Electronic Supplementary Material (ESI) for New Journal of Chemistry.

The role of non-covalent interactions in some 2-trifluoromethylchromones in the solid state

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Supporting Information

Experimental details and spectroscopic characterization of compounds **1** – **4**.

3-Cyanomethyl-2-trifluoromethylchromone (1). In a round-bottom flask a mixture of 2-bromomethyl-2-trifluoromethylchromone **6** (1.2 g, 3.92 mmol), potassium cyanide (0.3 g, 4.65 mmol) and DMSO (7.0 mL) were stirred at 60 °C for 3 h. The reaction mixture was extracted (4 x 10 mL ethyl acetate) and the organic layer was washed (2 x 10 mL water), dried over Na_2SO_4 and evaporated *in vacuum* to give a brown oil. The product was purified by flash chromatography (hexane/ethyl acetate, 7:3) and the solid recrystallized twice from hot hexane. The white crystalline solid (m.p. 109–112 °C) was suitable for spectroscopic studies. Yield 21 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ= 8.20 (d, 1H, H-5, *J*= 8 Hz), 7.81 (t, 1H, H-7, *J*= 7.5 Hz), 7.56 (d, 1H, H-8, *J*= 8.5 Hz), 7.52 (t, 1H, H-6, *J*= 7.5 Hz), 3.80 ppm (s, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ= 175.4 (C-4), 155.0 (C-8a), 150.5 (q, C-2, J_{CF}= 38 Hz), 135.7 (C-7), 127.1 (C-5), 126.3 (C-6), 122.2 (C-4a), 119.1 (q, $\underline{C}F_3$, $^1J_{CF}$= 277 Hz), 118.4 (C-8), 115.6 (CN), 114.8 (C-3), 12.2 ppm (d, $\underline{C}H_2CN$, $^4J_{CF}$= 2.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ= -66.5 ppm. MS: m/z (%) = 253 ($[M]^+$, 100); 234 ($[C_{12}H_6F_2NO_2]^+$, 10); ($[C_{12}H_6F_2NO_2]^+$, 10); 184 ($[M]^+$-CF_3, 50); 120 ($[C_7H_4O_2]^+$, 15); 92 ($[C_6H_4O]^+$, 30). *UV-Vis* (methanol): λ_{max}= 204, 221, 245 and 300 nm.

3-Nitromethyl-2-trifluoromethylchromone (2) and 3-Hydroxymethyl-2-trifluoromethylchromone (3). A mixture of 2-bromomethyl-2-trifluoromethylchromone **6** (1.1 g, 3.60 mmol), silver nitrite (1.1 g, 6.95 mmol) and H_2O (20.0 mL) were added in a round-bottom flask and the suspension heated at 60 °C with vigorous stirring for 24 h. The reaction mixture (yellow) was extracted with ethyl acetate (3 x 20 mL), the organic layer was dried over Na_2SO_4, filtered and the solution was brought to dryness in vacuum. The crude product was subjected to flash chromatography (hexane-ethyl acetate 9:1) to give compounds **2** and **3**. Attempts to maximize the yield of **2** by replacing water for other non-nucleophylic solvents failed due to the insolubility of the silver nitrite salt.

Compound **2** (recrystallized from ethanol, m.p. 110–113 °C), yield 11%. ^1H NMR (500 MHz, $CDCl_3$) δ= 8.23 (dd, 1H, H-5, *J*= 8 and 1.5 Hz), 7.84 (ddd, 1H, H-7, *J*= 8.5, 7 and 1.5 Hz), 7.60 (d, 1H, H-8, *J*= 8.5 Hz), 7.55 (t, 1H, H-6, *J*= 7.5 Hz), 5.64 ppm (br.d, 2H, CH_2, $^5J_{HF}$= 1 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ= 175.7 (C-4), 155.2 (C-8a), 152.9 (q, C-2, $^2J_{CF}$= 38 Hz), 135.9 (C-7), 127.3 (C-5), 126.5 (C-6), 122.6 (C-4a), 119.1 (q, CF_3, $^1J_{CF}$= 277 Hz), 118.6 (C-8), 113.7 (C-3), 66.7 ppm (d, CH_2NO_2, $^4J_{CF}$= 2.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ= -65.6 ppm. GC-MS: m/z (%) = 273 ($[M]^+$, 0.2); 227 ([M-NO_2], 100); 199 ($[C_{10}H_6F_3O]^+$, 10); 120 ($[C_7H_4O_2]^+$, 42); 92 ($[C_6H_4O]^+$, 75). DIP-EI-MS: m/z (%) = 274 ($[M+1]^+$, 83). *UV-Vis* (methanol): λ_{max}= 204, 220, 246 and 302 nm.

Compound **3** (recrystallized from methanol, m.p. 125–126 °C), yield 20 %. ^1H NMR (500 MHz, $CDCl_3$) δ= 8.19 (dd, 1H, H-5, *J*= 8 and 1.5 Hz), 7.77 (ddd, 1H, H-7, *J*= 8.5, 7 and 1.5 Hz), 7.53 (d, 1H, H-8, *J*= 8.5 Hz, 1H), 7.48 (ddd, 1H, H-6, *J*= 8, 7 and 1.5 Hz), 4.76 (br.s, 2H, CH_2, $^5J_{HF}$= 1 Hz), 3.18 ppm (s, 1H, HO). ^{13}C NMR (126 MHz, $CDCl_3$) δ= 179.0 (C-4), 155.2 (C-8a), 149.5 (q, C-2, $^2J_{CF}$= 38 Hz), 135.4 (C-7), 126.6 (C-5), 126.0 (C-6), 123.0 (C-4a), 122.7 (q, C-3, $^3J_{CF}$= 1 Hz), 119.5 (q, CF_3, $^1J_{CF}$= 277 Hz), 118.5 (C-8), 55.5 ppm (q, CH_2OH, $^4J_{CF}$= 3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ = -64.0 ppm. DIP-EI-MS: m/z (%) = 245 ($[M+1]^+$, 62). *UV-Vis* (methanol): λ_{max}= 204, 222, 243 and 303 nm.

3-Aminomethyl-2-trifluoromethylchromone (4). 2-Bromomethyl-2-trifluoromethylchromone (0.324 g, 1.1 mmol) was dissolved in absolute ethanol (10.0 mL).

The flask was connected to a vacuum line and ammonia gas (130 Torr, 2.31 mmol) was condensed into the solution. The reaction mixture was stirred at -30 °C for 4 h. The yellow solution was poured into 50 mL of ice-water and the mixture was brought to dryness in vacuum. The crude product was extracted (ethyl acetate 4 x 10 mL), the organic layer was washed, dried over Na_2SO_4 and filtered. The pure product was obtained by selective precipitation of a methanolic solution stored at -20 °C (white dust, m.p. 163–164 °C), yield 30 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ= 8.19 (dd, 1H, H-5, *J*= 8 and 1.5 Hz), 7.74 (ddd, 1H, H-7, *J*= 8.5, 7 and 1.5 Hz), 7.50 (d, 1H, H-8, *J*= 8.5 Hz), 7.45 (t, 1H, H-6, *J*= 8 Hz), 3.93 (s, 2H, CH_2), 3.26 ppm (s, < 2H, NH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ= 177.9 (C-4), 155.1 (C-8a), 149.9 (q, C-2, $^2J_{CF}$= 37 Hz), 135.1 (C-7), 126.4 (C-5), 126.2 (C-6), 122.9 (C-4a), 121.6 (C-3), 119.6 (q, CF_3, $^1J_{CF}$= 277 Hz), 118.3 (C-8), 42.2 ppm (d, CH_2NH_2, $^4J_{CF}$= 2 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ= -64.1 ppm. GC-MS: m/z (%) = 243 ($[M]^+$, 12); 242 ($[M-H]^+$, 100); 227 ($[M-NH_2]^+$, 7); 199 ($[M-CO_2]^+$, 2); 121 ($[C_7H_5O_2]^+$, 15); 92 ($[C_6H_4O]^+$, 10). *UV-Vis* (methanol): λ_{max}= 205, 225, 244 and 305 nm.

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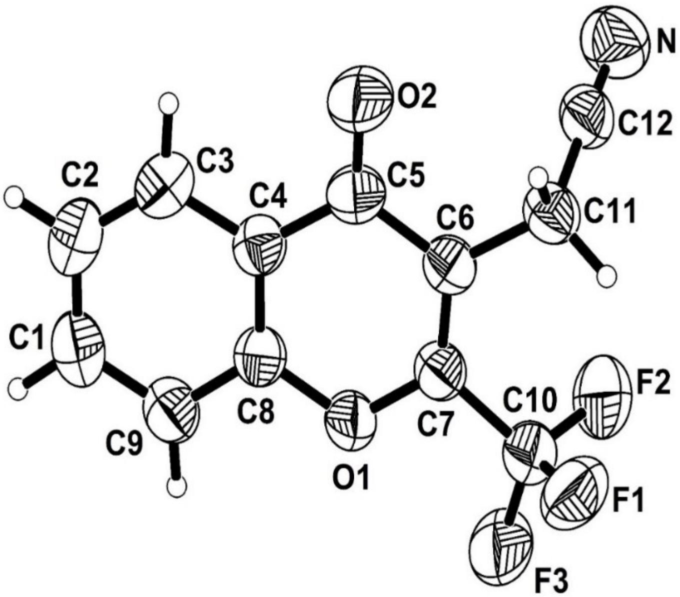

Figure S1. A view of molecular structure of compound **1** showing the atom-numbering scheme with displacement ellipsoids at the 30% probability level.

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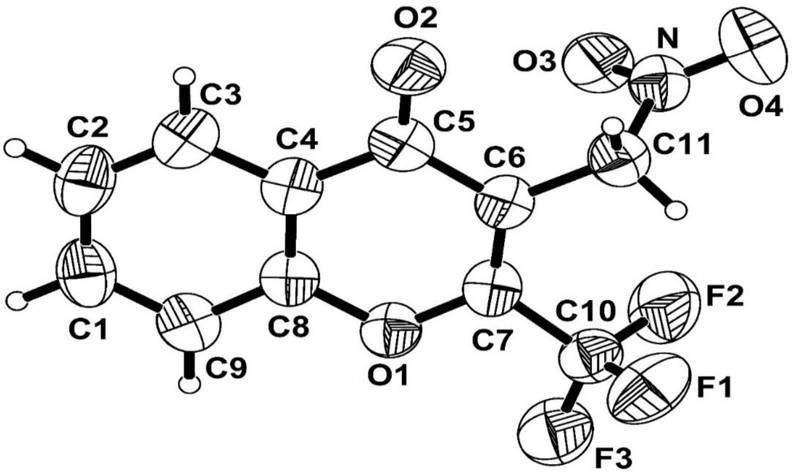


Figure S2. A view of molecular structure of compound **2** showing the atom-numbering scheme with displacement ellipsoids at the 30% probability level.

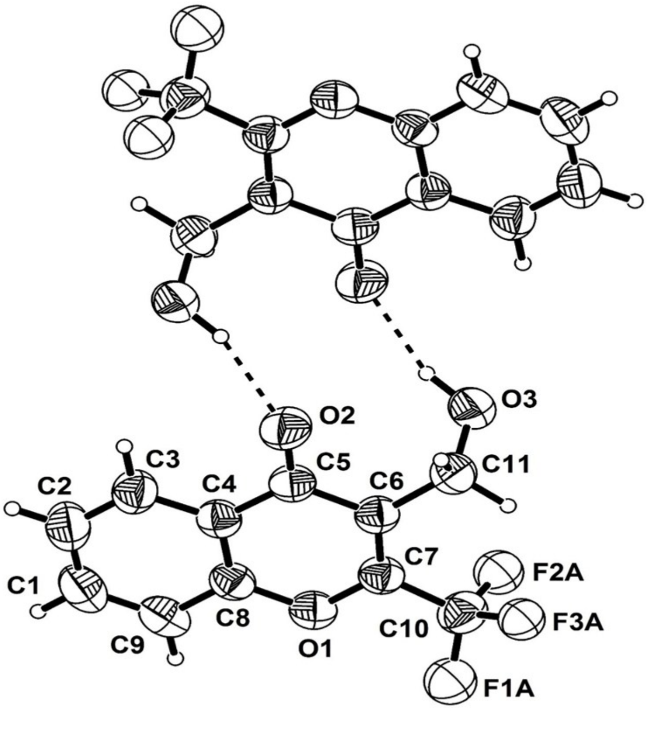


Figure S3. A view of molecular structure of compound **3** showing the atom-numbering scheme with displacement ellipsoids at the 30% probability level.

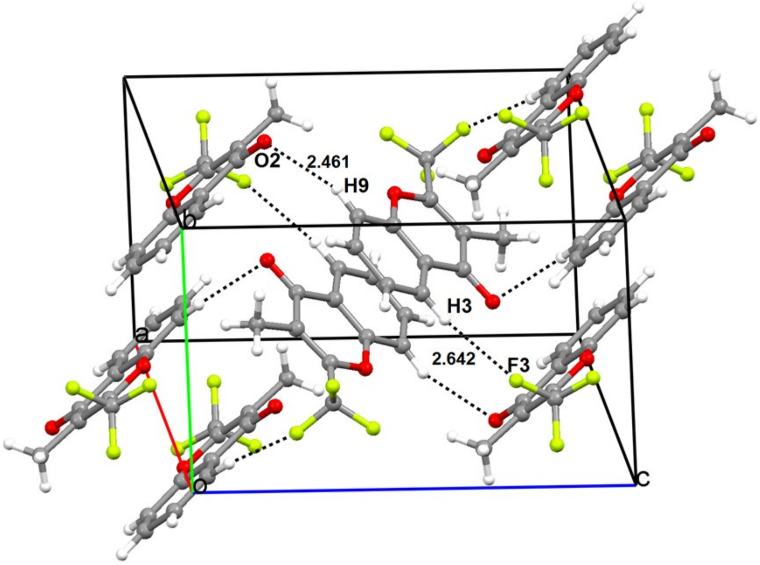


Figure S4. A view of the hydrogen-bonding interactions (dashed lines) for compound **5.**

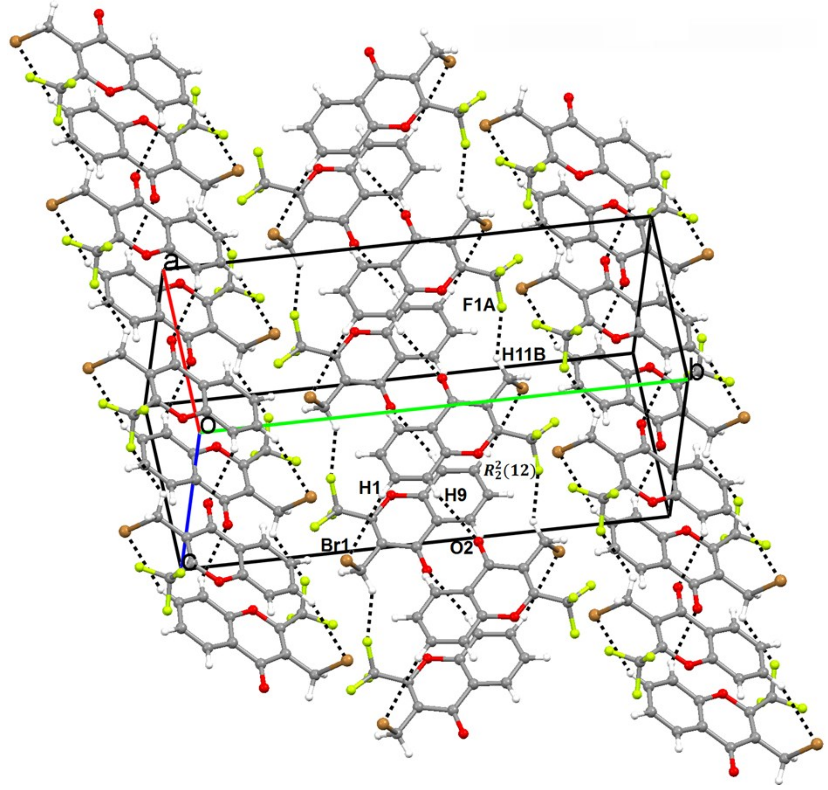


Figure S5. A view of the hydrogen-bonding interactions (dashed lines) for compound **6.**

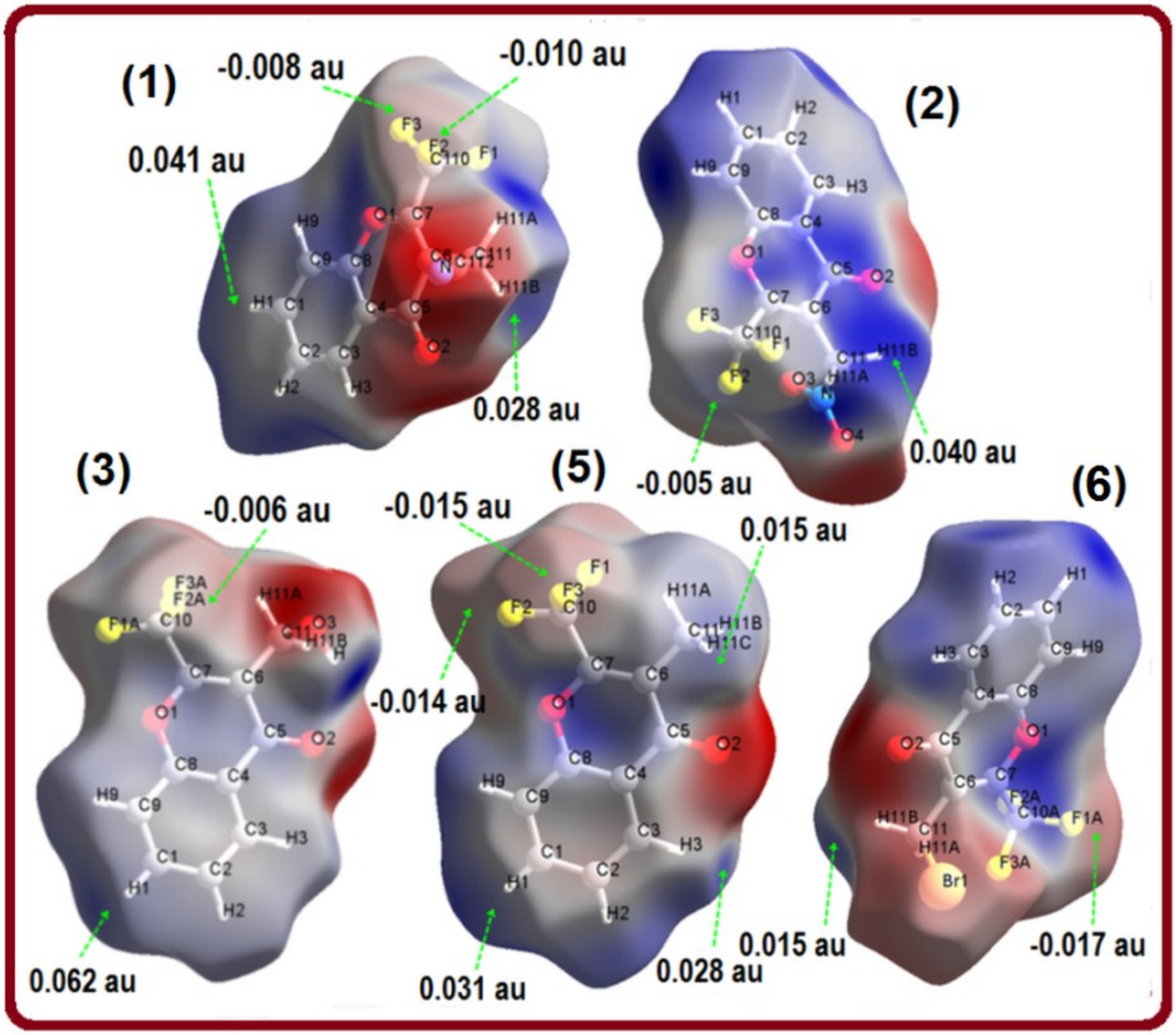


Figure S6. Hirshfeld surfaces mapped with electrostatic potential (ESP) showing selected electropositive and electronegative potentials (au).

