Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Materials:

New rhenium-tricarbonyl complexes bearing halogen-substituted bidentate ligands: Structural, computational and Hirshfeld surfaces studies

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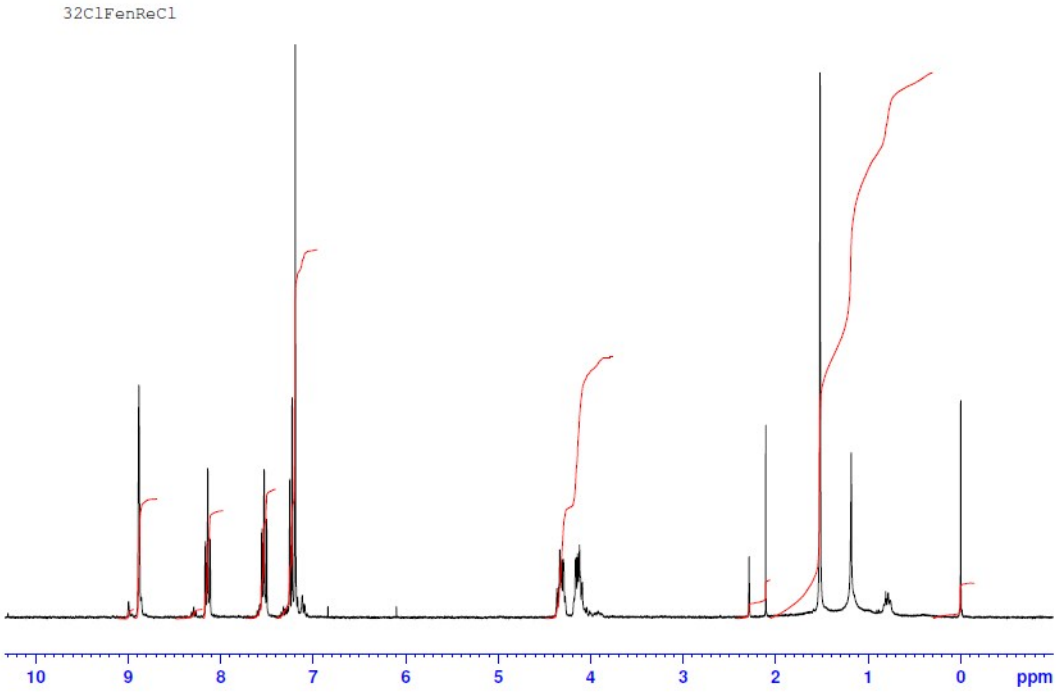

Fig. S1. ^{1}H-NMR spectrum of **C2** in $CDCl_3$.

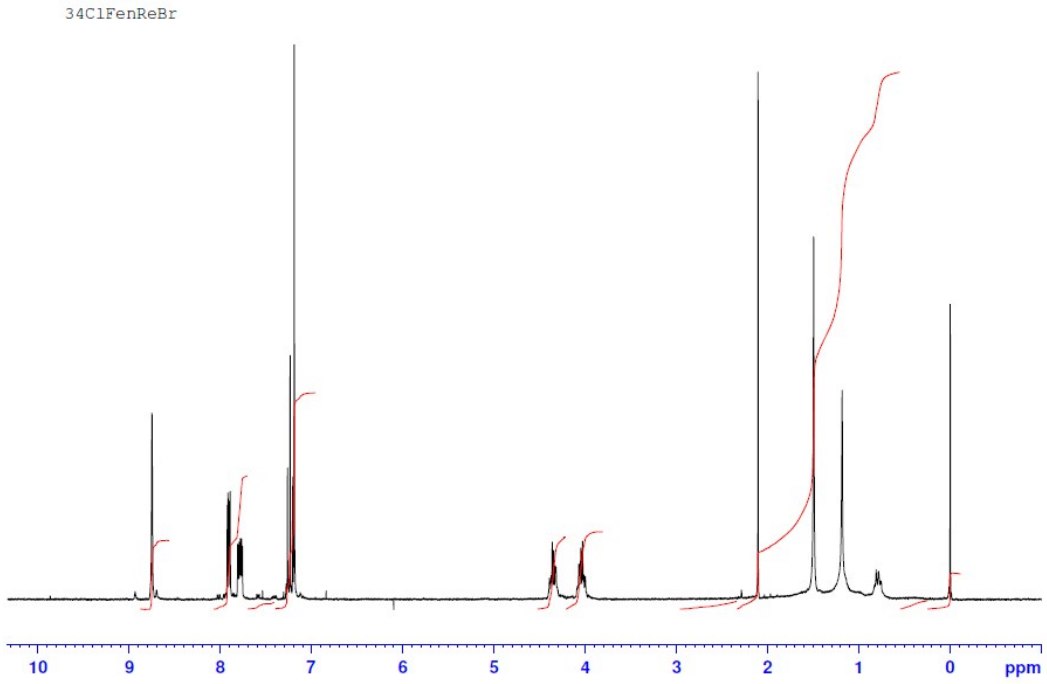

Fig. S2. ^{1}H-NMR spectrum of **C3** in $CDCl_3$.

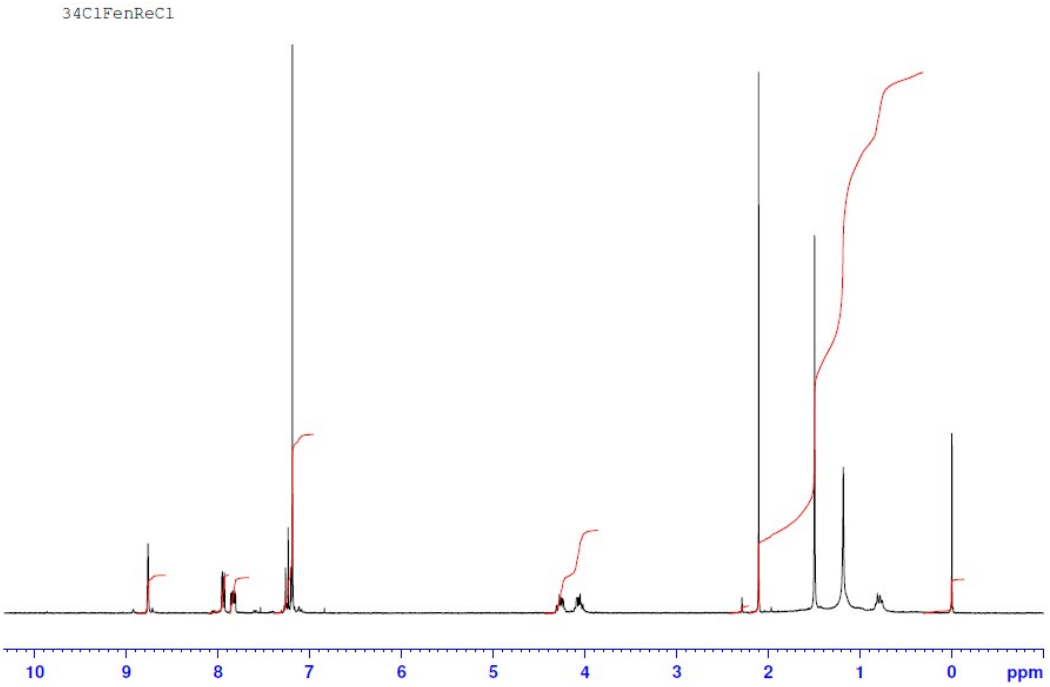

Fig. S3. ^{1}H-NMR spectrum of **C4** in $CDCl_3$.

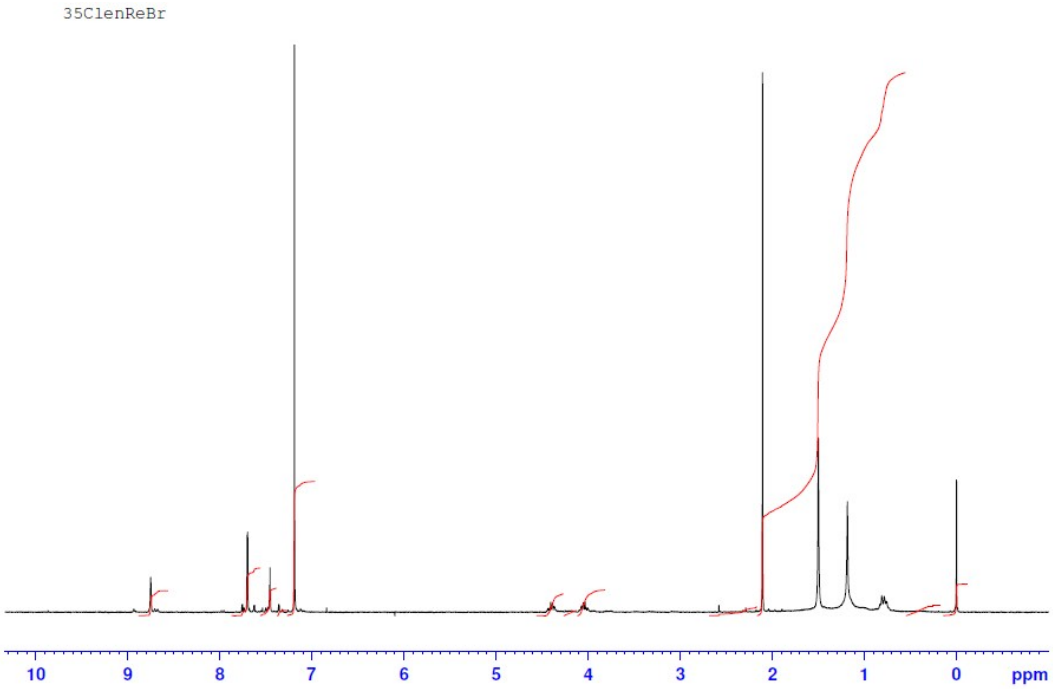

Fig. S4. ^{1}H-NMR spectrum of **C5** in $CDCl_3$.

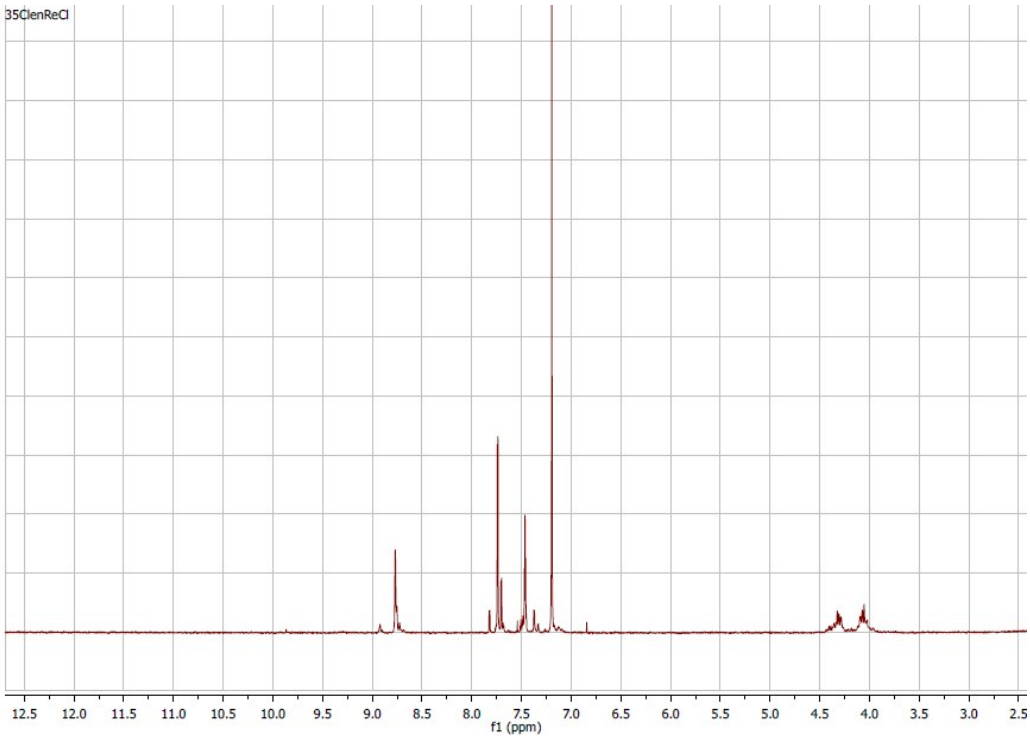

Fig. S5. ^{1}H-NMR spectrum of **C6** in $CDCl_3$.

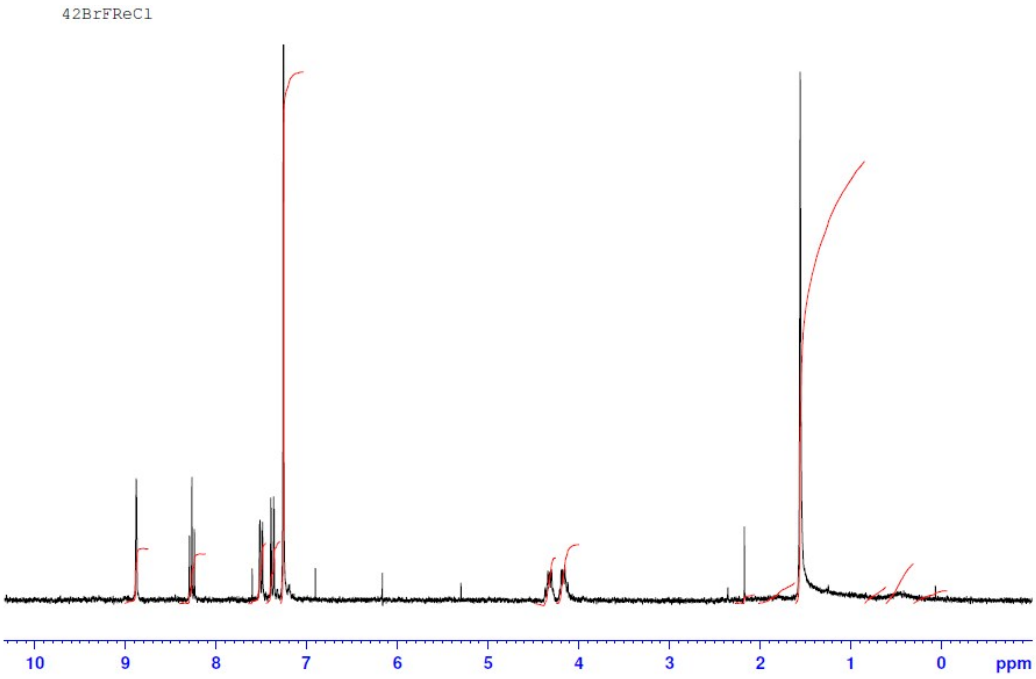

Fig. S6. ^{1}H-NMR spectrum of **C7** in $CDCl_3$.

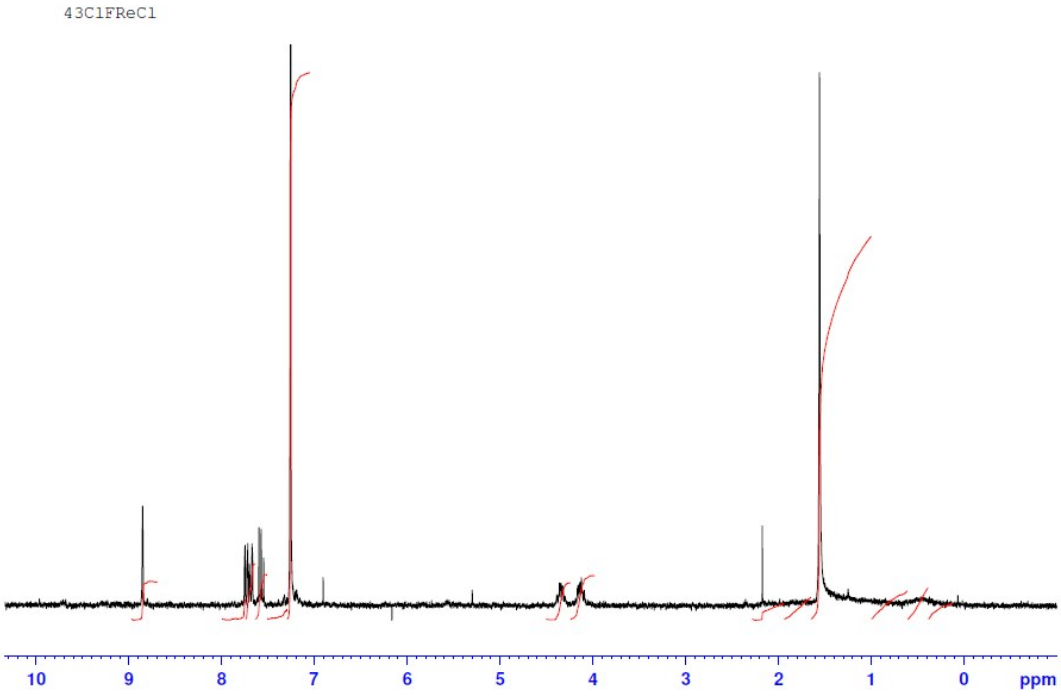

Fig. S7. ^{1}H-NMR spectrum of **C8** in $CDCl_3$.

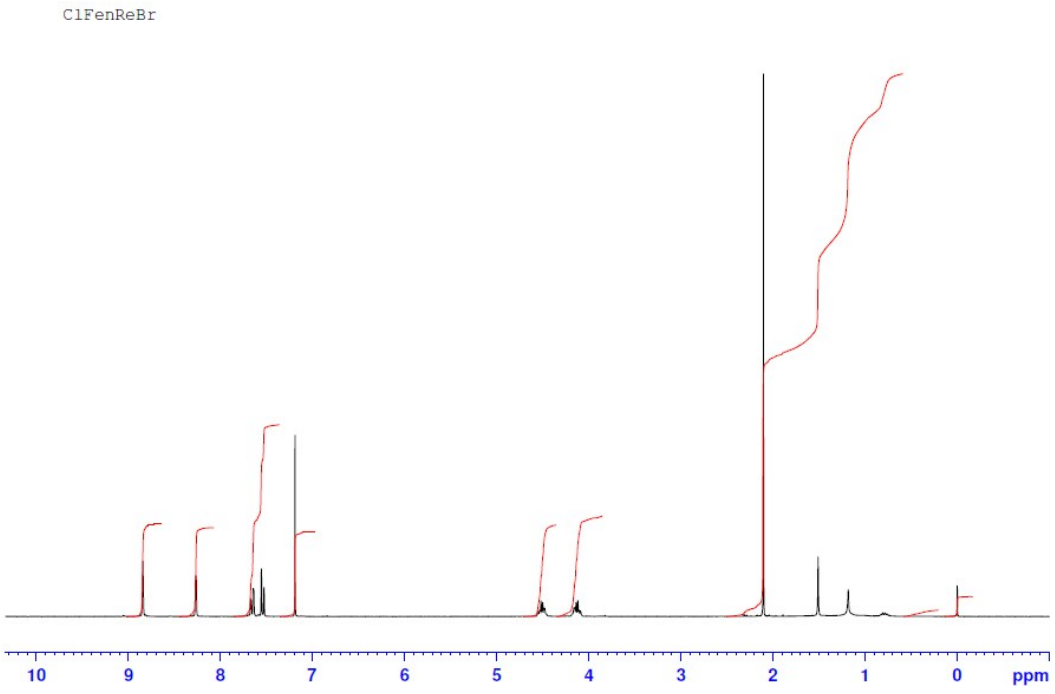

Fig. S8. ^{1}H-NMR spectrum of **C9** in $CDCl_3$.

