Iron-Porphyrin NO Complexes with Covalently Attached N-Donor Ligands: The Formation of a Stable Six-Coordinate Species in Solution

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Supporting Information

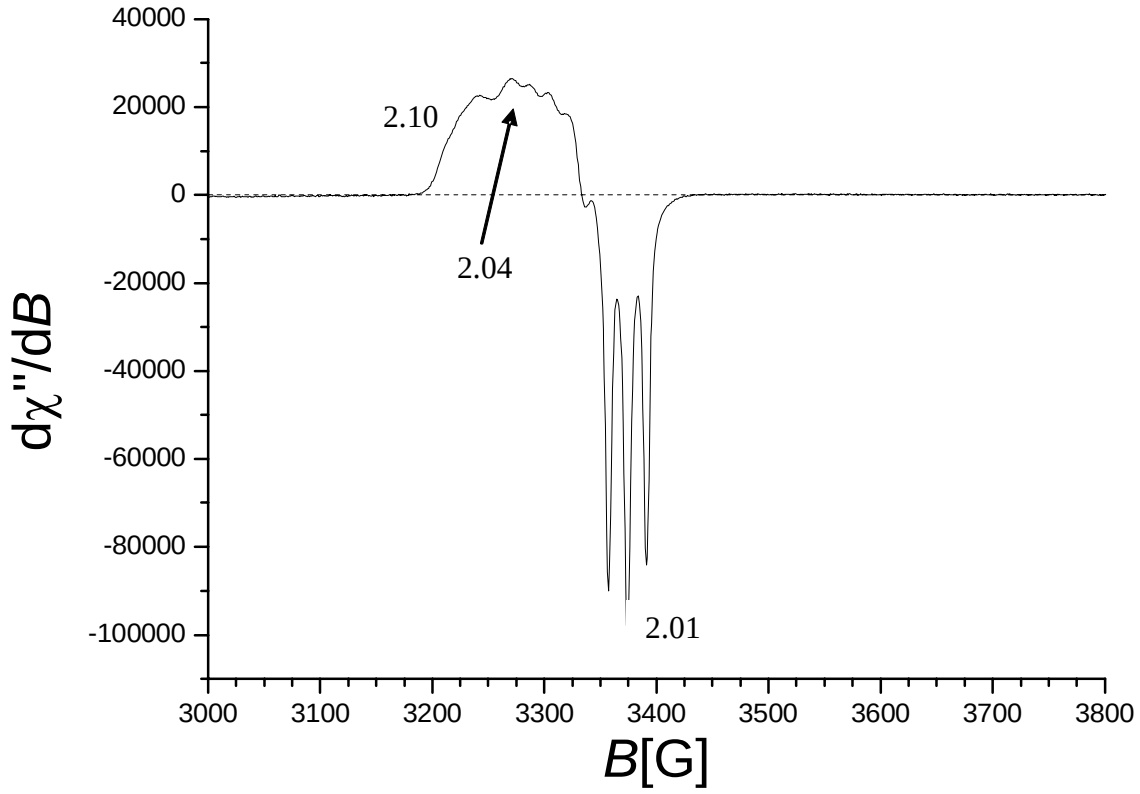

Figure S1. EPR spectrum of [Fe(TMP-*m*Py)(NO)] (**1**) recorded at 77 K in frozen toluene. Estimated g values are indicated.

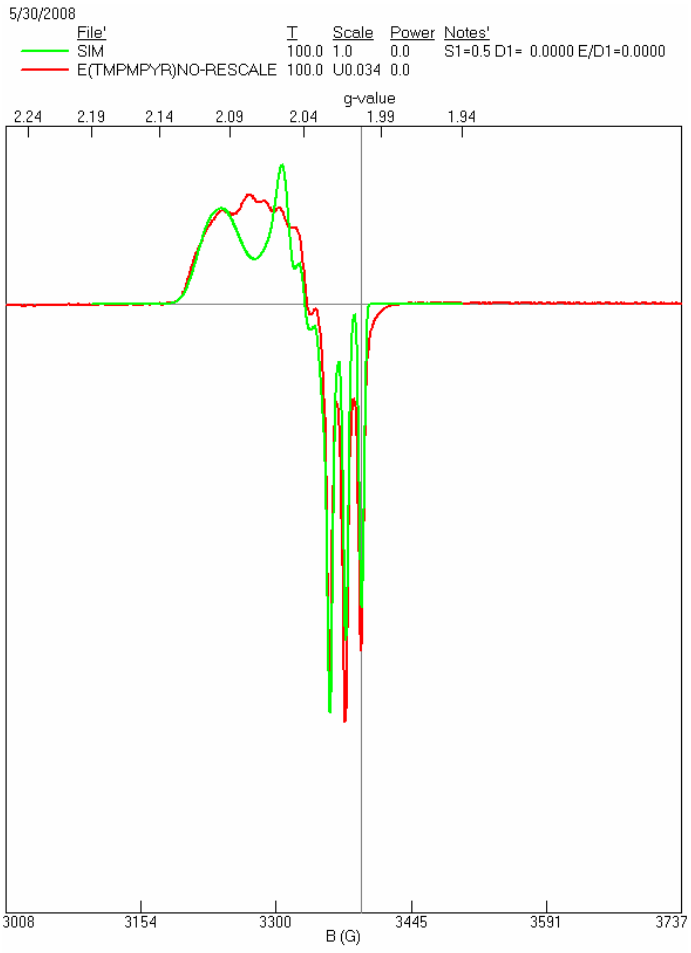

Figure S2. EPR spectrum of [Fe(TMP-*m*Py)(NO)] (**1**) recorded at 77 K in frozen toluene (red; cf. Figure S1) and fit of the spectrum using the program SpinCount (green).[1] Fit parameters: g_x = 2.099, g_y = 2.04, g_z = 2.012; ^{14}N hyperfine: $^{NO}A_x$ = 45 MHz, $^{NO}A_y$ = 48 MHz, $^{NO}A_z$ = 48 MHz.

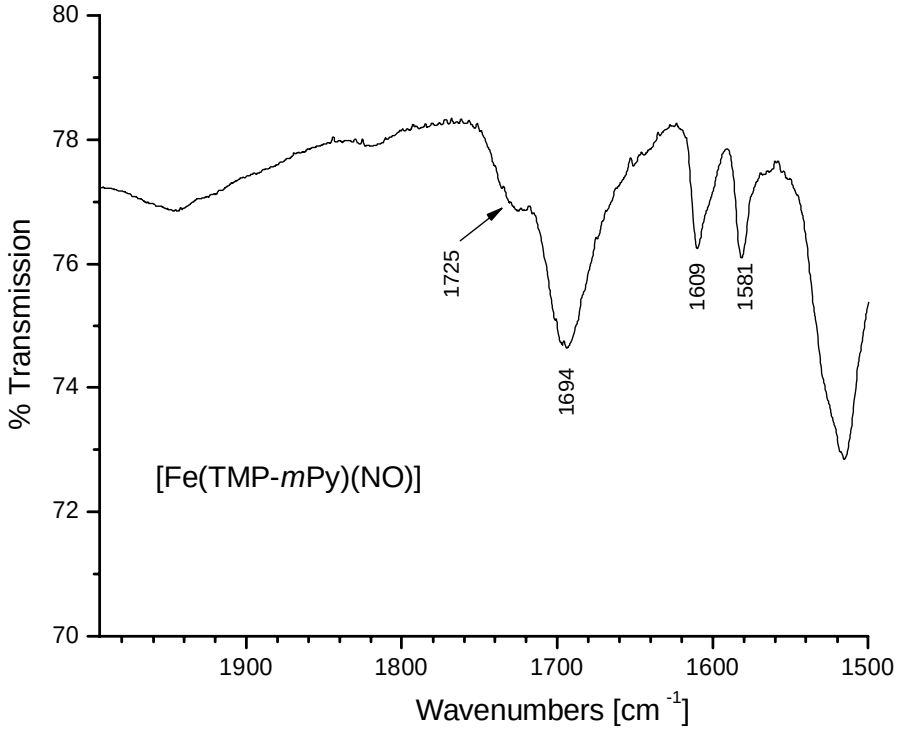

Figure S3. FT-IR spectrum of [Fe(TMP-*m*Py)(NO)] (**1**) in KBr. The band at 1694 cm^{-1} corresponds to the N-O stretch ν(N-O).

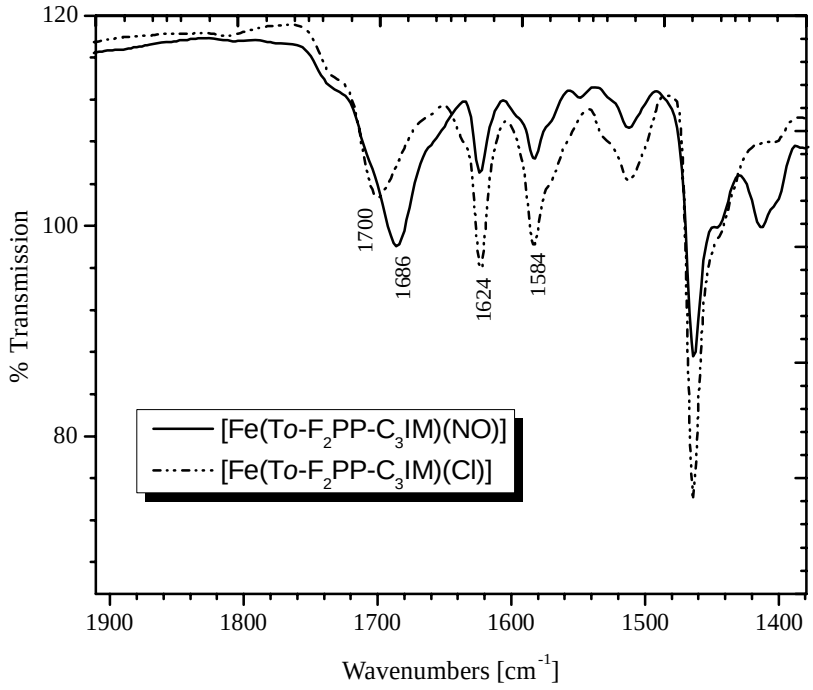

Figure S4. FT-IR spectra of [Fe(T*o*-F_2PP-C_3IM)(Cl)] (dashed line), and of the corresponding NO complex [Fe(T*o*-F_2PP-C_3IM)(NO)] (**2**; solid line) in KBr.

