Supporting Information:

Conformational adjustments over homo and hetero synthons of urea and thiourea based assemblies

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Supporting Experimental

General information and materials

All the materials for synthesis were purchased from commercial suppliers and used without further purification. IR spectra were recorded using a Perkin-Elmer Spectrum One FT-IR spectrometer with KBr pellets in the range 4000-400 cm^{-1}. ^{1}H-NMR spectra were recorded on a Varian 400 MHz FTNMR and a BRUKER Ascend-600 MHz spectrometer using TMS as internal standard. PXRD patterns were recorded on a Bruker D8 Advance (Germany) diffractometer with Cu Kα (1.542 Å) radiation operating at 40 kV and 40 mA on glass surface of air-dried samples. The mass spectra were obtained using Waters Q-ToF Premier mass spectrometer. The differential scanning calorimetry (DSC) plots were recorded by using a TA Instrument Q20 differential scanning calorimeter and SDT Q600 analyzer under nitrogen atmosphere. Calibration of the instrument was performed using indium standard with cell constant of 1.0609, and the experimental accuracy on temperature was ±0.1 °C.

1-(5-Methylthiazol-2-yl)-3-naphthalen-1-yl-thiourea (1): 5-Methylthiazol-2-yl-amine (23 mg, 2 mmol) and 1-naphthyl isothiocyanate (37 mg, 2 mmol) were dissolved in diethylether (20 mL), and the solution was stirred for 6 hrs. The resulting solution was evaporated, and the precipitate was dried in vacuum. Yield: 89 %.^{1}H-NMR (400 MHz, DMSO-d_6): δ 12.03 (s, 1H), 7.96 (m, 1H), 7.90 (m,1H), 7.86 (d, 8.0 Hz, 1H), 7.60 (s, 1H), 7.53 (m, 4H), 7.08 (s, 1H), 2.28 (s, 3H). ESI MS: calcd mass for (M+1) $C_{15}H_{13}N_3S_2$, 300.0631; found, 300.0600 [M+ 1]. IR (cm^{-1}): 3460 (w), 3250 (m), 1620 (m), 1550 (s), 1550 (s), 1500 (s), 1360 (s), 1190 (s), 824 (m), 774 (s), 708

(s), 651(s), 523 (s). Polymorph **1a** was crystallized from dimethylformamide, whereas polymorph **1b** was crystallized from dimethylsulfoxide.

1-(4-Methylthiazol-2-yl)-3-naphthalen-1-yl-thiourea (2): Compound **2** was prepared by following a procedure similar to the synthesis of **1**, but 4-methylthiazol-2-ylamine was used in place of 5-methylthiazol-2-ylamine. Yield 92 %. ^{1}H-NMR (600 MHz, DMSO-d_6): δ 12.16 (s, 1H), 7.96 (m, 3 H), 7.86 (d, 1H), 7.69 (s, 1H), 7.54 (m, 3H), 6.60 (s, 1H), 2.20 (s, 3H). ESI MS: calcd mass for (M+1) $C_{15}H_{13}N_3S_2$, 300.0631; found, 300.0639 [M+ 1]. IR (cm^{-1}): 3470 (w), 1570 (s), 1530 (s), 1510 (s), 1380 (m), 1210 (s), 857 (m), 768 (s), 695 (s), 513 (m). Polymorph **2a** was crystallized from diethylether, whereas polymorph **2b** was crystallized from dimethylformamide.

1-(5-Methylthiazol-2-yl)-3-naphthalen-1-yl-urea (3): 5-Methylthiazol-2-yl-amine (23 mg, 2 mmol) and 1-naphthyl isocyanate (35 mg, 2mmol) were dissolved in dry dichloromethane (20 mL), and the solution was stirred for 6 hrs. The resulting solution was evaporated, and the precipitate was dried in vacuum. Yield: 95 %. ^{1}H-NMR (400 MHz,DMSO-d_6): δ 10.67 (s, 1H), 9.16 (s, 1H), 8.08 (d, 8.0 Hz, 1H), 8.03 (d, 8.0 Hz, 1H), 7.96 (d, 8.0 Hz, 1H), 7.69 (d, 8.0 Hz, 1H), 7.62 (t, 8.0 Hz, 1H), 7.65 (d, 12.0 Hz, 1H), 7.50 (t, 8.0 Hz, 1H), 7.08 (s, 1H), 2.08 (s, 3H). ESI MS: calcd mass for (M+1) $C_{15}H_{11}N_3OS$, 284.0859; found, 284.0922 [M+ 1]. IR (cm^{-1}): 3430 (w), 2930 (w), 1720 (m), 1680 (s), 1610 (m), 1550 (s), 1510 (m), 1260 (s), 763 (s), 523 (s).

1-(4-Methylthiazol-2-yl)-3-naphthalen-1-yl-urea (4): Compound **4** was prepared by the procedure similar to the synthesis of **4**, but 4-methylthiazol-2-ylamine was used in place of 5-methylthiazol-2-ylamine. Yield 90 %. ESI MS: calcd mass for (M+1) $C_{15}H_{11}N_3OS$, 284.0859; found, 284.0900 [M+ 1]**.** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.03 (bs, 3H), 7.84 (d, 8.0 Hz, 1H), 7.64 (d, 8.0 Hz,1H), 7.46 (t, 12 Hz, 1H), 7.40 (t, 12 Hz, 1H), 6.43 (s, 1H), 2.37 (s, 3H). IR (cm^{-1}): 3460 (w), 2980 (m), 1690 (s), 1640 (s), 1590 (s), 1510 (s), 1410 (s), 1320 (s), 1250 (s), 1140 (s), 1020 (m), 796 (s), 770 (s), 741 (s), 668 (s), 558 (m).

(5-Methylthiazol-2-yl)-naphtho[1,2-d]thiazol-2-yl-amine (5): Compound **3** was obtained by adding few drops of inorganic acids such as hydrochloric acid, hydrobromic acid (37%, 0.4 mL) to a solution of **1** (29 mg, 0.1 mmol) in dimethylformamide:methanol (3:1) medium. After addition of acid, the solution was stirred at room temperature for 30 min and filtered. The filtrate, upon standing under ambient conditions, yielded pink colored crystals of **3** within 15 days. Yield

87 %. ESI MS: calcd mass for (M+1) $C_{15}H_{11}N_3S_2$, 298.0474; found, 298.0466 [M+ 1]. IR (cm^{-1}): 3470 (w), 1570 (s), 1540 (s), 1500 (s), 1360 (m), 1190 (m), 769 (s), 668 (s).

Salt [(4)H^+Cl^-].H_2O (6) : Salt **6** was obtained by adding a few drops of hydrochloric acid (37%, 0.4 mL) to a solution of compound **4** (28 mg, 0.1 mmol) in methanol (5 mL). After addition of acid, solution was stirred at room temperature for 30 min and filtered. The filtrate, upon standing under ambient conditions, yielded colorless crystals of **5** in 6-7 days. Yield 85%.^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.66 (m, 1H), 8.20 (t, 8.0 Hz, 1H), 7.98 (d, 8.0 Hz, 1H), 7.95 (d, 8.0 Hz, 1H), 7.68 (d, 8.0 Hz, 1H), 7.55 (m, 2H), 7.47 (t, 8.0 Hz, 1H), 7.14 (m, 1H), 2.31 (s, 3H). IR (cm^{-1}): 3350 (w), 1730 (s), 1550 (s), 1510 (m), 1340 (m), 1260 (s), 1200 (m), 796 (m), 668 (s).

Synthesis of Salt [(4)$H^+ClO_4^-$].H_2O (7) : Compound **4** (141 mg, 0.5 mmol) and perchloric acid (60%, 0.5 mL) were dissolved in methanol (10 mL), and the solution was left for crystallization. Colorless crystals were formed after 3 days. Yield 96 %. ^{1}H-NMR (400 MHz,DMSO-d_6): δ 9.21 (s, 1H), 8.05 (d, 8.0 Hz, 1H), 7.98 (d, 8.0 Hz, 1H), 7.94 (d, 8.0 Hz, 1H), 7.68 (d, 8.0 Hz, 1H), 7.62-7.52 (m, 2H), 7.48 (t, 8.0 Hz, 1H), 7.12 (s, 1H), 2.31 (s, 3H). IR (cm^{-1}): 3500 (w), 1720 (s), 1550 (s), 1330 (m), 1250 (s), 1090 (m), 798 (m), 627 (s).

Synthesis of cocrystals [(4)TBA$^+$Cl$^-$] (8), [(4)TBA$^+$Cl$^-$].H_2O (9 or 10) : Concomitant crystallization of **8**, **9** and **10** was performed by slow evaporation of a 15 mL methanol solution of **4** in the presence of excess TBACl. Crystals thus obtained were isolated by filtration and dried at room temperature. Isolated yield: 72% (considering formation of **8**, **9** and **10** in one pot). ^{1}H-NMR (400 MHz,DMSO-d_6): δ 8.05 (d, 8.0 Hz, 1H), 7.90 (m, 2H), 7.72 (d, 8.0 Hz, 1H) , 7.59-7.47 (m, 3H), 7.04 (s, 1H), 4.61 (s, 2H), 3.25-3.21 (m, 8H), 2.38 (s, 3H), 1.70-1.62 (m, 8H), 1.41 (h, 8.0 Hz, 8H), 1.02 (t, 12H). IR (cm^{-1}): 3450 (w), 2970 (m), 1700 (s), 1650 (w), 1550 (s), 1250 (s), 1030 (s), 806 (s), 668 (s).

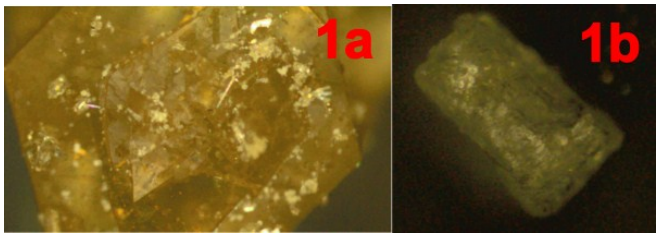


Figure S1: Photograph of crystals of polymorphs **1a** and **1b**.

