Supplementary Information

Ammonium chloride catalyzed Knoevenagel condensation in PEG-400 as ecofriendly solvent

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Supporting Information

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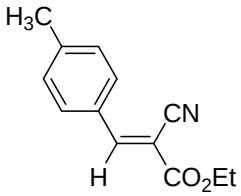
Experimental Section:

A commercially available reagents were used of analytical grade and employed without further purification. The products were purified using column chomatographywherever needed.All synthesizedcompounds identified by spectroscopic data,melting points and by comparison with available standards. FTIR spectra were obtained with a Shimadzu 8000 spectrophotometer. H^1 and C^{13} NMR spectra were recorded on varian spectrometer. Chemical shifts (δ) are reported in ppm and with 60 F_{254} plates and spots were rendered visible by exposing to UV light and Iodine. Melting points were determined with an electro thermal model 9100 apparatus and are uncorrected.

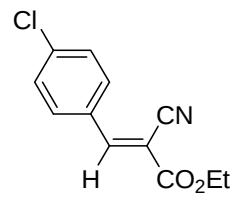
General procedure for the Knoevenagel Condensation:

A round bottom flask was charged with the aldehydes (10mmol), active methylene compound (10mmol), ammonium chloride catalyst (10 mol %) and solvent 10mL. The mixture was stirred at the room temperature. The formation of the products was monitored by TLC and after completion; title compound was isolated by quenching the reaction mixture with water at 5^0C and subsequent filtration. Traces of aldehyde if any, were removed by washing the product with hexane.



***(E)-ethyl-2-cyano-2-p-tolylacrylate*[3a][1]**

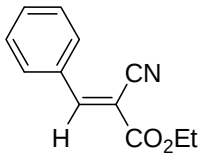
Colorless solid; **mp**: 91-92°C [Lit **mp**: 90-92°C]; **IR** (ν_{max}/cm^{-1}): 3100, 2850, 2210, 1710, 1600, 1460, 1370, 1270, 1200, 1100;**^{1}H NMR** (300 MHz; $CDCl_3$): *δ*1.40(t, *J*=7.06, 3H), 2.43(s, 3H), 4.38(q, *J*=7.06, 2H), 7.26(d, *J*=7.69, 2H,),7.86(d, *J*=8.14, 2H), 8.21(S, 1H).



***(E)-ethyl-3-(4-chlorophenyl)-2-cyanoacrylate* [3b][1,4]**

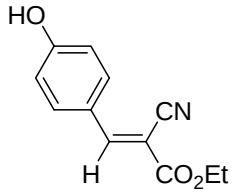
White solid; **mp**: 88-89°C [Lit **mp**: 89-90°C]; **IR** (ν_{max}/cm^{-1}): 2985, 2225, 1739, 1600, 1452, 1373, 1242, 1047, 933, 842, 788, 634; **^{1}H NMR** (300 MHz; $CDCl_3$): δ 1.38 (t, *J* =7.2 Hz, 3H), 4.38 (q, *J*= 7.2 Hz, 2H), 7.48 (d, *J*= 8.5 Hz, 2H), 7.93 (d, *J*= 8.5 Hz, 2 H), 8.18 (s, 1H); **^{13}C NMR** (75 MHz; $CDCl_3$): δ 14.26, 62.03, 103.37, 115.94, 129.50, 132.02, 139.49, 153.37, 161.87.

***(E)-ethyl-2-cyano-3-phenylacrylate* [3c][1,4]**



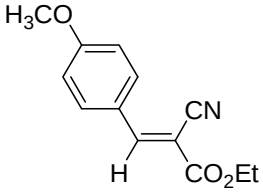
White crystalline solid; **mp**:49-50°C [Lit **mp**: 50-51°C]; **IR** (ν_{max}/cm^{-1}):2924, 2224, 1726, 1604, 1529, 1452, 1367, 1265, 1199, 1093, 1014, 954, 767, 684; **^{1}H NMR** (300 MHz; $CDCl_3$): δ 1.70(t, *J= 7.1,* 3H), 4.67 (q, *J* =7.1 Hz, 2H), 7.84 (t, *J* = 7.3 Hz, 2H), 8.30 (t, *J* = 7.3 Hz, 2H), 8.55 (s, 1H).

***(E)-ethyl -2-cyano-3(4-hydroxyphenyl)acrylate* [3d][1]**



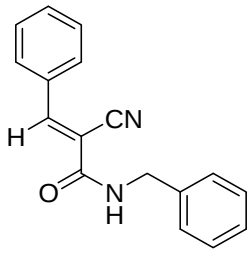
Yellow solid, **mp**: 169-171°C [Lit **mp**: 169-171°C]; **IR** (ν_{max}/cm^{-1}): 3414,2235, 1716, 1579, 1512, 1402, 1271, 1207, 1172, 1055, 910, 819, 734, 648; **^{1}H NMR** (300 MHz; $CDCl_3$):δ 1.40(t, 3H, *J* = 7.1 Hz),2.93 (s, 1H), 4.31(q, *J* = 7.1 Hz, 2H), 6.93(d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 8.30(s, 1H).

***(E)-ethyl -2-cyano-3-(4-methoxyphenyl)acrylate* [3e][1]**

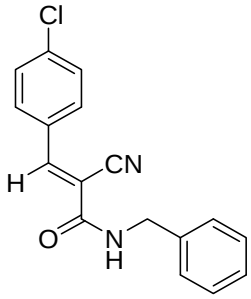


Yellow crystals, **mp**: 79-80°C[Lit **mp**:79-81°C]; **IR** (ν_{max}/cm^{-1}): 2990, 2916, 2215, 1710, 1584, 1561, 1513, 1431, 1262, 1211, 1184, 1127, 1089, 1017, 837; **^{1}H NMR** (300 MHz; $CDCl_3$):δ 1.44 (t, 3H, *J* = 7.1 Hz), 3.92 (s, 3H), 4.38 (q, 2H, *J* = 7.1 Hz), 6.97 (d, 2H, *J* = 9.0 Hz), 8.02 (d, *J* = 9.0 Hz, 2H), 8.20 (s, 1H); **^{13}C NMR** (75 MHz; $CDCl_3$): 14.2, 55.6, 62, 99.36, 114.7, 116.2, 124.37, 133, 154.4, 163.13, 163.79.

***(E)-N-benzyl-2-cyano-3-phenylacrylamide* [3f][5a,5b,8]**

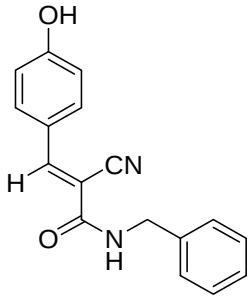


White solid, **mp**:138-139 °C [Lit **mp**: 138-139°C]; **IR** (ν_{max}/cm^{-1}): 3335, 3030, 2947, 2222, 1817, 1660, 1593, 1533, 1444,, 1363, 1271, 1207, 1159, 1078, 1028, 987, 819, 759, 690, 653; **^{1}H NMR** (300 MHz; $CDCl_3$):δ 4.60(s, 2H), 6.63(s, 1H), 6.98(d, *J*= 7.1 Hz, 3H), 7.35 (m, 5H), 7.94 (d, J= 7.1 Hz, 2H, *J* = 7.1 Hz), 8.31 (s, 1H); **^{13}C NMR** (75 MHz; $CDCl_3$):δ 44, 103, 116, 127, 128, 129, 130, 132, 137, 153, 160.



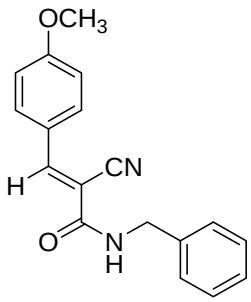
***(E)-N-benzyl-3-(4-chlorophenyl)-2-cyanoacrylamide* [3g][3,5c,8]**

White solid, **mp**: 174-175°C [Lit **mp**: 175-177°C]; **IR** (ν_{max}/cm^{-1}): 3358, 3217, 3026, 2931, 2216, 1896, 1672, 1591, 1527, 1494, 1452, 1419, 1356, 1317, 1274, 1203, 1089, 1018, 972, 831, 784,700, 624; **^{1}H NMR**(300 MHz; $CDCl_3$):δ 4.61 (d, 2H), 6.69 (s, 1H), 7.33 (m, 4H), 7.47 (m, 3H), 7.85(m, 2H), 8.29(s, 1H); **^{13}C NMR** (75 MHz; $CDCl_3$):δ 44.38, 104.65, 117.11, 127.63, 128,60, 129.20, 129.87, 130.46, 130.32, 136.65, 138.50;**HRMS**: 297$[M+H]^+$



***(E)-N-benzyl-2-cyano-3-(4-hydroxyphenyl)acrylamide* [3h][9]**

White solid, **mp**: 228-229°C [Lit **mp**: 227-236°C]; **IR** (ν_{max}/cm^{-1}): 3450, 3180, 3032, 2957, 2212, 1816, 1662, 1590, 1444,, 1362, 1261, 1267, 1158, 1074, 1026, 983, 812, 753, 692, 651; **^{1}H NMR** (300 MHz; $CDCl_3$):δ 3.51(s, 1H), 4.62 (d, 2H), 6.70 (s, 1H), 7.36 (m, 4H), 7.53 (m, 3H), 7.94 (d, 2H), 8.40 (s, 1H);**^{13}CNMR** (75 MHz; $CDCl_3$):δ 44.30, 103.72, 116.88, 127.94, 128.92, 129.27, 130.69, 131.76, 132.87, 137.20, 153.39, 160.19; **HRMS**: 279 $[M+H]^+$

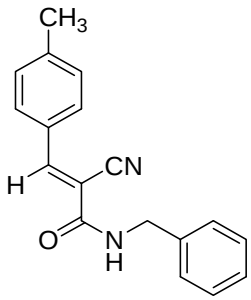


***(E)-N-benzyl-2-cyano-3-(4-methoxyphenyl)acrylamide* [3i][5c,8]**

White solid, **mp**: 144-145°C [Lit **mp**: 144°C]; **IR** (ν_{max}/cm^{-1}): 3335, 3030, 2947, 2222, 1817, 1660, 1593, 1533, 1444,, 1363, 1271, 1207, 1159, 1078, 1028, 987, 819, 759, 690, 653; **^{1}H NMR** (300 MHz; $CDCl_3$):δ 3.89 (s, 3H),4.60 (d, 2H), 6.63 (s, 1H), 6.98 (d, *J* = 6.2 Hz, 2H), 7.35 (m, 4H), 7.94 (d, *J* = 6.2 Hz, 3H), 8.31 (s, 1H); **^{13}C NMR** (75 MHz; $CDCl_3$):δ 44.91, 56.17, 100.02, 114.56, 117.41, 124.86, 127.31, 129.17, 133.15, 137.90, 152.82, 161.18, 163.04.

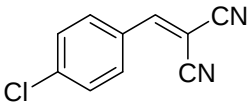
***(E)-N-benzyl-2-cyano-3-p-tolylacrylamide* [3j] [5c,8]**

White solid, **mp**: 110-112°C [Lit **mp**: 110-112°C]; **IR** (ν_{max}/cm^{-1}): 3360, 3020, 2929, 2785, 2590, 2461, 2397, 2324, 2216, 1952, 1901, 1803, 1753, 1678, 1595, 1525, 1425, 1356, 1271, 1197, 1030, 974, 808, 746,



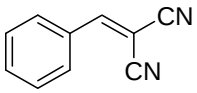
700, 615;**^{1}H NMR** (300 MHz; $CDCl_3$):δ 2.44 (s, *J* = 7.1 Hz, 3H), 4.61 (d, 2H), 6.66 (s, 1H), 7.33 (m, *J*= 6.5 Hz, 5H), 7.84 (d, *J* = 6.5 Hz, 4H), 8.35 (s, 1H);**^{13}C NMR** (75 MHz; $CDCl_3$):δ 21.85, 44.57, 102.40, 117.29, 127.91, 127.93, 128.91, 130.02, 130.87, 137.22, 144.10, 153.33, 160.52; **HRMS**: 277$(M+H)^+$

2-(4-chlorobenzylidene) malononitrile **[3k][4]**



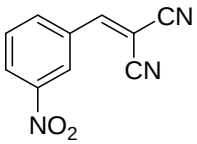
White solid, **mp**: 160-162°C [Lit **mp**: 161-162°C]; **IR** (ν_{max}/cm^{-1}): 3807, 3724, 3317, 3032, 2935, 2584, 2303, 2225, 2075, 1928, 1788, 1585, 1419, 1410, 1290, 1219, 1095, 937, 779, 704, 617; **^{1}H NMR** (300 MHz; $CDCl_3$):δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.74 (s,1H), 7.84 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (75 MHz; $CDCl_3$):δ 83.62, 111.63, 113.25, 129.28, 130.58, 132.17, 140.94, 158.01.

2-benzylidenemalononitrile**[3l][2,4]**



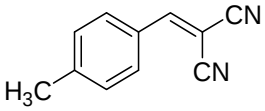
White solid, **mp**: 80-81°C [Lit **mp**: 82-83°C]; **IR** (ν_{max}/cm^{-1}): 3817, 3722, 3307, 2934, 2540, 2302, 2221, 2074, 1922, 1783 1583, 1413 1410, 1288, 1210, 1090, 933, 774, 732, 622; **^{1}H NMR** (300 MHz; $CDCl_3$):δ 7.52(t, *J* = 7.7 Hz, 1H), 7.64 (t, *J*= 7.4 Hz, 2H), 7.79 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 2H).

