (dd, *J* = 8.3 and 4.5 Hz, 1H), 3.18 (s, 3H); ^{13}C NMR (101 MHz) δ 150.6, 144.4, 135.6, 129.5, 126.7, 40.8; HRMS (ESI) calculated for $C_7H_7N_3O_4SNa$ $[M+Na]^+$: 240.004948, found: 240.004940.

2r (para): ^{1}H NMR (400 MHz, DMSO) δ 10.95 (br. s, 1H), 8.39 (d, *J* = 2.6 Hz, 1H), 8.34 (d, *J* = 8.9 Hz, 1H), 7.90 (dd, *J* = 8.9 and 2.7 Hz, 1H), 3.25 (s, 3H); ^{13}C NMR (101 MHz) δ 151.1, 140.7, 137.6, 126.9, 119.8, 40.5; HRMS (ESI) calculated for $C_7H_7N_3O_4SNa$ $[M+Na]^+$: 240.004948, found: 240.004916.

Literature

[1] W. L. F. Armarego and C. L. L Chai, *Purification of Laboratory Chemicals*; 5th ed.;Butterworthn Heinemann: Oxford, **2003**.

[2] S.-Y. Moon, J. Nam, K. Rathwell and W.-S. Kim, *Org. Lett.*, 2014, **16**, 338

[3] B. R. Rosen, J. C. Ruble, T. J. Beauchamp and A. Navarro, *Org. Lett.*, **2011**, 13, 2564

[4] S. Shekhar, T. B. Dunn, B. J. Kotecki, D. K. Montavon and S. C. Cullen, *J. Org. Chem.*, **2011**, 76, 4552

[5] B. S. Kim, S. Y. Lee and S. W. Youn, *Chem. Asian J.*, **2011**, 6, 1952

[6] V. Masevicius, G. Petraityte and S. Tumkevicius *Synthesis*, **2012**, 9, 1329

[7] C. Rossy, E. Fouquet and F.-X. Felpin, *Beilstein J. Org. Chem.*, **2013**, 9, 1426

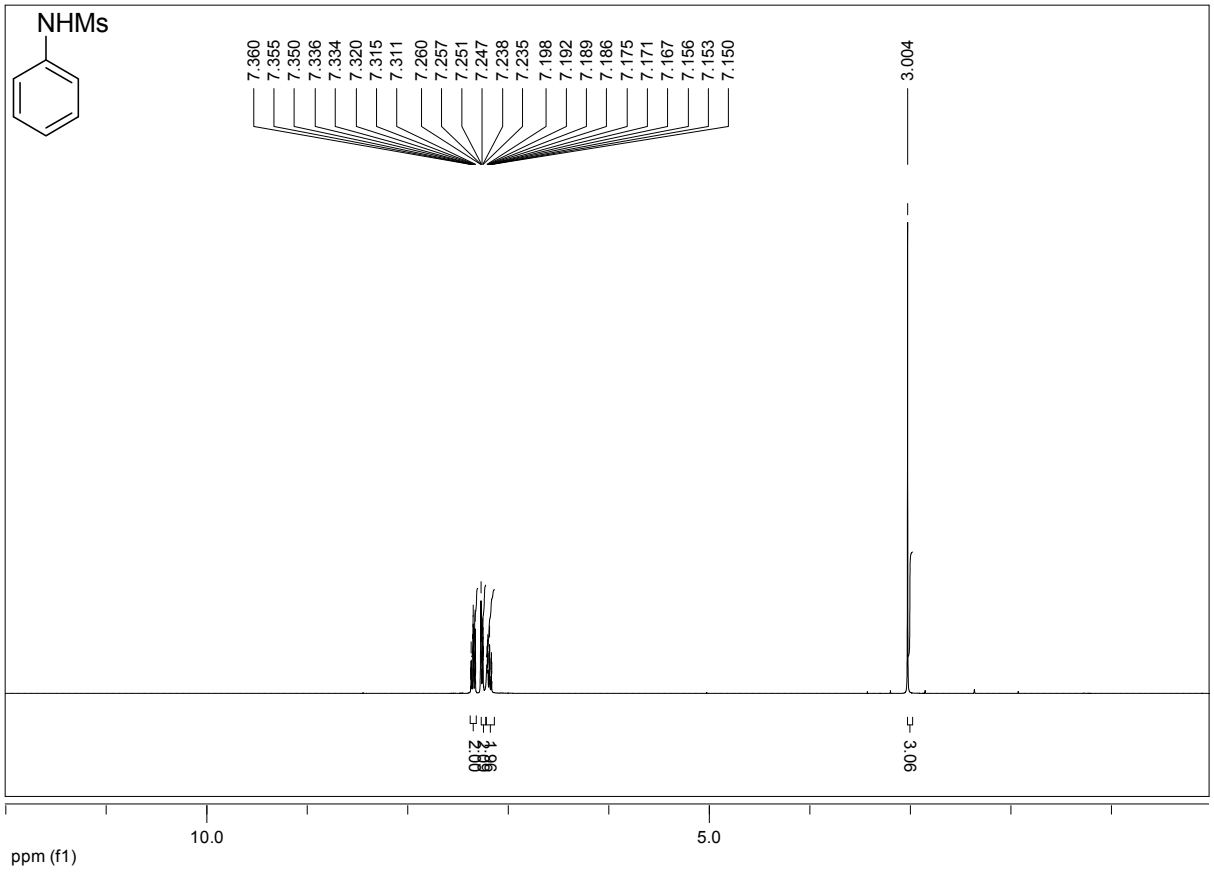
[8] S. Sridhar, B. Srinivas, V. P. Kumar, M. Narender and K. R. Rao, *Adv. Synth. Catal*, **2007**, 349, 1873

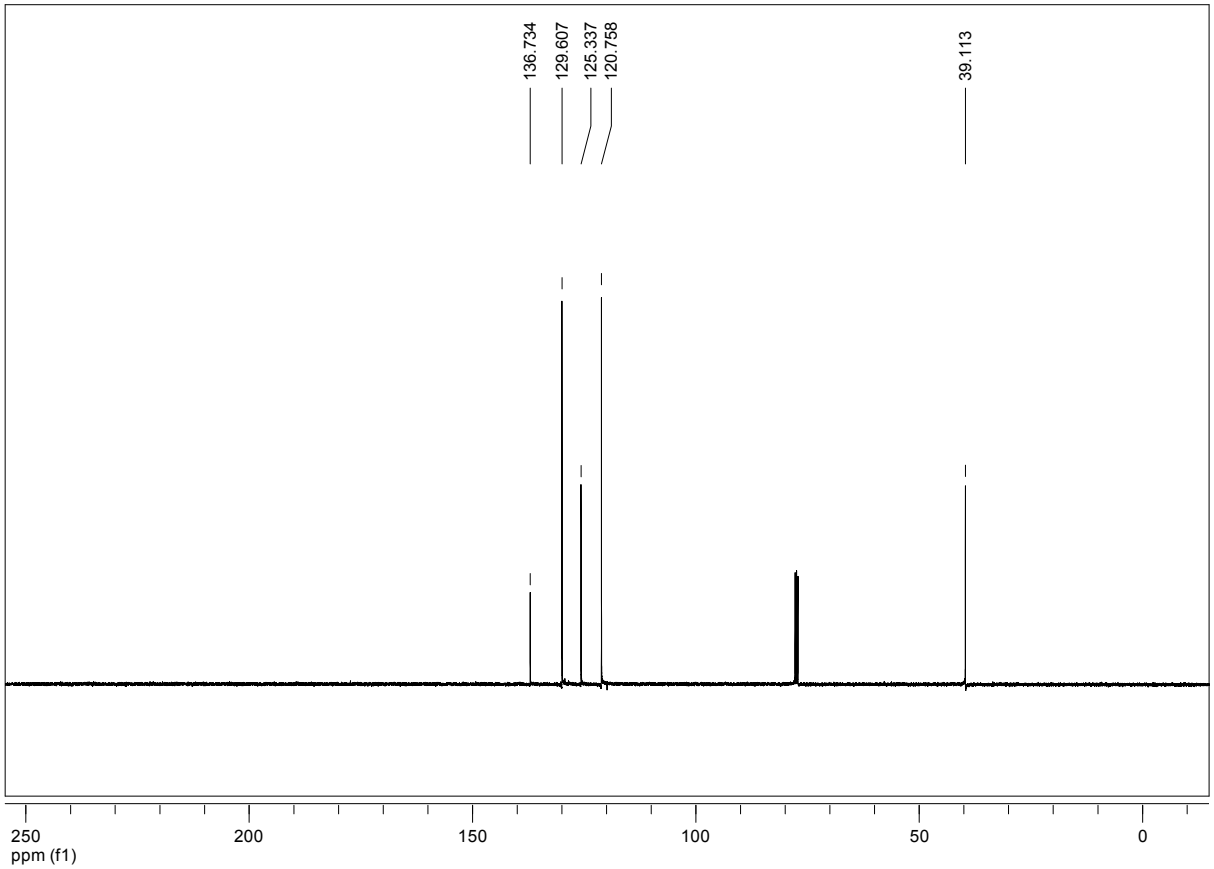
[9] Y.-G. Suh ,Y.-S. Lee ,K.-H. Min ,O.-H. Park ,J.-K. Kim ,H.-S. Seung ,S.-Y. Seo ,B.-Y. Lee ,Y.-H. Nam ,K. O. Lee ,H.-D. Kim ,H.-G. Park ,J. Lee ,U. Oh ,J.-O. Lim ,S.-U. Kang ,M.-J. Kil ,J.-y. Koo ,S. S. Shin ,Y.-H. Joo ,J. K. Kim ,Y.-S. Jeong ,S.-Y. Kim and Y.-H. Park *J. Med. Chem.*, **2005**, 48, 5823–5836

[10] A. F. Andrews, D. M. Smith, H. F. Hodson and P. B. Thorogood *J. Chem. Soc., Perkin Trans. 1*, **1982**, 2995-3006

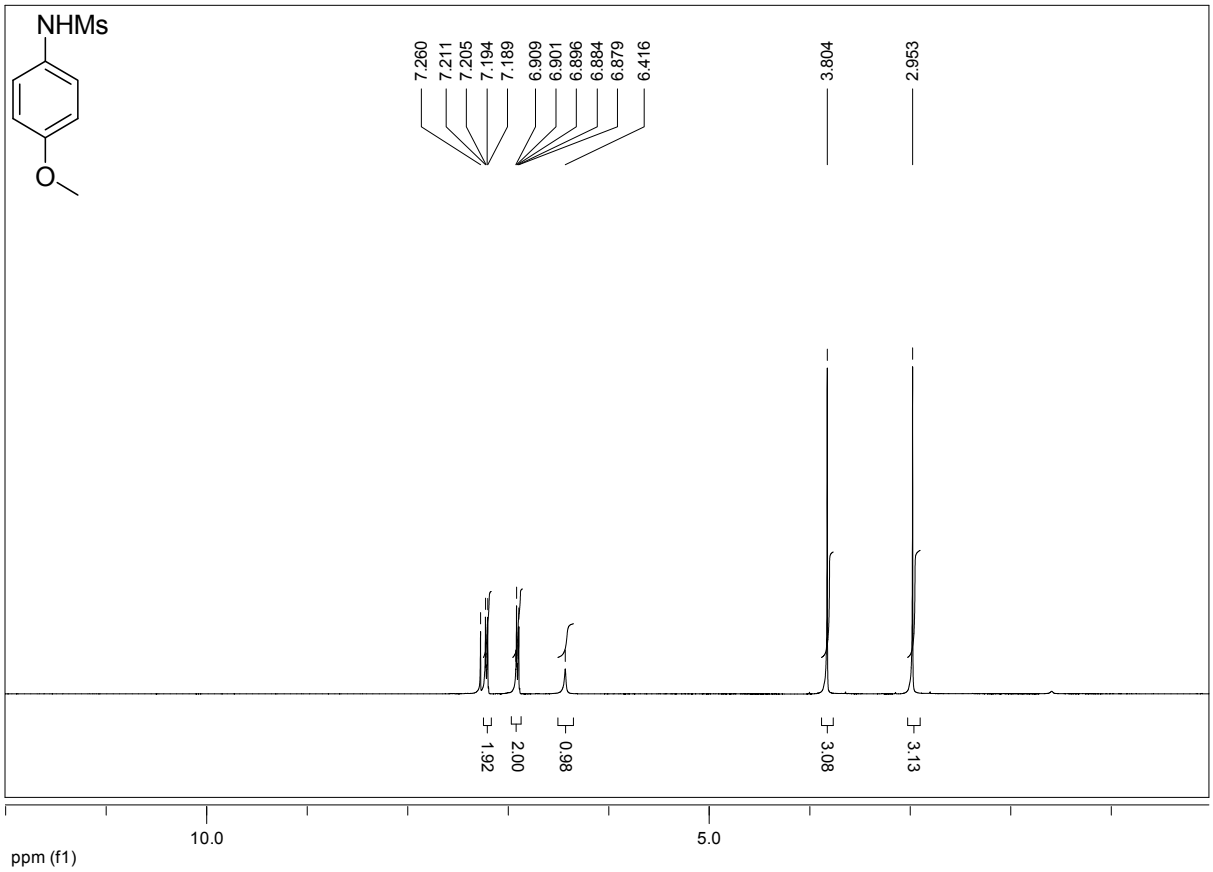
1H and 13C Spectra

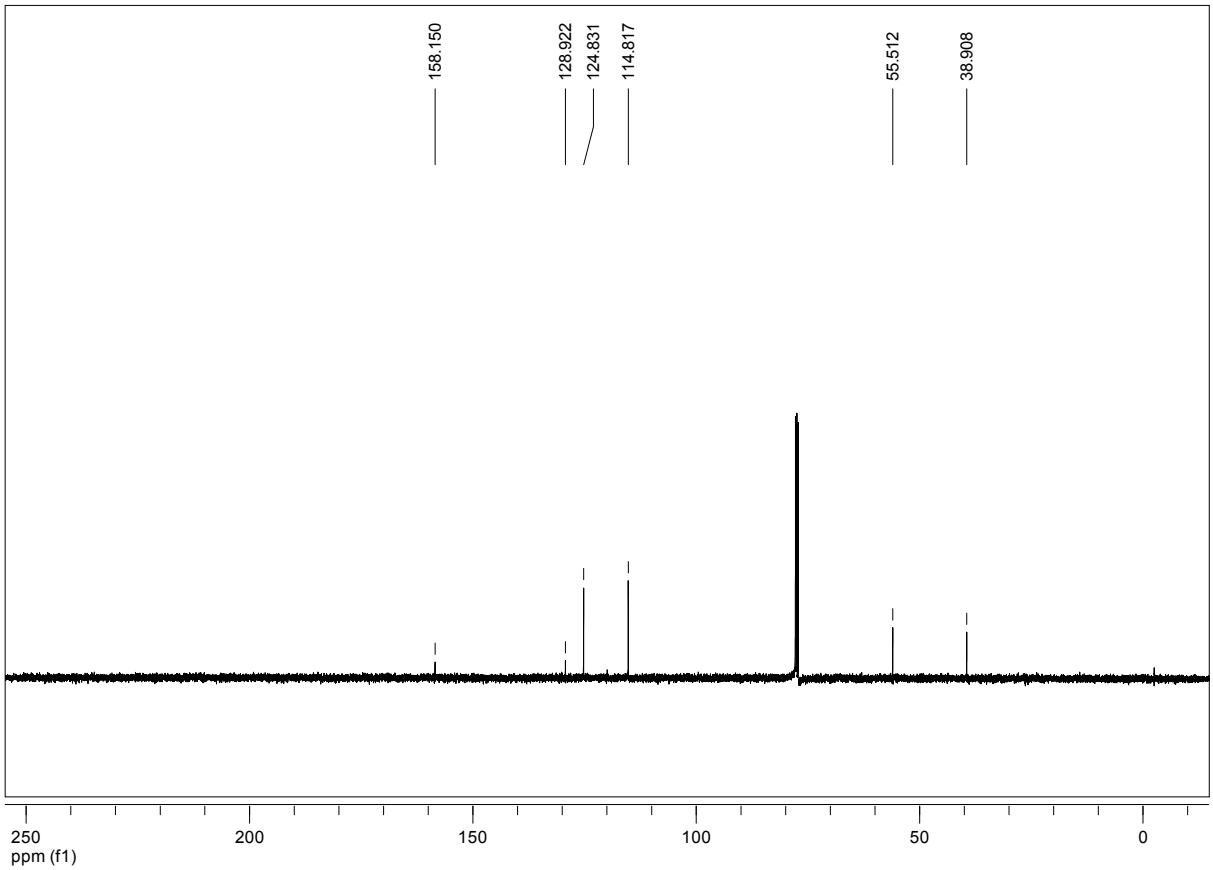
***N*-Phenylmethanesulfonamide** (**1a**)



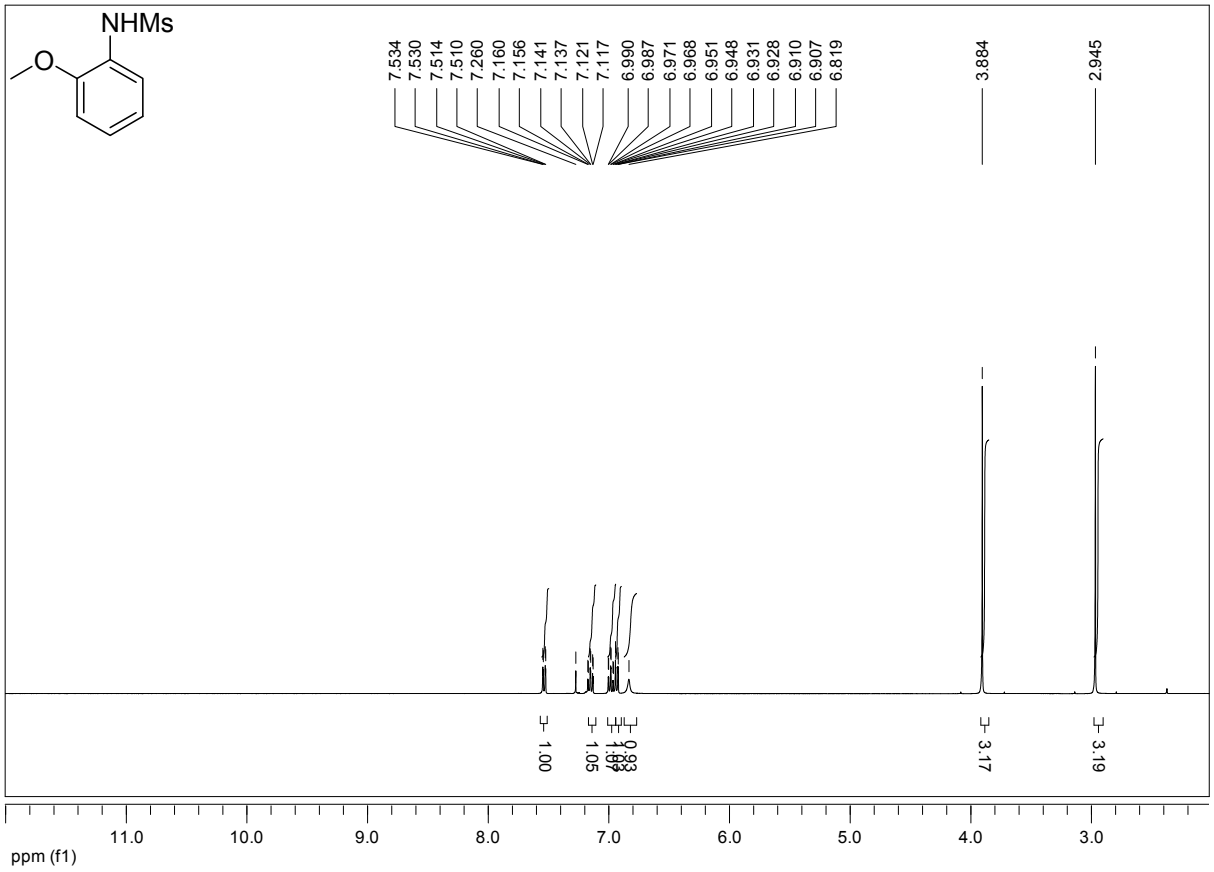


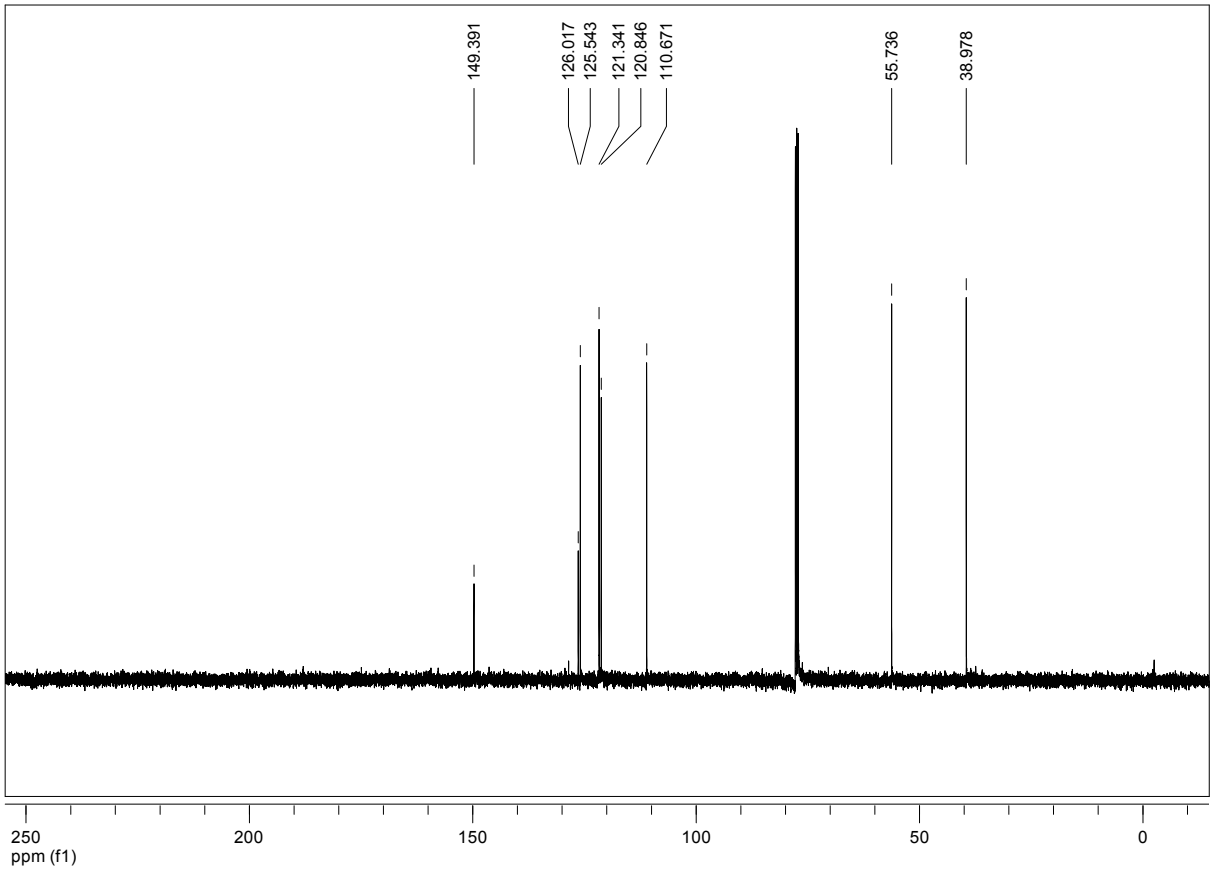
***N*-(4-Methoxyphenyl)methanesulfonamide (1b)**



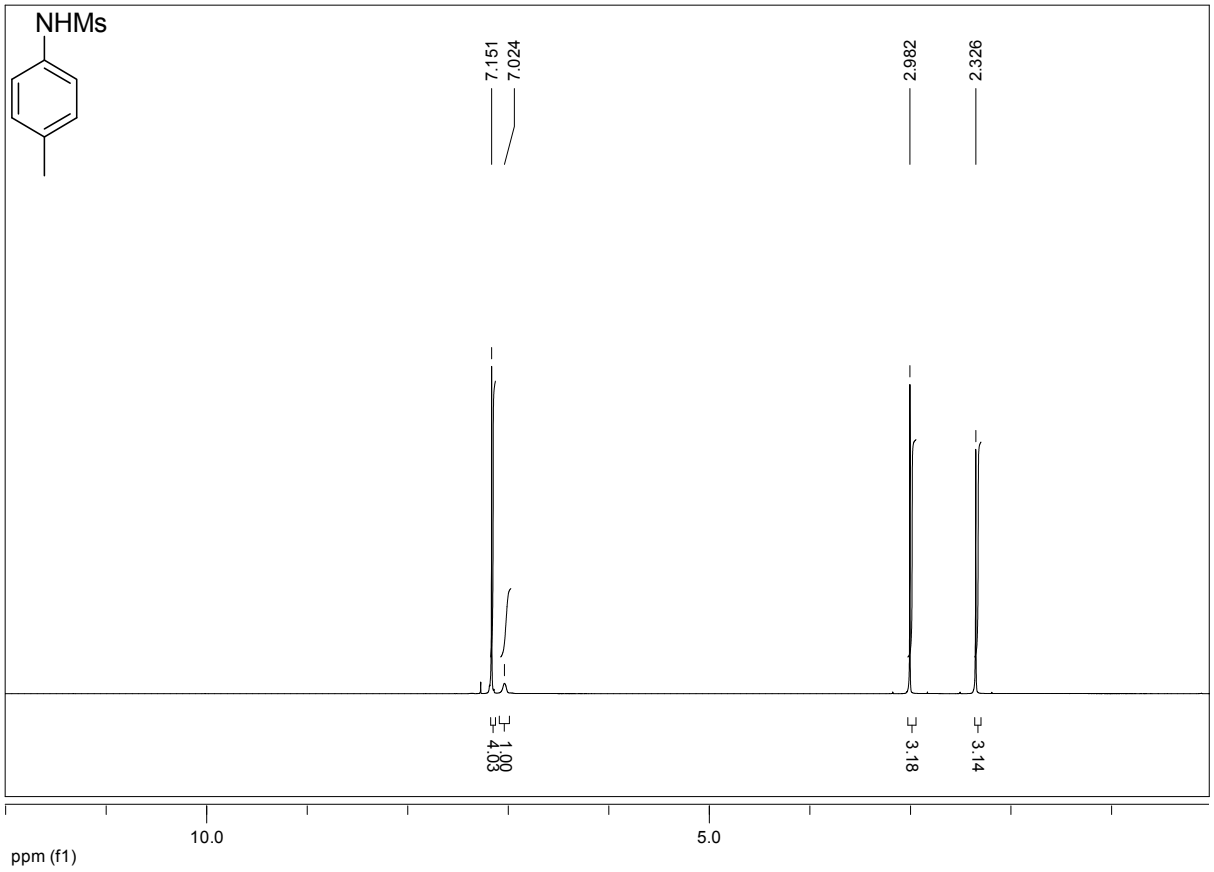


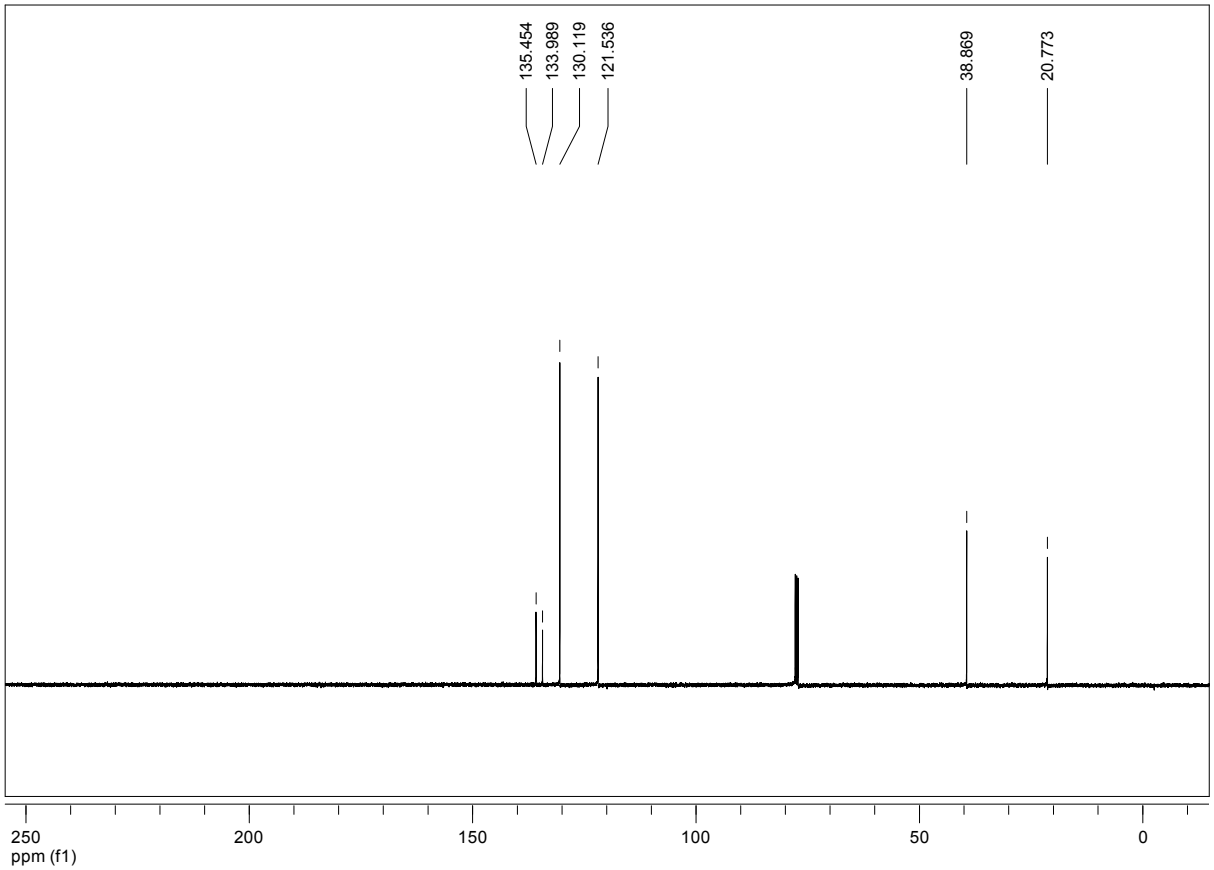
***N*-(2-Methoxyphenyl)methanesulfonamide (1c)**



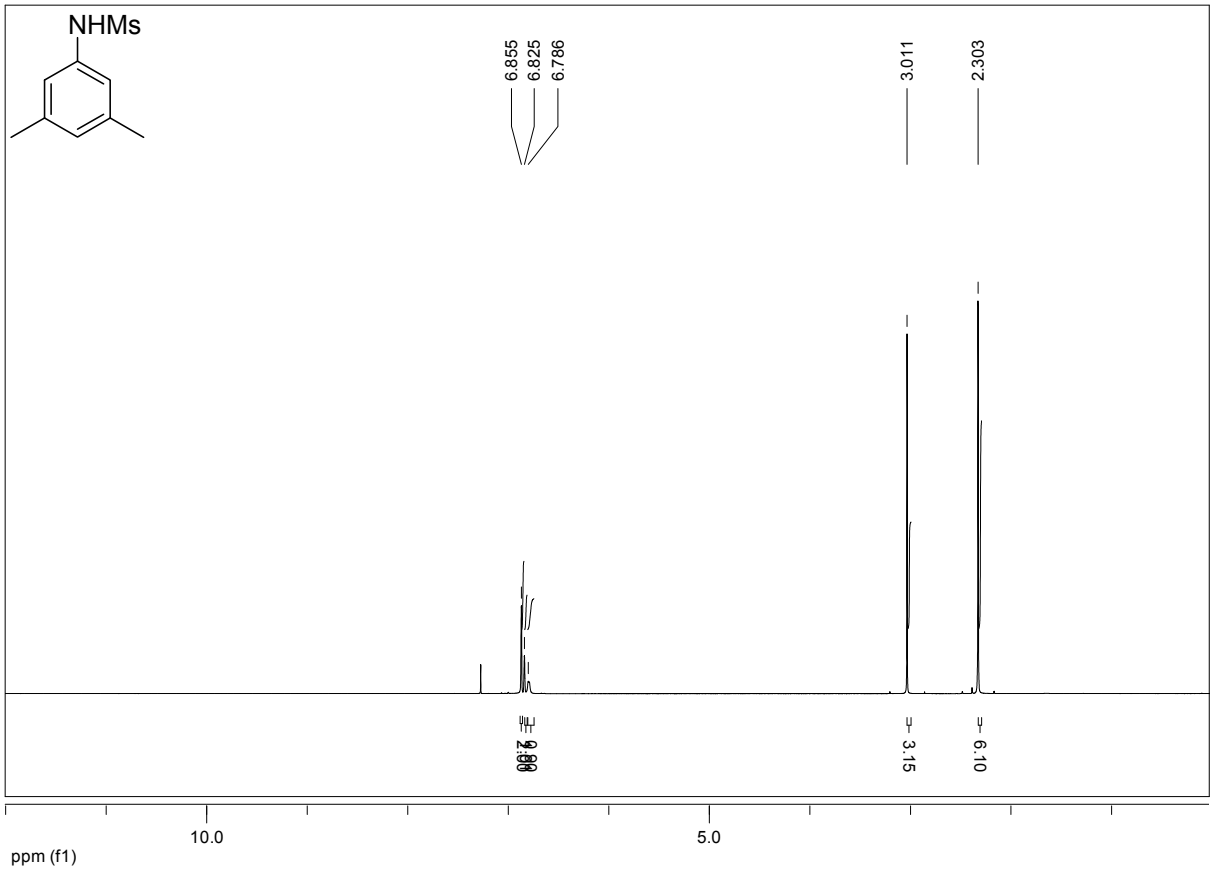


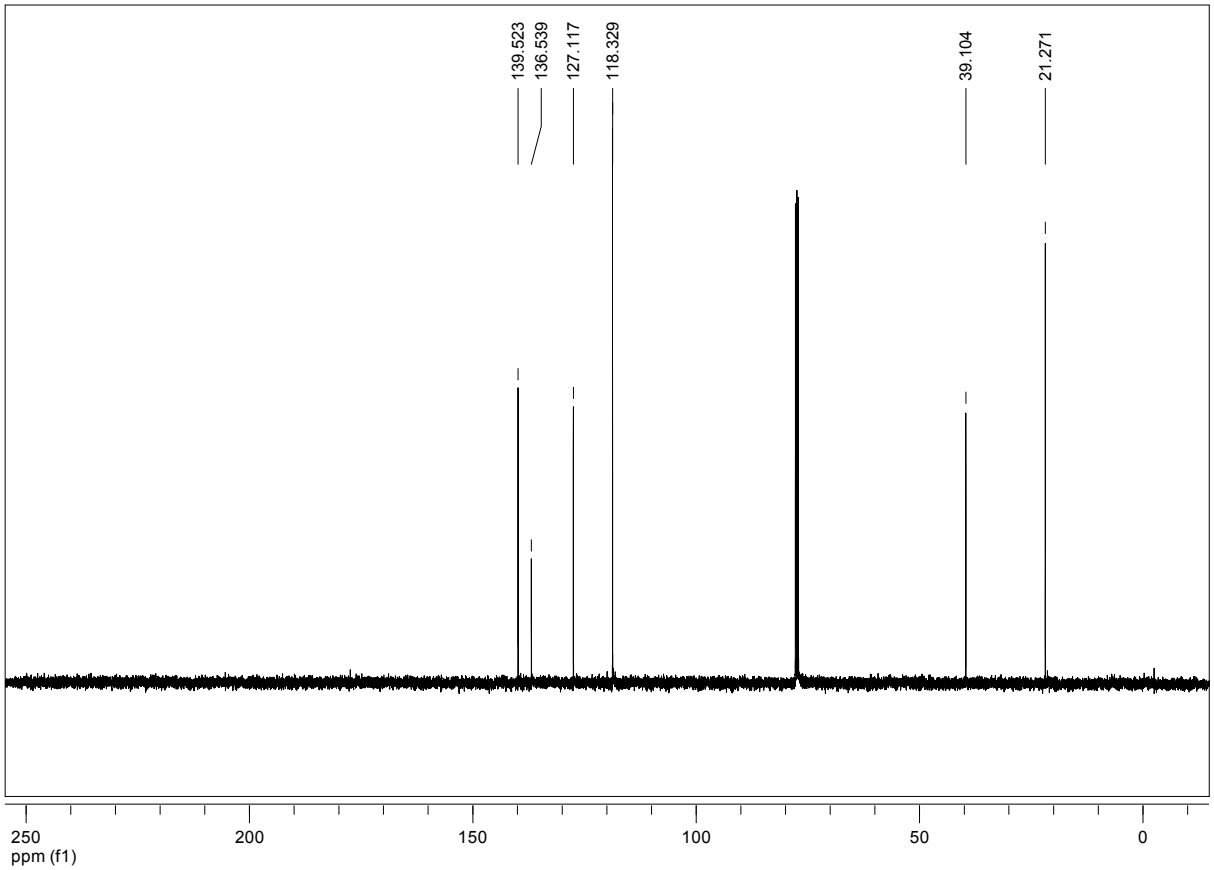
***N*-(*p*-tolyl)methanesulfonamide** (**1d**)



