Electronic Supplementary Information

Construction of 2D interwoven and 3D metal-organic frameworks (MOFs) of Cd(II): effect of ancillary ligands on the structure and the catalytic performance for Knoevenagel reaction

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catalytic cycle (d) sample obtained after second catalytic cycle (e) for sample obtained after third catalytic cycle.

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13. GC-MS data

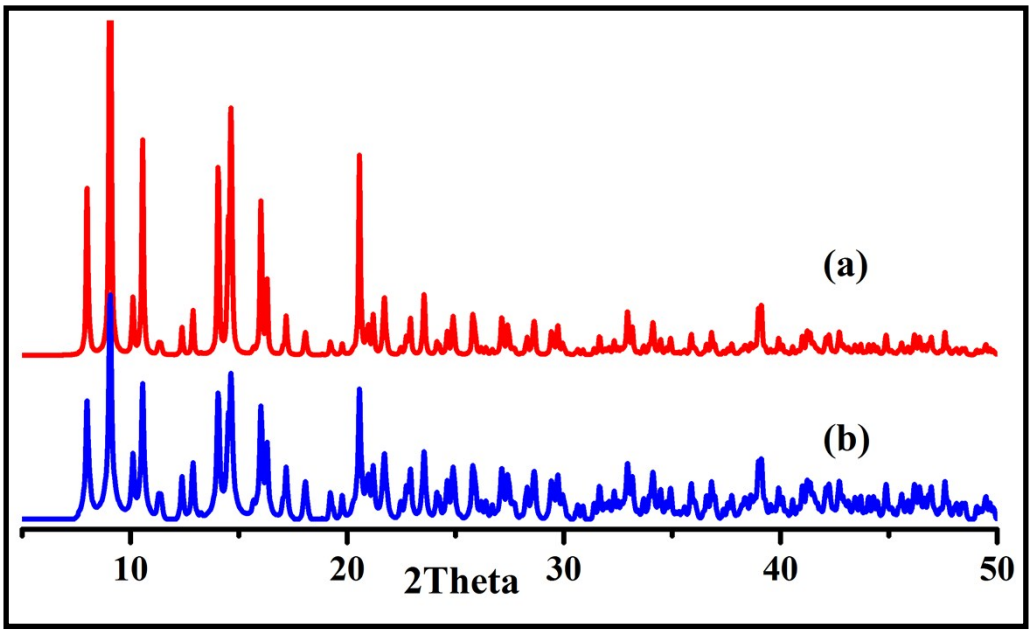


Fig. S1 PXRD patterns of compound **1**. (a) Simulated from X-ray single crystal data; (b) bulk as-synthesized compound.

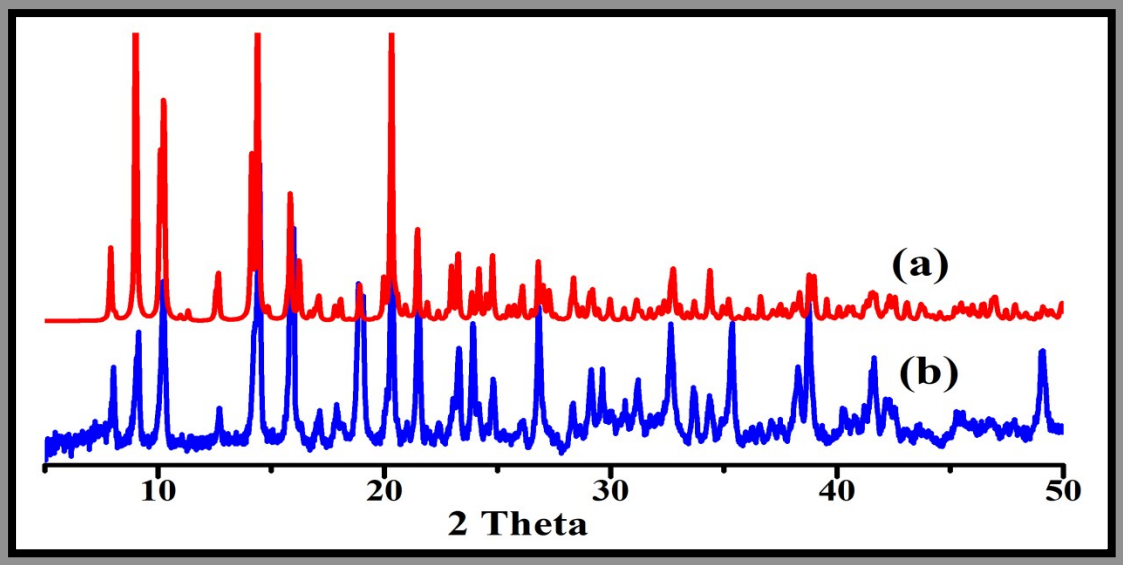


Fig S2 PXRD patterns of compound **2**. (a) Simulated from X-ray single crystal data; (b) bulk as-synthesized compound.

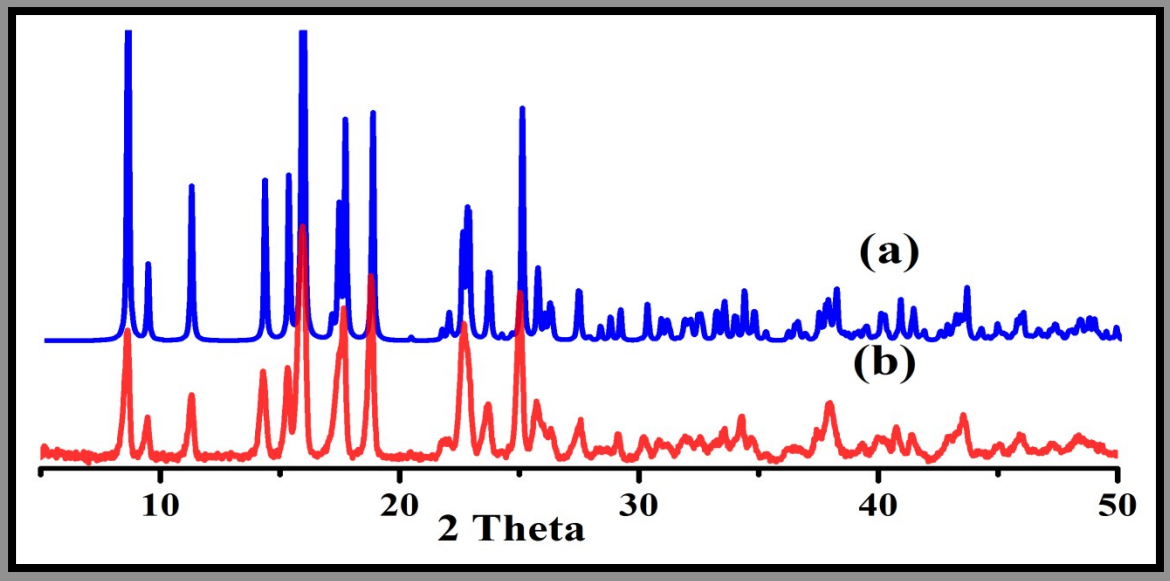


Fig. S3 PXRD patterns of compound **3**. (a) Simulated from X-ray single crystal data; (b) bulk as-synthesized compound.

Table S1. Selected bond lengths (Å) and angles (°) for compound **1**.

Cd1-O1	2.308(2)	O2-Cd1-O4	140.81(7)
Cd1-O2	2.483(2)	O2-Cd1-N1	83.03(8)
Cd1-O3	2.562(2)	O2-Cd1-N2	97.97(8)
Cd1-O4	2.335(2)	O2-Cd1-N3	86.12(8)
Cd1-N1	2.376(2)	O3-Cd1-O4	53.59(7)
Cd1-N2	2.337(2)	O3-Cd1-N1	81.99(8)
Cd1-N3	2.345(2)	O3-Cd1-N2	89.06(7)
O1-Cd1-O2	54.66(7)	O3-Cd1-N3	85.63(7)
O1-Cd1-O3	140.53(7)	O4-Cd1-N1	135.57(8)
O1-Cd1-O4	86.99(7)	O4-Cd1-N2	93.45(8)
O1-Cd1-N1	137.43(8)	O4-Cd1-N3	86.53(8)
O1-Cd1-N2	96.05(8)	N1-Cd1-N2	84.26(8)
O1-Cd1-N3	90.53(8)	N1-Cd1-N3	91.14(8)
O2-Cd1-O3	162.72(7)	N2-Cd1-N3	173.41(8)

Table S2 Selected bond lengths (Å) and angles (°) for compound **2**.

