Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Polymer supported ascorbate functionalized task specific ionic liquid: an efficient reusable catalyst for 1,3-dipolar cycloaddition

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A) General Information

Alkynes (Aldrich/Alfa Aesar), sodium azide (Spectrochem, Mumbai) and copper sulphate pentahydrate (Spectrochem, Mumbai) were used as received. All reactions were carried out in air atmosphere in predried glassware. Infrared spectra were measured with an Agilent Cary (IR-630) spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker AC spectrometer (300 MHz for^{1}H NMR and 75 MHz for ^{13}C

NMR), using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are expressed in parts per million (ppm) and coupling constants are expressed in hertz (Hz). Mass spectra were recorded on a Shimadzu QP2010 GCMS. FESEM was performed using a HITACHI S-4800.

B) Typical procedure for the preparation of Ascorbate functionalized polymer supported task specific ionic liquid catalyst (MR-IMZ-As)

Step-1 Preparation of imidazolium-loaded polymeric support (MR-IMZ-Cl)

In 100 mL round bottom flask were added Merrifield peptide resin (2 % cross linked, 2-4 mmol Cl/g) 5 g, N-methyl imidazole (0.0609 mmol) in toluene (25 mL) and refluxed for 24 hours. On completion, the reaction mixture was cooled to room temperature. It was then filtered and the residue obtained was washed with toluene, 0.1M HCl, water and methanol sequentially followed by drying under reduced pressure to afford imidazolium-loaded polymeric support. The catalyst was further characterized by FTIR to check the attachment of the ionic liquid. A strong band centred at 1561 cm^{-1} confirms the attachment of the imidazole on Merrifield resin.

Step-2 Preparation of imidazolium-loaded polymeric support (MR-IMZ-OH)

(MR-IMZ-Cl) (1.0 g) was suspended in 10 mL aqueous solution of KOH (0.448 g). The resulting mixture was stirred for 24 h at room temperature, Afterward the polymer was filtered and washed with Water, methanol and dried under vacuum to afford (MR-IMZ-OH). IR Shows absorption bands at 3386, 3029, 2923, 1572, 1451, 1332, 1159, 1113, 1020, 820 cm^{1}

Step-3 Preparation of polymer supported Ascorbate anionic ionic liquid catalyst (MR-IMZ-As)

A mixture of the imidazolium loaded polymeric support (MR-IMZ-OH) (1.0 g) and Ascorbic acid (1.408 g, 8mmol) was suspended in water (20 mL). The mixture was then stirred at room temperature for 24 h. On completion, the reaction mixture was filtered and the polymeric support was washed vigorously with distilled water (10 mL × 5), MeOH (10mL × 5) and dried under reduced pressure to give (MR-IMZ-As).

C) General procedure for synthesis of 1, 4-disubstituted 1, 2, 3-triazole

In a 50 mL round bottom flask aryldiazonium tetrafluoroborate (1 mmol), sodium azide (1.2 mmol), alkyne (1.0 mmol), $CuSO_4.5H_2O$ (10 mg, 0.04 mmol) and MR-IMZ-As (25 mg, 0.16 mmol) were mixed and stirred in 5 mL water. The reaction was allowed to proceed for 2 h at room temperature. Reactions were monitored by Thin Layer Chromatography (TLC) using aluminium backed silica gel 60 (F_{254}) plates. After completion of the reaction, the reaction mixture was filtered and quenched with water (10 mL) the organic products were separated from the reaction mixture by extraction with ethyl acetate (15 mL X 2). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure then the product was purified by silica gel column chromatography.

D) SEM, TEM-EDS analysis of polymer supported task specific ionic liquid:

(b)

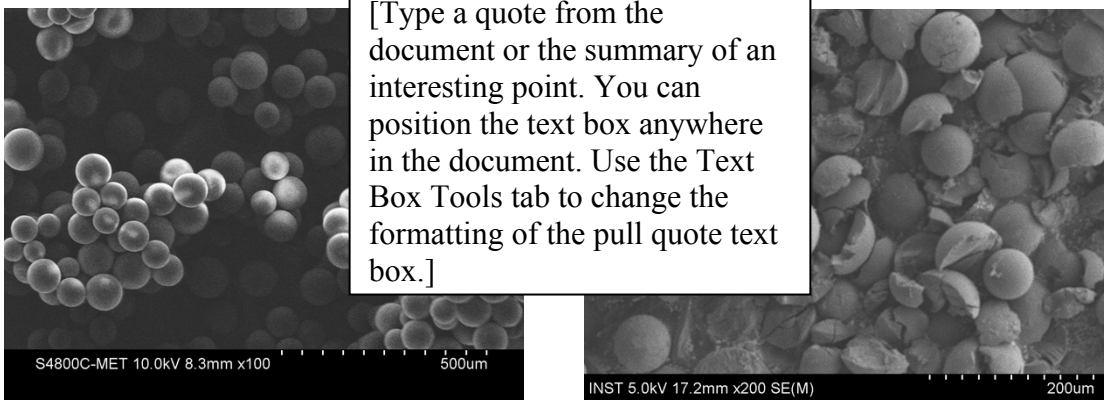

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Fig.1 SEM analysis of polymer supported task specific ionic liquid (MR-IMZ-As) before (a) and after (b) use respectively

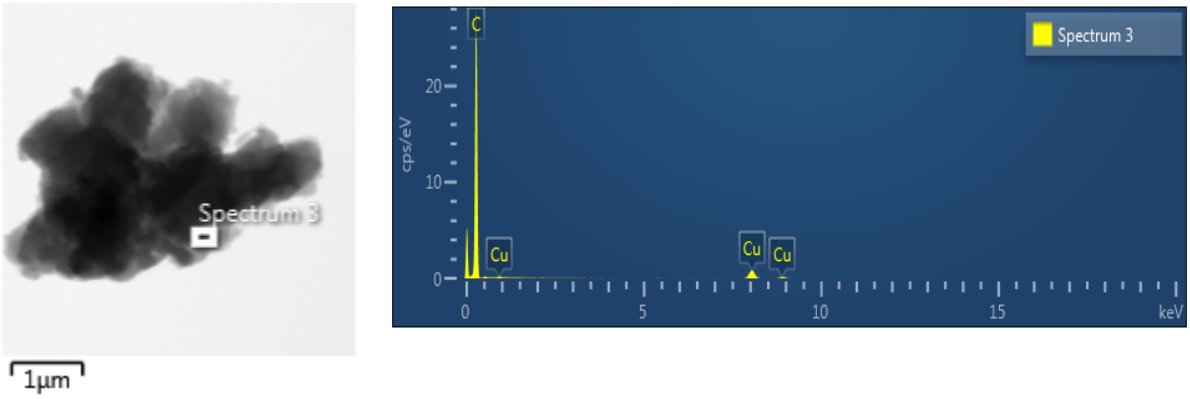


Fig.2 TEM-EDS analysis of polymer supported task specific ionic liquid after first cycle

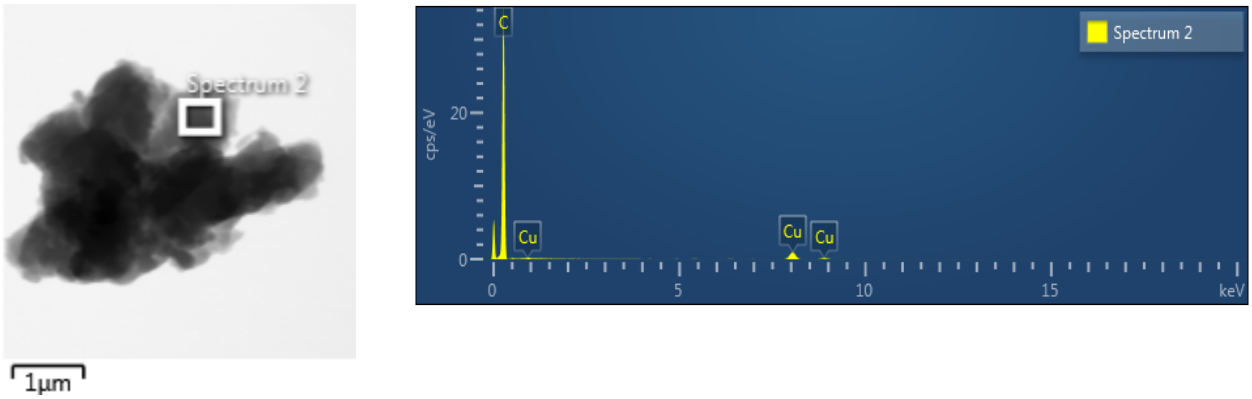
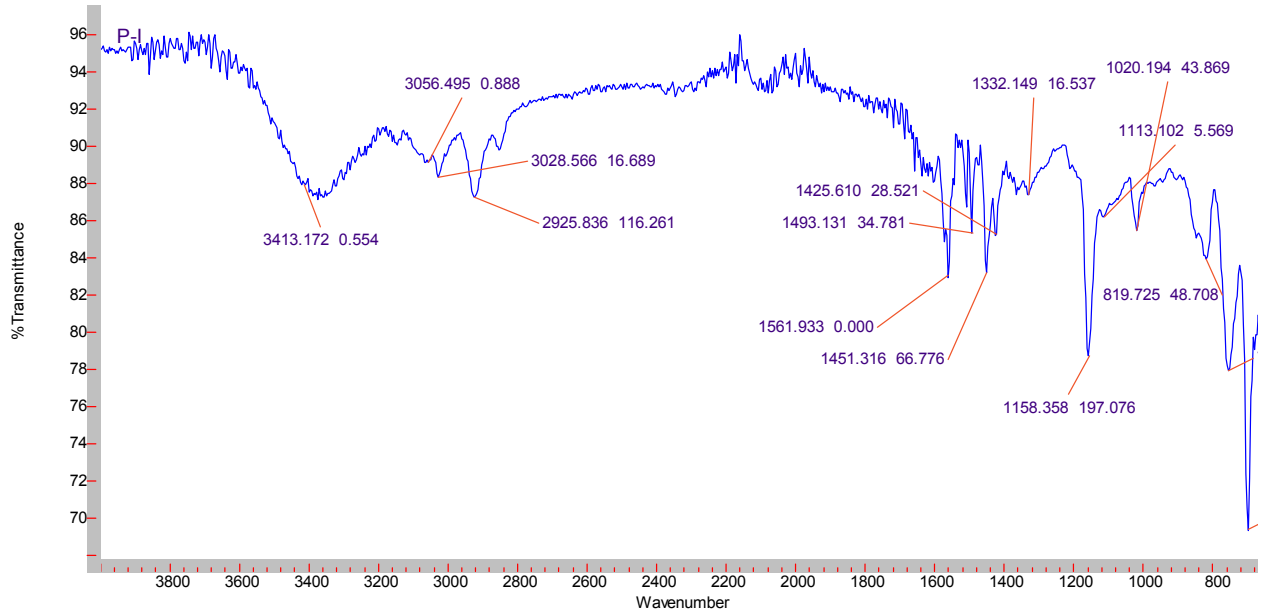
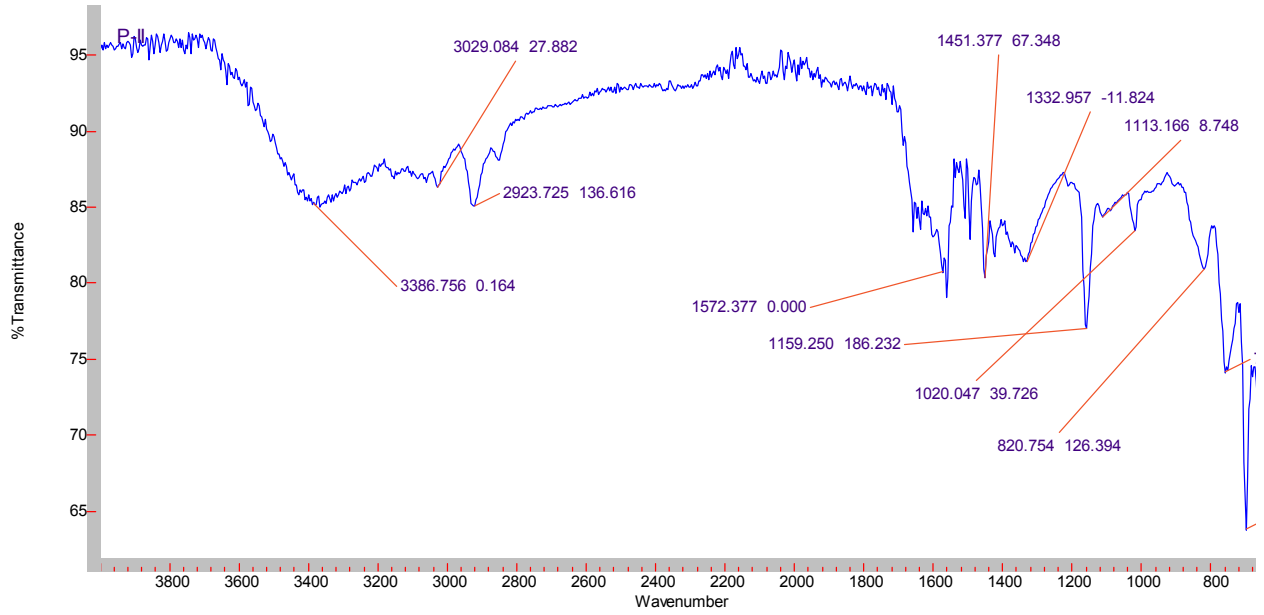


Fig.3 TEM-EDS analysis of polymer supported task specific ionic liquid after fifth cycle

