Electronic Supporting Information

Synthesis and structure of iron (II) complexes of functionalized 1,5-diaza-3,7-diphosphacyclooctanes.

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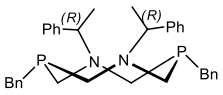
Content

General methods: ESI_{pos} MS were recorded with an AmazonX (Bruker Daltonic GmbH, Bremen, Germany) spectrometer at a capillary voltage of 4500 V. DataAnalysis 4.0 (Bruker Daltonic GmbH, Bremen, Germany) program was used to process the mass spectrometry data. MALDI MS were recorded with an Ultraflex III TOF/TOF (Bruker Daltonics, Germany) spectrometer on p-nitroaniline matrix. FlexAnalysis 3.0 (Bruker Daltonics) program was used to process the mass spectrometry data. The mass spectra are reported as m/z values. ^{1}H NMR (400 MHz and 600 MHz) and ^{31}P NMR (162 and 242 MHz) spectra were obtained with Bruker Avance-DRX 400 and Bruker Avance-600 spectrometers. The chemical shifts are reported in ppm relative to $SiMe_4$ (^{1}H, internal standard), and 85% H_3PO_4 (aq) (^{31}P; external standard). The coupling constants (*J*) are reported in Hz. Simultaneous thermogravimetry and differential scanning calorimetry (TG/DSC) analysis of samples of **11b** (solvate) (10.7 mg) were performed using the STA 449F1 Jupiter (Netzsch, Germany) thermoanalyzer (in the range of temperatures from 40 to 200 °C in aluminum crucible under dynamic atmosphere of argon (75 ml/min). The heating rate was 10 °C/min.

The spectra of the synthesized compounds.

3,7-dibenzyl-1,5-di(1'-(*R*)-phenylethyl)-1,5-diaza-3,7-diphosphacyclooctane (3).



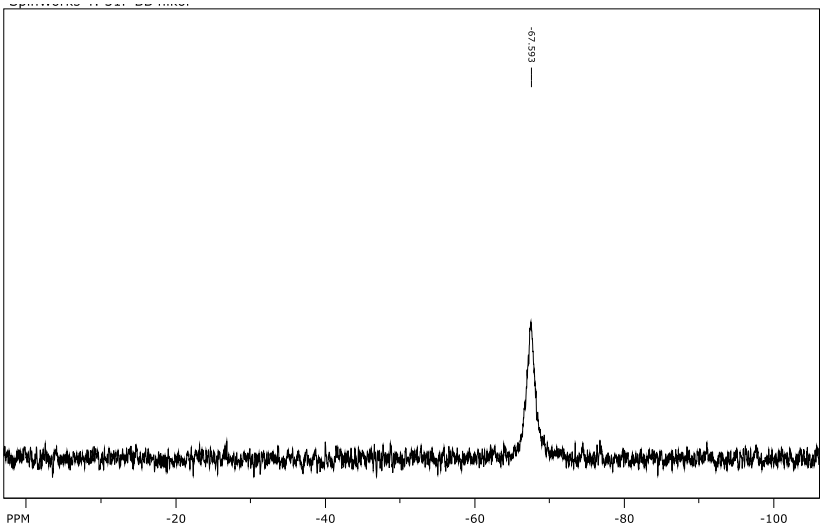


Figure S1. ^{31}P NMR spectrum of **3** in $CDCl_3$ (162 MHz).

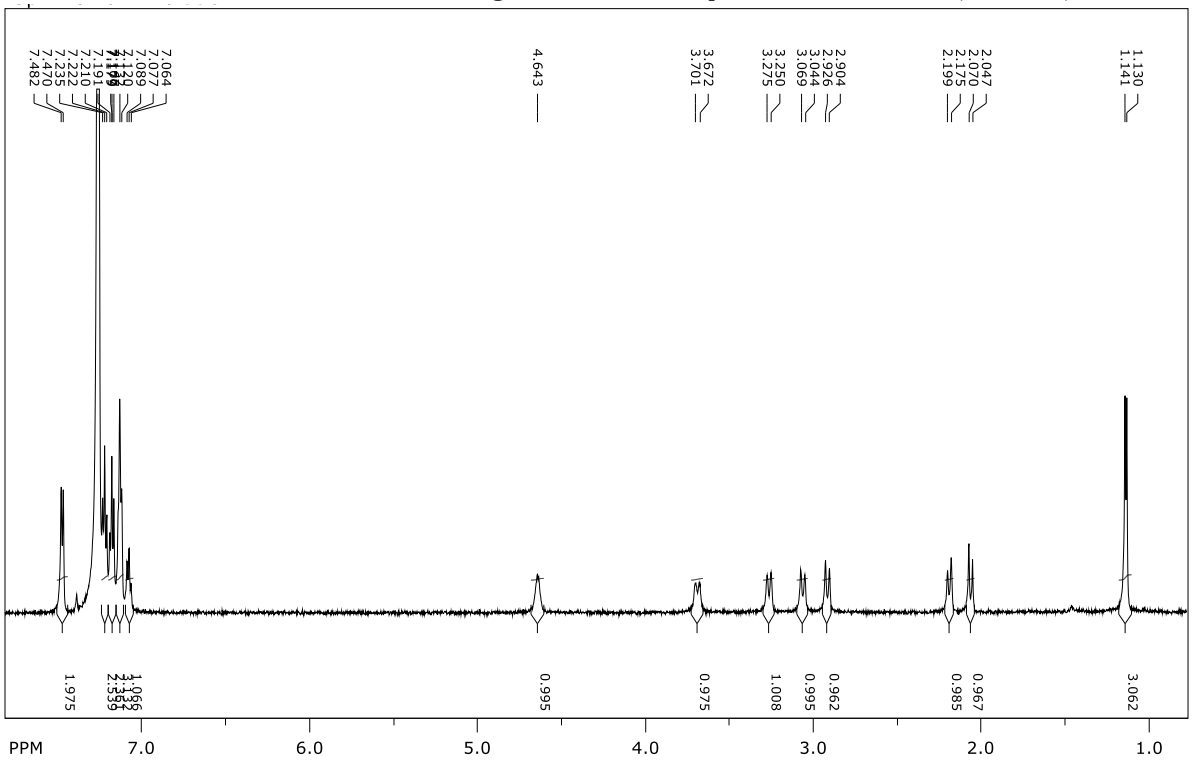
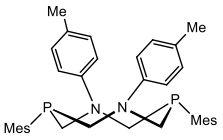


Figure S2. ^{1}H NMR spectrum of **3** ($CDCl_3$,400 MHz).

3,7-dimesityl-1,5-di(p-tolyl)-1,5-diaza-3,7-diphosphacyclooctane (5)



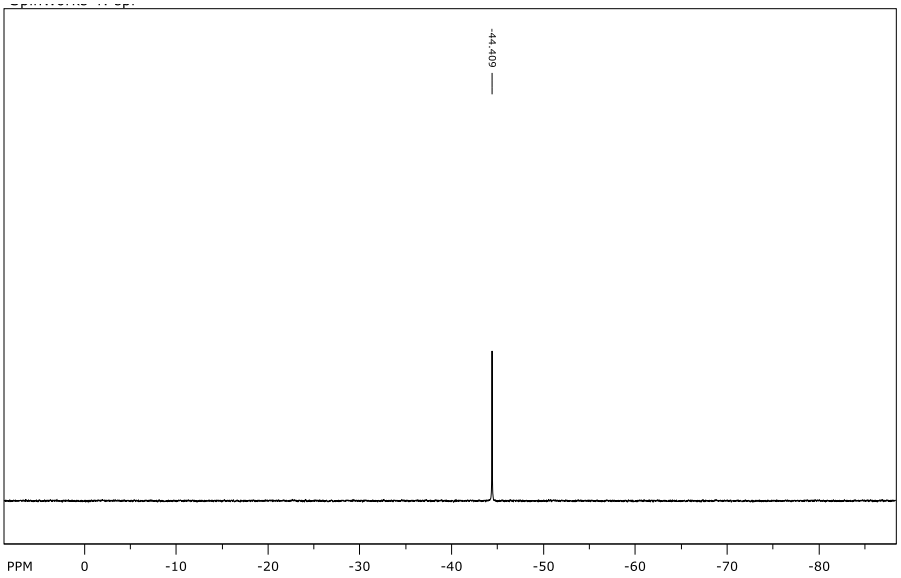


Figure S3. ^{31}P NMR spectrum of **5** ($CDCl_3$,162 MHz).

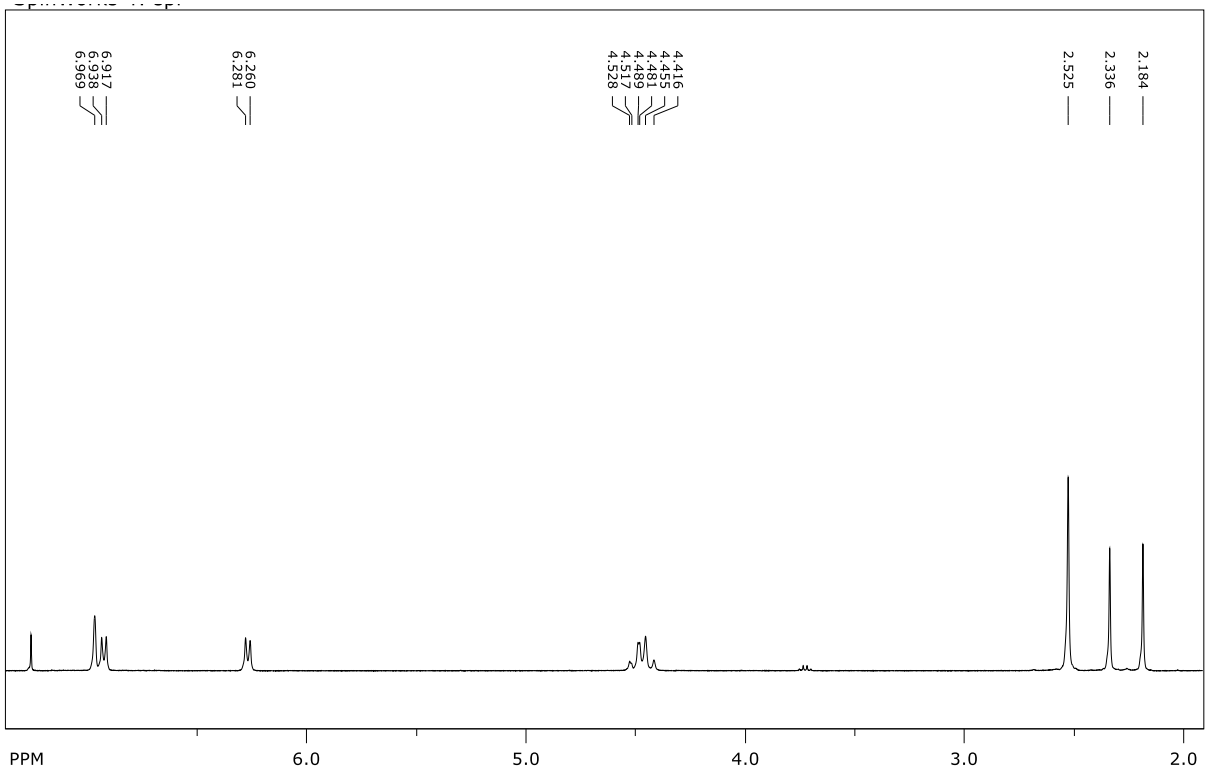


Figure S4. ^{1}H NMR spectrum of **5** ($CDCl_3$, 400 MHz).

