Electronic Supplementary Information

Construction of 3D homochiral metal-organic frameworks (MOF) of Cd(II): selective CO_2 adsorption and catalytic properties for Knoevenagel and Henry reaction

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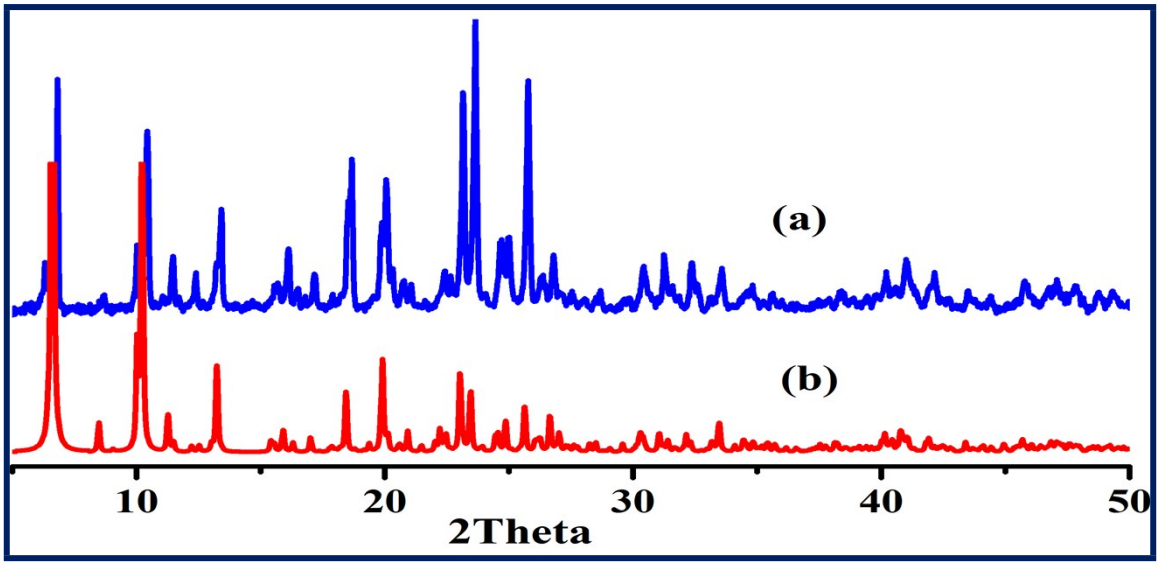


Fig. S1 PXRD patterns of compound **1**. (a) bulk as-synthesized compound; (b) Simulated from X-ray single crystal data.

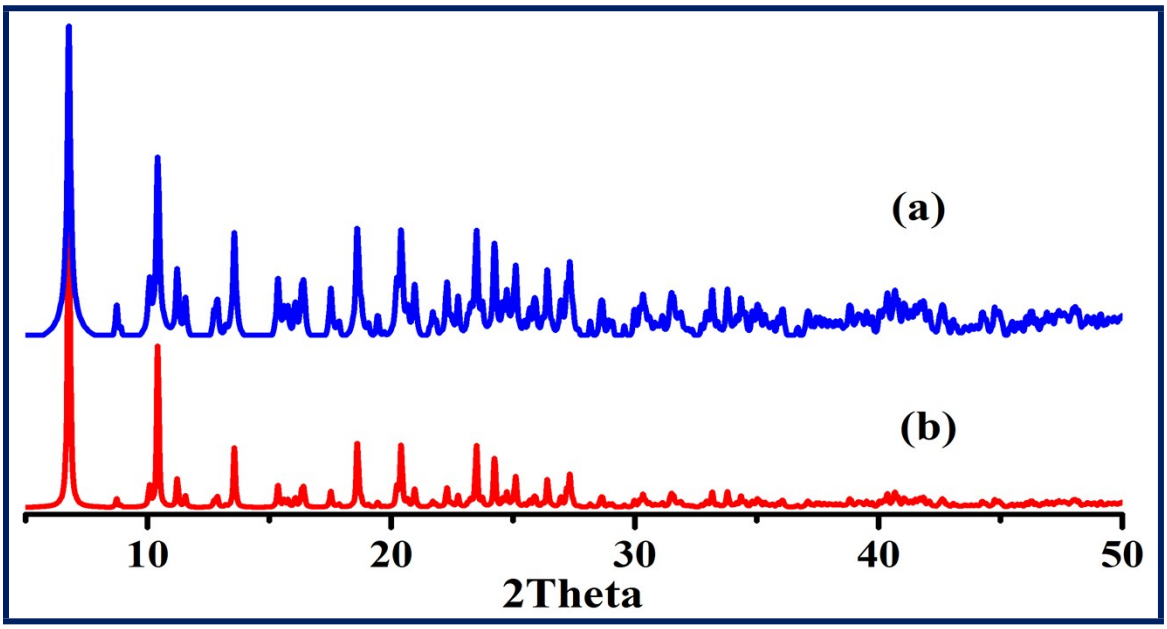


Fig. S2 PXRD patterns of compound **2**. (a) bulk as-synthesized compound; (b) Simulated from X-ray single crystal data

X-ray Crystallography

Single crystal X-ray structural data of compound **1** and **2** were collected on a CMOS based Bruker D8 Venture PHOTON 100 diffractometer equipped with a INCOATEC micro-focus source with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. The SAINT[1] program was used for integration of diffraction profiles and absorption correction was made with SADABS program.[2] The structures were solved by SIR 92[3] and refined by full matrix least square method using SHELXL-2013[4] and WinGX system, Ver 2013.3.[5] The non hydrogen atoms in all the structures were located from the difference Fourier map and refined anisotropically. All the hydrogen atoms were fixed by HFIX and placed in ideal positions and included in the refinement process using riding model with isotropic thermal parameters. The disordered guest water molecules in compound **1** were treated with SQUEEZE option of PLATON[6] multipurpose crystallographic software. The formula of compound **1** was determined based on the elemental analyses and TGA. The potential solvent accessible area or void space was calculated using the PLATON[6] software. All the crystallographic and structure refinement data of the compound **1** is summarized in Table S1. Selected bond lengths and angles are given in Table S2 and S4 and selected hydrogen bond details of the compound **1** and **2** are summarized in Table S3 and S5 respectively. The crystallographic information file is deposited with the CCDC number 1471921 and 1505243 for compound **1** and **2** respectively.

Table S1. Crystal data and structure refinement parameters for compounds **1** and **2**.

Parameters	**1**	**2**
Molecular formula	$C_{46}H_{50}N_8O_{11}Cd_2$	$C_{46}H_{50}N_{10}O_{17}Cd_3$
Molecular mass	1115.95	1352.17
Crystal system	Triclinic	Triclinic
Space group	P1(No.1)	P1(No.1)
a /Å	10.0425(5)	9.5471(11)
b /Å	10.7819(5)	11.7577(5)
c /Å	15.1215(7)	14.0097(15)
α (°)	74.980(2)	69.421(3)
β (°)	77.163(2)	87.400(4)
γ(°)	64.873(2)	67.391(3)
V(Å^3)	1419.91(12)	1351.8(3)
Z	1	1
ρ(g cm^{-3})	1.263	1.654
μ(mm^{-1})	0.801	1.246
F(000)	546	670
T(K)	298	298
λ(Mo K_α)(Å)	0.71073	0.71073
Θ_{min}(°)	2.3	2.0
Θ_{max}(°)	28.4	28.5
Total data	71932	26032
Unique data	14084	12392
R_{int}	0.060	0.034
Data[I>2σ(I)]	11867	11732
[a]R_1	0.0354	0.0371
[b]wR_2	0.0763	0.0916
S	1.01	1.03
Flack parameter(x)	0.002(10)	0.010(10)

$$^{a}R_1 = \sum \| F_0 | - | F_c \| / \sum | F_o |, \; ^{b}wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(Fo^2)^2]^{1/2}$$

Table S2. Selected bond lengths (Å) and angles (°) for compound **1**.

Cd1-O1	2.284(4)	O2-Cd1-N2	89.6(2)
Cd1-O1W	2.384(5)	O3-Cd1-N1	87.76(18)
Cd1-O2	2.453(4)	O3-Cd1-N2	94.2(2)
Cd1-O3	2.356(4)	N1-Cd1-N2	175.7(3)
Cd1-N1	2.331(7)	O3-Cd2-O4	73.16(15)
Cd1-N2	2.331(7)	O3-Cd2-O5	82.78(14)
Cd2-O3	2.486(4)	O3-Cd2-O6	135.04(16)
Cd2-O4	2.565(4)	O3-Cd2-O7	142.86(12)
Cd2-O5	2.469(4)	O3-Cd2-N3	88.4(2)
Cd2-O6	2.488(5)	O3-Cd2-N4	82.0(2)
Cd2-O7	2.341(4)	O4-Cd2-O5	155.84(16)
Cd2-N3	2.245(7)	O4-Cd2-O6	151.74(18)
Cd2-N4	2.259(7)	O4-Cd2-O7	70.81(14)
		O4-Cd2-N3	84.1(2)
O1-Cd1-O1W	84.31(19)	O4-Cd2-N4	87.13(18)
O1-Cd1-O2	175.55(13)	O5-Cd2-O6	52.41(16)
O1-Cd1-O3	121.54(15)	O5-Cd2-O7	132.40(13)
O1-Cd1-N1	92.9(2)	O5-Cd2-N3	97.5(2)
O1-Cd1-N2	89.3(3)	O5-Cd2-N4	87.4(2)
O1W-Cd1-O2	99.89(17)	O6-Cd2-O7	81.54(15)
O1W-Cd1-O3	154.14(19)	O6-Cd2-N3	93.6(2)
O1W-Cd1-N1	92.10(19)	O6-Cd2-N4	97.6(3)
O1W-Cd1-N2	84.4(2)	O7-Cd2-N3	96.6(2)
O2-Cd1-O3	54.25(13)	O7-Cd2-N4	87.5(2)
O2-Cd1-N1	88.4(2)	N3-Cd2-N4	168.5(2)

Table S3. Selected hydrogen bonding geometry (Å,°) for compound **1**

D–H···A	D···H	H···A	D···A	D–H···A
O1W --H1W1 .. N8	0.9300	2.1400	2.979(8)	149.00[i]
N7 --H1A .. O4	0.8600	2.3400	2.677(8)	103.00
N7--H1A .. O7	0.8600	2.2700	2.897(5)	130.00
N7--H1B .. O2	0.8600	2.0500	2.858(7)	155.00[ii]
O1W--H1W2 ..O6	0.9300	2.1800	2.750(8)	119.00[iii]
N8--H11B..O1	0.8600	2.2300	2.855(6)	129.00[iv]
N8--H11B..O1W	0.8600	2.2800	2.979(8)	138.00[iv]
Symmetry codes : (i) 1+x,-1+y,z; (ii) 1+x, y, z; (iii) x, -1+y, z; (iv) -1+x, 1+y, z.				

Table S4. Selected bond lengths (Å) and angles (°) for compound **2**.

Cd1-O1	2.345(5)	O2-Cd2-O5	99.3(2)
Cd1-O3	2.264(6)	O2-Cd2-N5	81.3(3)
Cd1-O6	2.339(6)	O2-Cd2-N6	88.4(3)
Cd1-N7	2.335(7)	O2-Cd2-N8	163.6(2)
Cd1-N1	2.369(7)	O3-Cd2-O5	166.1(2)
Cd1-N2	2.347(7)	O3-Cd2-N5	101.6(2)
Cd2-O2	2.246(5)	O3-Cd2-N6	86.6(2)
Cd2-O3	2.345(6)	O3-Cd2-N8	70.6(2)
Cd2-O5	2.307(6)	O5-Cd2-N5	81.9(2)
Cd2-N5	2.366(7)	O5-Cd2-N6	92.4(2)
Cd2-N6	2.351(7)	O5-Cd2-N8	95.8(2)
Cd2-N8	2.338(7)	N5-Cd2-N6	167.2(3)
Cd3-O1W	2.317(6)	N5-Cd2-N8	94.7(3)
Cd3-O6	2.456(6)	N6-Cd2-N8	97.3(3)
Cd3-O7	2.344(5)	O1W-Cd3-O6	79.8(2)
Cd3-O8	2.318(6)	O1W-Cd3-O7	133.0(2)
Cd3-N3	2.350(7)	O1W-Cd3-O8	84.0(2)
Cd3-N4	2.366(7)	O1W-Cd3-N3	93.8(2)
Cd3_O5^{i}	2.465(6)	O1W-Cd3-N4	85.5(2)
O1-Cd1-O3	93.8(2)	O1W-Cd3-O5^{i}	136.5(2)
O1-Cd1-O6	76.1(2)	O6-Cd3-O7	54.42(19)
O1-Cd1-N1	84.6(2)	O6-Cd3-O8	163.1(2)
O1-Cd1-N2	91.3(2)	O6-Cd3-N3	82.7(2)
O1-Cd1-N7	145.8(2)	O6-Cd3-N4	95.5(3)
O3-Cd1-O6	169.5(2)	O5^{i}-Cd3-O6	142.1(2)
O3-Cd1-N1	80.7(2)	O7-Cd3-O8	142.4(2)
O3-Cd1-N2	91.2(2)	O7-Cd3-N3	90.4(2)
O3-Cd1-N7	119.2(2)	O7-Cd3-N4	88.9(2)
O6-Cd1-N1	101.1(2)	O5^{i}-Cd3-O7	87.7(2)
O6-Cd1-N2	86.0(2)	O8-Cd3-N3	94.0(2)
O6-Cd1-N7	71.2(2)	O8-Cd3-N4	87.6(3)
N1-Cd1-N2	170.6(3)	O5^{i}-Cd3-O8	54.8(2)
N1-Cd1-N7	92.0(2)	N3-Cd3-N4	178.2(3)
N2-Cd1-N7	96.1(2)	O5^{i}-Cd3-N3	101.4(2)
O2-Cd2-O3	94.6(2)	O5^{i}-Cd3-N4	80.3(2)

Symmetry codes : (i) 1+x,-1+y,z.

Table S5. Selected hydrogen bonding geometry (Å,°) for compound **2**

D–H···A	D···H	H···A	D···A	D–H···A
N7--H7C .. O3w	0.8900	2.3200	3.054(10)	139.00
N7--H7D .. O8	0.8900	2.0200	2.865(9)	158.00[i]
N8--H8C..O7	0.8900	2.0400	2.853(8)	151.00[ii]
N8--H8D..O5W	0.8900	2.3400	3.183(11)	159.00[iii]
Symmetry codes : (i) -1+x,y,z; (ii) -1+x,1+y,z; (iii) -1+x,1+y,-1+z.				