Cd1-O1	2.337(3)	O2-Cd1-N3	82.81(12)
Cd1-O2	2.519(4)	O2-Cd1-O3^{i}	160.91(11)
Cd1-N1	2.355(4)	O2-Cd1-O4^{i}	138.57(10)
Cd1-N3	2.317(4)	O2-Cd1-N2^{ii}	105.15(12)
Cd1-O3^{i}	2.540(3)	N1-Cd1-N3	94.28(13)
Cd1-O4^{i}	2.398(3)	O3^{i}-Cd1-N1	84.35(12)
Cd1-N2^{ii}	2.328(4)	O4^{i}-Cd1-N1	136.99(13)
O1-Cd1-O2	53.79(11)	N1-Cd1-N2^{ii}	88.34(13)
O1-Cd1-N1	135.13(13)	O3^{i}-Cd1-N3	83.32(12)
O1-Cd1-N3	93.79(12)	O4^{i}-Cd1-N3	85.85(12)
O1-Cd1-O3^{i}	140.46(11)	N2^{ii} -Cd1-N3	171.87(14)
O1-Cd1-O4^{i}	87.59(11)	O3^{i}-Cd1-O4^{i}	52.88(11)
O1-Cd1-N2^{ii}	89.75(12)	O3^{i}-Cd1-N2^{ii}	89.29(12)
O2-Cd1-N1	83.67(12)	O4^{i}-Cd1-N2^{ii}	89.99(12)

Symmetry codes: (i) 1/2-x,1/2-y,-1/2+z; (ii) x,-y,1/2+z;

Table S3. Selected bond lengths (Å) and angles (°) for compound **3**.

Cd1-O1	2.436(6)	O1w-Cd1-N1	84.86(9)
Cd1-O1w	2.331(6)	$O1^{i}$-Cd1-O1w	84.75(9)
Cd1-O2	2.402(5)	O1w-Cd1-$O2^{i}$	135.27(13)
Cd1-N1	2.365(6)	O1w-Cd1-$N1^{i}$	84.86(14)
Cd1-$O1^{i}$	2.436(6)	O2-Cd1-N1	101.70(19)
Cd1-$O2^{i}$	2.402(5)	$O1^{i}$-Cd1-O2	136.48(15)
Cd1-$N1^{i}$	2.365(6)	O2-Cd1-$O2^{i}$	89.45(18)
O1-Cd1-O1w	84.75(9)	O2-Cd1-$N1^{i}$	85.7(2)
O1-Cd1-O2	53.49(15)	$O1^{i}$-Cd1-N1	97.60(2)
O1-Cd1-N1	81.4(2)	$O2^{i}$-Cd1-N1	85.7(2)
O1-Cd1-$O1^{i}$	169.49(13)	N1-Cd1-$N1^{i}$	169.70(2)
O1-Cd1-$O2^{i}$	136.48(15)	$O1^{i}$-Cd1-$O2^{i}$	53.49(15)
O1-Cd1-$N1^{i}$	97.60(2)	$O1^{i}$-Cd1-$N1^{i}$	81.4(2)
O1w-Cd1-O2	135.27(13)	$O2^{i}$-Cd1-$N1^{i}$	101.70(19)

Symmetry codes: (i) -x,y,1/2-z;

Table S4. Selected hydrogen bonding geometry (Å,°)for compound **1**

D–H···A	D···H	H···A	D···A	D–H···A
C10--H10 .. O4	0.9300	2.4600	3.381(4)	173.00[i]
C13--H13 .. O2	0.9300	2.4000	3.087(4)	131.00
O2w—H4A .. O1	0.9300	2.4000	3.085(4)	131.00

Symmetry codes: (i) 1/2-x,-1/2+y,z;

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

D–H···A	D···H	H···A	D···A	D–H···A
C7--H7 .. O3	0.9300	2.4500	3.137(6)	131.00[i]
C11--H11 .. O2	0.9300	2.5500	3.193(6)	127.00

Symmetry codes: (i) 1/2-x,1/2-y,-1/2+z;

Table S6. Selected hydrogen bonding geometry (Å,°) for compound **3**

D–H···A	D···H	H···A	D···A	D–H···A
O1w--H1w1 .. O1	0.9300	2.0600	2.698(5)	125.00[i]
O1w--H1w2 .. O1	0.9300	2.0600	3.698(5)	125.00[ii]
C4--H1 .. O2	0.9300	2.5400	3.202(9)	128.00[iii]
C8--H2 .. O1	0.9300	2.4000	3.243(9)	151.00[i]
C5--H5 .. O2	0.9300	2.5100	3.176(9)	128.00[iv]

Symmetry codes: (i) -x,1-y,-z; (ii) x,1-y,1/2+z; (iii) -x,y,1/2-z; (iv) -1/2+x,1/2-y,-1/2+z;

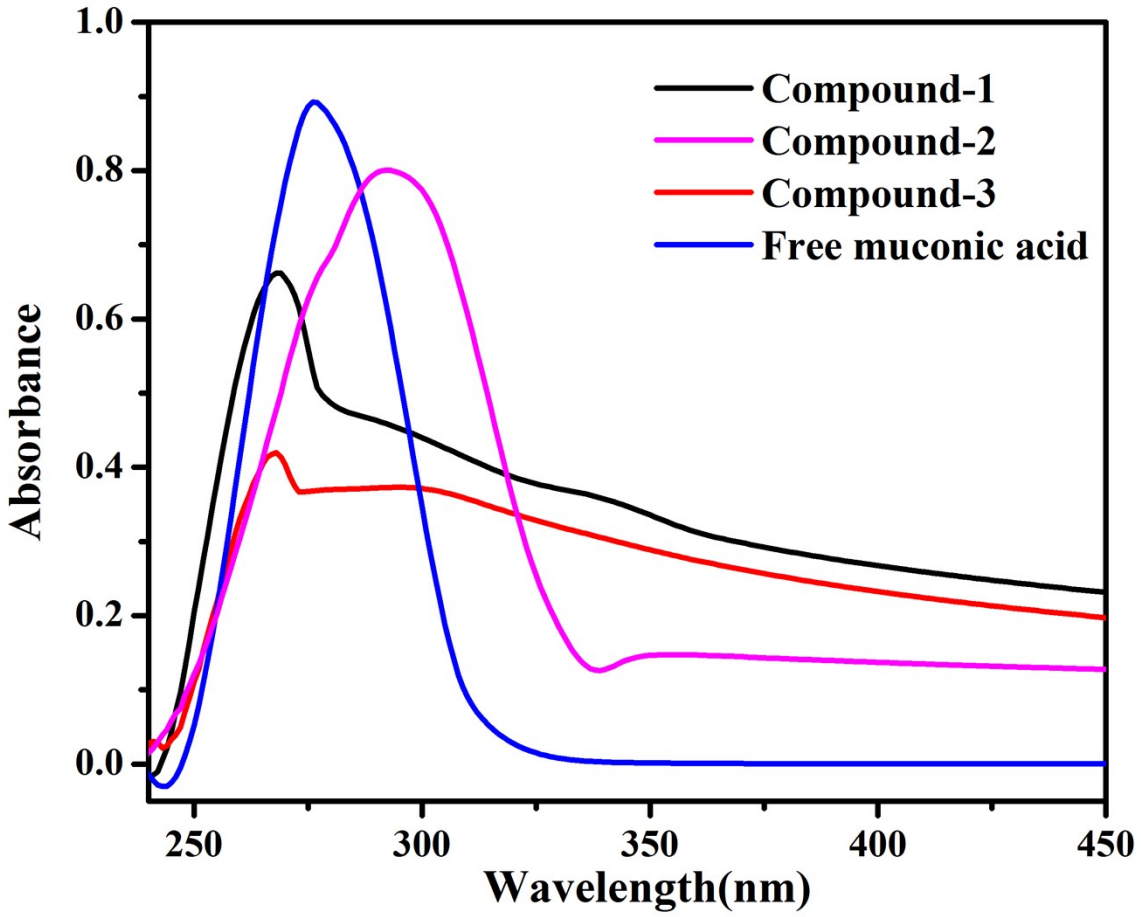


Fig. S4 Room temperature UV-Visible spectra of free muconic acid and compounds **1-3** dispersed in DMF**.**