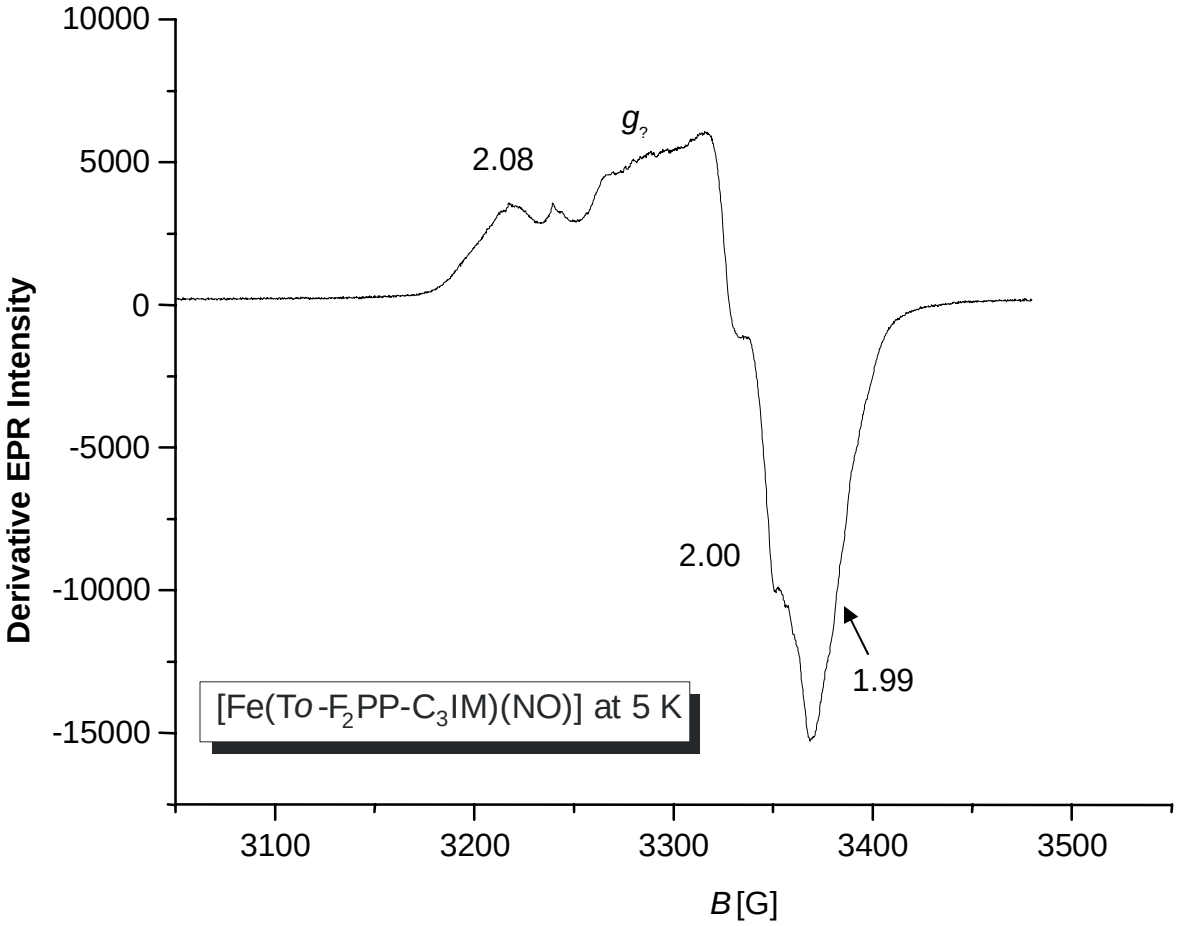

Figure S5. EPR spectrum of [Fe(T*o*-F_2PP-C_3IM)(NO)] (**2**) in frozen DMSO at 5 K. The additional species ($g_?$) is typically observes in 6C ferrous heme nitrosyls.[2] Estimated g values are indicated.

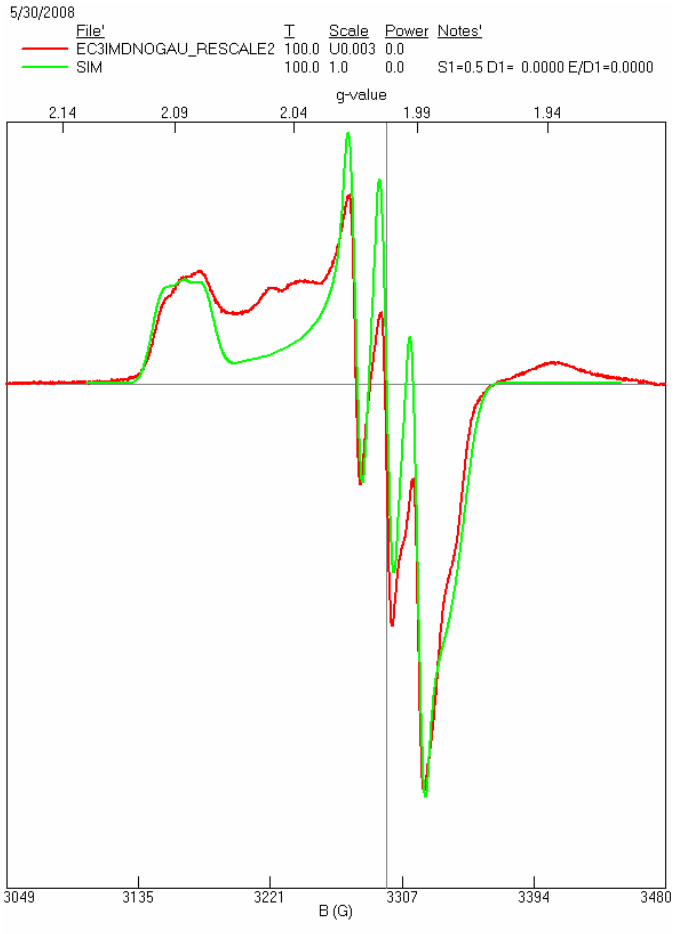

Figure S6. EPR spectrum of [Fe(T*o*-F_2PP-C_3IM)(NO)] (**2**) recorded at 77 K in frozen DMSO (red) and fit of the spectrum using the program SpinCount (green).[1] Fit parameters: g_x = 2.087, g_y = 2.002, g_z = 1.982; ^{14}N hyperfine: $^{NO}A_x$ = 40.5 MHz, $^{NO}A_y$ = 57 MHz, $^{NO}A_z$ = 37 MHz; $^{IM}A_y$ = 2 MHz.

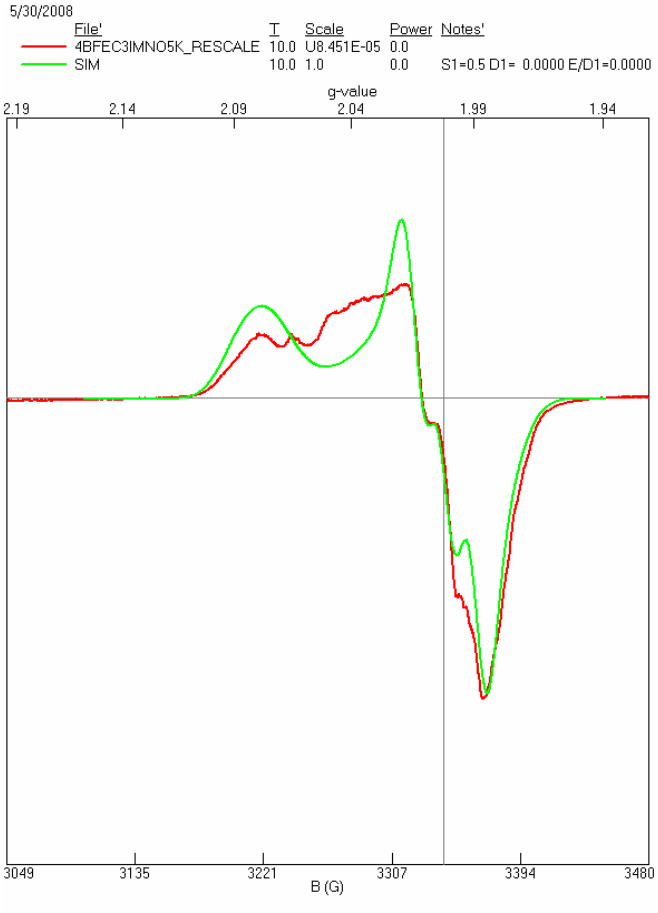

Figure S7. EPR spectrum of [Fe(T*o*-F_2PP-C_3IM)(NO)] (**2**) recorded at 5 K in frozen DMSO (red) and fit of the spectrum using the program SpinCount (green).[1] Fit parameters: g_x = 2.08, g_y = 2.001, g_z = 1.989; ^{14}N hyperfine: $^{NO}A_x$ = 40.5 MHz, $^{NO}A_y$ = 57 MHz, $^{NO}A_z$ = 50 MHz; $^{IM}A_y$ = 2 MHz.

