10.1071/CH16213_AC

Australian Journal of Chemistry 70(1), 44-51

Supplementary Material

$Mo(CO)_6$ as a Solid CO Source in the Synthesis of Aryl/Heteroaryl Weinreb Amides under Microwave-Enhanced Condition

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1. General information.

Reactions were set-up on fume hoods and carried out under nitrogen atmosphere in Schlenk tubes unless otherwise noted. Compounds were purified by column chromatography using silica gel (230-400 mesh). All the reagents and solvents were used as received from commercial sources, unless otherwise specified. 1H NMR, 19F NMR and 13C NMR data were recorded on Bruker 400MHz AVANCE series or Bruker300 MHz DPX Spectrometer with $CDCl_3$ or DMSO-d_6 as the solvent. ^1H chemical shifts were referenced to $CDCl_3$ at 7.26 ppm. ^{13}C chemical shifts were referenced to $CDCl_3$&DMSO-d_6 at 77 ppm &39ppm respectively and obtained with ^1H decoupling. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), sextet (sextet), septet (septet), multiplet (m), and broad (br). IR spectra were obtained on a Thermo Scientific ATR Nicolet 7200 FT-IR spectrometer. MS was measured on Agilent 7890A/5975C Series GC/MSD mass spectrometer or Agilent 1100 Series LC/MSD mass spectrometer.

2.General procedure for the preparation of Phenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate.

To a solution of Phenol(5g, 0.053mmol) in Acetonitrile (100 mL) potassiumcarbonate(11.01g 0.0796mmol) was added followed by the drop wise addition of perfluorobutane sulfonyl fluoride(16.0g,0.053mmol) The reaction mixture was stirred at room temperature for 5hrs. Distilled out solvent, add water (200mL), Extracted with Ethyl acetate twice (2×150 mL), combined organic layers were washed with brine solution (200mL), the organic layer was dried over Na_2SO_4 and concentrated. The crude compound was purified by column chromatography

packed with 60-120 silica gel, eluted with 15-20% ethyl acetate in petroleum ether to obtain the pure compound (18.97g, 95%) as a color less oil.

2.1. General procedure for the coupling of amine with different Aryl/Hetero aryl Nonaflates.

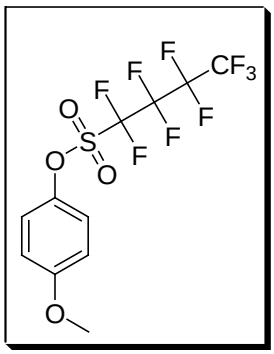
To a degassed solution of Aryl Nonaflates (250mg,1.0equiv) and we N,O-Dimehtyl hydroxyl amine hydrochloride(1.0 equiv) in 1,4-dioxane(10vol),DBU(3.0equiv), $Pd(OAc)_2$(0.02equiv), Molybdenum hexacarbonyl(0.35equiv) and Xantphos (0.04equiv) were added. The reaction mixture was heated at 120^0C under microwave condition for about 20 min. The reaction mixture was cooled to RT, passed through celite bed, washed with ethyl acetate (10mL), bi-phased with saturated NH_4Cl solution (10mL), washed with water (10mL), brine solution (10mL), the organic layer was dried over Na_2SO_4 and concentrated. The crude was purified by column chromatography packed with 230-400 silica gel, eluted with 25-45% ethyl acetate in petroleum ether which yielded pure compound (65-93%).

2.2.General procedure for the preparation of 4-methoxy phenyl methane sulfonate/4-Methyl benzene sulfonate/Trifluoromethane sulfonate.

To a solution of 4-Methoxy phenol(1.0eq) in anhydrous methylene dichloride (10 vol) Triethyl amine(1.5eq) was added followed by drop wise addition of methane sulfonyl chloride(1.0eq) at 0^0C.The reaction mixture was stirred at room temperature for 5hrs. Add water (20vol), separate organic and aqueous layer, extract aqueous layer with MDC(10vol),combined organic layers were washed with brine solution (5vol), the organic layer was dried over Na_2SO_4 and concentrated. The crude compound was purified by column chromatography packed with 60-120 silica gel, eluted with 15-20% ethyl acetate in petroleum ether to obtain the pure compound (90%) as a white solid.

2.3.Characterization data of compounds. 1a-v.

4-methoxy phenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1a). Yielded product as a white solid,(93%).

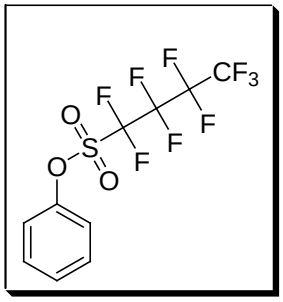


^{1}H NMR: (CD_3OD, 400MHz): δ=3.85(s, 3H) 7.05(d, J=8.6Hz,2H) 7.29(d, J=8.6Hz, 2H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -80.61 to -80.29 (m), -109.43 to -109.36 (m), -121.48 to -120.92 (m), -125.83 to -125.60 (m).

GC-MS: 406.

Phenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate, (1b). Yielded product as a colorless liquid**,**(95%).

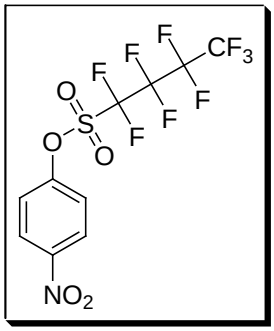


^{1}H NMR: (DMSO-d_6, 400MHz): δ=7.45-7.52(m, 3H) 7.55-7.59(m, 2H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -80.36 to -80.31 (m), -109.43 to -109.36 (m), -120.90 to -120.92 (m), -125.70 to -125.62 (m).

GC-MS: 376.

4-nitro phenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1c). Yielded product as a white solid, (89%).

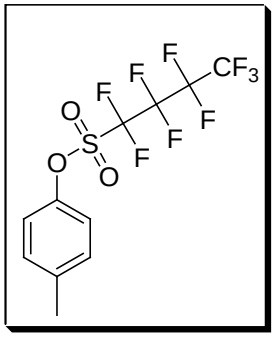


^{1}H NMR: (DMSO-d_6, 400MHz): δ=7.85(d, J=8.6Hz, 2H) 8.42(d, J=8.6Hz, 2H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -80.44 to -80.06 (m), -108.81 to -108.74 (m), -120.75 to -120.72 (m), -125.48 to -125.40 (m).

GC-MS: 420.9

p-tolyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1d). Yielded product as a white solid,(91%).

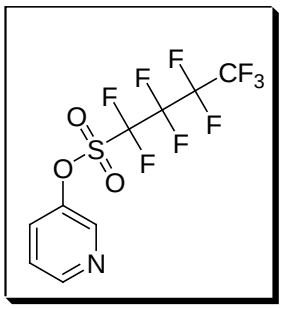


^{1}H NMR: (CD_3OD, 400MHz): δ=3.33(s, 3H) 7.24(d, J=8.0Hz, 2H) 7.34(d, J=8.0Hz, 2H).

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -80.84 to -80.68 (m), -109.66 to -109.58 (m), -121.58 to -121.12 (m), -125.98 to -125.90 (m).

GC-MS: 389.9

Pyridine-3-yl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1e) Yielded product as a colorless liquid,(90%).

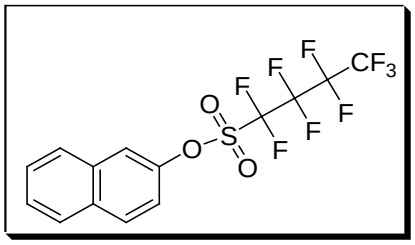


^{1}H NMR: (CD_3OD, 400MHz): δ7.62-7.65(m, 1H) 7.93-7.95(m, 1H) 8.67(d, J=2.8Hz, 2H)

F^{19} NMR: (DMSO-d_6, 376.2MHz): δ= -80.41 to -80.36 (m), -109.07 to -109.00 (m), -120.96 to -120.89 (m), -125.71 to -125.63(m).

GC-MS: 376.9

Naphthalen-3-yl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1f). Yielded product as a white solid,(94%).

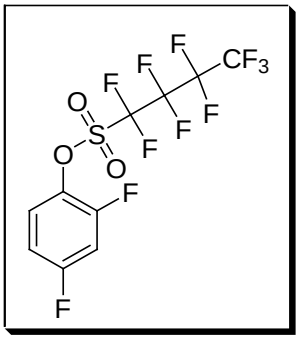


^{1}H NMR: (CD_3OD, 400MHz): δ 7.45(t, J=6.8Hz, 1H) 7.61(t, J=4.0Hz, 2H) 7.89-8.04(m, 4H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -80.62 to -80.30 (m), -109.35 to -109.28 (m), -121.47 to -120.85 (m), -125.83 to -125.58(m).

GC-MS: 426.

2,4-Difluorophenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1g). Yielded product as a white solid,(87%).

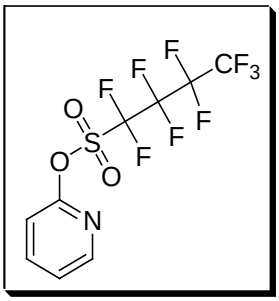


^{1}H NMR: (DMSO-d_6, 400MHz): δ 7.31(d, J=6.8Hz, 1H) 7.72-7.83(m, 2H).

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -80.79 to -80.58 (m), -107.58 to -107.51 (m), 109.82 to-109.73(m), 121.58 to -120.97(m), -123.83 to -123.77(m), -125.96 to-125.85(m).

GC-MS: 411.9

Pyridin-2-yl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1h) Yielded product as a white solid,(89%).

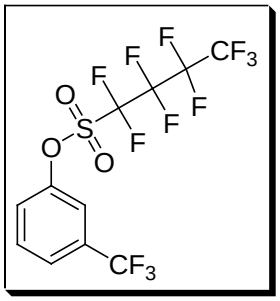


^{1}H NMR: (DMSO-d_6, 400MHz): δ=7.57(d, J=8.0Hz, 1H) 7.63(s, 1H) 8.16(t, J=8.0Hz, 1H) 8.48(s, 1H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -80.63 to -80.33 (m), -109.47 to -109.40 (m), -121.50 to -120.96 (m), -125.84 to -125.60(m).

GC-MS: 377.

3-(Trifluoromethyl) phenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1i). Yielded product as a white solid,(93%).

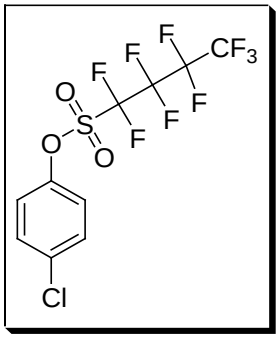


^{1}H NMR: (DMSO-d_6, 400MHz): δ=7.29(m, 1H) 7.80-7.84(m, 2H) 7.91(d, J=7.2Hz, 1H) 7.96(s, 1H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -61.61 to -61.50 (m), -80.64 to -80.38 (m), -109.14 to -109.07 (m), -121.52 to -120.89 (m), -125.84 to -125.62(m).

GC-MS: 444.

4-Chloro phenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1j). Yielded product as a white solid,(91%).

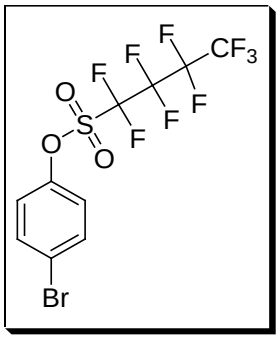


^{1}H NMR: (DMSO-d_6, 400MHz): δ=7.55(d, J=8.8Hz, 2H) 7.64(d, J=8.8Hz, 2H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -80.91 to -80.77 (m), -109.43 to -109.36 (m), -121.59 to -121.17 (m), -126.02 to -125.95(m).

GC-MS: 409.9.

4-Bromo phenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1k). Yielded product as a white solid,(89%).

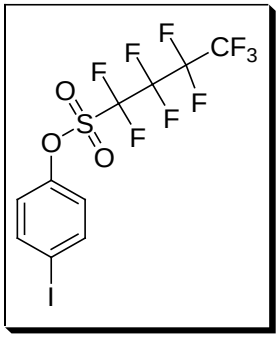


^{1}H NMR: (DMSO-d_6, 400MHz): δ=7.48(d, J=8.8Hz, 2H) 7.77(d, J=8.8Hz, 2H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -80.70 to -80.40 (m), -109.24 to -109.16 (m), -121.52 to -120.94 (m), -125.88 to -125.66(m).

GC-MS: 455.6

4-Iodo phenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1l). Yielded product as a white Solid,(90%).

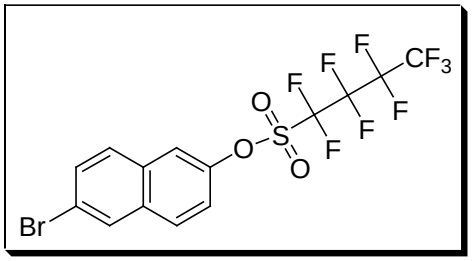


^{1}H NMR: (DMSO-d_6, 400MHz): δ=7.33(d, J=8.4Hz, 2H) 7.93(d, J=8.8Hz, 2H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -80.47 to -80.21 (m), -109.05, -121.31 to -120.80 (m), -125.66 to -125.51(m).

GC-MS: 501.88

2-Bromonaphthalen-6-yl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1m). Yielded product as a white solid, (93%).

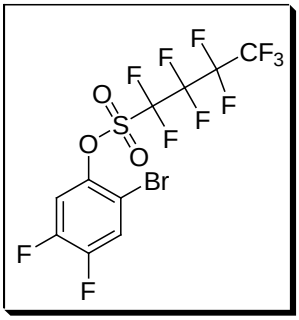


^{1}H NMR: (DMSO-d_6, 400MHz): δ=7.66(d, J=8.4Hz, 1H) 7.78(d, J=8.8Hz, 1H) 8.06(d, J=8.8Hz, 1H) 8.12(d, J=9.2Hz,1H) 8.19(s,1H) 8.36(s,1H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -80.68 to -80.33 (m), -109.34 to -109.22 (m), -121.40 to -120.86 (m), -125.82 to -125.60(m).

GC-MS: 503.91.

2-Bromo-4,5-difluorophenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate(1n). Yielded product as a white solid,(87%).

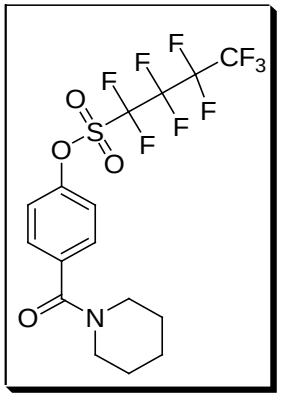


^{1}H NMR: (DMSO-d_6, 400MHz): δ=7.93-7.97(m, 1H) 8.21-8.26(m, 1H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ=-80.89 to -80.74 (m), -109.55 to -109.48 (m), -121.59 to -120.95 (m), -126.01 to -125.88(m), -133.39 to -133.29(m), -134.03 to -133.92 (m).

GC-MS: 491.87.

4-(Piperidine-1-carbonyl)phenyl1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1o). Yielded product as a white solid**,**(93%).

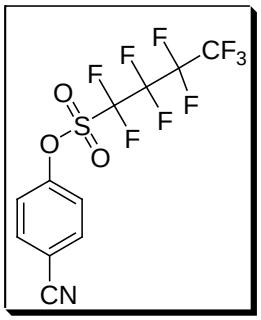


^{1}H NMR: (CD_3OD, 400MHz): δ=1.56-1.72(m, 6H) 3.30-3.35(m, 2H) 3.71(s, 2H) 7.48(d, J=8.8Hz, 2H) 7.59(d, J=2.0Hz, 2H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -80.73 to -80.44 (m), -109.36 to -109.29 (m), -121.56 to -120.92 (m), -125.92 to -125.65(m).

GC-MS: 487.05.

4-Cyano phenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1p). Yielded product as a white solid,(89%).

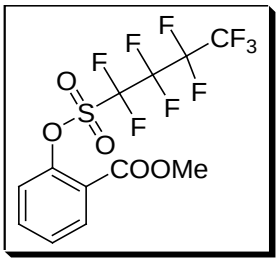


^{1}H NMR: (DMSO-d_6, 400MHz): δ=7.79(d, J=8.4Hz, 2H) 8.11(d, J=8.4Hz, 2H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -80.66 to -80.37 (m), -109.04, -121.50 to -120.94(m), -125.88 to -125.66(m).

GC-MS: 400.9.

2-(Methoxycarbonyl)phenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1q). Yielded product as a white solid**,**(91%).

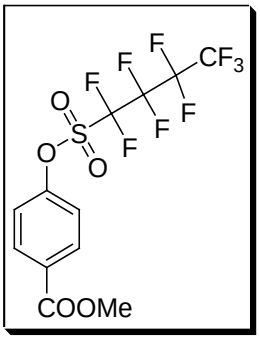


^{1}H NMR: (DMSO-d_6, 400MHz): δ=3.87(s, 3H) 7.56(d, J=5.6Hz, 1H) 7.66(t, J=7.2Hz, 1H) 7.83(d, J=6.8Hz,1H) 8.08(d, J=6.4Hz,1H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -80.62,-109.74 , -121.50 to -120.98 (m), -125.83.

GC-MS: 434.

4-(Methoxycarbonyl)phenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1r). Yielded product as a white solid,(93%).

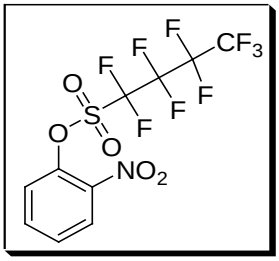


^{1}H NMR: (DMSO-d_6, 400MHz): δ= 3.87(s, 3H) 7.65(d, J=8.4Hz, 2H) 8.12(d, J=8.4Hz, 2H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ= -80.73 to -80.42 (m), -109.26 to -109.19 (m), -121.55 to -120.98 (m), -125.90 to -125.72 (m).

GC-MS: 434.

2-Nitro phenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1s). Yielded product as a pale yellow solid,(91%).

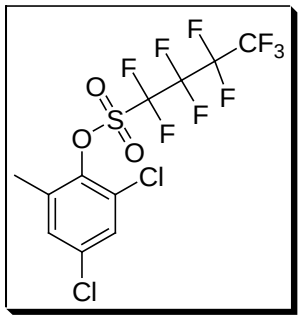


^{1}H NMR: (DMSO-d_6, 400MHz): δ= 7.81(d, J=8.0Hz, 2H) 7.99(t, J=7.2Hz, 1H) 8.35(d, J=8.0Hz, 1H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ=-80.65 to -80.30 (m), -109.20 to -109.12 (m), -121.52 to -120.77 (m), -125.85 to -125.61 (m).

GC-MS: 420.9

2,4-Dichloro-6-methylphenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1t). Yielded product as a white solid,(93%).

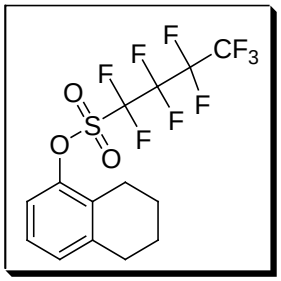


^{1}H NMR: (DMSO-d_6, 400MHz): δ= 2.37(s, 3H) 7.62(s, 1H) 7.81(s,1H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ=-80.62 to -80.31 (m), -108.66 to -108.59 (m), -121.50 to -120.57 (m), -125.84 to -125.55 (m).

GC-MS: 457.9

1,2,3,4-tetrahydronaphthalen-5-yl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1u). Yielded product as a white solid,(91%).



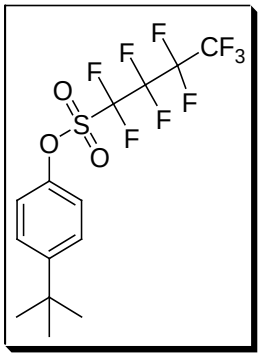
^{1}H NMR: (DMSO-d_6, 400MHz): δ= 1.74(s, 4H) 2.62(s, 2H) 2.79(s, 2H)

7.16(d, J=5.6Hz, 1H) 7.23(s, 1H) 7.28(t, J=4.4Hz, 1H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ=-80.83 to -80.52 (m), -110.43 to -110.36 (m), -121.69 to -121.10 (m), -126.04 to -125.82 (m).

GC-MS: 430.

4-tert-butyl phenyl 1,1,2,2,3,3,4,4-nonafluorobutane-1-sulfonate,(1v). Yielded product as a white solid,(90%).



^{1}H NMR: (CD_3OD, 400MHz): δ=1.34(s, 9H) 7.26(d, J=8.8Hz, 2H) 7.56(d, J=8.8Hz, 2H)

^{19}F NMR: (DMSO-d_6, 376.2MHz): δ=-80.67 to -80.31 (m), -109.49 to -109.42 (m), -121.49 to -120.94 (m), -125.82 to -125.62 (m).

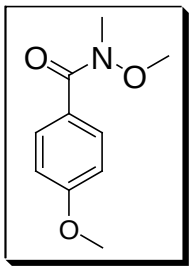
GC-MS: 432.

2.4. Characterization data of compounds 2 a-ze.

N, 4-Dimethoxy-N-methylbenzamide.(2a),Yielded product as a pale yellow oil, (87%).

Reaction was performed for 250mg scale, Yield= 104mg.(87%)

Same reaction carried out for 5g scale, Yield=2.05g. (85%)



^{1}H NMR: (CDCl3, 400MHz) δ=3.36(s, 3H) 3.57(s, 3H) 3.85(s, 3H) 6.91(d, J=8.8Hz, 2H) 7.73(d, J=8.4Hz, 2H).

^{13}C NMR: 34.01, 55.41, 60.99, 113.34, 126.06, 130.65, 161.63, 169.50 ppm

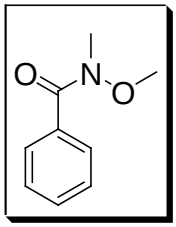
LCMS: 196.01(M+H).

Anal calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.18%,

Found: C, 61.50; H, 6.73; N, 7.20%,

N-Methoxy-N-methylbenzamide.(2b), Yielded product as a pale yellow oil,(91%).

Reaction was performed for 250mg scale, Yield= 99mg.



^{1}H NMR: (400MHz, $CDCl_3$): δ= 3.36(s, 3H) 3.55(s, 3H) 7.38-7.47(m, 3H) 7.67(d, J=7.2Hz, 2H)

^{13}C NMR: (400MHz, $CDCl_3$): δ= 33.87, 61.10, 128.09, 128.20, 130.64, 134.18, 170.04ppm

LCMS: 166.0 (M + H).

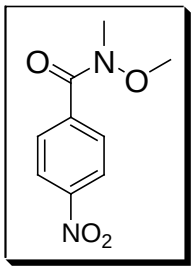
IR (KBr): 2924.15, 2853.68, 2726.75, 1658, 1602.34, 1577.91, 1462.18, 1407.95, 1377, 1302.67, 1212.33, 1156.97, 1111.11, 1063.77, 1029.18, 981.85, 887.97, 786.15, 721.78, 703.05, 629.55, 556.63, 475.67 cm^{-1}.

Anal. calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48%,

Found: C, 65.54; H, 6.76; N, 8.45%.

N-methoxy-N-methyl-4-nitrobenzamide. (2c), Yielded product as a light yellow colored solid. (92%).

Reaction was performed for 250mg scale, Yield= 114mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ=3.40(s, 3H) 3.54(s, 3H) 7.85(d, J=8.8Hz, 2H) 8.27 (d, J=8.8Hz, 2H)

^{13}C NMR: 32.29, 61.50, 123.35, 129.35, 140.15, 148.93, 167.81ppm

LCMS: 211.1 (M + H).

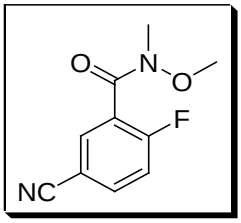
Anal calcd for $C_9H_{10}N_2O_4$: C, 51.43; H, 4.80; N, 13.33%,

Found: C, 51.40; H, 4.84; N, 13.31%.

IR (KBr): 3115.14, 2992.44, 2925.55, 2859.21, 1944.18, 1637.69, 1601.04, 1526.51, 1459.23, 1424.54, 1354.56, 1338.17, 1313.81, 1211.80, 1103.23, 1009.98, 976.68, 890.53, 863.63, 851.84, 772.32, 731.27, 710.05, 550.84, 521.43, 443.16 cm^{-1}.

5-Cyano-2-fluoro-N-methoxy-N-methylbenzamide.(2d) Yielded product as a colorless oil.(90%).

Reaction was performed for 250mg scale, Yield= 111mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ=3.36(s, 3H) 3.53(s, 3H) 7.24(t, J=8.8Hz, 1H) 7.75(t, J=8.4Hz, 2H).

^{13}C NMR: ($CDCl_3$, 400MHz) δ 32.31, 61.52, 108.80, 117.27, 117.46, 125.43, 133.48, 135.55, 159.71, 162.29ppm

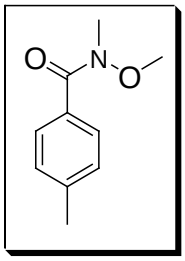
LCMS: 208.06 (M+H)

Anal calcd for $C_{10}H_9FN_2O_2$: C, 57.69; H, 4.36; N, 13.46%

Found: C, 57.72; H, 4.33; N, 13.48%

N-methoxy-N-4-dimethylbenzamide. (2e), Yielded product as a colorless oil. (90%).

Reaction was performed for 250mg scale, Yield= 103mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ=2.39(s, 3H) 3.35(s, 3H) 3.56(s, 3H) 7.21(d, J=8.0Hz, 2H) 7.60(d, J=8.0Hz, 2H)

^{13}C NMR: 21.54, 33.96, 61.03, 128.40, 129.10, 131.15, 140.99, 170.06ppm

LCMS: 180.0 (M + H)

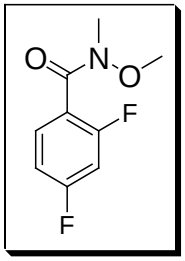
IR(Liquid Paraffin): 930.21, 2854.16, 2727.62, 1651.69, 1614.11, 1570.13, 1462.43, 1411.31, 1376.95, 1219.35, 1207.42, 1181.39, 1112.09, 1064.07, 1022.47, 999.93, 980.40, 888.66, 829.11, 794.13, 741.37, 722.44, 674.12, 636.63, 585.63, 556.90, 470.02 cm^{-1}.

Anal calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82%,

Found: C, 67.05; H, 7.29; N, 7.85%.

2, 4-difluoro-N-methoxy-N-methylbenzamide.(2f),Yielded product as a colorless oil.(79%).

Reaction was performed for 250mg scale, Yield= 95mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ=3.34(s, 3H) 3.56(s, 3H) 6.84-6.95(m, 2H) 7.42-7.47(m, 1H)

^{13}C NMR: 32.77, 61.38, 104.30, 111.73, 119.68, 130.47, 158.11, 160.75, 162.70, 165.21ppm

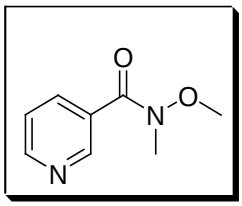
LCMS: 201.06 (M+H)

Anal calcd for $C_9H_9F_2NO_2$: C, 53.73; H, 4.51; N, 6.96%

Found: C, 53.75; H, 4.49, N, 6.99%

N-methoxy-N-methylnicotinamide.(2g), Yielded product as a colorless oil.(83%).

Reaction was performed for 250mg scale, Yield= 90mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ=3.39(s, 3H) 3.55(s, 3H) 7.37-7.40 (m, 1H) 8.05(d, J=7.6Hz, 1H) 8.69(s, 1H) 8.95 (s, 1H).

^{13}C NMR: 33.27, 61.40, 123.24, 130.08, 136.56, 149.09, 151.13, 167.31ppm

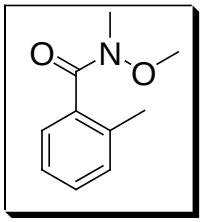
LCMS: 166.07(M+H)

Anal calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86%

Found: C, 57.85, H, 6.10, N, 16.83%

N-methoxy-N, 2-dimethylbenzamide,(2h). Yielded product as a colorless oil.(87%)

Reaction was performed for 250mg scale, Yield= 99mg.



H^1 NMR: ($CDCl_3$, 400MHz) δ2.49(s, 3H) 3.30(s, 3H) 3.49(s, 3H) 7.18-7.30(m, 4H)

C^{13}NMR: 19.15, 32.79, 61.11, 125.47, 126.24, 129.26, 130.20, 134.86, 135.29, 168.20.

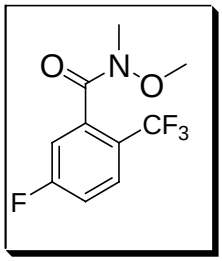
LCMS: 179.09 (M+H)

Anal calcd for $C_{10}H_{13}NO_2$: C, 67.02, H, 7.31, N, 7.82%

Found: C, 67.05, H, 7.29, N, 7.85%

5-fluoro-2-(trifluoromethyl)-N-methoxy-N-methylbenzamide.(2i), Yielded product as a colorless oil.(89%)

Reaction was performed for 250mg scale, Yield= 120mg.



H^1 NMR: ($CDCl_3$, 400MHz) δ3.36(s, 3H) 3.46(s, 3H) 7.13-7.15(m, 1H) 7.21-7.25(m, 1H) 7.69-7.72(m, 1H)

C^{13}NMR: 32.68, 61.20, 114.75, 115.53, 118.30, 122.06, 129.26, 136.66, 165.14, 167.93.

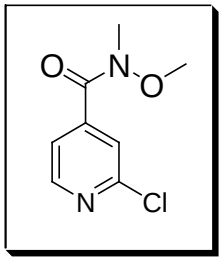
LCMS: 252.0 (M+H)

Anal calcd for $C_{10}H_9F_4NO_2$: C, 47.82; H, 3.61; N, 5.58%

Found: C, 47.79; H, 3.63; N, 5.60%

2-chloro-N-methoxy-N-methylpyridine-4-carboxamide.(2j), Yielded product as a colorless oil.(71%)**.**

Reaction was performed for 250mg scale, Yield= 85mg.



H^1 NMR: ($DMSO\text{-}d_6$, 400MHz) δ3.27(s, 3H) 3.50(s, 3H) 7.54(d, J=4.8Hz, 1H) 7.64 (s, 1H)

8.51(d, J=5.2Hz, 1H).

C^{13}NMR: 32.56, 61.30, 121.02, 122.10, 145.81, 150.39, 150.44, 165.68ppm

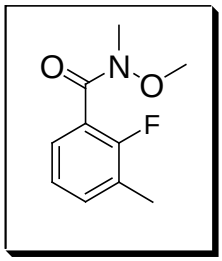
LCMS: 200.04 (M+H)

Anal calcd for $C_8H_9ClN_2O_2$: C, 47.89; H, 4.52; N; 13.96%

Found: C, 47.86; H, 4.55; N, 13.93%

2-fluoro-N-methoxy-N, 3-dimethylbenzamide,(2k). Yielded product as a white solid, (89%).

Reaction was performed for 250mg scale, Yield= 107mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ2.31(s, 3H) 3.35(s, 3H) 3.55(s, 3H) 7.06-7.09 (m, 1H) 7.22-7.28 (m, 2H).

^{13}C NMR: 14.63, 32.77, 61.33, 123.19, 123.37, 123.79, 126.26, 132.98, 155.97, 158.44ppm

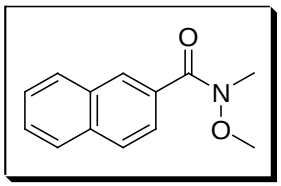
LCMS: 197.09 (M+H)

Anal calcd for $C_{10}H_{12}FNO_2$: C, 60.90; H, 6.13; N, 7.10%

Found: C, 60.92; H, 6.10; N, 7.08%.

N-methoxy-N-methyl-2-naphthamide.(2l),Yielded product as a colorless oil.(93%)

Reaction was performed for 250mg scale, Yield= 117mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ3.43(s, 3H) 3.58(s, 3H) 7.52-7.59 (m, 2H) 7.77(d, J=8.4Hz,1H) 7.87-7.93(m, 3H) 8.24(s, 1H)

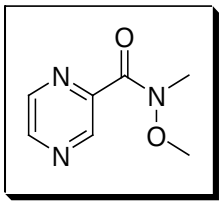
^{13}C NMR: 33.98, 61.23, 125.16, 126.58, 127.50, 127.73, 127.80, 128.78, 128.94, 131.51, 132.60 134.33, 170.02ppm

LCMS: 216.0 (M+H)

Anal calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51%

Found: C, 72.52; H, 6.11; N, 6.53%

N-methoxy-N-methylpyrazine-2-carboxamide,(2m). Yielded product as a colorless oil,(65%). Reaction was performed for 250mg scale, Yield= 71mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ3.34(s, 3H) 3.73(s, 3H) 8.59(d, J=1.6Hz, 1H) 8.65(d, J=1.6Hz,1H) 8.89(s, 1H)

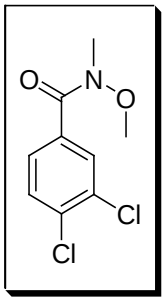
^{13}C NMR: 29.74, 61.87, 143.24, 144.48, 145.72, 148.73, 166.98ppm

LCMS: 167.07 (M+H)

Anal calcd for $C_7H_9N_3O_2$: C, 50.29; H, 5.43; N, 25.14%

Found: C, 50.32; H, 5.45; N, 25.11%

3, 4-dichloro-N-methoxy-N-methylbenzamide,(2n). Yielded product as a white solid,(89%). Reaction was performed for 250mg scale, Yield= 116mg.



^{1}H NMR: (DMSO-d_6, 400MHz) δ3.26(s, 3H) 3.44(s, 3H) 7.58(d d, J_1=1.6Hz, J_2=8.0Hz, 1H) 7.72(d, J=8.4Hz, 1H) 7.82(d, J=1.6Hz, 1H)

^{13}C NMR: 32.99, 60.95, 127.96, 129.58, 130.45, 130.92, 133.12, 134.74, 166.38ppm

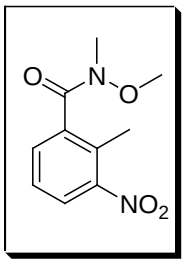
LCMS: 234 (M+H)

Anal calcd for $C_9H_9Cl_2NO_2$: C, 46.18; H, 3.88; N, 5.98%

Found: C, 46.15; H, 3.86; N, 5.99%

N-methoxy-N, 2-dimethyl-3-nitrobenzamide, (2o).Yielded product as a light yellow colored solid,(87%).

Reaction was performed for 250mg scale, Yield= 111mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ=2.48(s, 3H) 3.40(d, J=6.0Hz, 6H) 7.39(t, J=7.6Hz, 1H) 7.50(d, J=7.2Hz, 1H) 7.90(d, J=8.0Hz, 1H)

^{13}C NMR: 16.40, 32.35, 61.45, 125.01, 126.56, 130.22, 130.52, 138.79, 150.21, 169.23ppm

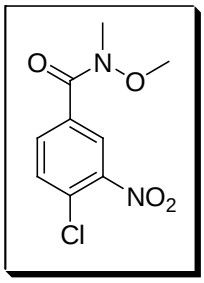
LCMS: 224.08 (M+H)

Anal calcd for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.39; N, 12.49%

Found: C, 53.55; H, 5.42; N, 12.51%

4-chloro-N-methoxy-N-methyl-3-nitrobenzamide,(2p). Yielded product as a light yellow colored solid,(88%).

Reaction was performed for 250mg scale, Yield= 117mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ=3.39(s, 3H) 3.57(s, 3H) 7.61(d, J=8.4Hz, 1H) 7.91(d d, J_1=1.2Hz, J_2=8.0Hz, 1H) 8.28(s, 1H)

^{13}C NMR: 33.30, 61.58, 126.05, 129.40, 131.74, 133.23, 133.57, 147.52, 165.95ppm

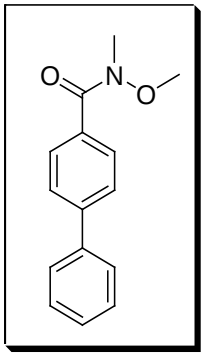
LCMS: 244.03 (M+H)

Anal calcd for $C_9H_9ClN_2O_4$: C, 44.19; H, 3.71; N, 11.45%

Found: C, 44.21; H, 3.69; N, 11.47%

4-Phenyl-N-methoxy-N-methylbenzamide, (2q). Yielded product as a white colored solid,(91%).

Reaction was performed for 250mg scale, Yield= 120mg.



^{1}H NMR: (DMSO-d_6, 400MHz) δ=3.36(s, 6H) 7.35(t, J=7.2Hz, 1H) 7.45(t, J=7.6Hz, 2H) 7.58(d, J=8.0Hz, 2H) 7.67(d, J=7.6Hz, 2H) 7.98(d, J=8.0Hz, 2H)

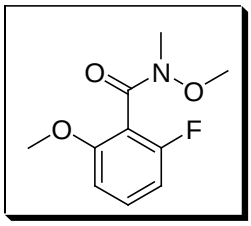
^{13}C NMR: (DMSO-d_6, 400MHz): 33.74, 60.75, 125.50, 126.78, 128.84, 129.76, 138.63, 140.11, 140.57, 170.42ppm.

LCMS: 241.11 (M+H)

Anal calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81%

Found: C, 75.65; H, 6.25; N, 5.83%.

2-fluoro-N, 6-dimethoxy-N-methylbenzamide,(2r). Yielded product as a white solid,(79%).
Reaction was performed for 250mg scale, Yield= 99mg.



^{1}H NMR: ($CDCl_3$, 400MHz): δ=3.38(s, 3H) 3.50(s, 3H) 3.84(s, 3H) 6.72(t, J=8.0Hz, 2H) 7.29(q, J=7.6Hz, 1H)

^{13}C NMR: ($CDCl_3$, 400MHz): 32.16, 56.29, 61.54, 106.80, 107.89, 108.10, 130.75, 157.24, 160.41, 164. 62ppm.

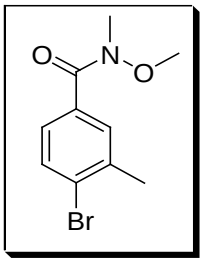
LCMS: 214.0 (M+H)

Anal calcd for $C_{10}H_{12}FNO_3$; C, 56.33; H, 5.67; N, 6.57%

Found: C, 56.30; H, 5.65; N, 6.59%

4-Bromo-N-methoxy-N, 3-dimethylbenzamide,(2s). Yielded product as a white solid, (26%).

Reaction was performed for 250mg scale, Yield= 35mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ=2.51(s, 3H) 3.35(s, 3H) 3.55(s, 3H) 7.37(d, J=8.0Hz, 1H) 7.56(d, J=7.6Hz, 2H)

^{13}C NMR: 22.99, 33.72, 61.21, 127.11, 127.63, 130.71, 132.07, 133.20, 137.96, 169.10ppm

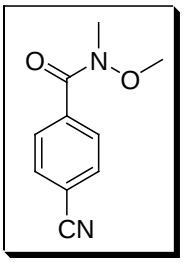
LCMS: 257.01(M+H)

Anal calcd for $C_{10}H_{12}BrNO_2$: C, 46.53; H, 4.69; N, 5.43%

Found: C, 46.55; H, 4.72; N, 5.40%.

4-Cyano-N-methoxy-N-methylbenzamide,(2t). Yielded product as a white solid, (90%).

Reaction was performed for 250mg scale, Yield= 106mg.



^{1}H NMR: (DMSO-d_6, 400MHz) δ=3.40(s, 3H) 3.54(s, 3H) 7.84(d, J=8.8Hz, 2H) 8.28 (d, J=8.8Hz, 2H)

^{13}C NMR: 33.6, 61.9, 115.8, 116, 128.2, 131.3, 138.3, 168.1ppm

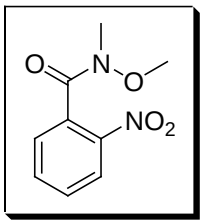
LCMS: 190.07 (M + H).

Anal calcd for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.30; N, 14.73%,

Found: C, 63.18; H, 5.27; N, 14.70%.

N-Methoxy-N-methyl-2-nitrobenzamide,(2u). Yielded product as a white solid, (79%).

Reaction was performed for 250mg scale, Yield= 98mg.



^{1}H NMR: (DMSO-d_6, 400MHz): δ= 3.38(s, 3H) 3.55(s, 3H) 7.78(d, J=8.0Hz, 2H) 8.02(t, J=7.2Hz, 1H) 8.33(d, J=8.0Hz, 1H).

^{13}C NMR: 33.4, 61.5, 121.3, 128.5, 128.8, 133.5, 134.5, 147.6, 168.6ppm.

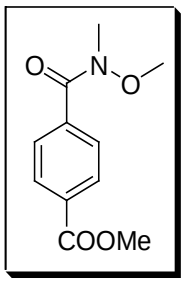
LCMS: 211.06 (M+H)

Anal calcd for $C_9H_{10}N_2O_4$: C, 51.43; H, 4.80; N, 13.33%,

Found: C, 51.40; H, 4.82; N, 13.30%,

Methyl 4-(N-methoxy-N-methylcarbamoyl)benzoate,(2v). Yielded product as a colorless oil, (83%)**.**

Reaction was performed for 250mg scale, Yield= 106mg.



^{1}H NMR: (DMSO-d_6, 400MHz): δ= 3.35(s, 3H) 3.56(s, 3H) 3.84(s, 3H) 7.68(d, J=8.4Hz, 2H) 8.32(d, J=8.4Hz, 2H)

^{13}C NMR: 33.7, 51.8, 62.3, 127.6, 130.5, 133.7, 138.7, 166.7, 168.4ppm

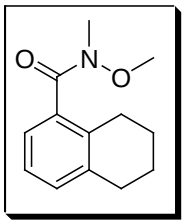
LCMS: 223.08 (M + H).

Anal calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27%,

Found: C, 59.16; H, 5.89; N, 6.26%,

5,6,7,8-tetrahydro-N-methoxy-N-methylnaphthalene-1-carboxamide,(2w). Yielded product as a white solid, (88%).

Reaction was performed for 250mg scale, Yield= 111mg.



^{1}H NMR: (DMSO-d_6, 400MHz): δ= 1.78(s, 4H) 2.60(s, 2H) 2.72(s, 2H) 3.39(s, 3H) 3.56(s, 3H) 7.18(d, J=5.6Hz, 1H) 7.25(s, 1H) 7.32(t, J=4.4Hz, 1H)

^{13}C NMR: 22.4, 22.8, 24.4, 31.4, 33.9, 62, 124.5, 125.7, 131.8, 134.8, 135.7, 137.8, 169.1ppm

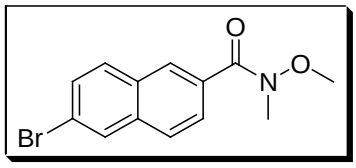
LCMS: 219.13 (M + H).

Anal calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39%,

Found: C, 71.20; H, 7.79; N, 6.36%,

6-Bromo-N-methoxy-N-methylnaphthalene-2-carboxamide,(2x). Yielded product as a white solid, (27%).

Reaction was performed for 250mg scale, Yield= 39mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ3.44(s, 3H) 3.59(s, 3H) 7.52-7.59 (m, 2H) 7.80(d, J=8.8Hz, 1H) 7.94(d, J=8.0Hz, 2H) 8.24(s, 1H)

^{13}C NMR: 33.98, 61.53, 125.16, 126.58, 127.50, 127.63, 127.80, 128.78, 128.94, 131.51, 132.50, 133.33, 169.02ppm

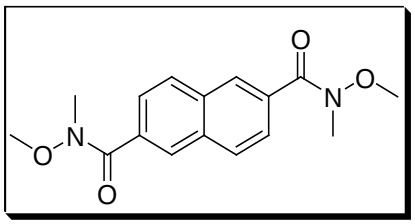
GC-MS: 293.01 (M+H).

Anal calcd for $C_{13}H_{12}BrNO_2$: C, 53.08; H, 4.11; N, 4.76%

Found: C, 53.05; H, 4.10; N, 4.73%

N^2, N^6-Dimethoxy-N^2, N^6-dimethylnaphthalene-2,6-dicarboxamide,(2x^c). Yielded product as a white solid, (25%).

Reaction was performed for 250mg scale, Yield= 37mg.



^{1}H NMR: (DMSO-d_6, 400MHz) δ3.45(s, 6H) 3.59(s, 6H) 6.86 (d, J=8.0Hz, 1H) 7.23-7.28(m, 2H) 7.81(d, J=8.8Hz, 1H) 7.94(d, J=8.0Hz, 1H) 8.25(s,1H)

^{13}C NMR: 32.56, 61.21, 124.16, 128.58, 129.50, 134.51, 136.50, 168.2ppm

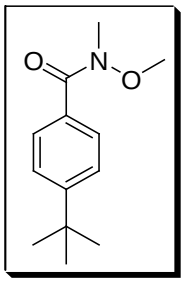
LCMS: 302.13 (M+H)

Anal calcd for $C_{16}H_{18}N_2O_4$: C, 63.56; H, 6.00; N, 9.27%

Found: C, 63.59; H, 6.02; N, 9.24%.

4-tert-butyl-N-methoxy-N-methylbenzamide, (2y). Yielded product as a white solid, (85%).

Reaction was performed for 250mg scale, Yield= 108mg.



^{1}H NMR: (DMSO-d_6, 400MHz): δ=1.29(s, J=9H) 3.34(s, 3H) 3.55(s,3H)7.40(t, J=5.2Hz, 2H) 7.57(t, J=3.2Hz, 2H).

^{13}C NMR: 31.3, 33.6, 40.7, 61.9, 125.7, 127.6, 132.5, 152.4, 168.2ppm

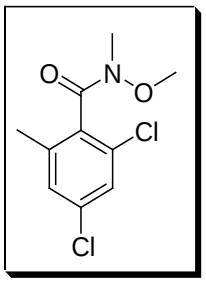
LCMS: 221.14 (M+H)

Anal calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33%

Found: C, 70.54; H, 8.68; N, 6.30% .

2, 4-Dichloro-N-methoxy-N, 6-dimethylbenzamide,(2z). Yielded product as a white solid.(77%).

Reaction was performed for 250mg scale, Yield= 103mg.



^{1}H NMR: (DMSO-d_6, 400MHz): δ= 2.37(s, 3H) 3.37(s, 3H) 3.54(s, 3H) 7.60(s, 1H) 7.87(s, 1H).

^{13}C NMR: 16.4, 33.7, 61.5, 127.5, 127.8, 132.8, 133.9, 139, 139.8, 168.7ppm

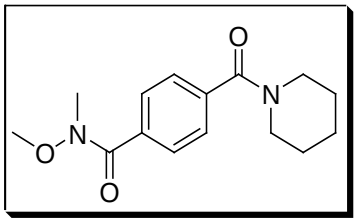
LCMS: 247.02 (M+H)

Anal calcd for $C_{10}H_{11}Cl_2NO_2$: C, 48.41; H, 4.47; N, 5.65%

Found: C, 48.44; H, 4.44; N, 5.67%.

N-Methoxy-N-Methyl-4-(piperidine-1-carbonyl)benzamide,(2za). Yielded product as a white solid, (84%).

Reaction was performed for 250mg scale, Yield= 118mg.



^{1}H NMR: (CD_3OD, 400MHz): δ=1.56-1.72(m, 6H) 3.30-3.35(m, 2H) 3.37(s, 3H) 3.54(s, 3H) 3.71(s, 2H) 7.46(d, J=8.8Hz, 2H) 7.79(d, J=2.0Hz, 2H)

^{13}C NMR: 25.4, 25.6, 33.5, 45.7, 61.9, 127.3, 127.5, 135.2, 138.6, 168.2, 172.8ppm

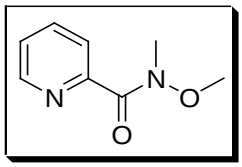
LCMS: 276.15 (M+H)

Anal calcd for $C_{15}H_{20}N_2O_3$: C, 65.20; H, 7.30; N, 10.14%

Found: C, 65.22; H, 7.33; N, 10.11%

N-Methoxy-N-methylpicolinamide,(2zb). Yielded product as a colorless oil, (67%)**.**

Reaction was performed for 250mg scale, Yield= 73mg.



^{1}H NMR: ($CDCl_3$, 400MHz): δ=3.38(s, 3H) 3.62(s, 3H) 7.32-7.35(m, 1H) 7.74-7.78(m, 2H) 8.59(d, J=4.4Hz, 1H).

^{13}C NMR: 33.27, 61.41, 123.24, 130.08, 136.67, 148.53, 153.11, 167.31ppm

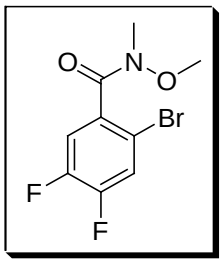
LCMS: 166.07(M+H)

Anal calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86%

Found: C, 57.84, H, 6.06, N, 16.85% .

