Supplementary Information:

Electron density distribution of thiourea-based anion-receptors

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1. Residual density analysis of the multipole model refinements

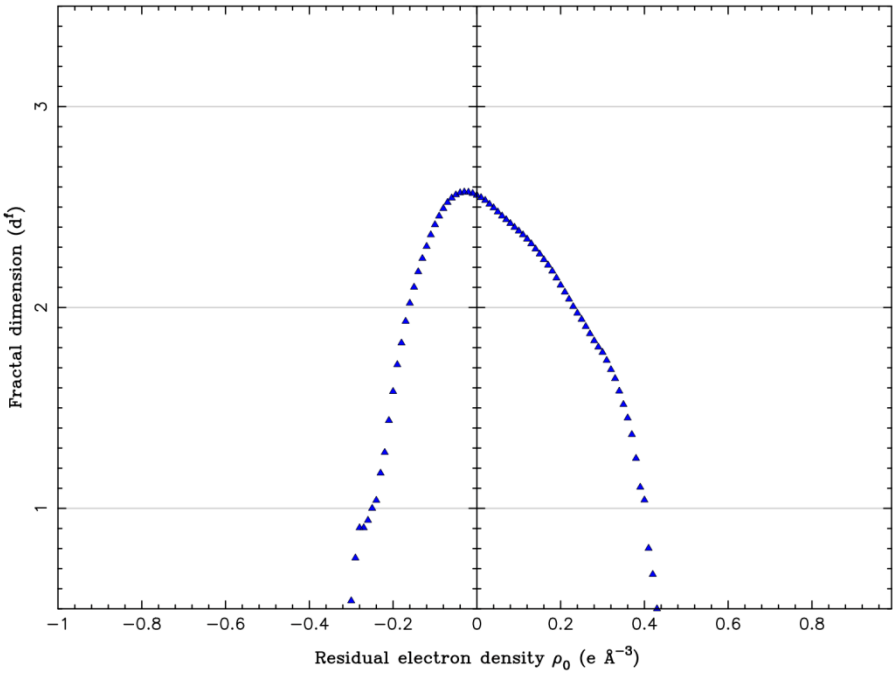


Figure S1: Fractal dimension distribution of residual density plot of **3**.

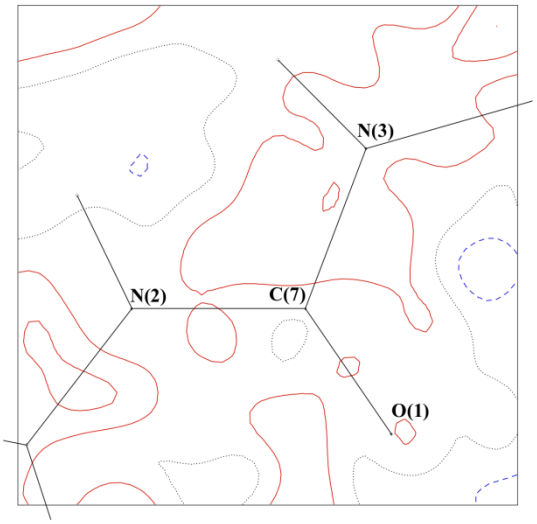


Figure S2: Residual density plot of **3** in the plane of the N(2) C(7) and N(3) atoms. Positive electron density is shown in red and negative electron density in blue. Zero-level contours are dashed. Contours are at 0.1 *e* Å^{-3}.

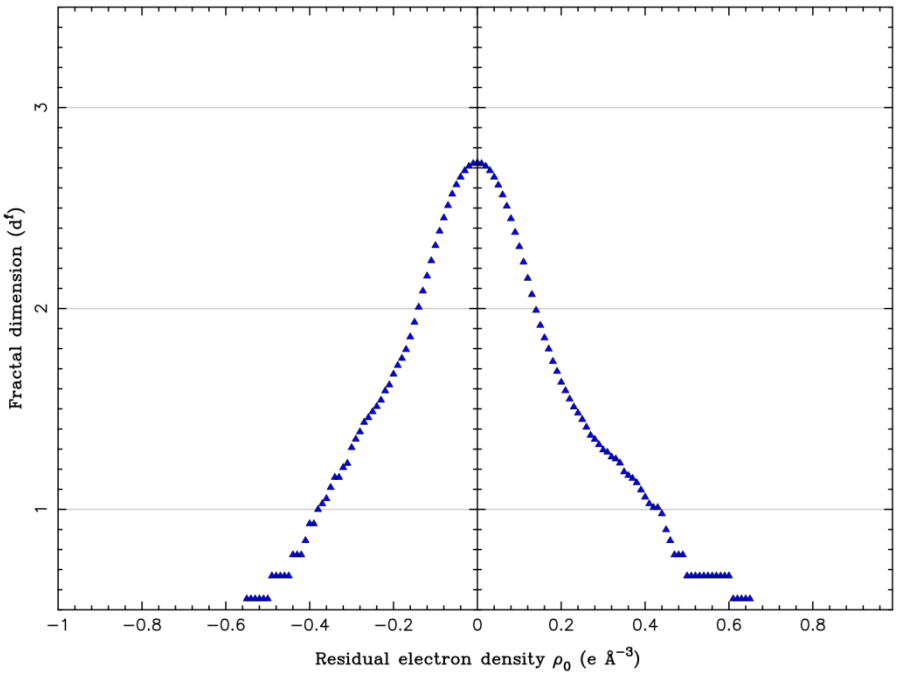


Figure S3: Fractal dimension distribution of residual density plot of **4**.

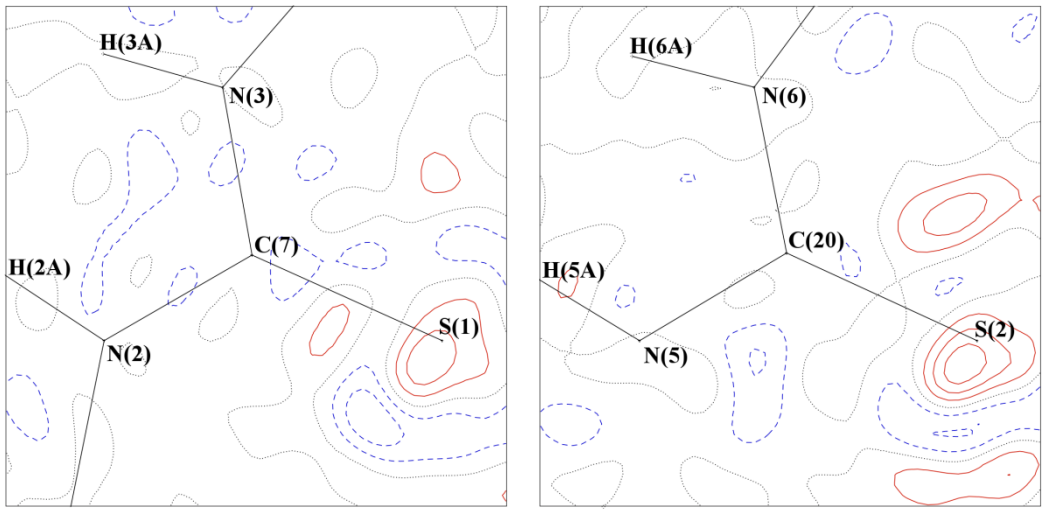


Figure S4: Residual density plots of **4** in the planes of the N(2) S(1) and N(3) atoms (*left*) and the N(5) S(2) and N(6) atoms (*right*). Positive electron density is shown in red and negative electron density in blue. Zero-level contours are dashed. Contours are at 0.1 *e* Å^{-3} and cut-off at 0.9 *e* Å^{-3}.

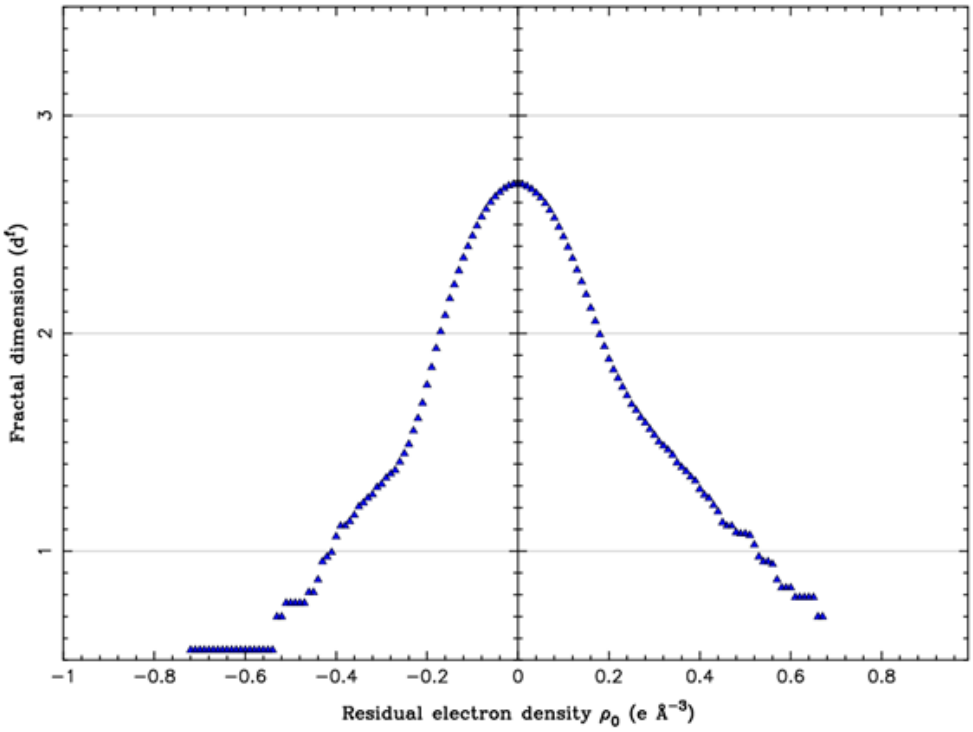


Figure S5: Fractal dimension distribution of residual density plot of **8**.

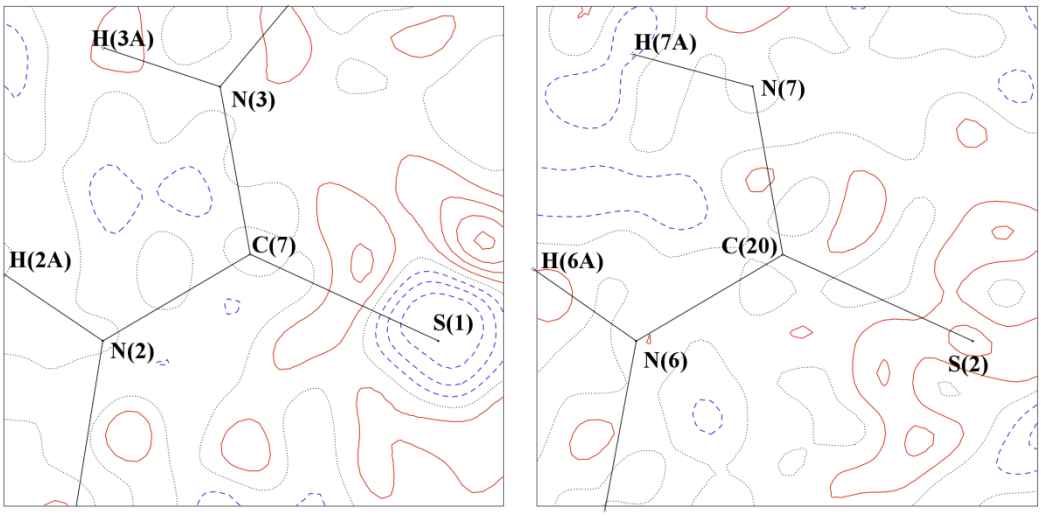


Figure S6: Residual density plots of **8** in the planes of the N(2) S(1) and N(3) atoms (*left*) and the N(6) S(2) and N(7) atoms (*right*). Positive electron density is shown in red and negative electron density in blue. Zero-level contours are dashed. Contours are at 0.1 *e* Å^{-3} with cut-off at 0.9 *e* Å^{-3}.

2. Critical point properties from theoretical studies of **3**, **4**, **7** and **8**.

Table S1: Theoretical CP properties for **3**.

Bond	$\rho(\mathbf{r})$ (e A^{-3})	$\nabla^2\rho(\mathbf{r})$ (e A^{-5})
O(1)−C(7)	2.749	-9.533
O(2)−N(1)	3.372	-25.599
O(3)−N(1)	3.317	-24.687
N(1)−C(1)	1.780	-16.068
N(2)−C(4)	2.019	-20.203
N(2)−H(2A)	2.294	-43.809
N(2)−C(7)	2.051	-21.618
N(3)−C(7)	2.144	-23.125
N(3)−C(8)	1.927	-18.764
N(3)−H(3A)	2.296	-43.324
N(5)−C(51)	1.565	-12.610
N(5)−C(53)	1.525	-11.635
N(5)−C(55)	1.577	-12.792
N(5)−C(57)	1.562	-12.572
C(1)−C(2)	2.099	-21.141
C(1)−C(6)	2.096	-21.055
C(2)−C(3)	2.109	-21.004
C(2)−H(2)	1.916	-23.798
C(3)−C(4)	2.027	-19.763
C(3)−H(3)	1.922	-23.380
C(4)−C(5)	2.048	-20.276
C(5)−C(6)	2.099	-20.907
C(5)−H(5)	1.931	-24.186
C(6)−H(6)	1.923	-24.002
C(8)−C(9)	2.075	-20.607
C(8)−C(13)	2.047	-20.061
C(9)−C(10)	2.071	-20.370
C(9)−H(9)	1.900	-23.237
C(10)−C(11)	2.056	-20.183
C(10)−H(10)	1.901	-23.341
C(11)−C(12)	2.079	-20.661
C(11)−H(11)	1.896	-23.195
C(12)−C(13)	2.068	-20.356
C(12)−H(12)	1.905	-23.443
C(13)−H(13)	1.922	-23.867
C(51)−C(52)	1.651	-13.574
C(53)−C(54)	1.658	-13.671
C(55)−C(56)	1.674	-14.018
C(57)−C(58)	1.675	-14.006
C(51)−H(alkyl)	1.913	-23.388
C(51)−H(alkyl)	1.909	-23.276
C(53)−H(alkyl)	1.940	-24.315
C(53)−H(alkyl)	1.906	-23.194
C(55)−H(alkyl)	1.911	-23.370
C(55)−H(alkyl)	1.914	-23.433
C(57)−H(alkyl)	1.924	-23.704
C(57)−H(alkyl)	1.911	-23.344
C(52)−H(alkyl)	1.987	-25.108
C(52)−H(alkyl)	1.985	-25.143
C(52)−H(alkyl)	2.003	-25.597

C(54)−H(alkyl)	1.986	-25.150
C(54)−H(alkyl)	1.989	-25.289
C(54)−H(alkyl)	1.979	-24.873
C(56)−H(alkyl)	1.985	-24.985
C(56)−H(alkyl)	1.980	-25.034
C(56)−H(alkyl)	1.988	-25.116
C(58)−H(alkyl)	1.984	-25.027
C(58)−H(alkyl)	1.984	-25.159
C(58)−H(alkyl)	1.985	-25.015
H(2A)···Cl(1)	0.166	1.549
H(3A)···Cl(1)	0.157	1.514

Table S2: Theoretical CP properties for **4**.

Bond	$\rho(\mathbf{r})$ (e A^{-3})	$\nabla^2\rho(\mathbf{r})$ (e A^{-5})
S(1)−C(7)	1.444	-1.940
S(2)−C(20)	1.424	-3.056
O(1)−N(1)	3.291	-24.237
O(2)−N(1)	3.294	-24.427
O(3)−N(4)	3.342	-25.077
O(4)−N(4)	3.313	-24.221
N(1)−C(1)	1.737	-14.398
N(2)−C(4)	1.987	-20.112
N(2)−C(7)	2.109	-21.581
N(2)−H(2A)	2.299	-44.540
N(3)−C(7)	2.146	-22.518
N(3)−C(8)	1.907	-18.123
N(3)−H(3A)	2.302	-42.892
N(7)−C(71)	1.624	-13.276
N(7)−C(72)	1.630	-13.671
N(7)−C(73)	1.659	-14.359
N(7)−C(74)	1.625	-12.531
C(1)−C(2)	2.097	-21.211
C(1)−C(6)	2.101	-21.243
C(2)−C(3)	2.107	-20.956
C(2)−H(2)	1.918	-23.877
C(3)−C(4)	2.047	-20.272
C(3)−H(3)	1.918	-23.773
C(4)−C(5)	2.058	-20.543
C(5)−C(6)	2.085	-20.557
C(5)−H(5)	1.931	-24.168
C(6)−H(6)	1.919	-23.859
C(8)−C(9)	2.077	-20.554
C(8)−C(13)	2.076	-20.655
C(9)−C(10)	2.069	-20.395
C(9)−H(9)	1.902	-23.300
C(10)−C(11)	2.090	-20.881
C(10)−H(10)	1.903	-23.408
C(11)−C(12)	2.072	-20.527
C(11)−H(11)	1.900	-23.311
C(12)−C(13)	2.070	-20.398
C(12)−H(12)	1.905	-23.449
C(13)−H(13)	1.921	-23.825
N(4)−C(14)	1.774	-15.869

N(5)−C(17)	1.980	-19.881
N(5)−C(20)	2.098	-21.608
N(6)−C(20)	2.178	-22.411
N(6)−C(21)	1.917	-18.097
N(5)−H(5A)	2.305	-43.612
N(6)−H(6A)	2.313	-43.203
C(14)−C(15)	2.096	-21.090
C(15)−C(16)	2.101	-20.872
C(16)−C(17)	2.049	-20.222
C(17)−C(18)	2.063	-20.567
C(18)−C(19)	2.089	-20.699
C(19)−C(14)	2.105	-21.254
C(15)−H(15)	1.914	-23.736
C(16)−H(16)	1.909	-23.481
C(18)−H(18)	1.930	-24.109
C(19)−H(19)	1.922	-23.983
C(21)−C(22)	2.069	-20.461
C(22)−C(23)	2.099	-20.990
C(23)−C(24)	2.083	-20.793
C(24)−C(25)	2.087	-20.815
C(25)−C(26)	2.069	-20.392
C(21)−C(26)	2.059	-20.320
C(22)−H(22)	1.904	-23.309
C(23)−H(23)	1.910	-23.548
C(24)−H(24)	1.896	-23.199
C(25)−H(25)	1.904	-23.417
C(26)−H(26)	1.926	-23.922
C(71)−H(alkyl)	2.031	-26.449
C(71)−H(alkyl)	2.027	-26.367
C(71)−H(alkyl)	2.055	-27.343
C(72)−H(alkyl)	2.032	-26.495
C(72)−H(alkyl)	2.042	-26.848
C(72)−H(alkyl)	2.031	-26.481
C(73)−H(alkyl)	2.033	-26.491
C(73)−H(alkyl)	2.032	-26.515
C(73)−H(alkyl)	2.031	-26.482
C(74)−H(alkyl)	2.027	-26.446
C(74)−H(alkyl)	2.022	-26.085
C(74)−H(alkyl)	2.049	-27.007
H(2A)···Cl(1)	0.182	1.663
H(3A)···Cl(1)	0.134	1.385
H(5A)···Cl(1)	0.180	1.718
H(6A)···Cl(1)	0.150	1.518

Table S3: Theoretical CP properties for **7**.