Bis(3,7-diphenyl-1,5-di(*p*-methoxyphenyl)-1,5-diaza-3,7-diphosphacyclooctane)-bis(acetonitrile)iron(II)] tetrafluoroborate (6)

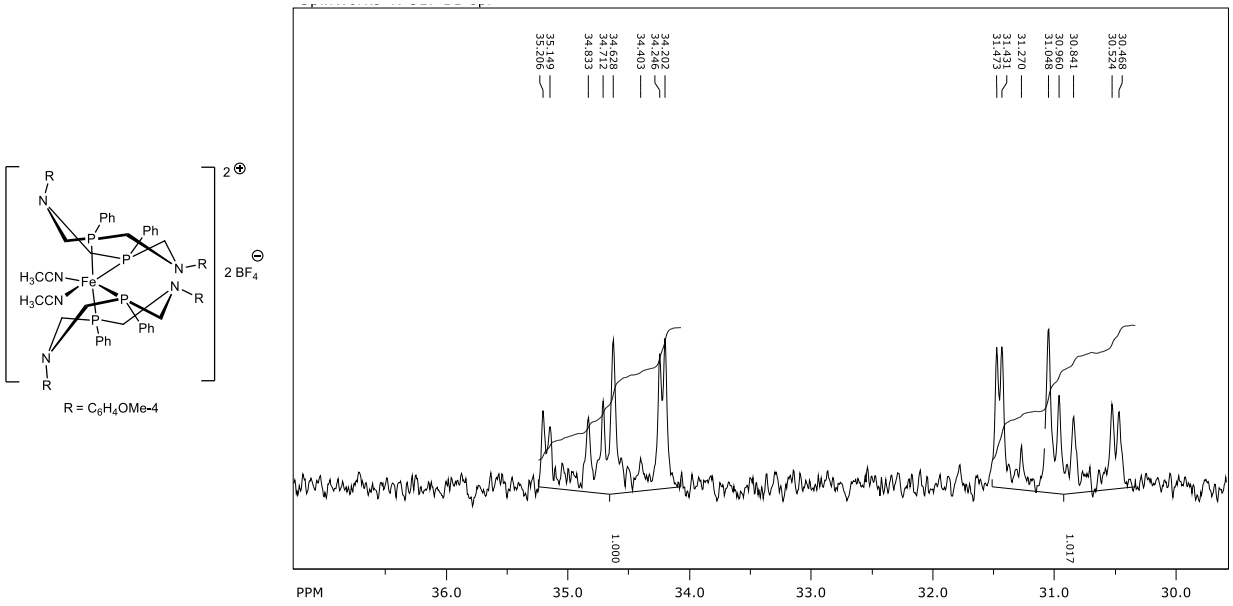


Figure S5. ^{31}P NMR spectrum of **6** (CD_3CN, 162 MHz).

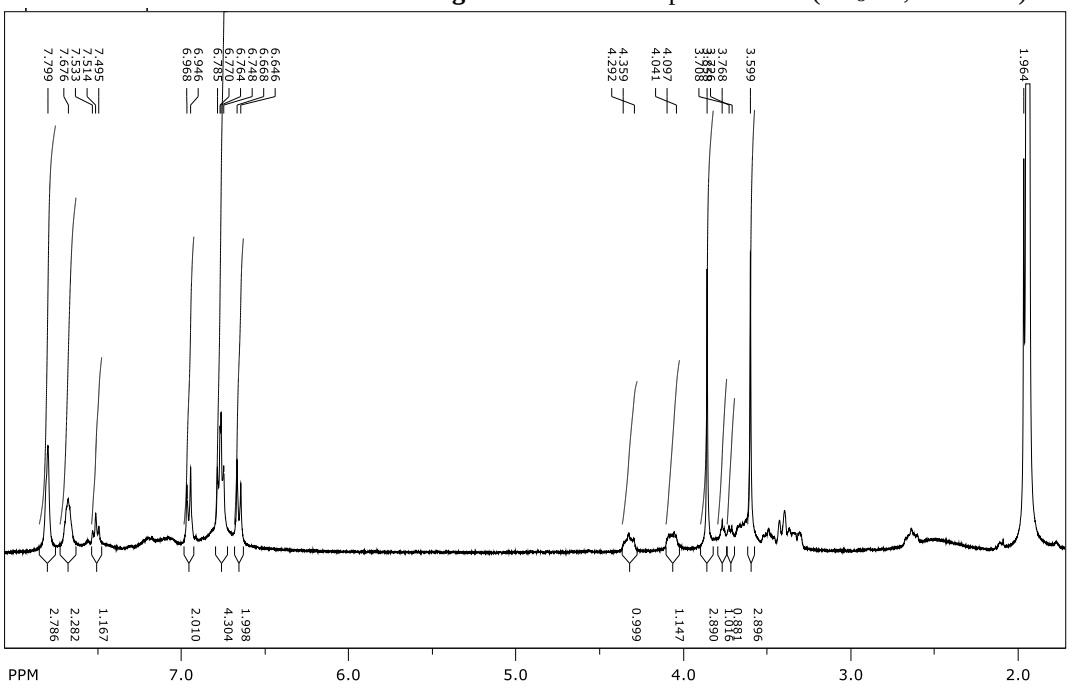


Figure S6. ^{1}H NMR spectrum of **6** (CD_3CN, 400 MHz).

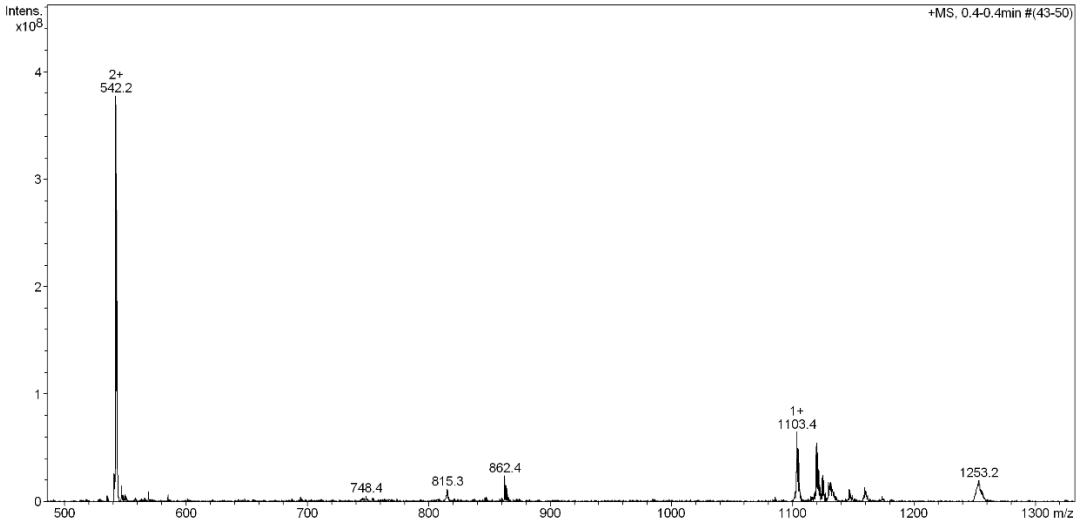


Figure S7. ESI-MS spectrum of **6** (CD_3CN).

[Bis(3,7-dibenzyl-1,5-diphenyl-1,5-diaza-3,7-diphosphacyclooctane)-bis(acetonitrile)iron(II)] tetrafluoroborate (7).

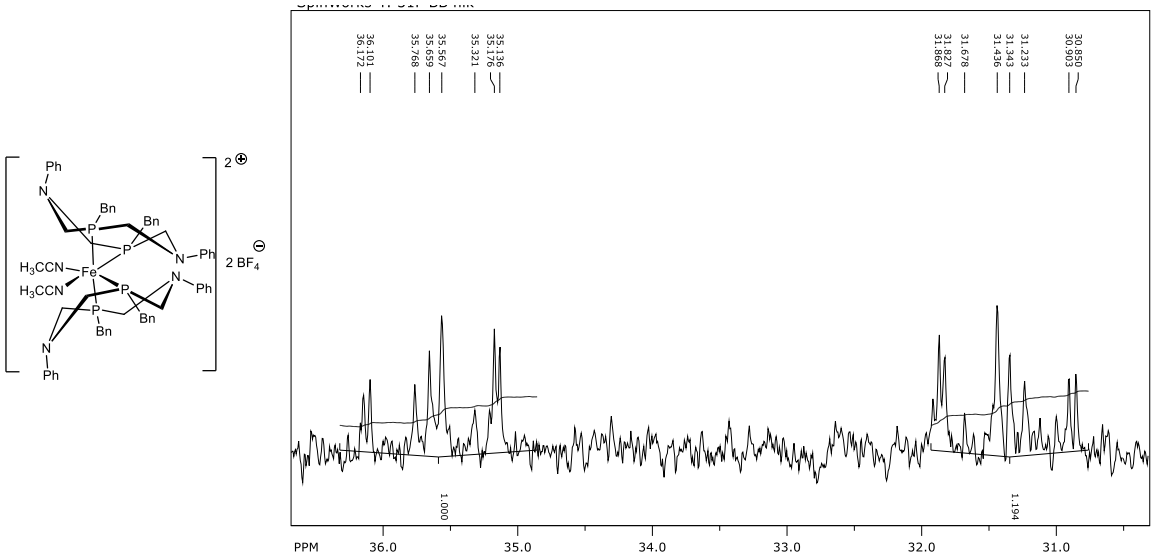


Figure S8. ^{31}P NMR spectrum of **7** (CD_3CN, 162 MHz).

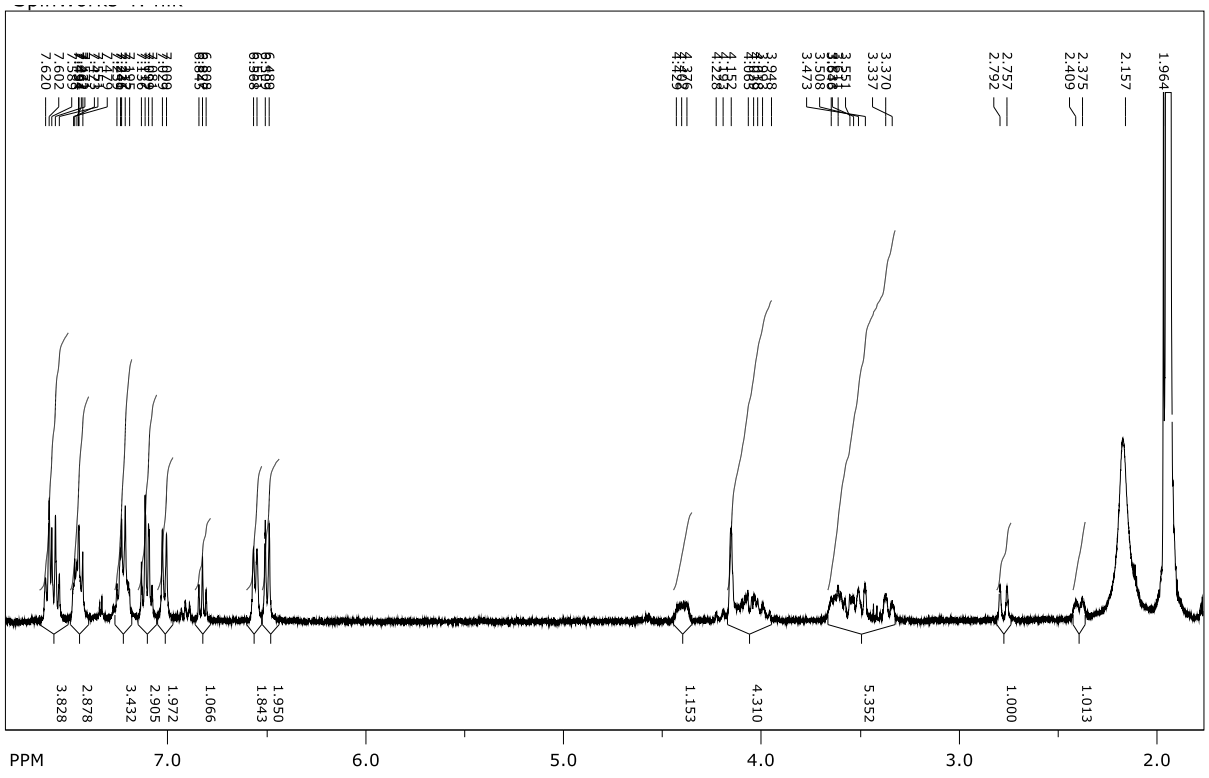


Figure S9. ^{1}H NMR spectrum of **7** (CD_3CN, 400 MHz) (2.16 s – H_2O in the solvent).

