Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

C–H bond cyanation of arenes using N, N-dimethylformamide and NH_4HCO_3 as CN source over hydroxyapatite supported copper catalyst

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1. Experimental section

i) General information

All chemicals were used reagent grade and as received without further purification. All solvents were dried and distilled by standard methods as described in the literature. ^1H NMR spectra were recorded by using Bruker VX NMR FT-300 or Varian Unity 500 and ^{13}C NMR spectra were recorded by using Bruker VX NMR FT-75 MHz spectrometers instrument in $CDCl_3$. The chemical shifts (δ) are reported in ppm units relative to TMS as an internal standard for ^1H NMR and $CDCl_3$ for ^{13}C NMR spectra. Coupling constants (J) are reported in hertz (Hz) and multiplicities are indicated as follows: s (singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quartet), m (multiplet). Mass spectra were obtained at an ionisation potential of 70 eV [scanned on VG 70-70H (micro mass)]. Column chromatography was carried out using silica gel (100-200 mesh). The surface properties of copper supported on HAP were measured by N_2 adsorption at −196 °C, in an Autosorb 3000 physical adsorption apparatus. The specific surface areas were calculated applying the BET method. TPD of CO_2 was carried out using an Auto Chem 2910 (Micromeritics, USA). The amount of desorbed CO_2 was calculated using GRAMS/32 software. TPR analysis was carried out in a quartz micro-reactor interfaced to a GC equipped with a TCD unit. Hydrogen consumption was measured by analyzing effluent gas using a calibration curve of TPR of Ag_2O under a similar protocol. The X-ray diffraction (XRD) patterns of the HAP supported CuO fresh and used samples were obtained on a Rigaku Rigaku Miniflex X-ray diffractometer using Ni filtered Cu K_α radiation ($\lambda = 0.15406$ nm) from $2\theta = 20$ to 65°, at a scan rate of $2° \min^{-1}$, with generator voltage and current of 30 kV and 15 mA respectively. The XPS patterns were recorded using a Kratos Axis Ultra Imaging X-ray photoelectron spectrometer, equipped with Mg anode and a multichannel detector. Charge referencing was done against adventitious carbon (C 1s, 284.8 eV). A Shirley-type background was subtracted from the signals. The recorded spectra were fitted using Gauss–Lorentz curves to determine the binding energies of the different elements. The morphological analysis was carried out using transmission electron microscopy (TEM on a JEOL100S microscope at high resolution (HR) on a JEOL 2010 micro-scope). The elemental analysis of the Cu supported on $Ca_5(PO_4)_3(OH)$ fresh and used samples were analysed by atomic absorption spectroscopy (AAS) Perkin Elmer, Analyst-300. The inductively coupled plasma-optimal emission spectrophotometer (ICP-OES) analysis was carried out by using iCAP-6500 DUO, Thermo Fisher Scientifics UK.

ii) N_2O decomposition studies

N_2O titration measurements were carried out on Auto Chem 2910 (Micrometrics, USA). For N_2O decomposition the sample was reduced at 450 °C (4.97% H_2/Ar) and then flushed in a pure He gas flow (purity 99.995%) for an hour at 450 °C and cooled to 90 °C in He gas stream. The N_2O decomposition is performed at 90 °C with pure N_2O (purity 99.995%) and the titration was stopped after the saturation of N_2O decomposition confirmed by GC-TCD. One molecule of N_2O is assumed to be adsorbed in stoichiometry of two atoms of Cu on the catalyst surface[1].

$$2Cu(s) + N_2O \rightarrow Cu_2O\ (s) + N_2$$

Determination of metal dispersion and Cu metal surface area

Metal surface area (MSA): MSA= (No. of Surface Cu moles per unit weight) (Avogadro number) (Cu-cross sectional area)

Units: $m^2\ g^{-1}$

Cu cross sectional area = $6.8 \times 10^{-20}\ m^2\ (Cu\ atom)^{-1}$

Surface Cu moles = $2 \times N_2O$ uptake (mol/g_{cat}), according to stoichiometric equation.

$$\% D = \left[\frac{(No.of\ surface\ metal\ sites)}{Total\ no.of\ metal\ sites\ in\ the\ sample}\right] \times 100$$

iii). Formula used for the normalized rate calculation (normalized with reaction temperature and reaction run time)

$$Rate = \frac{Fractional\ yield\ \times\ [Substrate\ concentration]}{g_{Cu}} \times \frac{1}{Reaction\ run\ time\ (h)} \times \frac{300\ K}{Reaction\ temperature\ K}$$

The rates are normalized with per gram of Cu in order to compare the product yields while correcting the rate with reaction time and reaction temperatures since various authors have conducted the cyanation reaction at various run times and temperatures.

Table S1: N_2O chemisorption studies over various loading of Cu on HAP catalysts

Cu loading (wt%) on HAP	N_2O uptake ($\mu mol/g_{cat}$)	D(%)	S_{Cu} (m^2/g_{Cu})	MCS (nm)
0.0	n.d	n.d	n.d	n.d
2.5	1.6	0.8	5.30	127.18
5.0	3.9	1.0	6.44	104.53
7.5	7.0	1.18	7.70	87.54
10.0	10.9	1.3	8.99	74.91
12.5	10.8	1.10	7.18	93.82

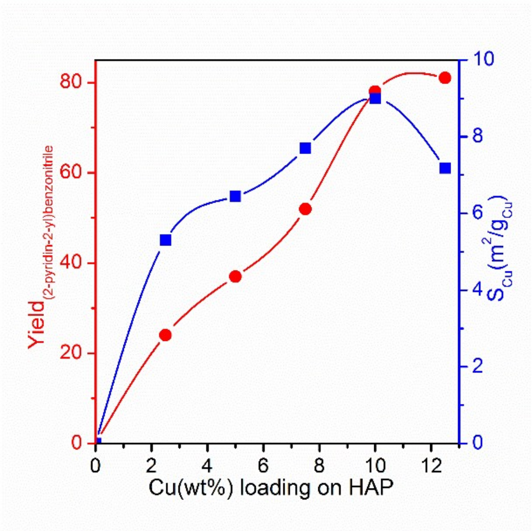


Figure S1: Relationship between Cu metal surface area and yield of (2-pyridin-2-yl) benzonitrile against Cu loading (wt%) on hydroxyapatite.

iii) TPD of CO_2 analysis

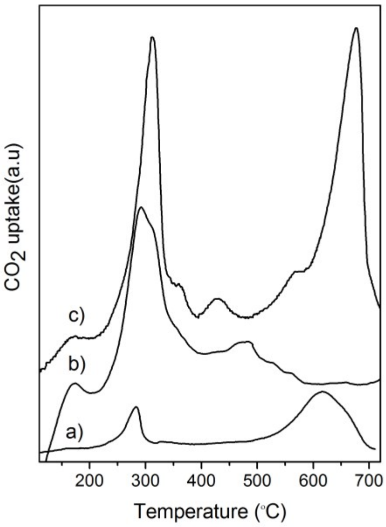


Figure S2: TPD of CO_2 over 10wt%Cu supported on (a) Al_2O_3 (b) MgO and (c) MgLaO catalysts.

iv) XRD analysis

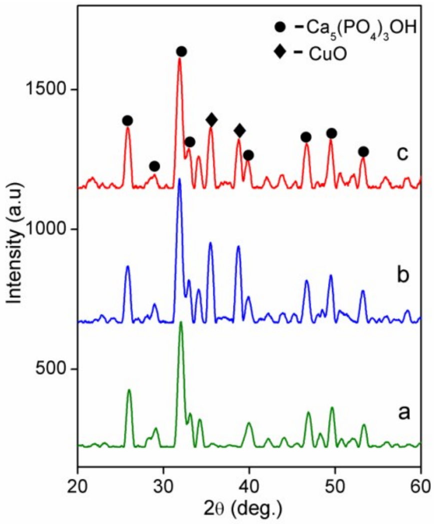


Figure S3: XRD patterns of a) Pure HAP, b) 10wt%Cu/HAP (fresh), c) 10wt%Cu/HAP (used).

Table S2: Atomic absorption spectroscopic analysis

Cu loading (wt%) on HAP	Ca	P	Metal	Ca/P
0.0	18.05	14.21	-	1.27
2.5	17.65	14.46	2.36	1.22
5	17.94	14.35	4.91	1.24
7.5	18.08	13.80	7.42	1.31
10	17.97	14.14	9.8	1.27
12.5	17.95	13.91	12.3	1.29

Table S3: Surface compositions obtained by XPS analysis of fresh and used 10wt%Cu/HAP catalyst.

Catalyst	**Metal (%)**	**Ca 2p**	**P 2p**	**O 1s**	**Metal/Ca**
10wt%Cu/HAP (F)	6.08	19.54	13.85	60.53	0.36
10wt%Cu/HAP (U)	6.03	19.91	13.96	60.10	0.35

Table S4: Elemental analysis of 10wt%Cu supported on HAP sample (measured for each recycle)

S. No	**Cycles**	**Cu wt.% from ICP-OES analysis**
1	Fresh	9.81
2	1st	9.79
3	2nd	9.79
4	3rd	9.72
5	4th	9.60

Table S5: Temperature programmed desorption of CO_2 of various loading of Cu on HAP catalysts

Catalyst (wt%)	Basicity from CO_2-TPD ($mmol/g_{cat}$)				
	Weak	Moderate	Strong	Very strong	Total
HAP	0.125	0.042	0.008	nf	0.173
2.5wt%Cu/HAP	0.103	0.035	0.043	nf	0.181
5wt%Cu/HAP	0.101	0.112	0.076	nf	0.289
7.5wt%Cu/HAP	0.127	0.082	0.086	nf	0.295
10wt%Cu/HAP	0.120	0.095	0.236	nf	0.451
12.5wt%Cu/HAP	0.129	0.123	0.087	nf	0.339
10wt%Cu/Al_2O_3	0.028	~Nil	0.054	0.08	0.162
10wt%Cu/MgO	0.033	0.217	0.042	nf	0.292
10wt%Cu/MgLaO	0.025	0.222	0.045	0.225	0.517

ix) General catalytic procedure for the cyanation reaction

A 10 mL round bottom flask was charged with 2-phenylpyridine (77.59 mg, 0.5 mmol), NH_4HCO_3 (118 mg, 1.5 mmol, 3.0 equiv.), Cu(II)/HAP (150 mg), and DMF (2 mL). The reaction mixture was stirred at 140 ºC for 18 h. After the completion of the reaction, as monitored by TLC, 5 mL of ethyl acetate was added in the reaction mixture. The catalyst was separated by simple centrifugation and the reaction mixture was treated with brine (10 mL). The organic layer was separated and the aqueous layer was back extracted with ethyl acetate (3×5 mL). The combined ethyl acetate extract was dried with anhydrous Na_2SO_4 and was concentrated under reduced pressure. The crude residue was further purified by flash column chromatography using silica gel (100-200 mesh) to afford pure desire product. All the products were identified on the basis of ^1H and ^{13}C NMR spectral data.

