Electronic Supplementary Material (ESI) for RSC Advances

Catalyst free tosylation of lipophylic alcohols in water.

Manuela Oliverio,*[a] Paola Costanzo,[a] Rosina Paonessa,[a] Monica Nardi[b] and Antonio Procopio[a]

Supplementary Informations

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Experimental

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker WM 300 and on Bruker Avance 500 instruments respectively, at 298 K, on samples dissolved in $CDCl_3$ Chemical shifts are given in parts per million (ppm) from tetramethylsilane as the internal standard (0.0 ppm). Coupling constants (J) are given in Hertz. Reactions were monitored by a GC–MS Thermo Scientific workstation, formed by a Focus GC (30-m VARIAN-VF-5ms, 0.25 mm diameter capillary column, working on spitless mode, 1.2 mL/min He as carrier gas) and by an DSQ II mass detector. MW-assisted reactions were performed in Synthos 3000 instrument from Anton Paar, equipped with a 64MG5 rotor and an IR probe as external control of the temperature. Using a temperature controlled program the instrument is able to tune the power magnetron in order to reach and to maintain the fixed temperature throughout the experiment. For each run 16 positions of the rotor were occupied by 0.3-3 ml glass vials sealed with a dedicated PEEK screw-cup together with a reliable PTFE seal. The high-power US-bath (19.6 kHz) for irradiation at 20 kHz were made by Danacamerini (Torino). TLC were performed using silica plates 60-F264 on alumina, commercially available from Merk. Liquid Flash chromatography was performed on a Supelco VERSA FLASH HTFP station on silica cartridges commercially available from Supelco. All solvents were distilled before using by standard methods. All chemicals were used as commercially available.

MW-assisted synthesis of Tosyl esters

In a general procedure 25 mg of alcohol were suspended in 1.0 ml of water and 1.2 equivalents of Ts_2O were added in a 0.3-3 ml glass vials from Anton Paar sealed with a dedicated PEEK screw-cup together with a reliable PTFE seal. The mixture was reacted in "power controlled mode" for 15 min. runs in a Synthos 3000 instrument from Anton Paar, equipped with a 64MG5 rotor and an IR probe as external control of the temperature, fixed on the temperature value of 110°C. On completion, monitored by TLC, the crude product was separated from the *p*-toluensulfonic acid by extraction whit CH_2Cl_2. The organic phases collected were dried on Na_2SO_4, filtered and then evaporated under vacuum giving rise to the pure product.

Pent-4-enyl-4-methylbenzenesulfonate (2). Colourless oil. Yield 15%; Rf (Hexane - Ethyl acetate 8:2) 0.48; ^{1}H-NMR: δ (ppm)(300MHz, $CDCl_3$): 7.7 (d, 2H, H_M,H_P,J=8Hz), 7.4 (d, 2H, H_N,H_O,J=9Hz,), 5.67-5.75 (m, 1H, H_C),4.90-5.00 (m, 2H, H_A,H_B), 4.05(t, 2H, H_H,H_I, J=7Hz), 2.45 (sb, 3H,H_I), 2.06-2.13 (m, 2H,H_D,H_E),1.68-1.78 (m, 2H, H_F,H_G).; m/z: 240 $[M]^+$, 155 $[CH_3\text{-}Ph\text{-}SO_2]^+$, 91 $[CH_3\text{-}Ph]^+$, 68 $[M–TsOH]^+$.

Octadecyl-9-enyl 4-methylbenzenesulfonate (8). Colourless oil. Yield 96%; Rf (Hexane - Ethyl acetate 9:1) 0.45; ^{1}H-NMR: δ (ppm)(300MHz, $CDCl_3$): 7.8 (d, 2H, H_N, J=8.2Hz), 7.35 (d, 2H, H_M, J=8Hz,), 5.30-5.40 (m, 2H, H_A,), 4.3 (t, 2H, H_C, J=7Hz), 2.45 (s, 3H, H_L), 2.05-1.92 (m, 4H, H_B), 1.57-1.67 (m, 2H, H_F), 1.4-1.2. (m, 22H), 0.87(t 3H, H_L J=6.6Hz); ^{13}C-NMR: δ (ppm)(500MHz, $CDCl_3$): 144.57, 133.44, 130.03, 129.80, 129.75, 127.90, 70.76, 31.92, 29.79, 29.70, 29.54 29.33, 29.39, 29.16, 28.93, 28.86, 27.24, 27.17, 25.36, 22.68, 21.61, 14.10. m/z: 155 $[CH_3\text{-}Ph\text{-}SO_2]^+$, 250,3 $[M–TsOH]^+$, 91 $[CH_3\text{-}Ph]^+$

4-ethylphenyl 4-methylbenzenesulfonate (14). Colourless oil. Yield 76%; Rf (Hexane - Ethyl acetate 9:1) 0.70; ^{1}H-NMR: δ (ppm)(300MHz, $CDCl_3$): 7.7 (d, 2H, H_F,J=9Hz), 7.3 (d, 2H, H_G,J=8Hz,), 7.07 (d, 2H, H_A,J=9Hz), 7.87 (d, 2H, H_B,J=8Hz),2.6 (q, 2H, H_C), 2.45(s 3H,H_E), 1.2 (t 3H, H_D J=7Hz); ^{13}C-NMR: δ (ppm)(500MHz, $CDCl_3$): 147.60, 145.17, 143.17, 129.69, 128.87, 128.52, 122.11, 28.22, 21.70, 15.37. m/z=: 276,1 $[M]^+$, 155 $[CH_3\text{-}Ph\text{-}SO_2]^+$, 121,1 $[M–\ CH_3\text{-}Ph\text{-}SO_2]^+$, 91 $[CH_3\text{-}Ph]^+$.

***o*-tolyl-4-methylbenzenesulfonate (15).** Colourless oil. Yield 56%; Rf (Hexane - Ethyl acetate 9:1) 0.53; ^{1}H-NMR: δ (ppm)(300MHz, $CDCl_3$): 7.74 (d, 2H, H_C, H_E J=9Hz), 7.33 (d, 2H, H_B, H_D J=8Hz,), 7.16-6.95 (m, 4H, H_H, H_F H_I H_G), 2.48 (S, 3H, H_L), 2.08 (s 3H, H_A); ^{13}C-NMR: δ (ppm)(500MHz, $CDCl_3$): 148.43, 145.26, 131.65, 131.58,129.78, 126.95, 126.90, 122.32, 21.70, 16.30. m/z=: 262.1 $[M]^+$, 155 $[CH_3\text{-}Ph\text{-}SO_2]^+$, 107 $[M–\ CH_3\text{-}Ph\text{-}SO_2]^+$, 91 $[CH_3\text{-}Ph]^+$

4-bromophenyl 4-methylbenzenesulfonate (16). Colourless oil. Yield 62%; Rf (Petroleum ether - Ethyl ether 8.5:1.5) 0.76; ^{1}H-NMR: δ (ppm)(300MHz, $CDCl_3$): 7.7 (d, 2H, H_C J=8Hz), 7.4 (m, 2H, H_D), 7.33 (d, 2H, H_B, J=9Hz,), 6.86 (m, 2H, H_E), 2.45 (s 3H,H_A); ^{13}C-NMR: δ (ppm)(500MHz, $CDCl_3$): 148.66, 145.65, 132.74, 129.87, 128.55, 124.17, 120.58, 21.73. m/z=: 326 $[M]^+$, 328 (50%) $[M+2]^+$, 155 $[CH_3\text{-}Ph\text{-}SO_2]^+$, 91 $[CH_3\text{-}Ph]^+$

2-allylphenyl 4-methylbenzenesulfonate (18). Colourless oil. Yield 60%; Rf (Hexane - Ethyl acetate 9:1) 0.65; ^{1}H-NMR: δ (ppm)(300MHz, $CDCl_3$): 7.76 (d, 2H, H_L,H_I, J=8Hz), 7.35 (d, 2H, H_M,H_H,J=9Hz,), 7-7.22 (m, 4H, H_G,H_F, H_E,H_D), 5.68-5.83 (m, 1H, H_C), 4.95-5.07(m, 2H, H_A,H_B), 3.22. (ddd, 2H_P, $J_{P\text{-}C}$=1.37Hz; $J_{P\text{-}B}$=5.5Hz), 2.45(s 3H,H_N); ^{13}C-NMR: δ (ppm)(500MHz, $CDCl_3$): 147.86, 145.35, 135.52, 133.44, 130.68, 129.69, 128.43, 127.37, 127.09, 122.27, 116.64, 33.92, 21.72. m/z=: 288.1 $[M]^+$, 155 $[CH_3\text{-}Ph\text{-}SO_2]^+$, 115,1 $[M–TsOH]^+$, 91 $[CH_3\text{-}Ph]^+$

EI/MS Spectra

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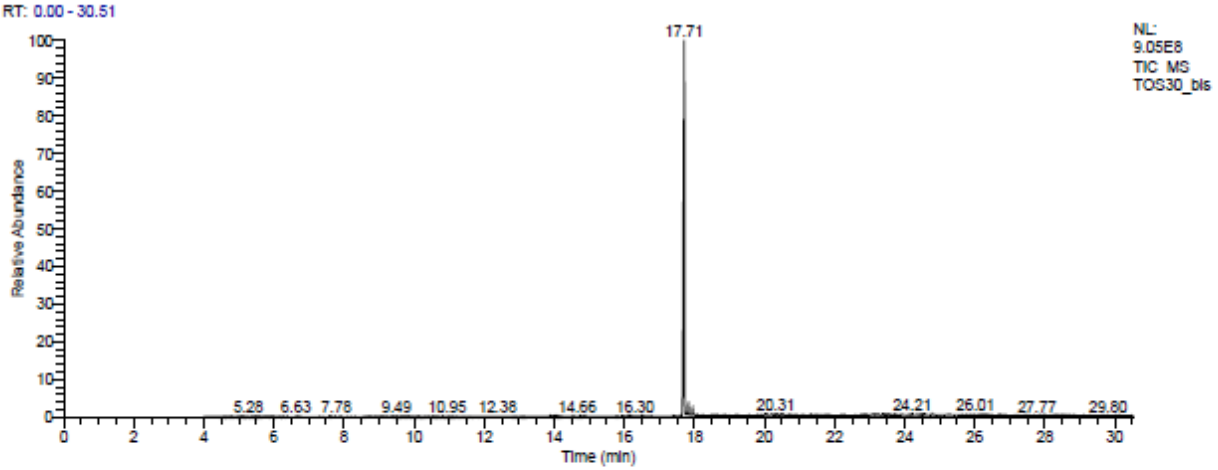

