Supporting Information for

Triazole-directed Fabrication of Polyoxovanadate-based Metal-organic Frameworks as Efficient Multifunctional Heterogeneous Catalysts for Knoevenagel Condensation and Oxidation of Alcohols

Jikun Li, Chuanping Wei, Yinfeng Han, Yu Mei, Xueli Cheng, Xianqiang Huang, and Changwen Hu

Table of contents

Table S1. Bond valance sum calculations for PMOFs **1-3**.

Table S2. Selected Bond lengths [Å] and angles [°] for PMOFs **1-3**.

Table S3. Comparison of Knoevenagel condensation with different POM-based catalysts.

Figure S1. The 2D inorganic-organic hybrid network of PMOF **2**.

Figure S2. The 3D supramolecular structure of PMOF **2**.

Figure S3. The FT-IR spectra of PMOF **1**.

Figure S4. The FT-IR spectra of PMOF **2**.

Figure S5. The FT-IR spectra of PMOF **3**.

Figure S6. The FT-IR spectra of the reused PMOF **1**.

Figure S7. The simulated, experimental and recycled PXRD patterns of PMOF **1**. Simulation based on the SXRD data.

Figure S8. The simulated (black) and experimental (red) PXRD patterns of PMOF **2**. Simulation based on the SXRD data.

Figure S9. The simulated (black) and experimental (red) PXRD patterns of PMOF **3**. Simulation based on the SXRD data.

Figure S10. The TG analysis curves of PMOFs **1-3**.

Figure S11. The ^{1}H and ^{13}C NMR spectra of the compounds isolated from Knoevenagel condensation.

Table S1. Bond valance sum calculations for PMOFs **1-3**.[a][1-3]

1	**V site**	V1	V2	V3	V4	V5
	BVS (V^{IV})	5.01	5.14	5.00	-	-
	BVS (V^{V})	5.27	5.41	5.26	-	-
	assigned O.S.	5	5	5	-	-
2	**V site**	V1	V2	V3	V4	V5
	BVS (V^{IV})	4.96	4.99	5.00	-	-
	BVS (V^{V})	5.22	5.25	5.26	-	-
	assigned O.S.	5	5	5	-	-
3	**V site**	V1	V2	V3	V4	V5
	BVS (V^{IV})	5.52	5.52	5.50	5.48	5.49
	BVS (V^{V})	5.81	5.82	5.79	5.77	5.78
	assigned O.S.	5	5	5	5	5

[a] The calculations were performed twice for each individual vanadium atom using bond-valence parameters presented by Brese and O'Keeffe. The oxidation state of atom *i* is given by $\sum v_{ij}=V$ with $v_{ij}=\exp[(R_{ij}-d_{ij})/b]$. Here b is taken to be a 'universal' constant equal to 0.37 Å, v_{ij} is the valence of a bond between two atoms *i* and *j*, R_{ij} is the empirical parameter, and d_{ij} is the observed bond length.

Table S2. Selected Bond lengths [Å] and angles [º] for PMOFs **1-3**.

PMOF **1**			
Ni(1)-O(4)	2.031(2)	Ni(1)-O(1)	2.055(2)
Ni(1)-N(9)	2.058(2)	Ni(1)-N(2)	2.063(3)
Ni(1)-N(6)	2.059(3)	Ni(1)-O(9)#3	2.062(2)
Ni(2)-N(5)	2.103(2)	Ni(2)-N(1)	2.110(2)
Ni(2)-N(10)	2.113(3)	V(1)-O(2)	1.617(3)
V(1)-O(1)	1.656(2)	V(1)-O(6)#1	1.777(3)
V(1)-O(3)	1.785(2)	V(2)-O(5)	1.611(3)
V(2)-O(4)	1.631(2)	V(2)-O(6)	1.774(3)
V(2)-O(7)	1.787(2)	V(3)-O(8)	1.625(3)
V(3)-O(9)	1.644(2)	V(3)-O(3)#2	1.785(2)
V(3)-O(7)	1.795(2)	N(1)-N(2)	1.373(4)
O(2)-V(1)-O(1)	109.79(12)	O(2)-V(1)-O(6)#1	110.64(16)
O(1)-V(1)-O(6)#1	107.17(12)	O(2)-V(1)-O(3)	107.71(13)
O(1)-V(1)-O(3)	110.68(11)	O(6)#1-V(1)-O(3)	110.86(15)
O(5)-V(2)-O(4)	107.45(15)	O(5)-V(2)-O(6)	109.09(18)
O(4)-V(2)-O(6)	108.22(14)	O(5)-V(2)-O(7)	110.41(15)
O(4)-V(2)-O(7)	110.01(12)	O(6)-V(2)-O(7)	111.55(13)
O(8)-V(3)-O(9)	109.30(14)	O(8)-V(3)-O(3)#2	108.51(15)
O(9)-V(3)-O(3)#2	109.00(13)	O(8)-V(3)-O(7)	109.38(13)
O(9)-V(3)-O(7)	109.76(12)	O(3)#2-V(3)-O(7)	110.87(12)
O(4)-Ni(1)-O(1)	89.63(10)	O(4)-Ni(1)-N(9)	93.64(10)
O(1)-Ni(1)-N(9)	89.79(9)	O(4)-Ni(1)-N(2)	93.21(10)
O(1)-Ni(1)-N(2)	175.31(9)	N(9)-Ni(1)-N(2)	86.31(10)
O(4)-Ni(1)-N(6)	171.61(10)	O(1)-Ni(1)-N(6)	87.79(9)
N(9)-Ni(1)-N(6)	94.33(10)	O(1)-Ni(1)-O(9)#3	90.87(9)
O(4)-Ni(1)-O(9)#3	84.50(10)	N(2)-Ni(1)-O(9)#3	93.11(10)
N(9)-Ni(1)-O(9)#3	178.02(10)	N(5)-Ni(2)-N(1)	90.33(10)
N(6)-Ni(1)-O(9)#3	87.56(10)	N(5)#4-Ni(2)-N(1)	89.67(10)
N(1)#4-Ni(2)-N(10)	90.96(10)	N(5)-Ni(2)-N(10)	90.71(10)
V(3)#5-O(3)-V(1)	145.38(15)	N(1)-Ni(2)-N(10)	89.04(10)
Symmetry transformations used to generate equivalent atoms: #1 -x+2, -y, -z+1; #2 x+1, y+1, z; #3 -x+2, -y+1, -z+1; #4 -x+1, -y, -z; #5 x-1, y-1, z.			
PMOF **2**			
V(1)-O(2)	1.627(2)	V(1)-O(1)	1.648(2)
V(1)-O(7)#1	1.792(2)	V(1)-O(4)	1.794(2)
V(2)-O(5)	1.619(3)	V(2)-O(3)	1.6612(19)
V(2)-O(9)#2	1.776(3)	V(2)-O(4)#3	1.779(2)
V(3)-O(8)	1.618(3)	V(3)-O(6)	1.645(2)
V(3)-O(9)	1.769(2)	V(3)-O(7)	1.795(2)
Co(1)-N(2)	2.145(3)	Co(1)-N(2)#4	2.145(3)
Co(1)-N(6)#4	2.153(2)	Co(1)-N(10)#4	2.160(2)
Co(2)-O(6)	2.058(2)	Co(2)-O(3)	2.064(2)
Co(2)-O(1)	2.076(2)	Co(2)-N(1)	2.118(2)
Co(2)-N(9)	2.119(2)	Co(2)-N(5)	2.122(3)

O(2)-V(1)-O(1)	109.02(13)	O(2)-V(1)-O(7)#1	109.71(13)
O(1)-V(1)-O(7)#1	109.86(12)	O(2)-V(1)-O(4)	107.91(15)
O(1)-V(1)-O(4)	109.48(12)	O(7)#1-V(1)-O(4)	110.82(11)
O(5)-V(2)-O(3)	109.70(13)	O(5)-V(2)-O(9)#2	111.45(16)
O(3)-V(2)-O(9)#2	106.76(11)	O(5)-V(2)-O(4)#3	107.53(13)
O(3)-V(2)-O(4)#3	110.77(11)	O(9)#2-V(2)-O(4)#3	110.66(15)
O(8)-V(3)-O(6)	107.55(15)	O(8)-V(3)-O(7)	110.78(16)
O(9)-V(3)-O(7)	111.62(12)	N(2)-Co(1)-N(2)#4	180.0
N(2)-Co(1)-N(6)	90.17(10)	N(2)-Co(1)-N(6)#4	89.83(10)
N(2)-Co(1)-N(10)	90.60(10)	N(2)-Co(1)-N(10)#4	89.40(10)
O(6)-Co(2)-O(3)	90.54(9)	O(3)-Co(2)-O(1)	91.77(9)
O(3)-Co(2)-N(5)	173.28(9)	N(1)-Co(2)-N(5)	89.11(10)

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z+2; #2 -x+1, -y, -z+2; #3 -x, -y, -z+2; #4 -x, -y, -z+1.

