Supporting Information

Mechanistic Studies of the Oxidative *N*-Dealkylation of a Substrate Tethered to Carboxylate-Bridged Diiron(II) Complexes, $[Fe_2(\mu\text{-}O_2CAr^{Tol})_2(O_2CAr^{Tol})_2(N,N\text{-}Bn_2en)_2]$

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Synthesis of Benzyl(4-R-benzyl)aminoacetonitrile Compounds. The general reaction pathway is shown in Scheme 2. A solution of 4-R-benzaldehyde (0.100 mole), where R = Cl, F, CH_3, *t*-Bu, or OCH_3, in 27 mL of benzene was cooled to 0 °C. To this solution was added 10.8 g (0.101 mol) of benzylamine in 17 mL of benzene. The solution was warmed to ambient temperature. The flask was connected to a Dean-Stark water separator, followed by heating at reflux overnight, resulting in separation of ca 1.5 mL of water. The volatile portion was removed under reduced pressure, resulting in a light yellow oil, which was dissolved in 150 mL of methanol. The solution was cooled to 0 °C and 5.4 g (0.14 mol) of $NaBH_4$ was added slowly. The reaction mixture was allowed to warm to ambient temperature and stored overnight. The volume was reduced to half under partial vacuum and water (200 mL) was added. The product was extracted with 3 × 50 mL portions of dichloromethane, dried using anhydrous $MgSO_4$ and filtered

through Celite. The volatile portion of the filtrate was removed under reduced pressure, resulting in a light yellow oil. To a rapidly stirred DMF (50 mL) solution of *N,N*-benzyl(4-R-benzyl)amine (96.7 mmol) were added first triethylamine (13.5 mL) and then 6.8 mL of chloroacetonitrile in a dropwise manner. The solution turned cloudy and was stirred overnight. DMF was removed under reduced pressure and 40 mL of water were added. Anhydrous Na_2CO_3 was added to increase the pH of the solution to ca 14. The product was extracted with 3 × 50 mL portions of dichloromethane, dried with $MgSO_4$, and filtered through Celite. The targeted compound was isolated by using silica column chromatography with ethylacetate as the eluent.

Benzyl(4-chlorobenzyl)aminoacetonitrile. Yield (77 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.32 (9 H, mm), 3.74 (2 H, s), 3.72 (2 H, s), 3.37 (2 H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.08, 135.84, 133.78, 130.43, 129.13, 129.05, 128.91, 128.11, 114.69, 58.43, 57.72, 40.99. FT-IR (NaCl disk, cm^{-1}) 3063 (w), 3030 (w), 2933 (w), 2831 (m), 2228 (w, $\nu_{C\equiv N}$), 1598 (w), 1492 (s), 1453 (m), 1419 (w), 1369 (w), 1324 (w), 1119 (w), 1090 (m), 1015 (m), 858 (w), 800 (m), 743 (m), 699 (m). GC/MS (EI) M^+: Calcd for $C_{16}H_{15}ClN_2$, 270; Found, 270.

Benzyl(4-fluorobenzyl)aminoacetonitrile. Yield (72 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.31 (7 H, mm), 7.07 (2H, t, 8.7 Hz), 3.74 (2 H, s), 3.72 (2 H, s), 3.37 (2 H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.57 (d, $^1J_{CF}$ = 246.1 Hz), 137.16, 133.02 (d, $^4J_{CF}$ = 3.1 Hz), 130.7 (d, $^3J_{CF}$ = 7.9 Hz), 129.01, 128.90, 128.08, 115.74 (d, $^2J_{CF}$ = 21.4 Hz), 114.74, 58.40, 57.66, 40.90. FT-IR (NaCl disk, cm^{-1}) 3031 (w), 2935 (w), 2826 (m), 2228 (w, $\nu_{C\equiv N}$), 1602 (w), 1509 (s), 1454 (w), 1419 (w), 1369 (w), 1350 (w), 1324 (w), 1294 (w), 1223 (s), 1156 (w), 1119 (w),

1093 (w), 976 (w), 855 (m), 820 (m), 743 (m), 699 (m), 504(w). GC/MS (EI) M^+: Calcd for $C_{16}H_{15}FN_2$, 254; Found, 254.

Benzyl(4-methylbenzyl)aminoacetonitrile. Yield (69 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43-7.29 (7 H, mm), 7.18 (2 H, d, 7.9 Hz), 3.75 (2 H, s), 3.73 (2 H, s), 3.38 (2 H, s), 2.37 (3 H, S). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.67, 137.41, 134.24, 129.50, 129.13, 129.10, 128.82, 127.94, 114.91, 58.39, 58.21, 40.86, 21.34. FT-IR (NaCl disk, cm^{-1}) 3028 (m), 2923 (m), 2826 (m), 2230 (w, $\nu_{C\equiv N}$), 1603 (w), 1515 (s), 1496 (m), 1454 (s), 1419 (m), 1369 (m), 1349 (w), 1324 (w), 1303 (w), 1249 (w), 1204 (w), 1179 (w), 1117 (m), 1105 (m), 1075 (w), 1022 (w), 975 (m), 858 (m), 803 (m), 758 (m), 742 (s), 699 (s), 488(m). ESI-MS $(M+H)^+$: Calcd for $C_{17}H_{19}N_2$, 251.3; Found, 275.3.

Benzyl(4-tert-butylbenzyl)aminoacetonitrile. Yield (87 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43-7.30 (9 H, mm), 3.76 (2 H, s), 3.74 (2 H, s), 3.39 (2 H, s), 1.33 (9 H, S). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.96, 137.45, 134.26, 129.13, 128.84, 128.83, 127.94, 125.73, 114.95, 58.45, 58.11, 40.96, 34.74, 31.55. FT-IR (NaCl disk, cm^{-1}) 3087 (w), 3062 (w), 3029 (w), 2963 (s), 2904 (m), 2868 (m), 2826 (m), 2228 (w, $\nu_{C\equiv N}$), 1513 (w), 1496 (w), 1454(m), 1417 (w), 1363 (m), 1393 (w), 1323 (w), 1269 (w), 1111 (m), 1076 (w), 1028 (w), 859 (m), 740 (m), 737 (m), 699 (m). GC/MS (EI) M^+: Calcd for $C_{20}H_{24}N_2$, 292; Found, 292.

Benzyl(4-methoxybenzyl)aminoacetonitrile. Yield (76 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43-7.32 (7 H, mm), 6.92 (2 H, d, 8.4 Hz), 3.83 (3 H, s), 3.75 (2 H, s), 3.71 (2 H, s), 3.37 (2 H, S). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.35, 137.39, 130.31, 129.25, 129.08, 128.78, 127.90, 114.87, 114.13, 58.28, 57.80, 55.42, 40.72. FT-IR (NaCl disk, cm^{-1}) 3062 (w), 3030 (w), 3004 (w), 2934 (w), 2835 (m), 2230 (w, $\nu_{C\equiv N}$), 1611 (m), 1512 (s), 1454 (m), 1419 (w),

1302 (m), 1250 (s), 1173 (m), 1105 (w), 1076 (w), 1034 (m), 854 (w), 813 (w), 743 (m), 700 (m). GC/MS (EI) M^+: Calcd for $C_{17}H_{18}N_2O$, 266; Found, 266.

Synthesis of Benzyl(4-R-benzyl)ethylenediamine Compounds (*N,N*-(4-R-Bn)Bnen). To a rapidly stirred diethylether (25 mL) suspension of lithium aluminum hydride (LAH) (1.5 g, 36 mmol) was added a diethylether solution (25 mL) of benzyl(4-R-benzyl)aminoacetonitrile (19 mmol) at -78 °C. The reaction mixture was stirred for 10 min, warmed to ambient temperature, and stirred overnight under argon. The sequential addition of 1.5 g of water, 1.5 g of 15 % NaOH(aq), and 3 × 1.5 g of water was performed cautiously. The product was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered through Celite, and evaporated under reduced pressure to afford light yellow oil.

