Supporting Information

Expanded Perlite-Polyphosphoric Acid (EP-PPA) as a Low-Cost Heterogeneous Solid Acid Catalyst for Green and Metal-Free Synthesis of Nitriles from Aldehydes

Mahdieh Mahmoodi[1], Batool Akhlaghinia[1a]

[1]Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad 9177948974, Iran.

Experimental

General

All chemical reagents and solvents were purchased from Merck Chemical Company and were used as received without further purification. The purity determination of the products and the progress of the reactions were monitored by TLC (Thin Layer Chromatography) on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR (Fourier Transform Infrared) spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer. The NMR (Nuclear Magnetic Resonance) spectra were recorded on Brucker Avance 300, 400 and 600 MHz instruments in $CDCl_3$ and DMSO-d_6. Mass spectra were recorded with a Shimadzu GC-MS-QP5050 and CH7A Varianmat Bremem instrument at 70 eV, in m/z (rel %). All the yields refer to isolated products after purification by thin layer chromatography.

Spectral Data

Benzonitrile [1]

Benzonitrile (Table 3, Entry 1). Oil (Lit.[1] Oil); 0.0976g (95%); FT-IR (neat): 3065, 2927, 2855, 2228 (CN), 1598, 1581, 1490, 1447, 1287, 1178, 1071, 1026, 926, 758, 687, 547 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.66-7.59 (m, 3H), 7.50-7.46 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 132.7, 132.0, 129.0, 118.7, 112.4; MS (EI) m/z (%): 103 $[M]^{+}$.

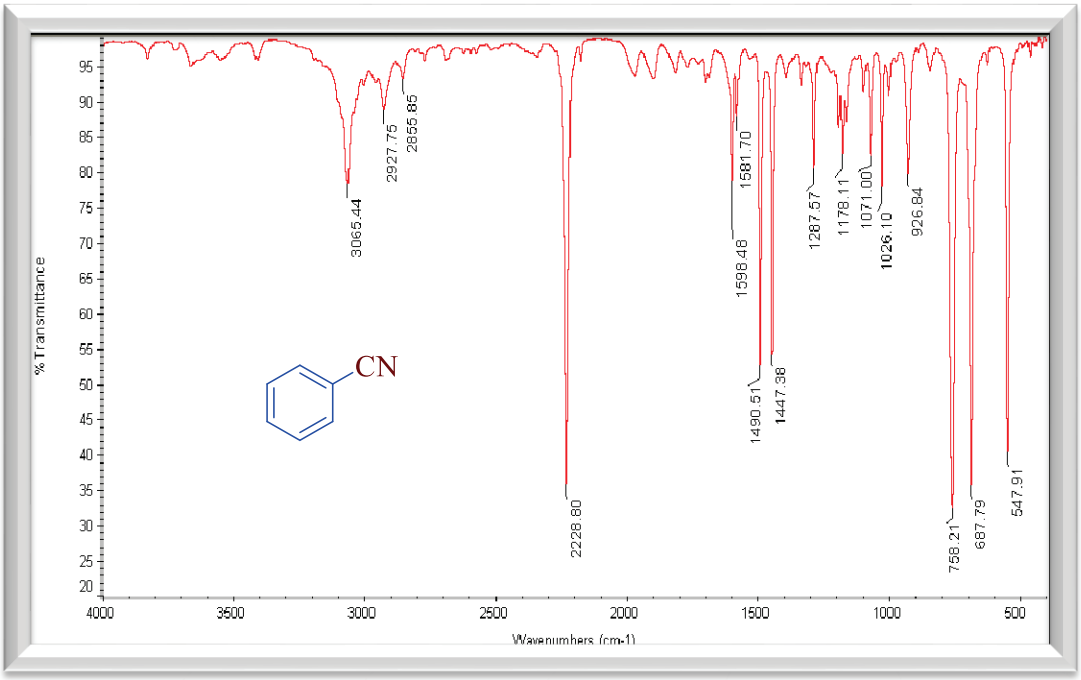

Fig S 1: FT-IR (neat) Spectrum of Benzonitrile (Table 3, Entry1)

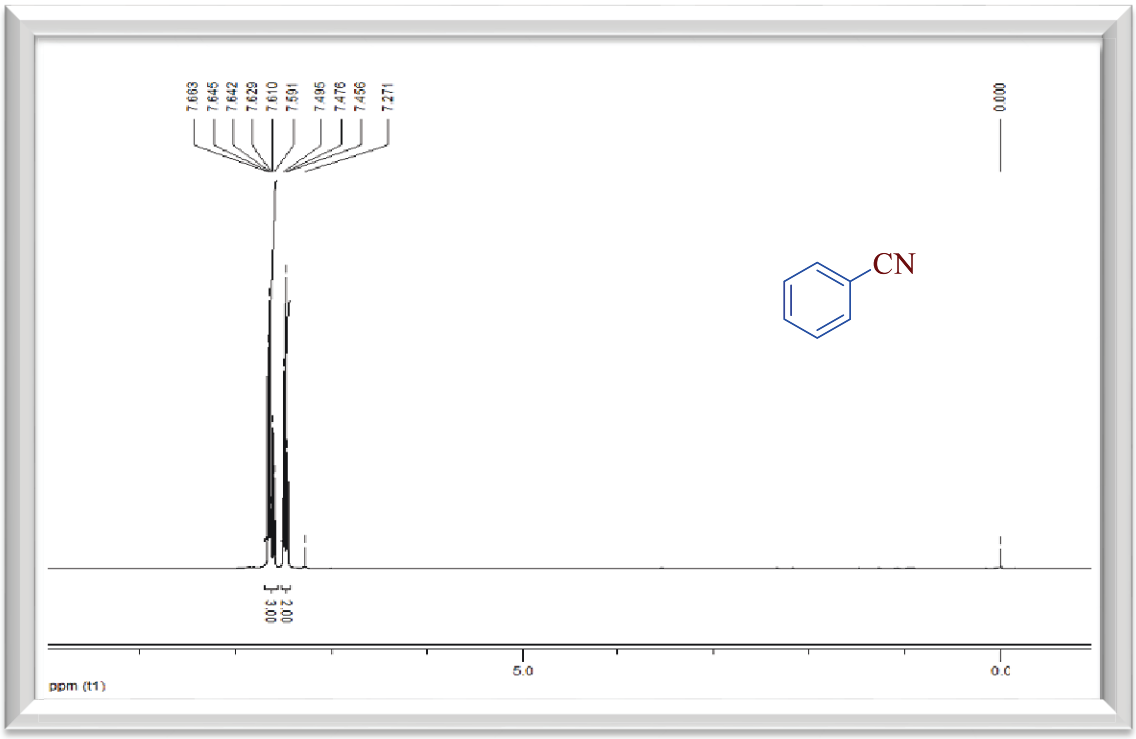

Fig S 2: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Benzonitrile (Table 3, Entry1)

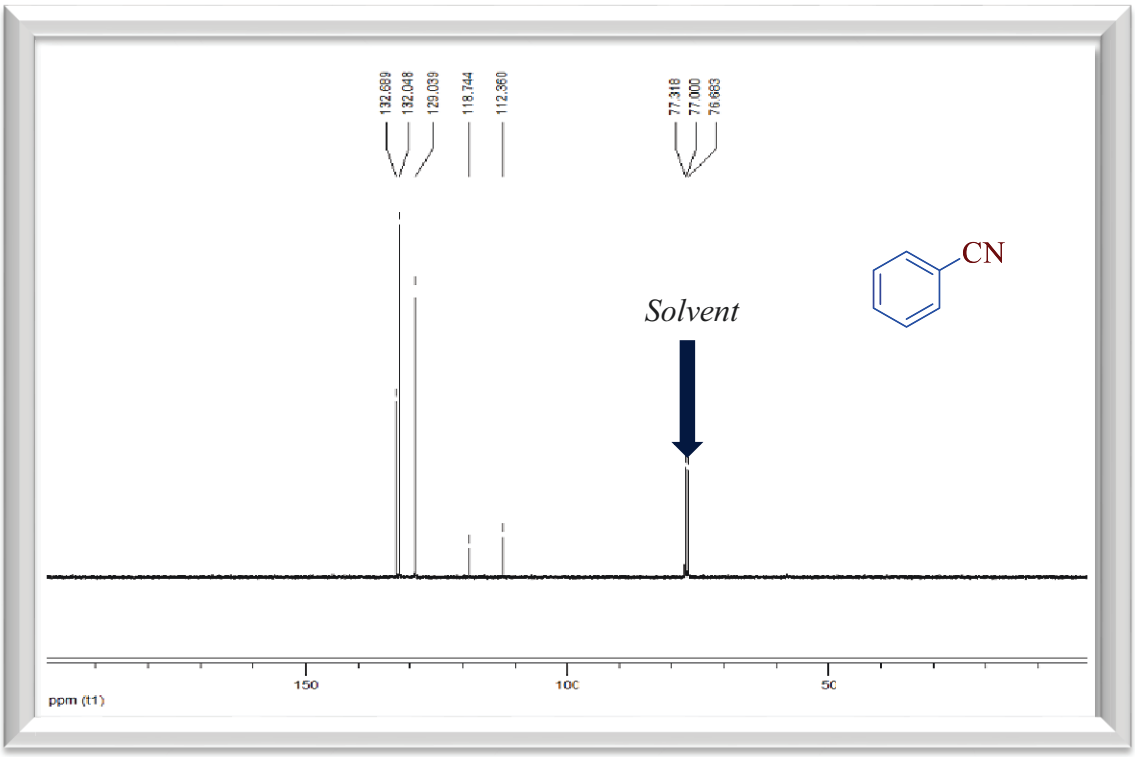

Fig S 3: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Benzonitrile (Table 3, Entry1)

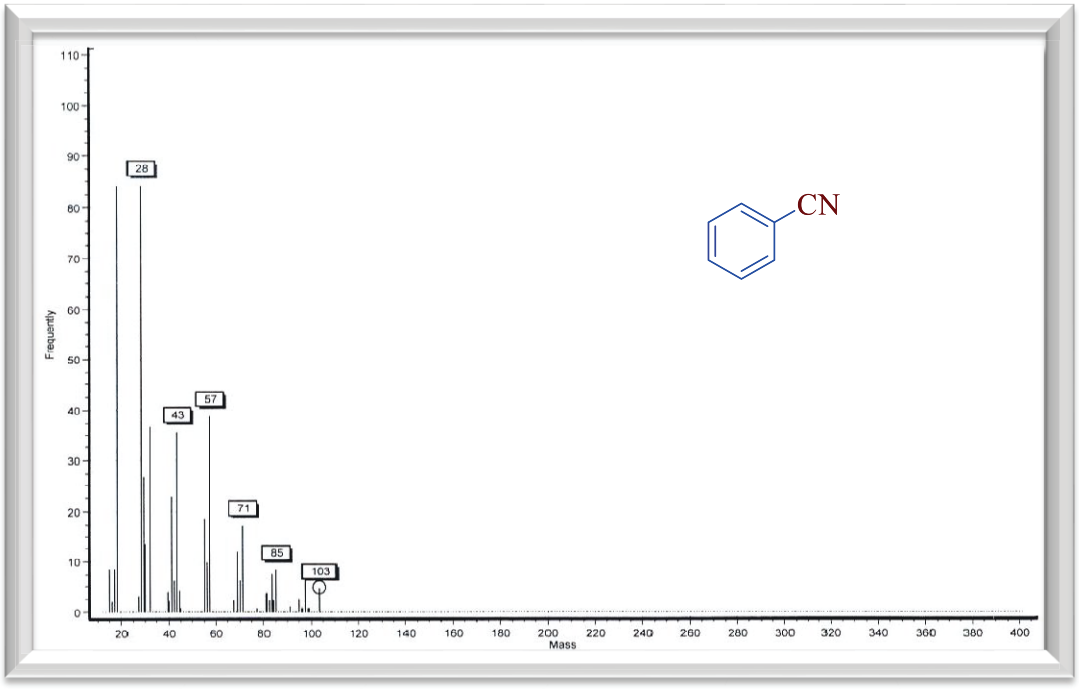

Fig S 4: Mass Spectrum of Benzonitrile (Table 3, Entry1)

4-Hydroxybenzonitrile [2]

4-Hydroxybenzonitrile (Table 3, Entry 2). 0.1154g (97%); Mp 110-111˚C (Lit.[2]111-112˚C); FT-IR (KBr): 3310, 2233 (CN), 1907, 1785, 1612, 1586, 1510, 1443, 1377, 1284, 1222, 1164, 1103, 967, 839, 701, 669, 547 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm]= 7.53 (2H, d, J=8.4 Hz), 6.93 (2H, d, J=8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm]= 160.5, 134.3, 119.3, 116.5, 102.6; MS (EI) m/z (%): 119 $[M]^{+}$.

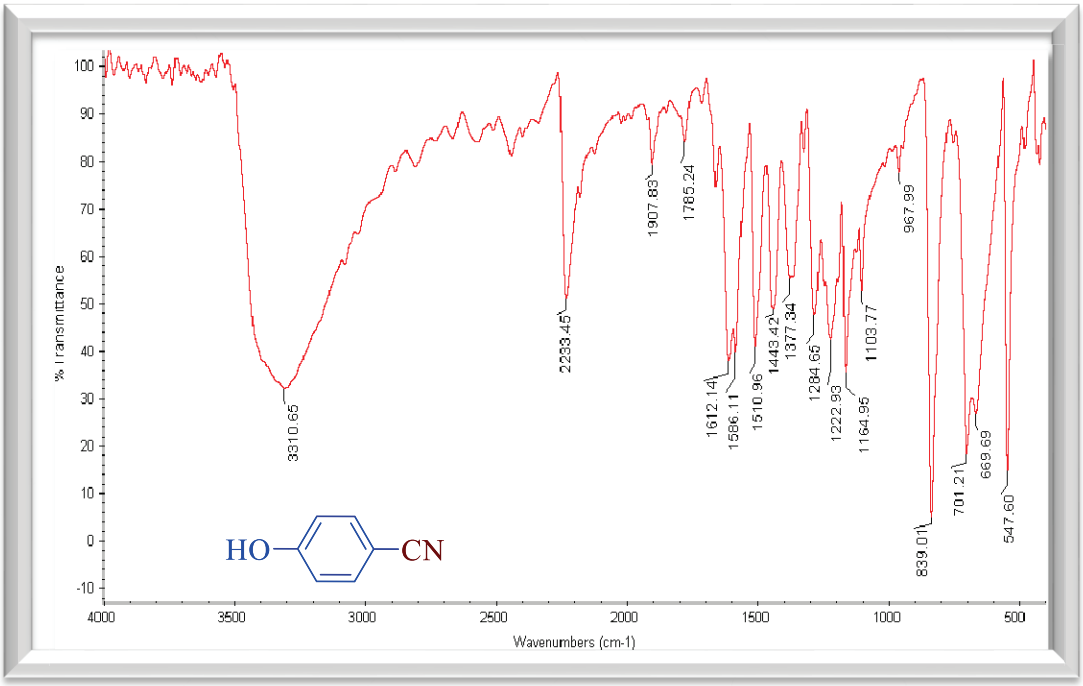

Fig S 5: FT-IR (KBr) Spectrum of 4-Hydroxybenzonitrile (Table 3, Entry 2)

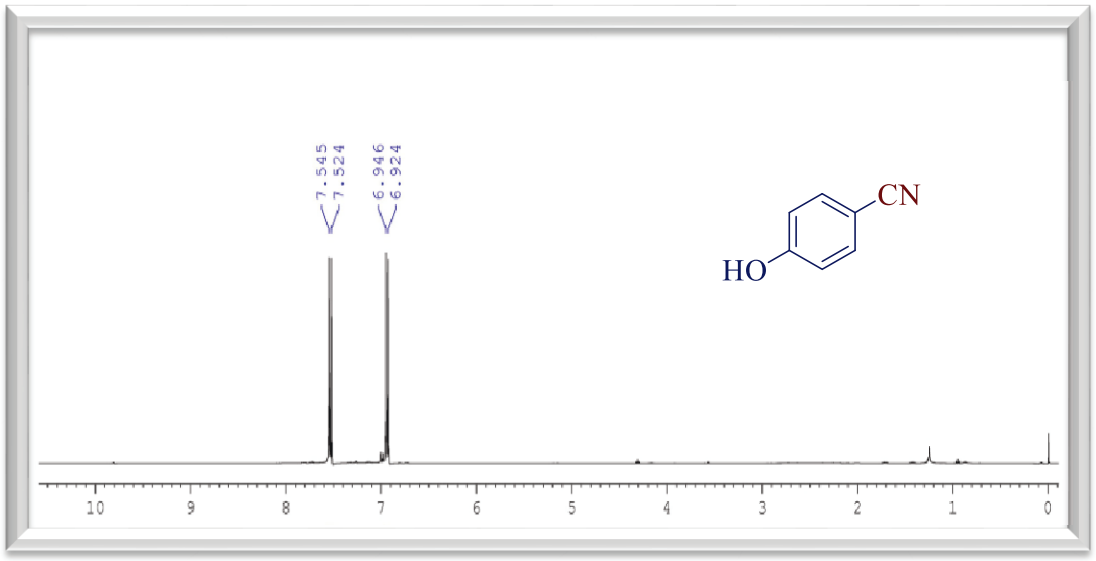

Fig S 6: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 4-Hydroxybenzonitrile (Table 3, Entry 2)

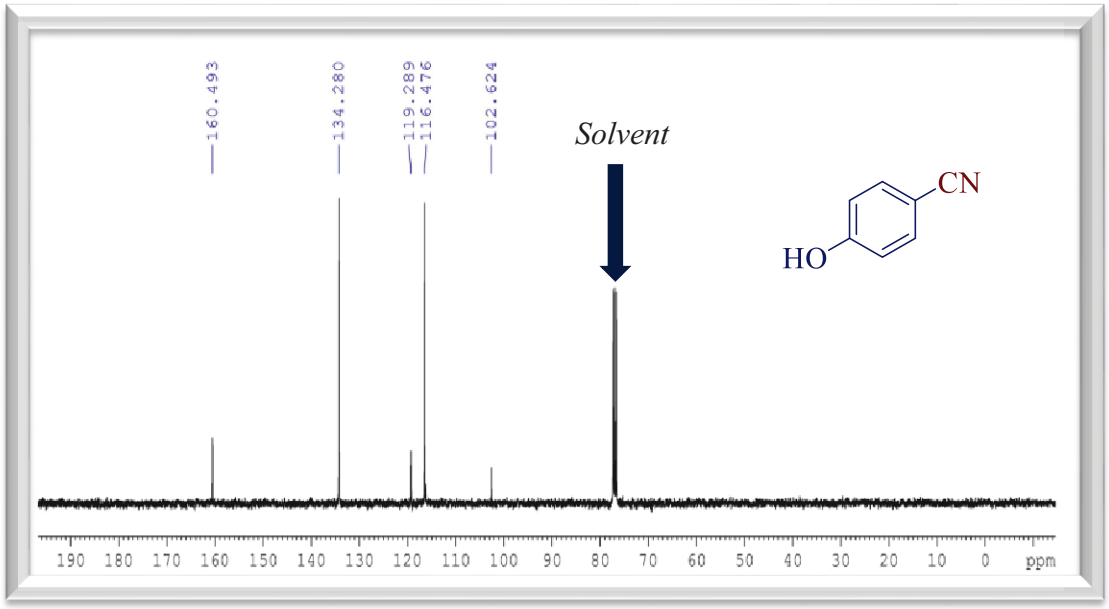

Fig S 7: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 4-Hydroxybenzonitrile (Table 3, Entry2)

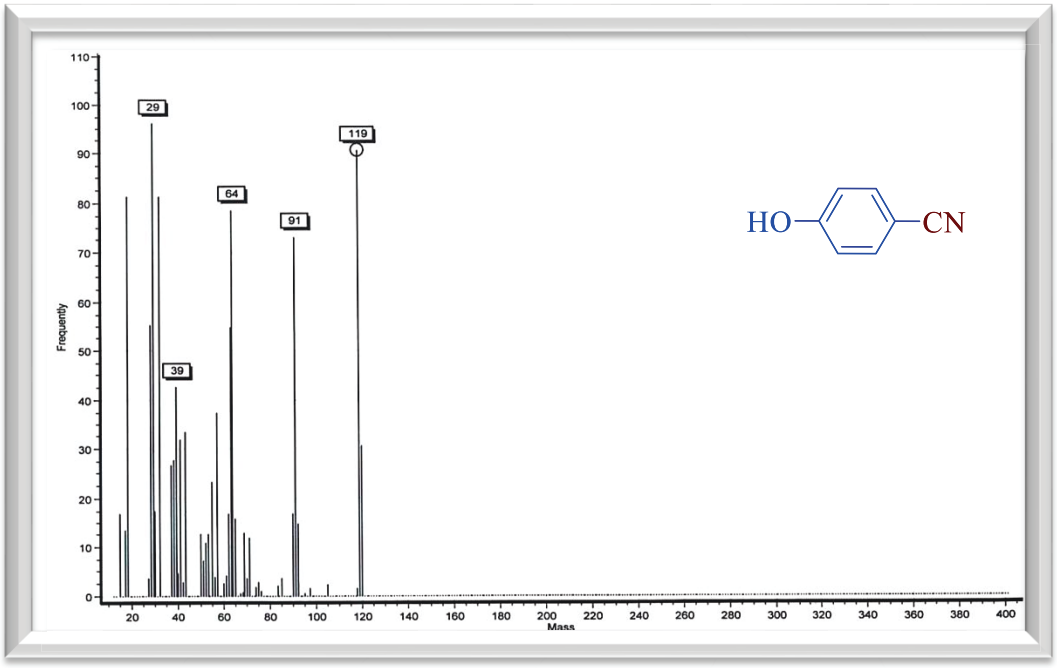

Fig S 8: Mass Spectrum of 4-Hydroxybenzonitrile (Table 3, Entry 2)

2-Hydroxybenzonitrile [3]

2-Hydroxybenzonitrile (Table 3, Entry 3). 0.1118g (94%); Mp 93-94˚C (Lit.[3] 94 ˚C); FT-IR (KBr): 3231, 3068, 2966, 2864, 2729, 2602, 2508, 2467, 2345, 2239 (CN), 1604, 1505, 1458, 1369, 1306, 1269, 1239, 1102, 1037, 947, 848, 769, 754, 731, 687, 567, 496, 465 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.56-7.49 (m, 2 H), 7.18-7.10 (m, 2 H), 5.46 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 158.9, 134.8, 133.0, 120.8, 117.0, 116.2, 100.0; MS (EI) m/z (%): 119 $[M]^+$.

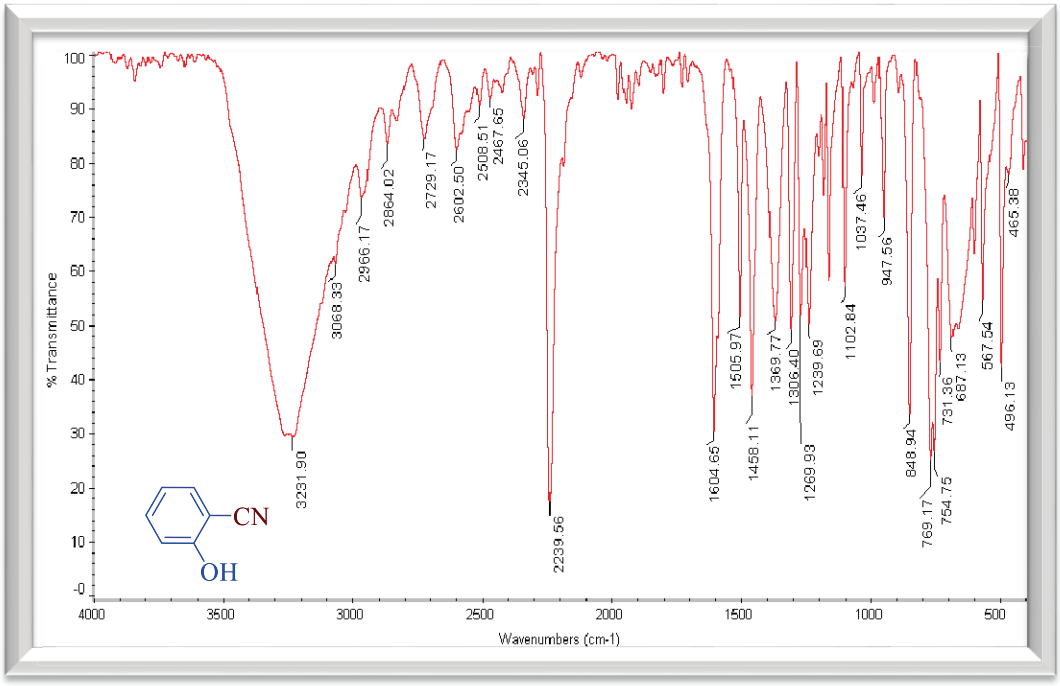

Fig S 9: FT-IR (KBr) Spectrum of 2-Hydroxybenzonitrile (Table 3, Entry 3)

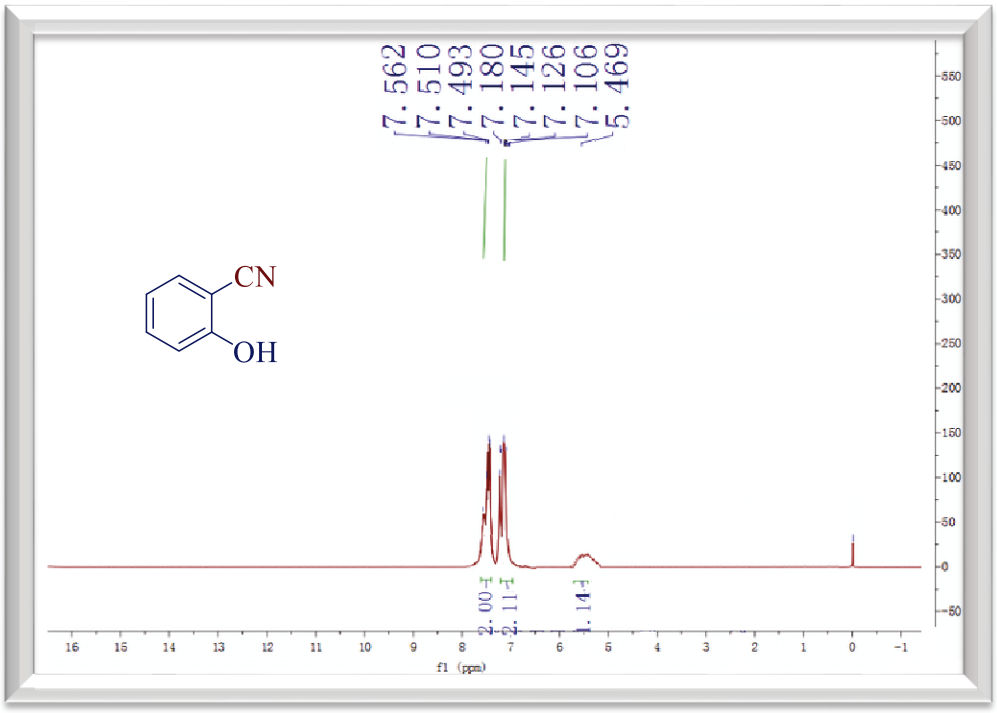

Fig S 10: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 2-Hydroxybenzonitrile (Table 3, Entry 3)

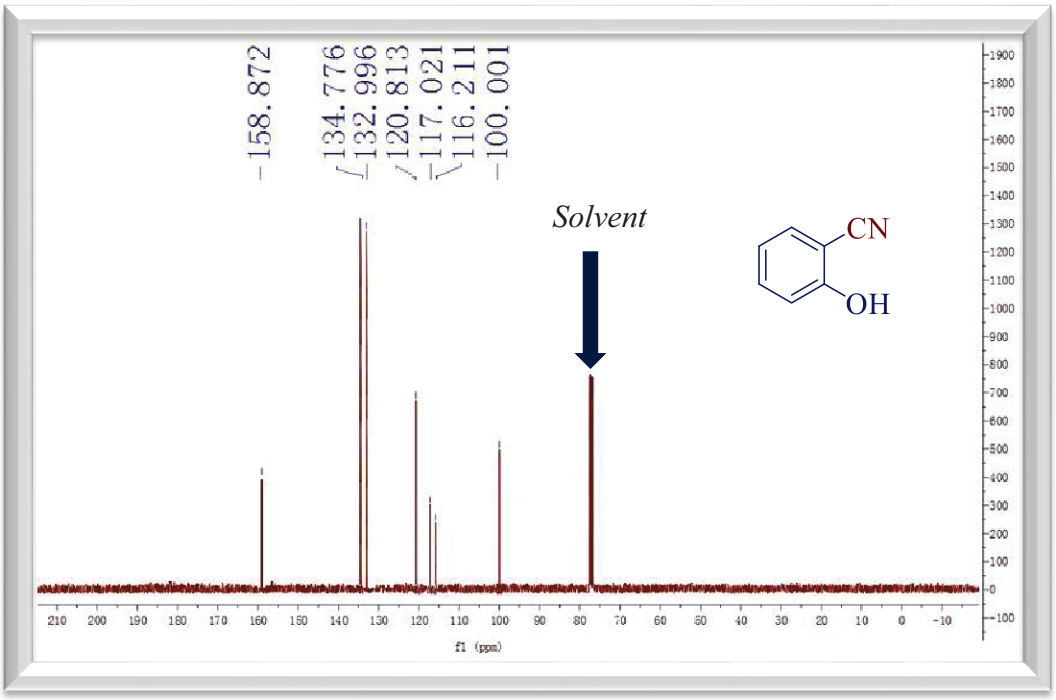

Fig S 11: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 2-Hydroxybenzonitrile (Table 3, Entry3)

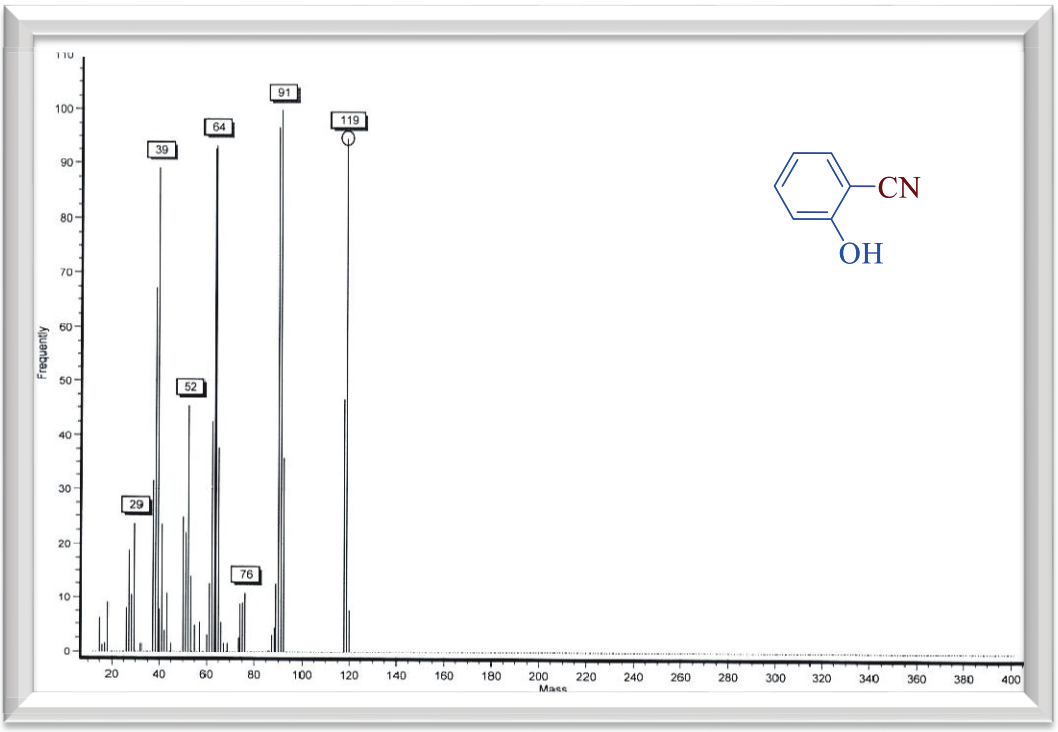

Fig S 12: Mass Spectrum of 2-Hydroxybenzonitrile (Table 3, Entry 3)

3,4-Dihydroxybenzonitrile [4]

3,4-Dihydroxybenzonitrile (Table 3, Entry 4). 0.1296g (96%); Mp 154-156˚C (Lit.[4]156 ˚C): FT-IR (KBr): 3423, 3377, 3211, 3072, 2957, 2926, 2854, 2226(CN), 1728, 1662, 1605, 1513, 1413, 1394, 1297, 1261, 1237, 1189, 1161, 1110, 1039, 1012, 850, 769, 686, 583 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ[ppm] = 9.90 (s, 2 H), 7.11 (d, J = 8.4 Hz, 1 H), 7.06 (s, 1 H), 6.86 (d, J = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ[ppm] = 150.99, 146.36, 125.24, 120.04, 118.81, 116.78, 101.36.