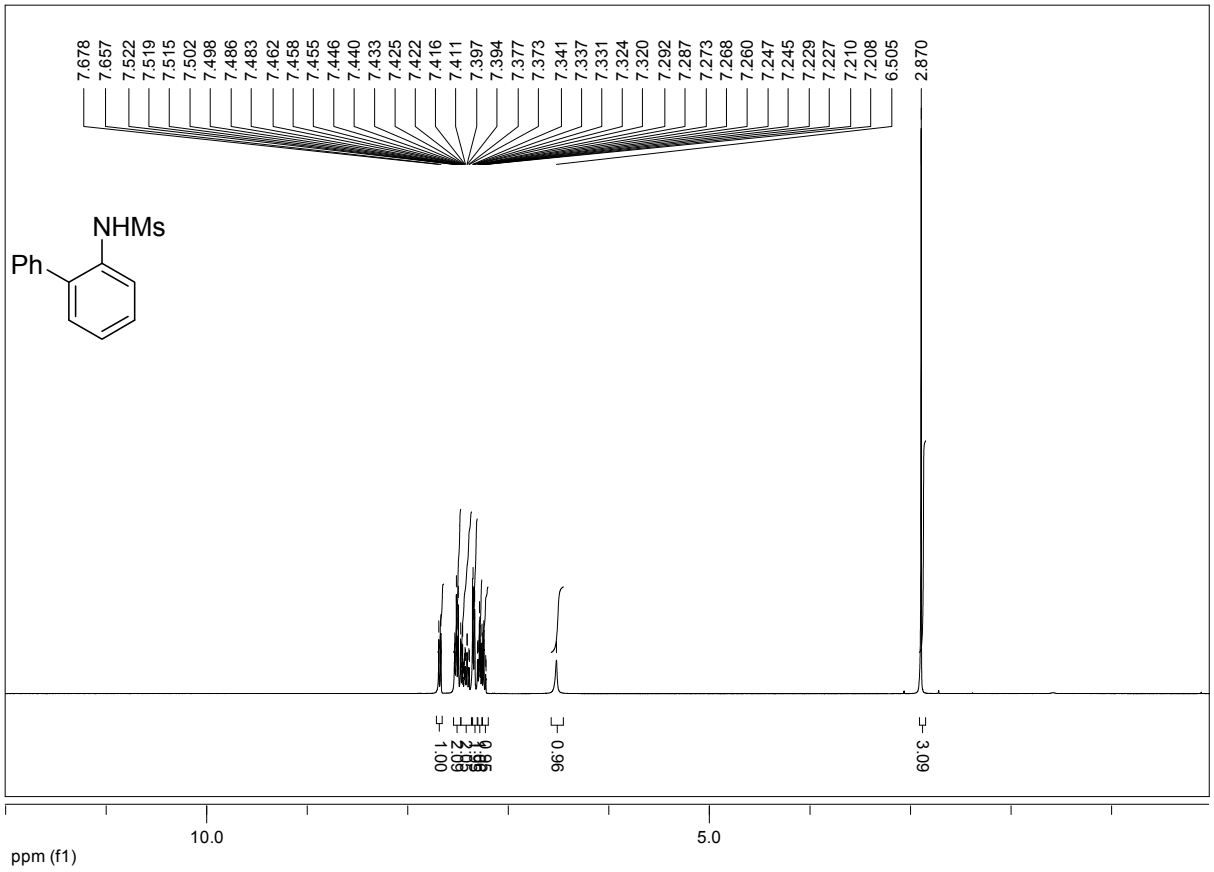


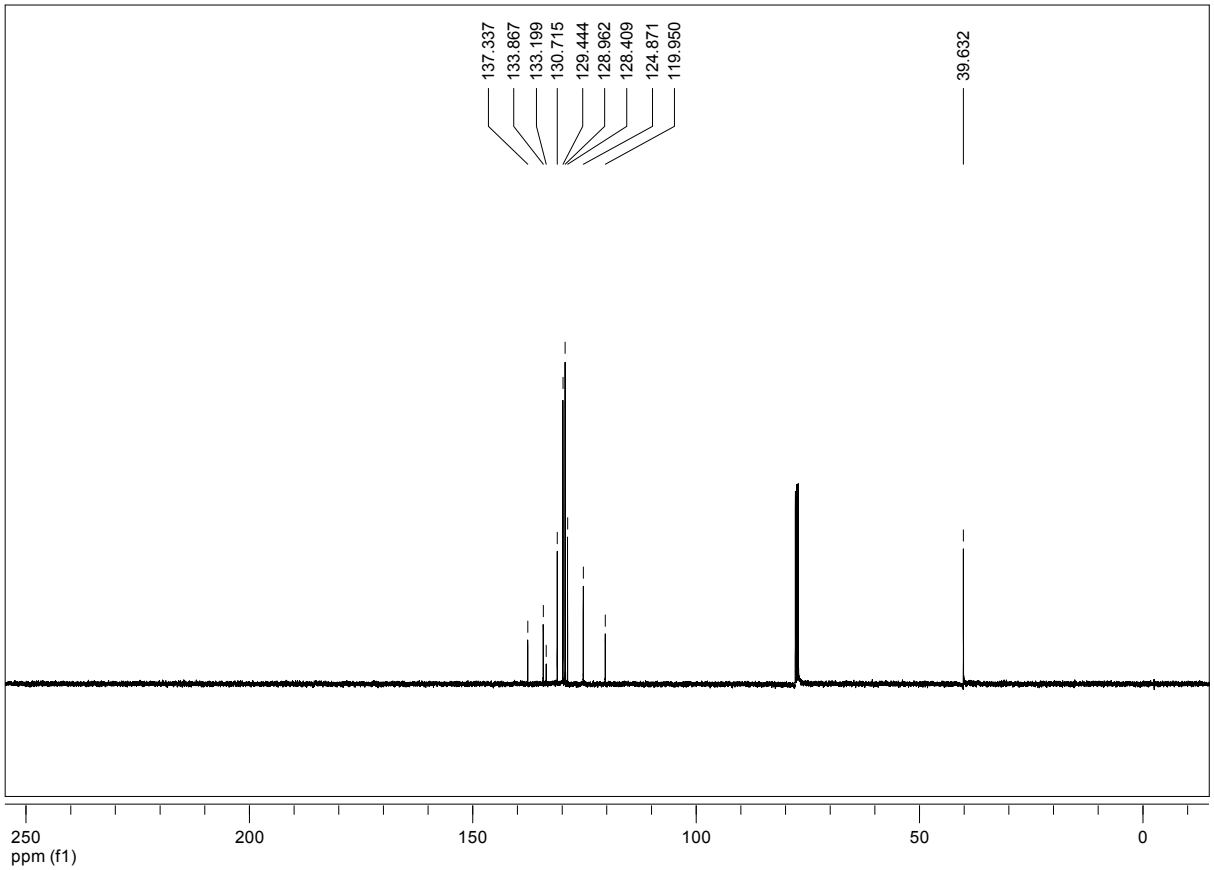
***N*-(3,5-Dimethylphenyl)methanesulfonamide (1e)**



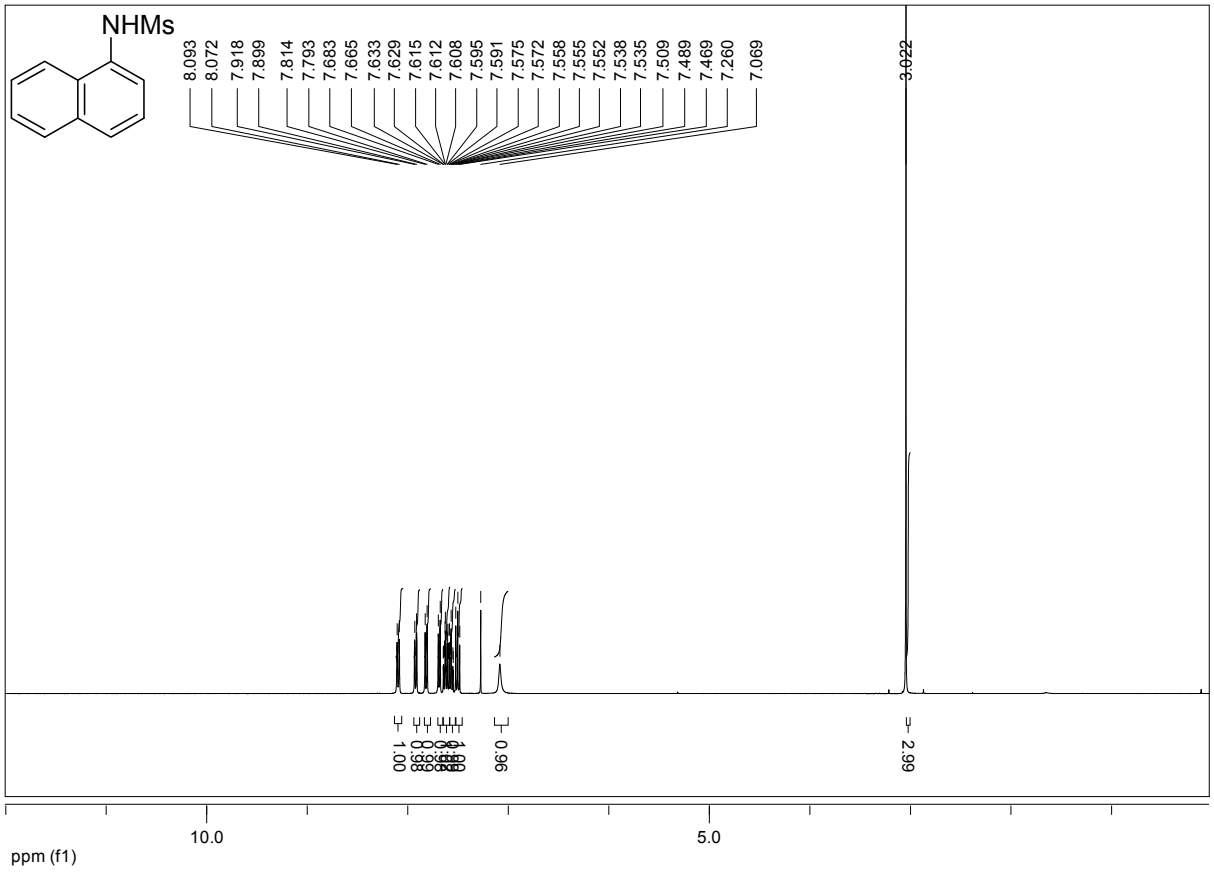


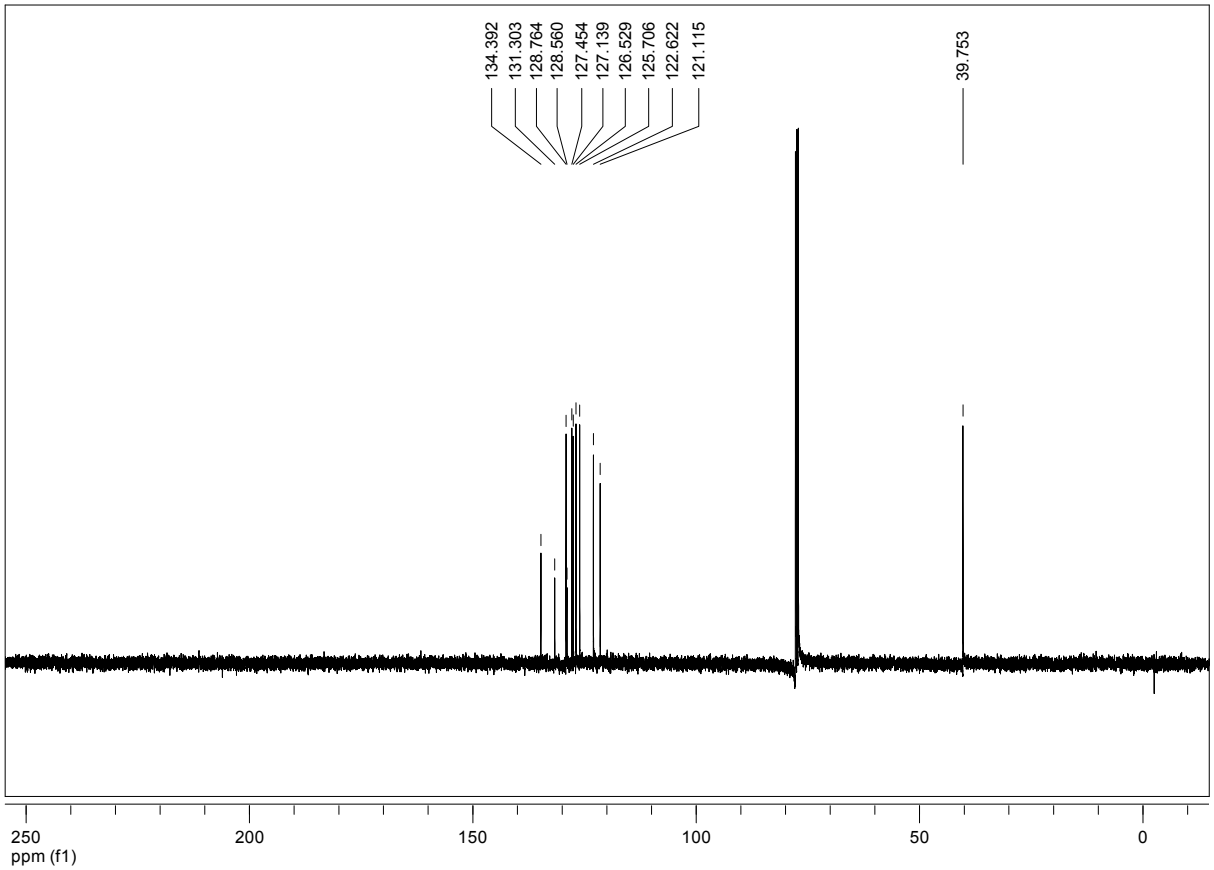
***N*-([1,1'-biphenyl]-2-yl)methanesulfonamide (1f)**



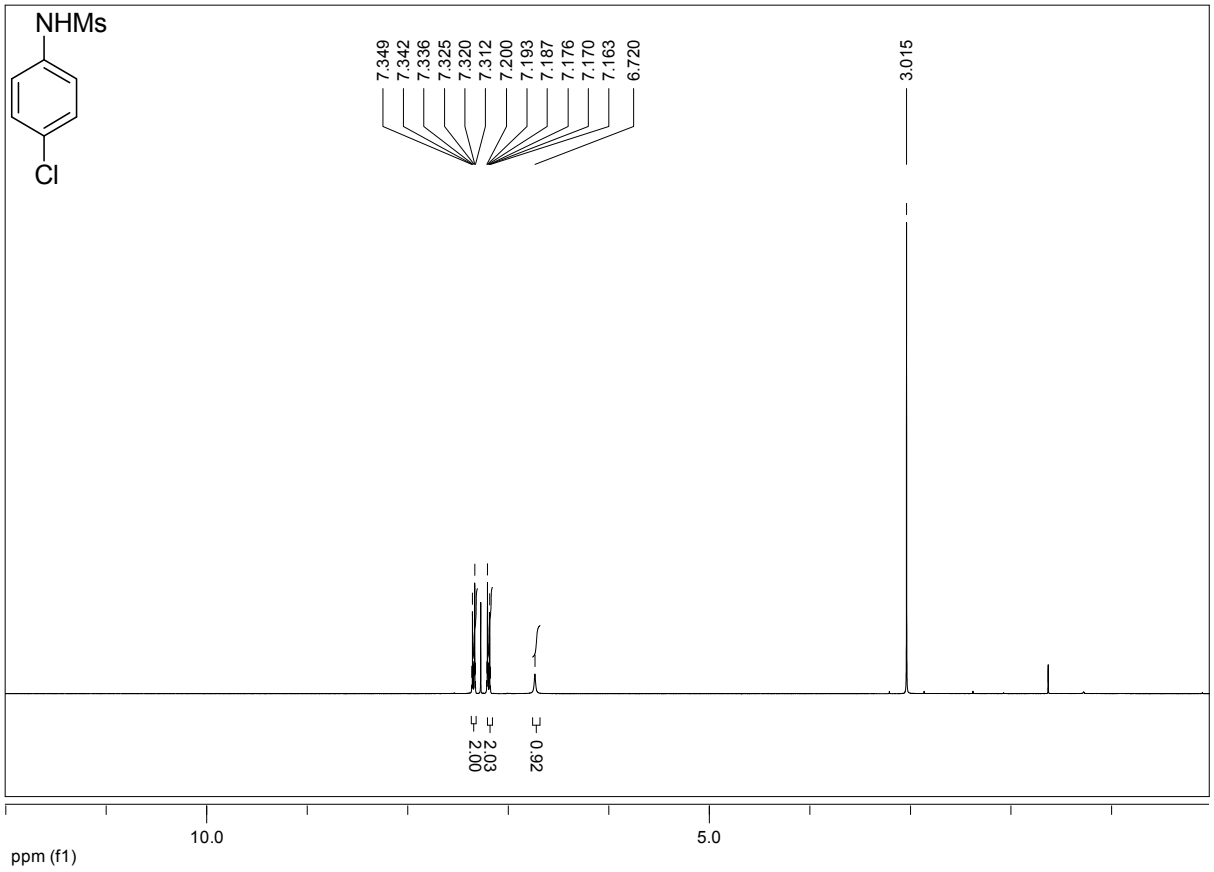


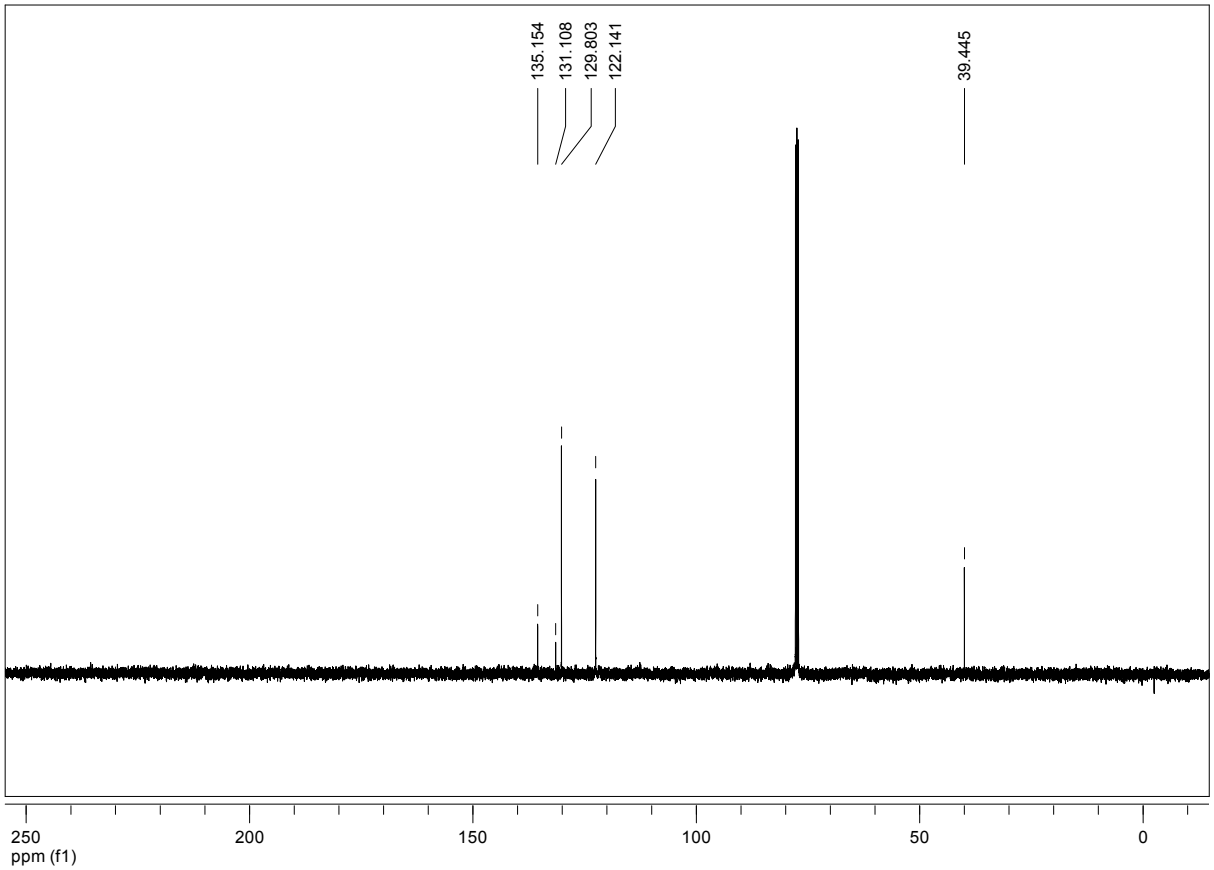
***N*-(Naphtalen-1-yl)-methanesulfonamide (1g)**



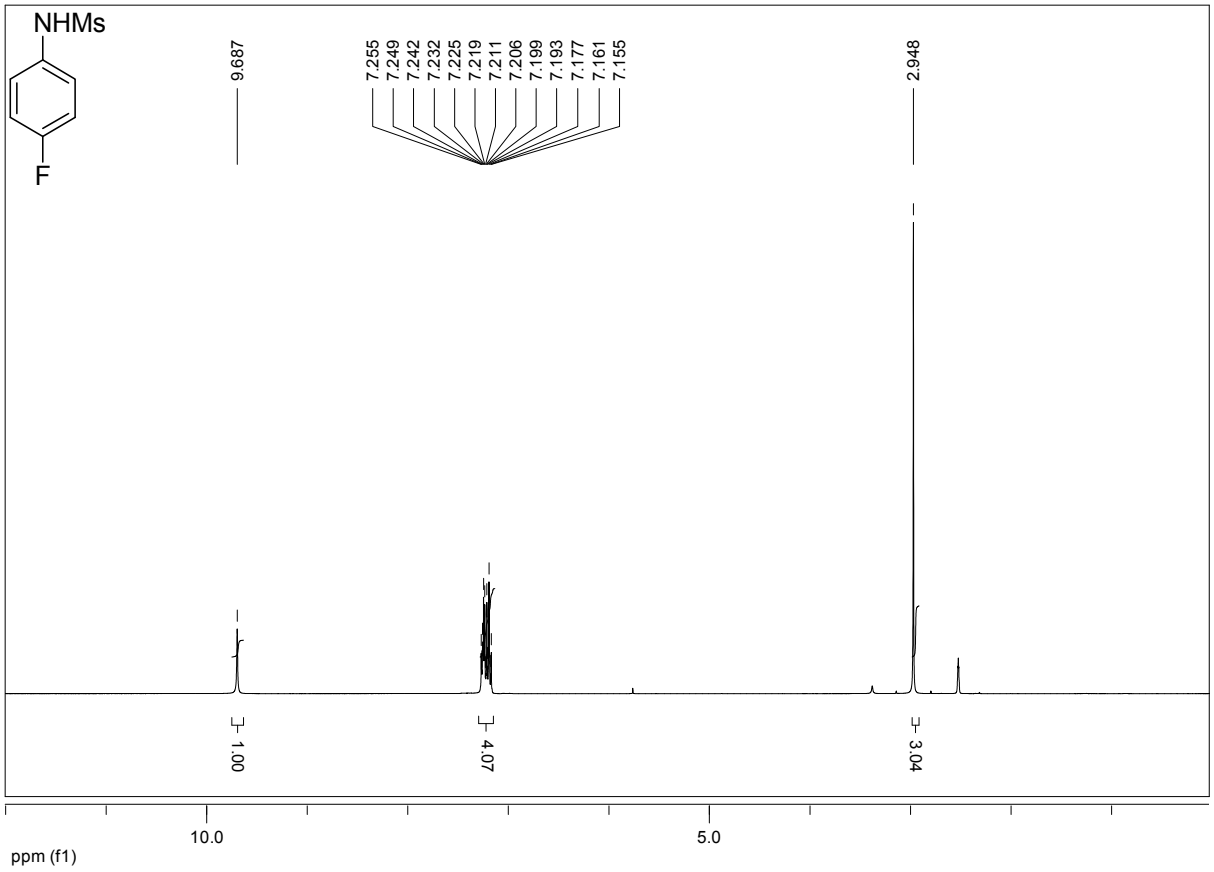


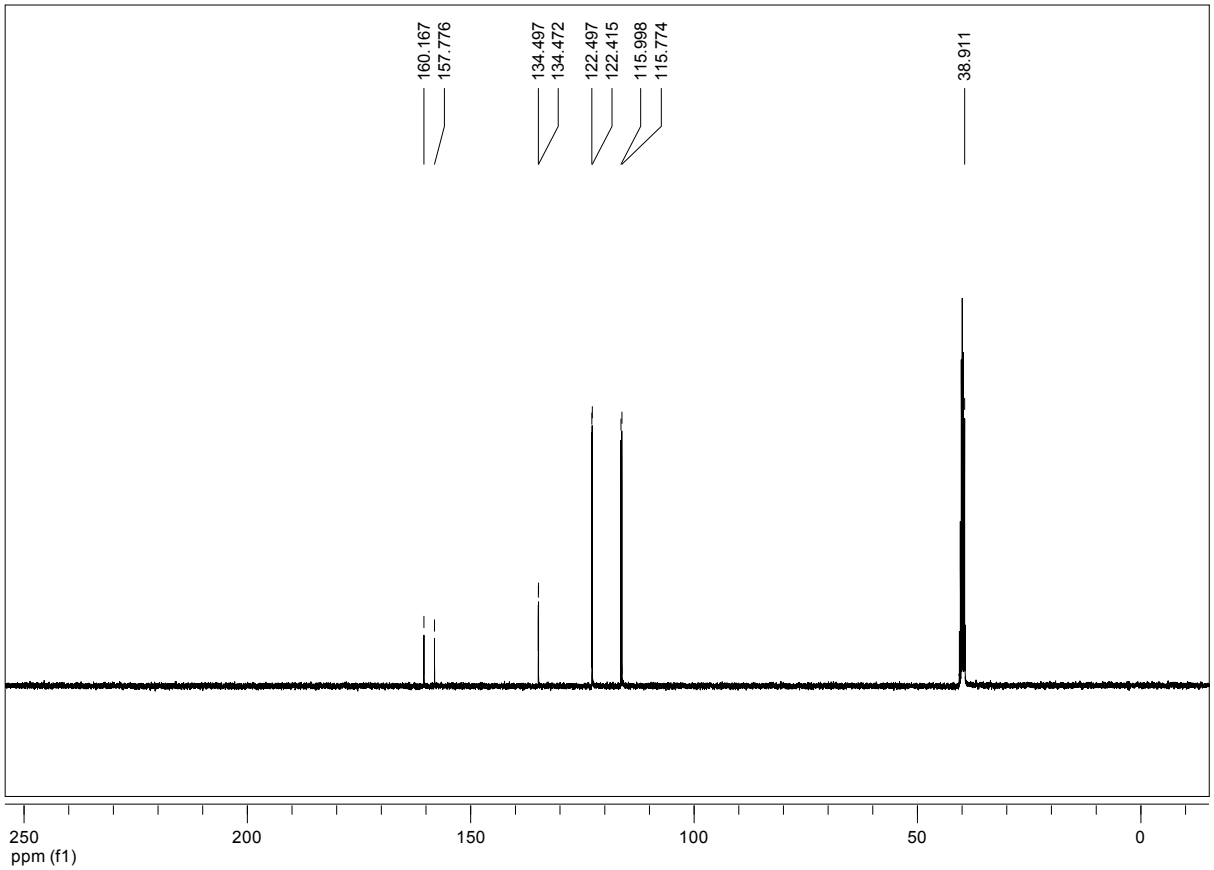
***N*-(4-Chlorophenyl)methanesulfonamide (1h)**



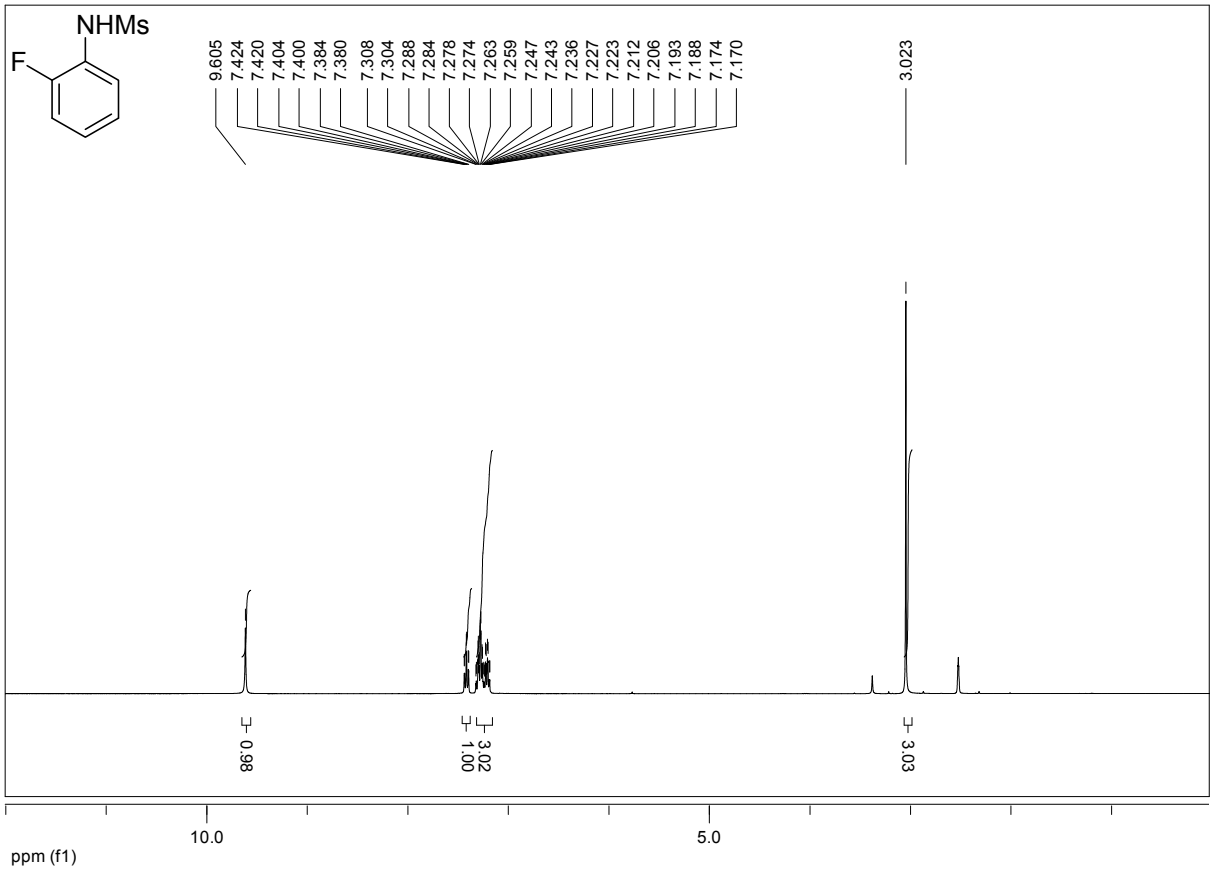


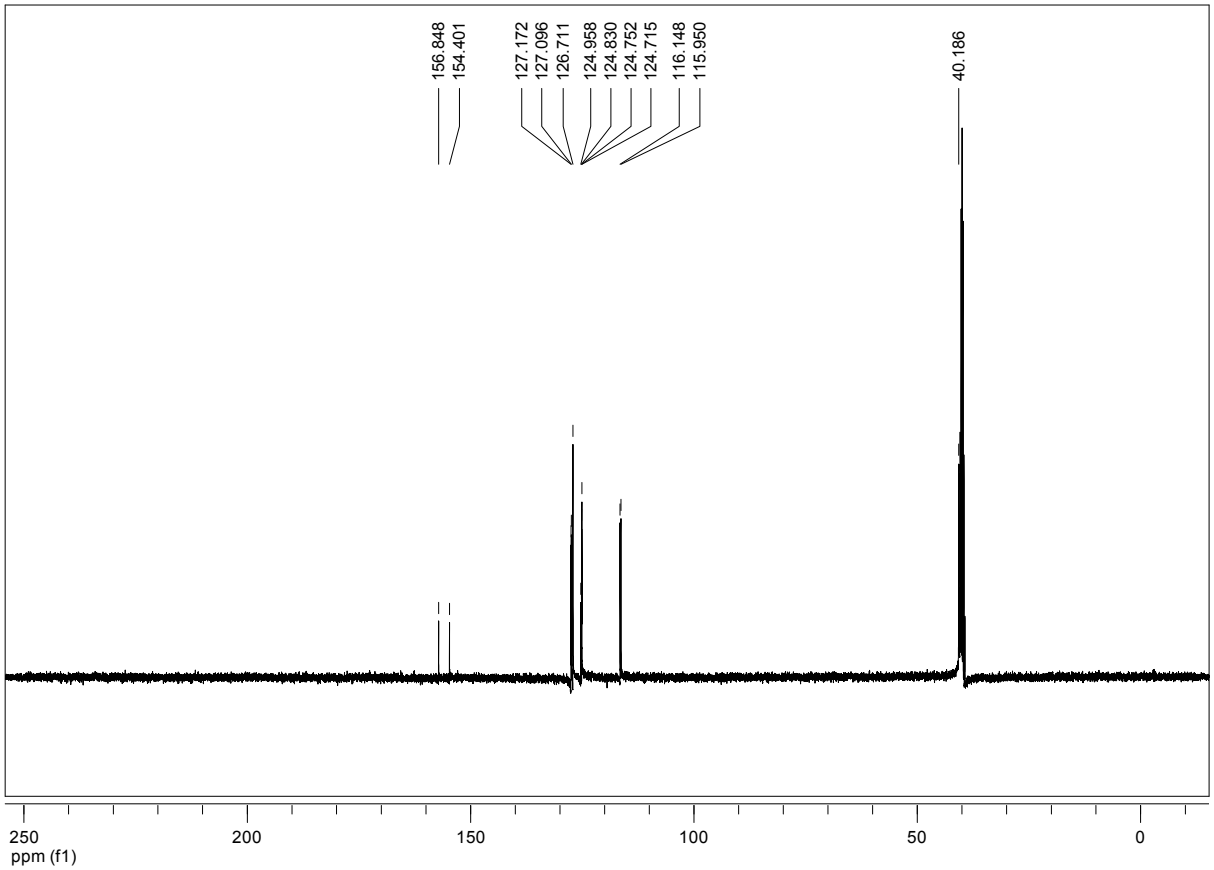
***N*-(4-Fluorophenyl)methanesulfonamide (1i)**