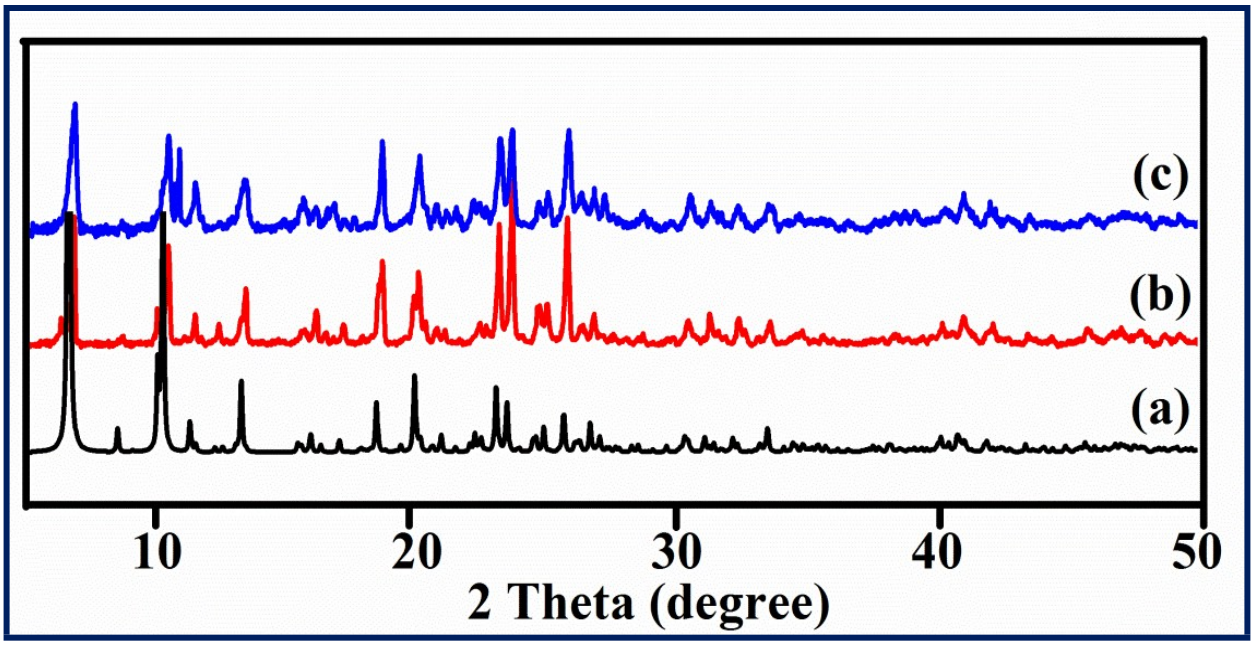


Fig. S3 PXRD patterns of compound **1** (a) pattern calculated from single crystal X- ray data; (b) for as synthesized sample before heating; (c) for the sample activated at 120^{o}C for 20 hours.

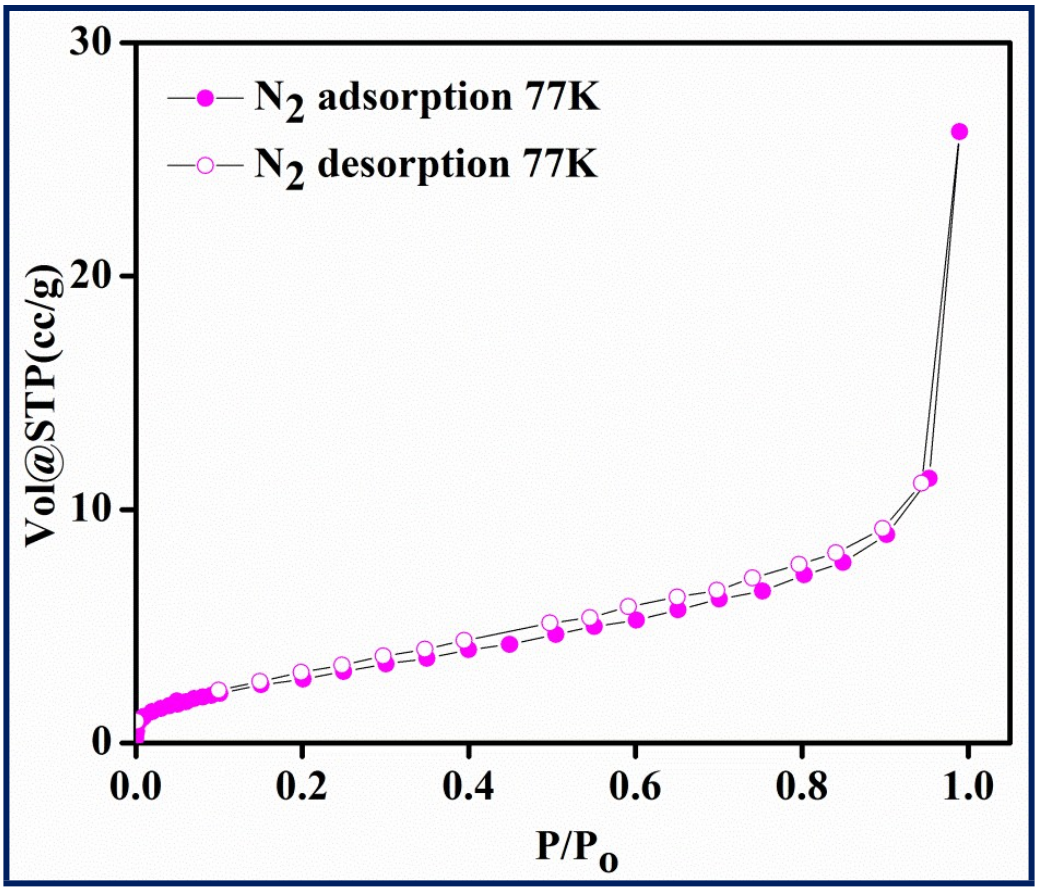


Fig. S4 Nitrogen adsorption-desorption isotherm of compound **1** carried out at 77K.

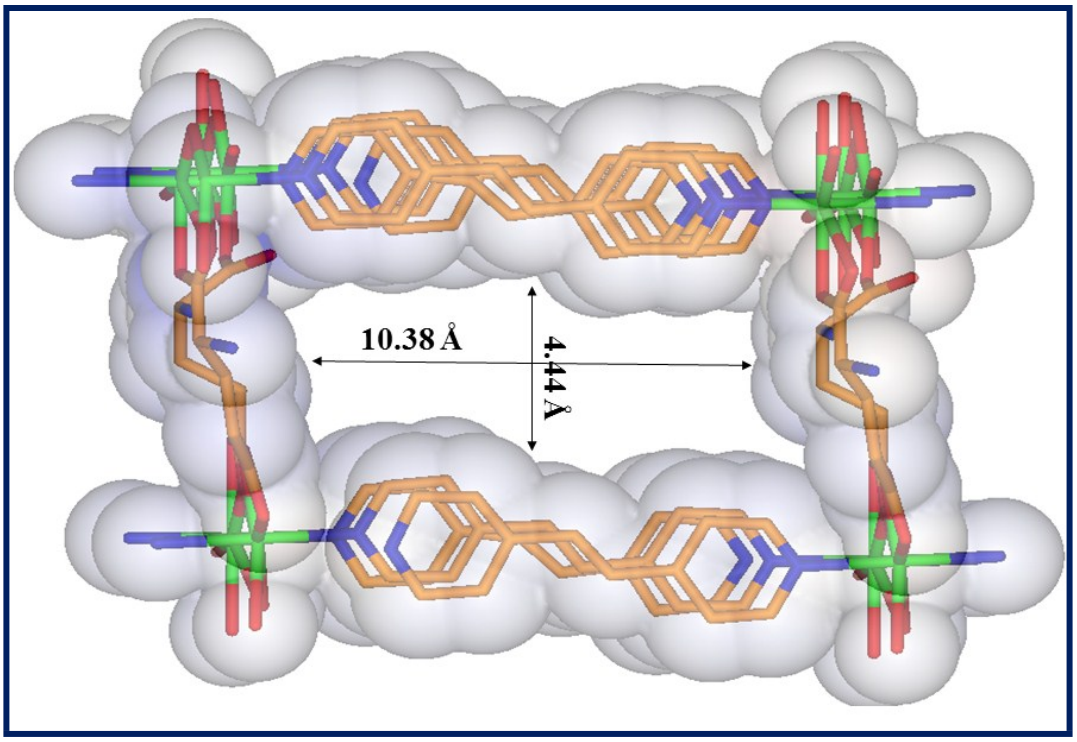


Fig. S5 Pore picture of 1D channel in compound **1**.

Analysis of Gas adsorption Isotherms

Clausius-Clapeyron Equation[1,2] was used to calculate the enthalpies of hydrogen adsorption. By using Langmuir Freundlich equation[3] an accurate fit was retrieved which gives a precise prediction of hydrogen adsorbed at saturation. A modification of Clausius-Clapeyron equation is used for calculations.

$$\ln\left[\frac{P_1}{P_2}\right] = \Delta H_{ads} \; X \left[\frac{T_2 - T_1}{R \; X \; T_2 T_1}\right] \qquad \text{------(i)}$$

where, P_1 and P_2 = pressures for isotherm at 273K and 298K respectively.

T_1 and T_2 = temperatures for isotherm at 273K and 298K respectively.

ΔH_{ads} = Enthalpy of adsorption.

R = Universal gas constant = 8.314 J/K/mol.

Pressure is a function of amount of gas adsorbed which was determined by using the Langmuir-Freundlich fit.

$$\frac{Q}{Q_m} = \frac{B \; X \; P^{(1/t)}}{1 + (B \; X \; P^{(1/t)})} \qquad \text{------(ii)}$$

where, Q = moles of gas adsorbed.

Q_m = moles of gas adsorbed at saturation.

B and t = constants.

P = Pressure.

By rearranging equation (ii) we get equation (iii)

$$P = \left[\frac{Q/Q_m}{B - (B \; X \; Q/Q_m)} \right]^t \qquad \text{------(iii)}$$

Substituting equation (iii) into equation (i) we get

$$\Delta H_{ads} = \frac{R \; X \; T_1 \; X \; T_2}{T_2 - T_1} \; \ln \frac{\left[\frac{Q/Q_{m1}}{B - (B \; X \; Q/Q_{m1})} \right]^{t1}}{\left[\frac{Q/Q_{m2}}{B - (B \; X \; Q/Q_{m2})} \right]^{t2}} \qquad \text{------(iv)}$$

In equation (iv), subscript 1 and 2 are representing data corresponding to 273K and 298K in case of carbon dioxide gas.

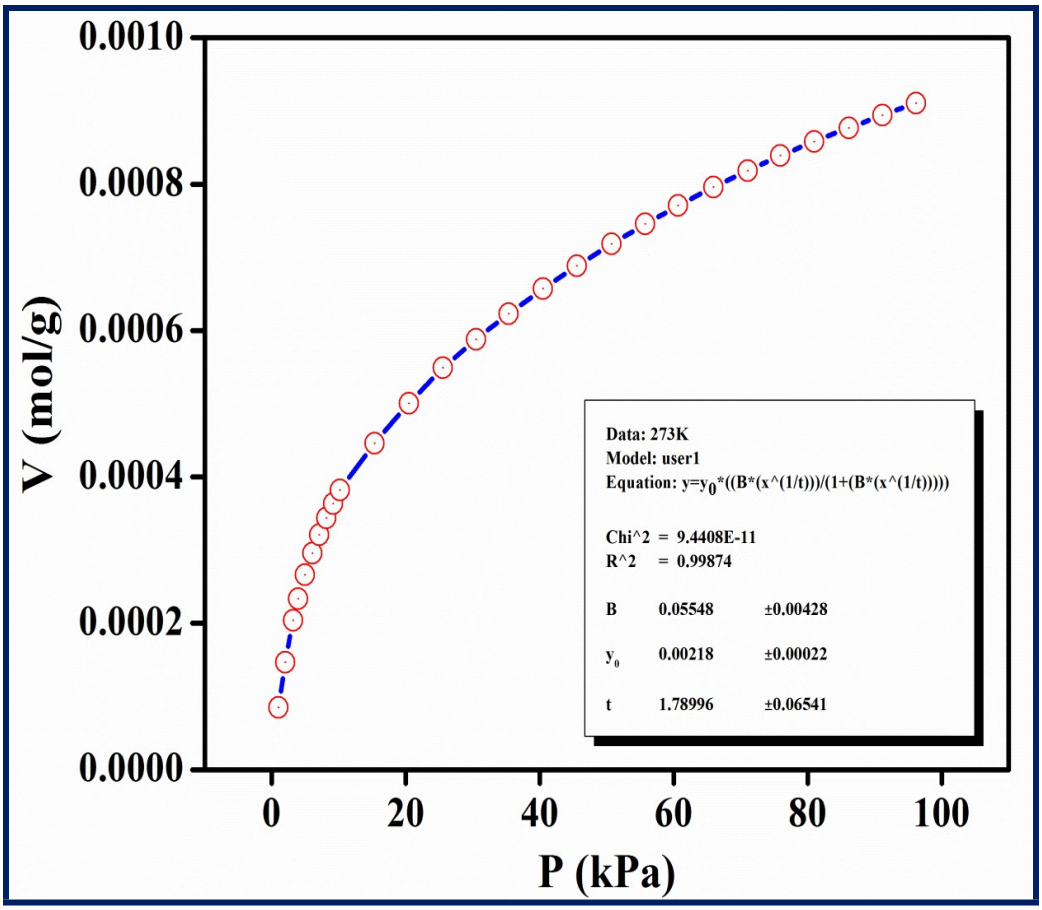


Fig. S6 Carbon dioxide adsorption isotherm for **1** at 273K. The solid line shows the best fit to the data using Langmuir- Freundlich Equation.

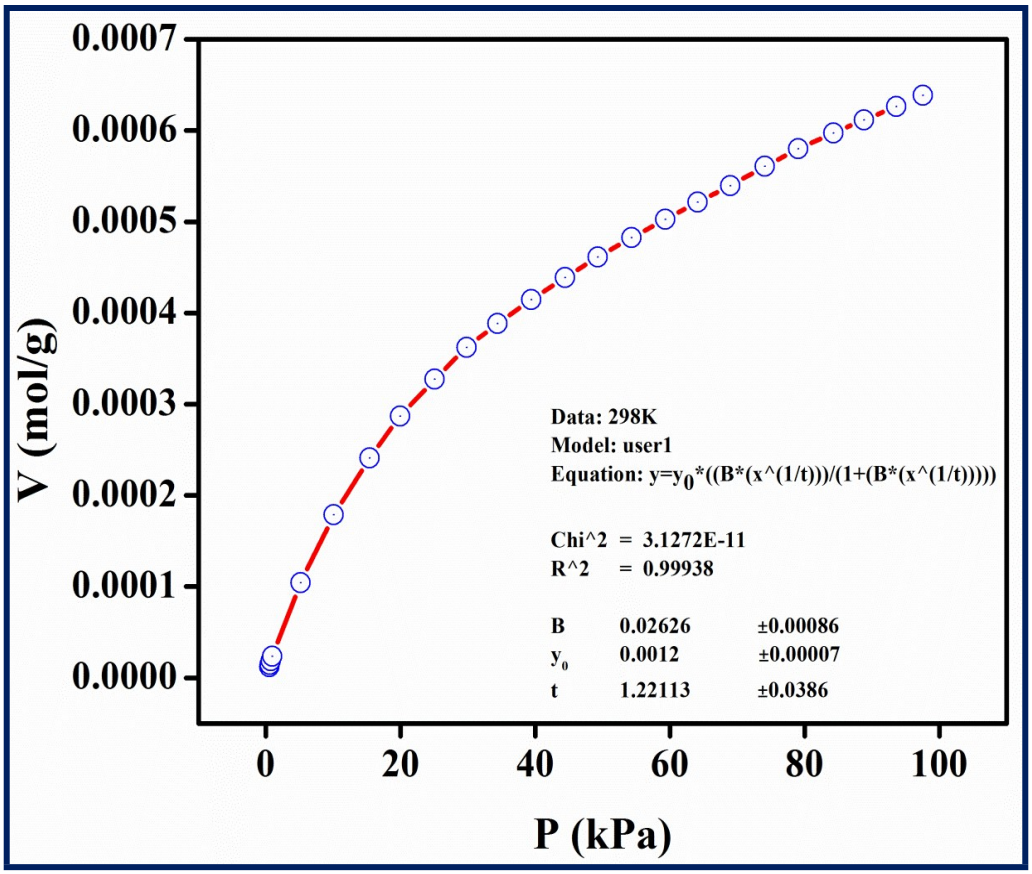


Fig. S7 Carbon dioxide adsorption isotherm for **1** at 298K. The solid line shows the best fit to the data using Langmuir- Freundlich Equation.

