Nitration of iron corrolates: further evidence for non-innocence of the corrole ligand

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Electronic Supplementary Information

Reagents and solvents (Sigma-Aldrich, Fluka and Carlo Erba Reagenti) were of synthetic grade and used without further purification. Silica gel 60 (70-230 mesh) was used for chromatography.
^{1}H NMR spectra were recorded on a Bruker AV300 (300 MHz) or Bruker Avance 400 (400 MHz) spectrometers. Chemical shifts are given in ppm relative to tetramethylsilane (TMS). UV-vis spectra were measured on a Cary 50 spectrophotometer. Mass spectra were recorded on a VGQuattro spectrometer in the positive-ion mode, using *m*-nitrobenzyl alcohol (NBA, Aldrich) as a matrix (FAB).

General procedure for preparation of β-nitro corrole iron complexes.

$NaNO_2$ (21 mmol) and the chloro iron corrolate complex (0.21 mmol) in 40 mL of DMF were refluxed and the reaction was monitored by TLC. When the starting material was no more present in the reaction mixture (20 min.), the solvent was removed under vacuum, and the residue was taken up in $CHCl_3$ and washed with H_2O (3 × 50 mL). The organic phase was reduced to a small volume and chromatography on a silica gel column (CH_2Cl_2/hexane 4:1 as eluant) afforded three main products.

The corrFeNO complexes have been characterized by comparison with authentic specimen prepared following literature methods (C. A. Joseph, P. C. Ford, *J. Am. Chem. Soc.* **2005**, *127*, 6737). Spectral data of ttcorr derivatives are reported in the manuscript.

3-NO_2tpcorrFeNO: ^{1}H NMR (300 MHz, $CDCl_3$, J [Hz]): δ = 8.52 (s, 1H), 8.02 (d, 1H, J= 4.28, β-pyrrolic), 7.88 (d, 4H, J= 4.28, β-pyrrolic), 7.83-7.53 (m, 15H, phenyl), 7.49 ppm (d, 1H, J= 4.80, β-pyrrolic); UV/Vis: λ_{max}(CH_2Cl_2), nm 401 (log ε 4.03), 581 (3.60); MS (FAB): m/z 624 (M^+-NO).

3,17-$(NO_2)_2$tpcorrFeNO: ^{1}H NMR (300 MHz, $CDCl_3$, J [Hz]): δ =8.53 (s, 2H), 7.84 (d, 2H, J= 4.80, β-pyrrolic), 7.77 (m, 6H, phenyl), 7.66 ppm (m, 11H, phenyl + β-pyrrolic); UV/Vis: λ_{max}(CH_2Cl_2), nm 408 (log ε 4.10), 604 (3.97); MS (FAB): m/z 669 (M^+-NO).

