

Supplementary Information

New Schiff base salts as sources of blue and green light in the solid state: the role of anion and protonation

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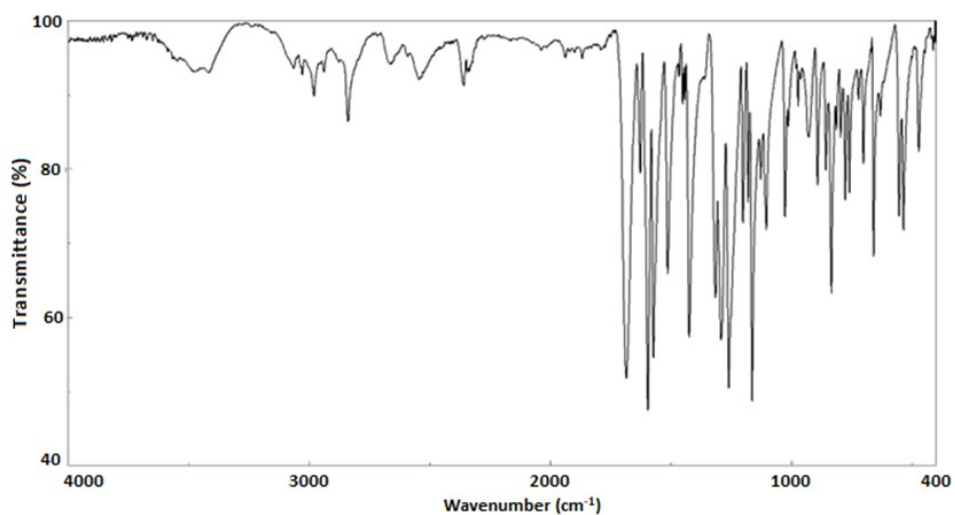


Figure S1. IR spectrum of *N*-(4'-methoxybenzylidene)-4-aminobenzoic acid (1a).

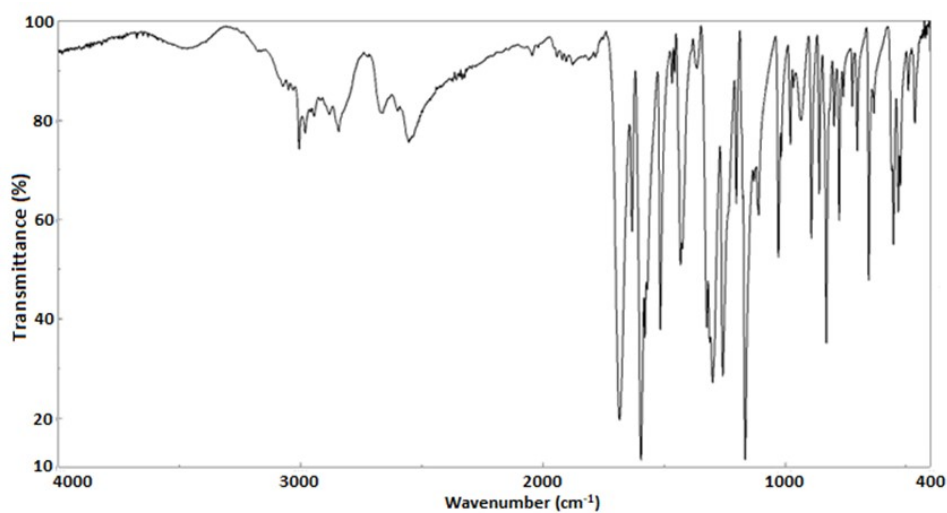


Figure S2. IR spectrum of *N*-(4'-methoxybenzylidene)-4-aminobenzoic acid (1b).

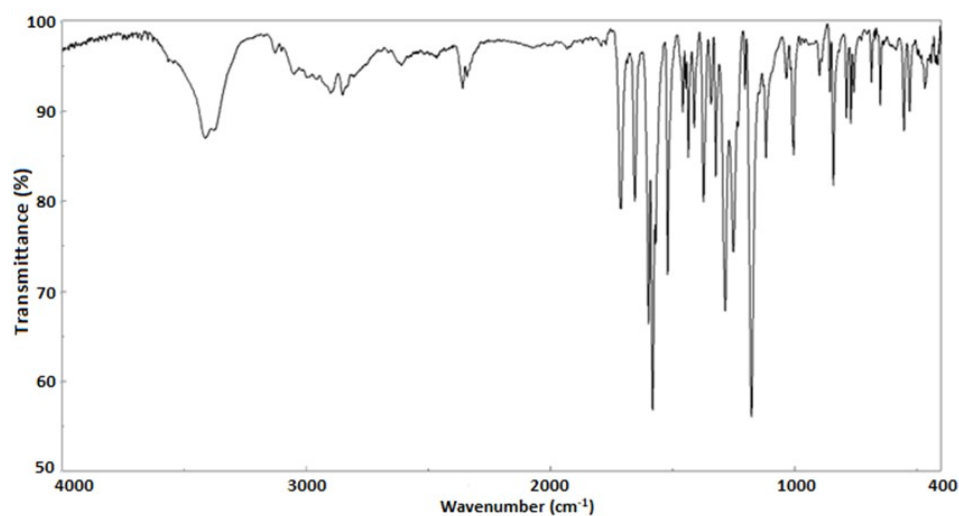


Figure S3. IR spectrum of 4-carboxy-*N*-(4'-methoxybenzylidene)anilium chloride monohydrate (2).

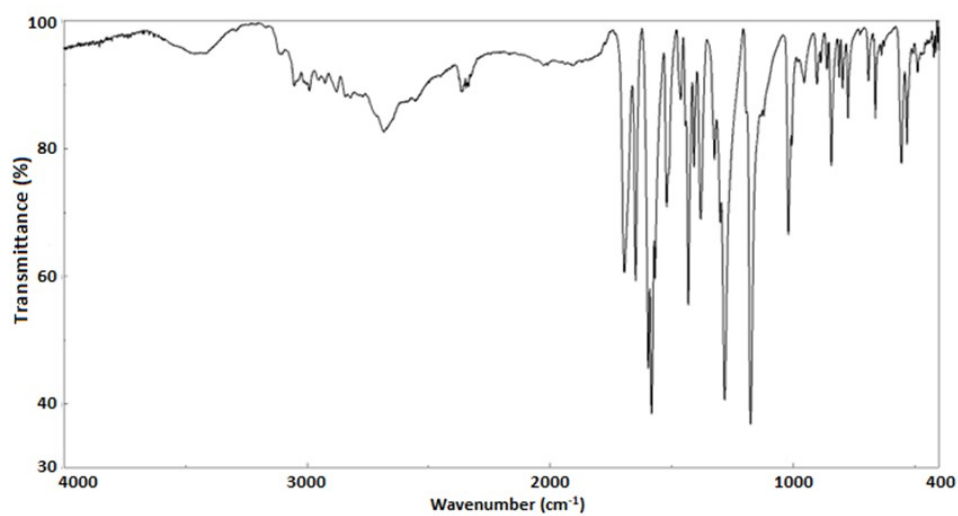


Figure S4. IR spectrum of 4-carboxy-*N*-(4'-methoxybenzylidene)anilium bromide monohydrate (3).

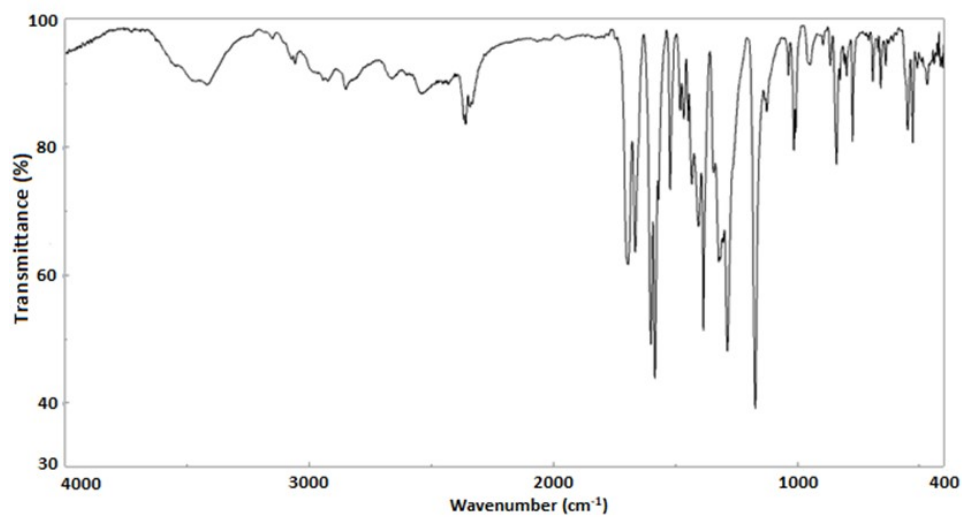


Figure S5. IR spectrum of 4-carboxy-*N*-(4'-methoxybenzylidene)anilium nitrate (4).

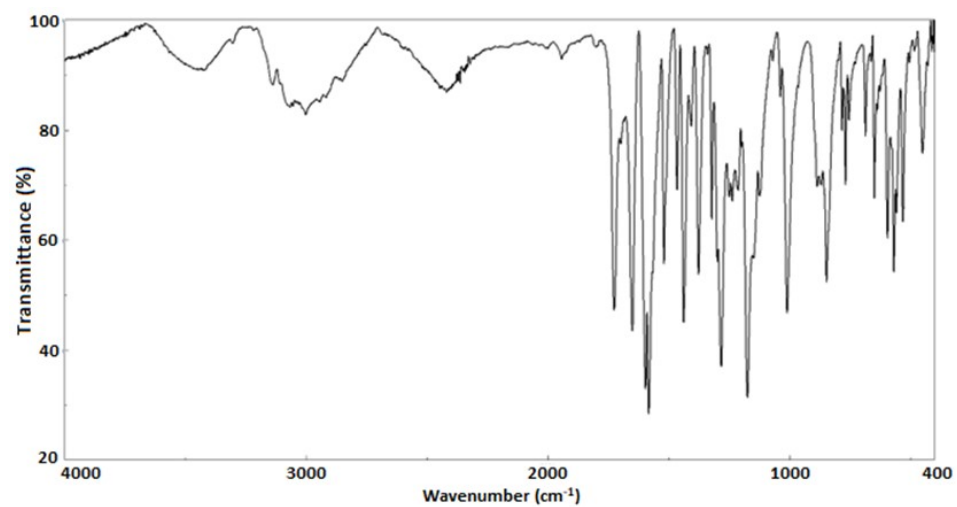


Figure S6. IR spectrum of 4-carboxy-*N*-(4'-methoxybenzylidene)anilium hydrogen sulfate (5).