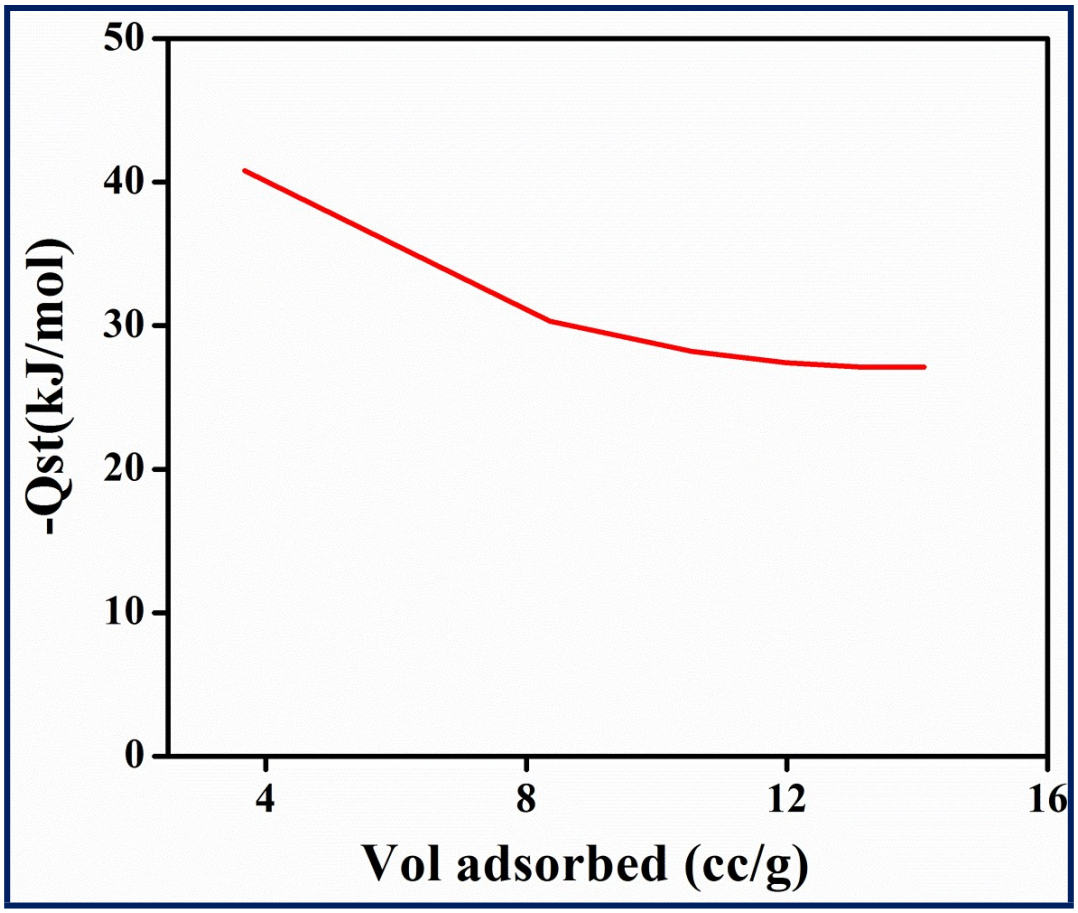


Fig. S8 Enthalpy of carbon dioxide adsorption for **1** using Clausius-Clapeyron Equation calculations.

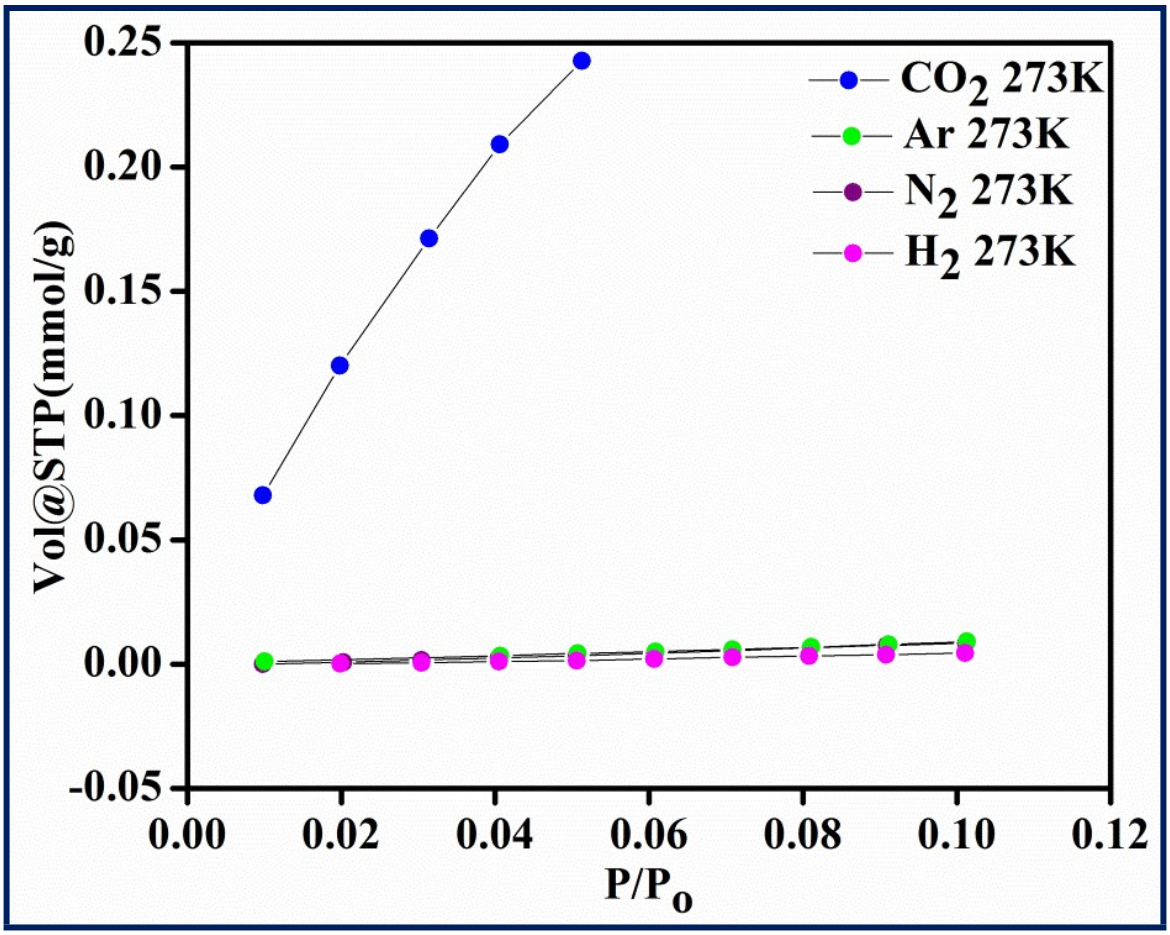


Fig. S9 Gas selectivity for compound **1** calculated following the Henry's law from the CO_2, N_2, Ar and H_2 isotherms at 273K.

Table S6. Optimization of the Knoevenagel condensation reaction of benzaldehyde with malononitrile catalyzed by compound **1**.

Entry no.	Catalyst	R_1	R_2,R_3	Time [h]	Temperature [°C]	Conversion [%][a]
1.	Blank	-H	R_2,R_3 = -CN	6	r.t.	15.6
2.	Free L-glutamic acid	-H	R_2,R_3 = -CN	6	r.t.	82.6
3.	$Cd(NO_3)_2.4H_2O$	-H	R_2,R_3 = -CN	6	r.t.	6
4.	Compound-**1**	-H	R_2,R_3 = -CN	6	r.t.	100
5.	Compound-**1** removed after 1 h	-H	R_2,R_3 = -CN	6	r.t.	63.4

[a] Reaction conditions: Aldehyde (2 mmol), malononitrile (2.2 mmol), MeOH 4ml and Catalyst (0.025eq), r.t, stirring . Yield calculated by GCMS, based on aromatic aldehydes.

Table. S7 Comparison of the catalytic activity of various MOFs in the Knoevenagel reaction of benzaldehyde and propanedinitrile.

Sr.no	Catalyst	Mol (%)	Time	Solvent	Temp [°C]	Yield (%)	Ref.
1.	$[Cd(4\text{-}btapa)_2(NO_3)_2].6H_2O.2DMF$	5	12 h	C_6H_6	r.t.	98	10
2.	$[Cd(bipd)_2(DMF)_2].(ClO_4)_2.(2DMF)$	4	30 min	C_6H_6	r.t.	93	11
3.	$Pb(cpna)_2.2DMF.6H_2O$	3	24 h	CH_3CN	r.t.	100	12
4.	ZIF-8	5	3 h	Toluene	r.t.	100	13
5.	ZIF-9	5	4 h	Toluene	r.t.	99	14
6.	$[Gd_2(tnbd)_3(DMF)_4].4DMF.3H_2O$	10	20 min	C_6H_6	r.t.	96	15
7.	$[Zn(oba)(4\text{-}bpdh)_{0.5}]_n.(DMF)_y$	2	30 min	H_2O	r.t.	100	16
8.	$[Cd(muco)(4bpdh)(H_2O)]$ (**3**)	2.5	90 min	MeOH	r.t	100	17
9.	**Compound 1**	**2.5**	**5 h**	**MeOH**	**r.t.**	**>99**	**This work**

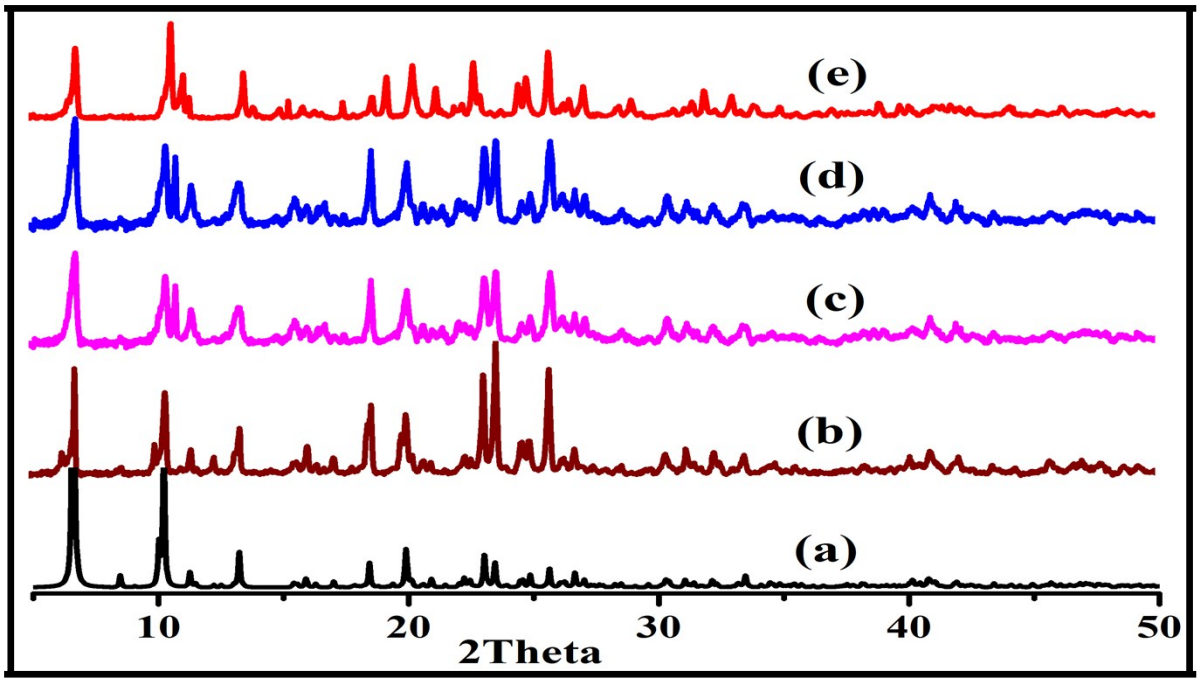


Fig. S10 PXRD patterns of compound **1** (a) simulated PXRD pattern from single crystal x-ray diffraction data. (b) for as-synthesized sample (c) for sample obtained after Knovenagel condensation reaction (d) for sample obtained after Henry reaction (e) for sample obtained after gas adsorption studies.

Table S8. Optimization table for the Henry reaction of benzaldehyde with nitroethane.

Entry no.	Catalyst	R	Time [h]	Temperature [°C]	Solvent	Conversion [%][a]
1.	MOF	-H	72	r.t.	MeOH	≈ 6
2.	$Zn(OAc)_2.2H_2O$	-H	72	r.t.	MeOH	9
3.	Glutamic acid	-H	72	r.t.	MeOH	14
4.	Glutamic acid + Zn(II)	-H	72	r.t.	MeOH	21.8
5.	**MOF + Zn(II)**	**-H**	**72**	**r.t.**	MeOH	**89.3**
6.	MOF + Zn(II)	-H	72	-10	MeOH	0
7.	MOF + Zn(II)	-H	72	-25	MeOH	0
8.	MOF removed after 24 [h]	-H	72	r.t.	MeOH	61.4

[a] Reaction conditions: Aldehyde (2 mmol), nitroethane (10 mmol), MeOH 5 ml and Catalyst (2.5 mol%), r.t, stirring. Conversion calculated based on ^{1}H NMR GCMS, based on aromatic aldehydes

