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**Supporting information for article:**

**X-ray constrained wavefunctions based on Hirshfeld atoms. II.  
Reproducibility of electron densities in crystals of  $\alpha$ -oxalic acid  
dihydrate**

**Max L. Davidson, Simon Grabowsky and Dylan Jayatilaka**

**S. Supplementary Information for "X-ray constrained wavefunctions based on Hirshfeld atoms. II. Reproducibility of electron densities in crystals of  $\alpha$ -oxalic acid dihydrate" by M. L. Davidson, S. Grabowsky and D. Jayatilaka**

*S.1. Power function fits for the Kaminski et al. (2014) data sets*

Figure S1 shows that the power function fits all the data very well. However, closer examination shows that for large  $\lambda$  the power function overestimates the  $\text{GoF}^2$  value. For  $\lambda$  values not so large, there is a tendency to underestimate the  $\text{GoF}^2$ . Especially in the oxa9 data set for  $\lambda < 0.08$ , the values of  $\text{GoF}^2(\lambda)$  are overestimated. Once again, the alternating over-, under-, over-estimation of  $\text{GoF}^2$  values evokes the change in curvature ideas of Genoni (2013) also seen for the Zobel (1996) data.

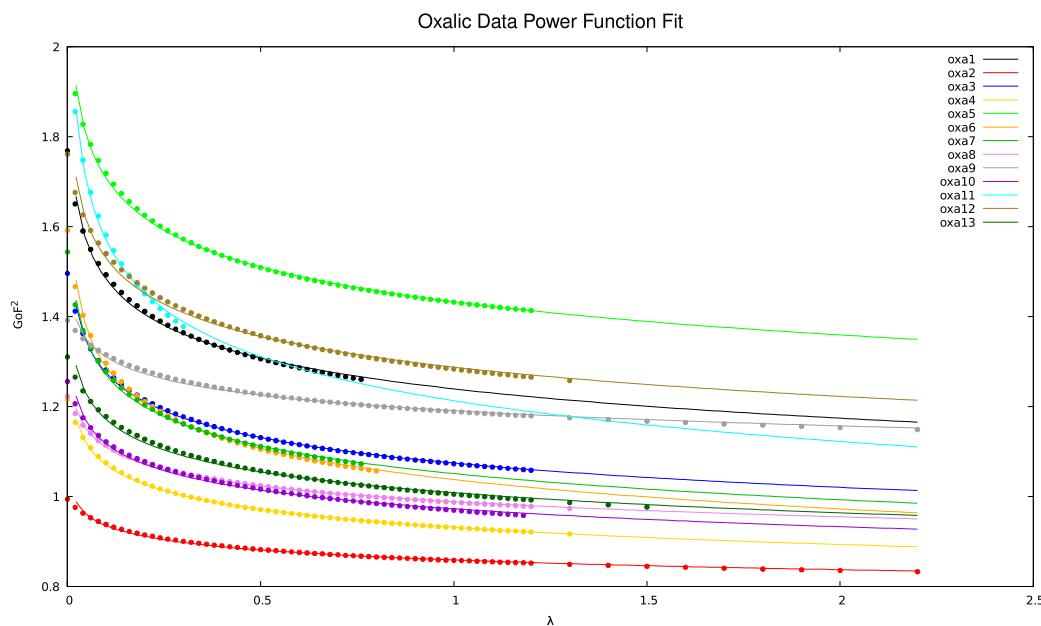


Figure S1:  $\text{GoF}^2$  vs.  $\lambda$  for HA-XCW using a RHF/def2-SVP wavefunction for all the Kaminski *et al.* (2014) data sets (dots). Power function fits are also shown (lines).  $\text{GoF}^2$  values at  $\lambda = \lambda_{\max}$  and  $\lambda = \lambda_{\text{opt}}$  for the different extrapolation methods are listed in Table 4. oxa11 has a data point at (0, 2.13) and oxa5 has a data point (0, 2.01).

For the power function model, we observe that  $0.86 < A < 1.43$  and  $-0.110 < B < -0.037$  for all the data sets (Table S1). In spite of the fact that the data have been

collected from separate experiments, most of the  $A$  values are close to unity, which lends some support to the notion that  $A$  is indeed a scaling factor associated with the  $\sigma$ s, i.e. it is a measure of the error in the errors, as was argued in section 2.1. Moreover, the smallest  $A$  parameters are associated with the best Q-Q plots (namely oxa2, oxa4, oxa8, oxa10 and oxa13, oxa9 is an exception with  $A = 1.19$ , see figure S9), further supporting the idea of the  $A$  parameter as a scale factor based on  $\sigma$  (figure S2). Still, this is somewhat surprising since, given the exponential nature of the power function form, one might have expected only an order of magnitude agreement. It was possible to terminate the XCW at  $\lambda = \lambda_{\text{pow}}$  in 9 out of 13 of the data sets.

Table S1: Model parameters for HA-XCW.  $A$  and  $B$  are for the power function model, equation (2).  $D$ ,  $E$  and  $F$  are for the even-order asymptotic fits, equation (7), for the last points in Table 4. “All” represents values for the simultaneous refinement of all Kaminski *et al.* data sets except oxa2, while “All<sub>min</sub>” is the same but using data only up to the minimum of all the  $\lambda_{\text{pen}}$  values, in this case  $\lambda = 0.28$ .

Data set	<i>A</i>	<i>B</i>	<i>D</i>	<i>E</i>	<i>F</i>	<i>D</i>	<i>E</i>	<i>F</i>
	3-point fit				6-point fit			
oxa1	1.239(2)	-0.0780(9)	1.195	0.046	-0.0044	1.188(3)	0.054(3)	-0.0066(7)
oxa2	0.8589(4)	-0.0369(4)	0.8123	0.122	-0.119	0.8143(5)	0.106(3)	-0.087(5)
oxa3	1.0744(7)	-0.0743(5)	0.981	0.164	-0.077	1.005(4)	0.10(1)	-0.031(7)
oxa4	0.9315(4)	-0.0605(3)	0.876	0.092	-0.039	0.881(1)	0.077(3)	-0.027(2)
oxa5	1.433(1)	-0.0761(5)	1.328	0.171	-0.070	1.346(3)	0.122(7)	-0.036(5)
oxa6	1.038(2)	-0.0936(9)	0.986	0.059	-0.0085	0.988(2)	0.056(2)	-0.0078(7)
oxa7	1.051(1)	-0.0821(8)	1.008	0.049	-0.0069	1.017(1)	0.040(1)	-0.0044(2)
oxa8	0.9886(5)	-0.0501(4)	0.938	0.080	-0.031	0.940(1)	0.074(3)	-0.027(2)
oxa9	1.1909(8)	-0.0415(5)	1.1183	0.181	-0.164	1.1201(7)	0.166(5)	-0.136(8)
oxa10	0.9727(8)	-0.0603(6)	0.9191	0.063	-0.012	0.9124(6)	0.081(2)	-0.025(1)
oxa11	1.213(6)	-0.112(2)	1.262	0.0132	-0.00024	1.282(3)	0.0102(4)	-0.00014(1)
oxa12	1.288(1)	-0.0747(8)	1.187	0.155	-0.062	1.195(2)	0.132(5)	-0.044(3)
oxa13	1.008(1)	-0.0651(8)	0.928	0.138	-0.068	0.934(1)	0.118(4)	-0.049(3)
All	1.4053(6)	-0.0554(3)	1.346	0.084	-0.026	1.350(4)	0.073(9)	-0.018(6)
All <sub>min</sub>	1.417(4)	-0.052(1)	1.441	0.0070	-0.000131	1.461(2)	0.0044(2)	-0.000050(5)

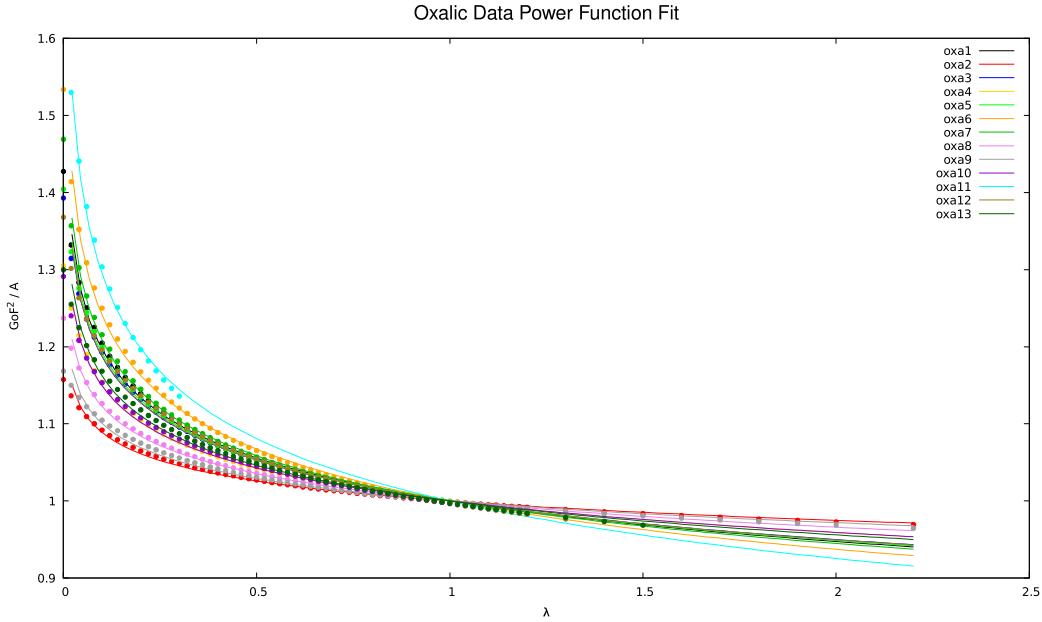


Figure S2:  $\text{GoF}_{\text{corr}}^2 = \text{GoF}^2/A$  vs.  $\lambda$  for HA-XCW using a RHF/def2-SVP wavefunction for all Kaminski *et al.* (2014) data sets. Dots represent actual data and lines are the power function fits. The  $A$  value is taken from the power function coefficient, see table S1. oxa11 has a data point at (0, 1.75).

### S.2. Asymptotic extrapolation halting procedure for the Kaminski *et al.* (2014) data sets

For the TIH halting method, Table S1 shows that for all data sets we have  $D > 0$ ,  $E > 0$  but  $F < 0$  and that  $|D| > |E| > |F|$  which superficially indicates that we are in the asymptotic region. However, a closer investigation shows that the lower-bound condition, equation (9), is always violated (as  $|F|/|E| > |E|/|D|$ ). In this case, as discussed in section 2.2, we employ only the upper-bound condition, equation (8), to estimate the value of  $\lambda$  to halt the fitting procedure.

Of all the three parameters, it is interesting to see that the  $D$  values are very similar for the 3- and 6-point fits: the largest difference is about 3% for data set oxa3. The  $E$  and  $F$  values are not as close to each other, sometimes being different by as much as 60%. The  $F$  values are the smallest of the three parameters by magnitude and differ by up to 150%.