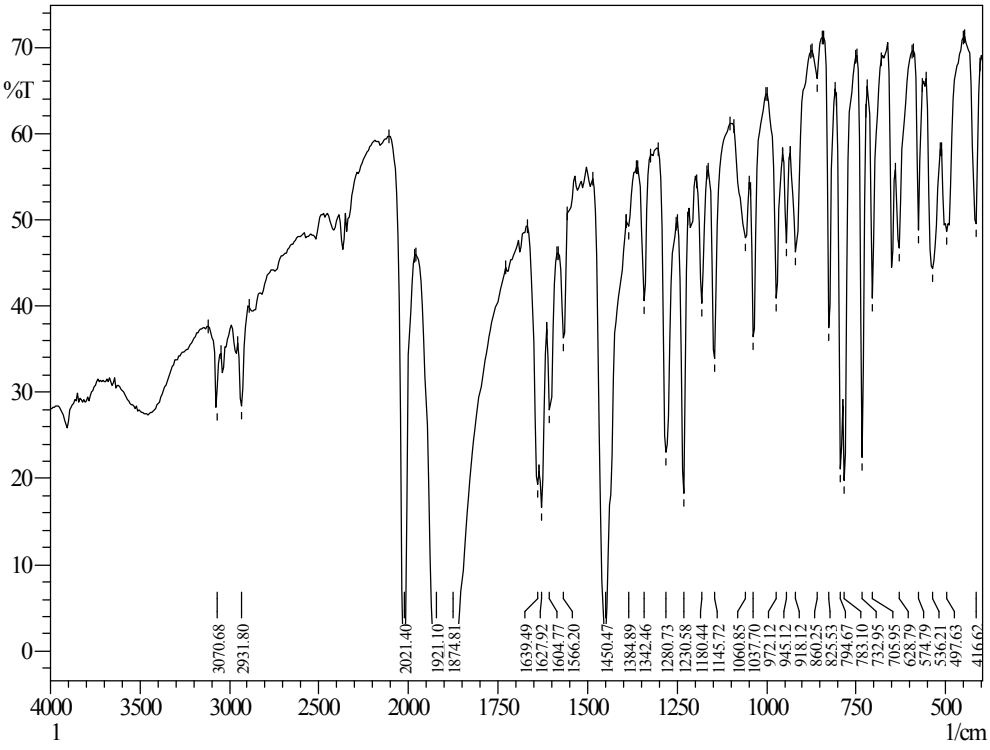

Fig. S9. FT-IR spectrum of **32ClFenReCl** (**C2**).

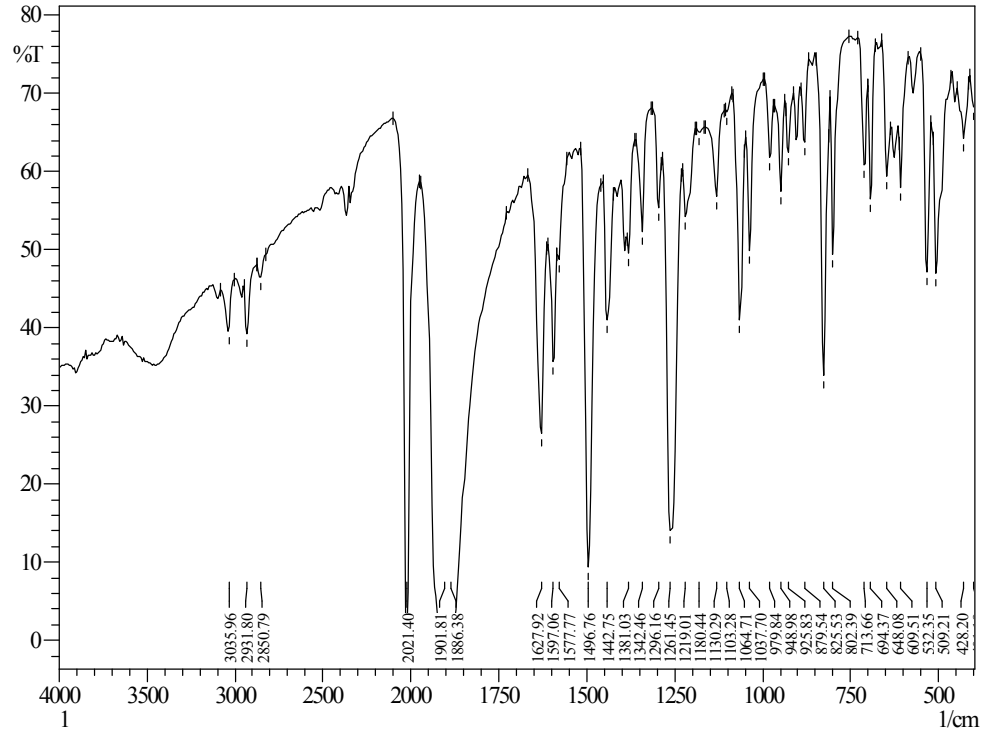

Fig. S10. FT-IR spectrum of **34ClFenReBr** (**C3**).

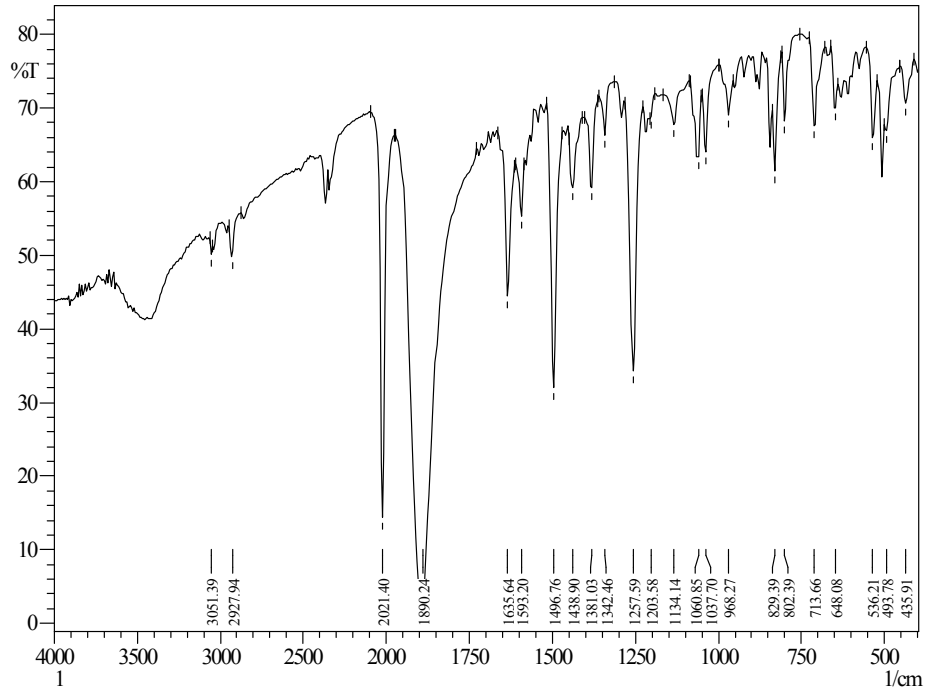

Fig. S11. FT-IR spectrum of **34ClFenReCl** (**C4**).

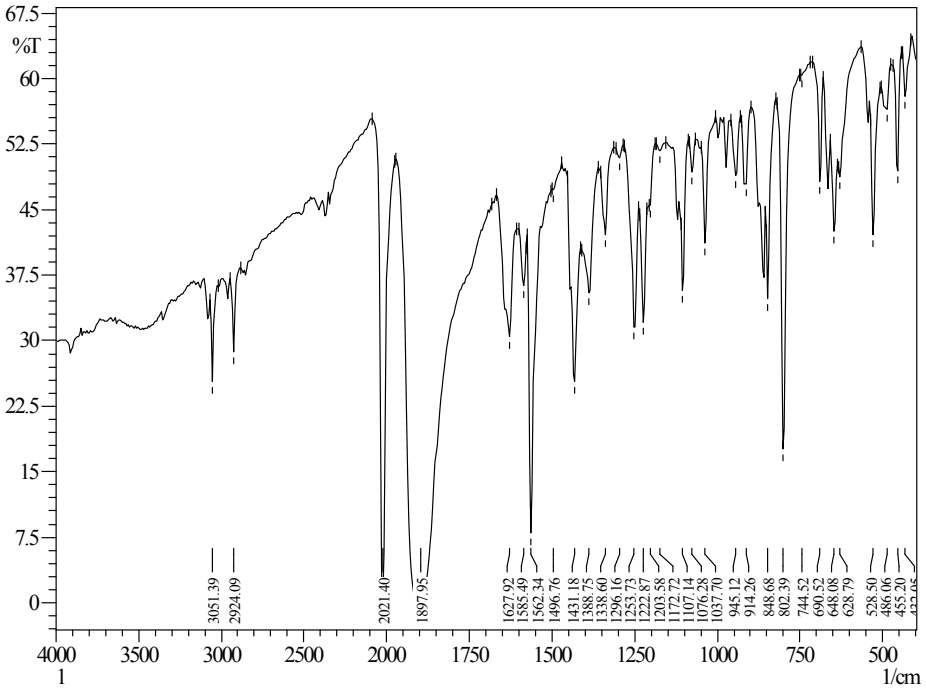

Fig. S12. FT-IR spectrum of **35ClenReBr** (**C5**).

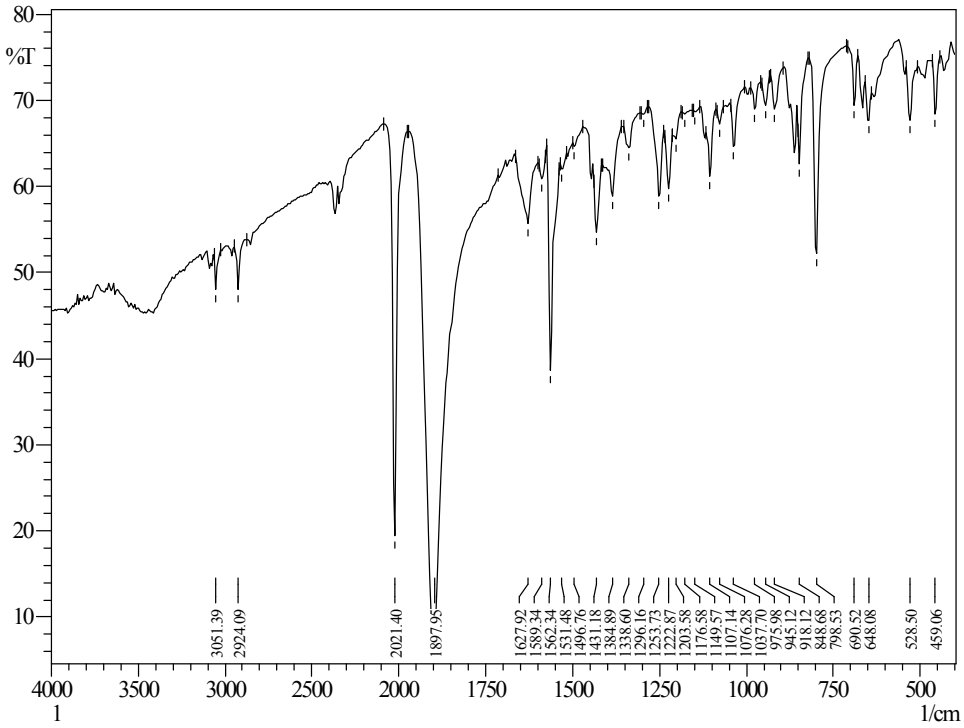

Fig. S13. FT-IR spectrum of **35ClenReCl** (**C6**).

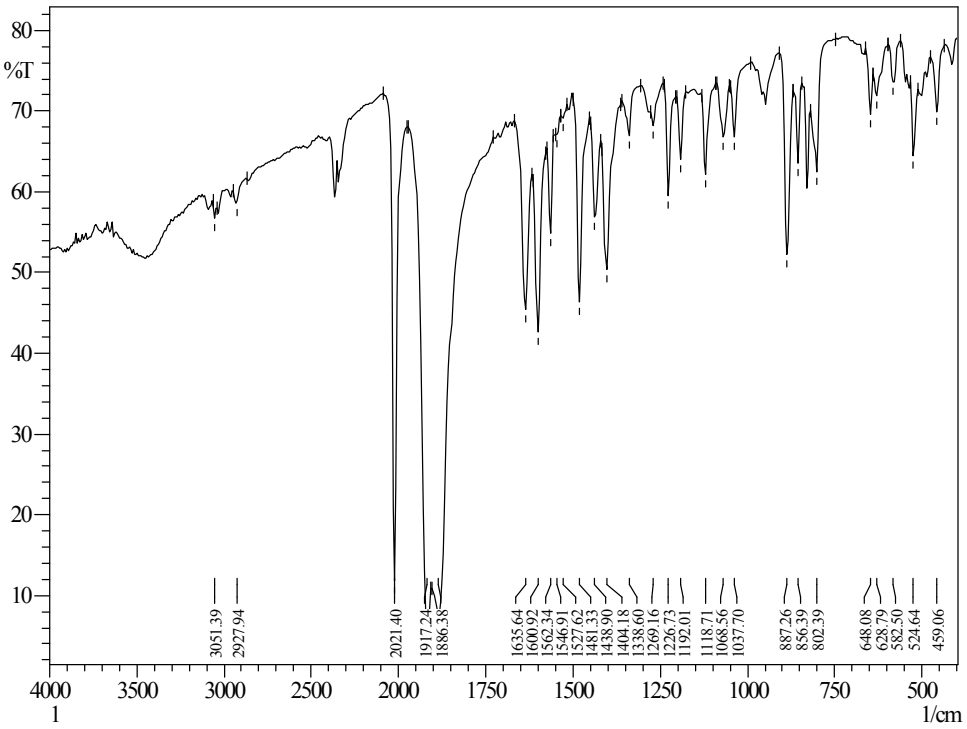

Fig. S14. FT-IR spectrum of **42BrFReCl** (**C7**).

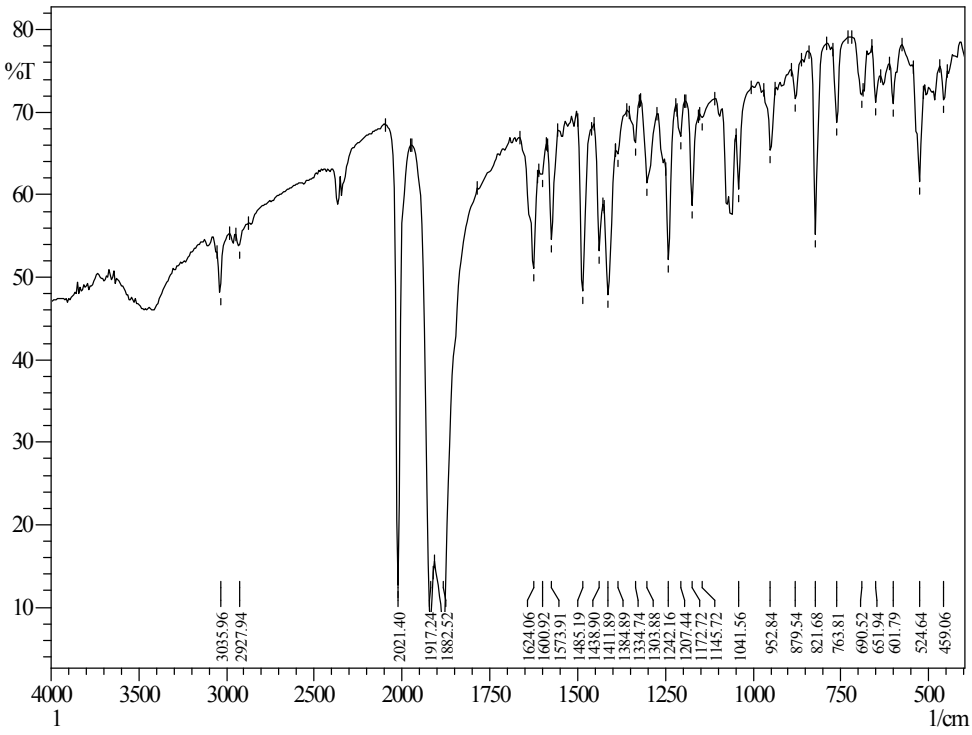

Fig. S15. FT-IR spectrum of **43ClFReCl** (**C8**).

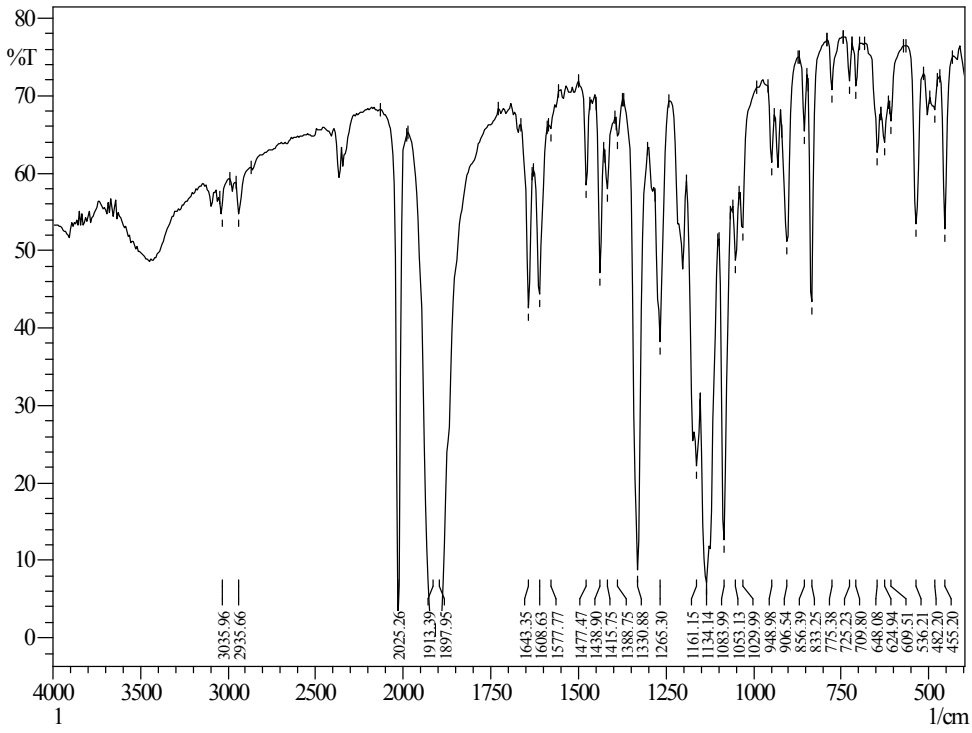

Fig. S16. FT-IR spectrum of **ClFenReBr** (**C9**).

Table S1. Crystal data and structure refinement for C2 = 32ClFReCl

Identification code	**C2**	
Empirical formula	C19 H12 Cl3 F2 N2 O3 Re	
Formula weight	646.86	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	*a* = 7.1480(2) Å	α= 105.7160(9)°
	b = 9.2830(2) Å	β= 98.7670(10)°
	c = 17.0670(6) Å	γ = 95.9490(14)°
Volume	1064.83(5) $Å^3$	
Z	2	
Density (calculated)	2.017 Mg/m^3	
Absorption coefficient	6.123 mm^{-1}	
F(000)	616	
Crystal size	0.060 x 0.050 x 0.010 mm^3	
Theta range for data collection	2.917 to 27.502°	
Index ranges	-9<=h<=9, -12<=k<=12, -22<=l<=22	
Reflections collected	15268	
Independent reflections	4817 [R(int) = 0.0728]	
Completeness to theta = 25.242°	99.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4817 / 0 / 271	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.0913	
R indices (all data)	R1 = 0.0456, wR2 = 0.0957	
Largest diff. peak and hole	1.992 and -3.339 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for C3 = 34clfrebr

Identification code	**C3**	
Empirical formula	C19 H12 Br Cl2 F2 N2 O3 Re	
Formula weight	691.32	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	*a* = 7.36000(10) Å	α= 101.5080(10)°
	b = 9.2080(3) Å	β= 94.970(2)°
	c = 16.5900(5) Å	γ = 98.653(2)°
Volume	1081.25(5) $Å^3$	
Z	2	
Density (calculated)	2.123 Mg/m^3	
Absorption coefficient	7.754 mm^{-1}	
F(000)	652	
Crystal size	0.200 x 0.050 x 0.050 mm^3	
Theta range for data collection	2.948 to 27.483°	
Index ranges	-9<=h<=9, -11<=k<=11, -21<=l<=21	
Reflections collected	15821	
Independent reflections	4940 [R(int) = 0.0512]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4940 / 0 / 271	
Goodness-of-fit on F^2	1.279	
Final R indices [I>2sigma(I)]	R1 = 0.0272, wR2 = 0.0783	
R indices (all data)	R1 = 0.0339, wR2 = 0.0988	
Largest diff. peak and hole	1.511 and -2.575 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for C4 = 34clfrecl.