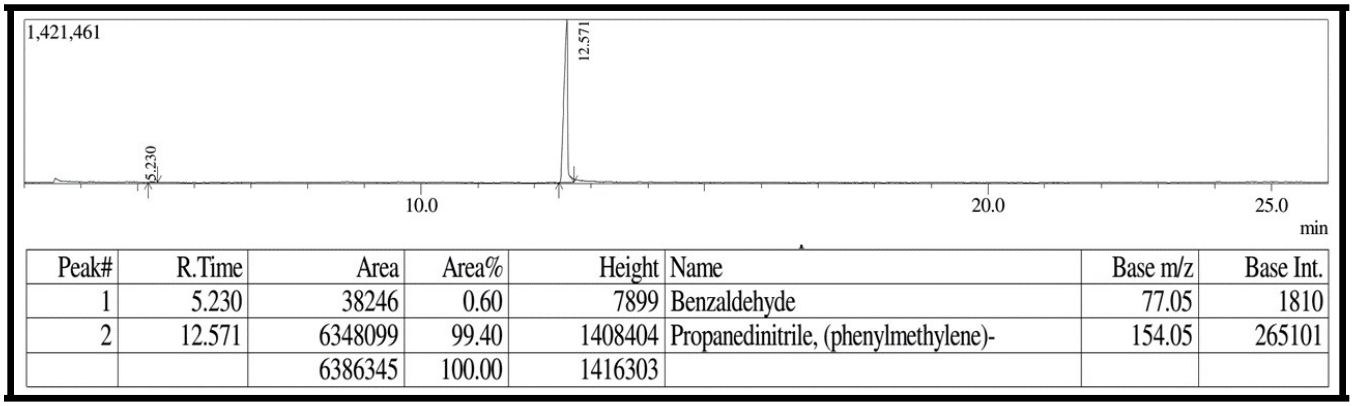
GC-MS DATA

Knovenagel condensation

(A) Standardisation of the reaction condition

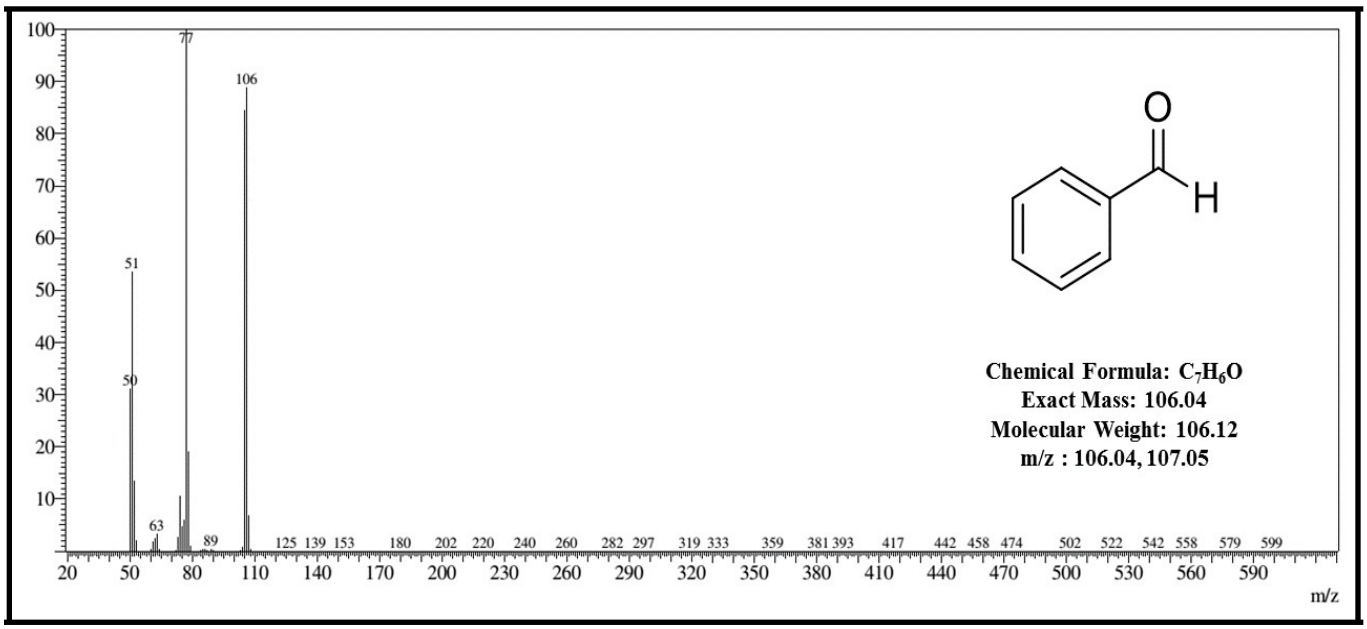
1. Compound 1 used as catalyst (benzaldehyde with malononitrile)

(i)GC data

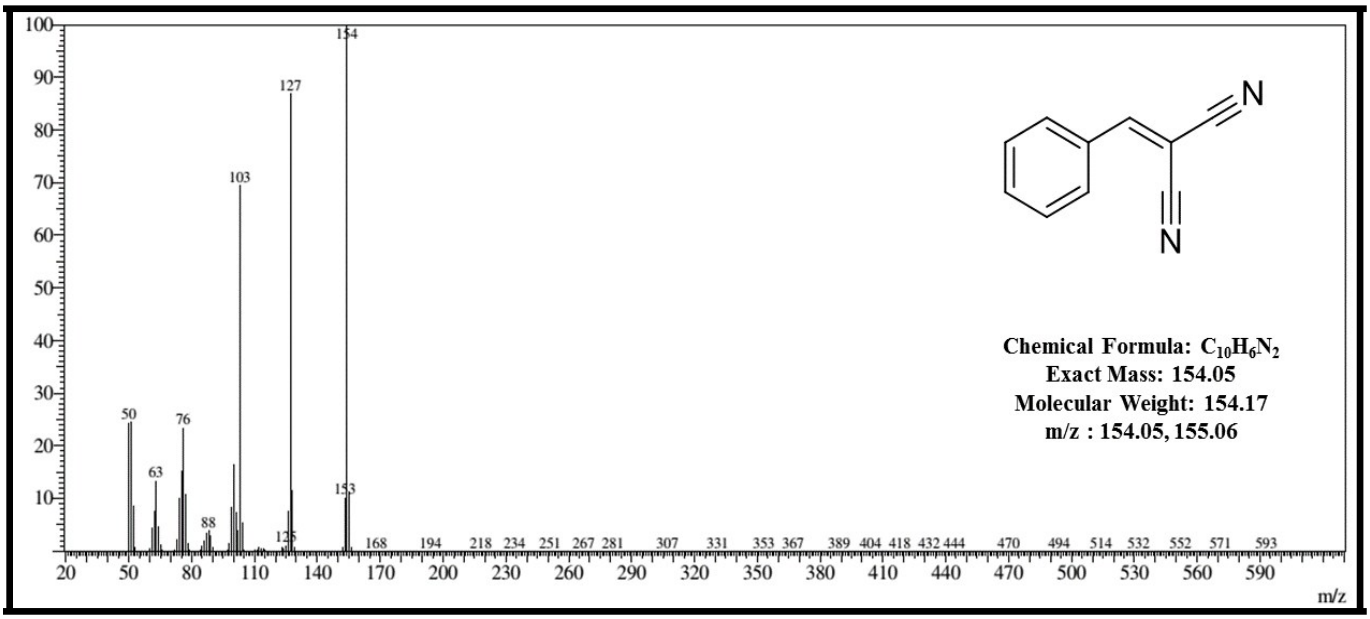


Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	5.230	38246	0.60	7899	Benzaldehyde	77.05	1810
2	12.571	6348099	99.40	1408404	Propanedinitrile, (phenylmethylene)-	154.05	265101
		6386345	100.00	1416303			

(ii) MS data **a. Reactant**

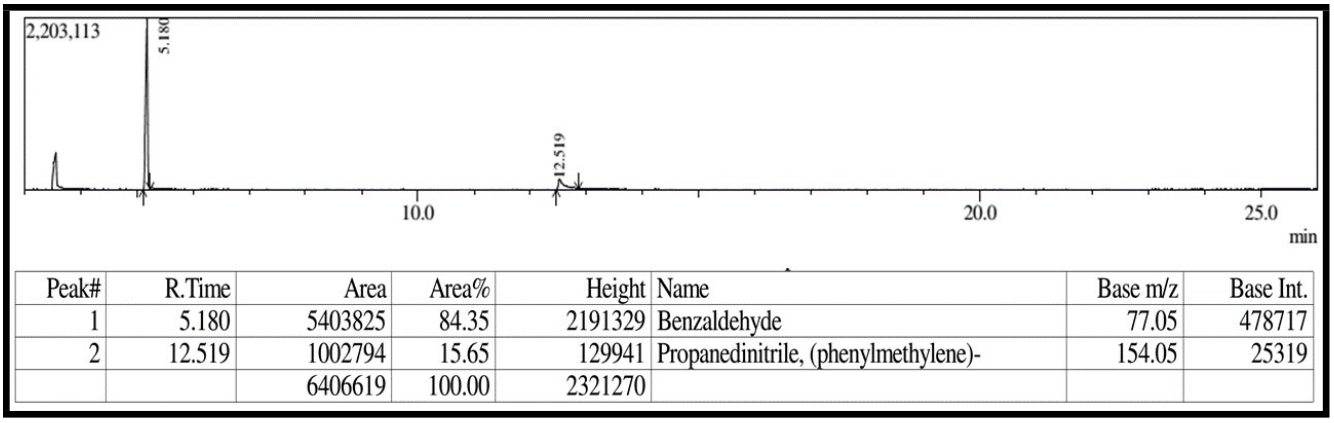


b. <u>Product</u>



2. <u>Blank reaction without catalyst</u> (benzaldehyde with malononitrile)

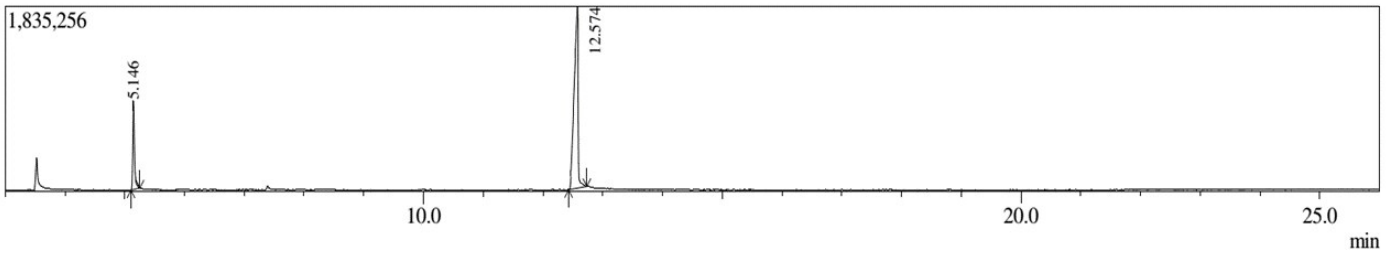
(i)GC data



Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	5.180	5403825	84.35	2191329	Benzaldehyde	77.05	478717
2	12.519	1002794	15.65	129941	Propanedinitrile, (phenylmethylene)-	154.05	25319
		6406619	100.00	2321270			

3. L-glutamic acid used as catalyst (benzaldehyde with malononitrile)

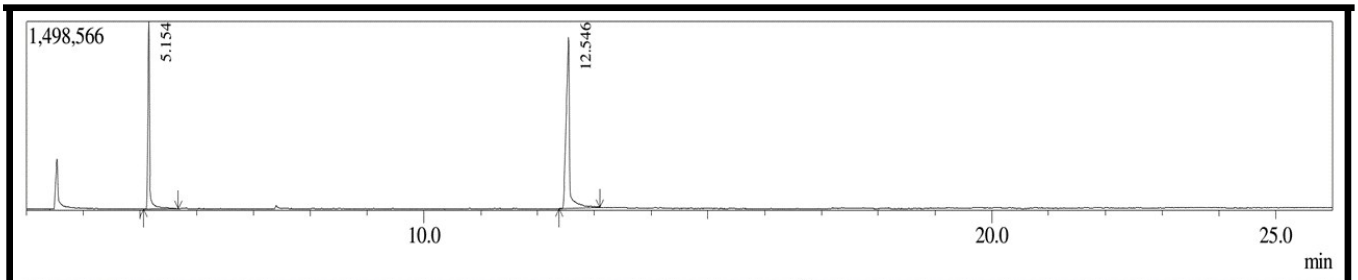
(i) GC data



Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	5.146	1734183	17.42	882792	Benzaldehyde	77.05	187978
2	12.574	8219414	82.58	1802102	Propanedinitrile, (phenylmethylene)-	154.05	334967
		9953597	100.00	2684894			

4. Compound-1 removed after 1hour (benzaldehyde with malononitrile)

(i) GC data

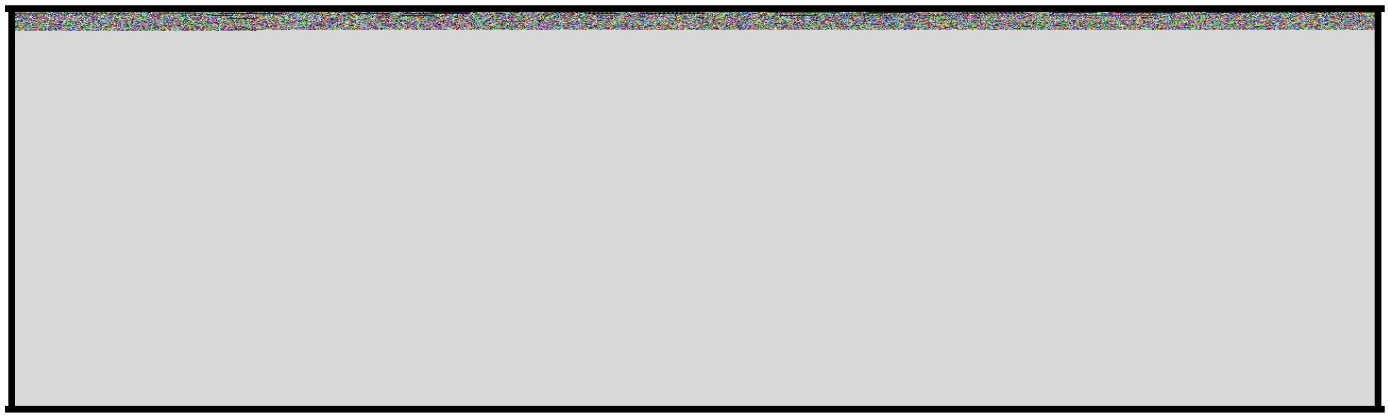


Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	5.154	3302742	36.62	1482965	Benzaldehyde	77.05	320226
2	12.546	5715345	63.38	1354257	Propanedinitrile, (phenylmethylene)-	154.05	255671
		9018087	100.00	2837222			

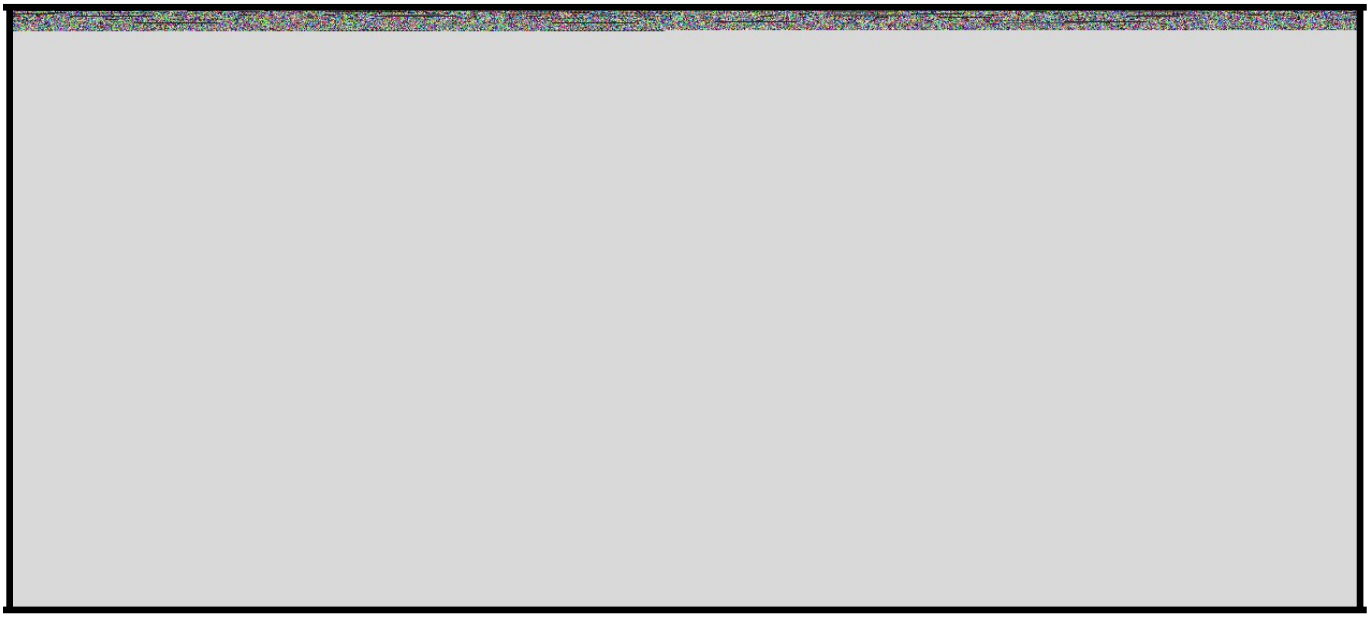
(B) Compound 1 as catalyst in reaction with different substrates