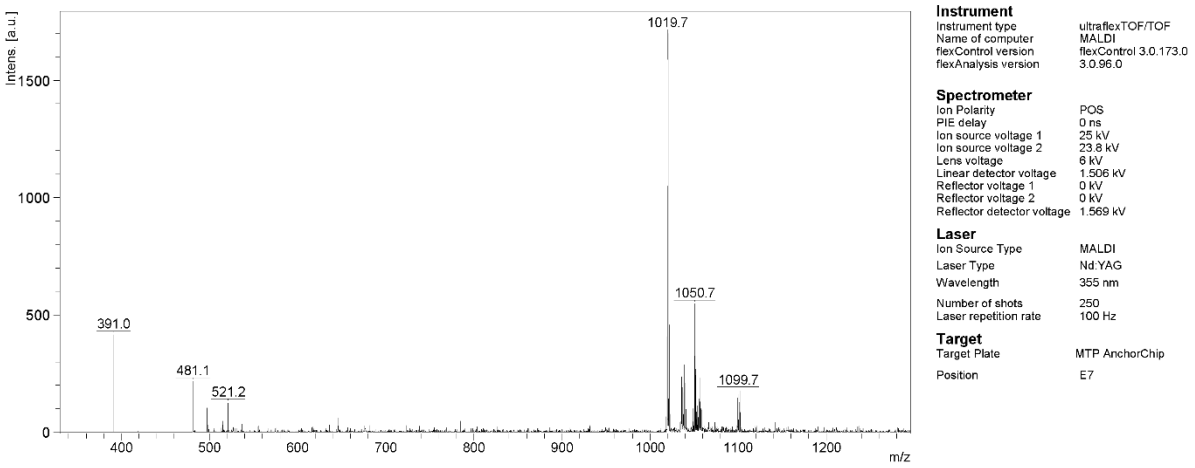


Figure S10. MALDI-MS spectrum of **7** (CD_3CN).

[Bis(3,7-dibenzyl-1,5-di(1'-(*R*)-phenylethyl)-1,5-diaza-3,7-diphosphacyclooctane)-bis(acetonitrile)iron(II)] tetrafluoroborate (8).

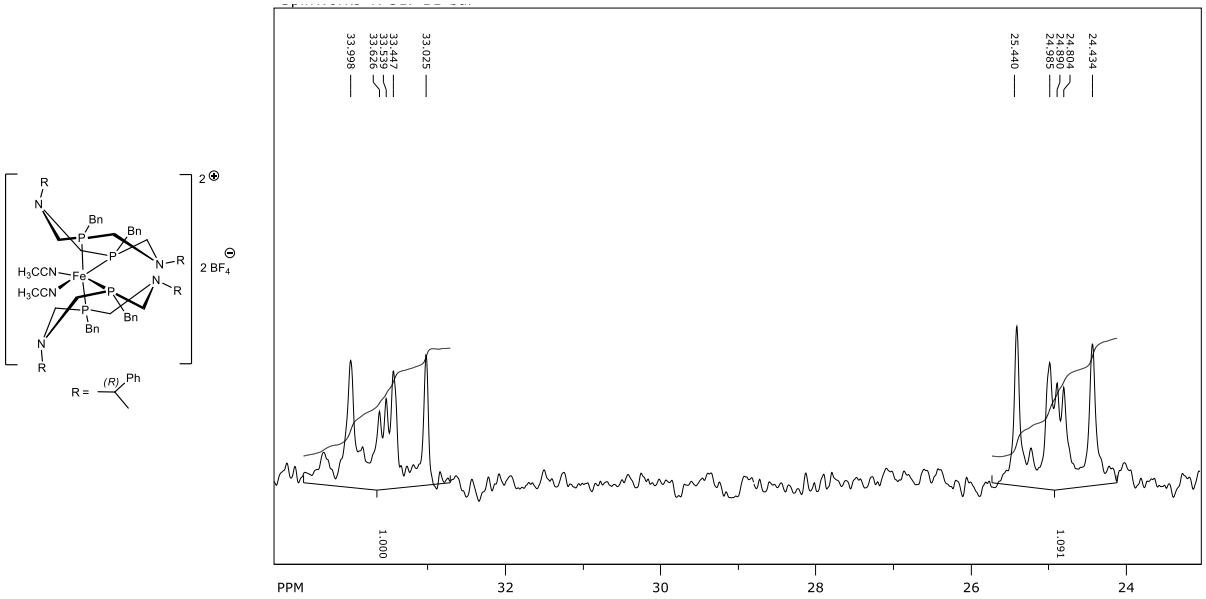


Figure S11. ^{31}P NMR spectrum of **8** (CD_3CN, 162 MHz).

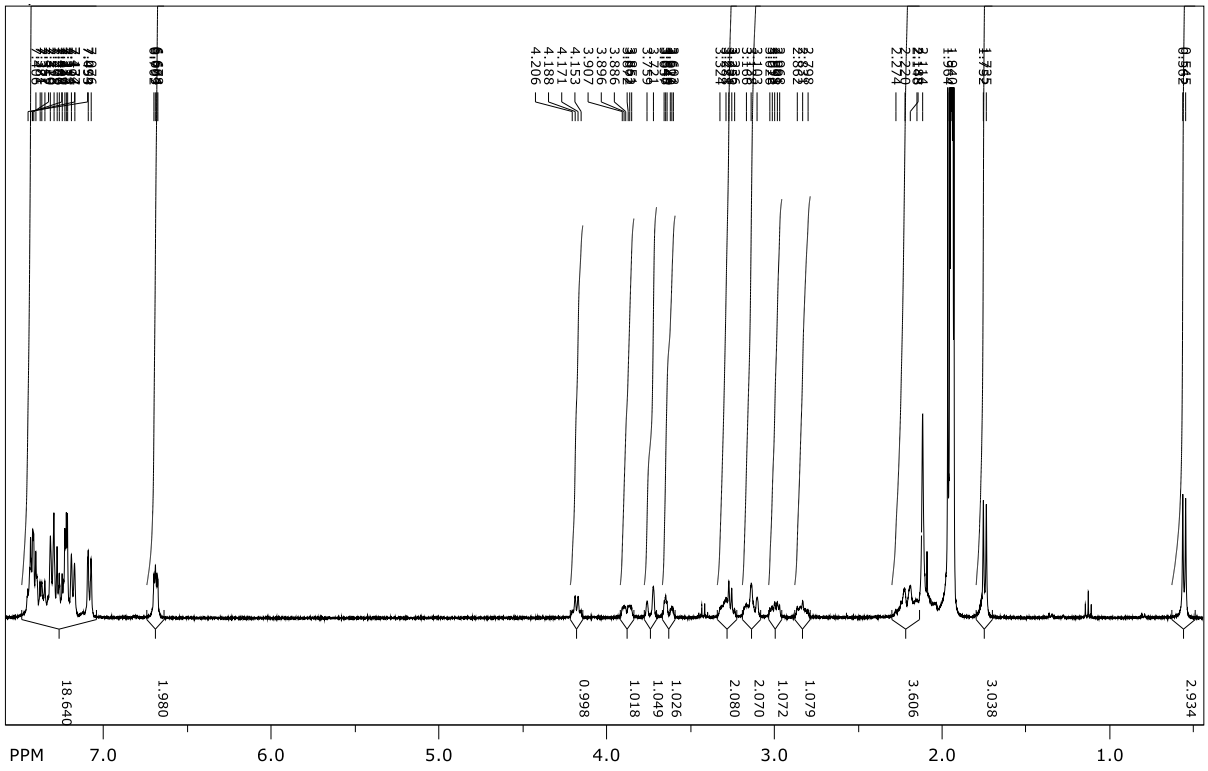


Figure S12. ^{1}H NMR spectrum of **8** (CD_3CN, 400 MHz) (2.11 s – H_2O in the solvent).

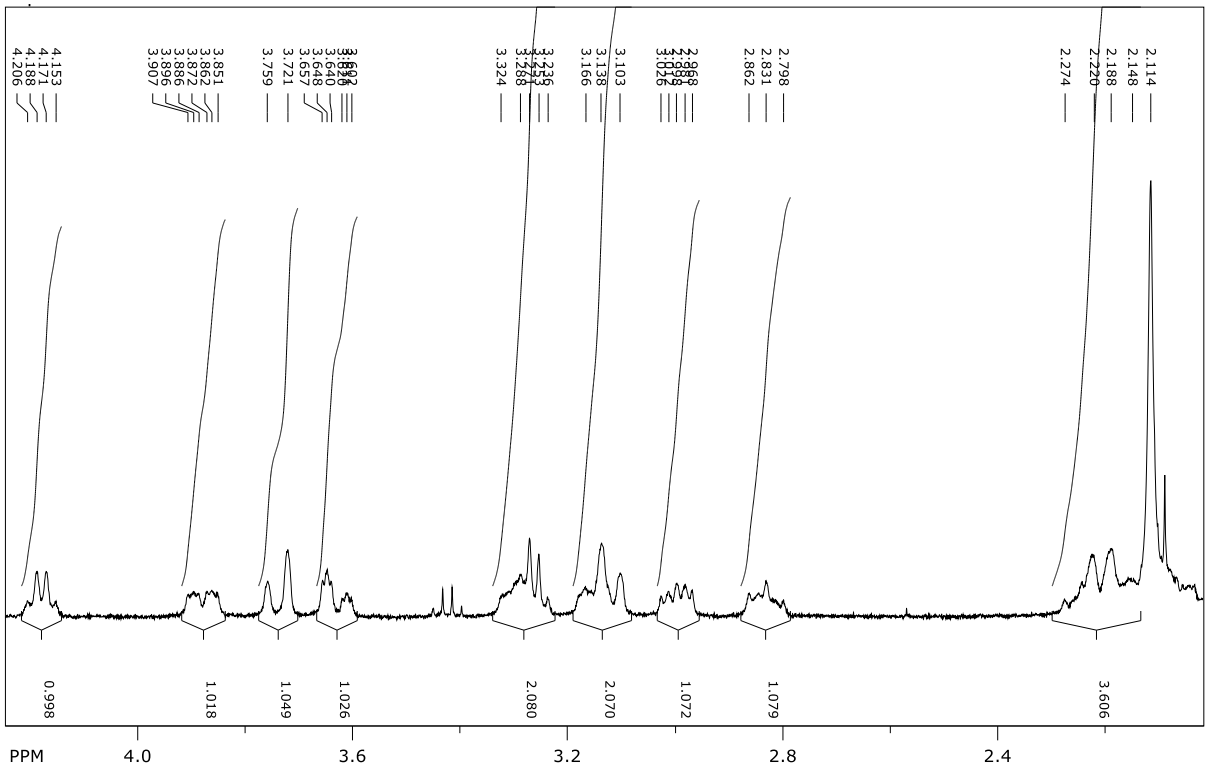


Figure S13. ^{1}H NMR spectrum of **8** (CD_3CN, 400 MHz), the region of protons of P-C*H*$_2$-N, P-C*H*$_2$-Ph, C*H*(Ph)Me fragments (2.11 s – H_2O in the solvent).

