

Supplementary information

Ligand and complex syntheses.

The new ligand¹ H(L-*t*Bu) and its mixed-valent complex² [Fe^{II}Fe^{III}(L-*t*Bu)(mpdp)(CH₃OH)](BPh₄)₂, **1b**, were prepared according to already reported general procedures and characterised by elemental analysis (**1b**: calcd. C: 70.54, H: 5.93, N: 7.75; exp C:70.9, H: 6.0, N: 7.7), ESI-MS (see figures S1 and S2) and ¹H NMR spectroscopy.

¹ E. Lambert, B. Chabut, S. Chardon-Noblat, A. Deronzier, G. Chottard, A. Bousseksou, J. P. Tuchagues, M. Bardet, J. Laugier, and J. M. Latour, *J. Am. Chem. Soc.*, 1997, **119**, 9424.

² S. Chardon-Noblat, O. Horner, B. Chabut, F. Avenier, N. Debaecker, P. Jones, J. Pécaut, L. Dubois, C. Jeandey, J.-L. Oddou, A. Deronzier, and J.-M. Latour, *Inorg. Chem.*, 2004, **43**, 1638.

Figure S1 : ESI-MS spectrum of the solution after reaction at room temperature of **1b** with 4 eq H₂O₂. Insert: ESI-MS spectrum of **1b**.

Figure S2 : ESI-MS spectra of the ligands recovered after iron extraction by sodium sulphide.

MS1: spectrum of the two ligands H(L-*t*Bu) and H(L-*t*Bu-H+OH)

MS2: fragmentation of the peaks at *m/z* 496 (left) and 512 (right)

MS3: fragmentation of the peaks at *m/z* 297 (left) and 313 (right)

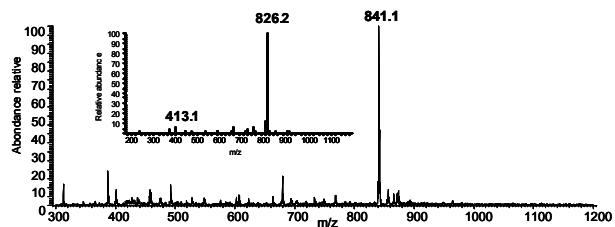


Figure S1 ESI-MS spectrum of the solution after reaction at room temperature of **1b** with 4 eq H_2O_2 . Insert: ESI-MS spectrum of **1b**.

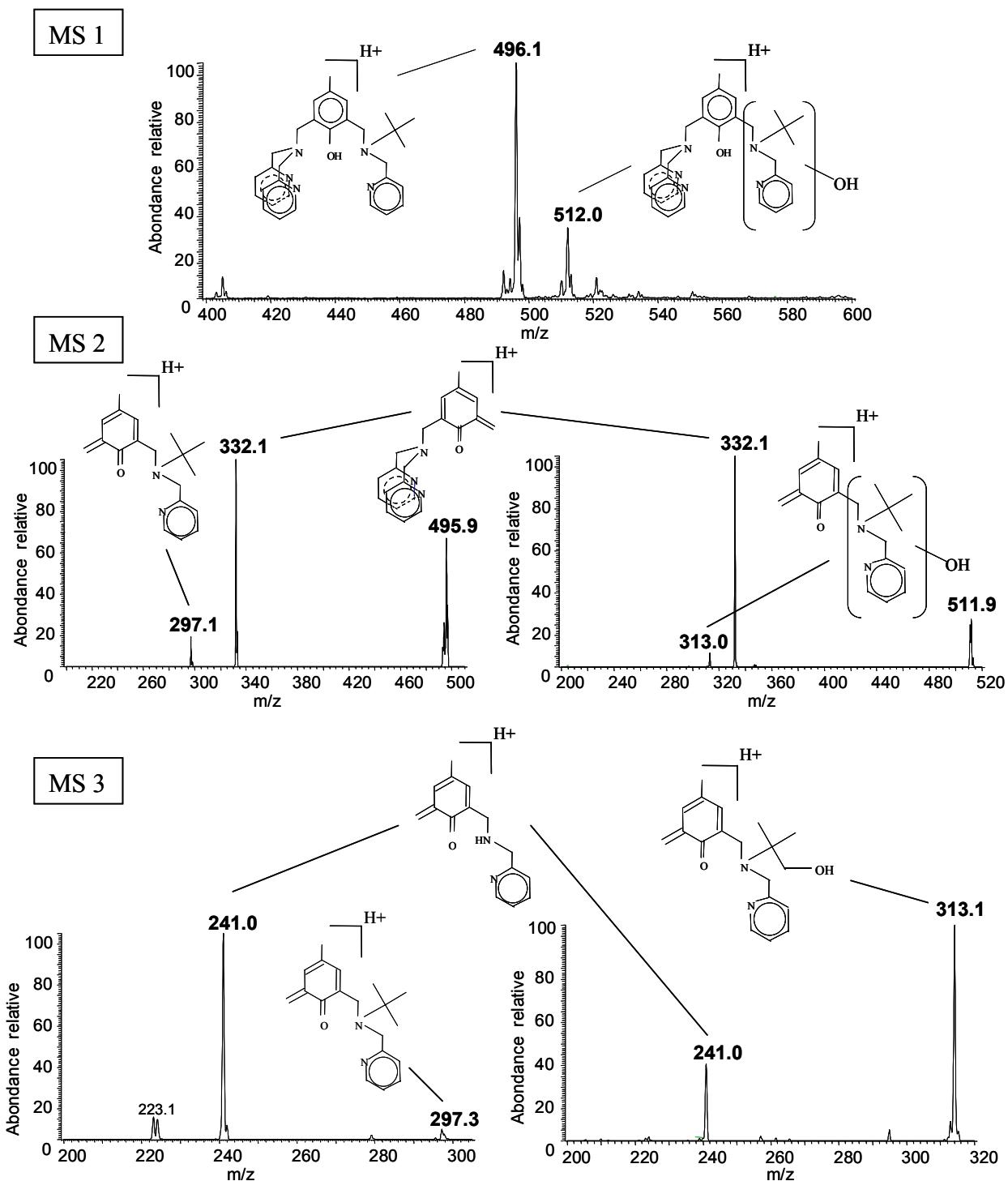


Figure S2 : ESI-MS spectra of the ligands recovered after iron extraction by sodium sulphide.
 MS1: spectrum of the two ligands $\text{H}(\text{L}-\text{tBu})$ and $\text{H}(\text{L}-\text{tBu}-\text{H}^+\text{OH})$
 MS2: fragmentation of the peaks at m/z 496 (left) and 512 (right)
 MS3: fragmentation of the peaks at m/z 297 (left) and 313 (right)