Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

Quantitative crystal structure analysis of thiadiazoles derivatives

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.

Section 1:

Table S1. Characterization data of 2-(4''-substituted benzamido)-5-(4'-fluoro-3'-phenoxyphenyl)-1,3,4-thiadiazoles

Compd. No.	R	M.P. (Onset Value from DSC plot)	Yield (%)	Nature of the Compd.	Molecular Formula	*Analysis(%) Found (Calculated)*		
						C	H	N
TDZ-1	H	260.59	73	white powder	$C_{21}H_{14}FN_3O_2S$	64.44 (64.35)	3.61 (3.68)	10.74 (10.47)
TDZ-2	F	233.88	65	white powder	$C_{21}H_{13}F_2N_3O_2S$	61.61 (61.47)	3.20 (3.18)	10.26 (10.41)
TDZ-3	CH_3	252.78	68	white powder	$C_{22}H_{16}F\ N_3O_2S$	65.17 (65.56)	3.98 (3.58)	10.36 (10.18)
TDZ-4	OCH_3	293.58	80	white powder	$C_{22}H_{16}FN_3O_3S$	62.70 (62.51)	3.83 (3.89)	9.97 (9.78)

TDZ-1: IR : ν cm^{-1}, 3214 (N-H str.), 1642(C=O str.), 1605-1500 (C=C / C=N str.), 1215 (C-O-C str.)

TDZ-2: IR : ν cm^{-1}, 3151 (N-H str.), 1676 (C=O str.), 1593- 1498 (C=C / C=N str.), 1216 (C-O-C str.).

TDZ-3: IR : ν cm^{-1}, 3149 (N-H str.), 1666 (C=O str.), 1595-1499 (C=C / C=N str.), 1212 (C-O-C str.).

TDZ-4: IR : ν cm^{-1}, 3150 (N-H str.), 1648 (C=O str.), 1597- 1498 (C=C / C=N str.) 1212 (C-O-C str.).

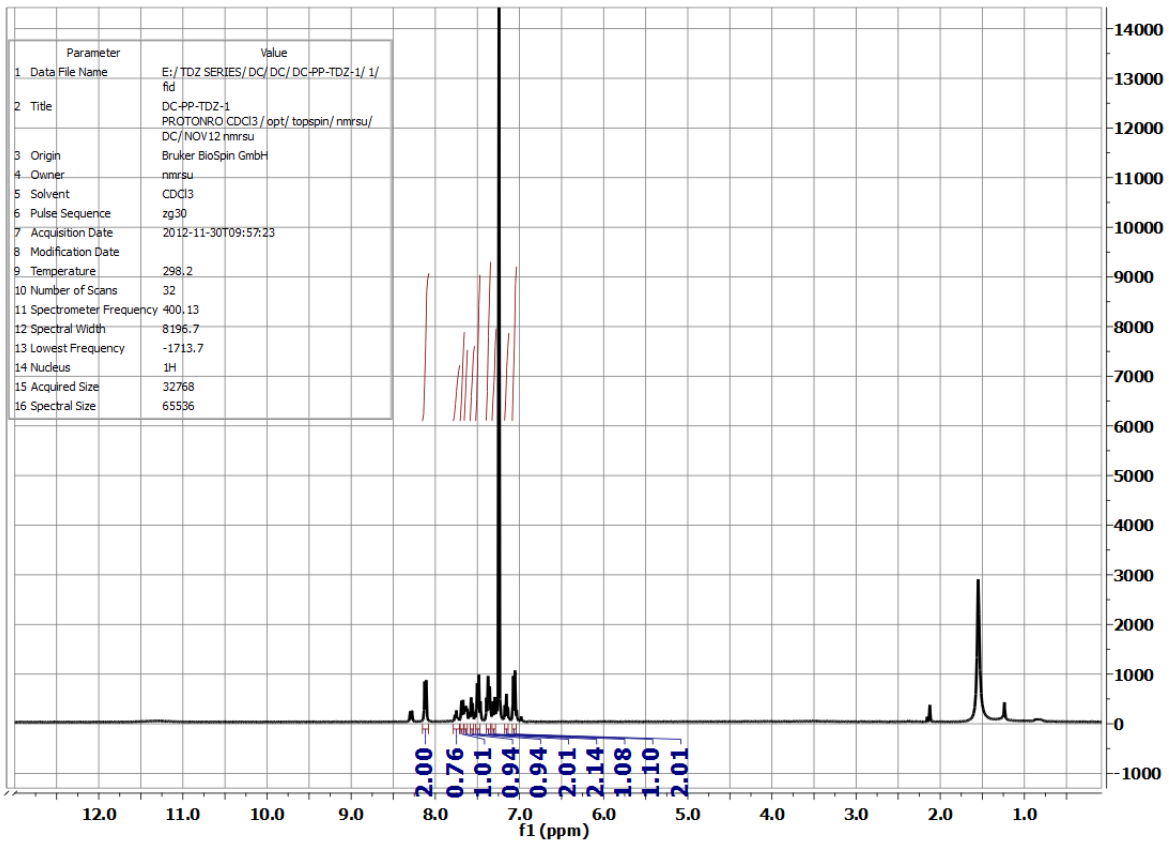
Table S2: Crystallization Experiments:

Compound Code	Solvents	Result
TDZ-1	(a) **Toluene*** (b) Ethanol	Crystals obtained and same Form observed.
TDZ-2	(a) **Ethanol + Hexane*** (b) DCM + Hexane (c) THF +Hexane	Crystals obtained and same Form observed.
TDZ-3	(a) **DCM + hexane*** (b) Chloroform +hexane (c) Ethanol + Hexane (d) Acetonitrile + Hexane	Crystals obtained and same Form observed.
TDZ-4	(a) **DCM + hexane*** (b) Acetone + Hexane	Crystals obtained and same Form observed.

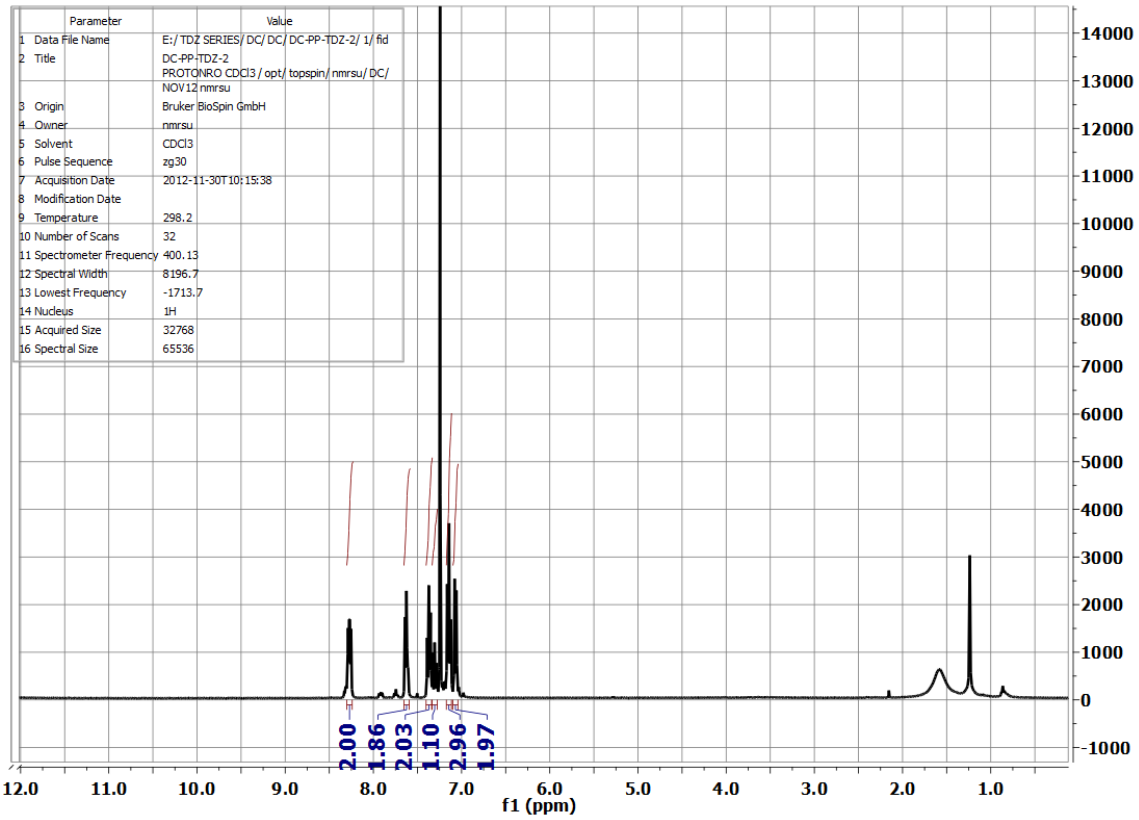
***: indicates the solvent system from which the obtained crystals were used for single crystal XRD.**

Figure S1: ^{1}H NMR of all compounds: All NMR experiments were recorded on 400MHz spectrometer (from Bruker) in $CDCl_3$ as solvent.

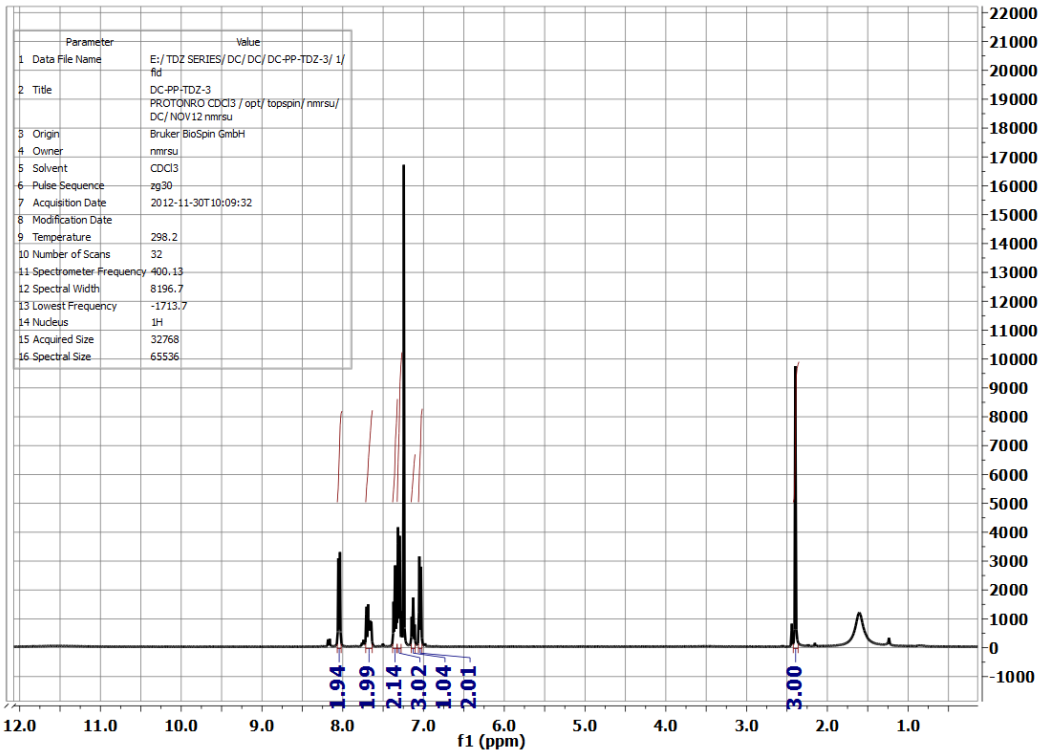
(a) TDZ-1: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 7.90 Hz, 2H), 7.79-7.71 (m, 1H), 7.70-7.66 (m, 1H), 7.65-7.62 (m, 1H), 7.59-7.55 (m, 1H), 7.52-7.47 (m, 2H), 7.39-7.35 (m, 2H), 7.33-7.29 (m, 1H), 7.16 (t, J = 7.20Hz, 1H), 7.06 (d, J = 8.10Hz, 2H)



(b) TDZ-2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30-8.24 (m, 2H), 7.65-7.59 (m, 2H), 7.37 (t, J = 8.02Hz, 2H), 7.31 (t, J = 9.30Hz, 1H), 7.14 (t, J = 8.41Hz, 3H), 7.07 (d, J = 8.08Hz, 2H).



(c) TDZ-3: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.19Hz, 2H), 7.72-7.63 (m, 2H), 7.35 (t, J = 8.03Hz, 2H), 7.30 (d, J = 8.51Hz, 3H), 7.13 (t, J = 7.43Hz, 1H), 7.04 (d, J = 7.85Hz, 2H), 2.40 (s, 3H).



(d) TDZ-4: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.89Hz, 2H), 7.77-7.71 (m, 2H), 7.39-7.32 (m, 3H), 7.15 (d, J = 7.39Hz, 1H), 7.04 (d, J = 7.94Hz, 3H), 7.00-6.96 (m, 2H), 3.90 (s, 3H).