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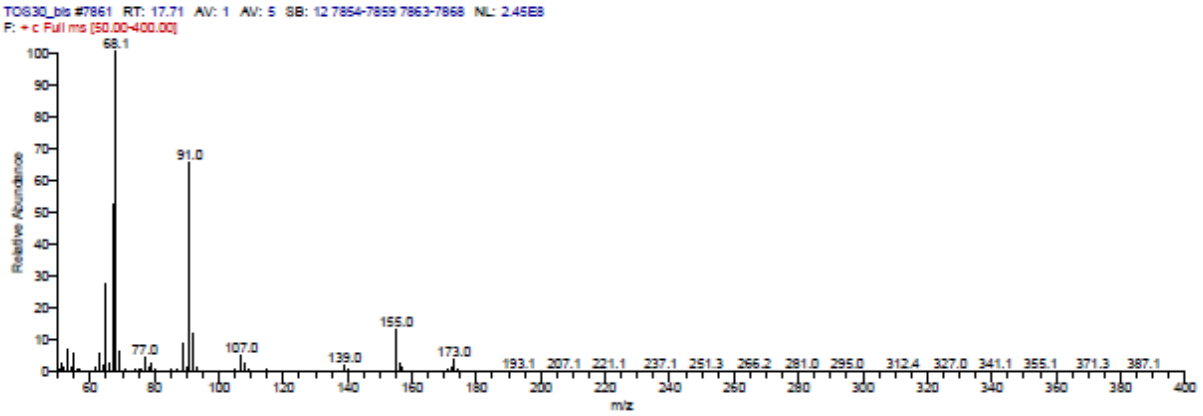

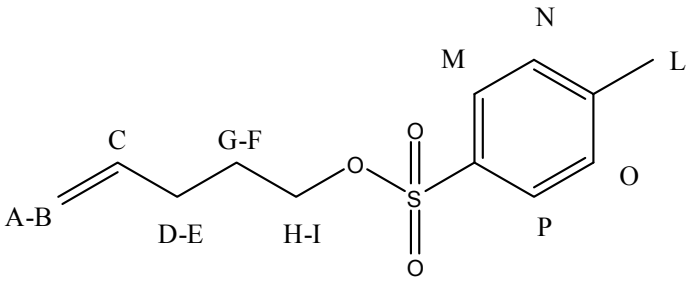

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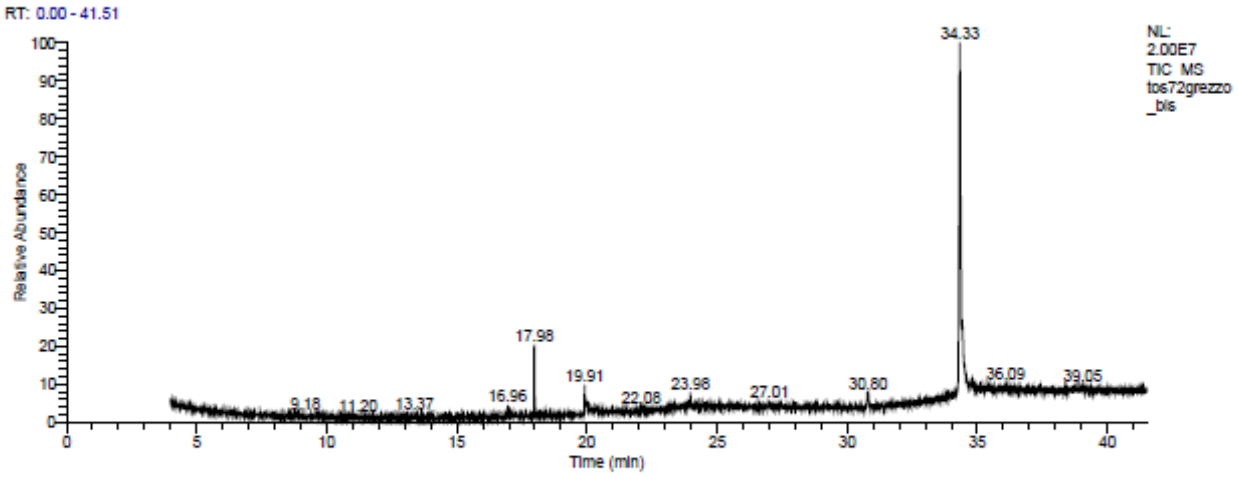

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30.80	3718389.67	783664.35	4.38	239.85
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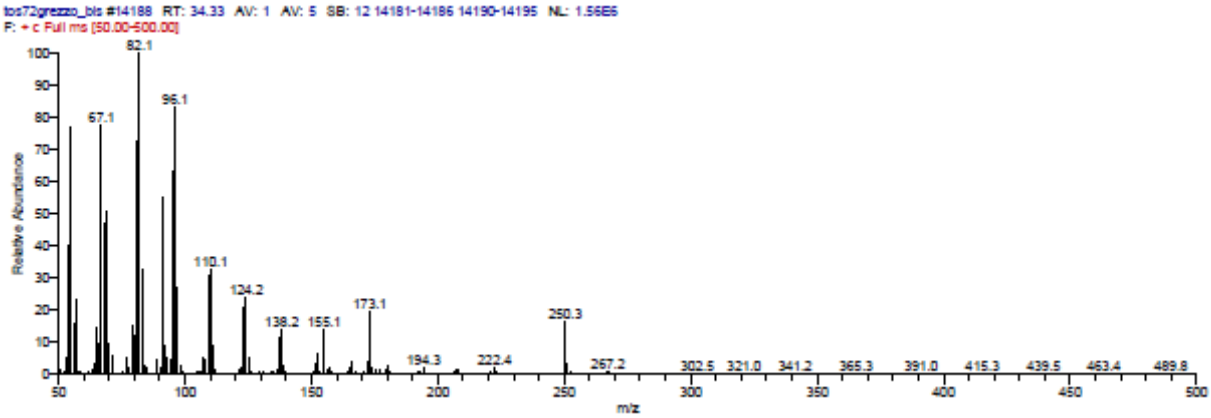

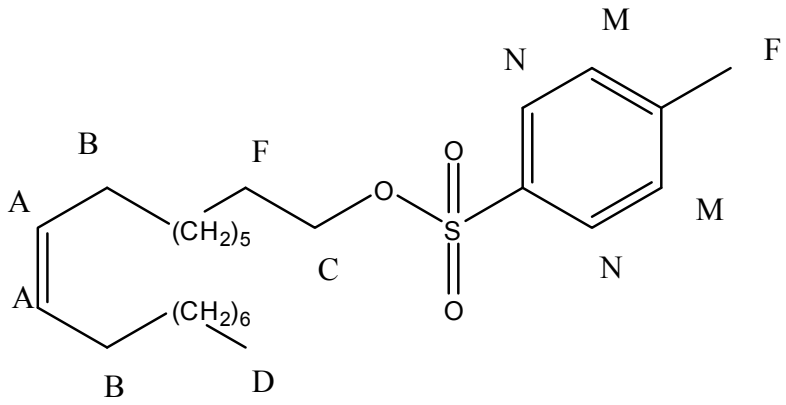

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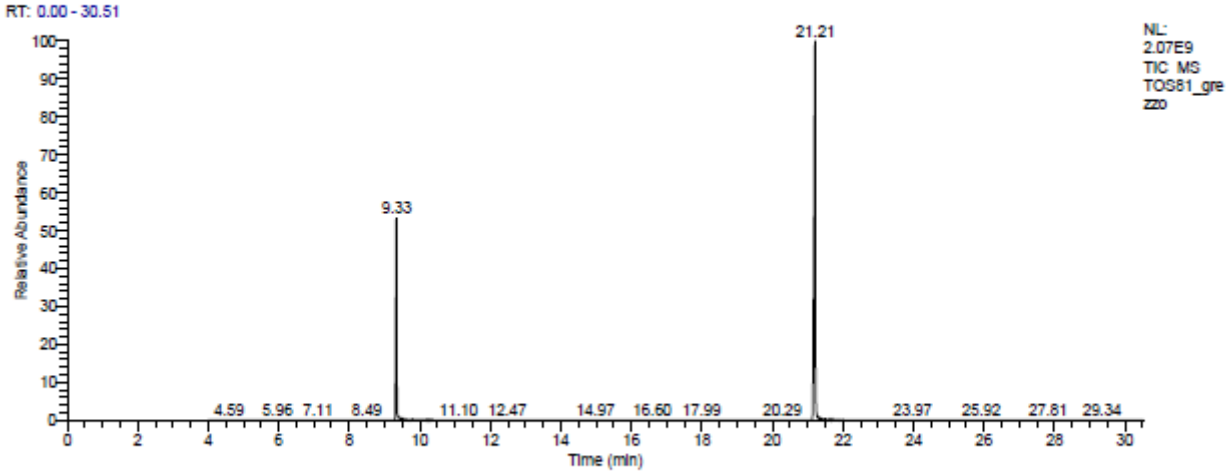

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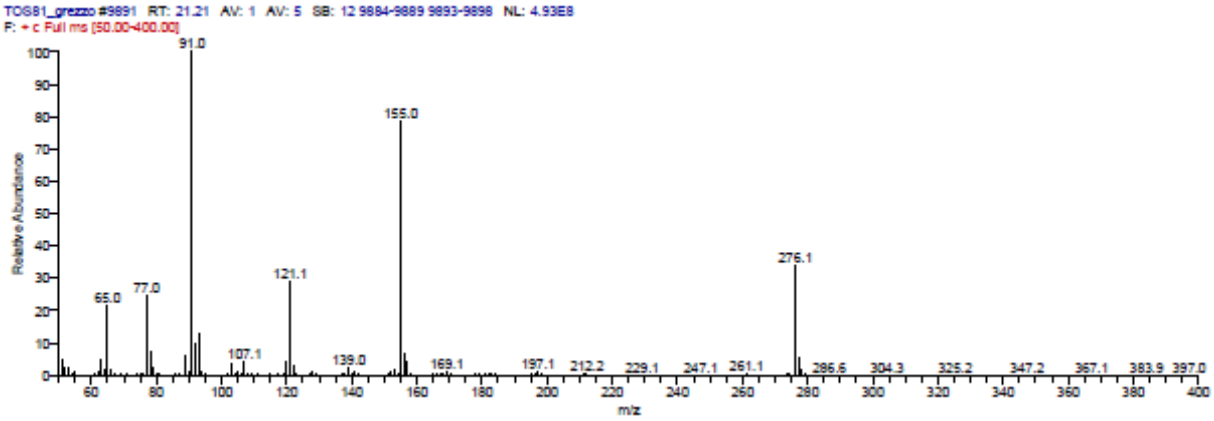