PMOF **3**

Cu(1)-O(2)	1.908(8)	Cu(1)-N(10)	1.928(10)
Cu(1)-N(1)	1.950(9)	Cu(1)-O(16)	1.953(7)
Cu(1)-O(6)#1	2.189(9)	Cu(2)-N(2)	1.934(10)
Cu(2)-O(14)#2	1.889(8)	Cu(2)-N(5)	1.943(10)
Cu(2)-O(16)	1.974(7)	Cu(2)-O(17)	2.324(9)
Cu(3)-O(9)	1.842(8)	Cu(3)-N(9)	1.899(10)
Cu(3)-N(6)	1.917(10)	Cu(3)-O(16)	1.943(8)
Cu(3)-O(10)#3	2.422(9)	V(1)-O(3)	1.569(9)
V(1)-O(2)	1.637(8)	V(1)-O(1)	1.726(9)
V(1)-O(4)	1.759(9)	V(2)-O(6)	1.587(8)
V(2)-O(5)	1.605(8)	V(2)-O(7)	1.738(8)
V(2)-O(1)	1.766(9)	V(3)-O(10)	1.568(9)
V(3)-O(9)	1.635(7)	V(3)-O(7)#4	1.723(9)
V(3)-O(8)	1.772(8)	V(4)-O(12)	1.594(9)
V(4)-O(13)	1.601(8)	V(4)-O(8)	1.749(8)
V(4)-O(11)	1.756(8)	V(5)-O(15)	1.575(9)
V(5)-O(14)	1.648(8)	V(5)-O(4)#1	1.716(8)
V(5)-O(11)	1.750(8)	N(1)-N(2)	1.341(13)
O(2)-Cu(1)-N(10)	90.5(4)	O(2)-Cu(1)-N(1)	91.5(4)
N(10)-Cu(1)-N(1)	171.2(4)	O(2)-Cu(1)-O(16)	165.5(3)
N(10)-Cu(1)-O(16)	89.4(4)	N(1)-Cu(1)-O(16)	86.6(4)
O(2)-Cu(1)-O(6)#1	93.4(3)	N(10)-Cu(1)-O(6)#1	96.1(4)
N(1)-Cu(1)-O(6)#1	92.3(4)	O(16)-Cu(1)-O(6)#1	101.0(3)
O(14)#2-Cu(2)-N(2)	89.6(4)	O(14)#2-Cu(2)-N(5)	92.1(4)
N(2)-Cu(2)-N(5)	173.6(4)	O(14)#2-Cu(2)-O(16)	170.7(4)
N(2)-Cu(2)-O(16)	87.8(3)	N(5)-Cu(2)-O(16)	89.5(3)
O(14)#2-Cu(2)-O(17)	98.4(4)	N(2)-Cu(2)-O(17)	99.0(4)
N(5)-Cu(2)-O(17)	86.9(4)	O(16)-Cu(2)-O(17)	90.8(3)
O(9)-Cu(3)-N(9)	91.1(4)	O(9)-Cu(3)-N(6)	91.7(4)
N(9)-Cu(3)-N(6)	167.1(4)	O(9)-Cu(3)-O(16)	171.5(3)
N(9)-Cu(3)-O(16)	89.3(4)	N(6)-Cu(3)-O(16)	89.8(3)
O(9)-Cu(3)-O(10)#3	94.4(3)	N(9)-Cu(3)-O(10)#3	95.0(4)
N(6)-Cu(3)-O(10)#3	97.4(4)	O(16)-Cu(3)-O(10)#3	77.1(3)
O(3)-V(1)-O(2)	107.9(5)	O(3)-V(1)-O(1)	109.3(5)
O(2)-V(1)-O(1)	110.2(4)	O(3)-V(1)-O(4)	108.9(5)
O(2)-V(1)-O(4)	106.7(4)	O(1)-V(1)-O(4)	113.7(5)
O(6)-V(2)-O(5)	109.5(4)	O(6)-V(2)-O(7)	110.3(4)
O(5)-V(2)-O(7)	109.0(4)	O(6)-V(2)-O(1)	108.6(4)
O(5)-V(2)-O(1)	110.0(5)	O(7)-V(2)-O(1)	109.3(4)
O(10)-V(3)-O(9)	111.5(5)	O(10)-V(3)-O(7)#4	110.1(5)
O(9)-V(3)-O(7)#4	109.4(4)	O(10)-V(3)-O(8)	109.4(4)
O(9)-V(3)-O(8)	106.6(4)	O(7)#4-V(3)-O(8)	109.9(4)
O(12)-V(4)-O(13)	108.4(5)	O(12)-V(4)-O(8)	106.4(5)
O(13)-V(4)-O(8)	111.7(4)	O(12)-V(4)-O(11)	107.1(5)
O(13)-V(4)-O(11)	111.4(5)	O(8)-V(4)-O(11)	111.6(4)
O(15)-V(5)-O(14)	109.4(5)	O(15)-V(5)-O(4)#1	107.6(5)
O(14)-V(5)-O(4)#1	112.0(5)	O(15)-V(5)-O(11)	111.2(5)
O(14)-V(5)-O(11)	107.9(4)	O(4)#1-V(5)-O(11)	108.8(4)

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z+1 ; #2 x, y, z-1; #3 -x+1, -y, -z+1; #4 x,y-1,z.

Table S3. Comparison of Knoevenagel condensation with different POM-based catalysts.

Entry	Catalysts	Solvent	T/℃	Yield.(%)[b]	Ref
1	Na-A-PW_9	MeOH	rt	92	14
2	Fe_3O_4@SiO_2@NH-NH_2-PW	H_2O	reflux	93	36
3	GO@ Fe_3O_4@POM	PEG/H_2O	rt	96	37
4	$P_2W_{18}O_{68}$	H_2O	rt	90	38
5	$[H_4Ta_6O_{19}]^{4-}$	EtOH	70	83	39
6	$K_7HNb_6O_{19}$	EtOH	rt	99	40
7	[Zn(bix)]{V_2O_6}	-	60	>99	22
8	PMOF **1**	-	45	>99	this work

Figure S1. The 2D inorganic-organic hybrid network of PMOF **2**.

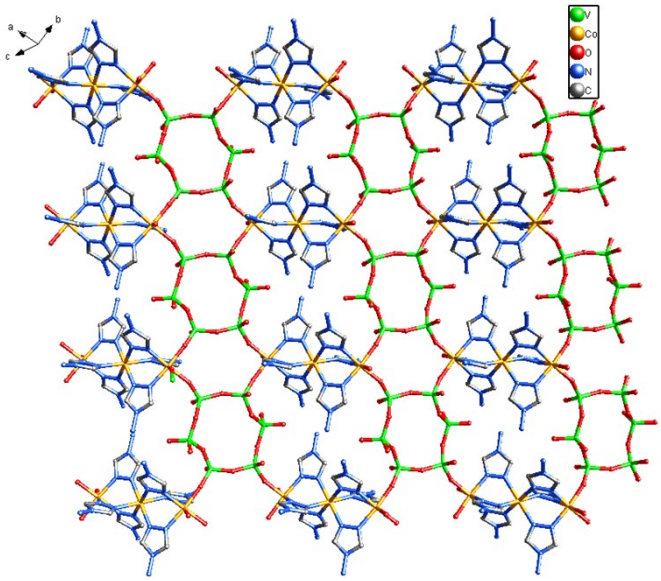


Figure S2. The 3D supramolecular structure of PMOF **2**.

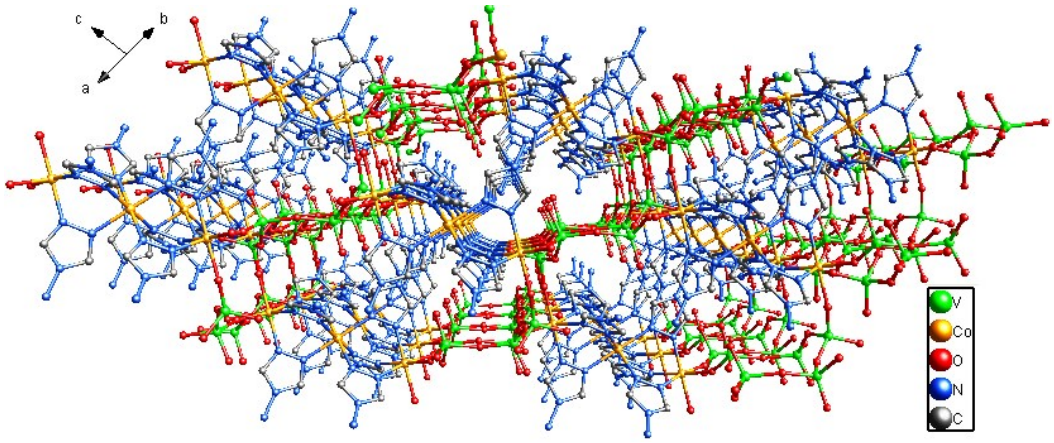


Figure S3. The FT-IR spectra of PMOF **1**.

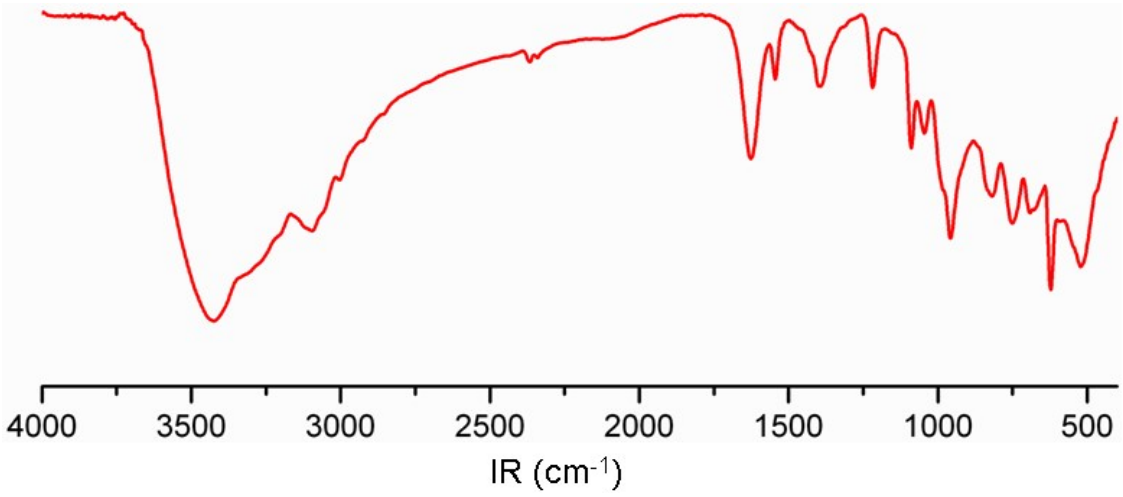


Figure S4. The FT-IR spectra of PMOF **2**.