2-Bromo-4, 5-difluoro-N-methoxy-N-methylbenzamide,(2zc) Yielded product as a white solid,(28%).

Reaction was performed for 250mg scale, Yield= 39mg.



^{1}H NMR: (DMSO-d_6, 400MHz): δ=3.40(s,3H) 3.56(s,3H)7.91-7.96(m, 1H) 819-8.24(m, 1H).

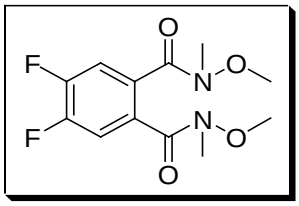
^{13}C NMR: 33.6, 61.9, 116.7, 117.5, 121.4, 134.5, 149.8, 156.7, 168.6ppm

LCMS: 278.97 (M+H)

Anal calcd for $C_9H_8BrF_2NO_2$: C, 38.60; H, 2.88; N, 5.0%

Found: C, 38.63; H, 2.85; N, 5.03%.

4, 5-Difluoro-N^{1}, N^{2}-dimethoxy-N^{1}, N^{2}-dimethylbenzene-1,2-diamide.(2zc^{c}) Yielded product as a white solid,(26%).



^{1}H NMR: (DMSO-d_6, 400MHz): δ=3.37(s, 6H) 3.52(s, 6H)7.90-7.95(m, 1H) 817-8.22(m, 1H).

^{13}C NMR: 33.5, 61.5, 114.7, 126.5, 153.6, 168.2ppm

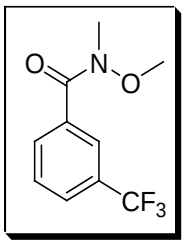
LCMS: 288.09 (M+H).

Anal calcd for $C_{12}H_{14}F_2N_2O_4$: C, 50.0; H, 4.90; N, 9.72%

Found: C, 50.03; H, 4.87; N, 9.70%.

3-(Trifluoromethyl)-N-methoxy-N-methylbenzamide,(2zd). Yielded product as a white solid, (86%).

Reaction was performed for 250mg scale, Yield= 112mg.



^{1}H NMR: ($CDCl_3$, 400MHz): δ=3.40(s, 3H) 3.56(s, 3H) 7.56(d, J=6.4Hz, 1H) 7.73(d, J=6.0Hz, 1H) 7.90(d, J=6.4Hz, 1H) 7.99(s, 1H)

^{13}C NMR: 33.40, 61.21, 122.42, 125.13, 127.24, 128.60, 130.70, 131.60, 134.74, 168.31ppm

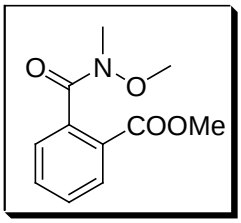
LCMS: 233.07 (M+H)

Anal calcd for $C_{10}H_{10}F_3NO_2$: C, 51.51; H, 4.32; N, 6.01%

Found: C, 51.49; H, 4.29; N, 6.04%.

Methyl 2-(N-methoxy-N-methylcarbamoyl)benzoate,(2ze). Yielded product as a colorless oil,(80%).

Reaction was performed for 250mg scale, Yield= 102mg.



^{1}H NMR: ($CDCl_3$, 400MHz): δ=3.37(s, 3H)3.52(s,3H)3.85(s, 3H) 7.52(d, J=5.6Hz,1H) 7.56(t, J=7.2Hz, 1H) 7.73(d, J=6.8Hz,1H) 8.18(d, J=6.4Hz,1H)

^{13}C NMR: 33.7, 51.8, 61.5, 127.6, 130.5, 131.7, 132.7, 133.3, 166.7, 168.4ppm

GC-MS: 223.08

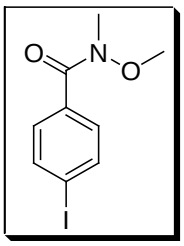
Anal calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27%,

Found: C, 59.16; H, 5.89; N, 6.26%,

2.5. Characterization data of compounds 3 a-c

4-Iodo-N-methoxy-N-methylbenzamide,(3a). Yielded product as a white solid.(28%)

Reaction was performed for 250mg scale, Yield= 40mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ=3.35(s, 3H) 3.56(s, 3H) 7.65(d, J=8.8Hz, 2H) 7.70 (d, J=8.8Hz, 2H)

LCMS: 290.98 (M + H).

^{13}C NMR: 33.50, 61.25, 122.08, 130.04, 131.16, 132.04, 168.56ppm

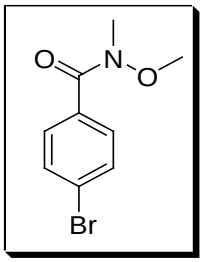
LCMS: 290.98 (M+H).

Anal calcd for $C_9H_{10}INO_2$: C, 37.14; H, 3.46; N, 4.81%,

Found: C, 37.11; H, 3.48; N, 4.80%,

4-Bromo-N-methoxy-N-methylbenzamide, (3b). Yielded product as a white solid.(26%)

Reaction was performed for 250mg scale, Yield= 35mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ=3.37(s, 3H) 3.54(s, 3H) 7.55(d, J=8.8Hz, 2H) 7.60 (d, J=8.8Hz, 2H) LCMS: 223.08 (M + H).

^{13}C NMR: 33.52, 61.15, 125.18, 130.04, 131.26, 132.74, 168.76ppm

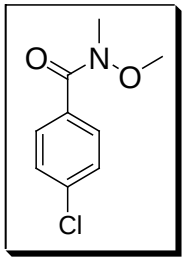
LCMS: 242.99 (M+H).

Anal calcd for $C_9H_{10}BrNO_2$: C, 44.29; H, 4.13; N, 5.74%,

Found: C, 44.32; H, 4.10; N, 5.72%,

4-Chloro-N-methoxy-N-methylbenzamide,(3c). Yielded product as a colorless oil.(90%)

Reaction was performed for 250mg scale, Yield= 108mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ=3.36(s, 3H) 3.53(s, 3H) 7.40(d, J=12.4Hz, 2H) 7.66(d, J=8.4Hz, 2H)

^{13}C NMR: 33.62, 61.21, 128.36, 129.95, 132.34, 136.84, 168.76ppm

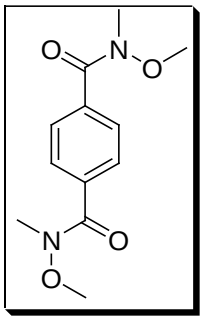
LCMS: 199.04 (M+H).

Anal calcd for $C_9H_{10}ClNO_2$: C, 54.15; H, 5.05; N, 7.02%,

Found: C, 54.12; H, 5.07; N, 7.05%,

2.6. Characterization data of compound 4.

N^1, N^4-dimethoxy-N^1, N^4-dimethylterephthalamide,(4). Yielded product as a light brown colored solid.



^{1}H NMR: ($CDCl_3$, 400MHz) δ=3.36(s, 6H) 3.63(s, 6H) 7.69(s, J=4H)

^{13}C NMR: 33.60, 61.19, 127.84, 136.05, 169.16ppm.

LC-MS: 252.11 (M+H).

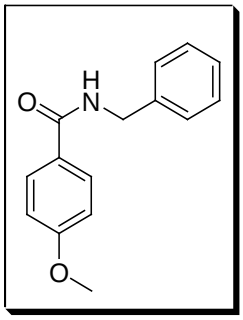
Anal calcd for $C_{12}H_{16}N_2O_4$: C, 57.13; H, 6.39; N, 11.10%,

Found: C, 57.10; H, 6.36; N, 11.12%,

2.7. Characterization data of compounds 5 a-f.

N-Benzyl-4-methoxybenzamide, (5a). Yielded product as a white solid, (91%),

Reaction was performed for 250mg scale, Yield= 135mg. MP (124-126^{0}C).



^{1}H NMR: (DMSO-d_6, 400MHz) δ=3.35(s, 3H) 4.47(d, J=6.0Hz, 2H) 7.01(d, J=8.8Hz, 2H) 7.23-7.32(m, 5H) 7.89(d, J=8.8Hz, 2H) 8.90(t, J=5.6Hz, 1H)

^{13}C NMR: 42.48, 55.28, 113.46, 126.53, 126.60, 127.12, 128.19, 129.02, 139.87, 161.54, 165.63 ppm.

LCMS: 242.0 (M + H).

IR(KBr) :3265.48, 3057.56, 2956.01, 2932.33, 2837.17, 1631.65, 1607.65, 1560.55, 1509.02, 1459.83, 1449.83, 1441.35, 1420.03, 1408.02, 1362.78, 1329.25, 1254.17, 1179.12, 1154.68, 1119.31, 1055.43, 1030.01, 1010.15, 990.09, 842.68, 723.49, 696.56, 686.80, 592.46,

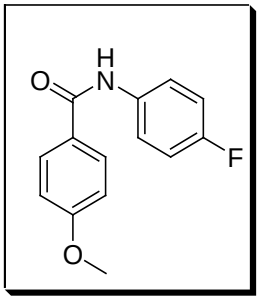
493.74cm^{-1}.

Anal calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81%

Found: C, 74.65; H, 6.30; N, 5.79%

N-(4-fluorophenyl)-4-methoxybenzamide,(5b). Yielded product as a white solid, (92%), (MP=110-114^{0}C).

Reaction was performed for 250mg scale, Yield= 138mg.



^{1}H NMR: (DMSO-d_6, 400MHz) δ=3.83(s, 3H) 7.06(d, J=8.8Hz, 2H) 7.17(t, J=8.8Hz, 2H) 7.77(q, J=5.2Hz, 2H) 7.95 (d, J=8.8Hz, 2H) 10.13 (s, 1H)

^{13}C NMR: 55.41, 113.60, 115.19, 122.15, 126.79, 129.55, 135.70, 156.96, 161.92, 164.81ppm

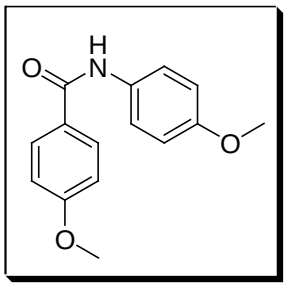
LCMS: 246.0 (M +H).

IR (KBr) :3335.01, 3081.01, 3020.85, 2969.76, 2935.07, 2840.92, 1650.89, 1608.90, 1578.47, 1512.26, 1458.67, 1438.81, 1405.34, 1332.86, 1311.25, 1257.29, 1214.52, 1181.44, 1159.02, 1106.46, 1095.11, 1025.30, 902.45, 844.77, 829.41, 763.14, 659.83, 636.32, 627.86, 611.62, 545.83, 514.24, 505.80 cm^{-1}.

Anal calcd for $C_{14}H_{12}FNO_2$: C, 68.56; H, 4.93; N, 5.71%

Found; C, 68.54; H, 4.95; N, 5.68%

4-Methoxy-N-(4-methoxyphenyl)benzamide,(5c). Yielded product as a white solid,(90%).
Reaction was performed for 250mg scale, Yield= 141mg.



^{1}H NMR: (DMSO-d_6, 400MHz) δ3.74(s, 3H) 3.83(s, 3H) 6.92(d, J=8.8Hz, 2H) 7.05(d, J=8.8Hz, 2H) 7.67(d, J=9.2Hz, 2H) 7.96 (d, J=8.8Hz, 2H) 9.98(s, 1H)

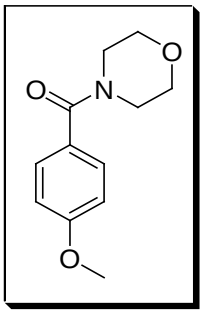
^{13}C NMR: 55.12, 55.36, 113.52, 11365, 121.94, 127.06, 129.42, 132.38, 155.37, 161.72, 164.47ppm.

LCMS: 257.11 (M+H).

Anal calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44%

Found: C, 70.05; H, 5.90; N, 5.41%.

(4-Methoxyphenyl)(morpholino)methanone,(5d). Yielded product as a colorless liquid,(91%). Reaction was performed for 250mg scale, Yield= 123mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ3.60-3.65(m, 8H) 3.78(s, 3H) 6.87(d, J=8.8Hz, 2H)

7.35(d, J=8.8Hz, 2H)

^{13}C NMR: 47.12, 55.29, 66.82, 113.73, 127.19, 129.14, 160.86, 170.35ppm

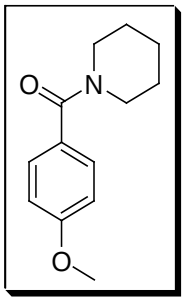
LCMS: 221.11 (M+H)

Anal calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33%

Found: C, 65.11; H, 6.85; N, 6.30%

(4-Methoxyphenyl)(piperidine-1-yl)methanone,(5e). Yielded product as a colorless liquid,(89%).

Reaction was performed for 250mg scale, Yield= 119mg.



^{1}H NMR: ($CDCl_3$, 400MHz) δ1.67 (d, J=4.0Hz, 6H) 3.64(s, 4H) 3.82 (s, 3H) 6.90(d, J=8.0Hz,

2H) 7.37 (d, J=8.4Hz, 2H)

^{13}CNMR: 24.69, 26.17, 45.3, 55.39, 113.71, 128.41, 128.97, 160.66, 170.43ppm

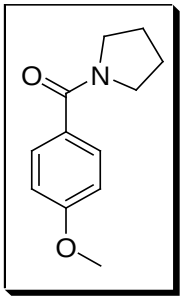
LCMS: 219.13(M+H).

Anal calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39%

Found; C, 71.19; H, 7.79; N, 6.40%

(4-Methoxyphenyl)(pyrrolidin-1-yl)methanone,(5f). Yielded product as a light yellow color liquid,(90%).

Reaction was performed for 250mg scale, Yield= 113mg.



^{1}H NMR: (DMSO-d_6, 400MHz): δ= 1.82(q, J=4.4Hz, 4H) 3.43(d, J=6.4Hz, 4H) 3.79(s, 3H) 6.96(d, J=8.8Hz, 2H) 7.50(d, J=8.4Hz, 2H)

C^{13} NMR: (DMSO-d_6, 400MHz): δ 26.03, 49.01, 55.17, 113.29, 129.05, 129.22, 160.25, 167.84 ppm.

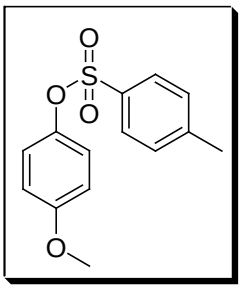
LCMS: 205.11 (M+H)

Anal calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82%

Found: C, 70.19; H, 7.39; N, 6.79%.

2.8. Characterization data of compounds 6 a-c.

4-Methoxyphenyl 4-methylbenzenesulfonate,(6a). Yielded product as a white solid,(90%).



^{1}H NMR: ($CDCl_3$, 400MHz): δ2.44(s, 3H) 3.75(s, 3H) 6.76(d, J=9.2Hz, 2H) 6.88(d, J=8.8Hz, 2H) 7.30(d, J=7.6Hz, 2H) 7.68(d, J=8.4Hz, 2H)

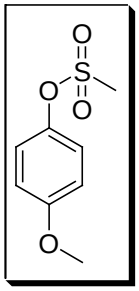
^{13}C NMR: ($CDCl_3$, 400MHz): δ21.71, 55.57, 114.52, 123.37, 128.57, 129.77, 132.37, 143.11, 145.35, 158.26ppm

LCMS: 278.06 (M+H)

Anal calcd for $C_{14}H_{14}O_4S$: C, 60.42; H, 5.07%

Found: C, 60.40; H, 5.10%.

4-Methoxyphenyl methanesulfonate,(6b). Yielded product as a yellow solid,(92%).



^{1}H NMR: ($CDCl_3$, 400MHz): δ=3.11(s, 3H) 3.81(s,3H) 6.91 (d, J=9.2Hz, 2H) 7.21(d, J=6.8Hz, 2H).

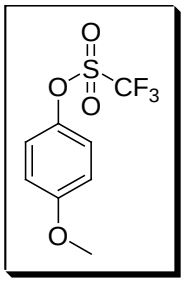
^{13}C NMR: ($CDCl_3$, 400MHz): δ 37.04, 55.72, 114.98, 123.11, 142.73, 158.58ppm.

LCMS; 202.03 (M+H).

Anal calcd for $C_8H_{10}O_4S$: C, 47.51, H, 4.98%

Found: C, 47.54, H, 4.95% .

4-Methoxyphenyl trifluoromethane sulfonate,(6c). Yielded product as a colorless oil,(88%).



^{1}H NMR: ($CDCl_3$, 400MHz): δ=3.84(s, 3H) 6.94(d, J=8.8Hz, 2H) 7.18(d, J=9.2Hz, 2H).

^{13}C NMR: ($CDCl_3$, 400MHz): δ 55.83, 115.18, 117.32, 122.69, 143.19, 159.25ppm.

LCMS: 256 (M+H)

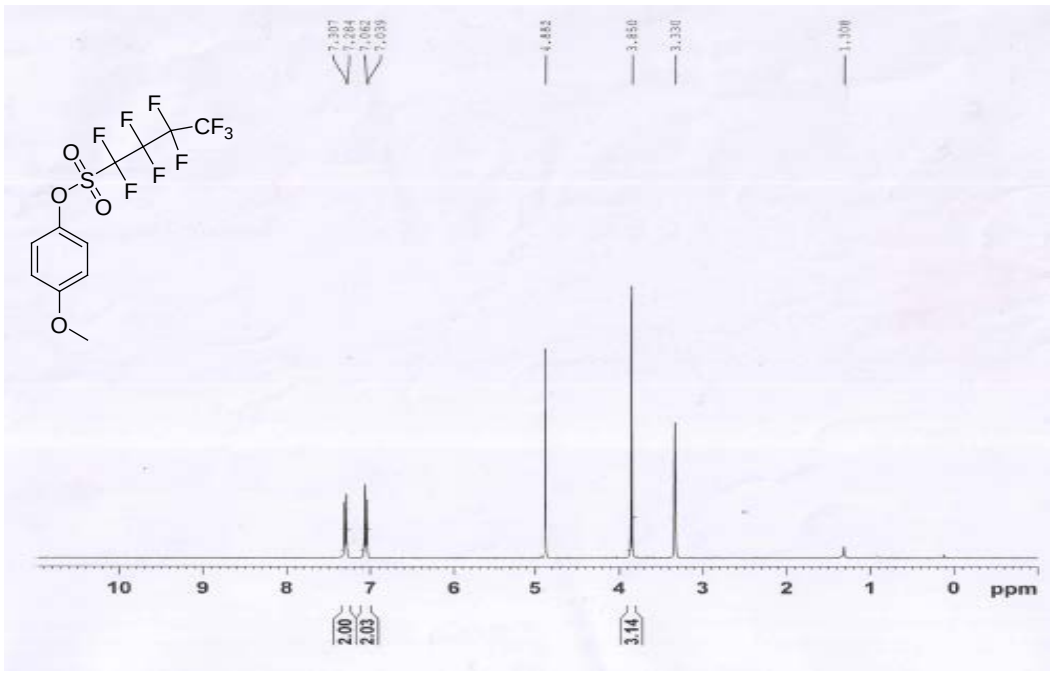
Anal calcd for $C_8H_7F_3O_4S$: C, 37.50; H, 2.75%

Found: C, 37.47; H, 2.78%.

3. Spectral data.

3.1 Spectral data of compounds 1a-v.

1. 1a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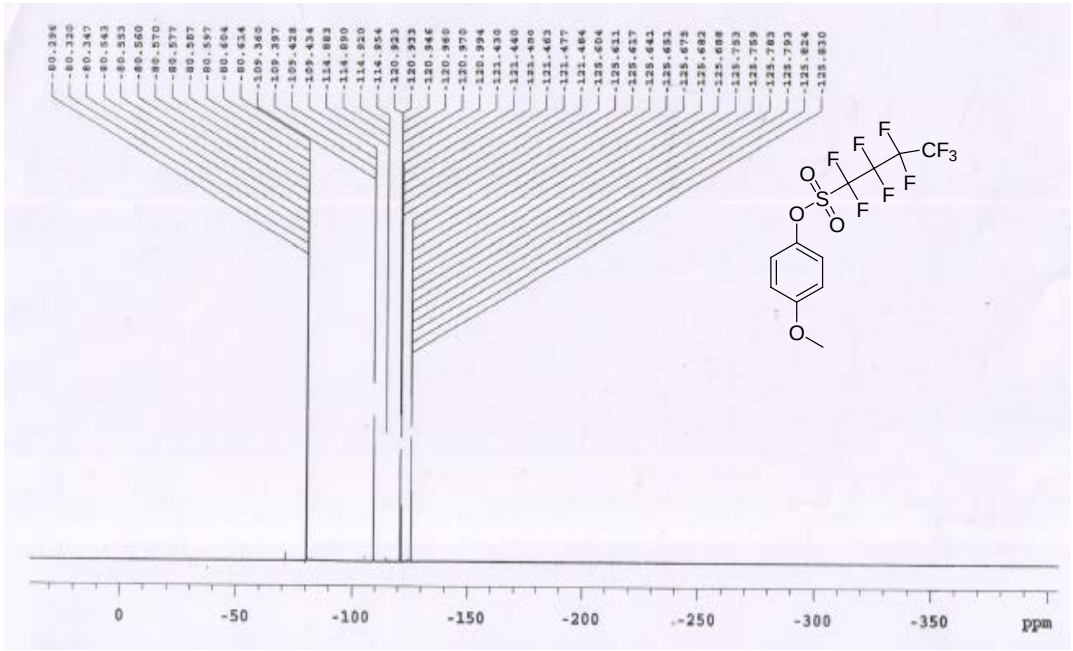
7.062
7.039
4.885
3.850
3.330
1.300
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.03
3.14


0
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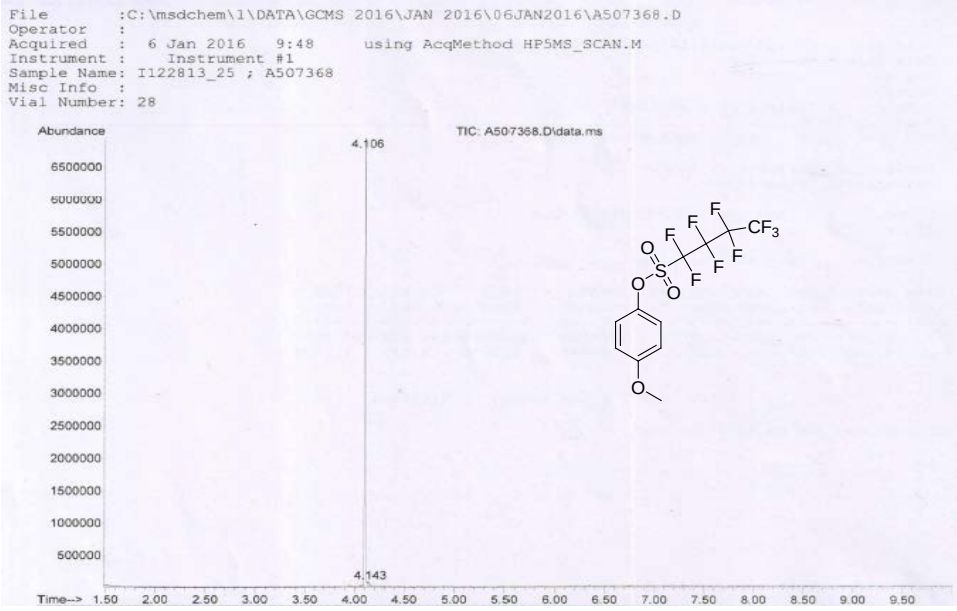
-150
-200
-250
-300
-350
ppm



Signal : TIC: A507368.D\data.ms

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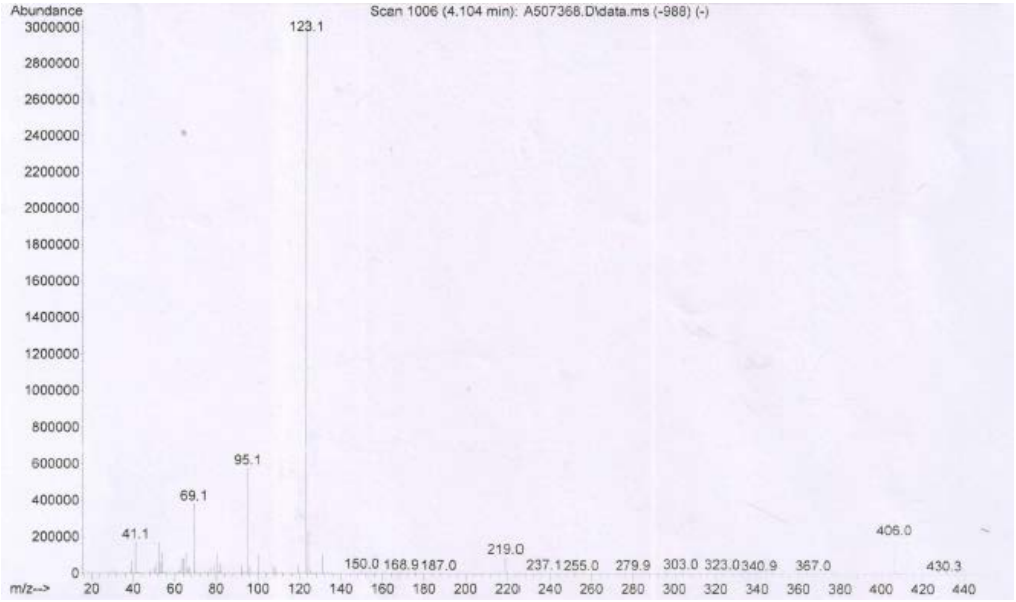
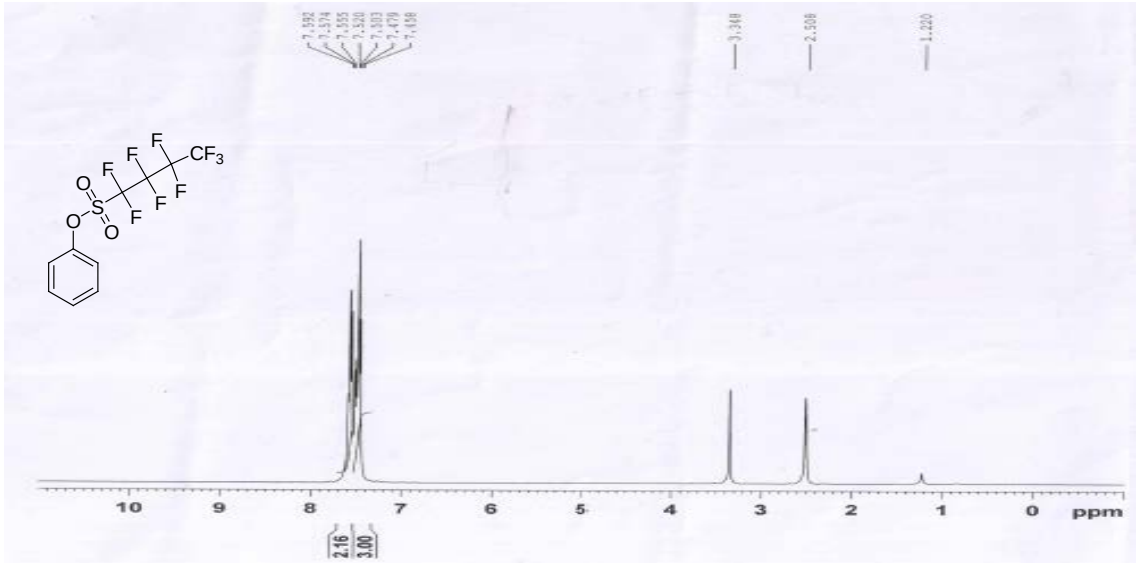
2	4.143	1017	1021	1030	VV 2	67975	623195	1.17%	1.153%



2. 1b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7.555
7.520
7.503
7.479
7.458
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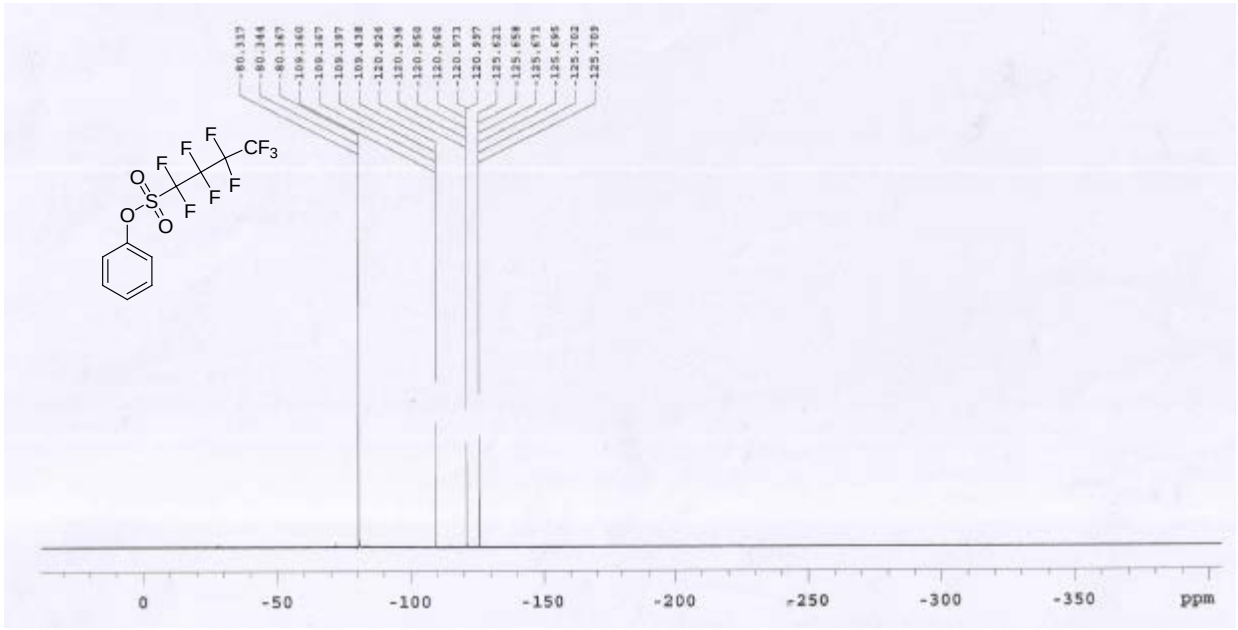
9
8
7
6
5
4
3
2
1
0
ppm
2.16
3.00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-80.367
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-109.367
-109.387
-109.438
-120.926
-120.934
-120.950
-120.960
-120.973
-120.997
-125.621
-125.658
-125.671
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-125.702
-125.709
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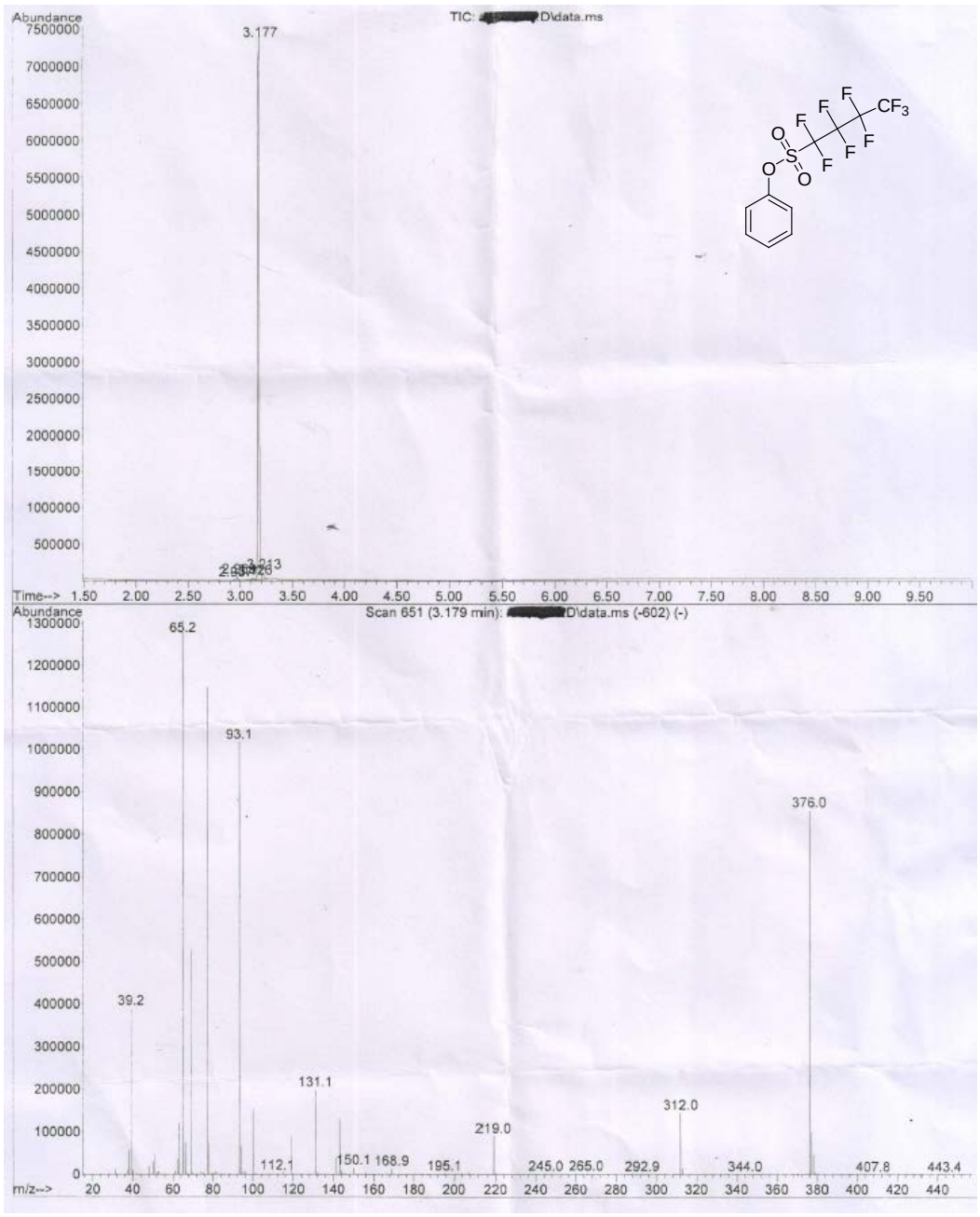
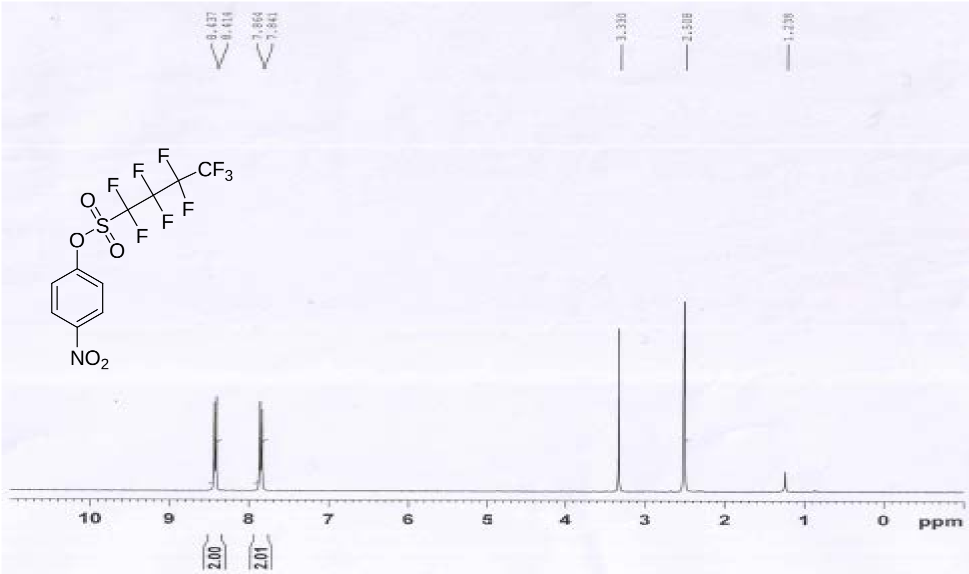
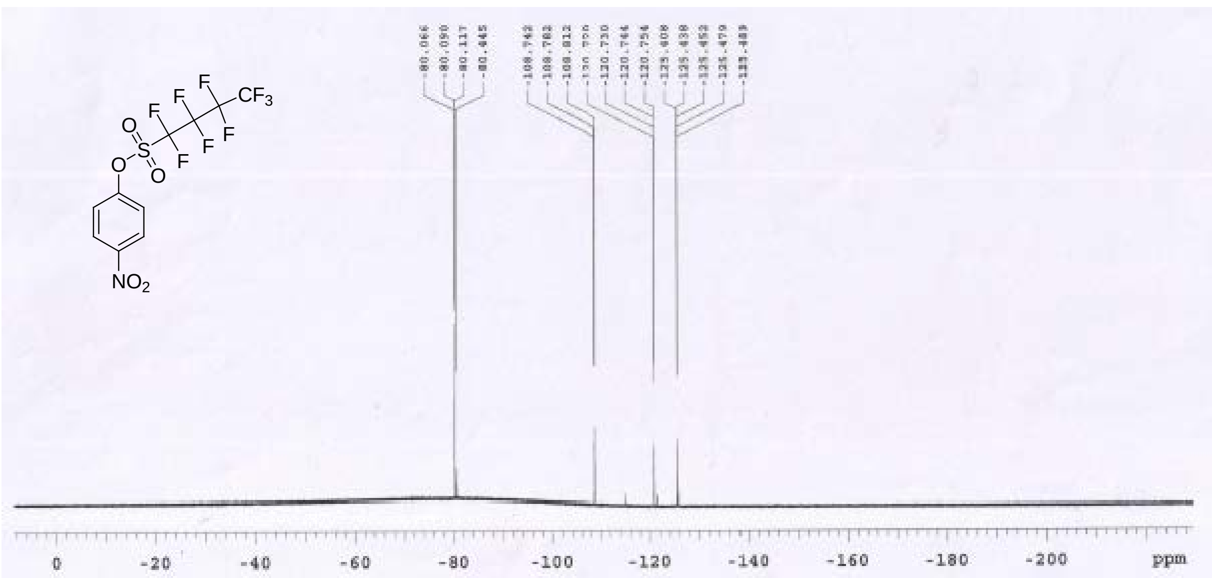
-100
-150
-200
-250
-300
-350
ppm


TIC: [redacted]D\data.ms
Abundance
3.177
Time--> 1.50 2.00 2.50 3.00 3.50 4.00 4.50 5.00 5.50 6.00 6.50 7.00 7.50 8.00 8.50 9.00 9.50
Scan 651 (3.179 min): [redacted]D\data.ms (-602) (-)
65.2
93.1
376.0
39.2
131.1
312.0
219.0
112.1
150.1 168.9
195.1
245.0 265.0
292.9
344.0
407.8
443.4
m/z--> 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440

3. 1c





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File       :C:\msdchem\1\DATA\Y2015\DEC2015\28DEC2015\A498813.D
Operator   :
Acquired   : 28 Dec 2015  12:50     using AcqMethod HP5MS_SCAN.M
Instrument :    Instrument #1
Sample Name: I122813-25 ; A498813
Misc Info  :
Vial Number: 5
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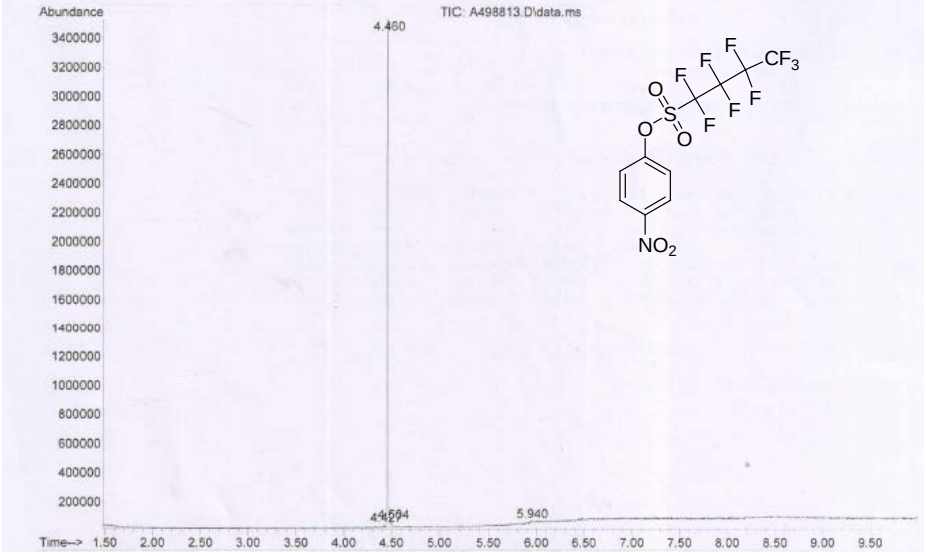

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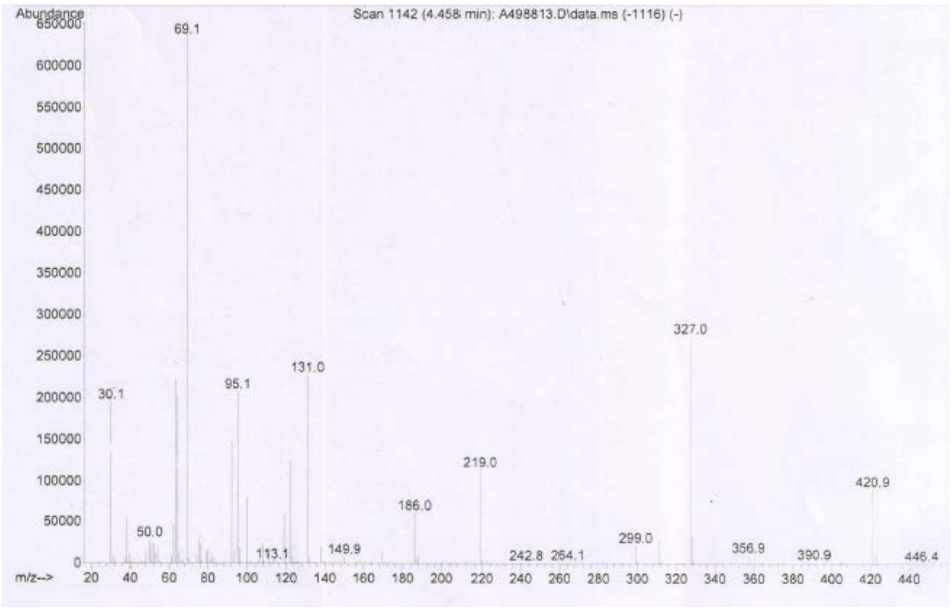
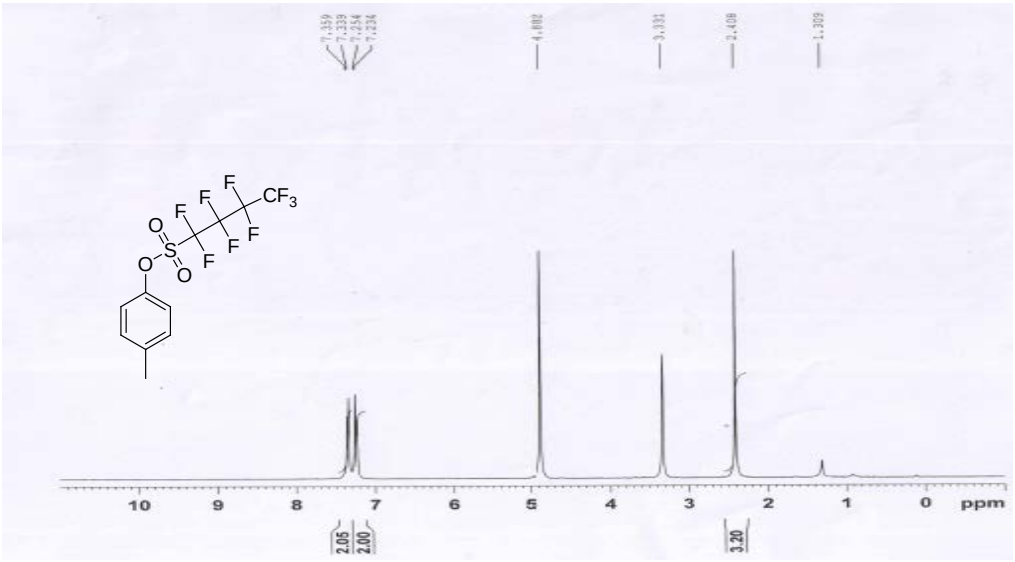
2	4.460	1135	1143	1156	VV	3496352	26865346	100.00%	98.168%
3	4.504	1156	1160	1167	VV 8	33636	306860	1.14%	1.121%
4	5.940	1706	1711	1716	PV 8	9465	80186	0.30%	0.293%