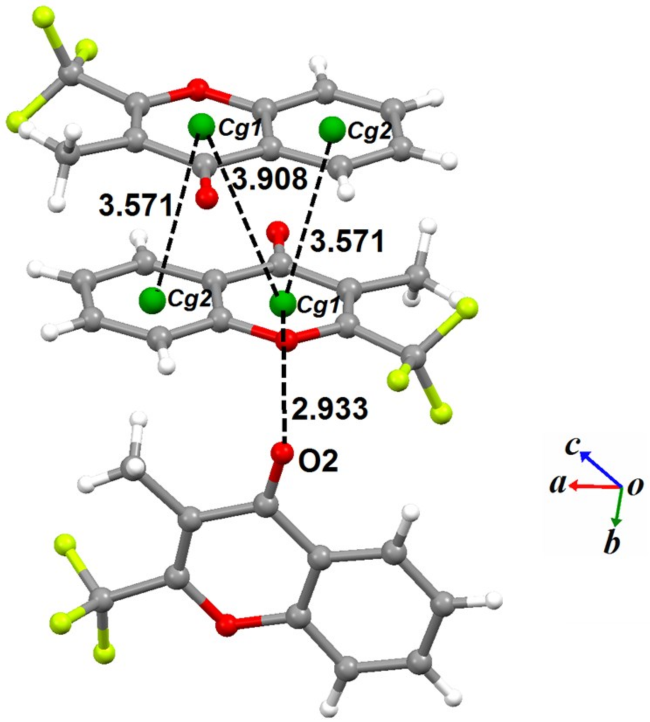


Figure S7. A view of the π-π stacking and C-O···π (dashed lines) interactions showing intercentroid and O···Cg1 distances for compound **5.**

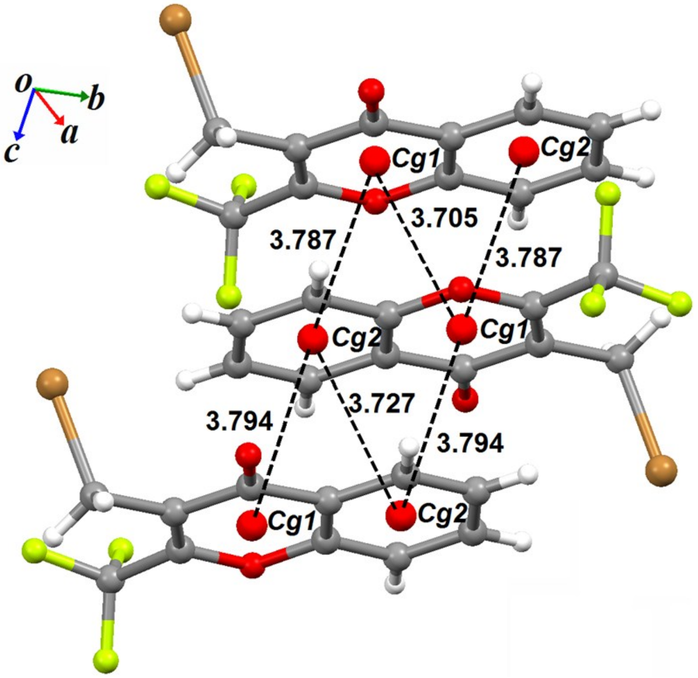


Figure S8. A view of the π-π stacking (dashed lines) interactions showing intercentroid distances for compound **6.**

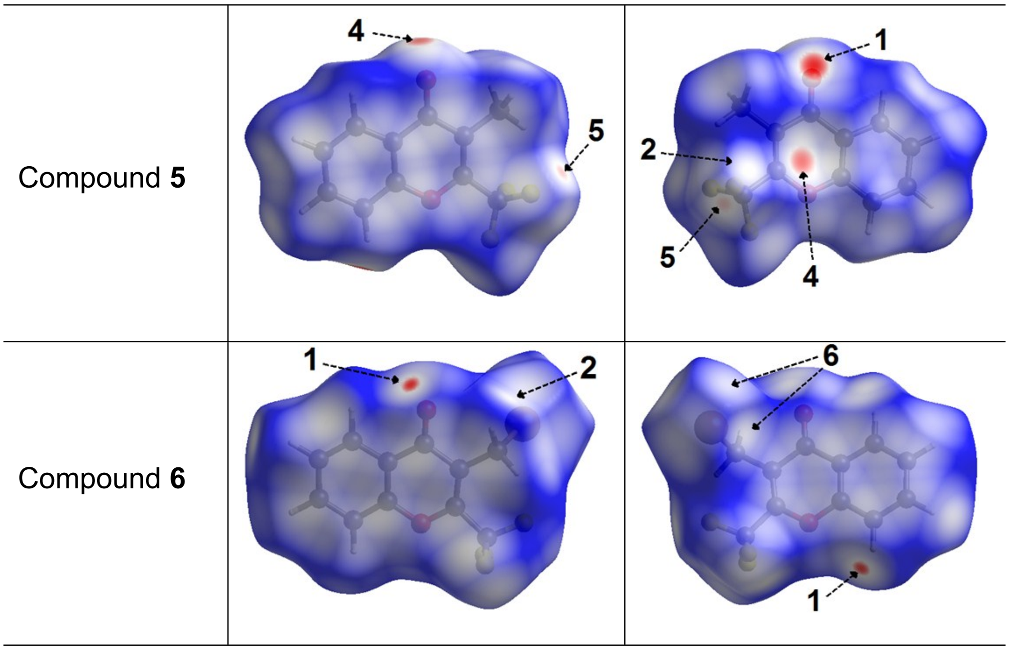


Figure S9 Views of the Hirshfeld surfaces in two orientations for compounds **5** and **6**. The surfaces in column 3 are 180° rotated around the vertical axis of the plot; labels denote hydrogen bonding contacts:1: C-H···O; 2: C-H···F; 4: C=O···π; 5: F···F¸ 6: C-H·· Br.

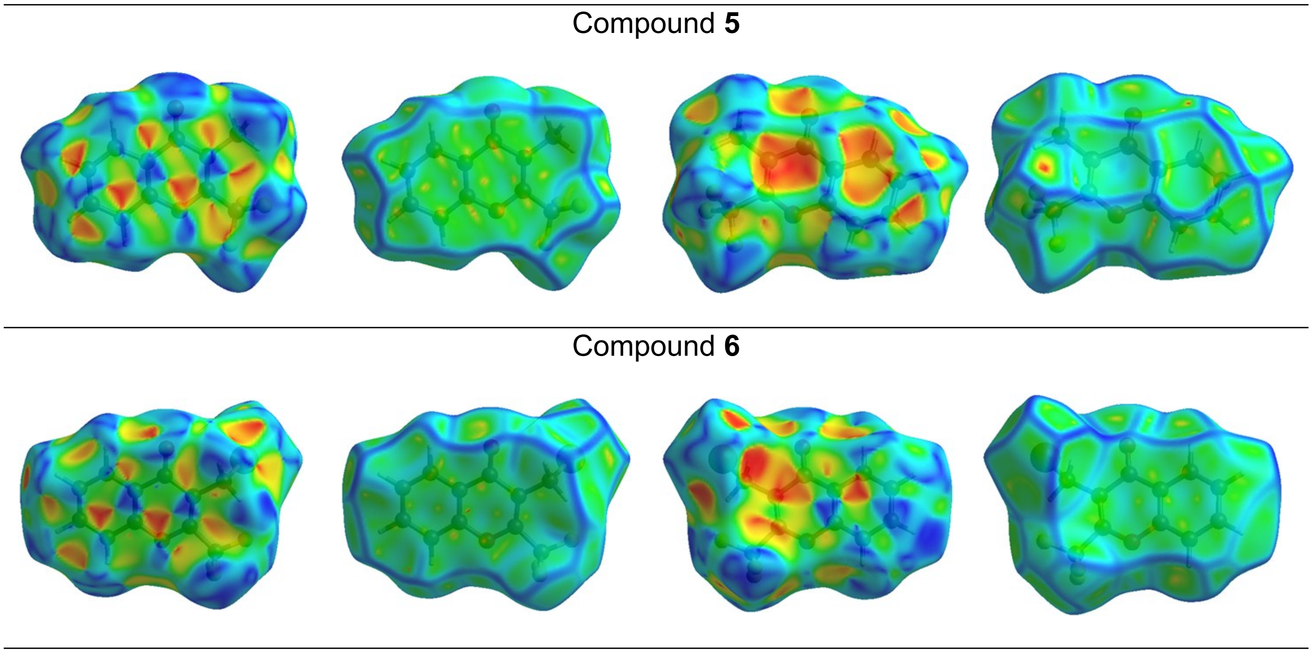


Figure S10 Hirshfeld surfaces mapped with *shape index* and *curvedness* for compounds **5** and **6**. The surfaces in columns 3 and 4 are 180° rotated around the horizontal axis of the plot.

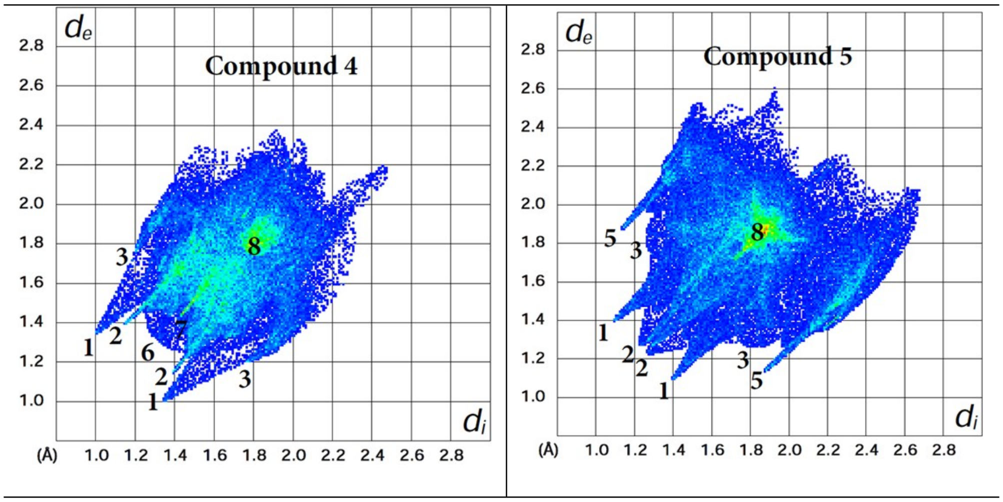
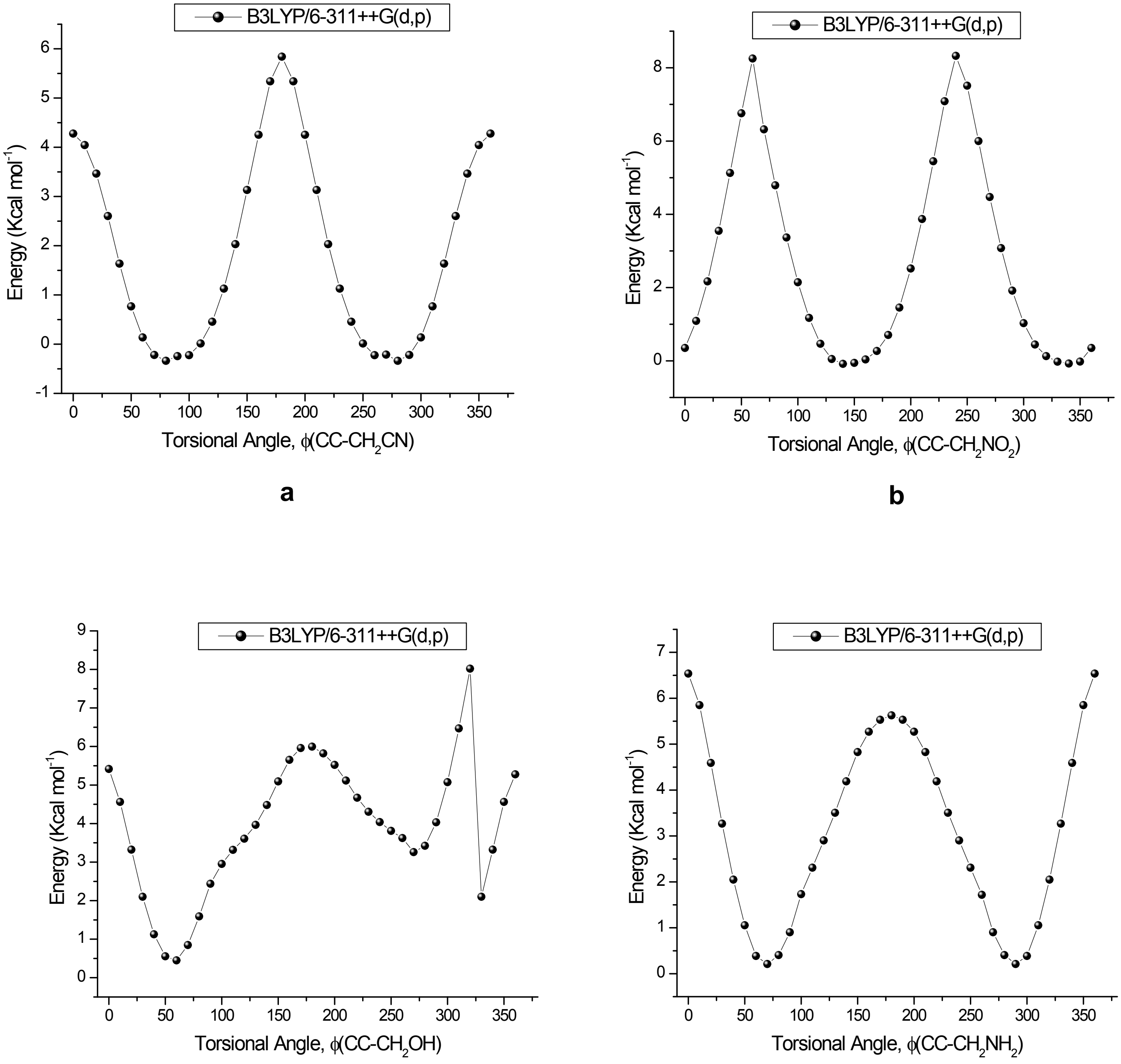


Figure S11. Fingerprint plots of compounds **5** and **6**. Close contacts are llabelled as (1) O···H, (2) F···H, (3) C···H, (4) N···H, (5) Br···H, (6) H···H, (7) F···F and (8) C···C.



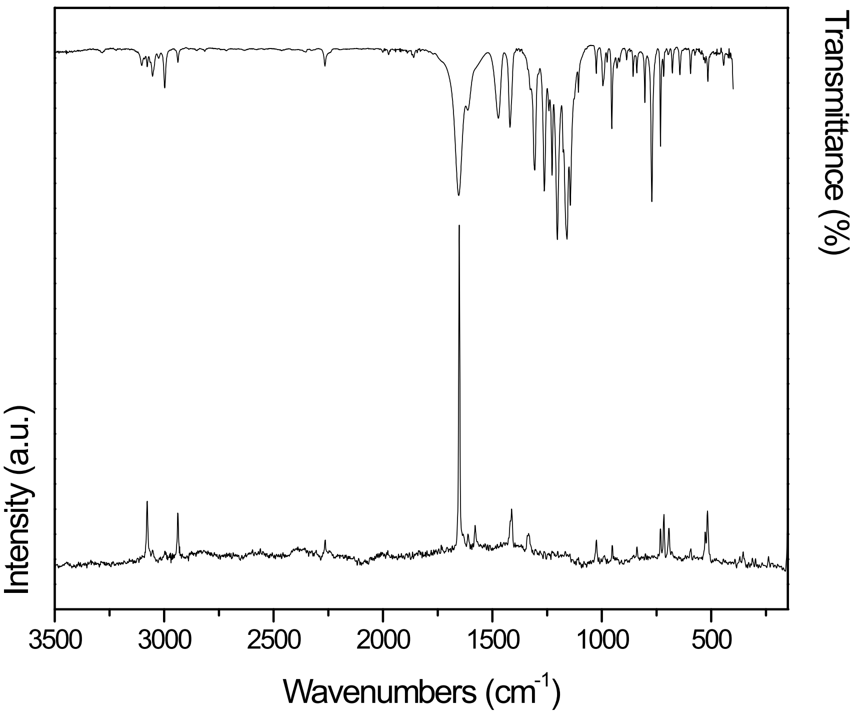
a

b

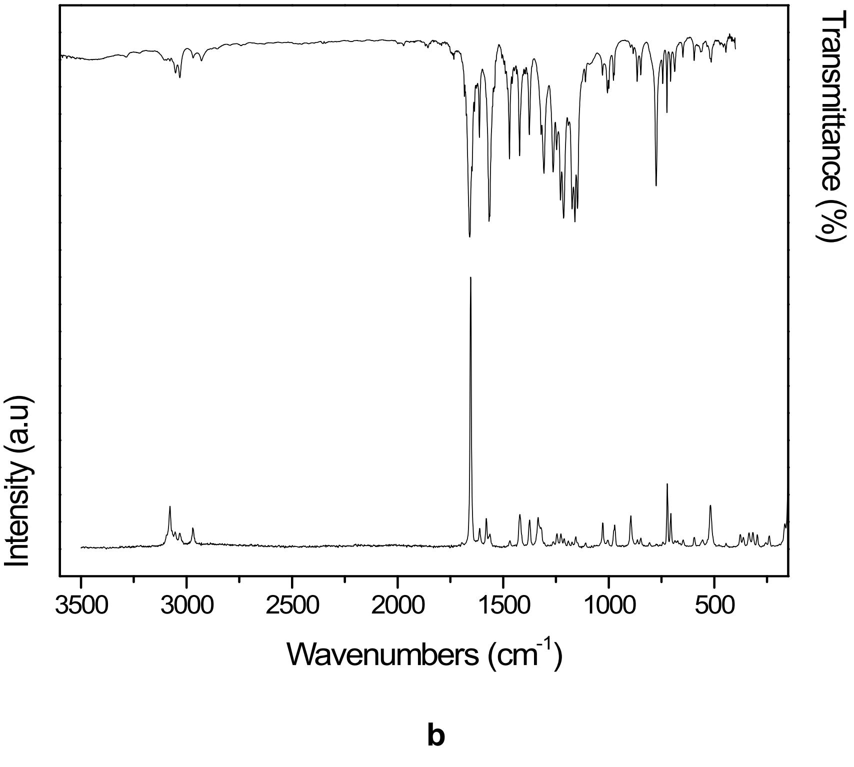
c

d

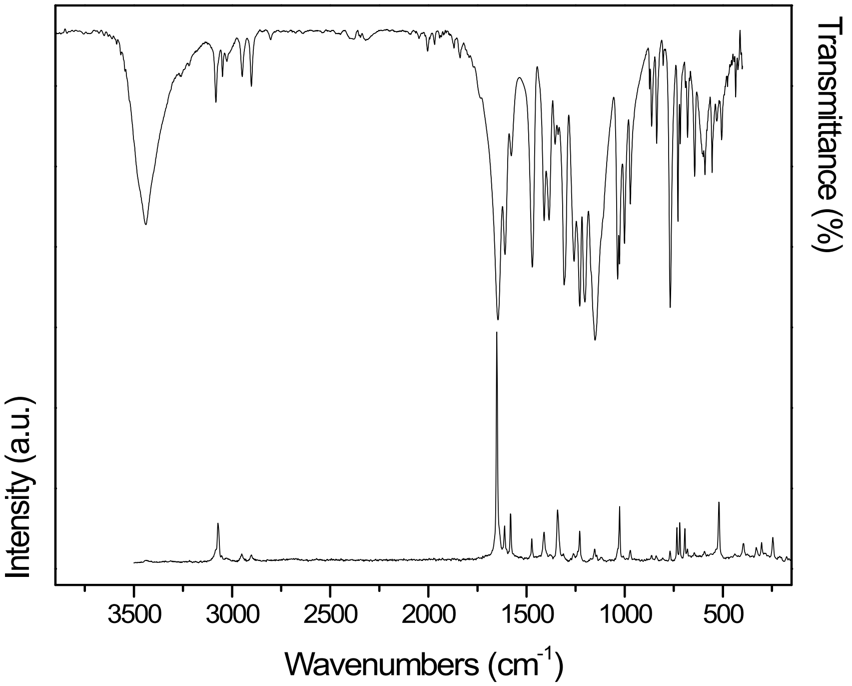
Figure S12. Potential energy curve for the torsional angle around ϕ (CC-CCH$_2$R) of **1 (a), 2 (b), 3 (c) and 4 (d)**, calculated at the B3LYP/6-311++G(d,p) level of theory.