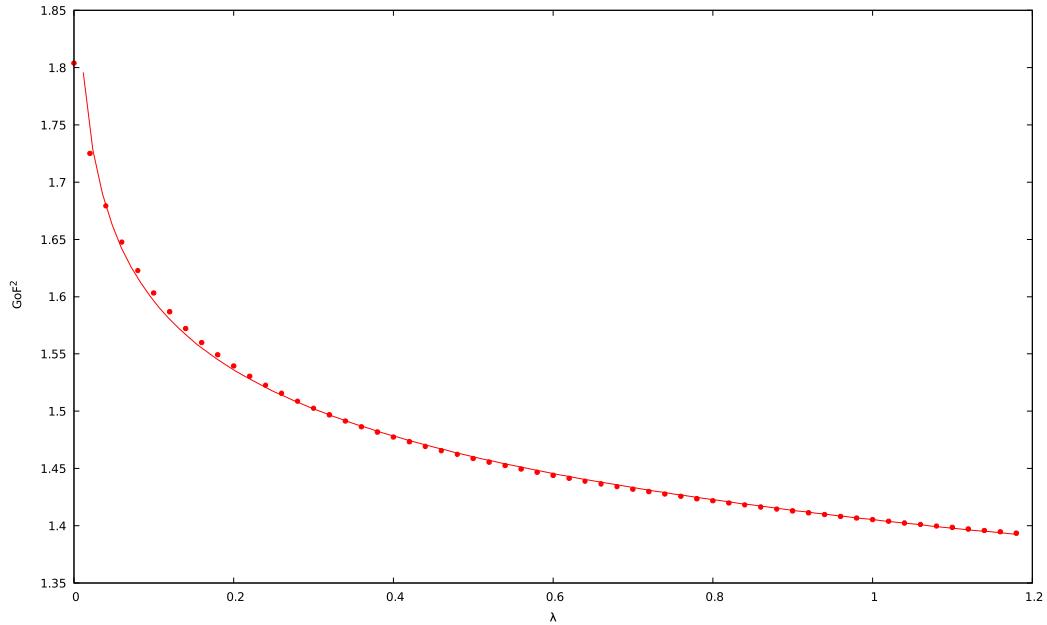


Figure S3:  $\text{GoF}^2$  versus  $\lambda$  for a simultaneous HA-XCW using a RHF/def2-SVP wavefunction for 12 of the Kaminski *et al.* (2014) data sets, with a fitted power function  $A\lambda^B$ , with  $A = 1.4053(6)$ , and  $B = -0.0554(3)$ .

### S.3. Power function fits for the joint refinement

For the joint refinement, figure S3 shows the power function fit. Table S1 shows that, although parameter uncertainties are small for  $A$  and  $B$ , the  $A$  parameter is significantly larger in magnitude than values obtained for the individual data sets, except for  $A$  in oxa5. The  $B$  parameter is more in line with the others, except for oxa11, which is nearly double in size.

### S.4. Asymptotic extrapolation halting procedure for the joint refinement

A similar observation is true for the  $D$  parameters of both the 3- and 6-point asymptotic extrapolation fittings, as it is larger than the average of the parameters from the individual refinements, but still smaller than for individual data sets oxa1, oxa5, oxa11 and oxa12. By comparison, the  $E$  parameter is smaller than the average of the individual data sets, but  $E$  values were highly variable between data sets. The

corresponding  $\lambda_{\text{TIH}3} = 0.25$  and  $\lambda_{\text{TIH}6} = 0.23$  values are nearly the same, as with the individual data sets, but still quite different from the halting value of the power function procedure of  $\lambda_{\text{pow}} = 1$ . Nevertheless, as already explained, the corresponding GoF<sup>2</sup> values for  $\lambda_{\text{TIH}6}$  and  $\lambda_{\text{pow}}$  are 1.516 and 1.405, respectively, and are very similar.

amplitudes

### S.5. GoF<sup>2</sup> versus $\lambda$ exponential form for Kaminski et al. (2014) data

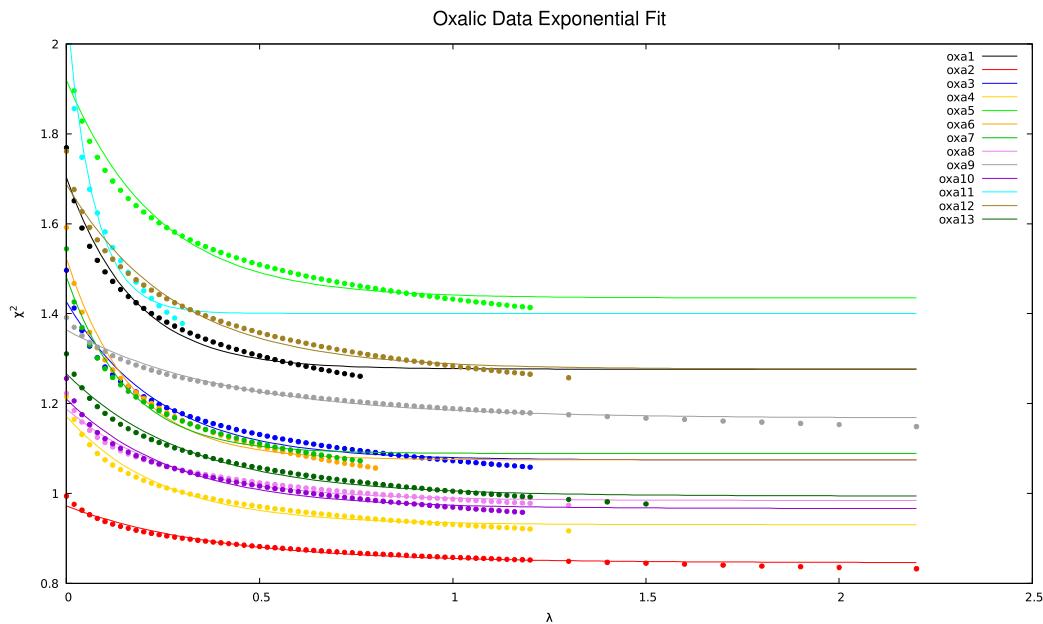


Figure S4: GoF<sup>2</sup> versus  $\lambda$  for a HA-XCW using a RHF/def2-SVP wavefunction for the Zobel (1996) data set, with fitted exponential functions of the form  $Ae^{B\lambda} + C$ .

S.6.  $\text{GoF}^2$  versus  $\lambda$  Padé approximant form for Kaminski et al. (2014) data

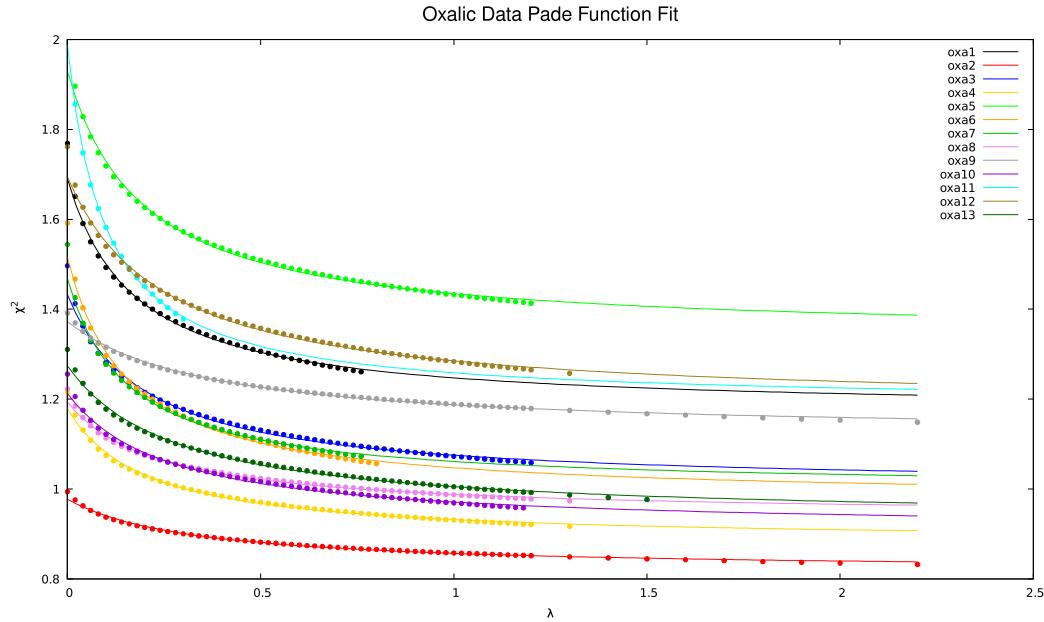


Figure S5:  $\text{GoF}^2$  versus  $\lambda$  for a HA-XCW using a RHF/def2-SVP wavefunction for the Zobel (1996) data set, with a [1/1]-Padé function of the form  $\text{GoF}^2(\lambda) = a + \frac{b\lambda}{1+c}$ .

*S.7. Distribution of A and B parameters for the power function method applied to the Kaminski et al. (2014) data sets.*

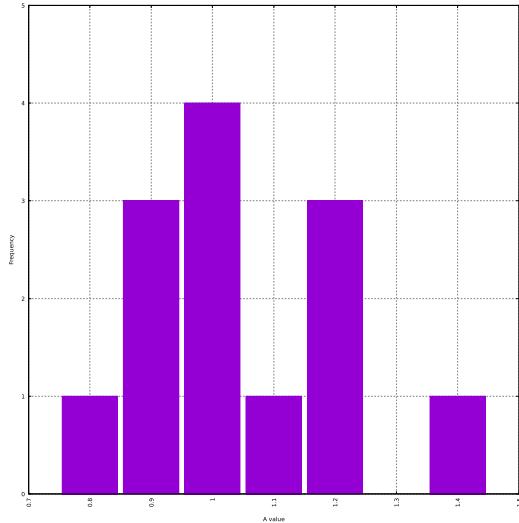


Figure S6: Distribution of the  $A$  parameter across the Kaminski et al. (2014) data sets.

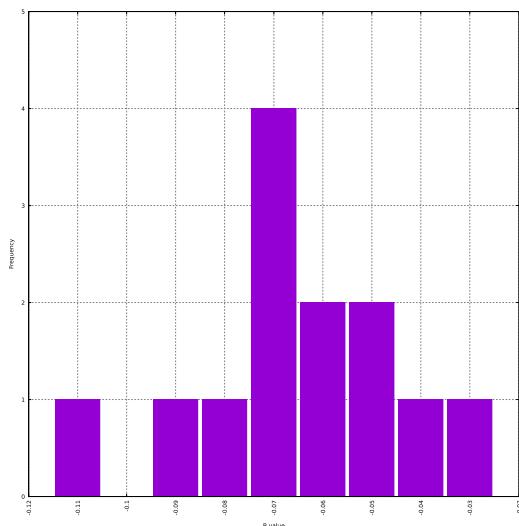


Figure S7: Distribution of the  $B$  parameter across the Kaminski et al. (2014) data sets.