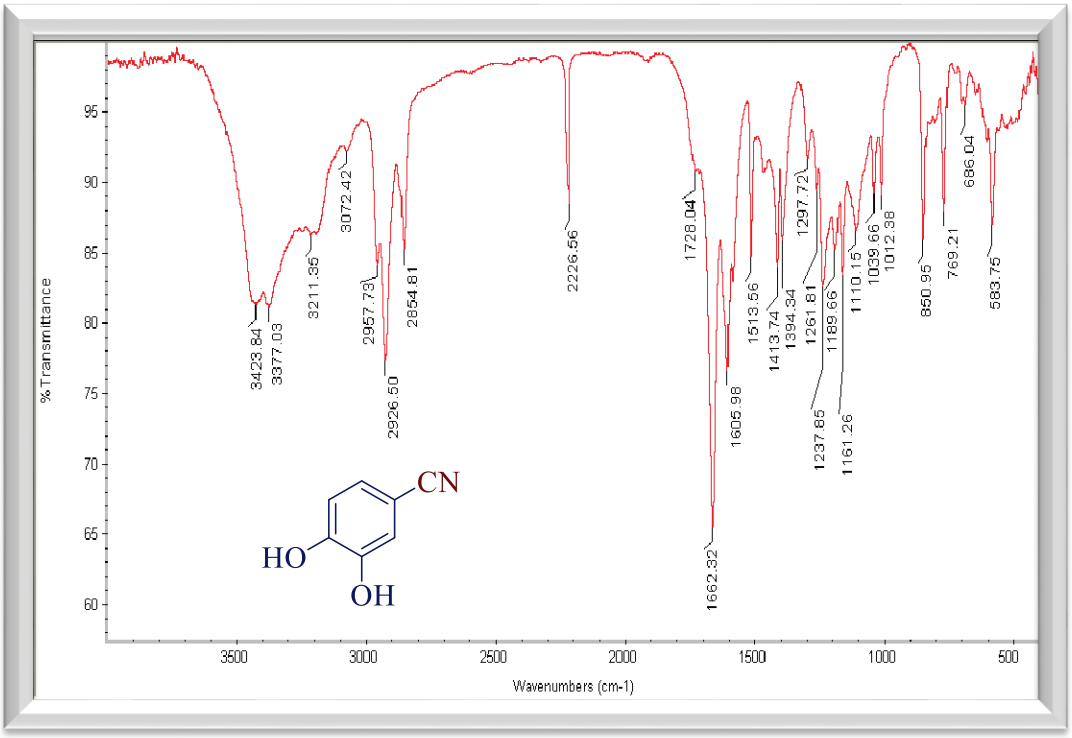

Fig S 13: FT-IR (KBr) Spectrum of 3,4-Dihydroxybenzonitrile (Table 3, Entry 4)

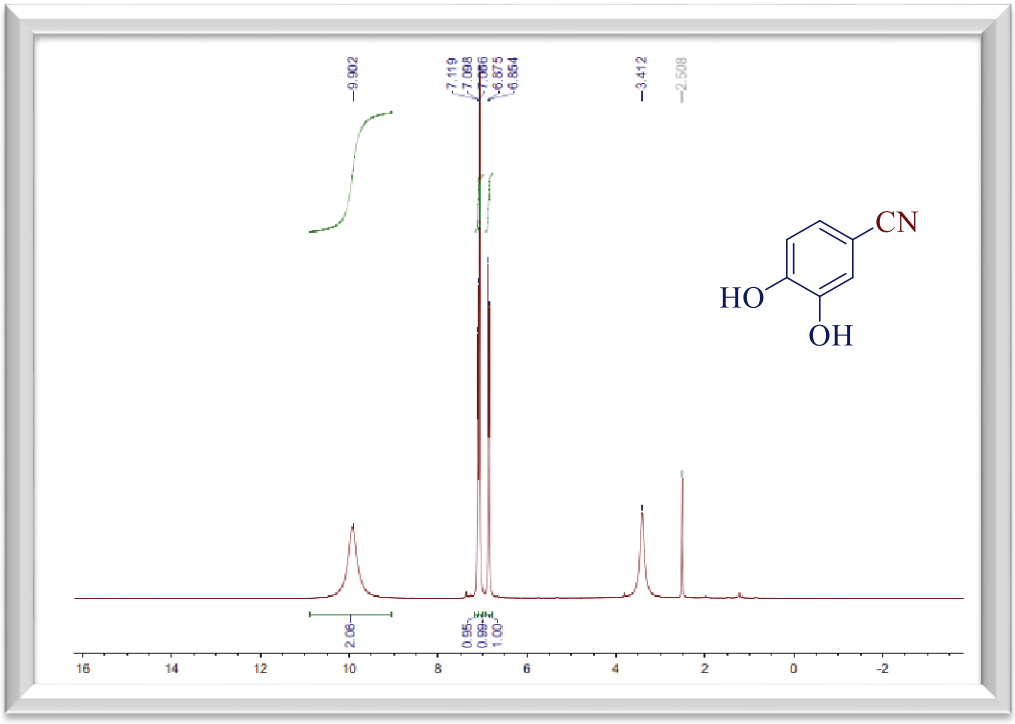

Fig S 14: ^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of 3,4-Dihydroxybenzonitrile (Table 3, Entry 4)

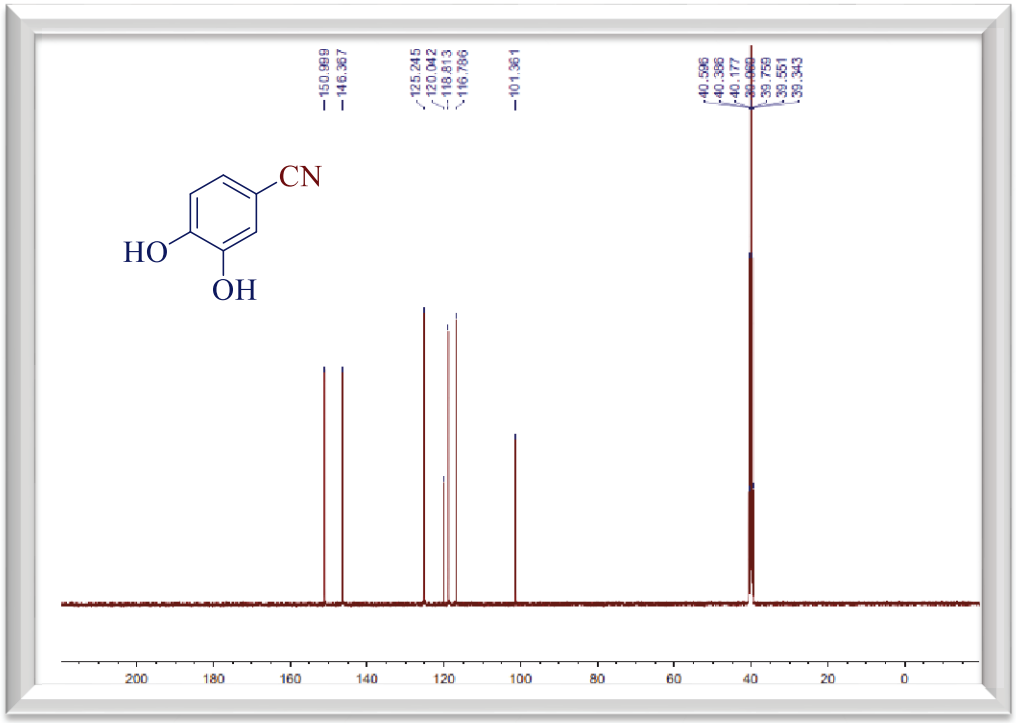

Fig S 15: ^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of 3,4-Dihydroxybenzonitrile (Table 3, Entry4)

4-(Dimethylamino) benzonitrile [5]

4-(Dimethylamino) benzonitrile (Table 3, Entry 5). 0.1430g (98%); Mp 73 ˚C (Lit.[5] 72-75˚C); FT-IR (KBr): 2917, 2864, 2814, 2207 (CN), 1606, 1524, 1446, 1368, 1227, 1171, 1125, 1066, 938, 817, 645, 544 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 7.46 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 8.8 Hz, 2H), 3.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ[ppm] = 152.4, 133.3, 120.7, 111.3, 97.2, 39.9; MS (EI) m/z (%) 146 $[M]^+$.

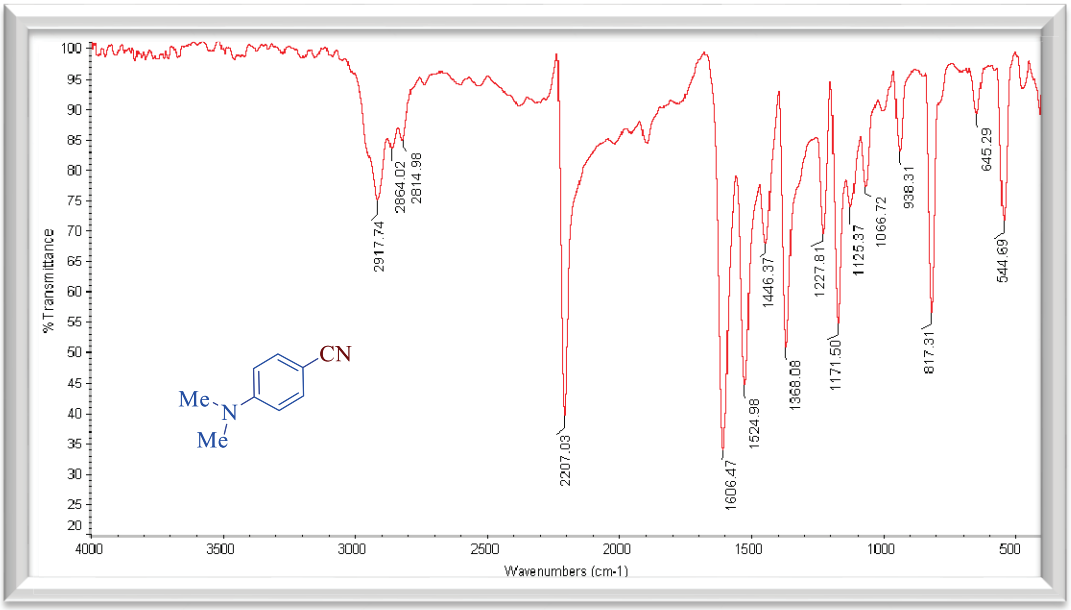

Fig S 16: FT-IR (KBr) Spectrum of 4-(Dimethylamino) benzonitrile (Table 3, Entry 5)

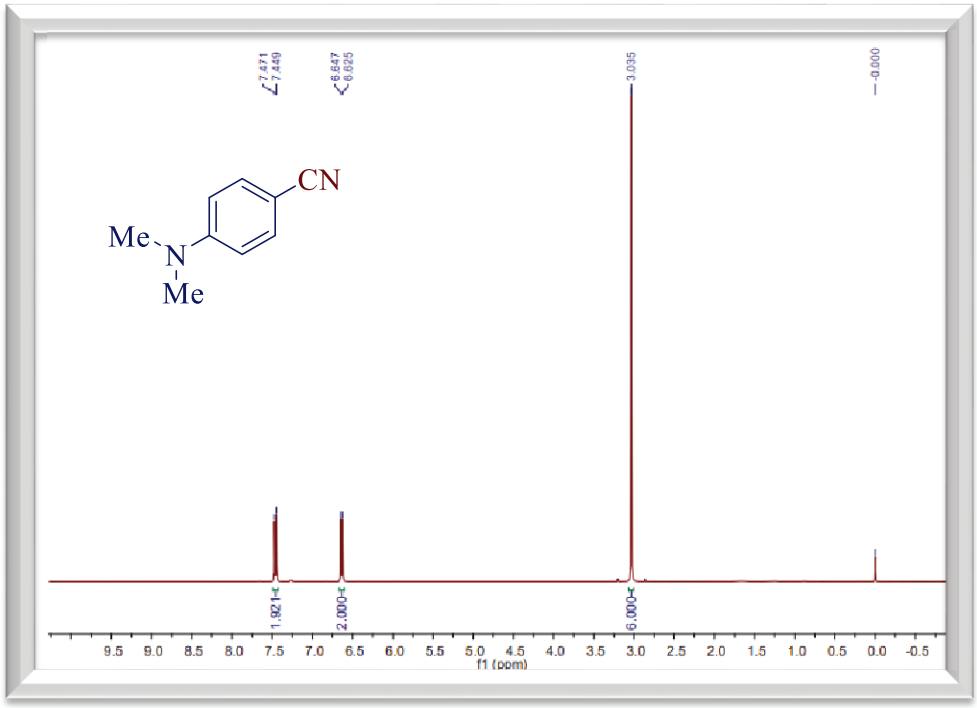

Fig S 17: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 4-(Dimethylamino) benzonitrile (Table 3, Entry 5)

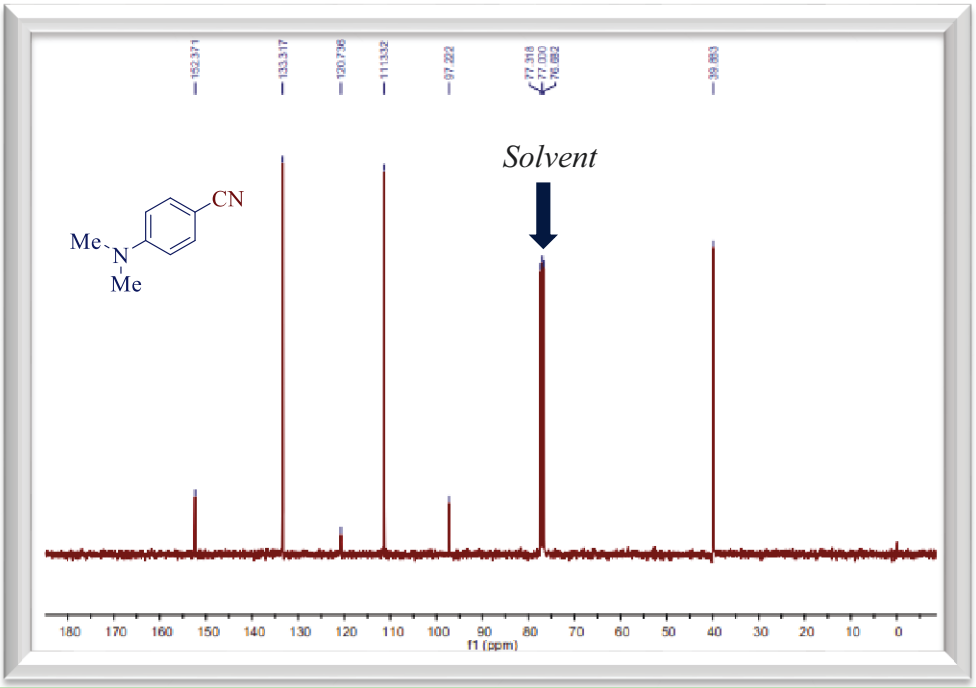

Fig S 18: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 4-(Dimethylamino) benzonitrile (Table 3, Entry5)

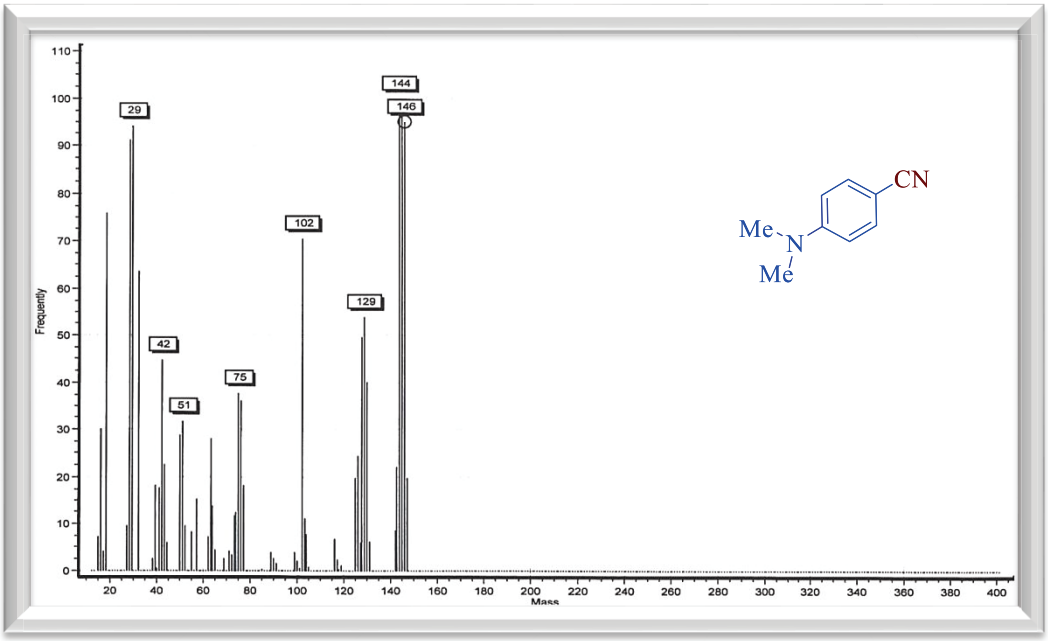

Fig S 19: Mass Spectrum of 4-(Dimethylamino) benzonitrile (Table 3, Entry 5)

4-Methoxybenzonitrile [6]

4-Methoxybenzonitrile (Table 3, Entry 6). 0.1236g (93%); Mp 57-58 ˚C (Lit.[6] 58-59 ˚C); FT-IR (KBr): 3050, 2931, 2847, 2213 (CN), 1604, 1506, 1454, 1303, 1256, 1170, 1020, 828, 678, 546, 406 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm]= 7.59 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 8.6 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm]= 162.9, 133.9, 119.2, 114.8, 103.9, 55.5; MS (EI) m/z (%): 133 $[M]^{+}$.

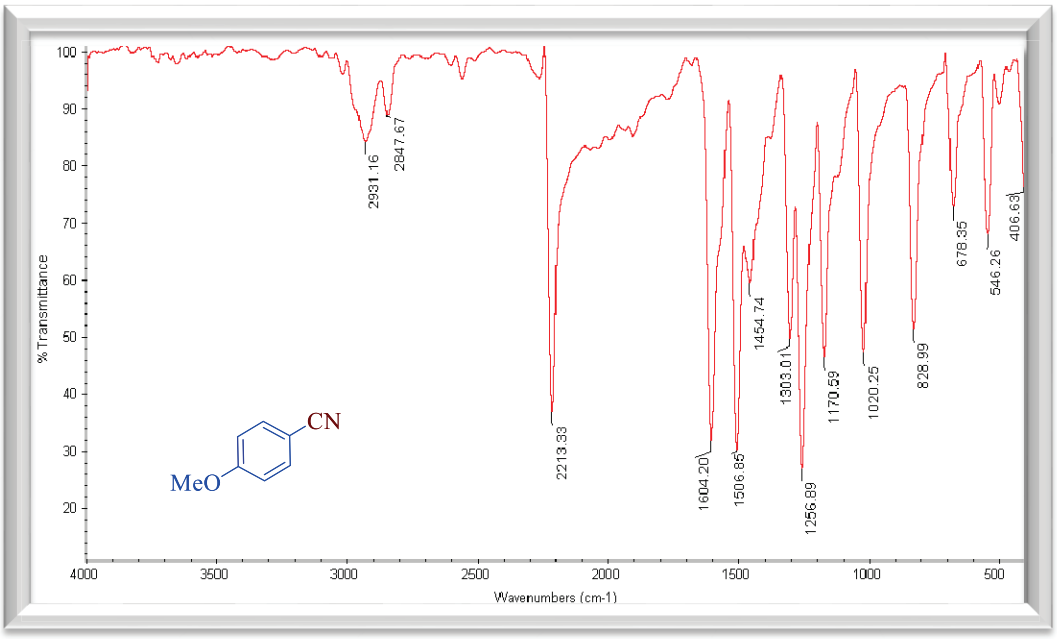

Fig S 20: FT-IR (KBr) Spectrum of 4-Methoxybenzonitrile (Table 3, Entry 6)

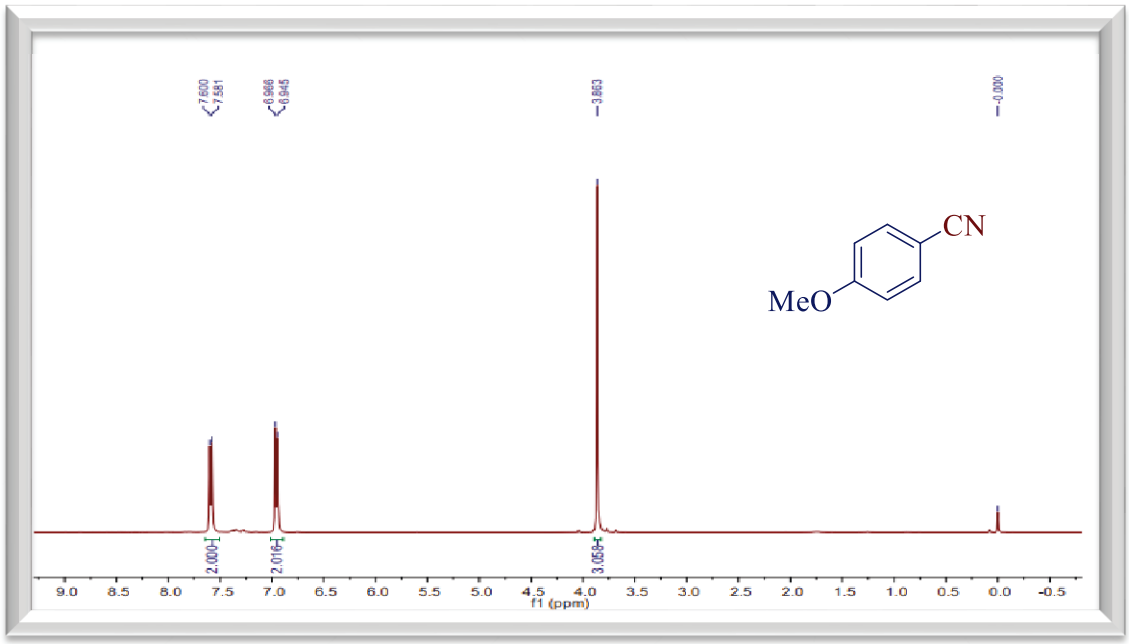

Fig S 21: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 4-Methoxybenzonitrile (Table 3, Entry 6)

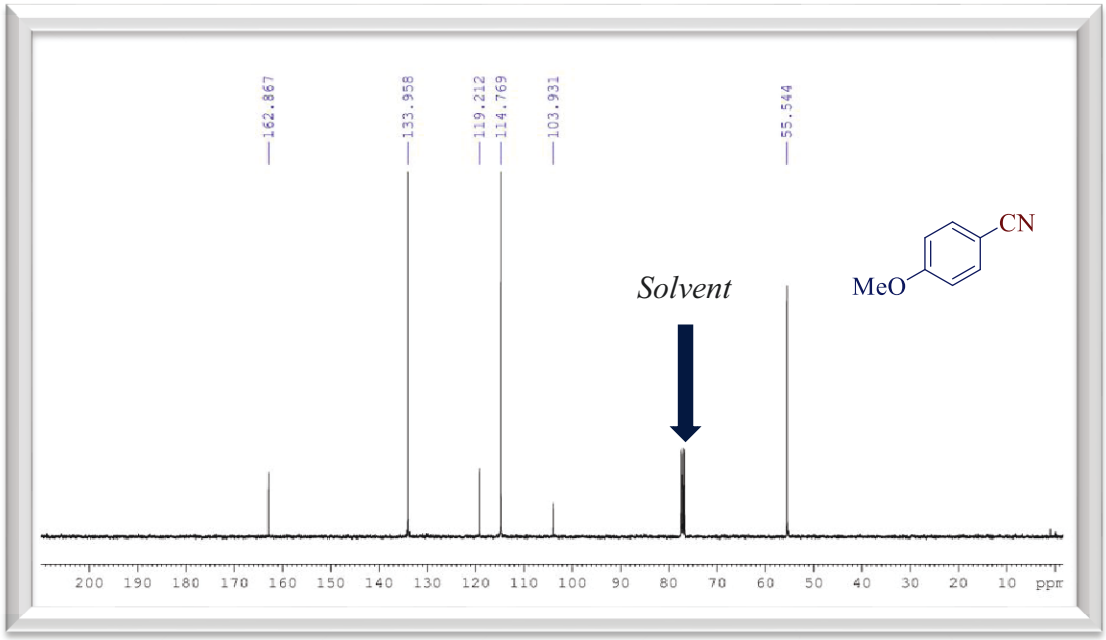

Fig S 22: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 4-Methoxybenzonitrile (Table 3, Entry6)

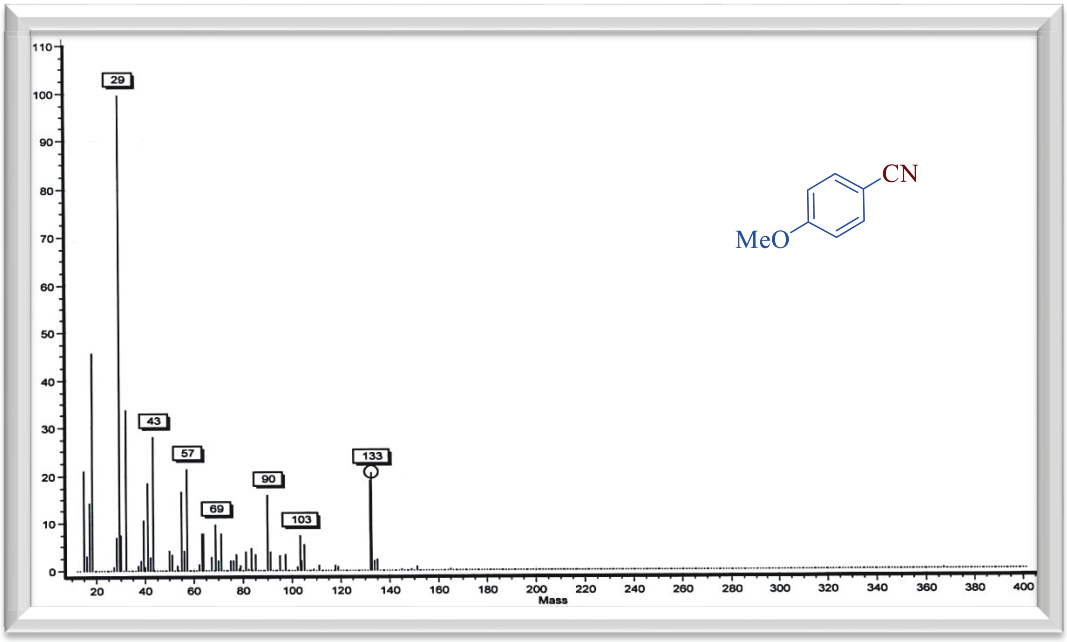

Fig S 23: Mass Spectrum of 4-Methoxybenzonitrile (Table 3, Entry 6)

4-Methylbenzonitrile [7]

4-Methylbenzonitrile (Table 3, Entry 7). 0.1111g (95%); Mp 26-27 ˚C (Lit.[7] 26-28 ˚C); FT-IR (neat): 3041, 2926, 2861, 2227 (CN), 1918, 1739, 1608, 1507, 1452, 1379, 1245, 1177, 1113, 1047, 957, 819, 703, 547, 438 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.53 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 143.6, 131.9, 129.7, 119.1, 109.2, 21.7; MS (EI) m/z (%): 117 $[M]^{+}$.