N,N-Benzyl(4-chlorobenzyl)ethylenediamine (N,N-(4-Cl-Bn)Bnen). Yield (88 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.25 (9 H, mm), 3.57 (2 H, s), 3.54 (2 H, s), 2.75 (2 H, t, J = 6.0 Hz), 2.50 (2 H, t, J = 6.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.42, 138.27, 132.76, 130.30, 128.57, 128.50, 127.24, 58.74, 58.10, 56.81, 39.72. FT-IR (NaCl disk, cm^{-1}) 3084 (w), 3061 (w), 3027 (w), 2939 (m), 2801 (s), 1597 (w), 1490 (s), 1452 (m), 1407 (w), 1366 (m), 1244 (w), 1126 (w), 1088 (m), 1028 (w), 1015 (m), 978 (w), 908 (w), 841 (m), 804 (m), 739 (m), 699 (m), 671 (w). ESI-MS $(M+H)^+$: Calcd for $C_{16}H_{20}ClN_2$, 275.4; Found, 275.4.

N,N-Benzyl(4-fluorobenzyl)ethylenediamine (*N,N-(4-F-Bn)Bnen*). Yield (87 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34-7.25 (7 H, mm), 7.01 (2H, t, 8.7 Hz), 3.57 (2 H, s), 3.54 (2 H, s), 2.75 (2 H, t, J = 6.0 Hz), 2.51 (2 H, t, J = 6.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.06 (d, $^1J_{CF}$ = 244.7 Hz), 139.56, 135.36 (d, $^4J_{CF}$ = 3.0 Hz), 130.43 (d, $^3J_{CF}$ = 7.9 Hz),

128.98, 128.46, 127.19, 115.21 (d, $^2J_{CF}$ = 21.3 Hz), 58.69, 58.01, 56.77, 39.74. FT-IR (NaCl disk, cm^{-1}) 3028 (w), 2939 (w), 2802 (m), 1602 (w), 1508 (s), 1452 (w), 1366 (w), 1292 (w), 1220 (s), 1154 (w), 1126 (w), 1091 (w), 1070 (w), 1028 (w), 1015 (w), 978 (w), 824 (m), 791 (w), 767 (w), 739 (m), 699 (m), 502 (w). ESI-MS $(M+H)^+$: Calcd for $C_{16}H_{20}FN_2$, 259.3; Found, 259.4.

N,N-Benzyl(4-methylbenzyl)ethylenediamine (N,N-(4-Me-Bn)Bnen). Yield (78 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40-7.27 (7 H, mm), 7.16 (2 H, d, 7.5 Hz), 3.61 (2 H, s), 3.58 (2 H, s), 2.77 (2 H, t, J = 6.0 Hz), 2.53 (2 H, t, J = 5.9 Hz), 2.37 (3 H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.82, 136.62, 136.56, 129.10, 129.00, 128.98, 128.39, 127.05, 58.70, 58.45, 56.84, 39.82, 21.28. FT-IR (NaCl disk, cm^{-1}) 3372 (w), 3084 (w), 3025 (m), 2924 (s), 2798 (s), 1602 (w), 1513 (m), 1494 (m), 1452 (m), 1365 (m), 1104 (w), 1070 (w), 1027 (m), 845 (m), 737 (s), 698 (s), 486 (w). ESI-MS $(M+H)^+$: Calcd for $C_{17}H_{23}N_2$, 255.4; Found, 255.4.

N,N-Benzyl(4-tert-butylbenzyl)ethylenediamine (N,N-(4-^{t}Bu-Bn)Bnen). Yield (85 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.24 (9 H, mm), 3.59 (2 H, s), 3.57 (2 H, s), 2.76 (2 H, t, J = 6.0 Hz), 2.52 (2 H, t, J = 6.0 Hz), 1.32 (9 H, S). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.97, 139.88, 136.60, 129.03, 128.66, 128.43, 127.09, 125.34, 58.95, 58.38, 56.85, 39.82, 34.65, 31.61. FT-IR (NaCl disk, cm^{-1}) 3375 (w), 3085 (w), 3060 (w), 3026 (w), 2961 (s), 2903 (m), 2868 (m), 2798 (m), 1602 (w), 1512 (w), 1494 (w), 1453 (m), 1362 (m), 1269 (w), 1109 (w), 1070 (w), 1027 (w), 834 (m), 741 (m), 698 (m), 546 (w). ESI-MS $(M+H)^+$: Calcd for $C_{20}H_{29}N_2$, 297.5; Found, 297.5.

N,N-Benzyl(4-methoxybenzyl)ethylenediamine (*N,N-(4-OMe-Bn)Bnen*). Light brown yellow crystals. Yield (83 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34-7.22 (7 H, mm), 6.86 (2

H, d, 8.6 Hz), 3.79 (3 H, s), 3.57 (2 H, s), 3.53 (2 H, s), 2.76 (2 H, t, J = 6.0 Hz), 2.59 (2 H, t, J = 5.9 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.88, 139.36, 131.12, 130.29, 129.11, 128.55, 127.26, 113.92, 58.54, 58.01, 55.44, 54.92, 39.09. FT-IR (NaCl disk, cm^{-1}) 3027 (w), 2998 (w), 2933 (w), 2833 (m), 1611 (w), 1584 (w), 1511 (s), 1494 (w), 1452 (w), 1366 (w), 1301 (w), 1248 (s), 1178 (w), 1104 (w), 1035 (w), 819 (w), 740 (w), 699 (w). ESI-MS $(M+H)^+$: Calcd for $C_{17}H_{23}N_2O$, 271.4; Found, 271.4.

***α,α′-d*$_2$-*N,N*-Dibenzylethylene-1,2-diamine ($(C_6H_5CDH)_2$en).** To a stirred anhydrous suspension of lithium aluminum deuteride (2.6 g, 62 mmol) in diethylamine (25 mL) was added a solution of benzaldehyde oxime (3.0 g, 25 mmol), using a pressure-compensated dropping funnel at -78 °C. The mixture was warmed to room temperature and stirred for 6 h before being carefully hydrolyzed by sequential addition of 2.6 g of water, 2.6 g of 15 % NaOH (aq), and 3 × 2.6 g of water. Inorganic salts were removed by filtration and washed with 200 mL of ethylacetate. The filtrate was dried over $MgSO_4$ and concentrated. The amine product was separated from the starting oxime by extraction with $CHCl_3$, resulting in a turbid solution. The solution was filtered through Celite and concentrated. To a solution of *d*$_1$-benzylamine (1.6 g, 15 mmol) in 5 mL of benzene in a 50 mL round-bottom flask, cooled to 0 °C, was added a solution of PhCHO (2.0 g, 19 mmol) in 5 mL of benzene. The solution was warmed to room temperature, resulting in a turbid suspension. After 1 h of stirring, the flask was connected to a Dean-Stark water separator and heated at reflux overnight at 92 °C. The solution was concentrated under vacuum and, without further purification, the resulting Schiff base was taken up in 60 mL of methanol and the solution was cooled to

0 °C. A 0.8 g (19 mmol) portion of solid $NaBD_4$ was carefully added, and the reaction mixture was allowed to warm to room temperature and then stirred for an additional 12 h. The solvent was concentrated under vacuum, 100 mL of water was added, and the solution was extracted with 4 × 50 mL portions of ethylacetate. The solution was dried ($MgSO_4$) and concentrated. With the resulting *d*$_2$-*N,N*-dibenzylamine, $(C_6H_5CDH)_2$en was prepared as a colorless oil in the manner described for the synthesis of benzyl(4-R-benzyl)ethylenediamine. Yield (54 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.24 (9 H, mm), 3.59 (1 H, s), 3.57 (1 H, s), 2.76 (2 H, t, J = 6.0 Hz), 2.52 (2 H, t, J = 6.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.49, 129.14, 128.57, 127.37, 58.13 (t, $^1J_{CD}$ = 18.98 Hz), 52.48, 38.04. FT-IR (NaCl disk, cm^{-1}) 3059 (w), 3025 (w), 2938 (w), 2080 (w), 1662 (m), 1603 (m), 1494 (s), 1449 (s), 1397 (w), 1342 (w), 1313 (w), 1213 (w), 1155 (w), 1075 (w), 1028 (w), 924 (w), 738 (s), 698 (s), 614 (w). ESI-MS $(M+H)^+$: Calcd for $C_{16}H_{19}D_2N_2$, 243.4; Found, 243.4.