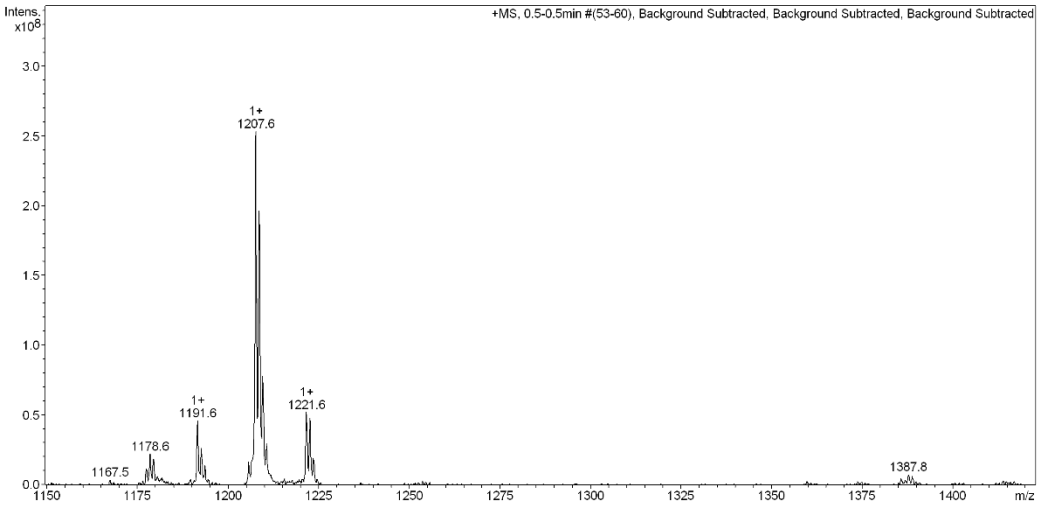


Figure S14. ESI-MS spectrum of **8** (CD_3CN).

[Bis(3,7-di(pyridine-2'-yl)-1,5-di(p-tolyl)-1,5-diaza-3,7-diphosphacyclooctane)-bis(acetonitrile)iron(II)] tetrafluoroborate (9).

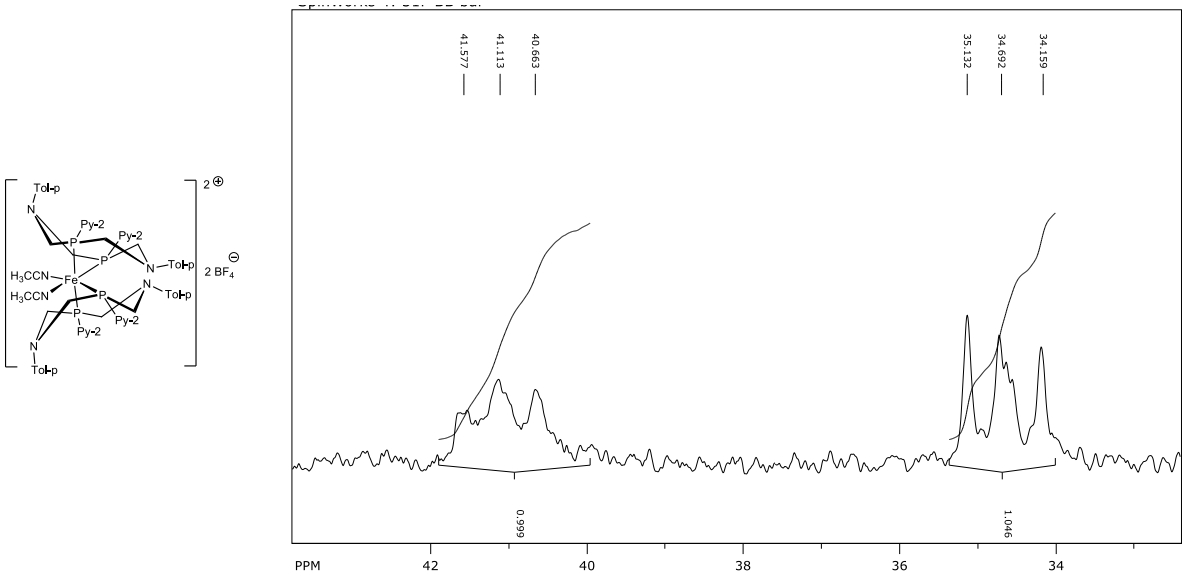


Figure S15. ^{31}P NMR spectrum of **9** (CD_3CN, 162 MHz).

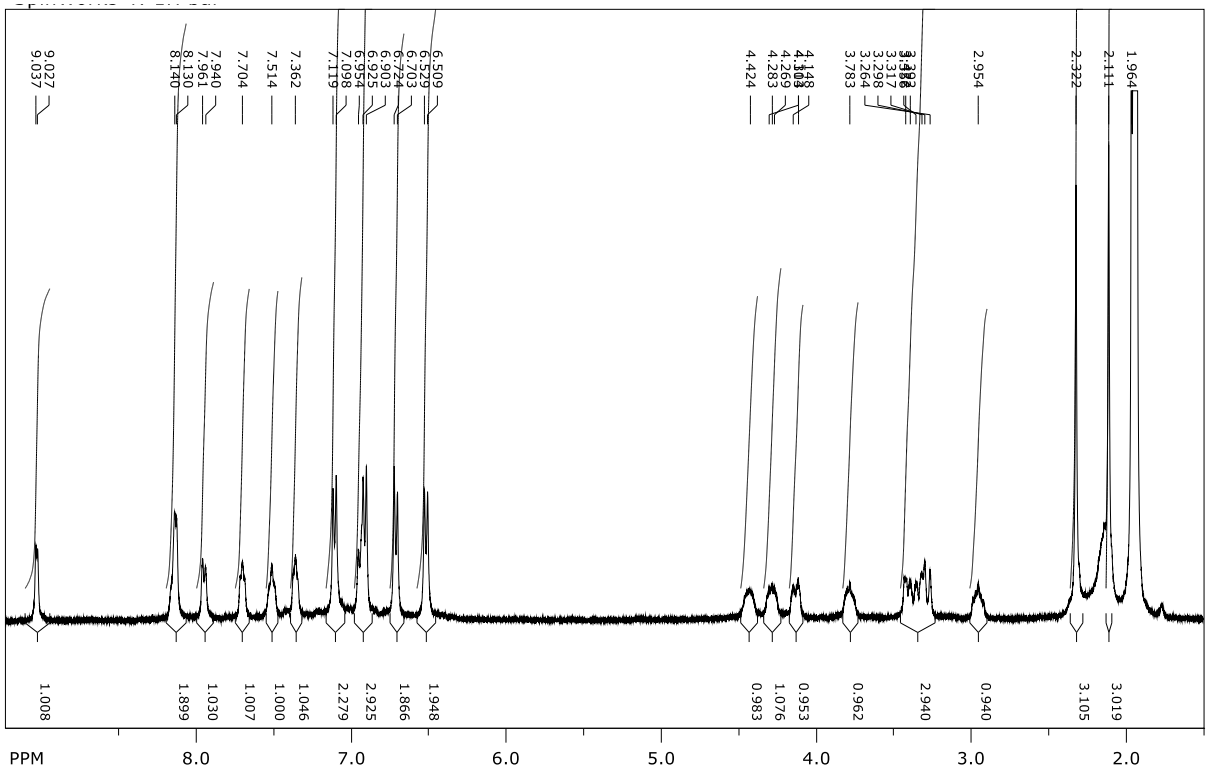


Figure S16. ^{1}H NMR spectrum of **9** (CD_3CN, 400 MHz).

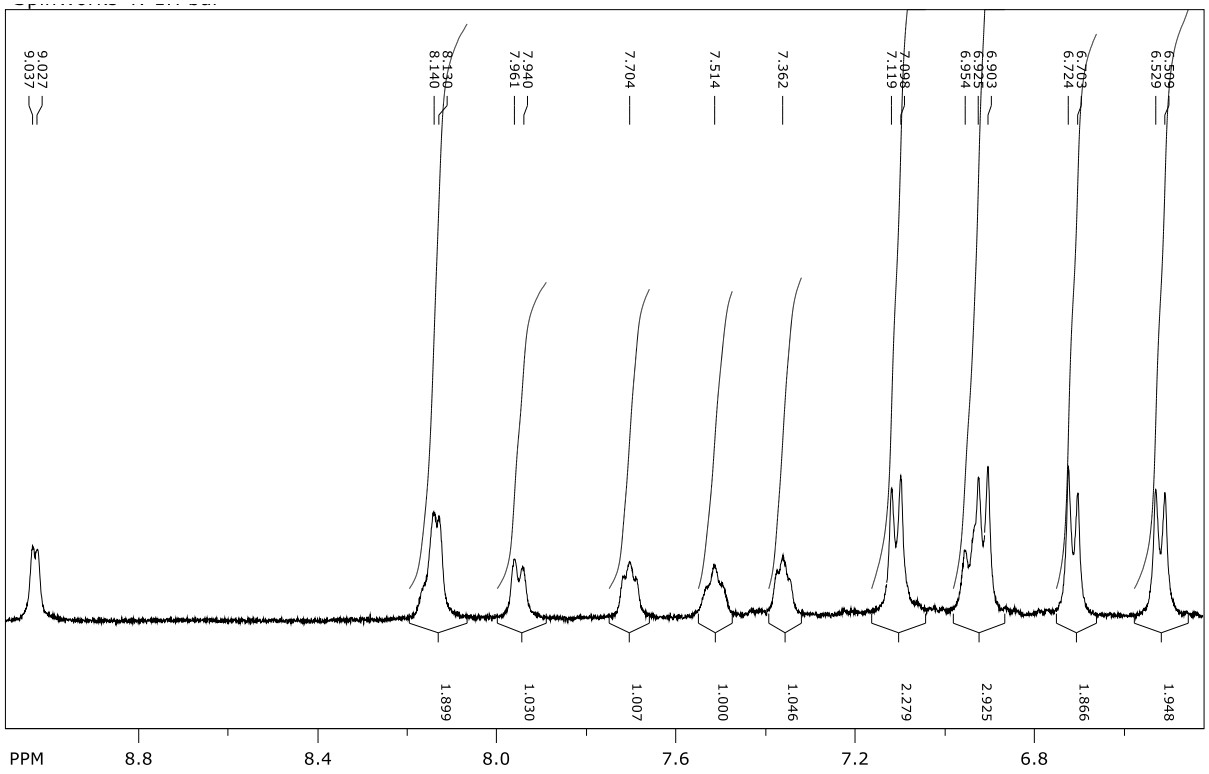


Figure S17. ^{1}H NMR spectrum of **9**, the region of aromatic protons (CD_3CN, 400 MHz).