*S.8. HAR & XCW simultaneous refinement on Kaminski et al. data; refinement of scale factors*

Table S2: Scale factors for each data set in the simultaneous HAR and XCW of all Kaminski *et al.* (2014) (except oxa2).

Data set	HAR	XCW		
		$\lambda_{\text{TIH6}}$	$\lambda_{\min}$	$\lambda_{\text{pen}}$
	0.23	0.28	1.16	
oxa1	1.005	1.004	1.004	1.002
oxa3	1.006	1.005	1.005	1.003
oxa4	1.018	1.016	1.016	1.014
oxa5	0.985	0.984	0.984	0.982
oxa6	1.001	1.000	1.000	0.998
oxa7	0.983	0.981	0.981	0.979
oxa8	0.996	0.994	0.994	0.992
oxa9	1.012	1.011	1.010	1.008
oxa10	0.988	0.986	0.985	0.983
oxa11	0.999	0.998	0.998	0.996
oxa12	1.009	1.008	1.008	1.006
oxa13	0.994	0.992	0.992	0.990

### S.9. Abrahams-Keeve QQ Plots

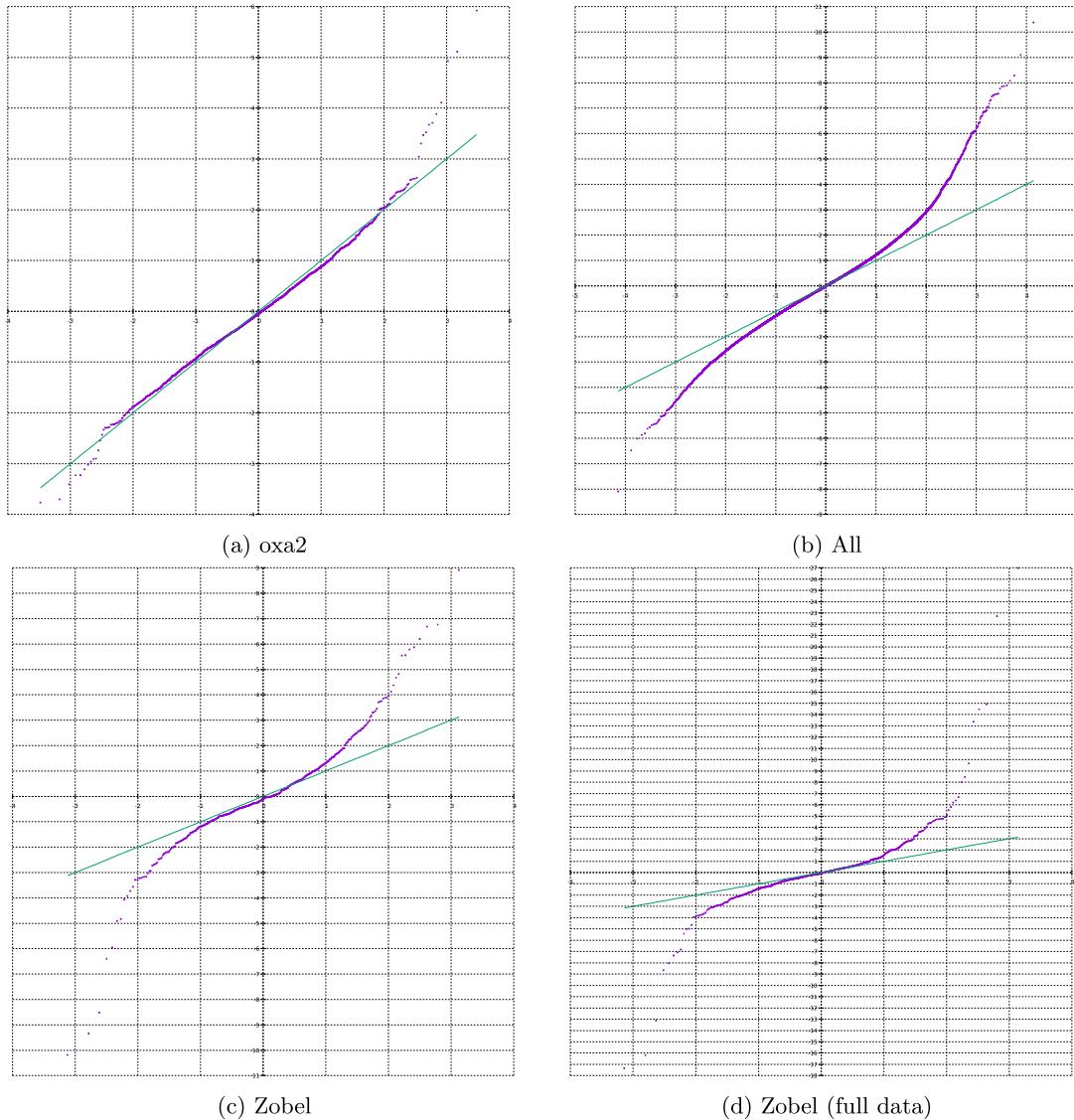


Figure S8: QQ plots for HAR after outlier removal and after pruning according to the  $|F| > 4\sigma$  criterion for (a) the oxa2 Kaminski *et al.* (2014) data set, (b) the simultaneous refinement of all data sets of Kaminski *et al.* (2014) except oxa2, and (c) the Zobel (1996) data set used in GJ2001. (d) The Zobel (1996) data set before outlier removal and pruning.

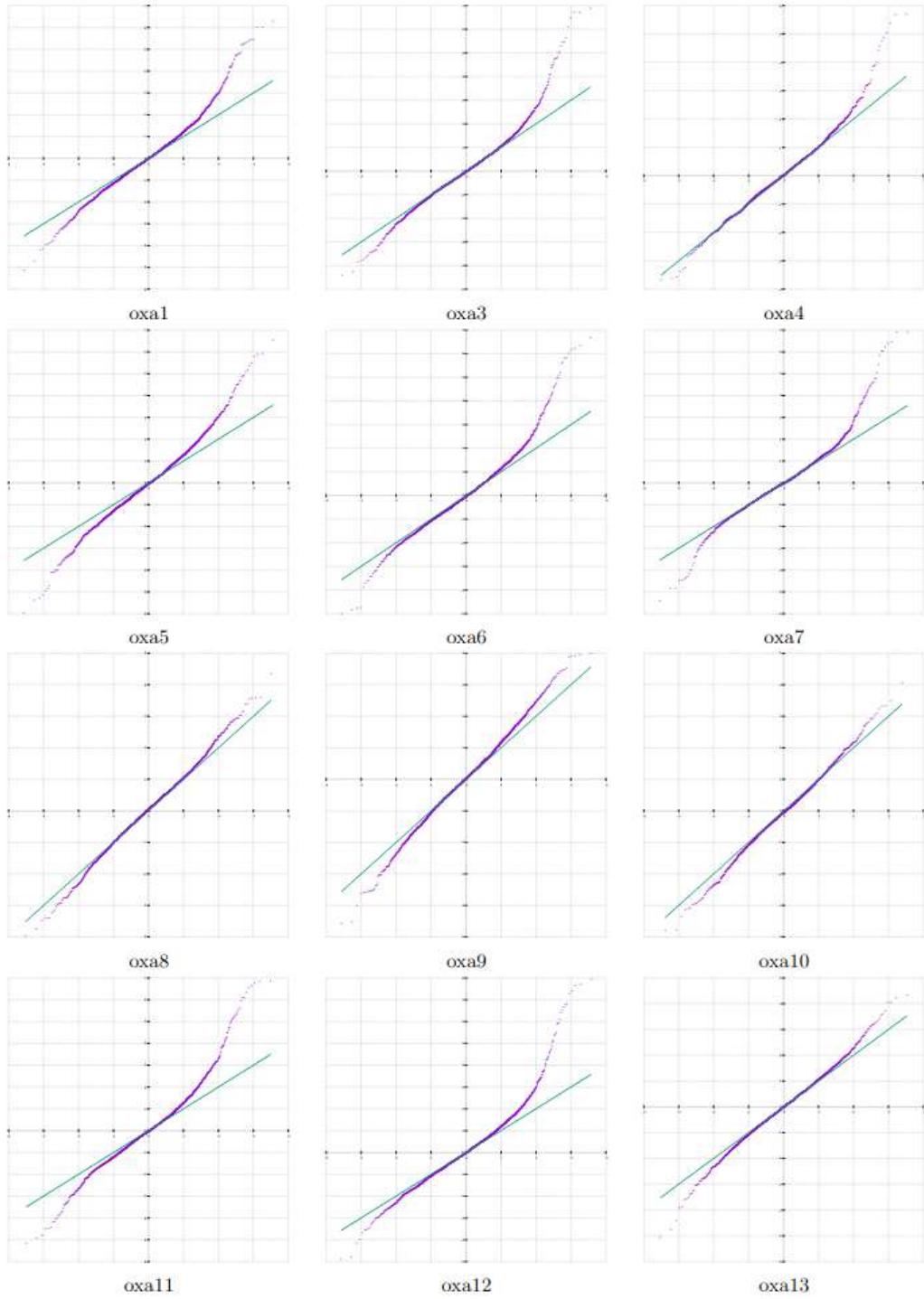


Figure S9: QQ plots for HAR after outlier removal and after pruning according to the  $|F| > 4\sigma$  criterion for the Kaminski *et al.* (2014) data sets (except for oxa2).

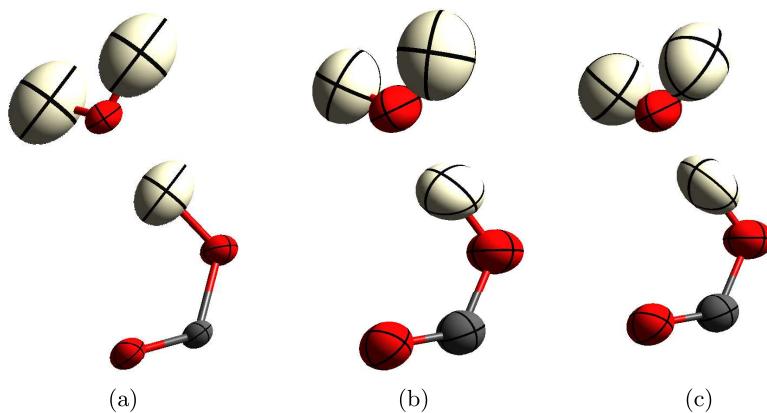
*S.10. ORTEP plots for Kaminski et al. (2014) data*

Figure S10: HAR ORTEP plots (after outlier removal) for (a) the Zobel (1996) data set used in GJ2001, (b) the oxa2 Kaminski *et al.* (2014) data set, (c) the simultaneous refinement of all Kaminski *et al.* (2014) data sets (except oxa2). All views are in approximately the same orientation relative to the unit cell with the 99% probability level.