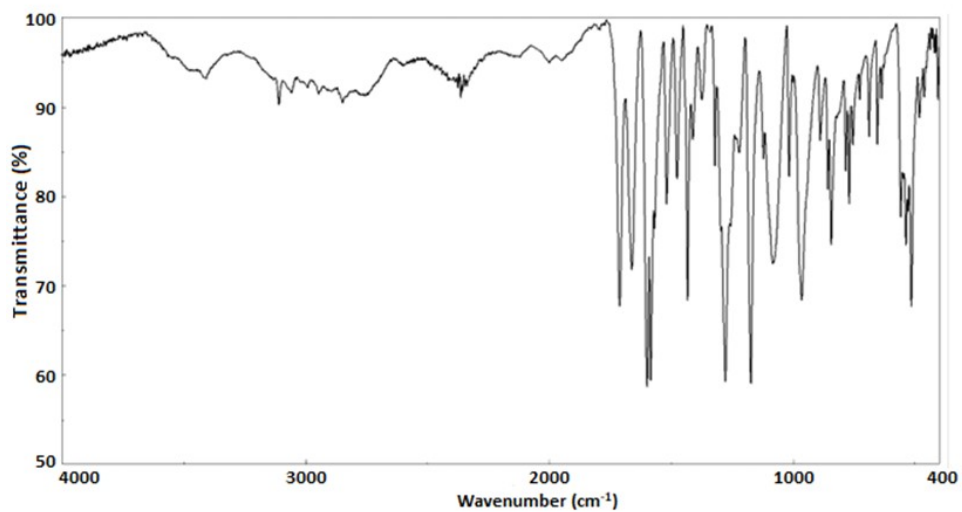


Figure S7. IR spectrum of 4-carboxy-*N*-(4'-methoxybenzylidene)anilium dihydrogen phosphate (6).

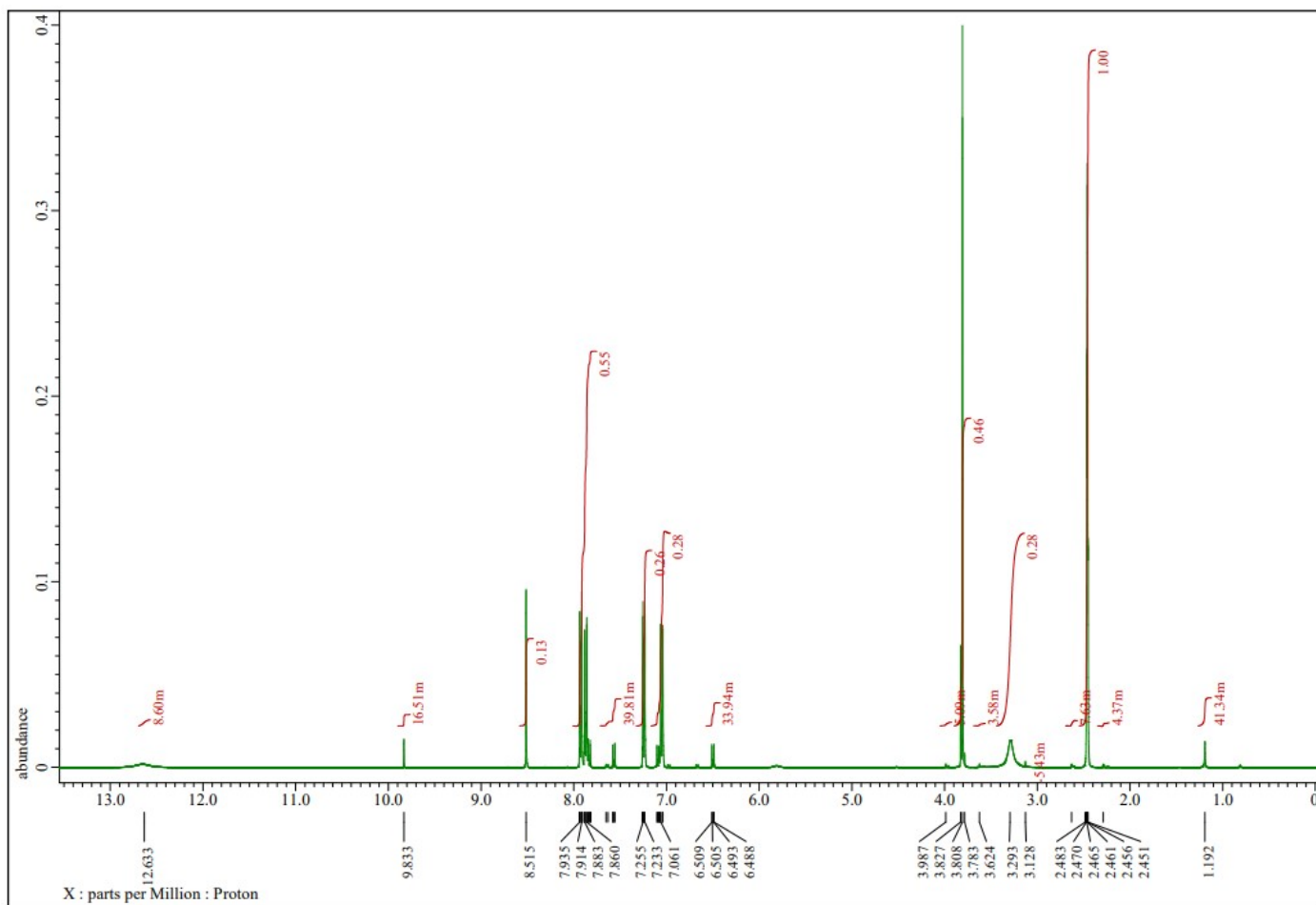


Figure S8. NMR spectrum of *N*-(4'-methoxybenzylidene)-4-aminobenzoic acid (1a).

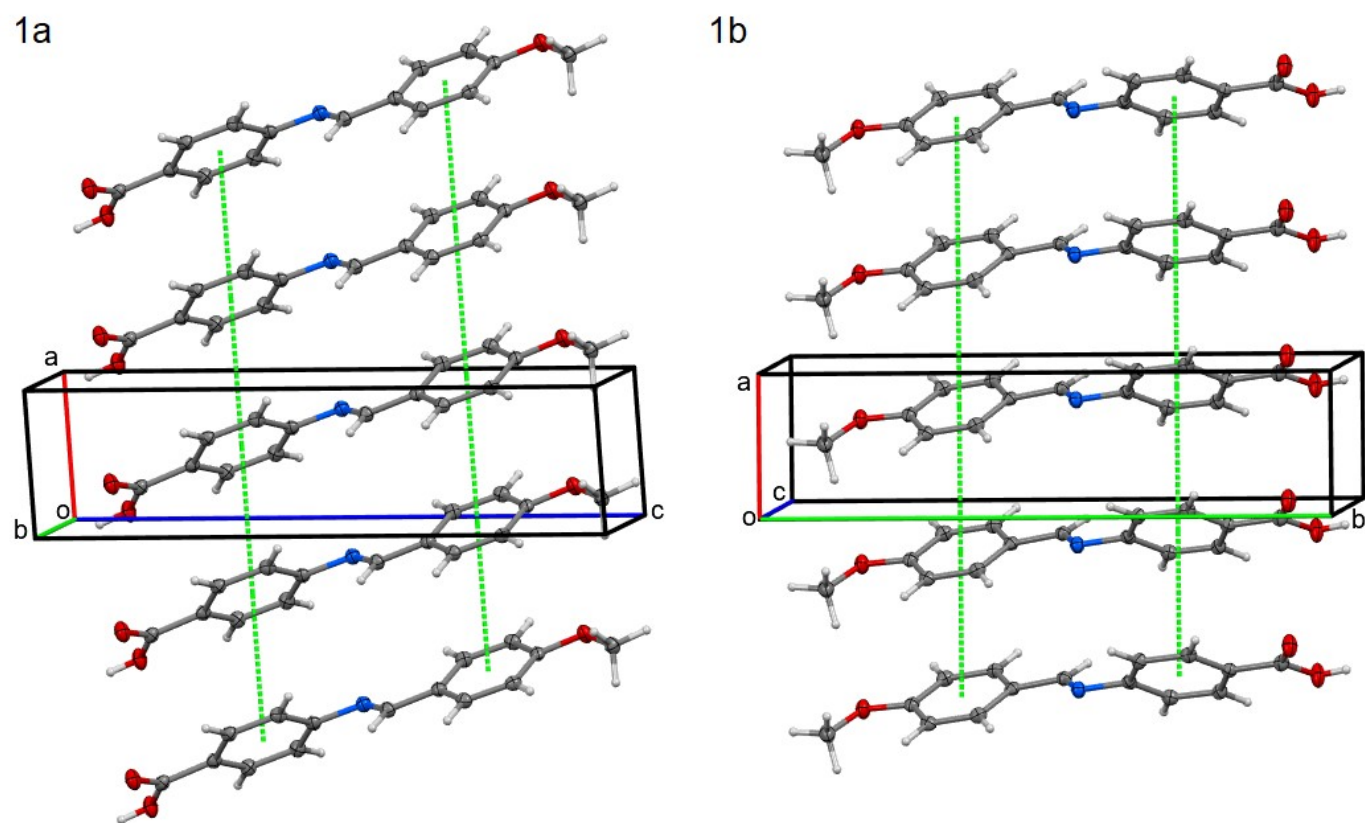


Figure S9. The $\pi \cdots \pi$ interactions in **1a** and **1b**.