4. 1d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1.309
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F
F
CF3
F
F
F
F
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S
O
O
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9
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7
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5
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3
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1
0
ppm
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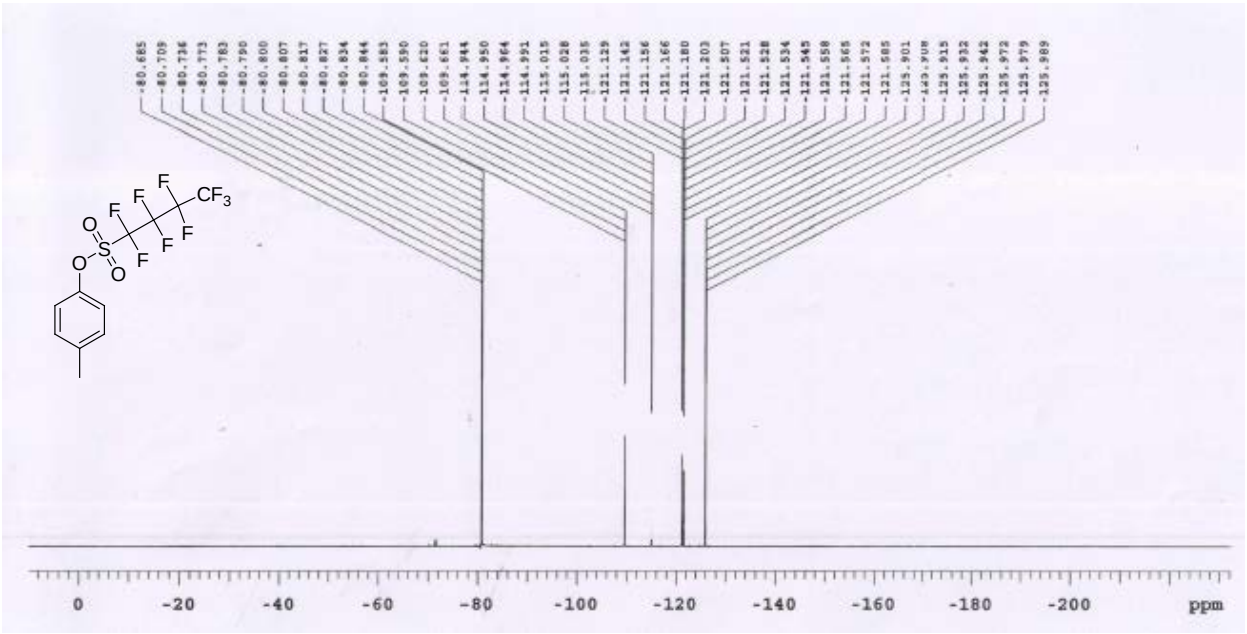
2.00
3.20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-80.807
-80.817
-80.827
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-80.844
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-109.590
-109.620
-109.661
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-114.950
-114.964
-114.991
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-115.028
-115.035
-121.129
-121.142
-121.156
-121.166
-121.180
-121.203
-121.507
-121.521
-121.528
-121.534
-121.545
-121.558
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-125.989
F
F
F
CF3
F
F
F
F
O
S
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O
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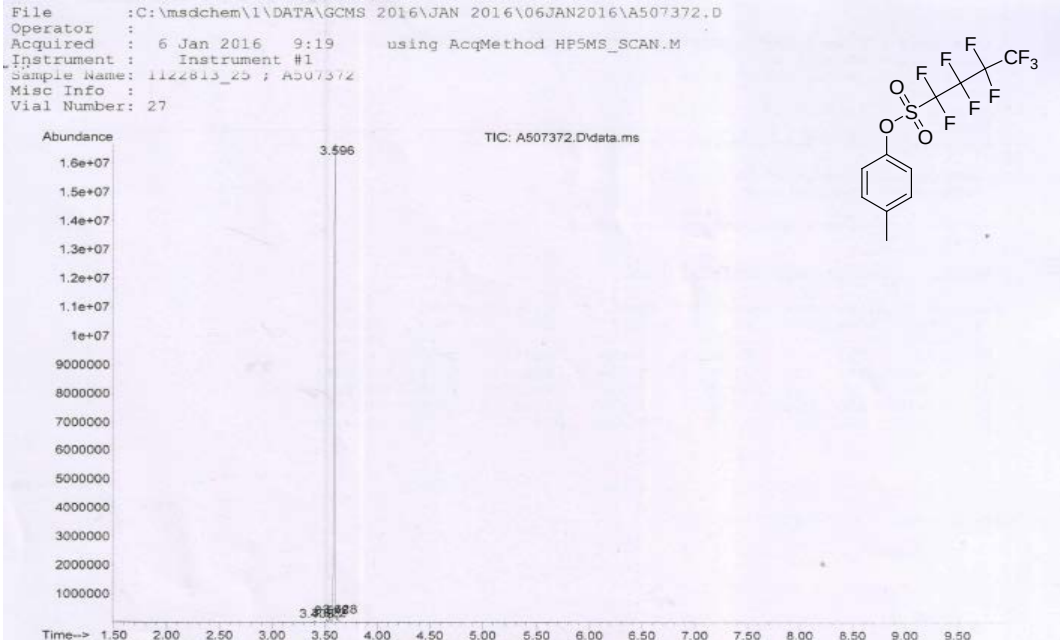
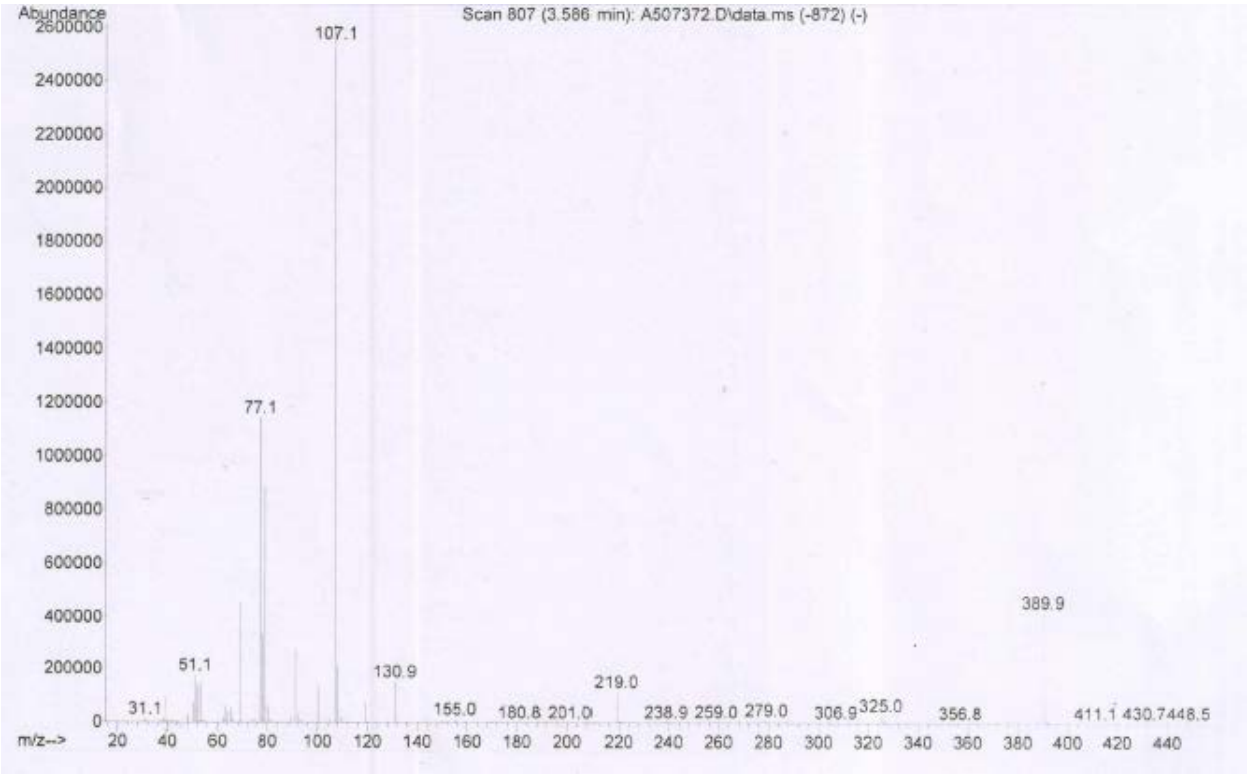
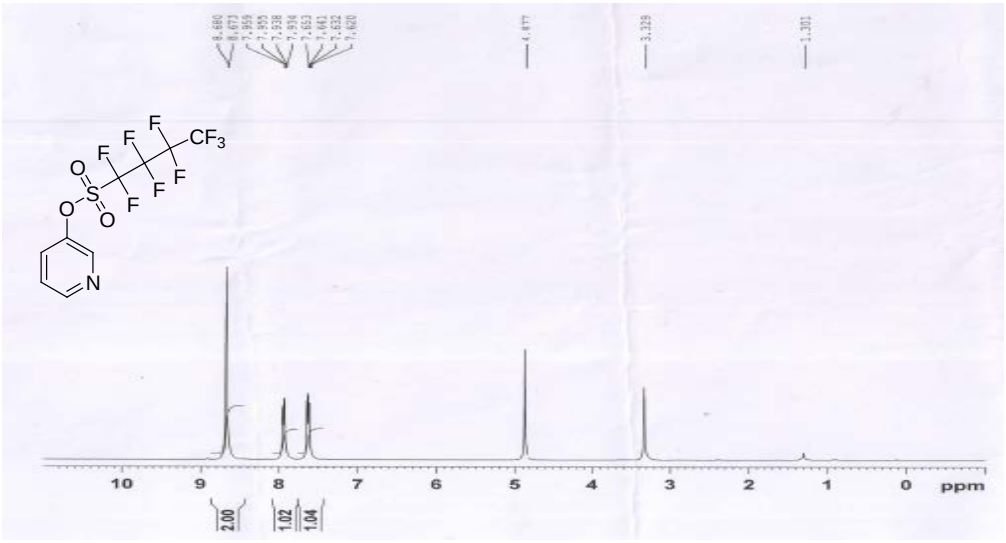
ppm



peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	3.406	732	738	754	PB 3	65286	542844	0.37%	0.355%
2	3.522	762	783	787	BV 2	89316	682097	0.46%	0.446%
3	3.548	787	793	800	VV	175836	1406370	0.95%	0.920%
4	3.596	800	811	819	PV	16149641	148152717	100.00%	96.964%
5	3.628	819	823	843	VV 2	206794	2006702	1.35%	1.313%



5. 1e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7.661
7.632
7.620
4.877
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CF3
F
F
F
F
O
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O
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9
8
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5
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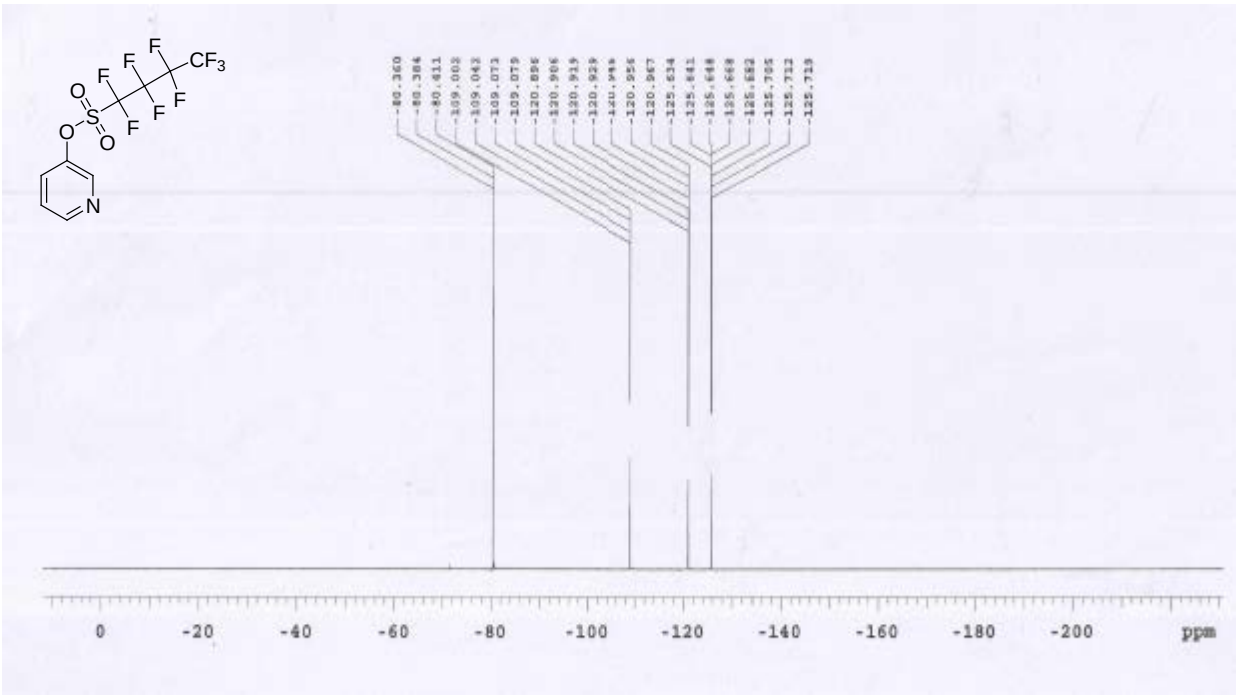
1.02
1.04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S
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-125.705
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-60
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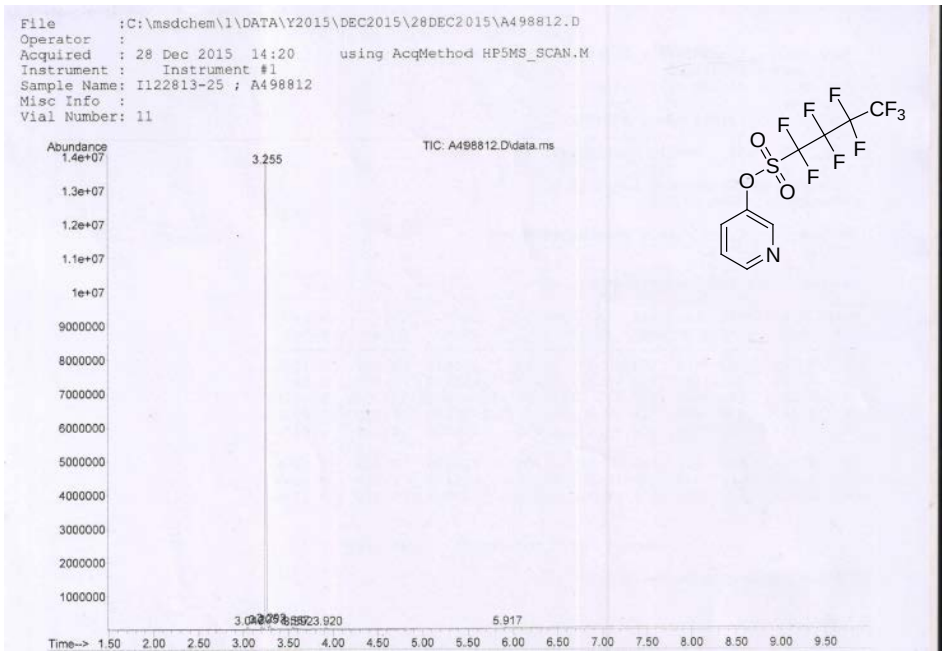
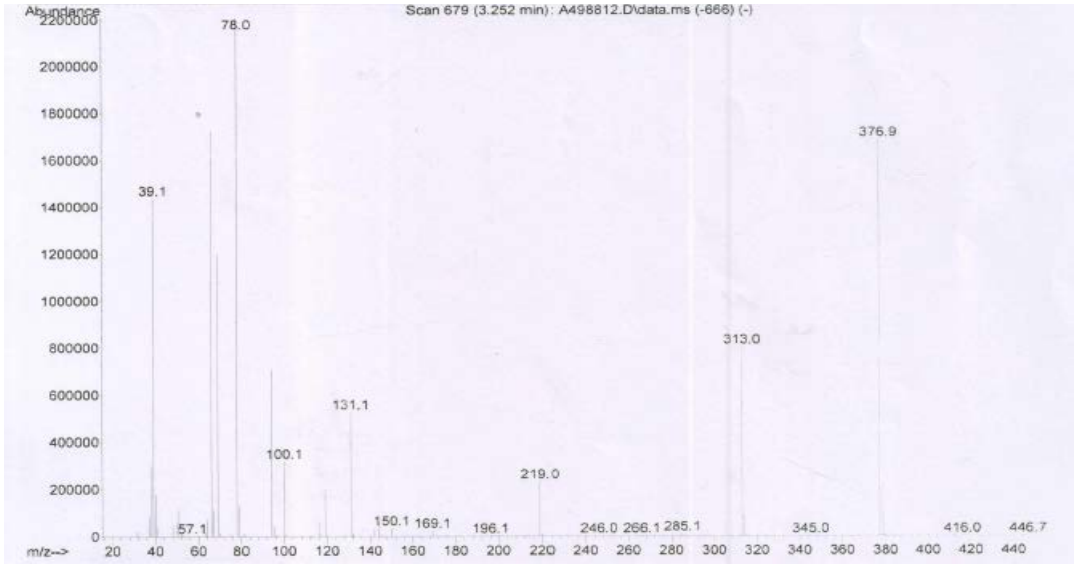
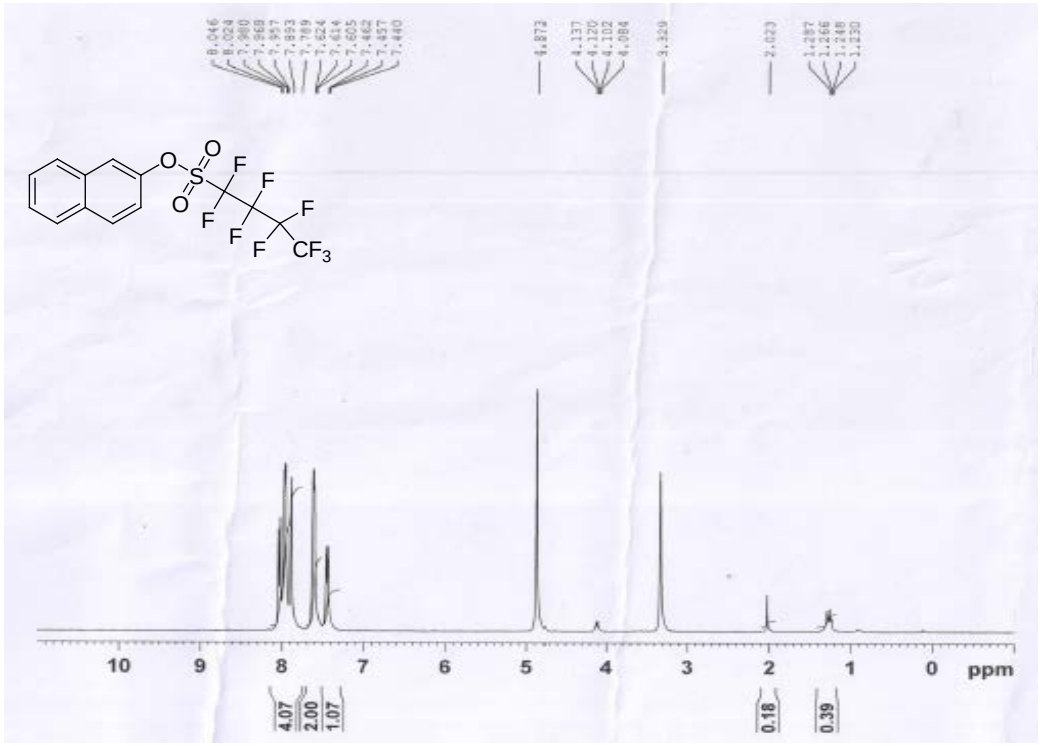
ppm

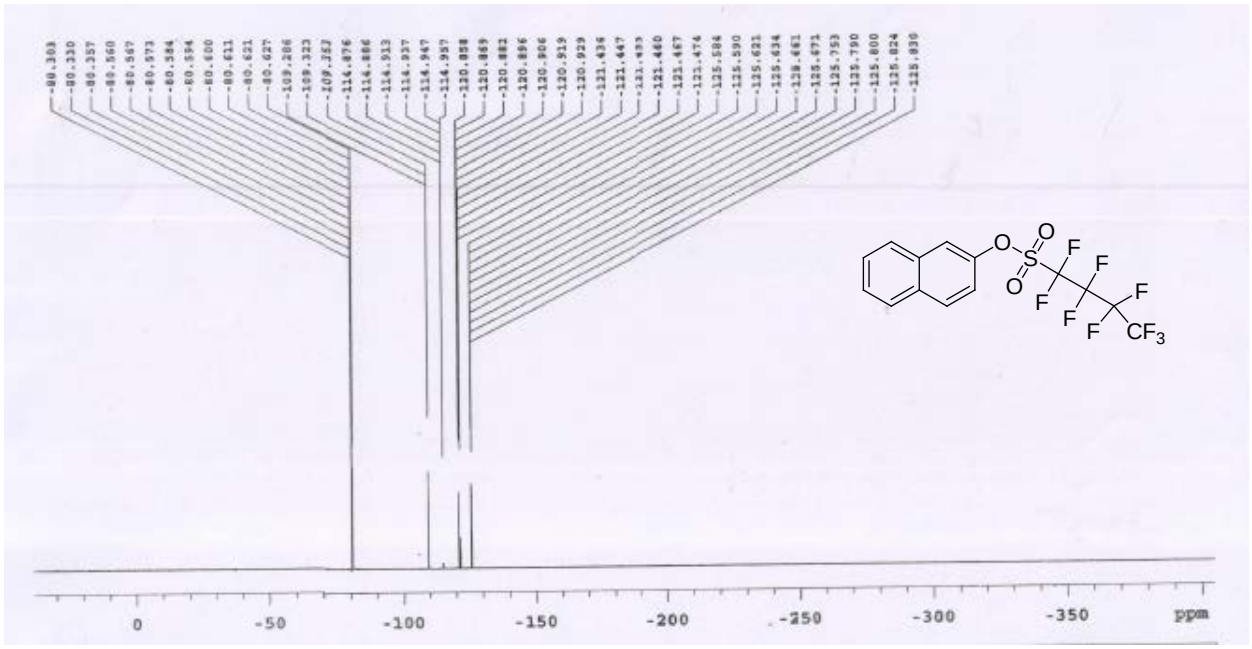


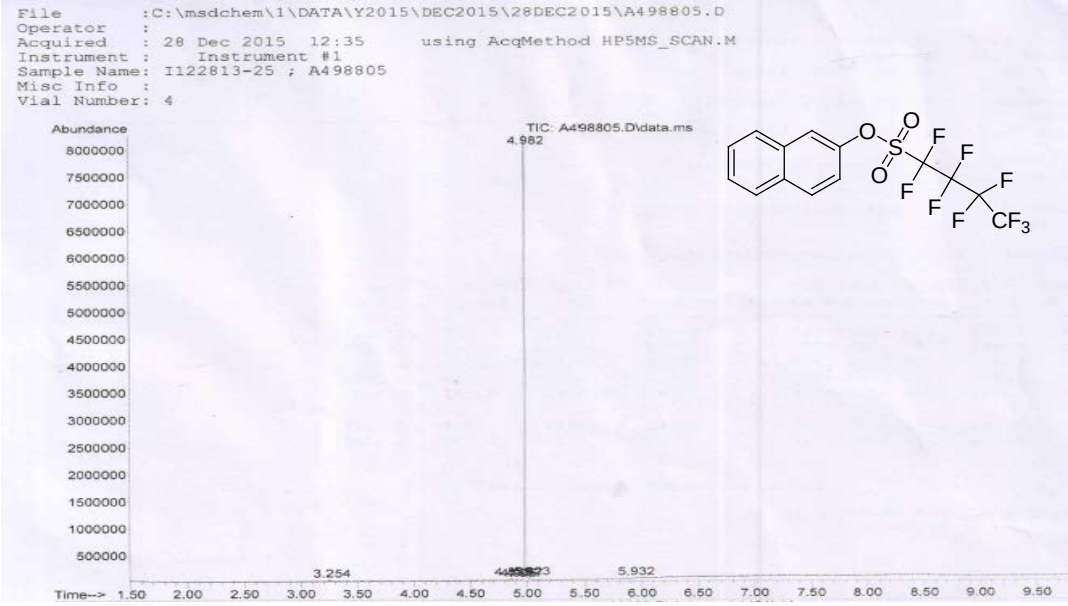
peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	3.046	593	600	609	PV 3	70309	600678	0.45%	0.434%
2	3.205	655	661	668	VV 3	99892	888770	0.67%	0.643%
3	3.255	668	680	690	VV	13868541	133596648	100.00%	96.616%
4	3.292	690	694	715	VV 2	142074	1700100	1.27%	1.230%
5	3.557	787	796	804	PV 4	69962	590019	0.44%	0.427%
6	3.592	804	810	816	VV 2	37355	311160	0.23%	0.225%
7	3.920	928	936	943	PV 3	49168	425472	0.32%	0.308%
8	5.917	1692	1703	1708	PV 3	20221	162441	0.12%	0.117%



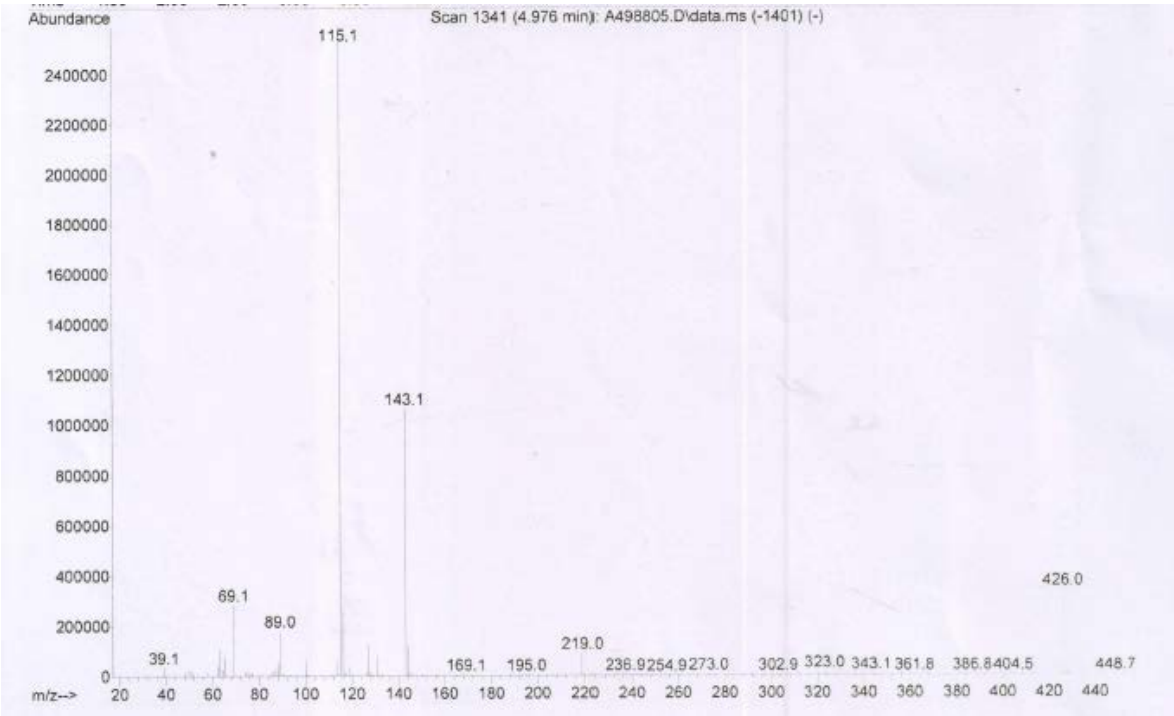
6. 1f


8.046
8.024
7.980
7.969
7.957
7.893
7.789
7.624
7.614
7.605
7.462
7.457
7.440
4.873
4.137
4.120
4.102
4.084
3.329
2.023
1.267
1.266
1.248
1.230
O
O
O
S
F
F
F
F
F
F
F
CF3
10
9
8
7
6
5
4
3
2
1
0
ppm
4.07
2.00
1.07
0.18
0.39

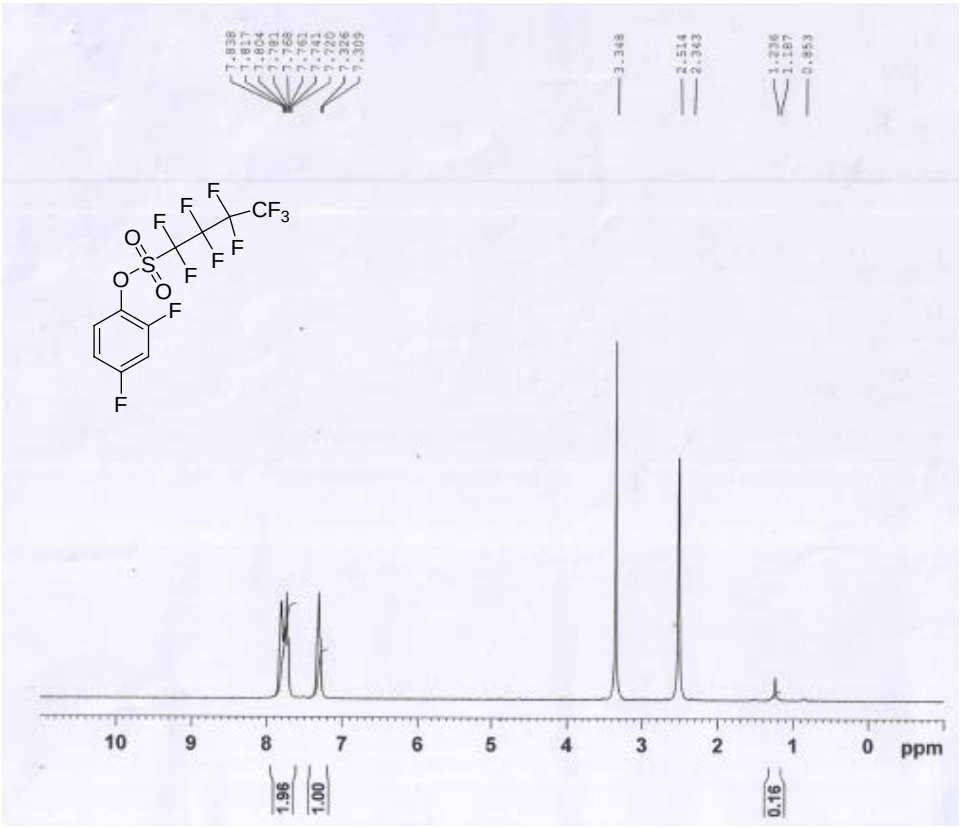

-80.303
-80.330
-80.357
-80.560
-80.567
-80.573
-80.584
-80.594
-80.600
-80.611
-80.621
-80.627
-109.286
-109.333
-109.382
-114.876
-114.886
-114.913
-114.937
-114.947
-114.957
-120.858
-120.869
-120.882
-120.896
-120.906
-120.919
-120.929
-121.434
-121.447
-121.493
-121.460
-121.467
-121.474
-125.584
-125.590
-125.621
-125.634
-125.661
-125.671
-125.753
-125.790
-125.800
-125.824
-125.830
O
O
O
S
F
F
F
F
F
F
F
CF3
0
-50
-100
-150
-200
-250
-300
-350
ppm

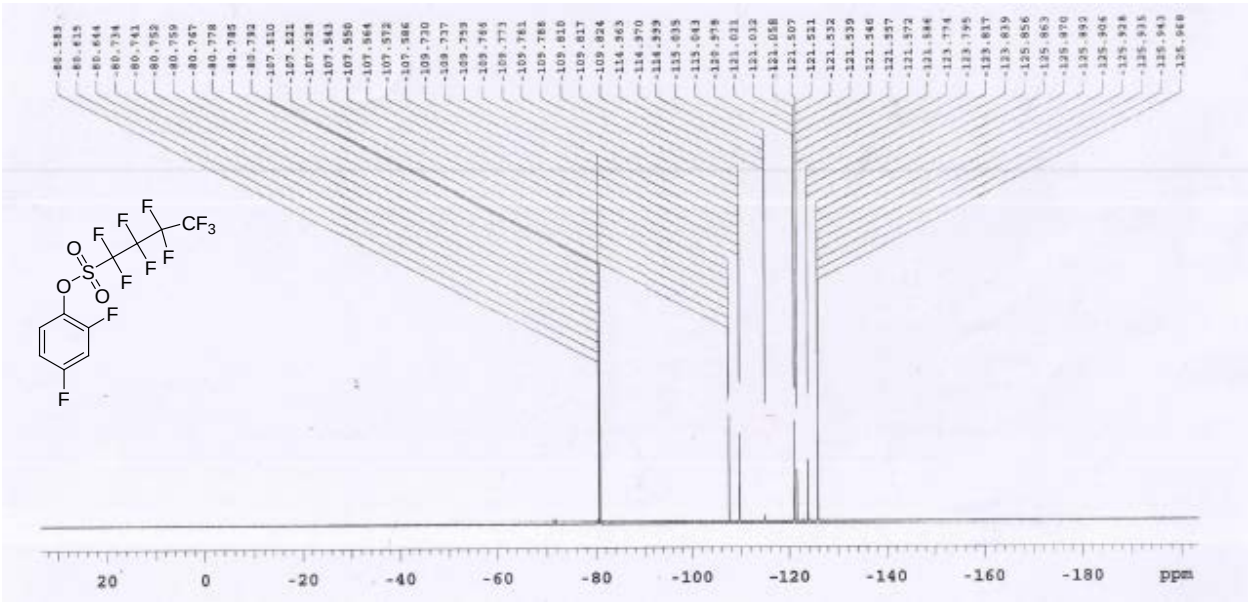


peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	3.254	673	680	685	PV 5	30253	261335	0.39%	0.382%
2	4.855	1289	1295	1303	VV 3	41746	360656	0.54%	0.527%
3	4.906	1303	1314	1319	PV 5	22794	221760	0.33%	0.324%
4	4.957	1325	1333	1335	VV 8	19410	142729	0.21%	0.209%
5	4.982	1335	1343	1354	VV	8199197	66862527	100.00%	97.684%
6	5.023	1354	1359	1375	VV 3	47148	578227	0.86%	0.845%
7	5.932	1703	1708	1711	PV 7	5128	20598	0.03%	0.030%

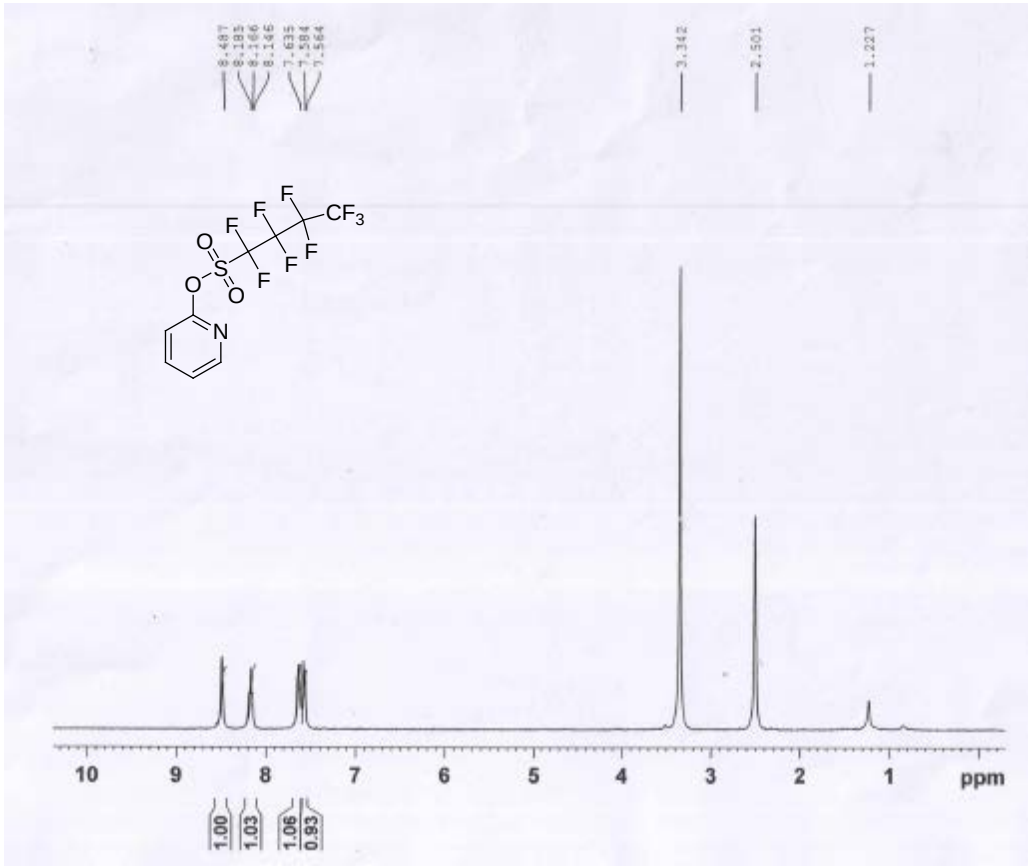


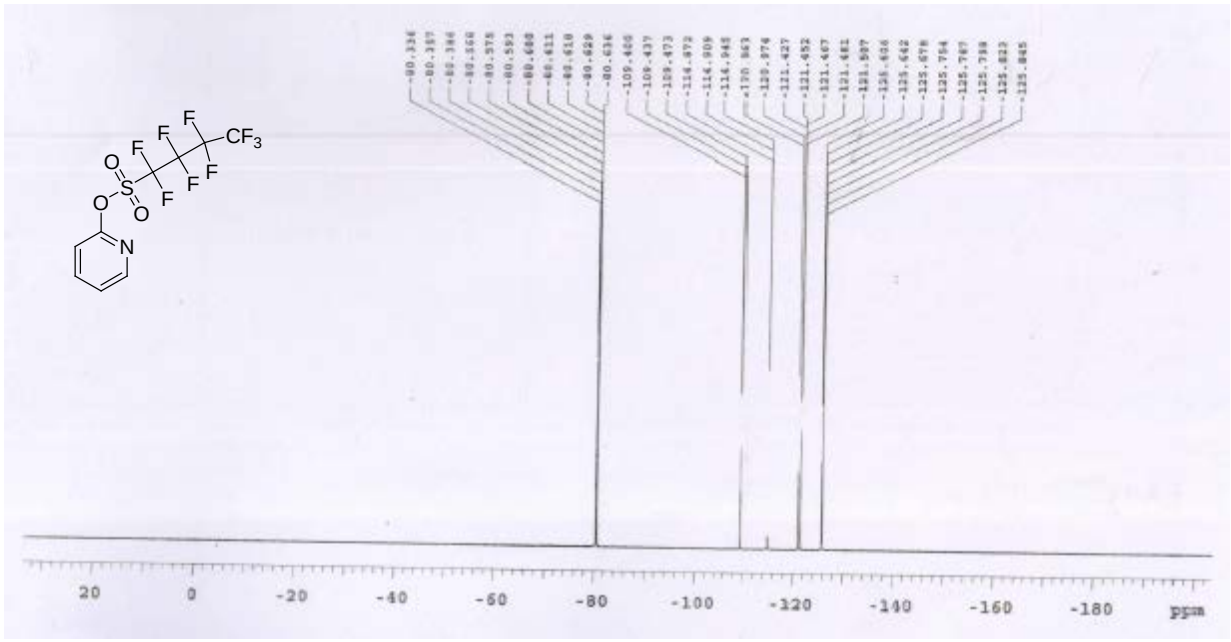
7. 1g


7.838
7.817
7.804
7.781
7.768
7.761
7.741
7.720
7.326
7.309
3.348
2.514
2.363
1.236
1.187
0.853
10
9
8
7
6
5
4
3
2
1
0
ppm
1.96
1.00
0.16

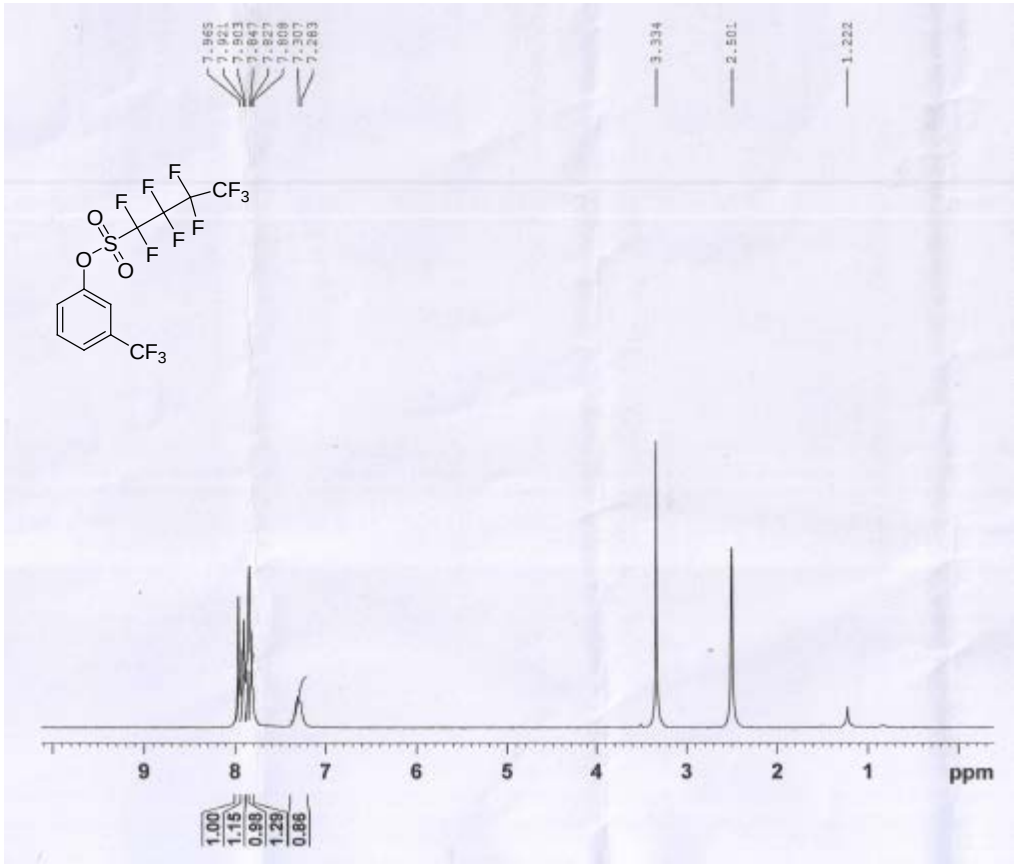

20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

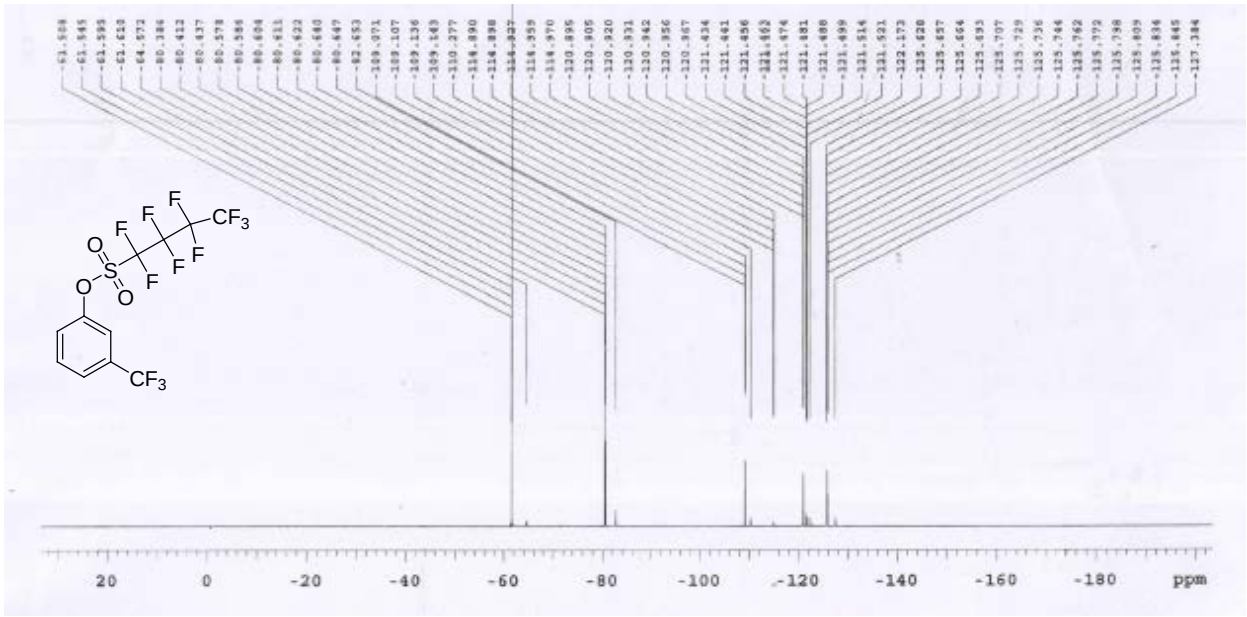
8.1h


8.487
8.185
8.166
8.146
7.635
7.584
7.564
3.342
2.501
1.227
F
F
F
CF3
F
O
S
O
F
F
F
O
O
N
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.03
1.06
0.93

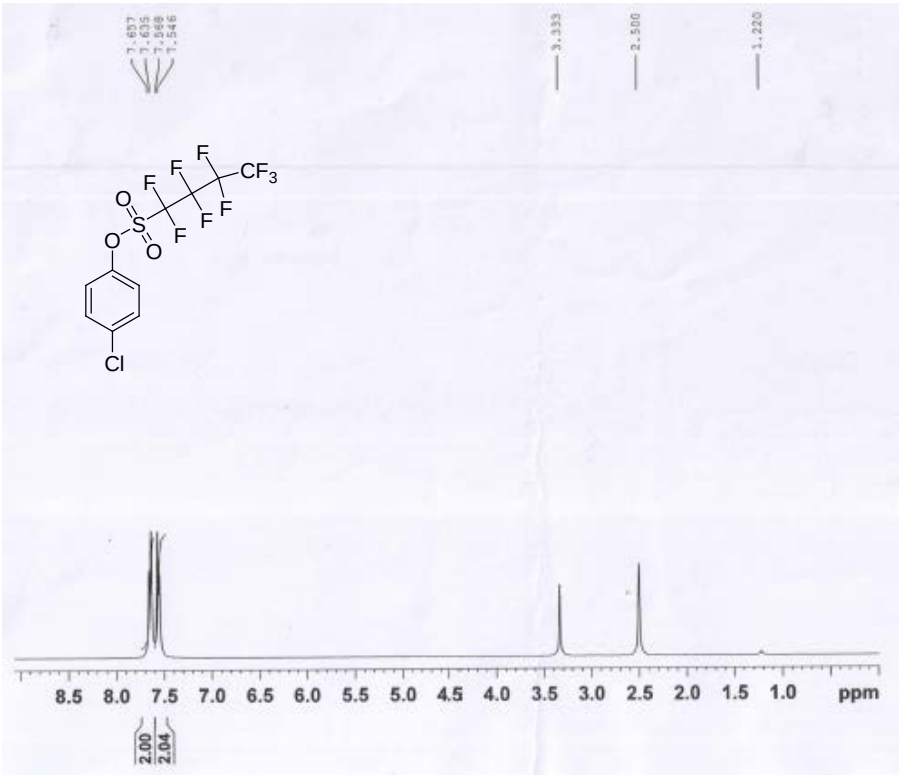

F
F
F
CF3
F
O
S
O
F
F
F
O
O
N
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

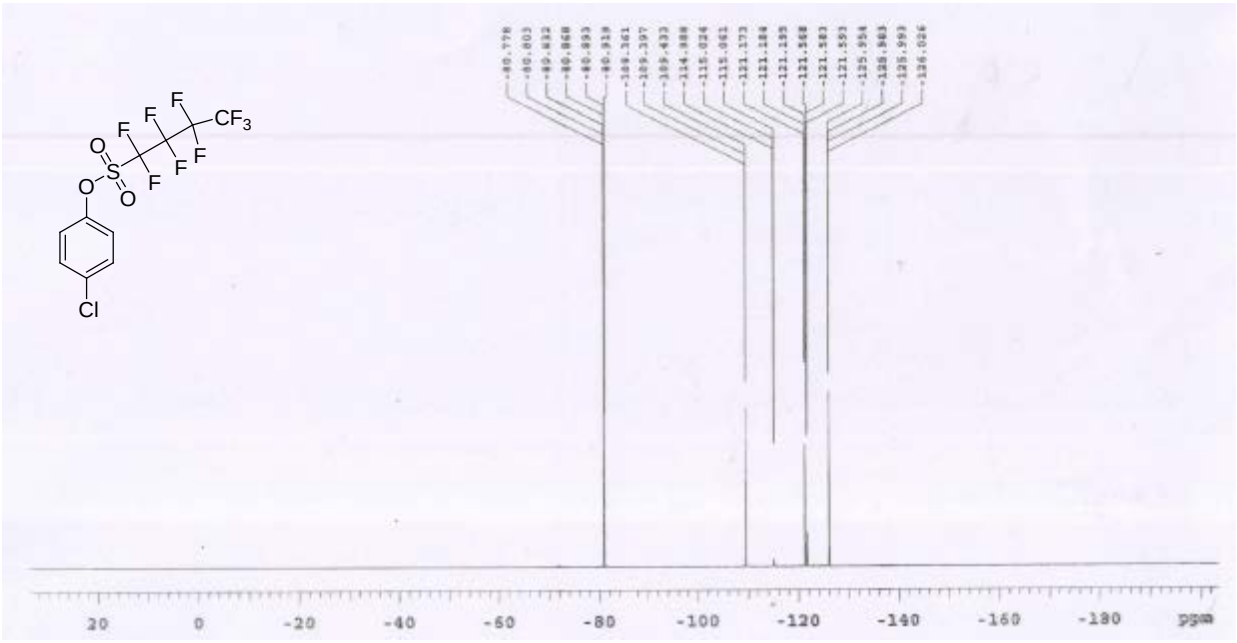
9. 1i


7.965
7.921
7.903
7.847
7.827
7.809
7.307
7.283
3.334
2.501
1.222
F
F
F
CF3
F
F
F
F
O
S
O
O
O
CF3
9
8
7
6
5
4
3
2
1
ppm
1.00
1.15
0.98
1.29
0.86

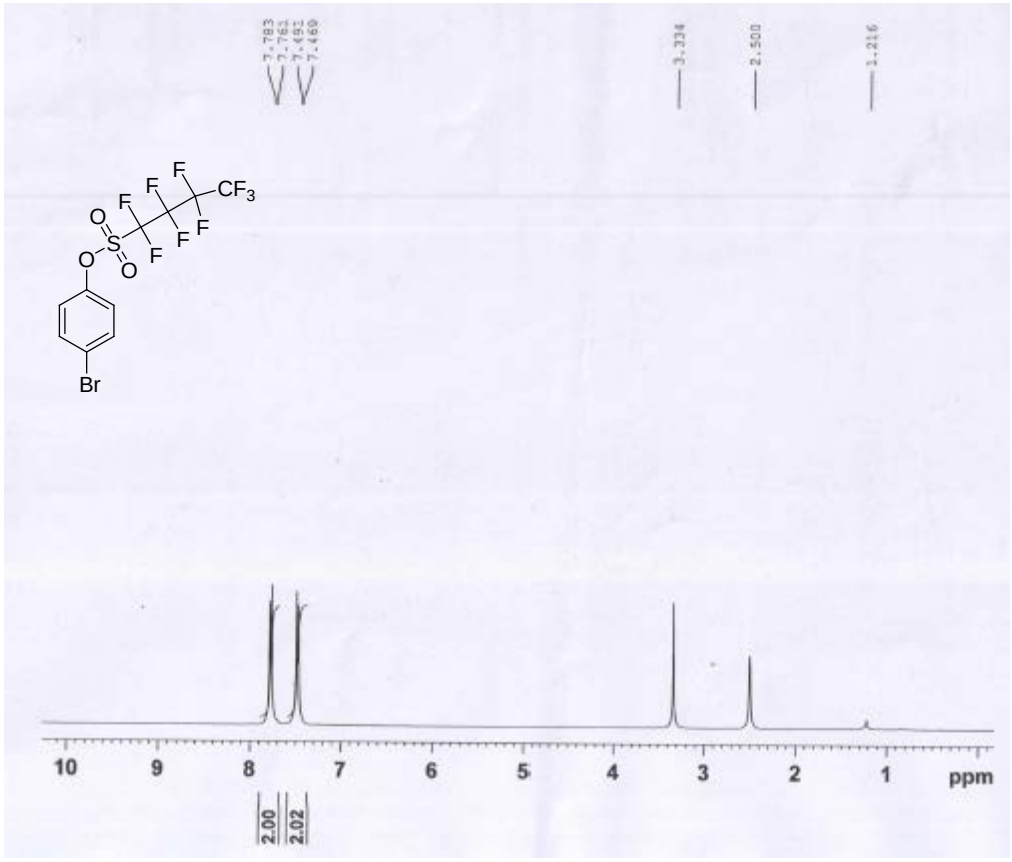

F
F
F
CF3
F
F
F
F
O
S
O
O
O
CF3
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

