Supporting Information for

Iron Complexes of Dendrimer-Appended Carboxylates for Activating Dioxygen and Oxidizing Hydrocarbons

Min Zhao[1], Brett Helms[2], Elena Slonkina[3], Simone Friedle[1], Dongwhan Lee[1], Jennifer DuBois[3], Britt Hedman[3], Keith O. Hodgson[3*], Jean M. J. Fréchet[2]*, and Stephen J. Lippard[1]**

[1]Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139

[2]Department of Chemistry, University of California, 718 Latimer Hall, Berkeley, CA 94720-1460

[3]Department of Chemistry and Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford, CA 94305

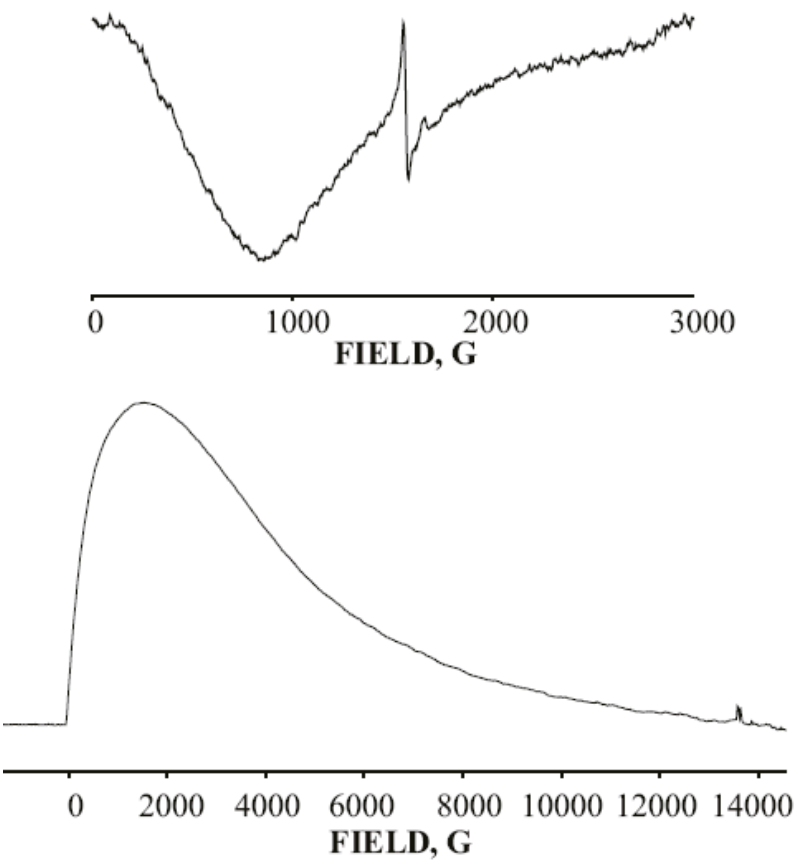

Figure S1. X-band (top, 3.7 K, 9.367 GHz, 13 db) and Q-band (bottom, 2 K, 35.251 GHz, 20 db) EPR spectra of compound **9**-P in frozen toluene solution.

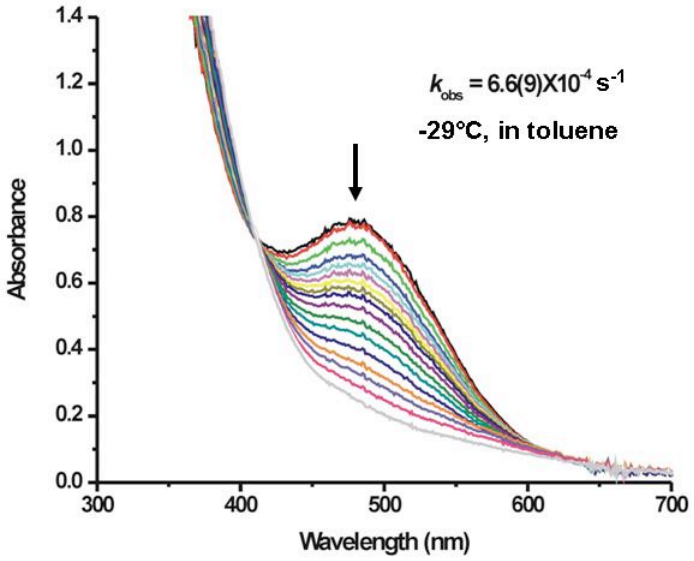

Figure S2. Optical changes when **9**-CN reacts with O_2 in toluene at -29 ºC. The spectra were recorded every 30 s up to 15 min, and with an increment of 20% in the cycle time afterwards.

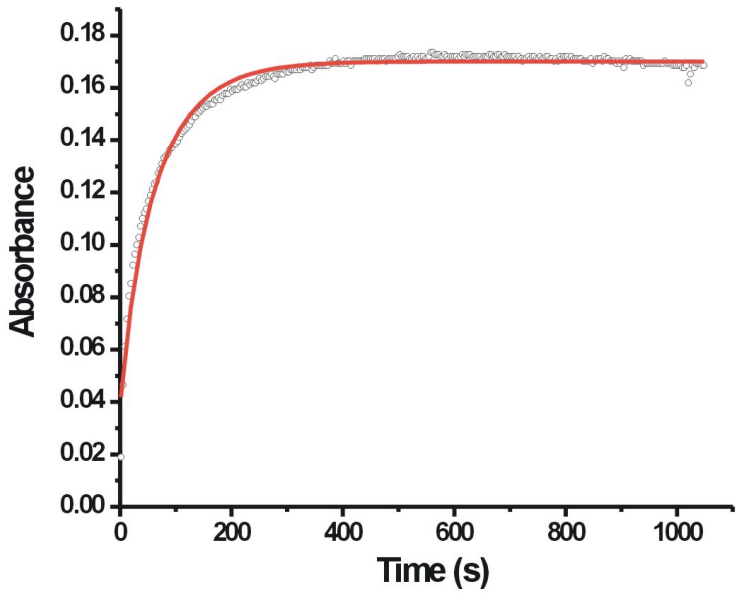

Figure S3. Plot of the evolution in absorbance at 442 nm after mixing **9**-P (0.0376 mM in CH_2Cl_2) with a large excess of dioxygen at 20 ºC. The data were fit to eq. 1 fixing ε_{10} as 6000 $cm^{-1}M^{-1}$ and $\varepsilon_{9\text{-}P}$ as 1000 cm^{-1} M^{-1} to afford k_1' = 0.0132(8) s^{-1}, k_2 = 0.04 (2) s^{-1}, , and ε_{11} = 4523(5) cm^{-1} M^{-1}.

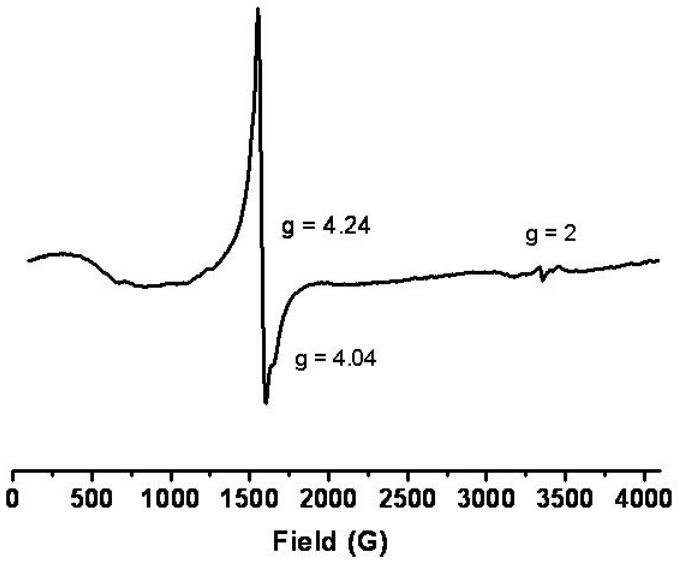

Figure S4. X-band EPR spectrum of a toluene sample of **9**-P at 4.2 K.

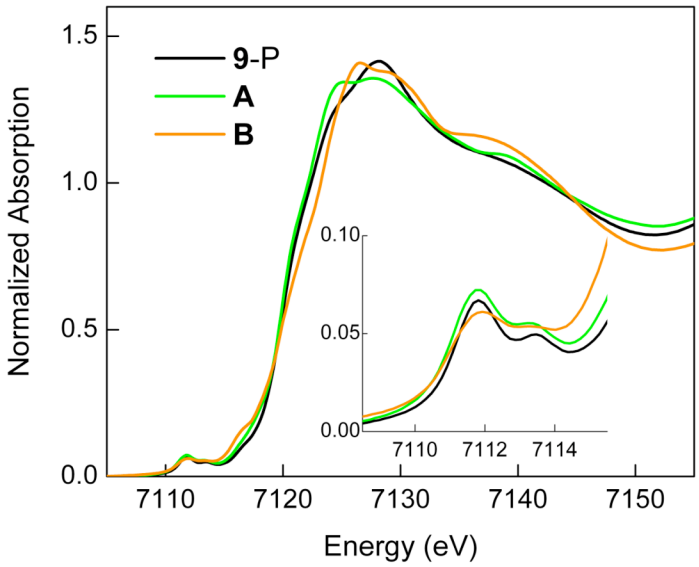

Figure S5. Fe K-edge XAS spectra for **9**-P (black), **A** (green), and **B** (orange). The inset shows the magnified pre-edge region.

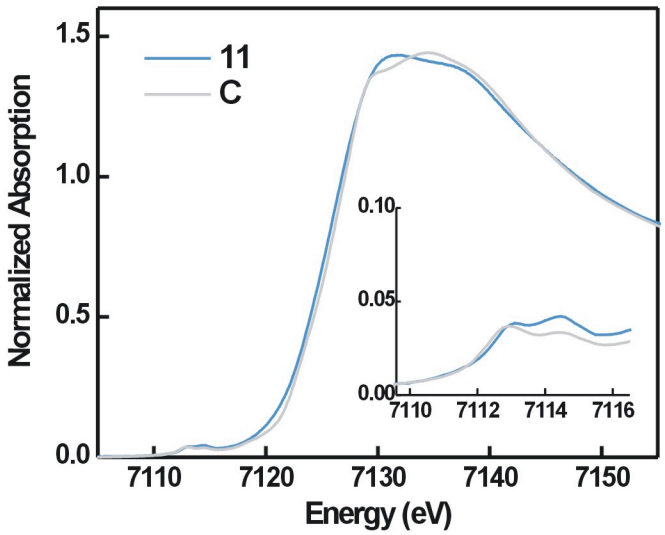

Figure S6. Fe K-edge XAS spectra for **11** (blue) and **C** (gray). The inset shows the magnified pre-edge region.

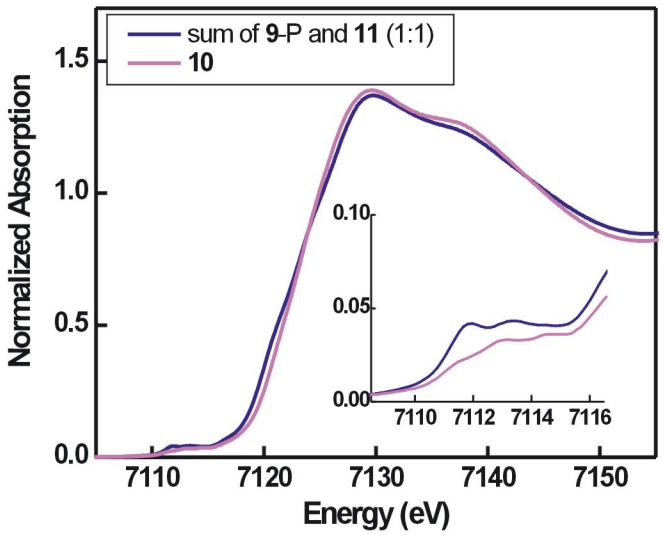

Figure S7. Simulated spectrum of a 1:1 mixture of **9**-P and **11** (navy) and experimental spectrum of **10** (magenta). The inset shows the magnified pre-edge region.

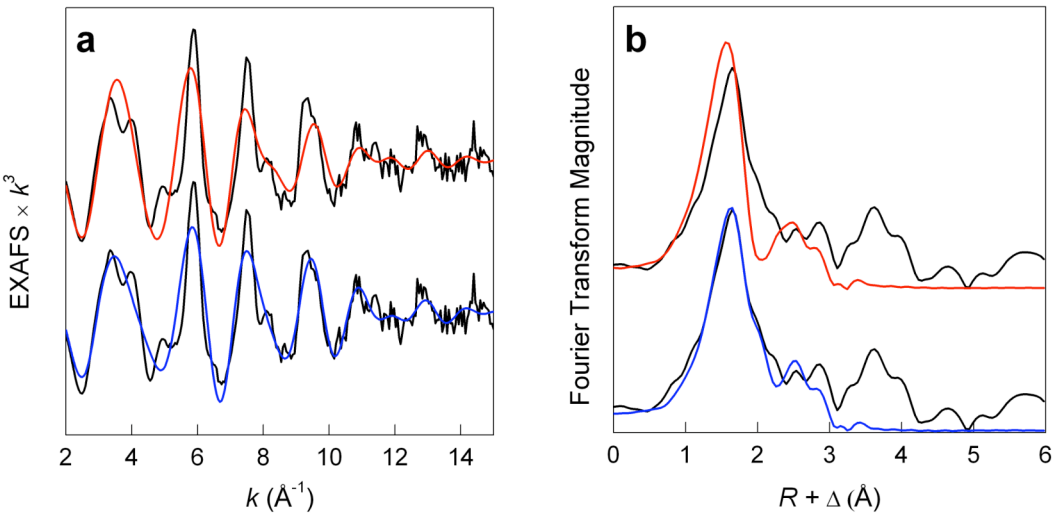

Figure S8. (**a**) EXAFS and (**b**) Fourier transforms of **9**-P (black) and (top to bottom) Fits 1 (red) and 2 (blue) from Table 2.

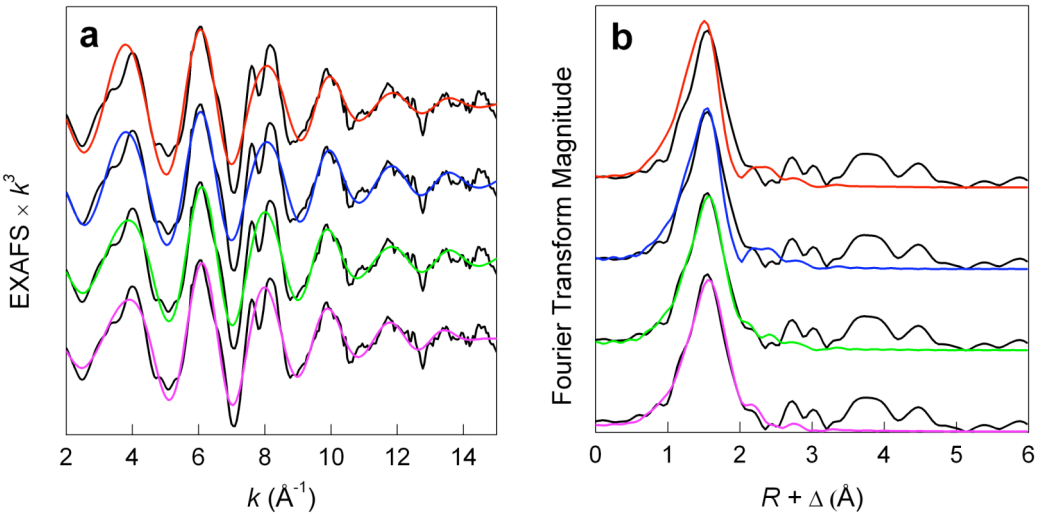

Figure S9. (**a**) EXAFS and (**b**) Fourier transforms of **A** (black) and (top to bottom) Fits 1 (red), 2 (blue), 3 (green), 4 (magenta) from Table S1.

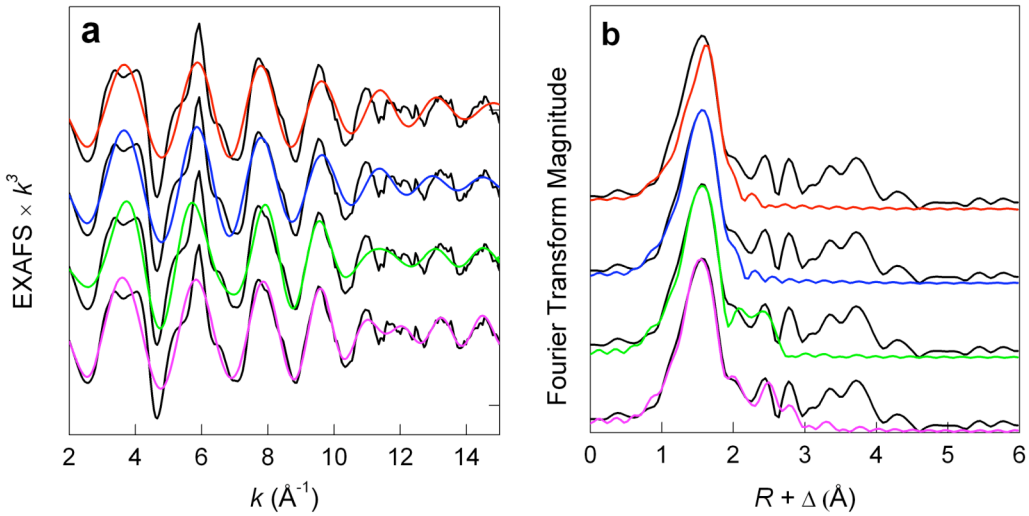

Figure S10. (**a**) EXAFS and (**b**) Fourier transforms of **B** (black) and (top to bottom) Fits 1 (red), 2 (blue), 3 (green), 4 (magenta) from Table S2.

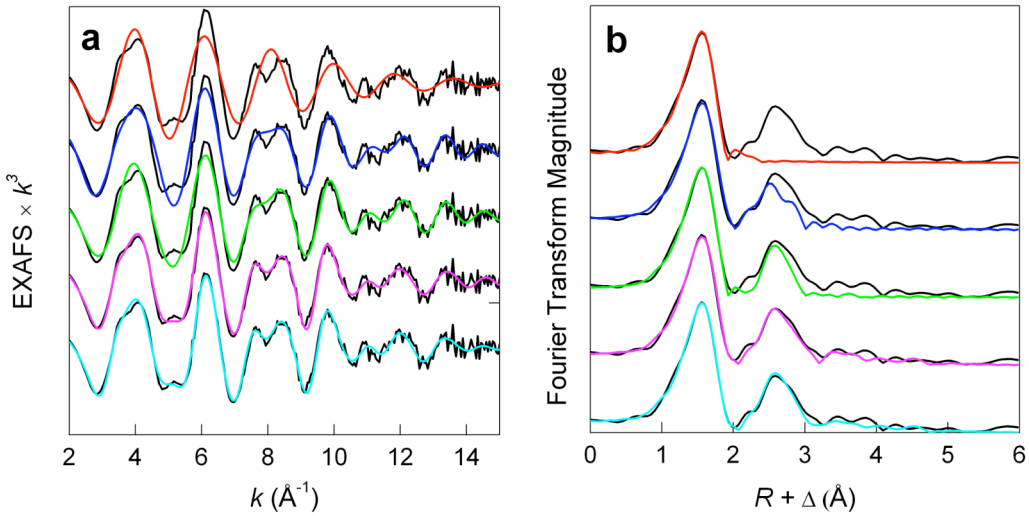

Figure S11. (**a**) EXAFS and (**b**) Fourier transforms of **11** (black) and (top to bottom) Fits 1 (red), 2 (blue), 3 (green), 4 (magenta), and 5 (cyan) from Table S3.

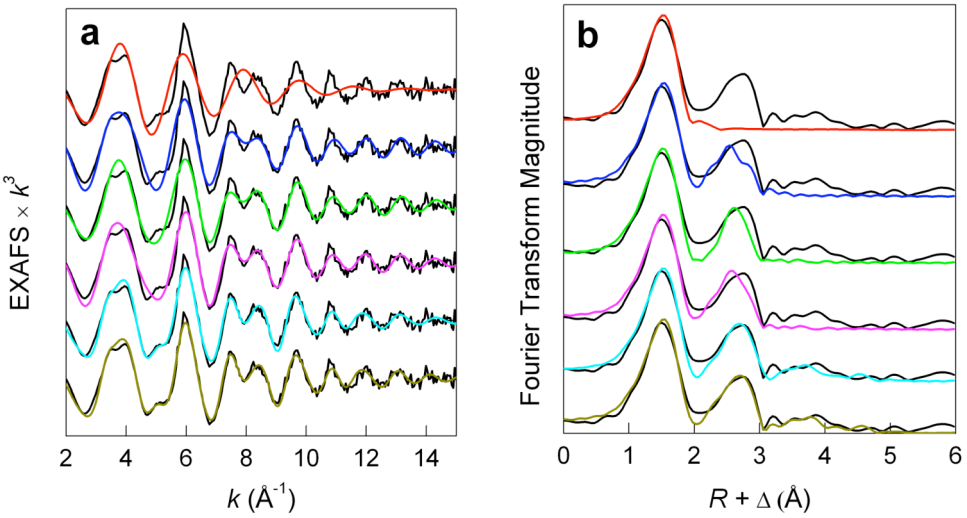

Figure S12. (a) EXAFS and (b) Fourier transforms of **10** (black) and (top to bottom) Fits 1 (red), 2 (blue), 3 (green), 4 (magenta), 5 (cyan) and 6 (dark yellow) from Table S4.

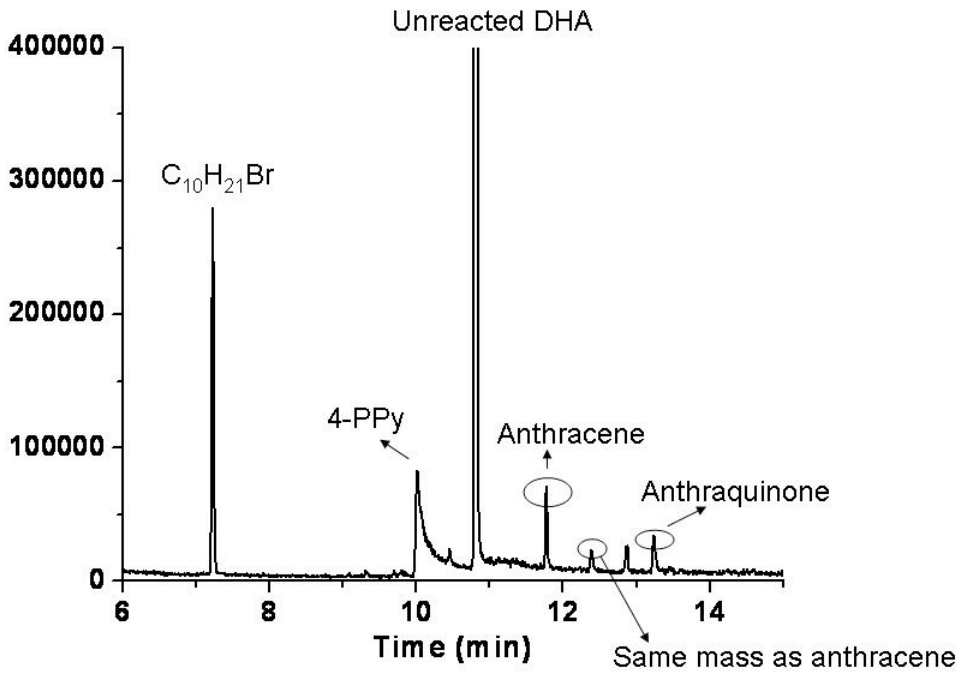

Figure S13. A typical total ion chromatogram from reaction of **9**-P and dihydroanthracene.

Table S1. EXAFS Fit Results for **A**.[a]

Fit number		R (Å) (EXAFS)	R (Å) (crystallography)[b]	$\sigma^2 \times 10^6$ (Å^2)	F[c]
1	5 O/N[d]	2.00	2.03	890	0.399
	4 C	2.97	3.04	1090	
2	4 O/N	2.00	2.03	710	0.356
	4 C	2.98	3.04	1100	
3	4 O/N	2.00	2.03	720	0.314
	2 C/O	2.44	2.44	880	
	4 C	2.97	3.04	1100	
4	4 O/N	2.00	2.03	730	0.314
	1 O	2.35	2.36	450	
	1 C	2.53	2.53	330	
	4 C	2.97	3.04	1400	

[a] Errors are estimated to be 25 % for coordination numbers and 0.01 – 0.03 Å for distances.
[b] *JACS*, **1998**, *120*, 12153-12154.
[c] Error (F) is defined as $F = [\Sigma k^6(\chi_{exptl} - \chi_{calcd})^2]/\Sigma k^6 \chi_{exptl}^2]$.
[d] Scatterers differing by Z = ±1 are not distinguishable by EXAFS. The first element in a pair indicates the type of atom used to model the backscattered wave in the theoretical fit.

Table S2. EXAFS Fit Results for **B**.[a]

Fit number		R (Å) (EXAFS)	R (Å) (crystallography)[b]	$\sigma^2 \times 10^6$ (Å^2)	F[c]
1	5 O/N[c]	2.08	2.09	580	0.446
	6 C	2.98	3.00	5080	
2	2 O	1.99	2.03	300	0.416
	3 O/N	2.10	2.13	280	
	6 C	2.92	3.00	3900	
3	2 O	1.98	2.03	280	0.408
	3 O/N	2.09	2.13	260	
	1 Fe	2.76	2.82	840	
4	2 O	1.99	2.03	240	0.334
	3 O/N	2.11	2.13	250	
	1 Fe	2.77	2.82	490	
	6 C	2.97	3.00	660	

[a] Errors are estimated to be 25 % for coordination numbers and 0.01 – 0.03 Å for distances.
[b] *JACS*, **1999**, *121*, 9893-9894.
[c] Error (F) is defined as $F = [\Sigma k^6(\chi_{exptl} - \chi_{calcd})^2]/\Sigma k^6 \chi_{exptl}^2]$.
[d] Scatterers differing by Z = ±1 are not distinguishable by EXAFS. The first element in a pair indicates the type of atom used to model the backscattered wave in the theoretical fit.

Table S3. EXAFS Fit Results for **11**.[a]

Fit number		R (Å)	$\sigma^2 \times 10^6$ (Å^2)	F^b
1	6 O/N[c]	2.00	830	0.464
2	6 O/N	2.02	840	0.298
	5 C	3.00	270	
3	6 O/N	2.01	830	0.276
	1 Fe	2.99	380	
4	6 O/N	2.02	820	0.241
	1 Fe	3.00	400	
	5 C	2.94	1160	
5	6 O/N	2.02	840	0.178
	5 C	3.00	270	
	3 O/C	3.32	380	
	8 C/N-C	4.28	880	
	10 C	4.92	930	
6	6 O/N	2.01	830	0.174
	1 Fe	3.00	480	
	5 C	2.97	1430	
	3 O/C	3.30	710	
	8 C/N-C	4.27	860	
	10 C	4.91	940	

[a] Errors are estimated to be 25 % for coordination numbers and 0.01 – 0.03 Å for distances.
[b] Error (F) is defined as $F = [\Sigma k^6(\chi_{exptl} - \chi_{calcd})^2]/\Sigma k^6 \chi_{exptl}^2]$.
[c] Scatterers differing by Z = ±1 are not distinguishable by EXAFS. The first element in a pair indicates the type of atom used to model the backscattered wave in the theoretical fit.

Table S4. EXAFS Fit Results for **10**.[a]

Fit number		R (Å)	$\sigma^2 \times 10^6$ (Å^2)	F^b
1	6 O/N	2.04	1290	0.525
2	6 O/N	2.05	1300	0.331
	5 C	3.04	340	
3	6 O/N	2.04	1290	0.311
	1 Fe	3.02	460	
4	6 O/N	2.05	1280	0.280
	1 Fe	3.03	500	
	5 C	3.00	1524	
5	6 O/N	2.05	1290	0.235
	5 C	3.03	380	
	3 O	3.34	530	
	8 C/N-C	4.38	890	
	10 C	4.99	1000	
6	6 O	2.05	1290	0.217
	1 Fe	3.07	470	
	5 C	2.99	580	
	3 O	3.27	850	
	8 C/N-C	4.38	760	
	10 C	4.99	1000	

[a] Errors are estimated to be 25 % for coordination numbers and 0.01 – 0.03 Å for distances.
[b] Error (F) is defined as $F = [\Sigma k^6(\chi_{exptl} - \chi_{calcd})^2]/\Sigma k^6 \chi_{exptl}^2]$.
[c] Scatterers differing by Z = ±1 are not distinguishable by EXAFS. The first element in a pair indicates the type of atom used to model the backscattered wave in the theoretical fit.