2-(3-nitrobenzylidene)malononitrile **[3m][7]**



White solid, **mp**:100-102°C [Lit **mp**: 99-100°C]; **IR** (ν_{max}/cm^{-1}): 3088, 3045, 2949, 2866, 2742, 2636, 2571, 2461, 2301, 2229, 2000, 1942, 1892, 1795, 1763, 1602, 1425, 1344, 1313, 1217, 1153, 1105, 1035, 999, 943, 823, 736, 690, 671, 623; **^{1}H NMR** (300 MHz; $CDCl_3$):δ 7.81 (t, 2H), 7.91 (s, 1H), 8.32 (d, 2H), 8.47(m, 2H), 8.64(t, 2H).

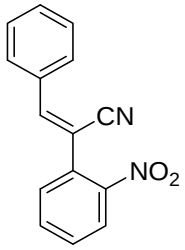
2-(4-methylbenzylidene)malononitrile **[3n][2]**



White solid, **mp**: 134-136°C [Lit **mp**: 133-134°C]; **IR** (ν_{max}/cm^{-1}): 3827, 3712, 3300, 2928, 2530, 2302, 2201, 2064, 1922, 1783 1583, 1418 1425, 1290, 1210, 1098, 933, 778, 732, 628; **^{1}H NMR** (300 MHz; $CDCl_3$):δ

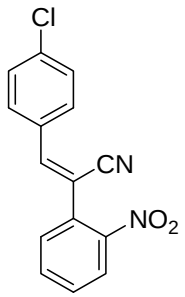
2.46 (s, 3H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.72 (s, 1H), 7.80(d, *J* = 8.0 Hz, 2H).

***(Z)-2-(2-nitrophenyl)-3-phenylacrylonitrile* [3o][13]**



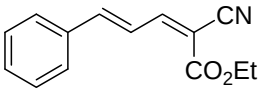
White solid, **mp**: 101-105°C [Lit **mp**: 99-101°C]; **IR** (ν_{max}/cm^{-1}): 3098, 2936, 2845, 2506, 2401, 2204, 1930, 1900, 1802, 1502, 1511, 1332, 1204, 1087, 1028, 901, 840, 810, 742, 630; **^{1}H NMR** (300 MHz; $CDCl_3$): δ 7.51(t, 2H), 7.69 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.95 (s, *J* = 7.9 Hz, 2H), 8.31(t, *J* = 7.9 Hz, 2H).

***(Z)-3-(4-chlorophenyl)-2-(2-nitrophenyl)acrylonitrile* [3p][11]**



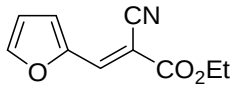
White solid, **mp**: 140-142°C [Lit **mp**: 140-142°C]; **IR** (ν_{max}/cm^{-1}): 3099, 2926, 2835, 2596, 2441, 2214, 1940, 1911, 1817, 1519, 1510, 1342, 1203, 1097, 1008, 910,858, 828, 750, 669; **^{1}H NMR** (300 MHz; $CDCl_3$): δ 7.51 (d, *J* = 6.8 Hz, 2H),7.63 (s, 1H), 7.87 (m, 4H), 8.31(d, *J* =6. 8 Hz, 2H); **^{13}C NMR** (75 MHz; $CDCl_3$): δ 110.08, 116.94, 124.44, 126.80, 129.57, 130.93, 131.30, 137.80, 140.24, 143.95, 148.03.

***(2Z,4E)-ethyl 2-cyano-5-phenylpenta-2,4-dienoate* [3q][6,10]**



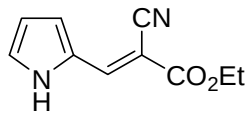
Brown solid, **mp**: 115-116°C [Lit **mp**: 115°C]; **IR** (ν_{max}/cm^{-1}): 3090, 2985, 2251, 1730,1640, 1221, 1023, 961, 857, 749, 669;**^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.38 (t, *J*=7.1 Hz, 3H), 4.34 (q, *J*= 7.1 Hz, 2H), 7.28 (m, 3H), 7.43 (m, 2H), 7.59 (m, 2H), 8.0(d, *J* =10.8 Hz, 1H);**^{13}C NMR** (75 MHz; $CDCl_3$):δ 13.88, 62.06, 104.36, 114.95, 123.06, 128.46, 129.07, 131.35, 134.20, 148.85, 155.01, 162.16; **MS(m/z)**: 227[M^+]

***(E)-ethyl 2-cyano-3-(furan-2-yl)acrylate* [3r][1]**



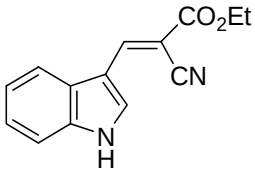
Colorless solid, **mp**: 90-91°C [Lit **mp**: 89-91°C]; **IR** (ν_{max}/cm^{-1}):3030, 2215, 1760, 1618, 1530, 1460, 1380, 1215, 1091, 756; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.38 (t, *J* = 7.1 Hz, 3H), 4.35 (q, *J* =7.1 Hz, 2H), 6.65 (dd, *J*=1.9, 4.0 Hz, 1H), 7.40 (d, *J*=4.0 Hz, 1 H), 7.75 (d, *J*=1.9 Hz, 1H), 8.0 (s, 1H);**^{13}C NMR** (75 MHz, $CDCl_3$): δ 13.9, 62.3,98.3, 113.7, 115.1, 121.6, 139.2, 148.1, 148.5, 162.3.

***(E)-ethyl 2-cyano-3-(1H-pyrrol-2-yl)acrylate* [3s][1]**



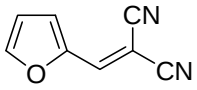
Light gray solid, **mp**:135-136°C [Lit **mp**: 135-137°C]; **IR** (ν_{max}/cm^{-1}): 3307, 2206, 1695, 1585, 1427, 1355, 1281, 1217, 1142, 1047, 750. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.39 (t, *J* =7.0 Hz, 3H), 4.39 (q, *J* =7.0 Hz, 2H),6.40 (dd, *J* =3.2, 2.0 Hz, 1H), 6.90 (d, *J* =2.0 Hz, 1H), 7.25 (d, *J* =3.2 Hz, 1H), 8.0 (s, 1H), 10.05 (br. s, 1H, NH). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 14.1, 61.9, 91.5, 112.4, 118.2, 123.9, 126.6, 128.4, 142.6, 163.5.

***(E)-ethyl -2-cyano-3-(1H-indol-3-yl)acrylate* [3t][1]**



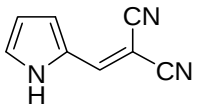
Yellow solid, **mp**: 160-161°C [Lit **mp**: 161-162°C]; **IR** (ν_{max}/cm^{-1}):3325, 2212, 1697, 1565, 1505, 1363, 1263, 1136, 1012, 880, 746;**^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.40 (t, *J* =7.0 Hz, 3H), 4.40 (q, *J*= 7.0 Hz, 2H),7.20-7.38 (m, 2H), 7.40-7.50 (m, 1 H), 7.78-7.85 (m, 1H), 8.60 (s, 1 H), 8.65 (s, 1H), 9.45 (br. s, 1H, NH);**^{13}C NMR** (75MHz, $CDCl_3$): δ 14.2, 29.6, 62.0, 94.3, 111.0, 112.3, 118.2, 122.5, 124.1, 127.3, 130.8, 135.6, 146.6, 163.8.

***2-((furan-2-yl)methylene)malononitrile*[3u][1]**

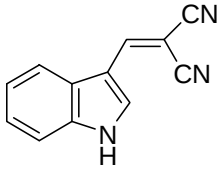


Pale-yellow solid, **mp**: 67-69°C [Lit **mp**: 67-68°C]; **IR** (ν_{max}/cm^{-1}): 3415, 3043, 2224, 1609, 1523, 1451, 1391, 1294, 1149, 1019, 935, 767, 584; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 6.75 (dd, *J*= 3.9, 1.8 Hz, 1H), 7.40 (d, *J* = 3.9 Hz,1 H), 7.55 (d, *J* =1.8 Hz, 1 H), 7.8 (s,1 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ149.5, 147.9, 143.0, 123.5, 114.3, 113.7, 112.5, 77.2.

***2-((1H-pyrrol-2-yl)methylene)malononitrile* [3v][1]**

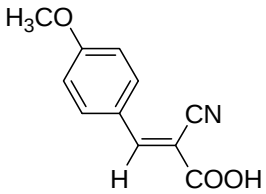


Light gray solid, **mp**:120-121°C [Lit **mp**: 120-122°C]; **IR** (ν_{max}/cm^{-1}): 3368, 1589, 1511, 1393, 1322, 1123, 1045, 927, 868, 769, 700, 583;**^{1}H NMR** (300 MHz, $CDCl_3$): δ 6.40 (dd, *J*= 2.5, 3.4 Hz, 1 H), 7.20 (d, *J*= 2.5 Hz,1H), 7.40 (d, *J*= 3.4 Hz, 1H), 7.65 (s, 1 H), 11.5 (br. s, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 69.5, 113.2, 114.5, 115.5, 125.2, 126.6, 130.2, 145.9.



***2-((1H-indol-3-yl)methylene)malononitrile*[3w][1]**

Brown solid, **mp**: 221-222°C [Lit **mp**: 221-223°C]; **IR** (ν_{max}/cm^{-1}):3270, 2915, 2215, 1566, 1499, 1336, 1225, 1139, 825, 789; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.20-7.30 (m, 2H), 7.40-7.50 (m, 1H), 7.50-7.78 (m, 1H), 8.10-8.20 (s, 1H), 8.45 (s, 1H), 12.30 (br. s, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 69.5, 110.2, 112.1, 114.9, 117.2, 121.9, 123.2, 126.0, 131.8, 135.4, 150.2.

