STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 73 (2017)

Supporting information for article:

Quantitative analysis of solid-state diversity in trifluoromethylated phenylhydrazones

Dhananjay Dey and Deepak Chopra

Characterization

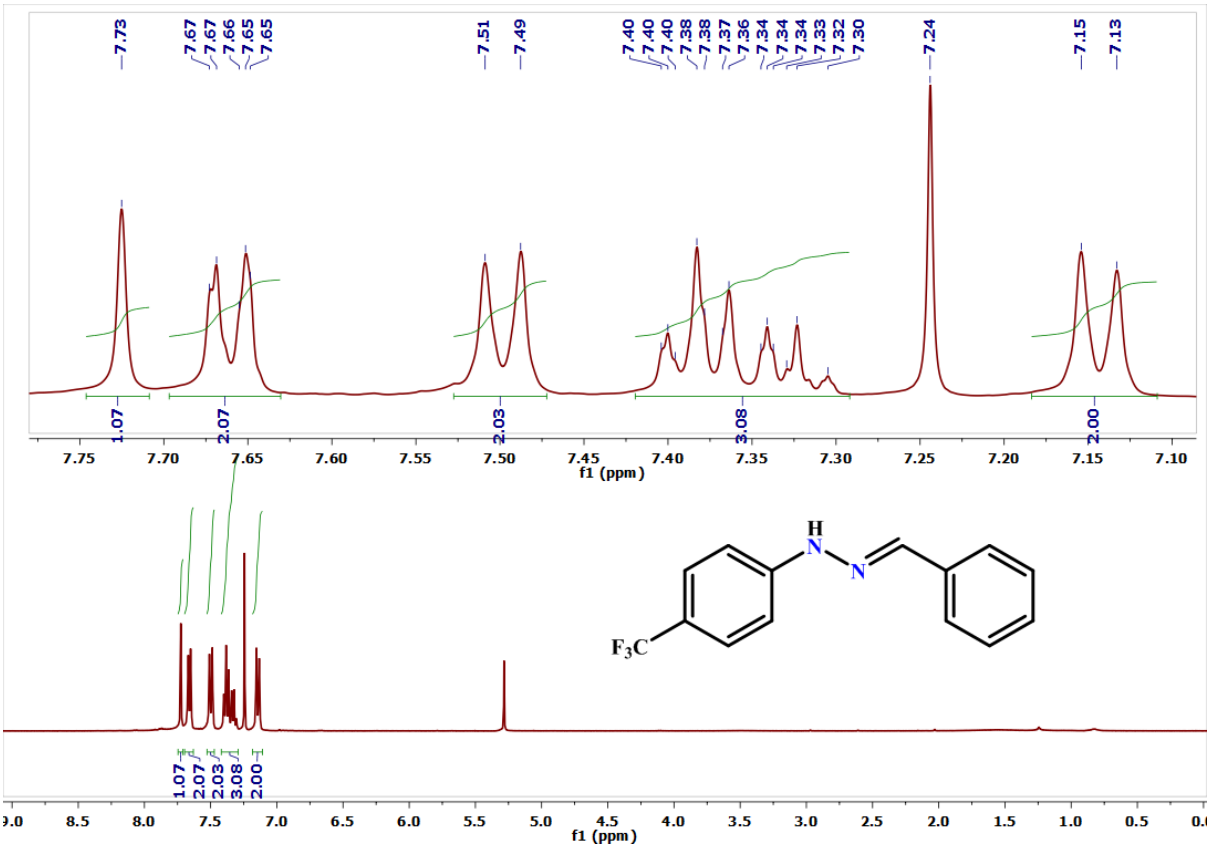

Figure S1a. ^{1}H-NMR spectra of the synthesized compound **HT03** in $CDCl_3$.

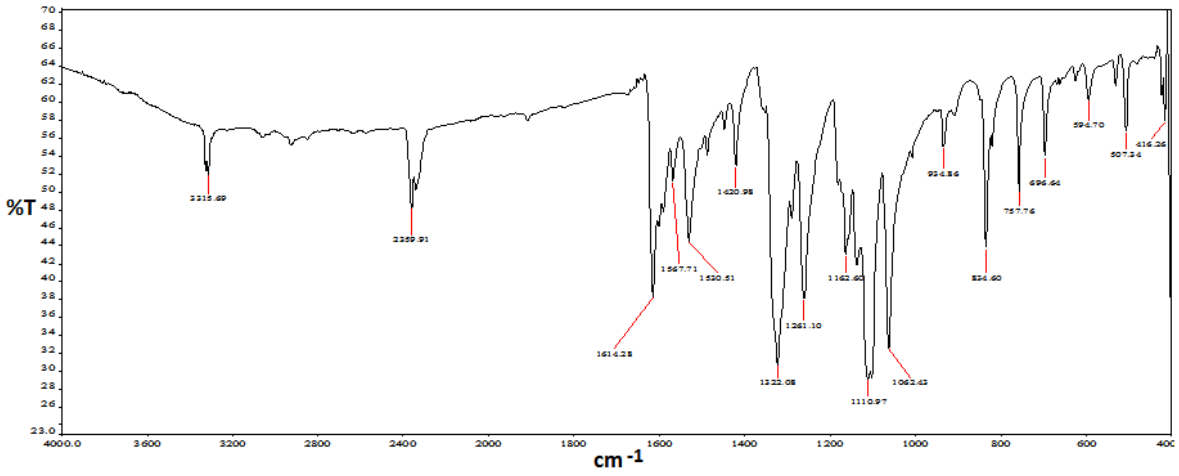

Figure S1b. FTIR spectra of **HT03**.

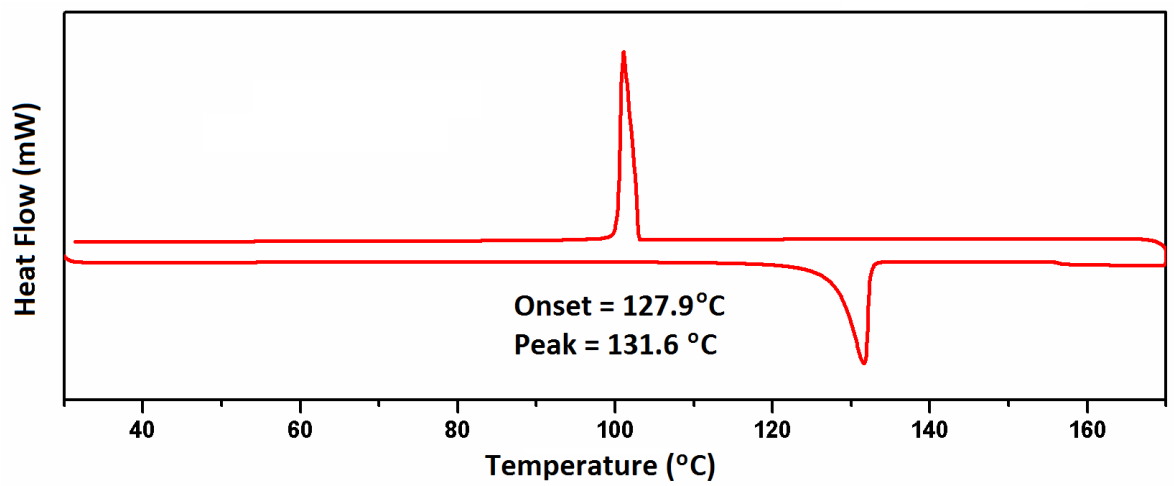

Figure S1c. DSC plot of **HT03** heated/cooled at 5ºC/min.

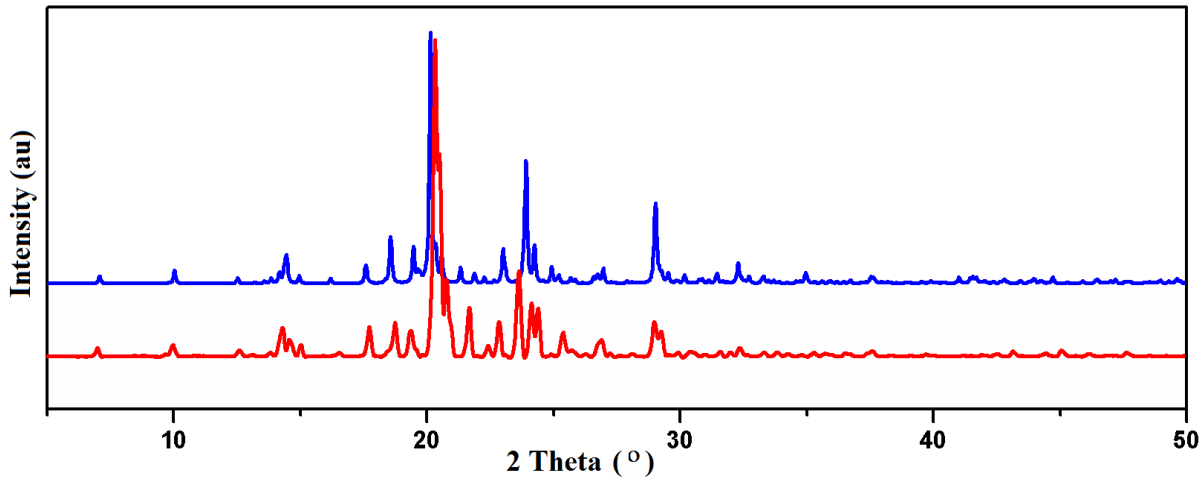

Figure S1d. Powder diffraction pattern of **HT03** (red: experimental; blue: calculated).

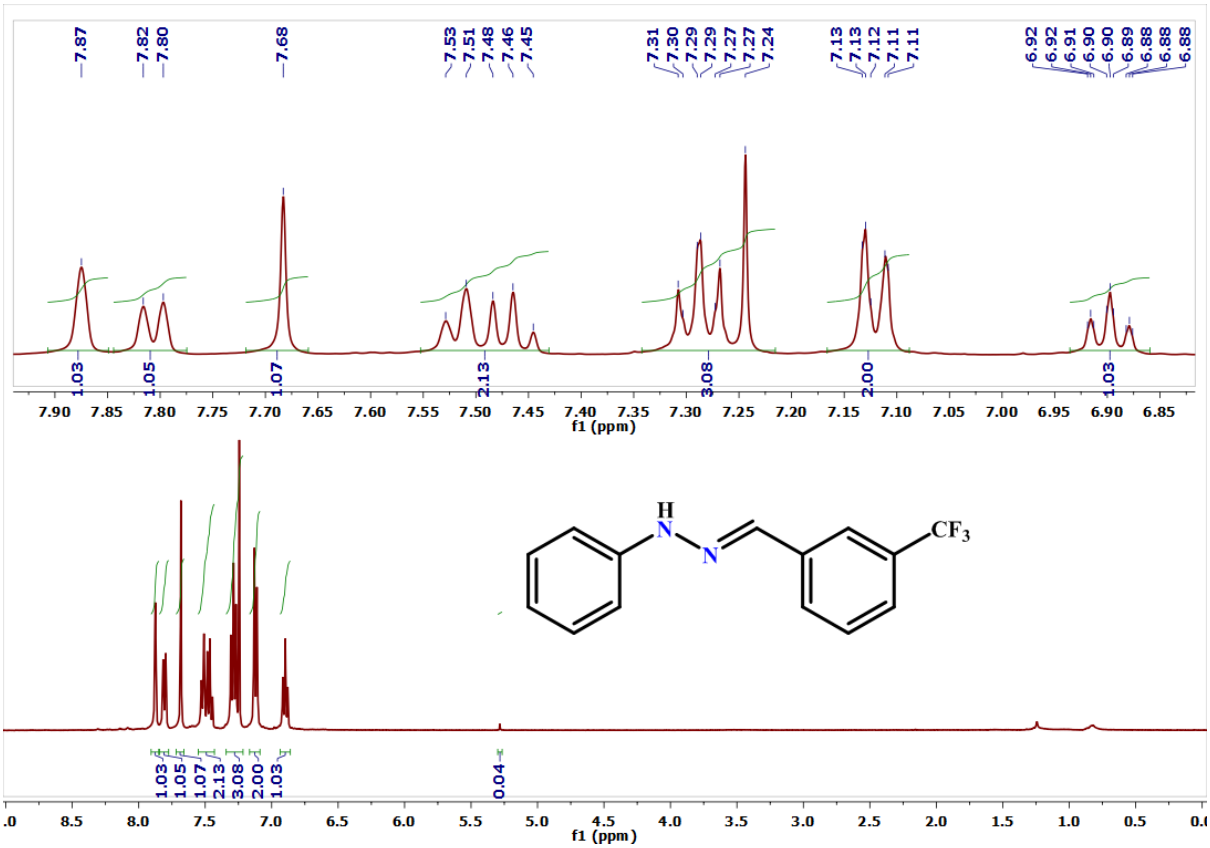

Figure S2a. ^{1}H-NMR spectra of the synthesized compound HT20 in $CDCl_3$.

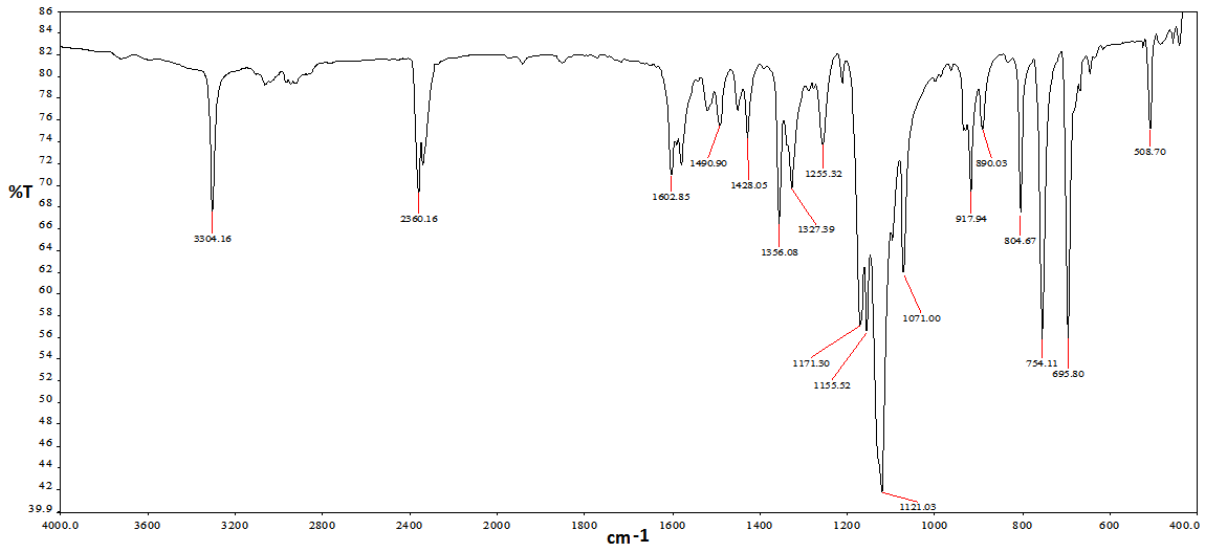

Figure S2b. FTIR spectra of **HT20**.

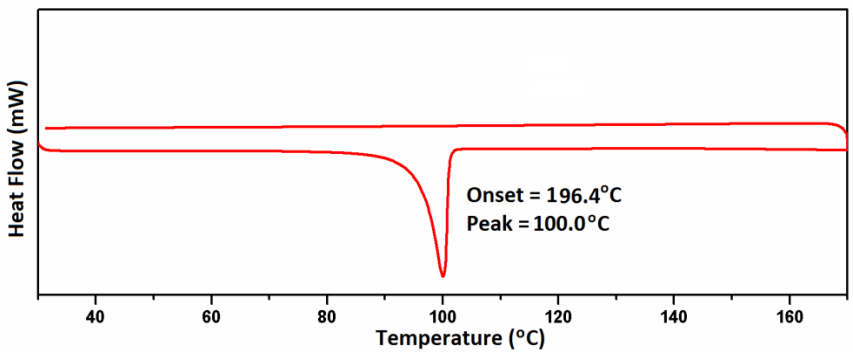

Figure S2c. DSC plot of **HT20** heated/cooled at 5ºC/min.

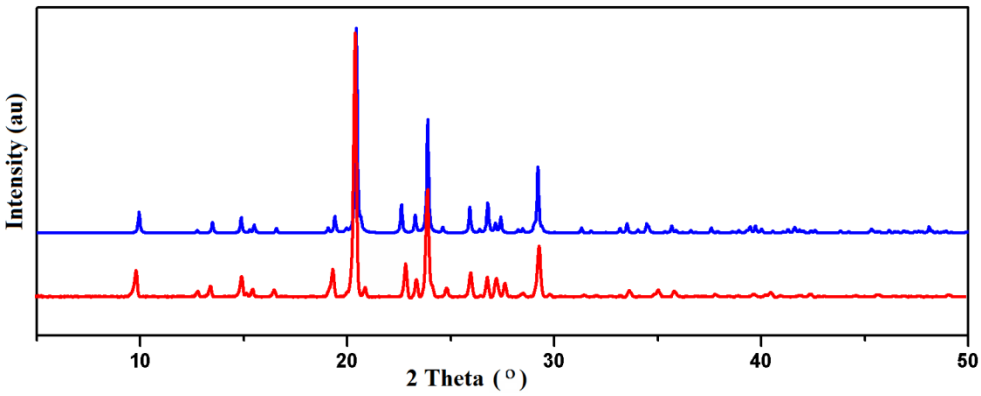

Figure S2d. Powder diffraction pattern of **HT20** (red: experimental; blue: calculated).

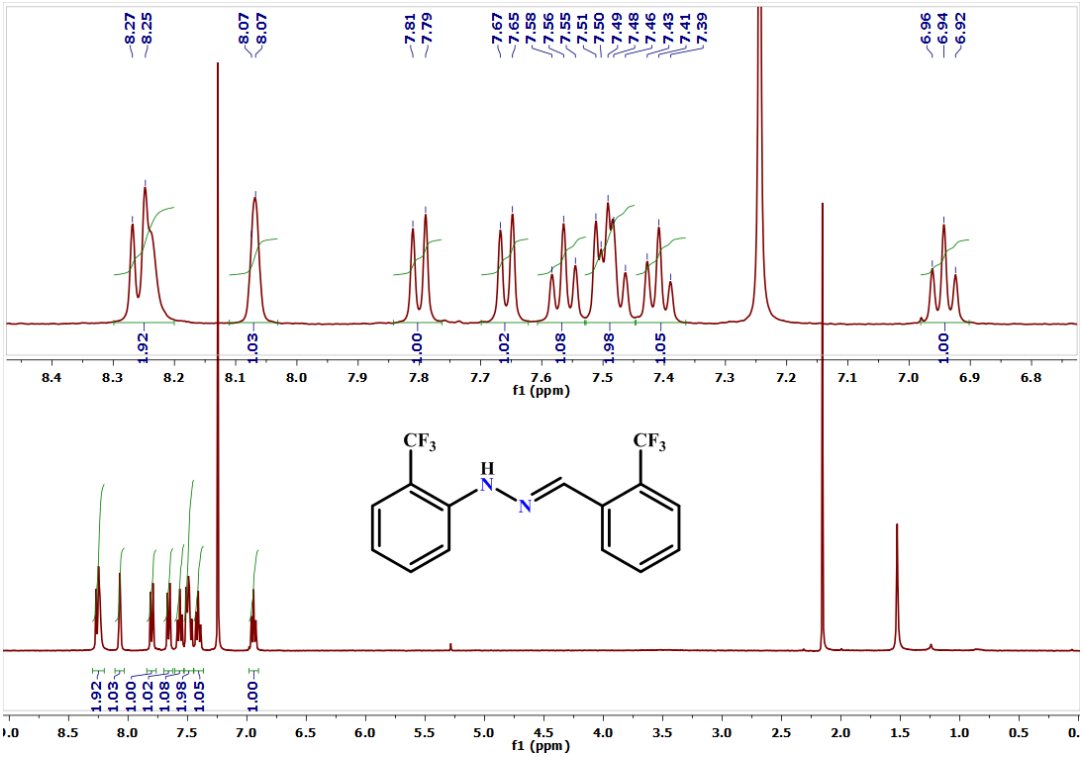

Figure S3a. ^{1}H-NMR spectra of the synthesized compound **HT11** in $CDCl_3$.