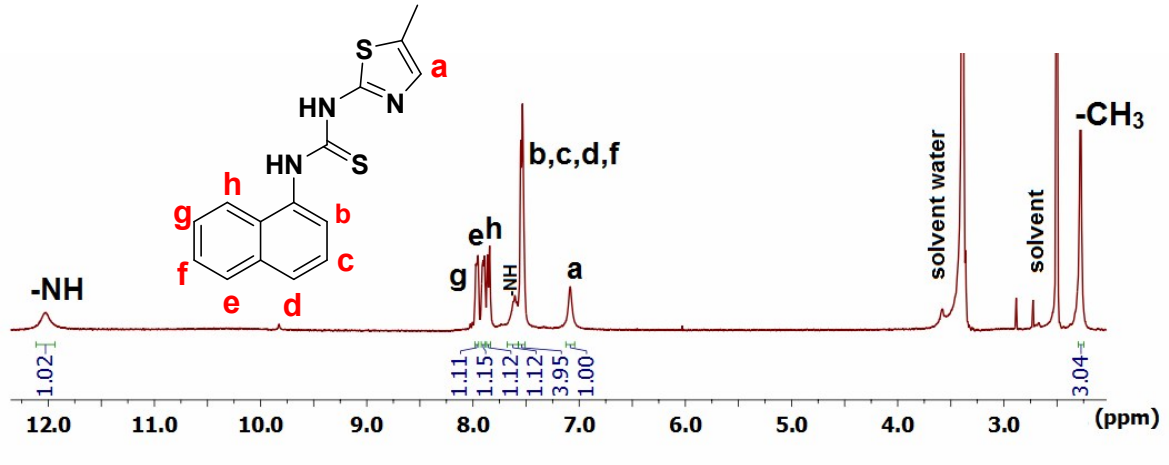


Figure S2: ^{1}H-NMR (DMSO-d_6, 600 MHz) of compound 1

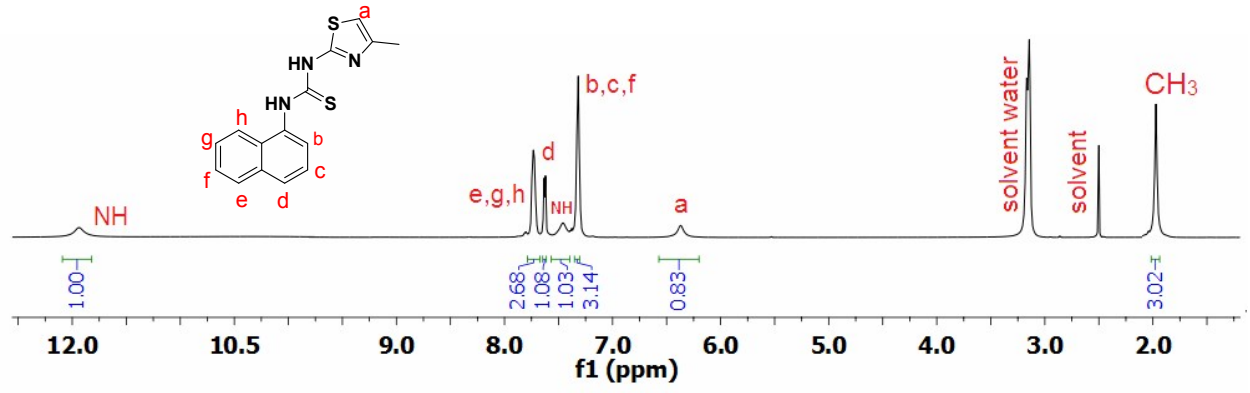


Figure S3: ^{1}H-NMR (DMSO-d_6 , 600 MHz) of compound 2

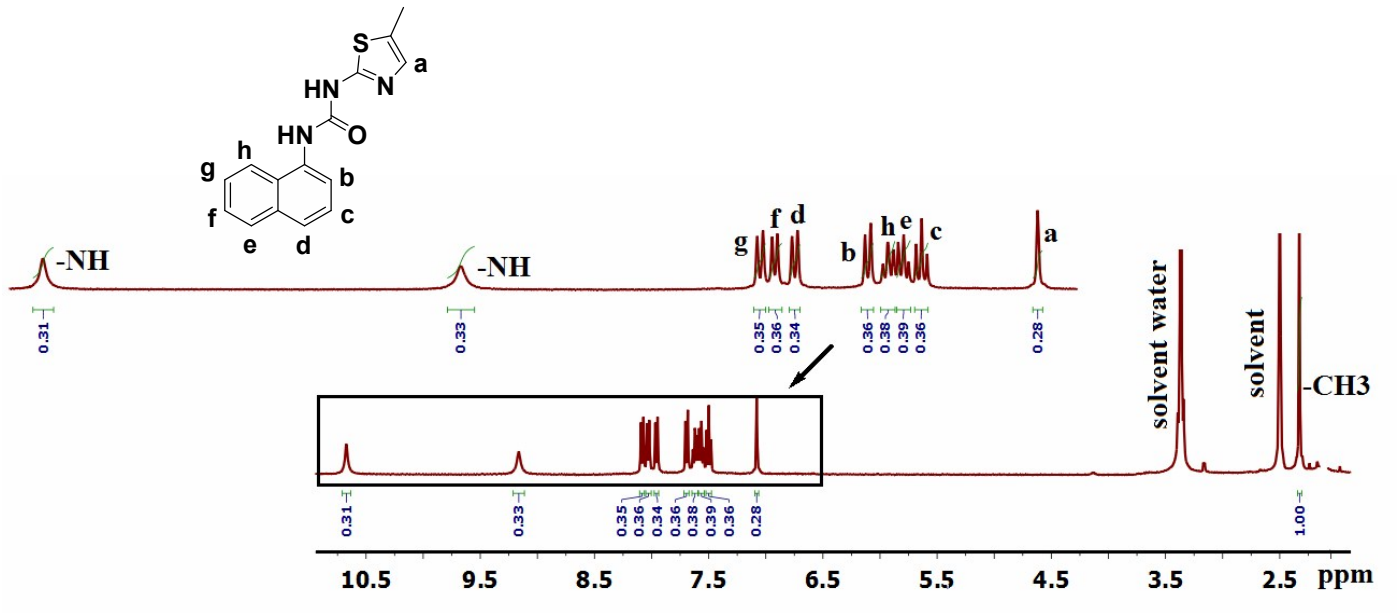


Figure S4: ^{1}H-NMR (DMSO-d_6 , 400 MHz) of compound **4**

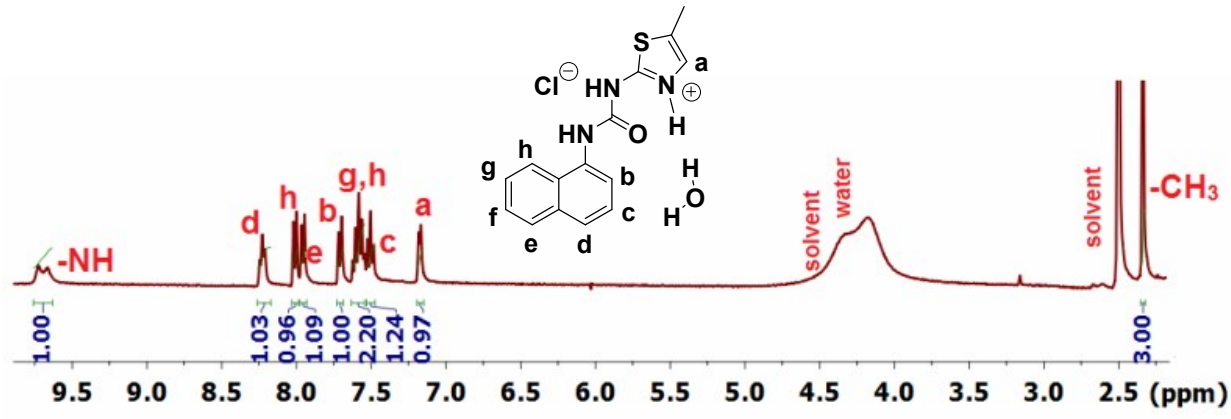


Figure S5: ^{1}H-NMR (DMSO-d_6, 400 MHz) of compound **5**

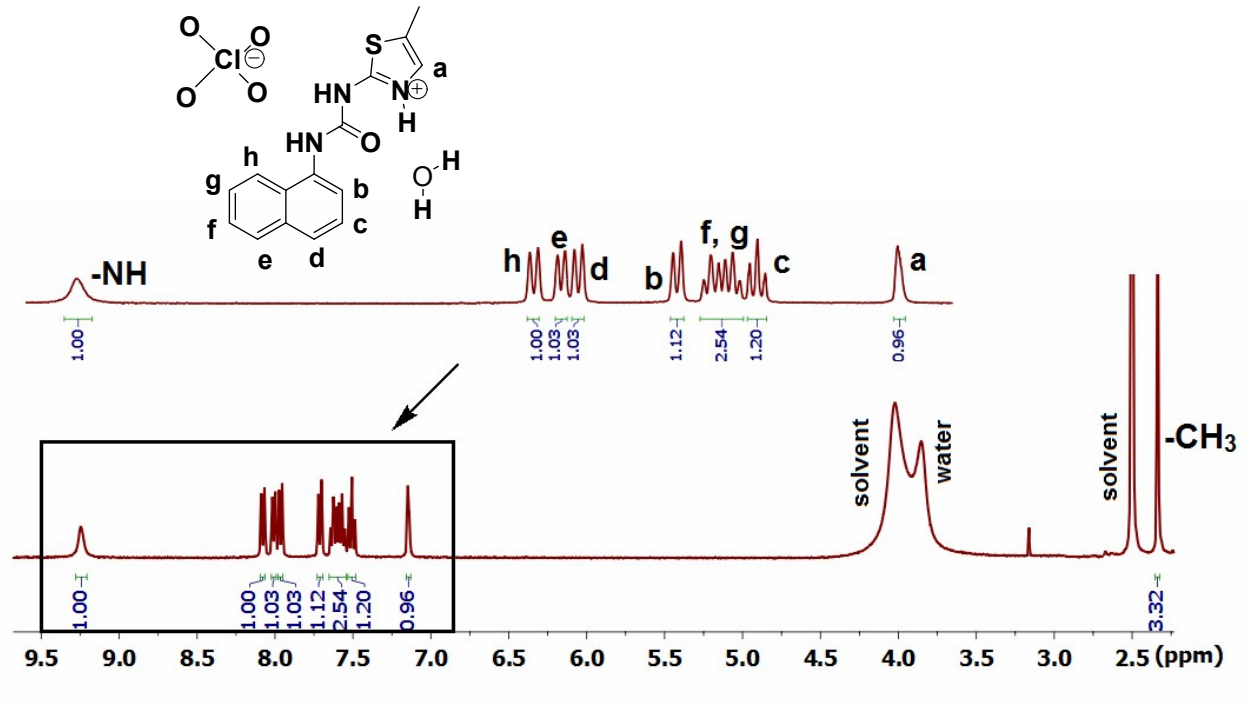


Figure S6: ^{1}H-NMR (DMSO-d_6 , 400 MHz) of compound **6**

