Assembling Triple Helical Amide-to-Amide Hydrogen Bonded Columns of tris(4-halophenyl)Benzene-1,3,5-tricarboxamides into Porous Materials via Halogen···Halogen interactions

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Supporting Information

FESEM Images of **1**F & **2**, I_2, N_2 and CO_2 gas absorption data for **2**-**4**, IR and ^{1}H NMR spectra, Guest Exchange Study, Powder XRD patterns and crystallographic information of compounds and experimental details.

Experimental Section:

General: FTIR spectra were recorded with a Perkin Elmer Instrument Spectrum Rx Serial No. 73713. Melting point measurement was carried out using Fisher Scientific instrument Cat. No. 12-144-1. ^{1}H NMR (200 MHz) spectra were recorded on a BRUKER-AC 200MHz spectrometer. Elemental analysis has been carried out by Perkin Elmer *Series II* 2400 and the powder XRD patterns were recorded with a PHILIPS Holland PW-1710 diffractometer. FESEM analysis was performed with a supra 40, Carl Zeiss Pvt. Ltd instrument.

Synthesis of 1F**:** 4-Fluoroaniline (1.2556 gm, 11.30 mmol) and triethyl amine (1.9056 gm, 18.83 mmol) in THF was cooled to 0°C. To this solution, THF solution of trimesyl chloride (1.0 gm, 3.77 mmol) was added drop wise with continuous stirring under nitrogen atmosphere. The reaction mixture was stirred overnight. THF was distilled off and the solid product thus obtained was washed with water and recrystallized from THF. Yield: 47.25%. Mp: 312-314°C. Elemental Analysis for $C_{27}H_{18}N_3O_3F_3$ Calc (%): C, 66.26; H, 3.71; N, 8.59; Obs (%): C, 66.36; H, 3.89, N, 8.77.

Similar procedure was adopted for the synthesis of compounds 1Cl, 1Br and 1I.

1I: Yield: 91.21%. Mp: 309-312°C. Elemental Analysis for $C_{27}H_{18}N_3O_3I_3$ Calc (%): C, 39.88; H, 2.23; N, 5.17; Obs (%): C, 40.10; H, 2.34, N, 5.37.

2, (1I•2THF): Mp: 295-298°C. Elemental Analysis for $C_{35}H_{34}N_3O_5I_3$ Calc (%): C, 43.91; H, 3.58; N, 4.39; Obs (%): C, 43.83; H, 2.96, N, 4.61.

1I-(THF-Removed): Elemental Analysis for $C_{27}H_{18}N_3O_3I_3$ Calc (%): C, 39.88; H, 2.23; N, 5.17; Obs (%): C, 39.99; H, 2.51, N, 5.01.

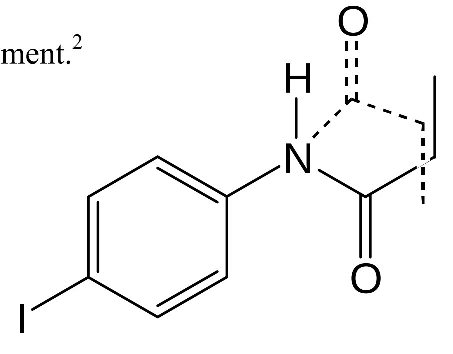
1Br**:** Yield: 83.53%. Mp: 310-312°C. Elemental Analysis for $C_{27}H_{18}N_3O_3Br_3$ Calc (%): C, 48.25; H, 2.70; N, 6.25; Obs (%): C,47.96; H, 2.84, N, 6.17.

3, (**1**Br•2THF): Mp: 308-310°C. Elemental Analysis for $C_{35}H_{34}N_3O_5Br_3$ Calc (%):C, 51.49%; H, 4.20% , N, 5.15%; Obs (%): C,52.17; H, 3.86 , N, 5.30.

1Cl**:** Yield: 74.94%. Mp: 311-314°C. Elemental Analysis for $C_{27}H_{18}N_3O_3Cl_3$ Calc (%): C, 60.19; H, 3.37; N, 7.80; Obs (%): C, 59.79; H, 3.74 , N,7.65.

4, (**1**Cl•THF): Mp: 296-298°C Elemental Analysis for $C_{31}H_{26}N_3O_4Cl_3$ Calc (%): C,60.95; H, 4.29 , N, 6.88. 1-THF Obs (%): C,60.09; H, 3.74 , N, 6.90.

X-ray Crystallography: The single crystal data was collected on Bruker APEX-2 CCD X-ray diffractometer that uses graphite monochromated MoKα radiation (λ=0.71073 Å) by hemisphere method. The structures are solved by direct methods and refined by least square methods on F^2 using SHELX-97.[1] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. PLATON was used for the calculation of guest available volumes.[2] In **2**, the central C_6 ring and amide CO groups are disordered over two sites which was modeled and refined. The THF molecules could not be located platon squeeze option was used in the final refinement.[2]



Model of the disorder

The powder patterns for **3** and **4** were measured in transmission mode using a G670 Guinier camera diffractometer ($CuK_{\alpha1}$ radiation, λ=1.54059 Å) at ambient conditions (*T* = 295(2) K) (Figure S4). The trigonal unit-cell dimensions were determined with TREOR90.[3] Based on systematic extinctions the space group *P31c* was assigned for **3** and **4**. The unit-cell parameters and space group were further tested using Pawley's fit [4] and confirmed by crystal structure solution. The crystal data, data collection and refinement parameters for **3** and **4** are given in Table S2. The crystal structures were solved with the use of simulated annealing technique.[5] The solution found for each structure was fitted with the program MRIA[6] in the bond-restrained Rietveld refinement using a split-type pseudo-Voigt peak profile function.[7]

In both structures **3** and **4**, the geometry of preliminary refined four neighbouring hydrogen-bonded molecules was optimised by density functional theory (DFT) calculations, which were performed *in vacuo* using the quantum-chemical code Priroda [8] employing the generalized-gradient approximation (GGA) and PBE exchange correlation function.[9] The optimised geometry of one molecule from the middle of the stack was further used as template in the final bond-restrained refinements. The THF molecule was treated as rigid molecule disordered between two positions with occupancies fixed to 0.5. Five isotropic displacement parameters were refined for each structure: two parameters for two independent halogen atoms, two common displacement parameters for the rest non-H atoms in two independent molecules, and one common parameter for all non-H atoms in two parts of disordered THF molecule. Restraints were applied to the intramolecular bond lengths and contacts (< 2.6 Å) in the main and solvent molecules. The strength of the restraints was a function of interatomic separation and, for intramolecular bond lengths, corresponded to an r.m.s. deviation of 0.03 Å. Additional restraints were applied to the planarity of chloro- and bromo-benzene fragments, with the maximal allowed deviation from the mean plane 0.05 Å. To keep the central benzene ring planar, the z-coordinates of independent atoms C1, C8 and C9 were constrained to be equal (and C10, C17, C18 in another molecule). The H-atoms were placed in geometrically idealized positions (C-H 0.93-0.97 Å, N-H 0.86 Å) and not refined.

Table S1: Crystallographic parameters for **1**F and **2**.

Compound	**1**F	**2**
Formula	$C_{27}H_{18}N_3O_3F_3$	$C_{35}H_{34}N_3O_5I_3$
M. Wt.	489.44	957.35
***T* (K)**	293(2)	293(2)
System	Orthorhombic	Trigonal
Space Group	Pbca	P-31c
a(Å)	7.1319(3)	22.5852(4)
b(Å)	25.1912(1))	22.5852(4)
c(Å)	25.6790(1)	7.5192(3)
α (°)	90	90
β (°)	90	90
γ (°)	90	120
Vol. (Å^3)	4613.5(4)	3321.6(2)
Z	8	4
D_{calc} (Mg/m^3)	1.409	1.914
R_1 (I>2σ(I))	0.0534	0.0772
wR_2 (on F^2, all data)	0.1600	0.1928

Table S2: Crystal data for **3** and **4** deduced from powder XRD.

Compound	**3**	**4**
Formula	$C_{27}H_{18}Br_3N_3O_3$ $1.5(C_4H_8O)$	$C_{27}H_{18}Cl_3N_3O_3$ $1.5(C_4H_8O)$
M. Wt.	780.33	646.91
System	Trigonal	Trigonal
Space group	P31c	P31c
a (Å)	21.9892(18)	21.6250(17)
c (Å)	7.3478(5)	7.3012(6)
Vol. (Å^3)	3076.9(4)	2956.9(4)
Z	4	4
D (Mg m^{-3})	1.684	1.453
μ, mm^{-1}	5.236	3.192
$2\theta_{min}$ - $2\theta_{max}$ (^{o})	3.00-85.00	3.00-85.00
2θ step (^{o})	0.01	0.01
No. parameters/restraints & constraints	151/116	151/116
R_p, R_{wp}, R_{exp} *	0.0144, 0.0187, 0.0099	0.0184, 0.0237, 0.0112

* - R_p, R_{wp} and R_{exp} are defined according to Young & Wiles.[10]

Table S3: Geometrical parameters of amide-to-amide hydrogen bonds in the crystal structures of **1**F, and **2-4**.

Compond	**Type**	**H···A (Å)**	**D···A (Å)**	**D-H···A (°)**
1F	N(11)-H(11)···O(9)[a]	2.15	2.938(3)	152
	N(21)-H(21)···O(7)	2.12	2.945(3)	159
	N(31)-H(31)···O(8)	2.11	2.931(3)	159
	C(12)-H(12)···O(7)	2.30	2.895(4)	122
	C(26)-H(26)···O(8)	2.36	2.889(4)	116
	C(36)-H(36)···O(9)	2.34	2.867(4)	115
2	N(11)-H(11)···O(11A)	1.81	2.626(7)	155
3	N(1)-H(1)···O(2)[b]	2.12	2.895(2)	150
	N(2)-H(2)···O(1)[c]	2.19	2.968(2)	151
	C(16)-H(16)···O(1)	2.52	3.213(2)	132
4	N(1)-H(1)···O(2)[d]	2.09	2.890(1)	155
	N(2)-H(2)···O(1)[e]	2.15	2.962(1)	157
	C(16)-H(16)···O(1)	2.59	3.230(1)	126

Symmetry operators: (a) 1/2+x,1/2-y,1-z; (b) 1-y,1+x-y,z; (c) x,y,-1+z; (d) 1-y,1+x-y,z; (e) x,y,-1+z.