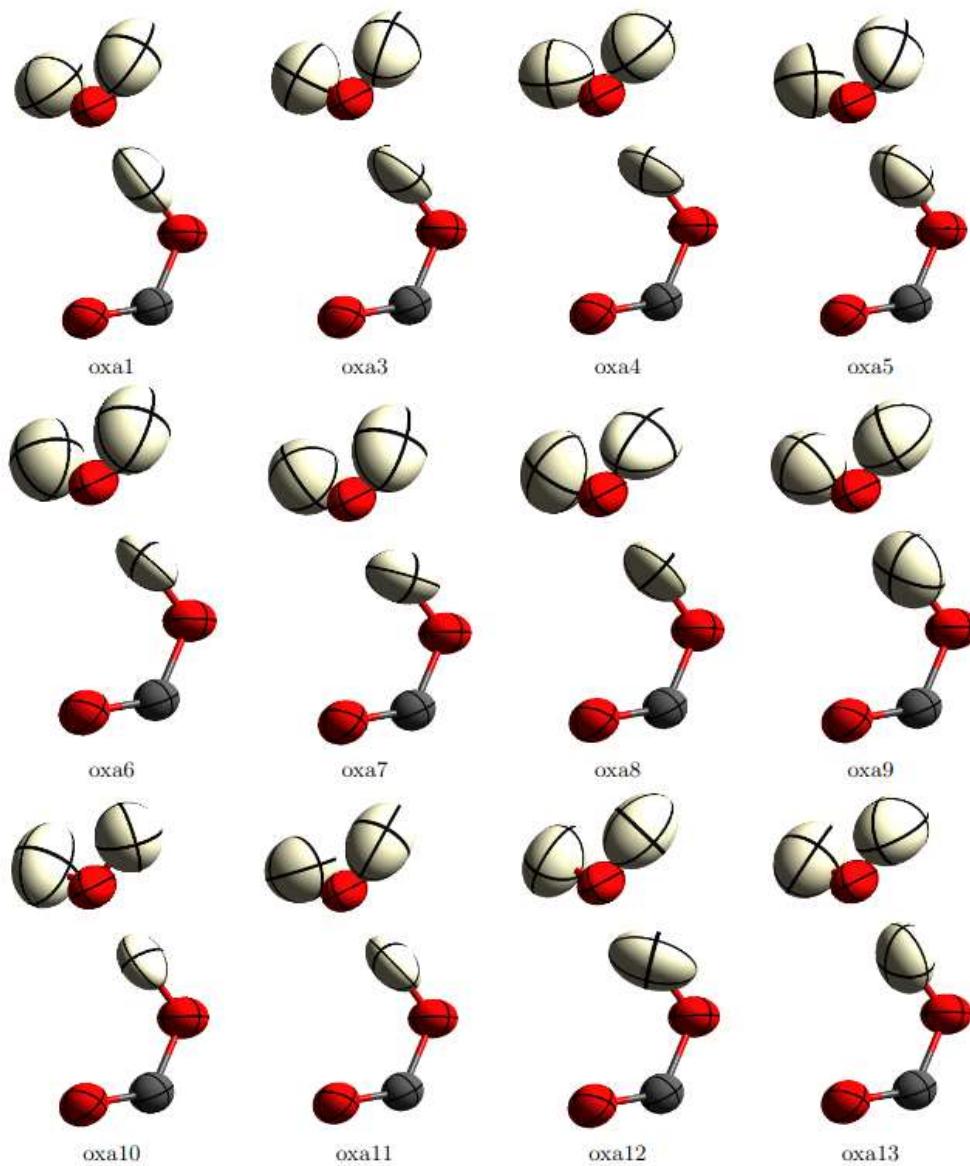


Figure S11: HAR ORTEP plots after outlier removal for the Kaminski *et al.* (2014) data sets (except *oxa2*). All views are in the same orientation relative to the unit cell with the 99% probability level.

*S.11. Outlier reflections removed*

Table S3: Outlier reflections removed from the Zobel (1996) data set, and associated  $(|F_r^{\text{obs}}| - |F_r^{\text{calc}}|)/\sigma(|F_r^{\text{obs}}|)$  values.

$h_1$	$h_2$	$h_3$	$\Delta F/\sigma$
0	0	2	22.41
1	0	-1	13.22
1	1	0	-16.24
1	2	-3	14.66
2	0	2	-13.07
2	0	-4	-17.37
2	1	4	27.30
5	1	-2	14.91



*S.12. GoF<sup>2</sup> versus  $\lambda$  data*

Table S5: GoF<sup>2</sup> versus  $\lambda$  for data set oxa1 of Kaminski *et al.* (2014)

$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>
0.00	1.769137	0.50	1.306158
0.02	1.650938	0.52	1.301819
0.04	1.590622	0.54	1.297723
0.06	1.549561	0.56	1.293702
0.08	1.518286	0.58	1.289799
0.10	1.493065	0.60	1.286158
0.12	1.471856	0.62	1.282657
0.14	1.453882	0.64	1.279074
0.16	1.437918	0.66	1.275887
0.18	1.424166	0.68	1.272583
0.20	1.411826	0.70	1.269562
0.22	1.400508	0.72	1.266485
0.24	1.390443	0.74	1.263497
0.26	1.381032	0.76	1.260659
0.28	1.372180		
0.30	1.364306		
0.32	1.356741		
0.34	1.349749		
0.36	1.343293		
0.38	1.336988		
0.40	1.331408		
0.42	1.325760		
0.44	1.320607		
0.46	1.315530		
0.48	1.310744		

Table S6: GoF<sup>2</sup> versus  $\lambda$  for data set oxa2 of Kaminski *et al.* (2014)

$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>
0.00	0.994179	0.50	0.882121	1.00	0.857927
0.02	0.975925	0.52	0.880722	1.02	0.857336
0.04	0.962843	0.54	0.879389	1.04	0.856635
0.06	0.952791	0.56	0.878064	1.06	0.856001
0.08	0.944794	0.58	0.876833	1.08	0.855393
0.10	0.937834	0.60	0.875667	1.10	0.854774
0.12	0.931881	0.62	0.874439	1.12	0.854187
0.14	0.926997	0.64	0.873367	1.14	0.853571
0.16	0.922414	0.66	0.872255	1.16	0.852964
0.18	0.918414	0.68	0.871197	1.18	0.852417
0.20	0.914710	0.70	0.870219	1.20	0.851889
0.22	0.911428	0.72	0.869231	1.30	0.849210
0.24	0.908419	0.74	0.868295	1.40	0.846825
0.26	0.905514	0.76	0.867336	1.50	0.844599
0.28	0.902968	0.78	0.866442	1.60	0.842505
0.30	0.900282	0.80	0.865578	1.70	0.840584
0.32	0.898099	0.82	0.864752	1.80	0.838729
0.34	0.895891	0.84	0.863880	1.90	0.837053
0.36	0.893884	0.86	0.863143	2.00	0.835441
0.38	0.891948	0.88	0.862308	2.20	0.832488
0.40	0.890121	0.90	0.861539		
0.42	0.888379	0.92	0.860775		
0.44	0.886691	0.94	0.860048		
0.46	0.885111	0.96	0.859354		
0.48	0.883567	0.98	0.858655		

Table S7: GoF<sup>2</sup> versus  $\lambda$  for data set oxa3 of Kaminski *et al.* (2014)

$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>
0.00	1.496472	0.50	1.130996	1.00	1.072893
0.02	1.412423	0.52	1.127591	1.02	1.071323
0.04	1.362855	0.54	1.124251	1.04	1.069808
0.06	1.328006	0.56	1.121074	1.06	1.068293
0.08	1.302266	0.58	1.118089	1.08	1.066848
0.10	1.281630	0.60	1.115143	1.10	1.065379
0.12	1.264278	0.62	1.112380	1.12	1.063921
0.14	1.249588	0.64	1.109705	1.14	1.062592
0.16	1.236723	0.66	1.107148	1.16	1.061192
0.18	1.225460	0.68	1.104508	1.18	1.059891
0.20	1.215346	0.70	1.102072	1.20	1.058566
0.22	1.206267	0.72	1.099746		
0.24	1.198025	0.74	1.097526		
0.26	1.190512	0.76	1.095254		
0.28	1.183655	0.78	1.093099		
0.30	1.177248	0.80	1.091031		
0.32	1.171288	0.82	1.088998		
0.34	1.165755	0.84	1.087071		
0.36	1.160494	0.86	1.085121		
0.38	1.155429	0.88	1.083187		
0.40	1.150996	0.90	1.081431		
0.42	1.146492	0.92	1.079637		
0.44	1.142170	0.94	1.077944		
0.46	1.138305	0.96	1.076190		
0.48	1.134550	0.98	1.074562		

Table S8:  $\text{GoF}^2$  versus  $\lambda$  for data set oxa4 of Kaminski *et al.* (2014)

$\lambda$	$\text{GoF}^2$	$\lambda$	$\text{GoF}^2$	$\lambda$	$\text{GoF}^2$
0.00	1.215416	0.50	0.970900	1.00	0.930942
0.02	1.164582	0.52	0.968499	1.02	0.929870
0.04	1.131420	0.54	0.966229	1.04	0.928839
0.06	1.108501	0.56	0.964177	1.06	0.927840
0.08	1.088913	0.58	0.962012	1.08	0.926788
0.10	1.075100	0.60	0.959929	1.10	0.925755
0.12	1.063143	0.62	0.958047	1.12	0.924819
0.14	1.053064	0.64	0.956218	1.14	0.923861
0.16	1.044158	0.66	0.954379	1.16	0.922972
0.18	1.036265	0.68	0.952656	1.18	0.922011
0.20	1.029236	0.70	0.950936	1.20	0.921142
0.22	1.023070	0.72	0.949393	1.30	0.916872
0.24	1.017296	0.74	0.947785		
0.26	1.012212	0.76	0.946232		
0.28	1.007133	0.78	0.944814		
0.30	1.002838	0.80	0.943405		
0.32	0.998589	0.82	0.941959		
0.34	0.994887	0.84	0.940591		
0.36	0.991236	0.86	0.939287		
0.38	0.987855	0.88	0.938052		
0.40	0.984666	0.90	0.936773		
0.42	0.981623	0.92	0.935482		
0.44	0.978741	0.94	0.934371		
0.46	0.976040	0.96	0.933234		
0.48	0.973333	0.98	0.932067		

Table S9:  $\text{GoF}^2$  versus  $\lambda$  for data set oxa5 of Kaminski *et al.* (2014)