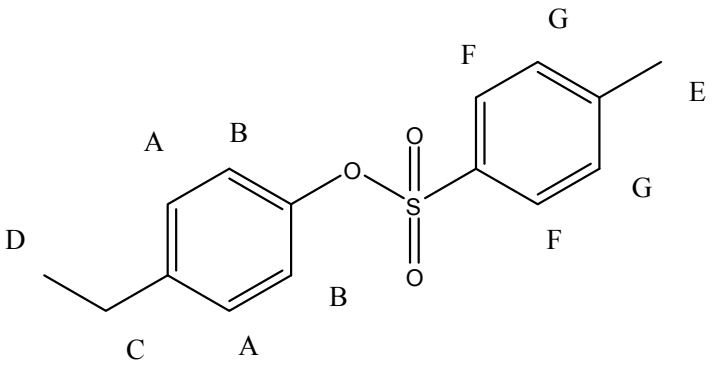

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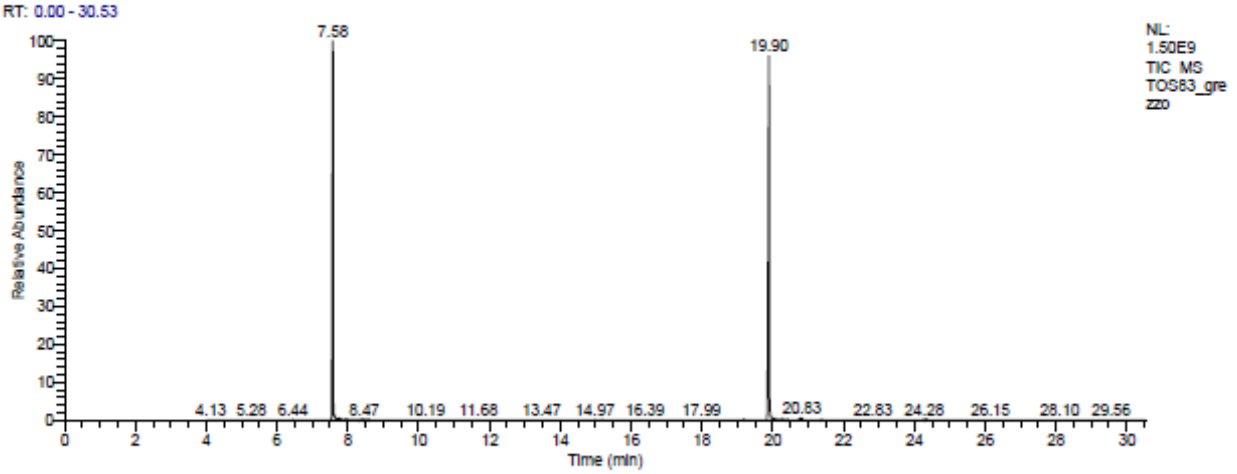

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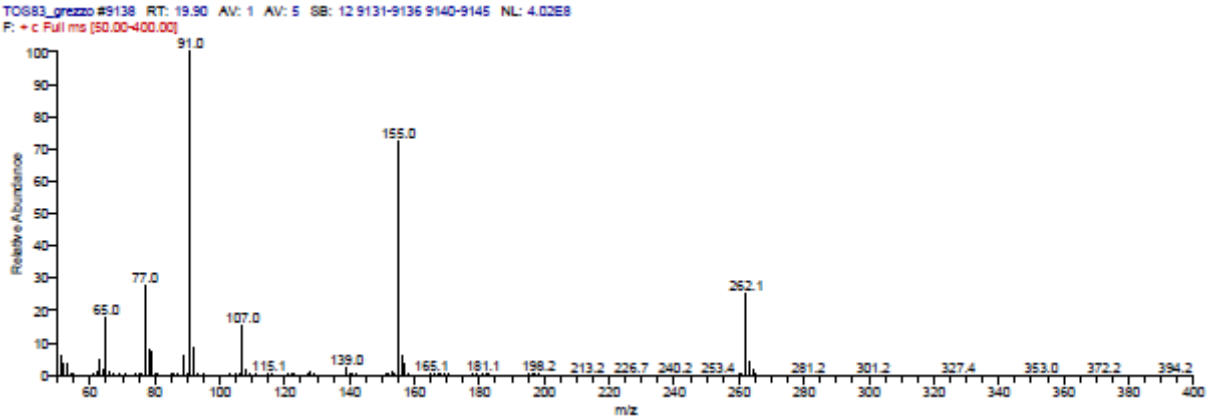

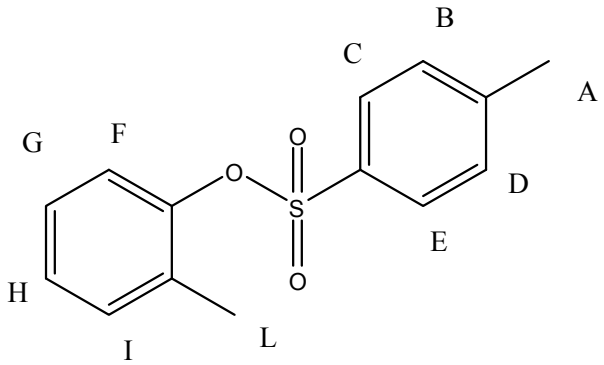

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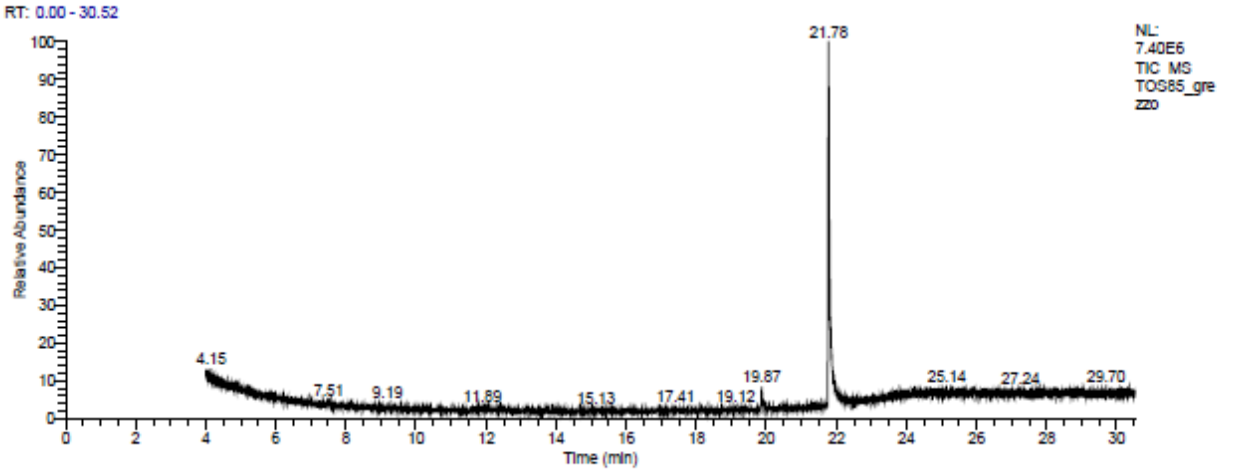

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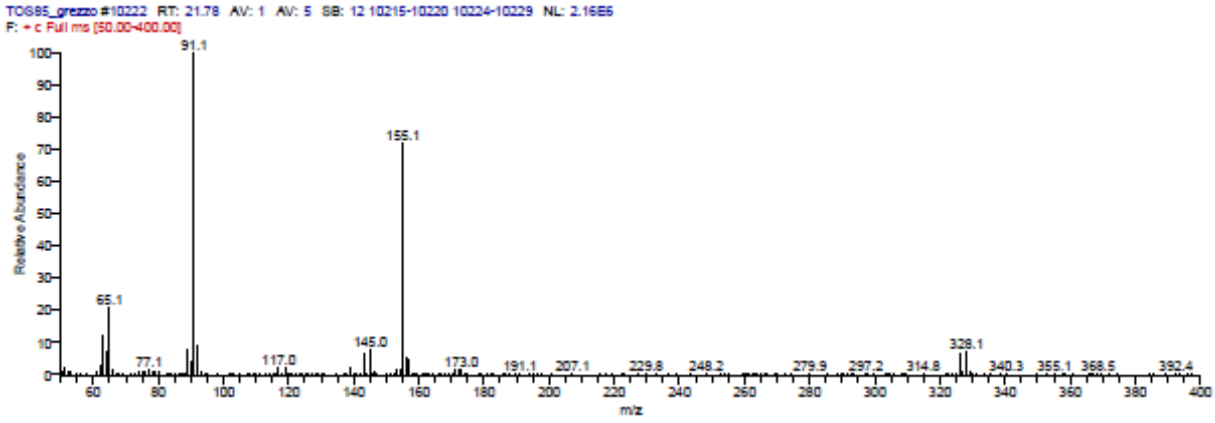