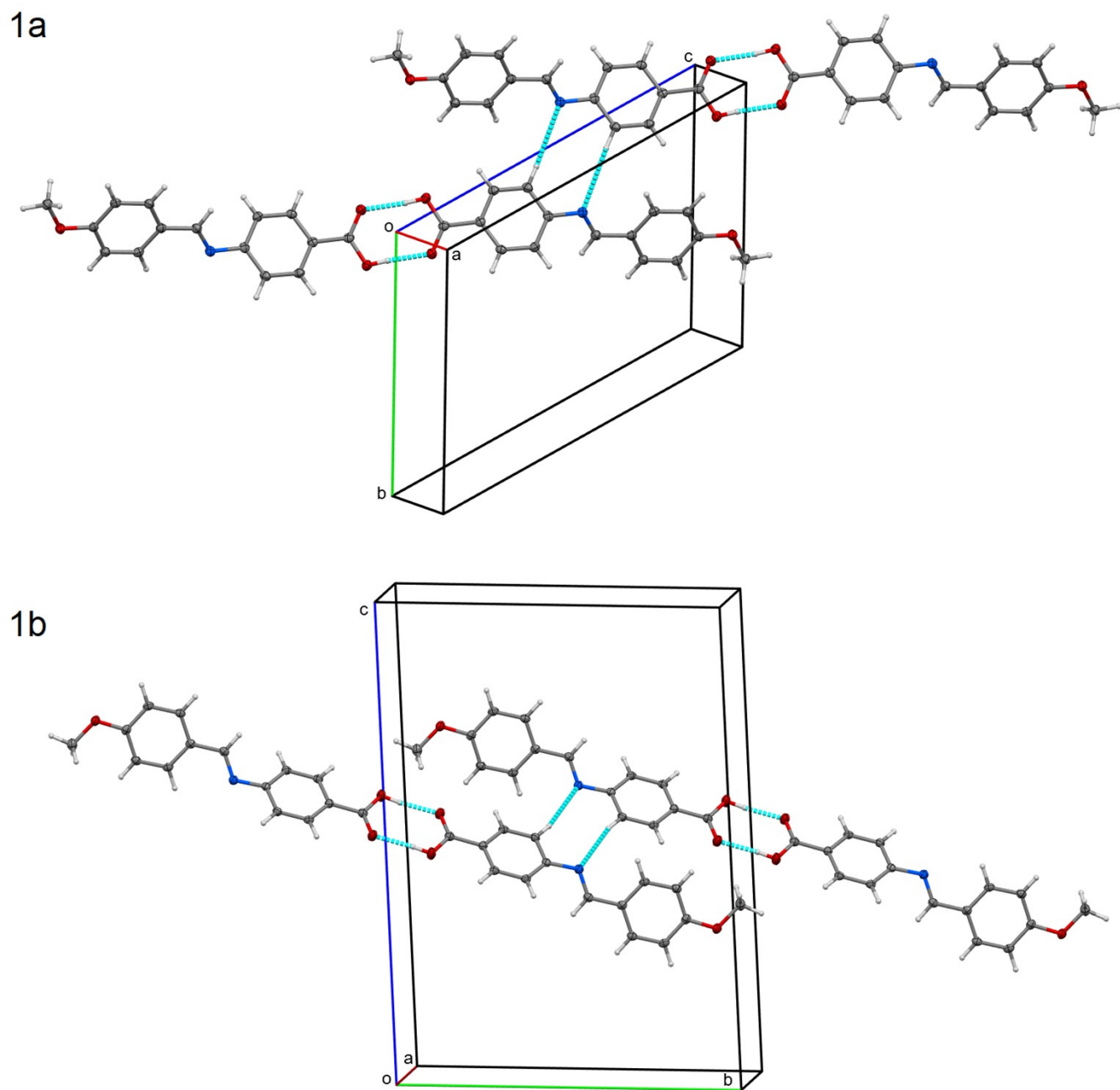
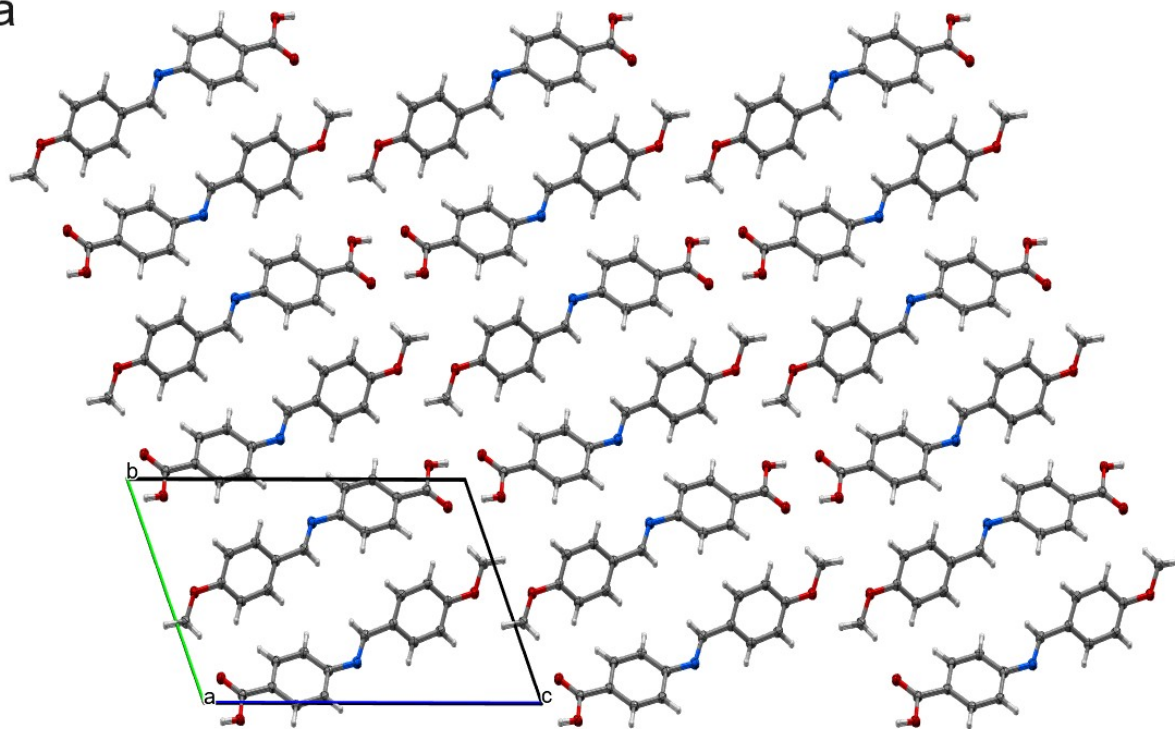


Figure S10. The hydrogen bond $R_2^2(8)$ synthons in **1a** and **1b**.

1a



1b

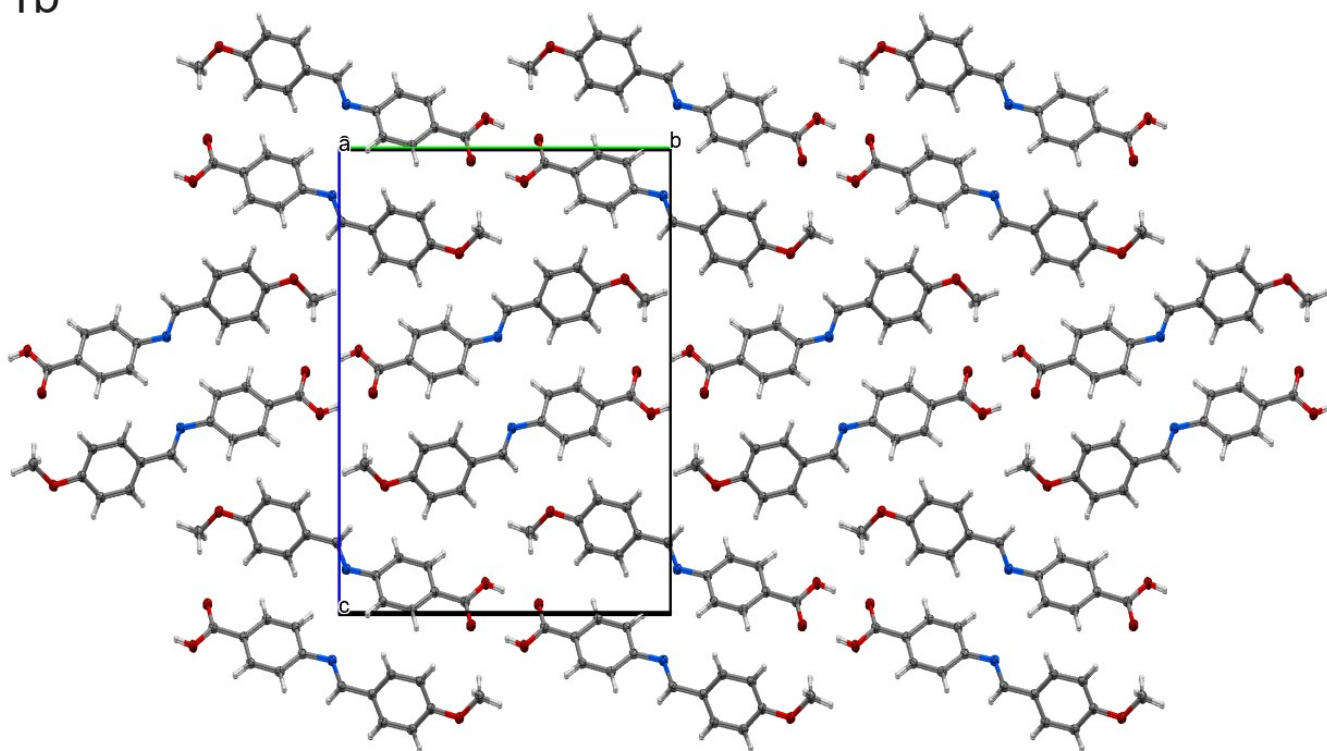


Figure S11. The molecular packing in **1a** and **1b** along (100) plane.

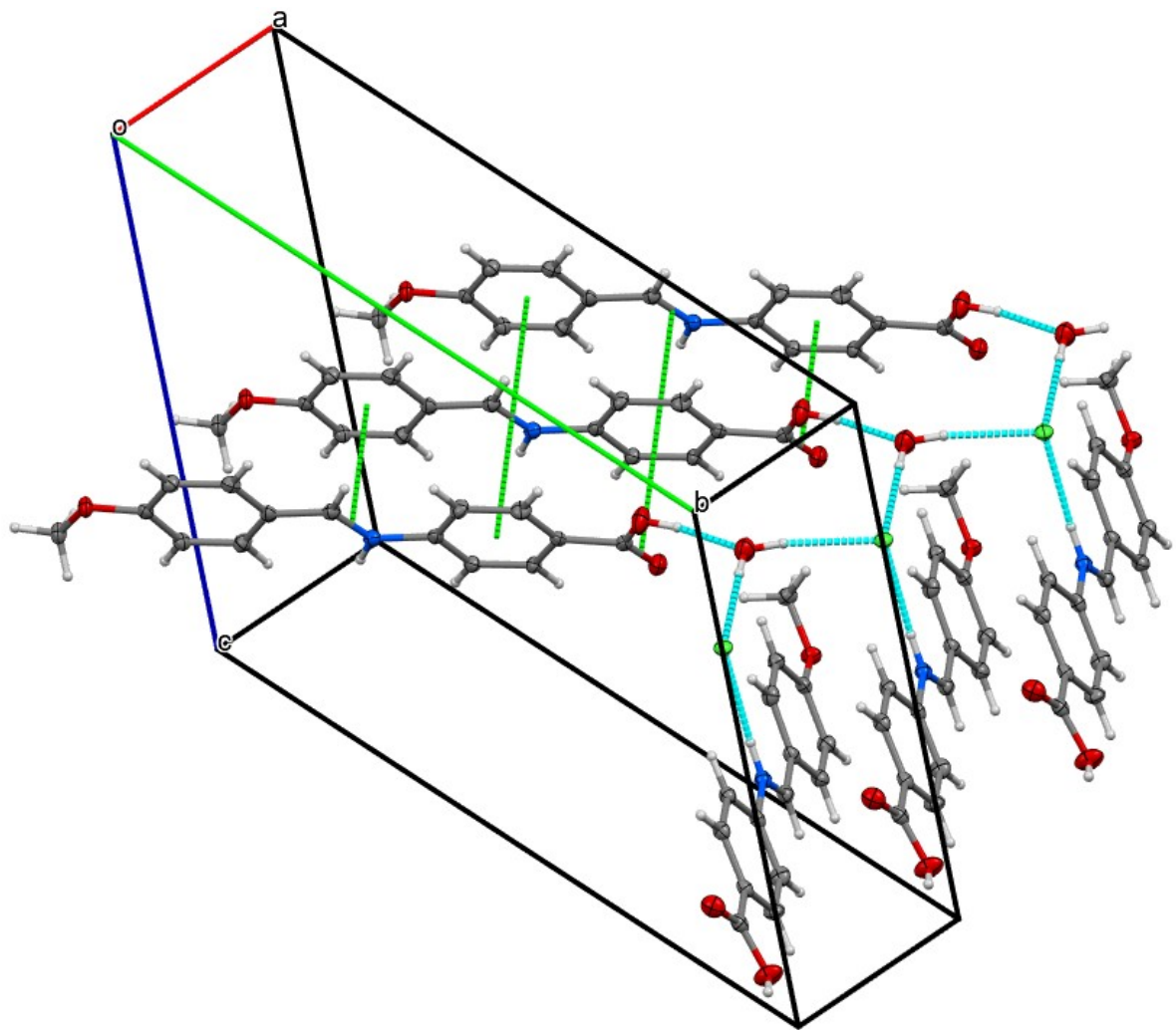


Figure S12. The hydrogen bond network (cyan) and $\pi \cdots \pi$ interactions (green) in **2**.

