Electronic Supplementary Information

Coordination driven self-assembly of [2+2+2] molecular squares: synthesis, crystal structures, catalytic and luminescence properties

Vijay Gupta[a] and Sanjay K. Mandal[a]

[a]*Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali, Sector 81, Manauli PO, S.A.S. Nagar, Mohali (Punjab) 140306, INDIA*

Author for correspondence:
Prof. Sanjay K. Mandal, E-mail: sanjaymandal@iisrmohali.ac.in.

Table of Contents

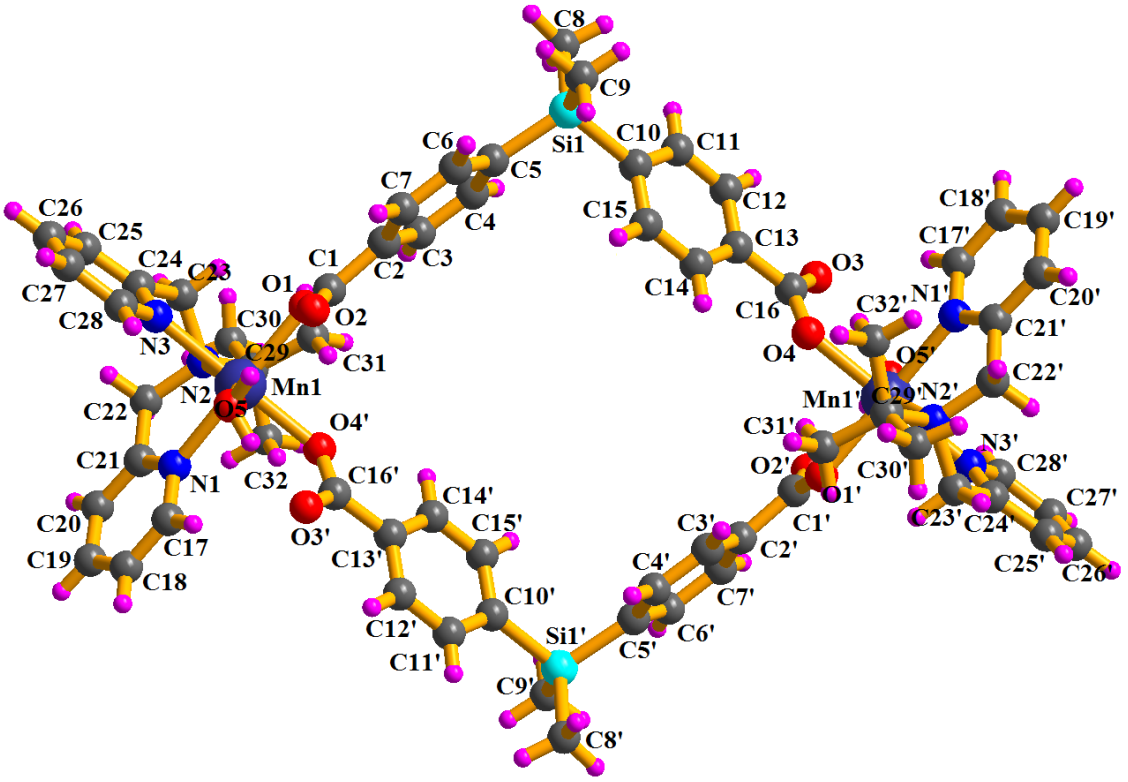


Fig. S1 Structure of molecular square **1** with nonhydrogen atoms labelled; symmetry related atoms are designated with a ‘.

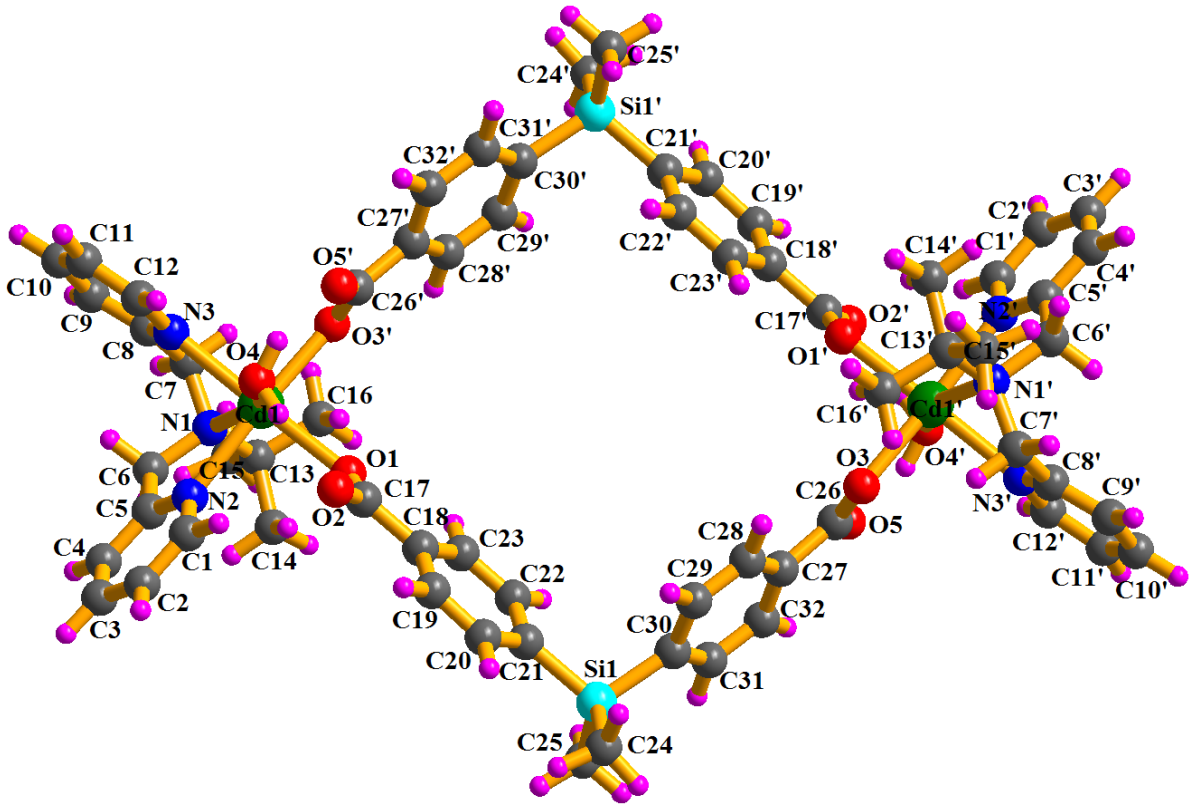


Fig. S2 Structure of molecular square **4** with nonhydrogen atoms labelled; symmetry related atoms are designated with a ‘.

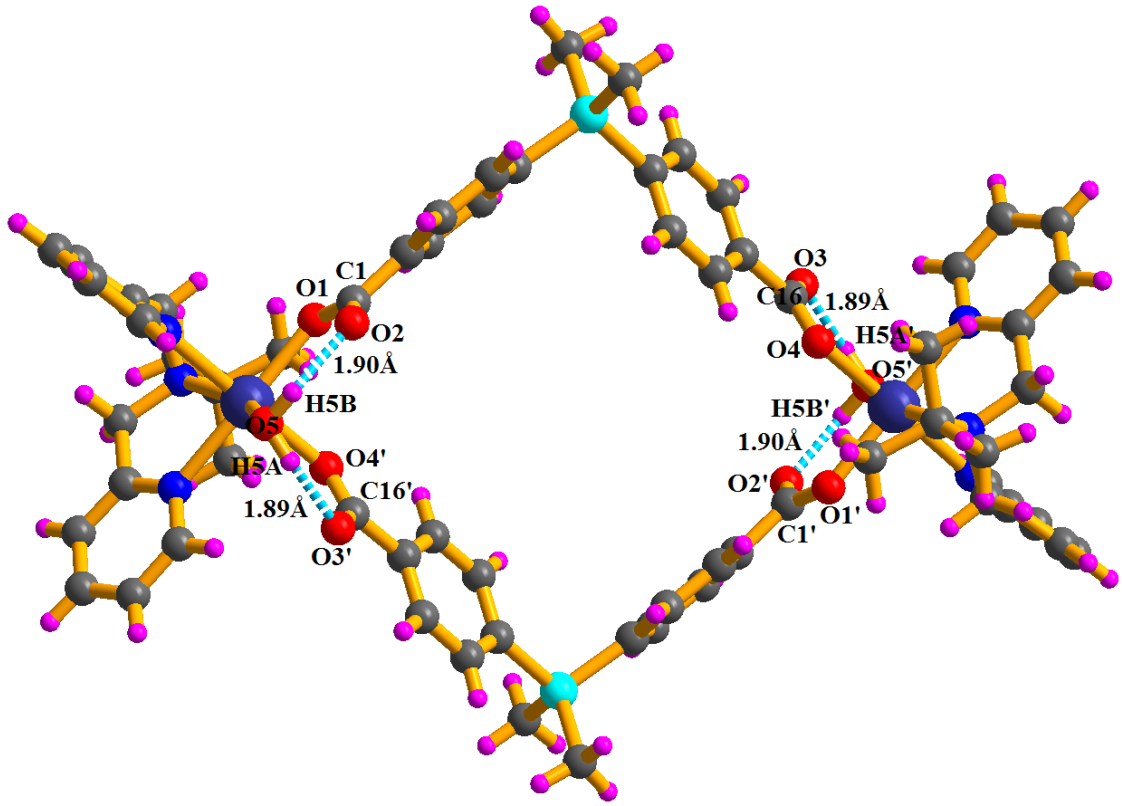


Fig. S3 View of bifurcated intramolecular hydrogen bonding between coordinated water molecule and the carboxylate oxygen atom in **1** forming two six membered rings $R_1^1(6)$.

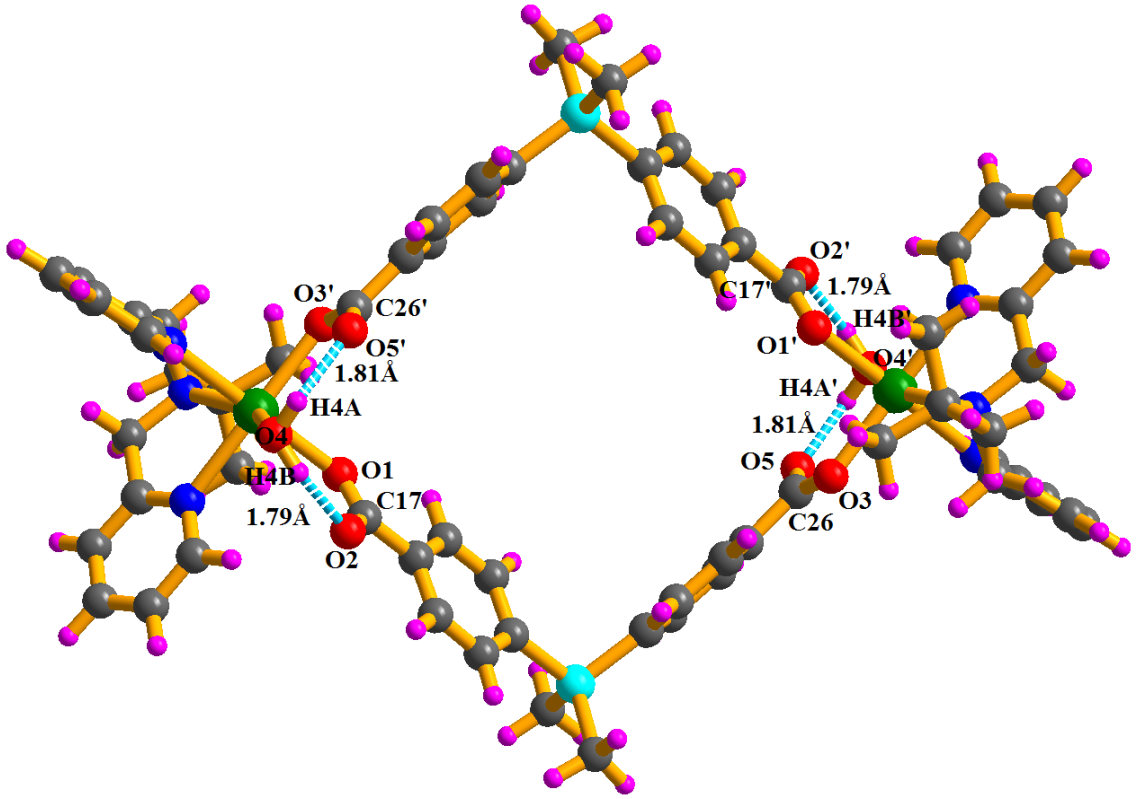


Fig. S4 View of bifurcated intramolecular hydrogen bonding between coordinated water molecule and the carboxylate oxygen atom in **4** forming two six membered rings $R_1^1(6)$.

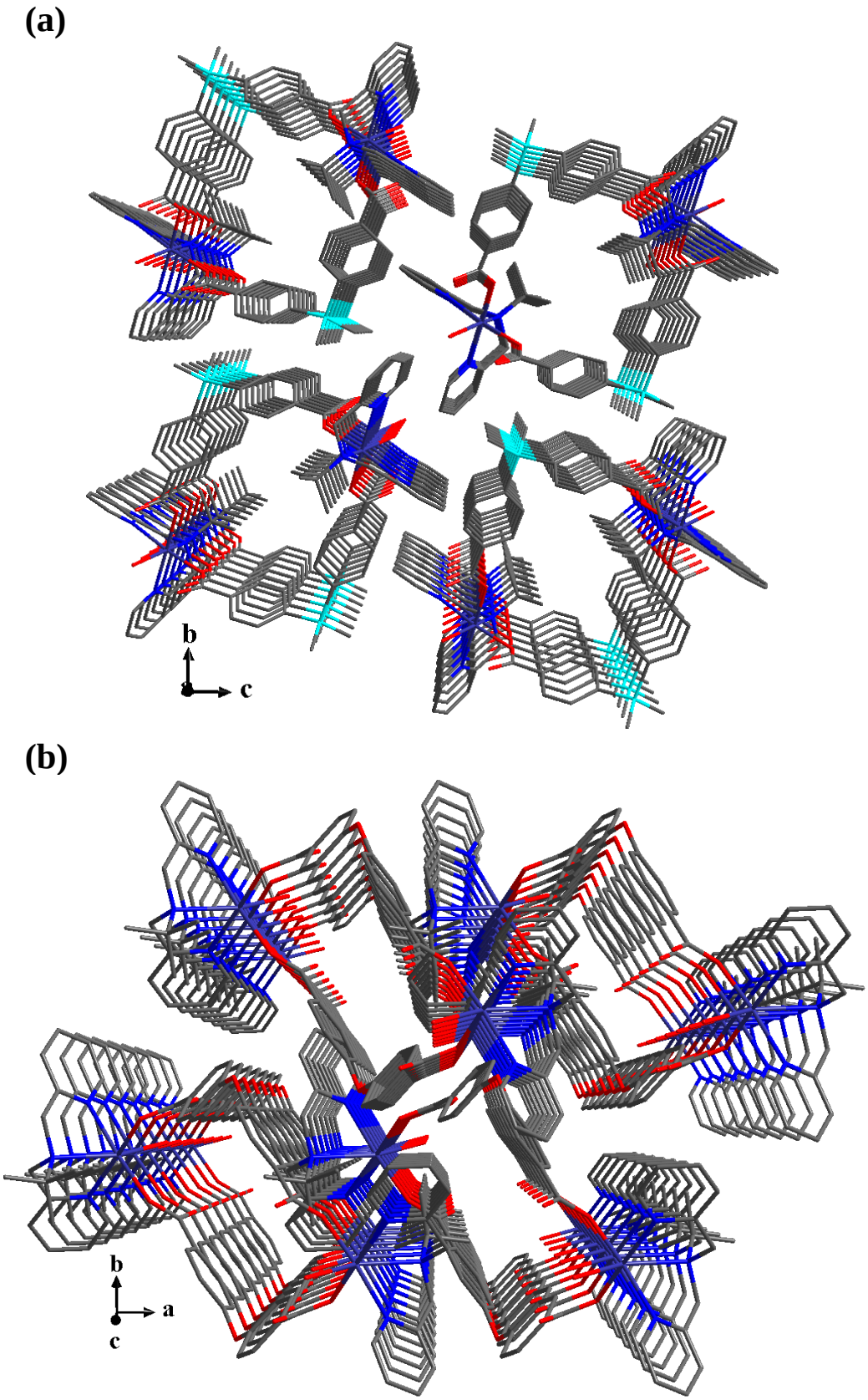


Fig. S5 Packing diagram of the molecular squares in **1** (a) and **5** (b), viewing along the a-axis. All hydrogen atoms are omitted for clarity.

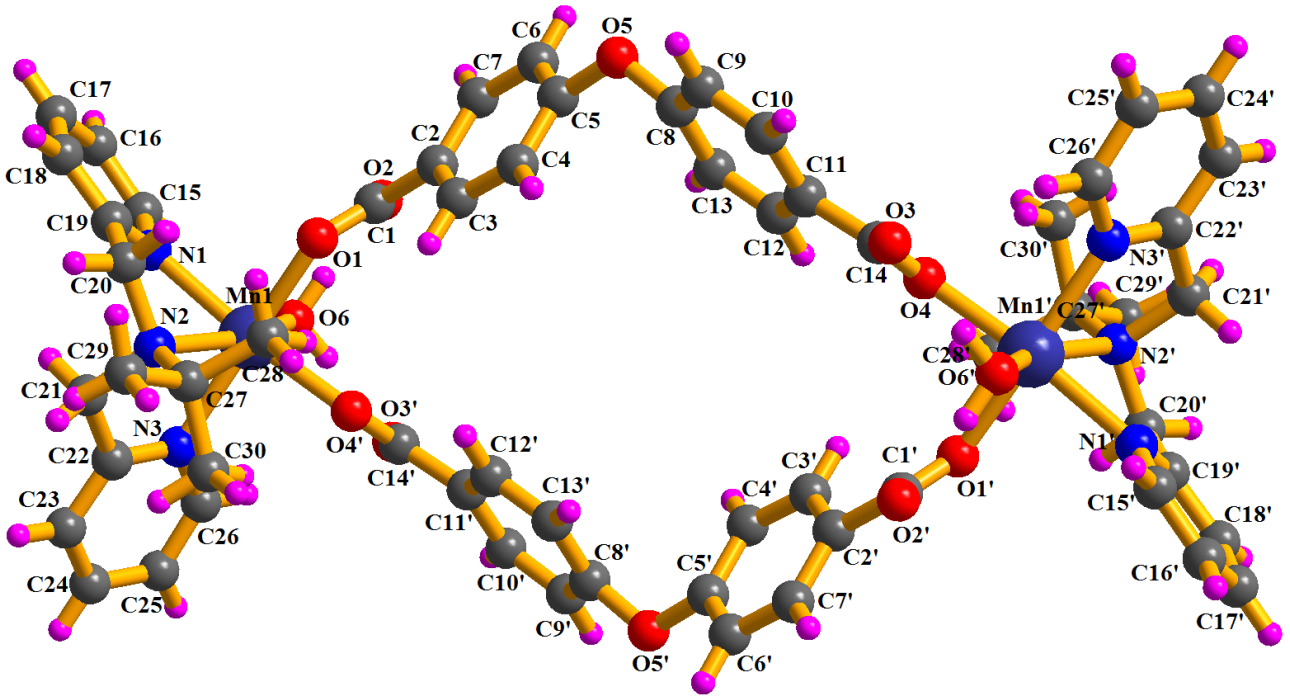


Fig. S6 Structure of molecular square **5** with nonhydrogen atoms labelled; symmetry related atoms are designated with a ‘.

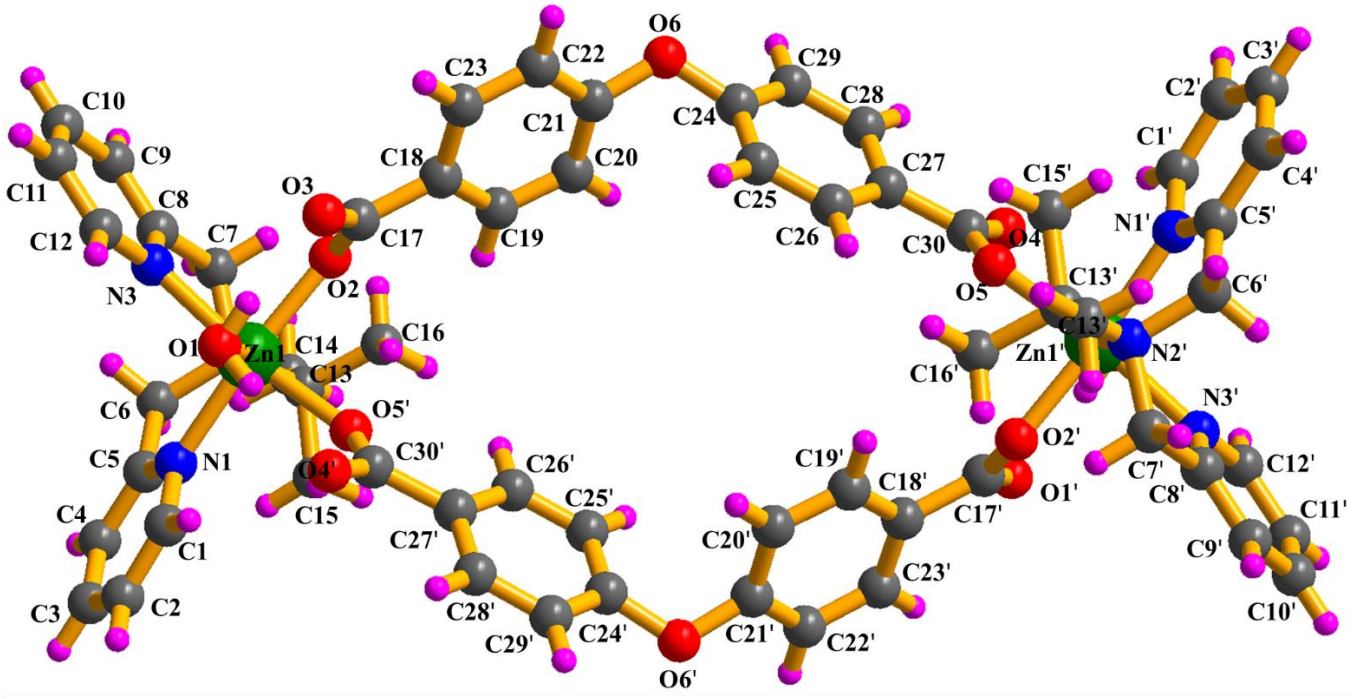


Fig. S7 Structure of molecular square **9** with nonhydrogen atoms labelled; symmetry related atoms are designated with a ‘.

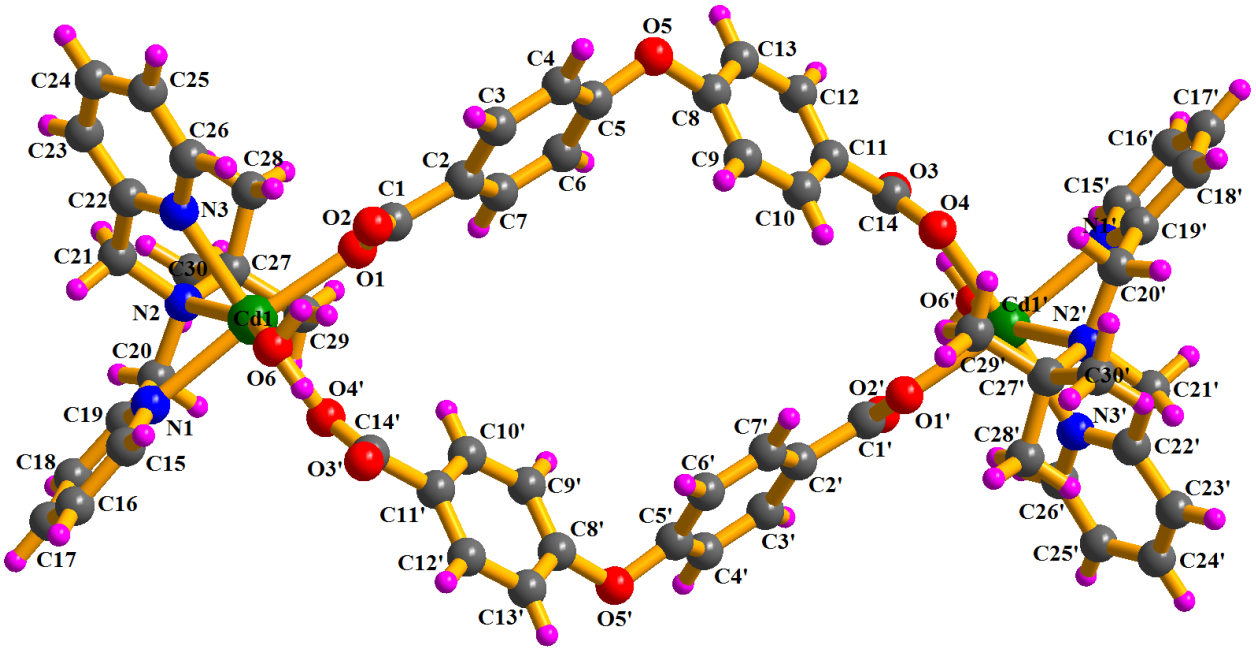


Fig. S8 Structure of molecular square **10** with nonhydrogen atoms labelled; symmetry related atoms are designated with a ‘.

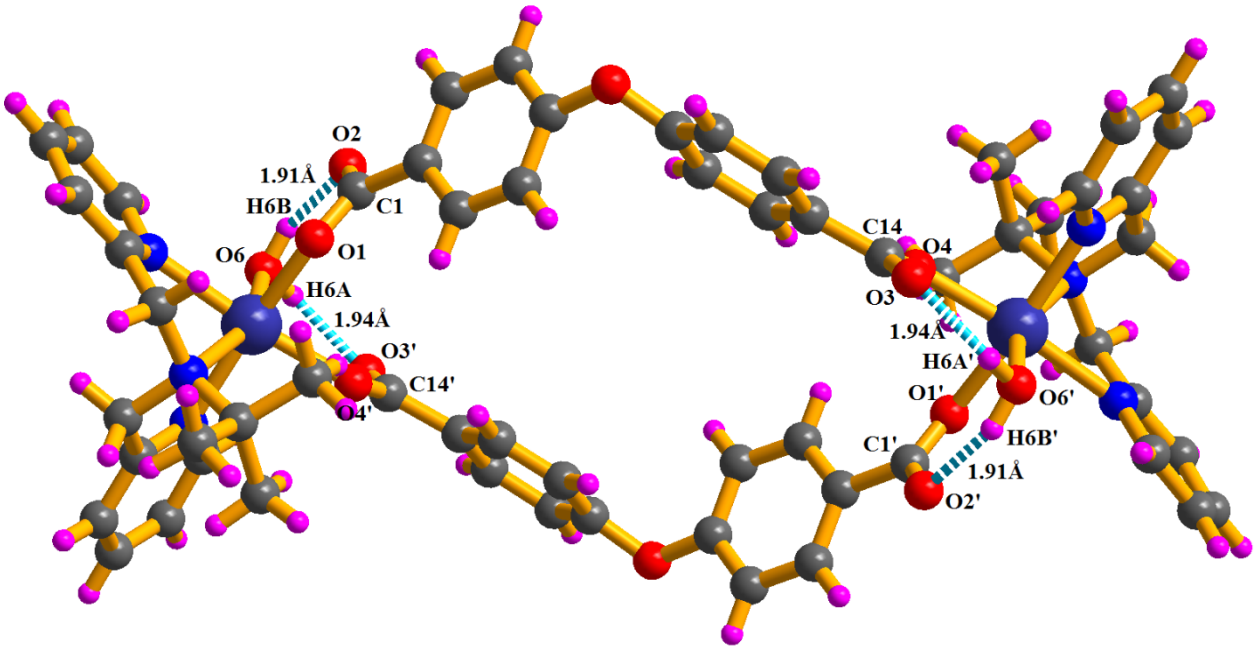


Fig. S9 View of bifurcated intramolecular hydrogen bonding between coordinated water molecule and the carboxylate oxygen atom in **5** forming two six membered rings $R_1^1(6)$.