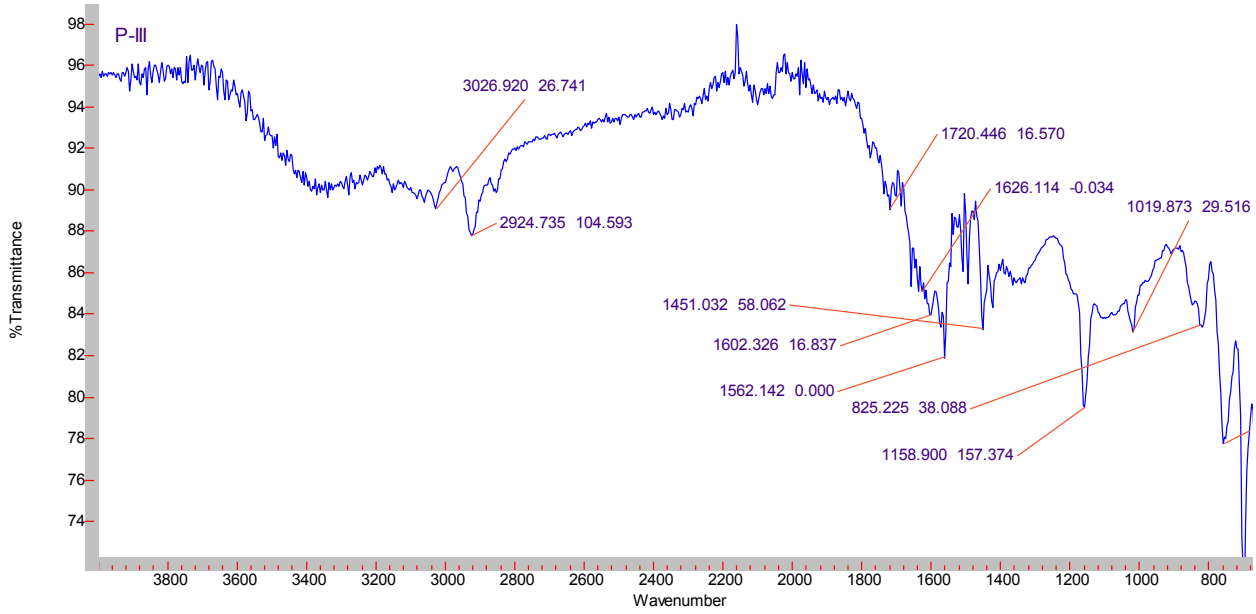
a) IR spectra of imidazolium-loaded polymeric support (MR-IMZ-Cl)



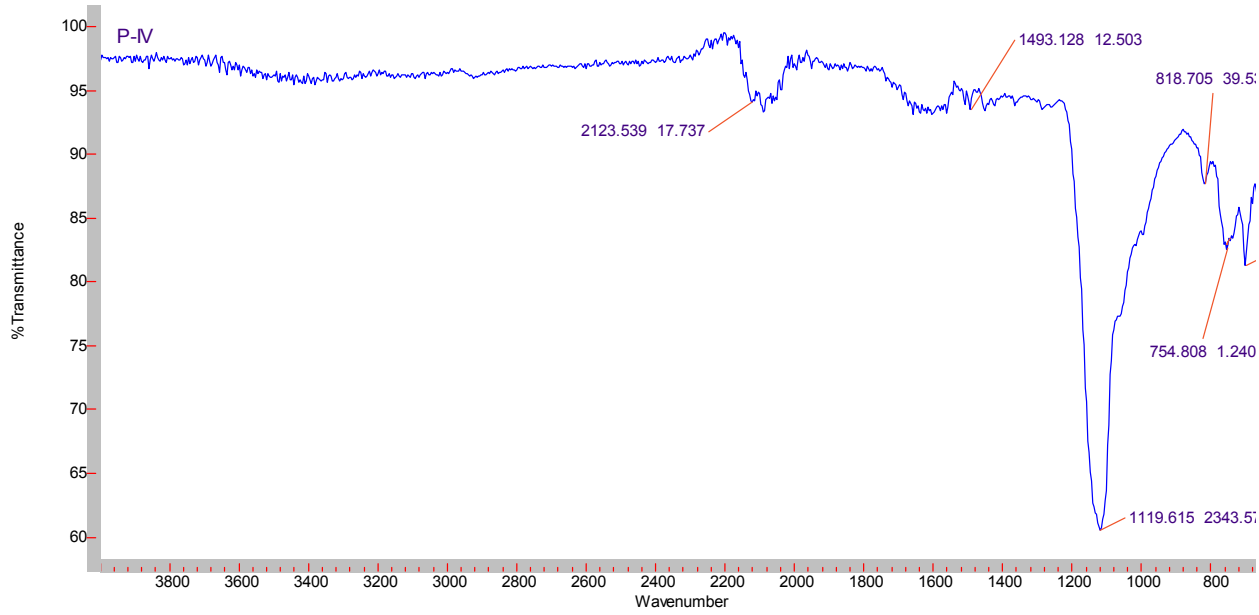
b) IR spectra of imidazolium-loaded polymeric support (MR-IMZ-OH)



c) IR spectra of Ascorbate functionalized polymer supported task specific ionic liquid catalyst (MR-IMZ-As)

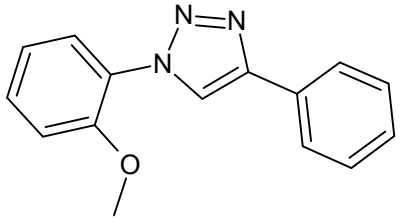


d) IR spectra of copper incorporated ascorbate functionalized polymer supported task specific ionic liquid catalyst (MR-IMZ-As-Cu)



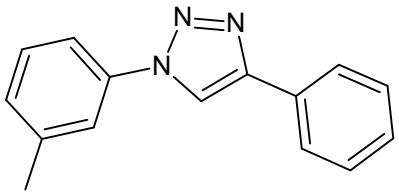
E) Spectral data of synthesized 1,2,3-triazole compounds:

Entry 1, Table 1: 1-(2-methoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole



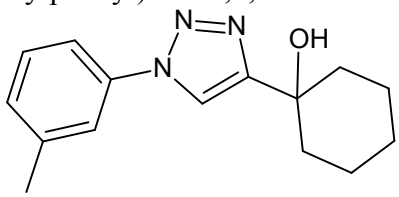
IR (Znse): 3126, 2940, 2842, 2286, 1879, 1725, 1656, 1610, 1562, 1517, 1440, 1302, 1230, 1183, 1110, 1073, 1028, 918, 826, 800 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 3.88 (s, 3H), 7.02-7.07 (dd, 2H, *J*= 3, 3 Hz), 7.35- 7.40 (t, 1H, *J*= 15 Hz), 7.44-7.49 (t, 2H, *J*= 15 Hz), 7.67-7.71 (dt, 2H, *J*= 3, 9 Hz), 7.91-7.93 (d, 2H, *J*= 6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 55.65, 114.82, 117.94, 122.19, 125.87, 128.41, 128.92, 130.18, 130.46, 148.10, 159.91; MS (EI): 237 (M^{+}-14), 222, 207, 194, 179, 165, 152, 130, 115, 103, 91, 77, 51 m/z.

Entry 2, Table 1: 1-(3-methylphenyl)-4-phenyl-1*H*-1,2,3-triazole



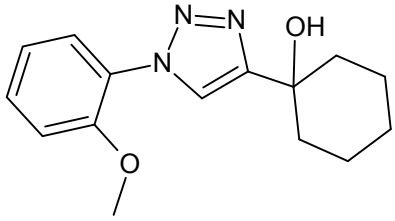
IR (Znse): 3126, 2921, 2856, 2305, 2114, 2092, 1872, 1664, 1610, 1592, 1475, 1396, 1228, 1085, 1044, 1022, 971, 898, 832, 785, 765 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 2.49 (s, 3H), 7.29 (s, 1H), 7.36-7.41 (m, 2H), 7.44- 7.51 (m, 2H), 7.57-7.60 (d, 1H, *J*= 9 Hz), 7.65 (s, 1H), 7.91-7.95 (m, 2H), 8.20 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 21.44, 117.61, 117.67, 121.22, 125.86, 128.40, 129.55, 130.30, 137.02, 140.04, 148.30; MS (EI): 235, 207, 192, 179, 165, 152, 130, 116, 103, 91, 76, 65, 51 m/z.

Entry 6, Table 1: 1-[1-(3-methylphenyl)-1*H*-1,2,3-triazol-4-yl]cyclohexanol



IR (Znse): 3236, 3111, 3066, 2936, 2855, 2108, 2088, 1726, 1610, 1594, 1491, 1446, 1259, 1234, 1170, 1057, 1022, 967, 898, 869, 848, 780 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 1.27-1.42 (m, 2H), 1.64-1.82 (m, 3H), 1.93-2.12 (m, 6H), 2.46 (s, 3H), 7.26-7.28 (d, 1H, *J*= 6 Hz), 7.37-7.43 (t, 1H, *J*= 9 Hz), 7.50-7.53 (d, 1H, *J*= 9 Hz), 7.57 (s, 1H), 7.90 (s,1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 21.40, 21.98, 25.34, 38.14, 117.67, 121.28, 129.47, 129.50, 139.97; MS (EI): 256, 239,210, 196, 182, 168, 167, 144, 131, 118, 91, 79, 65, 51, 41, 40 m/z.

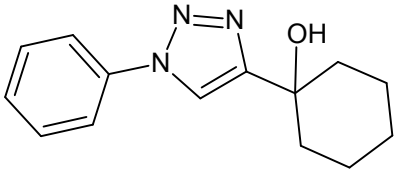
Entry 7, Table 1: 1-[1-(2-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl]cyclohexanol



IR (Znse): 3229, 3107, 3063, 2934, 2855, 1872, 1726, 1613, 1595, 1516, 1438, 1413, 1364, 1305, 1255, 1225, 1155, 1106, 1080, 1058, 1036, 968, 895, 876, 826 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 1.26-1.41 (m, 2H), 1.64 (s, 2H), 1.77-1.82 (t, 2H, *J*= 6 Hz), 1.92-1.97 (m, 2H), 2.03-2.07 (m, 2H), 2.32 (s, 1H, -OH), 3.87 (s, 3H), 7.00-7.03 (d, 2H, *J*= 9 Hz), 7.61-7.64 (d, 2H, *J*= 9 Hz), 7.83 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):

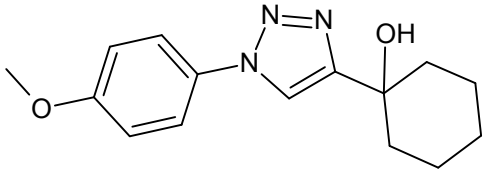
δ (ppm): 21.99, 25.35, 38.12, 55.63, 69.67, 114.74, 122.22; MS (EI): 244 (M^+-29), 227, 212, 198, 184, 160, 147, 132, 115, 103, 92, 77, 64, 51, 41, 40 m/z.

Entry 8, Table 1: 1-(1-phenyl-1*H*-1,2,3-triazol-4-yl)cyclohexanol



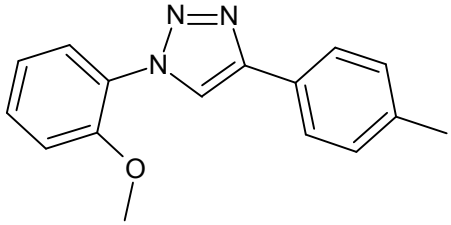
^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 1.01-1.38 (m, 2H), 1.43-1.66 (m, 3H), 1.79 (s, 2H), 1.98-2.06 (m, 3H), 2.30 (s, 1H, -OH), 7.53 (s, 3H), 7.75 (s, 2H), 7.92 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 21.98, 25.34, 38.12, 69.71, 117.98,120.57, 128.68, 129.73, 137.15; MS (EI): 243, 215, 196, 182, 168, 154, 141, 130, 117, 104, 91, 77, 66, 51, 41, 40 m/z.

Entry 9, Table 1: 1-[1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl]cyclohexanol



^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 1.26-1.46 (m, 2H), 1.59-1.64 (s, 2H), 1.81-1.82 (d, 2H, *J*= 3 Hz), 1.93-2.10 (m, 4H), 2.67 (s, 1H, -OH), 3.88 (s, 3H), 7.00-7.03 (d, 2H, *J*= 9 Hz), 7.61-7.64 (d, 2H, *J*= 9 Hz), 7.85 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 21.98, 22.17, 22.46, 25.35, 26.42, 38.14, 55.63, 69.64, 114.76, 122.08, 122.22, 125.85, 130.62, 159.81; MS (EI): 244 (M^+-29), 227, 212, 198, 184, 160, 147, 132, 115, 103, 92, 77, 64, 51, 41, 40 m/z.

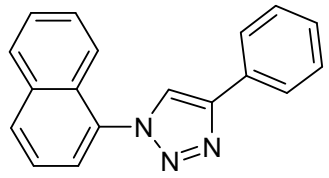
Entry 10, Table 1: 1-(2-methoxyphenyl)-4-(4-methylphenyl)-1*H*-1,2,3-triazole



IR (Znse): 3159, 3017, 2925, 2856, 2111, 2086, 1913, 1725, 1603, 1590, 1516, 1493, 1475, 1289, 1256, 1227, 1179, 1126, 1088, 1020, 932 809, 749, 715 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 2.41 (s, 3H), 3.92 (s, 3H), 7.10-7.15 (t, 2H, *J*= 9 Hz), 7.26- 7.29 (d, 1H, *J*= 9 Hz), 7.44 (t, 1H), 7.81-7.85 (dd, 3H, *J*= 6, 3 Hz), 8.30 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 21.30, 56.06, 112.36, 121.17, 121.51, 125.49, 125.78, 126.40,

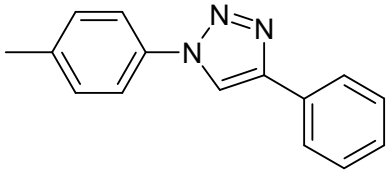
127.75, 130.11, 137.99, 147.22, 151.18; MS (EI): 265, 238, 237, 222, 207, 194, 179, 165, 152, 130, 115, 103, 91, 77, 51 m/z.