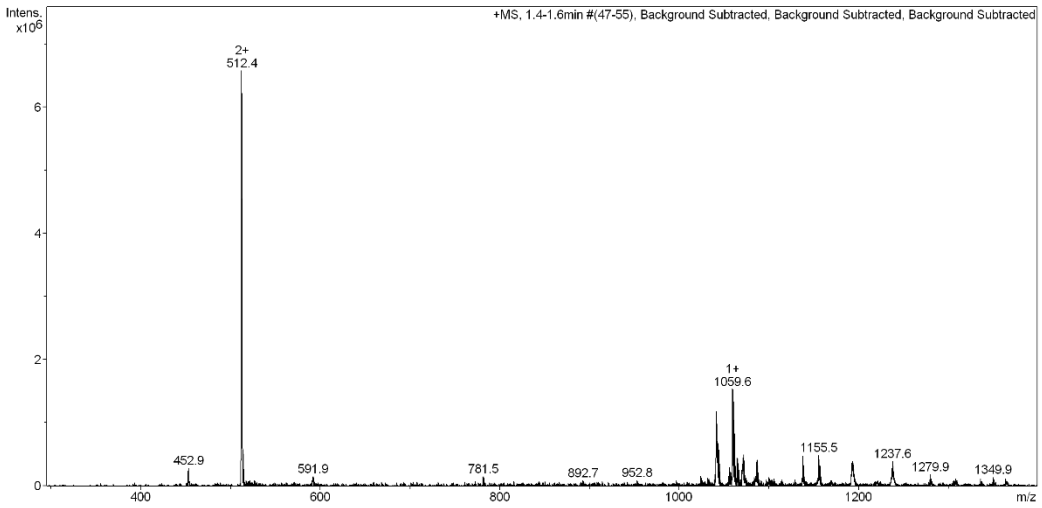
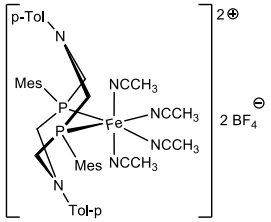


Figure S18. ESI-MS spectrum of **9** (CD_3CN).

[(3,7-dimesityl-1,5-di(p-tolyl)-1,5-diaza-3,7-diphosphacyclooctane)tetrakis-(acetonitrile)iron(II)] tetrafluoroborate (10).



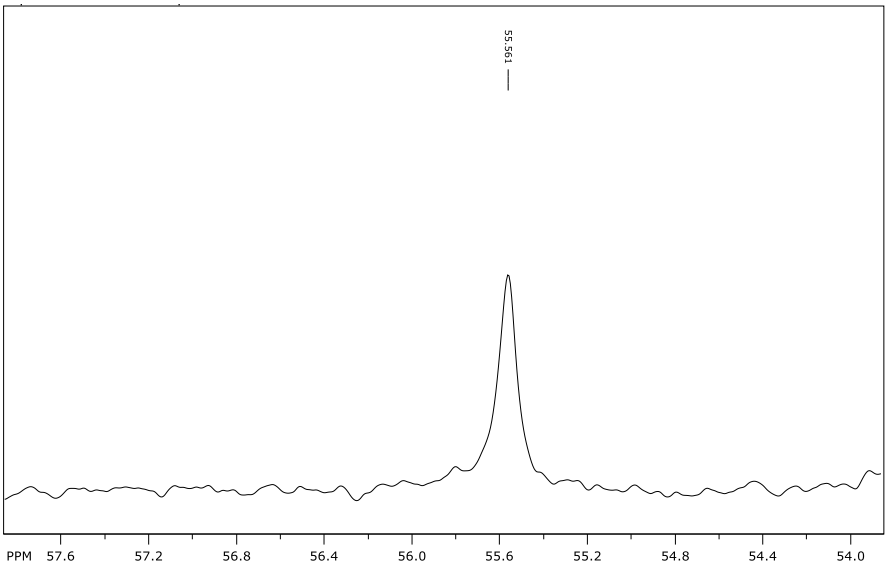


Figure S19. ^{31}P NMR spectrum of **10** (CD_3CN, 162 MHz).

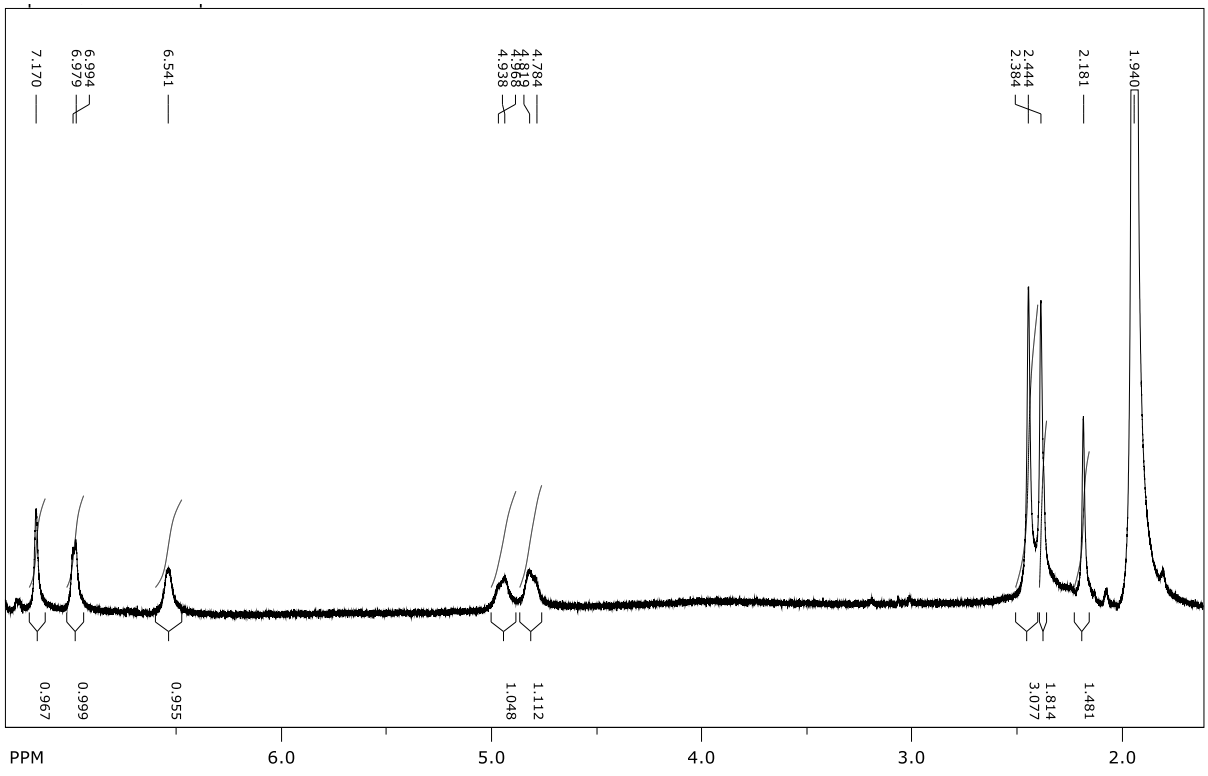


Figure S20. ^{1}H NMR spectrum of **10** (CD_3CN, 400 MHz).

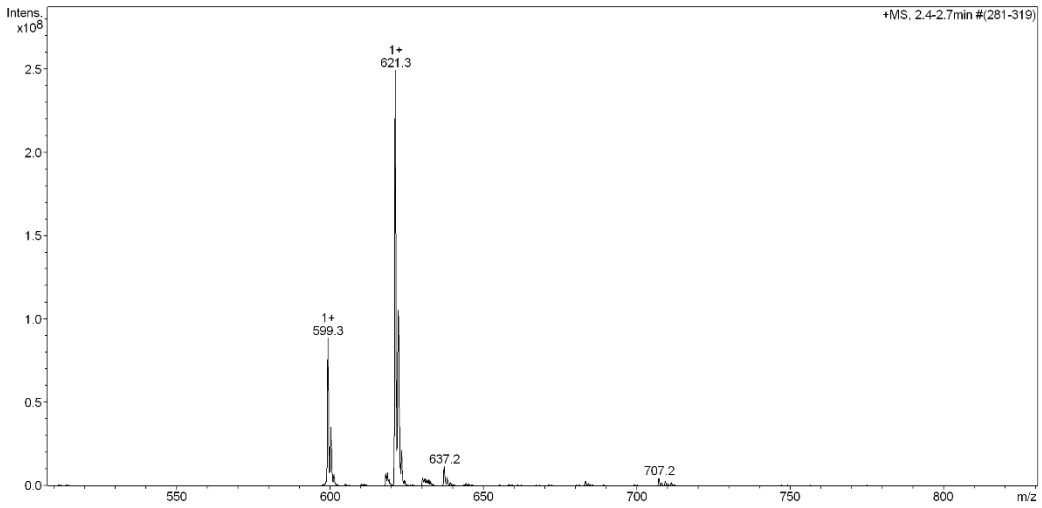


Figure S21. ESI-MS spectrum of **10** (CD_3CN).

[Bis(3,7-dibenzyl-1,5-di(1'-(*R*)-phenylethyl)-1,5-diaza-3,7-diphosphacyclooctane)- tetrafluoroboratoiron(II)] tetrafluoroborate (11b).

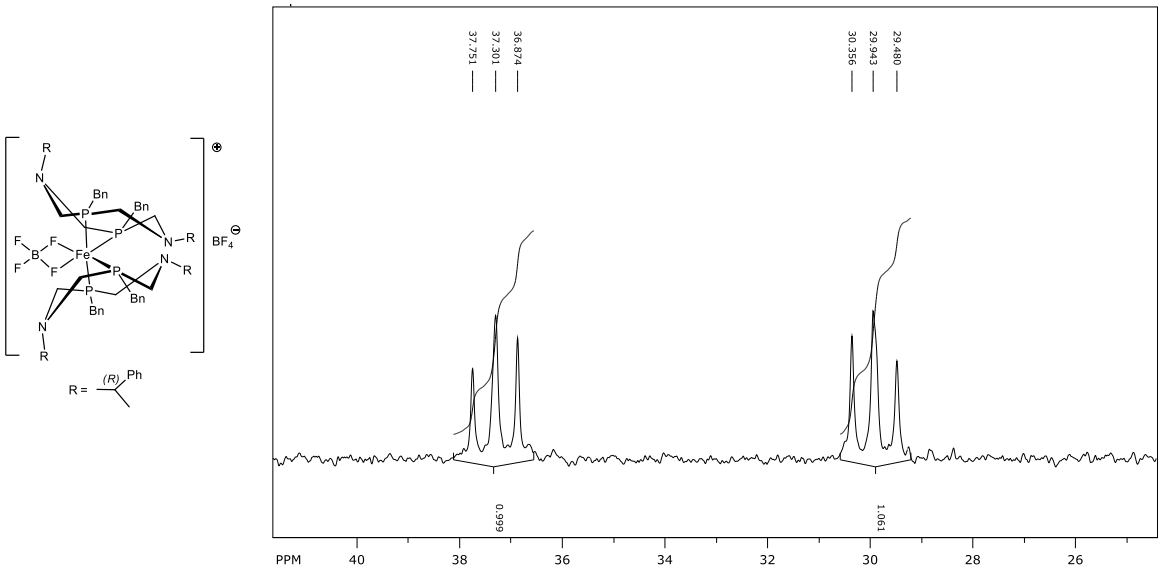


Figure S22. ^{31}P NMR spectrum of **11b** ($(CD_3)_2CO$, 162 MHz).