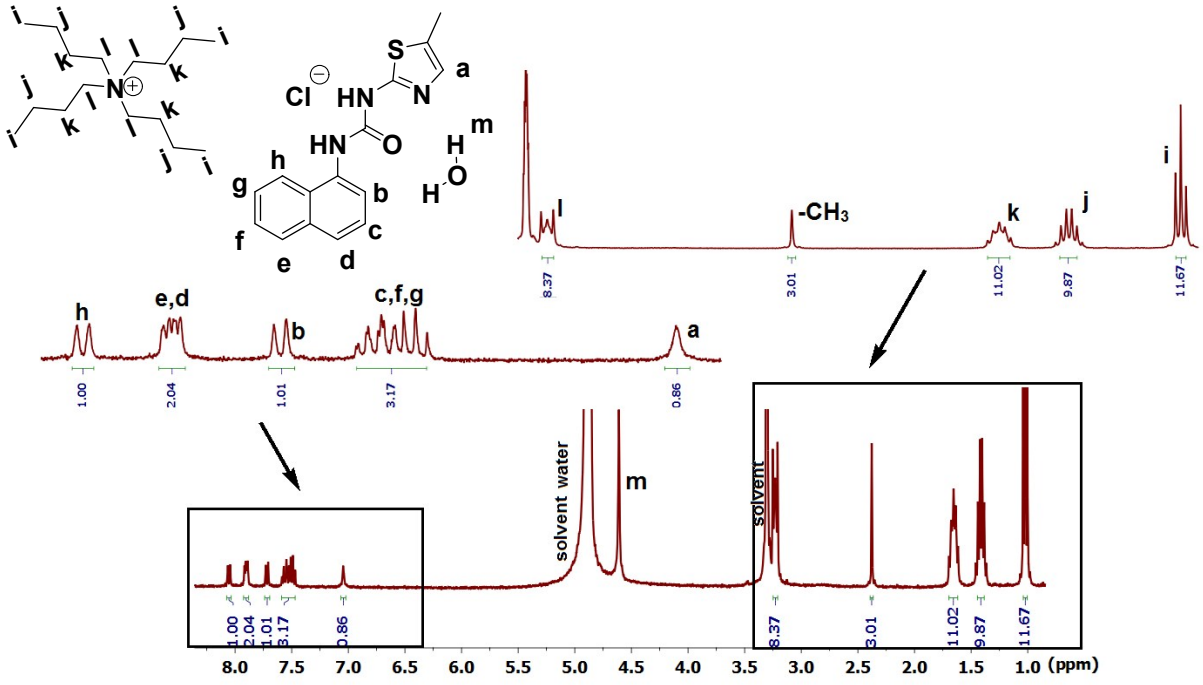


Figure S7: ^{1}H-NMR (DMSO-d_6 , 400 MHz) of compound **8**

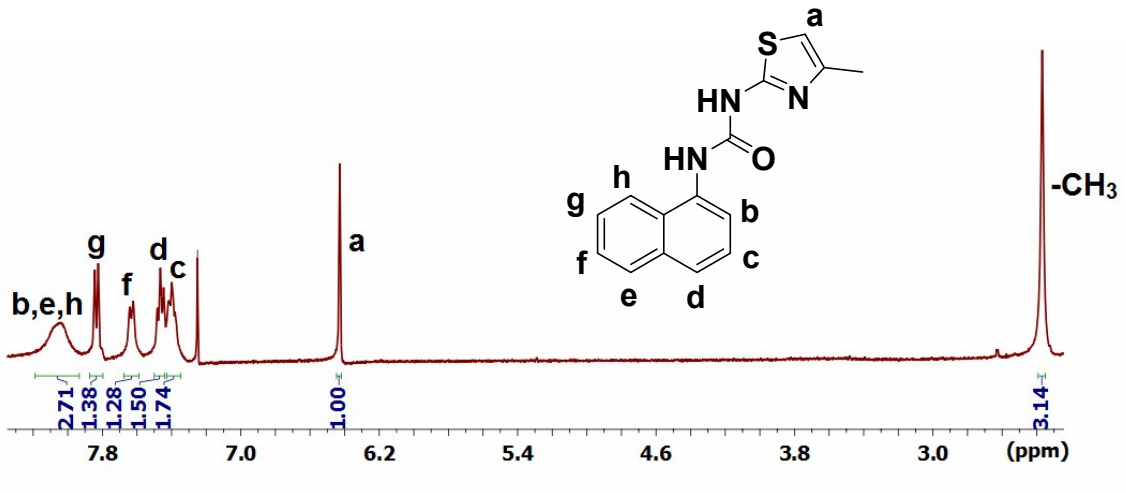


Figure S8: ^{1}H-NMR (DMSO-d_6 , 400 MHz) of compound **10.**

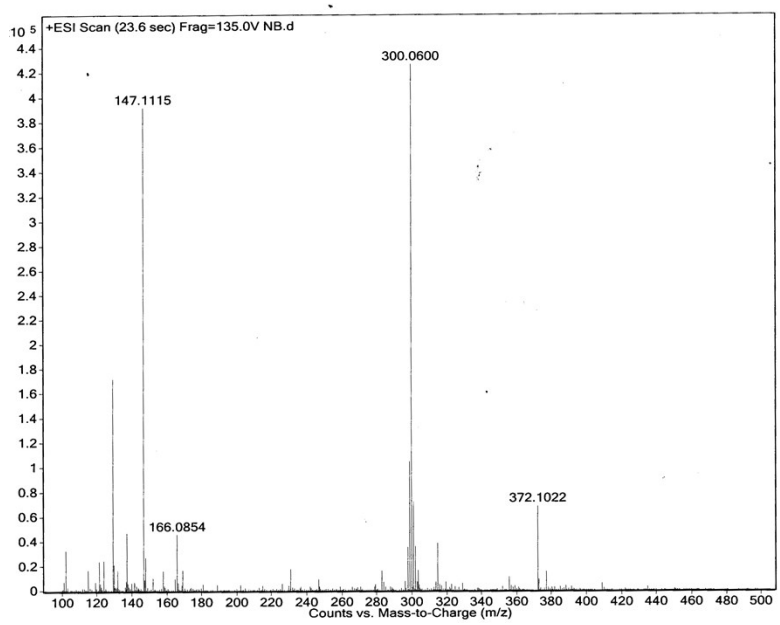


Figure S9: ESI mass spectra of compound **1**.

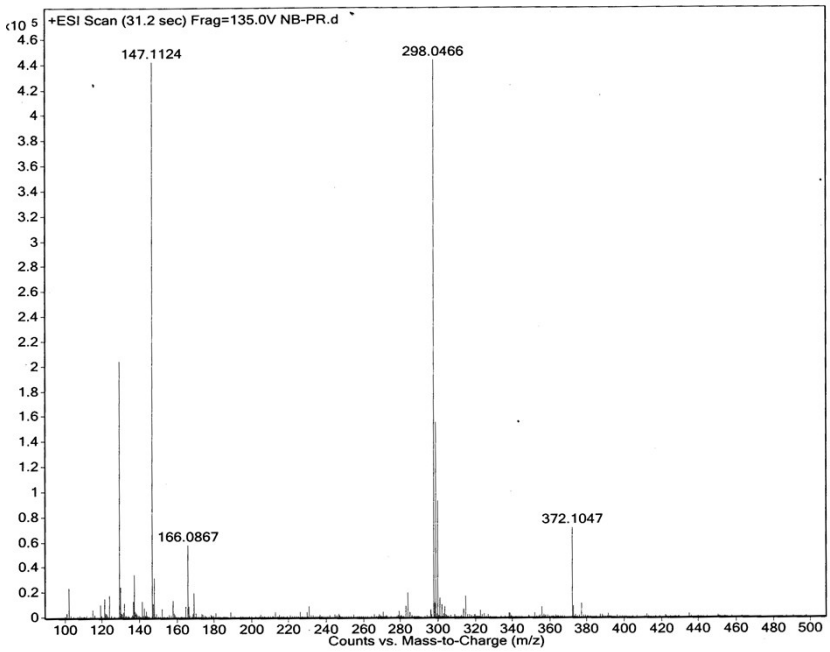


Figure S10: ESI mass spectra of compound **3**.

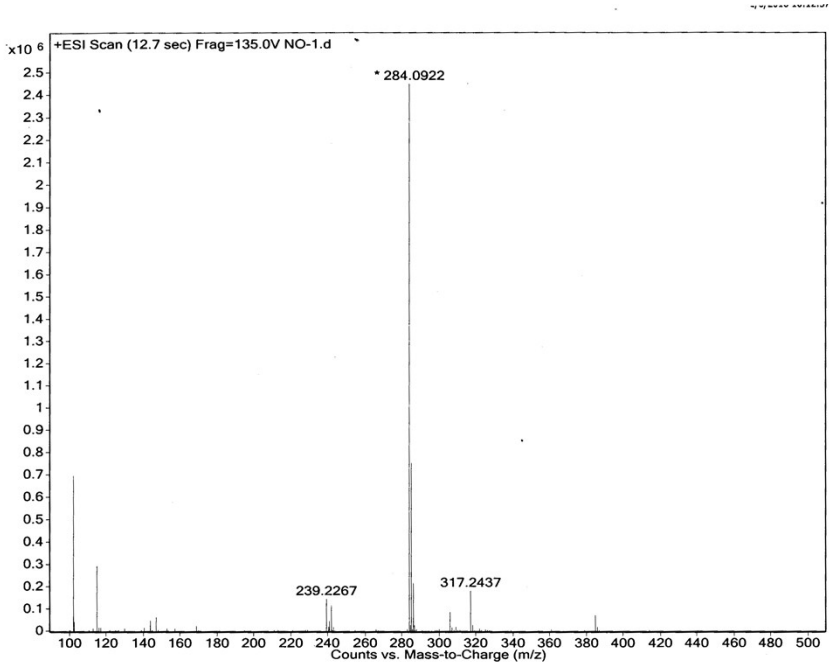


Figure S11: ESI mass spectra of compound **4**.