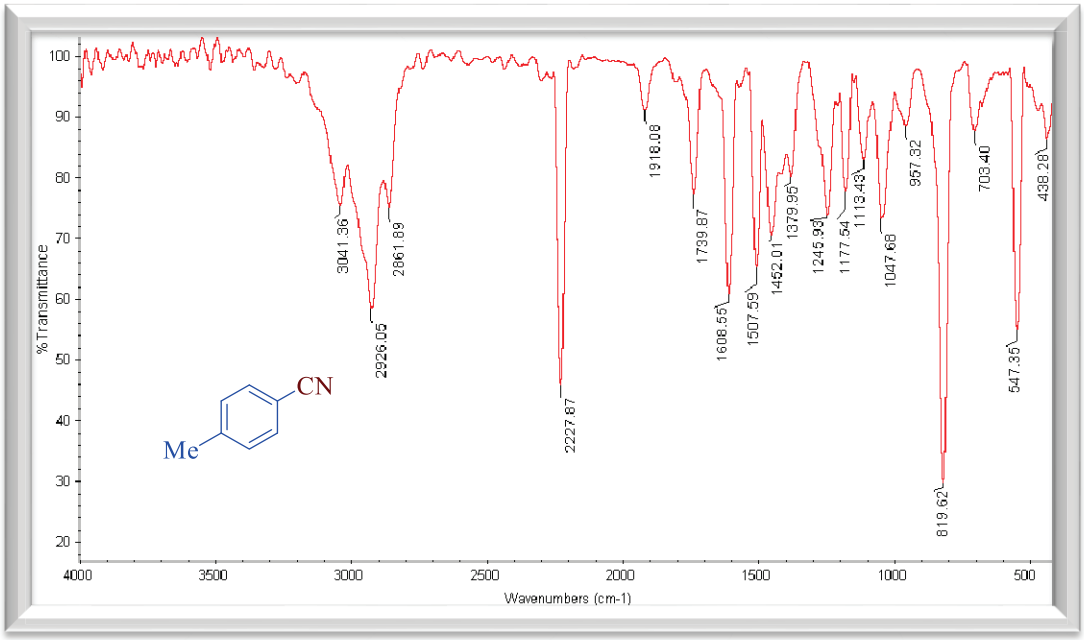

Fig S 24: FT-IR (neat) Spectrum of 4-Methylbenzonitrile (Table 3, Entry 7)

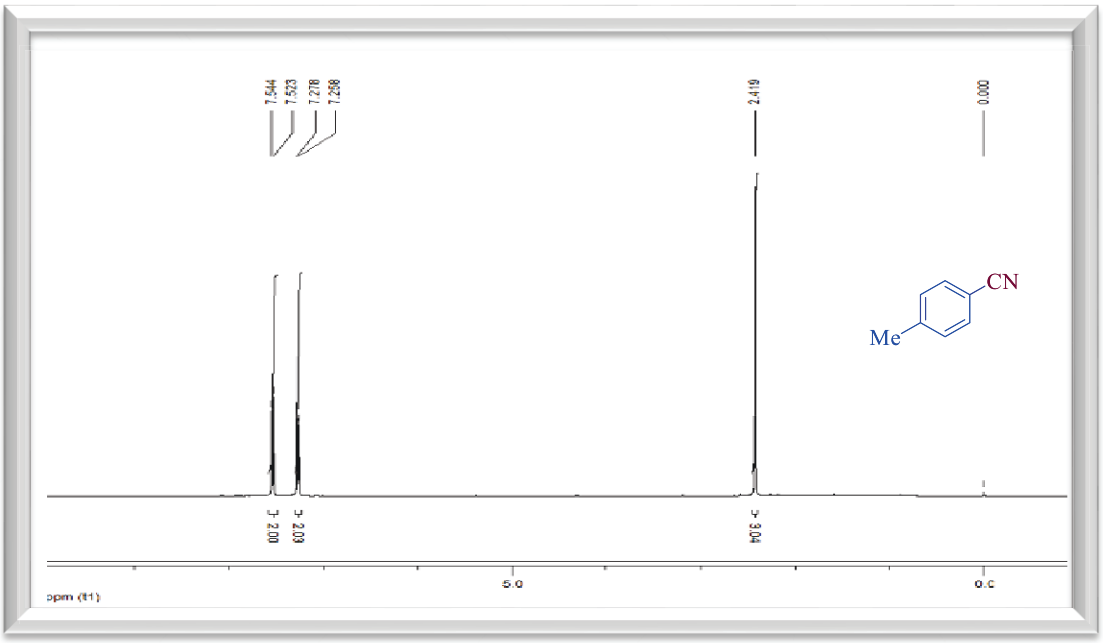

Fig S 25: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 4-Methylbenzonitrile (Table 3, Entry 7)

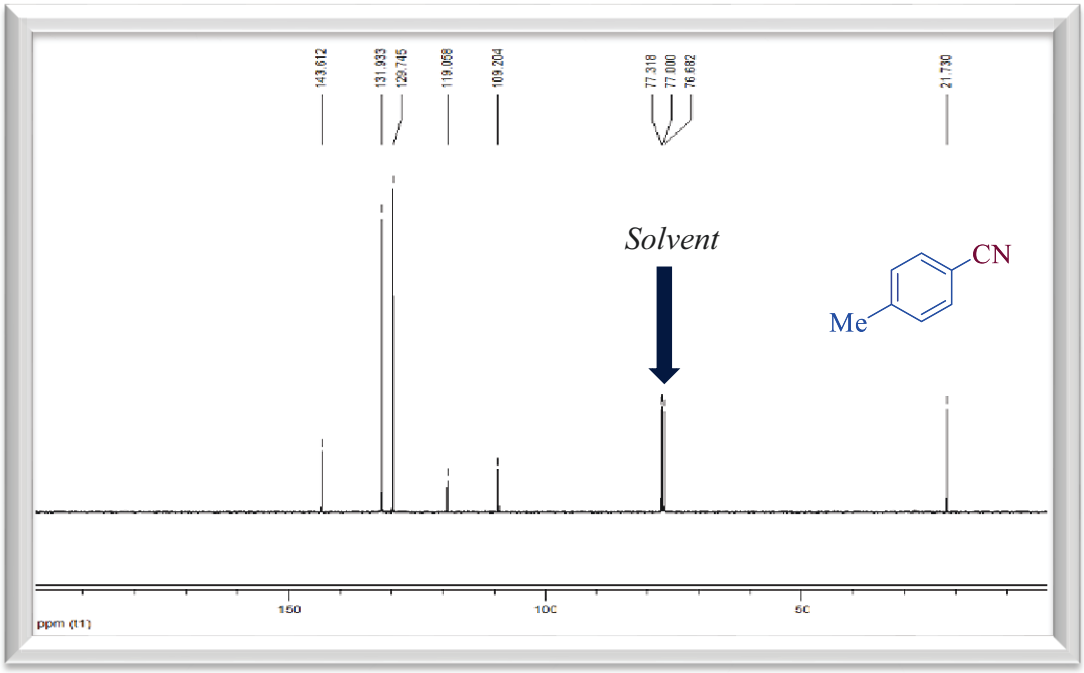

Fig S 26: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 4-Methylbenzonitrile (Table 3, Entry 7)

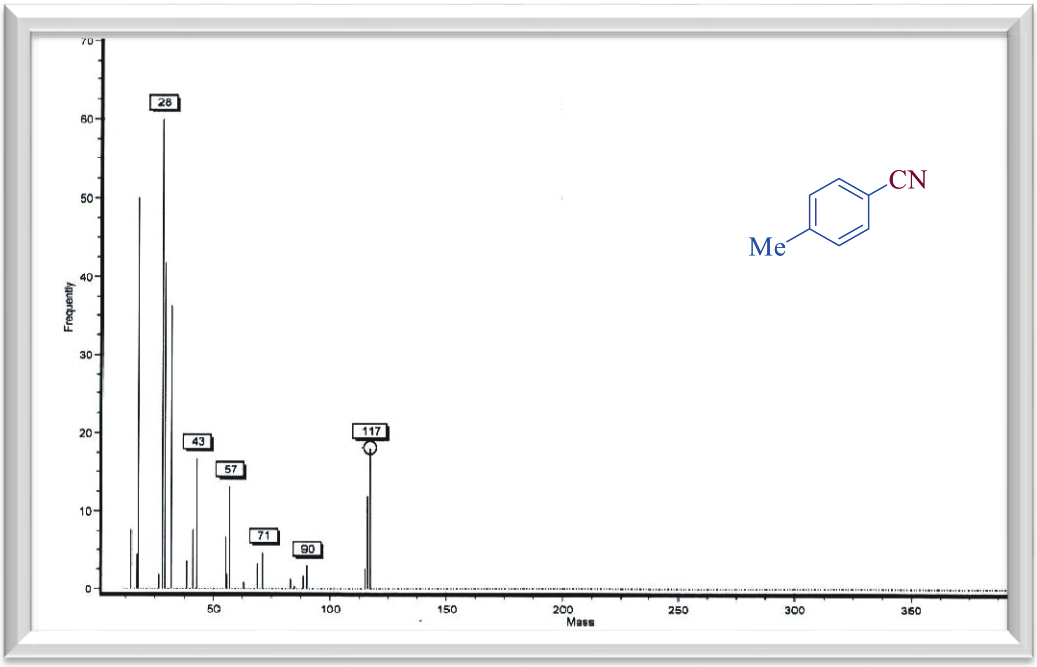

Fig S 27: Mass Spectrum of 4-Methylbenzonitrile (Table3, Entry 7)

3-Methylbenzonitrile [8]

3-Methylbenzonitrile (Table 3, Entry 8). Colorless Oil (Lit.[8] Oil); 0.1076g (92%); FT-IR (neat): 3059, 3026, 2924, 2859, 2229(CN), 1600, 1584, 1484, 1453, 1382, 1285, 1151, 1097, 1040, 922, 882, 788, 686, 579, 447 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.37–7.30 (m, 3 H), 2.34 (q, J = 8.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 139.1, 133.6, 132.4, 129.2, 128.9, 118.9, 112.1, 21.1.

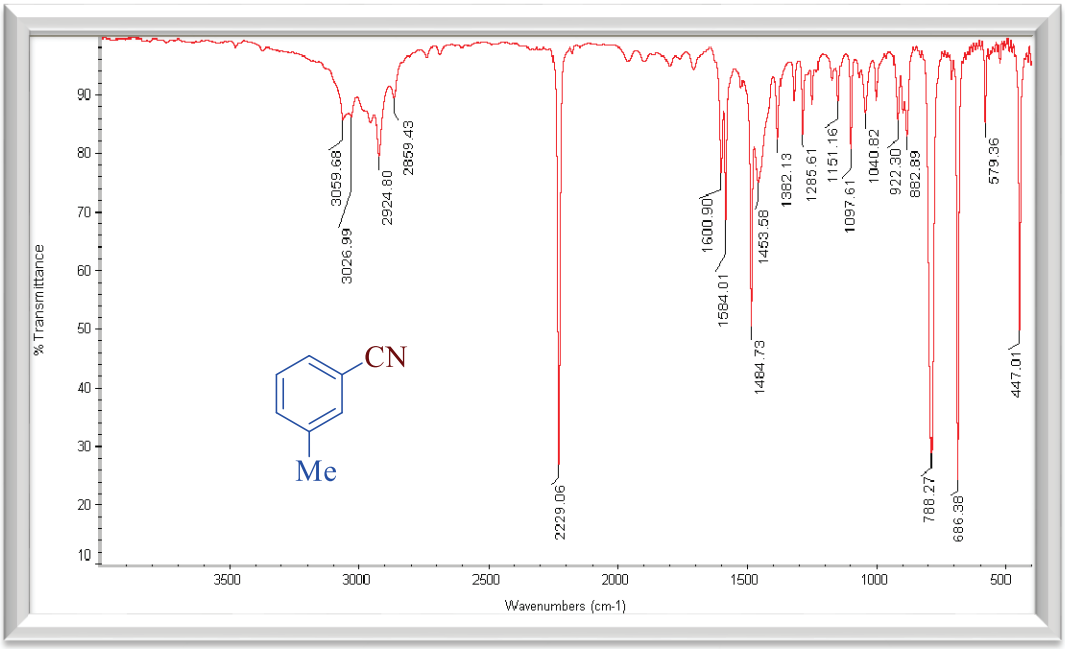

Fig S 28: FT-IR (neat) Spectrum of 3-Methylbenzonitrile (Table 3, Entry 8)

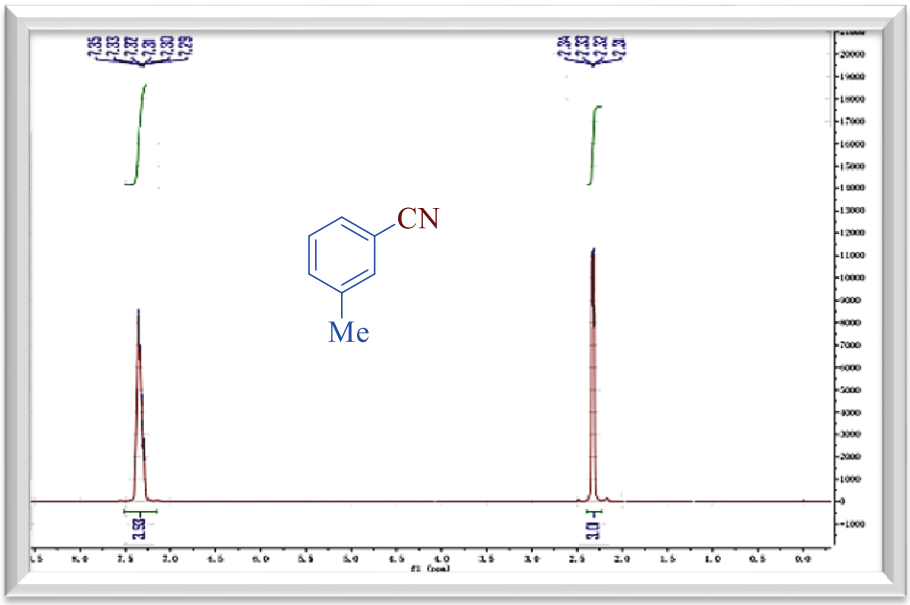

Fig S 29: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3-Methylbenzonitrile (Table 3, Entry 8)

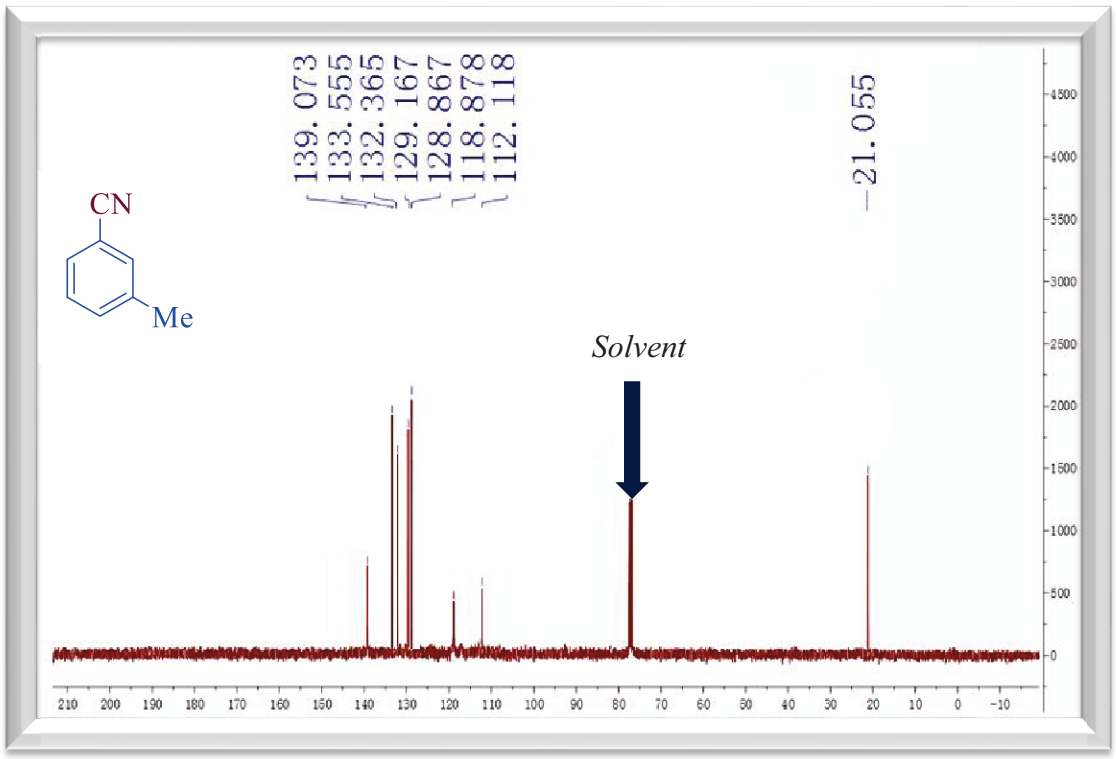

Fig S 30: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 3-Methylbenzonitrile (Table 3, Entry 8)

4-Isopropylbenzonitrile [2]

4-Isopropylbenzonitrile (Table 3, Entry 9). Oil (Lit.[2] Oil); 0.1348g (93%); FT-IR (neat): 3078, 2965, 2929, 2872, 2228 (CN), 1737, 1684, 1606, 1503, 1460, 1366, 1244, 1197, 1100, 1053, 1018, 838, 761, 695, 566 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm]= 7.60-7.52 (d, 2H), 7.34-7.29 (d, 2H), 2.95 (dt, J = 13.8, 6.9 Hz, 1H), 1.25 (d, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ[ppm] =154.4, 132.3, 127.4, 119.2, 109.7, 34.5, 23.6; MS (EI) m/z (%): 145 $[M]^+$.

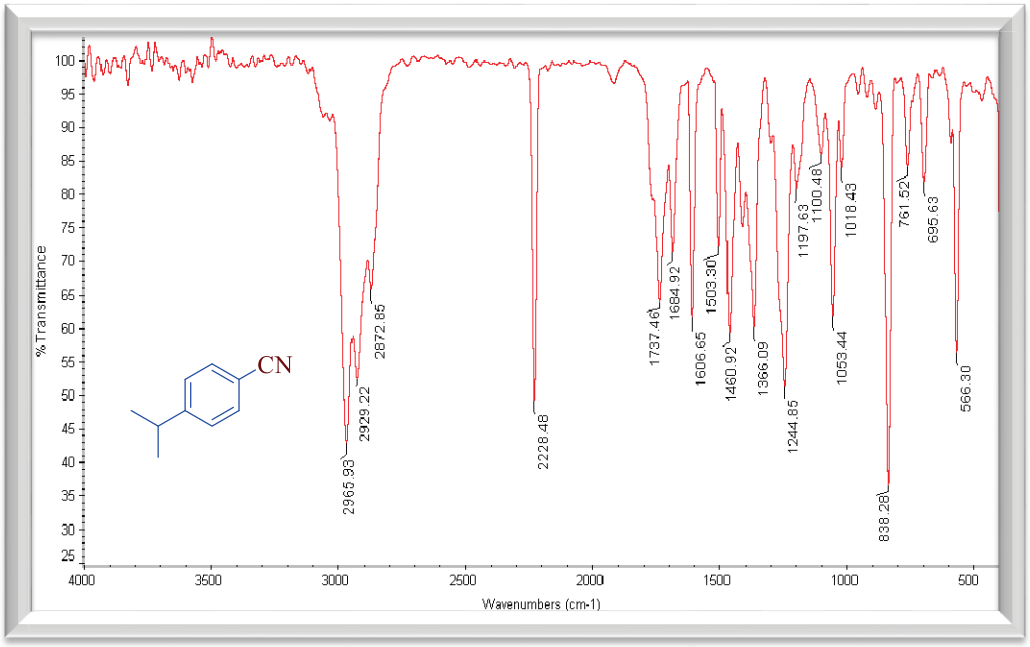

Fig S 31: FT-IR (neat) spectrum of 4-Isopropylbenzonitrile (Table 3, Entry 9)

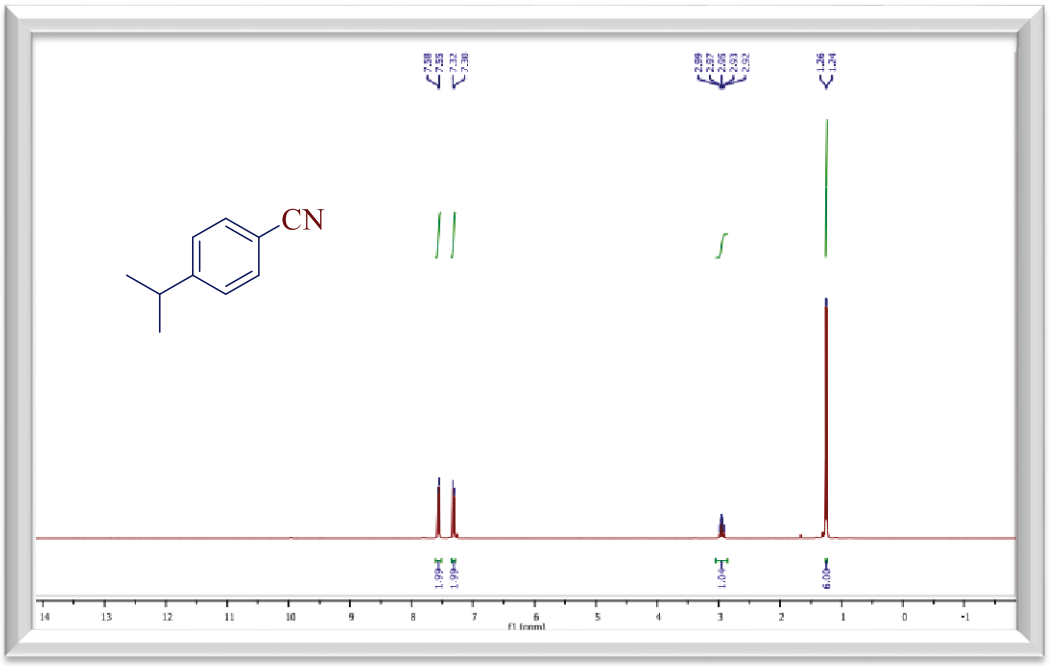

Fig S 32: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 4-Isopropylbenzonitrile (Table 3, Entry 9)

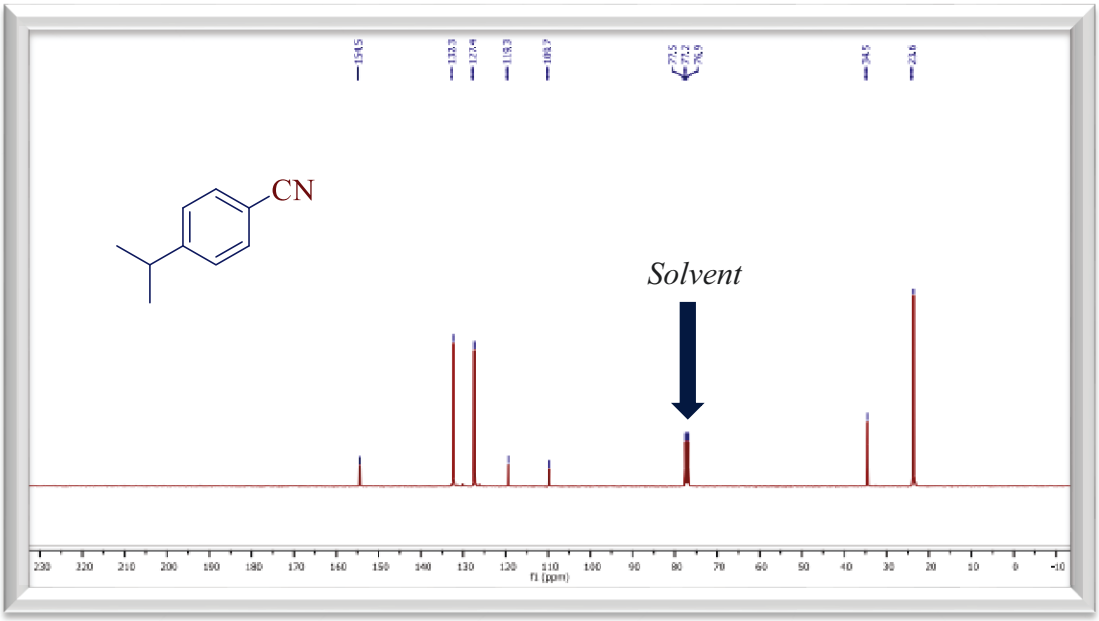

Fig S 33: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 4-Isopropylbenzonitrile (Table 3, Entry 9)

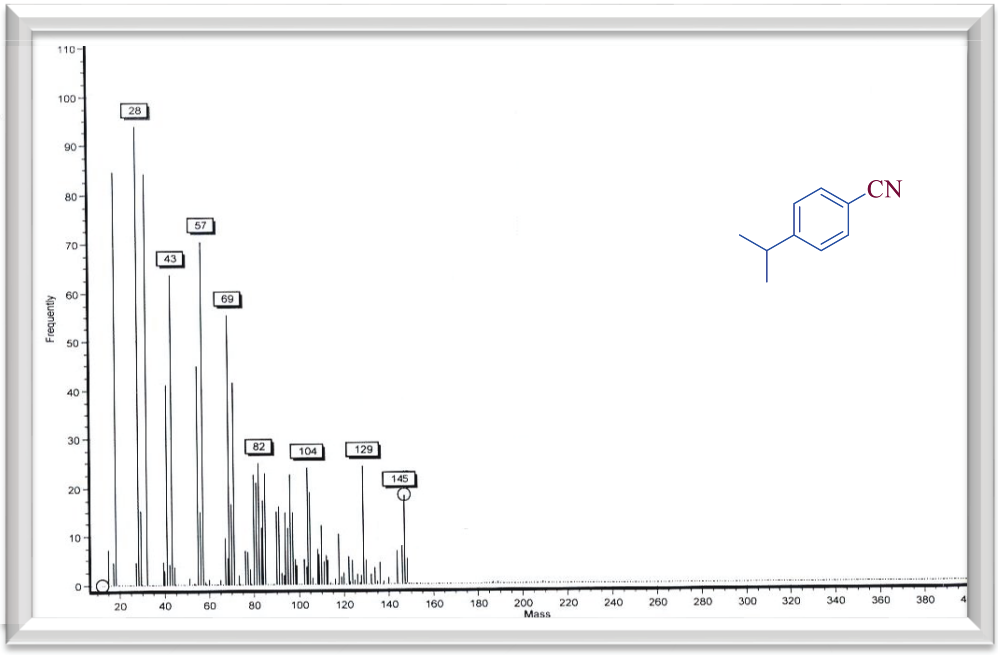

Fig S 34: Mass Spectrum of 4-Isopropylbenzonitrile (Table 3, Entry 9)

5-Bromo-2-hydroxybenzonitrile [9]

5-Bromo-2-hydroxybenzonitrile (Table 3, Entry 10). 0.1910g (97%); Mp 155-156 ˚C (Lit.[9] 156 - 157 ˚C); FT-IR (KBr): 3456, 3285, 3096, 3064, 2235(CN), 1899, 1748, 1683, 1646, 1597, 1489, 1407, 1349, 1297, 1238, 1116, 878, 821, 757, 638, 485 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6): δ [ppm]= 11.70 (s, 1H), 7.80 (d, 1H), 7.60 (d, 1H), 6.93 (d, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ[ppm] =160, 137, 134, 118, 115, 109, 100.