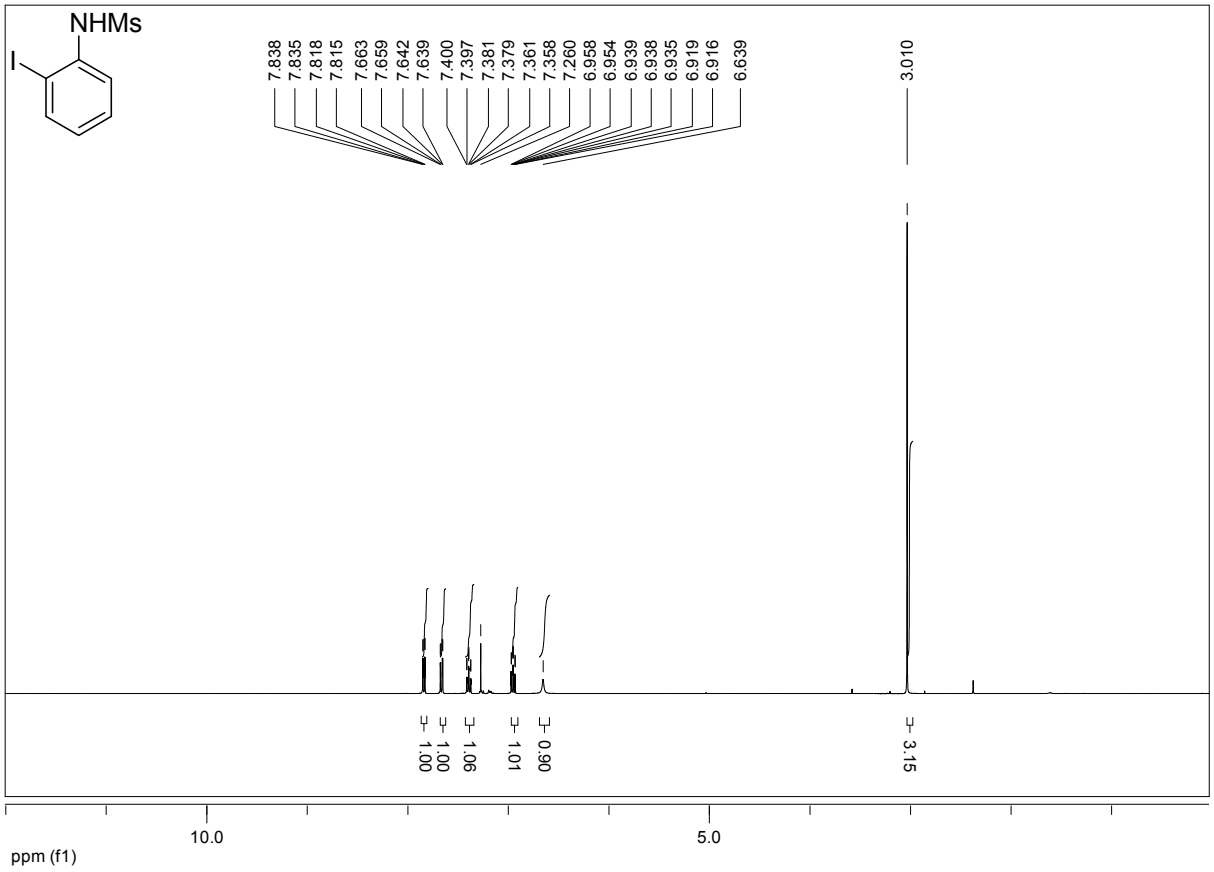


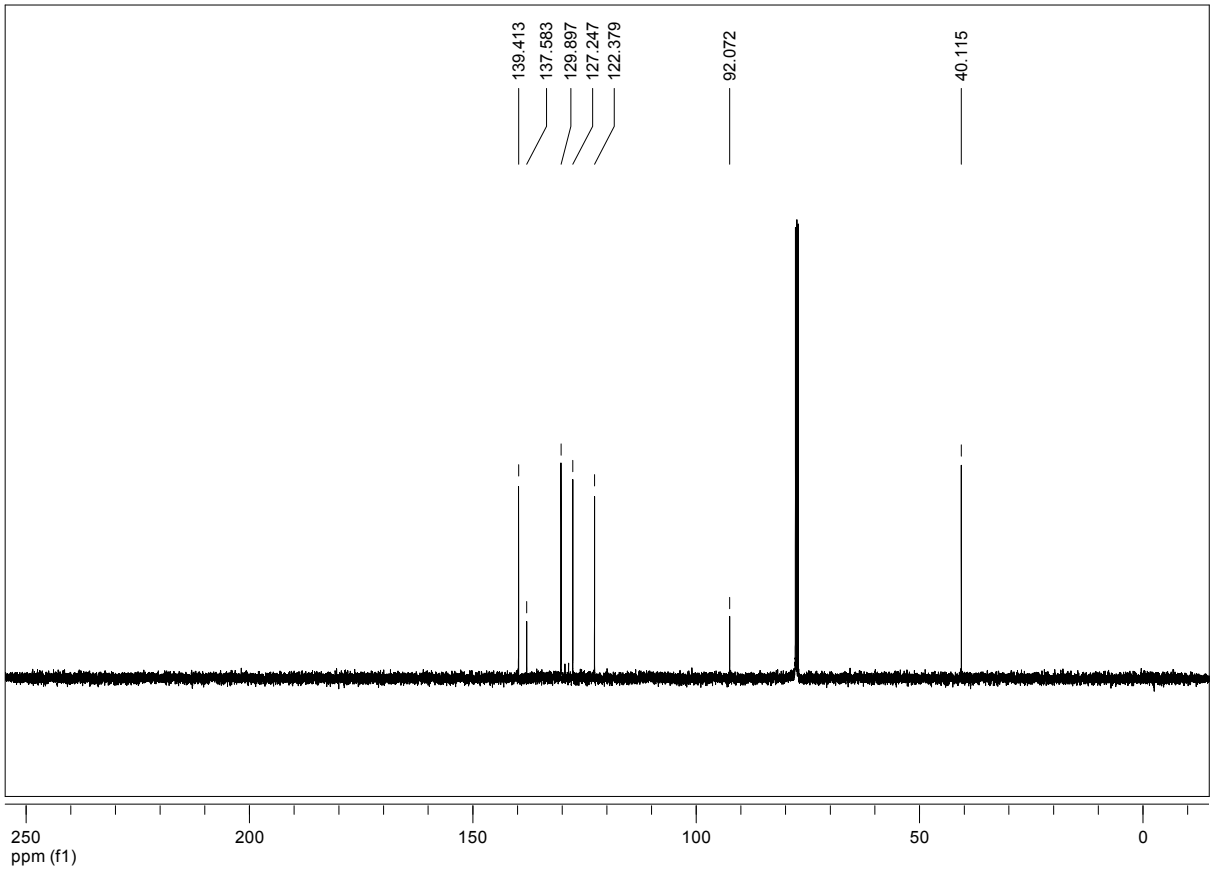
***N*-(2-Fluorophenyl)methanesulfonamide (1j)**



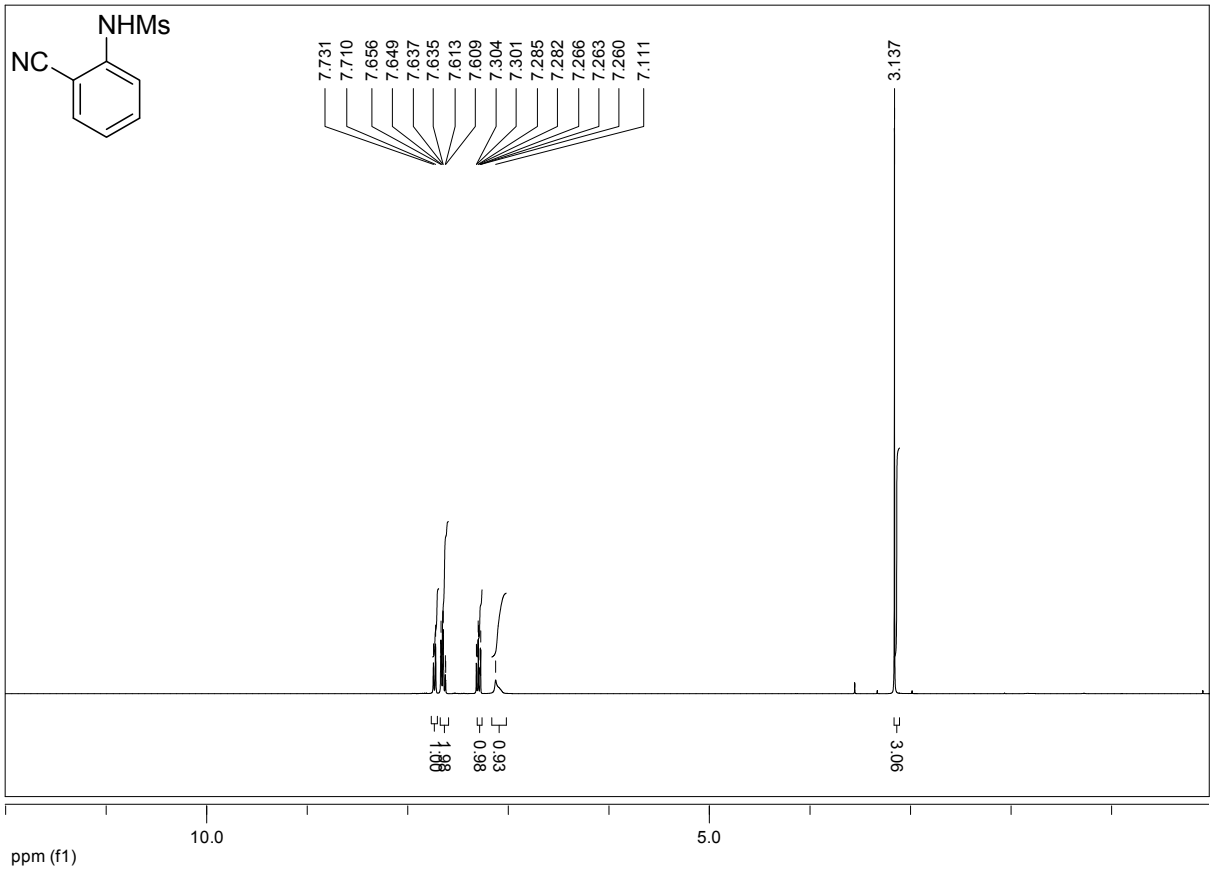


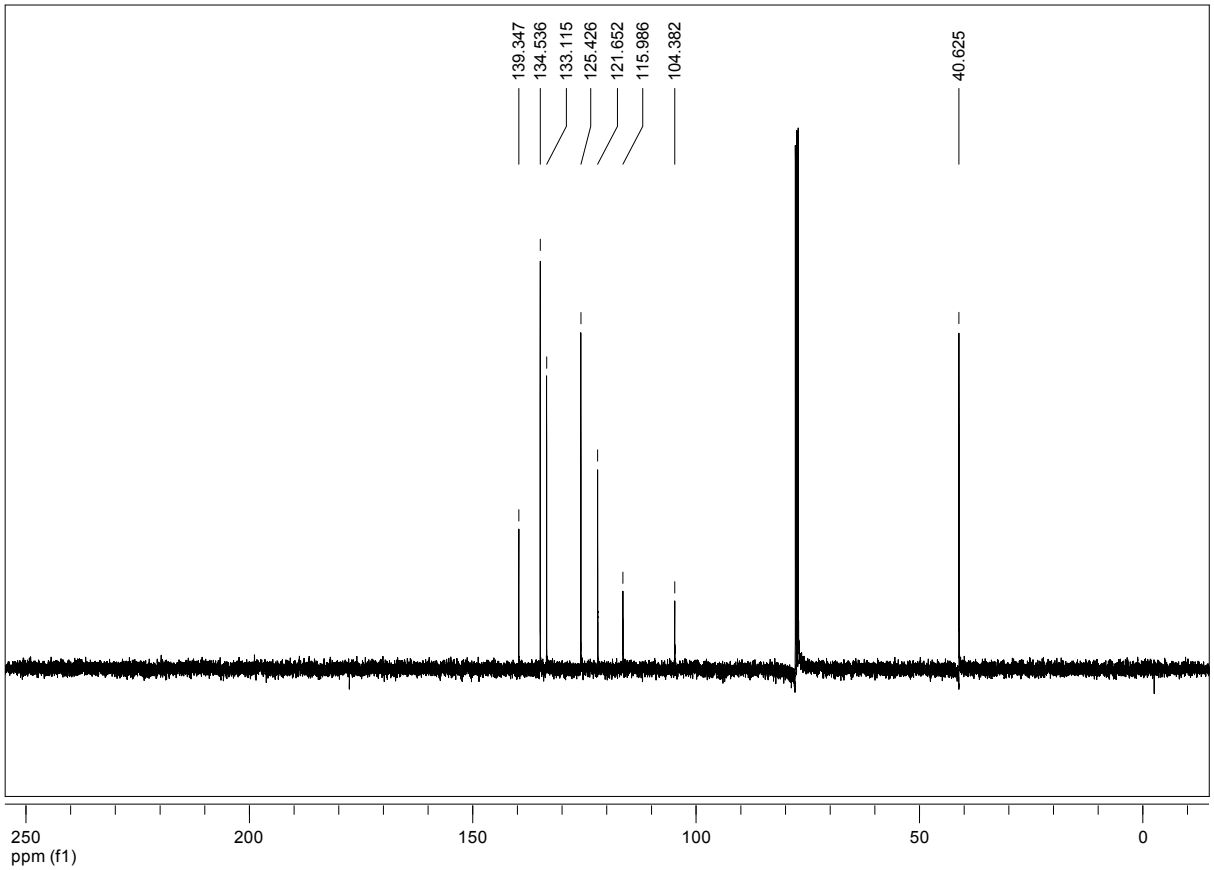
***N*-(2-Iodophenyl)methanesulfonamide (1k)**



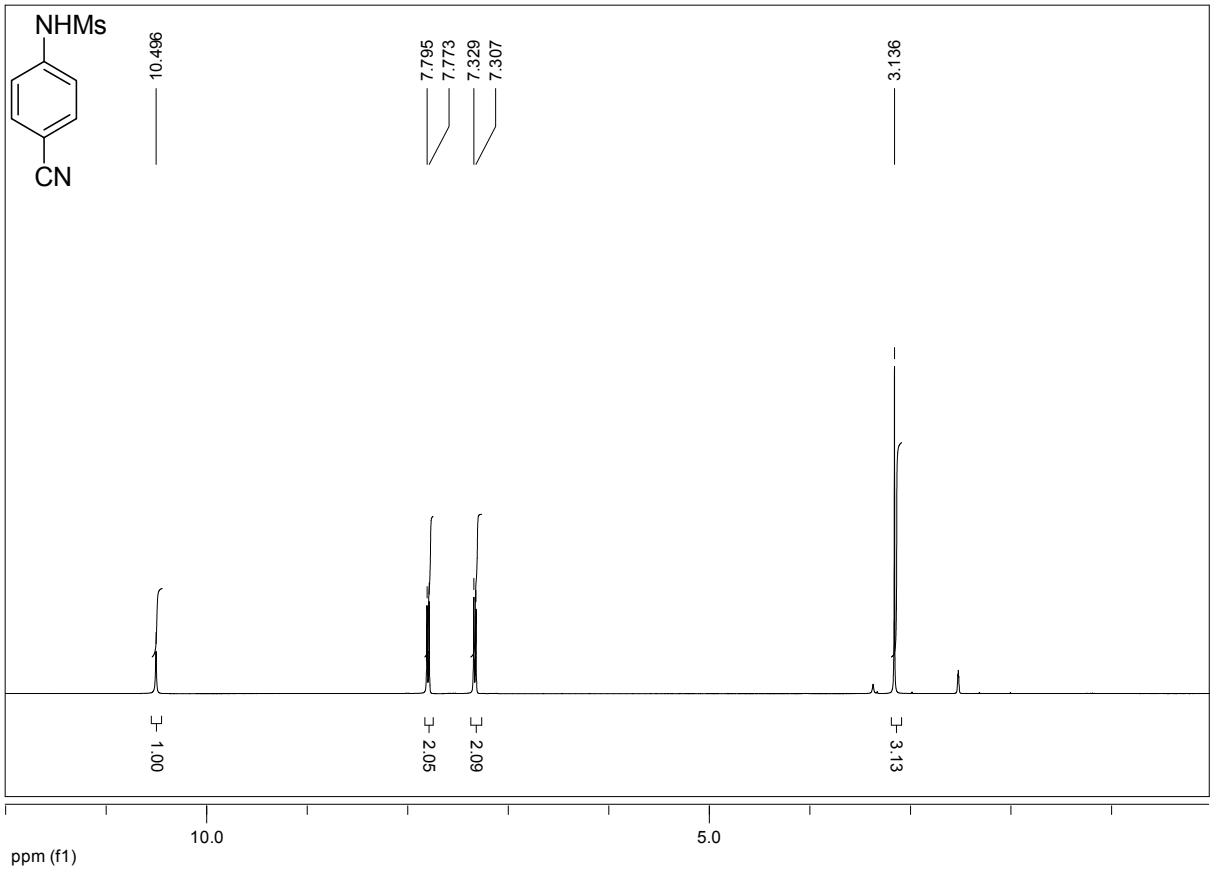


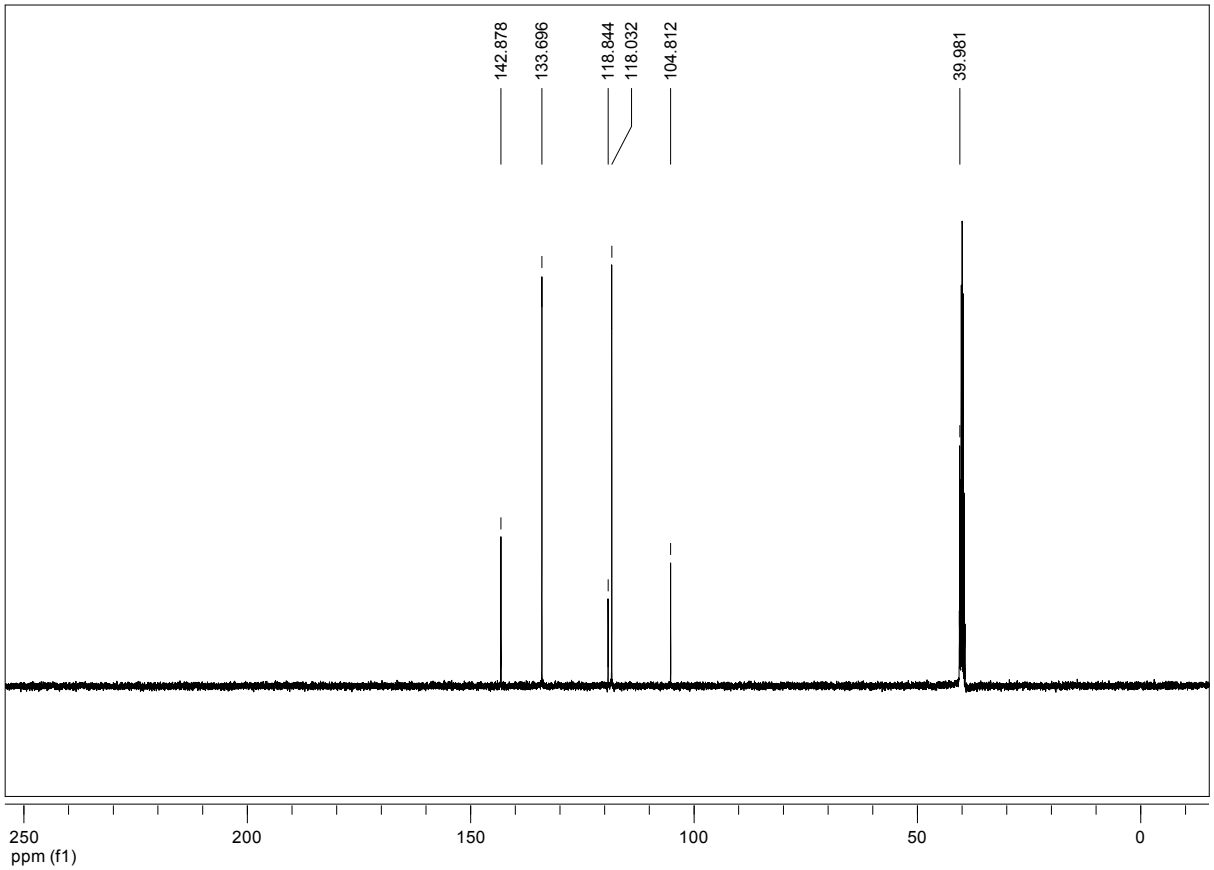
***N*-(2-Cyanophenyl)methanesulfonamide (1m)**



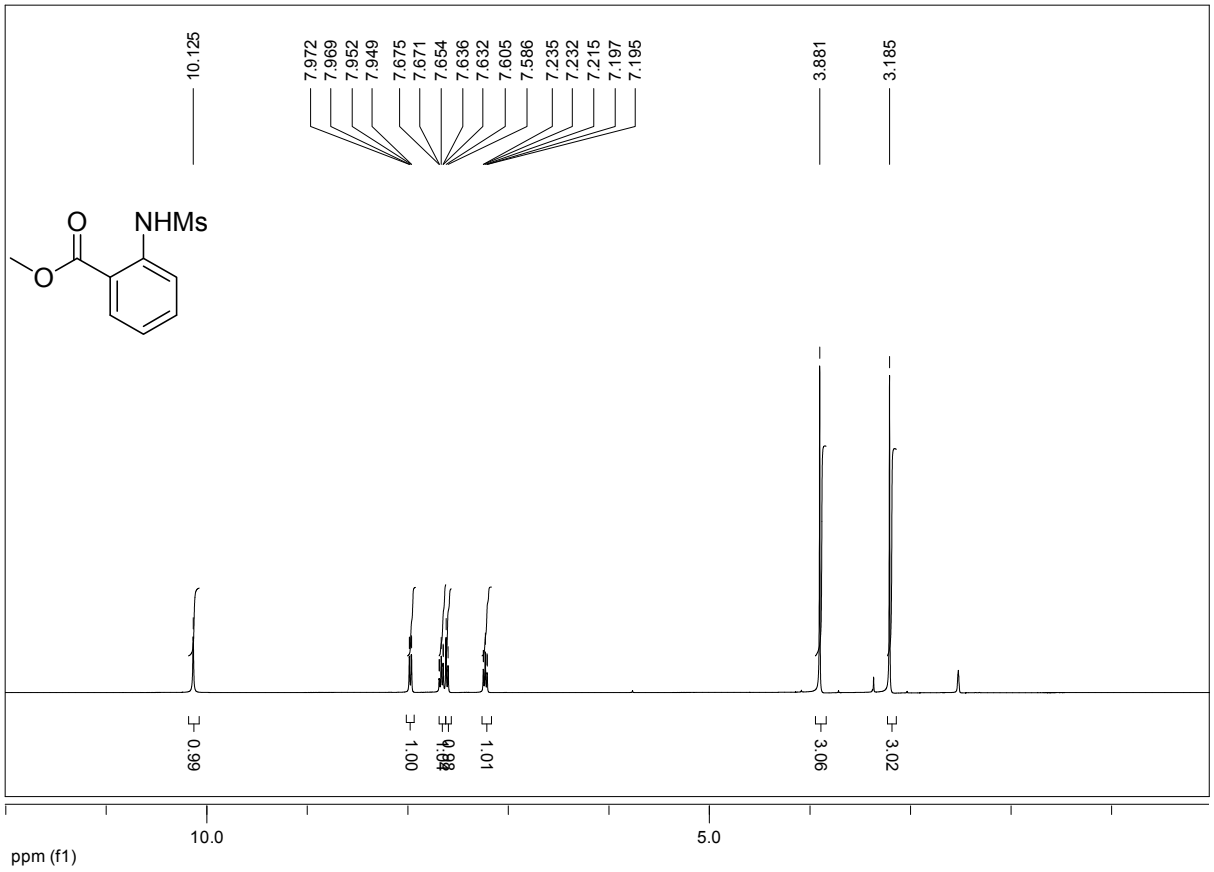


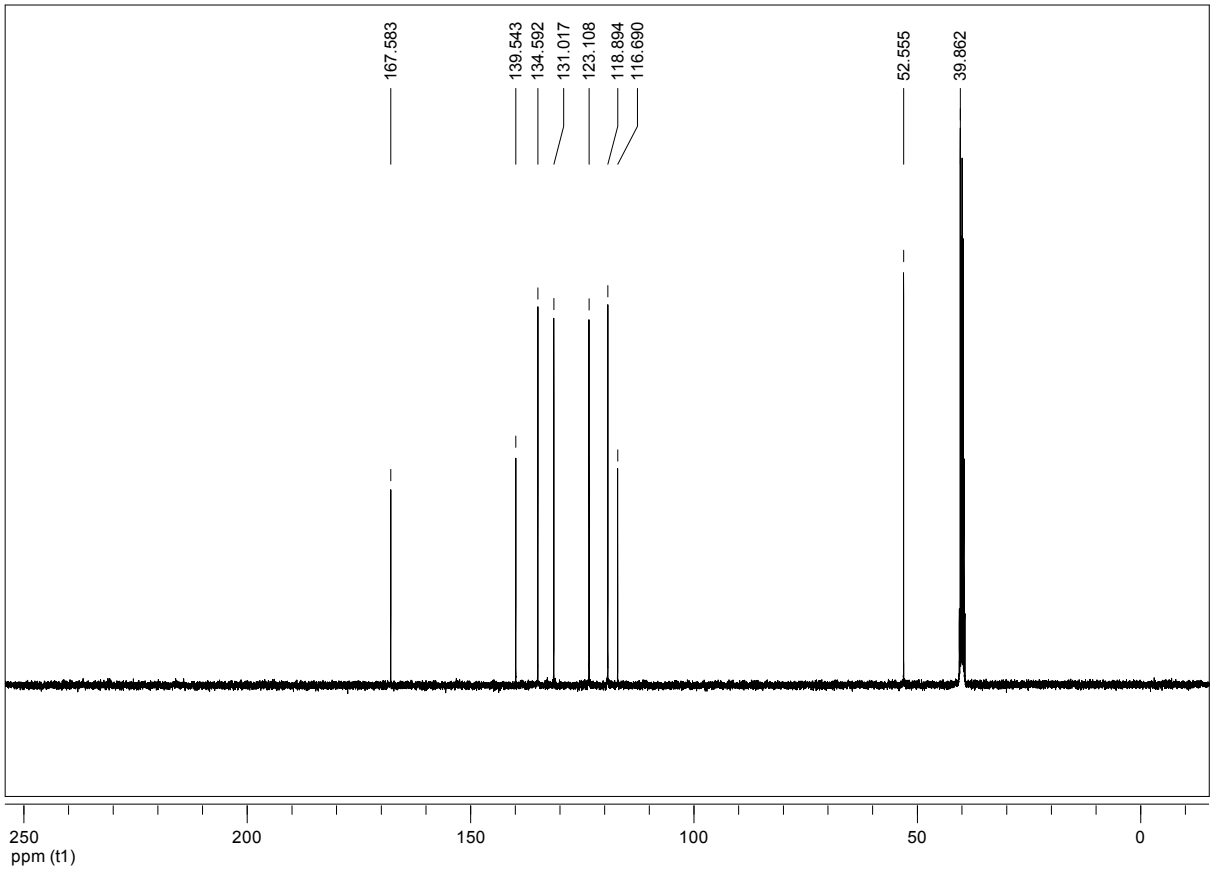
***N*-(4-Cyanophenyl)methanesulfonamide (1n)**



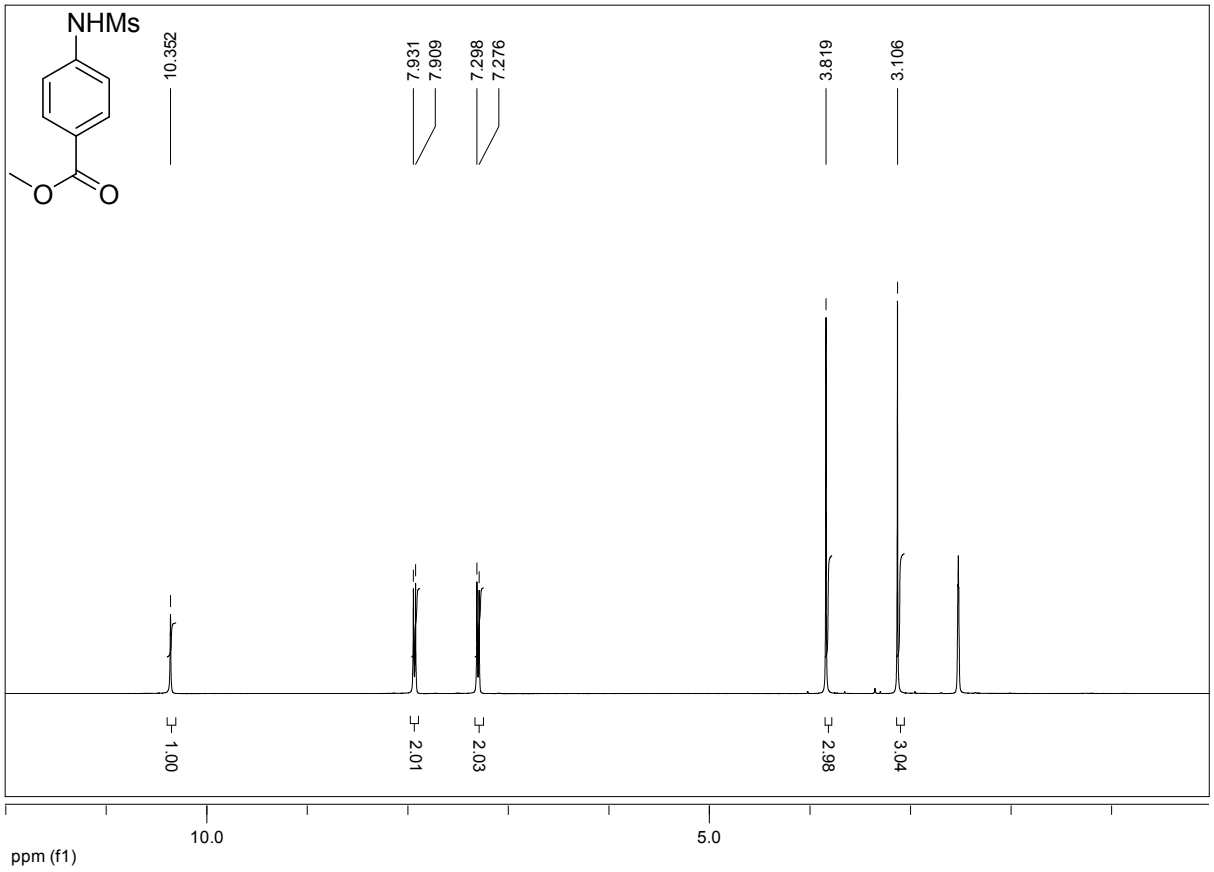


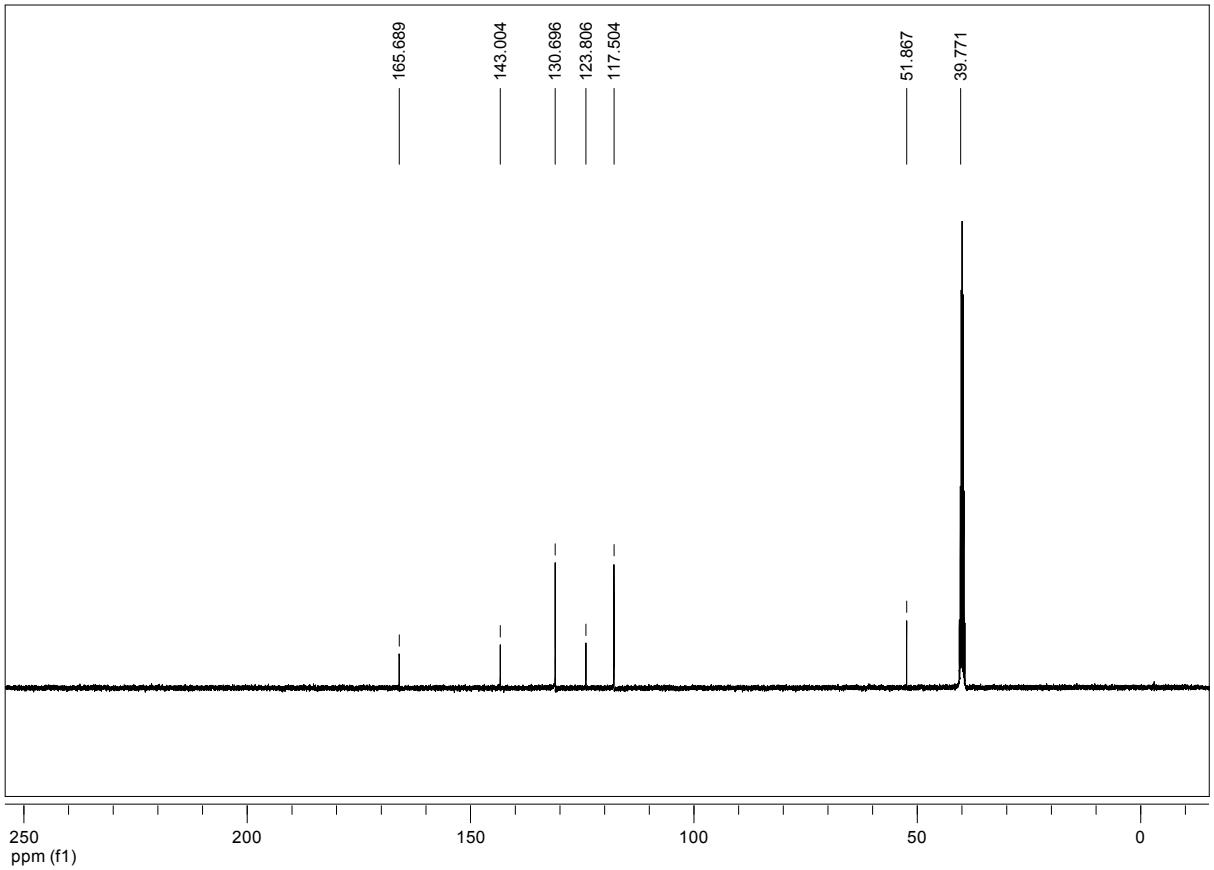
Methyl 2-(methylsulfonamido)benzoate (1o)



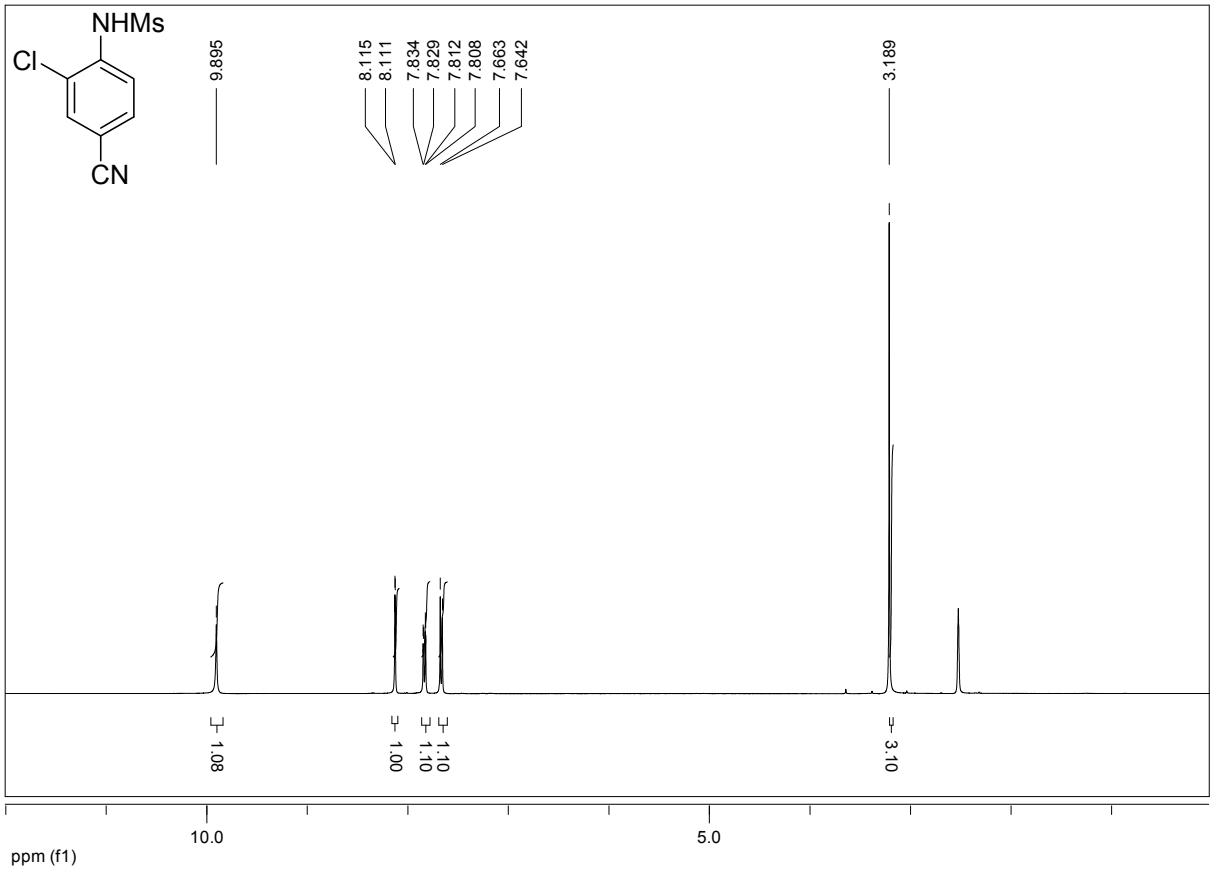


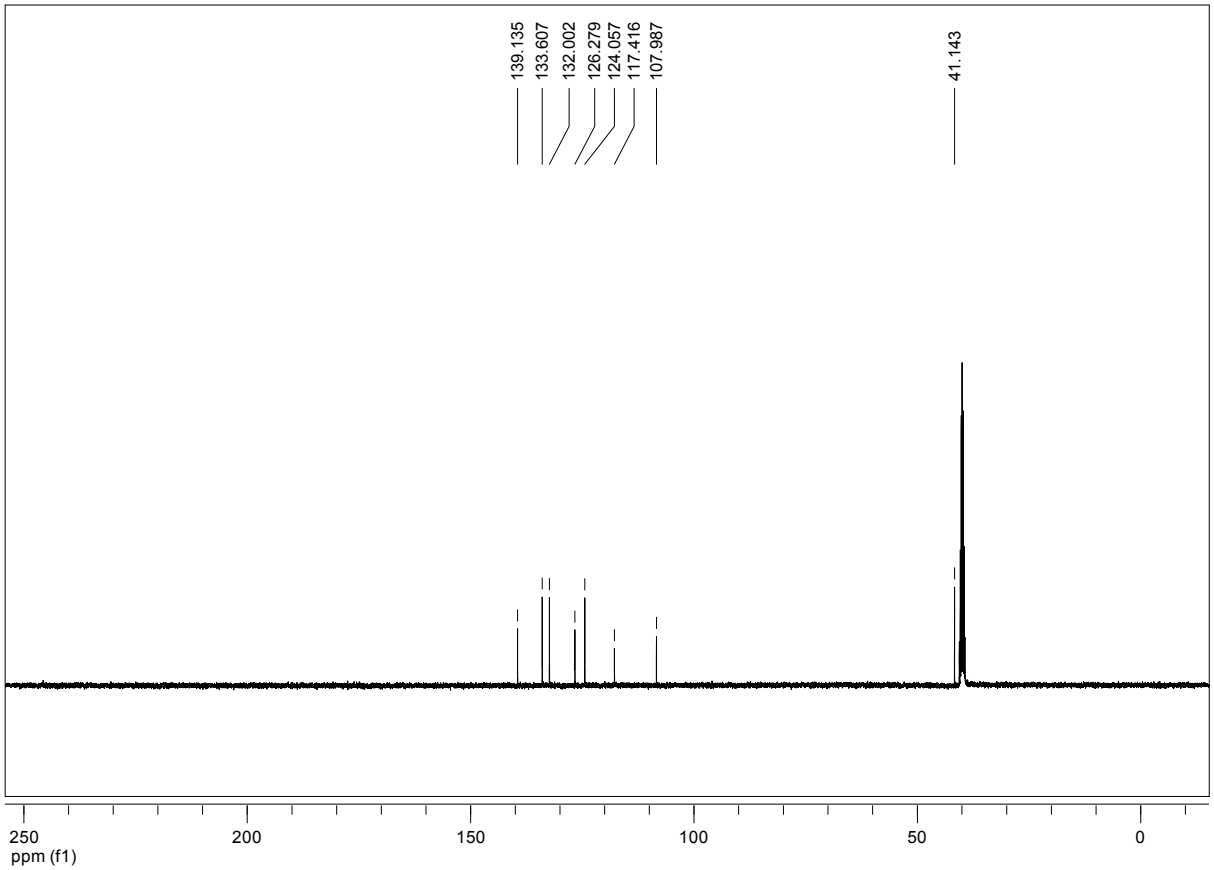
Methyl 4-(methylsulfonamido)benzoate (1p)