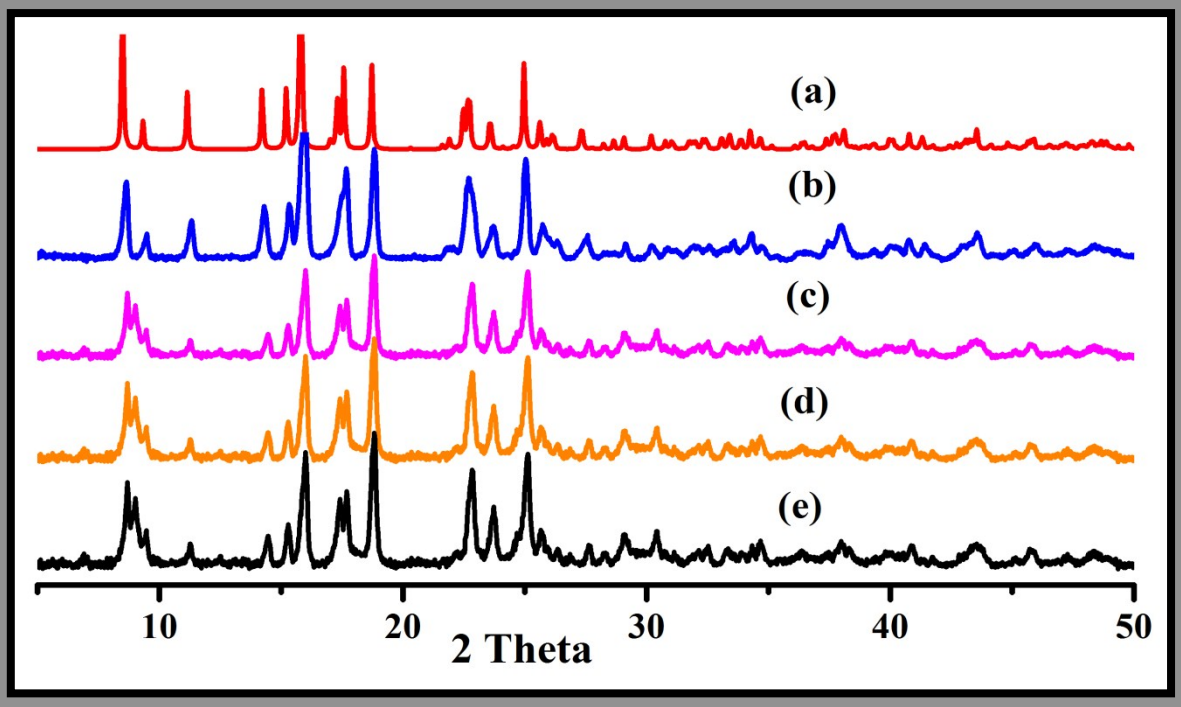
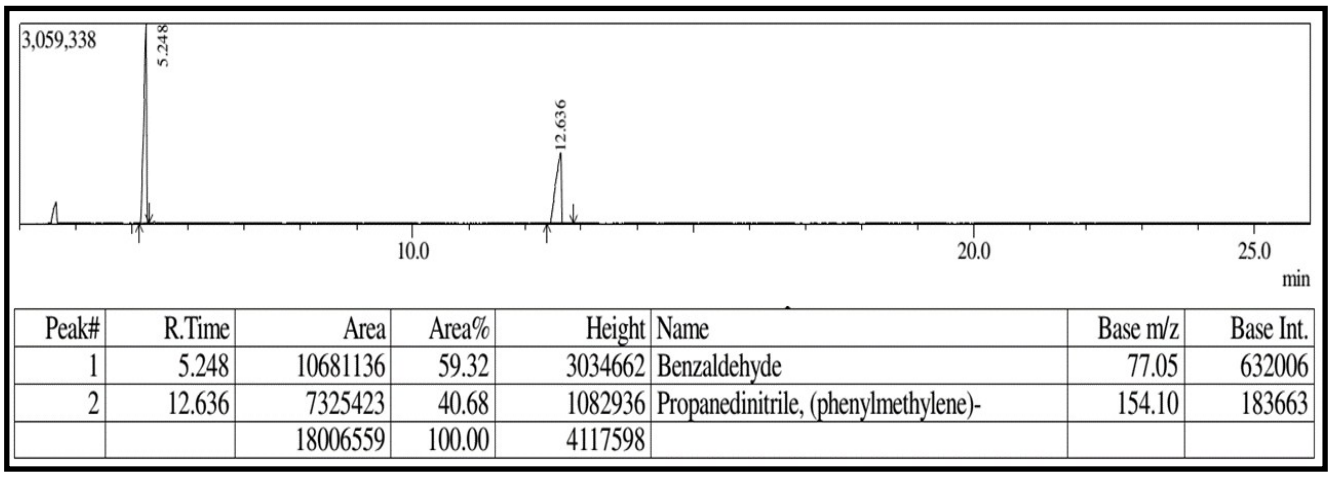


Fig. S5. PXRD patterns of compound **3**(a) simulated PXRD pattern from single crystal x-ray diffraction data. (b) for as-synthesized sample (c) sample obtained after first catalytic cycle (d) sample obtained after second catalytic cycle (e) for sample obtained after third catalytic cycle.

GC-MS DATA

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

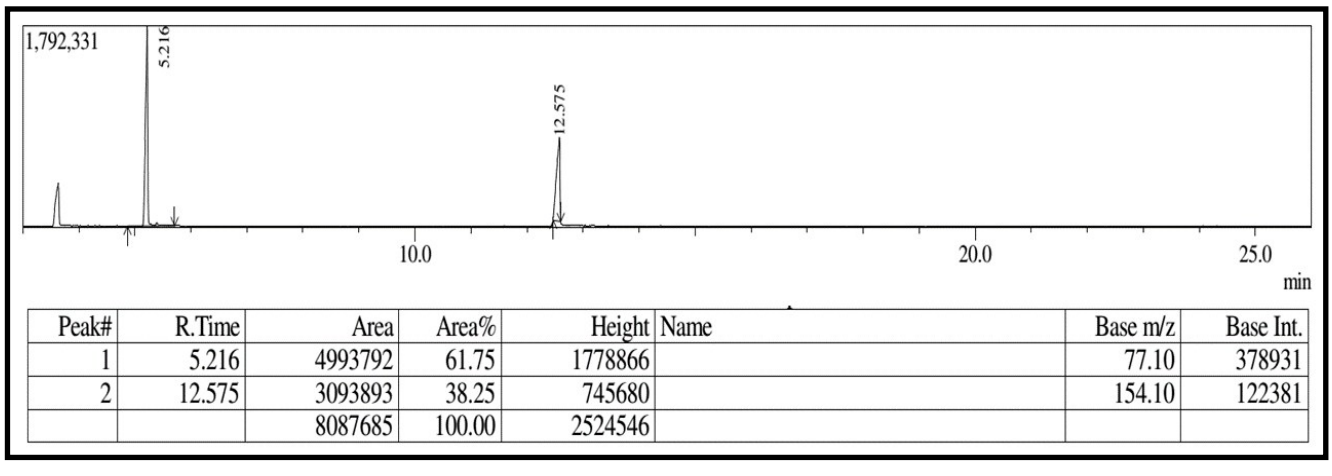
(i)GC data



Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	5.248	10681136	59.32	3034662	Benzaldehyde	77.05	632006
2	12.636	7325423	40.68	1082936	Propanedinitrile, (phenylmethylene)-	154.10	183663
		18006559	100.00	4117598			

2. Compound 2 used as catalyst (benzaldehyde with malononitrile)

(i)GC data

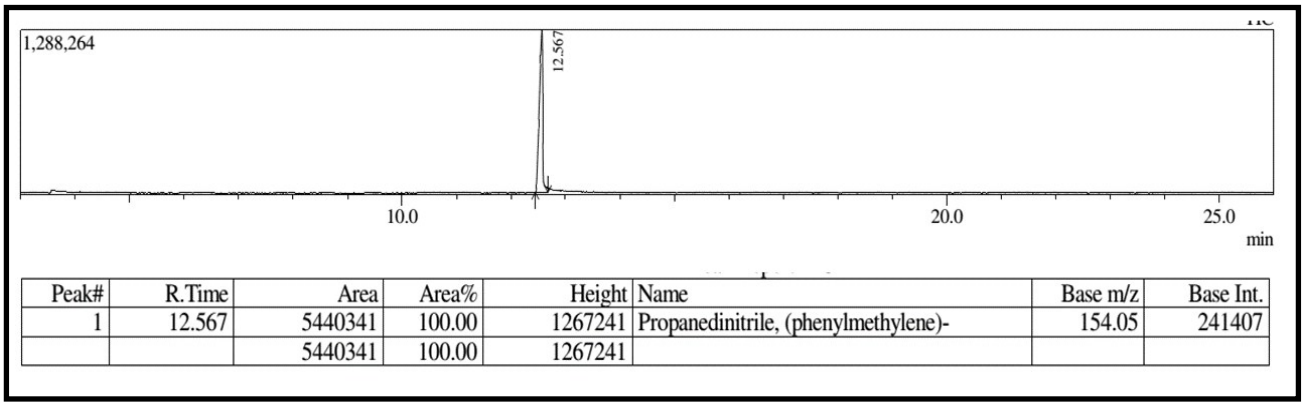


Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	5.216	4993792	61.75	1778866		77.10	378931
2	12.575	3093893	38.25	745680		154.10	122381
		8087685	100.00	2524546			