***α,α-d*$_2$*-N,N*-Dibenzylethylene-1,2-diamine ($(C_6H_5CD_2)(C_6H_5CH_2)$en)**. The chemical *α,α-d*$_2$-benzylamine was prepared by reduction of cyanobenzene using lithium aluminum deuteride as described in the literature.[10] With the resulting *α,α-d*$_2$-benzylamine, the colorless oil (D_2-Bn)Bnen was prepared as described in synthesis of benzyl-(4-R-benzyl)ethylenediamine. Yield (71 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.24 (9 H, mm), 3.60 (2 H, s), 2.76 (2 H, t, J = 6.0 Hz), 2.52 (2 H, t, J = 6.0 Hz). ESI-MS MH^+: Calcd for $C_{16}H_{19}D_2N_2$, 243.4; Found, 243.4.

Table S1. Summary of X-ray Crystallographic Data

Compound	**2**·2CH_2Cl_2	**3**·2CH_2Cl_2	**4**·2CH_2Cl_2	**5**·2CH_2Cl_2
empirical formula	$Fe_2C_{118}H_{110}N_4O_8Cl_6$	$Fe_2C_{118}H_{110}N_4O_8Cl_4F_2$	$Fe_2C_{120}H_{116}N_4O_8Cl_4$	$Fe_2C_{126}H_{128}N_4O_8Cl_4$
weight	2036.50	2003.60	1993.65	2079.82
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a,Å	13.341(3)	13.2882(18)	13.373(2)	12.044(2)
b, Å	14.160(3)	14.107(2)	14.135(3)	21.855(4)
c, Å	16.147(3)	16.170(2)	16.105(3)	21.563(4)
α, deg	68.32(3)	102.139(2)	68.356(2)	
β, deg	66.26(3)	114.168(2)	66.356(2)	103.068(2)
γ, deg	79.14(3)	100.610(2)	79.231(3)	
V, Å^3	2591.7(9)	2576.5(6)	2589.6(7)	5528.7(16)
Z	1	1	1	2
ρ_{calc}, g/cm^3	1.305	1.291	1.280	1.249
crystal size, mm	0.15×0.15×0.10	0.20×0.10×0.10	0.15×0.15×0.10	0.15×0.12×0.10
T, °C	-70	-90	-100	-100
μ□(Mo K□), mm^{-1}	0.494	0.449	0.443	0.418
total no. of data	14296	16297	20062	41700
no. of unique data points	9536	9458	9540	10284
no. of parameters	638	636	638	675
R1 (%)[a]	5.34	4.33	5.49	5.52
wR2 (%)[b]	11.32	11.63	13.99	14.37
max, min peaks, e/Å^3	0.587, -0.529	0.795, -0.731	0.764, -0.703	0.930, -0.794

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S1 Continued

Compound	**6**·2CH_2Cl_2	**7**	**8**·CH_2Cl_2
empirical formula	$Fe_2C_{119}H_{114}N_4O_{10}Cl_2$	$Fe_2C_{116}H_{104}N_4O_8D_4$	$Fe_2C_{117}H_{106}N_4O_8D_4Cl_2$
weight	1942.74	1801.79	1886.71
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a,Å	13.444(2)	11.3905(10)	11.620(3)
b Å	14.246(2)	14.7167(13)	12.720(3)
c Å	16.066(3)	15.2859(14)	18.030(5)
α, deg	68.220(3)	77.822(2)	77.717(6)
β, deg	66.366(3)	72.178(2)	84.601(5)
γ, deg	77.837(3)	82.189(2)	87.871(6)
V, Å^3	2610.8(7)	2377.5(4)	2592.1(12)
Z	1	1	1
ρ_{calc}, g/cm^3	1.236	1.258	1.209
crystal size, mm	0.10×0.10×0.08	0.10×0.07×0.02	0.20×0.20×0.10
T, ^{o}C	-80	-75	-90
μ (Mo Kα), mm^{-1}	0.390	0.367	0.389
total no. of data	16598	18881	16592
no. of unique data points	9619	8802	9562
no. of parameters	656	600	615
R1 (%)[a]	6.77	7.79	7.34
wR2 (%)[b]	16.96	20.18	16.13
max, min peaks, e/ Å^3	0.767, -0.706	0.476, -0.379	0.404, -0.366

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

List of Supporting Figures

Figure S1. ORTEP drawing of $[Fe_2(\mu\text{-}O_2CAr^{Tol})_2(O_2CAr^{Tol})_2(N,N\text{-}(4\text{-Cl-Bn})Bnen)_2]$ (**2**) showing 50 % probability thermal ellipsoids. Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+2. The solvent molecules and hydrogen atoms are omitted for clarity. (Bottom) All atoms of $Ar^{Tol}CO_2^-$ ligands in **2**, except for the carboxylate groups and the α–carbon atoms, were omitted for clarity.

Figure S2. ORTEP drawing of $[Fe_2(\mu\text{-}O_2CAr^{Tol})_2(O_2CAr^{Tol})_2(N,N\text{-}(4\text{-F-Bn})Bnen)_2]$ (**3**) showing 50 % probability thermal ellipsoids. Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1. The solvent molecules and hydrogen atoms are omitted for clarity. (Bottom) All atoms of $Ar^{Tol}CO_2^-$ ligands in **3**, except for the carboxylate groups and the α–carbon atoms, were omitted for clarity.

Figure S3. ORTEP drawing of $[Fe_2(\mu\text{-}O_2CAr^{Tol})_2(O_2CAr^{Tol})_2(N,N\text{-}(4\text{-Me-Bn})Bnen)_2]$ (**4**) showing 50 % probability thermal ellipsoids. Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z+1. The solvent molecules and hydrogen atoms are omitted for clarity. (Bottom) All atoms of $Ar^{Tol}CO_2^-$ ligands in **4**, except for the carboxylate groups and the α–carbon atoms, were omitted for clarity.

Figure S4. ORTEP drawing of $[Fe_2(\mu\text{-}O_2CAr^{Tol})_2(O_2CAr^{Tol})_2(N,N\text{-}(4\text{-}^t\text{Bu-Bn})Bnen)_2]$ (**5**) showing 50 % probability thermal ellipsoids. Symmetry transformations used to

generate equivalent atoms: #1 -x+1,-y+1,-z+1. The solvent molecules and hydrogen atoms are omitted for clarity. (Bottom) All atoms of $Ar^{Tol}CO_2^-$ ligands in **5**, except for the carboxylate groups and the α–carbon atoms, were omitted for clarity.

Figure S5. ORTEP drawing of $[Fe_2(\mu\text{-}O_2CAr^{Tol})_2(O_2CAr^{Tol})_2(N,N\text{-}(4\text{-}OMe\text{-}Bn)Bnen)_2]$ (**6**) showing 50 % probability thermal ellipsoids. Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z+1. The solvent molecules and hydrogen atoms are omitted for clarity. (Bottom) All atoms of $Ar^{Tol}CO_2^-$ ligands in **6**, except for the carboxylate groups and the α–carbon atoms, were omitted for clarity.

