Electronic Supplementary Information (ESI)

Synthesis and Biological Evaluation of New Pyranopyridine Derivatives Catalyzed by Guanidinium Chloride-Functionalized γ-Fe_2O_3/HAP Magnetic Nanoparticles†

Davood Azarifar[a]*, Masoumeh Ghaemi[a], Maryam Golbaghi[a], Roya Karamian[b], Mostafa Asadbegy[b]

Department of Chemistry, Bu-Ali Sina University, Zip Code 65178, Hamedan, Iran

Department of Biology, Faculty of Science, Bu-Ali Sina University, P. O. Box 65175/4161, Hamedan, Iran

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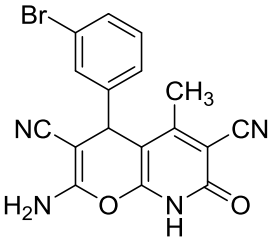
A1. ***2-Amino-7,8-dihydro-5-methyl-7-oxo-4-(3-bromophenyl)-4H-pyrano[2,3-b]pyridine-3,6-dicarbonitrile(C_1)(Table 2, Entry 1):***

White solid, mp 140-145 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.13 (s, 3H, CH_3), 4.83 (s, 1H, C_4-H), 7.11–8.11 (m, 6H, Ar-H and NH_2), 9.54 (s, 1H, NH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.6, 57.4, 93.2, 114.8, 119.4, 122, 126.2, 128.9, 129.7, 130.0, 131.2, 131.5, 132.8, 136.5, 146.8, 159.0 ppm; IR (KBr) (ν_{max}/cm^{-1}): 3641, 3488, 3355, 2224, 2196, 1683; Anal. Calcd for $C_{17}H_{11}BrN_4O_2$: C, 53.28; H, 2.89, N, 14.62; %. Found: C, 53.33; H, 2.91; N, 14.63; MS: m/z = 383 (M^+). ***(Table 2, Entry 2):***



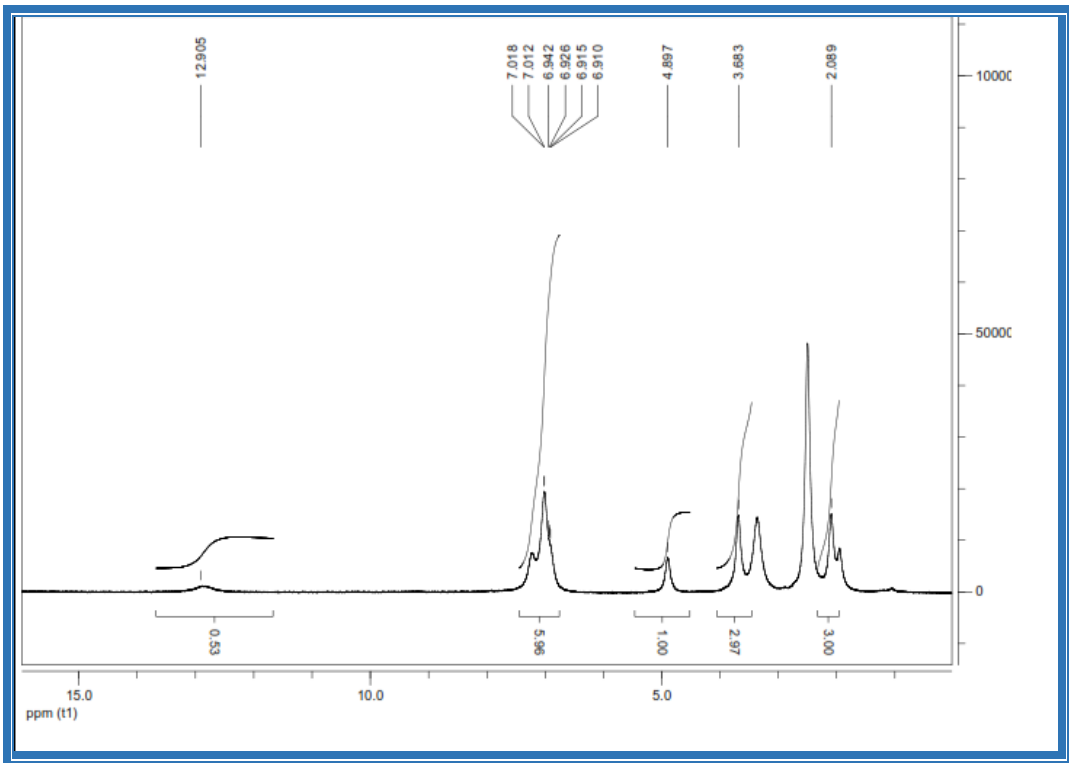


Fig. A1 The ^{1}H NMR (500 MHz) spectrum of product (**C_1**)

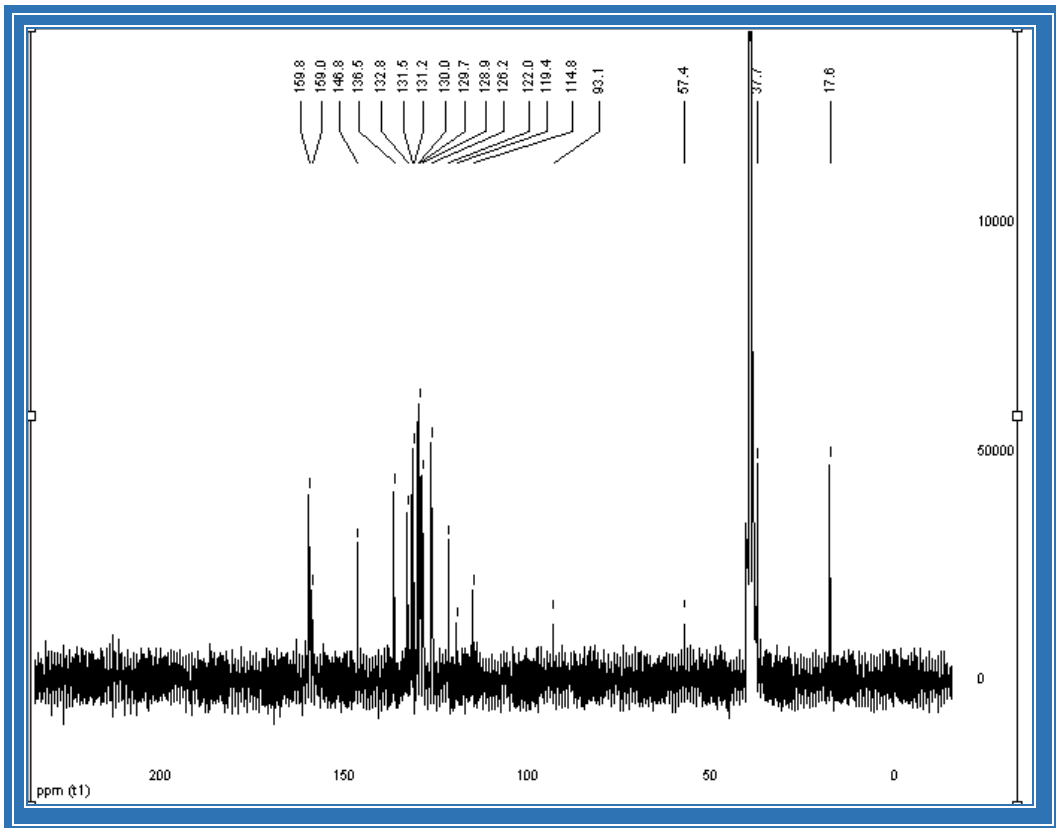


Fig. A2 The ^{13}C NMR (125 MHz) spectrum of product (**C_1**)

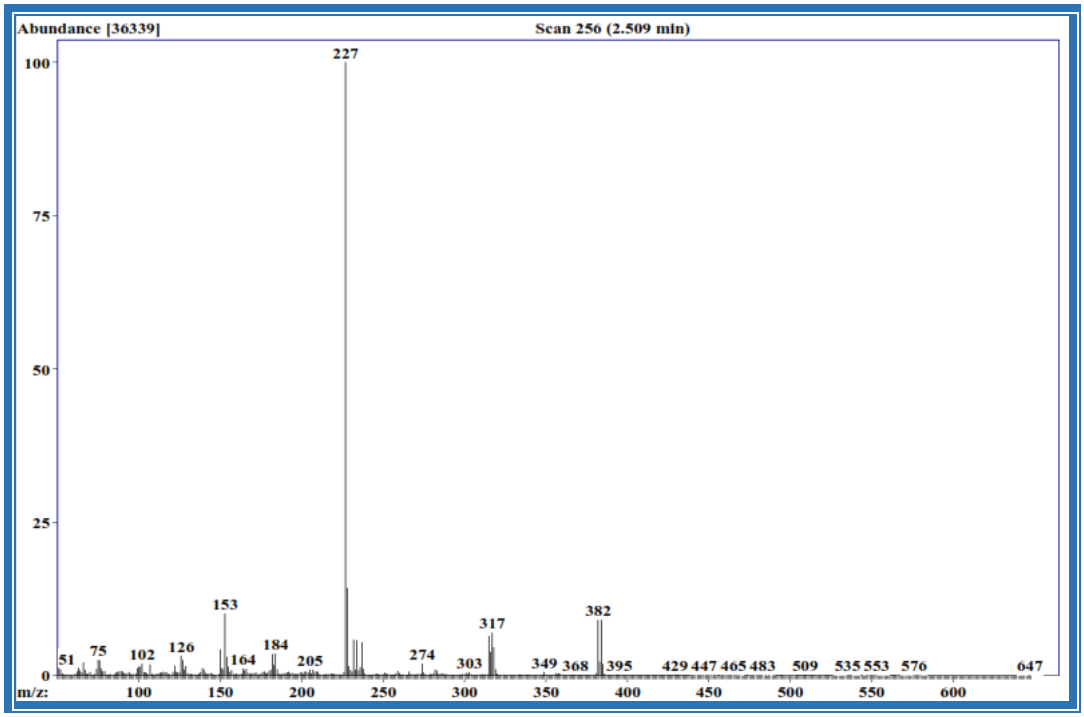


Fig. A3 The MS spectrum of product (**C_1**)

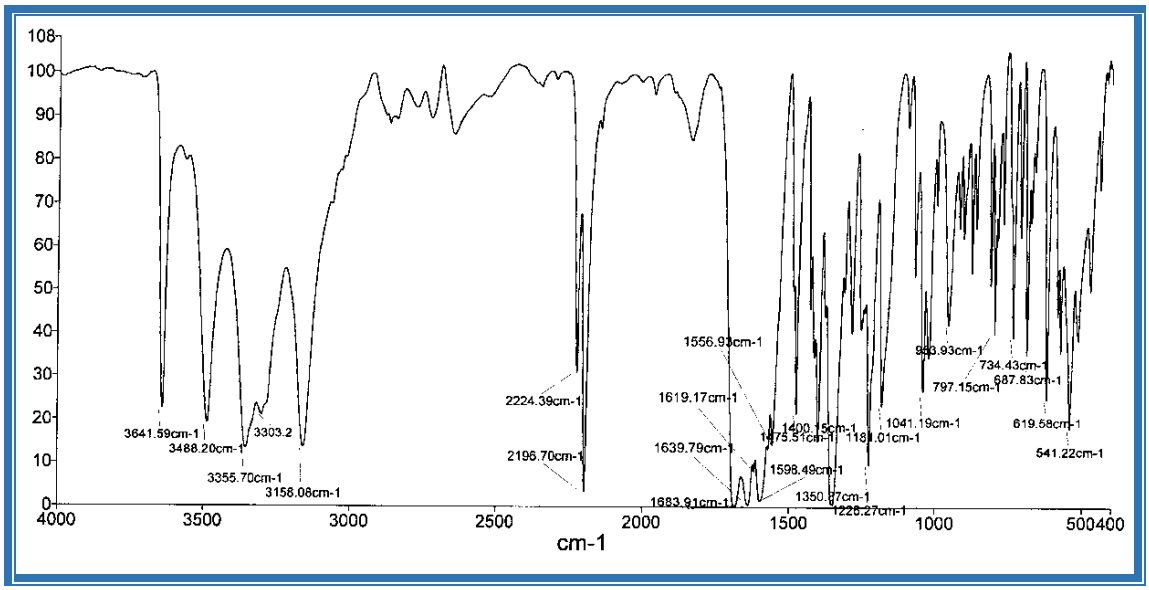
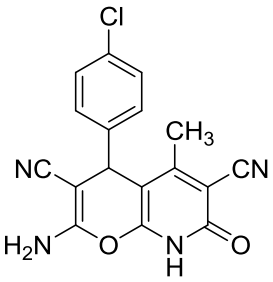


Fig. A4 The IR spectrum of product (C_1)

2-Amino-7,8-dihydro-5-methyl-7-oxo-4-(4-chlorophenyl)-4H-pyrano[2,3-b]pyridine-3,6-dicarbonitrile (**C_2**)

White solid, mp 180-184 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.11 (s, 3H, CH_3), 5.02 (s, 1H, C_4-H), 7.42-8.73 (m, 6H, Ar-H, and NH_2), 10.17 (s, 1H, NH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.2, 66.1, 92, 112, 113.2, 114.4, 120.9, 126.8, 131.1, 141.1, 167.1 ppm; IR (KBr) (ν_{max}/cm^{-1}): 3650, 3504, 3344, 2225, 2200, 1683; Anal. Calcd for $C_{17}H_{11}ClN_4O_2$: C, 60.28; H, 3.27, N, 16.54; %. Found: C, 60.32; H, 3.29; N, 16.54; MS: *m/z* = 338 (M^+). ***(Table 2, Entry 2):***



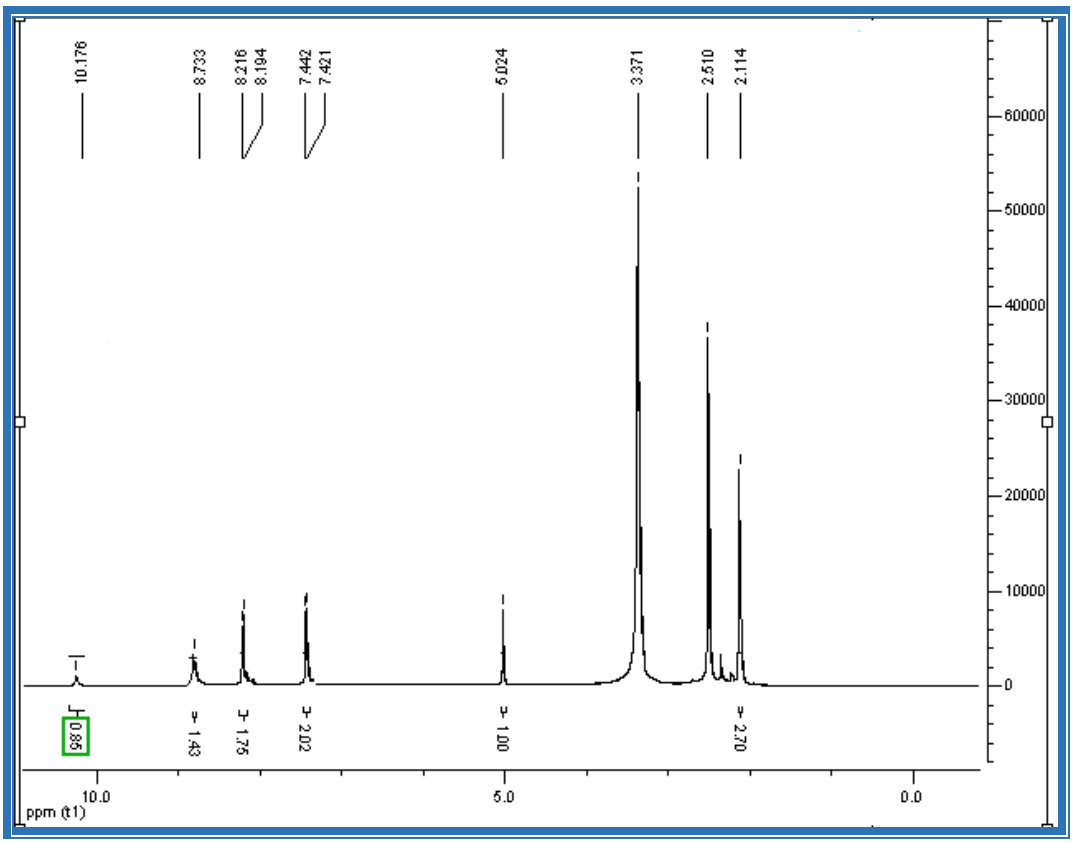


Fig. B1 The ^{1}H NMR (500 MHz) spectrum of product (**C_2**)