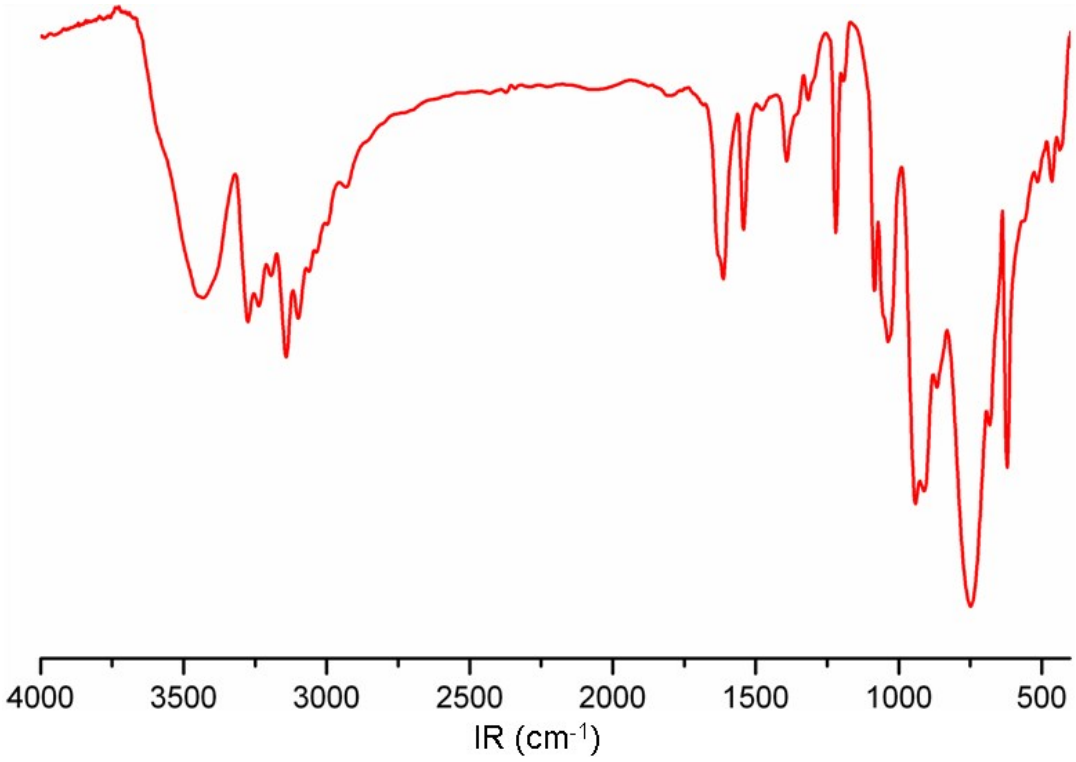


Figure S5. The FT-IR spectra of PMOF **3**.

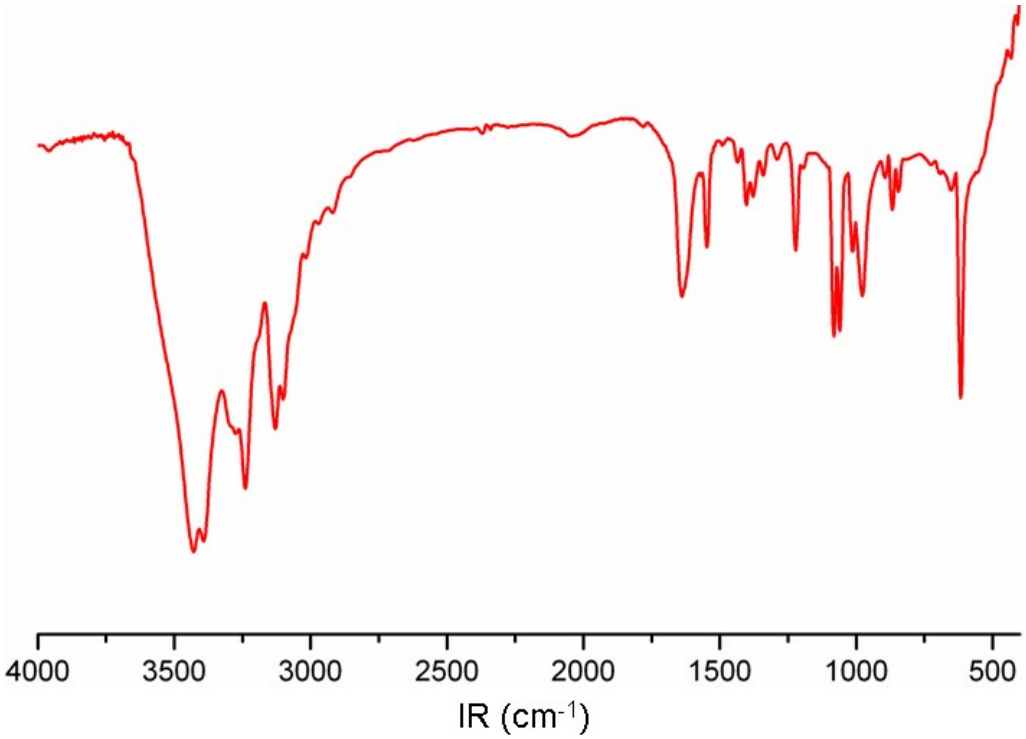


Figure S6. The FT-IR spectra of the reused PMOF **1**.

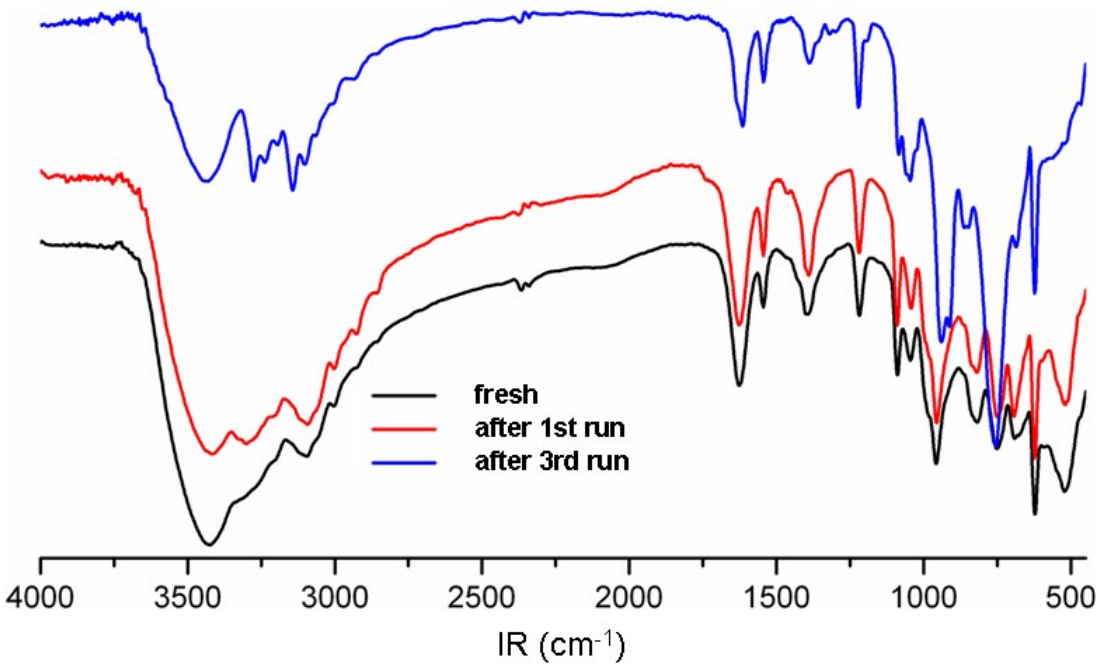


Figure S7. The simulated, experimental and recycled PXRD patterns of PMOF **1**. Simulation based on the SXRD data.

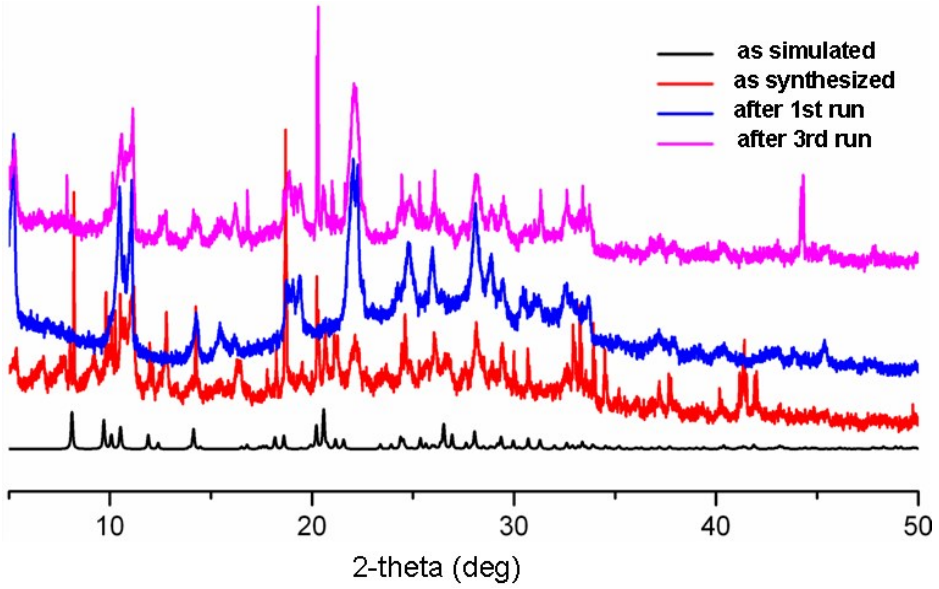


Figure S8. The simulated (black) and experimental (red) PXRD patterns of PMOF **2**. Simulation based on the SXRD data.

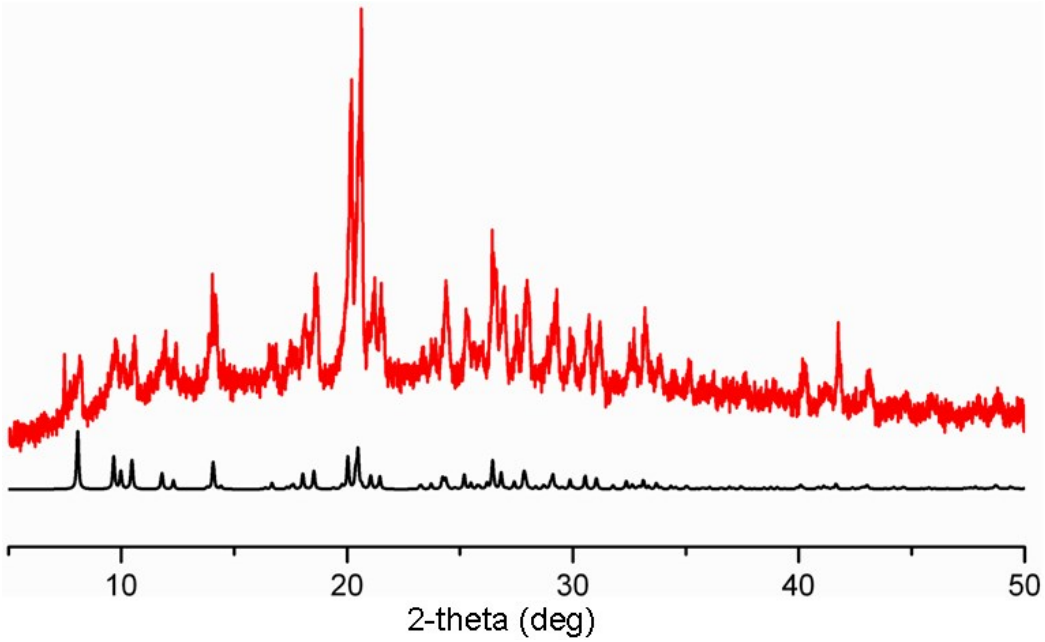


Figure S9. The simulated (black) and experimental (red) PXRD patterns of PMOF **3**. Simulation based on the SXRD data.