Bond	$\rho(\mathbf{r})$ (e A^{-3})	$\nabla^2\rho(\mathbf{r})$ (e A^{-5})
O(1)−C(7)	2.740	-9.832
O(2)−N(1)	3.266	-23.038
O(3)−N(1)	3.320	-24.484
O(4)−N(4)	3.259	-23.038
O(5)−N(4)	3.259	-22.942
N(1)−C(1)	1.795	-16.291
N(2)−C(4)	2.018	-20.339

N(2)−C(7)	2.072	-21.978
N(2)−H(2A)	2.294	-43.763
N(3)−C(7)	2.105	-22.460
N(3)−C(8)	2.004	-19.665
N(3)−H(3A)	2.294	-44.052
N(4)−C(11)	2.004	-19.665
N(5)−C(14)	1.620	-13.592
N(5)−C(15)	1.640	-14.170
N(5)−C(16)	1.593	-12.531
N(5)−C(17)	1.593	-12.917
C(1)−C(2)	2.072	-20.436
C(1)−C(6)	2.078	-20.725
C(2)−C(3)	2.112	-21.110
C(2)−H(2)	1.910	-20.821
C(3)−C(4)	2.031	-19.857
C(3)−H(3)	1.896	-23.135
C(4)−C(5)	2.031	-19.857
C(5)−C(6)	2.092	-20.821
C(5)−H(5)	1.930	-24.195
C(6)−H(6)	1.923	-24.099
C(8)−C(9)	2.031	-19.761
C(8)−C(13)	2.024	-19.761
C(9)−C(10)	2.112	-21.207
C(9)−H(9)	1.910	-23.520
C(10)−C(11)	2.072	-20.532
C(10)−H(10)	1.917	-23.906
C(11)−C(12)	2.078	-20.725
C(12)−C(13)	2.085	-20.629
C(12)−H(12)	1.923	-24.002
C(13)−H(13)	1.930	-24.099
C(14)−H(14A)	2.031	-26.509
C(14)−H(14B)	2.024	-26.316
C(14)−H(14C)	2.045	-26.991
C(15)−H(15A)	2.031	-26.412
C(15)−H(15B)	2.031	-26.412
C(15)−H(15C)	2.031	-26.412
C(16)−H(16A)	2.564	-40.775
C(16)−H(16B)	2.578	-41.064
C(16)−H(16C)	2.126	-29.015
C(17)−H(17A)	2.024	-26.219
C(17)-H(17B)	2.058	-27.473
C(17)−H(17C)	2.024	-26.219
H(2A)···CL(1)	0.165	1.562
H(3A)···CL(1)	0.182	1.735

Table S4: Theoretical CP properties of **8**.

Bond	$\rho(\mathbf{r})$ (e A^{-3})	$\nabla^2\rho(\mathbf{r})$ (e A^{-5})
N(1)−O(1)	3.320	-24.224
N(1)−O(2)	3.341	-24.740
N(1)−C(1)	1.779	-16.494
C(1)−C(2)	2.098	-21.073
C(2)−C(3)	2.096	-20.841
C(3)−C(4)	2.063	-20.404

C(4)−C(5)	2.076	-20.753
C(5)−C(6)	2.099	-20.940
C(6)−C(1)	2.113	-21.424
C(2)−H(2)	1.919	-23.934
C(3)−H(3)	1.902	-23.318
C(6)−H(6)	1.924	-24.068
C(5)−H(5)	1.926	-23.980
C(4)−N(2)	1.956	-19.064
N(2)−H(2A)	2.300	-42.762
N(2)−C(7)	2.122	-22.246
C(7)−S(1)	1.437	-2.128
C(7)−N(3)	2.142	-22.132
N(3)−H(3A)	2.302	-43.289
N(3)−C(8)	1.983	-19.602
C(8)−C(9)	2.058	-20.341
C(9)−C(10)	2.105	-20.981
C(10)−C(11)	2.092	-20.946
C(11)−C(12)	2.118	-21.520
C(12)−C(13)	2.084	-20.635
C(13)−C(8)	2.060	-20.439
C(9)−H(9)	1.898	-23.087
C(10)−H(10)	1.913	-23.719
C(12)−H(12)	1.925	-24.104
C(13)−H(13)	1.931	-24.151
C(11)−N(4)	1.789	-16.566
N(4)−O(3)	3.328	-24.348
N(4)−O(4)	3.312	-24.141
N(5)−O(5)	3.346	-24.887
N(5)−O(6)	3.350	-24.917
N(5)−C(14)	1.780	-16.459
C(14)−C(15)	2.104	-21.220
C(15)−C(16)	2.106	-21.070
C(16)−C(17)	2.068	-20.501
C(17)−C(18)	2.049	-20.180
C(18)−C(19)	20.89	-20.736
C(19)−C(14)	2.114	-21.440
C(15)−H(15)	1.921	-23.966
C(16)−H(16)	1.904	-23.349
C(18)−H(18)	1.928	-24.026
C(19)−H(19)	1.922	-24.003
C(17)−N(6)	1.972	-19.318
N(6)−C(20)	2.133	-22.064
N(6)−H(6A)	2.307	-42.780
N(7)−C(20)	2.105	-21.799
C(20)−S(2)	1.454	-0.956
N(7)−C(21)	1.970	-19.475
N(7)−H(7A)	2.307	-42.308
C(21)−C(22)	2.065	-20.444
C(22)−C(23)	2.093	-20.753
C(23)−C(24)	2.106	-21.228
C(24)−C(25)	2.097	-21.065
C(25)−C(26)	2.092	-20.793
C(21)−C(26)	2.051	-20.274
C(22)−H(22)	1.904	-23.281
C(23)−H(23)	1.917	-23.858
C(25)−H(25)	1.922	-23.978
C(26)−H(26)	1.929	-24.070
C(24)−N(8)	1.780	-16.509

N(8)−O(7)	3.344	-24.772
N(8)−O(8)	3.363	-25.291
N(9)−C(93)	1.575	-12.750
C(93)−C(94)	1.669	-13.878
C(93)−H(alkyl)	1.914	-23.416
C(93)−H(alkyl)	1.912	-23.393
C(94)−H(alkyl)	1.989	-25.205
C(94)−H(alkyl)	1.985	-25.093
C(94)−H(alkyl)	1.995	-25.174
N(9)−C(95)	1.566	-12.523
C(95)−C(96)	1.640	-13.368
C(95)−H(alkyl)	1.912	-23.361
C(95)−H(alkyl)	1.927	-23.795
C(96)−H(alkyl)	1.986	-24.967
C(96)−H(alkyl)	1.989	-25.366
C(96)−H(alkyl)	1.986	-25.070
N(9)−C(97)	1.615	-12.715
C(97)−C(98)	1.685	-14.170
C(97)−H(alkyl)	1.914	-23.441
C(97)−H(alkyl)	1.916	-23.467
C(98)−H(alkyl)	1.989	-25.206
C(98)−H(alkyl)	1.980	-24.973
C(98)−H(alkyl)	1.981	-24.846
N(9)−C(91)	1.566	-12.644
C(91)−C(92)	1.665	-13.860
C(91)−H(alkyl)	1.908	-23.237
C(91)−H(alkyl)	1.920	-23.540
C(92)−H(alkyl)	1.977	-24.637
C(92)−H(alkyl)	1.980	-25.079
C(92)−H(alkyl)	1.989	-25.097
H(2A)···Cl(1)	0.158	1.588
H(3A)···Cl(1)	0.194	1.804
H(5A)···Cl(1)	0.140	1.445
H(6A)···Cl(1)	0.124	1.279

3. Electron density distribution plots of **3**, **4**, **7** and **8**

Static deformation charge density distribution maps show the whole receptor molecule (*left*) and the anion binding region (*right*) of the structure. Positive electron density is shown in red, negative electron density in blue. Zero contours are dashed. Contours are at 0.1 *e* Å^{-3}.

Negative Laplacian ($-\nabla^2\rho(\mathbf{r})$) charge density distribution maps are also drawn in the plane of urea group of the receptor molecule. Positive electron density is shown in red, negative electron density in blue. Contours are in a logarithmic scale, *e* Å^{-5}.

Bond path plots display the nuclear positions of the atoms in each structure, the bond paths (paths of maximum electron density linking these nuclear positions), and the position of the bond critical points (saddle points along the bond paths where electron density is at a minimum along the nuclear axis and at a maximum in the direction perpendicular to the molecular axis.).

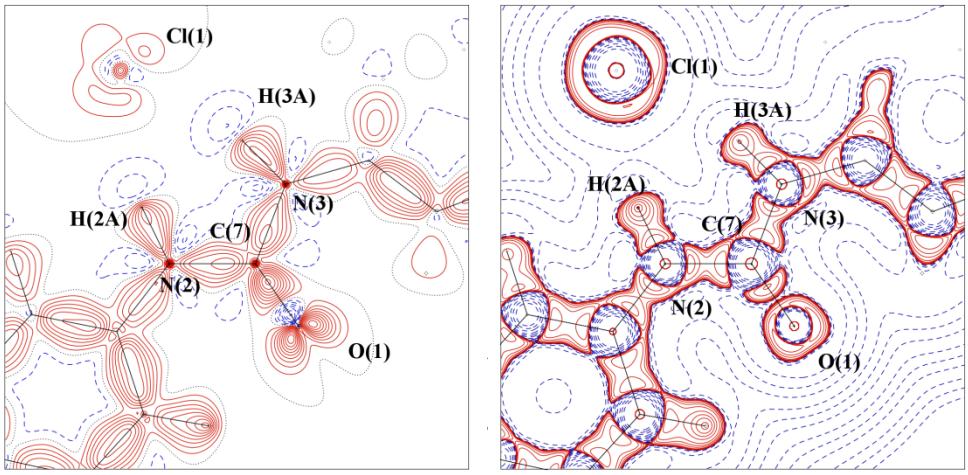


Figure S7: Electron density distribution across the urea portion of **3**. Static deformation charge density map (*left*) and $-\nabla^2\rho(\mathbf{r})$ charge density plot (*right*).

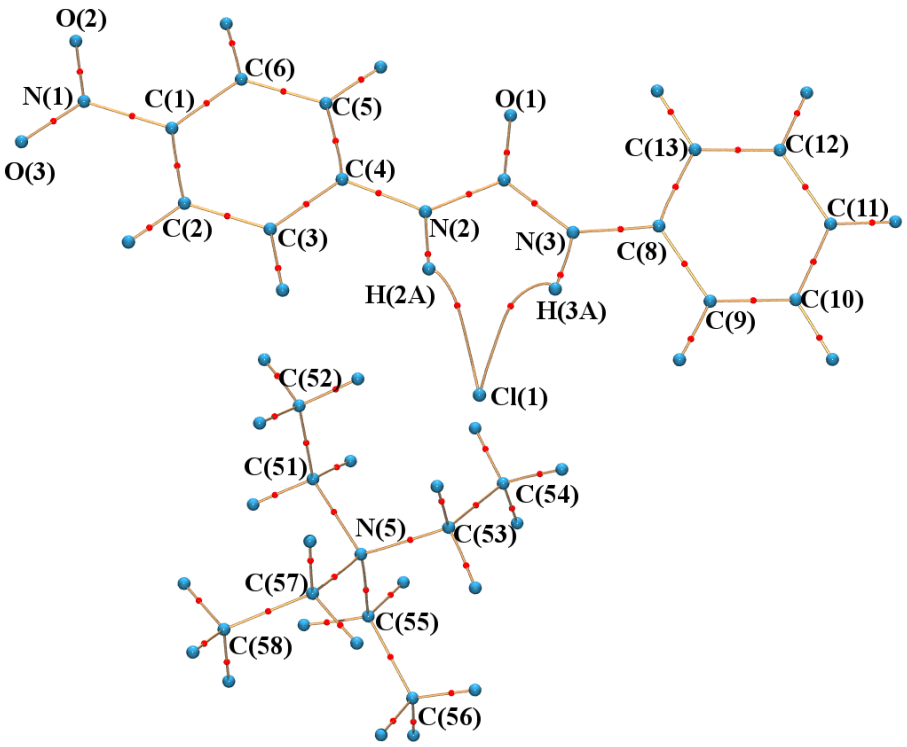


Figure S8: Bond path plot of **3** displaying the nuclear positions of the atoms in the structure, the bond paths and the position of the bond critical points.

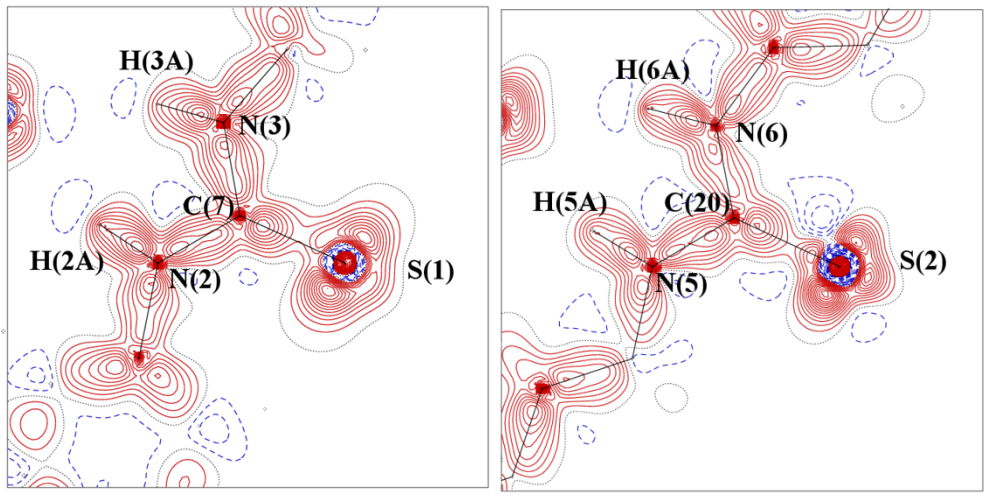


Figure S9: Static deformation charge density distribution maps of receptor molecules in **4** in the plane of the N(2) C(7) S(1) atoms (*left*) and the plane of N(5) C(20) S(2) atoms (*right*).

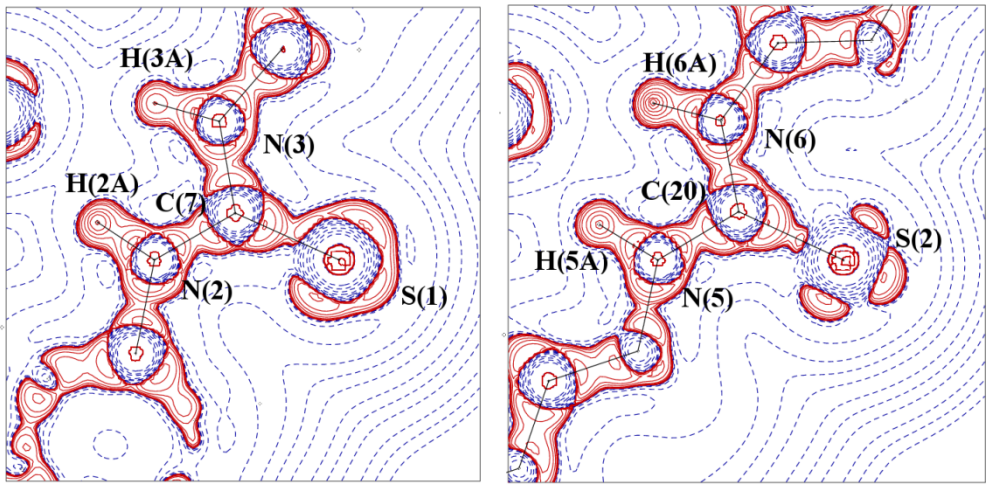


Figure S10: $-\nabla^2\rho(\mathbf{r})$ charge density distribution maps of receptor molecules in **4** in the plane of the N(2) S(1) N(3) atoms (*left*) and the N(5) S(2) N(6) atoms (*right*).

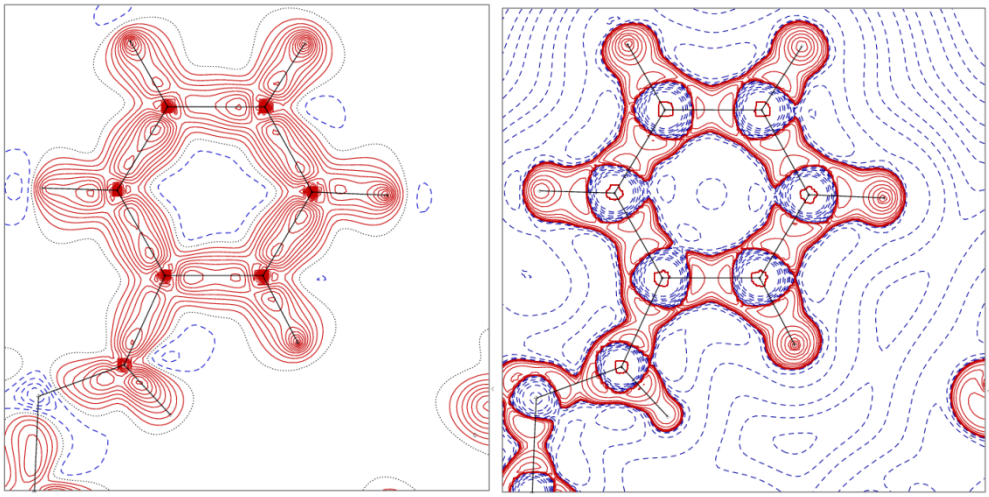


Figure S11: Electron density distribution across a representative phenyl ring (drawn in the plane of the C(21) C(22) and C(23) atoms) in **4**. Static deformation charge density map (*left*) and $-\nabla^2\rho(\mathbf{r})$ charge density plot (*right*).

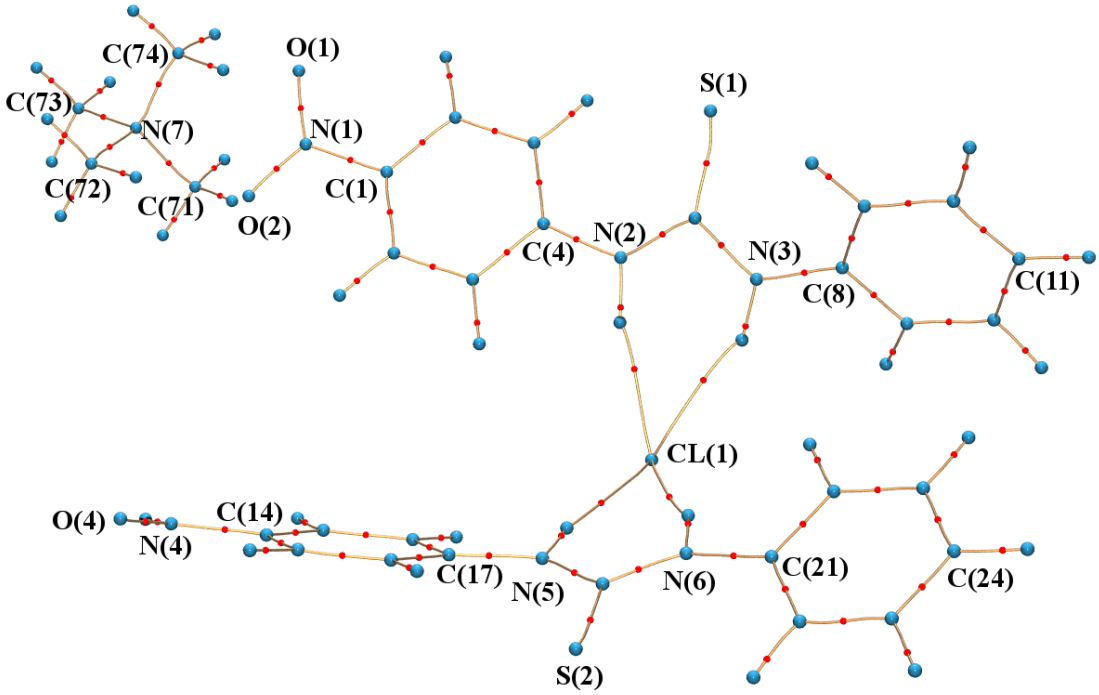


Figure S11: Bond path plot of **4** displaying the nuclear positions of the atoms in the structure, the bond paths and the position of the bond critical points.