Transmittance (%)
Intensity (a.u.)
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm^{-1})

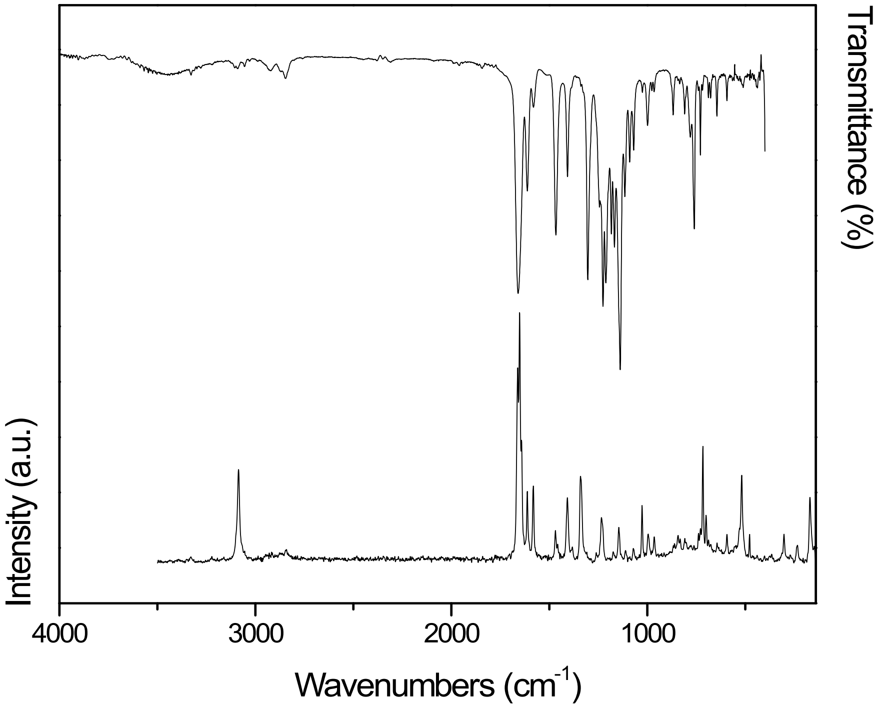
a


Transmittance (%)
Intensity (a.u)
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm^{-1})

b



c



d

Figure S13. Infrared spectra of the solid at room temperature (upper trace, KBr pellets) and Raman spectra (lower trace) of **1 (a), 2 (b), 3 (c) and 4 (d)**.

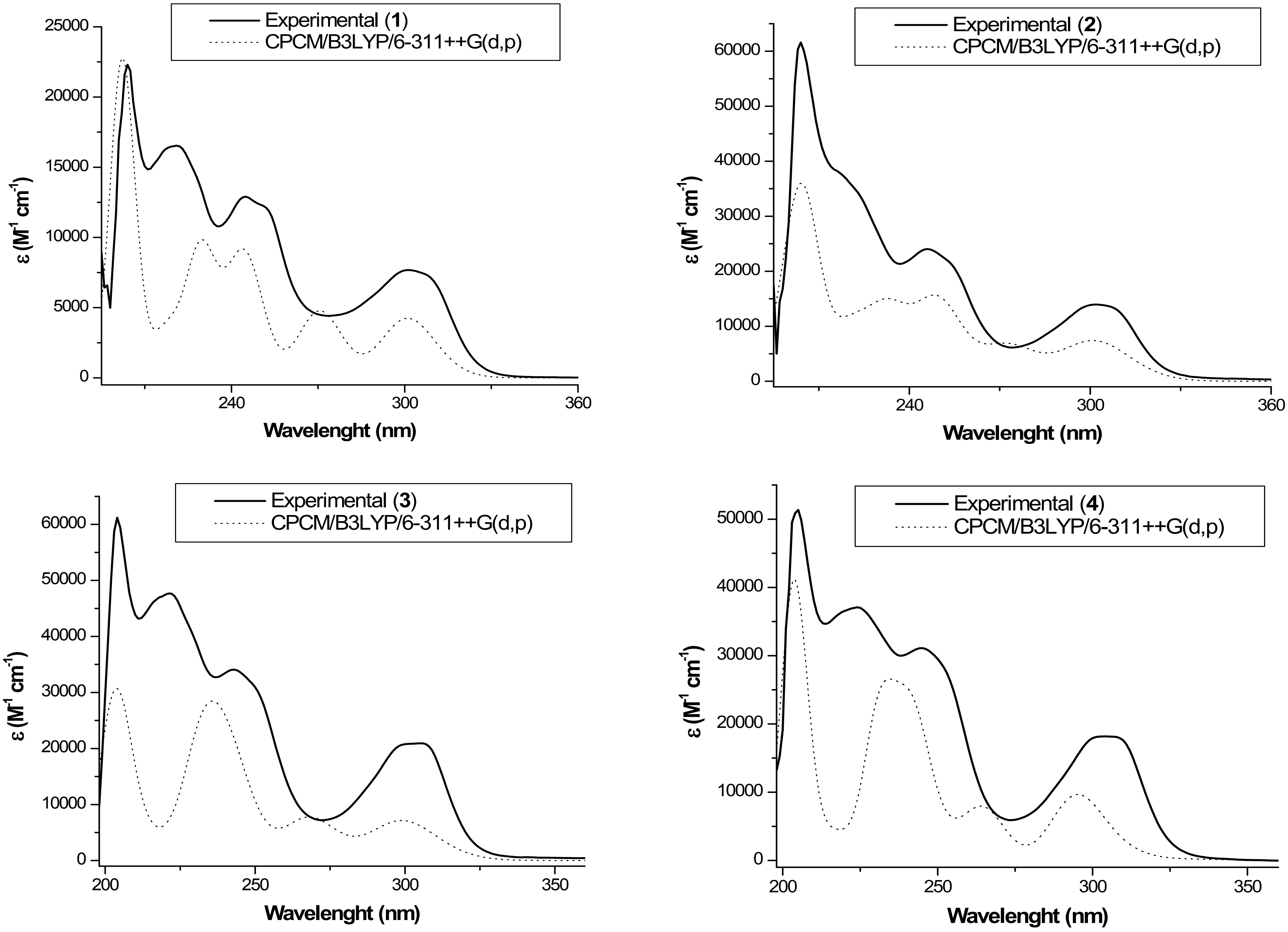


Figure S14. Experimental (full trace, in methanol) and calculated electronic spectra CPCM/ B3LYP/6-311++G(d,p), dashed and full trace) for **1 - 4** compounds.

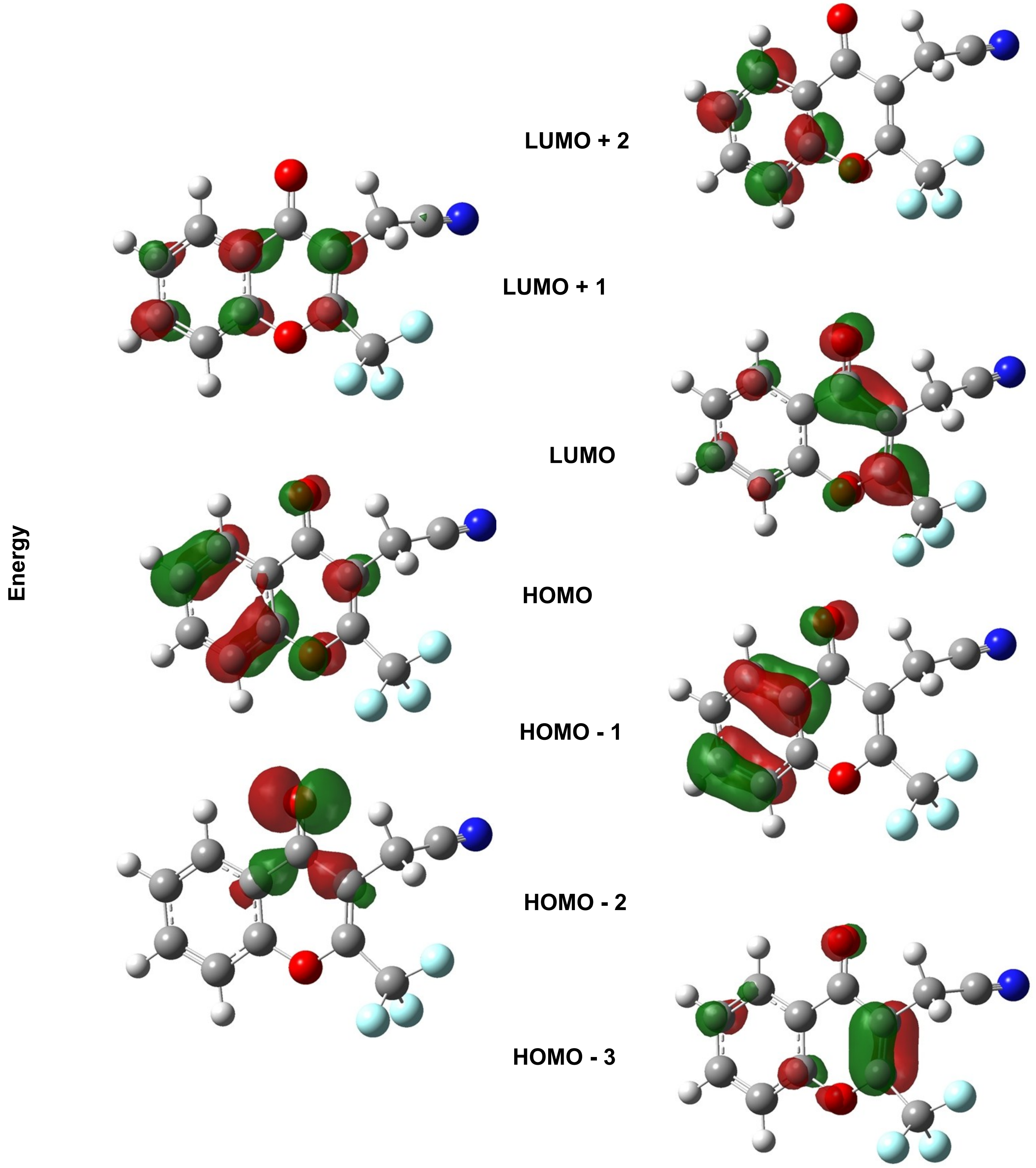


Figure S15. Molecular orbitals involved in the electronic transitions of **1**. The energy scale is only qualitative and does not represent the actual energy of the molecular orbitals

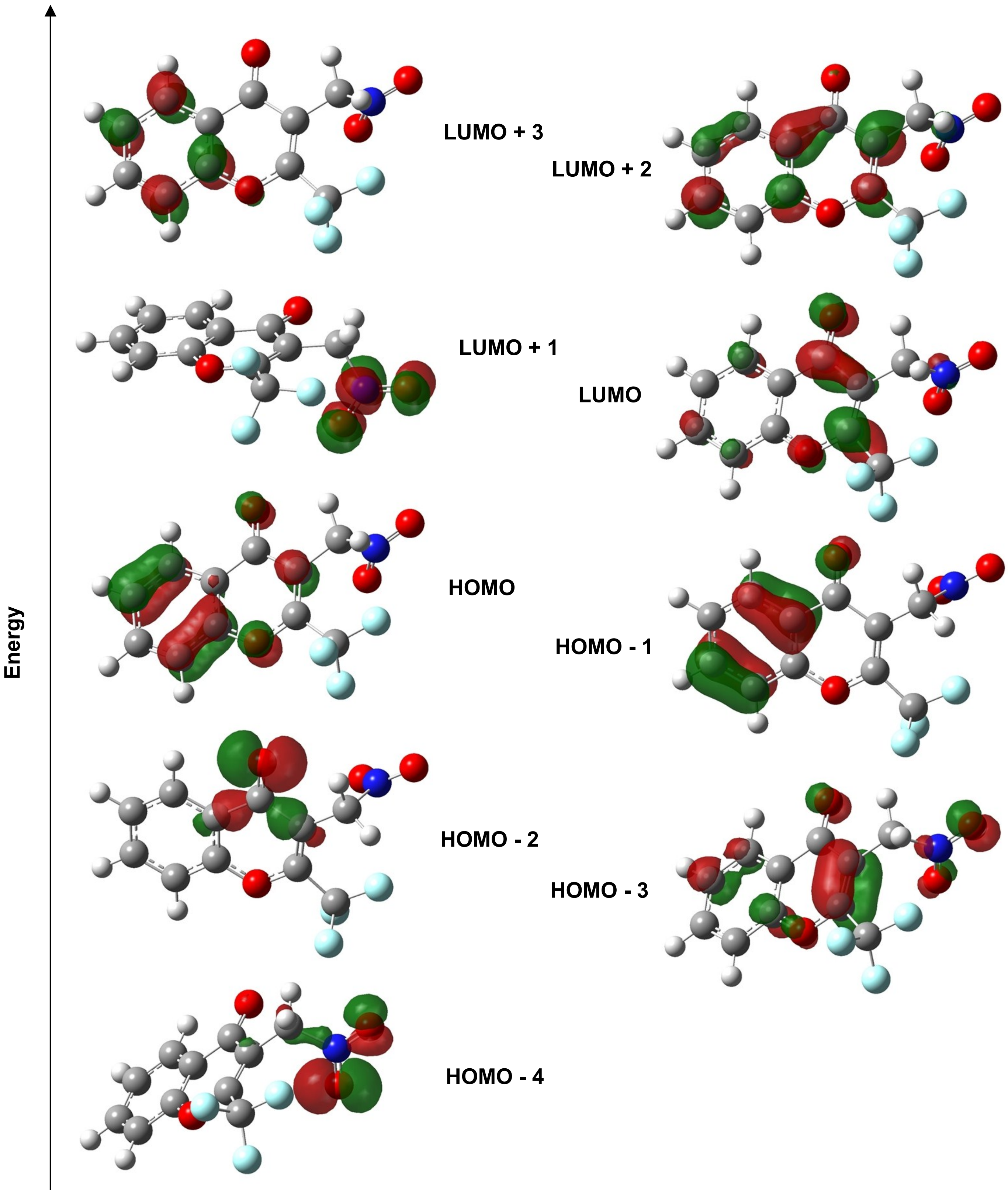


Figure S16. Molecular orbitals involved in the electronic transitions of **2**. The energy scale is only qualitative and does not represent the actual energy of the molecular orbitals

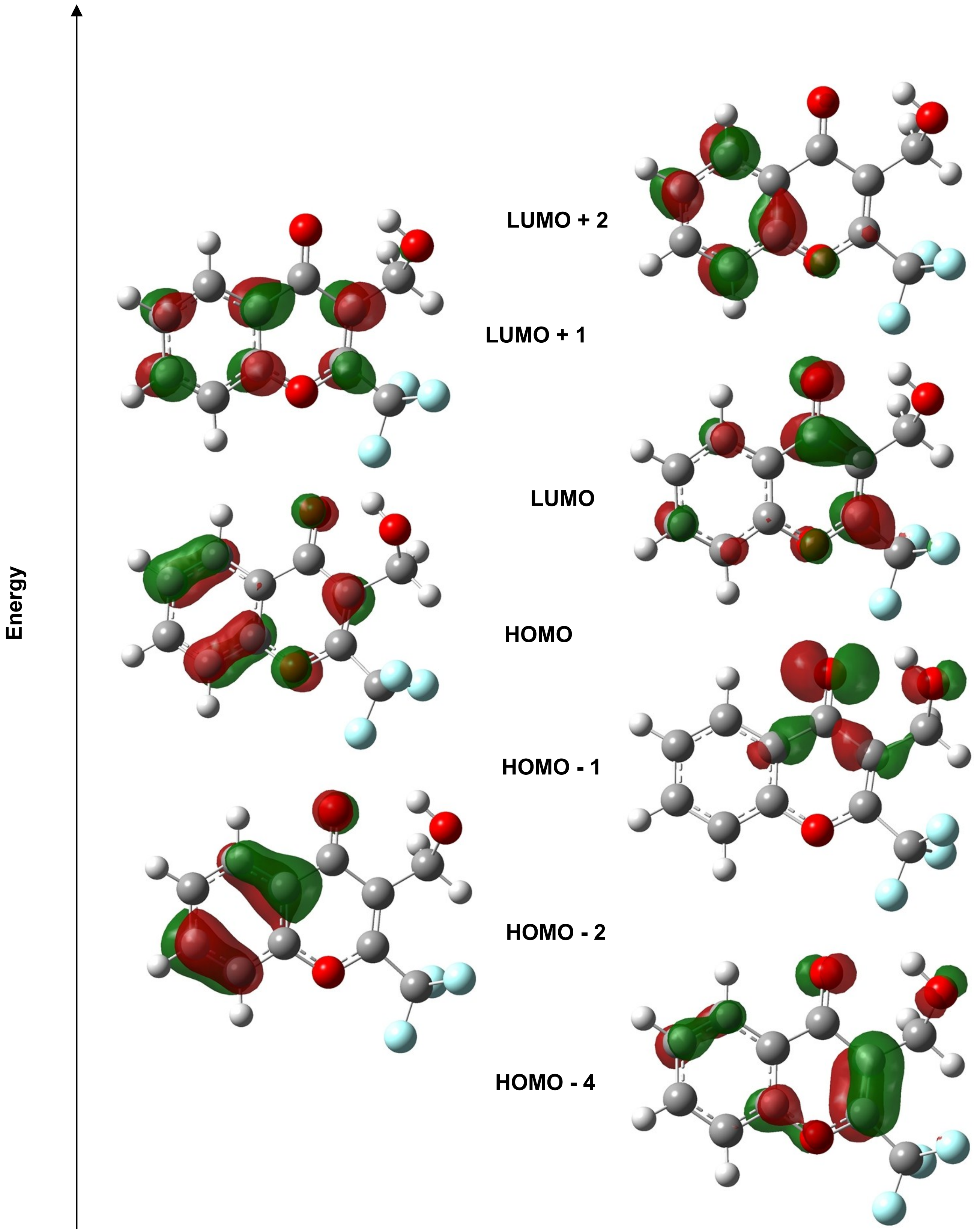


Figure S17. Molecular orbitals involved in the electronic transitions of **3**. The energy scale is only qualitative and does not represent the actual energy of the molecular orbitals