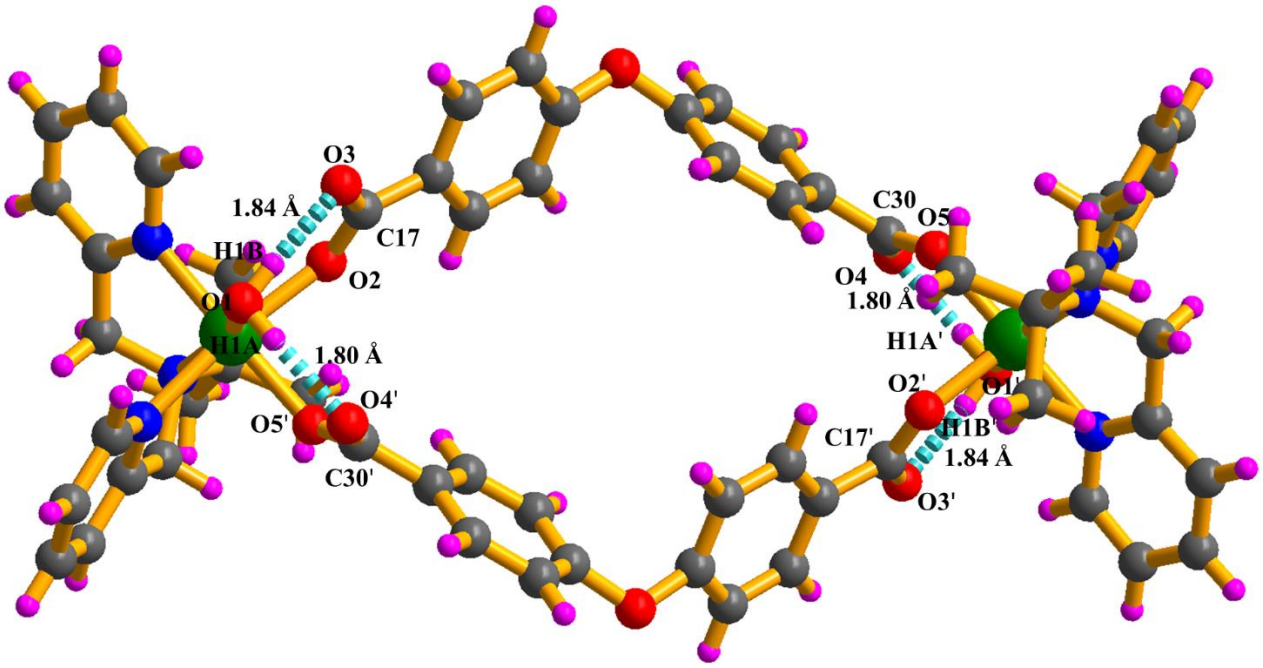


Fig. S10 View of bifurcated intramolecular hydrogen bonding between coordinated water molecule and the carboxylate oxygen atom in **9** forming two six membered rings $R_1^1(6)$.

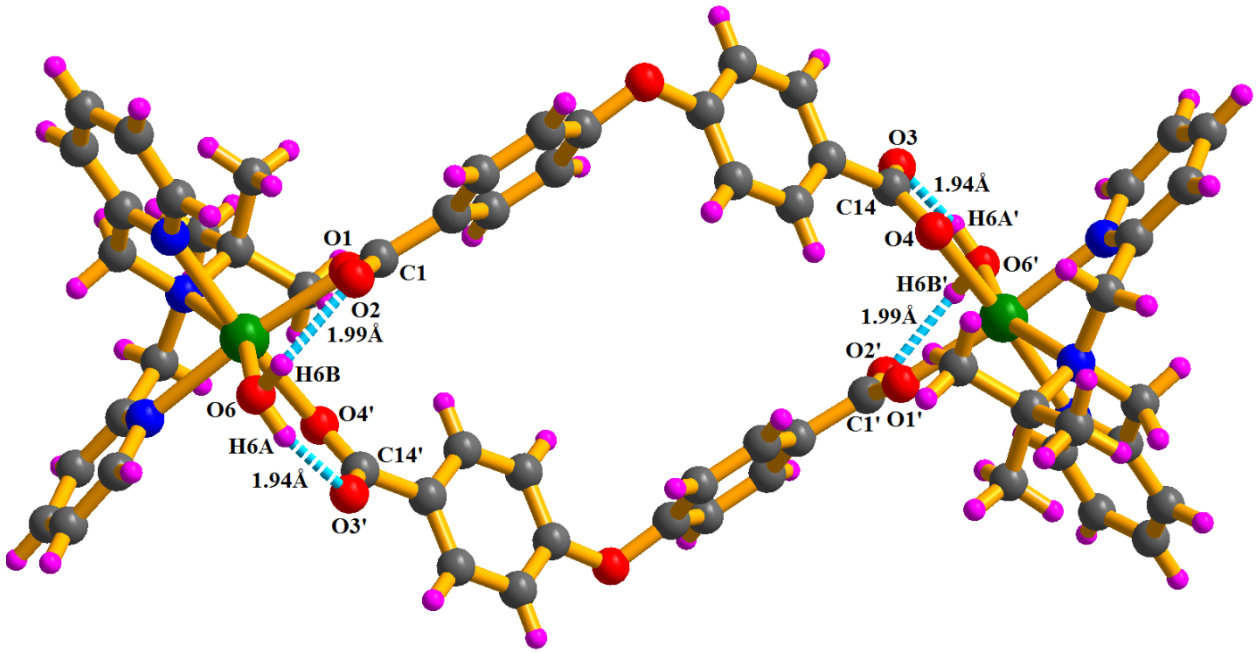


Fig. S11 View of bifurcated intramolecular hydrogen bonding between coordinated water molecule and the carboxylate oxygen atom in **10** forming two six membered rings $R_1^1(6)$.

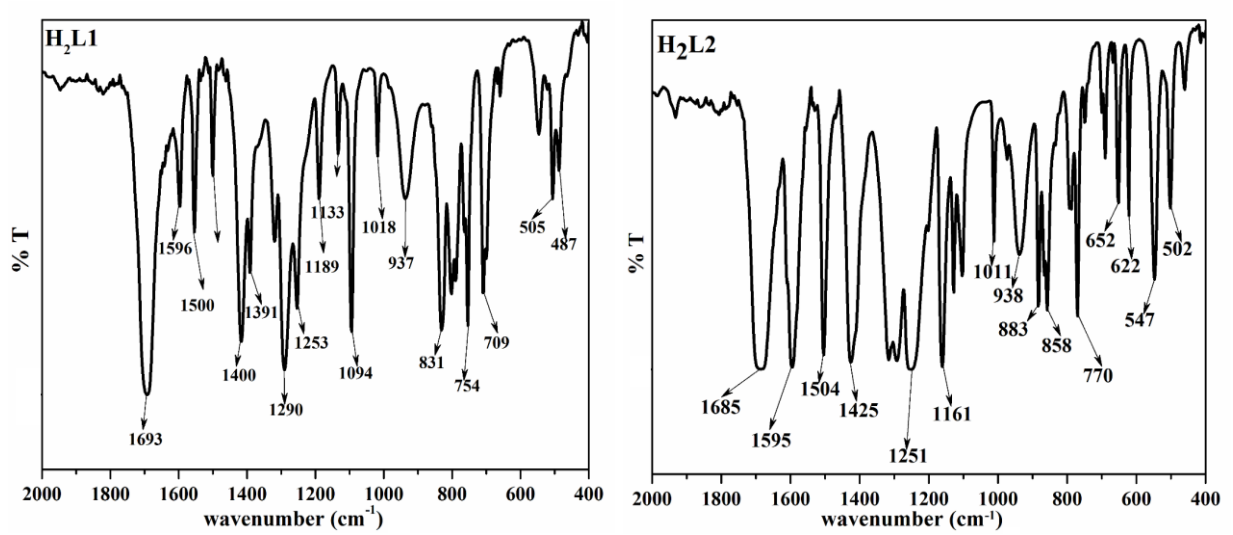


Fig. S12 FTIR spectra of the ligands **H_2L1**, **H_2L2**.

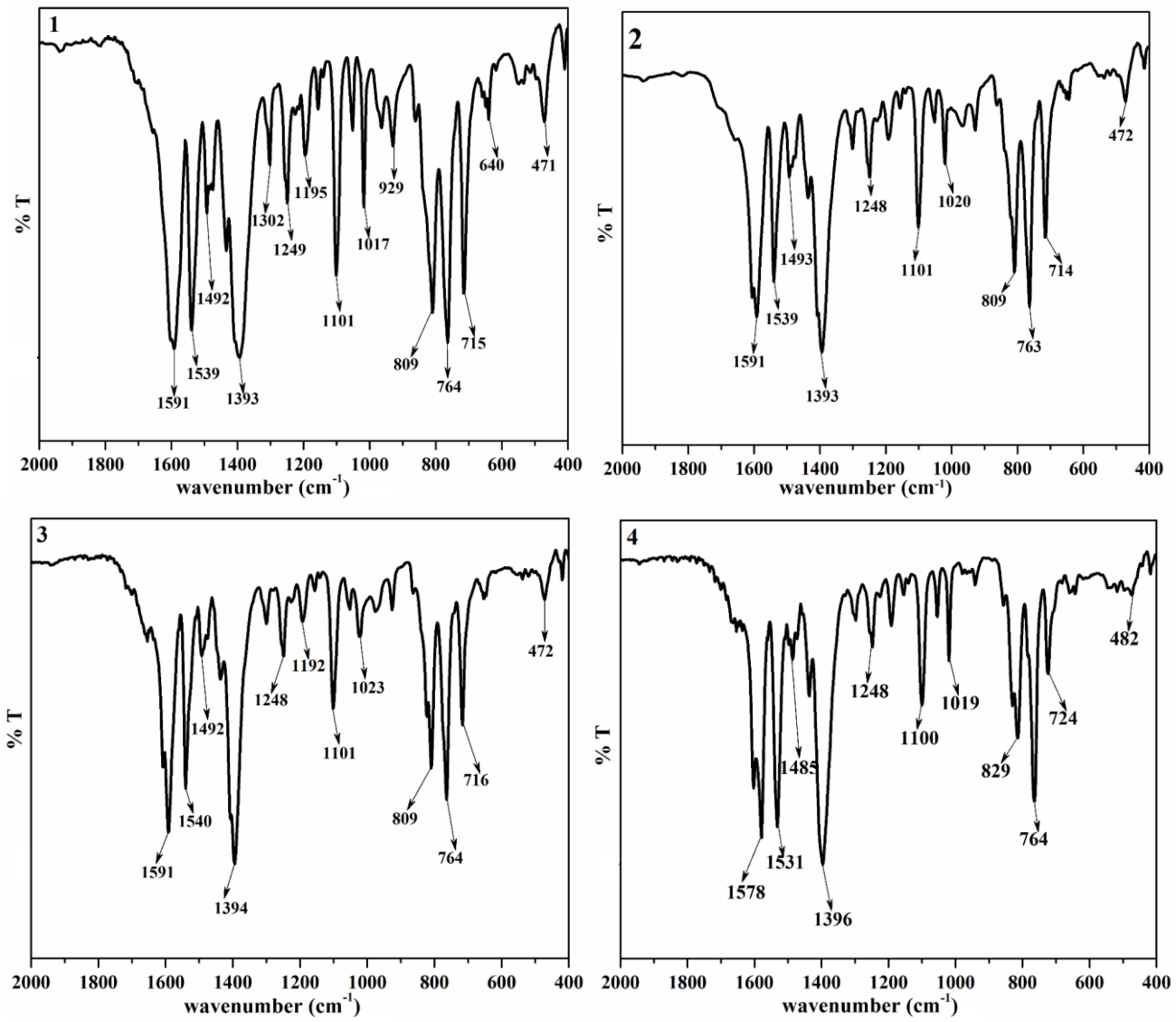


Fig. S13 FTIR spectra of the molecular squares **1-4**.

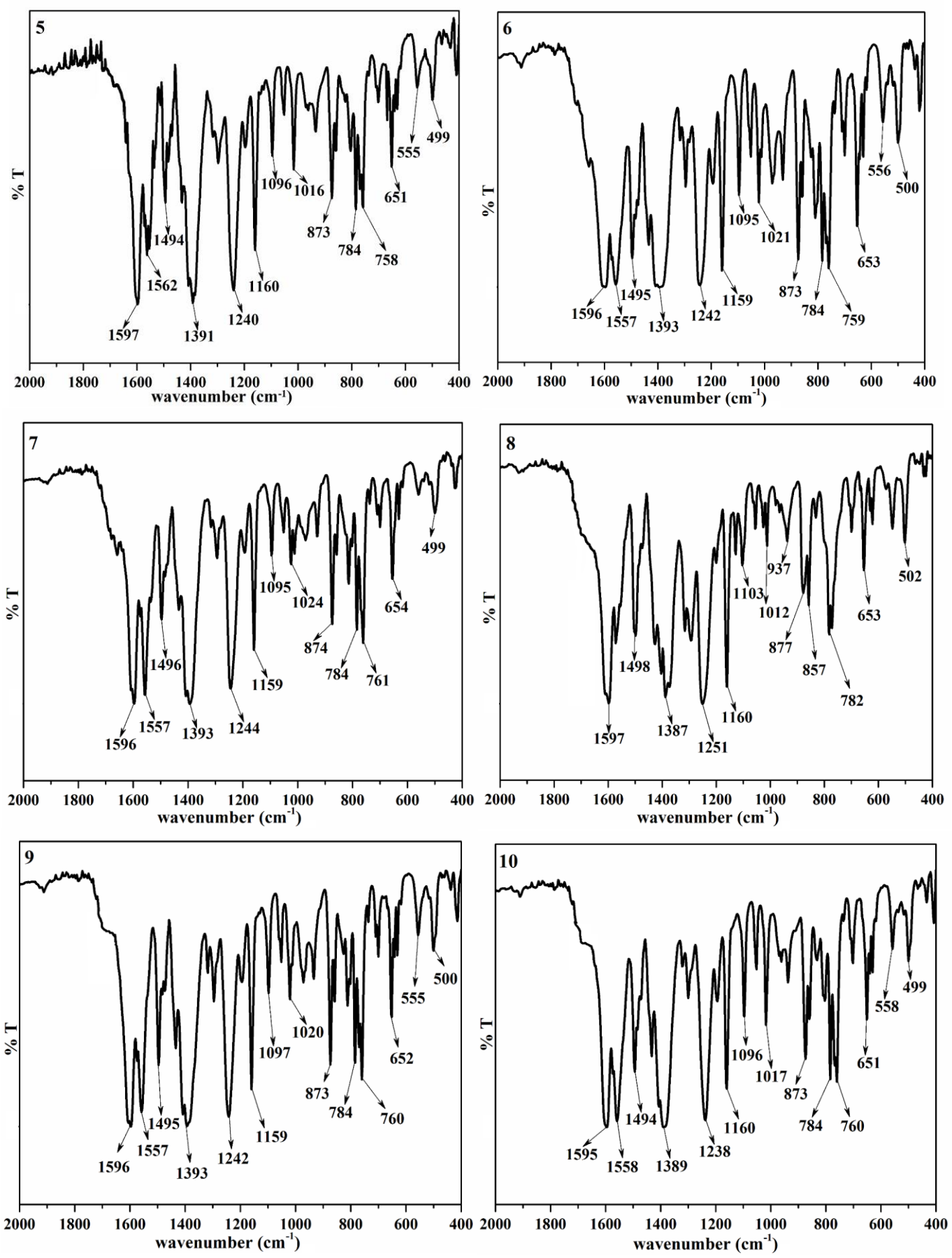


Fig. S14 FTIR spectra of the molecular squares **5**-**10**.

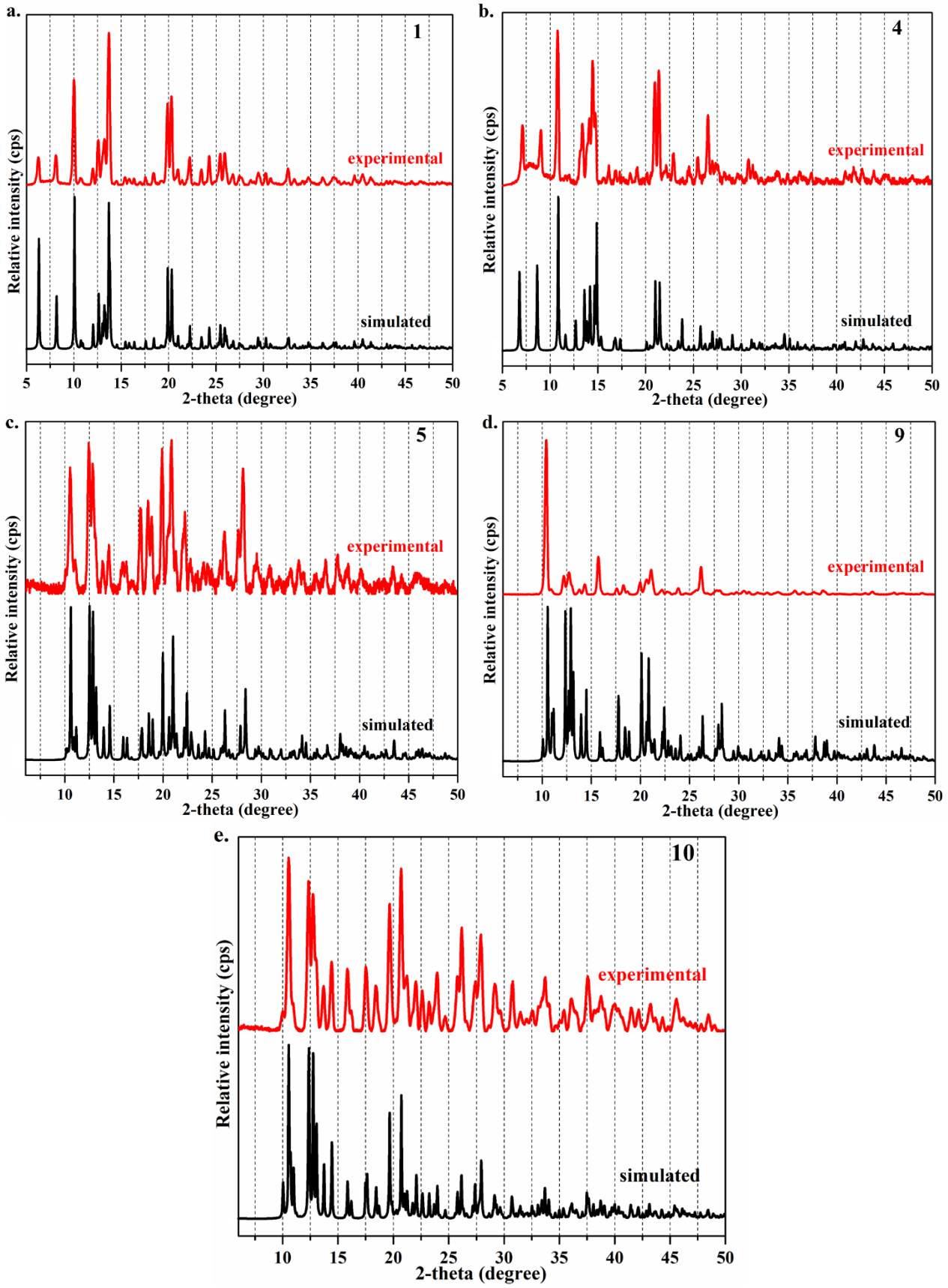


Fig. S15 PXRD patterns of the as-synthesized molecular squares **1** (a), **4** (b), **5** (c), **9** (d) and **10** (e) compared to the corresponding simulated powder patterns obtained from single crystal structures.

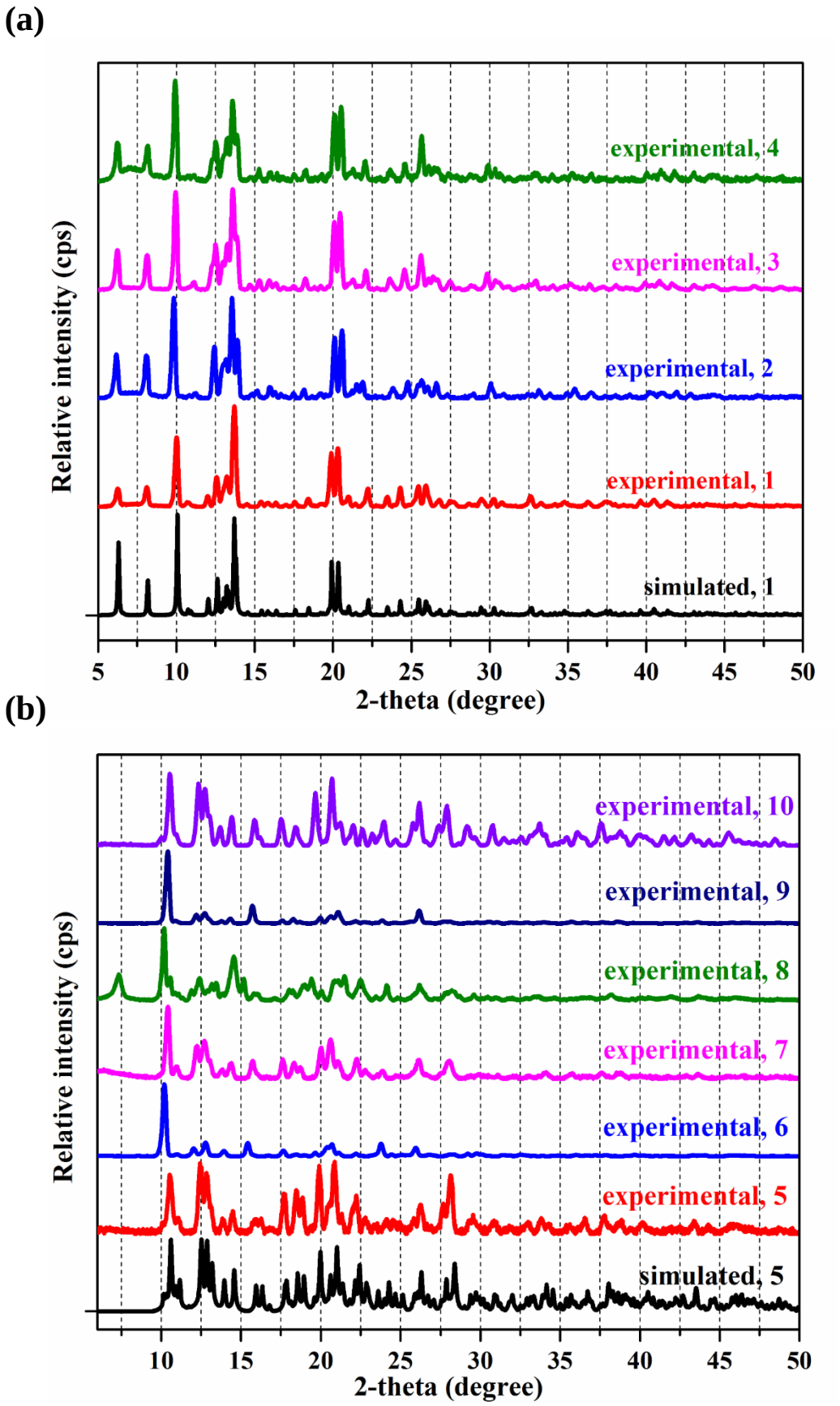


Fig. S16 Powder X-ray diffraction patterns of the as synthesized samples of (a) **1**-**4** and (b) **5**-**10** compared to the simulated powder patterns obtained from the single crystal structures of **1** and **5**, respectively.

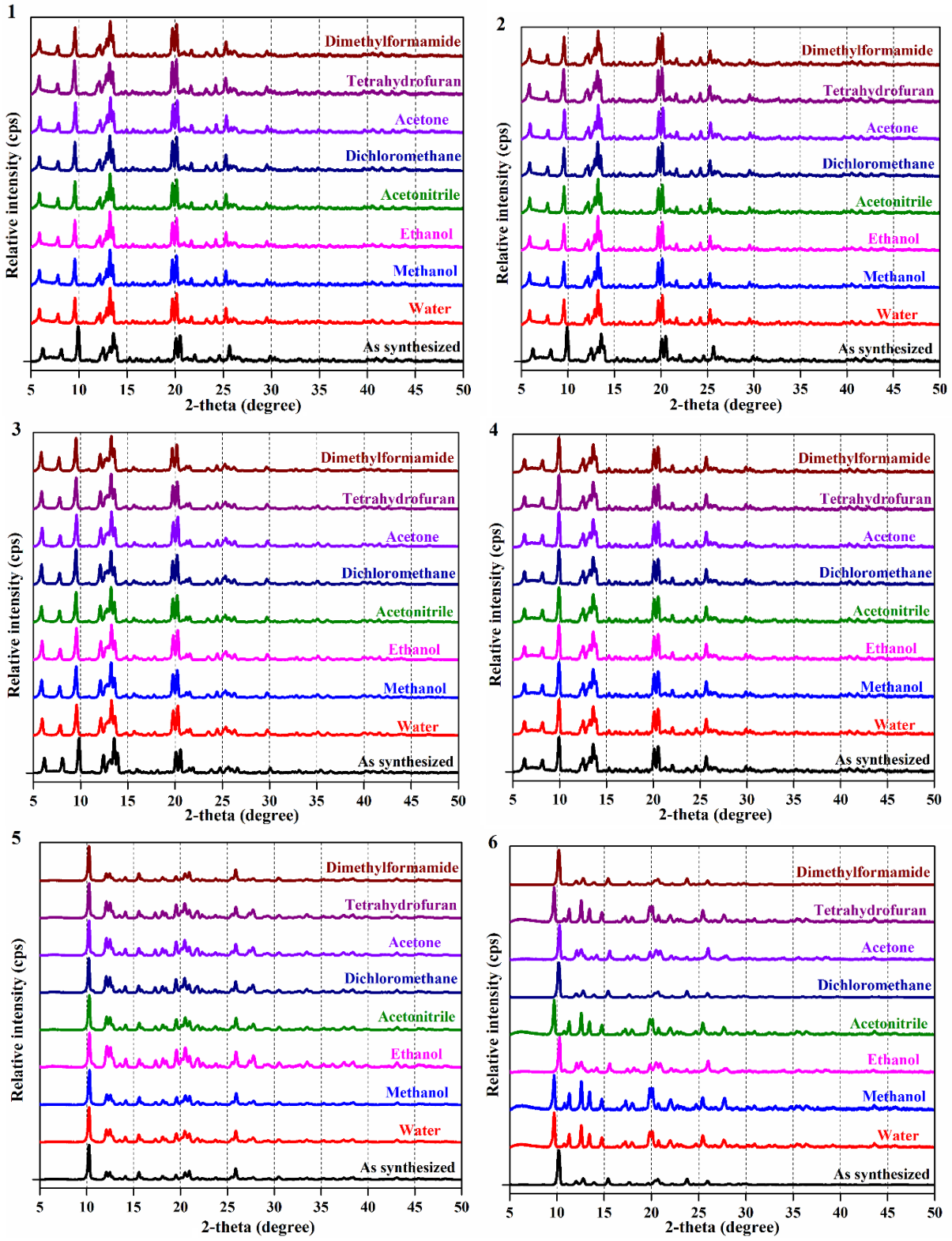


Fig. S17 PXRD pattern of **1-6** after socking in different solvents compared with their as synthesized powder pattern.