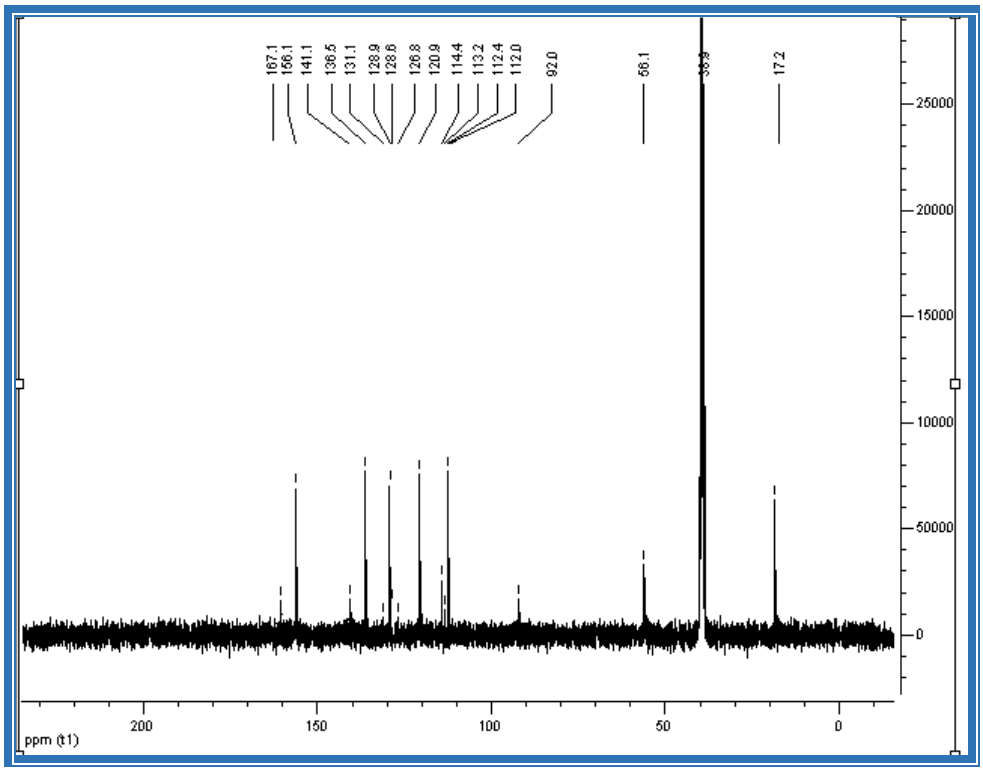


Fig. B2 The ^{13}C NMR (125 MHz) spectrum of product (**C_2**)

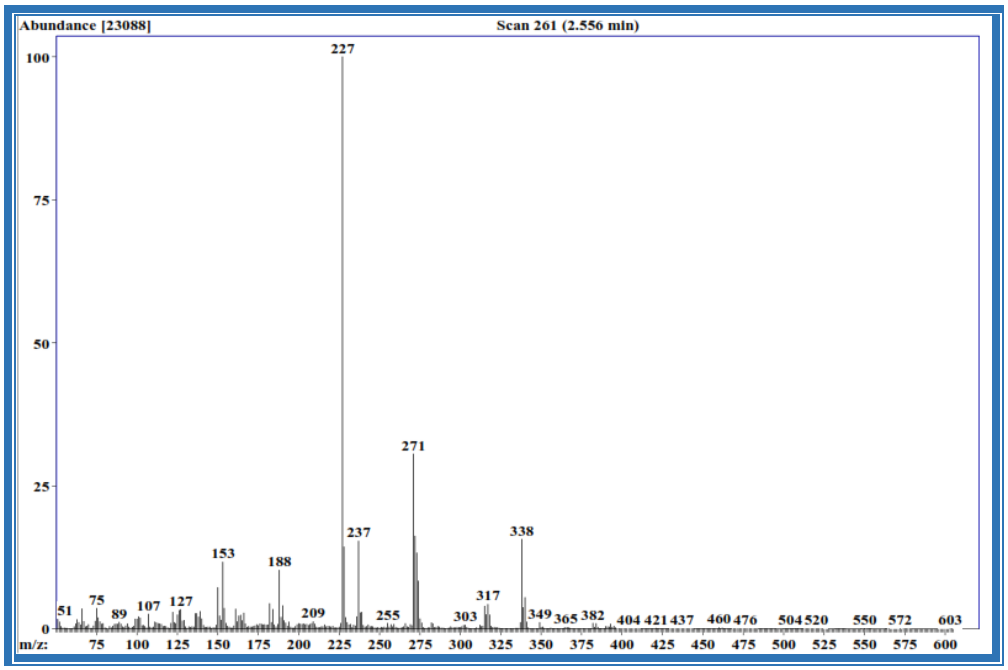


Fig. B3 The MS spectrum of product (**C_2**)

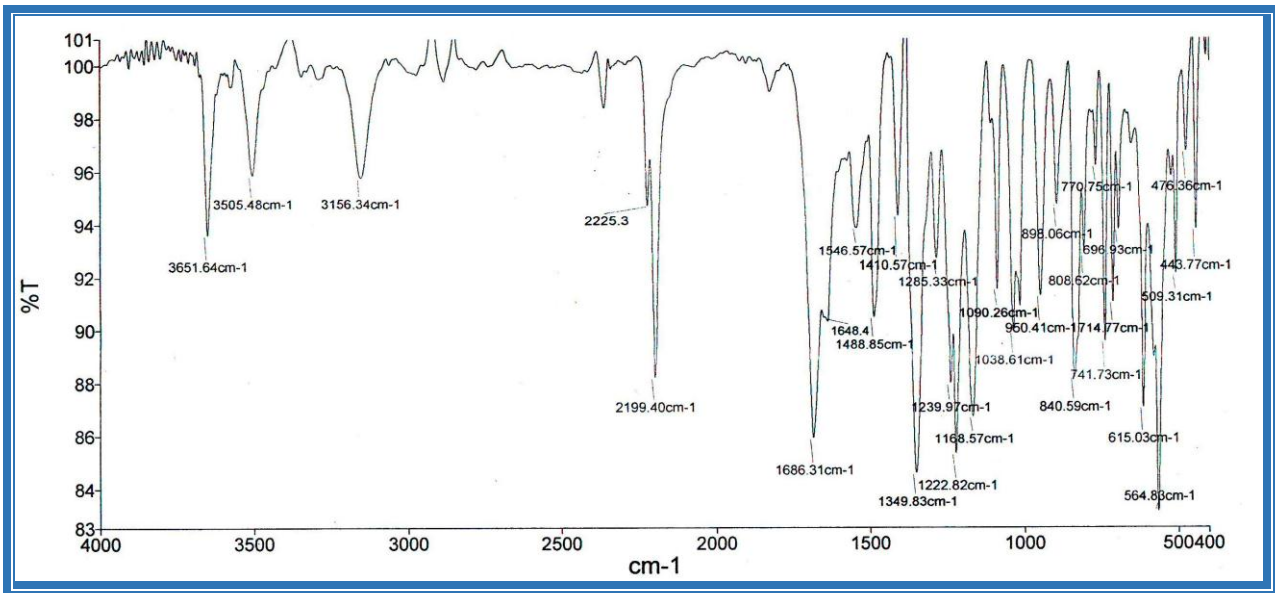
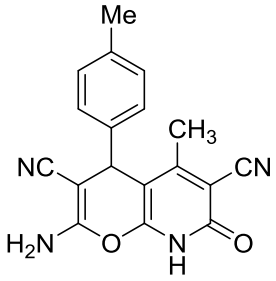


Fig. B4 The IR spectrum of product (**C_2**)

2-Amino-7,8-dihydro-5-methyl-7-oxo-4-(p-tolyl)-4H-pyrano[2,3-b]pyridine-3,6-dicarbonitrile (**C_3**)

White solid, mp 139-142 °C; ^{1}H NMR (400 MHz, $DMSOd_6$): δ = 2.20 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 5.52 (s, 1H, C_4-H), 6.98–8.49 (m, 6H, Ar-H and NH_2), 9.96 (s, 1H, NH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 26, 69.6, 92.9, 100.2, 109.7, 126.1, 126.9, 127.6, 127.7, 129.4, 129.7, 130.7, 153.4 ppm; IR (KBr) (ν_{max}/cm^{-1}): 3640, 3506, 3349, 2224, 2200, 1686; Anal. Calcd for $C_{18}H_{14}N_4O_2$: C, 67.92; H, 4.43, N, 17.60 %. Found: C, 67.95; H, 4.44; N, 17.65; MS: *m/z*= 318 (M^+).

(Table 2, Entry 3):



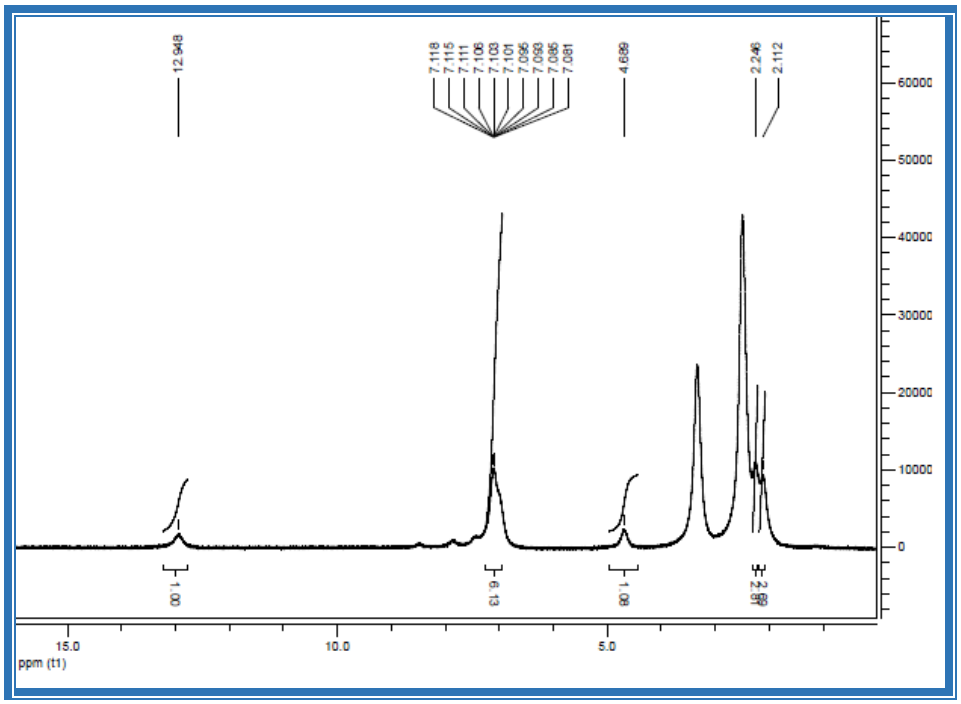


Fig. C1 The ^{1}H NMR (500 MHz) spectrum of product (**C_3**)

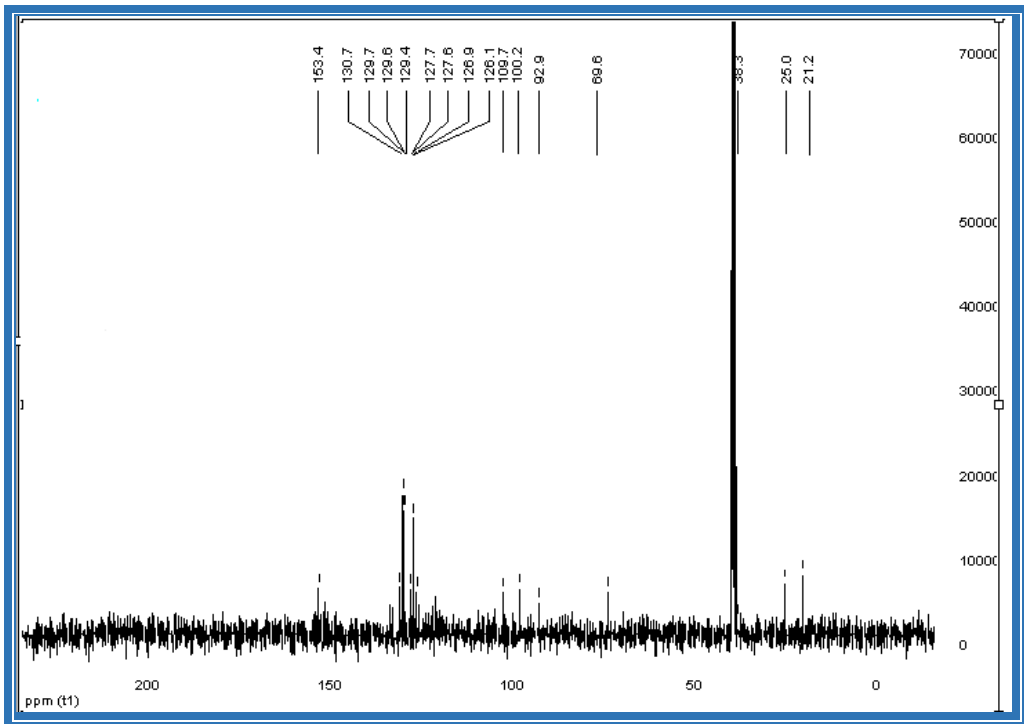


Fig. C2 The ^{13}C NMR (125 MHz) spectrum of product (**C_3**)

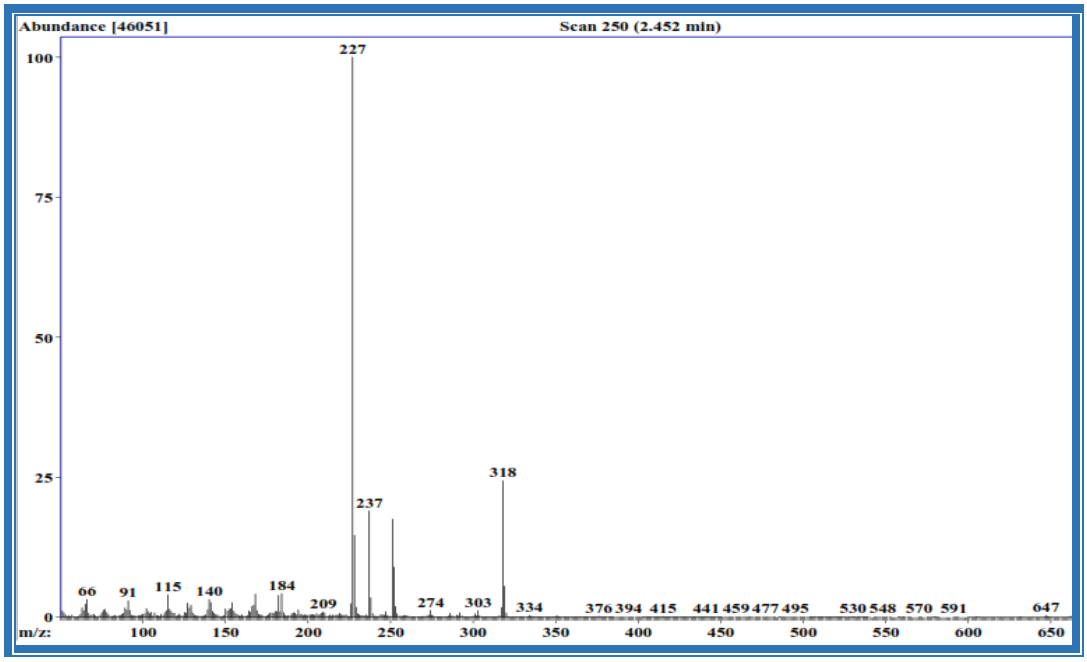


Fig. C3 The MS spectrum of product (**C_3**)