Entry 13, Table 1: 1-(naphthalen-1-yl)-4-phenyl-1*H*-1,2,3-triazole



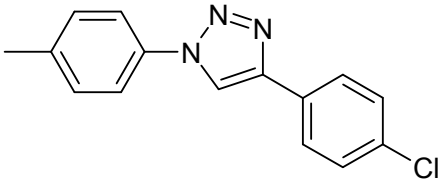
^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 7.28-7.30 (d, 2H, *J*= 6 Hz), 7.46- 7.59 (m, 5H), 7.57-7.59 (d, 2H, *J*= 6 Hz), 7.66- 7.68 (d, 2H, *J*= 6 Hz), 7.84- 7.87 (m, 1H), 8.13-8.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 113.95, 122.61, 124.73, 125.70, 126.18, 126.45, 126.93, 127.78, 134.39, 136.54.

Entry 14, Table 1: 1-(4-methylphenyl)-4-phenyl-1*H*-1,2,3-triazole



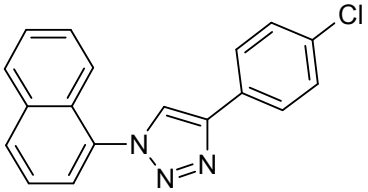
^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 2.40 (s, 3H), 7.23-7.26 (m, 6H), 7.34- 7.35 (m, 3H), 7.85 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 21.18, 124.99, 126.86, 128.54, 129.10, 129.89, 133.28, 134.12, 137.61, 139.33.

Entry 15, Table 1: 4-(4-chlorophenyl)-1-(4-methylphenyl)-1*H*-1,2,3-triazole



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 2.41 (s, 3H), 7.15-7.17 (d, 2H, *J*= 6 Hz), 7.23-7.26 (m, 4H), 7.31-7.33 (d, 2H, *J*= 6 Hz), 7.85 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 21.17, 125.29, 129.12, 129.74, 130.02, 133.27, 133.82, 135.31, 136.54, 139.61.

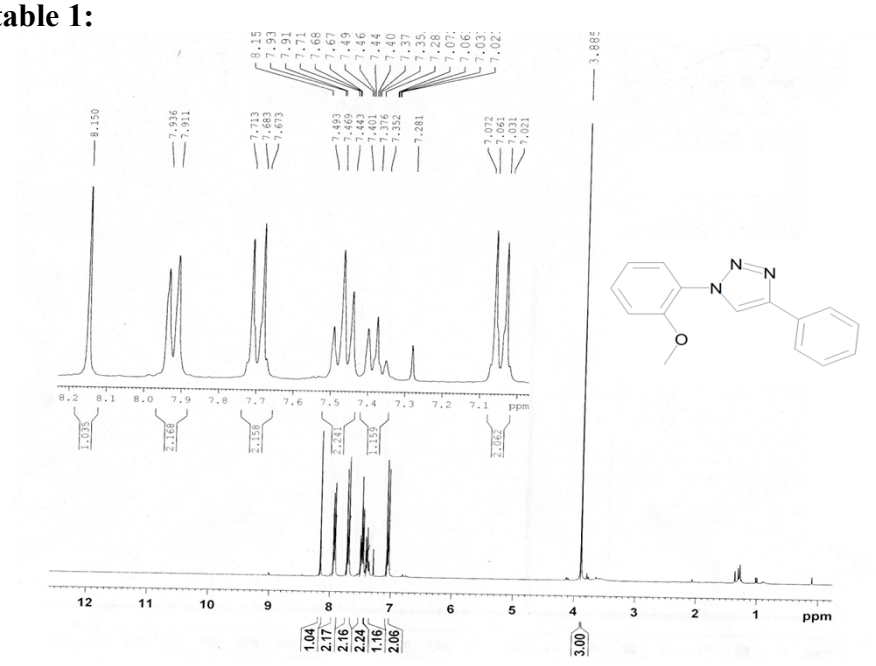
Entry 16, Table 1: 4-(4-chlorophenyl)-1-(naphthalen-1-yl)-1*H*-1,2,3-triazole

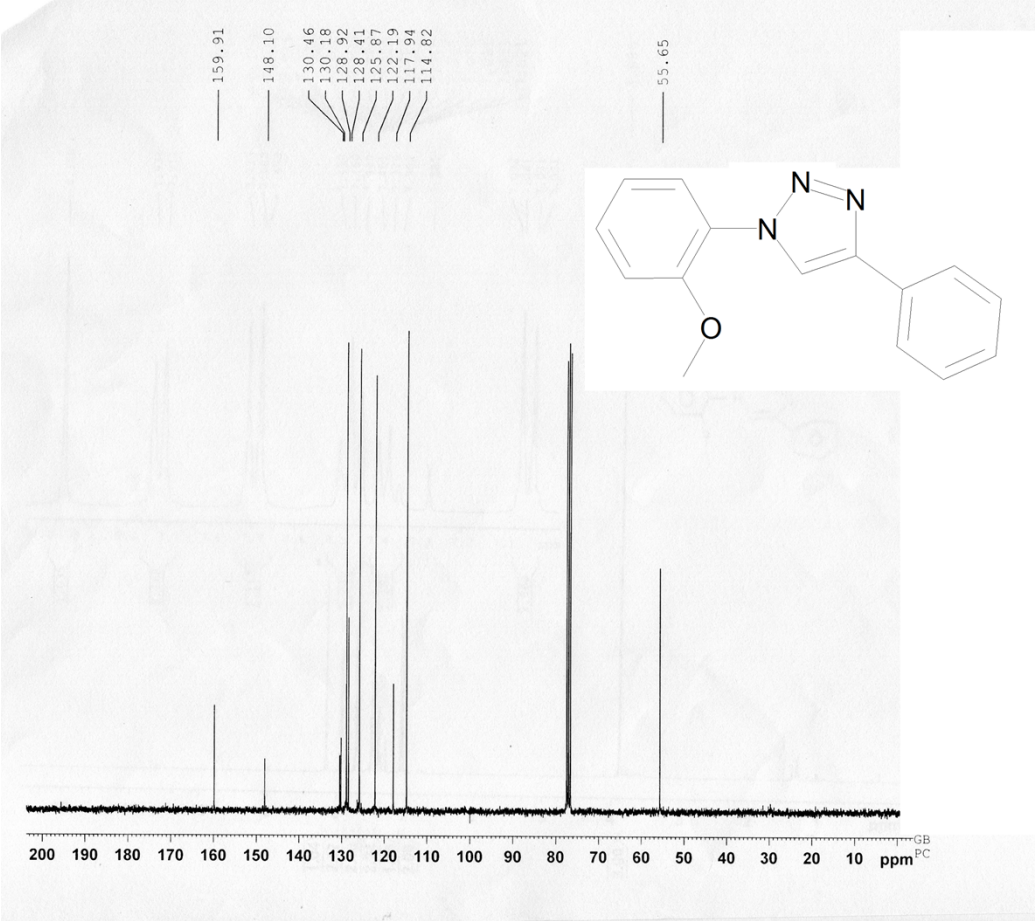


^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 7.30 (s, 1H), 7.47- 7.60 (m, 6H), 7.60-7.66 (d,

1H, *J*= 12 Hz), 7.85- 7.88 (dd, 2H, *J*= 6, 3 Hz), 8.14- 8.18 (t, 2H, *J*= 6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 113.93, 122.57, 124.71, 125.68, 126.16, 126.43, 126.90, 127.75, 134.36, 136.53.

Entry 1, table 1:

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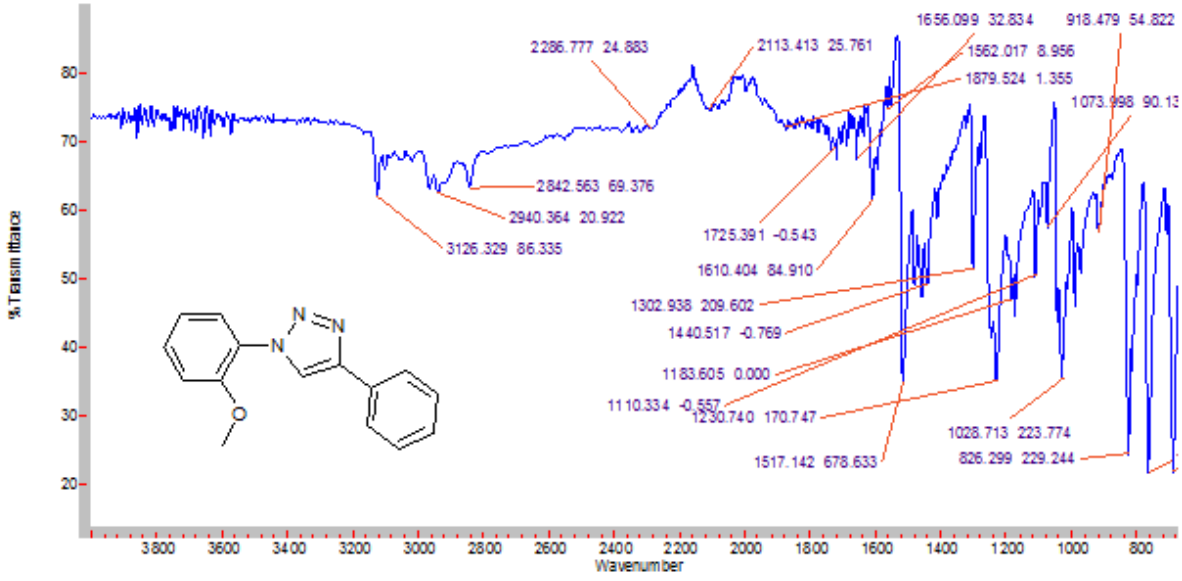
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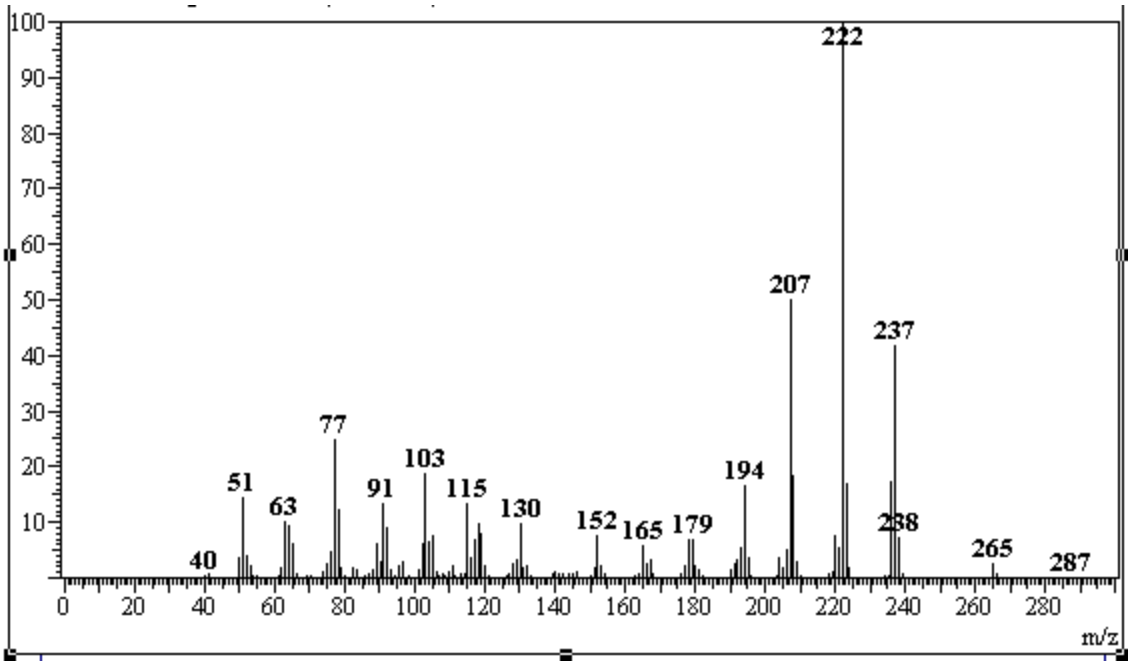