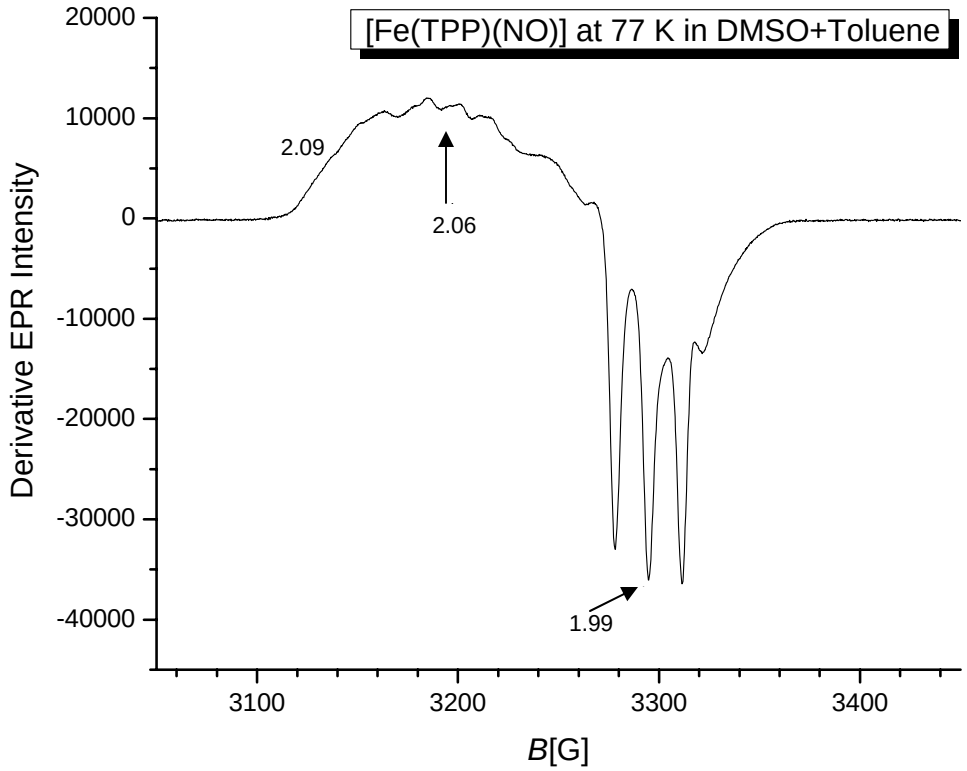

Figure S8. EPR spectrum of [Fe(TPP)(NO)] in a frozen 1:1 mixture of toluene and DMSO at 77 K.

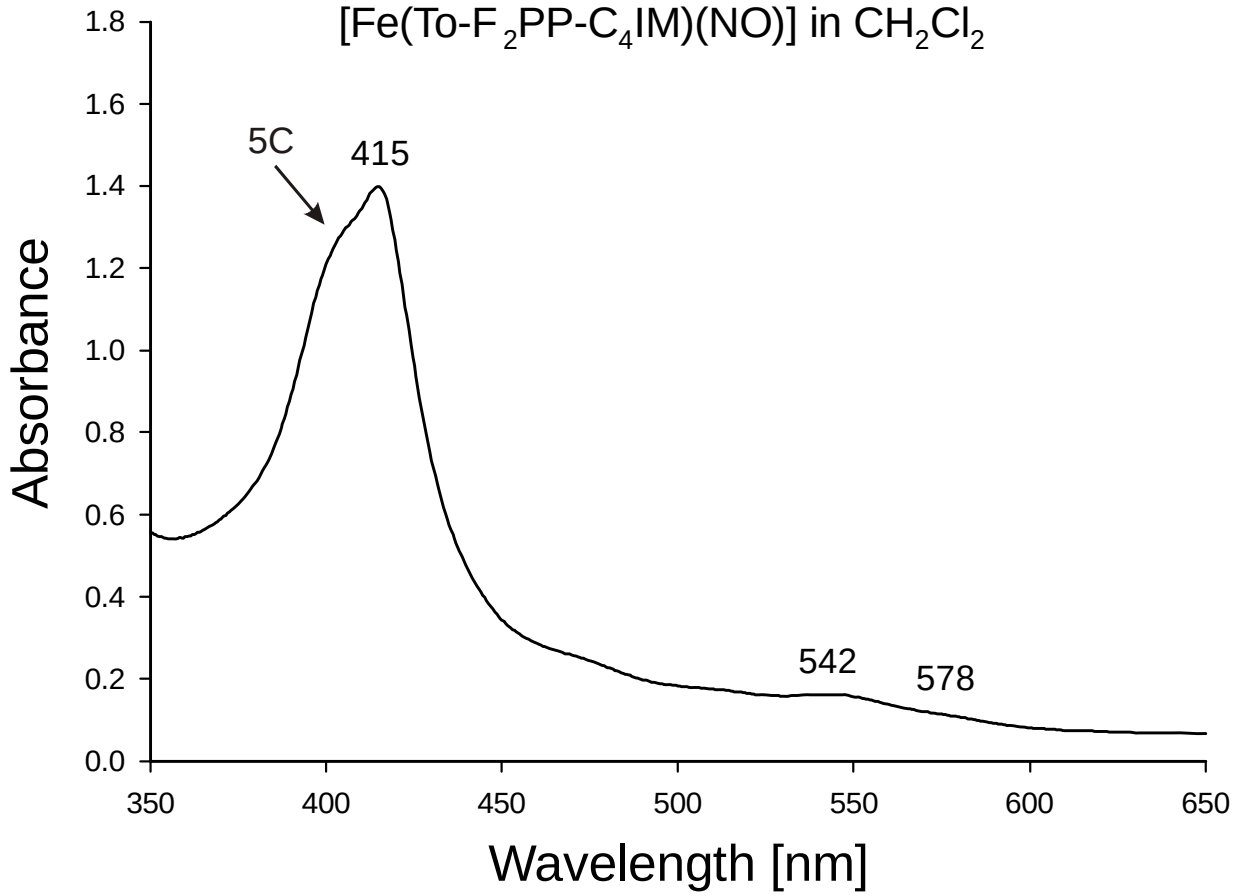

Figure S9. UV-Vis spectrum of [Fe(T*o*-F_2PP-C_4IM)(NO)] (**3**) in CH_2Cl_2 at room temperature.

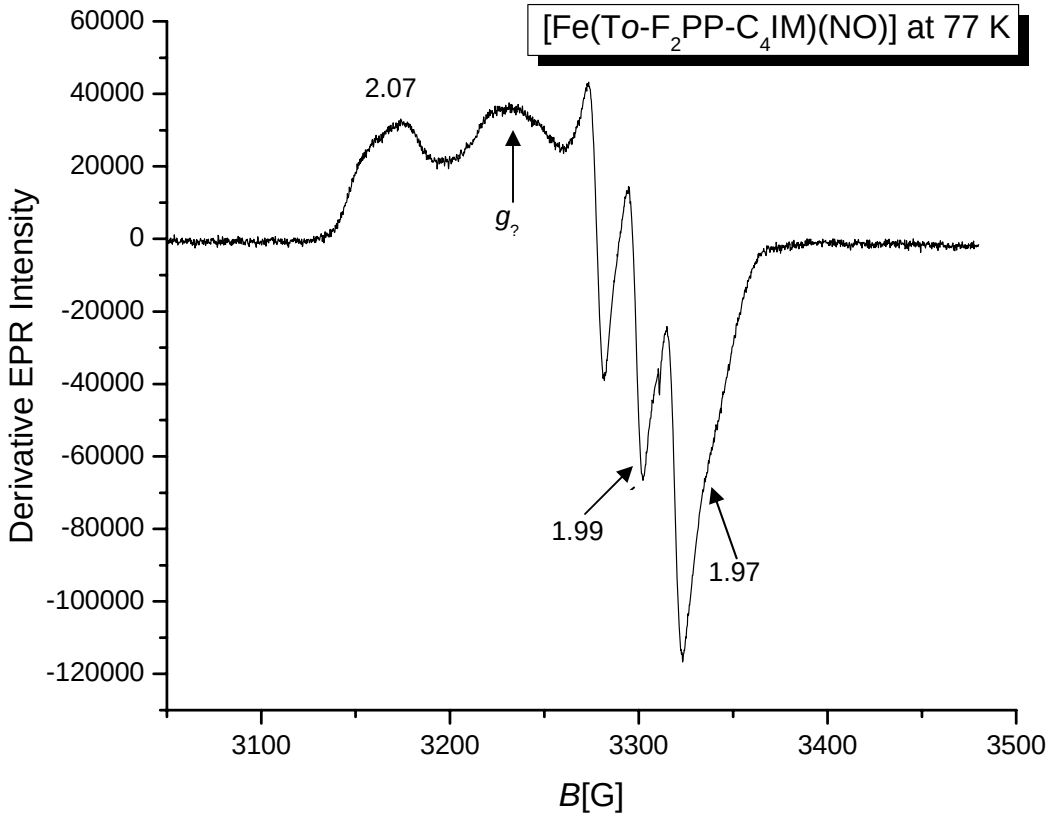

Figure S10. EPR spectrum of [Fe(T*o*-F_2PP-C_4IM)(NO)] (**3**) in frozen DMSO at 77 K. The additional species ($g_?$) is typically observes in 6C ferrous heme nitrosyls.[2] Estimated g values are indicated.

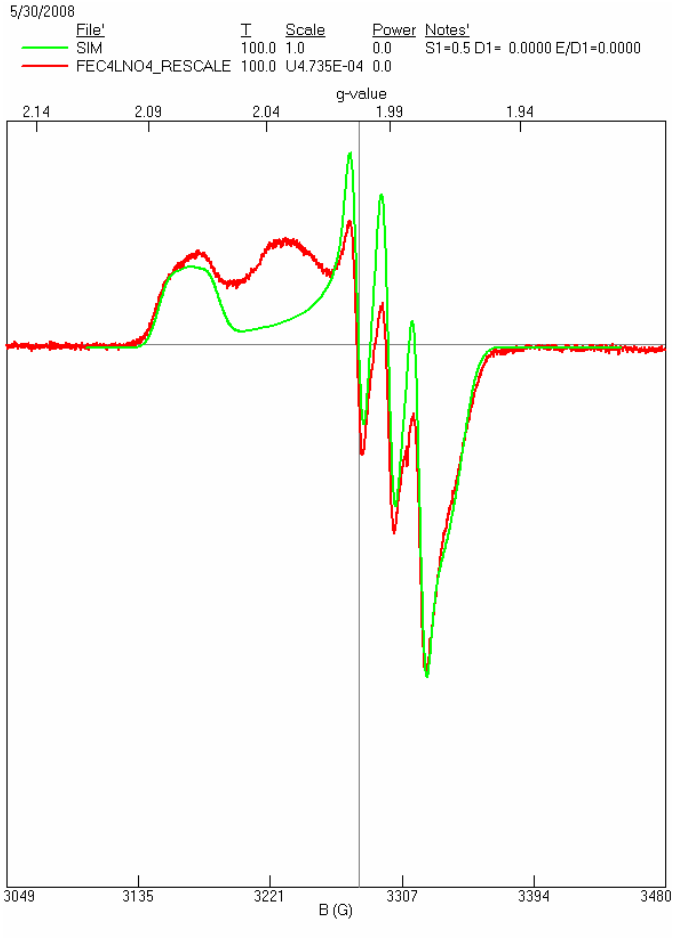

Figure S11. EPR spectrum of [Fe(T*o*-F_2PP-C_4IM)(NO)] (**3**) recorded at 77 K in frozen toluene (red) and fit of the spectrum using the program SpinCount (green).[1] Fit parameters: g_x = 2.073, g_y = 1.9905, g_z = 1.971; ^{14}N hyperfine: $^{NO}A_x$ = 39 MHz, $^{NO}A_y$ = 57 MHz, $^{NO}A_z$ = 37 MHz; $^{IM}A_y$ = 2 MHz.

