Supporting Information

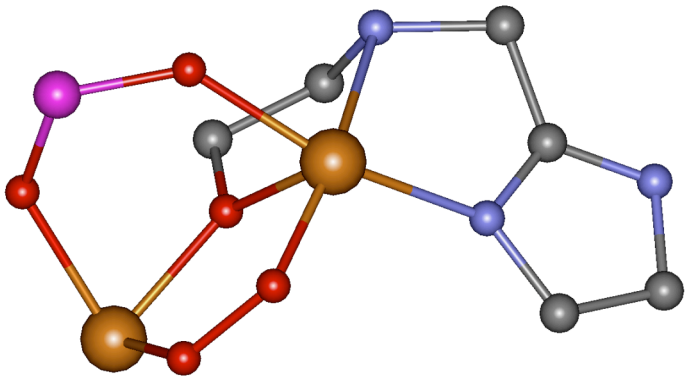

Figure S1. FEFF models for **2**•O_2PPh_2 and **2**•O_2AsMe_2, based on combination of crystal structures of **1**•O_2PPh_2, **1**•O_2AsMe_2 and $[Fe_2(N\text{-}EtHPTB)(O_2)(OPPh_3)_2]^{3+}$ (Dong *et al.*)[1] using Accelrys DS Visualizer 1.7 and ChemBio 3D Ultra 11.0. Black = C, Blue = N, Red = O, Brown = Fe, Pink = P/As.

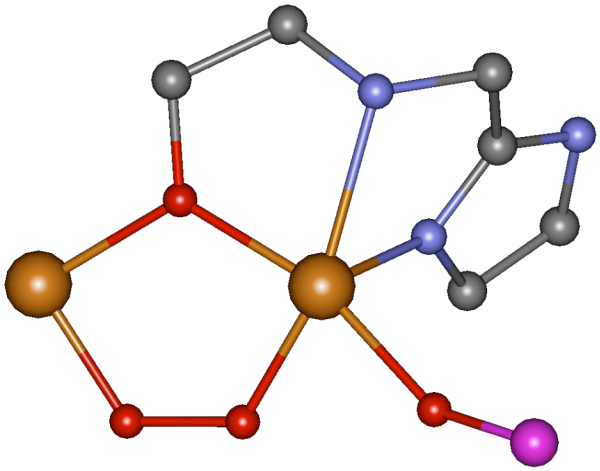

Figure S2. FEFF model for **3**•O_2PPh_2, based on crystal structures of $[Fe_2(N\text{-}EtHPTB)(O_2)(OPPh_3)_2]^{3+}$ (Dong *et al.*)[1] using Accelrys DS Visualizer 1.7 and ChemBio 3D Ultra 11.0. Black = C, Blue = N, Red = O, Brown = Fe, Pink = P.