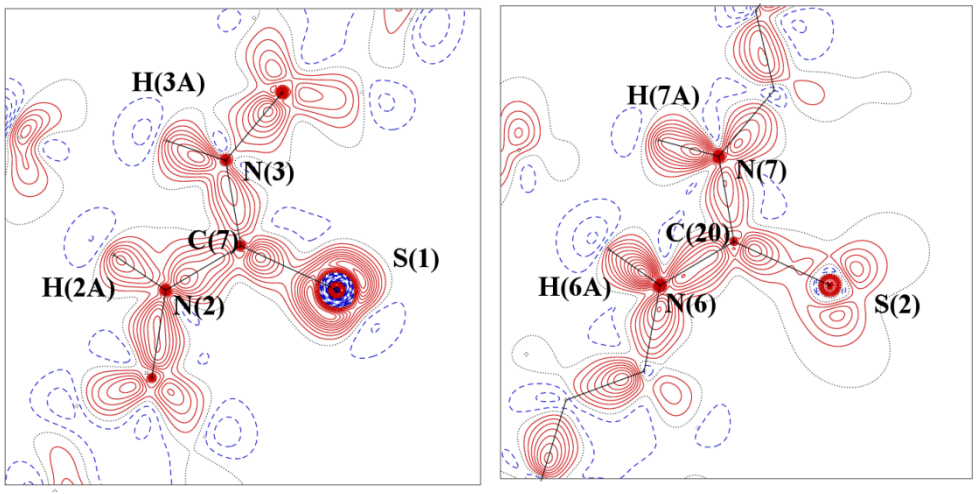


Figure S12: Static deformation charge density distribution maps of receptor molecules in **8** in the plane of N(2) S(1) N(3) atoms (*left*) and the N(6) S(2) N(7) atoms (*right*).

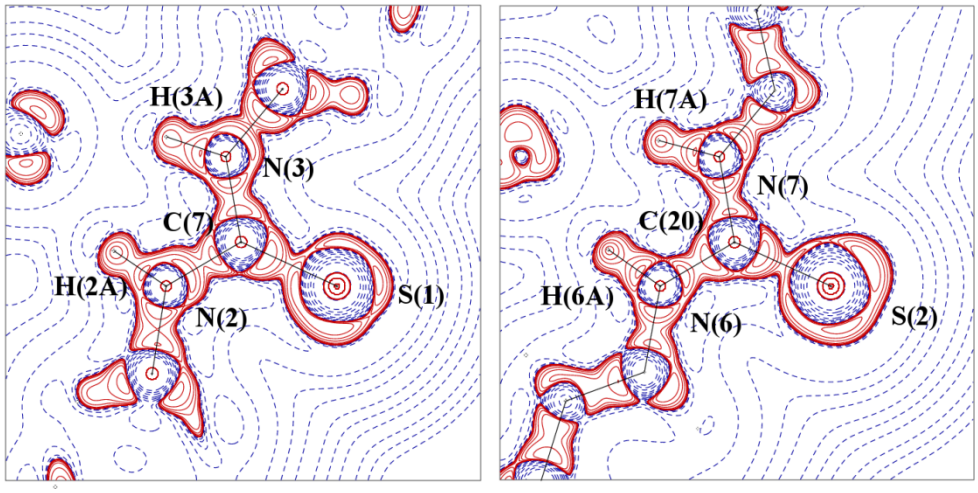


Figure S13: $-\nabla^2\rho(\mathbf{r})$ charge density distribution maps of receptor molecules in **8** in the plane of N(2) S(1) N(3) atoms (*left*) and the N(6) S(2) N(7) atoms (*right*).

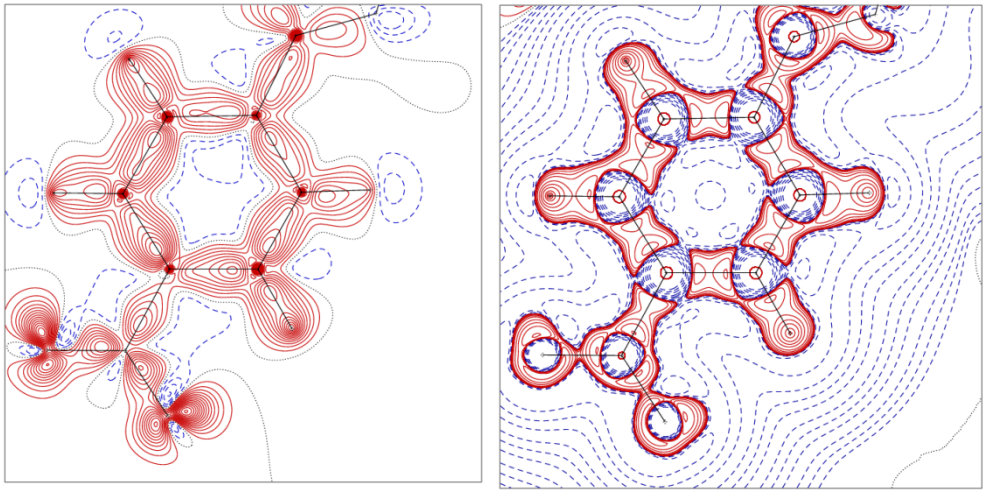


Figure S14: Electron density distribution across a representative phenyl ring (drawn in the plane of the C(24) C(25) and C(26) atoms) in **8**. Static deformation charge density map (*left*) and $-\nabla^2\rho(\mathbf{r})$ charge density plot (*right*).

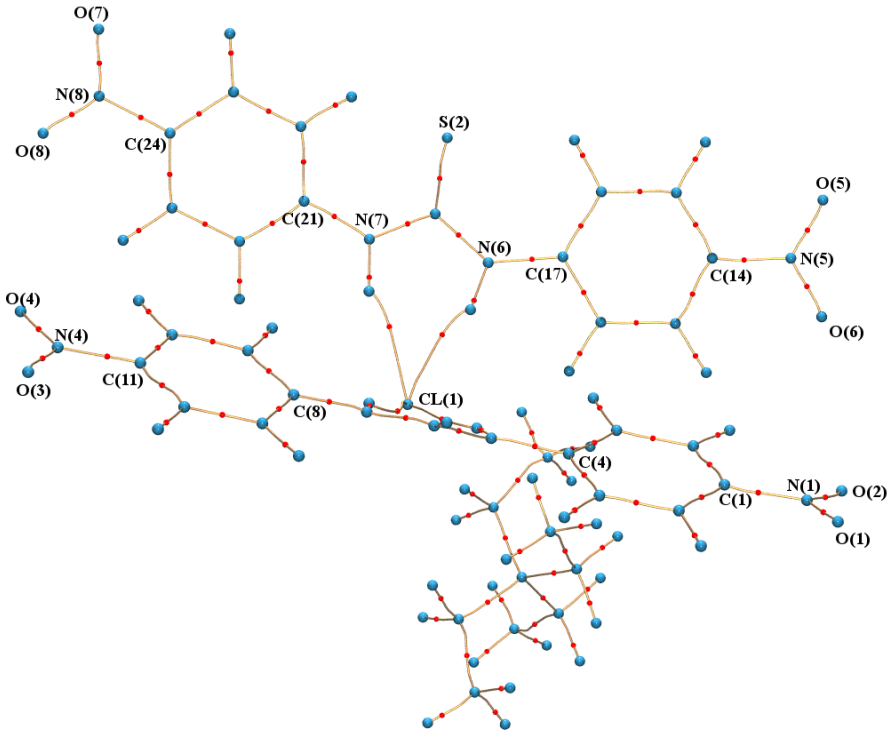


Figure S15: Bond path plot of **8** displaying the nuclear positions of the atoms in the structure, the bond paths and the position of the bond critical points.

4. NMR titrations

NMR titration Methodology:

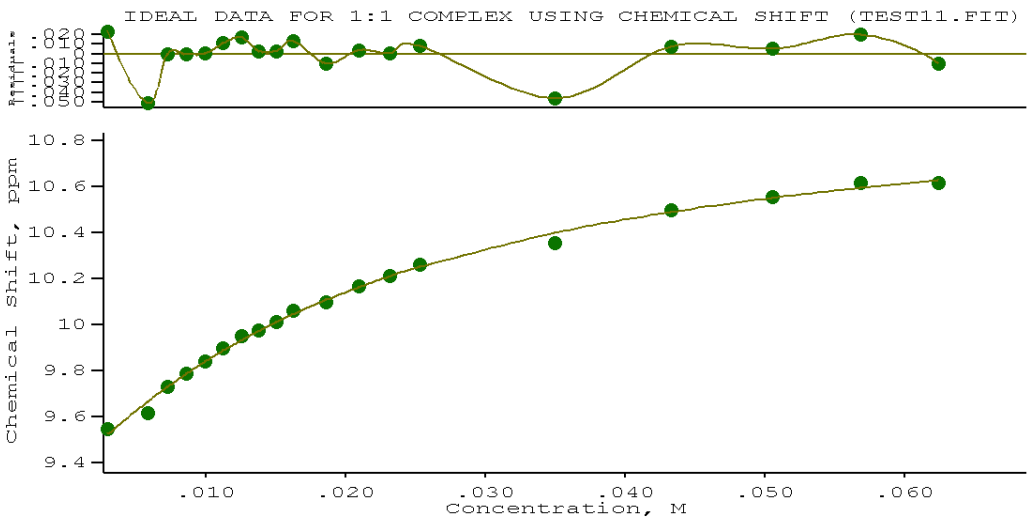
1.5 mL of a 0.01 M solution of the appropriate receptor in a 0.5% H_2O d_6-DMSO solvent mixture was prepared. Of this solution, 0.5 mL was added to a NMR tube, which was then sealed with an air tight suber seal. The remaining 1 mL of the receptor solution was used to make a 0.15 M solution of the desired guest. The anion/receptor solution was titrated into the NMR tube in small aliquots and a ^{1}H NMR spectrum was recorded after each addition. This resulted in an increasing concentration of guest throughout the experiment while the receptor concentration was kept constant. Chemical shifts for each peak were calibrated to the solvent peak. The data was fitted to a relevant binding model using WinEQNMR2[1] in order to generate values for the binding constant(s).

Job Plot Methodology:

Two solutions were prepared; the first was a 3 mL 0.01 M solution of the receptor and the second was a 3 mL 0.01 M of the guest. 0.5 mL of the receptor was added to an NMR tube. The volume of receptor solution was then decreased by 0.05 mL and the amount of guest solution was increased by 0.05 mL for each successive NMR tube until a 9:1 anion: receptor ratio was reached. A ^{1}H NMR spectrum was recorded for each of the ten samples, and calibrated to the solvent peak. This data was used to produce a Job Plot in accordance with the methods described by Job.[2] The molar fraction of the receptor (χ_r) was plotted against the values given by the formula given in Equation 7.1.

$$y = \frac{\delta_{obs} - \delta_{int}}{\delta_{fin} - \delta_{int}} \chi_r \qquad \text{(Eq. 7.1)}$$

where δ_{obs} is the observed chemical shift, δ_{int} is the initial chemical shift and δ_{fin} is the final chemical shift.



$K_1 = 58\ M^{-1}$, Error 9%

Figure S16: Fit Plot for titration of receptor **1** with TBA chloride

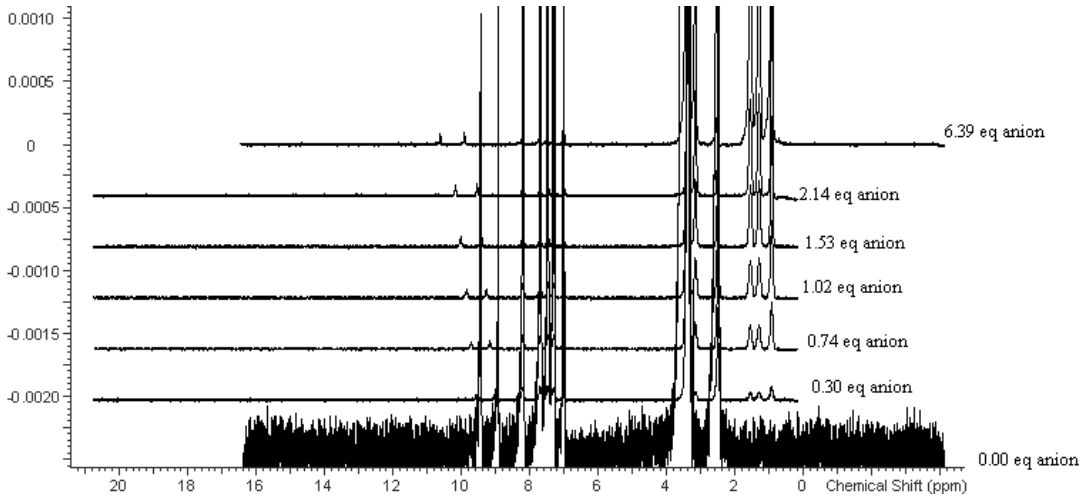


Figure S17: Stack plot for titration of receptor **1** with TBA chloride

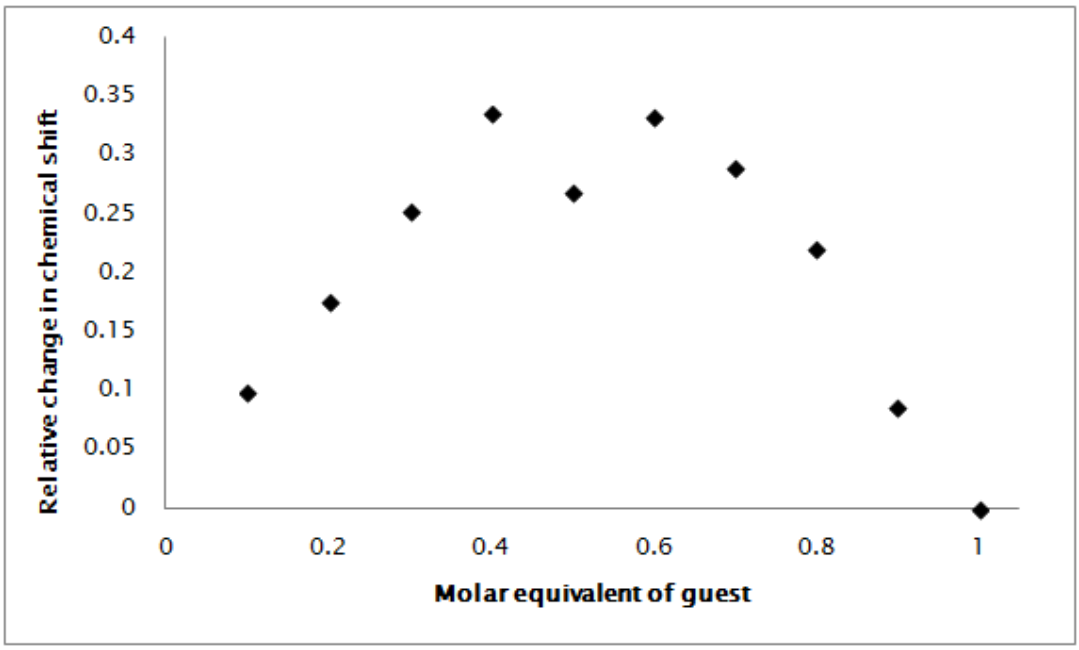
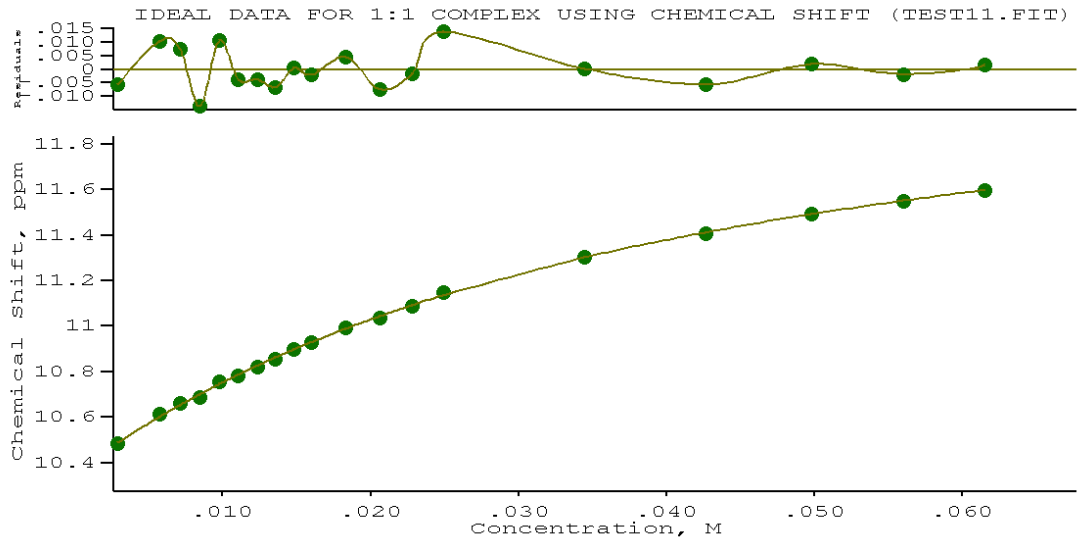