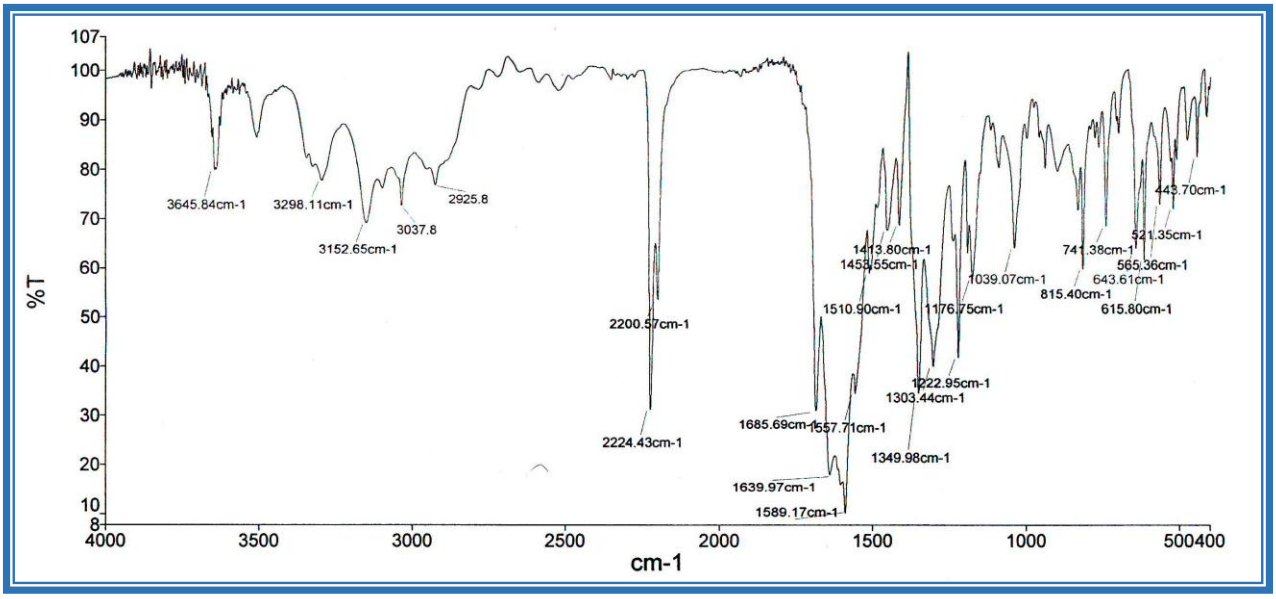
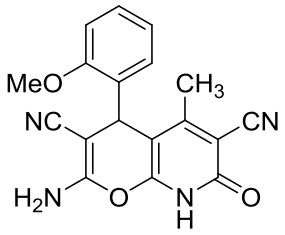


Fig. C4 The IR spectrum of product (**C_3**)

2-Amino-7,8-dihydro-5-methyl-7o-xo-4-(2-methoxyphenyl)-4H-pyrano[2,3-b]pyridine-3,6-dicarbonitrile (**C_4**)

White solid, mp 216-220 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.10 (s, 3H, CH_3), 3.69 (s, 3H, OCH_3), 4.89 (s, 1H, C_4-H), 7.01–8.48 (m, 6H, Ar-H and NH_2), 10.36 (s, 1H, NH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.2, 55.6, 92, 111.3, 112.0, 113.2, 114.4, 120.9, 126.8, 128.6, 128.9, 131.1, 136.5, 141.1, 156.1 ppm; IR (KBr) (ν_{max}/cm^{-1}): 3640, 3508, 3349, 2224, 2200, 1686; Anal. Calcd for $C_{18}H_{14}N_4O_3$: C, 64.67; H, 4.22, N, 16.76; %. Found: C, 64.68; H, 4.25; N, 16.78; MS: *m/z* = 334 (M^+).***(Table 2, Entry 4):***



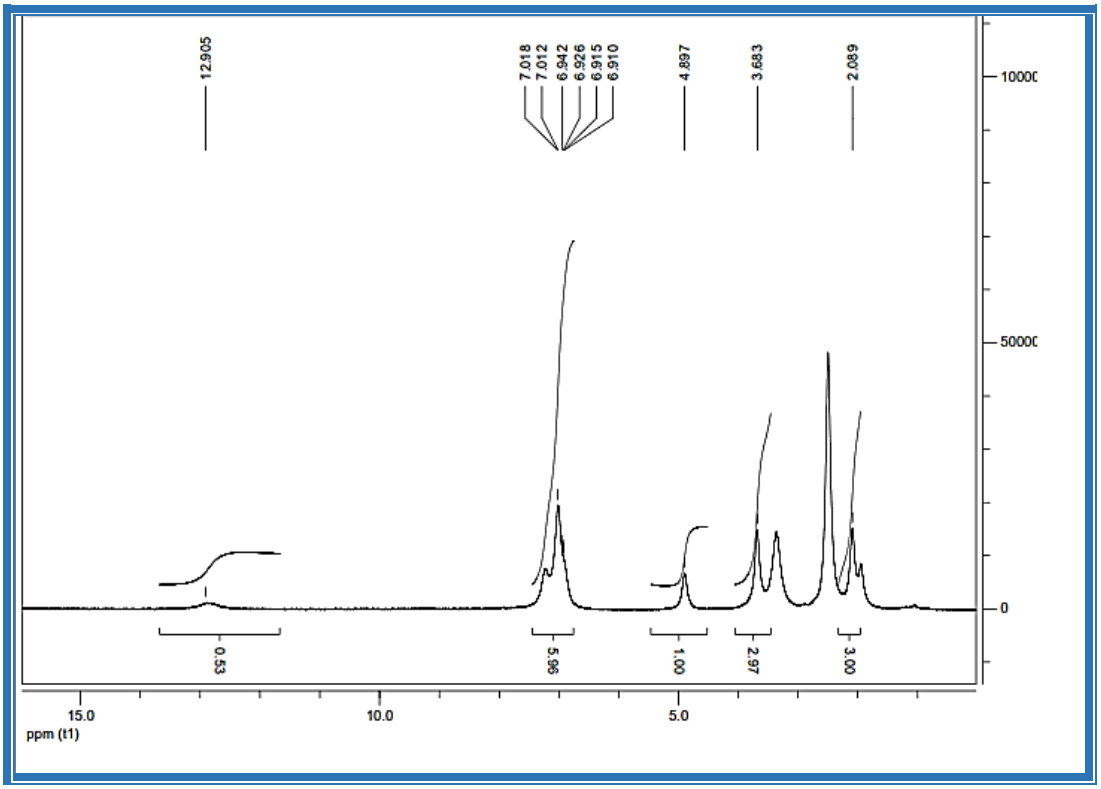


Fig. D1 The ^{1}H NMR (500 MHz) spectrum of product (**C_4**)

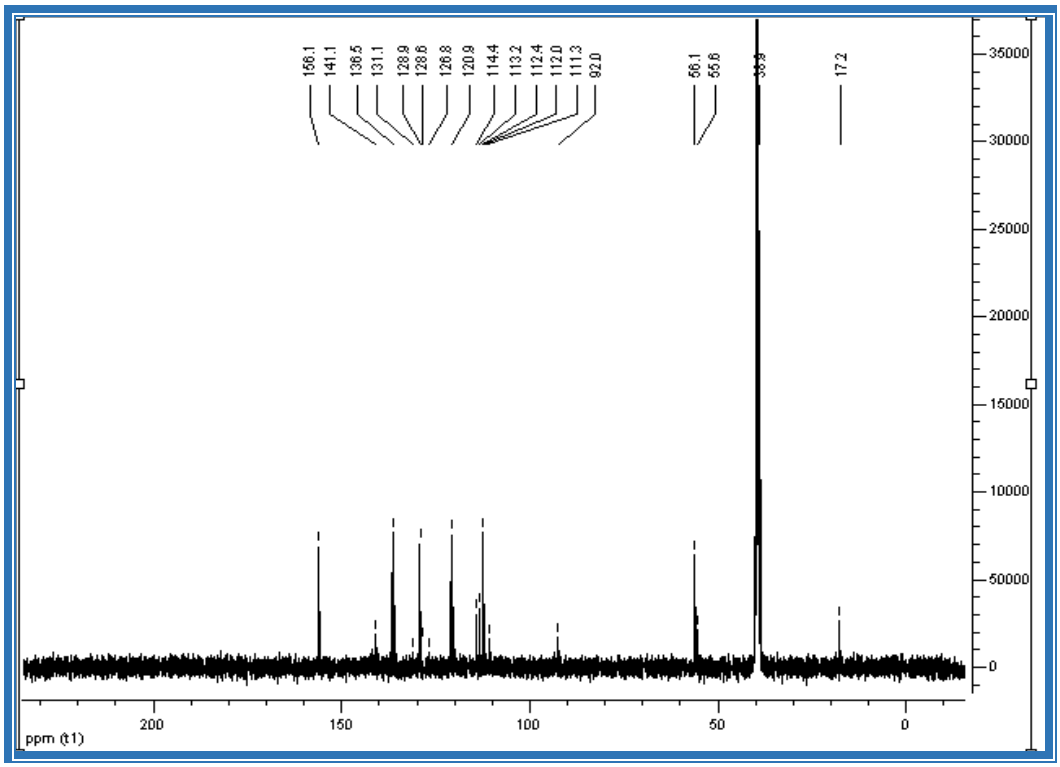


Fig. D2 The ^{13}C NMR (125 MHz) spectrum of product (**C_4**)

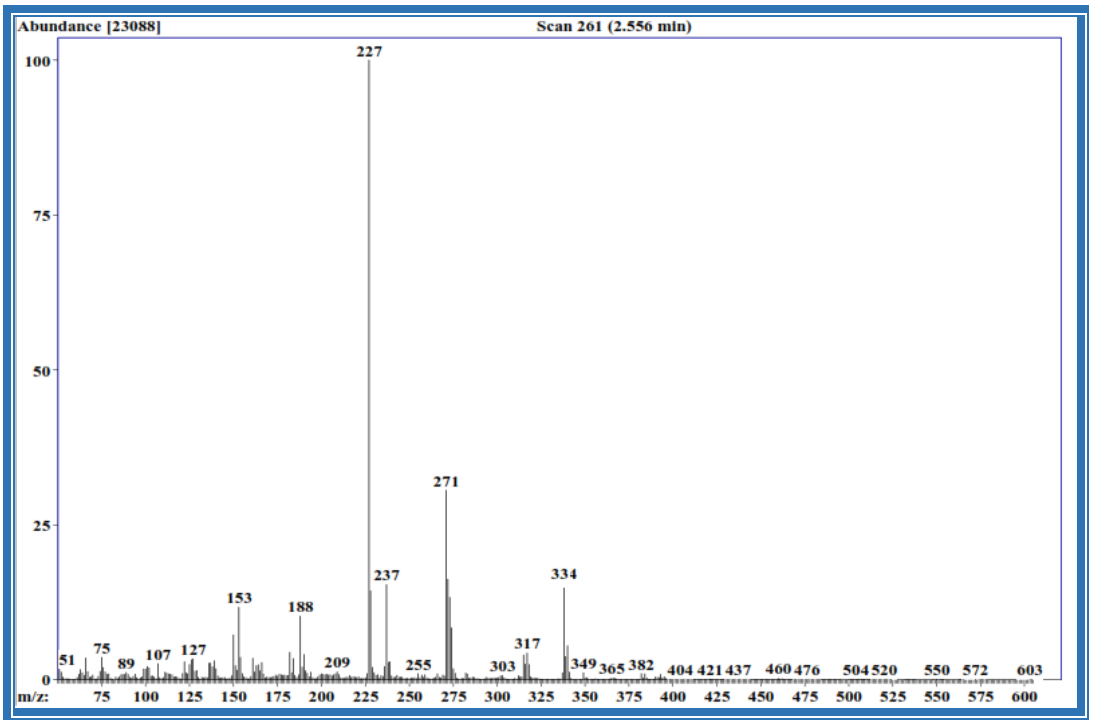


Fig. D3 The MS spectrum of product (**C_4**)

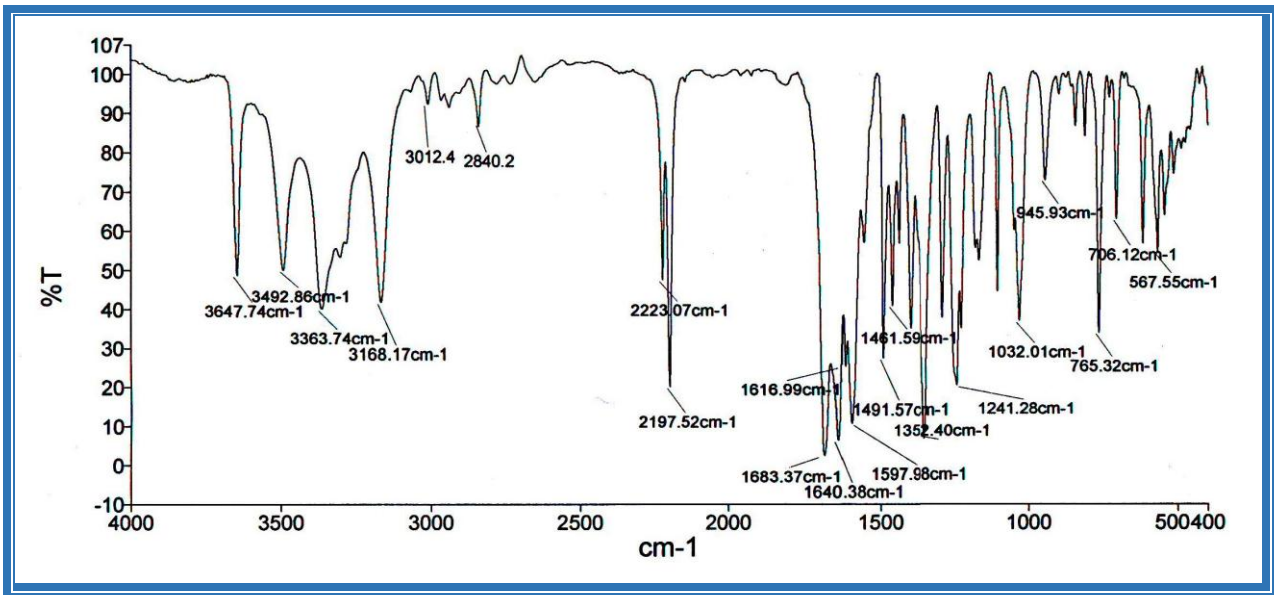
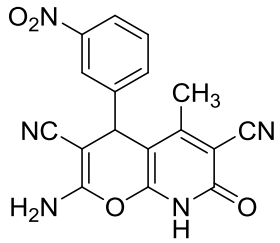


Fig. D4 The IR spectrum of product (**C_4**)

2-Amino-7,8-dihydro-5-methyl-7-oxo-4-(3-nitrophenyl)-4H- pyrano[2,3-b]pyridine-3,6-dicarbonitrile (**C_5**)

Yellow solid, mp 228-233 °C; ^{1}H NMR (FT-400 MHz, DMSO-d_6/TMS): δ = 2.12 (s, 3H, CH_3), 5.07 (s, 1H, C_4-H), 7.31–8.14 (m, 6H, Ar-H and NH_2), 13.01 (s, 1H, NH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.2, 93.6, 107.3, 115.2, 119.7, 122.1, 122.6, 131.0, 134.3, 146.6, 148.4, 156.0, 156.8, 159.6, 164.0 ppm; IR (KBr) (ν_{max}/cm^{-1}): 3648, 3484, 3356, 2225, 2197, 1681; Anal. Calcd for $C_{17}H_{11}N_5O_4$: C, 58.46; H, 3.17; N, 20.05 %. Found: C, 58.48; H, 3.18; N, 20.06; MS: *m/z* = 349 (M^+). ***(Table 2, Entry 5):***