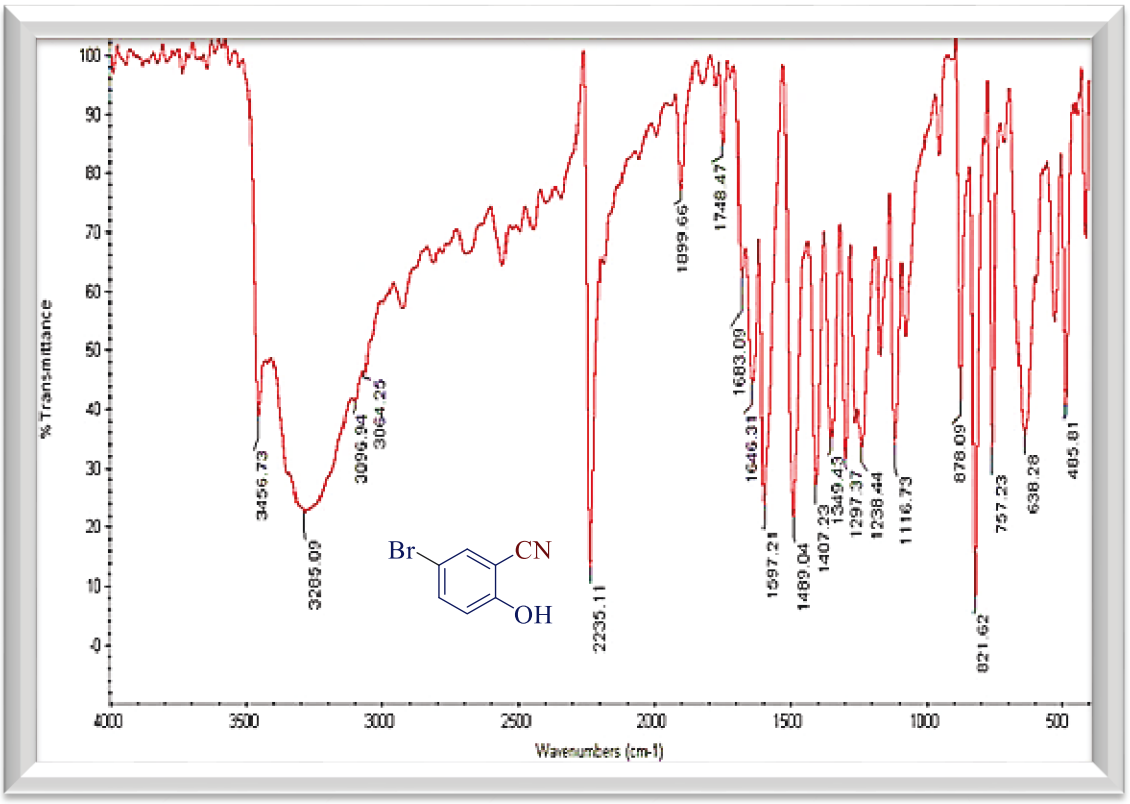

Fig S 35: FT-IR (KBr) spectrum of 5-Bromo-2-hydroxybenzonitrile (Table 3, Entry 10)

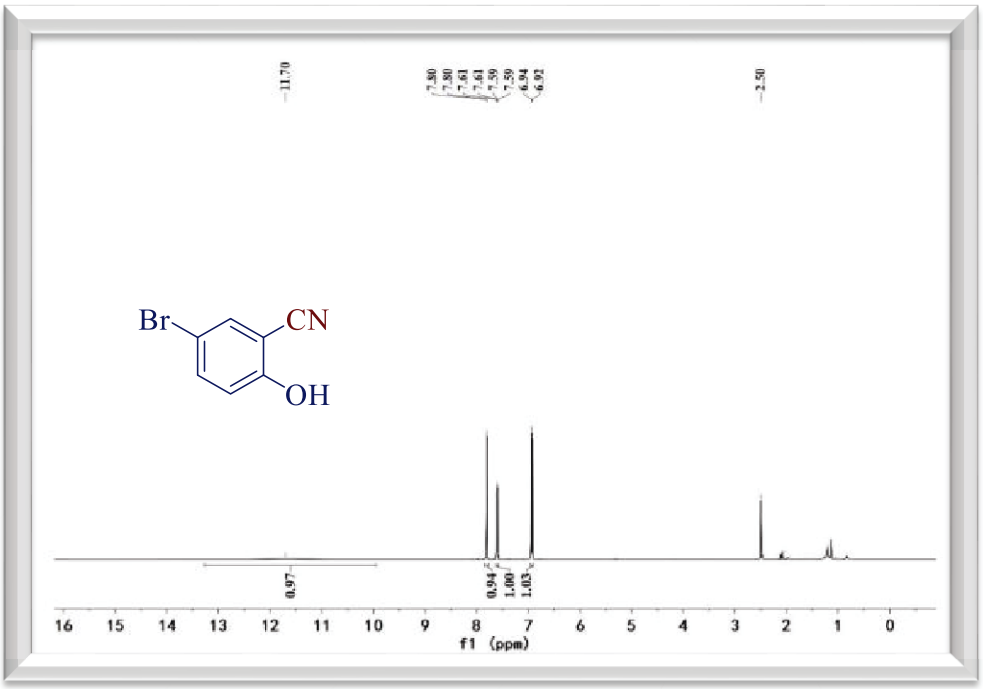

Fig S 36: ^{1}H NMR Spectrum (600 MHz, DMSO-d_6) of 5-Bromo-2-hydroxybenzonitrile (Table 3, Entry 10)

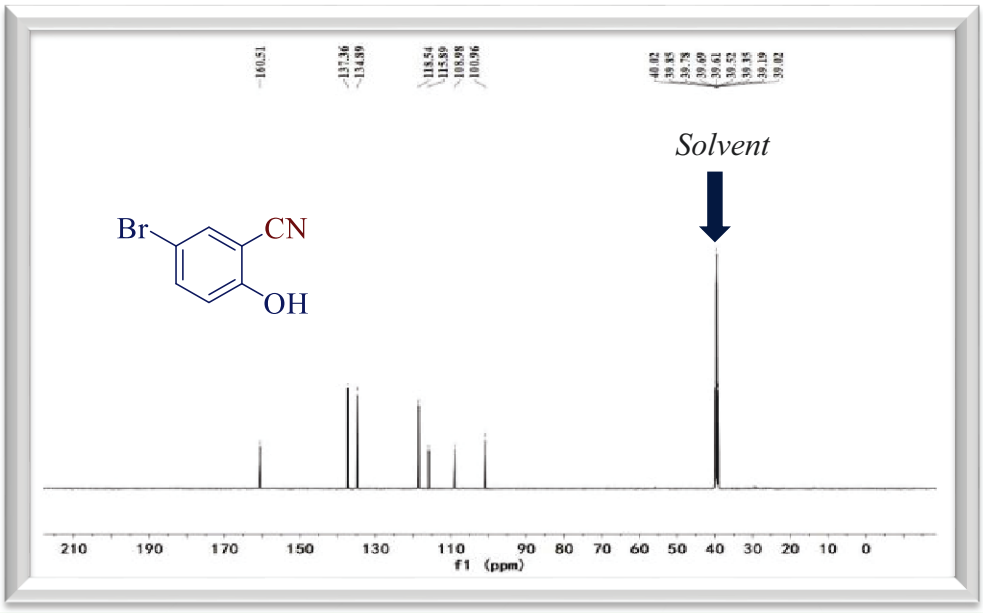

Fig S 37: ^{13}C NMR Spectrum (150 MHz, DMSO-d_6) of 5-Bromo-2-hydroxybenzonitrile (Table 3, Entry 10)

4-Iodobenzonitrile [10]

4-Iodobenzonitrile (Table 3, Entry 11). 0.2166g (95%); Mp 127 ˚C (Lit.[10] 124-128˚C); FT-IR (KBr): 3395, 3076, 2226(CN), 1911, 1793, 1642, 1577, 1499, 1474, 1390, 1273, 1055, 1010, 976, 818, 690, 540, 524, 428 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm]=7.41 (d, J = 8.3 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm]= 138.0, 132.7, 117.7, 111.2, 99.8; MS (EI) m/z (%):228 $[M]^+$.

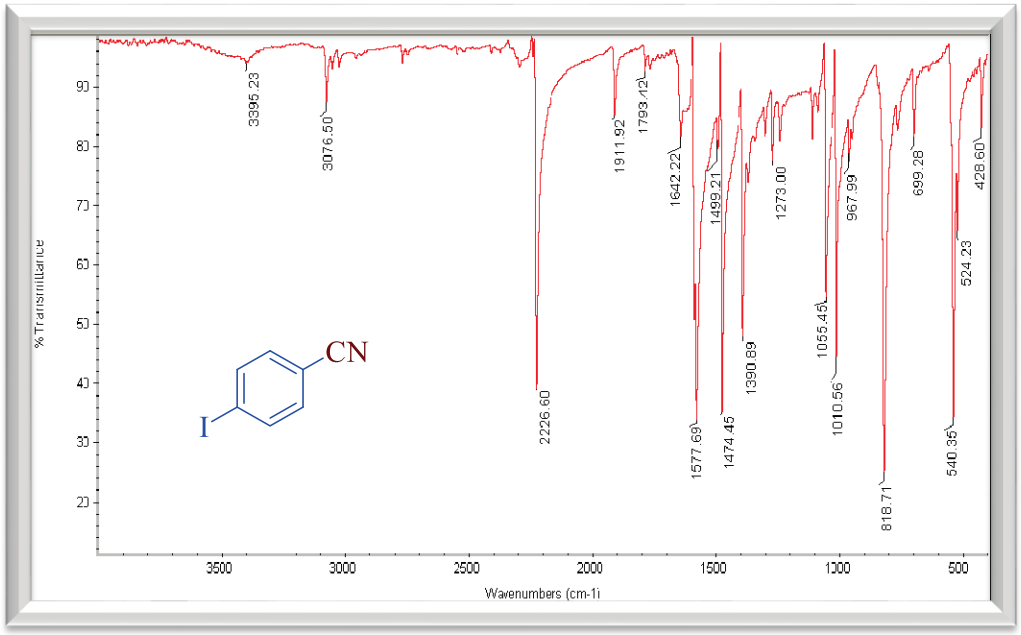

Fig S 38: FT-IR (KBr) spectrum of 4-Iodobenzonitrile (Table 3, Entry 11)

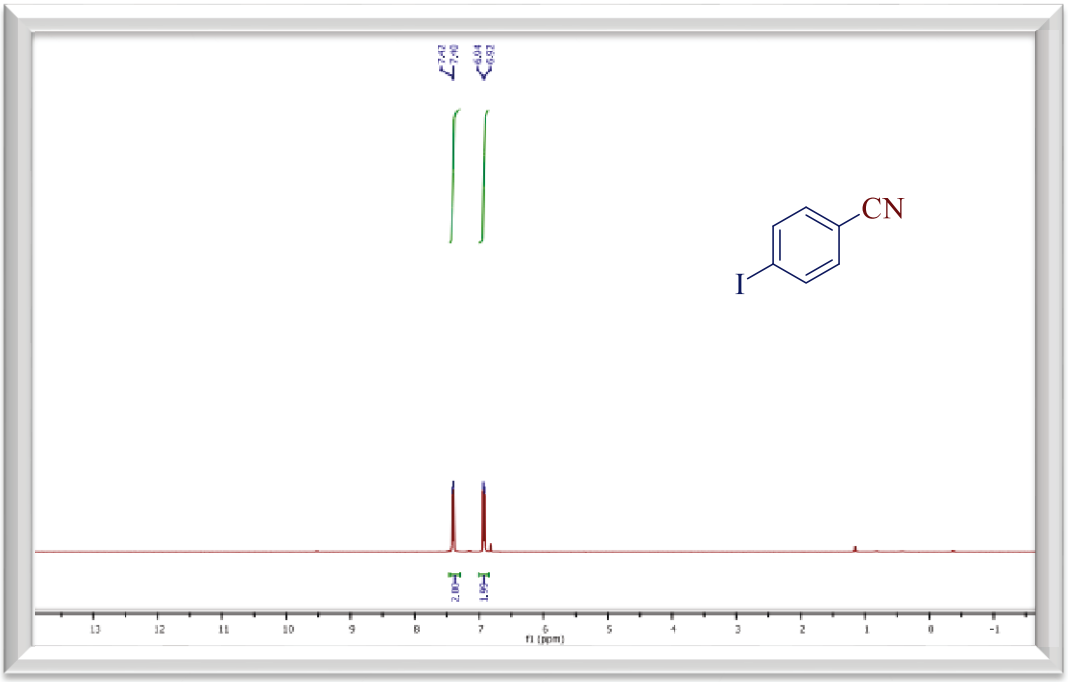

Fig S 39: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 4-Iodobenzonitrile (Table 3, Entry 11)

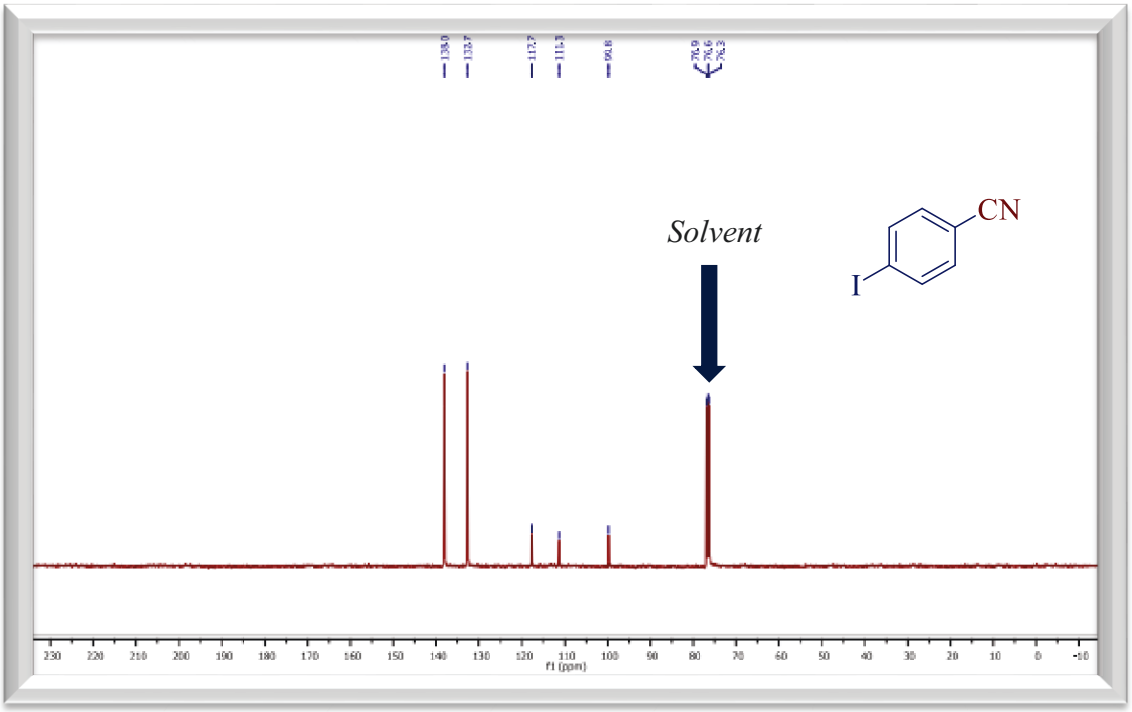

Fig S 40: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 4-Iodobenzonitrile (Table 3, Entry 11)

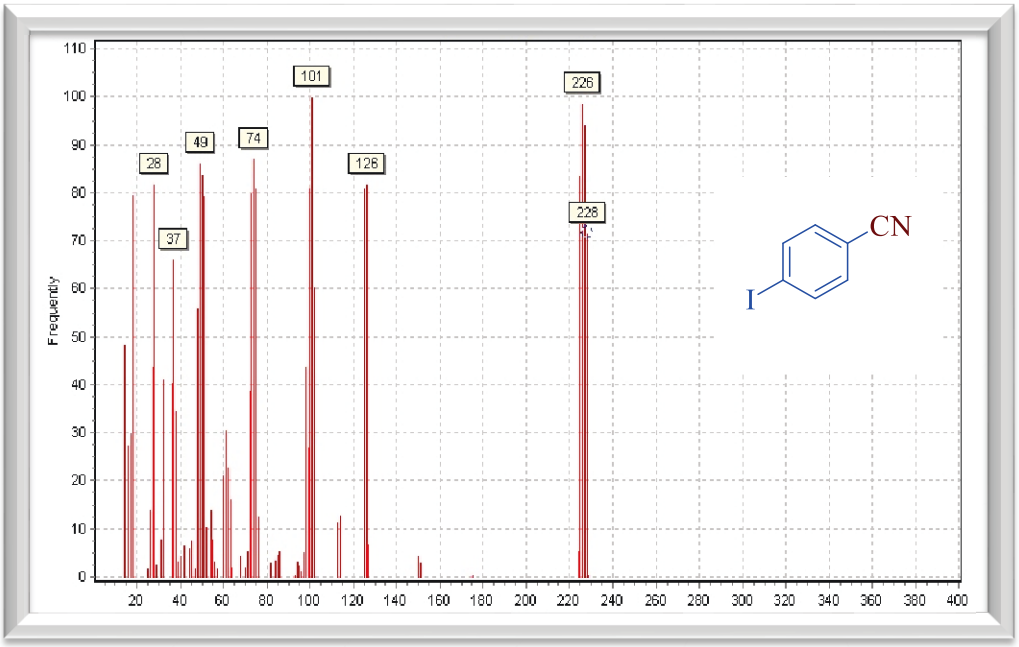

Fig S 41: Mass Spectrum of 4-Iodobenzonitrile (Table 3, Entry 11)

3-Bromobenzonitrile [11]

3-Bromobenzonitrile (Table 3, Entry 12). 0.1665g (92%); Mp 39˚C (Lit[11]. 38-40 ˚C); FT-IR (KBr): 3418, 3068, 2953, 2925, 2853, 2232(CN), 1700, 1592, 1563, 1471, 1409, 1382, 1266, 1191, 1076, 997, 915, 883, 820, 809, 788, 677, 577, 440 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] =7.79 (t, J = 1.56 Hz, 1H), 7.74 (ddd, J = 8.15 Hz, J = 1.84 Hz, J = 1.05 Hz, 1H), 7.60 (dt, J = 7.76 Hz, J = 1.13 Hz, 1H), 7.36 (t, J = 7.94 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$,): δ [ppm] = 136.3, 134.9, 130.9, 130.8, 123.1, 117.5, 114.4.

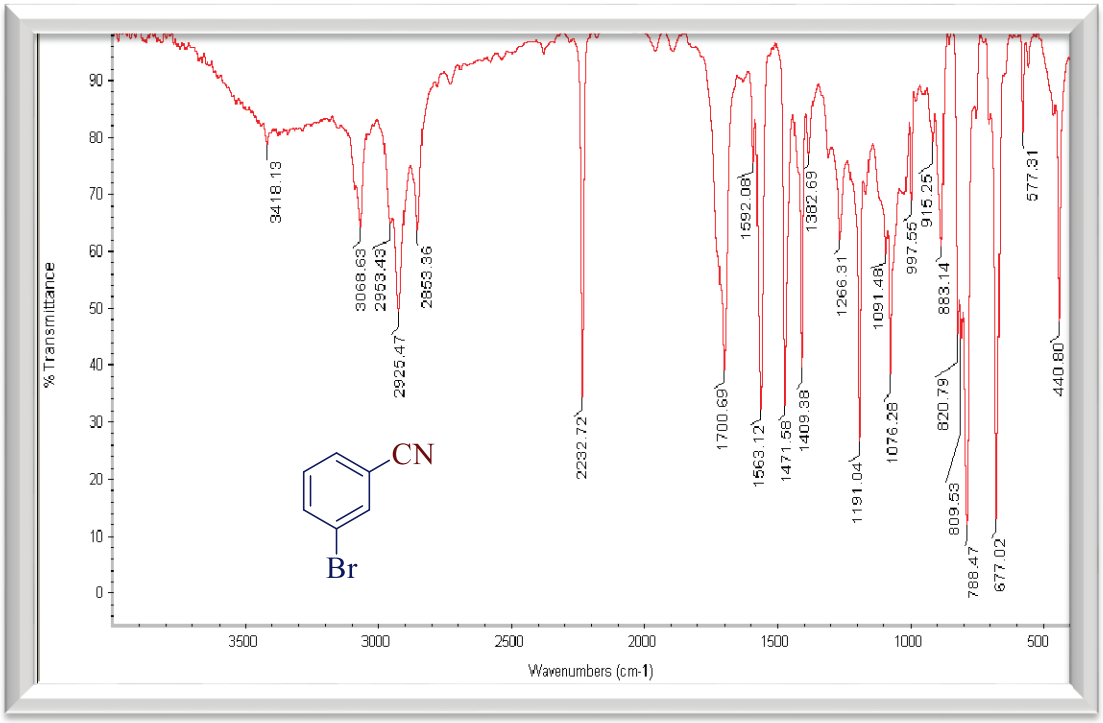

Fig S 42: FT-IR (KBr) spectrum of 3-Bromobenzonitrile (Table 3, Entry 12)

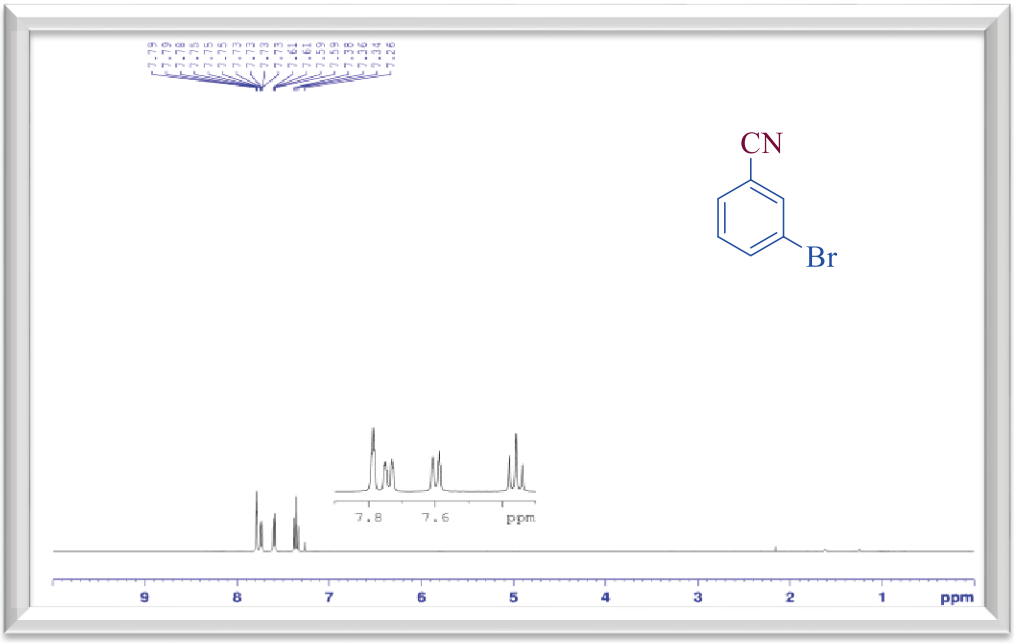

Fig S 43: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 3-Bromobenzonitrile (Table 3, Entry 12)

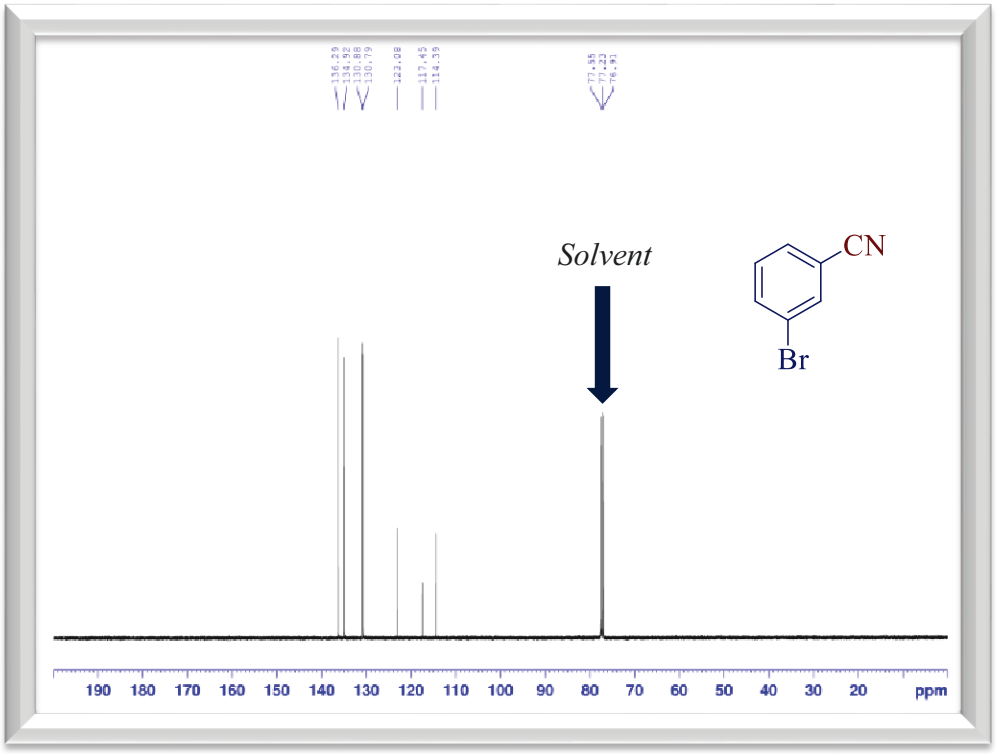

Fig S 44: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 3-Bromobenzonitrile (Table 3, Entry 12)

4-Clorobenzonitrile [6]

4-Clorobenzonitrile (Table 3, Entry 13). 0.1315g (96%); Mp 90-92 ˚C (Lit.[6] 92 ˚C); FT-IR (KBr): 3086, 3043, 2974, 2218 (CN), 1909, 1783, 1662, 1584, 1481, 1393, 1267, 1180, 1083, 1009, 826, 703, 580, 539 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.61 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 139.5, 133.3, 129.6, 117.9, 110.7; MS (EI) m/z (%): 137 $[M]^+$.