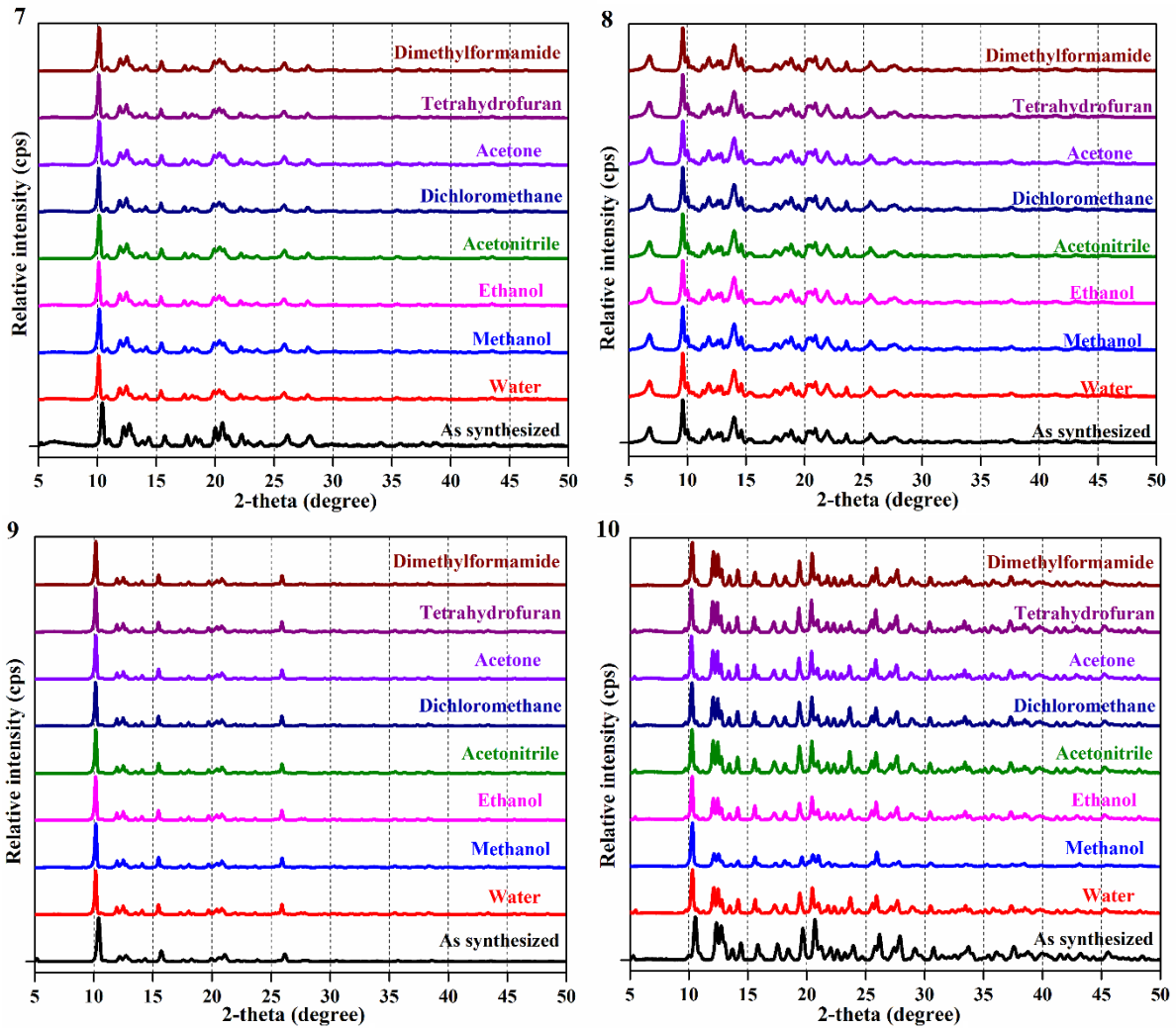


Fig. S18 PXRD pattern of **7-10** after socking in different solvents compared with their as synthesized powder pattern.

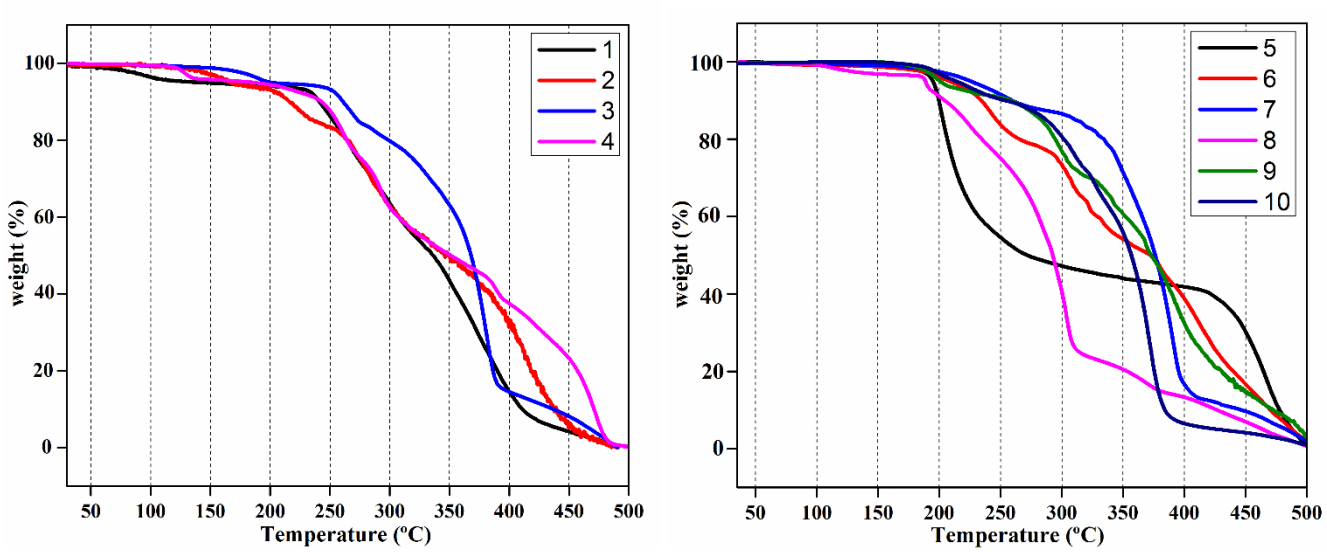


Fig. S19 TGA scans for **1-4** (left) and **5-10** (right).

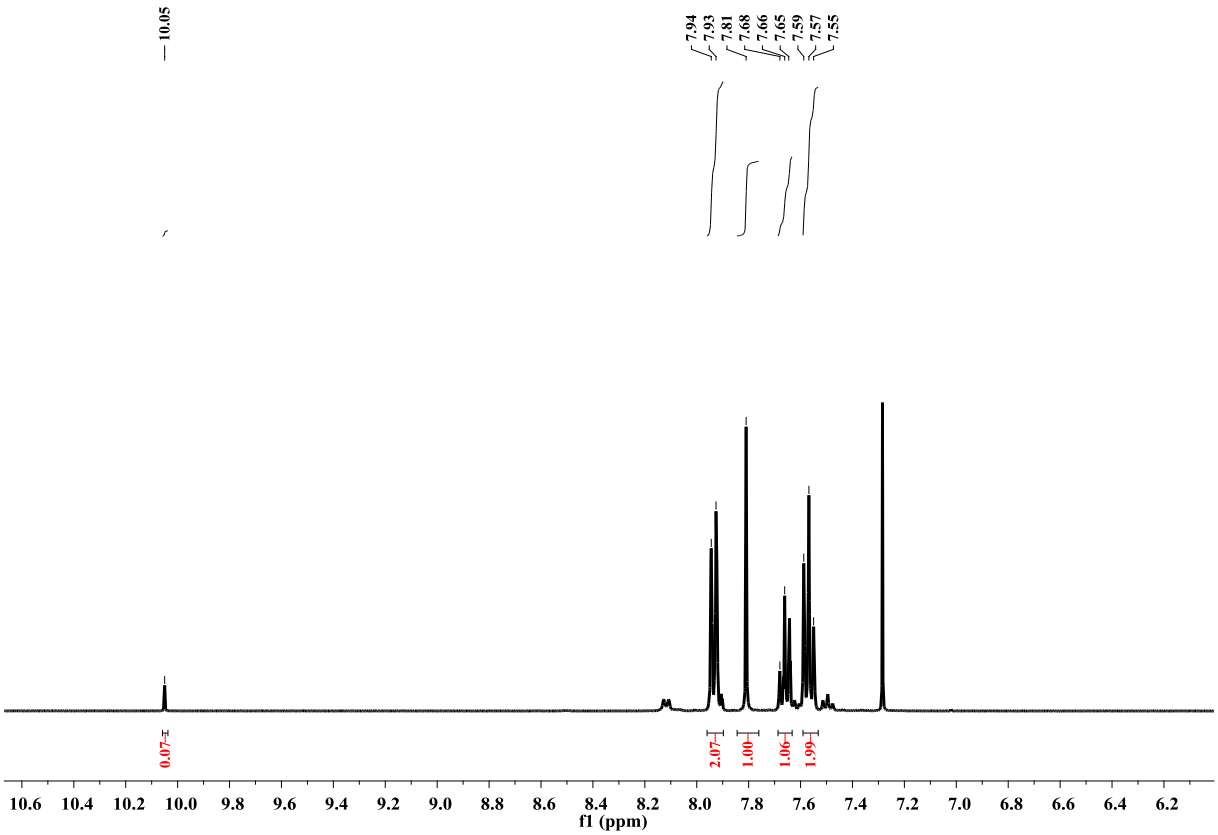


Fig. S20 Example of integration in the ^{1}H NMR spectrum for the determination of conversion in Knoevenagel condensation reaction of benzaldehyde with malononitrile (Table 1, entry 1)

Calculation of the product yield in the Knoevenagel condensation reaction of benzaldehyde with malononitrile catalyzed by 1

Total amount of compounds at the end (see Fig. S20):
Unreacted bezaldehyde (10.05 ppm) + 2-benzylidenemalononitrile (7.81 ppm) = 0.07 + 1.00 = 1.07
Yield of 2-benzylidenemalononitrile = (1/1.07) * 100 = 93.45 %.

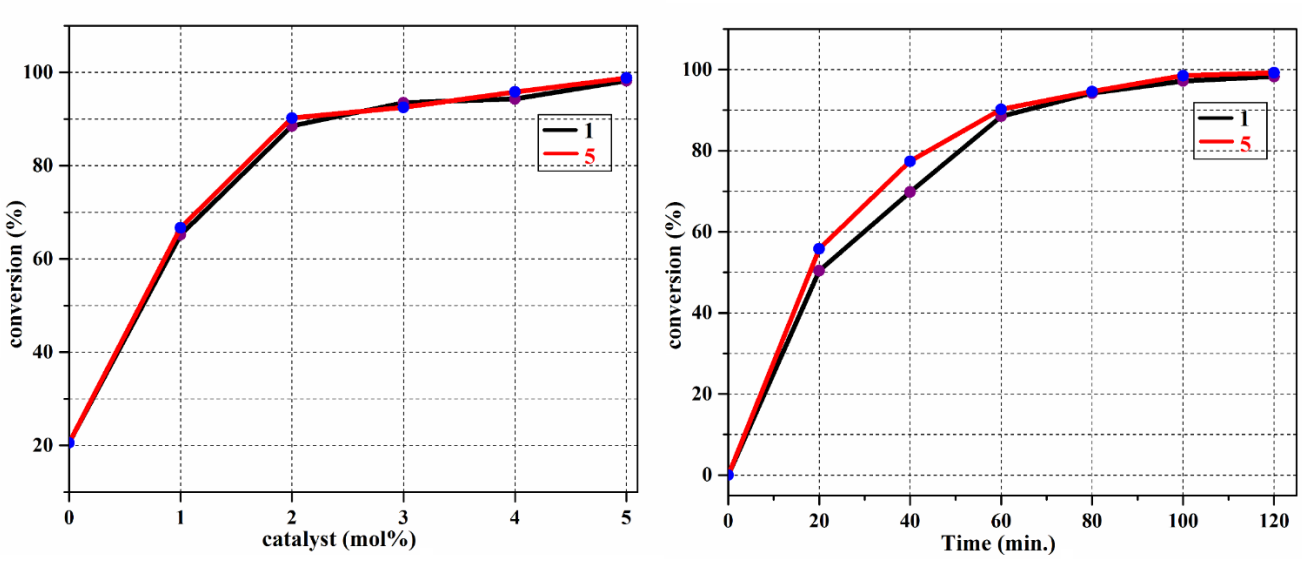


Fig. S21 Plot of % conversion versus catalyst amount (left) and time (right) for the Knoevenagel condensation reaction of benzaldehyde and malononitrile catalysed by **1** and **5**.

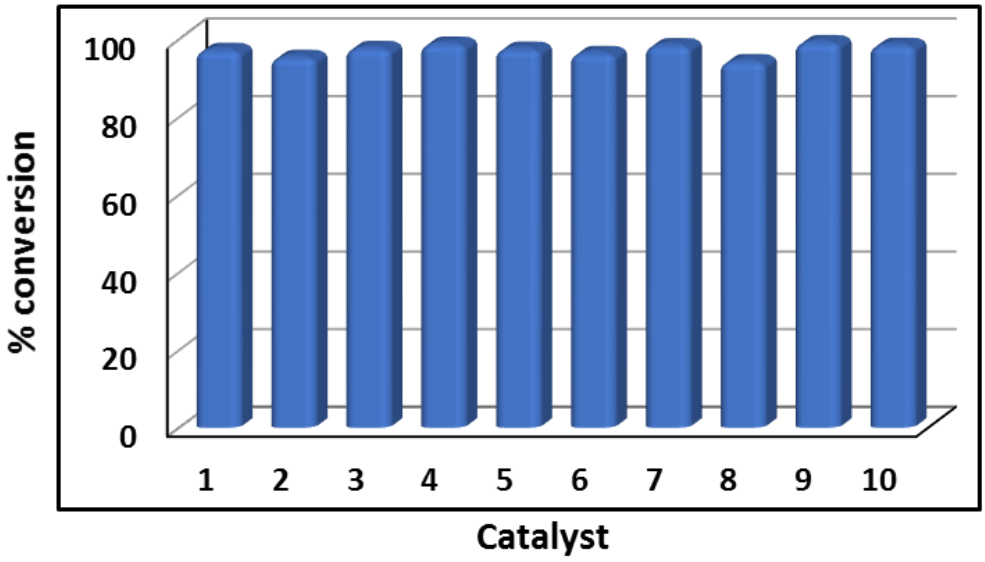


Fig. S22 % Conversion for the Knoevenagel condensation reaction of benzaldehyde and malononitrile catalysed by **1**-**10**.

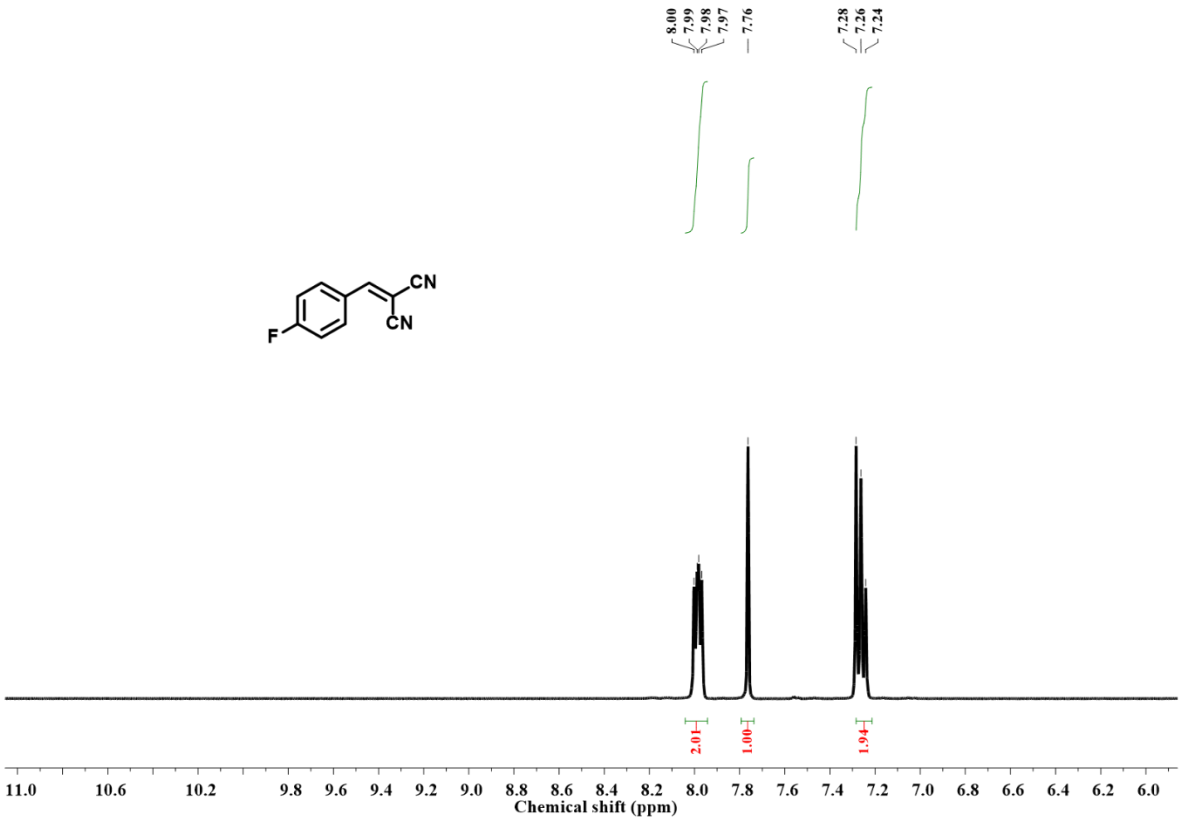


Fig. S23 ^{1}H NMR spectrum of 2-(4-fluorobenzylidene)malononitrile.

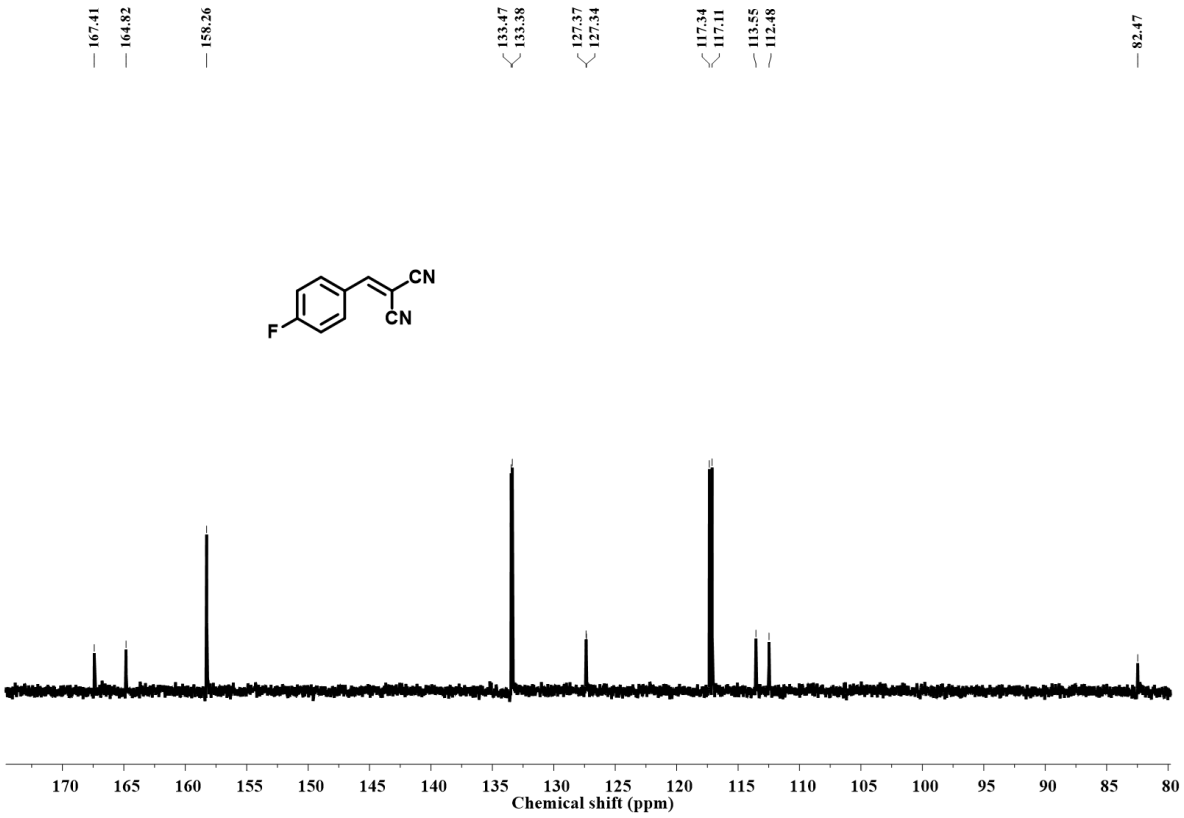


Fig. S24 ^{13}C NMR spectrum of 2-(4-fluorobenzylidene)malononitrile.

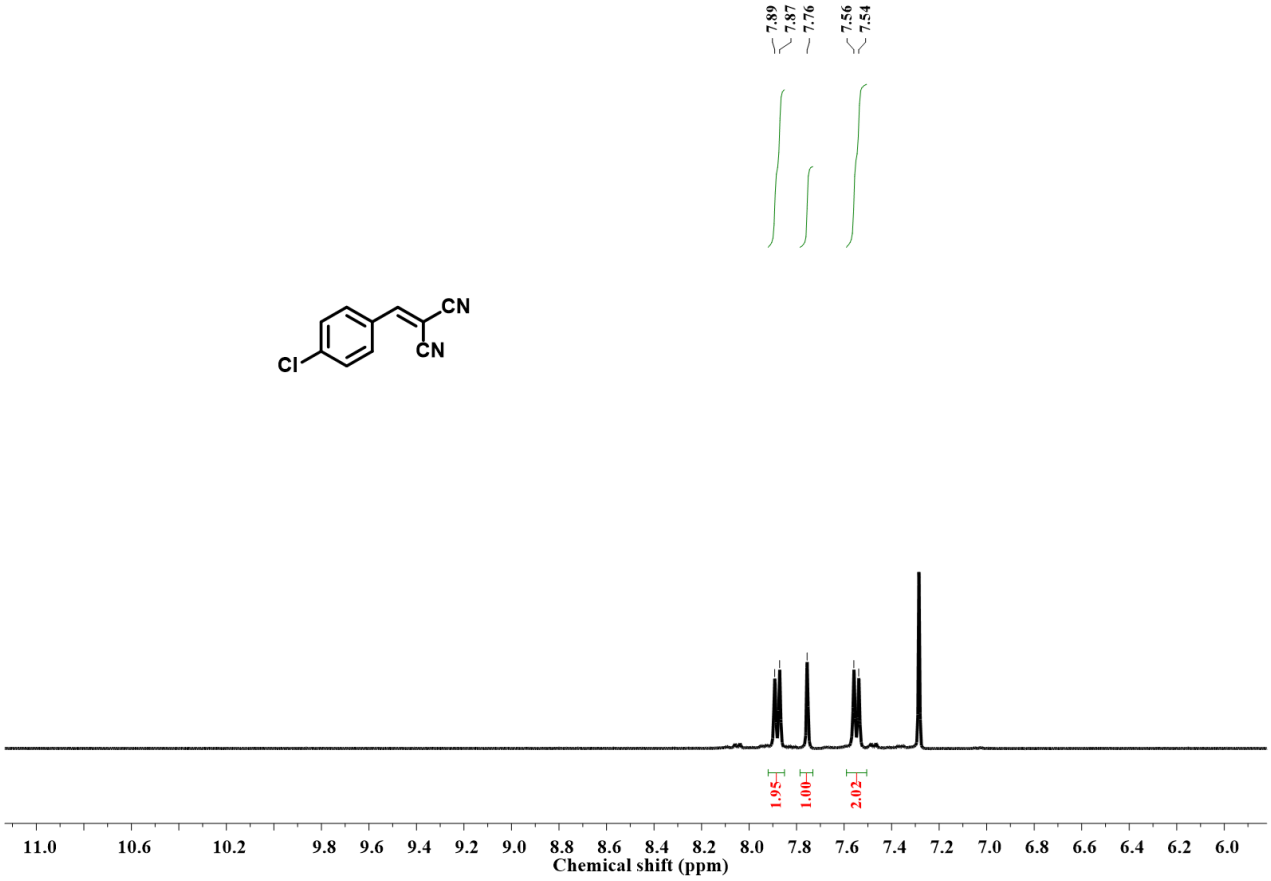


Fig. S25 ^{1}H NMR spectrum of 2-(4-chlorobenzylidene)malononitrile.