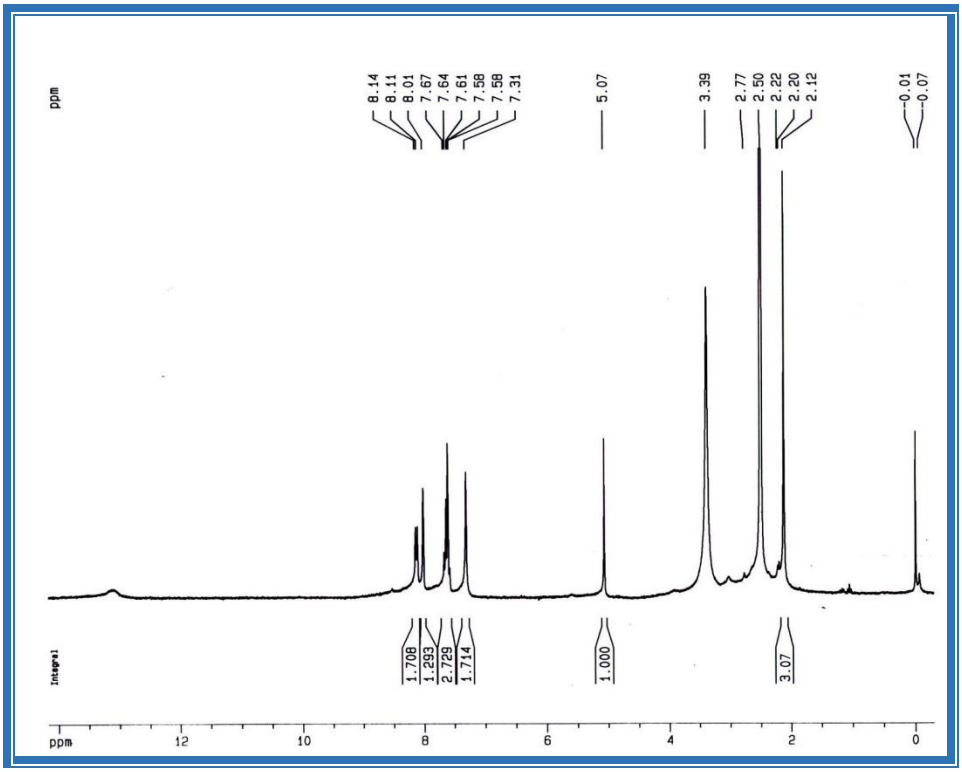


Fig. E1 The ^{1}H NMR (400 MHz) spectrum of product (**C_5**)

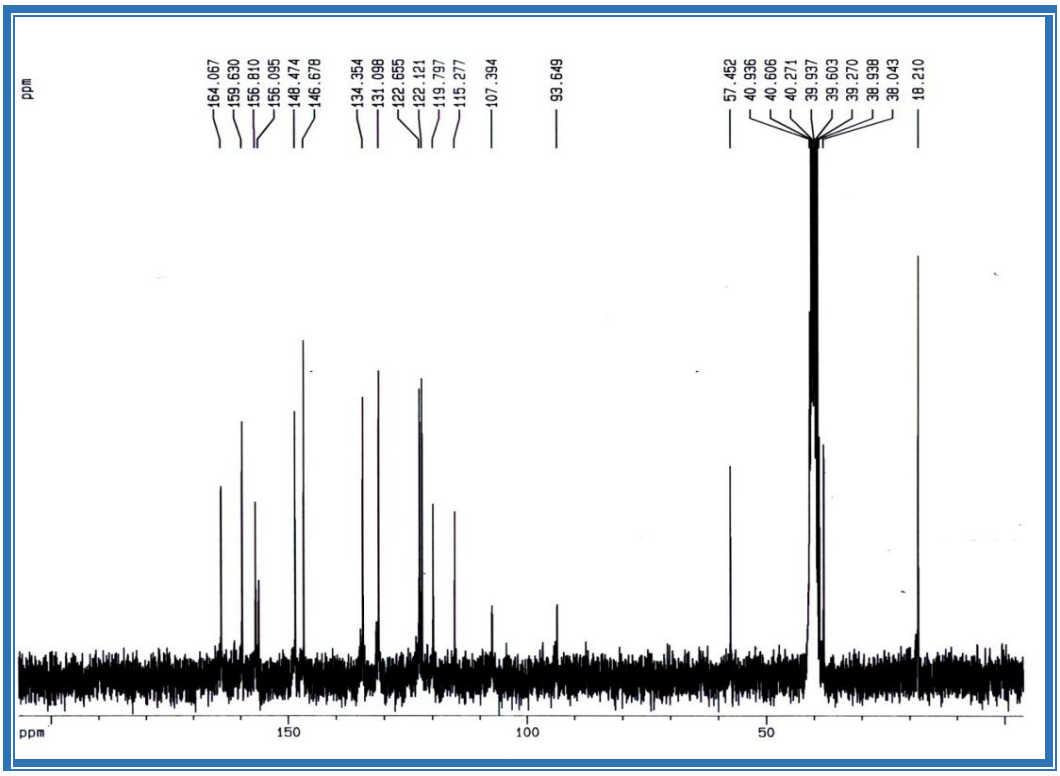


Fig. E2 The ^{13}C NMR (100 MHz) spectrum of product (**C_5**)

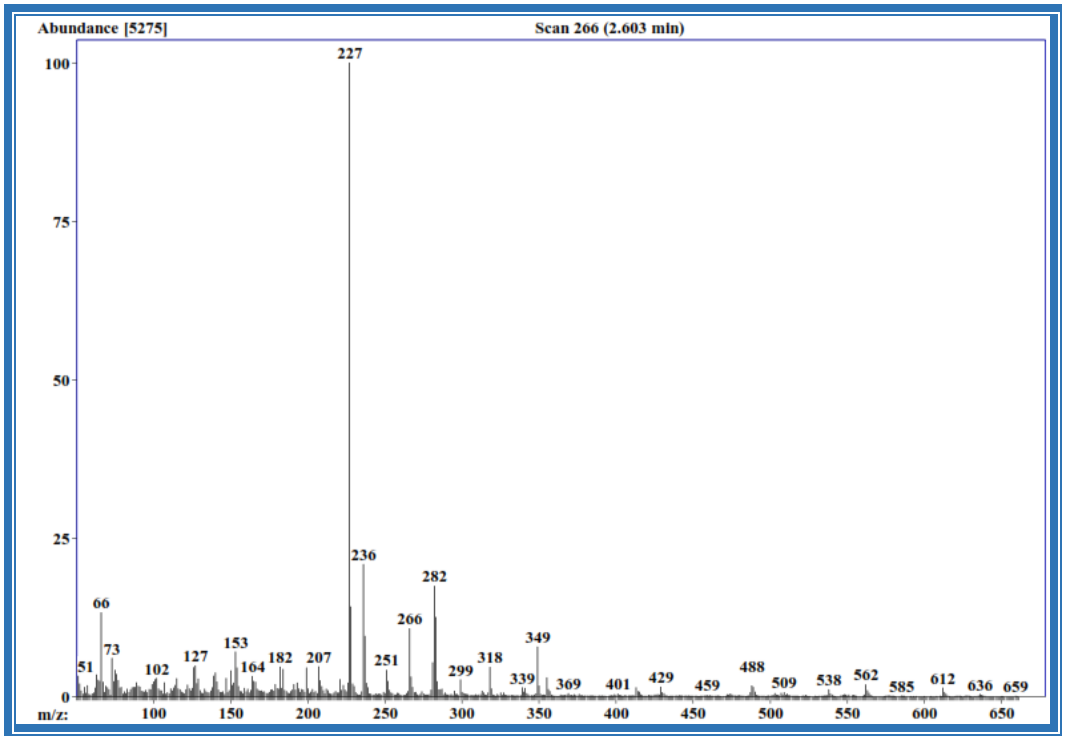


Fig. E3 The MS spectrum of product (**C_5**)

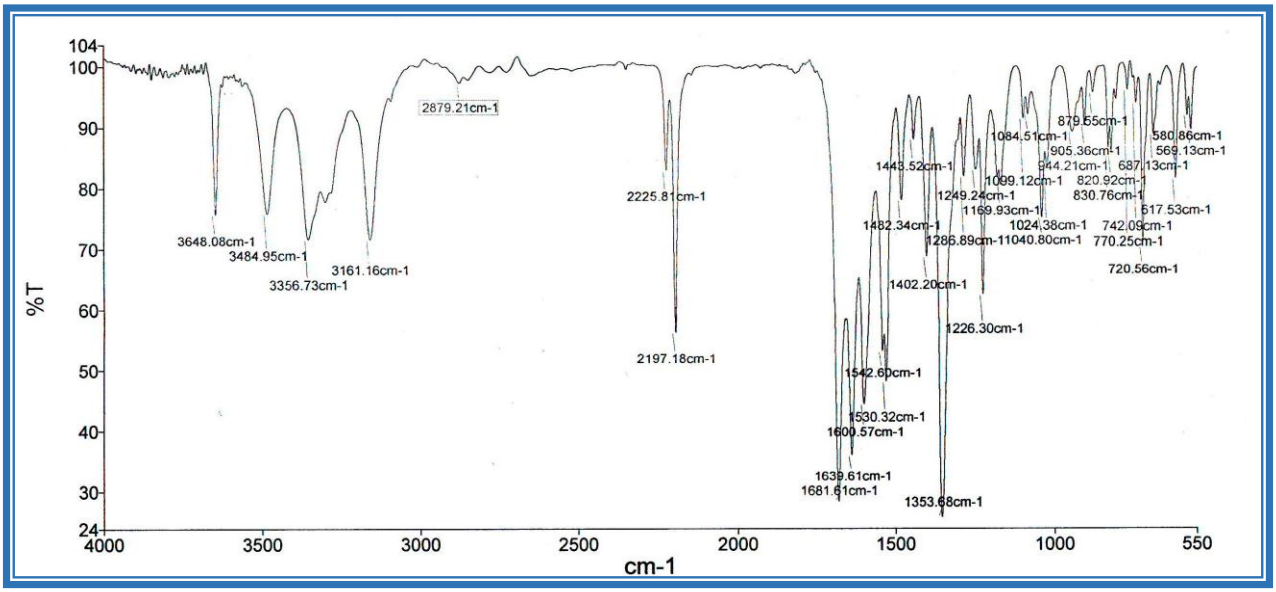
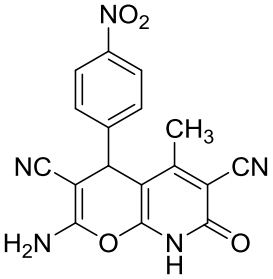


Fig. E4 The IR spectrum of product (**C_5**)

2-Amino-7,8-dihydro-5-methyl-7-oxo-4-(4-nitrophenyl)-4H- pyrano[2,3-b]pyridine-3,6-dicarbonitrile (**C_6**)

Yellow solid, mp 246-248 °C; ^{1}H NMR (FT-400 MHz, DMSO-d_6/TMS): δ = 2.28 (s, 3H, CH_3), 5.19 (s, 1H, C_4-H), 7.57–8.37 (m, 6H, Ar-H and NH_2), 13.28 (s, 3H, CH_3)ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.6, 56.5, 114.7, 119.2, 124.2, 128.4, 146.4, 151.3, 156.2, 159.1, 163.6, ppm; IR (KBr) (ν_{max}/cm^{-1}): 3648, 3484, 3355, 2225, 2197, 1682; Anal. Calcd for $C_{17}H_{11}N_5O_4$: C, 58.46; H, 3.17; N, 20.05 %. Found: C, 58.49; H, 3.18; N, 20.09; MS *m/z* = 349 (M^+).***(Table 2, Entry 5):***



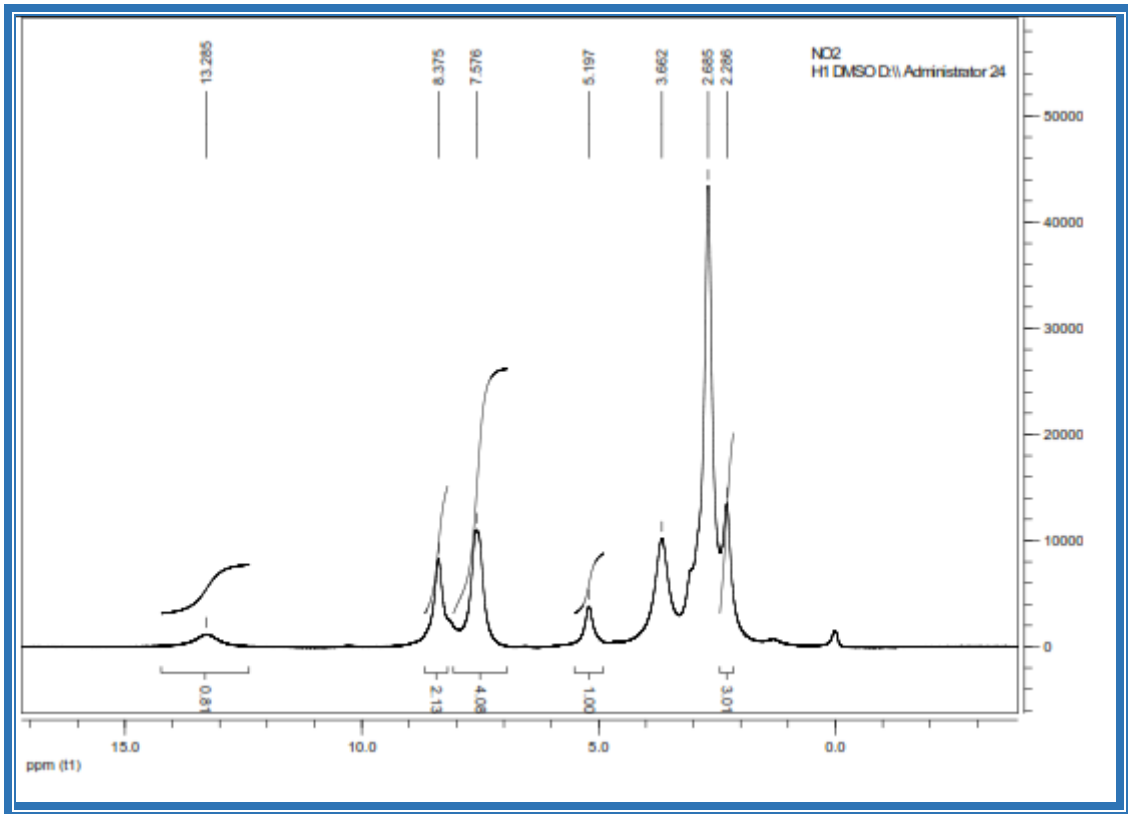


Fig. F1 The ^{1}H NMR (300 MHz) spectrum of product (**C_6**)