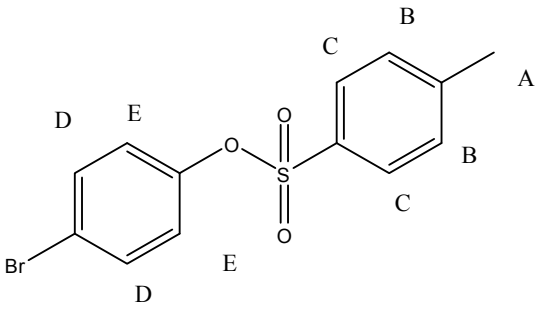

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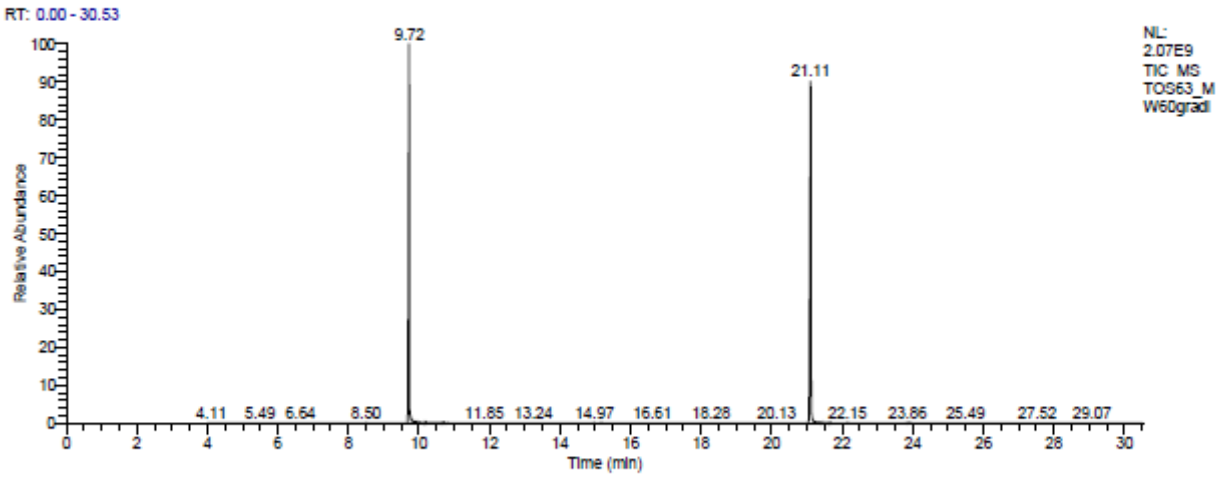

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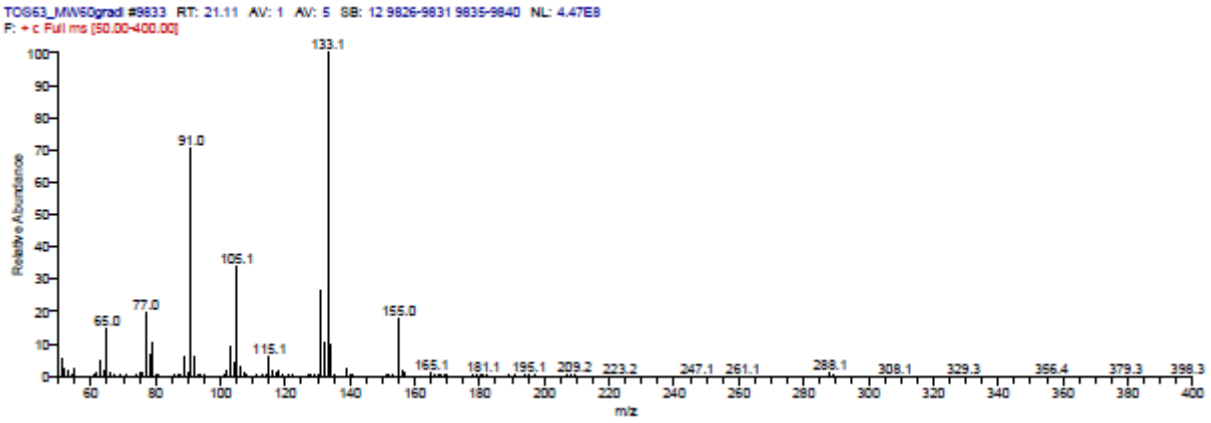

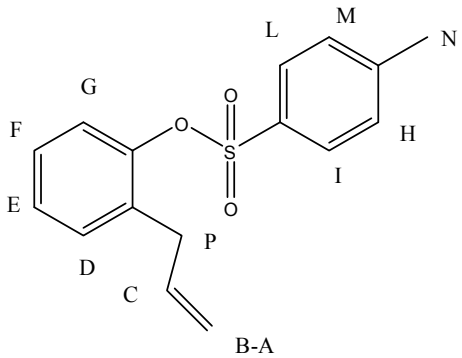

^{1}H-NMR Spectra

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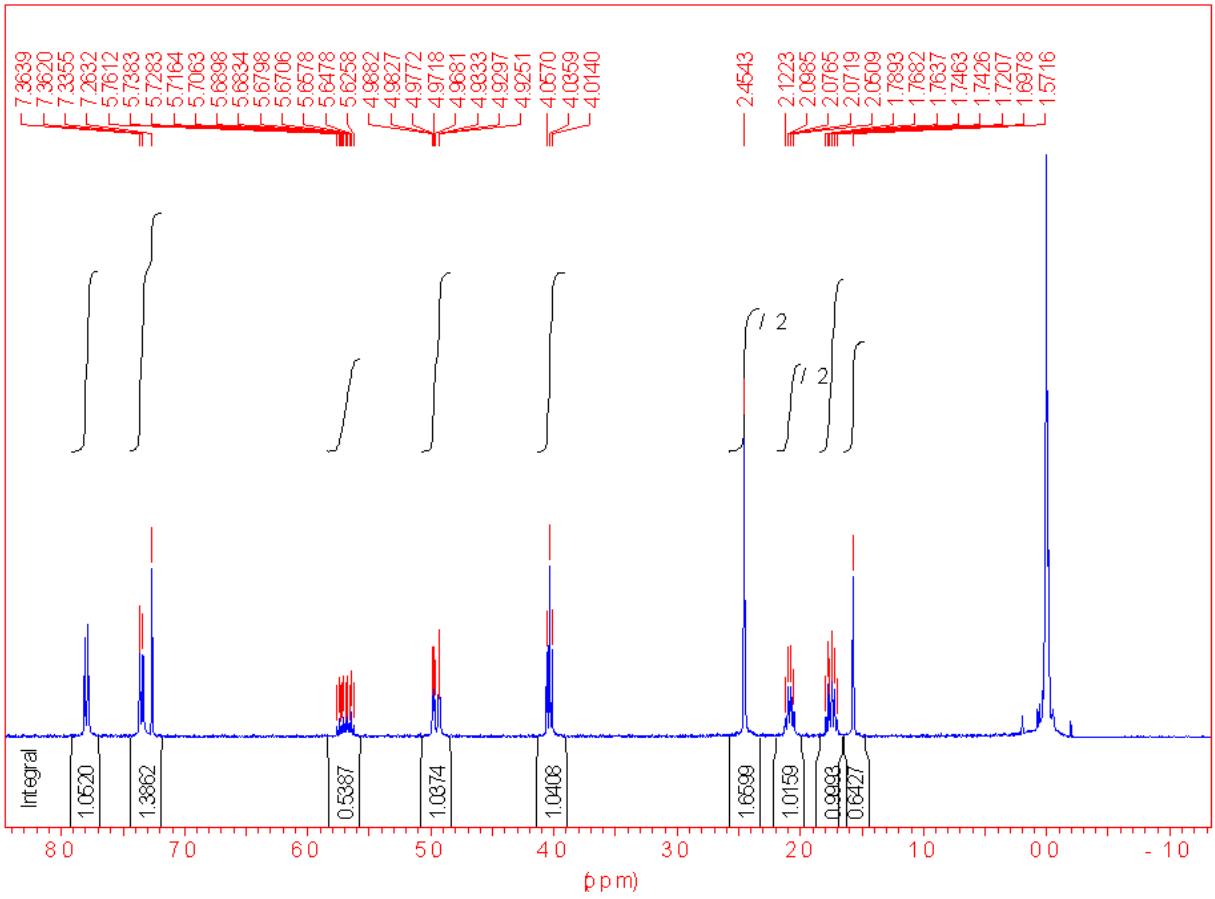

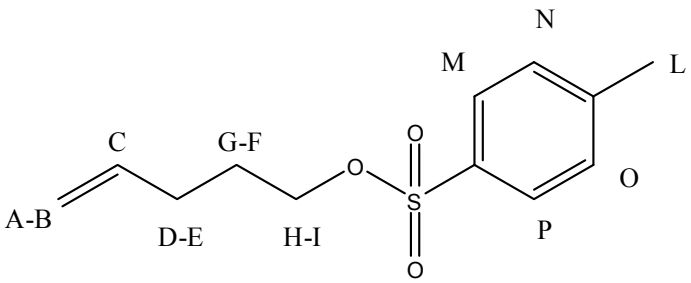

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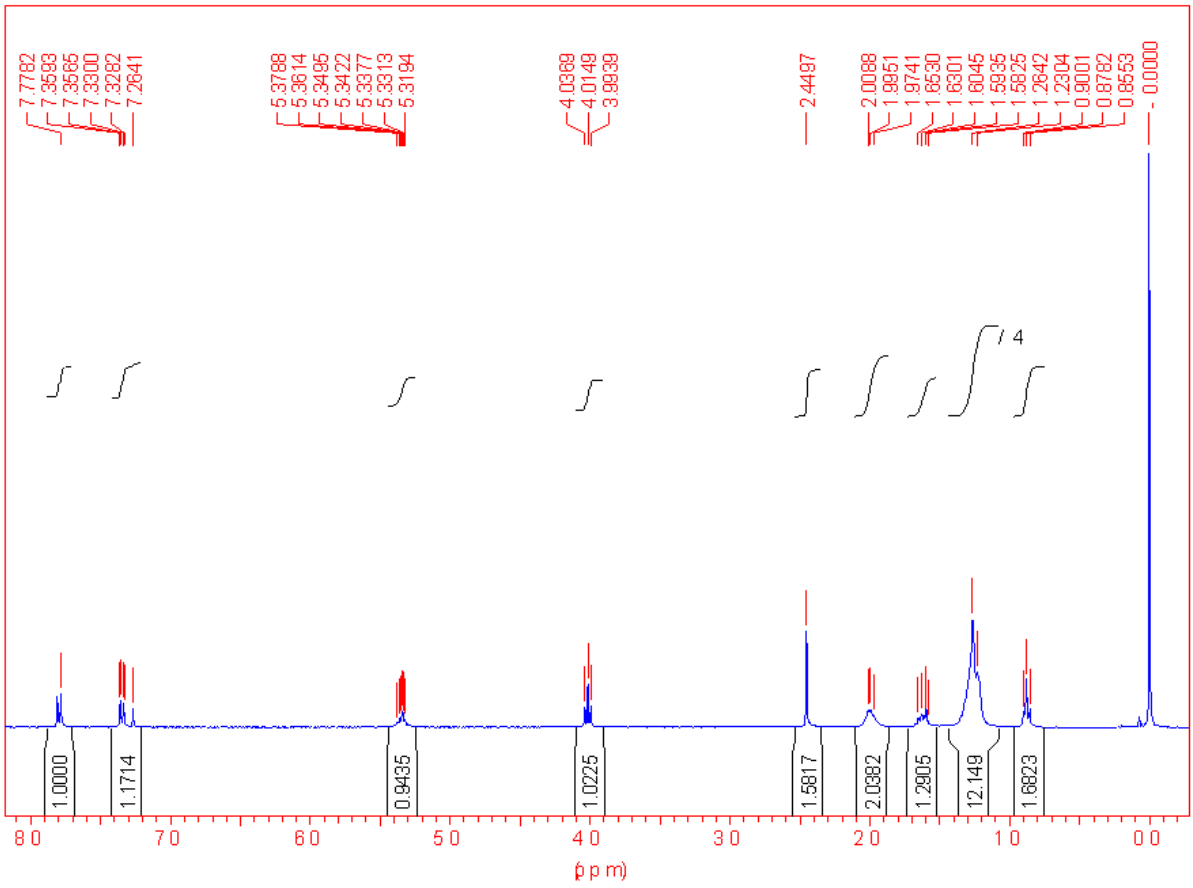