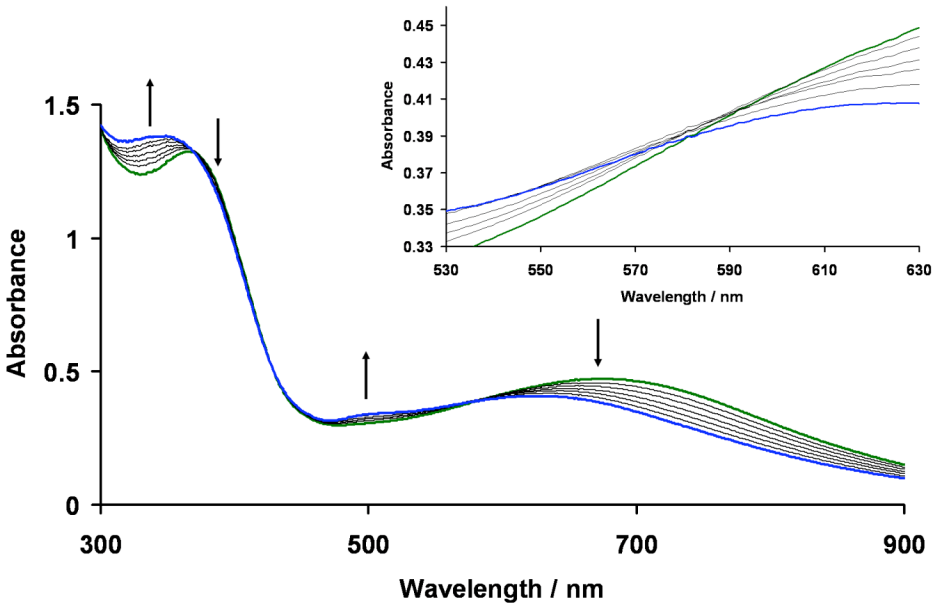

Figure S3. Partial conversion of a 0.5 mM solution of **2**•O_2PPh_2 to **3**•O_2PPh_2 in CH_2Cl_2 in a 0.5 cm cuvette at -30 °C. The inset reveals the pseudo-isosbestic point at ~580 nm.

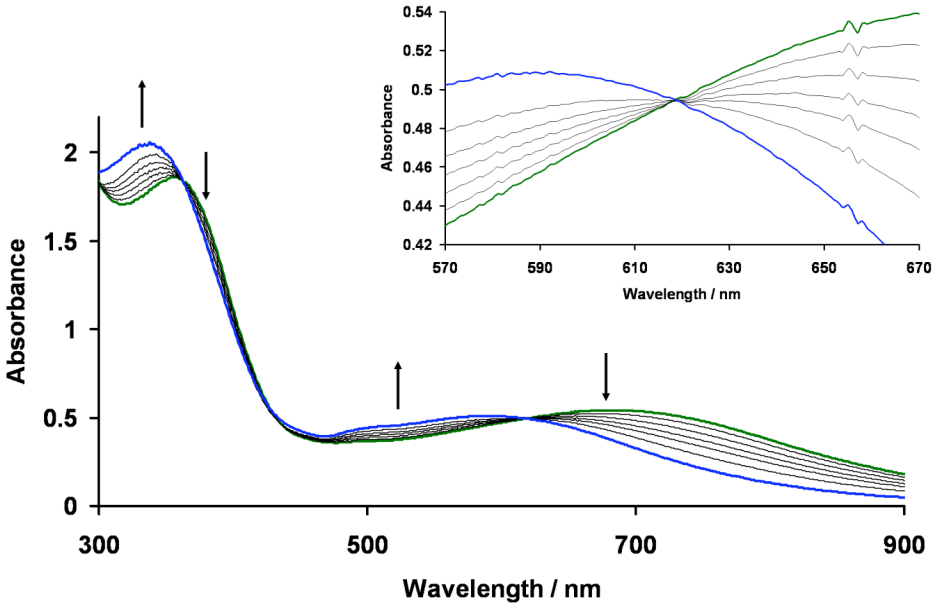

Figure S4. Conversion of a 0.5 mM solution of **2**•O_2PPh_2 to **3**•O_2PPh_2 in MeCN in a 0.5 cm cuvette at -30 °C. The inset reveals the isosbestic point at ~620 nm.