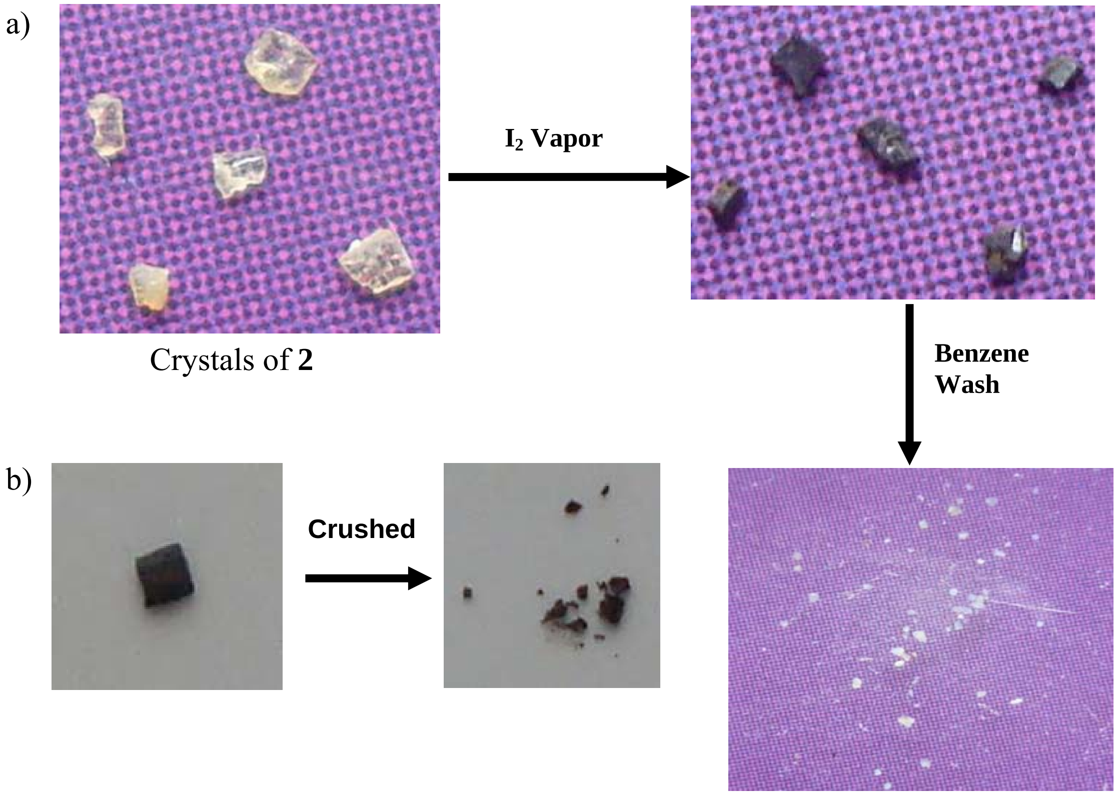


Figure S1: (a) Photographs of the crystals of **2** showing the color change after exposure to I_2 vapors and after their benzene wash and (b) photographs revealing the uniform absorption of I_2 vapors.

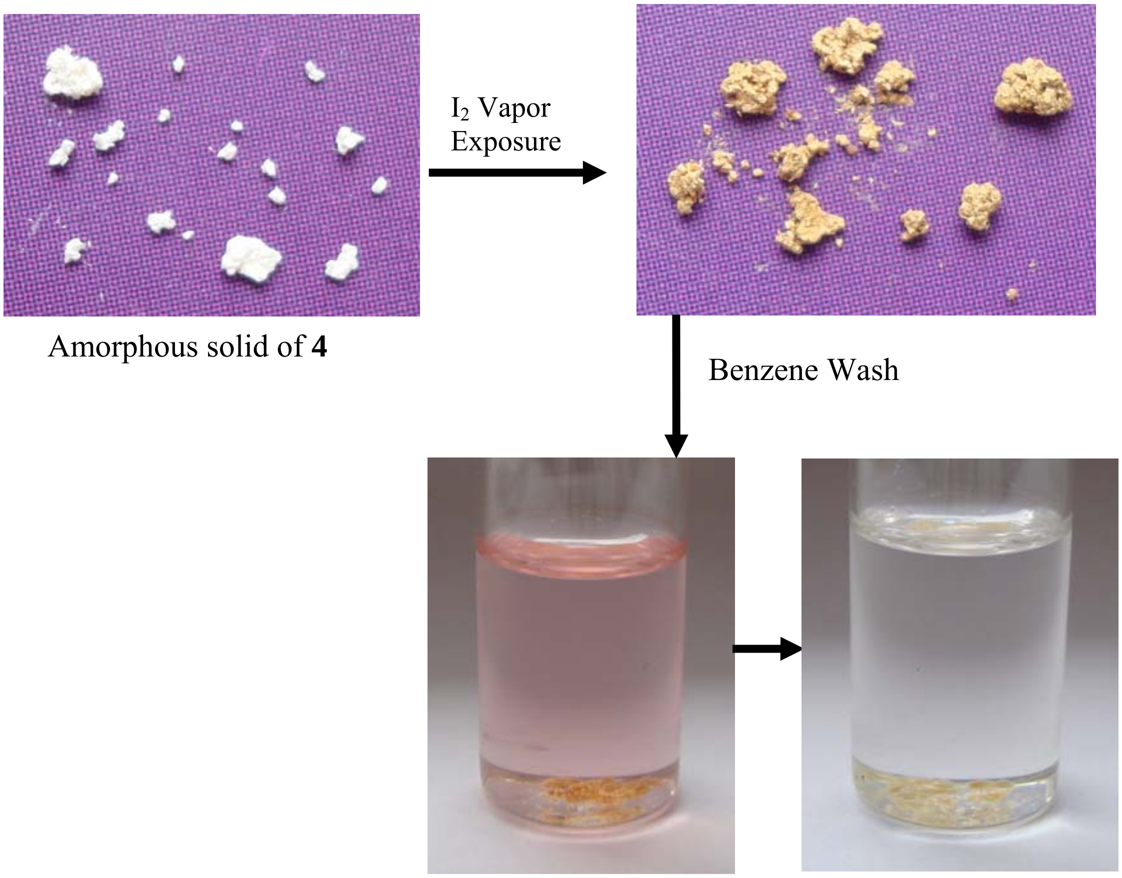


Figure S2: a) Photographs of the amorphous solid of **4** showing the colour change after exposure to I_2 vapours and their subsequent benzene wash to get the original solid.

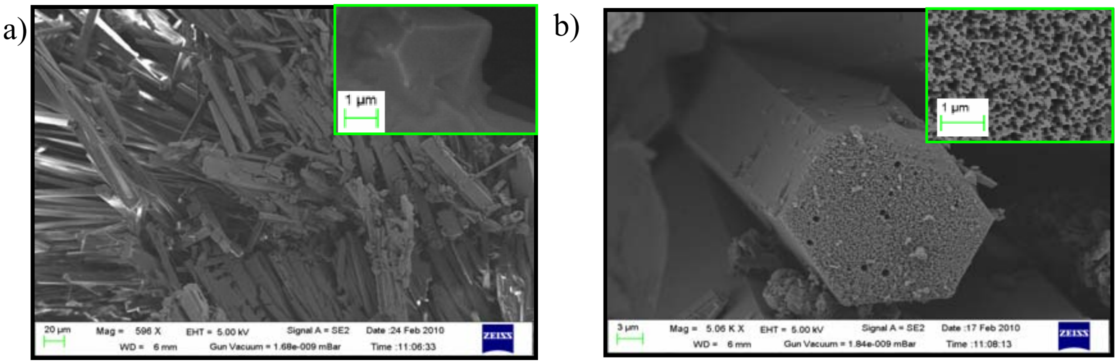


Figure S3: FESEM images showing the crystal morphology of (a) **1**F and (b) **2**.

Iodine Vapor Exposure Study:

Before exposure to I_2 vapors the compounds **2-4** were evacuated under vacuum at 80˚C. After exposure for 24h the compounds were kept in air and the weight loss at regular interval of time is monitored (Table S4-S6).

Compound 2:

Initial weight of the sample=47.7 mg

Table S4: Weight loss of I_2 exposed sample of **2** in air.

Time (min)	Weight of the sample (mg)	Weight Increase by (mg)	% Weight Increased
0	50.8	3.1	6.50
10	50.6	2.9	6.08
20	50.6	2.9	6.08
30	50.6	2.9	6.08
40	50.6	2.9	6.08
50	50.6	2.9	6.08
60	50.6	2.9	6.08
70	50.6	2.9	6.08
80	50.5	2.8	5.87
90	50.5	2.8	5.87
100	50.5	2.8	5.87
110	50.5	2.8	5.87
120	50.5	2.8	5.87
130	50.5	2.8	5.87
140	50.5	2.8	5.87
150	50.5	2.8	5.87
200	50.5	2.8	5.87
24h	50.5	2.8	5.87

Compound 3:

Initial weight of the sample=61.0mg

Table S5: Weight loss of I_2 exposed sample of **3** in air.

Time (min)	Weight of the sample (mg)	Weight Increase by (mg)	% Weight Increased
0	64.4	3.4	5.57
10	64.2	3.2	5.25
20	64.1	3.1	5.08
30	64.1	3.1	5.08
40	64.1	3.1	5.08
50	64.1	3.1	5.08
60	64.1	3.1	5.08
70	64.1	3.1	5.08
80	64.1	3.1	5.08
90	64.1	3.1	5.08
100	64.1	3.1	5.08
110	64.1	3.1	5.08
120	64.1	3.1	5.08
130	64.1	3.1	5.08
140	64.1	3.1	5.08
150	64.1	3.1	5.08
200	64.1	3.1	5.08
24h	64.1	3.1	5.08

Compound 4:

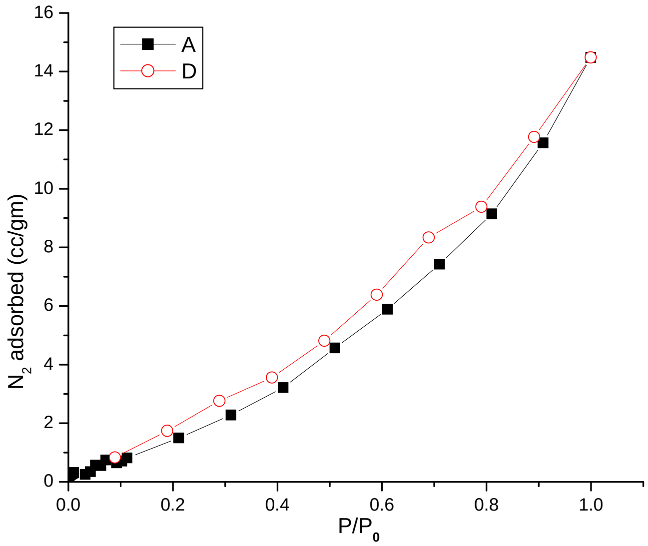
Initial weight of the sample=51.5mg

Table S6: Weight loss of I_2 exposed sample of **4** in air.