3. Compound 3 used as catalyst with different substrates shown below

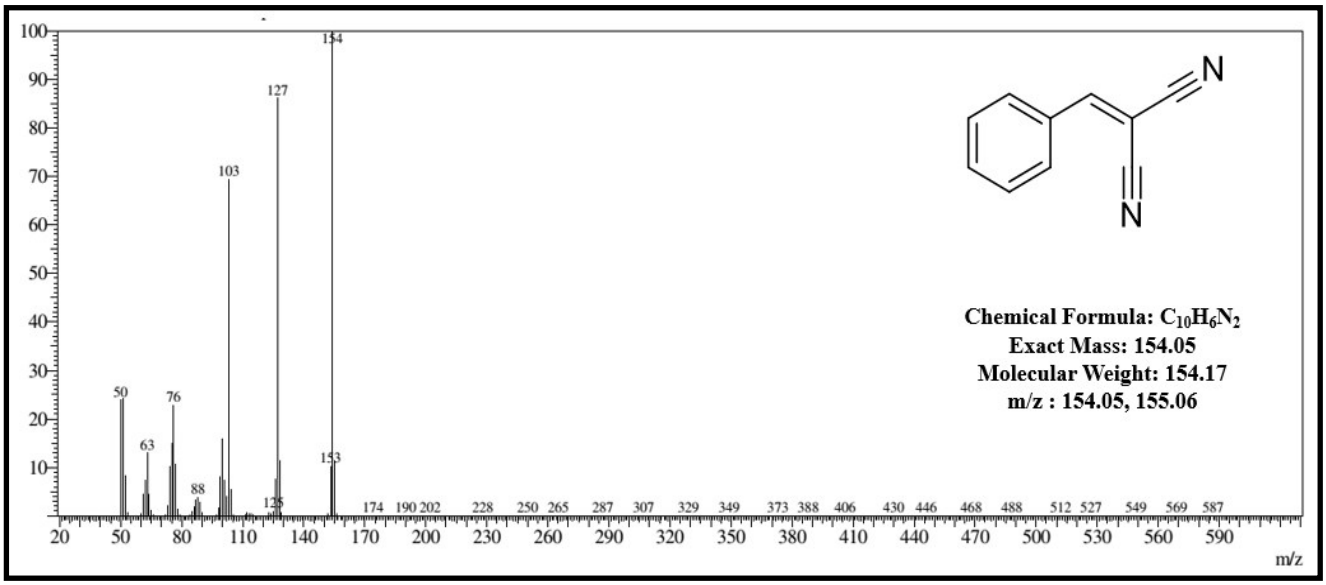
1. Benzaldehyde

(i)GC data



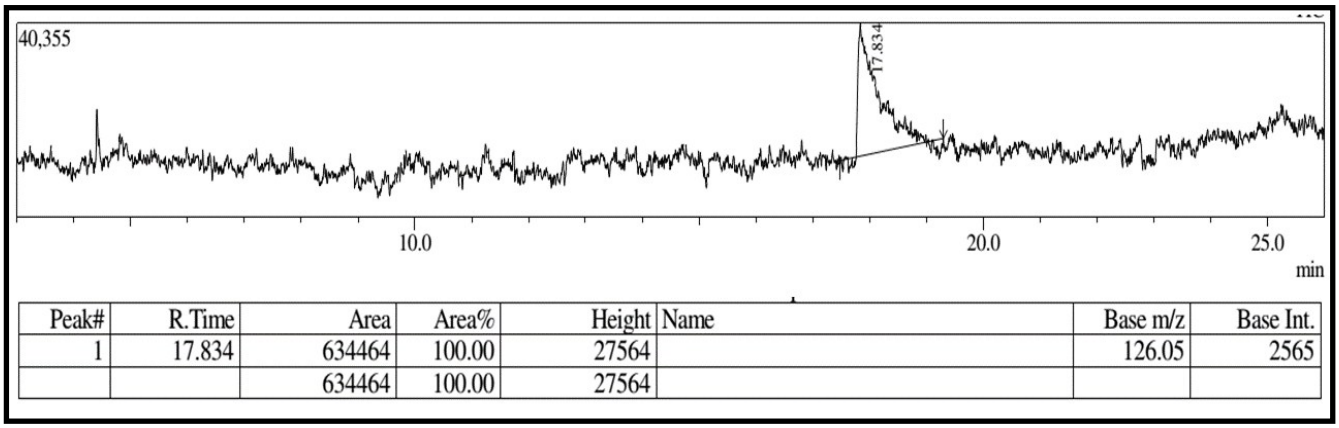
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	12.567	5440341	100.00	1267241	Propanedinitrile, (phenylmethylene)-	154.05	241407
		5440341	100.00	1267241			

(ii)MS data



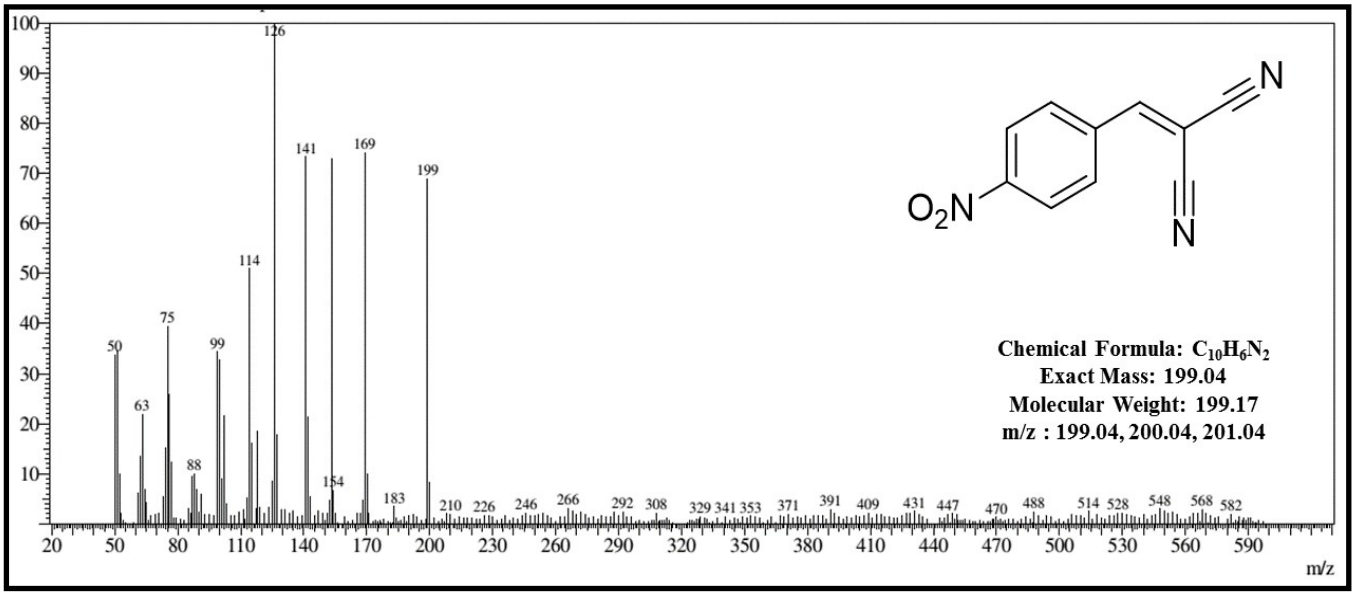
2. 4-Nitro benzaldehyde

(i)GC data



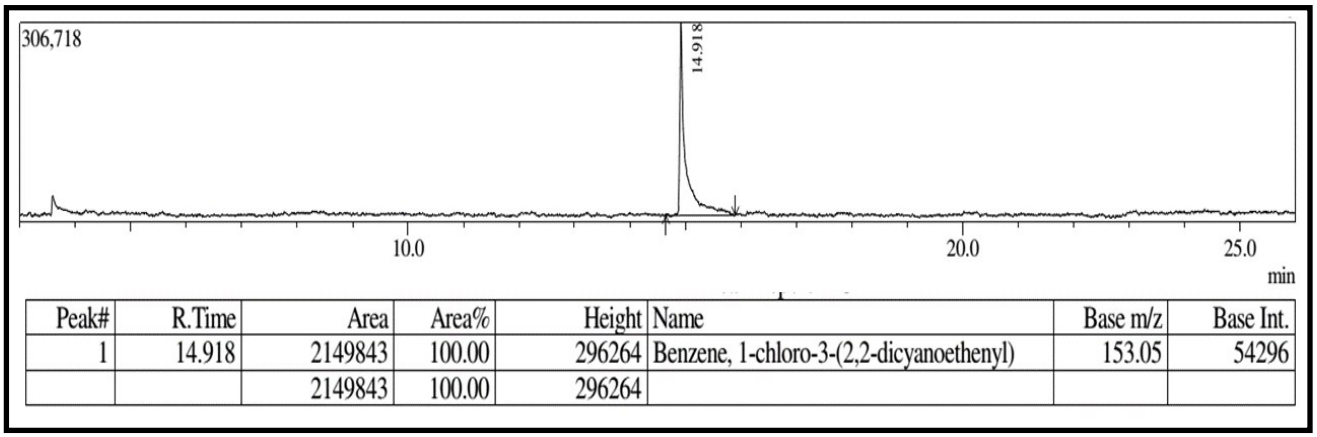
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	17.834	634464	100.00	27564		126.05	2565
		634464	100.00	27564			