1. Benzaldehyde (malononitrile)

(i)GC data

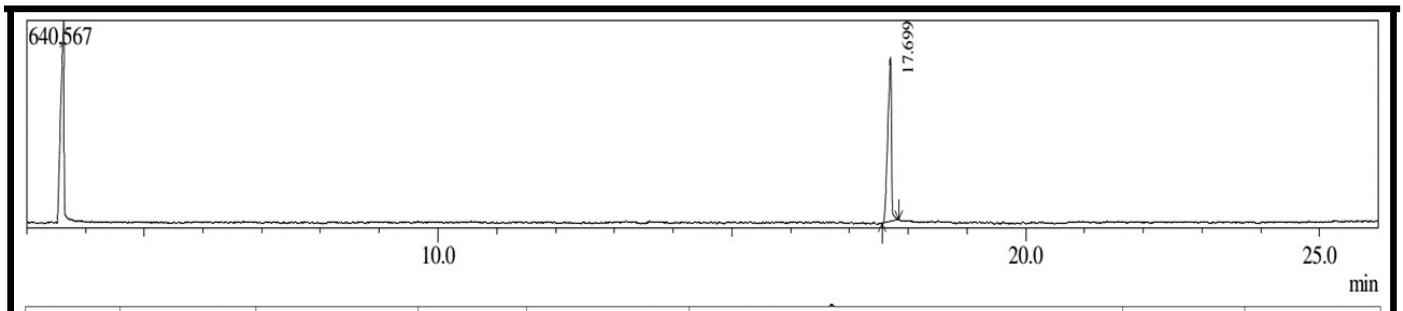


(ii)MS data



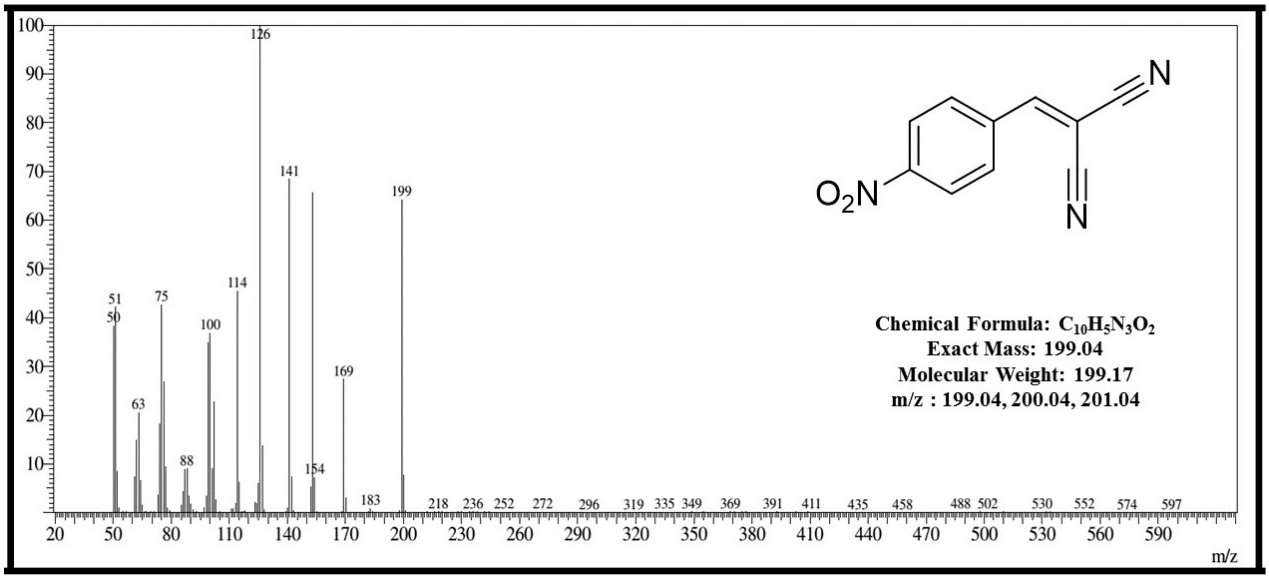
2. 4-Nitro benzaldehyde(malononitrile)

(i) GC data



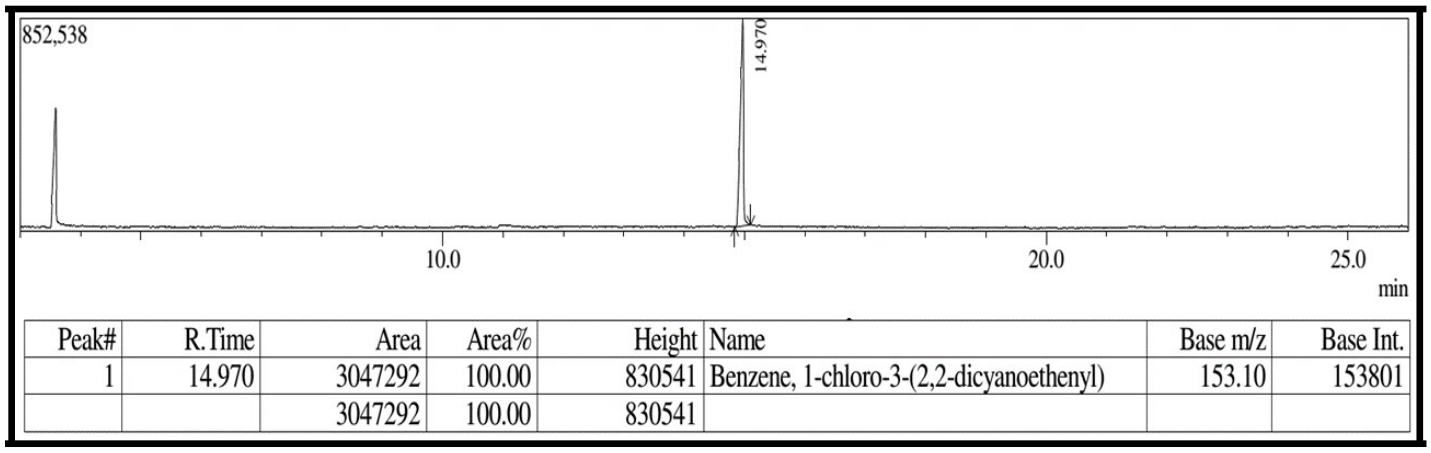
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	17.699	2186902	100.00	506376	Nitrobenzene, 4-(2,2-dicyanoethenyl)	126.05	59821
		2186902	100.00	506376			

(ii) MS data



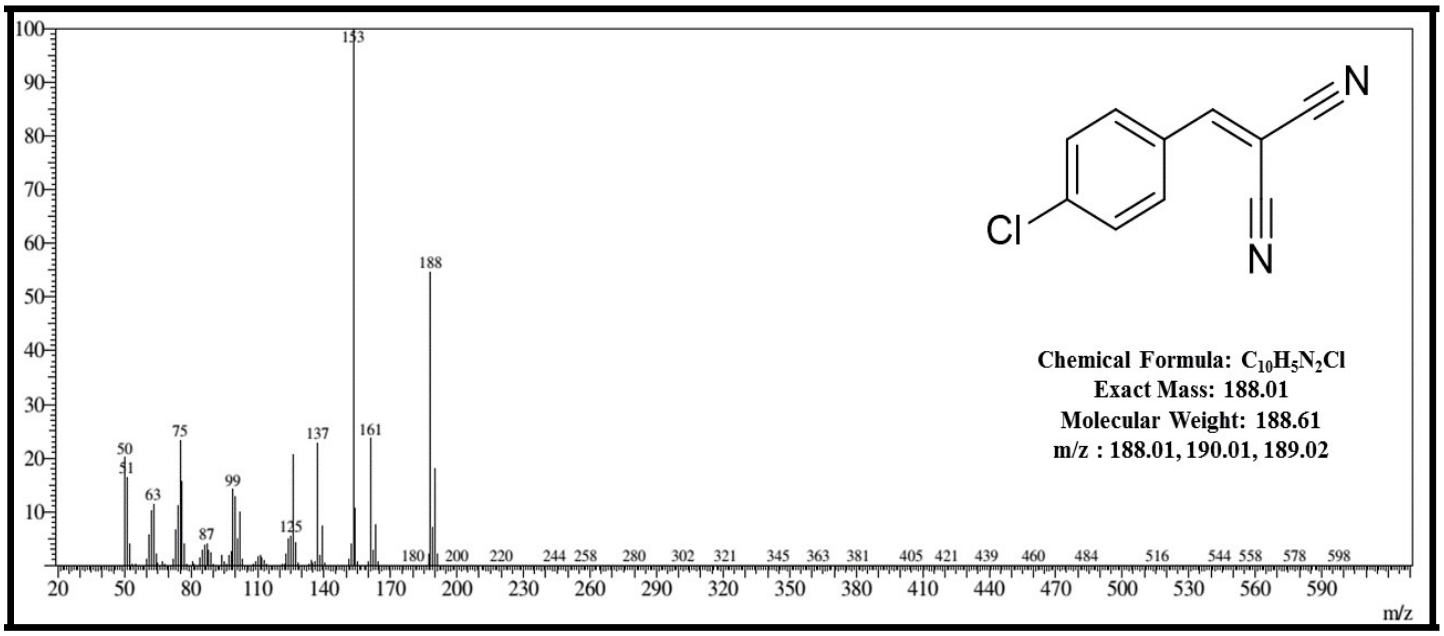
3. 4-Chloro benzaldehyde (malononitrile)

(i)GC data



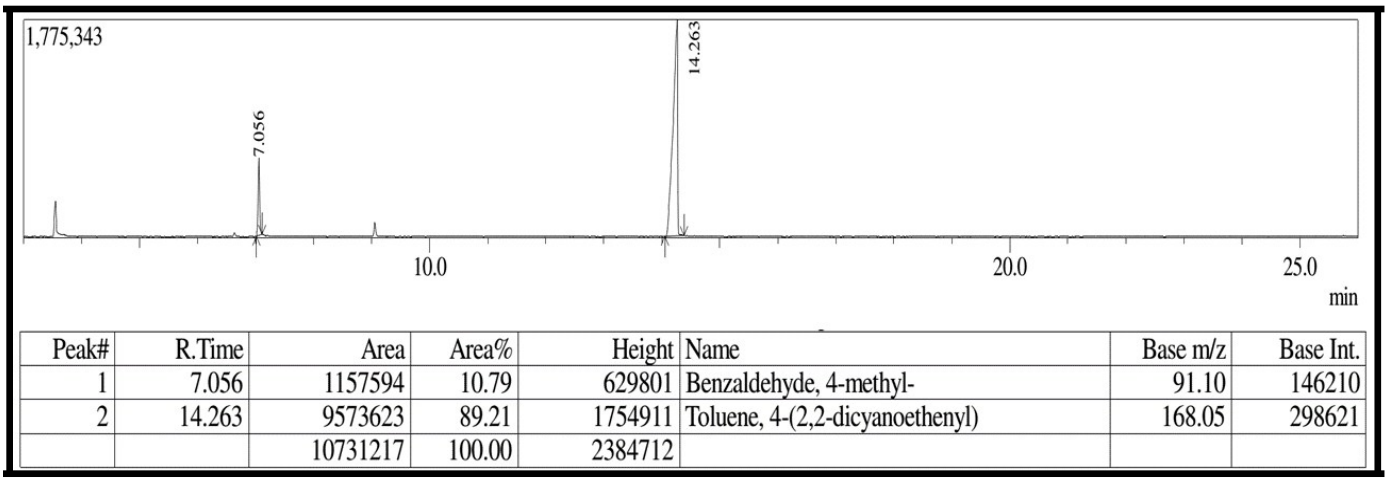
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	14.970	3047292	100.00	830541	Benzene, 1-chloro-3-(2,2-dicyanoethenyl)	153.10	153801
		3047292	100.00	830541			

(ii) MS data



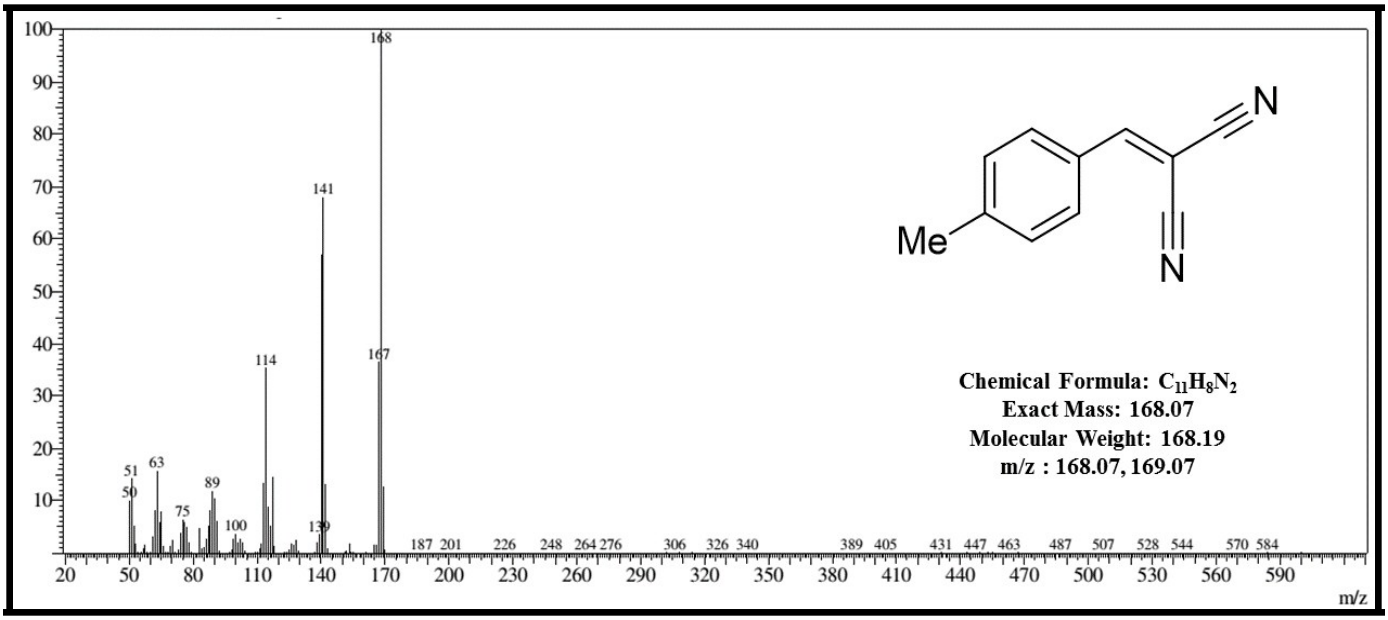
4. 4-Methyl benzaldehyde (malononitrile)