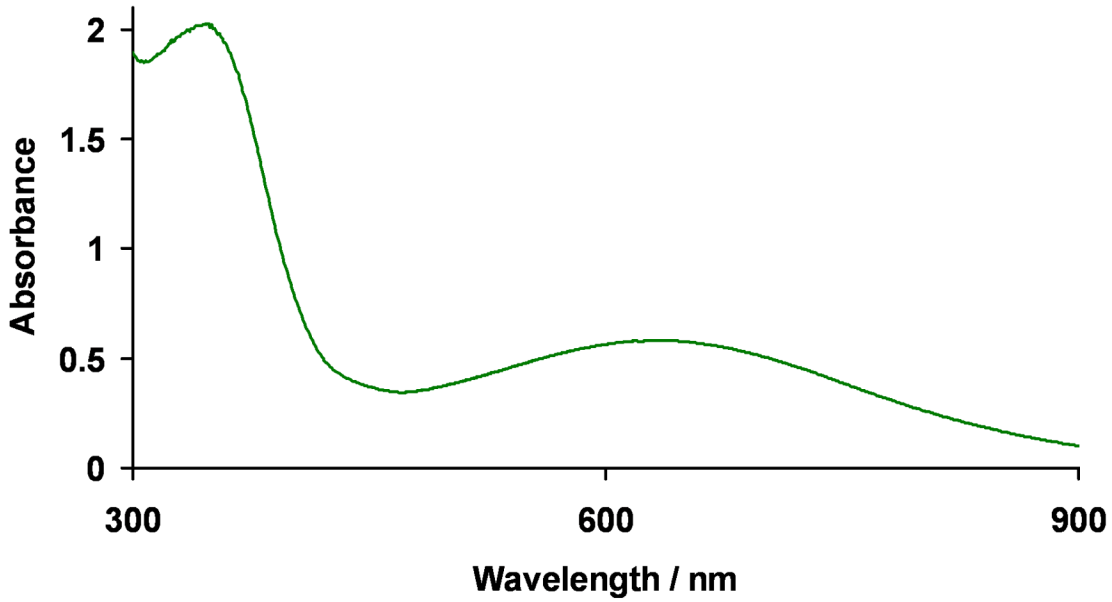

Figure S5. UV-Vis spectrum of a 0.5 mM solution of **2**•O_2AsMe_2 in MeCN in a 0.5 cm cuvette at -40 °C.

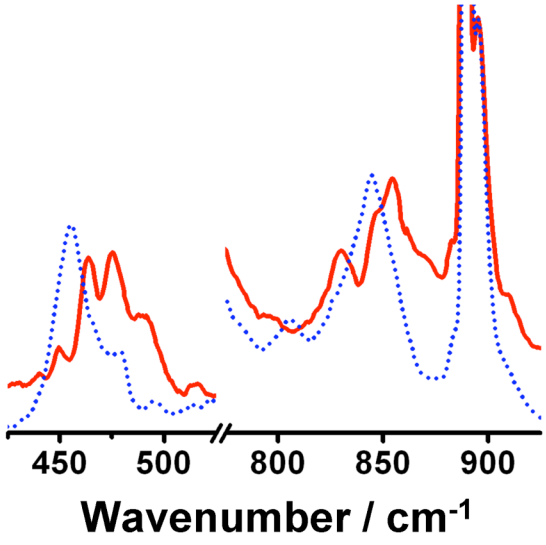

Figure S6. Resonance Raman spectra of frozen solutions of **3**•O_2PPh_2 in CH_2Cl_2. Samples are contaminated with **2**•O_2PPh_2. Solid-red = $^{16}O_2$. Dotted-blue = $^{18}O_2$.

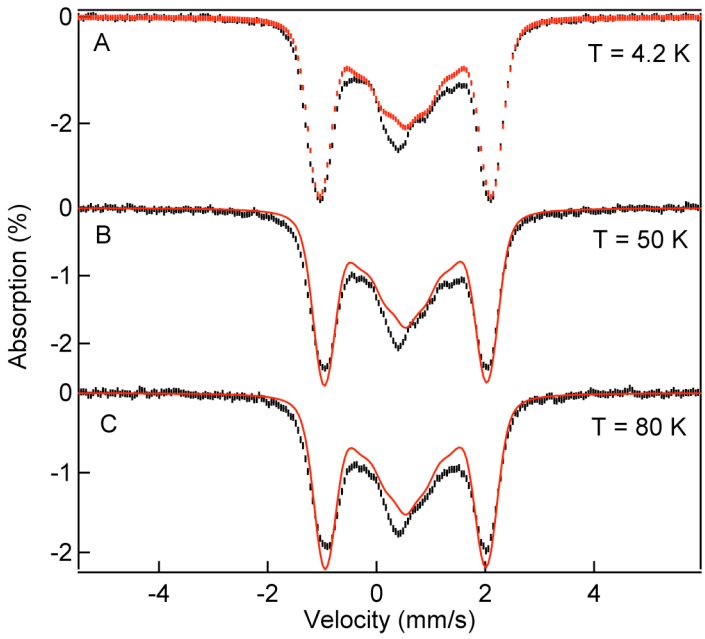

Figure S7. 8.0T Mössbauer spectra of **3**•O_2PPh_2 in MeCN recorded at 4.2 K (A) and 50 K (B) and 80 K (C). The solid lines are theoretical curves using the parameters listed in Table 3. The solid line in (B) was obtained for J = 60 cm^{-1}.