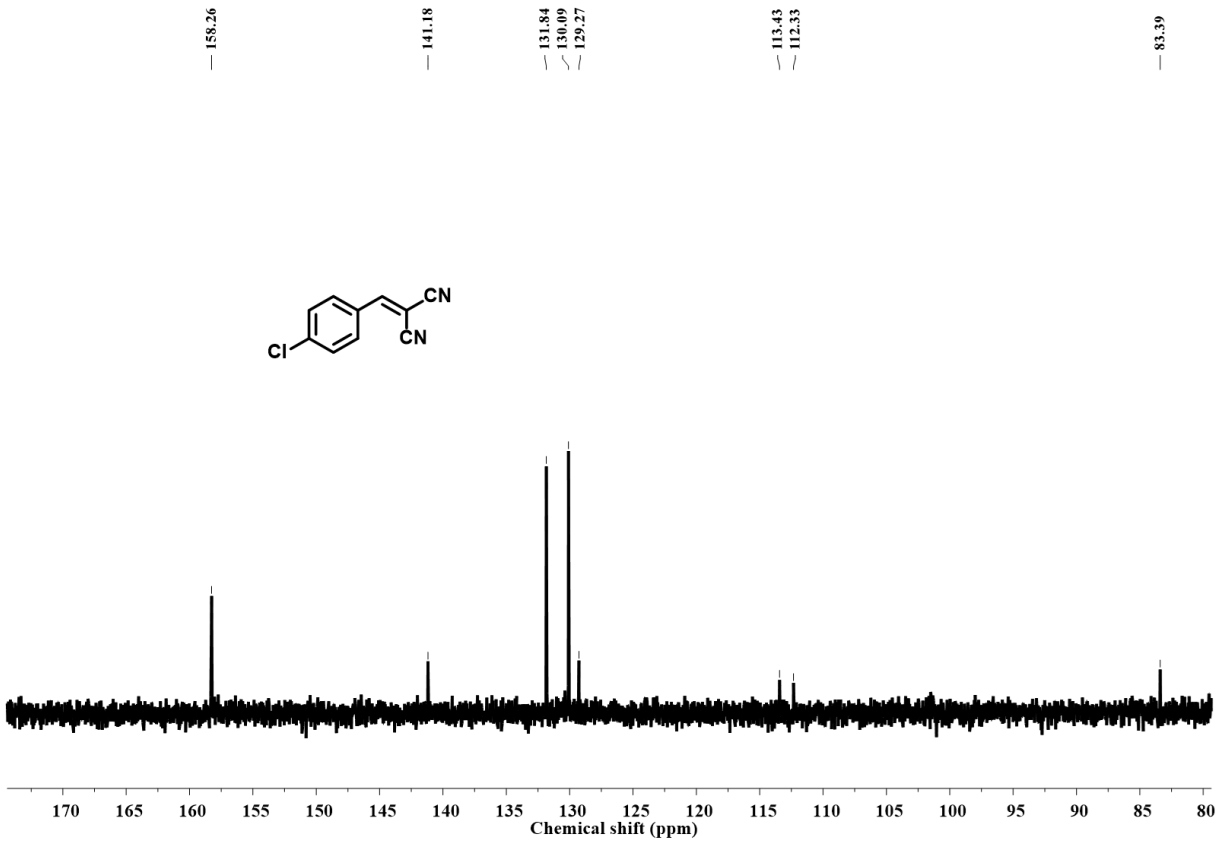


Fig. S26 ^{13}C NMR spectrum of 2-(4-chlorobenzylidene)malononitrile.

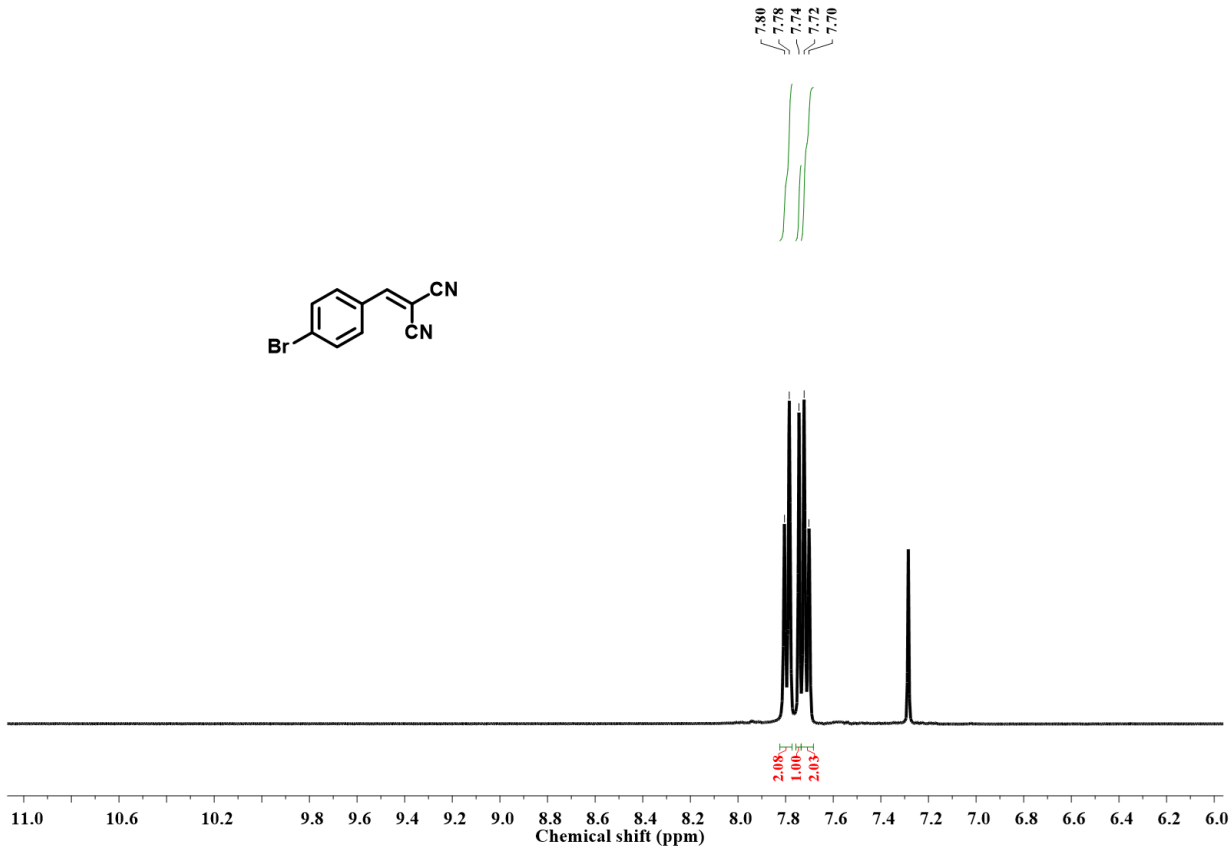


Fig. S27 ^{1}H NMR spectrum of 2-(4-bromobenzylidene)malononitrile.

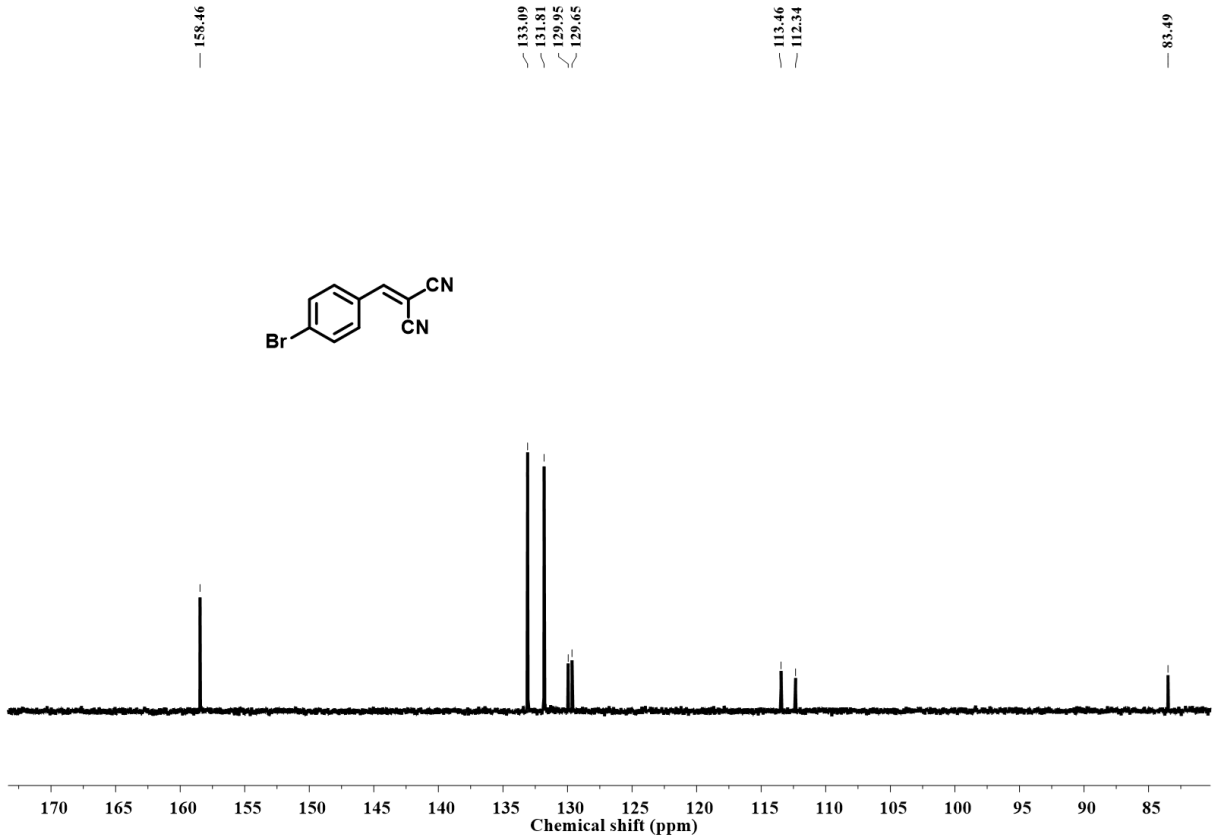


Fig. S28 ^{13}C NMR spectrum of 2-(4-bromobenzylidene)malononitrile.

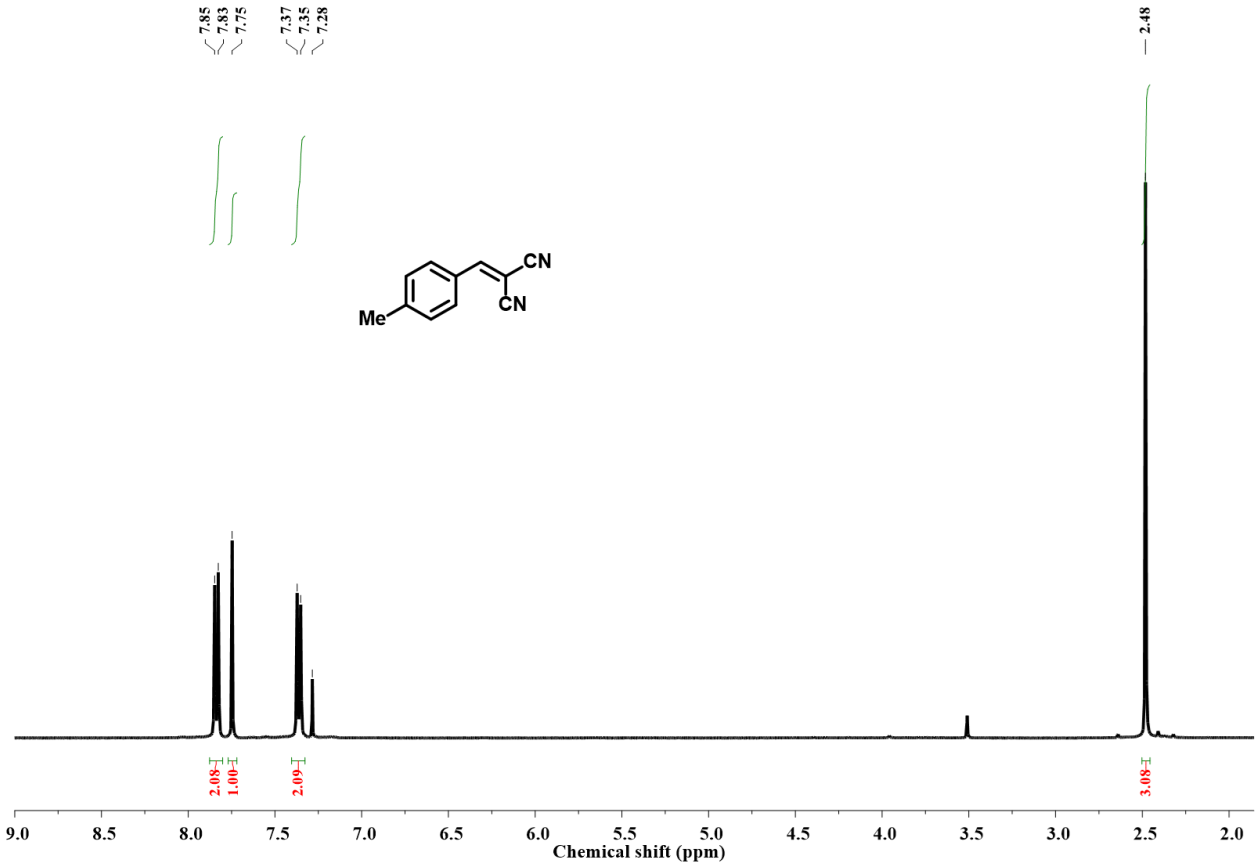


Fig. S29 ^{1}H NMR spectrum of 2-(4-methylbenzylidene)malononitrile.

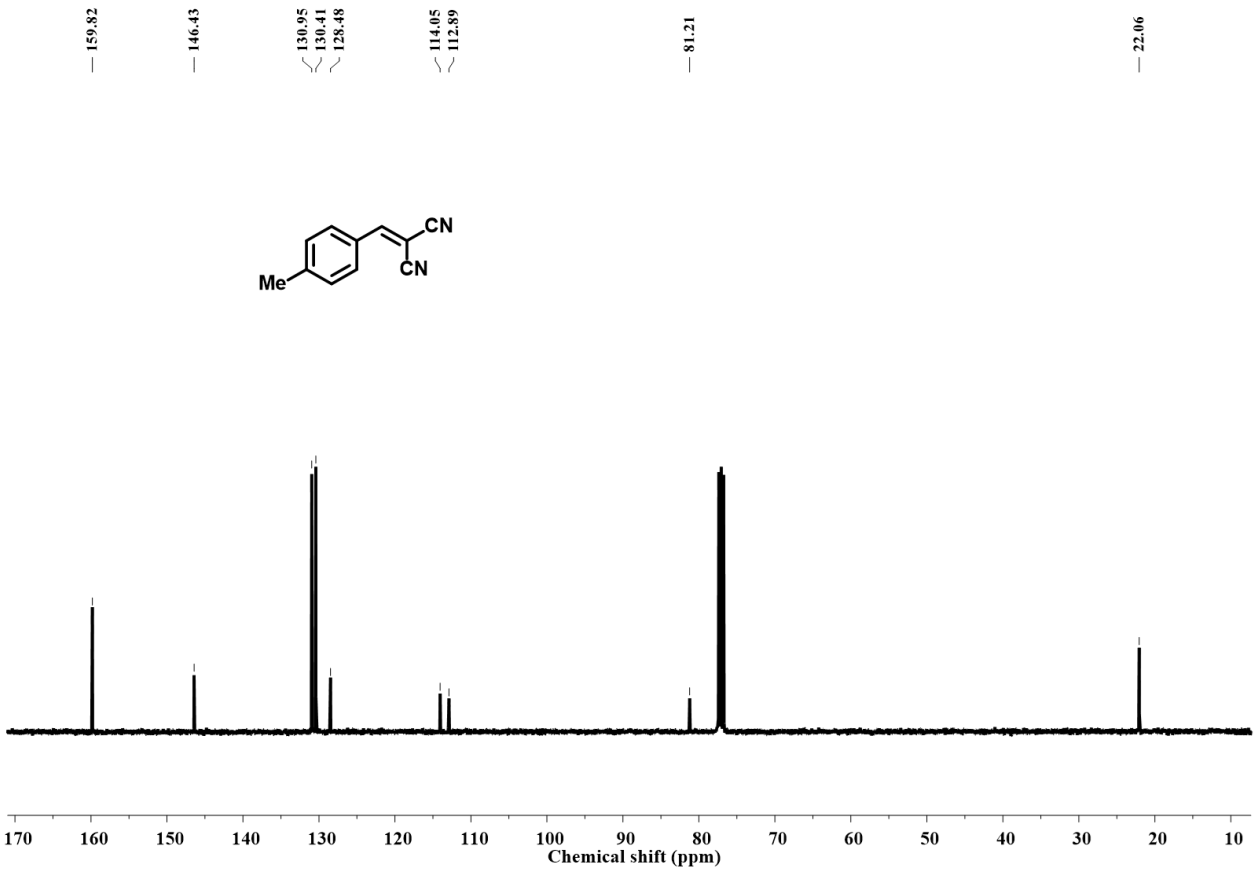


Fig. S30 ^{13}C NMR spectrum of 2-(4-methylbenzylidene)malononitrile.

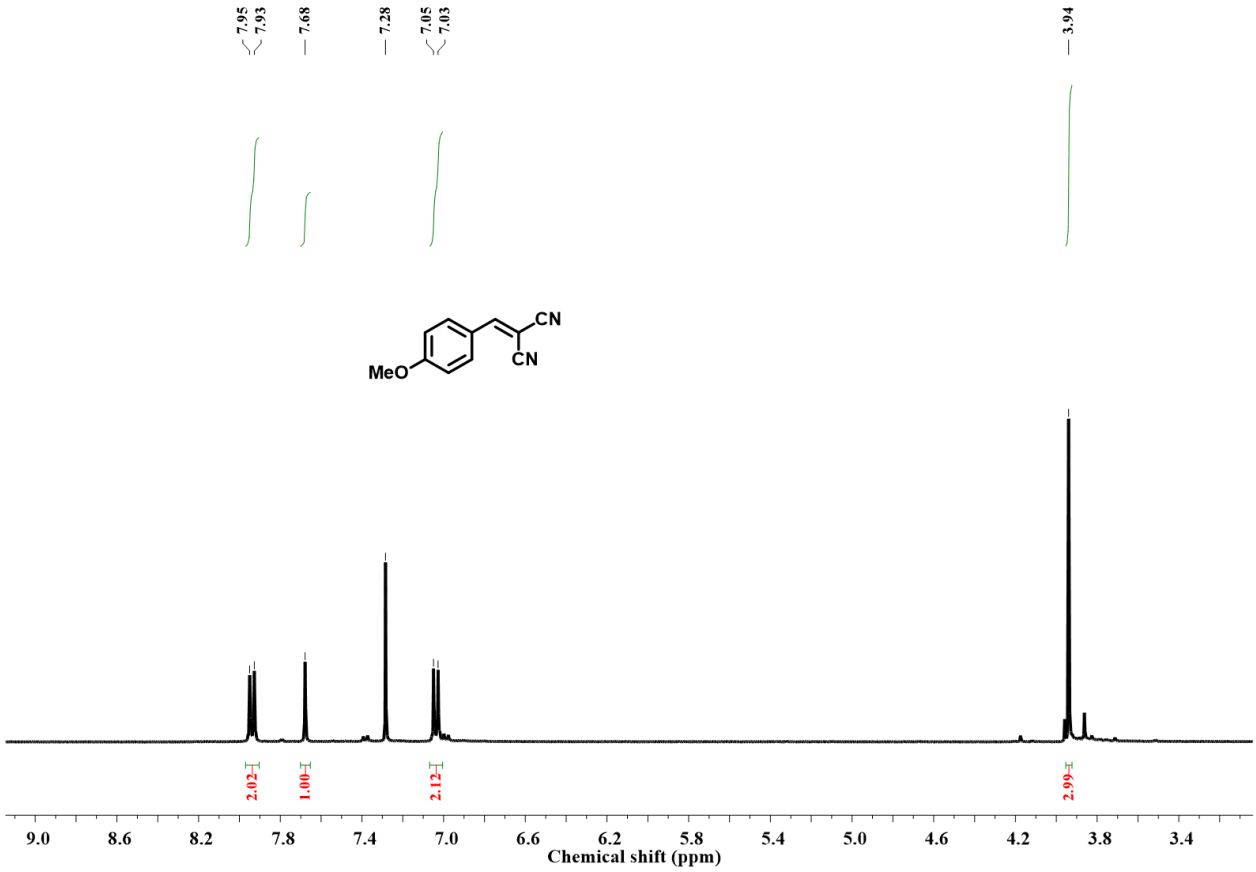


Fig. S31 ^{1}H NMR spectrum of 2-(4-methoxybenzylidene)malononitrile.

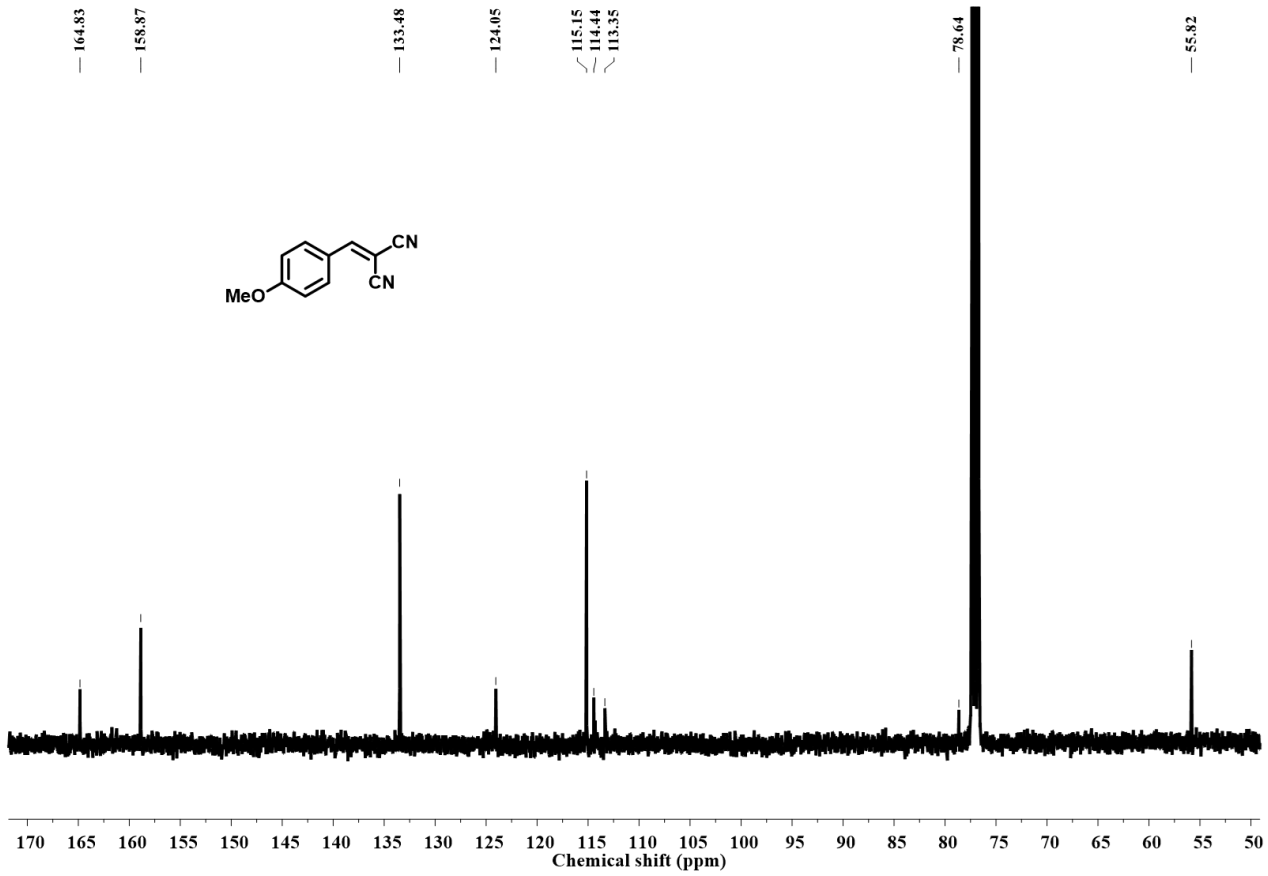


Fig. S32 ^{13}C NMR spectrum of 2-(4-methoxybenzylidene)malononitrile.

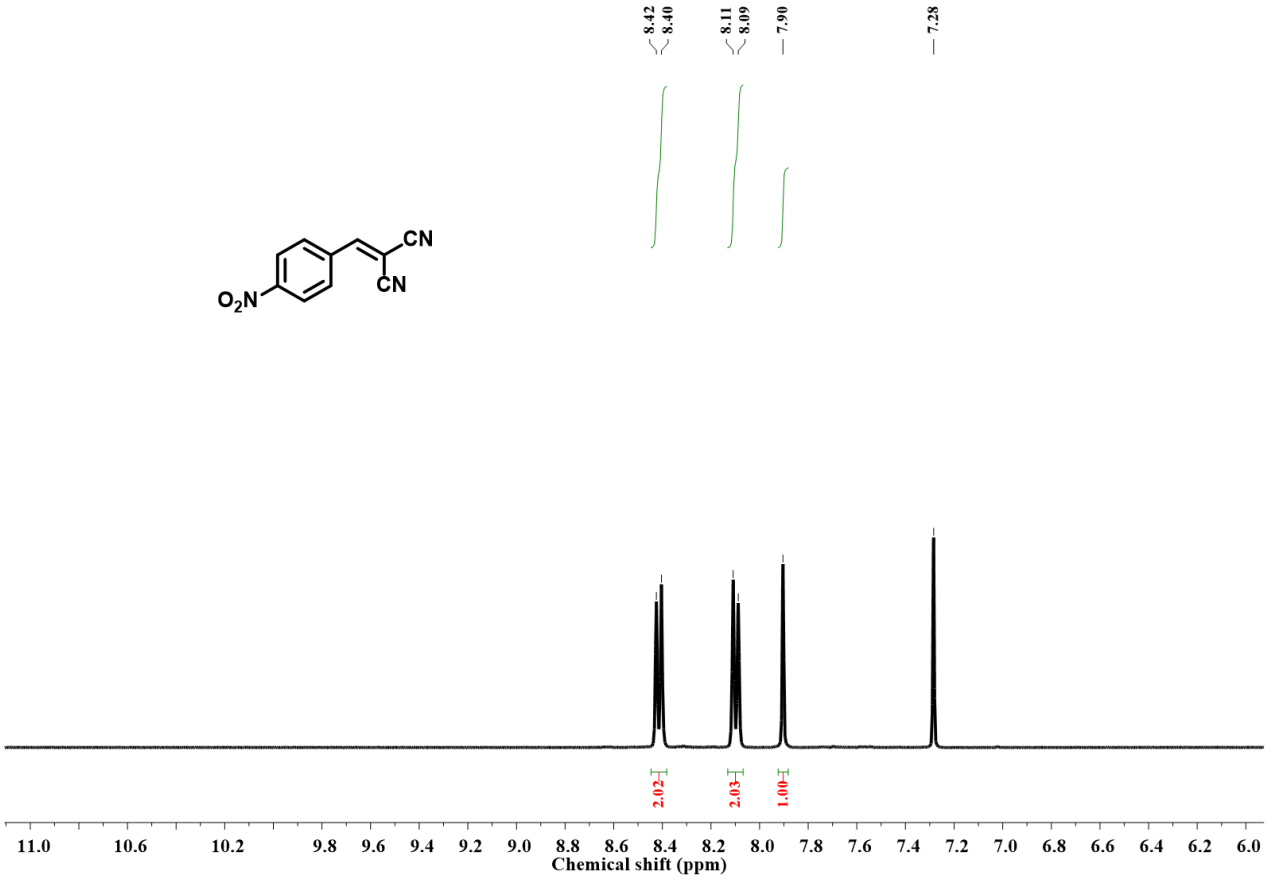


Fig. S33 ^{1}H NMR spectrum of 2-(4-nitrobenzylidene)malononitrile.

