Supporting information

Metal-free, high yielded synthesis of unsymmetrical biaryl, bi(heteroaryl), aryl vinyl, aryl alkyl sulfones *via* coupling of aryne with sulfinic acid salts

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Table of Contents

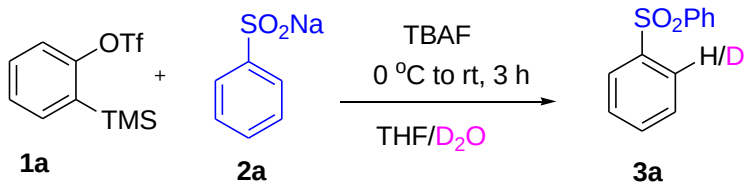
General Information:

All the chemicals for this study were purchased from Sigma-Aldrich, India. All the reactions were performed under nitrogen atmosphere. Analytical thin layer chromatography was performed using TLC pre-coated silica gel 60 F_{254} (20 x 20 cm). TLC plates were visualized by exposing UV light. Organic solvents were concentrated by rotary evaporation. Column chromatography was performed on flash silica gel 230-400 mesh size and ethyl acetate/hexane mixture used for elution. Melting points were recorded on BUCHI Melting Point B-545 instrument and are uncorrected. IR spectra were recorded on FT-IR instrument. ^{1}H NMR (400 MHz or 500 MHz) and ^{13}C NMR (101 MHz or 126 MHz) recorded on FT-NMR instruments. Chemical data for protons are reported in parts per million (ppm, scale) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent ($CDCl_3$: δ 7.26). All the NMR spectras were processed with MestReNova software. The coupling constant (*J*) are in Hz. ESI-MS and HRMS spectra were recorded on LC-Q-TOF and HRMS-6540-UHD machines.

General experimental procedure:

To a 10 ml round bottom flask equipped with a magnetic stir bar was added CsF (4.0 mmol). Then RB flask was evacuated and backfilled with nitrogen and dissolved in CH_3CN under nitrogen atmosphere (4.0 ml). To the stirring solution, sulfinic acid sodium salt **2a** (0.5 mmol) was added followed by the addition of aryne precursor **1a** (0.25 mmol). Then the reaction mixture was heated at 80 ^{o}C for 2-3 hours. The reaction mixture was diluted with CH_2Cl_2 and filtered off. The filtrate was evaporated under vaccum and the crude compounds were purified by column chromatography. Purified products were characterized through NMR and Mass analysis.

Experimental procedure for deuterium labelled reaction:



To a 10 ml round bottom flask equipped with a magnetic stir bar was added benzene sulfinic acid sodium salt **2a** (0.15 mmol). Then RB flask was evacuated and backfilled with nitrogen and dissolved in THF (1.5 ml) under nitrogen atmosphere. To the resulting stirring solution was added tetra butyl ammonium fluoride (0.2 mmol). Then the reaction mixture was cooled to 0 ^{o}C. After that 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.1 mmol) and D_2O (1 mmol) were added in 5 min intervals. Then the mixture was then stirred at rt for 3 h. The reaction mixture was diluted with diethyl ether (2.0 mL) and filtered off. The solvent was evaporated to obtain the crude product. LC-MS spectrum analysis of crude product showed 20% deuterium incorporation in the respective product **3a**.

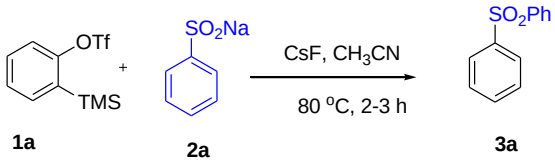
Chromatographic conditions and LC-ESI-MS of deuterated experiment:

LC-MS analysis was performed on an LC/MS-MS triple-stage quadrupole mass spectrometer equipped with electrospray ionization (ESI) interface and liquid chromatography. Analytical chromatographic separations of samples were carried out on a chromolith performance RP-18e column (50 x 4.6 mm, Merck, Germany) protected by a chromolith guard column. The flow rate was optimized to 0.5 ml/min. The mobile phase consisted of solvent A (water with 0.1% formic acid) and solvent B (acetonitrile). A gradient programme was used as follows: 0–7 min, 10–60% B; 7–10 min, 60% B; 10-11 min, 60-10% B and 11–12 min, 10% B. The injection volume was 5µL and the column temperature was maintained at 30 ^{o}C. A triple quad LC/MS system was used for the detection. The analysis was performed using an electrospray- ionisation (ESI) source in positive and negative modes. The operation conditions were as follows: scan range of 50–800 amu, ion source temperature

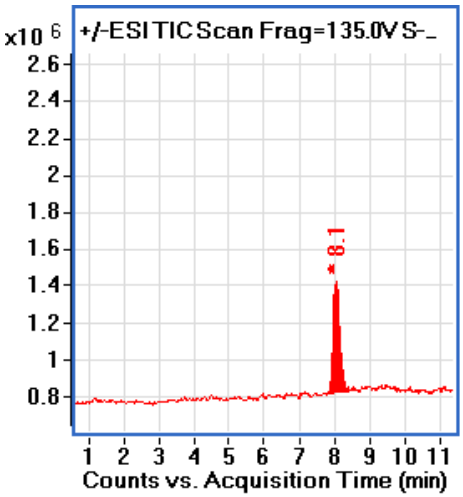
300 °C, nebulizer 40 psi, gas flow 12 L/min, capillary voltage 4000, collision gas nitrogen, dwell time of 50 ms and a step size of 0.1 amu. Nitrogen was used in all cases. Mass Hunter software (version B.04.00) was used for data acquisition and processing.

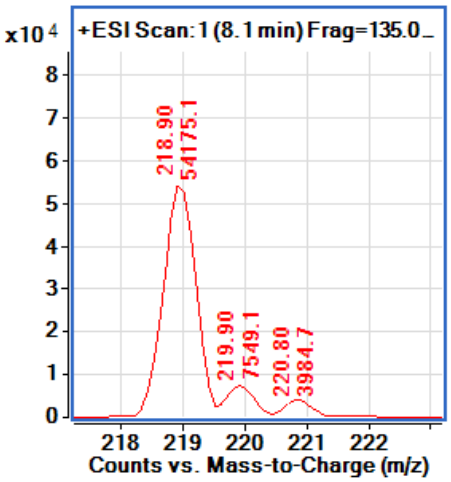
20% Increasing in the abundance of M+1 peak was observed in the reaction performed in the presence of D_2O.

LC-MS analasys of deuterated experiment:

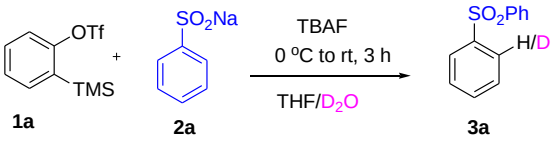


1a 2a 3a

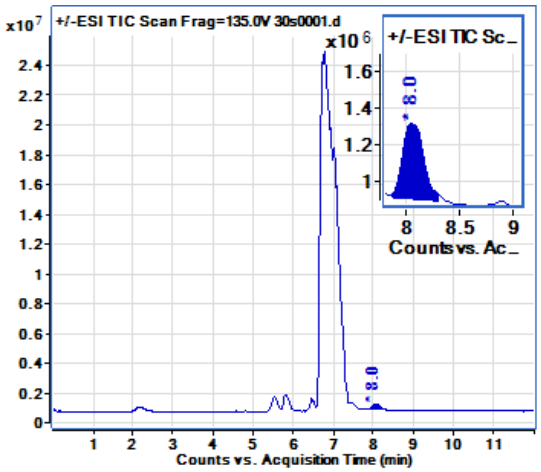


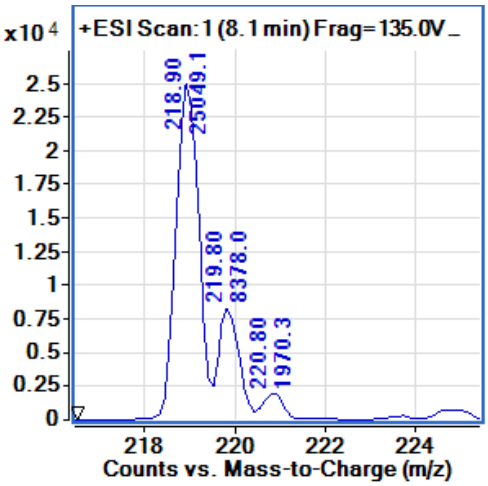


Abundance of M+1 peak = 13.93
Abundance of M+2 peak = 7.35



1a 2a 3a

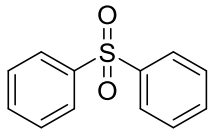




Abundance of M+1 peak = 33.44
Abundance of M+2 peak = 7.86

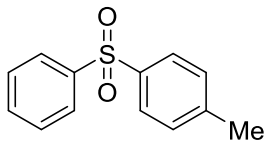
Spectral data:

1-(Phenylsulfonyl)benzene (3a)[1]:



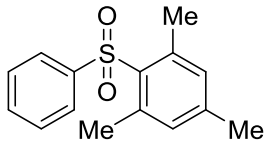
White solid; m.p.: 121-122 ^{o}C; IR (KBr): 1155, 1309, 1581, 2926, 3081 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.3 Hz, 4H), 7.51 – 7.38 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.62, 133.20, 129.29, 127.66, 127.33; HRMS (ESI-TOF) cald. for $C_{12}H_{10}O_2S$ $[M + H]^+$ 219.0480; found 219.0468.

1-Methyl-4-(phenylsulfonyl)benzene (3b)[1]:



White solid; m.p.: 127-129 ^{o}C; IR (KBr): 1157, 1308, 1593, 2854, 2926, 3065 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.53 (m, 1H), 7.50 - 7.47(m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 141.9, 138.6, 133.0, 129.9, 129.2, 127.7, 127.5, 21.6; HRMS (ESI-TOF)cald. for $C_{13}H_{12}O_2S$ $[M + H]^+$ 233.0636; found 233.0627.

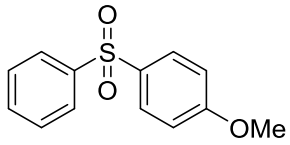
1,3,5-Trimethyl-2-(phenylsulfonyl)benzene (3c)[1]:



White solid; m.p.: 87-90 ^{o}C; IR (KBr): 1148, 1297, 1602, 2851, 2922, 2983 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.5 Hz, 2H), 7.56 – 7.52 (m, 1H), 7.49 –7.45 (m, 2H), 6.94 (s, 2H), 2.59 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.47, 140.11, 133.74,

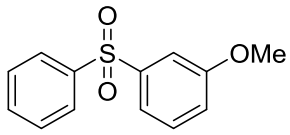
132.60, 132.23, 130.75, 128.91, 126.23, 77.30, 77.05, 76.79, 22.85, 21.06; HRMS (ESI-TOF) cald. for $C_{15}H_{16}O_2S$ $[M + H]^+$ 261.0949; found 261.0949.

1-Methoxy-4-(phenylsulfonyl)benzene (3d)[1]:



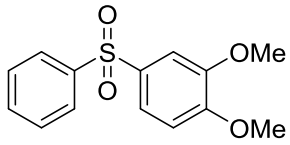
White solid; m.p.: 90-91 ^oC; IR (KBr): 1152, 1263, 1590, 2852, 2956, 2996 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 14.8, 8.1 Hz, 4H), 7.56 – 7.46 (m, 3H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.39, 142.37, 133.11, 132.85, 129.89, 129.21, 127.31, 114.52, 55.66; HRMS (ESI-TOF) cald. for $C_{13}H_{12}O_3S$ $[M + H]^+$ 249.0585; found 249.0578.

1-Methoxy-3-(phenylsulfonyl)benzene (3e)[2]:



White solid; m.p.: 88-91 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.57 (dd, *J* = 8.6, 6.0 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.47 – 7.44 (m, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.08 (dd, *J* = 8.6, 2.1 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.01, 142.67, 141.51, 133.24, 130.41, 129.30, 127.66, 119.94, 119.58, 112.22, 55.71; HRMS (ESI-TOF) cald. for $C_{13}H_{12}O_3S$ $[M + H]^+$ 249.0585; found 249.0576.

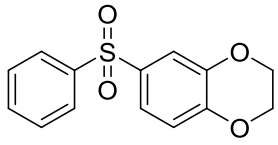
1,6-Dimethoxy-3-(phenylsulfonyl)benzene (3f)[3]:



White solid; m.p.: 115-117 ^oC; IR (KBr): 1147, 1305, 1583, 2846, 2936, 3014 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.0 Hz, 2H), 7.60 – 7.47 (m, 4H), 7.39 (d, *J* = 2.1 Hz, 1H),

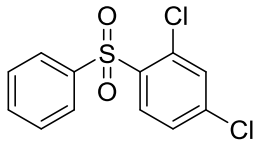
6.94 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 149.3, 142.3, 133.1, 132.8, 129.2, 127.2, 121.9, 110.9, 109.9, 56.2, 56.2.

6-(Phenylsulfonyl)-2,3-dihydrobenzo[b][1,4]dioxine (3g):



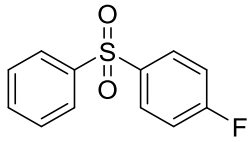
White solid; m.p.: 96-99 ^{o}C; IR (KBr): 1154, 1287, 1582, 2852, 2956, 3059 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.57 – 7.42 (m, 5H), 6.94 (d, *J* = 8.3 Hz, 1H), 4.27 (dd, *J* = 9.1, 5.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.91, 143.75, 142.18, 133.97, 132.89, 129.19, 127.42, 121.41, 118.05, 117.35, 64.55, 64.12; HRMS (ESI-TOF) cald. for $C_{14}H_{12}O_4S$ $[M + H]^+$ 277.0535; found 277.0528.

1,5-Dichloro-2-(phenylsulfonyl)benzene (3h)[4]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.5 Hz, 1H), 7.89 – 7.84 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.37 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.59, 138.64, 136.03, 132.88, 132.69, 130.96, 130.81, 127.96, 127.52, 126.64.

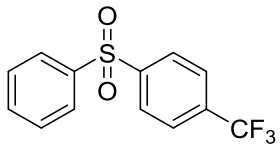
1-Fluoro-4-(phenylsulfonyl)benzene (3i)[1]:



White solid; m.p.: 111-113 ^{o}C; IR (KBr): 1154, 1322, 1587, 2853, 2926, 3100 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (ddd, *J* = 15.6, 7.4, 1.7 Hz, 4H), 7.59 – 7.49 (m, 3H), 7.21 – 7.16 (m, 2H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -104.18 (m, 1F); ^{13}C NMR (125 MHz, $CDCl_3$) δ

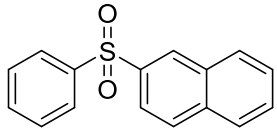
165.45 (d, *J* = 255.9 Hz), 141.43, 137.66 (d, *J* = 3.1 Hz), 133.39, 130.51 (d, *J* = 9.6 Hz), 129.42, 127.58, 116.64 (d, *J* = 22.6 Hz).

1-Trifluoromethyl-4-(phenylsulfonyl)benzene (3j)[1]:



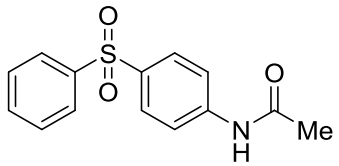
White solid; m.p.: 90-93 ^{o}C; IR (KBr): 1156, 1324, 1607, 2924, 3061, 3109 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.64 – 7.58 (m, 1H), 7.57 – 7.52 (m, 2H); ^{19}F NMR (375 MHz, $CDCl_3$) δ –63.21; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 140.5, 134.8 (q, *J* = 33.1 Hz), 133.8, 129.5, 128.2, 127.9, 126.4 (q, *J* = 3.6 Hz), 123.1 (q, *J* = 272Hz).

2-(Phenylsufonyl)naphthalene (3k)[1]:



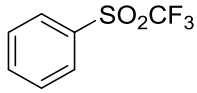
White solid; m.p.: 119-120 ^{o}C; IR (KBr): 1153, 1319, 1586, 2853, 2925, 3061 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.02 – 7.90 (m, 4H), 7.87 – 7.83 (m, 2H), 7.62 (ddd, *J* = 14.4, 7.0, 1.4 Hz, 2H), 7.55 – 7.47 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.65, 138.41, 135.02, 133.23, 132.22, 129.69, 129.41, 129.33, 129.19, 129.12, 127.95, 127.72, 127.68, 122.68; HRMS (ESI-TOF) cald. for $C_{16}H_{12}O_2S$ $[M + H]^+$ 269.0636; found 269.0623.

1- Acetamido-4-(phenylsulfonyl)benzene (3l)[5]:



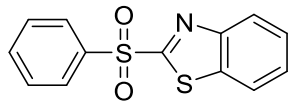
Yellow solid; m.p.: 190-193 ^{o}C; IR (KBr): 1155, 1318, 1591, 1691, 2853, 2926, 3094, 3326 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.90 (d, *J* = 7.9 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.51 – 7.47 (m, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.25, 142.83, 141.67, 135.68, 133.21, 129.35, 128.87, 127.37, 119.67, 24.56; HRMS (ESI-TOF) cald. for $C_{14}H_{13}NO_3S$ $[M + H]^+$ 276.0694; found 276.0683.

(Trifluoromethyl)sulfonylbenzene (3m)[6]:



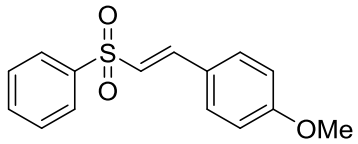
Colourless oil; IR (KBr): 576, 605, 1075, 1143, 1221, 1370, 1451, 1585, 3070 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.86 (t, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.42.

2-(phenylsulfonyl)benzo[d]thiazole (3o)[7]:



White solid; m.p.: 152-155 ^{o}C; IR (KBr): 1158, 1332, 1580, 2656, 2928, 3092 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.6, 7.5 Hz, 3H), 7.87 (d, *J* = 7.1 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (dt, *J* = 13.8, 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.28, 152.90, 138.51, 137.04, 134.60, 129.55, 128.94, 127.93, 127.54, 125.52, 122.25; HRMS (ESI-TOF) cald. for $C_{13}H_9NO_2S_2$ $[M + H]^+$ 276.0153; found 276.0151.