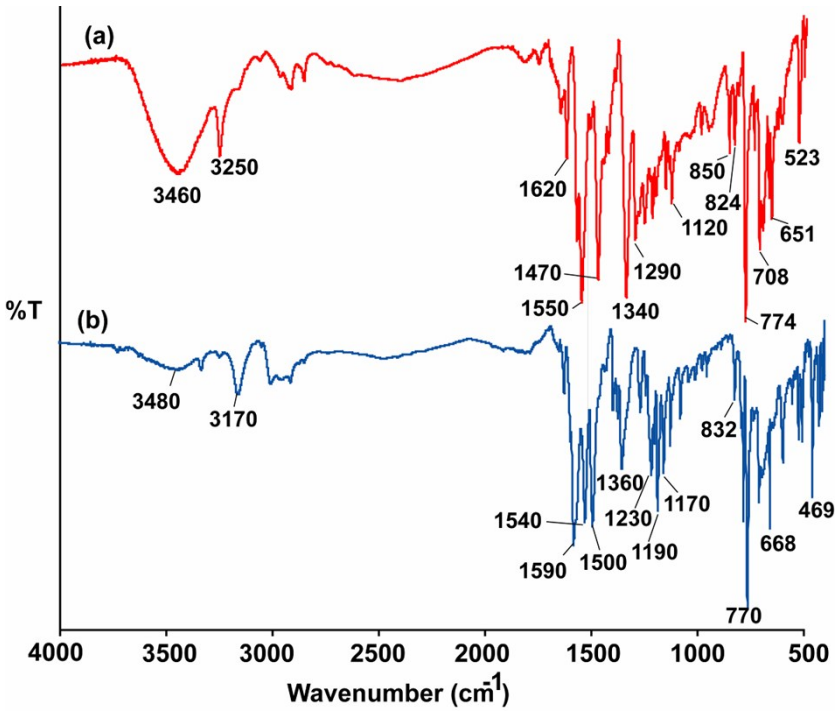


Figure S12 : FT-IR spectra (KBr, cm^{-1}) of (a) **1a,** (b) **1b.**

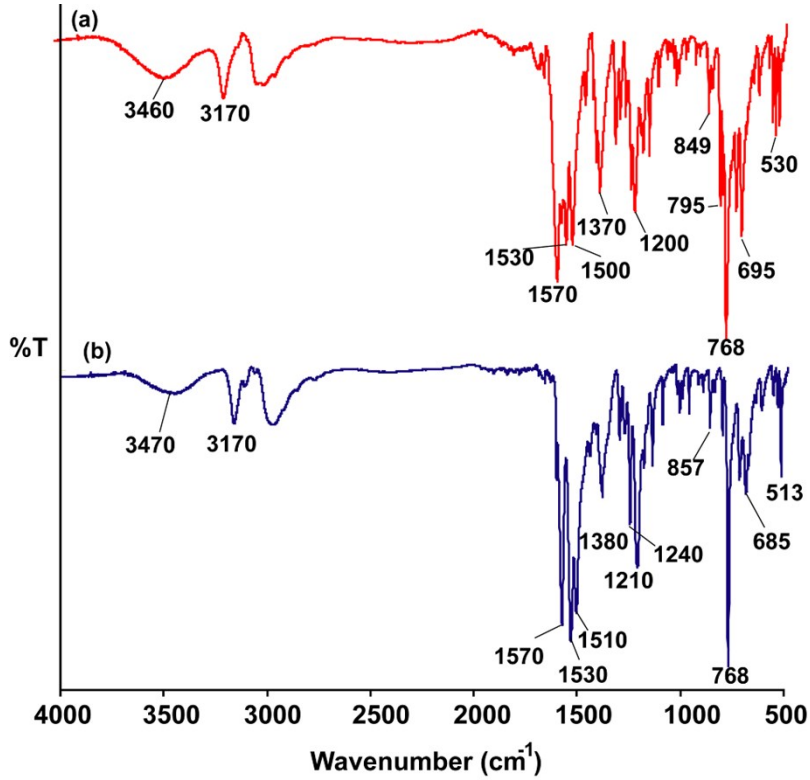


Figure S13 : FT-IR spectra (KBr, cm^{-1}) of (a) **2a,** (b) **2b.**

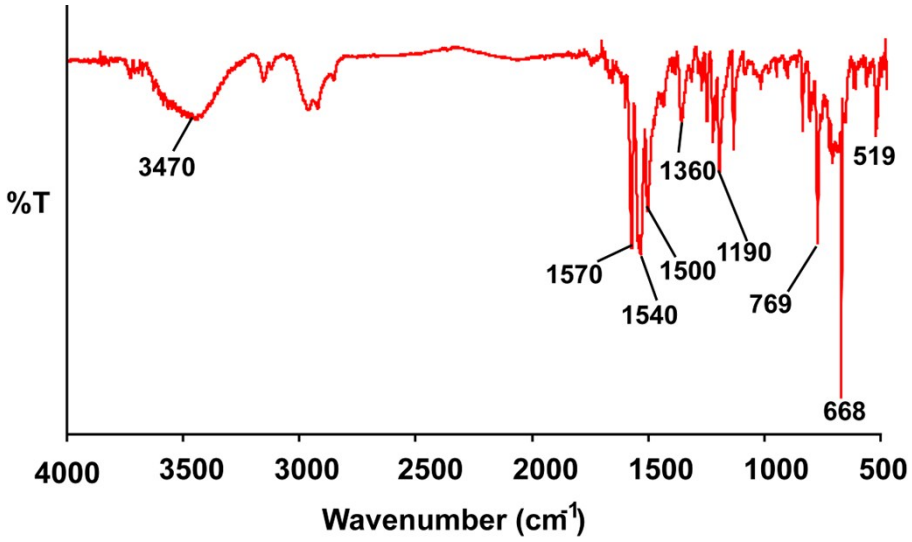


Figure S14: FT-IR spectra (KBr, cm^{-1}) of **3**.

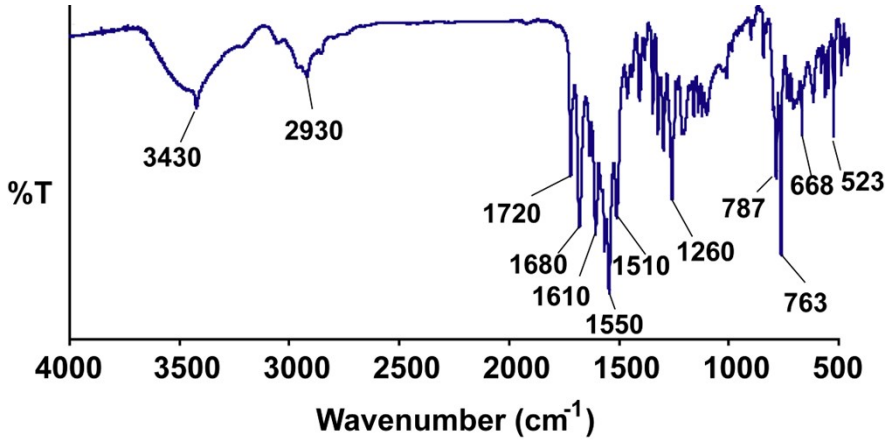


Figure S15 : FT-IR spectra (KBr, cm^{-1}) of **4**

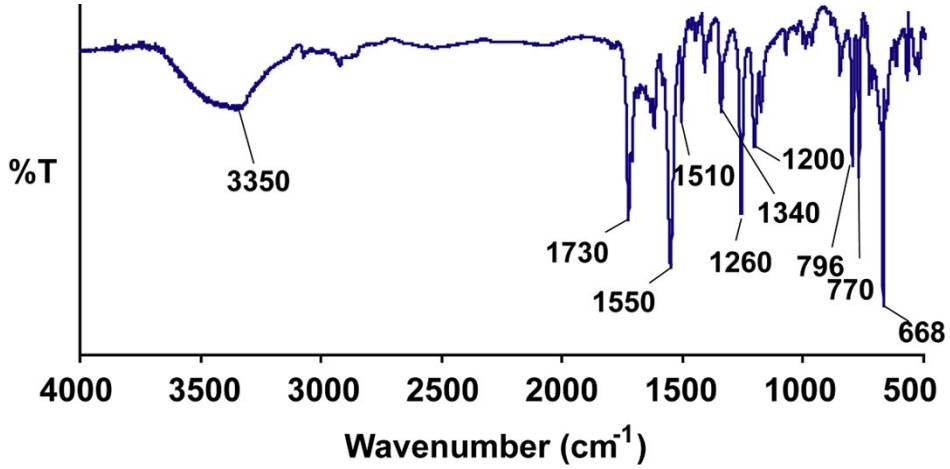


Figure S16 : FT-IR spectra (KBr, cm^{-1}) of **5**.

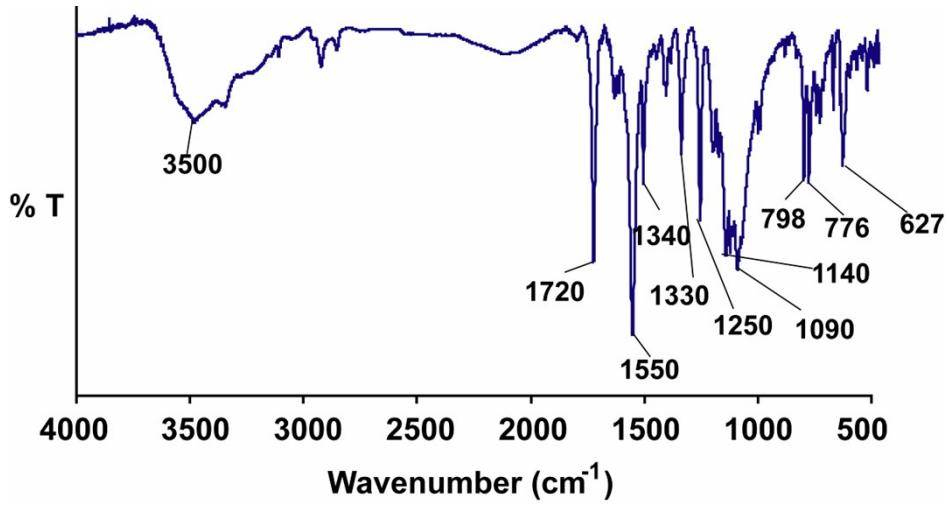


Figure S17: FT-IR spectra (KBr, cm^{-1}) of **6**.