$\lambda$	$\text{GoF}^2$	$\lambda$	$\text{GoF}^2$	$\lambda$	$\text{GoF}^2$
0.00	2.012446	0.50	1.508908	1.00	1.432119
0.02	1.896083	0.52	1.504239	1.02	1.430046
0.04	1.828072	0.54	1.499900	1.04	1.428039
0.06	1.783198	0.56	1.495658	1.06	1.426107
0.08	1.747753	0.58	1.491638	1.08	1.424169
0.10	1.718795	0.60	1.487621	1.10	1.422361
0.12	1.694749	0.62	1.483864	1.12	1.420494
0.14	1.674224	0.64	1.480268	1.14	1.418686
0.16	1.656113	0.66	1.476841	1.16	1.416952
0.18	1.640207	0.68	1.473448	1.18	1.415236
0.20	1.625981	0.70	1.470321	1.20	1.413524
0.22	1.613066	0.72	1.467212		
0.24	1.601602	0.74	1.464178		
0.26	1.591160	0.76	1.461281		
0.28	1.581399	0.78	1.458448		
0.30	1.572406	0.80	1.455605		
0.32	1.564178	0.82	1.453056		
0.34	1.556355	0.84	1.450486		
0.36	1.548991	0.86	1.447952		
0.38	1.542373	0.88	1.445453		
0.40	1.535975	0.90	1.443148		
0.42	1.529925	0.92	1.440817		
0.44	1.524328	0.94	1.438582		
0.46	1.518939	0.96	1.436314		
0.48	1.513686	0.98	1.434173		

Table S10:  $\text{GoF}^2$  versus  $\lambda$  for data set oxa6 of Kaminski *et al.* (2014)

$\lambda$	$\text{GoF}^2$	$\lambda$	$\text{GoF}^2$
0.00	1.591488	0.50	1.105268
0.02	1.467239	0.52	1.101090
0.04	1.402967	0.54	1.097028
0.06	1.358112	0.56	1.093125
0.08	1.324186	0.58	1.089351
0.10	1.297188	0.60	1.085935
0.12	1.274622	0.62	1.082544
0.14	1.255522	0.64	1.079245
0.16	1.238996	0.66	1.076085
0.18	1.224339	0.68	1.073011
0.20	1.211395	0.70	1.070044
0.22	1.200119	0.72	1.067167
0.24	1.189347	0.74	1.064489
0.26	1.179762	0.76	1.061811
0.28	1.170956	0.78	1.059194
0.30	1.162657	0.80	1.056654
0.32	1.155317		
0.34	1.148170		
0.36	1.141676		
0.38	1.135592		
0.40	1.129700		
0.42	1.124294		
0.44	1.119174		
0.46	1.114311		
0.48	1.109772		

Table S11: GoF<sup>2</sup> versus  $\lambda$  for data set oxa7 of Kaminski *et al.* (2014)

$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>
0.00	1.544145	0.50	1.110943
0.02	1.426215	0.52	1.107173
0.04	1.369107	0.54	1.103612
0.06	1.330474	0.56	1.100175
0.08	1.301151	0.58	1.096968
0.10	1.277576	0.60	1.093919
0.12	1.258099	0.62	1.090941
0.14	1.241575	0.64	1.088027
0.16	1.227347	0.66	1.085231
0.18	1.214709	0.68	1.082501
0.20	1.203539	0.70	1.079921
0.22	1.193423	0.72	1.077381
0.24	1.184243	0.74	1.074998
0.26	1.176055	0.76	1.072671
0.28	1.168279		
0.30	1.161254		
0.32	1.154641		
0.34	1.148450		
0.36	1.142837		
0.38	1.137306		
0.40	1.132415		
0.42	1.127561		
0.44	1.123094		
0.46	1.118790		
0.48	1.114742		

Table S12: GoF<sup>2</sup> versus  $\lambda$  for data set oxa8 of Kaminski *et al.* (2014)

$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>
0.00	1.222835	0.50	1.023910	1.00	0.987253
0.02	1.184381	0.52	1.021771	1.02	0.986215
0.04	1.158964	0.54	1.019709	1.04	0.985243
0.06	1.140334	0.56	1.017764	1.06	0.984227
0.08	1.124940	0.58	1.015872	1.08	0.983277
0.10	1.113560	0.60	1.014154	1.10	0.982340
0.12	1.103424	0.62	1.012290	1.12	0.981451
0.14	1.094965	0.64	1.010586	1.14	0.980519
0.16	1.087666	0.66	1.009002	1.16	0.979636
0.18	1.081041	0.68	1.007350	1.18	0.978802
0.20	1.074976	0.70	1.005839	1.20	0.977952
0.22	1.069680	0.72	1.004345	1.30	0.973869
0.24	1.064713	0.74	1.002907		
0.26	1.060322	0.76	1.001491		
0.28	1.056143	0.78	1.000167		
0.30	1.052132	0.80	0.998868		
0.32	1.048644	0.82	0.997552		
0.34	1.045301	0.84	0.996277		
0.36	1.042065	0.86	0.995039		
0.38	1.039123	0.88	0.993841		
0.40	1.036203	0.90	0.992694		
0.42	1.033595	0.92	0.991532		
0.44	1.030991	0.94	0.990414		
0.46	1.028514	0.96	0.989362		
0.48	1.026126	0.98	0.988257		

Table S13: GoF<sup>2</sup> versus  $\lambda$  for data set oxa9 of Kaminski *et al.* (2014)

$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>
0.00	1.391409	0.50	1.227476	1.00	1.188839
0.02	1.369572	0.52	1.225320	1.02	1.187805
0.04	1.350908	0.54	1.223214	1.04	1.186739
0.06	1.336360	0.56	1.221010	1.06	1.185749
0.08	1.325359	0.58	1.219141	1.08	1.184713
0.10	1.315561	0.60	1.217171	1.10	1.183770
0.12	1.306646	0.62	1.215272	1.12	1.182809
0.14	1.299064	0.64	1.213450	1.14	1.181820
0.16	1.292098	0.66	1.211725	1.16	1.180952
0.18	1.285865	0.68	1.210093	1.18	1.180042
0.20	1.280131	0.70	1.208428	1.20	1.179160
0.22	1.274650	0.72	1.206854	1.30	1.174967
0.24	1.269712	0.74	1.205365	1.40	1.171159
0.26	1.265173	0.76	1.203881	1.50	1.167638
0.28	1.260967	0.78	1.202418	1.60	1.164407
0.30	1.257040	0.80	1.200990	1.70	1.161341
0.32	1.253379	0.82	1.199595	1.80	1.158508
0.34	1.249859	0.84	1.198290	1.90	1.155836
0.36	1.246580	0.86	1.197032	2.00	1.153280
0.38	1.243352	0.88	1.195727	2.20	1.148674
0.40	1.240463	0.90	1.194535		
0.42	1.237623	0.92	1.193369		
0.44	1.234898	0.94	1.192136		
0.46	1.232334	0.96	1.191024		
0.48	1.229931	0.98	1.189924		

Table S14: GoF<sup>2</sup> versus  $\lambda$  for data set oxa10 of Kaminski *et al.* (2014)

$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>
0.00	1.255885	0.50	1.016344	1.00	0.969295
0.02	1.206127	0.52	1.013635	1.02	0.967974
0.04	1.175308	0.54	1.011127	1.04	0.966667
0.06	1.152869	0.56	1.008676	1.06	0.965364
0.08	1.135728	0.58	1.006201	1.08	0.964082
0.10	1.121843	0.60	1.004034	1.10	0.962844
0.12	1.110336	0.62	1.001762	1.12	0.961641
0.14	1.100546	0.64	0.999590	1.14	0.960454
0.16	1.092004	0.66	0.997525	1.16	0.959285
0.18	1.084385	0.68	0.995515	1.18	0.958159
0.20	1.077414	0.70	0.993534		
0.22	1.070898	0.72	0.991602		
0.24	1.065461	0.74	0.989742		
0.26	1.060087	0.76	0.987920		
0.28	1.055248	0.78	0.986266		
0.30	1.050710	0.80	0.984423		
0.32	1.046286	0.82	0.982807		
0.34	1.042382	0.84	0.981111		
0.36	1.038430	0.86	0.979499		
0.38	1.034926	0.88	0.978000		
0.40	1.031432	0.90	0.976473		
0.42	1.028132	0.92	0.974952		
0.44	1.024974	0.94	0.973546		
0.46	1.022000	0.96	0.972058		
0.48	1.019121	0.98	0.970652		

Table S15: GoF<sup>2</sup> versus  $\lambda$  for data set oxa11 of Kaminski *et al.* (2014)

$\lambda$	GoF <sup>2</sup>
0.00	2.127754
0.02	1.856252
0.04	1.748031
0.06	1.676462
0.08	1.623665
0.10	1.581642
0.12	1.546846
0.14	1.517480
0.16	1.492309
0.18	1.470388
0.20	1.451065
0.22	1.433600
0.24	1.417699
0.26	1.403476
0.28	1.390294
0.30	1.378188

Table S16: GoF<sup>2</sup> versus  $\lambda$  for data set oxa12 of Kaminski *et al.* (2014)

$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>
0.00	1.761539	0.50	1.357792	1.00	1.283428
0.02	1.676215	0.52	1.353444	1.02	1.281475
0.04	1.626834	0.54	1.349096	1.04	1.279469
0.06	1.591785	0.56	1.345041	1.06	1.277547
0.08	1.563985	0.58	1.341188	1.08	1.275743
0.10	1.540084	0.60	1.337476	1.10	1.273980
0.12	1.521048	0.62	1.333920	1.12	1.272093
0.14	1.504163	0.64	1.330531	1.14	1.270281
0.16	1.488993	0.66	1.327114	1.16	1.268595
0.18	1.475328	0.68	1.323900	1.18	1.266905
0.20	1.463350	0.70	1.320745	1.20	1.265293
0.22	1.452416	0.72	1.317731	1.30	1.257518
0.24	1.442268	0.74	1.314817		
0.26	1.432984	0.76	1.311954		
0.28	1.424247	0.78	1.309180		
0.30	1.416347	0.80	1.306440		
0.32	1.408737	0.82	1.303880		
0.34	1.401706	0.84	1.301457		
0.36	1.395324	0.86	1.298883		
0.38	1.388923	0.88	1.296645		
0.40	1.382992	0.90	1.294240		
0.42	1.377362	0.92	1.291912		
0.44	1.372357	0.94	1.289737		
0.46	1.367185	0.96	1.287593		
0.48	1.362406	0.98	1.285533		

Table S17: GoF<sup>2</sup> versus  $\lambda$  for data set oxa13 of Kaminski *et al.* (2014)

$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>	$\lambda$	GoF <sup>2</sup>
0.00	1.310560	0.50	1.056875	1.00	1.005211
0.02	1.265386	0.52	1.053913	1.02	1.003738
0.04	1.234875	0.54	1.050989	1.04	1.002364
0.06	1.211465	0.56	1.048200	1.06	1.001022
0.08	1.192844	0.58	1.045588	1.08	0.999664
0.10	1.177883	0.60	1.043043	1.10	0.998353
0.12	1.165081	0.62	1.040526	1.12	0.997093
0.14	1.154100	0.64	1.038137	1.14	0.995831
0.16	1.144157	0.66	1.035775	1.16	0.994600
0.18	1.135653	0.68	1.033640	1.18	0.993366
0.20	1.127451	0.70	1.031431	1.20	0.992155
0.22	1.120053	0.72	1.029356	1.30	0.986497
0.24	1.113564	0.74	1.027296	1.40	0.981337
0.26	1.107313	0.76	1.025376	1.50	0.976514
0.28	1.101601	0.78	1.023350		
0.30	1.096340	0.80	1.021492		
0.32	1.091238	0.82	1.019630		
0.34	1.086537	0.84	1.017933		
0.36	1.082117	0.86	1.016183		
0.38	1.077984	0.88	1.014503		
0.40	1.073925	0.90	1.012909		
0.42	1.070295	0.92	1.011293		
0.44	1.066581	0.94	1.009646		
0.46	1.063373	0.96	1.008178		
0.48	1.060115	0.98	1.006666		