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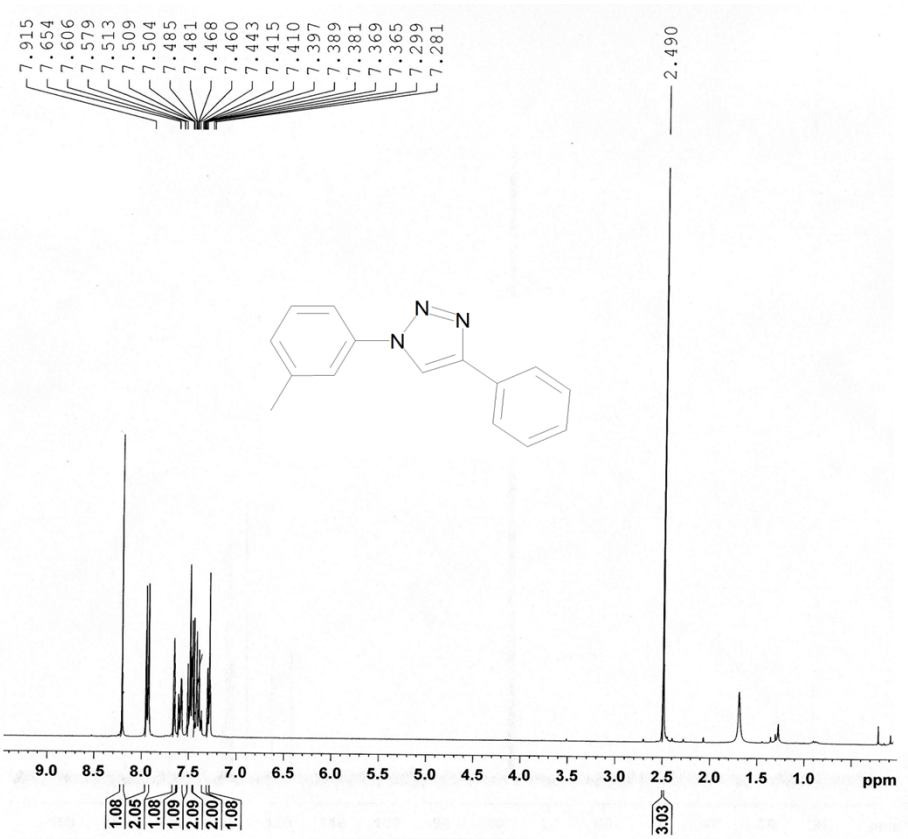
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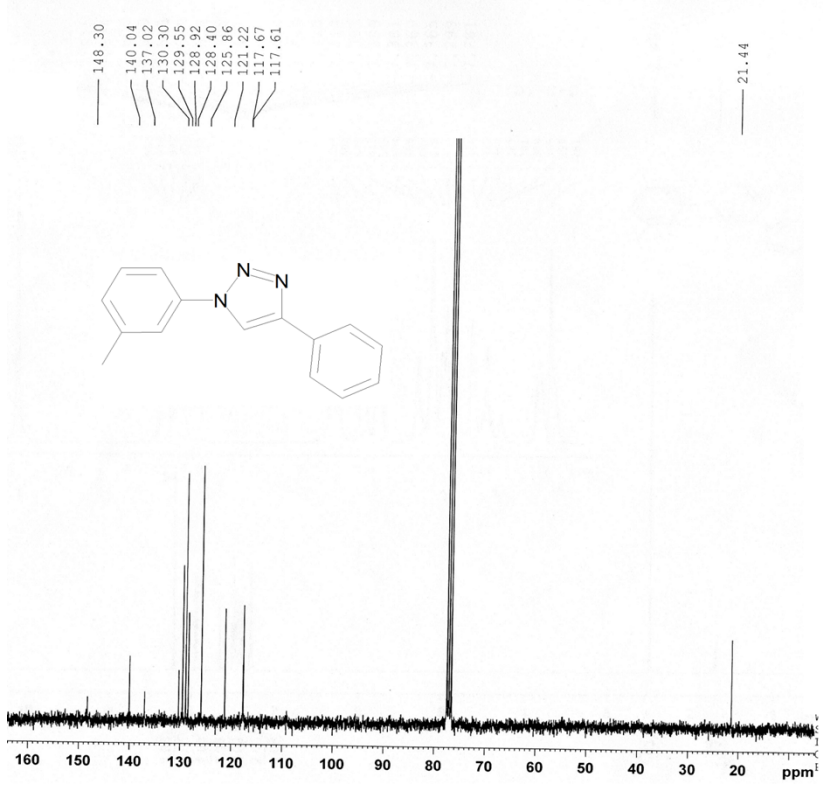
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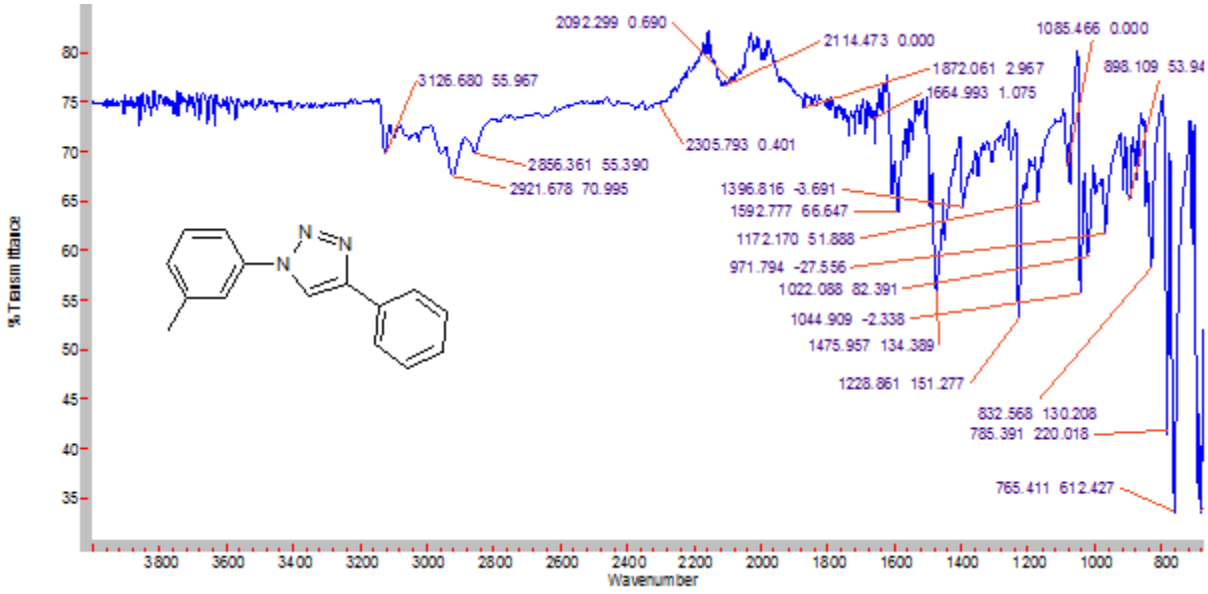
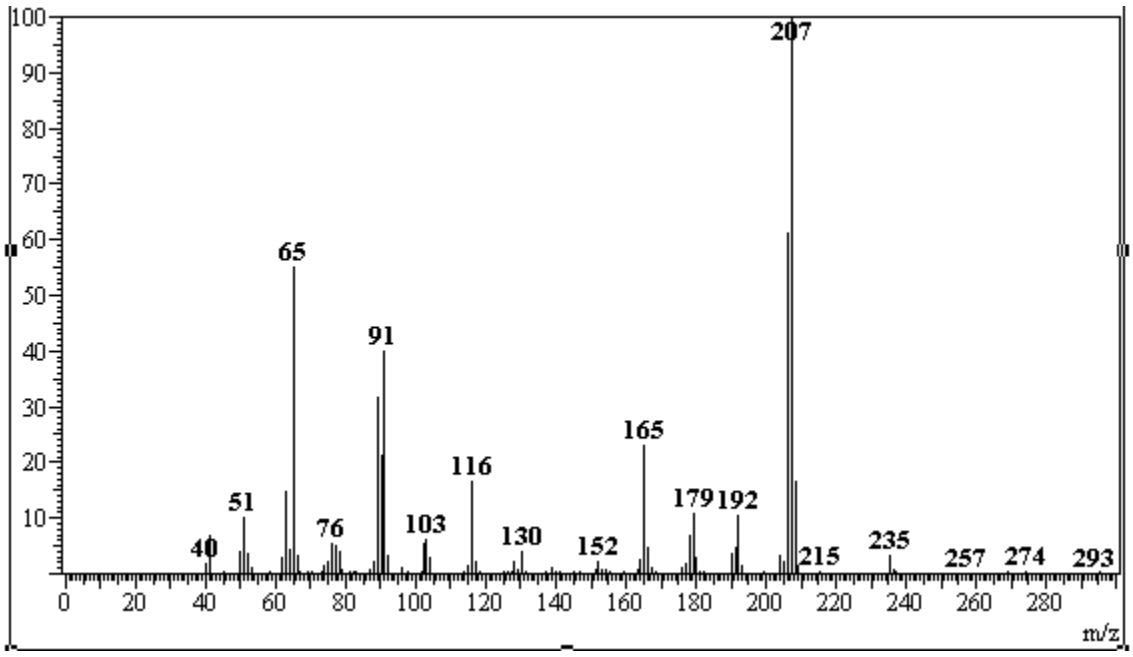
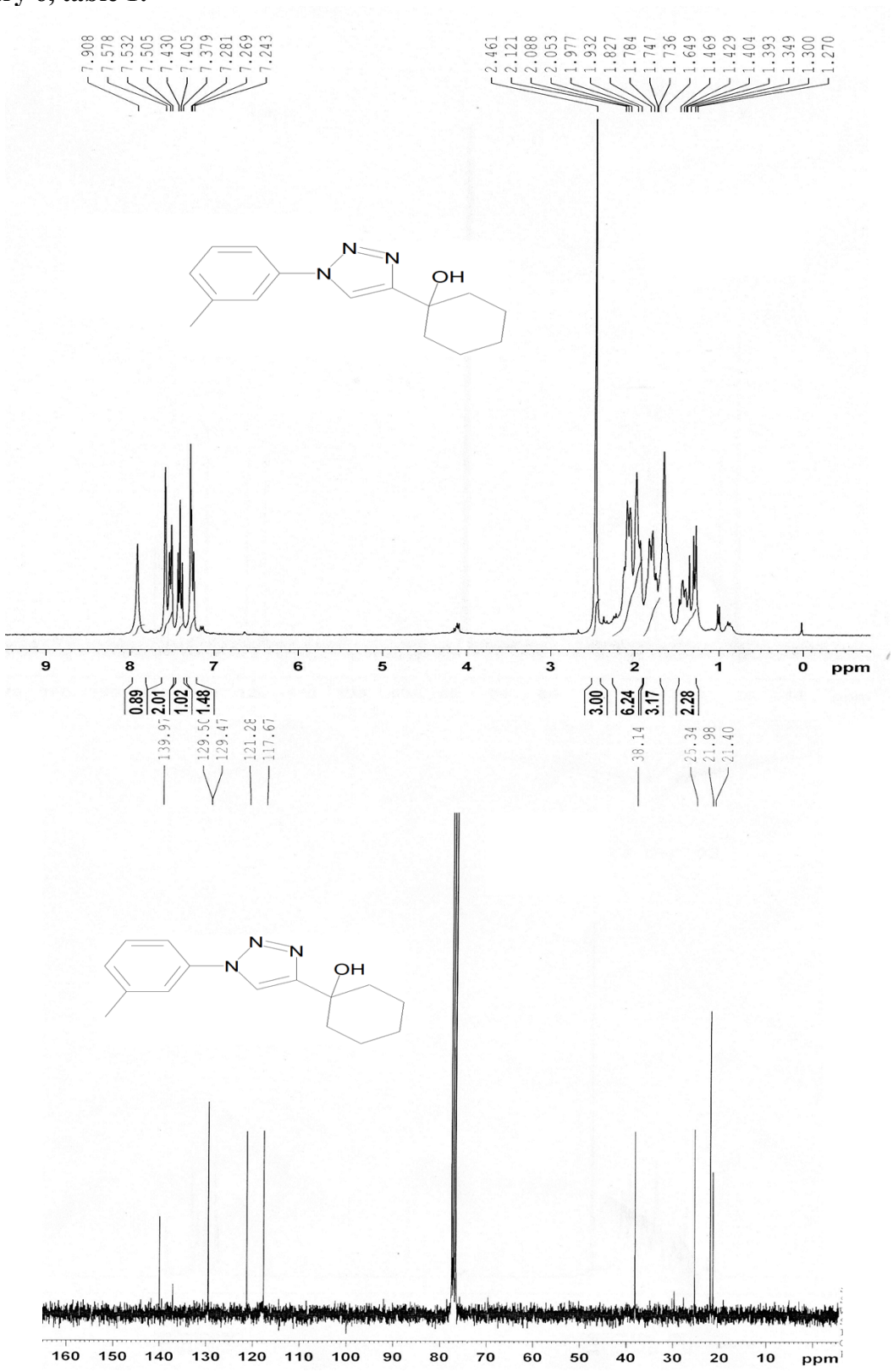
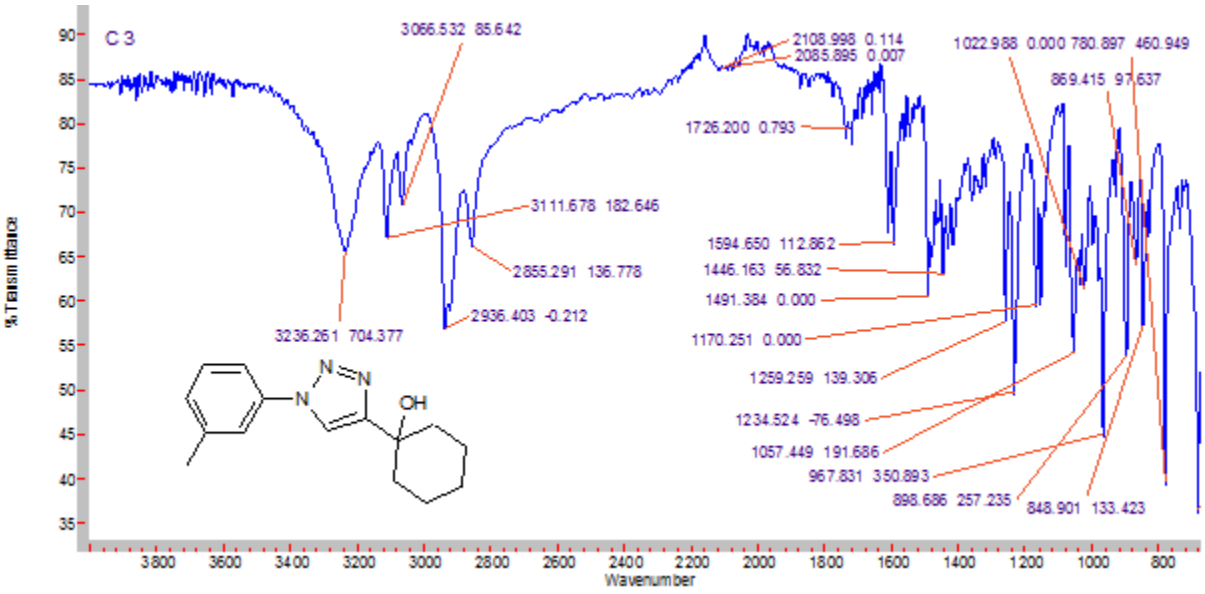
N
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