Preparation of substrates

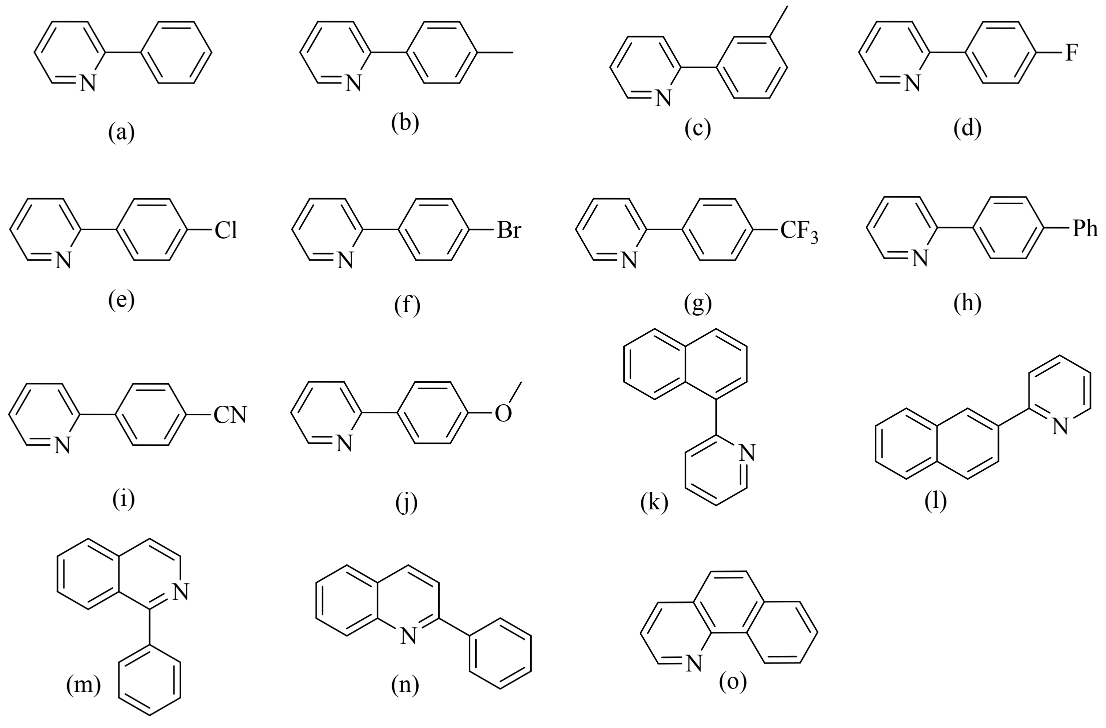
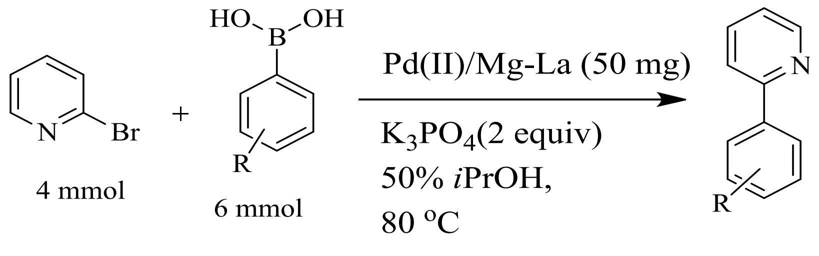


Figure S4: Substrates used for the cyanation reaction.

Substrates **a**, **b** and **n** (Figure S3) are commercially available and were purchased directly from Sigma-Aldrich. Other substrates (Figure S3, c-m, and o) were prepared by using Pd(II)/Mg-La mixed oxide catalyst via Suzuki coupling (Scheme S1).



Scheme S1: Synthesis of starting materials.

x) General catalytic procedure for the preparation of starting materials by Suzuki coupling

Aryl bromide (4 mmol), arylboronic acid (6 mmol), Pd(II)/Mg-La (50 mg), $K_3PO_4.7H_2O$ (1.698 g, 8 mmol), 50% aqueous isopropanol (20 mL) was taken in a 50 mL round bottom flask (RB) and was stirred at 80 º C. After the completion of the reaction (3 h), as monitored by TLC, the catalyst was separated by simple centrifugation and the reaction mixture was treated with brine (10 mL) and extracted with diethyl ether (4×15 mL). The combined organic extract was dried with anhydrous Na_2SO_4 and was concentrated under reduced pressure. The product was isolated by short column chromatography on silica gel column using ethyl acetate/hexane as eluent.

2. Spectral data of all products

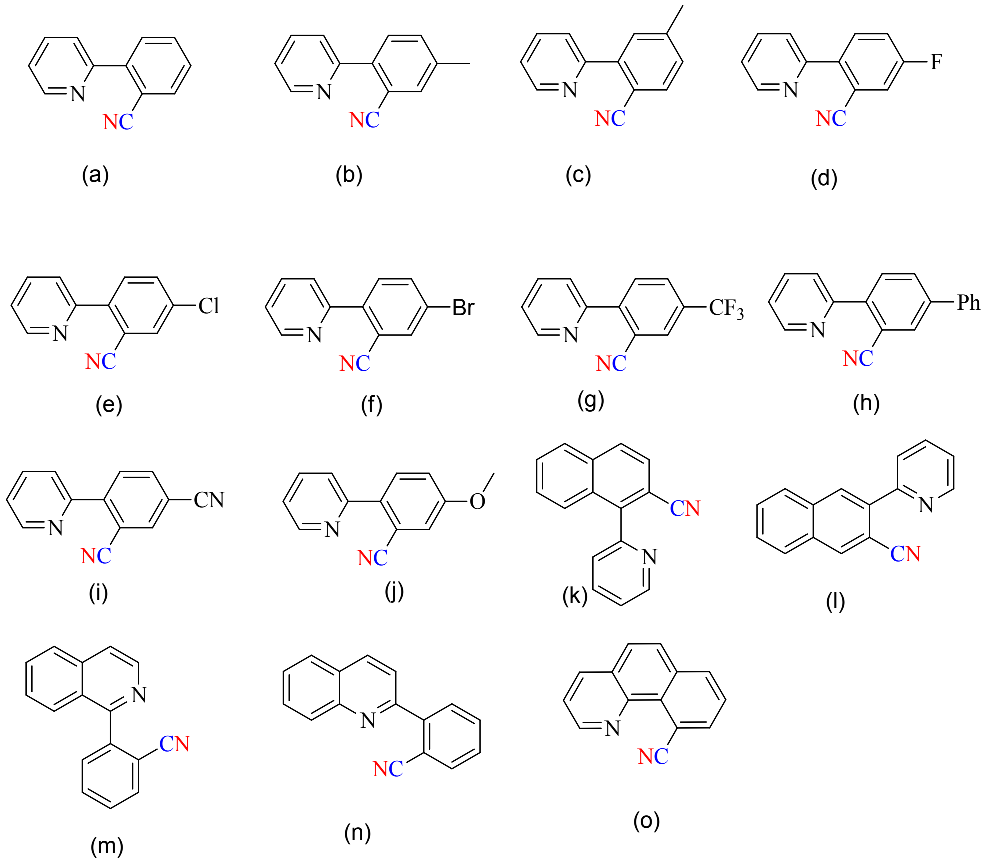
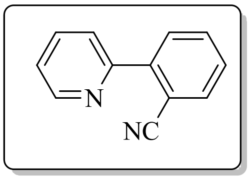
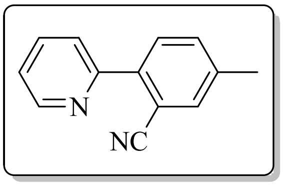


Figure S5: Products of the cyanation reaction.



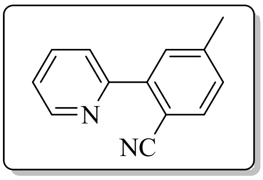
2-(Pyridin-2-yl)benzonitrile (Figure **S5a;** 85% yield)[2]; pale yellow oil;

^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) = 8.78-8.77 (m, 1H), 7.86-7.77 (m, 4H), 7.70 (td, J = 7.6, 1.3 Hz, 1H), 7.51 (td, J = 7.6, 1.2 Hz, 1H), 7.37-7.35 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm) = 155.1, 149.8, 143.4, 136.8, 134.0, 132.8, 129.9, 128.7, 123.3, 123.2, 118.6, 111.0; MS (ESI) 181 (M+H).



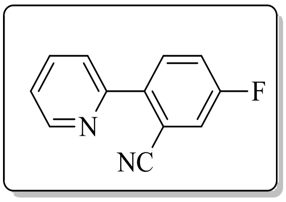
5-Methyl-2-(pyridin-2-yl)benzonitrile (Figure **S5b,** 72% yield)[3]; colorless solid;

^{1}H-NMR (CDCl$_3$, 400 MHz) δ (ppm) = 8.76 (d, J = 4.4 Hz, 1H), 7.83 (t, J = 7.4 Hz, 1H),7.77–7.73 (m, 2H), 7.59 (s, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.34–7.31 (m, 1H), 2.43 (s,3H); δ (ppm) = 13C-NMR (CDCl3, 100 MHz) δ:20.8, 110.6, 118.8, 123.0, 129.7, 133.6,134.3, 136.7, 139.0, 140.6, 149.7, 155.1; MS (ESI) 195 (M+H).

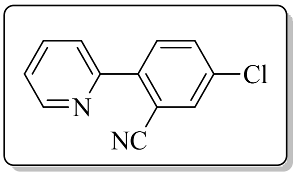


4-Methyl-2-(pyridin-2-yl)benzonitrile (Figure **S5c**, 62% yield)[2]; colorless solid;

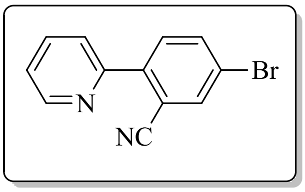
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) = 8.77-8.76 (m, 1H), 7.85-7.78 (m, 2H), 7.69-7.66 (m, 2H), 7.38-7.30 (m, 2H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) = 155.3, 149.8, 143.8, 143.3, 136.7, 133.9, 130.7, 129.5, 123.3, 123.2, 118.9, 107.9, 21.8; MS (ESI) 195 (M+H).



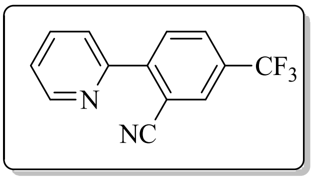
5-Fluoro-2-(pyridin-2-yl)benzonitrile (Figure **S5d**, 68% yield)[4]; colorless solid; ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) = 8.77-8.76 (m, 1H), 7.87-7.81 (m, 2H), 7.77-7.74 (m, 1H), 7.51 (dd, J = 8.0, 2.7 Hz, 1H), 7.44-7.34 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) = 161.9 (d, $J_{C\text{-}F}$ = 252.4 Hz), 154.1, 149.9, 139.9 (d, $J_{C\text{-}F}$ = 2.9 Hz), 136.8, 132.1 (d, $J_{C\text{-}F}$ = 8.8 Hz), 123.3, 123.0, 120.5 (d, $J_{C\text{-}F}$ = 25.4 Hz), 120.3, 117.4 (d, $J_{C\text{-}F}$ = 13.2 Hz), 112.4 (d, $J_{C\text{-}F}$ = 9.5 Hz); MS (ESI) 199 (M+H).



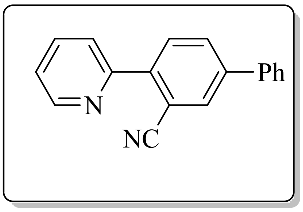
5-Chloro-2-(pyridin-2-yl)benzonitrile (Figure **S5e**, 62% yield)[5]; white solid; ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm) = 8.77 (d, J = 4.5Hz, 1H), 7.87-7.76 (m, 4H), 7.66 (dd, J = 8.4, 1.8Hz, 1H), 7.39-7.35 (m, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ (ppm) = 154.0, 149.9, 141.7, 136.9, 134.8, 133.5, 133.1, 131.2, 123.5, 123.0, 117.3, 112.3.



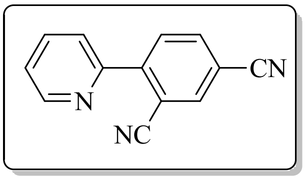
5-Bromo-2-(pyridin-2-yl)benzonitrile (Figure **S5f,** 60% yield)[3]; white solid; ^{1}H NMR (CDCl$_3$, 300 MHz) δ (ppm) = 8.78 (d, J = 4.7 Hz, 1H), 7.93 (d, J = 1.9 Hz, 1H), 7.86-7.73 (m, 4H), 7.39-7.36 (m, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ (ppm) = 154.0, 150.0, 142.2, 136.9, 136.4, 136.0, 131.3, 123.5, 123.0, 122.5, 117.2, 112.6; MS (ESI) 260 (M+H).



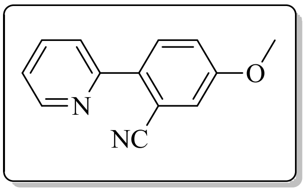
2-(Pyridin-2-yl)-5-(trifluoromethyl)benzonitrile (Figure **S5g,** 59% yield)[5]; white solid; ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm) = 8.82 (d, J = 4.3 Hz, 1H), 8.06 (s, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.89 (t, J = 7.3 Hz, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.45–7.40 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) = 153.7, 150.2, 146.5, 137.0, 131.4 (q, $J_{\text{C-F}}$ = 29.9 Hz), 131.1 (q, $J_{C\text{-}F}$ = 3.6 Hz), 130.7, 129.4 (q, $J_{\text{C-F}}$ = 3.6 Hz), 124.0, 123.3, 122.8 (q, $J_{\text{C-F}}$ = 272 Hz), 117.3, 111.9; MS (ESI) 249 (M+H).