Table S18:  $\text{GoF}^2$  versus  $\lambda$  for the simultaneous refinement of all Kaminski *et al.* (2014) data sets (except oxa2) of Kaminski *et al.* (2014)

$\lambda$	$\text{GoF}^2$	$\lambda$	$\text{GoF}^2$	$\lambda$	$\text{GoF}^2$
0	1.803959	0.5	1.458729	1	1.405239
0.02	1.725142	0.52	1.455543	1.02	1.403852
0.04	1.679277	0.54	1.452488	1.04	1.402403
0.06	1.647646	0.56	1.449526	1.06	1.401093
0.08	1.622811	0.58	1.446693	1.08	1.399738
0.1	1.603164	0.6	1.444053	1.1	1.398458
0.12	1.586829	0.62	1.441459	1.12	1.397106
0.14	1.572203	0.64	1.438933	1.14	1.395854
0.16	1.559865	0.66	1.436514	1.16	1.39465
0.18	1.549265	0.68	1.434142	1.18	1.393474
0.2	1.539436	0.7	1.431872		
0.22	1.530549	0.72	1.429783		
0.24	1.522742	0.74	1.427623		
0.26	1.515599	0.76	1.425639		
0.28	1.508702	0.78	1.423634		
0.3	1.502568	0.8	1.42175		
0.32	1.496879	0.82	1.419882		
0.34	1.491489	0.84	1.418092		
0.36	1.486442	0.86	1.416368		
0.38	1.481767	0.88	1.414634		
0.4	1.477436	0.9	1.412975		
0.42	1.473396	0.92	1.411327		
0.44	1.469243	0.94	1.40978		
0.46	1.465518	0.96	1.408199		
0.48	1.462317	0.98	1.406759		

*S.13. Effect on the electron density due to the XCW fitting process as a function of  $\lambda$*

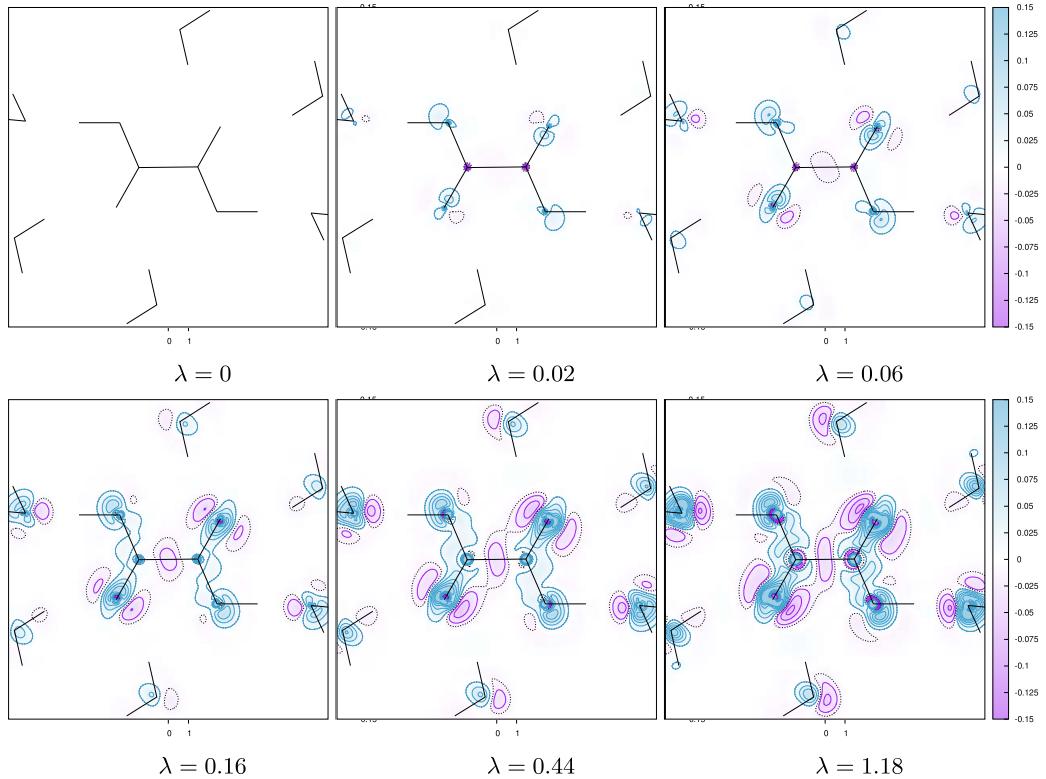


Figure S12: Comparison of features in electron density due to increasing  $\lambda$  values for refinement over all data sets of Kaminski *et al.* (2014). The plots presented are in logarithmic steps from the start to the end of the refinement at  $\lambda = 0, 0.02, 0.06, 0.16, 0.44, 1.18$ . Units are in  $e \text{ \AA}^{-3}$ , each contour indicates a change of  $0.025e \text{ \AA}^{-3}$ . Blue is an increase in the number of electrons while lilac is a decrease in the number of electrons.

S.14. Effect on the electron density due to the XCW on oxa2 data set of Kaminski et al (2014) at  $\lambda_{\text{TIH}6}$

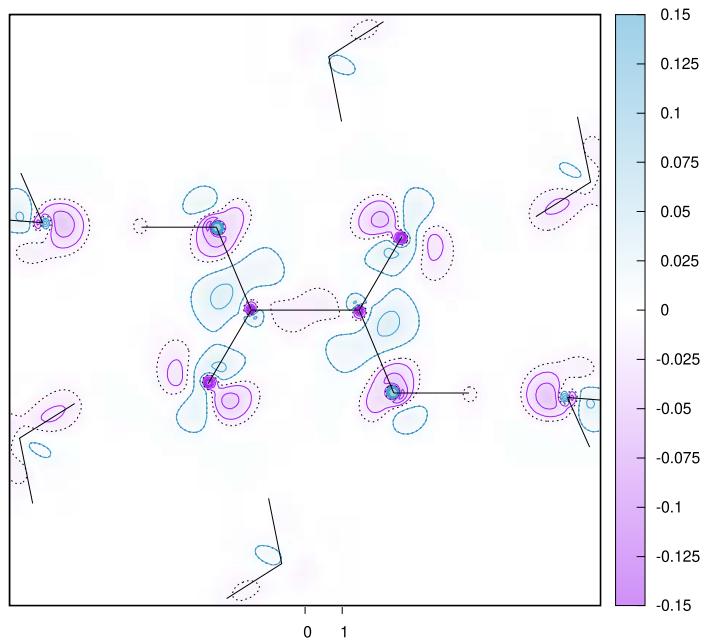


Figure S13: Difference in electron density due to the XCW fitting procedure on data set oxa2 of the Kaminski *et el.* (2014) series at  $\lambda = \lambda_{\text{TIH}6}$ . Units are in  $e \text{ \AA}^{-3}$ , difference between contour levels are  $0.025e \text{ \AA}^{-3}$ .

*S.15. Effect on the electron density due to the XCW fitting process at different halting values  $\lambda_{opt}$*

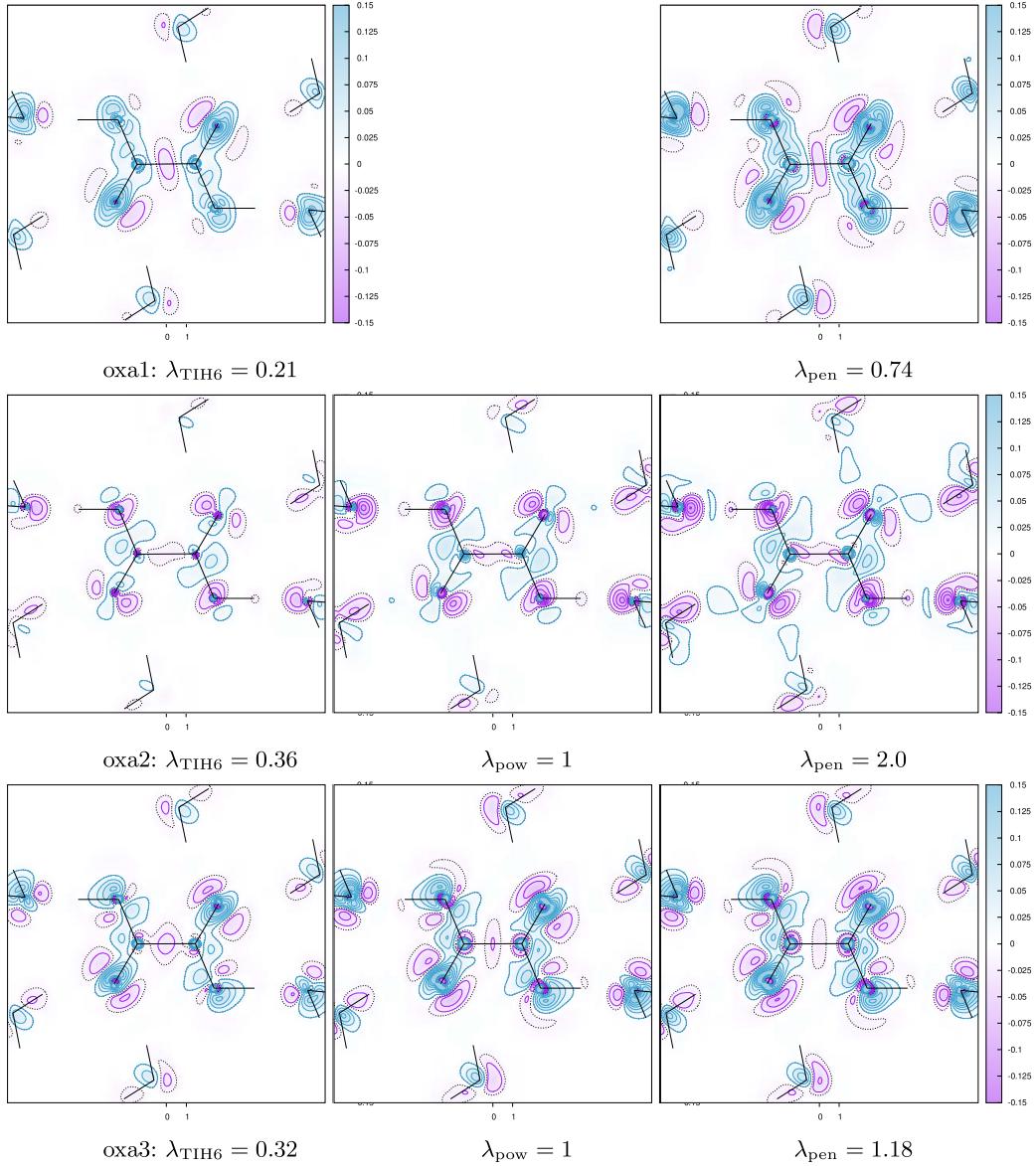


Figure S14: Comparison of changes in electron density due to the XCW procedure for the oxa1, oxa2 and oxa3 Kaminski *et al.*(2014) data sets at different halting points. A missing panel for  $\lambda_{pow} = 1$  indicates that it was not possible to obtain a converged fitting at that value. Contours are in units of  $0.025\text{e } \text{\AA}^{-3}$ .