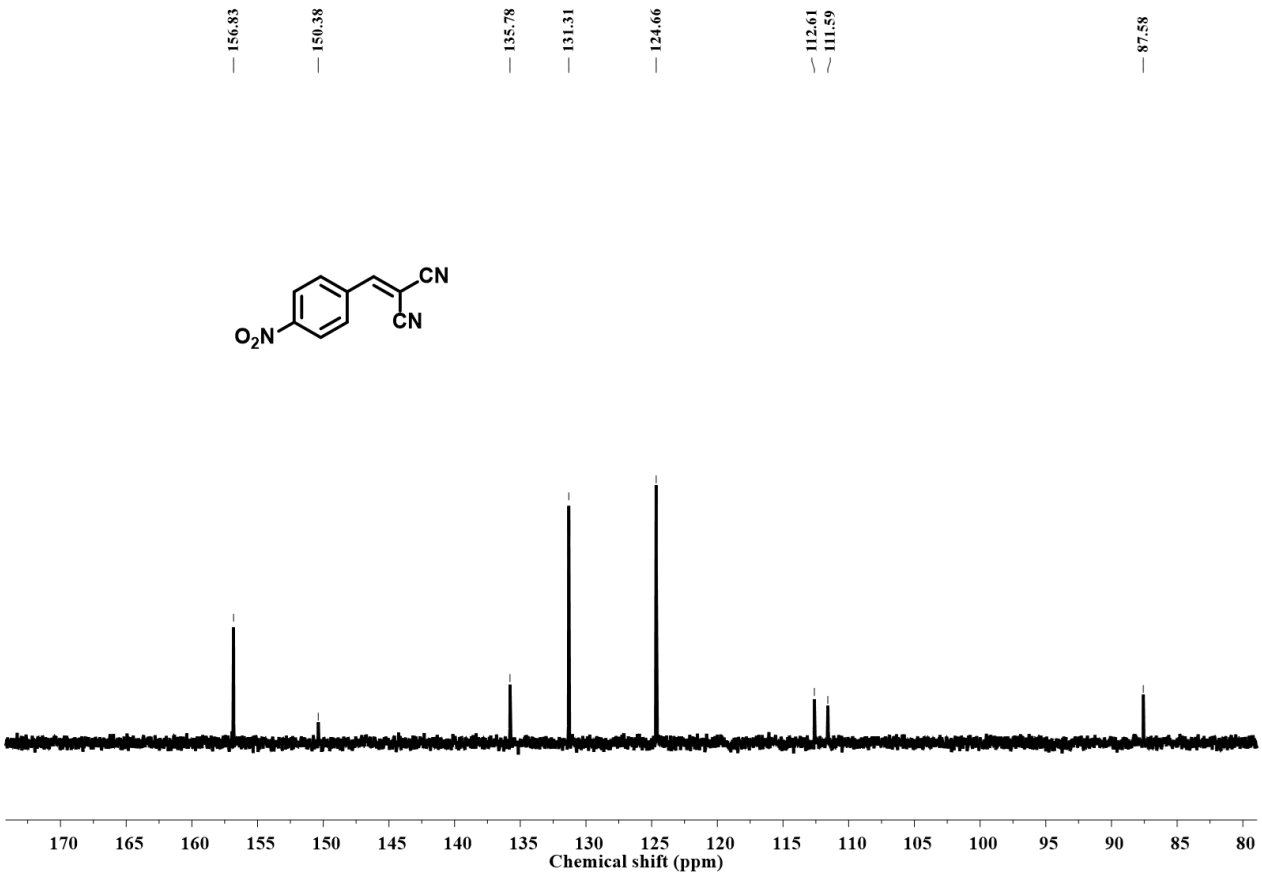


Fig. S34 ^{13}C NMR spectrum of 2-(4-nitrobenzylidene)malononitrile.

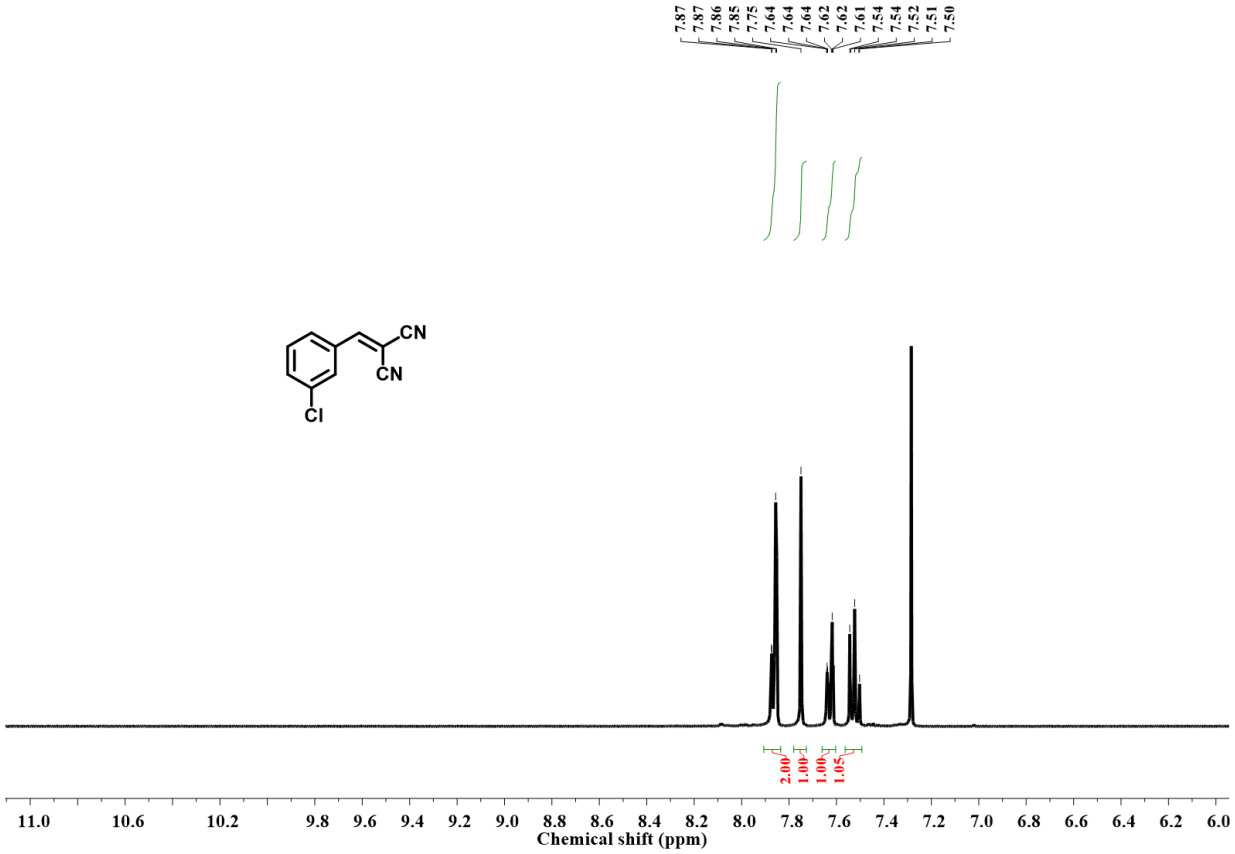


Fig. S35 ^{1}H NMR spectrum of 2-(3-chlorobenzylidene)malononitrile.

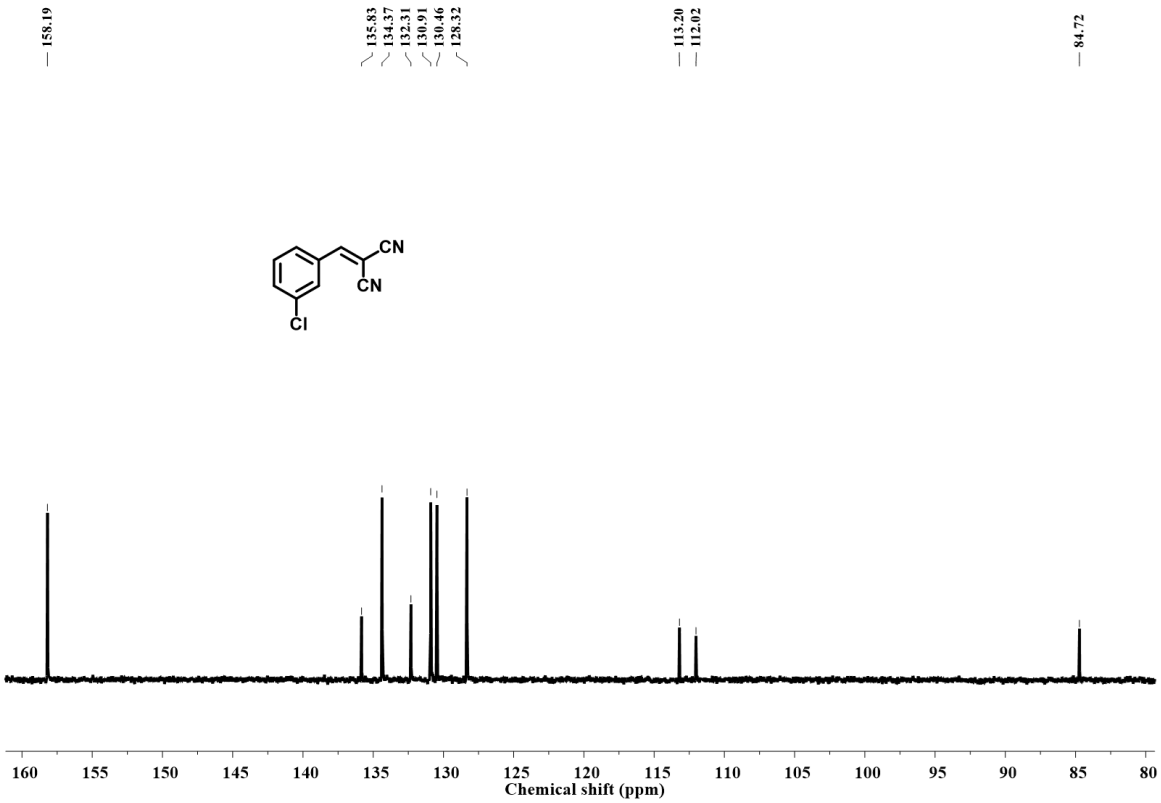


Fig. S36 ^{13}C NMR spectrum of 2-(3-chlorobenzylidene)malononitrile.

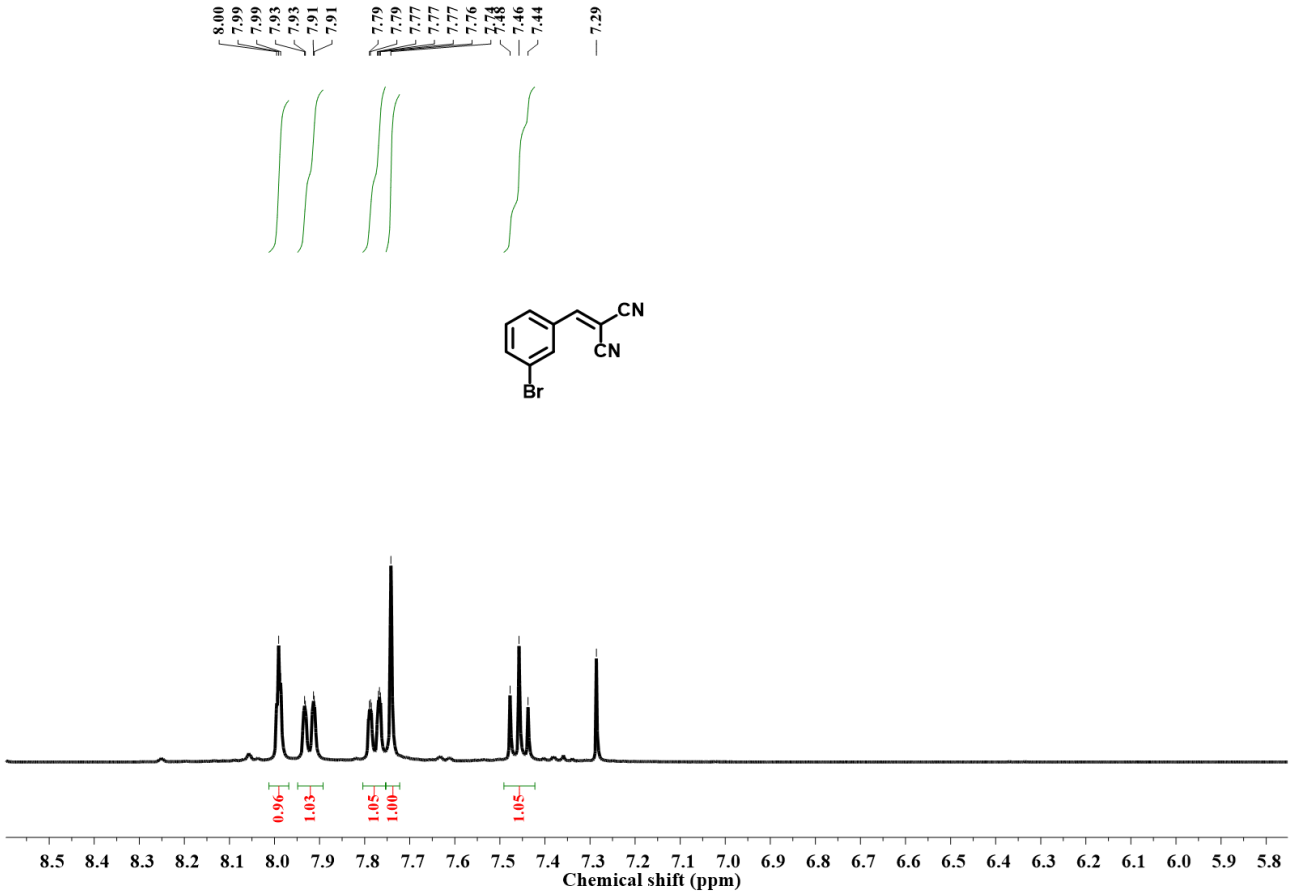


Fig. S37 ^{1}H NMR spectrum of 2-(3-bromobenzylidene)malononitrile.

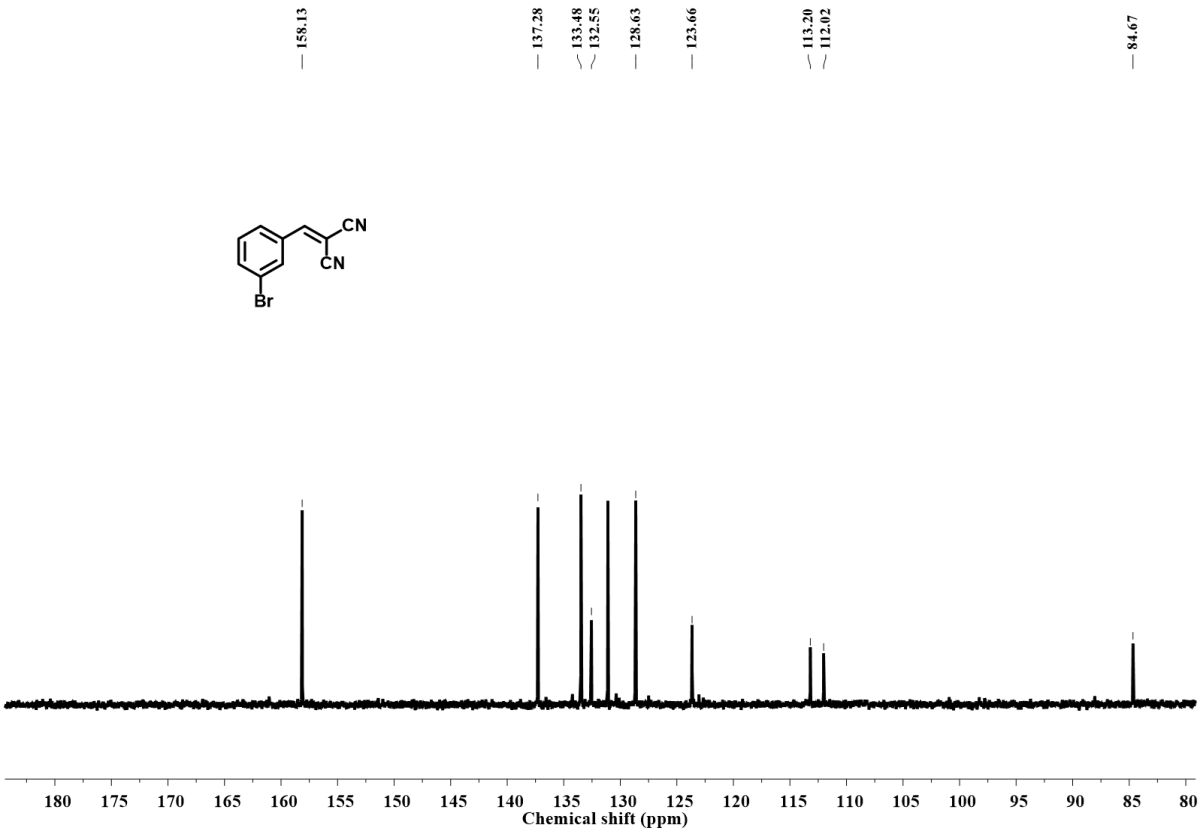


Fig. S38 ^{13}C NMR spectrum of 2-(3-bromobenzylidene)malononitrile.

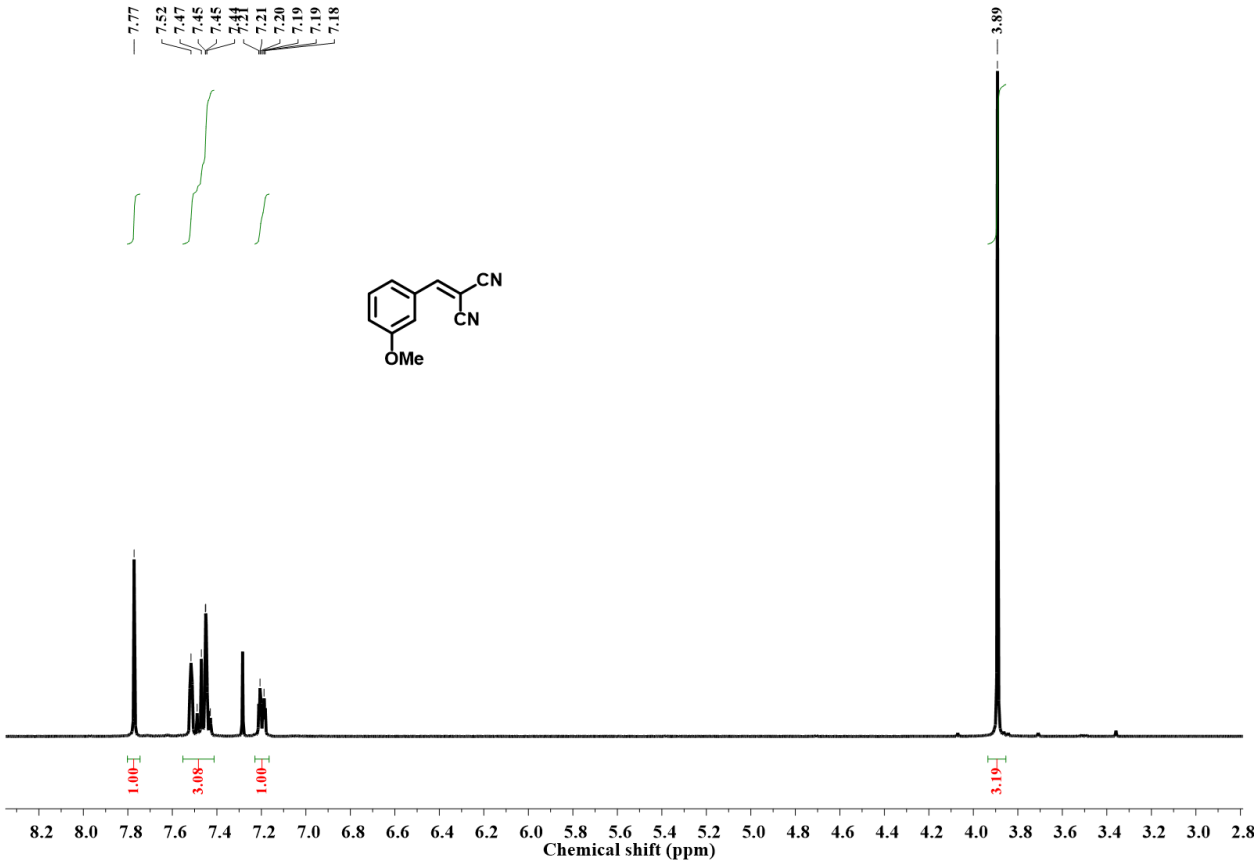


Fig. S39 ^{1}H NMR spectrum of 2-(3-methoxybenzylidene)malononitrile.

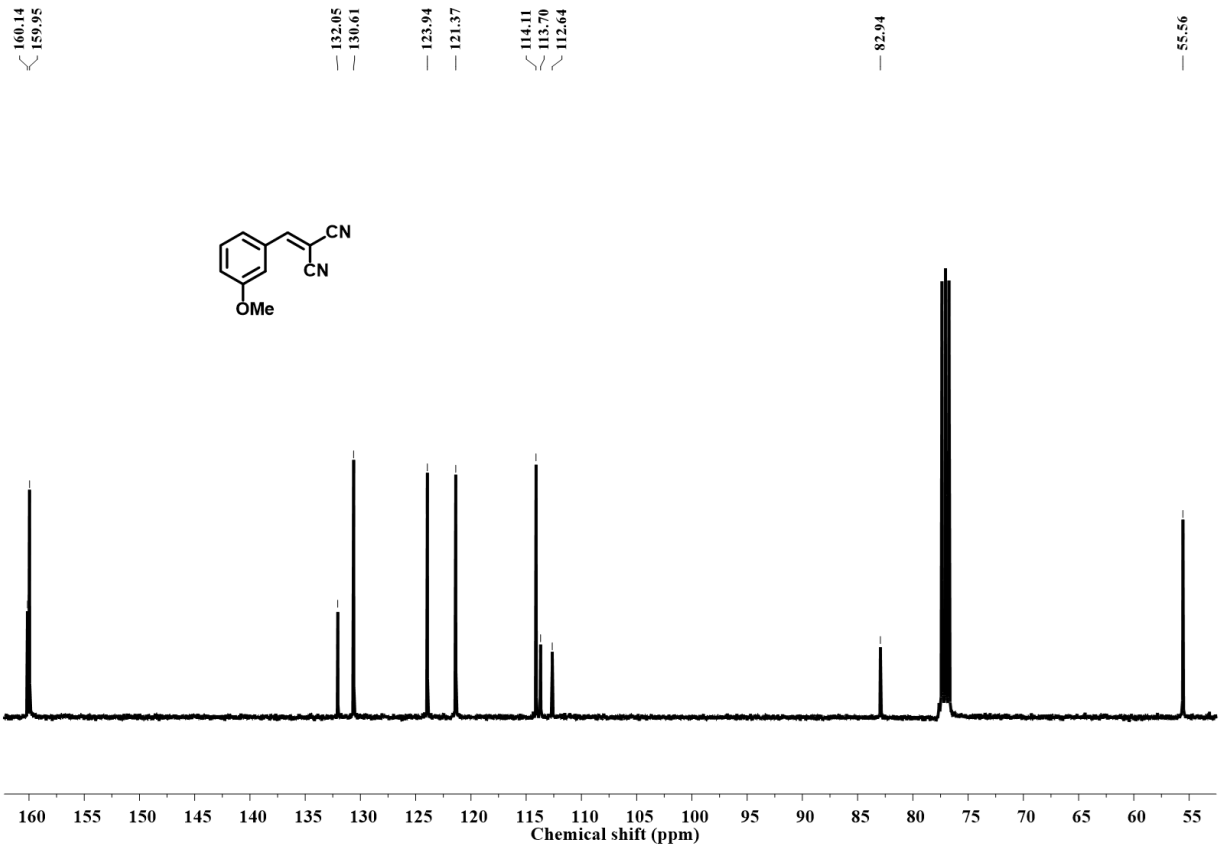


Fig. S40 ^{13}C NMR spectrum of 2-(3-methoxybenzylidene)malononitrile.

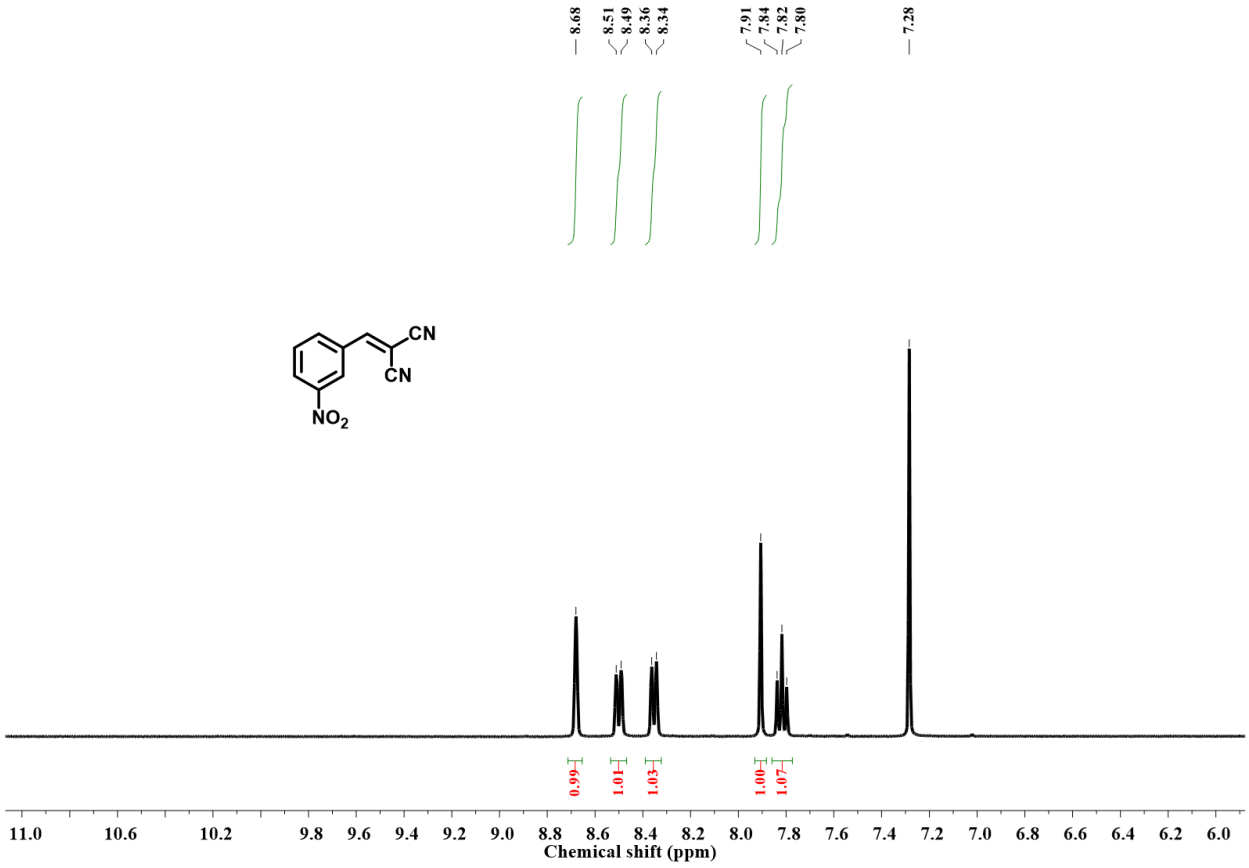


Fig. S41 ^{1}H NMR spectrum of 2-(3-nitrobenzylidene)malononitrile.