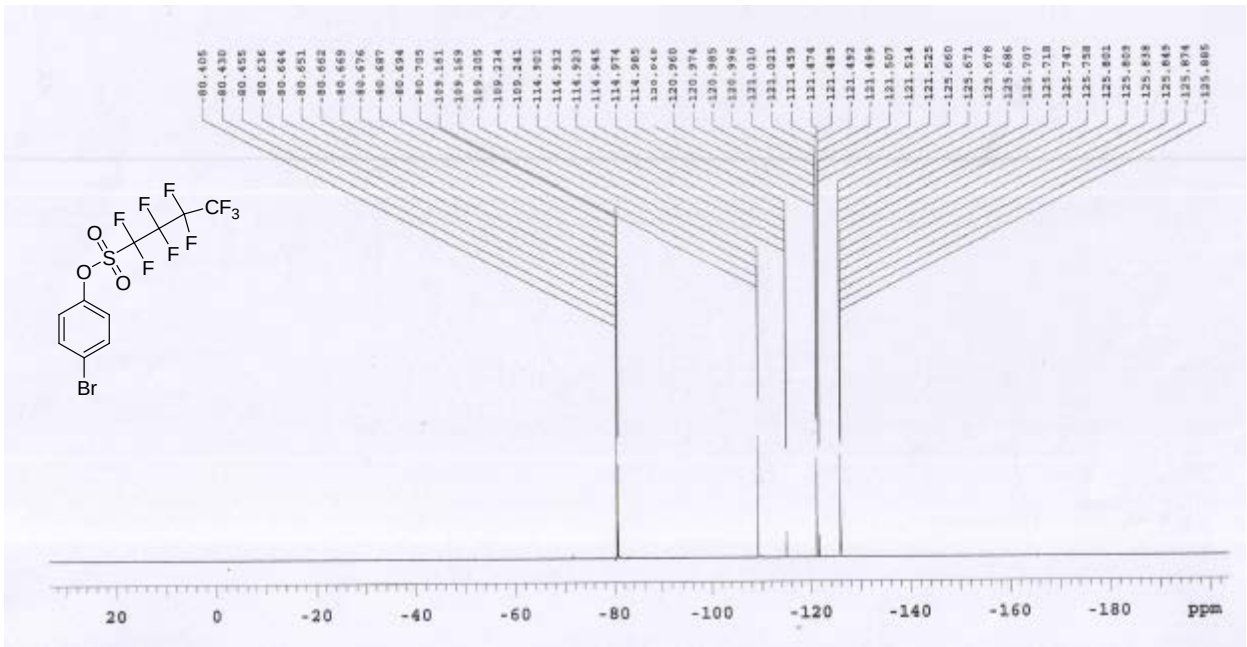
10. 1j


7.657
7.635
7.568
7.546
3.333
2.500
1.220
F
F
F
CF3
F
F
F
F
O
S
O
O
Cl
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00
2.04

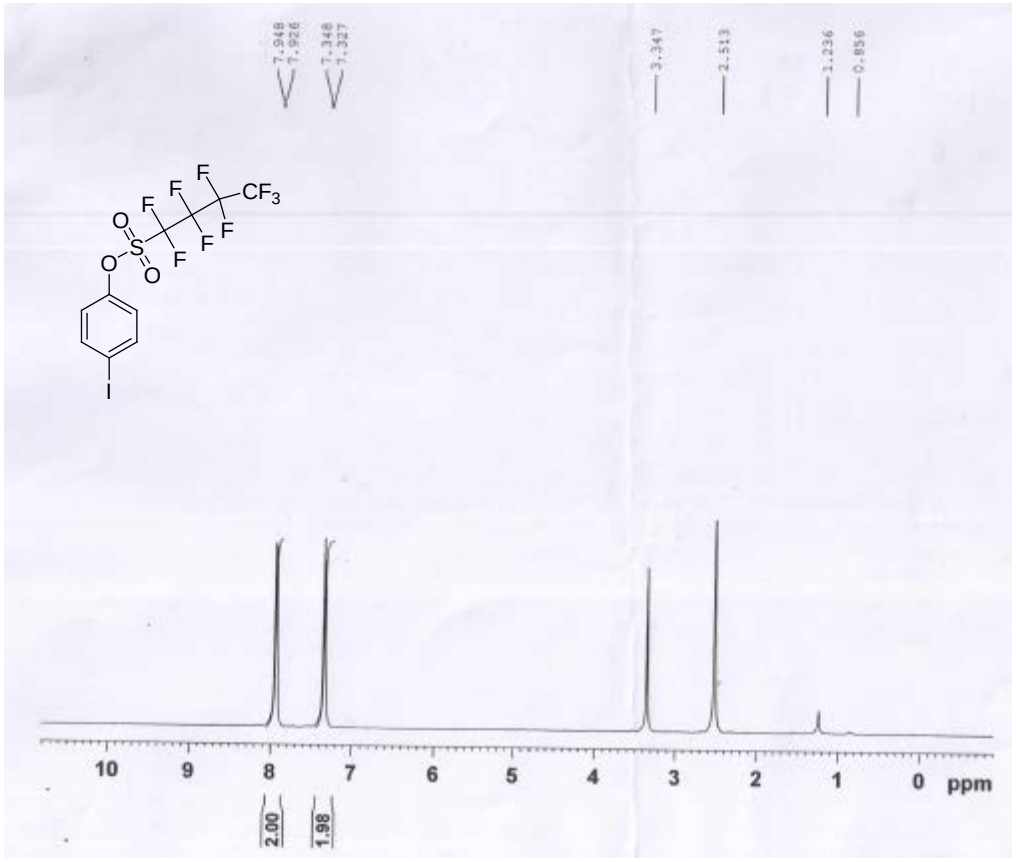

F
F
F
CF3
F
F
F
F
O
S
O
O
Cl
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 ppm

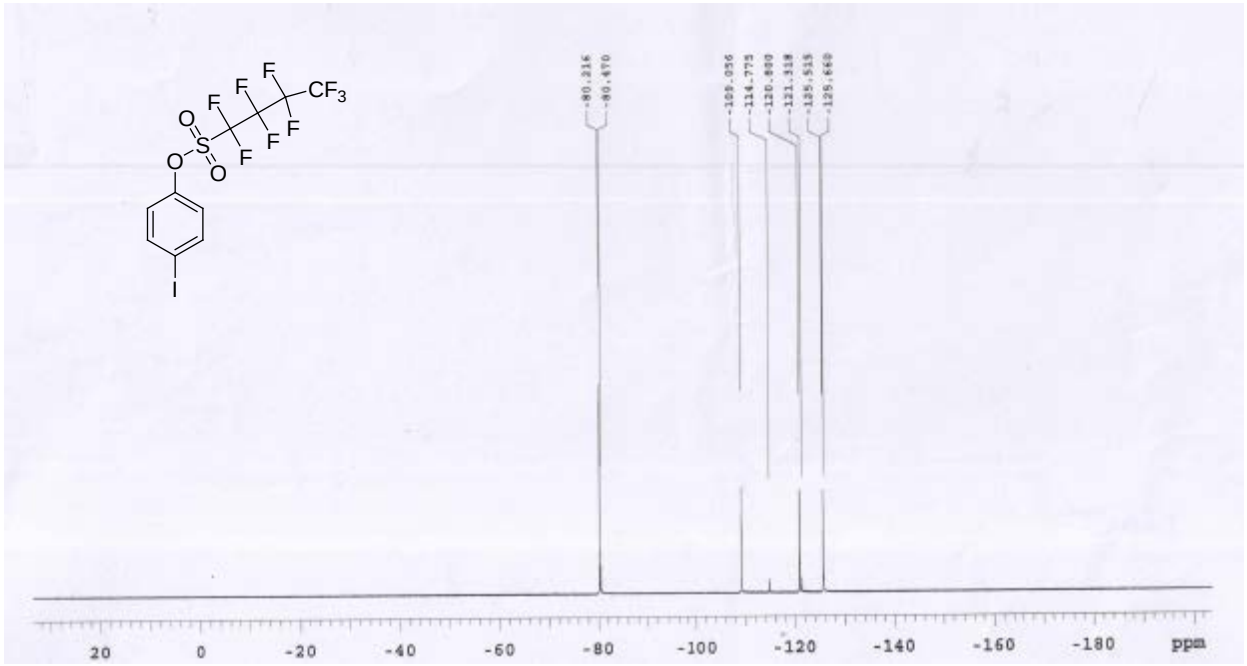
11. 1k


7.783
7.761
7.491
7.469
3.334
2.500
1.216
F
F
F
F
F
F
F
CF3
O
S
O
O
Br
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.02

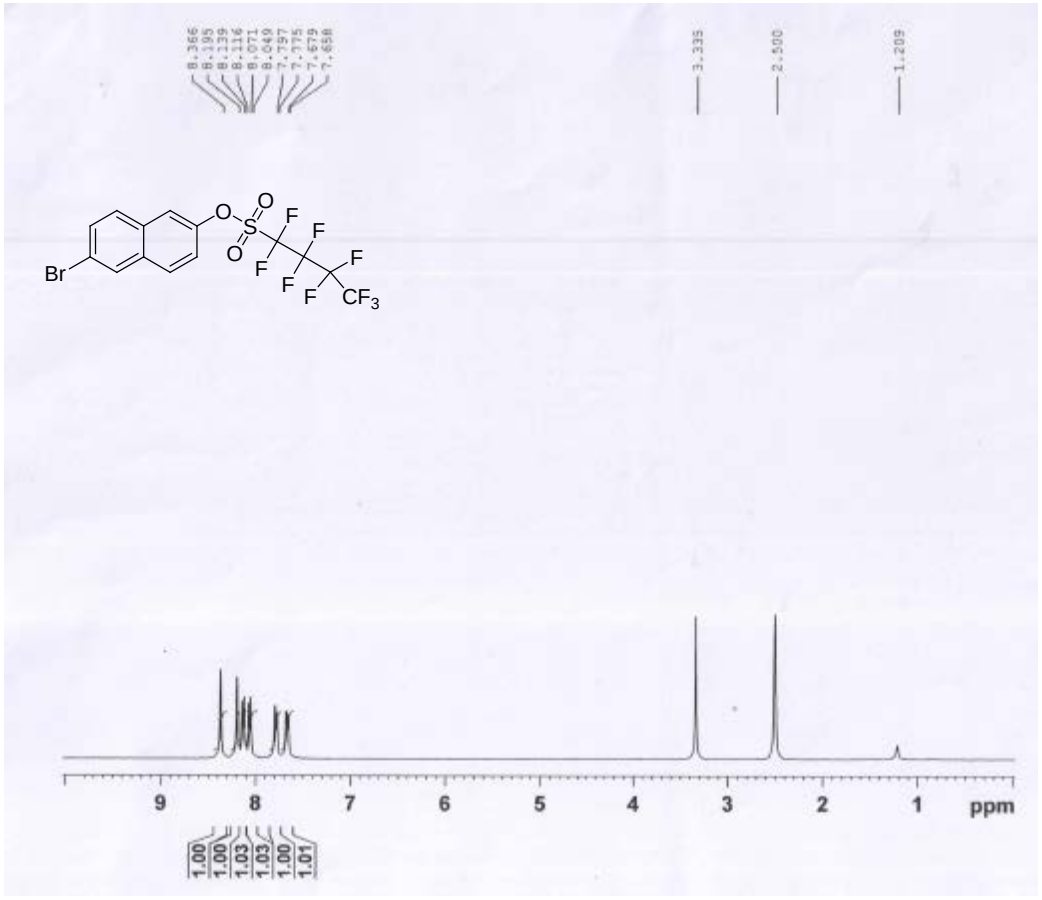

F
F
F
F
F
F
F
CF3
O
S
O
O
Br
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

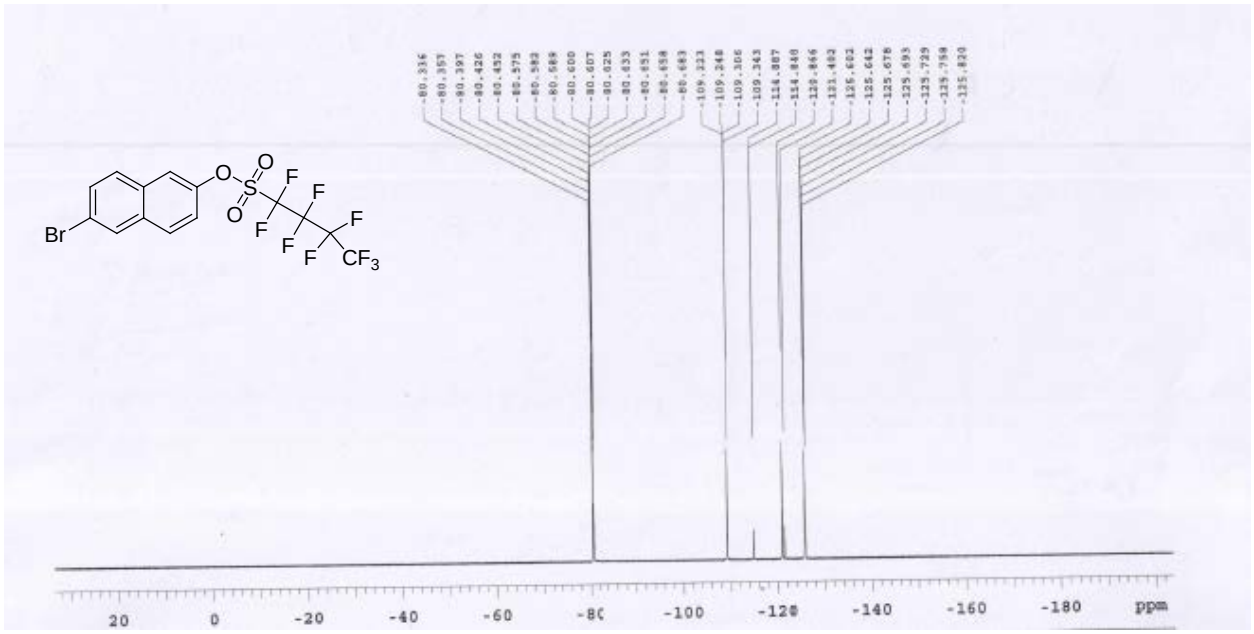
12. 1l


7.948
7.926
7.348
7.327
3.347
2.513
1.236
0.856
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.98

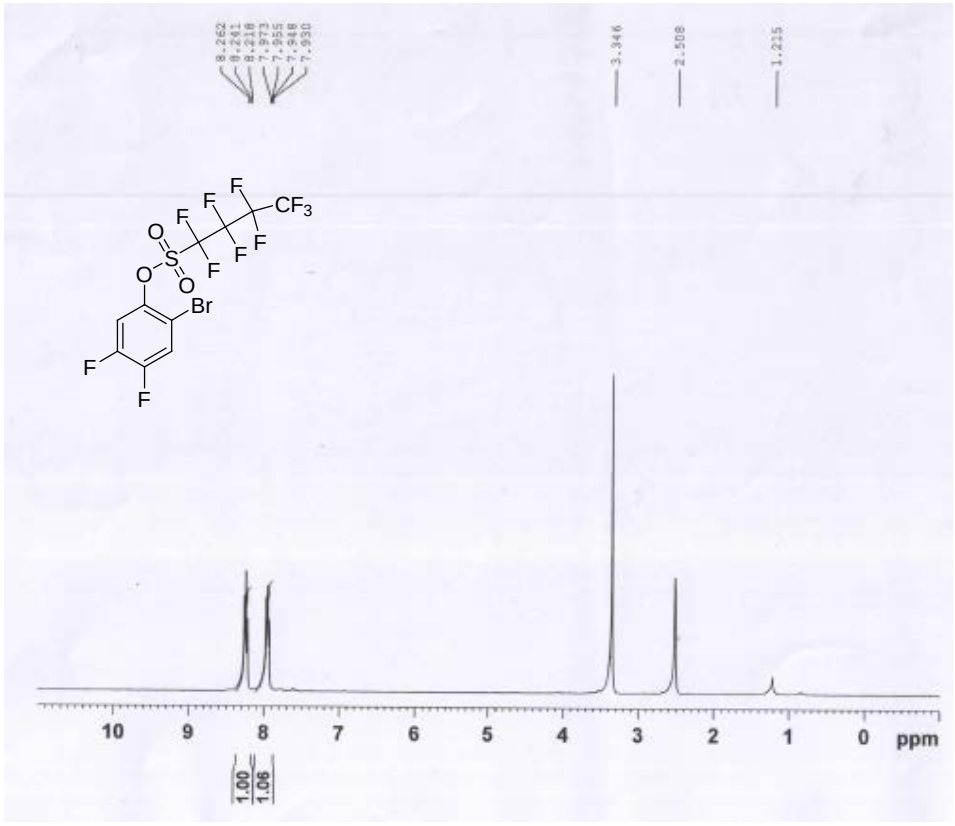

-80.216
-80.470
-109.056
-114.775
-120.890
-121.318
-125.535
-125.660
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

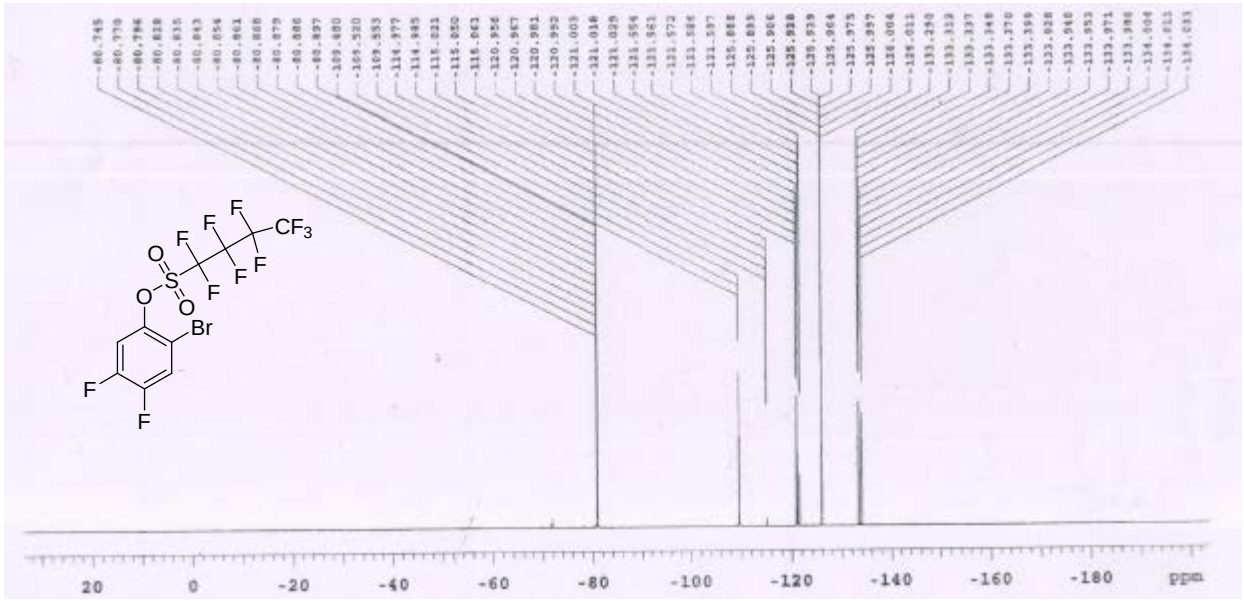
13. 1m


8.366
8.195
8.139
8.116
8.071
8.049
7.797
7.775
7.679
7.658
3.335
2.500
1.209
Br
O
S
O
O
F
F
F
F
F
F
CF3
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.03
1.03
1.00
1.01

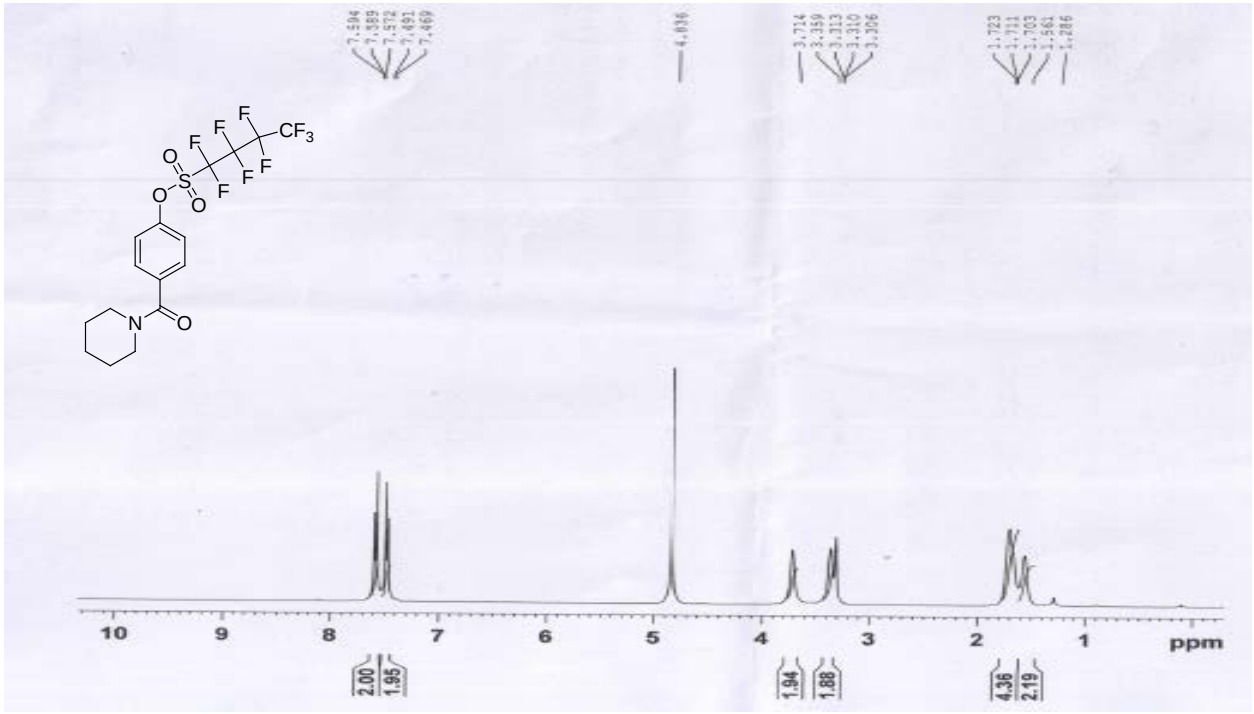

-80.336
-80.357
-80.397
-80.426
-80.452
-80.575
-80.588
-80.589
-80.600
-80.607
-80.625
-80.633
-80.651
-80.658
-80.683
-109.233
-109.248
-109.306
-109.343
-114.887
-114.940
-120.866
-121.402
-125.602
-125.642
-125.678
-125.693
-125.729
-125.764
-125.820
Br
O
S
O
O
F
F
F
F
F
F
CF3
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

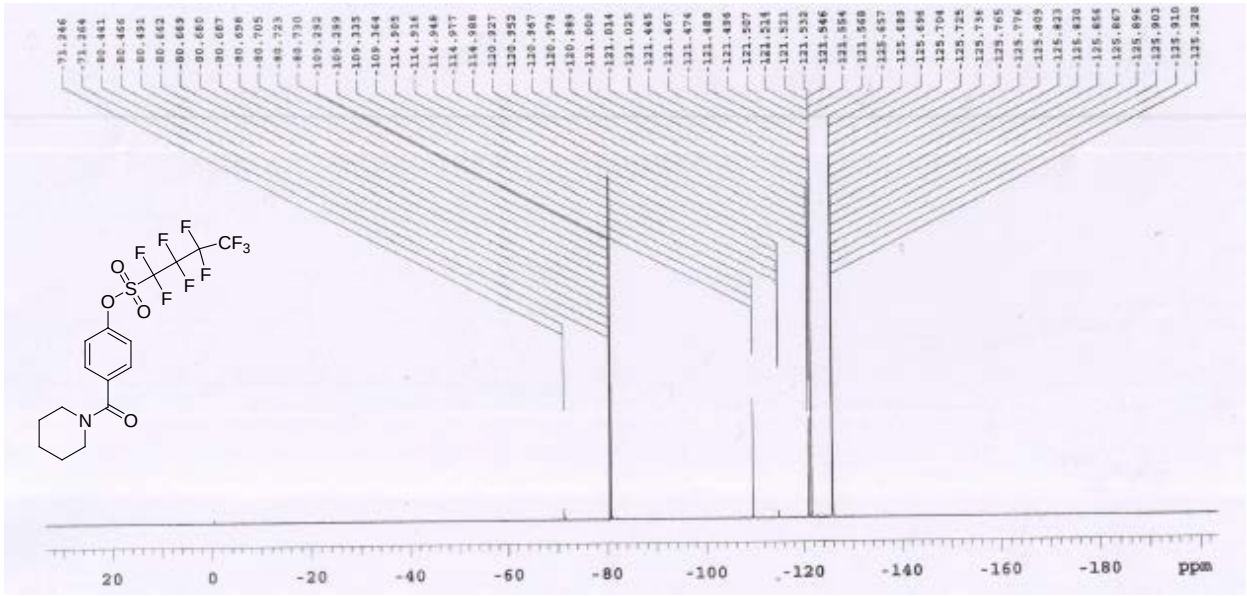
13. 1n


8.262
8.261
8.218
7.973
7.955
7.948
7.930
3.346
2.508
1.235
F
F
F
CF3
F
F
F
O
S
O
O
Br
F
F
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.06

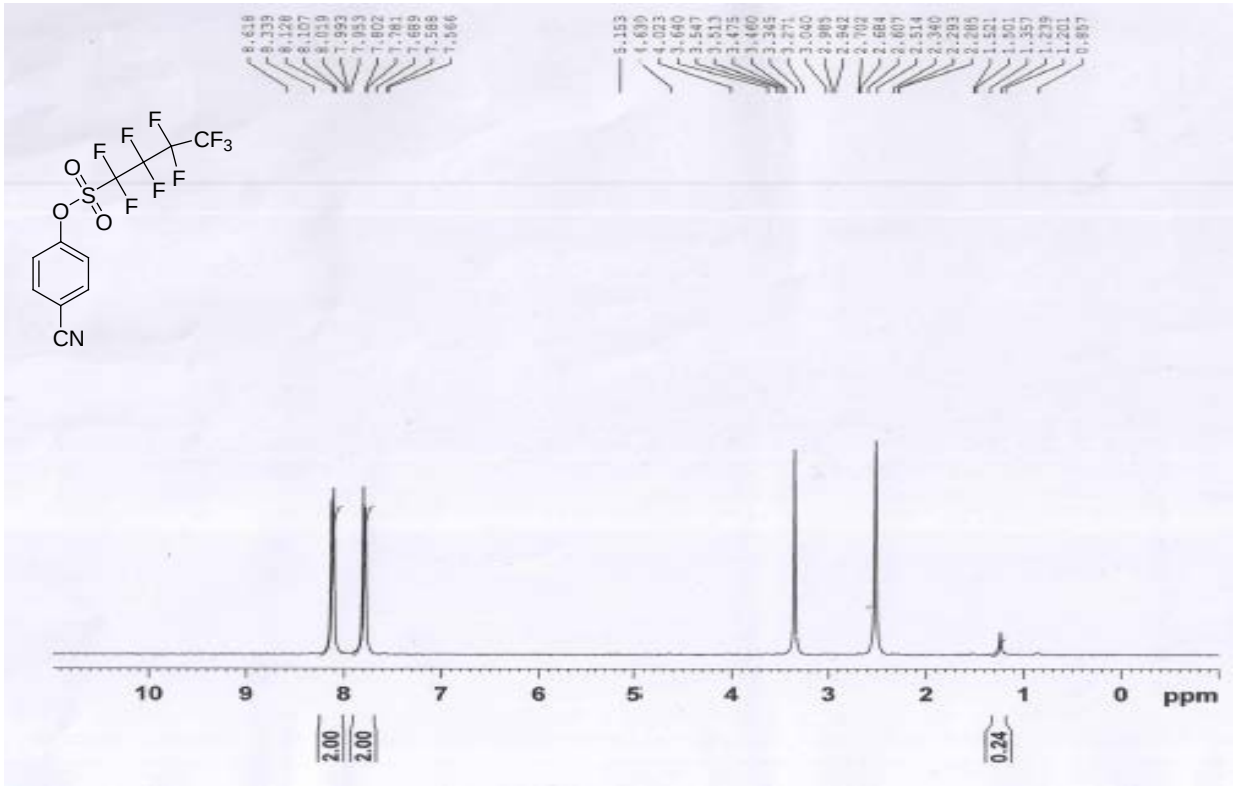

F
F
F
CF3
F
F
F
O
S
O
O
Br
F
F
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

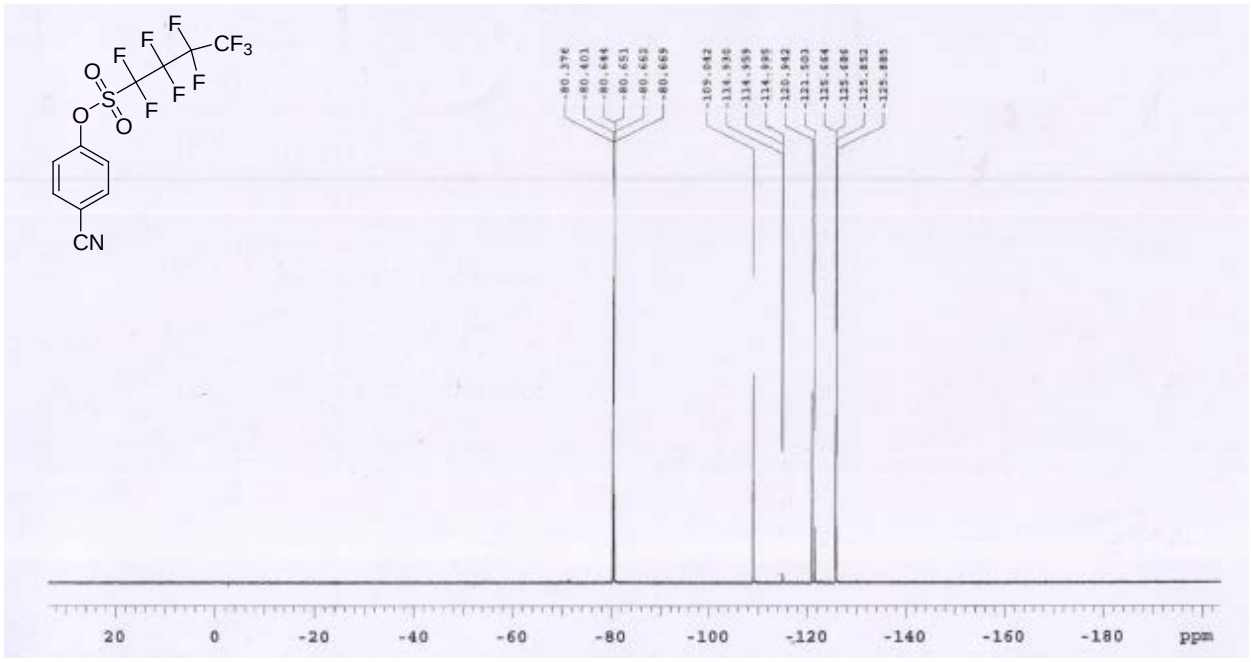
14. 1O


7.594
7.589
7.572
7.491
7.469
4.036
3.714
3.359
3.313
3.310
3.306
1.723
1.711
1.703
1.561
1.286
F
F
F
F
F
F
F
CF3
O
S
O
O
O
N
O
10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.95
1.94
1.88
4.36
2.19

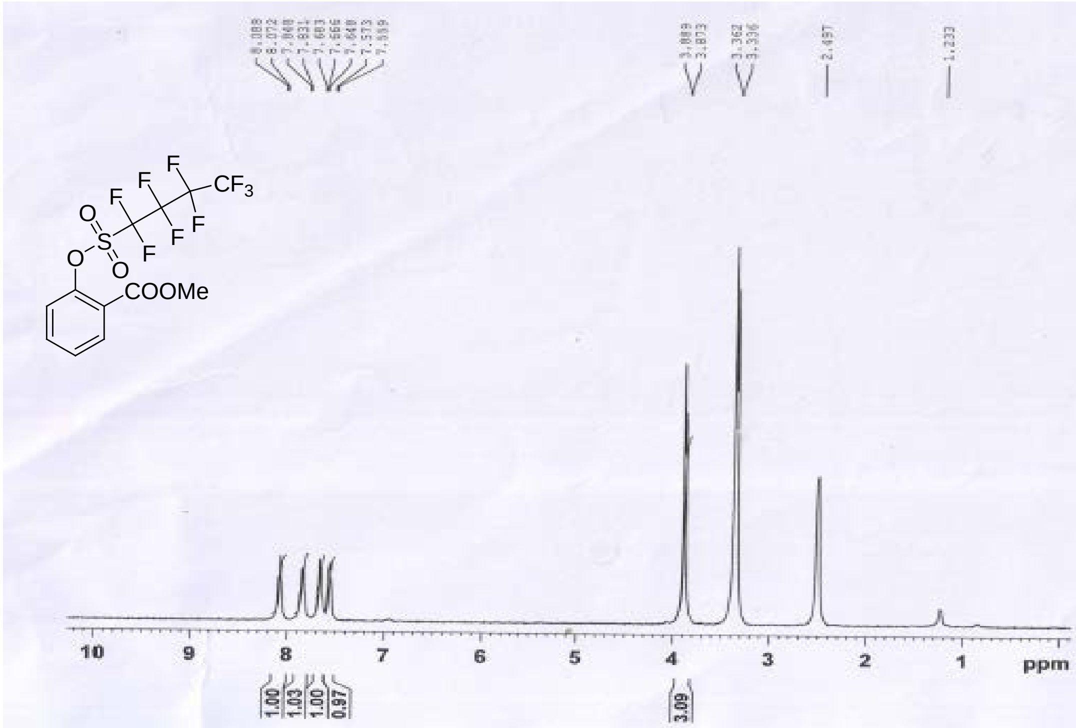

F
F
F
F
F
F
F
CF3
O
S
O
O
O
N
O
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

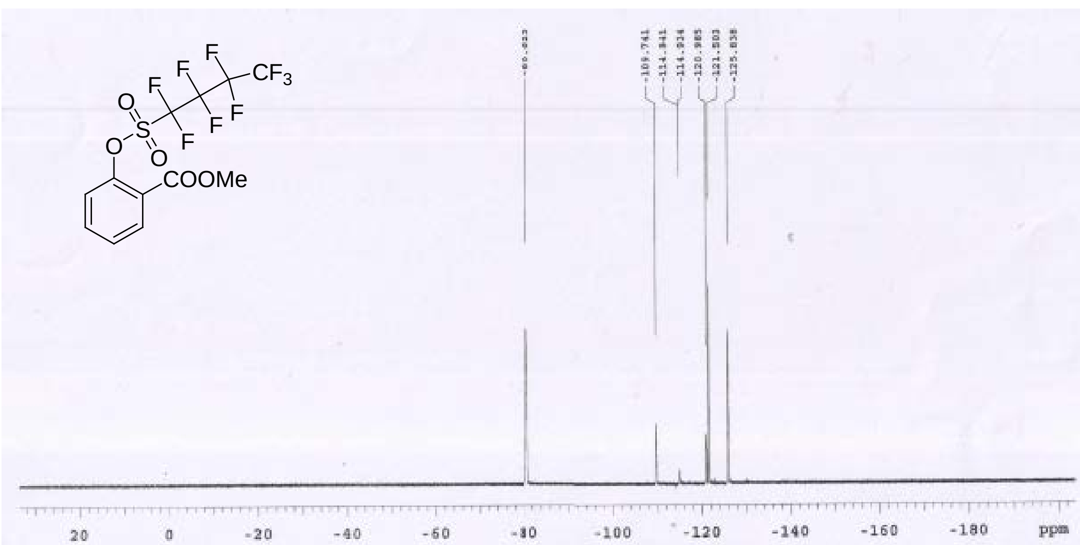
15. 1p


F
F
F
CF3
F
F
F
F
O
S
O
O
F
O
CN
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.00
0.24

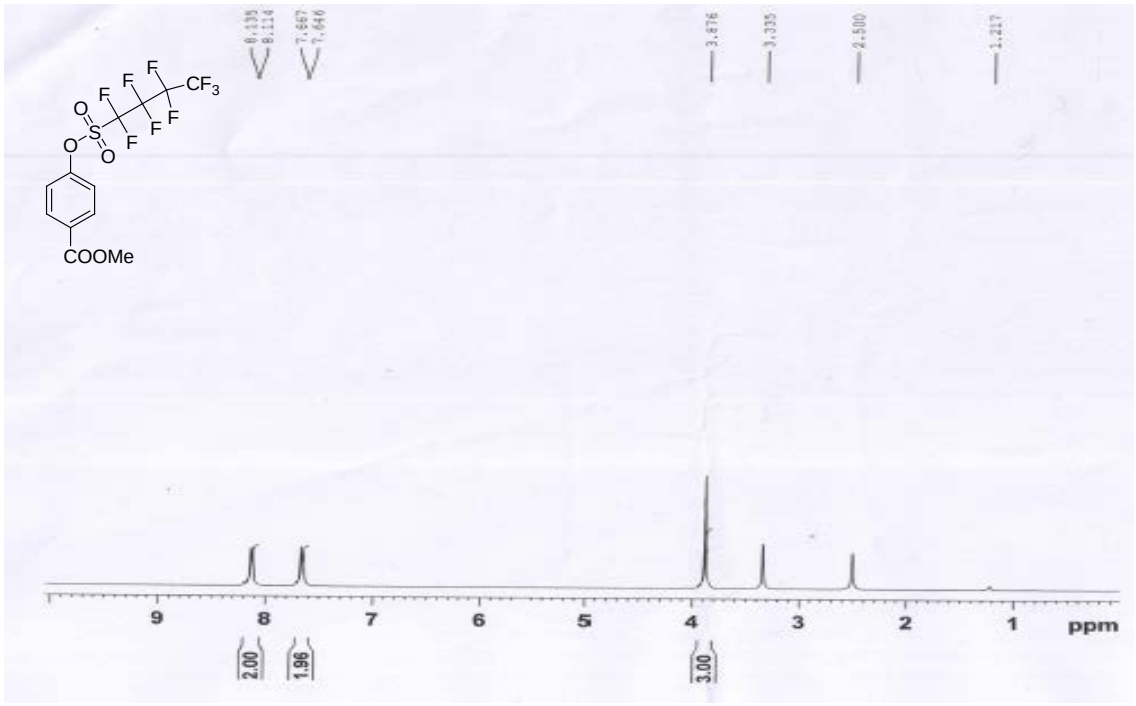

F
F
F
CF3
F
F
F
F
O
S
O
O
F
O
CN
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

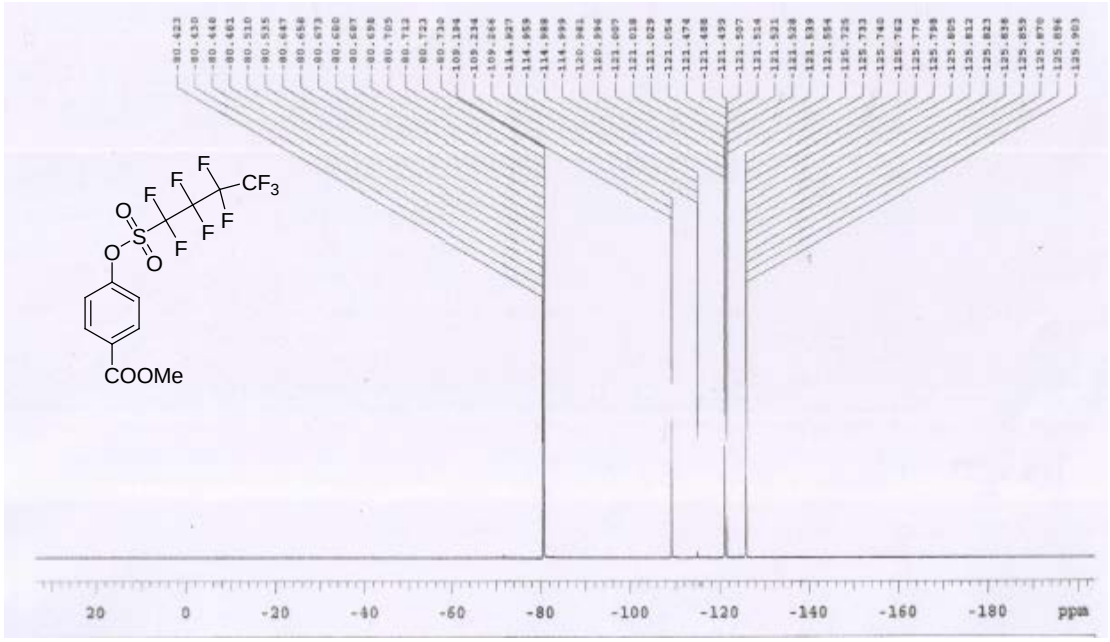
16. 1q


8.088
8.072
7.848
7.831
7.683
7.666
7.648
7.573
7.559
3.889
3.873
3.362
3.336
2.497
1.233
CF3
F
COOMe
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.03
1.00
0.97
3.09

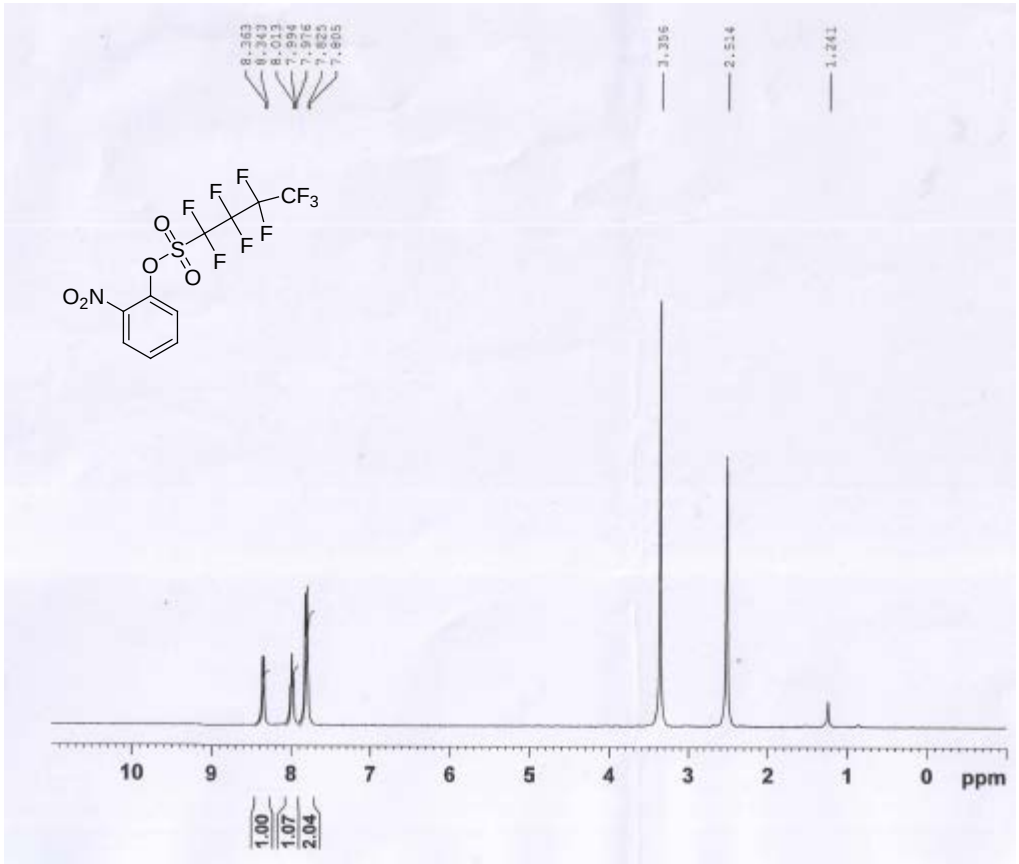

-109.741
-114.841
-114.934
-120.985
-121.503
-125.858
CF3
F
COOMe
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

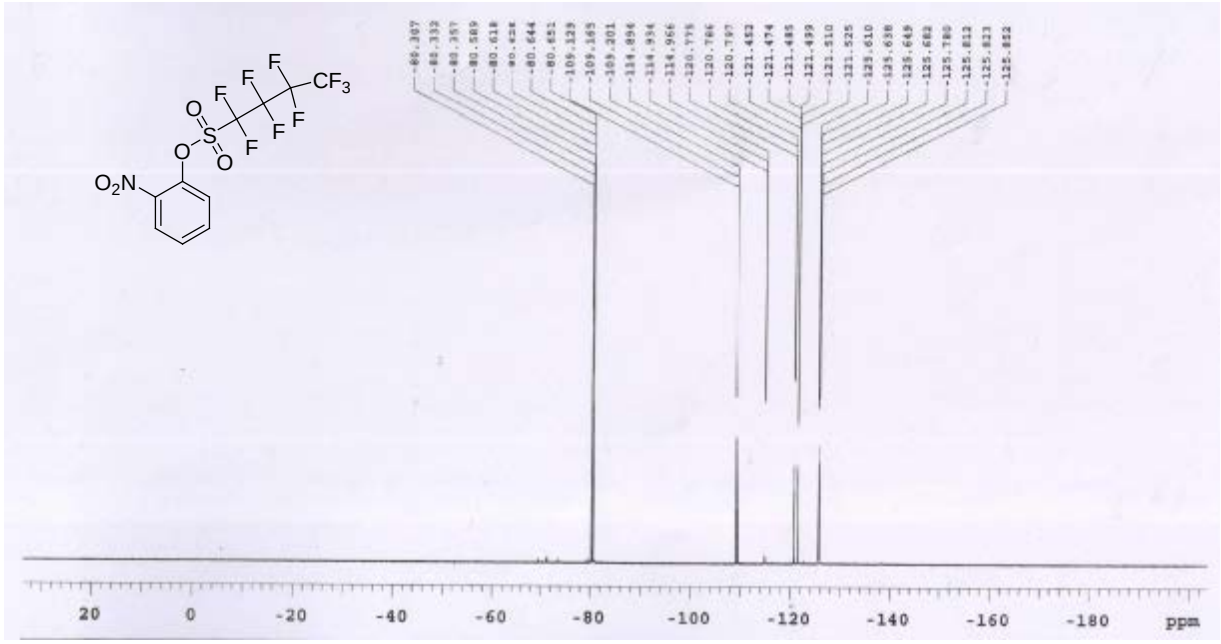
17. 1r


8.135
8.114
7.667
7.646
3.876
3.335
2.500
1.217
F
F
F
CF3
F
F
F
O
S
O
O
F
COOMe
9
8
7
6
5
4
3
2
1
ppm
2.00
1.96
3.00

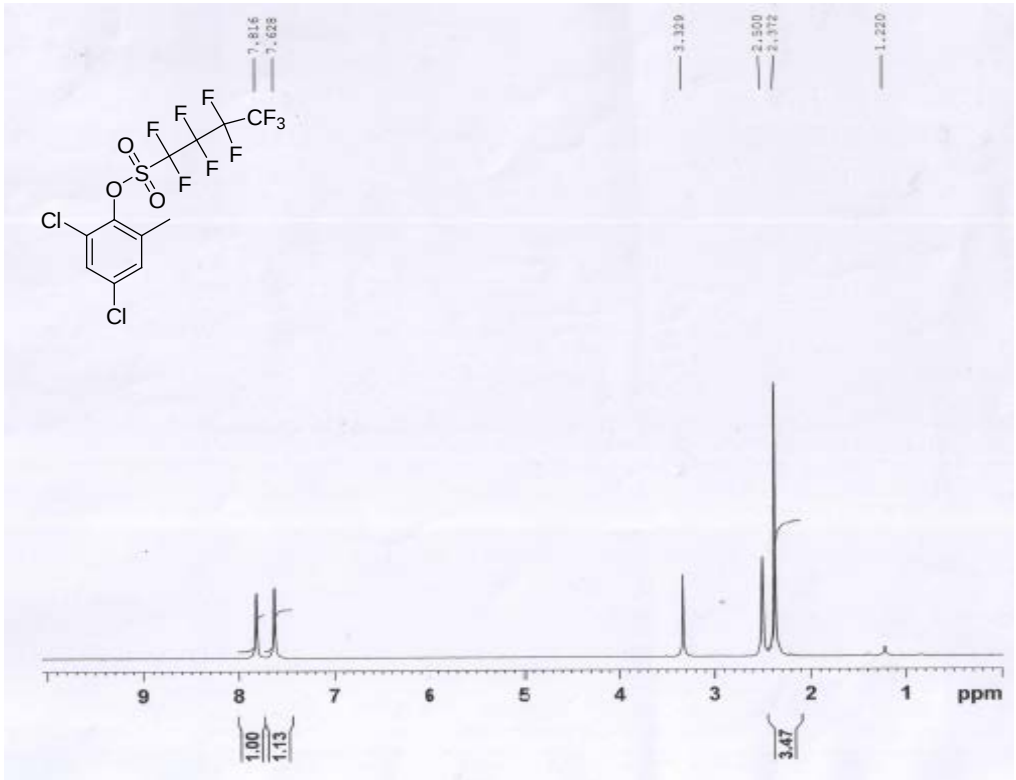

F
F
F
CF3
F
F
F
O
S
O
F
O
COOMe
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