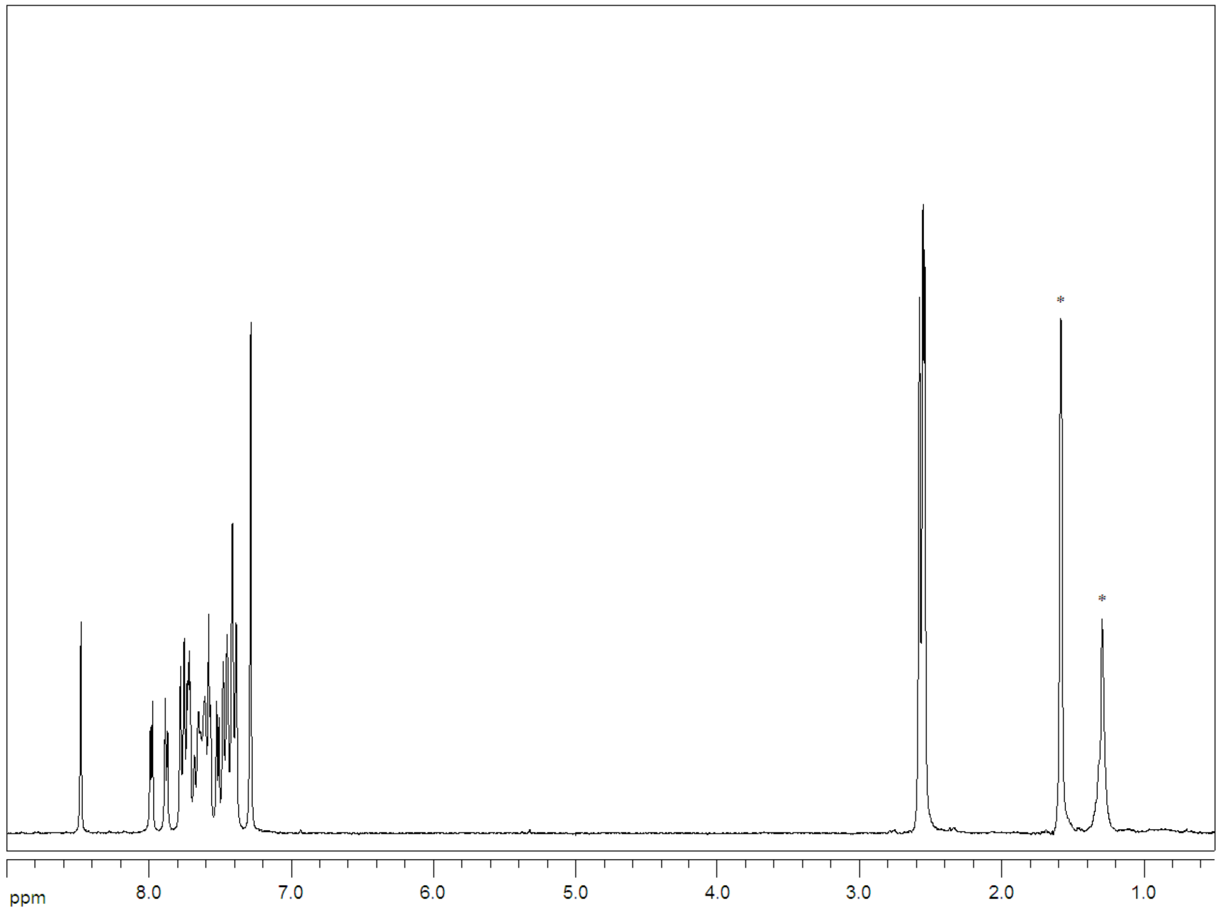

Figure S1. ^{1}H nmr spectrum of 3-NO_2ttcorrFeNO. Asterisks indicate water and impurity