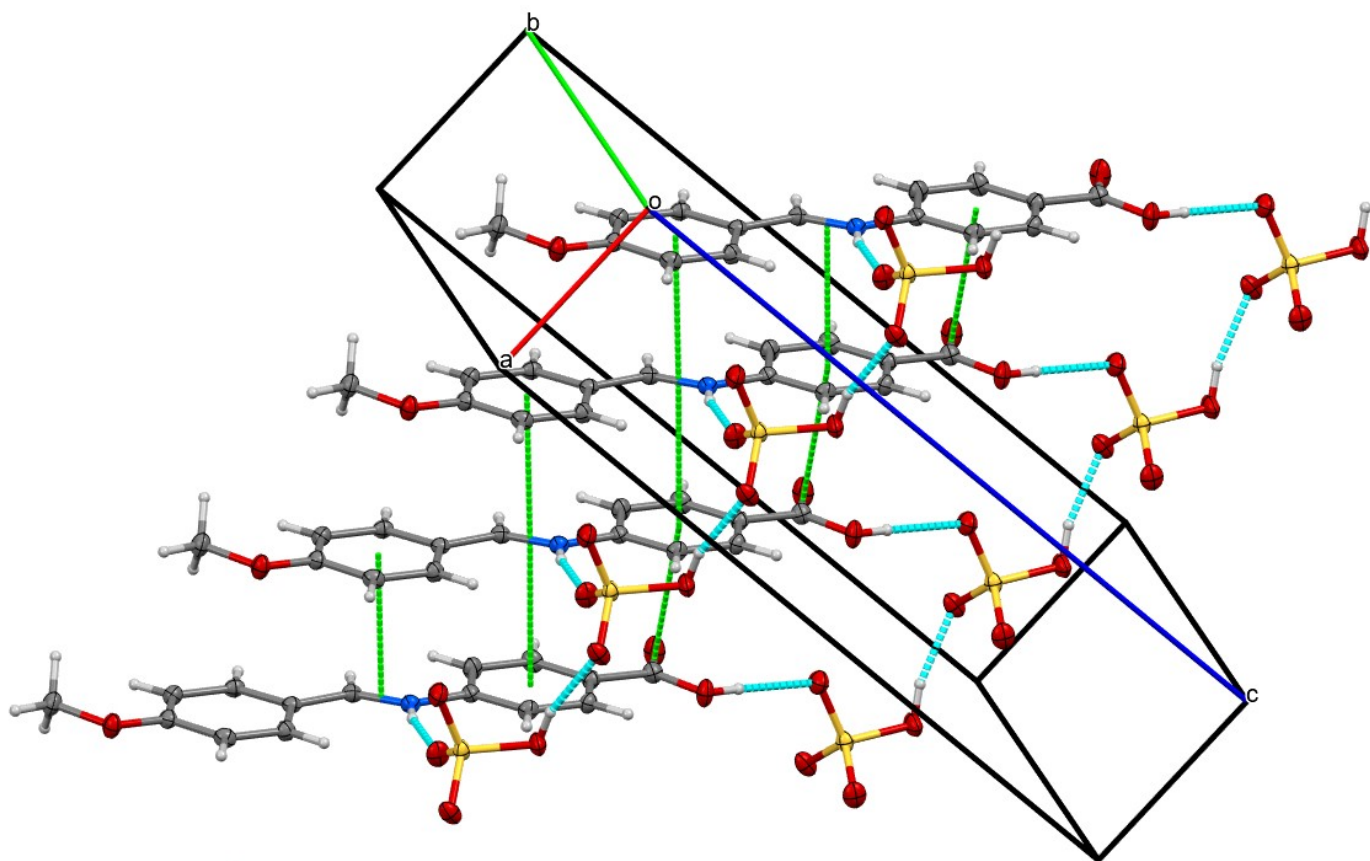


Figure S13. The hydrogen bond network (cyan) and $\pi \cdots \pi$ interactions (green) in **5**.

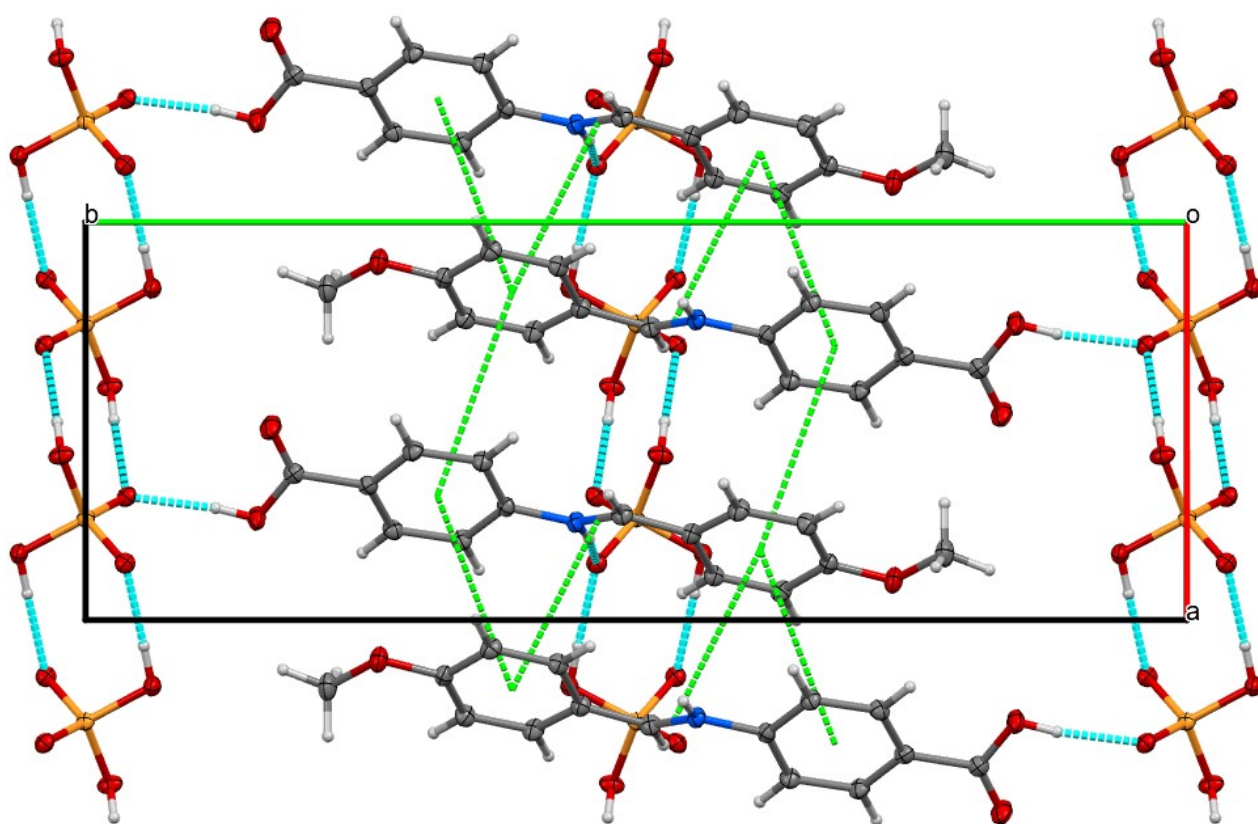


Figure S14. The hydrogen bond network (cyan) and $\pi \cdots \pi$ interactions (green) in **6**.

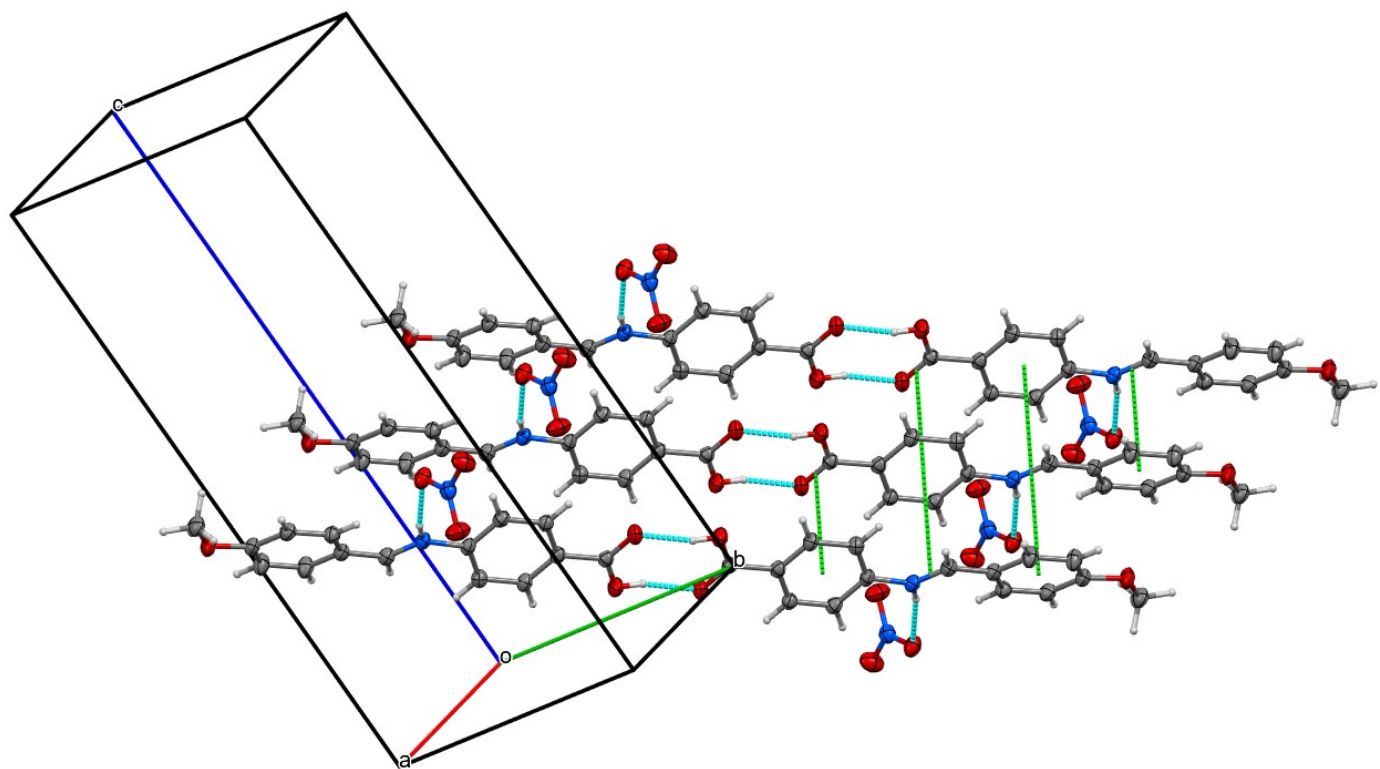


Figure S15. The hydrogen bond network (cyan) and $\pi \cdots \pi$ interactions (green) in **4**.