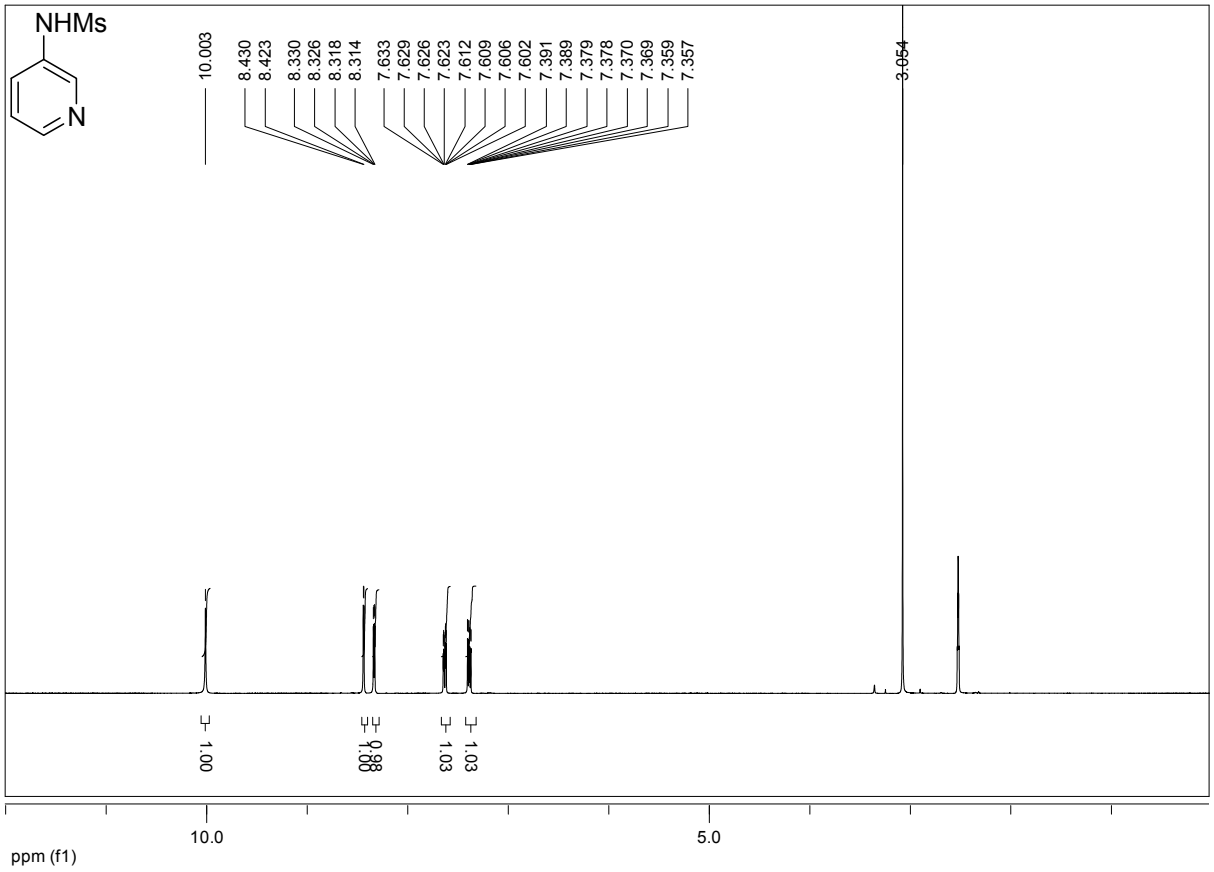


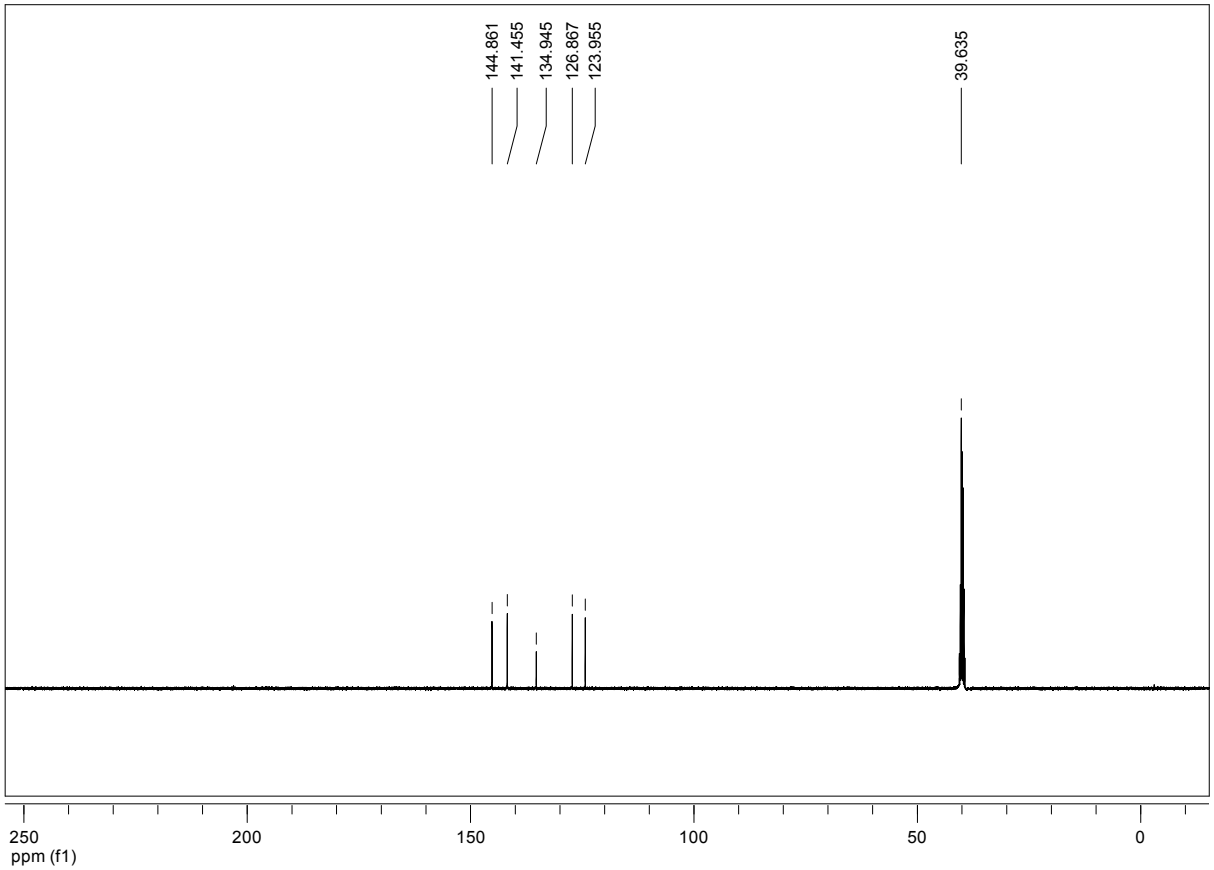
***N*-(2-Chloro-4-cyanophenyl)methanesulfonamide (1q)**



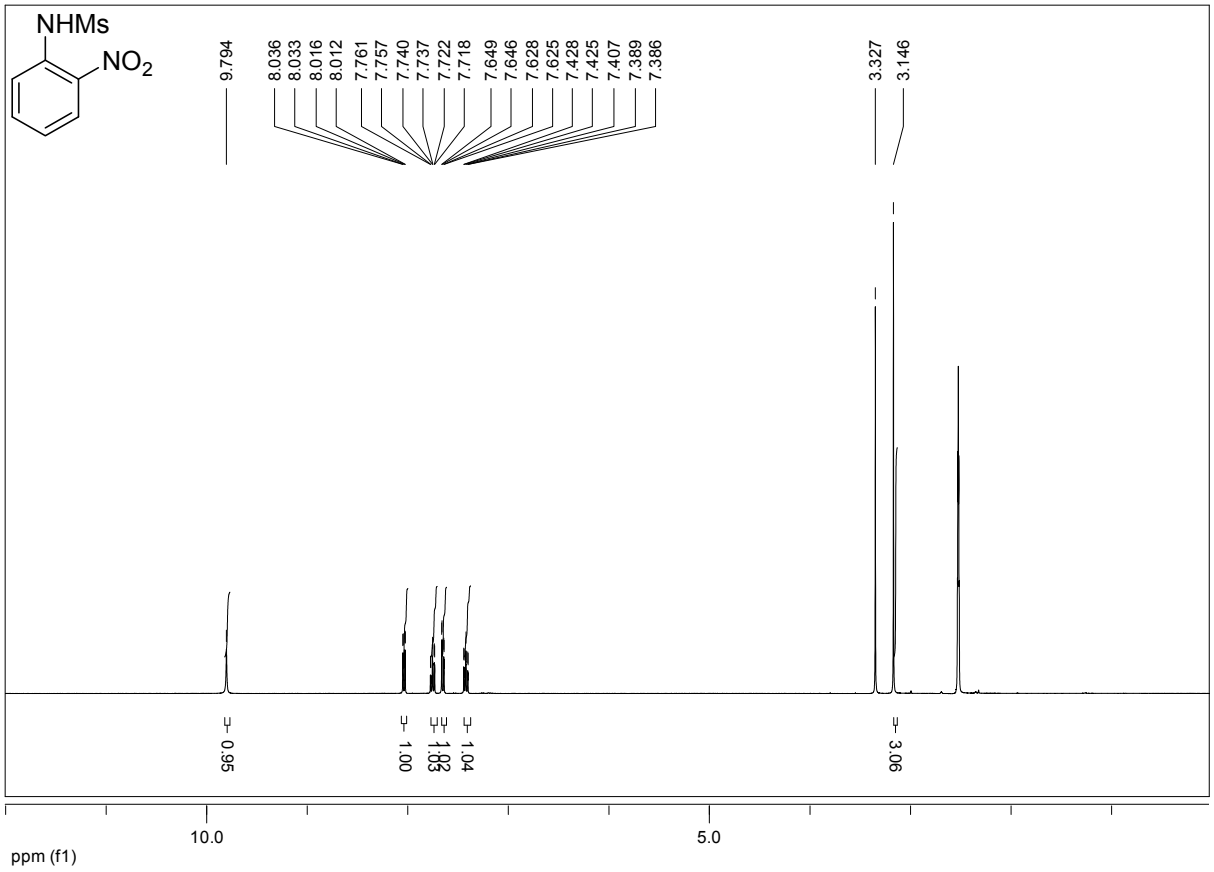


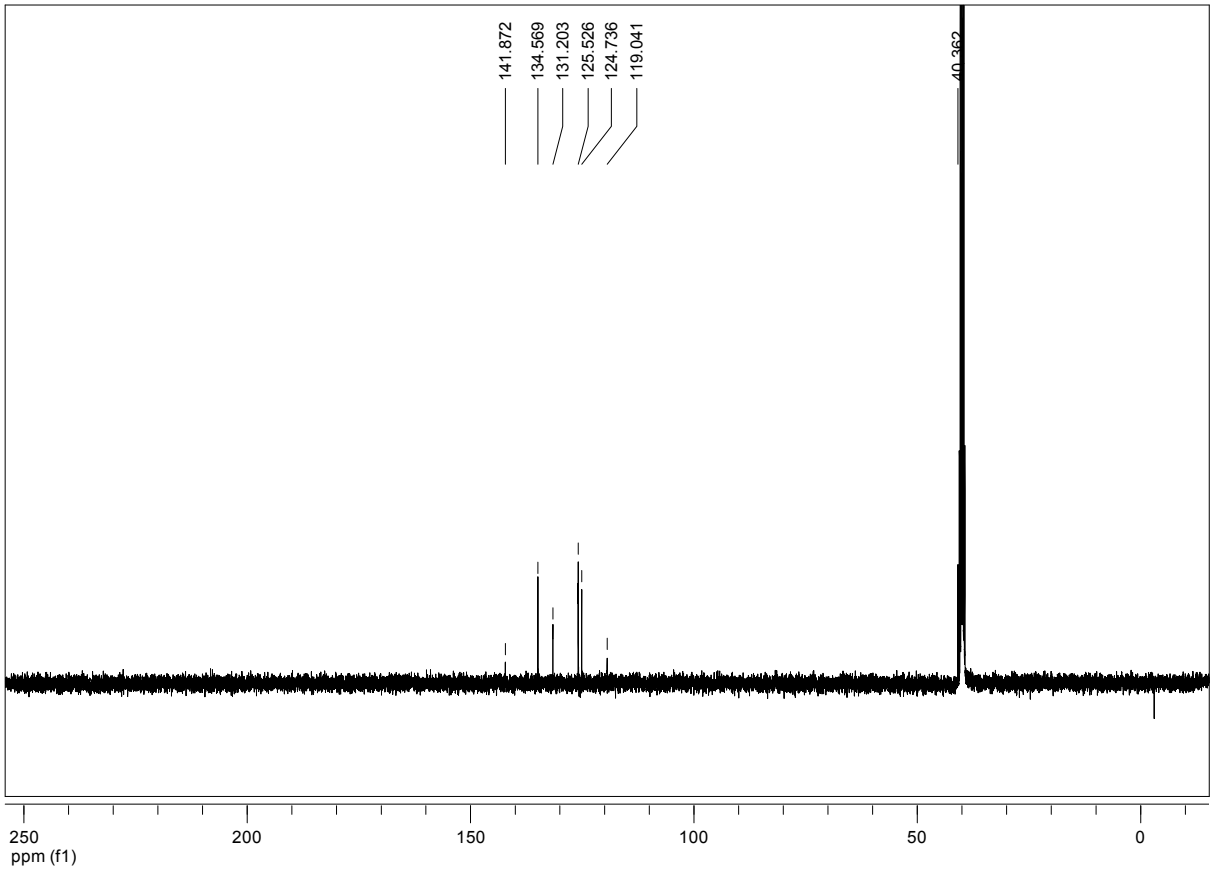
***N*-(Pyridin-3-yl)methanesulfonamide (1r)**



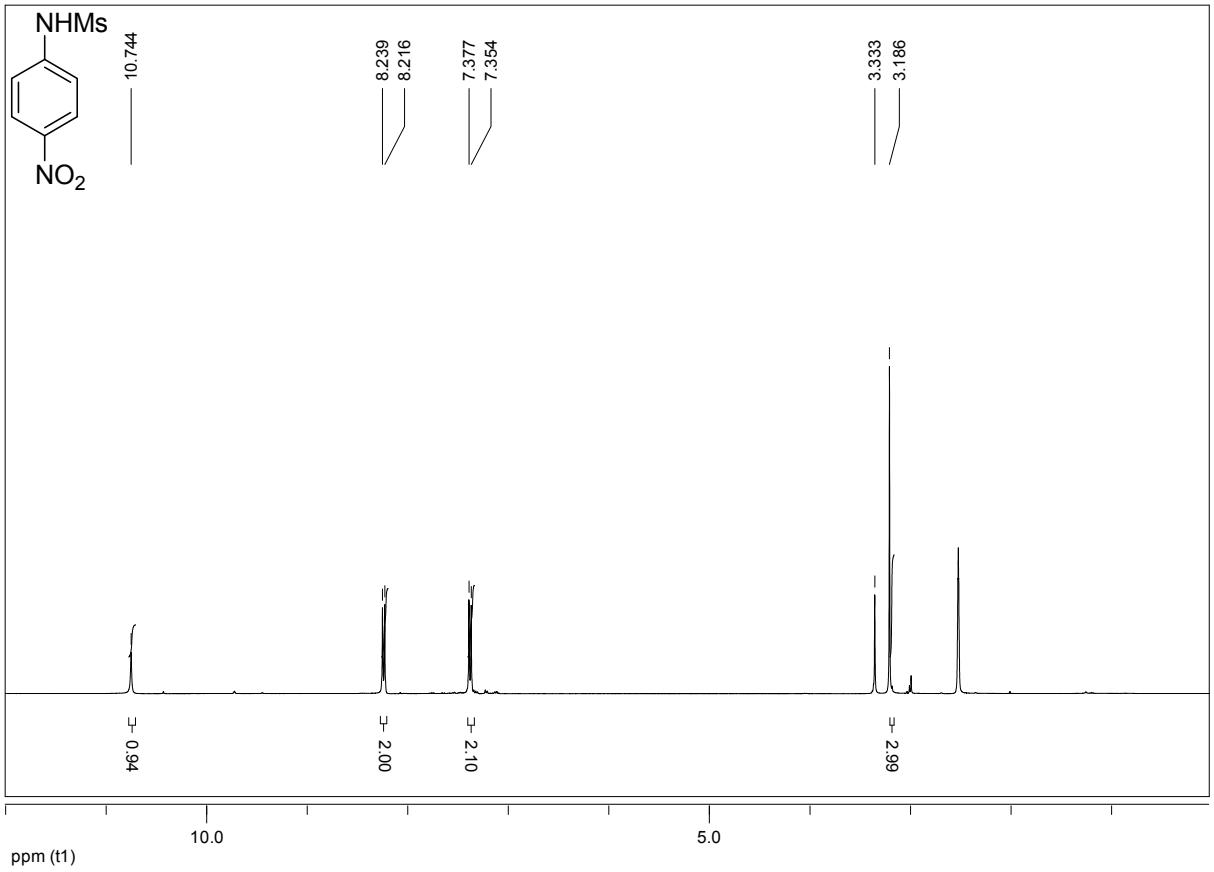


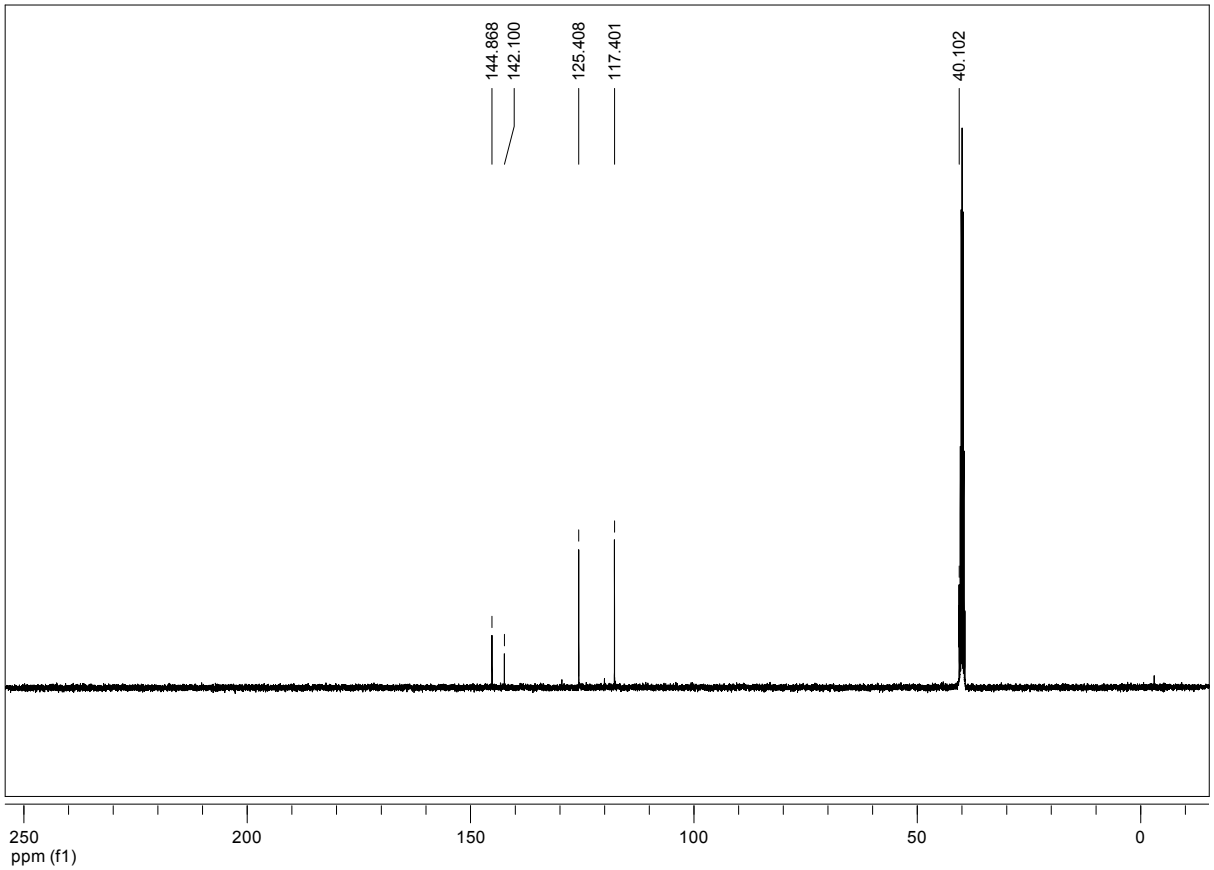
***N*-(2-Nitrophenyl)methanesulfonamide 2a** (ortho)



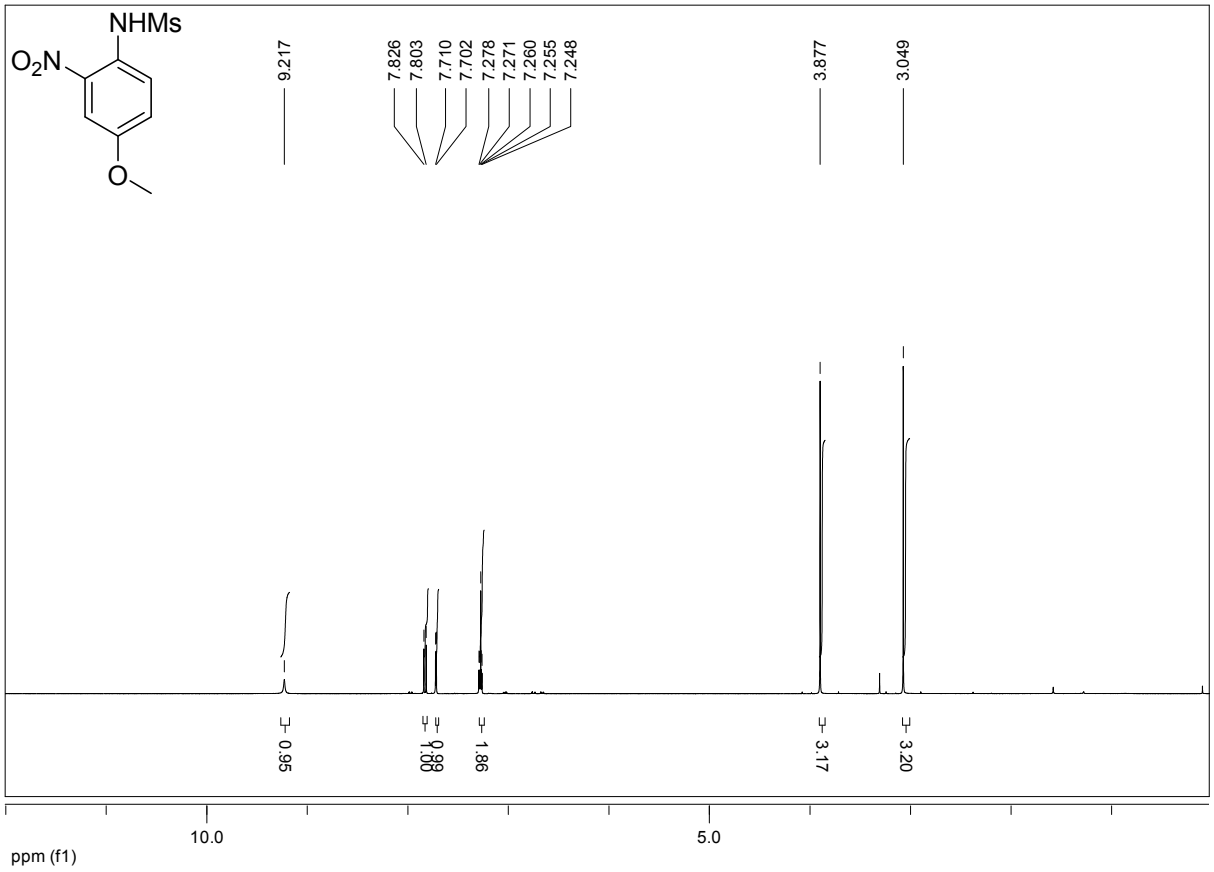


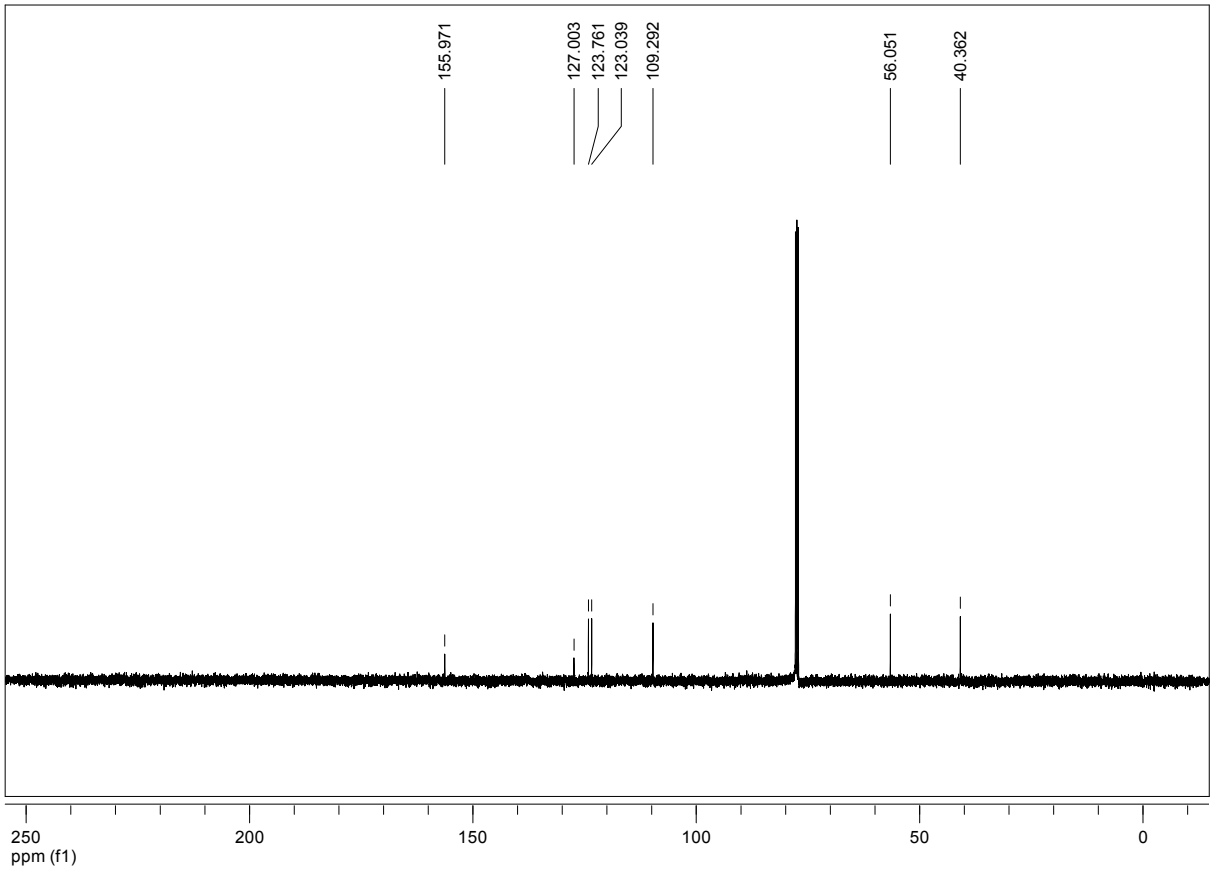
***N*-(4-Nitrophenyl)methanesulfonamide 2a** (para)



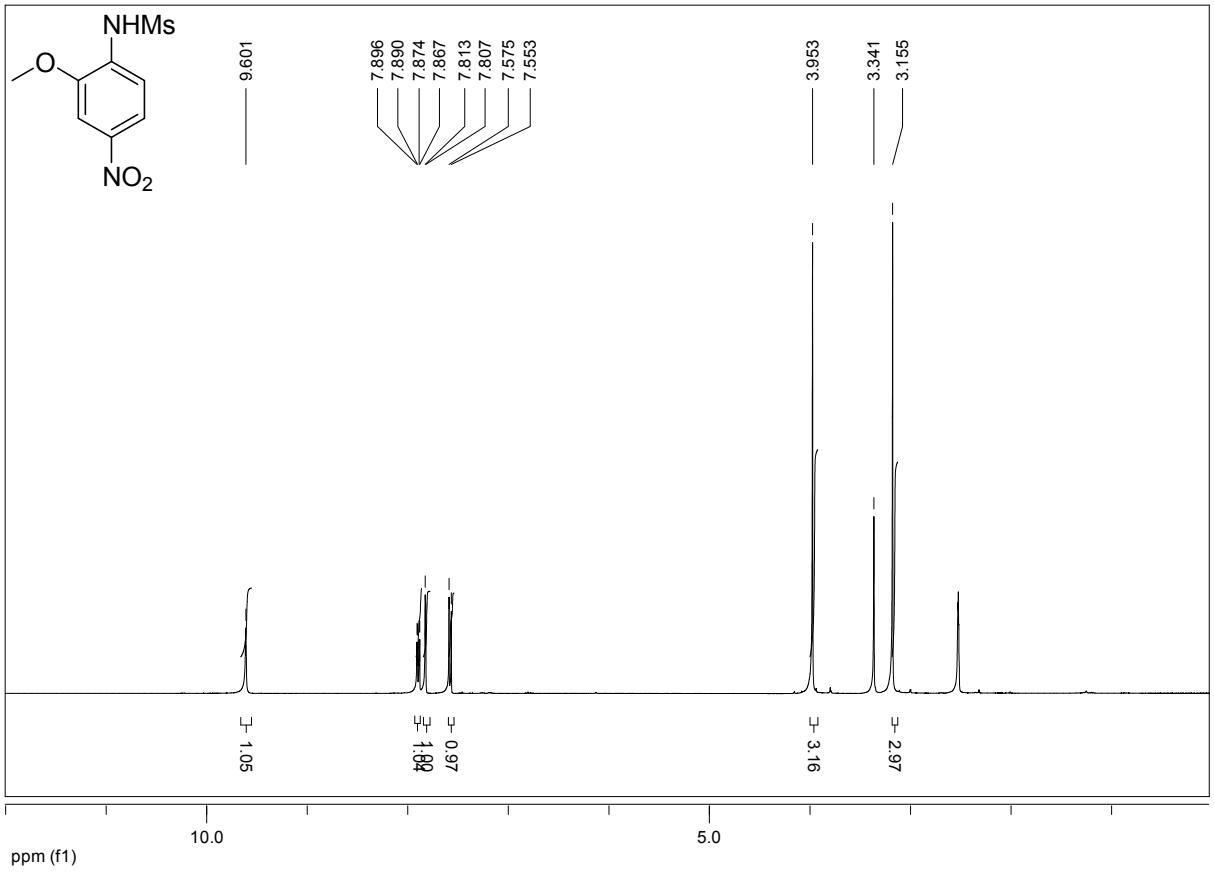


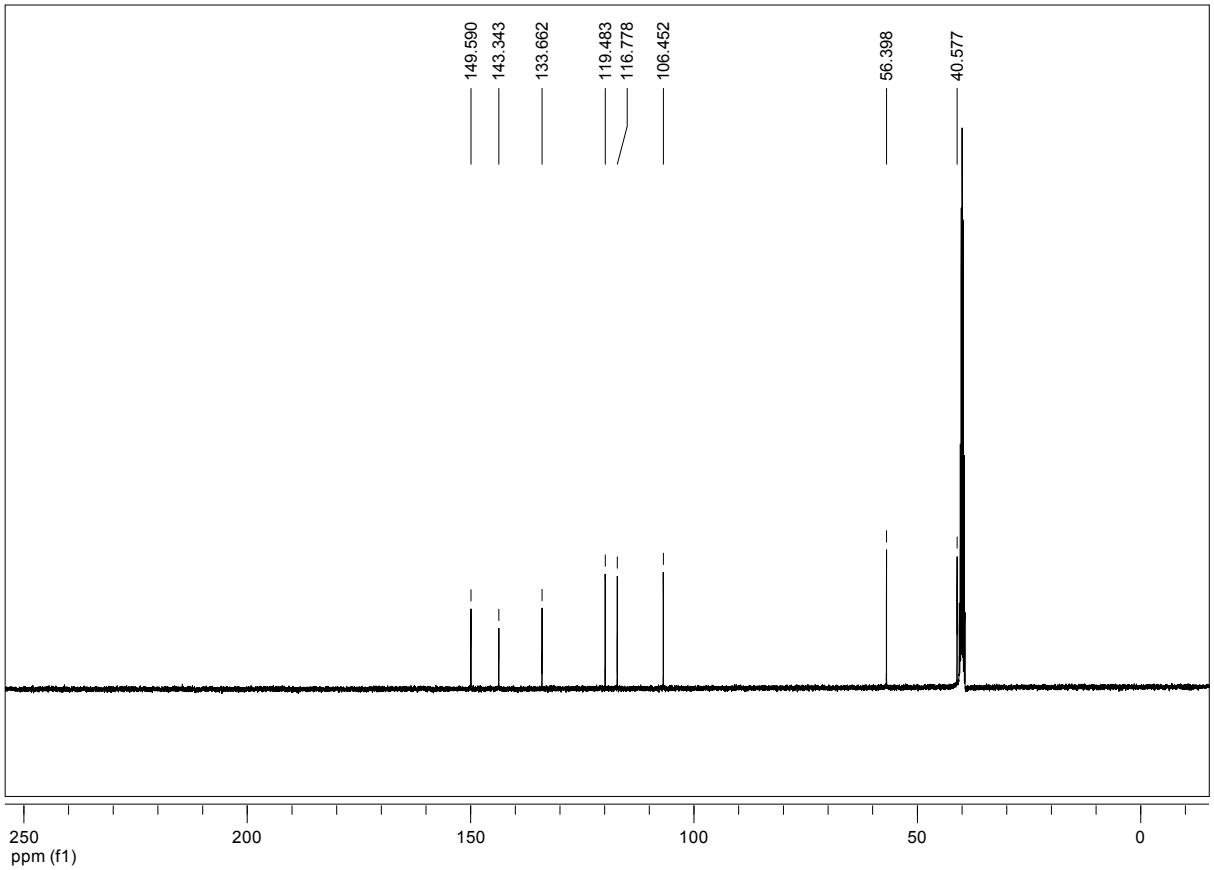
***N*-(4-Methox-2-nitroyphenyl)methanesulfonamide 2b**