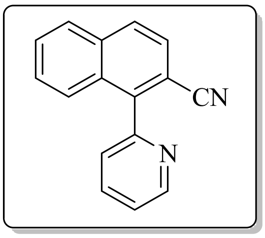
5-Phenyl-2-(pyridin-2-yl)benzonitrile (Figure **S5h**, 64% yield)[6]; yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) = 8.80-8.79 (m, 1H), 8.10 (d, J = 1.6 Hz, 1H), 7.94-7.89 (m, 2H), 7.87-7.83 (m, 2H), 7.63-7.61 (m, 2H), 7.51-7.48 (m, 2H), 7.45-7.41 (m, 1H), 7.38-7.35 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm) = 154.8, 149.9, 141.8, 141.8, 138.2, 136.8, 132.5, 131.3, 130.4, 129.1, 128.4, 127.0, 123.3, 123.1, 118.7, 111.4; MS (ESI) 257 (M+H).



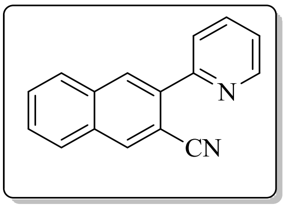
4-(pyridin-2-yl)isophthalonitrile (Figure **S5i,** 65% yield)[7]; white solid; ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm) = 8.82-8.81 (m, 1H), 8.09 (d, J = 1.6 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.96 (dd, J = 1.6, 8.2 Hz, 1H), 7.90 (td, J = 1.8, 7.8 Hz, 1H), 7.86-7.84 (m, 1H), 7.46–7.43 (m, 1H). ^{13}CNMR (CDCl$_3$, 125 MHz) δ (ppm) = 153.2, 150.3, 146.9, 137.4, 137.1, 135.7, 130.9, 124.3, 123.3, 116.6, 116.5, 113.2, 112.4; MS (ESI) 206 (M+H).



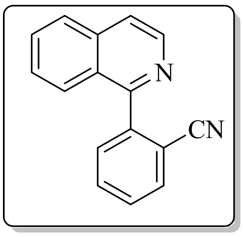
5-methoxy-2-(pyridin-2-yl)benzonitrile (Figure **S5j**, 67% yield)[2]; colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.74 (d, J = 4.7 Hz, 1H), 7.82-7.74 (m, 3H), 7.32-7.30 (m, 1H), 7.27 (d, J = 2.4 Hz, 1H), 7.22 (dd, J = 2.7, 8.8 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 159.4, 154.9, 149.7, 136.7, 136.0, 131.3, 122.8, 122.7, 119.3, 118.6, 118.4, 111.6, 55.7; MS (ESI) 211 (M+H).



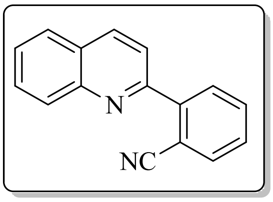
1-(Pyridin-2-yl)-2-naphthonitrile (Figure **S5k**, 55% yield)[4]; yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.87 (d, J = 3.0, Hz, 1H), 7.99-7.91 (m, 3H), 7.73-7.70 (m, 2H), 7.66-7.60 (m, 2H), 7.55-7.51 (m, 1H), 7.49-7.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 155.2, 149.9, 144.4, 136.7, 135.0, 131.1, 129.4, 128.7, 128.3, 127.9, 126.8, 126.7, 125.6, 123.5, 118.5, 109.7; MS (ESI) 231 (M+H).



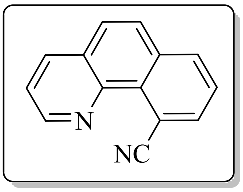
3-(pyridin-2-yl)naphthalene-2-carbonitrile (Figure **S5l** , 53% yield)[6]; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.84-8.81 (m, 1H), 8.39 (s, 1H), 8.27 (s, 1H), 7.96-7.84 (m, 4H), 7.68-7.60 (m, 2H), 7.41-7.36 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 154.8, 149.9, 141.8, 138.2, 136.8, 132.5, 131.3, 130.4, 129.1, 128.4, 126.9, 123.3, 123.1,118.7,113.3, 111.3; MS (ESI) 231 (M+H).



2-(Isoquinolin-1-yl)benzonitrile (Figure **S5m,** 61% yield)[4]; yellow solid; ^{1}H NMR (400 MHz, CDCl3) δ (ppm) = 8.69 (d, J = 5.8 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 7.7 Hz, 1H), 7.77-7.71 (m, 4H), 7.68-7.65 (m, 1H), 7.64-7.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 156.9, 143.0, 142.2, 136.6, 133.4, 132.3, 130.8, 130.4, 128.8, 127.7, 127.2, 126.7, 126.4, 121.3, 117.7, 113.2; MS (ESI) 231 (M+H).



2-(quinolin-2-yl)benzonitrile (Figure **S5n,** 63% yield)[6]; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.33 (d, J = 8.4 Hz , 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 7.7 Hz, 1H), 7.91-7.84 (m, 3H), 7.81-7.72 (m, 2H), 7.63-7.53 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 155.1, 148.0, 143.7, 137.0, 134.3, 132.8, 130.2, 130.1, 129.7, 128.9, 127.5, 127.3, 127.2, 120.5, 118.6, 111.5; MS (ESI) 231 (M+H).



Benzo[*h*]quinoline-10-carbonitrile (Figure **S5o ,** 57% yield)[2]; colorless solid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) = 9.14 (dd, J = 4.3, 1.5Hz, 1H), 8.23 (dd, J = 8.1, 1.5 Hz, 1H), 8.18-8.12 (m, 2H), 7.82 (q, J = 8.8 Hz, 2H), 7.74 (t, J = 7.7 Hz, 1H), 7.63 (dd, J = 8.1, 4.3 Hz, 1H). ^{13}CNMR ($CDCl_3$, 125 MHz) δ (ppm) = 148.5, 144.5, 136.2, 135.6, 134.0, 132.6, 130.7, 127.3, 127.2, 127.0, 126.9, 123.0, 120.7, 108.9. ; MS (ESI) 204.3 (M+H).

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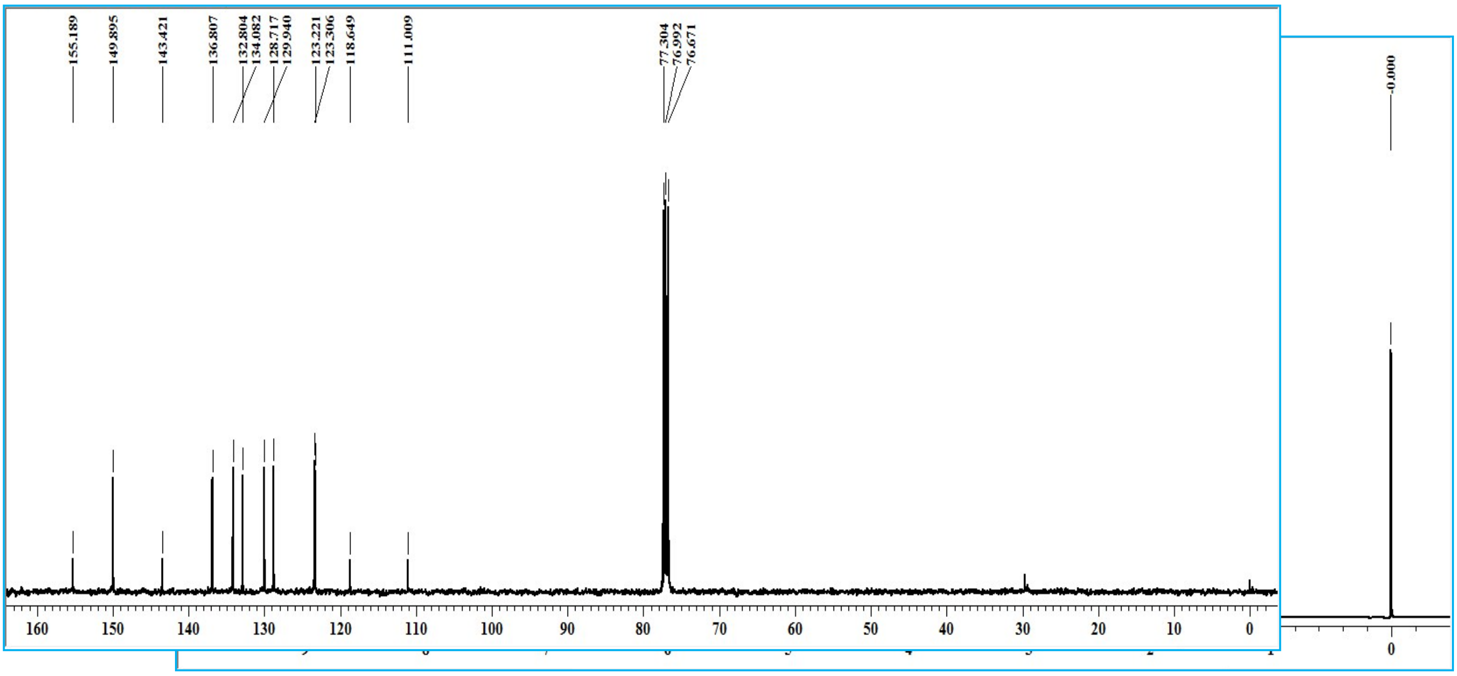
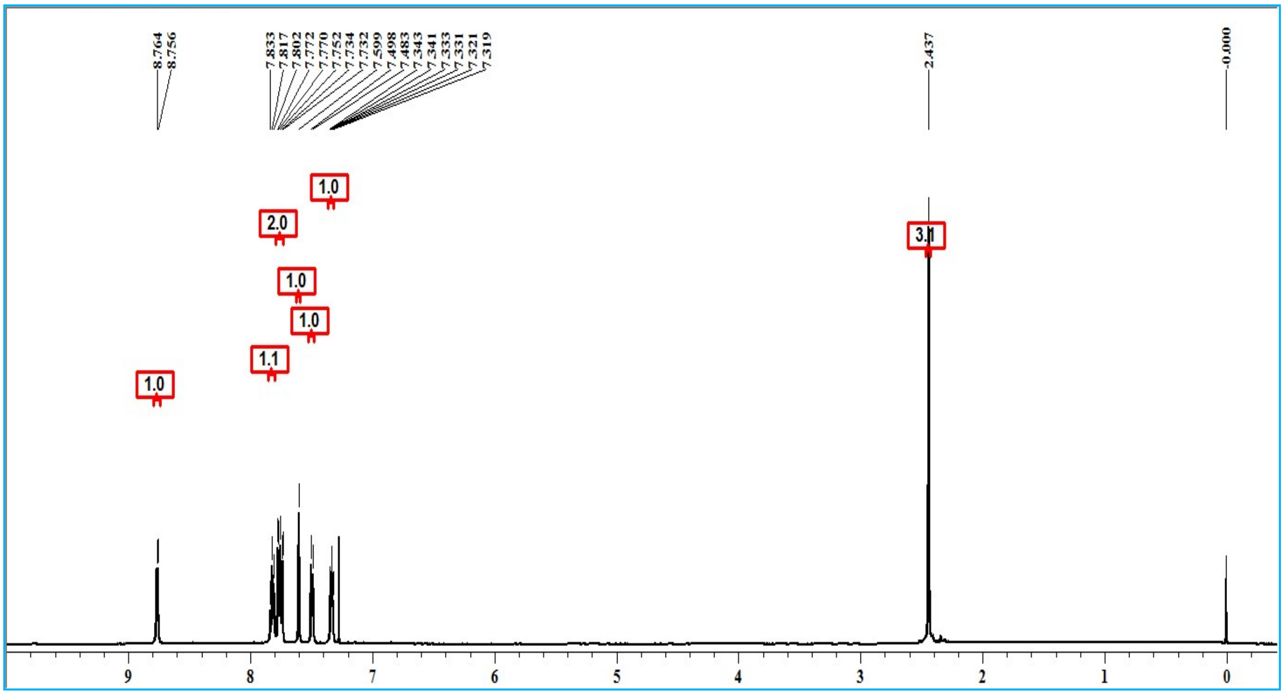
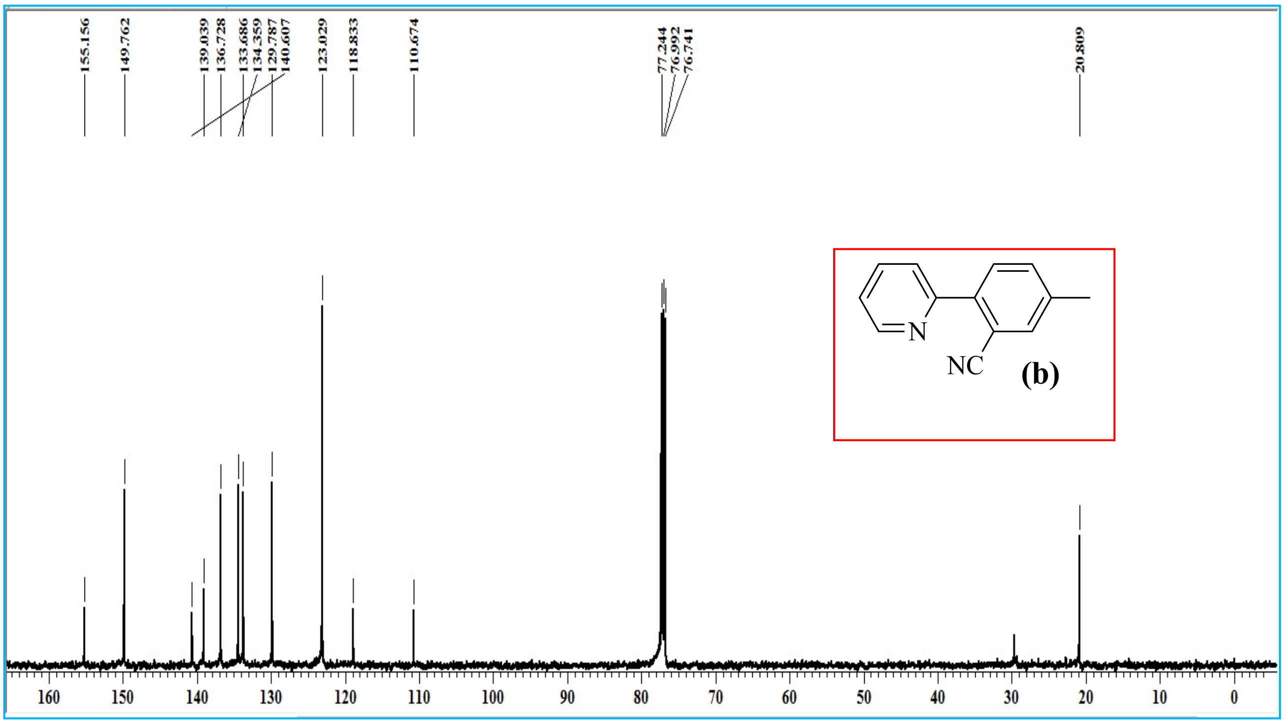
^1H and ^{13}C NMR spectra:

^1H and ^{13}C NMR Spectra of 2-(Pyridin-2-yl)benzonitrile (Figure S5a)

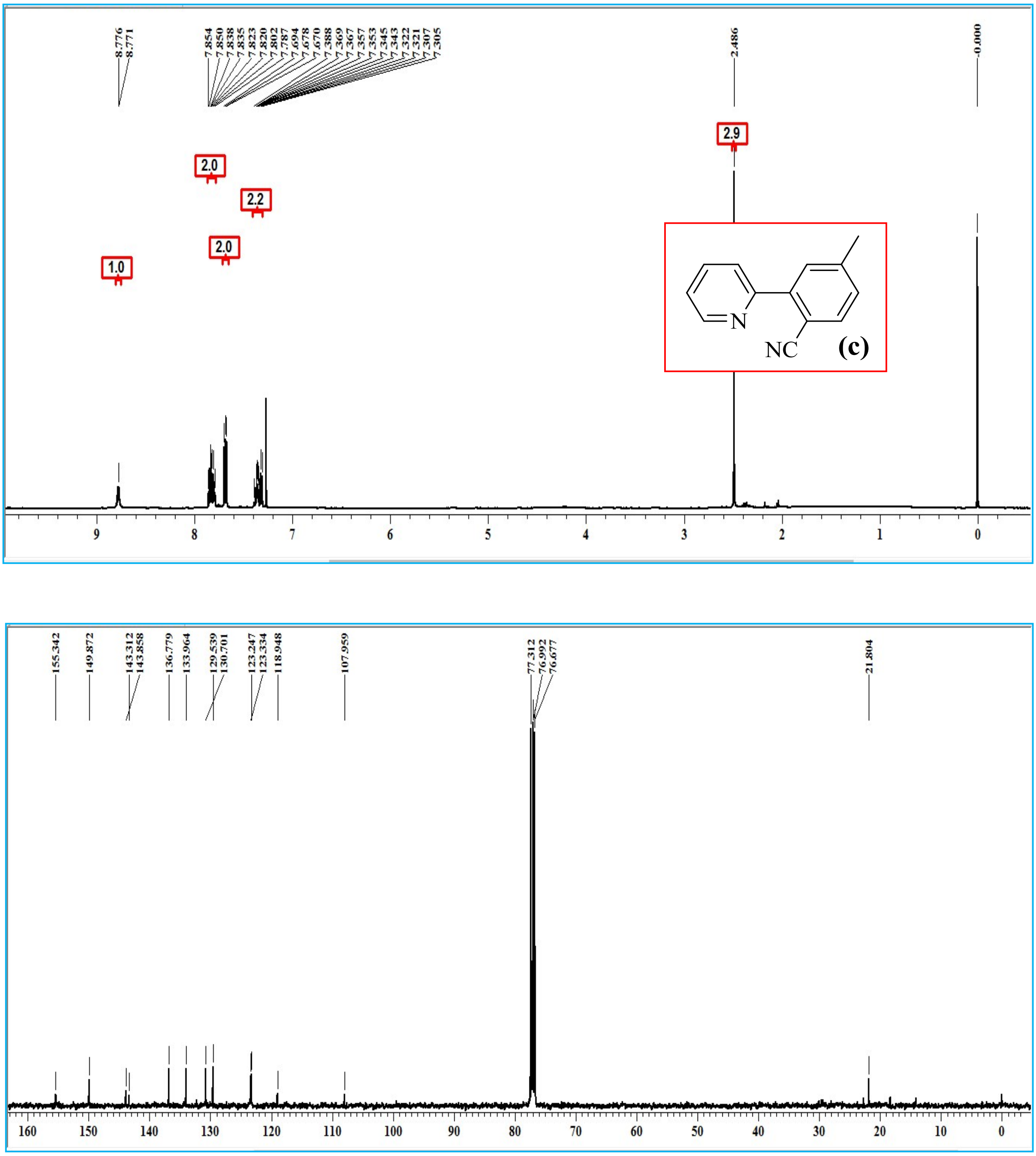


^1H and ^{13}C NMR Spectra of 5-Methyl-2-(pyridin-2-yl)benzonitrile (Figure S5b)

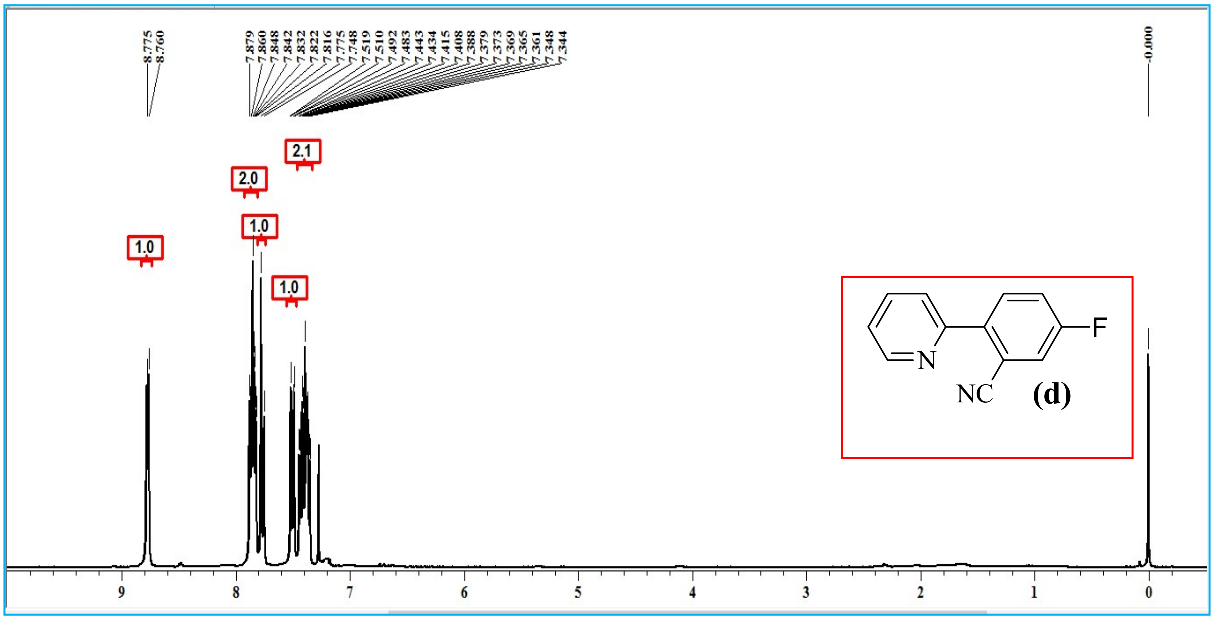


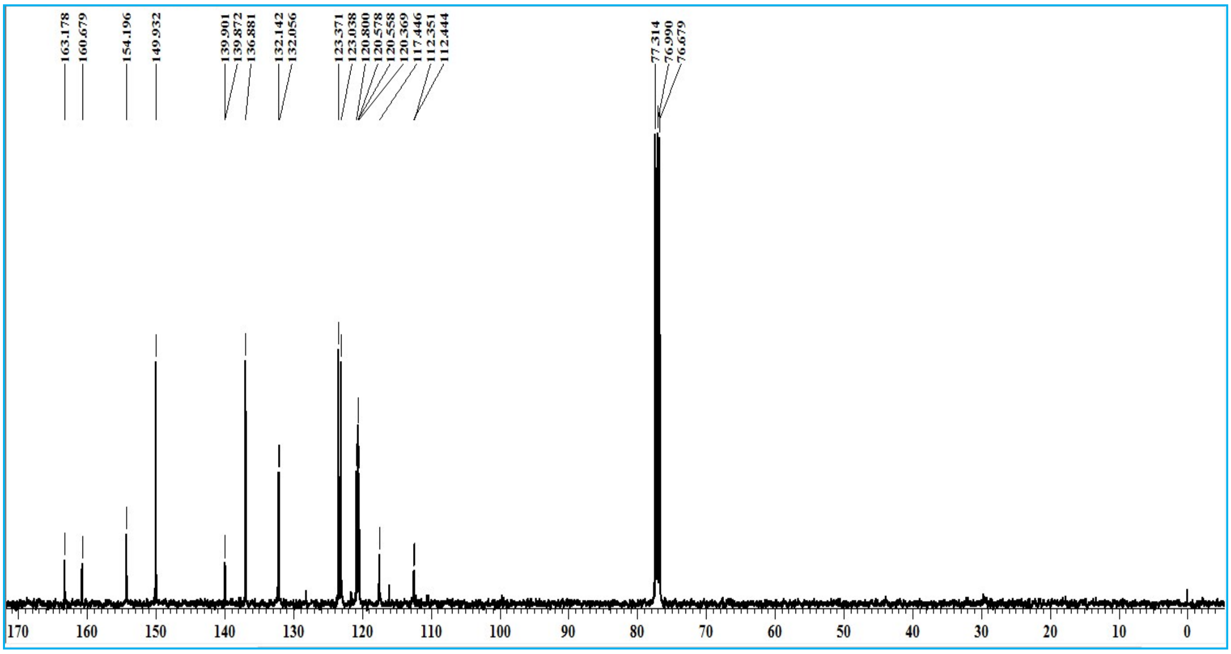


^{1}H and ^{13}C NMR Spectra of 4-Methyl-2-(pyridin-2-yl)benzonitrile (Figure S5c)