Identification code	**C4**	
Empirical formula	C19 H12 Cl3 F2 N2 O3 Re	
Formula weight	646.86	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P\,2_1/c$	
Unit cell dimensions	a = 15.4530(5) Å	α = 90°
	b = 7.0730(2) Å	β = 126.1351(11)°
	c = 23.5290(8) Å	γ = 90°
Volume	2076.98(12) Å^3	
Z	4	
Density (calculated)	2.069 Mg/m^3	
Absorption coefficient	6.278 mm^{-1}	
F(000)	1232	
Crystal size	0.090 x 0.040 x 0.010 mm^3	
Theta range for data collection	3.073 to 27.519°	
Index ranges	-20<=h<=17, -9<=k<=8, -30<=l<=26	
Reflections collected	9932	
Independent reflections	4688 [R(int) = 0.0633]	
Completeness to theta = 25.242°	99.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4688 / 0 / 271	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0435, wR2 = 0.0957	
R indices (all data)	R1 = 0.0671, wR2 = 0.1081	
Largest diff. peak and hole	1.990 and -3.422 e.Å^{-3}	

Table S4. Crystal data and structure refinement for C5 = 35clenbr

Identification code	**C5**	
Empirical formula	C19 H12 Br Cl4 N2 O3 Re	
Formula weight	724.22	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	*a* = 7.1653(3) Å	α= 86.971(4)°
	b = 10.1441(5) Å	β= 82.270(4)°
	c = 16.1968(10) Å	γ = 71.257(4)°
Volume	1104.65(10) $Å^3$	
Z	2	
Density (calculated)	2.177 Mg/m^3	
Absorption coefficient	7.817 mm^{-1}	
F(000)	684	
Crystal size	0.080 x 0.040 x 0.020 mm^3	
Theta range for data collection	3.424 to 29.262°	
Index ranges	-8<=h<=9, -12<=k<=13, -21<=l<=22	
Reflections collected	9299	
Independent reflections	5040 [R(int) = 0.0394]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5040 / 0 / 271	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0353, wR2 = 0.0691	
R indices (all data)	R1 = 0.0410, wR2 = 0.0722	
Largest diff. peak and hole	1.334 and -1.758 e.$Å^{-3}$	

Table S5. Crystal data and structure refinement for C6 = 35clencl

Identification code	**C6**	
Empirical formula	C19 H12 Cl5 N2 O3 Re	
Formula weight	679.76	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P\ 2_1/c$	
Unit cell dimensions	a = 7.12100(10) Å	α = 90°
	b = 33.7880(7) Å	β = 96.0240(8)°
	c = 9.4780(2) Å	γ = 90°
Volume	2267.86(7) $Å^3$	
Z	4	
Density (calculated)	1.991 Mg/m^3	
Absorption coefficient	5.971 mm^{-1}	
F(000)	1296	
Crystal size	0.060 x 0.030 x 0.020 mm^3	
Theta range for data collection	2.939 to 27.475°	
Index ranges	-8<=h<=9, -43<=k<=27, -12<=l<=12	
Reflections collected	13899	
Independent reflections	5136 [R(int) = 0.0561]	
Completeness to theta = 25.242°	99.3 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5136 / 0 / 271	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0339, wR2 = 0.0559	
R indices (all data)	R1 = 0.0642, wR2 = 0.0655	
Largest diff. peak and hole	1.650 and -1.628 e.$Å^{-3}$	

Table S6. Crystal data and structure refinement for C7 = 42BrFReCl

Identification code	**C7**	
Empirical formula	C19 H12 Br2 Cl F2 N2 O3 Re	
Formula weight	735.78	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	*a* = 7.3756(4) Å	*α* = 98.004(4)°
	b = 8.8914(4) Å	*β* = 90.442(5)°
	c = 16.9636(10) Å	*γ* = 105.113(4)°
Volume	1062.40(10) $Å^3$	
Z	2	
Density (calculated)	2.300 Mg/m^3	
Absorption coefficient	9.647 mm^{-1}	
F(000)	688	
Crystal size	0.100 x 0.060 x 0.020 mm^3	
Theta range for data collection	3.357 to 27.500°	
Index ranges	-9<=h<=9, -11<=k<=11, -22<=l<=22	
Reflections collected	15534	
Independent reflections	4862 [R(int) = 0.0526]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4862 / 0 / 281	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0527, wR2 = 0.1244	
R indices (all data)	R1 = 0.0727, wR2 = 0.1355	
Largest diff. peak and hole	3.252 and -1.709 e.$Å^{-3}$	

Table S7. Crystal data and structure refinement for C8 = 43ClFReCl

Identification code	**C8**	
Empirical formula	C38 H24 Cl6 F4 N4 O6 Re2	
Formula weight	1293.71	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	*a* = 7.3006(5) Å	a= 104.105(5)°
	b = 11.5980(7) Å	b= 97.855(5)°
	c = 12.6789(8) Å	g = 96.998(5)°
Volume	1017.88(12) $Å^3$	
Z	1	
Density (calculated)	2.111 Mg/m^3	
Absorption coefficient	6.405 mm^{-1}	
F(000)	616	
Crystal size	0.100 x 0.060 x 0.030 mm^3	
Theta range for data collection	3.364 to 29.201°	
Index ranges	-9<=h<=10, -15<=k<=15, -17<=l<=17	
Reflections collected	8612	
Independent reflections	4683 [R(int) = 0.0395]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4683 / 0 / 271	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0321, wR2 = 0.0557	
R indices (all data)	R1 = 0.0361, wR2 = 0.0583	
Largest diff. peak and hole	1.350 and -1.345 $e.Å^{-3}$	

Table S8. Crystal data and structure refinement for C9 = ClFReBr

Identification code	**C9**	
Empirical formula	C21 H12 Br Cl2 F6 N2 O3 Re	
Formula weight	791.34	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P\,2_1/c$	
Unit cell dimensions	a = 7.2547(4) Å	α = 90°
	b = 26.9040(16) Å	β = 93.127(6)°
	c = 12.6293(7) Å	γ = 90°
Volume	2461.3(2) $Å^3$	
Z	4	
Density (calculated)	2.136 Mg/m^3	
Absorption coefficient	6.850 mm^{-1}	
F(000)	1496	
Crystal size	0.120 x 0.080 x 0.050 mm^3	
Theta range for data collection	3.404 to 25.997°	
Index ranges	-8<=h<=8, -33<=k<=33, -15<=l<=15	
Reflections collected	21636	
Independent reflections	4820 [R(int) = 0.0477]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4820 / 0 / 325	
Goodness-of-fit on F^2	1.098	
Final R indices [I>2sigma(I)]	R1 = 0.0331, wR2 = 0.0542	
R indices (all data)	R1 = 0.0442, wR2 = 0.0571	
Largest diff. peak and hole	0.880 and -0.858 $e.Å^{-3}$	

Table S9. Crystal data and structure refinement for C10 = ClFReBr′.

Identification code	**C10**	
Empirical formula	C21 H12 Br Cl2 F6 N2 O3 Re	
Formula weight	791.34	
Temperature	100(2) K	
Wavelength	0.71073 ¦	
Crystal system	Monoclinic	
Space group	$P\,2_1/c$	
Unit cell dimensions	a = 9.6938(1)	α = 90°
	b = 12.9012(2)	β= 91.1190(10)°
	c = 22.2519(3)	γ = 90°
Volume	2782.33(6) ¦	
Z	4	
Density (calculated)	1.889 Mg/m^3	
Absorption coefficient	6.060 mm^{-1}	
F(000)	1496	
Crystal size	0.314 x 0.226 x 0.050 mm^3	
Theta range for data collection	1.825 to 30.856°	
Index ranges	-13<=h<=13, -18<=k<=18, -32<=l<=29	
Reflections collected	36476	
Independent reflections	8709 [R(int) = 0.0518]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8709 / 0 / 325	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0381, wR2 = 0.0905	
R indices (all data)	R1 = 0.0627, wR2 = 0.1031	
Largest diff. peak and hole	1.169 and -1.882 $e.^{3-}$¦	

Calculated electrostatic potential surfaces for complexes C1-C10 with G09-BP86-D3/def2-TZVP. Colour scale: positive (blue = +0.045 a.u.); negative (red = -0.045 a.u.).

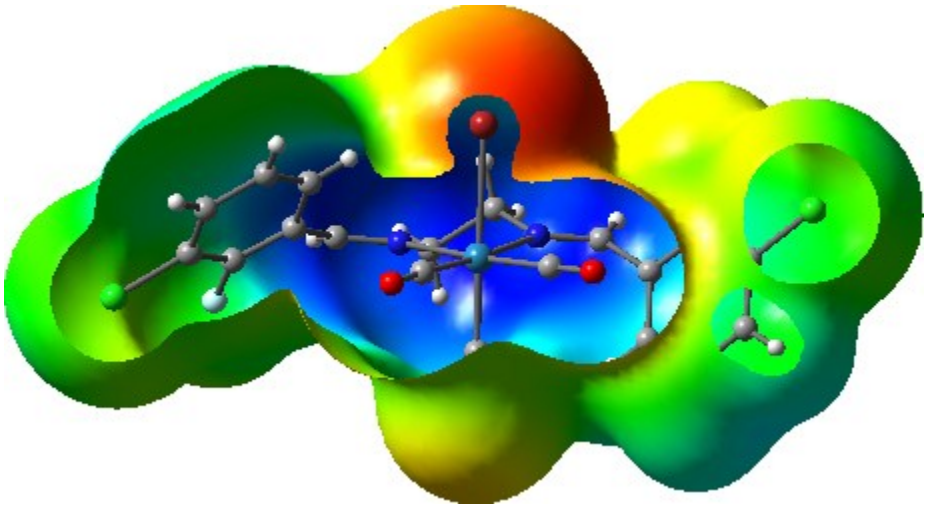

Fig. S17. MEP of **C1** [isovalue at -0.045 to 0.045].

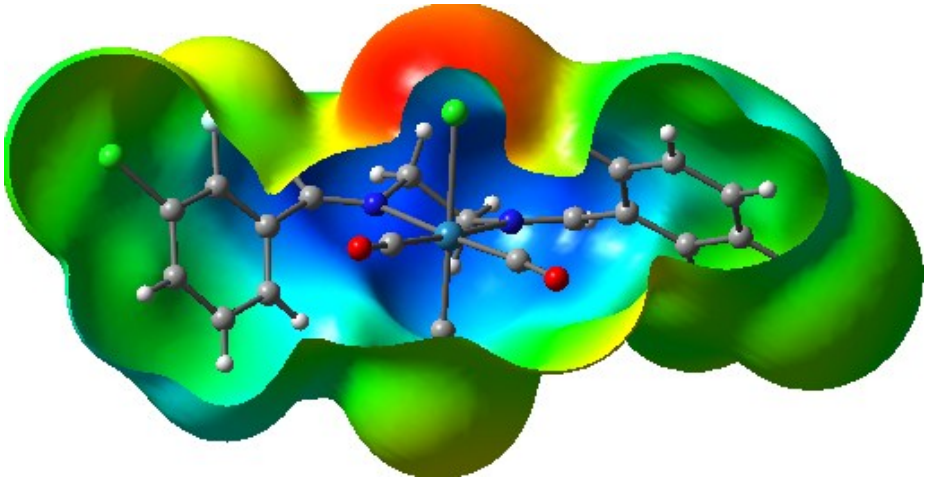

Fig. S18. MEP of **C2** [isovalue at -0.045 to 0.045].

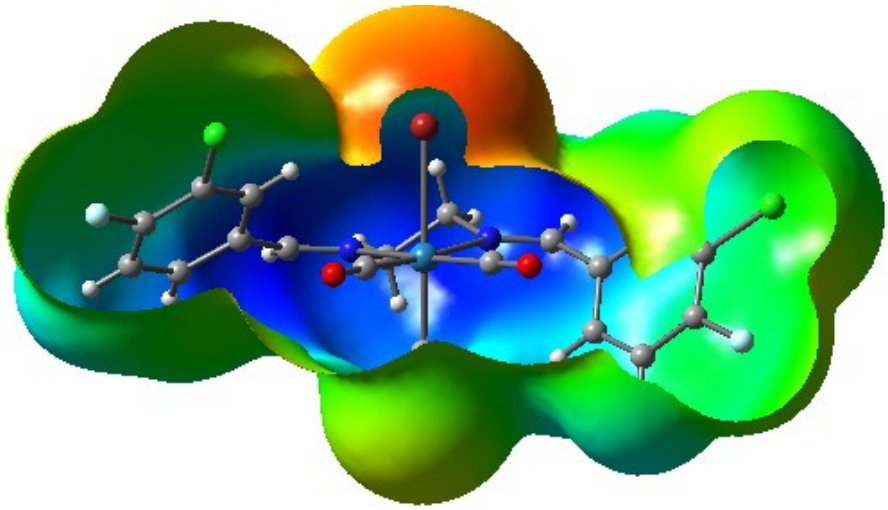

Fig. S19. MEP of **C3** [isovalue at -0.045 to 0.045].

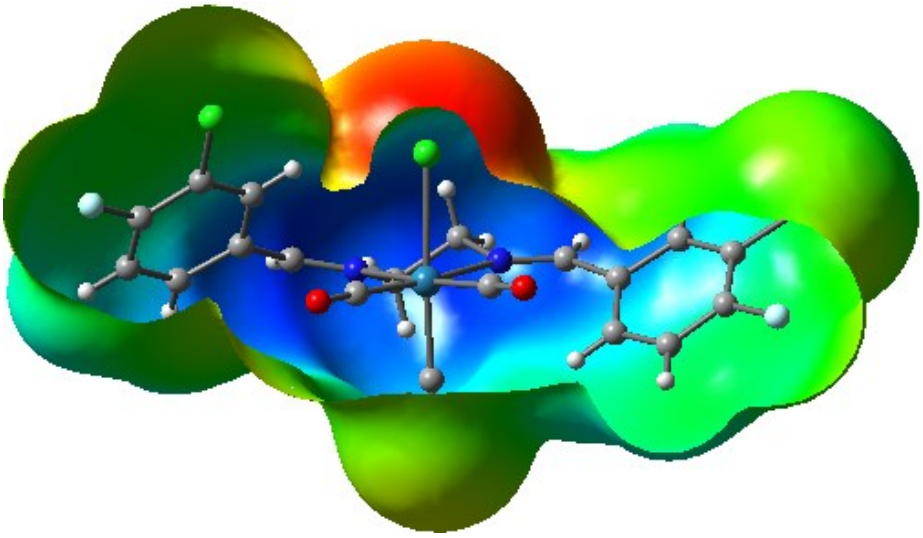

Fig. S20. MEP of **C4** [isovalue at -0.045 to 0.045].

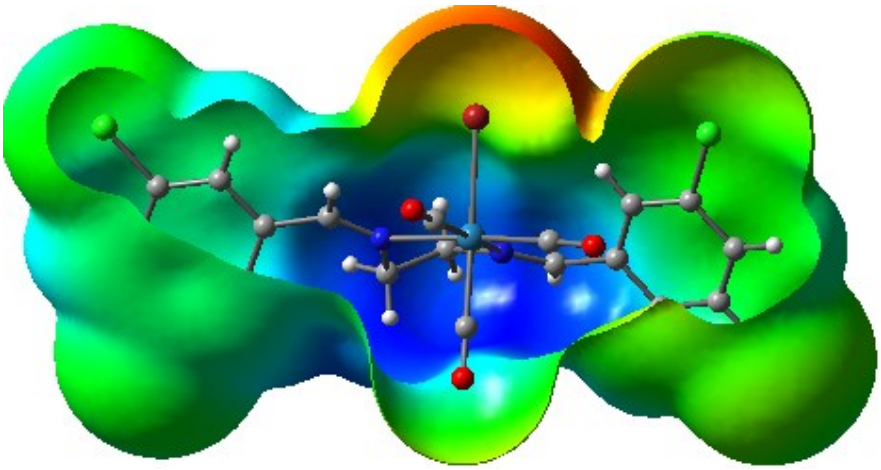

Fig. S21. MEP of **C5** [isovalue at -0.045 to 0.045].

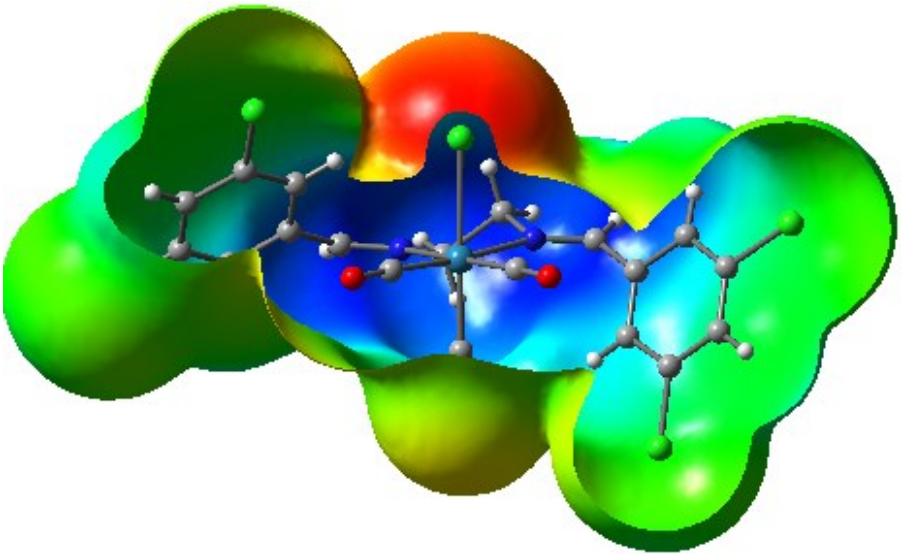

Fig. S22. MEP of **C6** [isovalue at -0.045 to 0.045].

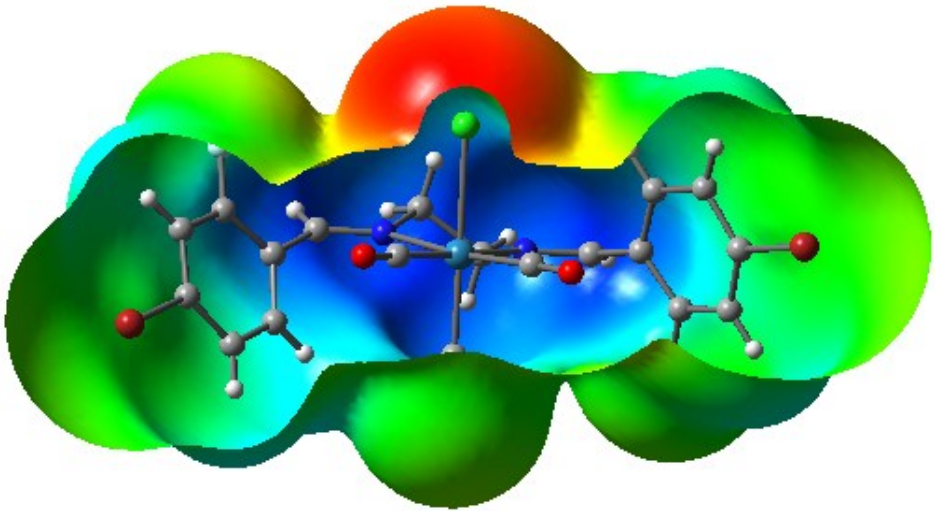

Fig. S23. MEP of **C7** [isovalue at -0.045 to 0.045].