(i)GC data



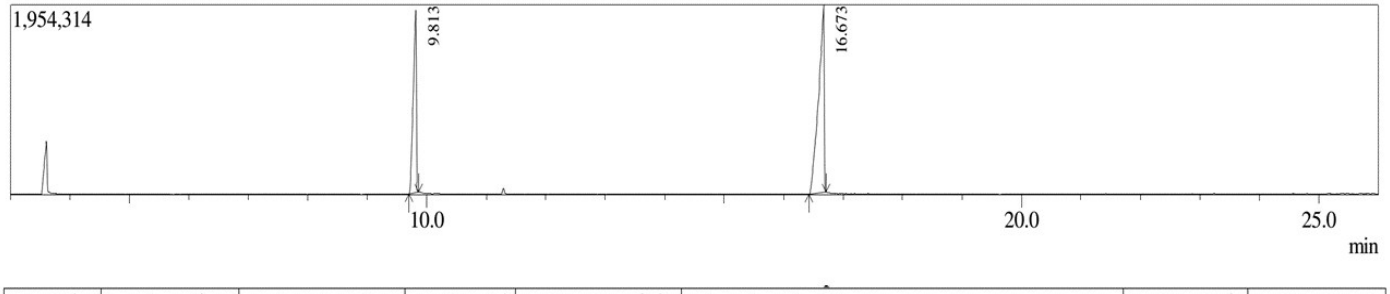
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	7.056	1157594	10.79	629801	Benzaldehyde, 4-methyl-	91.10	146210
2	14.263	9573623	89.21	1754911	Toluene, 4-(2,2-dicyanoethenyl)	168.05	298621
		10731217	100.00	2384712			

(ii) MS data



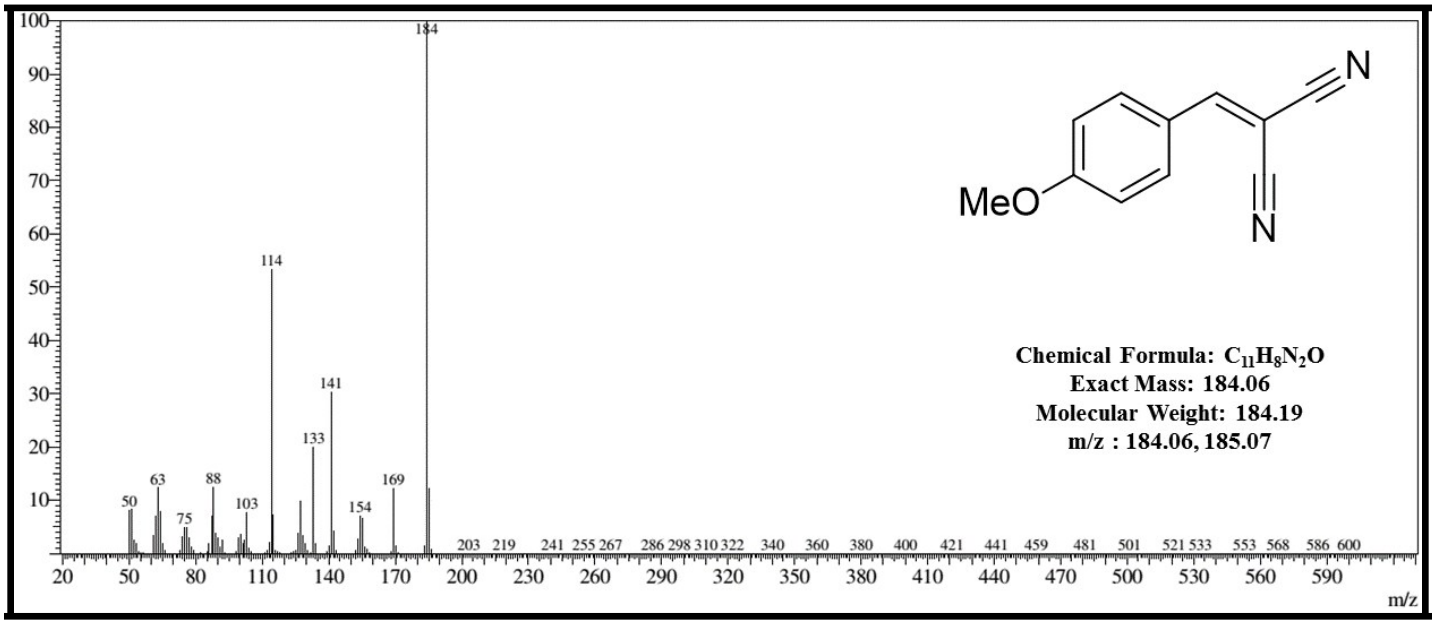
5. 4-Methoxy benzaldehyde (malononitrile)

(i)GC data



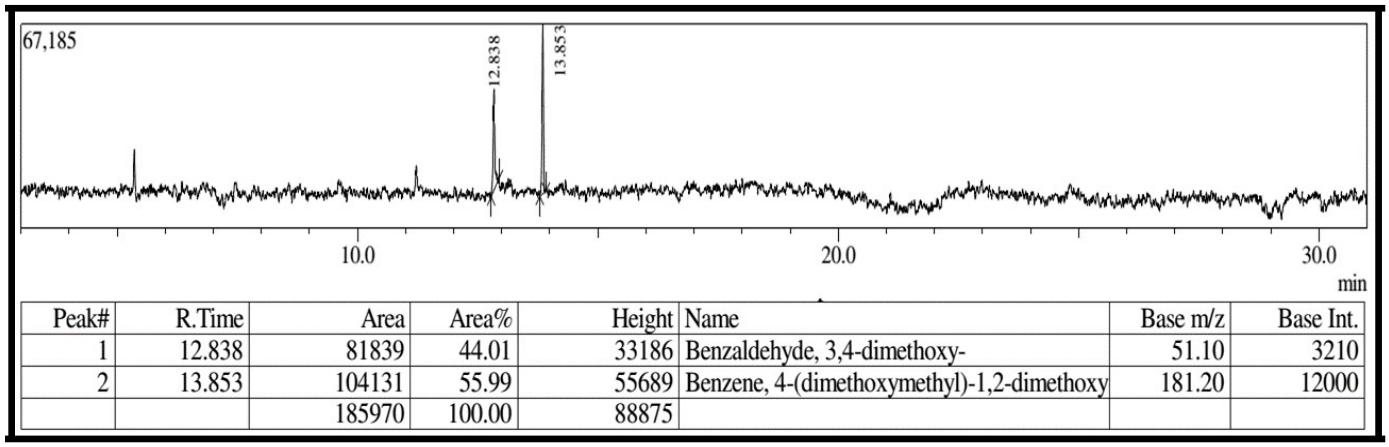
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	9.813	6761212	34.94	1874326	Benzaldehyde, 4-methoxy-	135.10	489378
2	16.673	12587770	65.06	1924019	Benzene, 1-methoxy-4-(2,2-dicyanoethenyl)	184.05	428255
		19348982	100.00	3798345			

(ii) MS data



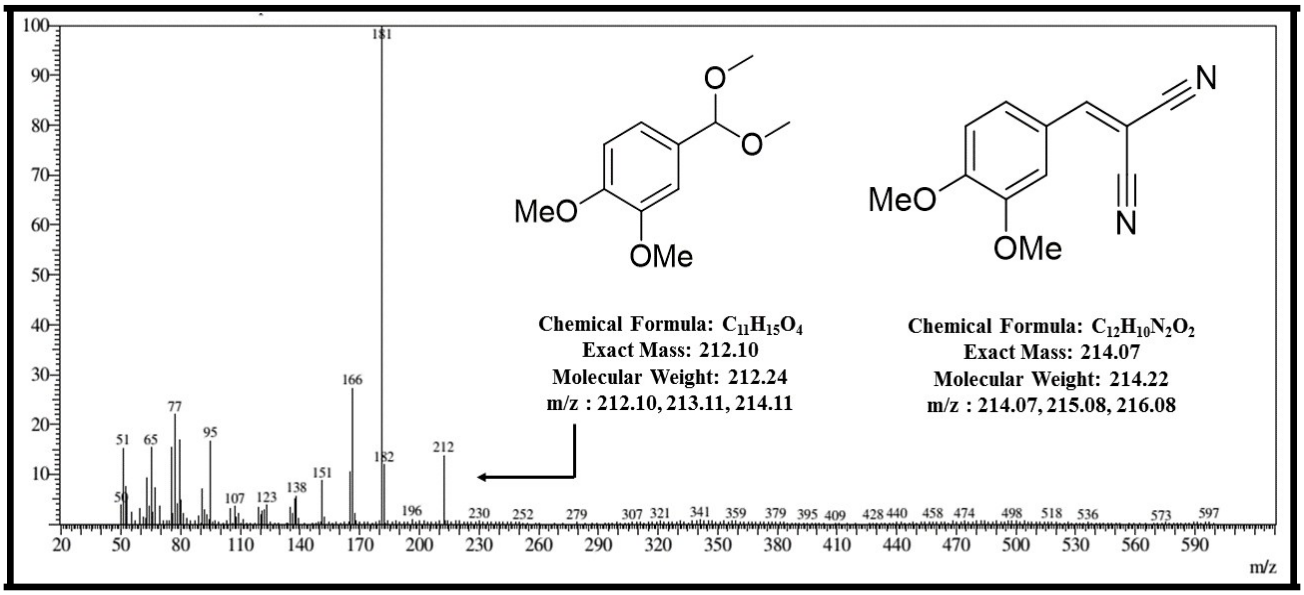
6. <u>3,4-di-Methoxy benzaldehyde</u> (malononitrile)

(i)GC data



Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	12.838	81839	44.01	33186	Benzaldehyde, 3,4-dimethoxy-	51.10	3210
2	13.853	104131	55.99	55689	Benzene, 4-(dimethoxymethyl)-1,2-dimethoxy	181.20	12000
		185970	100.00	88875			

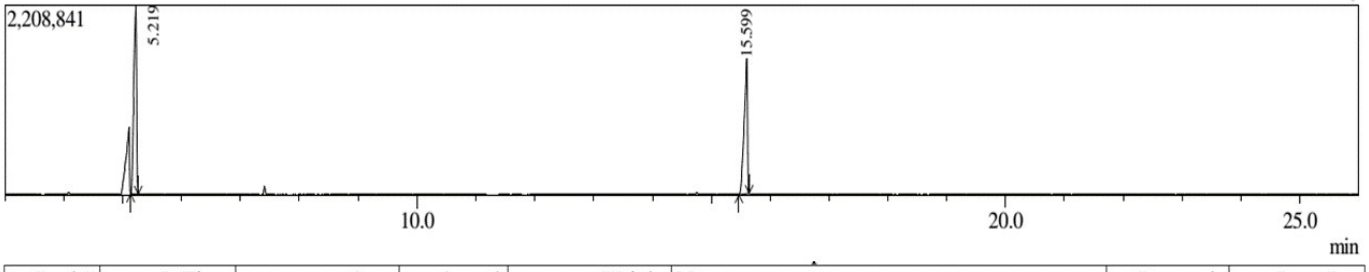
(ii) MS data



(C) Compound 1 as catalyst in reaction with different nitrile substrate

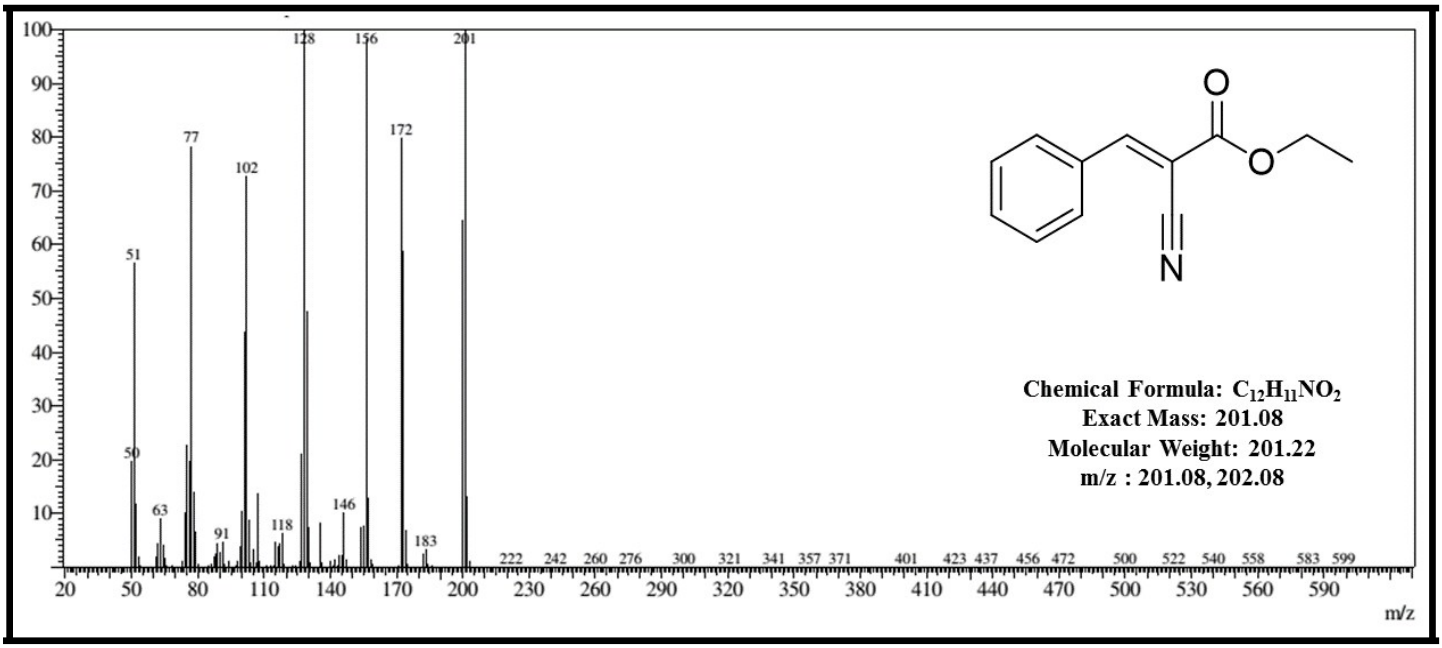
1. Benzaldehyde (Ethyl-2-cyanoacetate)

(i)GC data



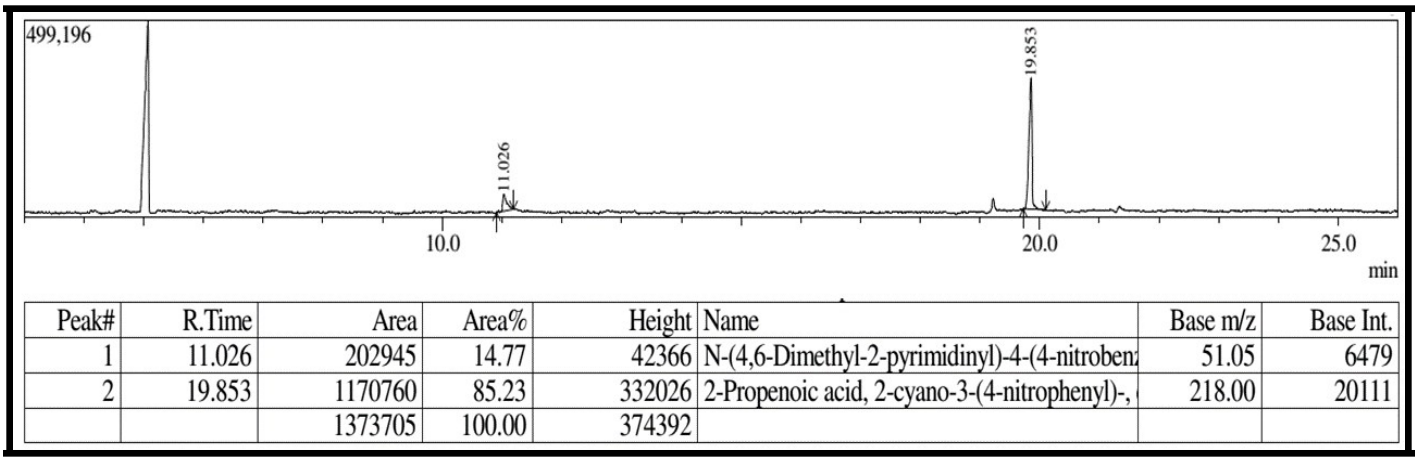
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	5.219	7170428	54.85	2187693	Benzaldehyde	106.10	495916
2	15.599	5902054	45.15	1566150	2-Propenoic acid, 2-cyano-3-phenyl-, ethyl est	128.10	132497
		13072482	100.00	3753843			