Figure S18: Job Plot of receptor **1** with TBA chloride



$K_1 = 32\ M^{-1}$, Error 4%

Figure S19: Fit Plot for titration of receptor **2** with TBA chloride

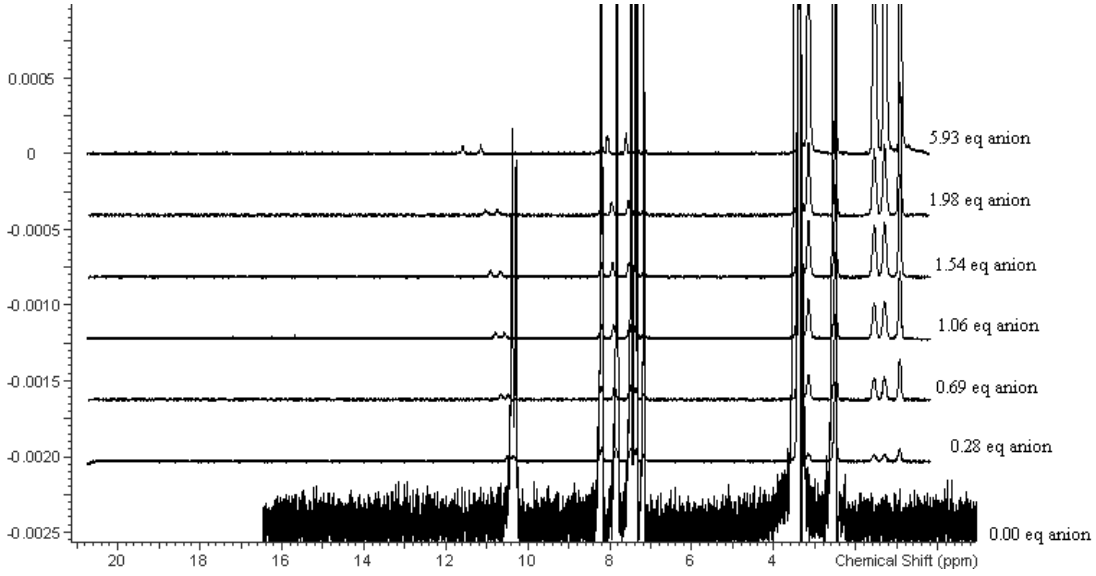


Figure S20: Stack plot for titration of receptor **2** with TBA chloride

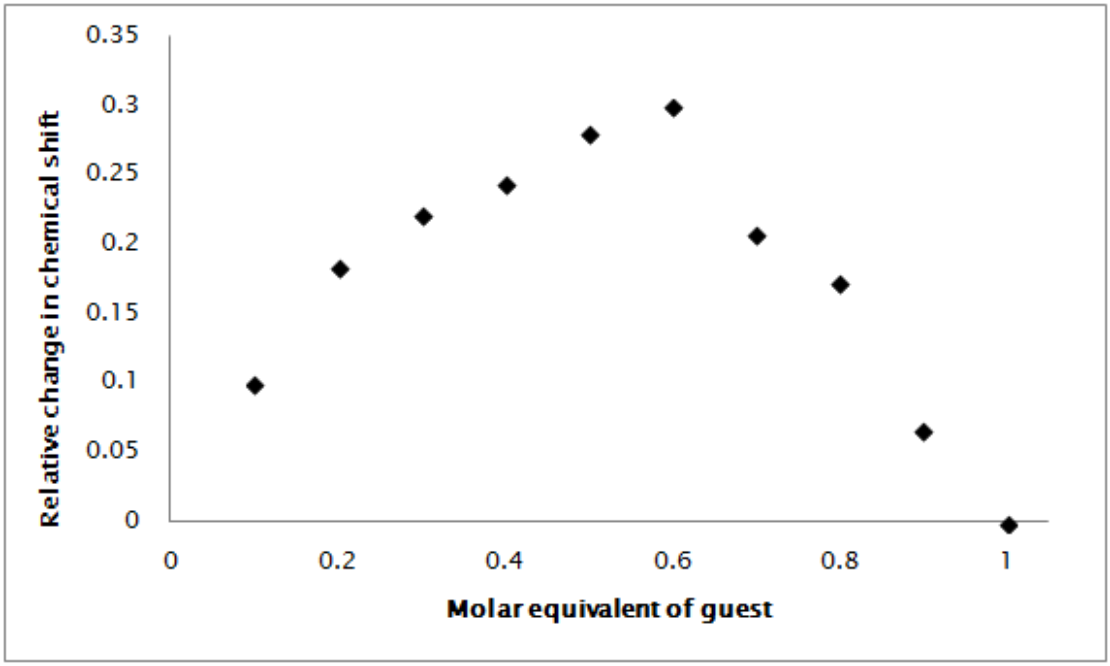
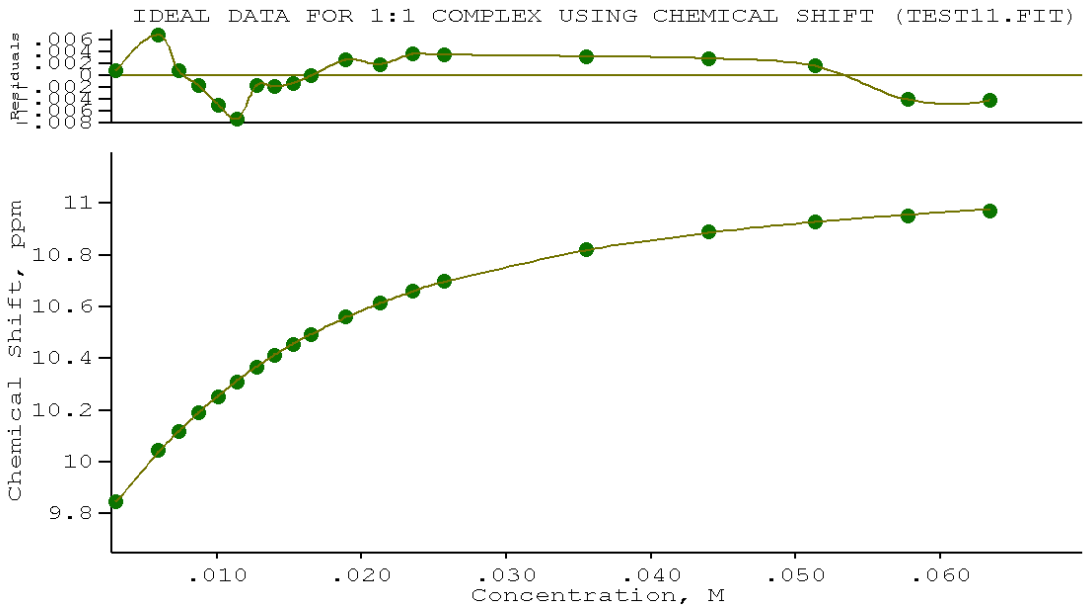


Figure S21: Job Plot of receptor **2** with TBA chloride



$K_1 = 118\ M^{-1}$, Error = 1.5%

Figure S22: Fit Plot for titration of receptor **5** with TBA chloride

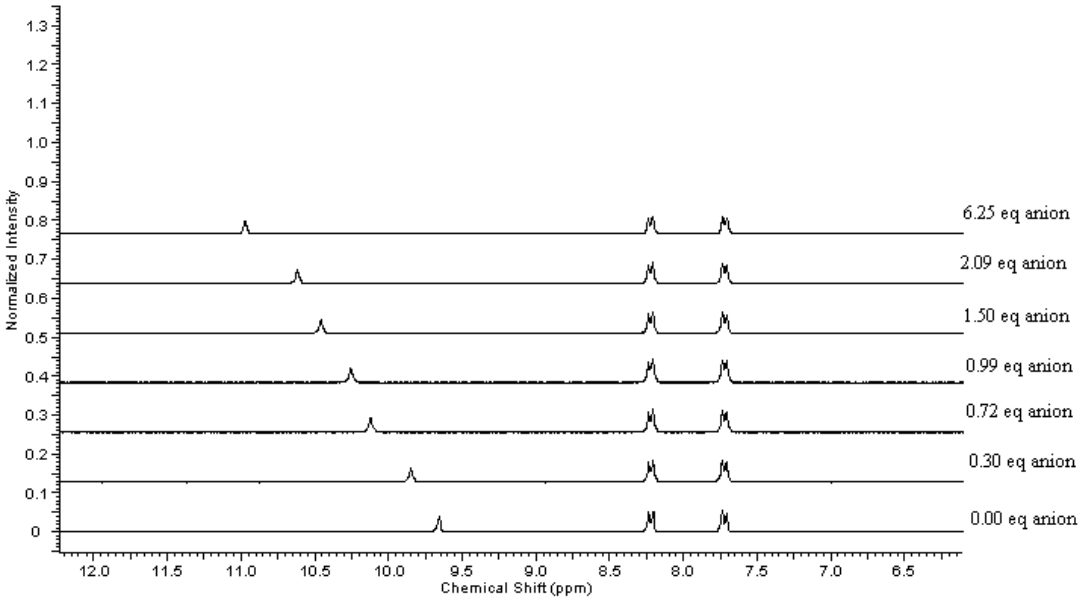


Figure S23: Stack plot for titration of receptor **5** with TBA chloride

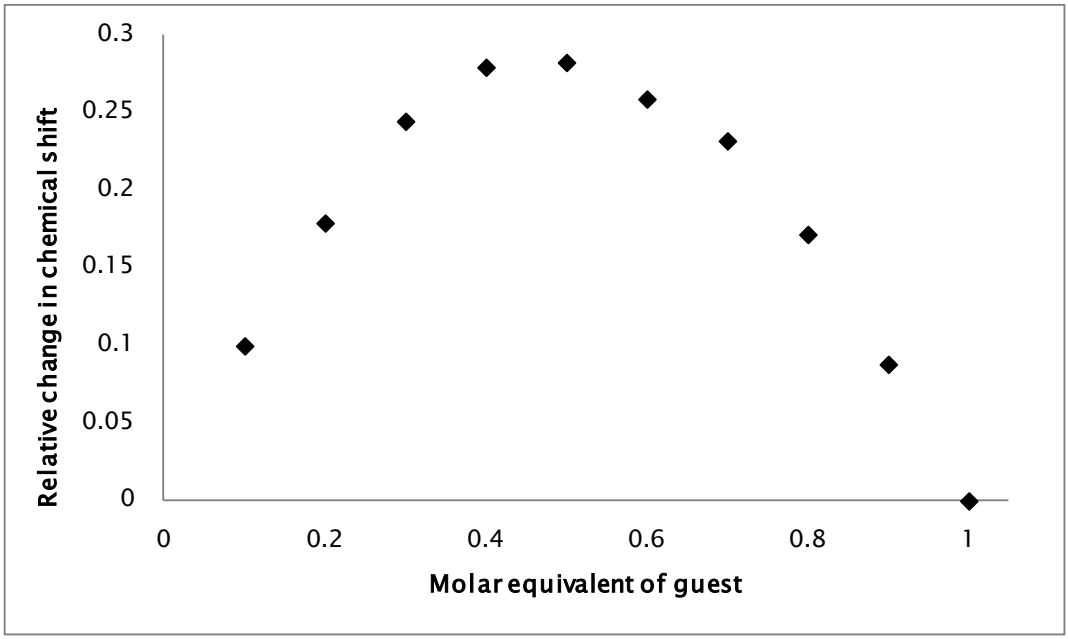
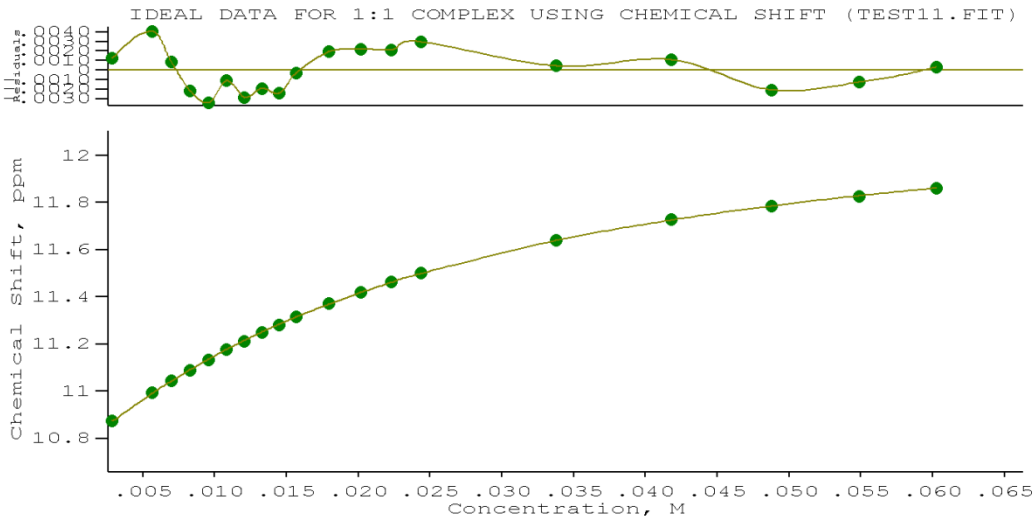


Figure S24: Job plot of receptor **5** with TBA chloride



K_1 = 50 M^{-1}, Error = 1%

Figure S25: Fit Plot for titration of receptor **6** with TBA chloride

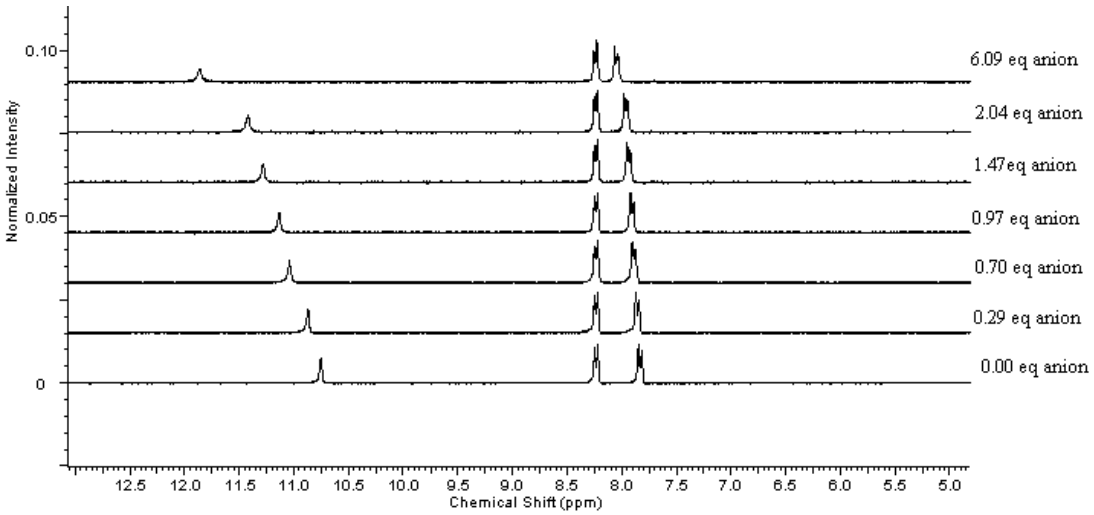


Figure S26: Stack plot for titration of receptor **6** with TBA chloride

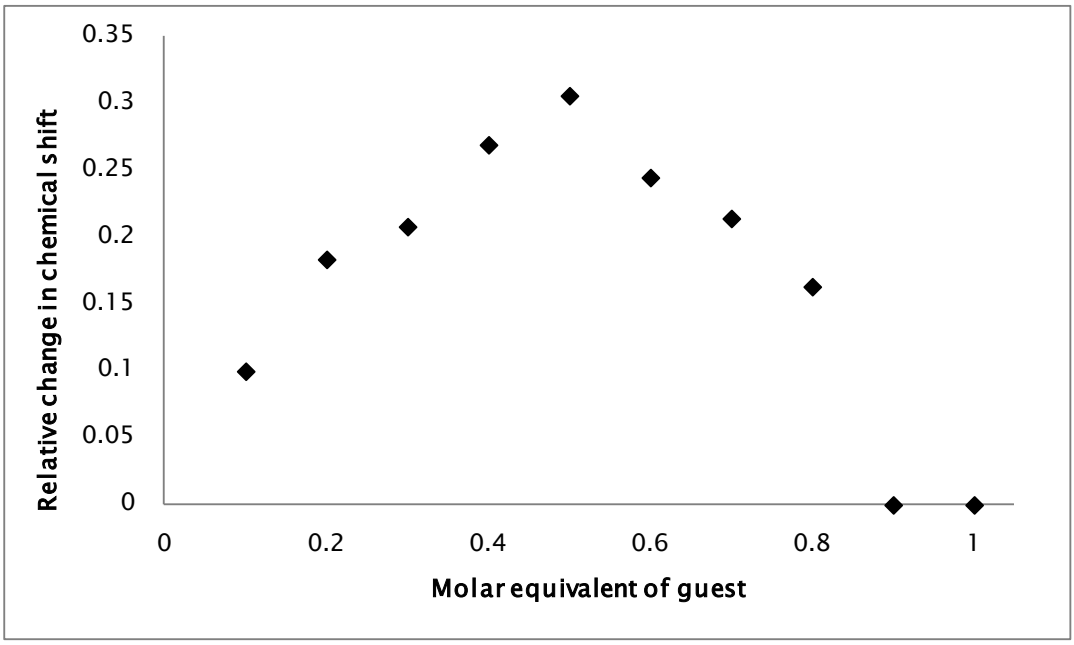


Figure S27: Job plot of receptor **6** with TBA chloride

5. Discussion of receptor molecules crystal structures

Table S5: Crystallographic details of receptor molecules crystal structures **1**, **2**, **5** and **6**.

Structure	**1**	**2**	**5**	**6**
Formula	$C_{13}H_{11}N_3O_3$	$C_{13}H_{11}N_3O_2S$	$C_{13}H_{10}N_4O_5$	$C_{13}H_{10}N_4O_4S$
Weight $gmol^{-1}$	257.25	273.31	302.25	318.31
System	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	P 2_1	P $2_1/n$	P $na2_1$	P $2_1/c$
a (Å)	4.590 (4)	5.6328 (7)	13.8899 (18)	8.2109 (5)
b (Å)	8.336 (7)	7.7579 (9)	24.389 (3)	25.4709 (18)
c (Å)	15.282 (13)	28.178 (4)	3.6682 (4)	12.5244 (9)
α (°)	90	90	90	90
β (°)	96.929 (17)	92.324 (7)	90	96.054 (2)
γ (°)	90	90	90	90
V (Å)	580.5 (9)	1230.3 (3)	1242.6 (3)	2604.7 (3)
Z	2	4	4	8
D (gcm^{-3})	1.472	1.476	1.616	1.623
Temp (K)	100 (2)	100 (2)	35 (2)	100 (2)
λ	0.71073	0.71073	0.68890	0.71073
μ (mm^{-1})	0.108	0.264	0.117	0.275
F(000)	268	568	624	1312
Crystal	Colourless Needle	Yellow Block	Yellow Lath	Yellow Plate
Crystal size (mm^3)	0.12 x 0.02 x 0.02	0.19 x 0.08 x 0.02	0.10 x 0.02 x 0.01	0.18 x 0.15 x 0.02
Data completeness	99.6	97.8	100	99.1
Index ranges	$-5 \le h \le 5$ $-10 \le k \le 10$ $-19 \le l \le 19$	$-6 \le h \le 6$ $-9 \le k \le 9$ $-33 \le l \le 33$	$0 \le h \le 18$ $0 \le k \le 31$ $-4 \le l \le 4$	$-9 \le h \le 9$ $-30 \le k \le 29$ $-13 \le l \le 14$
T_{min}/T_{max}	0.9872/ 0.9978	0.9515/ 0.9947	0.9873/0.9994	0.9521/0.9945
Final R indices [$F^2 > 2\sigma(F^2)$]	R1 = 0.0448 *w*R2 = 0.1159	R1 = 0.0428 *w*R2 = 0.1002	R1 = 0.0424 *w*R2 = 0.1101	R1 = 0.0502 *w*R2 = 0.1416
R indices (all data)	R1= 0.0492 *w*R2 = 0.1185	R1 = 0.0562 *w*R2 = 0.1066	R1 = 0.0429 *w*R2 = 0.1110	R1 = 0.0569 *w*R2 = 0.1463
Data/ restraints/ parameters	1408/ 1/ 173	2136/ 0/ 172	2790/1/199	4557/0/397
Δρ(r) (eÅ^{-3})	0.161/ -0.291	0.259/ -0.244	0.480/-0.263	0.771/-0.743

Both the unsymmetrical receptors (**1** and **2**) crystallise in monoclinic space groups, the urea (**1**) in $P2_1$ with two molecules in the unit cell and thiourea (**2**) in $P2_1/n$ with four molecules making up the unit cell. In structure **1** hydrogen bonding between the N−H···O unit of the urea follows the typically observed α-tape motif. This leads to columns of ureas with the nitro group on the same side linked by C−H···O contacts of nitro groups and unsubstituted phenyl rings extending the structure. The zigzag motif of thiourea N−H···S atom contacts is observed in **2** with the nitro group alternating position through the zigzag layer. These layers are linked as in **1** through C−H···O contacts of nitro groups and unsubstituted phenyl rings.

