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Supporting Information

HYDROGEN BONDING INTERACTIONS IN FLUORINATED 1,2,3-TRIAZOLE DERIVATIVES

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Table S1. Crystal data and structure refinement results for compounds **1**-**4**.

	(**1**)	(**2**)	(**3**)	(**4**)
Empirical formula	$C_{10}H_6F_3N_3O_2$	$C_{10}H_5F_3N_4O_4$	$C_{11}H_{10}F_3N_3O_3$	$C_{10}H_5ClF_3N_3O_2$
Formula weight	257.18	302.18	289.22	291.62
Temperature / K	297(2)	297(2)	297(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	C2/c	P-1
Unit cell dimensions	*a*=6.6999(3)Å	*a* =5.0192(2)Å	*a* =7.4429(3)Å	*a* =6.6403(9)Å
	b=20.5919(9)Å	*b* =17.4035(6)Å	*b* =21.4011(9)Å	*b* = 8.1037(7)Å
	c=7.6340(4)Å	*c* =13.0726(5)Å	*c* =15.5986(7)Å	*c*=11.1004(13)Å
				α= 6.450(9)°
	β= 107.377(5)°	β= 94.057(4)°	β= 97.343(4)°	β= 101.623(11)°
				γ= 93.168(9)°
Volume / Å^3	1005.15(9)	1139.05(7)	2464.3(2)	557.10(12)
Z	4	4	4	2
ρ calc./mg mm^{-3}	1.699	1.762	1.559	1.738
μ / mm^{-1}	0.158	0.169	0.144	0.386
F(000)	520	608	1184	292
Crystal shape/ color	Plate/yellow	Fragment/colorless	Fragment/yellow	Plate/yellow
Crystalsize / mm^3	0.45x0.17x0.07	0.37x0.18x0.15	0.51x0.47x0.37	0.34x0.18x0.03
Theta range for data collection	2.97 to 28.83°	3.34 to 28.79°	3.05 to 29.12°	3.32 to 28.50°
Index ranges	-8 ≤ *h* ≤ 8	-6 ≤ *h* ≤ 6	-9 ≤ *h* ≤ 6	-8 ≤ *h* ≤ 8
	-25 ≤ *k* ≤ 18	-14 ≤ *k* ≤ 23	-27 ≤ *k* ≤ 24	-9 ≤ *k* ≤ 10
	-10 ≤ *l* ≤ 10	17 ≤ *l* ≤ 17	-18 ≤ *l* ≤ 20	-13 ≤ *l* ≤ 13
Reflections collected	5024	4851	5772	4085
Indep. reflections	2214 [*R*(int) = 0.022]	2451 [*R*(int)=0.0252]	2722 [*R*(int)=0.024]	2373 [*R*(int) = 0.017]
Data / restraints / parameters	2214 / 0 / 187	2451 / 0 / 210	2722 / 0 / 195	2373 / 0 / 192
Goodness-of-fit on F^2	1.028	1.020	1.028	1.039
Final *R*indexes [$I > 2\sigma(I)$]	*R1* = 0.0397	*R1* = 0.0535	*R1* = 0.0516	*R1* = 0.0482
	wR2 = 0.931	*wR2* = 0.1287	*wR2* = 0.1328	*wR2* = 0.1044
Largest diff. peak/hole/ e Å^{-3}	0.242 / -0.219	0.269 / -0.248	0.463 / -0.348	0.242 / -0.260

Table S2 Lattice energies (kJ mol^{-1}) partitioned into coulombic (E_{coul}), polarization (E_{pol}), dispersion (E_{disp}) and repulsion (E_{rep}) components for **1** – **4**. Normalized % in parenthesis.[a]

Compound	E_{Coul}	E_{Pol}	E_{Dis}	E_{Rep}	E_{TOT}
1	-60.8 (31.0)	-22.5 (11.5)	-113.0 (57.6)	71.2	-125.1
2	-60.0 (30.8)	-19.1 (9.8)	-115.4 (59.3)	67.8	-126.7
3	-85.8 (43.4)	-43.0 (21.7)	-69.1 (34.9)	97.9	-100.0
4	-48.9 (25.5)	-23.0 (12.0)	-119.7 (62.5)	66.6	-125.0

[a] Value obtained after normalizing to 100% the sum of the attractive energy contributions.

Hirshfeld surface analysis

It is worthwhile to note a pair of small red spots labeled 4 in d_{norm} surface of structure **3** corresponding to H···C contacts, which are also visible as a pair of symmetrical spikes labeled 2 at (d_e + d_i) ≈ 2.8 Å (sum of r_{vdW} = 2.9 Å) in the FP. These contacts can be attributed to weak C–H···π interactions with (methyl)H11A···*C*g2 distance of 3.162(2) Å according to X-ray crystal determination. This distance value and the angle γ value of 30.2° (calculated for us) between the *C*g2–H11A vector and the normal to the phenyl ring are near but slightly larger than those commonly accepted for this type of interactions (H···*C*g < 3.0 Å, γ < 30°). Therefore, it is expected that they contribute little to the crystal stability. This result is in accordance with those obtained from PIXEL calculations in which, for this compound, dispersive forces are the ones that contribute the least to the lattice energies (see Table 2).

Table S3. Enrichment ratio (E_{XY})*of selected intermolecular contacts for compounds **1**-**4**.

Interaction	**1**	**2**	**3**	**4**
O···H/H···O	1.75	1.70	1.45	2.07
F···H/H···F	1.49	1.31	1.26	1.50
C···H/H···C	0.25	1.09	1.02	1.07
N···H/H···N	1.20	0.91	0.69	1.06
Cl···H/H···Cl	-	-	-	1.24
C···C	3.75	0.86	1.75	2.68
F···F	0.80	1.78	1.63	0.73
F···O/O···F	-	0.28	-	-
F···N/N···F	1.33	-	0.88	1.45
F···Cl/Cl···F	-	-	-	1.27
F···C/C···F	0.43	0.71	/	/
O···O	/	0.85	/	-
N···O/O···N	/	1.29	-	/
C···O/O···C	/	0.68	1.32	/
N···C/C···N	0.94	2.15	/	1.17
C···Cl/Cl··C	-	-	-	1.03
O···Cl/Cl··O	-	-	-	1.30

*The values were computed for interactions with C_{XY} >3.0%

In comparison with the unsubstituted compound **1** (Del% = 47.4%), the percentages of π-delocalization for compounds **2** (48.0%) and **4** (51.0%) are slightly higher due to the electron-withdrawing effect of the nitro and chlorine substituent groups, which destabilizes the phenyl ring favoring the formation of KE form.

The proportion of Hirshfeld surface contact C_{XY} (%), the proportion of chemical type on the molecular surface *S*x, and ratio of random contacts R_{XY} between two chemical elements X and Y are given in Table S3, ESI†. The enrichment ratio E_{XY} of a pair of elements (X,Y) is defined as the ratio between the proportion of actual contacts in the crystal (C_{XY}) and the theoretical proportion of random contacts (R_{XY}). An enrichment ratio larger than unity for a given pair of chemical species X···Y indicates that these contacts are over-represented in the crystal packing when compared to equi-probable contacts computed from the chemical composition on the Hirshfeld surface.

However, in comparison to the also favoured F···H contacts for **2** (E_{FH}= 1.31) and **3** (E_{FH}= 1.26), the corresponding F···F contacts are much more enriched for both the compounds (E_{FF}= 1.78/1.63), and hence with longer likelihood of occurrence as a consequence of close-packing effect bringing the trifluoromethyl groups nearer to each other.[1–3] These results suggest that the propensity for C-F group to form F···F inter-halogen bond in this type of compounds (CHFNO data set) may play an important role in stabilizing the crystal structures. Concerning compound **4**, the Cl···H contacts are also enriched with E_{ClH}= 1.24 larger than unity, as reported in literature[3] for various aromatic systems containing that type of halogen.

Table S4. Hirshfeld contact surfaces CXY(%)*, proportion of chemical type on the molecular surface Sx (%), and random contacts RXY(%) of intermolecular interactions for compounds **1**-**4**.

C_{XY}	**1**	**2**	**3**	**4**
H···H	13.0	1.6	20.2	2.5
C···H / H···C	3.4	9.5	12.4	9.5
N···H / H···N	10.0	5.9	9.7	7.2
O···H / H···O	12.8	23.0	13.9	12.4
F···H / H···F	28.4	16.6	21.3	21.8
Cl···H / H···Cl	-	-	-	8.8
C···C	10.5	1.9	2.8	5.1
C···O / O···C	2.4	4.7	3.3	-
O···O	-	4.6	-	-
F···F	4.5	8.4	4.9	3.3
F···O / O···F	-	2.8	-	-
F···C / C···F	3.4	4.6	2.2	1.9
F···N / N···F	6.5	2.6	4.4	6.8
N···O / O···N	-	6.7	-	-
N···C / C···N	3.2	7.1	-	3.4
N···N	-	-	1.6	-
C···Cl / Cl···C	-	-	-	3.1
O···Cl / Cl···O	-	-	-	2.6
F···Cl / Cl···F	-	-	-	6.2
Surface *S*x				
H	40.3	29.1	48.9	32.4
C	16.7	14.9	12.5	13.7
N	10.3	11.2	14.4	10.5
O	9.1	23.2	9.8	9.2
F	23.7	21.7	17.3	22.3
Cl	-	-	-	11.0
Random contacts R_{XY}				
H···H	16.2	8.5	23.9	10.5
C···H / H···C	13.5	8.7	12.2	8.9
N···H / H···N	8.3	6.5	14.1	6.8
O···H / H···O	7.3	13.5	9.6	6.0
F···H / H···F	19.1	12.6	16.9	14.5
Cl···H / H···Cl	-	-	-	7.1
C···C	2.8	2.2	1.6	1.9
C···O / O···C	3.0	6.9	2.5	-
O···O	0.8	5.4	1.0	-
F···F	5.6	4.7	3.0	4.5
F···O / O···F	-		-	-
F···C / C···F	7.9	6.5	4.3	6.1
F···N / N···F	4.9	4.9	5.0	4.7
N···O / O···N	-	5.2	-	-
N···C / C···N	3.4	3.3	-	2.9
N···N	-	-	2.1	-
C···Cl / Cl···C	-	-	-	3.0
O···Cl / Cl···O	-	-	-	2.0
F···Cl / Cl···F	-	-	-	4.9

*Data obtained from CrystalExplorer3.0, including reciprocal contacts.C_{XY} values lower than1.5% were not included.

Table S5. Pseudo ring **c**alculated geometrical parameters of **1**–**4**.

Compound	Basis set[b]	Parameters[a]							
		O-H	O···O	H···O	<OH···O	d_1	d_2	d_3	d_4
1	6-31(d.p)	0.992	2.543	1.648	147.8	1.336	1.430	1.463	1.245
	6-311++(d.p)	0.986	2.567	1.691	145.9	1.338	1.426	1.462	1.237
	CC-pVDZ	0.997	2.531	1.625	148.7	1.335	1.433	1.467	1.245
2	6-31(d.p)	0.996	2.531	1.632	147.9	1.328	1.433	1.471	1.243
	6-311++(d.p)	0.989	2.555	1.675	145.9	1.329	1.430	1.471	1.235
	CC-pVDZ	1.000	2.521	1.613	148.7	1.327	1.436	1.474	1.243
3	6-31(d.p)	0.992	2.544	1.649	147.7	1.337	1.427	1.462	1.246
	6-311++(d.p)	0.985	2.570	1.694	145.7	1.339	1.423	1.461	1.237
	CC-pVDZ	0.997	2.532	1.628	148.6	1.336	1.430	1.466	1.245
4	6-31(d.p)	0.993	2.539	1.645	147.6	1.335	1.429	1.467	1.244
	6-311++(d.p)	0.986	2.564	1.689	145.6	1.337	1.425	1.466	1.236
	CC-pVDZ	0.997	2.526	1.623	148.4	1.334	1.432	1.471	1.244

[a] Distances (Å) and angles (°); Experimental geometrical parameters defined in Table 1
[b]Functional B3LYP

Table S6. Experimental and calculated geometrical parameters of **1**.