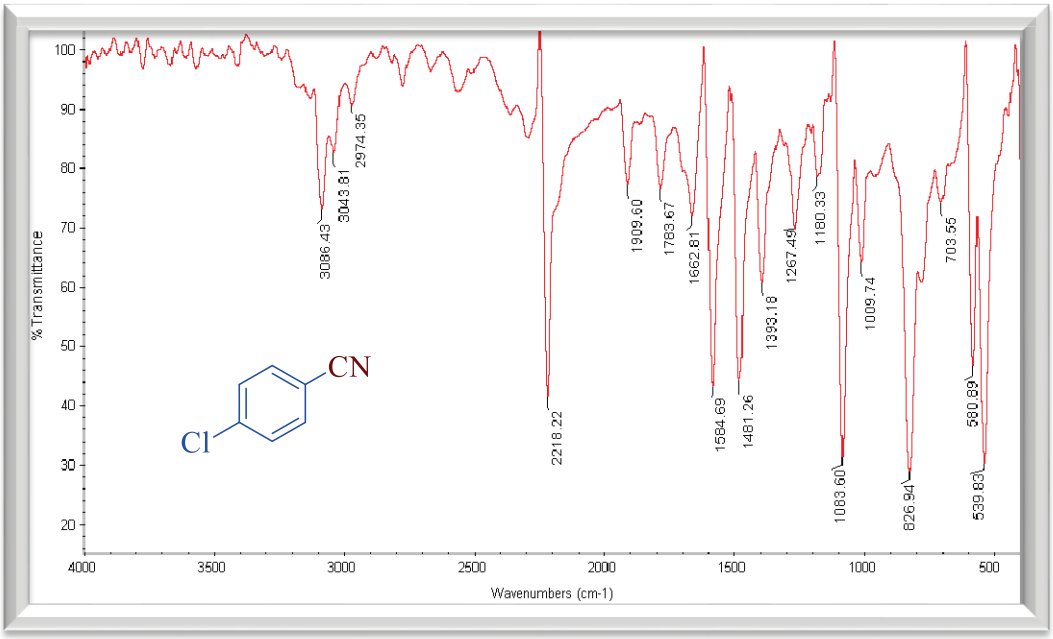

Fig S 45: FT-IR (KBr) Spectrum of 4-Chlorobenzonitrile (Table 3, Entry 13)

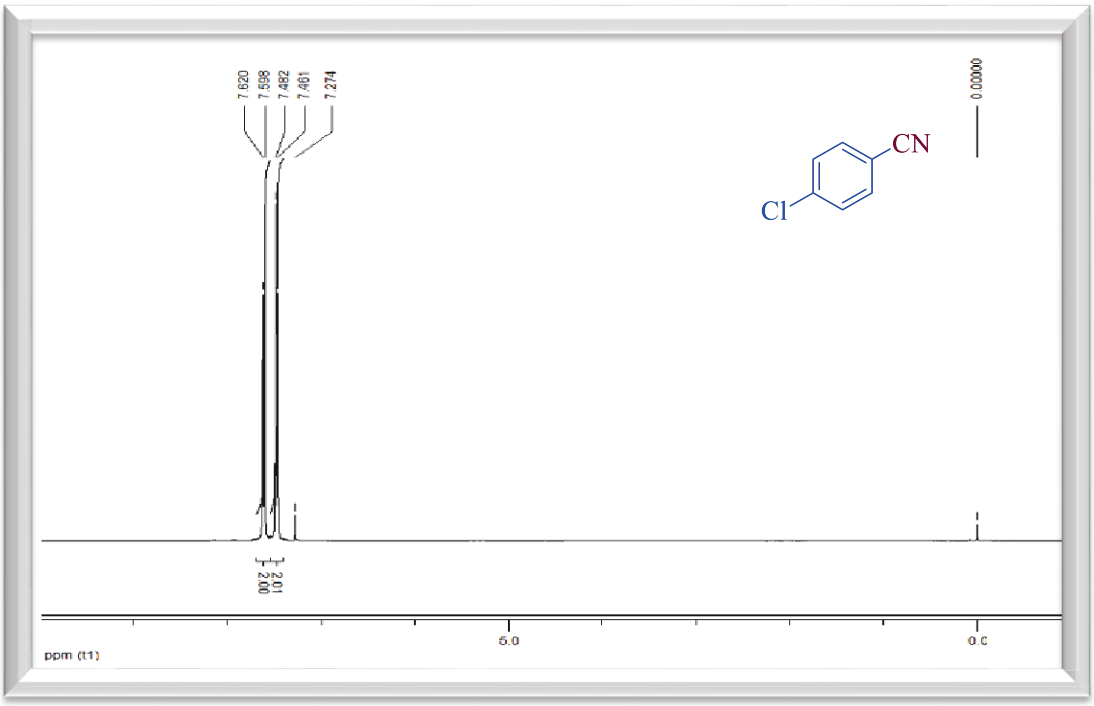

Fig S 46: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 4-Chlorobenzonitrile (Table 3, Entry 13)

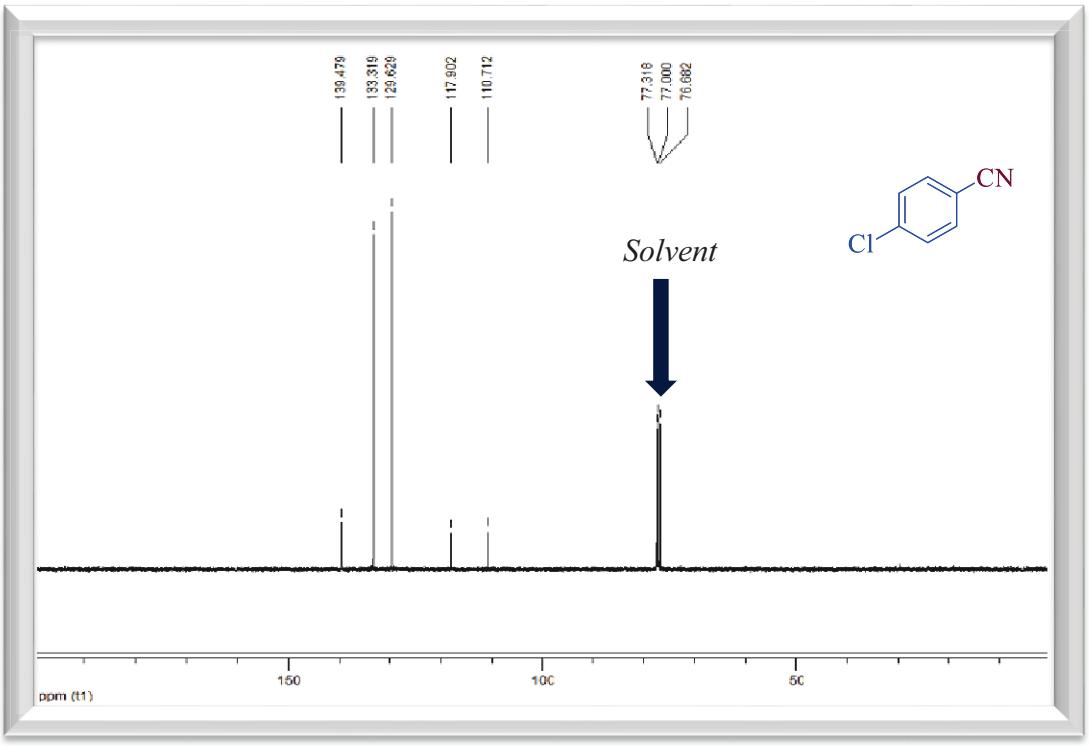

Fig S 47: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 4-Chlorobenzonitrile (Table 3, Entry 13)

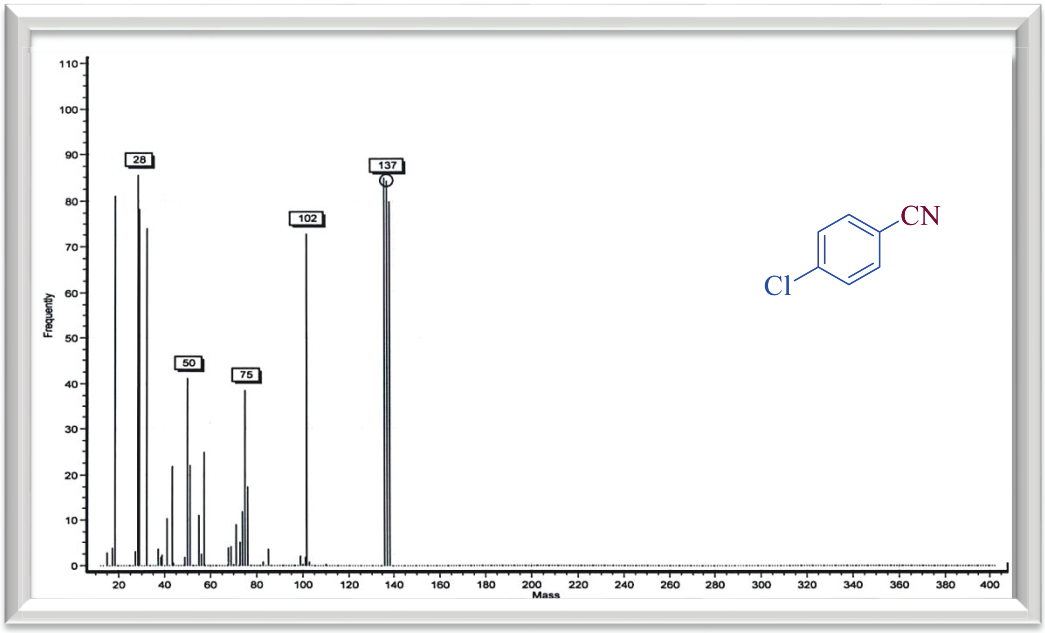

Fig S 48: Mass Spectrum of 4-Chlorobenzonitrile (Table 3, Entry 13)

2-Clorobenzonitrile [6]

2-Clorobenzonitrile (Table 3, Entry 14). 0.1246g (91%); Mp 41˚C (Lit.[6] 40-43 ˚C); FT-IR (KBr): 3064, 2926, 2859, 2226 (CN), 1582, 1469, 1437, 1339, 1275, 1200, 1135, 1059, 947, 758, 675, 558, 453 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm]= 7.61 (d, J = 7.8 Hz, 1H), 7.44-7.49 (m, 2H), 7.31 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ[ppm]= 136.7, 133.9, 133.8, 129.9, 127.1, 115.8, 113.3; MS (EI) m/z (%): 137 $[M]^+$.

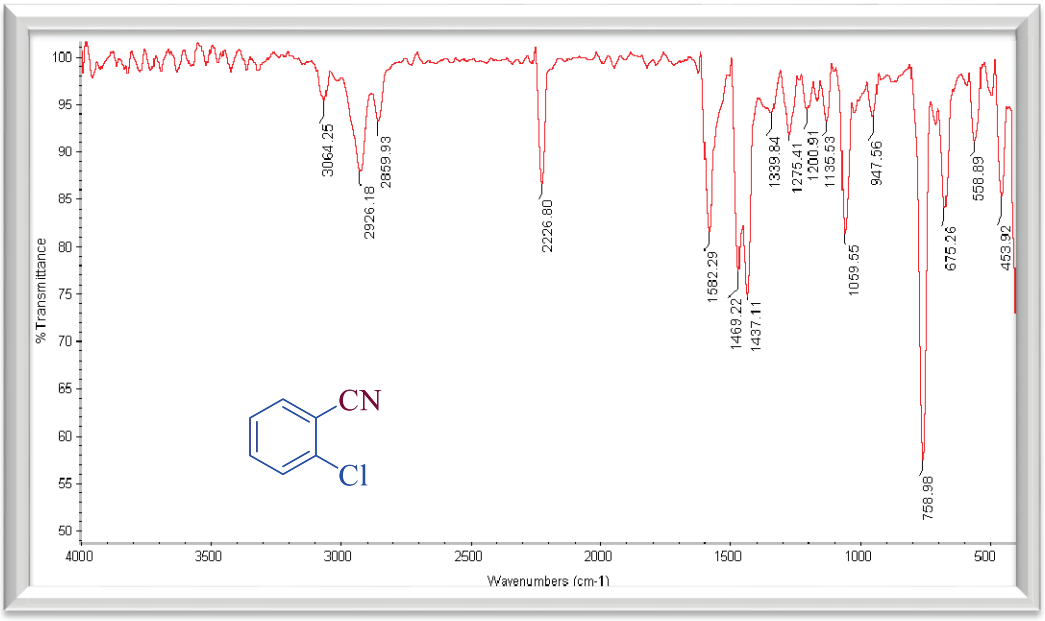

Fig S 49: FT-IR (KBr) Spectrum of 2-Chlorobenzonitrile (Table 3, Entry 14)

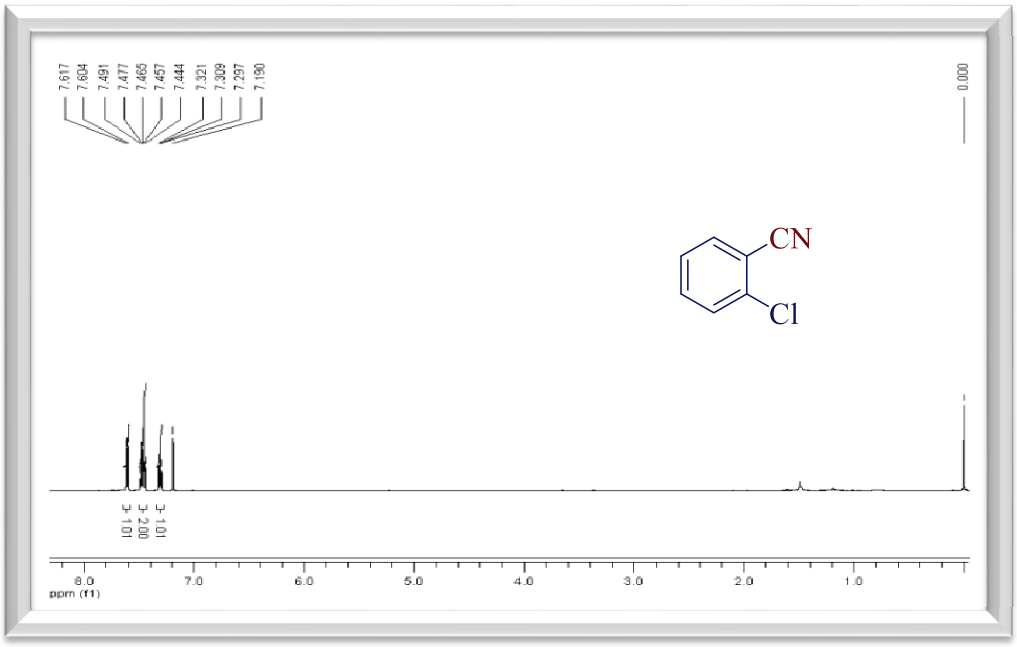

Fig S 50: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 2-Chlorobenzonitrile (Table 3, Entry 14)

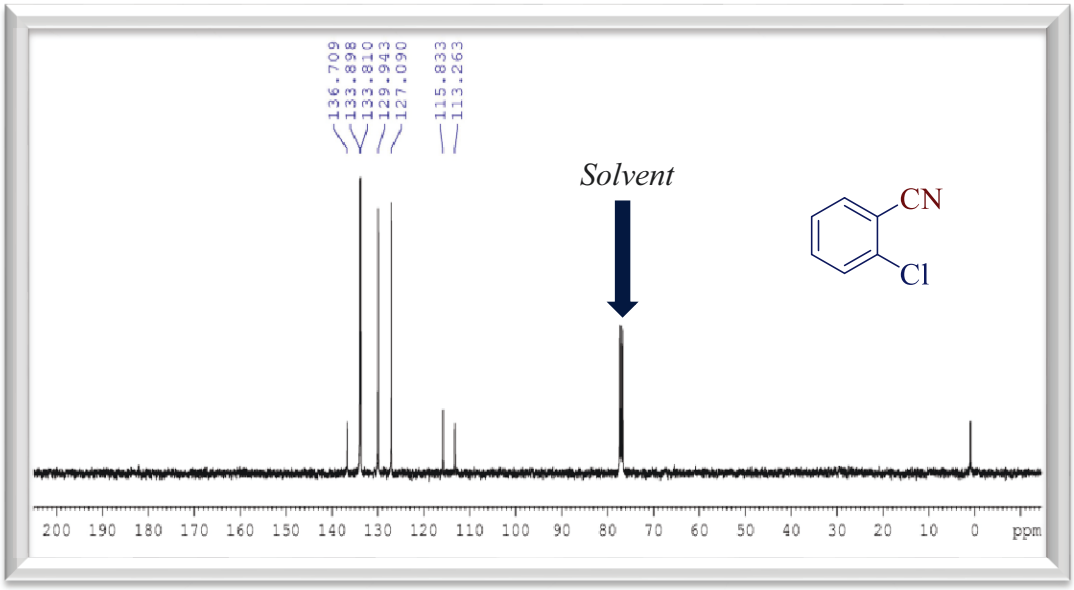

Fig S 51: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 2-Chlorobenzonitrile (Table 3, Entry 14)

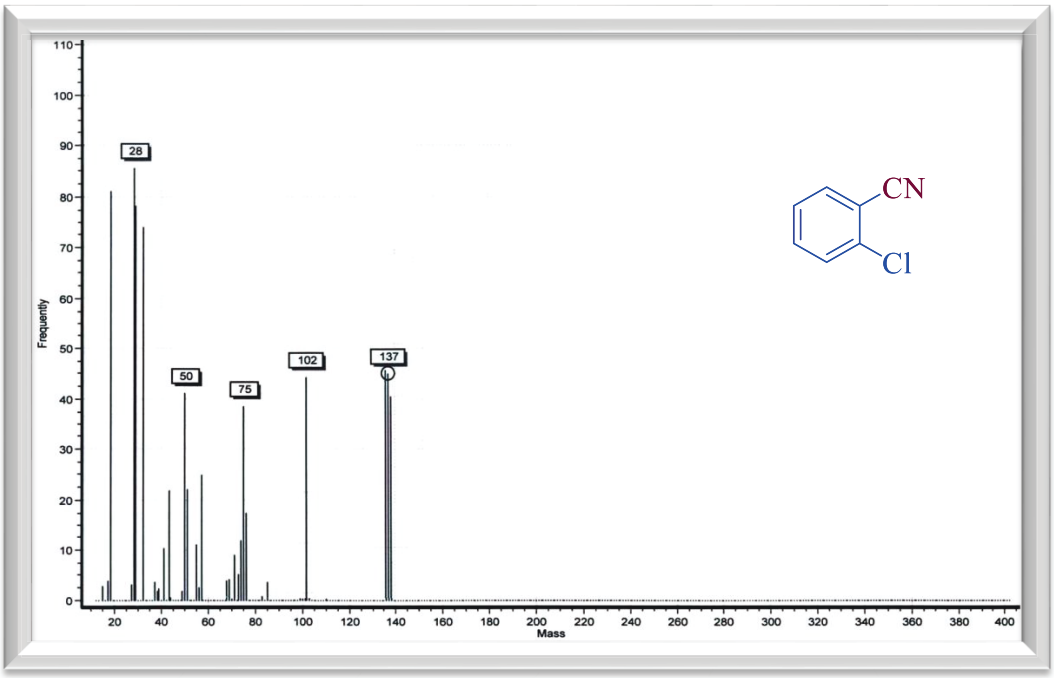

Fig S 52: Mass Spectrum of 2-Chlorobenzonitrile (Table 3, Entry 14)

4-Fluorobenzonitrile [12]

4-Fluorobenzonitrile (Table 3, Entry 15). Liquid (Lit[12]. Colorless Liquid); 0.1149g (95%); FT-IR (KBr):3362, 3117, 3068, 2962, 2925, 2232(CN), 1658, 1603, 1507, 1418, 1359, 1239, 1160, 1098, 1015, 841, 761, 685, 646, 564 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm]= 7.68-7.70 (m, 2H), 7.19 (t, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm]= 108.6 (d, J_{C-F} = 3.45 Hz), 116.9 (d, J_{C-F} = 22.65 Hz), 118.1, 134.7 (d, J_{C-F} = 9.3 Hz), 165.1 (d, J_{C-F} = 255 Hz).

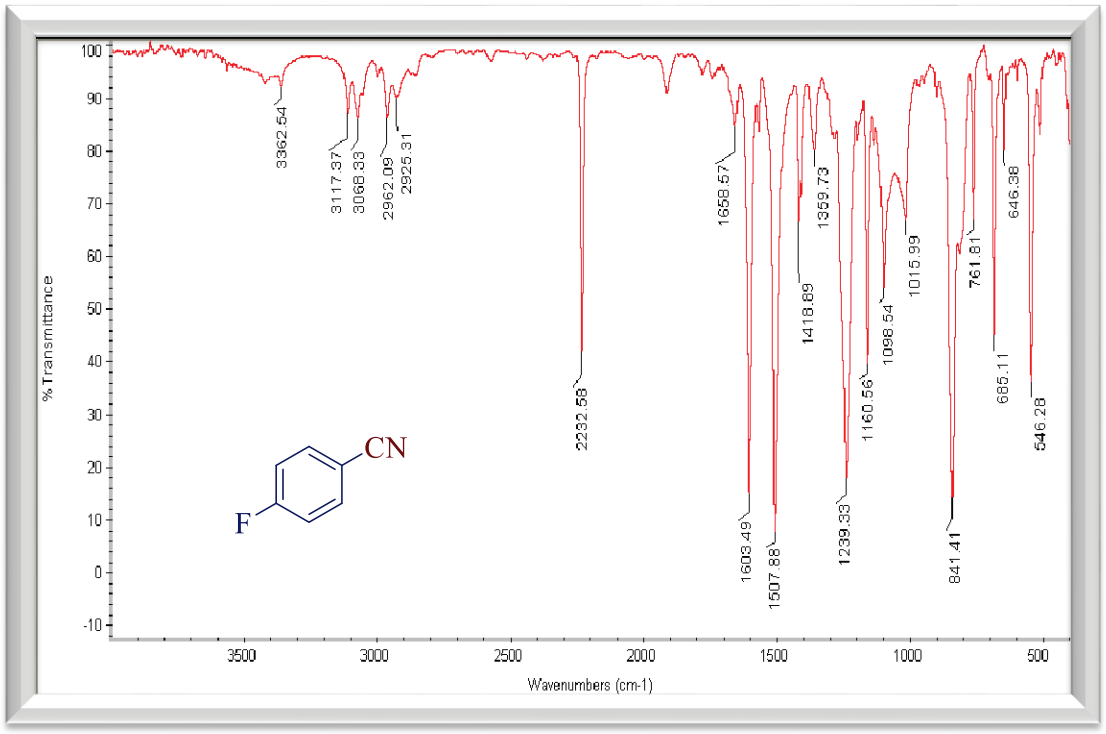

Fig S 53: FT-IR (KBr) Spectrum of 4-Fluorobenzonitrile (Table 3, Entry 15)

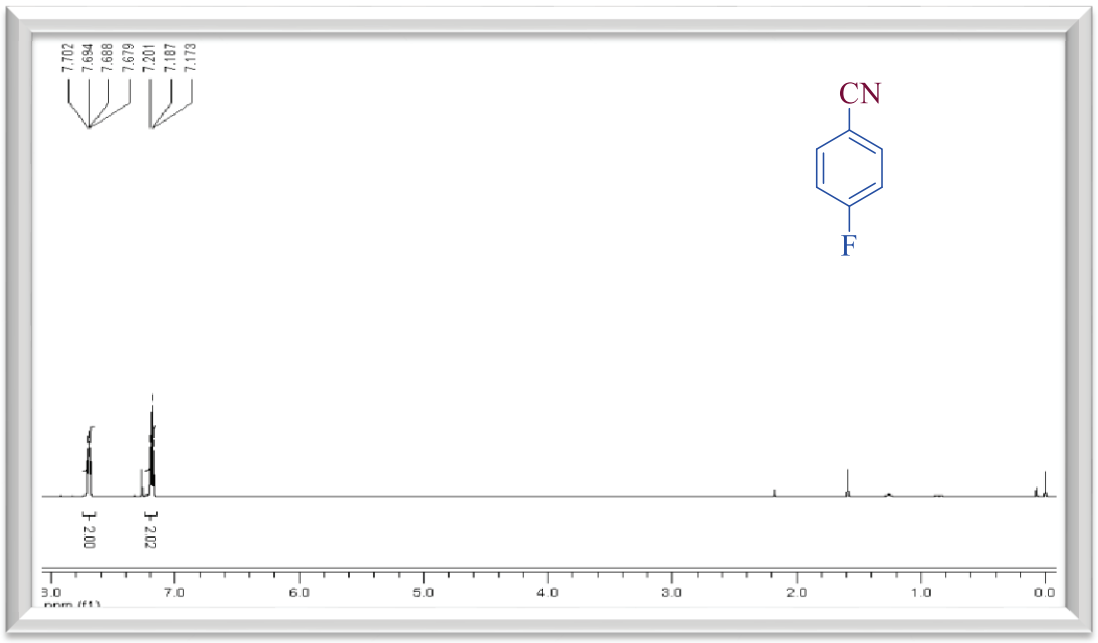

Fig S 54: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 4-Fluorobenzonitrile (Table 3, Entry 15)

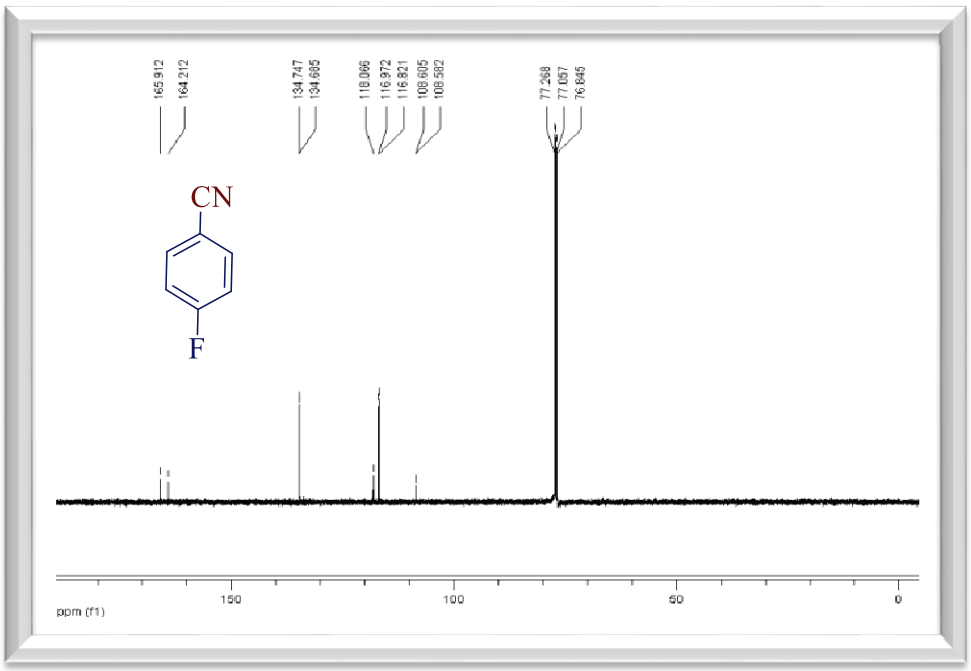

Fig S 55: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 4-Fluorobenzonitrile (Table 3, Entry 15)

1,4-Dicyanobenzene [13]

1,4-Dicyanobenzene (Table 3, Entry 16). 0.1190g (93%); Mp 225-227 ˚C (Lit.[13] 226-228˚C); FT-IR (KBr): 3096, 3050, 2962, 2924, 2854, 2230 (CN), 1941, 1809, 1692, 1500, 1402, 1276, 1198, 1025, 844, 641, 561 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.8 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 132.8, 117.0, 116.7; MS (EI) m/z (%): 128 $[M]^+$.