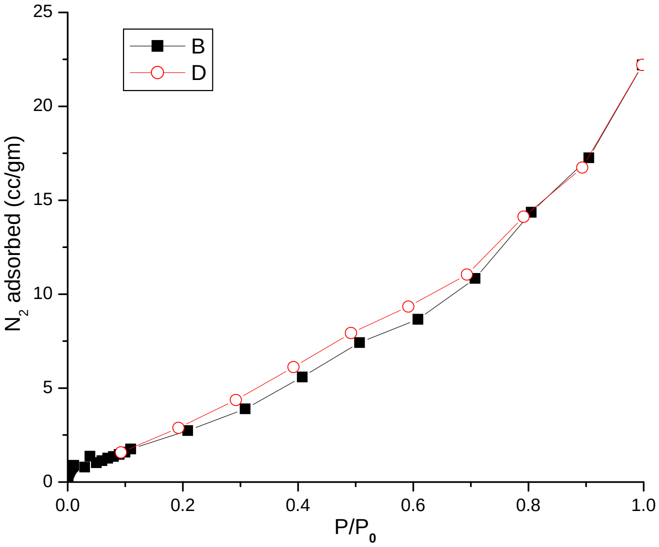
Time (min)	Weight of the sample (mg)	Weight Increase by (mg)	% Weight Increased
0	55.4	3.9	7.57
10	55.3	3.8	7.38
20	55.3	3.8	7.38
30	55.2	3.7	7.18
40	55.2	3.7	7.18
50	55.1	3.6	6.99
60	55.1	3.6	6.99
70	55.1	3.6	6.99
80	55.1	3.6	6.99
90	55.1	3.6	6.99
100	55.0	3.5	6.80
110	55.0	3.5	6.80
120	55.0	3.5	6.80
130	55.0	3.5	6.80
140	55.0	3.5	6.80
150	55.0	3.5	6.80
200	54.9	3.4	6.60
24h	54.8	3.3	6.40

N_2 Absorption Study:

Compound 2:



Compound 3:



P/P_0

Compound 4:

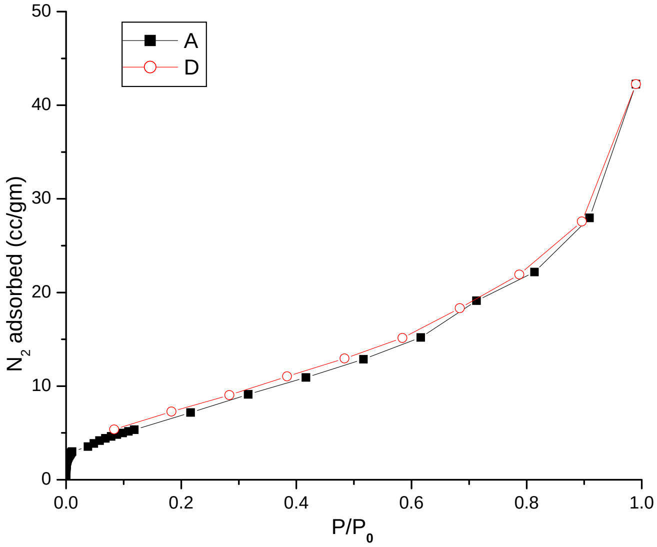
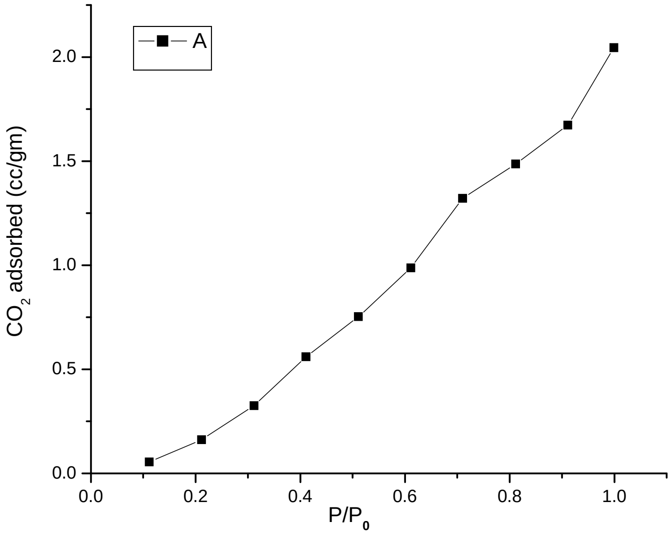


Table S7: N_2 absorption study at 77 K for samples **2-4**.

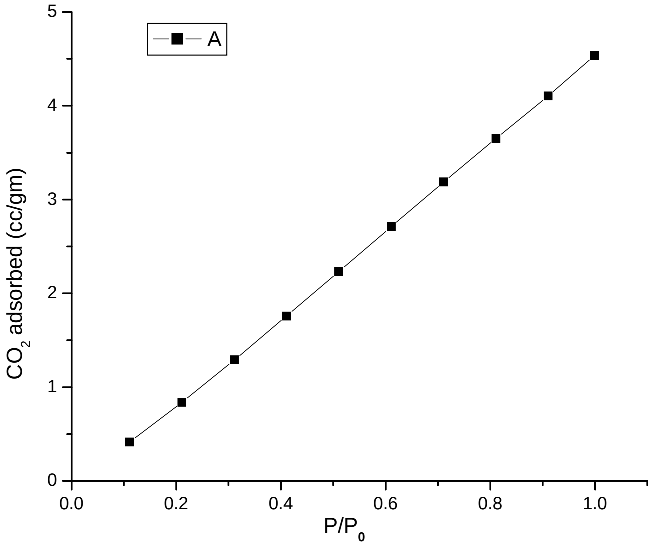
Property/Compound	**2**	**3**	**4**
Average Pore Diameter	71.74 Å	89.58 Å	87.97 Å
Surface Area	12.52 m^2/gm	15.38 m^2/gm	29.78 m^2/gm
Pore Volume	0.0207 cc/gm	0.0312 cc/gm	0.0591 cc/gm
Max Amount of Gas Ads.	14.48 cc/gm	22.21 cc/gm	42.24 cc/gm
Total Pore Volume	0.0225 cc/gm	0.0344 cc/gm	0.0655 cc/gm
Nature	mesoporous	mesoporous	mesoporous
% Wt. Absorbed	1.81	2.78	5.28
Isotherm type	III	III	III

CO_2 Absorption Study:

Compound 2:



Compound 3:



Compound 4:

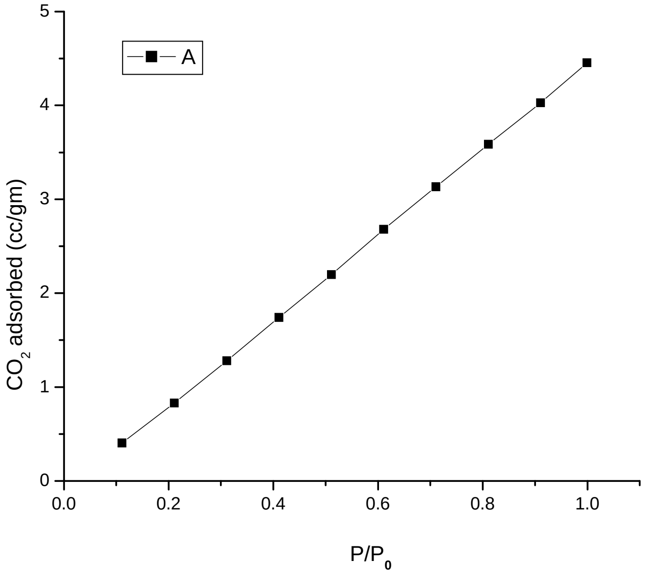


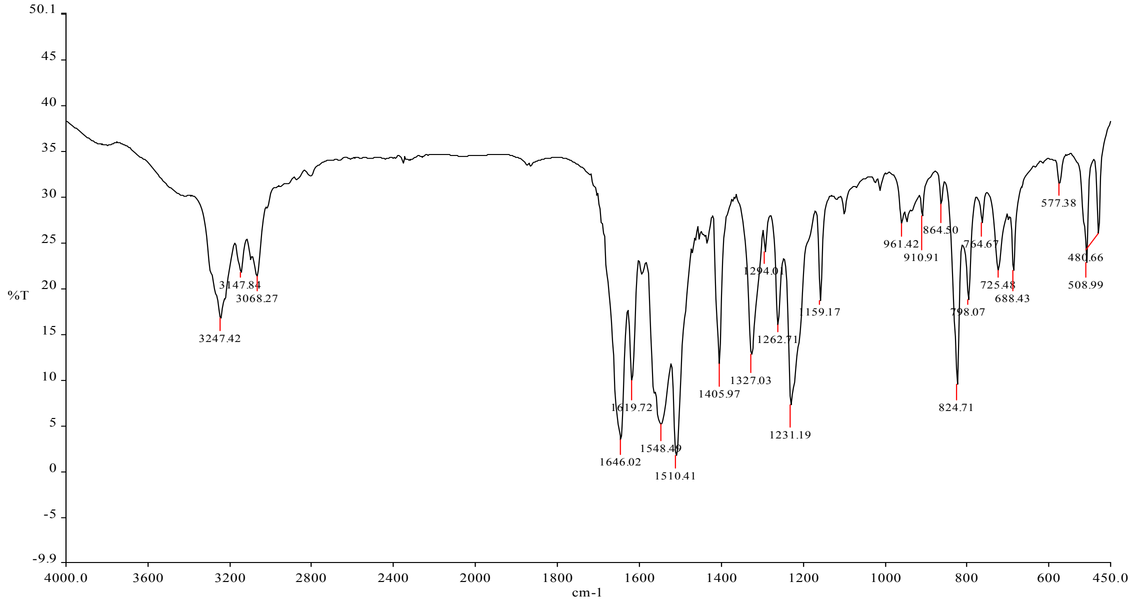
Table S8: CO$_2$ absorption study at 296 K for samples **2-4**.

Property/Compound	**2**	**3**	**4**
Max Amount of Gas Ads.	2.0450 cc/gm	4.5358cc/gm	4.4552 cc/gm
% Wt. Absorbed	0.40	0.88	0.87

Spectroscopic analysis:

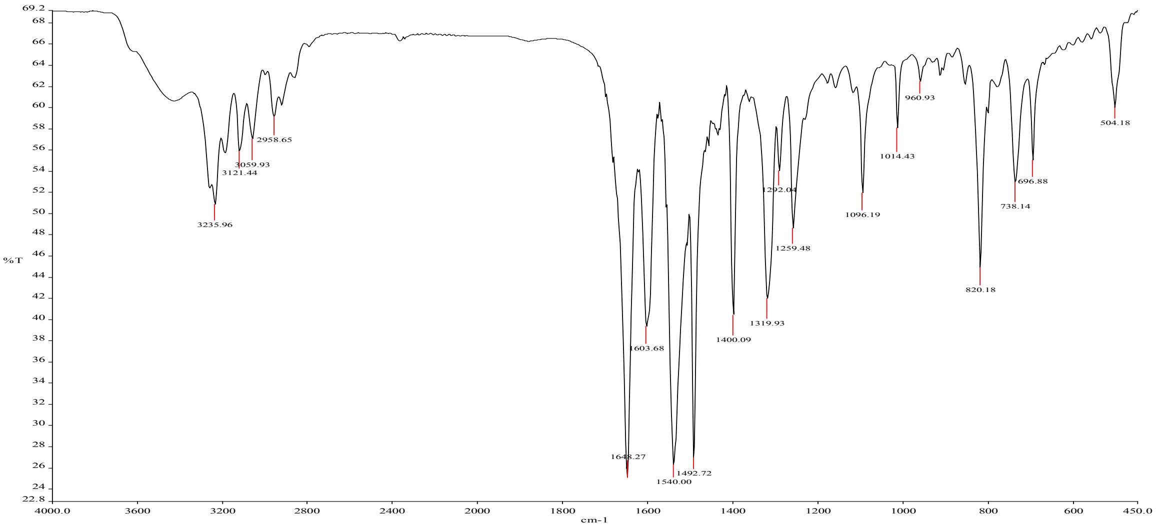
IR:

Compound **1**F**:**



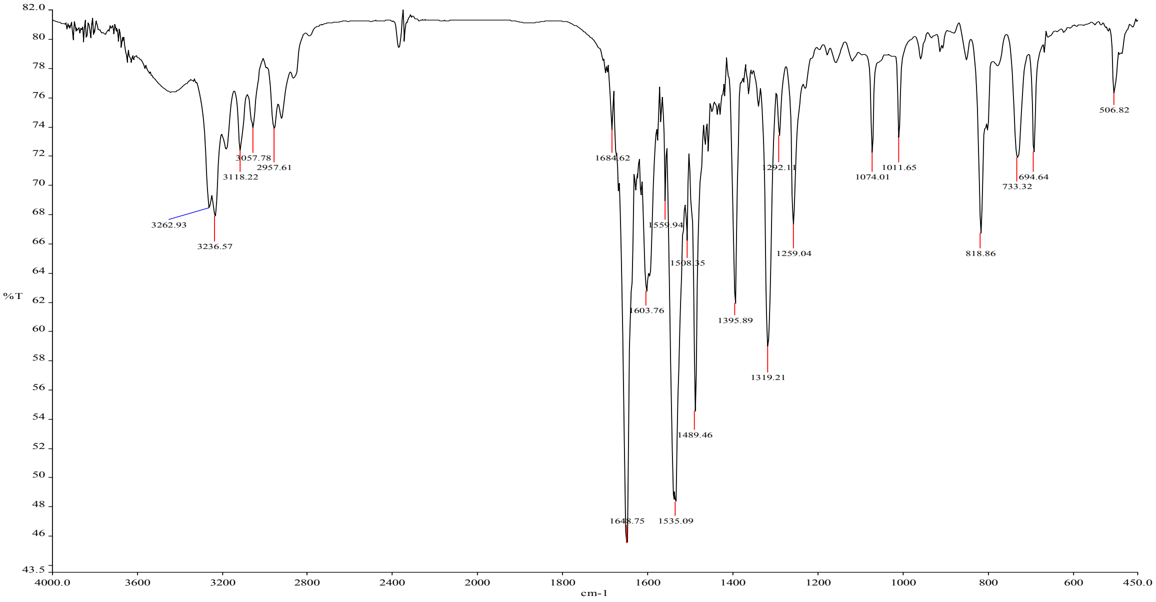
The N-H stretch, 3247 cm^{-1}; amide C=O stretch (amide-I band), 1646 cm^{-1}; N-H bending (amide-II band), 1548 cm^{-1}; interaction between the N-H bending and C-N stretching 1262 cm^{-1}; C-F stretching vibration, 1159 cm^{-1}, 1231 cm^{-1}, 1327 cm^{-1}.

Compound **1**Cl**:**



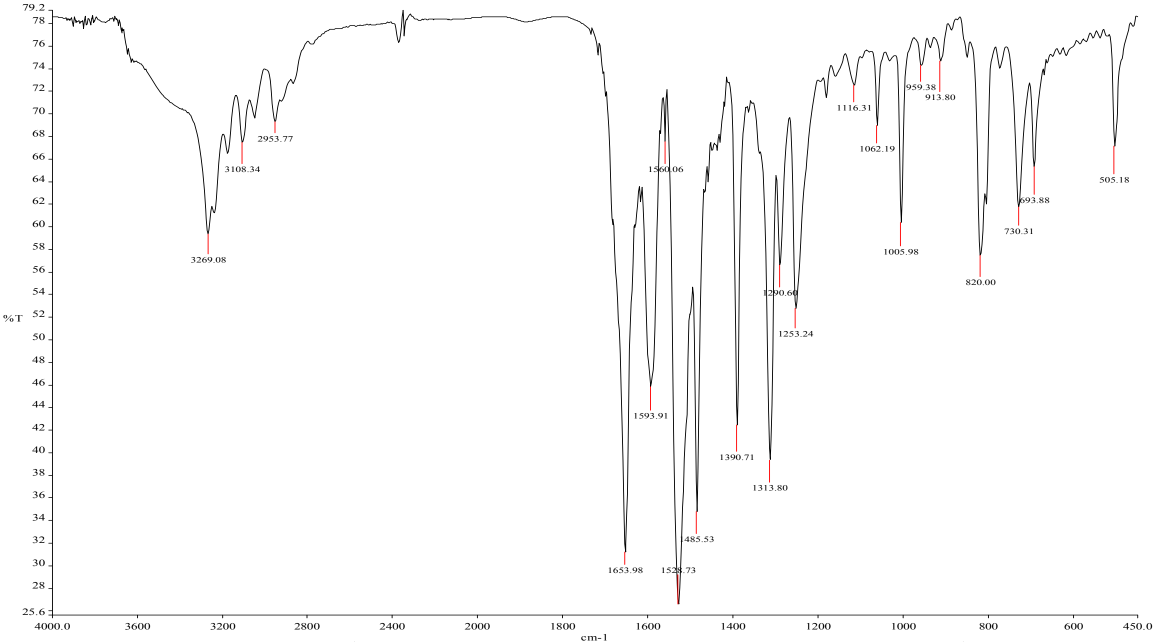
The N-H stretch, 3235 cm^{-1}; amide C=O stretch (amide-I band), 1648 cm^{-1}; N-H bending (amide-II band), 1540 cm^{-1}; interaction between the N-H bending and C-N stretching 1259 cm^{-1}; C-Cl absorption, 696 cm^{-1}, 738 cm^{-1}, 820 cm^{-1}.

Compound **1**Br**:**



The N-H stretch, 3236 cm^{-1}; amide C=O stretch (amide-I band), 1648 cm^{-1}; N-H bending (amide-II band), 1535 cm^{-1}; interaction between the N-H bending and C-N stretching 1259 cm^{-1}; C-Br absorption, 506 cm^{-1}, 694 cm^{-1}.

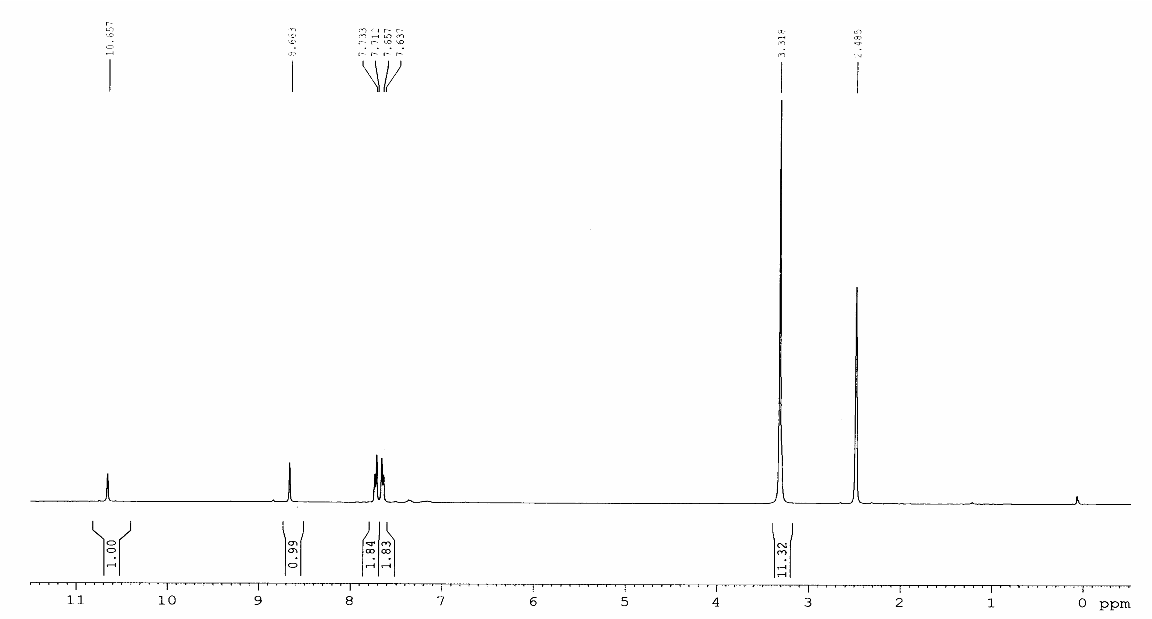
Compound **1I:**



The N-H stretch, 3269 cm^{-1}; amide C=O stretch (amide-I band), 1653 cm^{-1}; N-H bending (amide-II band), 1528 cm^{-1}; interaction between the N-H bending and C-N stretching 1253 cm^{-1}; C-I absorption, 505 cm^{-1}.

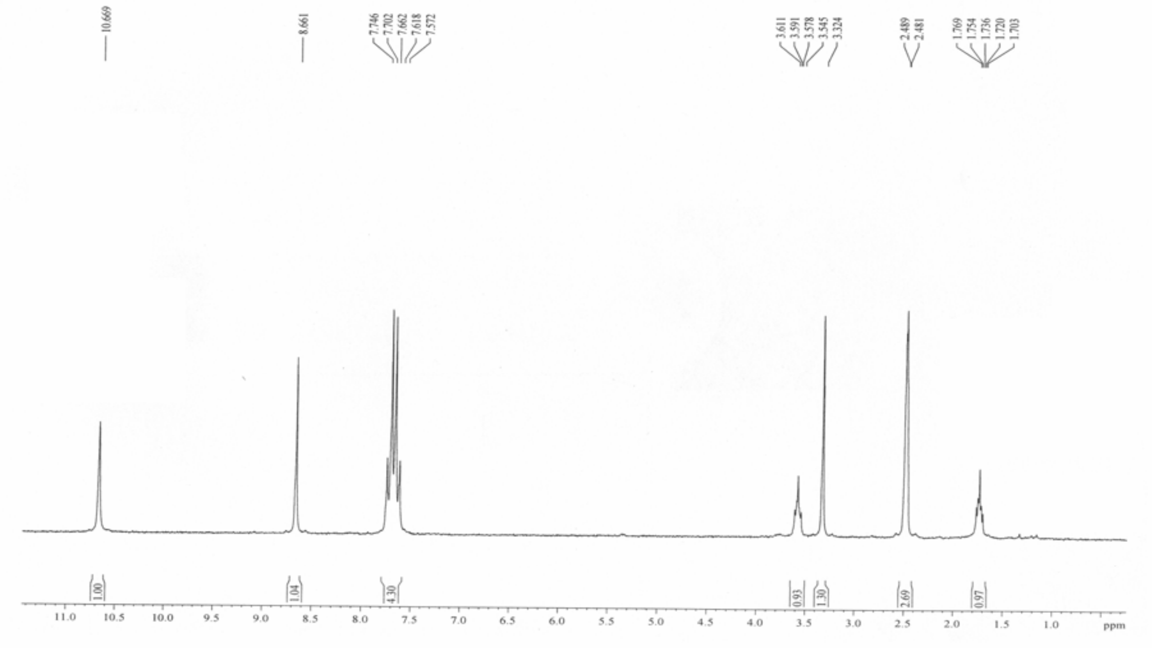
^{1}H-NMR for:

Compound **1I:**



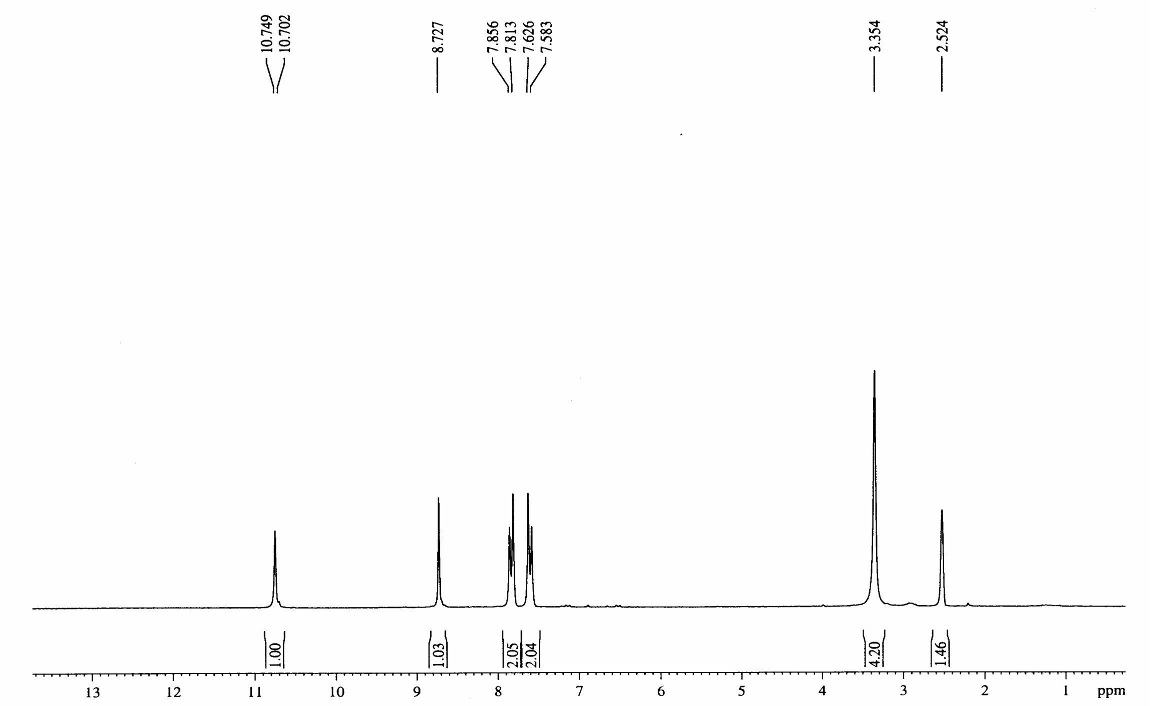
NMR: (D^{6}DMSO),δ_H(ppm)**:** 7.64(6H, d, iodophenyl m-H); 7.72(6H, d, iodophenyl o-H); 8.66(3H, s, Ar-H); 10.65(3H, s, NH).

Compound **2:** (Molecule: THF ratio observed is 1: 0.7)



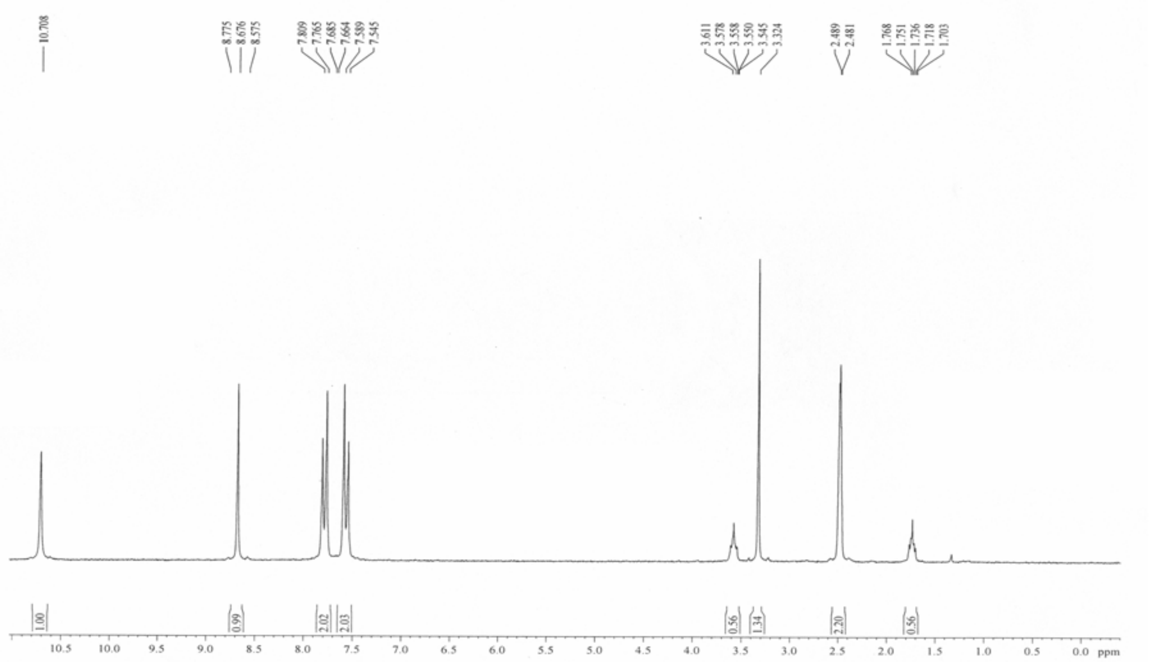
NMR: (D^{6}DMSO),δ_H(ppm)**:**1.73(4H, t, THF α-H); 3.58(4H, t, THF *β*-H); 7.57-7.75(12H, m, iodophenyl H); 8.66(3H, s, Ar-H); 10.67(3H, s, NH).

Compound **1**Br**:**



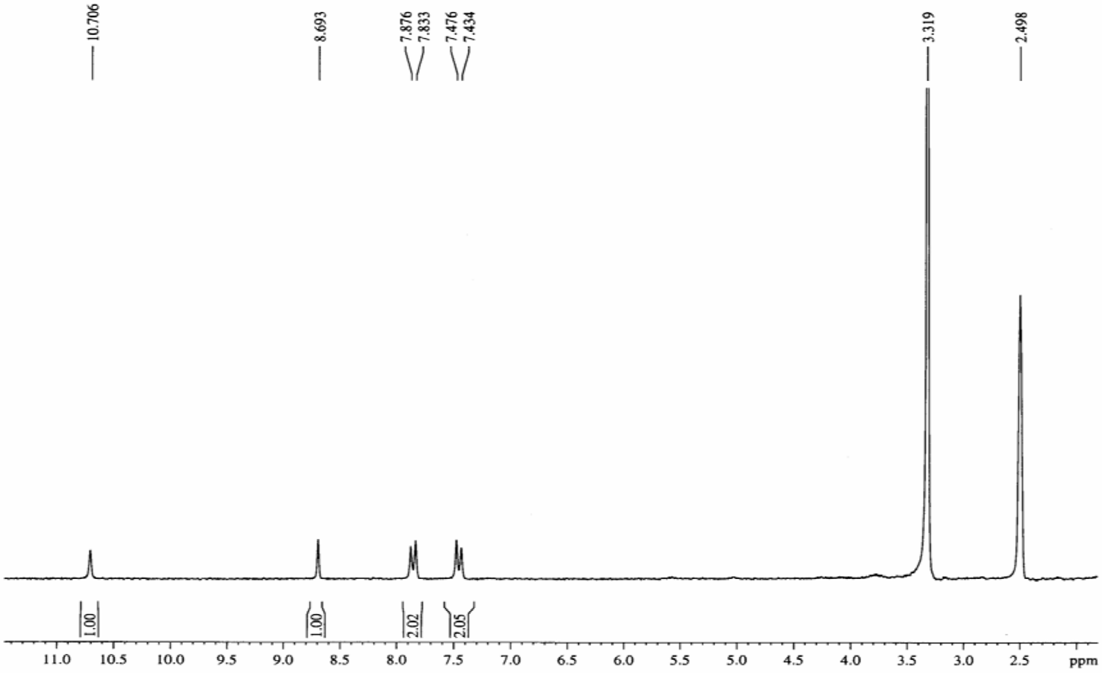
NMR: (D^{6}DMSO),δ_H(ppm)**:** 7.60(6H, d, o-H); 7.83(6H, d, m-H); 8.72(3H, s, Ar-H); 10.72(3H, s, NH).

Compound **3:** (Molecule: THF ratio observed is 1: 0.4)



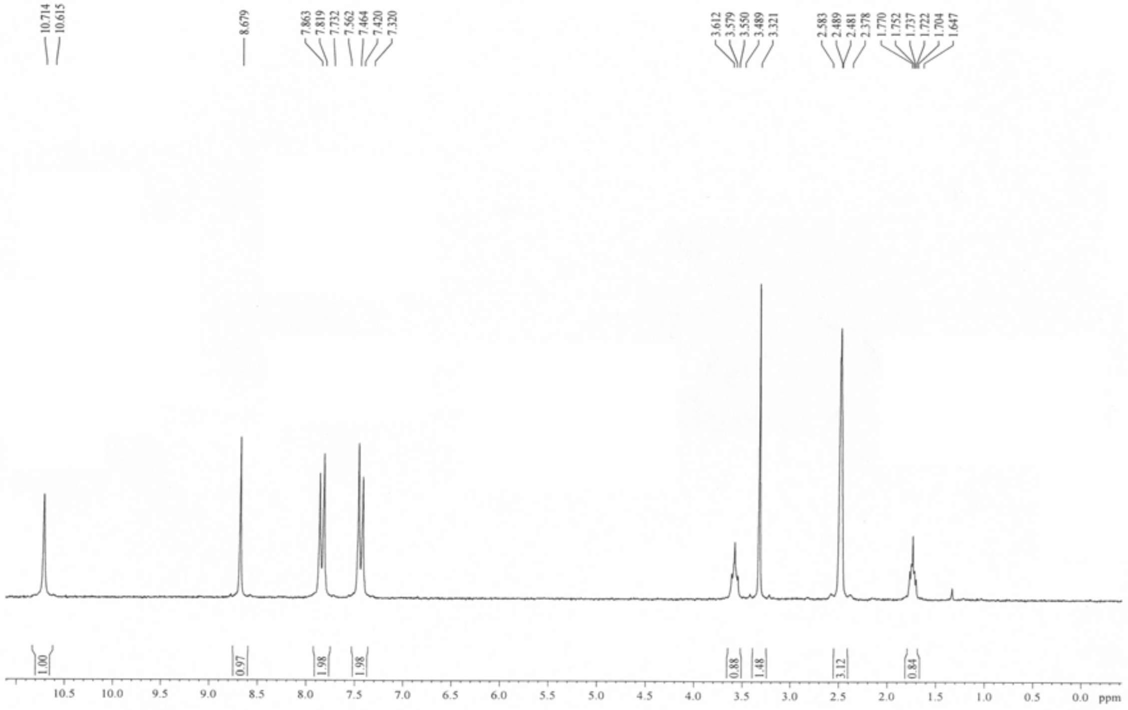
NMR: (D^{6}DMSO),δ_H(ppm)**:**1.73(4H, t, THF α-H); 3.55(4H, t, THF *β*-H); 7.60(6H, d, bromophenyl o-H); 7.74(6H, d, bromophenyl m-H); 8.67 (3H, s, Ar-H); 10.70(3H, s, NH).