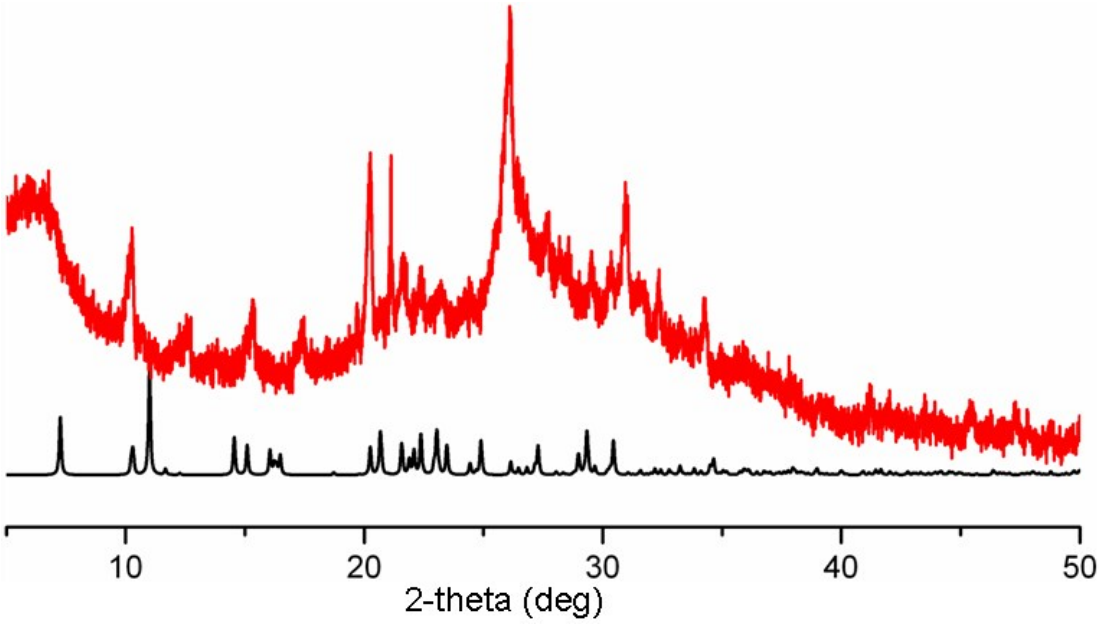
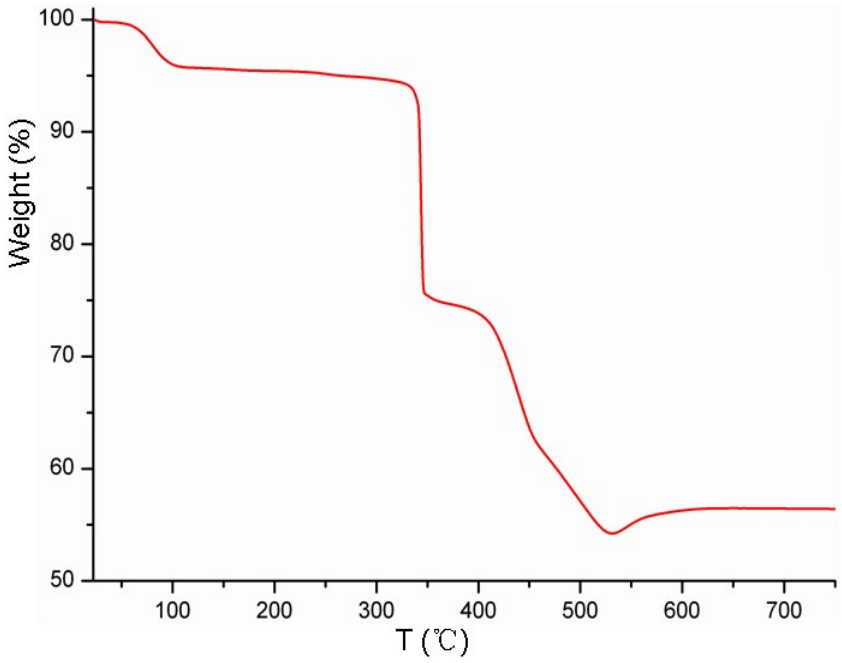
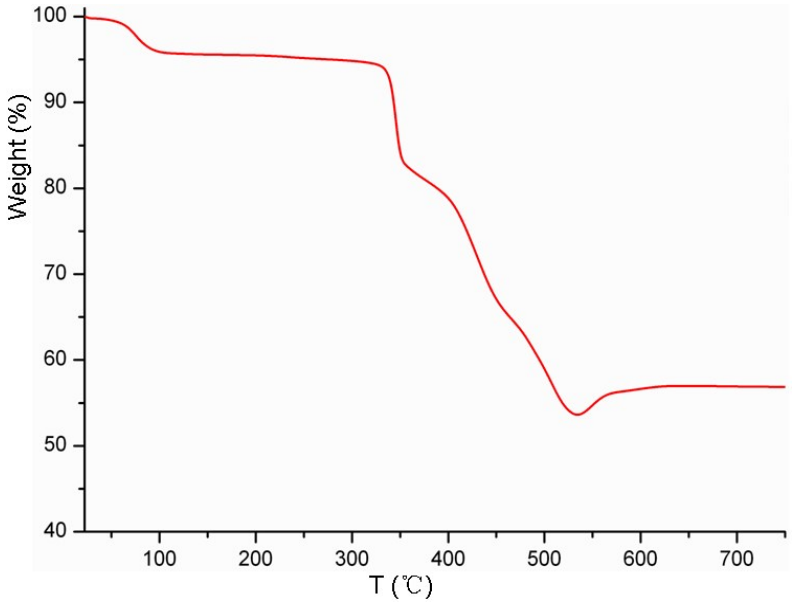


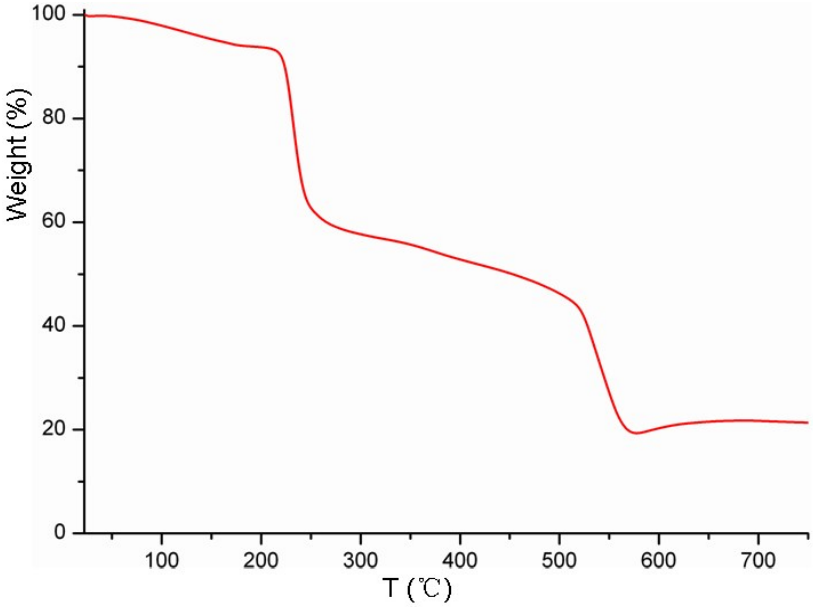
Figure S10. The TG analysis curves of PMOFs **1**-**3**.



(a) The TGA curve of PMOF **1**.

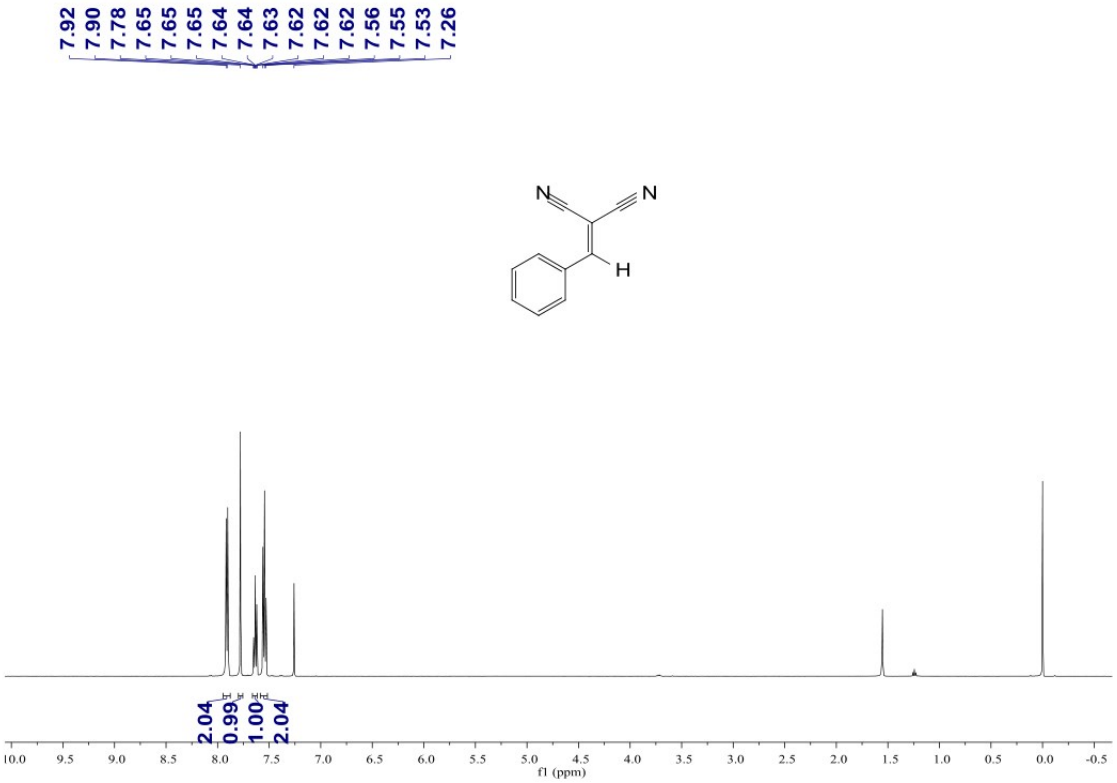


(b) The TGA curve of PMOF **2**.