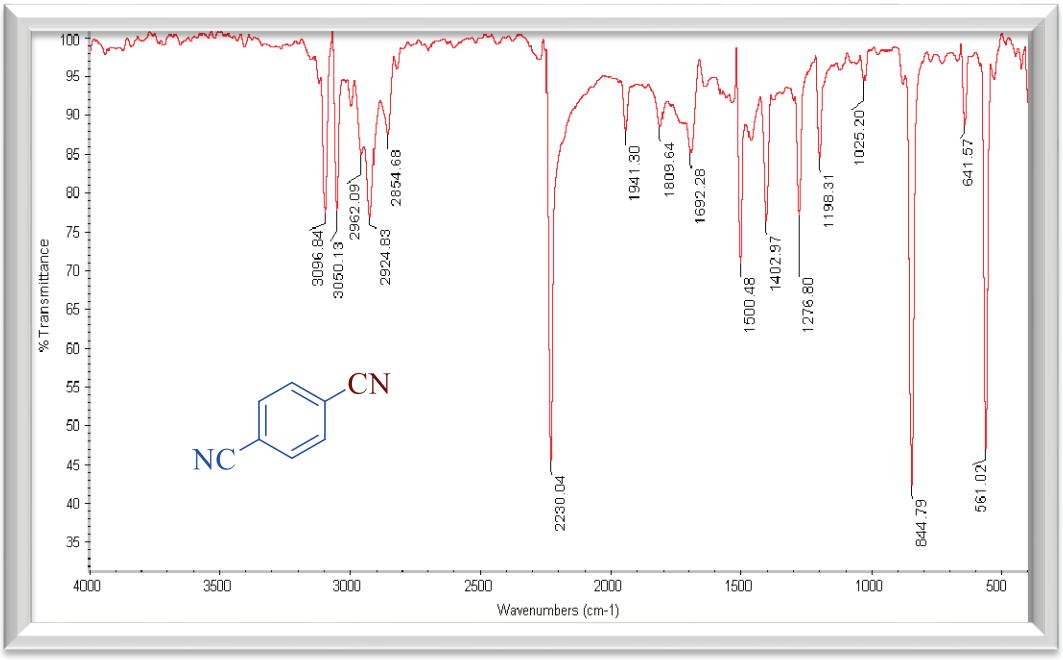

Fig S 56: FT-IR (KBr) Spectrum of 1,4-Dicyanobenzene (Table 3, Entry 16)

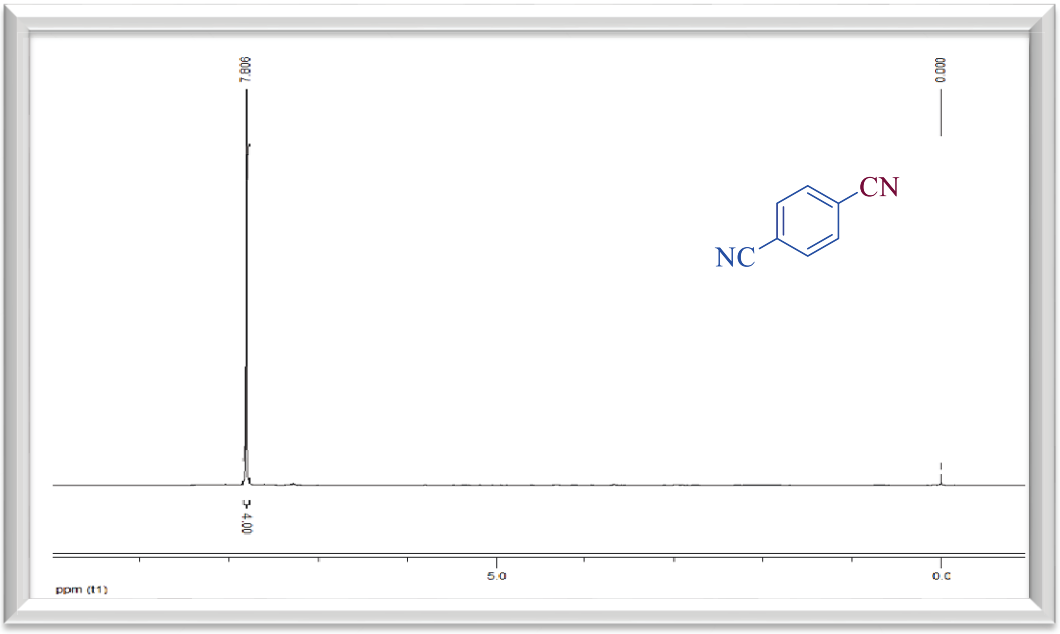

Fig S 57: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1,4-Dicyanobenzene (Table 3, Entry 16)

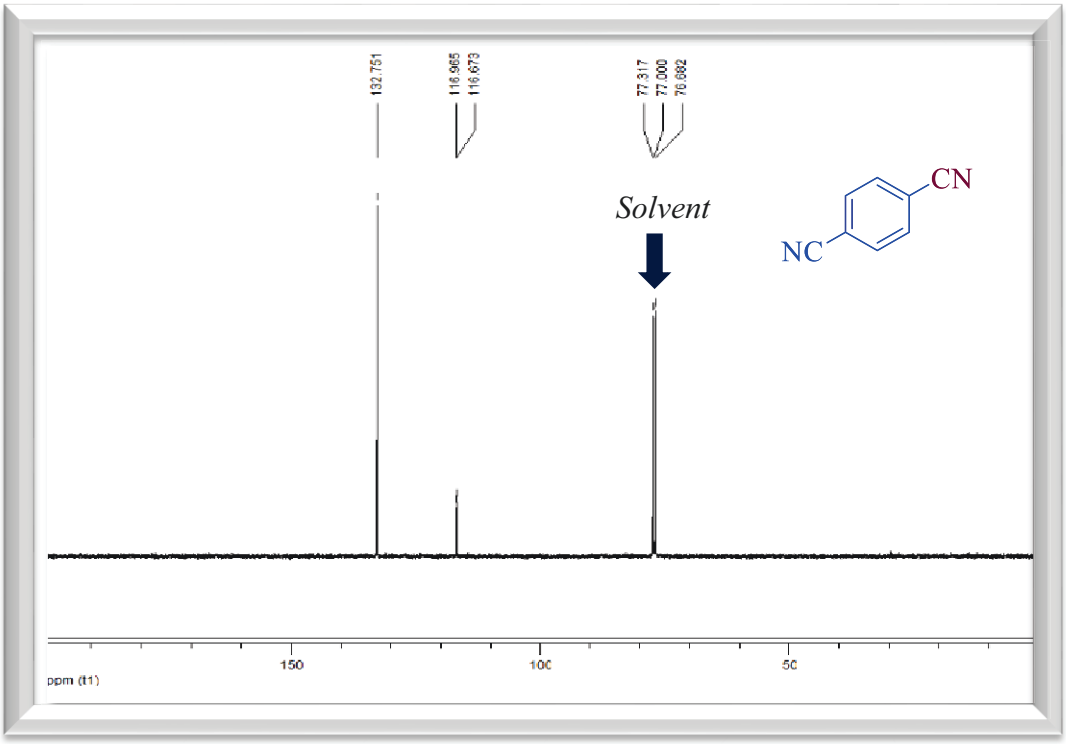

Fig S 58: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 1,4-Dicyanobenzene (Table 3, Entry 16)

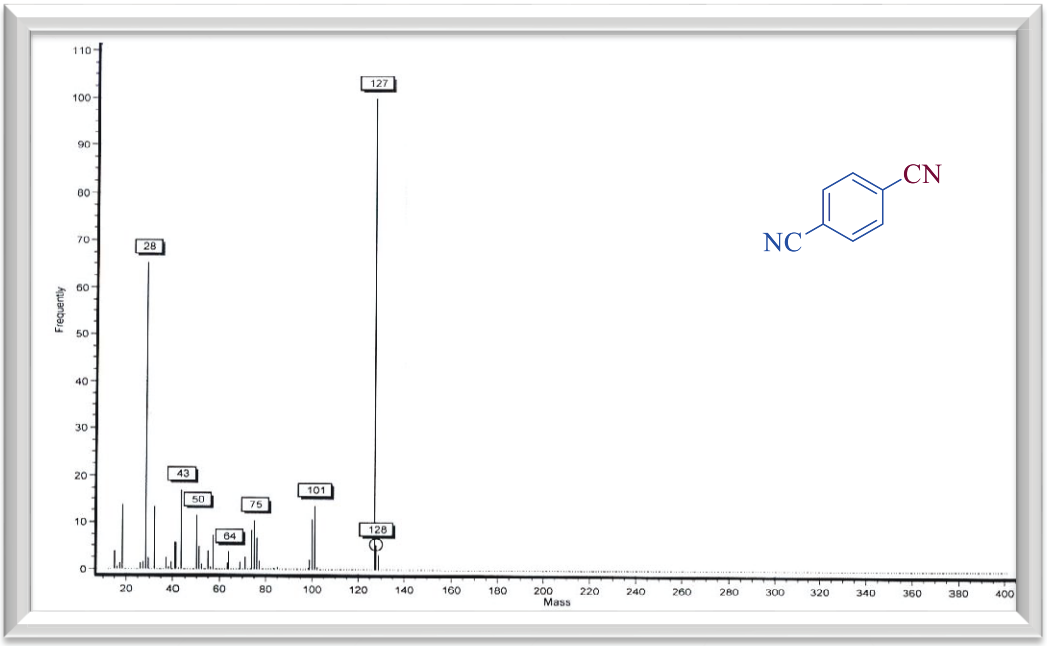

Fig S 59: Mass Spectrum of 1,4-Dicyanobenzene (Table 3, Entry 16)

4-Nitrobenzonitrile [14]

4-Nitrobenzonitrile (Table 3, Entry 17). 0.1406g (95%); Mp 147-148 ˚C (Lit.[14]149˚C); FT-IR (KBr): 3059, 2963, 2926, 2855, 2224 (CN), 1733, 1687,1584, 1503, 1380, 1343, 1240, 1157, 1062, 1013, 961, 806, 770, 693, 587, 457 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 8.37 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 150.0, 133.4, 124.2, 118.3, 116.8; Ms (EI) m/z (%): 148 $[M]^{+}$.

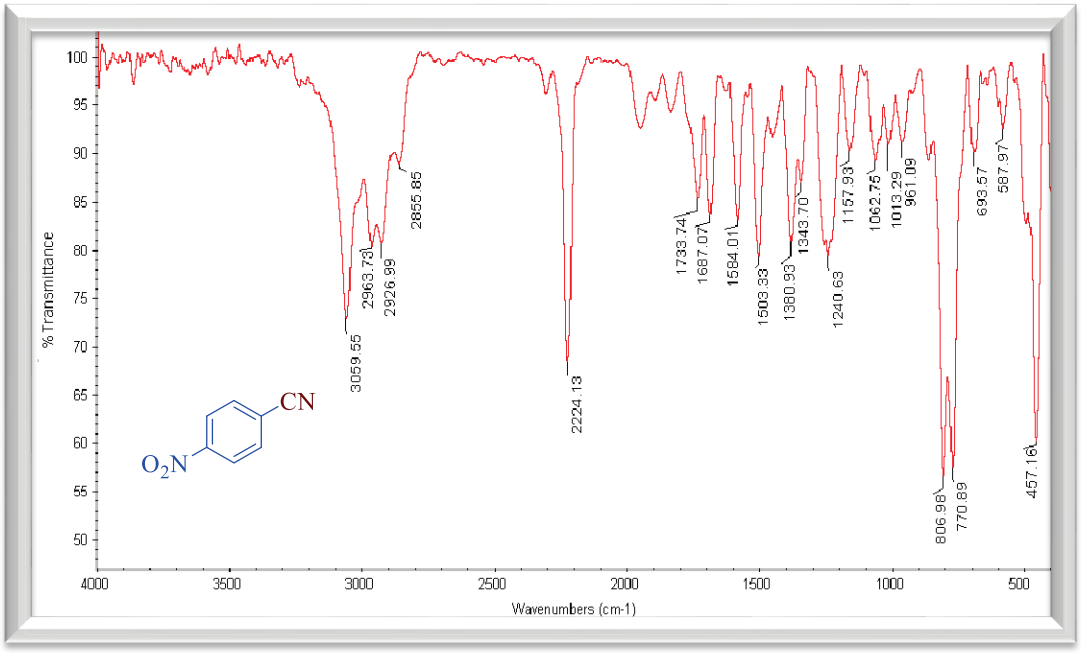

Fig S 60: FT-IR (KBr) Spectrum of 4-Nitrobenzonitrile (Table 3, Entry 17)

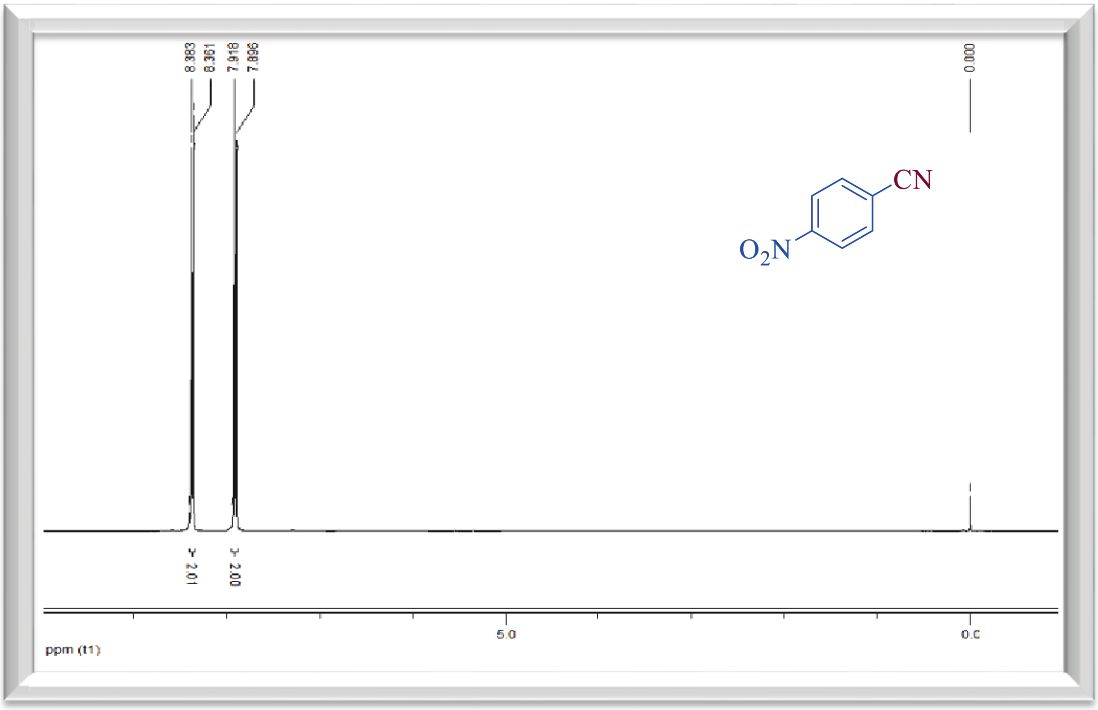

Fig S 61: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 4-Nitrobenzonitrile (Table 3, Entry 17)

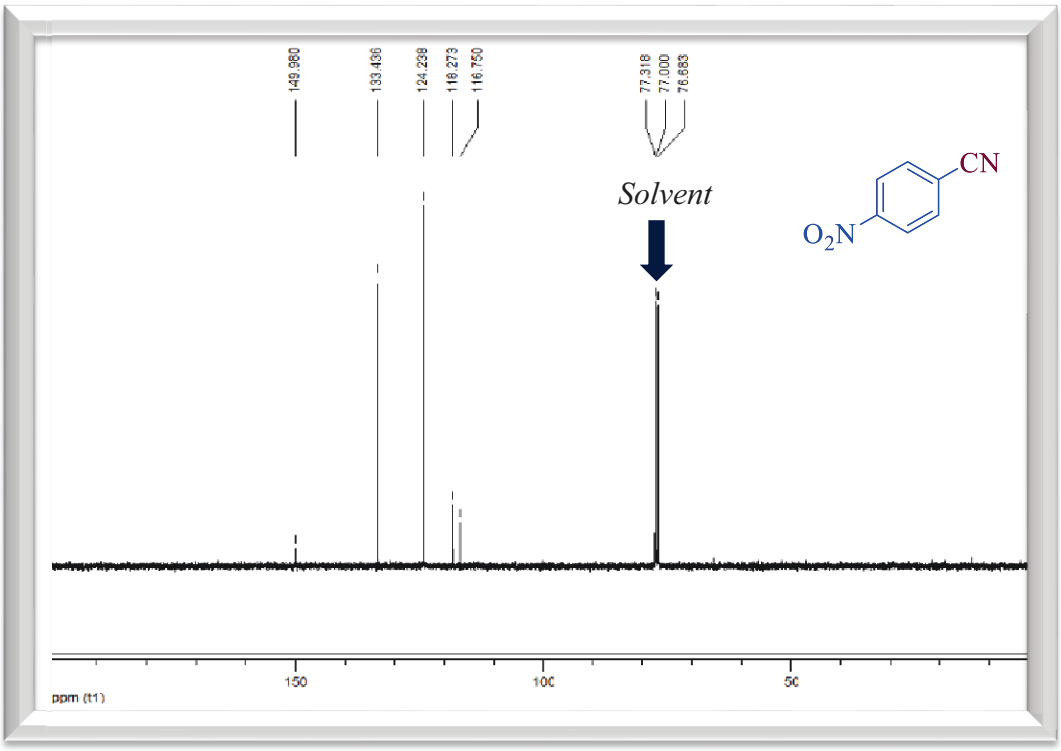

Fig S 62: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 4-Nitrobenzonitrile (Table 3, Entry 17)

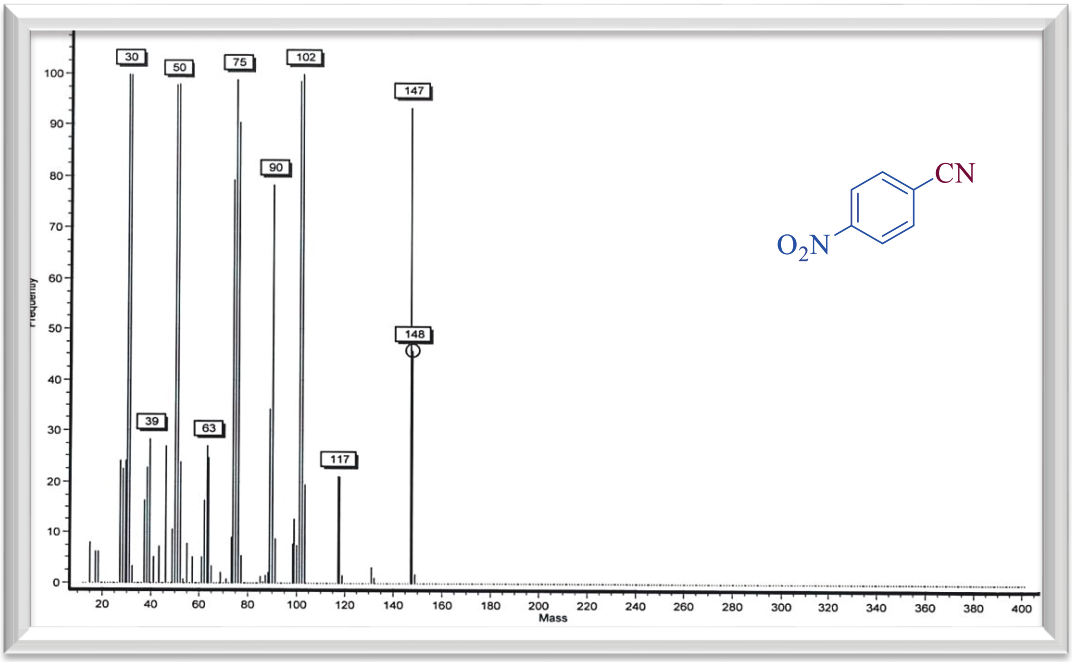

Fig S 63: Mass Spectrum of 4-Nitrobenzonitrile (Table 3, Entry 17)

4-Cyanopyridine [15]

4-Cyanopyridine (Table 3, Entry 18). 0.0956g (92%); Mp 75-76 ˚C (Lit.[15] 76-77˚C); FT-IR (KBr): 3056, 2239(CN), 1678, 1601, 1497, 1397, 1259, 1215, 1096, 993, 828, 738, 661, 564 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm]: 7.53 (dd, J1 = 1.6 Hz, J2 = 1.6 Hz, 2H), 8.79-8.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 150.7, 125.3, 120.3, 116.4.

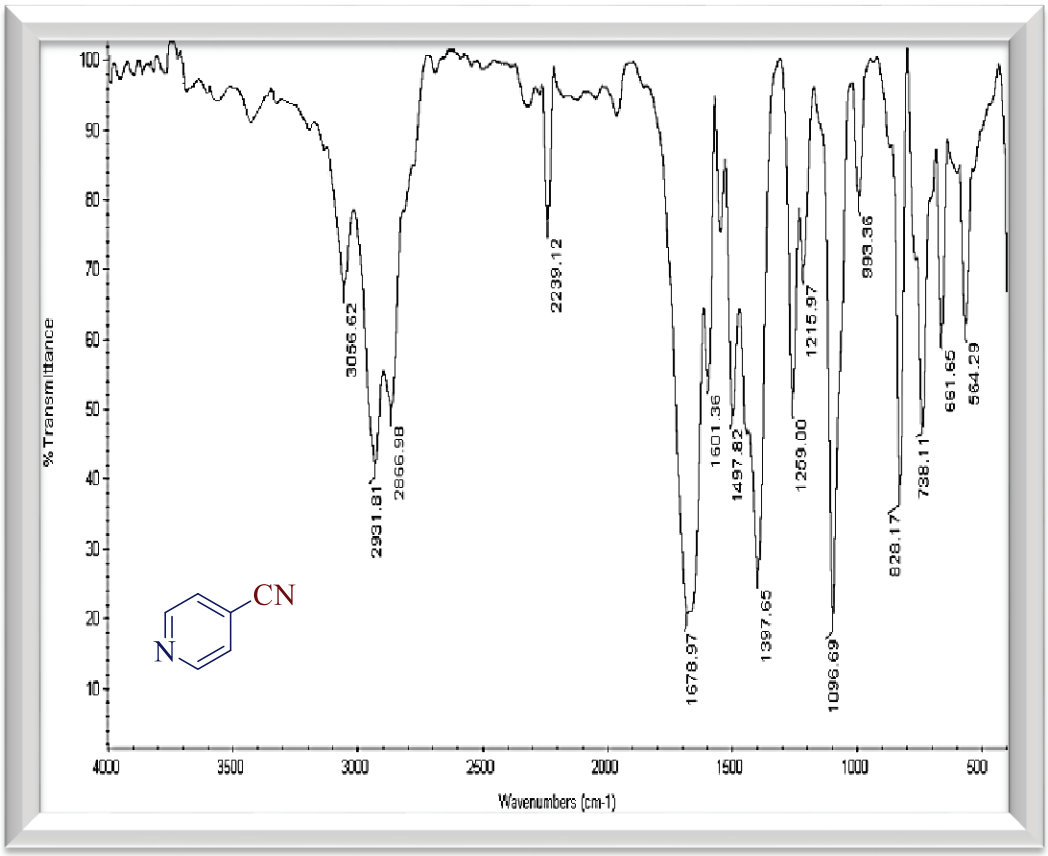

Fig S 64: FT-IR (KBr) Spectrum of 4-Cyanopyridine (Table 3, Entry 18)

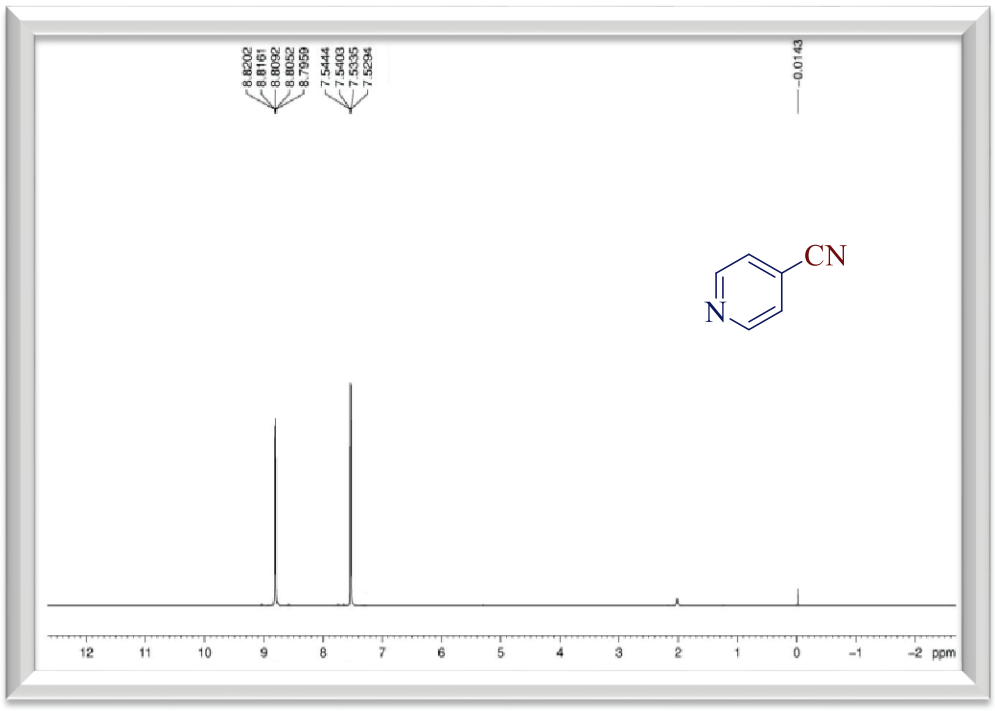

Fig S 65: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 4-Cyanopyridine (Table 3, Entry 18)

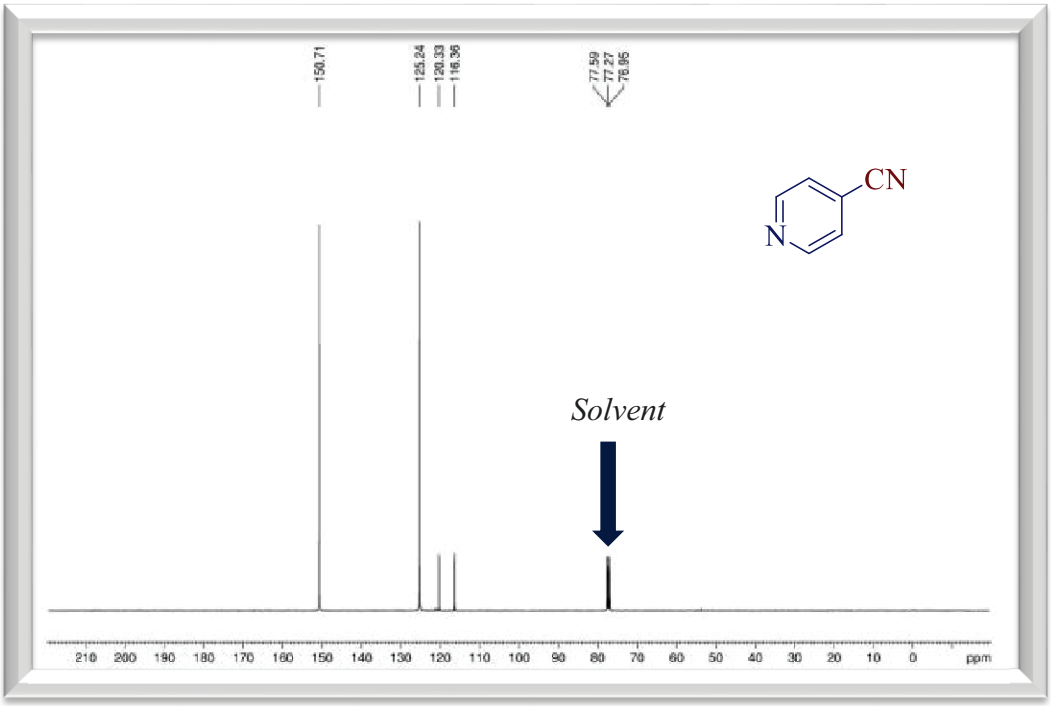

Fig S 66: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 4-Cyanopyridine (Table 3, Entry 18)

Thiophen-2-carbonitrile [16]

Thiophen-2-carbonitrile (Table 3, Entry 19). Oil (Lit[16]. Oil); 0.1057g (97%); FT-IR (neat): 3109, 3098, 2221 (CN), 1413, 1349, 1232, 1157, 1077, 1040, 856, 719, 567, 524, 486 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm]= 7.66 (d, *J* = 1.2 Hz, 1 H), 7.61 (d, *J* = 5.2 Hz, 1 H), 7.11 (t, *J* = 3.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm]= 137.3, 132.5, 127.6, 114.1, 109.8; MS (EI) m/z (%) 109 $[M]^+$.