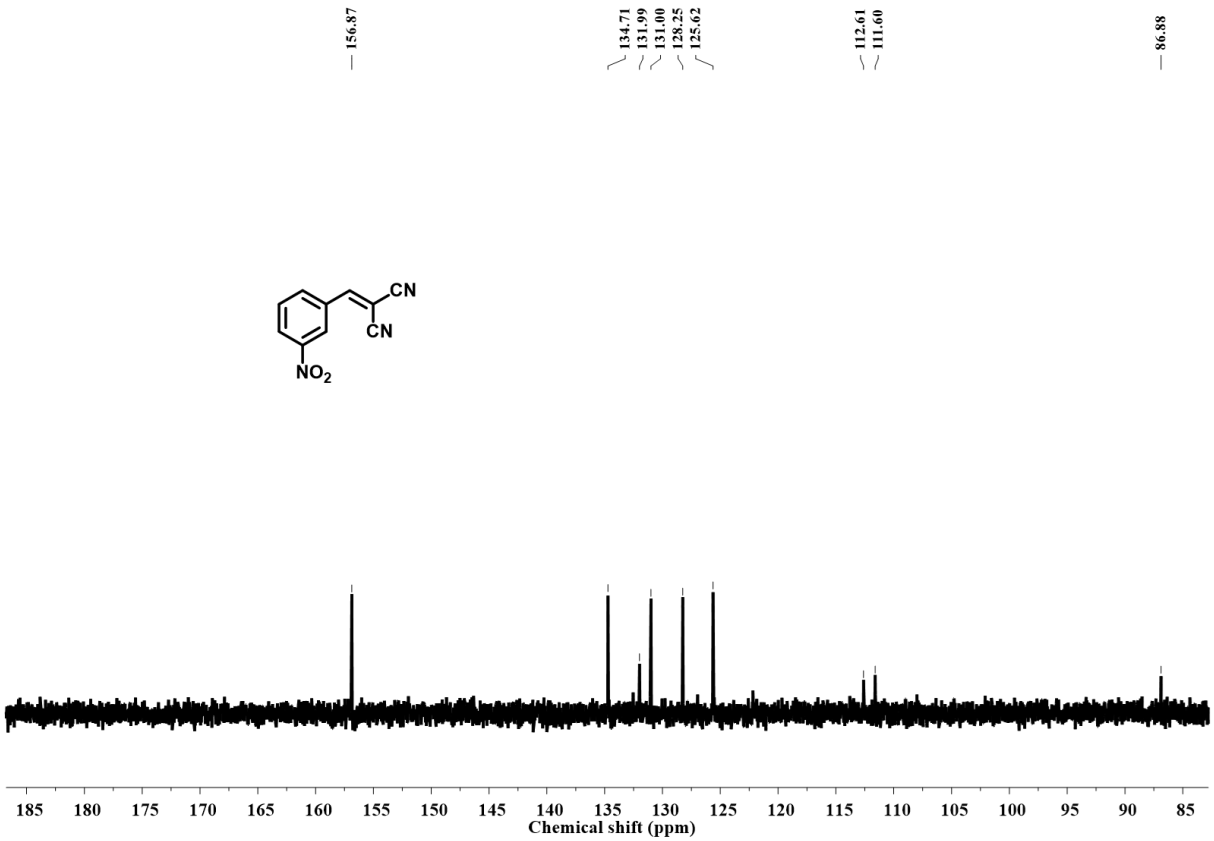


Fig. S42 ^{13}C NMR spectrum of 2-(3-nitrobenzylidene)malononitrile.

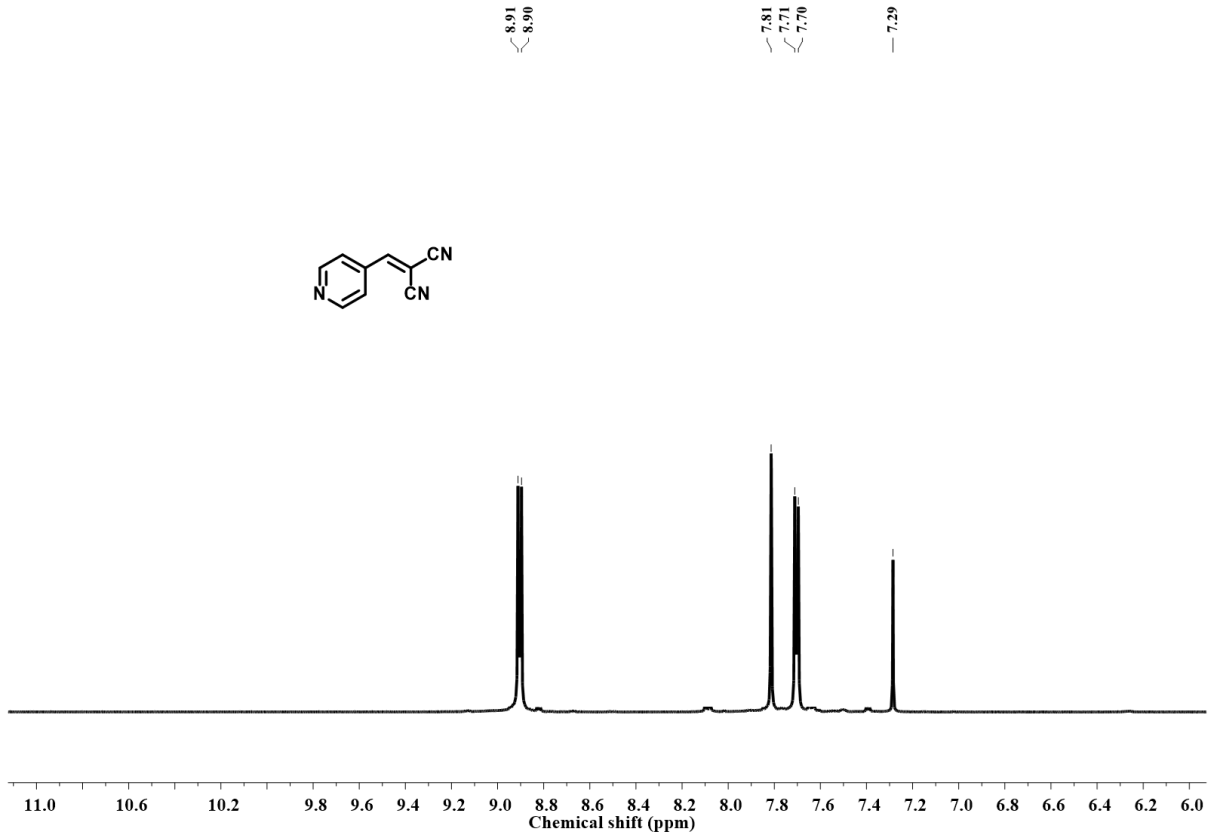


Fig. S43 ^{1}H NMR spectrum of 2-(pyridin-4-ylmethylene)malononitrile.

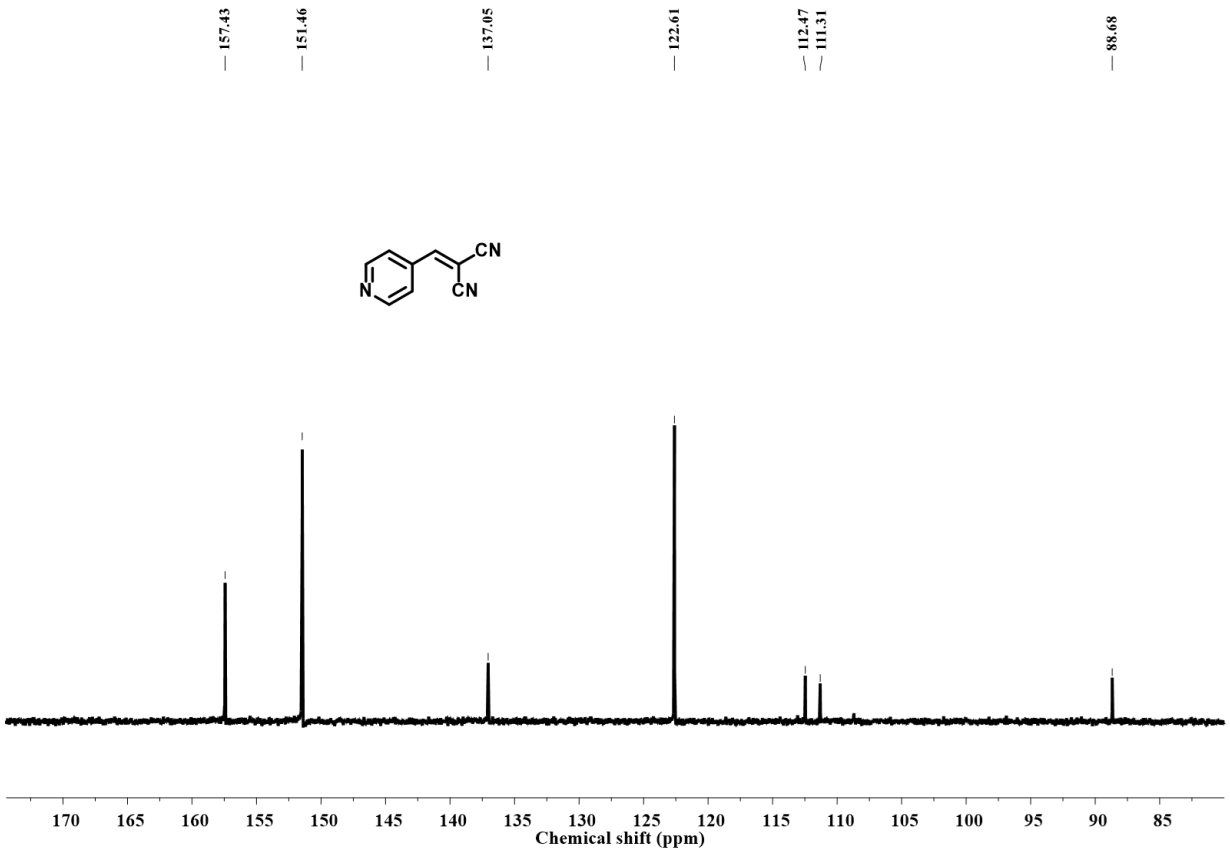


Fig. S44 ^{13}C NMR spectrum of 2-(pyridin-4-ylmethylene)malononitrile.

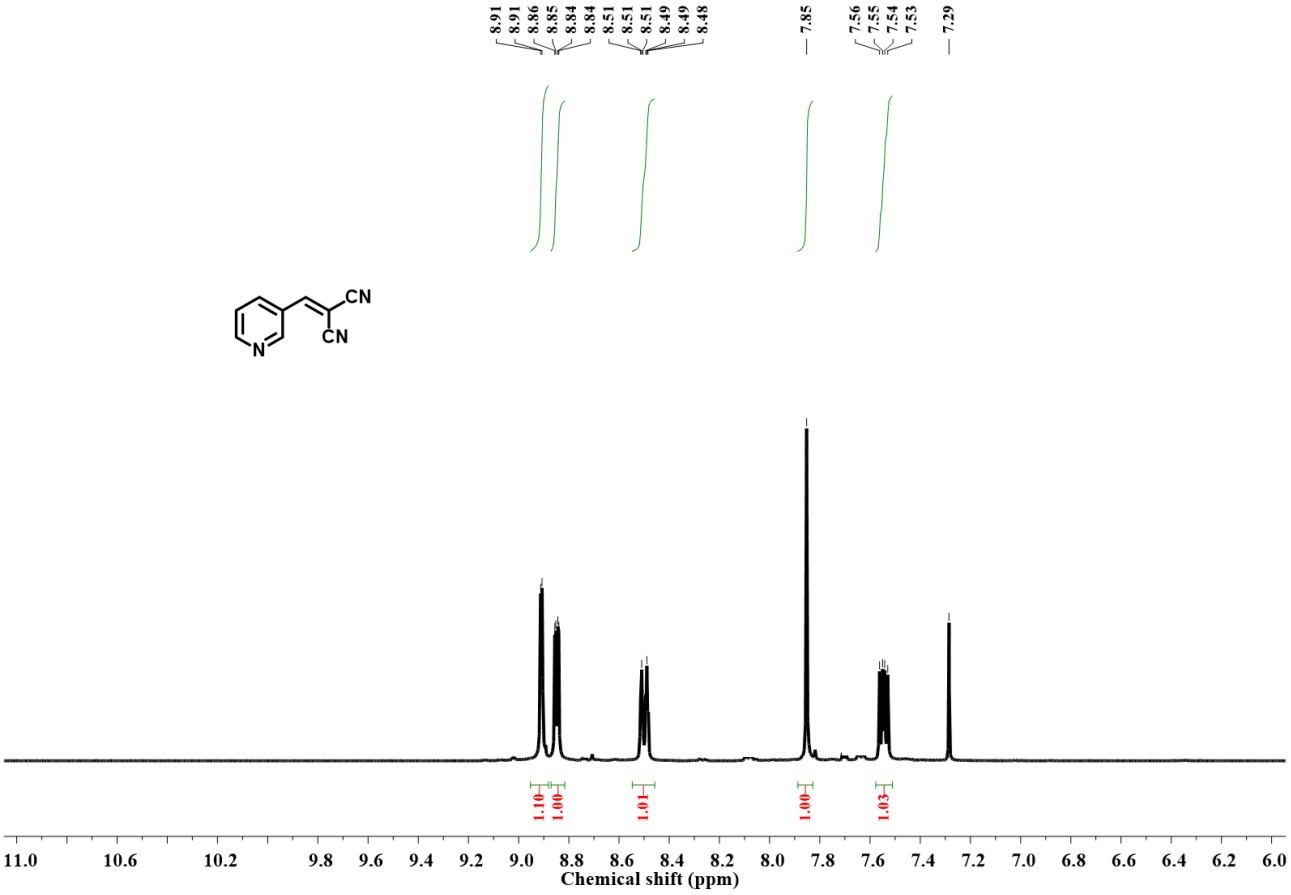


Fig. S45 ^{1}H NMR spectrum of 2-(pyridin-3-ylmethylene)malononitrile.

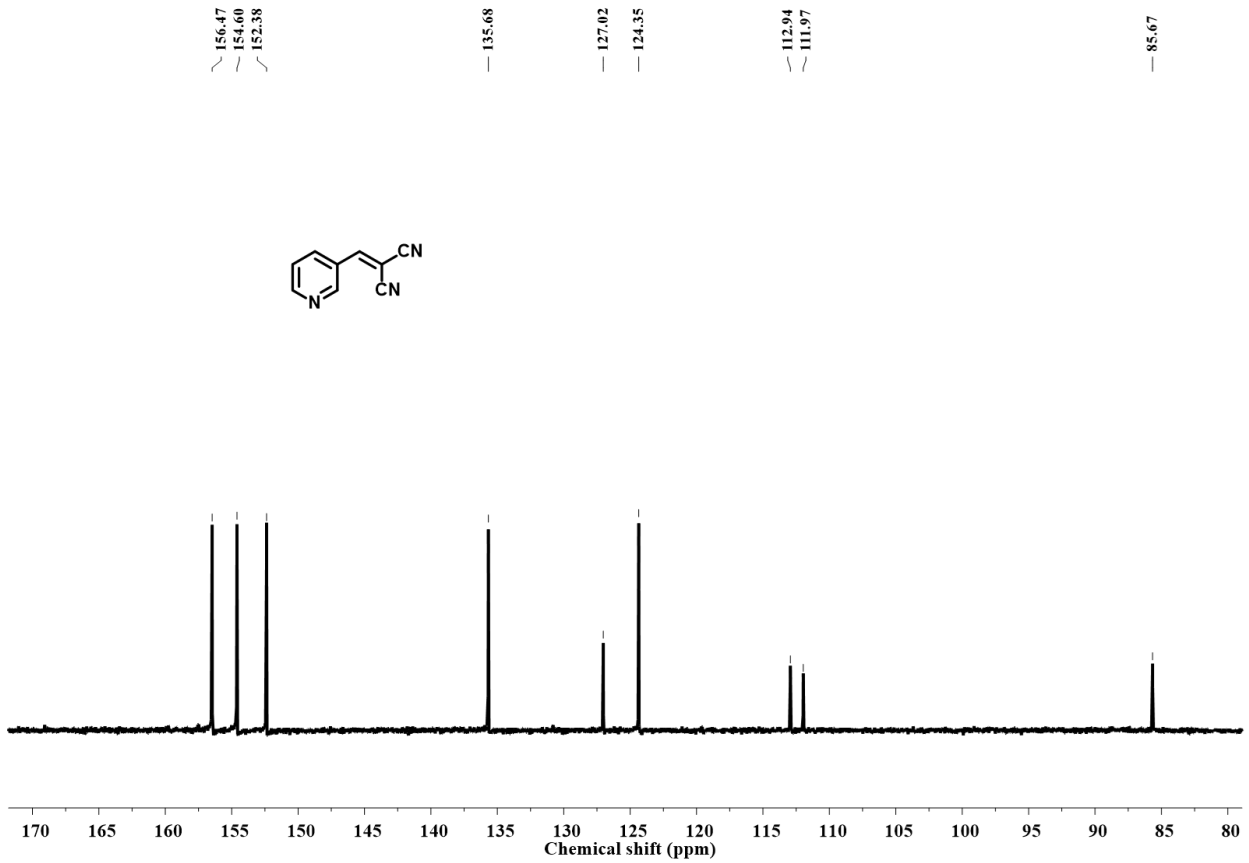


Fig. S46 ^{13}C NMR spectrum of 2-(pyridin-3-ylmethylene)malononitrile.

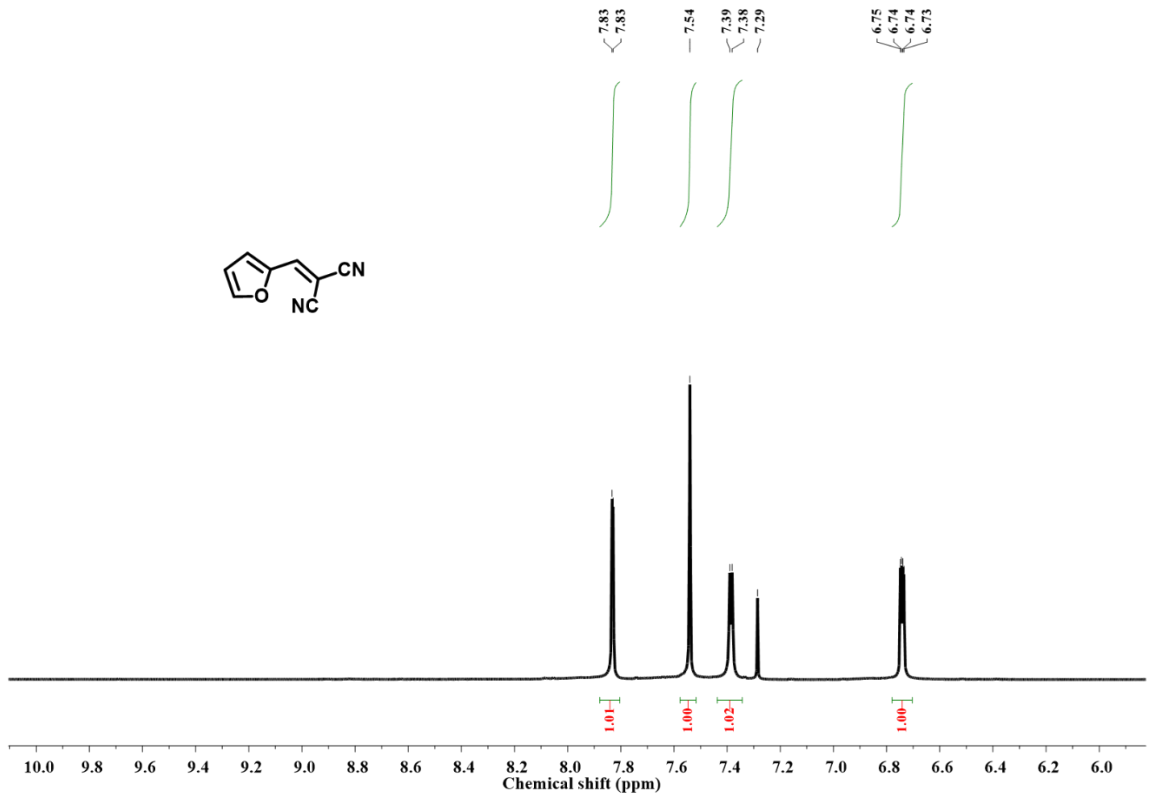


Fig. S47 ^{1}H NMR spectrum of 2-(furan-2-ylmethylene)malononitrile.

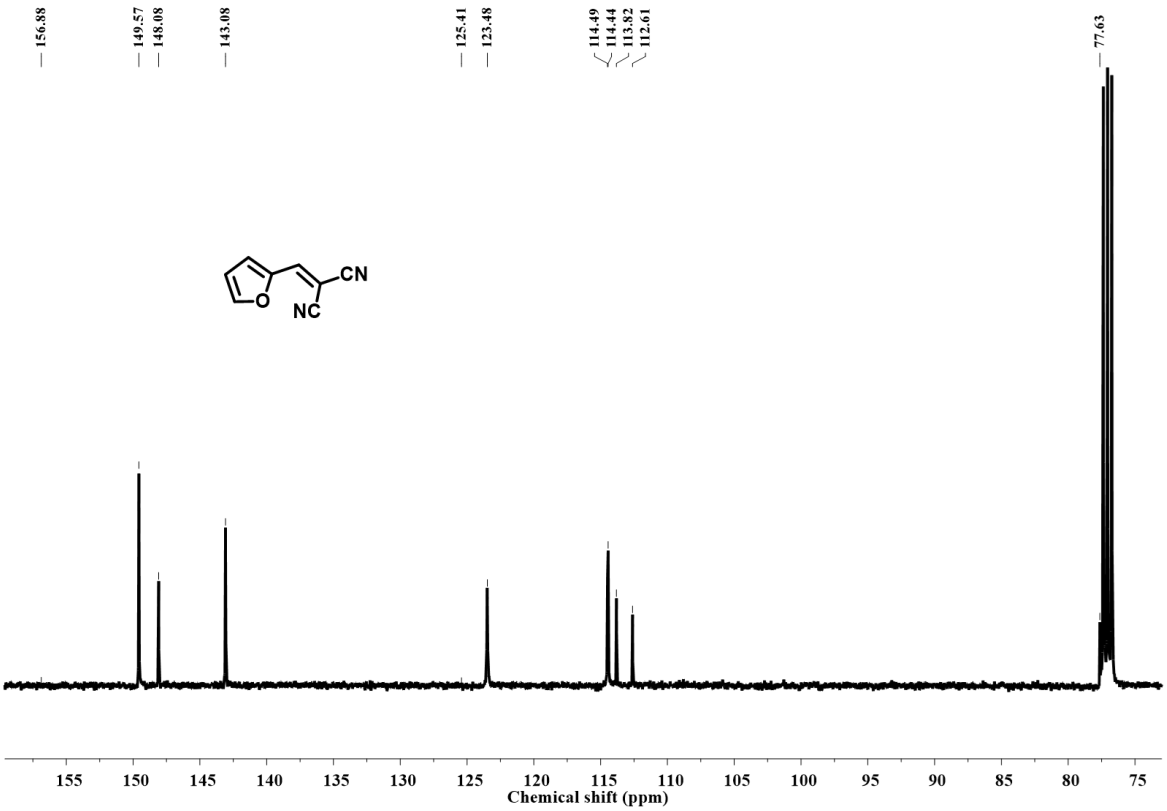


Fig. S48 ^{13}C NMR spectrum of 2-(furan-2-ylmethylene)malononitrile.

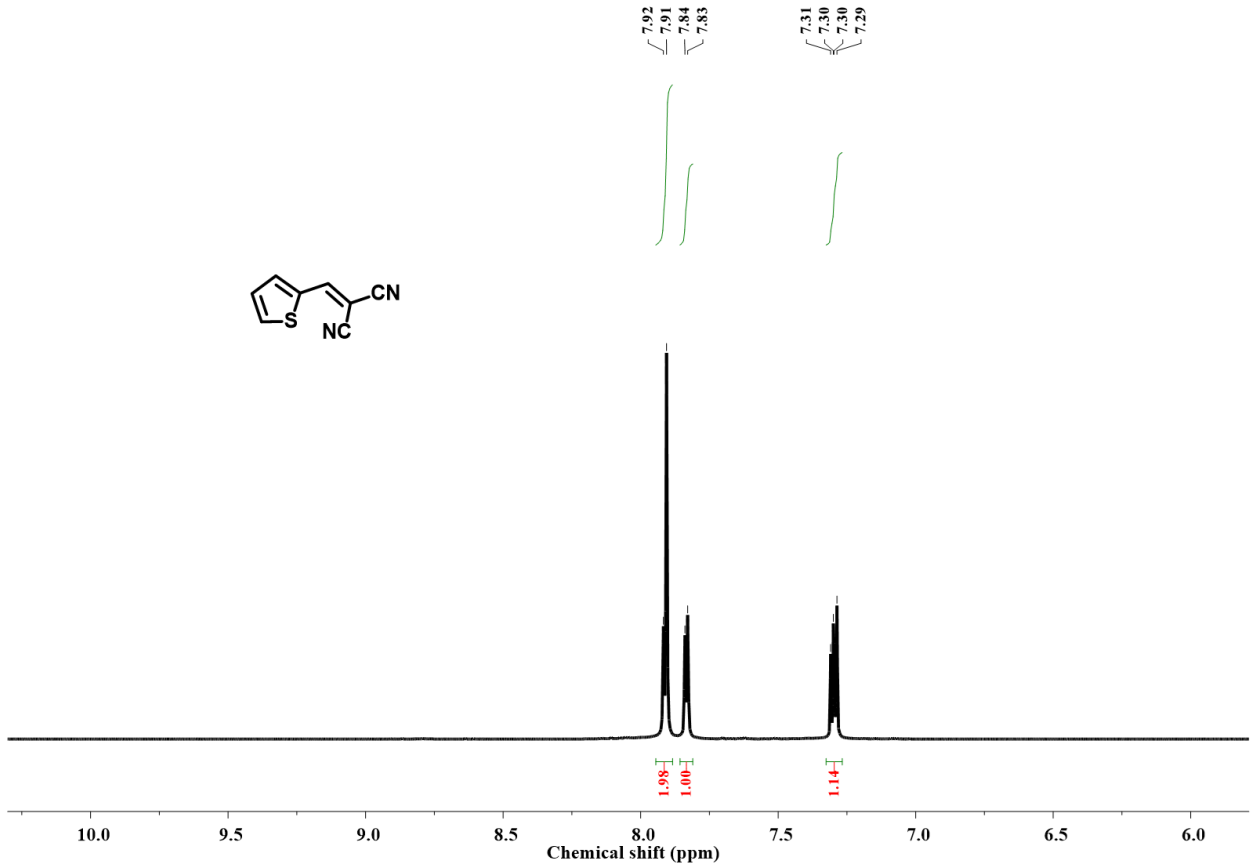


Fig. S49 ^{1}H NMR spectrum of 2-(thiophen-2-ylmethylene)malononitrile.