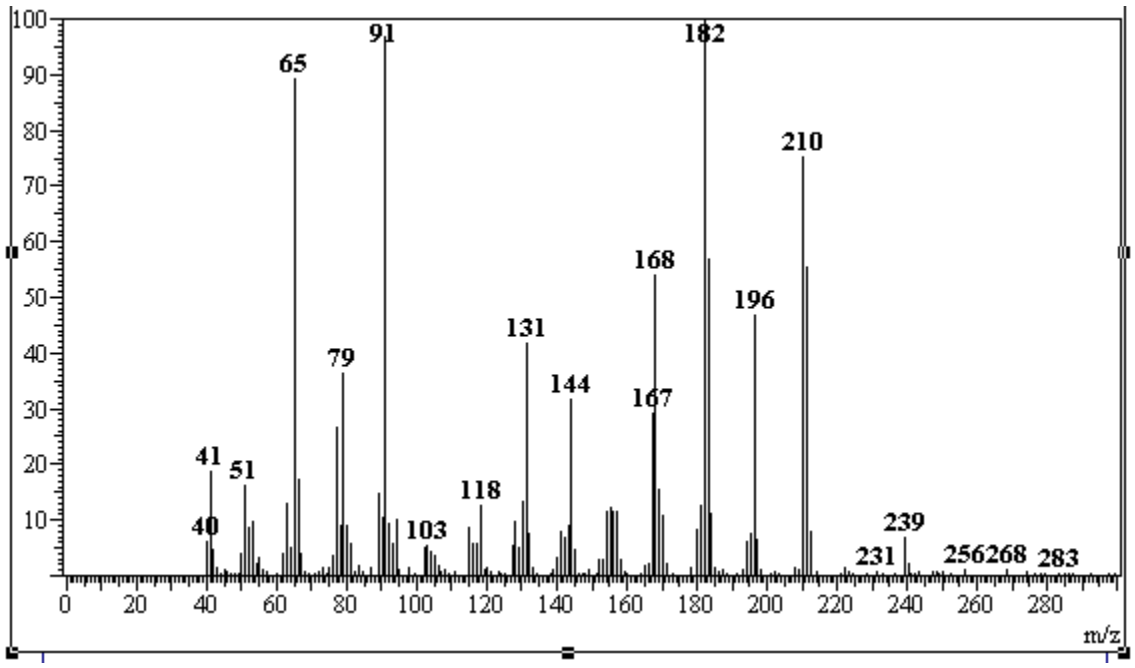

2092.299 0.690
2114.473 0.000
1085.466 0.000
1872.061 2.967
898.109 53.94
3126.680 55.967
1664.993 1.075
2856.361 55.390
2305.793 0.401
2921.678 70.995
1396.816 -3.691
1592.777 66.647
1172.170 51.888
971.794 -27.556
1022.088 82.391
1044.909 -2.338
1475.957 134.389
1228.861 151.277
832.568 130.208
785.391 220.018
765.411 612.427
%Transmittance
Wavenumber


207
65
91
165
116
179
192
51
76
103
130
152
40
215
235
257
274
293
m/z

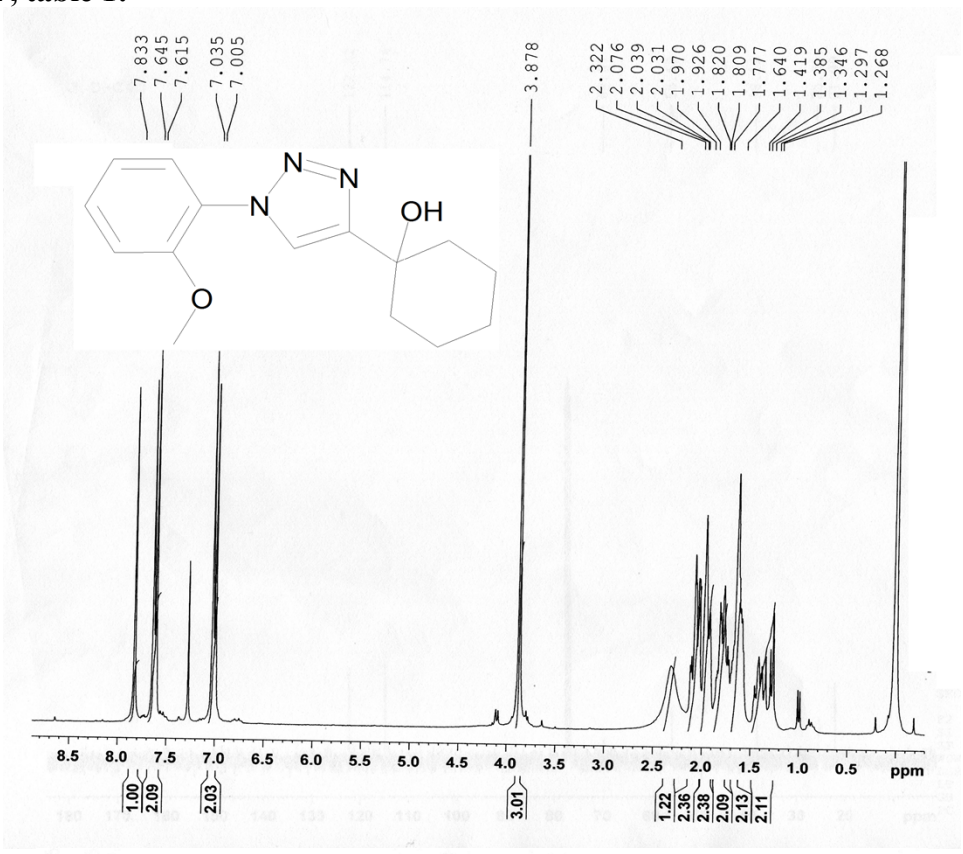
Entry 6, table 1:

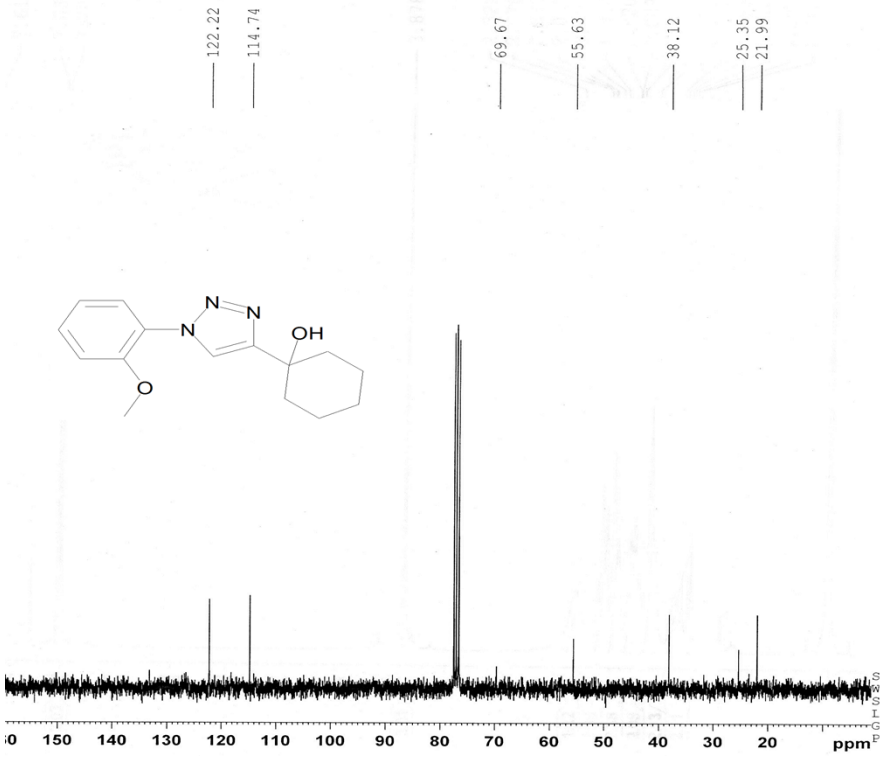


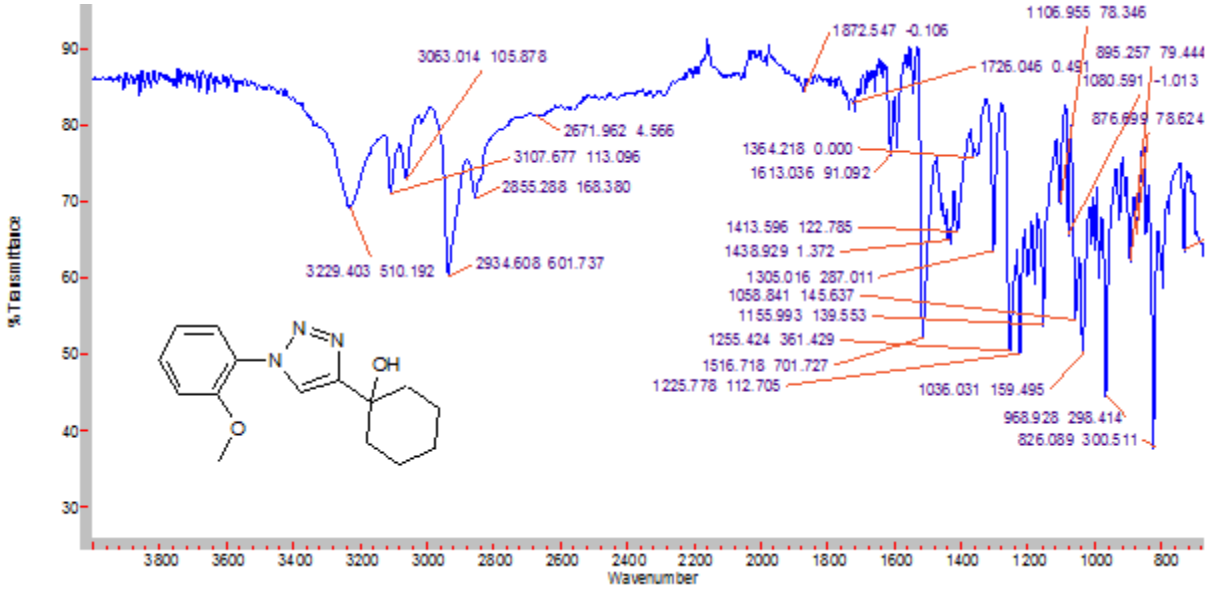

C 3
3066.532 85.642
2108.998 0.114
2085.895 0.007
1022.988 0.000
780.897 460.949
869.415 97.637
1726.200 0.793
3111.678 182.646
2855.291 136.778
2936.403 -0.212
3236.261 704.377
1594.650 112.862
1446.163 56.832
1491.384 0.000
1170.251 0.000
1259.259 139.306
1234.524 -76.498
1057.449 191.686
967.831 350.893
898.686 257.235
848.901 133.423
OH
%Transmittance
Wavenumber

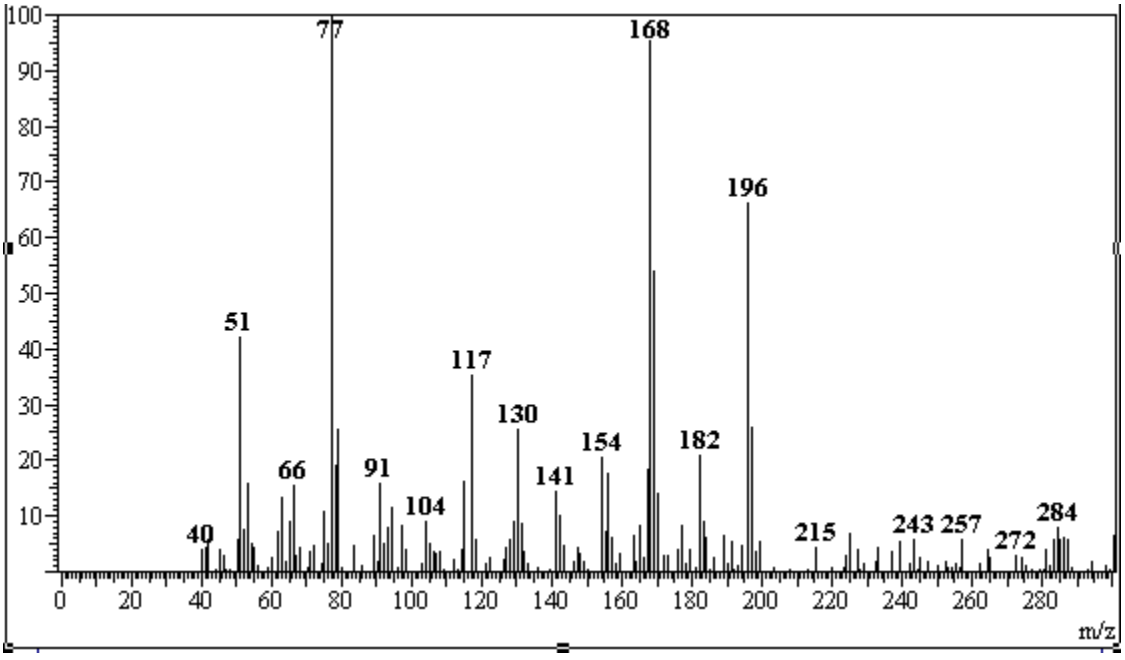

91
65
182
210
168
196
131
79
144
167
41
51
118
40
103
239
231
256268
283
m/z

Entry 7, table 1:

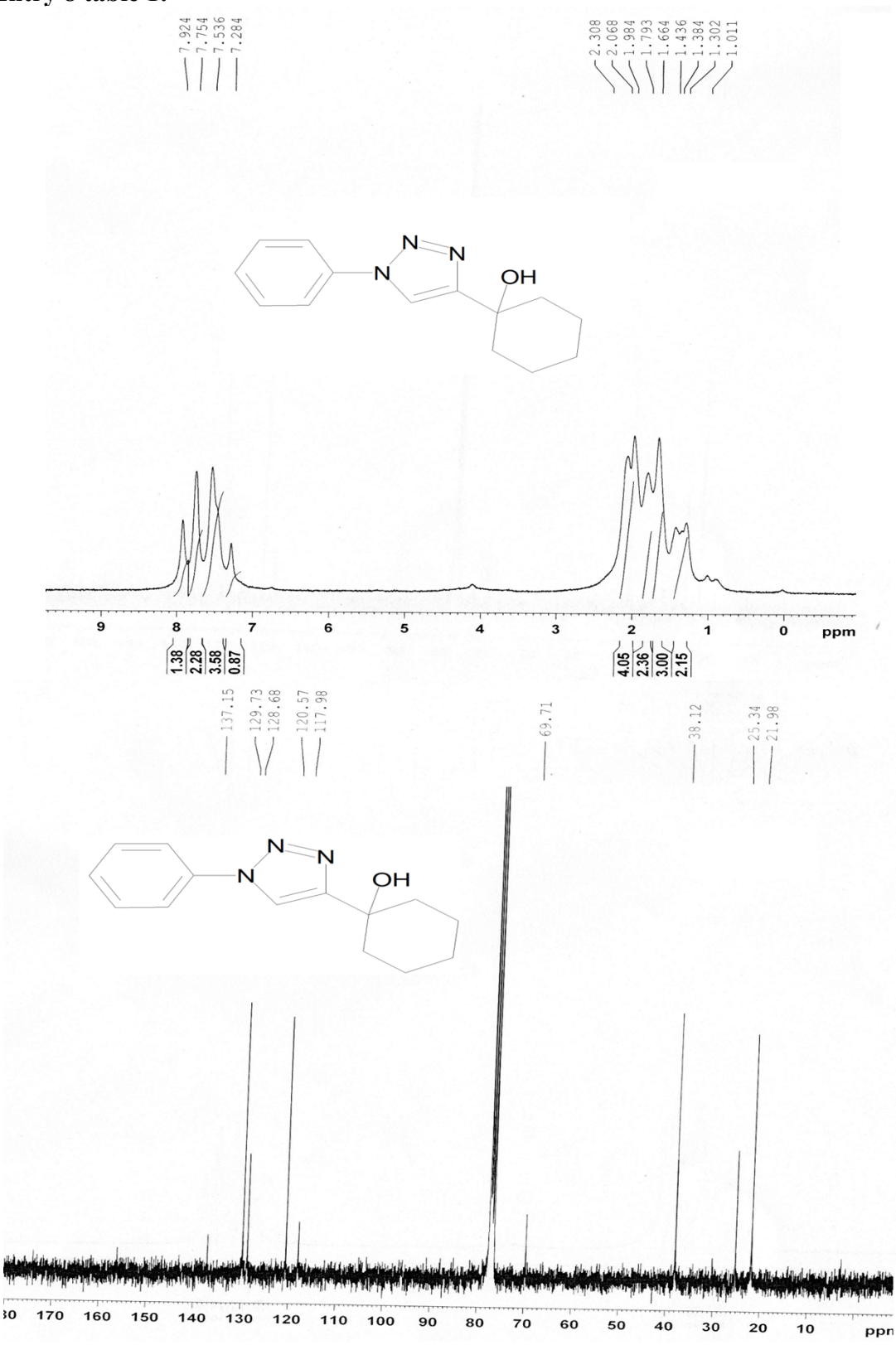


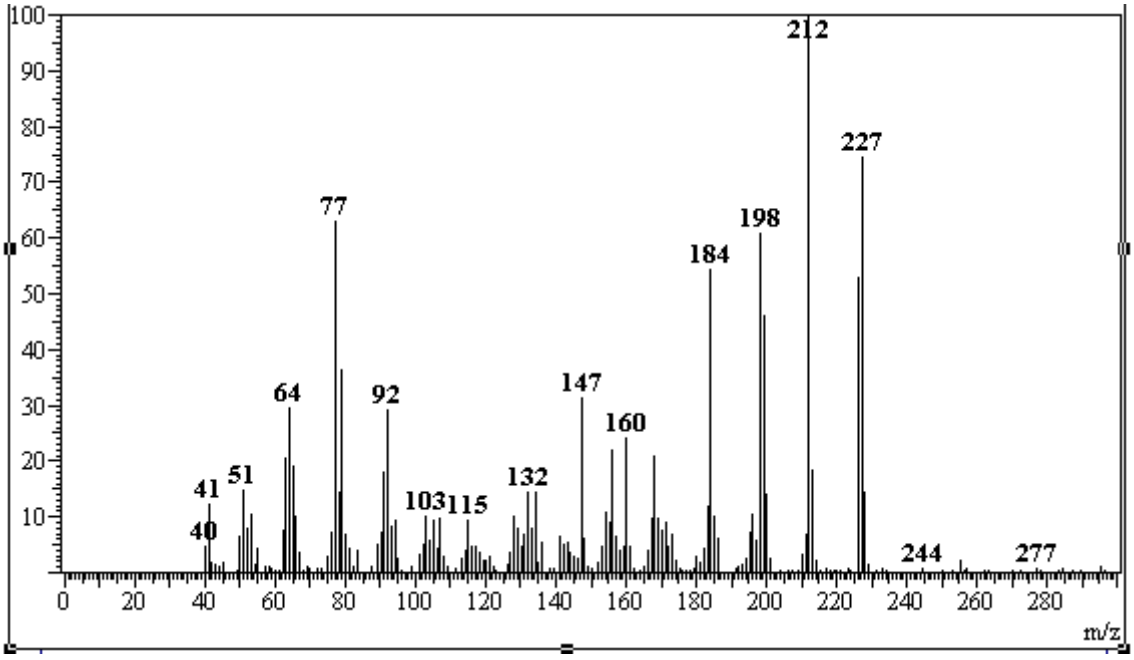



%Transmittance
Wavenumber
3063.014 105.878
3229.403 510.192
2934.608 601.737
2671.962 4.566
3107.677 113.096
2855.288 168.380
1872.547 -0.106
1726.046 0.491
1364.218 0.000
1613.036 91.092
1106.955 78.346
895.257 79.444
1080.591 -1.013
876.699 78.624
1413.596 122.785
1438.929 1.372
1305.016 287.011
1058.841 145.637
1155.993 139.553
1255.424 361.429
1516.718 701.727
1225.778 112.705
1036.031 159.495
968.928 298.414
826.089 300.511
OH
O
N
N

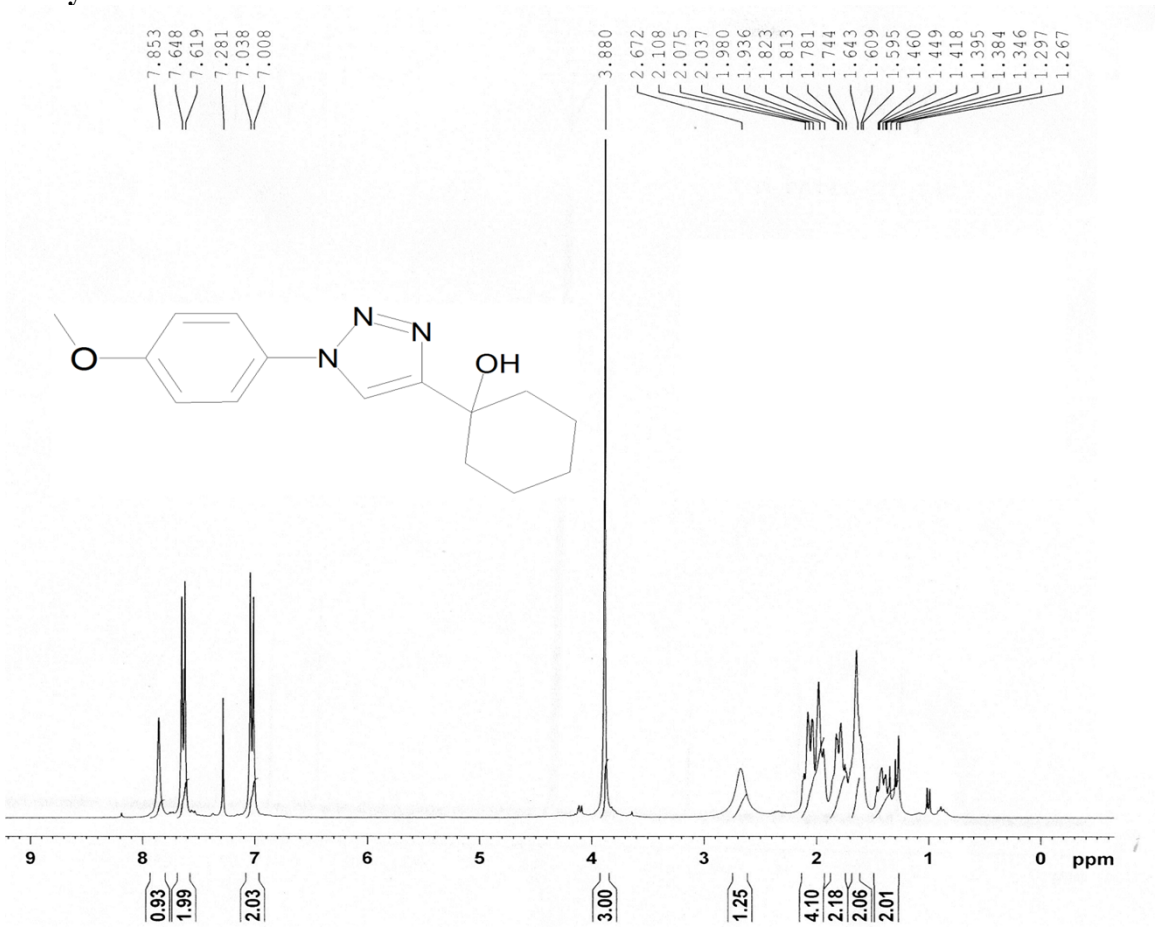

77
168
196
51
117
130
154
182
66
91
104
141
40
215
243
257
272
284
m/z

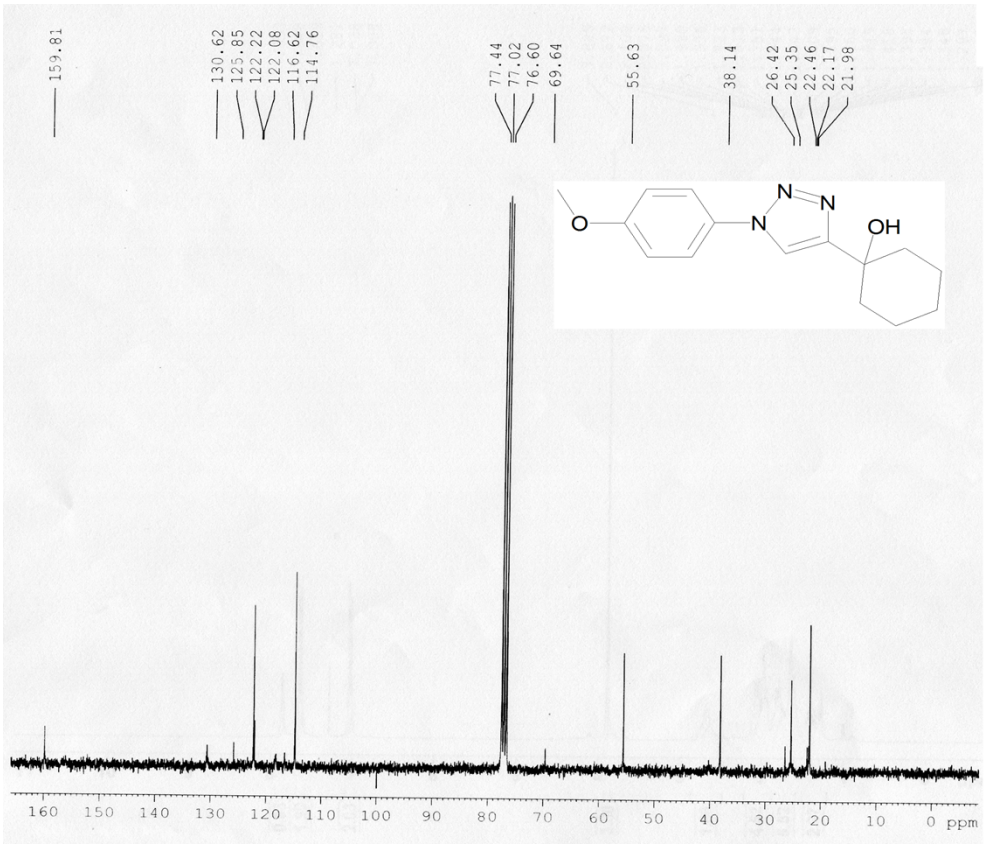
Entry 8 table 1:

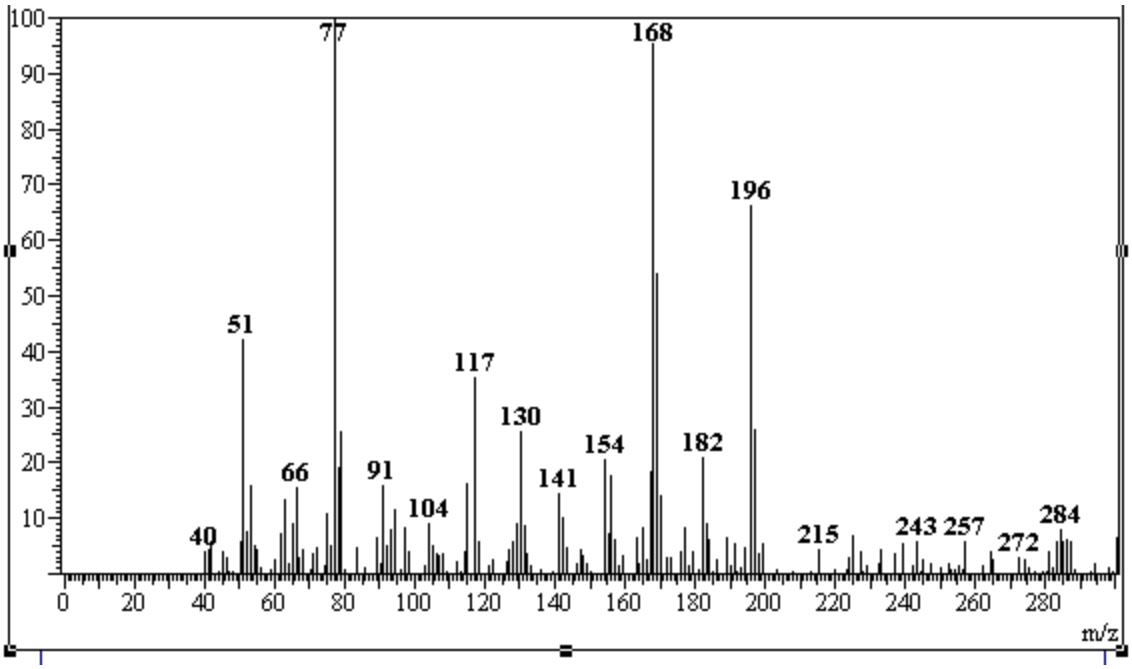




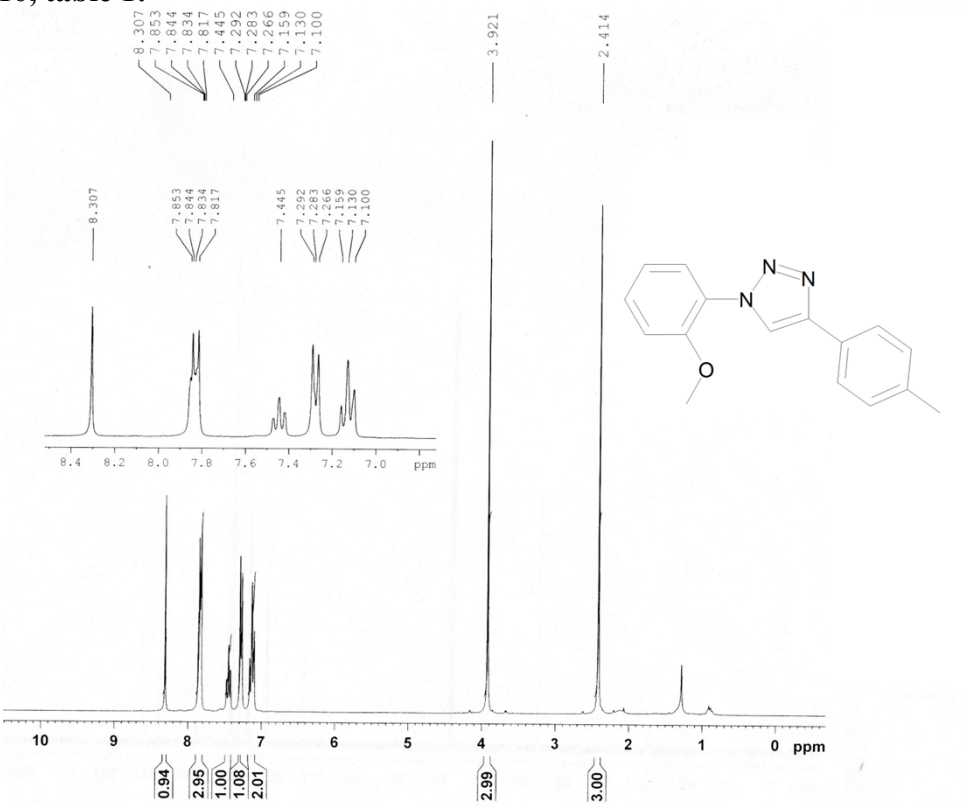
Entry 9 table 1:

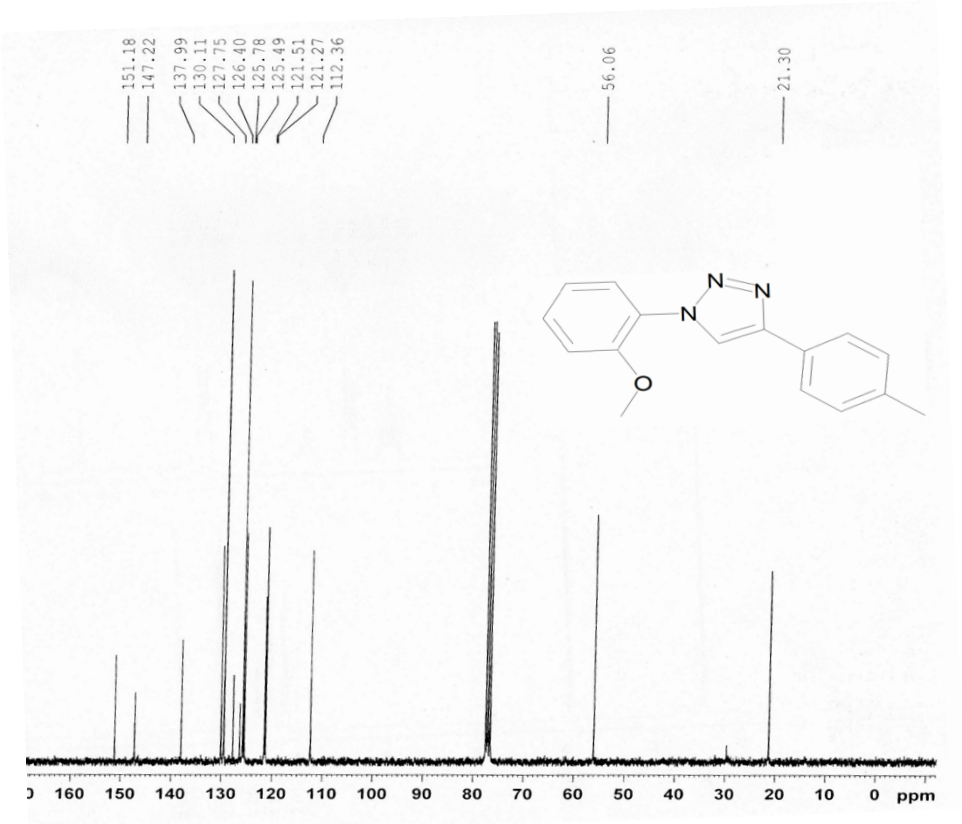


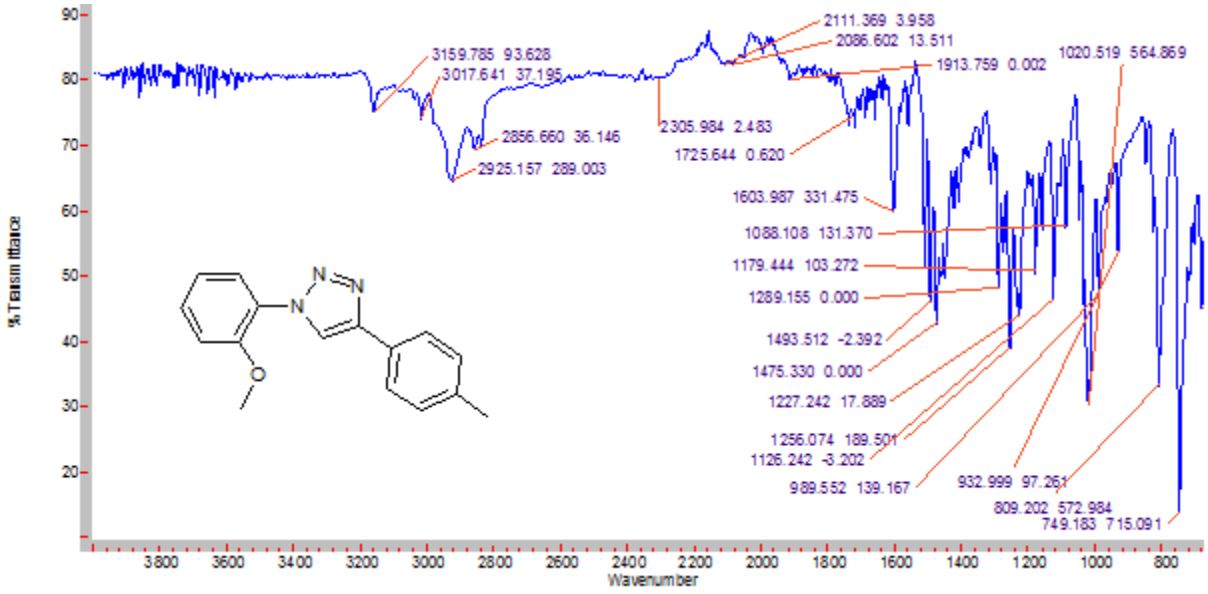

159.81
130.62
125.85
122.22
122.08
116.62
114.76
77.44
77.02
76.60
69.64
55.63
38.14
26.42
25.35
22.46
22.17
21.98
O
N
N
N
OH
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

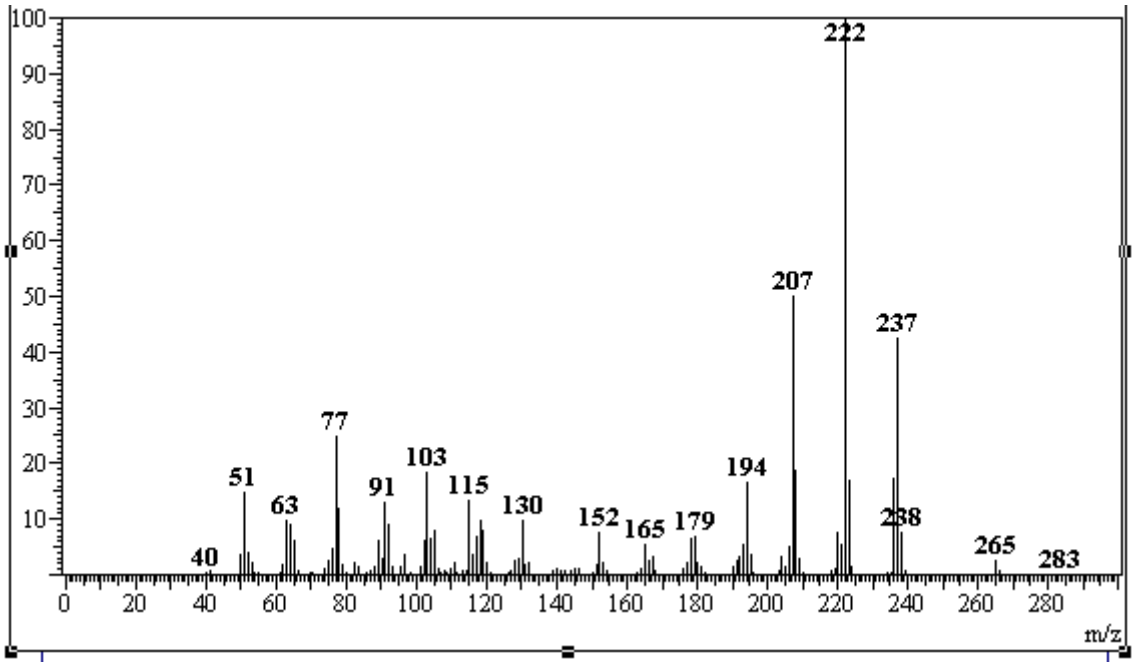

100
90
80
70
60
50
40
30
20
10
77
168
196
51
117
130
154
182
66
91
141
104
40
215
243
257
272
284
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280
m/z

Entry 10, table 1:

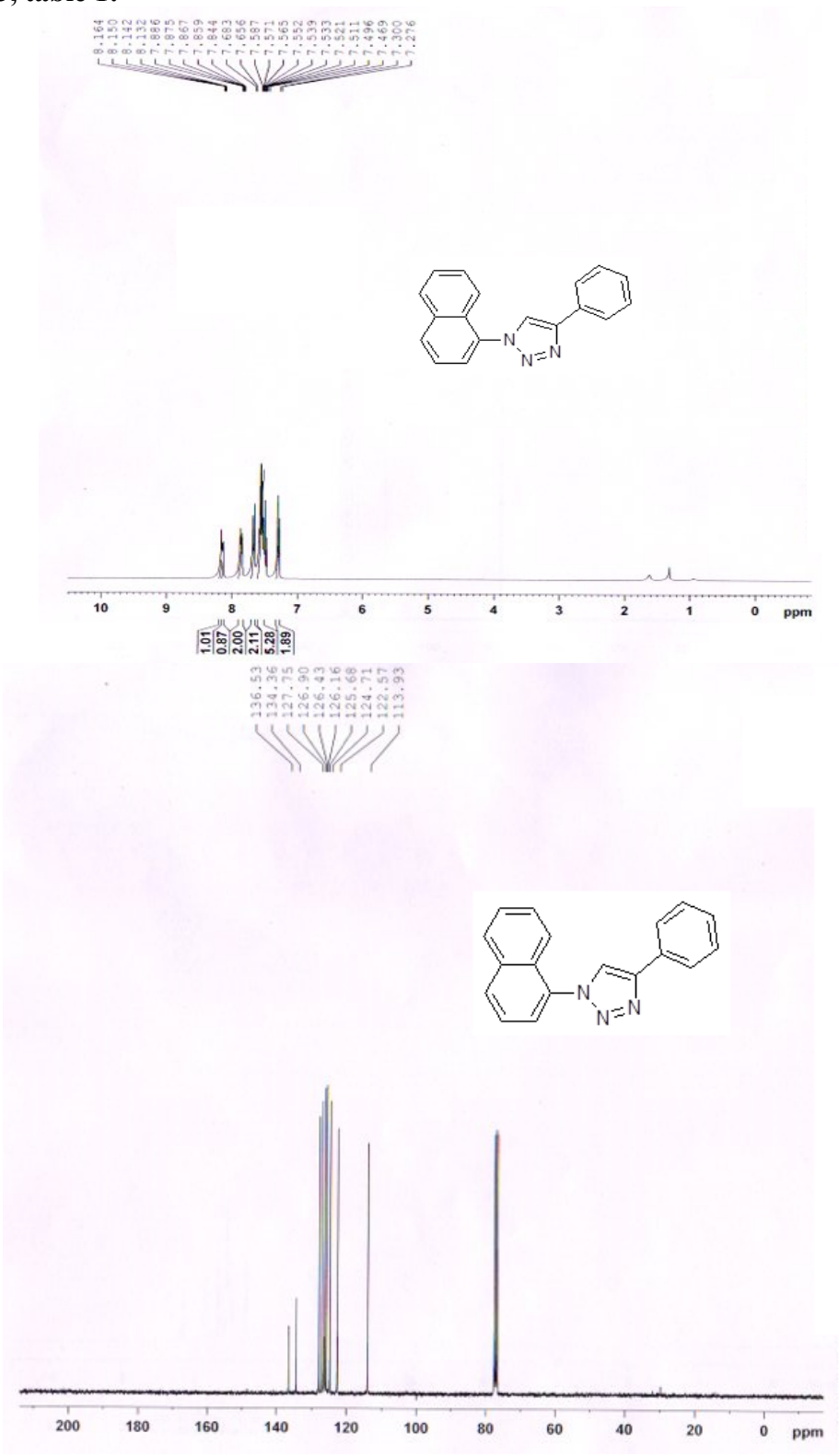




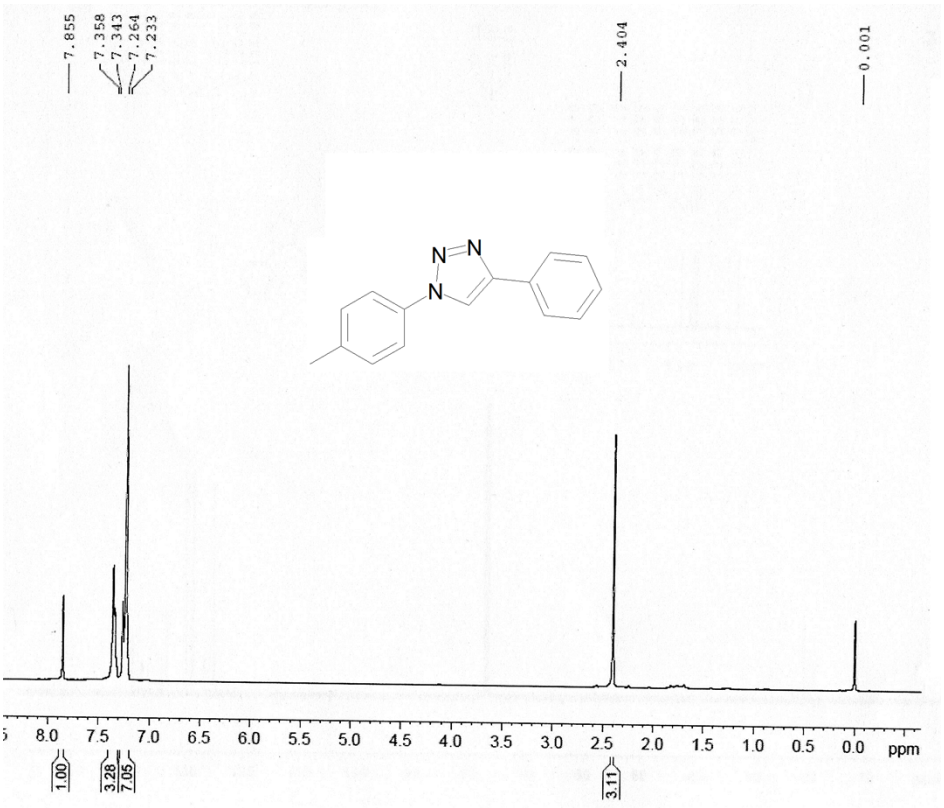

%Transmittance
Wavenumber
3159.785 93.628
3017.641 37.195
2856.660 36.146
2925.157 289.003
2111.369 3.958
2086.602 13.511
1913.759 0.002
1020.519 564.869
2305.984 2.483
1725.644 0.620
1603.987 331.475
1088.108 131.370
1179.444 103.272
1289.155 0.000
1493.512 -2.392
1475.330 0.000
1227.242 17.889
1256.074 189.501
1126.242 -3.202
989.552 139.167
932.999 97.261
809.202 572.984
749.183 715.091

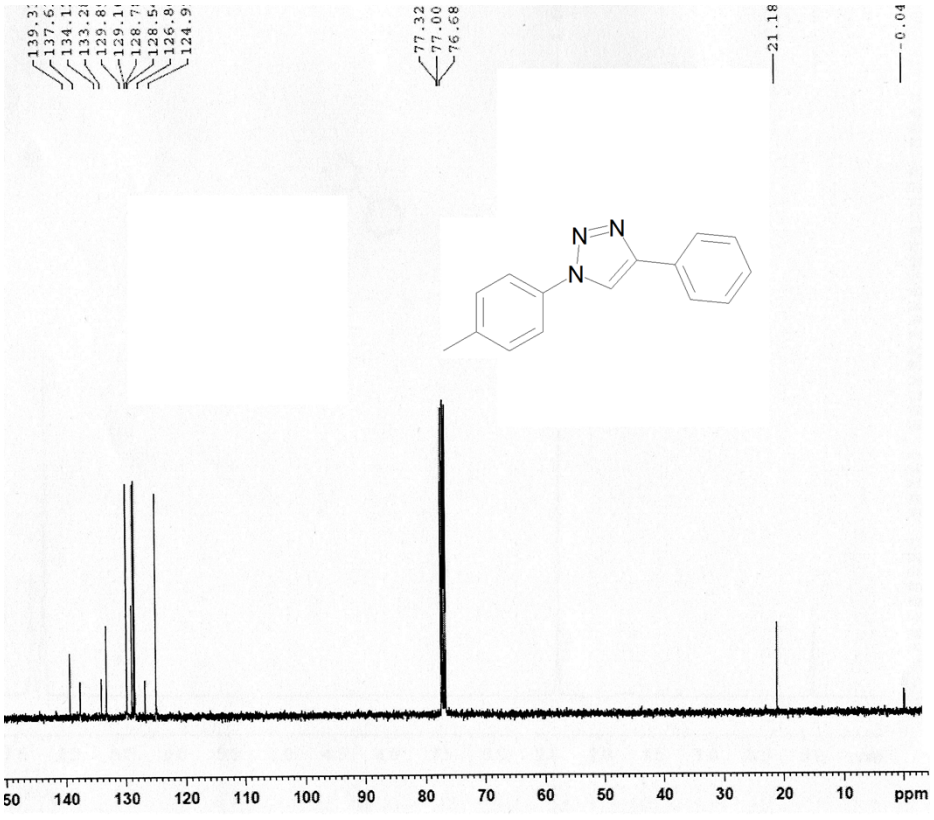

m/z
222
207
237
77
103
51
91
115
63
130
152
165
179
194
238
265
283
40

Entry 13, table 1:

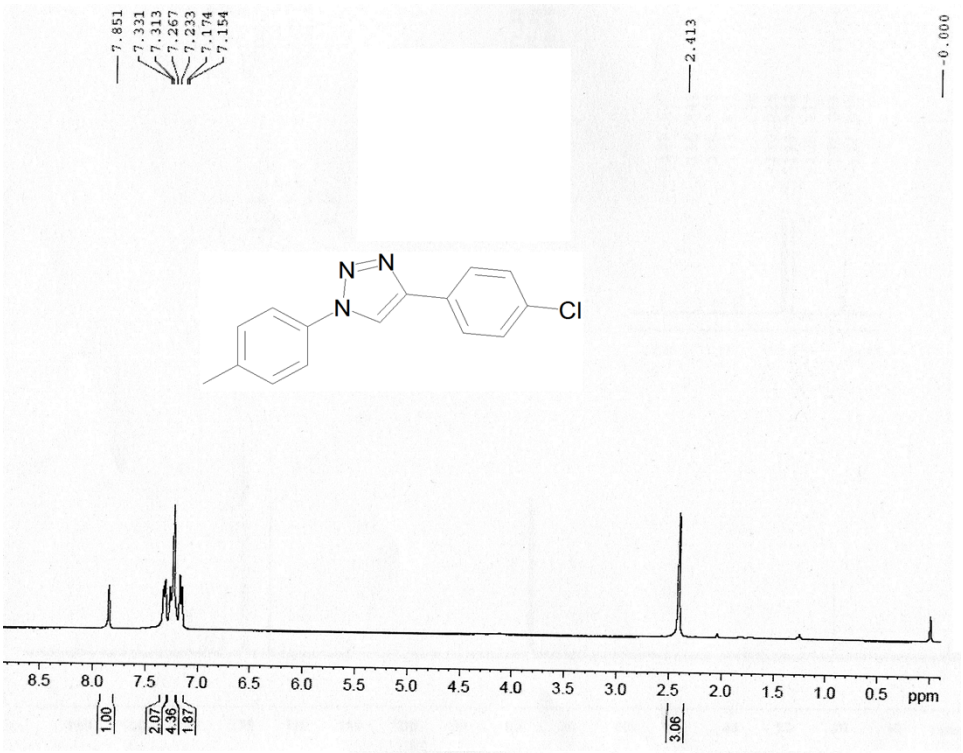


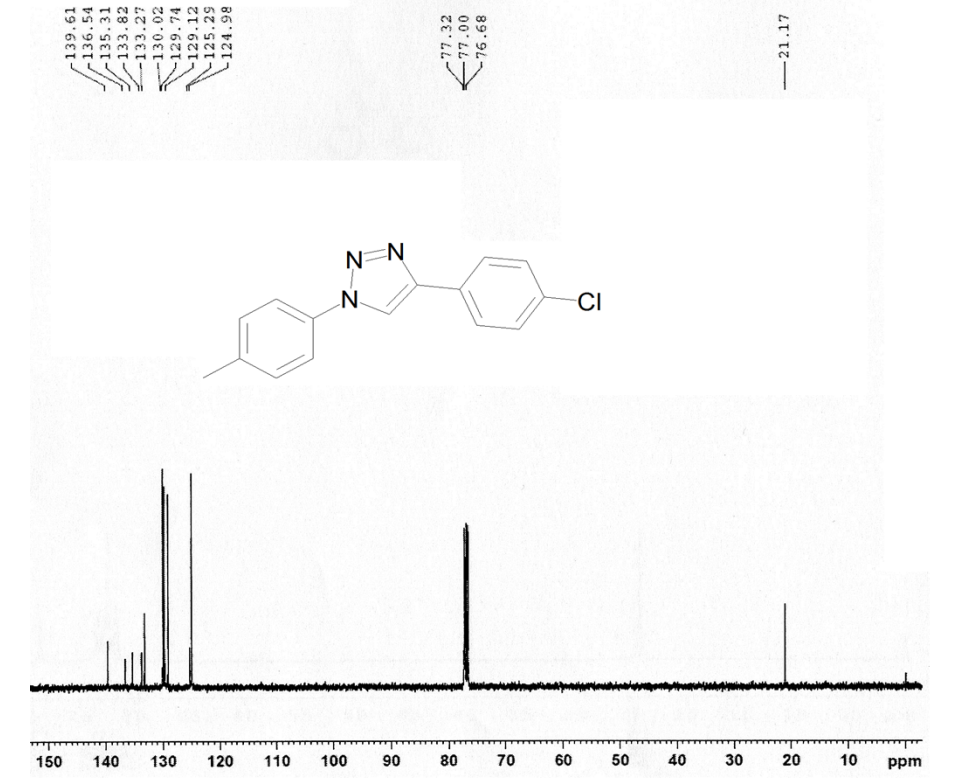
Entry 14, table 1:





Entry 15, table 1:





Entry 16, table 1: