Electronic Supplementary Material (ESI) for RSC Mechanochemistry.

Ball-milling for an efficient synthesis of pyridine-containing iron(II) photosensitizers

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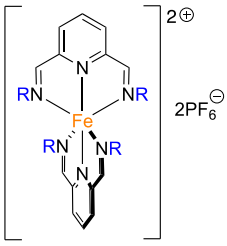
1 General information

Commercial reagents were used as received. Analyses were performed at the « Plateforme Technologique Laboratoire de Mesures Physiques » (IBMM, Université de Montpellier). ^{1}H NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer and are reported in ppm using deuterated solvent for calibration (acetone-d6 at 2.05 ppm). Data are reported as s = singlet, d = doublet, t = triplet, q = quadruplet, qt = quintuplet, sept = septuplet, m = multiplet; coupling constant in Hz; integration. ^{13}C NMR spectra were recorded on a Bruker Avance III HD 101 MHz spectrometer and are reported in ppm using deuterated solvent for calibration (acetone-d6 at 29.84 and 206.26 ppm). ^{19}F NMR spectra were recorded on a Bruker Avance III HD 376 MHz spectrometer and are reported in ppm. ^{31}P NMR spectra were recorded on a Bruker Avance III HD 162 MHz spectrometer and are reported in ppm.

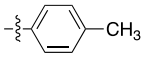
The milling treatments were carried out in Retsch® Mixer Mill 400 (MM400) at 25-30 Hz. Milling load is defined as the sum of the mass of the reactants per free volume in the jar and was fixed at 20 mg.mL^{-1}.

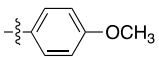
2 Description of procedures and compounds

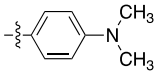
2.1 General procedure A: Synthesis of complexes **1a-d**

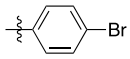


$FeCl_2{\cdot}4H_2O$ (1 equiv.), the corresponding amine (4 equiv.), KPF_6 (2 equiv.) and 2,6-pyridinedicarboxaldehyde (2 equiv.) were introduced in a 15 mL Teflon grinding jar with one stainless steel ball (10 mm diameter). The jar was closed, sealed with parafilm, placed in the vibratory ball-mill and subjected to grinding for 1 h at 30 Hz. The solid was dissolved in a minimum of acetone and then precipitated in ether. After washing with water and ether, the product was dried in vacuo.

Complex 1a: *p*-toluidine gave a dark blue solid (192 mg, 0.197 mmol, 86% yield). R =  ^{1}H NMR (acetone-d_6, 400 MHz) δ (ppm): 8.76 (s, 4 H), 8.59 (d, *J* = 8.0 Hz, 4 H), 8.51 (d, *J* = 8.0 Hz, 2 H), 7.01 (d, *J* = 7.6 Hz, 8 H), 6.52 (d, *J* = 7.9 Hz, 8 H), 2.22 (s, 12 H); ^{13}C NMR (acetone-d_6, 101 MHz) δ (ppm): 172.0, 160.9, 146.1, 140.6, 138.4, 131.0, 130.5, 121.9, 21.1; ^{19}F NMR (acetone-d_6, 376 MHz) δ (ppm): -73.43 (d, *J* = 706.9 Hz); ^{31}P NMR (acetone-d_6, 162 MHz) δ (ppm): -142.16 (hept, *J* = 707.9 Hz). Data in agreement with lit.[1]

Complex 1b: *p*-anisidine gave a dark blue solid (182 mg, 0.178 mmol, 82% yield). R =  ^{1}H NMR (acetone-d_6, 400 MHz) δ (ppm): 8.72 (s, 4 H), 8.60 - 8.58 (m, 4 H), 8.55 - 8.51 (m, 2 H), 6.71 (d, *J* = 8.8 Hz, 8 H), 6.57 (d, *J* = 8.8 Hz, 8 H), 3.74 (s, 12 H); ^{13}C NMR (acetone-d_6, 101 MHz) δ (ppm): 170.9, 161.7, 161.2, 141.9, 138.5, 130.3, 123.9, 115.7, 56.4; ^{19}F NMR (acetone-d_6, 376 MHz) δ (ppm): -73.43 (d, *J* = 706.9 Hz); ^{31}P NMR (acetone-d_6, 162 MHz) δ (ppm): -144.35 (hept, *J* = 706.3 Hz). Data in agreement with lit.[1]

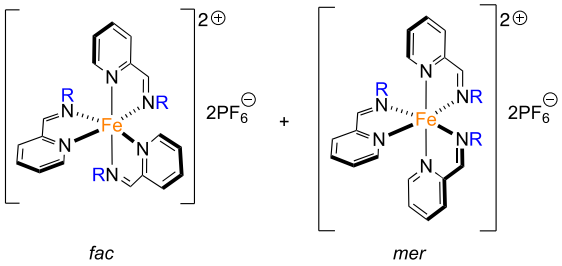
Complex 1c: 4-(dimethylamino)aniline gave a dark solid (195 mg, 0.184 mmol, 88% yield). R =  ^{1}H NMR (acetone-d_6, 400 MHz) δ (ppm): 8.56 (s, 4 H), 8.48 (s, 6 H), 6.42 (d, *J* = 8.9 Hz, 8 H), 6.36 (d, *J* = 8.9 Hz, 8 H), 2.91 (s, 16 H); ^{13}C NMR (acetone-d_6, 101 MHz) δ (ppm): 166.3, 161.3, 152.1, 138.1, 137.5, 128.6, 123.7, 112.5, 40.4; ^{19}F NMR (acetone-d_6, 376 MHz) δ (ppm): -73.46 (d, *J* = 706.9 Hz); ^{31}P NMR (acetone-d_6, 162 MHz) δ (ppm): -144.33 (hept, *J* = 707.9 Hz). Data in agreement with lit.[1]