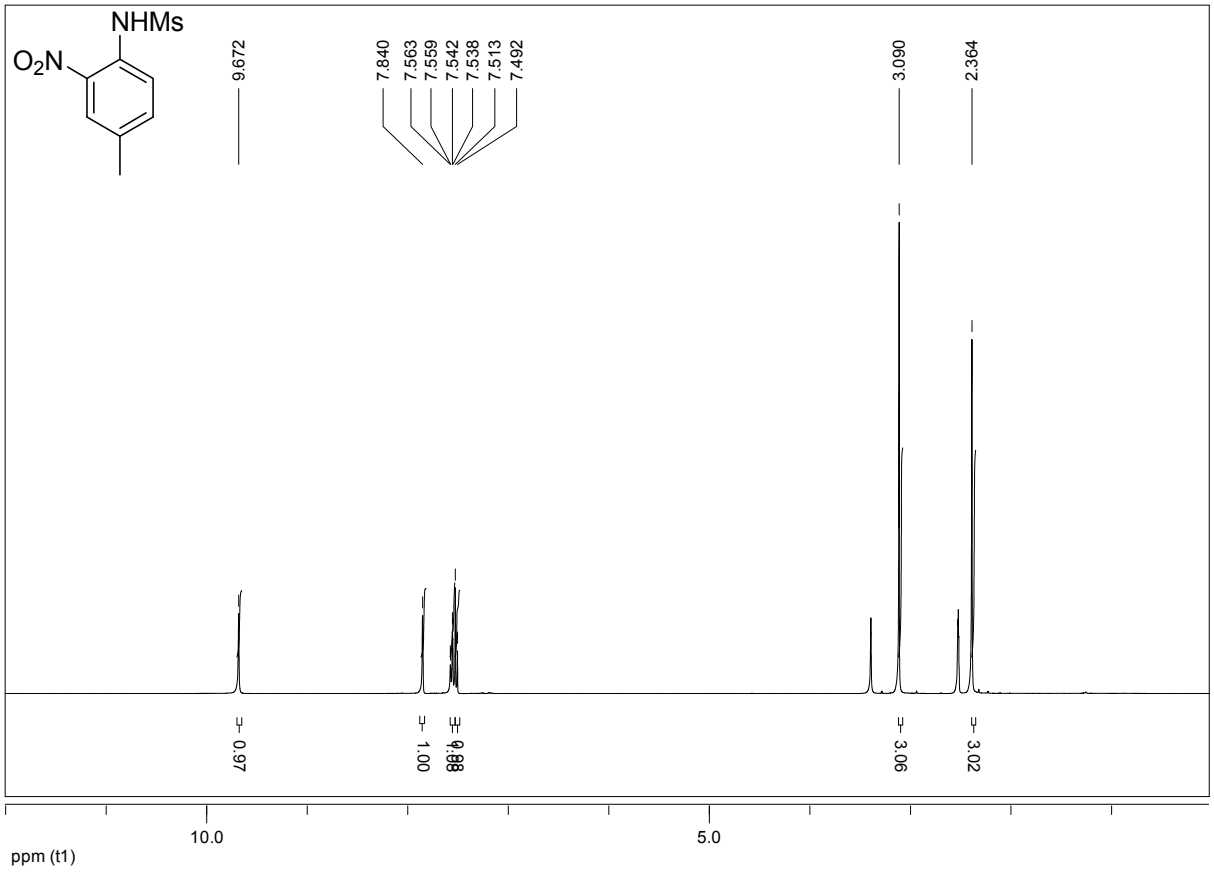


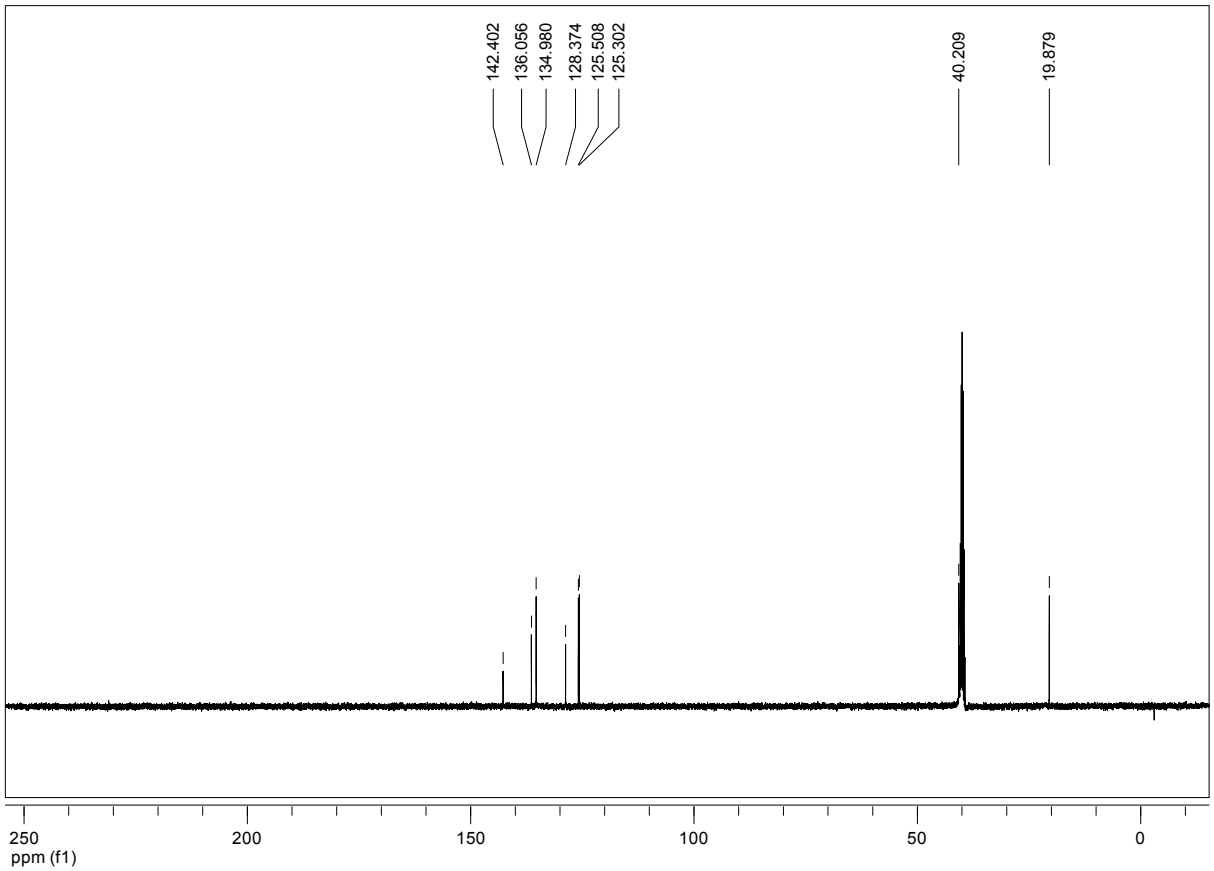
***N*-(2-Methoxy-4-nitrophenyl)methanesulfonamide 2c**



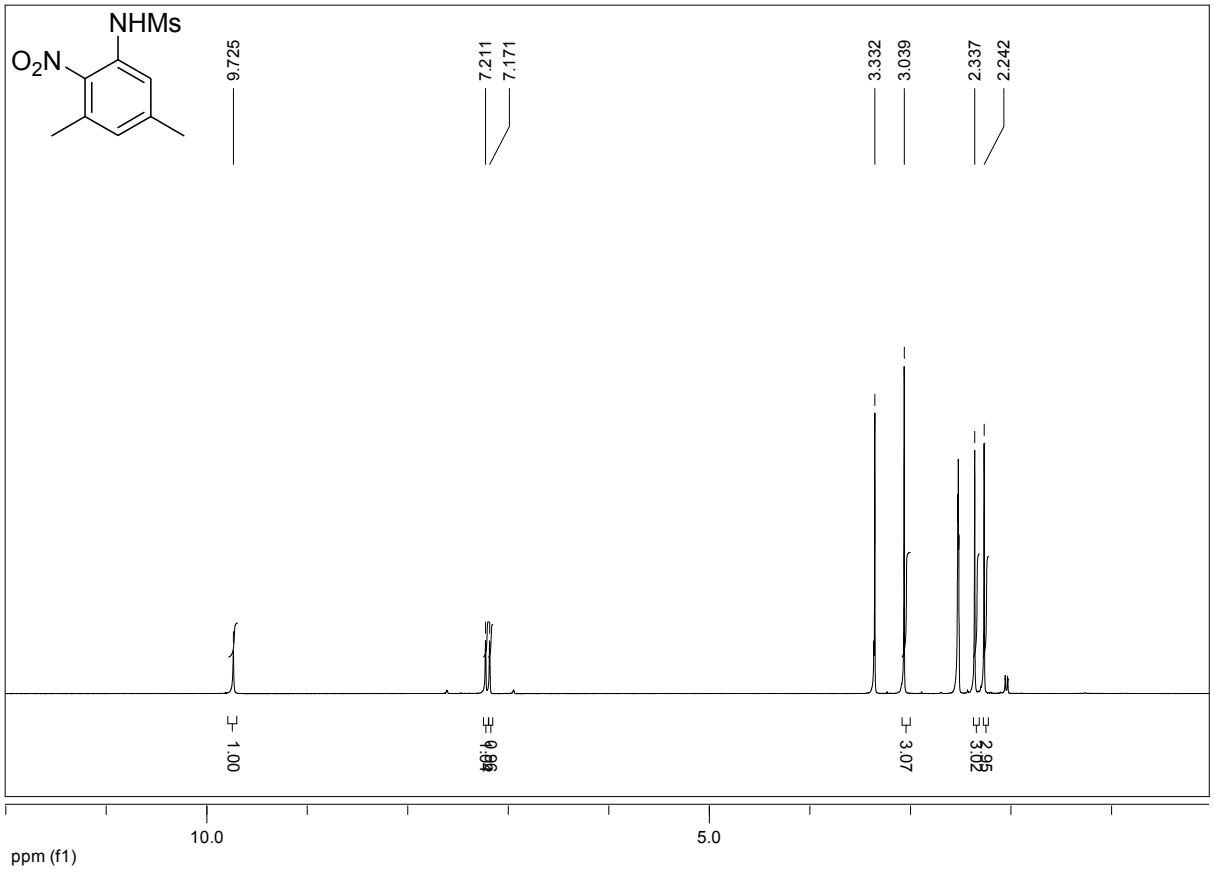


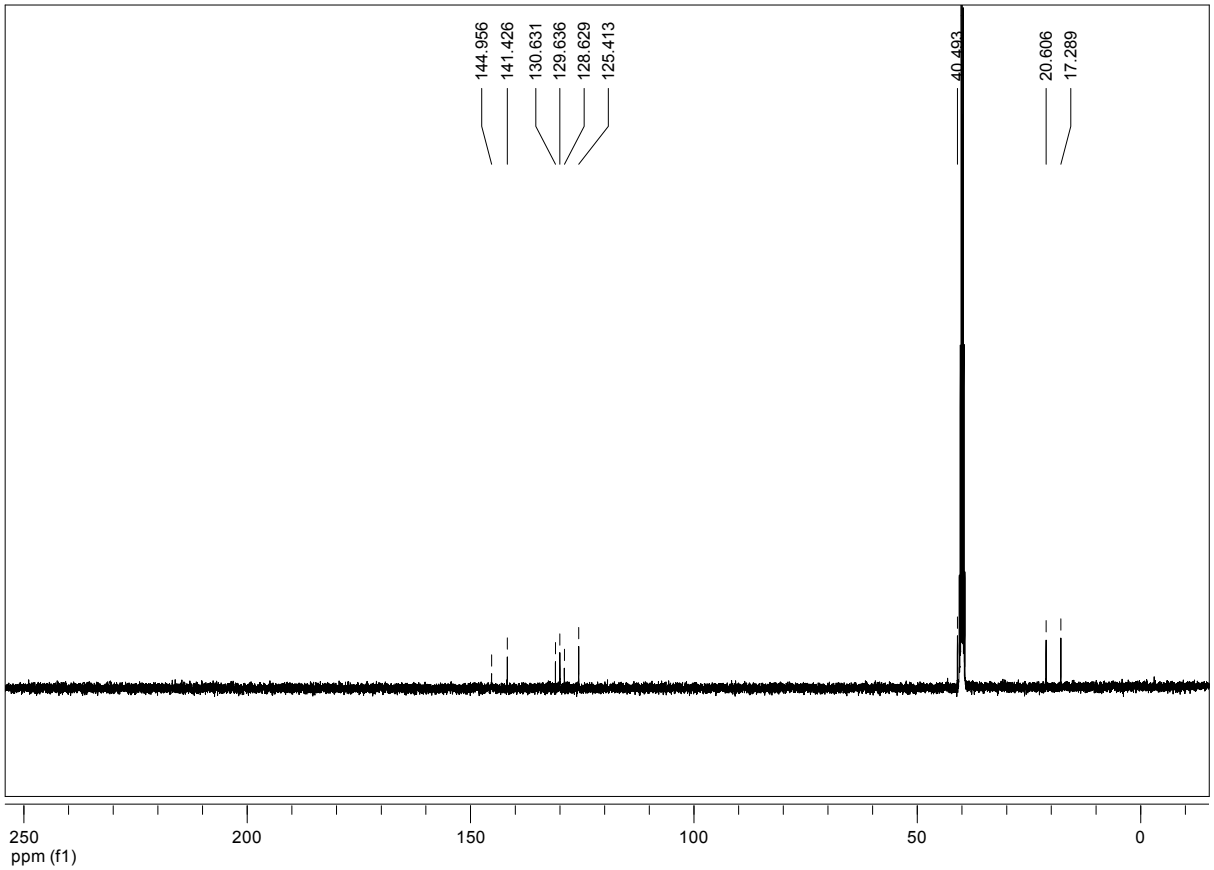
***N*-(4-Methyl-2-nitrophenyl)methanesulfonamide 2d**



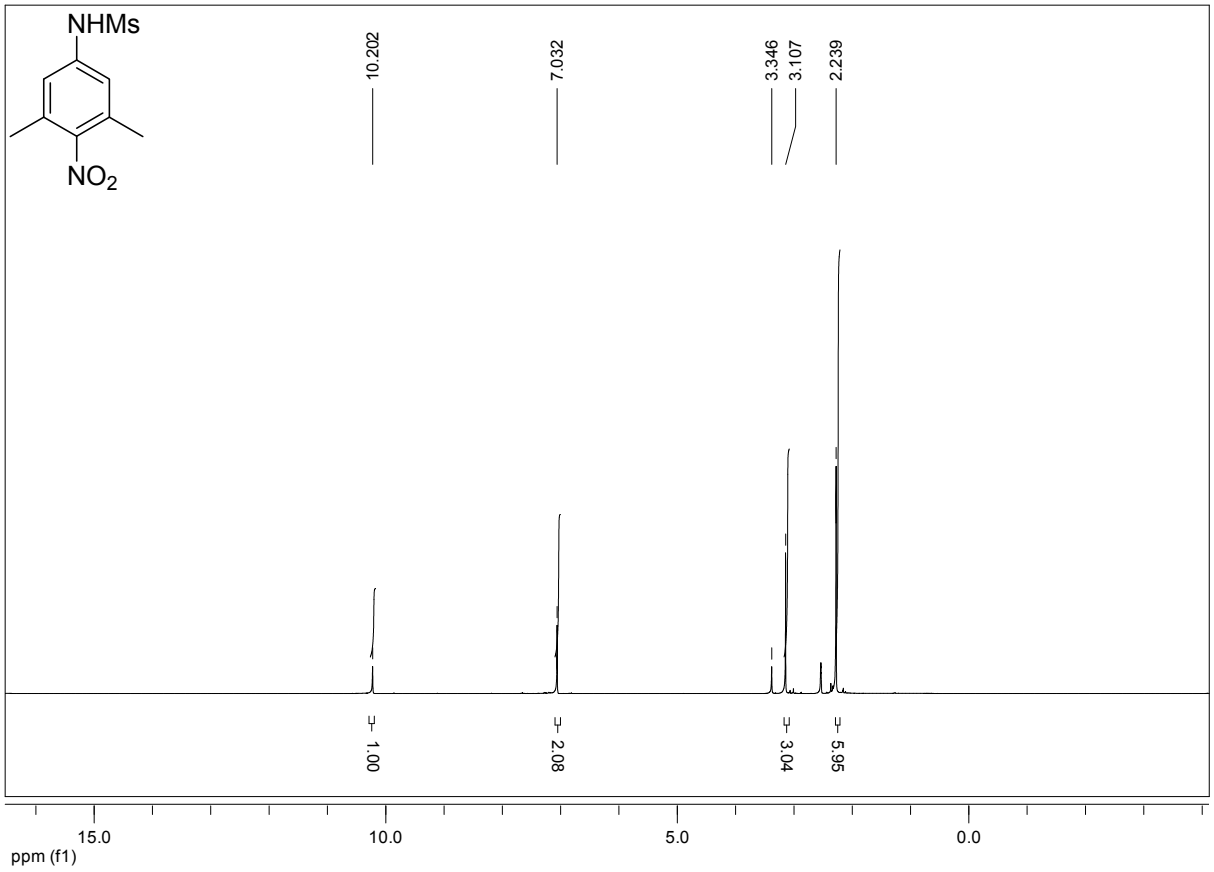


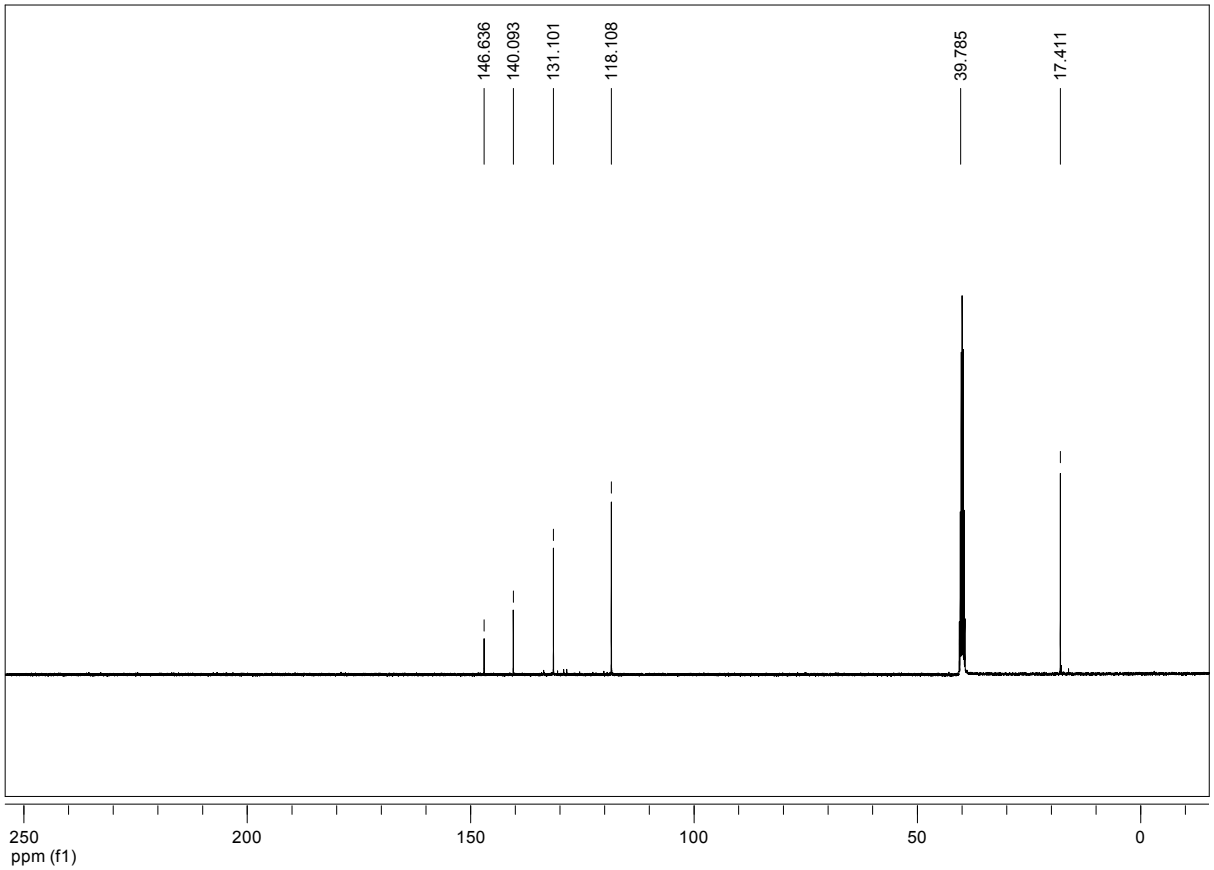
***N*-(3,5-Dimethyl-2-nitrophenyl)methanesulfonamide 2e**(ortho)



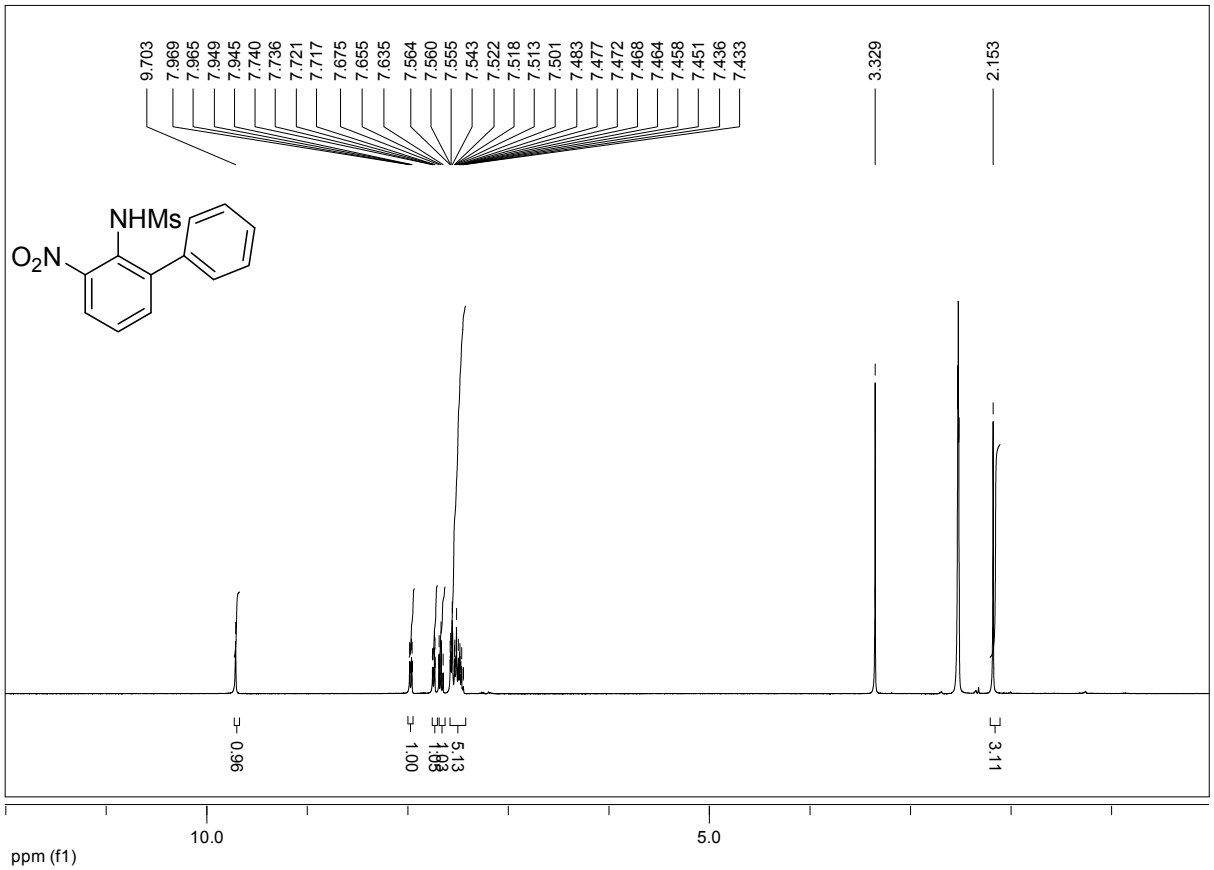


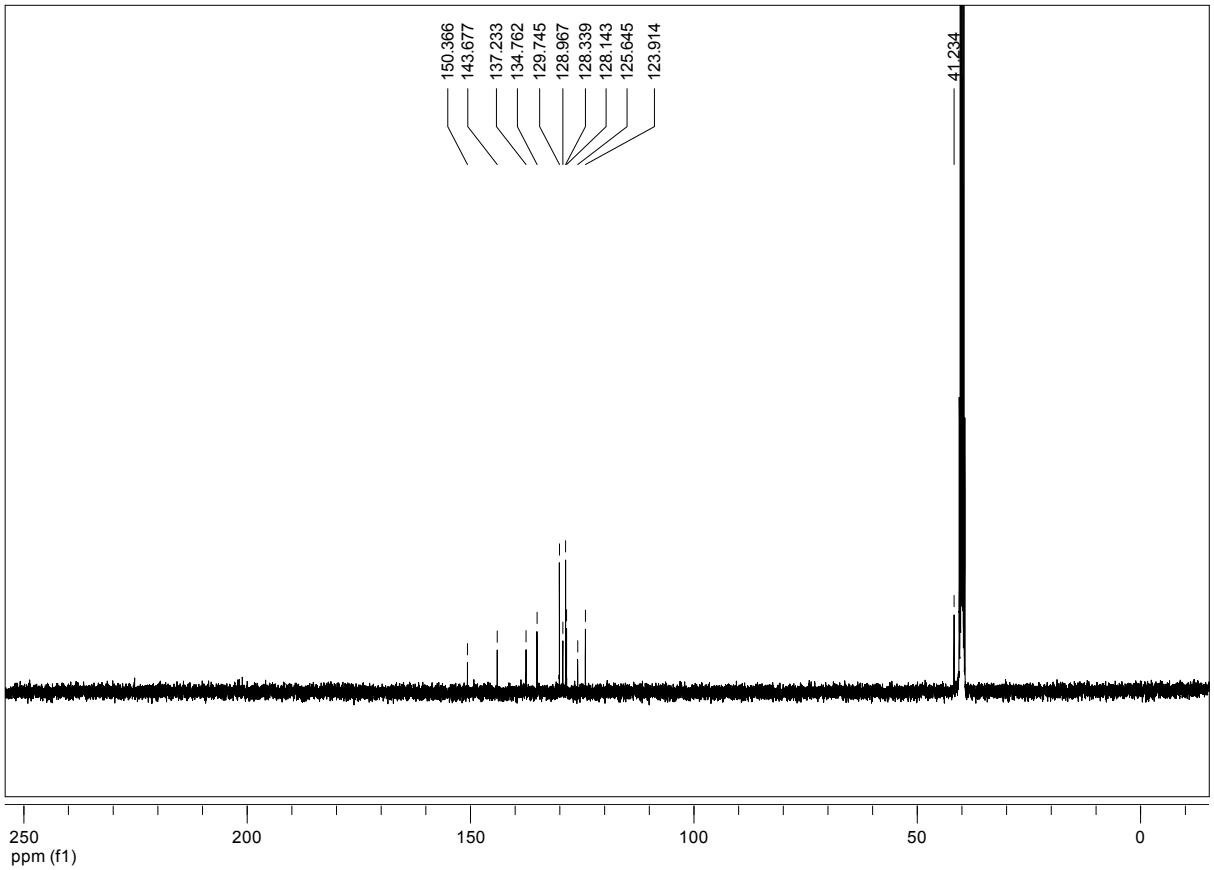
***N*-(3,5-Dimethyl-4-nitrophenyl)methanesulfonamide 2e** (para)



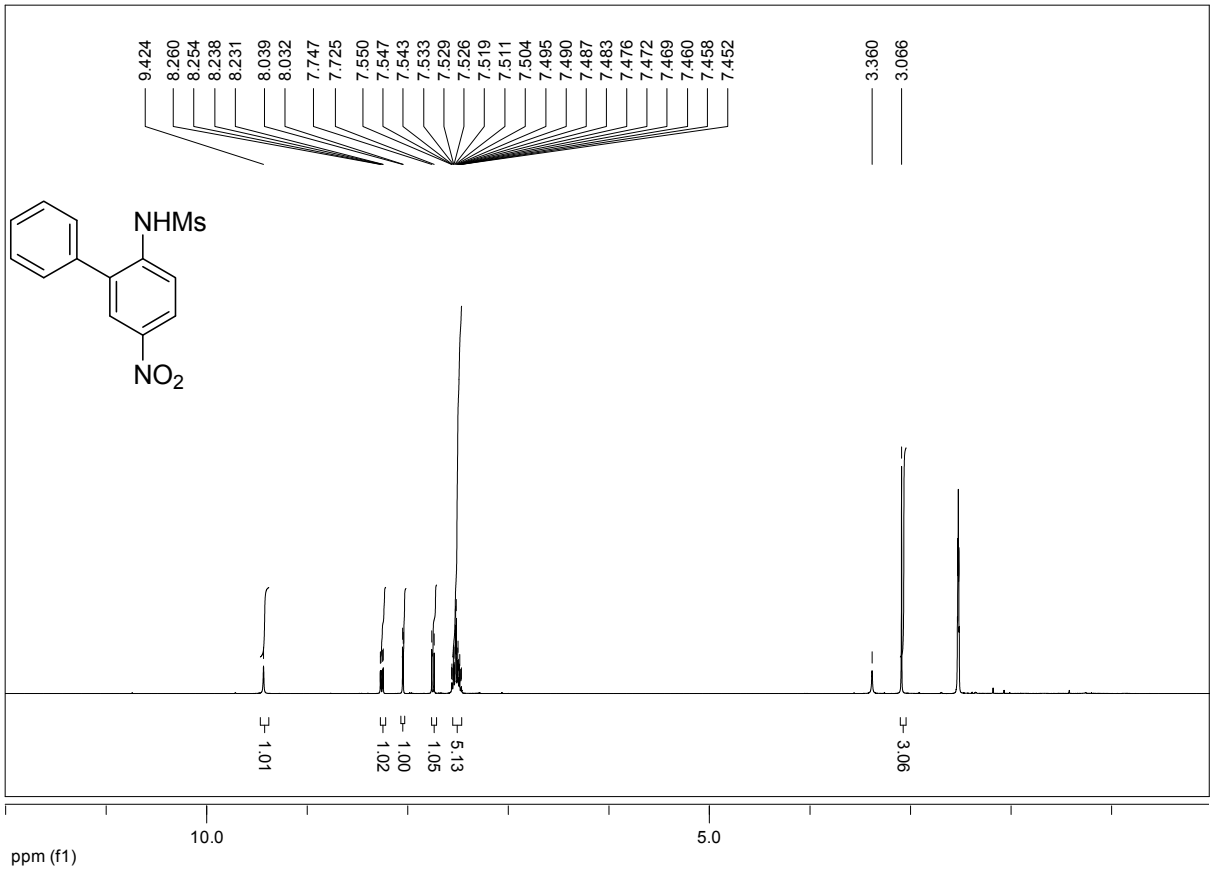


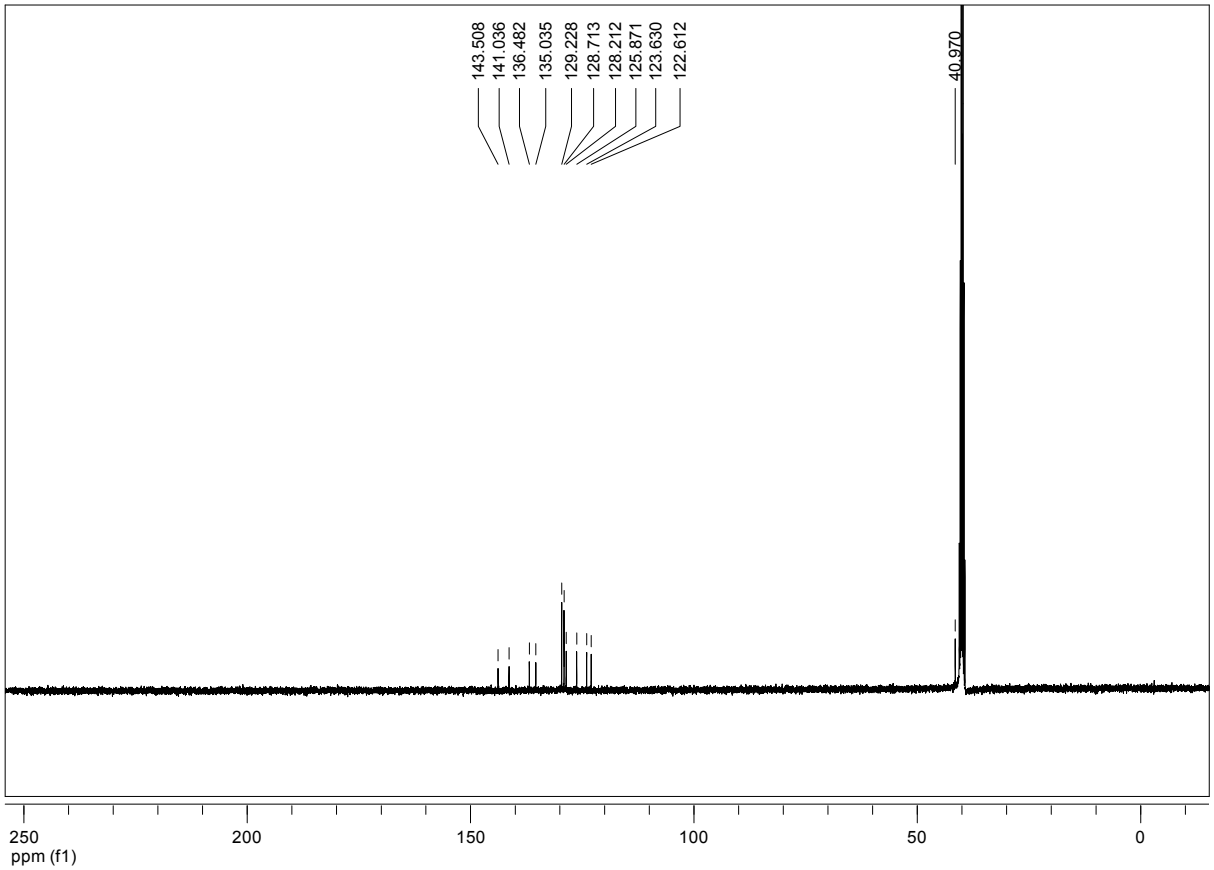
***N*-(3-nitro-[1,1'-biphenyl]-2-yl)methanesulfonamide 2f** (ortho)