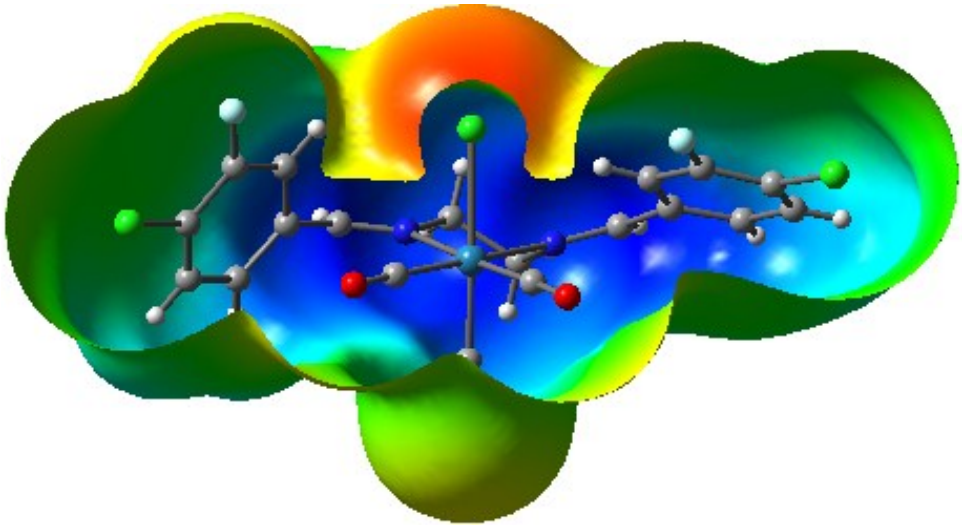

Fig. S24. MEP of **C8** [isovalue at -0.045 to 0.045].

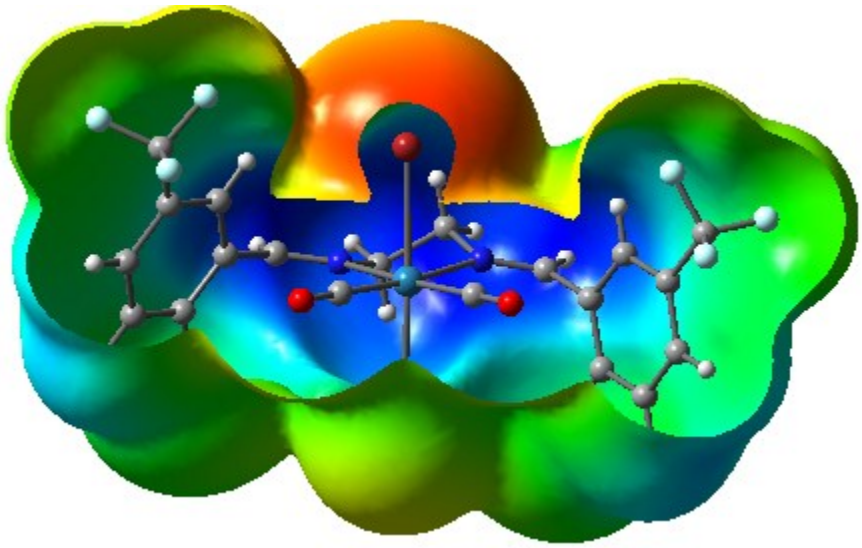

Fig. S25. MEP of **C9** [isovalue at -0.045 to 0.045].

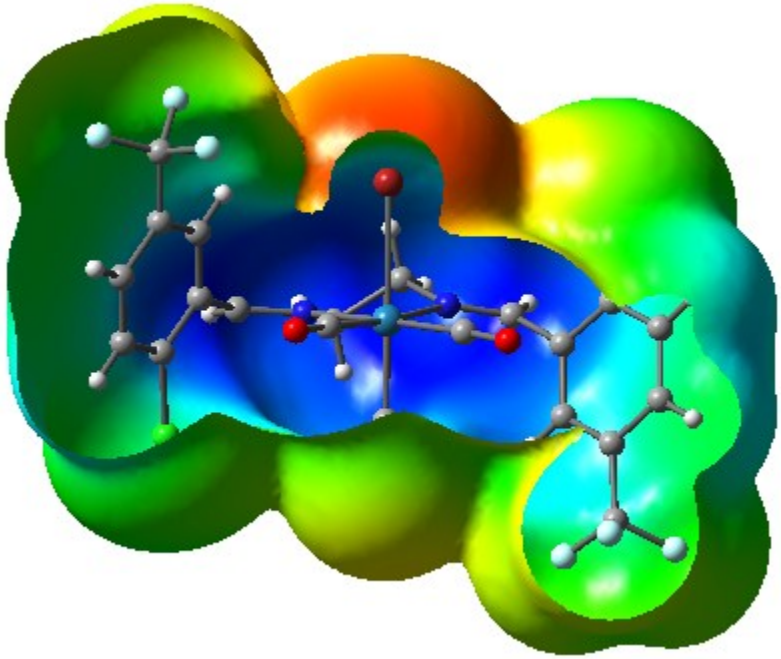

Fig. S26. MEP of **C10** [isovalue at -0.045 to 0.045].

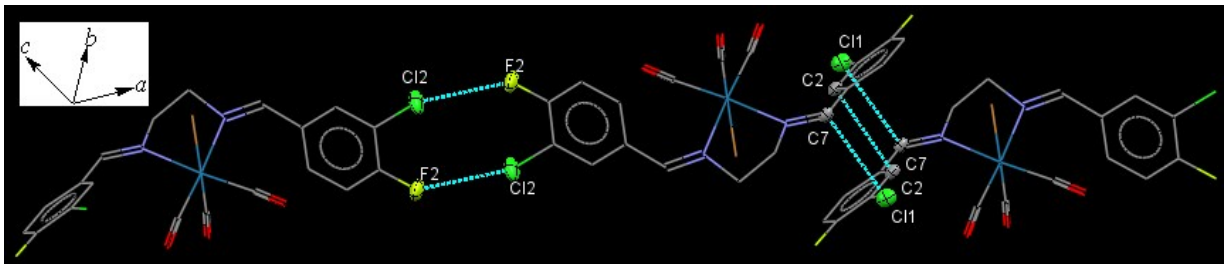

Fig. S27. Individual dimer formation in **C3** through the pair of intermolecular Cl···F interactions supported by C···Cl and C···C contacts.

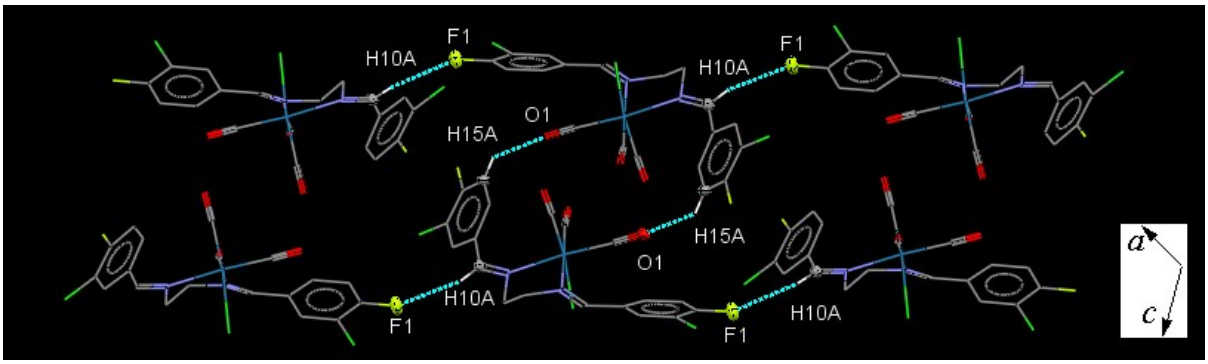

Fig. S28. Part of the crystal packing of **C4** viewed down the *b*-axis, showing head-to-tail individual dimer formation through C–H···O, further supported by the intermolecular C–H···F interactions.

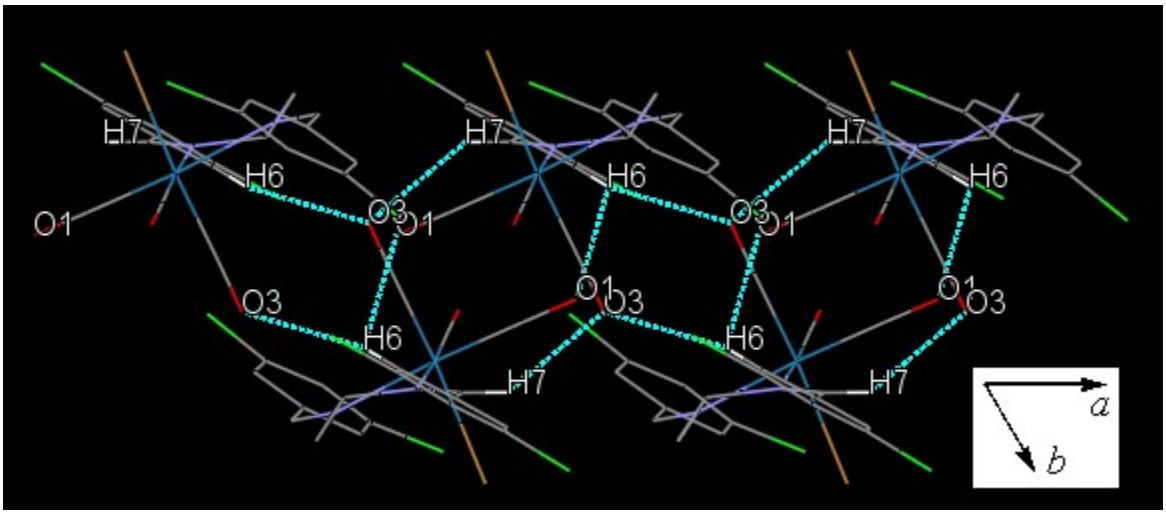

Fig. S29. Pair of intermolecular C7–H7···O3 and C6–H6···O1 hydrogen bonds form a centrosymmetric dimer in **C5**, linking molecules into an infinite chain along the *a*-axis.

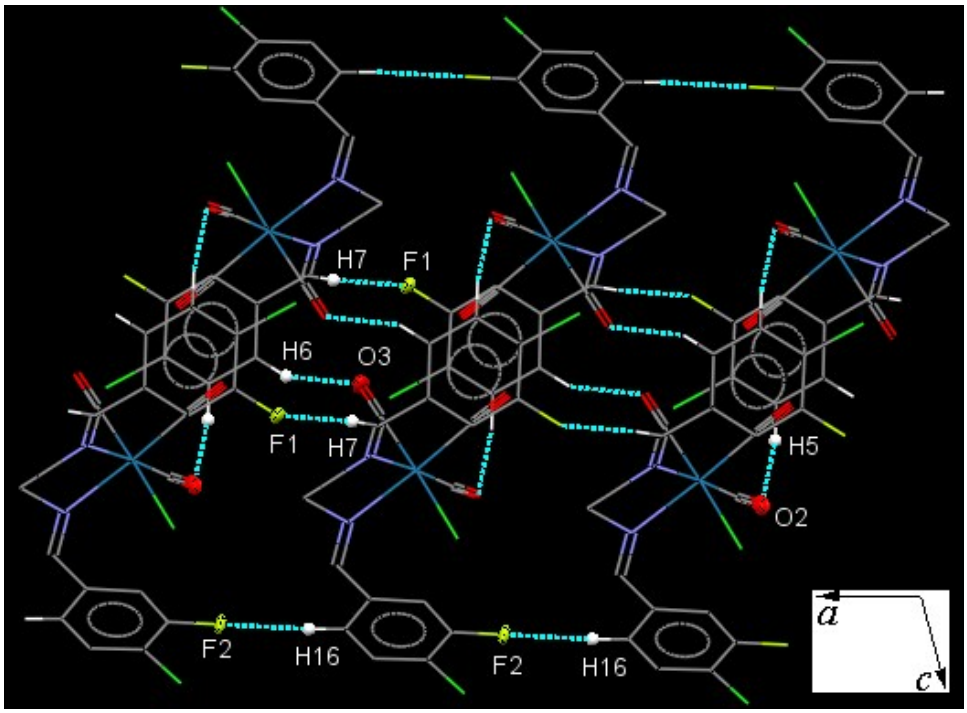

Fig. S30. Part of the crystal packing of **C8,** showing interconnected chains of neighboring molecules through the intermolecular Cl···Br halogen bond along [110] direction.

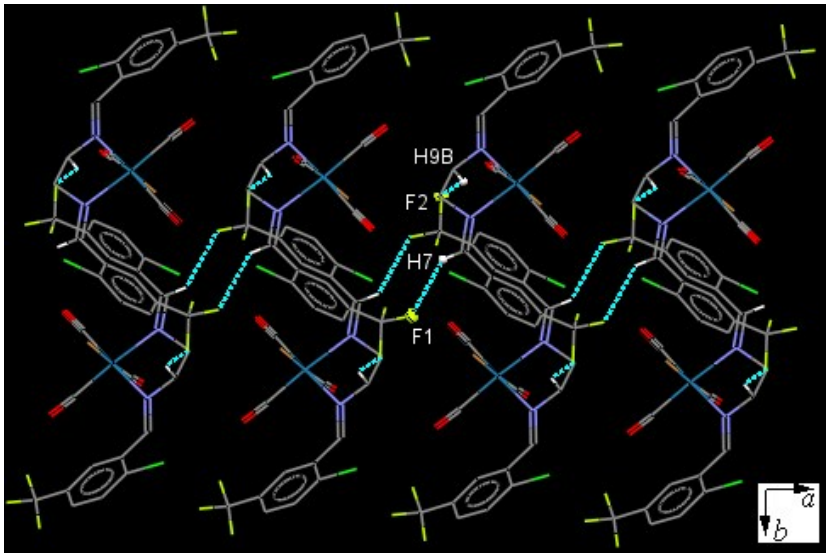

Fig. S31. Part of the packing of **C9**, showing connection of neighboring molecules into one-dimensional extended chain along the *c*-axis through C–H···F interactions.

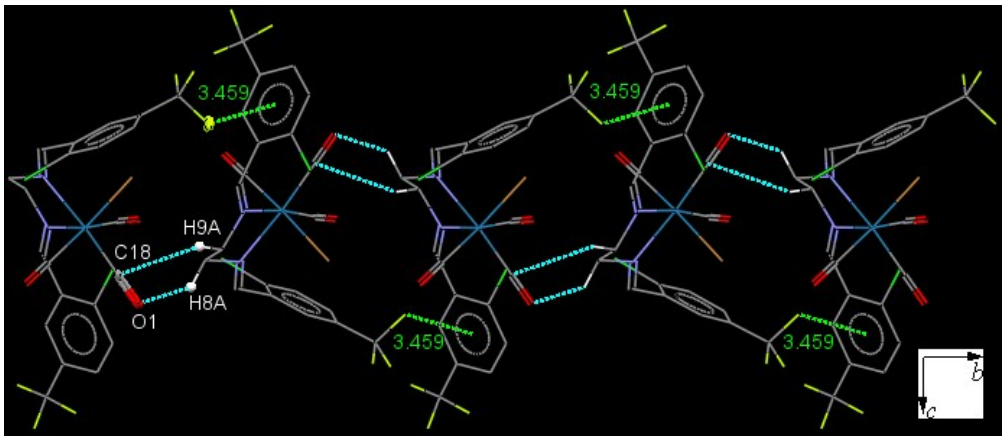

Fig. S32. One-dimensional extended chain of **C10** along the *b*-axis through intermolecular C–F···π, C–H···O and C–H···π interactions.

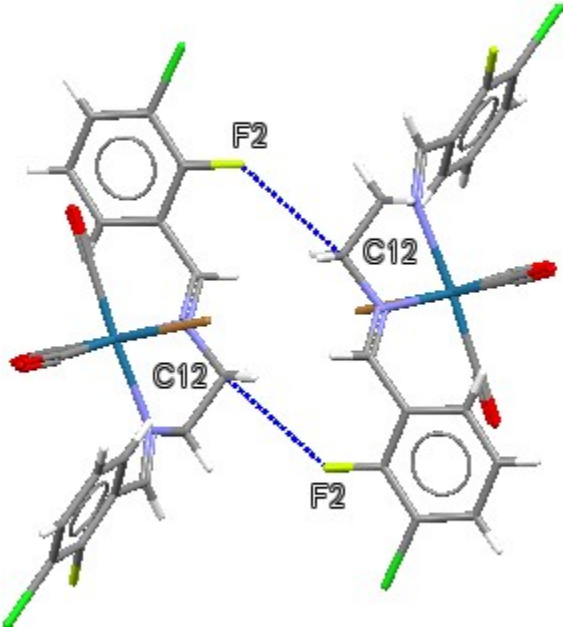

Fig. S33a. Dimer of **C1** formed from crystallographic coordinates.

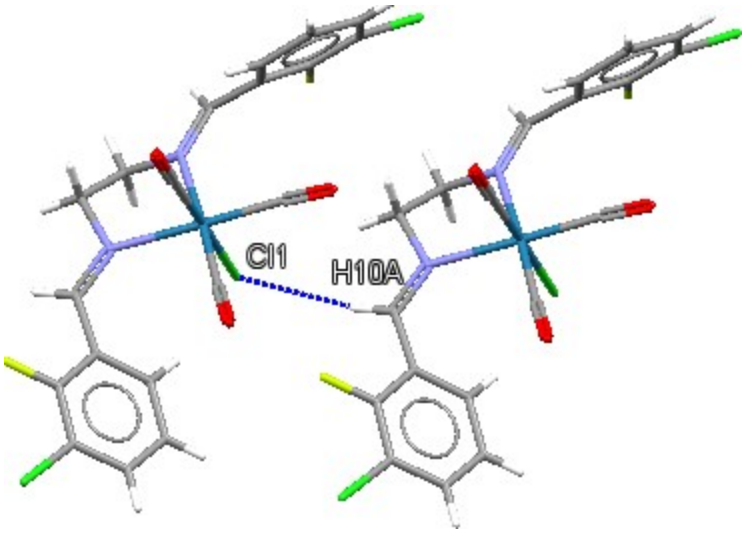

Fig. S33b. Dimer of **C2** formed from crystallographic coordinates.

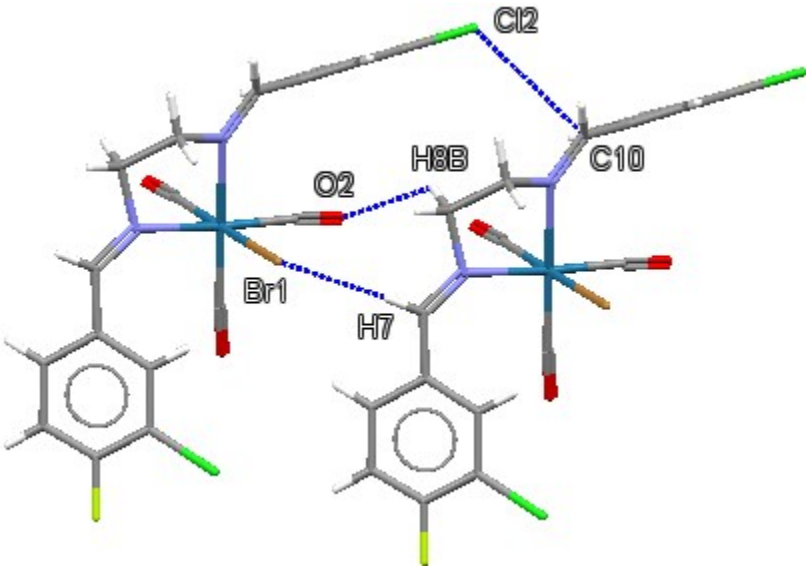

Fig. S33c. Dimer of **C3** formed from crystallographic coordinates.