Parameter	Bond lengths (Å)				Parameter	Angles (°)			
	Exp	Calculated (B3LYP)				Exp[b]	Calculated (B3LYP)		
	DRX	6-31g (d.p)	6-311++ g (d.p)	cc-PVDZ		DRX	6-31g (d.p)	6-311++ g (d.p)	cc-PVDZ
C(1)-C(6)	1.406	1.415	1.413	1.416	C(6)-C(1)-C(2)	117.4	118.3	118.3	118.2
C(1)-C(2)	1.412	1.430	1.426	1.430	C(6)-C(1)-C(7)	123.2	123.6	123.1	123.5
C(1)-C(7)	1.461	1.463	1.462	1.465	C(2)-C(1)-C(7)	119.4	118.0	118.5	118.3
C(2)-O(1)	1.343	1.336	1.338	1.339	O(1)-C(2)-C(3)	116.4	117.6	117.4	117.2
C(2)-C(3)	1.392	1.406	1.402	1.405	O(1)-C(2)-C(1)	123.5	122.8	122.9	123.1
C(3)-C(4)	1.367	1.384	1.383	1.385	C(3)-C(2)-C(1)	120.0	119.7	119.7	119.7
C(4)-C(5)	1.379	1.405	1.403	1.405	C(4)-C(3)-C(2)	120.7	120.3	120.3	120.3
C(5)-C(6)	1.372	1.383	1.381	1.383	C(3)-C(4)-C(5)	120.4	120.9	120.9	120.8
C(7)-O(2)	1.235	1.245	1.237	1.244	C(6)-C(5)-C(4)	120.0	119.6	119.5	119.6
C(7)-C(8)	1.488	1.492	1.495	1.492	C(5)-C(6)-C(1)	121.5	121.3	121.3	121.4
C(8)-N(3)	1.337	1.339	1.335	1.340	O(2)-C(7)-C(1)	121.2	121.8	122.1	121.9
C(8)-C(9)	1.408	1.421	1.419	1.422	O(2)-C(7)-C(8)	115.1	115.0	115.6	114.9
C(9)-N(1)	1.327	1.331	1.327	1.331	C(1)-C(7)-C(8)	123.8	123.2	122.3	123.2
C(9)-C(10)	1.486	1.506	1.505	1.506	N(3)-C(8)-C(9)	107.1	107.6	107.5	107.6
C(10)-F(3)	1.33	1.345	1.345	1.346	N(3)-C(8)-C(7)	124.9	125.3	124.3	125.4
C(10)-F(1)	1.334	1.344	1.346	1.343	C(9)-C(8)-C(7)	127.9	127.0	128.0	126.8
C(10)-F(2)	1.336	1.347	1.348	1.347	N(1)-C(9)-C(8)	109.3	108.9	108.8	108.9
N(1)-N(2)	1.317	1.327	1.322	1.326	N(1)-C(9)-C(10)	118.7	120.2	120.3	120.0
N(2)-N(3)	1.312	1.324	1.322	1.323	C(8)-C(9)-C(10)	132.0	130.9	130.9	131.0
					F(3)-C(10)-F(1)	106.9	107.7	107.4	107.7
					F(3)-C(10)-F(2)	107.0	107.8	107.6	107.8
					F(1)-C(10)-F(2)	105.9	108.2	107.8	108.2
					F(3)-C(10)-C(9)	111.3	110.4	111.0	110.4
					F(1)-C(10)-C(9)	112.8	111.7	112.0	111.8
					F(2)-C(10)-C(9)	112.6	110.8	111.0	110.9
					N(2)-N(1)-C(9)	102.7	103.0	103.3	103.0
					N(3)-N(2)-N(1)	117.1	116.9	116.6	117.0
					N(2)-N(3)-C(8)	103.7	103.5	103.7	103.5

Parameter	Dihedral (º)			
	Exp	Calculated (B3LYP)		
	DRX	6-31g (d.p)	6-311++ g (d.p)	cc-PVDZ
C(2)-C(1)-C(7)-(C8)	171.7	176.4	175.8	175.5
C(1)-C(7)-C(8)-(C9)	176.0	157.4	148.6	160.0

Table S7. Experimental and calculated geometrical parameters of **2**.

Parameter	Bond lengths (Å)				Parameter	Angles (°)			
	Exp	Calculated (B3LYP)				Exp[b]	Calculated (B3LYP)		
	DRX	6-31g (d.p)	6-311++g (d.p)	cc-PVDZ		DRX	6-31g (d.p)	6-311++g (d.p)	cc-PVDZ
C(1)-C(6)	1.396	1.406	1.404	1.409	C(6)-C(1)-C(2)	117.6	118.5	118.5	118.4
C(1)-C(2)	1.421	1.433	1.430	1.436	C(6)-C(1)-C(7)	123.7	123.5	123.0	123.8
C(1)-C(7)	1.467	1.471	1.471	1.474	C(2)-C(1)-C(7)	118.7	118.1	118.5	117.8
C(2)-O(3)	1.337	1.328	1.329	1.327	O(3)-C(2)-C(3)	116.6	117.5	117.3	117.4
C(2)-C(3)	1.395	1.410	1.407	1.413	O(3)-C(2)-C(1)	122.9	122.6	122.8	122.8
C(3)-C(4)	1.36	1.379	1.377	1.381	C(3)-C(2)-C(1)	120.5	119.9	119.9	119.8
C(4)-C(5)	1.386	1.404	1.401	1.405	C(4)-C(3)-C(2)	120.8	120.6	120.6	120.7
C(5)-C(6)	1.371	1.383	1.380	1.384	C(3)-C(4)-C(5)	118.7	119.3	119.3	119.2
C(5)-N(1)	1.455	1.464	1.470	1.470	C(6)-C(5)-C(4)	122.4	121.8	121.7	121.8
C(7)-O(4)	1.231	1.243	1.235	1.243	C(6)-C(5)-N(1)	118.8	119.0	119.0	119.0
C(7)-C(8)	1.484	1.487	1.489	1.489	C(4)-C(5)-N(1)	118.7	119.2	119.3	119.2
C(8)-N(2)	1.34	1.340	1.336	1.341	C(5)-C(6)-C(1)	120.0	120.0	120.1	120.1
C(8)-C(9)	1.4	1.422	1.420	1.426	O(4)-C(7)-C(1)	120.8	120.9	121.2	120.6
C(9)-N(4)	1.326	1.330	1.327	1.331	O(4)-C(7)-C(8)	115.8	115.8	116.4	115.5
C(9)-C(10)	1.495	1.507	1.506	1.509	C(1)-C(7)-C(8)	123.4	123.2	122.4	123.9
C(10)-F(1)	1.317	1.346	1.348	1.345	N(2)-C(8)-C(9)	107.6	107.7	107.5	107.4
C(10)-F(2)	1.322	1.344	1.345	1.345	N(2)-C(8)-C(7)	125.0	125.0	124.1	125.7
C(10)-F(3)	1.326	1.344	1.343	1.344	C(9)-C(8)-C(7)	127.4	127.3	128.2	127.0
N(1)-O(1)	1.217	1.232	1.226	1.227	N(4)-C(9)-C(8)	109.3	108.8	108.7	108.7
N(1)-O(2)	1.216	1.232	1.226	1.227	N(4)-C(9)-C(10)	118.2	120.2	120.2	119.5
N(2)-N(3)	1.312	1.321	1.319	1.317	C(8)-C(9)-C(10)	132.4	131.0	131.1	131.8
N(3)-N(4)	1.319	1.327	1.323	1.326	F(1)-C(10)-F(2)	106.1	108.2	107.8	108.1
					F(1)-C(10)-F(3)	107.1	107.9	107.6	107.6
					F(2)-C(10)-F(3)	107.6	107.9	107.5	107.6
					F(1)-C(10)-C(9)	113.2	110.7	110.9	111.5
					F(2)-C(10)-C(9)	112.2	111.5	111.8	111.5
					F(3)-C(10)-C(9)	110.4	110.5	110.9	110.3

Parameter	Dihedral (º)			
	Exp	Calculated (B3LYP)		
	DRX	6-31g (d.p)	6-311++g (d.p)	cc-PVDZ
C(2)-C(1)-C(7)-(C8)	174.7	177.1	175.3	-180.0
C(1)-C(7)-C(8)-(C9)	169.9	161.5	154.3	-180.0

O(1)-N(1)-O(2)	122.9	124.6	124.6	124.8
O(1)-N(1)-C(5)	118.5	117.9	117.9	117.8
O(2)-N(1)-C(5)	118.6	117.5	117.5	117.3
N(3)-N(2)-C(8)	103.3	103.5	103.8	103.8
N(2)-N(3)-N(4)	117.1	116.9	116.6	117.0
N(3)-N(4)-C(9)	102.7	103.1	103.4	103.2

Table S8. Experimental and Calculated geometrical parameters of **3.**

Parameter	Bond lengths (Å)				Parameter	Angles (°)			
	Exp	Calculated (B3LYP)				Exp[b]	Calculated (B3LYP)		
	DRX	6-31g (d.p)	6-311++g (d.p)	cc-PVDZ		DRX	6-31g (d.p)	6-311++g (d.p)	cc-PVDZ
C(1)-C(2)	1.405	1.427	1.423	1.430	C(2)-C(1)-C(6)	118.1	118.5	118.5	118.4
C(1)-C(6)	1.402	1.417	1.415	1.419	C(2)-C(1)-C(7)	118.9	118.0	118.5	117.7
C(1)-C(7)	1.458	1.462	1.461	1.466	C(6)-C(1)-C(7)	123.0	123.6	123.0	123.9
C(2)-O(1)	1.355	1.337	1.339	1.336	O(1)-C(2)-C(3)	118.3	117.7	117.6	117.7
C(2)-C(3)	1.381	1.406	1.402	1.409	O(1)-C(2)-C(1)	122.0	123.0	123.1	123.1
C(3)-C(4)	1.369	1.382	1.381	1.384	C(3)-C(2)-C(1)	119.7	119.2	119.2	119.2
C(4)-C(5)	1.389	1.412	1.410	1.414	C(4)-C(3)-C(2)	120.4	120.3	120.3	120.5
C(5)-C(6)	1.375	1.386	1.383	1.388	C(3)-C(4)-C(5)	121.7	121.9	121.9	121.8
C(5)-C(11)	1.509	1.510	1.510	1.510	C(6)-C(5)-C(4)	117.7	117.8	117.7	117.8
C(7)-O(2)	1.232	1.246	1.237	1.245	C(6)-C(5)-C(11)	121.2	121.7	121.8	121.8
C(7)-C(8)	1.486	1.492	1.495	1.494	C(4)-C(5)-C(11)	121.0	120.5	120.6	120.5
C(8)-N(3)	1.336	1.339	1.335	1.341	C(5)-C(6)-C(1)	122.3	122.3	122.3	122.4
C(8)-C(9)	1.397	1.421	1.419	1.426	O(2)-C(7)-C(1)	121.8	121.8	122.2	121.5
C(9)-N(1)	1.324	1.331	1.327	1.332	O(2)-C(7)-C(8)	115.6	115.0	115.6	114.7
C(9)-C(10)	1.483	1.505	1.504	1.508	C(1)-C(7)-C(8)	122.6	123.2	122.3	123.8
C(10)-F(1)	1.307	1.347	1.348	1.344	N(3)-C(8)-C(9)	107.4	107.7	107.5	107.4
C(10)-F(3)	1.309	1.346	1.345	1.346	N(3)-C(8)-C(7)	124.9	125.2	124.2	126.0
C(10)-F(2)	1.324	1.344	1.346	1.347	C(9)-C(8)-C(7)	127.5	127.0	128.0	126.6
N(1)-N(2)	1.312	1.327	1.322	1.325	N(1)-C(9)-C(8)	109.3	108.9	108.9	108.8
N(2)-N(3)	1.321	1.324	1.323	1.321	N(1)-C(9)-C(10)	119.5	120.2	120.2	119.7
					C(8)-C(9)-C(10)	131.3	130.9	130.9	131.5
					F(1)-C(10)-F(3)	108.4	107.8	107.5	107.4
					F(1)-C(10)-F(2)	106.1	108.1	107.8	108.1
					F(3)-C(10)-F(2)	104.9	107.7	107.4	107.5
					F(1)-C(10)-C(9)	112.3	110.8	111.0	112.0
					F(3)-C(10)-C(9)	112.0	110.4	111.0	110.3
					F(2)-C(10)-C(9)	112.7	111.7	112.0	111.3

Parameter	Dihedral (º)			
	Exp	Calculated (B3LYP)		
	DRX	6-31g (d.p)	6-311++g (d.p)	cc-PVDZ

					N(2)-N(1)-C(9)	103.5	103.0	103.3	103.1
C(2)-C(1)-C(7)-(C8)	170.8	176.5	175.0	178.5	N(1)-N(2)-N(3)	116.0	116.9	116.6	117.0
C(1)-C(7)-C(8)-(C9)	151.0	156.3	148.2	164.3	N(2)-N(3)-C(8)	103.9	103.5	103.7	103.7

Table S9. Experimental and Calculated geometrical parameters of **4**.

Parameter	Bond lengths (Å)				Parameter	Angles (°)			
	Exp	Calculated (B3LYP)				Exp[b]	Calculated (B3LYP)		
	DRX	6-31g (d.p)	6-311++g (d.p)	cc-PVDZ		DRX	6-31g (d.p)	6-311++g (d.p)	cc-PVDZ
C(1)-C(2)	1.410	1.429	1.425	1.432	C(2)-C(1)-C(6)	118.4	118.7	118.7	118.6
C(1)-C(6)	1.409	1.415	1.413	1.417	C(2)-C(1)-C(7)	119.6	118.0	118.5	117.7
C(1)-C(7)	1.453	1.467	1.466	1.471	C(6)-C(1)-C(7)	122.0	123.3	122.8	123.7
C(2)-O(1)	1.338	1.335	1.337	1.334	O(1)-C(2)-C(3)	116.6	117.5	117.3	117.4
C(2)-C(3)	1.397	1.407	1.403	1.409	O(1)-C(2)-C(1)	123.8	123.0	123.1	123.1
C(3)-C(4)	1.371	1.383	1.381	1.385	C(3)-C(2)-C(1)	119.6	119.5	119.5	119.4
C(4)-C(5)	1.385	1.404	1.401	1.406	C(4)-C(3)-C(2)	120.5	120.7	120.7	120.9
C(5)-C(6)	1.364	1.380	1.377	1.383	C(3)-C(4)-C(5)	120.1	119.8	119.8	119.7
C(5)-Cl	1.735	1.760	1.759	1.761	C(6)-C(5)-C(4)	120.8	120.9	120.8	120.9
C(7)-O(2)	1.239	1.244	1.236	1.244	C(6)-C(5)-Cl	119.7	119.8	119.9	119.8
C(7)-C(8)	1.49	1.490	1.492	1.492	C(4)-C(5)-Cl	119.4	119.2	119.3	119.2
C(8)-N(3)	1.337	1.340	1.336	1.341	C(5)-C(6)-C(1)	120.5	120.4	120.4	120.5
C(8)-C(9)	1.397	1.422	1.420	1.427	O(2)-C(7)-C(1)	122.0	121.3	121.7	120.9
C(9)-N(1)	1.336	1.330	1.327	1.332	O(2)-C(7)-C(8)	115.5	115.3	115.8	114.9
C(9)-C(10)	1.488	1.506	1.506	1.509	C(1)-C(7)-C(8)	122.5	123.4	122.5	124.2
C(10)-F(1)	1.334	1.344	1.345	1.345	N(3)-C(8)-C(9)	108.1	107.6	107.5	107.3
C(10)-F(3)	1.33	1.346	1.344	1.346	N(3)-C(8)-C(7)	123.6	125.3	124.4	126.0
C(10)-F(2)	1.328	1.345	1.348	1.345	C(9)-C(8)-C(7)	127.9	127.0	128.0	126.7
N(1)-N(2)	1.317	1.327	1.322	1.325	N(1)-C(9)-C(8)	109.3	108.9	108.8	108.8
N(2)-N(3)	1.326	1.3223	1.3207	1.3187	N(1)-C(9)-C(10)	119.5	120.1	120.2	119.3
					C(8)-C(9)-C(10)	131.1	131.0	131.1	131.9
					F(1)-C(10)-F(3)	107.8	107.8	107.4	107.5
					F(1)-C(10)-F(2)	105.8	108.2	107.8	108.2
					F(3)-C(10)-F(2)	107.2	107.9	107.6	107.5
					F(1)-C(10)-C(9)	112.9	111.6	111.9	111.6
					F(3)-C(10)-C(9)	111.5	110.4	110.9	110.2
					F(2)-C(10)-C(9)	111.3	110.8	111.0	111.6