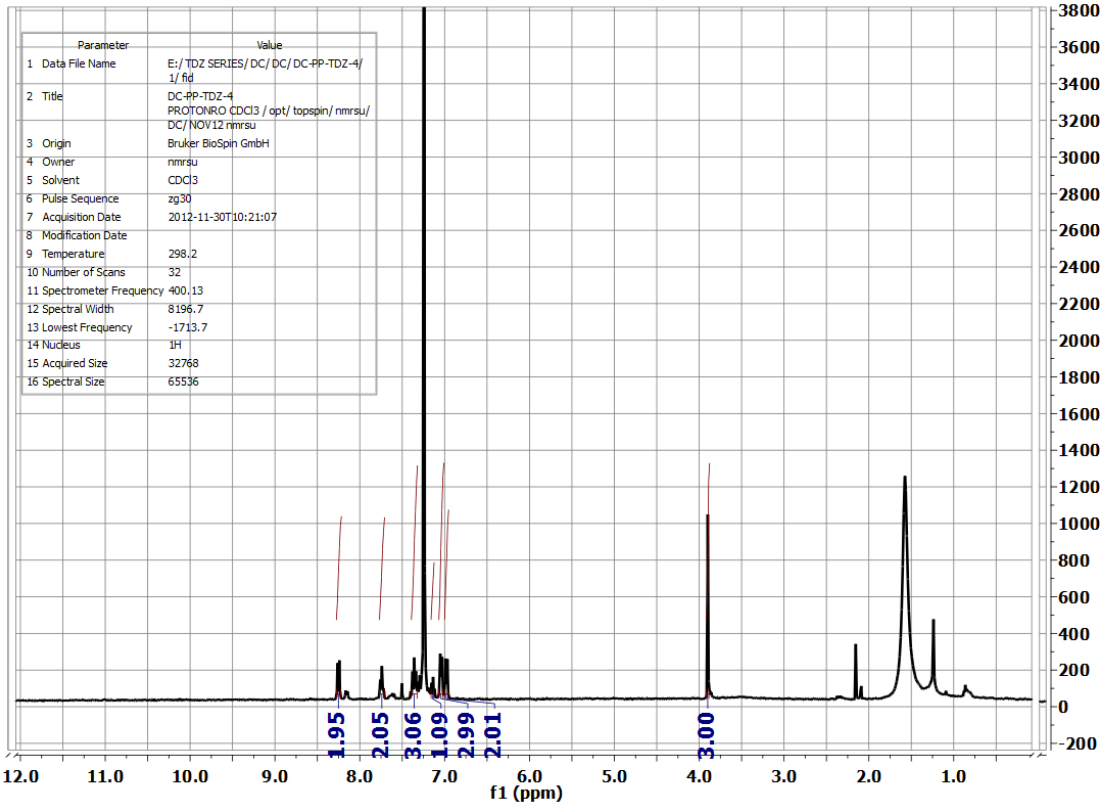
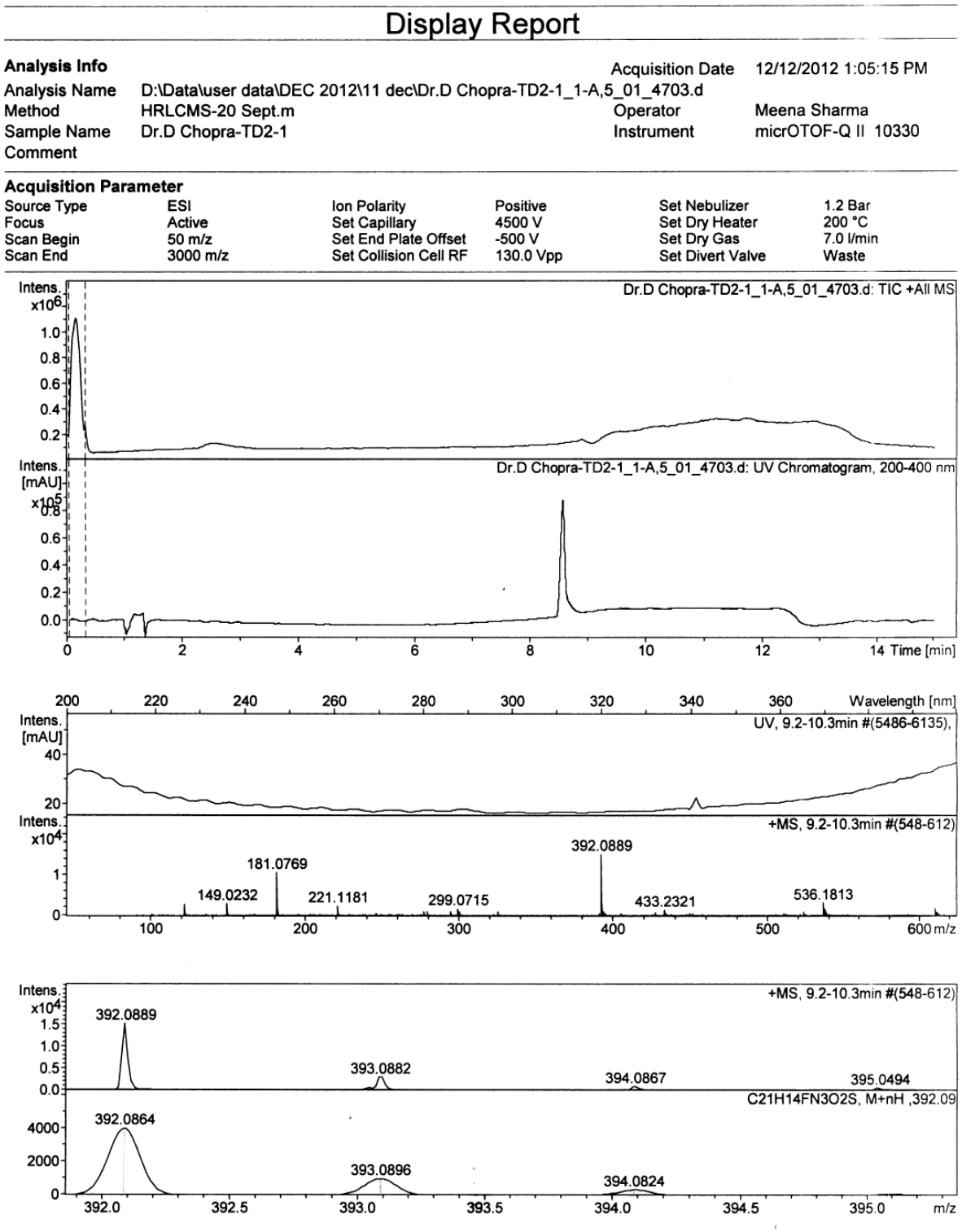


Figure S2: Mass spectra of all compounds:

(a) TDZ-1: HRMS-ESI$^+$ **:** 392.0889 (calculated for $C_{21}H_{14}FN_3O_2S + H^+$: 392.0864)



(b) TDZ-2: HRMS-ESI$^+$ **:** 410.0774 (calculated for $C_{21}H_{13}F_2N_3O_2S + H^+$: 410.0769)

Display Report

Analysis Info

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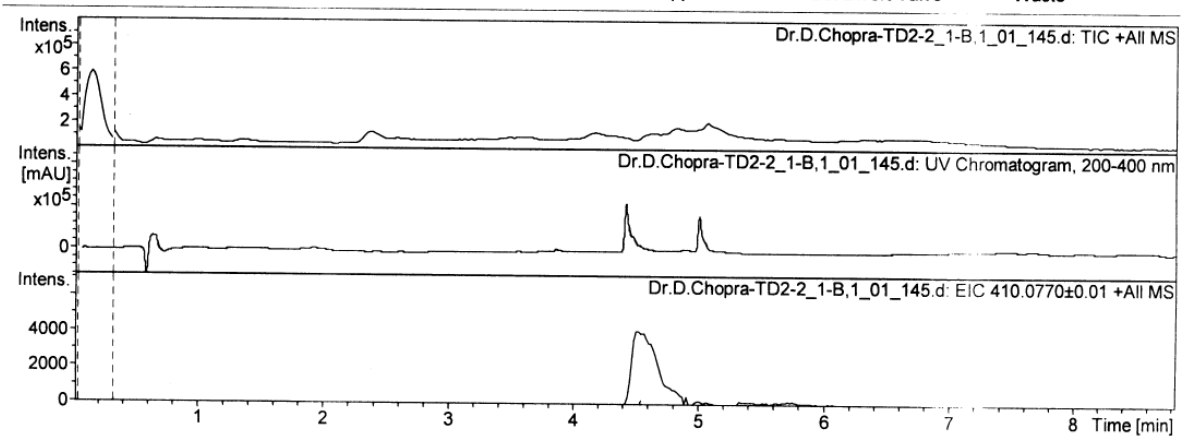
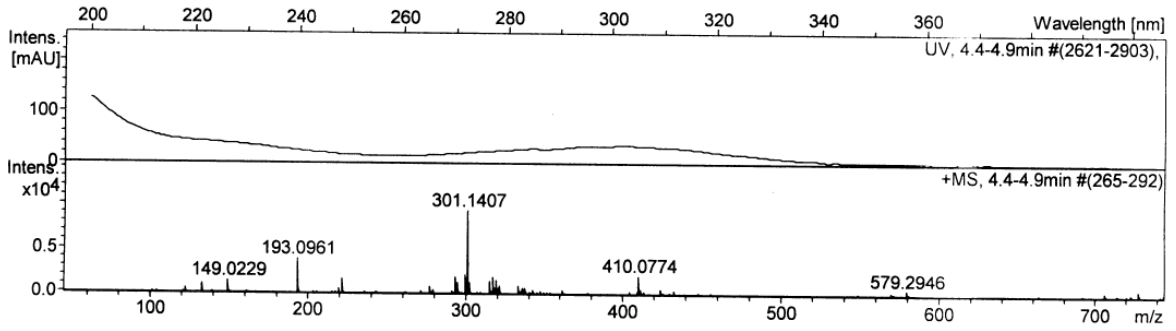
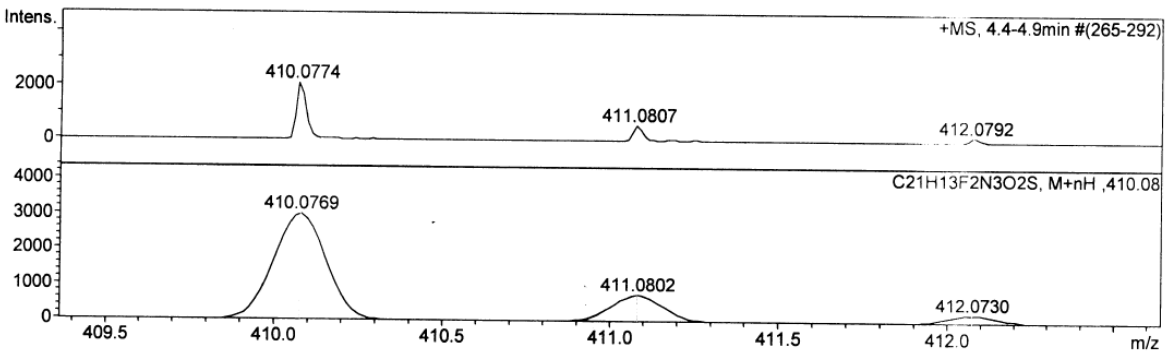
Method	HRLCMS-20 Sept.m	Operator	Amit
Sample Name	Dr.D.Chopra-TD2-2	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







(c) TDZ-3: HRMS-ESI$^+$ **:** 406.1030 (calculated for $C_{22}H_{16}FN_3O_2S + H^+$: 406.1020)