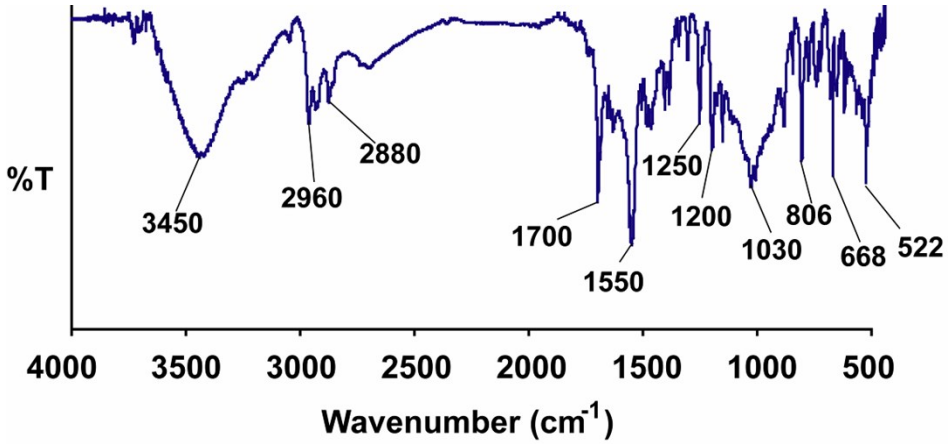


Figure S18 : FT-IR spectra (KBr, cm^{-1}) of **7**.

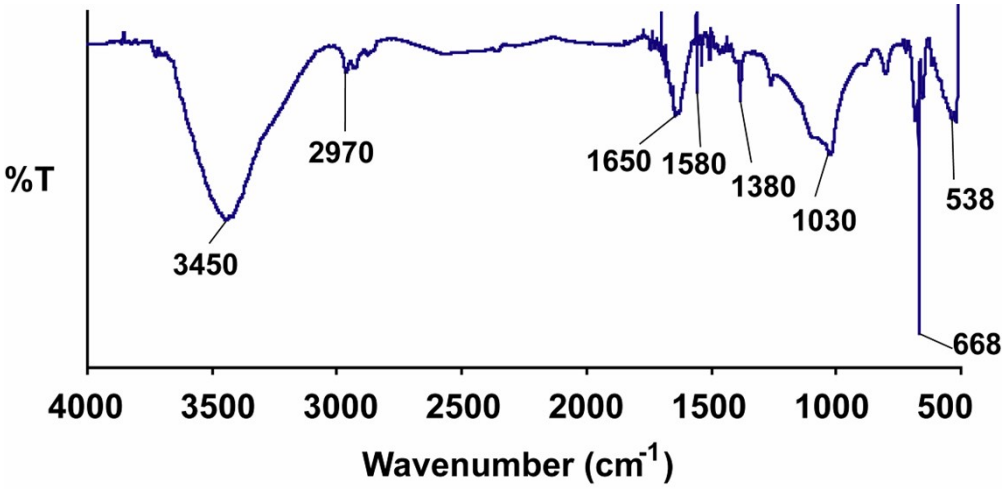


Figure S19 : FT-IR spectra (KBr, cm^{-1}) of **8**.

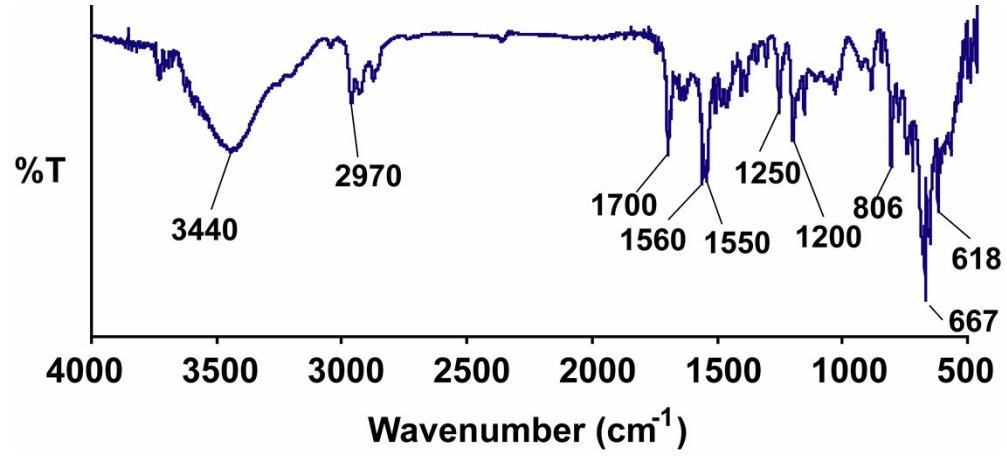


Figure S20: FT-IR spectra (KBr, cm^{-1}) of **9**.

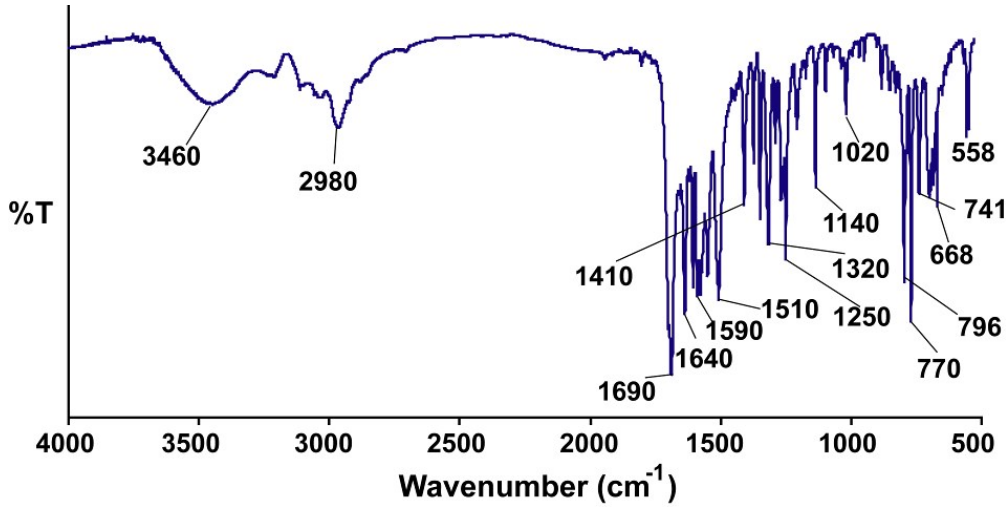
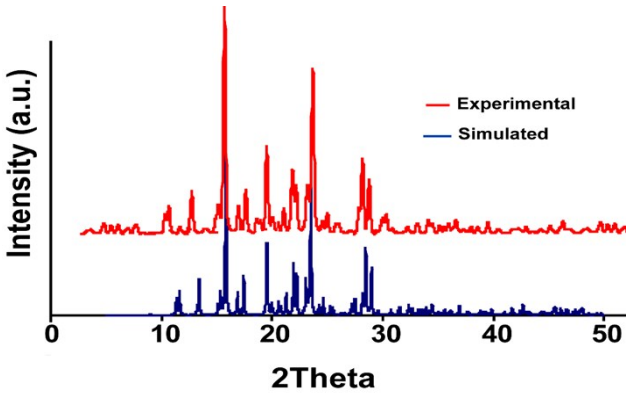
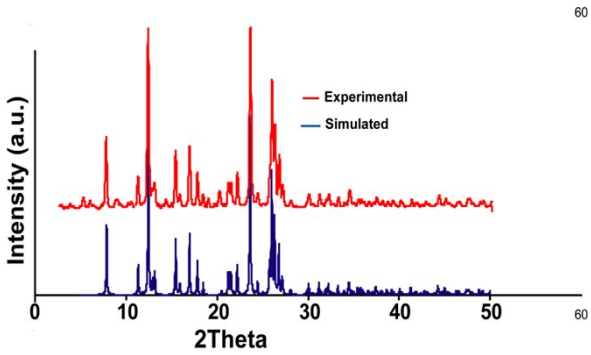


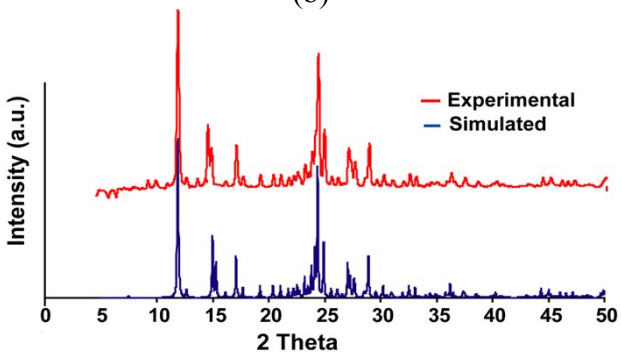
Figure S21: FT-IR spectra (KBr, cm^{-1}) of **10**.



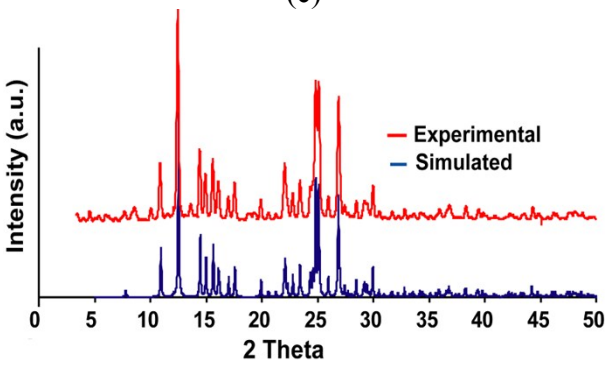
(a)



(b)



(c)



(d)

Figure S22: Powder XRD patterns of (a) **1a;** (b) **1b;** (c) **2a;** (d) **2b**.(top one are experimental pattern and lower one are generated from crystallographic information file

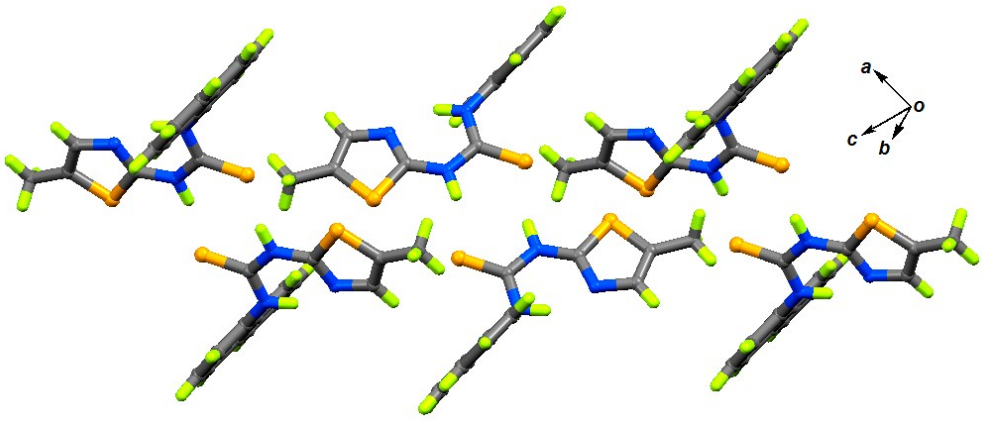


Figure S23: Packing pattern of polymorph **1b** along *b*-crystallographic axis.