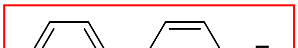


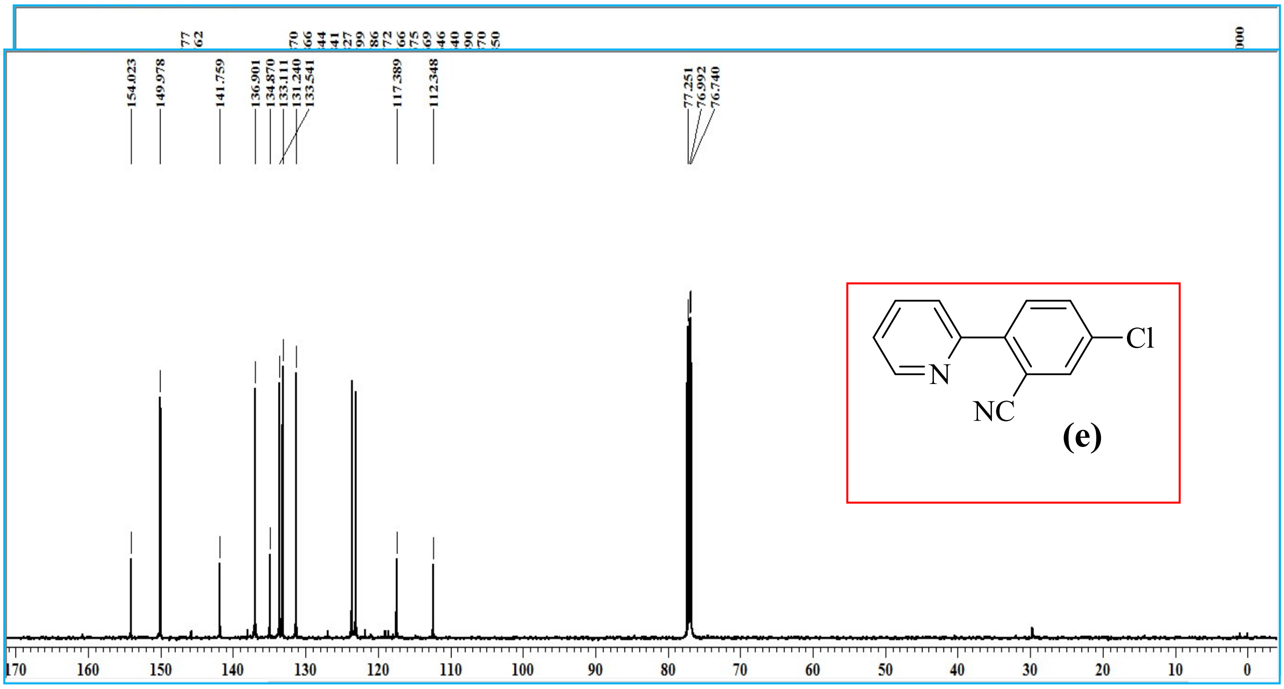
^{1}H and ^{13}C NMR Spectra of 5-Fluoro-2-(pyridin-2-yl)benzonitrile (Figure S5d)



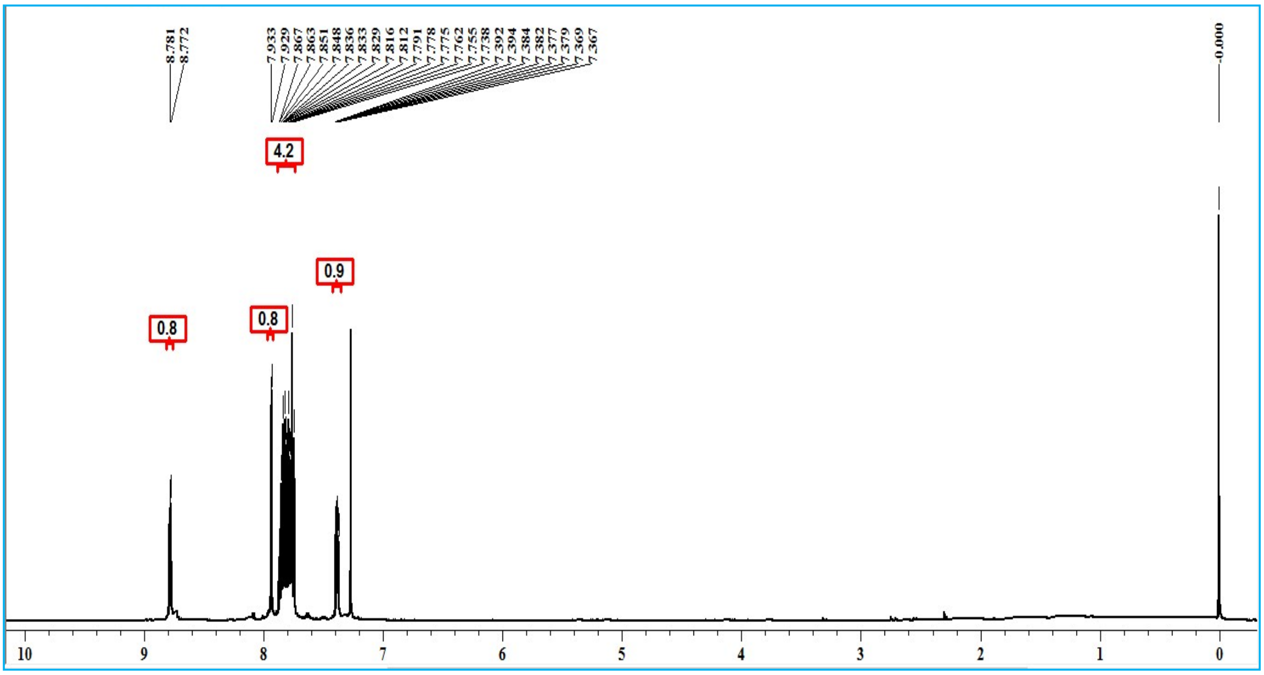


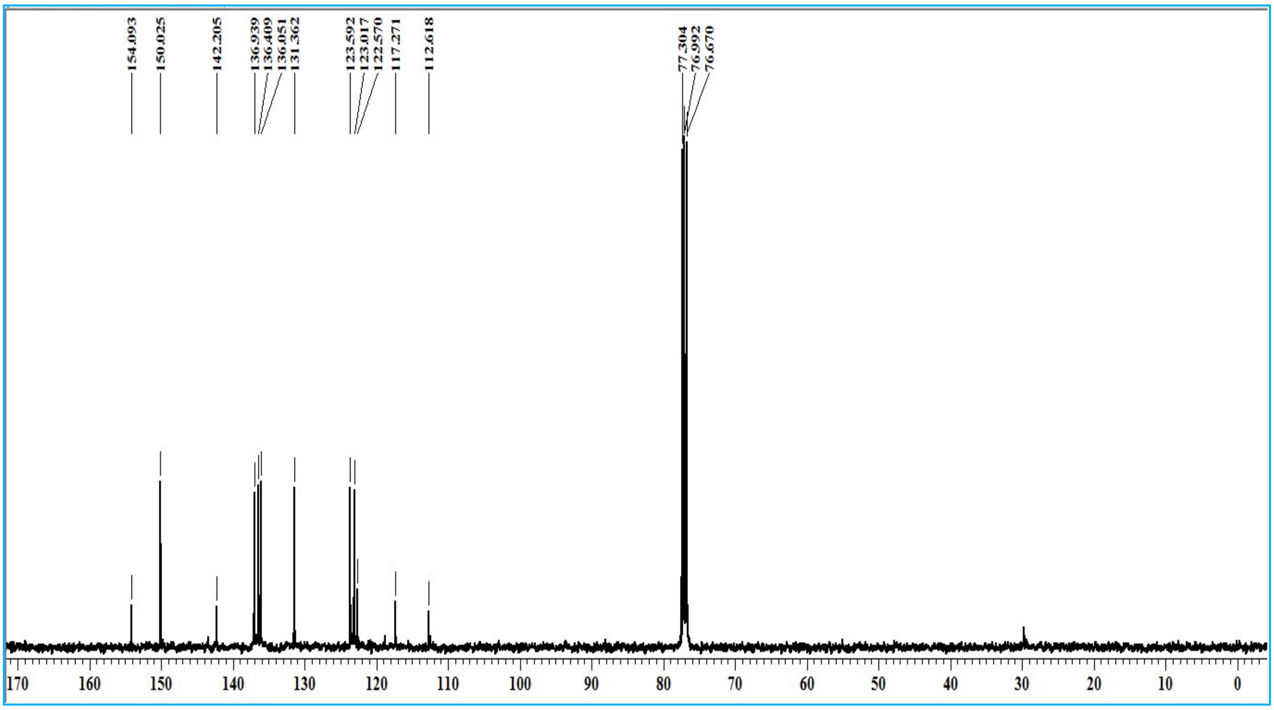
^{1}H and ^{13}C NMR Spectra of 5-Chloro-2-(pyridin-2-yl)benzonitrile (Figure S5e)