Display Report

Analysis Info

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Sample Name	Dr.D.Chopra-TD2-3	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
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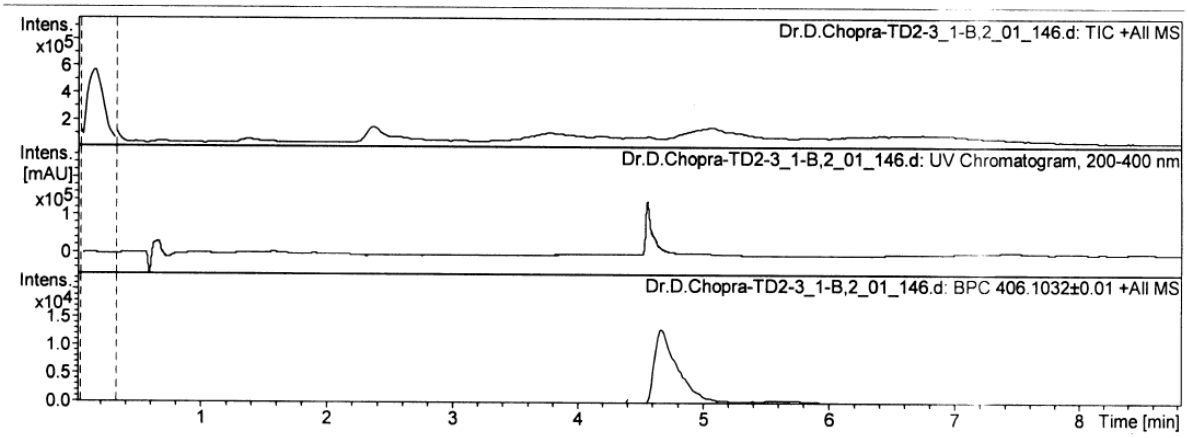
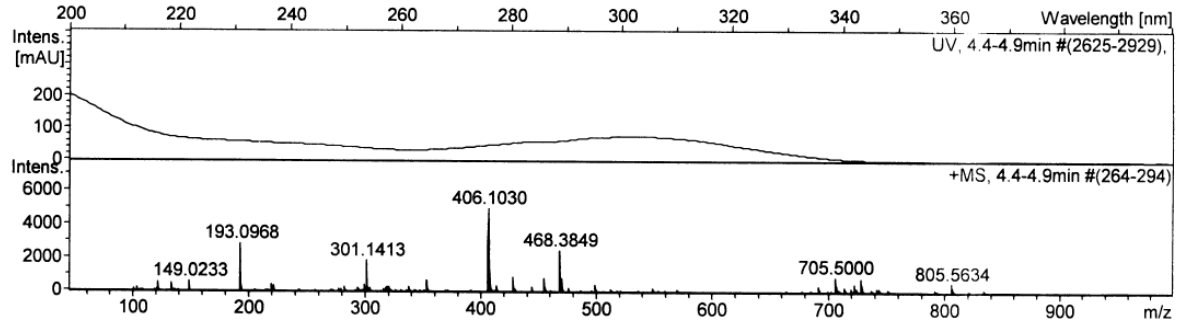
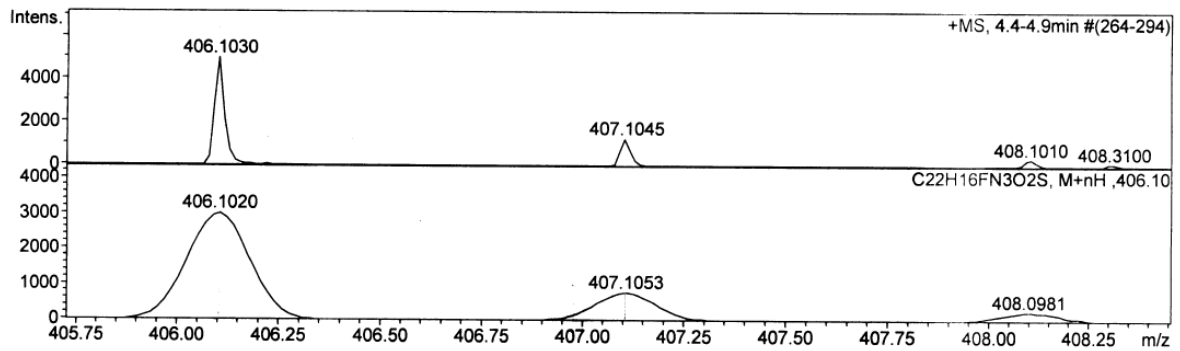
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







(d) TDZ-4: HRMS-ESI$^+$ **:** 422.1010 (calculated for $C_{22}H_{16}FN_3O_3S + H^+$: 422.0969)

Display Report

Analysis Info

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Sample Name	Dr.D Chopra-TD2-4	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
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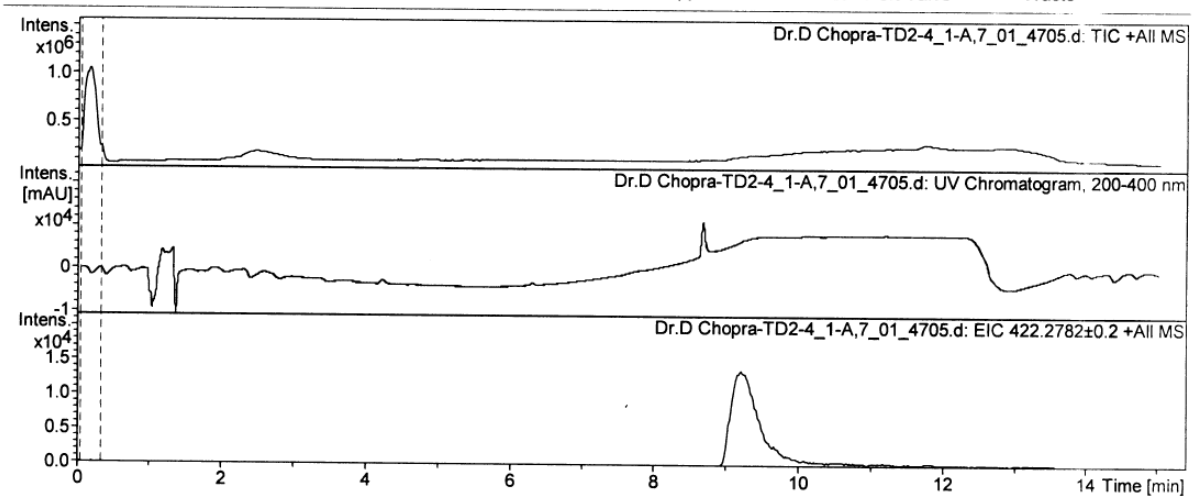
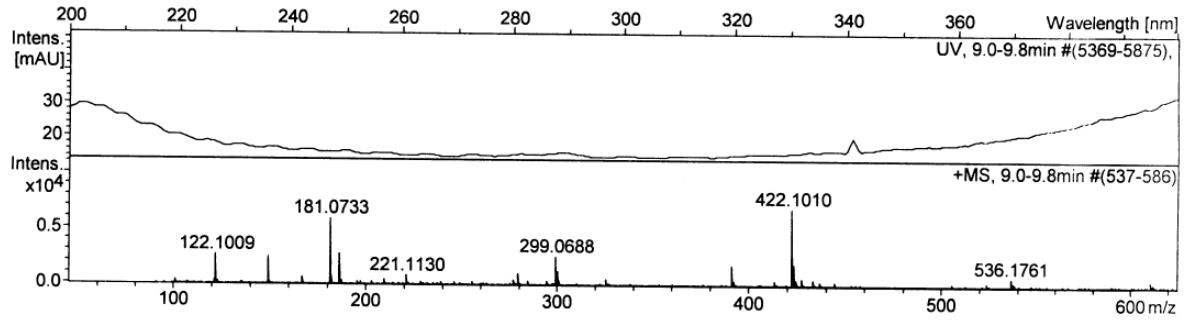
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste





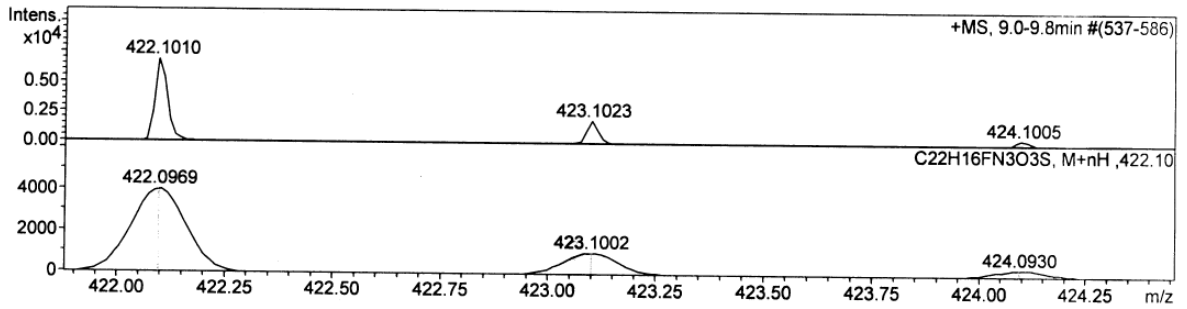
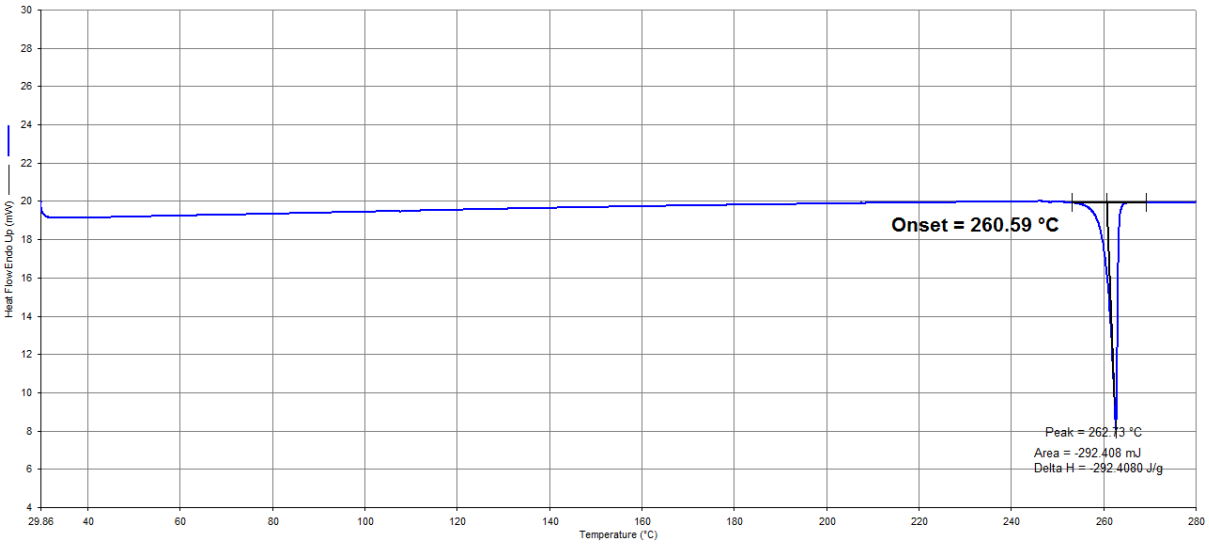
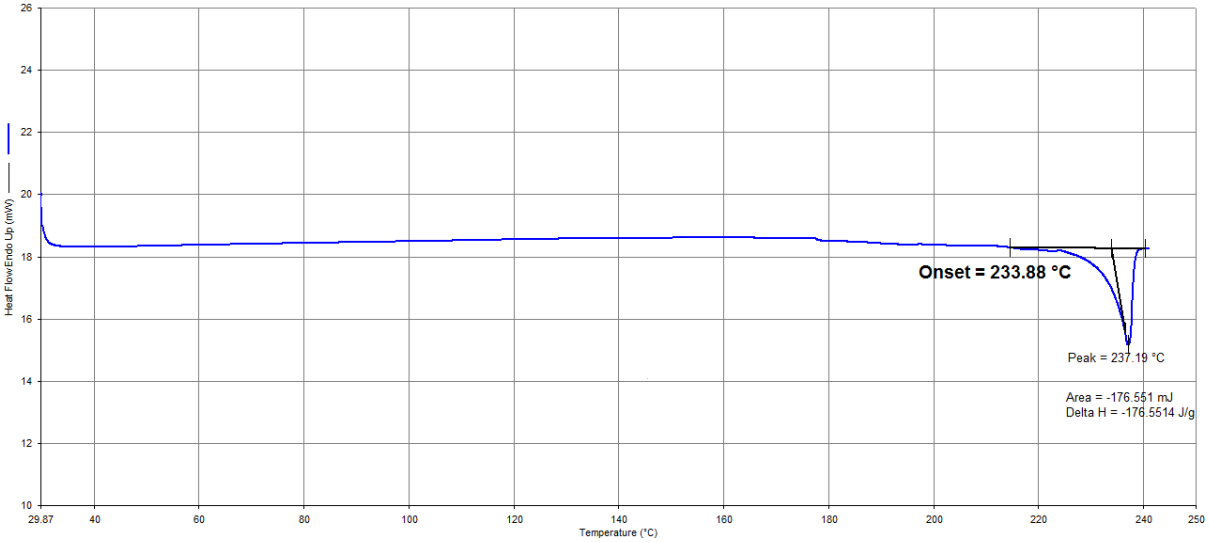


Figure S3: DSC curves of solids (@ 5°C/min) recorded on Perkin Elmer DSC 6000.