(E)-1-methoxy-4-(2-(phenylsulfonyl)vinyl)benzene (3p)[8]:

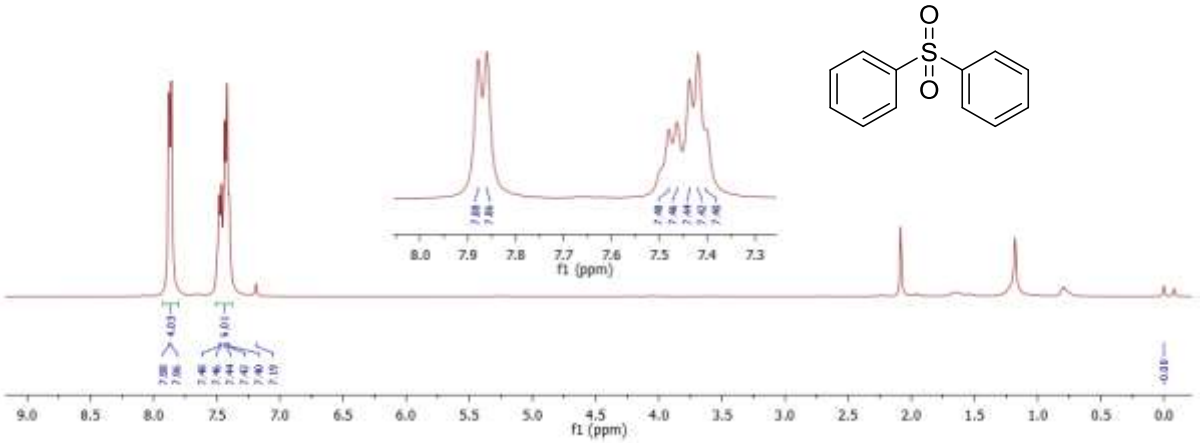


White solid; m.p.: 74-75 ^{o}C; IR (KBr): 1147, 1305, 1510, 1601, 2839, 2926, 3056 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 15.4 Hz, 1H), 7.54 – 7.44

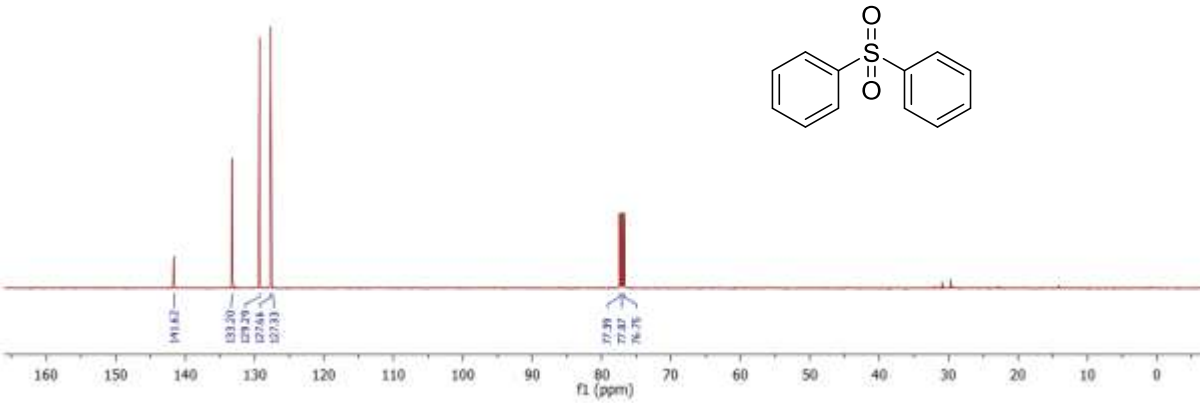
(m, 3H), 7.36 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 15.3 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.11, 142.32, 141.20, 133.18, 130.40, 129.29, 127.51, 124.99, 124.48, 114.54, 55.46.

Spectral copies of ^{1}H, ^{13}C NMR, DEPT and Mass data obtained in this Study:

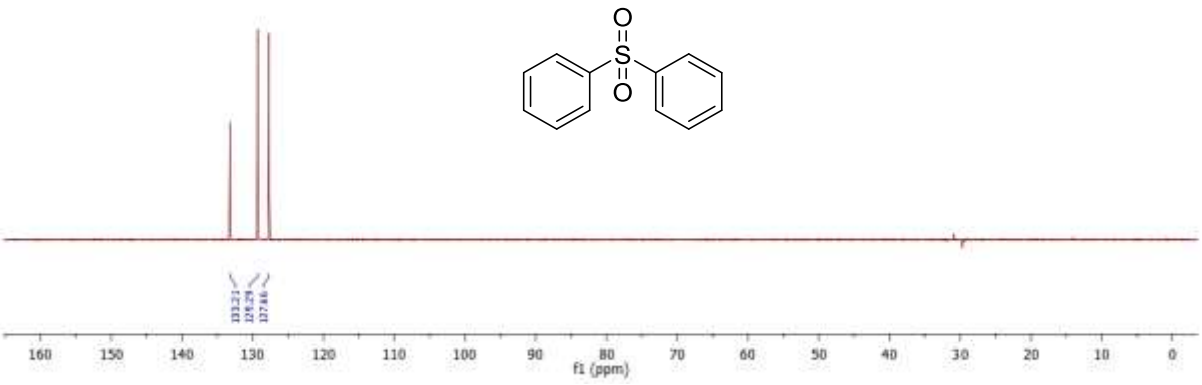
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**:



^{13}C NMR (100 MHz, $CDCl_3$) of compound **3a**:



DEPT (100 MHz, $CDCl_3$) of compound **3a**:



HRMS (ESI-TOF) of compound **3a**:

Qualitative Compound Report

Data File	Ph-SF.d	**Sample Name**	Ph-SF
Sample Type	Sample	**Position**	Vial 8
Instrument Name	Instrument 1	**User Name**	
Acq Method	new method.m	**Acquired Time**	29-05-2014 PM 3:16:16
IRM Calibration Status	Success	**DA Method**	daily_report.m
Comment			

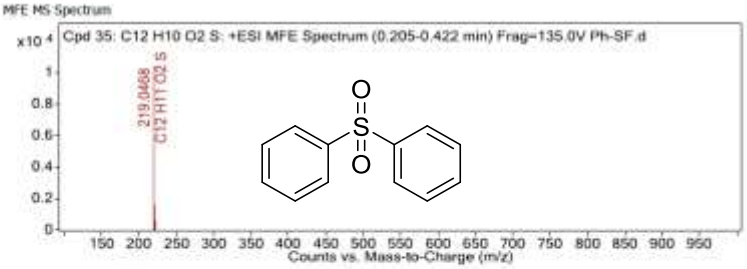
Sample Group **Info.**
Acquisition SW Version 6200 series TOF/6500 series Q-TOF B.05.01 (B5125)

Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 35: C12 H10 O2 S	0.262	218.0397	C12 H10 O2 S	C12 H10 O2 S	2.13	C12 H10 O2 S

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 35: C12 H10 O2 S	219.0468	0.262	Find by Molecular Feature	218.0397

MFE MS Spectrum



MS Spectrum Peak List

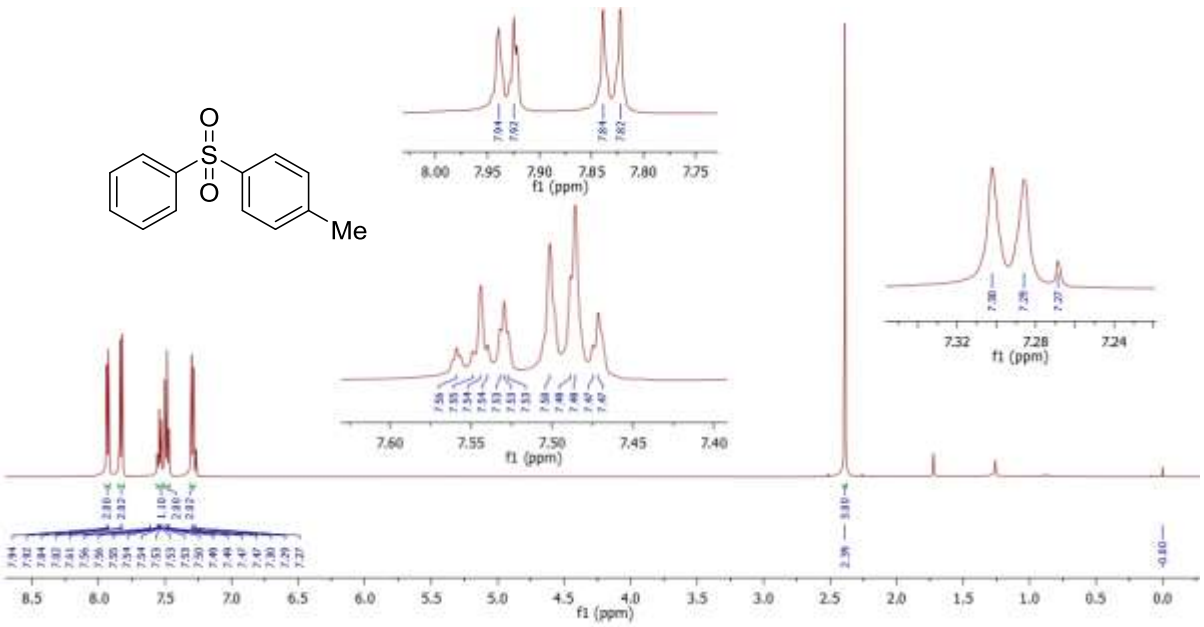
m/z	z	Abund	Formula	Ion
219.0468	1	10449.04	C12 H11 O2 S	(M+H)+
220.0513	1	1658.18	C12 H11 O2 S	(M+H)+
221.0453	1	670.48	C12 H11 O2 S	(M+H)+

Predicted Isotope Match Table

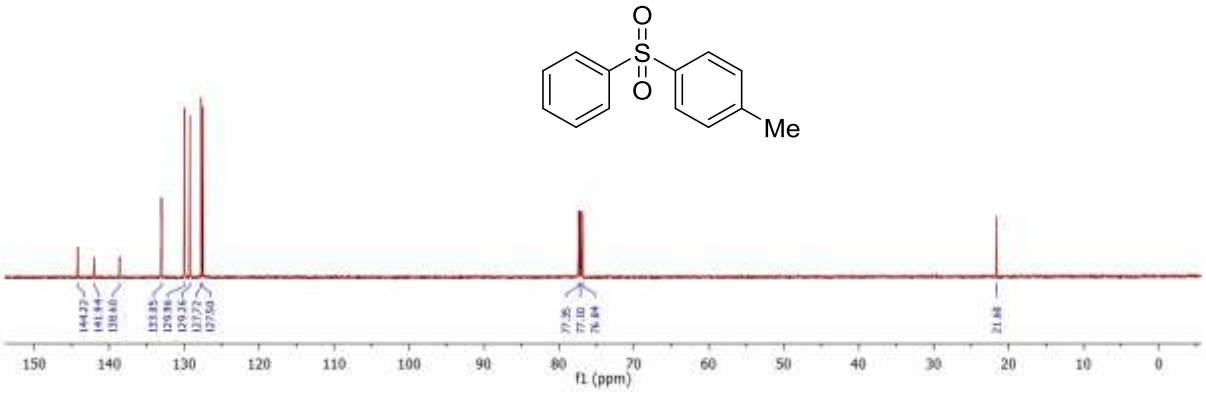
Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	219.0468	219.0474	3.07	100	100	81.78	83.5
2	220.0513	220.0506	-3.19	15.87	13.97	12.98	11.67
3	221.0453	221.0455	0.53	6.42	5.79	5.25	4.83

--- End Of Report ---

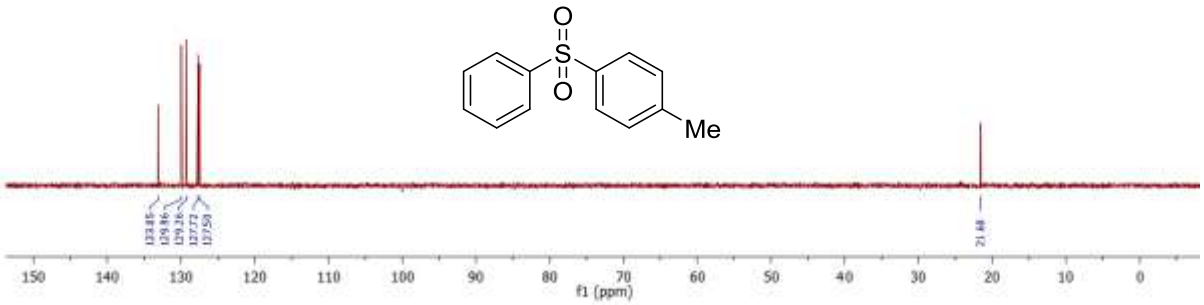
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3b**:



^{13}C NMR (125 MHz, $CDCl_3$) of compound **3b**:



DEPT (125 MHz, $CDCl_3$) of compound **3b**:



HRMS (ESI-TOF) of compound **3b**:

Qualitative Compound Report

Data File	Me-SOph.d	**Sample Name**	Me-SOph
Sample Type	Sample	**Position**	Vial 7
Instrument Name	Instrument 1	**User Name**	
Acq Method	new method.m	**Acquired Time**	29-05-2014 PM 3:11:46
IRM Calibration Status	Success	**DA Method**	daily_report.m
Comment			

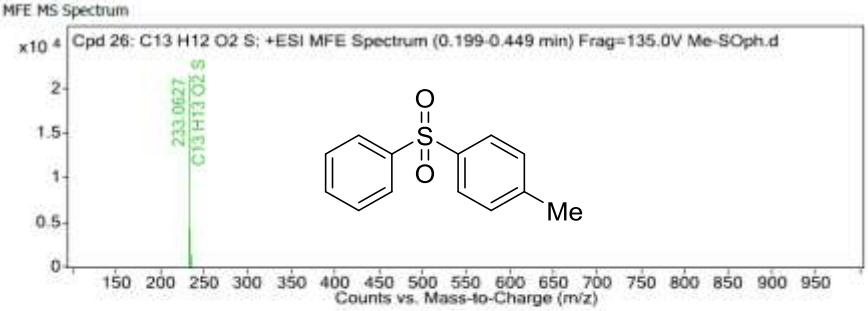
Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125)

Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 26: C13 H12 O2 S	0.263	232.0556	C13 H12 O2 S	C13 H12 O2 S	0.95	C13 H12 O2 S

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 26: C13 H12 O2 S	233.0627	0.263	Find by Molecular Feature	232.0556

MFE MS Spectrum



MS Spectrum Peak List

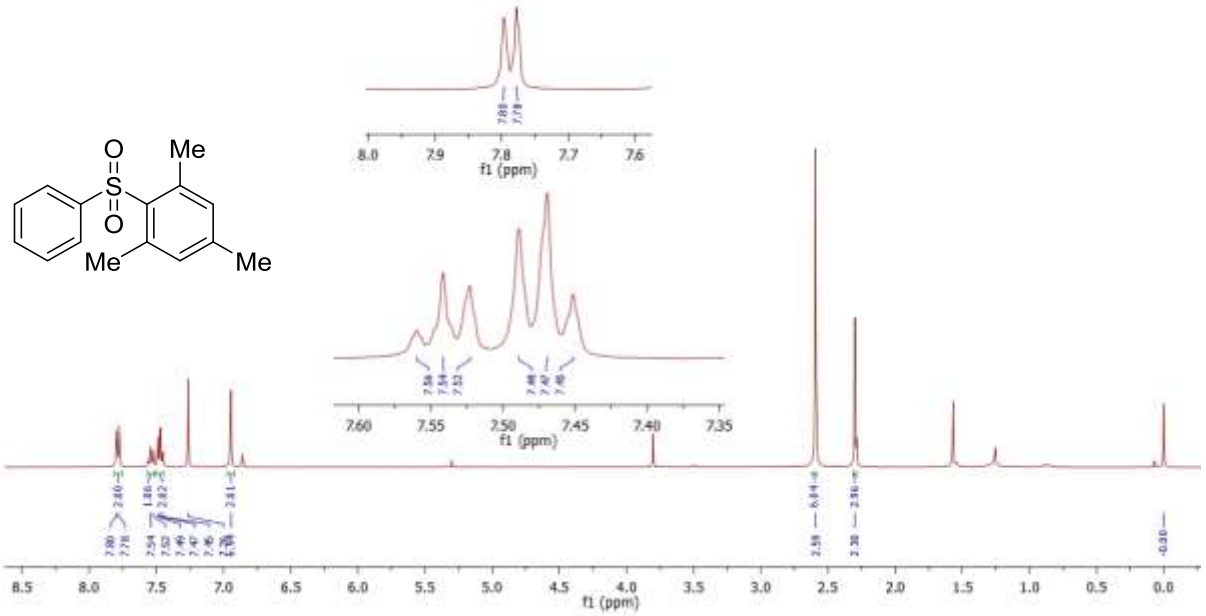
m/z	z	Abund	Formula	Ion
233.0627	1	21517.71	C13 H13 O2 S	(M+H)+
234.066	1	4414.5	C13 H13 O2 S	(M+H)+
235.0633	1	1508.21	C13 H13 O2 S	(M+H)+

Predicted Isotope Match Table

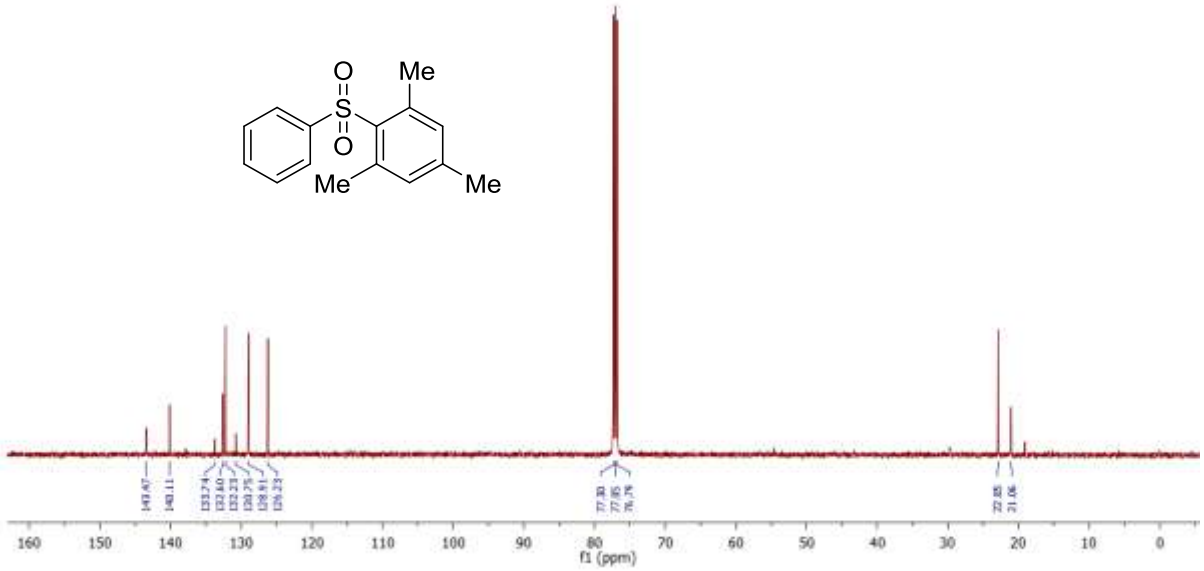
Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	233.0627	233.0631	1.57	100	100	78.42	82.63
2	234.066	234.0663	1.1	20.52	15.08	16.09	12.46
3	235.0633	235.0613	-8.24	7.01	5.94	5.5	4.91