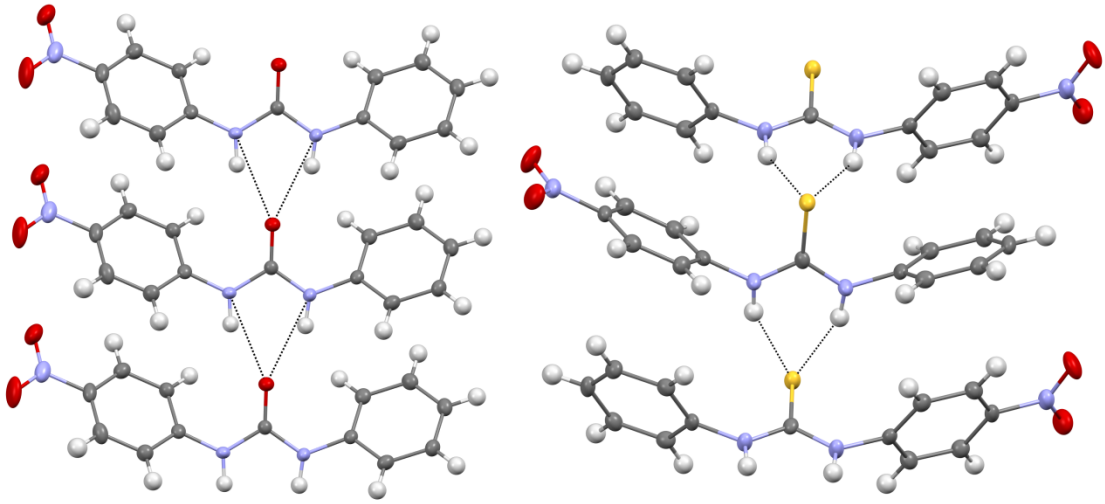


Figure S28: Asymmetric receptor crystal structures **1** (*left*) and **2** (*right*).

Table S6: Hydrogen bond and intermolecular interaction properties of asymmetrical receptor crystal structures **1** and **2** respectively.

Crystal Structure	H···A (Å)	D···A (Å)	∠ DHA (°)
1[#]	2.03 2.10	2.847 (4) 2.883 (3)	154.2 148.1
2[9]	2.70 2.63	3.514 (2) 3.4608 (19)	154.1 157.0

[#]symmetry used to generate equivalent atoms x-1, y, z; [9]symmetry used to generate equivalent atoms – x-1/2, y+1/2, -z+1/2

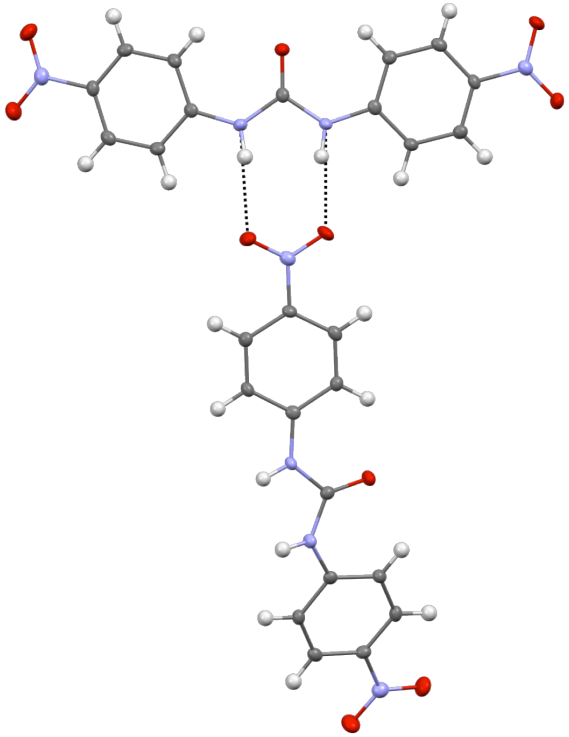


Figure S29: Hydrogen bonding in crystal structure of 1,3-bis(4-nitrophenyl)urea (**5**)

Table S7: Hydrogen bonding in 1,3-bis(4-nitrophenyl)urea (**5**) crystal structure

Hydrogen bond	D−H[†] (Å)	H···A (Å)	D···A (Å)	∠ DHA (°)
N2−H2A···O4[#]	0.88	2.20	3.070 (2)	170.4
N3−H3A···O5[#]	0.88	2.06	2.923 (2)	165.9

[#]symmetry used to generate equivalent atoms x+1/2, -y+1/2, z-1

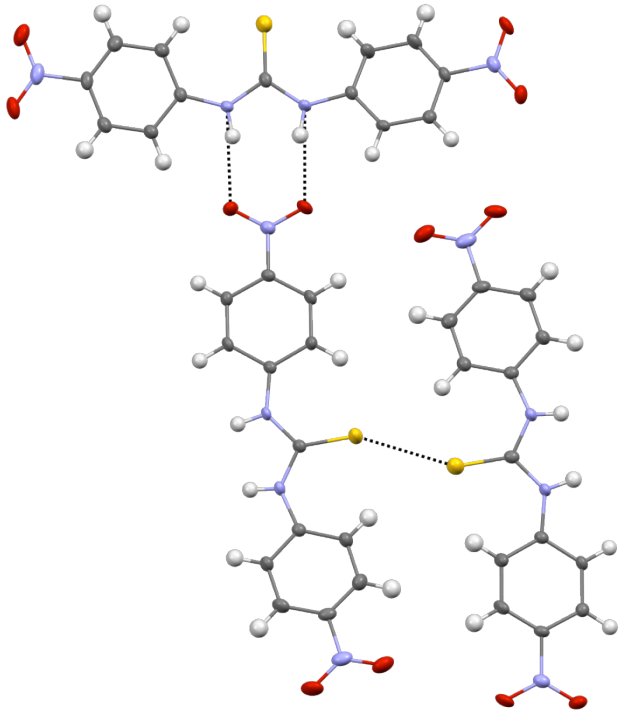


Figure S30: Hydrogen bonding in crystal structure of 1,3-bis(4-nitrophenyl)thiourea (**6**)

Table S8: Hydrogen bonding in 1,3-bis(4-nitrophenyl)thiourea crystal structure

Hydrogen bond	D−H[†] (Å)	H···A (Å)	D···A (Å)	∠ DHA (°)
N2−H2A···O5[#]	0.88	2.12	2.981 (3)	167.3
N3−H3A···O6[#]	0.88	2.11	2.978 (3)	166.9
N6−H6A···O1[ζ]	0.88	2.25	3.093 (3)	161.3
N6−H6A···S1[Ψ]	0.88	3.02	3.467 (2)	113.8
N7−H7A···O2[ζ]	0.88	2.15	3.011 (3)	166.8

[#] symmetry used to generate equivalent atoms x, -y+3/2, z-1/2; [ζ] symmetry used to generate equivalent atoms x+1, -y+3/2, z-1/2, [Ψ] symmetry used to generate equivalent atoms x+1, y, z

6. Hirshfeld surfaces and fingerprint plots for symmetrical receptor crystal structures (**5**, **6**, **7** and **8**)

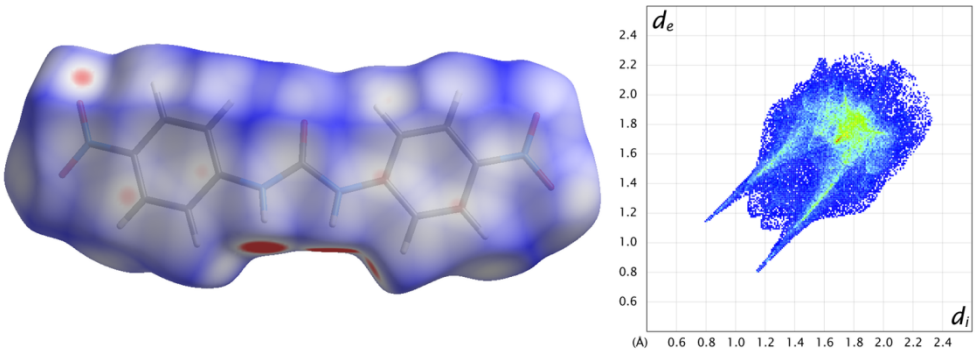


Figure S31: Hirshfeld surface (*left*) and fingerprint plot (*right*) of crystal structure **5**

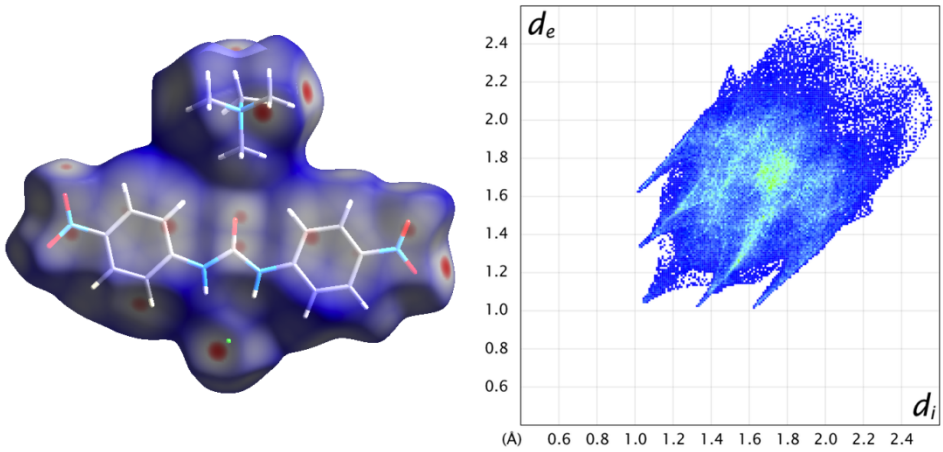


Figure S32: Hirshfeld surface (*left*) and fingerprint plot (*right*) of crystal structure **7**

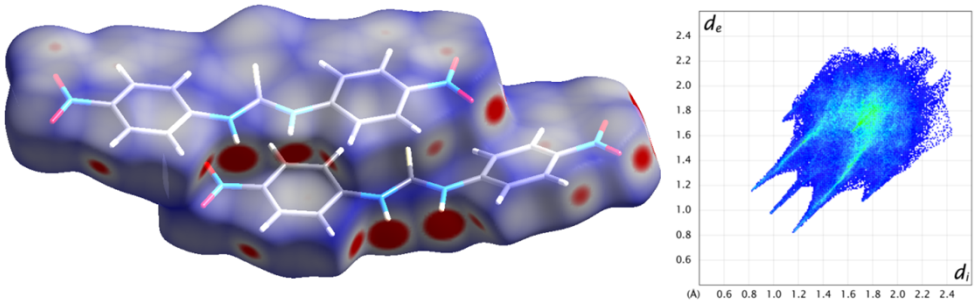


Figure S33: Hirshfeld surface (*left*) and fingerprint plot (*right*) of crystal structure **6**

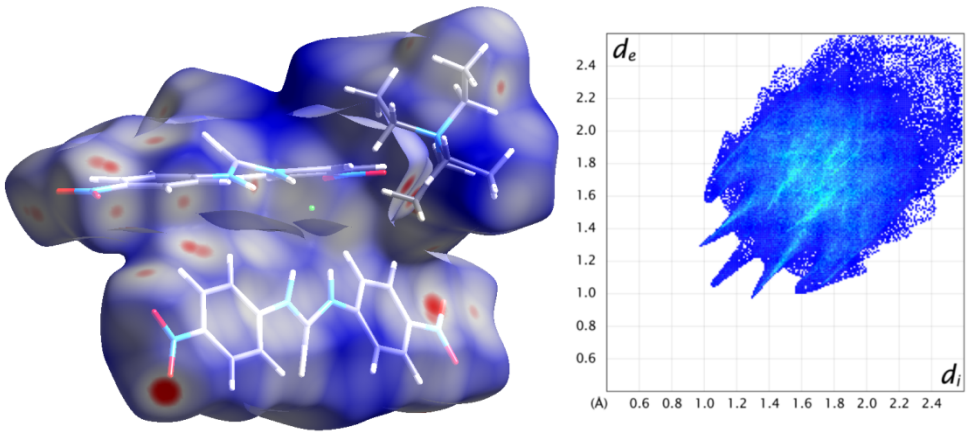


Figure S34: Hirshfeld surface (*left*) and fingerprint plot (*right*) of crystal structure **8**

7. Topological properties of the BCPs for the anion-receptors complexes

Table S9: Properties of the electron density distribution at the BCPs for the covalent bonds in **3**.

Bond	$\rho(\mathbf{r})$ (e A^{-3})	$\nabla^2\rho(\mathbf{r})$ (e A^{-5})	Rij (Å)	d_1 (Å)	d_2 (Å)	λ_1	λ_2	λ_3	ε
O(1)−C(7)	2.98(8)	-32.6(3)	1.2216	0.7064	0.5152	-27.31	-22.70	17.42	0.20
O(2)−N(1)	3.14(9)	4.7(4)	1.2247	0.6245	0.6001	-26.06	-21.34	52.09	0.22
O(3)−N(1)	3.09(4)	5.4(2)	1.2314	0.6268	0.6046	-25.58	-20.92	51.88	0.22
N(1)−C(1)	2.00(3)	-13.42(9)	1.4551	0.7990	0.6561	-16.34	-13.91	16.83	0.18
N(2)−C(4)	2.09(4)	-13.6(1)	1.3865	0.7796	0.6069	-16.44	-14.20	17.01	0.16
N(2)−C(7)	2.17(5)	-16.6(2)	1.3909	0.7677	0.6232	-18.62	-15.19	17.25	0.23
N(2)−H(2A)	2.19(9)	-29.6(4)	1.0090	0.7293	0.2597	-29.67	-26.93	27.05	0.10
N(3)−C(7)	2.21 (5)	-18.0(2)	1.3731	0.7613	0.6618	-18.93	-15.86	16.78	0.19
N(3)−C(8)	2.03(4)	-12.6(1)	1.4054	0.7783	0.6272	-15.85	-14.12	17.38	0.12
N(3)−H(3A)	2.25(9)	-34.0(5)	1.0094	0.7541	0.2553	-31.04	-28.61	25.62	0.09
N(5)−C(51)	1.63(3)	-6.84(7)	1.5175	0.8501	0.6674	-10.88	-10.88	14.92	0.00
N(5)−C(53)	1.67(1)	-8.49(4)	1.5210	0.8585	0.625	-11.53	-11.44	14.48	0.01
N(5)−C(55)	1.67(1)	-8.36(4)	1.5193	0.8571	0.6621	-11.54	-11.32	14.50	0.02
N(5)−C(57)	1.68(2)	-8.57(4)	1.5190	0.8578	0.6611	-11.56	-11.48	14.47	0.01
C(1)−C(2)	2.18(2)	-18.68(5)	1.3913	0.6986	0.6927	-17.53	-14.17	13.02	0.24
C(1)−C(6)	2.18(2)	-18.64(5)	1.3925	0.6991	0.6934	-17.51	-14.15	13.02	0.24
C(2)−C(3)	2.18(1)	-19.39(4)	1.3840	0.6925	0.6915	-17.89	-14.15	12.65	0.26
C(2)−H(2)	1.86(6)	-17.4(1)	1.0830	0.6836	0.3994	-17.27	-15.97	15.88	0.08
C(3)−C(4)	2.111(0)	-16.939(1)	1.4135	0.7041	0.7093	-16.73	-13.57	13.37	0.23
C(3)−H(3)	1.795(0)	-16.791(0)	1.0830	0.6967	0.3864	-16.95	-15.70	15.86	0.08
C(4)−C(5)	2.131(0)	-17.404(1)	1.4064	0.7036	0.7028	-16.97	-13.71	13.27	0.24
C(5)−C(6)	2.176(0)	-19.201(0)	1.3865	0.6938	0.6928	-17.84	-14.08	12.72	0.27
C(5)−H(5)	1.848(0)	-19.439(0)	1.0831	0.6991	0.3840	-17.96	-16.76	15.29	0.07
C(6)−H(6)	1.794(0)	-16.721(0)	1.0831	0.6969	0.3862	-16.92	-15.70	15.89	0.08
C(8)−C(9)	2.153(0)	-17.943(1)	1.4005	0.7032	0.6973	-17.15	-13.93	13.14	0.23
C(8)−C(13)	2.131(0)	-17.541(1)	1.4049	0.7040	0.7009	-17.02	-13.73	13.21	0.24
C(9)−C(10)	2.11(2)	-17.21(4)	1.3947	0.7013	0.6935	-16.67	-13.52	12.98	0.23
C(9)−H(9)	1.793(0)	-16.721(0)	1.0831	0.6967	0.3865	-16.90	-15.68	15.86	0.08
C(10)−C(11)	2.06(2)	-15.58(4)	1.3993	0.6997	0.6995	-15.71	-13.07	13.21	0.20
C(10)−H(10)	1.76(2)	-16.17(5)	1.0830	0.6917	0.3913	-16.01	-15.72	15.56	0.02
C(11)−C(12)	2.077(0)	-15.877(0)	1.3953	0.6975	0.6977	-15.83	-13.19	13.14	0.20
C(11)−H(11)	1.762(0)	-16.201(0)	1.0830	0.6915	0.3915	-16.02	-15.72	15.54	0.02

C(12)−C(13)	2.106(0)	-17.095(0)	1.3964	0.6944	0.7020	-16.63	-13.47	13.01	0.23
C(12)−H(12)	1.764(0)	-16.194(0)	1.0830	0.6918	0.3912	-16.02	-15.73	15.56	0.02
C(13)−H(13)	1.795(0)	-16.767(0)	1.0830	0.6966	0.3865	-16.92	-15.69	15.85	0.08
C(51)−C(52)	1.66(2)	-9.49(5)	1.5193	0.7604	0.7589	-11.35	-10.80	12.66	0.05
C(51)−H(51A)	1.82(6)	-16.5(1)	1.0920	0.6915	0.4005	-15.88	-15.39	14.81	0.03
C(51)−H(51B)	1.78(1)	-15.15(4)	1.0921	0.6937	0.3984	-15.45	-15.09	15.38	0.02
C(52)−H(52A)	1.77(6)	-15.7(2)	1.0594	0.6692	0.3902	-15.69	-14.68	14.71	0.07
C(52)−H(52B)	1.79(1)	-15.83(4)	1.0591	0.6616	0.3975	-16.00	-14.58	14.75	0.10
C(52)−H(53C)	1.79(1)	-15.88(4)	1.0590	0.6619	0.3971	-16.02	-14.62	14.76	0.10
C(53)−C(54)	1.663(0)	-9.628(0)	1.5165	0.7587	0.7578	-11.43	-10.86	12.66	0.05
C(53)−H(53A)	1.782(0)	-15.205(0)	1.0920	0.6937	0.3983	-15.55	-15.04	15.38	0.03
C(53)−H(53B)	1.779(0)	-15.015(0)	1.0922	0.6940	0.3982	-15.36	-15.09	15.43	0.02
C(54)−H(54A)	1.785(0)	-15.546(0)	1.0595	0.6624	0.3971	-15.69	-14.69	14.84	0.07
C(54)−H(54B)	1.790(0)	-15.867(0)	1.0590	0.6617	0.3973	-16.03	-14.59	14.75	0.10
C(54)−H(54C)	1.793(0)	-15.878(0)	1.0590	0.6621	0.3969	-16.03	-14.62	14.77	0.10
C(55)−C(56)	1.674(1)	-9.809(1)	1.5127	0.7575	0.7552	-11.52	-10.93	12.65	0.05
C(55)−H(55A)	1.75(6)	-15.1 (1)	1.0921	0.7023	0.3899	-15.35	-15.00	15.23	0.02
C(55)−H(55B)	1.780(1)	-15.203(1)	1.0921	0.6936	0.3985	-15.52	-15.06	15.37	0.03
C(56)−H(56A)	1.792(0)	-15.827(0)	1.0591	0.6622	0.3969	-15.93	-14.68	14.79	0.09
C(56)−H(56B)	1.795(0)	-15.864(0)	1.0591	0.6623	0.3967	-16.04	-14.61	14.78	0.10
C(56)−H(56C)	1.793(0)	-15.874(0)	1.0590	0.6620	0.3970	-16.05	-14.60	14.77	0.10
C(57)−C(58)	1.673(0)	-9.805(0)	1.5126	0.7570	0.7556	-11.53	-10.92	12.65	0.06
C(57)−H(57A)	1.782(0)	-15.153(0)	1.0921	0.6940	0.3981	-15.48	-15.08	15.41	0.03
C(57)−H(57B)	1.780(0)	-15.166(0)	1.0921	0.6937	0.3984	-15.50	-15.06	15.39	0.03
C(58)−H(58A)	1.790(0)	-15.794(0)	1.0591	0.6622	0.3970	-15.88	-14.70	14.79	0.08
C(58)−H(58B)	1.794(0)	-15.861(0)	1.0590	0.6622	0.3968	-15.99	-14.65	14.78	0.09
C(58)−H(58C)	1.793(0)	-15.881(0)	1.0590	0.6620	0.3970	-16.04	-14.61	14.77	0.10

Table S10: Properties of the electron density distribution at the BCPs for the covalent bonds in **4**.