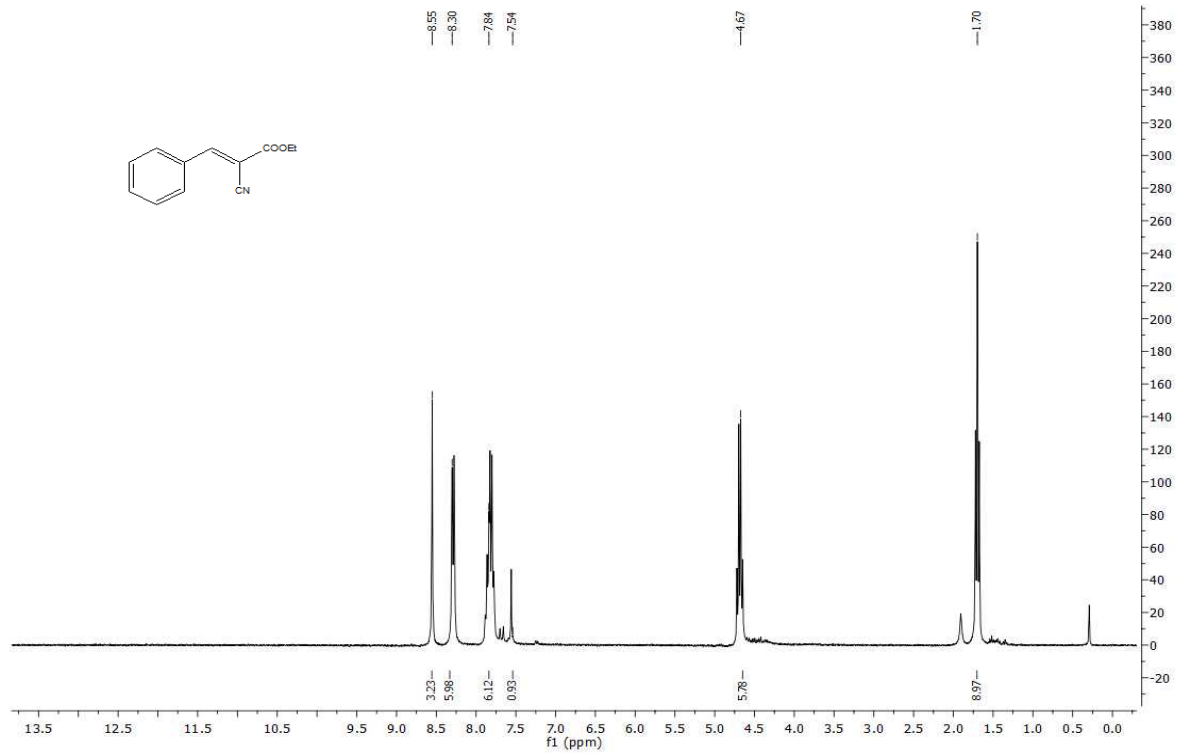


***(E)-2-cyano-3-(4-methoxyphenyl)acrylic acid* [3x][12]**

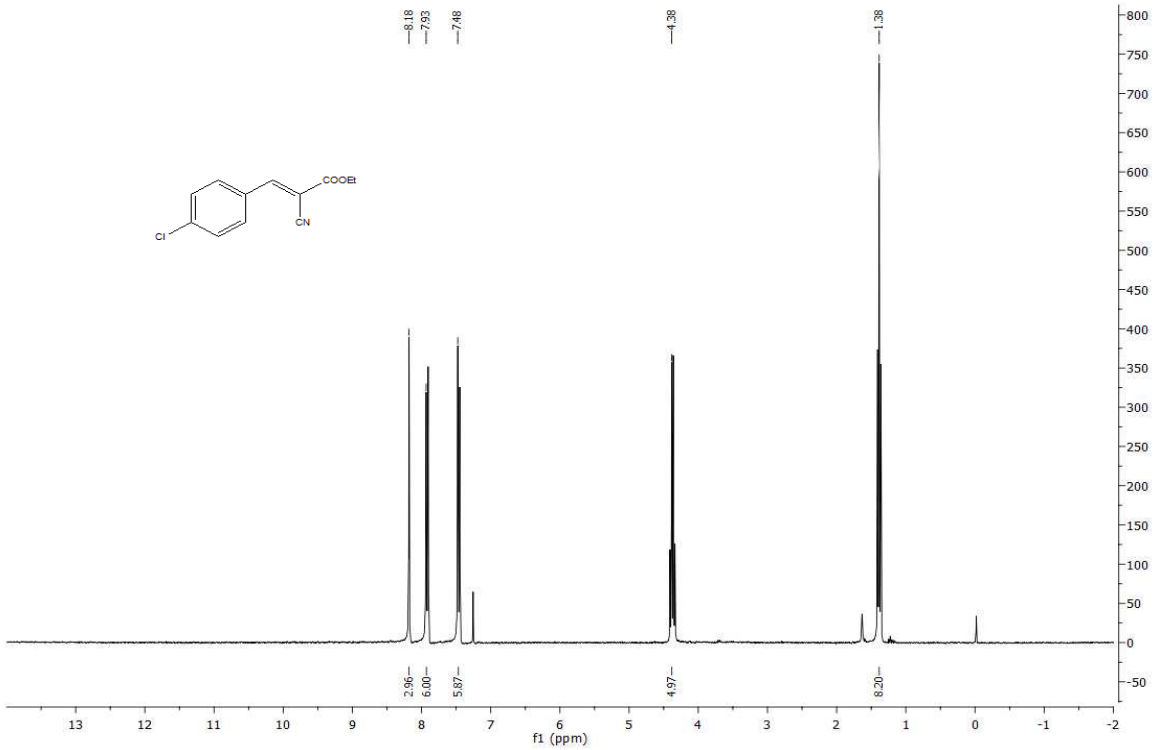
Yellow crystals, **mp**: 228-230°C [Lit **mp**: 228°C];**IR** (ν_{max}/cm^{-1}): 2824, 2550, 2230, 1697, 1602, 1587, 1492, 1430, 1290, 1213, 1094, 921, 833; **^{1}H NMR** (300 MHz; DMSO-*d6*): δ 3.85 (s, 3H), 7.11(d, 2H, *J* = 9 Hz), 8.03 (d, 2H, *J* = 9 Hz), 8.23 (s, 1H); **^{13}C NMR** (75MHz; DMSO-d_6): δ 53, 104, 119, 121, 128, 137, 158, 167, 168.

Analytical data:

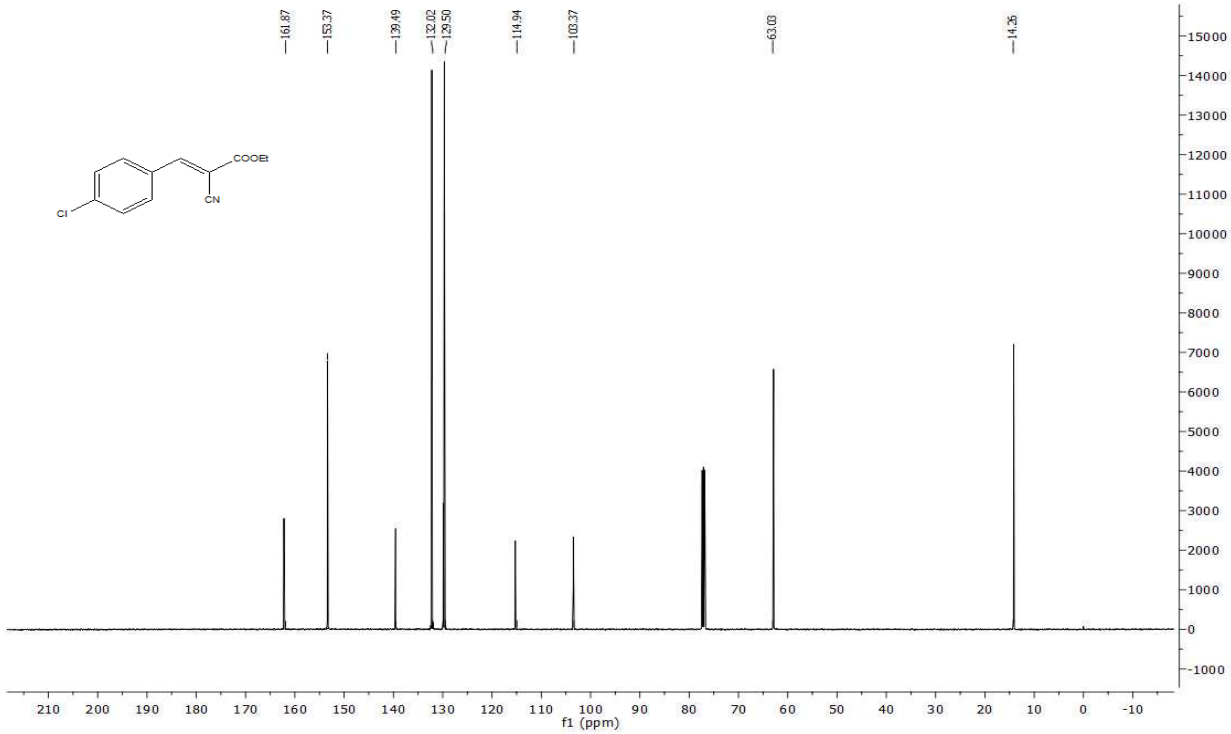
^{1}H-
NMR



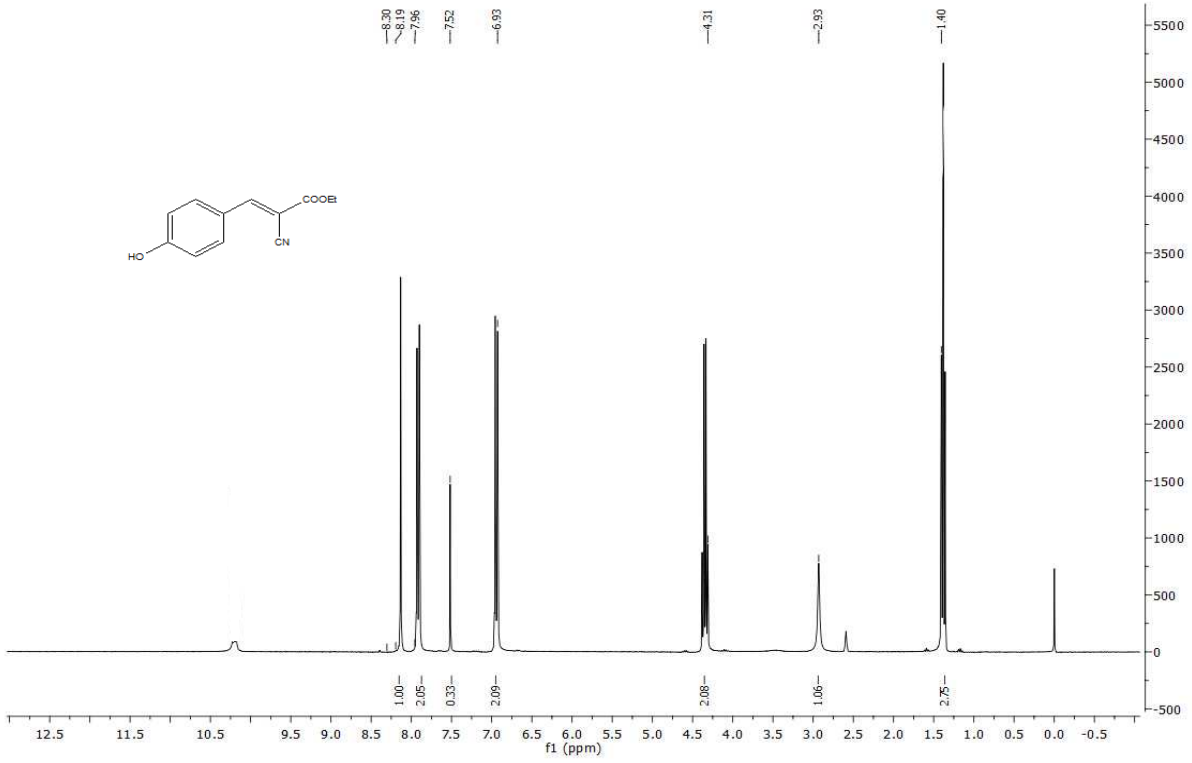
^{1}H
NMR



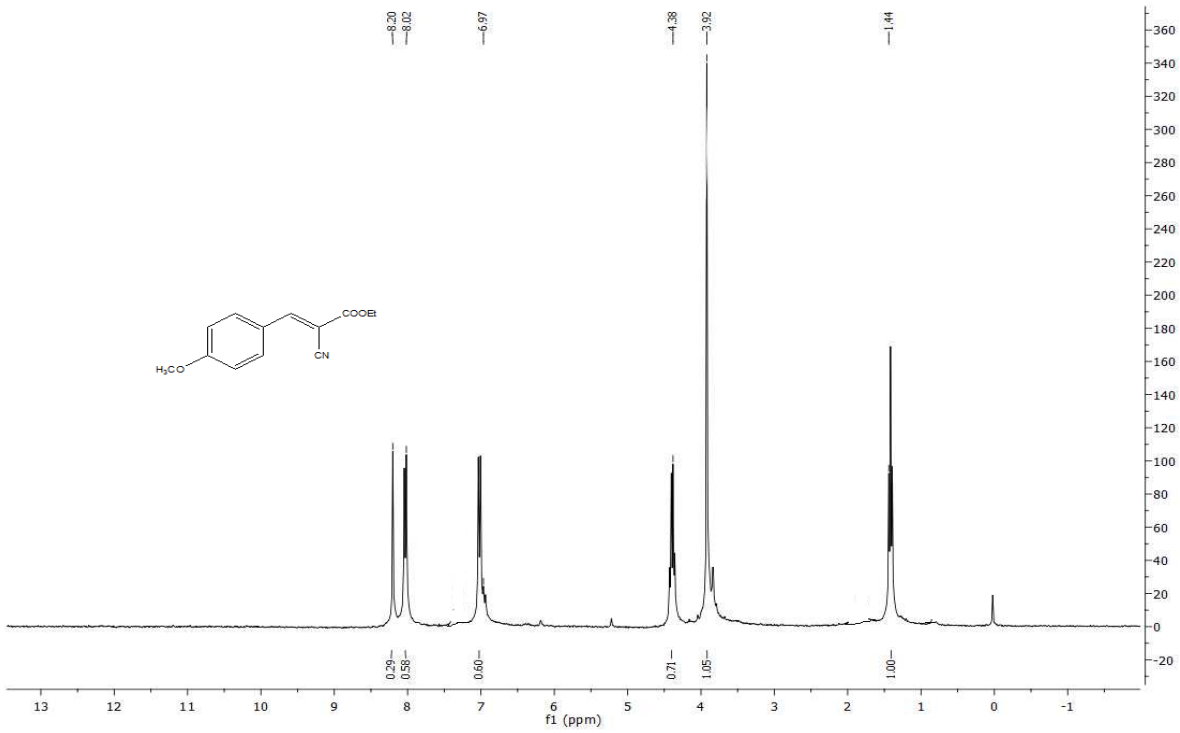
^{13}CNMR



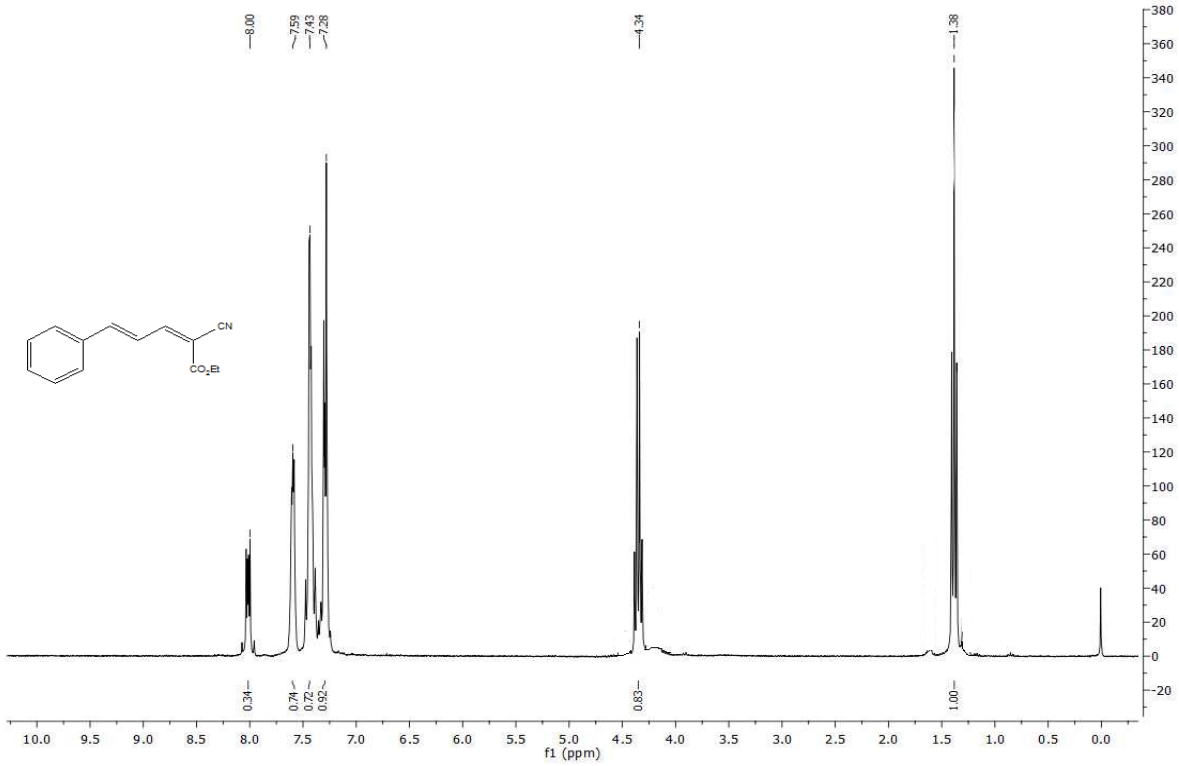
^{1}H-
NMR


8.30
8.19
7.96
7.52
6.93
4.31
2.93
1.40
COOEt
CN
HO
1.00
2.05
0.33
2.09
2.08
1.06
2.75
f1 (ppm)