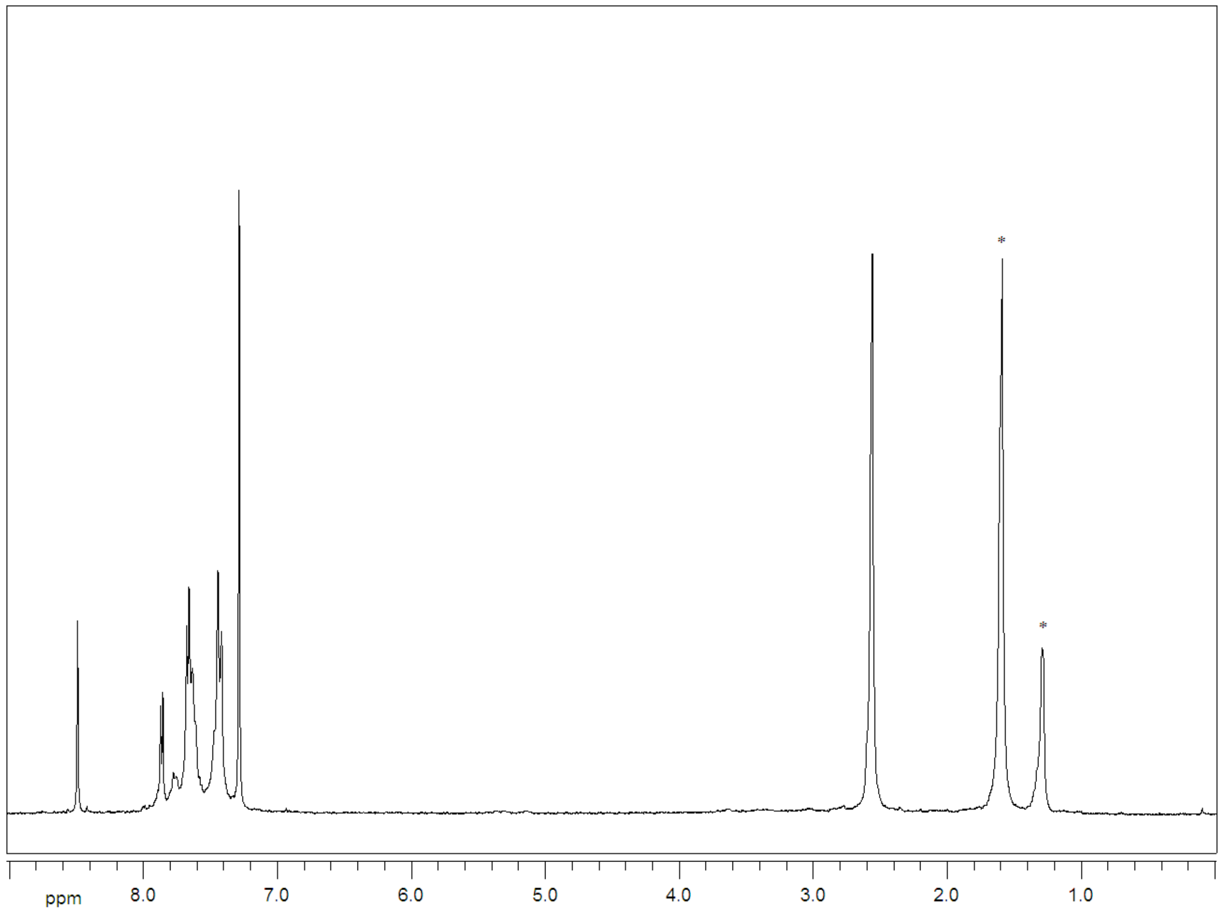

Figure S2. ^{1}H nmr spectrum of 3,17-$(NO_2)_2$ttcorrFeNO. Asterisks indicate water and impurity