(ii) MS data



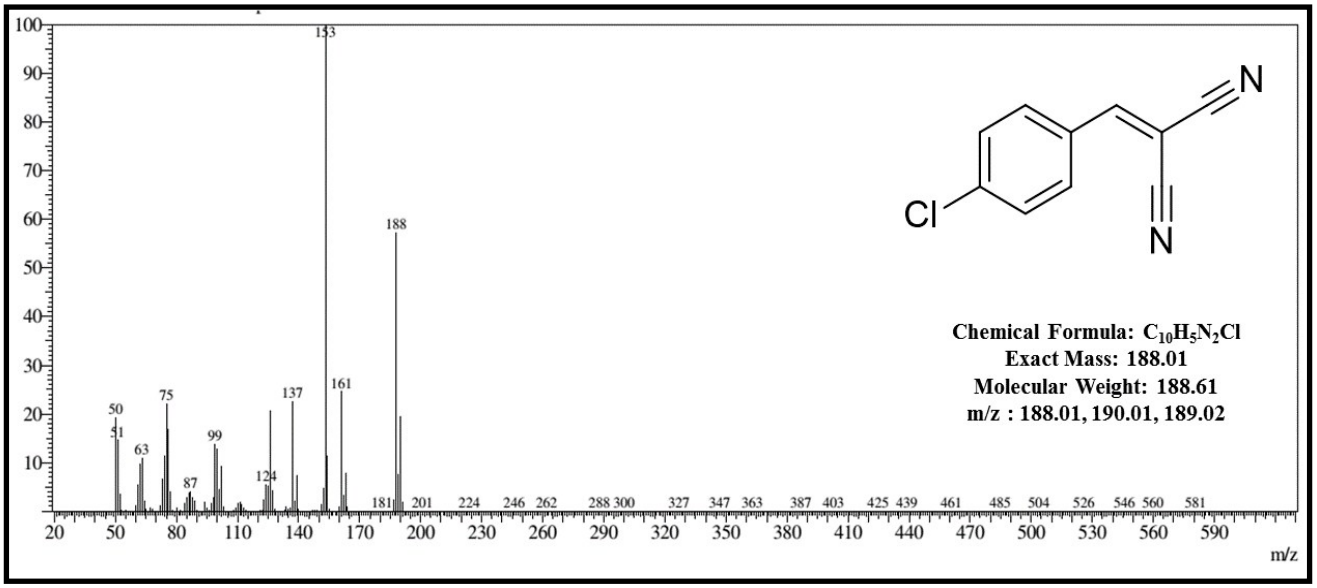
3. 4-Chloro benzaldehyde

(i)GC data



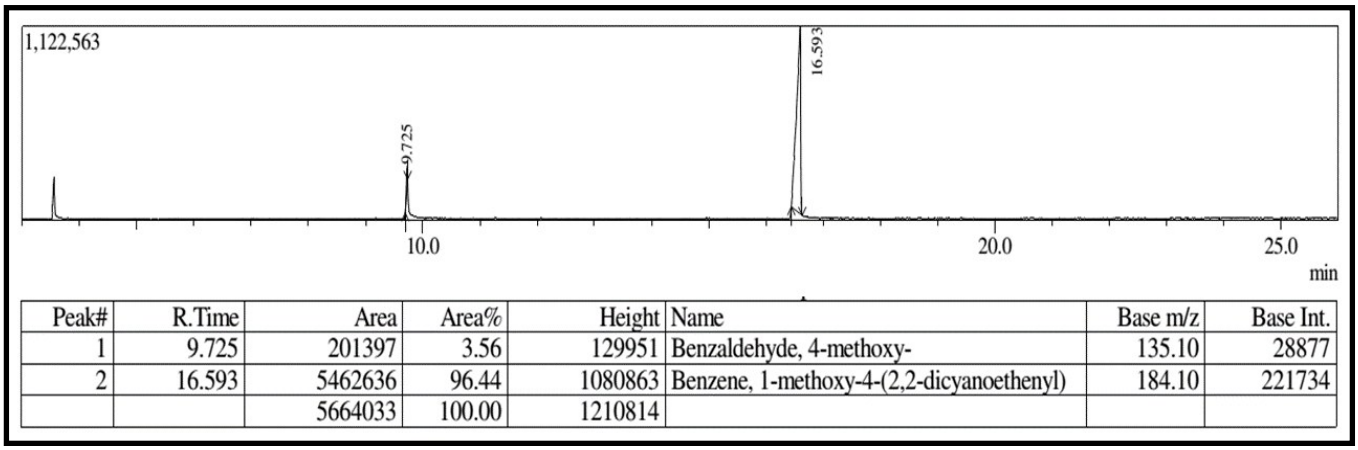
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	14.918	2149843	100.00	296264	Benzene, 1-chloro-3-(2,2-dicyanoethenyl)	153.05	54296
		2149843	100.00	296264			

(ii) MS data



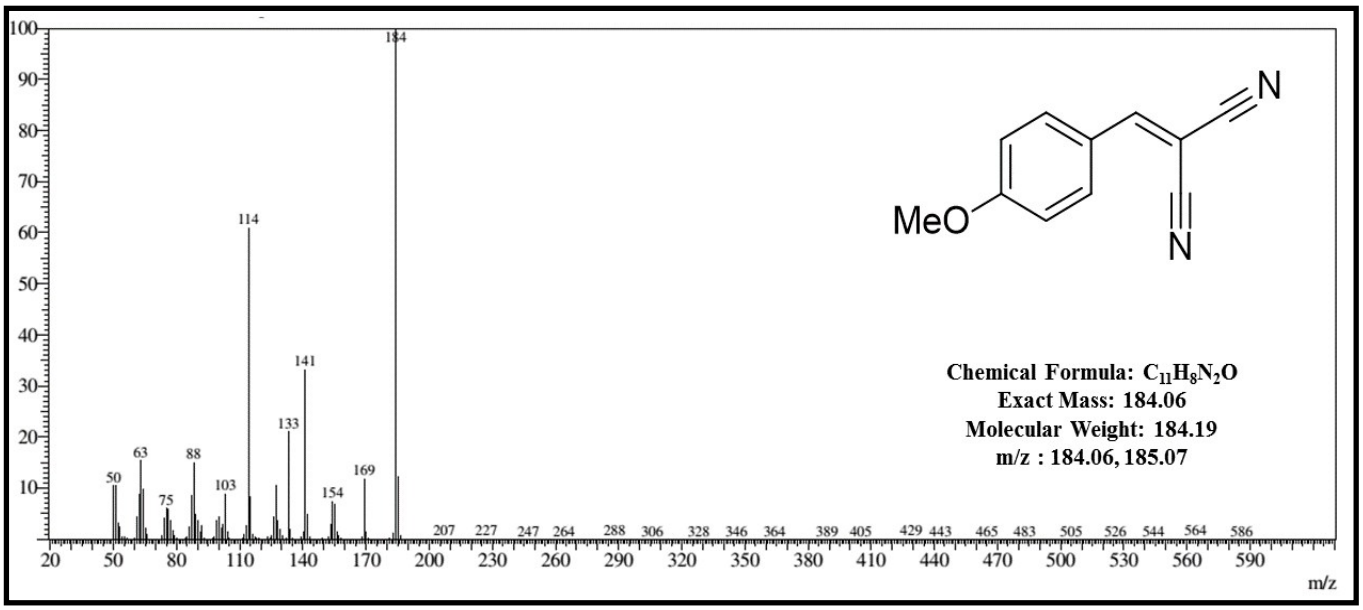
4. 4-Methoxy benzaldehyde

(i)GC data



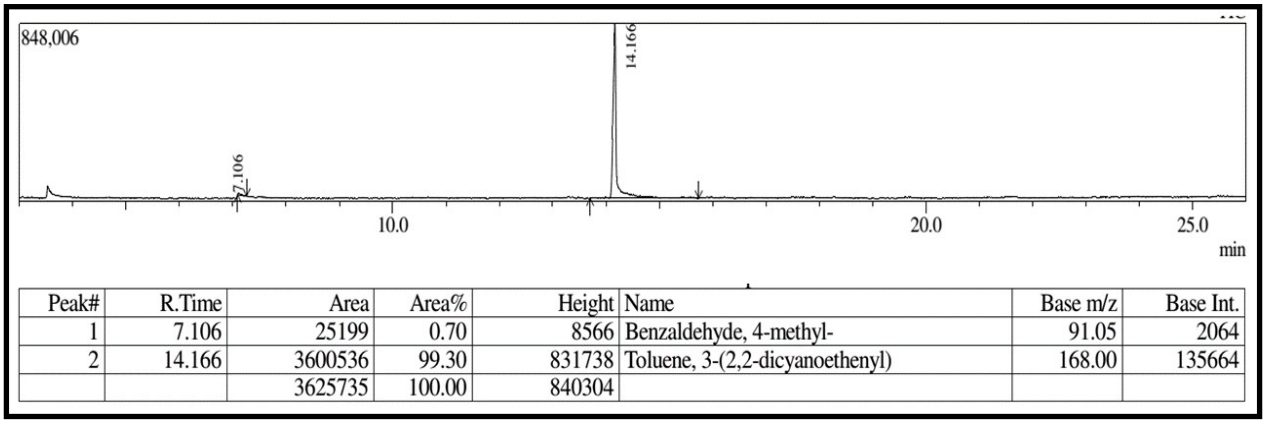
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	9.725	201397	3.56	129951	Benzaldehyde, 4-methoxy-	135.10	28877
2	16.593	5462636	96.44	1080863	Benzene, 1-methoxy-4-(2,2-dicyanoethenyl)	184.10	221734
		5664033	100.00	1210814			