Parameter	Dihedral (º)			
	Exp	Calculated (B3LYP)		
	DRX	6-31g (d.p)	6-311++g (d.p)	cc-PVDZ

					N(2)-N(1)-C(9)	102.6	103.1	103.3	103.2
C(2)-C(1)-C(7)-(C8)	167.0	177.3	175.9	-180.0	N(1)-N(2)-N(3)	117.0	116.9	116.6	117.0
C(1)-C(7)-C(8)-(C9)	158.2	160.2	152.0	-179.9	N(2)-N(3)-C(8)	103.1	103.5	103.8	103.8

Table S10 Experimental and calculated frequencies and tentative assignment of fundamental vibration modes of **1.**

Mode	Experimental[a]		Calculated[b]		Assignment[f]
	IR[c]	Raman[d]	Freq[a]	Int[e]	
ν_1			3660	143	ν(N2—H)
ν_2	3331 (vs)	3330 (23)	3295	316	ν(O1—H)
ν_3	3136 (w)	3136 (4)	3247	4	ν(C6—H)
ν_4		3100 (11)	3220	6	ν(C3—H)
ν_5			3209	13	ν(C5—H)
ν_6		3064 (9)	3189	9	ν(C4—H)
ν_7	1628 (vs)		1691	248	ν(C7—O2); δ(C2—O1—H); ν(C—C)
ν_8	1603 (vs)	1602 (69)	1661	60	ν(C7—O2)
ν_9	1567 (s)	1565 (25)	1628	105	δ(C2—O1—H)
ν_{10}	1517 (s)	1515 (35)	1561	35	δ(N2—H); ν(C9—N1)
ν_{11}	1492 (s)	1492 (47)	1534	117	$\delta(C—H)_{iph}$; δ(O1—H)
ν_{12}	1482 (s)		1532	27	ν(C8—C9)
ν_{13}	1446 (s)	1444 (23)	1494	65	$\delta(C3—H)_{iph}$; $\delta(C4—H)_{iph}$; $\delta(C5—H)_{iph}$
ν_{14}	1426 (vs)	1426 (14)	1461	137	δ(N2—H)
ν_{15}	1392 (sh)		1431	91	δ(O1—H); δ(C6—H)
ν_{16}	1338 (vs)	1338 (10)	1381	62	ν(C8—C9)
ν_{17}	1327 (vs)	1328 (10)	1374	24	ν(C8—N3)
ν_{18}	1321 (vs)	1322 (h)	1362	132	ν(C2—O1); $\delta(C—H)_{iph}$
ν_{19}	1261 (m)		1317	92	δ(C2—O1—H); ν(C1—C6); δ(C6—H); ν_{as}(N1—N2—N3)
ν_{20}	1236 (m)		1280	51	ν(C1—C7); $\delta(C6—H)_{iph}$; $\delta(C3—H)_{oph}$
ν_{21}	1212 (vs)	1212 (13)	1246	160	$\delta(C3—H—H)_{iph}$;$\delta(C5—H)_{oph}$;$\delta(C6—H)_{iph}$ ν_s(N1—N2—N3)
ν_{22}	1187 (vs)	1176 (41)	1227	110	ν(N2—N3)
ν_{23}	1158 (vs)		1218	252	$\nu_{as}(CF_3)$
ν_{24}		1154 (41)	1215	47	$\nu_{as}(CF_3)$
ν_{25}			1190	2	δ(C—H)
ν_{26}	1136 (vs)	1136 (35)	1184	110	ν(N1—N2)
ν_{27}	1120 (sh)	1120 (h)	1153	7	$\delta(C3—H)_{iph}$; $\delta(C3—H)_{oph}$; $\delta(C4—H)_{iph}$; $\delta(C6—H)_{oph}$
ν_{28}	1073 (vs)		1092	190	ν_s(CF3)
ν_{29}	1036 (m)	1036 (41)	1062	4	δ(C4—C5)
ν_{30}	993 (m)	993 (4)	1008	12	δ(C8—N3—N2); δ(C9—N1—N2)
ν_{31}			996	<1	$\gamma(C3—H)_{iph}$; $\gamma(C4—H)_{oph}$; $\gamma(C5—H)_{iph}$; $\gamma(C6—H)_{oph}$
ν_{32}			965	5	$\gamma(C3—H)_{iph}$; $\gamma(C4—H)_{oph}$; $\gamma(C5—H)_{oph}$; $\gamma(C6—H)_{iph}$
ν_{33}	919 (vs)	919 (4)	934	118	δ(C4—C5—C6)
ν_{34}	866 (w)		877	0	$\gamma(C3—H)_{iph}$; $\gamma(C4—H)_{iph}$; $\gamma(C5—H)_{oph}$; $\gamma(C6—H)_{oph}$
ν_{35}	818 (f)	819 (100)	850	78	γ(O1—H)
ν_{36}	808 (w)		839	21	δ(C4—C5—C6); $\delta(C4—H)_{iph}$; $\delta(C6—H)_{iph}$
ν_{37}			810	7	γ(O1—H); $\gamma(C—H)_{iph}$; γ(C7—C8—C9)
ν_{38}	753 (vs)	752 (85)	773	59	$\gamma(C—H)_{iph}$
ν_{39}			758	6	γ(O1—H); $\gamma(C—H)_{iph}$; γ(C8—C9—C10)
ν_{40}	745 (s)		749	13	$\delta s(CF_3)$
ν_{41}			725	36	γ(N2—H)

ν_{42}	690 (s)	690 (h)	695	23	δ(C2—C3—C4); δ(C1—C6—C5)
ν_{43}	681 (s)	679 (44)	693	35	γ(C1—C7—C8); $\gamma(C3—H)_{iph}$; $\gamma(C5—H)_{iph}$; γ(N2—H)
ν_{44}	613 (vw)	613 (15)	618	4	δ(N2—H); δ(C1—C7—C8); γ(N1—N2—N3)
ν_{45}			583	4	$\delta_{as}(CF_3)$
ν_{46}	583 (w)	583 (53)	571	42	γ(N2—H)
ν_{47}	563 (vw)	563 (19)	559	3	γ(N2—H); δ_{as}(CF3); γ(N1—N2—N3)
ν_{48}	542 (vw)	541 (33)	537	1	$\gamma(C—H)_{oph}$
ν_{49}	523 (w)	522 (7)	532	3	$\gamma(C—H)_{iph}$
ν_{50}	487 (w)	489 (7)	500	6	δ(C1—C2—O1)
ν_{51}	435 (vw)	437 (11)	443	7	δ(C7—O2)
ν_{52}	429 (w)	428 (26)	441	2	γ(C2—C1—C6); $\gamma(C3—H)_{iph}$; $\gamma(C6—H)_{iph}$
ν_{53}	407 (vw)	409 (14)	422	1	δ(C8—C9—C10); δ(C2—C1—C7)
ν_{54}			403	<1	$\delta(CF_3)$
ν_{55}		365 (10)	365	4	$\rho_{wag}(CF_3)$; δ(C2—C1—C7)
ν_{56}			275	3	δ(C2—C1—C7)
ν_{57}			265	<1	γ(C2—O1)
ν_{58}			249	2	$\rho_{tw}(CF_3)$
ν_{59}		214 (14)	213	<1	γ(C7—C8—C9)
ν_{60}		187 (11)	171	<1	γ(C8—C9—C10)
ν_{61}			147	<1	γ(C7—O2)
ν_{62}		157 (29)	137	<1	τ(C2—C1—C7—C8)
ν_{63}			100	<1	τ(C1—C7—C8—C9)
ν_{64}			57	<1	$\rho_r(CF_3)$
ν_{65}			40	<1	τ(C2—C1—C7—C8)
ν_{66}			15	<1	τ(C1—C7—C8—C9)

[a]In cm^{-1} [b]B3LYP 6-31g (d,p) [c]vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. [d]Intensity (arbitrary units). [e]Intensity (km/mol) [f]ν, δ, γ, τ, ρ_r, ρ_{tw} and ρ_{wag} represent stretching, in plane deformation, out-of-plane deformation, torsion, rocking, wagging and twisting modes. Iph and oph represent in phase and out-of-phase modes, respectively.

Table S11 Experimental and calculated frequencies and tentative assignment of fundamental vibration modes of **2.**

Mode	Experimental[a]		Calculated[b]		Assignment[f]
	IR[c]	Raman[d]	Freq[a]	Int[e]	
ν_1	3673 (vw)		3654	152	ν(N3—H)
ν_2			3273	25	ν(C6—H)
ν_3			3246	6	ν(C4—H)
ν_4	3271 (m)		3238	428	ν(O3—H)
ν_5	3120 (w)		3225	3	ν(C3—H)
ν_6	1637 (vs)	1642 (5)	1695	314	ν(C7—O4); δ(C2—O3—H); ν(C—C)
ν_7	1617 (s)	1620 (4)	1674	185	ν(C7—O4)
ν_8	1571 (m)	1573 (13)	1636	102	$\nu_{as}(NO_2)$
ν_9			1617	37	δ(C2—O3—H)
ν_{10}	1523 (s)		1561	32	δ(N3—H); ν(C9—N4)
ν_{11}	1515 (s)	1516 (6)	1533	33	ν(C8—C9)
ν_{12}	1493 (m)		1524	183	$\delta(C—H)_{iph}$; δ(O3—H)
ν_{13}			1480	2	ν(C5—C6); ν(C1—C6); δ(C4—H)
ν_{14}	1428 (m)	1427 (3)	1460	134	δ(N3—H)
ν_{15}	1411 (m)		1439	60	δ(O3—H); δ(C6—H)
ν_{16}	1342 (vs)	1343 (100)	1392	431	$\nu_s(NO_2)$
ν_{17}		1337 (45)	1381	118	ν(C8—C9)
ν_{18}	1328 (vs)		1376	89	ν(C8—N3)
ν_{19}	1302 (s)	1303 (25)	1350	72	$\nu(C2—O3); \delta(C—H)_{iph}$
ν_{20}	1277 (s)	1278 (3)	1324	116	$\delta(C2—O3—H); \nu(C1—C6); \delta(C6—H); \nu_{as}(N2—N3—N4)$
ν_{21}	1235 (m)	1233 (3)	1271	65	$\nu(C1—C7); \delta(C6—H)_{iph}; \delta(C3—H)_{oph}$
ν_{22}	1211 (s)		1241	94	$\delta(C3—H)_{iph}; \delta(C6—H)_{iph}; \nu_s(N2—N3—N4)$
ν_{23}	1186 (vs)		1235	197	ν(N2—N3)
ν_{24}	1164 (vs)		1218	242	$\nu_{as}(CF_3)$
ν_{25}			1214	46	$\nu_{as}(CF_3)$
ν_{26}	1150 (vs)		1183	83	ν(N4—N3)
ν_{27}	1127 (m)		1150	17	$\delta(C3—H)_{iph}; \delta(C4—H)_{oph}; \delta(C6—H)_{oph}$
ν_{28}	1114 (w)	1114 (15)	1133	20	$\delta(C4—H)_{iph}; \delta(C6—H)_{iph}$
ν_{29}	1070 (vs)		1089	236	$\nu_s(CF_3)$
ν_{30}	995 (w)	994 (4)	1009	11	δ(C8—N2—N3); δ(C9—N4—N3)
ν_{31}			999	<1	$\gamma(C3—H)_{iph}; \gamma(C4—H)_{oph}$
ν_{32}	948 (s)	948 (1)	970	100	δ(C4—C5—C6)
ν_{33}	938 (w)	935 (2)	959	10	γ(C6—H)
ν_{34}			886	60	γ(O3—H)
ν_{35}	866 (s)	865 (16)	878	53	$\delta_s(NO_2)$
ν_{36}	860 (m)		859	57	$\gamma(C3—H)_{iph}; \gamma(C4—H)_{iph}$
ν_{37}	813 (m)	811 (3)	830	4	$\delta(C4—C5—C6); \delta(C4—H)_{iph}; \delta(C6—H)_{iph}$
ν_{38}			808	<1	$\gamma(O3—H); \gamma(C—H)_{iph}; \gamma(C7—C8—C9)$
ν_{39}	753 (w)	757 (8)	761	7	$\delta(C2—C1—C7); \delta_s(CF_3)$
ν_{40}			754	10	γ(NO2); γ(C6—H); γ(C1—C2—C3)
ν_{41}			747	29	$\gamma(O3—H); \gamma(C—H)_{iph}; \gamma(C8—C9—C10); \gamma(NO_2)$