Compound **1**Cl**:**



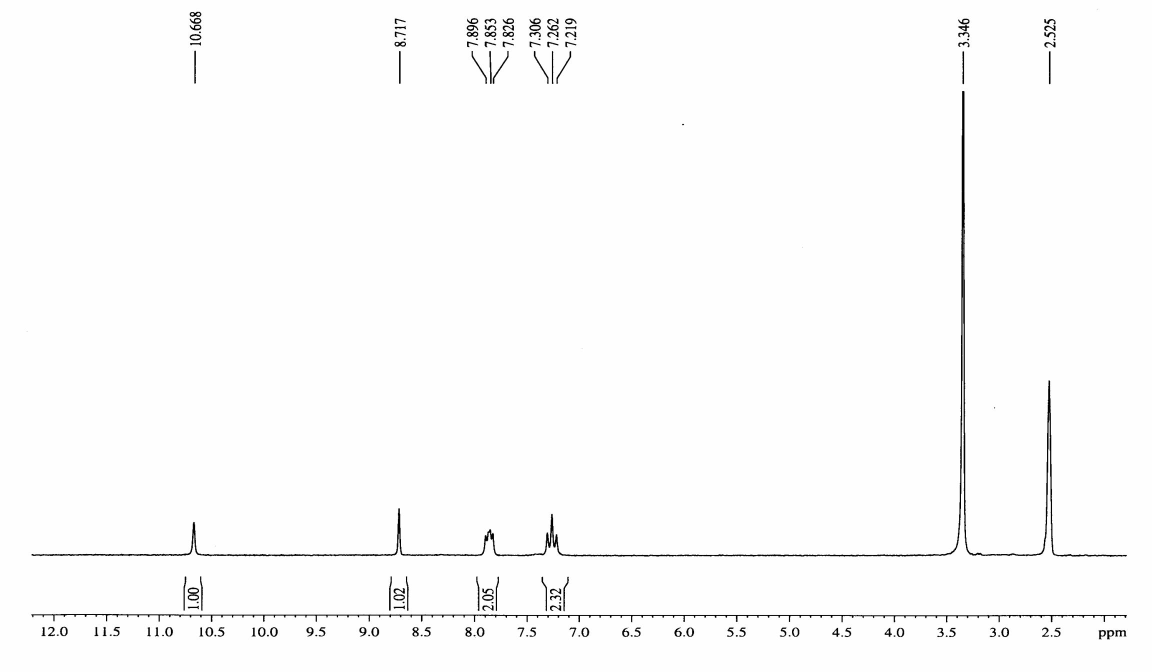
NMR: (D^{6}DMSO),δ_H(ppm)**:** 7.45(6H, d, chlorophenyl o-H); 7.85(6H, d, chlorophenyl m-H); 8.69(3H, s, Ar-H); 10.70(3H, s, NH).

Compound **4:** (Molecule: THF ratio observed is 1: 0.66)



NMR: (D^{6}DMSO),δ_H(ppm)**:** 1.73(4H, t, THF α-H); 3.58(4H, t, THF *β*-H); 7.44(6H, d, chlorophenyl o-H); 7.84(6H, d, chlorophenyl m-H); 8.67(3H, s, Ar-H); 10.71(3H, s, NH).

Compound **1F:**



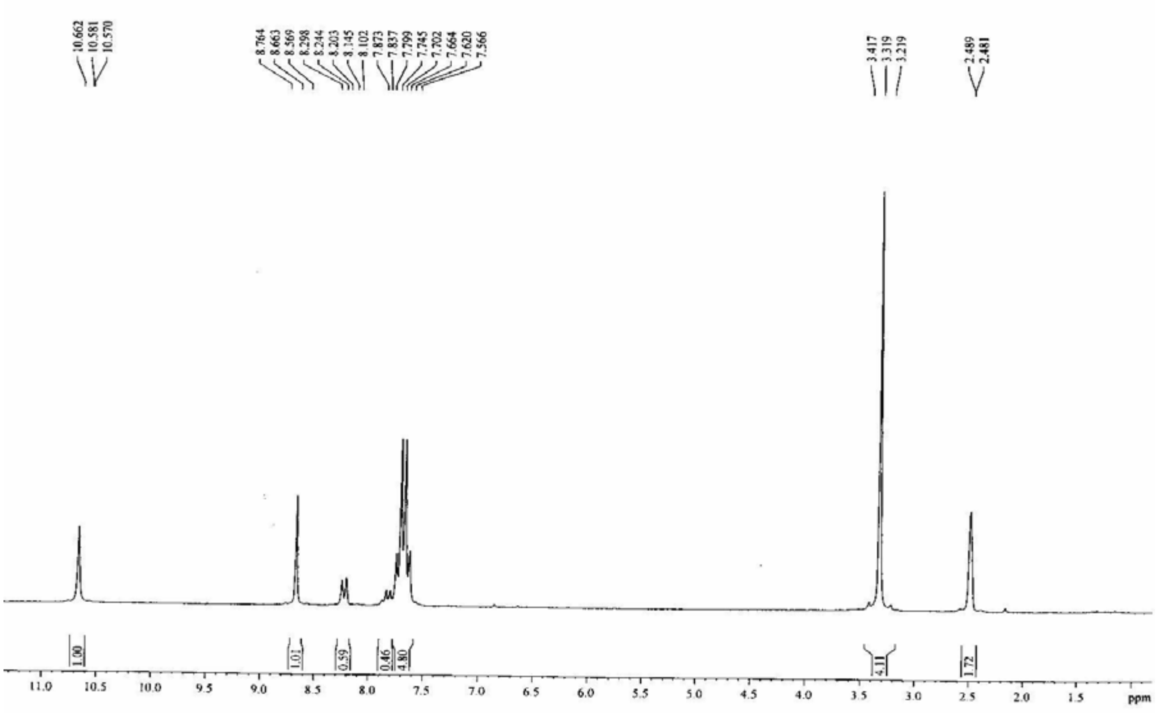
NMR:(D^{6}DMSO),δ_H(ppm): 7.26(6H, t, fluorophenyl o-H); 7.85(6H, t, fluorophenyl m-H); 8.71(3H, s, Ar-H); 10.67(3H, s, NH).

^{1}H-NMR for Guest Exchange Study:

Table S9: Guest exchange study of **2** in different solvents.

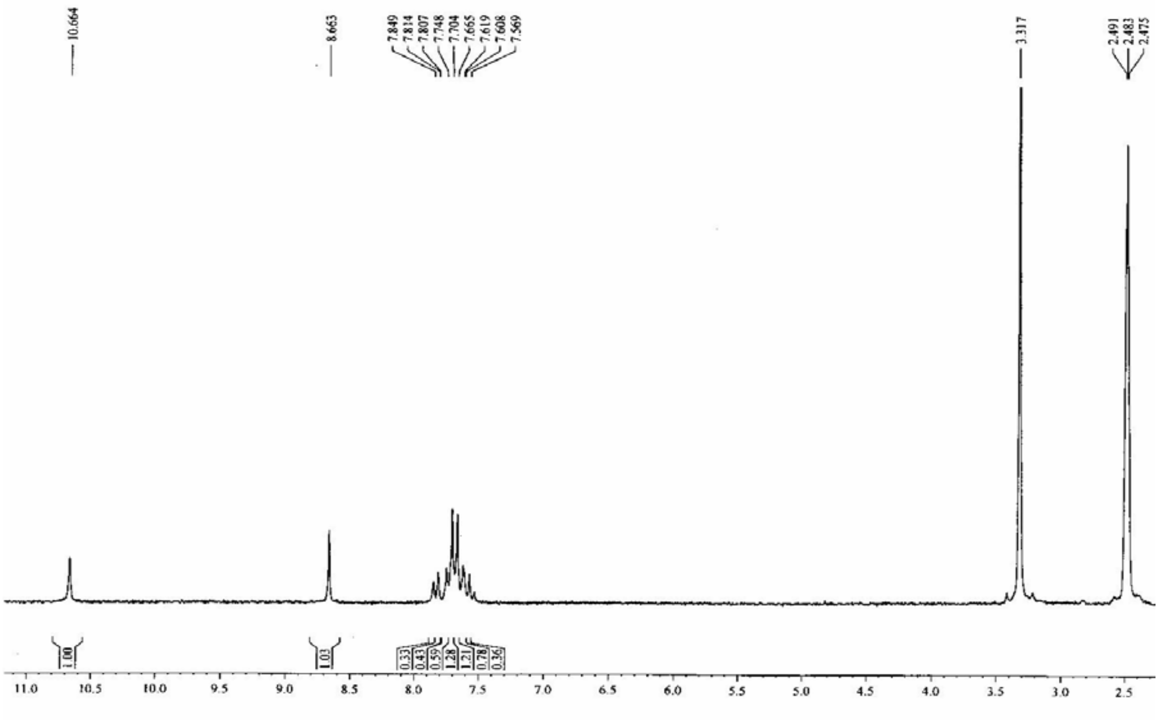
Guest	Ratio of **2: Guest** Observed
Nitrobenzene	1:1
Benzonitrile	1:1
Iodobenzene	1:1
Bromobenzene	1:0.6
Chlorobenzene	1:0.5
Mesitylene	1:0.2
$CHCl_3$	No inclusion

Nitrobenzene:



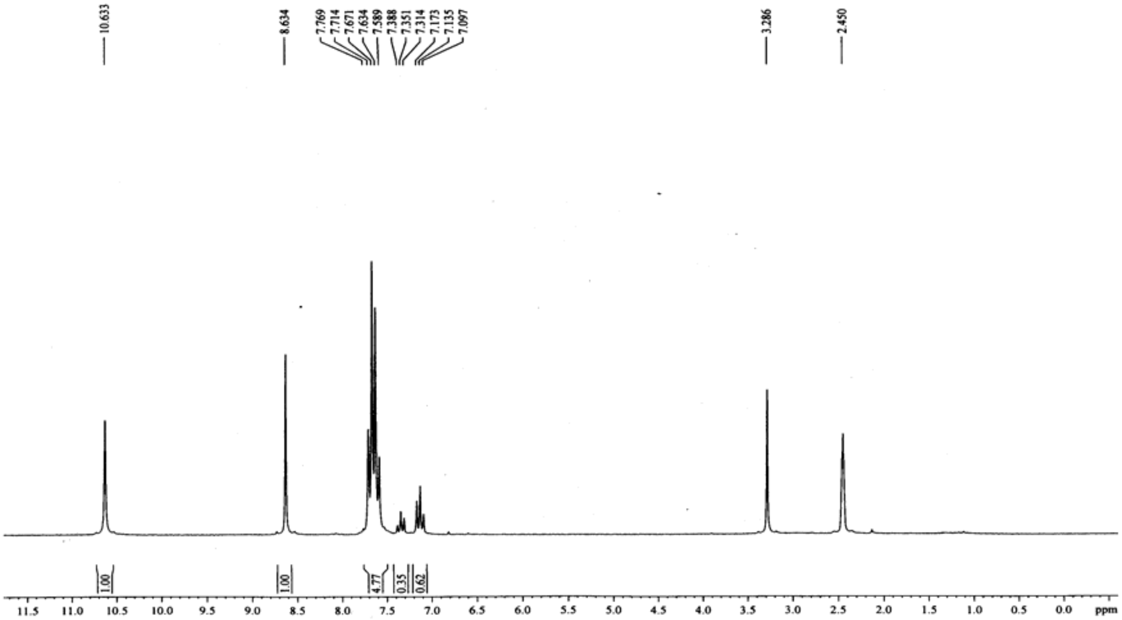
NMR: (D^{6}DMSO),δ_H(ppm): 7.57-7.79(12H, m, iodophenyl H); 8.66(3H, s, Ar-H); 10.67(3H, s, NH). Guest: 8.10-8.24 (2H, dd, *o*-H); 7.79-7.87 (1H, t, *p*-H); 7.57-7.79 (2H, dd, *m*-H).