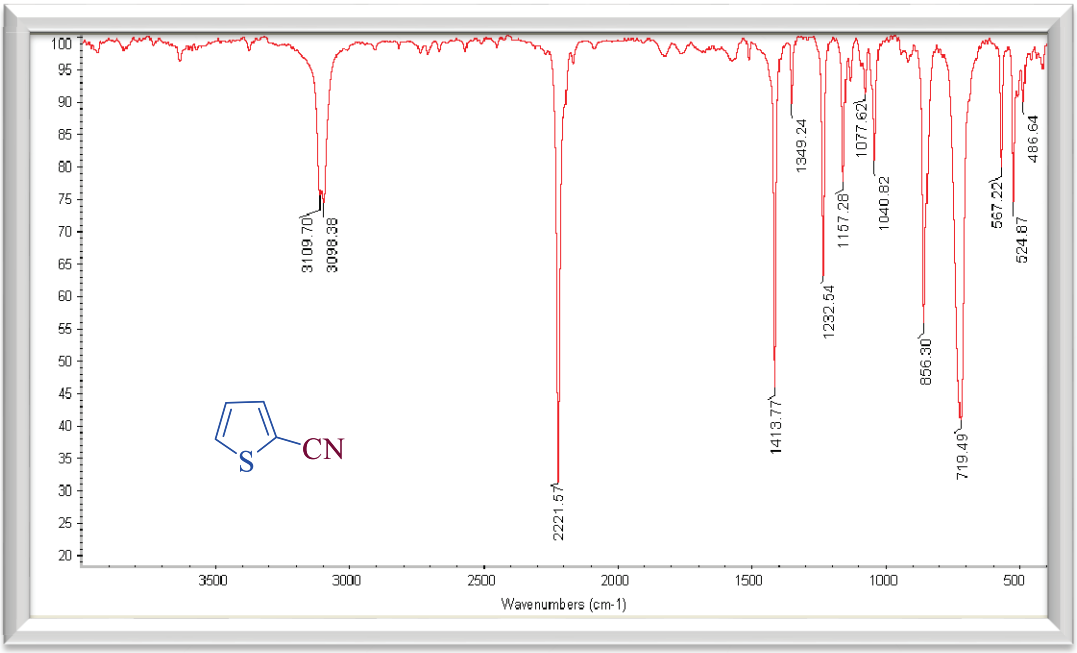

Fig S 67: FT-IR (neat) Spectrum of Thiophen-2-carbonitrile (Table 3, Entry19)

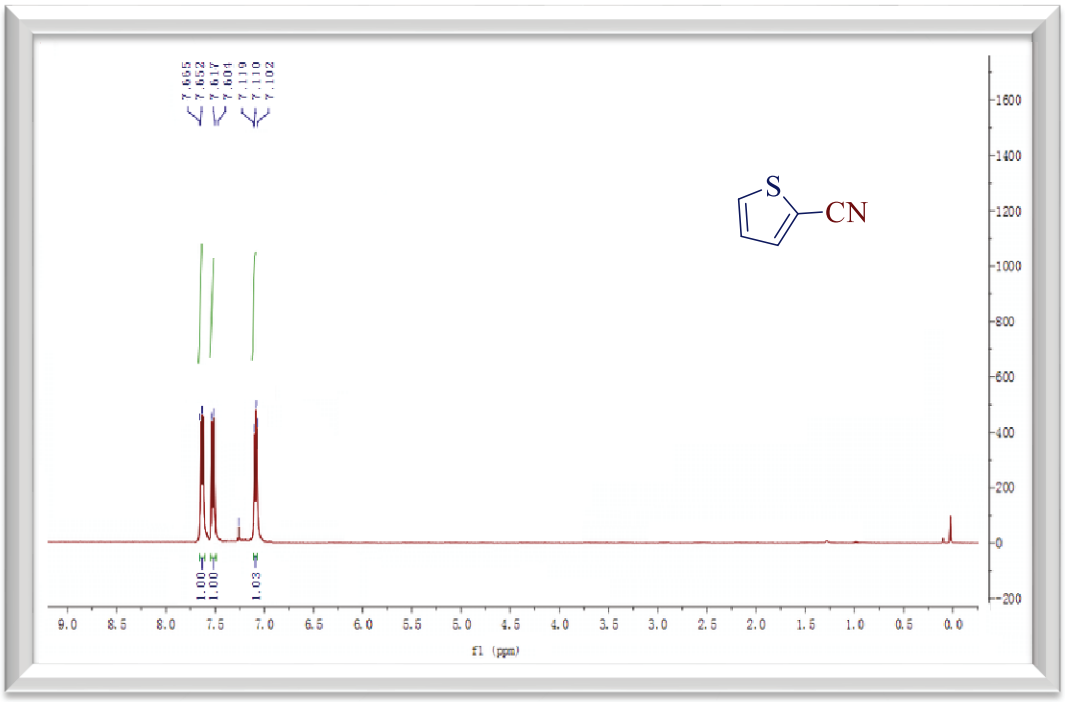

Fig S 68: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Thiophen-2-carbonitrile (Table 3, Entry 19)

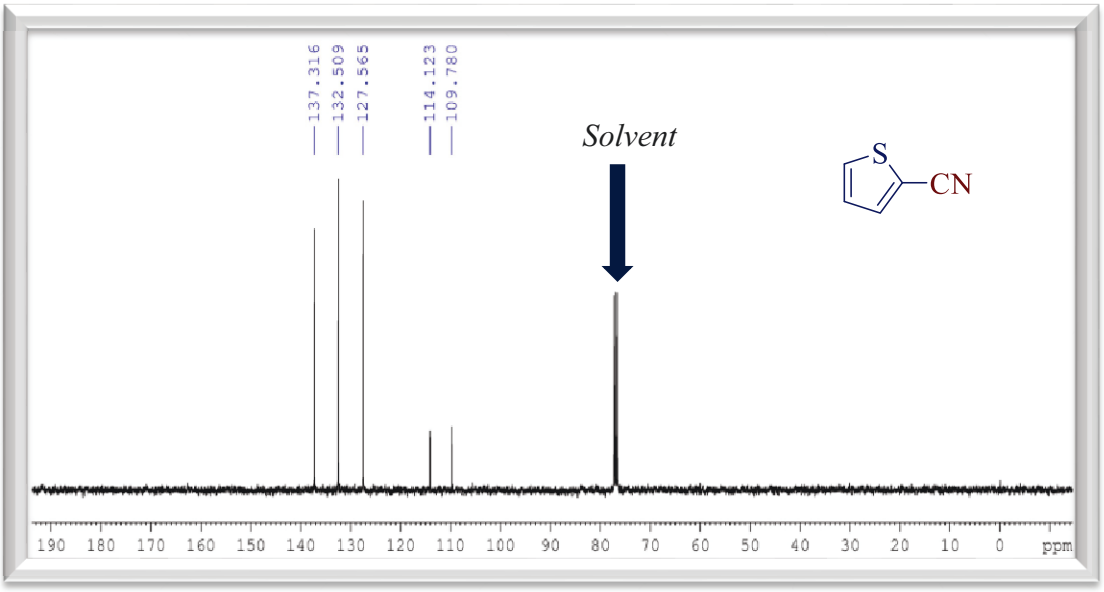

Fig S 69: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Thiophen-2-carbonitrile (Table 3, Entry 19)

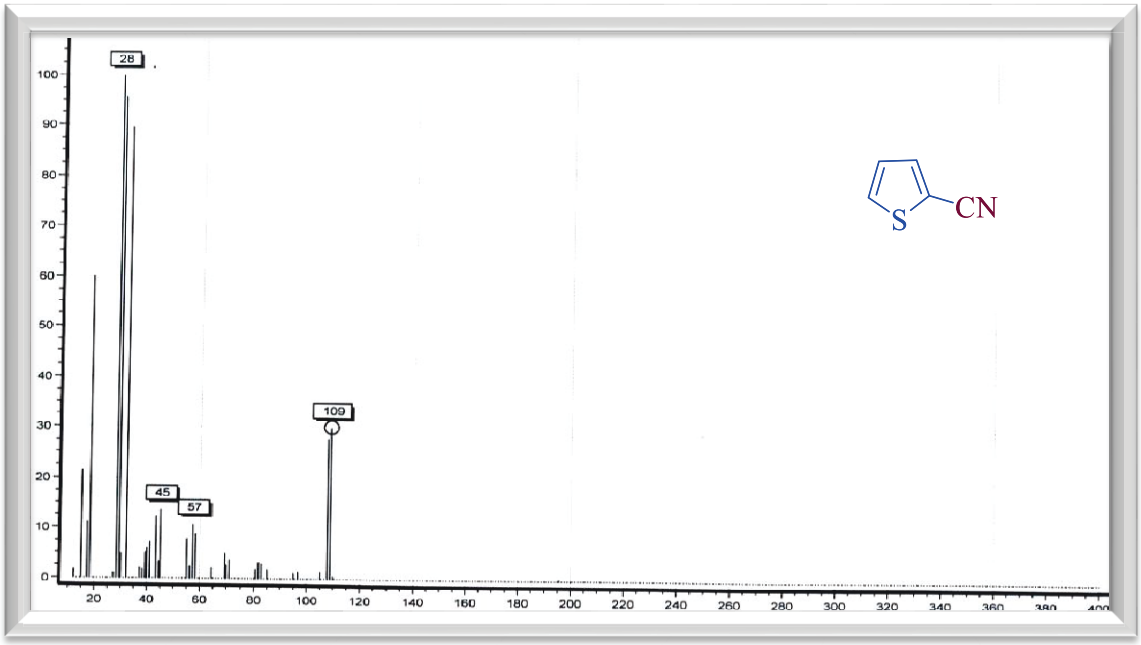

Fig S 70: Mass Spectrum of Thiophen-2-carbonitrile (Table 3, Entry19)

1-Naphthonitrile [17]

1-Naphthonitrile (Table 3, Entry 20). 0.1438g (94%); Mp 32-34 ˚C (Lit[17]. 34 ˚C); FT-IR (neat): 3058, 2926, 2847, 2222 (CN), 1625, 1586, 1508, 1375, 1342, 1242, 1162, 1047, 863, 803, 772, 689, 572, 453 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.21 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.92-7.88 (m, 2H), 7.69-7.66 (m, 1H), 7.62-7.7.58 (m, 1H), 7.52-7.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 133.2, 132.8, 132.5, 132.3, 128.6, 128.5, 127.5, 125.0, 124.8, 117.7, 110.1; MS (EI) m/z (%) 153 $[M]^{+}$.

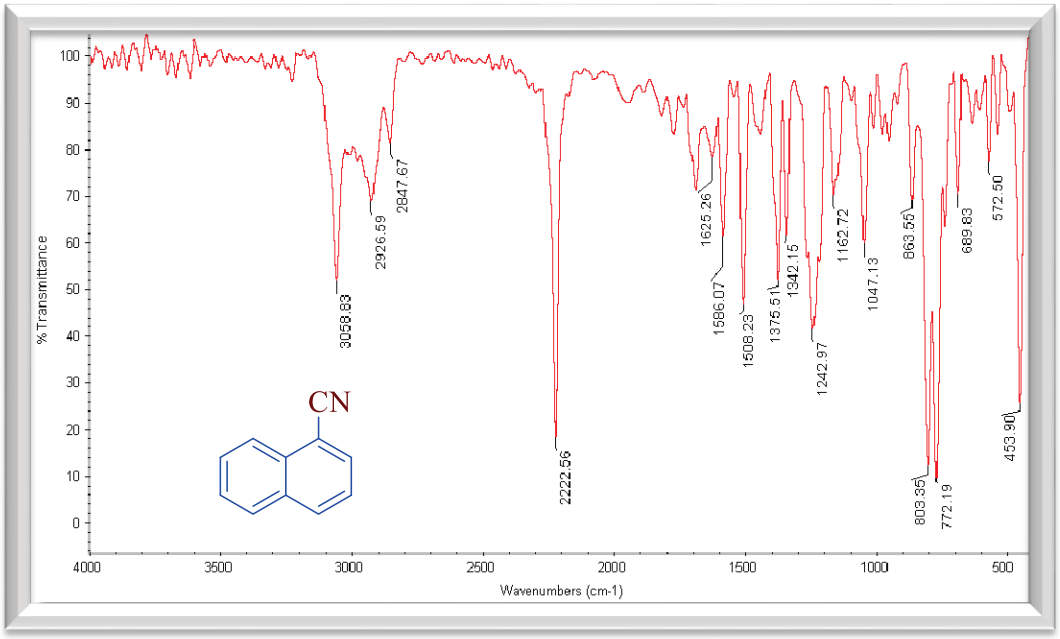

Fig S 71: FT-IR (neat) Spectrum of 1-Naphthonitrile (Table 3, Entry 20)

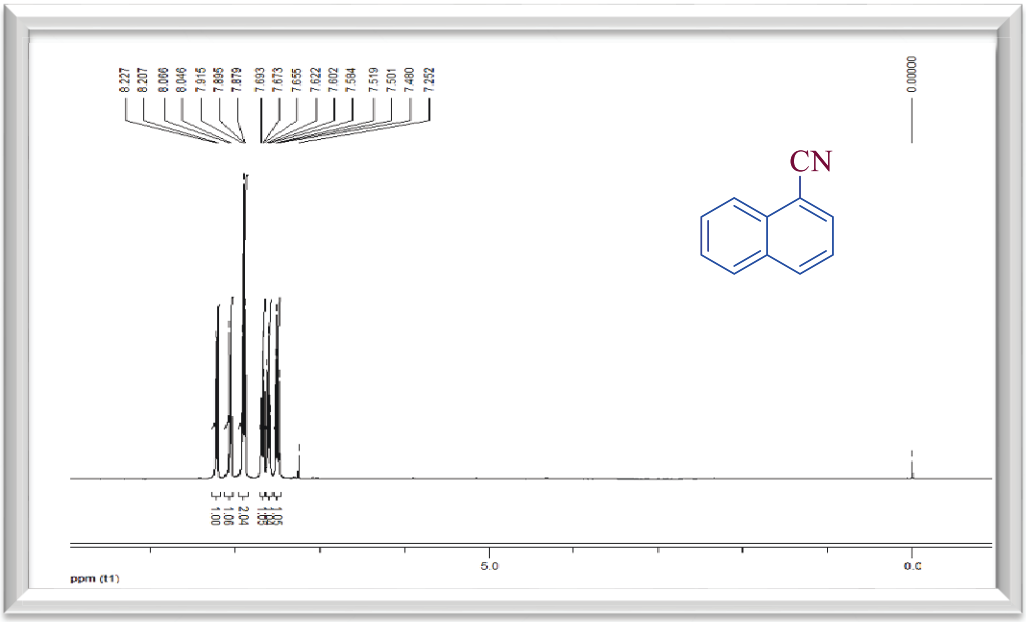

Fig S 72: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-Naphthonitrile (Table 3, Entry 20)

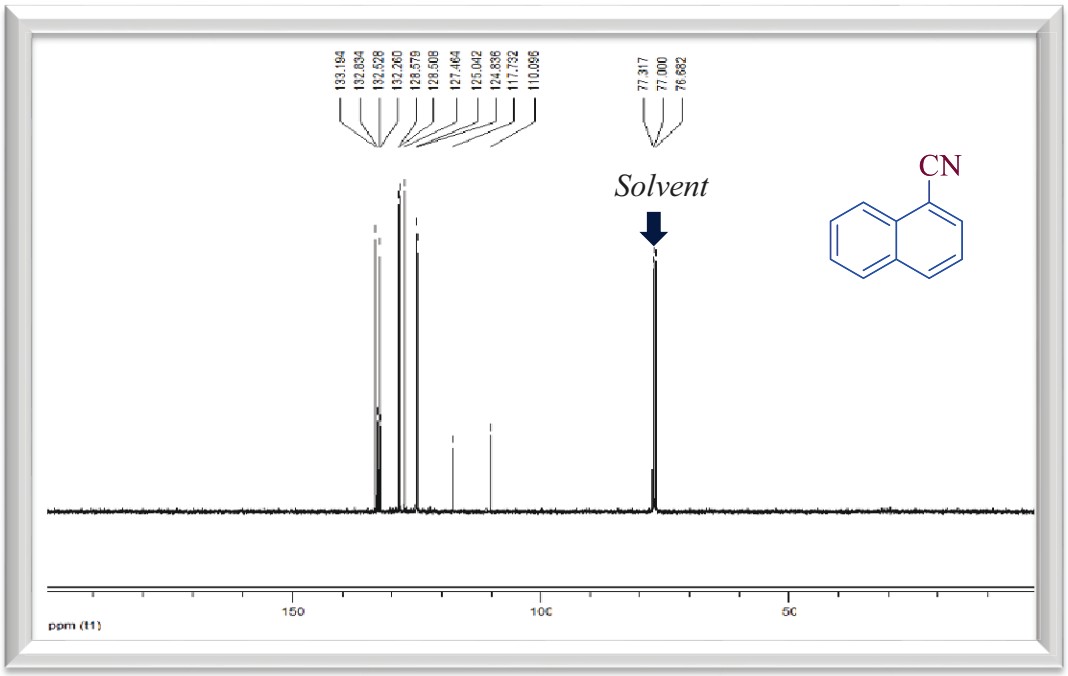

Fig S 73: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 1-Naphthonitrile (Table3, Entry 20)

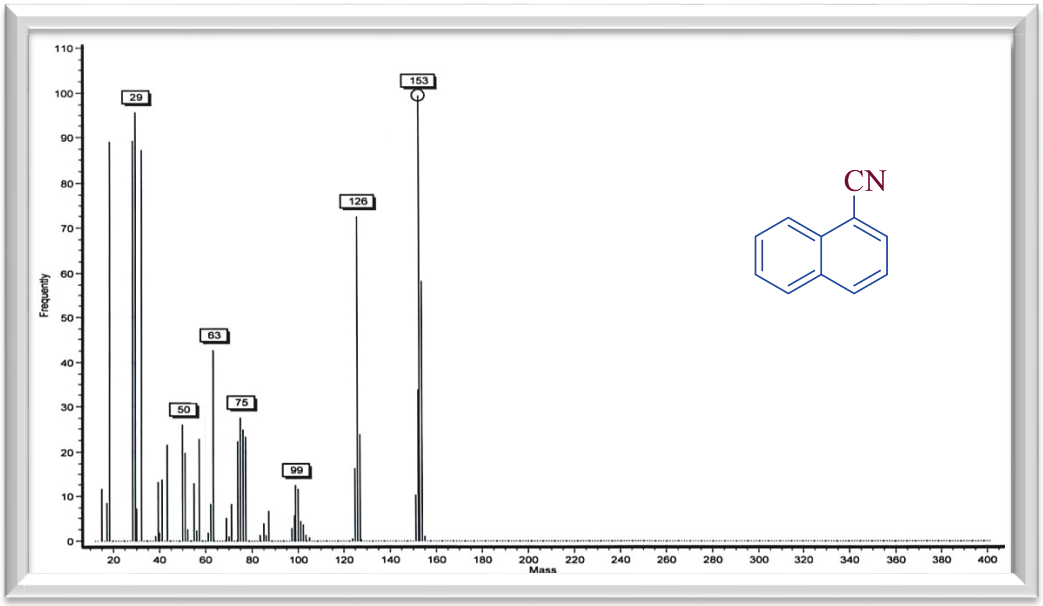

Fig S 74: Mass Spectrum of 1-Naphthonitrile (Table3, Entry 20)

2-Naphthonitrile [12]

2-Naphthonitrile (Table 3, Entry 21). 0.1422g (93%); Mp 64-68 ˚C (Lit.[12]64-69 ˚C); FT-IR (KBr): 3077, 2228(CN), 1626, 1594, 1435, 1381, 1273, 967, 904, 826, 755, 644, 483 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$,): δ [ppm]= 7.51-7.6 (m, 3H), 7.78-7.82 (m, 3H), 8.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm]= 134.5, 133.9, 132.1, 129.0, 128.9, 128.2, 127.9, 127.5, 126.1, 119.1, 109.2.

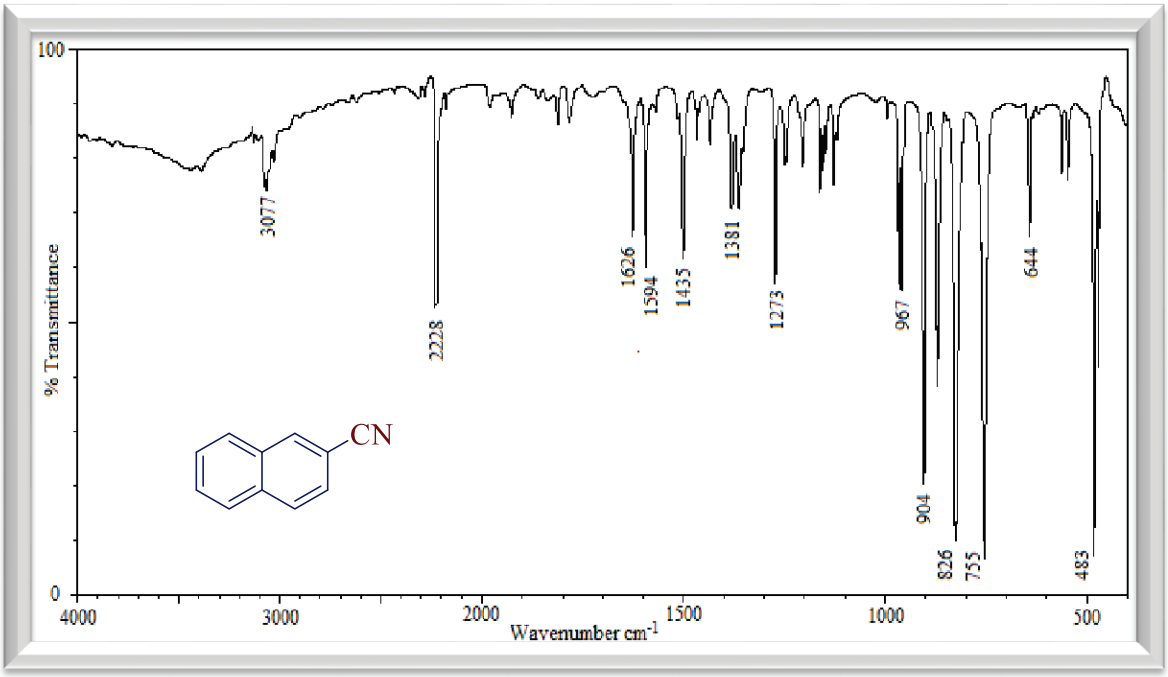

Fig S 75: FT-IR (KBr) Spectrum of 2-Naphthonitrile (Table 3, Entry 21)

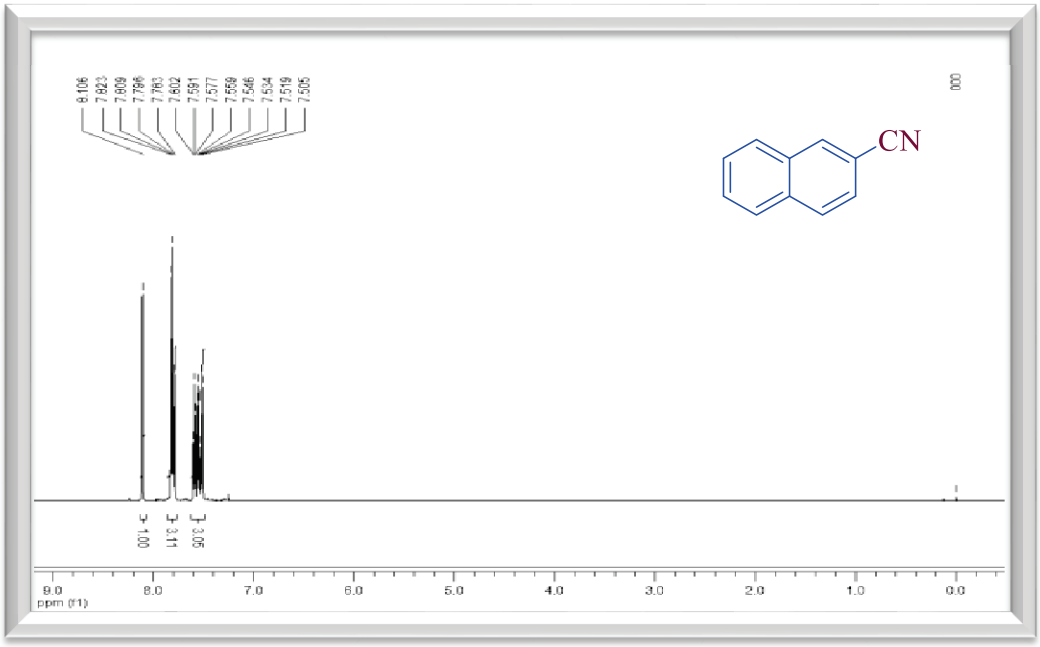

Fig S 76: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 2-Naphthonitrile (Table 3, Entry 21)

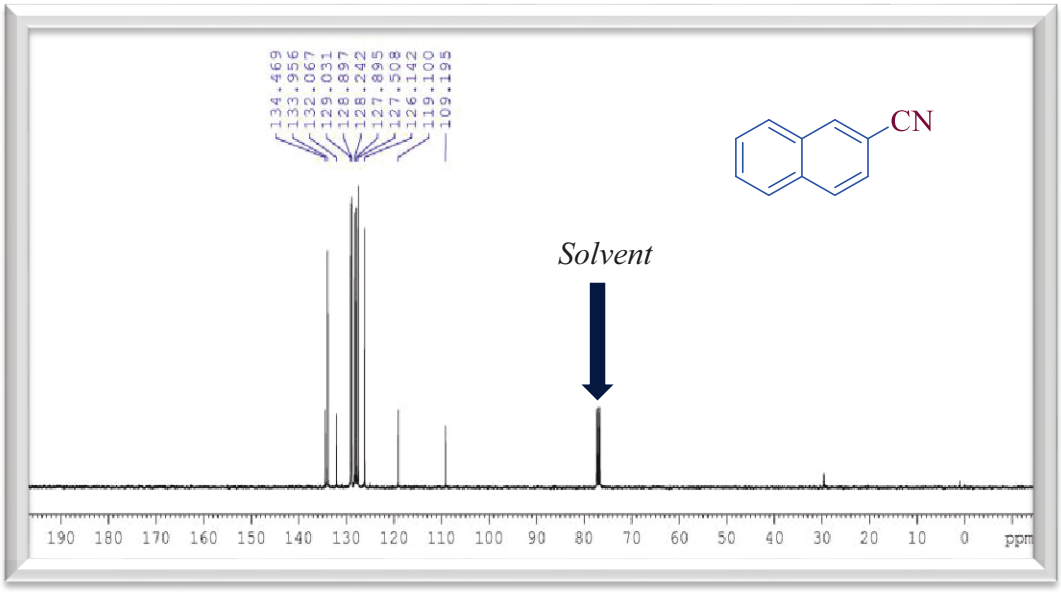

Fig S 77: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of 2-Naphthonitrile (Table3, Entry 21)

Cinnamonitrile *[18]*

Cinnamonitrile (Table 3, Entry 22). Oil (Lit.[18]Oil); 0.1225g (95%); FT-IR (neat): 3059, 2923, 2855, 2217 (CN), 1737, 1663, 1616, 1583, 1492, 1450, 1374, 1244, 1047, 969, 838, 749, 688, 622, 435 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.47–7.38 (m, 6 H), 5.87 (d, J = 16.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm]= 150.6, 133.5, 131.2, 129.1, 127.4, 118.2, 96.3; MS (EI) m/z (%): 129 $[M]^{+}$.

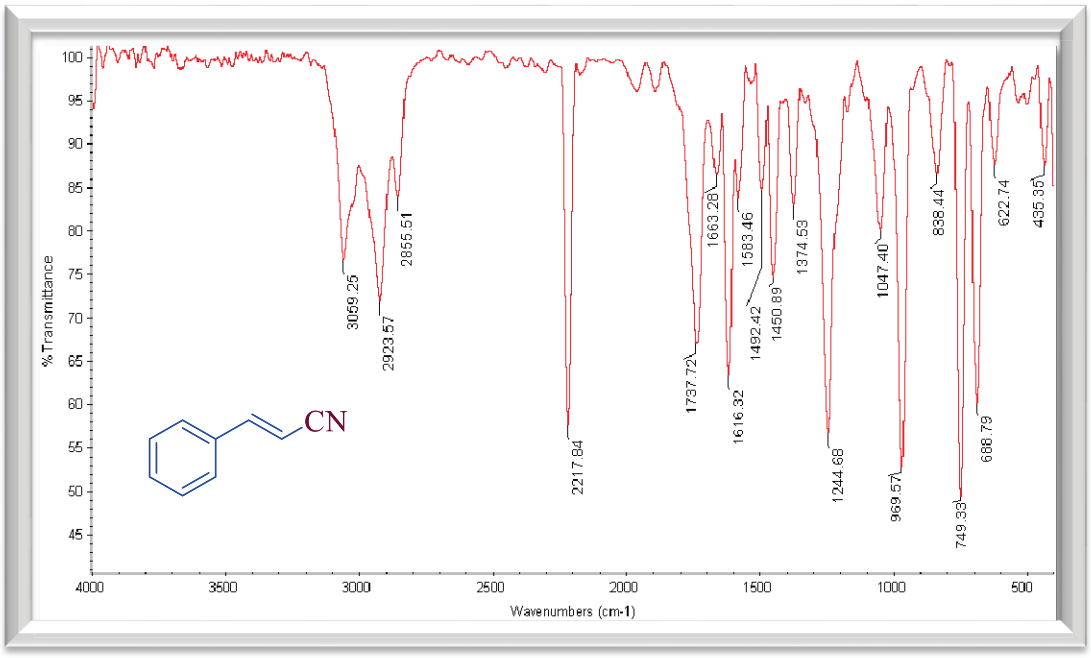

Fig S 78: FT-IR (neat) Spectrum of Cinnamonitrile (Table 3, Entry 22)

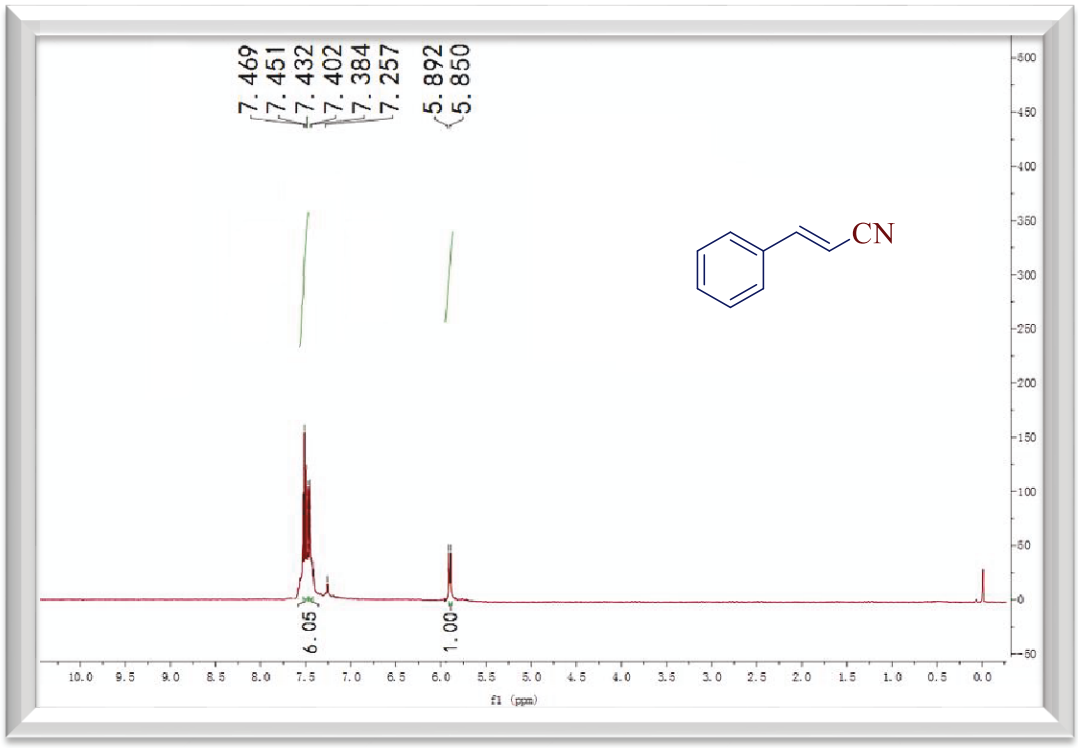

Fig S 79: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Cinnamonitrile (Table 3, Entry 22)