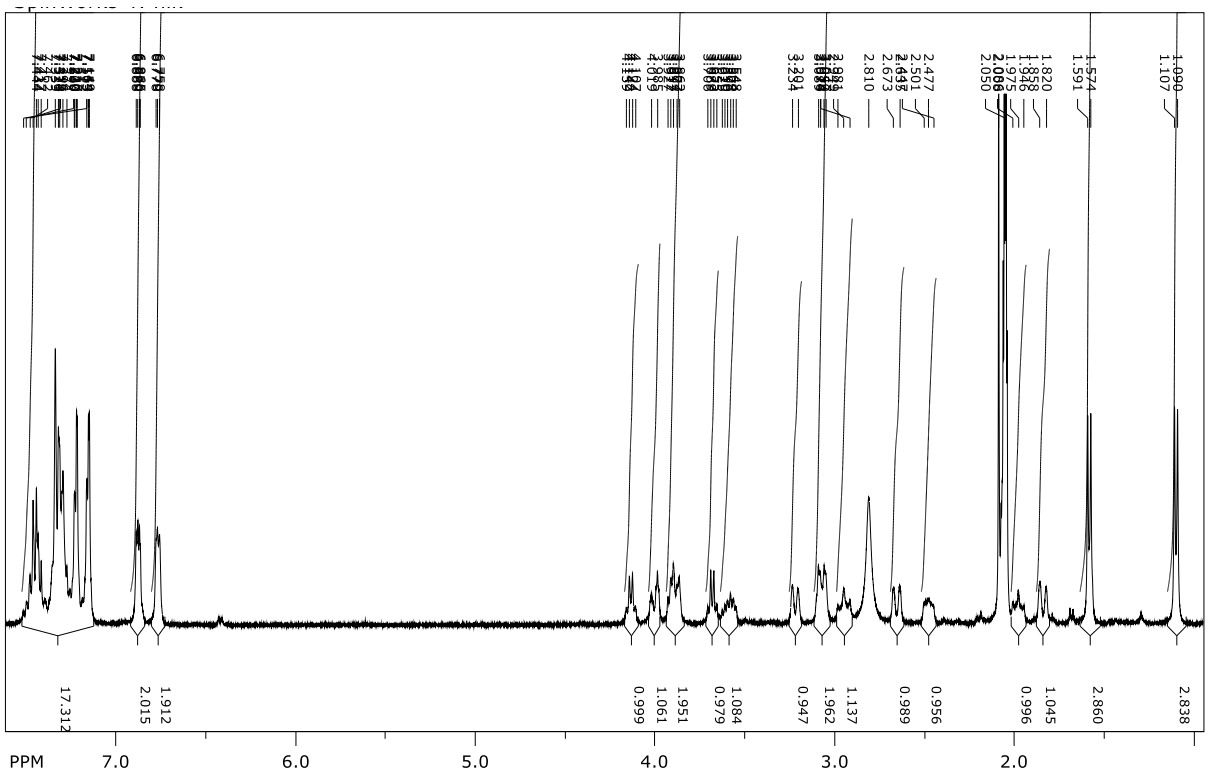


Figure S23. ^{1}H NMR spectrum of **11b** ($(CD_3)_2CO$, 400 MHz) (2.81 s – H_2O in the solvent).

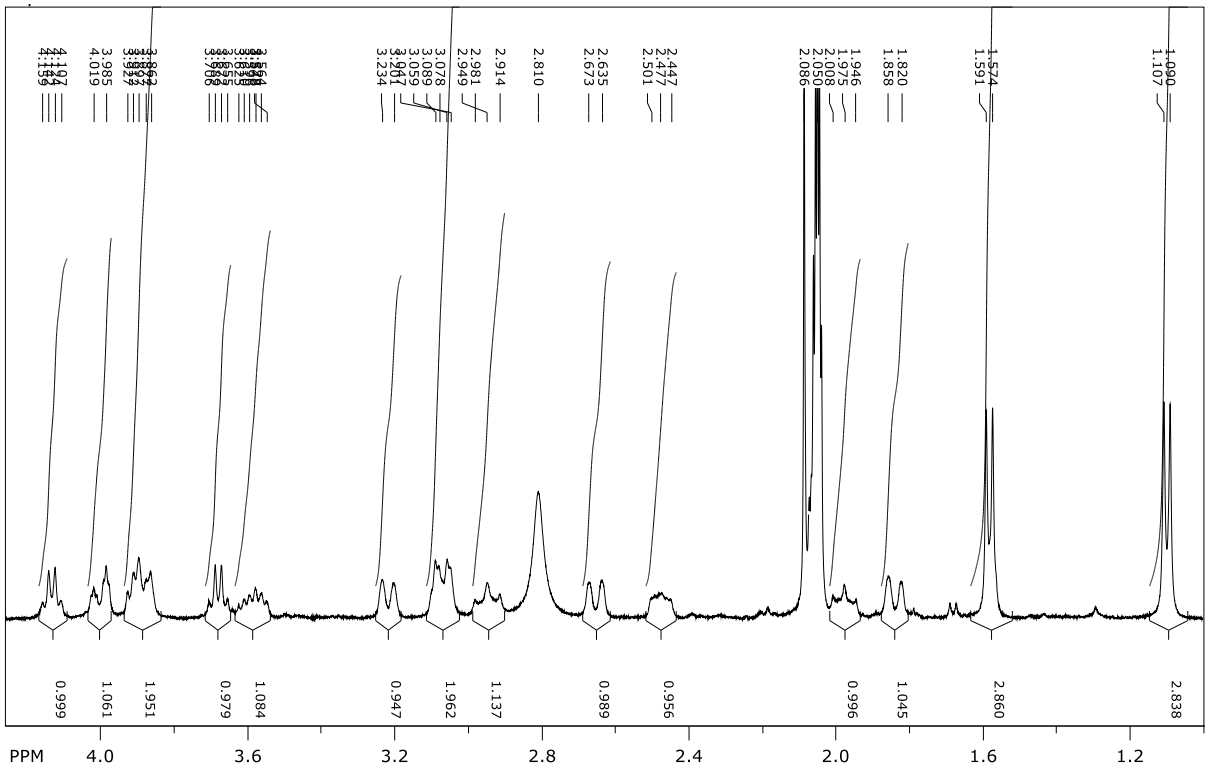


Figure S24. ^{1}H NMR spectrum of **11b** ($(CD_3)_2CO$, 400 MHz), the region of aliphatic protons (2.81 s – H_2O in the solvent).

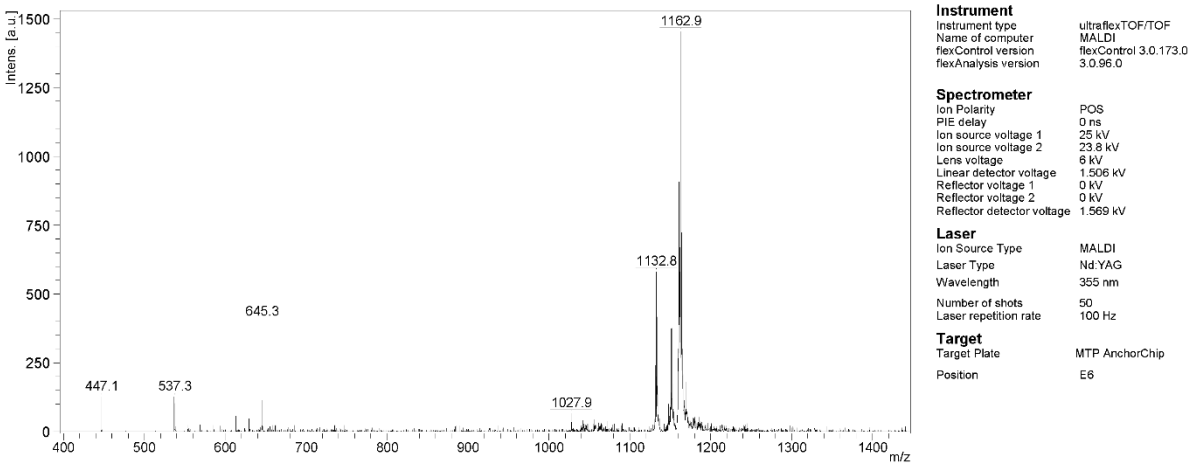


Figure S25. MALDI-MS spectrum of **11b** ($(CH_3)_2CO$).

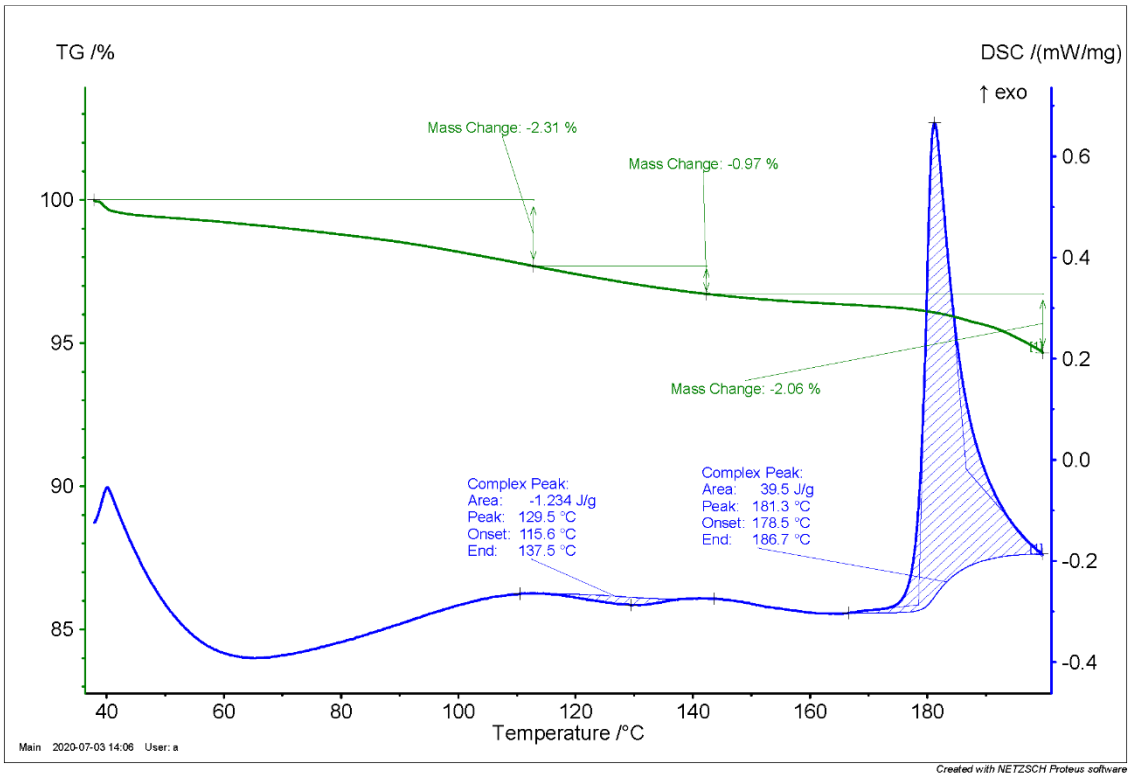


Figure S26. TG/DSK diagram of **11b** (single crystals containing solvate molecules).

[(Cyclopentadienyl)carbonyl(3,7-dibenzyl-1,5-di(1'-(*R*)-phenylethyl)-1,5-diaza-3,7-diphosphacyclooctane)iron(II)] tetrafluoroborate (12).