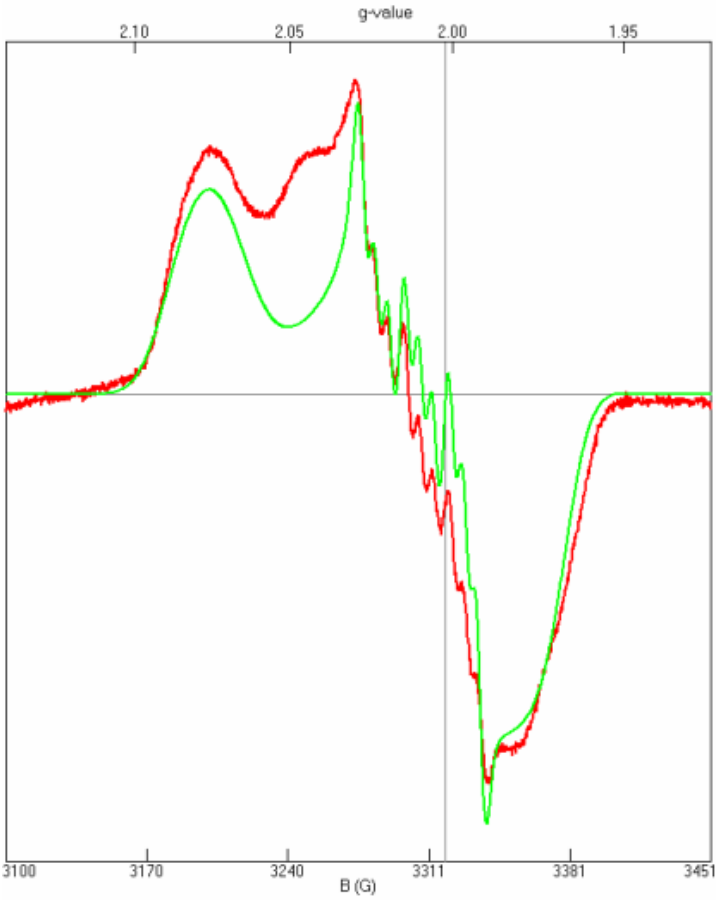

Figure S12. EPR spectrum of [Fe(T*o*-F_2PP-BzIM)(NO)] (**4**) in frozen DMSO at 77 K (red) and fit of the spectrum using the program SpinCount (green).[1] Fit parameters: g_x = 2.077, g_y = 2.009, g_z = 1.978; ^{14}N hyperfine: $^{NO}A_x$ = 37 MHz, $^{NO}A_y$ = 62 MHz, $^{NO}A_z$ = 39 MHz; $^{IM}A_y$ = 19 MHz.

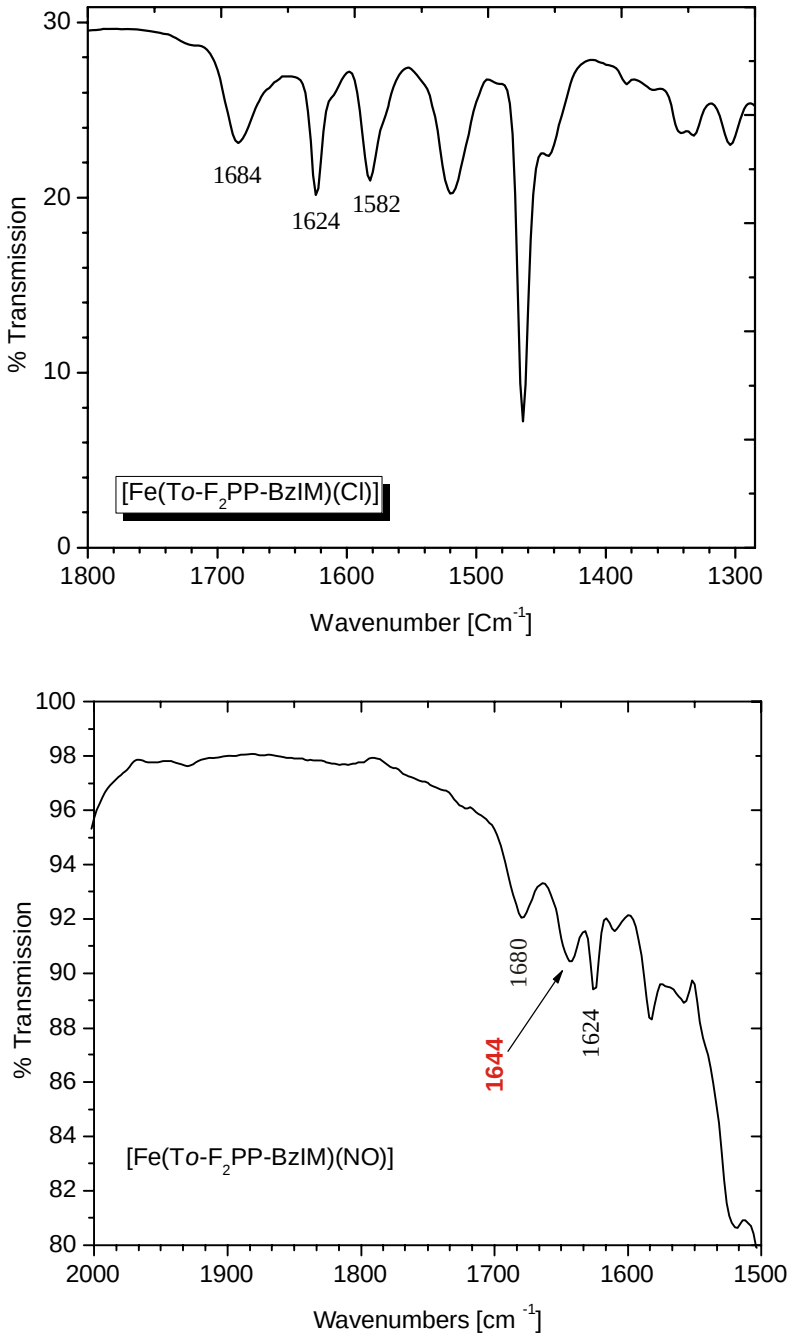

Figure S13. FT-IR spectra of the precursor [Fe(T*o*-F_2PP-BzIM)(Cl)] in KBr (top), and [Fe(T*o*-F_2PP-BzIM)(NO)] (**4**) in $CHCl_3$ (bottom). The FT-IR spectrum of **4** exhibits bands at 1680 cm^{-1} and 1624 cm^{-1}, which, however, are also present in the precursor complex [Fe(T*o*-F_2PP-BzIm)(Cl)] and have been assigned to ν(C=O) and phenyl ν(C-C) modes. In comparison with the precursor, a new, intense band at 1644 cm^{-1} is observed for the NO complex **4**, which is therefore assigned to ν(N-O).

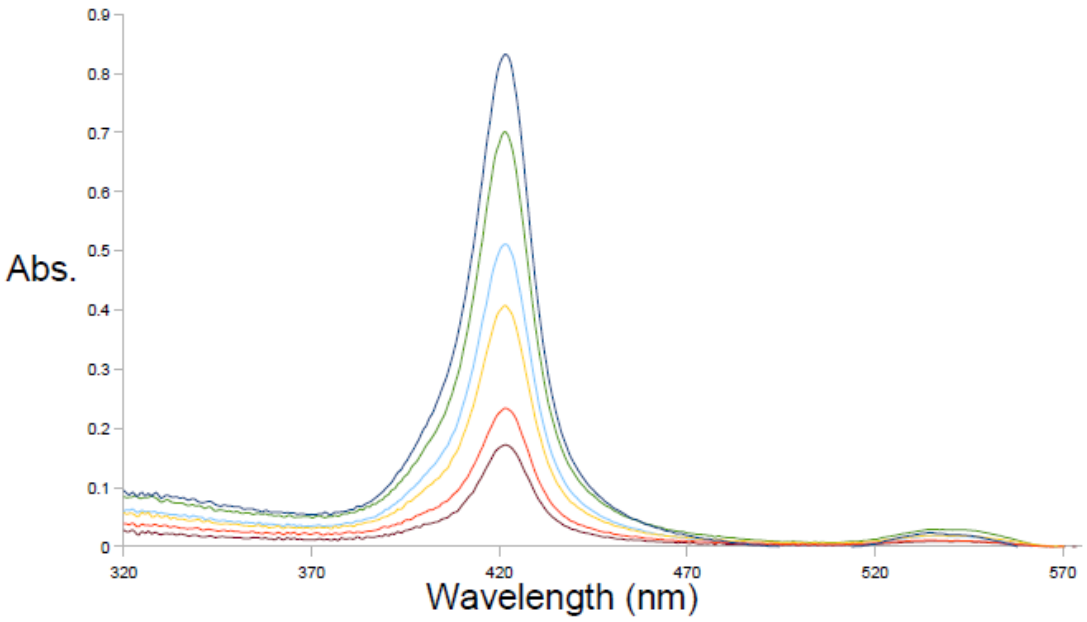

Figure S14. UV-Vis data for complex **4** recorded in CH_2Cl_2. This figure shows that the Soret position is independent of concentration in solution. As the concentration of complex **4** is increased (moving from the purple to the dark blue line) no change in Soret position is observed. This result implies that no intermolecular binding of the IM tether is occurring (see text for explanation).