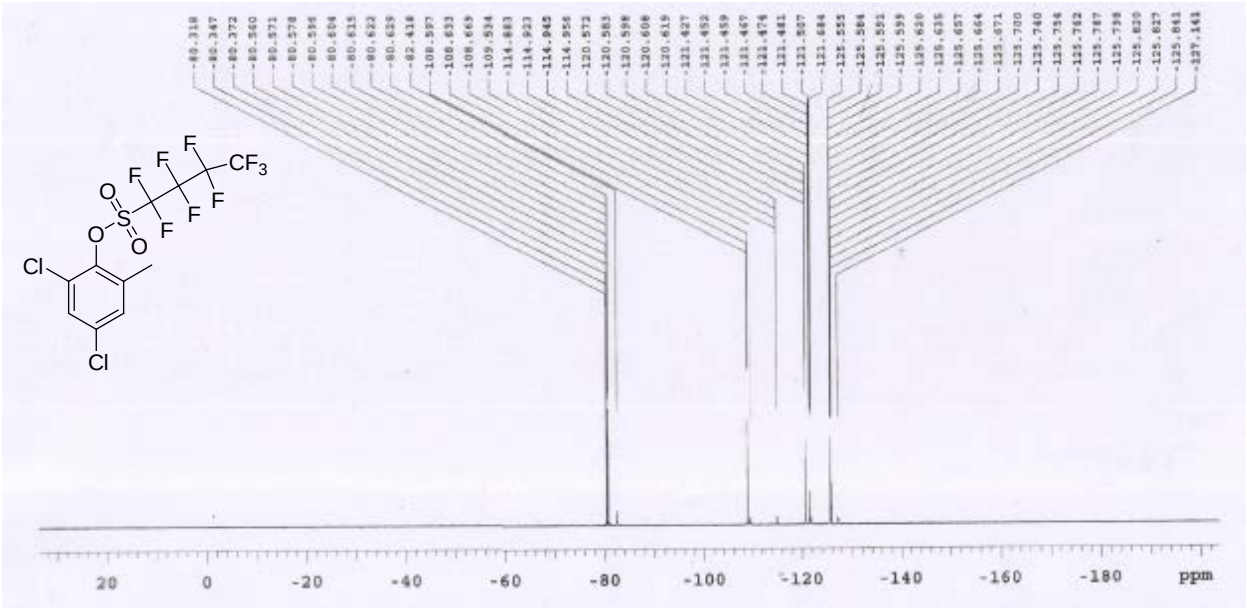
18. 1s


8.383
8.343
8.013
7.994
7.976
7.825
7.805
3.306
2.514
1.241
F
F
F
CF3
F
F
F
O
S
O
F
O
O2N
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.07
2.04

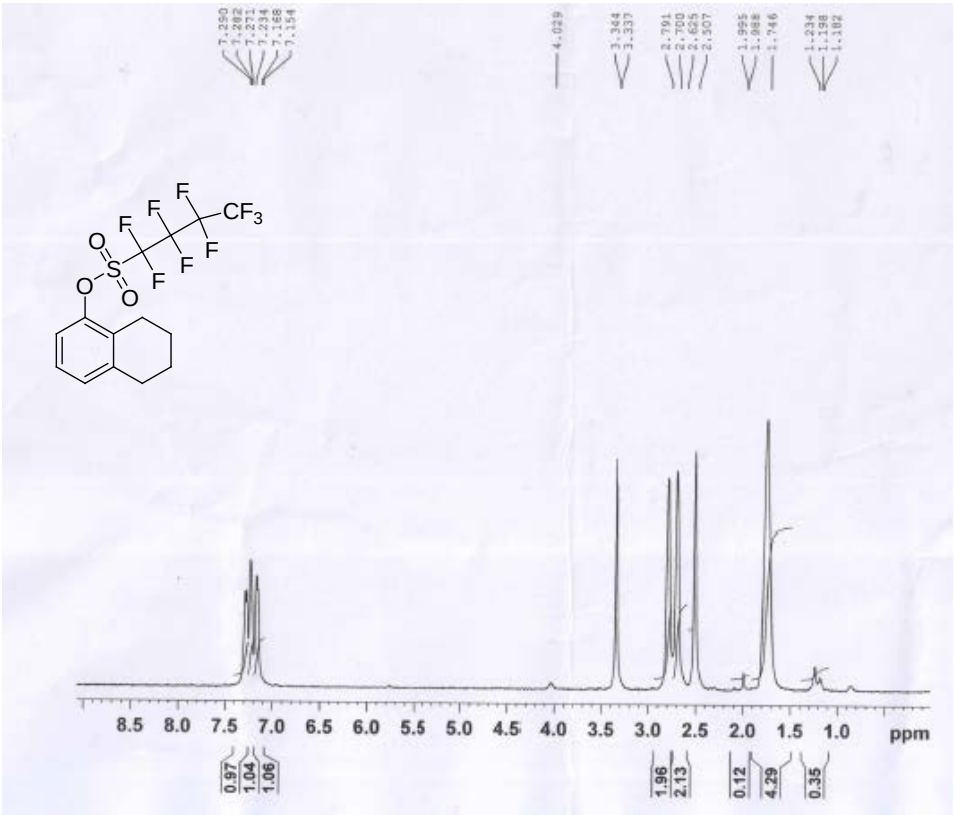

F
F
F
CF3
F
F
F
F
O
S
O
O
O
O2N
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

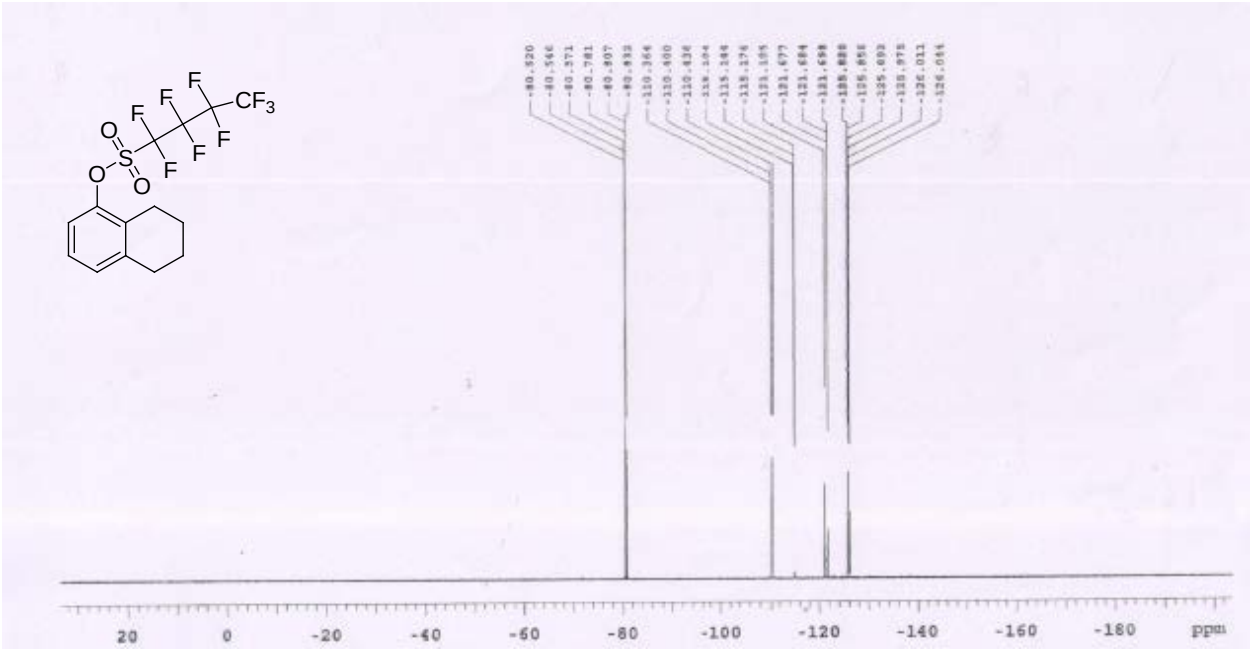
19. 1t


7.816
7.628
3.329
2.500
2.372
1.220
F
F
F
CF3
F
F
F
F
O
S
O
O
O
Cl
Cl
9
8
7
6
5
4
3
2
1
ppm
1.00
1.13
3.47

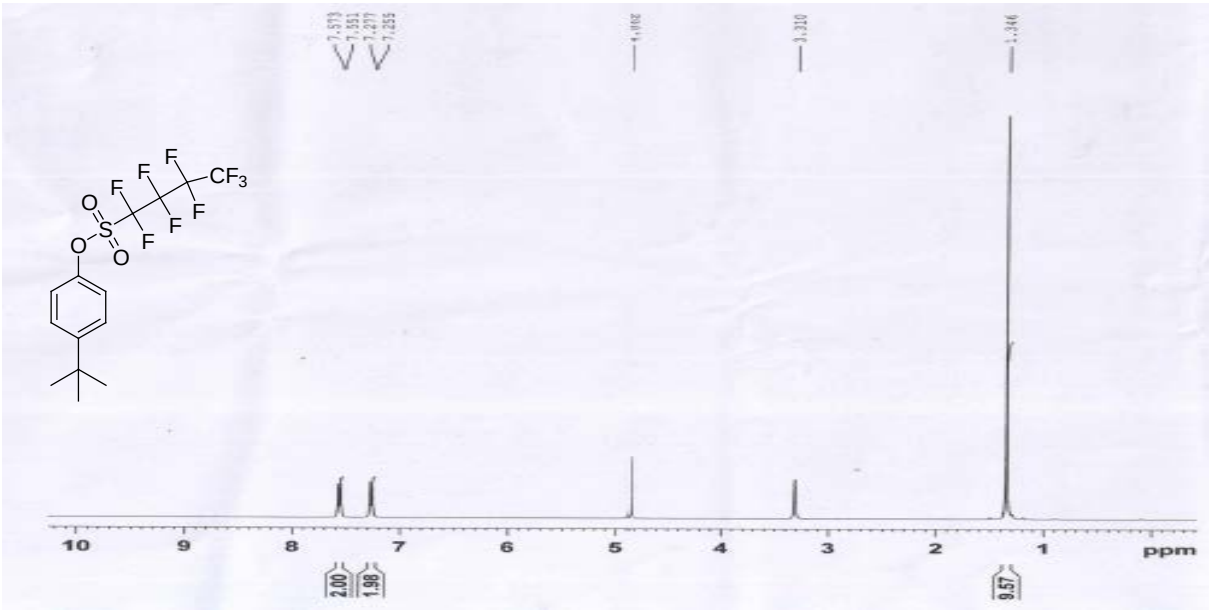

F
F
F
CF3
F
F
F
O
S
O
O
Cl
Cl
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

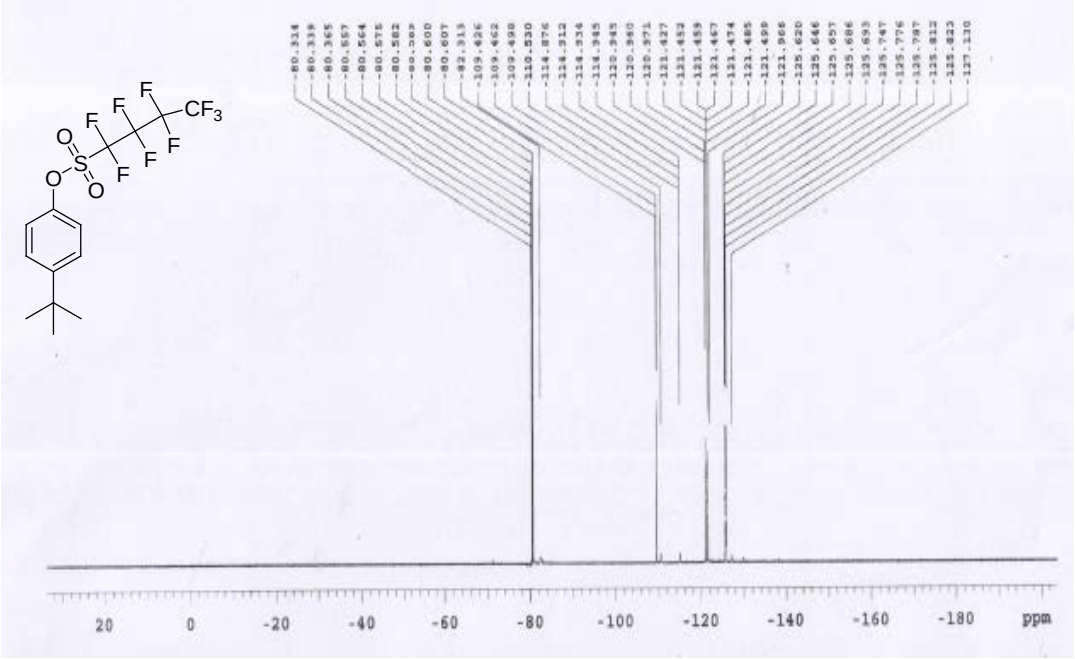
20. 1u


F
F
F
CF3
F
F
F
O
S
O
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.97
1.04
1.06
1.96
2.13
0.12
4.29
0.35


F
F
F
CF3
F
F
F
O
S
O
O
F
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

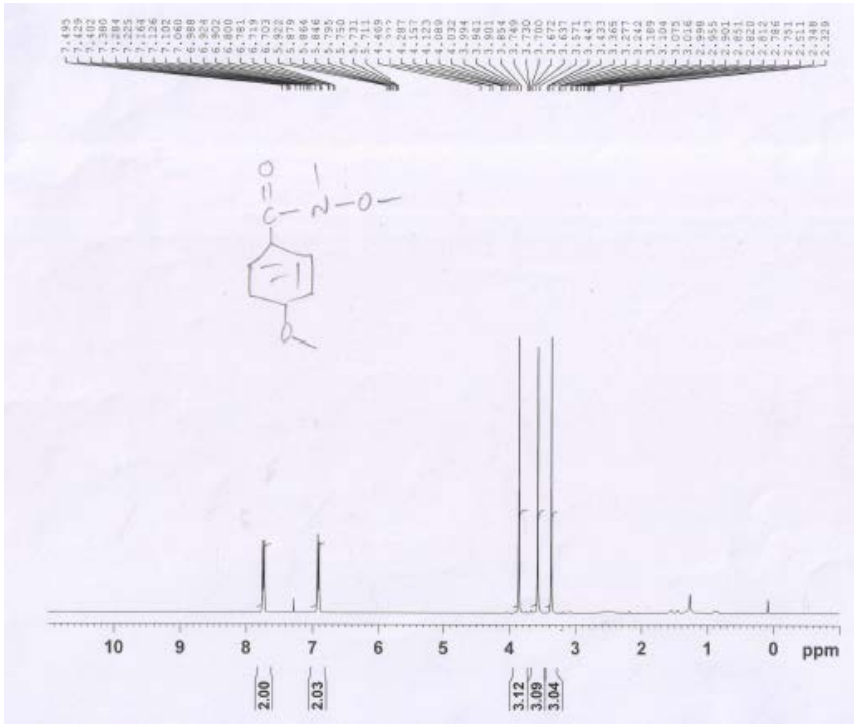
22. 1v

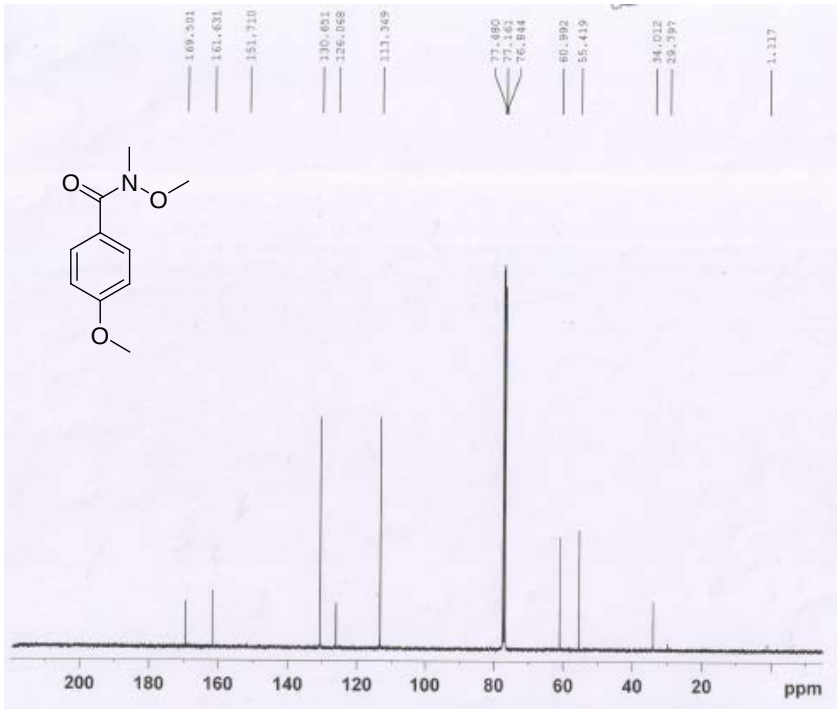

7.373
7.351
7.277
7.255
4.982
3.310
1.346
F
F
F
CF3
F
F
F
O
S
O
O
F
10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.98
9.57


F
F
F
CF3
F
F
F
O
S
O
F
O
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

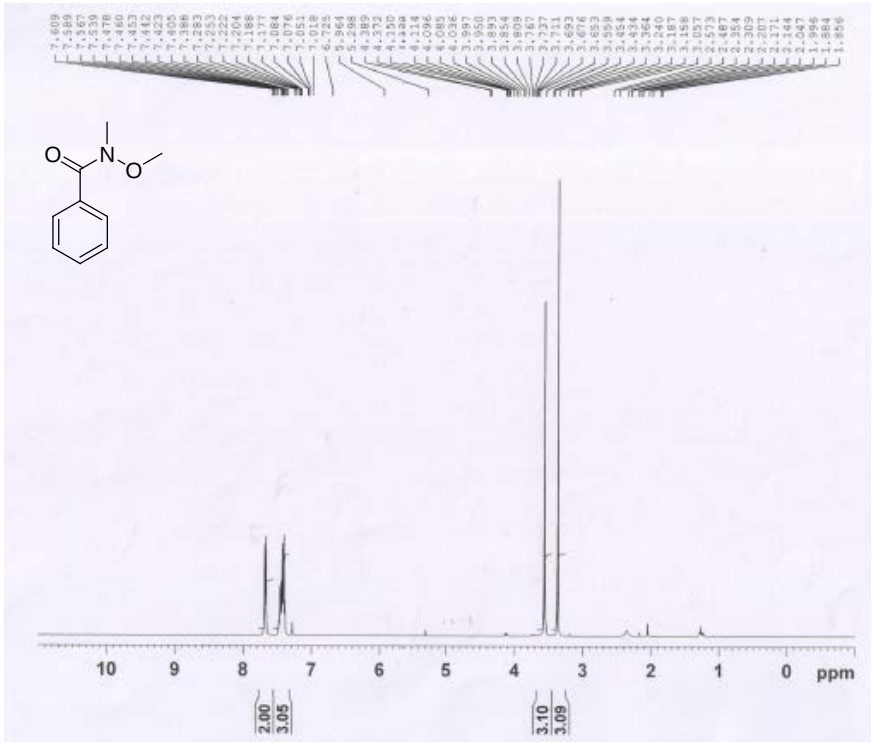
3.2 Spectral data of compounds 2a-2ze.

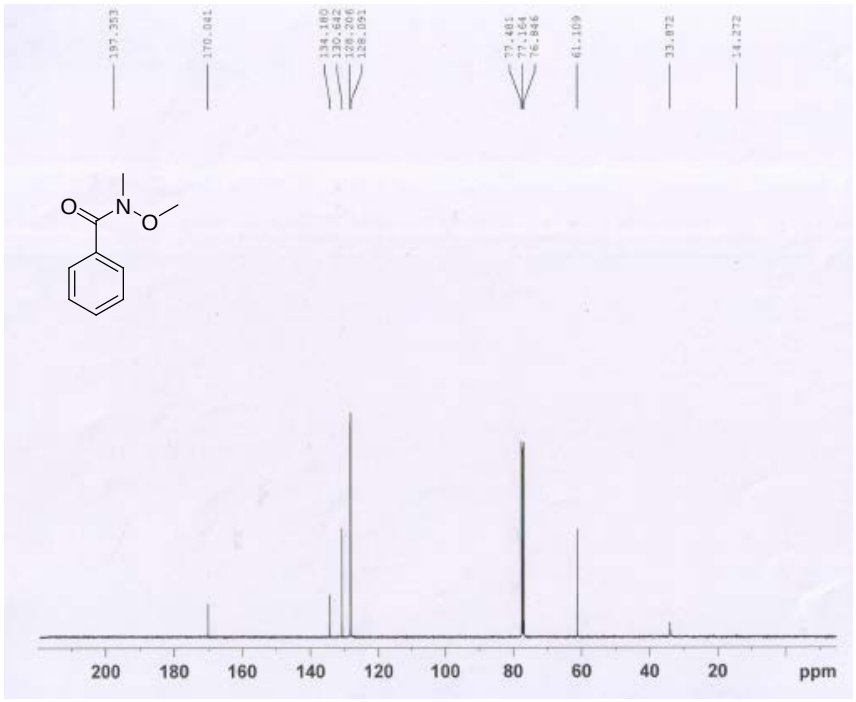
23. 2a

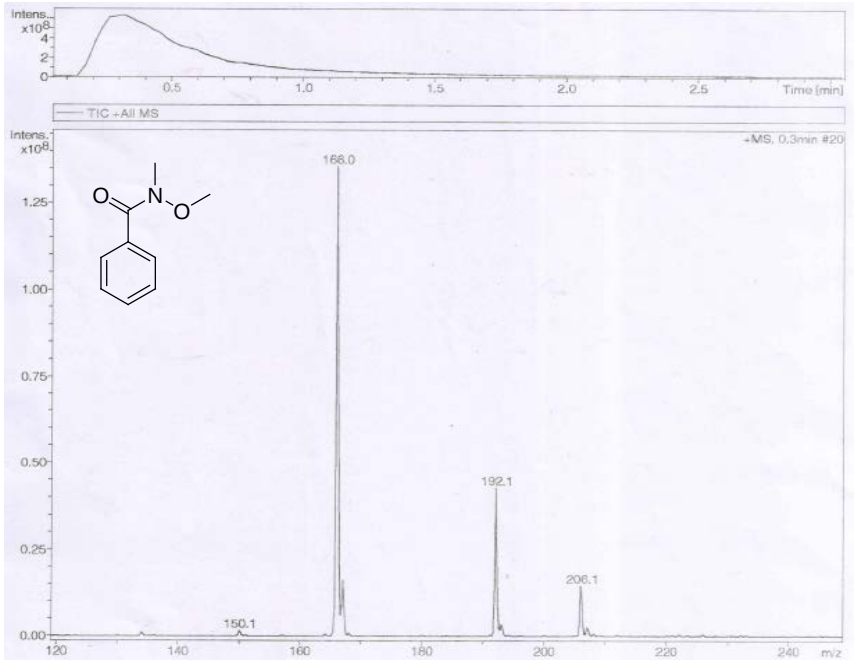


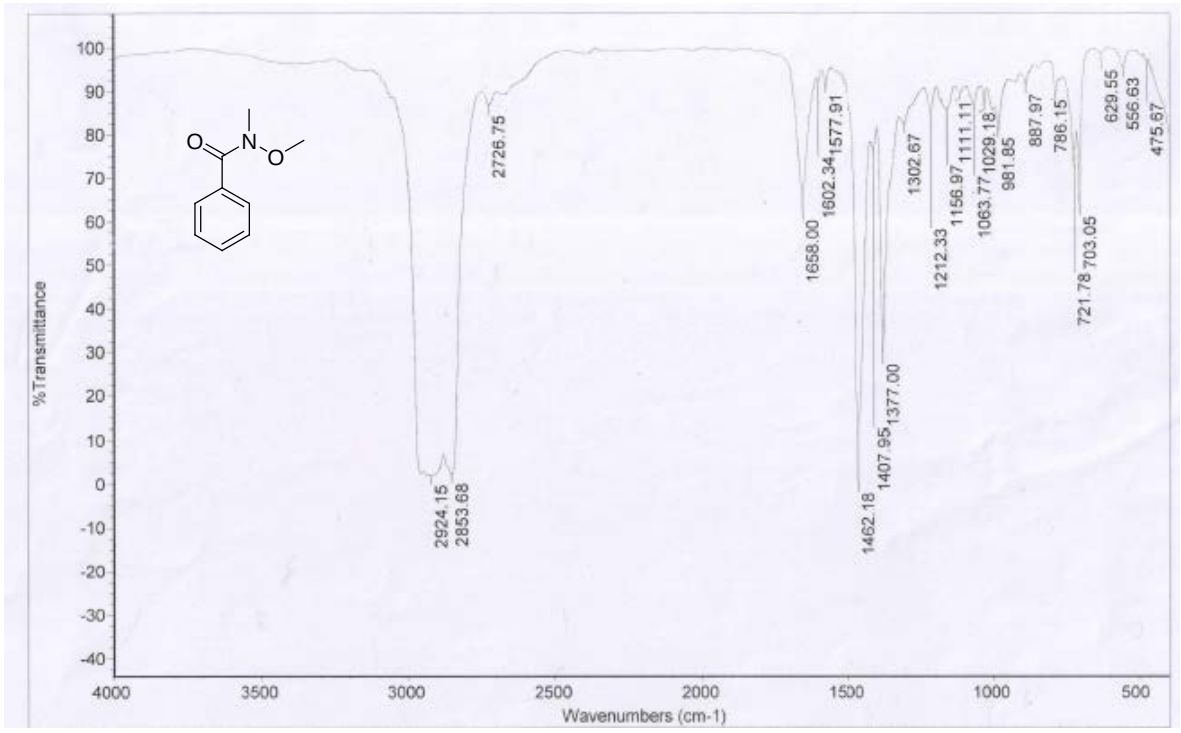


24. 2b

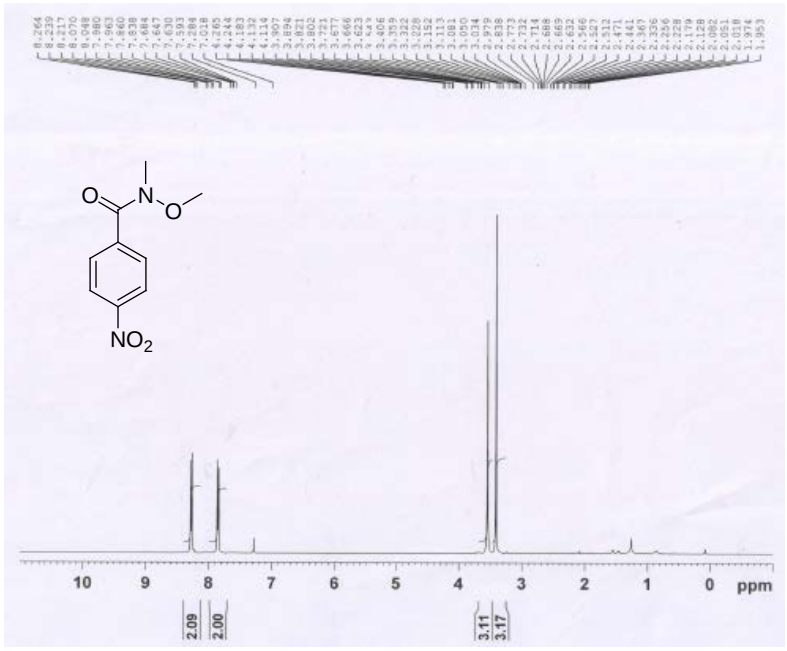

10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
3.05
3.10
3.09

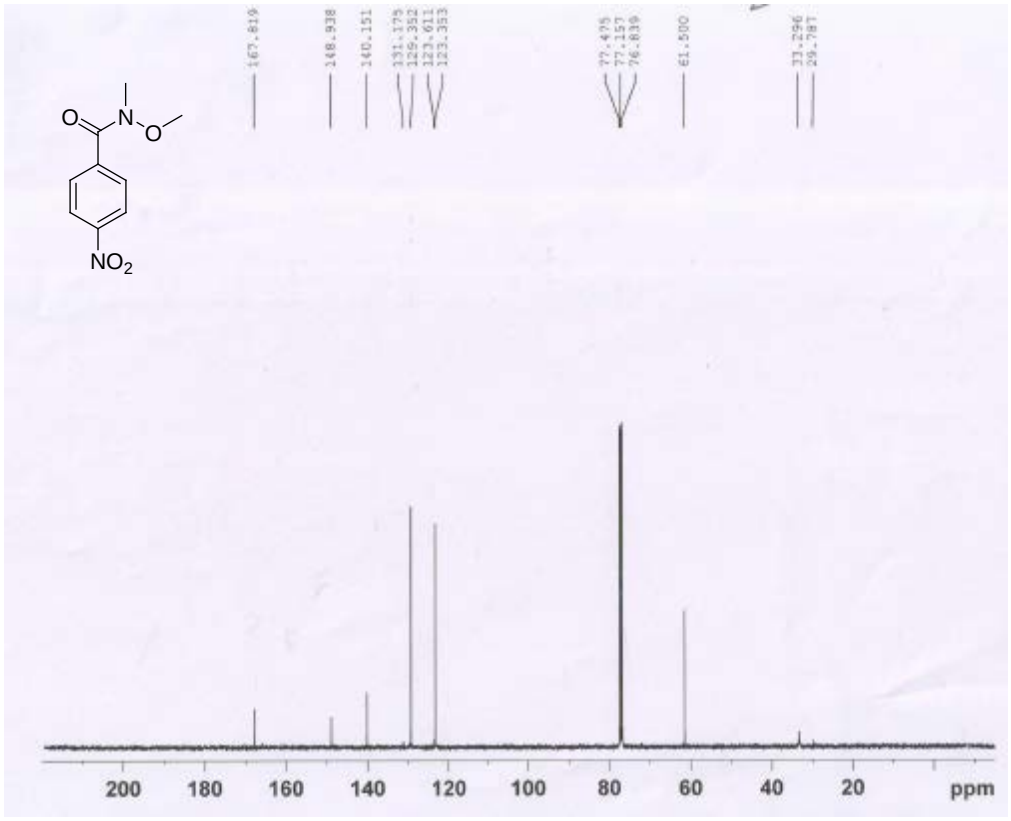

197.353
170.041
134.180
130.642
128.206
128.091
77.481
77.164
76.846
61.109
33.872
14.272
200
180
160
140
120
100
80
60
40
20
ppm

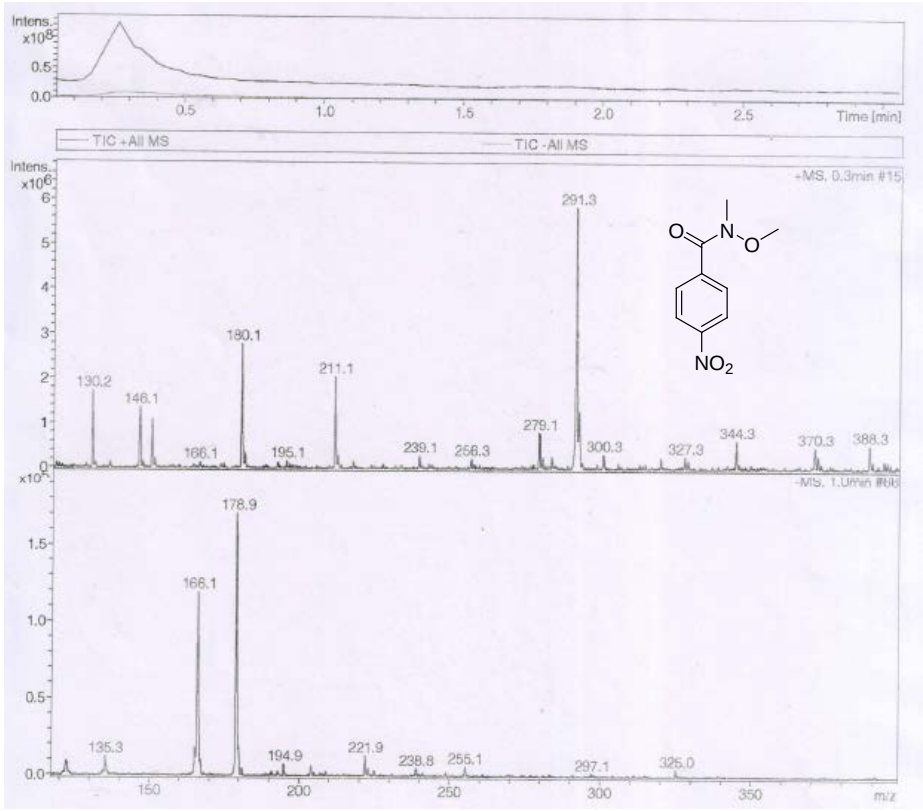

Intens.
x10^8
Time (min)
TIC +All MS
+MS, 0.3min #20
168.0
192.1
206.1
150.1
m/z

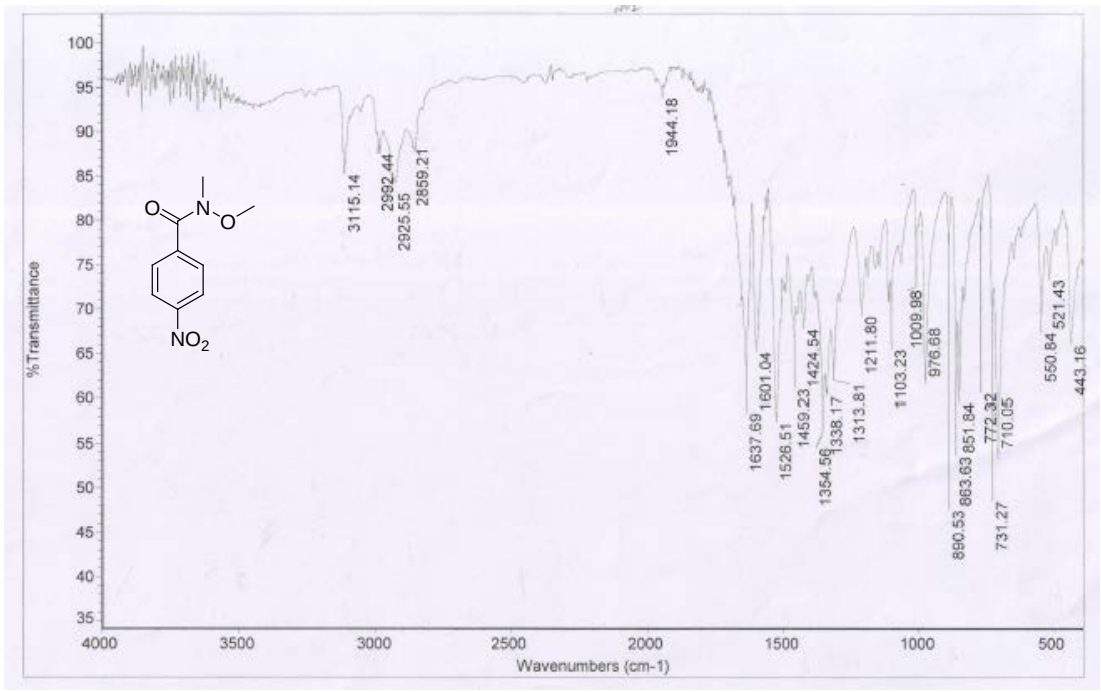

%Transmittance
Wavenumbers (cm-1)
2924.15
2853.68
2726.75
1658.00
1602.34
1577.91
1462.18
1407.95
1377.00
1302.67
1212.33
1156.97
1111.11
1063.77
1029.18
981.85
887.97
786.15
721.78
703.05
629.55
556.63
475.67

25. 2c

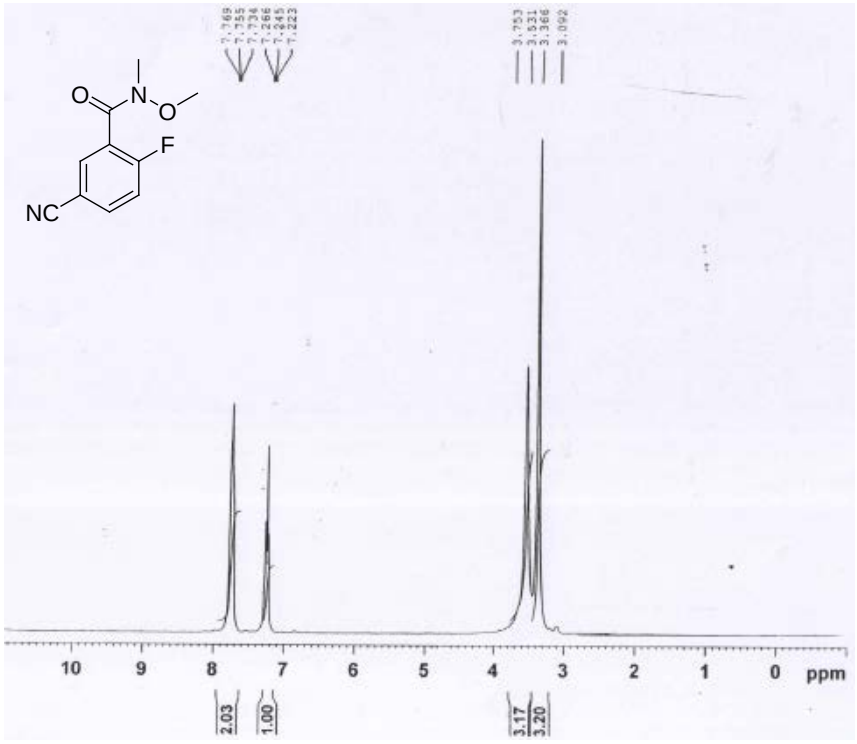

O
N
O
NO2
10
9
8
7
6
5
4
3
2
1
0
ppm
2.09
2.00
3.11
3.17

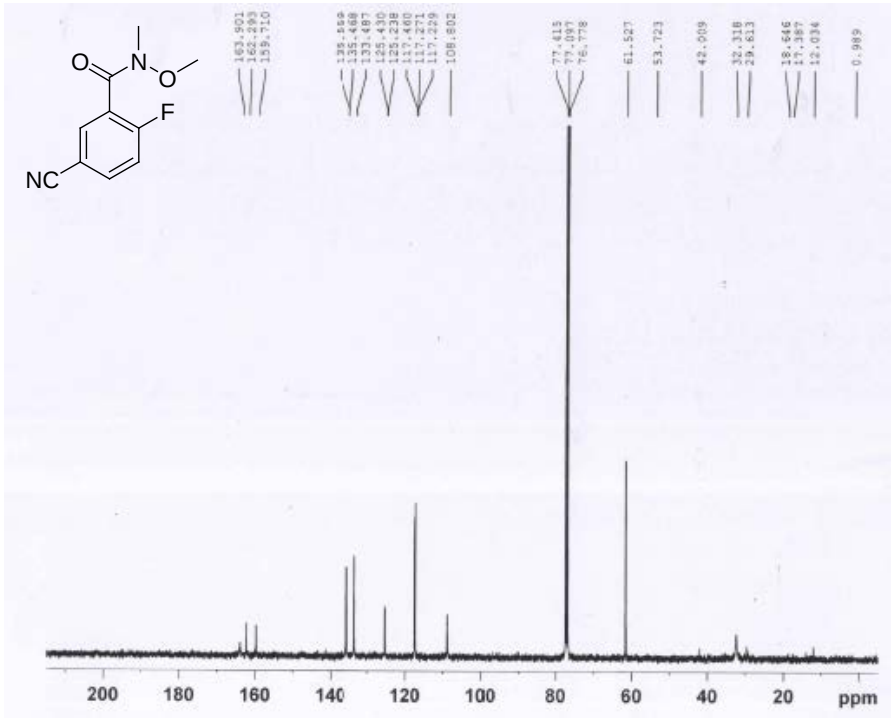

167.819
148.938
140.151
131.179
129.352
123.611
123.353
77.475
77.157
76.839
61.500
33.296
29.787
O
N
O
NO2
200
180
160
140
120
100
80
60
40
20
ppm


Intens.
x10^8
0.5
0.0
0.5
1.0
1.5
2.0
2.5
Time [min]
TIC +All MS
TIC -All MS
Intens.
x10^6
+MS, 0.3min #15
291.3
180.1
211.1
130.2
146.1
166.1
195.1
239.1
256.3
279.1
300.3
327.3
344.3
370.3
388.3
O
N
O
NO2
x10^5
-MS, 1.0min #60
178.9
166.1
135.3
194.9
221.9
238.8
255.1
297.1
325.0
150
200
250
300
350
m/z

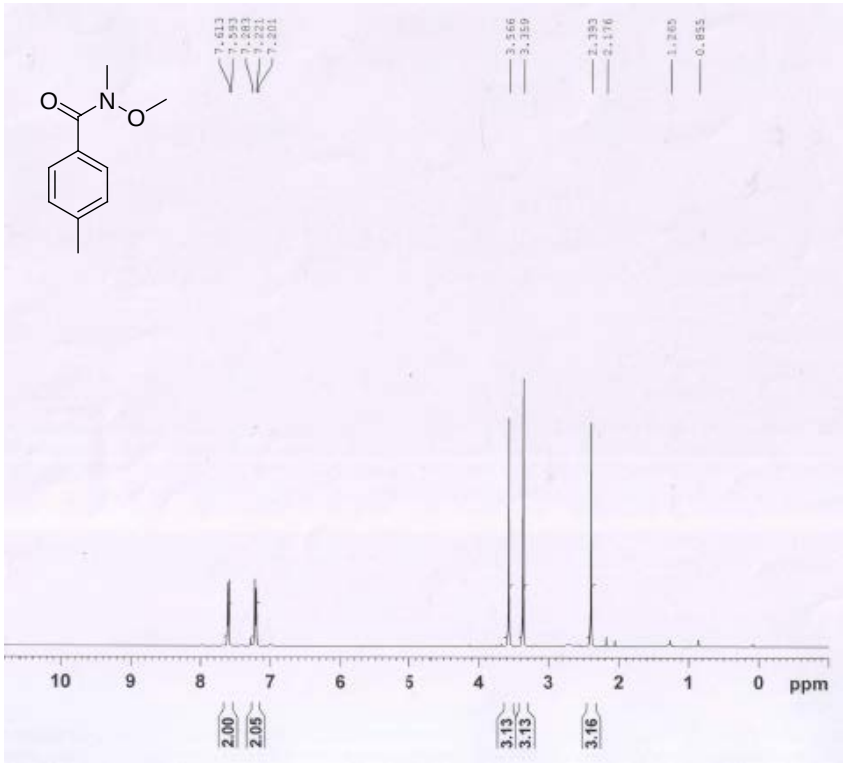

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
3115.14
2992.44
2925.55
2859.21
1944.18
1637.69
1601.04
1526.51
1459.23
1424.54
1354.56
1338.17
1313.81
1211.80
1103.23
1009.98
976.68
890.53
863.63
851.84
772.32
731.27
710.05
550.84
521.43
443.16
O
N
O
NO2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

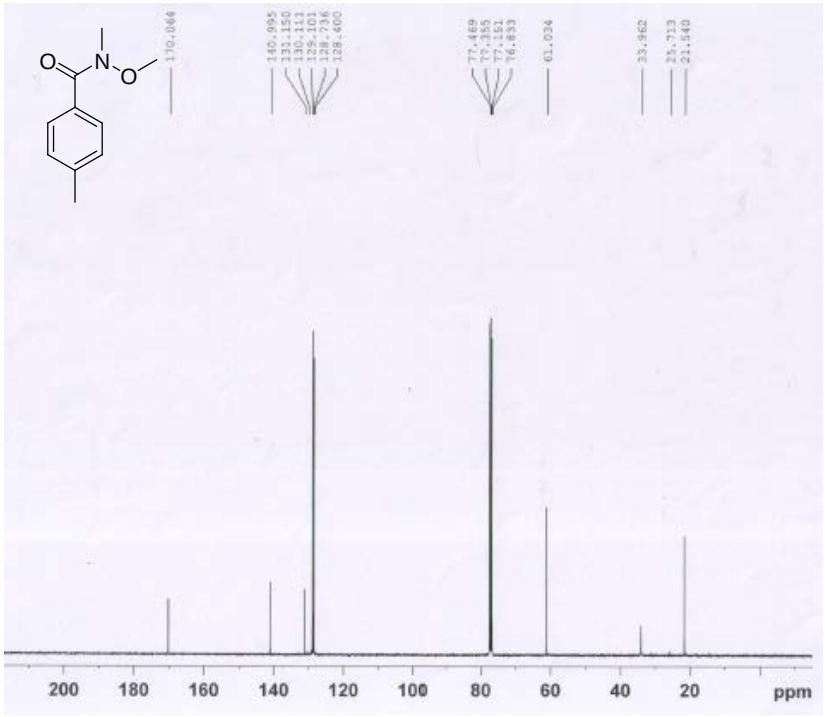
26. 2d

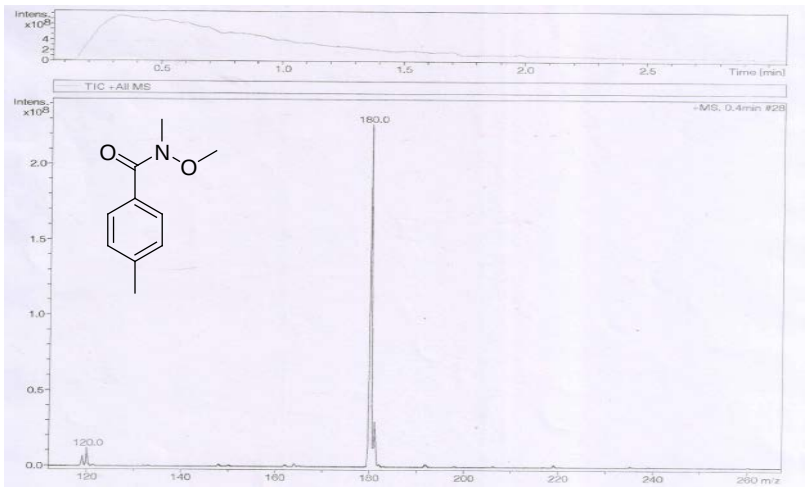

7.769
7.755
7.734
7.266
7.245
7.223
3.753
3.631
3.366
3.092
O
N
O
F
NC
10
9
8
7
6
5
4
3
2
1
0
ppm
2.03
1.00
3.17
3.20