Benzonitrile:



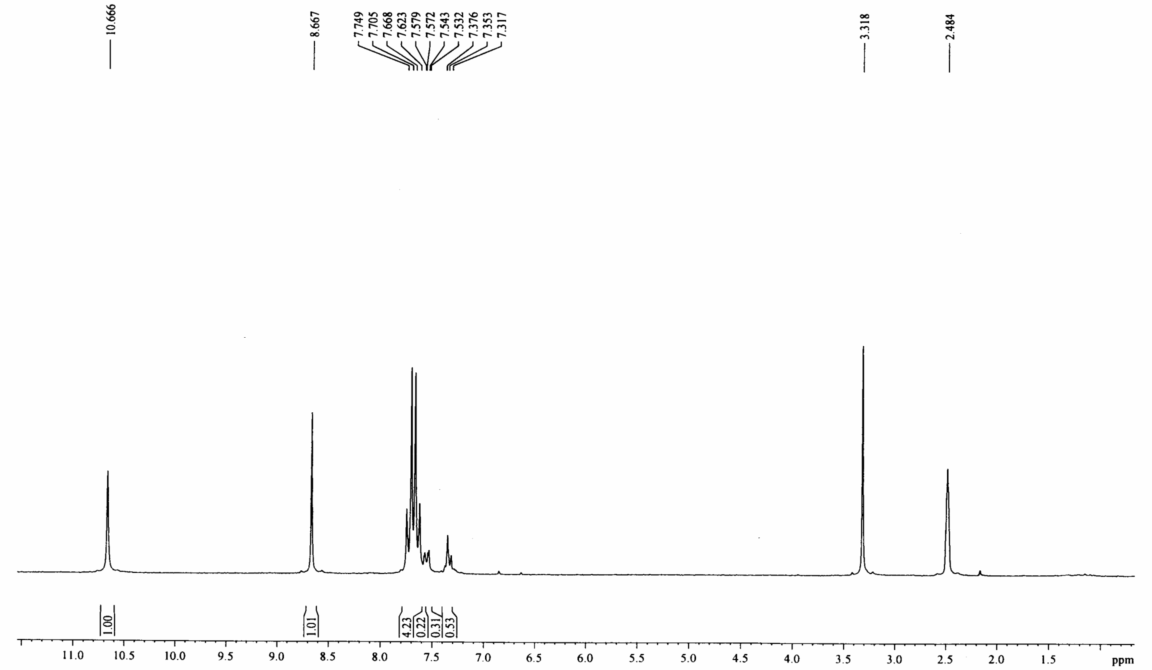
NMR: (D^6DMSO),δ_H(ppm): 7.57-7.79(12H, m, iodophenyl H); 8.66(3H, s, Ar-H); 10.67(3H, s, NH). Guest: 7.81-7.85 (1H, t, *p*-H); 7.57-7.80 (2H, m, *o*-H); 7.57-7.80 (2H, m, *m*-H).

Iodobenzene:



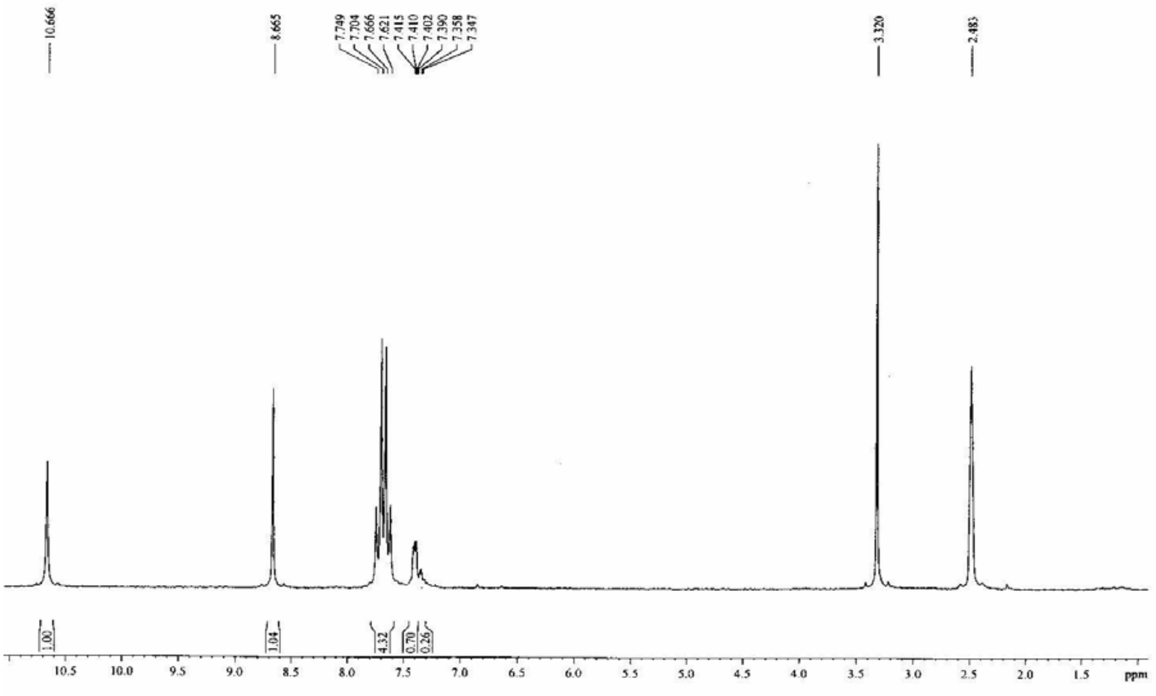
NMR: (D^6DMSO),δ_H(ppm): 7.56-7.77(12H, m, iodophenyl H); 8.66(3H, s, Ar-H); 10.67(3H, s, NH). Guest: 7.31-7.39 (1H, t, *p*-H); 7.09-7.17 (2H, t, *m*-H); 7.56-7.77 (2H, m, *o*-H).

Bromobenzene:



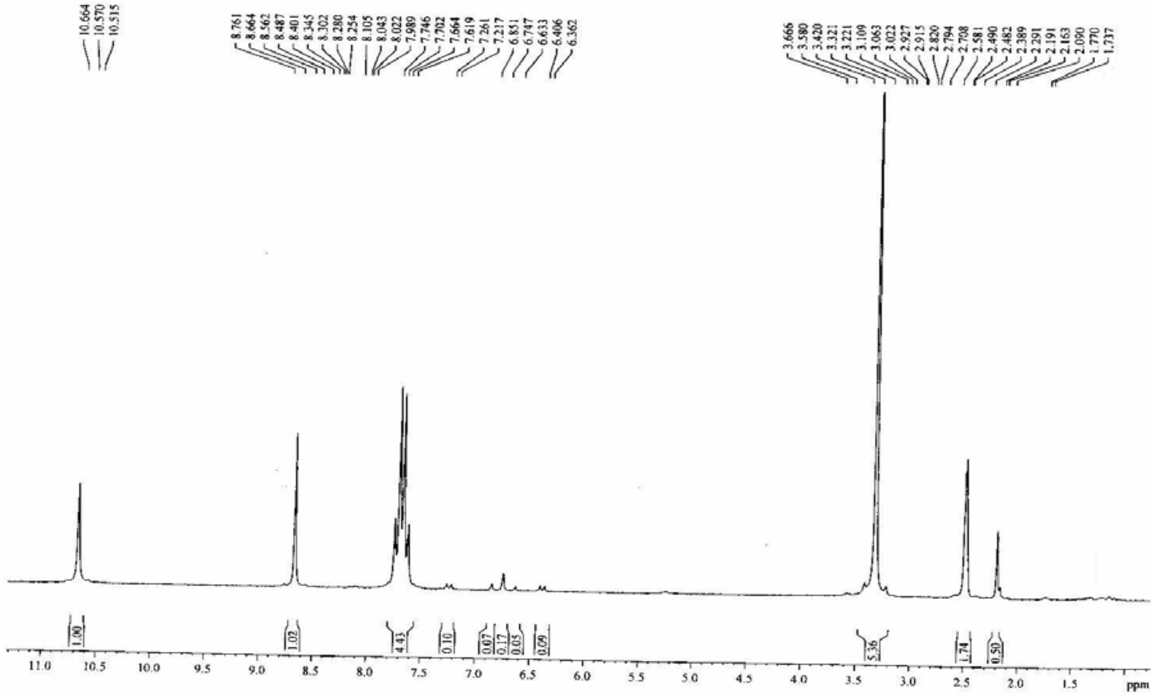
NMR: (D^{6}DMSO),δ_H(ppm): 7.56-7.77(12H, m, iodophenyl H); 8.66(3H, s, Ar-H); 10.67(3H, s, NH). Guest: 7.32-7.38 (2H, t, *m*-H); 7.53-7.54 (1H, dd, *p*-H); 7.53-7.75 (2H, m, *o*-H).

Chlorobenzene:



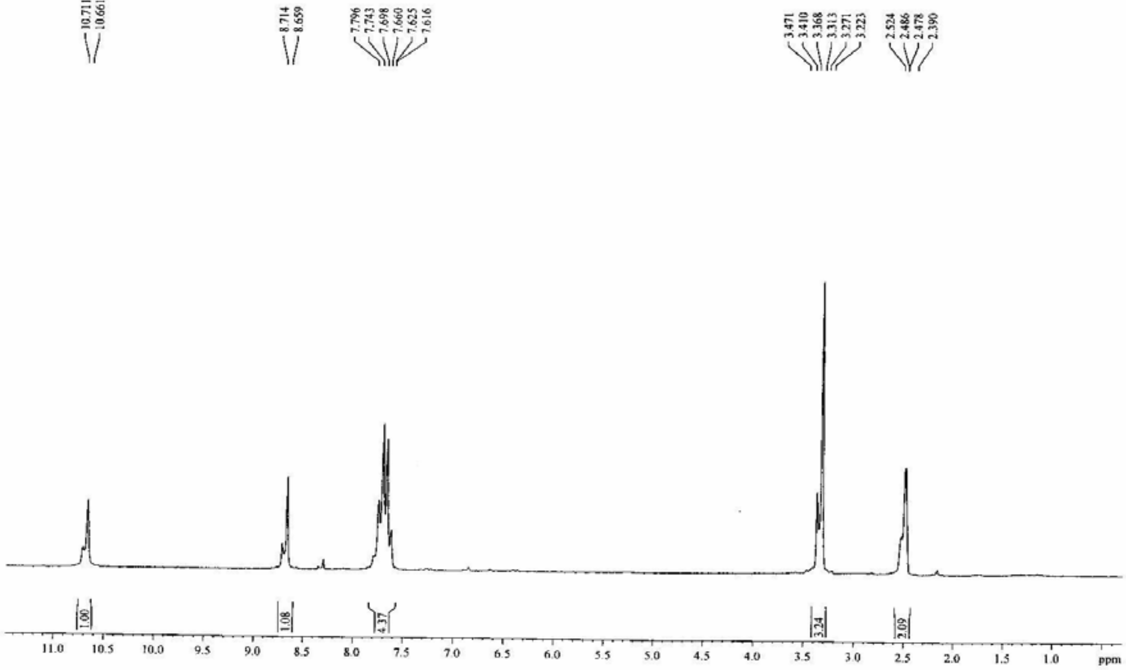
NMR: (D^{6}DMSO),δ_H(ppm): 7.56-7.77(12H, m, iodophenyl H); 8.66(3H, s, Ar-H); 10.67(3H, s, NH). Guest: 7.34-7.35 (1H, t, *p*-H); 7.39-7.42 (4H, m, *o* & *m*-H).