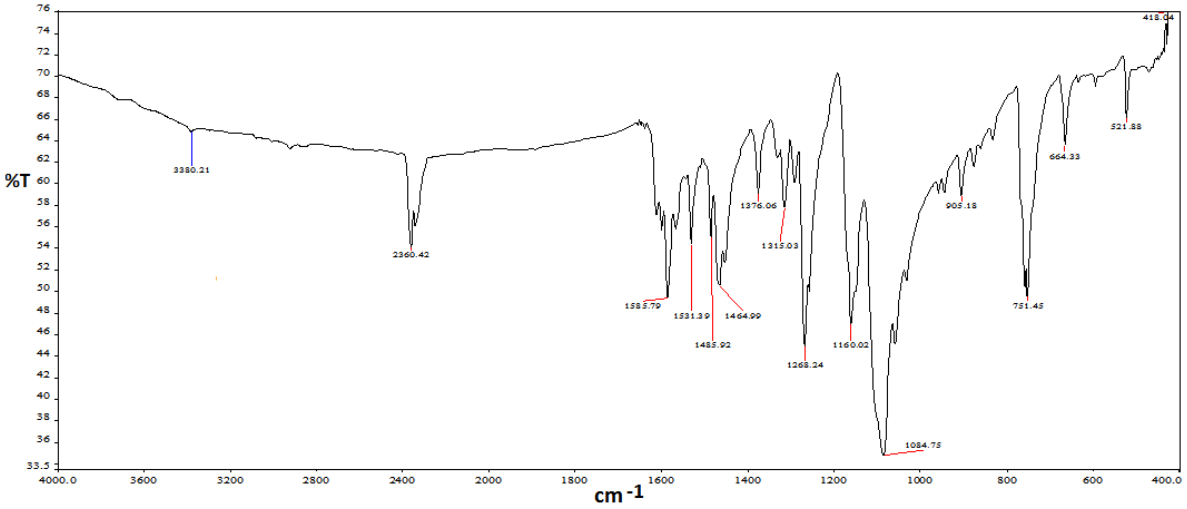

Figure S3b. FTIR spectra of **HT11.**

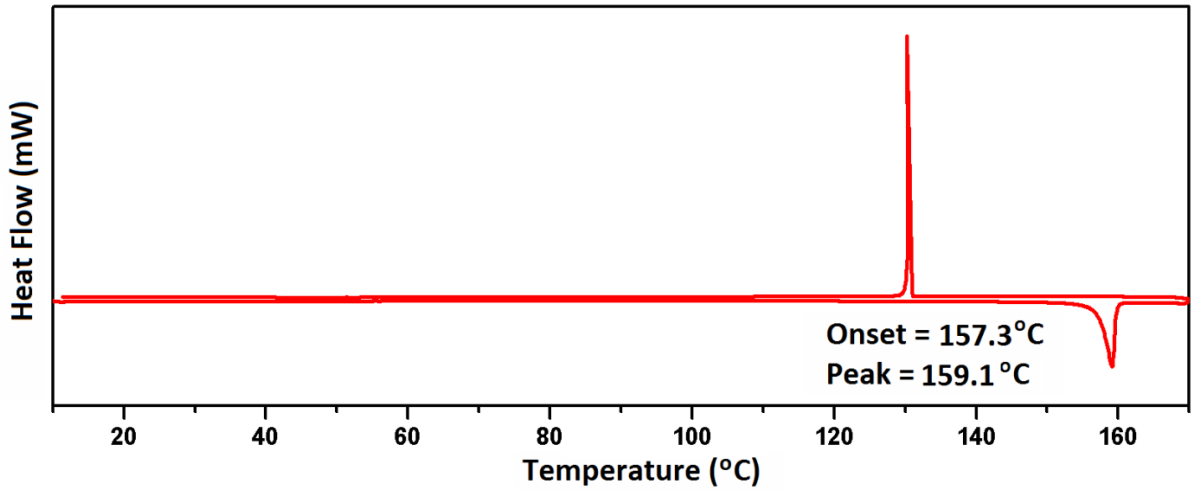

Figure S3c. DSC plot of **HT11** heated/cooled at 5ºC/min.

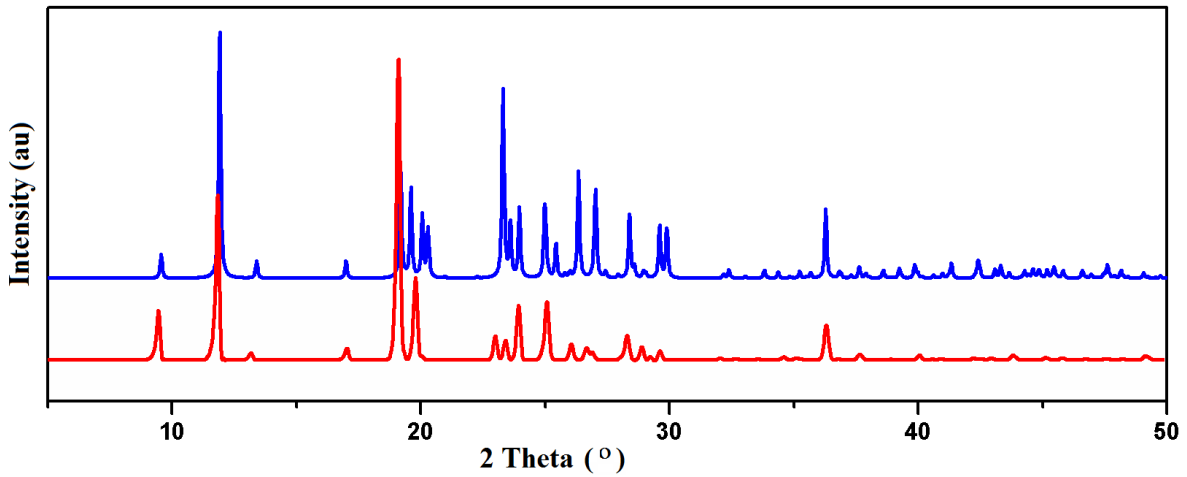

Figure S3d. Powder diffraction pattern of **HT11** (red: experimental; blue: calculated).

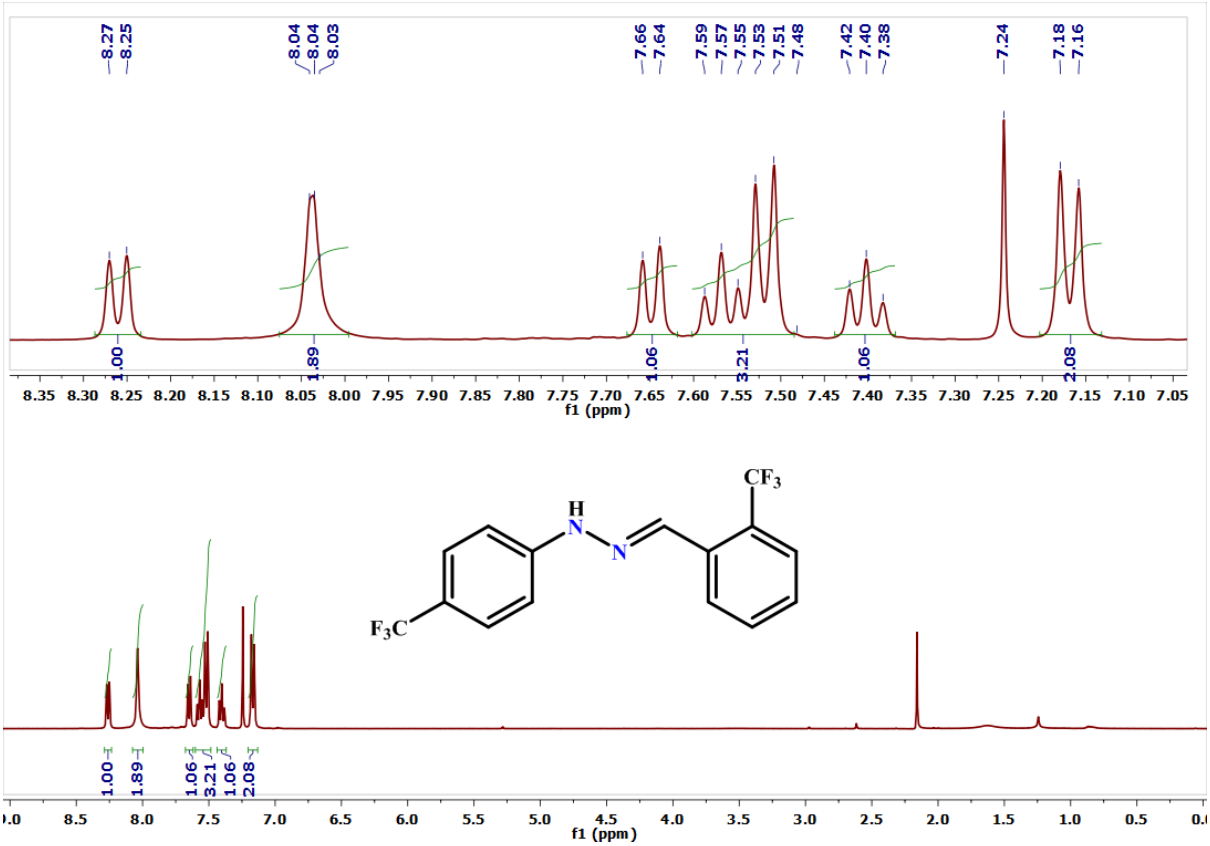

Figure S4a. ^{1}H-NMR spectra of the synthesized compound **HT13** in $CDCl_3$.

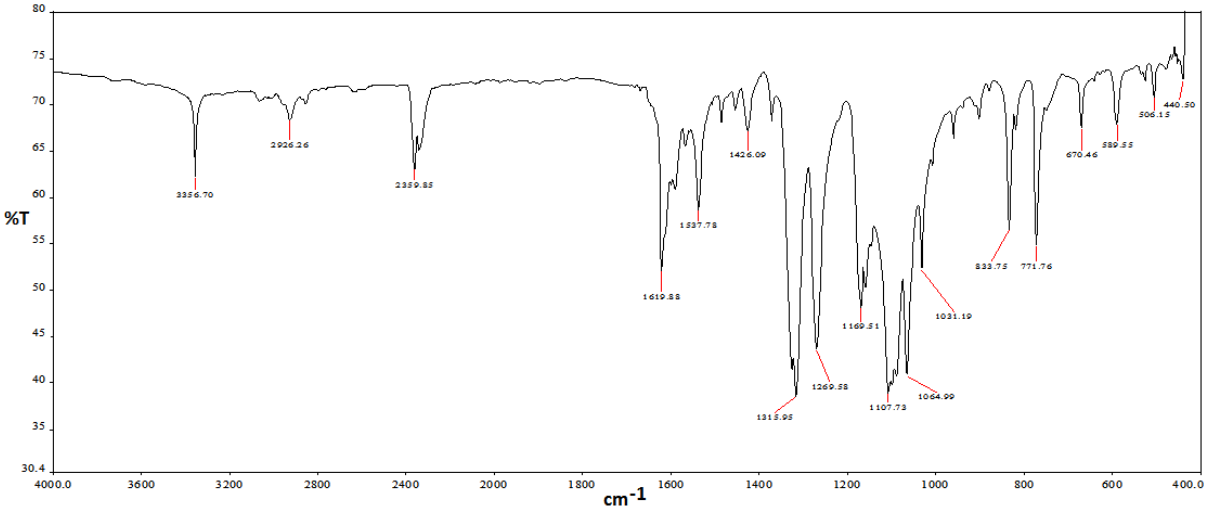

Figure S4b. FTIR spectra of **HT13**.

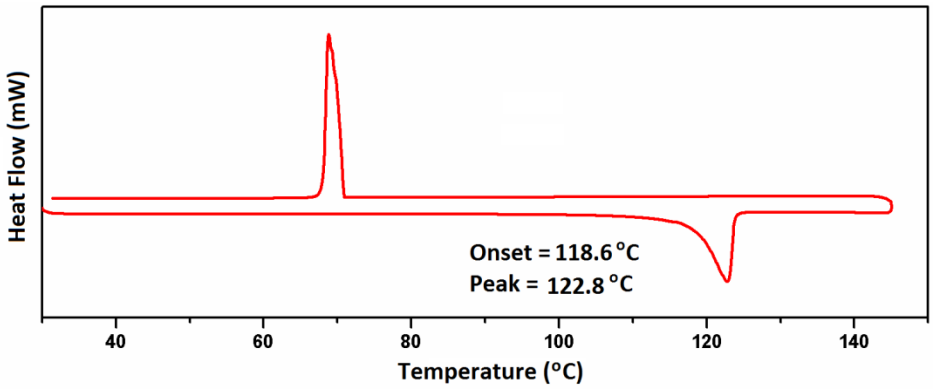

Figure S4c. DSC plot of **HT13** heated/cooled at 5ºC/min.

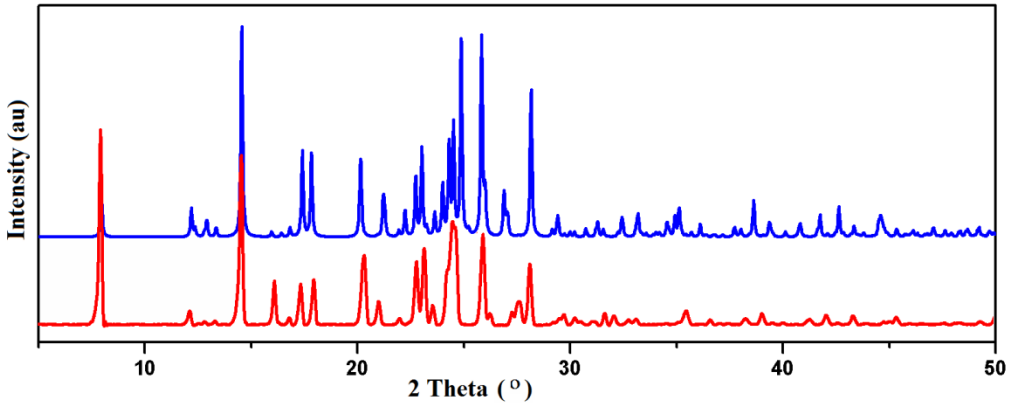

Figure S4d. Powder diffraction pattern of **HT13** (red: experimental; blue: calculated).

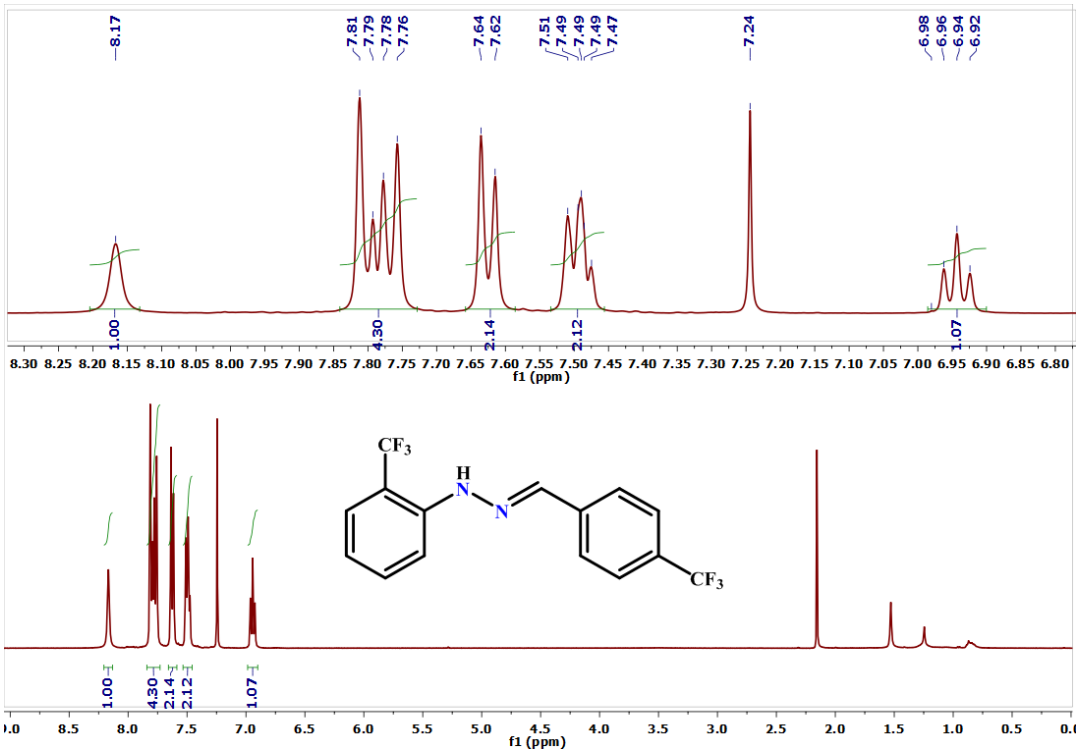

Figure S5a. ^{1}H-NMR spectra of the synthesized compound **HT31** in $CDCl_3$.

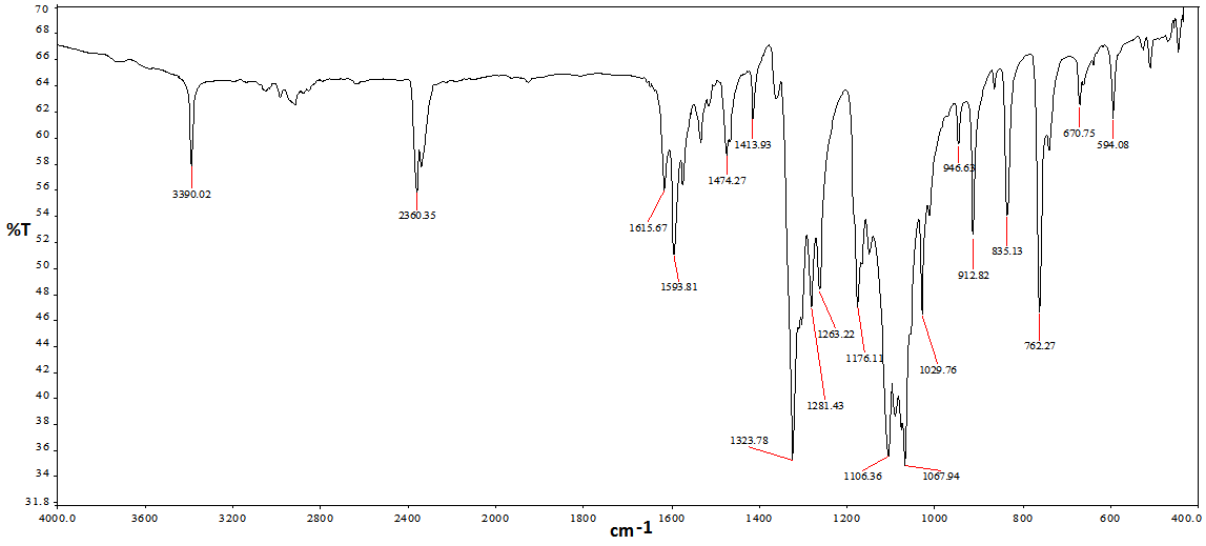

Figure S5b. FTIR spectra of **HT31**.