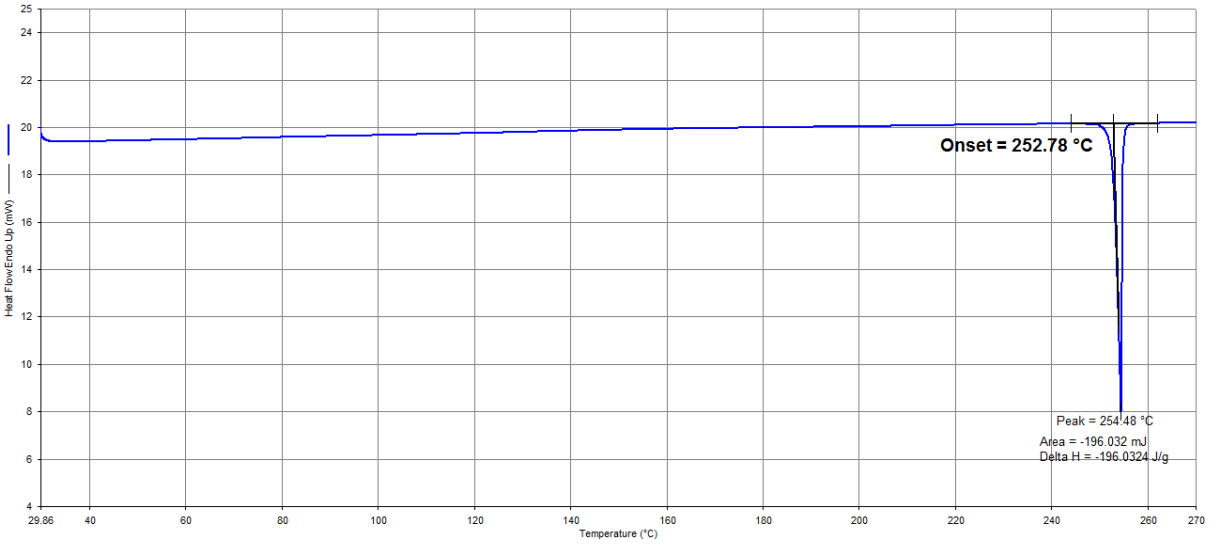
(a) TDZ-1:



(b) TDZ-2:



(c) TDZ-3:



(d) TDZ-4:

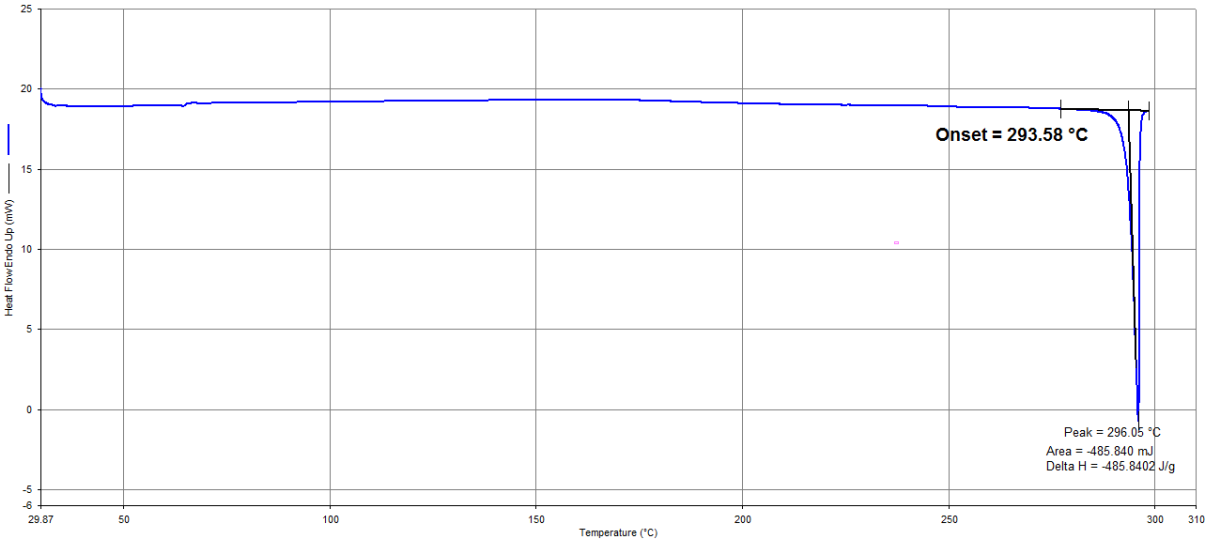
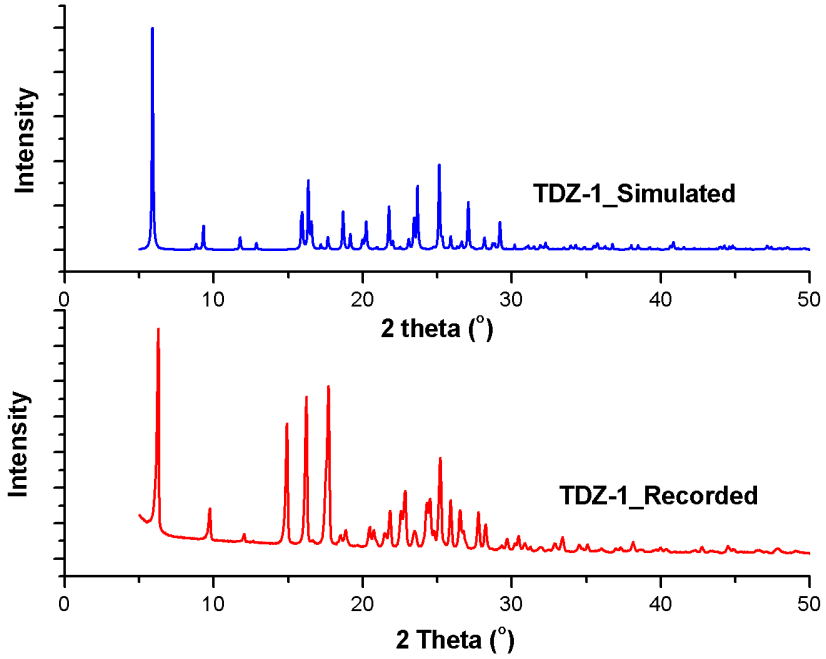
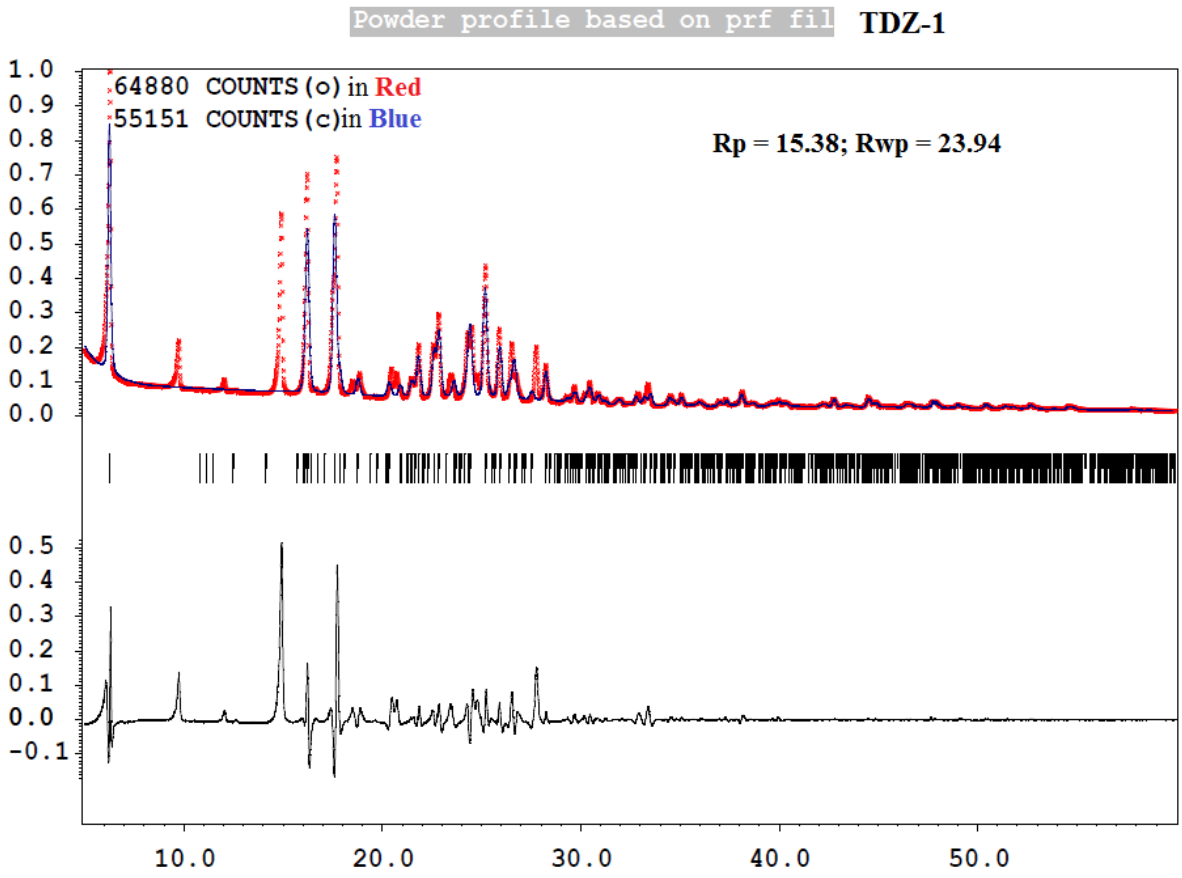


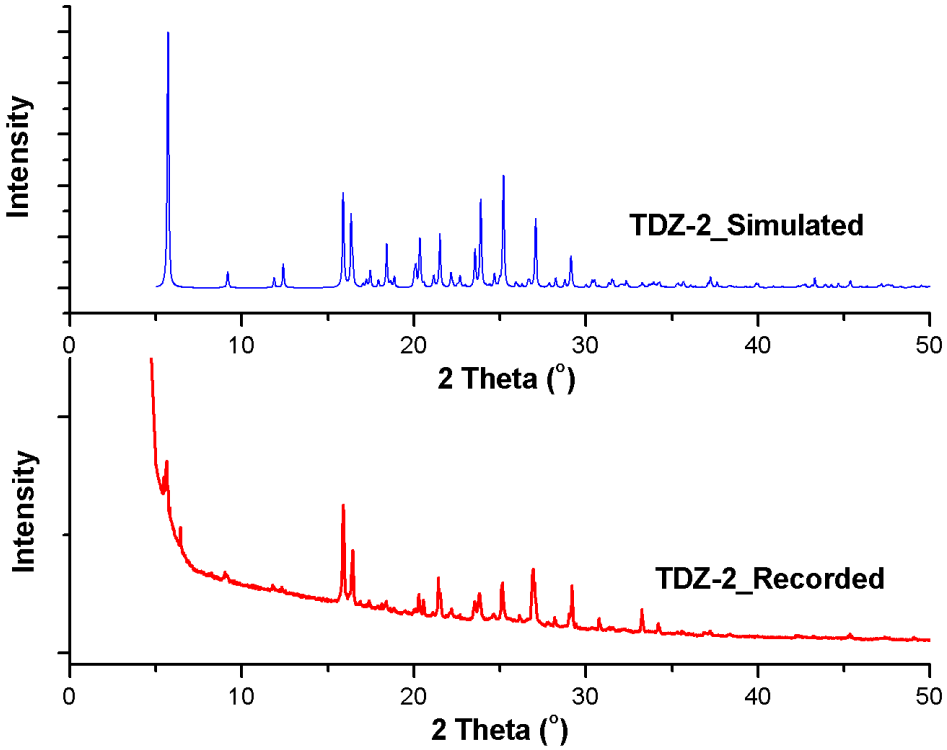
Figure S4: Comparison of Simulated powder pattern with experimental powder pattern recorded on PANalytical Empyrean (between 5 - 50° in 2θ):
Profile fitting Refinement was performed with JANA 2000. Profile fitting parameter R_p and R_{wp} are given the diagrams. The higher values of R_p and R_{wp} in case of **TDZ-1** may indicate the presence of more than one phase in the bulk powder.