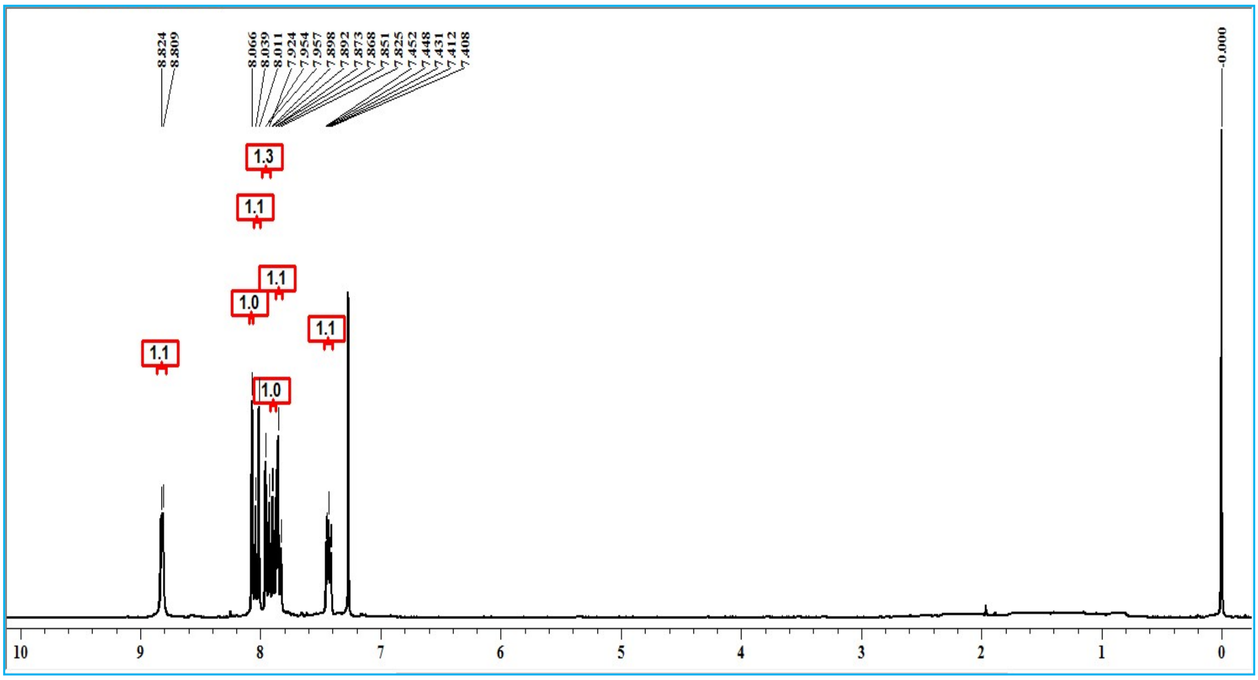


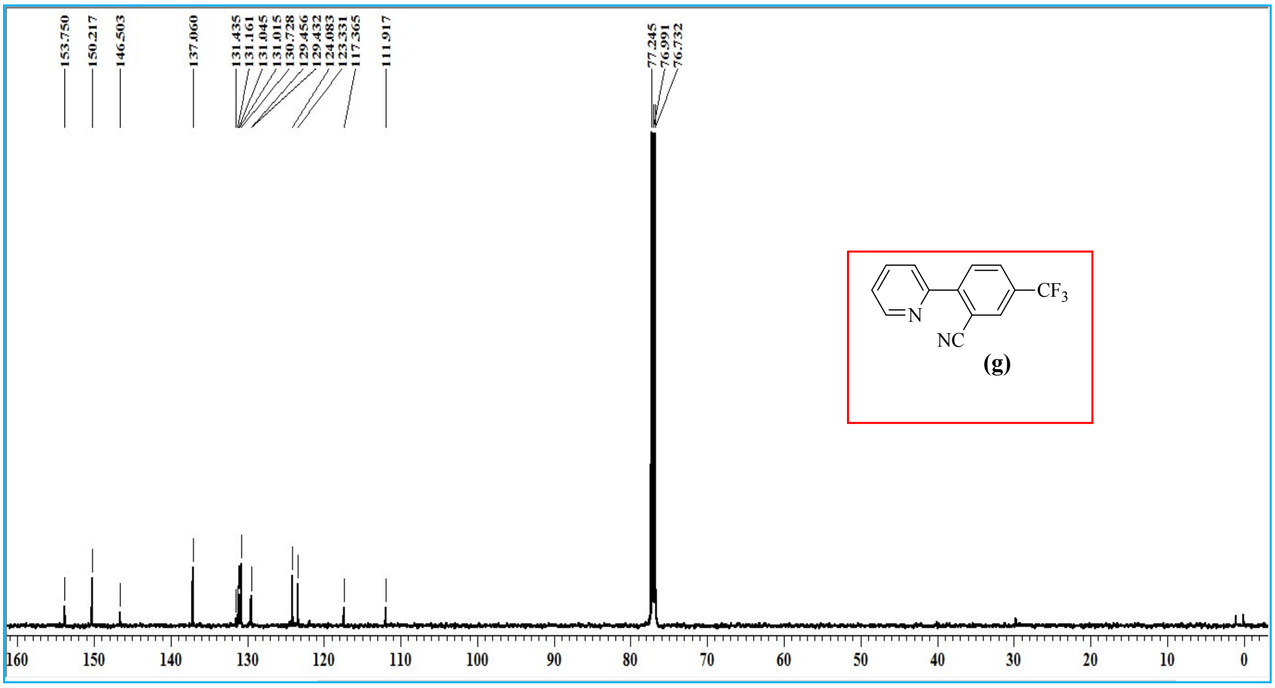
^{1}H and ^{13}C NMR Spectra of 5-Bromo-2-(pyridin-2-yl)benzonitrile (Figure S5f)



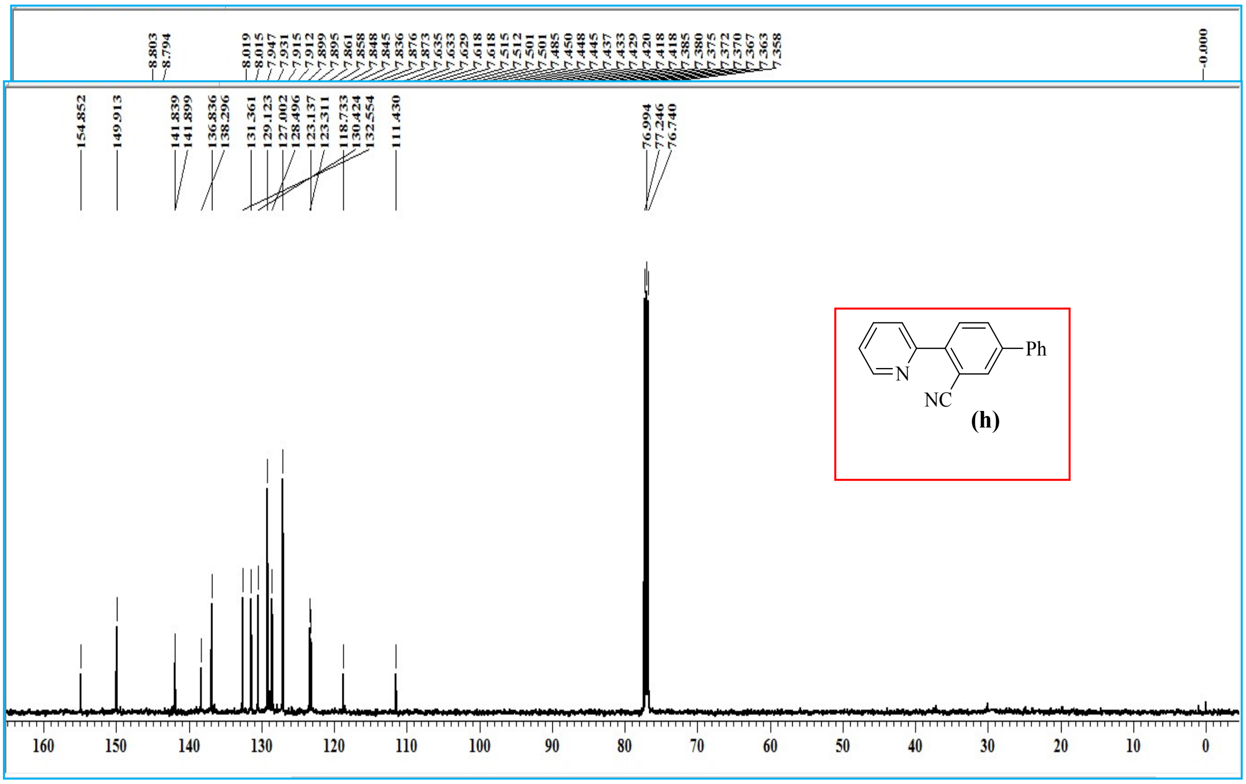


^{1}H and ^{13}C NMR Spectra of 2-(Pyridin-2-yl)-5-(trifluoromethyl)benzonitrile (Figure S5g)

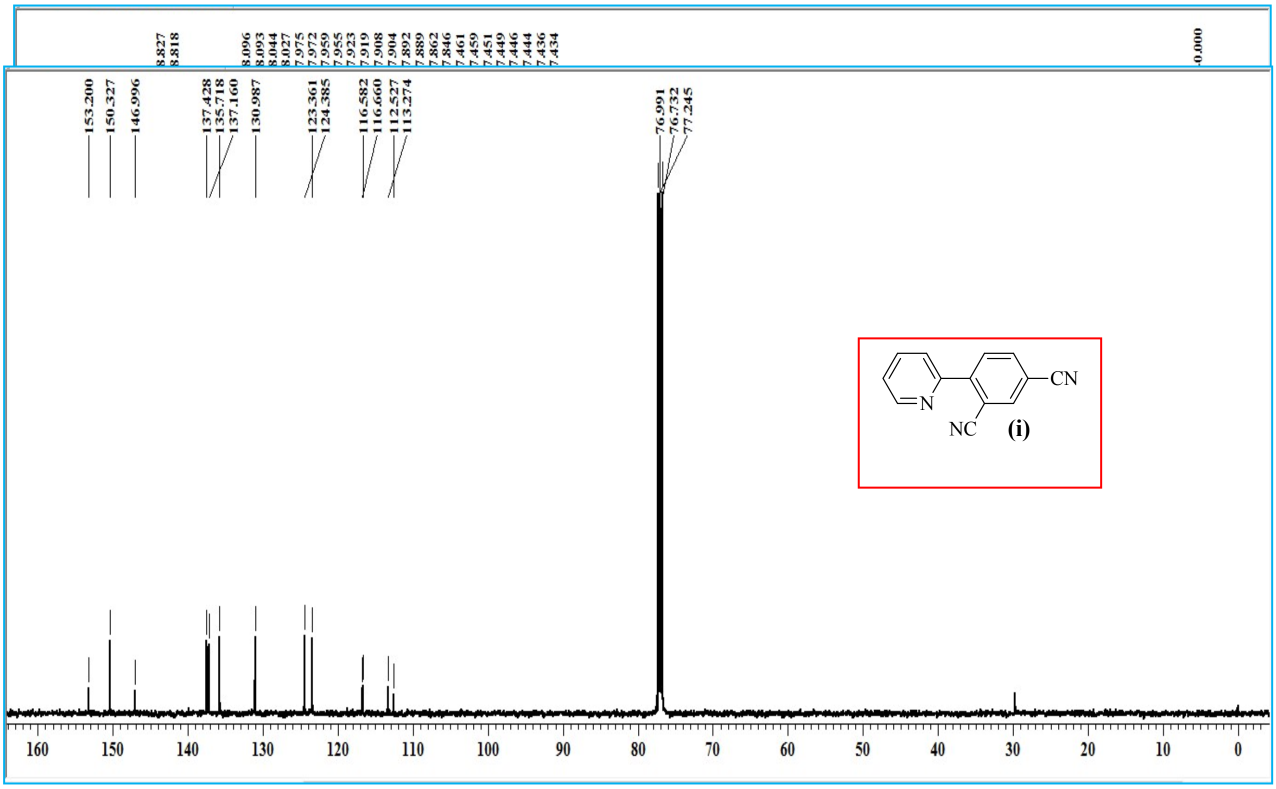




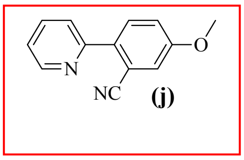
^{1}H and ^{13}C NMR Spectra of 5-Phenyl-2-(pyridin-2-yl)benzonitrile (Figure S5h)