(ii) MS data



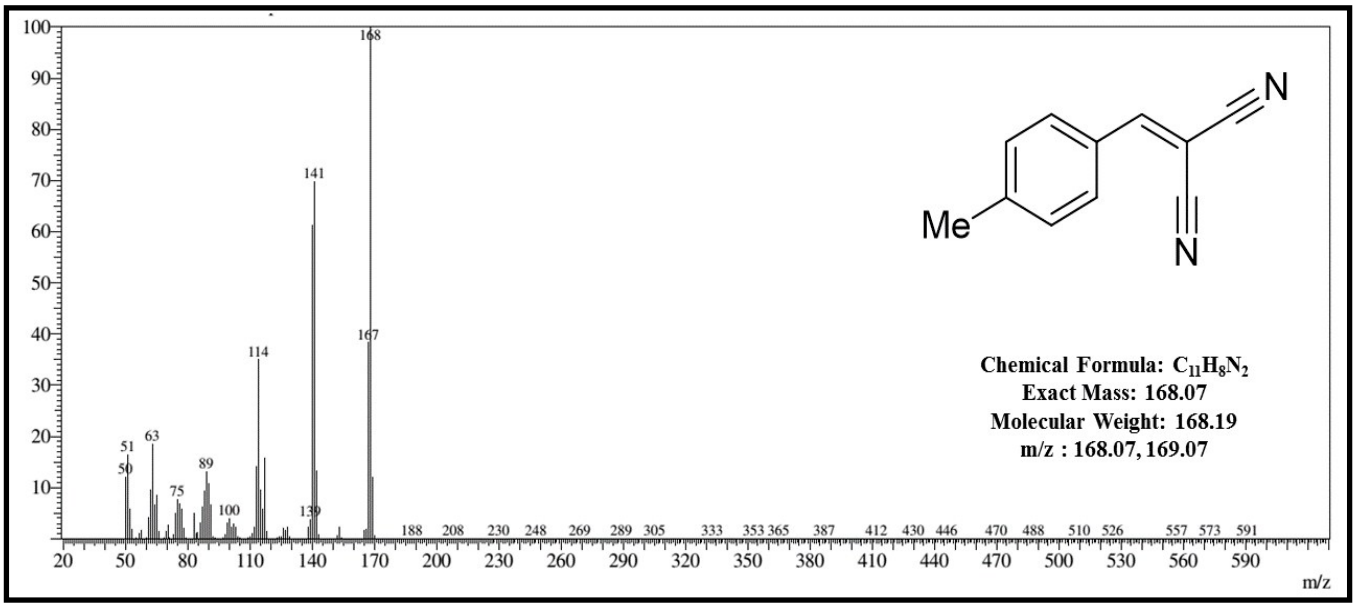
5. 4-Methyl benzaldehyde

(i)GC data



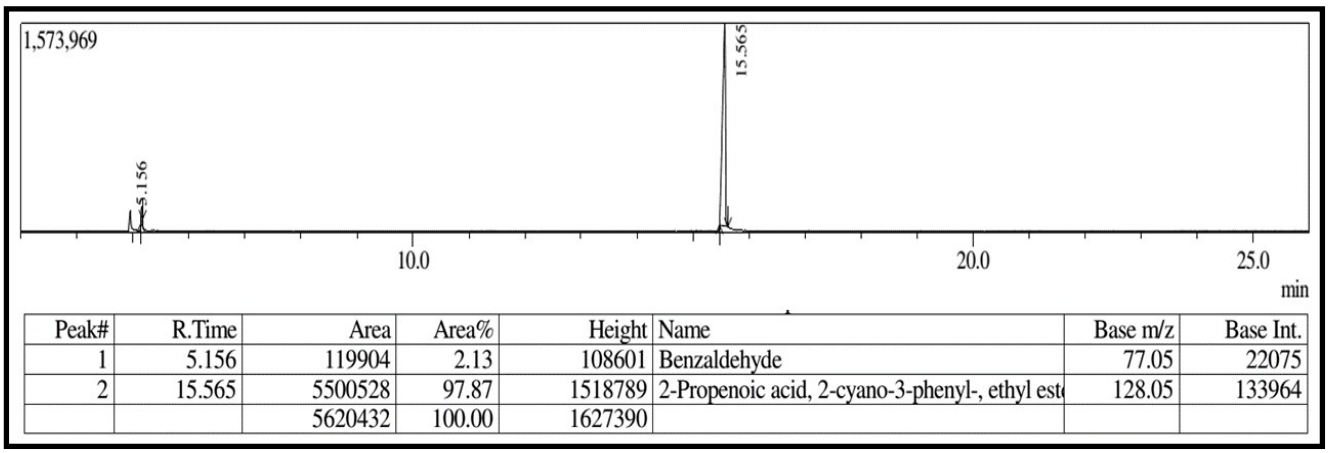
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	7.106	25199	0.70	8566	Benzaldehyde, 4-methyl-	91.05	2064
2	14.166	3600536	99.30	831738	Toluene, 3-(2,2-dicyanoethenyl)	168.00	135664
		3625735	100.00	840304			

(ii) MS data



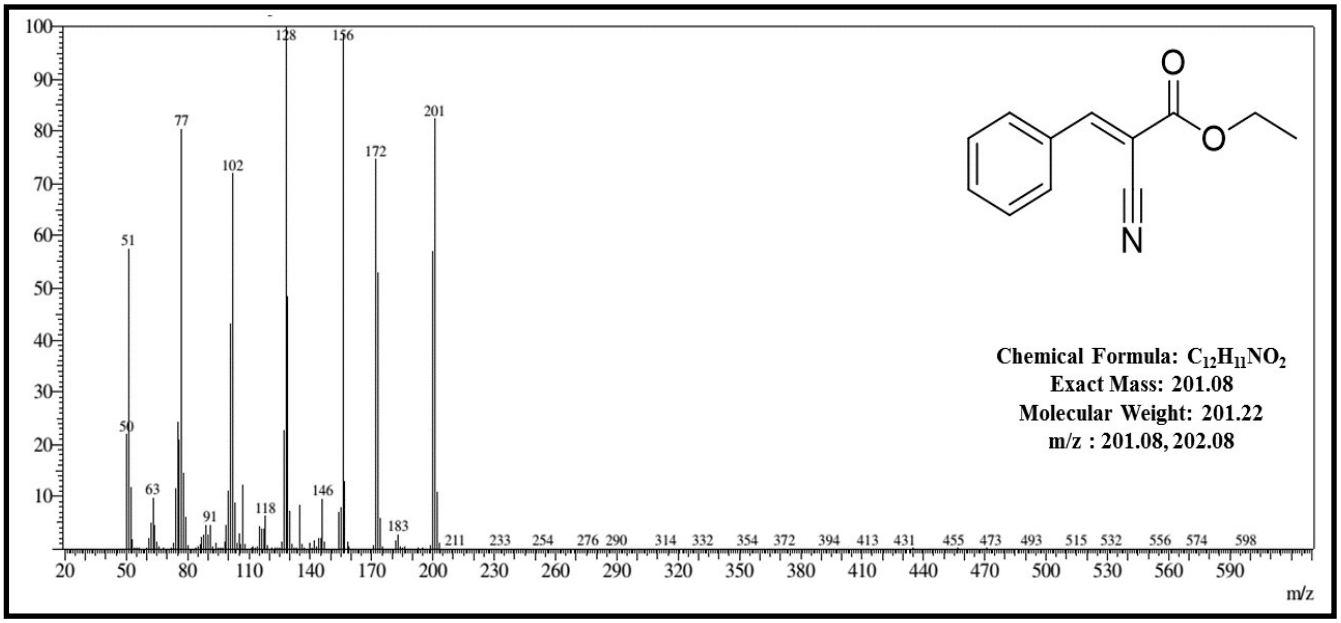
6. Benzaldehyde with Ethyl-2-cyanoacetate