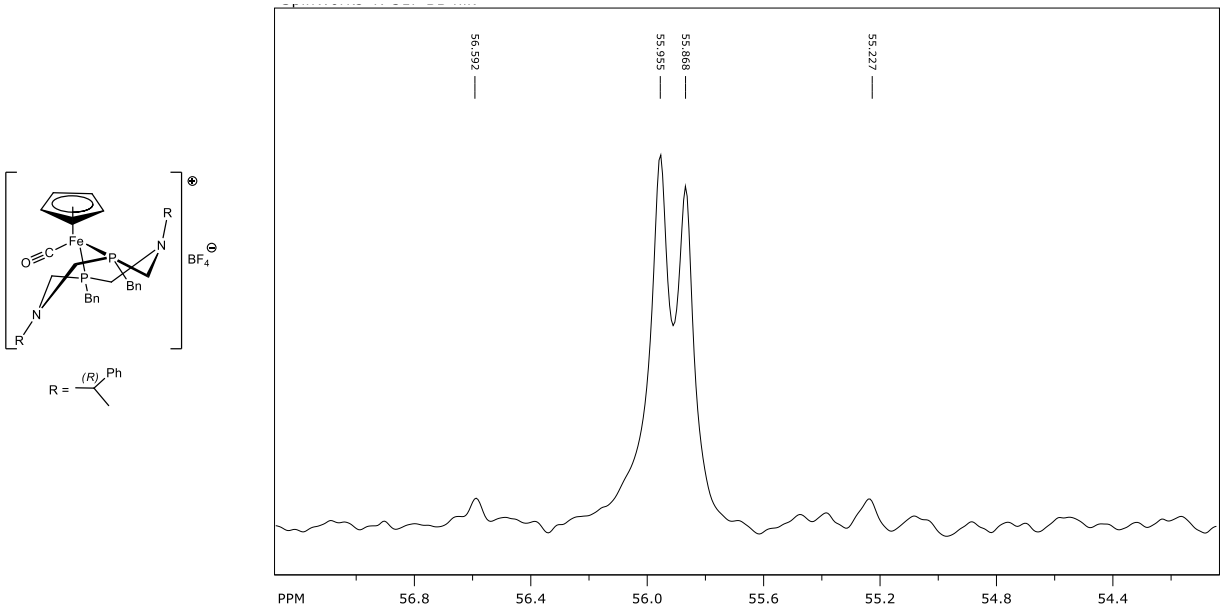


Figure S27. ^{31}P NMR spectrum of **12** ($(CD_3)_2CO$, 162 MHz).

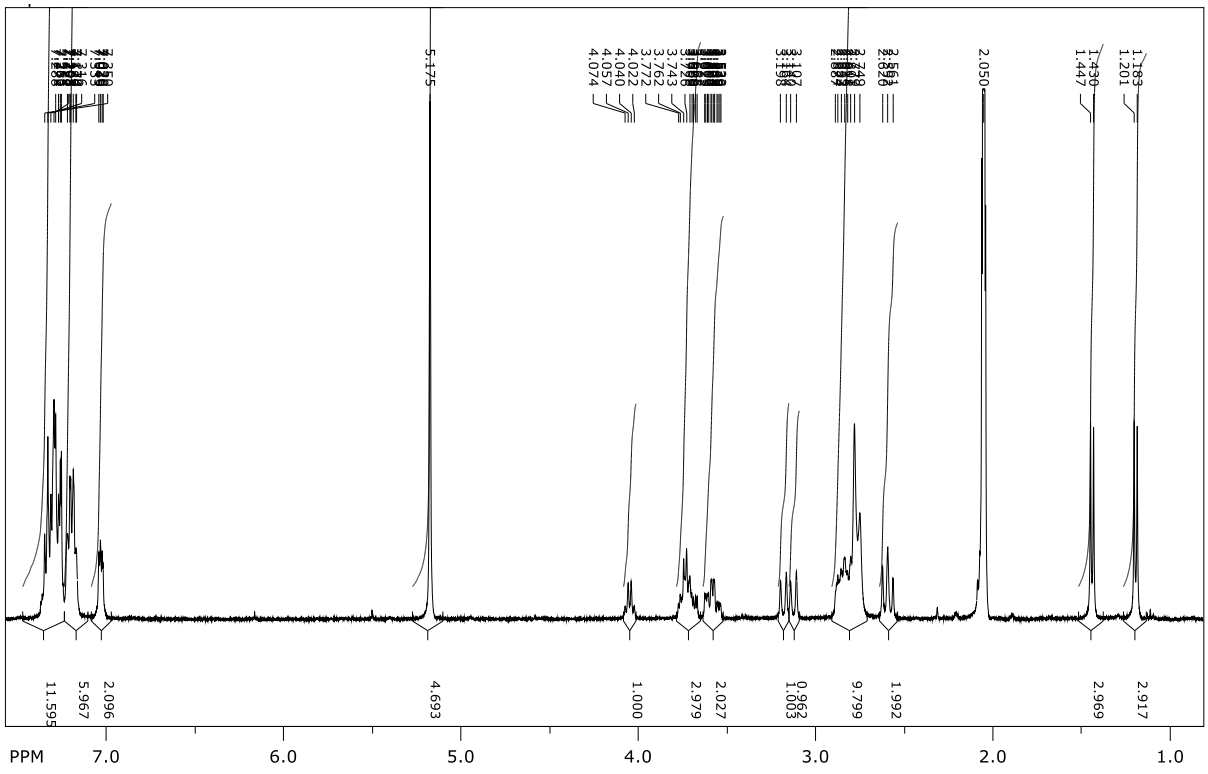


Figure S28. ^{1}H NMR spectrum of **12** ($(CD_3)_2CO$, 400 MHz) (2.79 s – H_2O in the solvent).

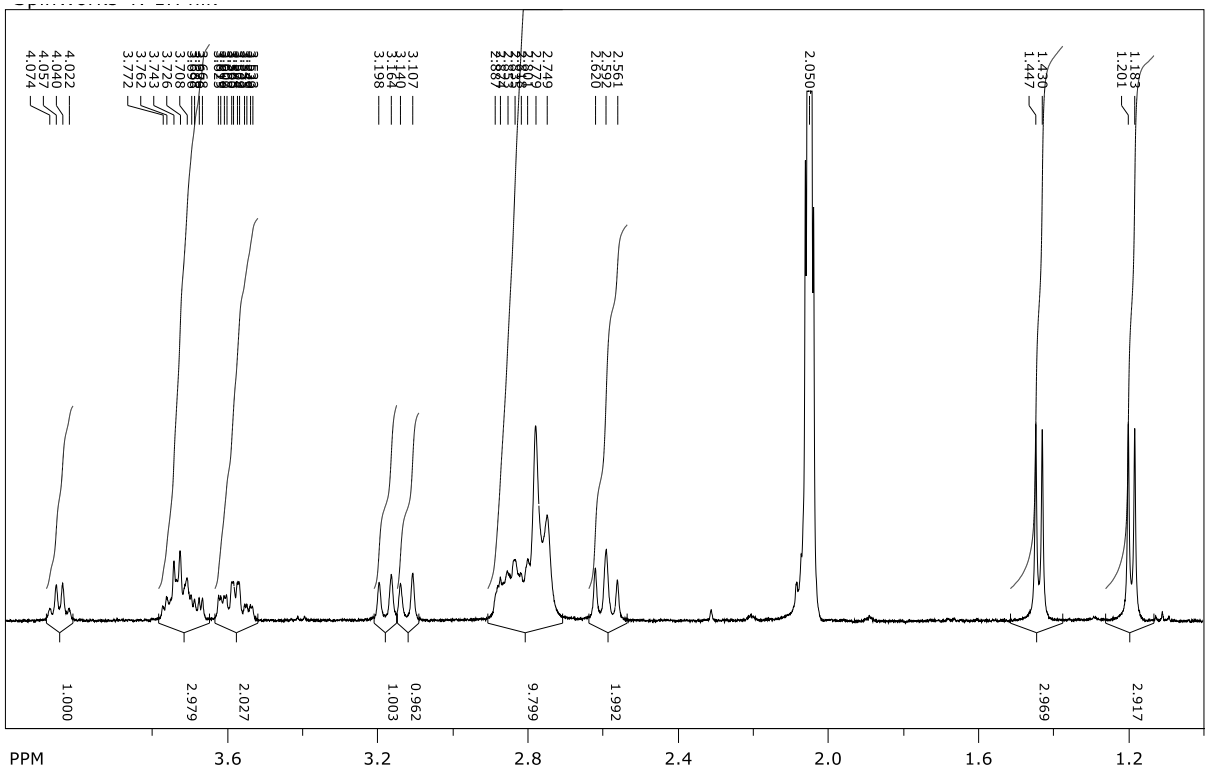


Figure S29. ^{1}H NMR spectrum of **12**, the region of aliphatic protons ($(CD_3)_2CO$, 400 MHz) (2.79 s – H_2O in the solvent).

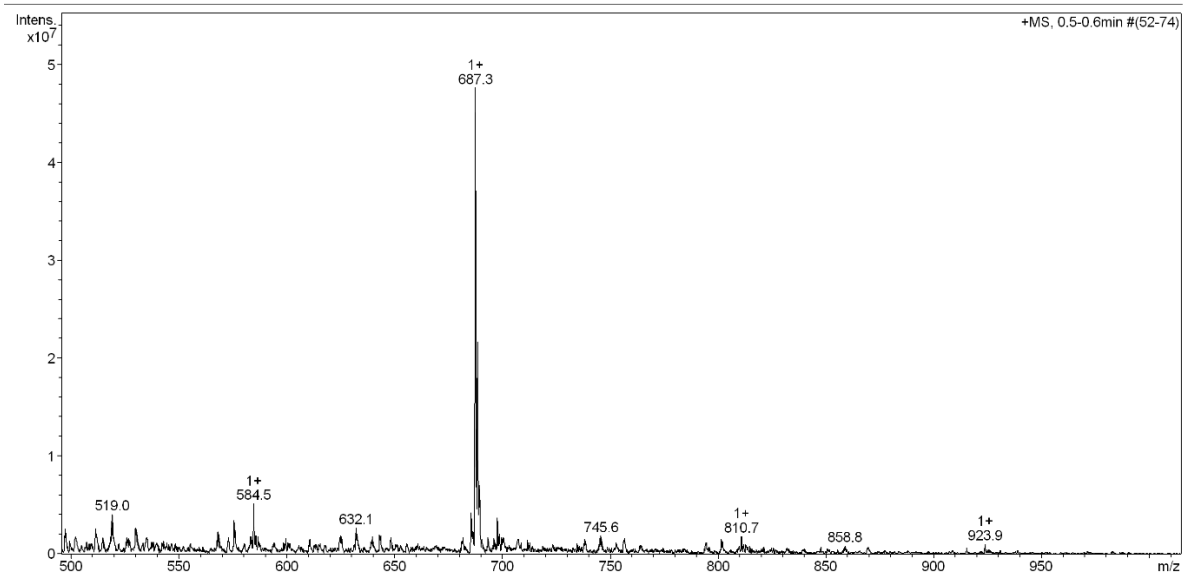


Figure S30. ESI-MS spectrum of **12** ($(CH_3)_2CO$).

[(Cyclopentadienyl)carbonyl(3,7-di(pyridine-2'-yl)-1,5-di(p-tolyl)-1,5-diaza-3,7-diphosphacyclooctane)iron(II)] tetrafluoroborate (13).