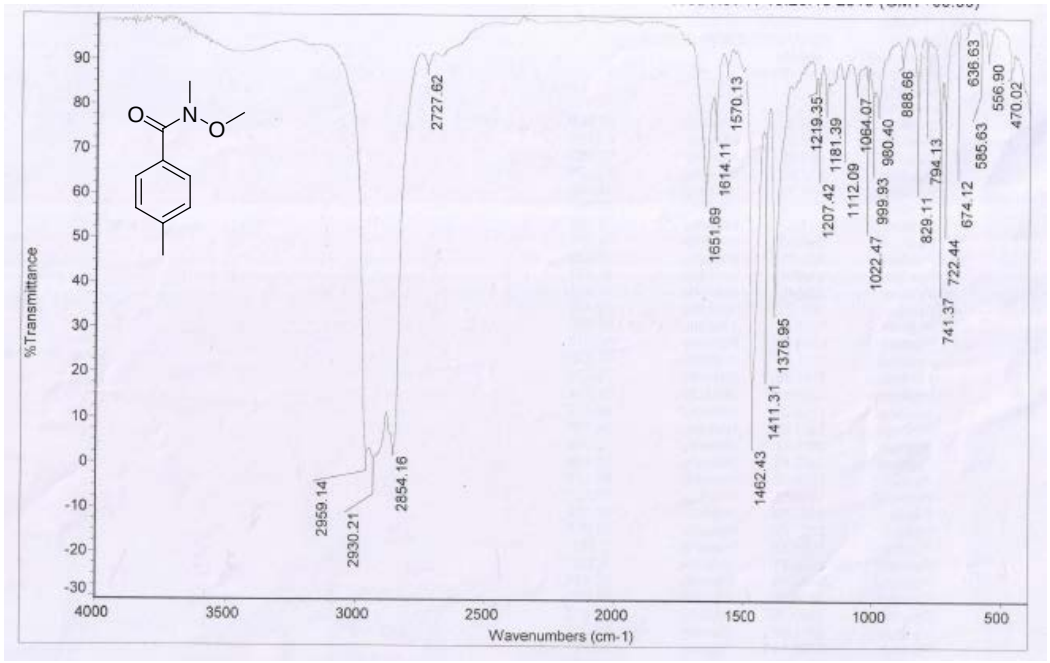

163.901
162.293
159.710
135.858
135.468
133.487
125.430
125.238
117.460
117.271
117.229
108.802
77.415
77.097
76.778
61.527
53.723
42.009
32.318
29.613
18.646
17.387
12.034
0.989
O
N
O
F
NC
200
180
160
140
120
100
80
60
40
20
ppm

27. 2e

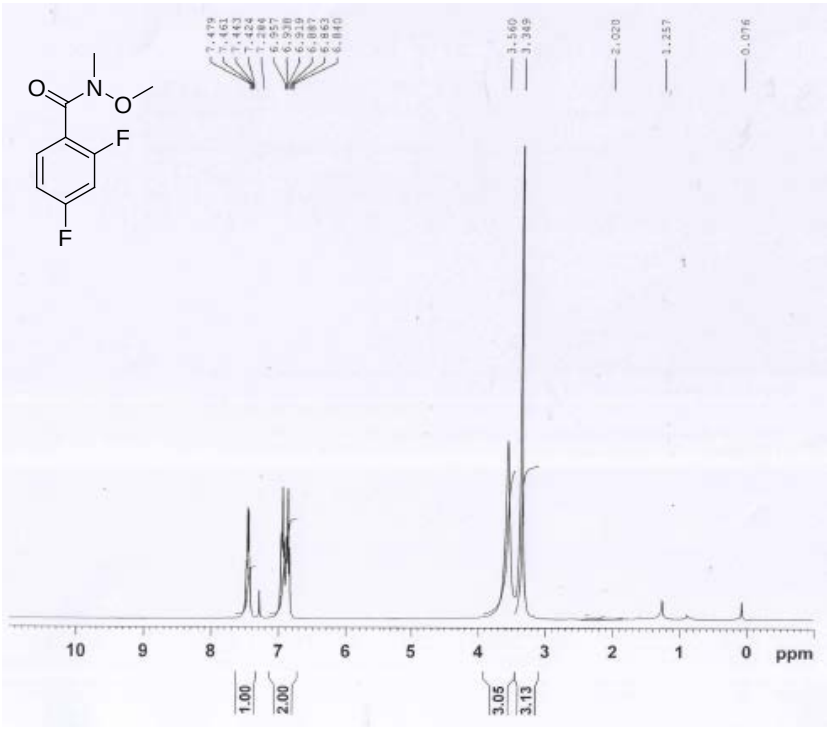

7.613
7.593
7.283
7.221
7.201
3.566
3.359
2.393
2.176
1.265
0.855
O
N
O
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.05
3.13
3.13
3.16

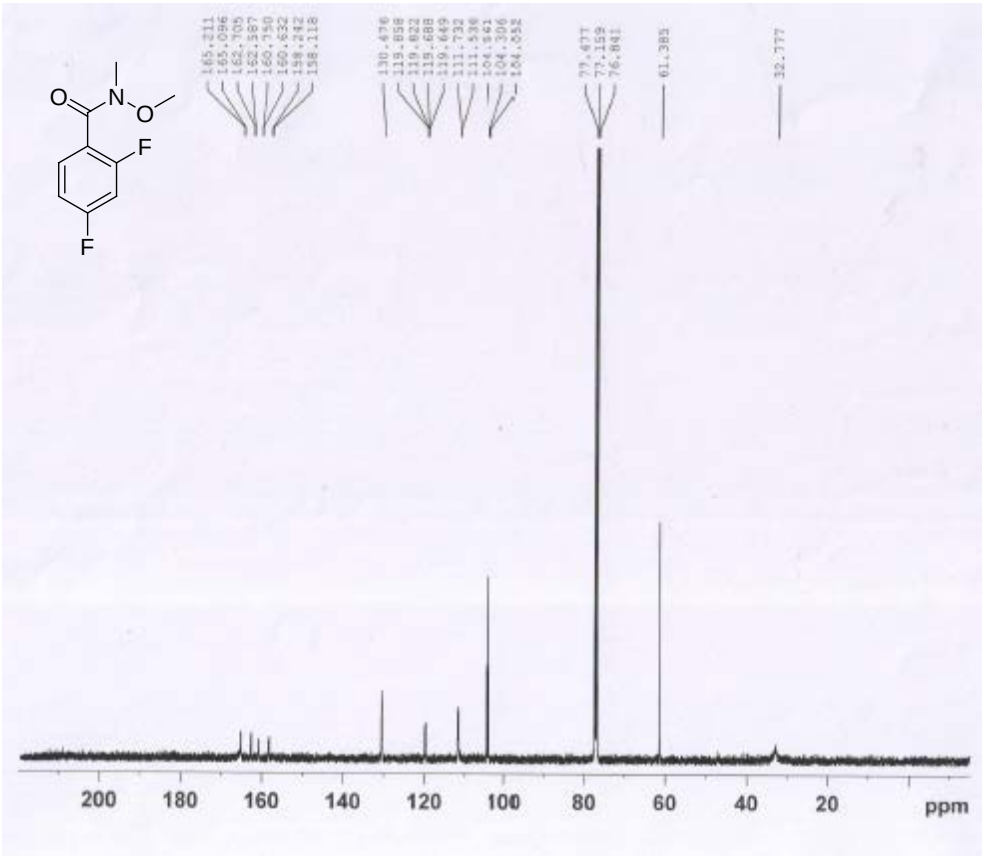

170.064
140.995
131.150
130.161
129.401
128.734
128.400
77.469
77.355
77.151
76.833
61.034
33.962
25.713
21.940
O
N
O
200
180
160
140
120
100
80
60
40
20
ppm


Intens.
x10^8
Time [min]
TIC +All MS
+MS, 0.4min #28
160.0
120.0
m/z

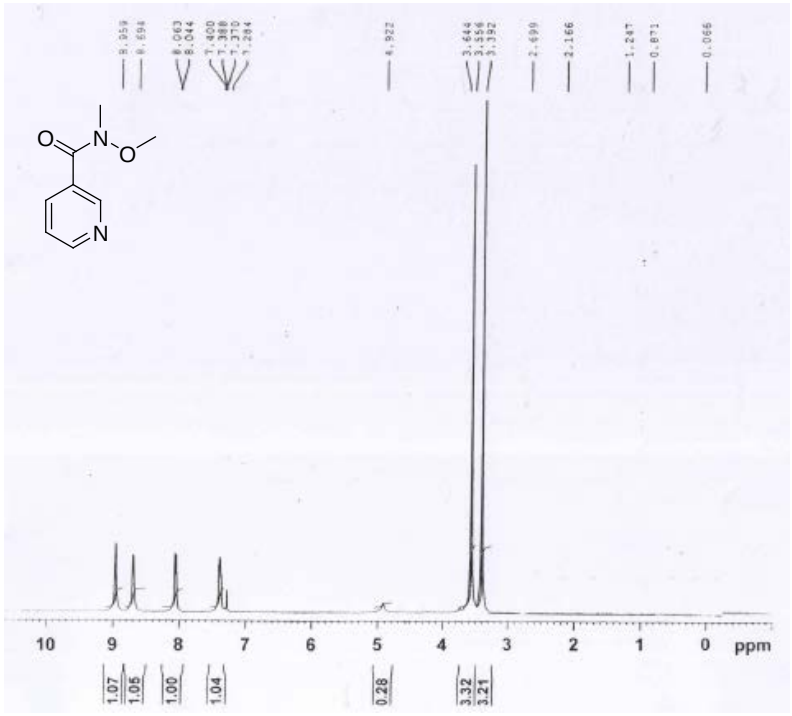

%Transmittance
Wavenumbers (cm-1)
2959.14
2930.21
2854.16
2727.62
1651.69
1614.11
1570.13
1462.43
1411.31
1376.95
1219.35
1207.42
1181.39
1112.09
1064.07
1022.47
999.93
980.40
888.66
829.11
794.13
741.37
722.44
674.12
636.63
585.63
556.90
470.02

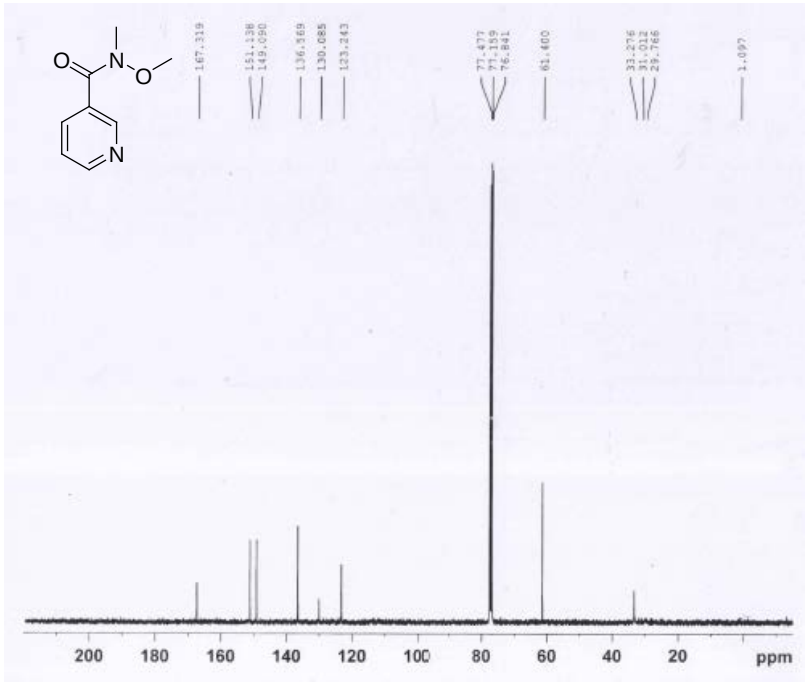
28. 2f


O
N
O
F
F
7.479
7.461
7.443
7.424
7.284
6.957
6.930
6.919
6.887
6.865
6.840
3.560
3.349
2.020
1.257
0.076
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.00
3.05
3.13

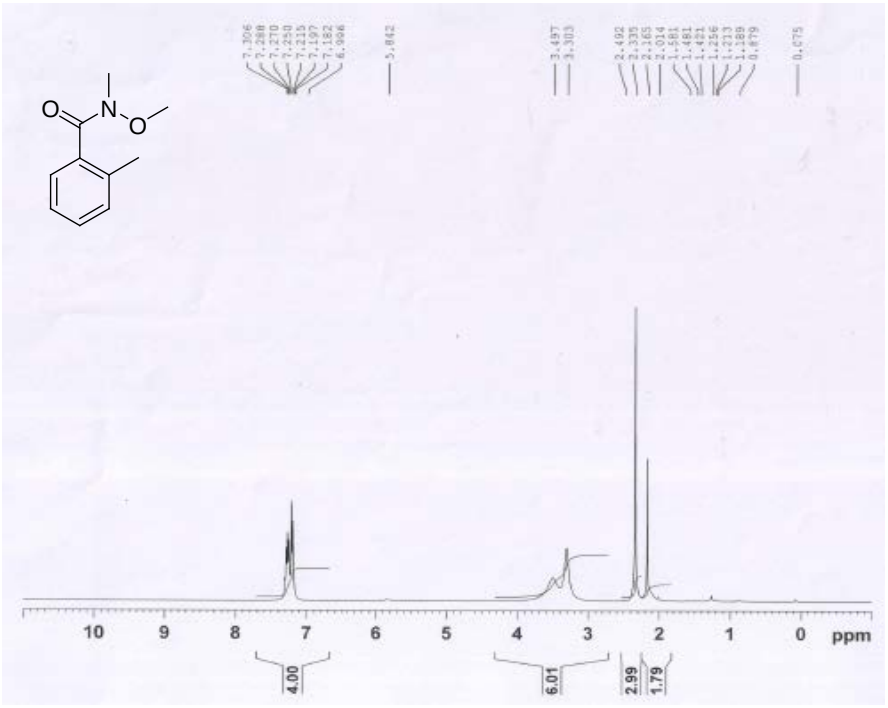

O
N
O
F
F
165.211
165.096
163.705
163.587
160.750
160.632
158.242
158.118
130.476
119.858
119.622
119.688
119.449
111.732
111.536
104.661
104.306
104.053
77.477
77.159
76.841
61.385
32.777
200
180
160
140
120
100
80
60
40
20
ppm

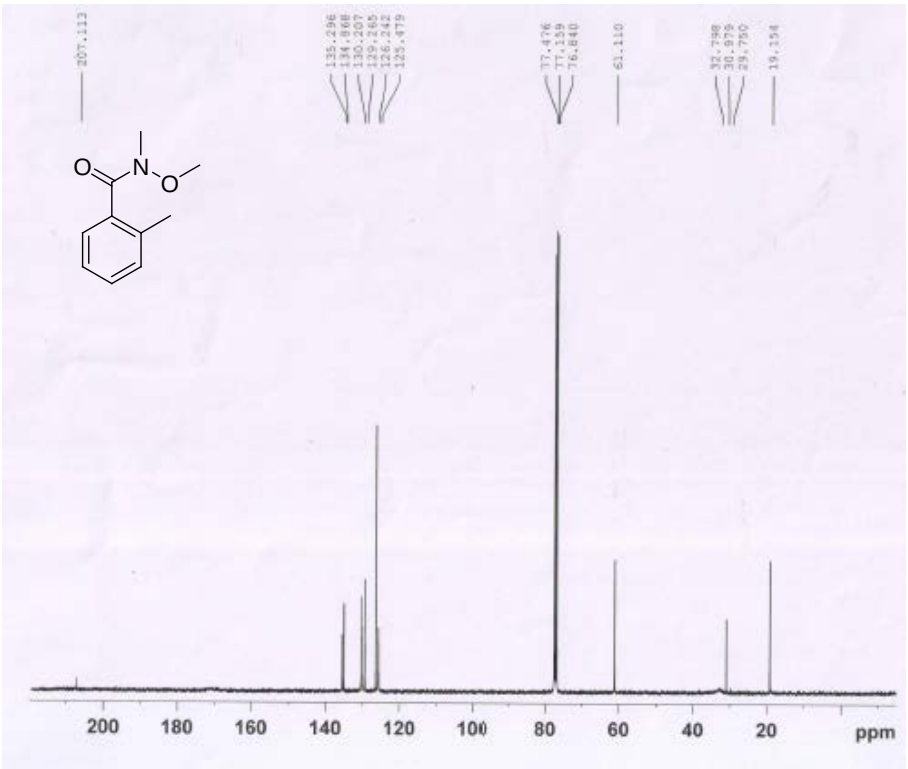
29. 2g


9.059
9.594
8.063
8.044
7.400
7.388
7.370
7.284
4.922
3.444
3.436
3.392
2.699
2.166
1.247
0.871
0.066
O
N
O
N
10
9
8
7
6
5
4
3
2
1
0
ppm
1.07
1.05
1.00
1.04
0.28
3.32
3.21

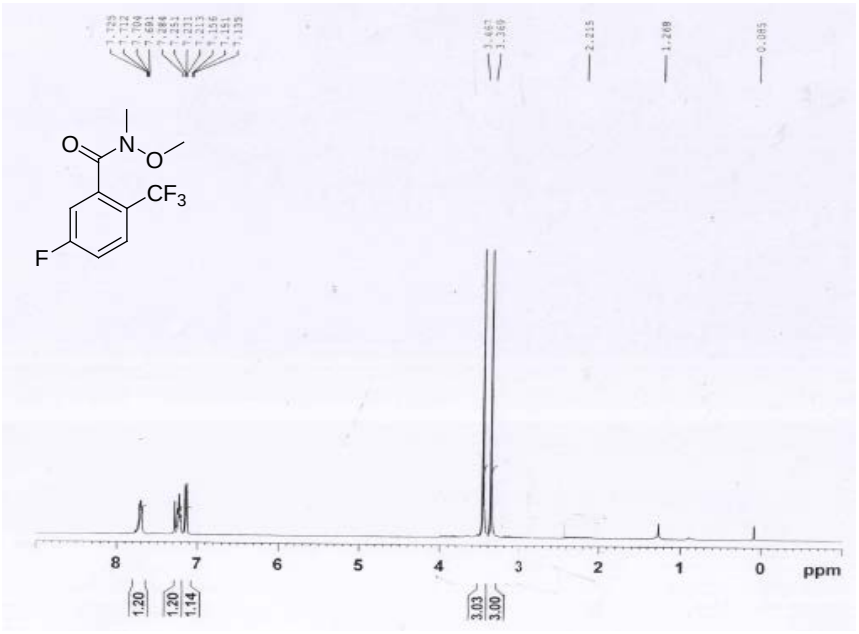

167.319
151.138
149.090
136.569
130.085
123.243
77.477
77.159
76.841
61.400
33.276
31.012
29.766
1.097
O
N
O
N
200
180
160
140
120
100
80
60
40
20
ppm

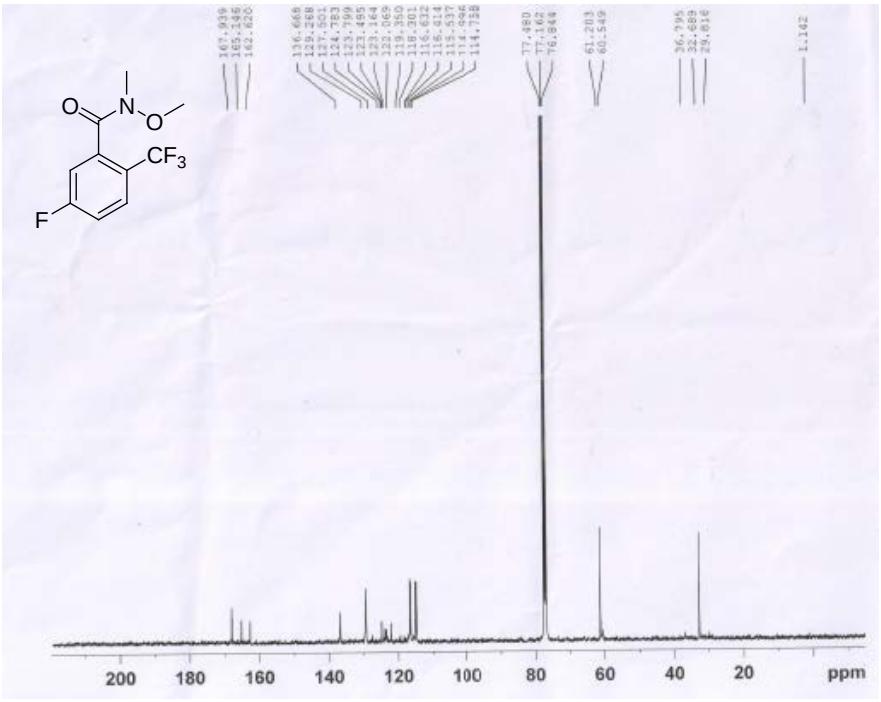
30. 2h

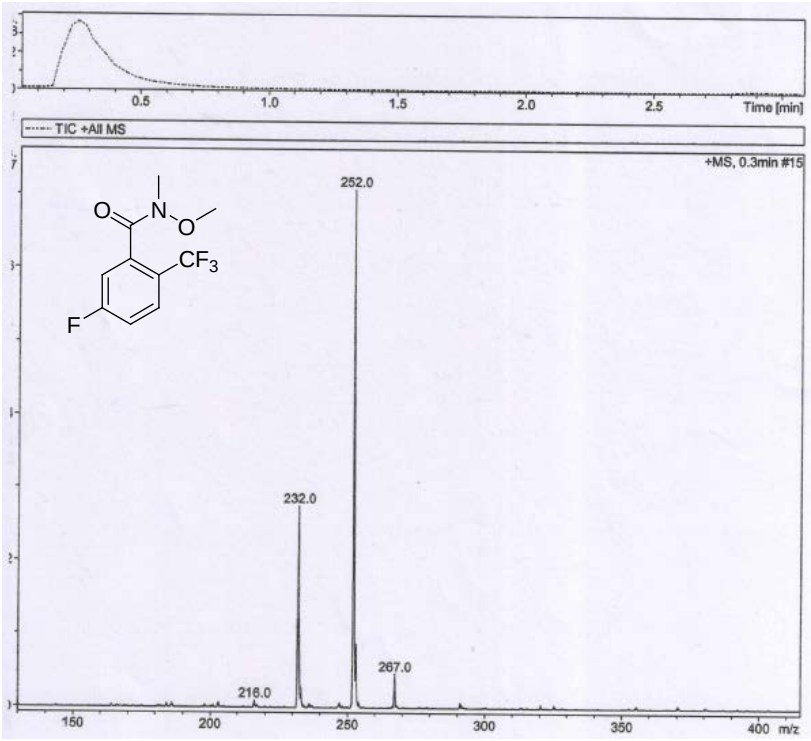

7.306
7.288
7.270
7.250
7.215
7.197
7.182
6.996
5.842
3.497
3.303
2.492
2.335
2.165
2.014
1.681
1.661
1.421
1.256
1.213
1.189
0.879
0.675
O
N
O
10
9
8
7
6
5
4
3
2
1
0
ppm
4.00
6.01
2.99
1.79


207.113
135.296
134.868
130.207
129.265
126.242
125.479
77.476
77.159
76.840
61.110
32.798
30.979
29.750
19.154
O
N
O
200
180
160
140
120
100
80
60
40
20
ppm

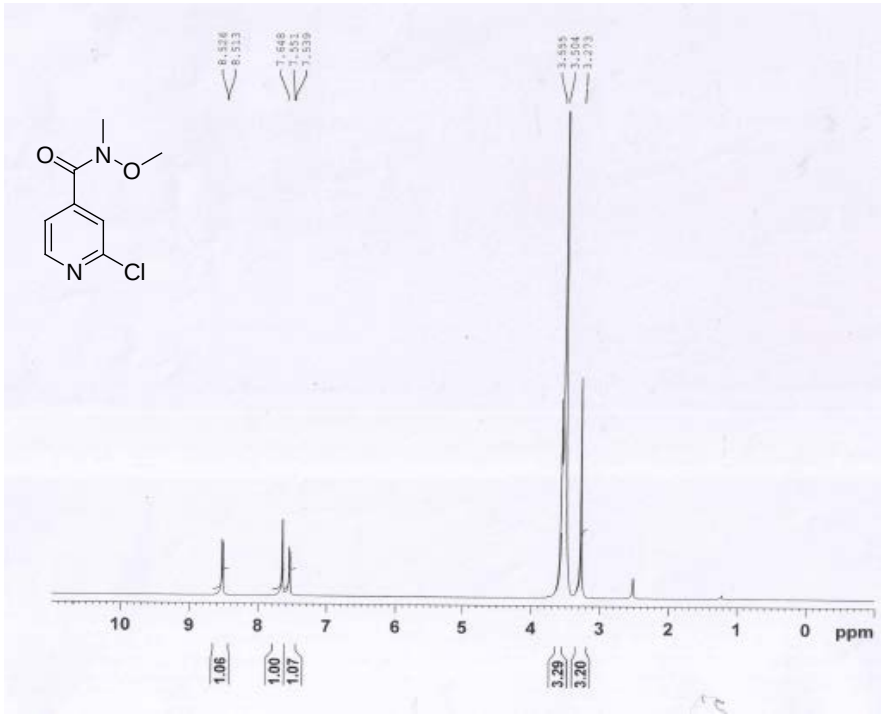
31. 2i

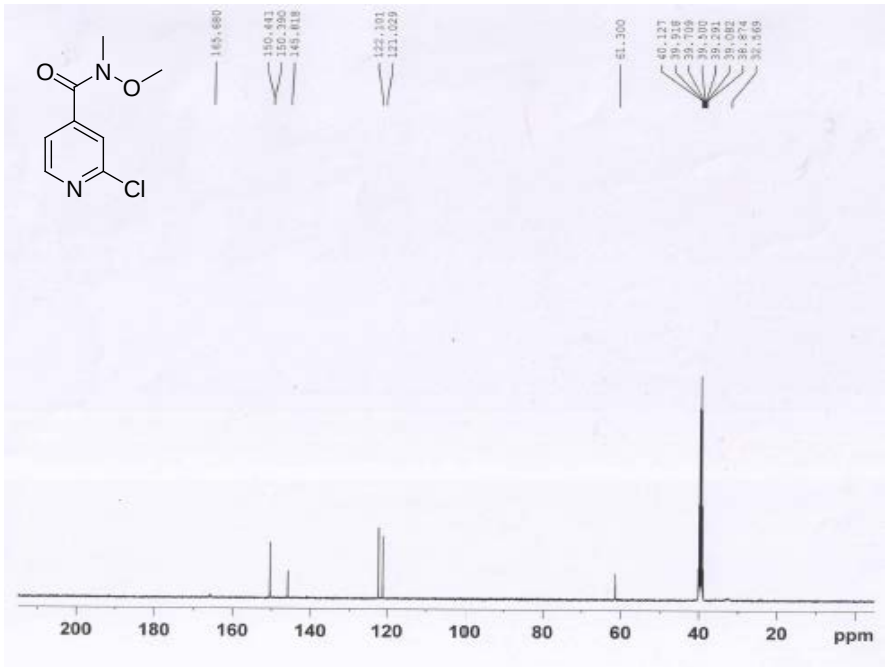

O
N
O
CF3
F
8
7
6
5
4
3
2
1
0
ppm


O
N
O
CF3
F
200
180
160
140
120
100
80
60
40
20
ppm

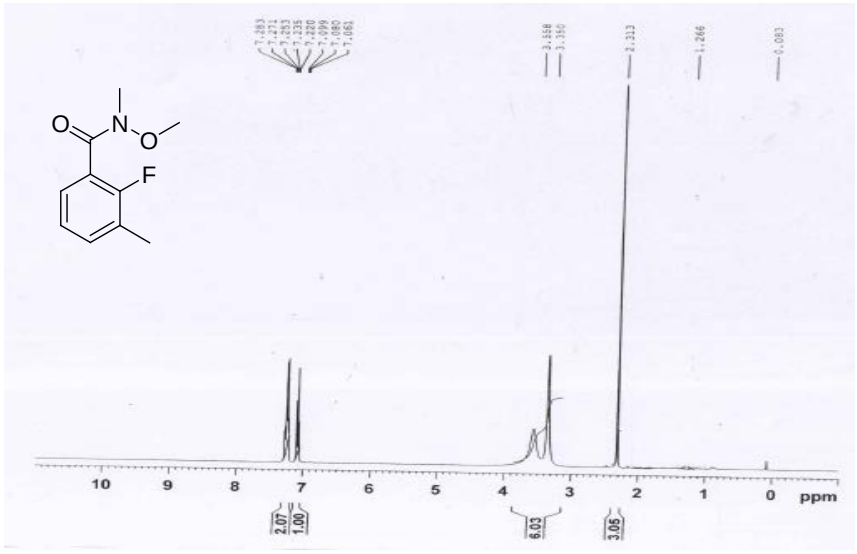

0.5
1.0
1.5
2.0
2.5
Time [min]
TIC +All MS
+MS, 0.3min #15
252.0
232.0
267.0
216.0
150
200
250
300
350
400 m/z
O
N
O
CF3
F

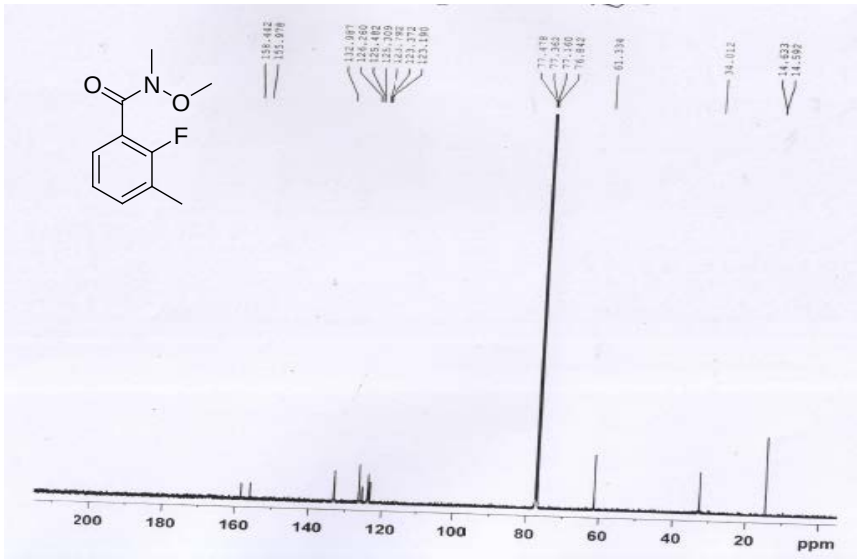
32.2j


8.526
8.513
7.648
7.551
7.539
3.595
3.504
3.273
O
N
O
N
Cl
10
9
8
7
6
5
4
3
2
1
0
ppm
1.06
1.00
1.07
3.29
3.20

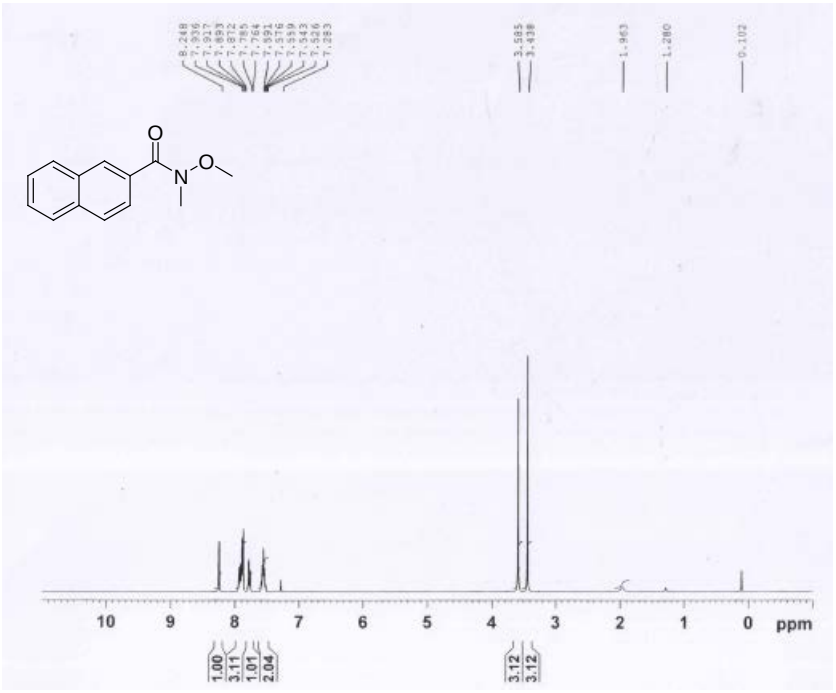

165.680
150.443
150.390
145.818
122.101
121.029
61.300
40.127
39.918
39.708
39.500
39.291
39.082
38.874
32.569
O
N
O
N
Cl
200
180
160
140
120
100
80
60
40
20
ppm

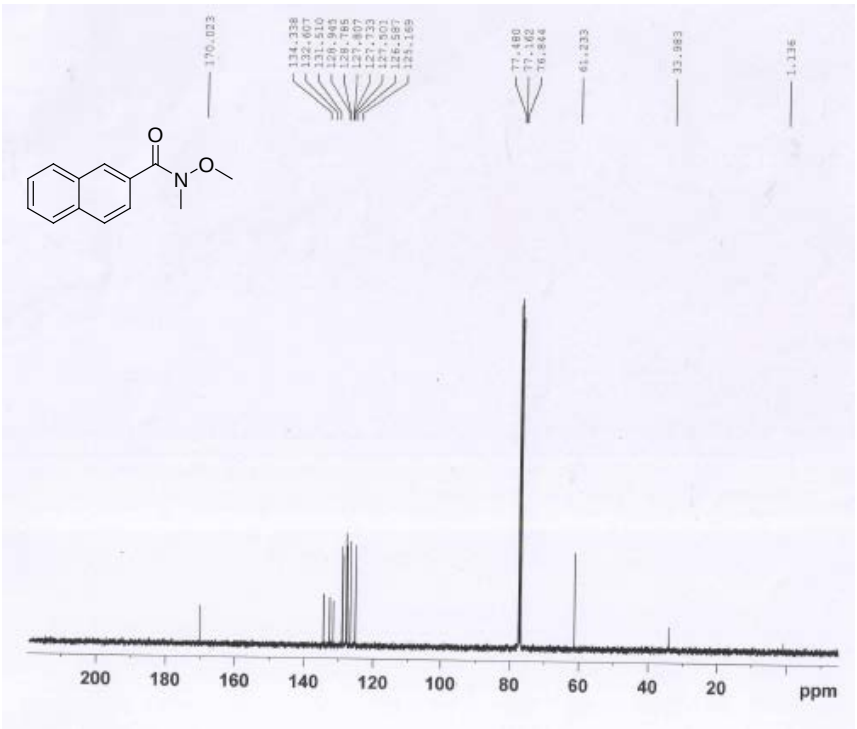
33. 2k

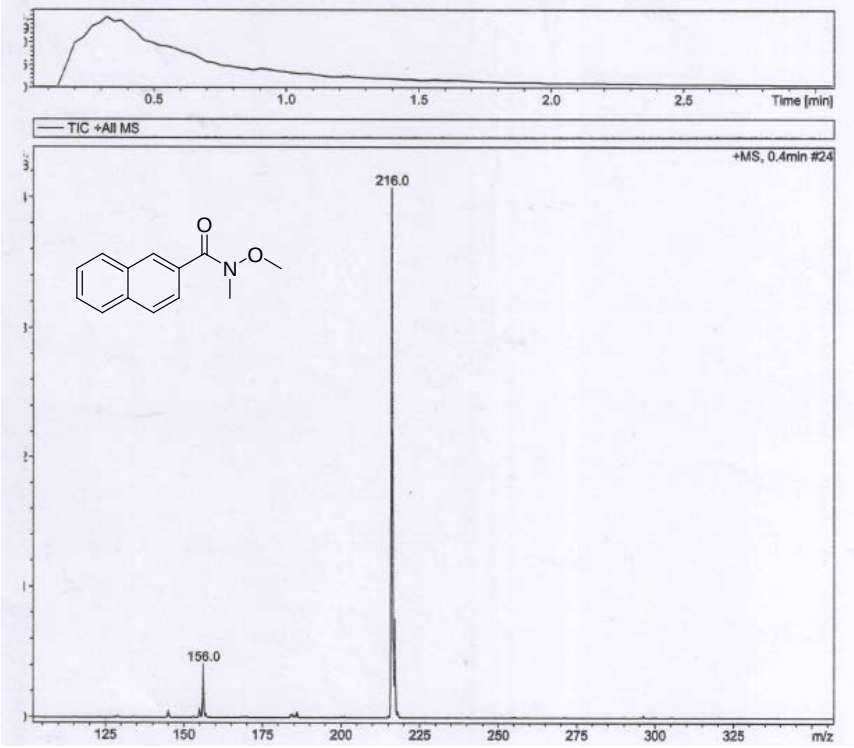

O
N
O
F
7.283
7.271
7.253
7.226
7.099
7.080
7.061
3.358
3.350
2.333
1.266
0.083
10
9
8
7
6
5
4
3
2
1
0
ppm
2.07
1.00
6.03
3.05


O
N
O
F
138.442
135.978
132.987
126.280
125.482
125.309
123.792
123.372
123.190
77.478
77.363
77.160
76.842
61.334
34.012
14.623
14.592
200
180
160
140
120
100
80
60
40
20
ppm

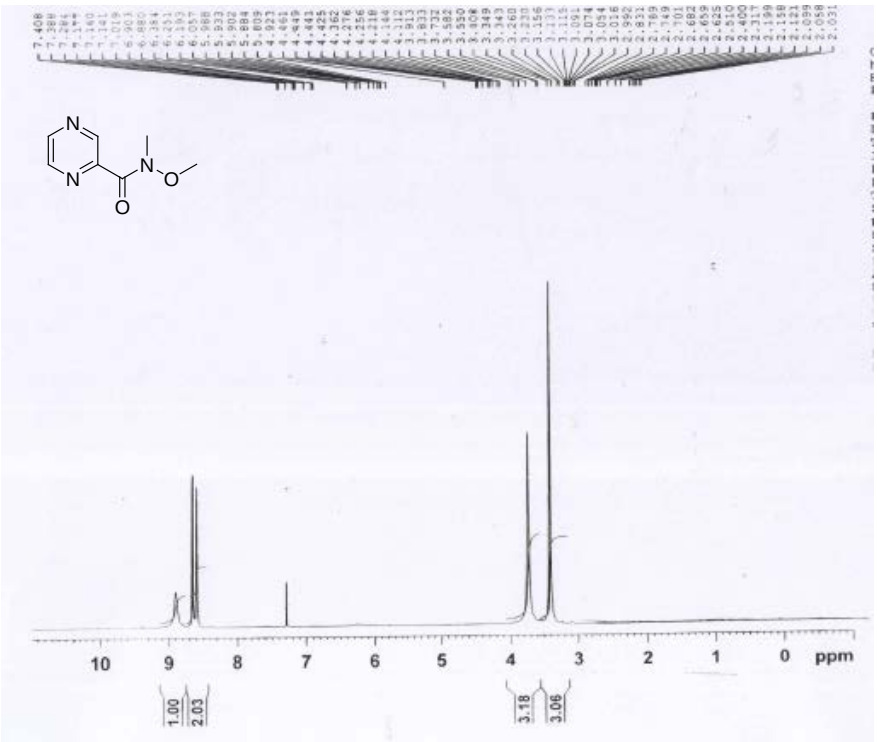
34. 2l

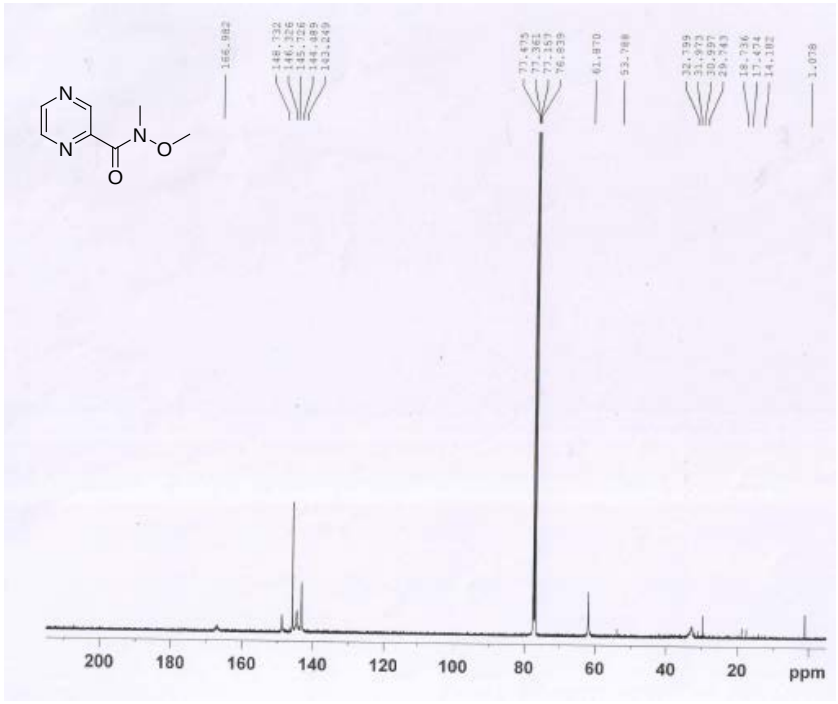

8.248
7.936
7.917
7.893
7.872
7.785
7.764
7.581
7.576
7.559
7.543
7.526
7.283
3.585
3.438
1.963
1.280
0.102
O
N
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
3.11
1.01
2.04
3.12
3.12


170.023
134.338
132.607
131.510
129.943
128.785
127.807
127.733
127.501
126.587
125.169
77.480
77.162
76.844
61.233
32.983
1.136
O
N
O
200
180
160
140
120
100
80
60
40
20
ppm

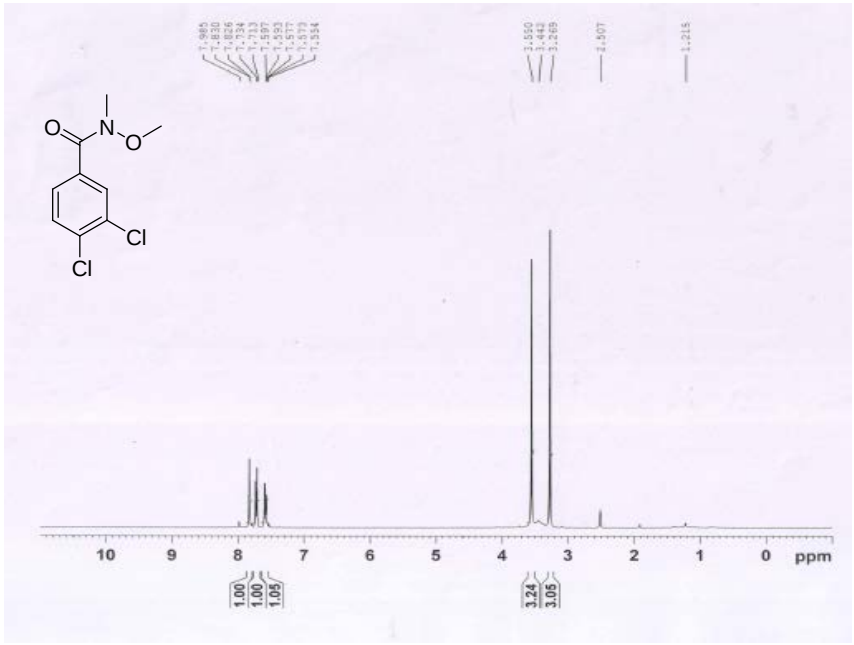


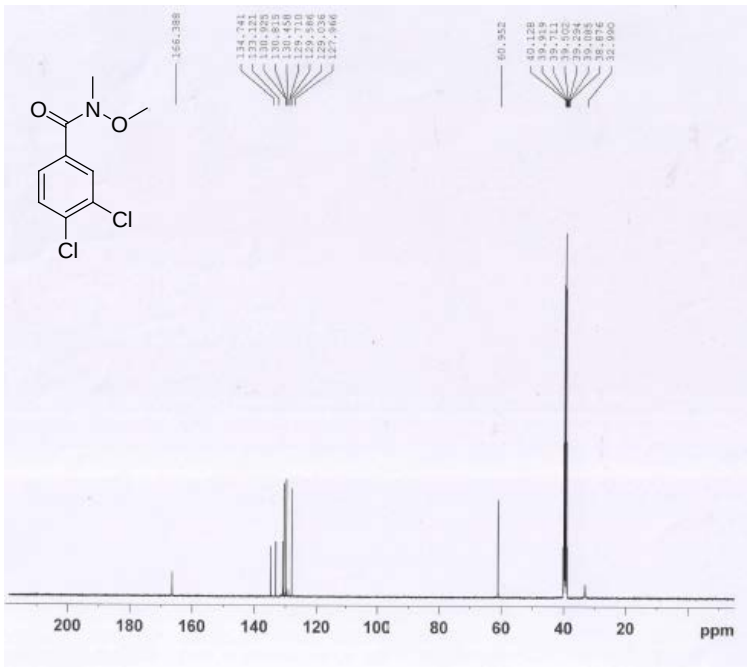
35. 2m

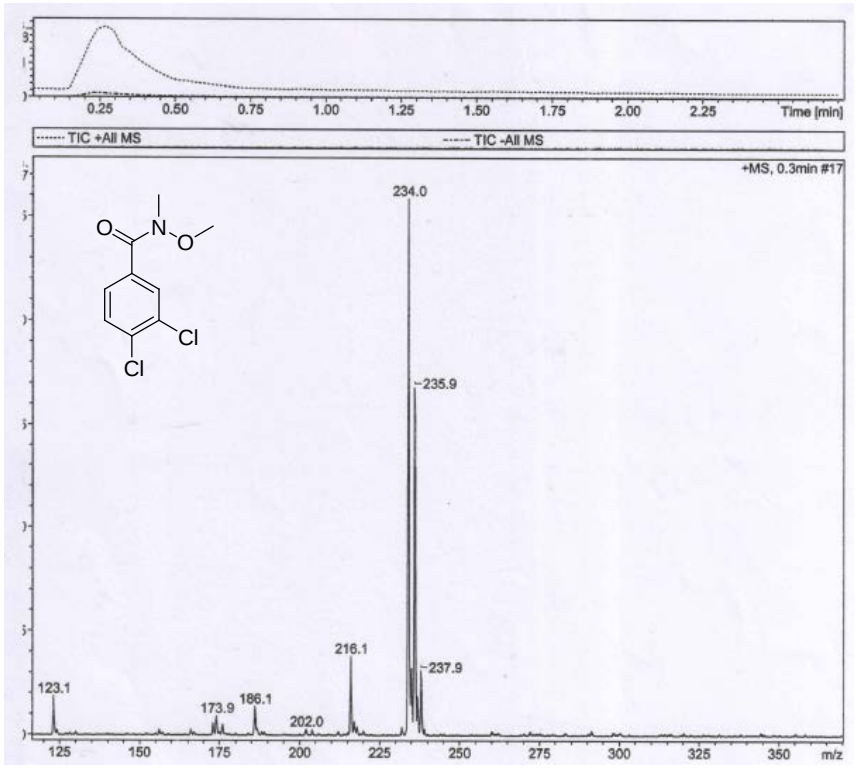



166.982
148.732
146.326
145.726
144.989
143.249
77.475
77.161
76.839
61.870
53.788
32.799
31.973
30.997
29.743
18.736
17.474
14.102
1.078
200
180
160
140
120
100
80
60
40
20
ppm

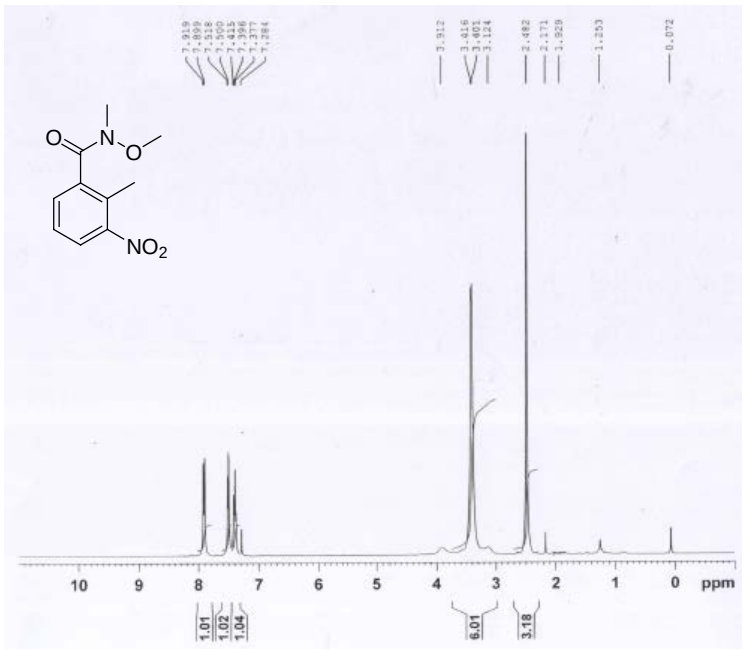
36. 2n

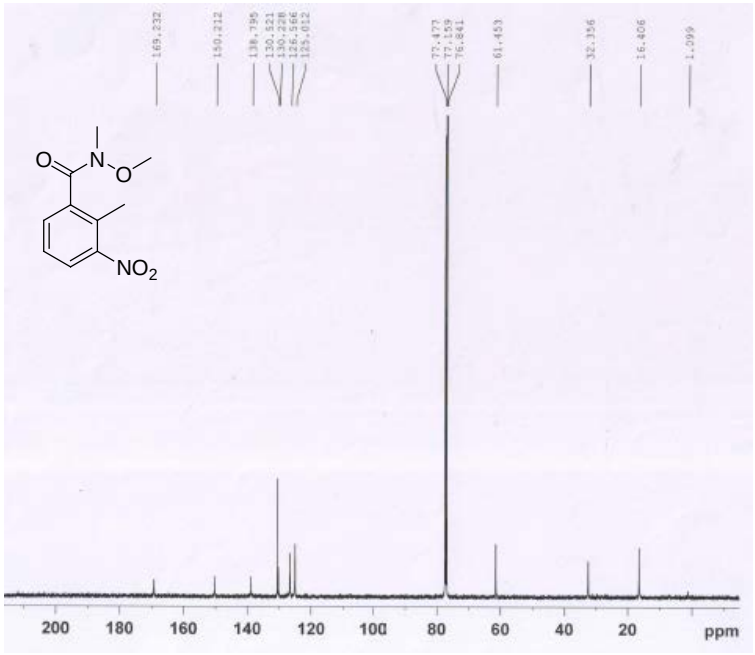

7.965
7.830
7.736
7.734
7.713
7.597
7.593
7.577
7.573
7.554
3.550
3.442
3.269
2.507
1.215
Cl
Cl
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.05
3.24
3.05