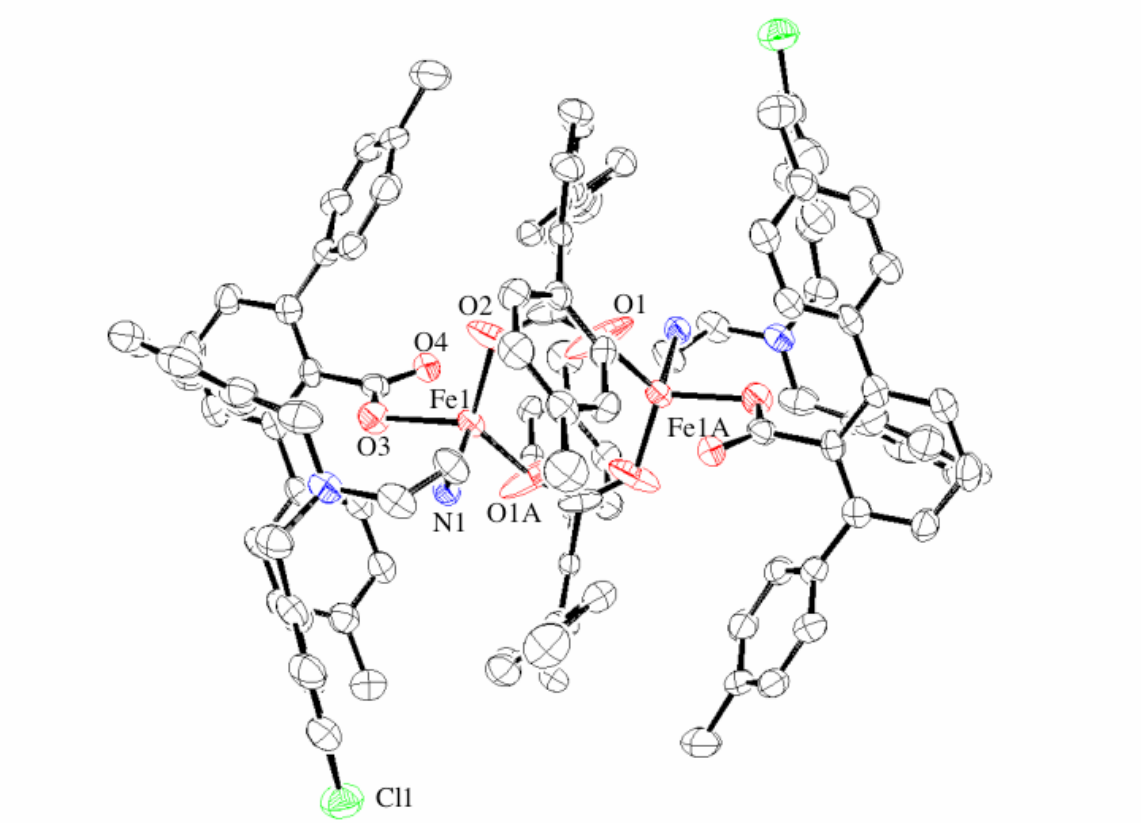
Figure S6. ORTEP drawings of $[Fe_2(\mu\text{-}O_2CAr^{Tol})_2(O_2CAr^{Tol})_2((C_6H_5CDH)_2en)_2]$ (**7**) (Top) showing 50 % probability thermal ellipsoids. Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+2. The solvent molecules and hydrogen atoms are omitted for clarity. (Bottom) All atoms of $Ar^{Tol}CO_2^-$ ligands in **7**, except for the carboxylate groups and the α–carbon atoms, were omitted for clarity.

Figure S7. The oxygenation product distributions of $[Fe_2(\mu\text{-}O_2CAr^{Tol})_2(O_2CAr^{Tol})_2(N,N\text{-}(4\text{-}F\text{-}Bn)Bnen)_2]$ (**3**) and $[Fe_2(\mu\text{-}O_2CAr^{Tol})_2(O_2CAr^{Tol})(N,N\text{-}(4\text{-}^t\text{Bu-}Bn)Bnen)_2]$ (**5**) at 23 °C, determined ^{1}H NMR spectroscopy, are shown in A) and B), respectively.

Figure S8. The oxygenation product distribution of $[Fe_2(\mu\text{-}O_2CAr^{Tol})_2(O_2CAr^{Tol})_2((C_6H_5CDH)_2en)_2]$ (**7**) at 23 °C. A) GC-MS: 20.011 min, $PhCHO(M^+$

= 106); 20.08 min, PhCDO (M^+ = 107) B) ^{1}H NMR spectrum: 10.01, (s, 1H from PhCHO), 7.88, (d, 2H from the combination of PhCHO and PhCDO).

Figure S9. The oxygenation product distribution of [$Fe_2(\mu$-$O_2CAr^{Tol})_2(O_2CAr^{Tol})_2$-$((C_6H_5CD_2)(C_6H_5CH_2)en)_2$] (**8**) at 23 °C. A) and B) ^{1}H NMR spectrum: 10.01, (s, 1H from PhCHO), 7.88, (d, 2H from the combination of PhCHO and PhCDO)



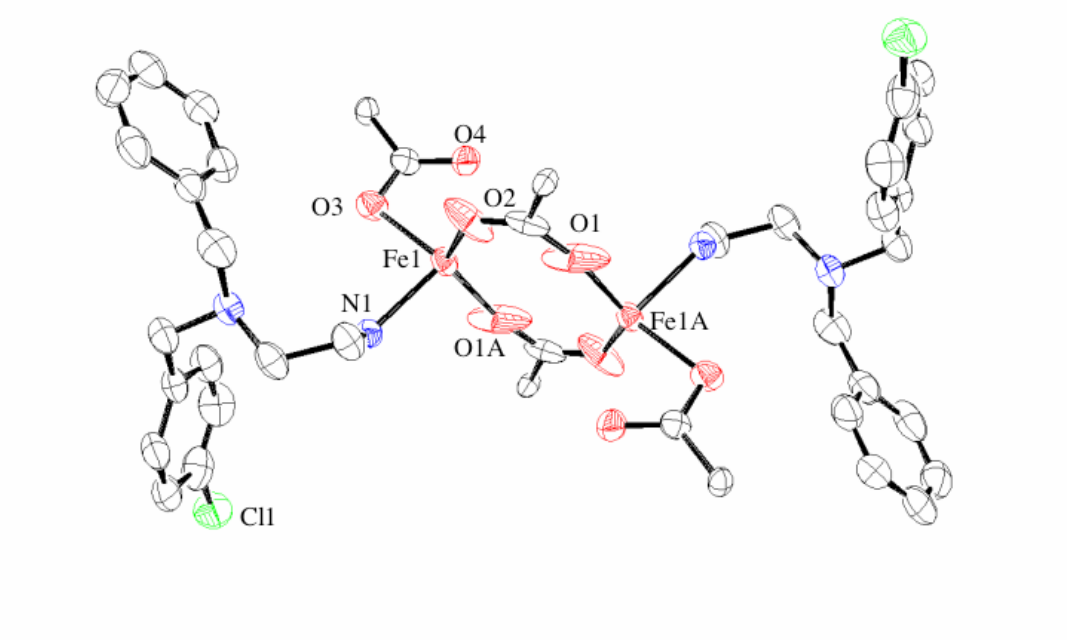
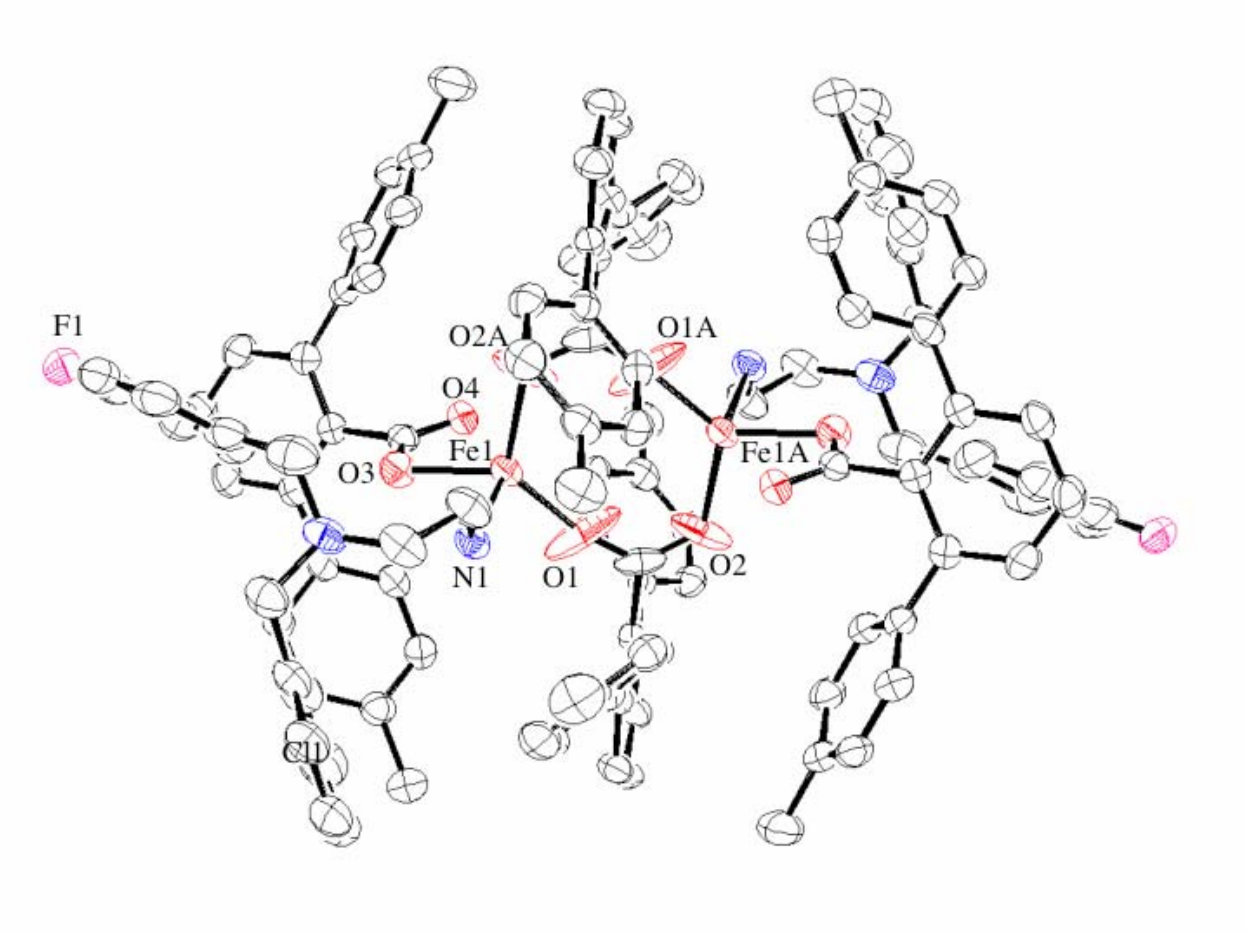