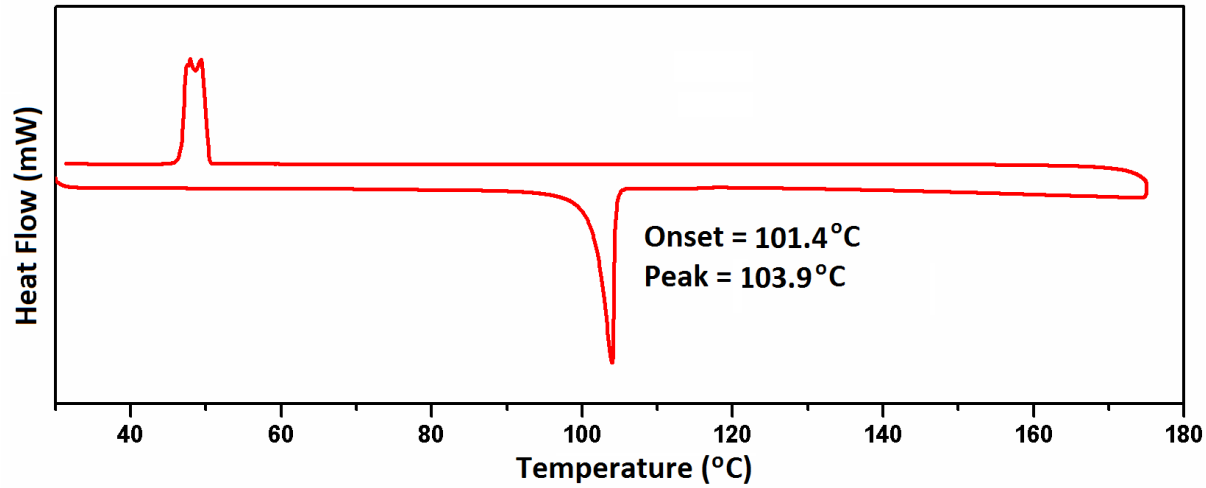

Figure S5c. DSC plot of **HT31** heated/cooled at 5ºC/min.

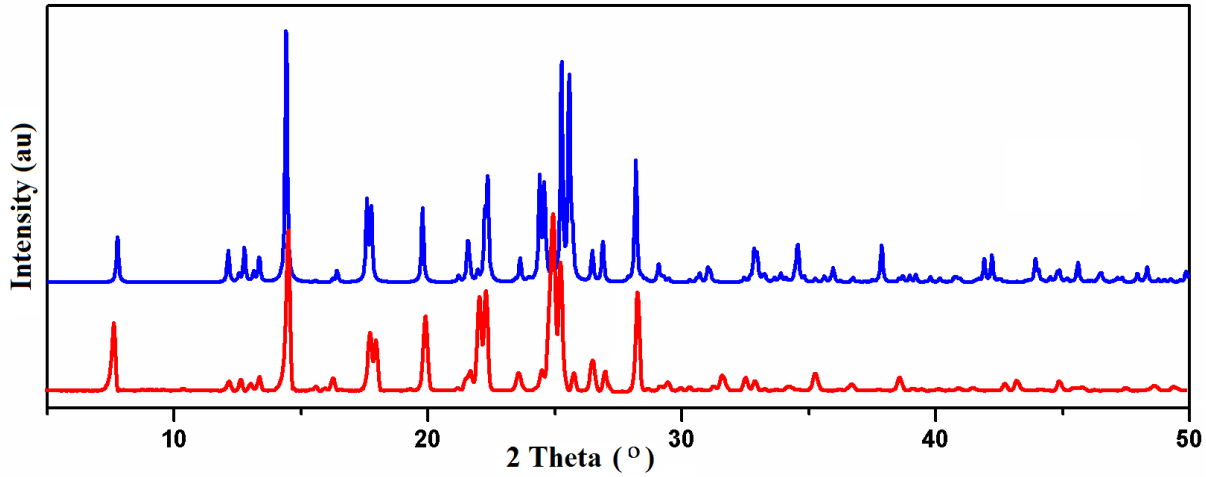

Figure S5d. Powder diffraction pattern of **HT31** (red: experimental; blue: calculated).

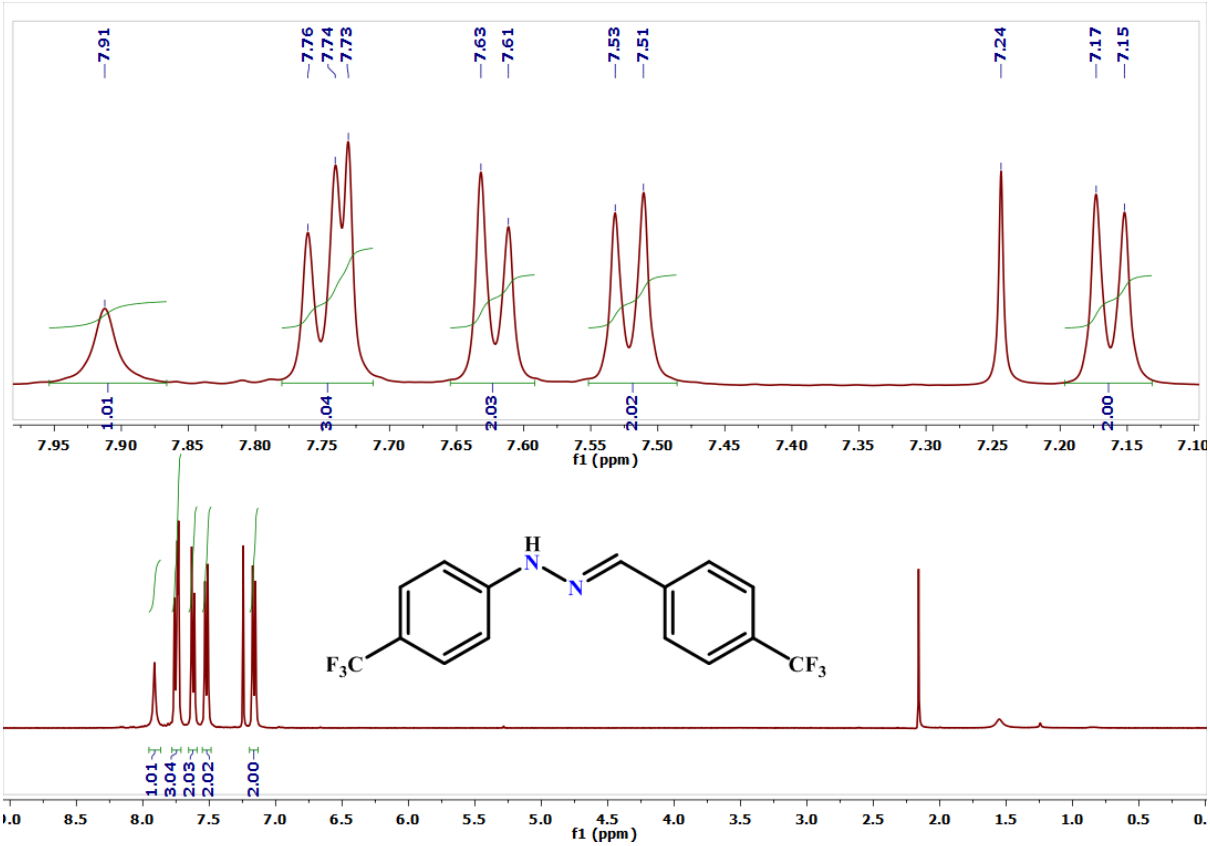

Figure S6a. ^{1}H-NMR spectra of the synthesized compound **HT33** in $CDCl_3$.

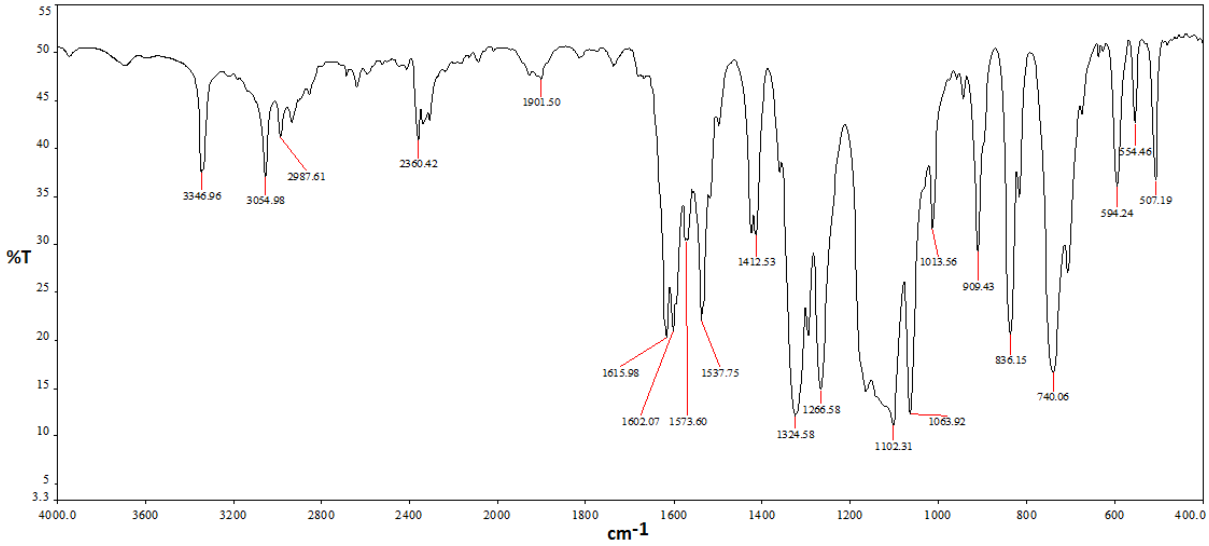

Figure S6b. FTIR spectra of **HT33**.

(*E*)-1-benzylidene-2-(3-(trifluoromethyl)phenyl)hydrazine: HT03 Yield = 89%, M. P. = 128ºC, FTIR (cm^{-1}): 3315(N-H), 1614 (C=N), 1261 (C-N); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.73 (s, 1H), 7.66 (d, *J* = 7.01 Hz, 2H), 7.50 (d, *J* = 8.53 Hz, 2H), 7.36 (m, 3H), 7.14 (d, *J* = 8.55 Hz, 2H).

(*E*)-1-phenyl-2-(3-(trifluoromethyl)benzylidene)hydrazine: HT20 Yield = 93%, M.P. = 196ºC, FTIR (cm^{-1}): 3304(N-H), 1602 (C=N), 1255 (C-N); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.87 (s, 1H), 7.81 (d, *J* = 7.59 Hz, 2H), 7.68 (s, 1H), 7.48 (m, 2H), 2.29 (t, *J* = 7.82 Hz, 2H), 7.12 (d, *J* = 7.73 Hz, 2H), 6.90 (t, *J* = 7.32 Hz, 1H).

(*E*)-1-(2-(trifluoromethyl)benzylidene)-2-(2-(trifluoromethyl)phenyl)hydrazine: HT11 Yield = 91%, M. P. = 157ºC, FTIR (cm^{-1}): 3380 (N-H), 1585 (C=N), 1268 (C-N); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.26 (d, *J* = 8.13 Hz, 2H), 8.07 (s, 1H) 7.80 (d, *J* = 8.37Hz, 1H), 7.66 (d, 7.81 Hz, 1H), 7.56 (t, *J* = 7.68, 1H), 7.49 (m, 2H), 7.41 (t, *J* = 7.55 Hz, 1H), 6.94 (t, *J* = 7.67 Hz, 1H).

(*E*)-1-(2-(trifluoromethyl)benzylidene)-2-(4-(trifluoromethyl)phenyl)hydrazine: HT13 Yield = 90%, M. P. = 119ºC, FTIR (cm^{-1}): 3356 (N-H), 1619 (C=N), 1269 (C-N); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.26, (d, *J* = 7.88 Hz, 1H), 8.04 (s, 2H), 7.65 (d, *J* = 7.82 Hz, 1H), 7.54 (m, 3H), 7.40 (t, *J* = 7.71Hz, 1H), 7.17 (d, *J* = 8.56 Hz, 2H).

(*E*)-1-(4-(trifluoromethyl)benzylidene)-2-(2-(trifluoromethyl)phenyl)hydrazine: HT31 Yield = 93%, M. P. = 101ºC, FTIR (cm^{-1}): 3390(N-H), 1615 (C=N), 1263 (C-N); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.17 (s, 1H), 7.78 (m, 4H), 7.63 (d, *J* = 8.20 Hz, 2H), 7.49 (t, *J* = 7.64 Hz, 2H), 6.94 (t, *J* = 7.57Hz, 1H).

(*E*)-1-(4-(trifluoromethyl) benzylidene)-2-(4-(trifluoromethyl)phenyl) hydrazine: HT33 Yield = 95%, M. P. = 128ºC, FTIR (cm^{-1}): 3346(N-H), 1615 (C=N), 1266 (C-N); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.91 (s, 1H), 7.76 (s, 1H), 7.74 (d, *J* = 7.87 Hz, 2H), 7.62 (d, *J* = 8.13 Hz, 2H), 7.52 (d, *J* = 8.56 Hz, 2H), 7.16 (d, *J* = 8.54Hz, 2H).

Data collection and structure refinements details

The data were collected at 100(2)K on a Bruker APEX II diffractometer equipped with a CCD area detector using monochromated Mo Kα radiation (λ = 0.71073 Å). Bruker Apex II program was used for the data collection. The data reduction and the cell refinement were done using the Bruker SAINT (Bruker, 2006a) suite of programs. The absorption corrections have been done using SADABS (Bruker, 2006b) program. The structures were refined by the full matrix least squares method using SHELXL-2014 (Sheldrick, 2008) present in the WinGX program (version 2014.1) (Farrugia, 1999). In the case of non-centrosymmetric space group, the inversion twin refinement has been performed using BASF command and TWIN instruction. The crystal packing and the molecular pairs were generated using Mercury 3.5.1 (CCDC)

program (Macrae, *et al*., 2008). Geometrical calculations were done using PARST (Nardelli, 1995) and PLATON (Spek, 2009).

Crystallographic Modelling of Disorder

The occupancies of the disordered fluorine atom in trifluoromethylated group (in case of HT03, HT33P and HT33C) at the two positions were refined by using the PART command in SHELXL 2014, namely F1A & F1B; F2A & F2B and F3A & F3B ('A' part contains the higher occupancy and 'B" part contains lower occupancy for that atom). The proper geometry (the C-F bond distances and the F-C-F bond angle) of the $–CF_3$ was fixed using SADI command. The anisotropic displacement parameters (ADP) of the disordered fluorine were fixed using SIMU and RIGU constraints.

Table S1. Single crystal data collection and refinement

Sample code	**HT03**	**HT20**	**HT11**
Formula	**$C_{14}H_{11}F_3N_2$**	**$C_{14}H_{11}F_3N_2$**	**$C_{15}H_{10}F_6N_2$**
Formula weight	**264.25**	**264.25**	**332.25**
Temperature/K	**100(2)**	**100(2)**	**100(2)**
Wavelength (Å)	**0.71073**	**0.71073**	**0.71073**
Solvent system	**Methanol, RT**	**Methanol, RT**	**Toluene, RT**
CCDC	**1524425**	**1524422**	**1524421**
Crystal system	**Triclinic**	**Orthorhombic**	**Monoclinic**
Space group	***P*-1**	***Pna*2$_1$**	***Cc***
***a* (Å)**	**9.6399(12)**	**11.5823(6)**	**15.2831(9)**
***b* (Å)**	**10.3142(14)**	**13.8757(7)**	**4.8177(3)**
***c* (Å)**	**13.4202(18)**	**7.4479(3)**	**19.0386(11)**
α (°)	**99.961(4)**	**90**	**90**
β (°)	**107.306(4)**	**90**	**103.740(3)**
γ(°)	**97.321(4)**	**90**	**90**
V(Å^3)	**1231.8(3)**	**1196.97(10)**	**1361.69(14)**
Z′*, *Z	**2, 4**	**1, 4**	**1, 4**
Density(g cm^{-3})	**1.425**	**1.466**	**1.621**
μ (mm^{-1})	**0.117**	**0.121**	**0.155**
F (000)	**544**	**544**	**672**
θ (min, max)	**2.254, 28.360**	**2.936, 30.525**	**2.202, 27.103**
Treatment of hydrogens	**Mixed**	**Fixed**	**Fixed**
$h_{min, max}$, $k_{min, max}$, $l_{min, max}$	**(-12, 12), (-13, 13), (-17, 17)**	**(-16, 16), (-19, 19), (-10, 9)**	**(-19, 19), (-6, 6), (-24, 21)**
No. of ref.	**30881**	**22984**	**9984**
No. of unique ref./ obs. Ref.	**6111, 4928**	**3414, 3036**	**2939, 2757**
No. parameters	**405**	**173**	**207**
R_all, R_obs	**0.0627, 0.0478**	**0.0455, 0.0368**	**0.0339, 0.0312**

wR2_all, wR2_obs	**0.1241, 0.1153**	**0.0897, 0.0856**	**0.0693, 0.0680**
Δρmin, max (eÅ^{-3})	**-0.330, 0.441**	**-0.245, 0.326**	**-0.235, 0.223**
G. o. F.	**1.030**	**1.043**	**1.061**