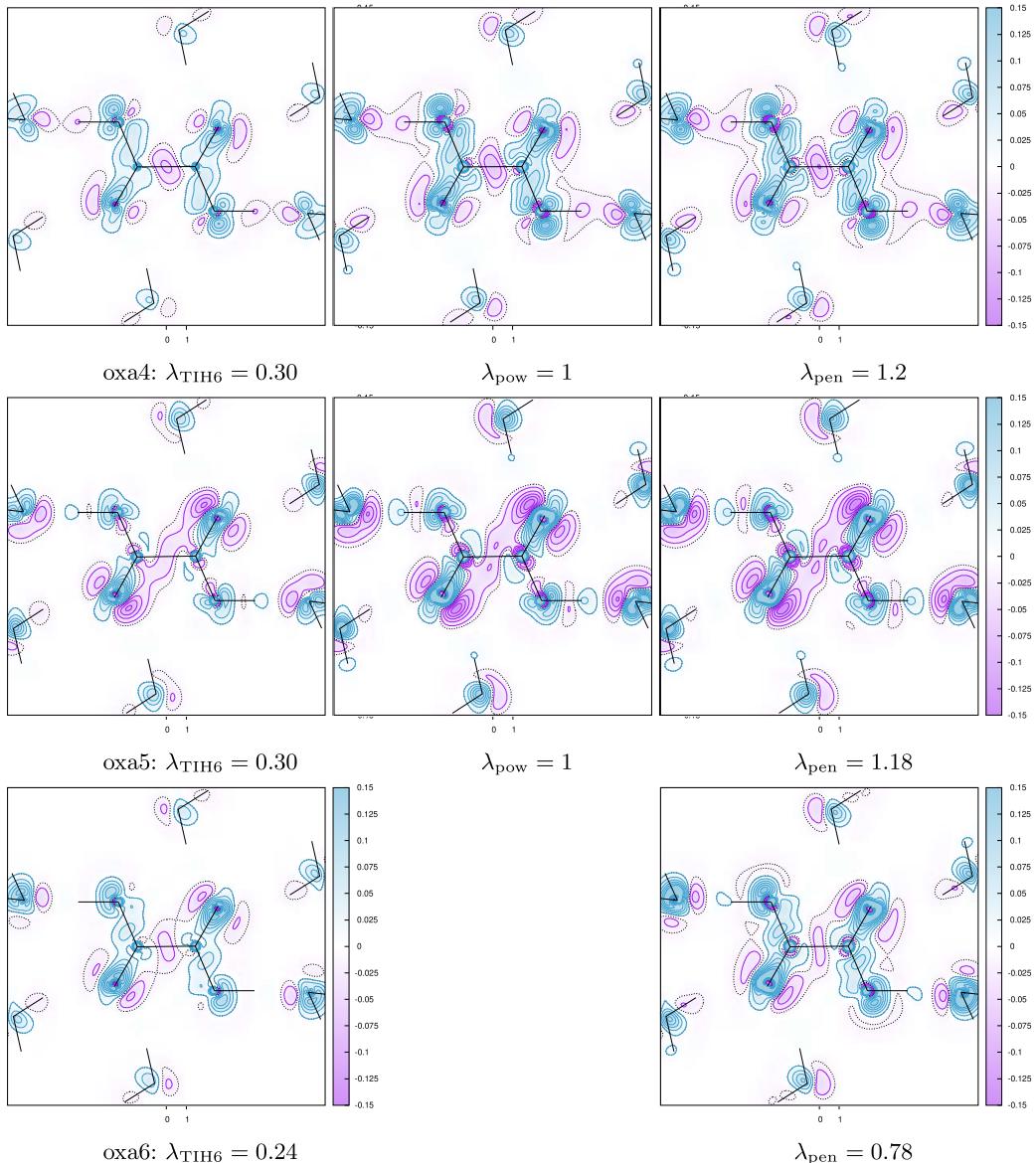


Figure S15: Comparison of changes in electron density due to the XCW procedure for the oxa4, oxa5 and oxa6 Kaminski *et al.* (2014) data sets at different halting points. A missing panel for  $\lambda_{\text{pow}} = 1$  indicates that it was not possible to obtain a converged fitting at that value. Contours are in units of  $0.025e \text{ \AA}^{-3}$ .

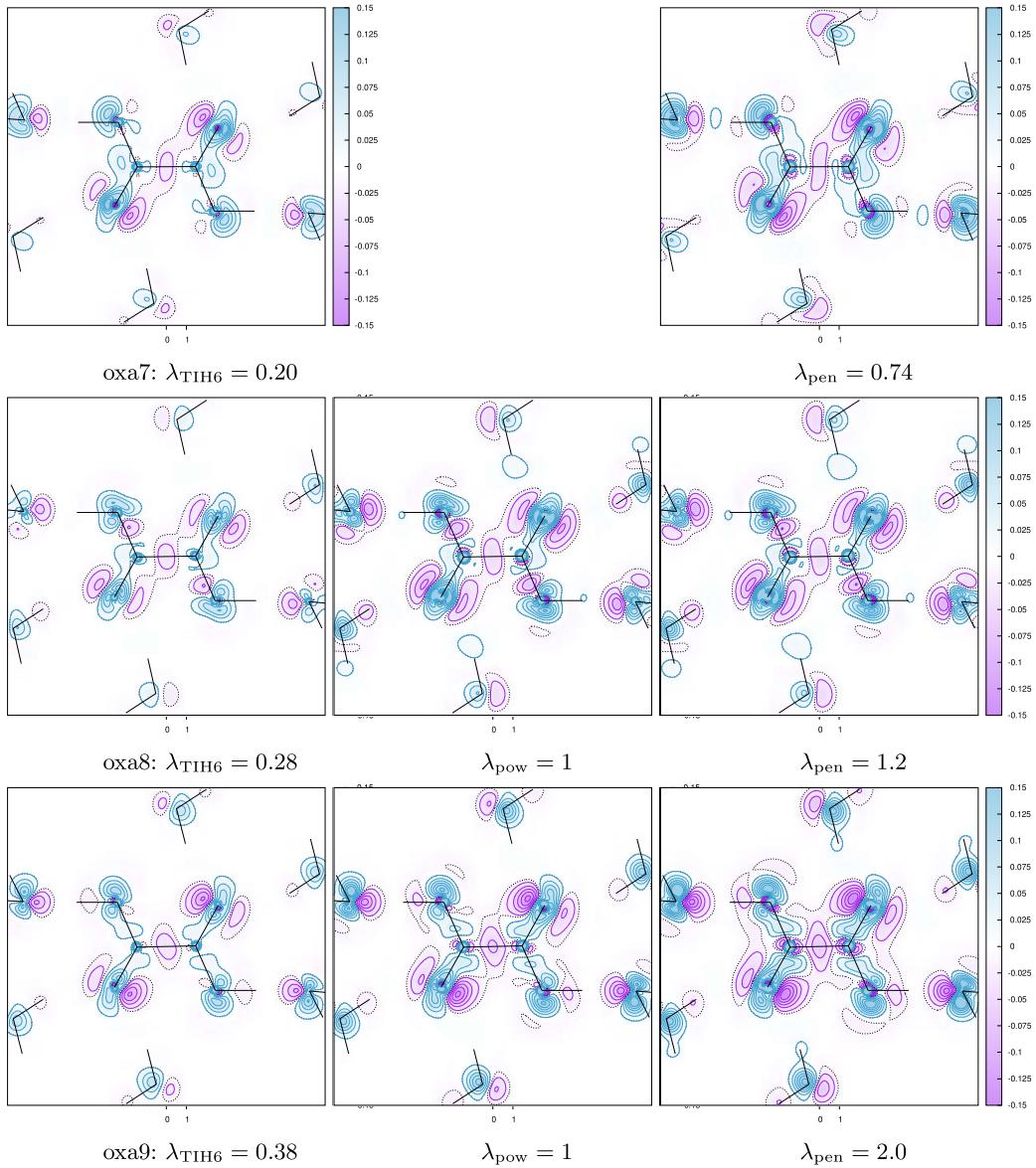


Figure S16: Comparison of changes in electron density due to the XCW procedure for the oxa7, oxa8, and oxa9 Kaminski *et al.* (2014) data sets at different halting points. A missing panel for  $\lambda_{\text{pow}} = 1$  indicates that it was not possible to obtain a converged fitting at that value. Contours are in units of  $0.025\text{e } \text{\AA}^{-3}$ .