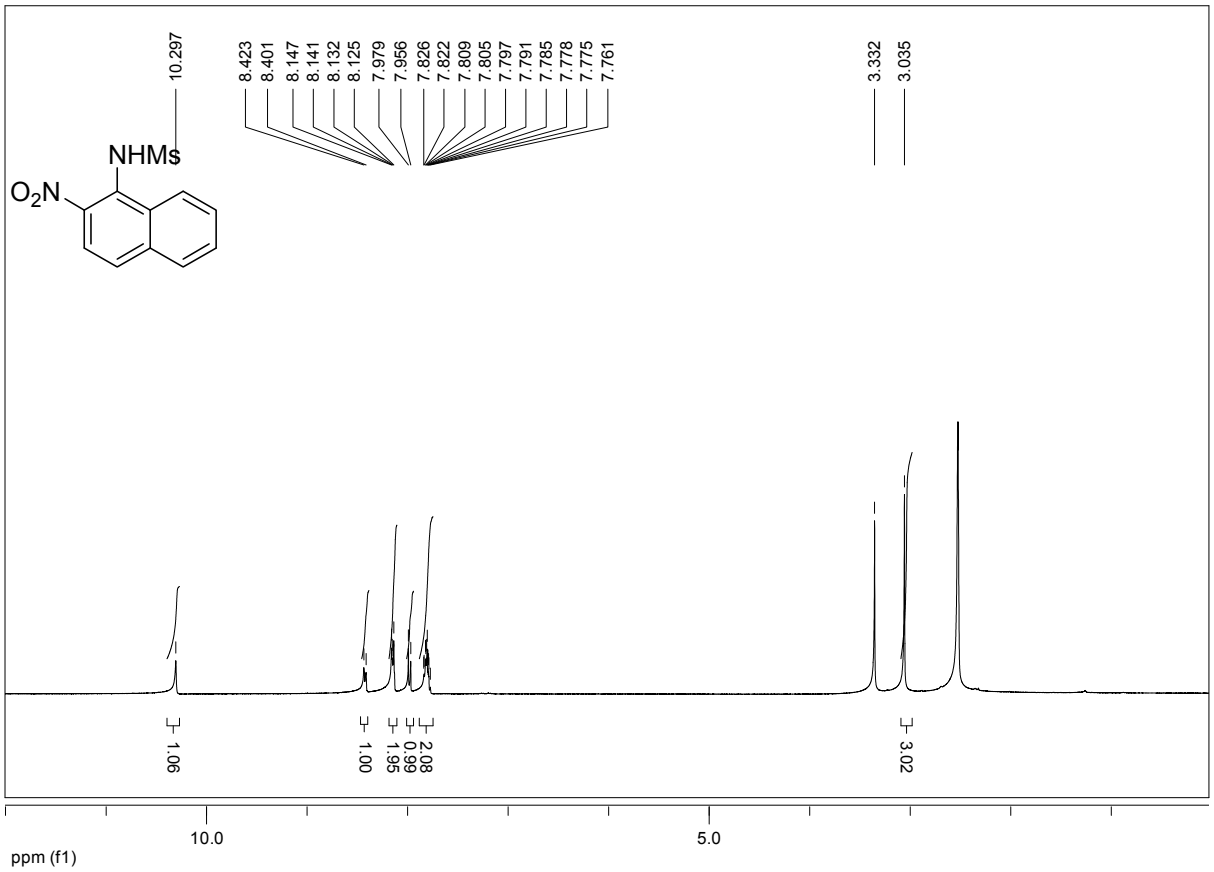


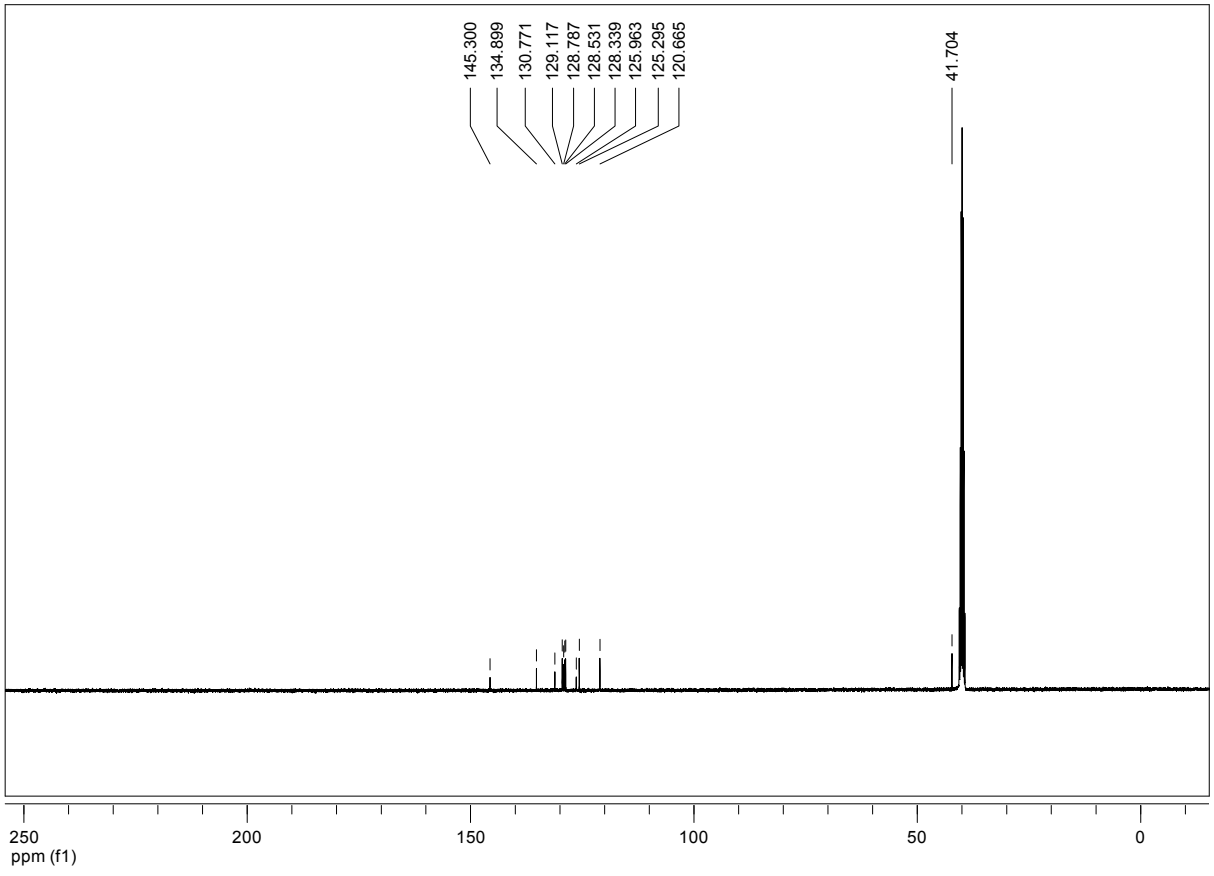
***N*-(5-nitro-[1,1'-biphenyl]-2-yl)methanesulfonamide 2f** (para)



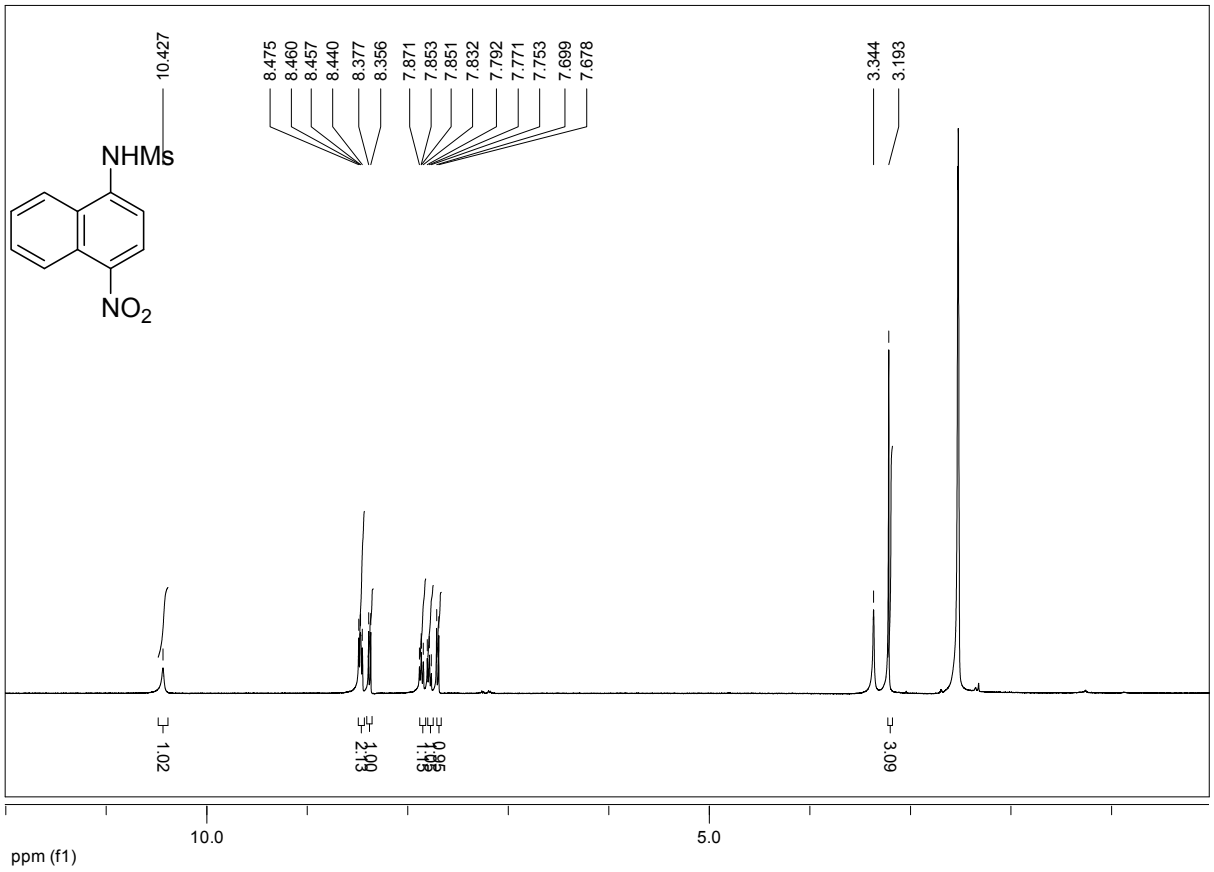


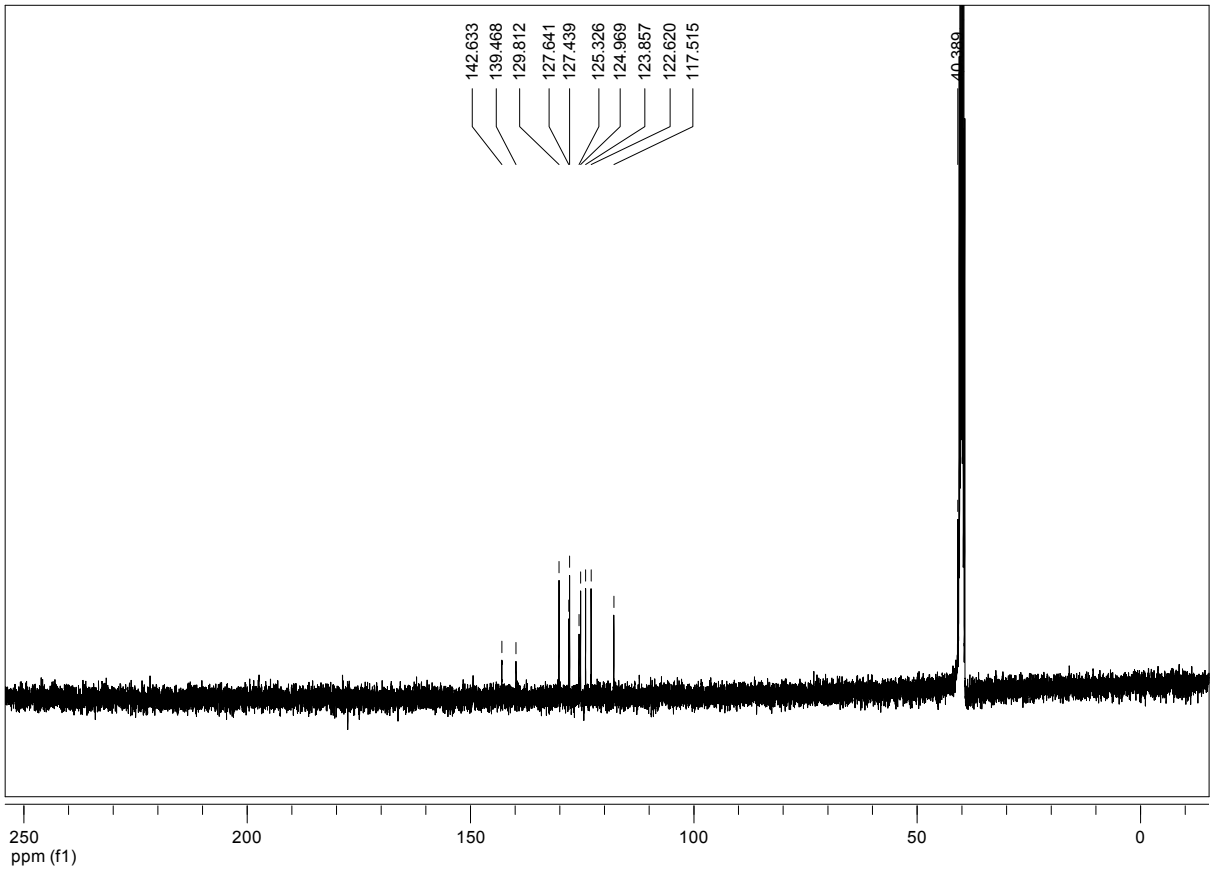
***N*-(2-Nitronaphtalen-1-yl)-methanesulfonamide 2g** (ortho)



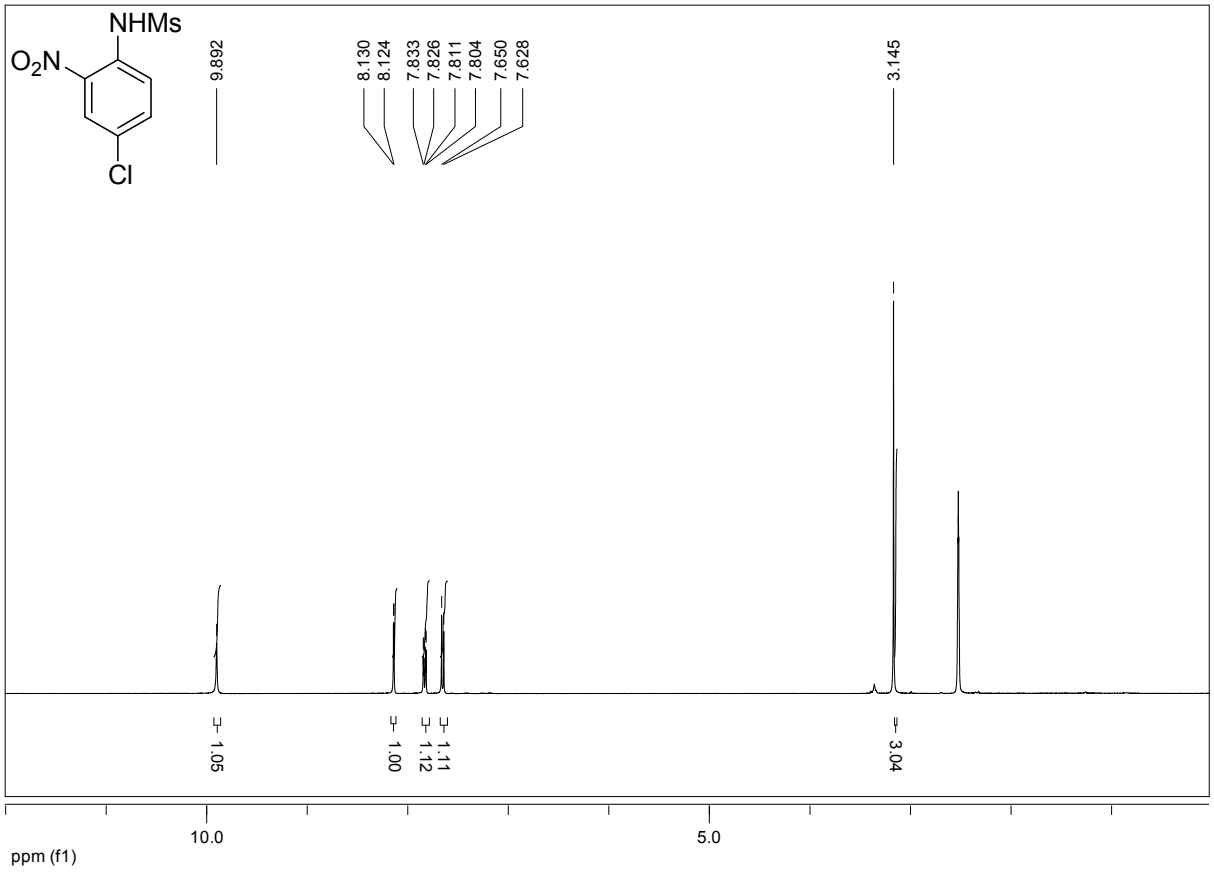


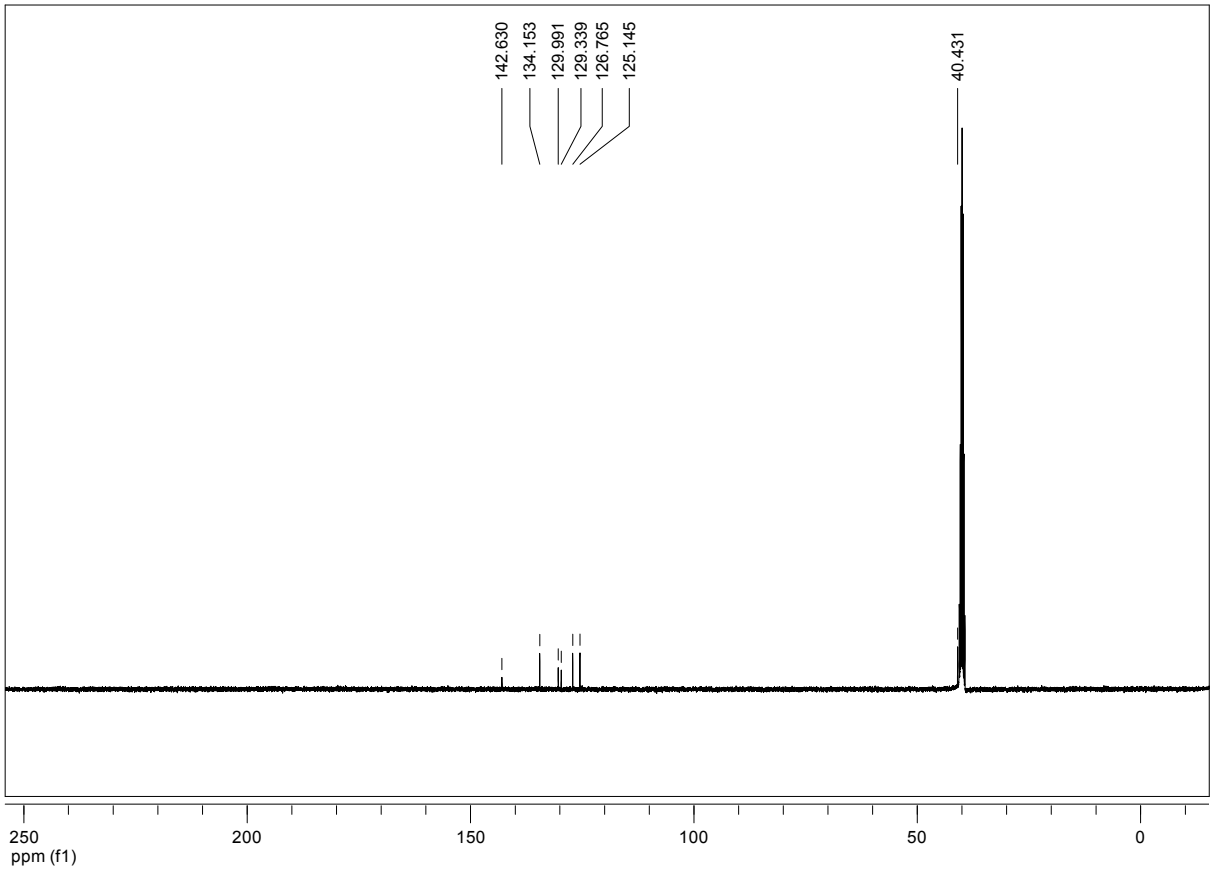
***N*-(4-Nitronaphtalen-1-yl)-methanesulfonamide 2g** (para)



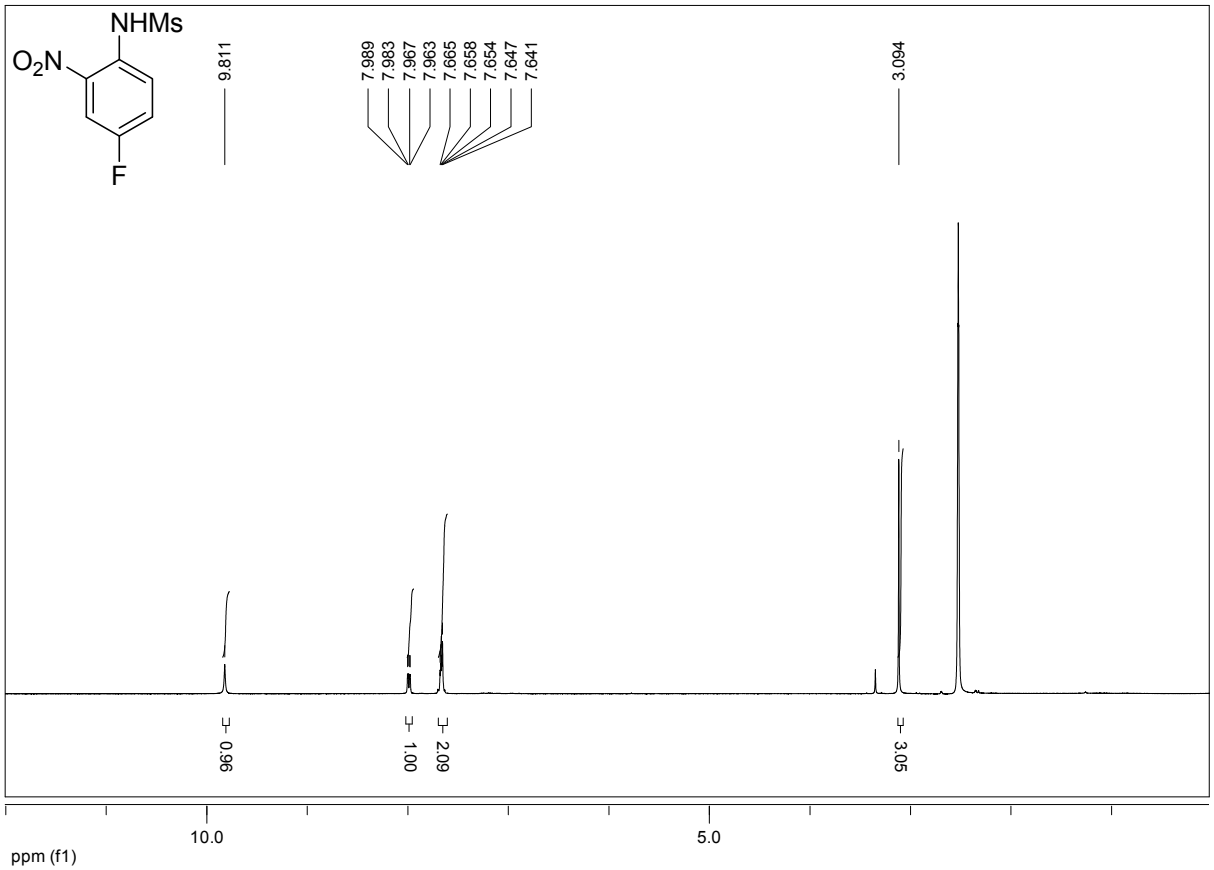


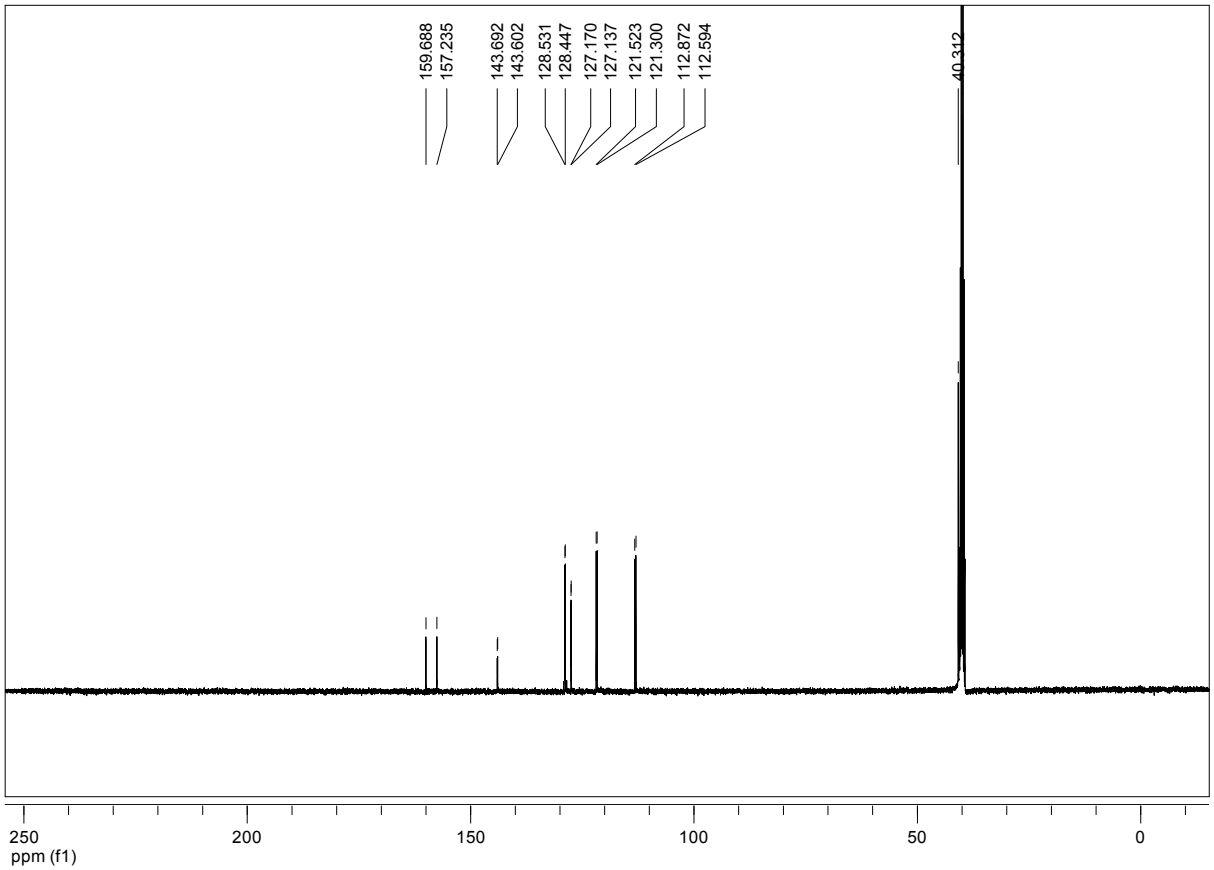
***N*-(4-Chloro-2-nitrophenyl)methanesulfonamide 2h**



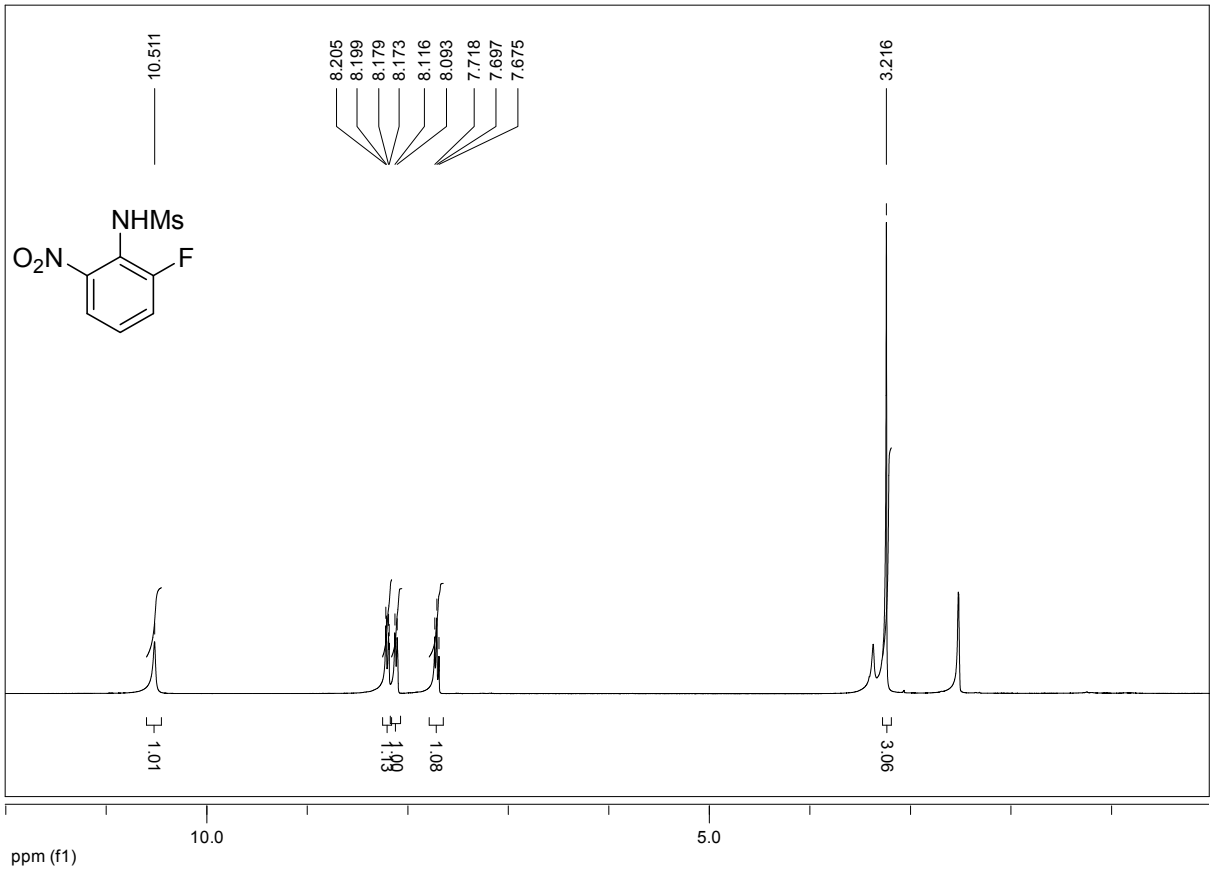


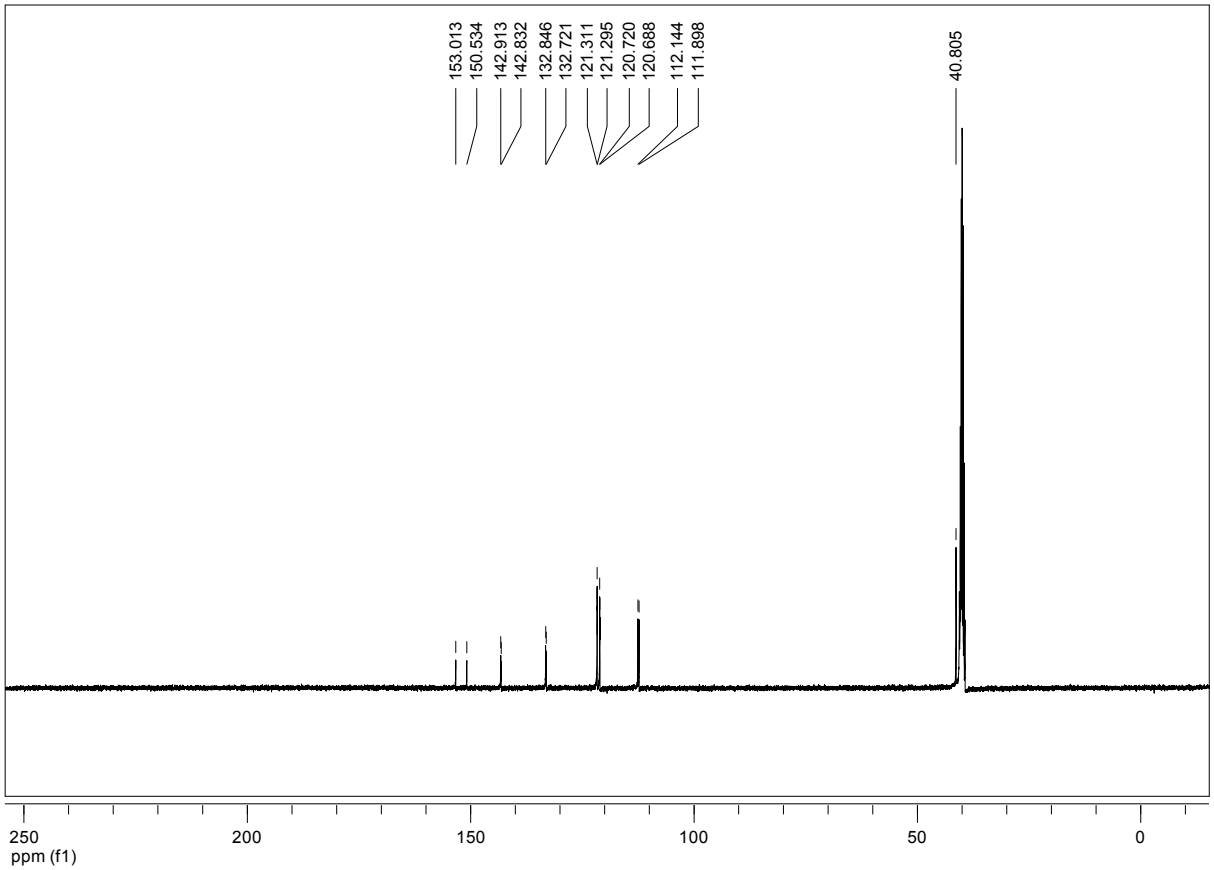
***N*-(4-Fluoro-2-nitrophenyl)methanesulfonamide 2i**