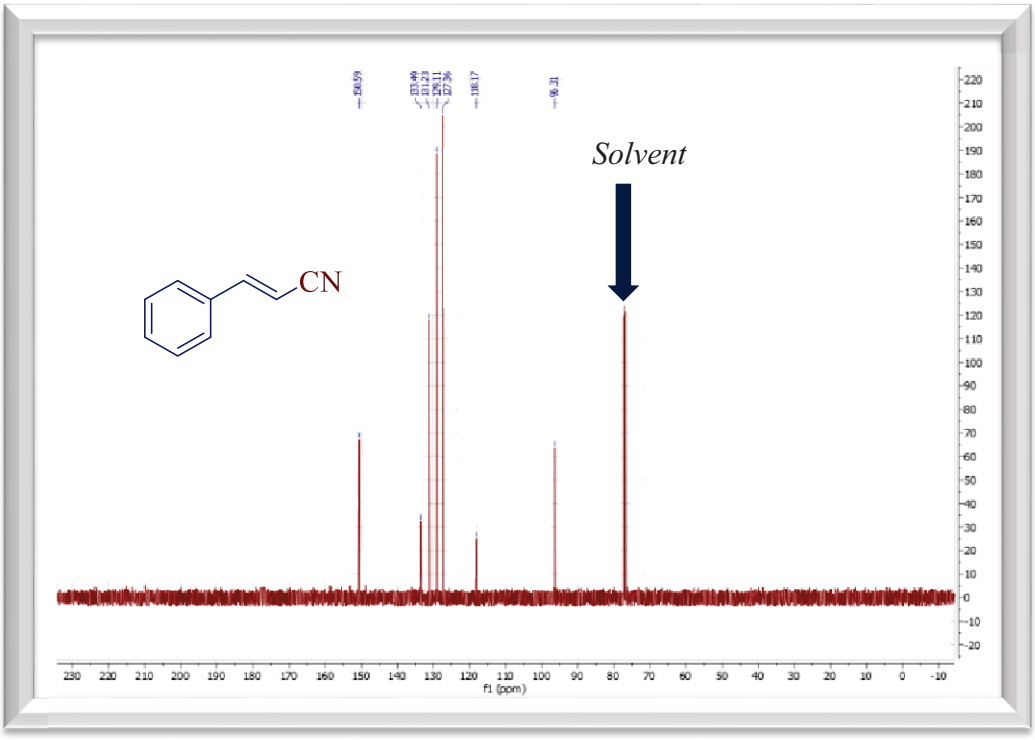

Fig S 80: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Cinnamonitrile (Table3, Entry 22)

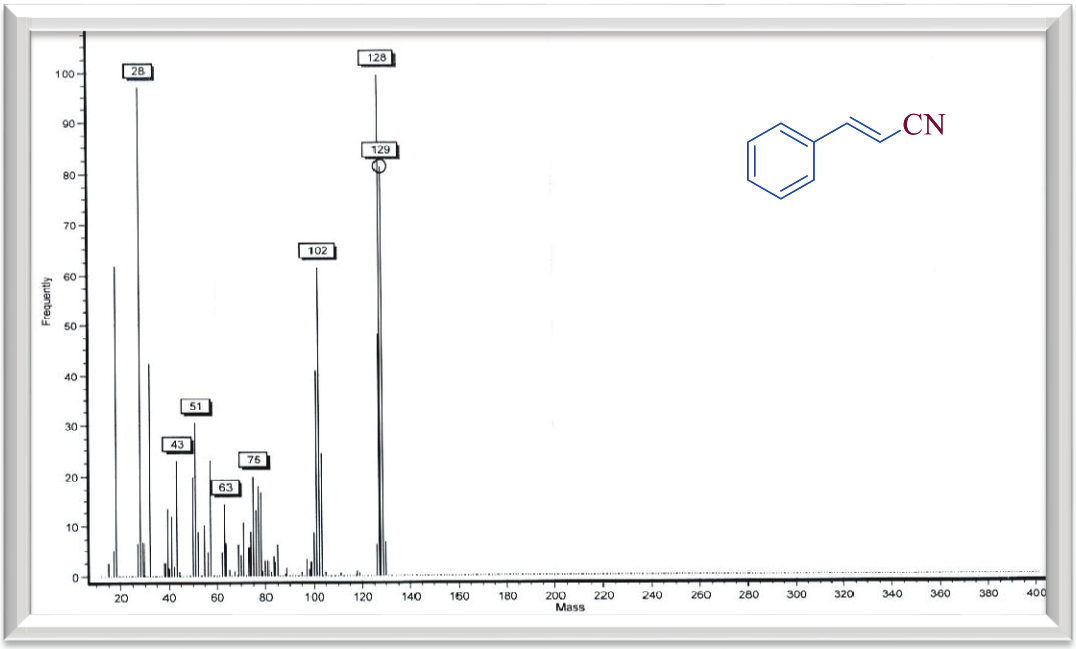

Fig S 81: Mass Spectrum of Cinnamonitrile (Table 3, Entry 22)

Heptanonitrile [13]

Heptanonitrile (Table 3, Entry 23). Pale Yellow Oil (Lit.[13]); 0.1021g (92%); FT-IR (neat): 3456, 2958, 2929, 2859, 2214(CN), 1737, 1466, 1378,1235, 1168, 1102, 1017, 726; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.36 (t, J = 7.2 Hz, 2 H), 1.64–1.59 (m, 2 H), 1.46–1.41 (m, 2 H), 1.33–1.26 (m, 4 H), 0.91 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 119.8, 30.9, 28.3, 25.3, 22.4, 17.1, 13.9.

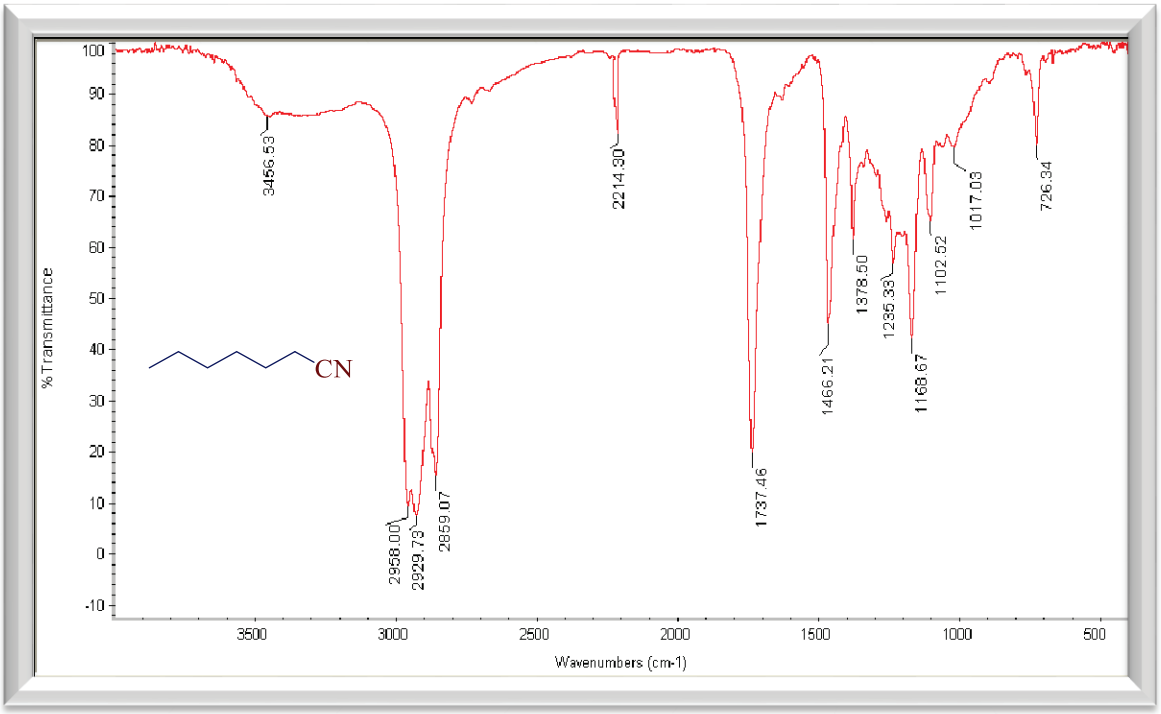

Fig S 82: FT-IR (neat) Spectrum of Heptanonitrile (Table 3, Entry 23)

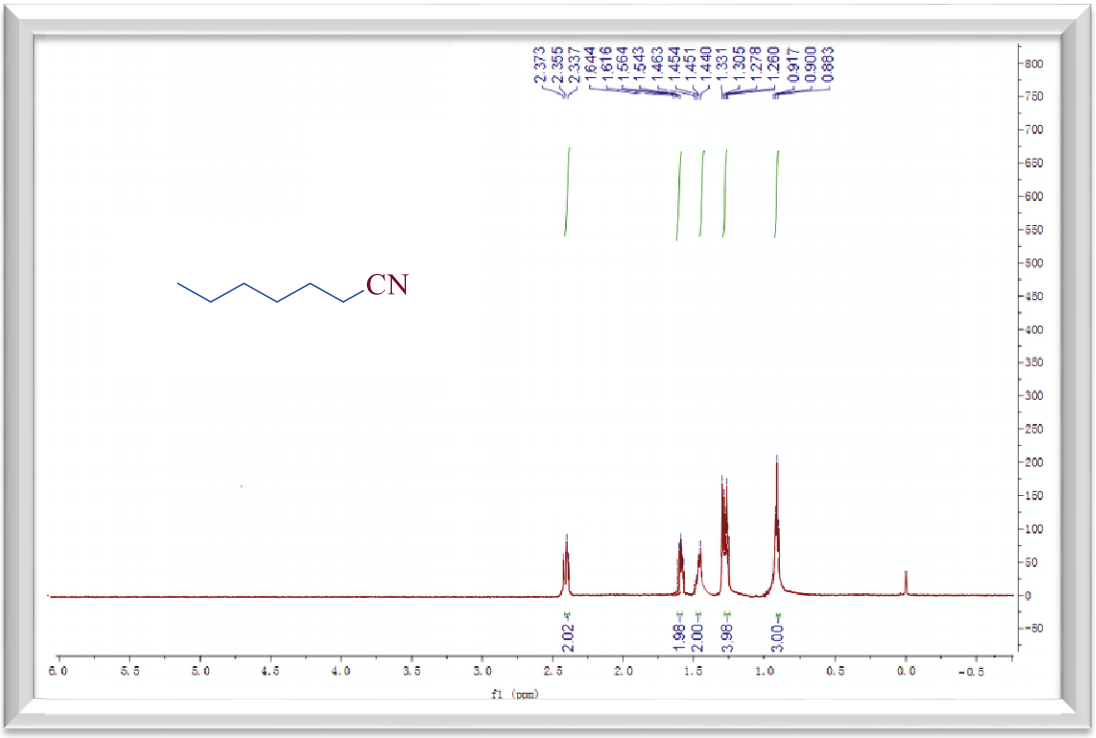

Fig S 83: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Heptanonitrile (Table 3, Entry 23)

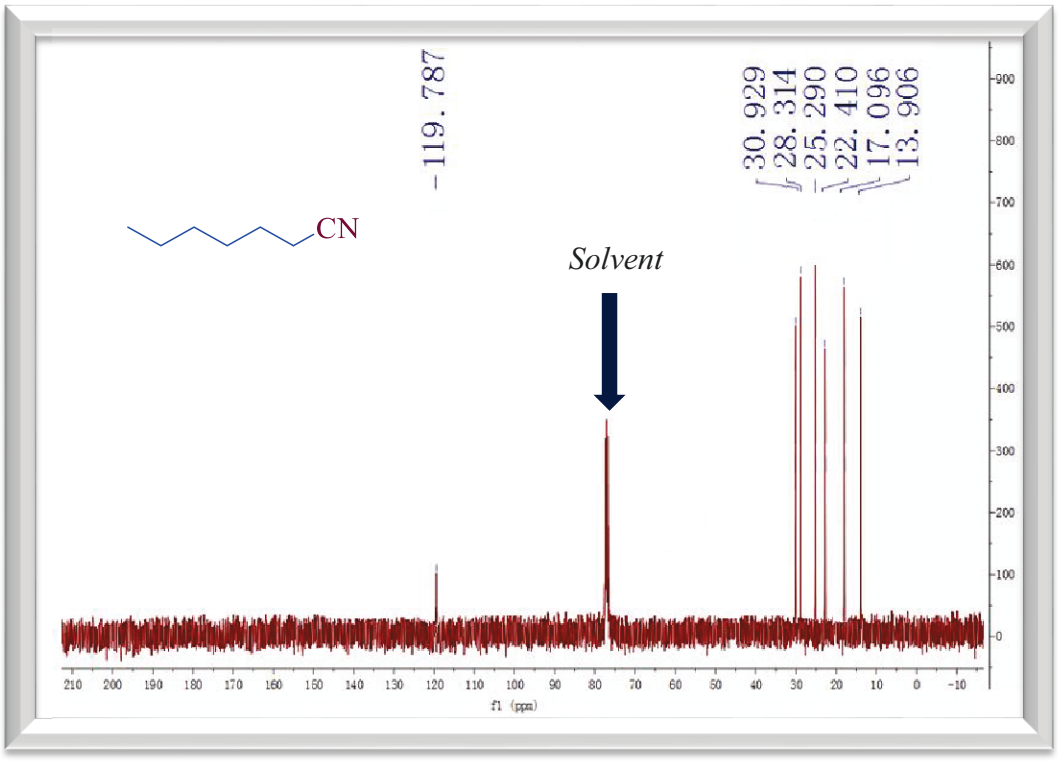

Fig S 84: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Heptanonitrile (Table3, Entry 23)

Octanenitrile [19]

Octanenitrile (Table 3, Entry 24). Oil (Lit.[19] Oil); 0.1200g (96%); FT-IR (neat): 2962, 2930, 2859, 2246 (CN), 1462, 1427, 1377, 1119, 723; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.91 (t, J = 7.0 Hz, 3H), 1.32 (s, 8H), 1.61 (q, J = 6.5 Hz, 2H), 3.68 (t, J = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 119.9, 31.5, 28.6, 28.4, 25.4, 22.5, 17.1, 14.0; MS (EI) m/z (%): 125 $[M]^+$.

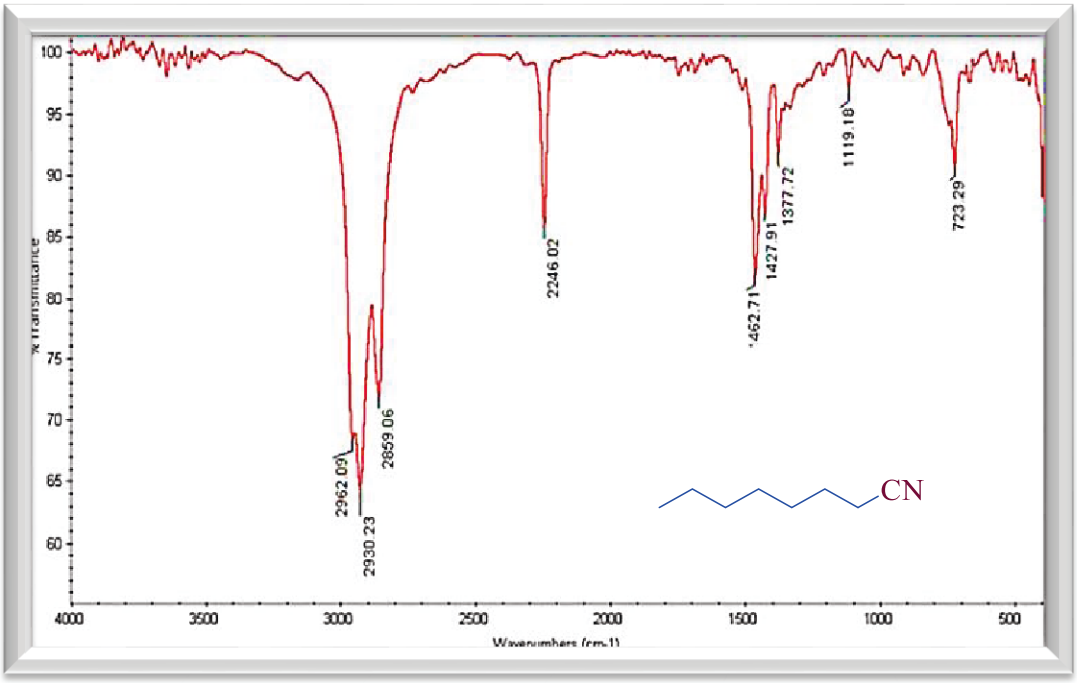

Fig S 85: FT-IR (neat) Spectrum of Octanenitrile (Table 3, Entry 24)

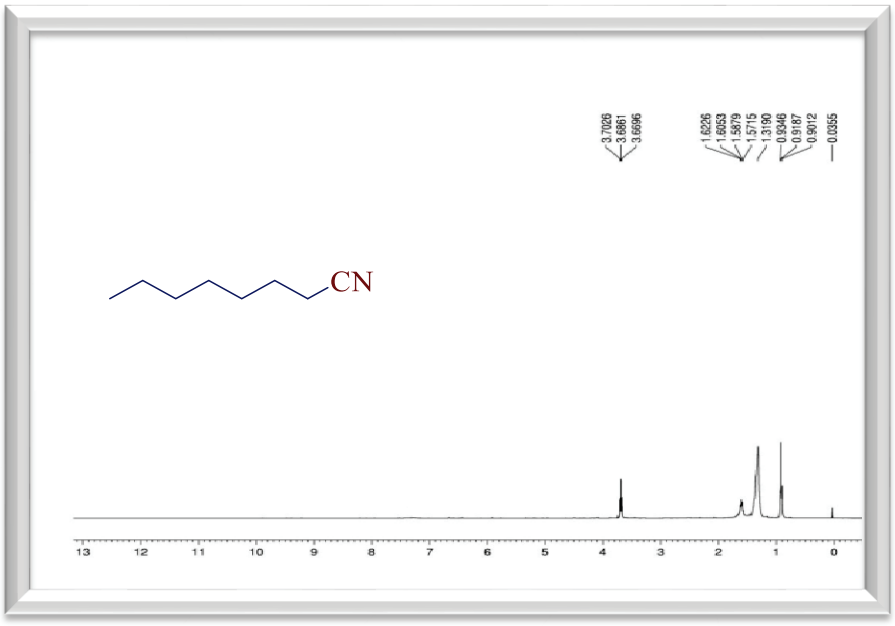

Fig S 86: ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Octanenitrile (Table 3, Entry 24)

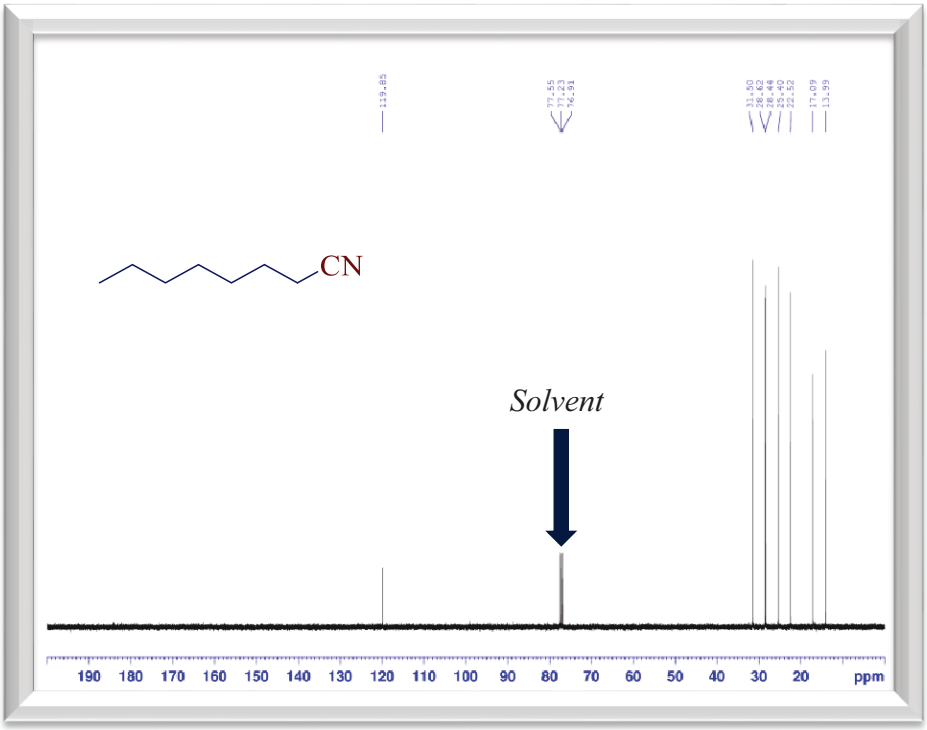

Fig S 87: ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Octanenitrile (Table3, Entry 24)

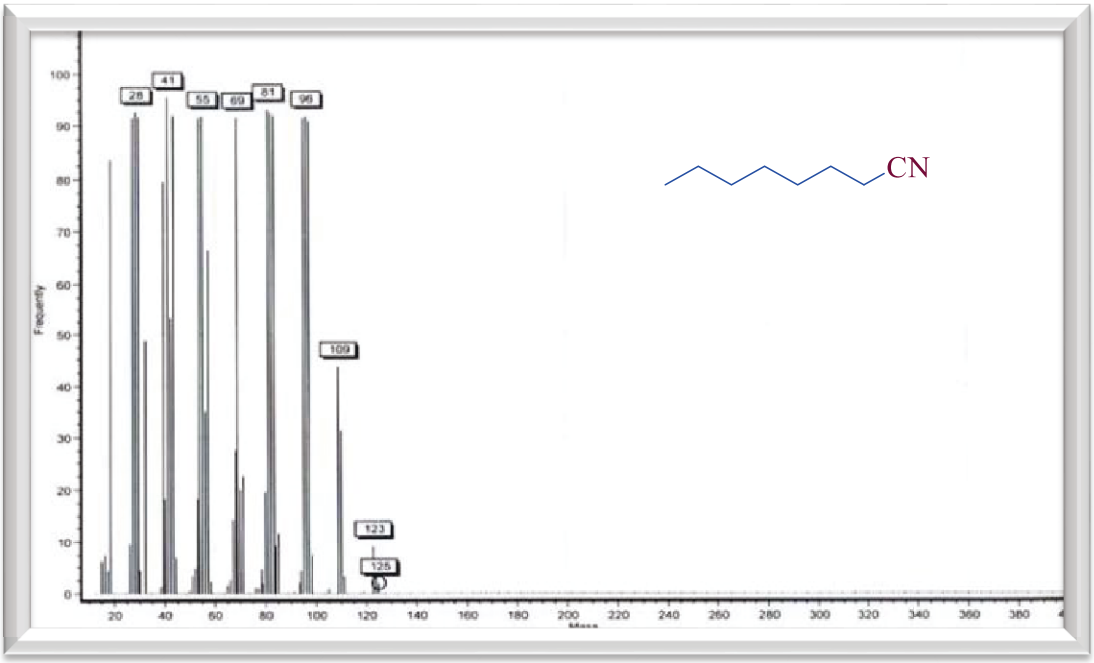

Fig S 88: Mass Spectrum of Octanenitrile (Table 3, Entry 24)

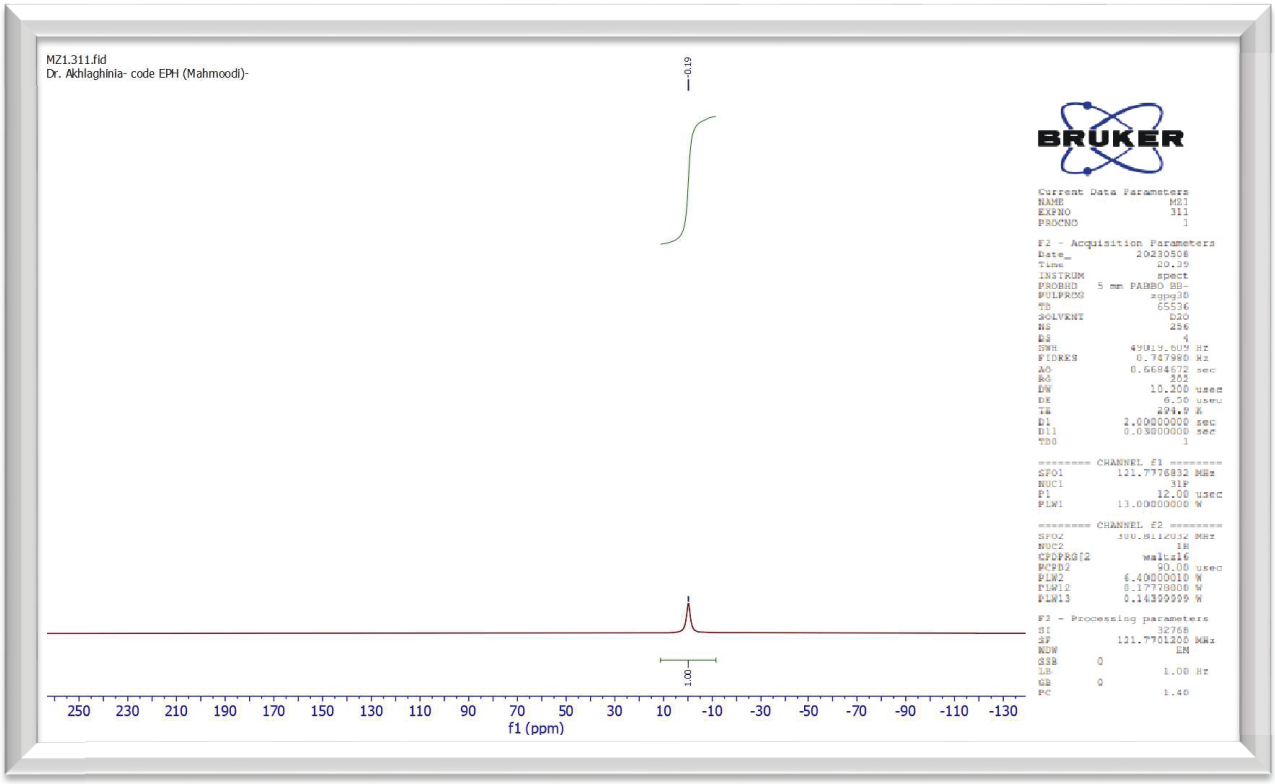

Fig S 89:[31] P NMR Spectrum (121 MHz) of dispersed Expanded Perlite-Polyphosphoric Acid (EP-PPA) in D_2O

References

[1] N. Coskun, *Synth. Commun.* **2004**, *34*, 1625. DOI: 10.1081/SCC-120030750.

[2] M. Sridhar, M. K. Kumar Reddy, V. V. Sairam, J. Raveendra, K. Reddy Godala, Ch. Narsaiah, B. Ch. Ramanaiah, C. Suresh Reddy, *Tetrahedron Lett.* **2012**, *53*, 3421. DOI:10.1016/j.tetlet.2012.04.057.

[3] X. C. Wang, L. Li, Zh. J. Quan, H. Peng Gong, H. Lin Ye, X. Feng Cao, *Chin. Chem. Lett.* **2009,** *20*, 651. DOI:10.1016/j.cclet.2009.02.004.

[4] Y-F. Liang ,X. Li, X. Wang, M. Zou, C. Tang, Y. Liang, S. Song, N. Jiao, *J. Am. Chem. Soc.* **2016**, *138*, 12271. DOI: 10.1021/jacs.6b07269.

[5] N. D. Kokare, D. B. Shinde, *Monatsh Chem.* **2009**, *140*, 185. DOI: 10.1007/s00706-008-0058-6.

[6] U. P. Patil, A. S. Kuwar, A. P. Nikum, K. Desale, *Int. J. Chemtech Res.* **2013**, *5*, 974.

[7] A. Gh. Choghamarani, M. A. Zolfigol, M. Hajjami, S. Sardari, *Synth. Commun.* **2013**, *43*, 52. DOI:10.1080/00397911.2011.591035.

[8] H. Shimojo, K. Moriyama, H. Togo, *Synth.* **2013**, *45*, 2155. DOI:10.1055/s-0033-1338489.

[9] Ph. Nimnal, J. Tummatorn, Ch. Thongsornkleep, S. Ruchirawat, *J. Org. Chem.* **2015**, *80*, 8657. DOI: 10.1021/acs.joc.5b01305.

[10] Zh. Yanling, Zh. Zhiguo, Hu. Yuanyuan, Liu. Yunkui, J. Hongwei, B. Zhou, *Org. Biomol. Chem.* **2022,** *20***,** 8049. DOI:10.1039/D2OB01240E.

[11] G. C. Nandi, K. K. Laali, *Tetrahedron Lett.* **2017**, *54*, 2177. DOI: 10.1016/j.tetlet.2013.02.051.

[12] A. V. Ushkov, V. V. Grushin, *J. Am. Chem. Soc.* **2011**, *133*, 10999. DOI:10.1021/ja2042035.

[13] H. Geng, P. Q. Huang, *Tetrahedron.* **2015**, *71*, 3795. DOI: 10.1016/j.tet.2015.03.094.

[14] A.R. Sardarian, Z. Shahsavari-Fard, H. R. Shahsavari, Z. Ebrahimi, *Tetrahedron Lett.* **2017**, *48*, 2639. DOI:10.1016/j.tetlet.2007.01.120.

[15] X. Ma, D. He, Zh. Chen, *J. Chem. Res.* **2018**, *42*, 595. DOI: 10.3184/174751918X15411700157951.

[16] N. S. Nandurkar, B. M. Bhanage, *Tetrahedron*. **2008**, *64*, 3655. DOI:10.1016/j.tet.2008.02.038.

[17] H. Sharghi, M. Hosseini Sarvari, *Synth.* **2003**, *3*, 0243. DOI:10.1055/s-2003-36830.

[18] R. M. Denton, J. An, P. Lindovska, W. Lewis, *Tetrahedron*. **2012**, *68*, 2899. DOI: 10.1016/j.tet.2012.01.067.

[19] J. A. Campbell, G. McDougald, H. McNab, L. V. C. Rees, R. G. Tyas, *Synth.* **2007**, *20*, 3179. DOI:10.1055/s-2007-990782.