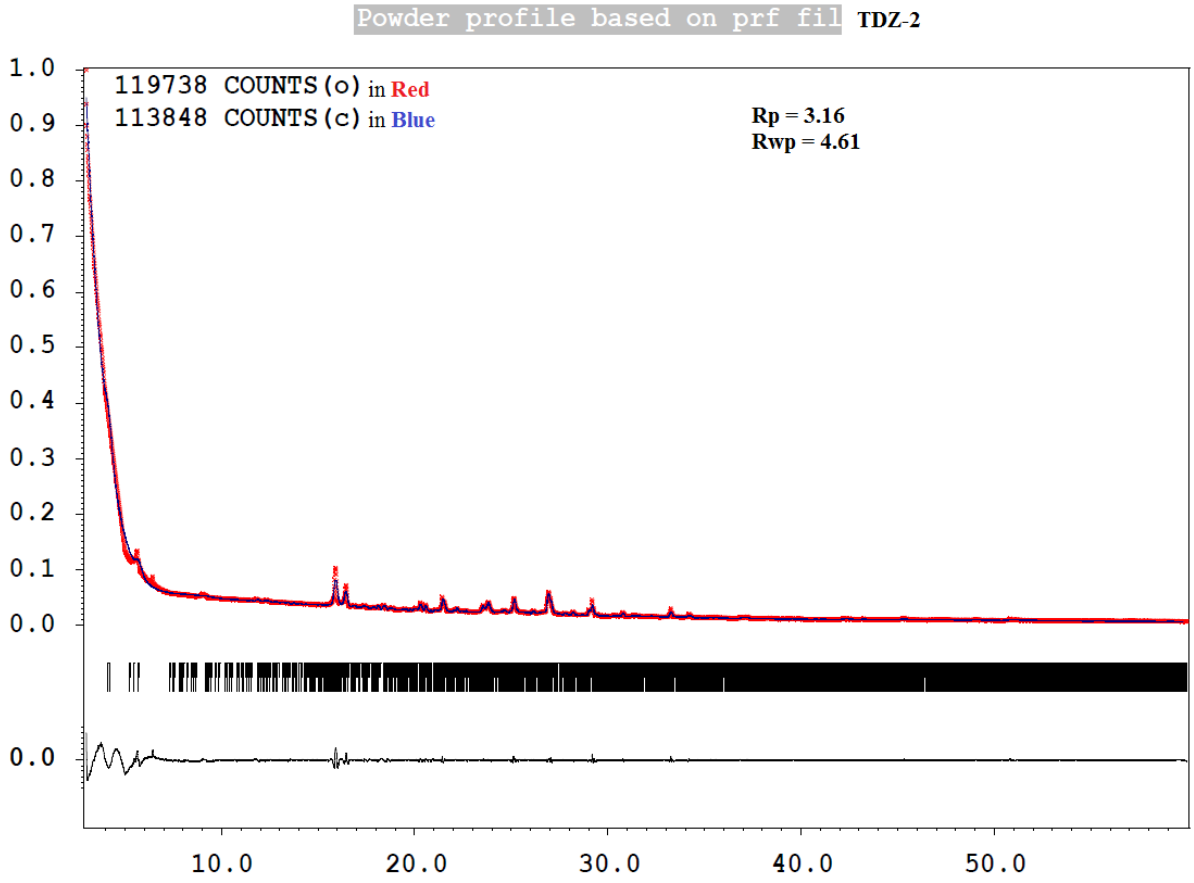
(a) TDZ-1:



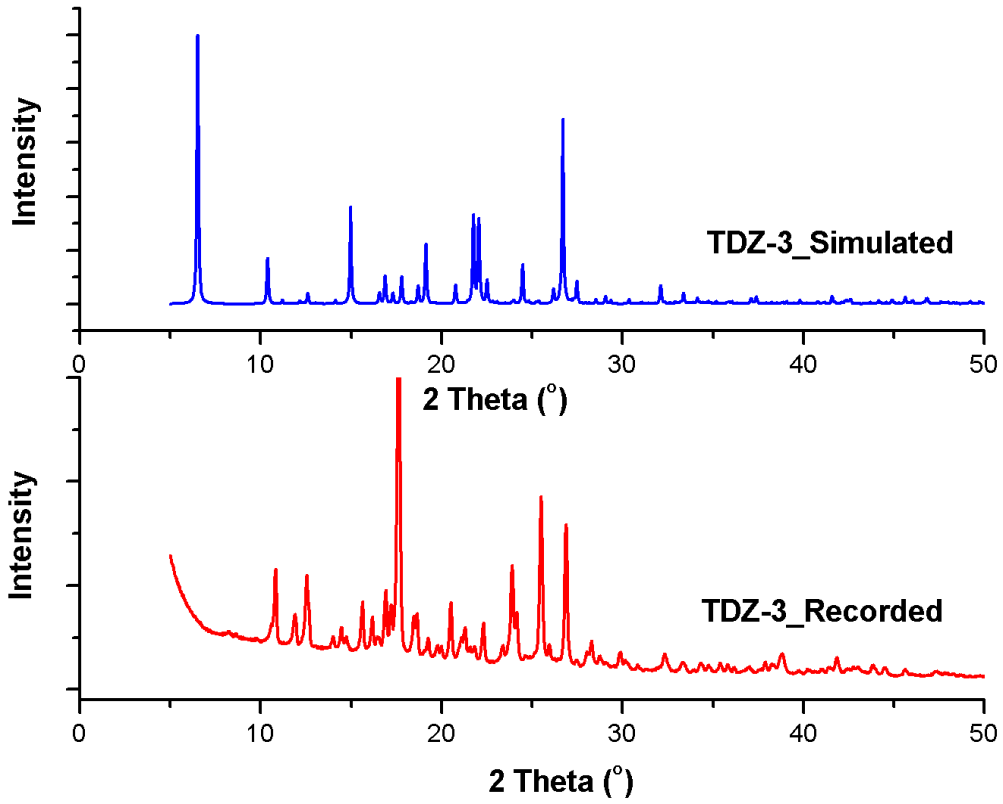


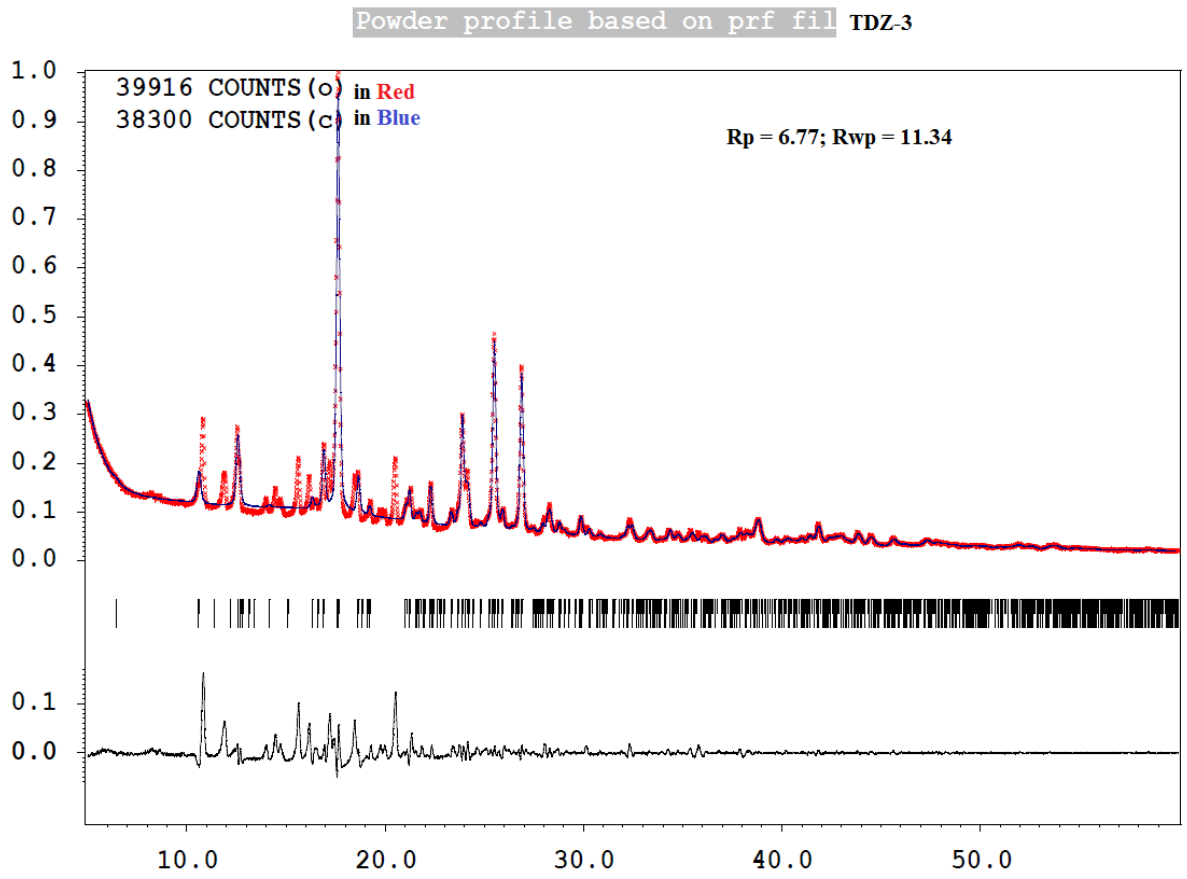
(b) TDZ-2:



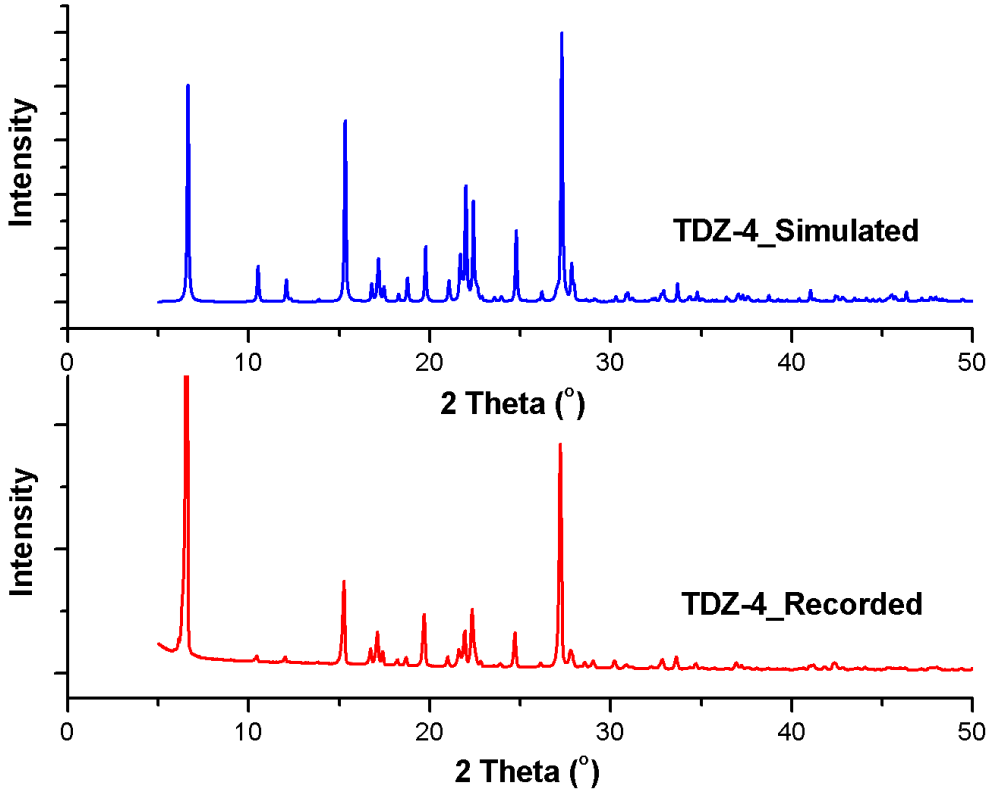


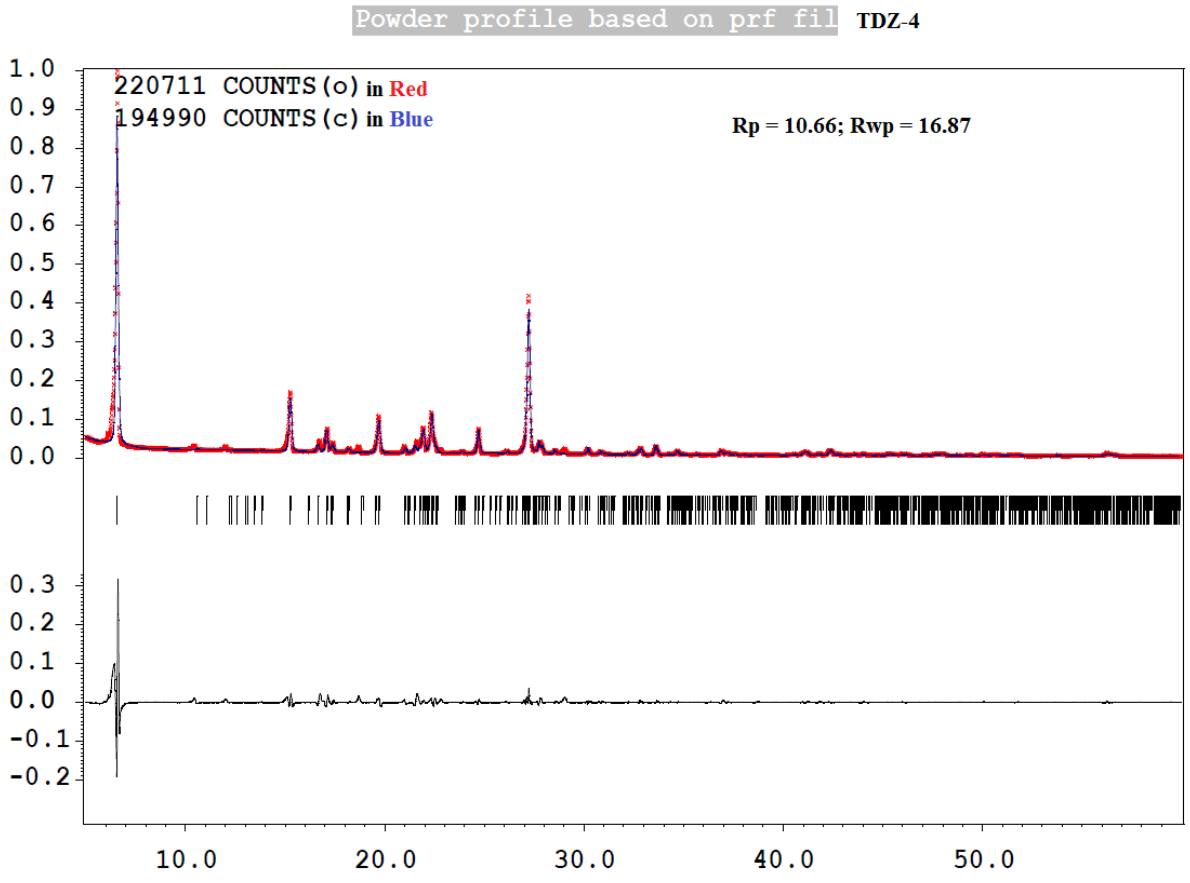
(c) TDZ-3:





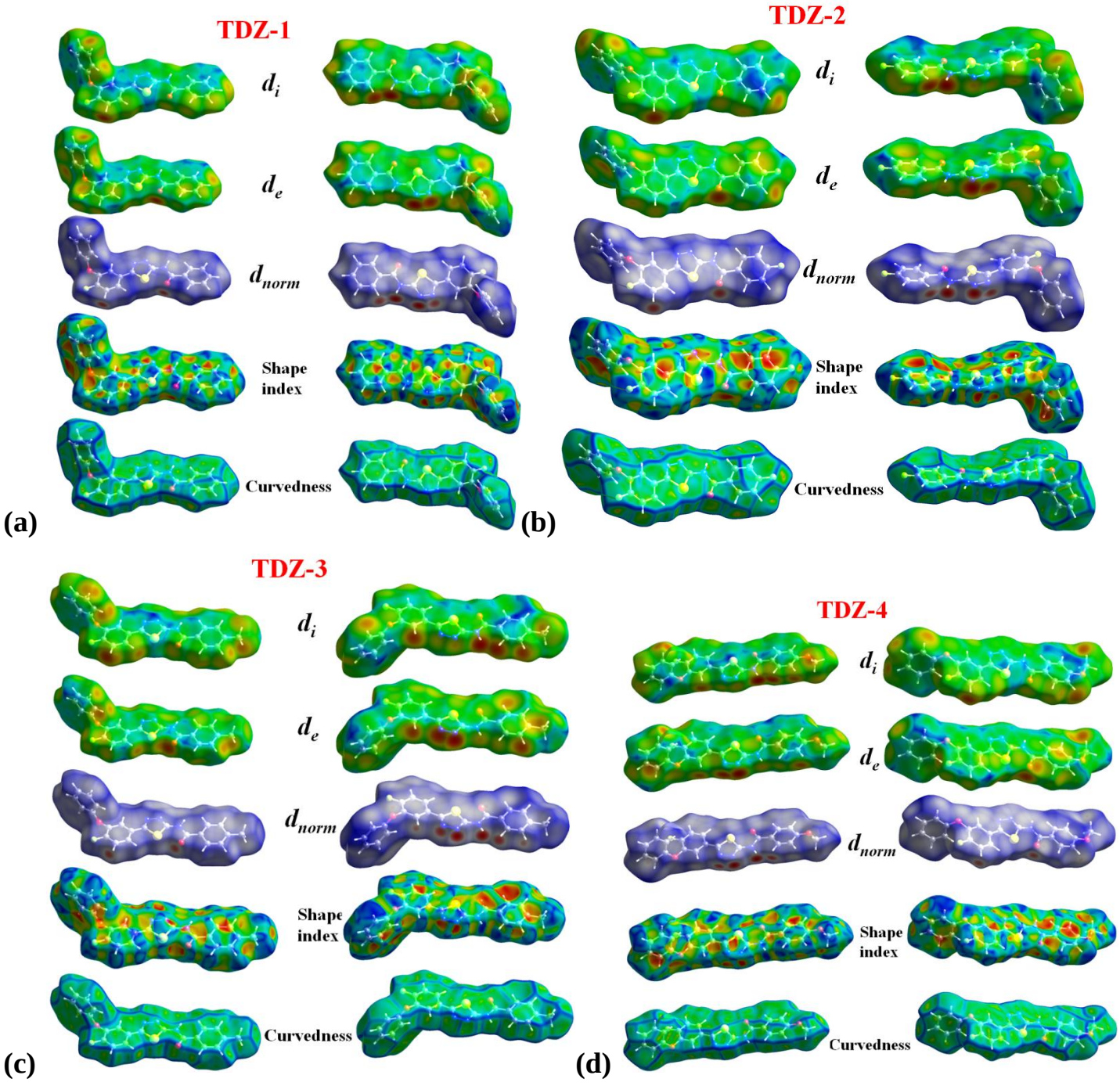
d) TDZ-4:





Section 2: Hirshfield surfaces from Crystal Explorer 3.0

Figure S5: Hirhfeld surfaces of four molecules mapped with different properties. Left column (front view) while right column (back view)



Section 3:

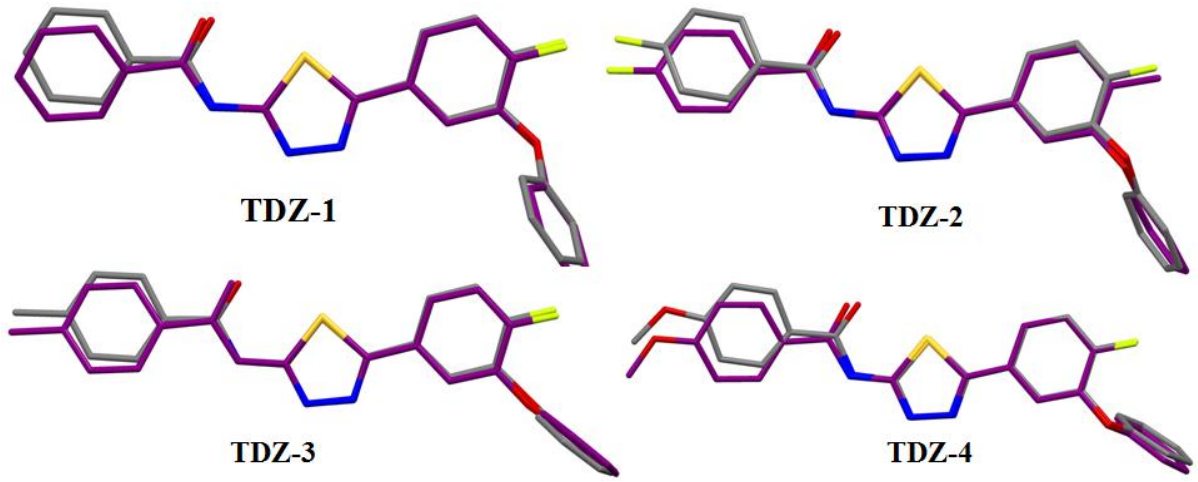


Figure S6: Molecular overlay diagram of all structures with the respective optimized geometry. Gray carbon corresponds to the solid state geometry and that of purple carbon corresponds to the gaseous state.

Section 4: XPAC analysis:

For XPAC analysis the circled atoms, labeled with C3, C4, C5, C7-C17, C21, N1-N3, S1, O1, O2, F1,were consider for '**corresponding ordered sets of points**' (COSPs) [**Fig S6**]. The filter setting a/p/d: 10/14/1.50 was applied for all comparisons.

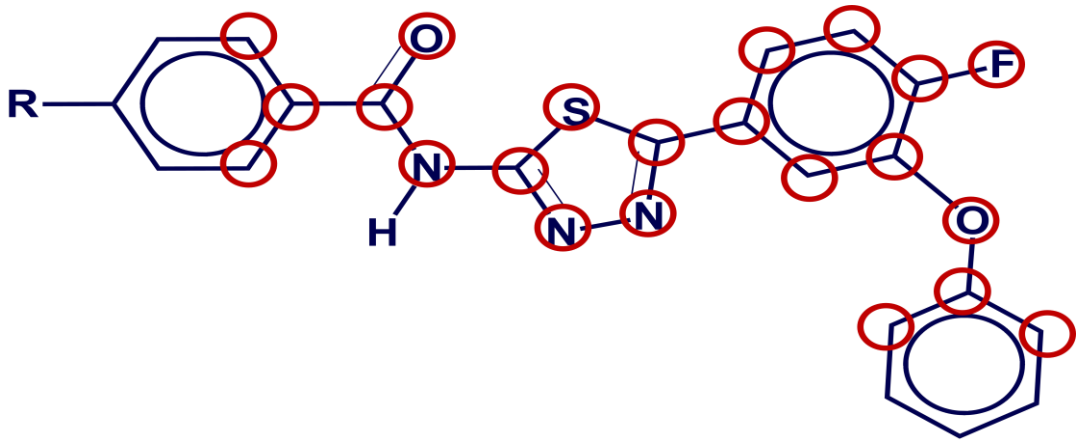


Figure S7: Selection of atoms for COSP denoted with red circles in all structures.

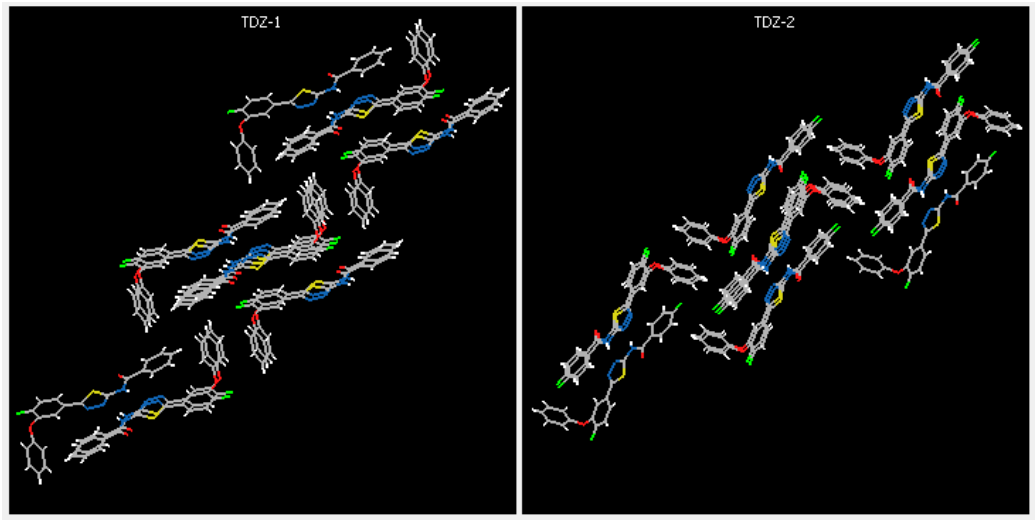


Figure S8(a): Comparison of crystal packing between TDZ-1 and TDZ-2 by XPAC depicting 3D SC.

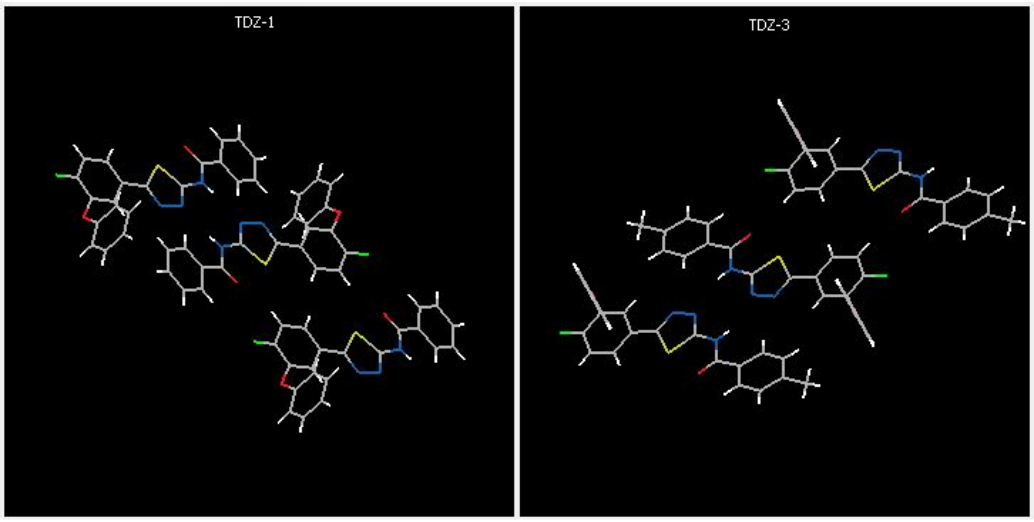


Figure S8(b): Comparison of crystal packing between TDZ-1 and TDZ-3 by XPAC depicting 1D SC.