(i)GC data



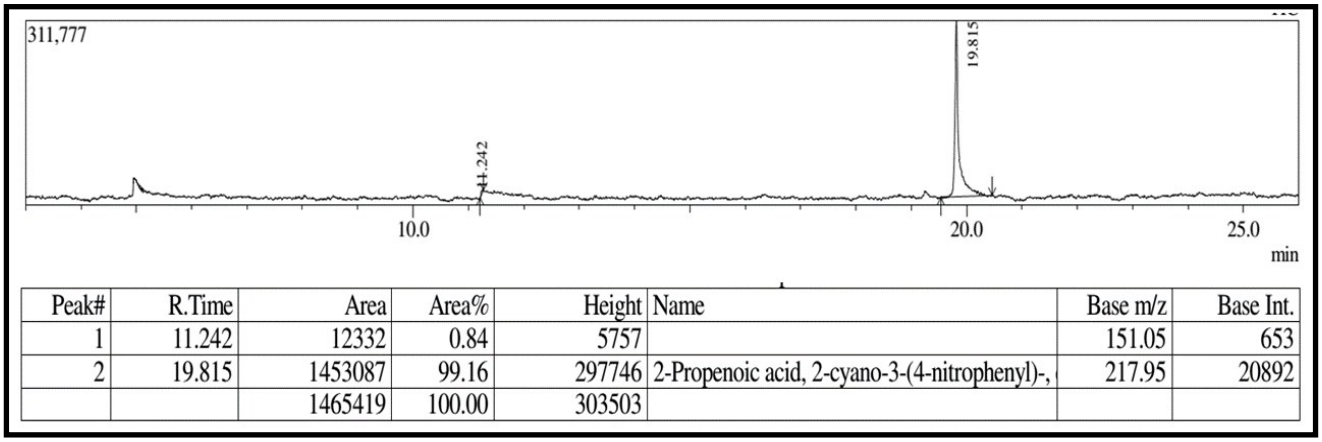
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	5.156	119904	2.13	108601	Benzaldehyde	77.05	22075
2	15.565	5500528	97.87	1518789	2-Propenoic acid, 2-cyano-3-phenyl-, ethyl est	128.05	133964
		5620432	100.00	1627390			

(ii) MS data



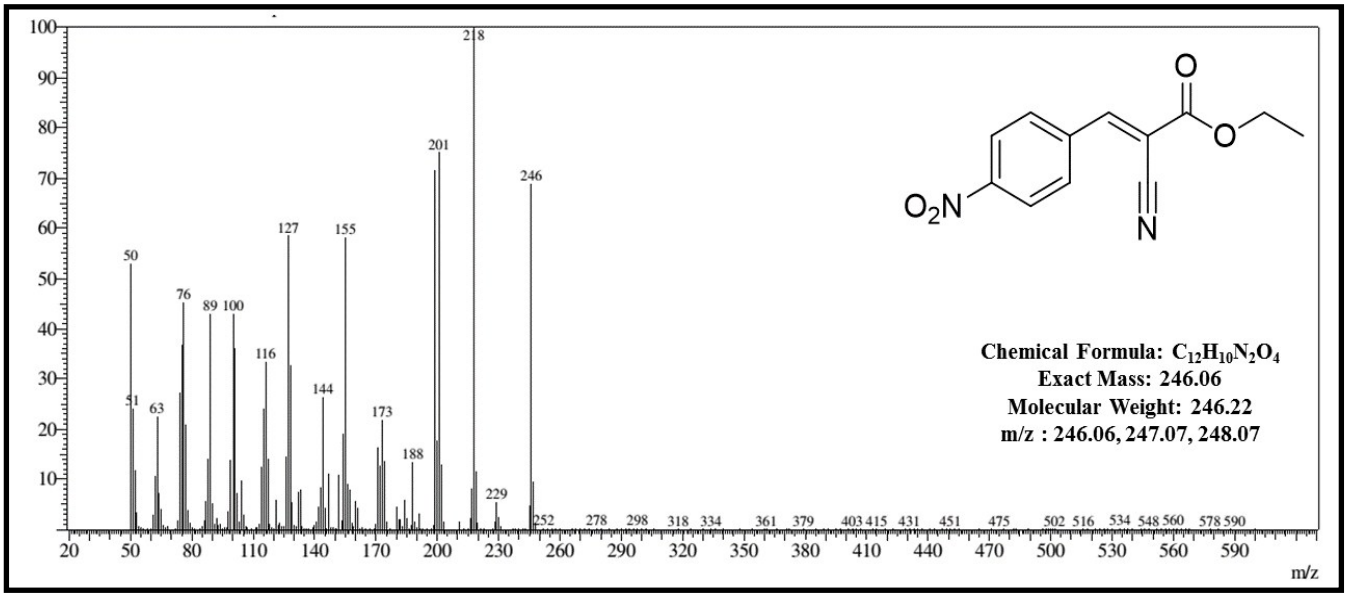
7. 4-Nitro benzaldehyde with Ethyl-2-cyanoacetate

(i)GC data



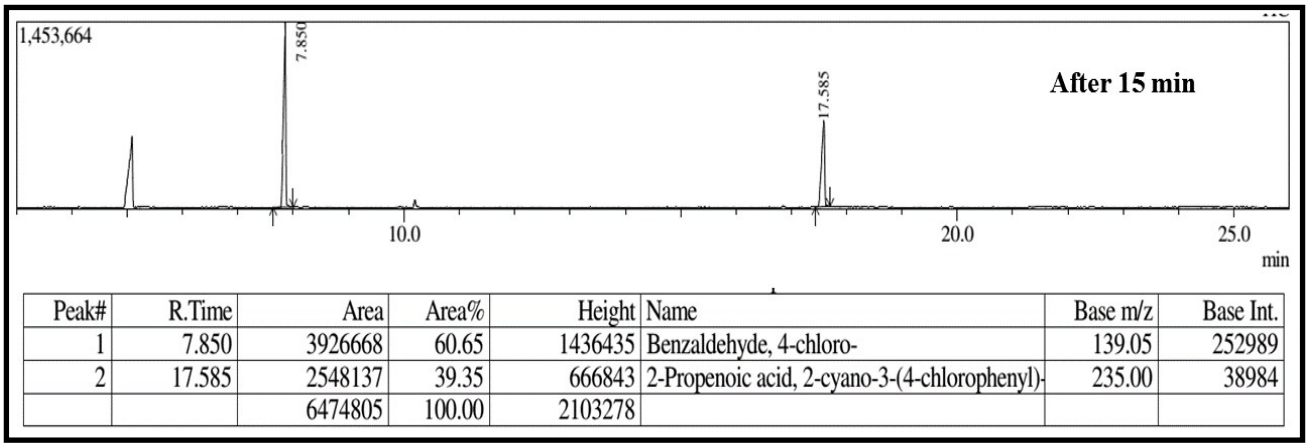
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	11.242	12332	0.84	5757		151.05	653
2	19.815	1453087	99.16	297746	2-Propenoic acid, 2-cyano-3-(4-nitrophenyl)-,	217.95	20892
		1465419	100.00	303503			

(ii) MS data



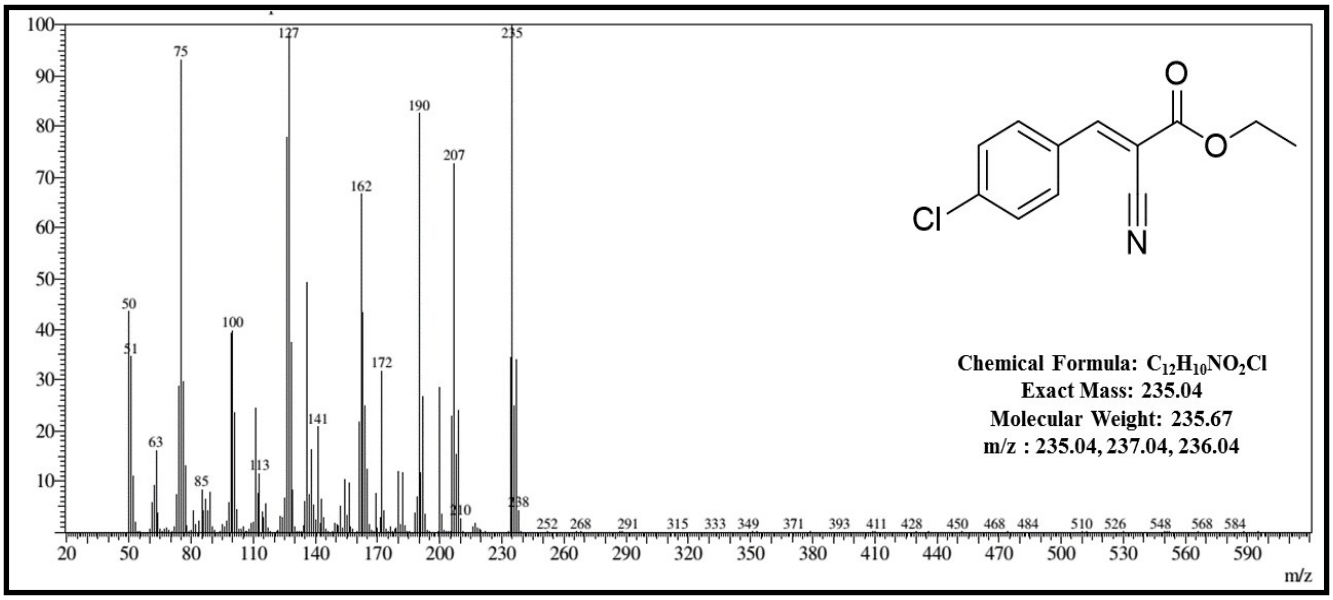
8. 4-Chloro benzaldehyde with Ethyl-2-cyanoacetate

