Table 1 $^{1}H$ and $^{19}F$ NMR chemical shifts of **1a-e** and **2** taken in $CD_2Cl_2$ ($\delta$, ppm)

| Complex | Porphyrin | | | | Axial Ligands | | |
|---|---|---|---|---|---|---|---|
| | py-H | *o*-$CH_3$ | *m*-H | *p*-$CH_3$ | *o*-H | *m*-H | *p*-X[a] |
| (a)298 K | | | | | | | |
| **1a** | 59.8 | 3.0 | 8.9 | 3.7 | -50.0[b] | 28.4[b] | - |
| **1b** | 63.6 | 2.9 | 8.8 | 3.6 | -48.5[b] | 29.2[b] | (-51.2)[b] |
| **1c** | 66.8 | 2.8 | 8.7 | 3.5 | -45.7 | 28.8 | (56.0) |
| **1d** | 67.8 | 2.7 | 8.4 | 3.4 | -38.6 | 22.4 | (3.7) |
| **1e** | 57.4 | 2.3 | 7.8 | 3.0 | -20.7 | 16.5 | (18.2) |
| **2** | 24.1 | -140[c] | -164[c] | -154[c] | -4.3 | 12.7 | (9.6) |
| (b)183 K | | | | | | | |
| **1a** | 110.2 | 5.3 | 11.7 | 5.7 | -106.5 | 37.3 | - |
| **1b** | 113.7 | 5.1 | 11.3 | 5.4 | -102.3 | 38.1 | (-93.6) |
| **1c** | 115.9 | 4.7 | 11.0 | 5.2 | -93.3 | 37.0 | (87.8) |
| **1d** | 112.3 | 4.3 | 10.5 | 4.8 | -77.6 | 29.2 | (3.2) |
| **1e** | 34.5 | 2.1 | 7.5 | 2.9 | -15.7 | 15.3 | (12.8) |
| **2** | -10.2 | -142[c] | -165[c] | -155[c] | 0.3 | 12.8 | (0.3) |

[a]Chemical shifts of the *para* substituents.

[b]Extrapolated from low temperature. [c] $^{19}F$ NMR chemical shifts.

Table 2. Selected structural parameters for **1a-e** and **2**.

| Complex | T (K) | Fe-N[a] | Fe-O[a] | N-O[a] | Fe-O-N[b] | $\theta$[c] |
|---|---|---|---|---|---|---|
| **1a** | 100 | 2.054(2) | 2.047(3) | 1.337(3) | 125.3(2) | 9.0 |
| **1c** | 300 | 2.048(2) | 2.048(2) | 1.336(6) | 123.7(1) | 7.8 |
| | 100 | 2.029(3) | 2.001(2) | 1.347(4) | 122.0(2) | 9.1 |
| **1e** | 100 | 1.997(4) | 1.904(3) | 1.364(6) | 120.2(2) | 9.1 |
| **2** | 100 | 1.996(6) | 1.908(3) | 1.368(7) | 119.7(3) | 6.2 |

[a]Averaged bond lengths(Å). [b]Averaged angles(°).

[c]Averaged angles between heme normal and Fe-O bonds.