Table S1. Continued

Sample code	**HT13**	**HT31**	**HT33P**	**HT33C**
Formula	**$C_{15}H_{10}F_6N_2$**	**$C_{15}H_{10}F_6N_2$**	**$C_{15}H_{10}F_6N_2$**	**$C_{15}H_{10}F_6N_2$**
Formula weight	**332.25**	**332.25**	**332.25**	**332.25**
Temperature/K	**100(2)**	**100(2)**	**100(2)**	**100(2)**
Wavelength (Å)	**0.71073**	**0.71073**	**0.71073**	**0.71073**
Solvent system	**Hexane, RT**	**Ethanol, RT**	**Ethanol, LT**	**Ethanol, RT**
CCDC	**1524423**	**1524424**	**1524427**	**1524426**
Crystal system	**Triclinic**	**Triclinic**	**Orthorhombic**	**Monoclinic**
Space group	***P*-1**	***P*-1**	***Pna*2$_1$**	***C*2/*c***
***a* (Å)**	**8.189(2)**	**8.2523(3)**	**11.2082(4)**	**14.330(4)**
***b* (Å)**	**8.376(2)**	**8.3039(4)**	**16.2891(5)**	**13.658(5)**
***c* (Å)**	**11.623(4)**	**11.7930(5)**	**15.2689(7)**	**7.938(2)**
***α* (˚)**	**72.723(18)**	**82.823(2)**	**90**	**90**
***β* (˚)**	**82.222(17)**	**74.769(2)**	**90**	**112.607(11)**
***γ* (˚)**	**62.417(15)**	**61.428(2)**	**90**	**90**
V(Å^3)	**674.7(4)**	**684.78(5)**	**2787.67(18)**	**1434.2(8)**
Z′*, *Z	**1, 2**	**1, 2**	**2, 8**	**0.5, 4**
Density(g cm^{-3})	**1.635**	**1.611**	**1.583**	**1.539**
μ (mm^{-1})	**0.156**	**0.154**	**0.151**	**0.147**
F (000)	**336**	**336**	**1344**	**672**
θ (min, max)	**1.835, 27.585**	**1.790, 28.279**	**2.501, 30.541**	**3.953, 28.683**
Treatement of hydrogens	**Fixed**	**Fixed**	**Fixed**	**Fixed**
$h_{min, max}$, $k_{min, max}$, $l_{min, max}$	**(-8, 10), (-10, 10), (-15, 15)**	**(-10, 10), (-11, 11), (-15, 15)**	**(-15, 16), (-22, 22), (-21, 21)**	**(-19, 18), (-17, 18), (-10, 10)**
No. of ref.	**9731**	**12775**	**36037**	**8765**
No. of unique ref./ obs. Ref.	**3006, 2297**	**3365, 2989**	**8421, 6821**	**1857, 1298**
No. parameters	**208**	**208**	**444**	**133**
R_all, R_obs	**0.0562, 0.0401**	**0.0400, 0.0365**	**0.0672, 0.0495**	**0.0794, 0.0505**
wR2_all, wR2_obs	**0.1309, 0.1136**	**0.1073, 0.1046**	**0.1325, 0.1212**	**0.1423, 0.1277**
Δρmin, max (eÅ^{-3})	**-0.307, 0.316**	**-0.350, 0.384**	**-0.261, 0.418**	**-0.215, 0.239**
G. o. F.	**1.164**	**1.064**	**1.029**	**1.069**

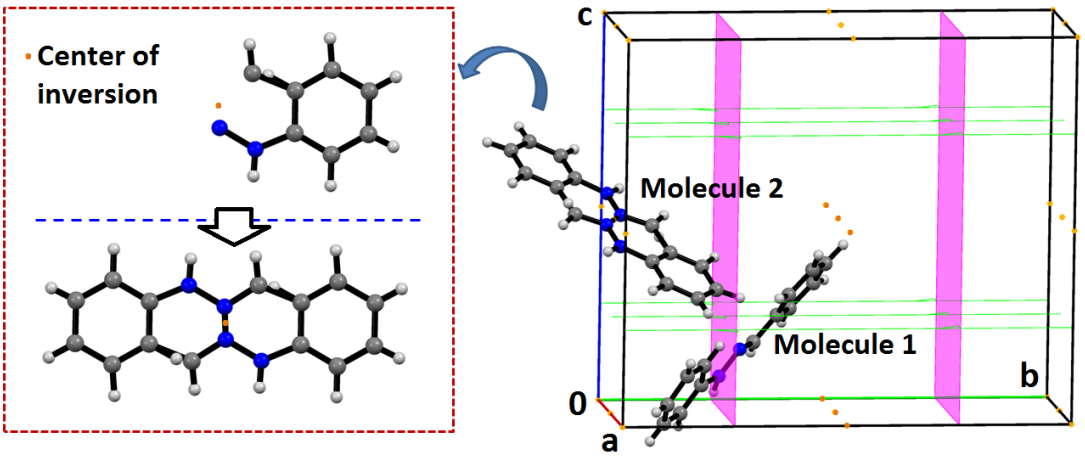

Figure S7. The asymmetric unit of **HT00** shows a complete molecule 1 and a half molecule 2 containing the center of inversion.

Table S2. Selected bond distances (Å)

Code			C-N	N-N	N-C	C-C
HT03		Molecule 1	N1-C1 1.387(2)	N2-N1 1.359(2)	N2-C13 1.286(1)	C7-C13 1.464(2)
		Molecule 2	C15-N3 1.382(2)	N3-N4 1.361(2)	N4-C27 1.280(2)	C27-C21 1.464(2)
HT20			N1-C1 1.400(2)	N1-N2 1.356(2)	N2-C13 1.288(2)	C13-C7 1.467(2)
HT11			N1A-C1 1.422(2)	N1A-N2A 1.29(3)	N2A-C13A 1.28(3)	C13A-C7 1.443(2)
HT13			N1-C1 1.382(2)	N1-N2 1.353(2)	N2-C13 1.275(2)	N2-C13-C7 1.468(2)
HT31			N1-C1 1.384(1)	N1-N2 1.358(1)	N2-C13 1.280(1)	C13-C7 1.462(1)
HT33	I	Molecule 1	C1-N1 1.407(4)	N2-N1 1.332(3)	C13-N2 1.299(4)	C13-C7 1.446(4)
		Molecule 2	C16-N3 1.414(4)	N4-N3 1.334(3)	C28-N4 1.319(4)	C28-C22 1.432(4)
	II		C1-C7/N1 1.407(2)	C7/N1-N2 1.326(2)	N2-C7/N1 1.326(2)	C7/N1-C1 1.407(2)

Table S3. Selected torsion angles (τ) and the dihedral angle (θ) between two phenyl rings

Code		τ_1(°)	τ_2(°)	τ_3(°)	τ_4(°)	θ (°)
HT03	Molecule 1	N2-N1-C1-C2 -174.3(1)	C13-N2-N1-C1 -177.6(2)	N1-N2-C13-C7 179.9(1)	C8-C7-C13-N2 -176.5(2)	10.31
	Molecule 2	C16-C15-N3-N4 166.9(2)	C15-N3-N4-C27 -172.7(2)	N3-N4-C27-C21 -178.7(1)	N4-C27-C21-C22 -173.8(2)	12.78
HT20		N2-N1-C1-C2 -174.1(2)	C1-N1-N2-C13 179.1(2)	N1-N2-C13-C7 -179.4(2)	N2-C13-C7-C8 166.3(2)	11.22

HT11			**N2A-N1A-C1-C2 -173.0(2)**	**C1-N1A-N2A-C13A 174.1(1)**	**N1A-N2A-C13A-C7 173.0(2)**	**N2A-C13A-C7-C8 -173.7(2)**	**7.23**
HT13			**N2-N1-C1-C2 175.9(1)**	**C1-N1-N2-C13 -173.5(1)**	**N1-N2-C13-C7 -179.5(1)**	**N2-C13-C7-C8 -176.5(1)**	**7.98**
HT31			**N2-N1-C1-C2 178.5(1)**	**C1-N1-N2-C13 -178.9(1)**	**N1-N2-C13-C7 178.6 (1)**	**N2-C13-C7-C8 179.9(1)**	**3.64**
HT33	**I**	**Molecule 1**	**C2-C1-N1-N2 -178.7(3)**	**C13-N2-N1-C1 180.0(3)**	**C7-C13-N2-N1 178.7(3)**	**N2-C13-C7-C8 -176.9(3)**	**3.45**
		Molecule 2	**C17-C16-N3-N4 175.1(3)**	**C28-N4-N3-C16 -176.2(3)**	**C22-C28-N4-N3 178.7(3)**	**N4-C28-C22-C23 171.8(3)**	**9.22**
	II		**C6-C1-C7-N1 175.8 (2)**	**C7-N1-C7-C1 -179.0(2)**	**C7-N1-C7-C1 -179.0(2)**	**C6-C1-C7-N1 175.8 (2)**	**5.14**

Computational details

Intermolecular Interaction energy

The interaction energies of the molecular dimers present in the crystal packing are determined using PIXEL (version 12.5.2014) program. The electron densities were calculated using Gaussian 09 program (Frisch, *et al.*,2009) at MP2/6-31G** level to generate the PIXEL input file. The total lattice energy of the molecule is classified into the corresponding Coulombic, polarization, dispersion and repulsion terms. In this study, all the analysis has been performed taking the atomic coordinates of the major conformer (**A** in the case of disorder molecule). We are not able to perform the PIXEL calculation in the case of HT33C due to the half-molecule.

The electrostatic contribution to the total stabilization of a particular molecular pair

$= [(E_{Coul} + E_{Pol}) / (E_{Coul} + E_{Pol} + E_{Disp})] \times 100\%$.

The dispersion contribution to the total stabilization of a particular molecular pair

$= [E_{Disp}) / (E_{Coul} + E_{Pol} + E_{Disp})] \times 100\%$.

XPac analysis

The structural similarities have been analyzed using *XPac* 2.0.2 program. It provides the information about the *extent of dissimilarity* (dissimilarity index x) as well as the dissimilarity parameters (Stretch parameter, change in angles and planes) between two crystal structures. For XPac analysis, we have taken all the atomic coordinates (in crystal geometry), except for the hydrogen atoms.

QTAIM analysis

A detail topological analysis was performed for some selected molecular dimers at the crystal geometry (version 13.05.06) (with the hydrogen atoms moved to their neutral value) using AIMALL (version 13.05.06) (Keith, 2013) calculation. The inputs were generated at the

MP2/6-311++G** level using Gaussian 09. The topological parameters like (i) electron density (ρ_b), (ii) Laplacian ($\nabla^2\rho_b$), (iii) local potential energy (V_b), and (iv) kinetic energy density (G_b) the bond critical points (BCPs) were obtained. The dissociation energies for the different intermolecular interactions were determined using the equation: $E_{int} = -0.5V_b$ (in au) (Espinosa, et al., 1998; Mata, *et al*., 2011).

Table S4. The stabilization energy (kJ/mol; obtained from PIXEL) of the molecular pairs for the **HT03** [CD = centroid-centroid distance between the two interacting molecules]

Motifs	Symmetry	CD (Å)	E_{Coul}	E_{Pol}	E_{Disp}	E_{Rep}	E_{Tot}	Possible interactions	Geometry (Å/º)
I (1-2)	1-x, 1-y, 1-z	5.055	-22.9	-12.5	-57.9	51.6	-41.7	C13-H13···Cg2′	2.63, 138
								C3-H3A···Cg1′	2.69, 134
								C5-H5···N4	2.56, 127
								N1-H1···C27	2.79, 134
								C2-H2···C20	2.66, 129
								C2-H2···N4	2.56, 127
II (1-1)	-x, 1-y, 1-z	7.227	-21.1	-8.9	-49.5	40.7	-38.8	C8-H8···C2	2.86, 109
								C8-H8···N1	2.92, 114
								C13-H13···N1	3.12, 104
								C13···C13	3.5302(4)
III (1-2)	x, y, z	6.053	-19.4	-12.8	-55.5	49.0	-38.7	C16-H16···Cg2	2.62, 129
								C22-H22···Cg1	2.61, 139
								N3-H3···C13	2.72, 173
								C27-H27···N2	2.67, 154
IV (2-2)	1-x, 1-y, 1-z	8.434	-7.2	-2.5	-21.3	4.6	-26.5	vdWaals interaction	
								C22-H22···N3	3.24, 118
V (1-2)	1+x, y, z	8.304	-5.1	-1.9	-29.1	12.0	-24.1	C25-H25···N2	2.83, 109
VI (1-1)	1-x, 2-y, 1-z	6.011	-6.9	-2.6	-22.1	12.6	-19.1	C12-H12···F2A	2.57, 154
								C6-H6···F2A	2.62, 133
								C5···C5	3.5868 (4)
VII (1-2)	1-x, 2-y, 1-z	8.508	-3.2	-1.9	-18.6	7.7	-16.0	C14-F2A···C27	3.2644(3), 112
								C5-H5···C21	2.85, 145
								C14-F3A···N4	3.4245(4), 116
VIII (2-2)	-x, -y, -z	10.217	-6.8	-1.4	-10.4	4.7	-13.9	C16-H16···F4A	2.99, 117
								C17-H17···F4A	2.88, 121
								H17···H17	2.49
IX (2-2)	1-x, 1-y, -z	5.694	-2.4	-1.1	-16.0	6.7	-12.7	C25-H25···F5A	2.62, 113
X (1-2)	-x, 1-y, -z	9.428	-5.3	-2.7	-20.3	16.9	-11.3	C11-H11···Cg1′	2.63, 132
XI (2-2)	2-x, 2-y, 1-z	14.908	-2.5	-0.7	-9.5	4.6	-8.2	C24-H24···C25	3.13, 117
XII (1-2)	-x, -y, -z	13.476	-2.8	-0.8	-6.3	2.3	-7.6	C29-F4A···C9	3.3812(4), 119
XIII (1-1)	-x, 1-y, -z	13.245	-2.2	-0.4	-7.3	2.6	-7.3	C11···C11	3.7389(2)
XIV (2-2)	1+x, 1+y, 1+z	15.140	-2.9	-0.9	-7.7	5.0	-6.5	C23-H23···F4A	2.49, 138
								C24-H24···F5A	2.69, 129
XV (1-2)	x, 1+y, 1+z	9.583	-1.3	-1.5	-8.5	5.5	-5.8	C19-H19···F3A	2.47, 165
								C29-F6A···C4	3.2945(3), 147
								C14-F3A···F6A-C28	3.1599(3), 105, 147
XVI (1-1)	1+x, 1+y, 1+z	15.140	-2.1	-0.7	-5.6	3.2	-5.3	C10-H10···F3A	2.50, 145
XVII (1-2)	-1+x, -1+y, -1+z	11.961	-0.4	-0.4	-3.5	0.9	-3.5	C17-H17···F1A	2.75, 135

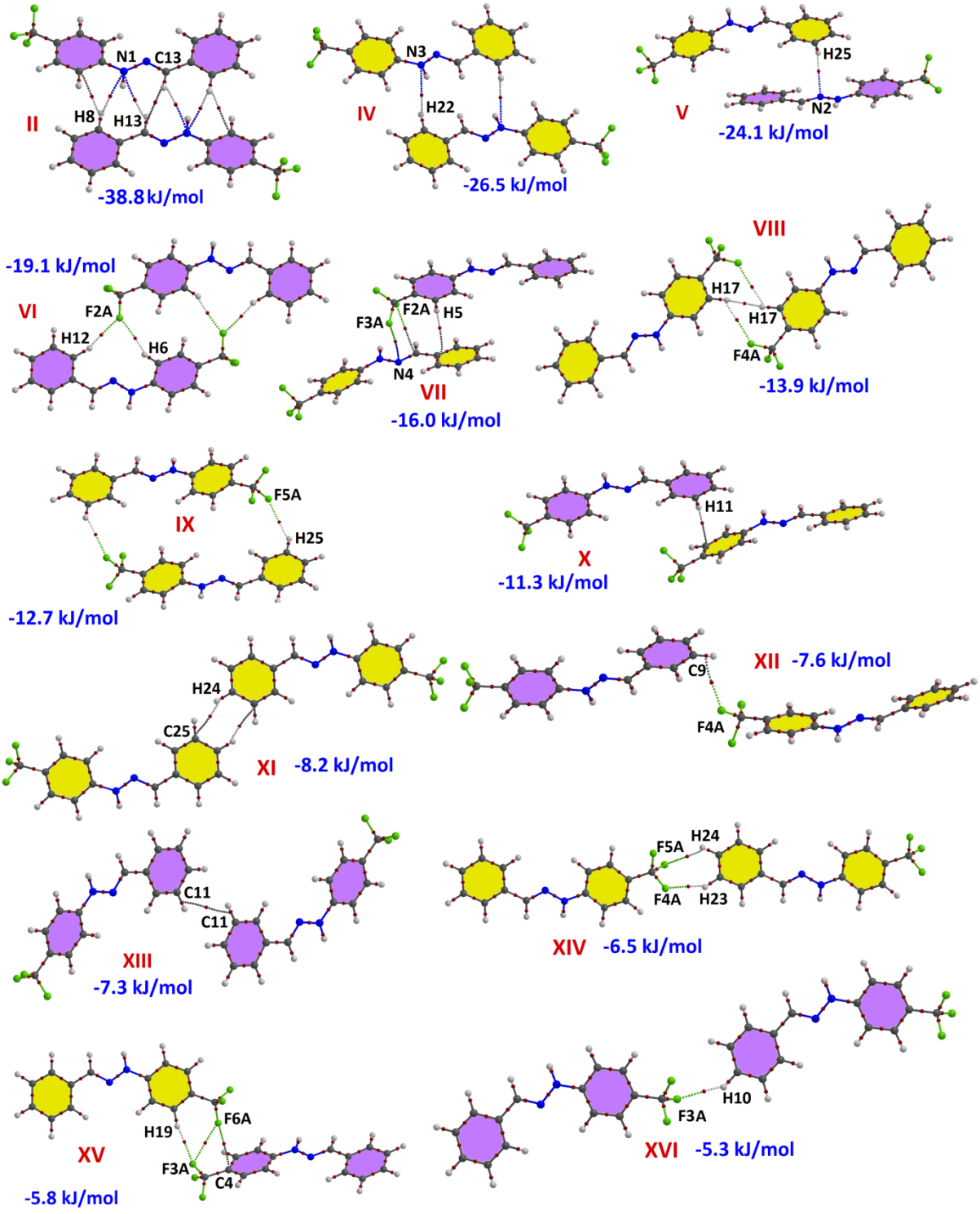

Figure S8. The molecular graphs for selected molecular pairs in **HT03** showing the bond critical points in deep red color. The corresponding value indicates the interaction energy (form PIXEL) between two interacting molecules.