ν_{42}	731 (s)		743	86	$\delta_s(CF_3)$
ν_{43}			726	32	γ(N3—H)
ν_{44}	691 (w)		690	17	γ(C1—C7—C8); γ(C3—H); γ(N3—H)
ν_{45}	642 (m)	641 (1)	653	17	δ(C1—C6—C5); δ(C2—C3—C4)
ν_{46}	608 (vw)	607 (1)	612	7	γ(N3—H); δ(C1—C7—C8)
ν_{47}			590	35	γ(N3—H)
ν_{48}	570 (vw)	570 (3)	571	<1	γ(N3—H); $\delta_{as}(CF_3)$; γ(N1—N2—N3)
ν_{49}		559 (1)	560	5	$\delta(C3—H)_{iph}$; $\delta(C4—H)_{iph}$; $\delta(C6—H)_{iph}$; $\delta(C5—NO_2)$
ν_{50}	549 (w)	550 (3)	549	4	$\delta_{as}(CF_3)$
ν_{51}	512 (vw)	511 (1)	521	3	$\gamma(C—H)_{iph}$
ν_{52}	488 (vw)	488 (2)	495	<1	δ(C1—C2—O3)
ν_{53}	444 (vw)		447	<1	γ(C2—C1—C6); $\gamma(C3—H)_{Iph}$; $\gamma(C6—H)_{Iph}$
ν_{54}	435 (vw)	435 (<1)	443	8	δ(C7—O3)
ν_{55}	410 (vw)	414 (<1)	414	<1	δ(C8—C9—C10); δ(C2—C1—C7)
ν_{56}			404	<1	$\delta(CF_3)$
ν_{57}		372 (1)	368	6	$\rho_{wag}(CF_3)$; δ(C2—C1—C7)
ν_{58}			358	1	δ(C1—C2—C3); δ(C4—C5—C6)
ν_{59}			316	<1	γ(C1—C2—C3); γ(4—C5—C6)
ν_{60}		290 (5)	292	2	δ(C2—C1—C7); $\delta(C5—NO_2)$
ν_{61}			251	1	$\rho_{tw}(CF_3)$
ν_{62}		220 (5)	233	2	δ(C7—C8—N2)
ν_{63}		182 (6)	204	3	γ(C7—C8—C9)
ν_{64}		161 (8)	165	<1	γ(C8—C9—C10)
ν_{65}			148	<1	γ(C7—O4)
ν_{66}			125	2	γ(C6—H)
ν_{67}			117	2	τ(C2—C1—C7—C8)
ν_{68}			82	1	τ(C1—C7—C8—C9)
ν_{69}			67	<1	$\rho_{tw}(CF_3)$
ν_{70}			55	<1	$\rho_{tw}(CF_3)$
ν_{71}			34	<1	τ(C2—C1—C7—C8)
ν_{72}			15	<1	τ(C1—C7—C8—C9)

[a]In cm^{-1} [b]B3LYP 6-31g (d,p) [c]vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. [d]Intensity (arbitrary units). [e]Intensity (km/mol) [f]ν, δ, γ, τ, ρ_r, ρ_{tw} and ρ_{wag} represent stretching, in plane deformation, out-of-plane deformation, torsion, rocking, wagging and twisting modes. Iph and oph represent in phase and out-of-phase modes, respectively.

Table S12 Experimental and calculated frequencies and tentative assignment of fundamental vibration modes of **3.**

Mode	Experimental[a]		Calculated[b]		Assignment[f]
	IR[c]	Raman[d]	Freq[a]	Int[e]	
ν_1			3661	139	ν(N2—H)
ν_2	3336 (vs)		3296	304	ν(O1—H)
ν_3			3236	3	ν(C6—H)
ν_4			3217	5	ν(C3—H)
ν_5			3177	16	ν(C4—H)
ν_6			3127	14	$\nu_{as}(CH_3)$
ν_7			3092	20	$\nu_{as}(CH_3)$
ν_8	2928 (w)	2931 (21)	3038	38	$\nu_s(CH_3)$
ν_9	1630 (vs)	1631 (53)	1695	191	ν(C7—O2); δ(C2—O1—H); ν(C—C)
ν_{10}	1612 (m)	1612 (11)	1662	80	ν(C7—O2)
ν_{11}	1576 (s)	1576 (100)	1633	131	δ(C2—O1—H)
ν_{12}	1523 (s)	1524 (34)	1560	37	δ(N2—H); ν(C9—N1)
ν_{13}	1495 (m)		1535	148	$\delta(C—H)_{iph}$; δ(O1—H)
ν_{14}		1517 (29)	1532	24	ν(C8—C9)
ν_{15}	1475 (s)	1476 (34)	1514	36	$\delta_{as}(CH_3)$
ν_{16}		1462 (h)	1499	5	$\delta_{as}(CH_3)$
ν_{17}	1427 (vs)		1462	142	δ(N2—H)
ν_{18}		1412 (53)	1457	<1	δ(O—H); δ(C6—H); δ_{as}(CH3)
ν_{19}	1382 (w)	1382 (12)	1435	63	$\delta_s(CH_3)$
ν_{20}			1429	34	$\delta_s(CH_3)$
ν_{21}	1346 (vs)	1347 (40)	1383	136	ν(C8—C9)
ν_{22}		1333 (17)	1376	10	ν(C8—N3)
ν_{23}	1312 (s)	1311 (46)	1353	110	ν(C2—O1); $\delta(C—H)_{iph}$
ν_{24}	1267 (m)	1266 (7)	1317	96	ν(C2—O1); ν(C1—C6); δ(C6—H); ν_{as}(N1—N2—N3)
ν_{25}		1241 (24)	1287	55	ν(C1—7); $\delta(3—H)_{iph}$; $\delta(C6—H)_{oph}$
ν_{26}	1234 (w)		1249	113	$\delta(C3—H)_{iph}$; $\delta(C6—H)_{iph}$; ν_s(N1—N2—N3)
ν_{27}		1206 (18)	1231	118	$\delta(CH_3)$; $\delta(C—H)_{iph}$; δ(N2—H)
ν_{28}	1189 (vs)	1190 (8)	1225	83	ν(N2—N3)
ν_{29}	1156 (vs)		1218	252	$\nu_{as}(CF_3)$
ν_{30}			1199	11	$\nu_{as}(CF_3)$
ν_{31}	1127 (vs)	1129 (42)	1183	100	ν(N1—N2)
ν_{32}			1162	8	$\delta(C3—H)_{iph}$; $\delta(C4—H)_{oph}$
ν_{33}	1074 (vs)	1072 (32)	1092	198	$\nu_s(CF_3)$
ν_{34}			1070	3	$\rho_r(CH_3)$
ν_{35}			1032	<1	$\rho_r(CH_3)$
ν_{36}	990 (m)	990 (15)	1008	15	δ(C8—N3—N2); δ(C9—N1—N2)
ν_{37}	979 (vw)	978 (6)	982	1	$\gamma(C3—H)_{iph}$; $\gamma(C4—H)_{oph}$
ν_{38}	950 (s)	949 (11)	966	77	δ(C4—C5—C6)
ν_{39}			906	3	$\gamma(C6—H)_{iph}$; $\gamma(C3—H)_{oph}$
ν_{40}		849 (69)	863	62	δ(C4—C5—C6); $\delta(C4—H)_{iph}$; $\delta(C6—H)_{iph}$
ν_{41}			855	8	$\gamma(O1—H)_{iph}$; $\gamma(C3—H)_{oph}$; $\gamma(C4—H)_{oph}$

ν_{42}	843 (s)		839	112	γ(O1—H)$_{iph}$; γ(C3—H)$_{iph}$; γ(C4—H$_{iph}$
ν_{43}			811	9	γ(O1—H); γ(C—H)$_{iph}$; γ(C8—C9—C10)
ν_{44}	788 (m)	787 (56)	805	10	γ(O1—H); γ(C6—H); γ(C7—C8—C9)
ν_{45}		745 (26)	757	7	γ(C8—C9—C10); γ(C1—C2—C3); δ(C4—H)$_{iph}$; δ(C6—H)$_{oph}$
ν_{46}	742 (s)		748	18	$\delta_s(CF_3)$
ν_{47}	700 (w)		725	39	γ(N2—H)
ν_{48}		684 (42)	697	10	γ(C1—C7—C8); γ(C3—H); γ(N2—H)
ν_{49}	680 (s)		694	26	δ(C1—C6—C5); δ(C2—C3—C4)
ν_{50}		607 (8)	613	5	γ(N2—H); δ(C1—C7—C8)
ν_{51}	579 (vw)	581 (46)	578	17	γ(N2—H)
ν_{52}			564	30	γ(N2—H)
ν_{53}	550 (vw)	550 (45)	551	2	$\delta_{as}(CF_3)$
ν_{54}	529 (m)	529 (13)	538	5	γ(C—H)$_{iph}$
ν_{55}	505 (w)	500 (42)	513	6	δ(C1—C2—O1)
ν_{56}	469 (vw)	469 (43)	472	3	δ(C1—C2—C3); δ(C4—C5—C6)
ν_{57}			447	<1	γ(C1—C2—C3); γ(C4—C5—C6)
ν_{58}	430 (vw)	430 (6)	442	8	δ(C7—O2)
ν_{59}	406 (vw)	400 (5)	426	2	δ(C8—C9—C10); δ(C2—C1—C7)
ν_{60}			403	<1	δ_{as}(CF3)
ν_{61}			370	6	ρ_{tw}(CF3); δ(C2—C1—C7)
ν_{62}		337 (28)	339	1	$\rho_{tw}(CH_3)$; γ(C2—C3—C4); γ(C1—C5—C6)
ν_{63}			331	2	$\rho_{tw}(CH_3)$
ν_{64}		257 (41)	261	2	$\rho_{tw}(CH_3)$
ν_{65}		244 (32)	242	2	$\rho_{tw}(CF_3)$; δ(C7—C8—N3)
ν_{66}		227 (20)	225	<1	$\rho_{tw}(CH_3)$; γ(C7—C8—C9)
ν_{67}			168	<1	γ(C8—C9—C10)
ν_{68}			152	<1	$\rho_r(CH_3)$
ν_{69}			146	<1	γ(C7—O2)
ν_{70}			126	<1	τ(C2—C1—C7—C8)
ν_{71}			95	<1	τ(C1—C7—C8—C9)
ν_{72}			84	<1	$\rho_r(CH_3)$
ν_{73}			56	<1	$\rho_r(CF_3)$
ν_{74}			38	<1	τ(C2—C1—C7—C8)
ν_{75}			16	<1	τ(C1—C7—C8—C9)

[a]In cm^{-1} [b]B3LYP 6-31g (d,p) [c]vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. [d]Intensity (arbitrary units). [e]Intensity (km/mol) [f]ν, δ, γ, τ, ρ_r, ρ_{tw} and ρ_{wag} represent stretching, in plane deformation, out-of-plane deformation, torsion, rocking, wagging and twisting modes. Iph and oph represent in phase and out-of-phase modes, respectively.

Table S13 Experimental and calculated frequencies and tentative assignment of fundamental vibration modes of **4**.

Mode	Experimental[a]		Calculated[b]		Assignment[f]
	IR[c]	Raman[d]	Freq[a]	Int[e]	
ν_1			3658	147	ν(N2—H)
ν_2	3334 (s)		3292	330	ν(O1—H)
ν_3	3109 (vw)		3261	9	ν(C6—H)
ν_4			3227	2	ν(C3—H)
ν_5		2921 (26)	3213	2	ν(C4—H)
ν_6	1623 (m)	1622 (100)	1691	196	ν(C7—O2); δ(C2—O1—H); ν(C—C)
ν_7	1601 (m)	1603 (4)	1654	65	ν(C7—O2)
ν_8	1560 (vw)	1568 (28)	1621	89	δ(C2—O1—H)
ν_9	1524 (w)	1520 (12)	1561	33	δ(N2—H); ν(C9—N1)
ν_{10}	1497 (vw)		1531	46	ν(C8—C9)
ν_{11}	1460 (m)	1459 (17)	1516	218	δ(O2—H); $\delta(C—H)_{iph}$
ν_{12}	1427 (m)		1460	134	δ(N2—H)
ν_{13}		1403 (24)	1458	14	δ(C1—C6—C5)
ν_{14}	1357 (vw)	1355 (4)	1423	98	δ(O1—H); δ(C6—H)
ν_{15}		1335 (25)	1379	48	ν(C8—C9)
ν_{16}	1341 (w)		1372	138	ν(C8—N3)
ν_{17}	1310 (w)		1345	76	ν(C2—O1); $\delta(C—H)_{iph}$
ν_{18}	1264 (w)		1313	90	δ(C2—O1—H); ν(C1—C6); δ(C6—H); ν_{as}(N1—N2—N3)
ν_{19}	1193 (m)		1274	75	ν(C1—C7); $\delta(C6—H)_{iph}$; $\delta(C3—H)_{oph}$
ν_{20}	1173 (m)		1239	165	$\delta(C3—H)_{iph}$; $\delta(C6—H)_{iph}$; ν_s(N1—N2—N3)
ν_{21}			1230	152	ν(N2—N3)
ν_{22}	1159 (m)		1219	256	$\nu_{as}(CF_3)$
ν_{23}			1209	3	$\nu_{as}(CF_3)$
ν_{24}	1128 (m)	1129 (16)	1184	87	ν(N1—N2)
ν_{25}			1157	11	$\delta(C3—H)_{iph}$; $\delta(C4—H)_{oph}$
ν_{26}	1097 (vw)	1093 (11)	1120	39	ν(C5—Cl)
ν_{27}	1075 (m)	1069 (2)	1092	208	$\nu_s(CF_3)$
ν_{28}	991 (w)		1009	14	δ(C8—N3—N2); δ(C9—N1—N2)
ν_{29}			975	0	$\gamma(C3—H)_{iph}$; $\gamma(C4—H)_{oph}$
ν_{30}	938 (m)	932 (1)	949	85	δ(C4—C5—C6)
ν_{31}	879 (vw)		908	6	γ(C6—H)
ν_{32}			855	15	$\gamma(O1—H)_{oph}$; $\gamma(C3—H)_{iph}$; $\gamma(C4—H)_{iph}$
ν_{33}			844	36	δ(C4—C5—C6); $\delta(C4—H)_{iph}$; $\delta(C6—H)_{iph}$
ν_{34}	824 (w)	822 (35)	841	110	γ(O1—H); $\gamma(C3—H)_{iph}$; $\gamma(C4—H)_{iph}$
ν_{35}			807	3	γ(O1—H); $\delta(C—H)_{iph}$; γ(C7—C8—C9)
ν_{36}	749 (w)	750 (17)	764	17	δ(C2—C1—C7); $\delta_s(CF_3)$
ν_{37}			748	27	γ(O1—H); $\gamma(C—H)_{oph}$; γ(C8—C9—C10)
ν_{38}	741 (m)		744	60	$\delta_s(CF_3)$
ν_{39}	695 (vw)		725	39	γ(N2—H)
ν_{40}	667 (vw)	671 (14)	689	7	γ(C1—C7—C8); γ(C3—H); γ(N2—H)
ν_{41}	645 (w)	646 (6)	659	23	δ(C1—C6—C5); δ(C2—C3—C4)