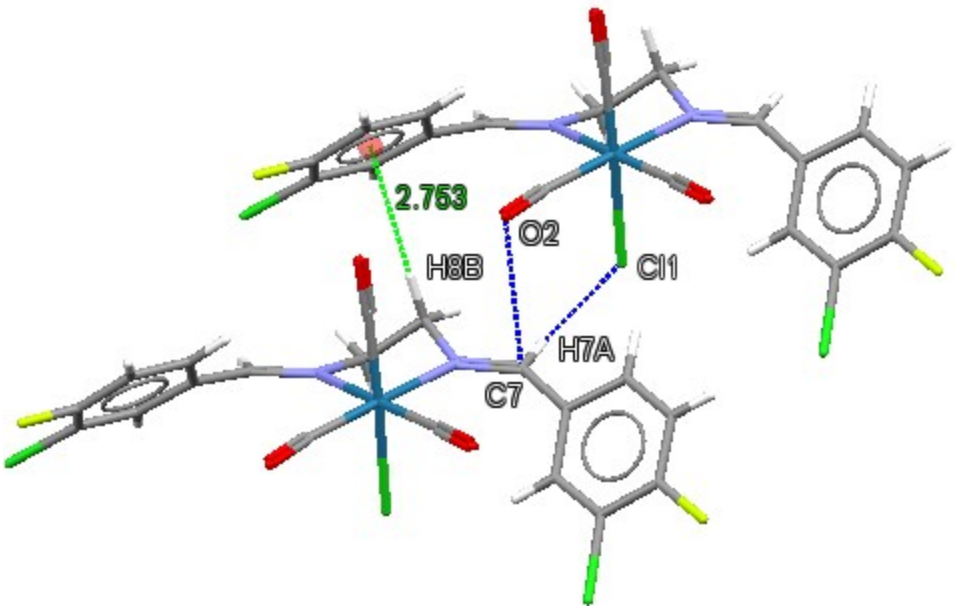

Fig. S33d. Dimer of **C4** formed from crystallographic coordinates.

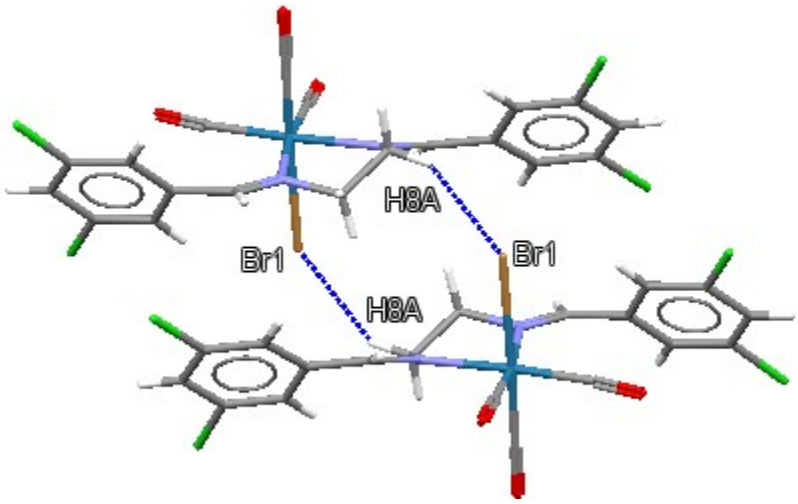

Fig. S33e. Dimer of **C5** formed from crystallographic coordinates.

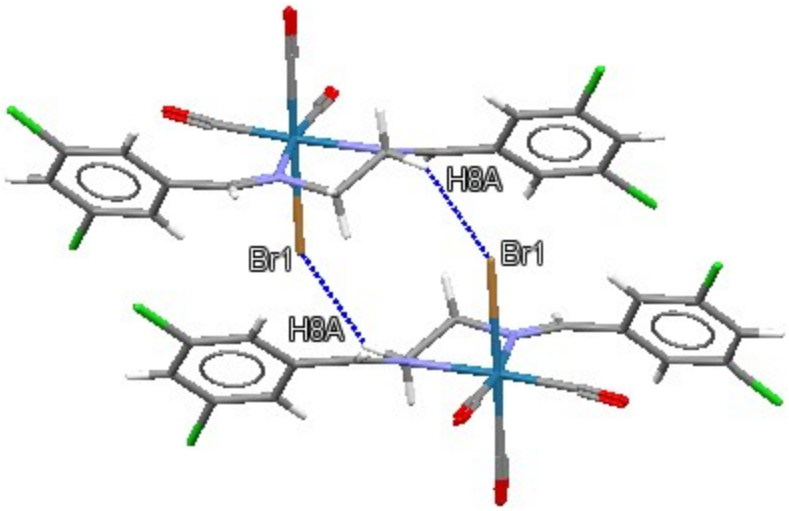

Fig. S33f. Dimer of **C5** formed from crystallographic coordinates.

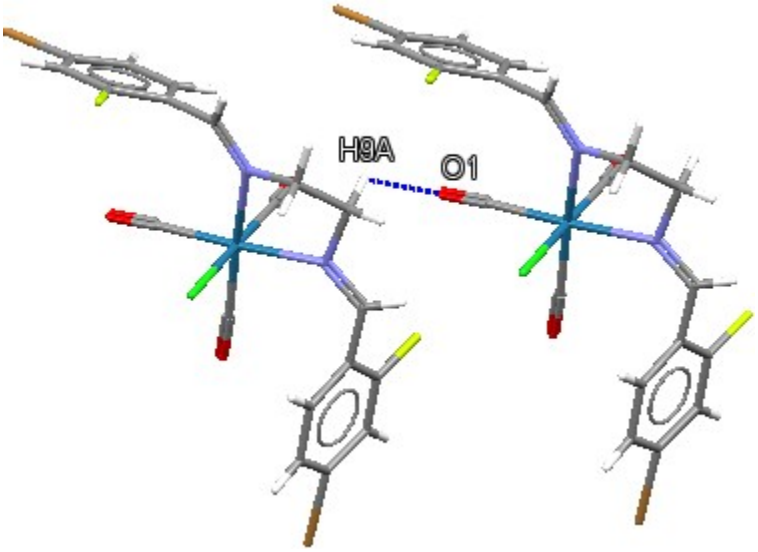

Fig. S33g. Dimer of **C7** formed from crystallographic coordinates.

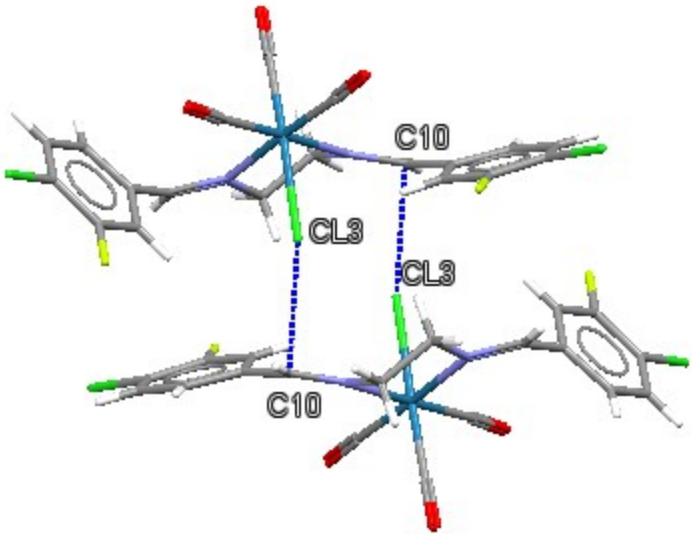

Fig. S33h. Dimer of **C8** formed from crystallographic coordinates.

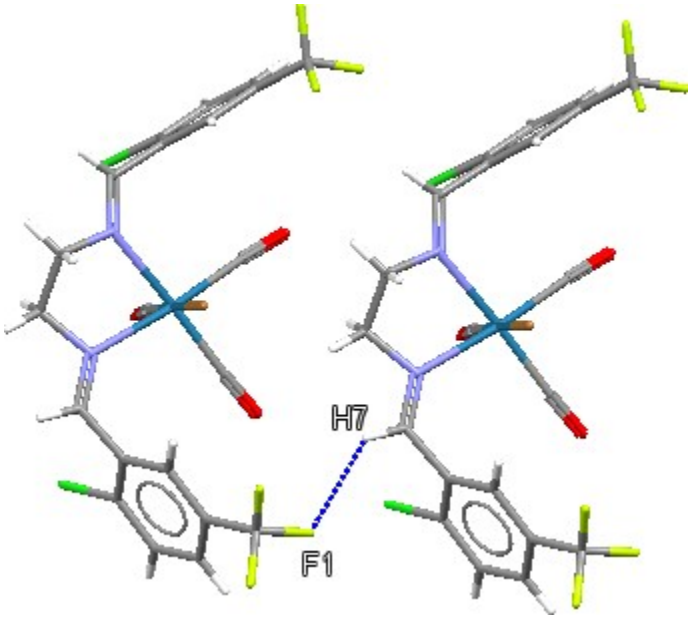

Fig. S33i. Dimer of **C9** formed from crystallographic coordinates.

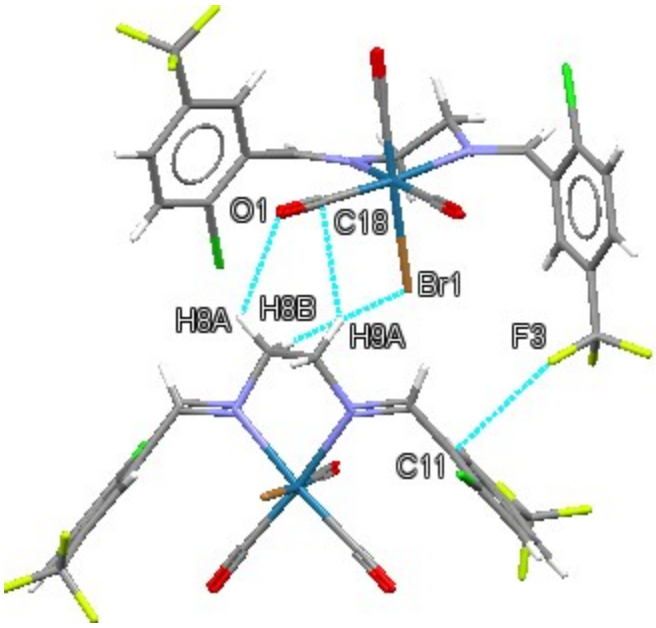

Fig. S33j. Dimer of **C10** formed from crystallographic coordinates.

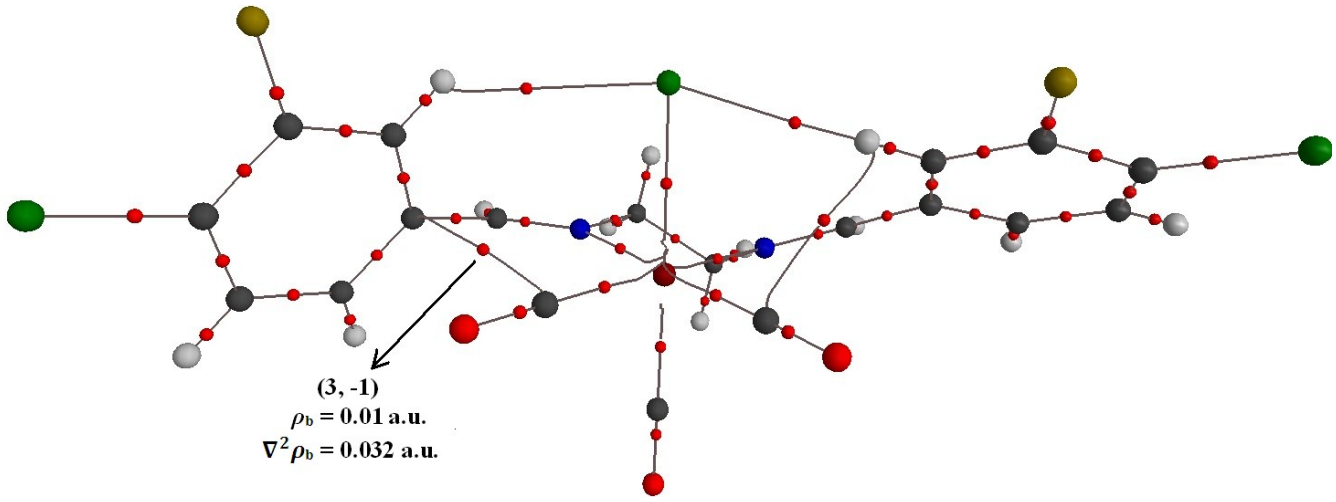

Fig. S34a. The bond critical points (BCPs) with their bond paths in **C8**. The specified BCP shows the interaction of the carbonyl group with the arene ring.

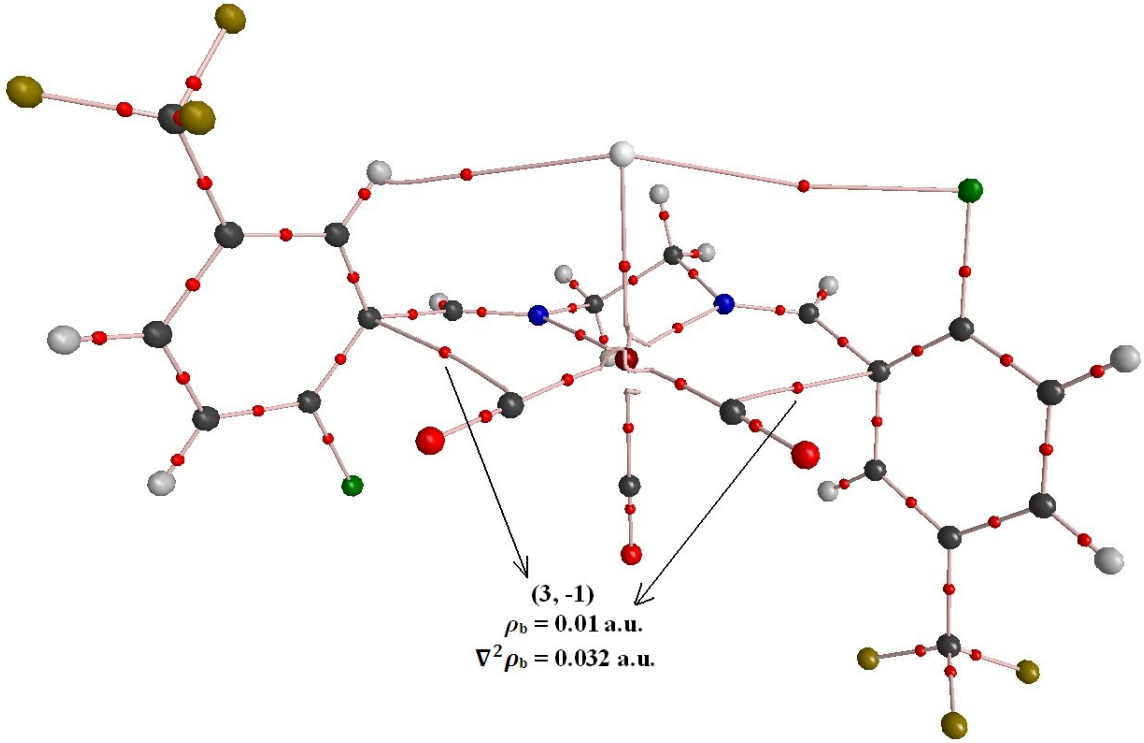

Fig. S34b. The bond critical points (BCPs) with their bond paths in **C10**. The specified BCP shows the interaction of the carbonyl group with the arene ring.

Fig. S35a-o:

The intermolecular interaction iso-surfaces generated by NCIPLOT for s = 0.3 and –0.03 < ρ*sign (λ_2) < +0.03 [colour scale: attractive (blue) → repulsive (red)] (top) and plots of ρ*sign (λ_2) vs. reduced density gradient highlighting the favorable interaction corresponding to the halogen bond (down).

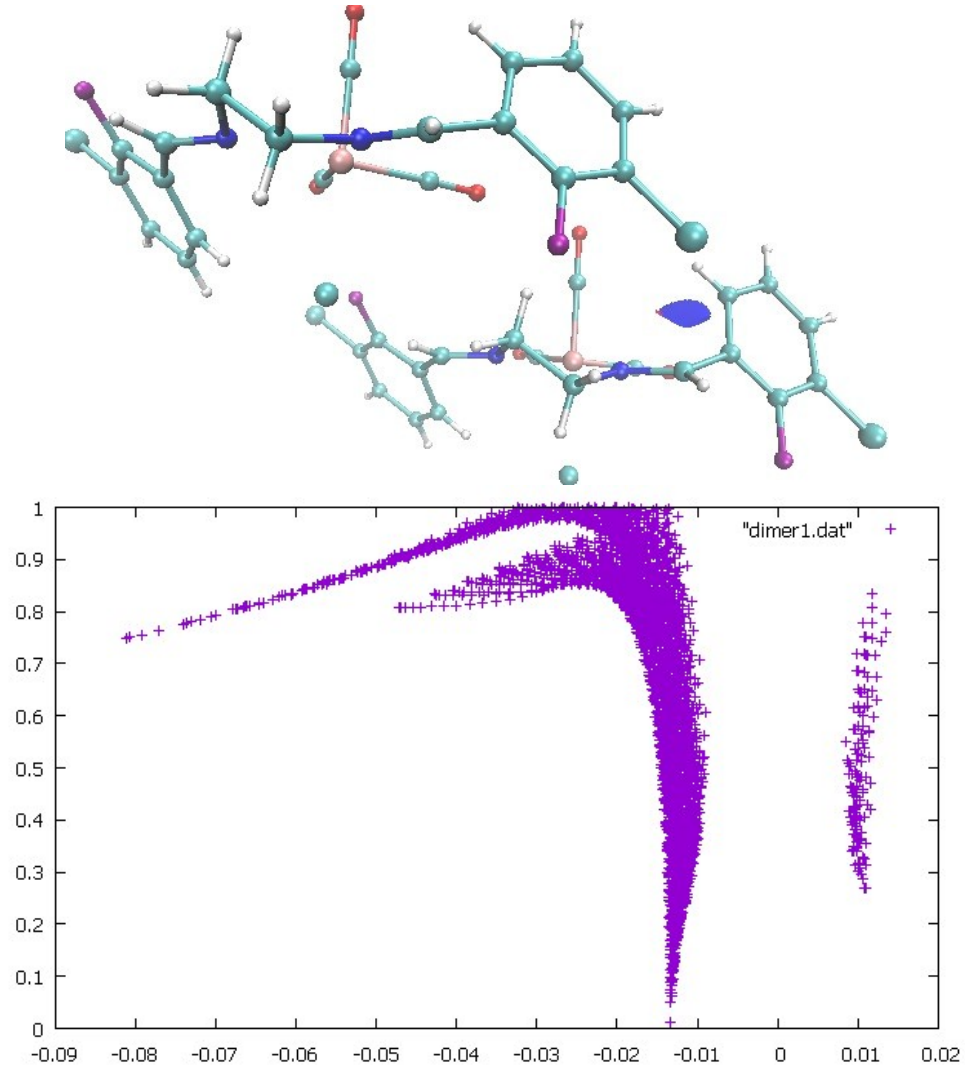

Fig. S35a. Intermolecular **Cl2···C13** isosurface (top) and its corresponding RDG vs. ρ*sign (λ_2) plot (down) in **C1 (32ClFReBr)**.