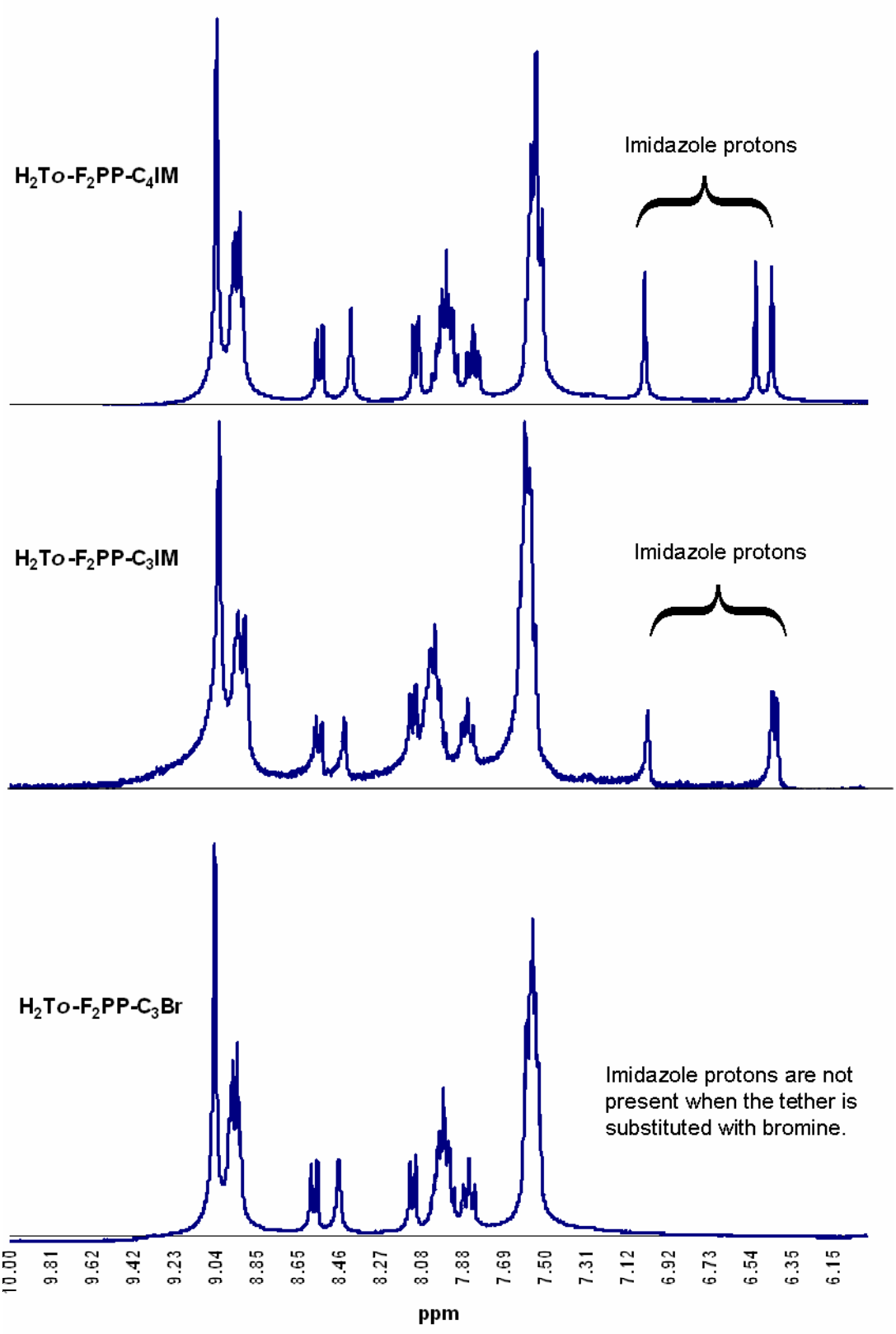

Figure S15. Overlay of ^{1}H-NMR data obtained for the alkyl chain substituted ligands **L2** and **L3** as compared to H_2To-F_2PP-C_3Br where imidazole has been replaced by bromine.

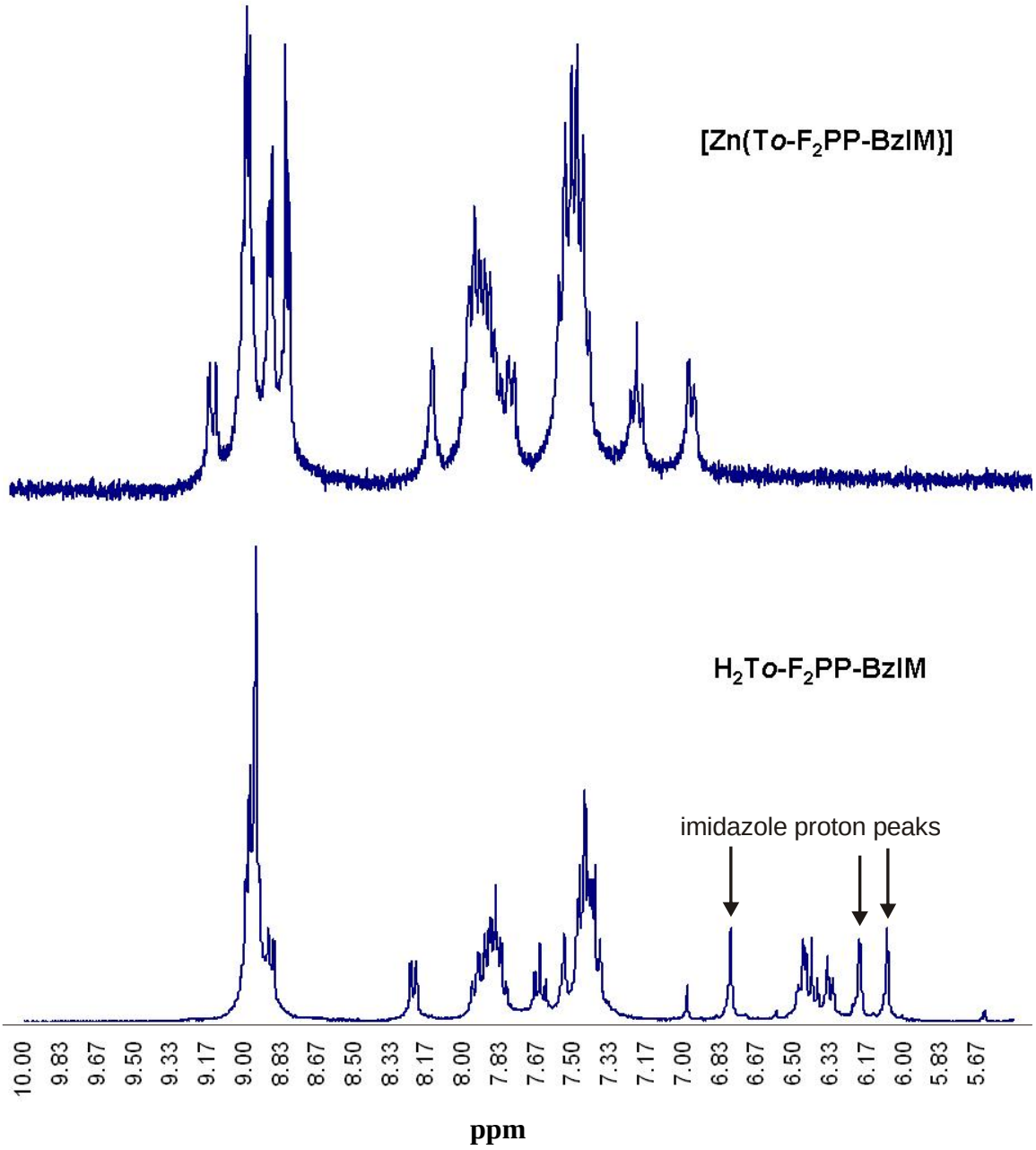

Figure S16. Overlay of ^{1}H-NMR data obtained for the benzyl substituted ligand **L4** and the corresponding zinc complex.