ν_{42}	598 (vw)	604 (9)	611	7	γ(N2—H); δ(C1—C7—C8)
ν_{43}	579 (vw)	573 (16)	580	37	γ(N2—H)
ν_{44}			568	5	γ(N2—H); δ_{as}(CF3); γ(N1—N2—N3)
ν_{45}		549 (25)	550	1	$\delta_{as}(CF_3)$
ν_{46}	526 (vw)	529 (3)	531	7	$\gamma(C—H)_{iph}$
ν_{47}	504 (vw)	501 (40)	512	6	δ(C1—C2—O1)
ν_{48}			446	0	$\gamma(C2—C1—C6); \gamma(C3—H)_{iph}; \gamma(C6—H)_{iph}$
ν_{49}	433 (vw)	432 (9)	444	9	δ(C7—O2)
ν_{50}	408 (vw)	404 (2)	427	2	δ(C8—C9—C10); δ(C2—C1—C7)
ν_{51}			404	<1	$\delta(CF_3)$
ν_{52}		373 (11)	376	2	δ(C1—C2—C3); δ(C4—C4—C5)
ν_{53}		364 (7)	369	4	$\rho_{wag}(CF_3)$; δ(C2—C1—C7)
ν_{54}		337 (14)	335	<1	γ(C1—C2—C3); δ(C4—C5—C6)
ν_{55}		304 (5)	310	1	δ(C2—C1—C7); δ(C5—Cl)
ν_{56}			258	1	δ(C7—C8—N3)
ν_{57}			238	2	$\rho_{tw}(CF_3)$
ν_{58}			211	1	γ(C7—C8—C9)
ν_{59}			163	<1	γ(C8—C9—C10)
ν_{60}		148 (8)	146	<1	γ(C7—O2)
ν_{61}			131	<1	τ(C2—C1—C7—C8)
ν_{62}		122 (50)	121	<1	τ(C1—C7—C8—C9)
ν_{63}			87	<1	$\rho_r(CF_3)$
ν_{64}			61	<1	$\rho_r(CF_3)$
ν_{65}			37	<1	τ(C2—C1—C7—C8)
ν_{66}			15	<1	τ(C1—C7—C8—C9)

[a]In cm^{-1} [b]B3LYP 6-31g (d,p) [c]vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. [d]Intensity (arbitrary units). [e]Intensity (km/mol) [f]ν, δ, γ, τ, ρ_r, ρ_{tw} and ρ_{wag} represent stretching, in plane deformation, out-of-plane deformation, torsion, rocking, wagging and twisting modes. Iph and oph represent in phase and out-of-phase modes, respectively.

Table S14. Experimental and calculated electronic spectra (in nm) for **1** – **4**, and tentative assignment of the absorption bands.

Comp.	Exp.[a, b]	Calc.[a,c]	*f*[d]	Assignment	%
1	212	201	0,2240	HOMO-3 → LUMO	30
				HOMO-1 → LUMO	32
		207	0,1183	HOMO-3 → LUMO	74
	269	249	0,2232	HOMO-1 → LUMO	94
	361	314	0,1305	HOMO → LUMO	100
2	250	242	0,3539	HOMO-1 → LUMO	82
	322	299	0,0756	HOMO → LUMO	74
3	217	208	0,1689	HOMO-3 → LUMO	38
	271	251	0,2130	HOMO-1 → LUMO	92
	369	326	0,1236	HOMO → LUMO	100
4	221	205	0,1656	HOMO-3 → LUMO	47
		212	0,1681	HOMO-3 → LUMO	45
	268	247	0,1820	HOMO-1 → LUMO	86
	372	328	0,1207	HOMO → LUMO	100

[a]In nm. [b]Diffuse Reflectance. [c]CAM-B3LYP/6-31+g (d,p). [d]Oscillator strength in atomic units.

Table S15. Calculated frontier MO energies and ΔHOMO-LUMO gaps (eV) for **1** – **4**.

	HOMO	LUMO	ΔE_{H-L} CAM-B3LYP/ 6-31+g(d,p)	ΔE_{H-L} B3LYP/ 6-31g(d,p)
1	-8.1030	-1.4838	6.62	3.94
2	-8.9003	-2.0417	6.86	4.17
3	-7.8510	-1.4232	6.43	3.78
4	-8.0989	-1.7388	6.36	3.74

Table S16. Natural Population Analysis for **1** and **4**.

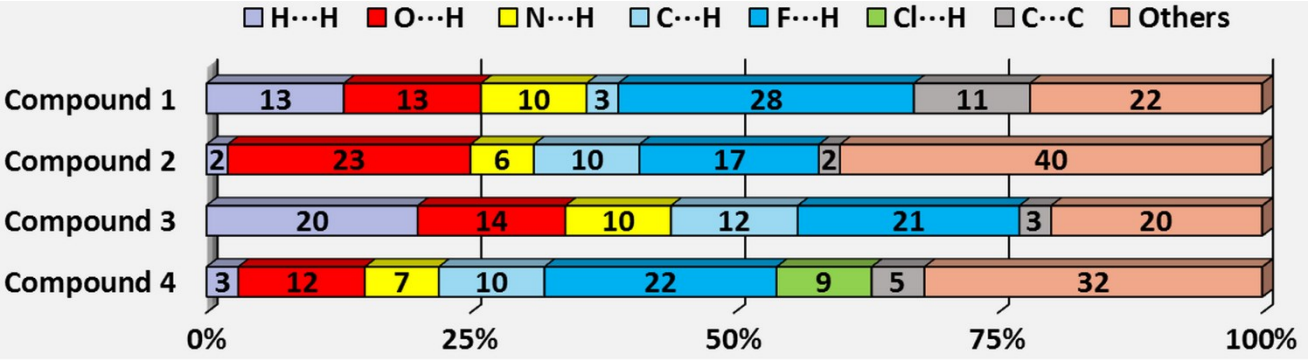
Atom	NPA					
	Monomers DRX		Dimers DRX			
	1	**4**	**1**		**4**	
			#1	**#2**	**#1**	**#2**
C1	-0.233	-0.216	-0.233	-0.235	-0.214	-0.220
C2	0.414	0.408	0.413	0.417	0.408	0.414
C3	-0.238	-0.212	-0.242	-0.237	-0.214	-0.205
C4	-0.126	-0.135	-0.130	-0.120	-0.138	-0.129
C5	-0.210	-0.057	-0.210	-0.207	-0.056	-0.056
C6	-0.121	-0.149	-0.115	-0.118	-0.145	-0.148
C7	0.537	0.536	0.538	0.553	0.538	0.554
C8	0.074	0.070	0.071	0.072	0.066	0.069
C9	0.039	0.033	0.034	0.037	0.029	0.030
C10	1.158	1.159	1.157	1.157	1.159	1.158
O1	-0.655	-0.612	-0.658	-0.655	-0.614	-0.604
H-(OH)	0.485	0.453	0.485	0.489	0.454	0.455
O2	-0.596	-0.586	-0.599	-0.641	-0.589	-0.637
N1	-0.247	-0.240	-0.246	-0.241	-0.239	-0.235
N2	-0.038	-0.098	-0.029	-0.034	-0.092	-0.094
H-(NH)	0.354	0.407	0.368	0.356	0.424	0.410
N3	-0.271	-0.265	-0.282	-0.265	-0.279	-0.259
F1	-0.363	-0.362	-0.365	-0.366	-0.364	-0.367
F2	-0.365	-0.367	-0.367	-0.369	-0.369	-0.369
F3	-0.364	-0.363	-0.365	-0.358	-0.364	-0.357
H(C3)	0.199	0.200	0.197	0.200	0.199	0.204
H(C4)	0.185	0.188	0.183	0.187	0.186	0.189
H(C5)	0.182		0.180	0.184		
H(C6)	0.203	0.216	0.205	0.204	0.217	0.216
Cl		-0.008			-0.015	-0.005

Table S17. Natural Population Analysis for **2**.

Atom	NPA				
	Monomer DRX	Dimers DRX			
		I		**II**	
		#1	**#2**	**#1**	**#2**
C1	-0.220	-0.220	-0.220	-0.216	-0.216
C2	0.433	0.432	0.433	0.436	0.436
C3	-0.236	-0.231	-0.236	-0.234	-0.234
C4	-0.086	-0.084	-0.085	-0.088	-0.088
C5	0.062	0.064	0.063	0.058	0.058
C6	-0.051	-0.054	-0.051	-0.044	-0.044
C7	0.548	0.550	0.549	0.551	0.551
C8	0.061	0.062	0.063	0.052	0.052
C9	0.046	0.046	0.045	0.043	0.043
C10	1.161	1.161	1.163	1.160	1.160
O3	-0.665	-0.681	-0.665	-0.663	-0.663
H-OH	0.506	0.505	0.506	0.507	0.507
O4	-0.586	-0.591	-0.587	-0.586	-0.586
N3	-0.260	-0.261	-0.259	-0.260	-0.260
N2	-0.002	-0.001	0.006	0.012	0.012
H-NH	0.327	0.327	0.329	0.335	0.335
N4	-0.245	-0.245	-0.254	-0.244	-0.244
F1	-0.362	-0.362	-0.360	-0.364	-0.364
F2	-0.361	-0.362	-0.359	-0.363	-0.363
F3	-0.364	-0.364	-0.371	-0.364	-0.364
H(C3)	0.222	0.232	0.222	0.223	0.223
H(C4)	0.177	0.177	0.177	0.177	0.177
H(C6)	0.168	0.168	0.168	0.171	0.171
N1	0.506	0.506	0.506	0.514	0.514
O1	-0.391	-0.391	-0.390	-0.425	-0.425
O2	-0.388	-0.387	-0.388	-0.389	-0.389

Table S18. Natural Population Analysis of **3**.

Atom	Monomer DRX	NPA	
		Dimers DRX	
		1	
		#1	**#2**
C1	-0,218	-0,217	
C2	0,404	0,401	
C3	-0,217	-0,218	
C4	-0,124	-0,122	
C5	-0,032	-0,028	
C6	-0,127	-0,132	
C7	0,539	0,541	
C8	0,074	0,076	
C9	0,033	0,031	
C10	1,161	1,161	
O1	-0,651	-0,674	
H-OH	0,475	0,481	
O2	-0,592	-0,589	
N1	-0,248	-0,245	
N2	-0,052	-0,040	
H-NH	0,361	0,386	
N3	-0,270	-0,313	
F1	-0,363	-0,364	
F2	-0,367	-0,368	
F3	-0,363	-0,363	
H3	0,187	0,183	
H4	0,172	0,174	
H5	0,000		
H6	0,181	0,182	
C11	-0,544	-0,544	
H11A	0,196	0,197	
H11B	0,193	0,193	
H11C	0,191	0,195	
O1			-0,843
H1A			0,443
H1B			0,422
O2			-0,843
H2A			0,432
H2B			0,406
O3			-0,832
H3A			0,415
H3B			0,414



FigureS1. Relative contributions of selected intermolecular contacts to the Hirshfeld surface area for structures **1** – **4**. Percentages are given on the histogram.