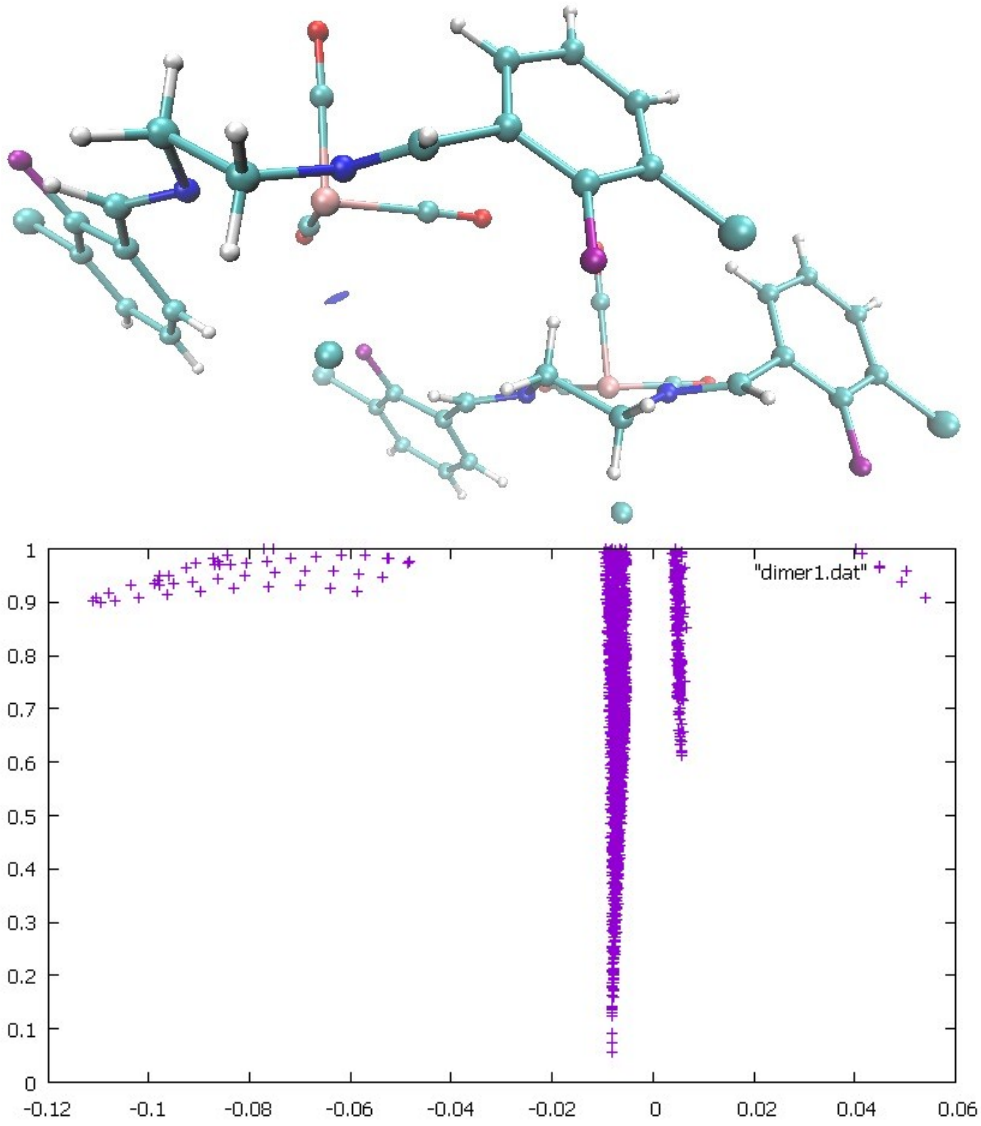

Fig. S35b. Intermolecular **F1···O2** isosurface (top) and its corresponding RDG vs. ρ*sign (λ_2) plot (down) in **C1 (32ClFReBr)**.

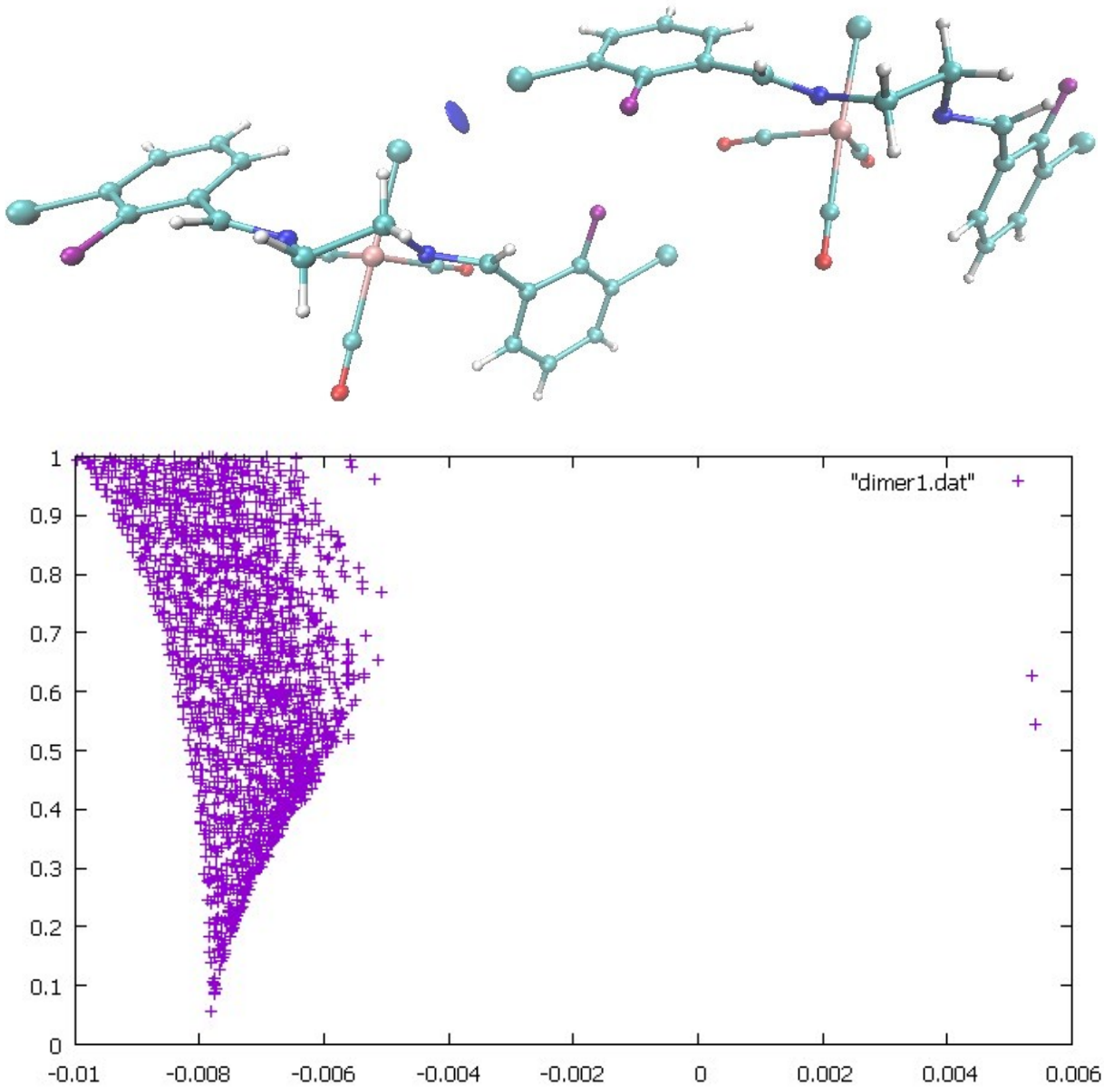

Fig. S35c. Intermolecular **Cl1···Cl3** isosurface (top) and its corresponding RDG vs. ρ*sign (λ_2) plot (down) in **C2 (32ClFReCl)**.

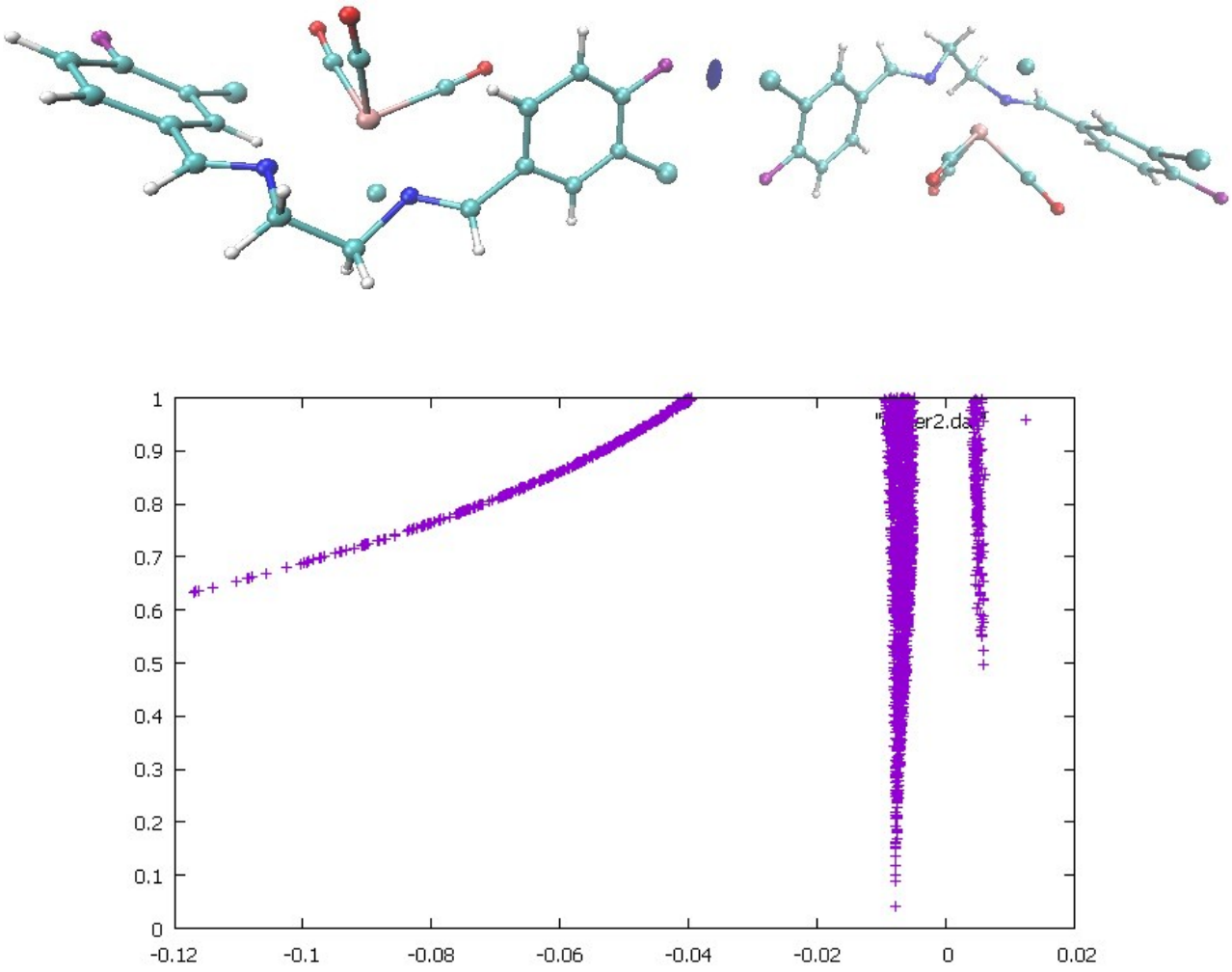

Fig. S35d. Intermolecular **Cl1···F1** isosurface (top) and its corresponding RDG vs. ρ*sign (λ_2) plot (down) in **C3 (34ClFReBr)**.

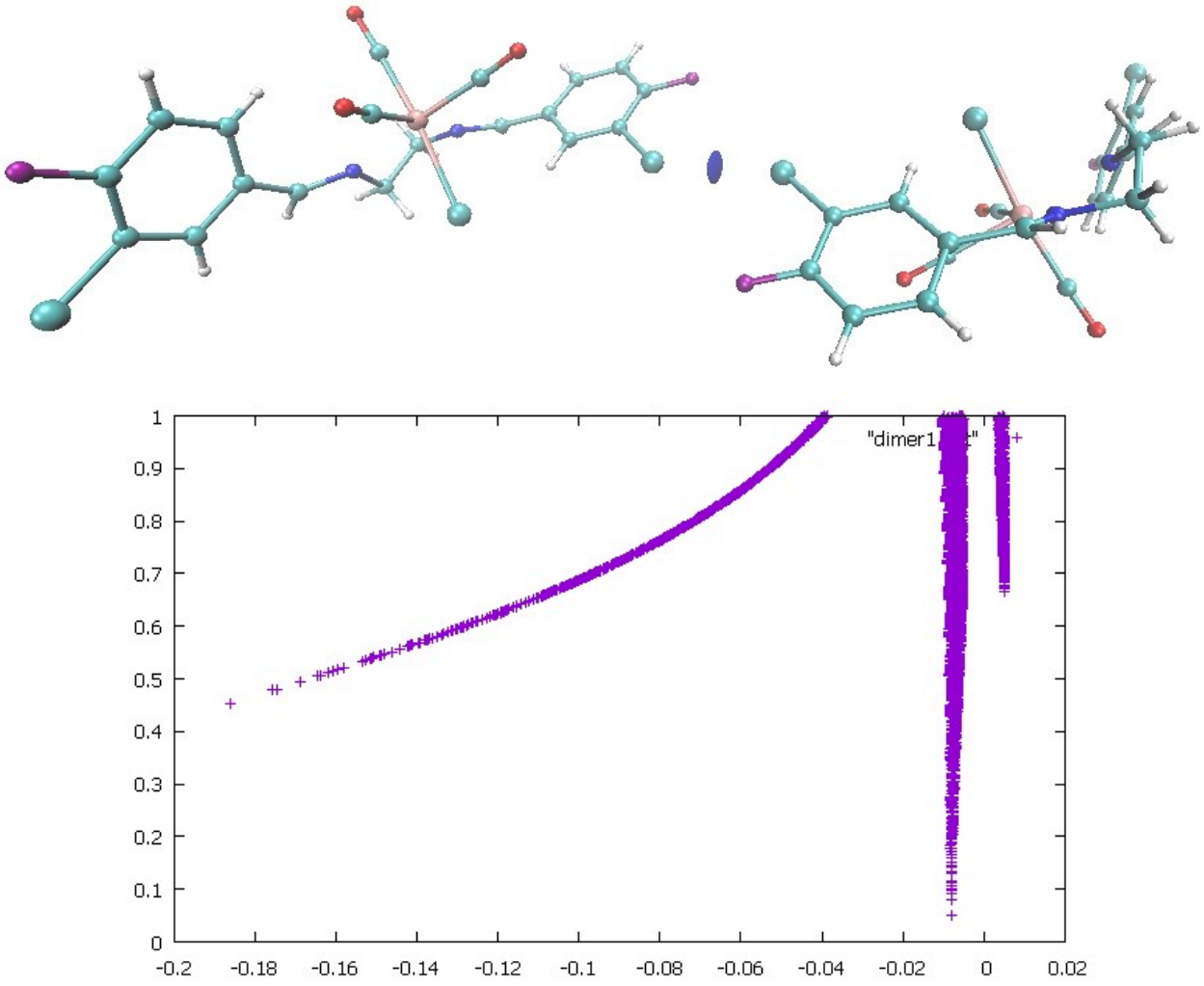

Fig. S35e. Intermolecular **Cl2···F2** isosurface (top) and its corresponding RDG vs. ρ*sign (λ_2) plot (down) in **C4 (34ClFReCl)**.

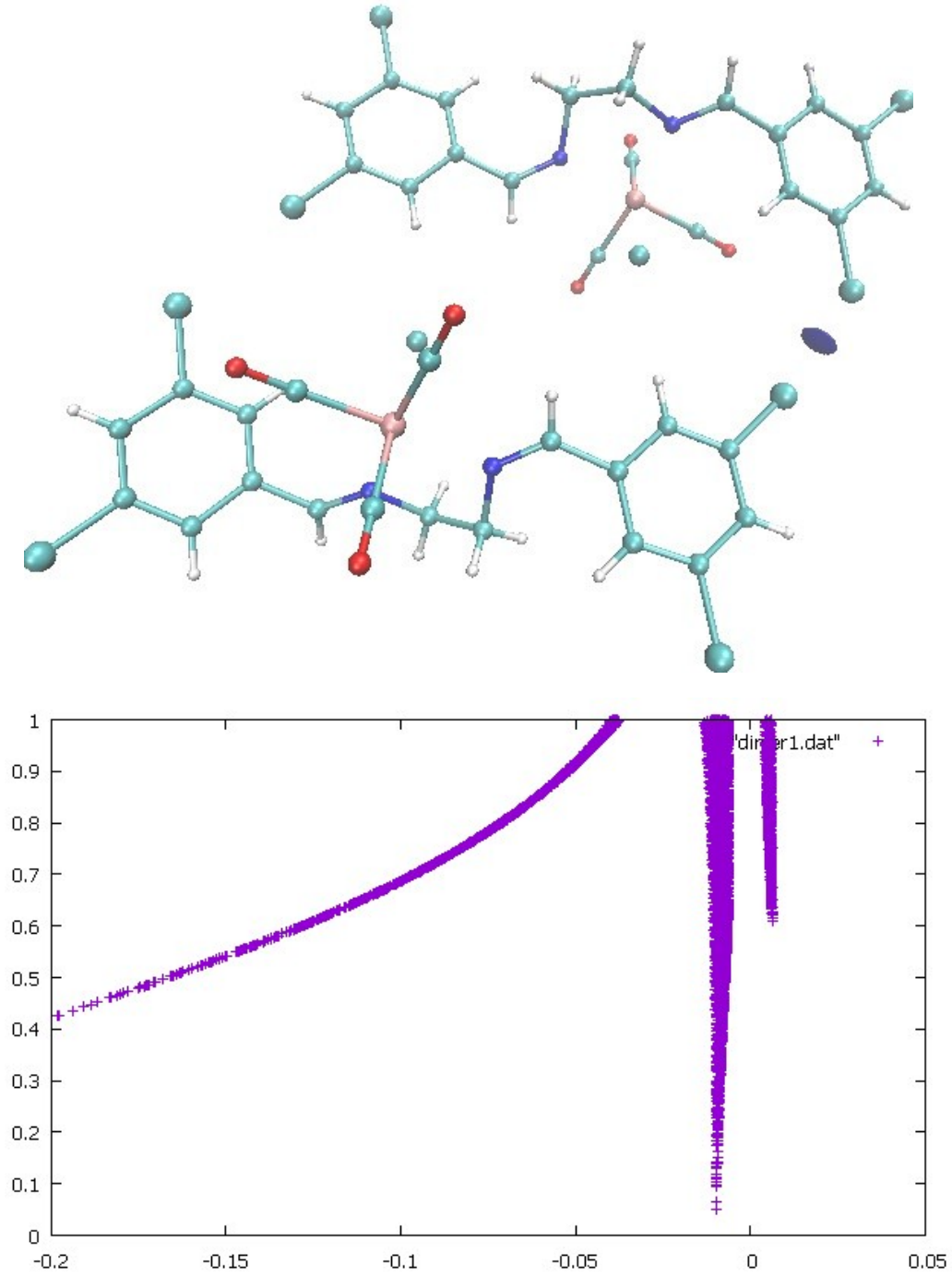

Fig. S35f. Intermolecular **Cl1···Cl3** isosurface (top) and its corresponding RDG vs. ρ*sign (λ_2) plot (down) in **C5 (35ClenReBr)**.