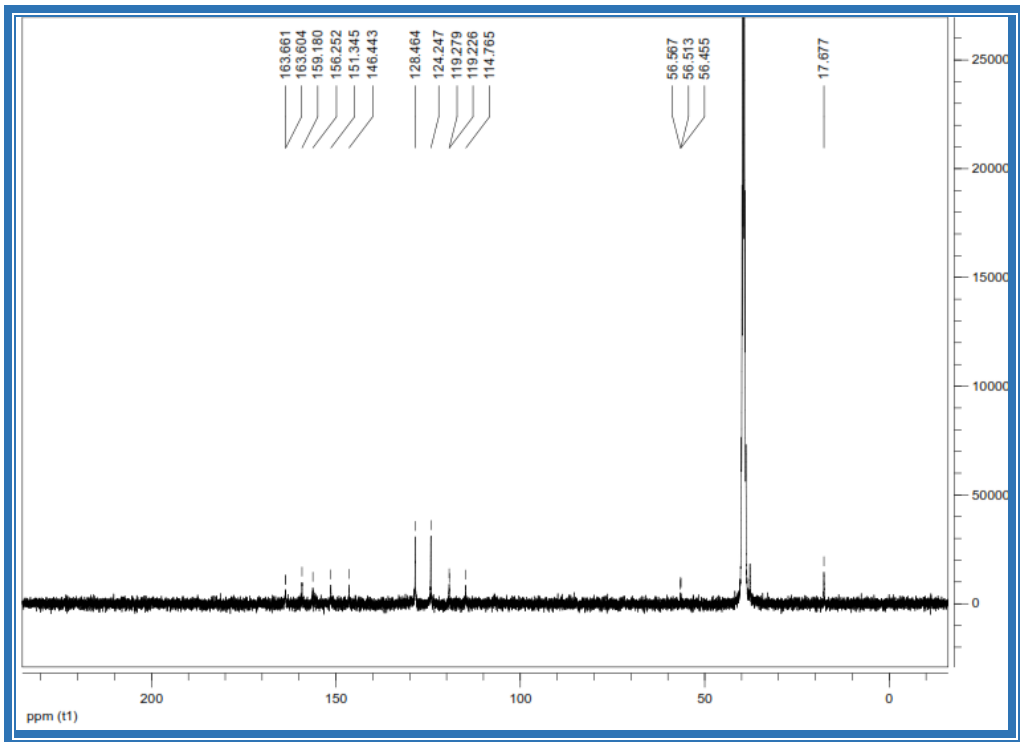


Fig. F2 The ^{13}C NMR (75 MHz) spectrum of product (**C_6**)

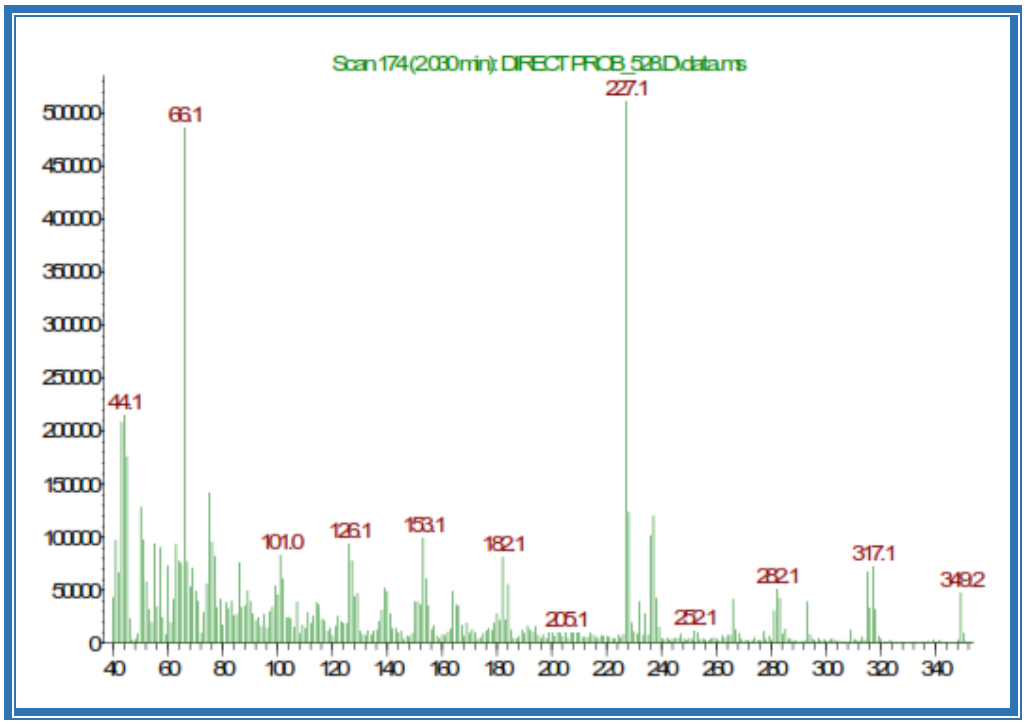


Fig. F3 The MS spectrum of product (**C_6**)

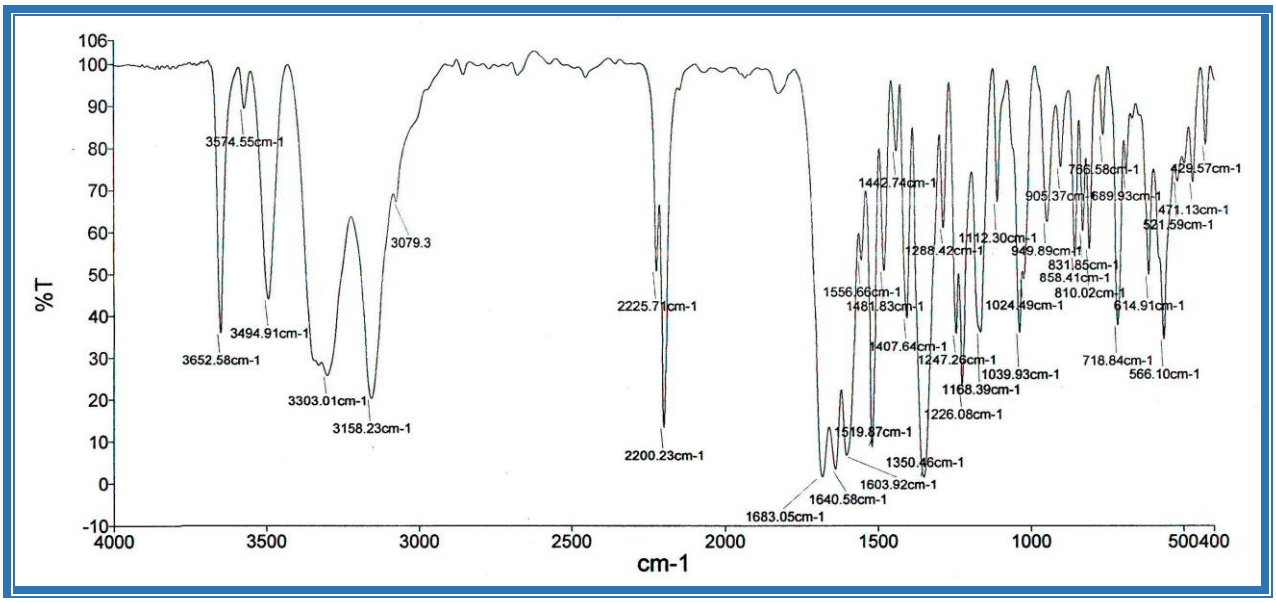
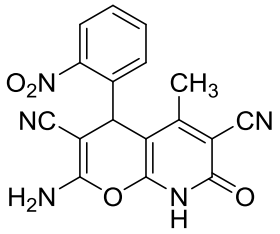


Fig. F4 The IR spectrum of product (**C_6**)

2-Amino-7,8-dihydro-5-methyl-7-oxo-4-(2-nitrophenyl)-4H- pyrano[2,3-b]pyridine-3,6-dicarbonitrile (**C_7**)

Yellow solid, mp 205-208 °C; ^{1}H NMR (FT-400 MHz, DMSO-d_6/TMS): δ = 2.07 (s, 3H, CH_3), 5.51 (s, 1H, C_4-H), 7.29–7.95 (m, 6H, Ar-H and NH_2) 13.12 (s, 3H, CH_3)ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.74, 33.8, 55.9, 114.7, 118.8, 124.6, 128.7, 130.6, 134.2, 137.3, 147.8, 156, 159.1, 162.2, 163.6 ppm; IR (KBr) (ν_{max}/cm^{-1}): 3648, 3484, 3355, 2225, 2197, 1682; Anal. Calcd for $C_{17}H_{11}N_5O_4$: C, 58.46; H, 3.17; N, 20.05 %. Found: C, 58.50; H, 3.19; N, 20.06; MS: *m/z* = 349 (M^+). ***(Table 2, Entry 7):***



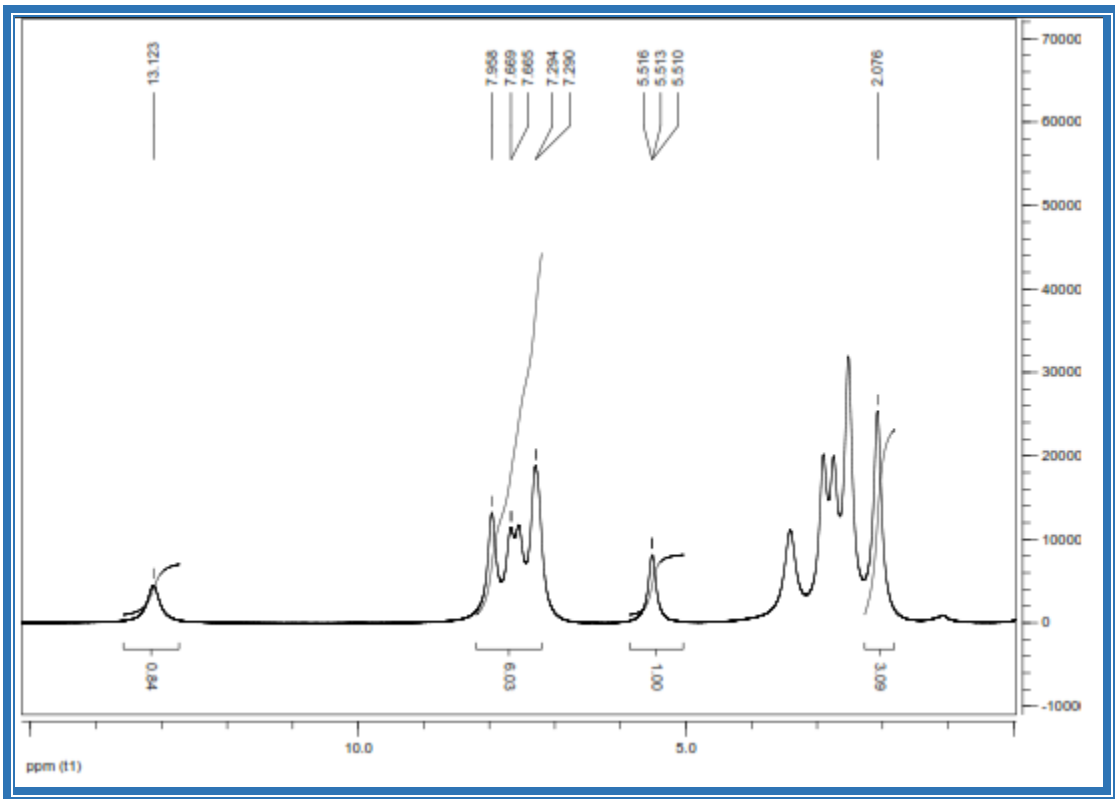


Fig. G1 The ^{1}H NMR (500 MHz) spectrum of product (**C_7**)

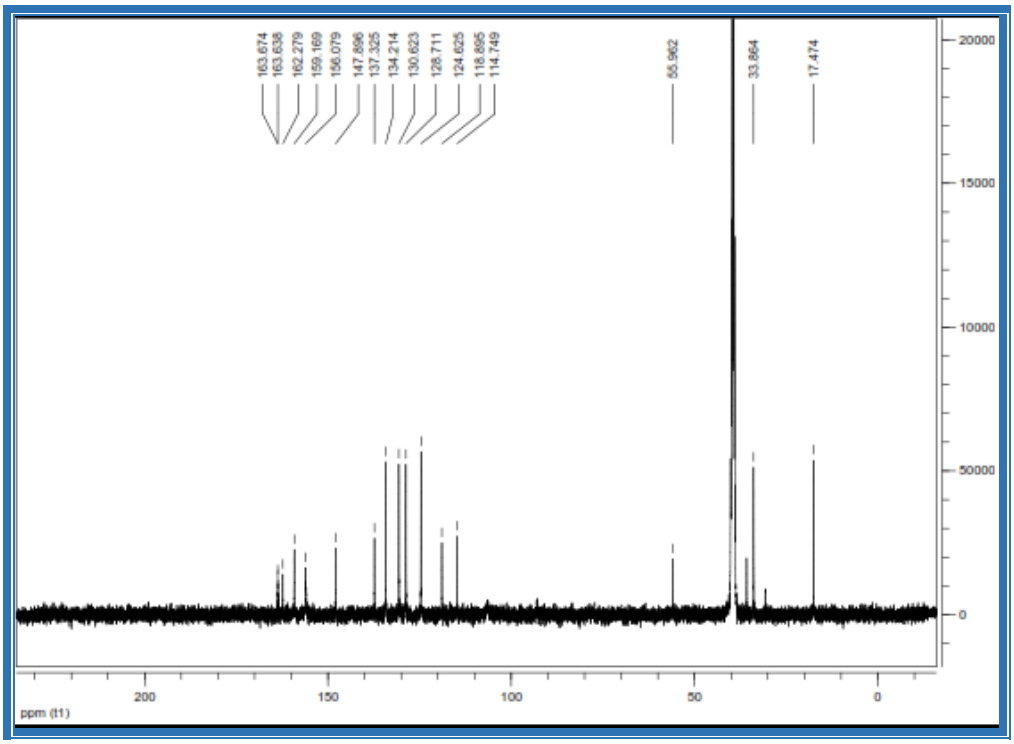


Fig. G2 The ^{13}C NMR (125 MHz) spectrum of product (**C_7**)

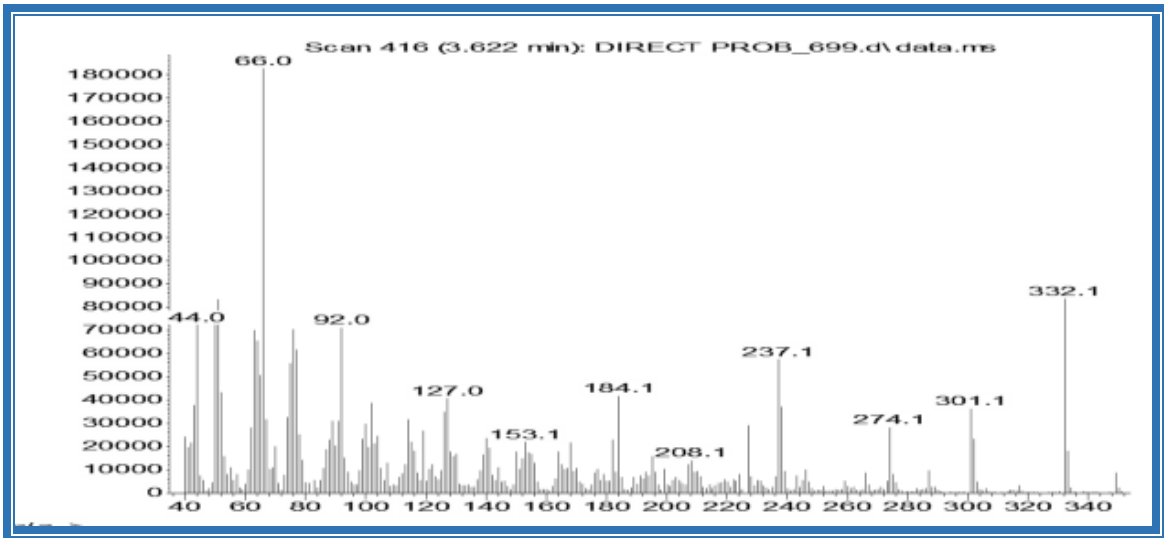


Fig. G3 The MS spectrum of product (**C_7**)