--- End Of Report ---

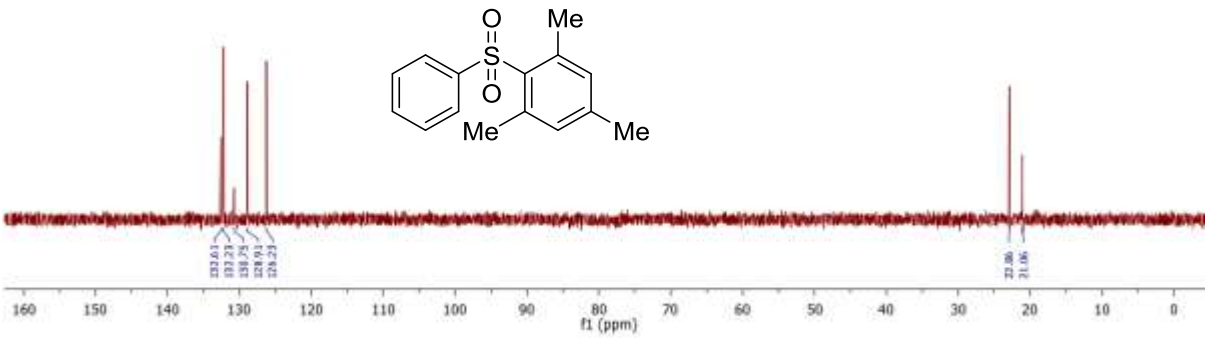
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c**:



^{13}C NMR (125 MHz, $CDCl_3$) of compound **3c**:



DEPT (125 MHz, $CDCl_3$) of compound **3c**:



HRMS (ESI-TOF) of compound **3c**:

Qualitative Compound Report

Data File	Mesityl.d	**Sample Name**	Mesityl
Sample Type	Sample	**Position**	Vial 12
Instrument Name	Instrument 1	**User Name**	
Acq Method	new method.m	**Acquired Time**	29-05-2014 PM 3:39:05
IRM Calibration Status	Success	**DA Method**	daily_report.m
Comment			

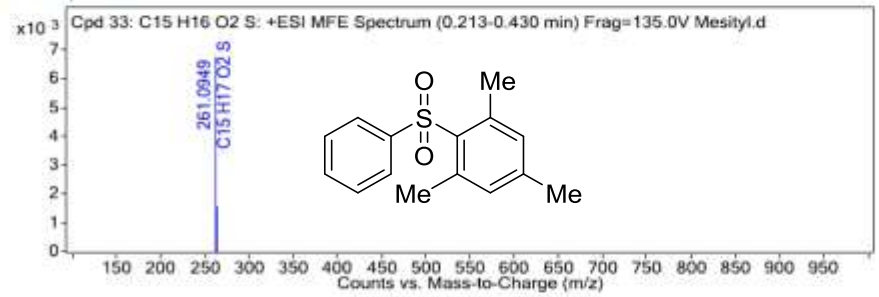
Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125)

Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 33: C15 H16 O2 S	0.264	260.0875	C15 H16 O2 S	C15 H16 O2 S	-1.37	C15 H16 O2 S

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 33: C15 H16 O2 S	261.0949	0.264	Find by Molecular Feature	260.0875

MFE MS Spectrum



MS Spectrum Peak List

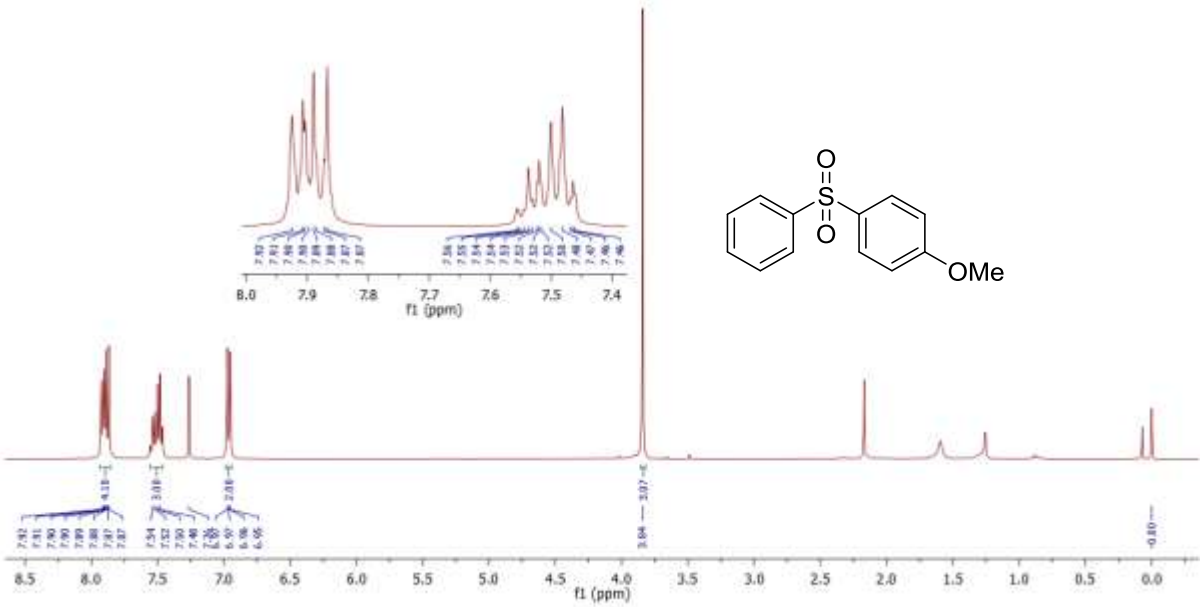
m/z	z	Abund	Formula	Ion
261.0949	1	6784.45	C15 H17 O2 S	(M+H)+
262.0983	1	1595.18	C15 H17 O2 S	(M+H)+
263.0902	1	555	C15 H17 O2 S	(M+H)+

Predicted Isotope Match Table

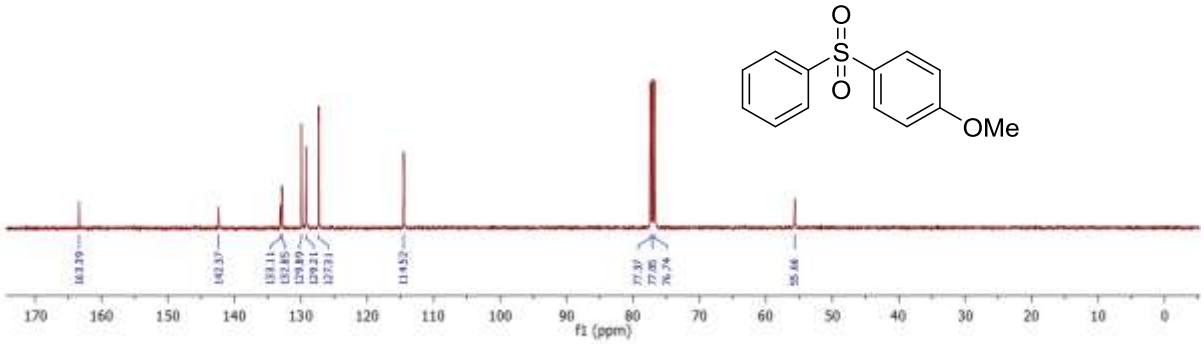
Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	261.0949	261.0944	-2.07	100	100	75.93	80.92
2	262.0983	262.0976	-2.67	23.51	17.28	17.85	13.99
3	263.0902	263.0931	10.98	8.18	6.29	6.21	5.09

--- End Of Report ---

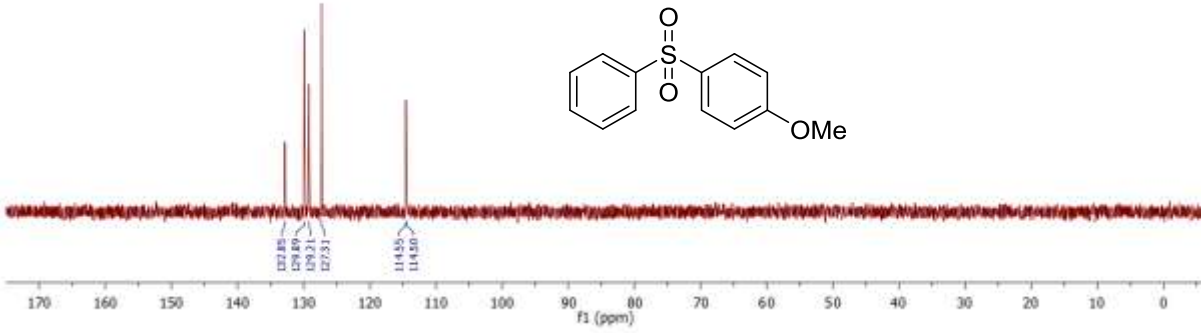
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**:



^{13}C NMR (100 MHz, $CDCl_3$) of compound **3d**:



DEPT (100 MHz, $CDCl_3$) of compound **3d**:



HRMS (ESI-TOF) of compound **3d**:

Qualitative Compound Report

Data File	OMe-SF.d	**Sample Name**	OMe-SF
Sample Type	Sample	**Position**	Vial 17
Instrument Name	Instrument 1	**User Name**	
Acq Method	new method.m	**Acquired Time**	29-05-2014 PM 4:06:19
IRM Calibration Status	Success	**DA Method**	daily_report.m
Comment			

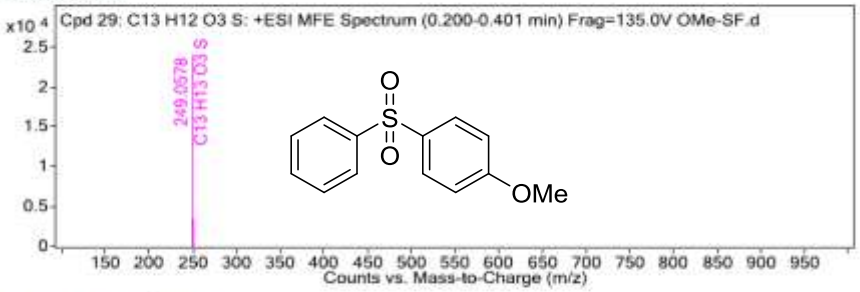
Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125)

Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 29: C13 H12 O3 S	0.261	248.0504	C13 H12 O3 S	C13 H12 O3 S	1.13	C13 H12 O3 S

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 29: C13 H12 O3 S	249.0578	0.261	Find by Molecular Feature	248.0504

MFE MS Spectrum



MS Spectrum Peak List

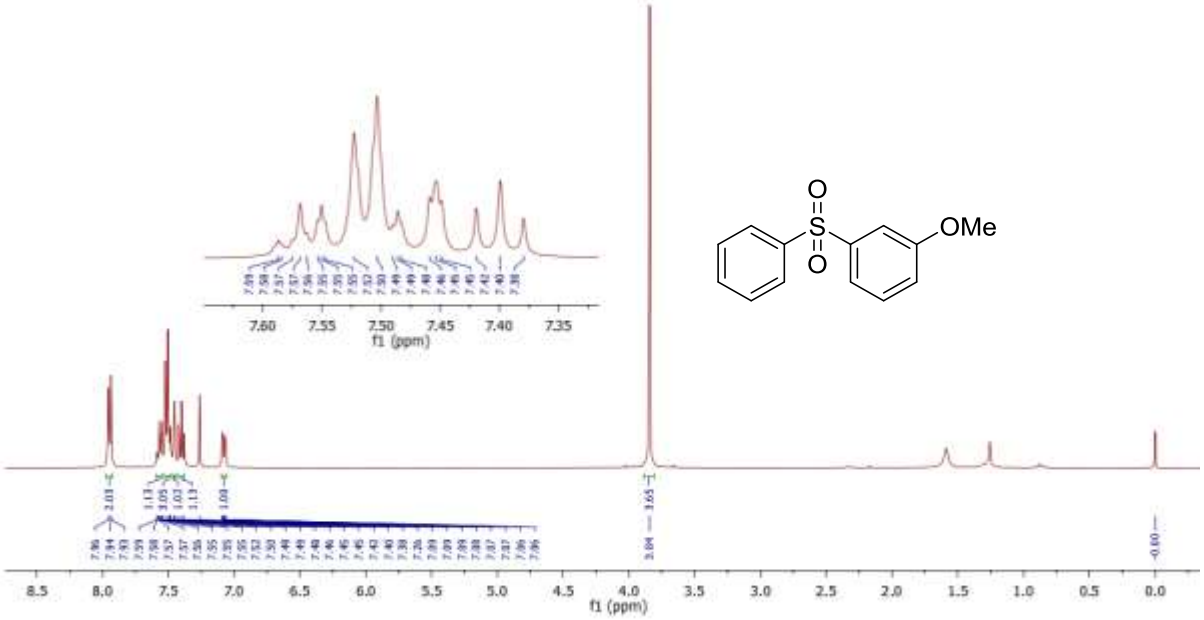
m/z	z	Abund	Formula	Ion
249.0578	1	24104.4	C13 H13 O3 S	(M+H)+
250.0613	1	3672.11	C13 H13 O3 S	(M+H)+
251.0541	1	1251.34	C13 H13 O3 S	(M+H)+

Predicted Isotope Match Table

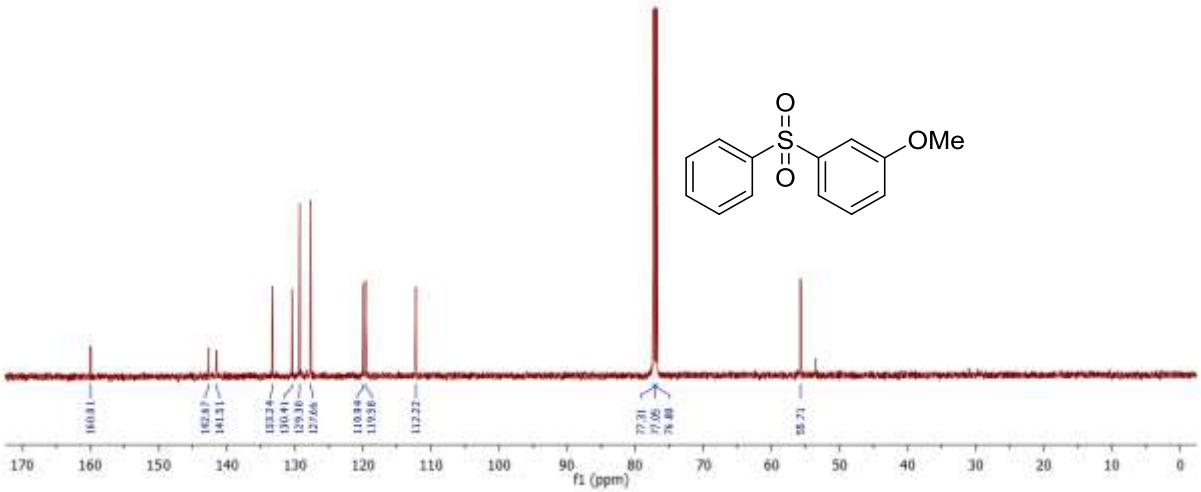
Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	249.0578	249.058	0.91	100	100	83.04	82.46
2	250.0613	250.0612	-0.33	15.23	15.11	12.65	12.46
3	251.0541	251.0565	9.41	5.19	6.15	4.31	5.07

--- End Of Report ---

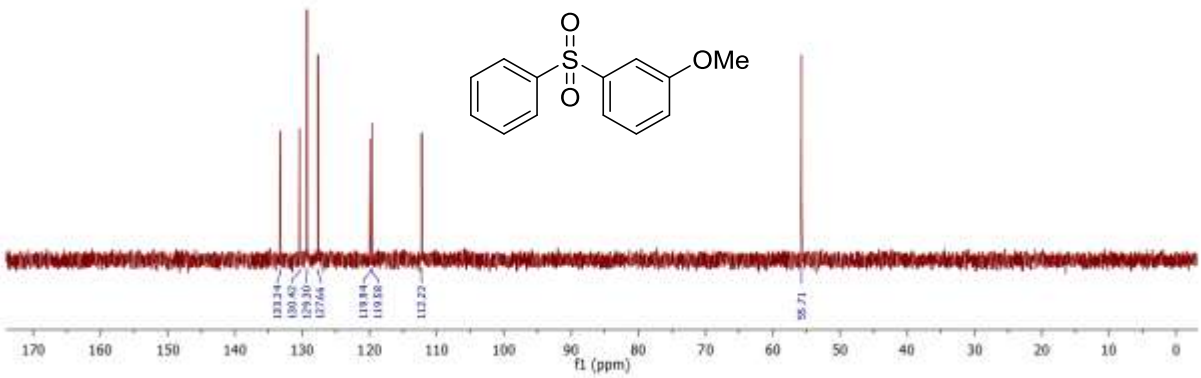
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e**:



^{13}C NMR (125 MHz, $CDCl_3$) of compound **3e**:



DEPT (125 MHz, $CDCl_3$) of compound **3e**:



HRMS (ESI-TOF) of compound **3e**:

Qualitative Compound Report

Data File	3-OMe-SO2ph.d	**Sample Name**	3-OMe-SO2ph
Sample Type	Sample	**Position**	Vial 13
Instrument Name	Instrument 1	**User Name**	
Acq Method	new method.m	**Acquired Time**	29-05-2014 PM 3:46:36
IRM Calibration Status	Success	**DA Method**	daily_report.m
Comment			

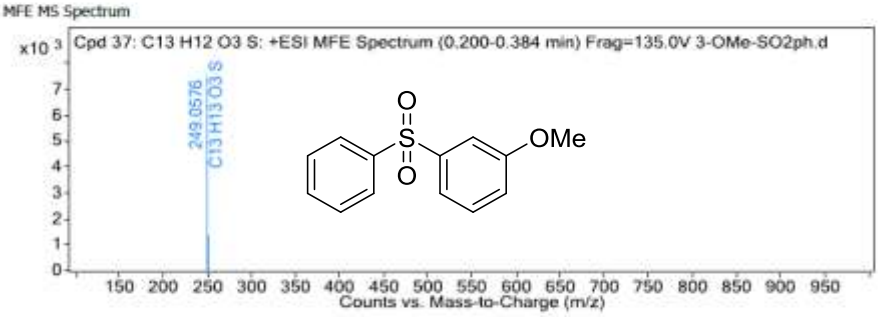
Sample Group **Info.**
Acquisition SW Version 6200 series TOF/6500 series Q-TOF B.05.01 (B5125)

Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 37: C13 H12 O3 S	0.262	248.0498	C13 H12 O3 S	C13 H12 O3 S	3.5	C13 H12 O3 S

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 37: C13 H12 O3 S	249.0576	0.262	Find by Molecular Feature	248.0498

MFE MS Spectrum



MS Spectrum Peak List

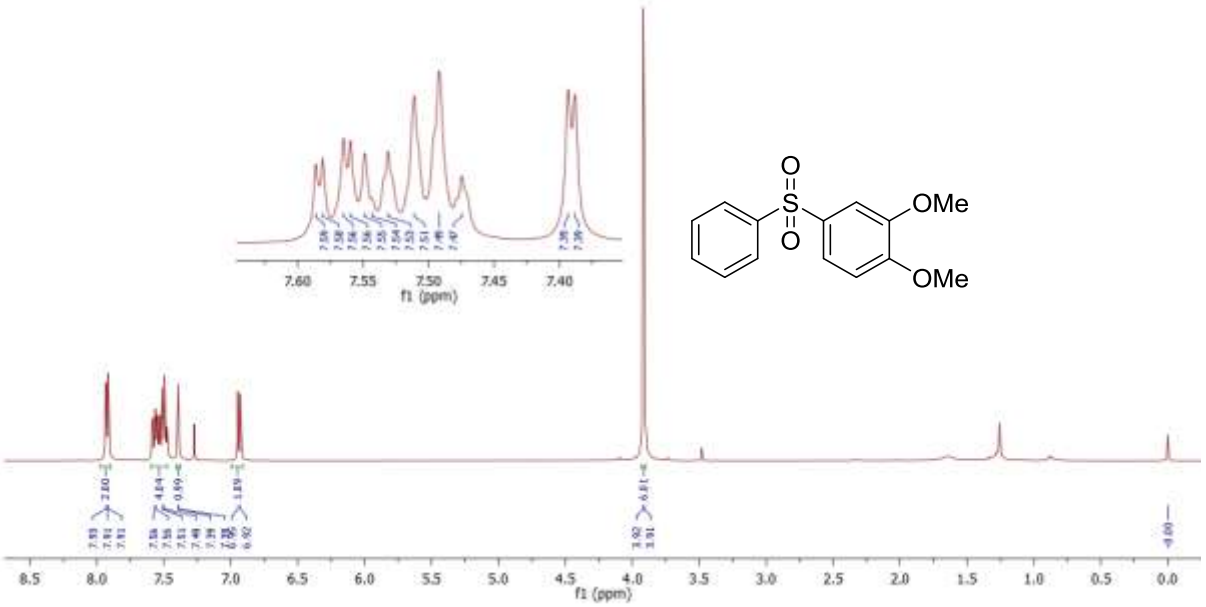
m/z	z	Abund	Formula	Ion
249.0576	1	7520.74	C13 H13 O3 S	(M+H)+
250.0612	1	1393.35	C13 H13 O3 S	(M+H)+
251.0487	1	710.02	C13 H13 O3 S	(M+H)+

Predicted Isotope Match Table

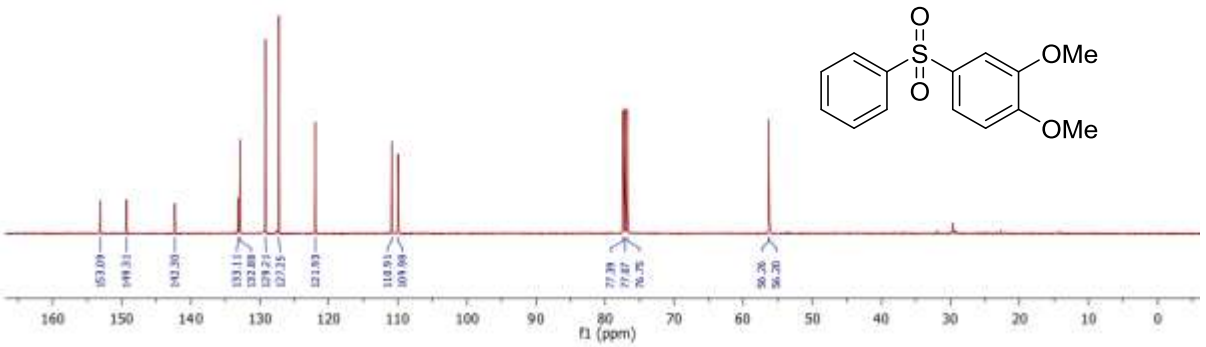
Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	249.0576	249.058	1.59	100	100	78.14	82.46
2	250.0612	250.0612	-0.28	18.53	15.11	14.48	12.46
3	251.0487	251.0565	30.75	9.44	6.15	7.38	5.07

--- End Of Report ---

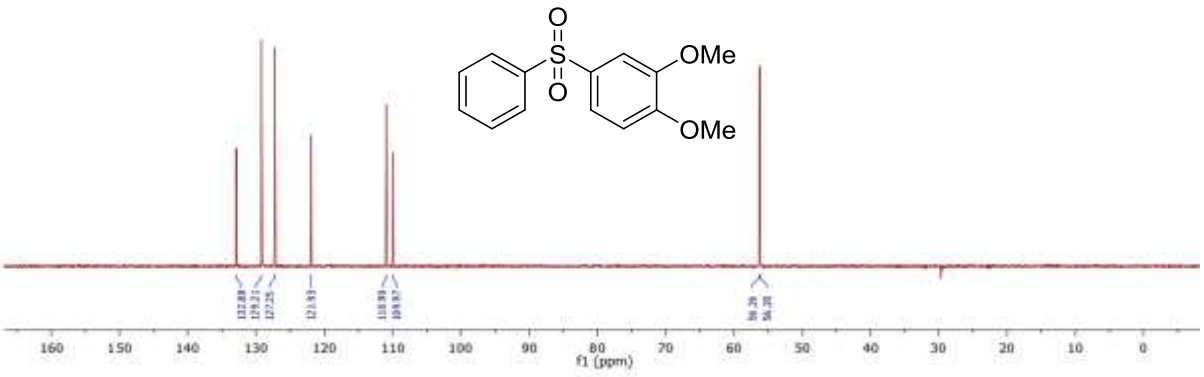
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f**:



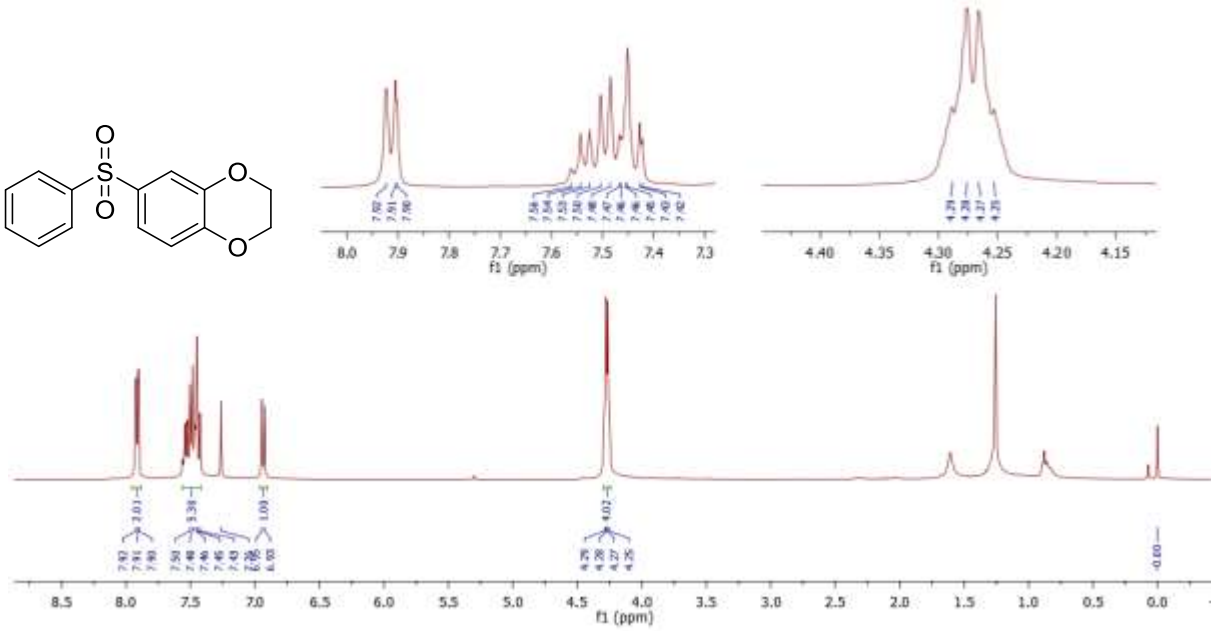
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3f**:



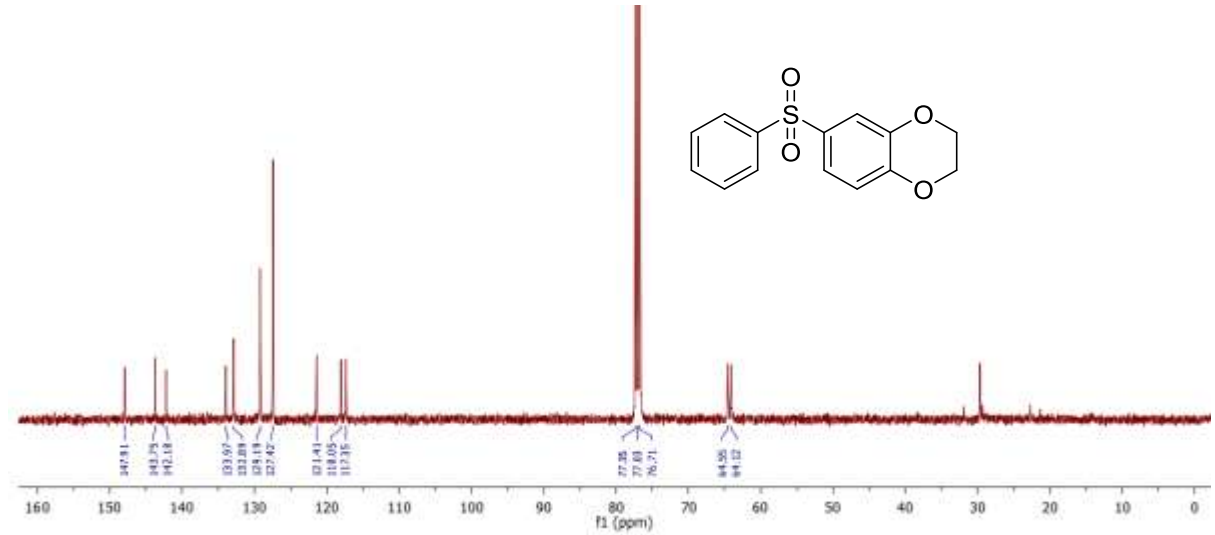
DEPT (100 MHz, $CDCl_3$) of compound **3f**:



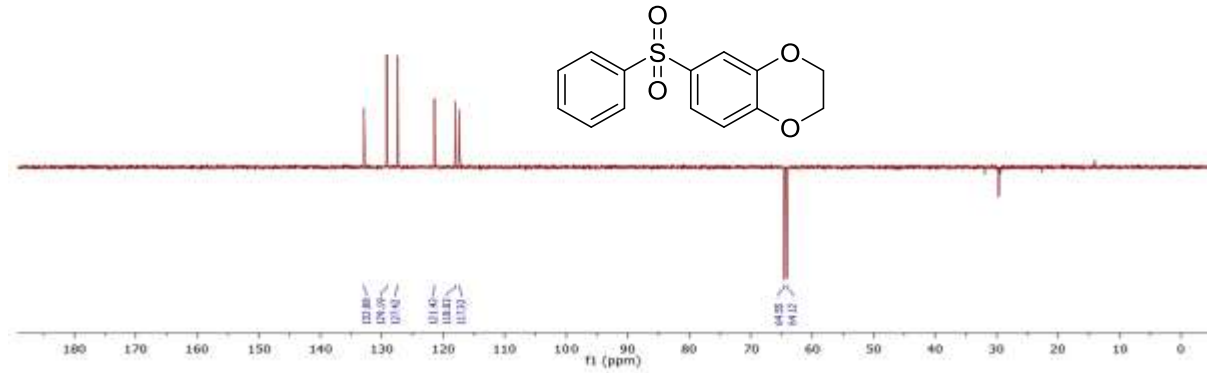
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g**:



^{13}C NMR (100 MHz, $CDCl_3$) of compound **3g**:



DEPT (100 MHz, $CDCl_3$) of compound **3g**:



HRMS (ESI-TOF) of compound **3g**:

Qualitative Compound Report

Data File	BOD-SF.d	**Sample Name**	BOD-SF
Sample Type	Sample	**Position**	Vial 9
Instrument Name	Instrument 1	**User Name**	
Acq Method	new method.m	**Acquired Time**	29-05-2014 PM 3:20:47
IRM Calibration Status	Success	**DA Method**	daily_report.m
Comment			

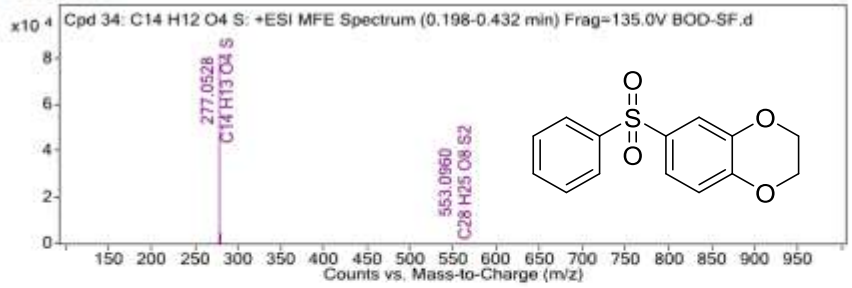
Sample Group **Info.**
Acquisition SW Version 6200 series TOF/6500 series Q-TOF B.05.01 (B5125)

Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 34: C14 H12 O4 S	0.262	276.0454	C14 H12 O4 S	C14 H12 O4 S	0.88	C14 H12 O4 S

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 34: C14 H12 O4 S	277.0528	0.262	Find by Molecular Feature	276.0454

MFE MS Spectrum



MS Spectrum Peak List

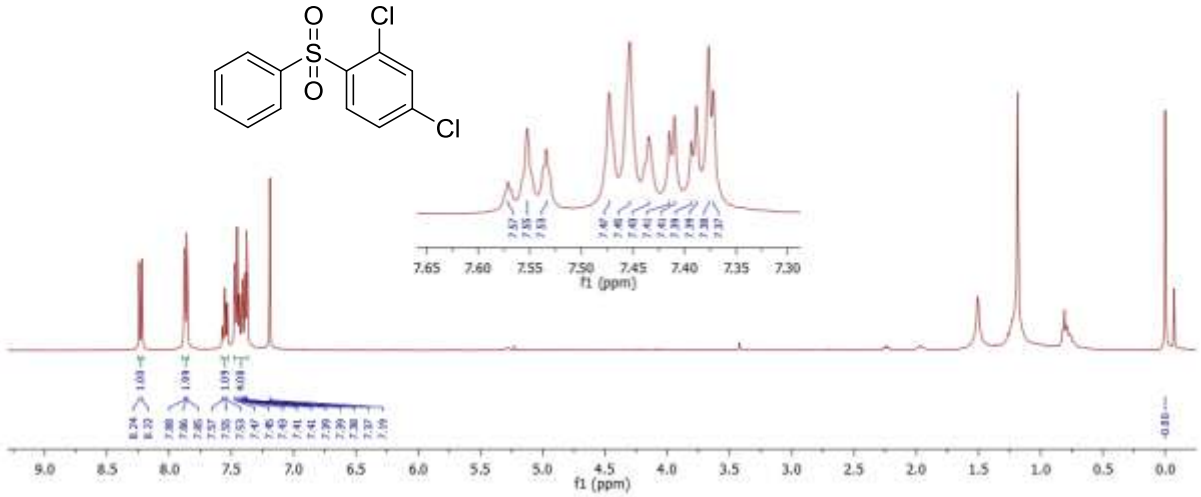
m/z	z	Abund	Formula	Ion
277.0528	1	81664.4	C14 H13 O4 S	(M+H)+
278.055	1	13367.83	C14 H13 O4 S	(M+H)+
279.0517	1	5267.01	C14 H13 O4 S	(M+H)+
553.096	1	347	C28 H25 O8 S2	(2M+H)+

Predicted Isotope Match Table

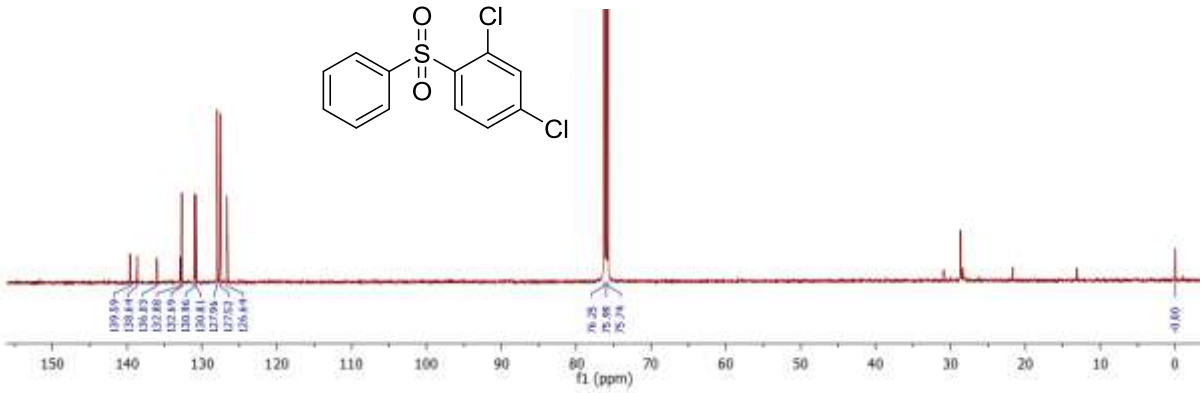
Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	277.0528	277.0529	0.42	100	100	81.42	81.46
2	278.055	278.0561	3.96	16.37	16.23	13.33	13.22
3	279.0517	279.0518	0.06	6.45	6.53	5.25	5.32