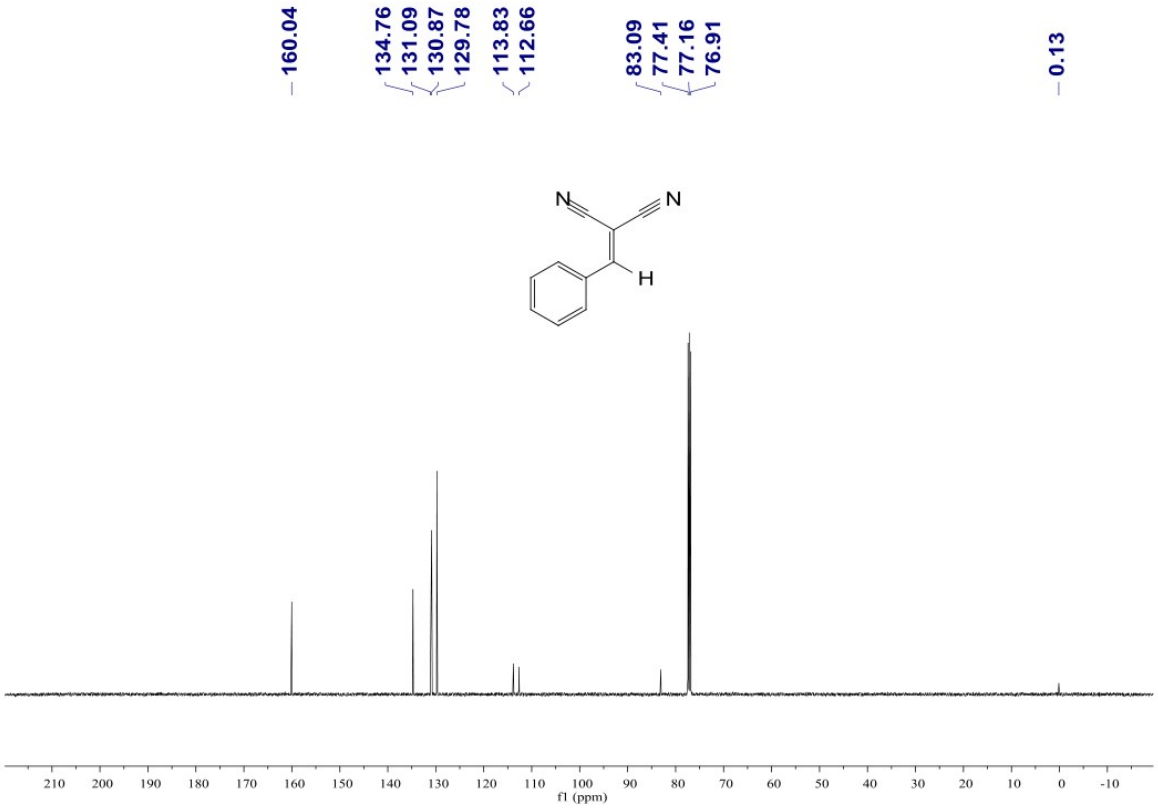


(c) The TGA curve of PMOF **3**.

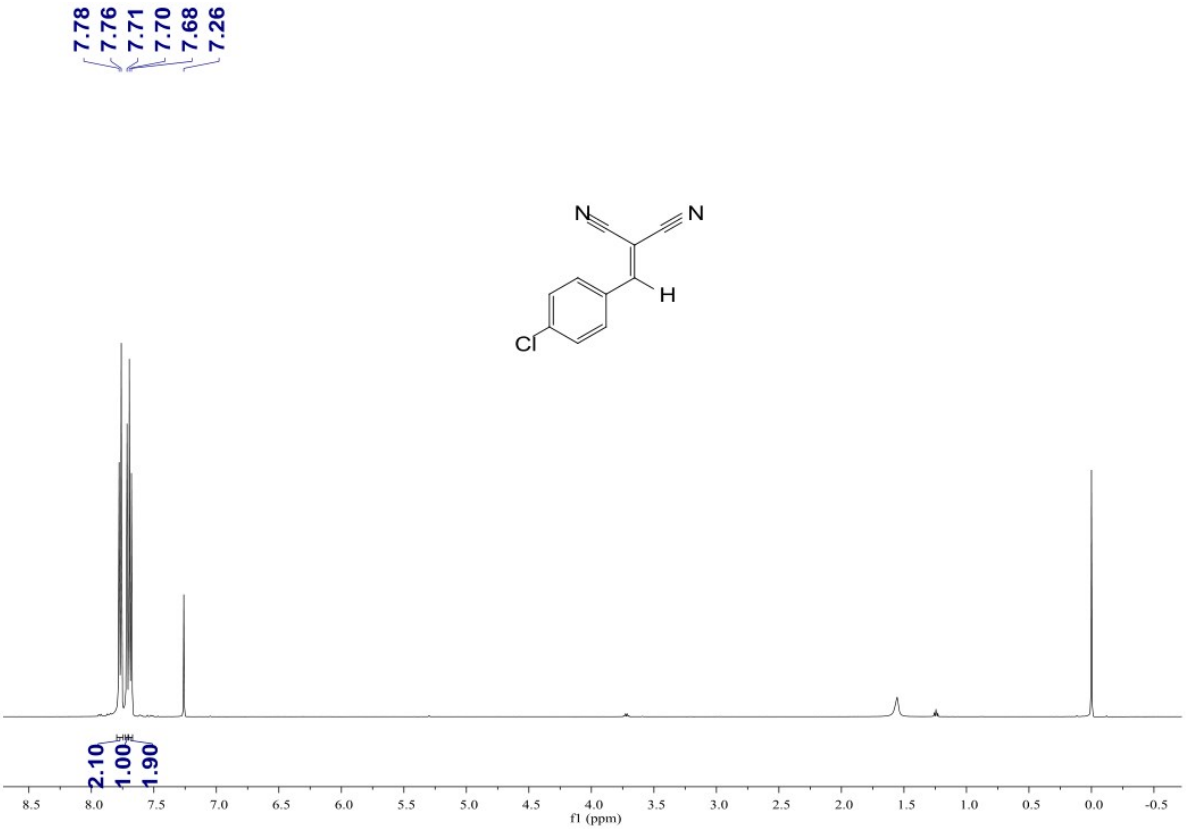
Figure S11. The ^{1}H NMR and ^{13}C NMR spectra of the compounds isolated from Knoevenagel condensation.



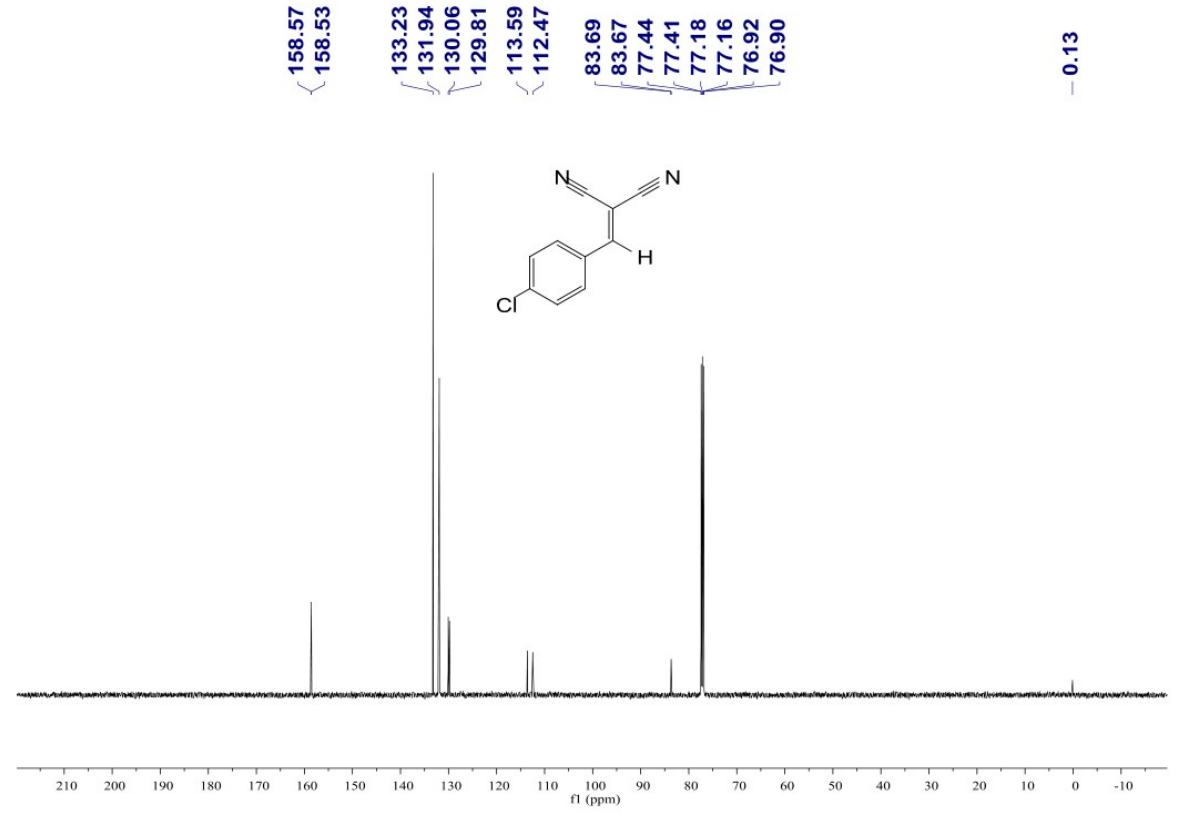
(a) ^{1}H NMR spectrum of 2-benzylidenemalononitrile in $CDCl_3$.