Figure S1. Yoon and Lippard.



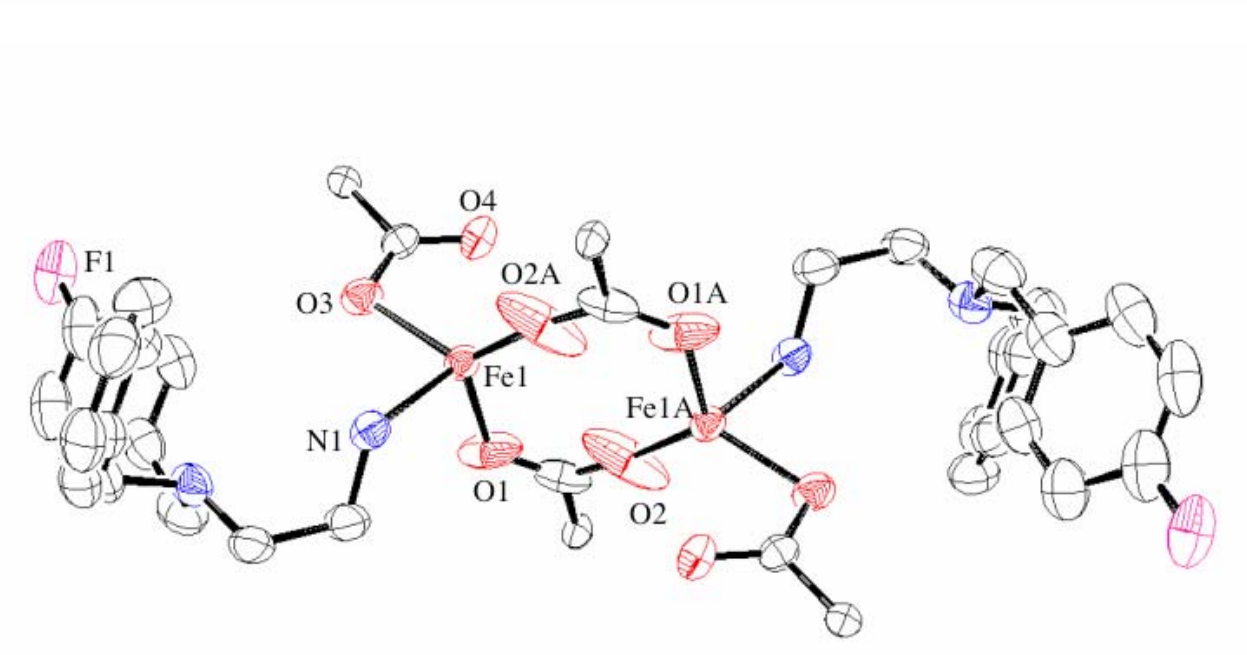


Figure S2. Yoon and Lippard.