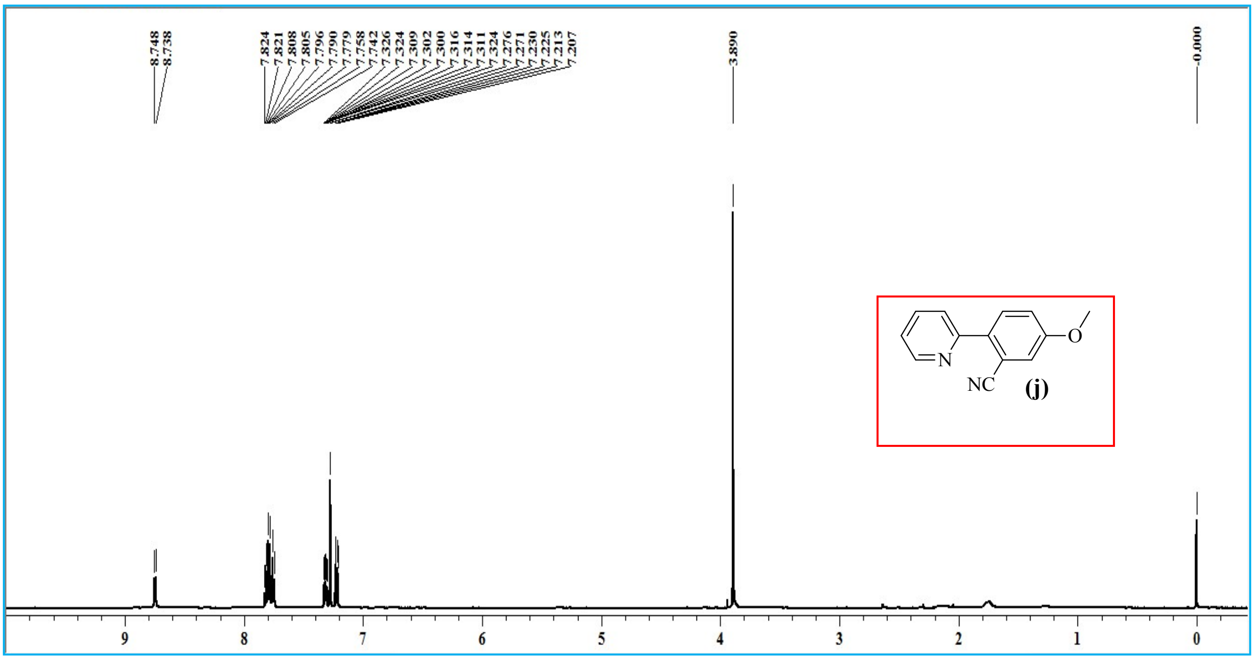


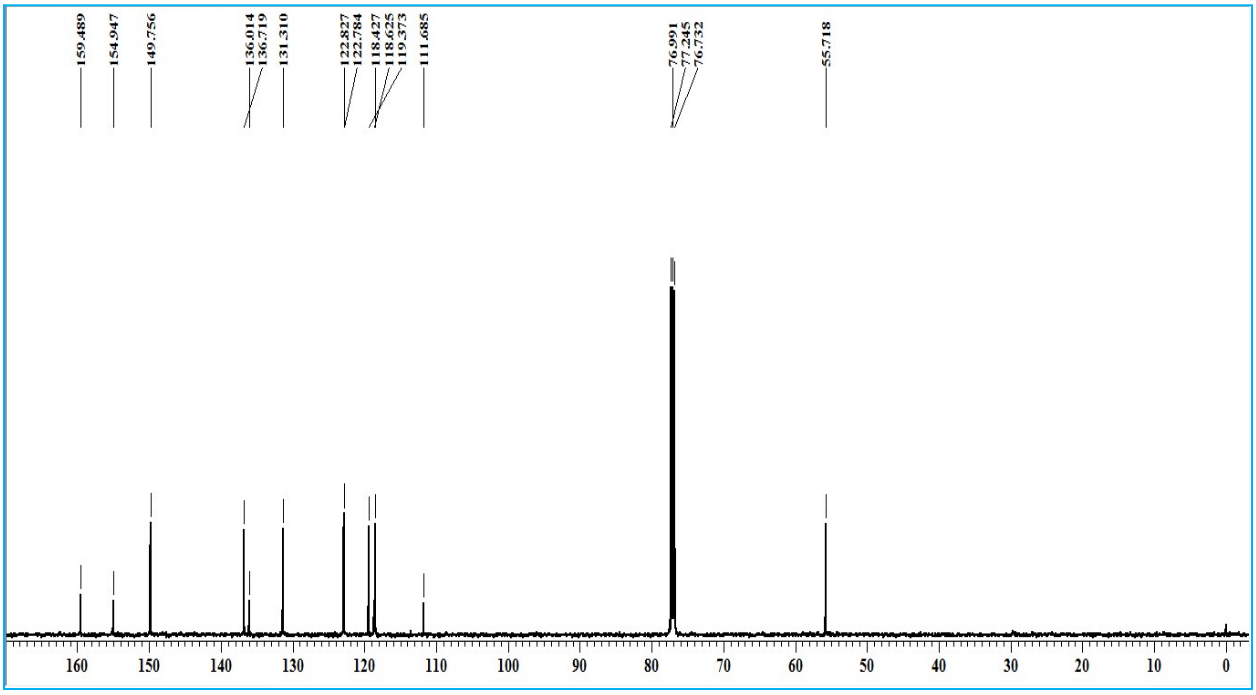
^{1}H and ^{13}C NMR Spectra of 4-(pyridin-2-yl)isophthalonitrile (Figure S5i)



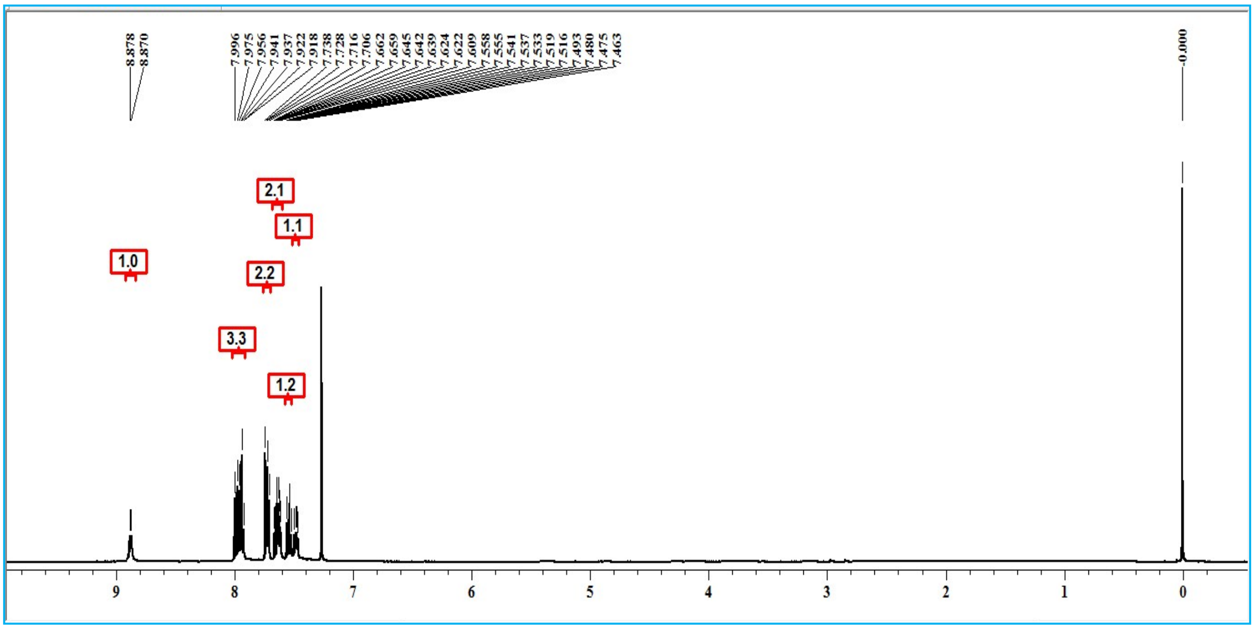
^{1}H and ^{13}C NMR Spectra of 5-methoxy-2-(pyridin-2-yl)benzonitrile (Figure S5j)

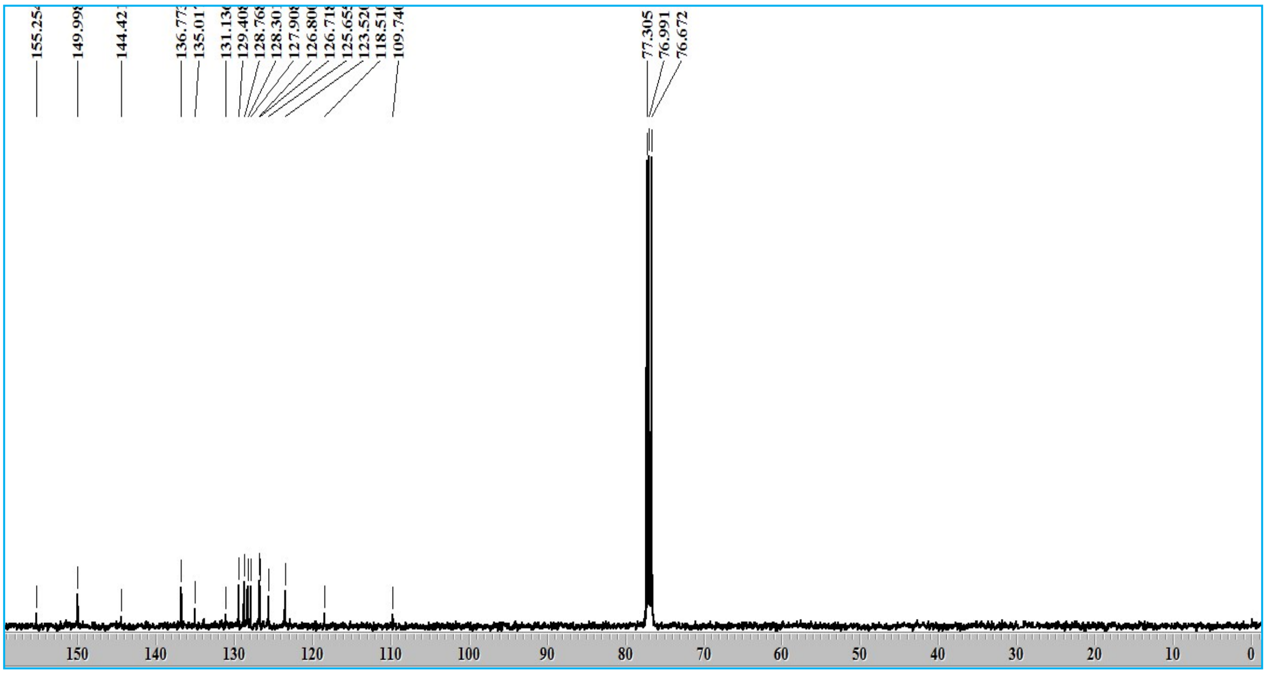




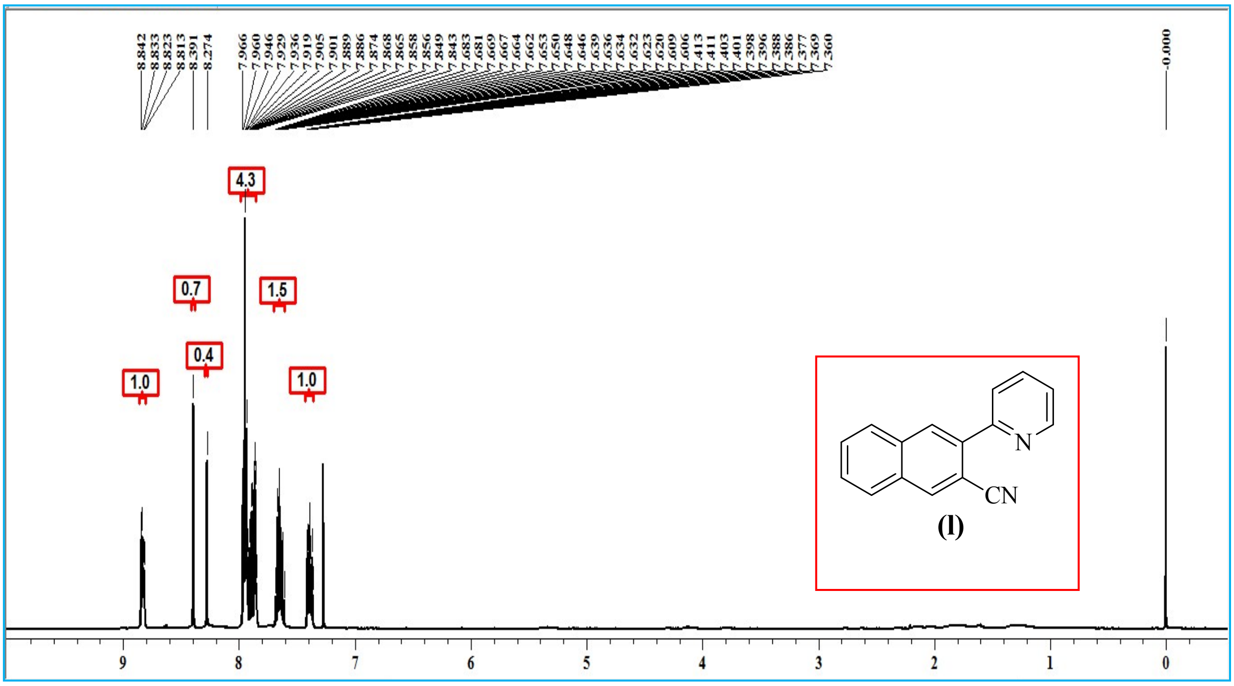


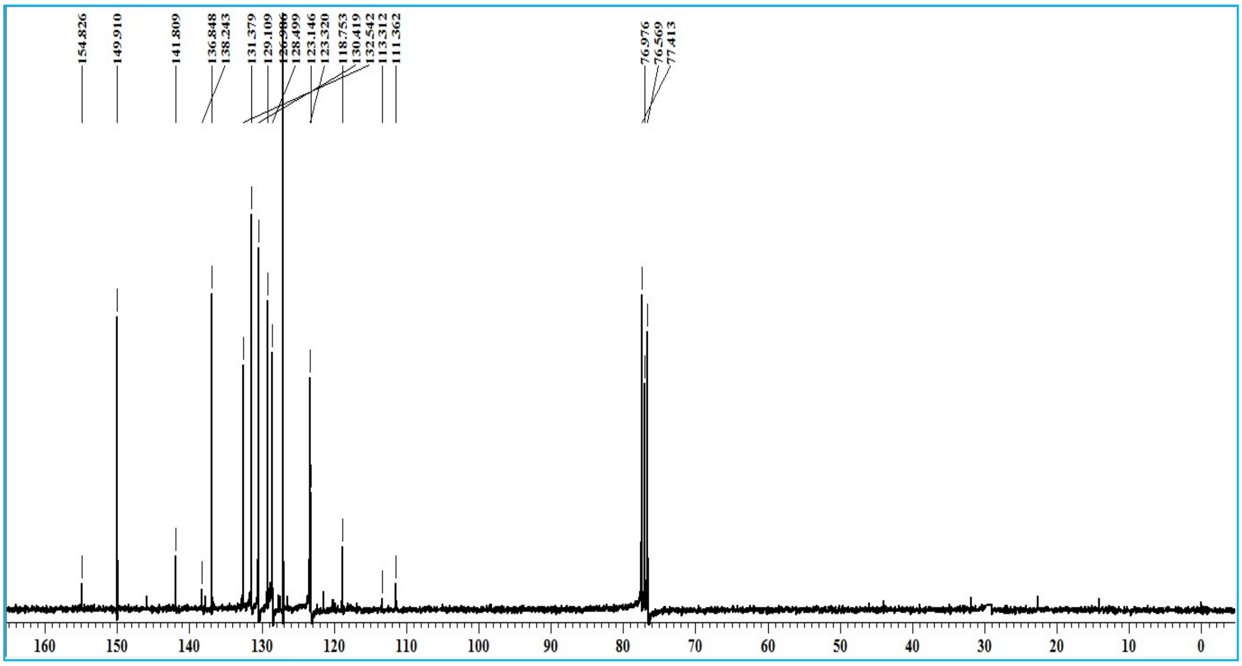
^{1}H and ^{13}C NMR Spectra of 1-(Pyridin-2-yl)-2-naphthonitrile (Figure S5k)