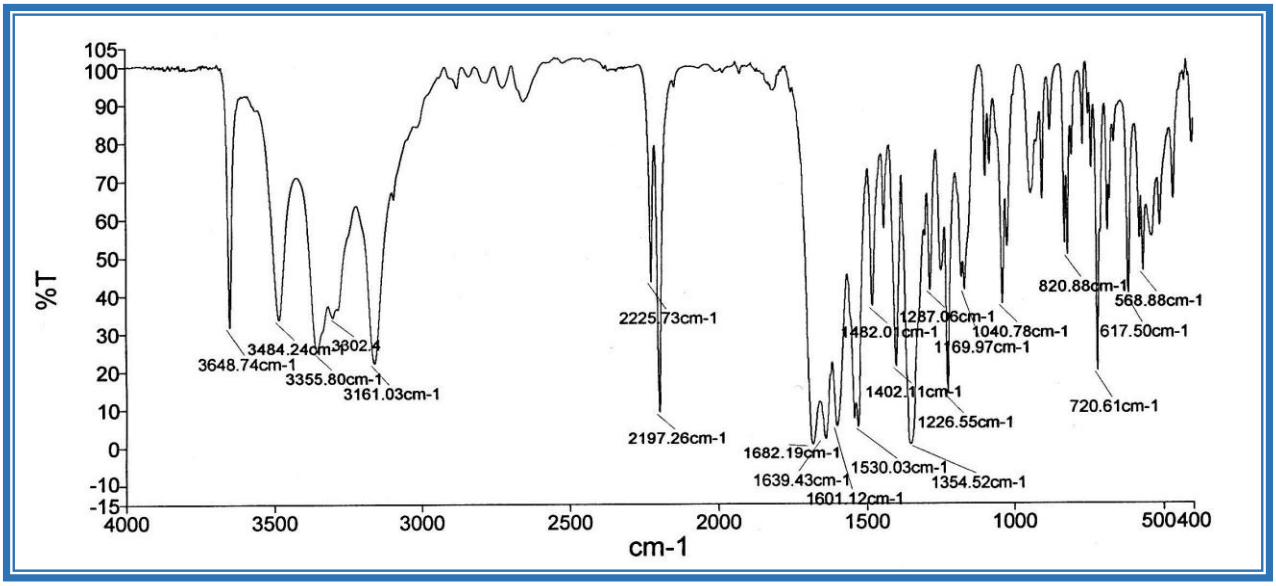
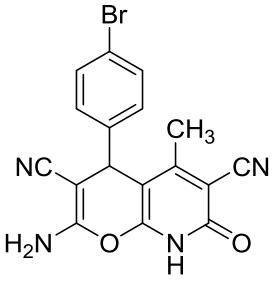


Fig. G4 The IR spectrum of product (C_7)

***2-Amino-7,8-dihydro-5-methyl-7-oxo-4-(4-bromophenyl)-4H-pyrano[2,3-b]pyridine-3,6-dicarbonitrile*(C$_8$)**

White solid, mp 238-241°C; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 2.21 (s, 3H, CH_3), 4.89 (s, 1H, C_4-H), 7.19–7.91 (m, 6H, Ar-H, and NH_2) 13.09 (s, 1H, NH)ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.6, 57.4, 114.8, 119.4, 120.1, 129.3, 131.7, 143.5, 155.5, 156.1, 158.9, 163.4 ppm; IR (KBr) (ν_{max}/cm^{-1}): 3649, 3504, 3349, 2220, 2199, 1683; Anal. Calcd for $C_{17}H_{11}BrN_4O_2$: C, 53.28; H, 2.89, N, 14.62; %. Found: C, 53.30; H, 2.93; N, 14.65; MS*: m/z* = 383 (M^+).***(Table 2, Entry 8):***



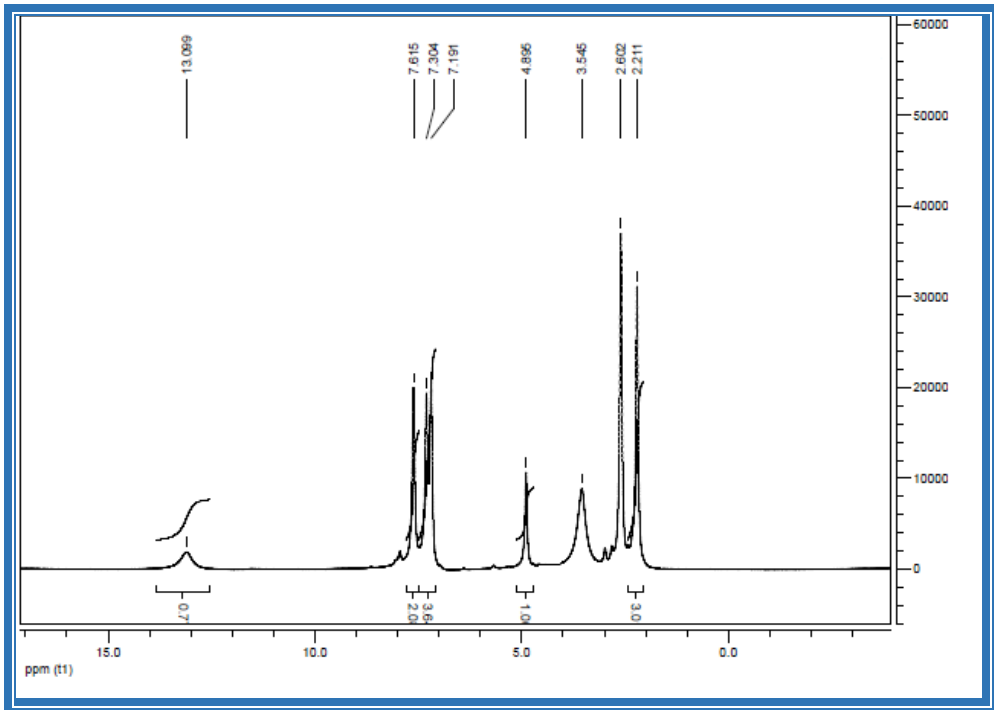


Fig. H1 The ^{1}H NMR (500 MHz) spectrum of product (**C$_8$**)

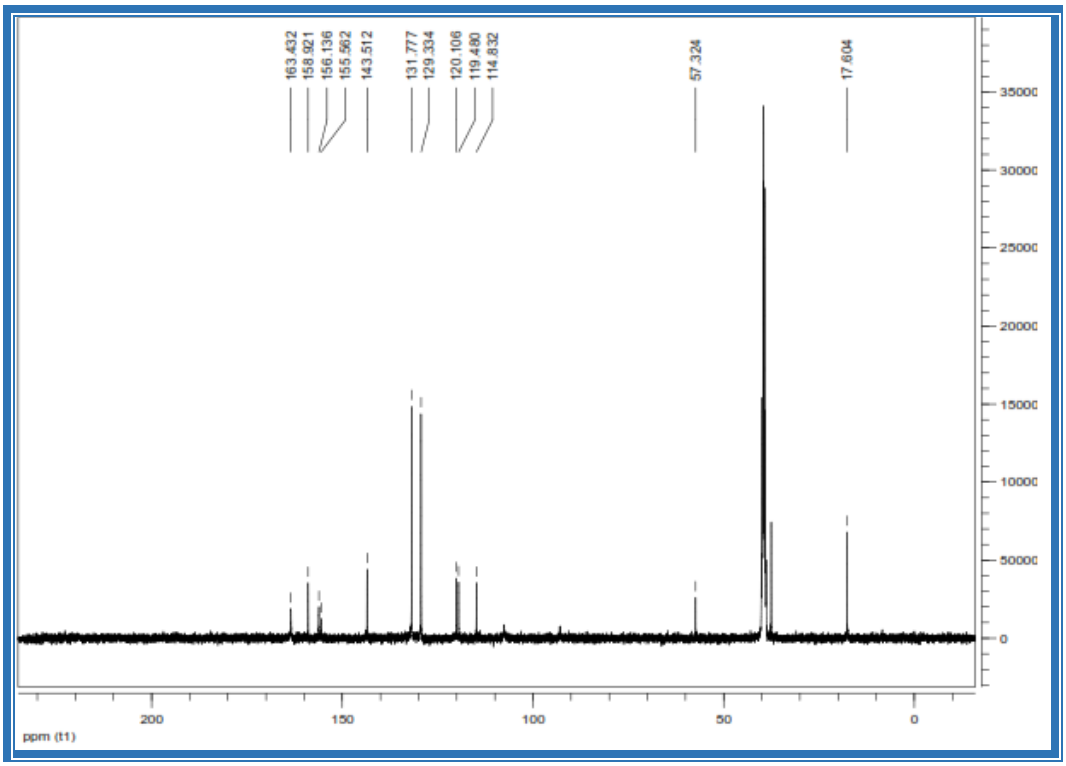


Fig. H2 The ^{13}C NMR (125 MHz) spectrum of product (**C_8**)

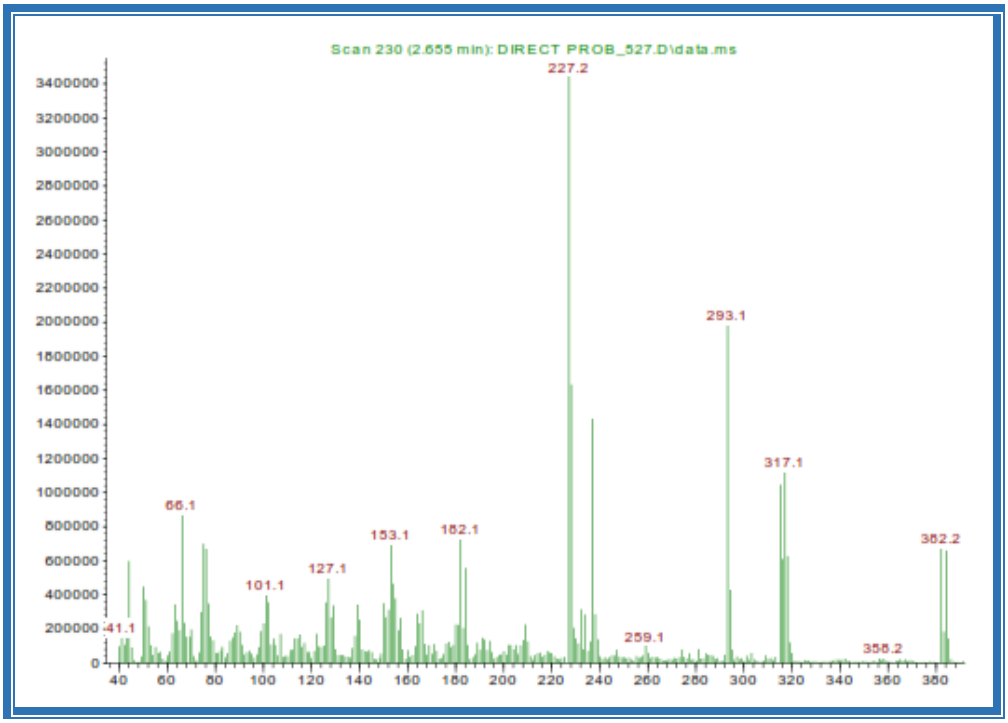


Fig. H3 The MS spectrum of product (**C_8**)

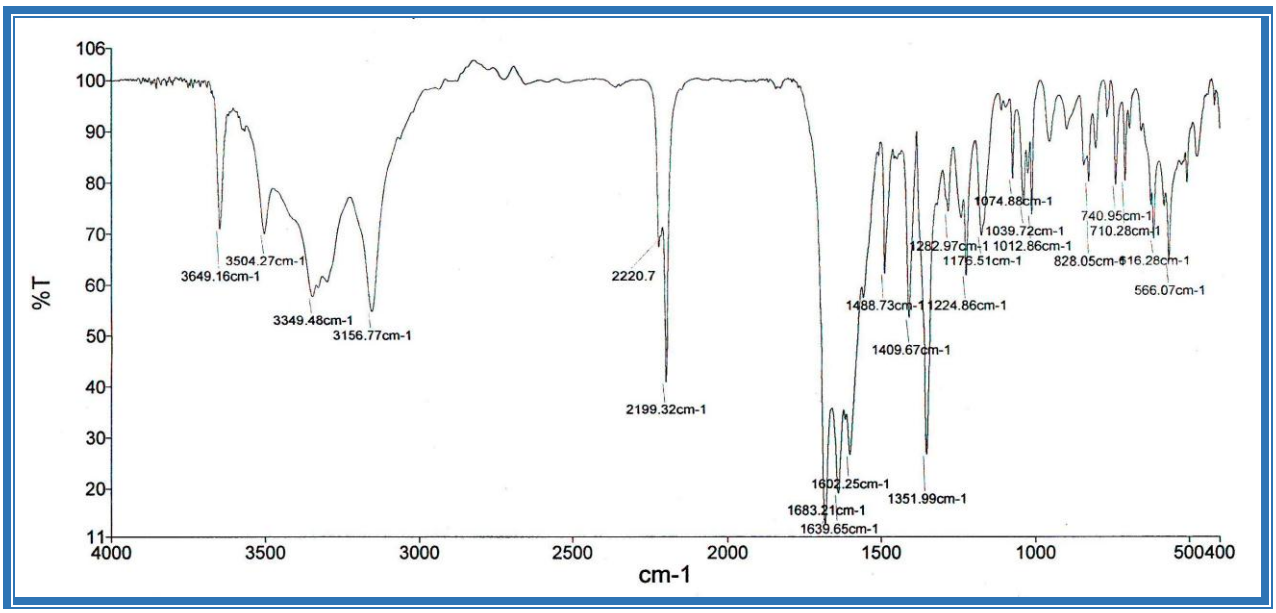
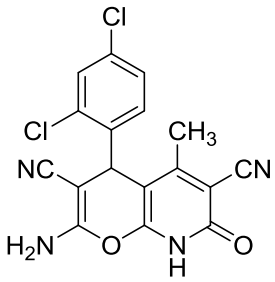


Fig. H4 The IR spectrum of product (C_8)

2-Amino-7,8-dihydro-5-methyl-7-oxo-4-(2,4-dichlorophenyl)-4H-pyrano[2,3-b]pyridine-3,6-dicarbonitrile (**C_9**)

White solid, mp 229-232 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.06 (s, 3H, CH_3), 5.17 (s, 1H, C_4-H), 7.25–7.62 (m, 5H, Ar-H, NH_2), 13.04 (s, 1H, NH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.5, 35.6, 55.3, 114.7, 118.9, 128.3, 129.2, 132.1, 139.6, 155.9, 159.2, 169, 174.9, 188.4 ppm; IR (KBr) (ν_{max}/cm^{-1}): 3650, 3499, 3348, 2225, 2200, 1683; Anal. Calcd for $C_{17}H_{10}Cl_2N_4O_2$: C, 54.71; H, 2.70, N, 15.01; %. Found: C, 57.75; H, 2.73; N, 15.04; MS: *m/z* = 372 (M^+). ***(Table 2, Entry 9):***