O
N
O
Cl
Cl
200
180
160
140
120
100
80
60
40
20
ppm

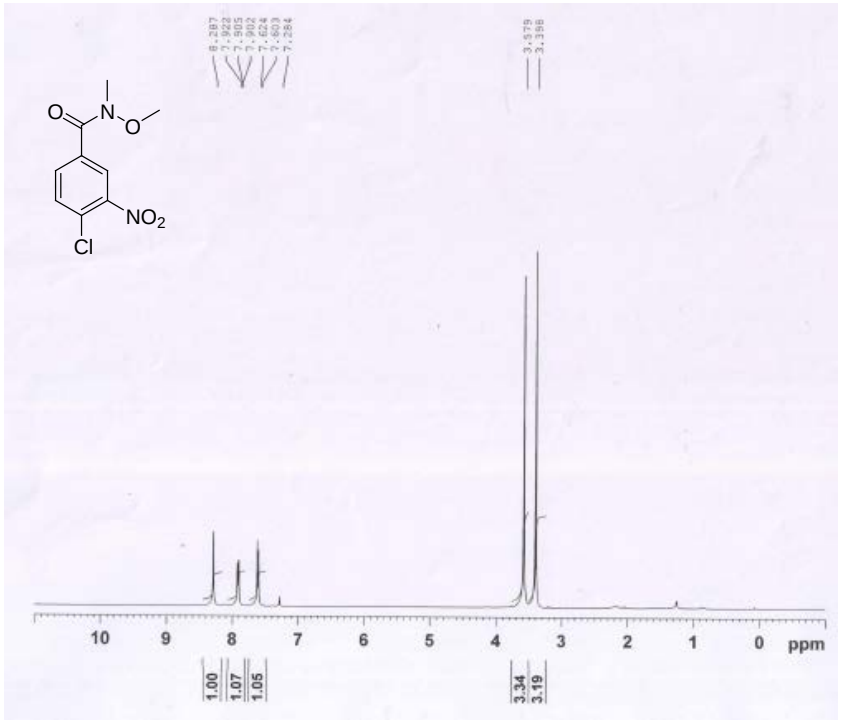

0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
2.25
Time [min]
TIC +All MS
TIC -All MS
+MS, 0.3min #17
234.0
235.9
216.1
237.9
123.1
173.9
186.1
202.0
125
150
175
200
225
250
275
300
325
350
m/z

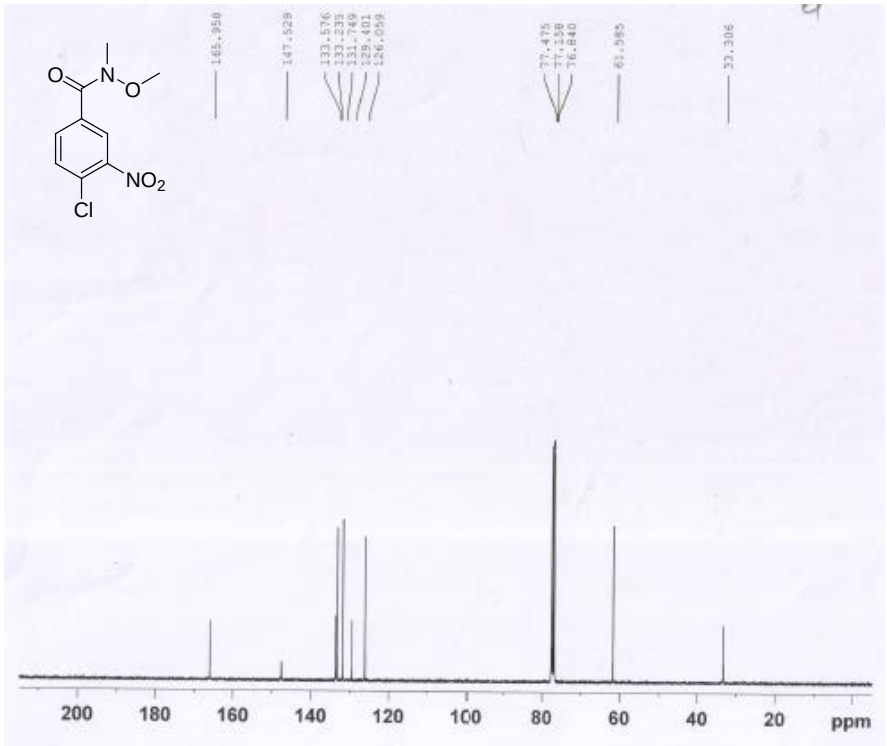
37. 2o


7.919
7.899
7.518
7.500
7.415
7.396
7.377
7.284
3.912
3.416
3.401
3.124
2.482
2.171
1.929
1.253
0.072
O
N
O
NO2
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.02
1.04
6.01
3.18

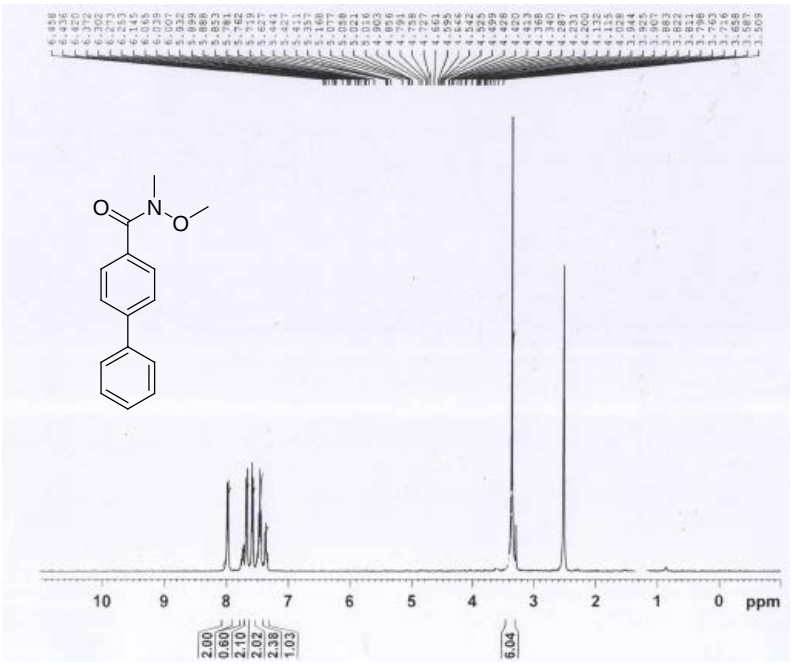

169.232
150.212
138.795
130.521
130.228
126.566
125.012
77.477
77.159
76.841
61.453
32.356
16.406
1.099
O
N
O
NO2
200
180
160
140
120
100
80
60
40
20
ppm

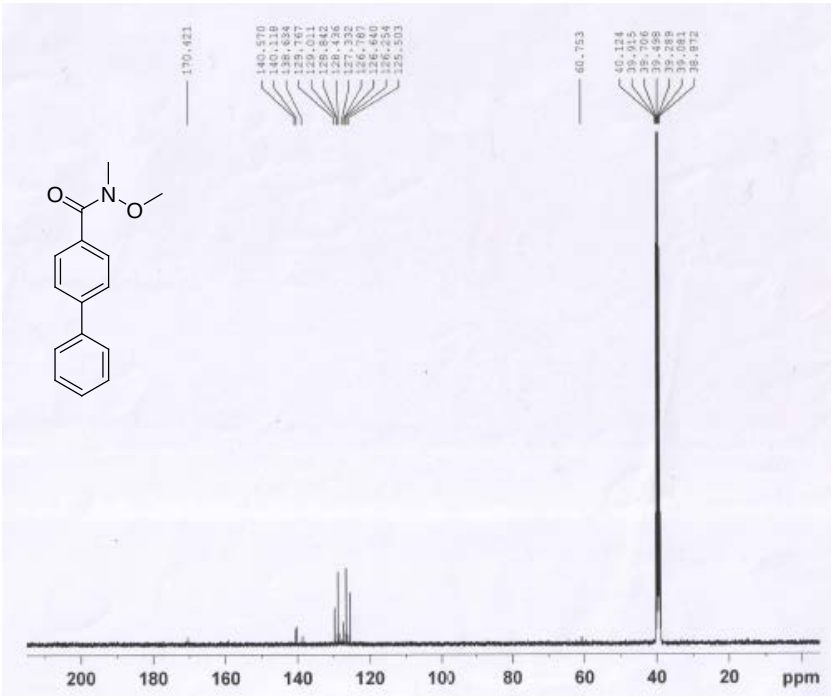
38.2p


8.287
7.922
7.905
7.902
7.624
7.609
7.284
3.379
3.398
O
N
O
NO2
Cl
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.07
1.05
3.34
3.19

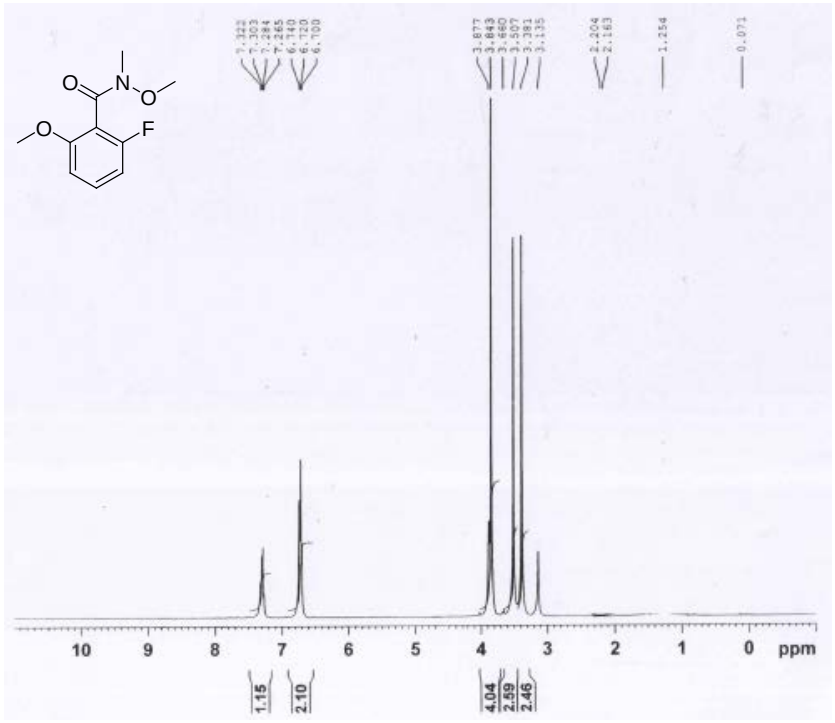

165.950
147.529
133.576
133.235
131.749
129.401
126.059
77.475
77.158
76.840
61.985
33.306
O
N
O
NO2
Cl
200
180
160
140
120
100
80
60
40
20
ppm

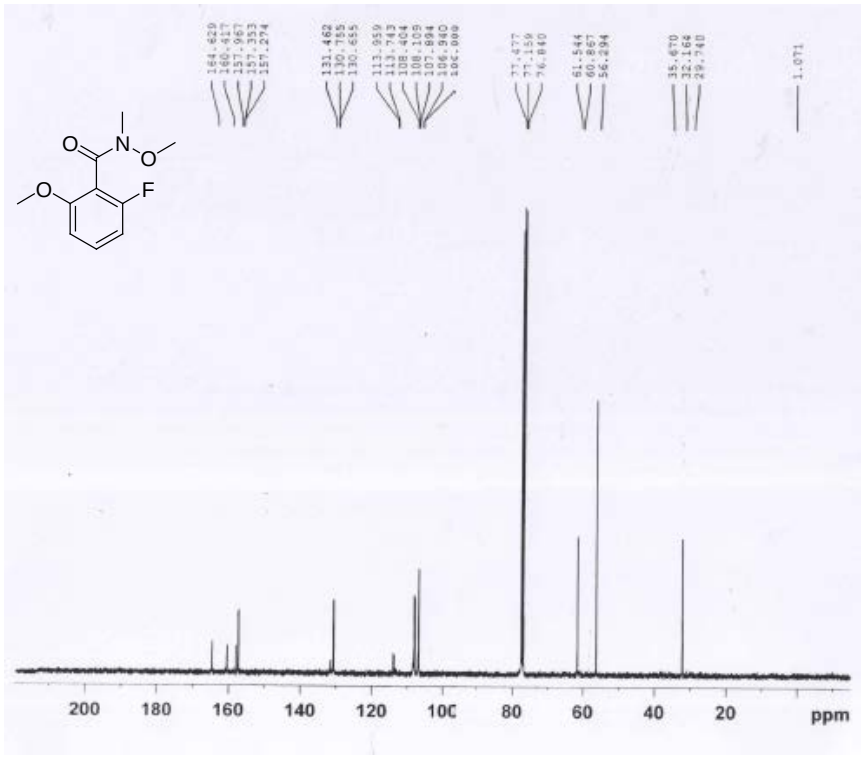
39. 2q

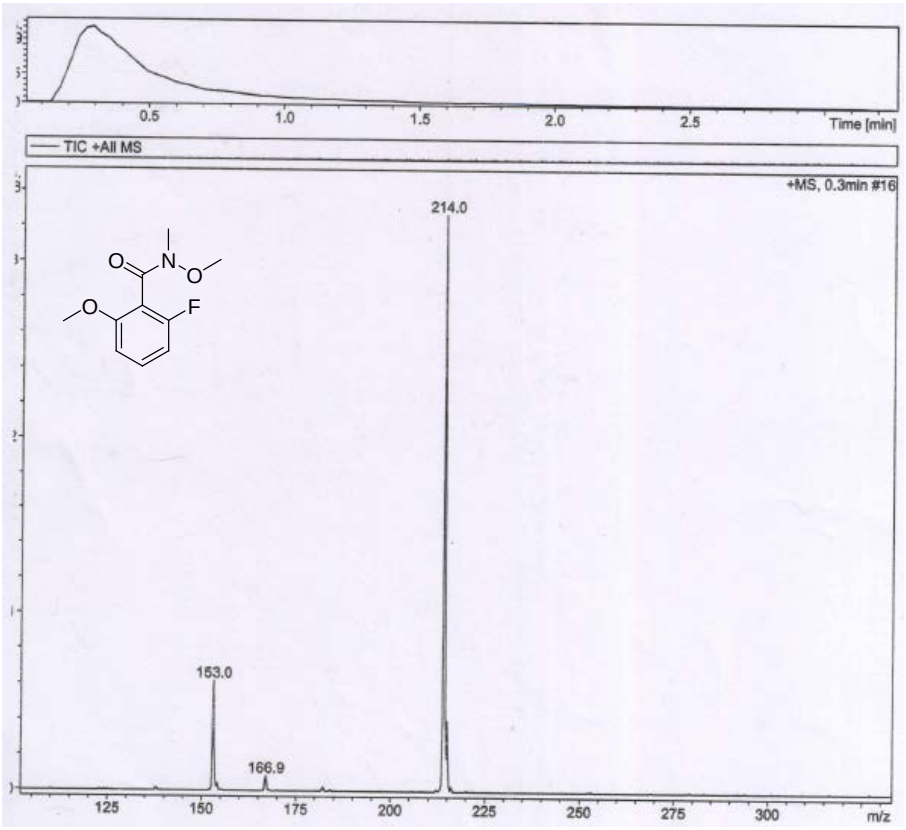

O
N
O
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
0.60
2.10
2.02
2.38
1.03
6.04


O
N
O
170.421
140.570
140.118
138.634
129.767
129.011
128.842
128.436
127.332
126.787
126.640
126.254
125.503
60.753
40.124
39.915
39.706
39.498
39.289
39.081
38.872
200
180
160
140
120
100
80
60
40
20
ppm

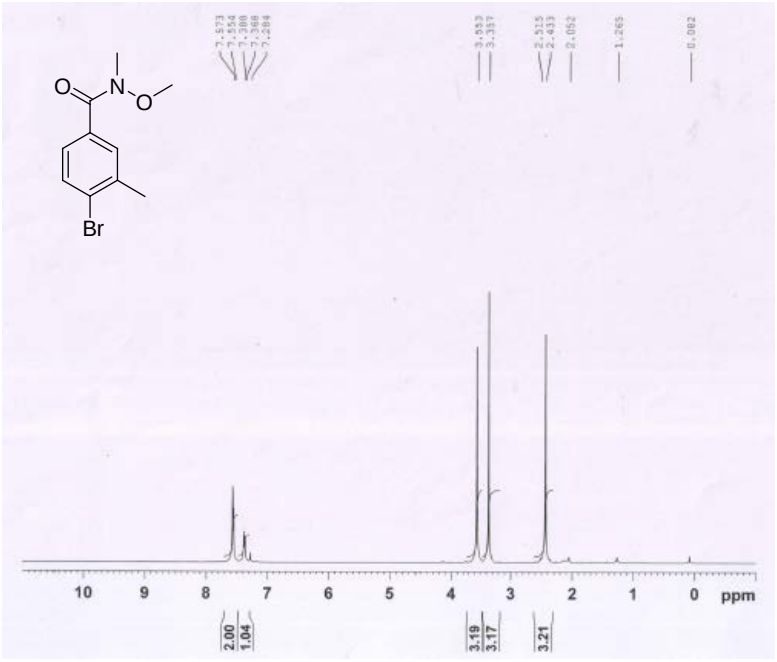
40. 2r

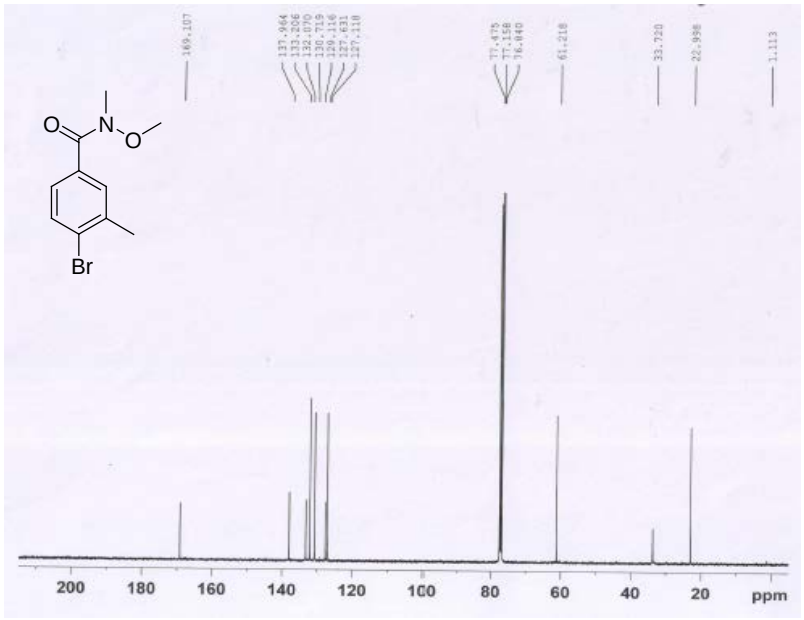

7.322
7.303
7.284
7.265
6.740
6.720
6.700
3.877
3.843
3.680
3.507
3.381
3.135
2.204
2.183
1.254
0.071
O
N
O
O
F
10
9
8
7
6
5
4
3
2
1
0
ppm
1.15
2.10
4.04
2.59
2.46


164.629
160.417
157.967
157.353
157.294
131.462
130.765
130.665
113.959
113.743
108.404
108.109
107.894
106.940
106.000
77.477
77.159
76.840
61.544
60.867
56.894
35.670
32.164
29.748
1.071
O
N
O
O
F
200
180
160
140
120
100
80
60
40
20
ppm

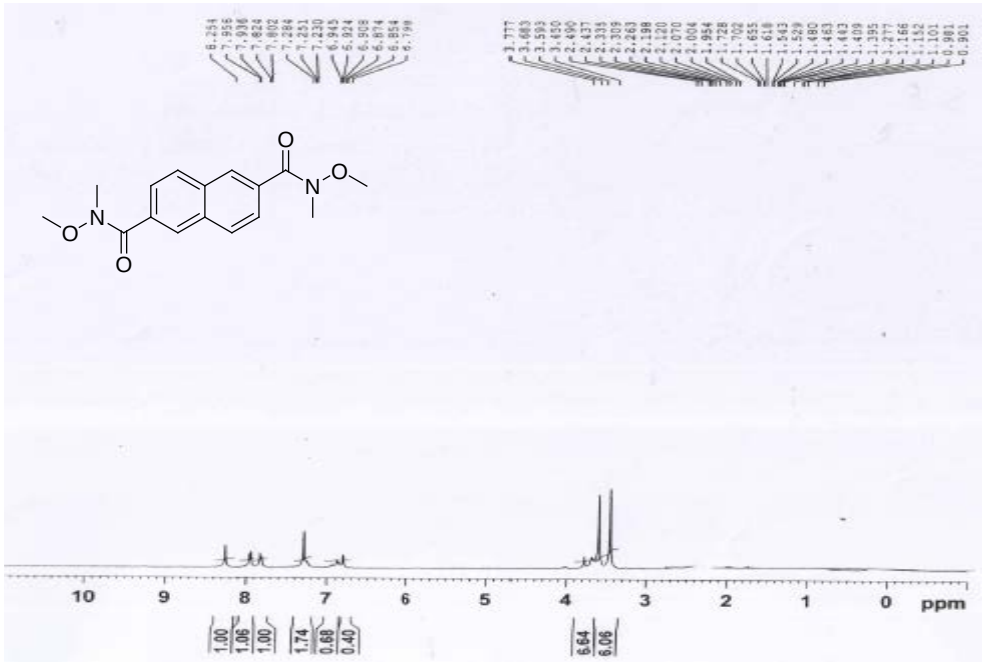


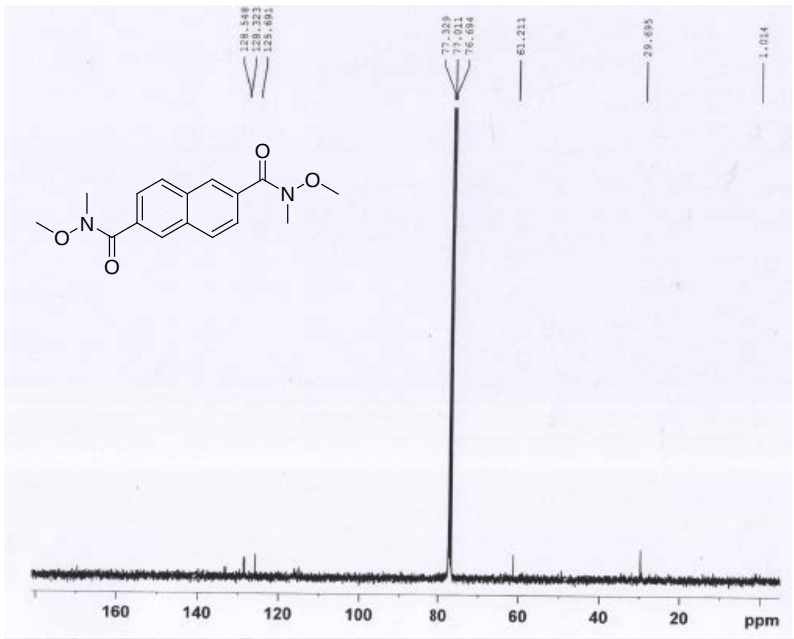
41. 2s

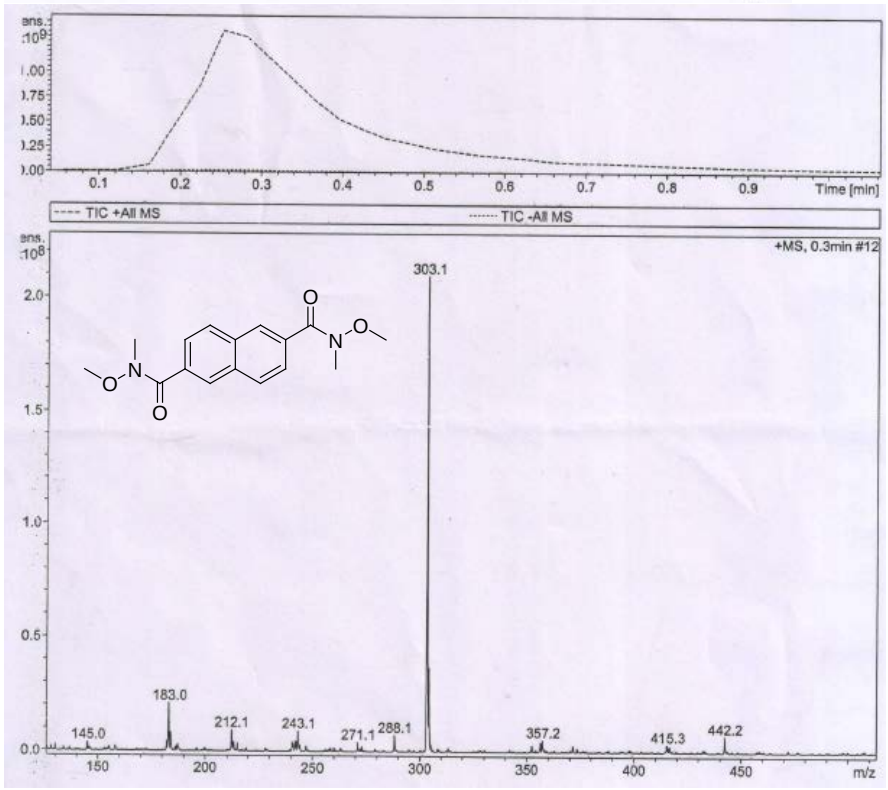



O
N
O
Br
200
180
160
140
120
100
80
60
40
20
ppm

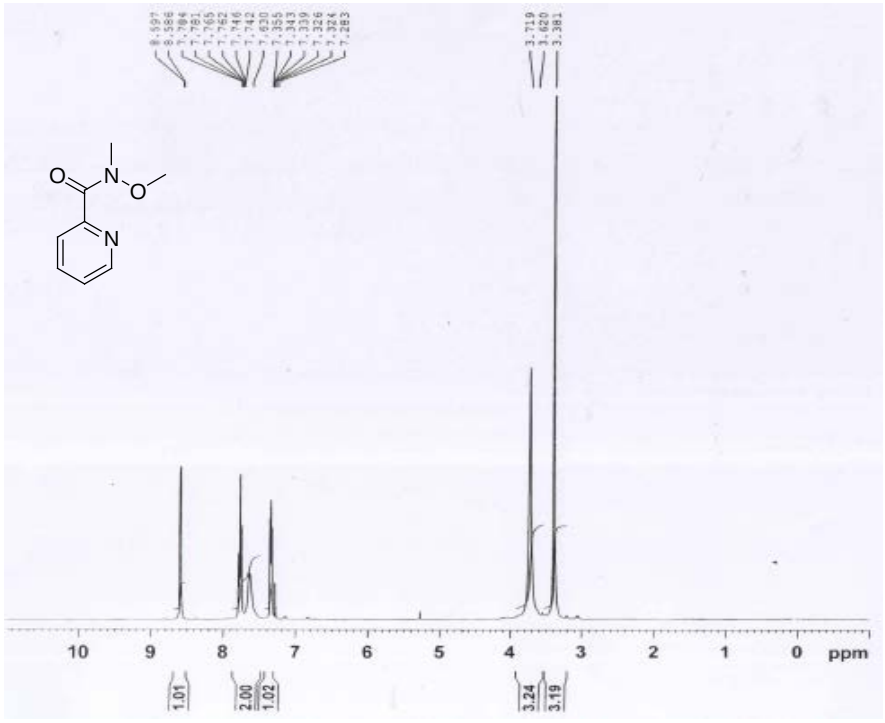
42.2x[c]

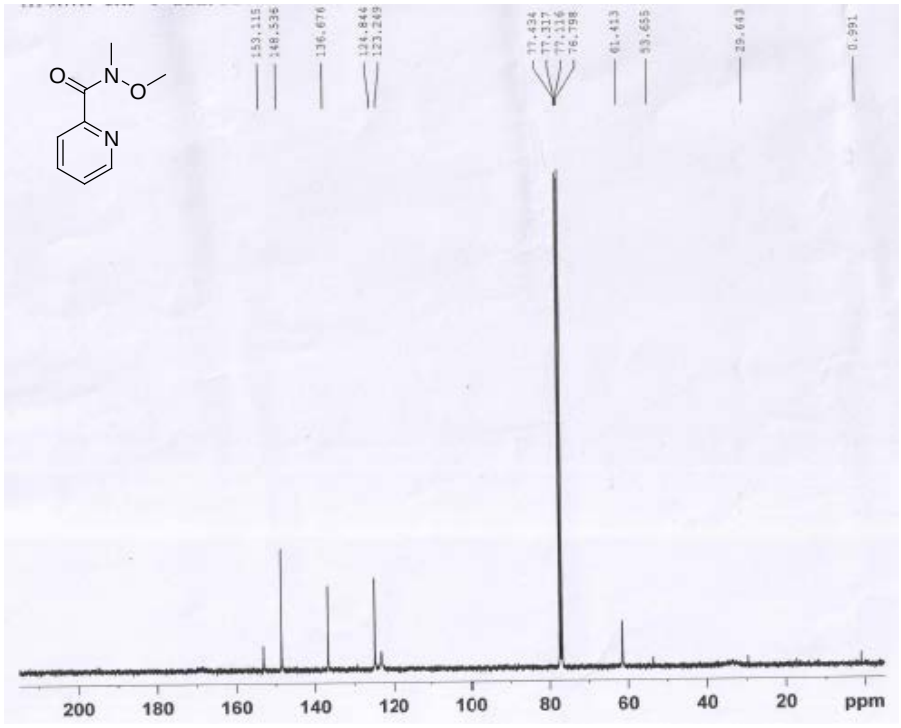

O
N
O
O
N
O
10
9
8
7
6
5
4
3
2
1
0
ppm


128.548
128.323
128.098
77.329
77.011
76.694
61.211
29.695
1.014
160
140
120
100
80
60
40
20
ppm

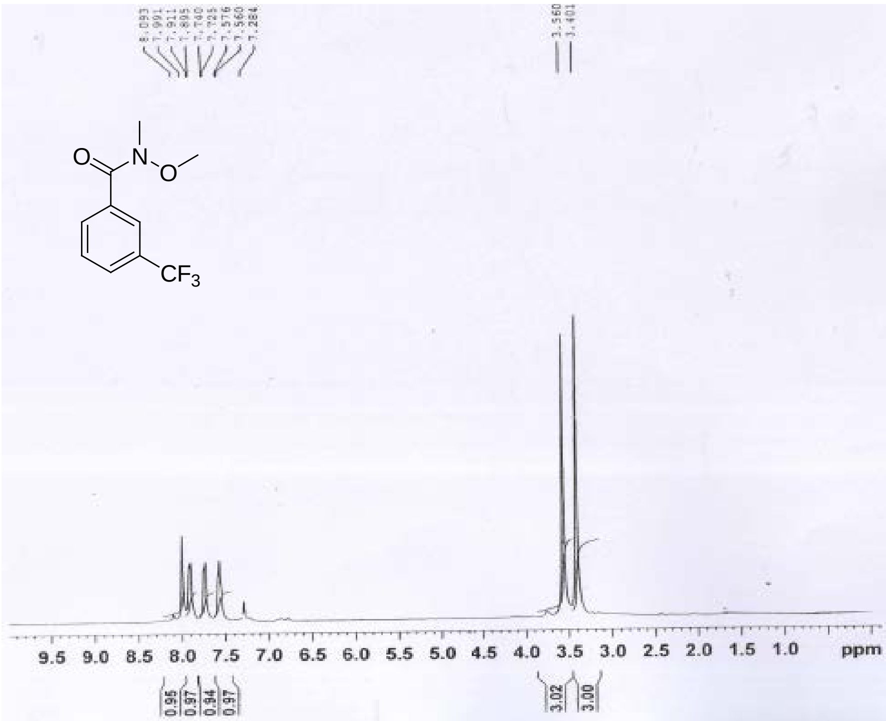

Time [min]
TIC +All MS
TIC -All MS
+MS, 0.3min #12
303.1
183.0
145.0
212.1
243.1
271.1
288.1
357.2
415.3
442.2
m/z

43.2zb

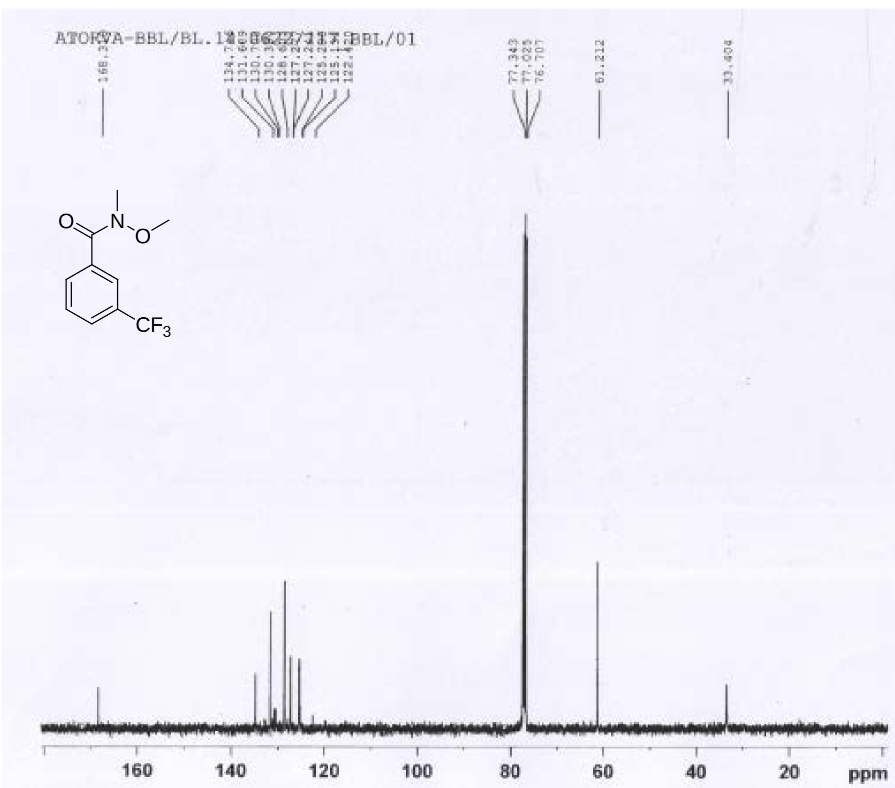

8.597
8.586
7.784
7.781
7.765
7.762
7.746
7.742
7.630
7.355
7.343
7.339
7.326
7.324
7.283
3.719
3.620
3.381
O
N
O
N
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
2.00
1.02
3.24
3.19


153.115
148.536
136.676
124.844
123.249
77.434
77.317
77.116
76.798
61.413
33.655
29.643
0.991
O
N
O
N
200
180
160
140
120
100
80
60
40
20
ppm

44 .2zd



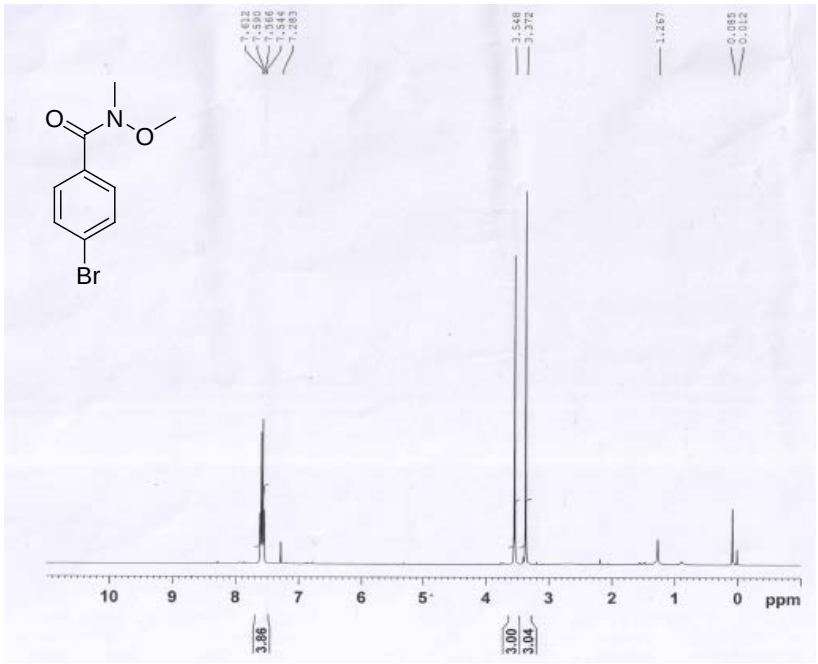
8.093
7.991
7.911
7.895
7.740
7.725
7.576
7.560
7.284
3.560
3.401
O
N
O
CF3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.95
0.97
0.94
0.97
3.02
3.00