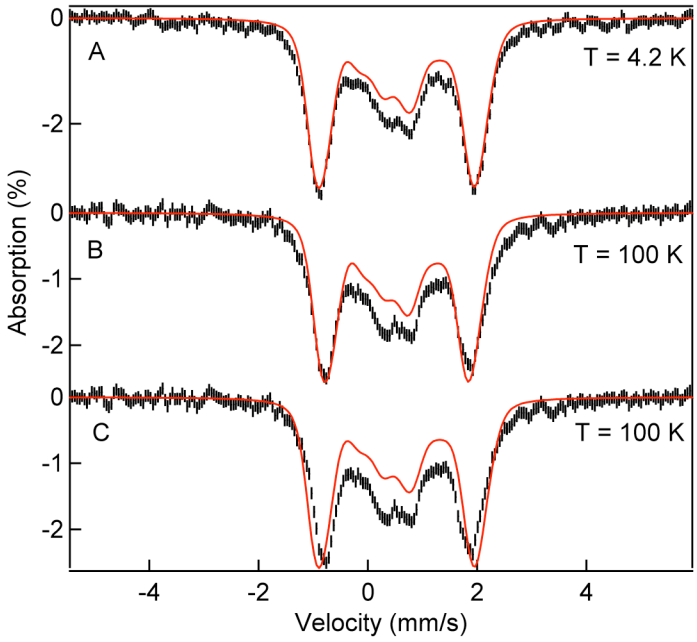

Figure S8. 8.0T Mössbauer spectra of **3**•O_2PPh_2 in CH_2Cl_2 recorded at 4.2 K (A) and 100 K (B). The solid lines are theoretical curves using the parameters listed in Table 3. The data in (C) are the same as in (B); the solid line in (C) is a simulation obtained by assuming that only the S = 0 ground state is occupied at 100 K, i. e. using J = 1000 cm^{-1}. The solid line in (B) was obtained for J = 60 cm^{-1}.

Table S1. EXAFS fitting results for **2**•O_2PPh_2, **2**•O_2AsMe_2, and **3**•O_2PPh_2.[a]