Bond	$\rho(\mathbf{r})$ (e A^{-3})	$\nabla^2\rho(\mathbf{r})$ (e A^{-5})	Rij (Å)	d_1 (Å)	d_2 (Å)	λ_1	λ_2	λ_3	ε
S(1)−C(7)	1.47(5)	-3.1(1)	1.6736	0.8074	0.8663	-9.08	-7.77	13.75	0.17
S(2)−C(20)	1.41(5)	-3.6(1)	1.6858	0.8414	0.8444	-10.60	-9.08	16.06	0.17
O(1)−N(1)	3.33(7)	-0.9(3)	1.2354	0.6256	0.6098	-31.82	-26.85	57.79	0.18
O(2)−N(1)	3.34(7)	-1.0(3)	1.2346	0.6254	0.6093	-31.89	-26.92	57.82	0.18
O(3)−N(4)	3.41(5)	-10.0(2)	1.2284	0.6121	0.6163	-34.18	-31.18	55.36	0.10
O(4)−N(4)	3.38(5)	-9.4(2)	1.2323	0.6135	0.6188	-33.80	-30.82	55.22	0.10
N(1)−C(1)	1.90(5)	-8.9(1)	1.4586	0.8086	0.655	-14.90	-13.49	19.46	0.10
N(2)−C(4)	2.09(5)	-11.9(2)	1.3970	0.7892	0.6077	-16.36	-14.77	19.26	0.11
N(2)−C(7)	2.32(5)	-19.8(2)	1.3688	0.7787	0.5901	-20.40	-16.91	17.47	0.21
N(2)−H(2A)	2.32(7)	-34.4(4)	1.0094	0.7752	0.2342	-33.68	-33.46	32.76	0.01
N(3)−C(7)	2.36(5)	-18.6(2)	1.3660	0.7657	0.6003	-19.37	-17.93	18.70	0.08
N(3)−C(8)	2.17(5)	-15.2(2)	1.4086	0.7879	0.6207	-17.45	-16.75	18.96	0.04
N(3)−H(3A)	2.19(7)	-29.9(4)	1.0091	0.7779	0.2312	-31.65	-31.00	32.78	0.02
N(4)−C(14)	1.84(4)	-8.4(1)	1.4561	0.8190	0.6371	-14.59	-12.86	19.04	0.13
N(5)−C(17)	2.06(4)	-12.8(1)	1.3970	0.7971	0.5998	-16.83	-14.79	18.86	0.14
N(5)−C(20)	2.34(5)	-16.9(2)	1.3721	0.7517	0.6204	-20.13	-16.99	20.20	0.18
N(5)−H(5A)	2.20(8)	-23.4(4)	1.0092	0.7595	0.2497	-29.85	-28.98	35.40	0.03
N(6)−C(20)	2.18(5)	-16.2(2)	1.3559	0.7737	0.5822	-17.13	-15.95	16.85	0.07
N(6)−C(21)	2.15(4)	-15.0(1)	1.4049	0.7855	0.6194	-17.98	-15.98	18.93	0.12
N(6)−H(6A)	2.14(8)	-27.8(5)	1.0092	0.7751	0.2341	-31.08	-29.31	32.55	0.06
N(7)−C(71)	1.58(5)	-3.2(1)	1.4966	0.8532	0.6433	-10.65	-9.92	17.33	0.07
N(7)−C(72)	1.56(5)	-4.3(1)	1.4927	0.8582	0.6345	-11.52	-9.12	16.33	0.26
N(7)−C(73)	1.69(5)	-2.9(1)	1.4918	0.8283	0.6635	-12.00	-10.37	19.42	0.16
N(7)−C(74)	1.66(5)	-8.1(1)	1.4937	0.8610	0.6327	-12.70	-11.38	16.03	0.12
C(1)−C(2)	2.20(4)	-17.6(1)	1.3912	0.6922	0.6990	-17.89	-14.47	14.77	0.24

C(1)−C(6)	2.16(5)	-17.1(1)	1.3918	0.7375	0.6542	-17.55	-14.07	14.54	0.25
C(2)−C(3)	2.26(4)	-18.5(1)	1.3858	0.6851	0.7007	-18.03	-15.64	15.13	0.15
C(2)−H(2)	1.93(6)	-17.2(2)	1.0839	0.7260	0.3579	-19.60	-18.15	20.57	0.08
C(3)−C(4)	2.10(4)	-15.8(1)	1.4100	0.6838	0.7262	-16.27	-14.34	14.82	0.13
C(3)−H(3)	1.84(6)	-16.4(2)	1.0831	0.7328	0.3503	-18.34	-17.94	19.93	0.02
C(4)−C(5)	2.08(4)	-15.3(1)	1.4033	0.7128	0.6905	-16.19	-13.80	14.68	0.17
C(5)−C(6)	2.23(4)	-18.0(1)	1.3907	0.6864	0.7043	-18.16	-15.10	15.23	0.20
C(5)−H(5)	1.77(6)	-15.1(2)	1.0843	0.7558	0.3285	-18.36	-17.89	21.19	0.03
C(6)−H(6)	1.77(7)	-16.7(2)	1.0833	0.7432	0.3401	-17.80	-17.70	18.79	0.01
C(8)−C(9)	2.09(4)	-14.5(1)	1.4002	0.6826	0.7176	-16.10	-13.11	14.68	0.23
C(8)−C(13)	2.16(4)	-17.7(1)	1.3996	0.6927	0.7069	-16.87	-15.05	14.26	0.12
C(9)−C(10)	2.25(4)	-18.0(1)	1.3948	0.6696	0.7252	-17.92	-15.16	15.06	0.18
C(9)−H(9)	1.82(6)	-15.6(2)	1.0838	0.7235	0.3603	-17.76	-17.22	19.34	0.03
C(10)−C(11)	2.21(4)	-18.9(1)	1.3925	0.6658	0.7267	-18.26	-14.83	14.23	0.23
C(10)−H(10)	1.79(6)	-14.7(2)	1.0834	0.7037	0.3797	-17.11	-15.92	18.36	0.07
C(11)−C(12)	2.08(5)	-16.2(1)	1.3967	0.7376	0.6591	-16.26	-13.74	13.75	0.18
C(11)−H(11)	1.84(7)	-14.5(2)	1.0831	0.7326	0.3505	-18.84	17.38	21.68	0.08
C(12)−C(13)	2.20(4)	-17.5(1)	1.3964	0.7001	0.6963	-17.42	-14.94	14.81	0.17
C(12)−H(12)	1.77(6)	-13.6(2)	1.0848	0.7199	0.3649	-17.09	-16.40	19.92	0.04
C(13)−H(13)	1.84(6)	-15.6(2)	1.0831	0.7403	0.3428	-18.46	-17.81	20.72	0.04
C(14)−C(15)	2.04(4)	-15.5(1)	1.3918	0.7239	0.6678	-16.16	-13.57	14.20	0.19
C(14)–C(19)	2.16(4)	-15.7(1)	1.3907	0.6953	0.6954	-17.75	-13.80	15.82	0.29
C(15)−C(16)	2.19(4)	-16.9(1)	1.3860	0.6606	0.7254	-18.10	-14.21	15.42	0.27
C(15)−H(15)	1.85(7)	-17.9(2)	1.0833	0.7402	0.3431	-19.15	-18.51	19.71	0.03
C(16)−C(17)	2.13(4)	-15.1(1)	1.4089	0.6725	0.7364	-17.18	-13.89	15.93	0.24
C(16)−H(16)	1.81(6)	-15.8(2)	1.0830	0.6993	0.3837	-17.27	-16.66	18.15	0.04
C(17)−C(18)	1.97(4)	-13.2(1)	1.4014	0.7363	0.6651	-15.27	-12.60	14.65	0.21
C(18)−C(19)	2.14(4)	-14.8(1)	1.3906	0.7270	0.6636	-17.29	-13.46	15.94	0.28
C(18)−H(18)	1.90(7)	-17.0(2)	1.0833	0.7352	0.3481	-19.32	-18.55	20.85	0.04
C(19)−H(19)	1.80(6)	-14.7(2)	1.0830	0.7310	0.3520	-17.84	-17.39	20.58	0.03
C(21)−C(22)	2.12(4)	-15.0(1)	1.4034	0.7078	0.6955	-16.59	-13.60	15.16	0.22
C(21)−C(26)	2.18(4)	-17.1(1)	1.3998	0.7091	0.6907	-17.45	-14.63	14.99	0.19
C(22)−C(23)	2.30(4)	-18.8(1)	1.3885	0.6792	0.7093	-18.79	-15.52	15.46	0.21
C(22)−H(22)	1.77(6)	-13.2(2)	1.0831	0.7310	0.3521	-17.60	-16.60	20.96	0.06
C(23)−C(24)	2.22(4)	-17.9(1)	1.3940	0.6988	0.6952	-18.00	-14.98	15.04	0.20
C(23)−H(23)	1.80(6)	-15.3(2)	1.0835	0.7191	0.3644	-17.46	-17.13	19.26	0.02
C(24)−C(25)	2.09(4)	-15.0(1)	1.3928	0.7324	0.6604	-15.93	-13.58	14.51	0.17
C(24)−H(24)	1.82(6)	-13.5(2)	1.0832	0.7194	0.3638	-18.20	-16.65	21.30	0.09
C(25)−C(26)	2.20(4)	-16.9(1)	1.3965	0.7259	0.6706	-17.60	-14.64	15.35	0.20
C(25)−H(25)	1.81(6)	-14.9(2)	1.0831	0.7127	0.3703	-17.42	-16.75	19.27	0.04
C(26)−H(26)	1.88(6)	-19.6(2)	1.0837	0.7467	0.3370	-19.42	-18.89	18.68	0.03
C(71)−H(71A)	1.88(7)	-16.0(2)	1.0592	0.7043	0.3550	-18.37	-17.92	20.32	0.02
C(71)−H(71B)	1.84(8)	-13.8(3)	1.0593	0.7039	0.3554	-17.95	-17.10	21.27	0.05
C(71)−H(71C)	1.91(7)	-16.3(2)	1.0595	0.6921	0.3674	-18.81	-17.55	20.05	0.07
C(72)−H(72A)	1.91(7)	-16.5(2)	1.0591	0.6913	0.3678	-19.02	-17.58	20.10	0.08
C(72)−H(72B)	1.76(7)	-11.8(2)	1.0616	0.6734	0.3882	-16.26	-15.27	19.72	0.06
C(72)−H(72C)	1.86(8)	-12.4(3)	1.0598	0.7326	0.3272	-18.80	-18.02	24.44	0.04
C(73)−H(73A)	1.77(7)	-13.0(2)	1.0591	0.6613	0.3978	-16.89	-14.72	18.56	0.15
C(73)−H(73B)	1.75(8)	-12.0(3)	1.0591	0.7031	0.3560	-17.05	-15.77	2082	0.08
C(73)−H(73C)	1.84(7)	-15.1(3)	1.0598	0.7135	0.3463	-18.42	-17.23	20.58	0.07
C(74)−H(74A)	1.86(7)	-16.7(2)	1.0599	0.6993	0.3606	-18.65	-17.20	19.17	0.08
C(74)−H(74B)	2.02(9)	-19.2(4)	1.0591	0.7646	0.2945	-22.47	-21.45	24.76	0.05
C(74)−H(74C)	1.73(7)	-13.6(2)	1.0604	0.6540	0.4064	-15.82	-14.76	17.03	0.07

Table S11: Properties of the electron density distribution at the BCPs for the covalent bonds in **7**.

Bond	$\rho(\mathbf{r})$ (e A^{-3})	$\nabla^2\rho(\mathbf{r})$ (e A^{-5})	R_{ij} (Å)	d_1 (Å)	d_2 (Å)	λ_1	λ_2	λ_3	ε
O(1)−C(7)	3.07(4)	- 39.1(2)	1.2237	0.7379	0.4859	-31.23	-25.99	18.09	0.20
O(2)−N(1)	3.36(3)	-10.1(1)	1.2377	0.6472	0.5905	-33.29	-29.95	53.11	0.11
O(3)−N(1)	3.40(4)	-11.0(2)	1.2314	0.6449	0.5865	-33.81	-30.44	53.27	0.11
O(5)−N(4)	3.29(4)	-3.2(2)	1.2411	0.6297	0.6114	-32.40	-26.36	55.54	0.23
O(4)−N(4)	3.29(3)	-3.3(1)	1.2404	0.6294	0.6110	-32.46	-26.39	55.56	0.23
N(1)−C(1)	1.83(3)	-13.43(9)	1.4505	0.8512	0.5993	-15.70	-12.20	14.48	0.29
N(2)−C(4)	2.10(3)	-17.13(9)	1.3867	0.7923	0.5944	-17.64	-15.20	15.72	0.16
N(2)−C(7)	2.17(3)	-19.0(1)	1.3851	0.7956	0.5896	-19.38	-15.61	15.95	0.24
N(2)−H(2A)	2.16(5)	-25.2(3)	1.0090	0.7647	0.2443	-29.46	-28.54	32.84	0.03
N(3)−C(7)	2.16(3)	-20.7(1)	1.3817	0.8010	0.5807	-19.43	-16.16	14.91	0.20
N(3)−C(8)	2.11(3)	-16.80(9)	1.3867	0.7936	0.5931	-17.57	-15.07	15.84	0.17
N(3)−H(3A)	2.22(5)	-29.7(3)	1.0090	0.7669	0.2421	-31.10	-30.08	31.47	0.03
N(5)−C(14)	1.62(3)	-6.61(8)	1.4984	0.8642	0.6343	-11.37	-10.91	15.67	0.04
N(5)−C(15)	1.66(3)	-5.89(8)	1.4956	0.8512	0.6443	-11.66	-10.98	16.75	0.06
N(5)−C(16)	1.70(3)	-7.09(8)	1.5012	0.8600	0.6412	-12.01	-11.94	16.86	0.01
N(5)−C(17)	1.63(3)	-6.99(8)	1.4969	0.8646	0.6323	-11.45	-11.16	15.61	0.03
N(4)−C(11)	1.85(3)	-13.07(9)	1.4532	0.8573	0.5959	-14.77	-13.02	14.71	0.13
C(1)−C(2)	2.18(2)	-18.48(6)	1.3969	0.7205	0.6764	-17.98	-14.12	13.61	0.27
C(1)−C(6)	2.15(2)	-18.02(6)	1.3957	0.7208	0.6749	-17.59	-13.86	13.43	0.27
C(2)−C(3)	2.16(2)	-17.46(6)	1.3840	0.6954	0.6886	-17.22	-13.83	13.59	0.24
C(2)−H(2)	1.88(4)	-17.1(1)	1.0830	0.7227	0.3604	-18.52	-17.82	19.27	0.04
C(3)−C(4)	2.10(2)	-16.97(6)	1.4119	0.6960	0.7159	-16.98	-13.62	13.63	0.25
C(3)−H(3)	1.83(4)	-16.6(1)	1.0830	0.7235	0.3595	-18.10	-17.20	18.67	0.05
C(4)−C(5)	2.07(2)	-17.35(6)	1.4083	0.7258	0.6825	-17.17	-13.39	13.21	0.28
C(5)−C(6)	2.14(2)	-17.50(6)	1.3898	0.6969	0.6929	-17.20	-13.84	13.53	0.24
C(5)−H(5)	1.86(4)	-18.5(1)	1.0831	0.7273	0.3558	-18.83	-17.74	18.09	0.06
C(6)−H(6)	1.83(4)	-16.2(1)	1.0831	0.7263	0.3567	-18.03	-17.29	19.10	0.04
C(8)−C(9)	2.08(2)	-16.70(6)	1.4130	0.7173	0.6957	-17.05	-13.18	13.52	0.29
C(8)−C(13)	2.08(2)	-17.12(6)	1.4093	0.7341	0.6751	-17.25	-13.22	13.35	0.30
C(9)−C(10)	2.19(3)	-19.11(7)	1.3838	0.6851	0.6987	-18.04	-14.33	13.25	0.26
C(9)−H(9)	1.86(4)	-18.9(1)	1.0830	0.7256	0.3574	-18.80	-17.81	17.74	0.06
C(10)−C(11)	2.15(3)	-17.19(7)	1.3983	0.7090	0.6893	-17.86	-13.28	13.94	0.35
C(10)−H(10)	1.83(4)	-17.5(1)	1.0830	0.7293	0.3537	-18.45	-17.64	1856	0.05
C(11)−C(12)	2.10(3)	-17.22(7)	1.3955	0.7211	0.6744	-17.19	-13.29	13.26	0.29
C(12)−C(13)	2.18(3)	-18.78(6)	1.3920	0.7194	0.6726	-17.62	-14.44	13.28	0.22
C(12)−H(12)	1.84(4)	-17.1(1)	1.0831	0.7223	0.3609	-18.39	-17.39	18.70	0.06
C(13)−H(13)	1.89(4)	-18.6(1)	1.0831	0.7256	0.3575	-19.06	-18.06	18.52	0.06
C(14)−H(14A)	1.92(4)	-16.7(1)	1.0592	0.6781	0.3811	-18.43	-17.39	19.08	0.06
C(14)−H(14B)	1.86(4)	-14.8(1)	1.0590	0.6921	0.3669	-18.03	-16.96	20.22	0.06
C(14)−H(14C)	1.91(4)	-16.7(1)	1.0591	0.6949	0.3642	-18.53	-17.84	19.66	0.04
C(15)−H(15A)	1.88(4)	-14.6(1)	1.0592	0.6842	0.3749	-17.92	-16.69	20.04	0.07
C(15)−H(15B)	1.84(5)	-13.9(1)	1.0592	0.6871	0.3721	-17.60	-16.34	20.02	0.08
C(15)−H(15C)	1.81(4)	-13.9(1)	1.0592	0.6405	0.4187	-16.02	-14.85	17.01	0.08
C(16)−H(16A)	1.89(4)	-15.7(1)	1.0591	0.6771	0.3821	-17.74	-17.20	19.29	0.03
C(16)−H(16B)	1.92(4)	-16.6(1)	1.0590	0.6991	0.3600	-18.89	-18.15	20.45	0.04
C(16)−H(16C)	1.88(4)	-16.0(1)	1.0591	0.6839	0.3751	-17.76	-17.22	19.02	0.03
C(17)−H(17A)	1.94(4)	-17.1(1)	1.0590	0.7061	0.3529	-19.22	-18.78	20.87	0.02
C(17)−H(17B)	1.88(4)	-16.0(1)	1.0592	0.6708	0.3884	-17.75	-16.87	18.61	0.05
C(17)−H(17C)	1.90(4)	-16.5(1)	1.0590	0.6863	0.3727	-18.35	-17.53	19.34	0.05

Table S12: Properties of the electron density distribution at the BCPs for the covalent bonds in **8**.