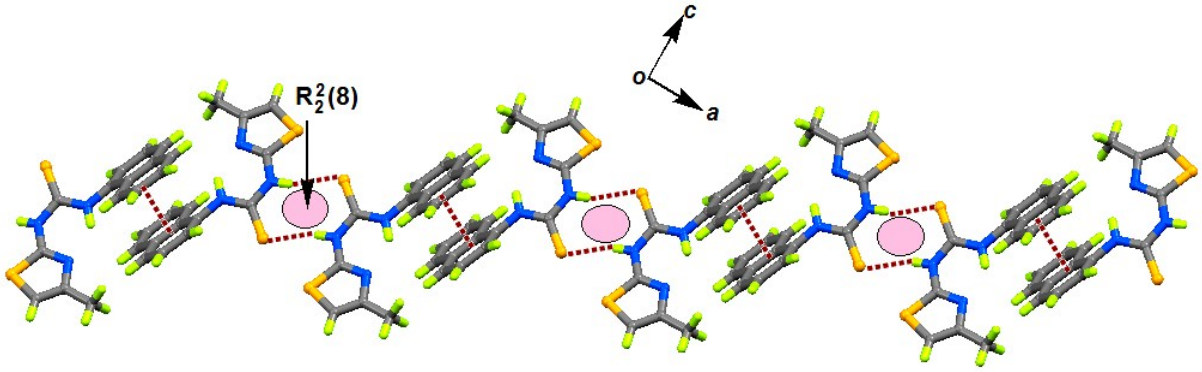
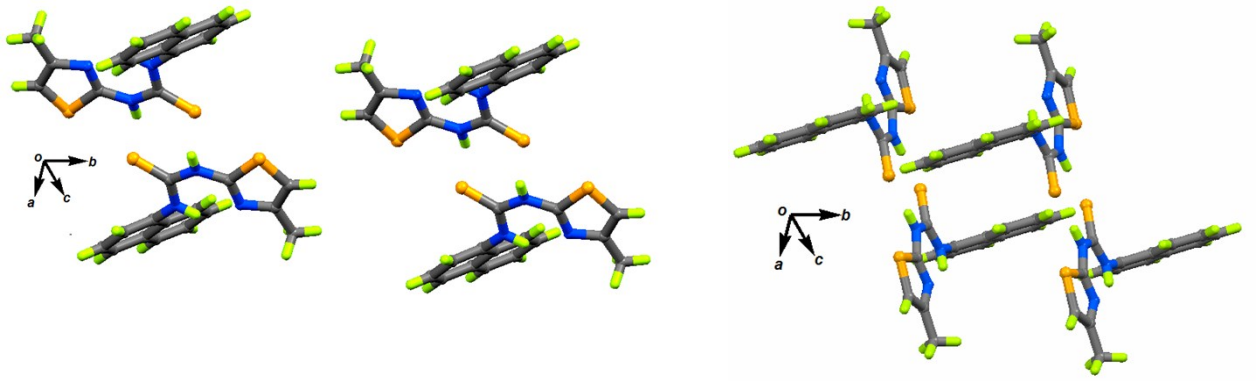


Figure S24: 1-Dimensional chain like arrangement of **2a** along ac-plane



(a) (b)

Figure S25: Packing pattern of (a) polymorph **2a** (b) polymorph **2b** along *c*-crystallographic axis

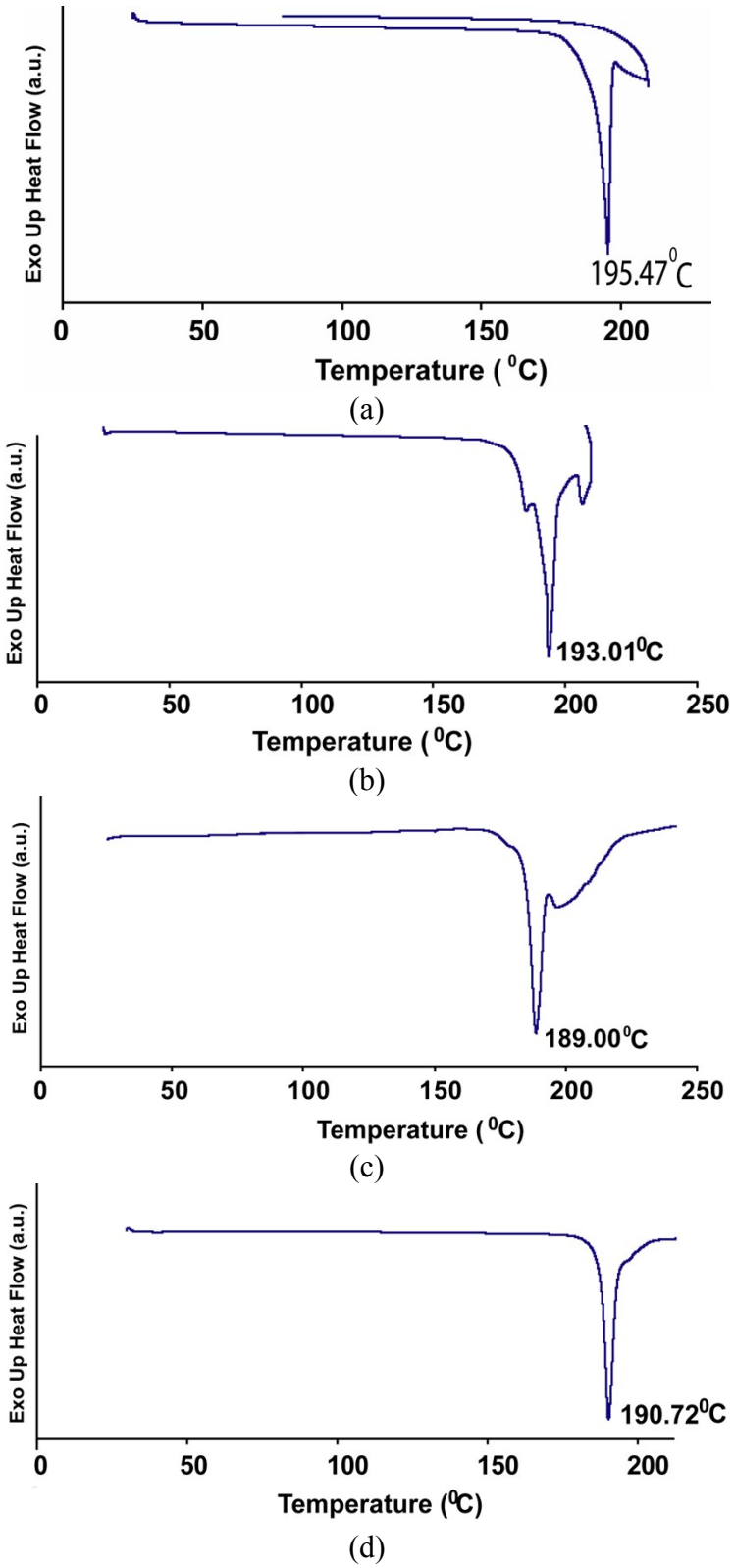
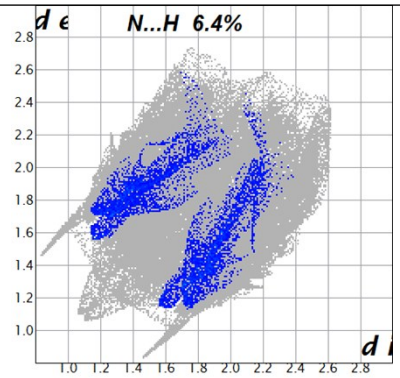
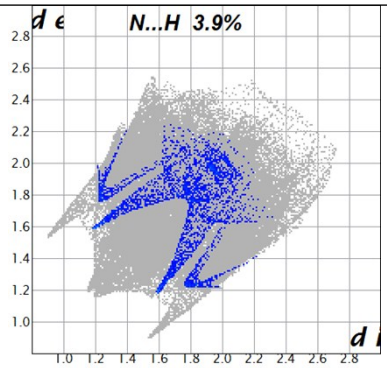
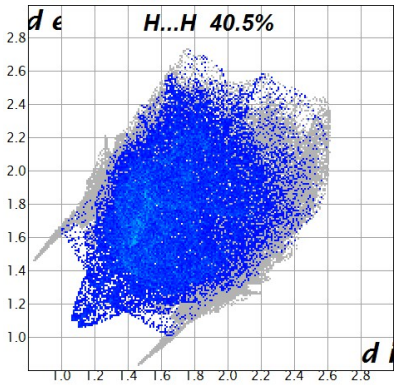
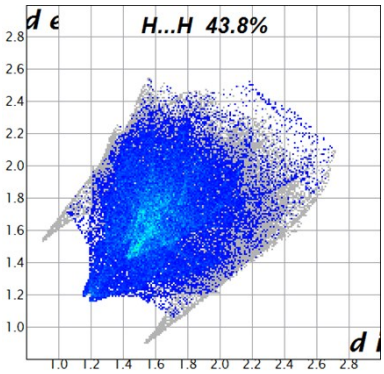
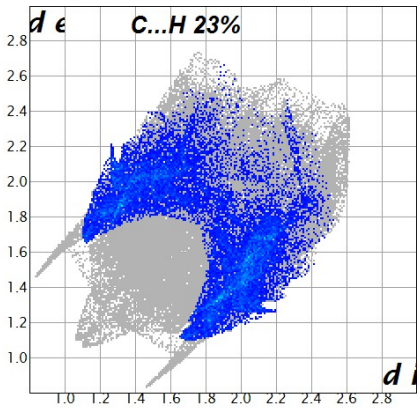
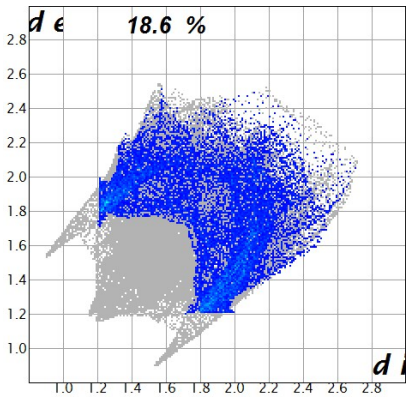
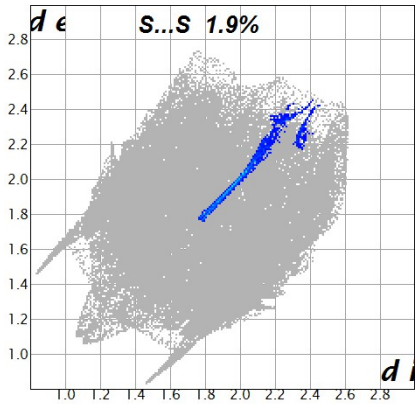
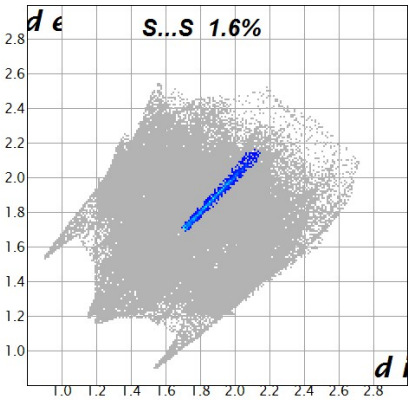