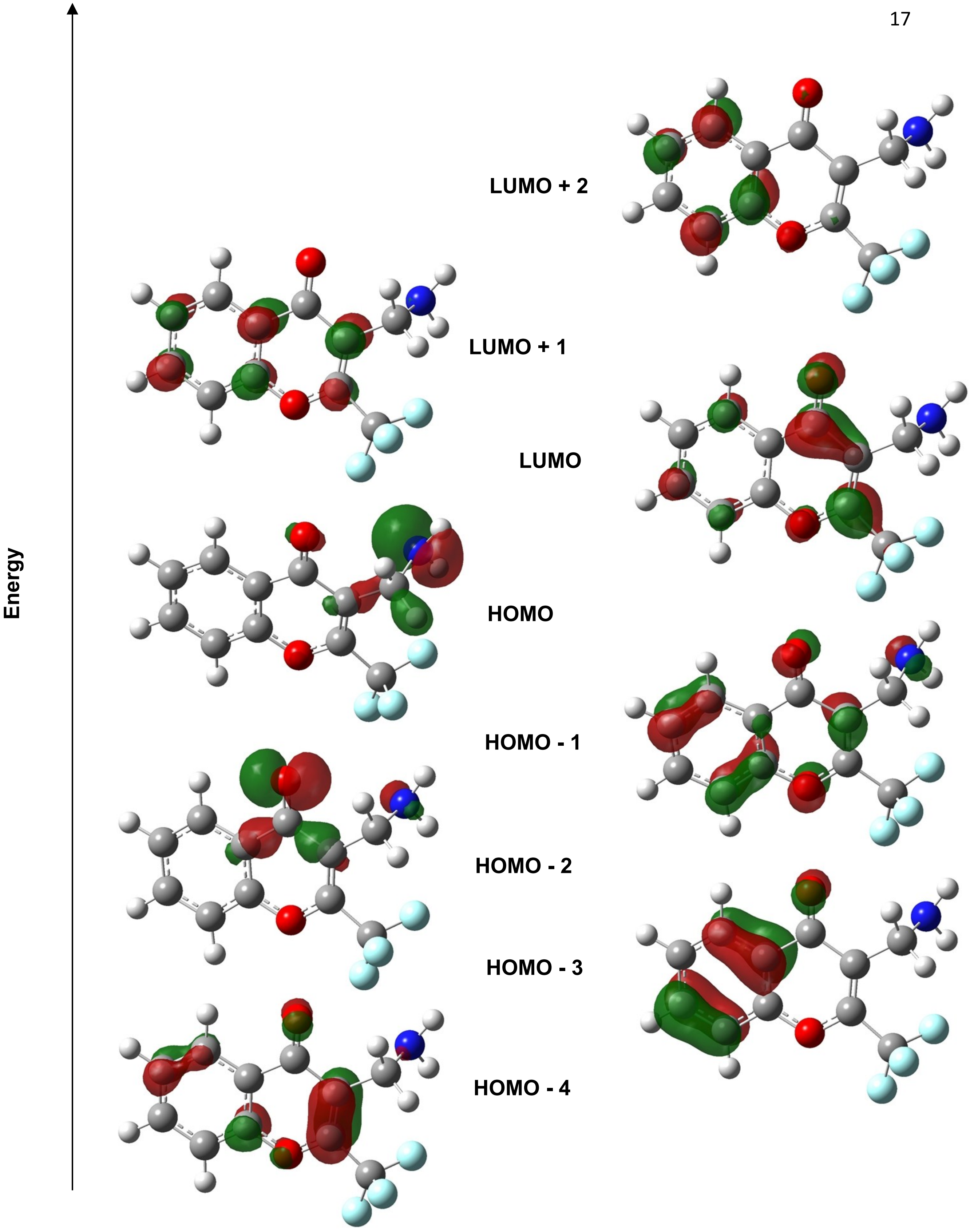
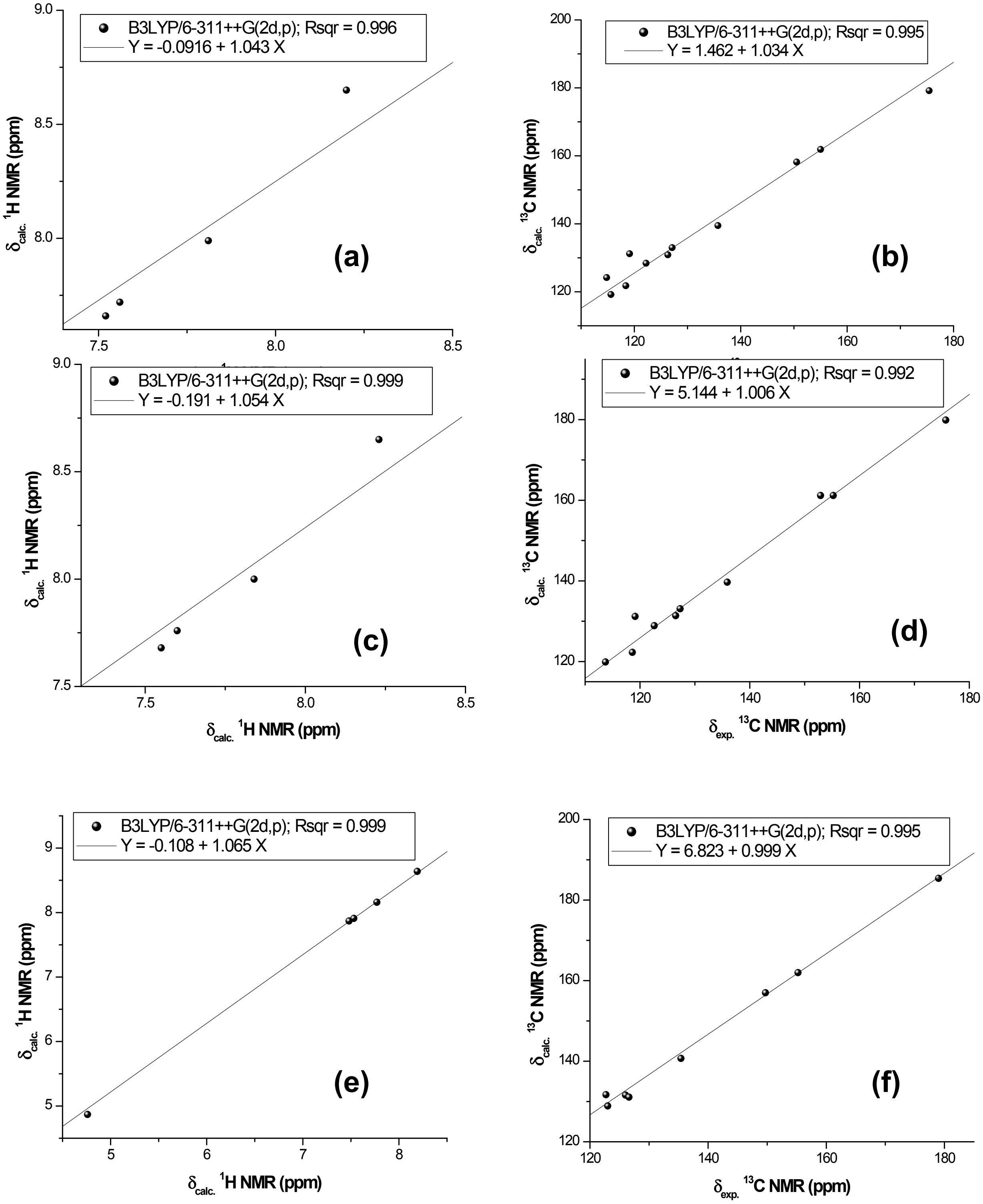


Figure S18. Molecular orbitals involved in the electronic transitions of **4**. The energy scale is only qualitative and does not represent the actual energy of the molecular orbitals.


B3LYP/6-311++G(2d,p); Rsqr = 0.996
Y = -0.0916 + 1.043 X
$\delta_{calc.}$ ^{1}H NMR (ppm)
9.0
8.5
8.0
7.5
8.0
8.5
(a)
B3LYP/6-311++G(2d,p); Rsqr = 0.995
Y = 1.462 + 1.034 X
$\delta_{calc.}$ ^{13}C NMR (ppm)
200
180
160
140
120
120
140
160
180
(b)
B3LYP/6-311++G(2d,p); Rsqr = 0.999
Y = -0.191 + 1.054 X
$\delta_{calc.}$ ^{1}H NMR (ppm)
9.0
8.5
8.0
7.5
7.5
8.0
8.5
$\delta_{calc.}$ ^{1}H NMR (ppm)
(c)
B3LYP/6-311++G(2d,p); Rsqr = 0.992
Y = 5.144 + 1.006 X
$\delta_{calc.}$ ^{13}C NMR (ppm)
180
160
140
120
120
140
160
180
$\delta_{exp.}$ ^{13}C NMR (ppm)
(d)
B3LYP/6-311++G(2d,p); Rsqr = 0.999
Y = -0.108 + 1.065 X
$\delta_{calc.}$ ^{1}H NMR (ppm)
9
8
7
6
5
5
6
7
8
$\delta_{calc.}$ ^{1}H NMR (ppm)
(e)
B3LYP/6-311++G(2d,p); Rsqr = 0.995
Y = 6.823 + 0.999 X
$\delta_{calc.}$ ^{13}C NMR (ppm)
200
180
160
140
120
120
140
160
180
$\delta_{exp.}$ ^{13}C NMR (ppm)
(f)

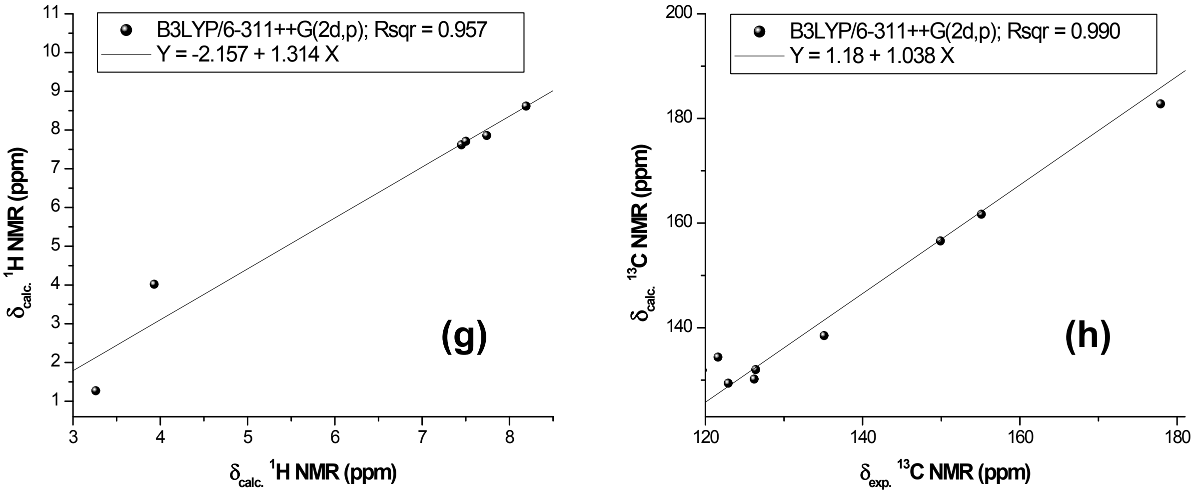


Figure S19: Comparison of experimental and theoretical chemical shifts of **1**: **(a)** ^{1}H, **(b)** ^{13}C; **2**: **(c)** ^{1}H, **(d)** ^{13}C; **3**: **(e)** ^{1}H, **(f)**; **4**: **(g)** ^{1}H, **(h)** ^{13}C calculated at the B3LYP/6-311+g(2d,p) level of the theory.

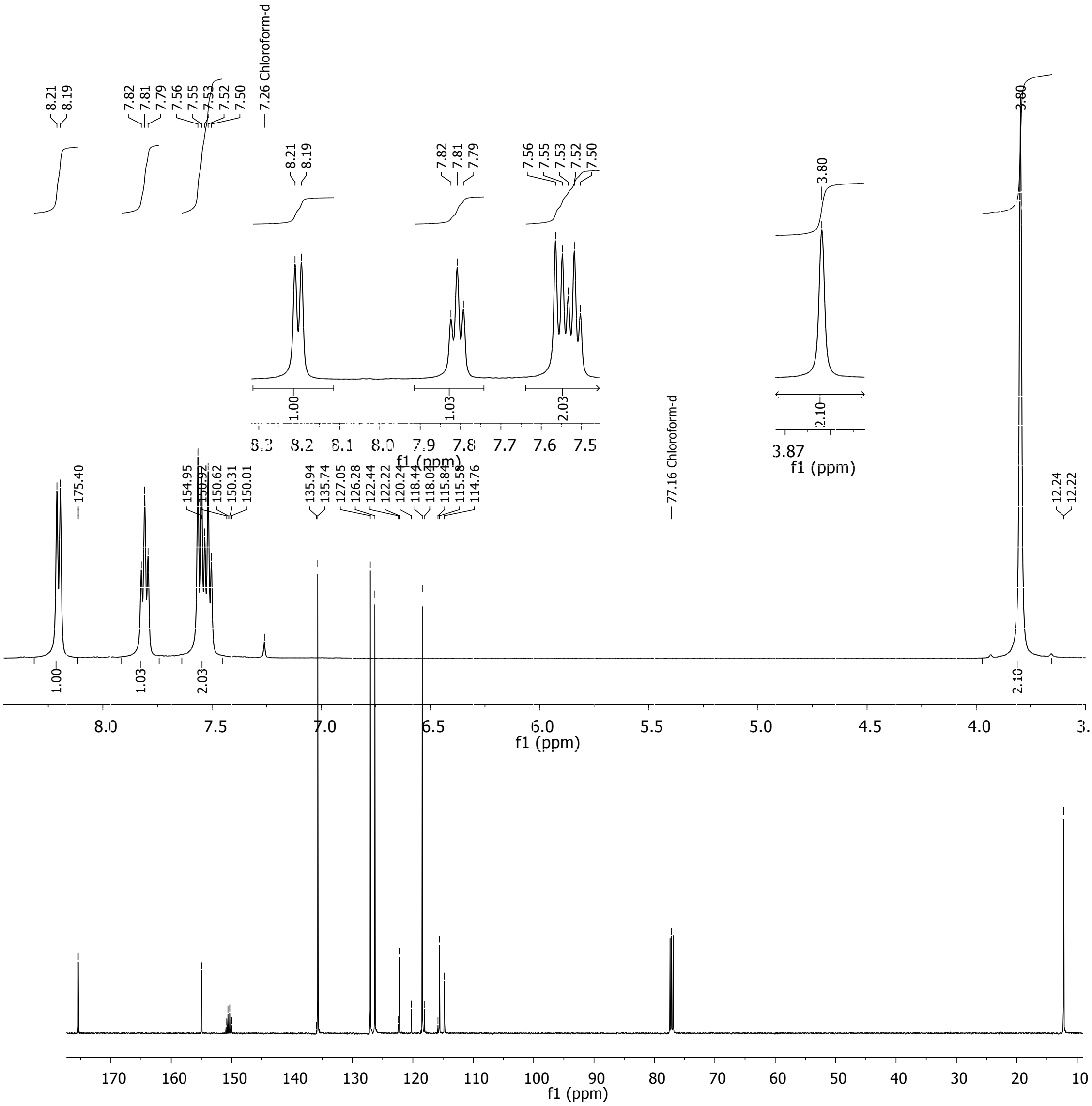


Figure S20: a) ^{1}H and b) ^{13}C NMR spectra of 3-cyanomethyl-2-trifluoromethylchromone **(1).**

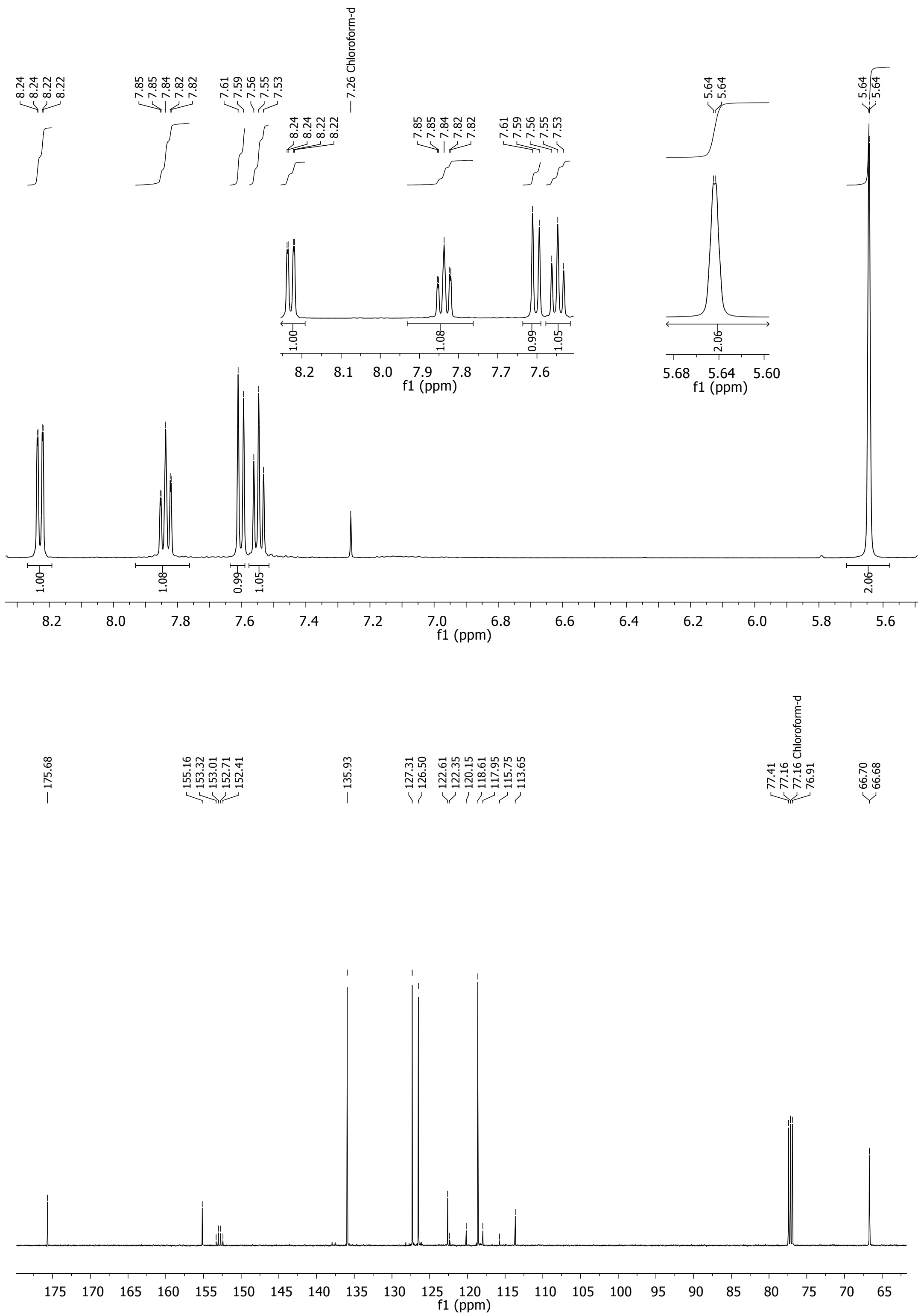
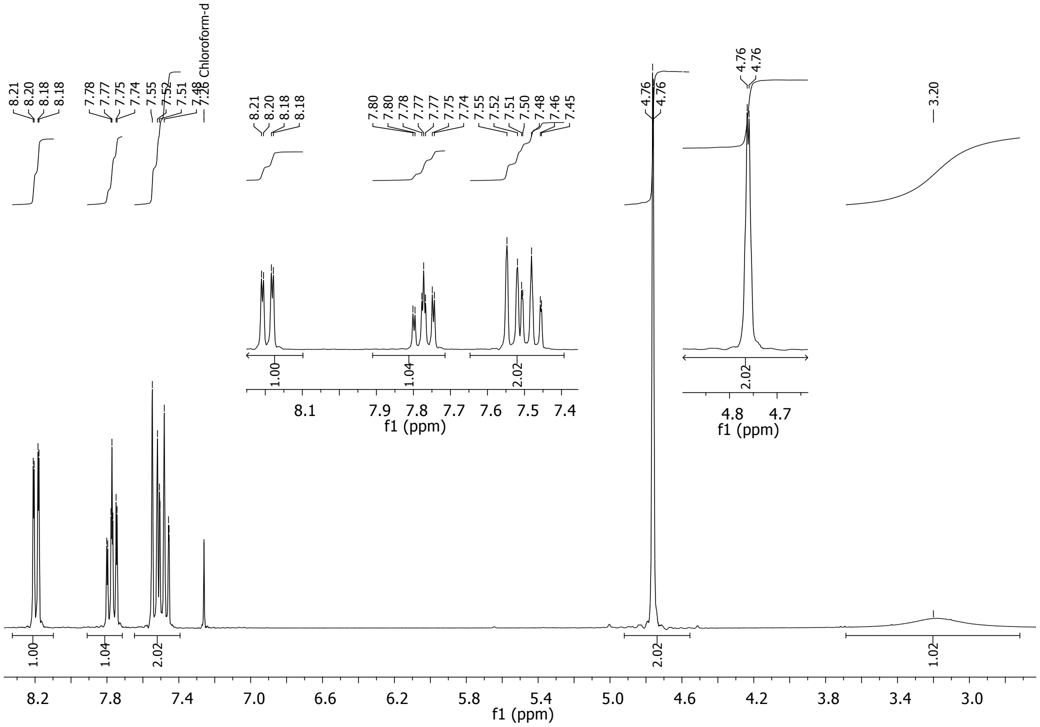