(ii) MS data



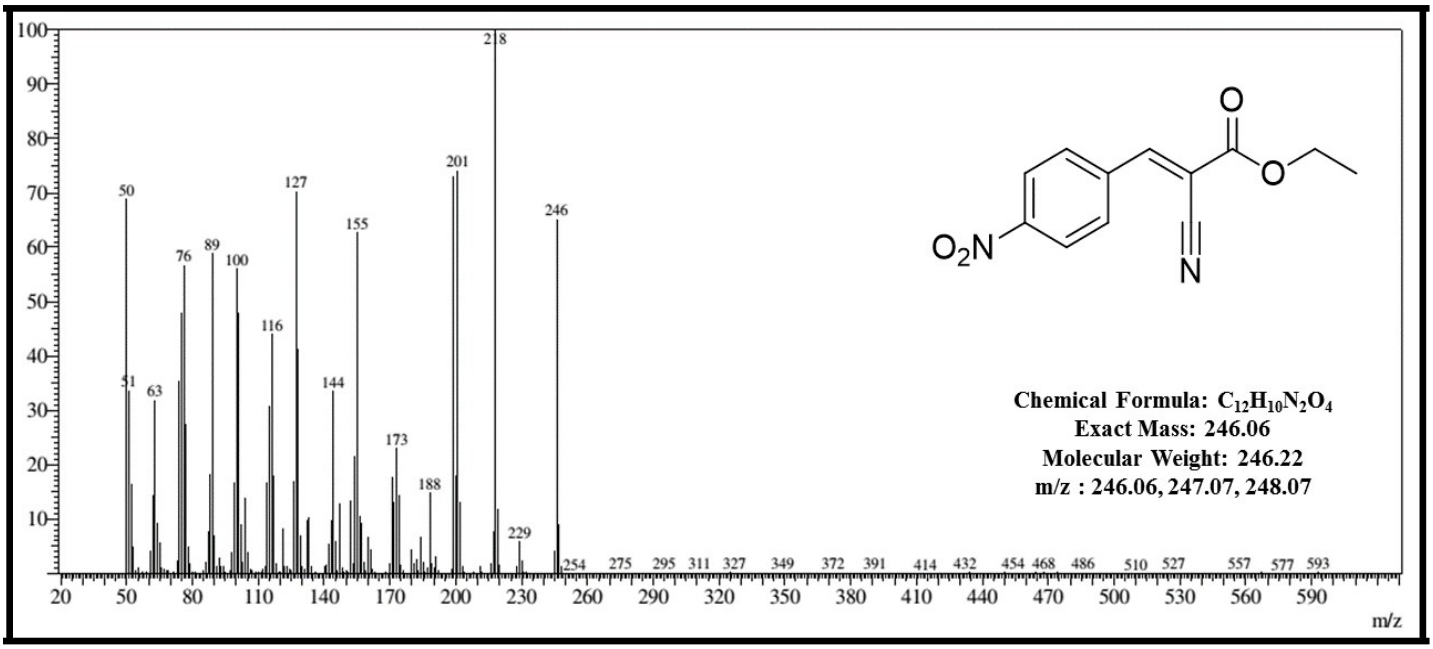
2. 4-Nitro benzaldehyde (Ethyl-2-cyanoacetate)

(i)GC data



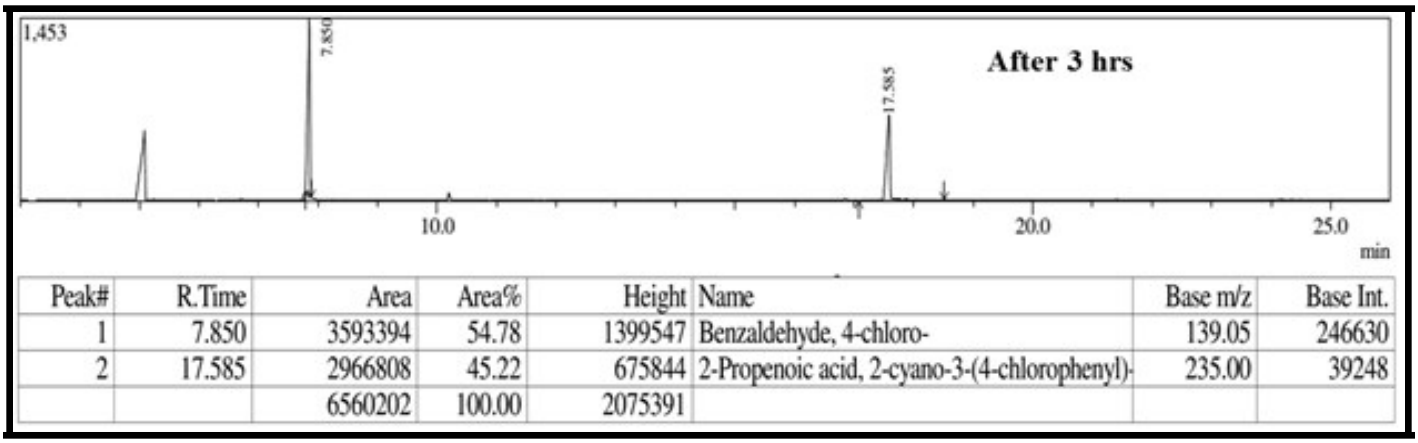
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	11.026	202945	14.77	42366	N-(4,6-Dimethyl-2-pyrimidinyl)-4-(4-nitrobenz	51.05	6479
2	19.853	1170760	85.23	332026	2-Propenoic acid, 2-cyano-3-(4-nitrophenyl)-,	218.00	20111
		1373705	100.00	374392			

(ii) MS data



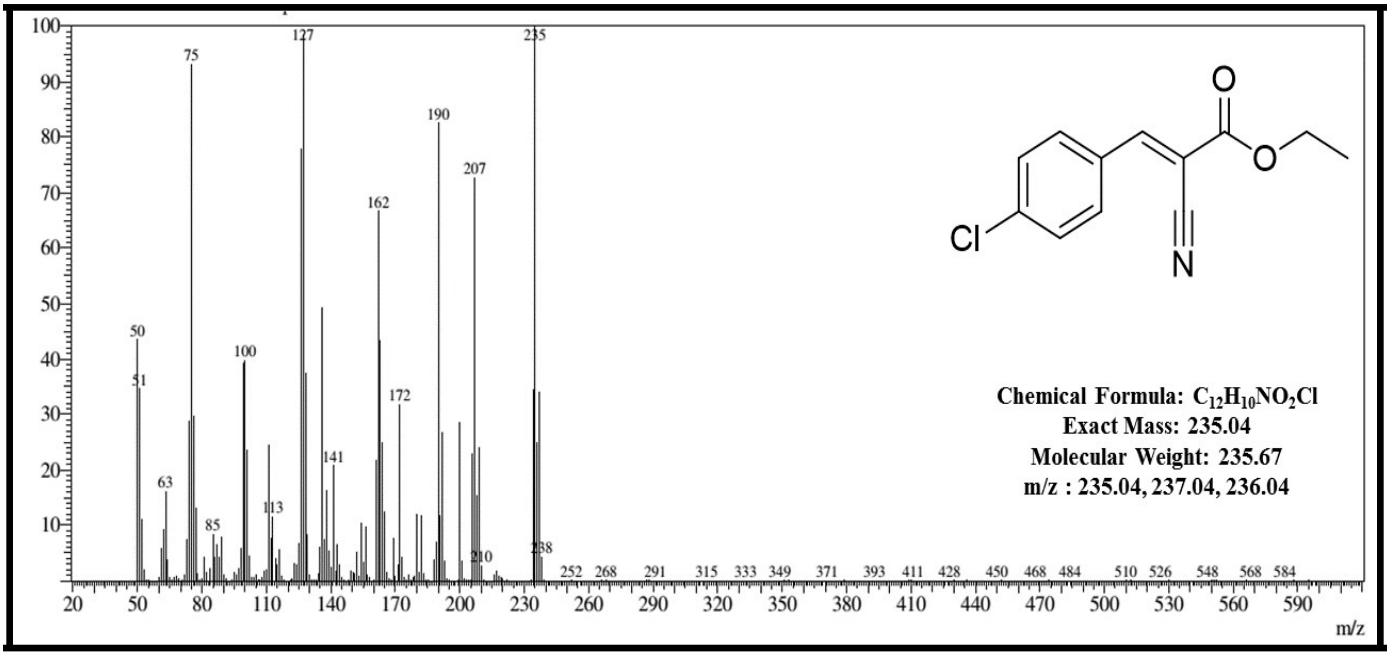
3. 4-Chloro benzaldehyde (Ethyl-2-cyanoacetate)

(i)GC data



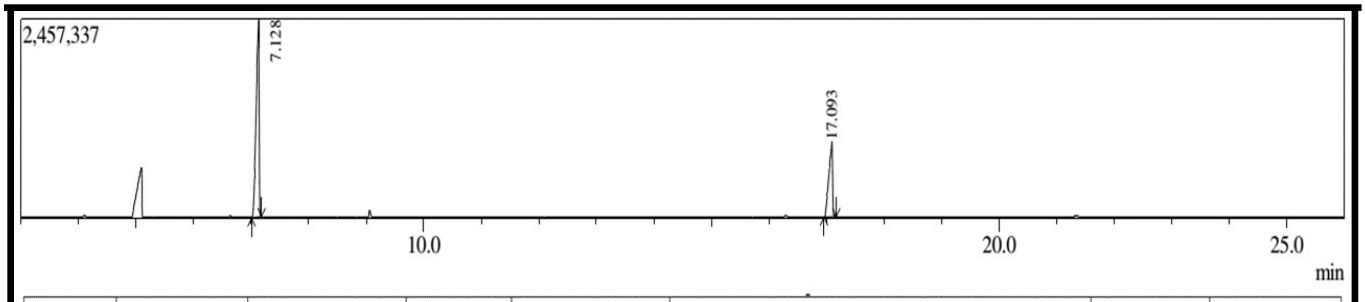
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	7.850	3593394	54.78	1399547	Benzaldehyde, 4-chloro-	139.05	246630
2	17.585	2966808	45.22	675844	2-Propenoic acid, 2-cyano-3-(4-chlorophenyl)-	235.00	39248
		6560202	100.00	2075391			

(ii) MS data



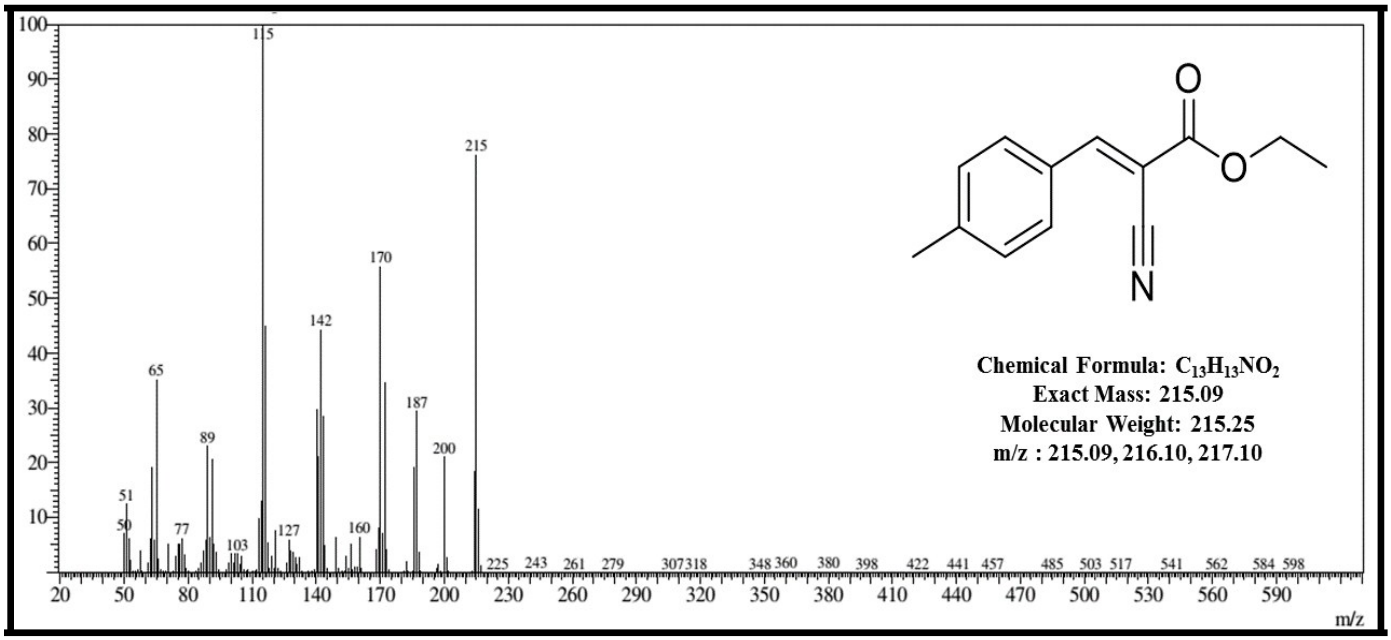
4. <u>4-Methyl benzaldehyde</u> (Ethyl-2-cyanoacetate)

(i)GC data



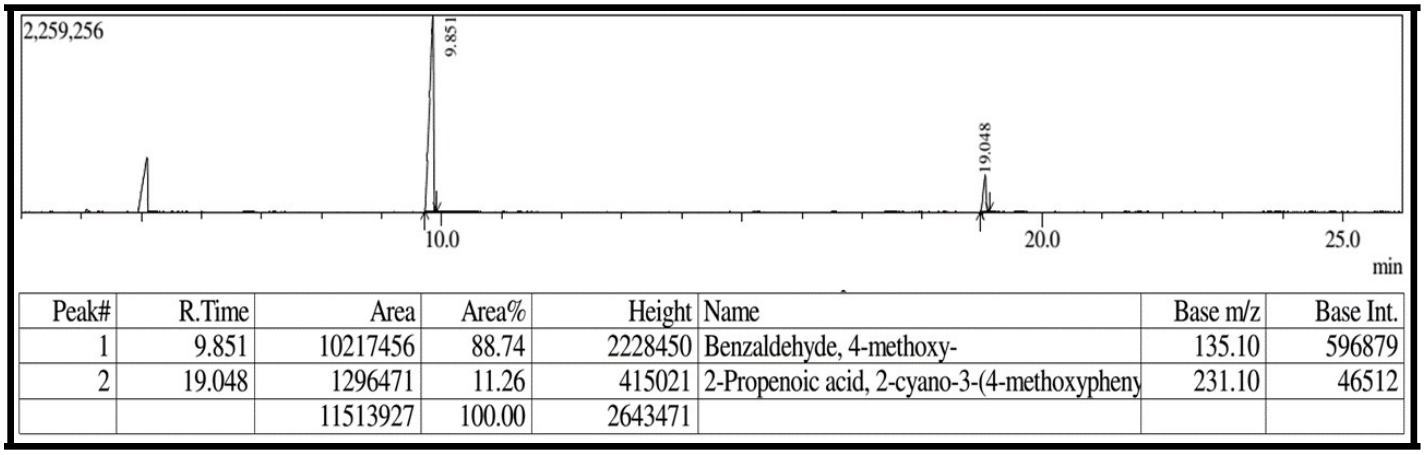
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	7.128	8800535	68.47	2435344	Benzaldehyde, 4-methyl-	91.10	558376
2	17.093	4052159	31.53	929258	2-Propenoic acid, 2-cyano-3-(3-methylphenyl)	115.10	99792
		12852694	100.00	3364602			