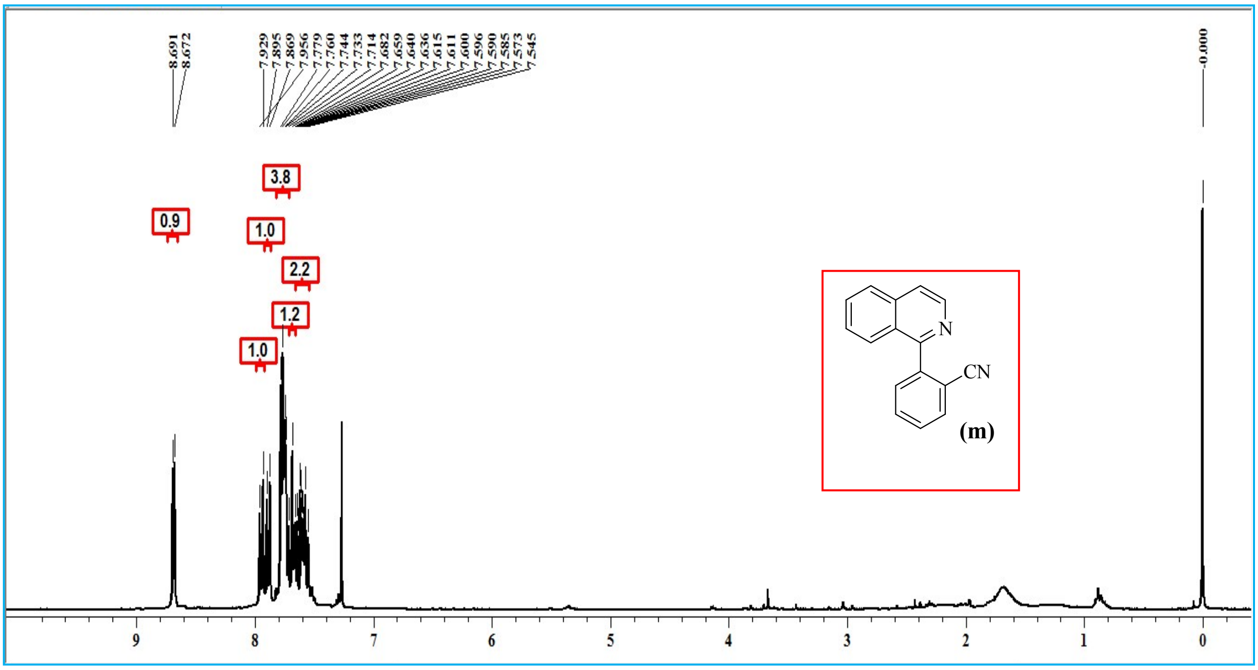


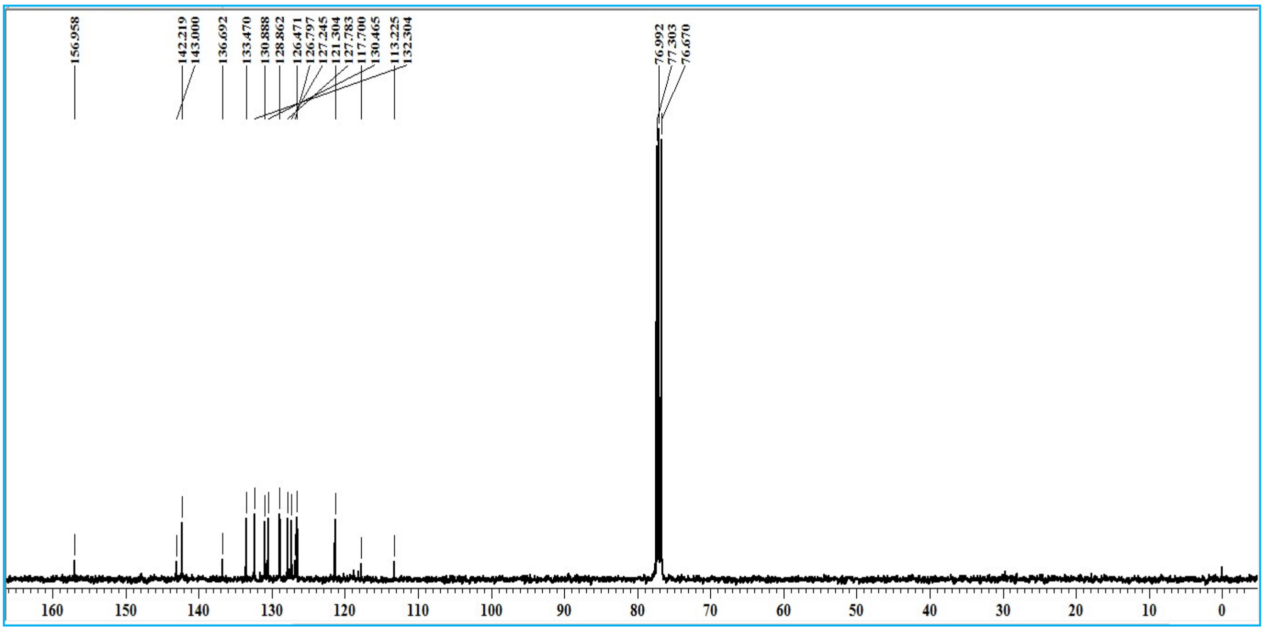
^{1}H and ^{13}C NMR Spectra of 3-(pyridin-2-yl)naphthalene-2-carbonitrile (Figure S5l)



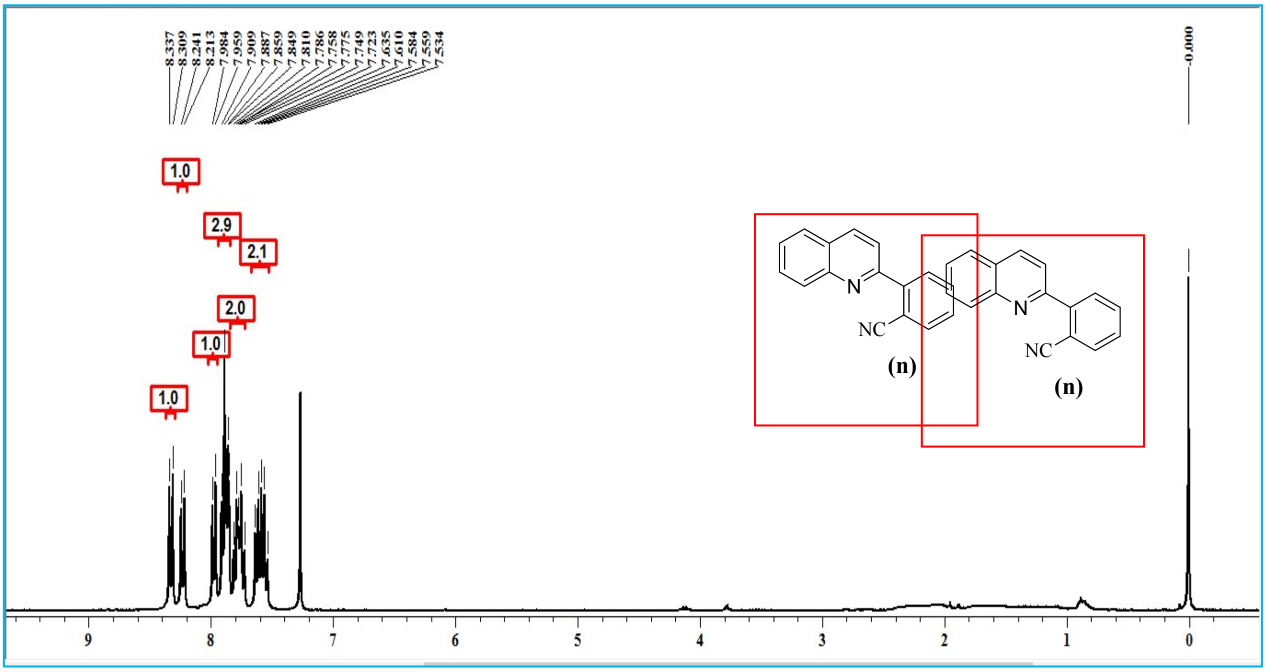


^{1}H and ^{13}C NMR Spectra of 2-(Isoquinolin-1-yl)benzonitrile (Figure S5m)





^{1}H and ^{13}C NMR Spectra of 2-(quinolin-2-yl)benzonitrile (Figure S5n)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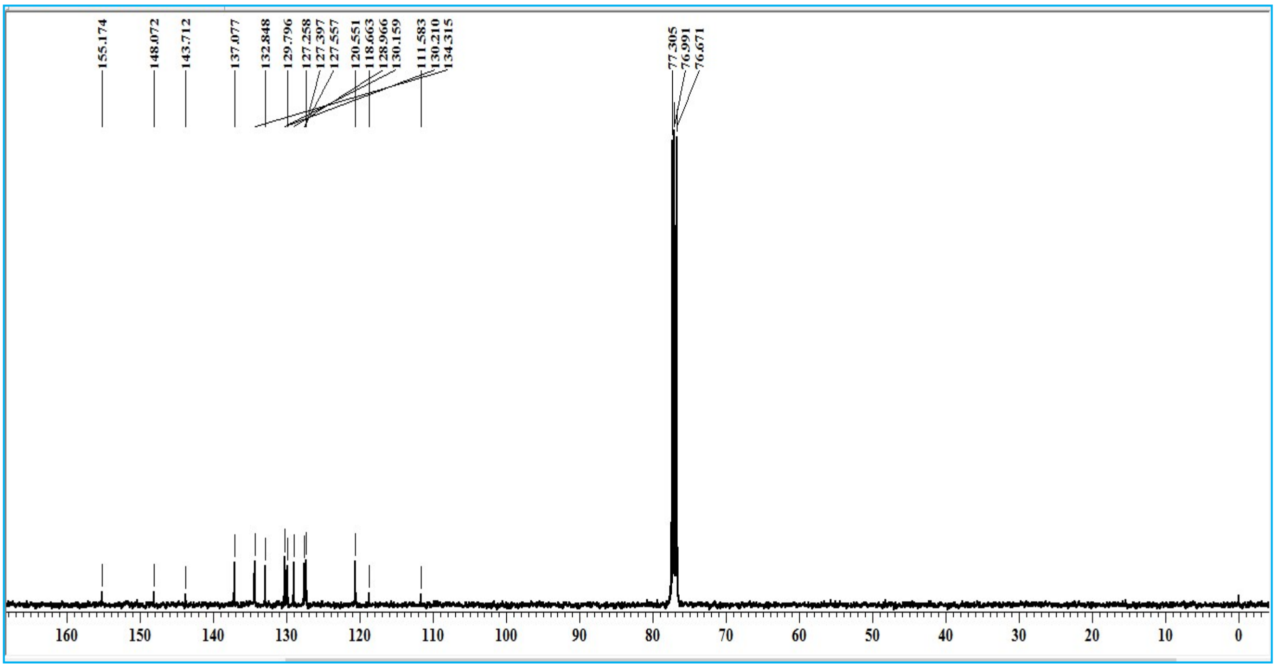
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140
130
120
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80
70
60
50
40
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20
10
0

^{1}H and ^{13}C NMR Spectra of Benzo[*h*]quinoline-10-carbonitrile (Figure S5o)