Figure S21: a) ^{1}H and b) ^{13}C NMR spectra of 3-nitromethyl-2-trifluoromethylchromone **(2).**



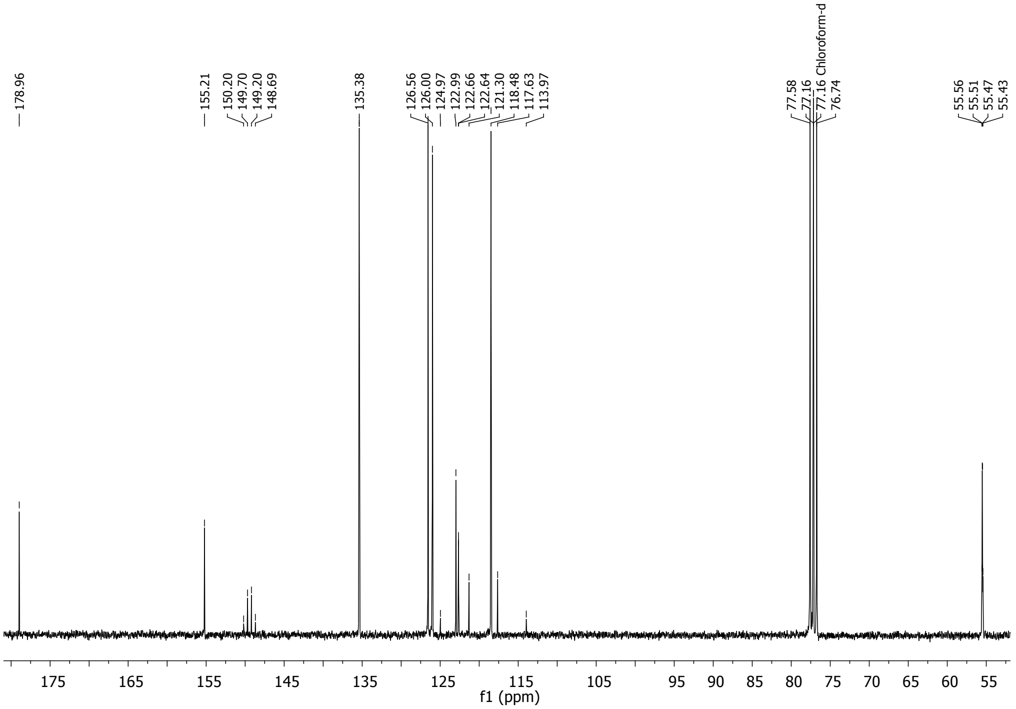
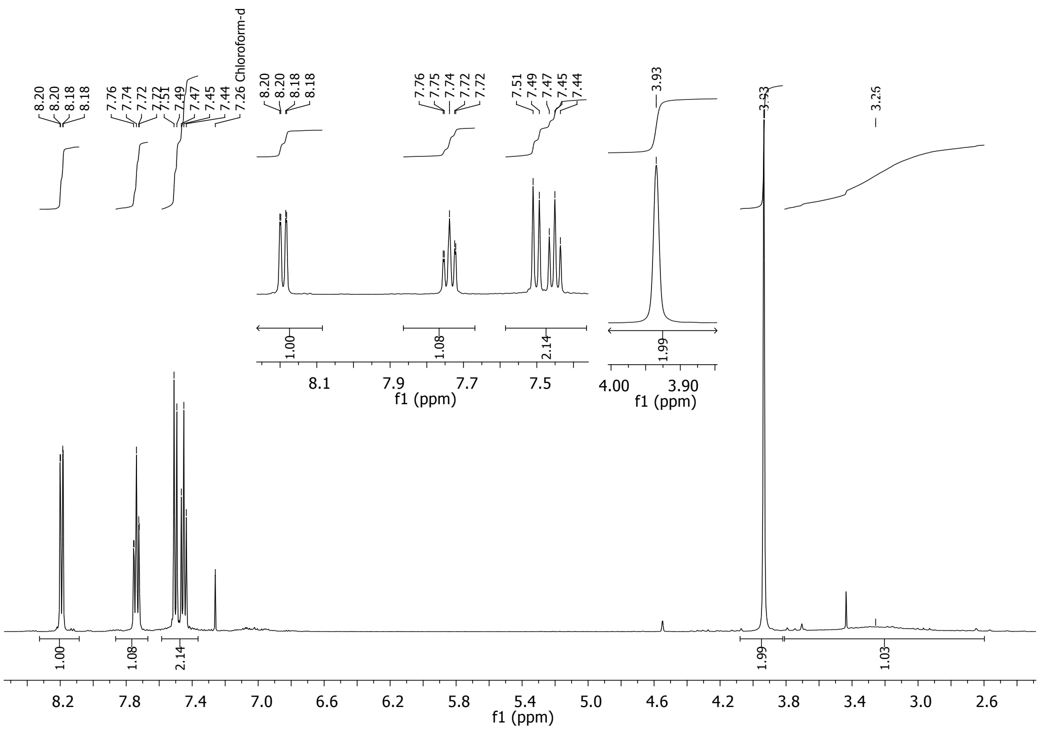


Figure S22: a) ^{1}H and b) ^{13}C NMR spectra of 3-hydroxymethyl-2-trifluoromethylchromone **(3).**



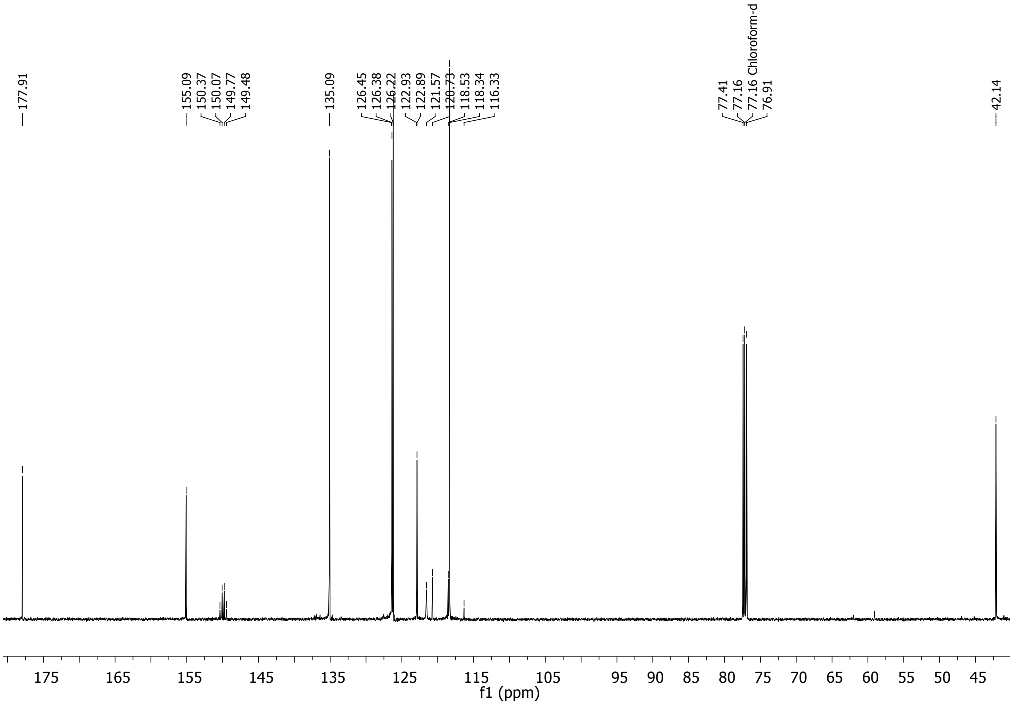


Figure S23: a) ^{1}H and b) ^{13}C NMR spectra of 3-aminomethyl-2-trifluoromethylchromone. **(4).**

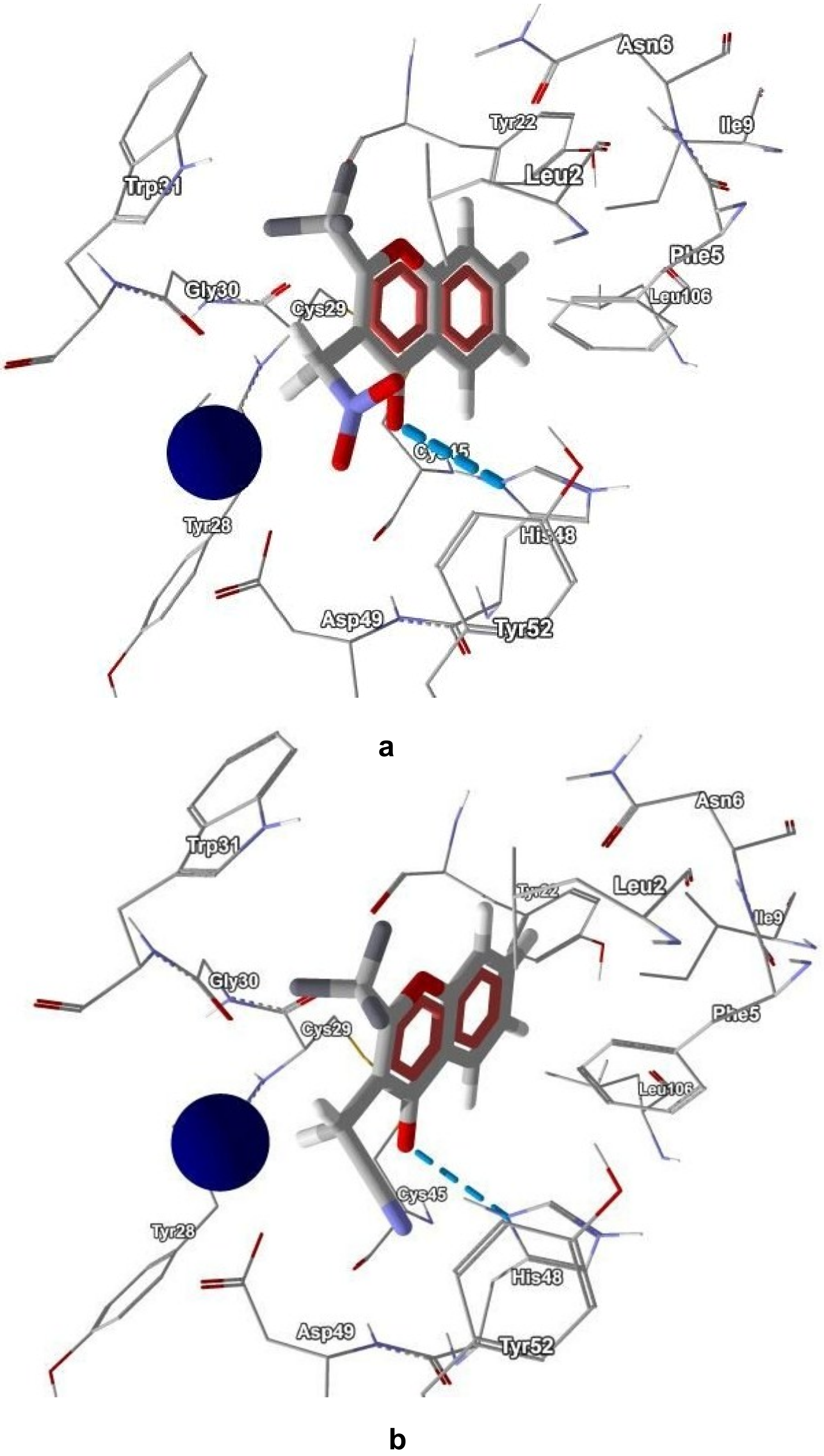


Figure S24. Docking results between compounds and a snake venom PLA$_2$ for compound **1 (a)** and **2 (b)**. Blue sphere represents Ca^{2+}. Dotted blue line represents a hydrogen bond.

Table S1. Selected experimental (X-ray diffraction) and calculated (B3LYP/6-311++g(d,p)) bond lengths [Å], bond angles [°], and torsion angles [°] [a] of **1**–**3**.

Parameter	**1**		**2**		**3**	
	Exp.	**Calc.**	**Exp.**	**Calc.**	**Exp.**	**Calc.**
r (C5-O2)	1.222(3)	1.223	1.225(6)	1.223	1.231(3)	1.230
r (C5-C6)	1.468(3)	1.486	1.476(7)	1.485	1.464(4)	1.474
r (C6-C7)	1.339(3)	1.351	1.497(6)	1.495	1.348(4)	1.350
r (C6-C11)	1.516(3)	1.519	1.497(6)	1.495	1.508(4)	1.517
r (C7-O1)	1.345(2)	1.349	1.343(5)	1.345	1.350(3)	1.350
r (C7-C10)	1.511(3)	1.523	1.525(7)	1.523	1.507(4)	1.526
r (C12-N)	1.134(3)	1.153				
r (C11-N)			1.514(7)	1.535		
r (N-O3)			1.206(5)	1.218		
r (C11-O3)					1.407(4)	1.418
∠(C5-C6-C11)	116.70(18)	115.2	116.2(4)	115.5	116.1(3)	116.1
∠(F1-C10-C7)	111.68(18)	112.7	111.8(4)	110.8	113.43	111.3
∠(C12-C11-C6)	111.44(18)	112.9				
∠(C6-C11-N)			111.8(4)	113.4		
∠(O3-C11-C6)					111.0(3)	111.7
∠(N-C12-C11)	179.2(3)	179.8				
Φ (O1-C7-C10-F1)	-113.9	-1.4	-115.2	172.9	-47.59	-121.0
Φ (C5-C6-C11-C12)	-75.44	-101.3				
Φ (C6-C11-C12-N)	-128.4	75.1				
Φ (C5-C6-C11-N)			-82.63	-98.5		
Φ (C5-C6-C11-O3)					-77.75	57.3

[a] Atom numbering scheme taken from Figures 1 - 3.

Crystallographic Supplementary Information (Tables S2-S13)

Table S2. Bond lengths [Å] and angles [°] in **1**.

C(1)-C(2)	1.384(4)	C(8)-C(4)-C(5)	120.2(2)
C(1)-C(9)	1.388(3)	C(3)-C(4)-C(5)	121.9(2)
C(2)-C(3)	1.369(3)	O(2)-C(5)-C(4)	123.7(2)
C(3)-C(4)	1.405(3)	O(2)-C(5)-C(6)	121.2(2)
C(4)-C(8)	1.383(3)	C(4)-C(5)-C(6)	115.1(2)
C(4)-C(5)	1.465(3)	C(7)-C(6)-C(5)	119.0(2)
C(5)-O(2)	1.222(3)	C(7)-C(6)-C(11)	124.3(2)
C(5)-C(6)	1.468(3)	C(5)-C(6)-C(11)	116.7(2)
C(6)-C(7)	1.339(3)	C(6)-C(7)-O(1)	125.6(2)
C(6)-C(11)	1.516(3)	C(6)-C(7)-C(10)	124.4(2)
C(7)-O(1)	1.345(2)	O(1)-C(7)-C(10)	110.0(2)
C(7)-C(10)	1.511(3)	O(1)-C(8)-C(4)	121.5(2)
C(8)-O(1)	1.381(2)	O(1)-C(8)-C(9)	115.7(2)
C(8)-C(9)	1.383(3)	C(4)-C(8)-C(9)	122.9(2)
C(10)-F(3)	1.322(3)	C(8)-C(9)-C(1)	117.7(2)
C(10)-F(1)	1.323(3)	F(3)-C(10)-F(1)	106.9(2)
C(10)-F(2)	1.324(3)	F(3)-C(10)-F(2)	107.4(2)
C(11)-C(12)	1.463(3)	F(1)-C(10)-F(2)	107.1(2)
C(12)-N	1.134(3)	F(3)-C(10)-C(7)	112.5(2)
		F(1)-C(10)-C(7)	111.7(2)
C(2)-C(1)-C(9)	120.6(2)	F(2)-C(10)-C(7)	111.0(2)
C(3)-C(2)-C(1)	120.8(2)	C(12)-C(11)-C(6)	111.4(2)
C(2)-C(3)-C(4)	120.0(2)	N-C(12)-C(11)	179.2(3)
C(8)-C(4)-C(3)	117.9(2)	C(7)-O(1)-C(8)	118.5(2)

Table S3. Bond lengths [Å] and angles [°] in **2**.

C(1)-C(9)	1.378(8)	C(9)-C(1)-C(2)	121.0(5)
C(1)-C(2)	1.393(9)	C(3)-C(2)-C(1)	120.0(5)
C(2)-C(3)	1.361(8)	C(2)-C(3)-C(4)	120.9(5)
C(3)-C(4)	1.403(7)	C(8)-C(4)-C(3)	117.4(4)
C(4)-C(8)	1.387(7)	C(8)-C(4)-C(5)	120.3(4)
C(4)-C(5)	1.461(7)	C(3)-C(4)-C(5)	122.4(5)
C(5)-O(2)	1.224(6)	O(2)-C(5)-C(4)	123.4(5)
C(5)-C(6)	1.476(7)	O(2)-C(5)-C(6)	122.0(4)
C(6)-C(7)	1.324(6)	C(4)-C(5)-C(6)	114.6(4)
C(6)-C(11)	1.497(6)	C(7)-C(6)-C(5)	119.9(4)
C(7)-O(1)	1.342(5)	C(7)-C(6)-C(11)	123.9(4)
C(7)-C(10)	1.523(7)	C(5)-C(6)-C(11)	116.2(4)
C(8)-C(9)	1.382(6)	C(6)-C(7)-O(1)	125.2(4)
C(8)-O(1)	1.388(5)	C(6)-C(7)-C(10)	125.3(4)
C(10)-F(3)	1.292(6)	O(1)-C(7)-C(10)	109.4(4)
C(10)-F(1)	1.309(6)	C(9)-C(8)-C(4)	122.9(4)
C(10)-F(2)	1.327(6)	C(9)-C(8)-O(1)	116.2(4)
C(11)-N	1.515(6)	C(4)-C(8)-O(1)	121.0(4)
N-O(3)	1.206(5)	C(1)-C(9)-C(8)	117.8(5)
N-O(4)	1.215(5)	F(3)-C(10)-F(1)	108.1(5)

F(3)-C(10)-F(2)	107.0(5)
F(1)-C(10)-F(2)	107.3(5)
F(3)-C(10)-C(7)	112.6(4)
F(1)-C(10)-C(7)	111.9(4)
F(2)-C(10)-C(7)	109.7(4)
C(6)-C(11)-N	111.8(4)
O(3)-N-O(4)	123.6(5)
O(3)-N-C(11)	120.0(4)
O(4)-N-C(11)	116.4(4)
C(7)-O(1)-C(8)	118.9(4)

Table S4. Bond lengths [Å] and angles [°] in **3**.