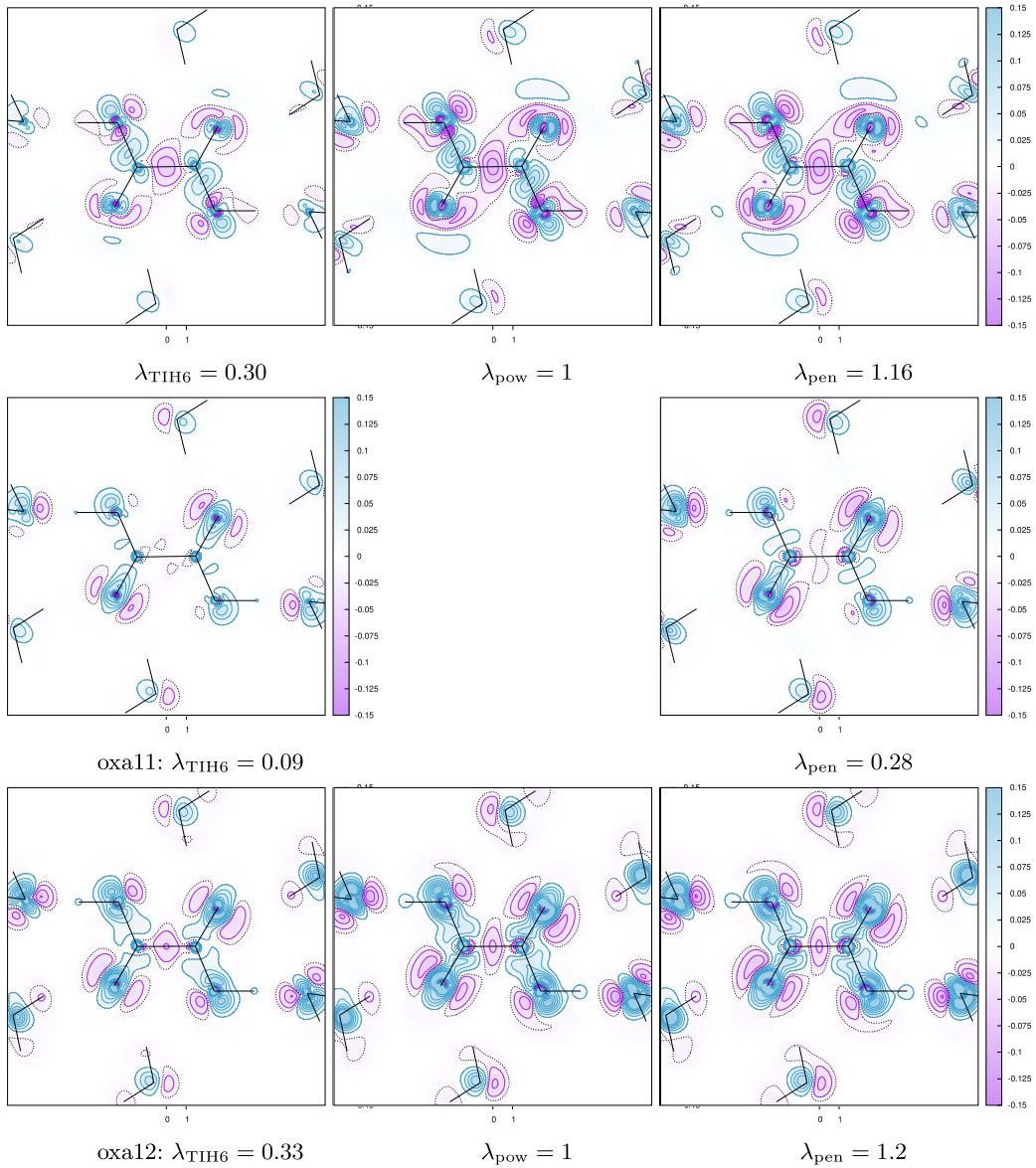


Figure S17: Comparison of changes in electron density due to the XCW procedure for the oxa10, oxa11, and oxa12 Kaminski *et al.* (2014) data sets at different halting points. A missing panel for  $\lambda_{\text{pow}} = 1$  indicates that it was not possible to obtain a converged fitting at that value. Contours are in units of  $0.025\text{e } \text{\AA}^{-3}$ .

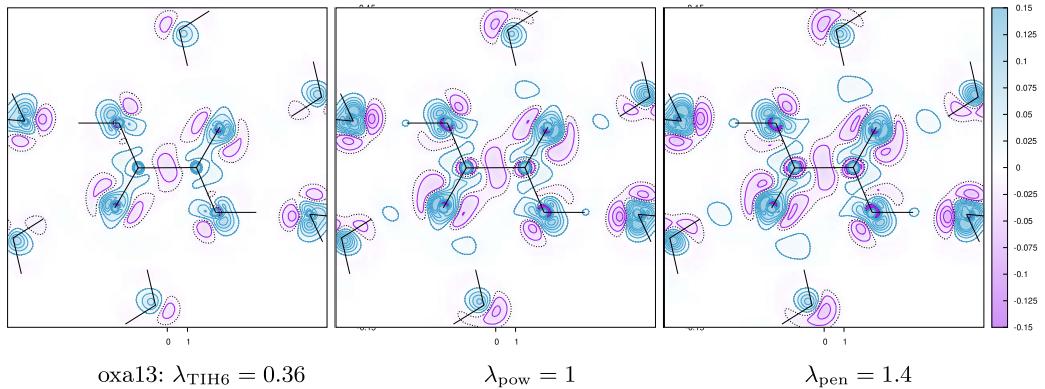


Figure S18: Comparison of changes in electron density due to the XCW procedure for the oxa13 Kaminski *et al.* (2014) data set at different halting points. Contours are in units of  $0.025\text{e } \text{\AA}^{-3}$ .

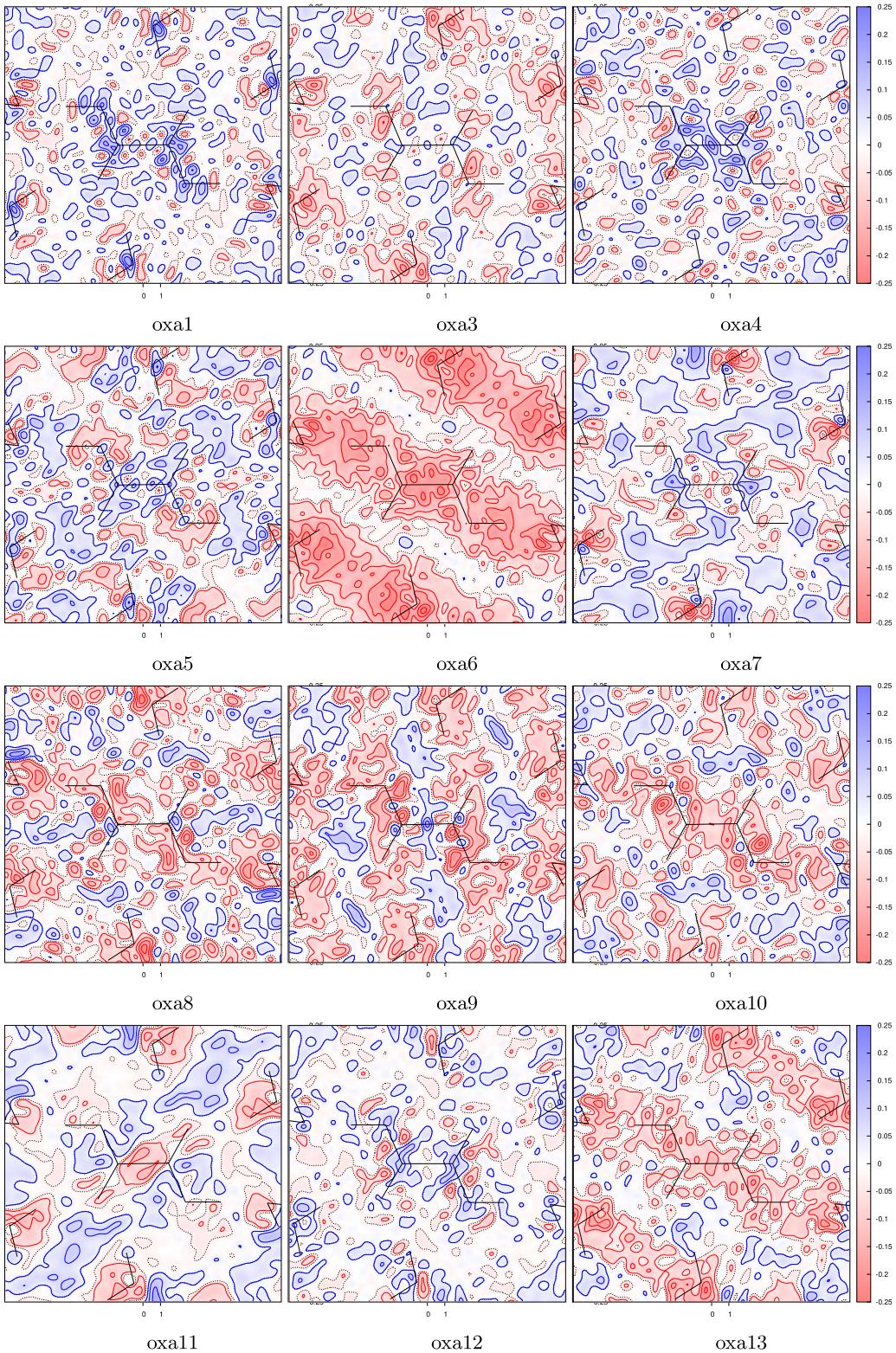


Figure S19: Residual electron density due to the XCW fitting procedure on the Kaminski *et al.* (2014) data sets at  $\lambda = \lambda_{\text{TIH}_6}$  for all data sets except oxa2. Units are in  $e \text{ \AA}^{-3}$ , difference between contour levels is  $0.025e \text{ \AA}^{-3}$ .

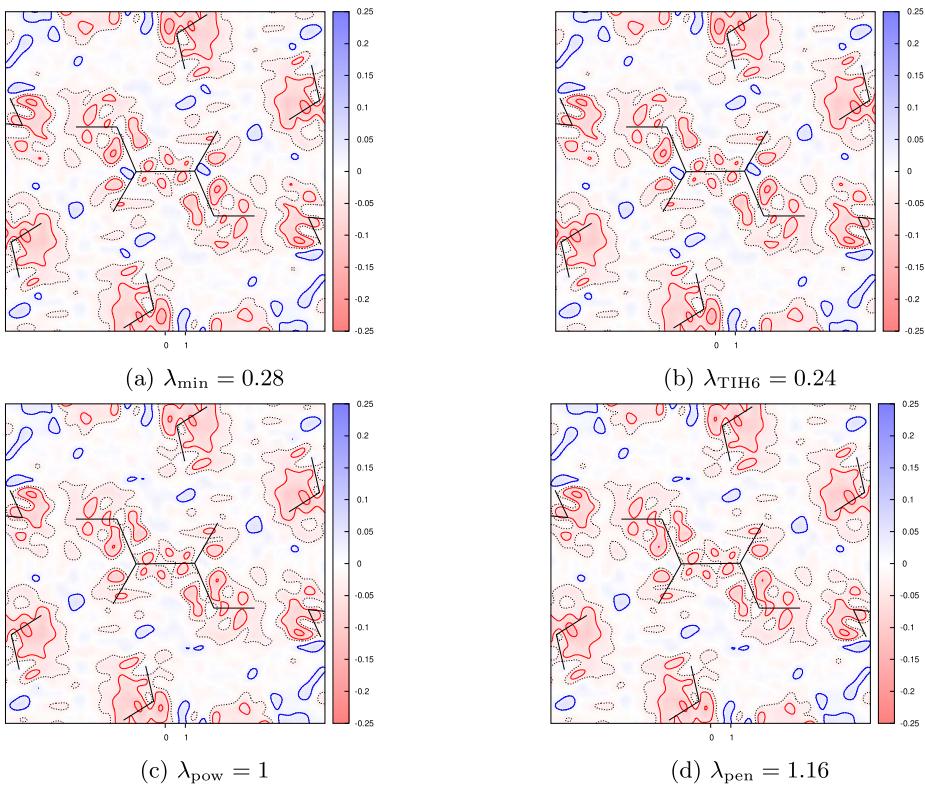


Figure S20: Residual due to the XCW fitting procedure simultaneously on all the Kaminski *et al.* (2014) data sets (except oxa2). Units are in  $e \text{ \AA}^{-3}$ . (a) at  $\lambda = \lambda_{\min} = 0.28$ , the smallest value of  $\lambda_{\text{pen}}$  across all refinements except oxa2. (b) At  $\lambda = \lambda_{\text{TIH6}} = 0.24$ , (c) at  $\lambda = \lambda_{\text{pow}} = 1$ , and (d) at  $\lambda = \lambda_{\text{pen}} = 1.16$ .

**References**

- Genoni, A. (2013). *J. Chem. Theory Comput.* **9**(7), 3004–3019.  
Zobel, D., (1996). Private Communication.