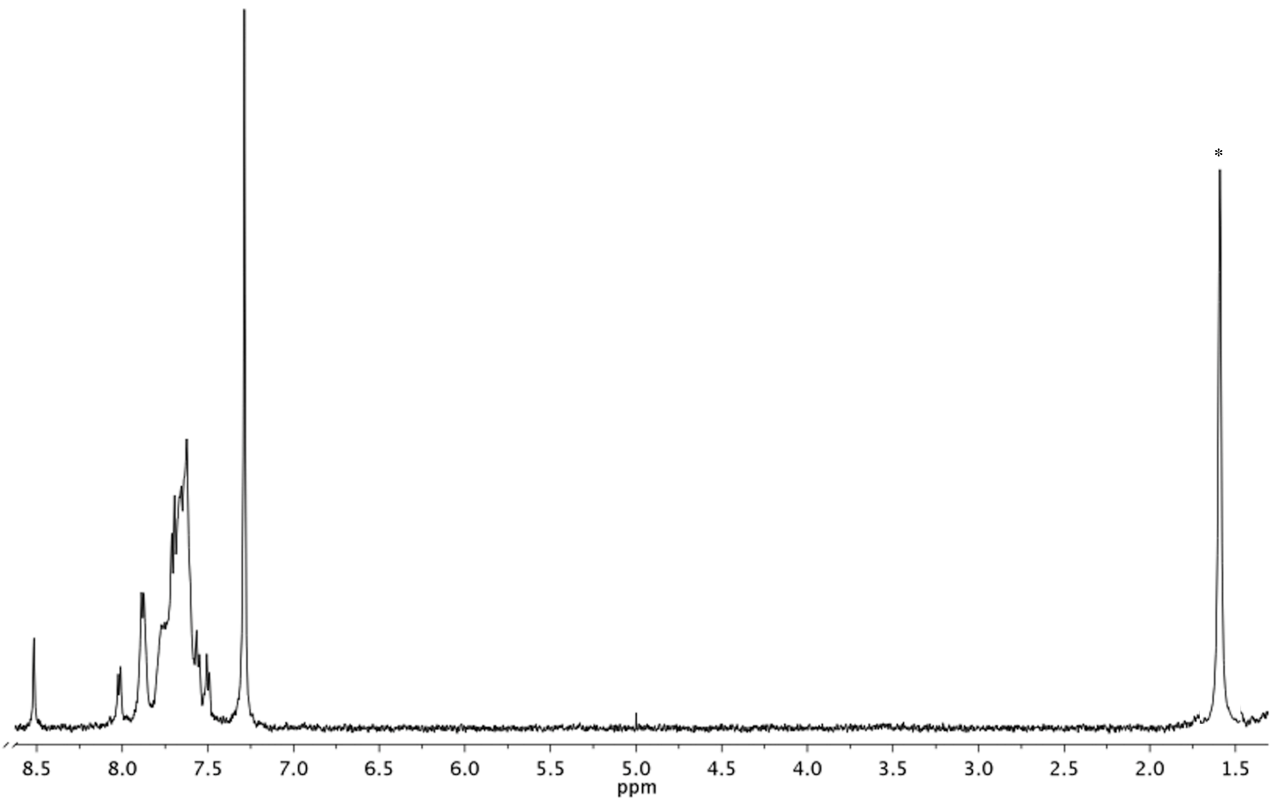

Figure S3. ^{1}H nmr spectrum of 3-NO_2tpcorrFeNO. Asterisk indicates water impurity