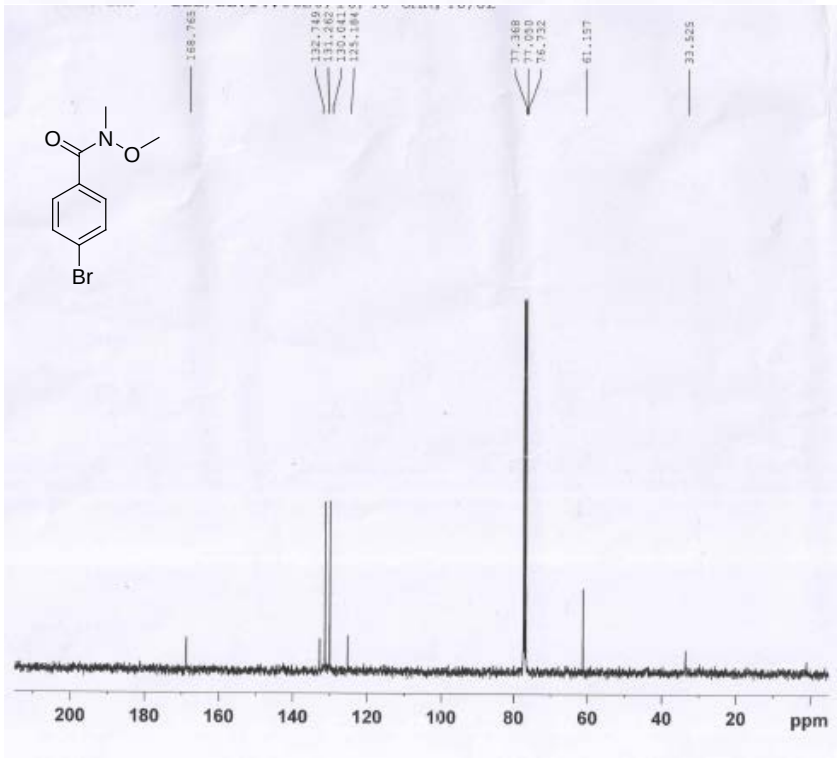


77.343
77.025
76.707
61.212
33.404
O
N
O
CF3
160
140
120
100
80
60
40
20
ppm

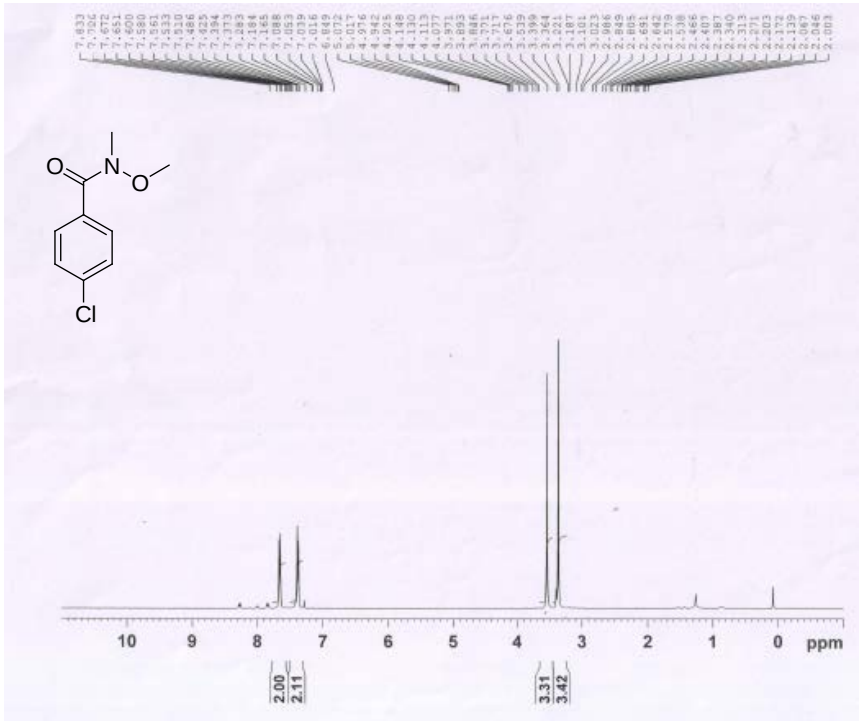
3.3 Spectral data of compounds 3a-c

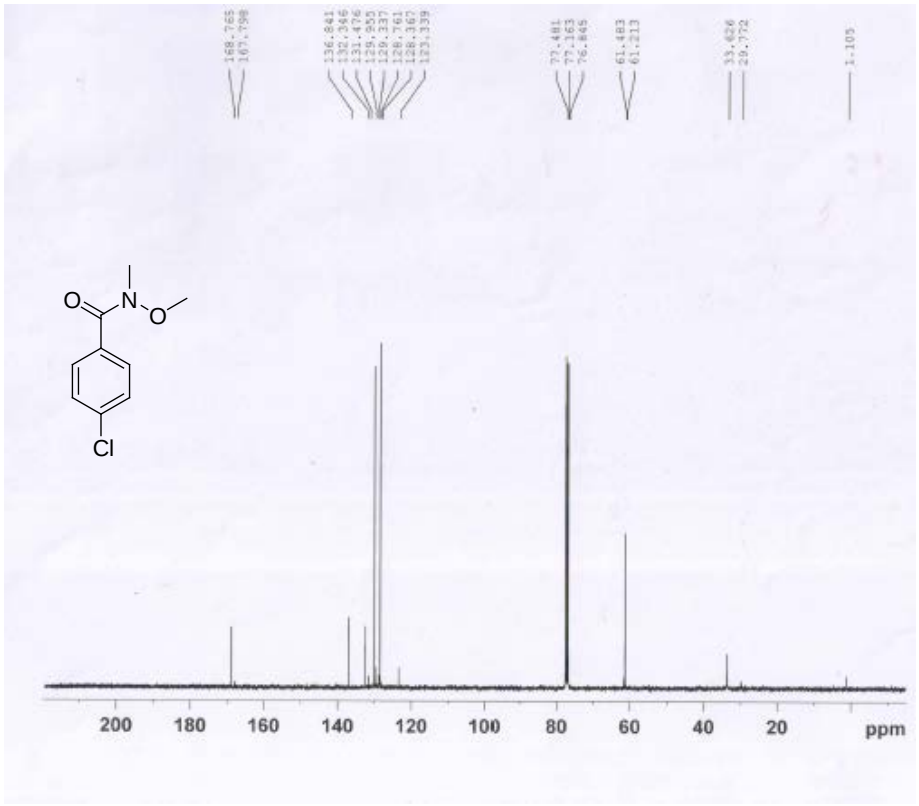
45. 3b





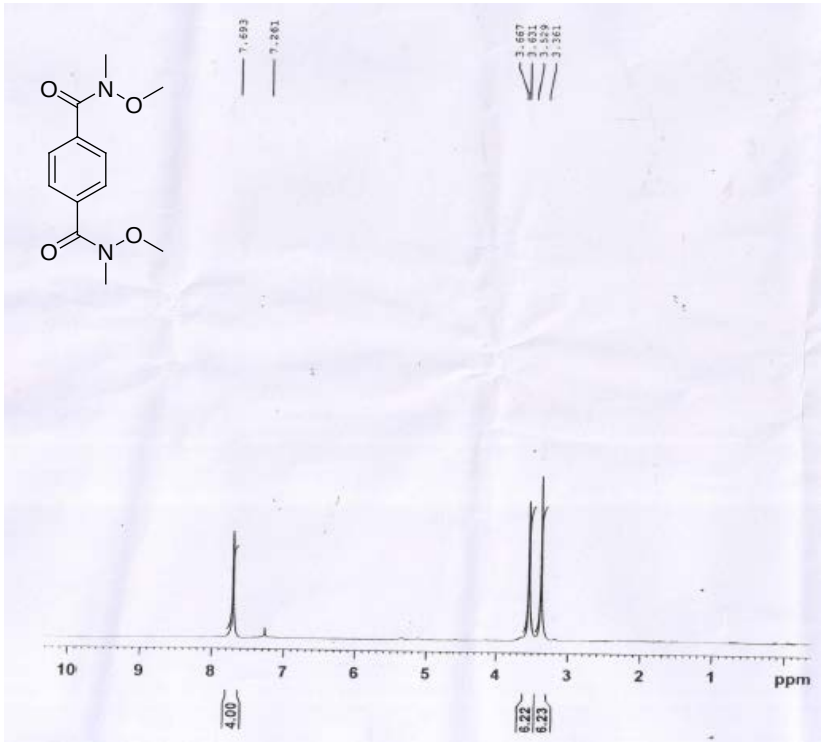
46. 3c

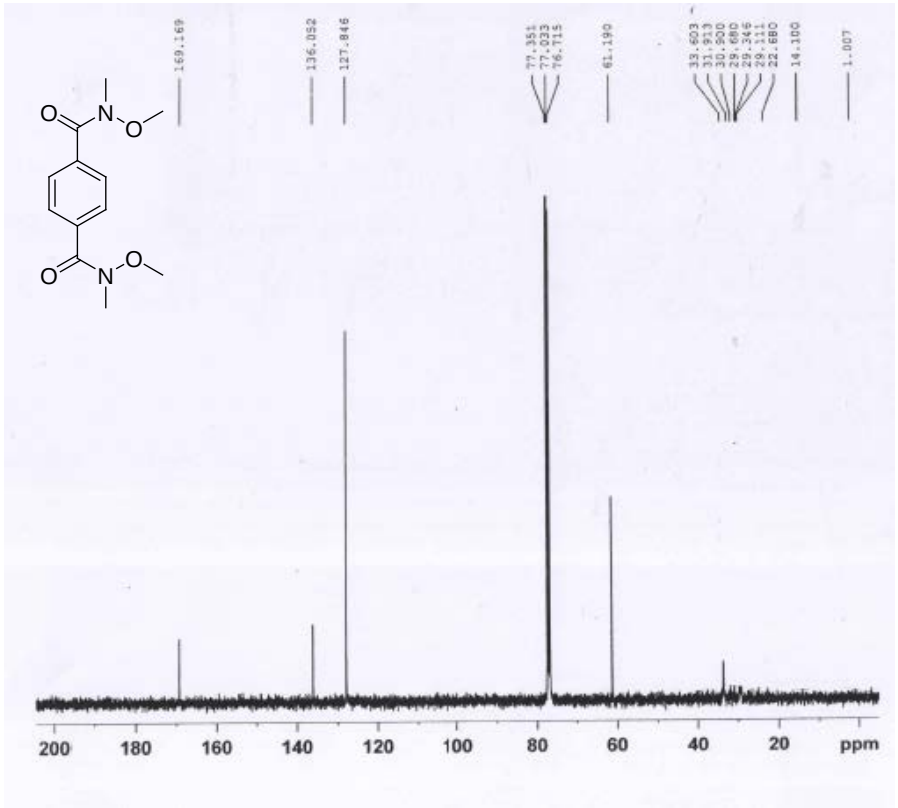

O
N
O
Cl
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.11
3.31
3.42

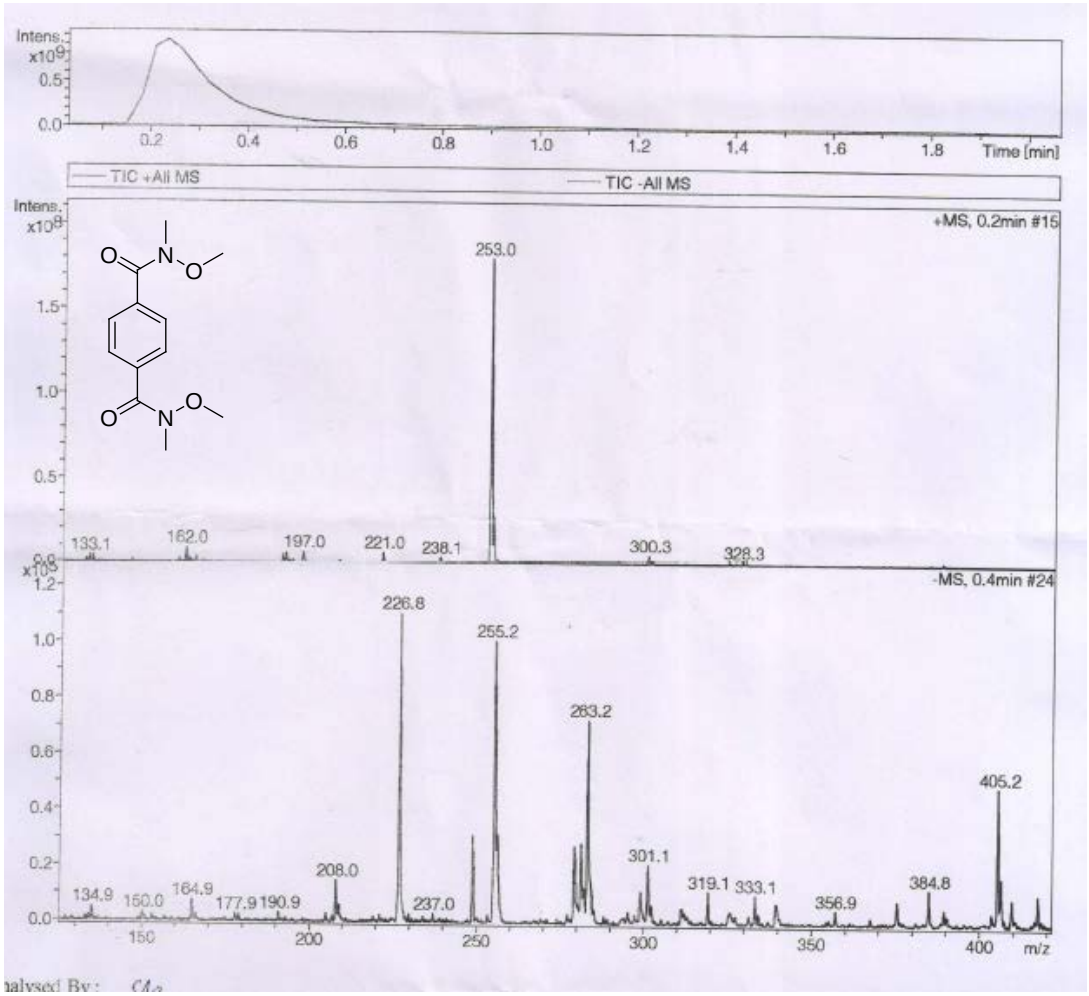

O
N
O
Cl
200
180
160
140
120
100
80
60
40
20
ppm

3.4 Spectral data of compound 4

47. 4

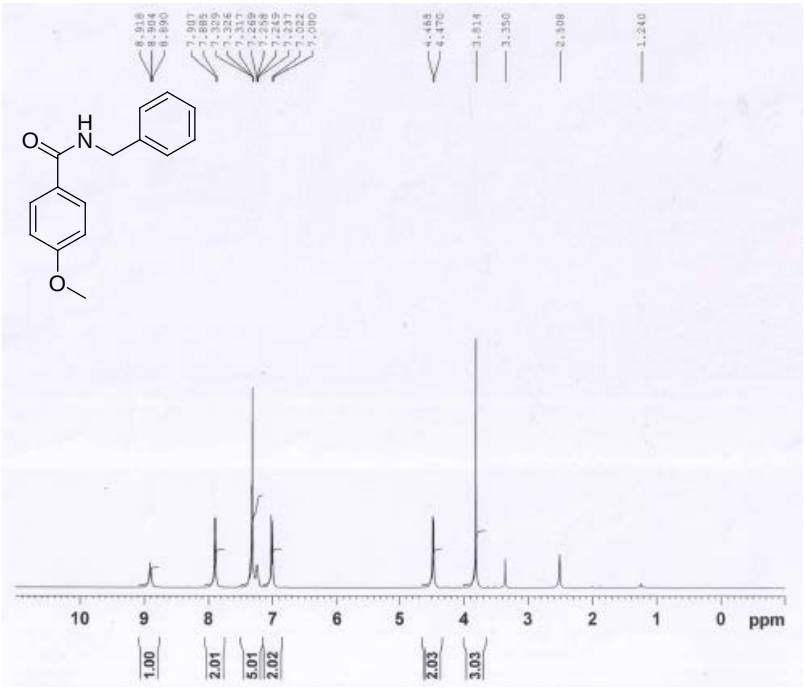


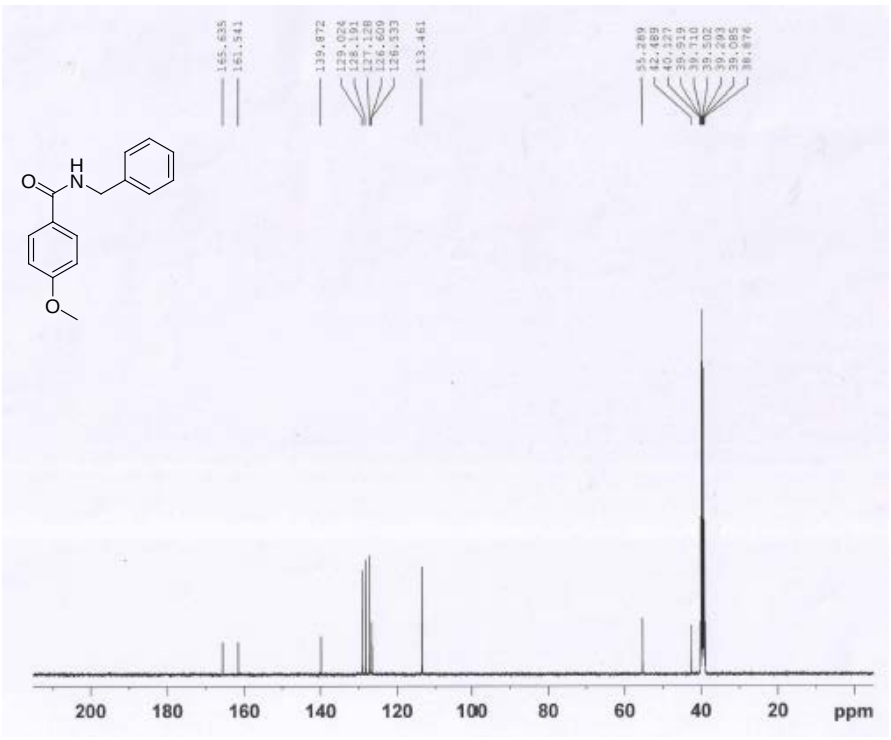


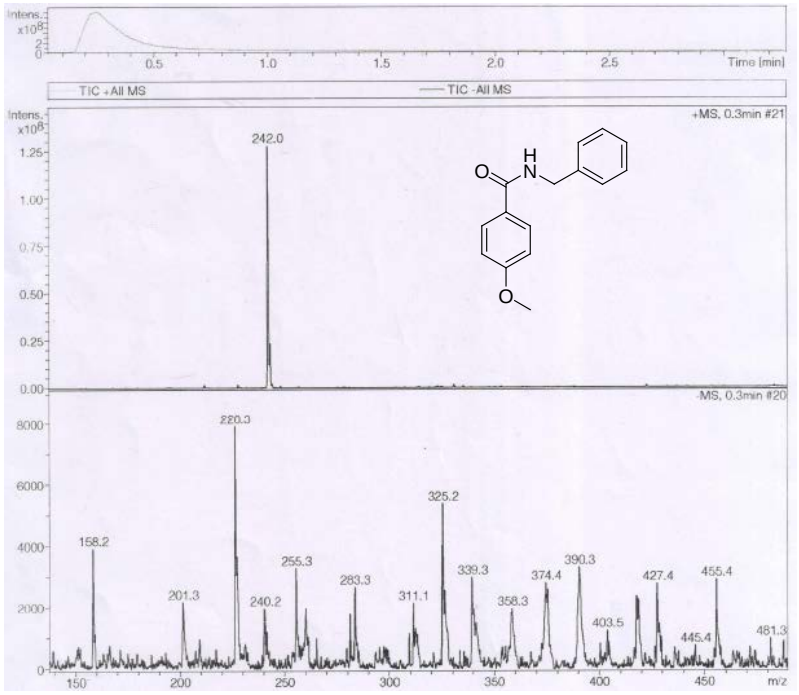

Intens.
x10^9
0.5
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
Time [min]
TIC +All MS
TIC -All MS
Intens.
x10^8
+MS, 0.2min #15
253.0
1.5
1.0
0.5
133.1
162.0
197.0
221.0
238.1
300.3
328.3
x10^5
-MS, 0.4min #24
226.8
255.2
263.2
405.2
1.2
1.0
0.8
0.6
0.4
0.2
0.0
208.0
301.1
319.1
333.1
384.8
134.9
150.0
164.9
177.9
190.9
237.0
356.9
150
200
250
300
350
400
m/z

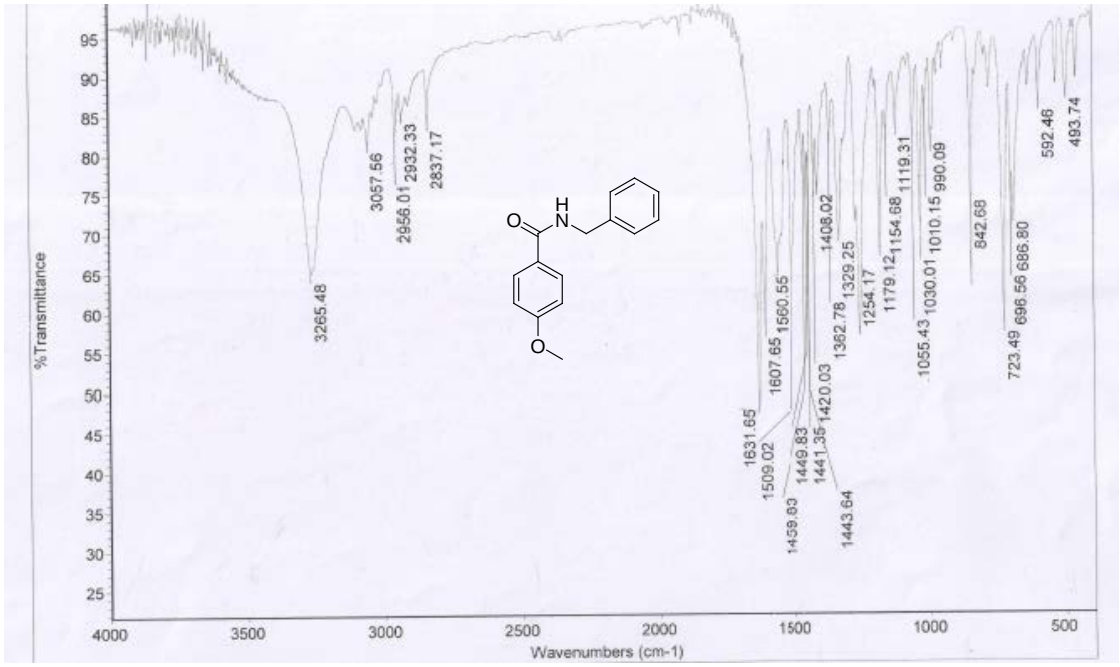
3.5 Spectral data of compounds 5a-f.

48. 5a

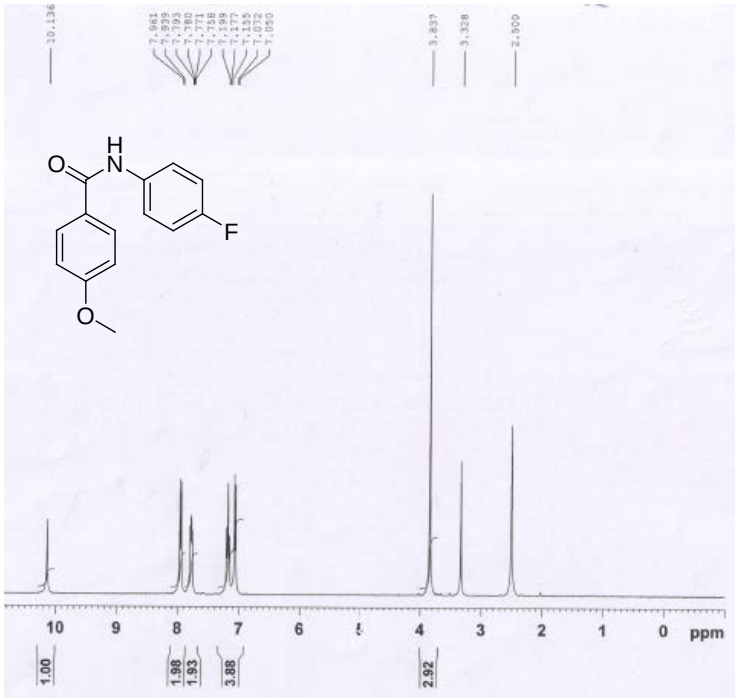


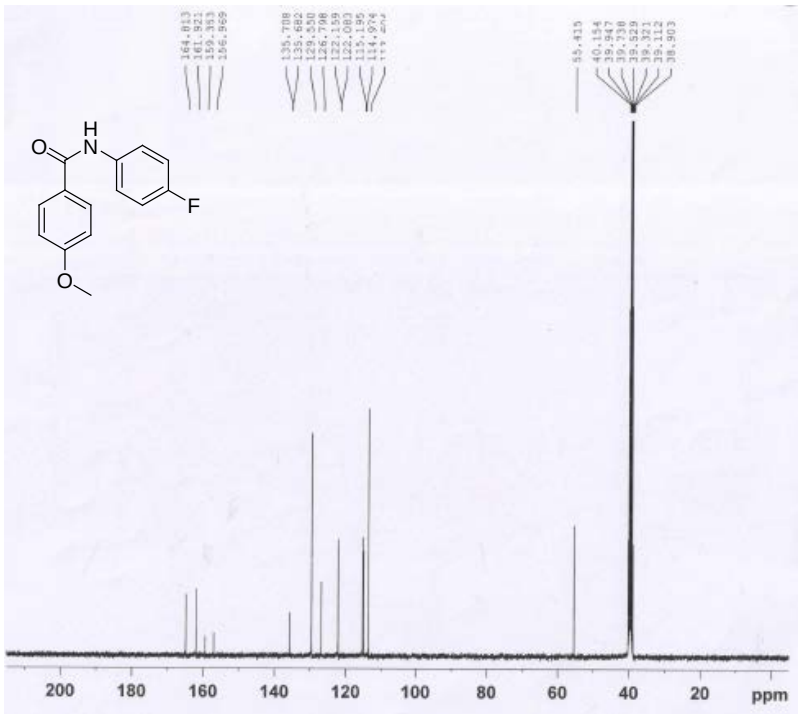


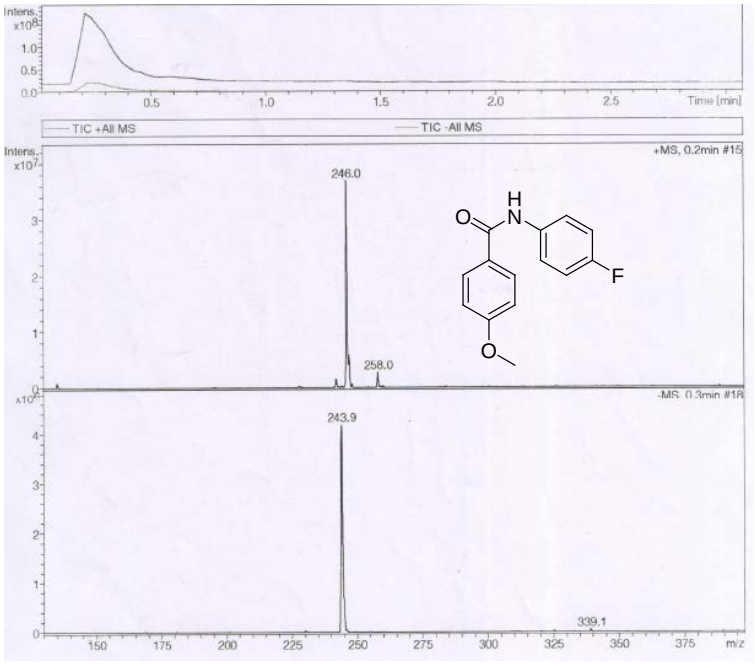

Intens.
x10^8
Time [min]
TIC +All MS
TIC -All MS
+MS, 0.3min #21
242.0
-MS, 0.3min #20
220.3
325.2
158.2
201.3
240.2
255.3
283.3
311.1
339.3
358.3
374.4
390.3
403.5
427.4
445.4
455.4
481.3
m/z

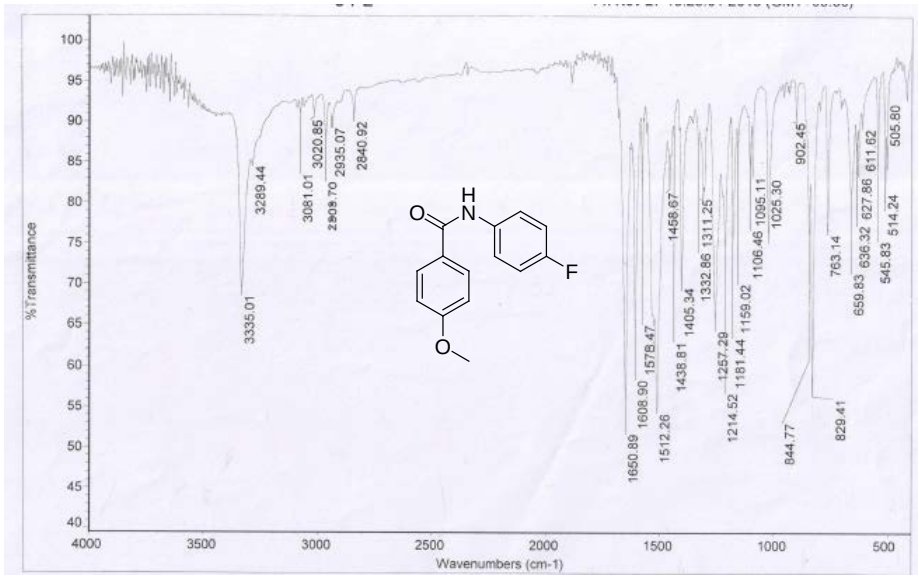

%Transmittance
Wavenumbers (cm-1)
3265.48
3057.56
2956.01
2932.33
2837.17
1631.65
1607.65
1560.55
1509.02
1449.83
1441.35
1439.63
1443.64
1420.03
1408.02
1362.78
1329.25
1254.17
1179.12
1154.68
1119.31
1055.43
1030.01
1010.15
990.09
842.68
723.49
696.56
686.80
592.46
493.74

49. 5b

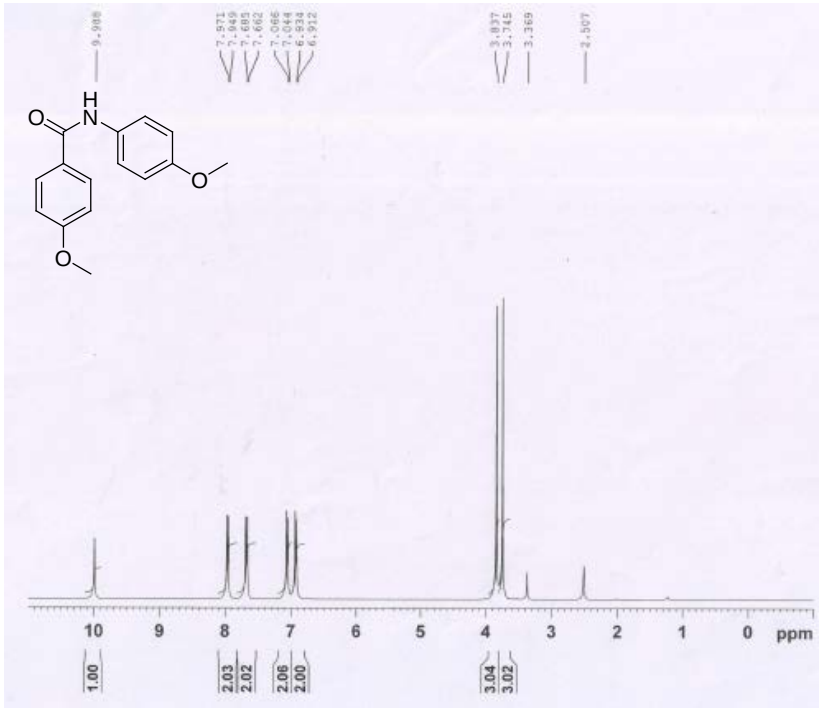

10.136
7.961
7.939
7.793
7.780
7.771
7.748
7.189
7.177
7.155
7.072
7.050
3.837
3.328
2.000
O
H
N
F
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.98
1.93
3.88
2.92

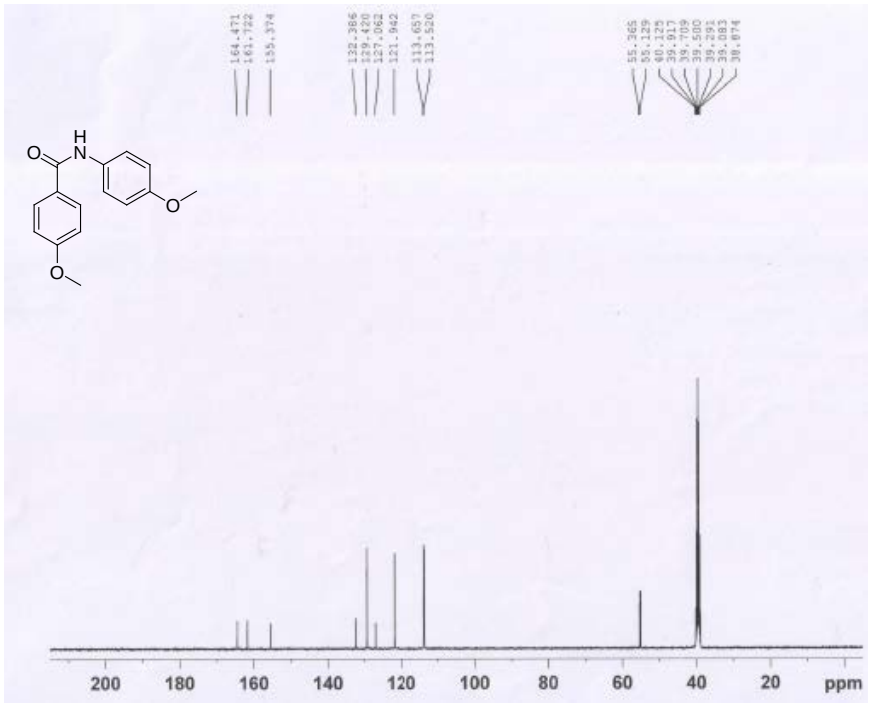

164.813
161.921
159.393
156.969
135.708
135.682
129.550
126.798
122.159
122.083
115.195
114.974
55.415
40.154
39.947
39.739
39.529
39.321
39.112
38.903
O
H
N
F
O
200
180
160
140
120
100
80
60
40
20
ppm


Intens.
x10^8
1.0
0.5
0.0
0.5
1.0
1.5
2.0
2.5
Time [min]
TIC +All MS
TIC -All MS
Intens.
x10^7
+MS, 0.2min #15
246.0
258.0
O
H
N
F
O
-MS, 0.3min #18
243.9
339.1
150
175
200
225
250
275
300
325
350
375
m/z

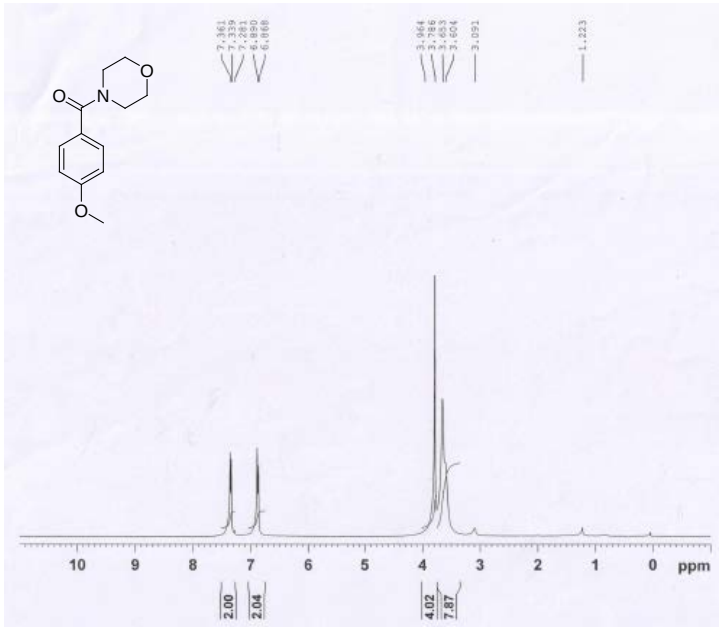

% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
3335.01
3289.44
3081.01
3020.85
2935.07
2840.92
1650.89
1608.90
1578.47
1512.26
1458.67
1438.81
1405.34
1332.86
1311.25
1257.29
1214.52
1181.44
1159.02
1106.46
1095.11
1025.30
902.45
844.77
829.41
763.14
659.83
636.32
627.86
611.62
545.83
514.24
505.80
O
H
N
F
O
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

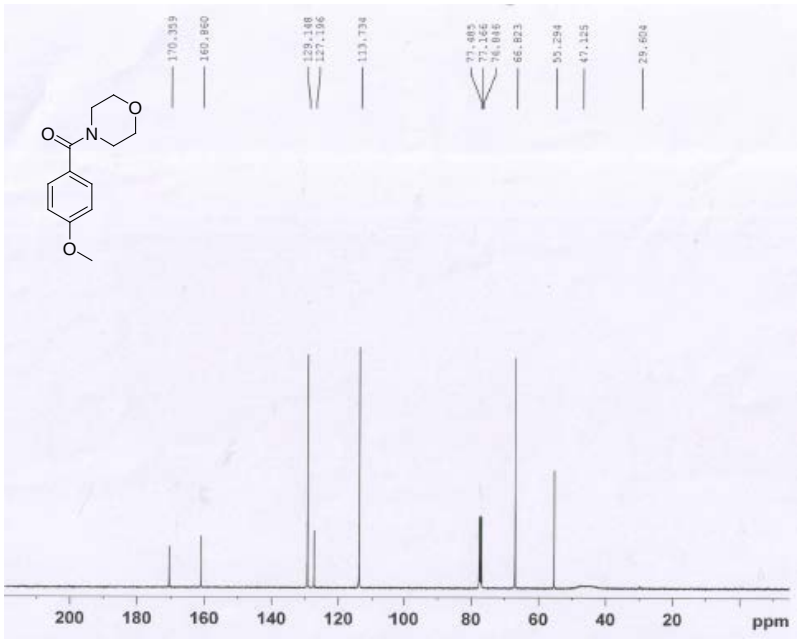
50. 5c


9.988
7.971
7.949
7.683
7.662
7.066
7.044
6.934
6.912
3.837
3.745
3.369
2.507
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.03
2.02
2.06
2.00
3.04
3.02

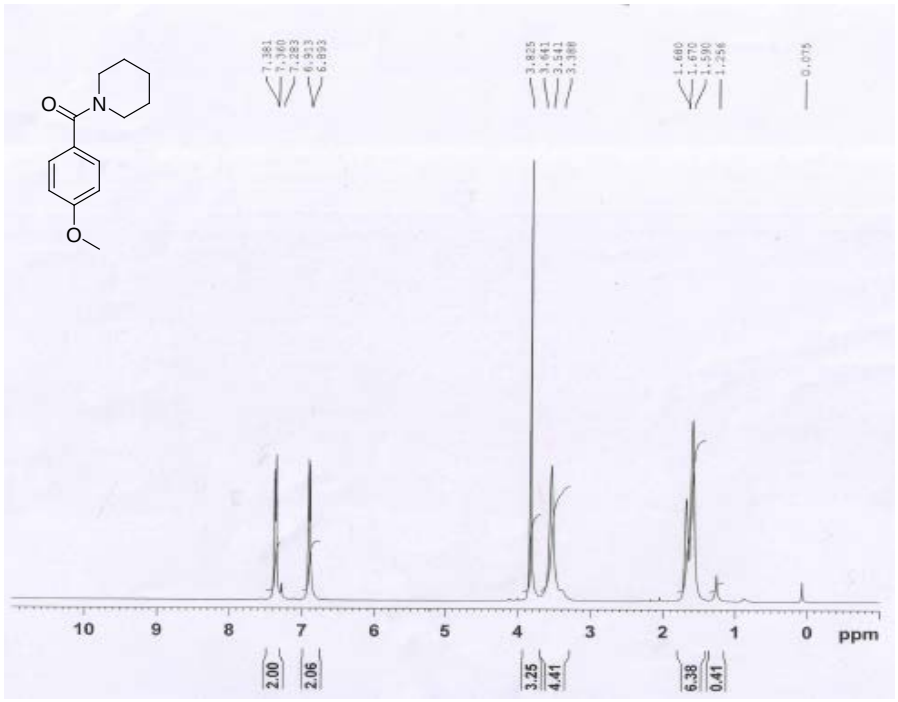

164.471
161.722
155.374
132.386
129.420
127.062
121.942
113.657
113.520
55.366
55.129
40.125
39.917
39.709
39.500
39.291
39.083
38.874
200
180
160
140
120
100
80
60
40
20
ppm

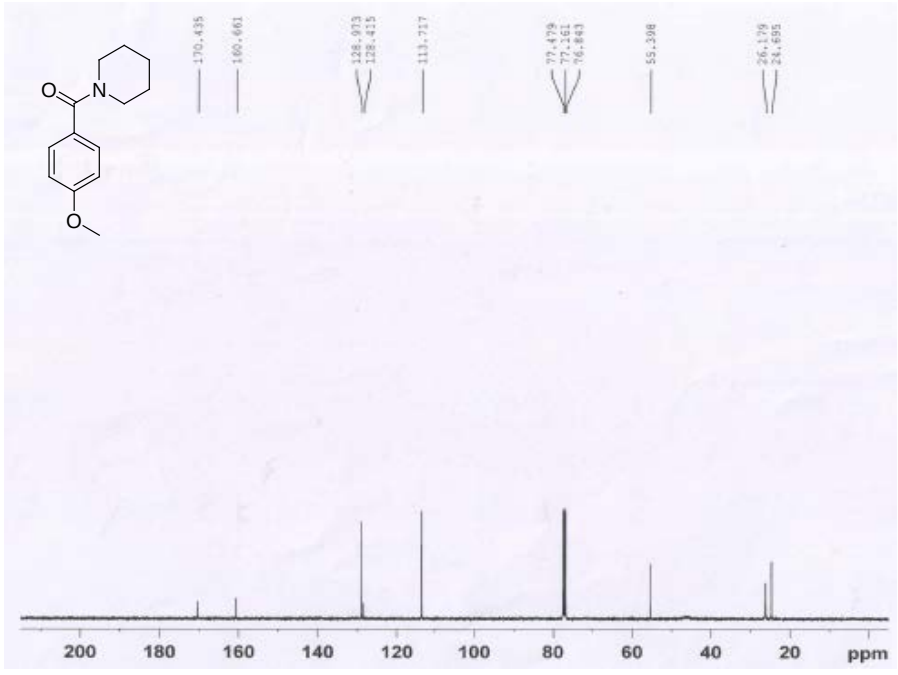
51. 5d


7.361
7.339
7.081
7.060
6.068
3.964
3.786
3.653
3.604
3.091
1.223
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.04
4.02
7.87

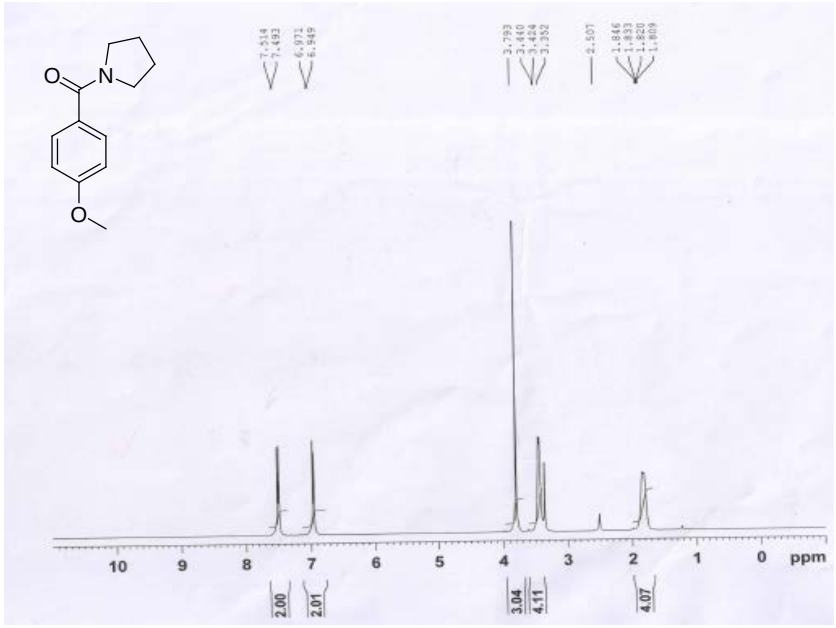

170.359
160.860
129.148
127.196
113.734
77.485
77.166
76.848
66.823
55.284
47.125
29.604
200
180
160
140
120
100
80
60
40
20
ppm

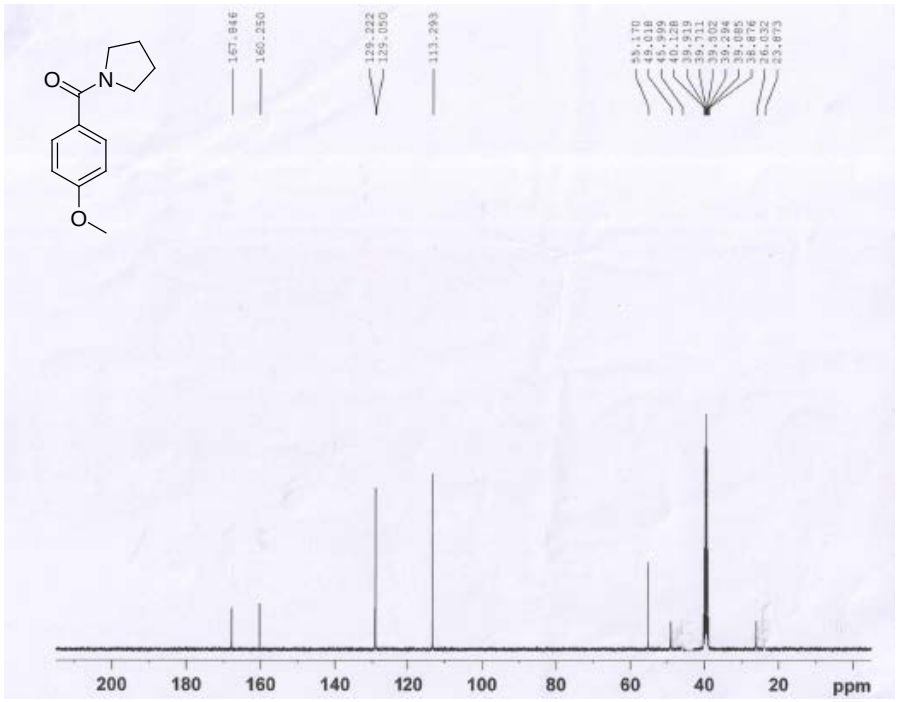
52. 5e


7.381
7.360
7.283
6.933
6.893
3.825
3.641
3.541
3.380
1.680
1.670
1.590
1.256
0.075
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.06
3.25
4.41
6.38
0.41


170.435
160.661
128.973
128.415
113.717
77.479
77.161
76.843
55.398
26.179
24.695
200
180
160
140
120
100
80
60
40
20
ppm

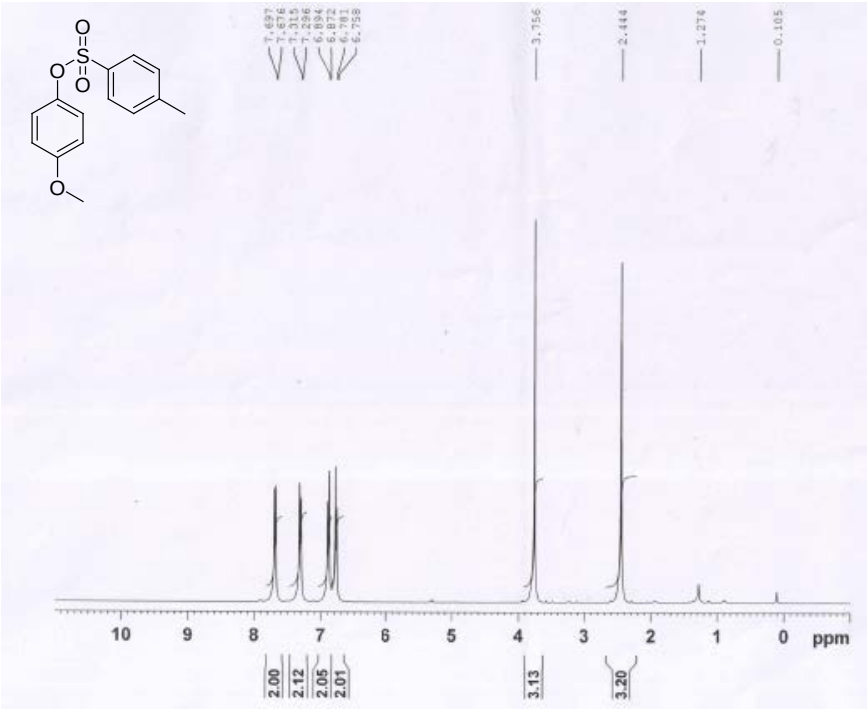
53. 5f

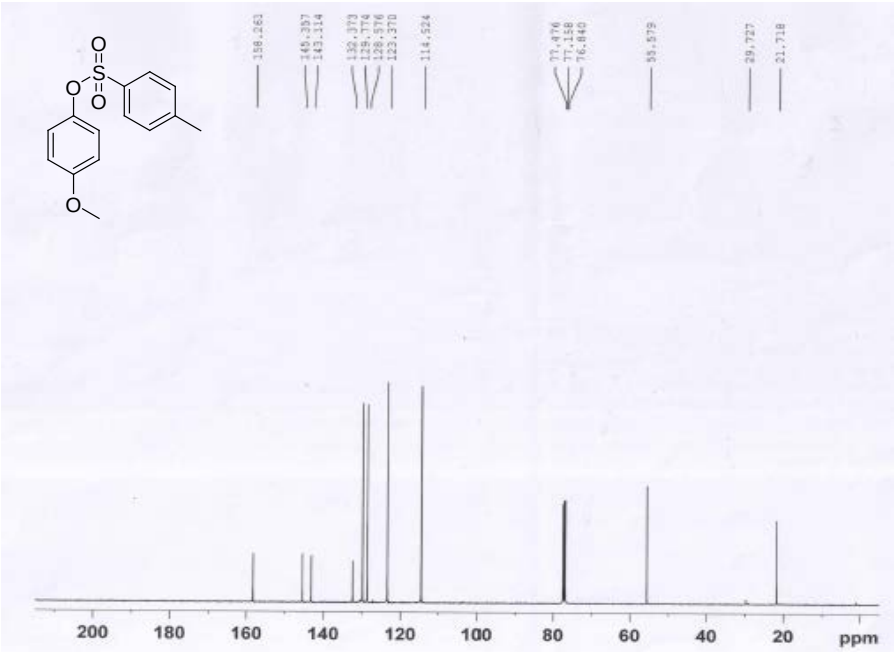

O
N
O
7.514
7.493
6.971
6.949
3.793
3.440
3.424
3.352
2.507
1.846
1.833
1.820
1.809
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.01
3.04
4.11
4.07


O
N
O
167.846
160.250
129.222
129.050
113.293
55.170
45.098
45.059
40.128
39.919
39.711
39.502
39.294
39.085
38.876
26.032
23.873
200
180
160
140
120
100
80
60
40
20
ppm

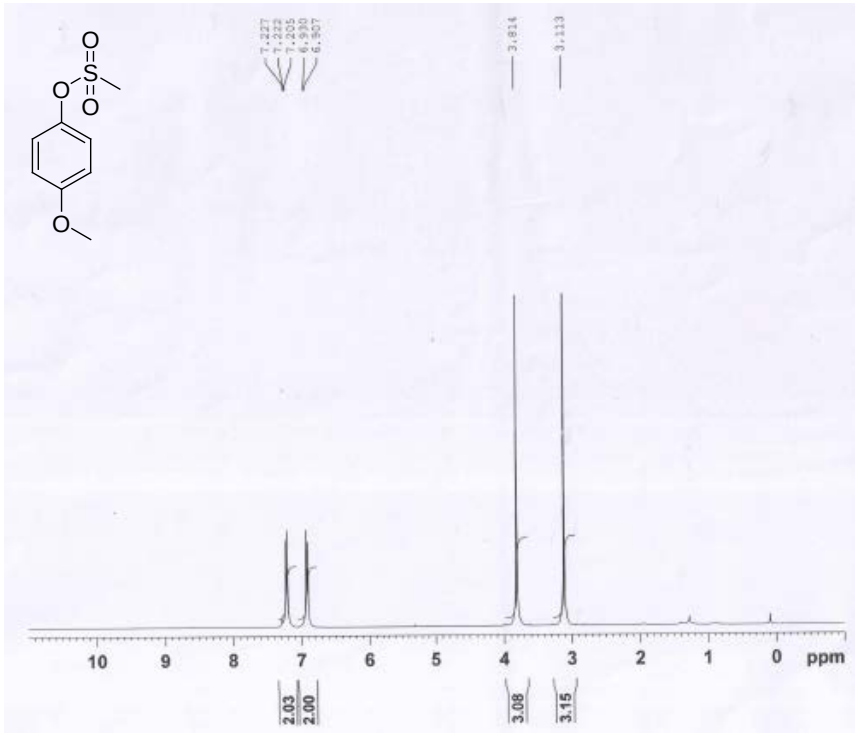
3.6 Spectral data of compounds 6 a-c

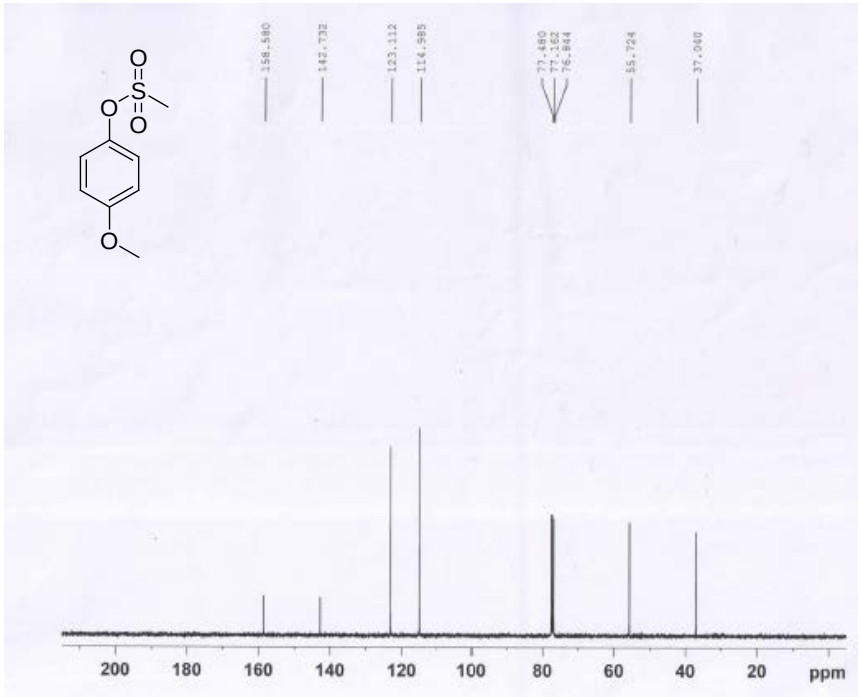
54.6a



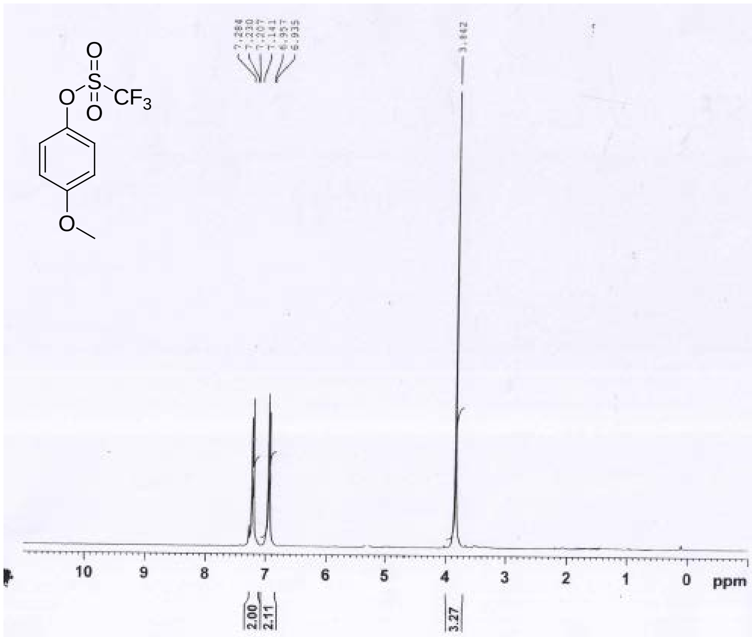


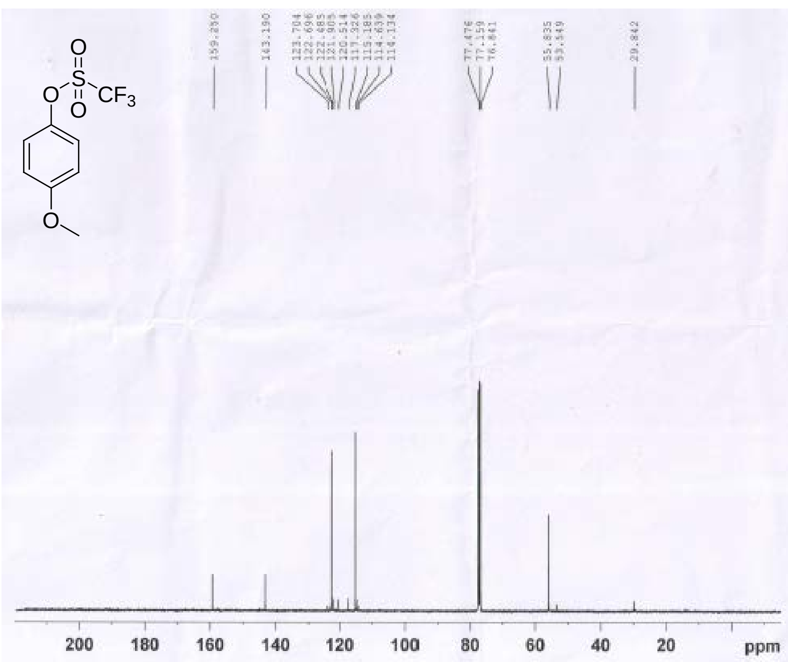
55. 6b


7.227
7.222
7.205
6.930
6.907
3.814
3.113
10
9
8
7
6
5
4
3
2
1
0
ppm
2.03
2.00
3.08
3.15


158.580
142.732
123.112
114.985
77.480
77.162
76.844
55.724
37.040
200
180
160
140
120
100
80
60
40
20
ppm

56. 6c


O
S
O
CF3
O
O
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.11
3.27


O
S
O
CF3
O
O
200
180
160
140
120
100
80
60
40
20
ppm