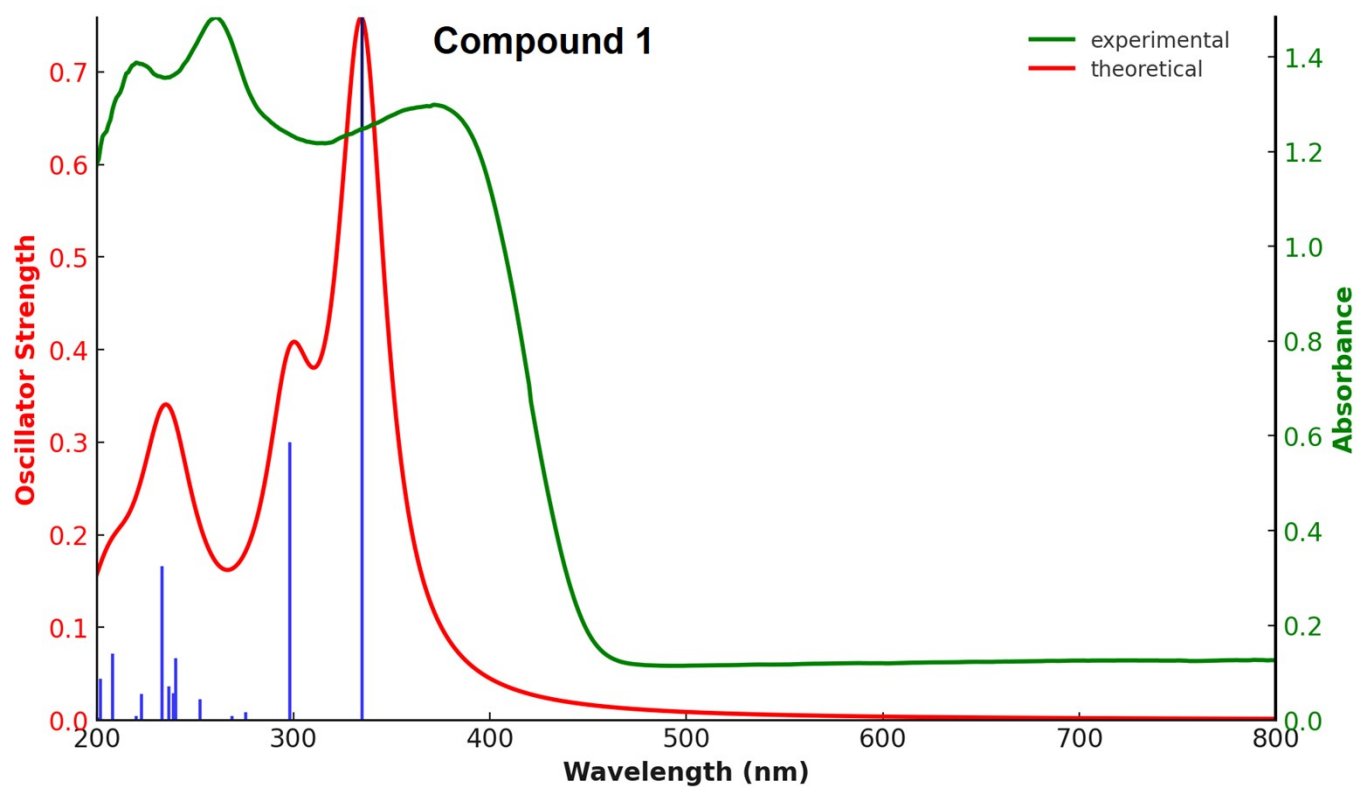


Figure S16. Experimental (green) and calculated (red) UV-Vis spectra of **1**. Oscillator strengths are represented as vertical navy-blue lines.

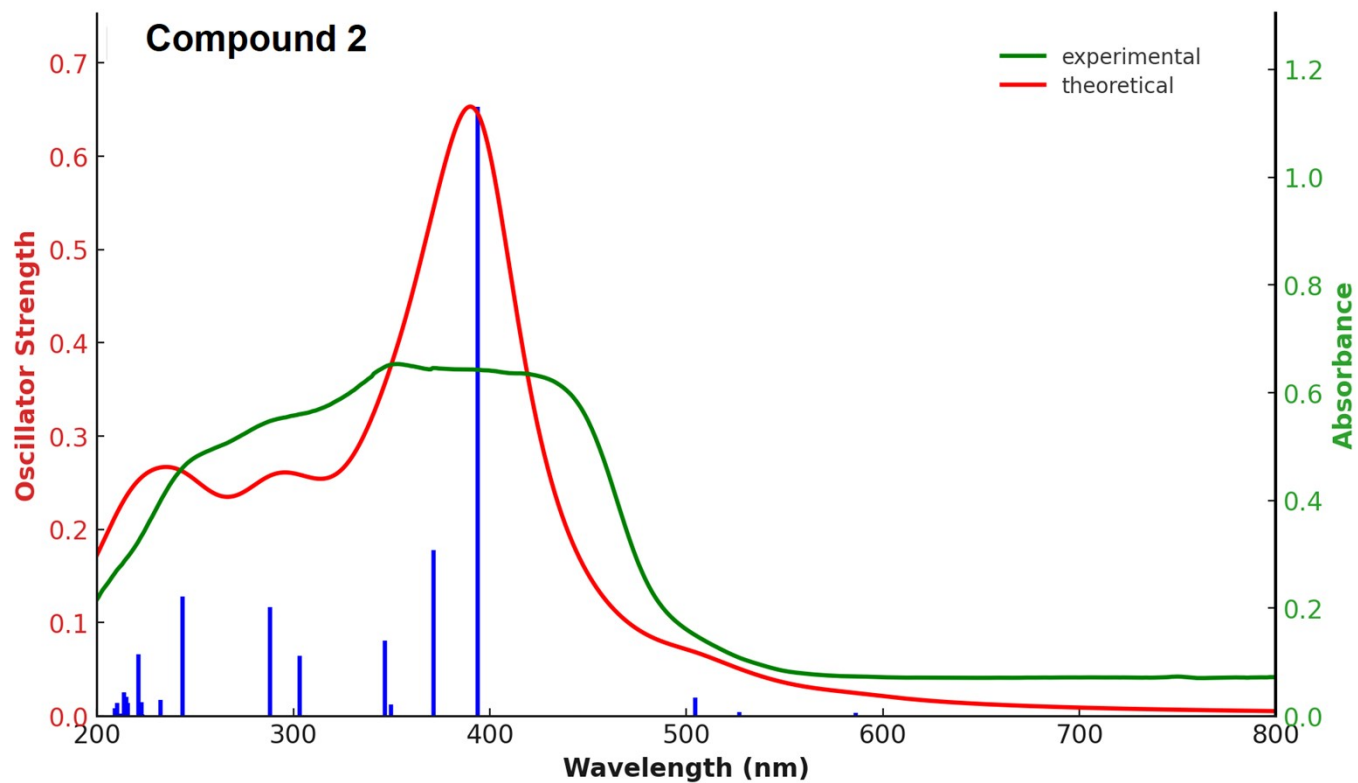


Figure S17. Experimental (green) and calculated (red) UV-Vis spectra of **2**. Oscillator strengths are represented as vertical navy-blue lines.

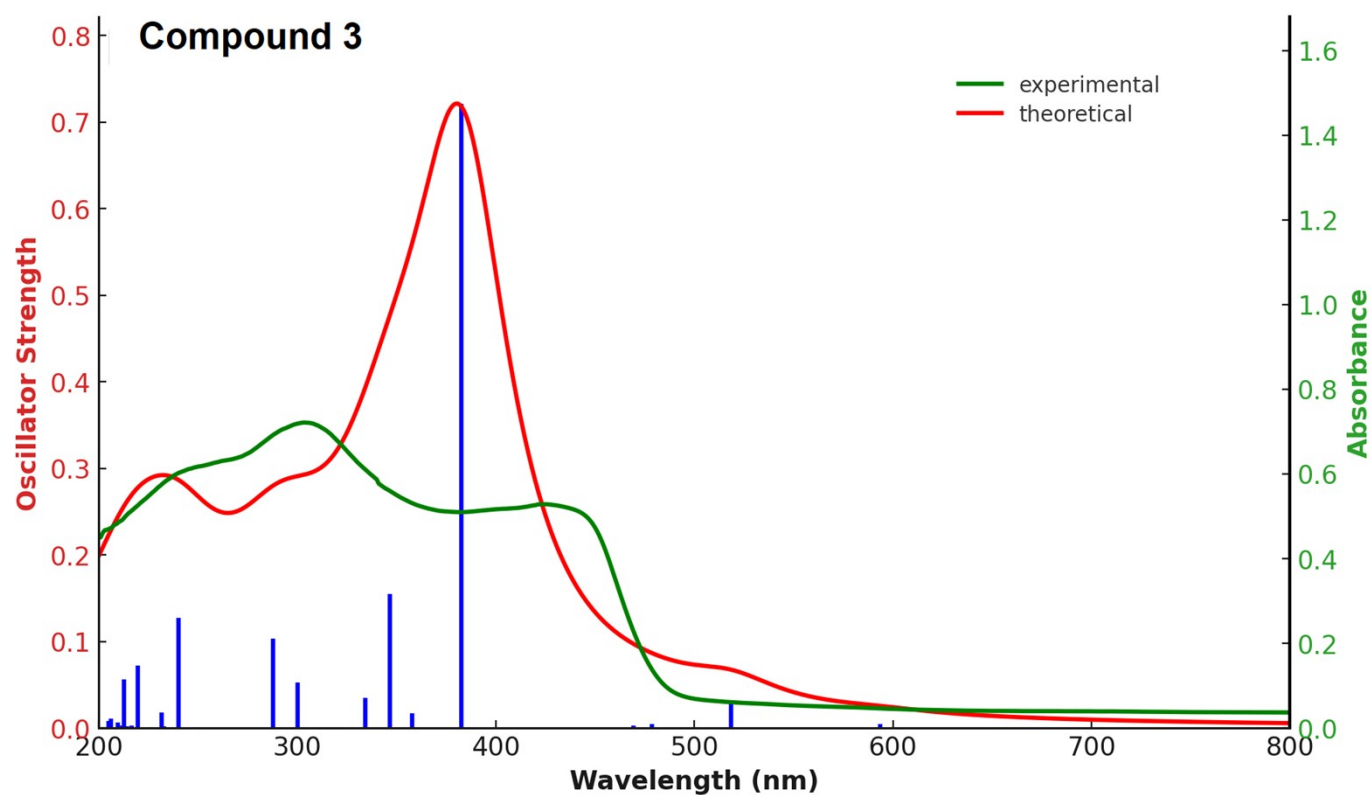


Figure S18. Experimental (green) and calculated (red) UV-Vis spectra of **3**. Oscillator strengths are represented as vertical navy-blue lines.