Complex 1d: 4-bromoaniline gave a dark blue solid (171 mg, 0.139 mmol, 73% yield). R =  ^{1}H NMR (acetone-d_6, 400 MHz) δ (ppm): 8.88 (br. s., 4 H), 8.76 - 8.68 (m, 4 H), 8.61 (br. s., 2 H), 7.41 - 7.32 (m, 8 H), 6.68 - 6.59 (m, 8 H); ^{13}C NMR (acetone-d_6, 101 MHz) δ (ppm): 173.9,

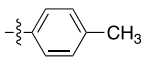
160.8, 147.3, 139.1, 133.8, 131.8, 124.2, 123.7; ^{19}F NMR (acetone-d_6, 376 MHz) δ (ppm): -73.34 (d, *J* = 706.9 Hz); ^{31}P NMR (acetone-d_6, 162 MHz) δ (ppm): -144.38 (hept, *J* = 709.6 Hz).

2.2 General procedure B: Synthesis of complexes **2a-c**

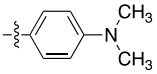
$FeCl_2{\cdot}4H_2O$ (1 eq), the corresponding amine (3 equiv.), KPF_6 (2 equiv.) and 2-pyridinecarboxaldehyde (3 equiv.) were introduced in a 15 mL Teflon grinding jar with one stainless steel ball (10 mm diameter). The jar was closed, sealed with parafilm, placed in the vibratory ball-mill and subjected to grinding for 1 h at 30 Hz. The solid was dissolved in a minimum of acetone and then precipitated in ether. After washing with water and ether, the product was dried in vacuo.



Complex 2a: *p*-toluidine gave a dark purple solid (164 mg, 0.175 mmol, 73% yield) in a 6:1 *mer*/*fac* ratio. ^{1}H NMR (acetone-d_6, 400 MHz) δ (ppm): *mer*: 9.64 (s, 1 H), 9.46 (s, 1 H), 9.14 (s, 1 H), 8.76 - 8.70 (m, 3 H), 8.39 (t, *J* = 7.8 Hz, 1 H), 8.23 - 8.17 (m, 3 H), 8.07 (t, *J* = 7.7 Hz 1 H), 7.83 (t, *J* = 6.4 Hz, 1 H), 7.74 - 7.66 (m, 3 H), 7.20 (d, *J* = 8.8 Hz, 2 H), 7.03 (d, *J* = 8.8 Hz, 2 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 6.83 (d, *J* = 8.7 Hz, 2 H), 6.76 (d, *J* = 8.7 Hz, 2 H), 6.23 (d, *J* = 8.8 Hz, 2 H), 2.27 (s, 3 H), 2.23 (s, 3 H), 2.12 (s, 3 H); *fac*: 9.14 (s, 3 H), 8.88 (d, *J* = 7.9 Hz, 6 H), 8.00 (d, *J* = 7.8 Hz, 6 H), 7.07 (d, *J* = 8.2 Hz, 6 H), 5.48 (d, *J* = 8.1 Hz, 6 H), 2.32 (s, 9 H); ^{13}C NMR (acetone-d_6, 101 MHz) δ (ppm): *mer*: 174.8, 172.9, 171.5, 159.1, 158.5, 158.4, 156.8, 156.5, 155.9, 149.4, 146.0, 145.0, 139.7, 139.2, 139.1, 138.9, 138.8, 138.6, 131.7, 130.7, 130.3, 130.1, 129.8, 129.5, 129.3, 129.1, 128.8, 122.3, 121,7, 20.0; *fac*: 174.3, 158.8, 155.7, 148.4, 139.2, 138.8, 131.1, 130.1, 129.7, 121.3, 19.9; ^{19}F NMR (acetone-d_6, 376 MHz) δ (ppm): -73.43 (d, *J* = 710.6 Hz); ^{31}P NMR (acetone-d_6, 162 MHz) δ (ppm): -144.37 (hept, *J* = 707.9 Hz). Data in agreement with lit.[2]

R = 

Complex 2b: *p*-anisidine gave a dark purple solid (197 mg, 0.200 mmol, 88% yield) in a 12:1 *mer*/*fac* ratio. ^{1}H NMR (acetone-d_6, 400 MHz) δ (ppm): *mer*: 9.67 (s, 1 H), 9.41 (s, 1 H), 9.16 (s, 1 H), 8.85 (d, *J* = 7.7 Hz, 1 H), 8.77 - 8.74 (m, 2 H) 8.39 (t, *J* = 7.8 Hz, 1 H), 8.22 - 8.17 (m, 3 H), 8.07 (t, *J* = 7.8 Hz 1 H), 8.02 (d, *J* = 6.6 Hz, 1 H), 7.82 (t, *J* = 6.7 Hz, 1 H), 7.75 - 7.67 (m, 2 H), 6.93 – 6.88 (m, 6 H), 6.74 (d, *J* = 8.6 Hz, 2 H), 6.57 (d, *J* = 8.8 Hz, 2 H), 6.37 (d, *J* = 8.7 Hz, 2 H), 3.75 (s, 6 H), 3.66 (s, 3 H); *fac*: 9.24 (s, 3 H), 8.70 (d, *J* = 7.9 Hz, 6 H), 8.48 (t, *J* = 7.8 Hz, 6 H), 6.83 (d, *J* = 8.1 Hz, 6 H), 5.75 (d, *J* = 8.1 Hz, 6 H), 3.80 (s, 9 H); ^{13}C NMR (acetone-d_6, 101 MHz) δ (ppm): *mer*: 174.1, 171.8, 170.3, 160.2, 159.9, 159.3, 158.8, 158.5, 157.0, 156.4, 155.9, 145.1, 141.4, 140.4, 139.1, 138.8, 138.7, 131.7, 130.6, 130.0, 129.3, 129.0, 128.8, 124.0, 123.4, 115.0, 114.6, 114.2, 55.3, 55.2; *fac*: 173.7, 160.0, 158.7, 155.9, 139.7, 139.2, 131.3, 130.3, 123.1, 114.5, 55.4; ^{19}F NMR (acetone-d_6, 376 MHz) δ (ppm): -73.41 (d, *J* = 706.9 Hz); ^{31}P NMR (acetone-d_6, 162 MHz) δ (ppm): -144.35 (hept, *J* = 707.9 Hz). Data in agreement with lit.[3]

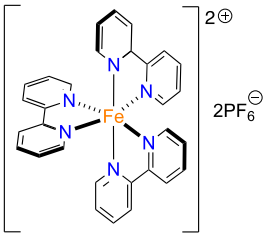
R = 

Complex 2c: 4-(dimethylamino)aniline gave a dark purple solid (220 mg, 0.215 mmol, 96% yield) and only the *mer* isomer. ^{1}H NMR (acetone-d_6, 400 MHz) δ (ppm): 9.65 (s, 1 H), 9.26 (s, 1 H), 9.10 (s, 1 H), 8.78 - 8.70 (m, 3 H), 8.34 (t, *J* = 7.4 Hz, 1 H), 8.19 - 8.10 (m, 2 H), 8.09 - 8.05 (m, 1 H), 8.04 - 7.98 (m, 2 H), 7.76 (t, *J* = 6.4 Hz, 1 H), 7.71 - 7.62 (m, 2 H), 6.88 (d, *J* = 8.9 Hz, 2 H), 6.72 (d, *J* = 8.8 Hz, 2 H), 6.62 (d, *J* = 8.8 Hz, 2 H), 6.47 (d, *J* = 8.7 Hz, 2 H), 6.34 - 6.27 (m, 4 H), 2.93 (s, 6 H), 2.91 (s, 6 H), 2.84 (s, 6 H); ^{13}C NMR (acetone-d_6, 101 MHz) δ (ppm): 170.9, 168.3, 167.1, 160.7, 160.2, 159.9, 157.7, 156.5, 156.2, 151.9, 151.7, 151.4, 142.6, 139.5, 139.1, 139.0, 138.5, 137.3, 131.7, 130.3, 129.9, 129.4, 128.8, 128.7, 124.6, 124.3, 112.8, 112.6, 112.1, 40.2, 40.1; ^{19}F NMR (acetone-d_6, 376 MHz) δ (ppm): -73.52 (d, *J* = 706.9 Hz); ^{31}P NMR (acetone-d_6, 162 MHz) δ (ppm): -144.36 (hept, *J* = 707.9 Hz). Data in agreement with lit.[1]

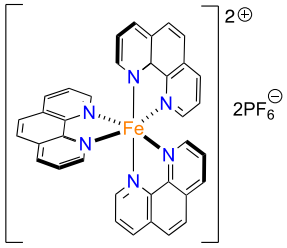
2.3 General procedure C: Synthesis of complexes **3a-c**

$FeSO_4 \cdot 7H_2O$ (1 equiv.), the corresponding bipyridine (3 equiv.) and KPF_6 (2 equiv.) were introduced in a 15 mL Teflon grinding jar with one stainless steel ball (10 mm diameter). The jar was closed, sealed with parafilm, placed in the vibratory ball-mill and subjected to grinding for a specific time at 30 Hz. The solid was dissolved in a minimum of acetone and then precipitated in ether. After washing with water and ether, the product was dried in vacuo.

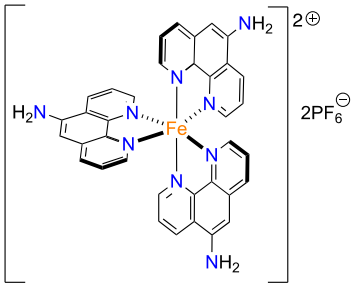
Complex 3a: With 2,2-bipyridine, grinding was carried out for 10 minutes and gave a red solid (176 mg, 0.216 mmol, 83% yield). ^{1}H NMR (acetone-d_6, 400 MHz) δ (ppm): 8.84 (d, *J* = 8.1 Hz, 6 H), 8.27 (t, *J* = 8.0 Hz, 6 H), 7.73 (d, *J* = 8.0 Hz, 6 H), 7.58 (t, *J* = 8.0 Hz, 6 H); ^{13}C NMR (acetone-d_6, 101 MHz) δ (ppm): 160.5, 155.3, 140.0, 128.8, 125.1; ^{19}F NMR (acetone-d_6, 376 MHz) δ (ppm): -73.48 (d, *J* = 706.9 Hz); ^{31}P NMR (acetone-d_6, 162 MHz) δ (ppm): -144.38 (hept, *J* = 707.9 Hz). Data in agreement with lit.[1]



Complex 3b: With 1,10-phenanthroline, grinding was carried out for 15 minutes and gave a red solid (194 mg, 0.219 mmol, 90% yield). ^{1}H NMR (acetone-d_6, 400 MHz) δ (ppm): 8.82 (d, *J* = 8.2 Hz, 6 H), 8.43 (s, 6 H), 8.04 (d, *J* = 5.1 Hz, 6 H), 7.79 (dd, *J* = 5.2, 8.3 Hz, 6 H); ^{13}C NMR (acetone-d_6, 101 MHz) δ (ppm): 157.3, 150.9, 138.5, 131.6, 129.2, 127.2; ^{19}F NMR (acetone-d_6, 376 MHz) δ (ppm): -73.46 (d, *J* = 706.9 Hz); ^{31}P NMR (acetone-d_6, 162 MHz) δ (ppm): -144.38 (hept, *J* = 707.9 Hz). Data in agreement with lit.[1]



Complex 3c: With 1,10-phenanthrolin-5-amine, grinding was carried out for 30 minutes and gave a red solid (218 mg, 0.234 mmol, quantitative yield). ^{1}H NMR (acetone-d_6, 400 MHz) δ (ppm): 8.93 (dd, *J* = 3.4, 8.0 Hz, 3 H), 8.35 - 8.31 (m, 3 H), 8.01 - 7.92 (m, 3 H), 7.78 - 7.71 (m, 3 H), 7.56 - 7.49 (m, 6 H), 7.29 (s, 3 H), 6.39 (s, 6 H); ^{13}C NMR (acetone-d_6, 101 MHz) δ (ppm): 156.5, 151.4, 145.9, 145.1, 134.8, 133.5, 132.9, 126.7, 125.6, 124.3, 103.8; ^{19}F NMR (acetone-d_6, 376 MHz) δ (ppm): -73.50 (d, *J* = 706.9 Hz); ^{31}P NMR (acetone-d_6, 162 MHz) δ (ppm): -144.37 (hept, *J* = 707.9 Hz). Data in agreement with lit.[4]



2.4 Powder X-Ray Diffraction (PXRD)

X-ray powder patterns were recorded in the Bragg-Brentano q-q reflection geometry, on a Bruker D8 Discover diffractometer equipped with primary monochromator ($CuK_{\alpha 1}$, λ = 1.54056 Å) and LYNXEYE_XE_T detector.
Measurements were performed at room temperature in the 5-45° 2θ range, using a step size of 0.033° and a counting time per step of 2.5 s.

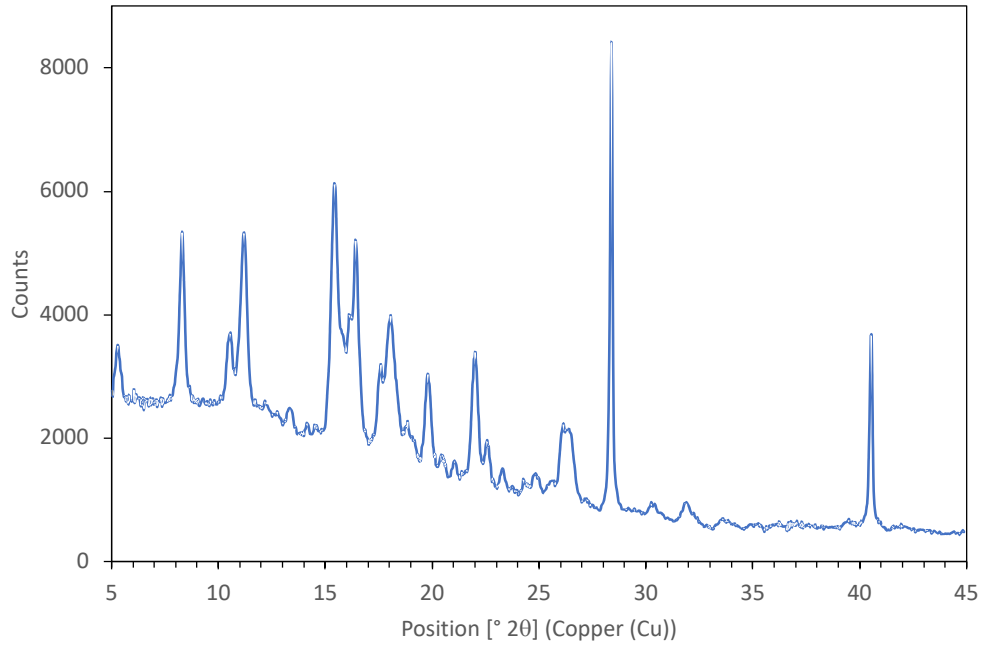


Figure S1 - PXRD pattern of complex **1a** (sample directly taken from the milling jar)

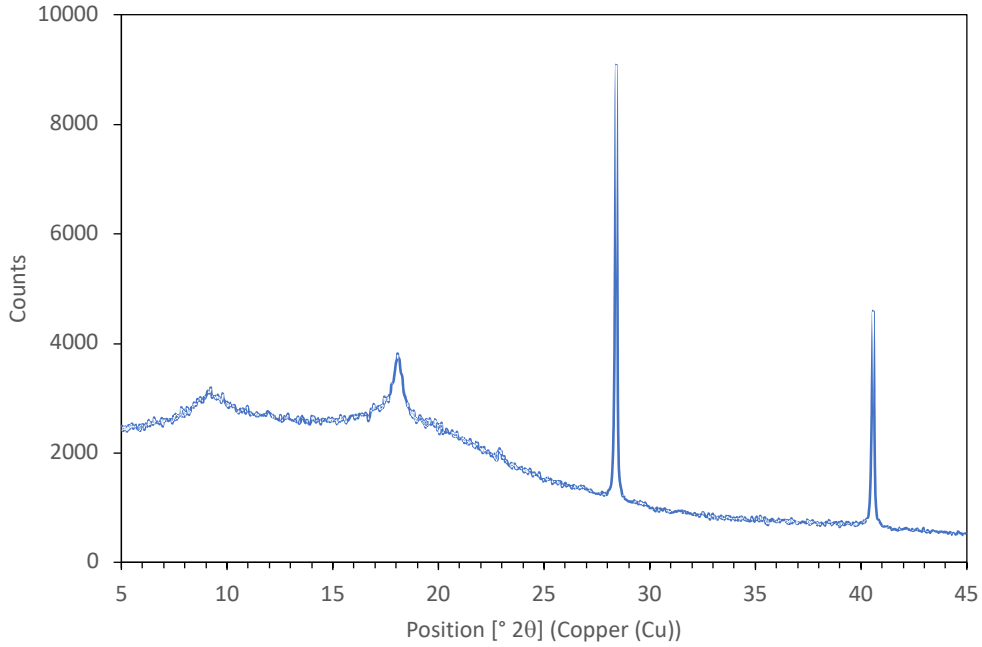


Figure S2 - PXRD pattern of complex **2a** (sample directly taken from the milling jar)