(ii) MS data



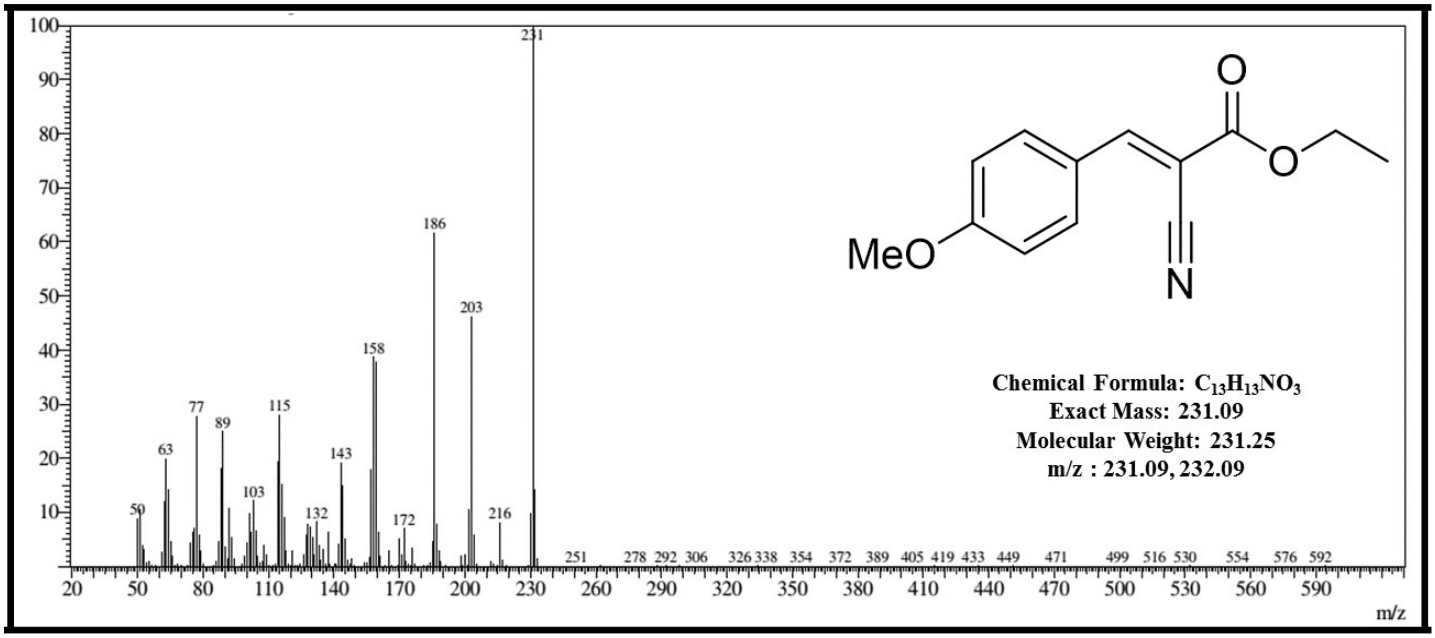
5. 4-Methoxy benzaldehyde (Ethyl-2-cyanoacetate)

(i)GC data



Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	9.851	10217456	88.74	2228450	Benzaldehyde, 4-methoxy-	135.10	596879
2	19.048	1296471	11.26	415021	2-Propenoic acid, 2-cyano-3-(4-methoxypheny	231.10	46512
		11513927	100.00	2643471			

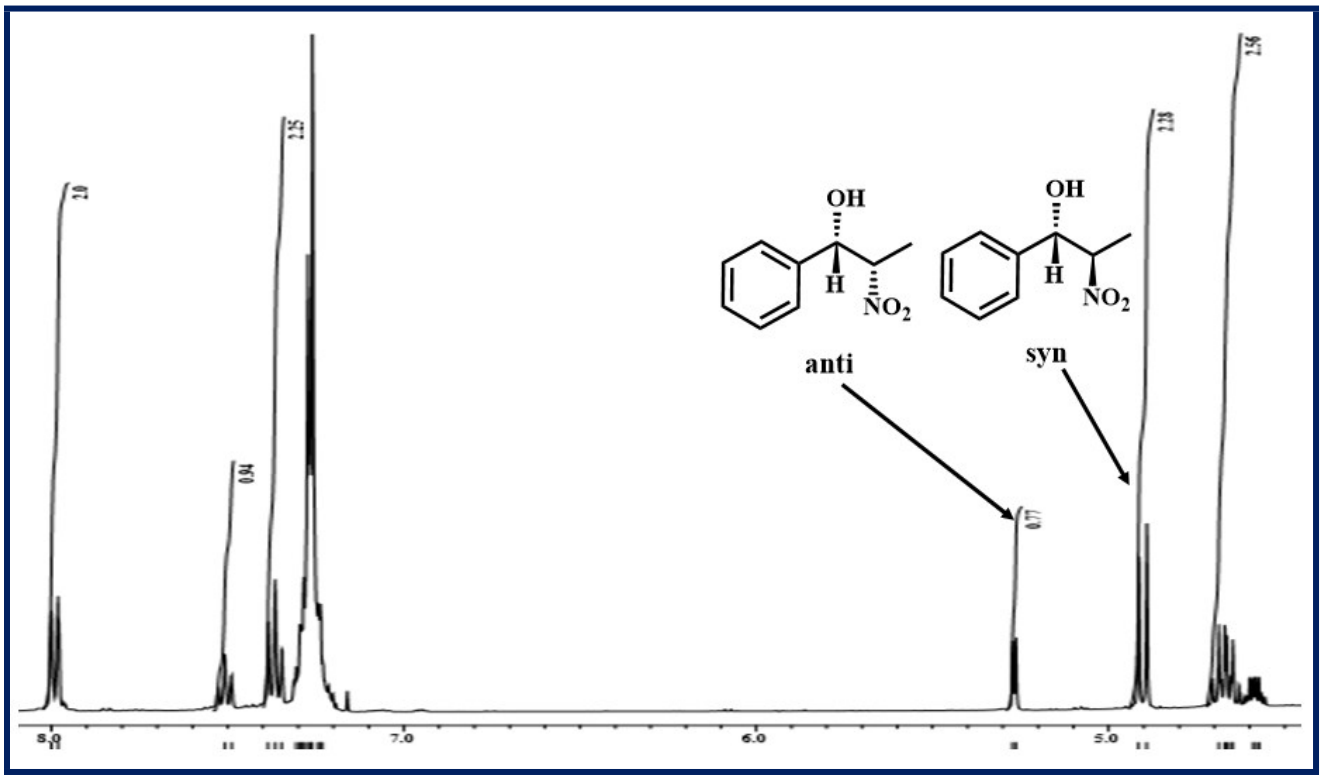
(ii) MS data



^{1}H NMR DATA

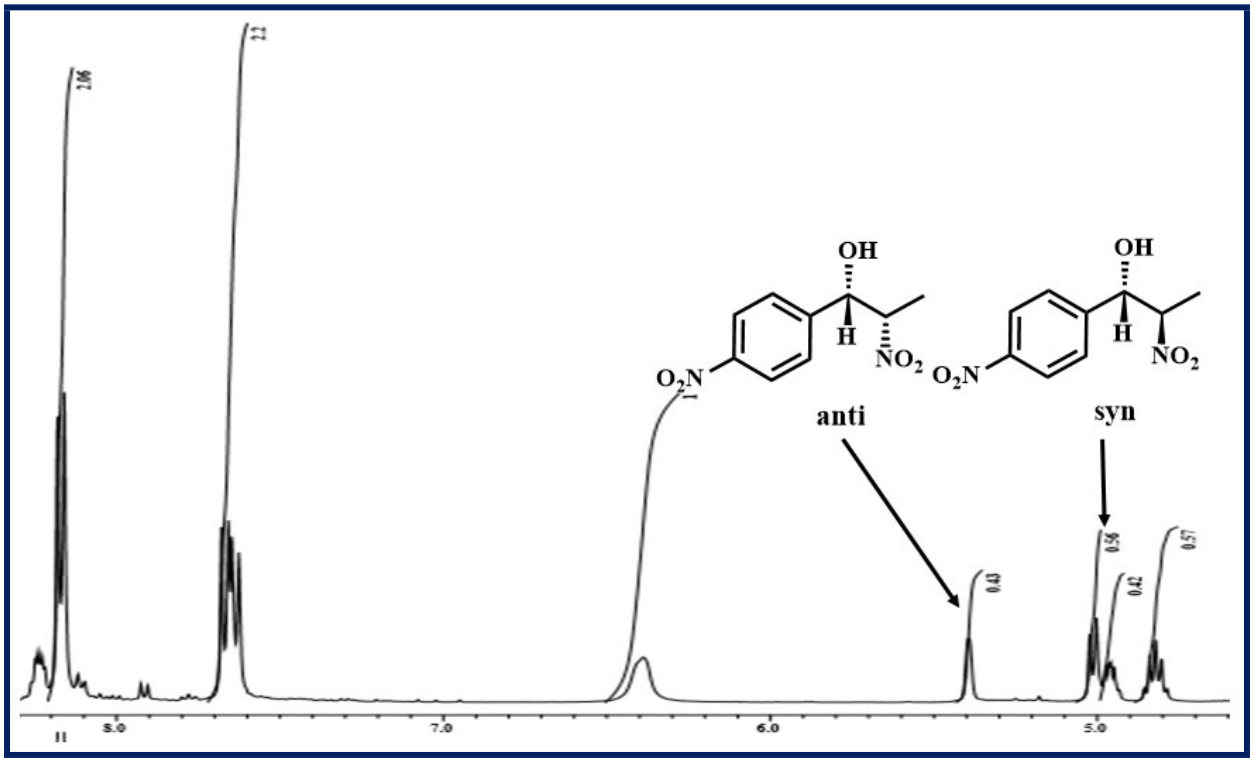
Henry (Nitro-Aldol) condensation

1. Benzaldehyde



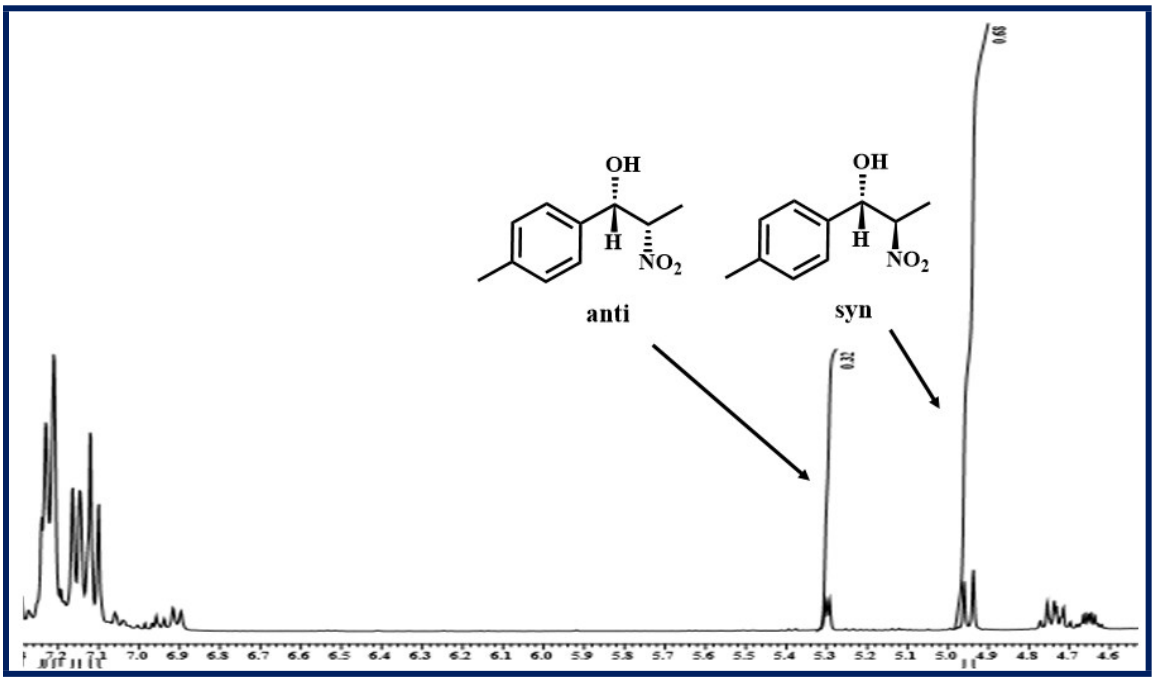
^{1}H NMR for the reaction of benzaldehyde with nitroethane showing the peaks for two different diastereoisomers.

2. 4-Nitro Benzaldehyde



^{1}H NMR for the reaction of 4-nitro benzaldehyde with nitroethane showing the peaks for two different diastereoisomers.

3. 4-Methyl Benzaldehyde



^{1}H NMR for the reaction of 4-methyl benzaldehyde with nitroethane showing the peaks for two different diastereoisomers.

References

(1) *SMART (V 5.628), SAINT (V 6.45a), XPREP, SHELXTL*; Bruker AXS Inc., Madison, Wisconsin, USA, **2004**.

(2) G. M. Sheldrick, *Siemens Area Detector Absorption Correction Program*, University of Göttingen, Göttingen, Germany, **2004**.

(3) A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Cryst*., **1993**, *26*, 343-350.

(4) G. M. Sheldrick, SHELXL-2014, *Program for Crystal Structure Solution and Refinement*; University of Göttingen, Göttingen,Germany, **2014**.

(5) L. J. Farrugia, WinGX-A Windows Programfor CrystalStructure Analysis, *J. Appl. Cryst*., **2012**, *45*, 849-854.

(6) A. L. Spek, *J. Appl. Crystallogr*., **2003**, *36*, 7-13.

(7) H. Pan, J. A. Ritter, P. B. Balbuena, *Langmuir* **1998**, *14*, 6323-6327.

(8) N. Sikdar, A. Hazra, T. K. Maji, *Inorg. Chem.* **2014,** *53*, 5993-6002.

(9) R. T. Yang, *Gas Separation by Adsorption Processes*, Butterworth, Boston, **1997**.

(10) S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita and S. Kitagawa, *J. Am. Chem. Soc*., **2007**, *129*, 2607-2614.

(11) M. K. Sharma, P. P. Singh and P. K. Bharadwaj, *J. Mol. Catal. A: Chem*., **2011**, *342-343*, 6-10.

(12) X.-M. Lin, T.-T. Li, L.-F. Chen, L. Zhang and C.-Y. Su, *Dalton Trans*, **2012**, *41*, 10422-10429.

(13) U. P. Tran, K. K. Le and N. T. Phan, *ACS Catal*., **2011**, *1*, 120-127.

(14) L. T. L. Nguyen, K. K. A. Le, H. X. Truong and N. T. S. Phan, *Catal. Sci. Technol*., **2012**, *2*, 521-528.

(15) R. K. Das, A. Aijaz, M. K. Sharma, P. Lama and P. K. Bharadwaj, *Chem. Eur. J*., **2012**, *18*, 6866-6872.

(16) M. Y. Masoomi, S. Beheshti and A. Morsali, J. Mater. Chem. A., **2014**, 2, 16863-16866.

(17) B. Ugale and C. M. Nagaraja, *RSC Adv*., **2016**, *6*, 28854-28864.