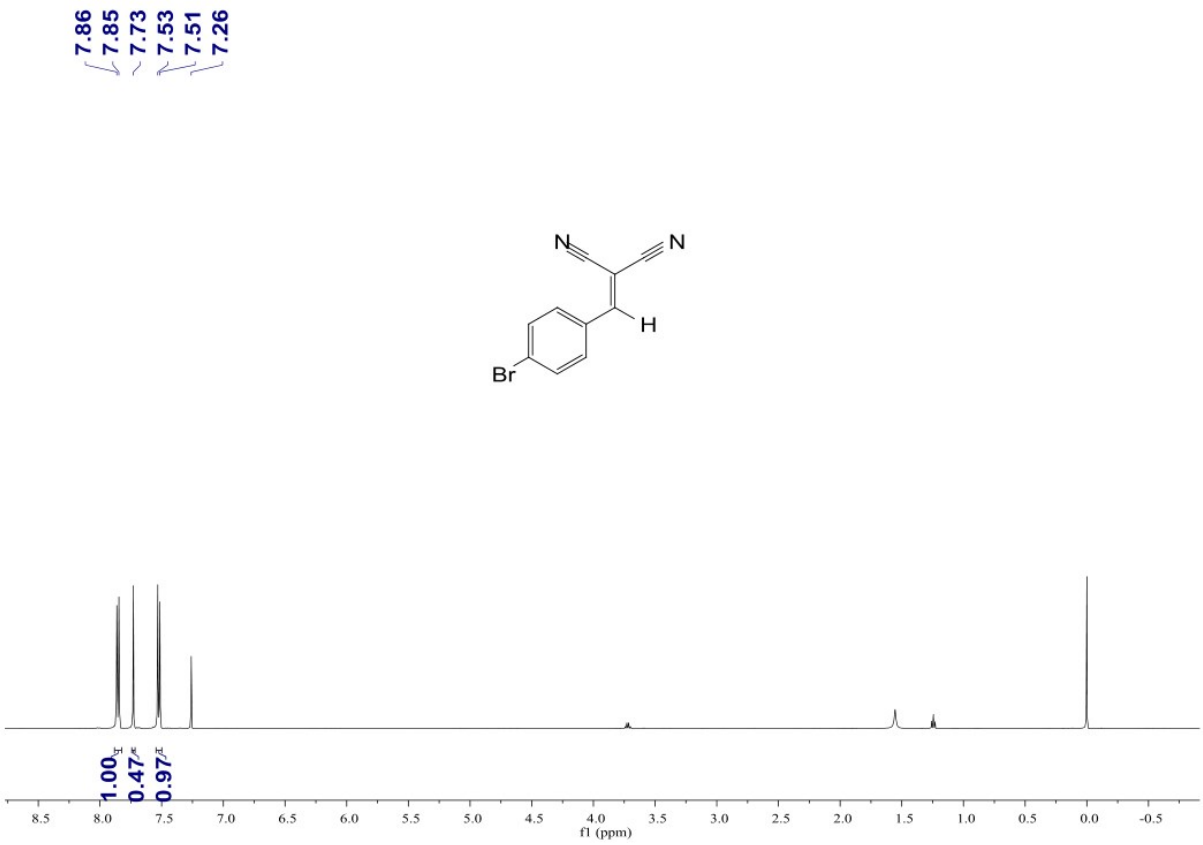
(b) ^{13}C NMR spectrum of 2-benzylidenemalononitrile in $CDCl_3$.



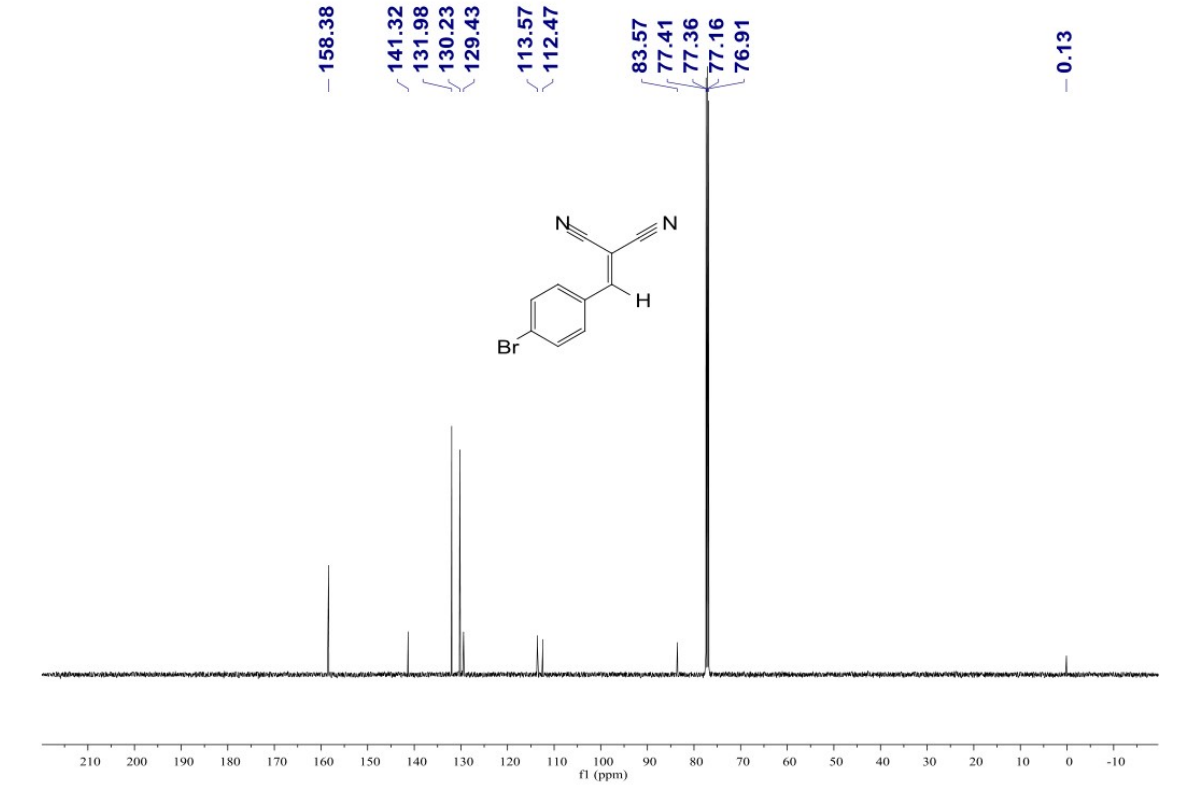
(c) ^{1}H NMR spectrum of 2-(4-chlorobenzylidene)malononitrile in $CDCl_3$.



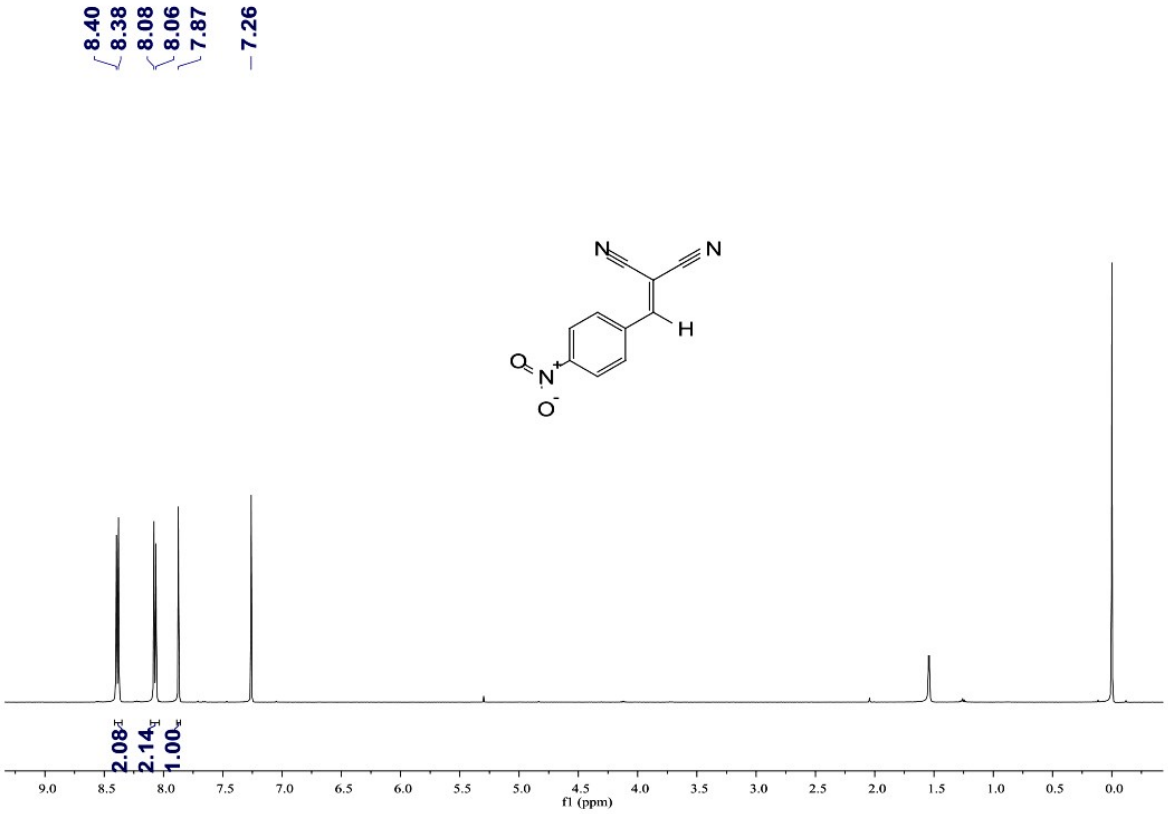
(d) ^{13}C NMR spectrum of 2-(4-chlorobenzylidene)malononitrile in $CDCl_3$.