Table S5. The stabilization energy (kJ/mol; obtained from PIXEL) of the molecular pairs for the **HT20** [CD = centroid-centroid distance between the two interacting molecules]

Motifs	Symmetry	CD (Å)	E_{Coul}	E_{Pol}	E_{Disp}	E_{Rep}	E_{Tot}	Possible interactions	Geometry (Å/º)
I	1-x, -y, 0.5+z	5.425	-19.1	-8.4	-50.0	35.0	-42.5	C8-H8···Cg1	2.81, 133
								C2-H2···Cg2	2.59, 136
								C3-H3···F1	2.71, 135
								N1-H1···N2	2.93, 137
								C13-H13···C1	2.94, 132
								F3···C4	3.2719(1)
II	0.5+x,0.5-y,z	7.337	-9.3	-2.6	-19.8	9.8	-21.9	C11-H11···F3	2.73, 120
								C13-H13···F2	2.75, 132
								N1-H1···F2	2.42, 140
III	1.5-x, -0.5+y, 0.5+z	8.320	-5.5	-2.8	-22.7	14.9	-16.2	C11-H11···C3	3.02, 146
								C10-H10···C1	2.77,128
								C10-H10···N1	2.79, 151
								C14-F1···N2	3.1632(1), 152
								C14-F1···C13	3.2554(1), 165
IV	0.5+x, -0.5-y, z	11.016	-4.8	-2.5	-20.4	12.6	-15.1	H3···H6	2.34
								H3···H12	2.38
								H12···H4	2.48
V	1.5-x, 0.5+y, 0.5+z	8.320	-4.0	-2.3	-20.9	13.7	-13.6	C12-H12···F2	2.47, 122
								C6-H6···F2	2.52, 141
								C5-H5···C12	3.00, 142
								C14-F2···N2	3.2812(1)
VI	x, 1+y, z	13.876	-1.3	-0.6	-5.5	3.8	-3.6	C4-H4···F3	2.51, 124

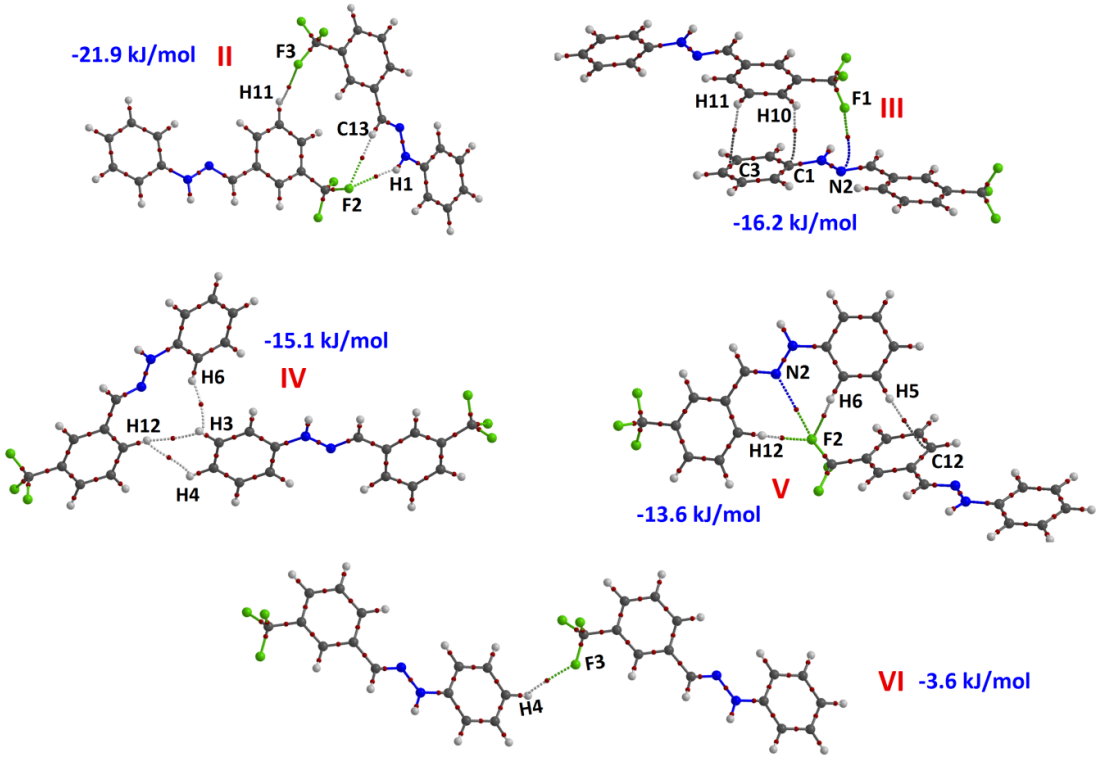

Figure S9. The molecular graphs for the molecular pairs in **HT20** showing the bond critical points in deep red color. The corresponding value indicates the interaction energy (form PIXEL) between two interacting molecules.

Table S6. The list of intramolecular interactions present in HT13, HT31 and HT11

Code	Interactions	Symmetry	D···A (Å)	H···A (Å)	D-H···A (°)
HT13	**Intramolecular**				
	C13-H13···F5	**x, y, z**	**2.966(1)**	**2.36**	**114**
	C13-H13···F4	**x, y, z**	**3.027(1)**	**2.52**	**108**
HT31	**Intramolecular**				
	N1-H1···F3	**x, y, z**	**2.968(1)**	**2.42**	**113**
	N1-H1···F1	**x, y, z**	**2.873(1)**	**2.25**	**117**
HT11	**Intramolecular**				
	N1A-H1A···F1	**x, y, z**	**3.073(1)**	**2.46**	**118**
	N1A-H1A···F3	**x, y, z**	**2.898(1)**	**2.37**	**110**
	C13A-H13A···F4	**x, y, z**	**2.961(1)**	**2.44**	**108**
	C13A-H13A···F6	**x, y, z**	**3.040(1)**	**2.40**	**116**

Table S7. The stabilization energy (kJ/mol; obtained from PIXEL) of the molecular pairs for the **HT11** [CD = centroid-centroid distance between the two interacting molecules]

Motifs	Symmetry	CD (Å)	E_{Coul}	E_{Pol}	E_{Disp}	E_{Rep}	E_{Tot}	Possible interactions	Geometry (Å/°)
I	**x, 1+y, z**	**4.818**	**-10.4**	**-4.6**	**-67.4**	**40.9**	**-41.5**	**C14-F2···F3-C14** **C14-F1···F6-C15** **C15-F5···F4-C15** **C13A···C9**	**2.9746(2), 106, 160** **3.1341(2), 133, 137** **2.9039(2), 158, 112** **3.5487(1)**

								C7···N1A F6···N1A C13A-H13A···F1 C13A···C1 N1A···C3	3.3945(1) 3.2167(2) 2.69, 125 3.3433(1) 3.4919(2)
II	**0.5+x, 0.5+y, z**	**8.012**	**-1.6**	**-1.8**	**-18.5**	**6.1**	**-15.8**	C5-H5···F2 C6-H6···F2 C10-H10···F6 C10-H10···F4 C12-H12···F3 C12-H12···F1	2.76, 118 2.65, 122 2.86, 132 2.98, 125 3.00, 137 2.91, 142
III	**x, 1-y, 0.5+z**	**9.849**	**-1.5**	**-1.8**	**-15.8**	**8.9**	**-10.2**	C4-H4···C10 C3-H3···C9 C15-F4···F2-C14	3.09, 123 2.81, 155 3.1634 (2)
IV	**x, -y, 0.5+z**	**9.791**	**-2.1**	**-2.1**	**-15.6**	**10.1**	**-9.6**	C9-H9···C3 C10-H10···C4 C15-F5···F2-C14 C15-F5···F3-C14	2.67, 153 3.04, 125 3.2159 (1) 3.1856 (2)
V	**-0.5+x, 0.5+y, z**	**8.012**	**-2.2**	**-0.8**	**-8.1**	**3.2**	**-7.8**	C5-H5···F3 C11-H11···F6	2.57, 129 2.89, 116
VI	**0.5+x, 0.5-y, 0.5+z**	**10.699**	**-2.8**	**-0.6**	**-4.6**	**2.3**	**-5.7**	C5-H5···F5	2.54, 149
VII	**0.5+x, 1.5+y, z**	**10.517**	**-0.5**	**-0.3**	**-4.0**	**1.7**	**-3.1**	C11-H11···F1	2.67, 121

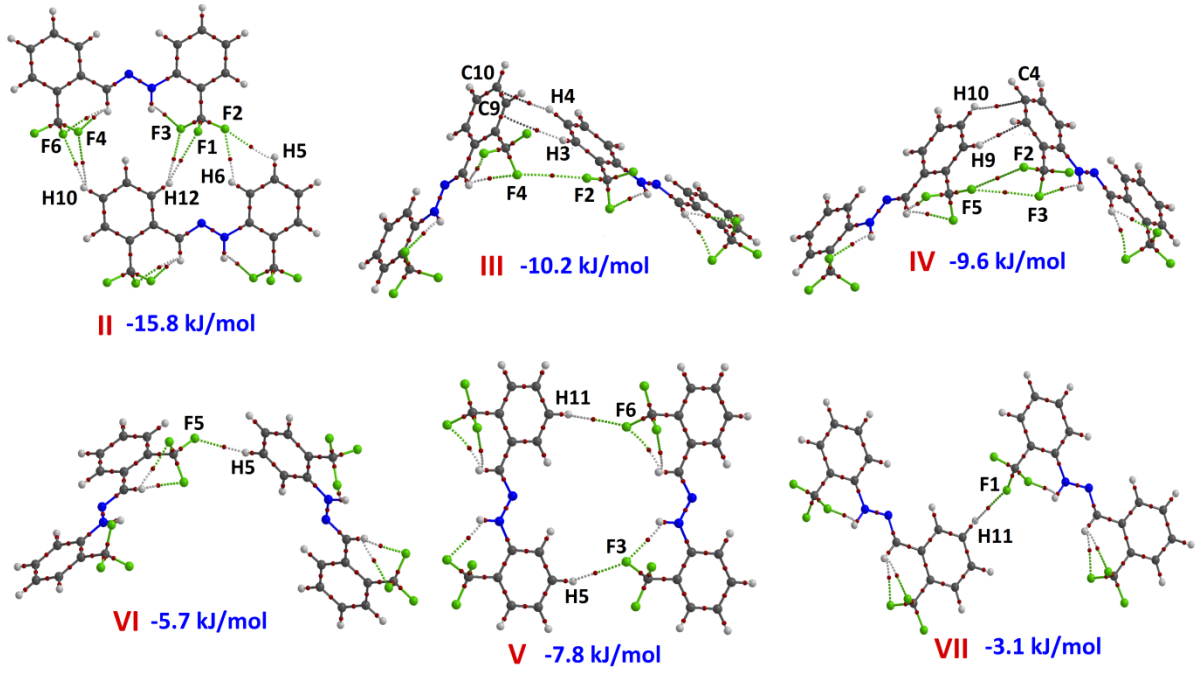

Figure S10. The molecular graphs for the molecular pairs in **HT11** showing the bond critical points in deep red color. The corresponding value indicates the interaction energy (form PIXEL) between two interacting molecules.

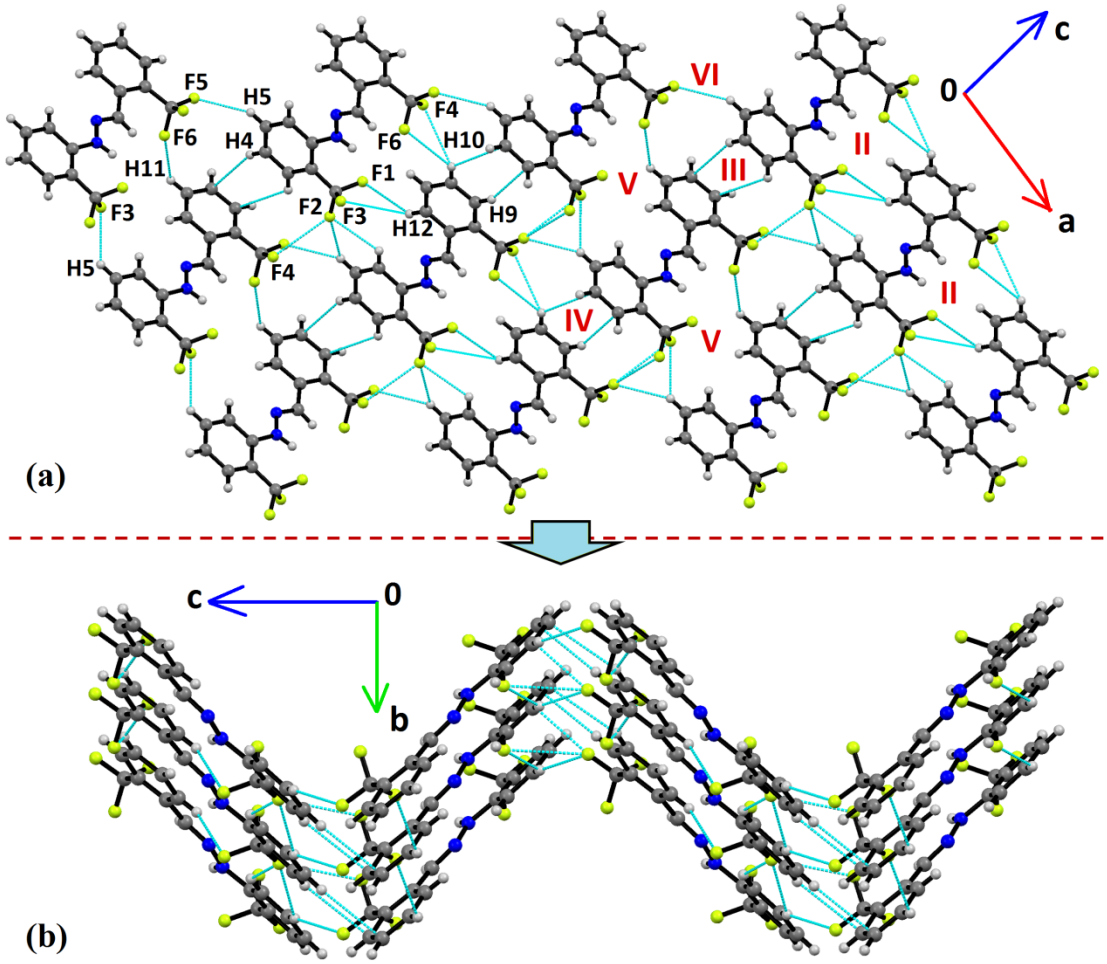

Figure S11. The formation of wave-like molecular sheet in **HT11** (a) view down the *ac* plane; (b) view down the *bc* plane.

Table S8. The stabilization energy (kJ/mol; obtained from PIXEL) of the molecular pairs for the isostructural **HT13** and **HT31** [CD = centroid-centroid distance between the two interacting molecules]

Motifs	Symmetry	CD (Å)	E_{Coul}	E_{Pol}	E_{Disp}	E_{Rep}	E_{Tot}	Possible interactions	Geometry (Å/°)
HT13 (*P*-1)									
I	1-x,1-y,2-z	5.565	-9.6	-3.7	-58.2	31.1	-40.4	C12-H12···F4 C9···C1 C9···N1 C8···N2 C7···C13	2.68, 115 3.4564(1) 3.5290(1) 3.5261(1) 3.5931(1)
II	1-x,-y,2-z	3.780	-4.5	-3.5	-63.1	35.1	-36.0	C14-F1···F5-C15 C15-F5···C5 C2···C12 C6···C13	2.9125(2), 99, 125 3.3181(2), 120 3.4464(1) 3.4871(1)
III	-x,1-y,2-z	7.135	-11.1	-3.0	-21.8	10.5	-25.5	C10-H10···F2 C11-H11···F2	2.81, 117 2.68, 125
IV	2-x,-y,2-z	8.060	-12.2	-4.6	-17.9	13.8	-21.0	N1-H1···F5 C13-H13···F5	2.35, 140 2.55, 130
V	1+x,y,z	8.189	-7.8	-3.0	-19.4	9.3	-20.9	N1-H1···F1 C2-H2···F1 C6-H6···F4	2.62, 146 2.60, 148 2.52, 131

								C12-H12···F6	2.59, 137
VI	1-x,-y,1-z	11.320	-7.5	-1.9	-10.6	6.1	-13.9	C2-H2···F3 H3···H3	2.91, 148 2.23
VII	x,y,1+z	11.623	-3.2	-1.4	-11.7	6.4	-9.8	C3-H3···C11 C10-H10···C2	2.94, 129 3.17, 123
VIII	1+x,y,1+z	15.097	-4.3	-1.0	-6.1	2.5	-8.8	C9-H9···F2 C9-H9···F3	2.64, 149 2.78, 139
IX	-x,1-y,1-z	11.519	1.6	-1.4	-8.5	3.9	-4.4	C14-F2···C4 C14-F2···F2-C14	3.303, 146 2.9692(7), 106, 106
X	-x,-y,1-z	15.406	4.1	-0.5	-3.8	1.4	1.3	F1···F3 C14-F3···F3-C14	3.0202(7), 147, 107 3.0425(7), 106, 106
HT31 (*P*-1)									
I	2-x,1-y,1-z	5.414	-11.1	-4.6	-63.3	35.9	-43.1	C12-H12···F3 C6-H6···F3 C3···C7 C2···N2 C1···N1	2.79, 127 2.73, 122 3.4247(1) 3.4924(1) 3.5153(1)
II	1-x,1-y,1-z	3.777	-4.5	-2.8	-62.8	29.6	-40.4	C14-F1···F5-C15 C15-F5···F2-C14 C14-F1···C11 C8···C6 N1···C12	3.0831(1), 90, 125 3.1125(1), 90, 143 3.2967(1), 117 3.5510(1) 3.5822(1)
III	2-x,-y,1-z	7.143	-6.2	-2.0	-20.6	9.2	-19.6	C5-H5···F4	2.61, 127
IV	1-x,2-y,1-z	8.057	-9.0	-2.5	-17.4	11.5	-17.4	C13-H13···F1 N1-H1···F1 C14-F1···F1-C14	2.50, 131 2.60, 130 3.0435(1), 138, 138
V	x,1+y,z	8.304	-4.1	-2.1	-17.3	7.0	-16.5	C8-H8···F5 C13-C13···F5 C12-H12···F3 C6-H6···F2	2.70, 154 2.74, 151 2.52, 135 2.70, 138
VI	1-x,1-y,-z	11.383	-2.6	-1.6	-10.1	5.0	-9.2	C8-H8···F6 H9···H9	2.94, 142 2.25
VII	x,y,1+z	11.793	-2.4	-1.3	-11.8	6.4	-9.0	C4-H4···C8 C9-H9···C5	3.12, 131 2.96, 133
VIII	x,1+y,1+z	15.248	-1.9	-0.5	-5.7	2.2	-5.9	C3-H3···F6 C3-H3···F4	2.79, 145 2.67, 149
IX	2-x,-y,-z	11.819	-0.5	-0.6	-8.2	3.6	-5.8	C15-F4···C10 C15-F4···F4-C15	3.3445(1), 146 2.9534(1), 106, 106
X	1-x,-y,-z	15.535	1.1	-0.2	-3.8	1.7	-1.3	C15-F6···F5-C15 C15-F6···F6-C15	2.9541(1), 142, 110 3.1400(1), 101, 101

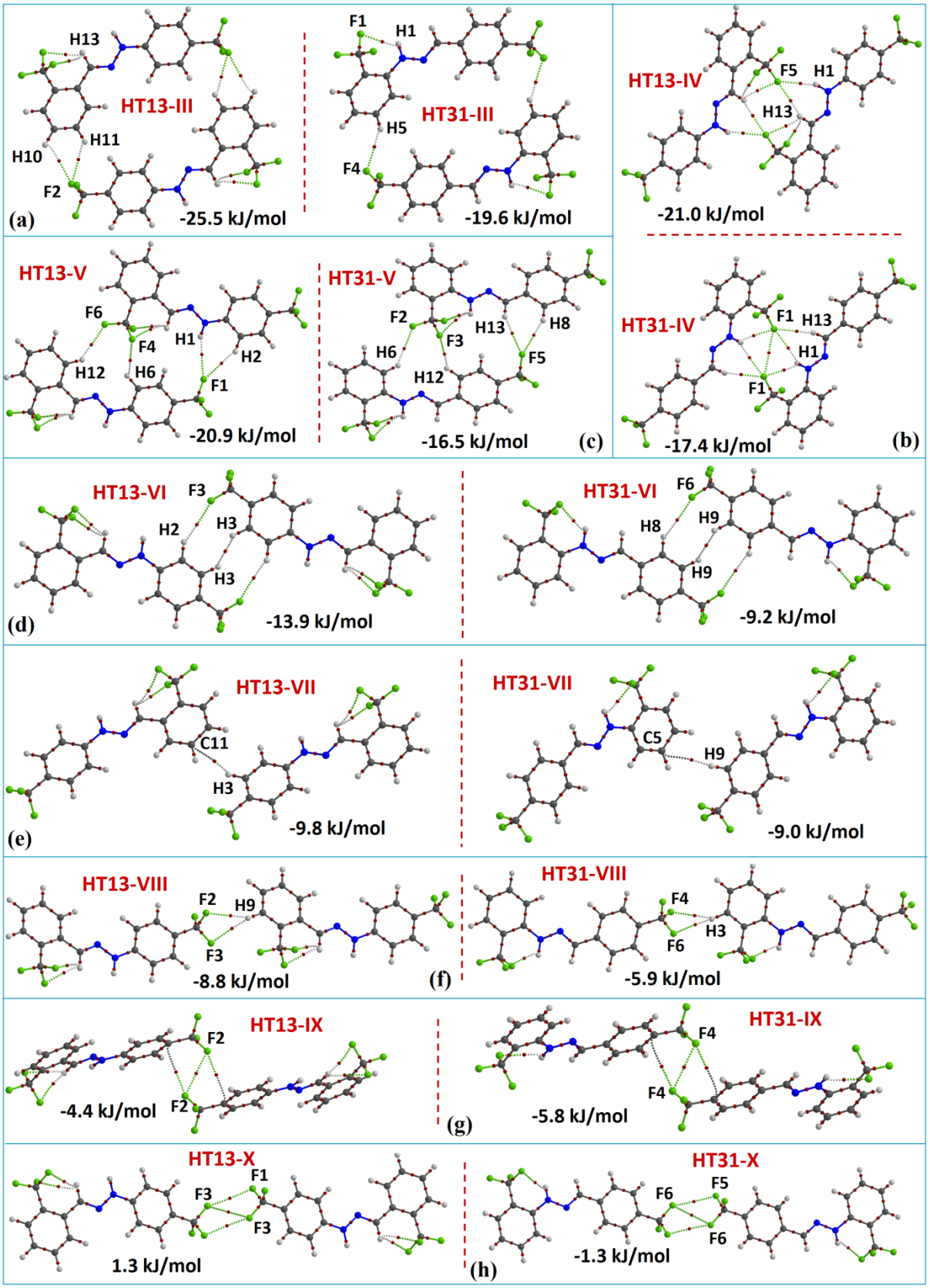

Figure S12. The molecular graphs for the molecular pairs in isostructural compounds **HT13** and **HT31** showing the bond critical points in deep red color. The corresponding value indicates the interaction energy (form PIXEL) between two interacting molecules.