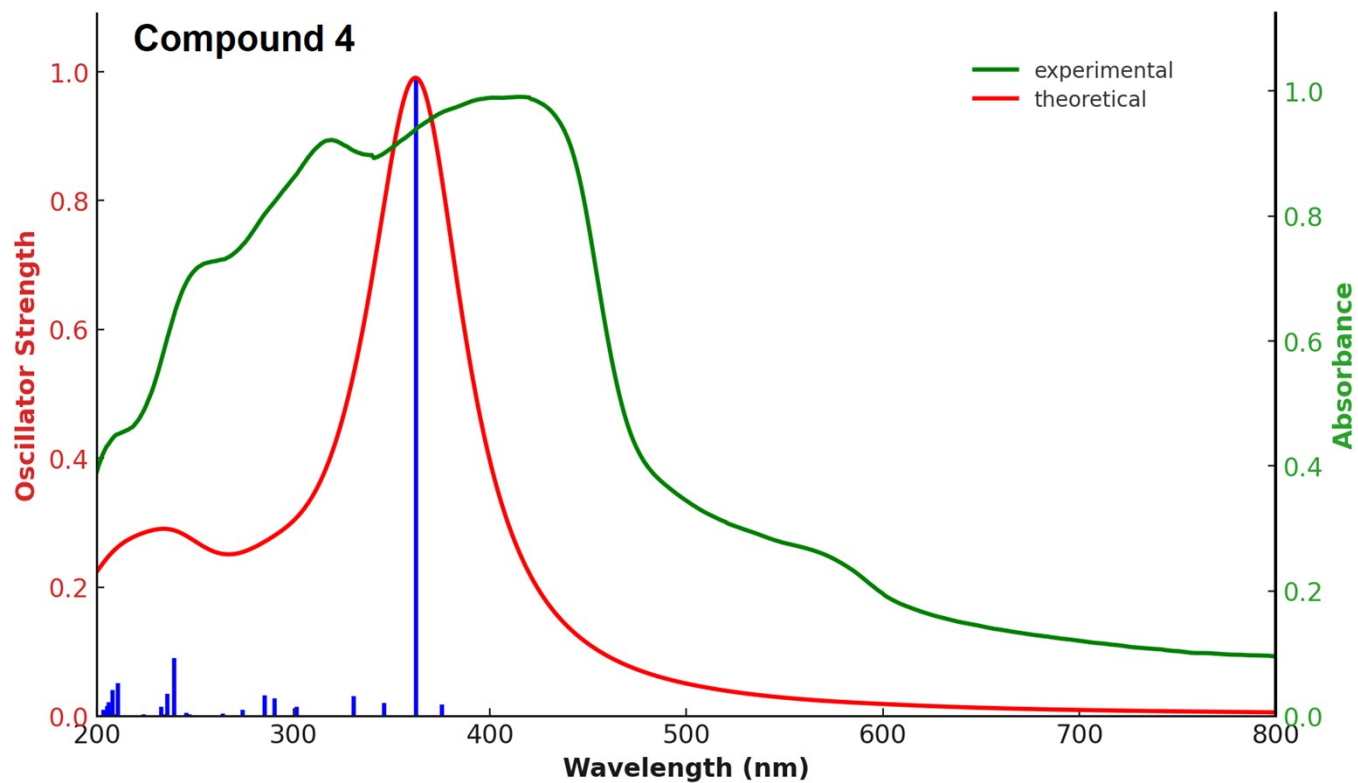


Figure S19. Experimental (green) and calculated (red) UV-Vis spectra of **4**. Oscillator strengths are represented as vertical navy-blue lines.

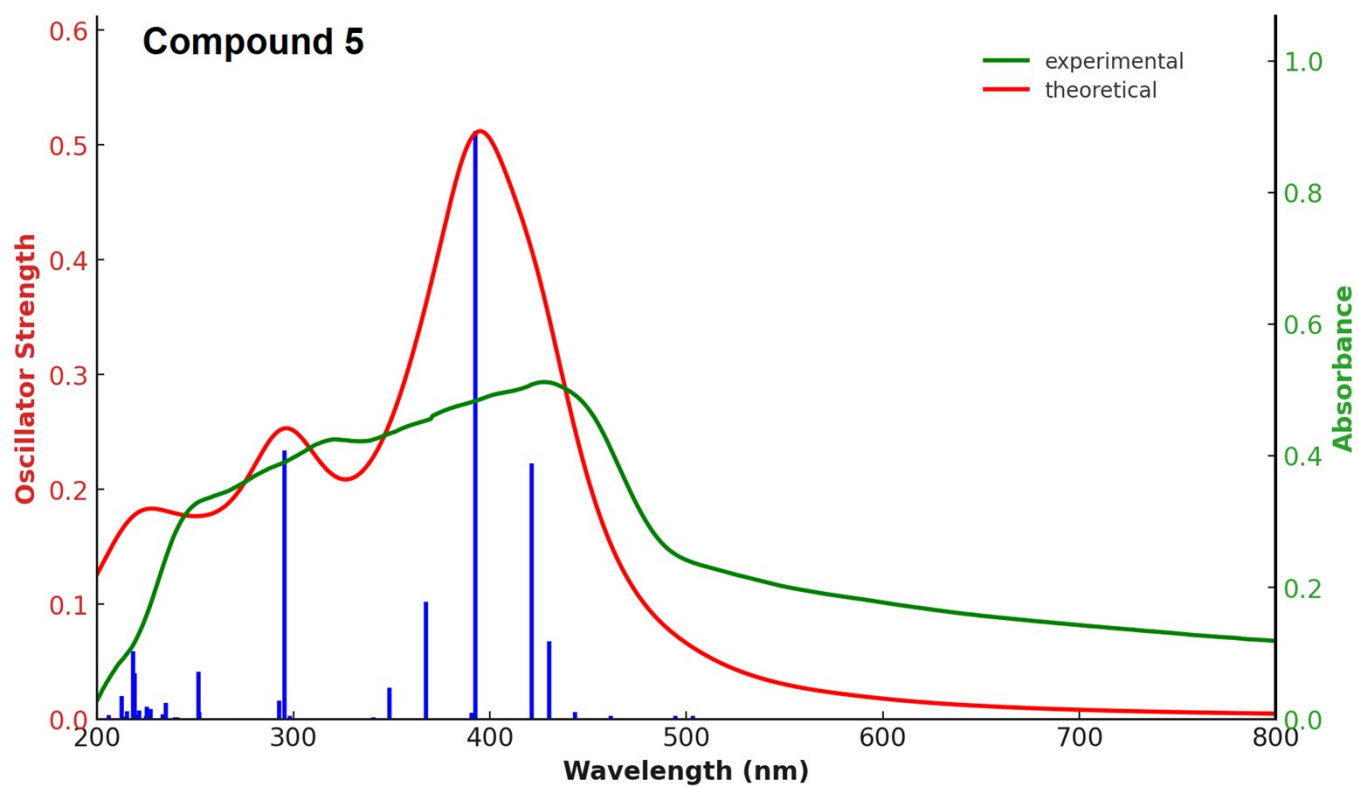


Figure S20. Experimental (green) and calculated (red) UV-Vis spectra of **5**. Oscillator strengths are represented as vertical navy-blue lines.

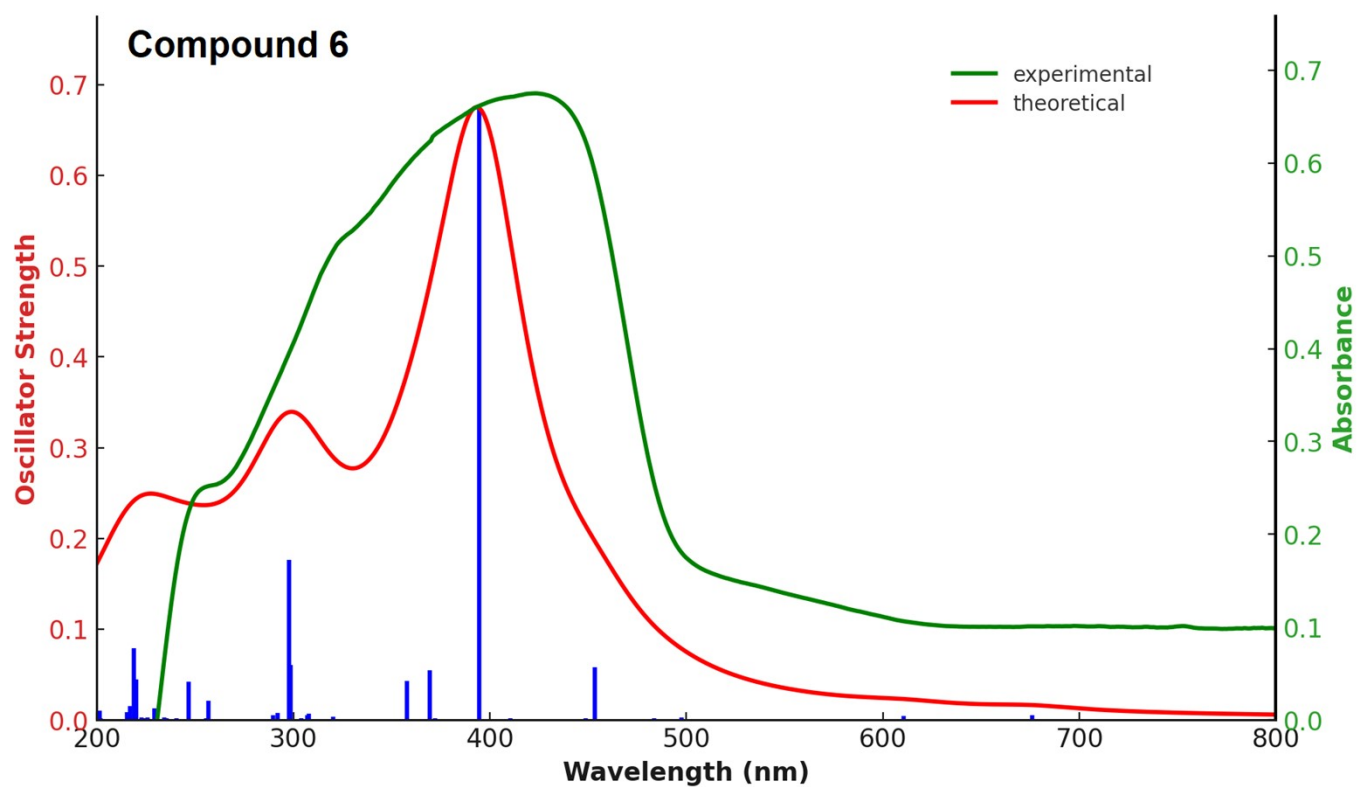


Figure S21. Experimental (green) and calculated (red) UV-Vis spectra of **6**. Oscillator strengths are represented as vertical navy-blue lines.