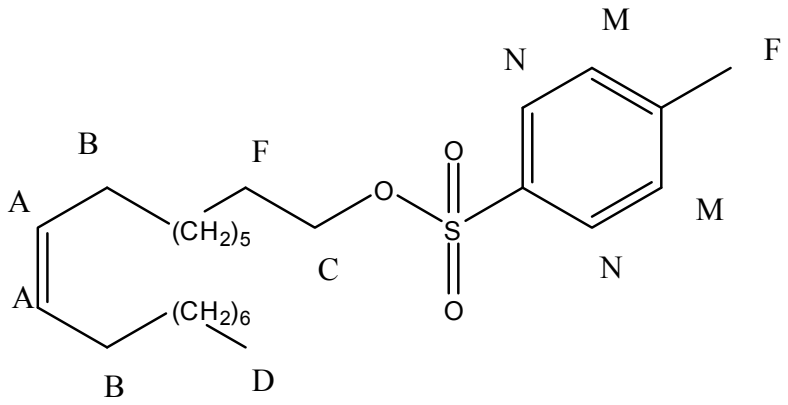

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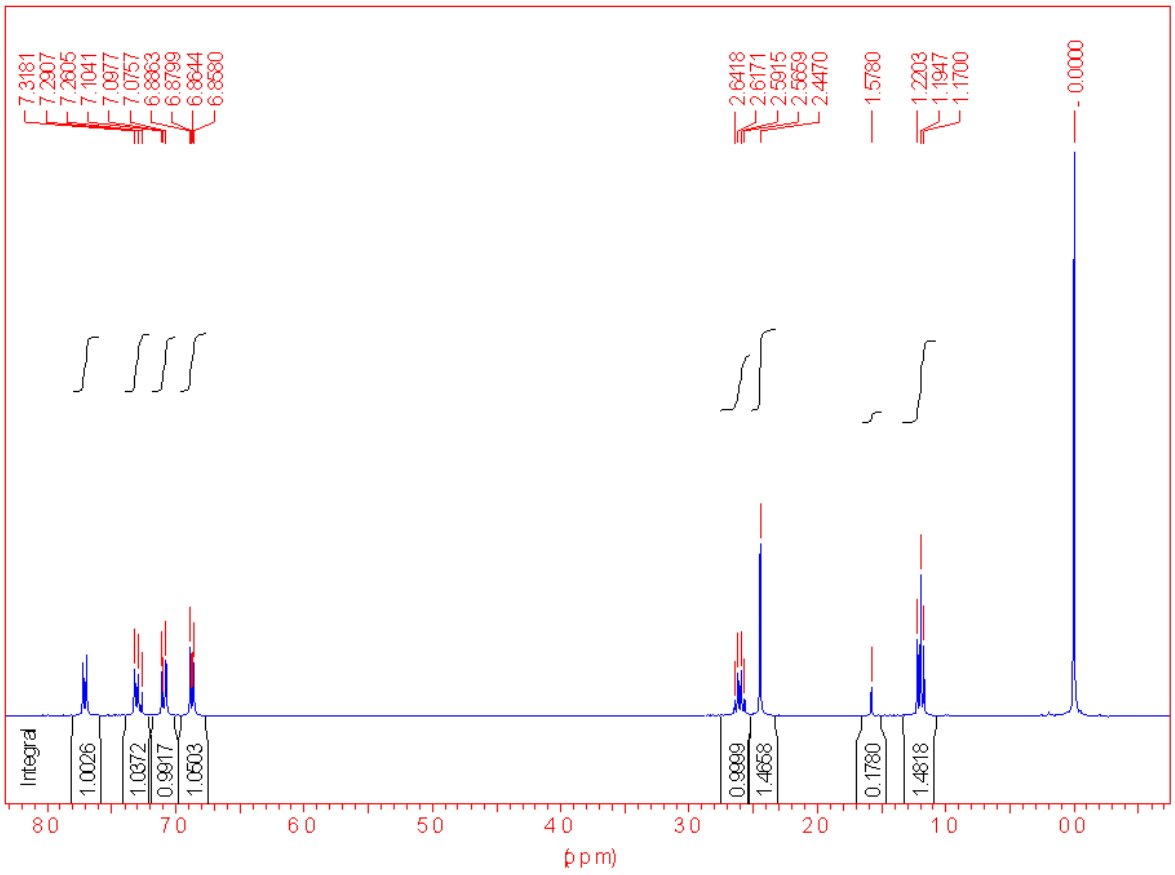

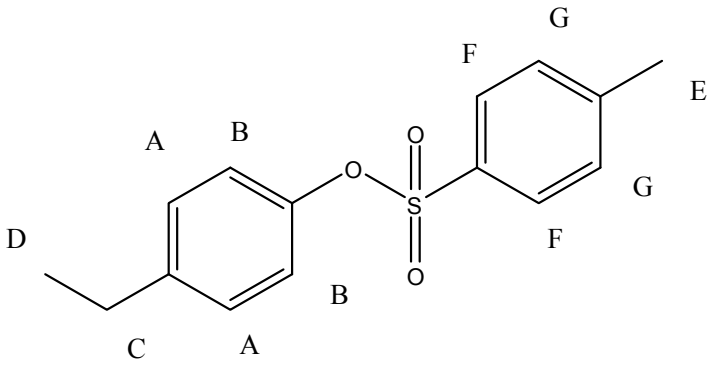

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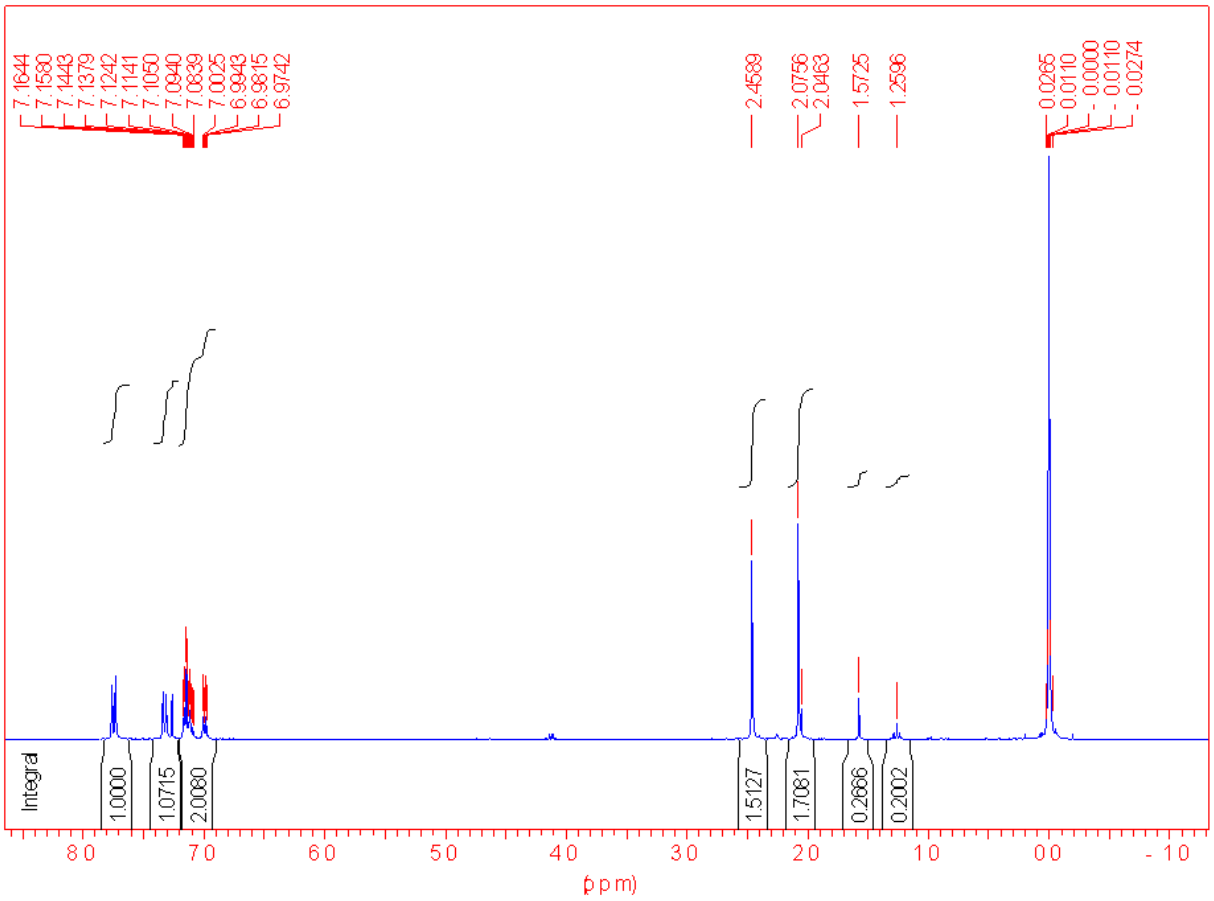