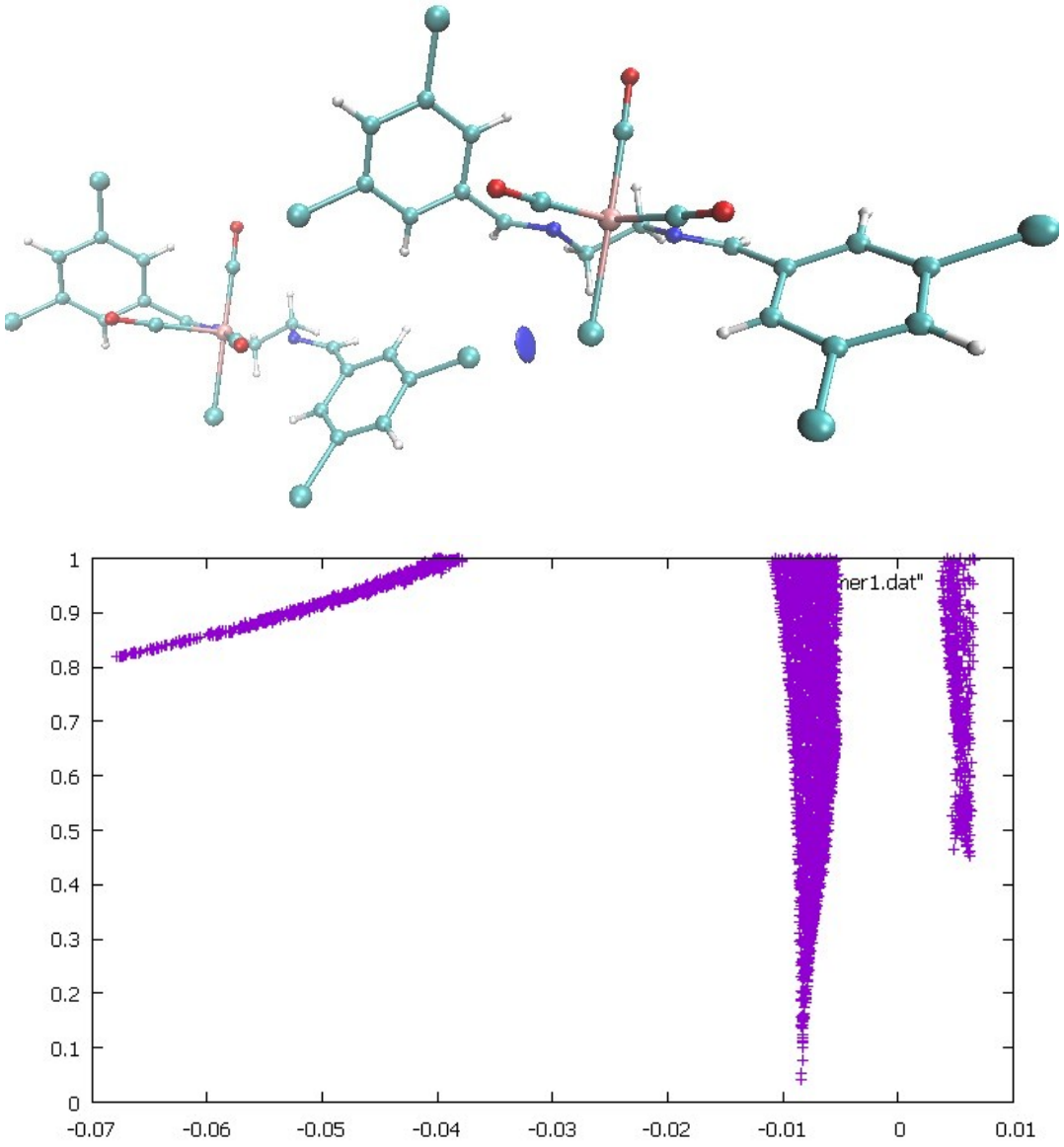

Fig. S35g. Intermolecular **Cl1···Cl3** isosurface (top) and its corresponding RDG vs. ρ*sign (λ_2) plot (down) in **C6 (35ClenReCl)**.

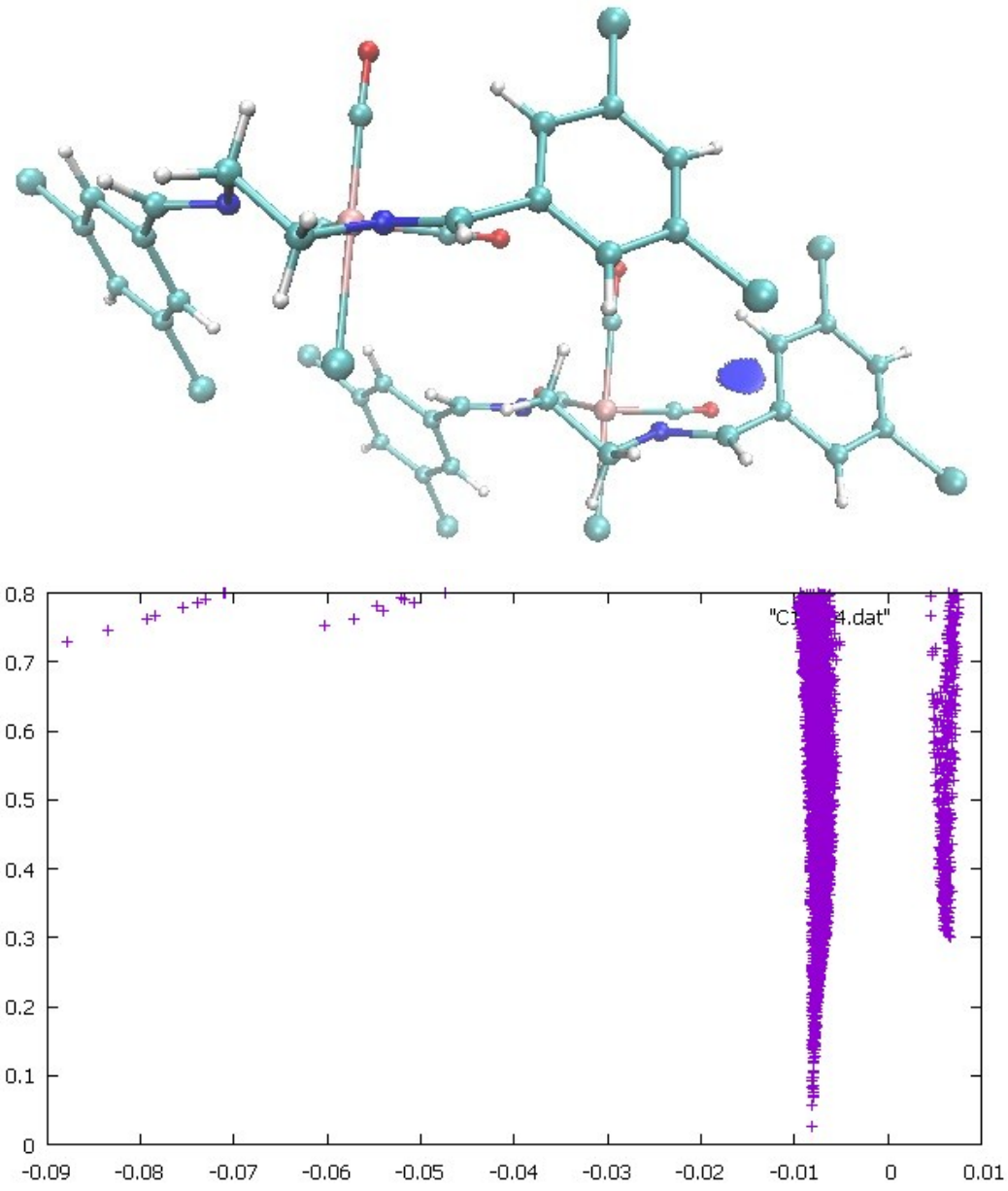

Fig. S35h. Intermolecular **Cl4···C10** isosurface (top) and its corresponding RDG vs. ρ*sign (λ_2) plot (down) in **C6 (35ClenReCl)**.

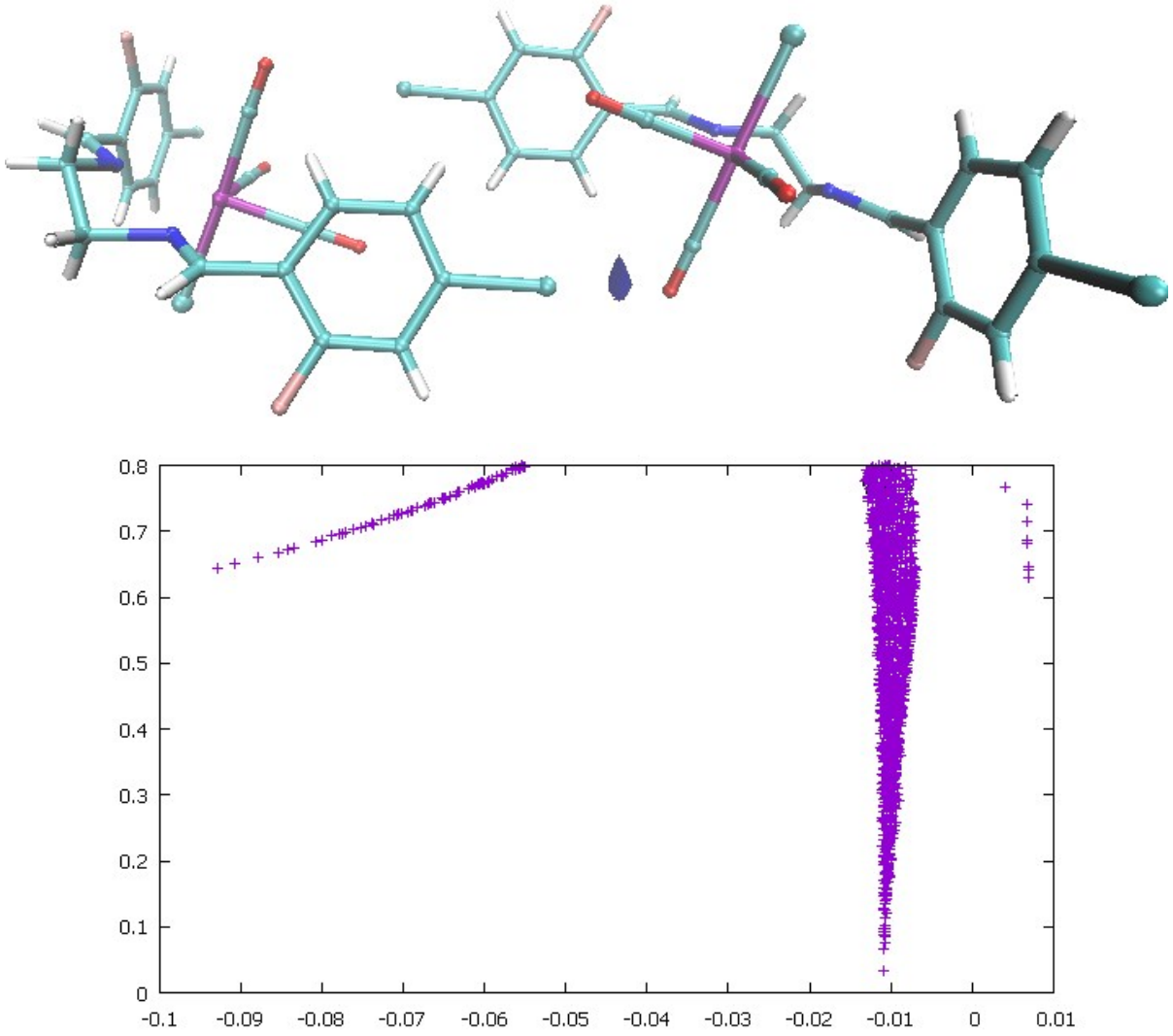

Fig. S35i. Intermolecular **Br1···O3** isosurface (top) and its corresponding RDG vs. ρ*sign (λ_2) plot (down) in **C7 (42BrFenReCl)**.

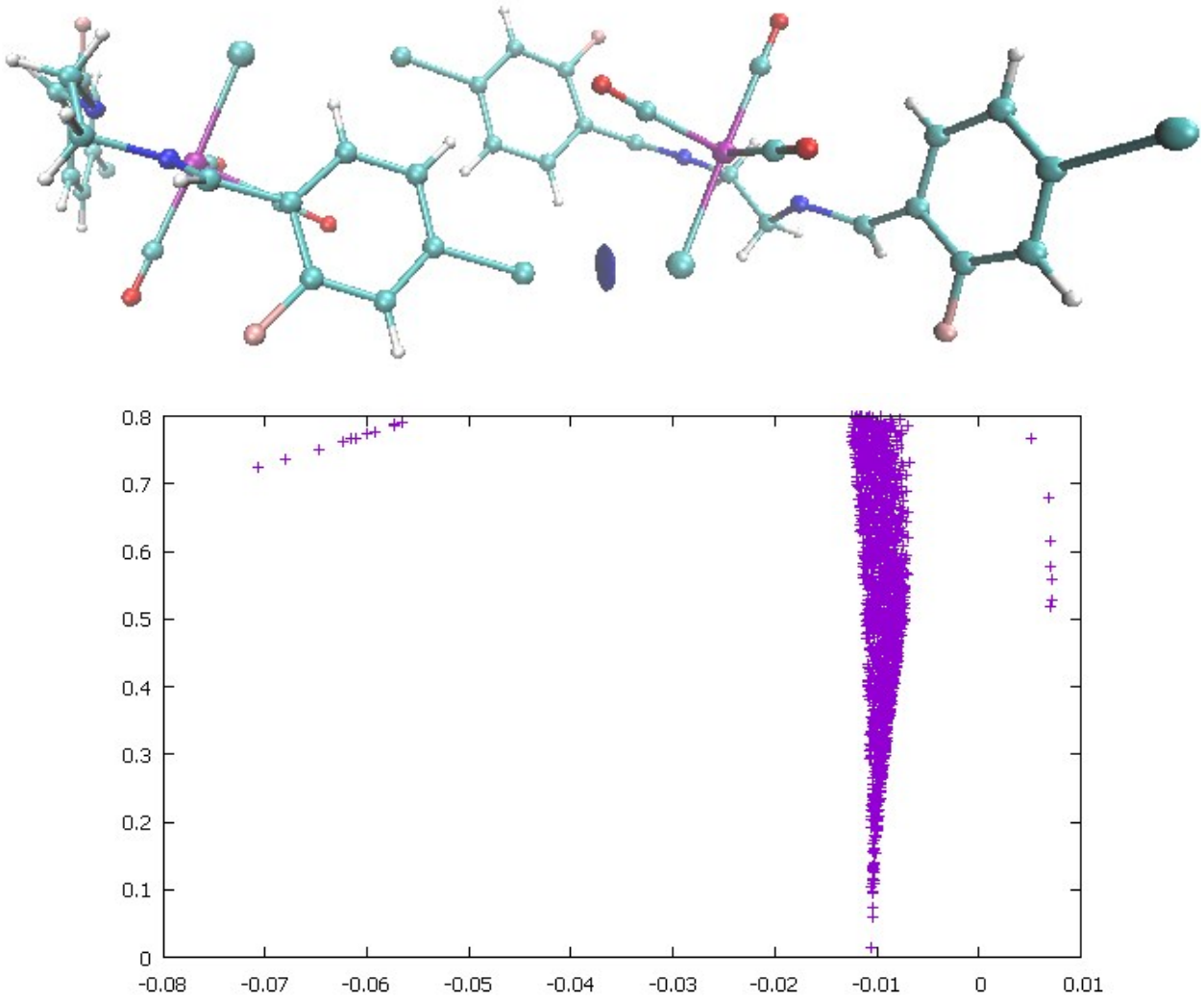

Fig. S35j. Intermolecular **Cl1···Br2** isosurface (top) and its corresponding RDG vs. ρ*sign (λ_2) plot (down) in **C7 (42BrFenReCl)**.

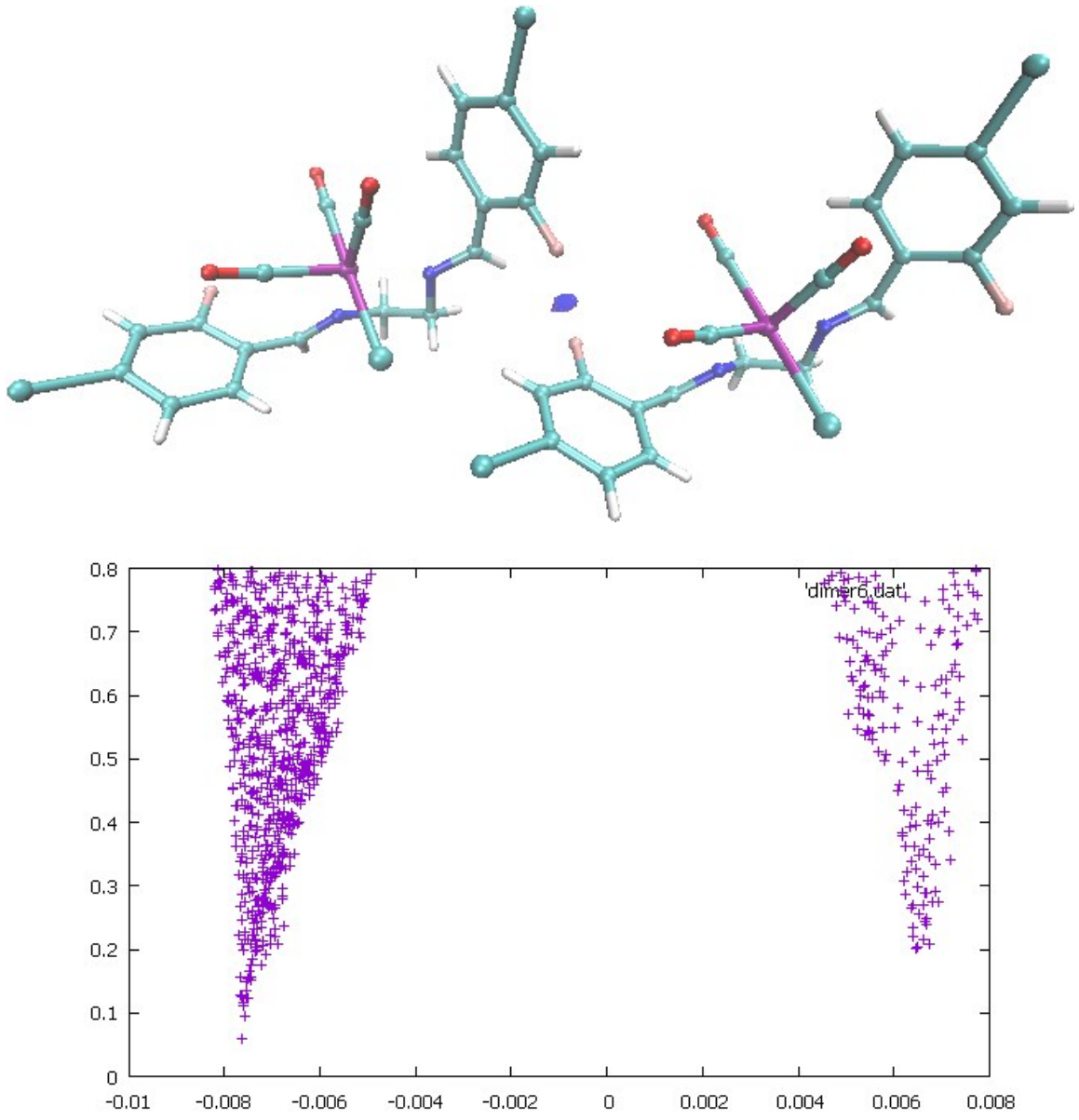

Fig. S35k. Intermolecular **F1···F2** isosurface (top) and its corresponding RDG vs. ρ*sign (λ_2) plot (down) in **C7 (42BrFenReCl)**.