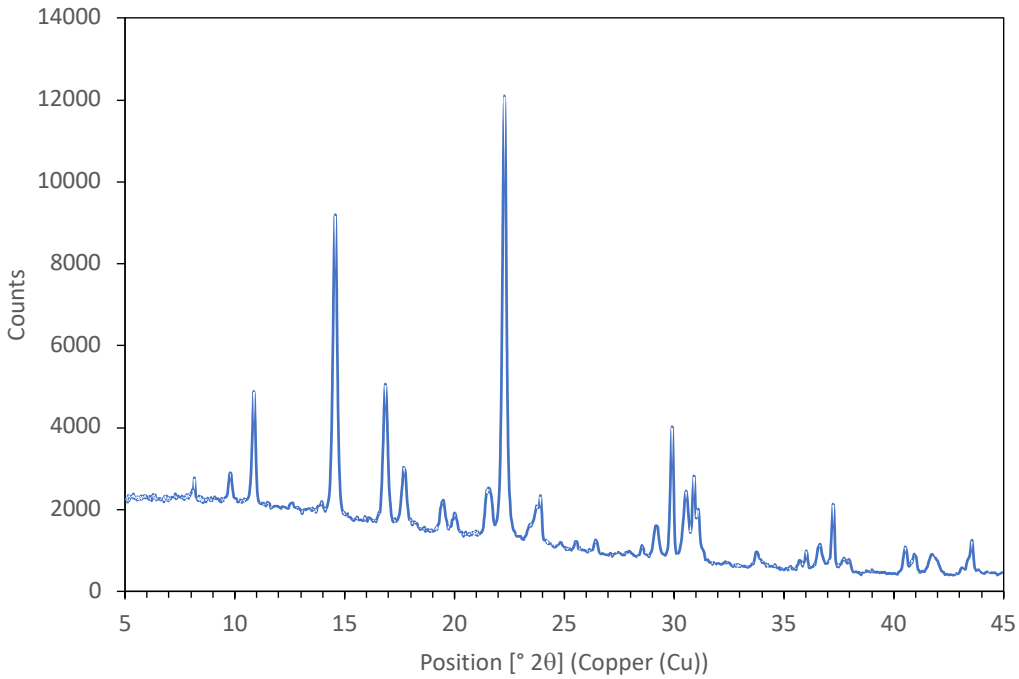


Figure S3 - PXRD pattern of complex **3a** (sample directly taken from the milling jar)

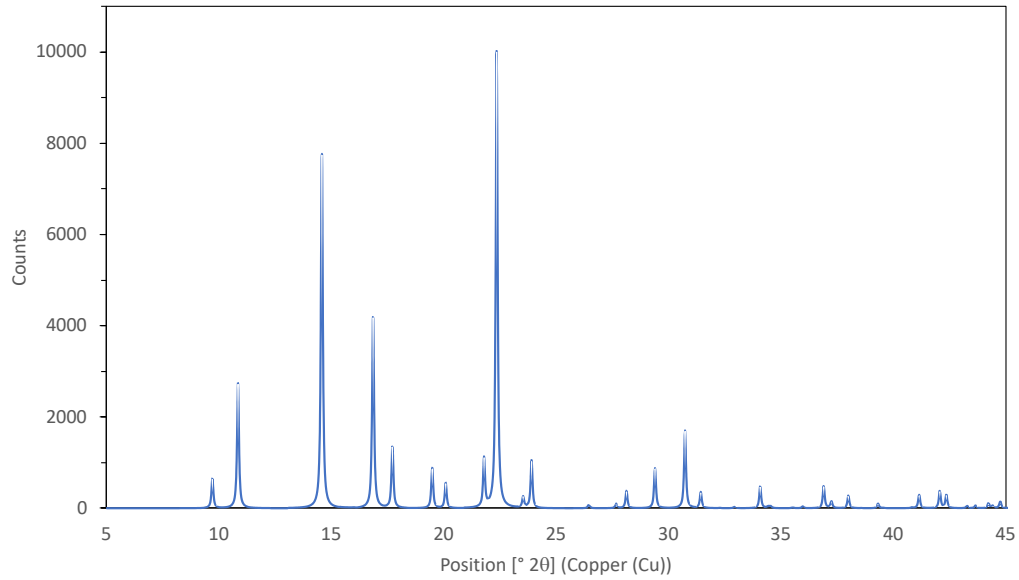


Figure S4 – Simulated PXRD pattern of complex **3a**

2.5 Raman spectroscopy

Raman measurements were conducted on a iRaman® analyser (Opton Laser International), equipped with a TE Cooled Linear Array detector (2048 pixels) and a non-contact Fiber-optic Raman probe (working distance: 5.4 mm). The excitation wavelength was 785 nm.
Ex situ measurements (pure samples, Fig. 1a in the manuscript) consisted in one spectrum with a radiation time of 500 ms.
In situ measurements (using a PMMA milling jar, Fig. 1b in the manuscript, Fig. S5) were performed every 30 s, consisting of one spectrum with a radiation time of 500 ms.