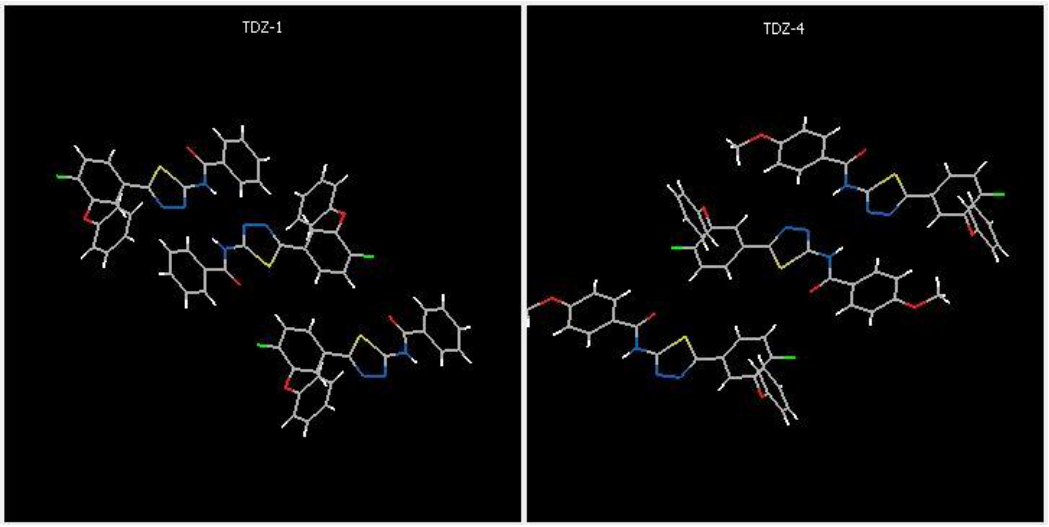


Figure S8(c): Comparison of crystal packing between TDZ-1 and TDZ-4 by XPAC depicting 1D SC.

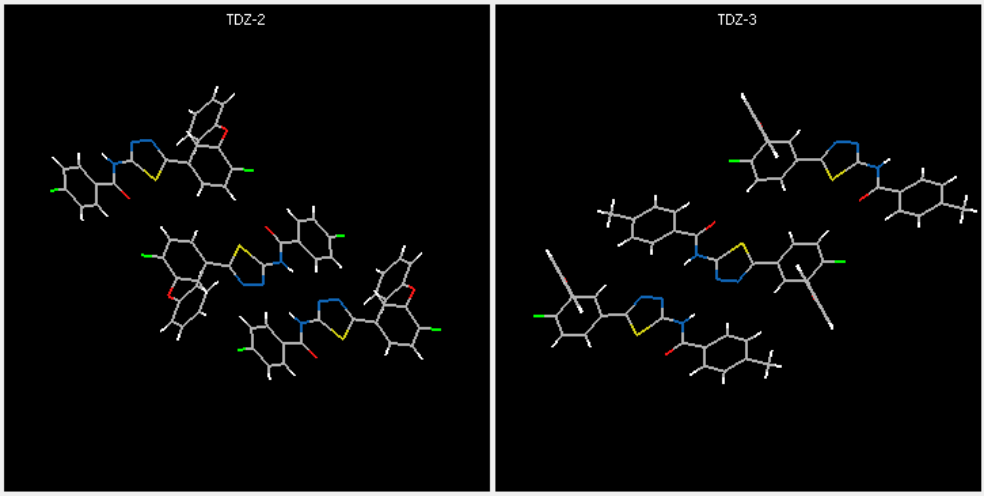


Figure S8(d): Comparison of crystal packing between TDZ-2 and TDZ-3 by XPAC depicting 1D SC.

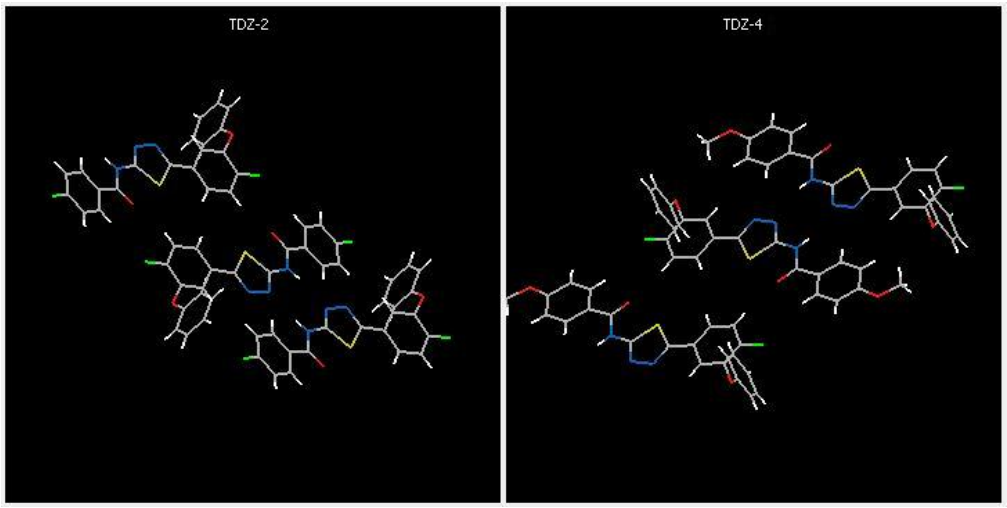


Figure S8(e): Comparison of crystal packing between TDZ-2 and TDZ-4 by XPAC depicting 1D SC.

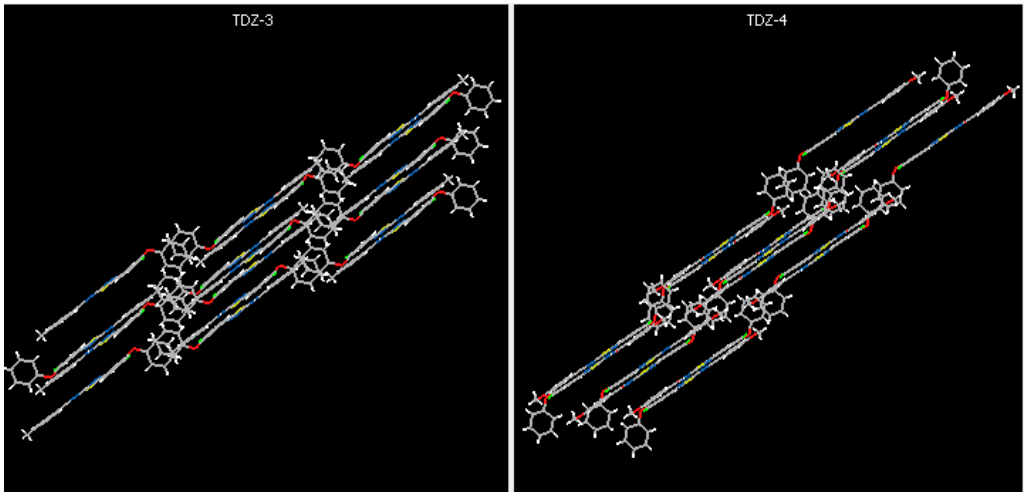


Figure S8(f): Comparison of crystal packing between TDZ-3 and TDZ-4 by XPAC depicting 3D SC.

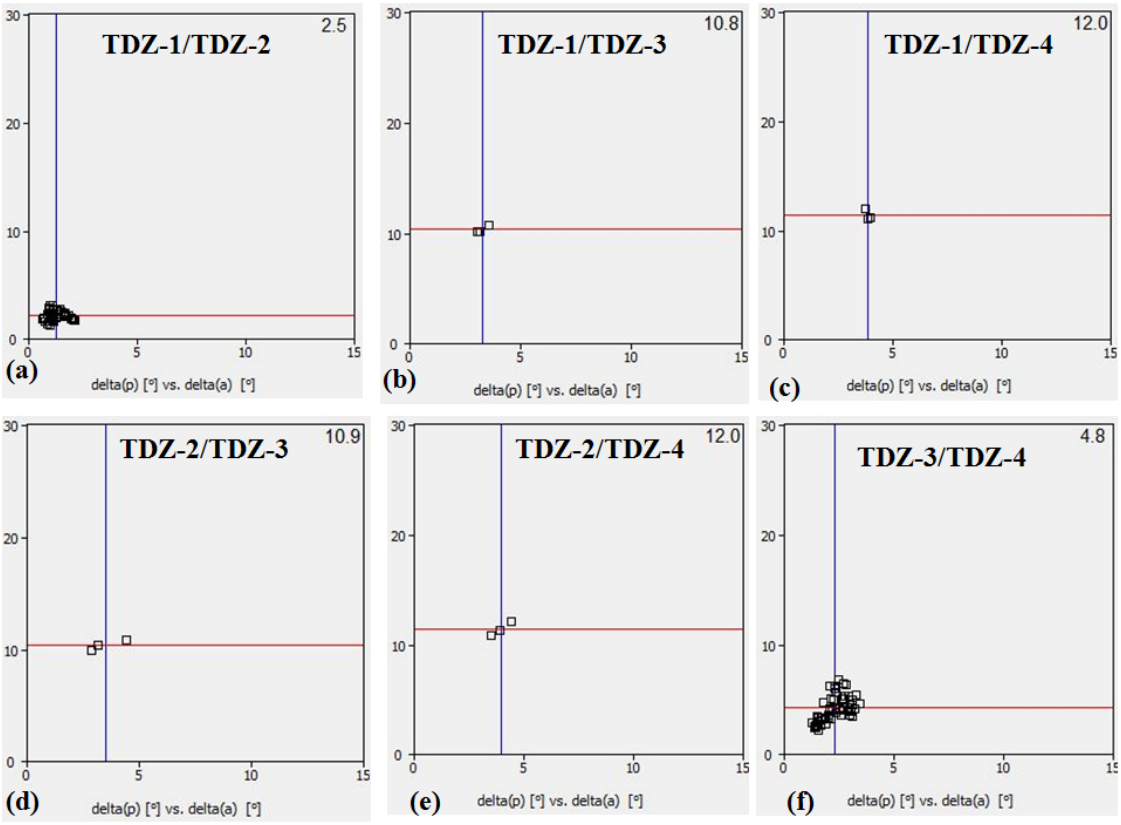


Figure S9: XPAC plots δp [y-axis] against δa [x-axis] (both in °), displaying the degree of similarity. Upper right corner is the dissimilarity index X, vertical and horizontal lines are the mean values of δa and δp, respectively.

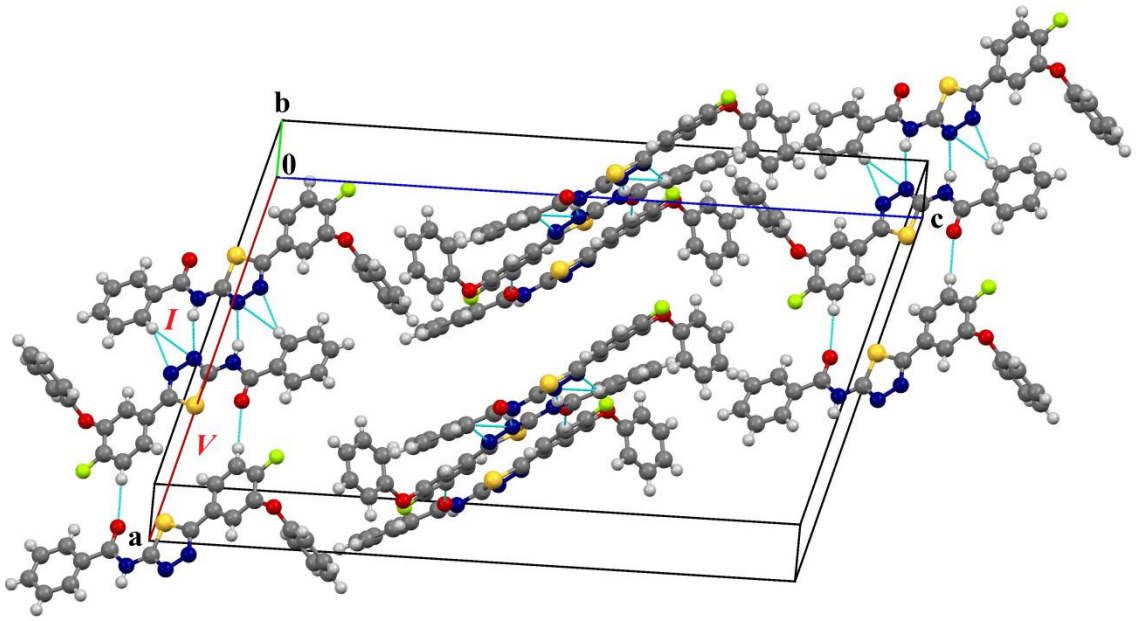


Figure S10(a): Packing of molecules *via* strong N-H···$N_{aromatic}$, weak C-H···$N_{aromatic}$ and C-H···O=C hydrogen bonds in **TDZ-1**.