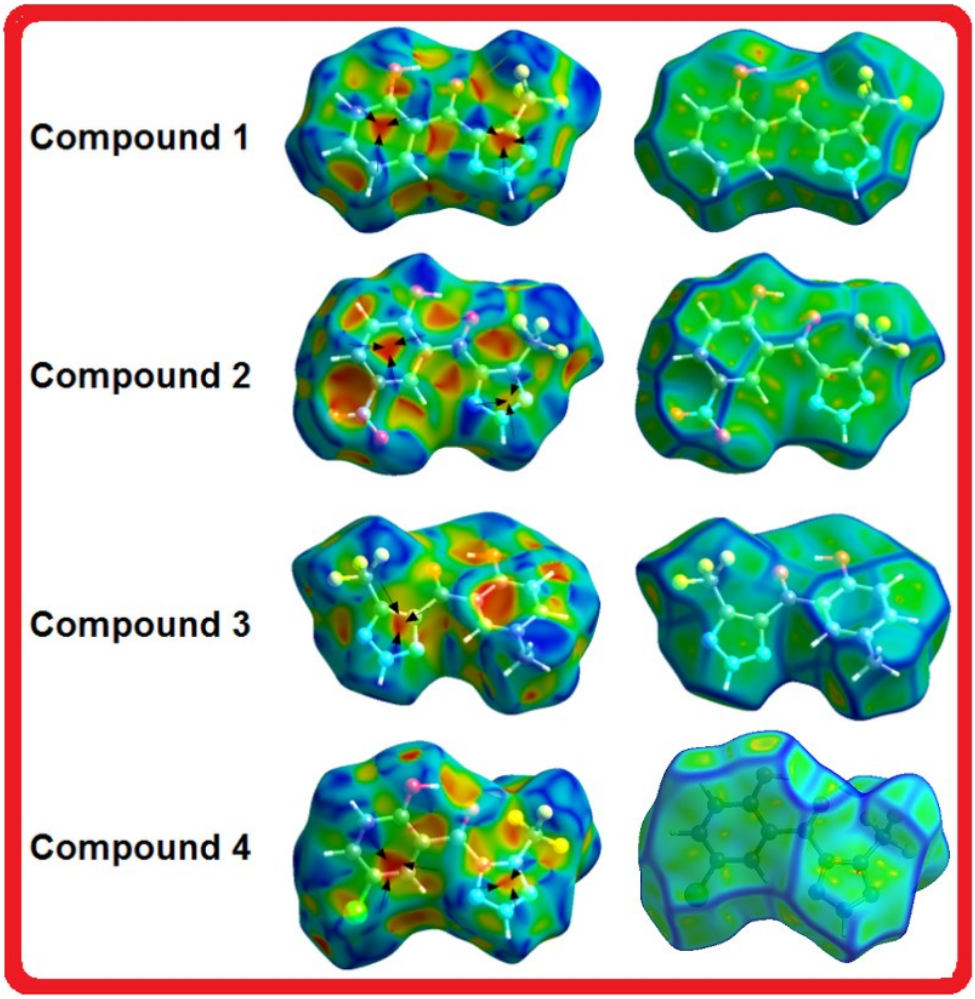


Figure S2. Hirshfeld surfaces for **1**-**4**, mapped over: (a) shape index, highlighting the regions involved in π-stacking interactions, and (b) curvedness**.**

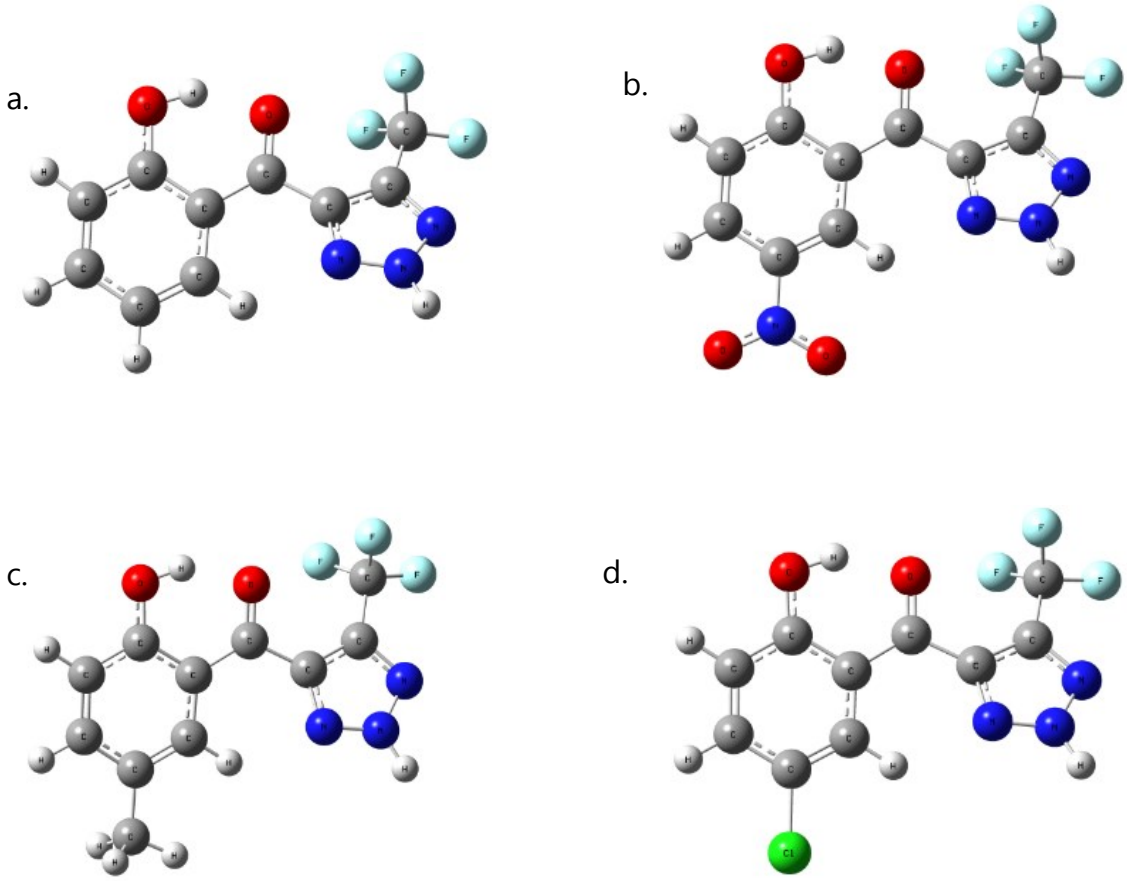


Figure S3. Optimized geometries calculated with B3LYP 6-31g(d.p): a. **1**. b. **2**. c. **3** and d. **4**.

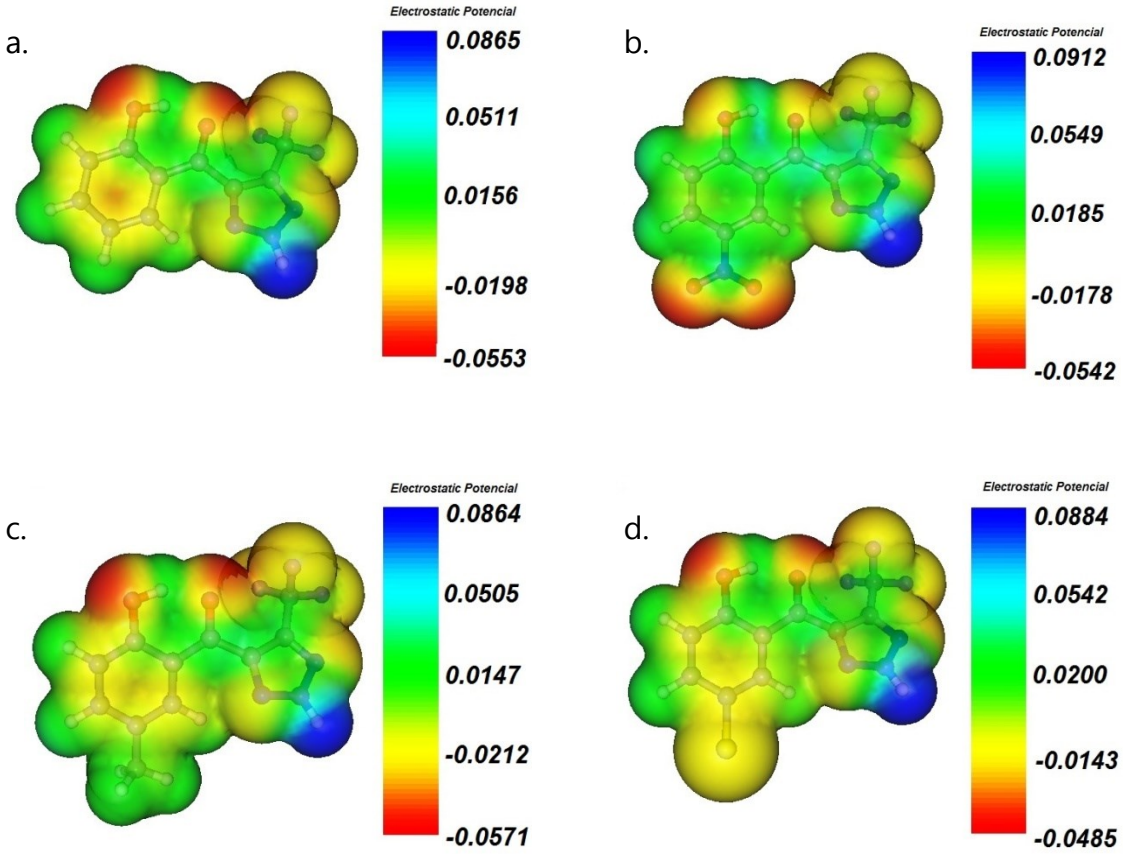
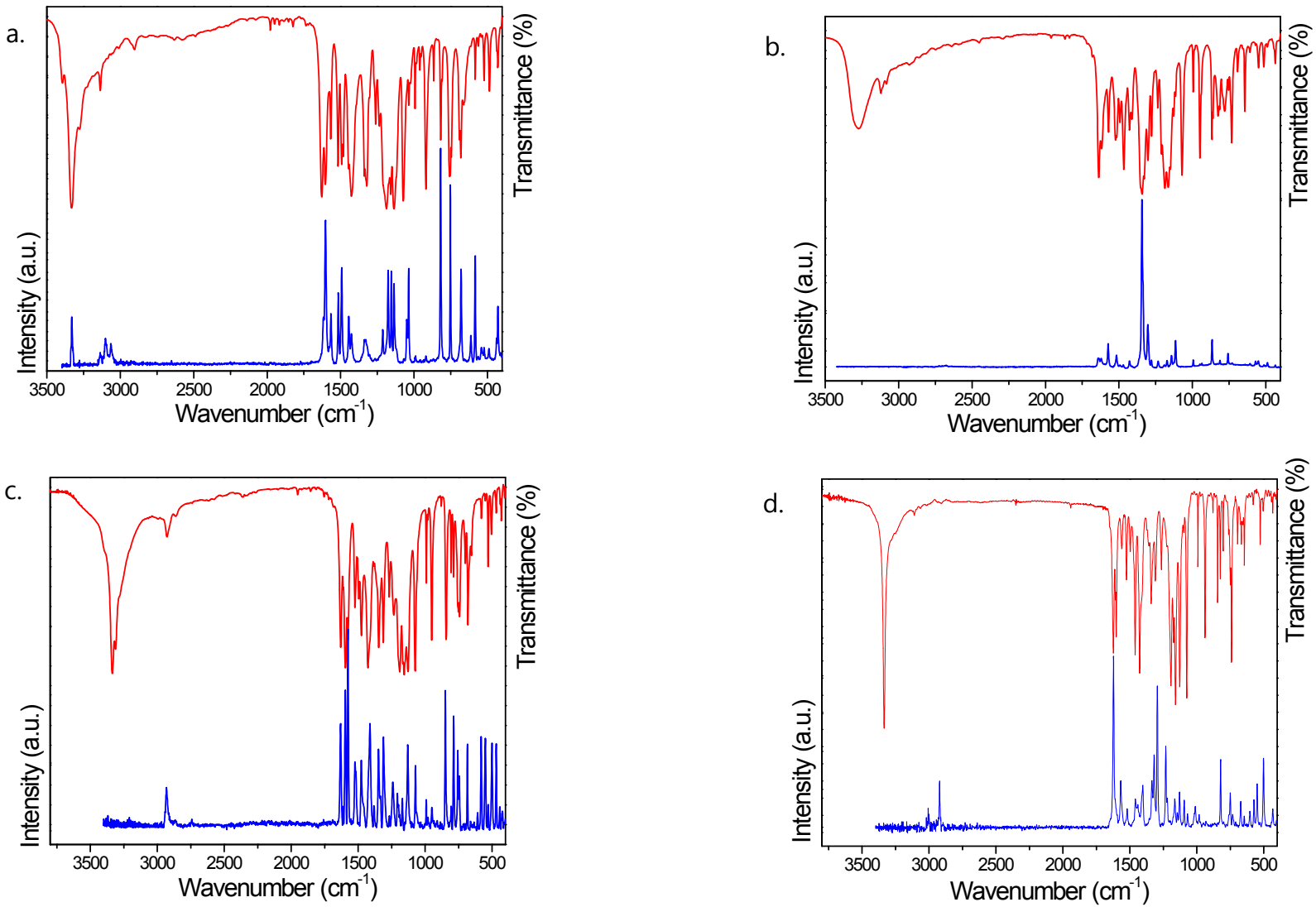
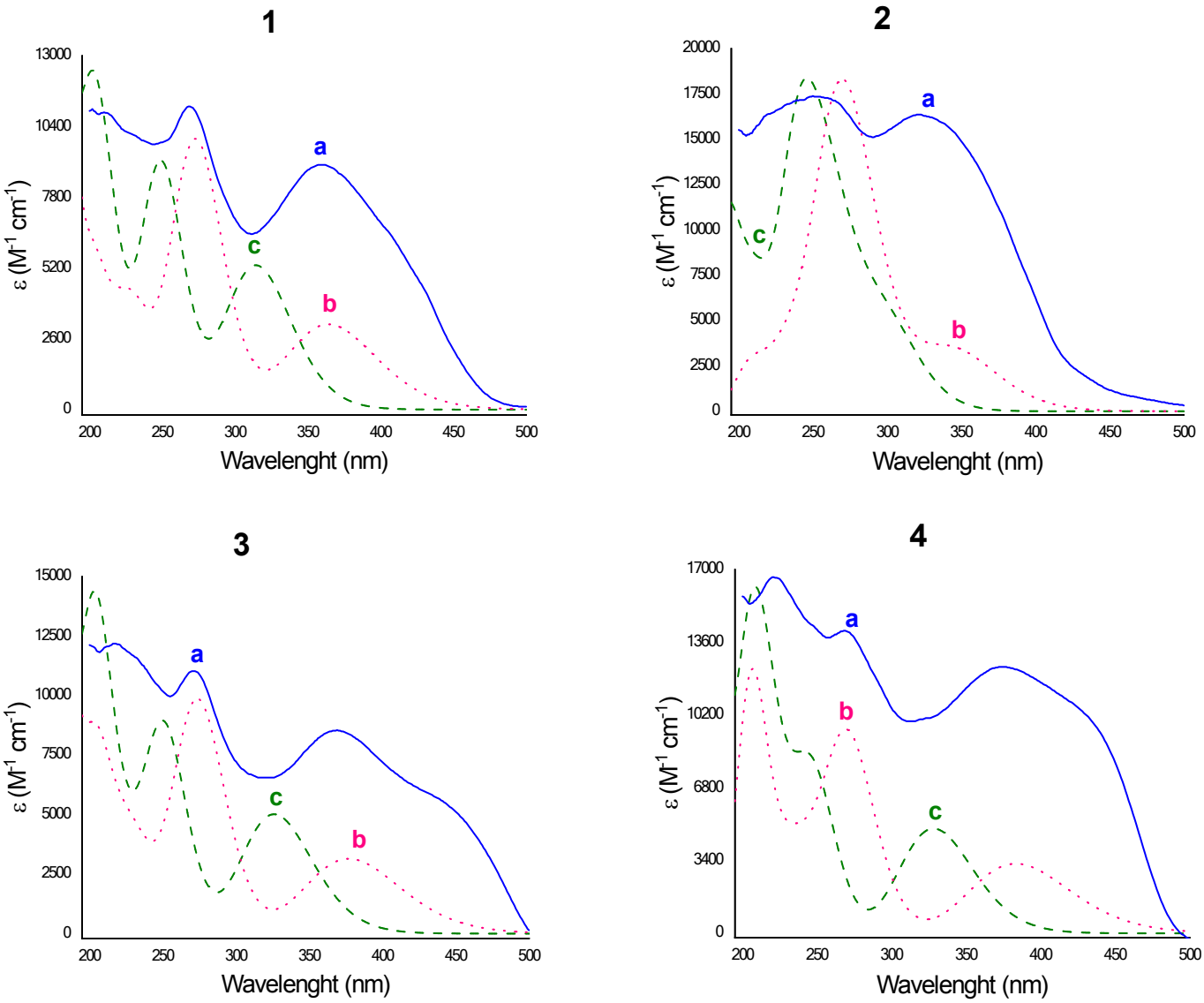


Figure S4. Molecular electrostatic potential maps (MEPs) calculated with B3LYP 6-31g(d.p): a. **1**. b. **2**. c. **3** and d. **4**.