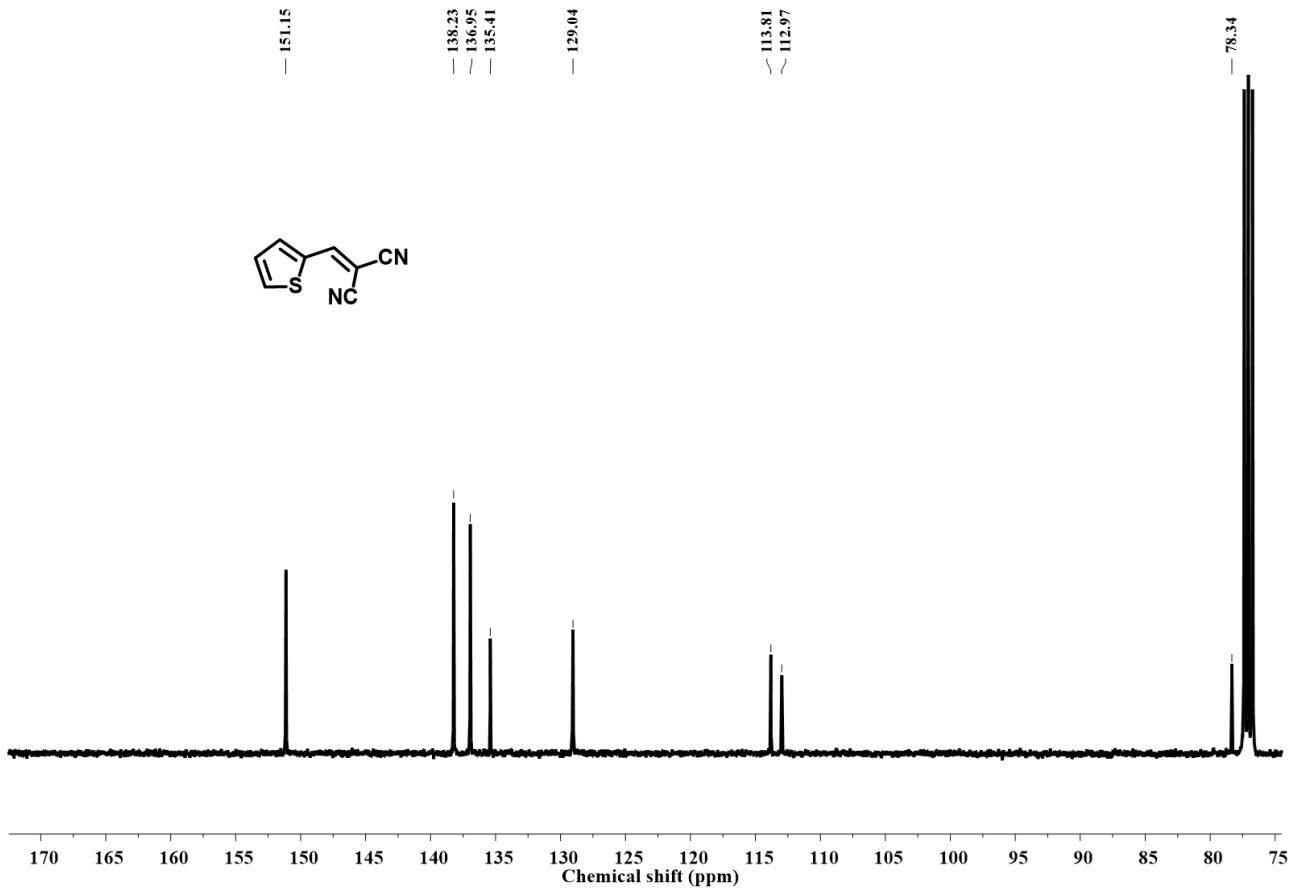


Fig. S50 ^{13}C NMR spectrum of 2-(thiophen-2-ylmethylene)malononitrile.

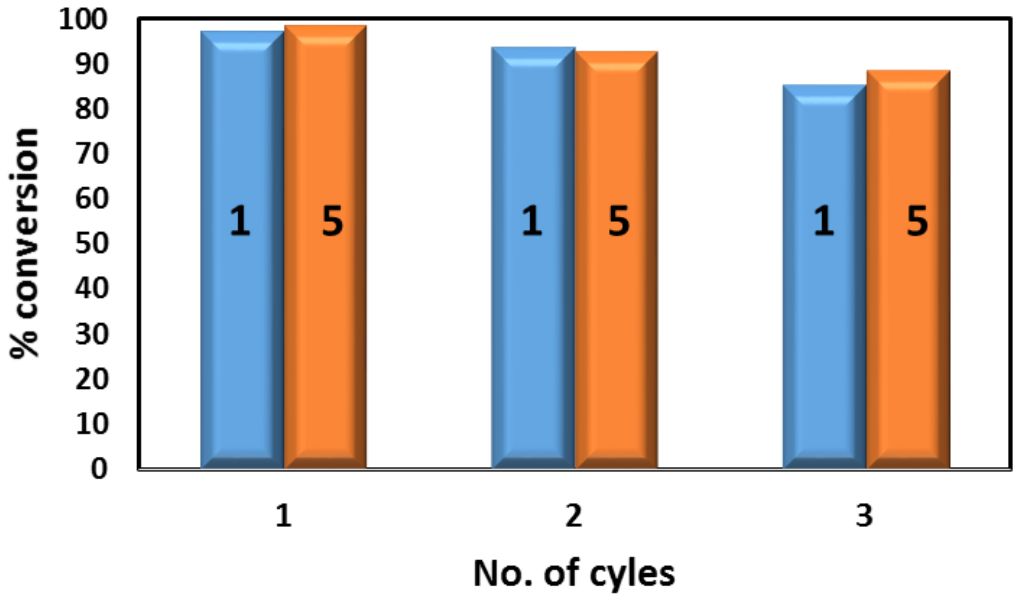


Fig. S51 Conversion for three consecutive cycles of Knoevenagel condensation reaction of benzaldehyde and malononitrile catalysed by **1** and **5**.

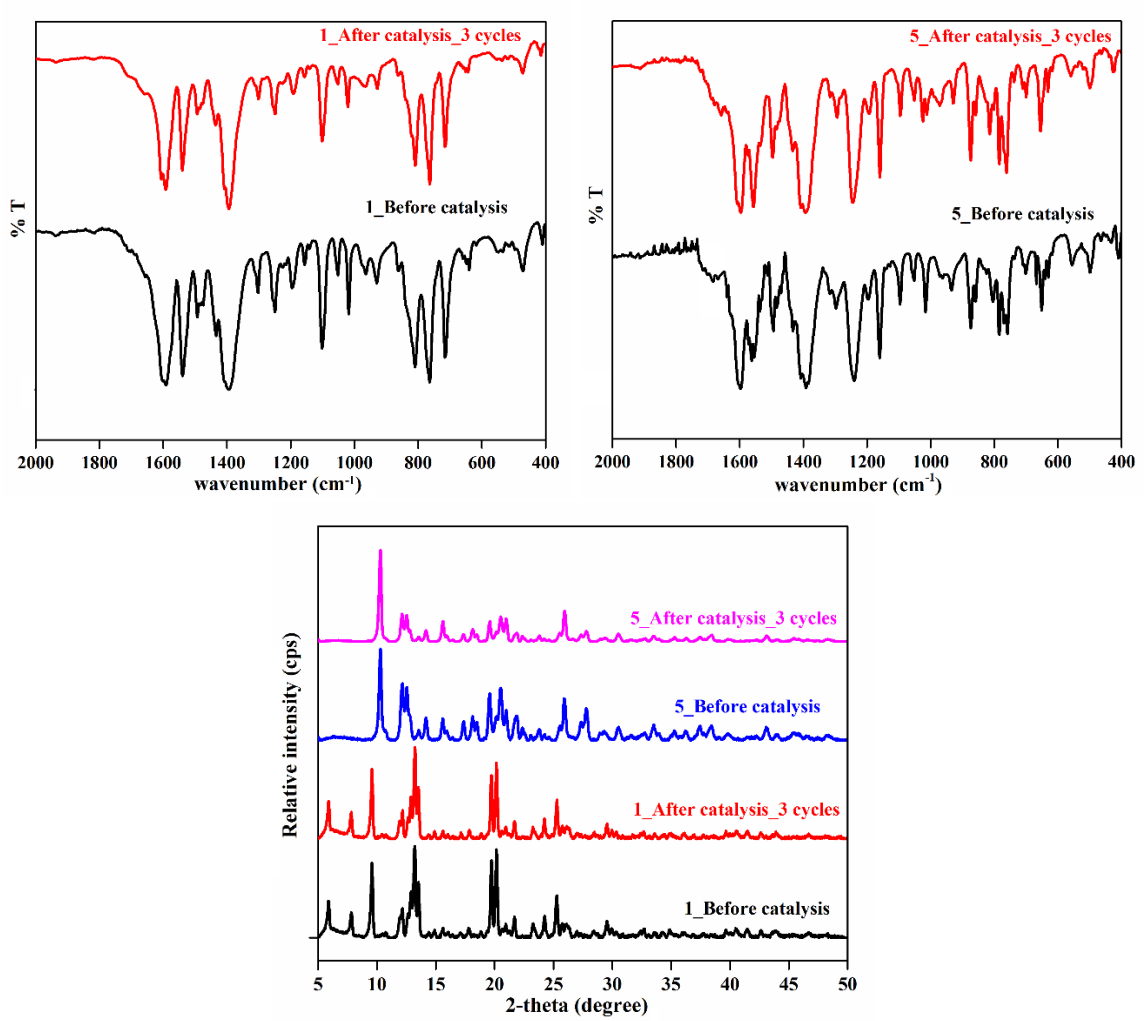


Fig. S52 FTIR spectra (top) and PXRD pattern (bottom) of **1** and **5** taken before and after catalysis experiments.

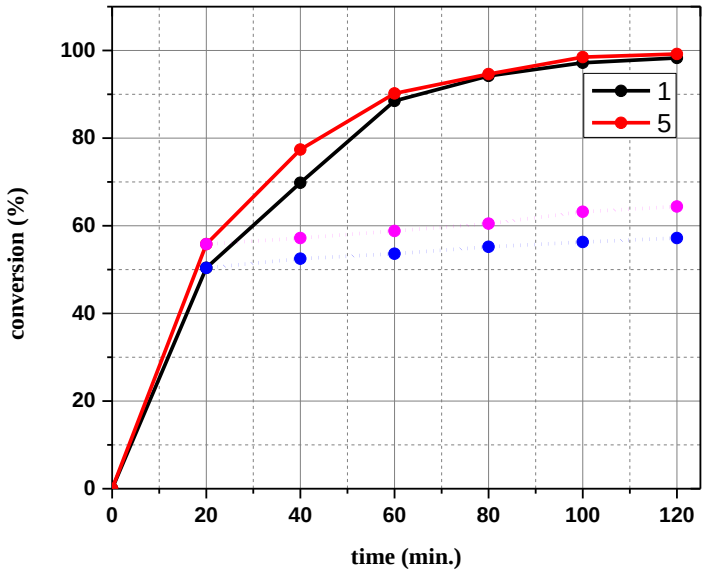


Fig. S53 Progress of the reaction with time in presence of catalysts **1** and **5** (solid lines) and after separating the catalyst from the reaction mixture (dotted lines).

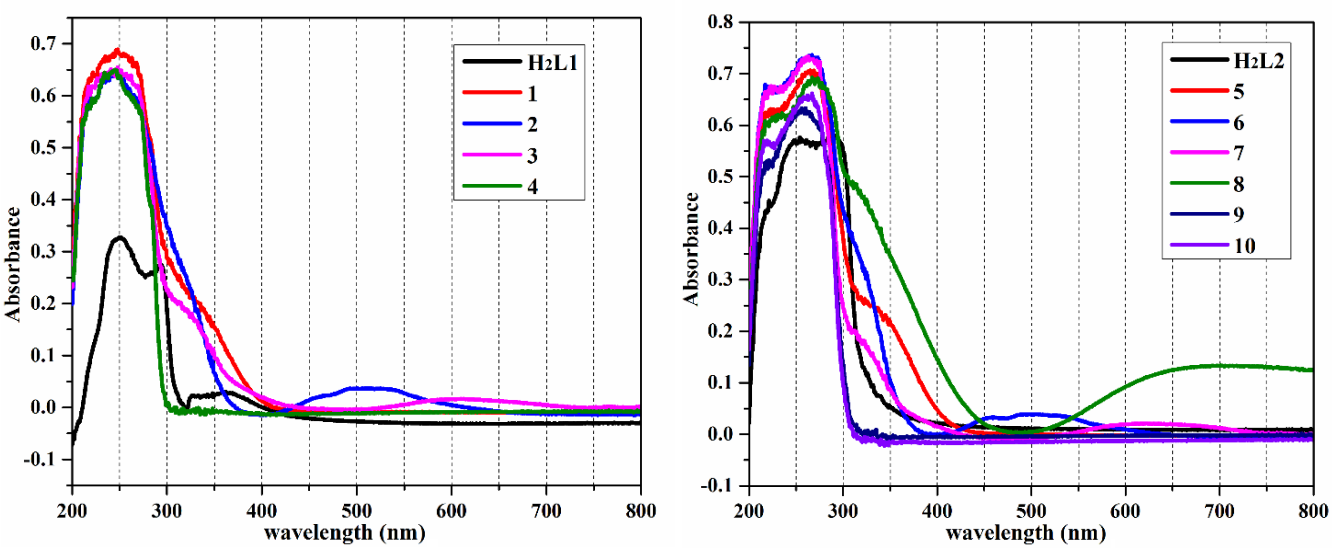


Fig. S54 Absorption spectra of **1-4** and **H_2L1** (left) and **5-10** and **H_2L2** (right)

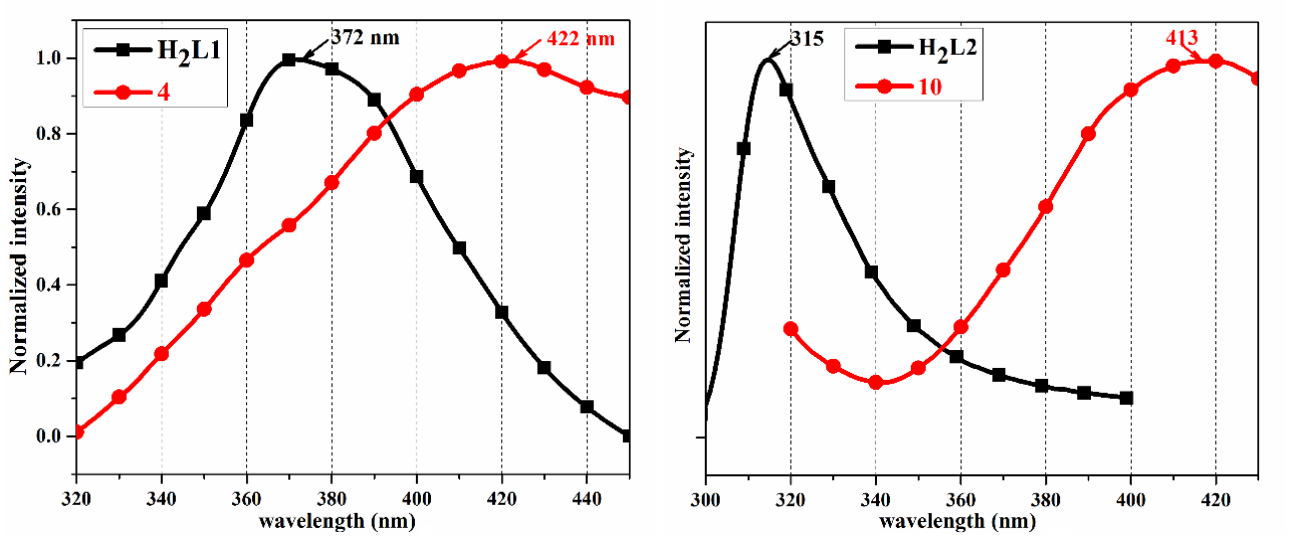


Fig. S55 Emission spectra of **4** (left) and **10** (right) compared with the free ligands **H_2L1** and **H_2L2** respectively.

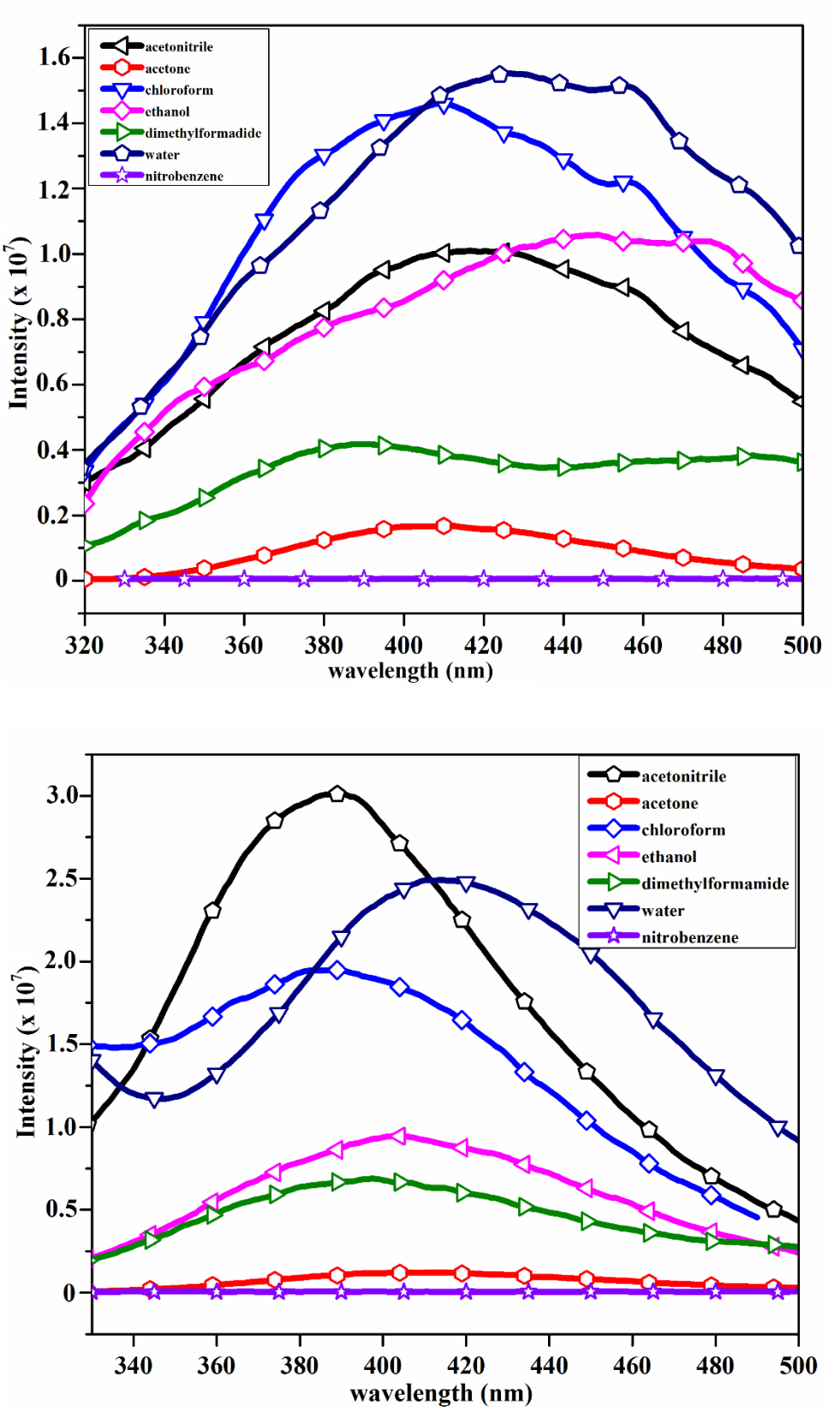


Fig. S56 Emission spectra of **4** (top) and **10** (bottom) in different solvents.

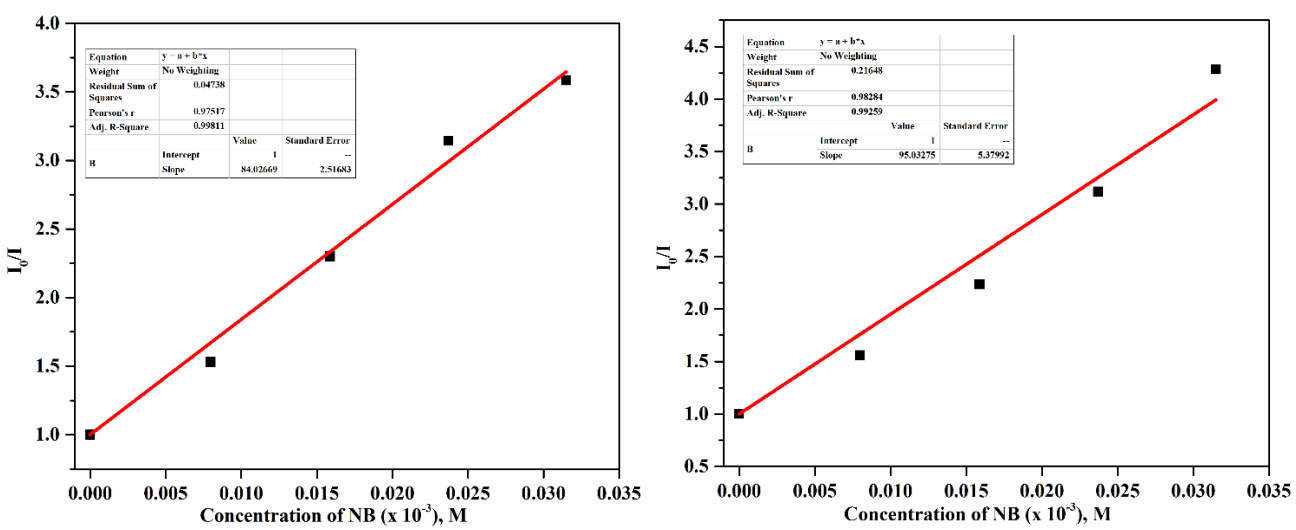


Fig. S57 Stern-Volmer (SV) plot for NB of **4** (left) and **10** (right). The relative fluorescence intensities are linear with NB concentration in the range of 0 – 0.035 mM, $I_0/I = 1 + 84.026[NB]$ ($R^2 = 0.998$) for **4** and $I_0/I = 1 + 95.032[NB]$ ($R^2 = 0.992$) for **10**.

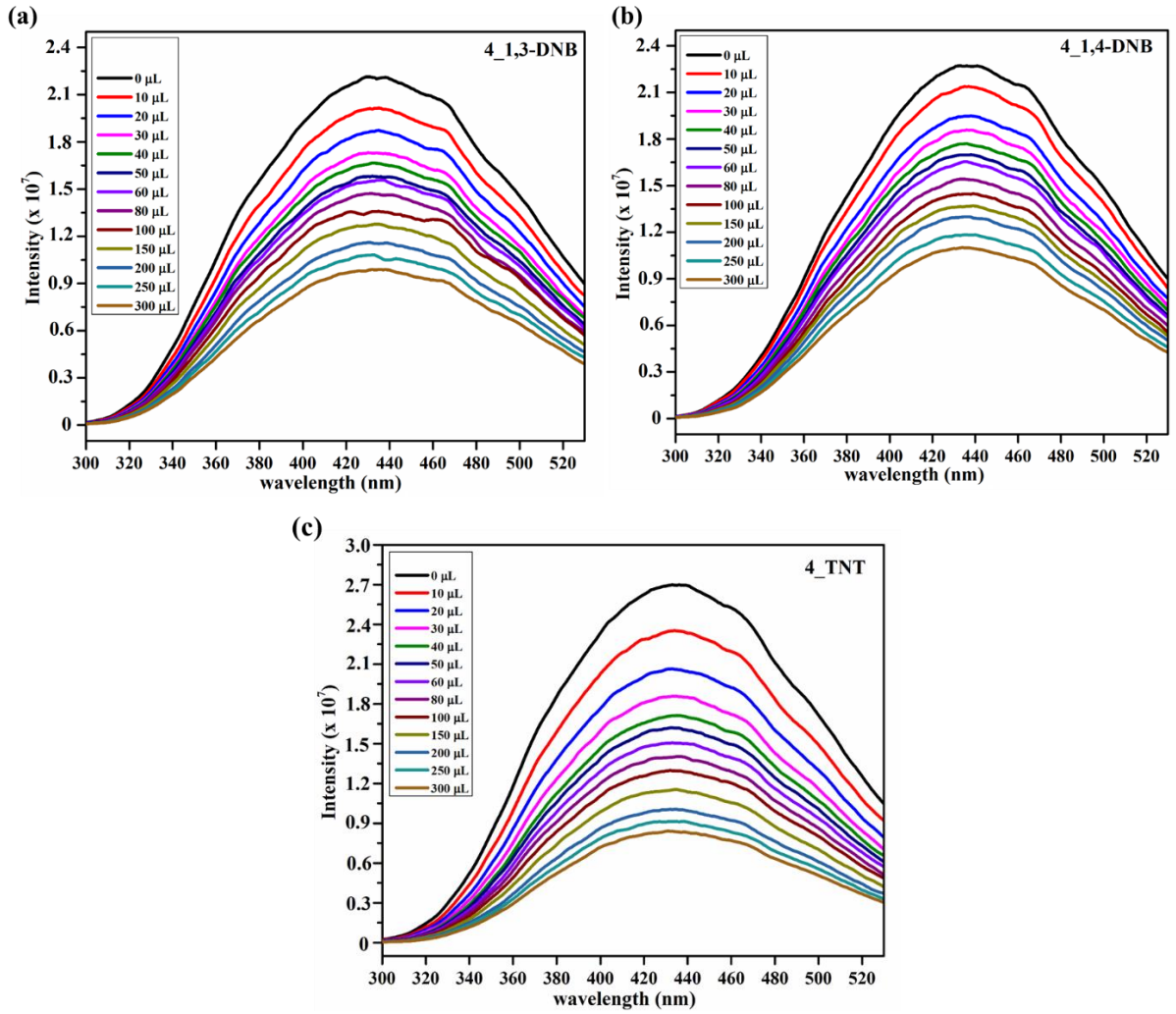


Fig. S58 Change in emission spectra of **4** dispersed in an aqueous medium upon incremental addition of (a) 1,3-DNB solution (2 mM), (b) 1,4-DNB solution (2 mM) and (c) 2,4,6-TNT solution (2 mM).