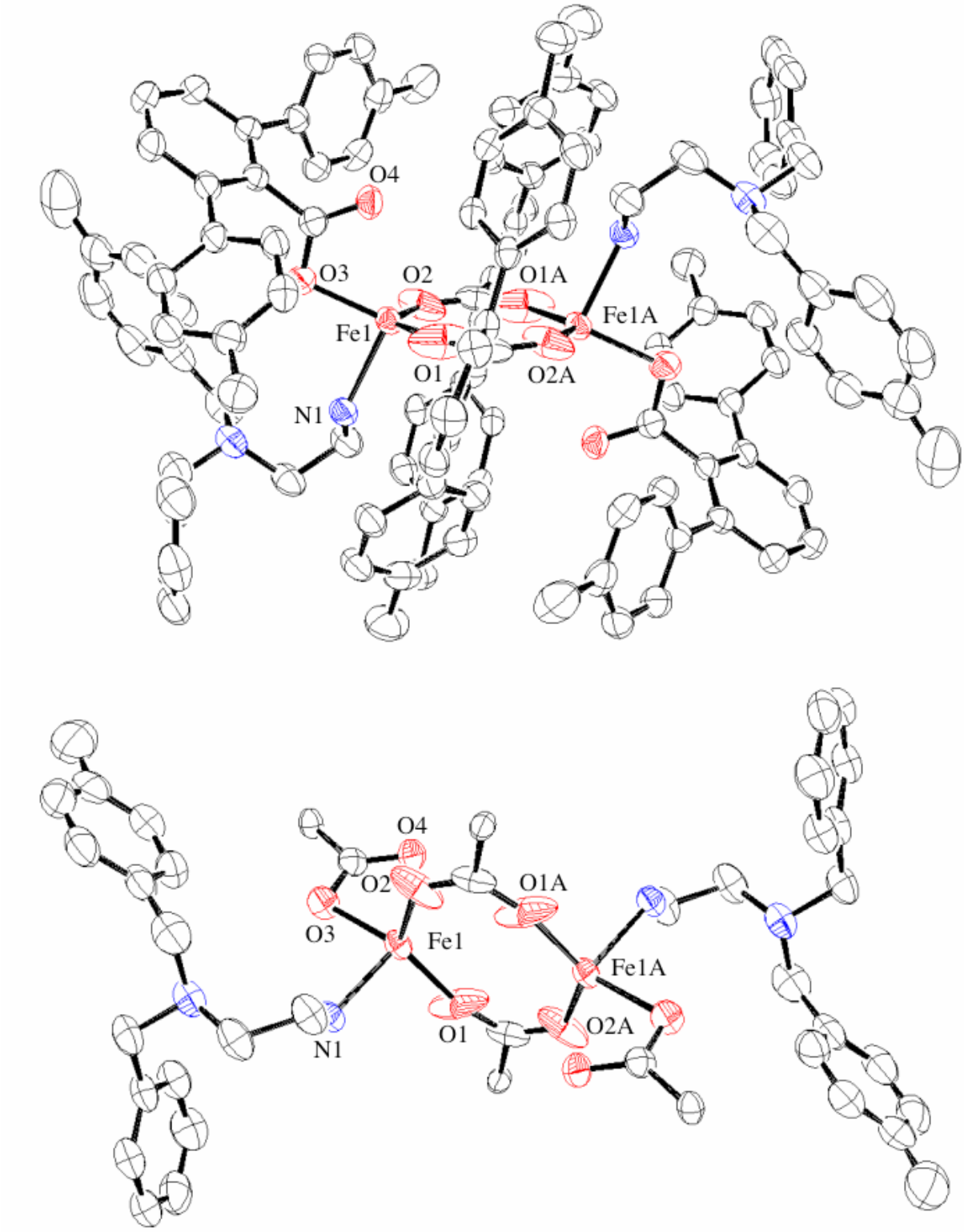


Figure S3. Yoon and Lippard.

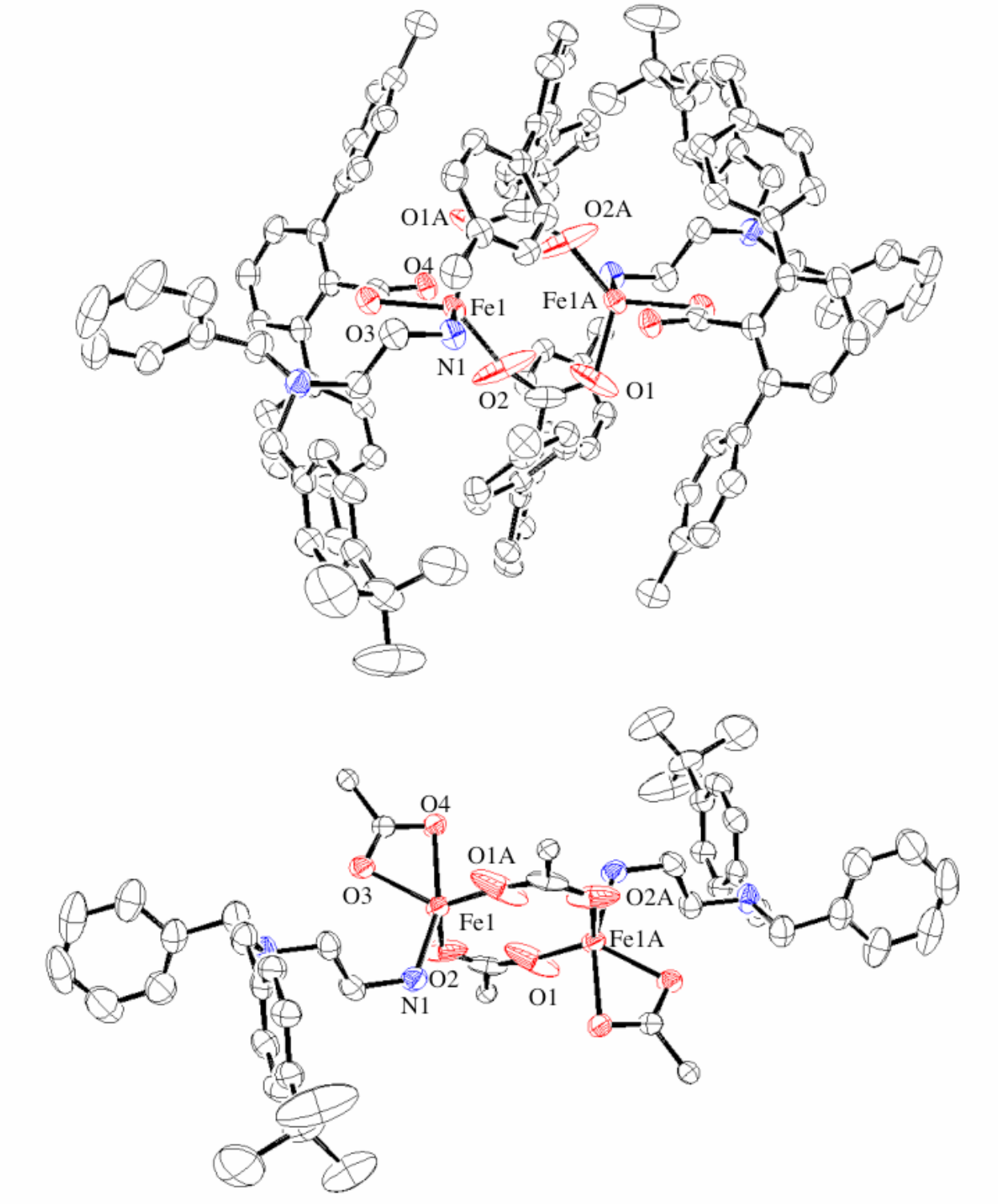


Figure S4. Yoon and Lippard.