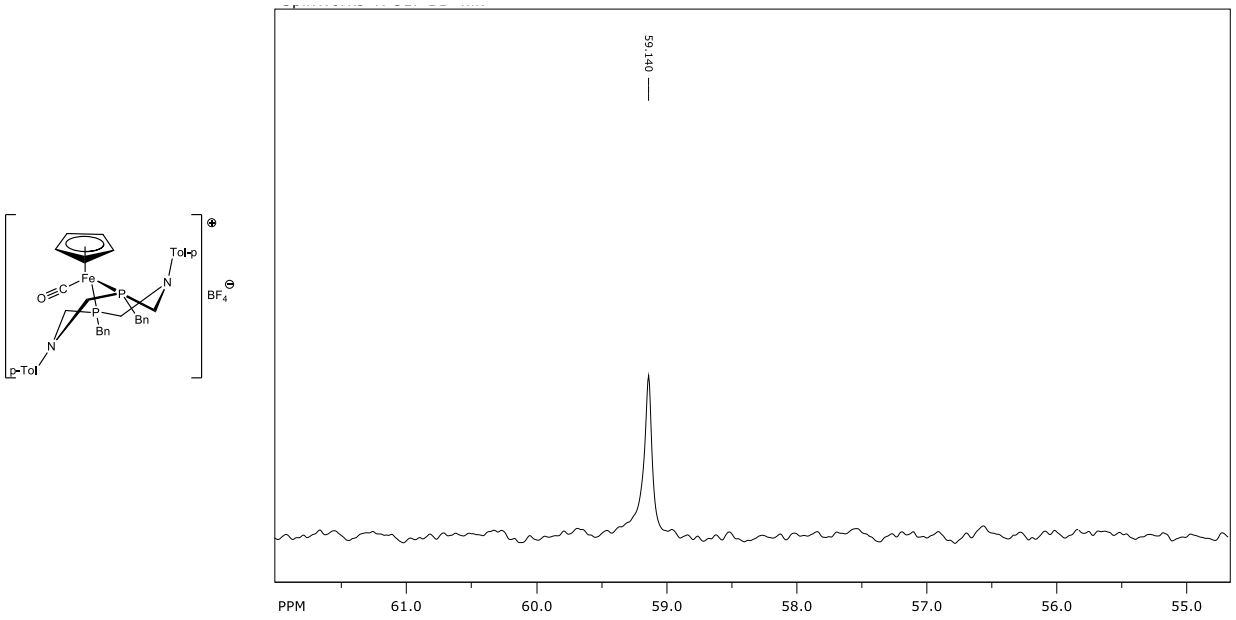


Figure S31. ^{31}P NMR spectrum of **13** ($(CD_3)_2CO$, 162 MHz).

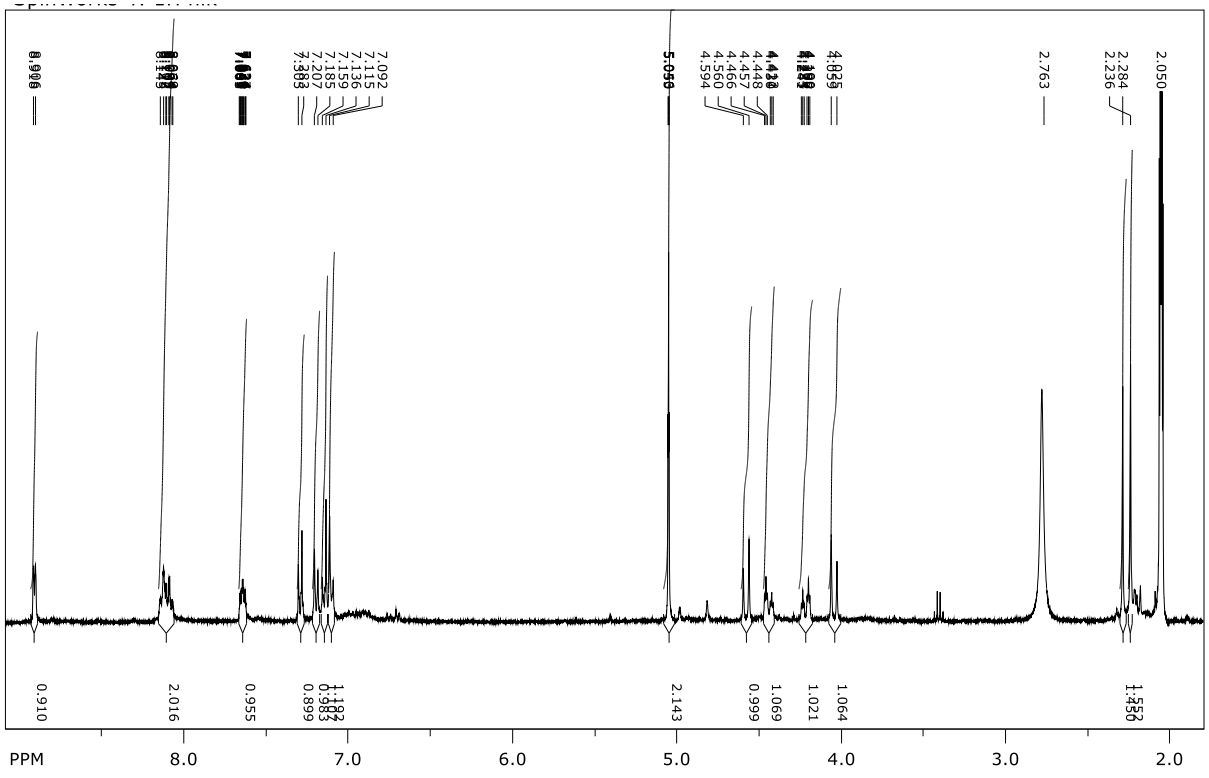


Figure S32. ^{1}H NMR spectrum of **13** ($(CD_3)_2CO$, 400 MHz) (2.76 s – H_2O in the solvent).

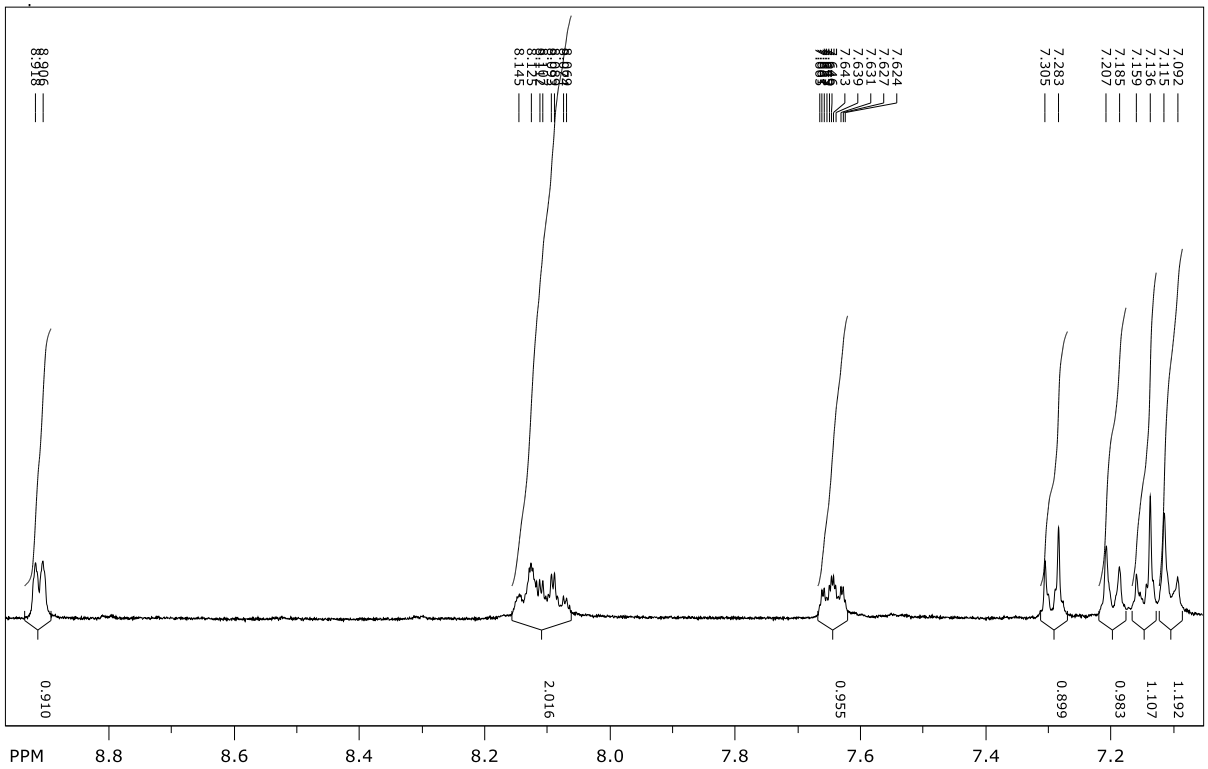


Figure S33. ^{1}H NMR spectrum of **13,** the region of aromatic protons ($(CD_3)_2CO$, 400 MHz)

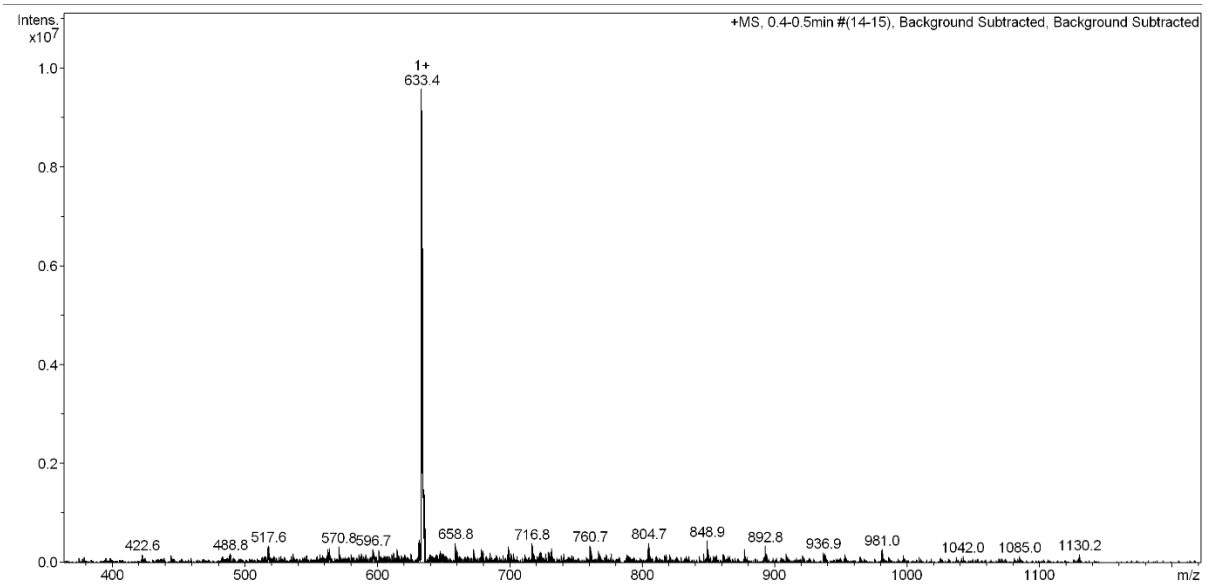


Figure S34. ESI-MS spectrum of **13** ($(CH_3)_2CO$).