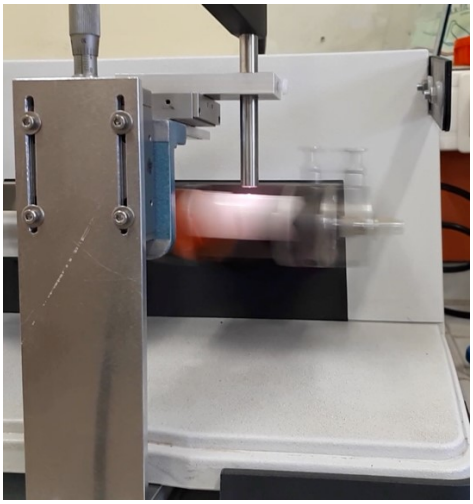
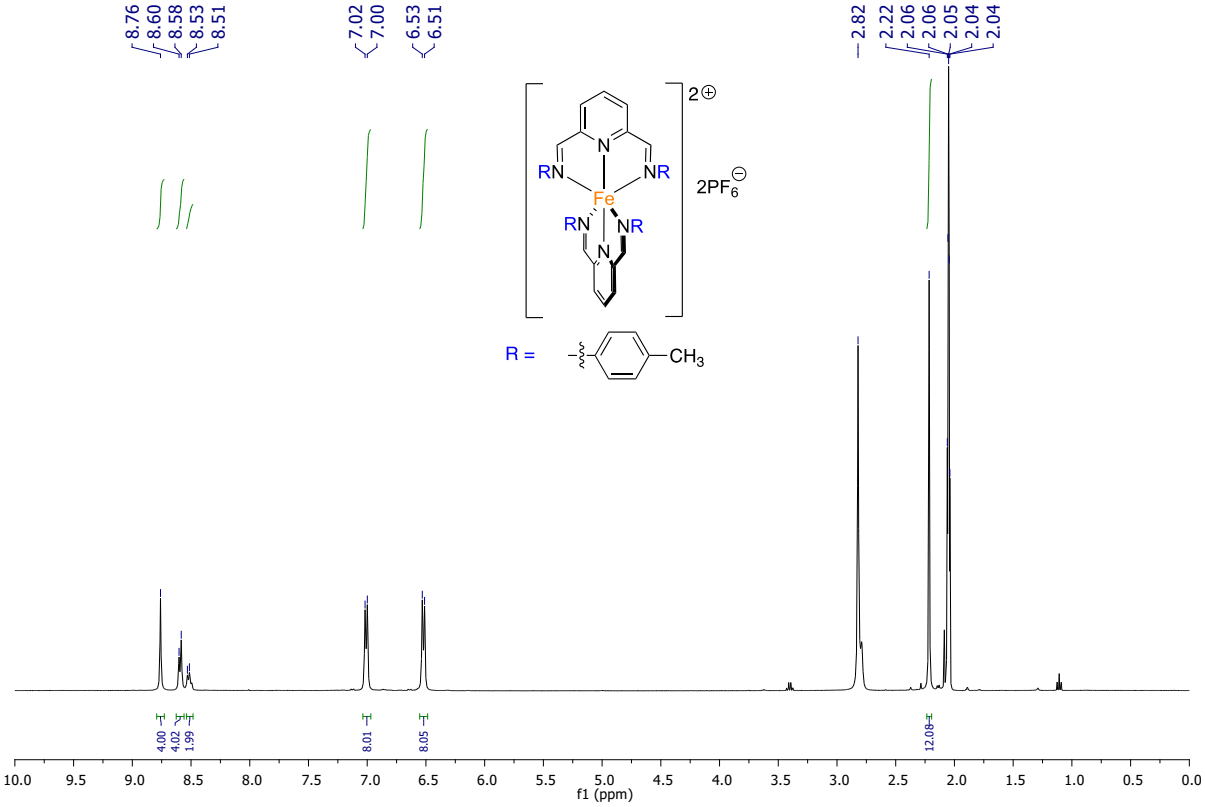


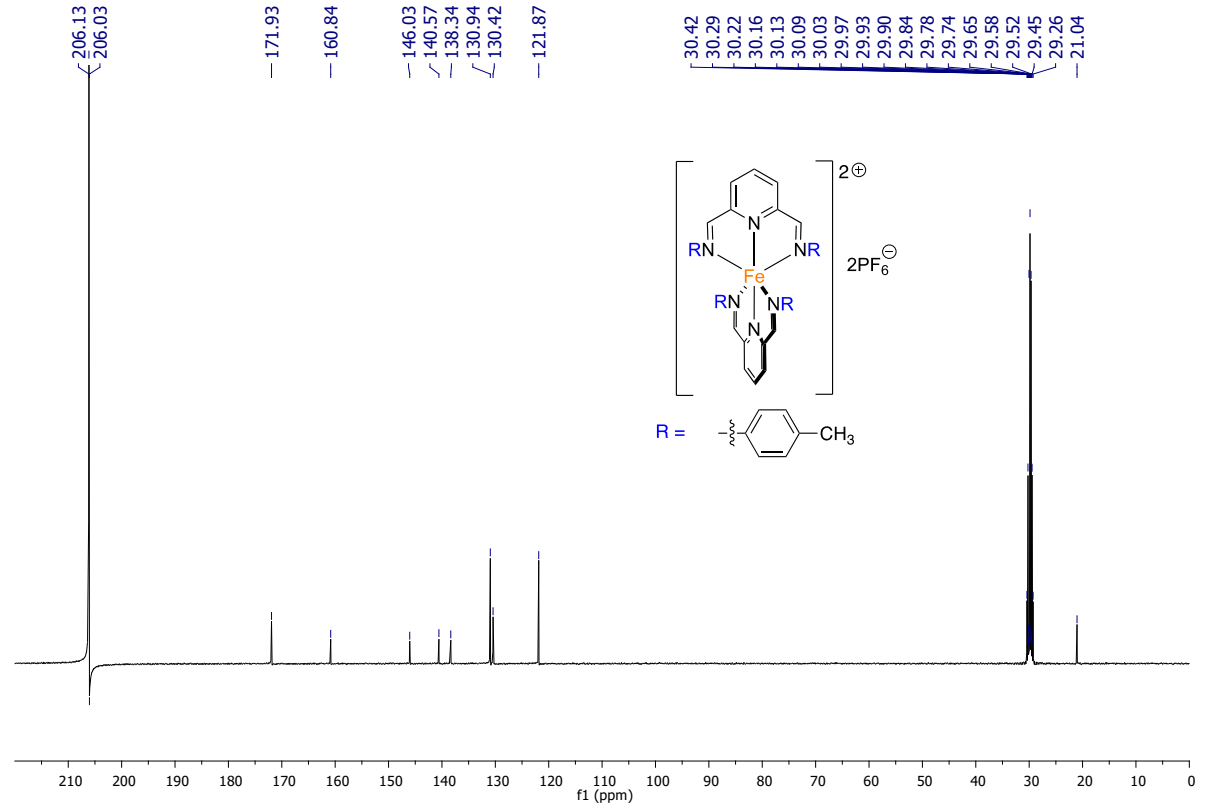
Figure S5. Set-up for in situ raman monitoring (PMMA milling jar with Raman probe – Retsch MM400)