Bond	$\rho(\mathbf{r})$ (e A^{-3})	$\nabla^2\rho(\mathbf{r})$ (e A^{-5})	R_{ij} (Å)	d_1 (Å)	d_2 (Å)	λ_1	λ_2	λ_3	ε
S(2)−C(20)	1.48(6)	-2.7(1)	1.6837	0.8508	0.8330	-8.10	-6.90	12.30	0.17
S(1)−C(7)	1.49(7)	-3.6(1)	1.6714	0.8564	0.8149	-11.98	-8.58	16.95	0.40
O(5)−N(5)	3.53(7)	-15.2(3)	1.2355	0.6284	0.6051	-36.89	-32.52	54.23	0.13
O(6)−N(5)	3.52(7)	-14.8(3)	1.2355	0.6289	0.6066	-36.70	-32.31	54.21	0.14
O(7)−N(8)	3.41(7)	-8.7(3)	1.2320	0.6271	0.6048	-33.56	-29.56	54.44	0.14
O(8)−N(8)	3.43(7)	-9.0(3)	1.2290	0.629	0.6031	-33.82	-29.69	54.52	0.14
O(1)−N(1)	3.53(8)	-16.0(3)	1.2309	0.6250	0.6059	-36.26	-33.29	53.55	0.09
O(2)−N(1)	3.54(8)	-16.1(3)	1.2281	0.6241	0.6041	-36.32	-33.43	53.66	0.09
O(3)−N(4)	3.52(8)	-7.4(4)	1.2287	0.6270	0.6017	-33.99	-30.86	57.47	0.10
O(4)−N(4)	3.53(8)	-7.4(3)	1.2283	0.6268	0.6016	-34.03	-30.89	57.48	0.10
N(9)−C(91)	1.36(7)	-5.7(2)	1.5186	0.8954	0.6232	-9.81	-6.49	10.62	0.51
N(9)−C(93)	1.50(7)	-7.1(2)	1.5147	0.8604	0.6543	-10.76	-9.32	12.95	0.16
N(9)−C(95)	1.48(7)	-6.1(2)	1.5120	0.8976	0.6144	-10.29	-7.79	11.98	0.32
N(9)−C(97)	1.63(7)	-6.4(2)	1.5198	0.8430	0.6767	-12.00	-10.00	15.64	0.20
N(5)−C(14)	1.71(7)	-8.5(2)	1.4580	0.8666	0.5914	-13.68	-9.55	14.68	0.43
N(6)−C(17)	2.09(7)	-19.1(2)	1.3935	0.8171	0.5764	-18.93	-14.25	14.10	0.33
N(6)−C(20)	2.37(7)	-21.1(2)	1.3640	0.7729	0.5911	-19.59	-18.48	16.97	0.06
N(6)−H(6A)	2.2(1)	-42.6(8)	1.0095	0.8046	0.2049	-3586	-34.40	27.66	0.04
N(7)−C(20)	2.12(7)	-16.7(2)	1.3711	0.7937	0.5774	-17.28	-14.59	15.13	0.18
N(7)−C(21)	2.15(7)	-14.6(2)	1.4002	0.7755	0.6246	-17.65	-15.49	18.52	0.14
N(7)−H(7A)	2.4(1)	-27.6(6)	1.0090	0.7378	0.2713	-32.45	-29.20	34.01	0.11
N(8)−C(24)	1.79(7)	-12.3(2)	1.4594	0.8520	0.6073	-15.18	-11.68	14.55	0.30
N(1)−C(1)	1.76(7)	-11.2(2)	1.4607	0.8581	0.6026	-13.50	-12.56	14.84	0.07
N(2)−C(4)	2.34(7)	-24.7(2)	1.3973	0.7847	0.6126	-21.20	-20.22	16.68	0.05
N(2)−C(7)	2.23(7)	-14.9(2)	1.3717	0.7821	0.5896	-17.39	-15.24	17.76	0.14
N(2)−H(2A)	2.3(1)	-25.3(5)	1.0095	0.7236	0.2859	-28.79	-26.91	30.42	0.07
N(3)−C(7)	2.20(7)	-21.2(2)	1.3673	0.7917	0.5755	-19.34	-16.69	14.79	0.16
N(3)−C(8)	2.14(7)	-8.5(2)	1.3966	0.7274	0.6692	-15.88	-14.57	21.96	0.09
N(3)−H(3A)	2.3(1)	-36.7(7)	1.0098	0.7623	0.2475	-32.38	-31.56	27.24	0.03
N(4)−C(11)	1.63(7)	-7.0(2)	1.4594	0.8765	0.5828	-11.48	-10.05	14.51	0.14
C(91)−C(92)	1.54(7)	-7.5(2)	1.5126	0.8251	0.6875	-9.90	-8.98	11.37	0.10
C(91)−H(91A)	1.6(1)	-9.4(4)	1.0922	0.7502	0.3421	-15.86	-14.83	21.25	0.07
C(91)−H(91B)	1.8(1)	-16.7(4)	1.0922	0.7332	0.3590	-18.65	-16.66	18.63	0.12
C(92)−H(92A)	1.8(1)	-12.7(3)	1.0610	0.6690	0.3921	-1518	-14.70	17.17	0.03
C(92)−H(92B)	1.7(1)	-13.1(4)	1.0618	0.6866	0.3752	-15.64	-14.92	17.49	0.05
C(92)−H(92C)	1.8(1)	-12.0(5)	1.0591	0.7161	0.3430	-17.23	-16.45	21.64	0.05
C(93)−C(94)	1.67(8)	-8.2(2)	1.5289	0.7501	0.7788	-12.13	-9.64	13.56	0.26
C(93)−H(93A)	1.8(1)	-14.6(5)	1.0933	0.7739	0.3195	-18.88	-17.41	21.70	0.08
C(93)−H(93B)	1.7(1)	-12.7(4)	1.0922	0.7176	0.3745	-15.96	-14.41	17.71	0.11
C(94)−H(94A)	1.7(1)	-7.7(4)	1.0637	0.5834	0.4803	-13.83	-6.91	13.07	1.00
C(94)−H(94B)	1.9(2)	-17.0(5)	1.0594	0.7259	0.3335	-19.52	-17.37	19.92	0.12
C(95)−C(96)	1.46(6)	-4.8(1)	1.5134	0.7194	0.7940	-9.46	-7.07	11.70	0.34
C(95)−H(95A)	1.8(1)	-14.9(3)	1.0925	0.6908	0.4017	-16.37	-14.54	16.00	0.13
C(95)−H(95B)	1.6(1)	-11.7(3)	1.0923	0.6922	0.4001	-14.22	-13.13	15.70	0.08
C(96)−H(96A)	1.7(1)	-13.2(4)	1.0597	0.6922	0.3675	-15.90	-15.34	18.07	0.04
C(96)−H(96B)	1.9(1)	-17.5(5)	1.0592	0.7413	0.3179	-20.10	-19.22	21.80	0.05
C(96)−H(96C)	1.7(1)	-11.2(4)	1.0641	0.6862	0.3779	-15.49	-14.77	19.01	0.05
C(97)−C(98)	1.71(8)	-9.7(2)	1.5141	0.7591	0.7550	-11.57	-11.05	12.96	0.05
C(97)−H(97A)	1.7(1)	-14.0(3)	1.0933	0.6947	0.3986	-15.73	-14.51	16.29	0.08
C(97)−H(97B)	1.9(1)	-15.2(3)	1.0930	0.6843	0.4087	-16.30	-15.59	16.70	0.05
C(98)−H(98A)	1.5(2)	-13.1(7)	1.0639	0.7597	0.3042	-15.70	-15.08	17.72	0.04
C(98)−H(98B)	1.6(2)	-14.4(9)	1.0593	0.7870	0.2723	-18.45	-16.89	20.95	0.09
C(98)−H(98C)	1.9(2)	-14.3(5)	1.0610	0.6988	0.3622	-17.83	-15.90	19.45	0.12
C(14)−C(15)	2.01(7)	-15.2(2)	1.3934	0.7599	0.6335	-15.42	-13.17	13.35	0.17

C(14)−C(19)	2.12(7)	-15.7(2)	1.3883	0.6948	0.6935	-16.63	-13.38	14.35	0.24
C(15)−C(16)	2.25(7)	-21.1(2)	1.3840	0.7248	0.6591	-18.29	-16.27	13.41	0.12
C(15)−H(15)	1.8(1)	-15.8(3)	1.0831	0.7116	0.3714	-17.86	-17.12	19.15	0.04
C(16)−C(17)	1.98(7)	-14.4(2)	1.4062	0.6400	0.7662	-15.78	-11.35	12.72	0.39
C(16)−H(16)	1.8(1)	-14.8(3)	1.0834	0.7016	0.3818	-17.20	-15.92	18.36	0.08
C(17)−C(18)	2.24(6)	-20.8(2)	1.4019	0.6653	0.7366	-19.61	-14.63	13.40	0.34
C(18)−C(19)	2.07(7)	-14.0(2)	1.3929	0.7144	0.6785	-16.11	-11.96	14.07	0.35
C(18)−H(18)	1.8(1)	-15.4(4)	1.0836	0.7622	0.3214	-19.16	-17.46	21.26	0.10
C(19)−H(19)	1.8(1)	-15.2(3)	1.0831	0.7170	0.3661	-18.55	-16.99	20.32	0.09
C(21)−C(22)	1.97(6)	-15.1(2)	1.4049	0.7136	0.6913	-16.51	-11.92	13.34	0.38
C(21)−C(26)	2.01(7)	-15.5(2)	1.3997	0.7370	0.6627	-15.86	-13.34	13.66	0.19
C(22)−C(23)	2.32(7)	-19.5(2)	1.3896	0.7156	0.6740	-18.49	-15.72	14.72	0.18
C(22)−H(22)	2.0(1)	-21.9(4)	1.0837	0.7404	0.3433	-20.75	-20.29	19.17	0.02
C(23)−C(24)	2.24(7)	-18.5(2)	1.3920	0.6292	0.7629	-18.08	-14.26	13.80	0.27
C(23)−H(23)	1.9(1)	-20.6(4)	1.0833	0.7437	0.3396	-20.10	-18.70	18.15	0.08
C(24)−C(25)	2.13(7)	-18.6(2)	1.3886	0.6427	0.7460	-17.87	-13.52	12.74	0.32
C(25)−C(26)	2.19(7)	-17.4(2)	1.3882	0.7334	0.6548	-17.79	-13.64	13.99	0.30
C(25)−H(25)	2.0(1)	-17.6(4)	1.0835	0.7236	0.3599	-20.40	-18.79	21.61	0.09
C(26)−H(26)	1.7(1)	-18.1(4)	1.0838	0.7501	0.3337	-18.05	-17.39	17.36	0.04
C(1)−C(2)	2.34(7)	-21.0(2)	1.3902	0.7147	0.6755	-19.30	-16.79	15.05	0.15
C(1)−C(6)	2.20(7)	-16.5(2)	1.3912	0.7010	0.6902	-17.48	-14.04	15.05	0.25
C(2)−C(3)	2.22(7)	-21.0(2)	1.3885	0.7281	0.6604	-19.12	-15.39	13.46	0.24
C(2)−H(2)	2.1(1)	-24.6(4)	1.0832	0.7418	0.3414	-22.20	-21.17	18.79	0.05
C(3)−C(4)	2.14(7)	-19.7(2)	1.4044	0.6863	0.7181	-18.76	-14.41	13.43	0.30
C(3)−H(3)	1.7(1)	-14.6(4)	1.0833	0.7526	0.3308	-17.57	-16.18	19.13	0.09
C(4)−C(5)	2.08(7)	-16.8(2)	1.4038	0.7238	0.6800	-16.71	-13.92	13.82	0.20
C(5)−C(6)	2.21(7)	-16.1(2)	1.3911	0.6433	0.7478	-17.53	-13.28	14.71	0.32
C(5)−H(5)	1.9(1)	-22.4(4)	1.0836	0.7385	0.3451	-19.93	-19.76	17.27	0.01
C(6)−H(6)	1.9(1)	-19.7(4)	1.0838	0.7460	0.3378	-20.27	-19.66	20.21	0.03
C(8)−C(9)	2.07(7)	-14.5(2)	1.4030	0.7493	0.6537	-14.81	-14.06	14.37	0.05
C(8)−C(13)	2.09(7)	-13.2(2)	1.4048	06932	0.7116	-16.27	-12.45	15.55	0.31
C(9)−C(10)	1.98(7)	-10.6(2)	1.3872	0.6522	0.7349	-14.44	-10.98	14.84	0.32
C(9)−H(9)	1.7(1)	-10.5(3)	1.0838	0.7300	0.3538	-16.51	-15.94	21.93	0.04
C(10)−C(11)	2.20(7)	-19.0(2)	1.3906	0.6689	0.7216	-16.99	-15.91	13.88	0.07
C(10)−H(10)	1.8(1)	-17.9(4)	1.0837	0.7345	0.3491	-18.87	-18.02	18.99	0.05
C(11)−C(12)	2.00(7)	-13.0(2)	1.3878	0.7060	0.6818	-14.62	-13.27	14.88	0.10
C(12)−C(13)	2.13(7)	-15.4(2)	1.3913	0.6817	0.7096	-16.03	-14.35	14.95	0.12
C(12)−H(12)	1.9(1)	-21.3(4)	1.0830	0.7514	0.3316	-20.60	-19.88	19.17	0.04
C(13)−H(13)	1.8(1)	-16.6(3)	1.0835	0.6849	0.3987	-17.06	-16.17	16.65	0.05

8. QTAIM charges of atoms in the crystal structures

Table S13: Bader charges of the atoms in **3**.

Atom	Atomic Population (*e*)	Net charge (*e*)	Atomic Lagrangian (a.u.)
CL(1)	17.455	-0.455	2.6778×10^{-3}
O(1)	8.723	-0.723	2.3375×10^{-4}
O(2)	8.244	-0.244	4.1304×10^{-4}
O(3)	8.239	-0.239	2.3057×10^{-4}
N(1)	6.640	0.360	3.7114×10^{-3}
N(2)	8.026	-1.026	-7.4668×10^{-4}
N(3)	7.991	-0.991	3.2880×10^{-3}
N(5)	7.872	-0.872	-2.7915×10^{-3}
C(1)	5.869	0.131	2.1109×10^{-3}
C(2)	6.002	-0.002	1.5442×10^{-3}
C(3)	6.010	-0.010	3.0996×10^{-3}
C(4)	5.769	0.231	-1.9438×10^{-3}
C(5)	6.057	-0.057	2.0125×10^{-3}
C(6)	6.011	-0.011	-5.2732×10^{-4}
C(7)	4.740	1.260	3.7362×10^{-3}
C(8)	5.807	0.193	-3.3356×10^{-3}
C(9)	6.013	-0.013	-1.4044×10^{-3}
C(10)	5.969	0.031	-2.0516×10^{-3}
C(11)	5.964	0.036	-1.1921×10^{-3}
C(12)	5.968	0.032	-6.2819×10^{-5}
C(13)	6.007	-0.007	2.0005×10^{-3}
C(51)	5.851	0.149	3.8923×10^{-3}
C(52)	5.925	0.075	-5.1691×10^{-3}
C(53)	5.839	0.161	-2.6094×10^{-4}
C(54)	5.897	0.103	7.3622×10^{-3}
C(55)	5.831	0.169	1.1645×10^{-2}
C(56)	5.902	0.098	-1.0808×10^{-3}
C(57)	5.837	0.163	9.5652×10^{-4}
C(58)	5.903	0.097	5.8561×10^{-4}
H(2)	1.011	-0.011	-6.8489×10^{-5}
H(3)	0.939	0.061	3.3147×10^{-5}
H(5)	0.897	0.103	-3.7812×10^{-4}
H(6)	0.933	0.067	-6.2537×10^{-5}
H(9)	0.936	0.064	1.9563×10^{-4}
H(10)	0.941	0.059	-1.2854×10^{-5}
H(11)	0.942	0.058	-2.1582×10^{-5}
H(12)	0.941	0.059	2.5240×10^{-6}
H(13)	0.937	0.063	5.8164×10^{-4}
H(51A)	0.958	0.042	5.9680×10^{-4}
H(51B)	1.013	-0.013	-1.9407×10^{-4}
H(52A)	0.935	0.065	-1.8360×10^{-5}
H(52B)	0.999	0.001	7.2376×10^{-4}
H(52C)	0.996	0.004	4.9287×10^{-4}

H(53A)	1.021	-0.021	-1.9219×10^{-3}
H(53B)	1.008	-0.008	-2.1643×10^{-5}
H(54A)	0.992	0.008	5.1548×10^{-5}
H(54B)	0.998	0.002	-4.2848×10^{-4}
H(54C)	0.997	0.003	-1.2467×10^{-4}
H(55A)	0.945	0.055	-1.2059×10^{-4}
H(55B)	1.012	-0.012	2.4829×10^{-4}
H(56A)	0.996	0.004	-3.0408×10^{-6}
H(56B)	0.996	0.004	4.8734×10^{-4}
H(56C)	0.997	0.003	-3.7008×10^{-5}
H(57A)	1.010	-0.010	6.3642×10^{-4}
H(57B)	1.012	-0.012	5.4721×10^{-4}
H(58A)	0.996	0.004	5.1694×10^{-6}
H(58B)	0.998	0.002	-8.3301×10^{-4}
H(58C)	0.996	0.004	-2.1272×10^{-4}
H(2A)	0.527	0.473	8.3198×10^{-4}
H(3A)	0.465	0.535	-4.5073×10^{-4}

Table S14: Bader charges of the atoms in **4**.