C(1)-C(9)	1.368(4)
C(1)-C(2)	1.394(5)
C(2)-C(3)	1.368(4)
C(3)-C(4)	1.402(3)
C(4)-C(8)	1.393(3)
C(4)-C(5)	1.455(3)
C(5)-O(2)	1.231(3)
C(5)-C(6)	1.464(3)
C(6)-C(7)	1.348(3)
C(6)-C(11)	1.508(3)
C(7)-O(1)	1.349(3)
C(7)-C(10)	1.507(3)
C(8)-O(1)	1.369(3)
C(8)-C(9)	1.394(3)
C(10)-F(3B)	1.248(6)
C(10)-F(2A)	1.283(6)
C(10)-F(3C)	1.266(9)
C(10)-F(1D)	1.291(6)
C(10)-F(1A)	1.302(6)
C(10)-F(2D)	1.324(6)
C(10)-F(1B)	1.333(7)
C(10)-F(2C)	1.354(9)
C(10)-F(2B)	1.423(6)
C(10)-F(3A)	1.425(6)
C(10)-F(1C)	1.418(8)
C(10)-F(3D)	1.434(6)
C(11)-O(3)	1.407(3)

C(9)-C(1)-C(2)	121.0(2)
C(3)-C(2)-C(1)	120.4(3)
C(2)-C(3)-C(4)	120.1(3)
C(8)-C(4)-C(3)	118.4(2)
C(8)-C(4)-C(5)	119.4(2)
C(3)-C(4)-C(5)	122.2(2)
O(2)-C(5)-C(4)	123.2(2)
O(2)-C(5)-C(6)	120.3(2)
C(4)-C(5)-C(6)	116.5(2)
C(7)-C(6)-C(5)	118.3(2)
C(7)-C(6)-C(11)	125.5(2)
C(5)-C(6)-C(11)	116.1(2)
C(6)-C(7)-O(1)	125.1(2)
C(6)-C(7)-C(10)	126.3(2)
O(1)-C(7)-C(10)	108.5(2)
O(1)-C(8)-C(4)	121.5(2)
O(1)-C(8)-C(9)	116.9(2)
C(4)-C(8)-C(9)	121.6(2)
C(1)-C(9)-C(8)	118.5(3)
F(2A)-C(10)-F(1A)	110.7(5)
F(1D)-C(10)-F(2D)	109.0(5)
F(3B)-C(10)-F(1B)	110.7(6)
F(3C)-C(10)-F(2C)	109.3(8)
F(3B)-C(10)-F(2B)	106.2(5)

F(1B)-C(10)-F(2B)	104.7(5)
F(2A)-C(10)-F(3A)	107.8(5)
F(1A)-C(10)-F(3A)	105.1(4)
F(3C)-C(10)-F(1C)	101.9(7)
F(2C)-C(10)-F(1C)	101.8(7)
F(1D)-C(10)-F(3D)	106.8(6)
F(2D)-C(10)-F(3D)	103.1(5)
O(3)-C(11)-C(6)	111.0(2)
C(7)-O(1)-C(8)	119.1(2)

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
C(1)	5226(4)	6169(1)	8591(3)	64(1)
C(2)	3615(4)	6326(1)	8910(3)	67(1)
C(3)	2143(3)	5873(1)	8502(3)	60(1)
C(4)	2257(3)	5238(1)	7751(3)	48(1)
C(5)	704(3)	4742(1)	7263(3)	53(1)
C(6)	1100(3)	4088(1)	6608(3)	48(1)
C(7)	2753(3)	4006(1)	6410(3)	47(1)
C(8)	3891(3)	5093(1)	7463(3)	47(1)
C(9)	5393(3)	5545(1)	7868(3)	58(1)
C(10)	3332(3)	3363(1)	5738(3)	59(1)
C(11)	-448(3)	3553(1)	6147(3)	56(1)
C(12)	-484(3)	3255(1)	7838(3)	57(1)
N	-511(3)	3017(1)	9142(3)	80(1)
O(1)	4127(2)	4477(1)	6757(2)	52(1)
O(2)	-824(2)	4850(1)	7380(3)	77(1)
F(1)	2186(2)	3229(1)	3984(2)	82(1)
F(2)	3248(2)	2839(1)	6750(2)	86(1)
F(3)	5102(2)	3391(1)	5828(3)	92(1)

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **2**.

Atom	x	y	z	U(eq)
C(1)	3626(7)	3907(3)	4883(8)	81(2)
C(2)	3967(8)	3753(3)	3275(9)	85(2)
C(3)	3535(6)	4199(3)	1866(7)	75(1)
C(4)	2740(6)	4815(2)	2004(6)	64(1)
C(5)	2233(6)	5300(3)	509(6)	66(1)
C(6)	1536(6)	5937(2)	953(6)	61(1)

C(7)	1317(6)	6016(2)	2565(6)	63(1)
C(8)	2414(6)	4949(2)	3624(6)	61(1)
C(9)	2849(7)	4507(3)	5079(6)	72(1)
C(10)	587(8)	6640(2)	3189(7)	74(1)
C(11)	1107(7)	6461(3)	-503(7)	70(1)
N	2875(6)	6831(2)	-441(5)	69(1)
O(1)	1660(4)	5552(2)	3882(4)	67(1)
O(2)	2360(6)	5194(2)	-1001(5)	87(1)
O(3)	4399(5)	6670(2)	648(5)	85(1)
O(4)	2652(7)	7282(2)	-1536(6)	108(2)
F(1)	-1160(5)	6775(2)	2139(6)	118(2)
F(2)	1647(6)	7153(2)	3093(7)	121(2)
F(3)	656(7)	6604(2)	4878(5)	118(2)

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **3**.

Atom	x	y	z	U(eq)
C(1)	-4128(6)	3145(2)	7022(2)	70(1)
C(2)	-4230(6)	2927(2)	6034(2)	69(1)
C(3)	-2530(5)	2289(2)	5709(2)	60(1)
C(4)	-677(4)	1847(1)	6370(2)	48(1)
C(5)	1132(4)	1152(1)	6063(2)	49(1)
C(6)	2855(4)	716(1)	6837(2)	47(1)
C(7)	2711(4)	998(1)	7764(2)	50(1)
C(8)	-609(4)	2079(1)	7353(2)	49(1)
C(9)	-2334(5)	2730(2)	7686(2)	61(1)
C(10)	4165(5)	601(2)	8665(2)	62(1)
C(11)	4534(5)	-54(2)	6525(2)	60(1)
O(1)	1126(3)	1669(1)	8040(1)	55(1)
O(2)	1215(4)	917(1)	5207(1)	67(1)
O(3)	2827(5)	-794(1)	6388(1)	68(1)
F(1A)	4390(20)	1129(5)	9408(5)	70(2)
F(2A)	2957(15)	-108(6)	8895(7)	62(2)
F(3A)	6970(10)	396(6)	8461(4)	56(2)
F(1C)	2250(20)	537(11)	9408(7)	62(3)
F(2C)	5000(40)	-235(7)	8580(7)	75(3)
F(3C)	6130(30)	1040(9)	9085(8)	69(3)
F(1B)	3120(30)	882(7)	9487(5)	69(2)
F(2B)	3610(20)	-307(4)	8647(6)	55(2)
F(3B)	6766(13)	680(7)	8710(7)	57(2)
F(1D)	2453(15)	204(9)	9203(8)	68(2)
F(2D)	6350(20)	93(7)	8549(5)	70(2)
F(3D)	5350(20)	1308(4)	9235(5)	61(2)

Table S8. Anisotropic displacement parameters (Å^2 x 10^3) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 hk a^*b^*U^{12}]$. To be deposited.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	68(1)	54(1)	65(1)	0(1)	22(1)	-12(1)
C(2)	82(2)	50(1)	64(1)	-8(1)	24(1)	1(1)
C(3)	62(1)	58(1)	60(1)	-5(1)	25(1)	6(1)
C(4)	50(1)	46(1)	49(1)	3(1)	20(1)	5(1)
C(5)	47(1)	59(1)	56(1)	1(1)	24(1)	6(1)
C(6)	45(1)	50(1)	49(1)	1(1)	19(1)	-2(1)
C(7)	45(1)	46(1)	51(1)	2(1)	21(1)	1(1)
C(8)	49(1)	45(1)	49(1)	4(1)	20(1)	4(1)
C(9)	54(1)	56(1)	64(1)	2(1)	25(1)	-3(1)
C(10)	59(1)	51(1)	74(1)	-5(1)	34(1)	-3(1)
C(11)	49(1)	60(1)	60(1)	-1(1)	25(1)	-5(1)
C(12)	53(1)	49(1)	74(1)	3(1)	31(1)	1(1)
N	91(2)	72(1)	91(2)	18(1)	51(1)	11(1)
O(1)	48(1)	46(1)	67(1)	-2(1)	29(1)	-1(1)
O(2)	58(1)	77(1)	108(1)	-14(1)	47(1)	3(1)
F(1)	90(1)	84(1)	77(1)	-25(1)	39(1)	-1(1)
F(2)	115(1)	47(1)	108(1)	11(1)	56(1)	9(1)
F(3)	67(1)	72(1)	153(2)	-24(1)	61(1)	2(1)

Table S9. Anisotropic displacement parameters (Å^2 x 10^3) for **2**. To be deposited.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	72(3)	68(3)	82(3)	10(3)	3(2)	-5(2)
C(2)	71(3)	64(3)	101(4)	-5(3)	7(3)	2(2)
C(3)	63(3)	74(3)	77(3)	-13(2)	12(2)	0(2)
C(4)	57(2)	62(3)	61(3)	-10(2)	6(2)	-8(2)
C(5)	58(2)	77(3)	55(3)	-3(2)	10(2)	-8(2)
C(6)	54(2)	63(2)	56(2)	-3(2)	9(2)	0(2)
C(7)	63(2)	60(2)	57(2)	-5(2)	9(2)	-2(2)
C(8)	58(2)	59(2)	57(3)	-6(2)	9(2)	-6(2)
C(9)	69(3)	74(3)	63(3)	0(2)	12(2)	-6(2)
C(10)	86(3)	69(3)	69(3)	-8(2)	30(2)	3(2)
C(11)	63(3)	73(3)	67(3)	5(2)	15(2)	-1(2)
N	75(2)	65(2)	62(2)	-1(2)	19(2)	0(2)
O(1)	74(2)	63(2)	58(2)	-7(1)	18(1)	0(1)
O(2)	103(3)	103(3)	56(2)	-4(2)	27(2)	6(2)
O(3)	64(2)	96(3)	89(3)	6(2)	21(2)	-2(2)
O(4)	119(4)	92(3)	97(3)	29(2)	19(2)	-14(2)
F(1)	86(2)	129(3)	126(3)	-15(2)	23(2)	29(2)
F(2)	136(3)	64(2)	178(4)	-15(2)	75(3)	-14(2)
F(3)	183(4)	94(3)	90(2)	-13(2)	64(3)	18(3)

Table S10. Anisotropic displacement parameters (Å^2 x 10^3) for **3**. To be deposited.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	63(2)	47(1)	101(2)	-4(1)	13(1)	5(1)
C(2)	63(2)	56(1)	88(2)	11(1)	-2(1)	6(1)
C(3)	59(1)	57(1)	62(1)	8(1)	-2(1)	0(1)
C(4)	47(1)	45(1)	53(1)	2(1)	5(1)	-5(1)
C(5)	49(1)	51(1)	47(1)	-2(1)	5(1)	-5(1)
C(6)	44(1)	49(1)	49(1)	-1(1)	3(1)	-3(1)
C(7)	48(1)	50(1)	52(1)	-3(1)	4(1)	-3(1)
C(8)	48(1)	44(1)	56(1)	-2(1)	6(1)	-6(1)
C(9)	63(1)	49(1)	71(2)	-11(1)	14(1)	-3(1)
C(10)	66(1)	70(2)	51(1)	0(1)	-1(1)	1(1)
C(11)	59(1)	61(1)	59(1)	-7(1)	1(1)	9(1)
O(1)	62(1)	55(1)	47(1)	-7(1)	3(1)	2(1)
O(2)	76(1)	78(1)	46(1)	-8(1)	1(1)	9(1)
O(3)	90(1)	51(1)	62(1)	-1(1)	-10(1)	5(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **1**.

Atom	x	y	z	U(eq)
H(1)	6250(40)	6477(14)	8810(30)	70(7)
H(2)	3520(40)	6740(14)	9390(30)	77(8)
H(3)	970(40)	5945(13)	8740(30)	73(7)
H(9)	6530(30)	5406(12)	7710(30)	60(6)
H(11A)	-310(40)	3193(15)	5300(40)	83(8)
H(11B)	-1660(40)	3780(12)	5520(30)	68(7)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **2**.

Atom	x	y	z	U(eq)
H(1)	39273601	584097		
H(2)	44893346	3162102		
H(3)	37714093	79890		
H(9)	26254611	615586		
H(11A)	2046772	-33084		
H(11B)	5296259	-170984		

Table S13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **3**.

Atom	x	y	z	U(eq)
H	1390(80)	-720(20)	5900(30)	102(12)
H(1)	-5350(70)	3560(20)	7260(20)	85(9)
H(2)	-5380(70)	3230(20)	5570(20)	77(9)
H(3)	-2610(60)	2123(19)	5000(20)	71(8)
H(9)	-2250(60)	2870(19)	8350(20)	66(8)
H(11A)	6070(70)	-220(20)	7050(20)	76(8)
H(11B)	5470(60)	92(18)	5900(20)	64(8)

Table S14. Lattice energies (kJ mol^{-1}) partitioned into coulombic (E_{coul}), polarization (E_{pol}), dispersion (E_{disp}) and repulsion (E_{rep}) components for **1–3, 5** and **6**.

Compound	E_{coul}	E_{pol}	E_{disp}	E_{rep}	E_{TOT}
1	-44.6	-14.3	-95.2	55.2	-98.8
2	-39.5	-11.8	-95.5	51.0	-95.8
3	-61.2	-22.1	-97.1	81.0	-99.5
5	-31.3	-10.6	-97.7	57.0	-82.6
6	-33.0	-10.1	-101.6	53.2	-91.5

Table S15. Geometrical parameters for the π-stacking moieties involved in the π···π interactions for compounds **1**-**3**, **5** and **6** (Å, º).

Rings i-j[a]	*R*c[b]	*R*1v[c]	*R*2v[d]	α[e]	β[f]	γ[g]	symmetry
Compound 1							
Cg(1) ··Cg(2)	3.7337(5)	3.4907(5)	3.5016(5)	2.00	20.3	20.8	1-x, -y, 1-z
Cg(2) ··Cg(1)	3.7337(5)	3.5016(5)	3.4907(5)	2.00	20.8	20.3	1-x, -y, 1-z
Cg(2) ··Cg(2)	3.8974(5)	3.5104(5)	3.5104(5)	2.03	28.3	27.0	1-x, -y, 1-z
Compound 2							
Cg(2) ··Cg(2)	3.9190(3)	3.4756(3)	3.4756(3)	0.00	27.5	27.5	-x, -y, 1-z
Cg(1) ··Cg(2)	3.9893(3)	3.4453(3)	3.4750(3)	2.00	29.4	30.3	-x, -y, 1-z
Cg(2) ··Cg(1)	3.9893(3)	3.4750(3)	3.4453(3)	2.00	30.3	29.4	-x, -y, 1-z
Compound 3							
Cg(1) ··Cg(2)	3.5995(2)	3.4739(2)	3.5090(2)	2.00	12.9	15.2	1+x, y, z
Cg(2) ··Cg(1)	3.5995(2)	3.5090(2)	3.4739(2)	2.00	15.2	12.9	-1+x, y, z
Compound 5							
Cg(1) ··Cg(1)	3.9083(3)	3.4565(3)	3.4565(3)	0.00	27.8	27.8	1-x, 1-y, 1-z
Cg(1) ··Cg(2)	3.5710(3)	3.4744(3)	3.4997(3)	2.00	11.5	13.4	1-x, 1-y, 1-z
Cg(2) ··Cg(1)	3.5710(3)	3.4997(3)	3.4744(3)	2.00	13.4	11.5	1-x, 1-y, 1-z
Compound 6							
Cg(1) ··Cg(1)	3.7050(2)	3.4551(2)	3.4551(2)	0.00	21.2	21.2	2-x, -y, 1-z
Cg(1) ··Cg(2)	3.7944(2)	3.5241(2)	3.5455(2)	2.00	20.9	21.8	2-x, -y, -z
Cg(1) ··Cg(2)	3.7869(2)	3.4742(2)	3.4928(2)	2.00	22.7	23.4	2-x, -y, 1-z
Cg(2) ··Cg(1)	3.7944(2)	3.5455(2)	3.5241(2)	2.00	21.8	20.9	2-x, -y, -z
Cg(2) ··Cg(1)	3.7869(2)	3.4928(2)	3.4742(2)	2.00	23.4	22.7	2-x, -y, 1-z
Cg(2) ··Cg(2)	3.7268(2)	3.5406(2)	3.5406(2)	0.00	18.2	18.2	2-x, -y, -z

[a] Cg(1) and Cg(2) are the centroids of O1/C4-C8 and C1-C4/C8-C9 rings, respectively. [b] Centroid distance between ring i and ring j. [c] Vertical distance from ring centroid i to ring j. [d] Vertical distance from ring centroid j to ring i. [e] Dihedral angle between mean planes i and j. [f] Angle between the centroid vector Cg(i) ·Cg(j) and the normal to the plane (i). [g] Angle between the centroid vector Cg(i) ·Cg(j) and the normal to the plane (j).

Table S16. Hirshfeld contact surfaces C_{XY} (%)*, proportion of chemical type on the molecular surface S_X (%) and random contacts R_{XY} (%) of the main intermolecular contacts for compounds **1-3, 5** and **6**.

Contact C_{XY}	**1**	**2**	**3**	**5**	**6**
C···H	14.6	11.7	10.7	12.0	7.7
N···H	16.2	0.8	-	-	-
O···H	11.4	35.3	23.4	11.9	13.6
F···H	28.4	24.0	21.0	39.9	28.1
Br···H	-	-	-	-	13.2
C···C	6.1	4.8	6.9	6.9	9.9
C···O	4.8	5.2	1.6	7.0	3.1
Surface S_X					
H	40.2	38.2	47.1	48.8	41.2
C	17.6	13.7	15.5	16.8	15.6
N	10.5	0.7	-	-	-
O	10.0	22.5	14.2	11.2	10.0
F	21.8	21.2	21.7	23.0	21.9
Br	-	-	-	-	11.4
Random contacts R_{XY}					
C···H	14.1	10.4	14.5	16.5	12.9
N···H	8.4	0.5	-	-	-
O···H	8.0	17.2	13.4	10.9	8.2
F···H	17.5	16.2	20.4	22.4	18.0
Br···H	-	-	-	-	9.4
C···C	3.1	1.9	2.4	2.9	2.4
C···O	3.5	6.1	4.4	3.8	3.1

*Data obtained from CrystalExplorer3.0, including reciprocal contacts.

Table S17. Enrichment ratios E_{XY} of the main intermolecular contacts for compounds **1–3, 5** and **6.**

Interaction	**1**	**2**	**3**	**5**	**6**
C···H	1.03	1.13	0.74	0.73	0.60
N···H	1.93	/	-	-	-
O···H	1.43	2.05	1.75	1.09	1.66
F···H	1.62	1.48	1.03	1.78	1.56
Br···H	-	-	-	-	1.40
C···C	1.98	2.58	2.89	2.41	4.07
C···O	1.38	0.85	0.23	1.85	1.00

E_{XY} values for random contacts R_{XY} lower than 0.7% were not calculated.

Table S18. Experimental and calculated frequencies (cm^{-1}) and tentative fundamental vibration modes assignment of 3-cyanomethyl-2-trifluoromethylchromone (**1**).