(i)GC data



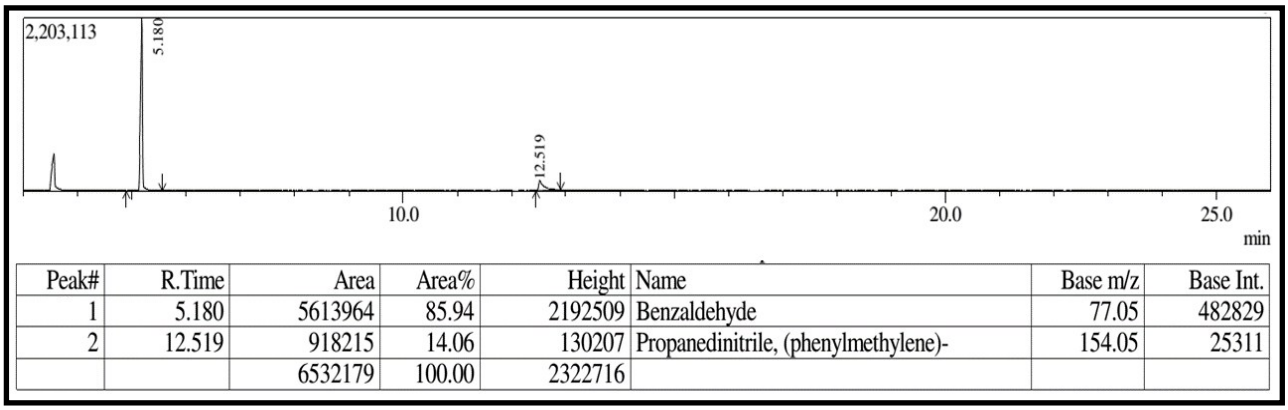
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	7.850	3926668	60.65	1436435	Benzaldehyde, 4-chloro-	139.05	252989
2	17.585	2548137	39.35	666843	2-Propenoic acid, 2-cyano-3-(4-chlorophenyl)-	235.00	38984
		6474805	100.00	2103278			

(ii) MS data



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

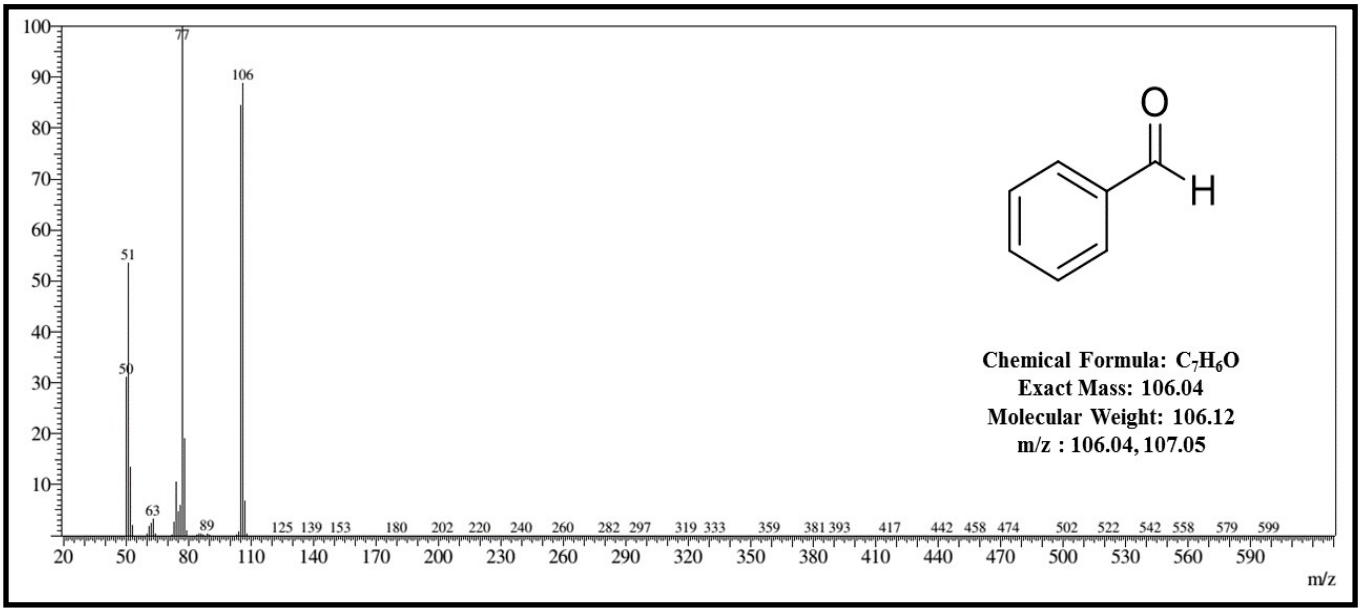
(i)GC data



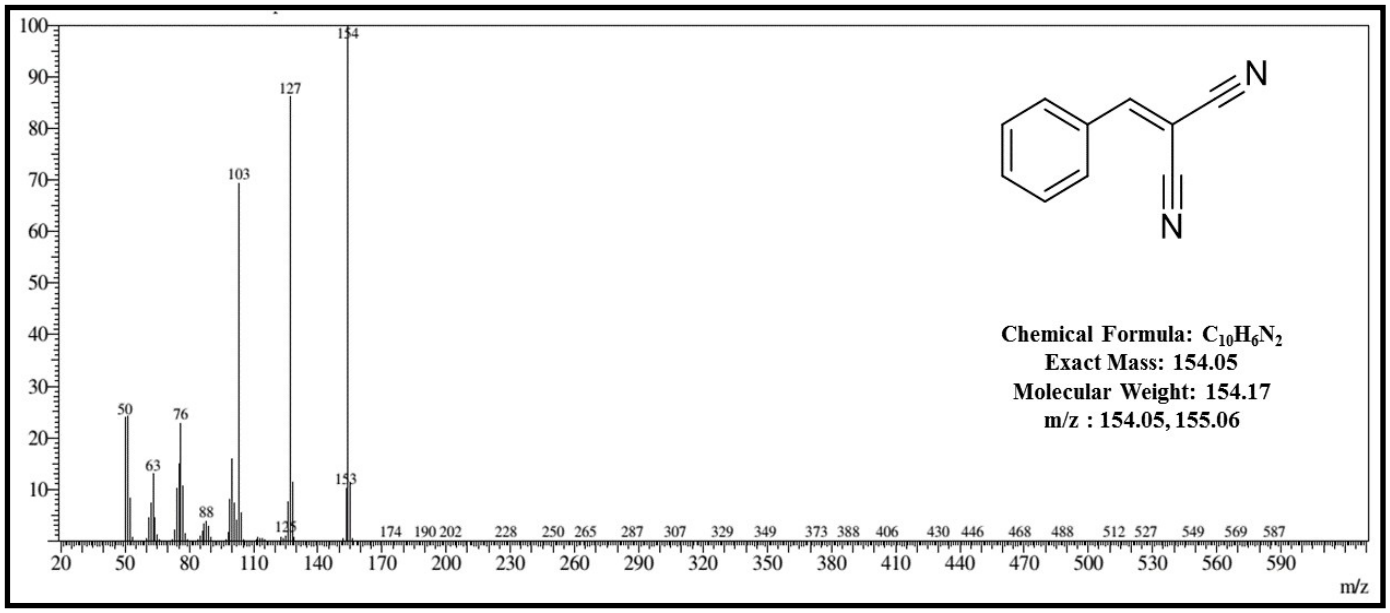
Peak#	R.Time	Area	Area%	Height	Name	Base m/z	Base Int.
1	5.180	5613964	85.94	2192509	Benzaldehyde	77.05	482829
2	12.519	918215	14.06	130207	Propanedinitrile, (phenylmethylene)-	154.05	25311
		6532179	100.00	2322716			

(ii) MS data

a. <u>Reactant</u>



b. Product


154
127
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76
63
88
153
N
N
Chemical Formula: $C_{10}H_6N_2$
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m/z : 154.05, 155.06
m/z