FigureS5. Infrared (upper trace, KBr pellets) and Raman (lower trace) spectra of the solid at room temperature of: a. **1**. b. **2**. c. **3** and d. **4**.



FigureS6. Electronic spectra of **1** – **4**: a) experimental; b) calculated at B3LYP/6-31g(d,p) level of theory; c) calculated at CAM-B3LYP/6-31+g(d,p) level of theory.

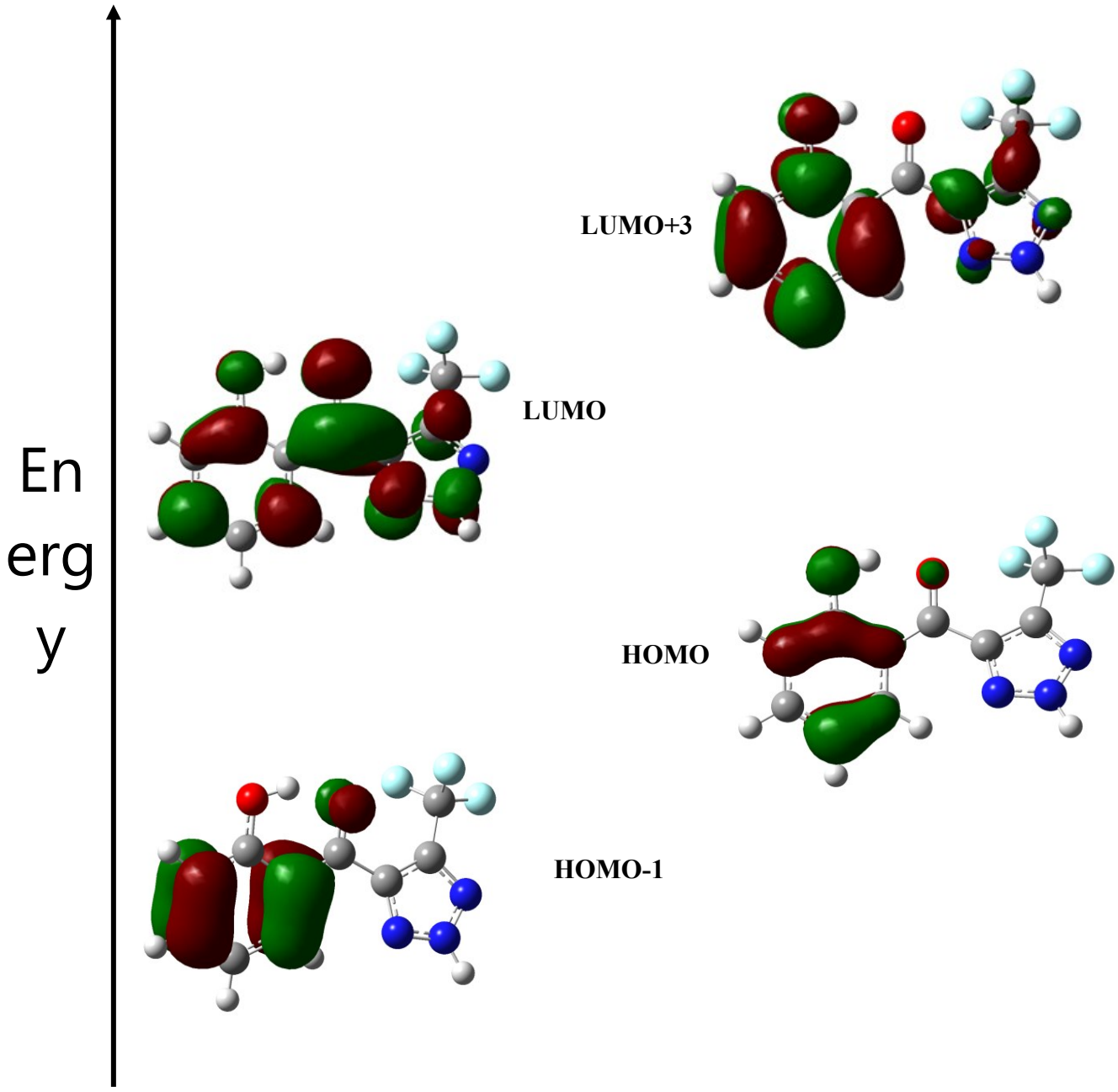


Figure S7. Molecular orbitals involved in the electronic transitions of **1**. The energy scale is only qualitative and does not represent the actual energy of the molecular orbitals.

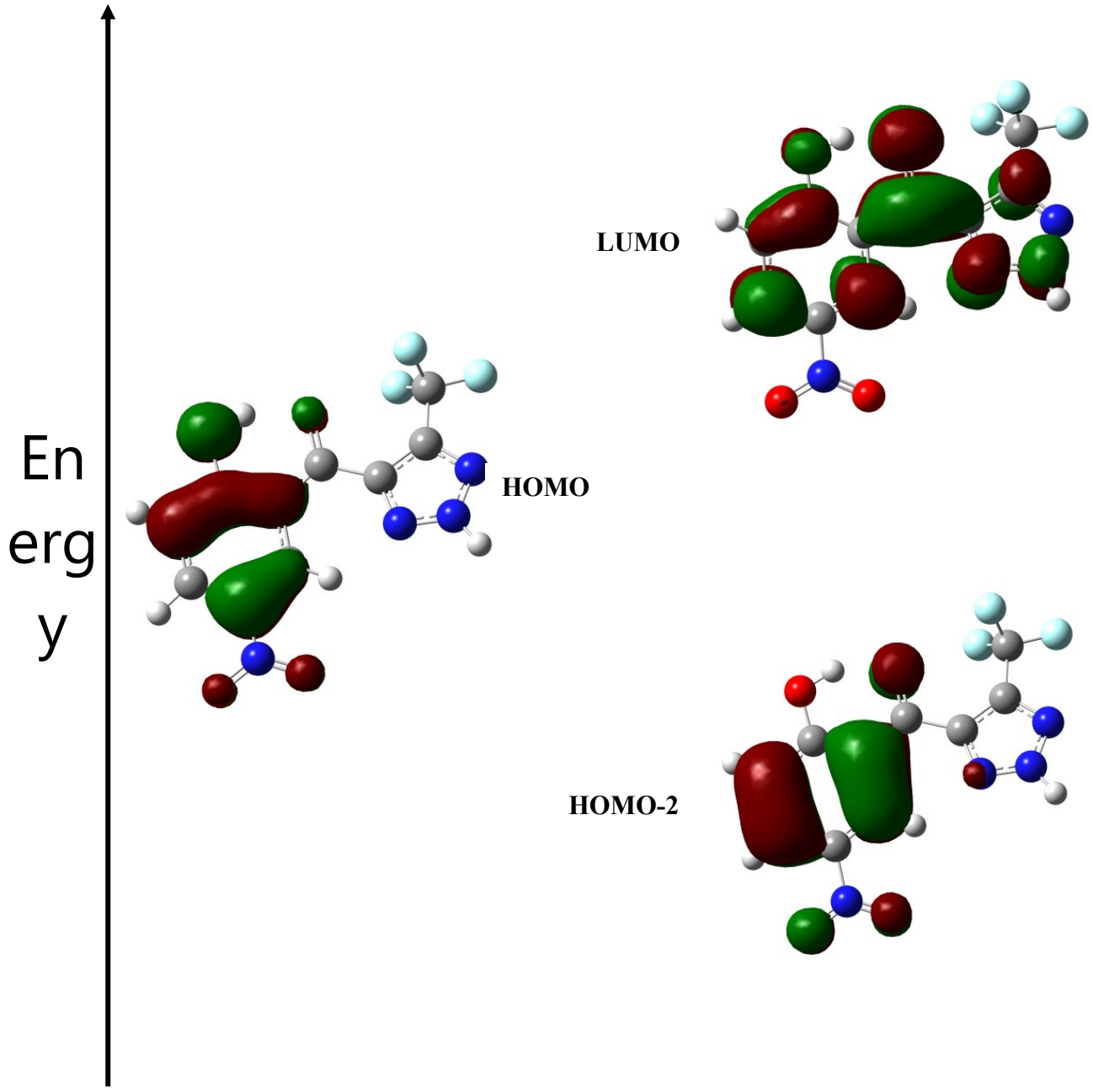


Figure S8. Molecular orbitals involved in the electronic transitions of **2**. The energy scale is only qualitative and does not represent the actual energy of the molecular orbitals.

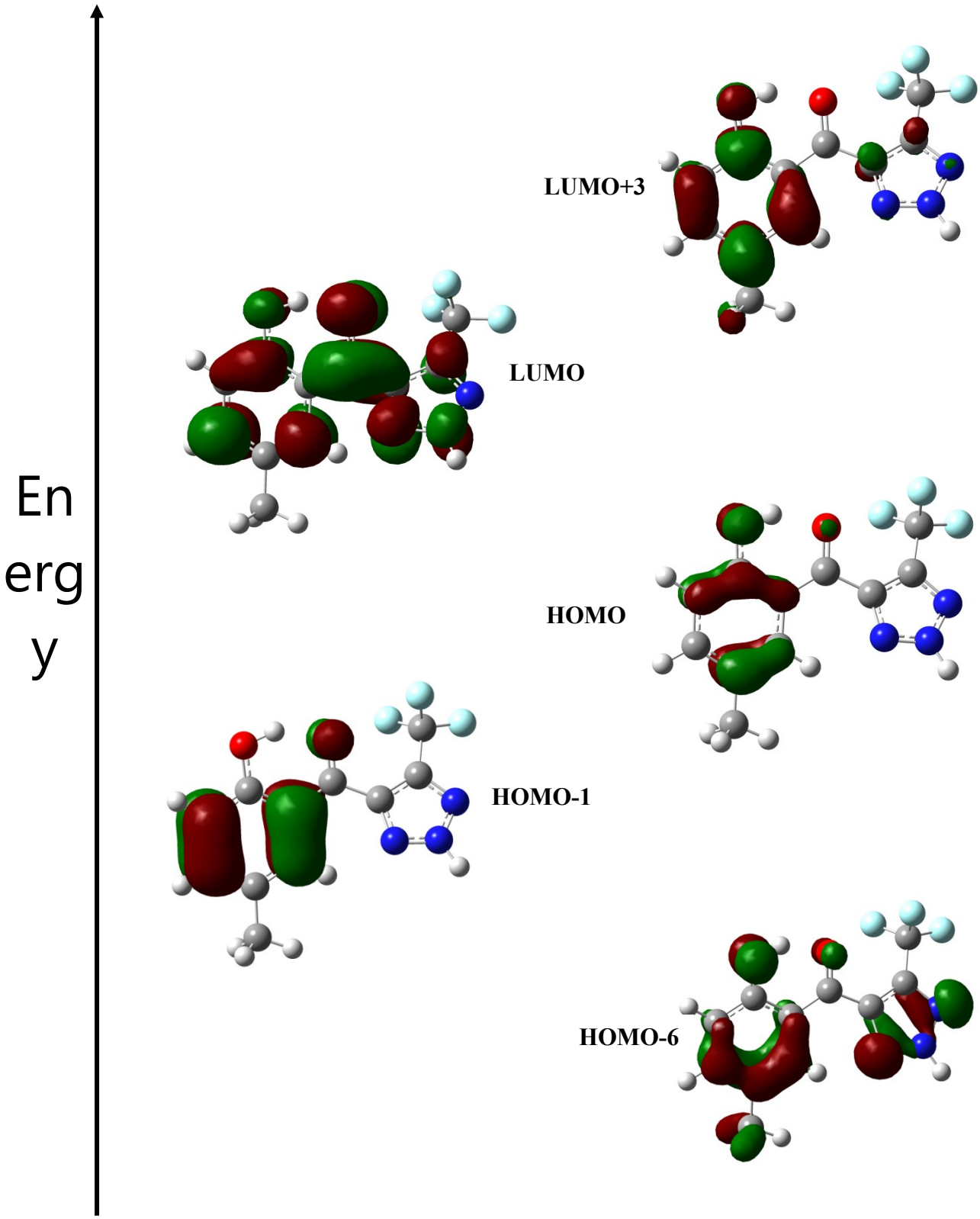


Figure S9. Molecular orbitals involved in the electronic transitions of **3**. The energy scale is only qualitative and does not represent the actual energy of the molecular orbitals.