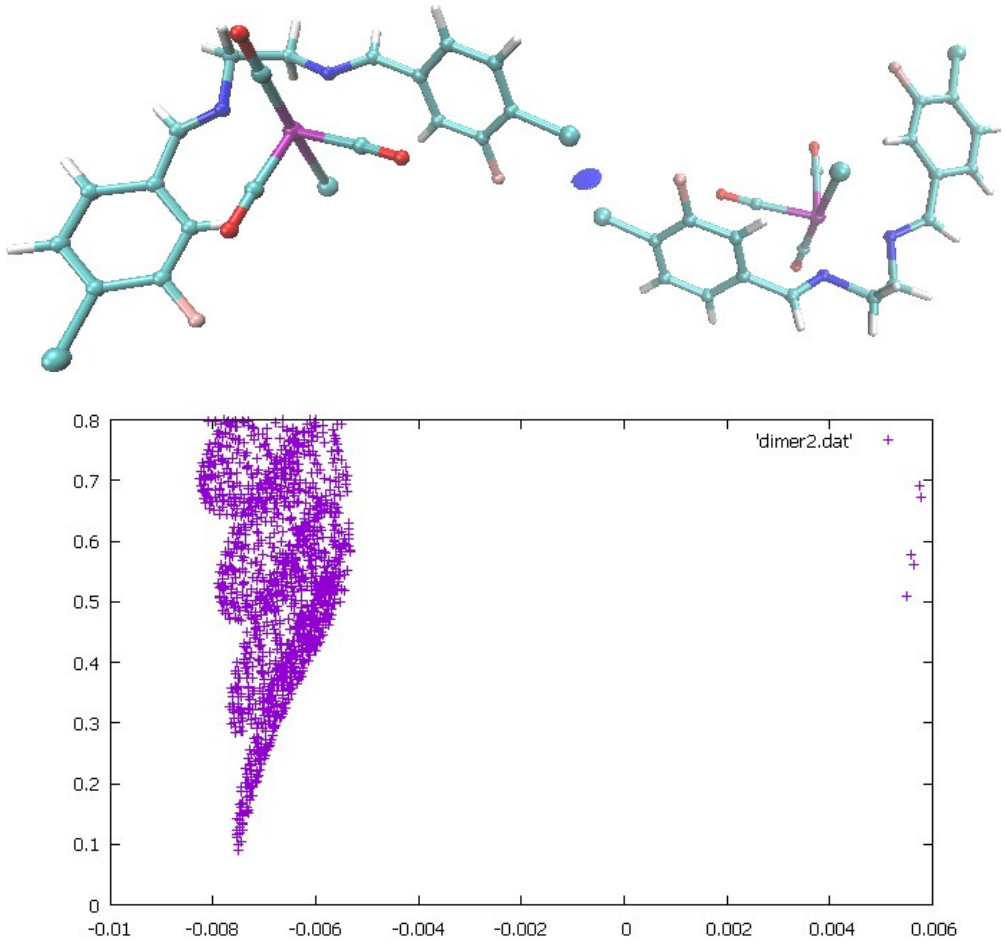

Fig. S35l. Intermolecular **Cl1···Cl1** isosurface (top) and its corresponding RDG vs. ρ*sign (λ_2) plot (down) in **C8 (43ClFenReCl)**.

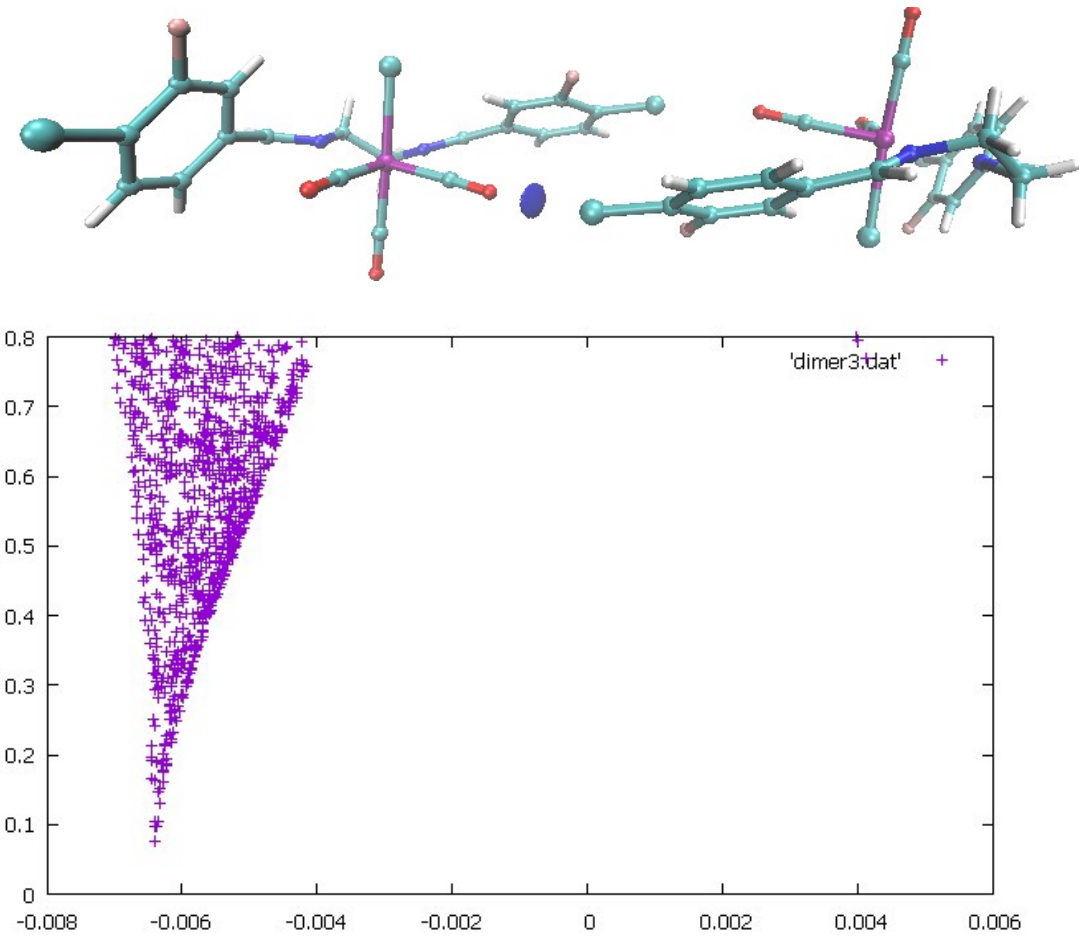

Fig. S35m. Intermolecular **Cl2···O2** isosurface (top) and its corresponding RDG vs. ρ*sign (λ_2) plot (down) in **C8 (43ClFenReCl)**.

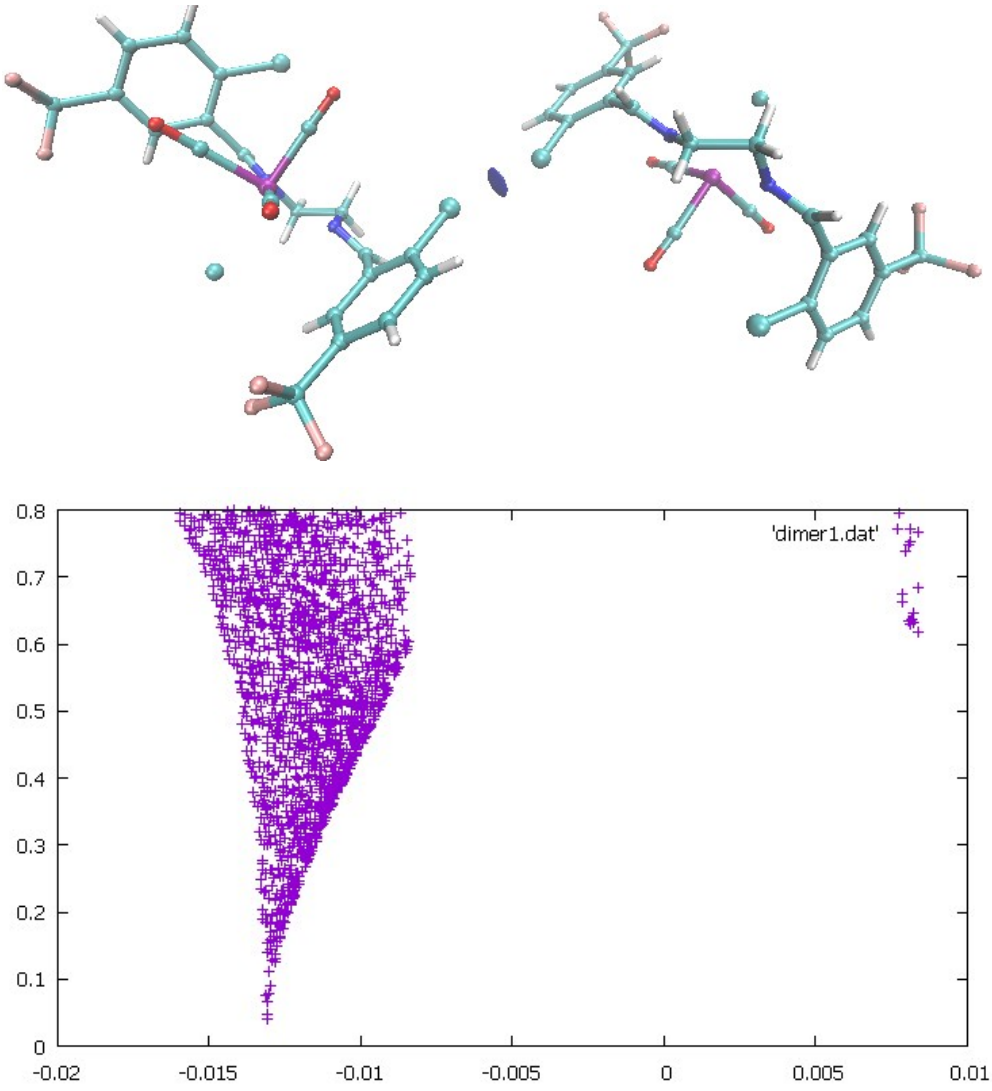

Fig. S35n. Intermolecular **Cl1···Cl1** isosurface (top) and its corresponding RDG vs. ρ*sign (λ_2) plot (down) in **C9 (ClFenReBr)**.

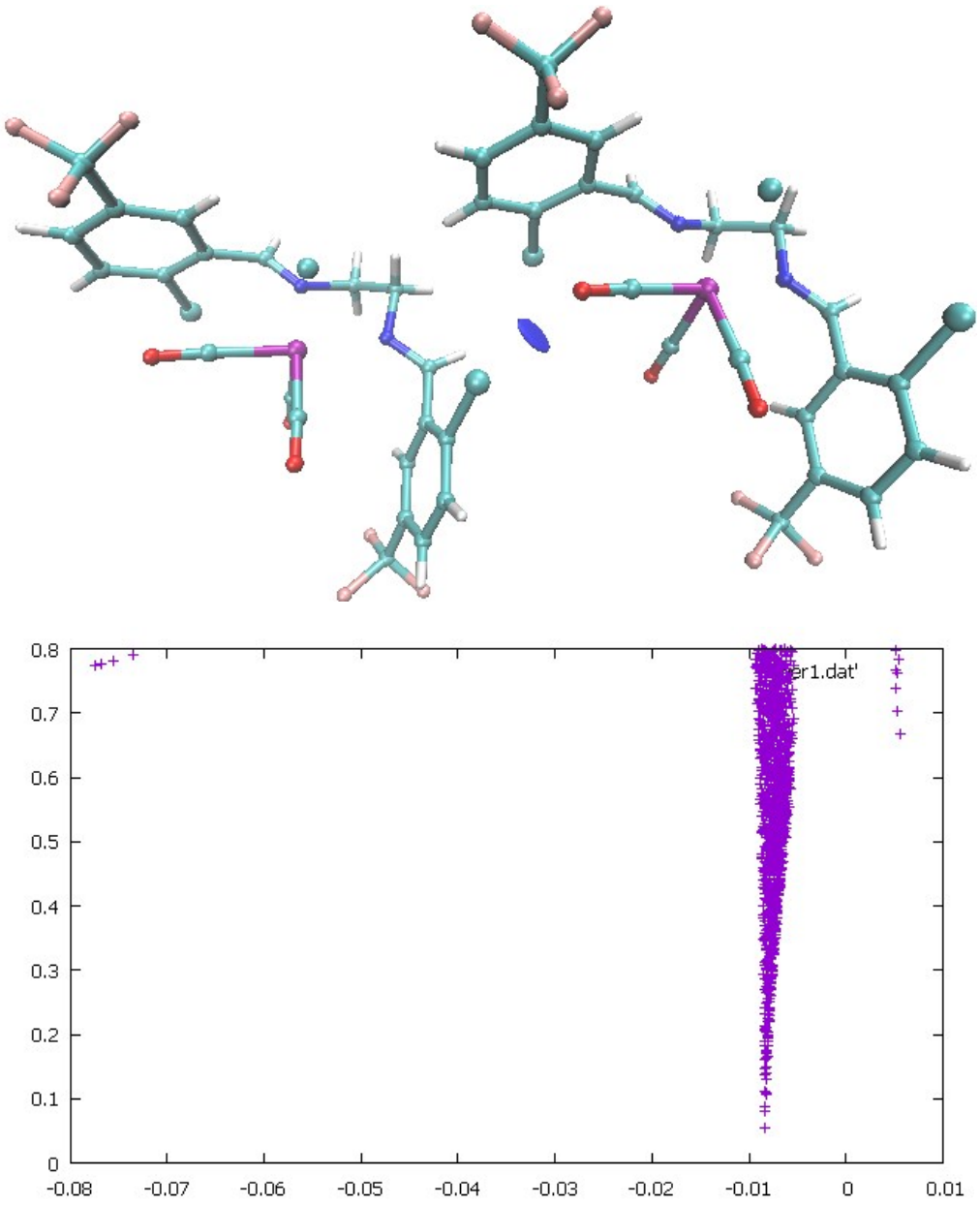

Fig. S35o. Intermolecular **Cl2···O2** isosurface (top) and its corresponding RDG vs. ρ*sign (λ_2) plot (down) in **C10 (ClFenReBr′)**.

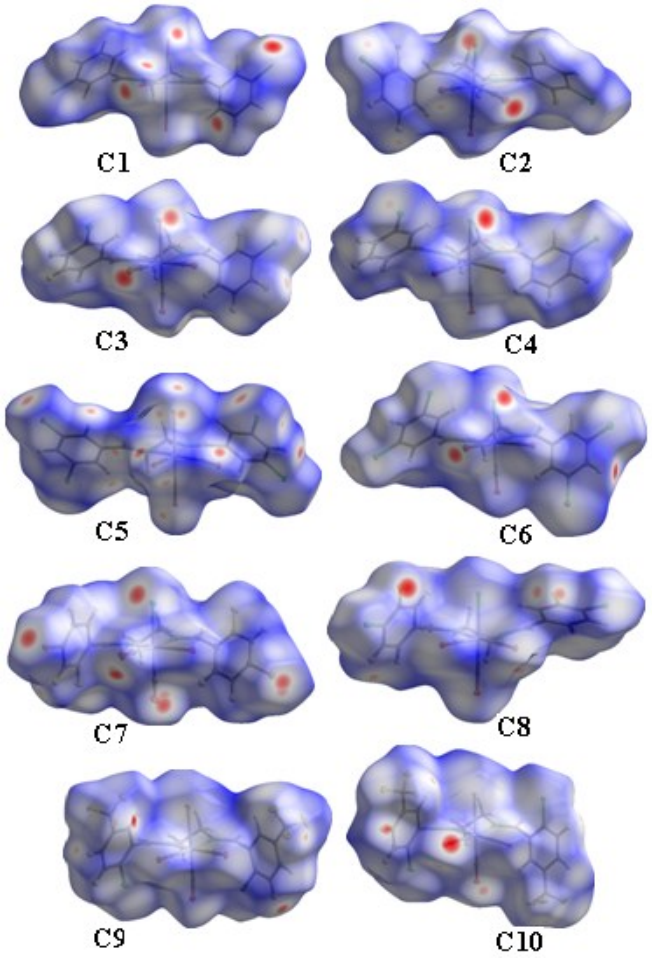

Figure S36. d_{norm} mapped on Hirshfeld surfaces in **C1–C10**.

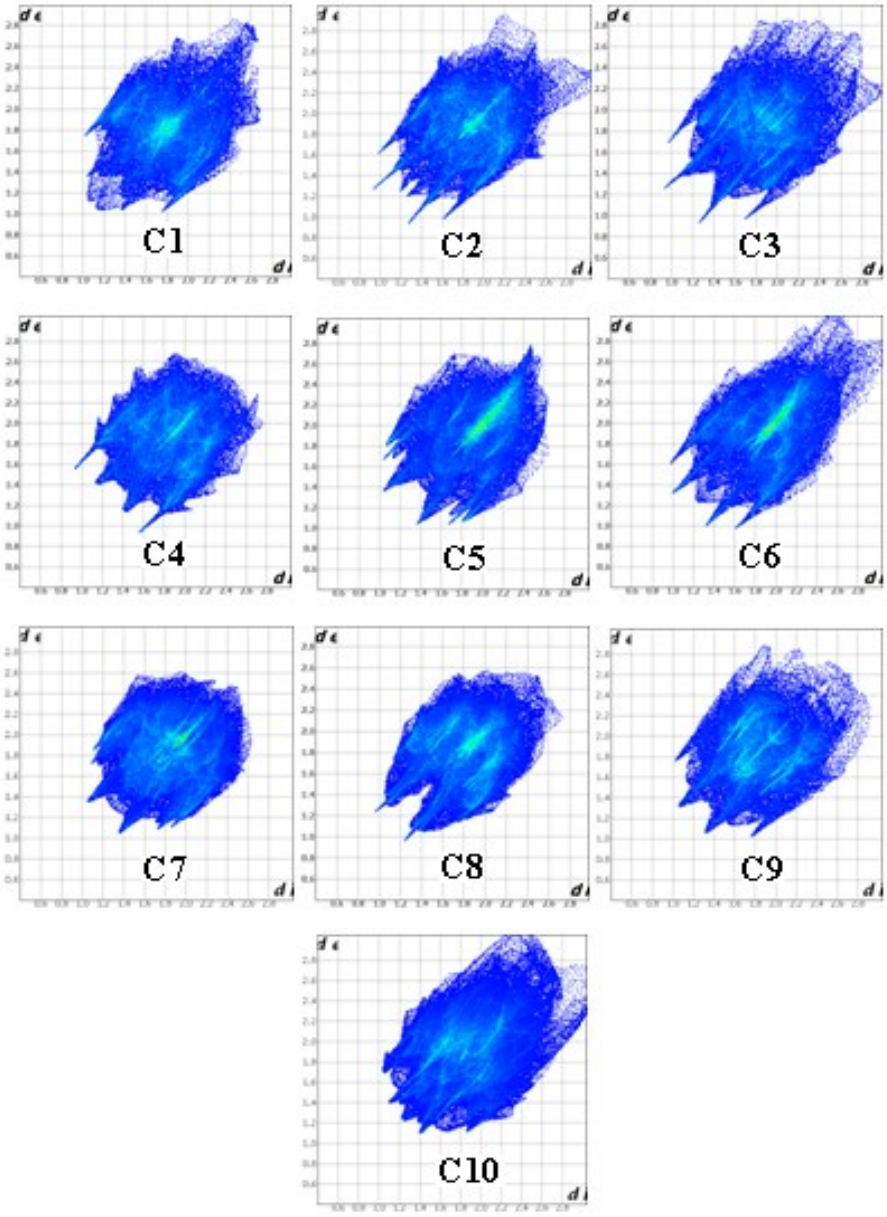

Figure S37. 2D fingerprint plots of observed contacts in **C1-C10**.