		Fe-O/N			Fe-O/N			Fe-O/N			Fe···C			Fe···X				
Complex	**Fit**	**N**	**R**	**σ^2**	**N**	**R**	**σ^2**	**N**	**R**	**σ^2**	**N**	**R**	**σ^2**	**N**	**R**	**σ^2**	**F[c]**	**F'[d]**
2•O_2PPh_2	1	6	1.97	11.37													1.384	0.117
	2	5	2.00	8.64	1	2.30	1.13										1.225	0.104
	3	4	2.00	6.23	1	2.29	2.92				5	2.99	1.98				0.799	0.052
	4	4	2.00	6.32	1	2.29	2.00				5	2.98	3.84	1Fe	3.27	3.59	0.601	0.035
	5	4	1.99	6.14	1	2.29	3.31				5	2.94	10.66	1P	3.12	-0.30	0.488	0.023
	6	4	2.00	6.54	1	2.31	3.64				5	2.99	2.19	5C	2.21	2.26	0.662	0.042
	7	4	1.99	6.22	1	2.29	2.50				5	2.95	9.28	1Fe	3.24	9.60	0.430	0.022
														1P	3.12	0.00		
	8	4	2.00	6.69	1	2.31	2.71	1	2.54	0.58	5	2.99	3.55	1Fe	3.28	3.18	0.392	0.018
	9	***4***	***2.00***	***6.57***	***1***	***2.30***	***1.50***	***1***	***2.51***	***3.00[b]***	***5***	***2.96***	***7.95***	***1Fe***	***3.25***	***4.06***	***0.304***	***0.013***
														1P	***3.14***	***3.00[b]***		
2•O_2AsMe_2	1	6	1.94	14.63													1.517	0.149
	2	5	1.97	10.13	1	2.26	1.35										1.368	0.140
	3	5	1.99	10.86	1	2.25	0.12				3	2.97	-1.00				1.091	0.104
	4	5	1.97	10.82	1	2.25	2.19				3	2.93	3.86	1Fe	3.25	0.98	0.611	0.040
	5	5	1.97	10.95	1	2.26	2.85				3	2.90	7.46	1As	3.19	1.94	0.595	0.038
	6	5	1.97	10.66	1	2.25	1.03				3	2.95	1.63	6C	3.28	0.40	0.809	0.079
	7	***3***	***1.97***	***3.94***	***2***	***2.17***	***4.28***	***1***	***2.35***	***5.35***	***3***	***2.94***	***2.76***	***1Fe***	***3.27***	***1.24***	***0.381***	***0.018***
	8	***3***	***1.97***	***3.87***	***2***	***2.17***	***3.82***	***1***	***2.36***	***3.80***	***3***	***2.93***	***5.20***	***1As***	***3.21***	***2.24***	***0.369***	***0.019***
	9	3	1.97	3.85	2	2.17	3.89	1	2.35	4.24	3	2.92	3.34	1Fe	3.13	19.43	0.344	0.022
														1As	3.21	1.97		
	10	3	1.97	3.84	2	2.17	3.90	1	2.36	4.71	3	2.94	2.22	1Fe	3.27	1.02	0.316	0.019
														1As	3.45	12.71		
3•O_2PPh_2	1	6	1.98	14.22													1.200	0.081
	2	5	2.00	7.84				1	1.84	1.30							1.143	0.083
	3	5	2.00	11.17	1	2.34	0.34										0.976	0.061
	4	4	2.03	5.68	1	2.34	1.01	1	1.87	1.16							0.914	0.061
	5	4	2.03	5.64	1	2.34	0.42	1	1.88	1.14	4	2.96	2.20				0.568	0.028
	6	***4***	***2.04***	***5.73***	***1***	***2.33***	***0.48***	***1***	***1.88***	***1.23***	***4***	***2.95***	***2.39***	***1Fe***	***3.47***	***4.59***	***0.366***	***0.012***
	7	4	2.04	5.74	1	2.33	0.52	1	1.88	1.28	4	2.95	2.30	1P	3.61	1.50	0.452	0.018
	8	4	2.03	5.73	1	2.33	0.67	1	1.88	1.24	4	2.95	2.63	5C	3.50	2.99	0.494	0.021
	9	4	2.04	5.58	1	2.33	0.80	1	1.88	1.12	4	2.95	2.43	1Fe	3.44	3.73	0.332	0.011
														0.5P	3.39	0.69		

[a] Resolution ~ 0.12 Å for **2**•O_2PPh_2 and **3**•O_2PPh_2 and ~ 0.14 Å for **2**•O_2AsMe_2; σ^2 = respective Debye-Waller factor in units of 10^{-3} Å^2.

[b] σ^2 value held fixed during optimization.

[c] F = goodness of fit calculated as $F = \sqrt{\sum k^6 (\div_{exp} - \div_{cal})^2 / N}$, where N = the number of data points.[2]

[d] F' = F^2/ν, where $\nu = n_{idp} - n_{var}$, n_{idp} is the number of independent points in each data set and n_{var} is the number of variables used in each optimization step. F' is used to indicate the improvement of fit upon the introduction of a shell.[2]

The σ^2 values of the Fe···Fe path (1.24) and the Fe···As path (2.24) in **2**•O_2AsMe_2 (Fits 7 and 8, respectively) are significantly smaller than the σ^2 value of 4.06 found for the Fe···Fe paths in **2**•O_2PPh_2 (Fit 9). Smaller σ^2 leads to larger calculated amplitudes of Fe···Fe or Fe···As peaks in **2**•O_2AsMe_2 as compared to the Fe···Fe path in **2**•O_2PPh_2 (Figure S9). In fact, two Fe···Fe/As paths can also lead a good simulation of data in the k-range of 8 to 13 $Å^{-1}$ (Figure S10).