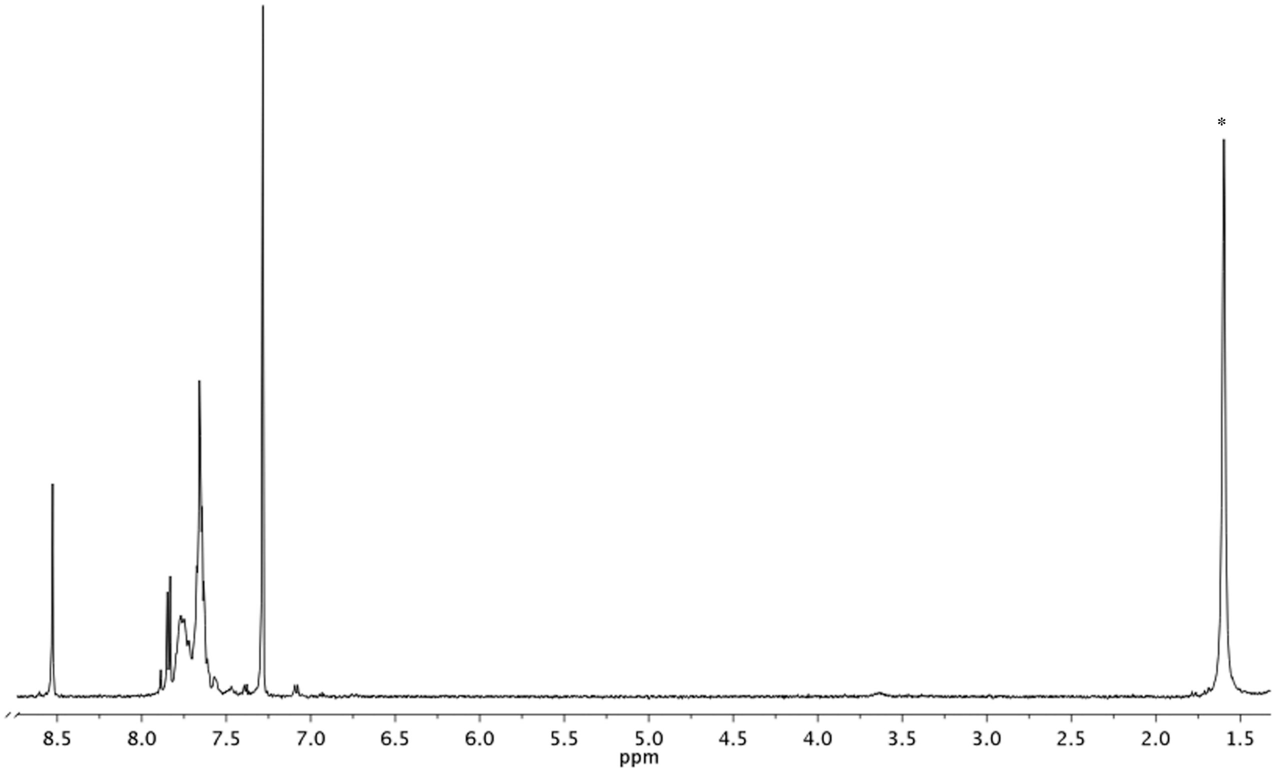

Figure S4. ^{1}H nmr spectrum of 3,17-$(NO_2)_2$tpcorrFeNO. Asterisk indicates water impurity