Mesitylene:



NMR: (D^{6}DMSO),δ_H(ppm): 7.56-7.77(12H, m, iodophenyl H); 8.66(3H, s, Ar-H); 10.67(3H, s, NH). Guest: 2.16-2.29 (9H, d, -CH_3); 6.74 (3H, s, Ar-H).

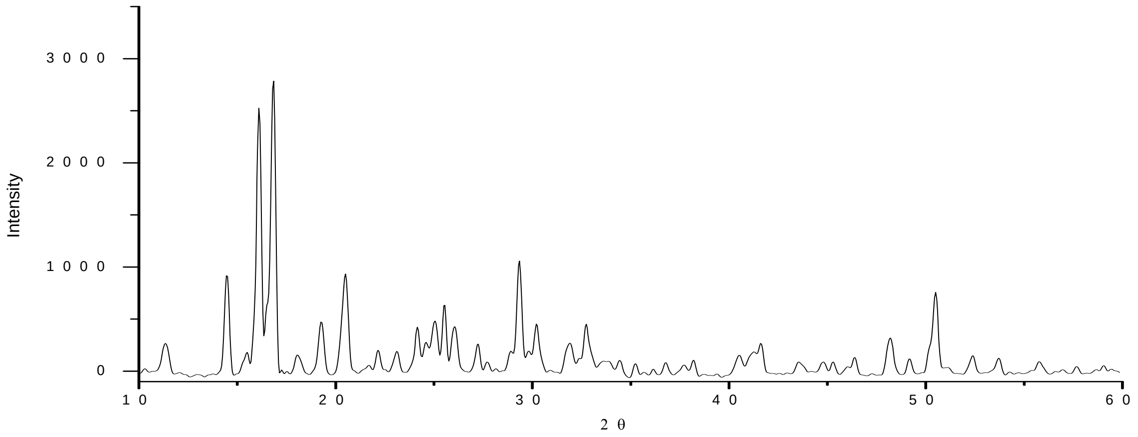
$CHCl_3$:



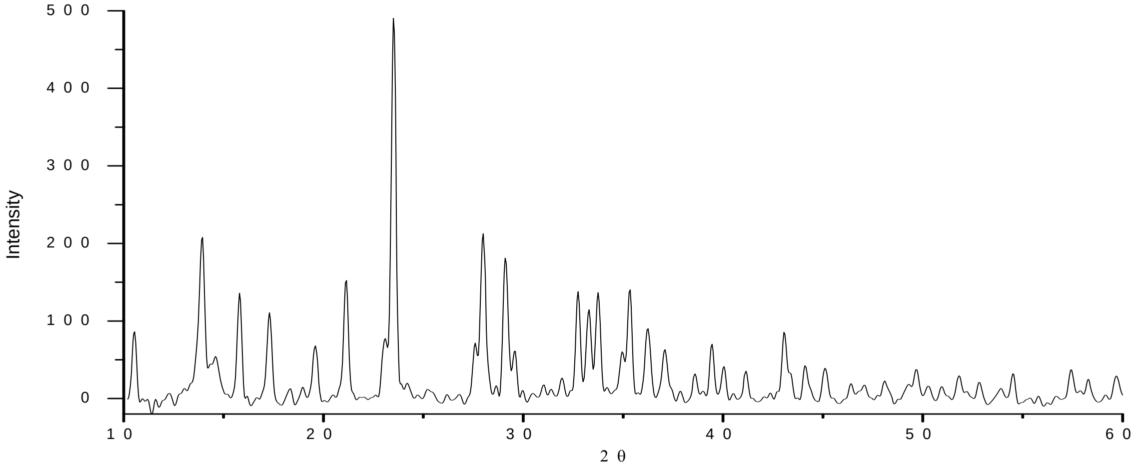
NMR: (D^{6}DMSO),δ_H(ppm): 7.56-7.77(12H, m, iodophenyl H); 8.66(3H, s, Ar-H); 10.67(3H, s, NH). Guest: No guest inclusion.

Powder XRD Pattern (Cu Target):

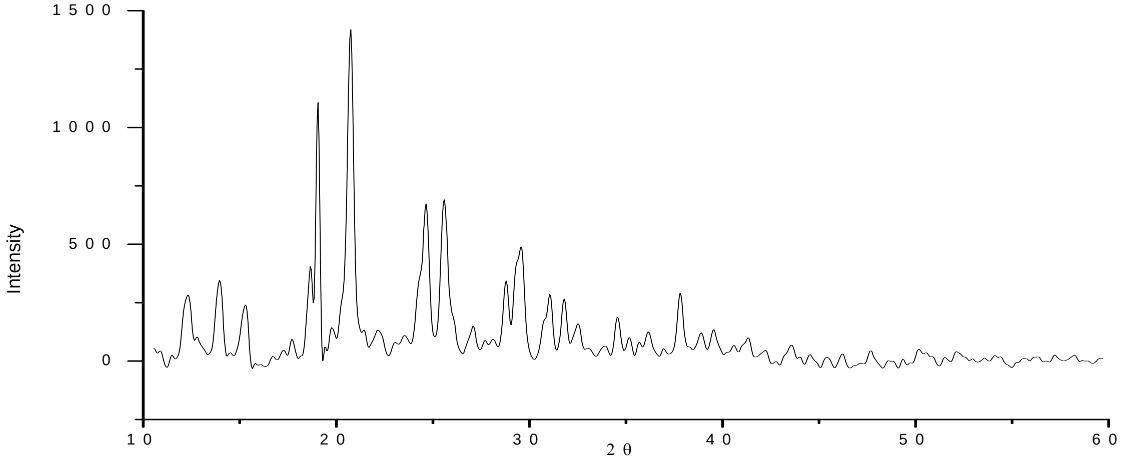
Compound **1**F**:**



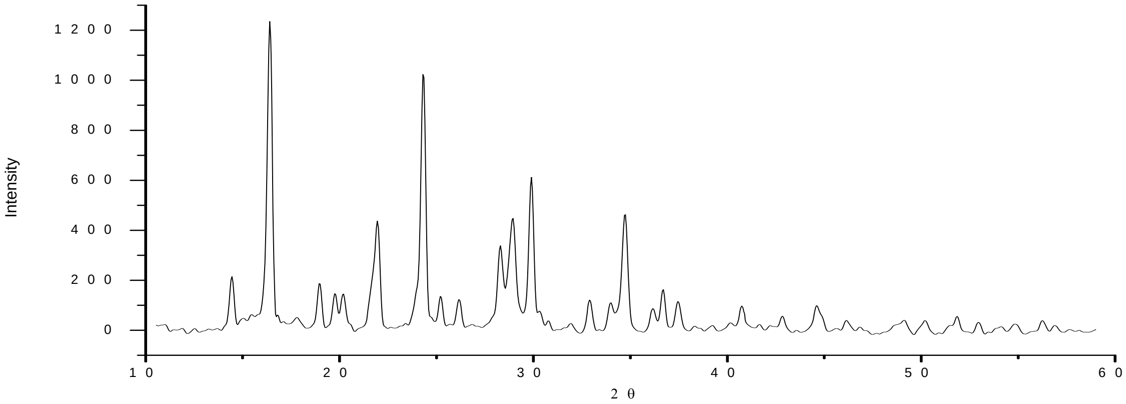
Compound **2:**



Compound **3:**



Compound **4:**



X-ray powder diffraction (*Structure refinement)*:

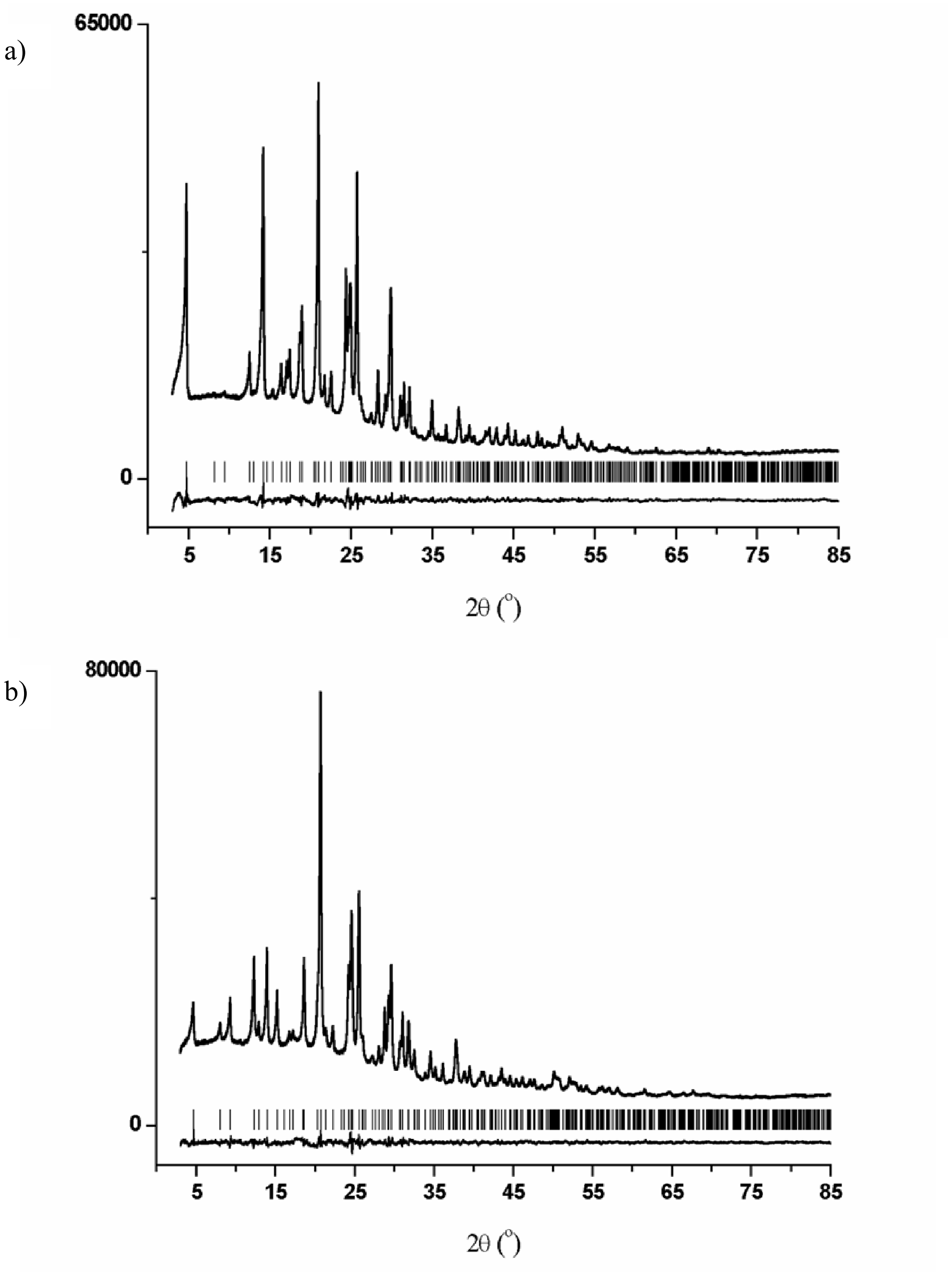


Figure S4: The Rietveld plots, showing the observed and difference profiles for a) **3** and b) **4**. The reflection positions are shown above the difference profiles.

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