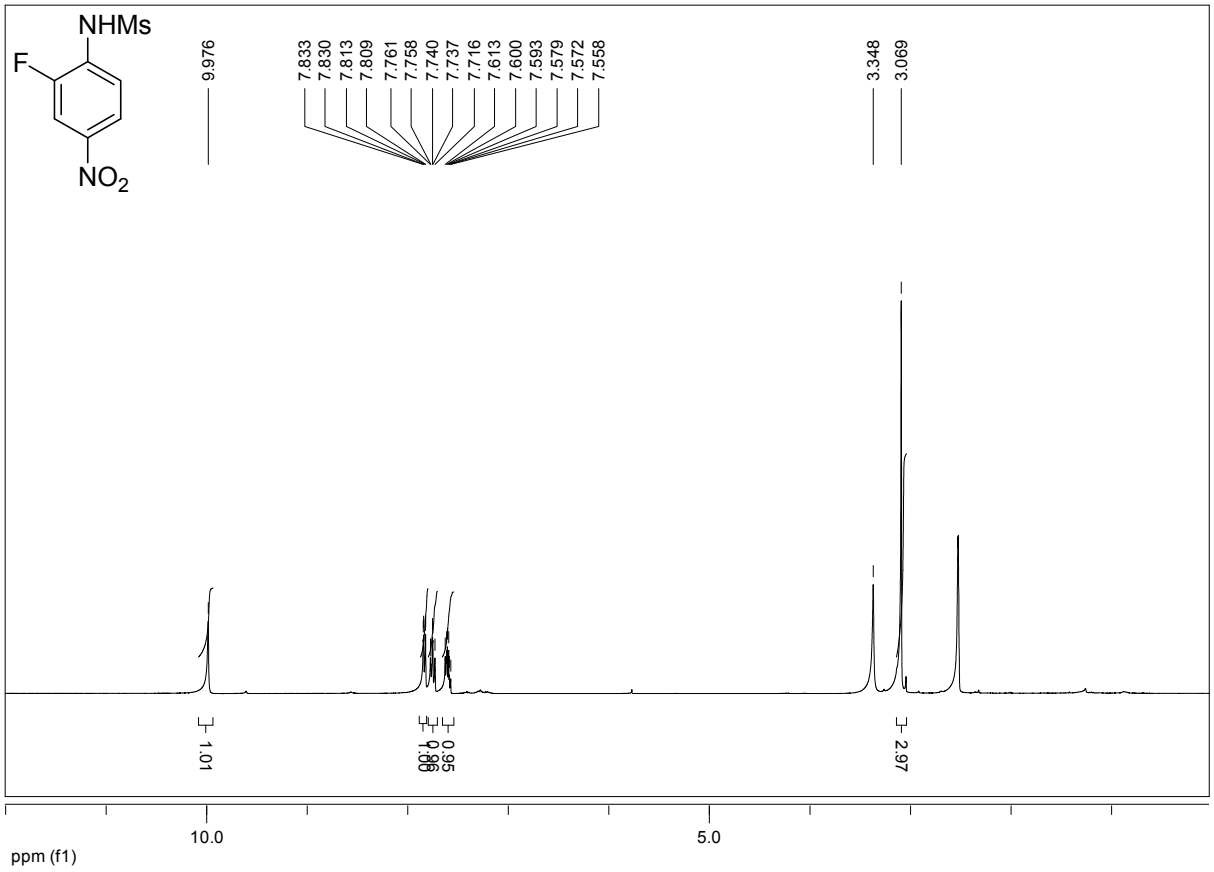


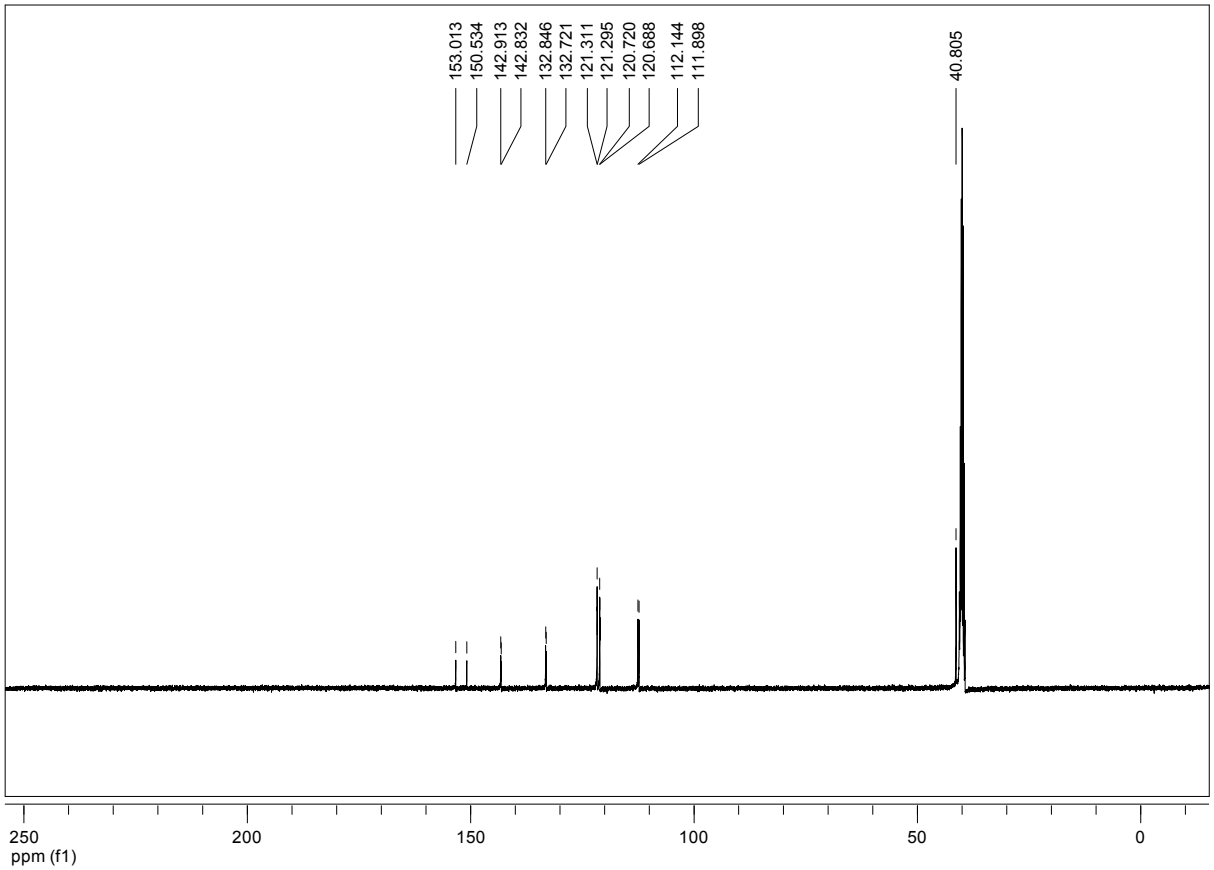
***N*-(2-Fluoro-6-nitrophenyl)methanesulfonamide 2j** (ortho)



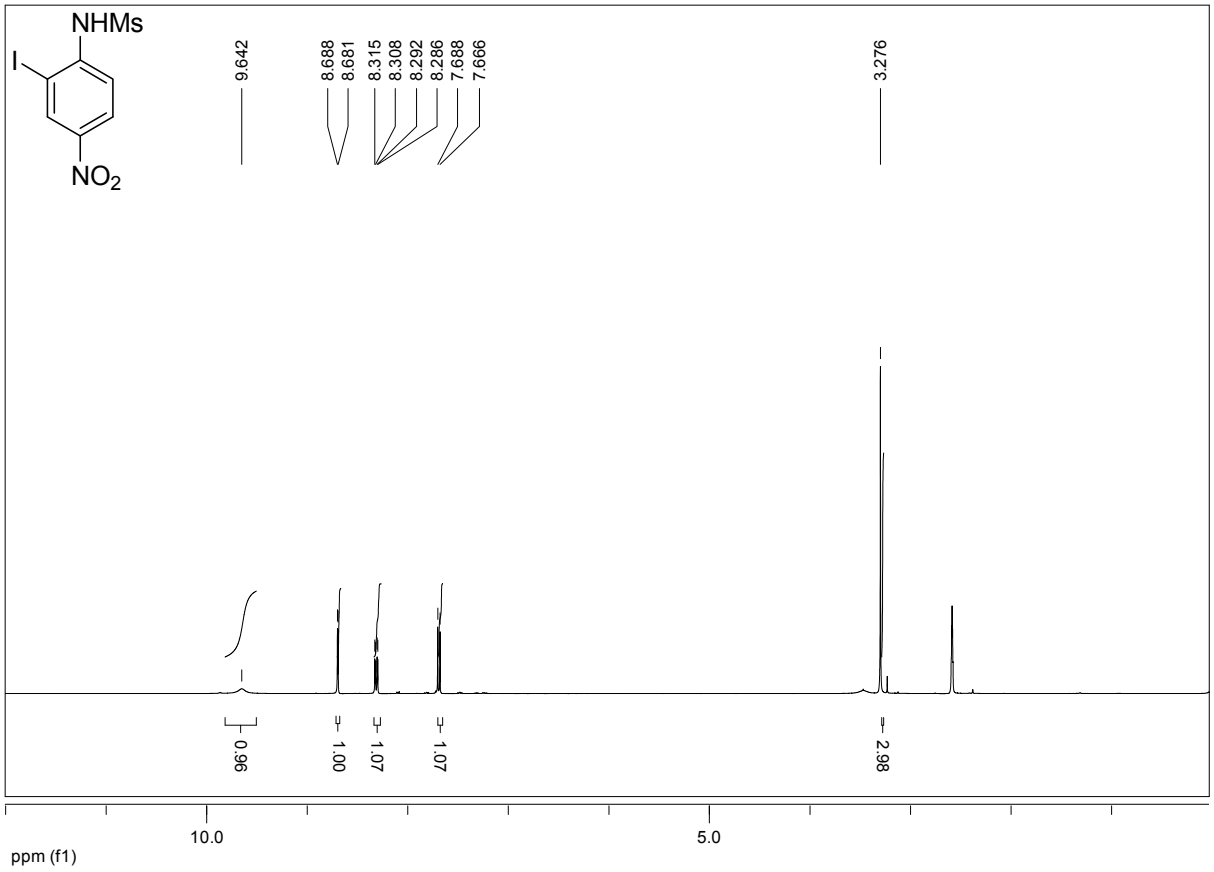


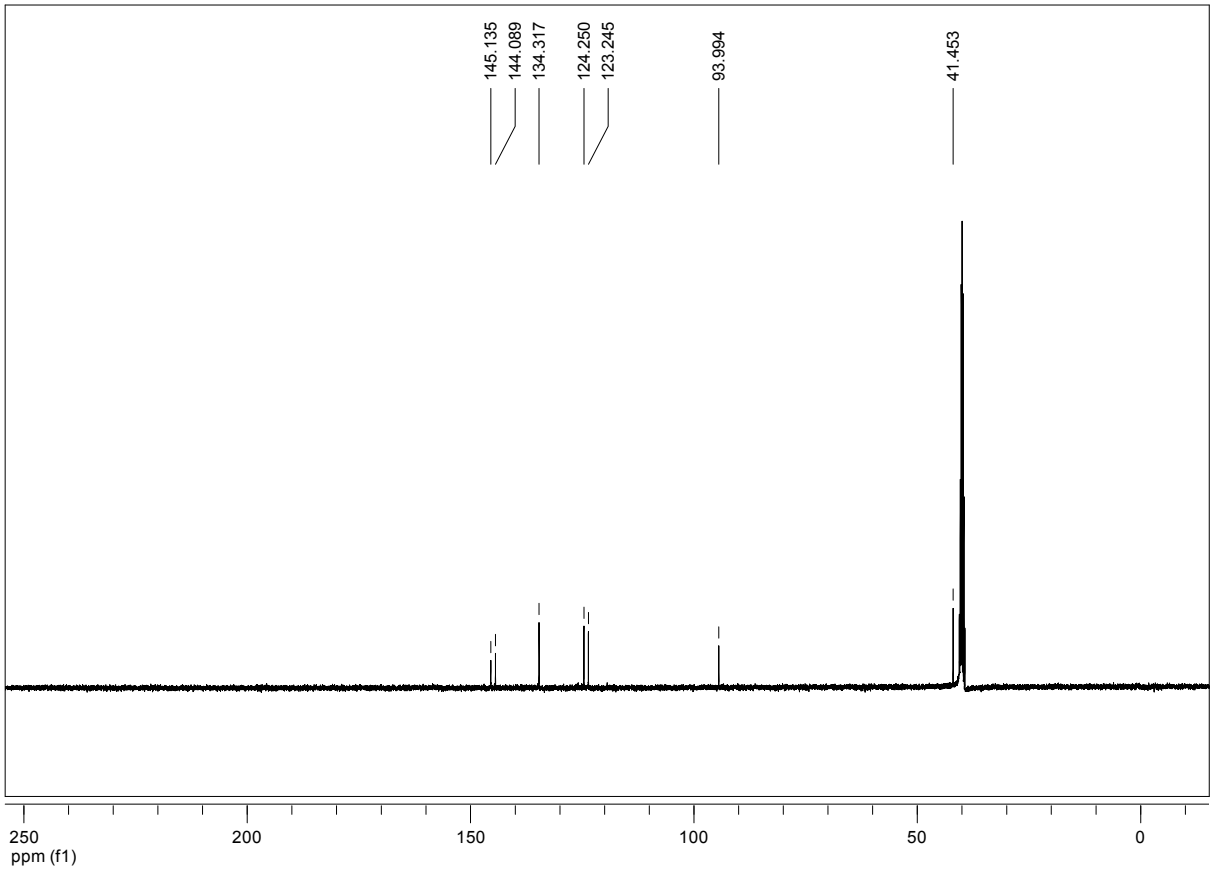
***N*-(2-Fluoro-4-nitrophenyl)methanesulfonamide 2j** (para)



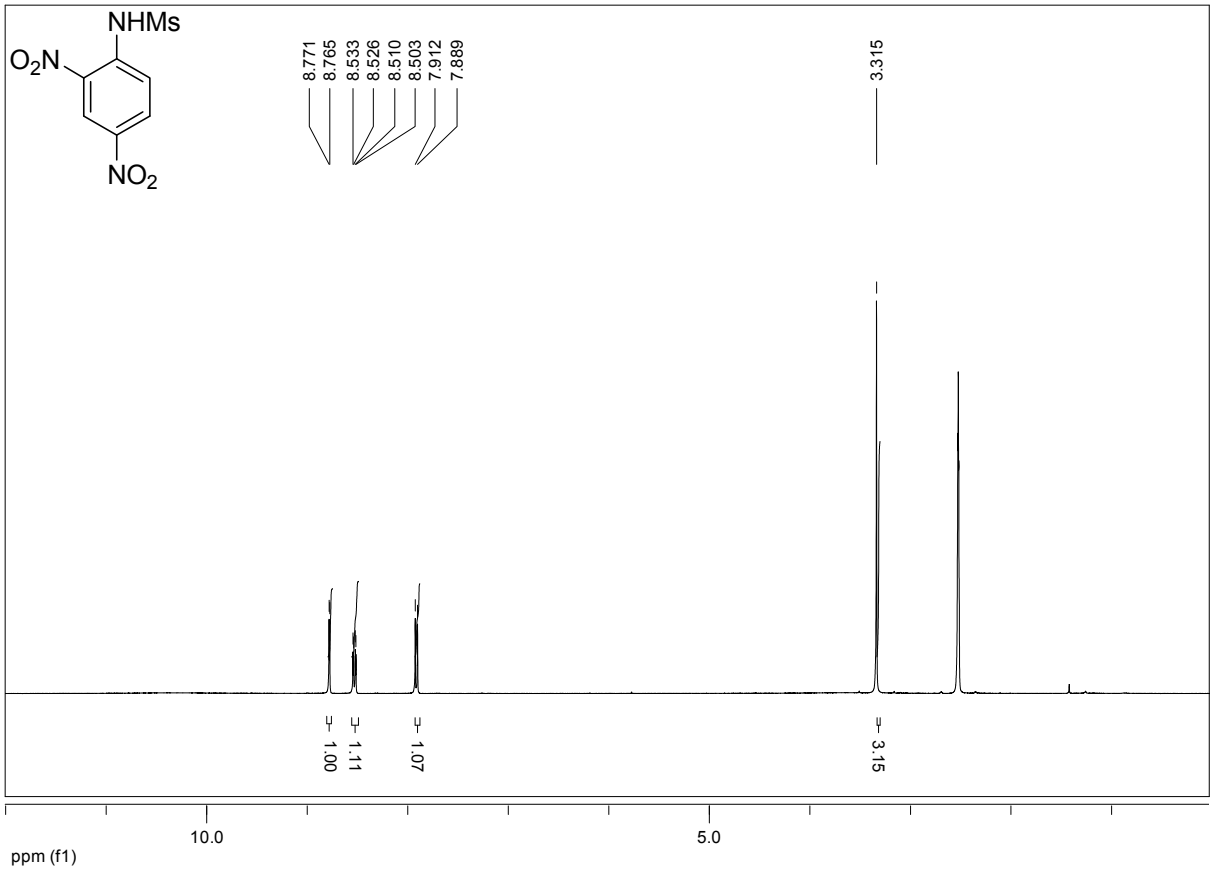


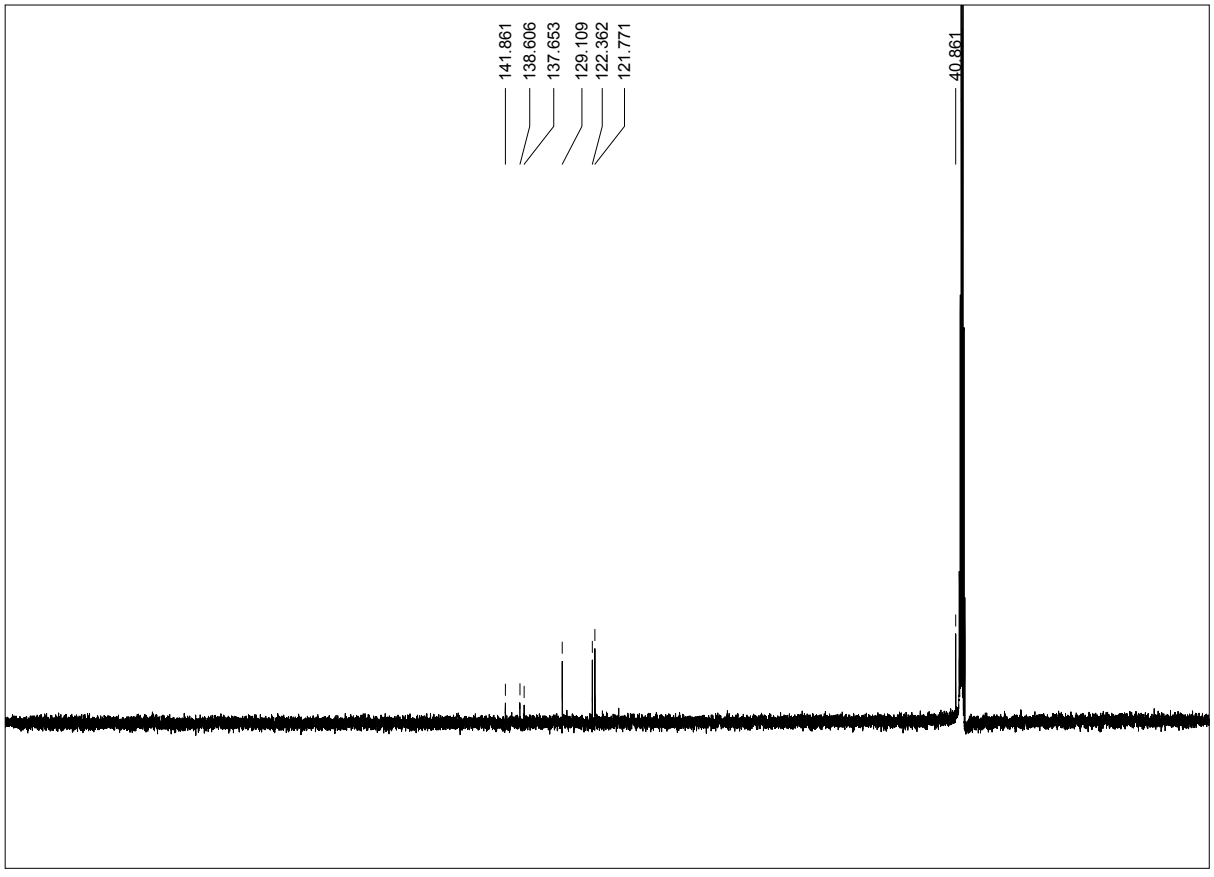
***N*-(2-Iodo-4-nitrophenyl)methanesulfonamide 2k**



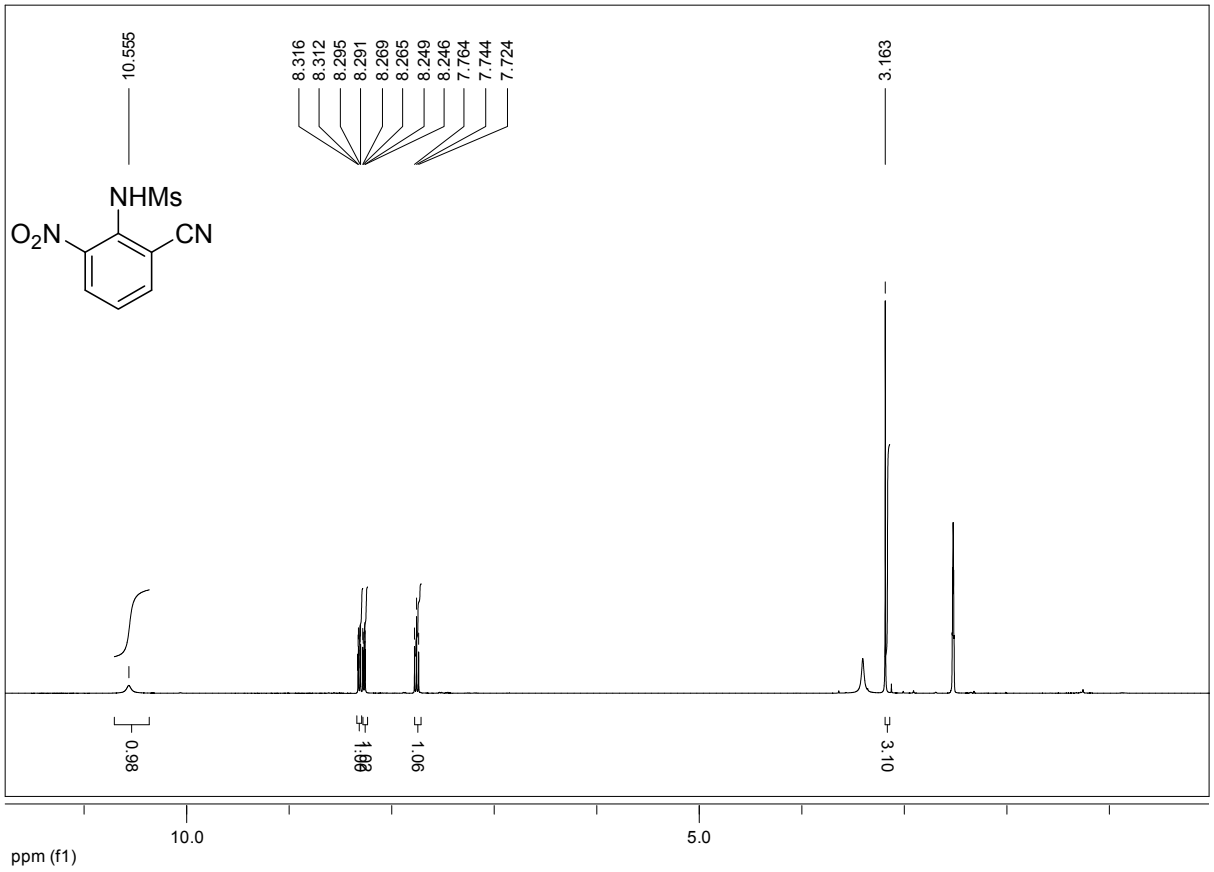


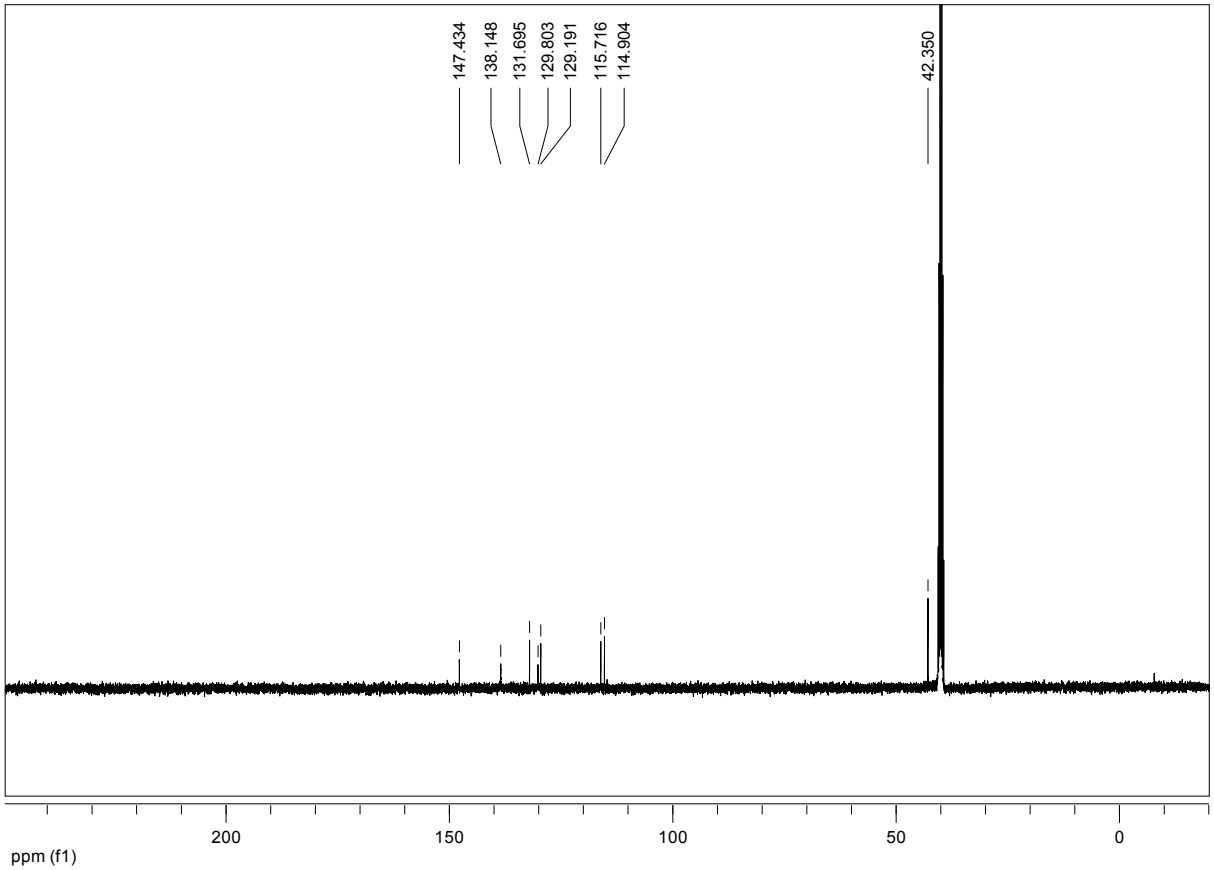
***N*-(2,4-Dinitrophenyl)methanesulfonamide 2l**



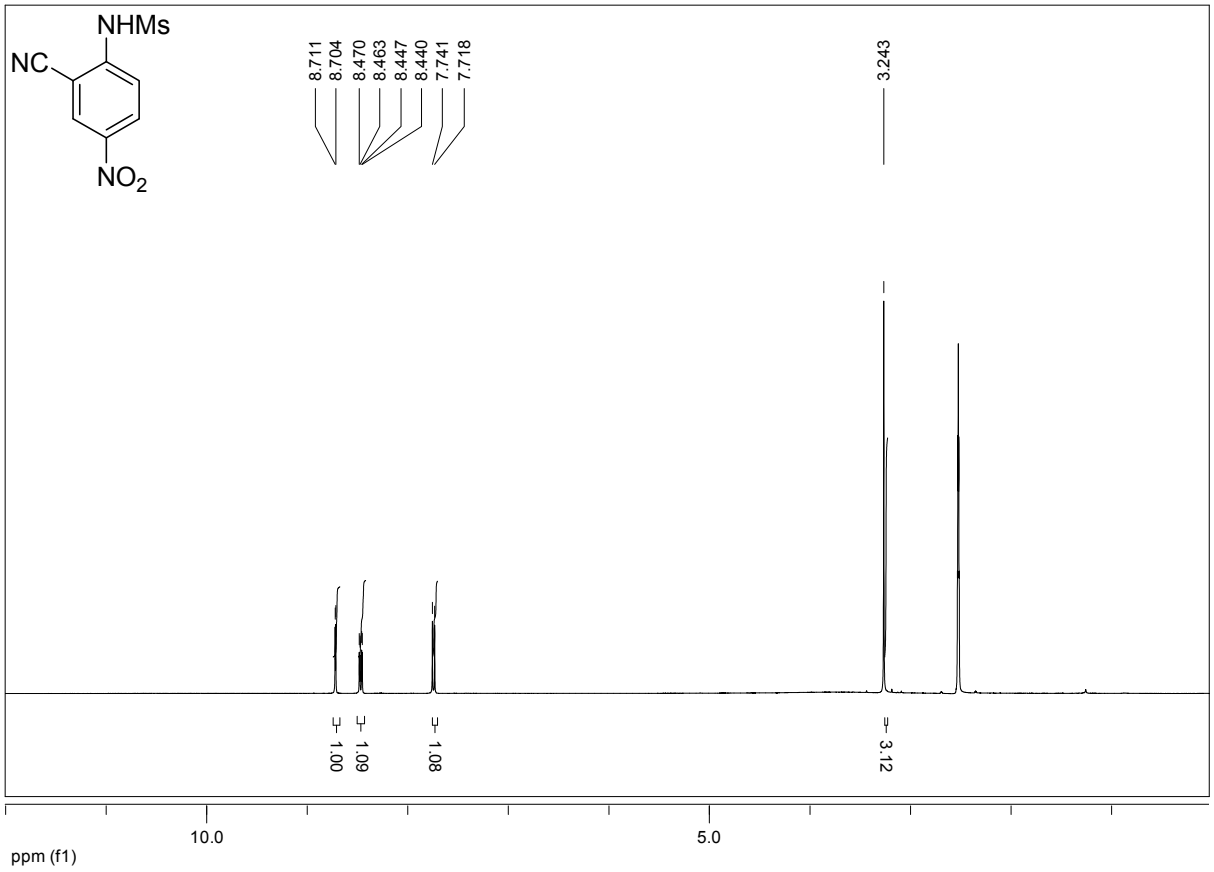


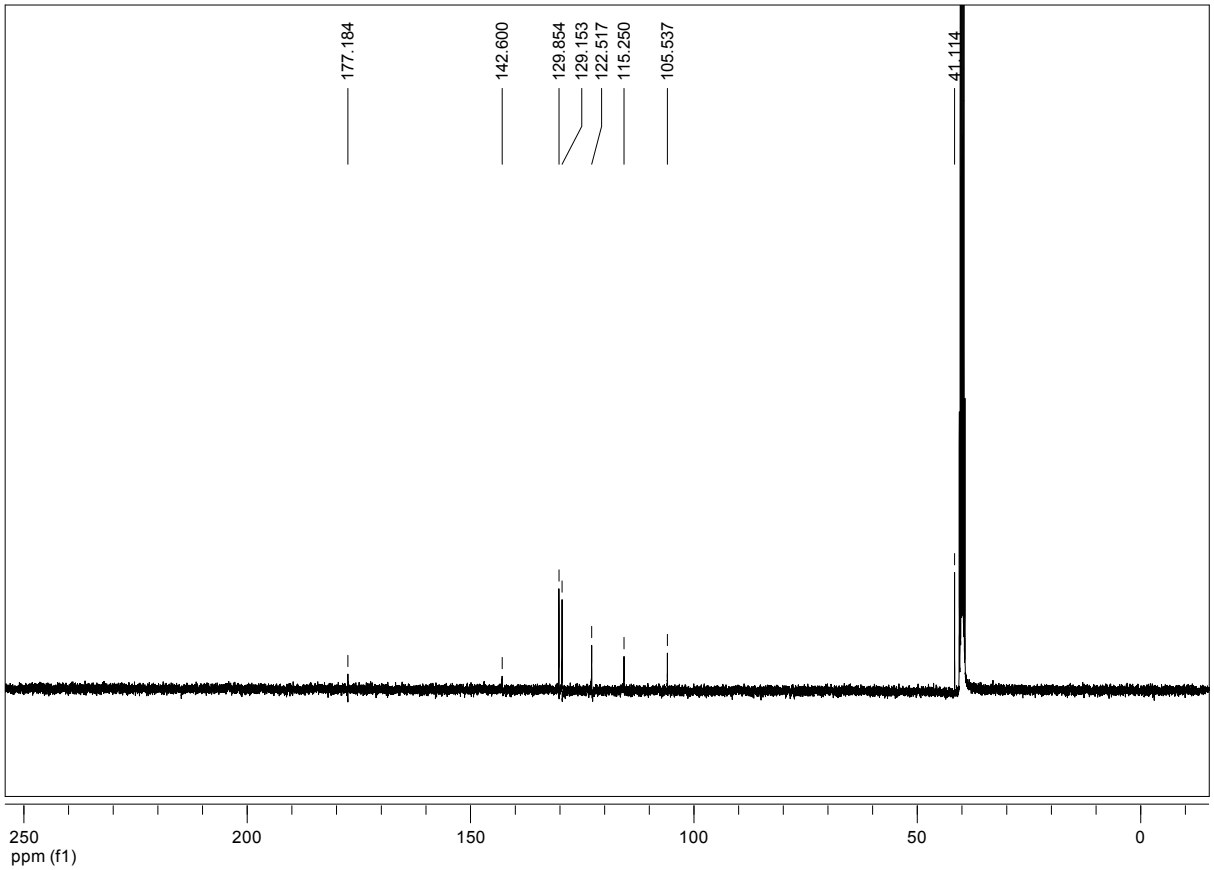
***N*-(2-Cyano-6-nitrophenyl)methanesulfonamide 2m** (ortho)



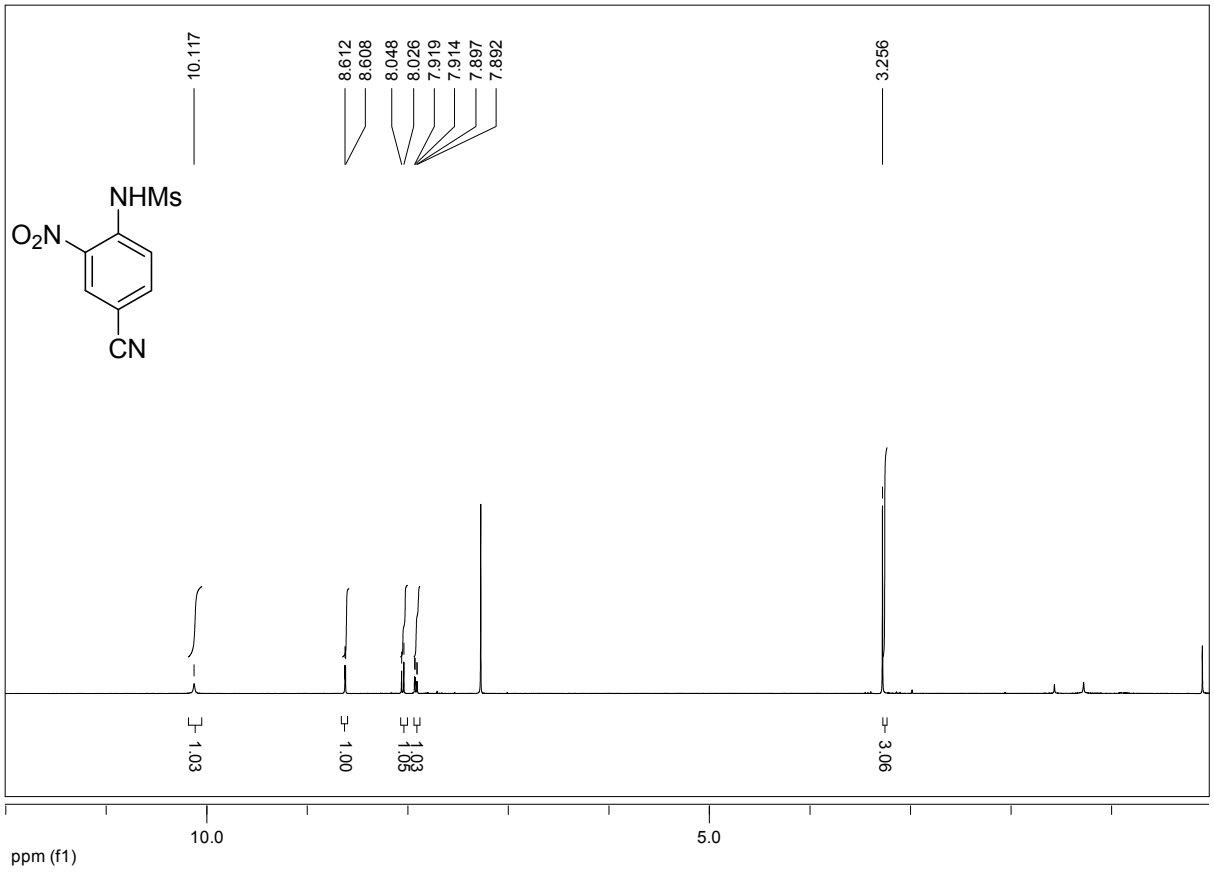


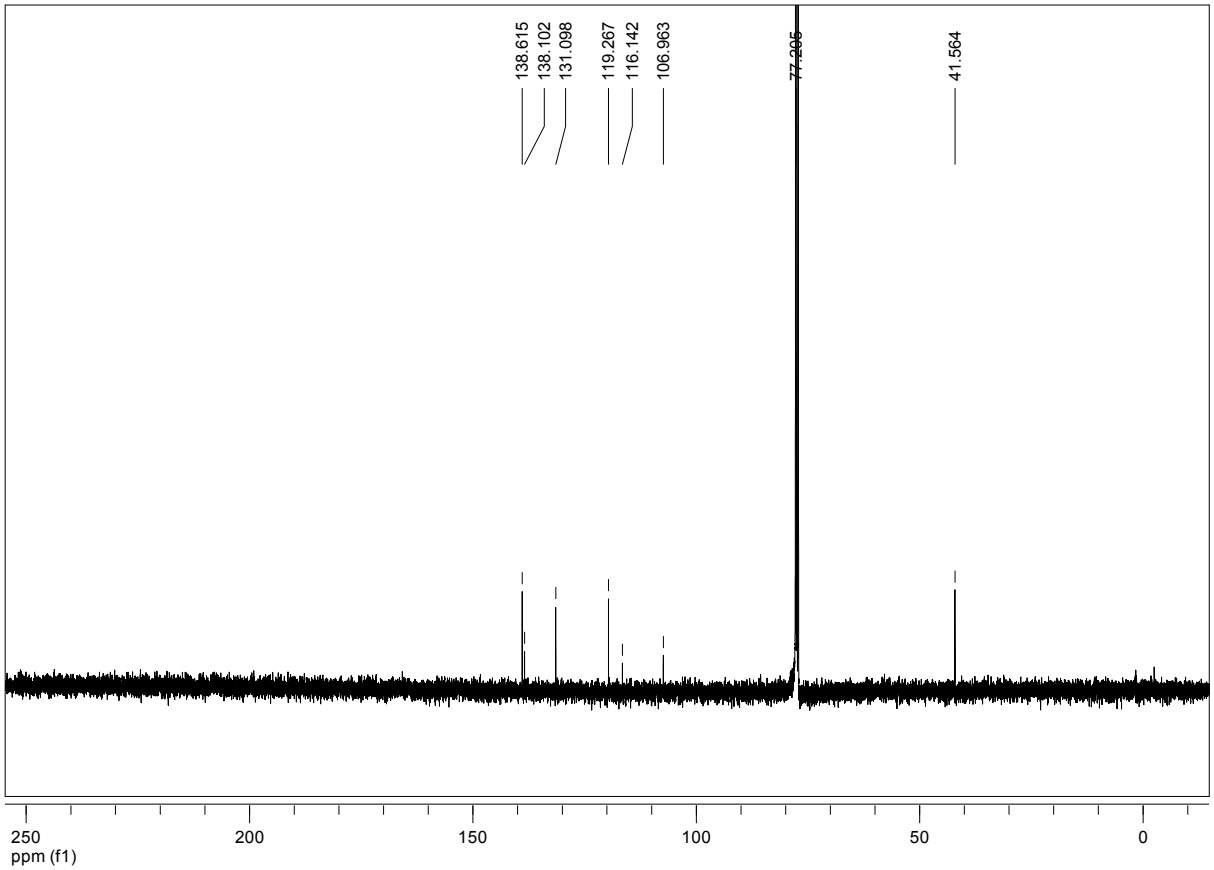
***N*-(2-Cyano-4-nitrophenyl)methanesulfonamide 2m** (para)