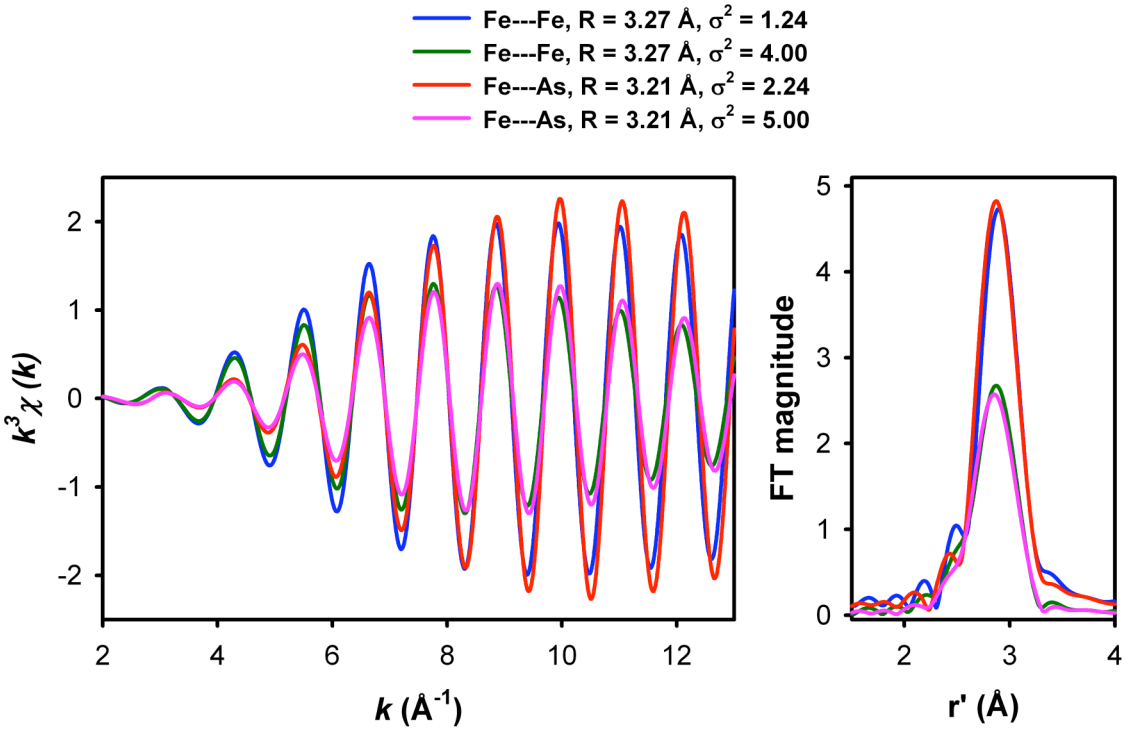

Figure S9. Theoretical EXAFS amplitudes and phases and FT amplitudes at different σ^2 values using FEFF84_87[3,4] and Artemis.[5]

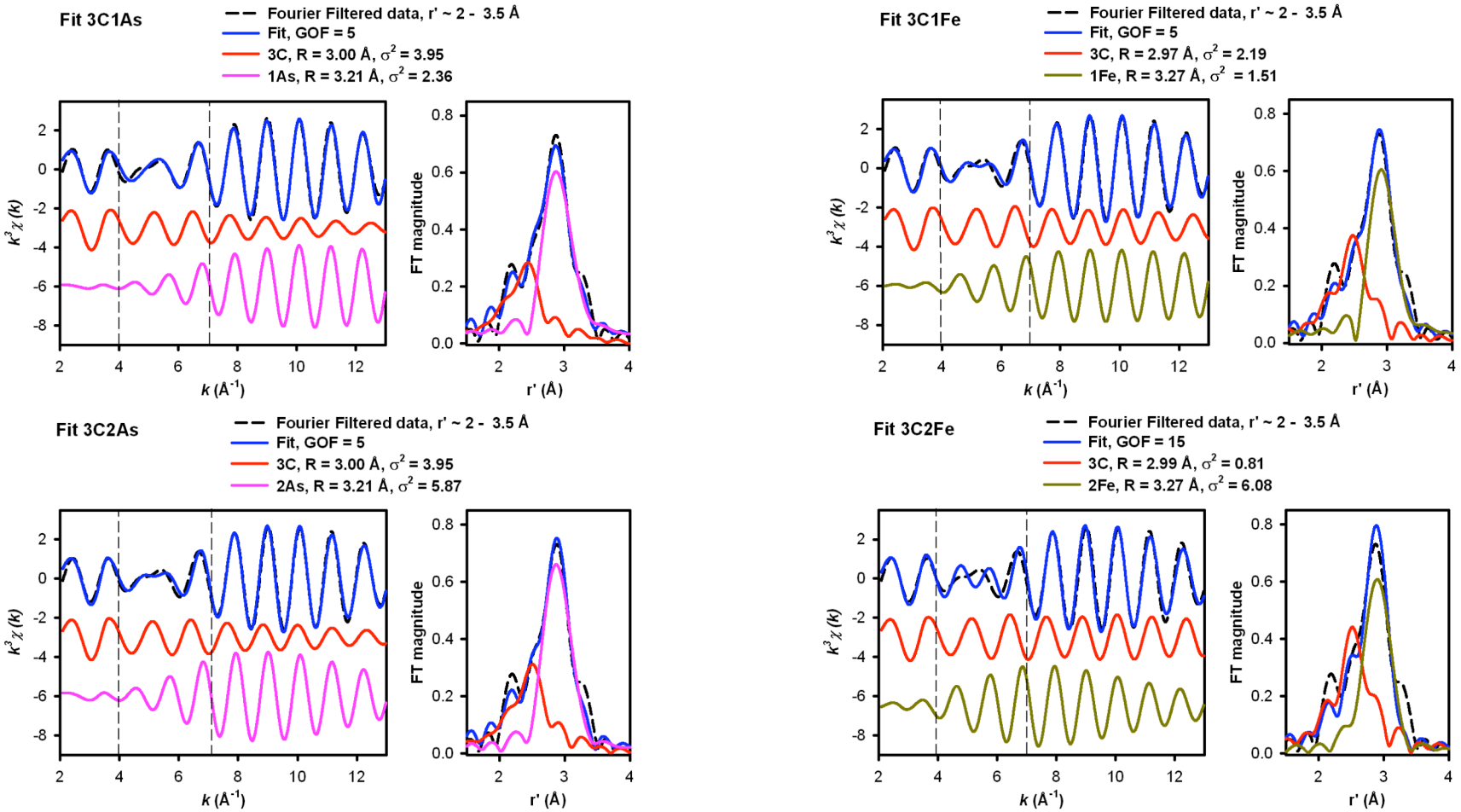

Figure S10. Fits to the outer shell with three Fe···C and one (3C1Fe, 3C1As) or two (3C2Fe, 3C2As) Fe···Fe/As paths. Fits 3C1Fe, 3C1As, and 3C2As are equally good. In fit 3C2Fe, the feature corresponding to the high Z scatterers is also well fitted. However, the destructive effect of two Fe···Fe paths on the 3 Fe···C paths in the range of 4 to 7 $Å^{-1}$ results in a lower quality of fit for 3C2Fe.

(1) Dong, Y.; Yan, S.; Young, V. G., Jr.; Que, L., Jr. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 618-620.

(2) Riggs-Gelasco, P. J.; Stemmler, T. L.; Penner-Hahn, J. E. *Coord. Chem. Rev.* **1995**, *144*, 245-286.

(3) Rehr, J. J.; Mustre de Leon, J.; Zabinsky, S. I.; Albers, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 5135-5140.

(4) Leon, J. M. d.; Rehr, J. J.; Zabinsky, S. I.; Albers, R. C. *Phys. Rev. B* **1991**, *44*, 4146-4156.

(5) Ravel, B.; Newville, M. *J. Synchrotron Rad.* **2005**, *12*, 537-541.