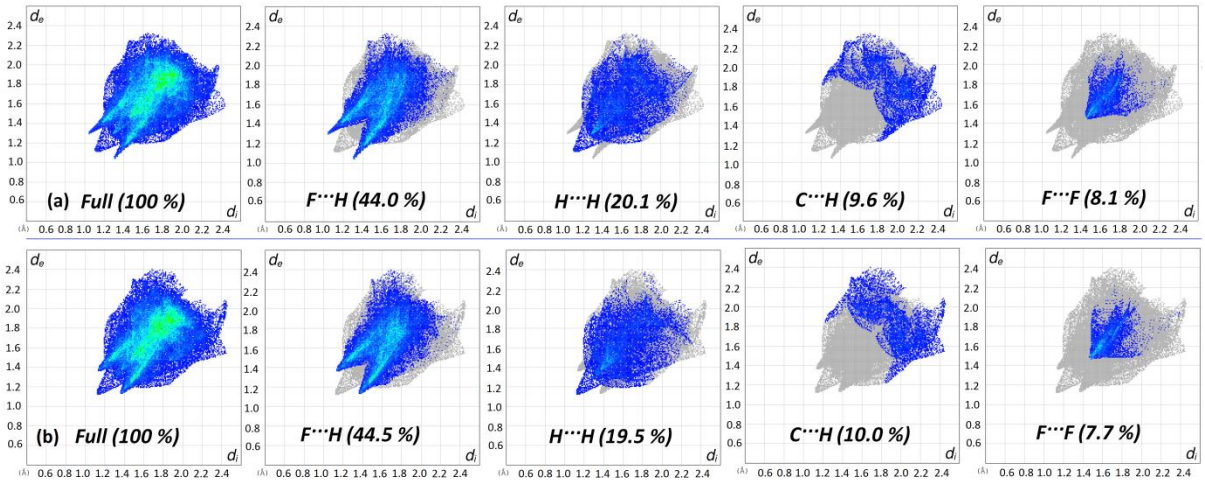

Figure S13. The fingerprint plots for the isostructural HT13 & HT31 and the contribution due to the various intermolecular contacts

Table S9. The stabilization energy (kJ/mol; obtained from PIXEL) of the molecular pairs for **HT33P** [CD = centroid-centroid distance between the two interacting molecules]

Motifs	Symmetry	CD (Å)	E_{Coul}	E_{Pol}	E_{Disp}	E_{Rep}	E_{Tot}	Possible interactions	Geometry (Å/°)
I (1-2)	-0.5+x, 1.5-y, z	4.843	-10.5	-9.5	-54.4	37.7	-36.8	C3-H3···F12A C9-H9···F8 C8-H8···C17 C13-H13···N3 N1-H1···N4 C2-H2···C23	2.59, 117 2.71, 118 2.94, 150 2.81, 150 2.86, 153 2.67, 153
II (1-2)	x, y, z	6.082	-9.4	-6.6	-40.9	27.7	-29.3	C14-F2···N3 C28-H28···C1 C23-H23···N2 C24-H24···C7	3.1573 (1) 2.96, 136 2.56, 132 3.05, 133
III (1-1)	0.5+x, 1.5-y, z	6.598	-6.8	-4.4	-31.1	13.7	-28.6	C8-H8···F3 C13-H13···F3 C11-H11···F1 C15-F6···F1-C14 C3-H3···C11	2.75, 142 2.94, 137 2.61, 149 3.0586 (1), 132, 168 2.89, 138
IV (2-2)	0.5+x, 1.5-y, z	6.612	-8.7	-4.8	-32.6	17.8	-28.3	C29-F9···F11A-C30 C20-H20···F11A C28-H28···C26 C17-H17···F12A N3-H3A···F12A	3.0130(1), 125, 172 2.46, 149 3.03, 129 2.62, 153 2.98, 145
V (1-2)	1-x, 1-y, 0.5+z	9.000	-3.7	-1.8	-28.7	13.9	-20.3	C29-F7···C1 C5···C18 C14-F1···C21 C14-F2···N3 C4···C20	3.1712(1), 115 3.6176(2) 3.2525(1), 103 3.1573(1), 103 3.8547(1)
VI (1-2)	1-x, 2-y, 0.5+z	9.024	-2.8	-1.3	-24.9	9.1	-19.8	C15-F4···C22 C9···C26 C11···C25 C30-F11A···C12 C30-F10A···C13	3.2854(1), 113 3.8573(2) 3.8015 (1) 3.5188(2), 93 3.2715 (1), 130
VII (1-2)	0.5-x, 0.5+y, 0.5+z	7.245	-6.4	-2.7	-21.7	12.1	-18.7	C6-H6···F9 C27-H27···F6	2.41, 126 2.43, 135
VIII (2-2)	0.5+x, 0.5-y, z	13.955	-4.2	-1.1	-8.2	4.7	-8.9	C18-H18···F8 C17-H17···F8 C18-H18···F9	2.67,123 2.73, 121 2.63, 130

IX (1-1)	**0.5+x, 2.5-y, z**	**13.979**	**-2.5**	**-0.6**	**-6.7**	**2.4**	**-7.4**	**C8-H8···F5** **C9-H9···F5** **C9-H9···F6**	**2.80, 120** **2.84, 118** **2.90, 118**
X (1-2)	**0.5-x, -0.5+y, 0.5+z**	**12.899**	**-1.6**	**-0.4**	**-4.5**	**2.6**	**-3.8**	**C30-F10A···F2-C14** **C26-H26···F2**	**2.7830(1), 146, 152** **2.87, 157**
XI (2-2)	**x,-1+y,z**	**16.289**	**2.1**	**-0.3**	**-4.3**	**1.1**	**-1.4**	**C30-F11A···F7-C29** **C30-F10A···F7-C29**	**3.0730(1), 97, 129** **3.0224(1), 98, 134**
XII (1-1)	**x,-1+y,z**	**16.289**	**2.2**	**-0.3**	**-4.4**	**1.5**	**-1.1**	**C15-F4···F1-C14** **C15-F4···F2-C14**	**2.9355(1), 142, 97** **3.1341(1), 137, 88**

Characterization of the polymorphs

The PXRD patterns (represented with various colored lines) of the two polymorphic forms HT33P and HT33C, including the bulk compound are shown in **Figure S14a**. The experimental diffraction patterns were collected with the 2θ range from 5 º to 50 º on a PAN analytical instrument with Cu Kα radiation (λ = 1.5406 Å) at room temperature. It is observed that the experimental (green) and simulated (indigo) PXRD patterns of HT33C are similar. Furthermore, the experimental PXRD pattern (red) of the bulk compound resembles both the experimental and the calculated patterns for HT33C form. Hence the bulk material completely corresponds to the HT33C form. The calculated diffraction pattern (pink) for the polymorphic form HT33P is completely different from the bulk material and the form HT33C. The low-intensity peaks in the low angle region (7 º-15 º) for both the forms also account for the remarkable differences between the PXRD patterns of the two polymorphic forms.

The thermal stability of these two polymorphic forms are investigated via differential scanning calorimetry (DSC) method using Perkin-Elmer DSC 6000 instrument under nitrogen gas atmosphere. For this experiment, 1-2 mg accurately weighted samples were taken in a aluminium pan and then the experiment was carried out from 30 ºC to 135 ºC with a heating rate 2 ºC/min with respect to a empty covered aluminium pan. In **Figure S14b**, the DSC traces are presented in red (first cycle) and blue color (second cycle) line for the different heating/cooling cycles for the bulk and the two polymorphic forms. In each cycle, one endothermic peak (during heating) and one sharp exothermic peak (during cooling) are observed. It is observed that the bulk compound HT33 started to melt at an onset value of 128.2 ºC and then completely melted at 129.5 ºC (ΔH = -64.5 J/g). The onset value (128.7 ºC, ΔH = -63.9 J/g) and the melting temperature (129.7 ºC) of the polymorphic forms HT33C (1.486 mg) is similar to the bulk compound. It is also interest to observe that nature of the endothermic peak (at onset value 126.7 ºC, ΔH = -60.3 J/g; melting temperature is 128.5 ºC) appeared for HT33P (1.428 mg) is quite broad in nature which differentiates from the bulk and HT33C form.

In all the cases, the endothermic peak comes at the similar position during heating, but the exothermic peak appears at various positions at the time of cooling. So, the melting temperatures for these two polymorphic forms are very close to each other.

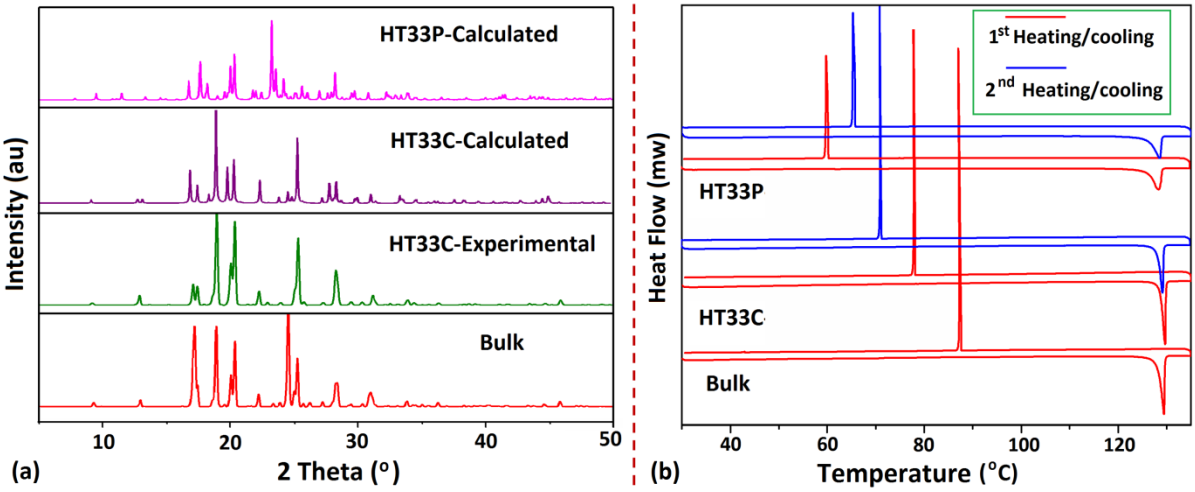

Figure S14. (a) PXRD patterns of the two polymorphic forms including the bulk compound; (b) DSC traces of two polymorphic forms and the bulk compound.

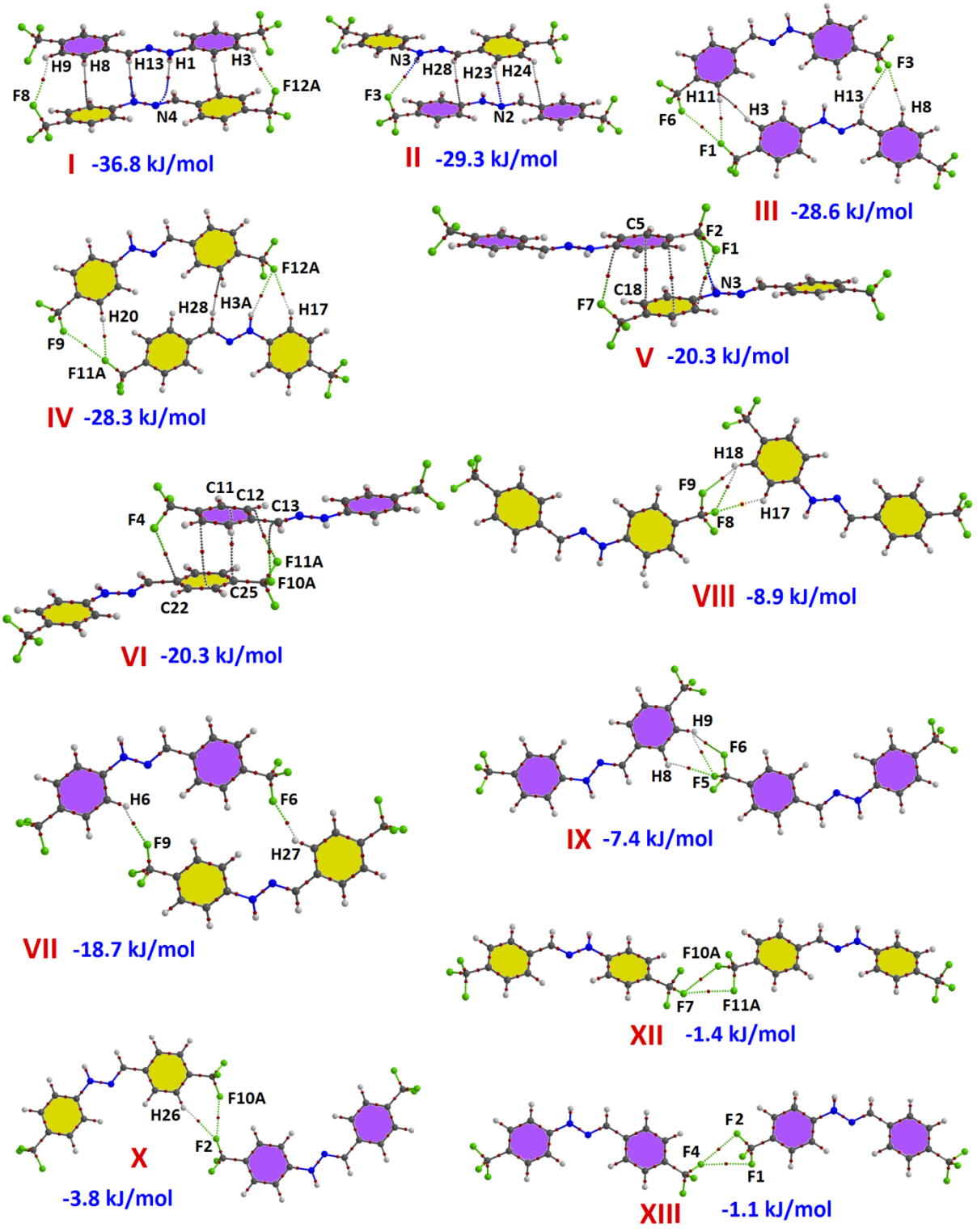

Figure S15. Molecular graphs for the molecular pairs of the polymorphic form **HT33P** showing the bond critical point in deep red color. The corresponding value indicates the interaction energy (form PIXEL) between two interacting molecules.

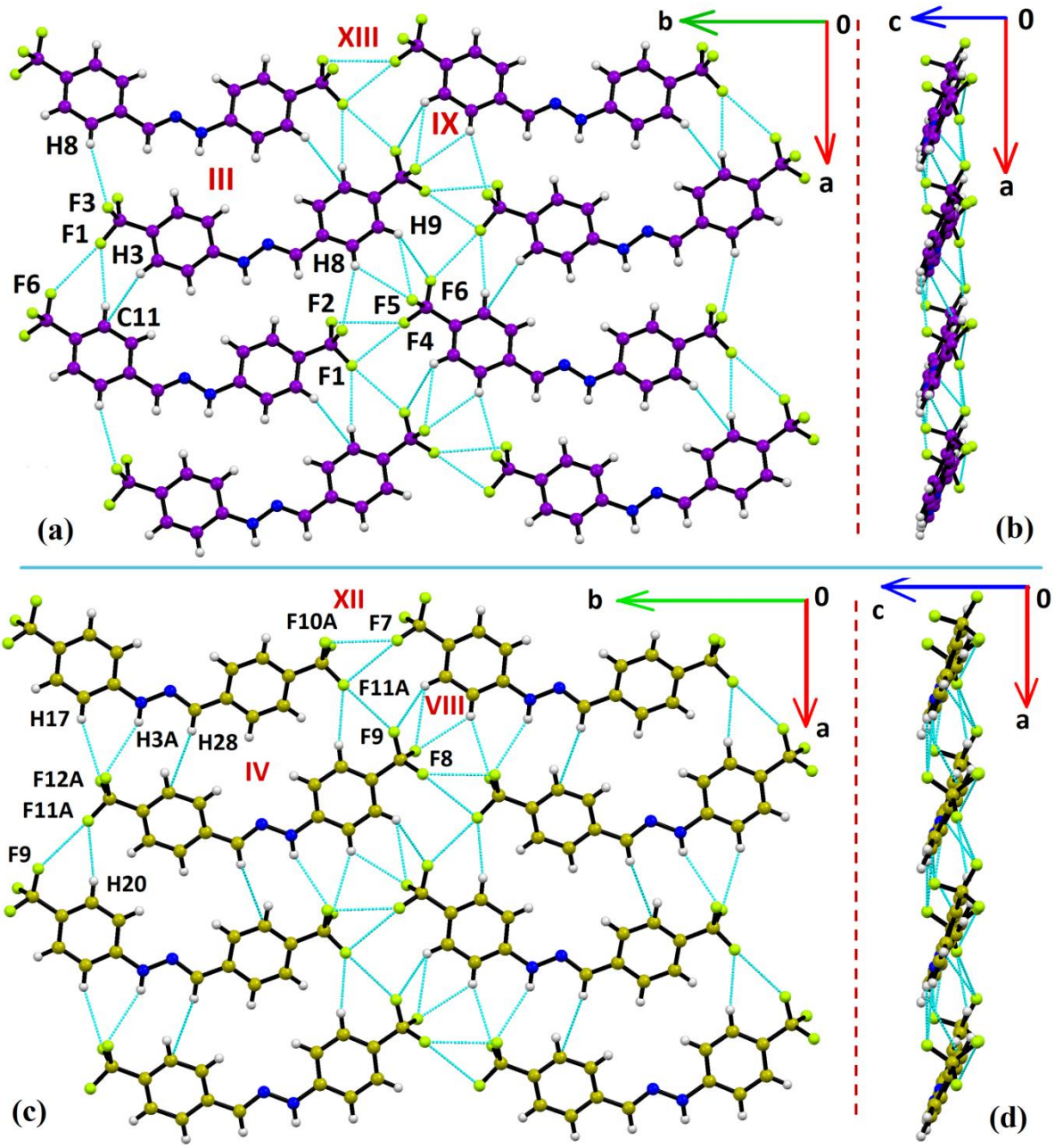

Figure S16. The formation of the molecular sheet associated with (a) the molecules **1** and (c) molecules **2** down the *ab* plane in HT33P; (b) and (d) are the corresponding view along the *b* direction.