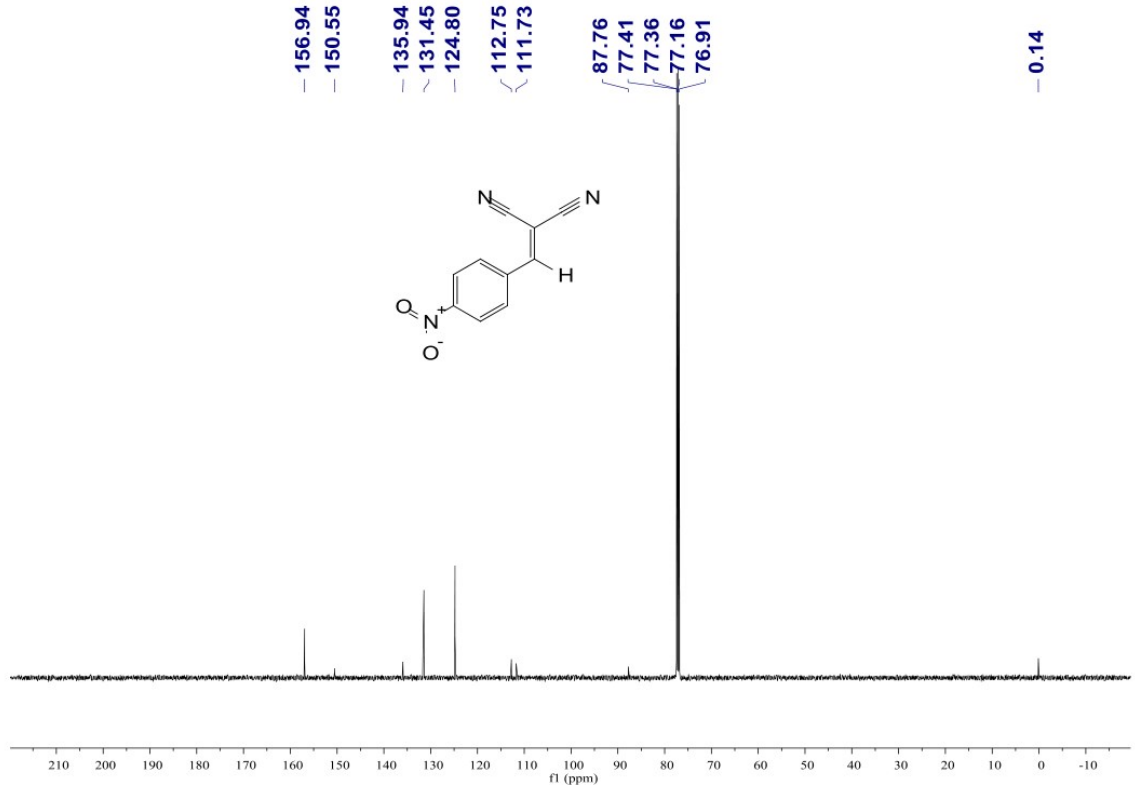
(e) ^{1}H NMR spectrum of 2-(4-bromobenzylidene)malononitrile in $CDCl_3$.



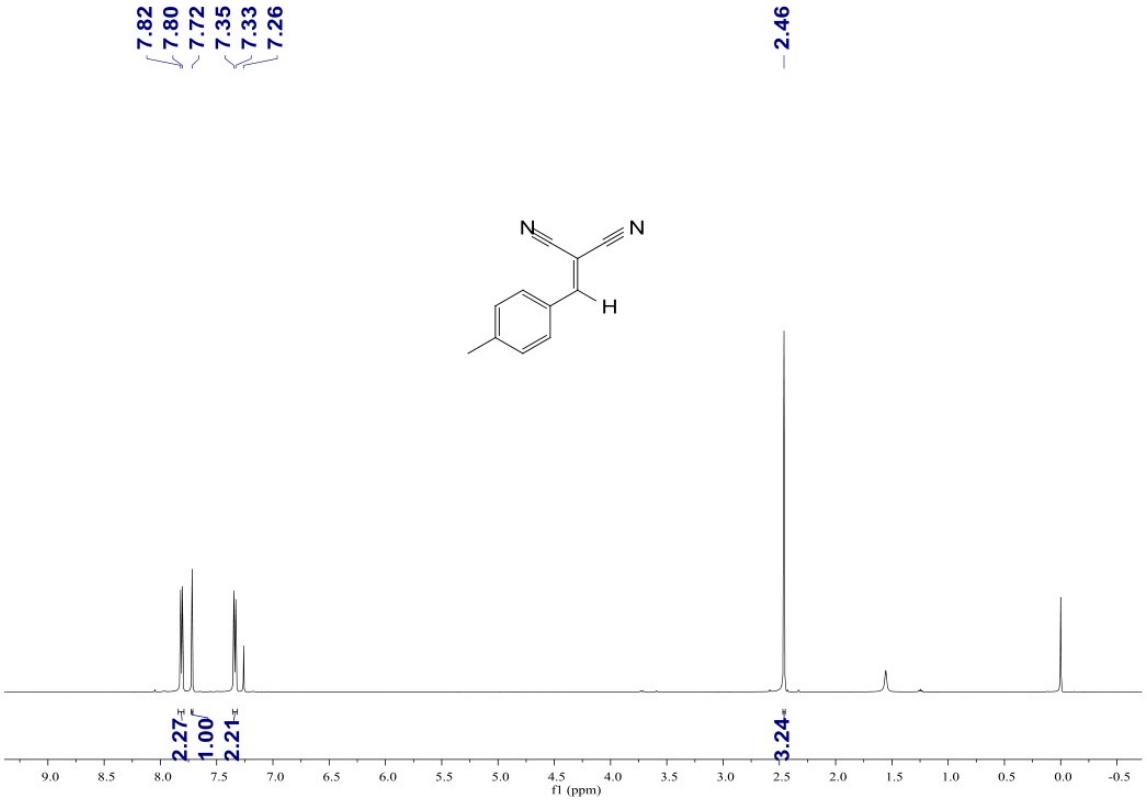
(f) ^{13}C NMR spectrum of 2-(4-bromobenzylidene)malononitrile in $CDCl_3$.



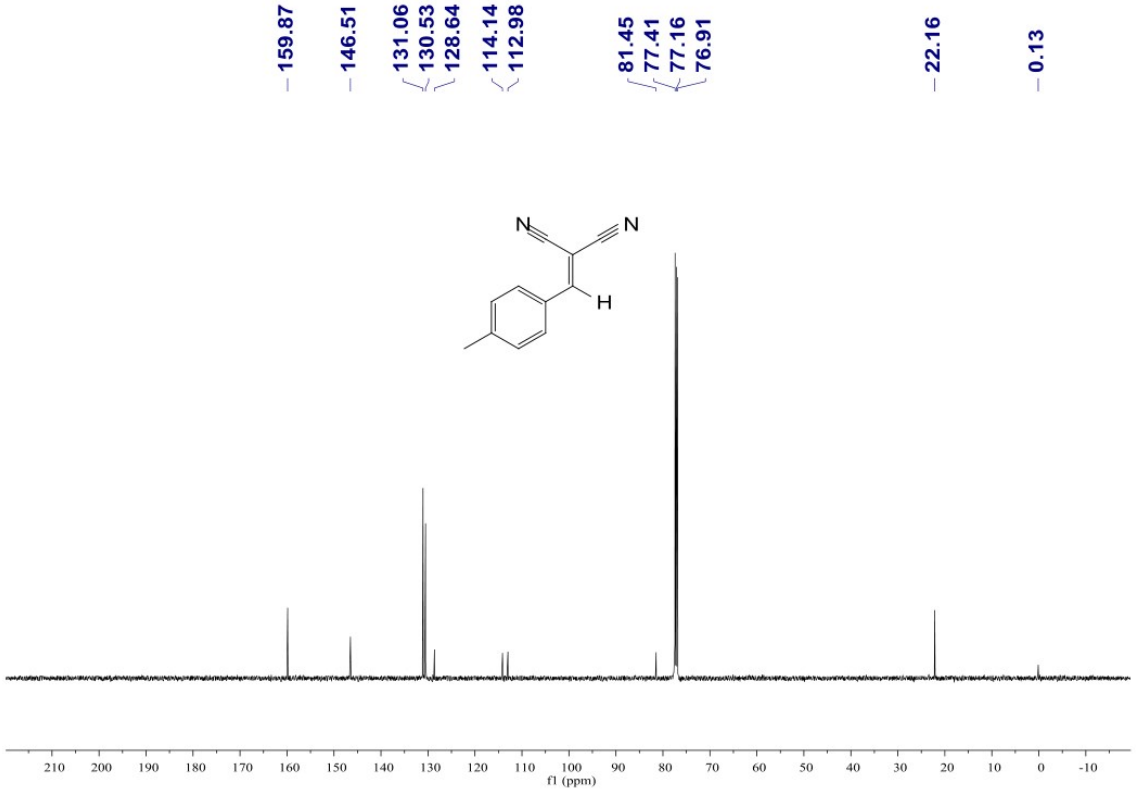
(g) ^{1}H NMR spectrum of 2-(4-nitrobenzylidene)malononitrile in $CDCl_3$.



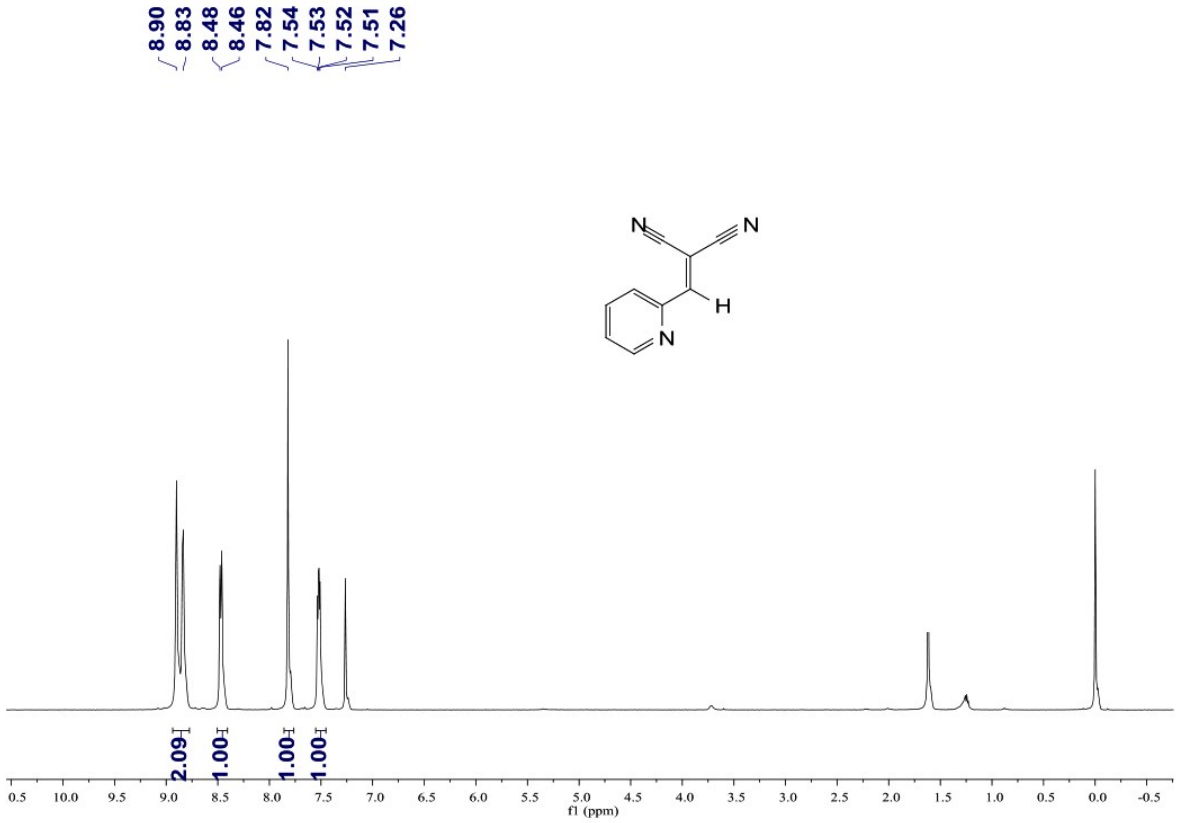
(h) ^{13}C NMR spectrum of 2-(4-nitrobenzylidene)malononitrile in $CDCl_3$.