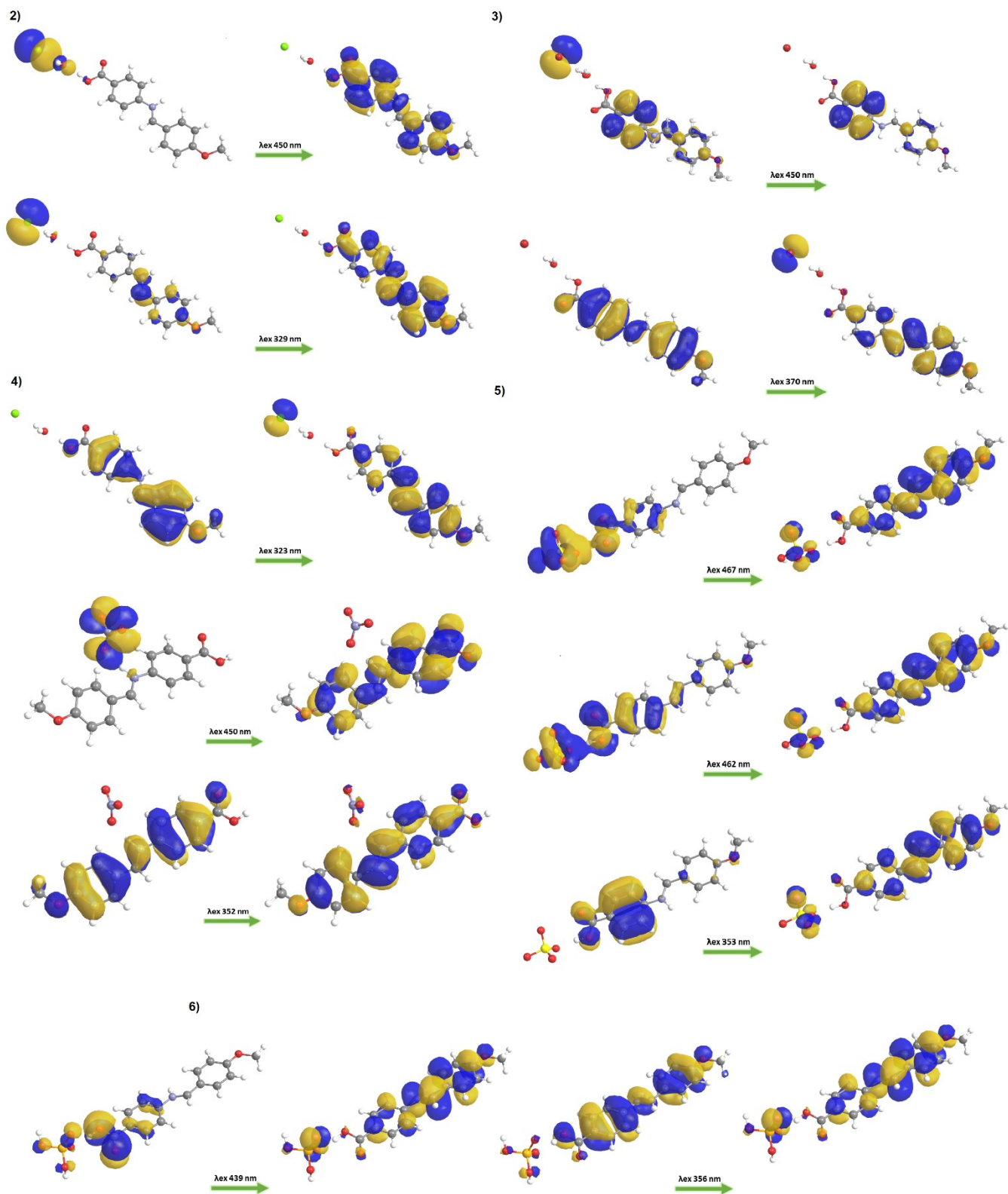


Figure S22. Calculated molecular orbital transition in the studied compounds (2-6), corresponding to the fluorescence emission maxima.

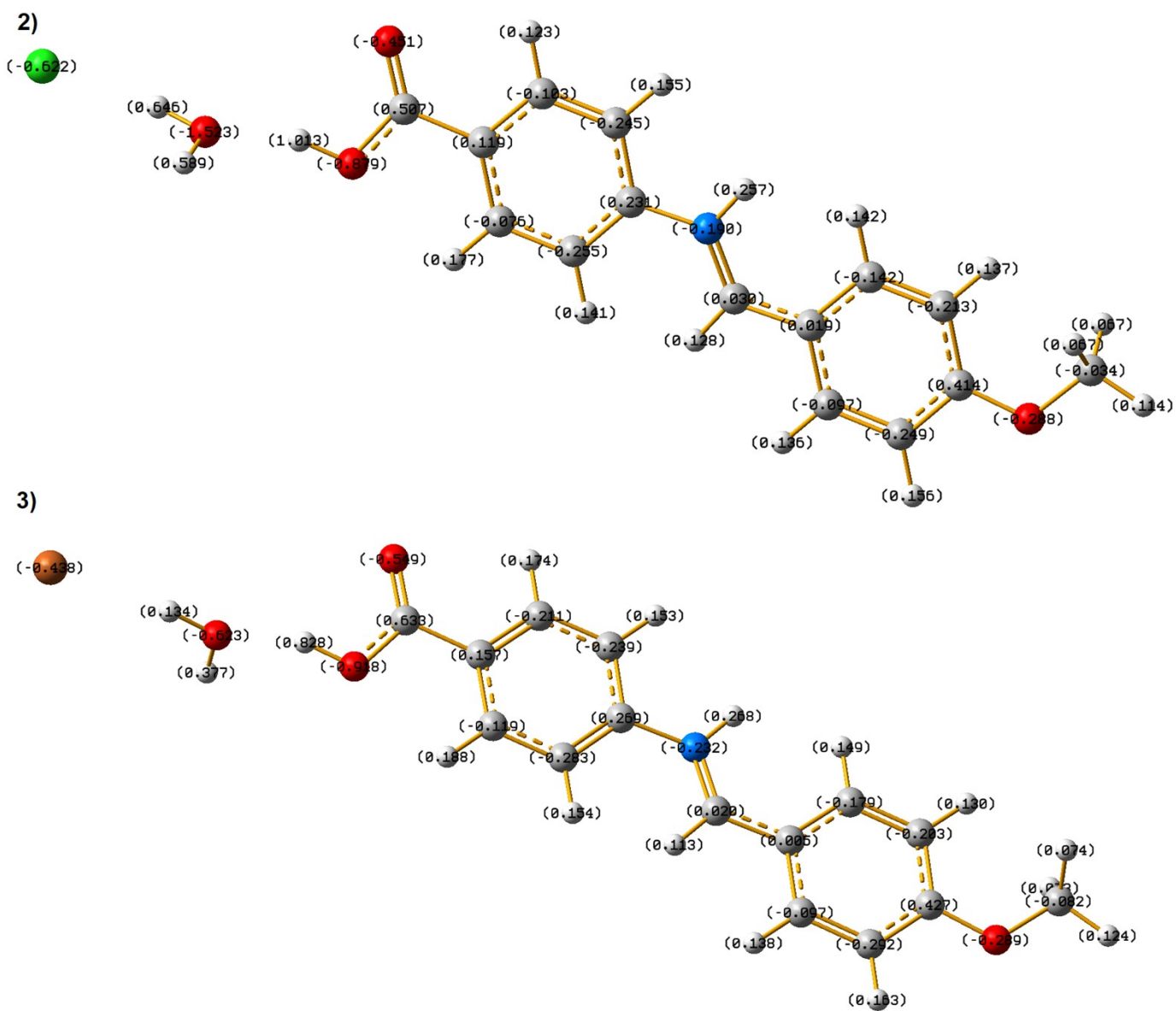


Figure S23. Calculated charge distribution in compounds **2** and **3**.

Table S1. Crystal data and structure refinement details for studied compounds.

Compound (CCDC number)	1a (2285252)	1b (2285249)	2 (2285251)	3 (2285248)	4 (2285246)	5 (2285247)	6 (2285250)
Empirical formula	C ₁₅ H ₁₃ NO ₃	C ₁₅ H ₁₃ NO ₃	C ₁₅ H ₁₆ ClNO ₄	C ₁₅ H ₁₆ BrNO ₄	C ₁₅ H ₁₄ N ₂ O ₆	C ₁₅ H ₁₅ NO ₇ S	C ₁₅ H ₁₆ NO ₇ P
Formula weight	255.26	255.26	309.74	354.20	318.28	353.34	353.26
Temperature (K)	100.00(10)	100.01(10)	100.00(13)	100.00(10)	99.9(8)	100.0(1)	100.01(10)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pc</i>	<i>P</i> 2 ₁ / <i>c</i>
a (Å)	3.89223(4)	3.82566(3)	4.70370(10)	4.72040(10)	4.83768(17)	4.47140(10)	7.99120(10)
b (Å)	10.76523(10)	15.07160(6)	20.9656(3)	21.1550(5)	14.8178(5)	9.3275(2)	21.7863(2)
c (Å)	15.40737(14)	21.19950(9)	14.8427(2)	15.1364(3)	20.0275(6)	17.7797(5)	9.04030(10)
α (°)	109.0366(8)	90	90	90	90	90	90
β (°)	94.0110(8)	92.4431(5)	92.1960(10)	92.616(2)	95.964(3)	90.109(2)	100.0910(10)
γ (°)	90.8565(8)	90	90	90	90	90	90
Volume (Å ³)	608.291(11)	1221.225(11)	1462.65(4)	1509.95(6)	1427.87(9)	741.54(3)	1549.56(3)
Z	2	4	4	4	4	2	4
ρ _{calc} (g/cm ³)	1.394	1.388	1.407	1.558	1.481	1.582	1.514
μ (mm ⁻¹)	0.803	0.800	2.458	3.854	0.988	2.327	1.946
<i>F</i> (000)	268.0	536.0	648.0	720.0	664.0	368.0	736.0
Crystal size (mm ³)	0.23 × 0.165 × 0.08	0.221 × 0.2 × 0.086	0.230 × 0.029 × 0.020	0.367 × 0.054 × 0.034	0.137 × 0.044 × 0.021	0.230 × 0.054 × 0.024	0.29 × 0.176 × 0.044
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
θ range for data collect. (°)	8.696 to 157.488	7.198 to 157.82	7.3 to 156.822	8.36 to 157.764	7.436 to 158.888	9.482 to 159.22	8.116 to 157.81
Index ranges	-4 ≤ h ≤ 4, -13 ≤ k ≤ 13, -19 ≤ l ≤ 19	-4 ≤ h ≤ 4, -19 ≤ k ≤ 19, -26 ≤ l ≤ 26	-5 ≤ h ≤ 4, -25 ≤ k ≤ 26, -18 ≤ l ≤ 18	-5 ≤ h ≤ 5, -26 ≤ k ≤ 26, -19 ≤ l ≤ 18	-5 ≤ h ≤ 5, -18 ≤ k ≤ 18, -25 ≤ l ≤ 25	-5 ≤ h ≤ 5, -11 ≤ k ≤ 11, -21 ≤ l ≤ 22	-10 ≤ h ≤ 10, -27 ≤ k ≤ 27, -9 ≤ l ≤ 11
Reflections collected / independent	33767 / 2543	85187 / 2622	14626/2923	22483/3130	3740/3740	24898/2993	37063/3198
R _{int}	0.0391	0.0490	0.0291	0.0516	0.0791	0.0405	0.0367
Data/restraints/parameters	2543/0/174	2622/0/174	2923/0/195	3130/0/195	3740/0/211	2993/2/221	3198/0/221
Goodness-of-fit on <i>F</i> ²	1.086	1.057	1.031	1.080	1.092	1.073	1.063
Final <i>R</i> indexes [<i>I</i> > 2σ(<i>I</i>)]	R ₁ = 0.0337, wR ₂ = 0.0934	R ₁ = 0.0339, wR ₂ = 0.0887	R ₁ = 0.0391, wR ₂ = 0.1008	R ₁ = 0.0445, wR ₂ = 0.1056	R ₁ = 0.0568, wR ₂ = 0.1666	R ₁ = 0.0260, wR ₂ = 0.0708	R ₁ = 0.0284, wR ₂ = 0.0737
R indexes (all data)	R ₁ = 0.0353, wR ₂ = 0.0944	R ₁ = 0.0346, wR ₂ = 0.0893	R ₁ = 0.0459, wR ₂ = 0.1046	R ₁ = 0.0496, wR ₂ = 0.1084	R ₁ = 0.0649, wR ₂ = 0.1731	R ₁ = 0.0265, wR ₂ = 0.0711	R ₁ = 0.0293, wR ₂ = 0.0744
Largest diff. peak and hole (e ⁻ Å ⁻³)	0.24/-0.23	0.25/-0.20	0.80/-0.28	1.26/-0.61	0.39/-0.31	0.23/-0.20	0.21/-0.49