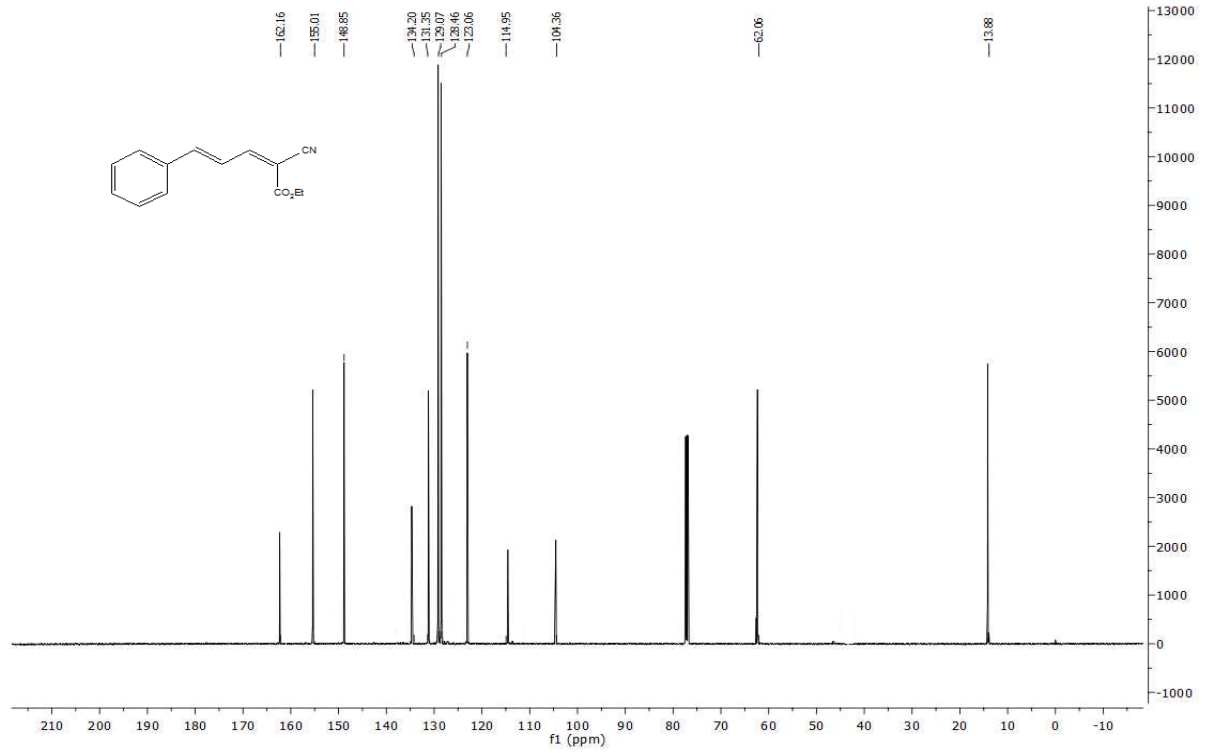
^{1}H-
NMR


8.20
8.02
6.97
4.38
3.92
1.44
COOEt
CN
H3CO
0.29
0.58
0.60
0.71
1.05
1.00
f1 (ppm)

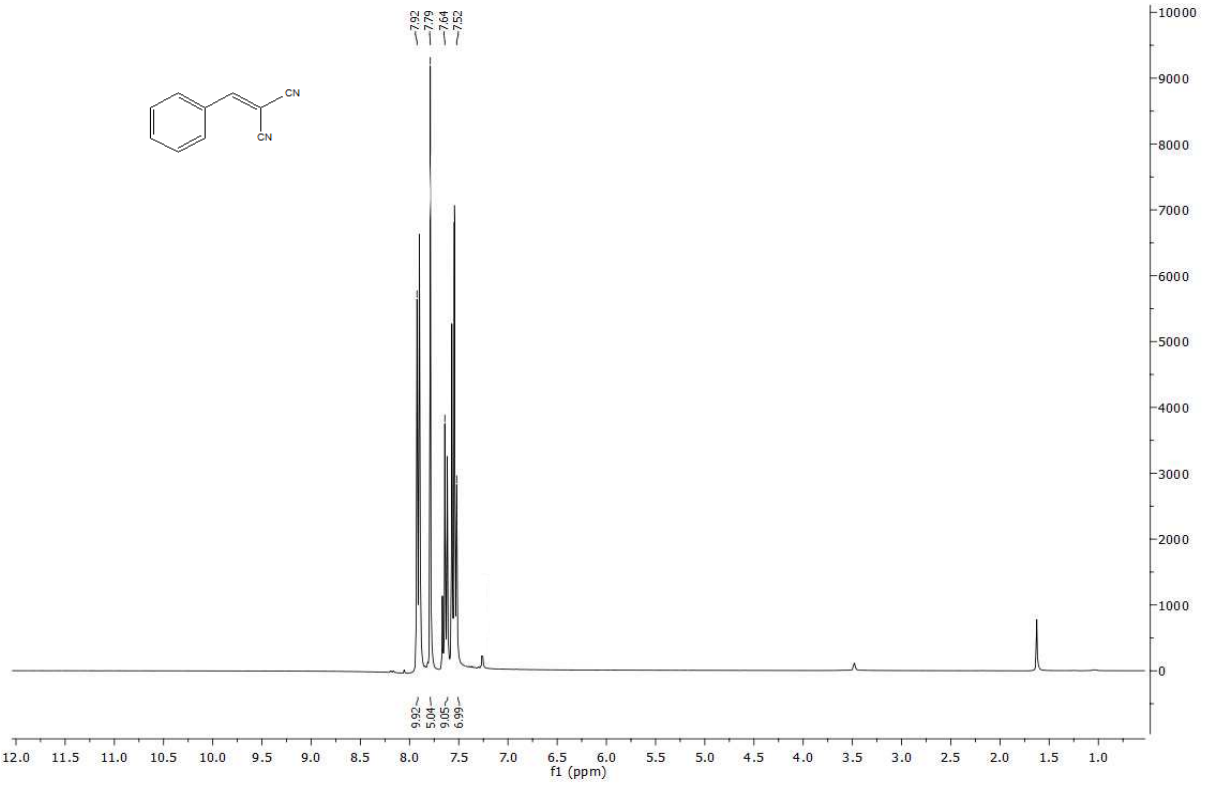
^{1}H-
NMR



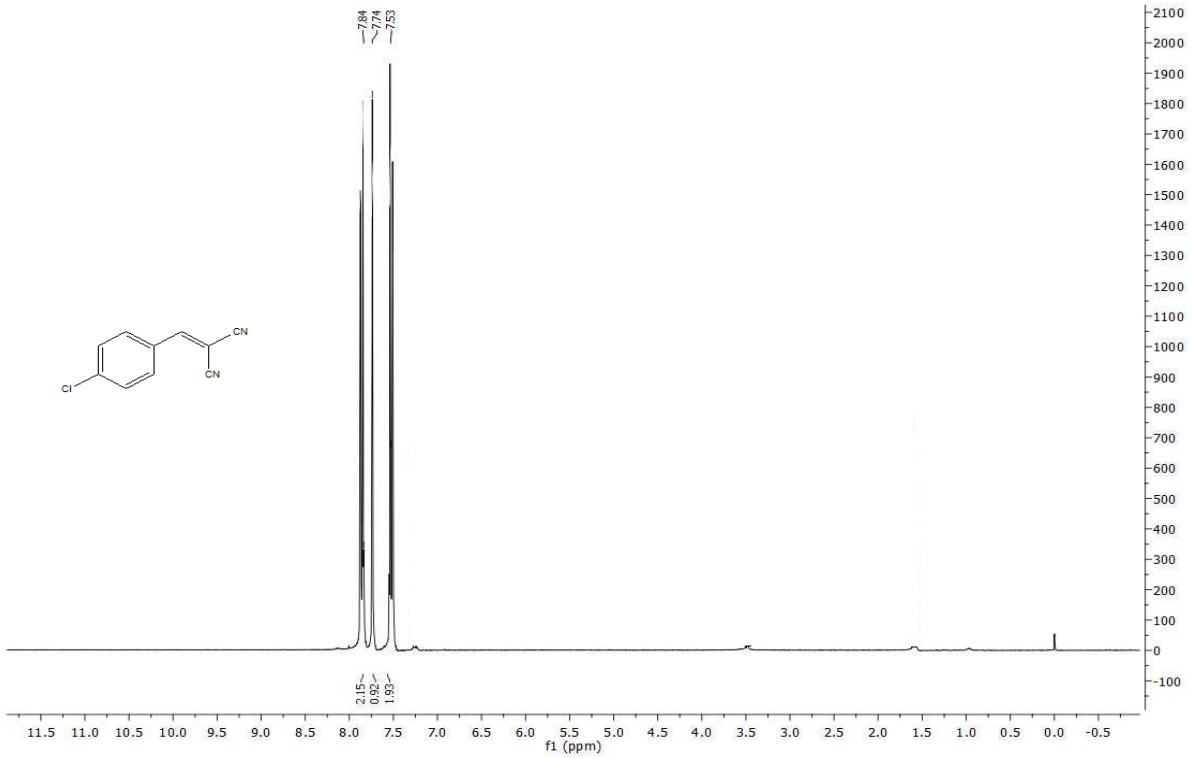
^{13}C-
NMR


162.16
155.01
148.85
134.20
131.35
129.07
128.46
123.06
114.95
104.36
62.06
13.88
CN
CO2Et
f1 (ppm)

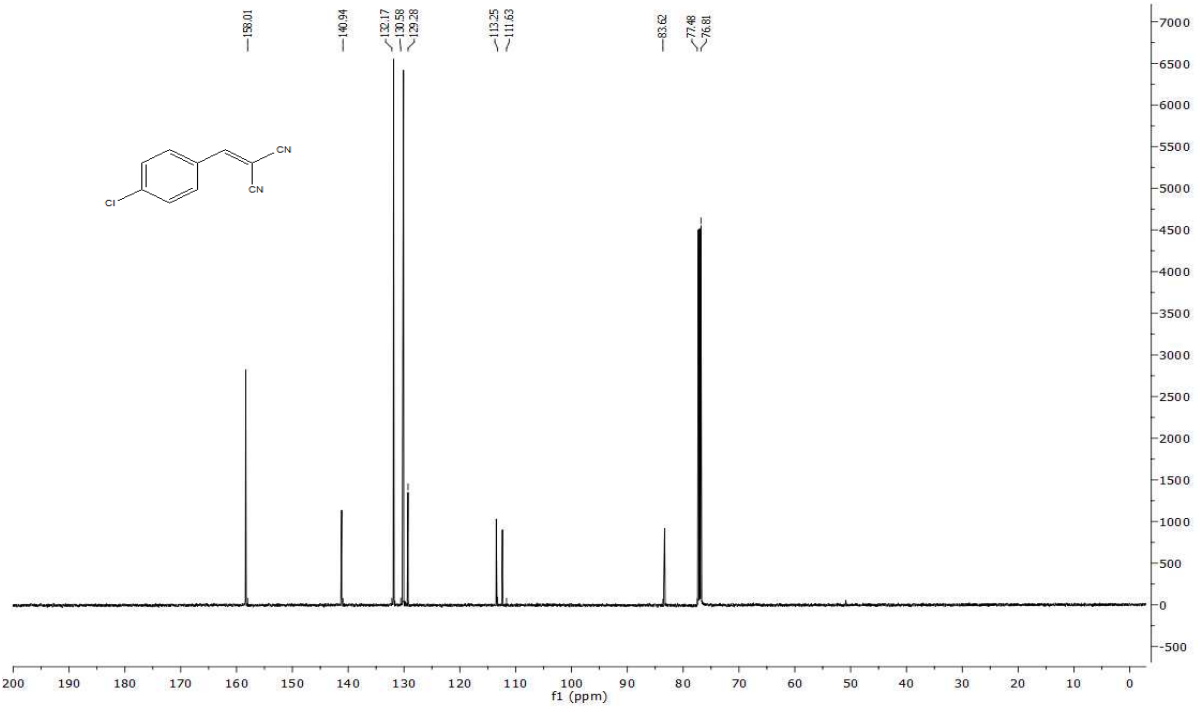
^{1}H-
NMR


7.92
7.79
7.64
7.52
CN
CN
9.92
5.04
9.05
6.99
f1 (ppm)