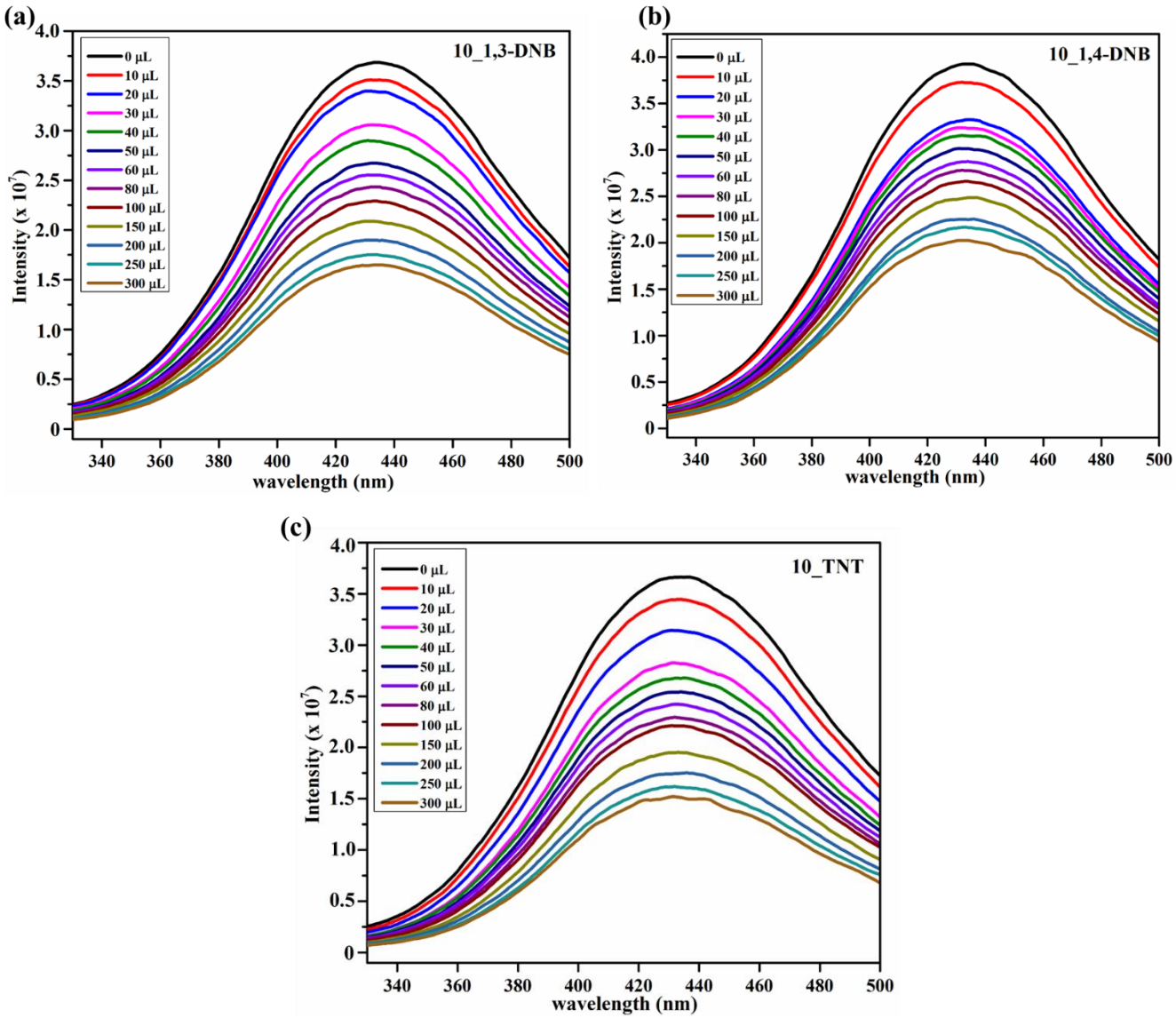


Fig. S59 Change in emission spectra of **10** dispersed in an aqueous medium upon incremental addition of (a) 1,3-DNB solution (2 mM), (b) 1,4-DNB solution (2 mM) and (c) 2,4,6-TNT solution (2 mM).

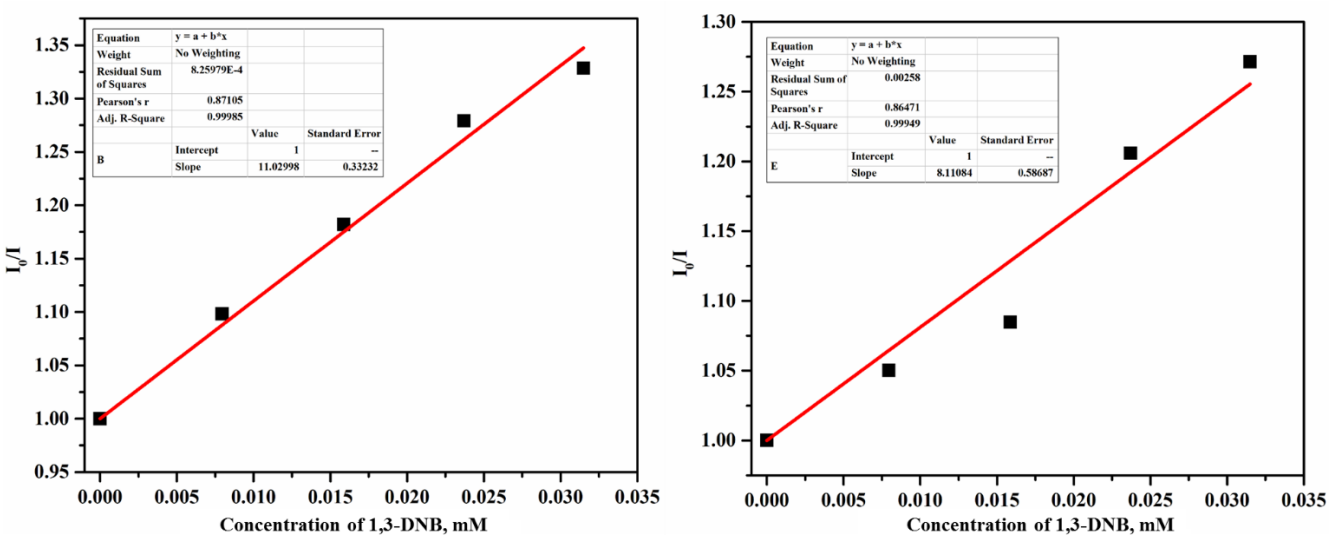


Fig. S60 Stern-Volmer (SV) plot for 1,3-DNB of **4** (left) and **10** (right). The relative fluorescence intensities are linear with 1,3-DNB concentration in the range of 0 – 0.035 mM, $I_0/I = 1 + 11.029[1,3\text{-DNB}]$ ($R^2 = 0.998$) for **4** and $I_0/I = 1 + 8.110[1,3\text{-DNB}]$ ($R^2 = 0.999$) for **10**.

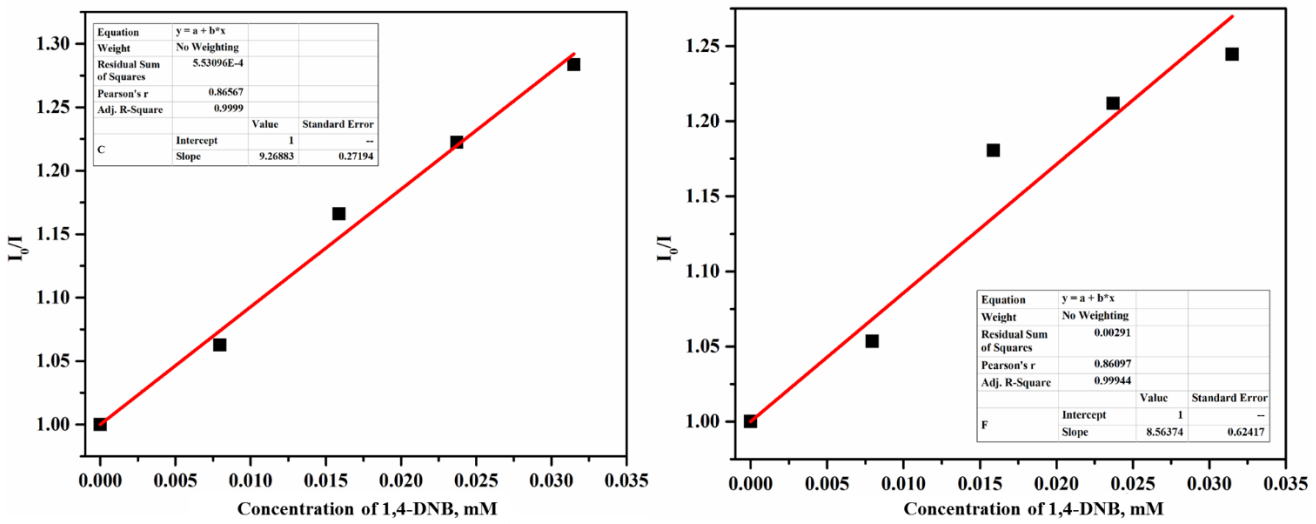


Fig. S61 Stern-Volmer (SV) plot for 1,4-DNB of **4** (left) and **10** (right). The relative fluorescence intensities are linear with 1,3-DNB concentration in the range of 0 – 0.035 mM, $I_0/I = 1 + 9.268[1,4\text{-DNB}]$ ($R^2 = 0.999$) for **4** and $I_0/I = 1 + 8.563[1,4\text{-DNB}]$ ($R^2 = 0.999$) for **10**.

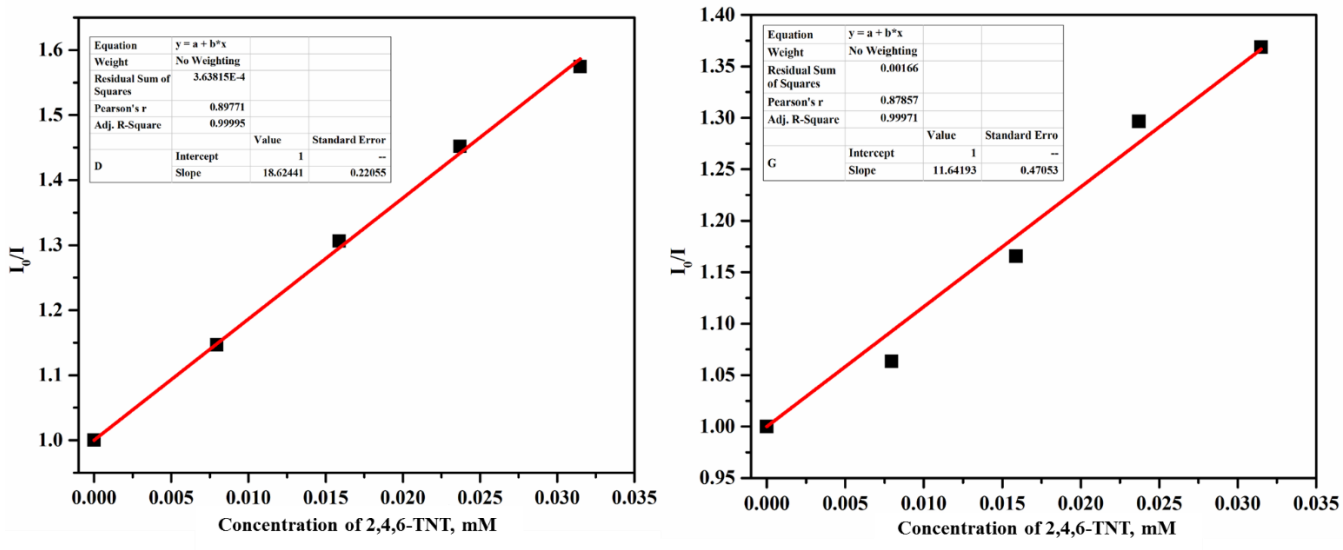


Fig. S62 Stern-Volmer (SV) plot for 2,4,6-TNT of **4** (left) and **10** (right). The relative fluorescence intensities are linear with 2,4,6-TNT concentration in the range of 0 – 0.035 mM, $I_0/I = 1 + 18.624[2,4,6\text{-TNT}]$ ($R^2 = 0.999$) for **4** and $I_0/I = 1 + 11.641[2,4,6\text{-TNT}]$ ($R^2 = 0.999$) for **10**.

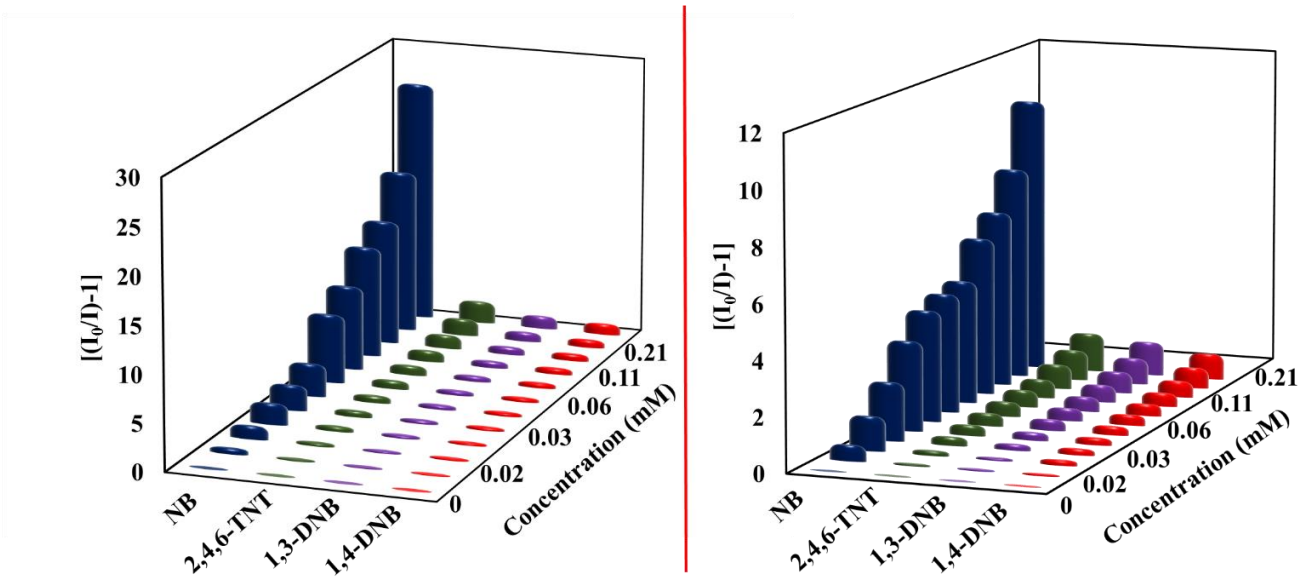


Fig. S63 A comparison of 3D Stern-Volmer plots of different nitro analytes (left) for **4** and (right) for **10**.

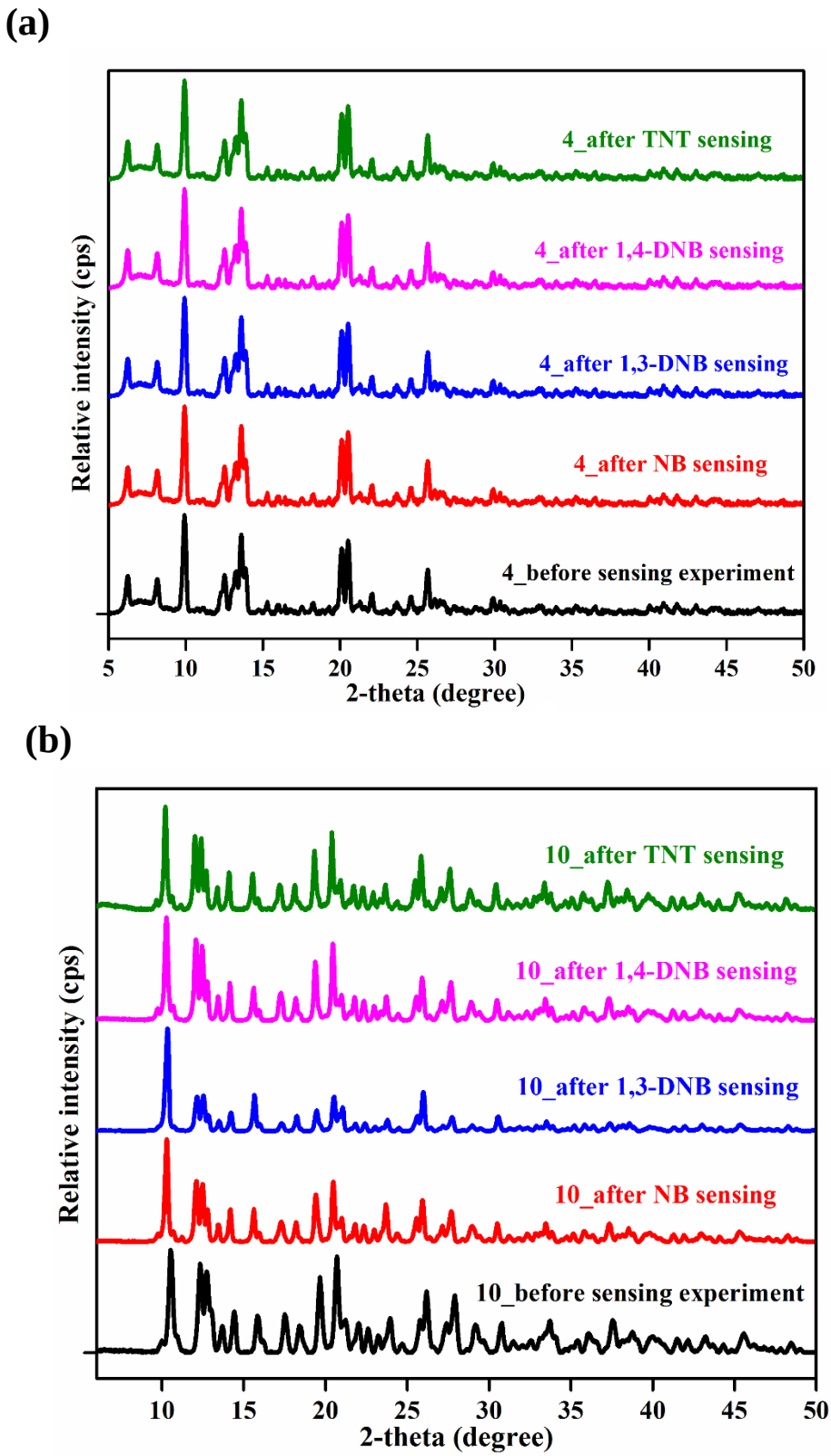


Fig. S64 PXRD patterns of (a) **4** and (b) **10** recorded before and after the sensing experiments for different nitroanalytes.

Table S1 Selected bond lengths (Å) and bond angles (degree) in **1**, **4**, **5**, **9** and **10**.

			1
Mn1-O5	2.2371(12)	Mn1-N2	2.4091(13)
Mn1-O4’	2.1354(12)	Mn1-O1	2.1395(12)
Mn1-N1	2.2809(14)	Mn1-N3	2.2647(14)
O5-Mn1-N2	155.35(5)	O5-Mn1-N1	86.62(5)
O5-Mn1-N3	92.18(5)	O4’-Mn1-O5	94.73(5)
O4’-Mn1-O1	89.92(5)	O4’-Mn1-N2	100.04(5)
O4’-Mn1-N1	89.71(5)	O4’-Mn1-N3	173.03(5)
O1-Mn1-O5	90.40(5)	O1-Mn1-N2	109.12(5)
O1-Mn1-N3	89.11(5)	O1-Mn1-N1	176.95(5)
N3-Mn1-N2	73.79(5)	N1-Mn1-N2	73.92(5)
N3-Mn1-N1	91.61(5)		
Symmetry codes:			
(#1) 'x, y, z',	(#2) '-x, -y, -z'		

			4
Cd1-O1	2.121(2)	Cd1-O3	2.117(2)
Cd1-N1	2.314(3)	Cd1-O4	2.236(2)
Cd1-N3	2.219(3)	Cd1-N2	2.209(3)
O1-Cd1-O4	90.52(9)	O1-Cd1-N1	110.30(10)
O1-Cd1-N2	88.91(10)	O1-Cd1-N3	177.31(10)
O3-Cd1-O1	89.13(10)	O3-Cd1-O4	96.60(9)
O3-Cd1-N1	101.13(9)	O3-Cd1-N2	172.06(10)
O3-Cd1-N3	90.52(10)	O4-Cd1-N1	152.62(9)
N2-Cd1-O4	91.11(9)	N2-Cd1-N1	72.39(9)
N2-Cd1-N3	91.80(10)	N3-Cd1-O4	86.86(10)
N3-Cd1-N1	72.39(10)		
Symmetry codes:			
(#1) 'x, y, z',	(#2) '-x, -y, -z'		

			5
Mn1-O1	2.1178(16)	Mn1-O4’	2.1293(16)
Mn1-O6	2.2262(16)	Mn1-N1	2.268(2)
Mn1-N2	2.3927(19)	Mn1-N3	2.2398(19)
O1-Mn1-O4’	88.27(7)	O1-Mn1-N1	86.84(7)
O1-Mn1-O6	91.33(6)	O1-Mn1-N2	98.75(6)
O1-Mn1-N3	172.13(6)	O4’-Mn1-O6	89.72(6)
O41-Mn1-N1	174.78(7)	O4’-Mn1-N2	109.86(7)
O41-Mn1-N3	89.52(7)	O6-Mn1-N1	88.56(7)
O6-Mn1-N2	158.10(6)	O6-Mn1-N3	96.22(6)
N1-Mn1-N2	72.75(7)	N3-Mn1-N1	95.57(7)
N3-Mn1-N2	74.92(7)		
Symmetry codes:			
(#1) 'x, y, z',	(#2) '-x, -y, -z'		

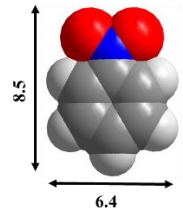
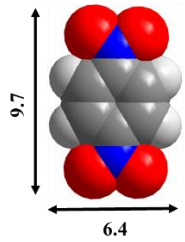
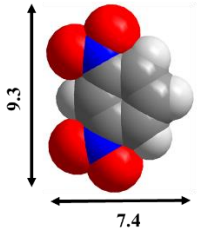
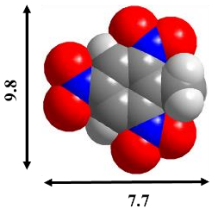
Table S1 (Continued)

		9	
Zn1-O1	2.155(2)	Zn1-O2	2.060(2)
Zn1-O5	2.076(2)	Zn1-N1	2.128(3)
Zn1-N2	2.334(3)	Zn1-N3	2.183(3)
O1-Zn1-N2	160.80(9)	O5-Zn1-O1	91.41(10)
O1-Zn1-N3	88.50(11)	O5-Zn1-N1	89.77(11)
O5-Zn1-N2	106.27(10)	O5-Zn1-N3	173.08(10)
O2-Zn1-O1	93.78(10)	O2-Zn1-O5	86.53(11)
O2-Zn1-N1	170.47(10)	O2-Zn1-N2	94.82(9)
O2-Zn1-N3	86.58(11)	N1-Zn1-O1	95.08(11)
N1-Zn1-N2	77.79(10)	N1-Zn1-N3	97.14(11)
N3-Zn1-N2	74.93(10)		
Symmetry codes:			
(#1) 'x, y, z',	(#2) '-x, -y, -z'		
		10	
Cd1-O1	2.235(2)	Cd1-O6	2.364(2)
Cd1-O4’	2.238(2)	Cd1-N1	2.348(2)
Cd1-N2	2.473(2)	Cd1-N3	2.327(2)
O1-Cd1-O41	87.20(10)	O1-Cd1-N1	174.15(9)
O1-Cd1-O6	89.55(8)	O1-Cd1-N2	109.99(8)
O1-Cd1-N3	90.10(10)	O4’-Cd1-O6	89.99(8)
O4’-Cd1-N1	86.97(9)	O4’-Cd1-N2	100.06(8)
O4’-Cd1-N3	171.38(9)	O6-Cd1-N2	158.28(8)
N1-Cd1-O6	89.96(8)	N1-Cd1-N2	71.58(8)
N3-Cd1-O6	98.18(8)	N3-Cd1-N1	95.75(9)
N3-Cd1-N2	73.20(8)		
Symmetry codes:			
(#1) 'x, y, z',	(#2) '-x, -y, -z'		

Table S2 Hydrogen bonding parameters in **1**, **4**, **5**, **9** and **10**.

D-H-A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
			1	
O5-H5A-O3’	0.89	1.89	2.6308(17)	140.0
O5-H5B-O2	0.89	1.90	2.6616(18)	143.7
D-H-A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
			4	
O4-H4A-O5	0.87	1.81	2.484(3)	135.8
O4-H4B-O2	0.85	1.79	2.512(3)	141.8
			5	
O6-H6A-O3’	0.88	1.94	2.702(2)	143.9
O6-H6B-O2	0.88	1.91	2.681(2)	145.8
			9	
O1-H1A-O4	0.89	1.80	2.675(4)	170.5
O1-H1B-O3’	0.84	1.84	2.661(4)	165.5
			10	
O6-H6A-O3’	0.88	1.94	2.696(3)	143.2
O6-H6B-O2	0.88	1.99	2.726(3)	140.7

Table S3 Approximate size of the nitro-analytes.

Nitro-analytes	Approximate size (L X W) Å	Number of Nitro Groups
Nitrobenzene (NB)	 8.5 X 6.4	1
1,4-dinitrobenzene (1,4-DNB)	 9.7 X 6.4	2
1,3-dinitrobenzene (1,3-DNB)	 9.3 X 7.4	2
2,4,6-trinitrotoluene (TNT)	 9.8 X 7.7	3