--- End Of Report ---

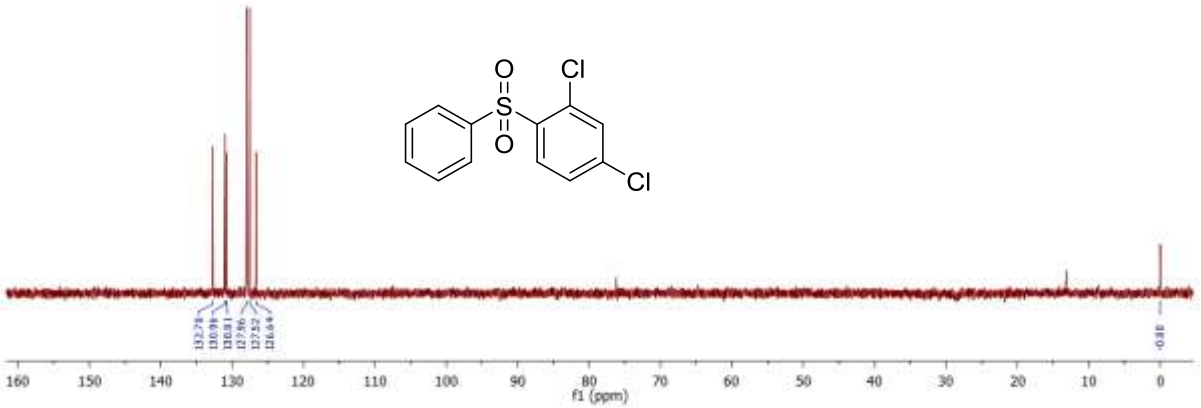
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h**:



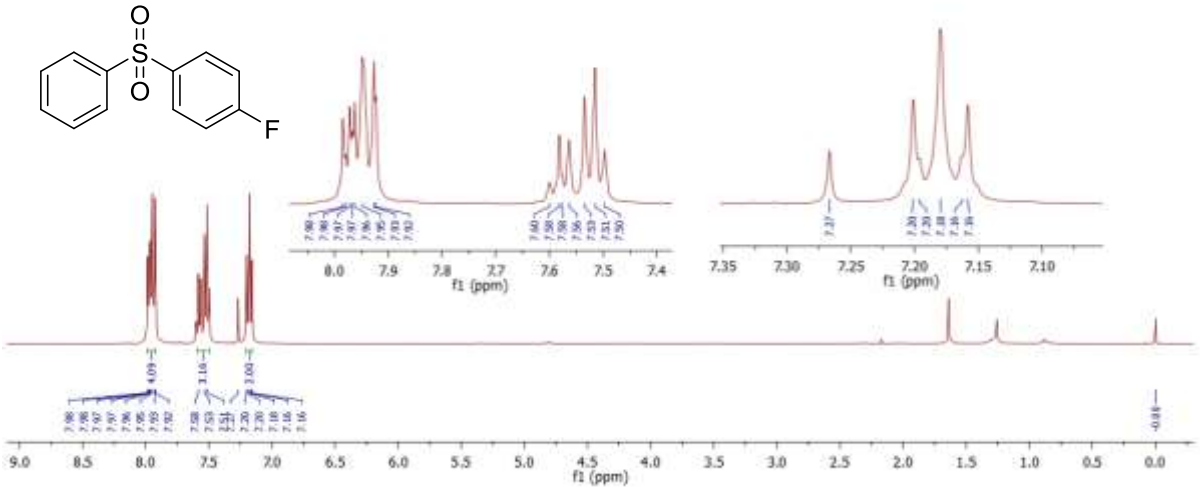
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3h**:



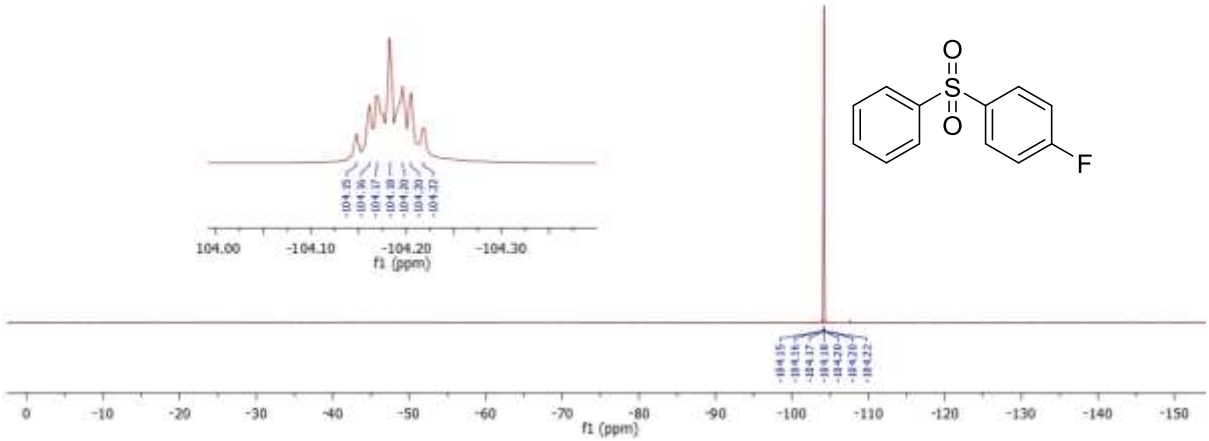
DEPT (125 MHz, $CDCl_3$) of compound **3h**:



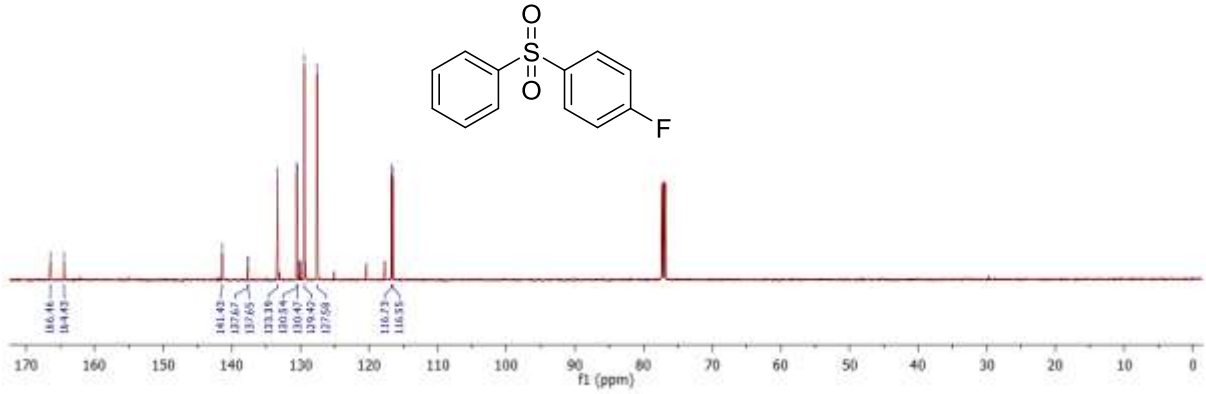
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**:



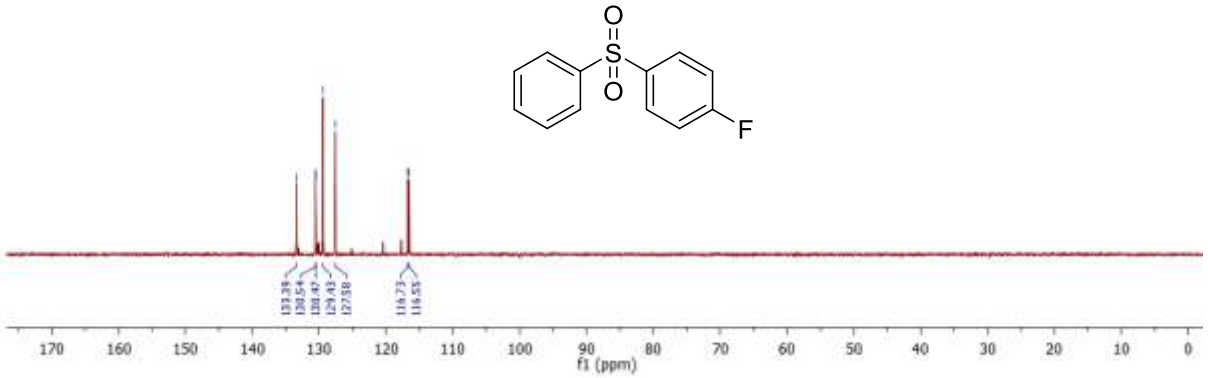
^{19}F NMR (375 MHz, $CDCl_3$) of compound **3i:**



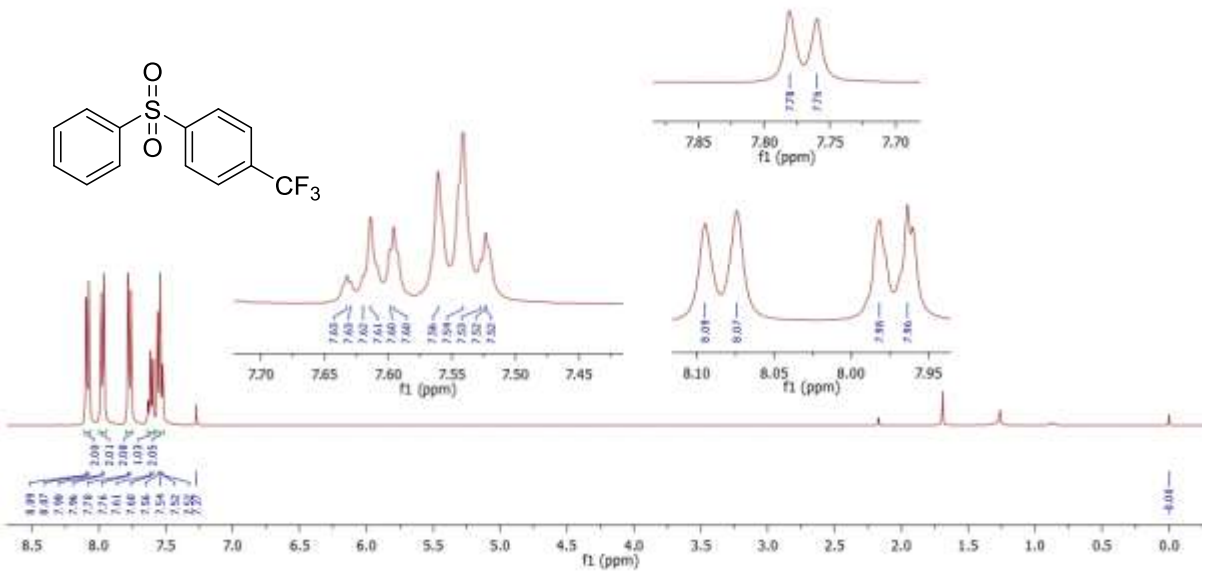
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3i**:



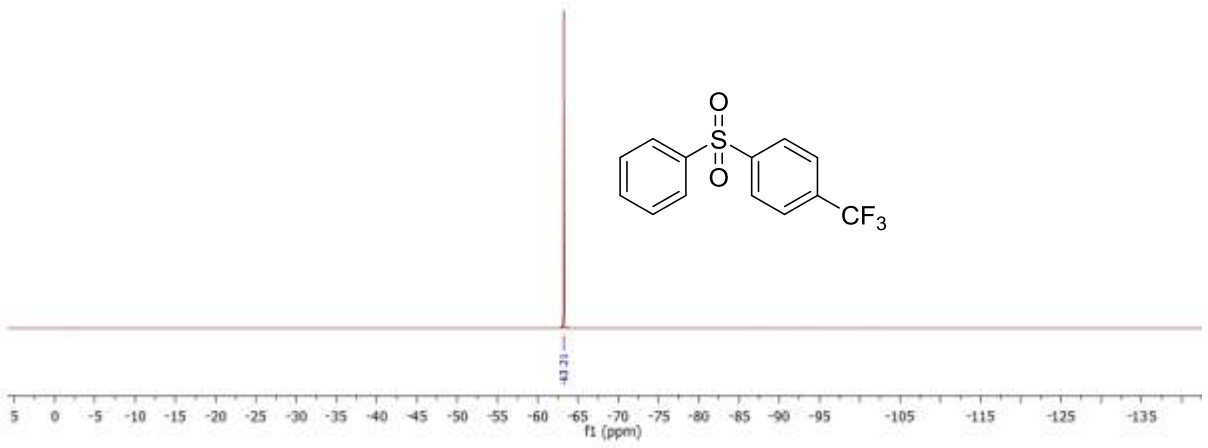
DEPT (125 MHz, $CDCl_3$) of compound **3i**:



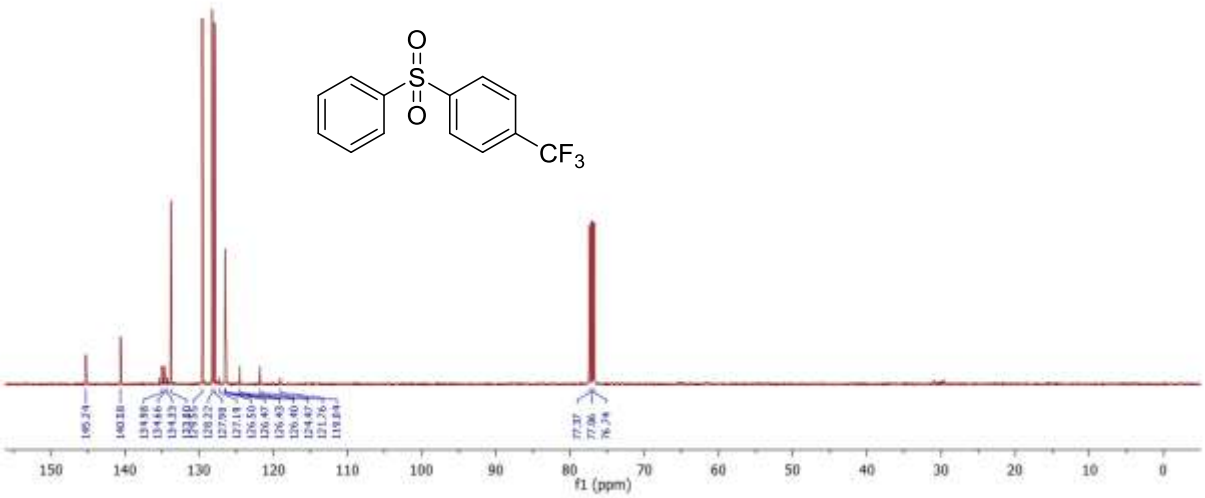
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3j**:



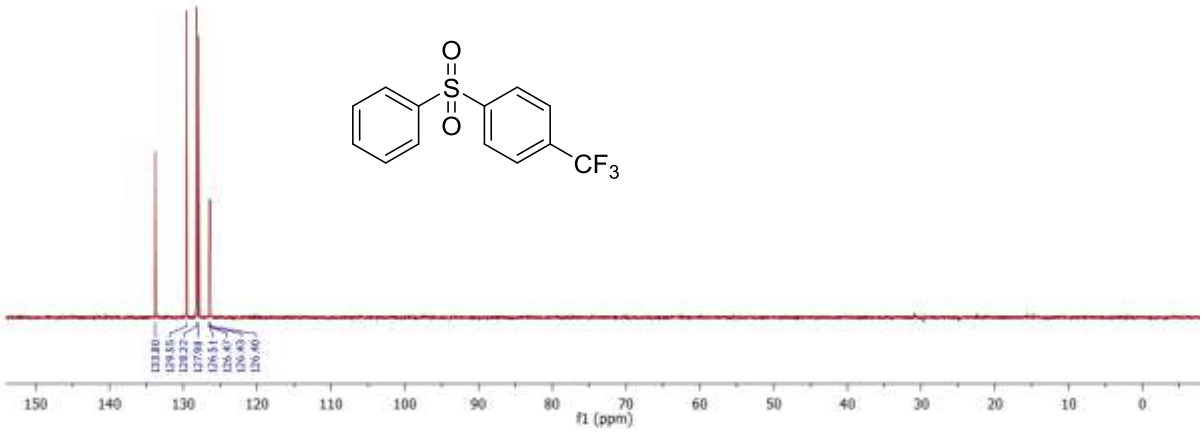
^{19}F NMR (375 MHz, $CDCl_3$) of compound **3j:**



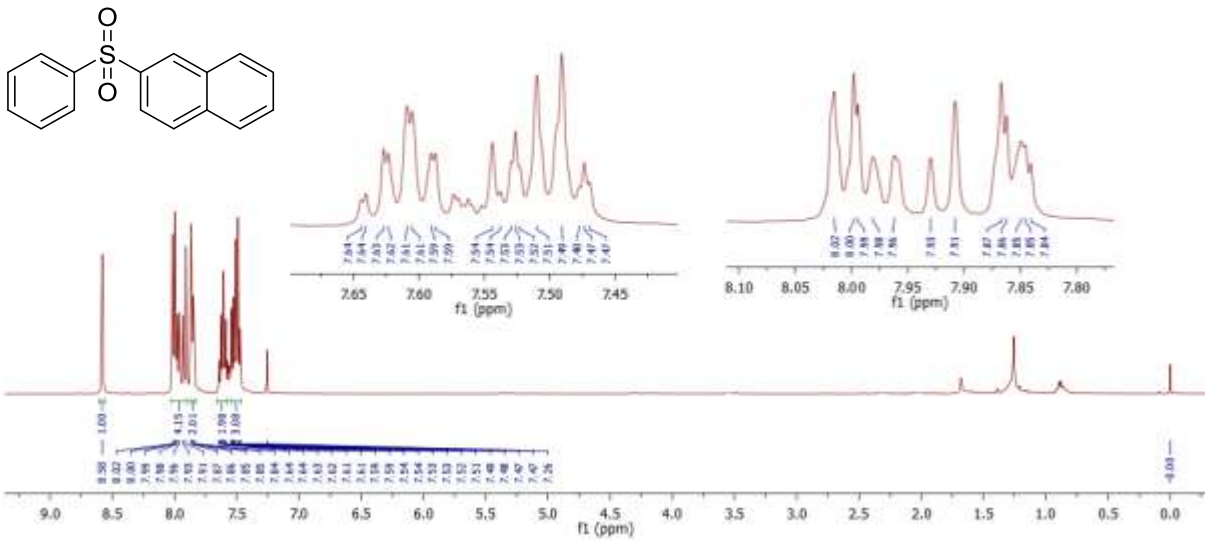
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3j**:



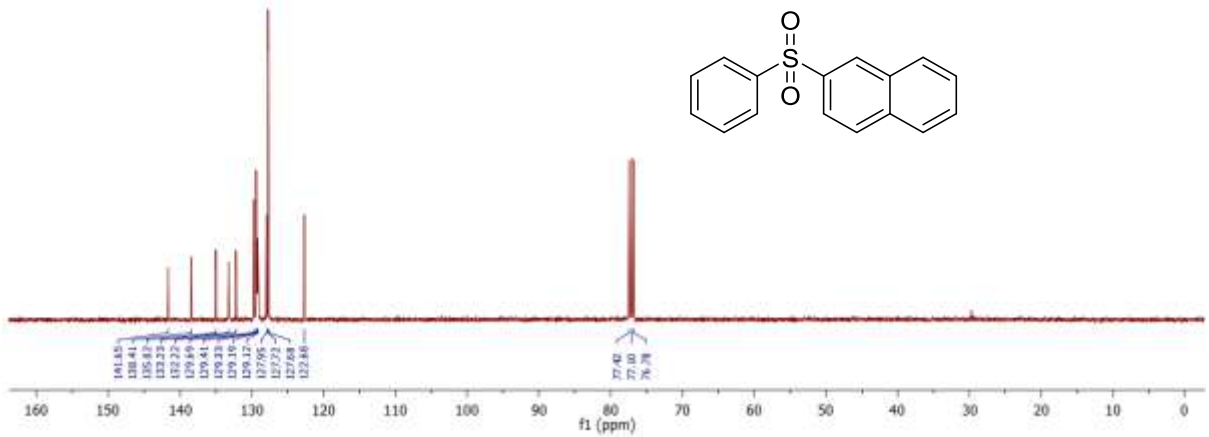
DEPT (100 MHz, $CDCl_3$) of compound **3j**:



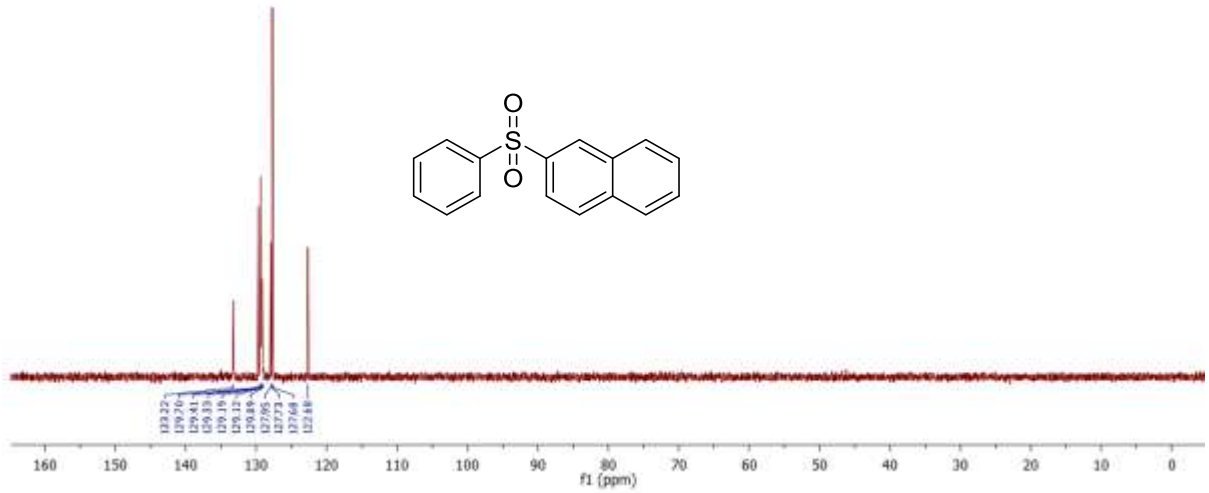
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3k**:



^{13}C NMR (100 MHz, $CDCl_3$) of compound **3k**:



DEPT (100 MHz, $CDCl_3$) of compound **3k**:



HRMS (ESI-TOF) of compound **3k**:

Qualitative Compound Report

Data File	Naph-SOph.d	**Sample Name**	Naph-SOph
Sample Type	Sample	**Position**	Vial 5
Instrument Name	Instrument 1	**User Name**	
Acq Method	new method.m	**Acquired Time**	29-05-2014 PM 2:58:07
IRM Calibration Status	Success	**DA Method**	daily_report.m
Comment			

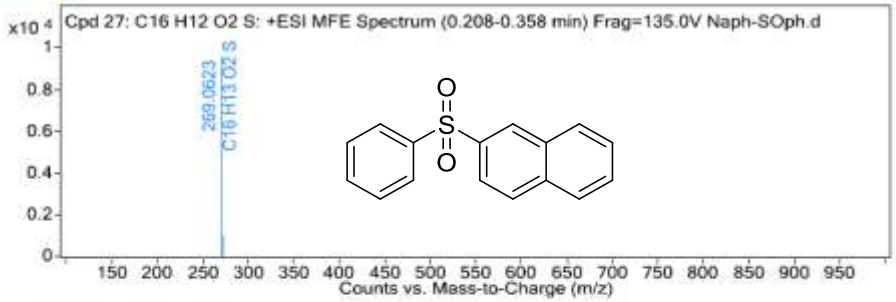
Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (85125)

Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 27: C16 H12 O2 S	0.26	268.055	C16 H12 O2 S	C16 H12 O2 S	2.88	C16 H12 O2 S

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 27: C16 H12 O2 S	269.0623	0.26	Find by Molecular Feature	268.055

MFE MS Spectrum



MS Spectrum Peak List

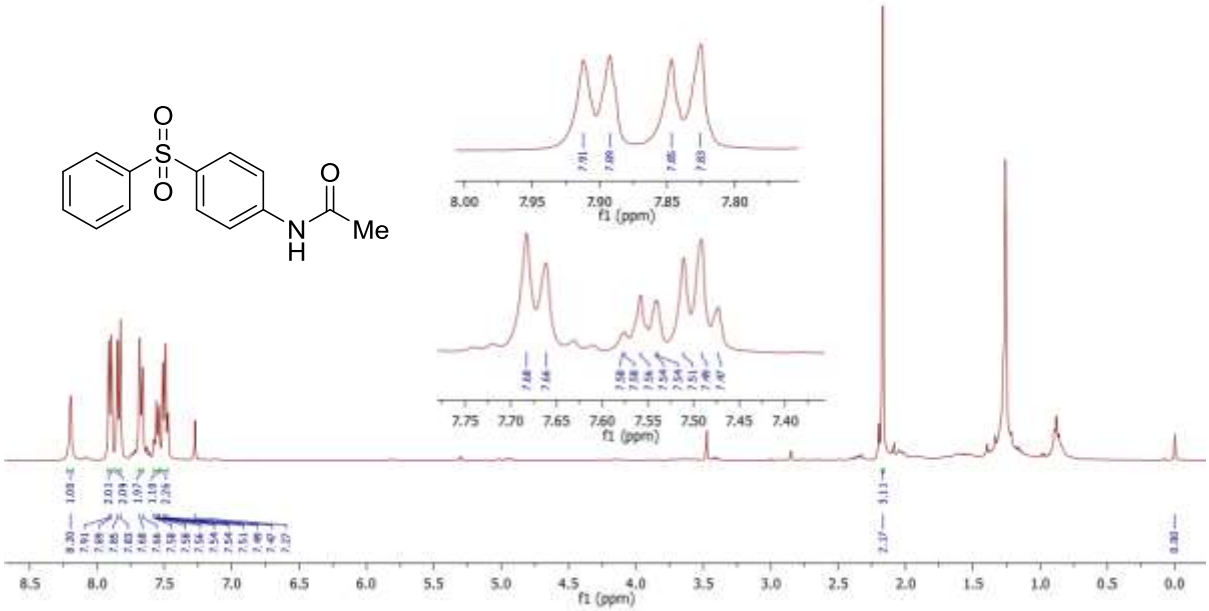
m/z	z	Abund	Formula	Ion
269.0623	1	9614.66	C16 H13 O2 S	(M+H)+
270.0654	1	2143.6	C16 H13 O2 S	(M+H)+
271.0617	1	1081.41	C16 H13 O2 S	(M+H)+

Predicted Isotope Match Table

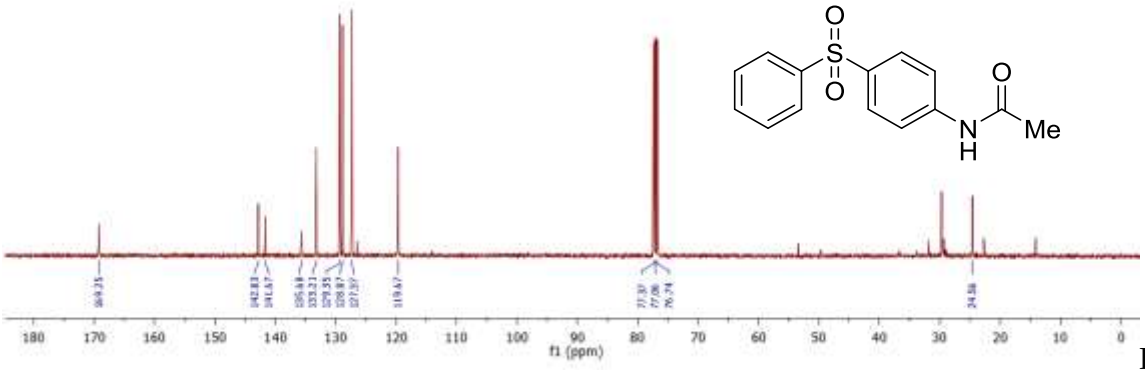
Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	269.0623	269.0631	2.93	100	100	74.88	80.14
2	270.0654	270.0663	3.44	22.3	18.32	16.7	14.68
3	271.0617	271.062	1.18	11.25	6.47	8.42	5.18

--- End Of Report ---

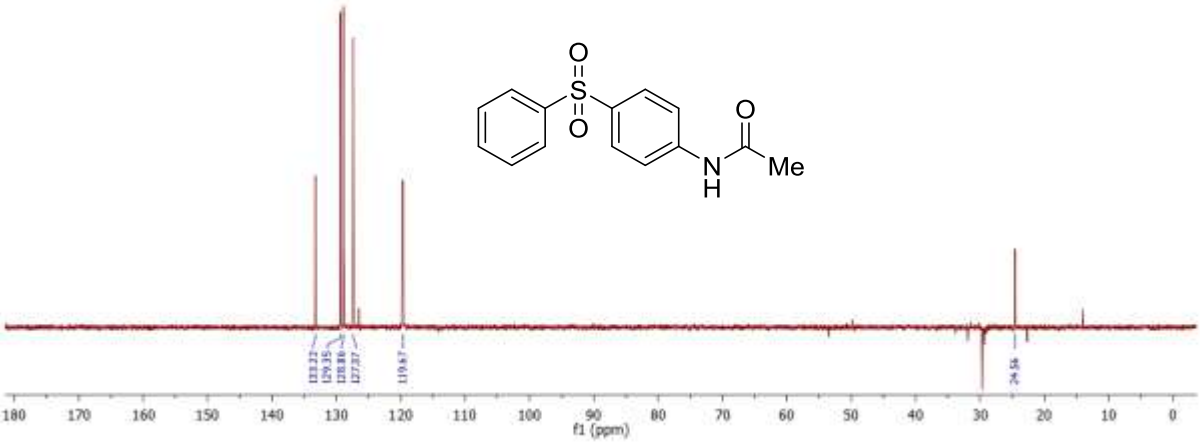
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3l**:



^{13}C NMR (100 MHz, $CDCl_3$) of compound **3l**:



DEPT (100 MHz, $CDCl_3$) of compound **3l**:



HRMS (ESI-TOF) of compound **3l**:

Qualitative Compound Report

Data File	N-ASO2ph.d	**Sample Name**	N-ASO2ph
Sample Type	Sample	**Position**	Vial 11
Instrument Name	Instrument 1	**User Name**	
Acq Method	new method.m	**Acquired Time**	29-05-2014 PM 3:34:34
IRM Calibration Status	Success	**DA Method**	daily_report.m
Comment			

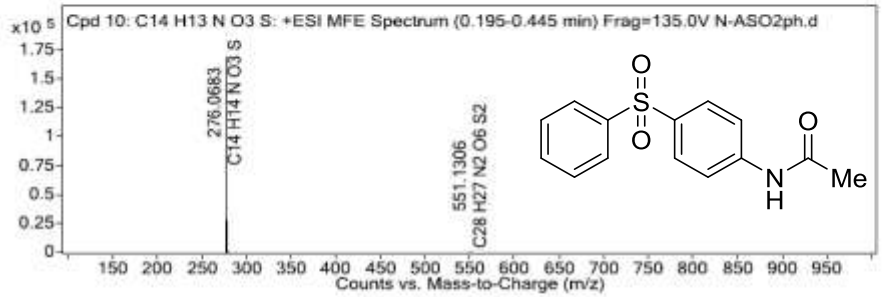
Sample Group **Info.**
Acquisition SW Version 6200 series TOF/6500 series Q-TOF B.05.01 (B5125)

Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 10: C14 H13 N O3 S	0.245	275.061	C14 H13 N O3 S	C14 H13 N O3 S	2.13	C14 H13 N O3 S

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 10: C14 H13 N O3 S	276.0683	0.245	Find by Molecular Feature	275.061

MFE MS Spectrum



MS Spectrum Peak List

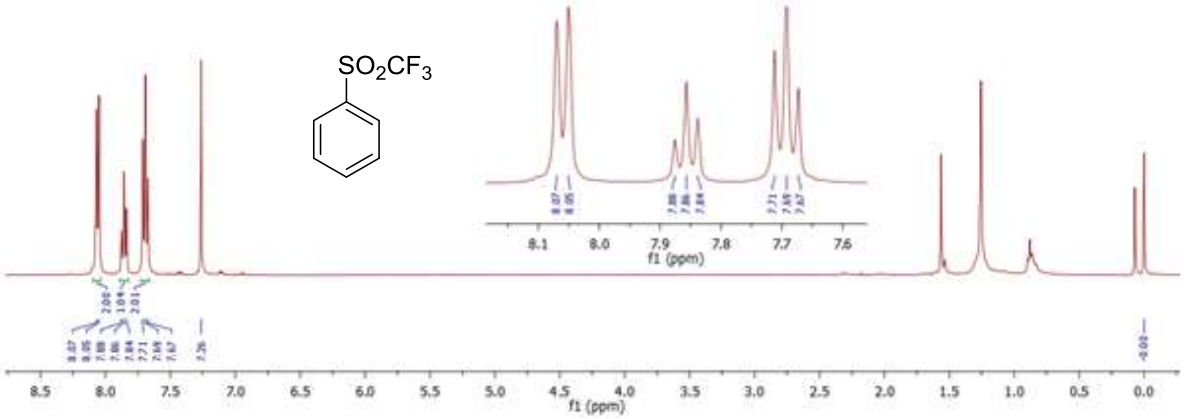
m/z	z	Abund	Formula	Ion
276.0683	1	169186.67	C14 H14 N O3 S	(M+H)+
277.0712	1	27675.43	C14 H14 N O3 S	(M+H)+
278.0675	1	8506.05	C14 H14 N O3 S	(M+H)+
279.0648	1	807.61	C14 H14 N O3 S	(M+H)+
551.1306	1	907.78	C28 H27 N2 O6 S2	(2M+H)+
552.1254	1	384.32	C28 H27 N2 O6 S2	(2M+H)+

Predicted Isotope Match Table

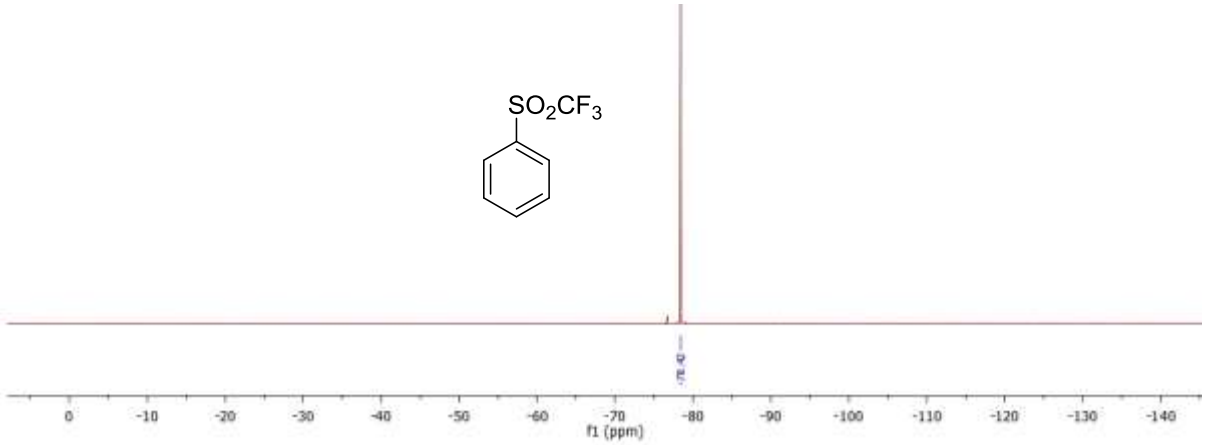
Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	276.0683	276.0689	2.05	100	100	82.06	80.76
2	277.0712	277.072	2.67	16.36	16.57	13.42	13.38
3	278.0675	278.0676	0.47	5.03	6.38	4.13	5.15
4	279.0648	279.0696	17.24	0.48	0.87	0.39	0.7

--- End Of Report ---

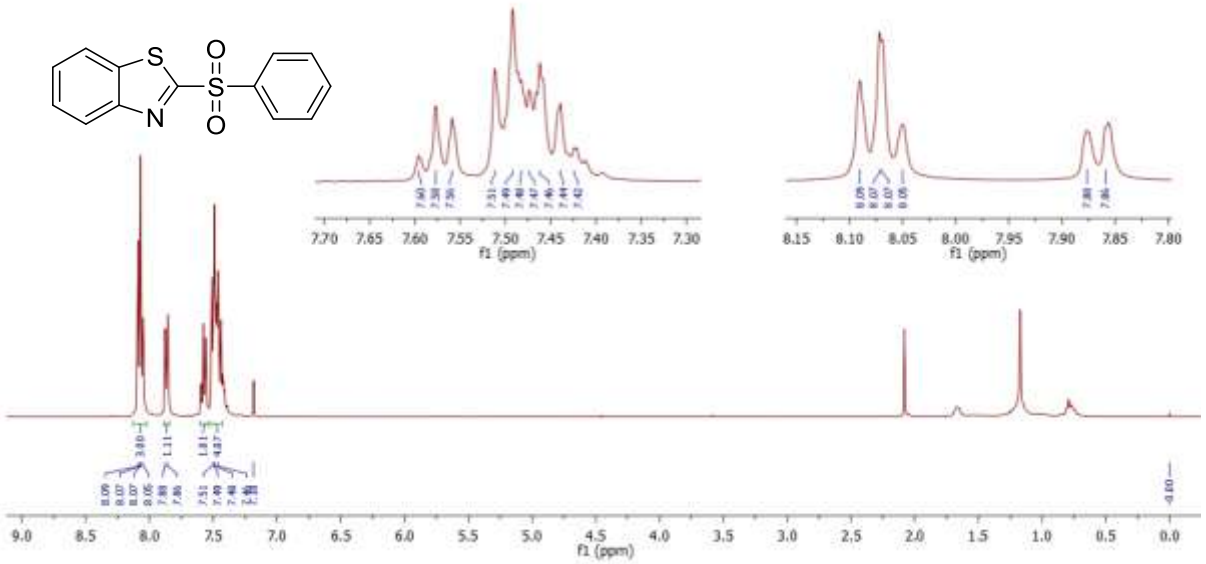
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3m**:



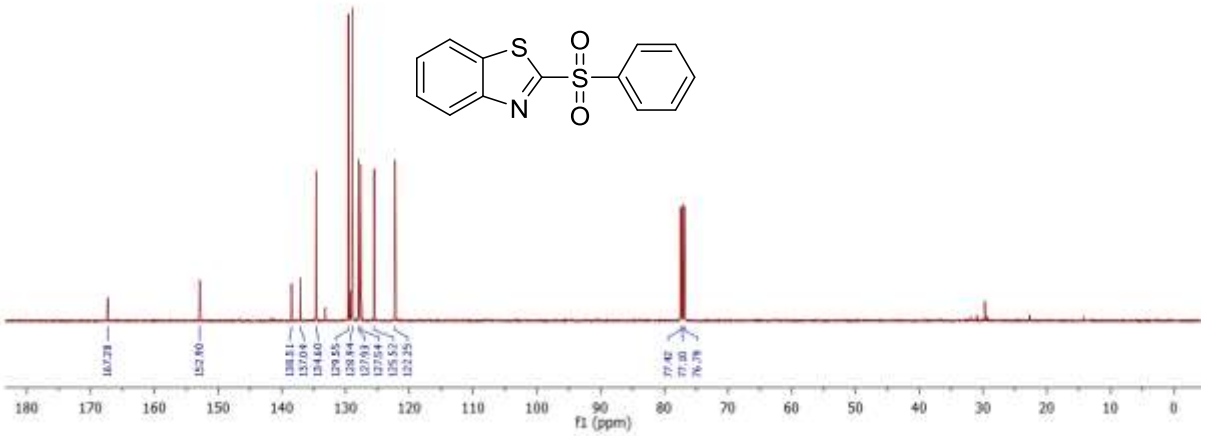
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3m:**



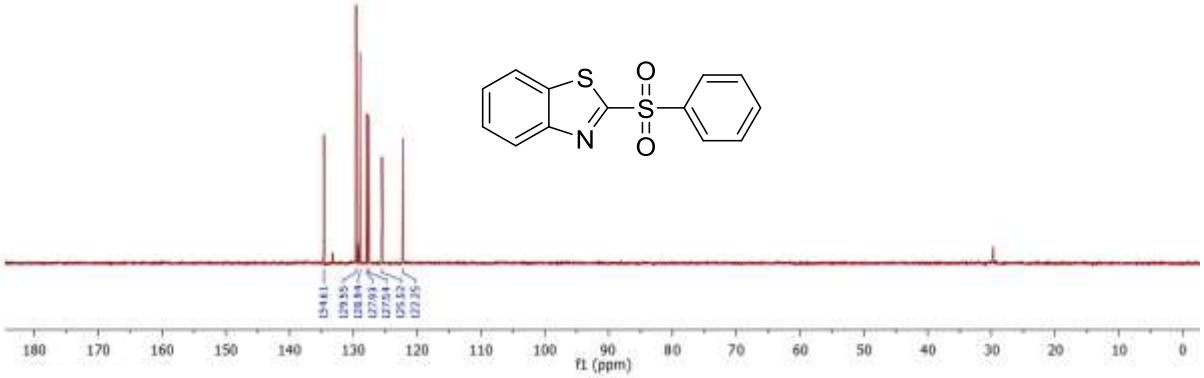
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3o**:



^{13}C NMR (100 MHz, $CDCl_3$) of compound **3o**:



DEPT (100 MHz, $CDCl_3$) of compound **3o**:



HRMS (ESI-TOF) of compound **3o**:

Qualitative Compound Report

Data File	BT-SOph.d	**Sample Name**	BT-SOph
Sample Type	Sample	**Position**	Vial 4
Instrument Name	Instrument 1	**User Name**	
Acq Method	new method.m	**Acquired Time**	29-05-2014 PM 2:53:32
IRM Calibration Status	Success	**DA Method**	daily_report.m
Comment			

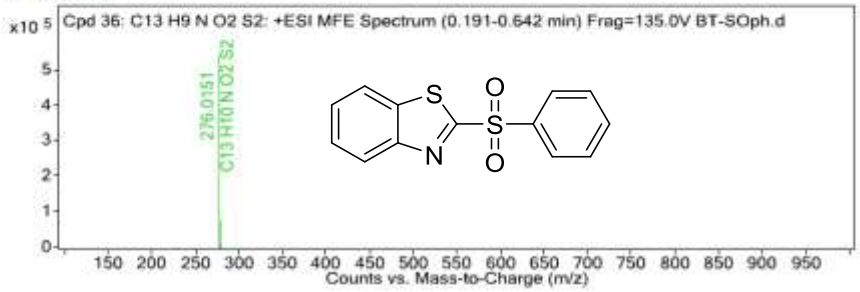
Sample Group **Info.**
Acquisition SW Version 6200 series TOF/6500 series Q-TOF B.05.01 (B5125)

Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 36: C13 H9 N O2 S2	0.261	275.0078	C13 H9 N O2 S2	C13 H9 N O2 S2	-1.13	C13 H9 N O2 S2

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 36: C13 H9 N O2 S2	276.0151	0.261	Find by Molecular Feature	275.0078

MFE MS Spectrum



MS Spectrum Peak List

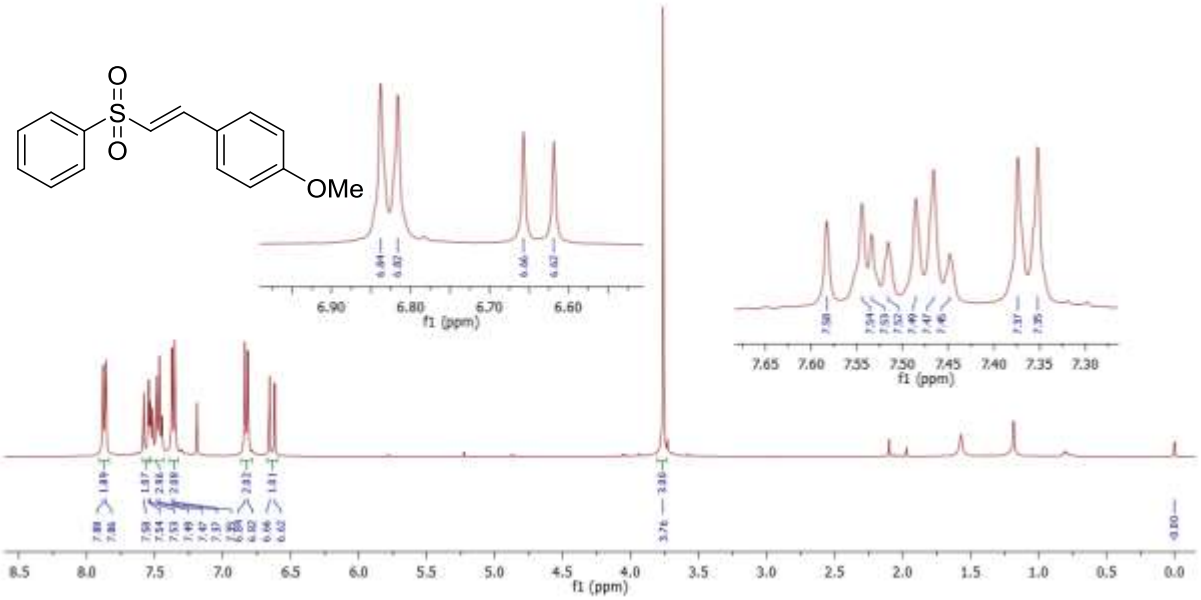
m/z	z	Abund	Formula	Ion
276.0151	1	538699.44	C13 H10 N O2 S2	(M+H)+
277.0176	1	78830.97	C13 H10 N O2 S2	(M+H)+
278.012	1	50456.3	C13 H10 N O2 S2	(M+H)+
279.0145	1	7993.95	C13 H10 N O2 S2	(M+H)+

Predicted Isotope Match Table

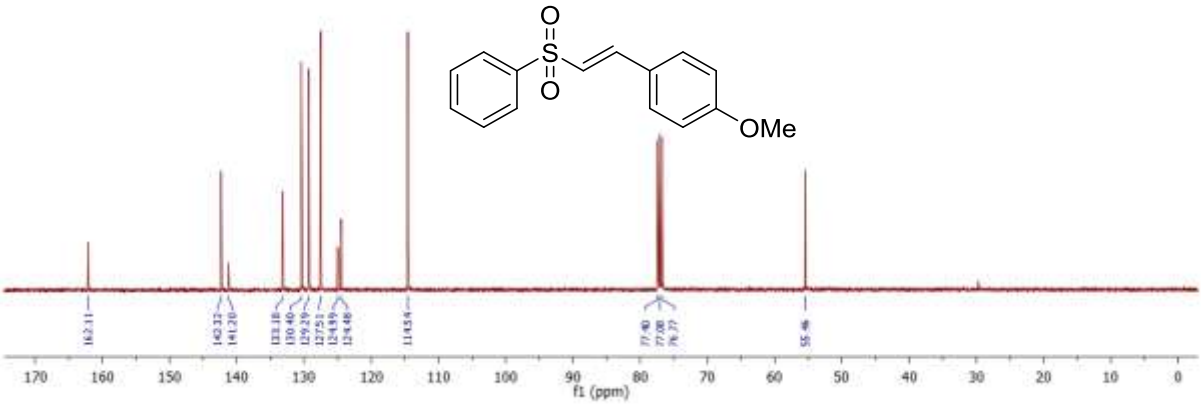
Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	276.0151	276.0147	-1.42	100	100	79.69	77.95
2	277.0176	277.0176	0.1	14.63	16.2	11.66	12.62
3	278.012	278.012	0.04	9.37	10.59	7.46	8.25
4	279.0145	279.0143	-0.77	1.48	1.5	1.18	1.17

--- End Of Report ---

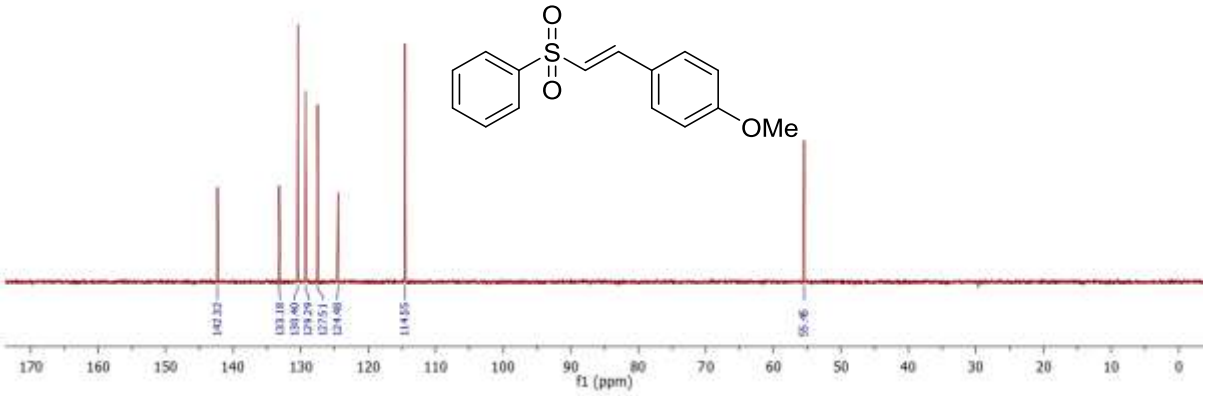
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3p**:



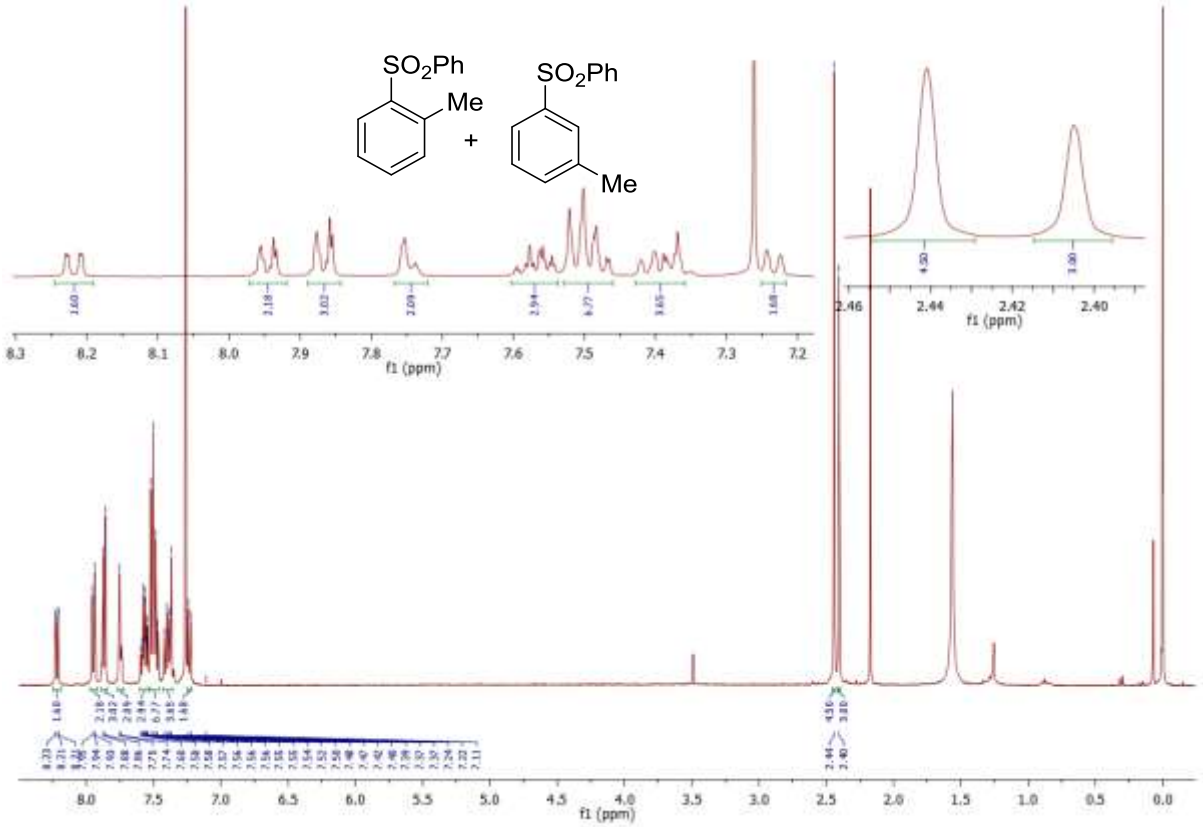
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3p**:



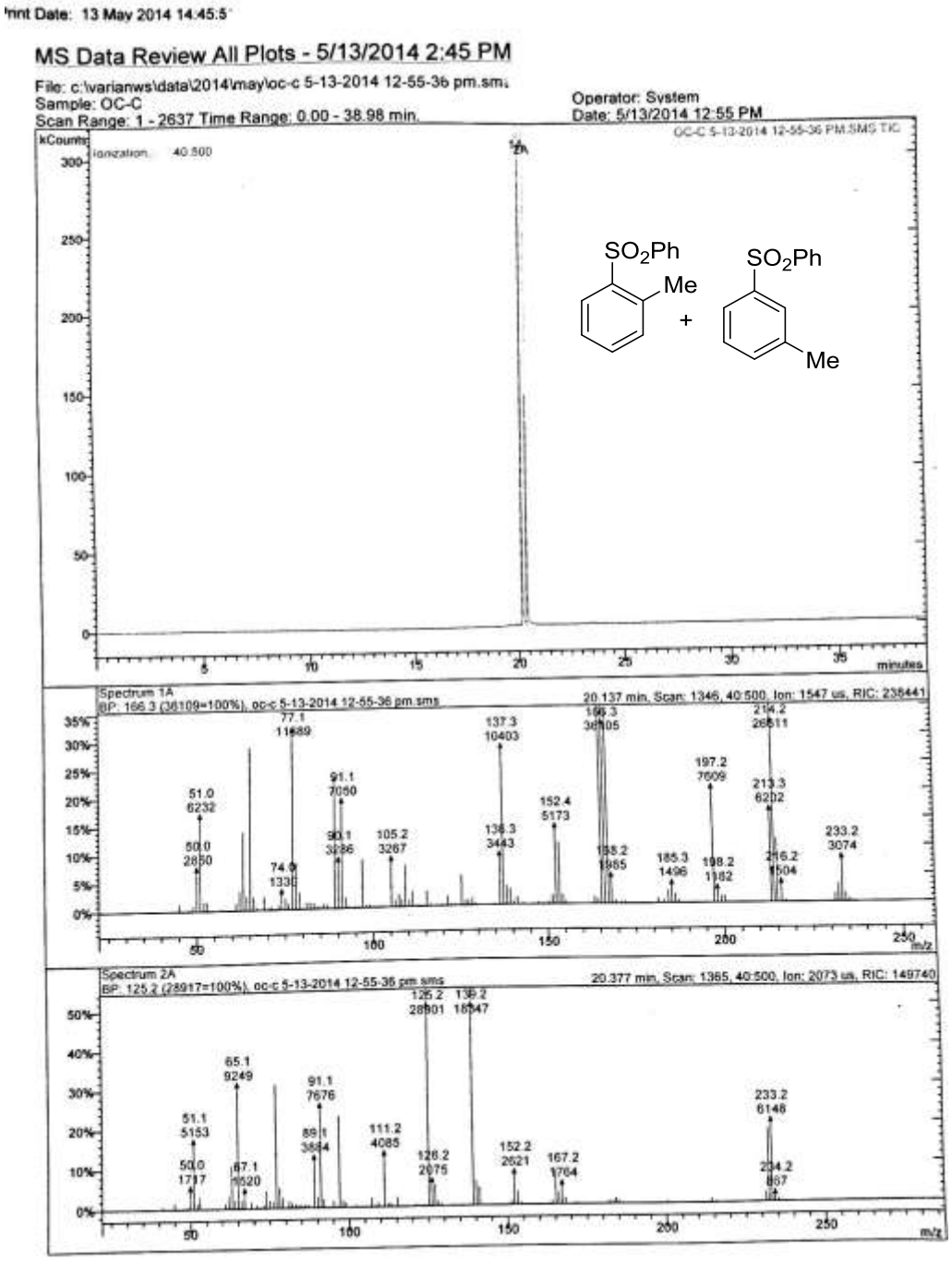
DEPT (100 MHz, $CDCl_3$) of compound **3p**:



^{1}H NMR (400 MHz, CDCl3) of compounds **4a & 4a′** (**37:63**) mixture:



GC-MS of compounds **4a & 4a′** (**37:63**) mixture:



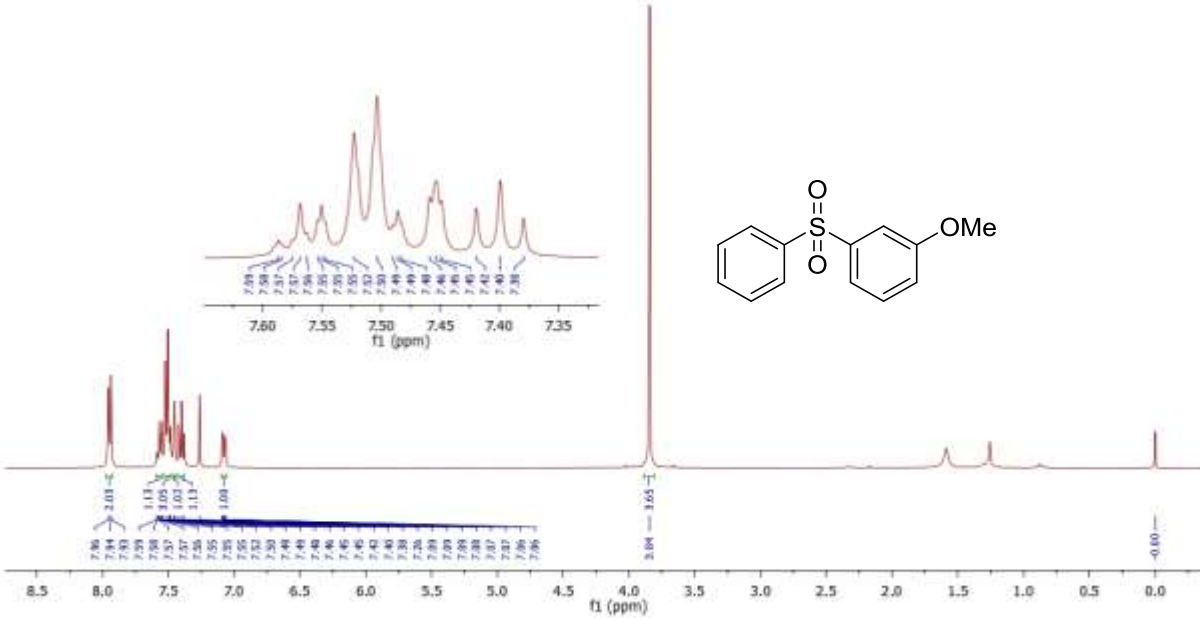
int Date: 13 May 2014 14:46:59

Plot 1. oc-c 5-13-2014 12-55-36 pm.sms - 5/13/2014 12:55 PM

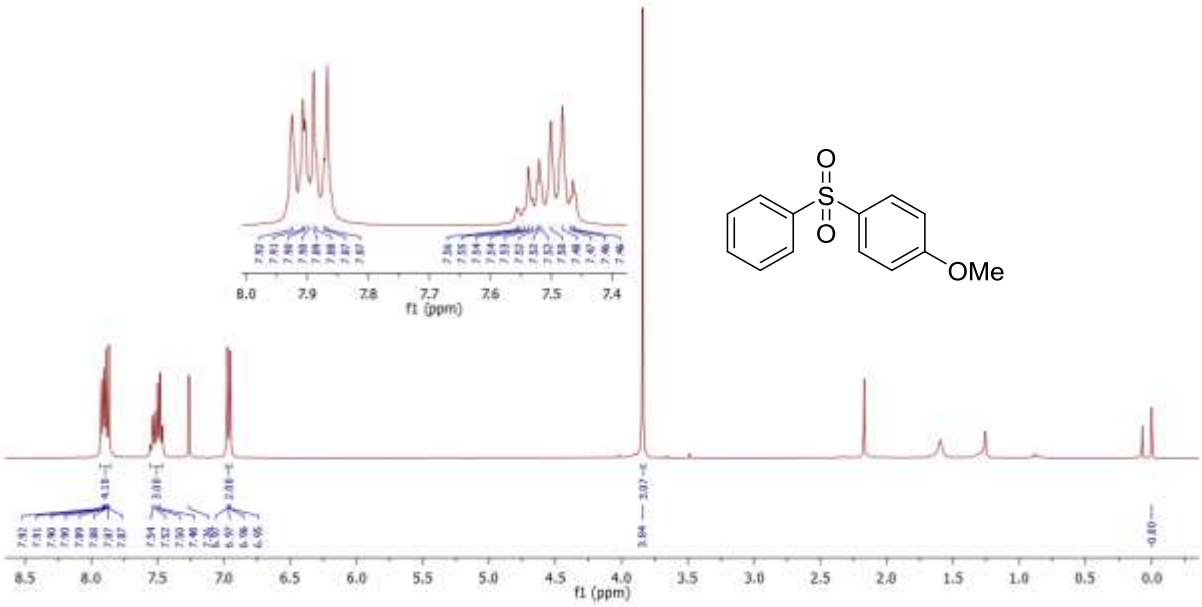
Lock Peak Width:	No
Parameters:	Local
Peak Width (sec):	4.0
Slope Sensitivity (SN):	20
Tangent %:	10
Peak Size Reject (counts):	2000
Smoothing:	None
Spike Threshold Factor:	None
Noise:	Peak to Peak

	Retention Time	Area	% of Total	Signal/Noise	Scan Description
1.	20.147	717280	63.043	1960	Merged
2.	20.373	420474	36.957	1052	Merged

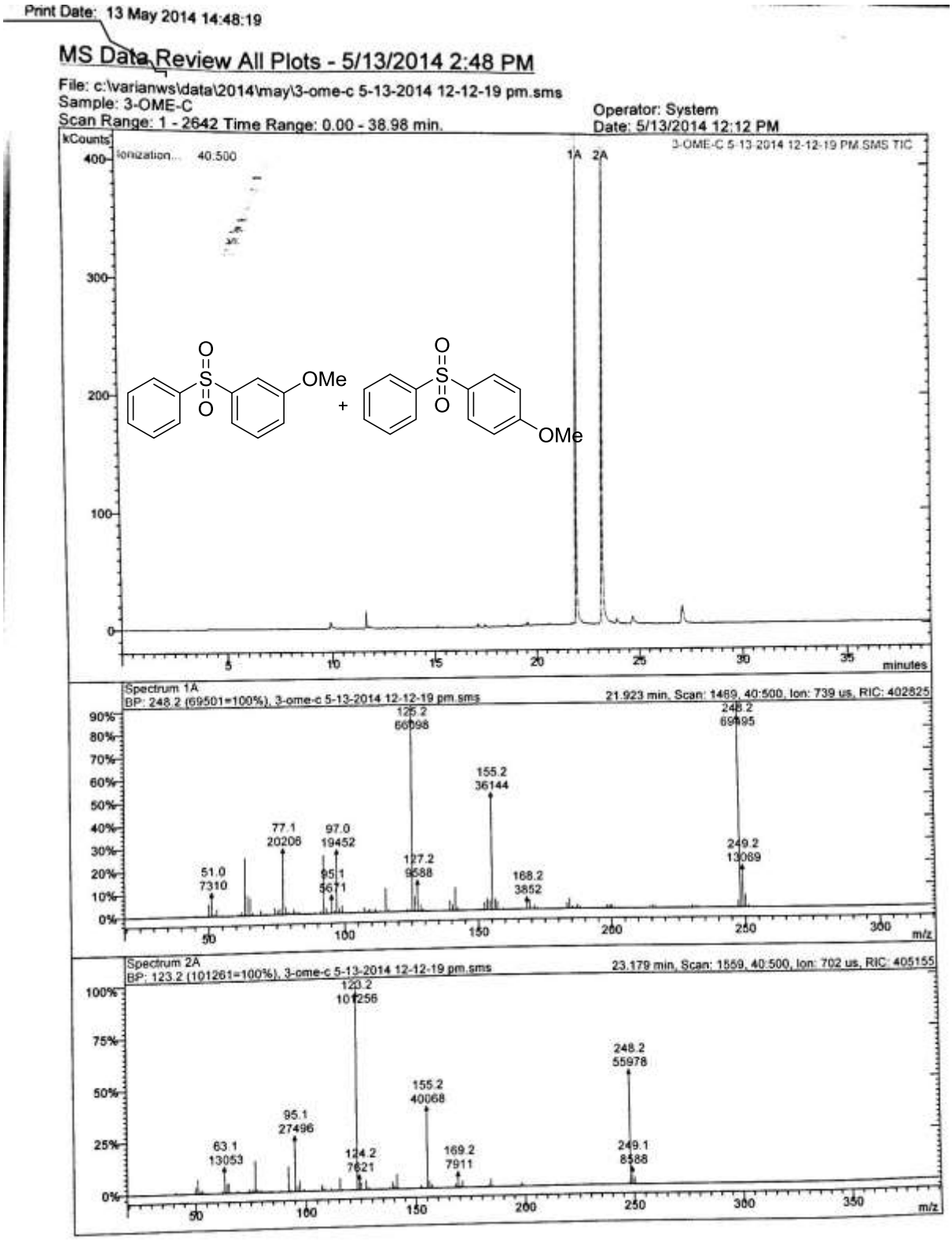
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4b**:



^{1}H NMR (400 MHz, $CDCl_3$) of compound **4b′**:



GC-MS of compounds **4b & 4b′** (**45:55**) mixture:



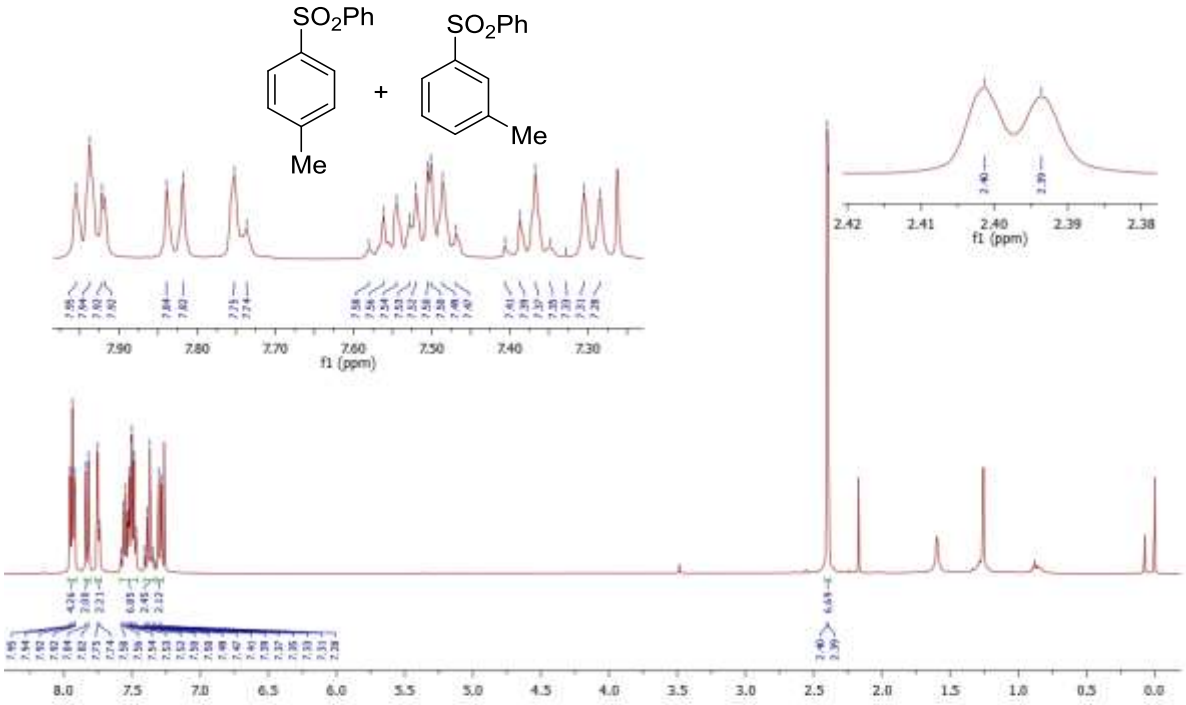
Print Date: 13 May 2014 14:50:30

Plot 1. 3-ome-c 5-13-2014 12-12-19 pm.sms - 5/13/2014 12:12 PM

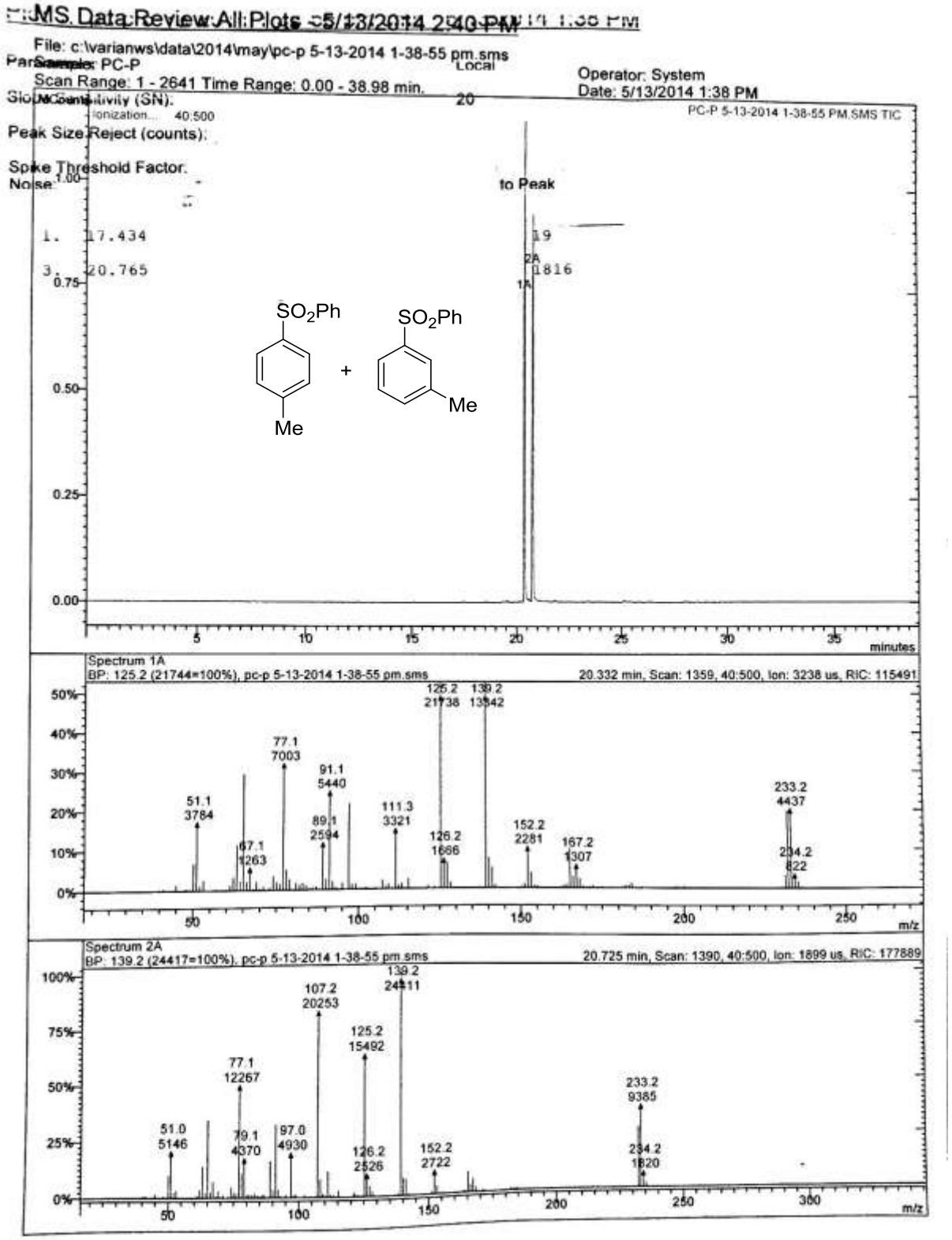
Lock Peak Width:	No
Parameters:	Local
Peak Width (sec):	4.0
Slope Sensitivity (SN):	256
Tangent %:	10
Peak Size Reject (counts):	50
Smoothing:	None
Spike Threshold Factor:	None
Noise:	Peak to Peak

	Retention Time	Area	% of Total	Signal/Noise	Scan Description
1.	21.922	1.374e+6	44.574	1890	Merged
2.	23.175	1.709e+6	55.426	1733	Merged

^{1}H NMR (400 MHz, CDCl3) of compounds **4c & 4c′** (**1:1.1**) mixture:



GC-MS of compounds **4c & 4c′** (**53:47**) mixture:



Plot 1. pc-p 5-13-2014 1-38-55 pm.sms - 5/13/2014 1:38 PM

Lock Peak Width:	
Parameters:	Local
Peak Width (sec):	
Slope Sensitivity (SN):	20
Tangent %:	
Peak Size Reject (counts):	2000
Smoothing:	
Spike Threshold Factor:	None
Noise:	Peak to Peak

	Retention Time	Area	% of Total	Classification	Scan Description
1.	17.434	4535	0.072	19	Merged
2.	20.370	3.350e+6	53.122	3053	Merged
3.	20.765	2.952e+6	46.806	1816	Merged

References:

1. Umierski, N.; Manolikakes, G. *Org. Lett*. **2013**, *15*, 188.
2. Umierski, N.; Manolikakes, G. *Org. Lett*. **2013**, *15*, 4972.
3. Burton, H.; Hoggarth, E. *J. Chem. Soc*. **1945**, 14.
4. Marquie, J.; Laporterie, A.; Dubac, J. *J. Org. Chem.* **2001**, *66*, 421.
5. Zhu, W.; Ma, D. *J. Org. Chem*. **2005**, *70*, 2696.
6. Steven, C. C.; Shashank, S.; Nandkishor, K. N. *J. Org. Chem*. **2013**, *78*, 12194.
7. Liang, S.; Zhang, R.-Y.; Xi, L.-Y.; Chen, S.-Y.; Yu, X.-Q. *J. Org. Chem*. **2013**, *78*, 11874.
8. Chawl, R.; Kapoor, R.; Singh, A. K.; Yadav, L. D. S. *Green Chem*. **2012**, *14*, 1308.