Mode	Experimental		Calculated[b]		Assignment[c]
	IR[a]	Raman	Frequency	Intensity	
ν_1	3102(w)	3078(34)	3207	4(265)	ν(C1-H)$_{iph}$; ν(C2-H)$_{iph}$; ν(C3-H)$_{iph}$; ν(C9-H)$_{iph}$
ν_2	3091(vw)		3204	1(28)	ν(C1-H)$_{iph}$; ν(C2-H)$_{oph}$; ν(C3-H)$_{oph}$; ν(C9-H)$_{iph}$
ν_3	3077(w)	3064(23)	3192	5(130)	ν(C1-H)$_{iph}$; ν(C2-H)$_{iph}$; ν(C3-H)$_{oph}$; ν(C9-H)$_{oph}$
ν_4	3053(w)	3053(27)	3179	3(64)	ν(C1-H)$_{iph}$; ν(C2-H)$_{oph}$; ν(C3-H)$_{iph}$; ν(C9-H)$_{oph}$
ν_5	3025(vw)	2997(23)	3116	3(57)	ν_{as} (CH_2)
ν_6	2997(w)	2938(32)	3063	10(110)	ν_s (CH_2)
ν_7	2265(w)	2264(25)	2357	13(122)	ν (C-N)
ν_8	1654(m)	1652(100)	1709	295(78)	ν(C5-O2)
ν_9	1612(w)	1612(27)	1674	88(105)	ν(C6-C7)
ν_{10}		1598(20)	1648	51(21)	ν(C8-C9)$_{iph}$; ν(C2-C3)$_{iph}$; ν(C6-C7)$_{iph}$
ν_{11}		1579(29)	1614	13(35)	ν(C4-C8)$_{iph}$; ν(C1-C2)$_{iph}$; δ(C9-C1-H)
ν_{12}		1486(15)	1504	4(1)	δ(C4-C3-H); δ(C1-C2-H); δ(C9-C8-H)
ν_{13}	1473(w)	1478(17)	1494	117(4)	δ(C1-C2-H); δ(C9-C1-H); δ(C4-C8-C9)
ν_{14}		1462(18)	1465	23(9)	δ (CH_2)
ν_{15}	1419(w)	1419(30)	1409	55(38)	δ(C6-C11-H11B); δ(C6-C7-C1); ν(C7-C10)
ν_{16}	1386(vw)	1412(33)	1364	3(33)	δ(C4-C3-H); δ(C9-C8-H); ρ_{wag} (CH_2)
ν_{17}	1374(vw)	1396(16)	1349	18(4)	ρ_{wag} (CH_2)
ν_{18}	1306(m)	1335(27)	1314	147(1)	δ(C2-C3-H); δ(C1-C2-H);δ(C9-C1-H); δ(C8-C9-H)
ν_{19}	1288(vw)		1273	43(4)	ρ_{tw} (CH_2)
ν_{20}	1263(m)		1248	183(7)	δ(C4-C3-H)$_{oph}$; δ(C9-C8-H)$_{iph}$; ν(C8-O1); ρ_{tw} (CH_2)
ν_{21}	1242(w)	1264(18)	1242	21(49)	δ(C3-C2-H); δ(C9-C1-H); δ(C8-O1); ν(C4-C5)
ν_{22}	1227(m)	1202(12)	1185	239(2)	ν_{as} (CF_3); δ(C9-C1-H); δ(C3-C2-H)
ν_{23}		1188(10)	1177	58(1)	δ(C3-C4-H); δ(C2-C1-H); δ(C3-C2-H); ν_{as} (CF_3)
ν_{24}	1203(vs)	1181(9)	1171	193(1)	ρ_{tw} (CH_2); δ(C3-C2-H); ν_s (CF_3)
ν_{25}	1177(m)	1168(15)	1164	41(9)	ρ_{wag} (CH_2); δ(C9-C8-H); δ(C9-C1-H); ν(C7-O1)
ν_{26}	1159(vs)	1157(9)	1136	283(3)	ν_{as} (CF_3)
ν_{27}	1144(m)	1146(9)	1127	13(3)	δ(C1-C2-H); δ(C1-C9-H); δ(C2-C1-H)
ν_{28}	1025(w)	1025(25)	1048	5(27)	δ(C2-C3-H); δ(C1-C9-H); ν(C1-C2)
ν_{29}		1015(12)	1009	<1(<1)	γ(C3-C4-H); γ(C2-C1-H); γ(C3-C2-H)
ν_{30}	995(w)	988(18)	998	27(8)	δ(C6-C7-O1); δ(C4-C5-O2); ρ_r (CH_2)
ν_{31}	976(w)		986	1(<1)	γ(C4-C3-H); γ(C9-C8-H); γ(C9-C1-H)
ν_{32}	955(w)	975(10)	971	39(5)	ρ_r (CH_2)
ν_{33}	931(w)	952(24)	939	9(5)	ν(C11-C12); γ(C6-C11-C12)$_{op}$
ν_{34}			884	<1(<1)	γ(C4-C3-H); γ(C1-C2-H); γ(C9-C8-H)
ν_{35}	887(vw)	840(24)	867	3(3)	ρ_r (CH_2); δ(C1-C2-C3); ν(C8-O1)
ν_{36}	840(w)		828	7(2)	ρ_r (CH_2); δ (CF_3); δ(C9-C8-O1)
ν_{37}	803(w)	801(6)	811	1(1)	γ(C4-C5-C6); γ(C9-C8-H); γ(C2-C1-H)
ν_{38}	772(m)	792(7)	777	71(<1)	γ(C4-C3-H); γ(C3-C2-H); γ(C2-C1-H)
ν_{39}	732(m)	732(28)	742	10(1)	γ(C11-C12-N)$_{op}$; γ(C4-C3-C2)$_{iph}$; γ(O1-C7-C6)$_{oph}$

ν_{40}	717(w)	716(31)	722	13(13)	δ (CF$_3$)
ν_{41}	709^{sh}(vw)	693(28)	704	3(7)	γ(C11-C12-N); γ(O1-C7-C6); γ(C2-C1-C9)
ν_{42}	697(vw)	680(15)	691	5(<1)	γ(C7-C6-C5); γ(C8-O1-C7); γ(C1-C9-C8)
ν_{43}	678(w)	665(12)	654	11(2)	ρ$_r$ (CH$_2$); δ(C6-C5-O2)$_{oph}$; δ(C1-C2-C9)$_{iph}$
ν_{44}	643(w)	593(23)	604	5(1)	γ(C11-C12-N)$_{op}$; δ(C2-C3-C4)$_{oph}$; δ (CF$_3$)
ν_{45}	594(w)	578(11)	581	1(2)	γ(C6-C11-CN); δ(C4-C8-O1)
ν_{46}	546(vw)	544(10)	536	2(<1)	γ(C1-C2-C3); γ(C4-C9-C8)
ν_{47}	535(vw)	528(27)	528	1(1)	δ (CF$_3$); ρ$_r$ (CH$_2$)
ν_{48}	528(vw)	517(32)	521	2(10)	δ(C3-C4-C5)$_{iph}$; δ(C9-C8-O1)$_{iph}$; δ(C5-C6-C7)$_{oph}$
ν_{49}	515(w)		512	2(1)	δ (CF$_3$); γ(C11-C12-N); γ(C9-C8-C4)
ν_{50}	443(w)		448	2(<1)	γ(C2-C3-C4); γ(C1-C9-C8)
ν_{51}		392(10)	392	6(4)	ρ$_r$ (CH$_2$); δ(C6-C5-O2)
ν_{52}			385	8(1)	γ(C11-C12-N)$_{ip}$; ρ$_r$ (CH$_2$)
ν_{53}		370(8)	360	3(<1)	γ(C11-C12-N)$_{ip}$; δ(C6-C5-O2)
ν_{54}		354(22)	355	5(2)	γ(C6-C11-C-N)
ν_{55}		312(10)	310	1(1)	ρ$_r$ (CH$_2$); ρ$_r$ (CF$_3$); γ(C8-O1-C7)
ν_{56}		298(8)	308	1(1)	γ(C8-O1-C7); ρ$_r$ (CH$_2$); γ(C2-C1-C9)
ν_{57}		282(5)	293	4(3)	γ(C7-C10-F3); ρ$_r$ (CH$_2$); τ(O2-C5-C4-C3)
ν_{58}		268(9)	271	7(3)	γ(C11-C12-N)
ν_{59}		238(21)	229	<1 (1)	τ(O1-C7-C10-F3); τ(C1-C9-C8-C4)
ν_{60}		150(29)	159	4(<1)	ρ$_r$ (CF$_3$)
ν_{61}			142	<1 (<1)	τ(C3-C4-C5-O2); τ(C2-C1-C9-C8)
ν_{62}		96(24)	117	5(1)	τ(C6-CH2-CN); τ(C7-C6-C5-O2)
ν_{63}		72(32)	70	<1 (3)	τ(O1-C7-C10-F2)
ν_{64}			53	3(5)	τ(O2-C6-C11-C12)
ν_{65}			46	2(3)	τ(C6-CH2-CN)
ν_{66}			26	1(1)	τ(O1-C7-CF$_3$); τ(C6-CH2-CN)

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. [b] 6-311++g(d,p) calculated IR frequencies (cm^{-1}) and intensities (km mol^{-1}) in parentheses. [c] ν, δ, γ, τ, ρ$_r$, ρ$_{wag}$ and ρ$_{tw}$ represent stretching, in-plane deformation, out-of-plane deformation, torsion, rocking, wagging and twisting modes. Moreover, iph, ip, op and oph represent in phase, in plane, out plane and out of phase modes.

Table S19. Experimental and calculated frequencies (cm^{-1}) and tentative fundamental vibration modes assignment of 3-nitromethyl-2-trifluoromethylchromone (**2**).

Mode	Experimental		Calculated[b]		Assignment[c]
	IR[a]	Raman	Frequency	Intensity	
ν_1	3095(vw)	3078(15)	3208	4(266)	ν(C1-H)$_{iph}$; ν(C2-H)$_{iph}$; ν(C3-H)$_{iph}$; ν(C9-H)$_{iph}$
ν_2	3079(vw)	3069(6)	3204	1(29)	ν(C1-H)$_{iph}$; ν(C2-H)$_{oph}$; ν(C3-H)$_{oph}$; ν(C9-H)$_{iph}$
ν_3	3065(vw)	3054(6)	3192	5(133)	ν(C1-H)$_{iph}$; ν(C2-H)$_{iph}$; ν(C3-H)$_{oph}$; ν(C9-H)$_{oph}$
ν_4	3052(w)	3033(6)	3180	3(63)	ν(C1-H)$_{iph}$; ν(C2-H)$_{oph}$; ν(C3-H)$_{iph}$; ν(C9-H)$_{oph}$
ν_5		3026(5)	3177	2(42)	ν_{as} (CH$_2$)
ν_6	3032(w)	2970(8)	3107	10(89)	ν_s (CH$_2$)
ν_7	1659(vs)	1654(100)	1713	308(100)	ν(C5-O2)
ν_8	1613(m)	1654^{sh}(70)	1675	103(129)	ν(C6-C7)
ν_9	1581^{sh}(w)	1611(7)	1648	39(17)	ν(C8-C9)$_{iph}$; ν(C2-C3)$_{iph}$
ν_{10}	1567(vs)		1632	358(4)	ν_{as} (NO$_2$); ρ_{wag} (CH$_2$)
ν_{11}	1543^{sh}(w)	1580(11)	1614	14(32)	δ(C2-C1-H)$_{iph}$; δ(C3-C2-H)$_{iph}$; δ(C9-C8-H)$_{oph}$
ν_{12}	1480^{sh}(w)		1504	3(1)	δ(C3-C4-H)$_{iph}$; δ(C9-C8-H)$_{iph}$; δ(C9-C1-H)$_{iph}$
ν_{13}	1470(m)	1480(5)	1494	113(5)	δ(C8-C9-H)$_{iph}$; δ(C9-C1-H)$_{iph}$; ν(C8-C1)
ν_{14}	1457(w)	1468(3)	1464	34(6)	δ (CH$_2$)
ν_{15}	1422(m)		1418	159(13)	ν_s (NO$_2$); ρ_{wag} (CH$_2$); ν(C5-C6); ν(C7-C10)
ν_{16}	1418^{sh}(w)	1421(12)	1405	48(24)	ρ_{wag} (CH$_2$)
ν_{17}	1394(vw)	1375(10)	1362	2(44)	δ(C4-C3-H)$_{iph}$; δ(C8-C9-H)$_{iph}$;δ(C9-C1-H)$_{oph}$
ν_{18}	1387(vw)		1343	29(22)	ρ_{wag} (CH$_2$)
ν_{19}	1376(m)		1314	135(1)	δ(C4-C3-H)$_{iph}$; δ(C8-C9-H)$_{oph}$; ν(C7-C10)
ν_{20}	1320(m)		1279	32(7)	ρ_{tw} (CH$_2$)
ν_{21}	1312^{sh}(m)		1247	168(4)	ν_{as} (CF$_3$); δ(C4-C3-H)$_{iph}$; δ(C8-C9-H)$_{iph}$
ν_{22}	1307(m)	1335(11)	1244	83(58)	δ(C2-C3-H)$_{iph}$; δ(C9-C1-H)$_{oph}$; δ(C6-C11-H)
ν_{23}	1263(m)	1245(5)	1198	93(4)	ρ_{wag} (CH$_2$); δ(C3-C2-H)$_{iph}$; δ(C9-C1-H)$_{iph}$; ν(C6-C11)
ν_{24}	1229(m)	1227(5)	1187	194(1)	ν_{as} (CF$_3$); ρ_{tw} (CH$_2$)
ν_{25}	1214(vs)	1211(4)	1179	160(2)	ν_s (CF$_3$); ρ_{tw} (CH$_2$); δ(C8-C9-H)
ν_{26}	1192(w)	1191(3)	1171	28(8)	δ(C1-C2-H)$_{iph}$; δ(C1-C9-H)$_{iph}$; δ(C2-C1-H)$_{oph}$; δ(C1-C2-H)$_{oph}$
ν_{27}	1160(vs)	1174(2)	1136	269(3)	ν_{as} (CF$_3$)
ν_{28}	1148(m)	1156(4)	1128	32(5)	δ(C1-C2-H)$_{iph}$; δ(C1-C9-H)$_{iph}$; δ(C1-C2-H)$_{oph}$
ν_{29}	1030(w)	1028(9)	1049	6(22)	δ(C3-C4-H)$_{iph}$; δ(C9-C8-H)$_{oph}$
ν_{30}	1006(w)	1004(3)	1010	59(6)	ρ_r (CH$_2$)
ν_{31}	1000(w)		1008	<1(<1)	γ(C4-C3-H); γ(C1-C2-H); γ(C9-C8-H)
ν_{32}	978(w)	972(9)	988	18(13)	ρ_r (CH$_2$); δ(C6-C5-O2); δ(C2-C3-C4)
ν_{33}	974(w)		985	2(<1)	γ(C4-C3-H); γ(C1-C2-H)
ν_{34}	865(w)	895(12)	899	17(33)	δ (NO$_2$)
ν_{35}			884	1(<1)	γ(C2-C3-C4); γ(C1-C9-C8)
ν_{36}		864(3)	870	7(4)	ρ_r (CH$_2$); δ(C1-C2-C3); δ(C6-C5-O2)
ν_{37}	848(w)	848(4)	847	19(5)	γ(C6-C11-H); δ (CF$_3$); δ(C6-C7-O1)
ν_{38}		807(2)	818	3(1)	γ(C4-C5-C6); γ(C2-C3-C4); δ (NO$_2$)
ν_{39}	775(m)	775(1)	779	80(<1)	γ(C4-C5-H); γ(C3-C2-H); γ(C9-C1-H)
ν_{40}	744(w)	743(1)	757	14(1)	γ(C2-C3-C4); γ(C5-C4-C8); δ(C6-C11-H)

ν_{41}	724(w)	723(24)	724	19(10)	δ (CF$_3$); γ(O1-C7-C6)
ν_{42}			714	6(9)	γ(C2-C3-C4); γ(C1-C9-C8); γ(O1-C7-C10)
ν_{43}	707(w)		695	6(1)	γ(O1-C7-C10); γ(C4-C5-C6); γ(C1-C2-C3)
ν_{44}		706(13)	673	1(6)	γ(C11-N-O); γ(C8-C4-C5)
ν_{45}	688(w)	686(3)	658	11(2)	ρ_{wag} (NO$_2$); γ(C6-C5-O2); γ(C2-C1-C9); ρ_{tw} (CH$_2$)
ν_{46}	649(w)	647(3)	602	5(2)	γ(C1-C9-C8); γ(C2-C3-C4); δ (CF$_3$)
ν_{47}	595(w)	595(4)	577	5(1)	ρ_r (CH$_2$); ρ_{wag} (NO$_2$)
ν_{48}	565(w)	556(3)	562	9(3)	γ(C8-O1-C7); γ(C11-N-O4); δ (CF$_3$)
ν_{49}	534(vw)	533(1)	536	2(<1)	γ(C1-C9-C8); γ(C1-C2-C3)
ν_{50}	521(vw)	518(16)	522	4(8)	δ(C4-C5-C6); δ (CF$_3$)
ν_{51}			519	2(3)	δ (CF$_3$); ρ_r (CH$_2$); δ(C4-C5-O2)
ν_{52}	515(w)		513	3(1)	δ (CF$_3$)
ν_{53}	445(w)	444(2)	450	2(<1)	γ(C1-C2-C3); γ(C3-C4-C8)
ν_{54}		377(5)	380	7(2)	ρ_r (CH$_2$); γ(C3-C4-C5)
ν_{55}			375	3(1)	γ(C11-N-O3); ρ_r (CH$_2$)
ν_{56}		363(4)	333	5(6)	ρ_r (NO$_2$); τ(C5-C6-C11-H11B)
ν_{57}			314	2(1)	ρ_r (CH$_2$); τ(O1-C7-C10-F3)
ν_{58}		336(6)	307	1(2)	ρ_r (CF$_3$); ρ_r (CH$_2$)
ν_{59}		317(6)	293	5(2)	τ(C3-C4-C5-O2); ρ_r (CH$_2$)
ν_{60}		296(5)	280	5(3)	τ(C6-C7-C10-F2); τ(C2-C5-C6-C11); ρ_r (CH$_2$)
ν_{61}		239(5)	228	<1 (1)	τ(O1-C6-C10-F1); τ(C4-C8-C9-C1)
ν_{62}		166(9)	163	3(<1)	ρ_r (CF$_3$); τ(C6-C11-N-O3)
ν_{63}			144	<1 (1)	τ(C2-C3-C4-C5); τ(C4-C8-C9-C1)
ν_{64}			116	3(<1)	τ(O2-C5-C6-C11); γ(C11-N-O3)
ν_{65}			72	<1 (2)	τ(O1-C7-CF$_3$); τ(O1-C8-C4-C3)
ν_{66}			50	2(3)	τ(C5-C6-C11-N)
ν_{67}			45	1(2)	τ(C6-C7-C10-F2)
ν_{68}			36	1(2)	τ(C6-C11-NO$_2$)
ν_{69}			16	<1(<1)	τ(O1-C7-CF$_3$)

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. [b] 6-311++g(d,p) calculated IR frequencies (cm^{-1}) and intensities (km mol^{-1}) in parentheses. [c] ν, δ, γ, τ, ρ_r, ρ_{wag} and ρ_{tw} represent stretching, in-plane deformation, out-of-plane deformation, torsion, rocking, wagging and twisting modes. Moreover, iph, ip and oph represent in phase, in plane and out of phase modes.

Table S20. Experimental and calculated frequencies (cm^{-1}) and tentative fundamental vibration modes assignment of 3-hydroxymethyl-2-trifluoromethylchromone (**3**).