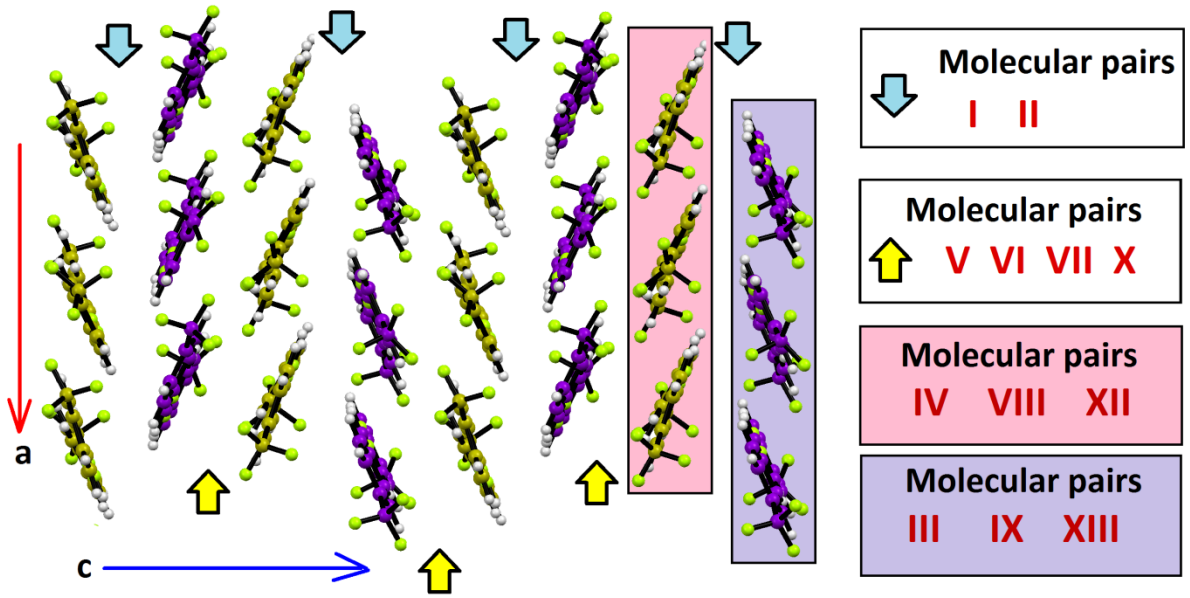

Figure S17. The overall molecular arrangement in **HT33P** showing the zigzag array involving the molecular pairs I, II, III, IV, V, VI, VII, VIII, IX, X, XII and XIII down the *ac* plane.

Table S10. The list of intermolecular interactions present in HT33C

Interactions	Symmetry	D···A (Å)	H···A (Å)	D-H···A (°)
N1-H1···F2A	0.5-x, 0.5+y, 1.5-z	3.545(1)	2.75	135
N1-H1···F3A	0.5-x, 0.5+y, 1.5-z	3.709(1)	2.72	162
C6-H6···F2A	0.5-x, 0.5+y, 1.5-z	3.600(1)	2.81	130
C7-H7···F2A	0.5-x, 0.5+y, 1.5-z	3.545(1)	2.71	133
C7-H7···F3A	0.5-x, 0.5+y, 1.5-z	3.709(1)	2.67	161
C2-H2···F2A	-0.5+x, 1.5-y, -0.5+z	3.386(1)	2.51	144
C5-H5···F1A	1-x, 2-y, 2-z	3.387(1)	2.36	158
C6-H6···F3A	x, 2-y, -0.5+z	3.333(1)	2.66	120
C7/N1···C7/N1	x , 2-y, 0.5+z	3.409(1)	-	-
N2···C1	x , 2-y, 0.5+z	3.406(1)	-	-
C6···C7	x , 2-y, 0.5+z	3.538(1)	-	-
C5···C1	x , 2-y, 0.5+z	3.494(1)	-	-
C5···C6	x , 2-y, 0.5+z	3.503(1)	-	-

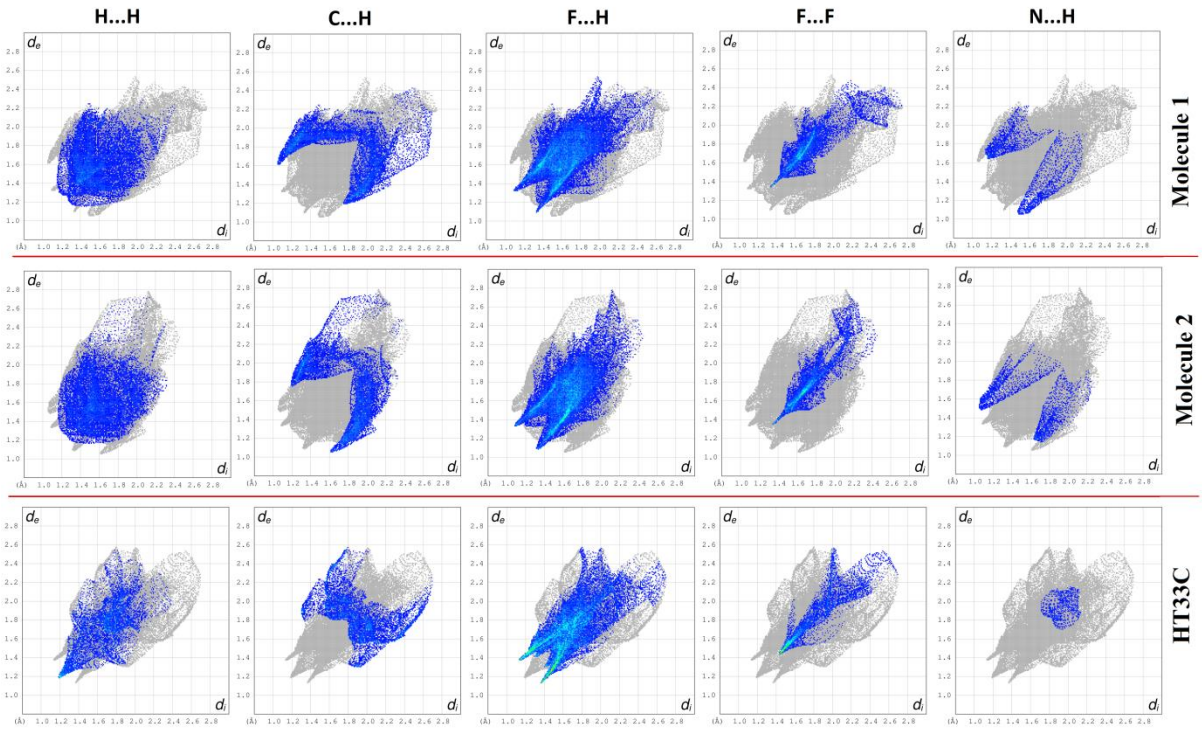

Figure S18. The decomposed fingerprint plots obtained from Hirshfeld surface of two symmetry independent molecules 1 (first row) and 2 (second row) in **HT33P** and the polymorphic form **HT33C** (third row).

Table S11. The lattice energies (in kJ/mol obtained from PIXEL) for the trifluoromethylated phenyl hydrazones

Code	E_{Coul}	E_{Pol}	E_{Disp}	E_{Rep}	E_{Tot}
HT03	**-44.9**	**-22.0**	**-147.2**	**96.1**	**-118.0**
HT20	**-45.1**	**-17.7**	**-147.1**	**89.8**	**-120.3**
HT11	**-18.9**	**-10.6**	**-139.9**	**71.7**	**-102.5**
HT13	**-32.1**	**-10.8**	**-138.9**	**70.1**	**-111.7**
HT31	**-23.5**	**-9.2**	**-137.5**	**64.7**	**-105.5**
HT33P	**-30.7**	**-16.7**	**-140.1**	**72.7**	**-114.8**

Table S12. The topological parameters at the bond critical points for the various interactions

Motifs	Interactions	R_{ij} (Å)	ρ_{BCP}(e/Å^3)	$\nabla^2\rho_{BCP}$ (e/Å^5)	V_b (a.u.)	G_b (a.u.)	D.E^V (kJ/mol)
HT20							
I	**C14-F3···C4**	**3.38**	**0.0319**	**0.466**	**-0.002928**	**0.003875**	**3.8**
	C8-H8···C5	**2.92**	**0.0424**	**0.423**	**-0.003151**	**0.003764**	**4.1**
	C13-H13···C6	**3.06**	**0.0399**	**0.388**	**-0.002885**	**0.003453**	**3.8**
	N1-H1···N2	**2.99**	**0.0294**	**0.323**	**-0.002440**	**0.002895**	**3.2**
	C2-H2···C11	**2.84**	**0.0463**	**0.487**	**-0.003620**	**0.004333**	**4.8**
	C3-H3···F1	**2.75**	**0.0330**	**0.472**	**-0.003339**	**0.004113**	**4.4**
II	**C11-H11···F3**	**2.79**	**0.0330**	**0.497**	**-0.003366**	**0.004255**	**4.4**

	C13-H13···F2	**2.78**	**0.0317**	**0.458**	**-0.003176**	**0.003958**	**4.2**
	N1-H1···F2	**2.47**	**0.0521**	**0.740**	**-0.005715**	**0.006690**	**7.5**
III	**C14-F1···N2**	**3.27**	**0.0337**	**0.486**	**-0.003501**	**0.004267**	**4.6**
	C10-H10···C1	**2.81**	**0.0446**	**0.531**	**-0.003829**	**0.004664**	**5.0**
	C11-H11···C3	**3.60**	**0.0316**	**0.318**	**-0.002354**	**0.002822**	**3.1**
IV	**H3···H6**	**2.50**	**0.0405**	**0.578**	**-0.003136**	**0.004563**	**4.1**
	H3···H12	**2.46**	**0.0267**	**0.441**	**-0.001866**	**0.003219**	**2.4**
	H12···H4	**2.55**	**0.0250**	**0.392**	**-0.001854**	**0.002958**	**2.4**
V	**C5-H5···C12**	**3.12**	**0.0328**	**0.328**	**-0.002434**	**0.002914**	**3.2**
	C6-H6···F2	**2.54**	**0.0464**	**0.652**	**-0.004897**	**0.005826**	**6.4**
	N2···F2	**3.29**	**0.0273**	**0.418**	**-0.002896**	**0.003611**	**3.8**
	C12-H12···F2	**2.53**	**0.0541**	**0.789**	**-0.005899**	**0.007037**	**7.7**
VI	**C4-H4···F3**	**2.56**	**0.0499**	**0.719**	**-0.005408**	**0.006428**	**7.1**
HT03							
I	**C3A-H3A···C15**	**3.53**	**0.0369**	**0.4472**	**-0.002862**	**0.003746**	**3.8**
	C2-H2···C20	**2.72**	**0.0541**	**0.620**	**-0.004099**	**0.005260**	**5.4**
	C2-H2··· N4	**2.61**	**0.0623**	**0.705**	**-0.005122**	**0.006211**	**6.7**
	N1-H1···C21	**3.15**	**0.0435**	**0.448**	**-0.002974**	**0.003805**	**3.9**
	C13-H13···C25	**3.03**	**0.0426**	**0.437**	**-0.003140**	**0.003830**	**4.1**
II	**C8-H8···C2**	**2.98**	**0.0458**	**0.543**	**-0.003552**	**0.004588**	**4.7**
	C8-H8···N1	**2.99**	**0.0400**	**0.470**	**-0.003521**	**0.004197**	**4.6**
	C13-H13···N1	**3.18**	**0.0348**	**0.422**	**-0.003030**	**0.003702**	**4.0**
	C13···C13	**4.20**	**0.0358**	**0.468**	**-0.002897**	**0.003872**	**3.8**
III	**C16-H16···C8**	**2.66**	**0.0621**	**0.633**	**-0.004377**	**0.005466**	**5.7**
	N3-H3···C13	**2.75**	**0.0446**	**0.483**	**-0.003208**	**0.004103**	**4.2**
	C27-H27···N2	**2.69**	**0.0466**	**0.514**	**-0.003956**	**0.004642**	**5.2**
	C22-H22···C2	**2.83**	**0.0518**	**0.526**	**-0.003645**	**0.004545**	**4.8**
IV	**C22-H22···N3**	**3.35**	**0.0210**	**0.226**	**-0.001593**	**0.001965**	**2.1**
V	**C25-H25···N2**	**2.95**	**0.0448**	**0.514**	**-0.003649**	**0.004488**	**4.8**
VI	**C12-H12···F2A**	**2.57**	**0.0398**	**0.561**	**-0.004165**	**0.004987**	**5.5**
	C6-H6···F2A	**2.64**	**0.0360**	**0.541**	**-0.003861**	**0.004735**	**5.1**
IX	**C25-H25···F5A**	**2.74**	**0.0338**	**0.498**	**-0.003477**	**0.004317**	**4.6**
VII	**F3A···N4**	**3.30**	**0.0269**	**0.395**	**-0.002690**	**0.003389**	**3.5**
	F2A···C28	**3.37**	**0.0255**	**0.372**	**-0.002276**	**0.003064**	**3.0**
	C5-H5···C21	**3.04**	**0.0418**	**0.406**	**-0.003005**	**0.003606**	**3.9**
X	**C11-H11···C17**	**2.71**	**0.0541**	**0.577**	**-0.004235**	**0.005105**	**5.6**
VIII	**H17···H17**	**2.54**	**0.0268**	**0.310**	**-0.002102**	**0.002657**	**2.8**
	C17-H17···F4A	**2.93**	**0.0218**	**0.359**	**-0.002192**	**0.002956**	**2.9**
XIV	**C24-H24···F5A**	**2.76**	**0.0349**	**0.531**	**-0.003628**	**0.004566**	**4.8**
	C23-H23···F4A	**2.62**	**0.0399**	**0.586**	**-0.004283**	**0.005175**	**5.6**
XI	**C24-H24···C25**	**3.30**	**0.0260**	**0.297**	**-0.001776**	**0.002424**	**2.3**
XIII	**C11···C11**	**4.29**	**0.0233**	**0.275**	**-0.001545**	**0.002195**	**2.0**
XV	**C19-H19···F3A**	**2.53**	**0.0405**	**0.577**	**-0.004281**	**0.005130**	**5.6**
	F6A···F3A	**2.96**	**0.0363**	**0.675**	**-0.004988**	**0.005992**	**6.5**
	C29-F6A···C4	**3.27**	**0.0303**	**0.439**	**-0.002945**	**0.003746**	**3.9**

XVI	**C10-H10···F3A**	**2.57**	**0.0431**	**0.585**	**-0.004451**	**0.005255**	**5.8**
XII	**C29-F4A···C9**	**3.59**	**0.0348**	**0.553**	**-0.003538**	**0.004632**	**4.6**
HT11							
Intra	**C13-H13···F4**	**2.42**	**0.0876**	**1.275**	**-0.010308**	**0.011754**	**13.5**
	C13-H13···F6	**2.56**	**0.0700**	**1.081**	**-0.008230**	**0.009711**	**10.8**
	N1-H1···F3	**2.40**	**0.0865**	**1.268**	**-0.010521**	**0.011829**	**13.8**
I	**F4···F5**	**2.91**	**0.0390**	**0.715**	**-0.005445**	**0.006423**	**7.1**
	C9···C13A	**3.96**	**0.0384**	**0.358**	**-0.002600**	**0.003152**	**3.4**
	F6···N1A	**3.37**	**0.0338**	**0.525**	**-0.003688**	**0.004562**	**4.8**
	C13A···C1	**3.56**	**0.0387**	**0.387**	**-0.002813**	**0.003412**	**3.7**
	N1A···C7	**3.46**	**0.0347**	**0.371**	**-0.002889**	**0.003366**	**3.8**
	F6···F1	**3.14**	**0.0231**	**0.467**	**-0.002926**	**0.003879**	**3.8**
	C13-H13A···F6	**2.90**	**0.0320**	**0.492**	**-0.003235**	**0.004163**	**4.2**
	C3···N1A	**3.49**	**0.0379**	**0.367**	**-0.002980**	**0.003393**	**3.9**
	F2···F3	**2.98**	**0.0328**	**0.622**	**-0.004486**	**0.005465**	**5.9**
II	**C10-H10···F4**	**3.02**	**0.0183**	**0.307**	**-0.001719**	**0.002447**	**2.3**
	C10-H10···F6	**2.89**	**0.0228**	**0.357**	**-0.002234**	**0.002964**	**2.9**
	C12-H12···F1	**2.94**	**0.0193**	**0.304**	**-0.001819**	**0.002484**	**2.4**
	C12-H12···F3	**3.02**	**0.0164**	**0.273**	**-0.001504**	**0.002163**	**2.0**
	C6-H6···F2	**2.69**	**0.0373**	**0.562**	**-0.003966**	**0.004892**	**5.2**
	C5-H5···F2	**2.82**	**0.0271**	**0.451**	**-0.002952**	**0.003810**	**3.9**
III	**C4-H4···C10**	**2.95**	**0.0427**	**0.409**	**-0.002975**	**0.003607**	**3.9**
	C3-H3···C9	**3.56**	**0.0278**	**0.289**	**-0.001976**	**0.002485**	**2.6**
	F4···F2	**3.17**	**0.0214**	**0.443**	**-0.002707**	**0.003650**	**3.6**
IV	**C10-H10···C4**	**3.11**	**0.0288**	**0.293**	**-0.002010**	**0.002521**	**2.6**
	C9-H9···C3	**2.71**	**0.0507**	**0.505**	**-0.003702**	**0.004466**	**4.9**
	F5···F2	**3.22**	**0.0176**	**0.378**	**-0.002172**	**0.003044**	**2.9**
	F5···F3	**3.19**	**0.0203**	**0.422**	**-0.002537**	**0.003456**	**3.3**
V	**C11-H11···F6**	**2.99**	**0.0221**	**0.361**	**-0.002167**	**0.002953**	**2.8**
	C5-H5···F3	**2.61**	**0.0427**	**0.616**	**-0.004543**	**0.005461**	**6.0**
VI	**C5-H5···F5**	**2.56**	**0.0427**	**0.593**	**-0.004476**	**0.005306**	**5.9**
VII	**C11-H11···F1**	**2.74**	**0.0332**	**0.513**	**-0.003531**	**0.004420**	**4.6**
HT13							
I	**C9···C1**	**3.48**	**0.0309**	**0.356**	**-0.002166**	**0.002925**	**2.8**
	C9···N1	**3.94**	**0.0325**	**0.335**	**-0.002480**	**0.002973**	**3.3**
	N2···C8	**3.55**	**0.0284**	**0.297**	**-0.002106**	**0.002592**	**2.8**
	C7···C13	**3.73**	**0.0286**	**0.296**	**-0.001905**	**0.002487**	**2.5**
	C12-H12···F4	**2.79**	**0.0352**	**0.534**	**-0.003517**	**0.004525**	**4.6**
Intra	**C13-H13···F5**	**2.43**	**0.0815**	**1.166**	**-0.009457**	**0.010765**	**12.4**
	C13-H13···F4	**2.67**	**0.0640**	**1.017**	**-0.007482**	**0.009009**	**9.8**
II	**F1···F5**	**2.91**	**0.0437**	**0.741**	**-0.005843**	**0.006757**	**7.7**
	F5···C5	**3.46**	**0.0272**	**0.416**	**-0.002373**	**0.003338**	**3.1**
	C12···C2	**3.47**	**0.0366**	**0.338**	**-0.002283**	**0.002894**	**3.0**
	C6···C13	**3.51**	**0.0331**	**0.317**	**-0.002081**	**0.002684**	**2.7**
III	**C10-H10···F2**	**2.90**	**0.0263**	**0.434**	**-0.002727**	**0.003613**	**3.6**