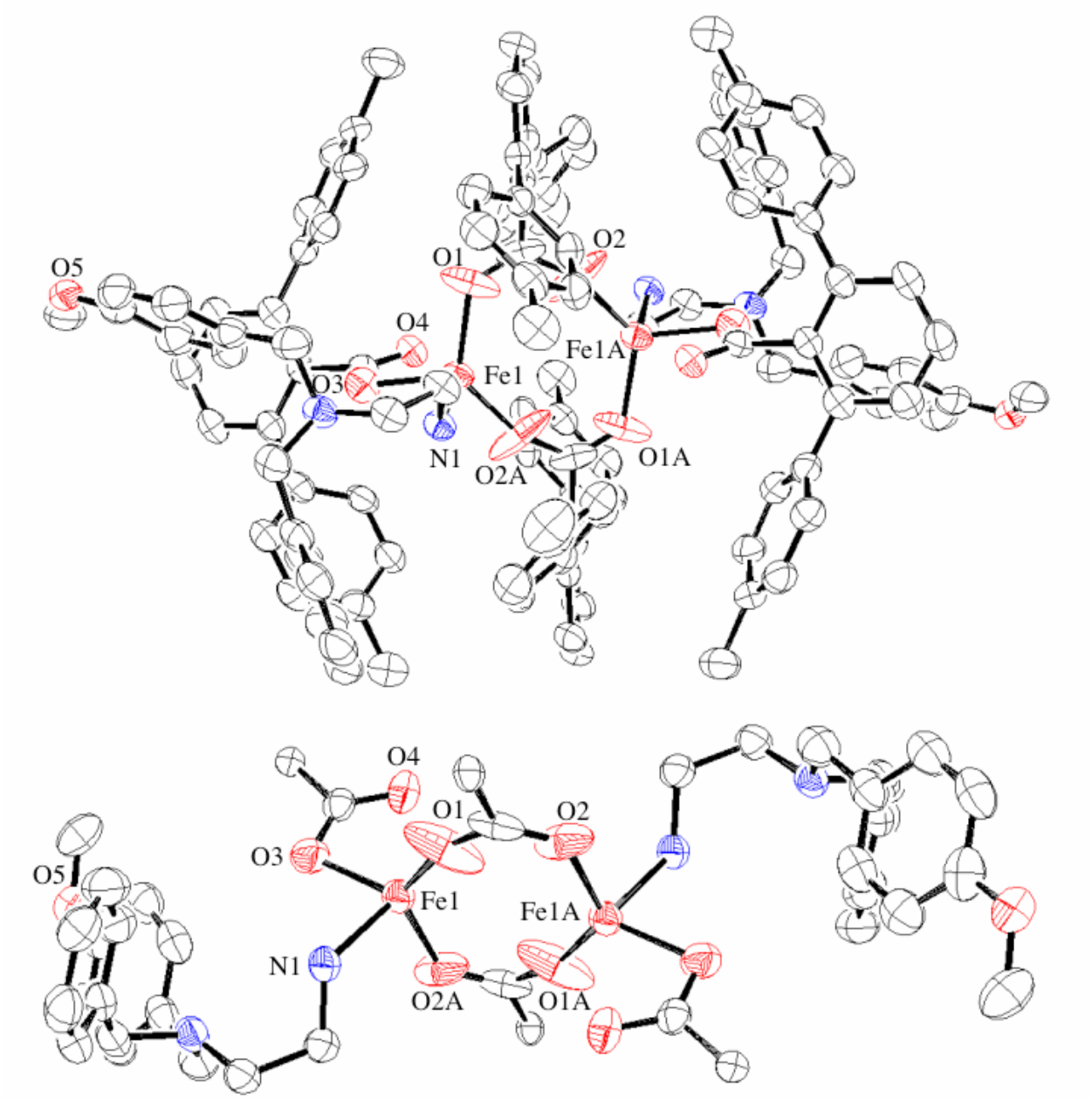


Figure S5. Yoon and Lippard.

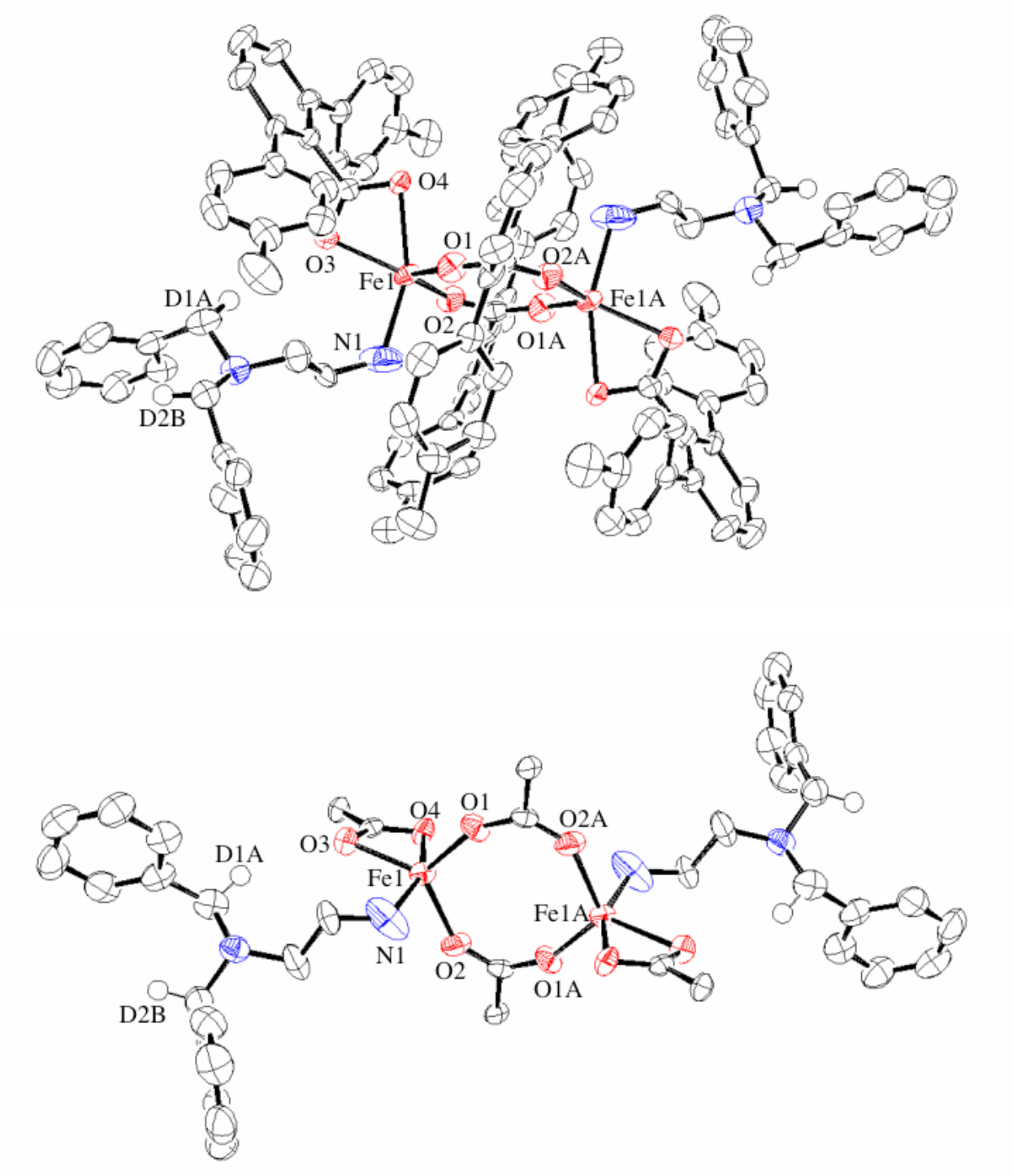
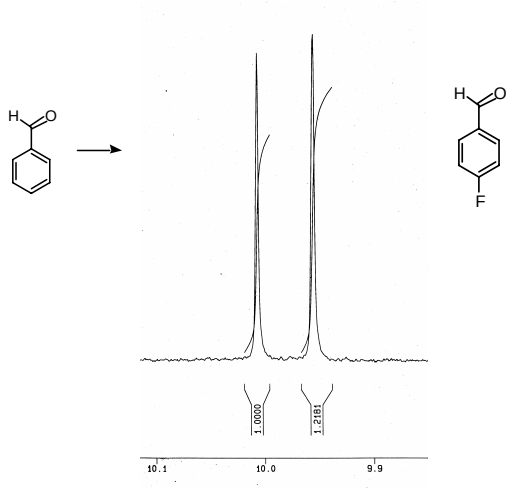


Figure S6. Yoon and Lippard.

A)



B)

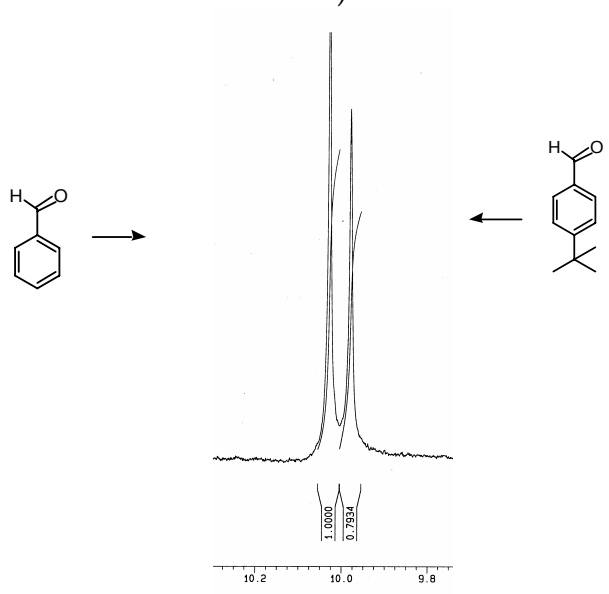
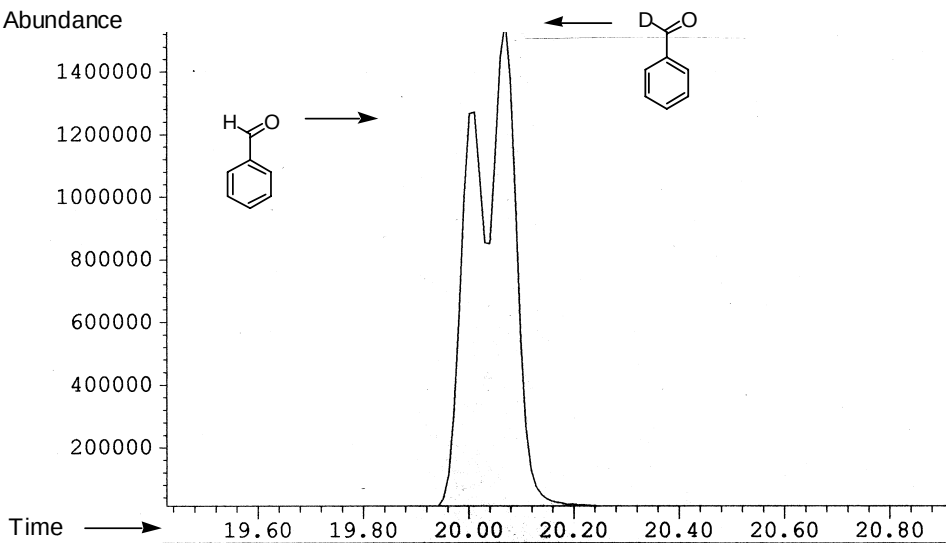


Figure S7. Yoon and Lippard.