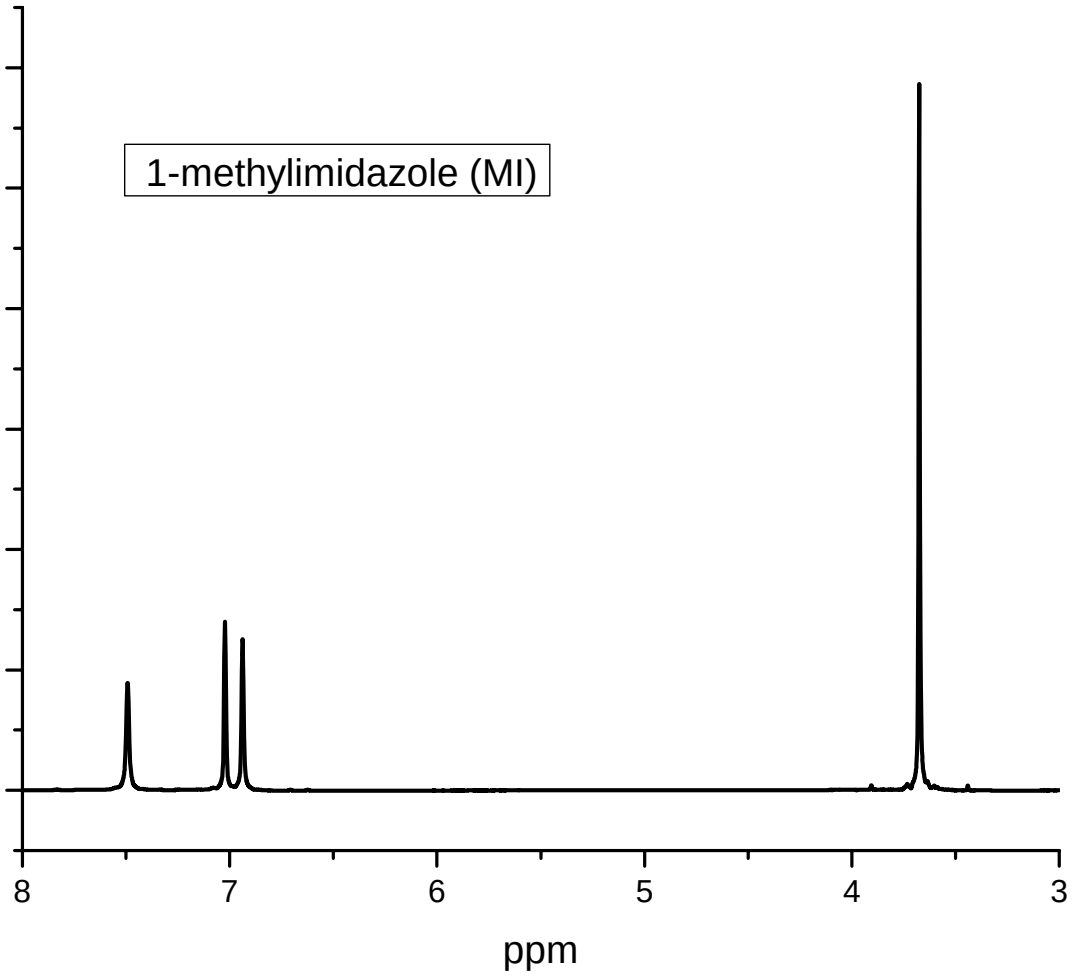

Figure S17. ^{1}H-NMR data obtained for 1-methylimidazole (MI) in deuterated acetone. The aromatic protons are observed as singlets as in the case of our imidazole (IM) tethered porphyrins, indicating very weak couplings between the IM ring protons.

Table S1. Crystal data and structure refinement for [Zn(T*o*-F_2PP-BzIM)].

Identification code	znbzim
Empirical formula	C56 H33 Cl2 F6 N7 O Zn
Formula weight	1070.16
Temperature	85(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.5223(8) A alpha = 103.955(1)deg. b = 13.2057(10) A beta = 101.557(1)deg. c = 19.7516(15) A gamma = 100.116(1)deg
Volume	2536.1(3) A^3
Z, Calculated density	2, 1.401 Mg/m^3
Absorption coefficient	0.659 mm^-1
F(000)	1088
Crystal size	0.14 x 0.14 x 0.10 mm
Theta range for data collection	1.63 to 28.32 deg.
Limiting indices	-14<=h<=14, -17<=k<=17, -26<=l<=26
Reflections collected / unique	54977 / 12597 [R(int) = 0.0460]
Completeness to theta = 28.32	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9370 and 0.9134
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12597 / 153 / 749
Goodness-of-fit on F^2	1.075
Final R indices [I>2sigma(I)]	R1 = 0.0570, wR2 = 0.1630
R indices (all data)	R1 = 0.0778, wR2 = 0.1770
Largest diff. peak and hole	1.301 and -0.655 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [Zn(T*o*-F_2PP-BzIM)]. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	5290(2)	3769(2)	9175(1)	39(1)
Zn(1)	455(1)	6873(1)	7550(1)	23(1)
F(1)	4139(2)	10523(1)	9279(1)	39(1)
F(2)	748(2)	9370(1)	10334(1)	35(1)
F(5)	-4266(2)	3837(2)	5650(1)	45(1)
F(6)	-80(2)	3633(2)	5238(1)	47(1)
N(1)	-71(2)	5223(2)	7378(1)	24(1)
N(2)	1259(2)	7020(2)	8639(1)	23(1)
N(3)	380(2)	8465(2)	7860(1)	26(1)
N(4)	-971(2)	6676(2)	6608(1)	24(1)
N(5)	3529(2)	4474(2)	8809(1)	28(1)
N(6)	3972(2)	6524(2)	6911(1)	33(1)
N(7)	2228(2)	6994(2)	7230(1)	27(1)
C(1)	-803(3)	4477(2)	6746(1)	25(1)
C(2)	-849(3)	3408(2)	6818(2)	31(1)
C(3)	-160(3)	3521(2)	7501(2)	31(1)
C(4)	334(3)	4660(2)	7853(1)	24(1)
C(5)	1084(2)	5111(2)	8569(1)	22(1)
C(6)	1550(2)	6212(2)	8921(1)	23(1)
C(7)	2384(2)	6664(2)	9651(1)	24(1)
C(8)	2578(2)	7744(2)	9799(1)	25(1)
C(9)	1860(2)	7962(2)	9167(1)	24(1)
C(10)	1758(3)	8985(2)	9112(1)	25(1)
C(11)	1052(3)	9214(2)	8508(1)	27(1)
C(12)	888(3)	10268(2)	8480(2)	33(1)
C(13)	115(3)	10145(2)	7814(2)	34(1)
C(14)	-213(3)	9016(2)	7429(1)	31(1)
C(15)	-1020(3)	8561(2)	6728(1)	28(1)
C(16)	-1378(3)	7471(2)	6347(1)	26(1)
C(17)	-2238(3)	7018(2)	5628(1)	29(1)
C(18)	-2354(3)	5944(2)	5459(1)	29(1)
C(19)	-1563(3)	5731(2)	6075(1)	25(1)
C(20)	-1465(3)	4707(2)	6131(1)	24(1)
C(21)	1343(3)	4346(2)	9006(1)	23(1)
C(22)	339(3)	3918(2)	9293(2)	29(1)
C(23)	522(3)	3189(2)	9686(2)	30(1)
C(24)	1715(3)	2877(2)	9786(1)	27(1)
C(25)	2739(3)	3296(2)	9514(1)	27(1)
C(26)	2548(3)	4027(2)	9120(1)	24(1)
C(27)	4778(3)	4317(2)	8836(1)	28(1)
C(28)	5515(3)	4882(2)	8408(1)	28(1)
C(29)	6905(3)	5203(2)	8644(2)	30(1)
C(30)	7620(3)	5726(2)	8262(2)	34(1)
C(31)	6970(3)	5917(3)	7634(2)	34(1)

C(32)	5591(3)	5591(3)	7388(2)	33(1)
C(33)	4866(3)	5084(2)	7782(2)	31(1)
C(34)	4857(3)	5813(3)	6716(2)	40(1)
C(35)	4383(3)	7588(3)	7301(2)	36(1)
C(36)	3306(3)	7873(2)	7494(2)	31(1)
C(37)	2670(3)	6202(2)	6887(1)	29(1)
C(38)	2398(3)	9912(2)	9773(1)	26(1)
C(39)	3553(3)	10662(2)	9837(2)	29(1)
C(40)	4138(3)	11536(2)	10437(2)	32(1)
C(41)	3530(3)	11682(2)	11001(2)	34(1)
C(42)	2386(3)	10953(2)	10975(2)	33(1)
C(43)	1867(3)	10094(2)	10367(1)	28(1)
F(3)	371(4)	9712(3)	5933(2)	56(1)
F(4)	-3447(4)	9028(3)	6770(2)	42(1)
C(44)	-1605(3)	9303(2)	6360(1)	32(1)
C(45)	-854(6)	9862(4)	5982(3)	37(1)
C(46)	-1355(7)	10552(4)	5628(3)	42(1)
C(47)	-2604(8)	10713(6)	5659(4)	40(2)
C(48)	-3342(8)	10229(6)	6045(4)	38(2)
C(49)	-2797(6)	9543(6)	6379(3)	31(2)
F(3A)	-299(8)	9200(6)	5582(4)	58(2)
F(4A)	-3260(6)	9376(5)	7080(3)	33(1)
C(44A)	-1605(3)	9303(2)	6360(1)	32(1)
C(45A)	-1309(11)	9578(9)	5775(5)	37(2)
C(46A)	-1901(11)	10241(9)	5432(6)	41(2)
C(47A)	-2959(13)	10568(12)	5660(8)	34(3)
C(48A)	-3392(13)	10250(11)	6205(7)	27(2)
C(49A)	-2712(11)	9623(10)	6547(6)	25(2)
C(50)	-2138(3)	3772(2)	5479(1)	26(1)
C(51)	-3504(3)	3362(2)	5255(2)	32(1)
C(52)	-4137(3)	2496(2)	4658(2)	37(1)
C(53)	-3354(3)	2009(2)	4256(2)	37(1)
C(54)	-1990(3)	2388(2)	4443(2)	36(1)
C(55)	-1416(3)	3259(2)	5050(2)	32(1)
Cl(98)	3684(2)	1520(1)	5773(1)	44(1)
Cl(99)	2284(2)	3084(2)	6350(1)	68(1)
C(99)	3757(7)	2656(5)	6469(4)	48(2)
Cl(91)	4209(2)	791(2)	7588(1)	64(1)
Cl(90)	6815(2)	2222(2)	7881(1)	64(1)
C(90)	5713(8)	1441(6)	8212(4)	55(2)

Table S3. Bond lengths [A] and angles [deg] for [Zn(T*o*-F_2PP-BzIM)].