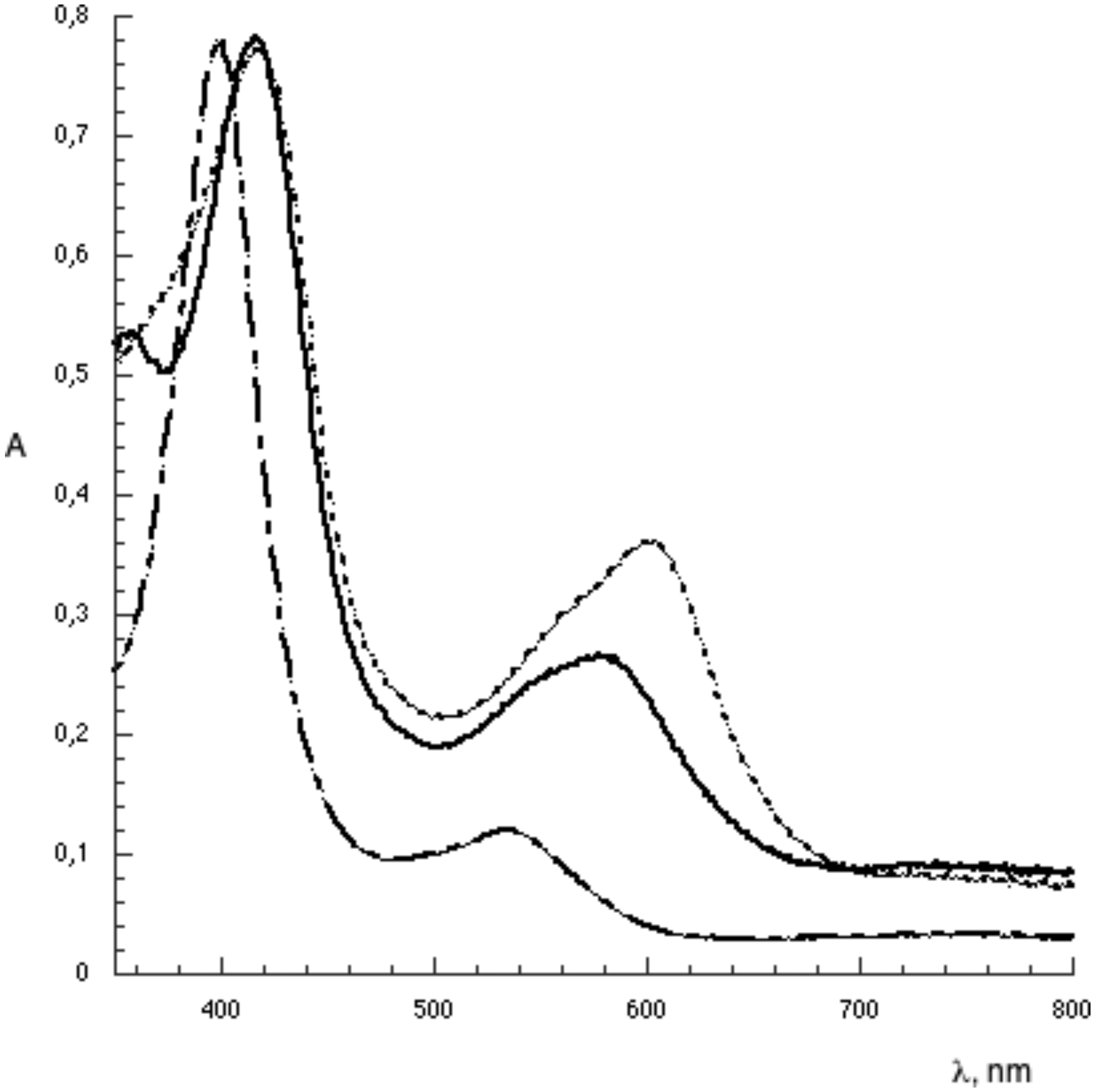

Figure S5. UV-vis spectra of ttcorrFeNO (dashed line), 3-(NO_2)ttcorrFeNO (solid line), 3,17-(NO_2)$_2$ttcorrFeNO (dotted line) in CH_2Cl_2 solutions. Absorbances are normalized to their maxima.