Figure S26: DSC plots obtained from heating at a rate of 5º C/min. of the polymorph (a) **1a**; (b) **1b**; (c) **2a** and (d) **2b.**

Interactions in **1a**	Interactions in **1b**
	
	
	
	

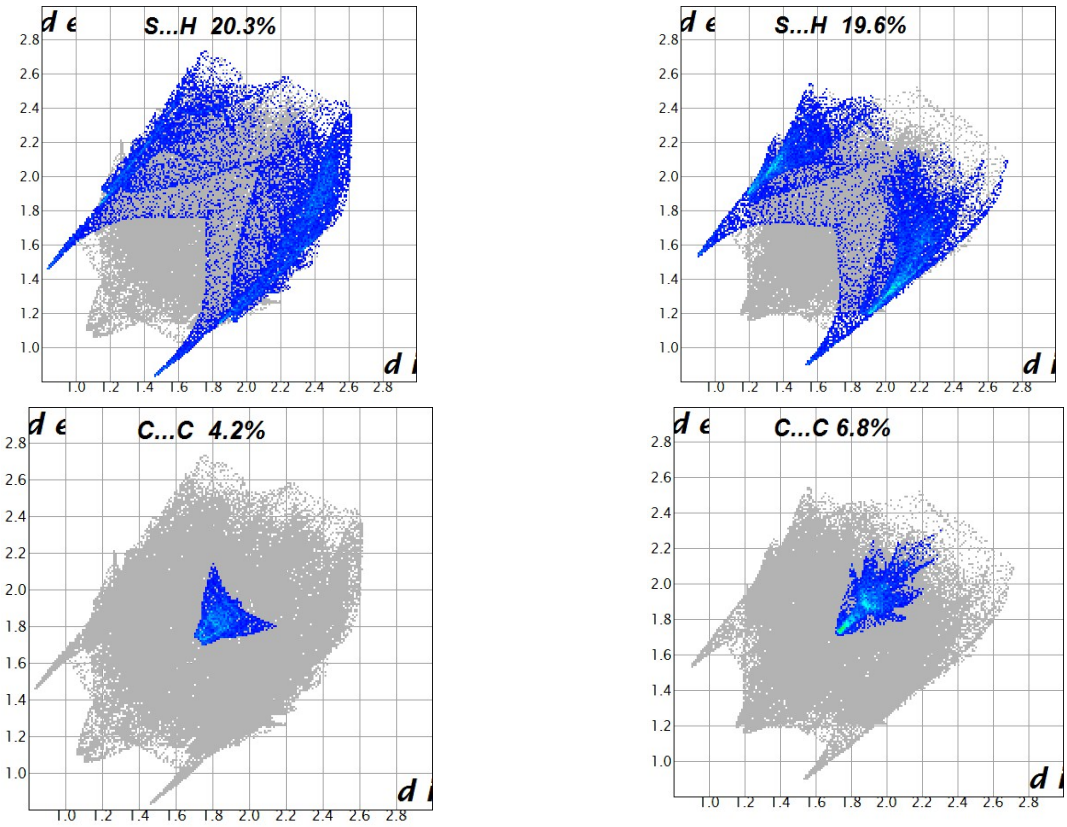
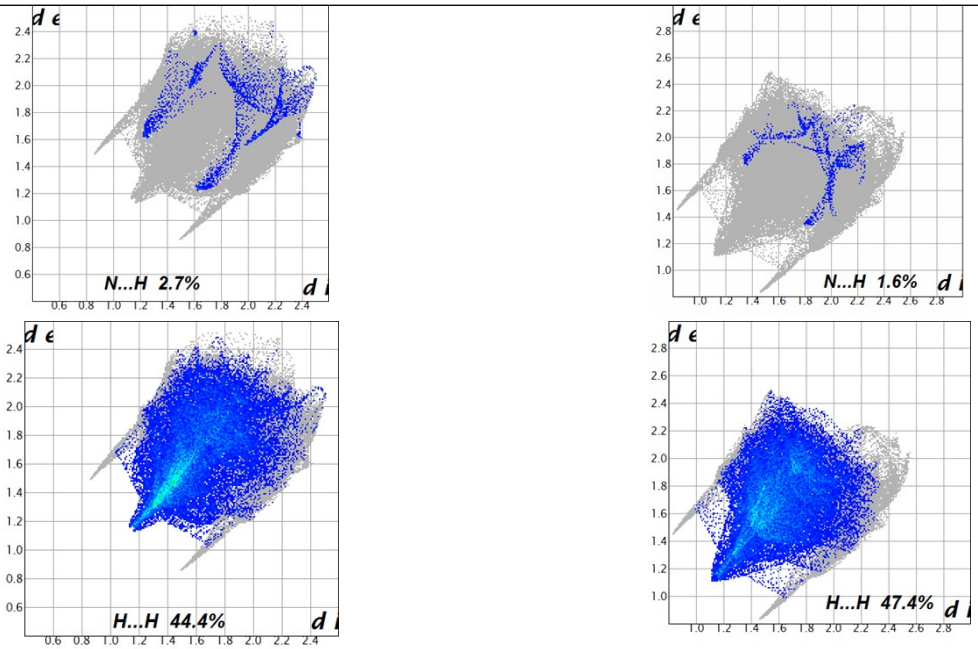


Figure S27: Fingerprint plots for polymorphs **1a** and **1b**, broken down into contributions from specific pairs of atom types.

Interactions in **2a**	Interactions in **2b**



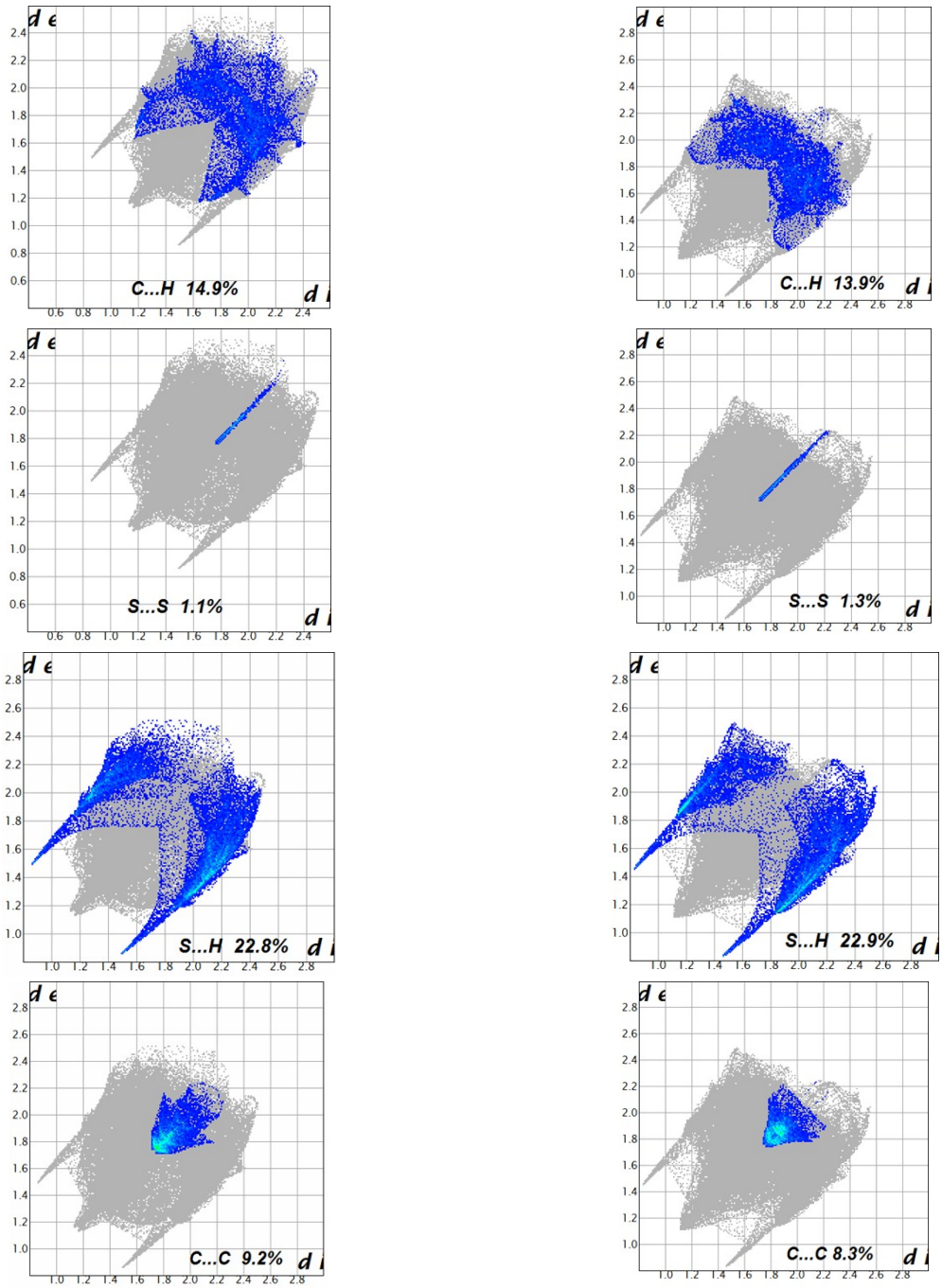


Figure S28: Fingerprint plots for polymorphs **2a** and **2b**, broken down into contributions from specific pairs of atom types.