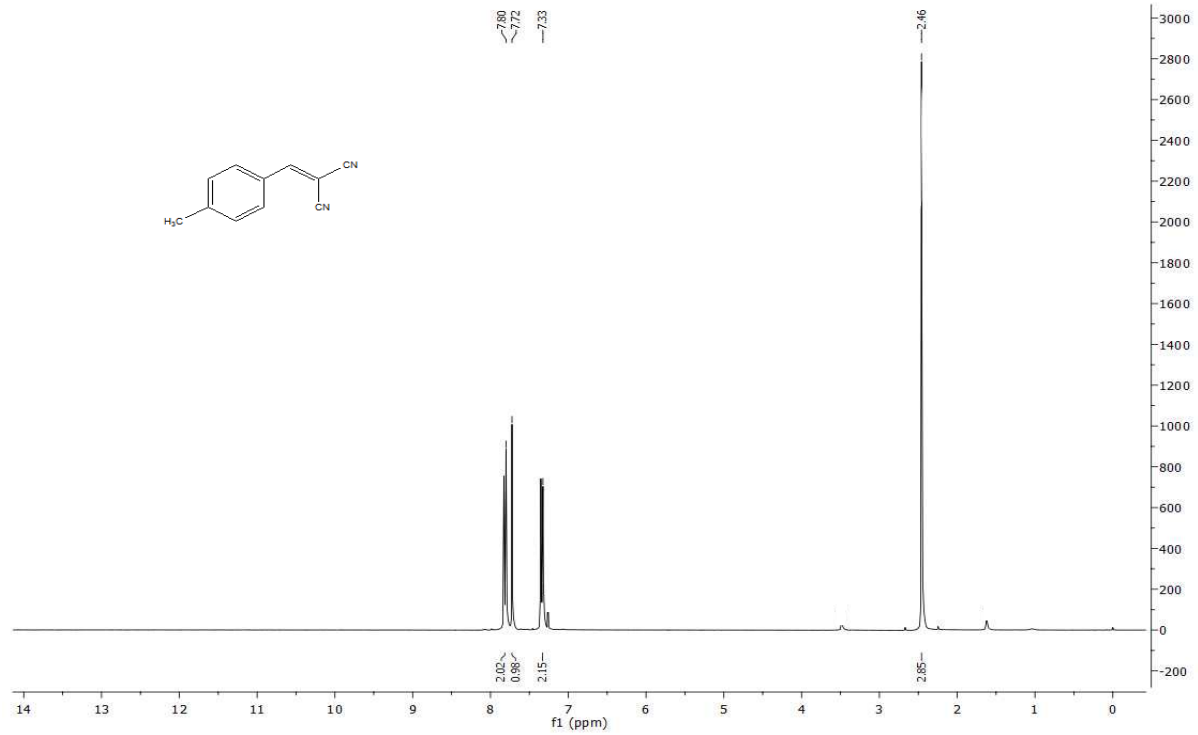
^{1}H-
NMR



^{13}C-
NMR

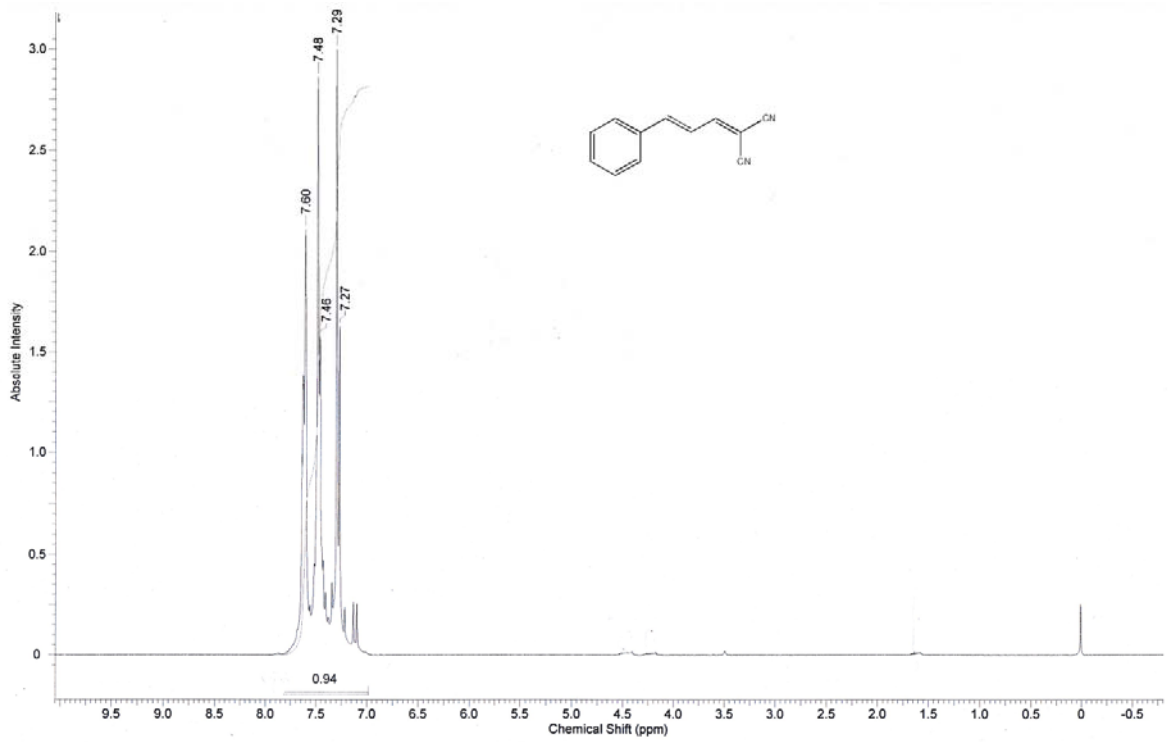


^{1}H-
NMR

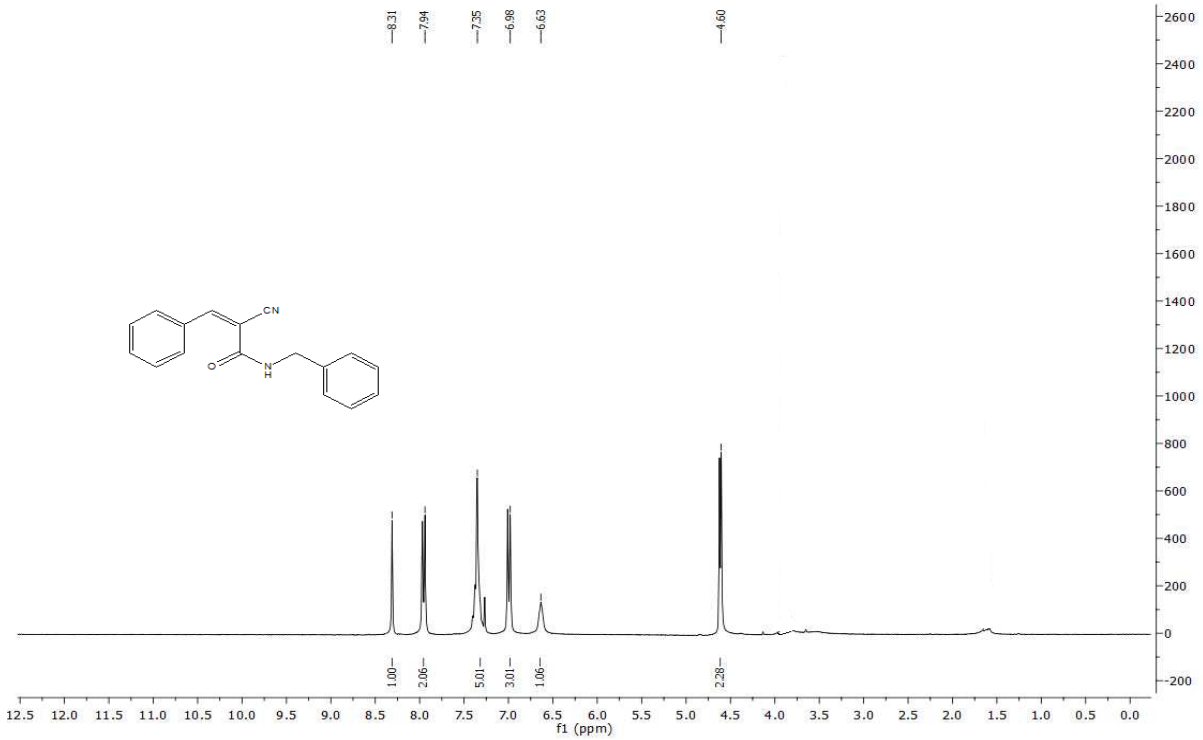


^{1}H-

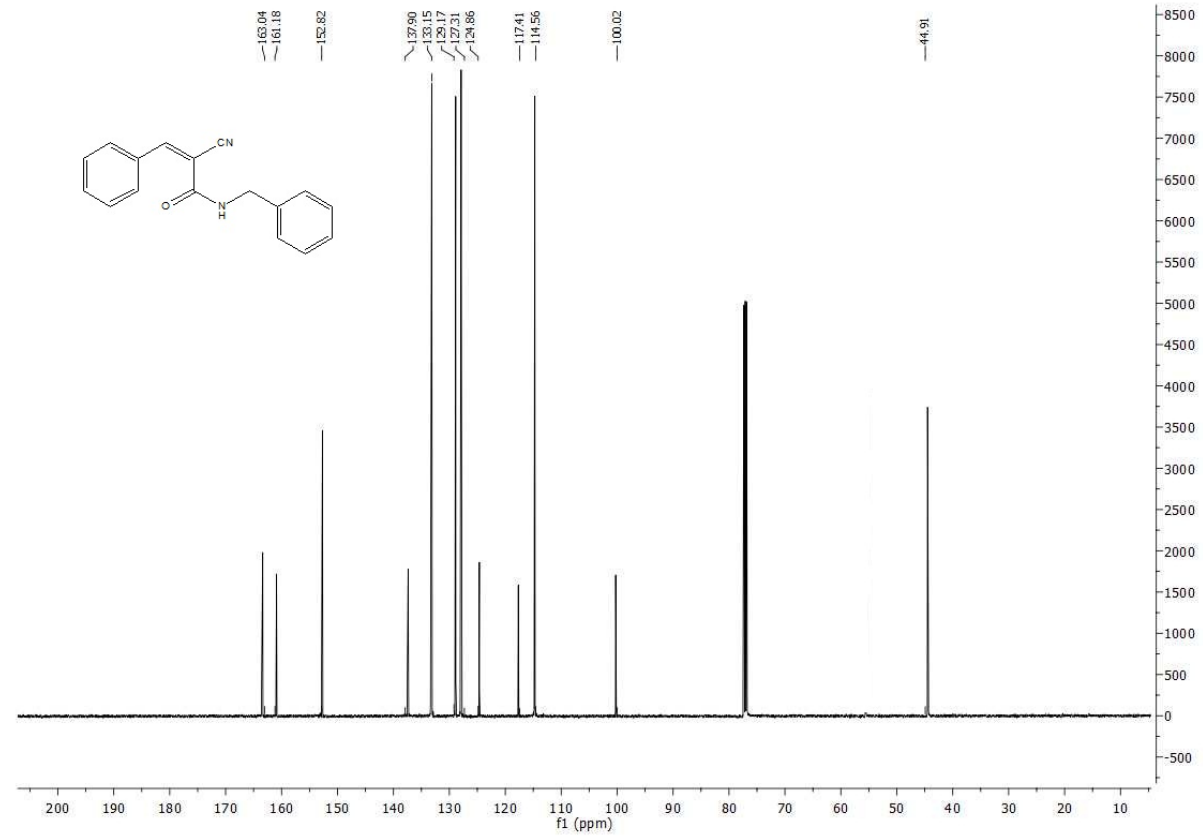
NMR


7.60
7.48
7.46
7.29
7.27
0.94
Absolute Intensity
Chemical Shift (ppm)
CN
CN

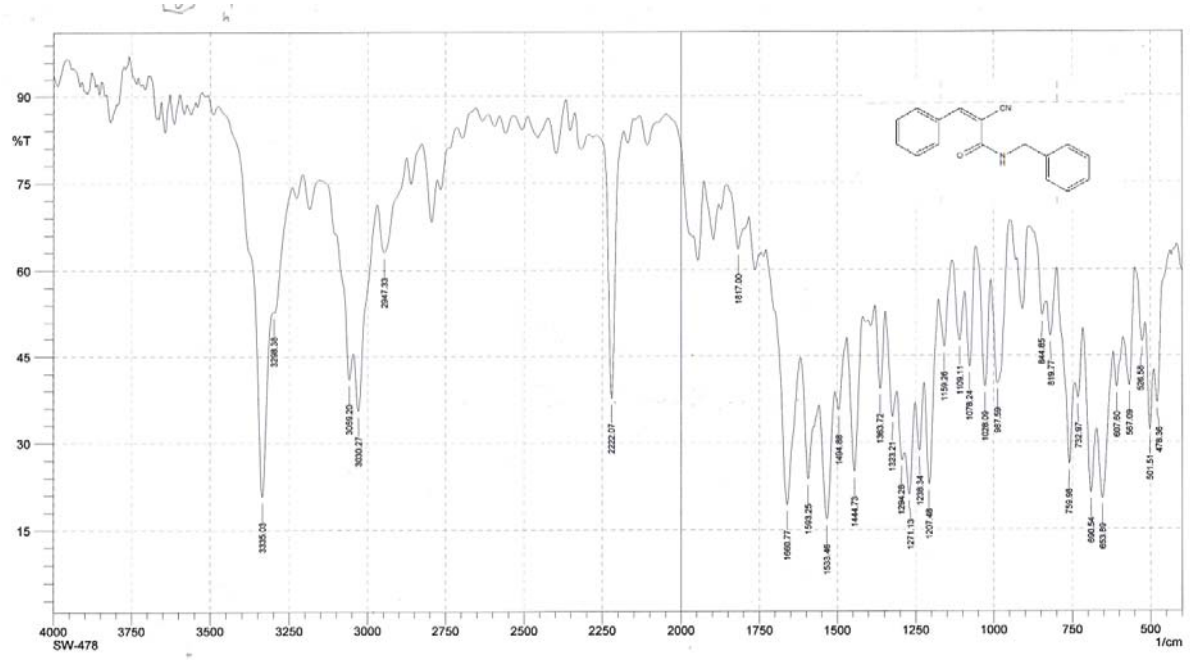
^{1}H-
NMR


8.31
7.94
7.35
6.98
6.63
4.60
CN
O
N
H
1.00
2.06
5.01
3.01
1.06
2.28
f1 (ppm)