	C11-H11···F2	**2.72**	**0.0363**	**0.540**	**-0.003806**	**0.004701**	**5.0**
IV	**N1-H1···F5**	**2.38**	**0.0607**	**0.866**	**-0.006759**	**0.007862**	**8.9**
	C13-H13···F5	**2.58**	**0.0424**	**0.624**	**-0.004665**	**0.005563**	**6.1**
V	**C12-H12···F6**	**2.61**	**0.0382**	**0.552**	**-0.004042**	**0.004880**	**5.3**
	C6-H6···F4	**2.54**	**0.0488**	**0.685**	**-0.005204**	**0.006147**	**6.8**
	N1-H1···F1	**2.63**	**0.0311**	**0.471**	**-0.003290**	**0.004084**	**4.3**
	C2-H2···F1	**2.65**	**0.0348**	**0.494**	**-0.003632**	**0.004373**	**4.8**
VI	**C2-H2···F3**	**2.94**	**0.0166**	**0.276**	**-0.001647**	**0.002251**	**2.2**
	H3···H3	**2.28**	**0.0462**	**0.513**	**-0.003712**	**0.004511**	**4.9**
VII	**C3-H3···C11**	**3.02**	**0.0333**	**0.391**	**-0.002464**	**0.003258**	**3.2**
VIII	**C9-H9···F2**	**2.65**	**0.0353**	**0.496**	**-0.003583**	**0.004361**	**4.7**
	C9-H9···F3	**2.80**	**0.0269**	**0.419**	**-0.002726**	**0.003534**	**3.6**
IX	**C14-F2···C4**	**3.37**	**0.0288**	**0.409**	**-0.002669**	**0.003451**	**3.5**
	F2···F2	**2.97**	**0.0397**	**0.703**	**-0.005416**	**0.006350**	**7.1**
X	**F1···F3**	**3.03**	**0.0302**	**0.582**	**-0.004083**	**0.005054**	**5.4**
	F3···F3	**3.04**	**0.0321**	**0.605**	**-0.004300**	**0.005281**	**5.6**
HT31							
I	**H12···F3**	**2.84**	**0.0276**	**0.415**	**-0.002628**	**0.003464**	**3.4**
	H6···F3	**2.84**	**0.0296**	**0.457**	**-0.002927**	**0.003830**	**3.8**
	C3···C7	**3.50**	**0.0347**	**0.376**	**-0.002348**	**0.003120**	**3.1**
	C2···N2	**3.53**	**0.0333**	**0.328**	**-0.002397**	**0.002899**	**3.1**
	C1···N1	**3.76**	**0.0292**	**0.317**	**-0.002299**	**0.002789**	**3.0**
II	**F2···F5**	**3.12**	**0.0258**	**0.492**	**-0.003179**	**0.004137**	**4.2**
	F5···F1	**3.09**	**0.0293**	**0.545**	**-0.003681**	**0.004663**	**4.8**
	F1···C11	**3.61**	**0.0302**	**0.464**	**-0.002751**	**0.003778**	**3.6**
	C8···C6	**3.61**	**0.0320**	**0.287**	**-0.001957**	**0.002466**	**2.6**
	N1···C12	**3.61**	**0.0267**	**0.264**	**-0.001960**	**0.002349**	**2.6**
Intra	**N1-H1···F1**	**2.45**	**0.0766**	**1.244**	**-0.009431**	**0.011160**	**12.4**
III	**C5-H5···F4**	**2.64**	**0.0414**	**0.597**	**-0.004382**	**0.005282**	**5.8**
IV	**C13-H13···F5**	**2.53**	**0.0519**	**0.711**	**-0.005544**	**0.006454**	**7.3**
	N1-H1···F5	**2.66**	**0.0332**	**0.536**	**-0.003787**	**0.004671**	**5.0**
	F1···F1	**3.05**	**0.0287**	**0.557**	**-0.003817**	**0.004795**	**5.0**
V	**C6-H6···F2**	**2.71**	**0.0296**	**0.472**	**-0.003133**	**0.004009**	**4.1**
	C12-H12···F3	**2.53**	**0.0492**	**0.726**	**-0.005413**	**0.006466**	**7.1**
	C13-H13···F5	**2.76**	**0.0274**	**0.432**	**-0.002844**	**0.003658**	**3.7**
	C8-H8···F5	**2.72**	**0.0287**	**0.450**	**-0.003019**	**0.003841**	**4.0**
VI	**C8-H8···F6**	**2.97**	**0.0155**	**0.264**	**-0.001543**	**0.002141**	**2.0**
	H9···H9	**2.30**	**0.0424**	**0.471**	**-0.003415**	**0.004148**	**4.5**
VII	**C9-H9···C5**	**3.09**	**0.0322**	**0.385**	**-0.002428**	**0.003208**	**3.2**
VIII	**C3-H3···F4**	**2.69**	**0.0329**	**0.468**	**-0.003335**	**0.004090**	**4.4**
	C3-H3···F6	**2.81**	**0.0258**	**0.399**	**-0.002598**	**0.003367**	**3.4**
IX	**C15-F4···C10**	**3.54**	**0.0270**	**0.385**	**-0.002449**	**0.003216**	**3.2**
	F4···F4	**2.95**	**0.0410**	**0.720**	**-0.005617**	**0.006537**	**7.4**
X	**F6···F5**	**2.96**	**0.0362**	**0.662**	**-0.004970**	**0.005915**	**6.5**

	F6···F6	**3.14**	**0.0257**	**0.521**	**-0.003325**	**0.004361**	**4.4**
HT33P							
I	**C9-H9···F8**	**2.80**	**0.0344**	**0.524**	**-0.003521**	**0.004474**	**4.6**
	C8-H8···C17	**3.02**	**0.0362**	**0.358**	**-0.002705**	**0.003206**	**3.6**
	C13-H13···N3	**2.83**	**0.0421**	**0.419**	**-0.003664**	**0.003999**	**4.8**
	N1-H1···N4	**3.10**	**0.0391**	**0.384**	**-0.002993**	**0.003487**	**3.9**
	C2-H2···C23	**2.71**	**0.0568**	**0.573**	**-0.004279**	**0.005106**	**5.6**
	C3-H3···F12A	**2.63**	**0.0467**	**0.672**	**-0.004935**	**0.005948**	**6.5**
II	**N3···F3**	**3.35**	**0.0335**	**0.536**	**-0.003713**	**0.004630**	**4.9**
	C28-H28···C1	**3.04**	**0.0353**	**0.350**	**-0.002582**	**0.003103**	**3.4**
	C23-H23···N2	**2.58**	**0.0592**	**0.730**	**-0.005432**	**0.006497**	**7.1**
	C24-H24···C7	**3.11**	**0.0276**	**0.289**	**-0.002009**	**0.002499**	**2.6**
III	**F6···F1**	**3.06**	**0.0246**	**0.504**	**-0.003304**	**0.004263**	**4.3**
	H11-H11···F1	**2.64**	**0.0350**	**0.510**	**-0.003661**	**0.004473**	**4.8**
	C3-H3···C11	**3.22**	**0.0369**	**0.443**	**-0.002858**	**0.003725**	**3.8**
	C13-H13···F3	**2.96**	**0.0202**	**0.311**	**-0.001878**	**0.002549**	**2.5**
	C8-H8···F3	**2.77**	**0.0277**	**0.414**	**-0.002809**	**0.003547**	**3.7**
IV	**F9···F11A**	**2.98**	**0.0303**	**0.601**	**-0.004193**	**0.005207**	**5.5**
	C20-H20···F11A	**2.44**	**0.0534**	**0.744**	**-0.005711**	**0.006709**	**7.5**
	C28-H28···C26	**3.16**	**0.0303**	**0.337**	**-0.002162**	**0.002825**	**2.8**
	N3-H3A···F12A	**3.01**	**0.0149**	**0.250**	**-0.001347**	**0.001969**	**1.8**
	C17H17···F12A	**2.73**	**0.0295**	**0.425**	**-0.002974**	**0.003688**	**3.9**
V	**F7···C1**	**3.18**	**0.0370**	**0.572**	**-0.003891**	**0.004909**	**5.1**
	C5···C18	**3.64**	**0.0288**	**0.258**	**-0.001870**	**0.002273**	**2.5**
	C4···C20	**4.04**	**0.0230**	**0.203**	**-0.001529**	**0.001818**	**2.0**
	F1···C21	**3.26**	**0.0321**	**0.448**	**-0.002907**	**0.003773**	**3.8**
	F2···N3	**3.17**	**0.0404**	**0.567**	**-0.004408**	**0.005142**	**5.8**
VI	**F4···C22**	**3.29**	**0.0317**	**0.462**	**-0.002962**	**0.003874**	**3.9**
	C9···C26	**4.35**	**0.0220**	**0.190**	**-0.001419**	**0.001694**	**1.9**
	C11···C25	**4.11**	**0.0244**	**0.210**	**-0.001554**	**0.001866**	**2.0**
	C12···F11A	**3.56**	**0.0248**	**0.377**	**-0.002183**	**0.003044**	**2.9**
	C13···F10A	**3.57**	**0.0273**	**0.402**	**-0.002440**	**0.003302**	**3.2**
VII	**C6-H6···F9**	**2.46**	**0.0587**	**0.852**	**-0.006489**	**0.007659**	**8.5**
	C27-H27···F6	**2.47**	**0.0526**	**0.759**	**-0.005775**	**0.006820**	**7.6**
VIII	**C18-H18···F9**	**2.66**	**0.0389**	**0.565**	**-0.004057**	**0.004954**	**5.3**
	C18-H18···F8	**2.78**	**0.0325**	**0.510**	**-0.003425**	**0.004357**	**4.5**
	C17-C17···F8	**2.71**	**0.0352**	**0.533**	**-0.003717**	**0.004618**	**4.9**
IX	**C8-H8···F5**	**2.86**	**0.0271**	**0.433**	**-0.002779**	**0.003634**	**3.6**
	C9-H9···F5	**2.91**	**0.0259**	**0.420**	**-0.002620**	**0.003486**	**3.4**
	C9-H9···F6	**2.97**	**0.0237**	**0.383**	**-0.002284**	**0.003125**	**3.0**
X	**C26-H26···F2**	**2.89**	**0.0176**	**0.302**	**-0.001782**	**0.002454**	**2.3**
	F10A···F2	**2.70**	**0.0587**	**1.055**	**-0.008677**	**0.009804**	**11.4**
XI	**F7···F11A**	**3.05**	**0.0304**	**0.575**	**-0.004030**	**0.004991**	**5.3**
	F7···F10A	**3.06**	**0.0303**	**0.569**	**-0.003975**	**0.004935**	**5.2**
XII	**F4···F1**	**2.94**	**0.0390**	**0.695**	**-0.005366**	**0.006285**	**7.0**

	F4···F2	**3.14**	**0.0247**	**0.495**	**-0.003137**	**0.004132**	**4.1**

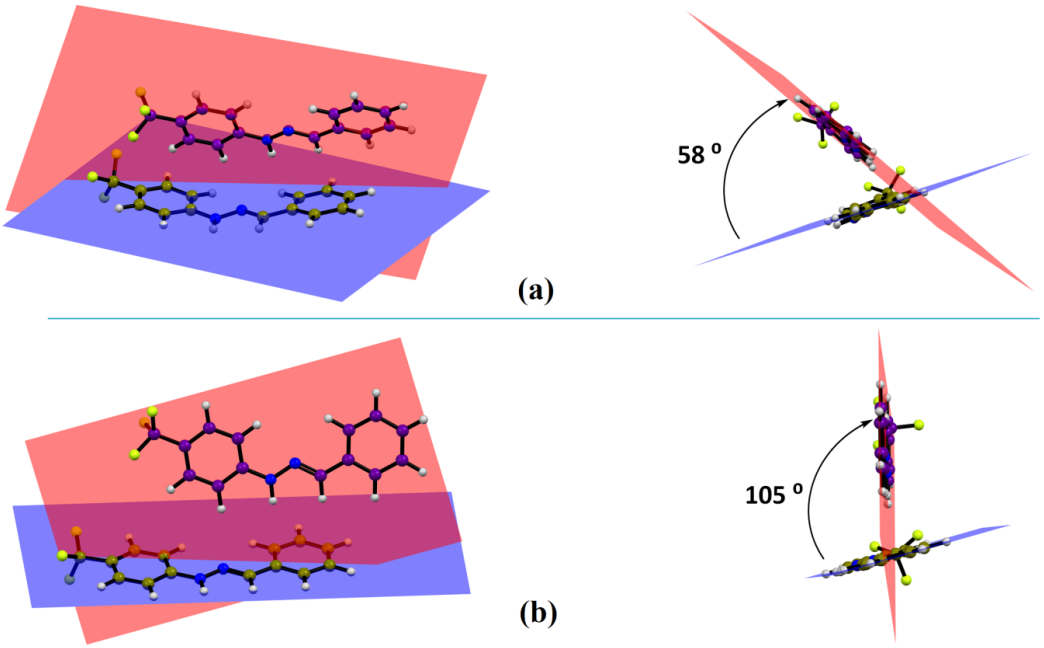

Figure S19. Molecular pair HT03-I in (a) the crystal geometry and (b) after optimization.

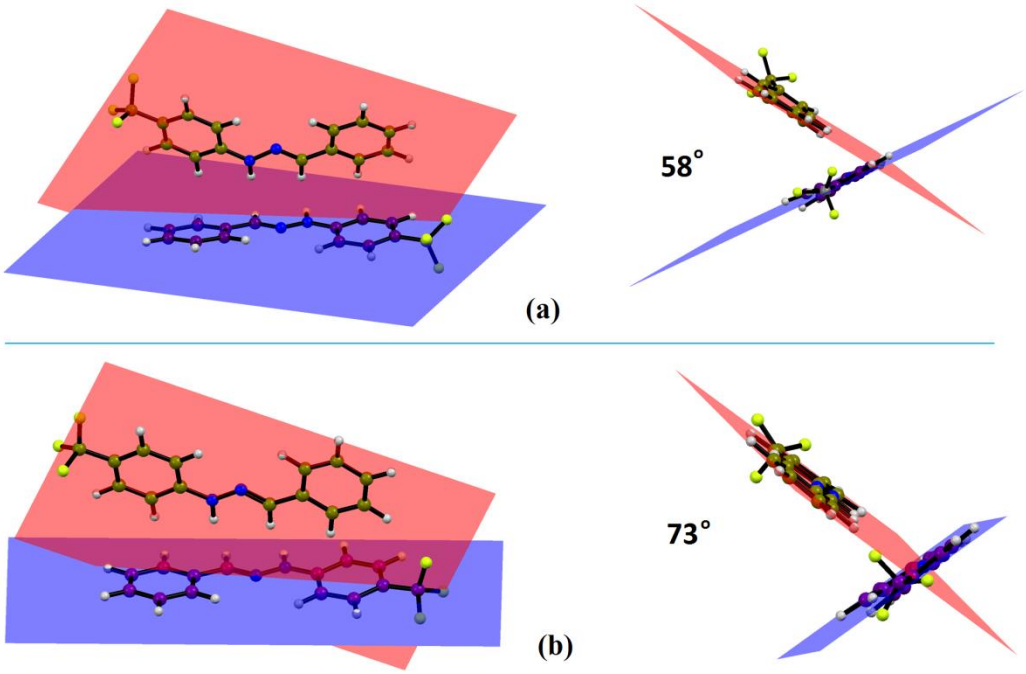

Figure S20. Molecular pair HT03-III in (a) the crystal geometry and (b) after optimization.

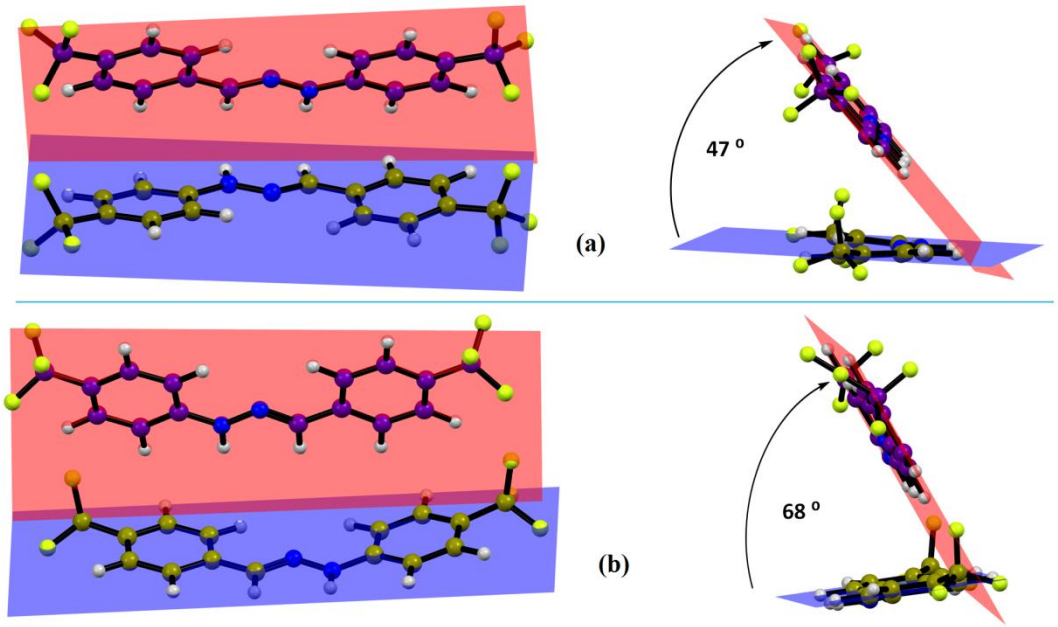

Figure S21. Molecular pair HT33-I in (a) the crystal geometry and (b) after optimization.

References

Bruker (2006a). SAINT, Version 7.60a. Bruker AXS Inc., Madison,Wisconsin, USA.

Bruker (2006b). SADABS, Version 2.05. Bruker AXS Inc., Madison, Wisconsin, USA.

Espinosa, E., Molins, E. & Lecomte, C. (1998). *Chem. Phys. Lett.* **285**, 170–173.

Farrugia, L. J. (1999). *J. Appl. Cryst*. **32**, 837–838.

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Jr. Montgomery, J. A.;, Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. (2009). Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT.

Keith, T. A. (2013). AIMALL, version 13.05.06, TK Gristmill Software, Overland Park KS, aim.tkgristmill.com.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466-470.

Mata, I., Alkorta, I., Espinosa, E. & Molins, E. (2011). *Chem. Phys. Lett.* **507**, 185–189.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Sheldrick, G. M. (2008). *Acta Cryst*. **A64**, 112–122.

Spek, A. L. (2009). *Acta Cryst.* **D65**, 148-155.