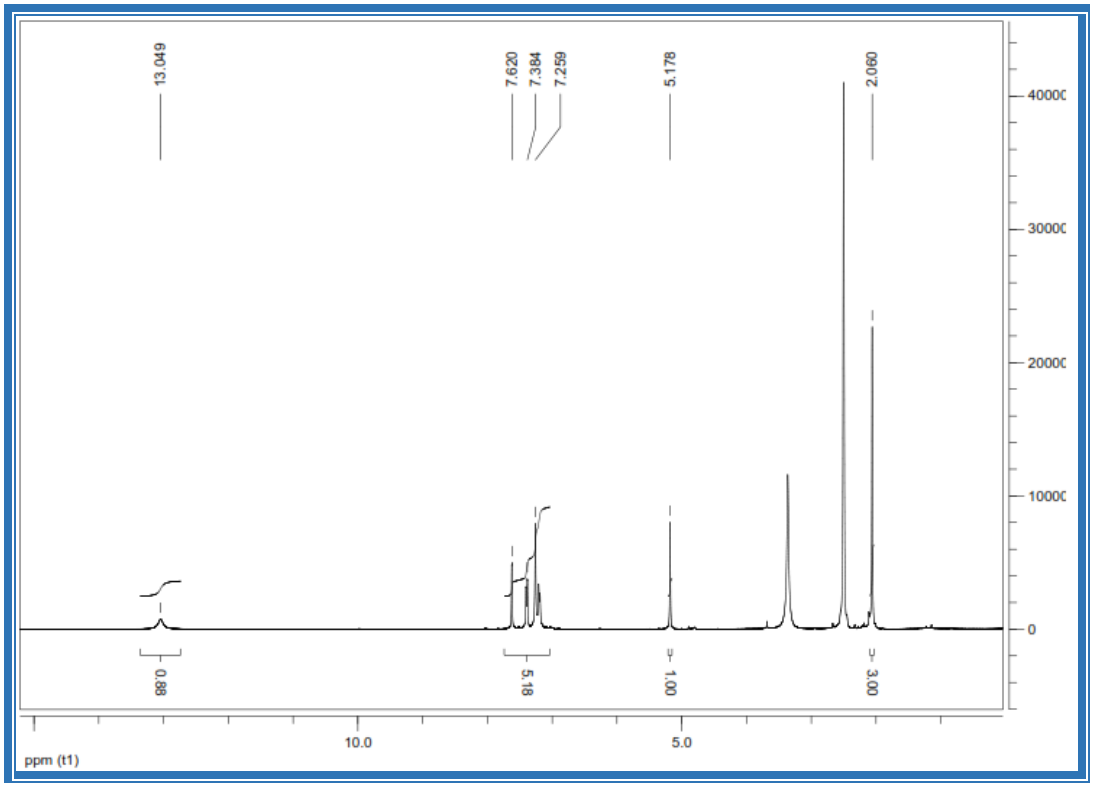


Fig. I1 The ^{1}H NMR (500 MHz) spectrum of product (**C_9**)

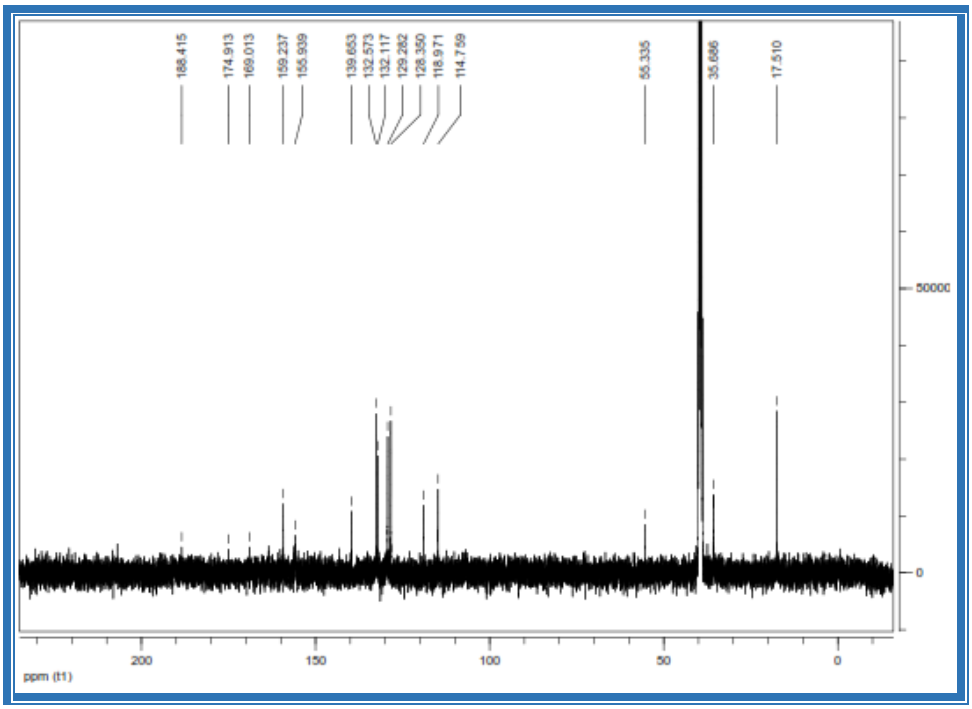


Fig. I2 The ^{13}C NMR (125 MHz) spectrum of product (**C_9**)

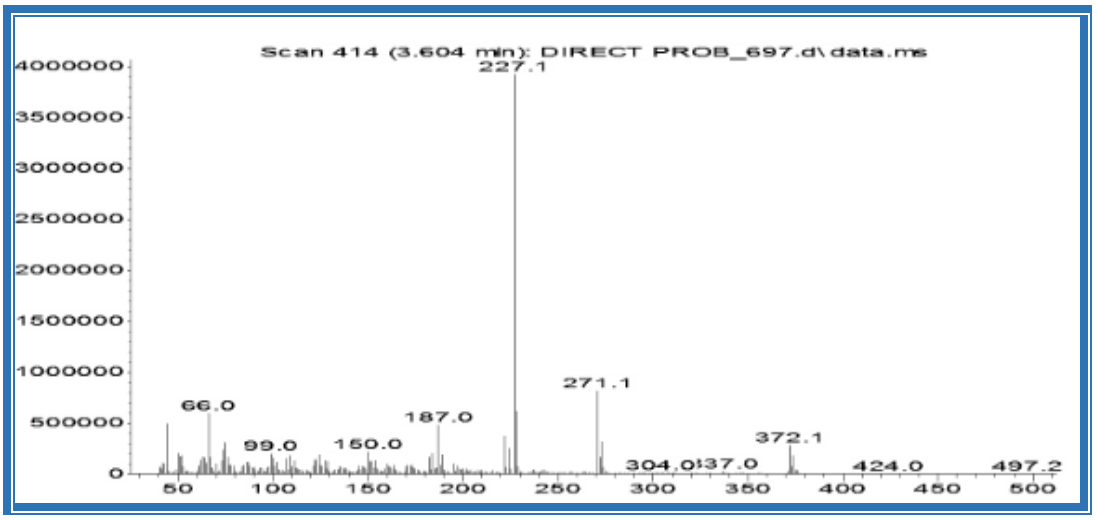


Fig. I3 The MS spectrum of product (**C_9**)

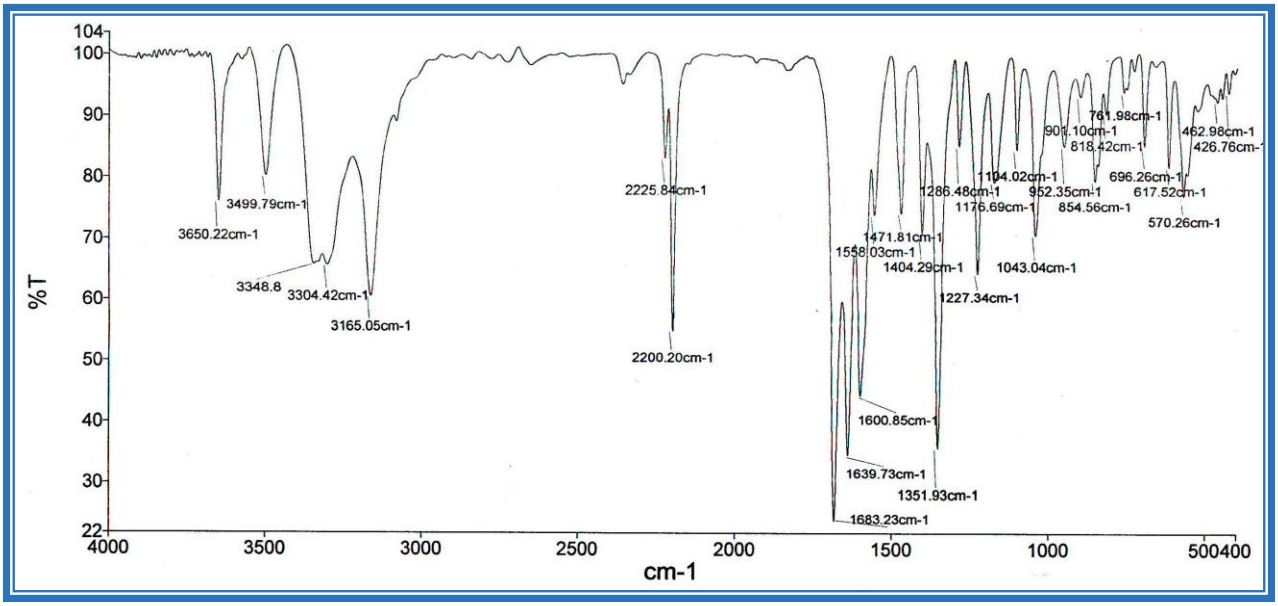
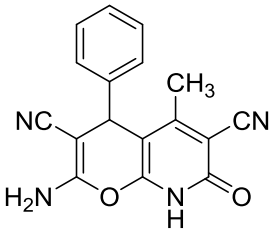


Fig. I4 The IR spectrum of product (**C_9**)

2 -Amino-7,8-dihydro-5-methyl-7-oxo-4-(phenyl)-4H-pyrano[2,3-b]pyridine-3,6-dicarbonitrile (**C_{10}**)

White solid, mp 221-223 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.21 (s, 3H, CH_3), 4.74 (s, 1H, C_4-H), 7.61–8.56 (m, 8H, Ar-H, NH and NH_2) ppm; ^{13}CNMR (100 MHz, $CDCl_3$): δ = 17.5, 38.8, 54.2, 81.5, 113.1, 114.1, 129.5, 130.4, 131.2, 134.3, 161.5 ppm; IR (KBr) (ν_{max}/cm^{-1}): 3639, 3498, 3349, 3152, 2222, 2198, 1685; Anal. Calcd for $C_{17}H_{12}N_4O_2$: C, 67.10; H, 3.97; N, 18.41 %. Found: C, 67.13; H, 4.01; N, 18.43; MS *m/z* = 304 (M^+). ***(Table 2, Entry 10):***



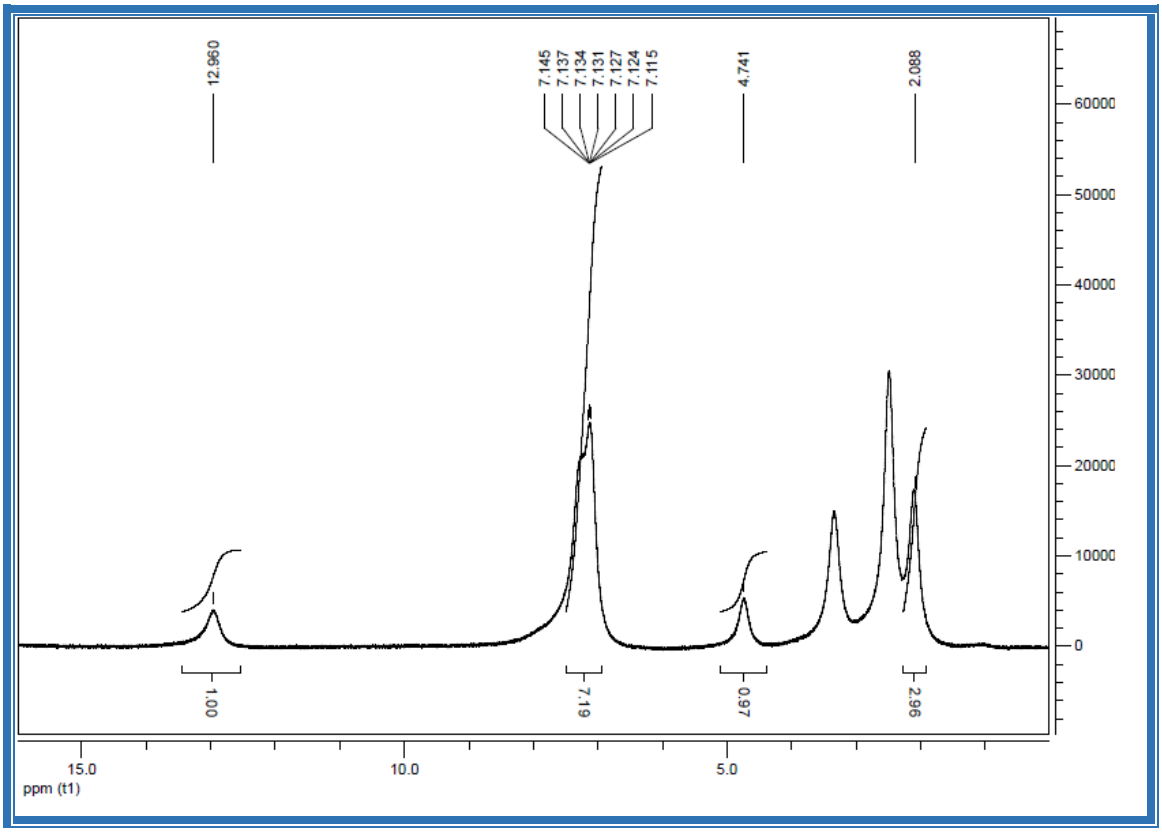


Fig. J1 The ^{1}H NMR (400 MHz) spectrum of product (**C_{10}**)

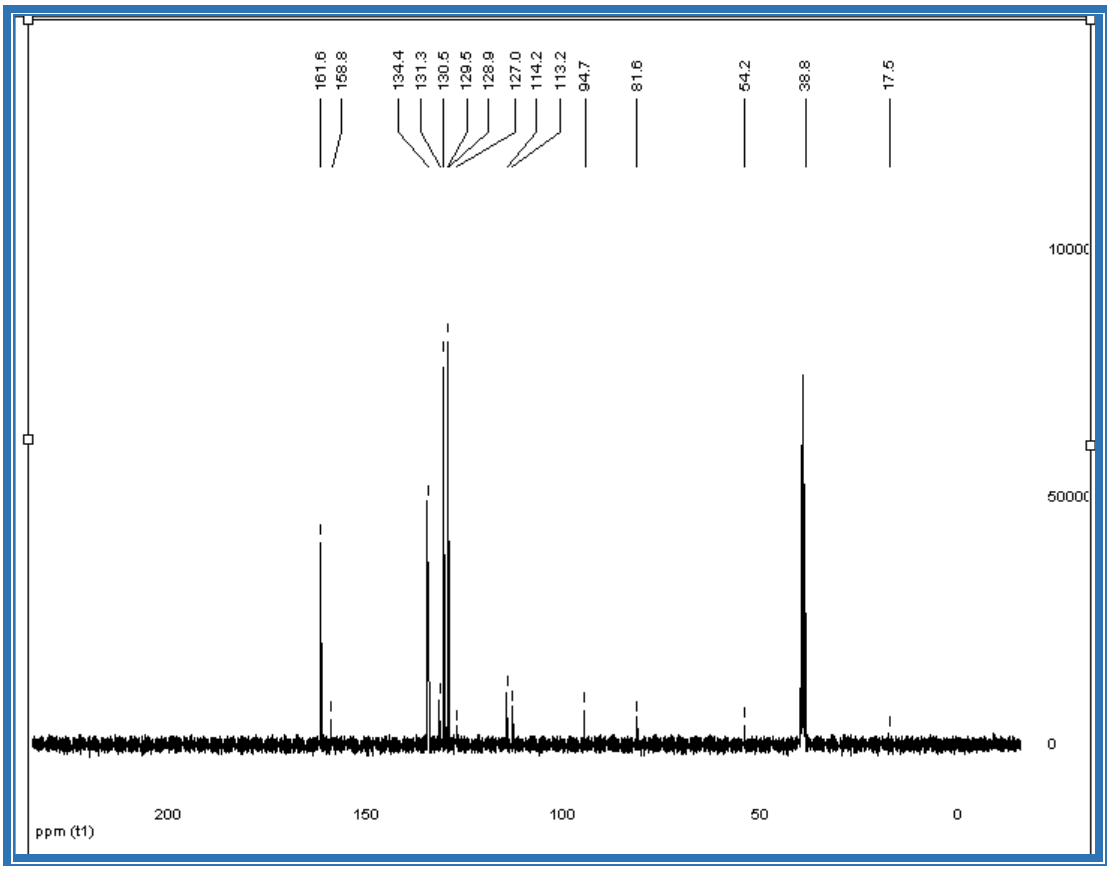


Fig. J2 The ^{13}C NMR (100 MHz) spectrum of product (**C_{10}**)