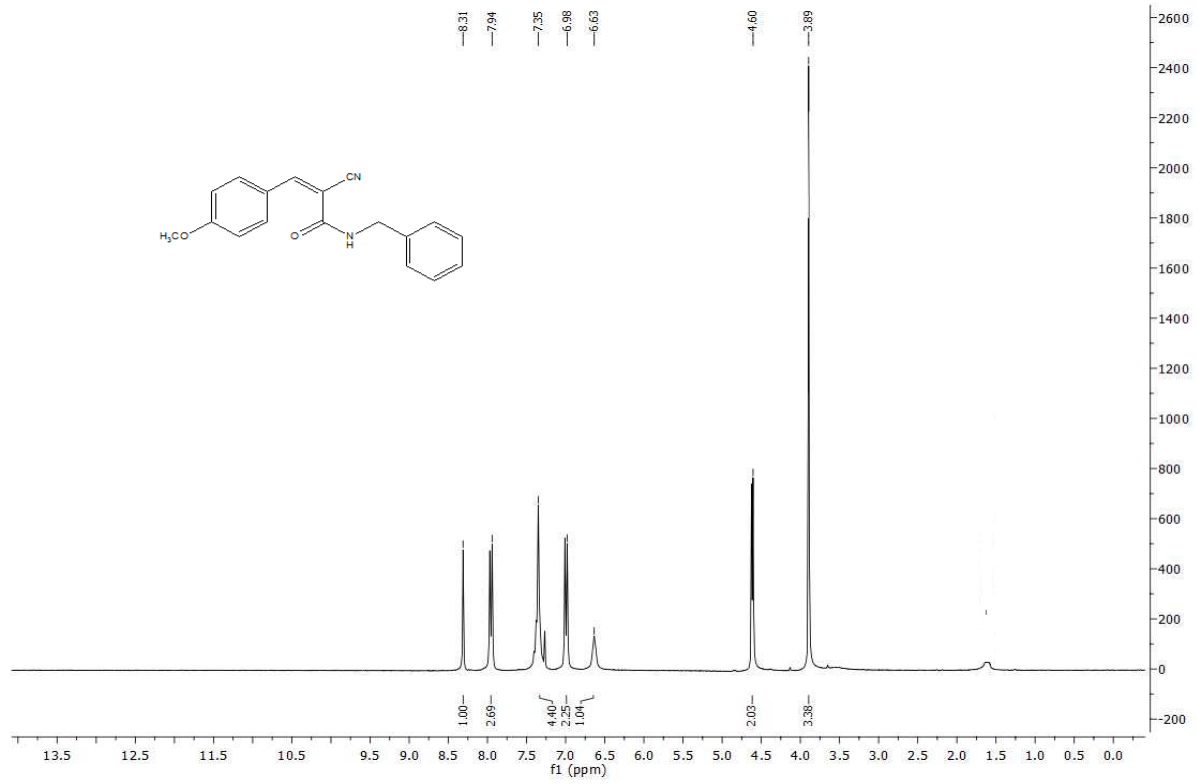
^{13}C-NMR


163.04
161.18
152.82
137.90
133.15
129.17
127.31
124.86
117.41
114.56
100.02
44.91
CN
O
N
H
f1 (ppm)

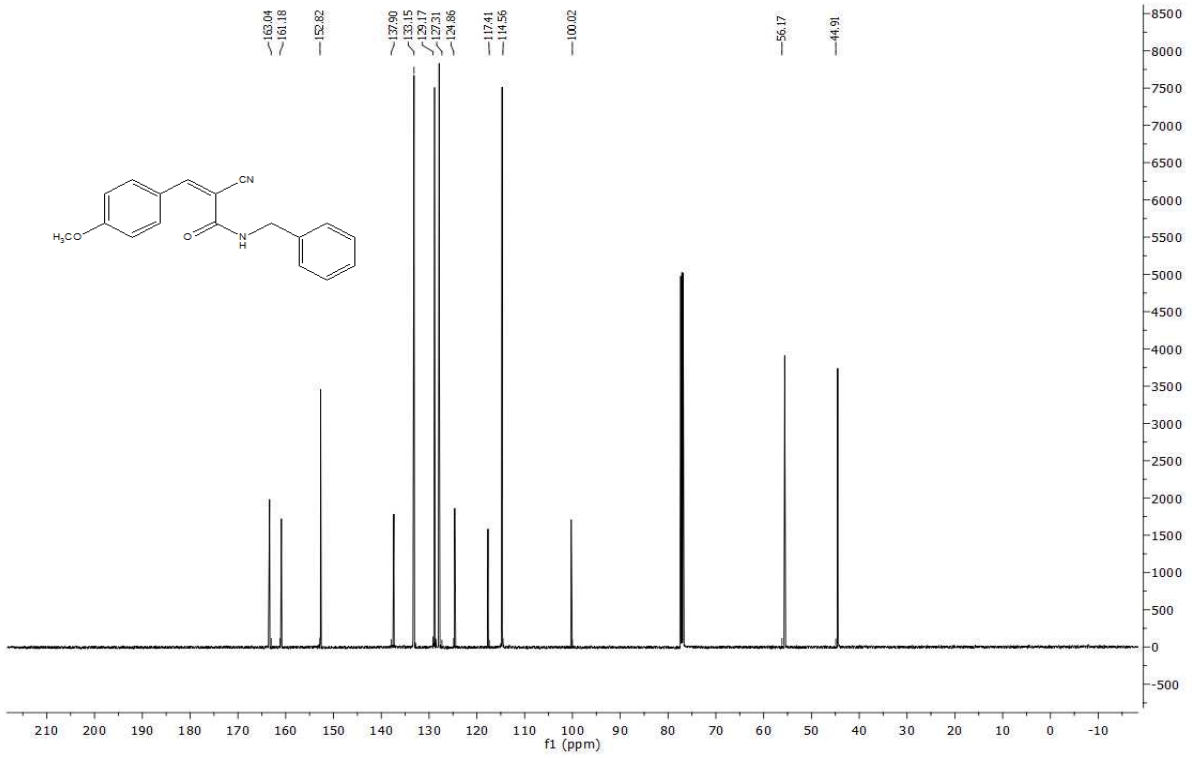
IR


%T
90
75
60
45
30
15
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
1/cm
SW-478
3336.03
3258.38
3059.20
3030.27
2947.33
2222.07
1617.00
1580.77
1569.25
1533.46
1494.88
1444.73
1383.72
1333.21
1294.29
1271.13
1236.34
1207.48
1159.26
1109.11
1078.24
1026.09
957.59
844.65
819.77
755.68
732.97
690.54
653.99
607.60
567.08
526.56
501.51
478.36

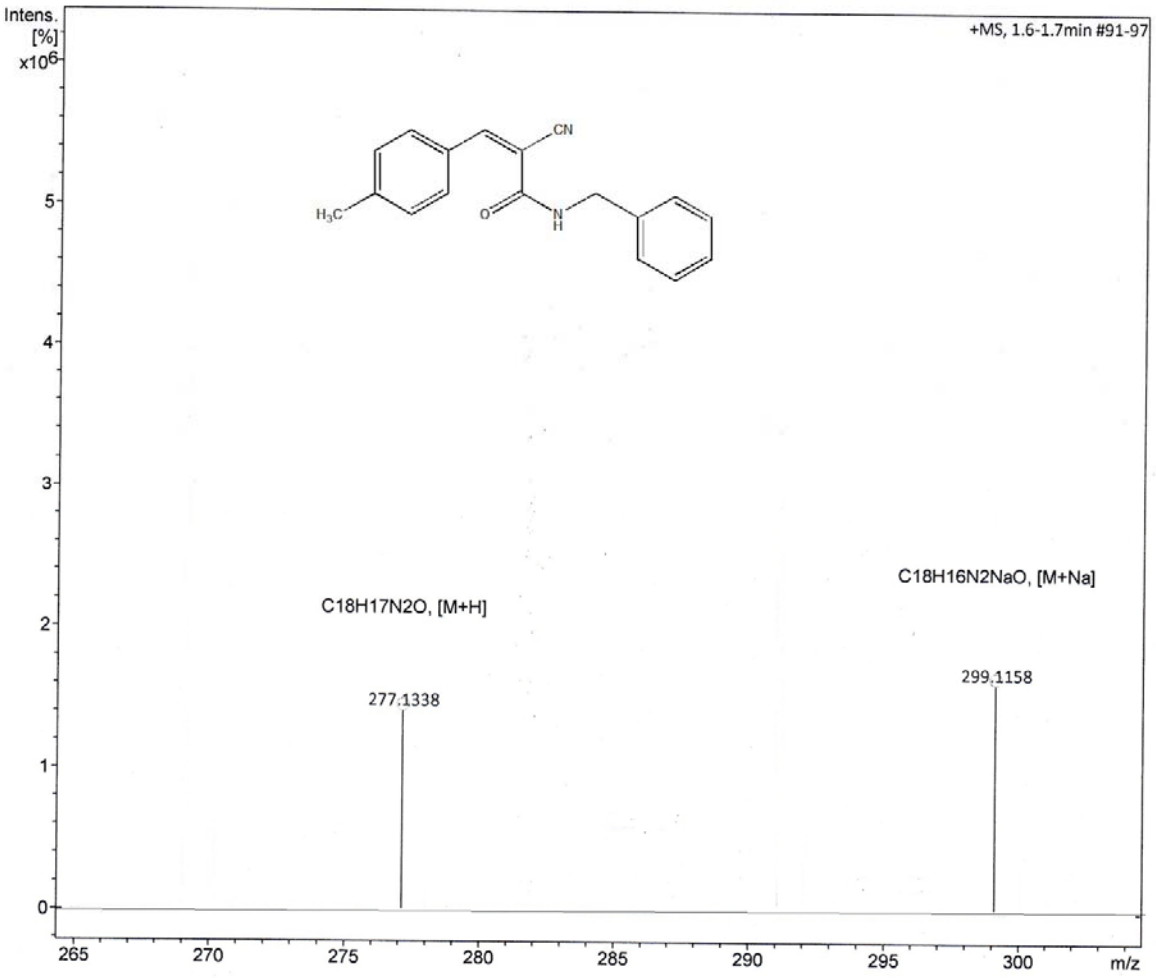
^{1}H-
NMR


8.31
7.94
7.35
6.98
6.63
4.60
3.89
CN
H3CO
O
N
H
1.00
2.69
4.40
2.25
1.04
2.03
3.38
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
13.5
12.5
11.5
10.5
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
0.5
0.0
f1 (ppm)