3 NMR Spectra

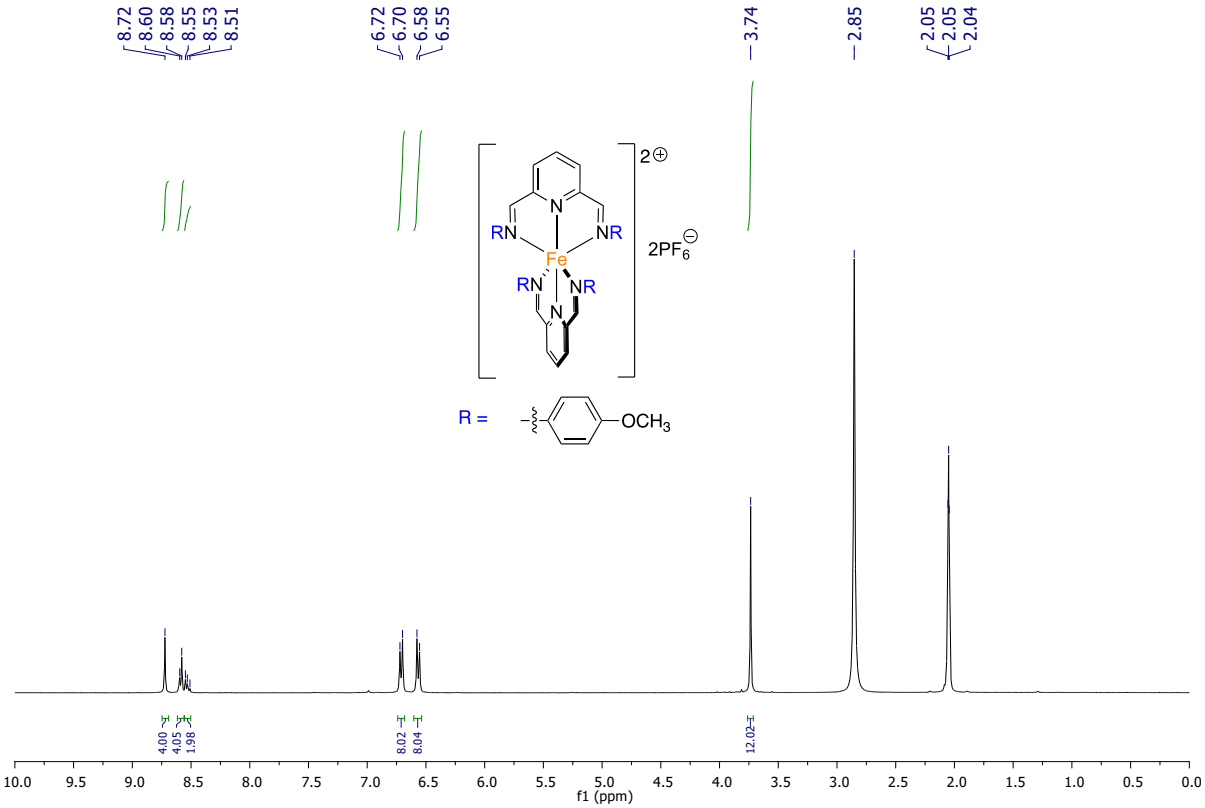
^{1}H NMR for complex **1a** (acetone-d_6, 400 MHz)