Mode	Experimental		Calculated[b]		Assignment[c]
	IR[a]	Raman	Frequency	Intensity	
ν_1	3438(m)	3437(6)	3758	71(54)	ν (O-H)
ν_2	3082(vw)	3071(19)	3206	4(263)	ν(C1-H)$_{iph}$; ν(C2-H)$_{iph}$; ν(C3-H)$_{iph}$; ν(C9-H)$_{iph}$
ν_3	3069^{sh}(vw)		3203	2(27)	ν(C1-H)$_{iph}$; ν(C2-H)$_{oph}$; ν(C3-H)$_{oph}$; ν(C9-H)$_{iph}$
ν_4	3049(vw)	3050(2)	3191	5(131)	ν(C1-H)$_{iph}$; ν(C2-H)$_{iph}$; ν(C3-H)$_{oph}$; ν(C9-H)$_{oph}$
ν_5	3026(vw)	3029(2)	3178	3(63)	ν(C1-H)$_{iph}$; ν(C2-H)$_{oph}$; ν(C3-H)$_{iph}$; ν(C9-H)$_{oph}$
ν_6	2948(vw)	2951(2)	3147	9(66)	ν$_{as}$ (CH$_2$)
ν_7	2902(vw)	2903(2)	3002	31(142)	ν$_s$ (CH$_2$)
ν_8	1646(vs)	1651(100)	1688	330(114)	ν(C5-O2)
ν_9	1610(m)	1638^{sh}(10)	1666	47(88)	ν(C6-C7)
ν_{10}	1578(w)	1611(12)	1647	67(24)	ν(C8-C9)$_{iph}$; ν(C2-C3)$_{iph}$; ν(C6-C7)$_{oph}$
ν_{11}		1581(23)	1611	10(35)	ν(C4-C8)$_{iph}$; ν(C1-C2)$_{iph}$
ν_{12}			1503	4(<1)	δ(C4-C3-H); δ(C1-C2-H); δ(C9-C8-H)
ν_{13}	1471(m)	1517(1)	1497	62(6)	δ(CH$_2$)
ν_{14}		1510(1)	1493	52(5)	δ(CH$_2$); δ(C9-C1-H); δ(C8-C9-H)
ν_{15}	1410(m)	1503(1)	1442	49(7)	δ(C11-O3-H)
ν_{16}	1385(m)	1473(9)	1418	128(18)	δ(O1-C7-C6); ν(C7-C10); δ(C11-O3-H)
ν_{17}	1355(w)	1417(7)	1373	5(7)	δ(C11-O3-H11B); ρ$_{wag}$ (CH$_2$)
ν_{18}	1340(w)	1411^{sh}(12)	1363	4(39)	ν(C4-C8)$_{iph}$; ν(C1-C9)$_{iph}$; δ(C11-O3-H)
ν_{19}	1308(m)	1383(3)	1314	117(2)	δ(C3-C4-H); δ(C9-C8-H)
ν_{20}	1298^{sh}(m)	1347(10)	1271	110(8)	ρ$_{tw}$ (CH$_2$); γ(C11-O3-H); ν(C7-C10)
ν_{21}	1258(m)		1246	86(5)	δ(C2-C3-H); δ(C8-C9-H); ν(C4-C5); ρ$_{tw}$ (CH$_2$)
ν_{22}		1342(20)	1243	71(44)	ν(C1-O1); δ(C9-C1-H); δ(C3-C2-H); δ(C3-C4-H)
ν_{23}	1229(m)	1260(4)	1188	285(5)	δ(C3-C2-H); ρ$_{tw}$ (CH$_2$); γ(C11-O3-H)
ν_{24}			1180	34(1)	γ(C6-C11-H11A); δ(C3-C2-H); ν(C7-O1)
ν_{25}		1240(11)	1167	82(4)	δ(C8-C9-H); δ(C2-C1-H); γ(C6-C11-H11A)
ν_{26}	1203(m)	1229(11)	1157	161(9)	ν$_{as}$ (CF$_3$); ν(C7-O1); δ(C4-C3-H); δ(C9-C1-H)
ν_{27}	1151(vs)	1153(5)	1128	211(2)	ν$_{as}$ (CF$_3$)
ν_{28}	1119^{sh}(m)	1141(2)	1126	81(2)	ν$_{as}$ (CF$_3$); δ(C3-C4-H); δ(C1-C9-H); δ(C3-C2-H)
ν_{29}	1036(m)	1036^{sh}(5)	1060	108(6)	ν(C11-O3)
ν_{30}	1027(m)	1026(22)	1046	12(33)	ν(C1-C2); δ(C3-C4-H); δ(C8-C9-H)
ν_{31}			1008	<1(<1)	γ(C4-C3-H); γ(C3-C2-H); γ(C2-C1-H)
ν_{32}	1001(m)	1006(1)	1004	36(1)	ρ$_r$ (CH$_2$)
ν_{33}			985	2(<1)	γ(C4-C3-H); γ(C3-C2-H); γ(C2-C1-H)
ν_{34}	971(w)	972(6)	978	24(4)	γ(C4-C3-H); γ(C9-C1-H); γ(C8-C9-H)
ν_{35}	873(vw)	862(3)	888	18(1)	ρ$_r$ (CH$_2$); δ(C4-C5-O2); δ(C2-C3-C4); γ(C11-O3-H)
ν_{36}	863(w)		882	7(<1)	γ(C4-C3-H); γ(C8-C9-H); γ(C6-C11-H11B)
ν_{37}	837(w)	839(3)	851	4(3)	ν$_s$ (CF$_3$); δ(C2-C3-C4); ν(C7-O1); δ(C6-C5-O2)
ν_{38}	804(vw)	806(2)	799	5(1)	γ(C6-C5-O2); γ(C4-C6-C6) ; γ(C9-C1-H); γ(C8-C9-H)
ν_{39}	768(m)		775	67(<1)	γ(O1-C8-C9); γ(C4-C3-H) ; γ(C3-C2-H); γ(C1-C2-H)
ν_{40}	729(m)	769(5)	727	21(3)	δ$_s$ (CF$_3$); γ(O1-C8-C4)

ν_{41}	717(w)	734(17)	718	10(11)	δ_s (CF$_3$); γ(C5-C6-C7); γ(C4-C8-C9)
ν_{42}	691(vw)	719(18)	694	5(8)	ν(C6-C11); γ(C5-C6-C7); γ(C2-C1-C9)
ν_{43}	680(w)	693(17)	681	4(1)	γ(C5-C6-C7); δ(C7-C10-F2A); γ(C1-C9-C8)
ν_{44}	643(w)	680(7)	650	9(<1)	δ(C9-C8-O1); δ(O2-C5-C6); ρ_r (CH$_2$); γ(C7-C10-F1A)
ν_{45}	601^{sh}(vw)	645(4)	600	3(2)	δ_s (CF$_3$); δ(C1-C9-C8); δ(C1-C2-C3)
ν_{46}	591(w)	594(5)	571	170(1)	γ (C11-O3-H)
ν_{47}	555(w)	537^{sh}(7)	546	11(4)	γ (C6-C11-O3); τ(C6-C11-O3-H)
ν_{48}	547^{sh}(vw)		537	3(1)	γ(C1-C2-C3); γ(C1-C9-C8); γ(C9-C8-O1)
ν_{49}			526	1(1)	δ_{as} (CF$_3$)
ν_{50}	531(w)	520(29)	519	9(8)	δ(C5-C4-C8); γ (C11-O3-H)
ν_{51}	506(w)	481^{sh}(1)	502	3(1)	δ_{as} (CF$_3$); γ (C6-C11-O3)
ν_{52}	435(vw)	437(3)	444	6(1)	γ(C1-C2-C3); γ(C4-C8-C9)
ν_{53}		395(7)	382	1(4)	δ(C6-C5-O2); δ(O2-C7-C6)
ν_{54}		375(1)	357	8(1)	ρ_r (CH$_2$); δ(C6-C5-O2); δ(C7-C10-F1A)
ν_{55}		329(6)	323	<1 (1)	γ(C8-O1-C7); γ(C1-C2-C3); ρ_r (CF$_3$)
ν_{56}			314	7(1)	δ(C6-C10-F1A); ρ_r (CH$_2$); δ(C4-C5-O2)
ν_{57}		302(8)	295	1(3)	ρ_r (CH$_2$)
ν_{58}		263(3)	260	7(1)	ρ_r (CH$_2$); γ(C6-C11-O3)
ν_{59}		245(10)	235	1(<1)	τ(O1-C7-C10-F2A); τ(C7-C6-C11-H11B)
ν_{60}		211(2)	191	2(<1)	γ(C6-C11-O3); τ(C5-C6-C11-O3)
ν_{61}		176(3)	155	3(1)	ρ_r (CF$_3$); ρ_r (CH$_2$)
ν_{62}		165(3)	144	1(<1)	τ(O2-C5-C4-C8); τ(C6-C7-C10-F2A)
ν_{63}			90	2(1)	τ(C5-C6-C11-O3)
ν_{64}			73	<1(3)	τ(C6-C7-C10-F2A)
ν_{65}			69	2(1)	τ(C6-CH$_2$-OH)
ν_{66}			29	<1 (1)	τ(C7-CF$_3$)

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. [b] 6-311++g(d,p) calculated IR frequencies (cm^{-1}) and intensities (km mol^{-1}) in parentheses. [c] ν, δ, γ, τ, ρ_r, ρ_{wag} and ρ_{tw} represent stretching, in-plane deformation, out-of-plane deformation, torsion, rocking, wagging and twisting modes. Moreover, iph, ip and oph represent in phase, in plane and out of phase modes.

Table S21. Experimental and calculated frequencies (cm^{-1}) and tentative fundamental vibration modes assignment of 3-aminomethyl-2-trifluoromethylchromone (**4**).

Mode	Experimental		Calculated[b]		Assignment[c]
	IR[a]	Raman	Frequency	Intensity	
ν_1	3328(w)	3329(16)	3606	7(90)	$\nu_{as}(NH_2)$
ν_2		3222(16)	3522	<1 (199)	$\nu_s(NH_2)$
ν_3	3105(w)	3086(46)	3205	6(265)	$\nu(C1\text{-}H)_{iph}$; $\nu(C2\text{-}H)_{iph}$; $\nu(C3\text{-}H)_{iph}$; $\nu(C9\text{-}H)_{iph}$
ν_4	3091(w)	3067(12)	3202	2(27)	$\nu(C1\text{-}H)_{iph}$; $\nu(C2\text{-}H)_{oph}$; $\nu(C3\text{-}H)_{oph}$; $\nu(C9\text{-}H)_{iph}$
ν_5	3056(w)	3055(10)	3189	7(134)	$\nu(C1\text{-}H)_{iph}$; $\nu(C2\text{-}H)_{iph}$; $\nu(C3\text{-}H)_{oph}$; $\nu(C9\text{-}H)_{oph}$
ν_6	3031(vw)	2917(15)	3176	3(64)	$\nu(C1\text{-}H)_{iph}$; $\nu(C2\text{-}H)_{oph}$; $\nu(C3\text{-}H)_{iph}$; $\nu(C9\text{-}H)_{oph}$
ν_7	2920(w)	2877(19)	3100	2(53)	$\nu_{as}(CH_2)$
ν_8	2845(w)	2841(18)	3022	44(110)	$\nu_s(CH_2)$
ν_9	1659(m)	1661(80)	1714	302(78)	$\nu(C5\text{-}O2)$
ν_{10}	1612(w)	1652(100)	1671	50(110)	$\nu(C6\text{-}C7)$; $\delta(NH_2)$; $\delta(C6\text{-}C11\text{-}H)$
ν_{11}	1581(w)	1641(56)	1655	46(15)	$\delta(NH_2)$
ν_{12}		1612(38)	1648	47(18)	$\nu(C8\text{-}C9)_{iph}$; $\nu(C2\text{-}C3)_{iph}$; $\nu(C6\text{-}C7)_{oph}$
ν_{13}		1582(40)	1613	13(34)	$\nu(C4\text{-}C8)_{iph}$; $\nu(C1\text{-}C2)_{iph}$
ν_{14}		1521(6)	1503	9(4)	$\delta(CH_2)$
ν_{15}		1505(7)	1501	12(6)	$\delta(CH_2)$; $\delta(C4\text{-}C3\text{-}H)$; $\delta(C9\text{-}C1\text{-}H)$
ν_{16}	1467(m)	1494(6)	1493	107(4)	$\delta(C2\text{-}C3\text{-}H)$; $\delta(C8\text{-}C9\text{-}H)$; $\delta(C9\text{-}C1\text{-}H)$
ν_{17}		1469(25)	1420	43(4)	$\rho_{wag}(CH_2)$; $\rho_{tw}(NH_2)$
ν_{18}		1408(36)	1409	62(22)	$\rho_{wag}(CH_2)$; $\delta(O1\text{-}C7\text{-}C6)$; $\nu(C7\text{-}C10)$; $\nu(C6\text{-}C7)$
ν_{19}	1407(w)	1341(43)	1362	1(37)	$\nu(C3\text{-}C2)_{iph}$; $\nu(C1\text{-}C9)_{iph}$; $\nu(C3\text{-}C4)_{oph}$; $\nu(C9\text{-}C8)_{oph}$
ν_{20}	1330(vw)	1324(18)	1333	22(3)	$\rho_{tw}(CH_2)$; $\rho_{tw}(NH_2)$
ν_{21}	1304(m)	1310(15)	1313	121(1)	$\delta(C3\text{-}C4\text{-}H)$; $\delta(C3\text{-}C2\text{-}H)$; $\delta(C9\text{-}C1\text{-}H)$; $\delta(C8\text{-}C9\text{-}H)$
ν_{22}	1226(m)	1261(17)	1250	258(2)	$\rho_{tw}(NH_2)$; $\rho_{tw}(CH_2)$; $\nu(C7\text{-}C10)$; $\delta(C3\text{-}C4\text{-}H)$
ν_{23}	1212(m)	1234(29)	1242	56(46)	$\delta(C3\text{-}C2\text{-}H)$; $\delta(C9\text{-}C1\text{-}H)$; $\nu(C4\text{-}C5)$; $\nu(C8\text{-}O1)$
ν_{24}	1199^{sh}(m)		1235	15(2)	$\rho_{tw}(NH_2)$; $\gamma(C6\text{-}C11\text{-}H)$; $\nu(C4\text{-}C5)$; $\delta(C3\text{-}C4\text{-}H)$
ν_{25}	1183(m)	1173(15)	1191	76(6)	$\nu(C6\text{-}C11)$; $\nu(O1\text{-}C7)$; $\delta(C3\text{-}C2\text{-}H)$; $\delta(C9\text{-}C1\text{-}H)$
ν_{26}	1168(m)		1172	123(4)	$\nu_{as}(CF_3)$
ν_{27}		1167(14)	1170	29(7)	$\delta(C8\text{-}C9\text{-}H)$; $\delta(C9\text{-}C1\text{-}H)$; $\delta(C1\text{-}C2\text{-}H)$
ν_{28}	1146^{sh}(m)		1142	210(2)	$\rho_{tw}(NH_2)$; $\rho_{tw}(CH_2)$; $\nu(C7\text{-}O1)$; $\delta(C4\text{-}C3\text{-}H)$
ν_{29}		1145(26)	1125	50(2)	$\delta(C9\text{-}C1\text{-}H)$; $\delta(C2\text{-}C3\text{-}H)$
ν_{30}	1138(vs)	1071(19)	1117	266(3)	$\nu_{as}(CF_3)$
ν_{31}	1115(m)	1041(17)	1057	19(4)	$\nu(C11\text{-}N)$
ν_{32}	1070(w)	1026(33)	1044	2(42)	$\nu(C1\text{-}C2)$; $\nu(C2\text{-}C3)$; $\nu(C1\text{-}C9)$
ν_{33}	1025(w)		1006	0(0)	$\gamma(C4\text{-}C3\text{-}H)$; $\gamma(C3\text{-}C2\text{-}H)$; $\gamma(C2\text{-}C1\text{-}H)$
ν_{34}		1010(3)	983	1(1)	$\gamma(C4\text{-}C3\text{-}H)$; $\gamma(C8\text{-}C9\text{-}H)$; $\gamma(C9\text{-}C1\text{-}H)$
ν_{35}	1001(w)	996(24)	983	17(3)	$\delta(C5\text{-}C6\text{-}C7)$; $\delta(O1\text{-}C7\text{-}C6)$; $\gamma(C11\text{-}N\text{-}H)$
ν_{36}	999(w)	965(23)	980	34(1)	$\rho_{tw}(NH_2)$; $\rho_r(CH_2)$
ν_{37}	977(w)		883	1(0)	$\gamma(C4\text{-}C3\text{-}H)$; $\gamma(C3\text{-}C2\text{-}H)$; $\gamma(C8\text{-}C9\text{-}H)$
ν_{38}	965(w)	861(20)	867	7(2)	$\rho_r(CH_2)$; $\delta(C1\text{-}C2\text{-}C3)$
ν_{39}	868(w)	832(22)	827	24(1)	$\gamma(C11\text{-}N\text{-}H)$; $\rho_r(CH_2)$
ν_{40}	809(w)	808(22)	816	11(3)	$\rho_{wag}(NH_2)$; $\rho_r(CH_2)$; $\delta(O2\text{-}C5\text{-}C6)$

ν_{41}	760(m)	777(20)	792	126(1)	ρ_{wag} (NH$_2$)
ν_{42}		762(20)	774	30(0)	γ(C4-C3-H); γ(C3-C2-H); γ(C2-C1-H)
ν_{43}	739(w)		724	14(2)	ρ_{wag} (NH$_2$); γ(C9-C8-O1); γ(C2-C3-C4)
ν_{44}	729(w)	738(24)	719	11(13)	δ_s (CF$_3$); δ(C8-O2-C7)
ν_{45}	718(w)	716(54)	690	25(8)	ν(C6-C11); δ(C9-C1-C2); δ(C3-C4-C8); γ(C11-N-H)
ν_{46}	688(w)	700(30)	678	3(1)	γ(C5-C6-C7); γ(C7-C10-F); γ(C1-C9-C8)
ν_{47}	677(w)	688(22)	648	6(1)	δ(C3-C4-C5); δ(C9-C8-O1); ρ_r (CH$_2$)
ν_{48}	645(w)	644(21)	600	4(2)	δ(C3-C4-C5); δ(C2-C3-C4); δ_{as} (CF$_3$)
ν_{49}	626(vw)	593(23)	556	10(2)	γ (C6-C11-N)
ν_{50}	614(vw)	548(20)	537	4(1)	γ(C9-C8-O1); γ(C1-C2-C3)
ν_{51}	594(w)	530(20)	524	1(5)	δ_{as} (CF$_3$)
ν_{52}	511(vw)	518(44)	521	2(6)	δ_{as} (CF$_3$); δ(C4-C5-O2); δ(C8-O1-C7)
ν_{53}		478(23)	499	14(1)	δ_{as} (CF$_3$); γ (C8-O1-C7); γ (C11-N-H)
ν_{54}	426(w)	440(16)	441	3(1)	γ(C1-C2-C3); γ(C4-C8-C9)
ν_{55}		402(16)	396	0(3)	ν(O1-C7); ν(C6-C11); τ(C1-C9-C8-C4)
ν_{56}		365(17)	361	8(1)	ρ_r (CH$_2$); δ(C6-C5-O2); δ(C7-C10-F)
ν_{57}			325	4(0)	ρ_r (CH$_2$); γ (C7-C10-F); ρ_r (NH$_2$)
ν_{58}		313^{sh}(17)	320	1(1)	γ (C4-C8-O1); τ(H-C11-N-H); δ(C7-C10-F)
ν_{59}		303(23)	300	4(4)	ρ_r (CH$_2$); δ(C3-C4-C5); δ(C9-C8-O1)
ν_{60}		271(16)	260	1(2)	ρ_r (CH$_2$); ρ_r (NH$_2$)
ν_{61}		234(20)	237	0(1)	τ(O1-C7-C10-F); τ(C7-C6-C11-H)
ν_{62}		205(15)	212	35(0)	ρ_r (NH$_2$)
ν_{63}		170(36)	188	0(0)	γ (C6-C11-N); τ(C5-C4-C8-O1)
ν_{64}		148(19)	153	1(0)	ρ_{wag} (CF$_3$)
ν_{65}			132	1(1)	τ(C3-C4-C5-O2); τ(C6-C11-C5-N)
ν_{66}			102	1(0)	τ(C6-C11-C5-N)
ν_{67}			75	0(4)	τ(C6-C7-C10-F)
ν_{68}			62	5(1)	τ(C6-CH$_2$-NH$_2$)
ν_{69}			26	0(1)	τ(O1-C7-CF$_3$)

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. [b] 6-311++g(d,p) calculated IR frequencies (cm^{-1}) and intensities (km mol^{-1}) in parentheses. [c] ν, δ, γ, τ, ρ_r, ρ_{wag} and ρ_{tw} represent stretching, in-plane deformation, out-of-plane deformation, torsion, rocking, wagging and twisting modes. Moreover, iph, ip and oph represent in phase, in plane and out of phase modes.