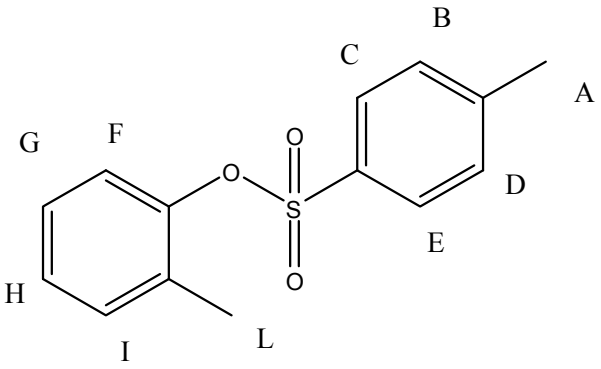

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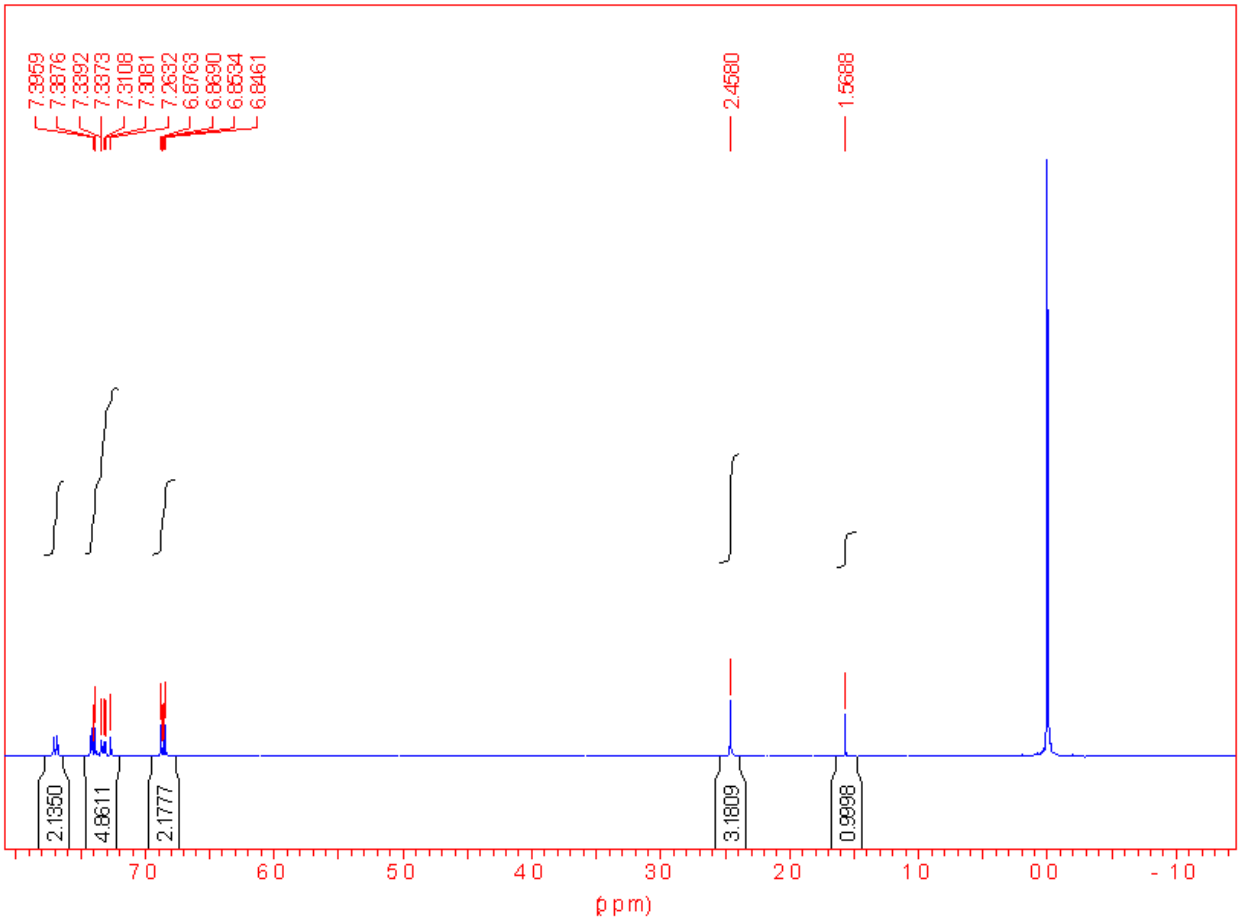