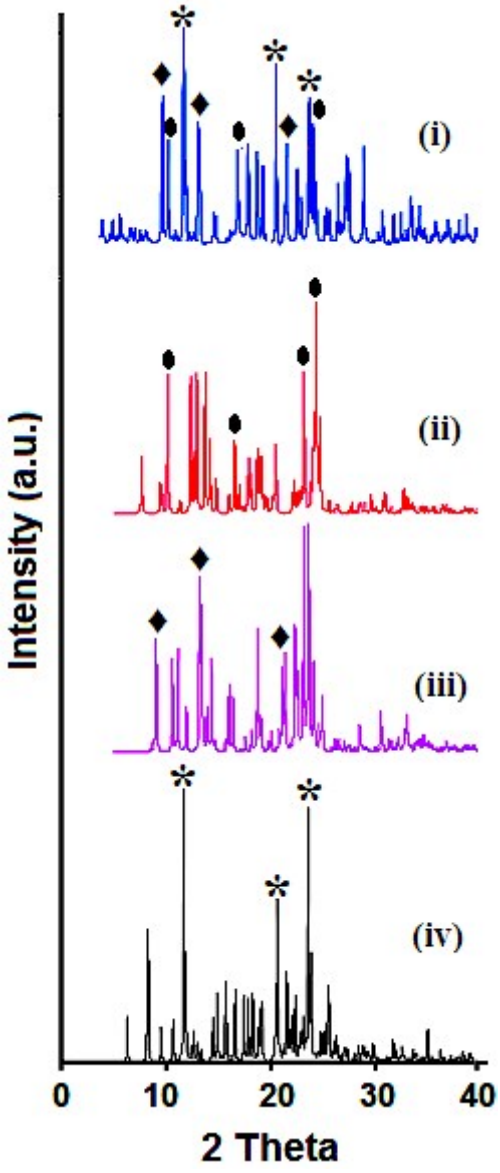


Figure S29: (i) Experimental PXRD pattern of concomitant polymorphs **8-10**. Individual PXRD of cocrystals generated from respective crystallographic information file of (ii) cocrystal **10**, (iii) cocrystal **9** and (iv) cocrystal **8** (Principal peaks of each polymorph marked ⁎ = cocrystal **8,** ♦ = cocrystal **9,** • = cocrystal **10** respectively**).**

(a) (b) (c)

Figure S30: Photograph of co crystals (a) **8** (b) **9** and (c) **10**.

Table S1: Crystallization of Polymorphs of **1** and **2** from Different Solvents

Solvent	**1** (type of crystals)	**2** (type of crystals)
Acetone	-[a]	-[a]
Acetonitrile	-[a]	**2a**
Methanol	-[a]	**2a**
Ethanol	-[a]	**2a**
THF	-[a]	-[a]
DMF	**1a**	**2b**
DMSO	**1b**	**2b**
Diethylether	-[a]	**2a**
Ethyl acetate	-[a]	-[a]
Methanol: DMF (1:1)	**1a**	**2b**
Diethylether:DMSO (1:1)	**1a**	**2b**

[a]No suitable crystal with adequate edges.

Table S2: Energy calculated at B3LYP/6-31++G(d,p) level

Polymorph	**Energy (in HF)**	**Energy (in kcal/mol)**	**Difference (in kcal/mol)**
1a	**-1540.1338736**	**-966448.80333737**	**0.00006903**
1b	**-1540.13387371**	**-966448.8034064**	
2a	**-1522.0354983**	**-955091.89894688**	**0.00006275**
2b	**-1522.0354984**	**-955091.89900963**	

Table S3: Hydrogen Bond Parameters of **1a**, **1b**, **2a**, **2b**, **3, 4, 5, 6, 7, 8, 9** and **10.**

Compound No.	Hydrogen Bond	Bond distances (Å)			Angle(°)
		d_{D-H}	$d_{H\cdots A}$	$d_{D\cdots A}$	D-H···A
1a	N2-H2 ···S2 [-x,-y,-z]	0.91(3)	2.39(3)	3.27(3)	164(3)
	N3-H3A ···N1 (Intra)	0.92(3)	1.94(3)	2.71(4)	140(3)
	C14-H14 ···N3 (Intra)	0.93	2.56	2.86(4)	100
1b	N2-H2···S2 [-x,1-y,-z]	0.86	2.56	3.32(2)	147
	N3-H3A···N1 (Intra)	0.86	2.00	2.69(3)	138
	C7-H7 ···S2 (Intra)	0.93	2.78	3.20(2)	108
	C14-H14 ···N3 (Intra)	0.93	2.54	2.85(3)	100
2a	N2-H2···S2 [3-x,1-y,1-z]	0.86	2.50	3.34(18)	164
	N3-H3A ···N1 (Intra)	0.86	1.99	2.70(2)	140
	C14-H14 ···N3 (Intra)	0.93	2.55	2.86(3)	100
2b	N2-H2 ···S2 [2-x,1-y,1-z]	0.84(2)	2.45(2)	3.26(18)	162(2)
	N3-H3A ···N1 (Intra)	0.85(2)	2.05(2)	2.74(2)	138(2)
	C14-H14 ···N3 (Intra)	0.93	2.58	2.89(3)	100
3	N2-H2 ···O1 [1-x,1-y,-z]	0.78(3)	2.010(3)	2.78(4)	173(19)
	N3-H3A ···N1 (Intra)	0.87(19)	2.04(19)	2.75(3)	138(16)
	C14-H14 ···N3 (Intra)	0.93	2.54	2.85(4)	100
4	N2-H2 ···O1 [2-x,-y,1-z]	0.89(3)	1.94(3)	2.83(3)	173(2)
	N3-H3A ···N1(Intra)	0.91(2)	1.92(2)	2.70(3)	144(2)
	C7-H7 ···O1 (Intra)	0.95(2)	2.22(2)	2.88(3)	126(19)
5	N2-H2 ···N4 [-x,-y,-z]	0.86	2.00	2.86(8)	175
	N5-H5 ···N1 [-x,-y,-z]	0.86	2.02	2.88(8)	174
6	N1-H1 ···O2 [1/2-x,1/2+y,z]	0.86	1.89	2.74(4)	174
	N2-H2 ···Cl1 [1/2-x,1/2+y,z]	0.88(2)	2.28(2)	3.14(2)	166(2)
	O2-H2P ···Cl1 [1/2-x,1/2+y,z]	0.83(5)	2.33(5)	3.13(4)	162(4)
	O2-H2Q ···Cl1	0.94(5)	2.21(5)	3.13(3)	166(4)
	N3-H3A ···Cl1 [1/2-x,1/2+y,z]	0.90(2)	2.58(2)	3.41(2)	153(18)
	C3-H3 ···Cl1 [-x,1-y,-z]	0.93	2.62	3.55(3)	171
	C7-H7 ···O1 (Intra)	0.93	2.31	2.86(3)	117
	C14-H14 ···N3 (Intra)	0.93	2.58	2.88(4)	100
7	N1-H1 ···O4 [1-x,3/2+y,-z]	0.86	2.09	2.92(8)	163
	N2-H2 ···O6 [x,1+y,z]	0.89(6)	1.99(5)	2.80(9)	150(5)
	N3-H3A ···O6 [x,1+y,z]	0.86	2.21	2.98(8)	151
	O6-H6P ···O2	0.93(9)	2.26(11)	2.95(10)	130(7)
	O6-H6Q ···O5 [1-x,-1/2+y,-z]	0.93(7)	2.15(8)	3.04(10)	161(7)
	C1-H1A ···O3 [-1+x,2+y,z]	0.96	2.52	3.43(11)	156
	C7-H7 ···O1 (Intra)	0.93	2.23	2.86(10)	124
	C14-H14 ···N3 (Intra)	0.93	2.56	2.87(11)	100
8	N2-H2 ···Cl1 [1-x,1/2+y,1/2-z]	0.80(4)	2.37(4)	3.13(4)	161(3)
	N3-H3A···Cl1 [1-x,1/2+y,1/2-z]	0.81(3)	2.47(3)	3.24(4)	159(3)
	C7-H7 ···O1 (Intra)	0.93	2.47	2.90(5)	108
	C14-H14 ···N3 (Intra)	0.93	2.61	2.91(5)	100
	C20-H20A ···Cl1 [1+x,y,z]	0.97	2.76	3.73(4)	171
9	N2-H2 ···Cl1	0.84(4)	2.39(4)	3.18(4)	159(4)
	O2-H2P ···Cl1	0.92(3)	2.32(4)	3.23(4)	168(4)
	O2-H2Q ···N1	0.93(6)	2.06(6)	2.98(6)	173(5)
	N3-H3A ···Cl1	0.86(4)	2.40(4)	3.22(4)	160(3)
	C1-H1A ···O2	0.96	2.56	3.48(6)	162
	C7-H7 ···O1 (Intra)	0.93	2.40	2.90(6)	114
	C14-H14 ···N3 (Intra)	0.93	2.56	2.87(6)	100
	C20-H20B ···O2 [1+x,1+y,z]	0.97	2.59	3.43(6)	146

10	O1-H1P···N1	0.93(10)	2.01(11)	2.92(8)	163(10)
	N2-H2···Cl1	0.86	2.40	3.23(5)	161
	O1-H2Q···Cl1	0.93(4)	2.31(5)	3.23(7)	170(4)
	N3-H3A···Cl1	0.86	2.45	3.27(5)	158
	C7-H7···O2 (Intra)	0.93	2.52	2.96(7)	110
	C14-H14···N3 (Intra)	0.93	2.56	2.87(8)	100
	C27-H27A···O1[1-x,-1/2+y,1/2-z]	0.97	2.55	3.43(8)	150