O(1)-C(27)	1.221(3)
Zn(1)-N(3)	2.064(2)
Zn(1)-N(4)	2.073(2)
Zn(1)-N(1)	2.077(2)
Zn(1)-N(7)	2.079(2)
Zn(1)-N(2)	2.095(2)
F(1)-C(39)	1.357(3)
F(2)-C(43)	1.359(3)
F(5)-C(51)	1.356(3)
F(6)-C(55)	1.348(3)
N(1)-C(1)	1.370(3)
N(1)-C(4)	1.378(3)
N(2)-C(9)	1.367(3)
N(2)-C(6)	1.369(3)
N(3)-C(14)	1.374(3)
N(3)-C(11)	1.376(3)
N(4)-C(16)	1.371(3)
N(4)-C(19)	1.373(3)
N(5)-C(27)	1.359(3)
N(5)-C(26)	1.417(3)
N(6)-C(37)	1.348(4)
N(6)-C(35)	1.374(4)
N(6)-C(34)	1.474(4)
N(7)-C(37)	1.314(4)
N(7)-C(36)	1.383(3)
C(1)-C(20)	1.403(4)
C(1)-C(2)	1.446(4)
C(2)-C(3)	1.355(4)
C(3)-C(4)	1.446(4)
C(4)-C(5)	1.400(4)
C(5)-C(6)	1.402(4)
C(5)-C(21)	1.504(3)
C(6)-C(7)	1.449(3)
C(7)-C(8)	1.353(4)
C(8)-C(9)	1.444(3)
C(9)-C(10)	1.402(4)
C(10)-C(11)	1.402(4)
C(10)-C(38)	1.498(4)
C(11)-C(12)	1.445(4)
C(12)-C(13)	1.357(4)
C(13)-C(14)	1.445(4)
C(14)-C(15)	1.396(4)
C(15)-C(16)	1.398(4)
C(15)-C(44)	1.499(4)
C(16)-C(17)	1.441(4)
C(17)-C(18)	1.353(4)
C(18)-C(19)	1.447(4)
C(19)-C(20)	1.403(4)
C(20)-C(50)	1.497(4)
C(21)-C(22)	1.395(4)
C(21)-C(26)	1.398(4)

C(22)-C(23)	1.389(4)
C(23)-C(24)	1.381(4)
C(24)-C(25)	1.387(4)
C(25)-C(26)	1.394(3)
C(27)-C(28)	1.496(4)
C(28)-C(29)	1.396(4)
C(28)-C(33)	1.397(4)
C(29)-C(30)	1.382(4)
C(30)-C(31)	1.394(4)
C(31)-C(32)	1.387(4)
C(32)-C(33)	1.395(4)
C(32)-C(34)	1.517(4)
C(35)-C(36)	1.351(4)
C(38)-C(43)	1.387(4)
C(38)-C(39)	1.389(4)
C(39)-C(40)	1.384(4)
C(40)-C(41)	1.383(4)
C(41)-C(42)	1.387(4)
C(42)-C(43)	1.375(4)
F(3)-C(45)	1.357(6)
F(4)-C(49)	1.353(7)
C(44)-C(49)	1.352(7)
C(44)-C(45)	1.422(6)
C(45)-C(46)	1.387(7)
C(46)-C(47)	1.378(9)
C(47)-C(48)	1.375(9)
C(48)-C(49)	1.379(7)
F(3A)-C(45A)	1.334(10)
F(4A)-C(49A)	1.374(10)
C(45A)-C(46A)	1.386(11)
C(46A)-C(47A)	1.381(12)
C(47A)-C(48A)	1.375(12)
C(48A)-C(49A)	1.393(12)
C(50)-C(51)	1.383(4)
C(50)-C(55)	1.384(4)
C(51)-C(52)	1.381(4)
C(52)-C(53)	1.388(4)
C(53)-C(54)	1.376(5)
C(54)-C(55)	1.388(4)
Cl(98)-C(99)	1.752(6)
Cl(99)-C(99)	1.733(7)
Cl(91)-C(90)	1.729(8)
Cl(90)-C(90)	1.745(8)

N(3)-Zn(1)-N(4)	88.39(9)
N(3)-Zn(1)-N(1)	159.51(9)
N(4)-Zn(1)-N(1)	88.37(8)
N(3)-Zn(1)-N(7)	101.12(9)
N(4)-Zn(1)-N(7)	103.42(8)
N(1)-Zn(1)-N(7)	99.31(9)
N(3)-Zn(1)-N(2)	87.90(8)
N(4)-Zn(1)-N(2)	158.82(9)
N(1)-Zn(1)-N(2)	87.85(8)
N(7)-Zn(1)-N(2)	97.76(8)
C(1)-N(1)-C(4)	106.7(2)
C(1)-N(1)-Zn(1)	126.16(17)
C(4)-N(1)-Zn(1)	126.95(17)

C(9)-N(2)-C(6)	106.6(2)
C(9)-N(2)-Zn(1)	125.63(16)
C(6)-N(2)-Zn(1)	126.33(17)
C(14)-N(3)-C(11)	106.4(2)
C(14)-N(3)-Zn(1)	126.48(18)
C(11)-N(3)-Zn(1)	126.70(17)
C(16)-N(4)-C(19)	106.1(2)
C(16)-N(4)-Zn(1)	127.00(17)
C(19)-N(4)-Zn(1)	126.35(17)
C(27)-N(5)-C(26)	129.1(2)
C(37)-N(6)-C(35)	107.1(2)
C(37)-N(6)-C(34)	125.7(3)
C(35)-N(6)-C(34)	125.5(3)
C(37)-N(7)-C(36)	105.9(2)
C(37)-N(7)-Zn(1)	126.84(19)
C(36)-N(7)-Zn(1)	125.40(19)
N(1)-C(1)-C(20)	125.5(2)
N(1)-C(1)-C(2)	109.7(2)
C(20)-C(1)-C(2)	124.7(2)
C(3)-C(2)-C(1)	107.0(2)
C(2)-C(3)-C(4)	107.2(2)
N(1)-C(4)-C(5)	125.8(2)
N(1)-C(4)-C(3)	109.4(2)
C(5)-C(4)-C(3)	124.8(2)
C(4)-C(5)-C(6)	125.5(2)
C(4)-C(5)-C(21)	116.9(2)
C(6)-C(5)-C(21)	117.5(2)
N(2)-C(6)-C(5)	125.5(2)
N(2)-C(6)-C(7)	109.8(2)
C(5)-C(6)-C(7)	124.7(2)
C(8)-C(7)-C(6)	106.6(2)
C(7)-C(8)-C(9)	107.1(2)
N(2)-C(9)-C(10)	125.1(2)
N(2)-C(9)-C(8)	109.8(2)
C(10)-C(9)-C(8)	125.0(2)
C(11)-C(10)-C(9)	126.0(2)
C(11)-C(10)-C(38)	117.0(2)
C(9)-C(10)-C(38)	117.0(2)
N(3)-C(11)-C(10)	125.1(2)
N(3)-C(11)-C(12)	109.9(2)
C(10)-C(11)-C(12)	124.9(2)
C(13)-C(12)-C(11)	106.7(2)
C(12)-C(13)-C(14)	107.2(2)
N(3)-C(14)-C(15)	125.5(2)
N(3)-C(14)-C(13)	109.7(2)
C(15)-C(14)-C(13)	124.7(2)
C(14)-C(15)-C(16)	126.2(2)
C(14)-C(15)-C(44)	117.0(2)
C(16)-C(15)-C(44)	116.8(2)
N(4)-C(16)-C(15)	124.7(2)
N(4)-C(16)-C(17)	110.2(2)
C(15)-C(16)-C(17)	125.1(2)
C(18)-C(17)-C(16)	106.8(2)
C(17)-C(18)-C(19)	107.0(2)
N(4)-C(19)-C(20)	125.1(2)
N(4)-C(19)-C(18)	109.8(2)
C(20)-C(19)-C(18)	125.0(2)

C(1)-C(20)-C(19)	125.8(2)
C(1)-C(20)-C(50)	116.9(2)
C(19)-C(20)-C(50)	117.3(2)
C(22)-C(21)-C(26)	118.6(2)
C(22)-C(21)-C(5)	119.1(2)
C(26)-C(21)-C(5)	122.3(2)
C(23)-C(22)-C(21)	121.1(3)
C(24)-C(23)-C(22)	119.3(3)
C(23)-C(24)-C(25)	121.0(2)
C(24)-C(25)-C(26)	119.3(2)
C(25)-C(26)-C(21)	120.6(2)
C(25)-C(26)-N(5)	123.0(2)
C(21)-C(26)-N(5)	116.4(2)
O(1)-C(27)-N(5)	124.6(3)
O(1)-C(27)-C(28)	121.1(2)
N(5)-C(27)-C(28)	114.4(2)
C(29)-C(28)-C(33)	119.4(3)
C(29)-C(28)-C(27)	118.2(2)
C(33)-C(28)-C(27)	122.4(2)
C(30)-C(29)-C(28)	119.8(3)
C(29)-C(30)-C(31)	120.6(3)
C(32)-C(31)-C(30)	120.2(3)
C(31)-C(32)-C(33)	119.2(3)
C(31)-C(32)-C(34)	121.2(3)
C(33)-C(32)-C(34)	119.5(3)
C(32)-C(33)-C(28)	120.7(3)
N(6)-C(34)-C(32)	109.5(2)
C(36)-C(35)-N(6)	106.4(3)
C(35)-C(36)-N(7)	109.3(3)
N(7)-C(37)-N(6)	111.2(3)
C(43)-C(38)-C(39)	114.8(2)
C(43)-C(38)-C(10)	122.2(2)
C(39)-C(38)-C(10)	123.0(2)
F(1)-C(39)-C(40)	118.4(2)
F(1)-C(39)-C(38)	117.9(2)
C(40)-C(39)-C(38)	123.6(3)
C(41)-C(40)-C(39)	118.3(3)
C(40)-C(41)-C(42)	120.9(3)
C(43)-C(42)-C(41)	117.9(3)
F(2)-C(43)-C(42)	118.7(3)
F(2)-C(43)-C(38)	116.8(2)
C(42)-C(43)-C(38)	124.5(3)
C(49)-C(44)-C(45)	114.9(4)
C(49)-C(44)-C(15)	125.4(4)
C(45)-C(44)-C(15)	119.6(3)
F(3)-C(45)-C(46)	117.1(5)
F(3)-C(45)-C(44)	121.0(4)
C(46)-C(45)-C(44)	121.8(5)
C(47)-C(46)-C(45)	118.7(6)
C(48)-C(47)-C(46)	121.6(6)
C(47)-C(48)-C(49)	117.0(7)
C(44)-C(49)-F(4)	112.7(5)
C(44)-C(49)-C(48)	125.9(6)
F(4)-C(49)-C(48)	121.4(6)
F(3A)-C(45A)-C(46A)	121.4(8)
C(47A)-C(46A)-C(45A)	116.8(10)
C(48A)-C(47A)-C(46A)	121.1(11)