A)



B)

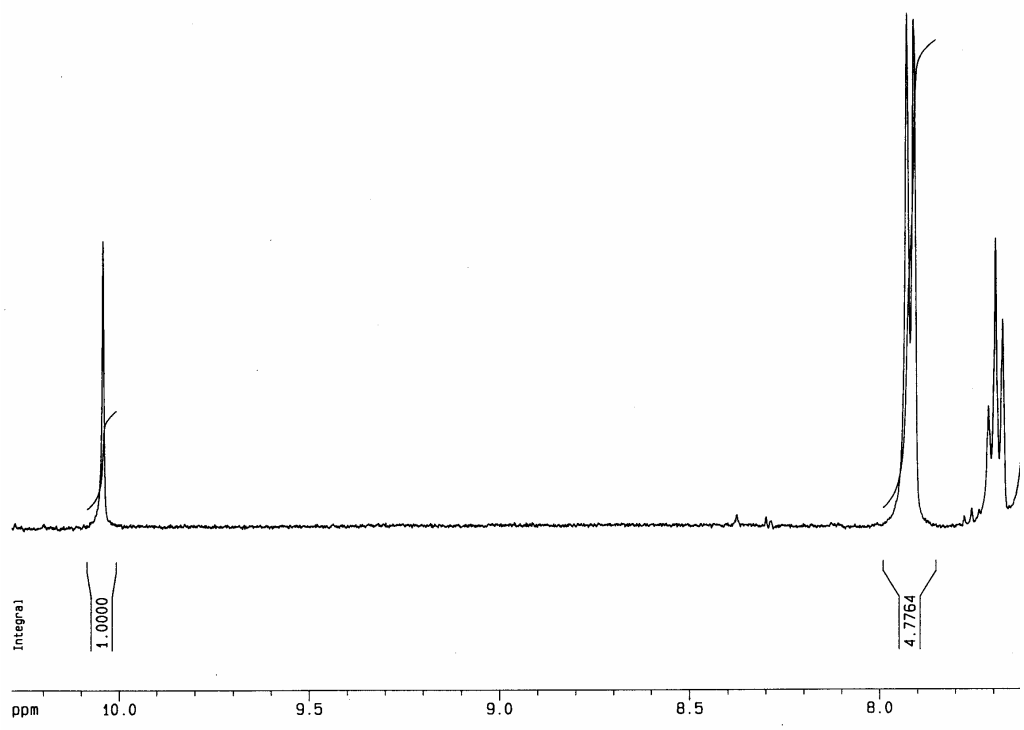
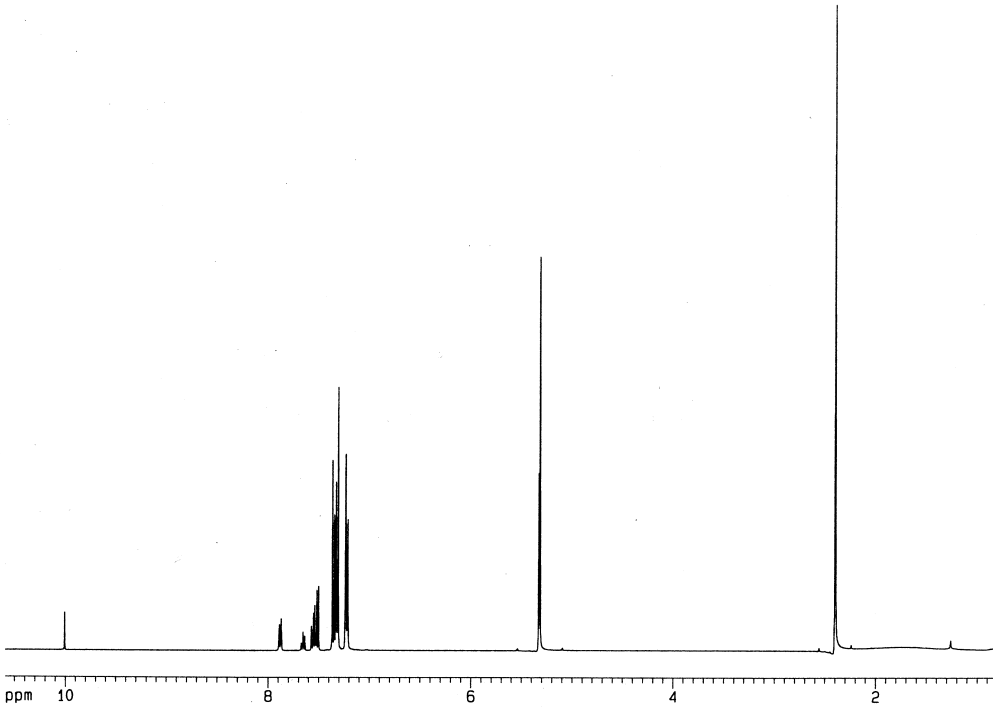


Figure S8. Yoon and Lippard.

A)



B)

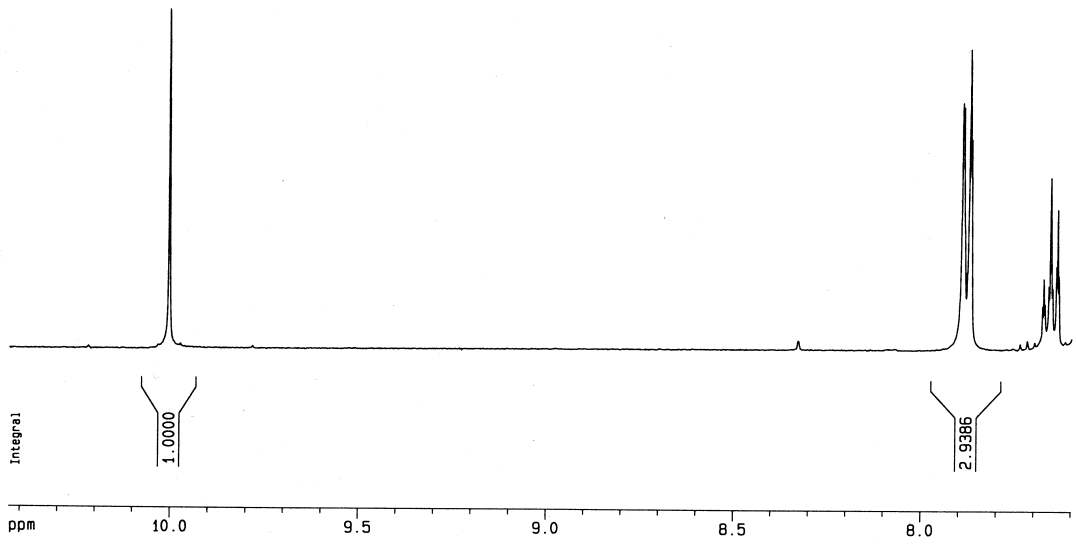


Figure S9. Yoon and Lippard.