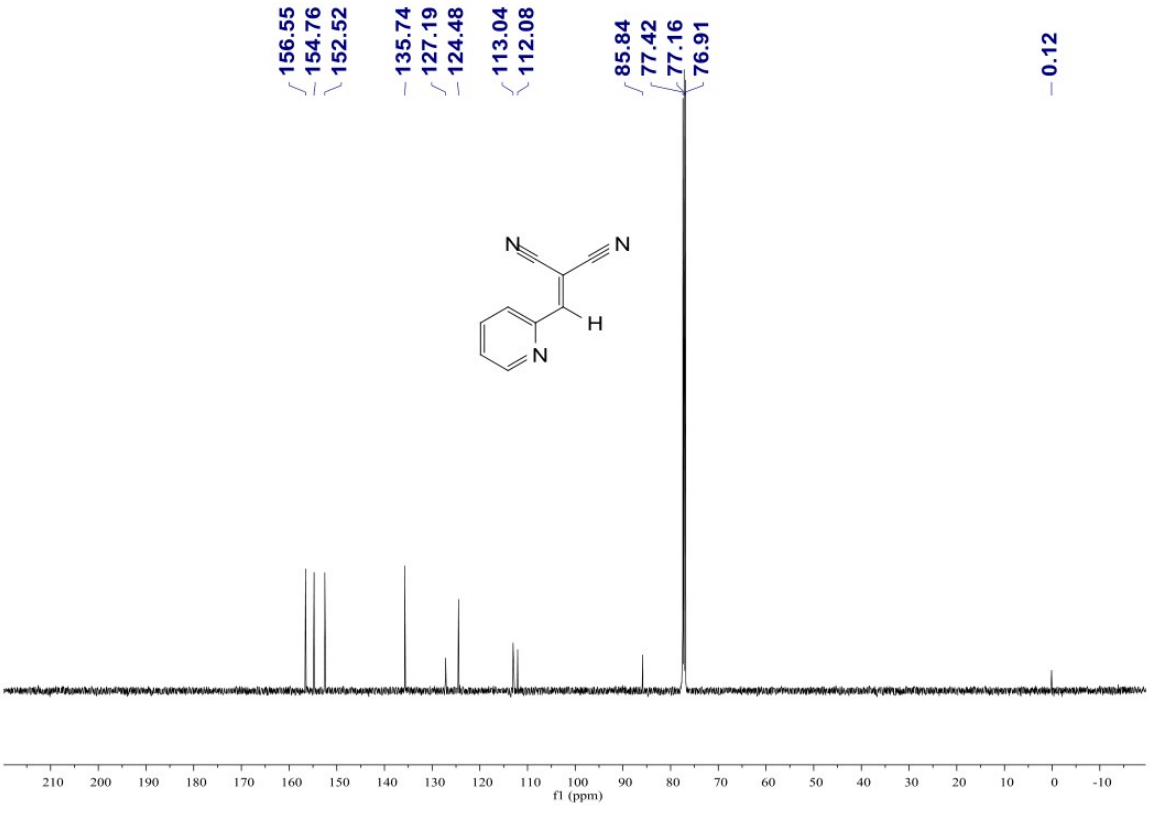
(i) ^{1}H NMR spectrum of 2-(4-methylbenzylidene)malononitrile in $CDCl_3$.



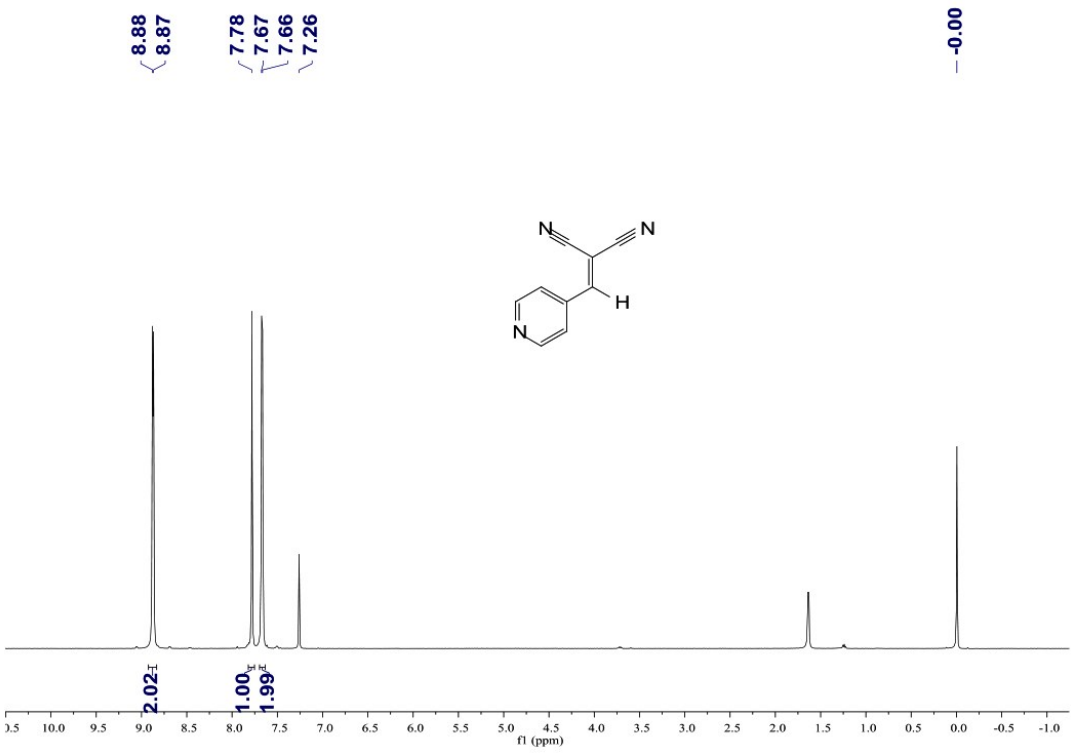
(j) ^{13}C NMR spectrum of 2-(4-methylbenzylidene)malononitrile in $CDCl_3$.



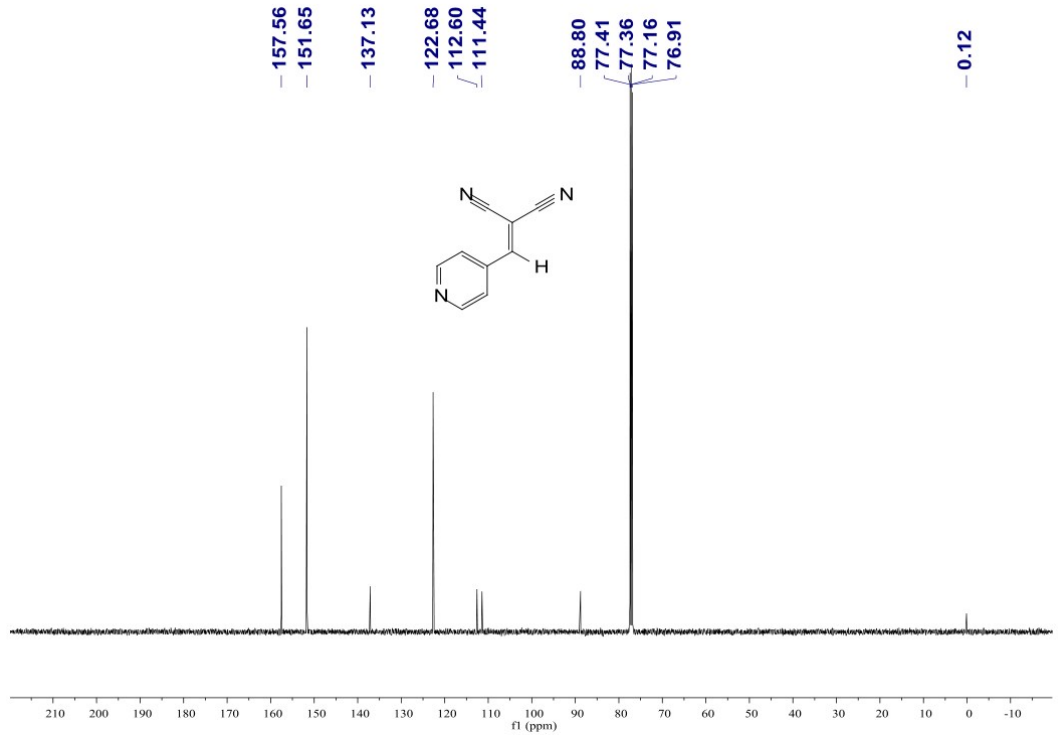
(k) ^{1}H NMR spectrum of 2-(2-pyridinylidene)malononitrile in $CDCl_3$.



(l) ^{13}C NMR spectrum of 2-(2-pyridinylidene)malononitrile in $CDCl_3$.



(m) ^{1}H NMR spectrum of 2-(4-pyridinylidene)malononitrile in $CDCl_3$.



(n) ^{13}C NMR spectrum of 2-(4-pyridinylidene)malononitrile in $CDCl_3$.

Reference:

[1] N. E. Brese and M. O'Keeffe, *Acta Cryst. Sect. B,* 1991, **47**, 192.

[2] I. D. Brown and D. Altermatt, *Acta. Cryst.* **1985**, *B41*, 244.

[3] H. H. Thorp, *Inorg. Chem.* **1992**, *31*, 1585.