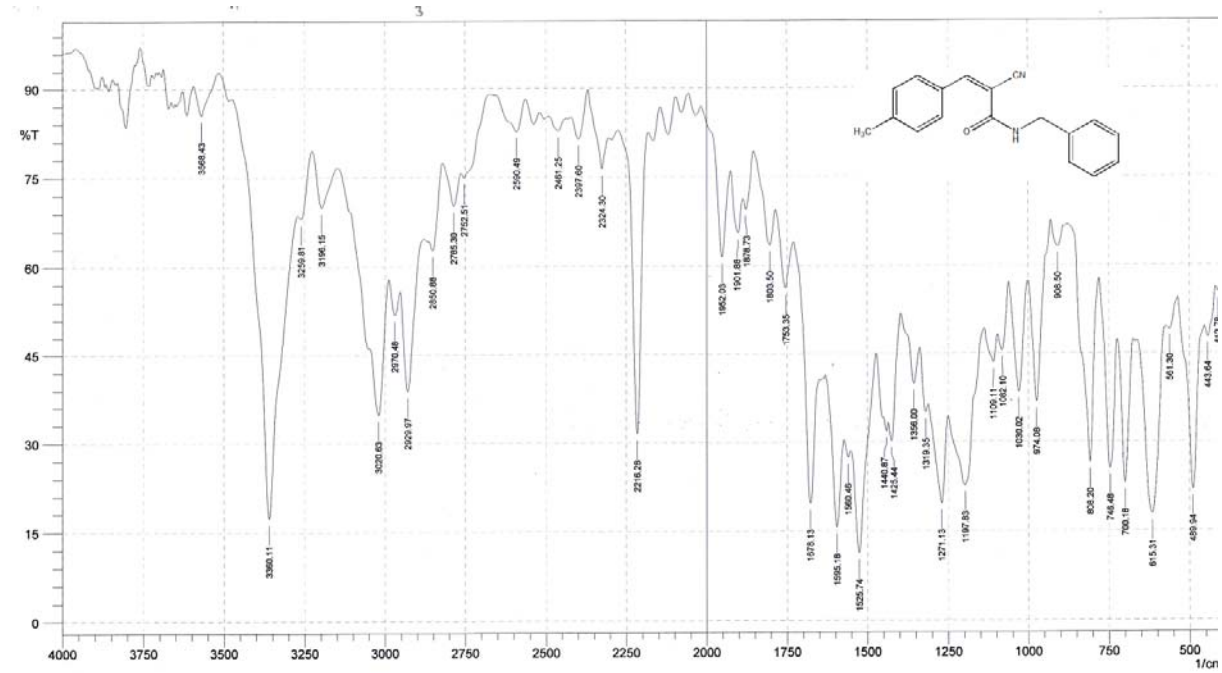
^{13}CNMR


163.04
161.18
152.82
137.90
133.15
129.17
127.31
124.86
117.41
114.56
100.02
56.17
44.91
CN
H3CO
O
N
H
f1 (ppm)

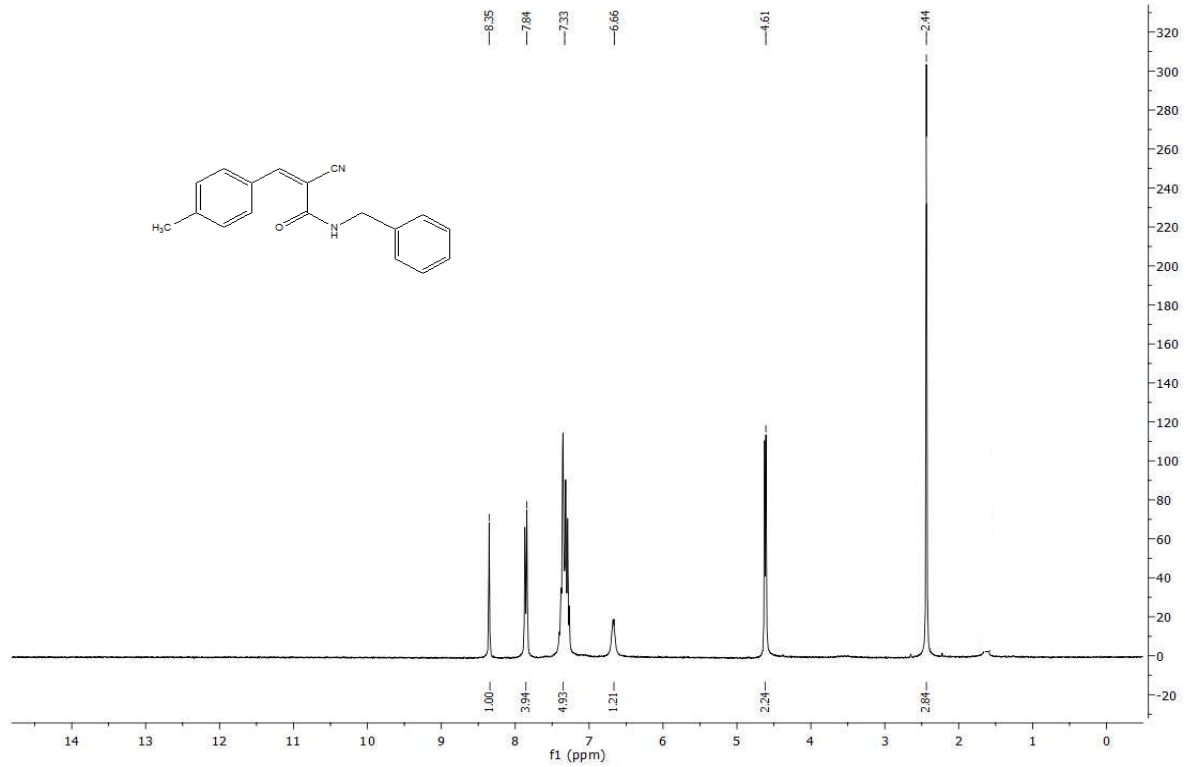
MASS


Intens.
[%]
x10^6
+MS, 1.6-1.7min #91-97
CN
H3C
O
N
H
C18H17N2O, [M+H]
277.1338
C18H16N2NaO, [M+Na]
299.1158
0
1
2
3
4
5
265
270
275
280
285
290
295
300
m/z

IR

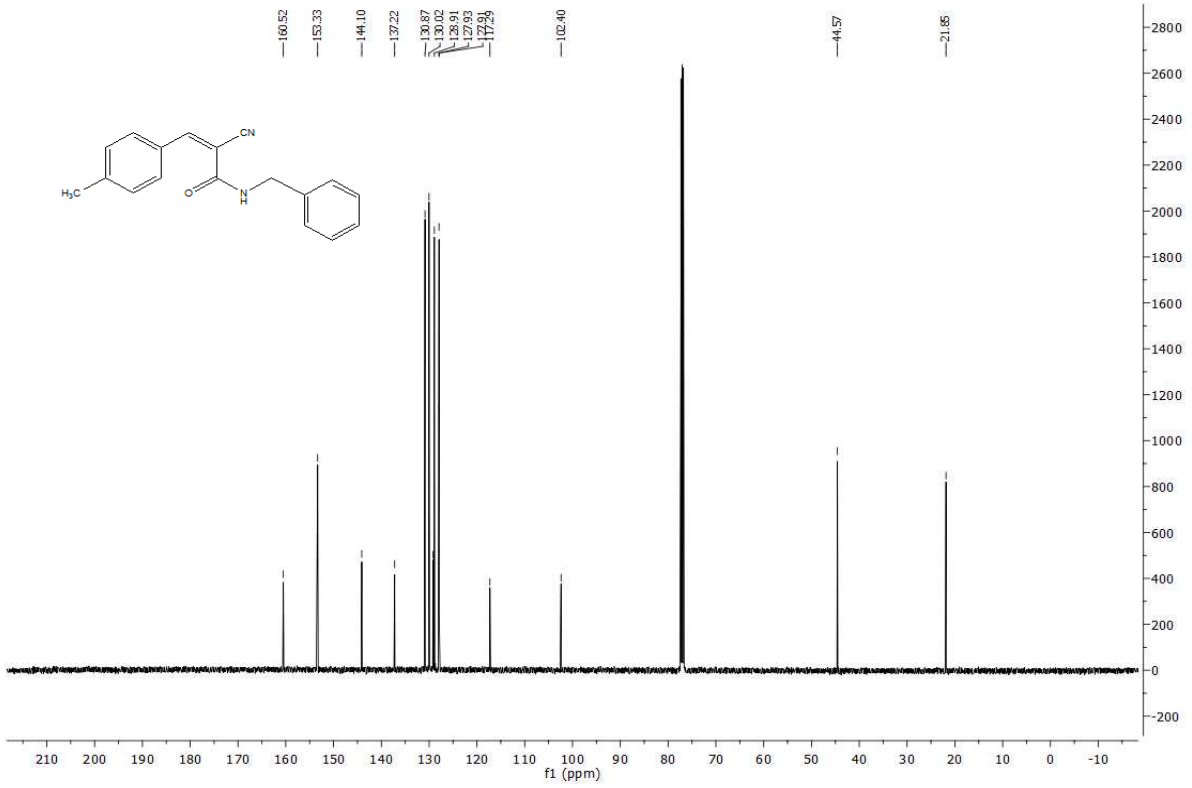


^{1}H-NMR

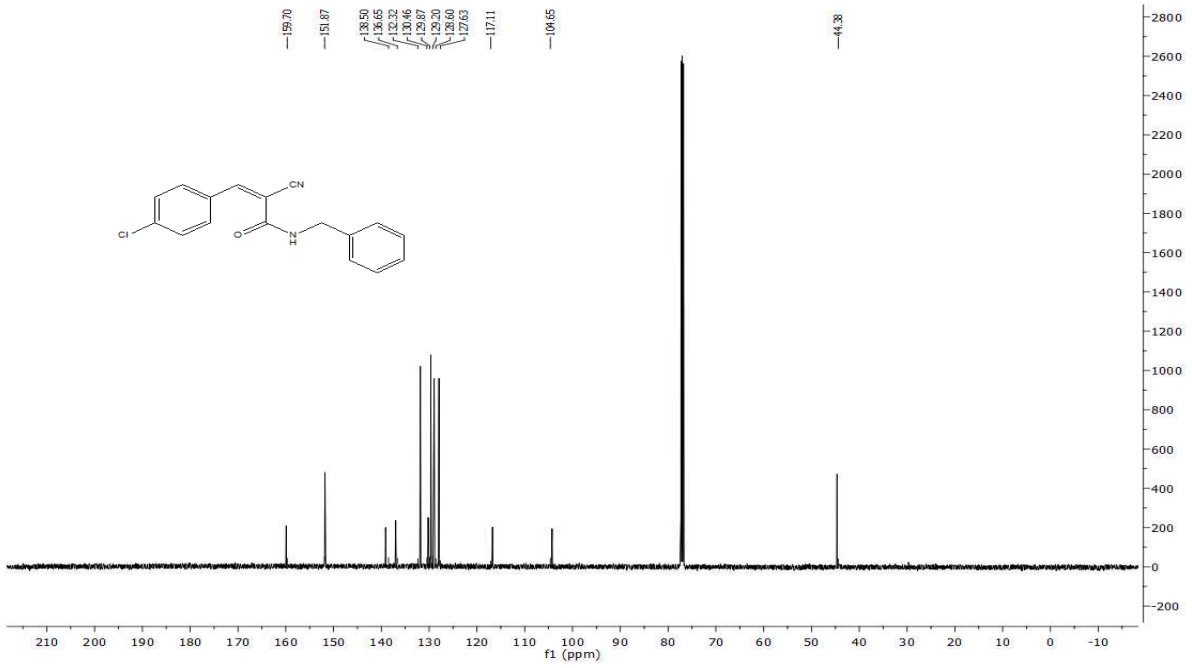


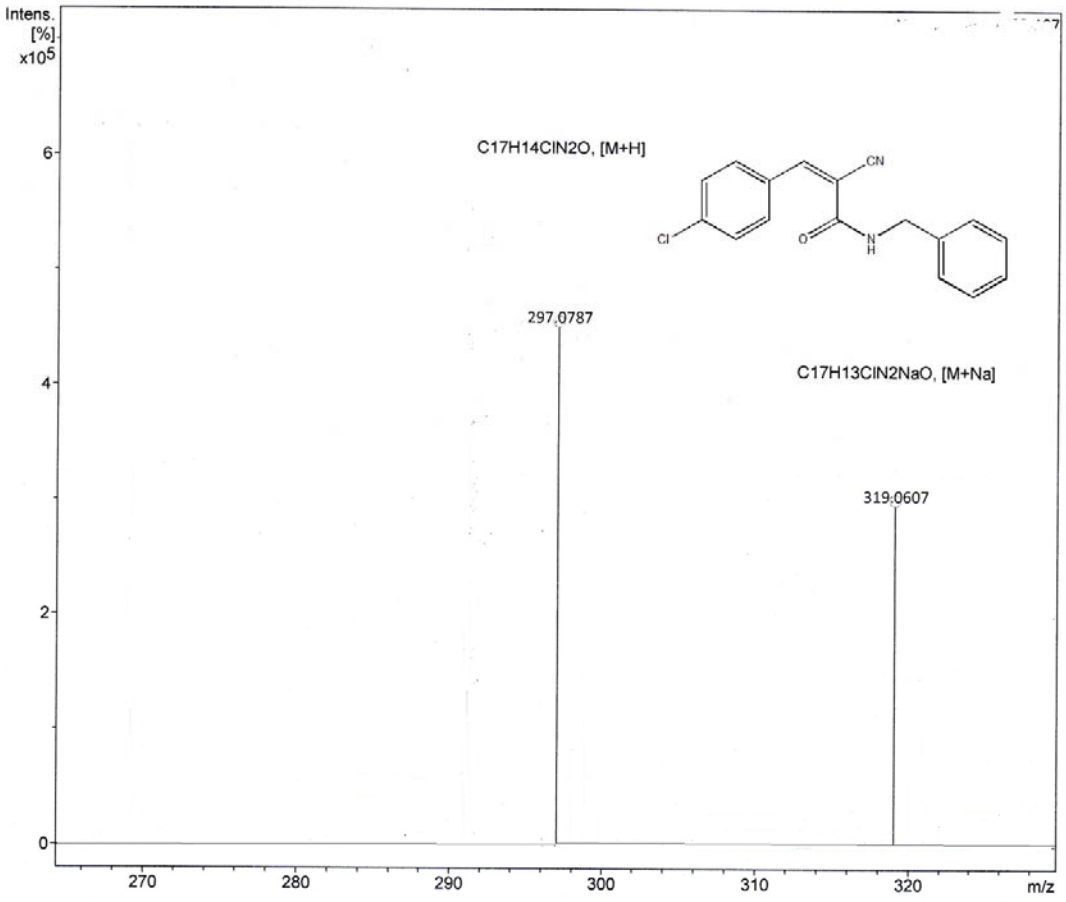
^{13}C-

NMR


160.52
153.33
144.10
137.22
130.87
130.02
128.91
127.93
117.29
102.40
44.57
21.65
CN
H3C
O
N
H
f1 (ppm)