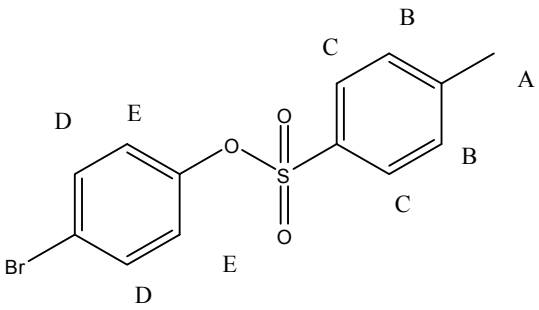

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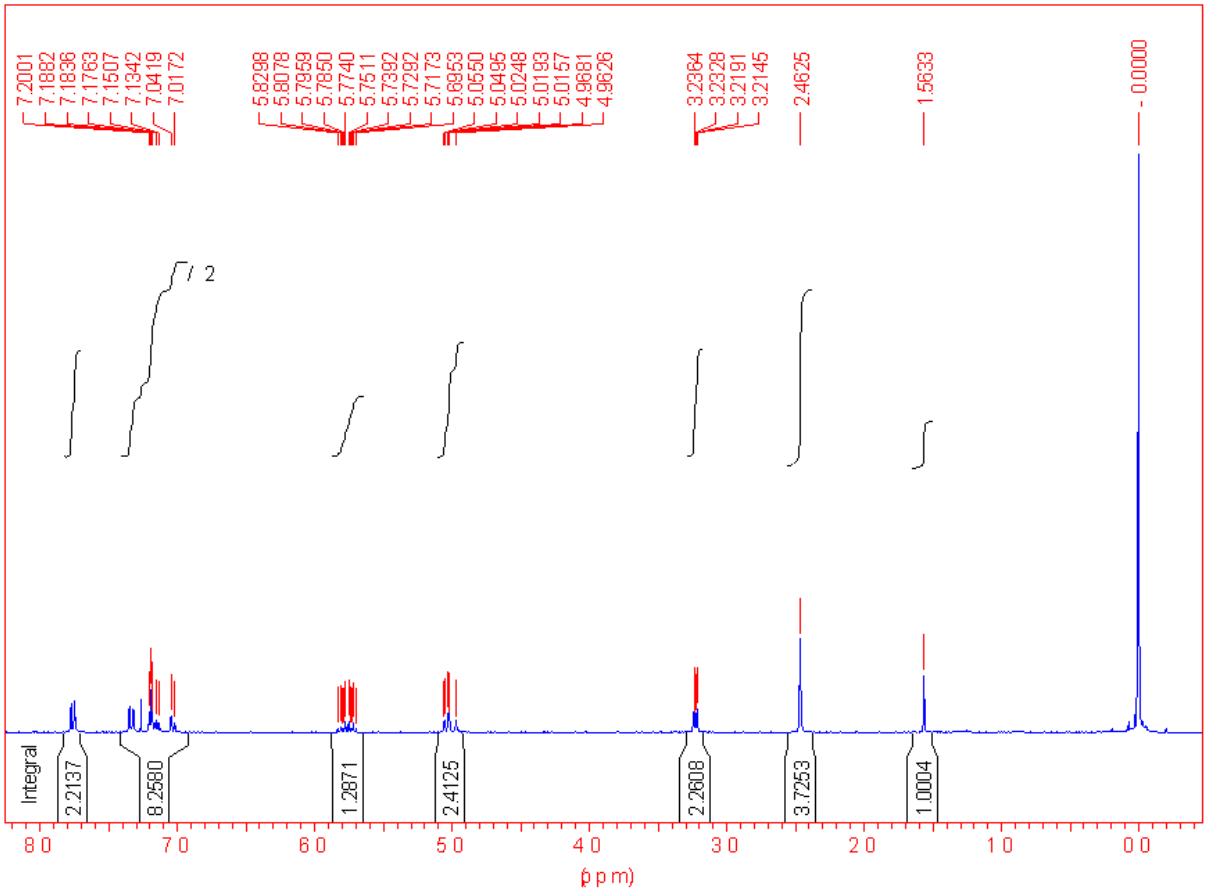
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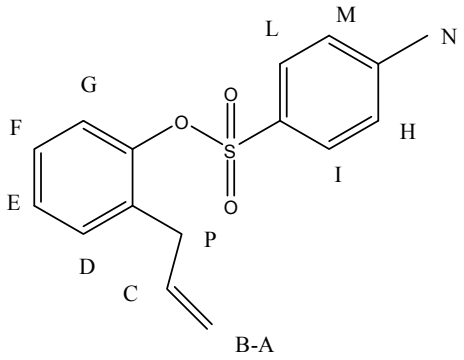
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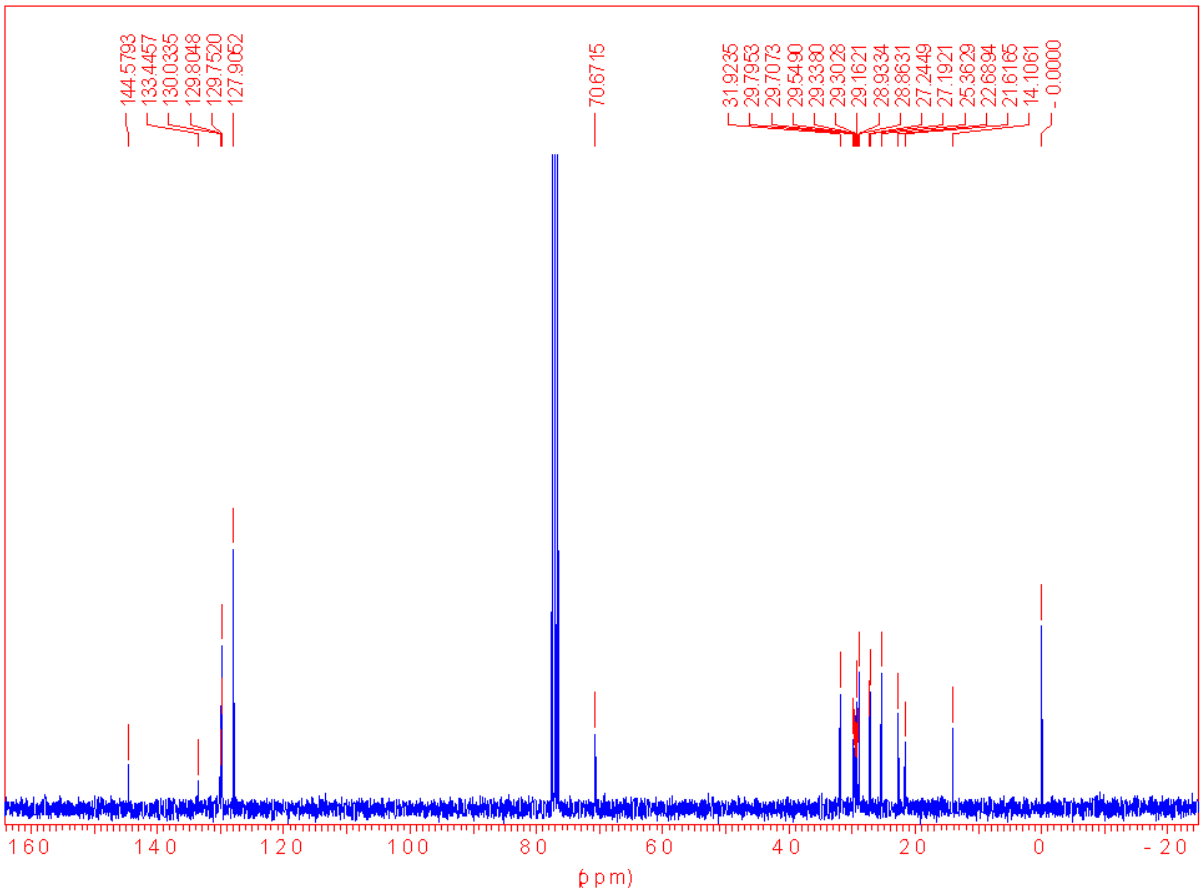
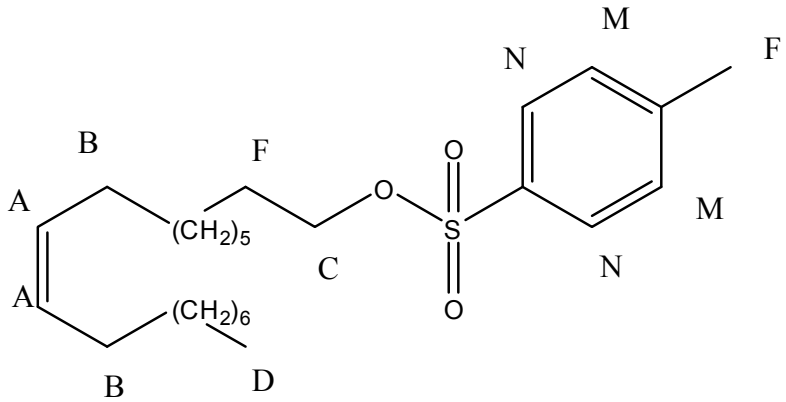
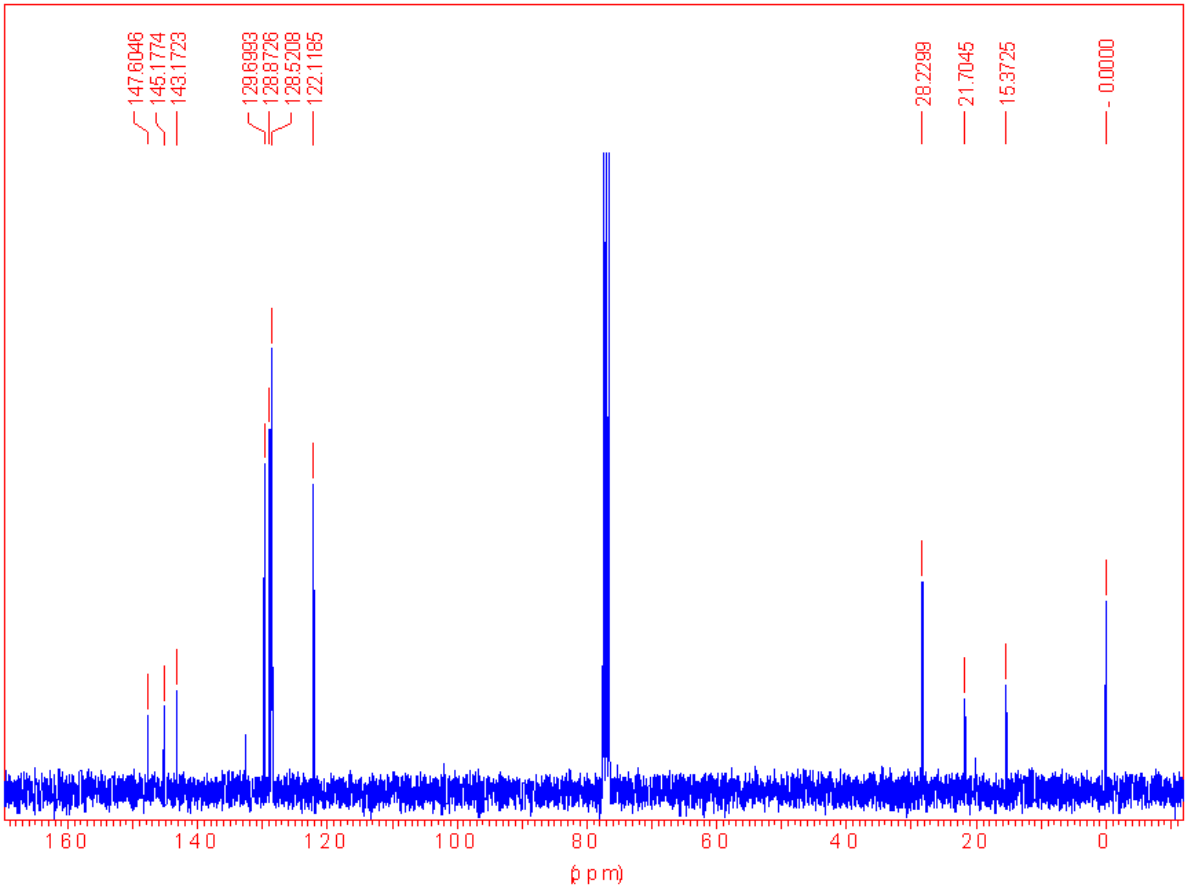
^{13}C-NMR Spectra

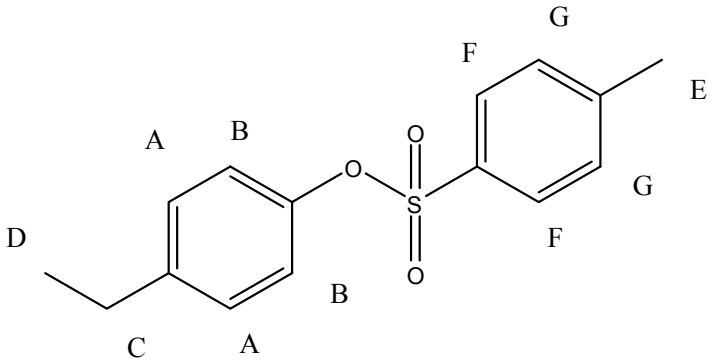
Sample **8**



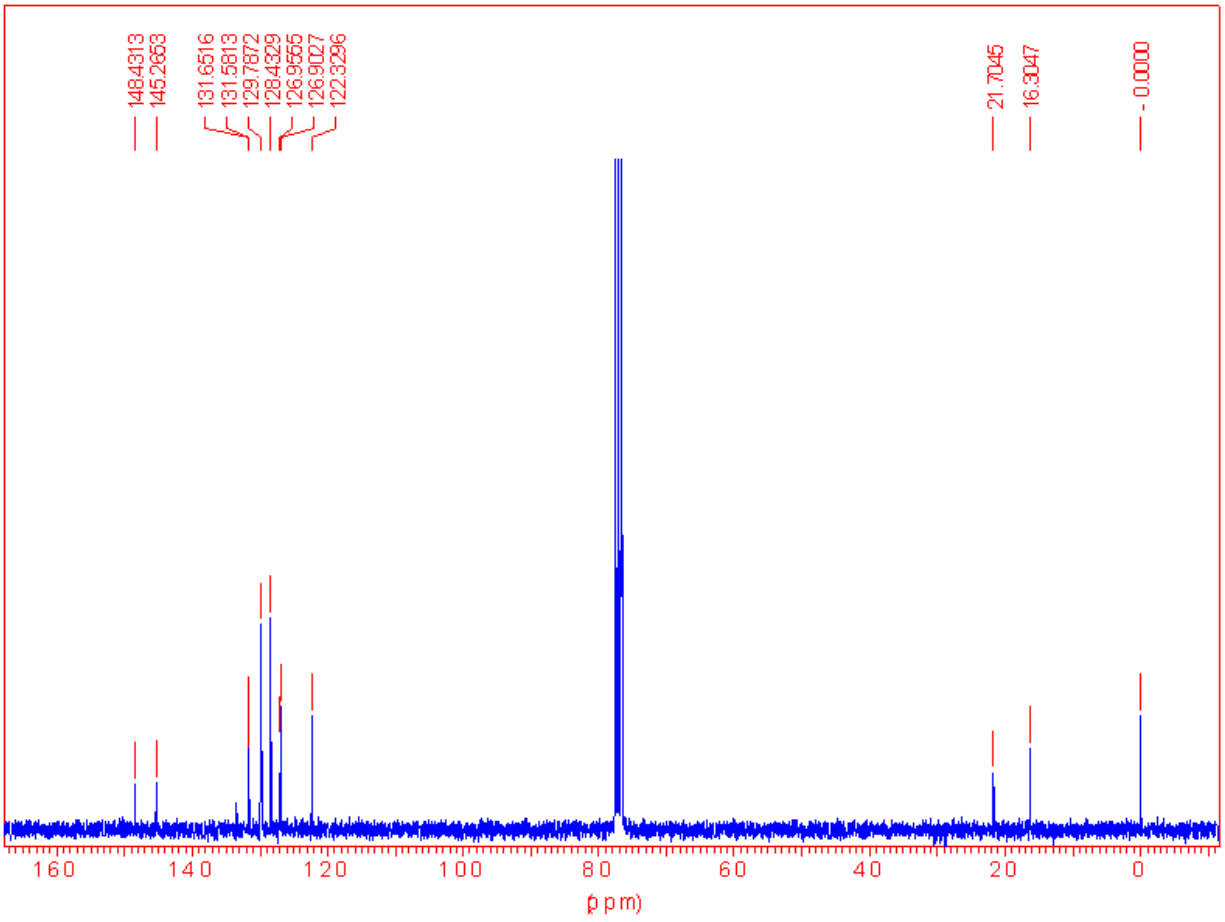


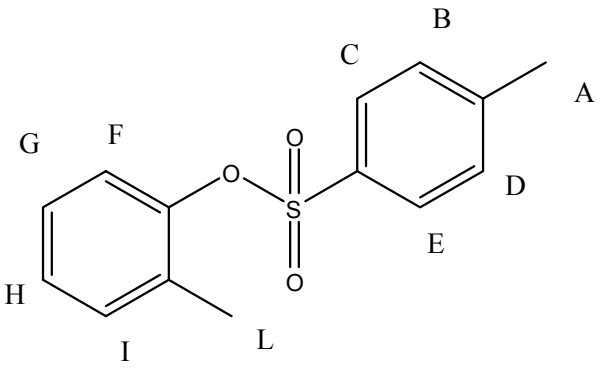
Sample **14**



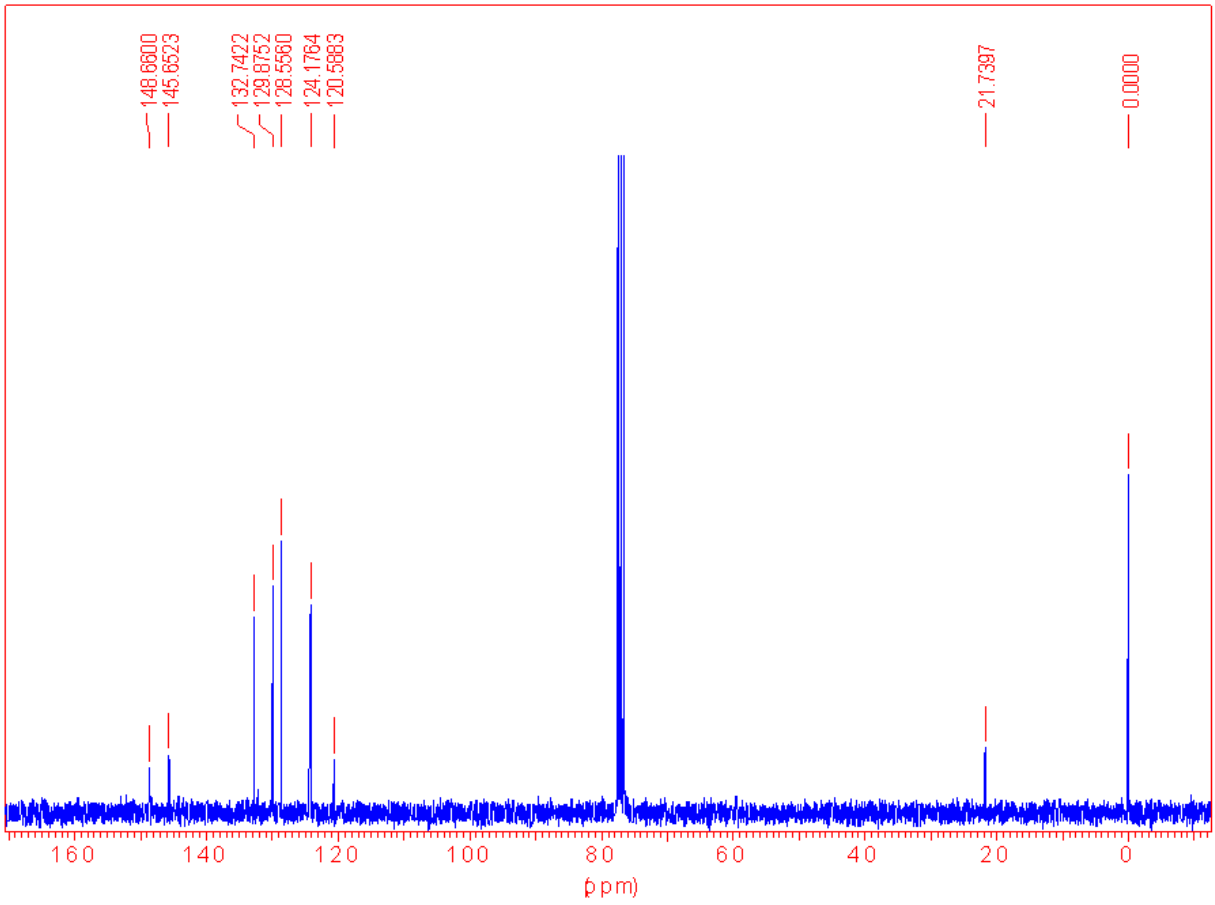


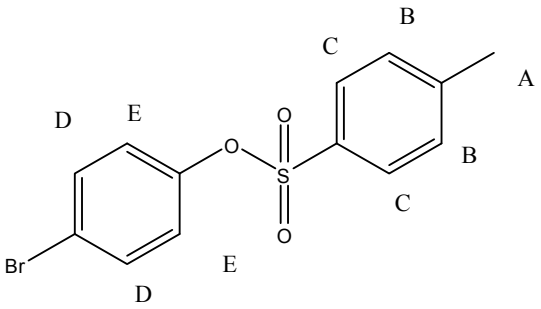
Sample **15**



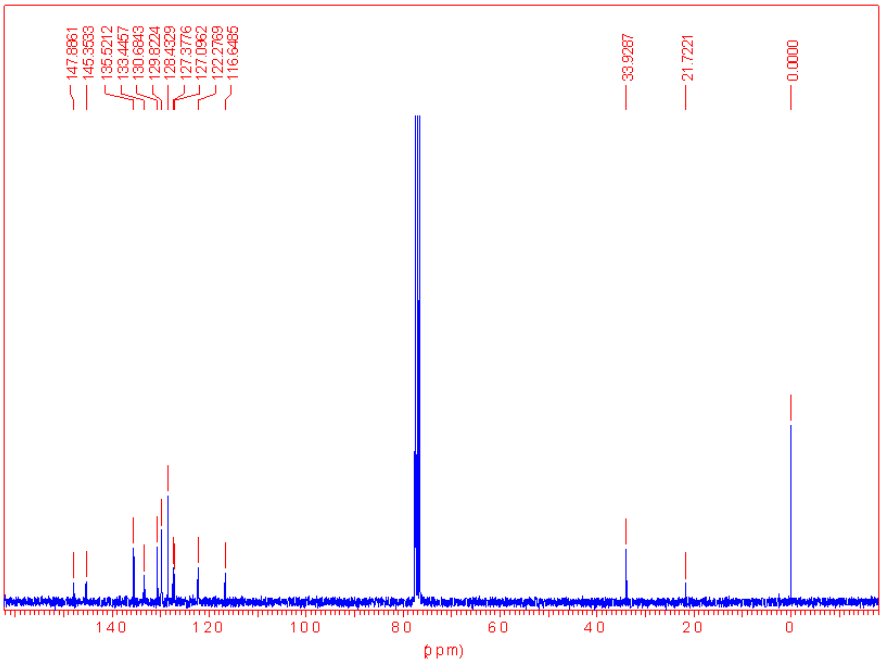


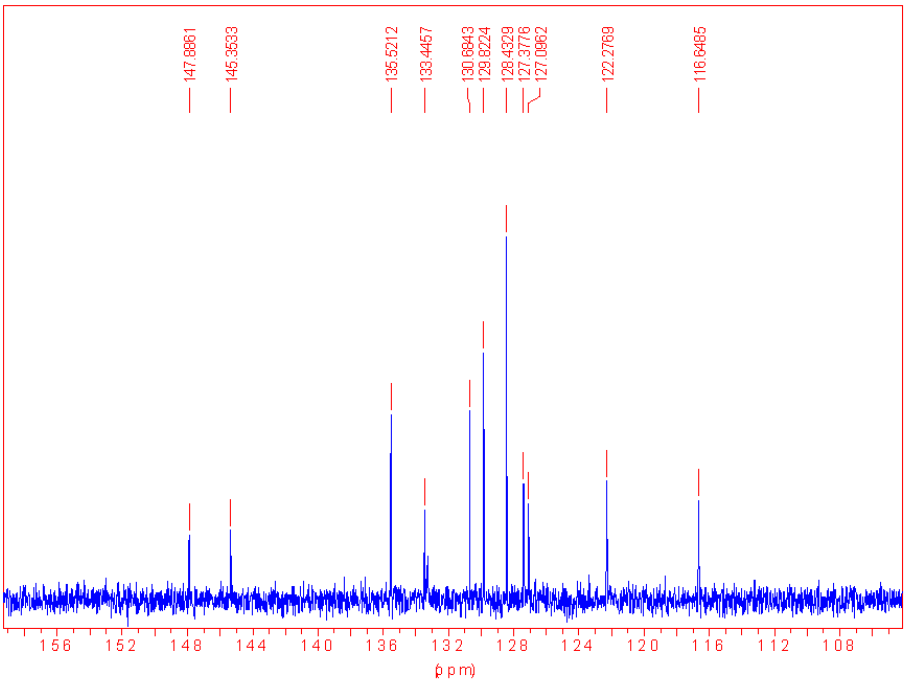
Sample **16**

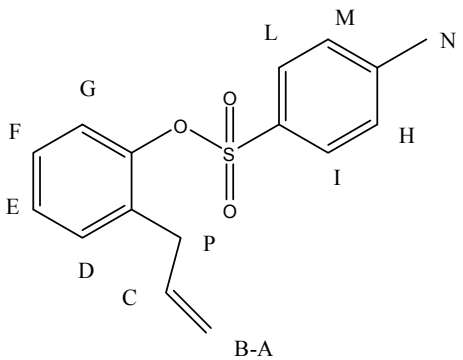

148.6600
145.6523
132.7422
129.8752
128.5660
124.1764
120.5883
21.7397
0.0000
160
140
120
100
80
60
40
20
0
ppm)


B
C
A
D
E
O
O
S
O
B
C
Br
E
D

Sample **18**


147.8861
145.3533
135.5212
133.4457
130.6843
129.8224
128.4329
127.3776
127.0962
122.2769
116.6485
33.9287
21.7221
0.0000
140
120
100
80
60
40
20
0
(ppm)


147.8861
145.3533
135.5212
133.4457
130.6843
129.8224
128.4329
127.3776
127.0962
122.2769
116.6485
156
152
148
144
140
136
132
128
124
120
116
112
108
(ppm)


L
M
N
G
F
O
O
S
O
H
I
E
P
D
C
B-A