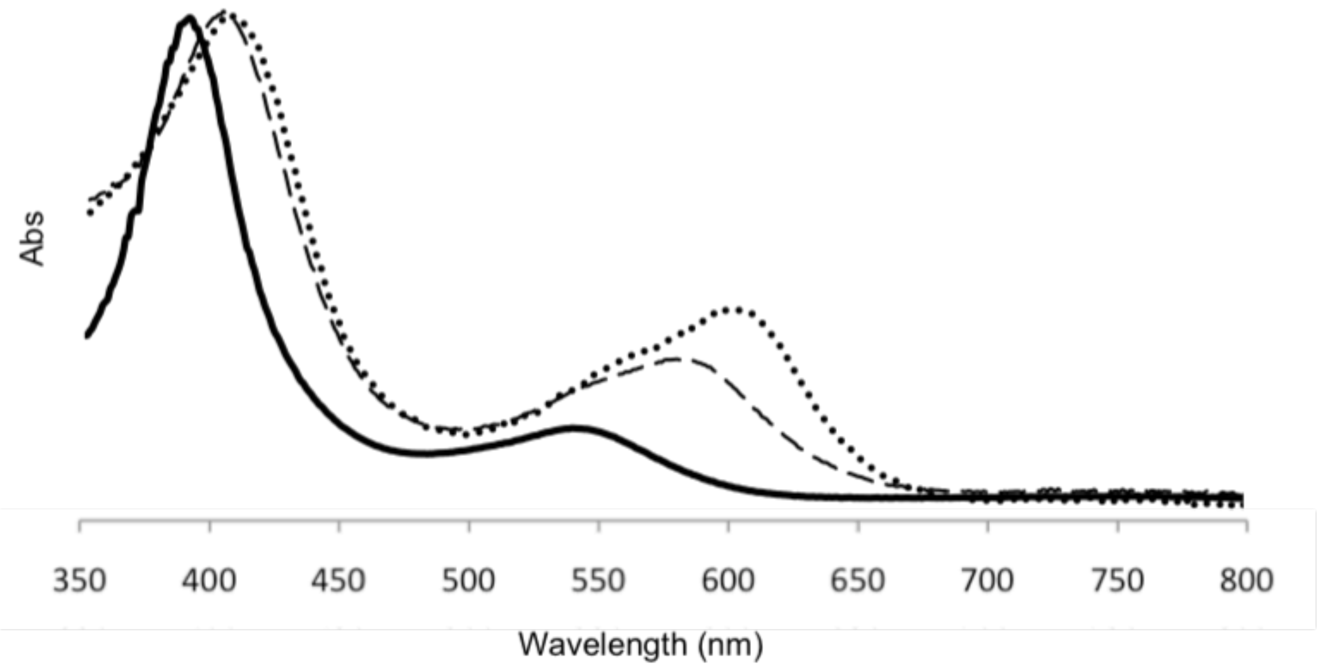

Figure S6. UV-vis spectra of tpcorrFeNO (solid line), 3-(NO_2)tpcorrFeNO (dashed line), 3,17-(NO_2)$_2$tpcorrFeNO (dotted line) in CH_2Cl_2 solutions. Absorbances are normalized to their maxima.

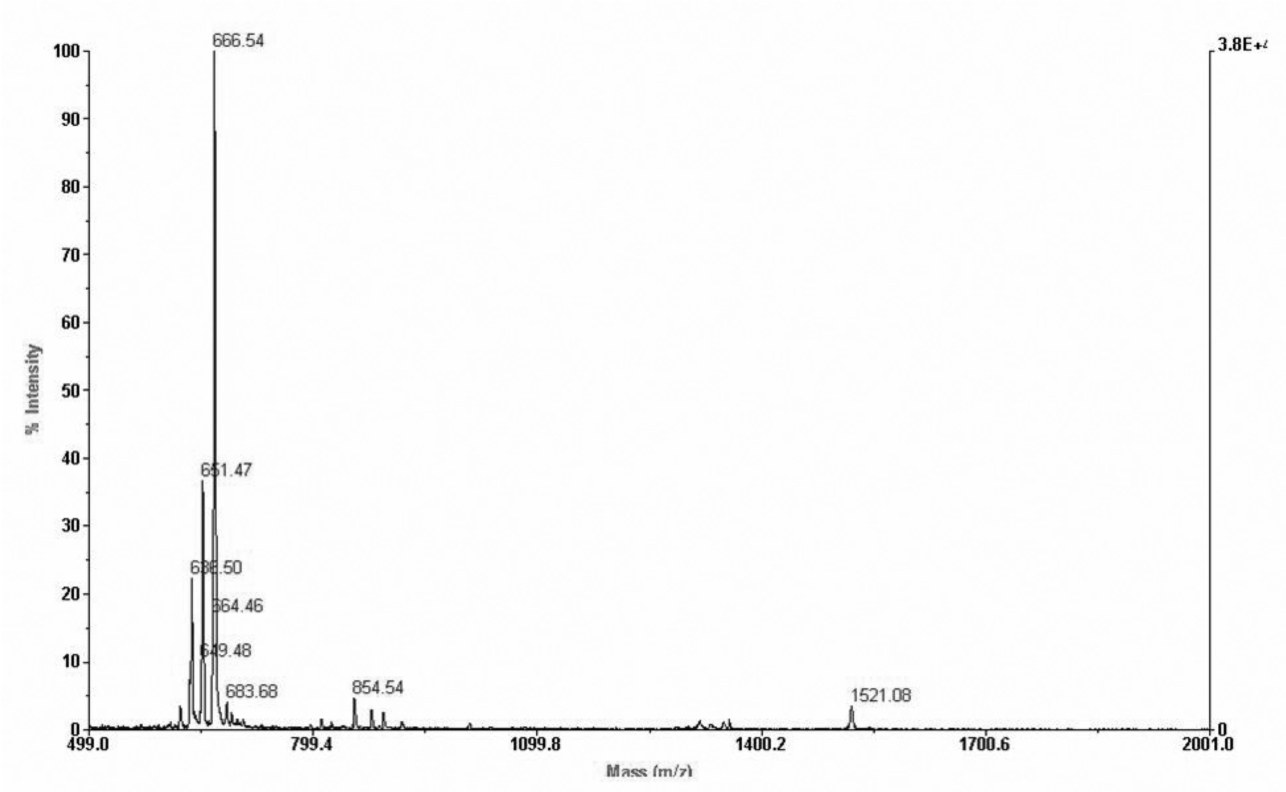

Figure S7. MALDI mass spectrum of 3-NO_2ttcorrFeNO.