Atom	Atomic Population (*e*)	Net charge (*e*)	Atomic Lagrangian (a.u.)
CL(1)	17.066	-0.066	8.9024×10^{-4}
S(1)	15.845	0.155	1.4899×10^{-4}
S(2)	15.349	0.651	3.3757×10^{-4}
O(1)	8.492	-0.492	-9.8845×10^{-4}
O(2)	5.495	-0.495	6.3093×10^{-4}
O(3)	8.442	-0.442	3.0141×10^{-4}
O(4)	8.441	-0.441	-6.3917×10^{-5}
N(1)	6.860	0.140	-2.5521×10^{-3}
N(2)	8.154	-1.154	2.2538×10^{-3}
N(3)	8.176	-1.176	2.8037×10^{-3}
N(4)	6.792	0.208	1.3227×10^{-2}
N(5)	8.026	-1.026	3.1553×10^{-3}
N(6)	8.104	-1.104	3.8156×10^{-4}
N(7)	7.841	-0.841	1.3133×10^{-2}
C(1)	5.918	0.082	-4.1264×10^{-3}
C(2)	6.155	-0.155	-1.5715×10^{-4}
C(3)	6.145	-0.145	8.4241×10^{-4}
C(4)	5.747	0.253	-3.3121×10^{-4}
C(5)	6.035	-0.035	1.9198×10^{-3}
C(6)	6.040	-0.040	2.1305×10^{-3}
C(7)	5.519	0.481	-9.3525×10^{-3}
C(8)	5.699	0.301	5.7106×10^{-3}
C(9)	6.193	-0.193	-2.9944×10^{-3}
C(10)	6.105	-0.105	1.3673×10^{-3}
C(11)	6.186	-0.186	3.1607×10^{-3}
C(12)	6.025	-0.025	4.3938×10^{-3}

C(13)	6.160	-0.160	-1.1413×10^{-3}
C(14)	5.807	0.193	6.8894×10^{-3}
C(15)	5.933	0.067	4.3421×10^{-3}
C(16)	6.069	-0.069	8.8341×10^{-4}
C(17)	5.785	0.215	7.4541×10^{-3}
C(18)	6.160	-0.160	4.9312×10^{-3}
C(19)	6.033	0.033	2.5632×10^{-3}
C(20)	5.440	0.560	5.4929×10^{-3}
C(21)	5.782	0.218	1.3686×10^{-3}
C(22)	6.129	-0.129	9.6846×10^{-4}
C(23)	6.204	-0.204	9.9124×10^{-4}
C(24)	6.126	-0.126	5.2539×10^{-3}
C(25)	6.108	-0.108	3.0719×10^{-3}
C(26)	6.170	-0.170	-5.3078×10^{-3}
C(71)	5.979	0.021	-3.8269×10^{-3}
C(72)	5.927	0.073	8.9041×10^{-3}
C(73)	5.934	0.066	-1.2340×10^{-3}
C(74)	5.888	0.112	-1.8631×10^{-4}
H(2)	0.855	0.145	4.2892×10^{-5}
H(3)	0.813	0.187	-4.7243×10^{-5}
H(5)	0.793	0.207	7.2176×10^{-4}
H(6)	0.701	0.299	6.8204×10^{-5}
H(9)	0.817	0.183	2.8342×10^{-6}
H(10)	0.876	0.124	2.0878×10^{-5}
H(11)	0.950	0.050	-3.5827×10^{-6}
H(12)	0.877	0.123	-1.5333×10^{-5}
H(13)	0.834	0.166	1.8868×10^{-6}
H(15)	0.752	0.248	9.2766×10^{-6}
H(16)	0.836	0.164	-1.2174×10^{-4}
H(18)	0.821	0.179	1.1655×10^{-4}
H(19)	0.852	0.148	1.5474×10^{-4}
H(22)	0.889	0.111	-1.0688×10^{-4}
H(23)	0.872	0.128	1.5323×10^{-4}
H(24)	0.976	0.024	8.6745×10^{-6}
H(25)	0.860	0.140	2.3856×10^{-6}
H(26)	0.679	0.321	-1.3997×10^{-4}
H(71A)	0.898	0.102	-6.0493×10^{-5}
H(71B)	0.924	0.076	-1.3698×10^{-5}
H(71C)	0.921	0.079	5.2644×10^{-5}
H(72A)	0.949	0.051	4.2802×10^{-5}
H(72B)	1.026	-0.026	-1.2603×10^{-5}
H(72C)	0.930	0.070	-5.9085×10^{-5}
H(73A)	0.983	0.017	9.9322×10^{-6}
H(73B)	0.940	0.060	2.1117×10^{-5}
H(73C)	0.851	0.149	-2.2433×10^{-6}
H(74A)	0.842	0.158	-6.7710×10^{-5}
H(74B)	0.808	0.192	3.7203×10^{-4}
H(74C)	0.983	0.017	-1.1498×10^{-4}

H(2A)	0.570	0.430	-8.2355×10^{-5}
H(3A)	0.539	0.461	1.3115×10^{-4}
H(5A)	0.695	0.305	-4.0549×10^{-5}
H(6A)	0.541	0.459	1.9354×10^{-4}

Table S15: Bader charges of the atoms in **7**.

Atom	Atomic Population (*e*)	Net charge (*e*)	Atomic Lagrangian (a.u)
Cl(1)	17.296	-0.296	4.8178×10^{-3}
O(1)	9.047	-1.047	1.0811×10^{-4}
O(2)	8.528	-0.528	2.358×10^{-4}
O(3)	8.532	-0.532	6.5751×10^{-5}
O(4)	8.500	-0.500	1.0146×10^{-4}
O(5)	8.500	-0.500	-1.4803×10^{-4}
N(1)	6.740	0.260	-1.0396×10^{-3}
N(2)	8.098	-1.098	2.8992×10^{-3}
N(3)	8.121	-1.121	7.7730×10^{-5}
N(4)	6.782	0.218	-2.7230×10^{-3}
N(5)	7.930	-0.930	1.7449×10^{-2}
C(1)	5.823	0.177	1.3921×10^{-3}
C(2)	6.096	-0.096	6.2566×10^{-4}
C(3)	6.111	-0.111	-2.4336×10^{-3}
C(4)	5.652	0.348	2.3717×10^{-3}
C(5)	6.007	-0.007	2.8160×10^{-3}
C(6)	6.049	-0.049	-3.3163×10^{-3}
C(7)	4.494	1.506	-4.8031×10^{-3}
C(8)	5.660	0.340	5.3388×10^{-3}
C(9)	6.114	-0.114	-2.4080×10^{-3}
C(10)	6.071	-0.071	4.3161×10^{-3}
C(11)	5.787	0.213	5.5666×10^{-3}
C(12)	5.979	0.021	2.7422×10^{-3}
C(13)	6.008	-0.008	3.1211×10^{-3}
C(14)	5.826	0.174	-7.4033×10^{-3}
C(15)	5.782	0.218	-6.5715×10^{-3}
C(16)	5.851	0.149	-2.8639×10^{-3}
C(17)	5.806	0.194	-6.0781×10^{-3}
H(2)	0.846	0.154	1.3955×10^{-4}
H(3)	0.819	0.181	-9.6069×10^{-6}
H(5)	0.766	0.234	1.0429×10^{-4}
H(6)	0.817	0.183	8.8546×10^{-5}
H(9)	0.749	0.251	-2.9003×10^{-5}
H(10)	0.803	0.197	-8.5883×10^{-5}
H(12)	0.844	0.156	-3.7284×10^{-4}
H(13)	0.794	0.206	3.3874×10^{-4}
H(14A)	0.949	0.051	-1.0725×10^{-5}
H(14B)	0.952	0.048	1.4915×10^{-4}
H(14C)	0.881	0.119	-1.3456×10^{-5}
H(15A)	0.950	0.050	-2.5833×10^{-5}

H(15B)	0.940	0.060	-1.2954 x10^{-4}
H(15C)	0.976	0.024	1.5374 x10^{-4}
H(16A)	0.966	0.034	6.0685 x10^{-5}
H(16B)	0.932	0.068	6.8646 x10^{-5}
H(16C)	0.908	0.092	5.9650 x10^{-5}
H(17A)	0.906	0.093	1.2846 x10^{-4}
H(17B)	0.974	0.026	7.4247 x10^{-5}
H(17C)	0.929	0.071	7.6634 x10^{-5}
H(2A)	0.566	0.434	-4.7707 x10^{-5}
H(3A)	0.539	0.461	4.3218 x10^{-4}

Table S16: Bader charges of the atoms in **8**.

Atom	Atomic Population (*e*)	Net charge (*e*)	Atomic Lagrangian (a.u)
CL(1)	17.163	-0.163	-1.3670 x10^{-4}
S(2)	16.099	-0.099	1.9872 x10^{-3}
S(1)	14.834	1.166	-5.1875 x10^{-3}
O(5)	8.476	-0.476	-2.1651 x10^{-4}
O(6)	8.471	-0.471	-7.8857 x10^{-4}
O(7)	8.518	-0.518	-1.8368 x10^{-4}
O(8)	8.517	-0.517	9.9540 x10^{-4}
O(1)	8.483	-0.483	-1.5416 x10^{-4}
O(2)	8.478	-0.478	-8.9338 x10^{-4}
O(3)	8.429	-0.429	-1.9486 x10^{-5}
O(4)	8.436	-0.436	1.4695 x10^{-4}
N(9)	7.998	-0.998	-1.7926 x10^{-2}
N(5)	6.940	0.060	4.9791 x10^{-3}
N(6)	8.369	-1.369	5.6059 x10^{-3}
N(7)	8.180	-1.180	8.0997 x10^{-4}
N(8)	6.891	0.109	1.2905 x10^{-2}
N(1)	6.869	0.131	2.0621 x10^{-3}
N(2)	8.122	-1.122	5.6545 x10^{-3}
N(3)	8.050	-1.050	2.0733 x10^{-4}
N(4)	7.009	-0.009	-9.5107 x10^{-3}
C(91)	5.801	0.199	-4.6434 x10^{-3}
C(92)	6.243	-0.243	1.3602 x10^{-3}
C(93)	6.163	-0.163	-4.3021 x10^{-3}
C(94)	6.059	-0.059	-1.6923 x10^{-3}
C(95)	5.687	0.313	4.6441 x10^{-3}
C(96)	6.451	-0.451	4.9070 x10^{-3}
C(97)	6.075	-0.075	-4.6154 x10^{-3}
C(98)	6.469	-0.469	1.4031 x10^{-3}
C(14)	5.909	0.091	4.0715 x10^{-3}
C(15)	5.875	0.125	6.9612 x10^{-3}
C(16)	5.751	0.249	4.1558 x10^{-3}
C(17)	5.679	0.321	5.0052 x10^{-3}
C(18)	6.285	-0.285	2.2258 x10^{-3}
C(19)	6.030	-0.030	4.0248 x10^{-3}

C(20)	5.366	0.634	3.7315×10^{-3}
C(21)	5.693	0.307	6.0971×10^{-3}
C(22)	6.186	-0.186	2.3537×10^{-3}
C(23)	6.021	-0.021	4.9192×10^{-3}
C(24)	5.708	0.292	1.0539×10^{-2}
C(25)	6.227	-0.227	2.4606×10^{-3}
C(26)	5.993	0.007	4.7077×10^{-3}
C(1)	6.068	-0.068	-3.4557×10^{-4}
C(2)	6.180	-0.180	1.6268×10^{-3}
C(3)	5.760	0.240	3.0662×10^{-3}
C(4)	5.599	0.401	3.9262×10^{-3}
C(5)	5.950	0.050	-1.9109×10^{-4}
C(6)	6.260	-0.260	5.3956×10^{-3}
C(7)	5.372	0.628	7.3313×10^{-5}
C(8)	5.940	0.060	-3.0168×10^{-2}
C(9)	6.123	-0.123	-8.4004×10^{-3}
C(10)	5.796	0.204	-1.0460×10^{-2}
C(11)	5.902	0.098	-6.8950×10^{-3}
C(12)	6.103	-0.103	-6.2890×10^{-3}
C(13)	6.148	-0.148	-1.0448×10^{-3}
H(91A)	0.964	0.036	2.7153×10^{-4}
H(91B)	0.909	0.091	-5.3411×10^{-4}
H(92A)	0.949	0.051	2.2923×10^{-5}
H(92B)	0.926	0.074	-3.5095×10^{-4}
H(92C)	0.983	0.017	-5.9359×10^{-4}
H(93A)	0.820	0.180	3.2059×10^{-4}
H(93B)	0.825	0.175	-1.7879×10^{-4}
H(94A)	0.924	0.076	1.5616×10^{-4}
H(94B)	0.878	0.122	1.2667×10^{-4}
H(94C)	1.107	-0.107	3.4531×10^{-4}
H(95A)	0.859	0.141	-1.6295×10^{-4}
H(95B)	0.815	0.185	3.2919×10^{-4}
H(96A)	0.992	0.008	6.4572×10^{-4}
H(96B)	0.862	0.138	4.1537×10^{-4}
H(96C)	1.011	-0.011	-1.7034×10^{-4}
H(97A)	0.970	0.030	-2.2839×10^{-4}
H(97B)	0.956	0.044	-8.1533×10^{-4}
H(98A)	0.615	0.385	6.8477×10^{-6}
H(98B)	0.630	0.370	2.2196×10^{-4}
H(98C)	1.013	-0.013	-7.2442×10^{-6}
H(15)	0.912	0.088	3.5507×10^{-4}
H(16)	0.906	0.094	1.7707×10^{-4}
H(18)	0.805	0.195	3.7795×10^{-4}
H(19)	0.991	0.009	-2.3435×10^{-4}
H(22)	0.758	0.242	-9.3760×10^{-6}
H(23)	0.683	0.316	-3.6946×10^{-5}
H(25)	1.012	-0.012	-7.0310×10^{-4}
H(26)	0.623	0.377	3.8575×10^{-4}

H(6A)	0.339	0.661	1.2913×10^{-4}
H(7A)	0.648	0.352	-5.2983×10^{-4}
H(2)	0.728	0.272	-5.7177×10^{-5}
H(3)	0.726	0.274	1.7195×10^{-5}
H(5)	0.638	0.362	7.2990×10^{-5}
H(6)	0.796	0.204	5.2521×10^{-5}
H(9)	0.909	0.091	-2.2350×10^{-4}
H(10)	0.807	0.193	-1.0460×10^{-4}
H(12)	0.669	0.331	-8.5111×10^{-5}
H(13)	0.803	0.197	3.4751×10^{-4}
H(2A)	0.602	0.398	-2.1886×10^{-4}
H(3A)	0.446	0.554	6.0440×10^{-4}

9. Electrostatic potential distribution in **7** and **8**

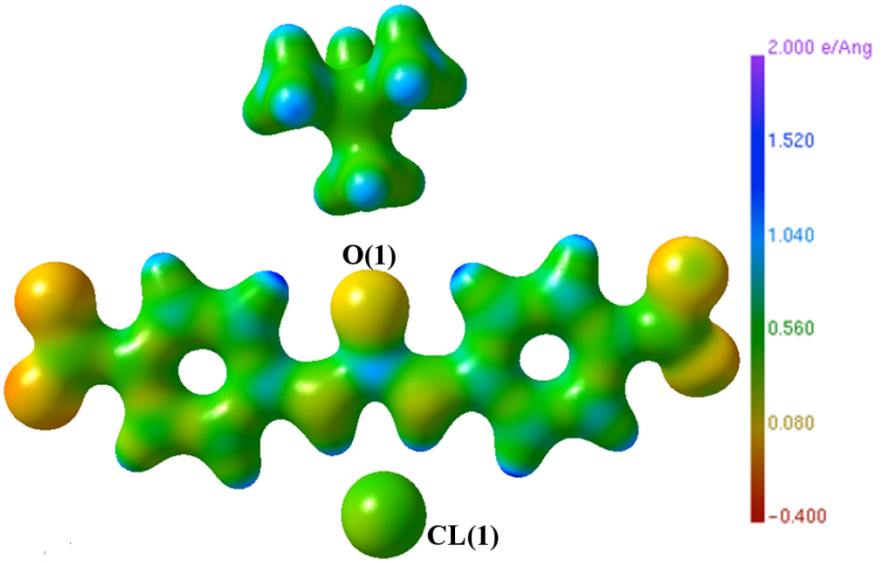


Figure S35: Electrostatic potential distribution in crystal structure **7**

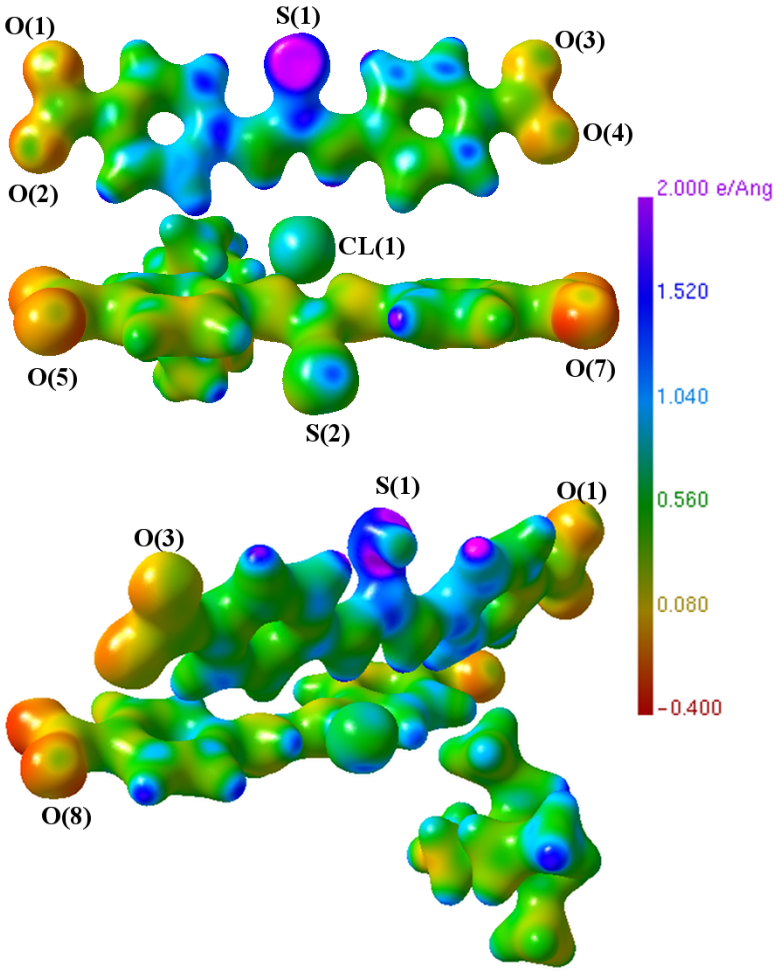


Figure S36: Electrostatic potential distribution in crystal structure **8** shown in two views

10. References

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