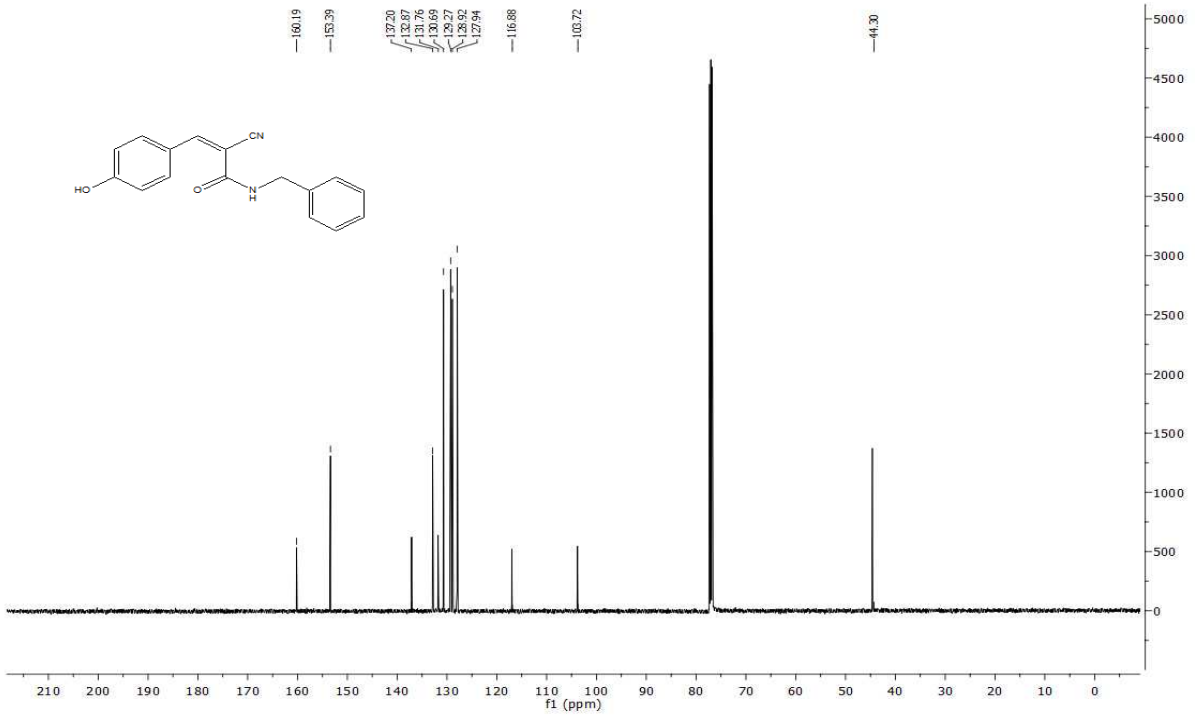
^{13}C-
NMR


159.70
151.87
138.50
136.65
132.32
130.46
129.87
129.20
128.60
127.63
117.11
104.65
44.38
CN
Cl
O
N
H
f1 (ppm)

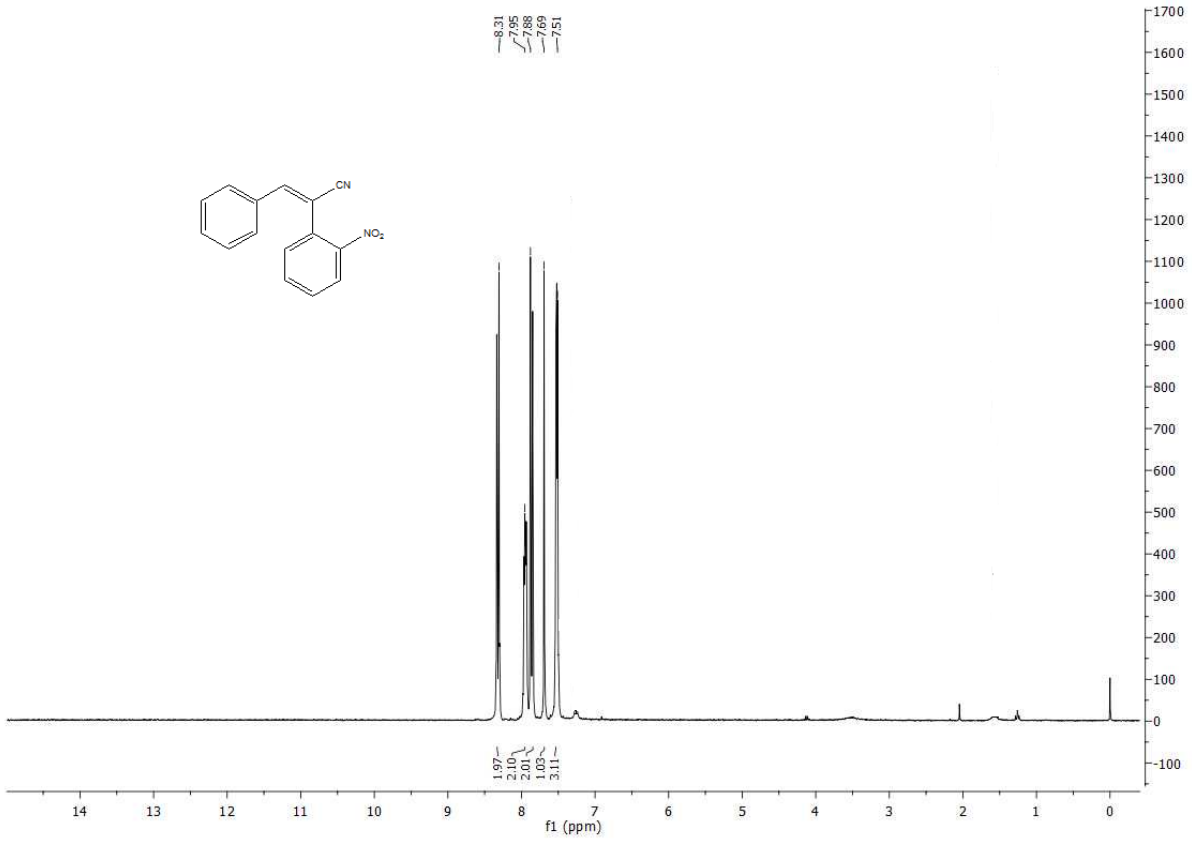

Intens.
[%]
x10^5
6
4
2
0
C17H14ClN2O, [M+H]
297.0787
C17H13ClN2NaO, [M+Na]
319.0607
270
280
290
300
310
320
m/z
CN
Cl
O
N
H

MASS

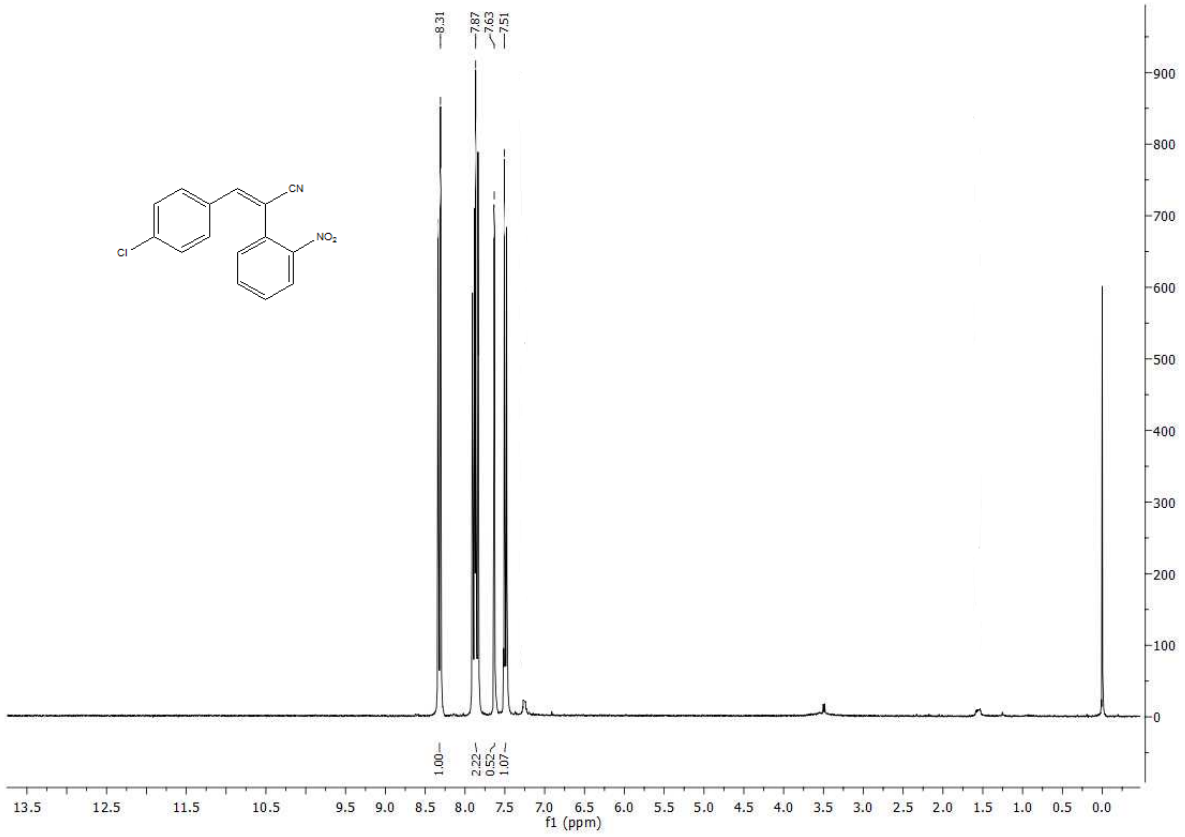
^{13}CMR


160.19
153.39
137.20
132.87
131.76
130.69
129.27
128.92
127.94
116.88
103.72
44.30
CN
HO
O
N
H
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H-
NMR



^{1}H-
NMR


8.31
7.87
7.63
7.51
CN
Cl
NO2
900
800
700
600
500
400
300
200
100
0
1.00
2.22
0.52
1.07
13.5 12.5 11.5 10.5 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 0.5 0.0
f1 (ppm)

Reference for the Supporting Data

1) Yadav J S, Subba Reddy B V, Basak A K, Visali B,Narsaiah A V, Nagaiah K, *Eur. J. Org. Chem.* **2004**, 546
2) Xu D Z, Liu Y, Shi S, Wang Y, *Green Chem.*, **2010**, 12, 514.
3) Kobayashi Y, Li S, Takemoto Y, *Asian J. Org. Chem*., **2014**, 3, 403.
4) a) Chtourou M, Lahyani A, Trabelsi M, *Reaction Kinetics, Mechanisms and Catalysis,* 126, 2019, 237. b)Zhao S, Wang X, Zhang L, *RSC Adv*, 3, **2013**, 11691. c) Liu Y, Liang J, Liu X H, Fan J C, Shang Z C, *Chin ChemLett*,19, **2008**,1043.
5) a) Nie X, Wang Y, Yang L, Yang Z, Kang T, *Tetrahedron Letters*, 58, **2017**, 3003. b) Kang T R, Chen L M, *ActaCryst*., E67, **2011**, 08. c) He Y, Kang T R, Liu Q Z, Chen L M, Tu Y L, Liu Y J, Chen T B, Wang Z Q, Liu J, Xie Y M, Yang J L, He L,*Org. Lett*., 15(16), **2013**, 4054.
6) Shanthan Rao P, Venkataratnam R V, *Tetrahedron Lett*.,32, **1991**, 5821.
7) Keithellakpam S, Moirangthen N, Laitonjam W S, Indian J Chem, 54B, **2015**, 1157.
8) a) Gomez C V, Cruz D C, Mose R, Jorgensen K A, *Chem. Commun.*,**2014**, 50, 6035. b) Ryabukhin S V, Plaskon A S, Volochnyuk D M, Pipko S E, Shivanyuk A N, Tolmachev A A, *J. Comb. Chem.* **2007,** 9*,* 1073.
9) Wilde F, Specker E, Neuenschwander M, Nazare M, Bodtke A, Link A, *Mol Divers*, 18, **2014**, 483.
10) Oskooie H A, Roomizadeh E, Heravi M M, J Chem Res, **2006**, 246.
11) FormentiD,Ferretti F.R Fabio, *Chem Cat Chem,* 10,**2018**, 148.
12) Sharma Y O, Degani M S, *Green Chem.*, 11,**2009**, 526.
13) Yang K, Zhou F, Kuang Z, Gao G, Driver T G, Song Q, *Org. Lett*., 18, **2016**, 4088.