C(47A)-C(48A)-C(49A)	118.9(11)
F(4A)-C(49A)-C(48A)	112.0(9)
C(51)-C(50)-C(55)	114.9(2)
C(51)-C(50)-C(20)	123.5(2)
C(55)-C(50)-C(20)	121.5(2)
F(5)-C(51)-C(52)	118.1(3)
F(5)-C(51)-C(50)	117.7(2)
C(52)-C(51)-C(50)	124.2(3)
C(51)-C(52)-C(53)	118.0(3)
C(54)-C(53)-C(52)	120.8(3)
C(53)-C(54)-C(55)	118.3(3)
F(6)-C(55)-C(50)	117.6(2)
F(6)-C(55)-C(54)	118.6(3)
C(50)-C(55)-C(54)	123.8(3)
Cl(99)-C(99)-Cl(98)	111.9(4)
Cl(91)-C(90)-Cl(90)	113.5(4)

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for [Zn(T*o*-F_2PP-BzIM)]. The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a^{*2} U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	29(1)	52(1)	51(1)	35(1)	12(1)	18(1)
Zn(1)	26(1)	20(1)	27(1)	12(1)	6(1)	6(1)
F(1)	35(1)	34(1)	49(1)	10(1)	19(1)	3(1)
F(2)	40(1)	29(1)	37(1)	14(1)	15(1)	1(1)
F(5)	32(1)	44(1)	51(1)	0(1)	10(1)	9(1)
F(6)	38(1)	54(1)	48(1)	8(1)	18(1)	12(1)
N(1)	24(1)	22(1)	27(1)	12(1)	6(1)	5(1)
N(2)	23(1)	20(1)	28(1)	12(1)	5(1)	5(1)
N(3)	36(1)	22(1)	26(1)	13(1)	7(1)	9(1)
N(4)	27(1)	22(1)	29(1)	14(1)	9(1)	7(1)
N(5)	26(1)	34(1)	36(1)	24(1)	9(1)	12(1)
N(6)	29(1)	48(1)	32(1)	26(1)	11(1)	11(1)
N(7)	26(1)	30(1)	26(1)	13(1)	5(1)	4(1)
C(1)	30(1)	20(1)	28(1)	11(1)	9(1)	7(1)
C(2)	43(2)	20(1)	29(1)	9(1)	4(1)	7(1)
C(3)	43(2)	21(1)	31(1)	13(1)	8(1)	10(1)
C(4)	26(1)	21(1)	29(1)	12(1)	9(1)	8(1)
C(5)	22(1)	23(1)	28(1)	14(1)	7(1)	8(1)
C(6)	20(1)	24(1)	28(1)	15(1)	6(1)	6(1)
C(7)	22(1)	25(1)	29(1)	13(1)	5(1)	5(1)
C(8)	22(1)	26(1)	28(1)	11(1)	5(1)	4(1)
C(9)	22(1)	24(1)	27(1)	13(1)	7(1)	3(1)
C(10)	24(1)	22(1)	30(1)	11(1)	8(1)	3(1)
C(11)	32(1)	21(1)	30(1)	11(1)	8(1)	6(1)
C(12)	49(2)	21(1)	30(1)	12(1)	7(1)	8(1)
C(13)	55(2)	22(1)	29(1)	13(1)	8(1)	13(1)
C(14)	45(2)	23(1)	29(1)	15(1)	10(1)	11(1)
C(15)	39(1)	24(1)	28(1)	16(1)	8(1)	12(1)
C(16)	29(1)	27(1)	27(1)	14(1)	7(1)	9(1)
C(17)	34(1)	30(1)	27(1)	13(1)	7(1)	13(1)
C(18)	33(1)	29(1)	27(1)	12(1)	6(1)	10(1)
C(19)	26(1)	25(1)	26(1)	11(1)	6(1)	7(1)
C(20)	25(1)	23(1)	26(1)	10(1)	7(1)	6(1)
C(21)	26(1)	20(1)	26(1)	11(1)	6(1)	5(1)
C(22)	28(1)	30(1)	37(1)	18(1)	10(1)	11(1)
C(23)	30(1)	29(1)	37(1)	19(1)	11(1)	6(1)
C(24)	34(1)	23(1)	26(1)	14(1)	4(1)	6(1)
C(25)	28(1)	28(1)	30(1)	15(1)	6(1)	10(1)
C(26)	27(1)	24(1)	25(1)	13(1)	7(1)	6(1)
C(27)	25(1)	32(1)	31(1)	14(1)	7(1)	9(1)
C(28)	26(1)	33(1)	30(1)	14(1)	9(1)	11(1)
C(29)	28(1)	36(1)	32(1)	15(1)	8(1)	12(1)
C(30)	25(1)	41(2)	42(2)	18(1)	10(1)	11(1)
C(31)	30(1)	45(2)	38(1)	21(1)	16(1)	13(1)

C(32)	29(1)	50(2)	31(1)	21(1)	13(1)	18(1)
C(33)	25(1)	42(2)	32(1)	17(1)	9(1)	12(1)
C(34)	36(2)	65(2)	37(2)	30(1)	18(1)	23(1)
C(35)	27(1)	46(2)	38(2)	27(1)	4(1)	1(1)
C(36)	29(1)	33(1)	30(1)	15(1)	2(1)	-2(1)
C(37)	26(1)	35(1)	29(1)	15(1)	7(1)	6(1)
C(38)	29(1)	21(1)	29(1)	12(1)	2(1)	6(1)
C(39)	27(1)	26(1)	38(1)	12(1)	8(1)	9(1)
C(40)	24(1)	24(1)	45(2)	10(1)	1(1)	4(1)
C(41)	35(2)	26(1)	33(1)	7(1)	-5(1)	5(1)
C(42)	42(2)	31(1)	29(1)	14(1)	5(1)	8(1)
C(43)	31(1)	25(1)	29(1)	13(1)	6(1)	4(1)
F(3)	79(2)	54(2)	69(2)	41(2)	50(2)	38(2)
F(4)	34(2)	41(2)	58(2)	30(2)	8(2)	8(1)
C(44)	52(2)	24(1)	24(1)	13(1)	7(1)	13(1)
C(45)	60(3)	32(3)	27(2)	14(2)	16(2)	19(2)
C(46)	76(4)	31(3)	27(3)	14(2)	16(3)	17(3)
C(47)	75(4)	22(3)	26(3)	12(2)	7(3)	17(3)
C(48)	46(3)	28(3)	34(4)	14(2)	-9(2)	9(2)
C(49)	33(2)	29(3)	21(3)	12(2)	-12(2)	-3(2)
F(3A)	84(5)	72(4)	67(4)	53(3)	55(3)	57(4)
F(4A)	33(3)	38(3)	35(3)	23(2)	8(2)	9(2)
C(44A)	52(2)	24(1)	24(1)	13(1)	7(1)	13(1)
C(45A)	54(5)	47(6)	25(4)	19(4)	17(4)	33(4)
C(46A)	59(6)	50(6)	36(5)	32(4)	17(4)	32(5)
C(47A)	48(6)	34(6)	33(5)	22(4)	11(4)	22(4)
C(48A)	27(4)	29(5)	24(5)	15(4)	-2(3)	-2(3)
C(49A)	33(4)	24(5)	15(4)	13(3)	-7(3)	2(4)
C(50)	35(1)	21(1)	24(1)	11(1)	5(1)	9(1)
C(51)	33(1)	31(1)	32(1)	8(1)	5(1)	11(1)
C(52)	40(2)	33(2)	32(1)	8(1)	-3(1)	6(1)
C(53)	54(2)	30(1)	24(1)	10(1)	2(1)	13(1)
C(54)	54(2)	32(1)	29(1)	12(1)	15(1)	18(1)
C(55)	33(1)	34(1)	31(1)	12(1)	9(1)	10(1)
Cl(98)	61(1)	35(1)	34(1)	7(1)	5(1)	22(1)
Cl(99)	46(1)	56(1)	83(1)	-13(1)	6(1)	20(1)
C(99)	63(4)	37(3)	46(4)	6(3)	24(3)	17(3)
Cl(91)	83(1)	52(1)	52(1)	29(1)	6(1)	-8(1)
Cl(90)	58(1)	66(1)	64(1)	11(1)	21(1)	8(1)
C(90)	65(5)	56(4)	47(4)	21(3)	10(3)	18(4)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for [Zn(T*o*-F_2PP-BzIM)].

	x	y	z	U(eq)
H(5A)	3296	4916	8564	34
H(2A)	-1280	2751	6456	37
H(3A)	-27	2958	7709	37
H(7A)	2728	6278	9965	29
H(8A)	3091	8261	10236	30
H(12A)	1252	10921	8856	40
H(13A)	-161	10699	7634	41
H(17A)	-2645	7400	5330	35
H(18A)	-2858	5428	5019	34
H(22A)	-485	4128	9219	35
H(23A)	-166	2907	9883	36
H(24A)	1837	2368	10046	33
H(25A)	3563	3087	9594	32
H(29A)	7357	5063	9066	36
H(30A)	8564	5959	8430	41
H(31A)	7473	6270	7373	41
H(33A)	3919	4875	7623	37
H(34A)	5508	6159	6493	48
H(34B)	4324	5130	6361	48
H(35A)	5253	8036	7413	44
H(36A)	3291	8567	7768	38
H(37A)	2142	5494	6653	35
H(40A)	4936	12024	10461	39
H(41A)	3900	12290	11411	41
H(42A)	1976	11044	11366	40
H(46A)	-846	10907	5370	51
H(47A)	-2963	11169	5408	48
H(48A)	-4189	10361	6080	45
H(46B)	-1593	10460	5057	50
H(47B)	-3395	11019	5437	41
H(48B)	-4143	10456	6346	33
H(52A)	-5080	2242	4527	45
H(53A)	-3765	1406	3847	44
H(54A)	-1454	2061	4164	43
H(99A)	3941	2486	6936	57
H(99B)	4503	3244	6488	57
H(90A)	6142	898	8369	66
H(90B)	5537	1907	8640	66

Complete Ref. 2d.

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