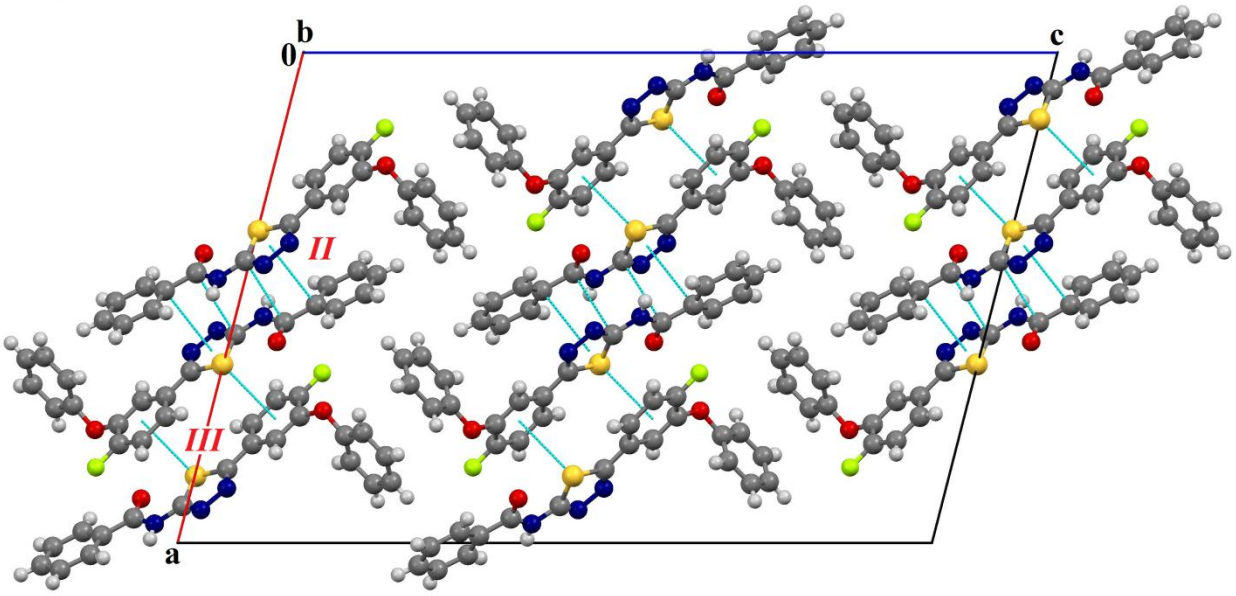


Figure S10(b): Packing view down the ac plane in **TDZ-1,** displays weak π···π and S(lp)···π interactions.

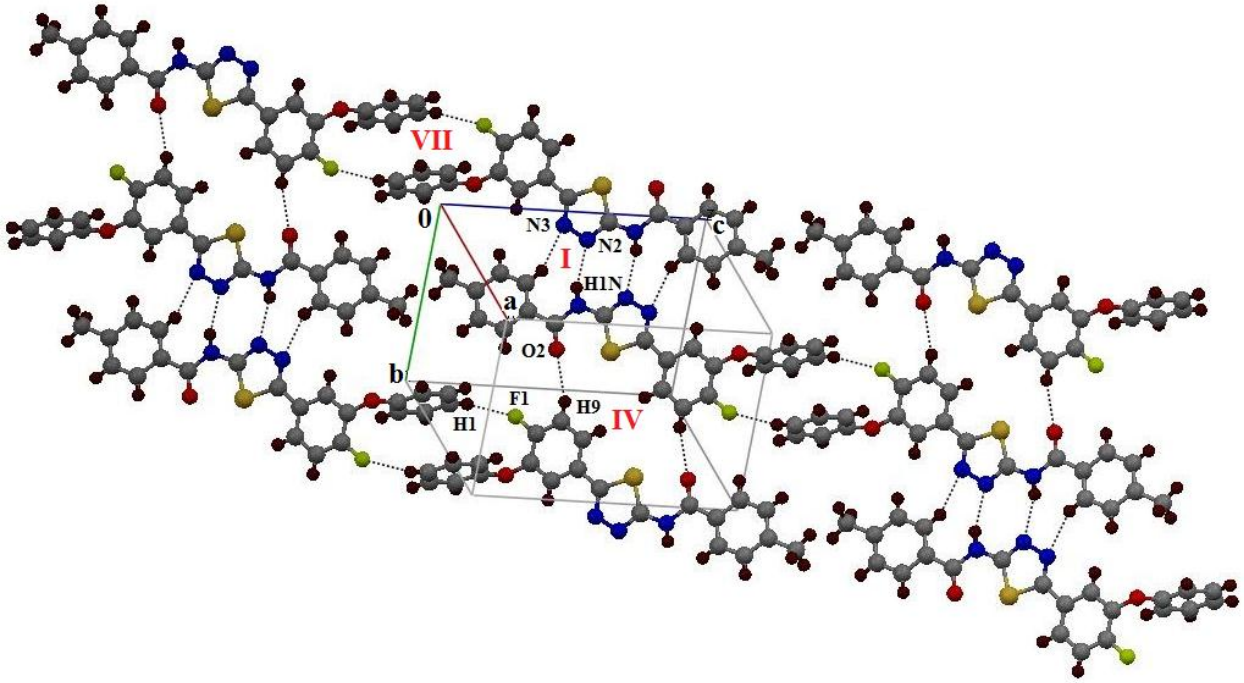


Figure S11: Packing of molecules in **TDZ-3** *via* strong N-H···$N_{aromatic}$, weak C-H···$N_{aromatic}$, C-H···O=C and C-H···F hydrogen bonds.

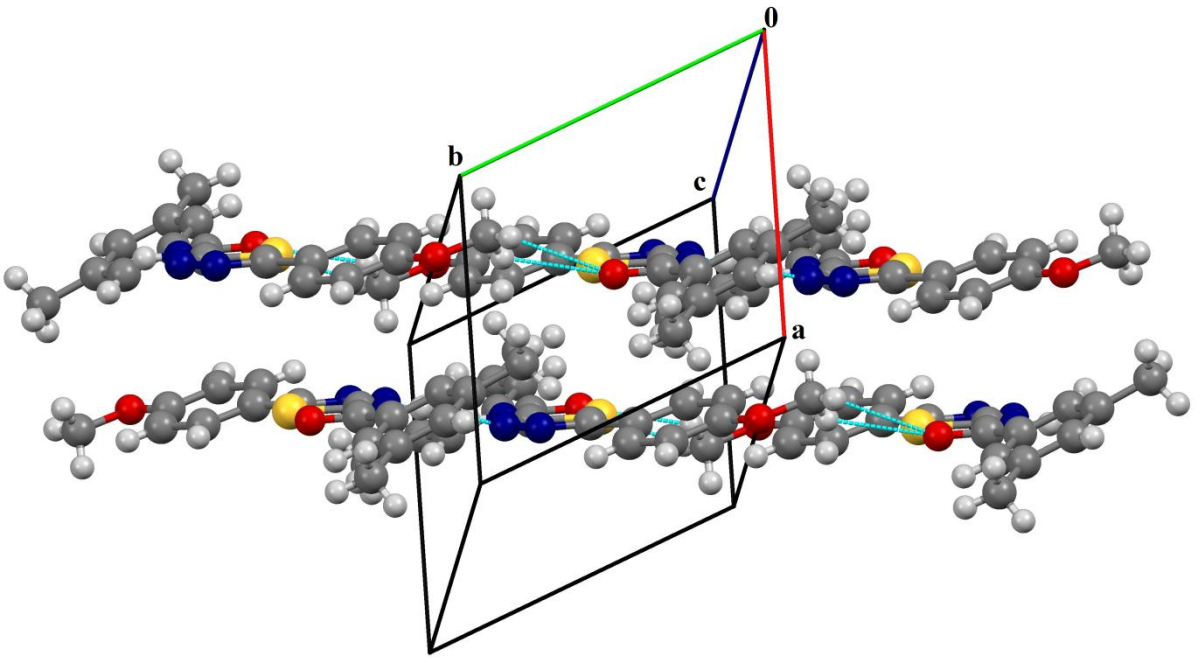


Figure S12 (a): Packing diagram of **NEQPAB** depicting N-H···$N_{aromatic}$ and C-H···O=C H-bonds.

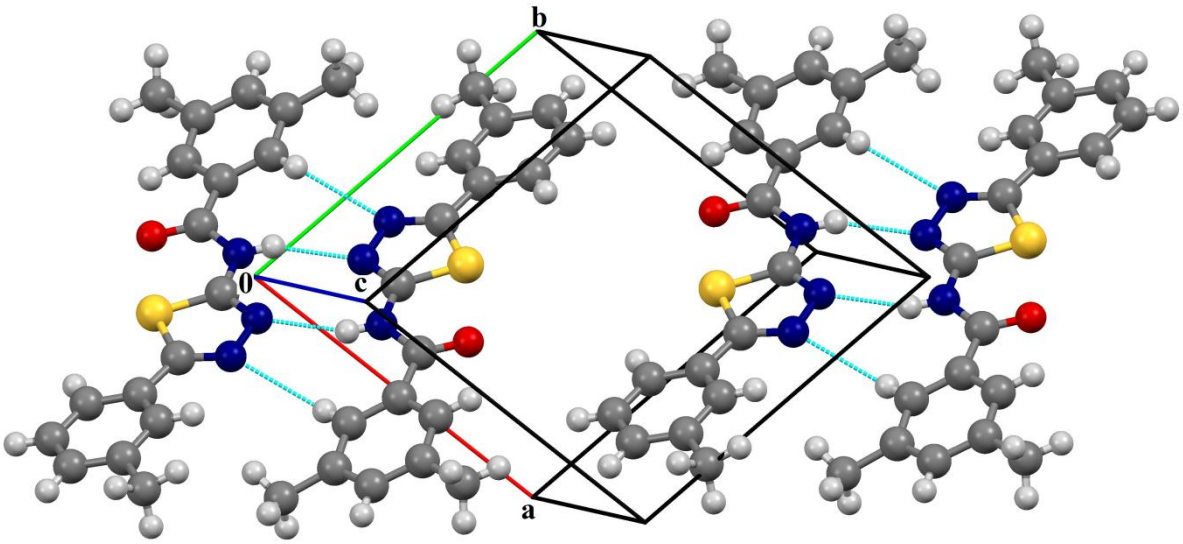


Figure S12 (b): Packing diagram of **REWBUR** depicting N-H···$N_{aromatic}$ and C-H···$N_{aromatic}$ H-bonds.

Section 5: Results from Theoretical Calculations performed using TURBOMOLE:

Molecular motifs	Interaction Energy calculated by DFT+Disp/B97-D/ cc-pVTZ (kcal/mol)	Counter Poise corrected Interaction Energy (kcal/mol)	BSSE (kcal/mol)
TDZ-1			
I	-27.22	-25.24	1.98
II	-17.28	-15.63	1.65
III	-16.45	-13.94	2.51
IV	-10.6	-8.96	1.64
V	-7.45	-6.10	1.35
Common SC(Fig 8 in Manuscript)	-34.8	-31.4	3.40
TDZ-2			
I	-27.69	-25.09	2.60
II	-23.54	-15.96	7.58
III	-17.14	-14.54	2.60
IV	-10.43	-8.73	1.70
V	-7.92	-6.53	1.39
Common SC (Fig 8 in Manuscript)	-35.7	-31.7	4.00
TDZ-3			
I	-23.98	-21.95	2.03
II	-19.07	-16.70	2.37
III	-17.22	-15.57	1.65
IV	-7.49	-6.28	1.21
V	-8.16	-6.88	1.28
VI	-6.43	-5.76	0.67
VII	-5.79	-4.30	1.49
Common SC (Fig 8 in Manuscript)	-31.5	-28.3	3.20
TDZ-4			
I	-27.19	-24.96	2.23
II	-20.32	-17.73	2.59
III	-19.67	-17.31	2.36
IV	-7.94	-6.67	1.27
V	-8.71	-7.40	1.31
VI	-7.51	-6.74	0.77
VII	-6.32	-4.86	1.46
Common SC(Fig 8 in Manuscript)	-35.2	-31.7	3.50