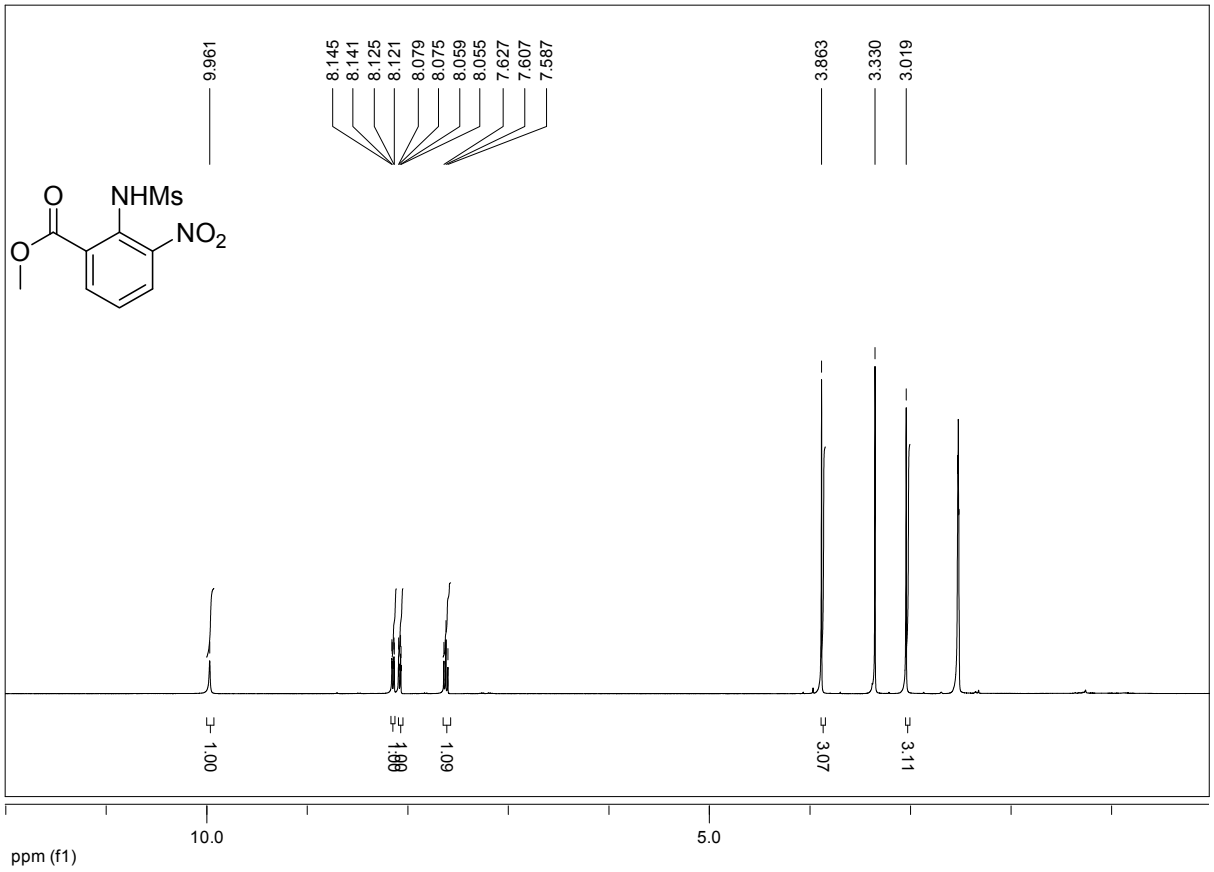


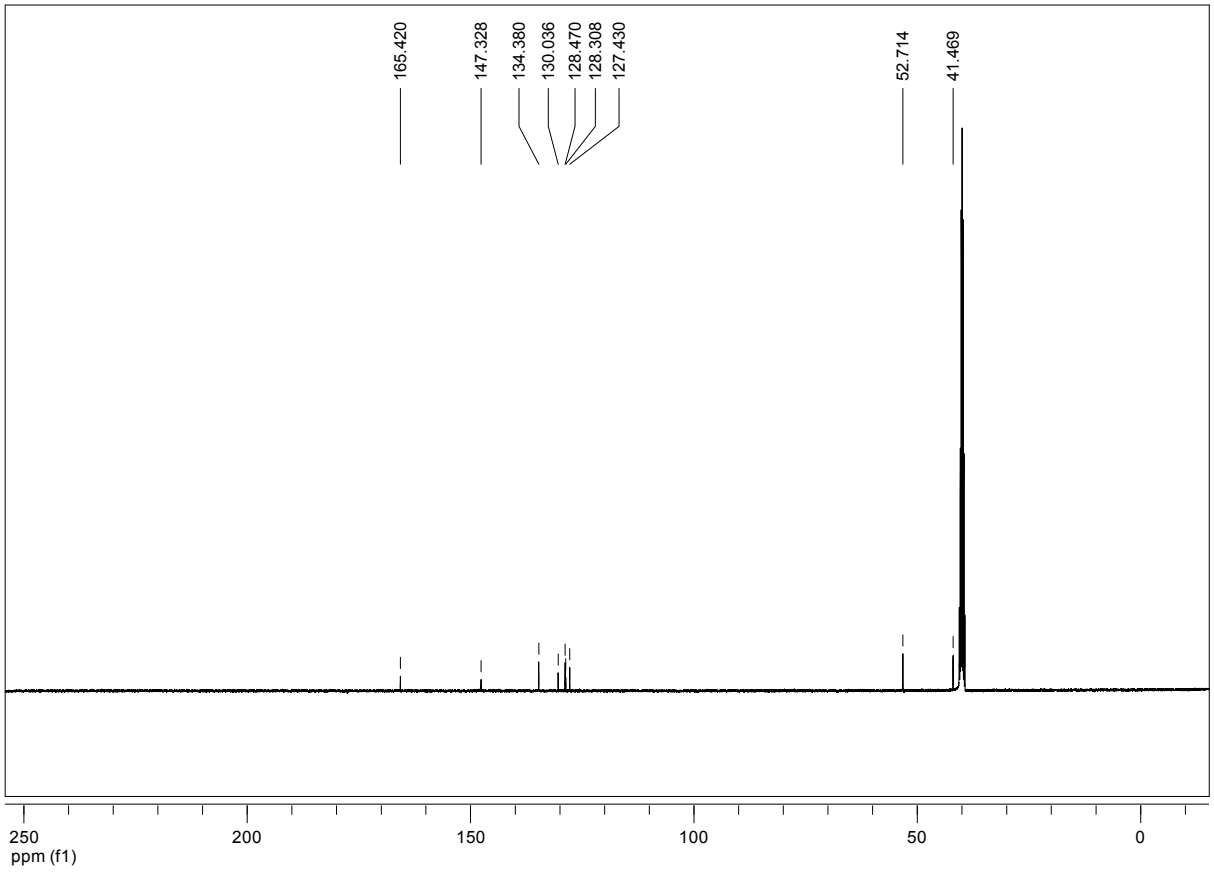
***N*-(4-Cyano-2-nitrophenyl)methanesulfonamide 2n**



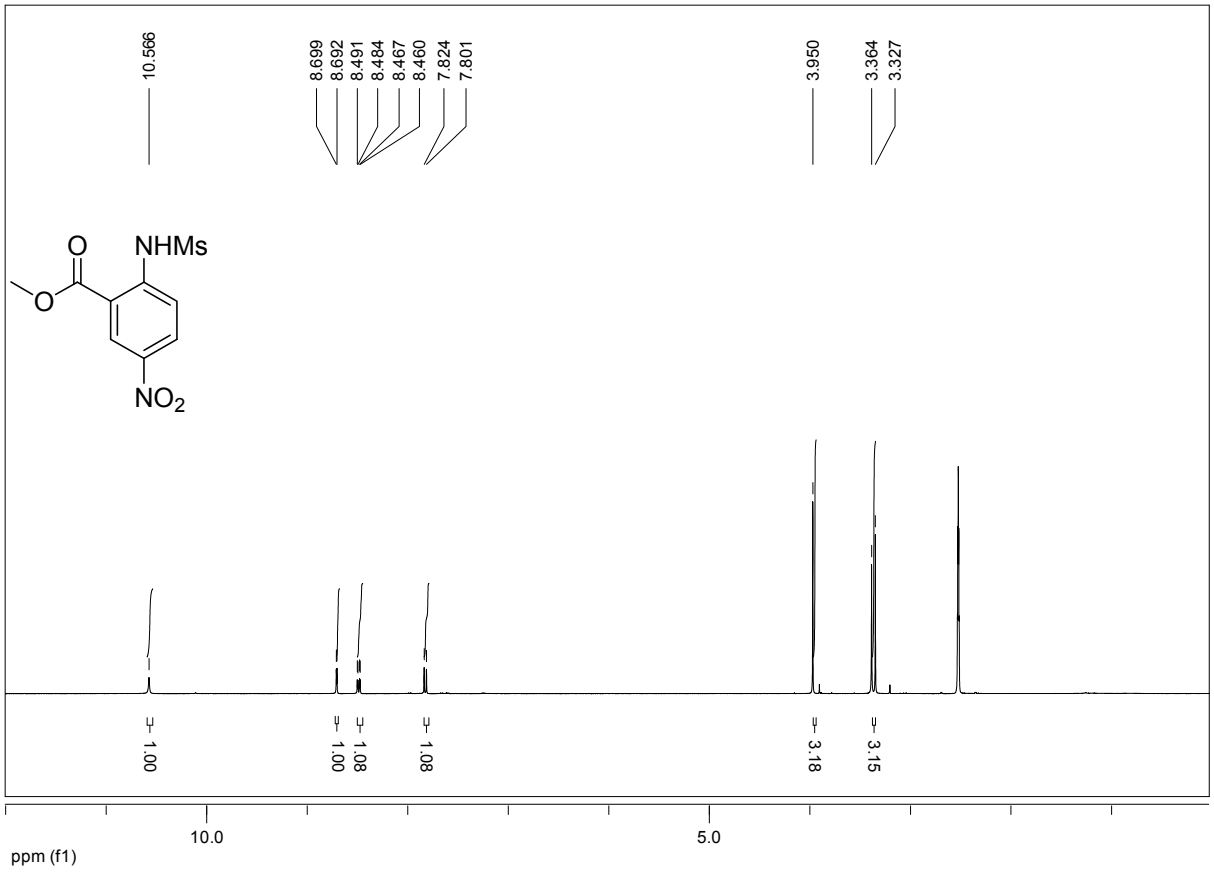


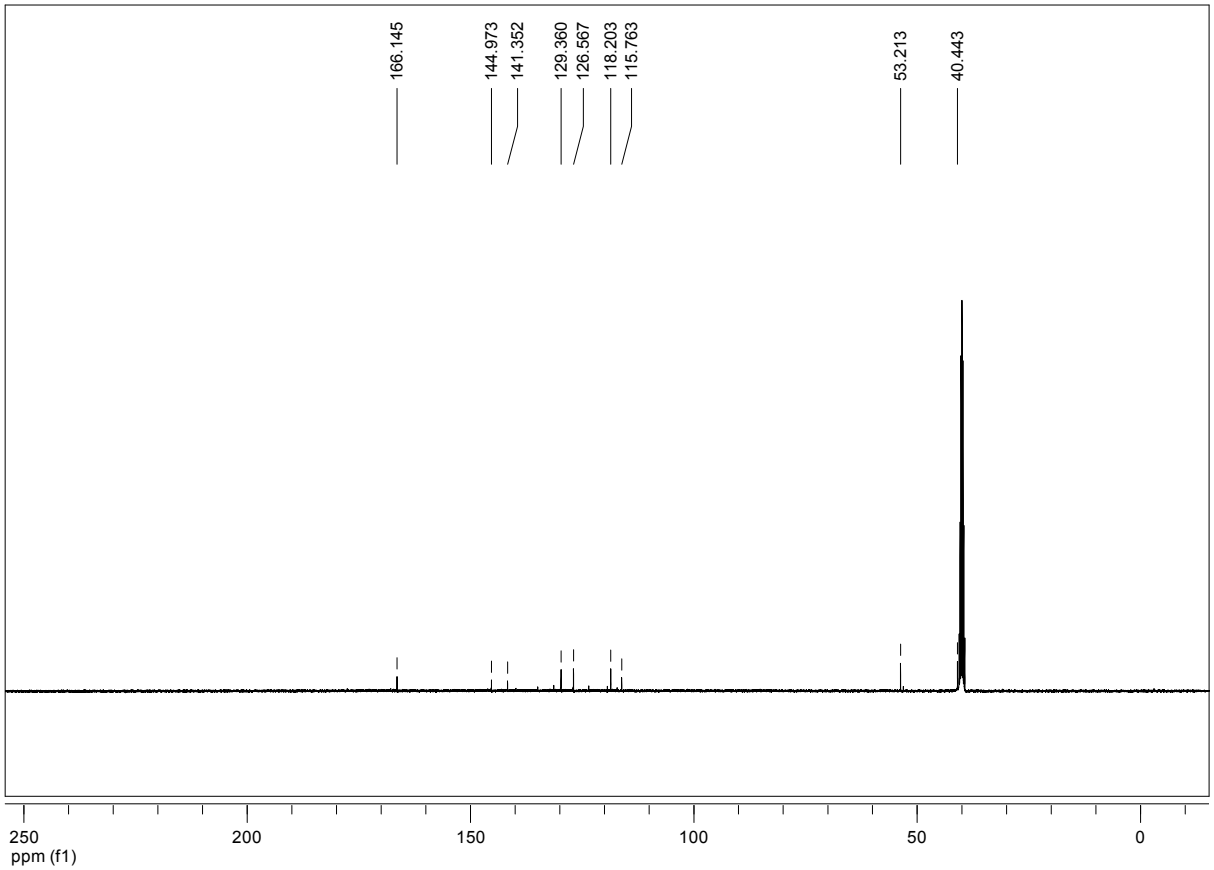
Methyl-2-(methylsulfonamido)-3-nitrobenzoate 2o (ortho)



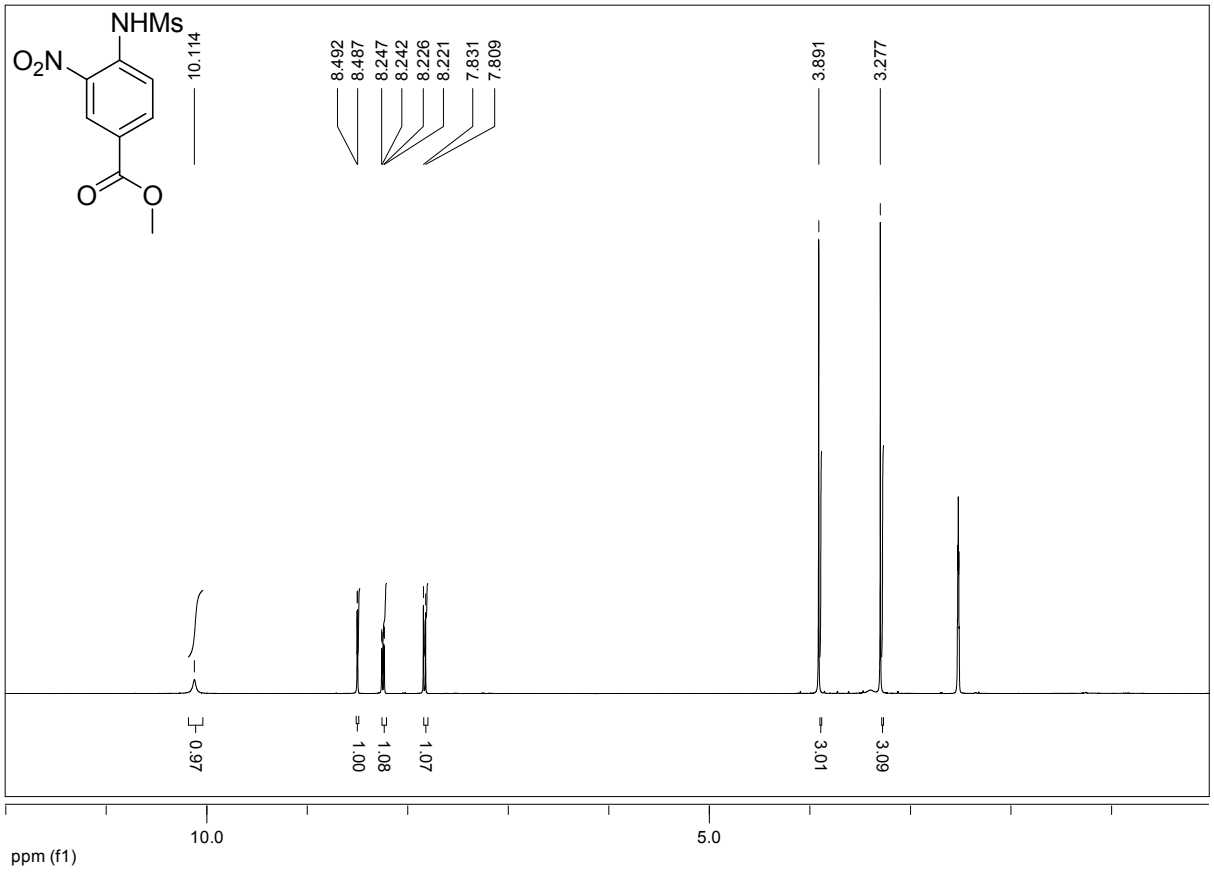


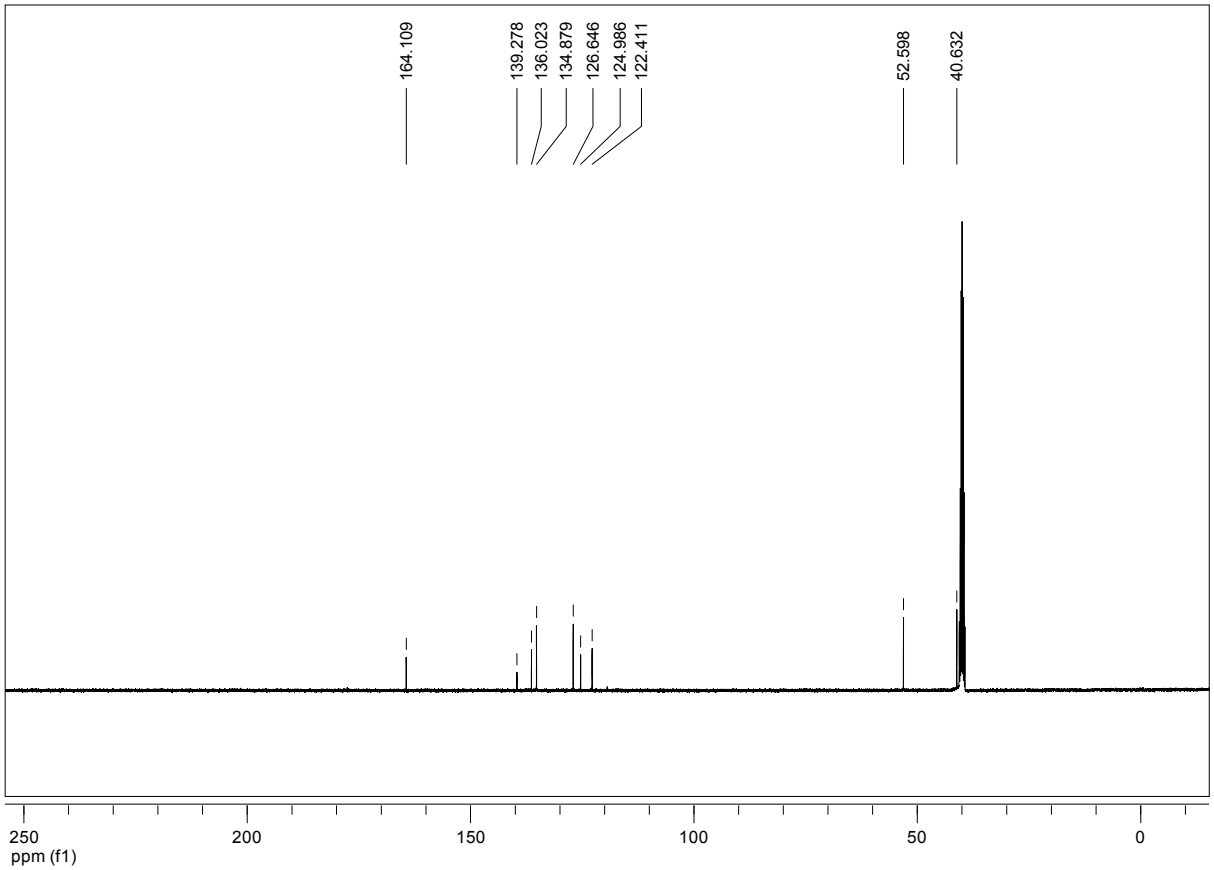
Methyl-2-(methylsulfonamido)-5-nitrobenzoate 2o (para)



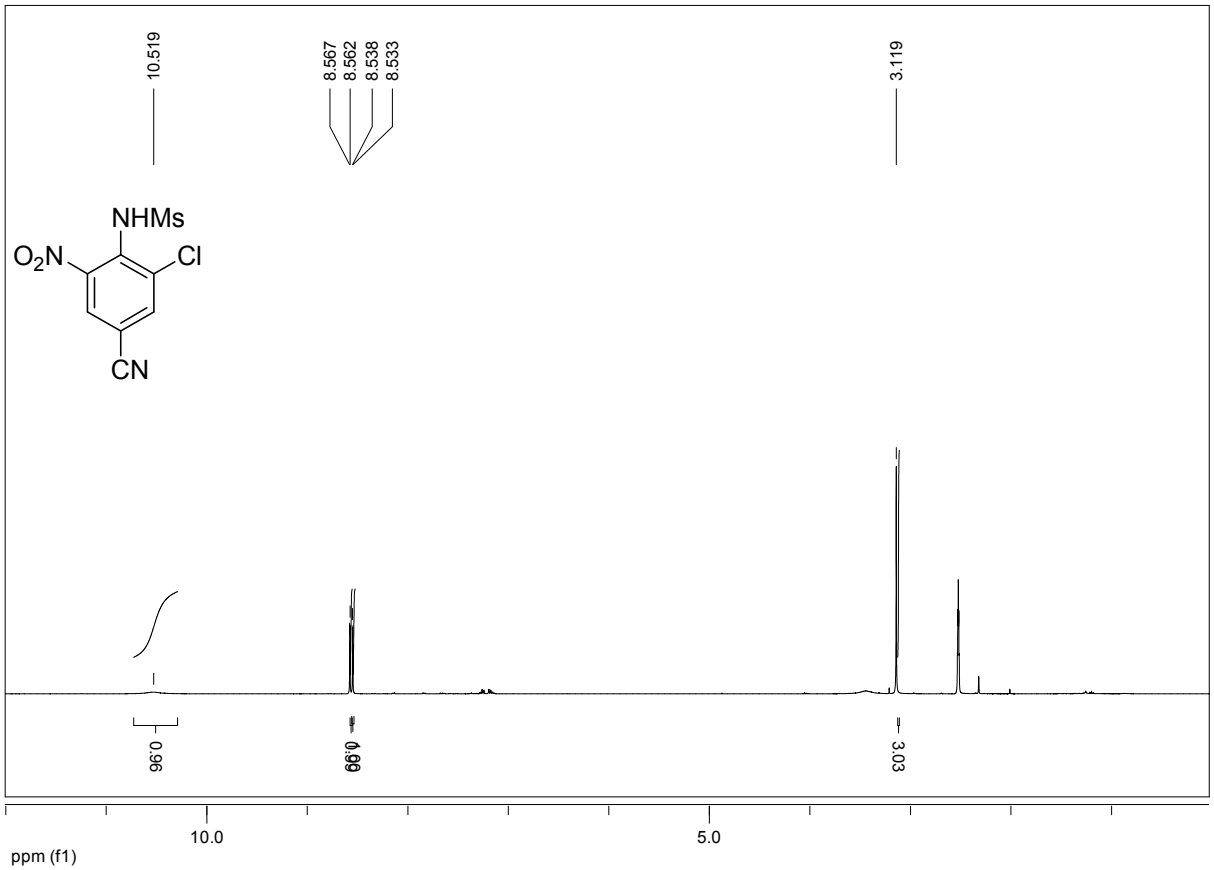


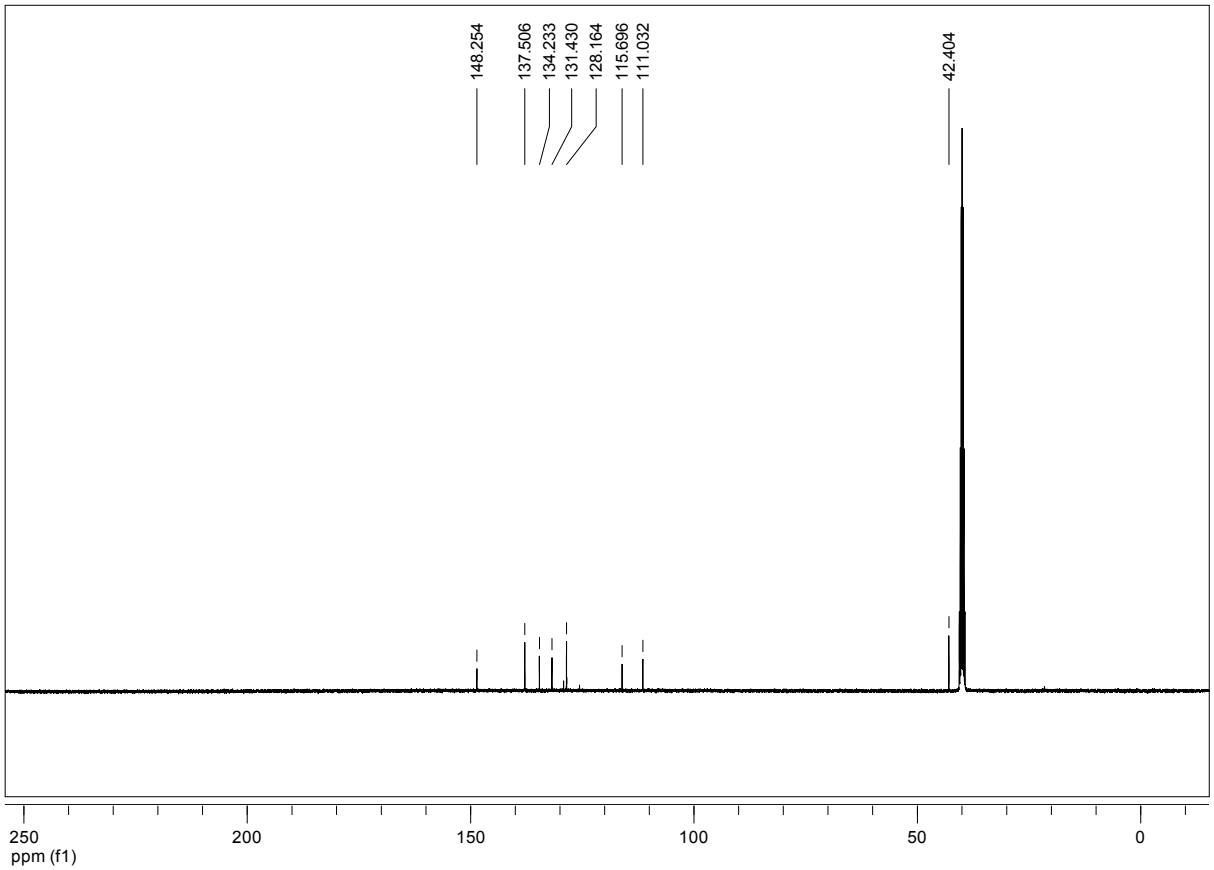
Methyl 4-(methylsulfonamido)-3-nitrobenzoate 2p



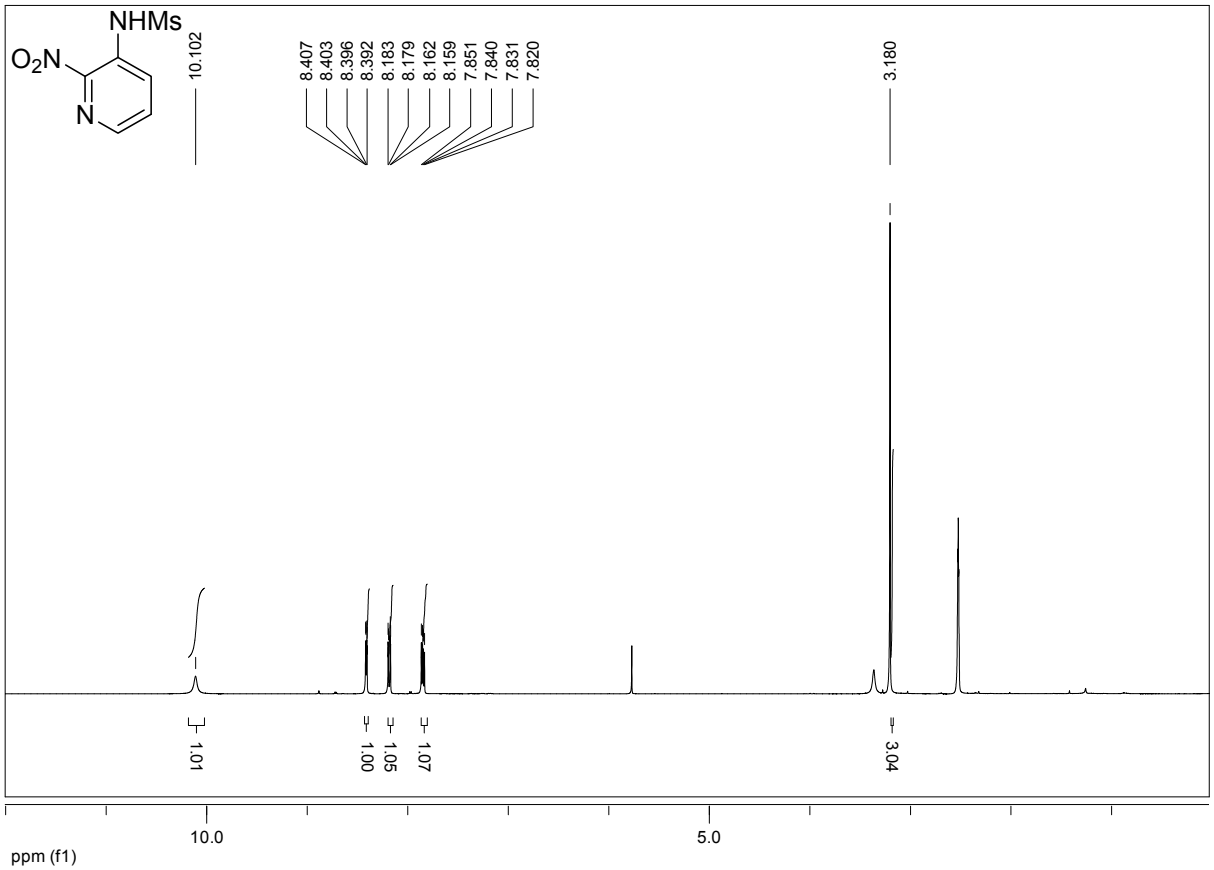


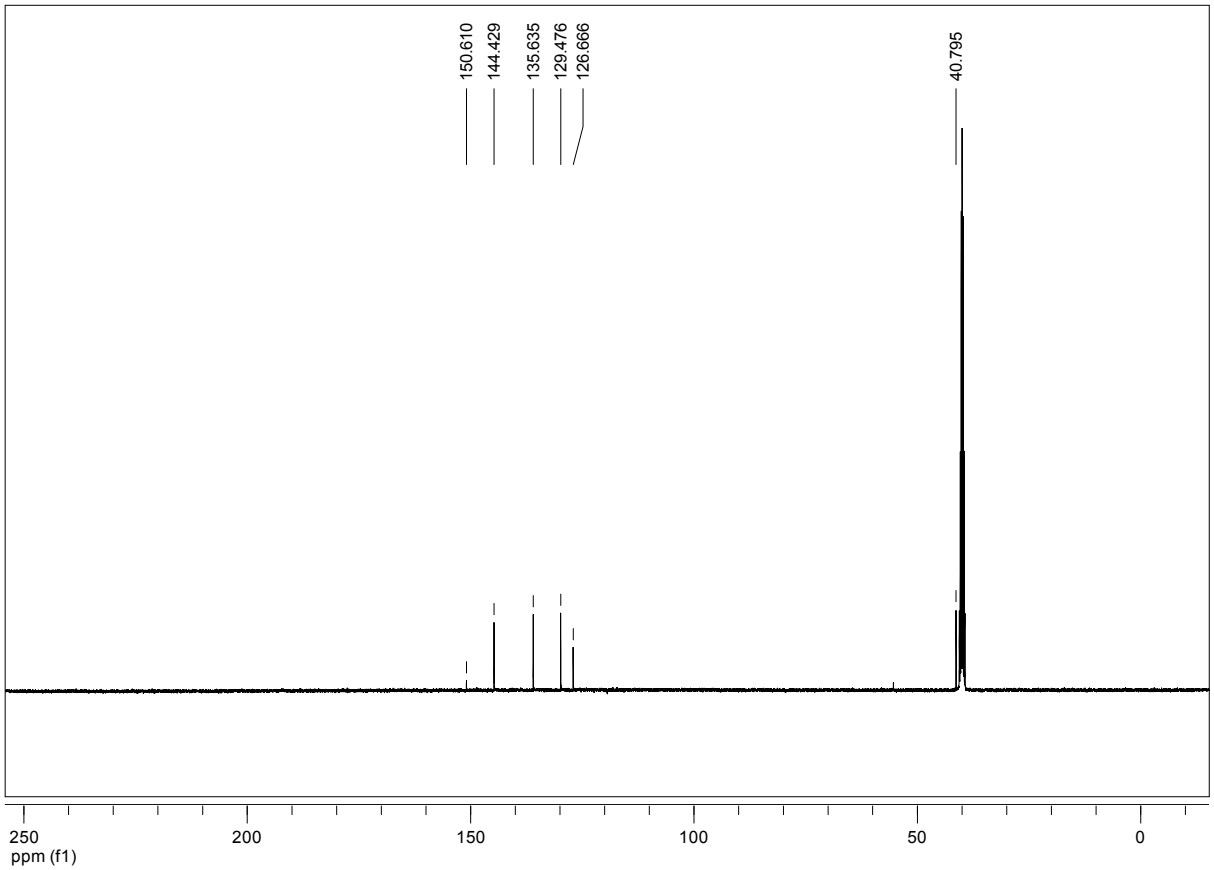
***N*-(2-Chloro-4-cyano-6-nitrophenyl)methanesulfonamide 2q**





***N*-(2-nitropyridin-3-yl)methanesulfonamide 2r** (ortho)





***N*-(6-nitropyridin-3-yl)methanesulfonamide 2r** (para)