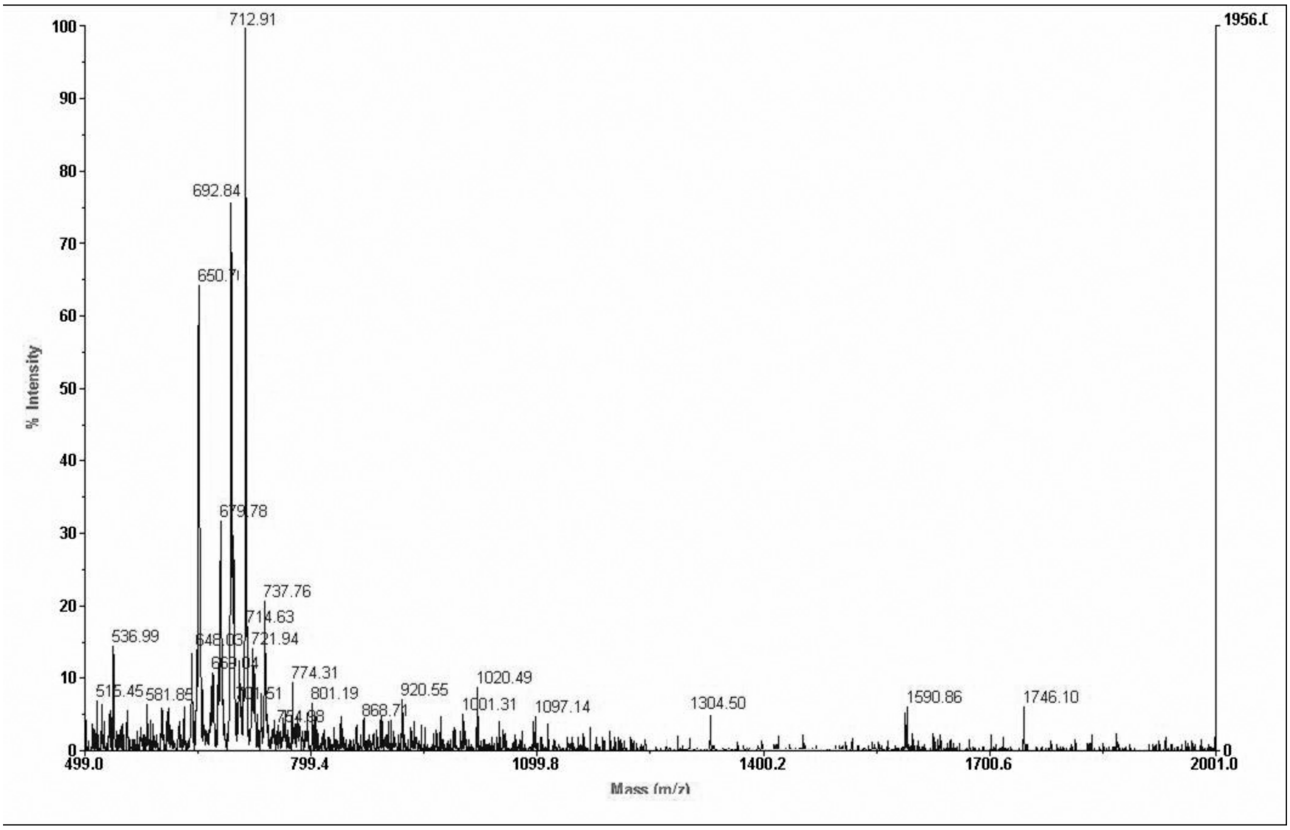

Figure S8. MALDI mass spectrum of 3,17-$(NO_2)_2$ttcorrFeNO