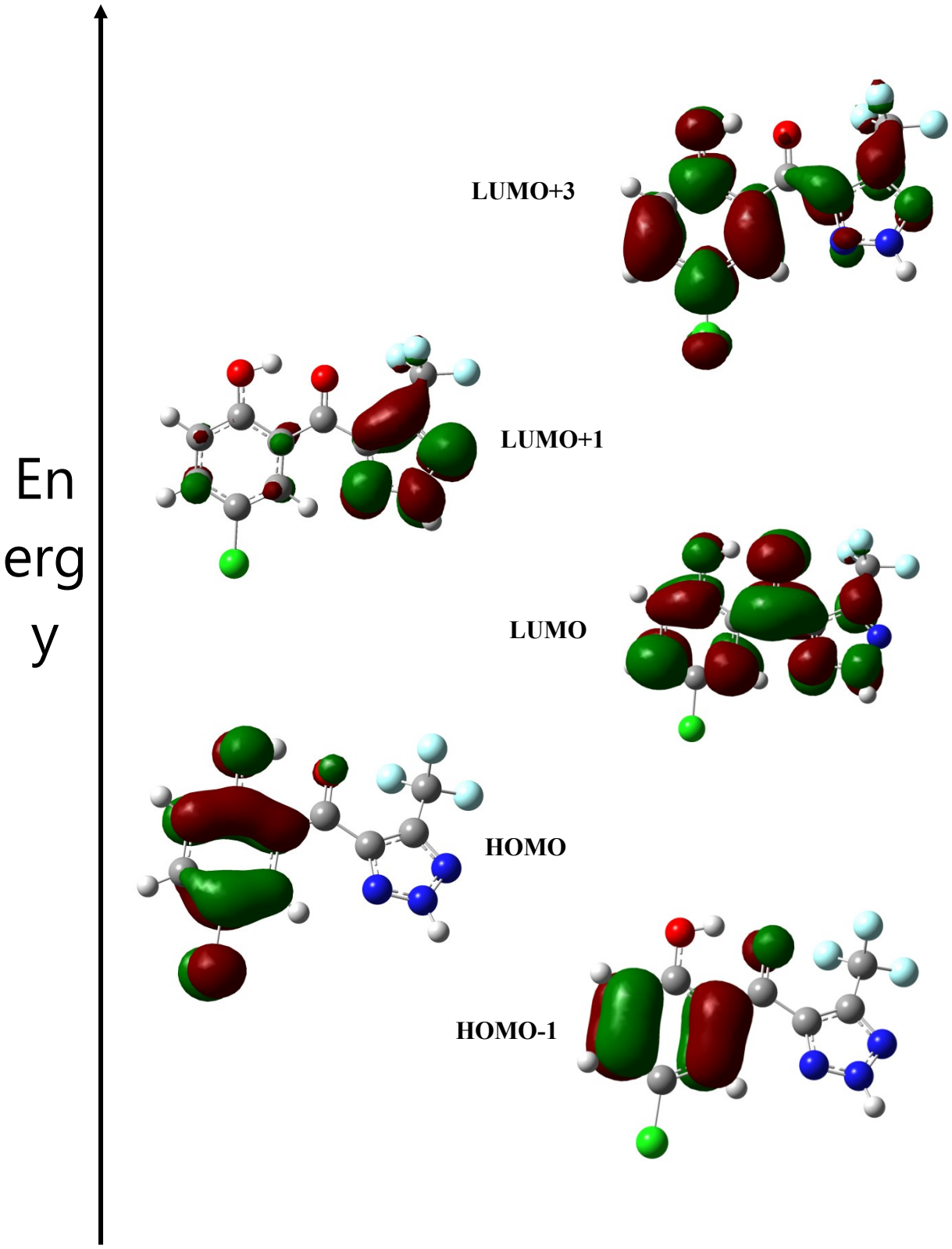
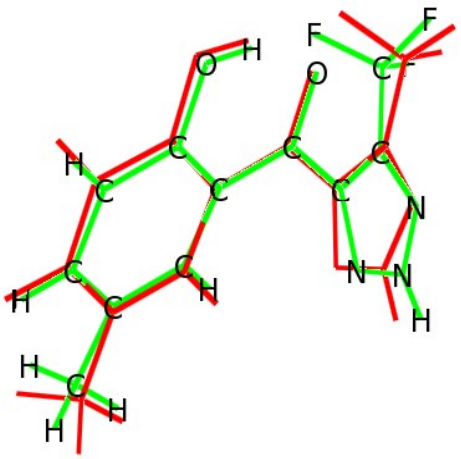


Figure S10. Molecular orbitals involved in the electronic transitions of **4**. The energy scale is only qualitative and does not represent the actual energy of the molecular orbitals.

a.



b.

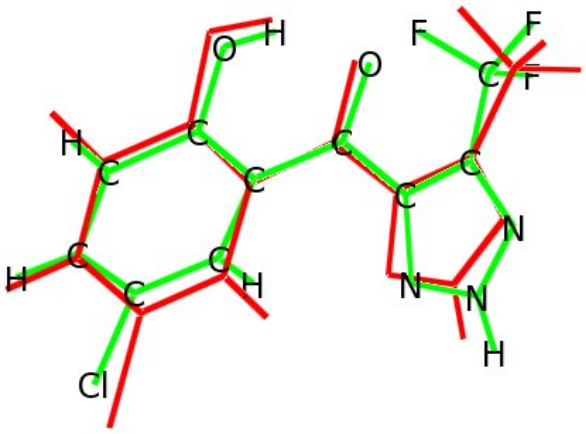
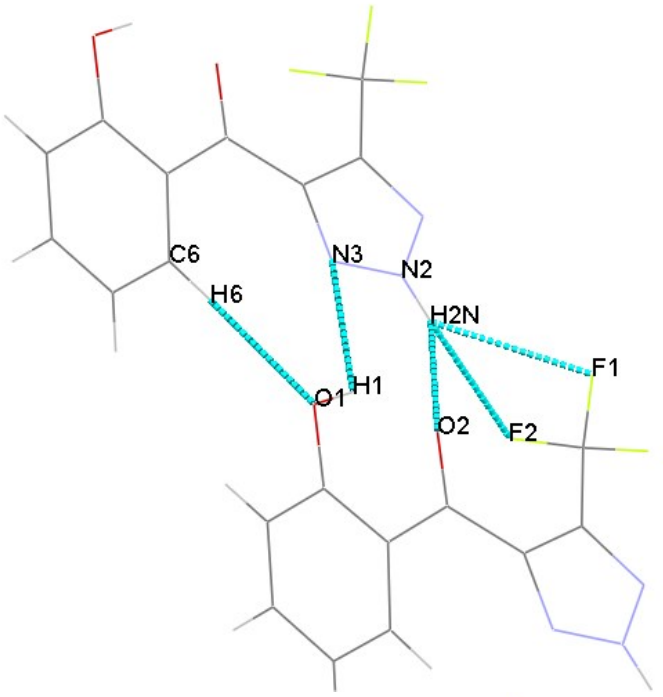


Figure S11. Calculated (B3LYP/cc-PVDZ, red) and experimental geometries (green) for: a. **3** and b. **4**.

a.



b.

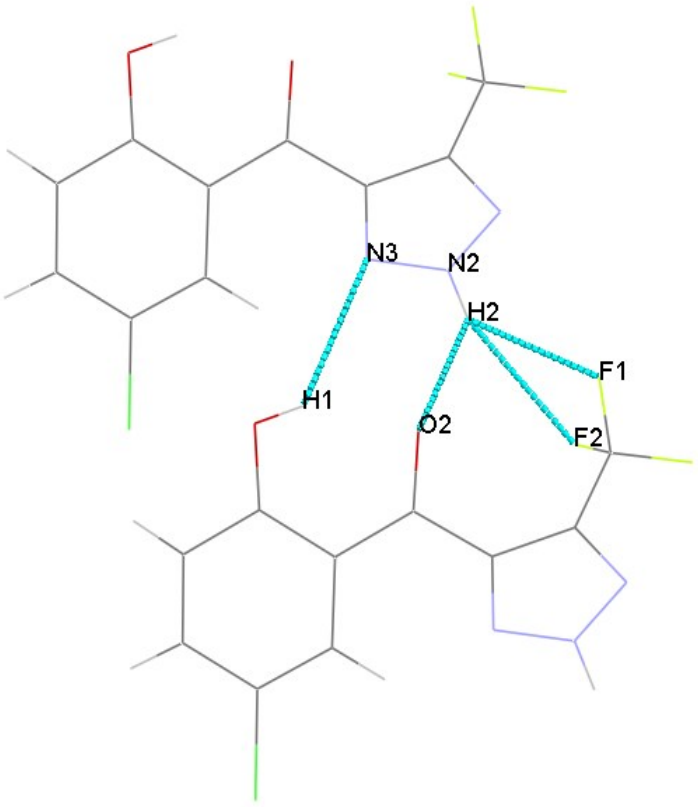


Figure S12. Dimers of: a. **1** and b. **4**.

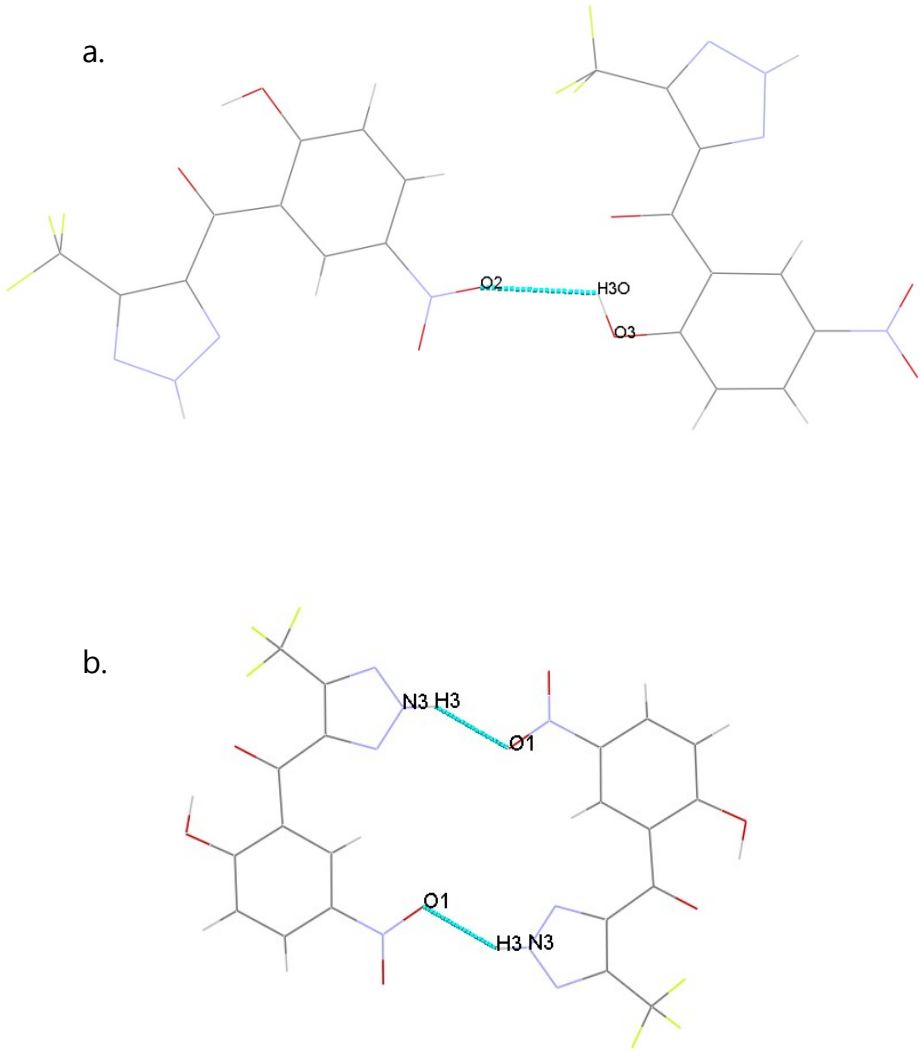


Figure S13. Dimers of **2**. a. I and b. II.

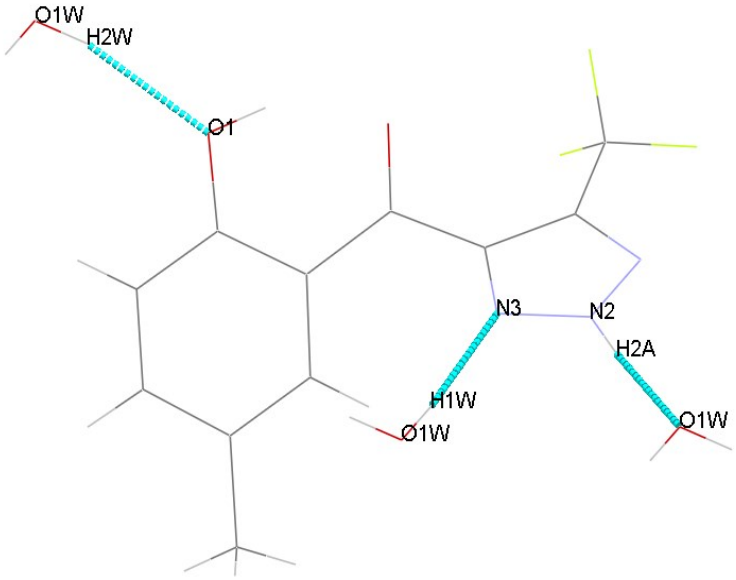


Figure S14. Dimer of **3.**

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