Table S2. Bond lengths (Å) for the studied compounds.

Compound	1a	1b	2	3	4	5	6
O3—C12	1.3559(12)	1.3692(12)	1.351(2)	1.356(4)	1.343(3)	1.351(6)	1.3511(14)
O3—C15	1.4354(12)	1.4314(13)	1.433(2)	1.423(4)	1.435(4)	1.439(6)	1.4386(15)
O1—C1	1.2352(12)	1.3105(12)	1.334(2)	1.333(4)	1.279(3)	1.212(6)	1.2096(15)
O2—C1	1.3144(12)	1.2396(12)	1.196(2)	1.188(4)	1.260(3)	1.324(6)	1.3244(15)
N1—C5	1.4085(13)	1.4076(13)	1.439(2)	1.449(4)	1.426(3)	1.431(6)	1.4251(15)
N1—C8	1.2798(13)	1.2773(14)	1.299(2)	1.291(4)	1.301(3)	1.306(6)	1.2984(16)
C9—C8	1.4580(14)	1.4656(14)	1.430(3)	1.436(5)	1.432(4)	1.425(7)	1.4325(17)
C2—C1	1.4784(13)	1.4751(14)	1.487(2)	1.489(4)	1.487(3)	1.494(7)	1.4950(16)

Table S3. Bond angles (°) for the studied compounds.

Compound	1a	1b	2	3	4	5	6
C12—O3—C15	117.46(8)	117.12(8)	117.50(13)	117.7(2)	118.9(2)	117.9(4)	117.88(10)
C8—N1—C5	117.94(8)	119.80(9)	125.33(16)	125.0(3)	125.9(2)	124.5(4)	125.87(10)
C14—C9—C8	121.94(9)	120.70(9)	123.93(17)	124.2(3)	124.0(2)	124.5(4)	122.84(11)
C10—C9—C8	119.42(9)	120.78(9)	117.12(16)	116.7(3)	117.6(2)	116.8(4)	118.42(11)
O3—C12—C13	115.44(9)	124.14(9)	123.68(16)	123.5(3)	124.5(2)	114.7(4)	114.73(10)
O3—C12—C11	124.48(9)	115.56(9)	115.53(15)	115.8(3)	115.5(2)	125.0(4)	124.80(11)
O1—C1—O2	122.93(9)	122.83(9)	124.07(17)	125.1(3)	124.2(2)	123.7(5)	124.05(11)
C3—C2—C1	118.71(9)	121.74(9)	121.90(17)	121.9(3)	121.2(2)	117.5(4)	119.05(10)
C7—C2—C1	121.78(9)	118.60(9)	118.83(16)	119.1(3)	118.4(2)	122.9(4)	121.37(11)
C6—C5—N1	118.85(9)	117.98(9)	116.25(16)	116.5(3)	116.5(2)	117.0(4)	116.37(10)
C4—C5—N1	121.70(9)	122.12(9)	122.80(16)	122.5(3)	122.1(2)	121.9(4)	122.45(11)
N1—C8—C9	123.51(9)	121.23(9)	125.47(17)	125.5(3)	124.7(2)	125.4(4)	124.39(11)
O1—C1—C2	121.82(9)	115.59(9)	112.08(15)	111.6(3)	117.0(2)	122.6(4)	123.20(11)
O2—C1—C2	115.23(8)	121.57(9)	123.85(17)	123.3(3)	118.8(2)	113.6(4)	112.75(10)

Table S4. Interplane angles (°) between phenylene ring mean planes in the studied compounds.

1a	52.4
1b	49.2
2	1.8
3	0.9
4	23.2
5	1.0
6	7.2

Table S5. Stacking interactions in the studied compounds. Each ring, R, is indicated by one membered atom. Each bond, B, is indicated by both membered atoms. The d is a distance between centroid of I, Cg(I), and centroid of J, Cg(J), α is a dihedral angle between planes of rings I and J, β is an angle between Cg(I)-Cg(J) vector and normal to plane I, d_p is a perpendicular distance of Cg(J) on the ring I plane.

I...J	d (Å)	α (°)	β (°)	d_p (Å)
1a				
R(C2)•••R(C2) ⁽ⁱ⁾	3.892(2)	0	29.5	3.3865(6)
R(C9)•••R(C9) ⁽ⁱ⁾	3.892(2)	0	30.2	3.3640(6)
1b				
R(C2)•••R(C2) ⁽ⁱ⁾	3.826(2)	0	27.9	3.3799(7)
R(C9)•••R(C9) ⁽ⁱ⁾	3.826(2)	0	27.3	3.3995(7)
2				
R(C2)•••B(N1C8) ⁽ⁱⁱⁱ⁾	3.345(2)	-	-	-
R(C2)•••B(C1-O2) ⁽ⁱ⁾	3.373(2)	-	-	-
R(C9)•••B(N1-C8) ⁽ⁱⁱⁱ⁾	3.340(2)	-	-	-
3				
R(C2)•••B(N1-C8) ⁽ⁱⁱⁱ⁾	3.347(2)	-	-	-
R(C2)•••B(C1-O2) ⁽ⁱⁱⁱ⁾	3.371(2)	-	-	-
R(C9)•••B(N1-C8) ⁽ⁱⁱⁱ⁾	3.374(2)	-	-	-
4				
R(C2)•••B(N1-C8) ⁽ⁱ⁾	3.554(2)	-	-	-
R(C2)•••B(C1-O2) ⁽ⁱⁱ⁾	3.441(2)	-	-	-
R(C9)•••B(N1-C8) ⁽ⁱⁱⁱ⁾	3.430(2)	-	-	-
5				
R(C2)•••B(N1-C8) ⁽ⁱ⁾	3.384(2)	-	-	-
R(C2)•••B(C1-O1) ⁽ⁱⁱⁱ⁾	3.760(2)	-	-	-
R(C9)•••B(N1-C8) ⁽ⁱⁱⁱ⁾	3.330(2)	-	-	-
6				
R(C9)•••B(N1-C8) ^(iv)	3.880(2)	-	-	-
R(C9)•••R(C2) ^(iv)	4.232(2)	7.2(6)	34.1	3.4320(5)
R(C9)•••R(C2) ⁽ⁱⁱ⁾	4.310(2)	7.2(6)	31.0	3.3880(5)

Symmetry transformations used to generate equivalent atoms: (i) $x-1, y, z$; (ii) x, y, z ; (iii) $x+1, y, z$; (iv) $-x, -y+1, -z+1$;

Table S6. Hydrogen bonds in studied compounds [$G_d^a(n)$ – unitary graph set].

D-H...A	d(D—H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (°)	$G_d^a(n)$
1a					
O2—H2...O1 ⁽ⁱ⁾	0.84	1.80	2.6374(15)	176	$R_2^2(8)$
C6—H6...N1 ⁽ⁱⁱ⁾	0.95	2.87	3.814(2)	176	$R_2^2(8)$
1b					
O1—H1...O2 ⁽ⁱⁱⁱ⁾	0.84	1.78	2.6146(16)	175	$R_2^2(8)$
C6—H6...N1 ^(iv)	0.95	2.78	3.716(2)	168	$R_2^2(8)$
2					
N1—H1A...Cl1 ^(v)	0.88	2.37	3.2247(15)	165	D(2)
O1—H1...O4	0.84	1.79	2.597(2)	160	D(2)
O4—H4A... Cl1	0.87	2.28	3.1352(15)	167	D(2)
O4—H4B... Cl1 ^(vi)	0.87	2.31	3.1706(15)	172	D(2)
3					
N1—H1A...Br1 ^(vii)	0.88	2.50	3.360(3)	164	D(2)
O1—H1...O4	0.84	1.79	2.584(4)	158	D(2)
O4—H4A... Br1	1.00	2.29	3.262(3)	164	D(2)
O4—H4B... Br1 ^(viii)	1.07	2.25	3.305(3)	168	D(2)
4					
N1—H1A...O4	0.88	1.97	2.828(3)	163	D(2)
O1—H1...O2 ^(ix)	0.84	1.78	2.605(3)	167	$R_2^2(8)$
5					
N1—H1...O5 ^(x)	0.88	1.95	2.810(3)	167	D(2)
O2—H2...O4	0.84	1.86	2.692(3)	172	D(2)
O7—H7A... O6 ^(vi)	0.84	1.77	2.584(3)	164	C(4)
6					
N1—H1...O4 ^(xi)	0.88	1.82	2.6845(13)	166	D(2)
O2—H2...O5	0.84	1.78	2.6079(12)	169	D(2)
O6—H6A... O4 ^(xii)	0.84	1.76	2.5987(12)	179	$R_2^2(8)$
O7—H7A... O5 ^(xiii)	0.84	1.71	2.5324(11)	167	$R_2^2(8)$

Symmetry transformations used to generate equivalent atoms: (i) $-x, -y, -z$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+2, -y-2, -z+1$; (iv) $-x+2, -y+1, -z+1$; (v) $-x+2, y-1/2, -z+3/2$; (vi) $x-1, y, z$; (vii) $-x, y+1/2, -z+1/2$; (viii) $x+1, y, z$; (ix) $-x-1, -y+1, -z$; (x) $x+1, -y+1, z-1/2$; (xi) $x, -y+1/2, z-1/2$; (xii) $-x, -y, -z+1$; (xiii) $-x+1, -y, -z+1$.