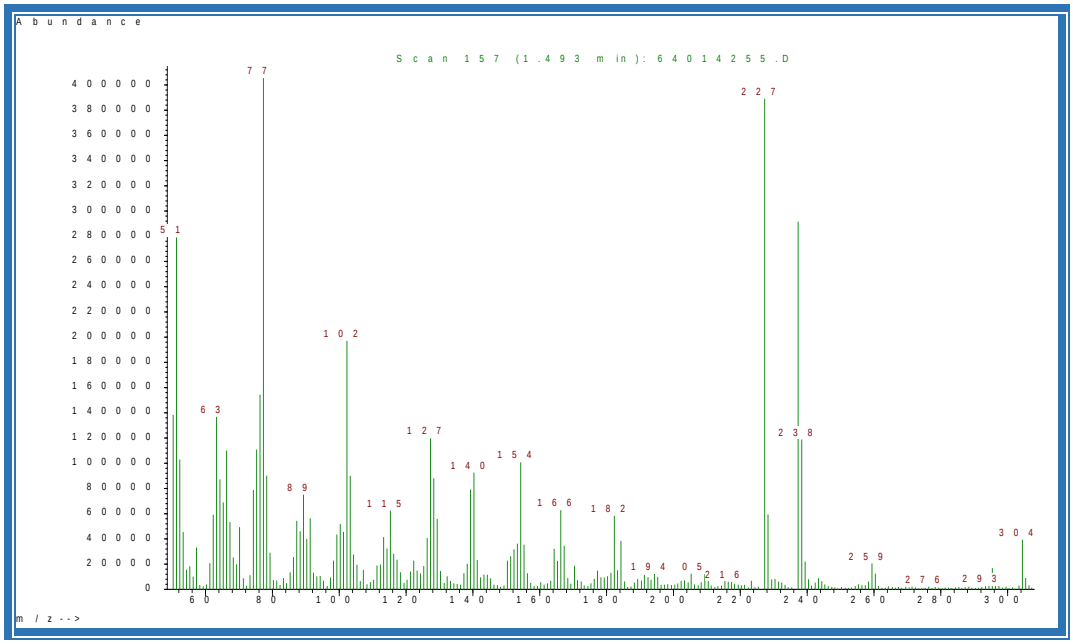


Fig. J3 The MS spectrum of product (**C_{10}**)

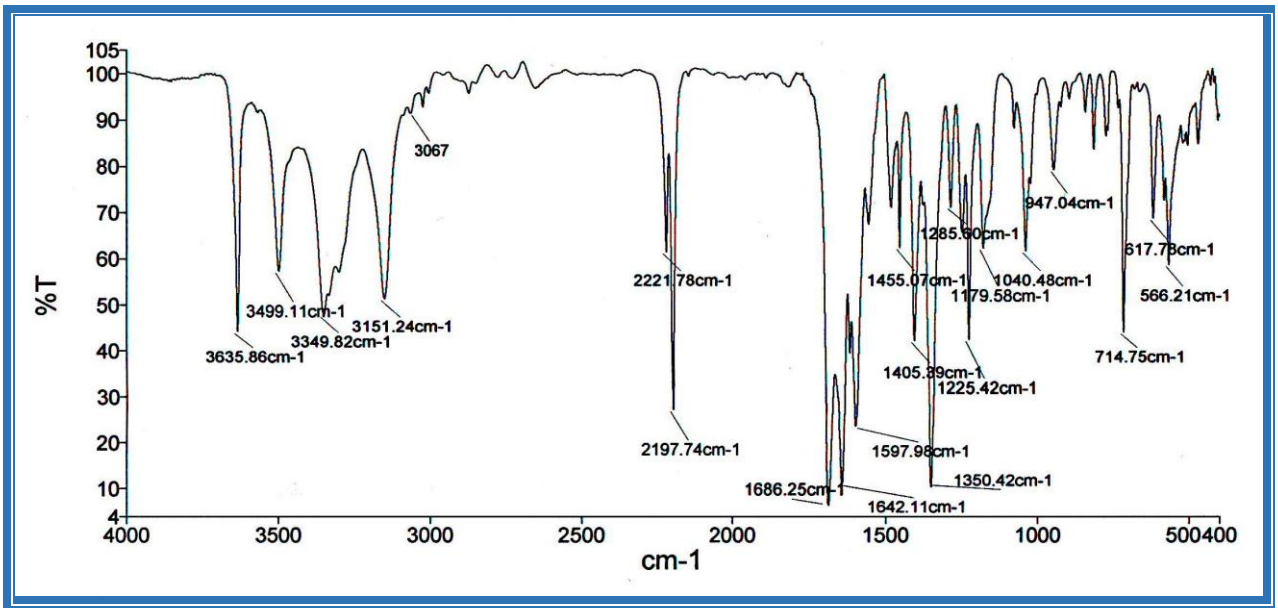
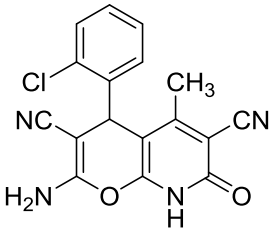


Fig. J4 The IR spectrum of product (C_{10})

2-Amino-7,8-dihydro-5-methyl-7-oxo-4-(2-chlorophenyl)-4H-pyrano[2,3-b]pyridine-3,6-dicarbonitrile (**C_{11}**)

White solid, mp 253–258°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.08 (s, 3H, CH_3), 5.19 (s, 1H, C_4-H), 7.26–7.28 (m, 6H, Ar-H, and NH_2) 13.04 (s, 1H, NH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.4, 55.7, 114.7, 119.1, 128.1, 129.8, 130.7, 140.5, 151.3, 159.2 163.5, 170.8 ppm; IR (KBr) (ν_{max}/cm^{-1}): 3648, 3496, 3356, 2225, 2199, 1683; Anal. Calcd for $C_{17}H_{11}ClN_4O_2$: C, 60.28; H, 3.27, N, 16.54; %. Found: C, 60.31; H, 3.30; N, 16.57; MS: *m/z* = 338 (M^+). ***(Table 2, Entry 11):***



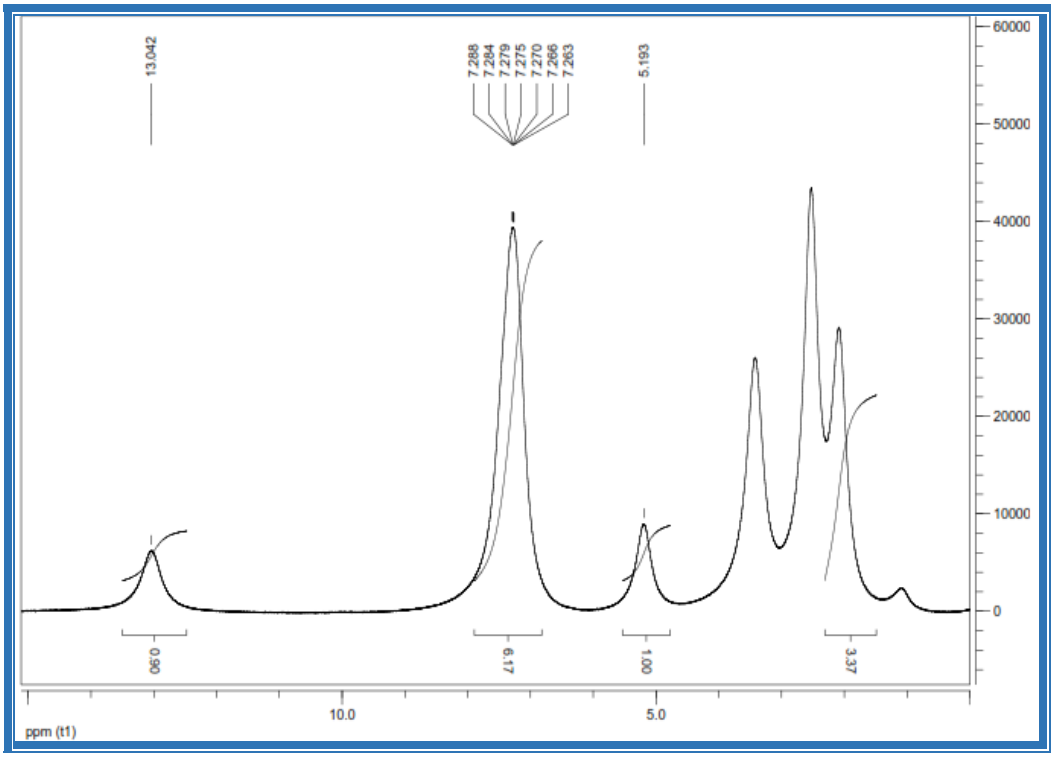


Fig. K1 The ^{1}H NMR (400 MHz) spectrum of product (**C_{11}**)

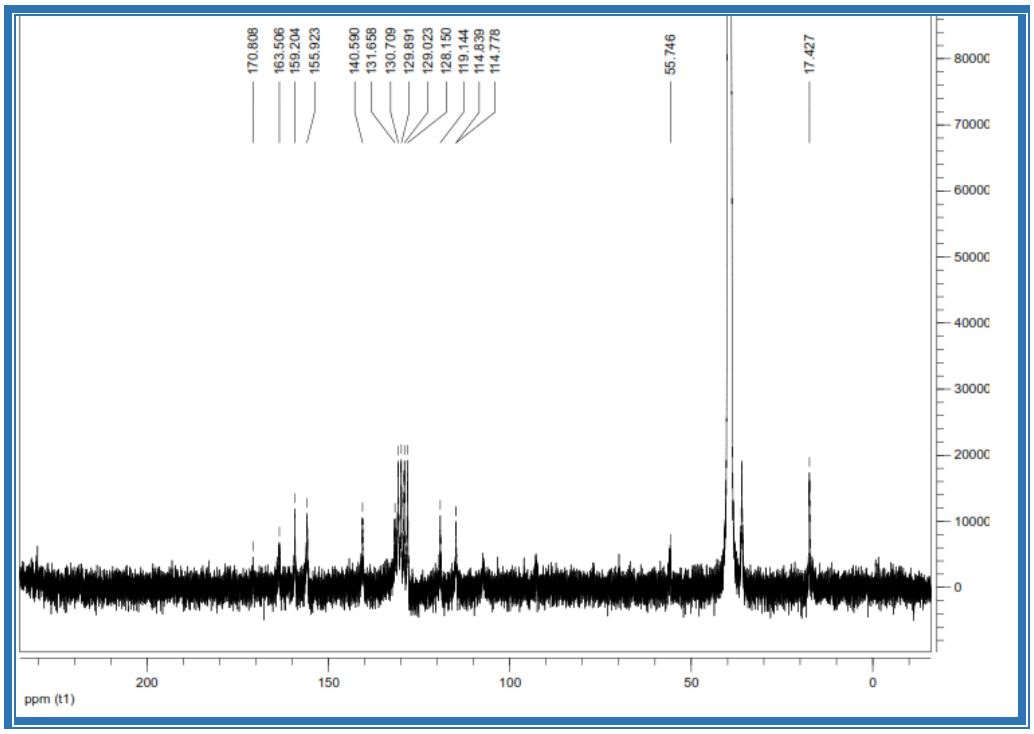


Fig. K2 The ^{13}C NMR (100 MHz) spectrum of product (C_{11})

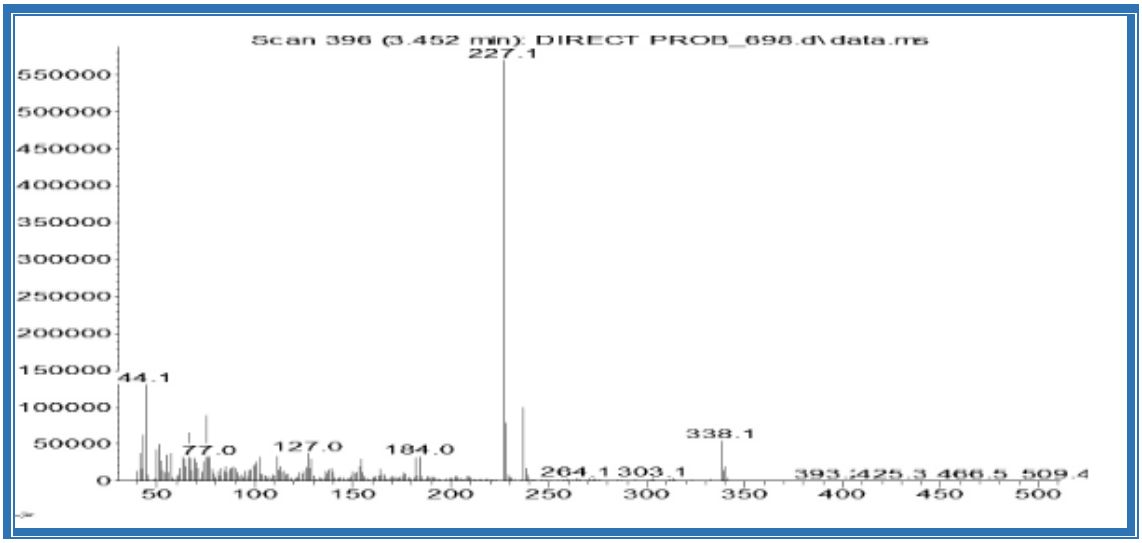


Fig. K3 The MS spectrum of product (C_{11})

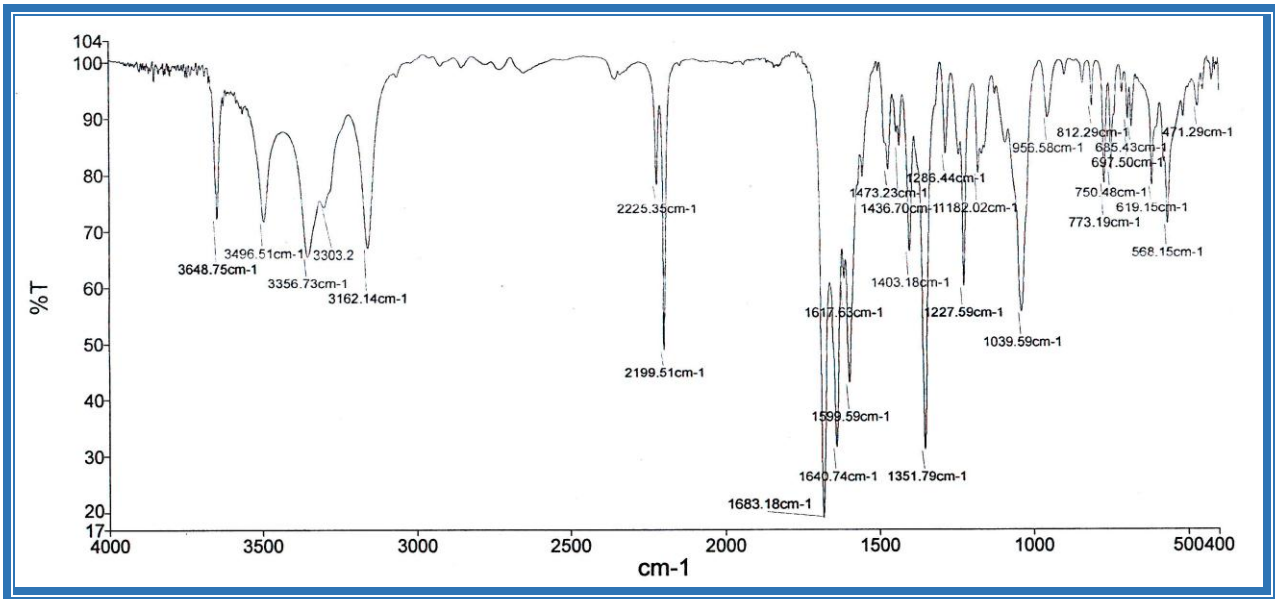


Fig. K4 The IR spectrum of product (C_{11})