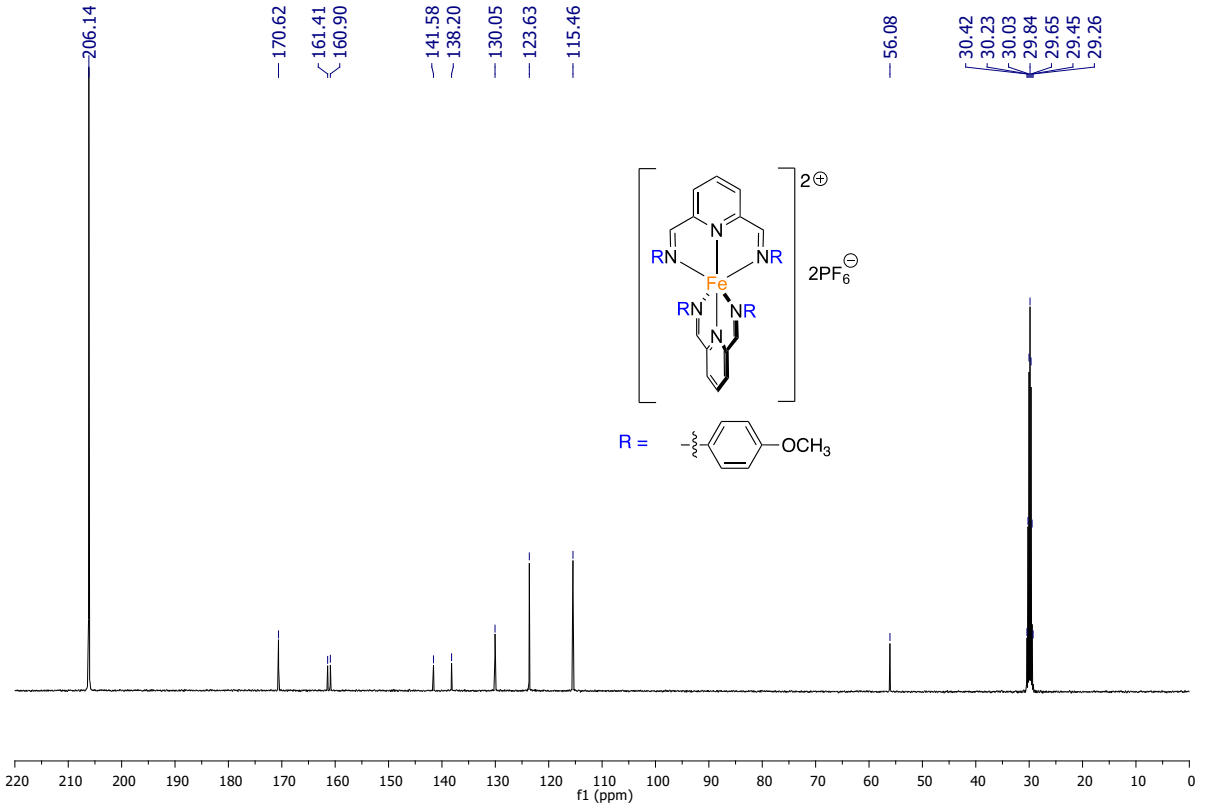
^{13}C NMR for complex **1a** (acetone-d_6, 101 MHz)



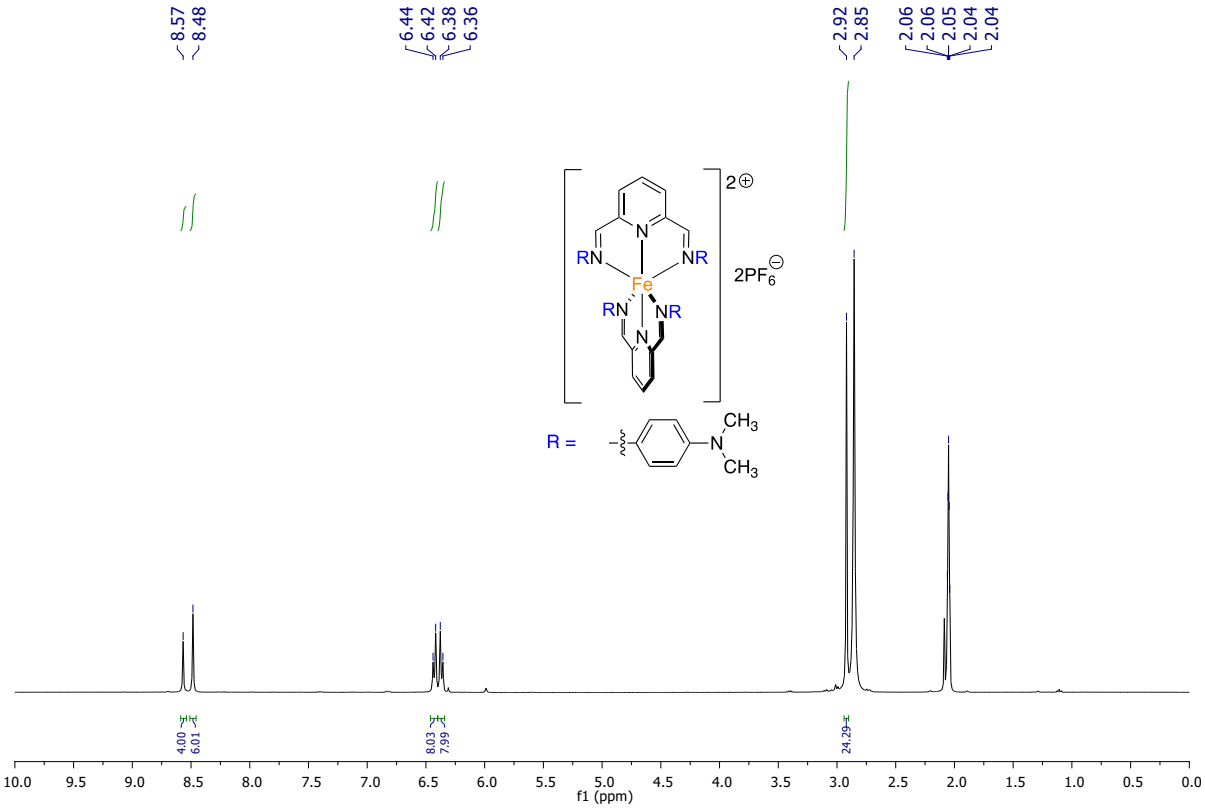
^{1}H NMR for complex **1b** (acetone-d_6, 400 MHz)



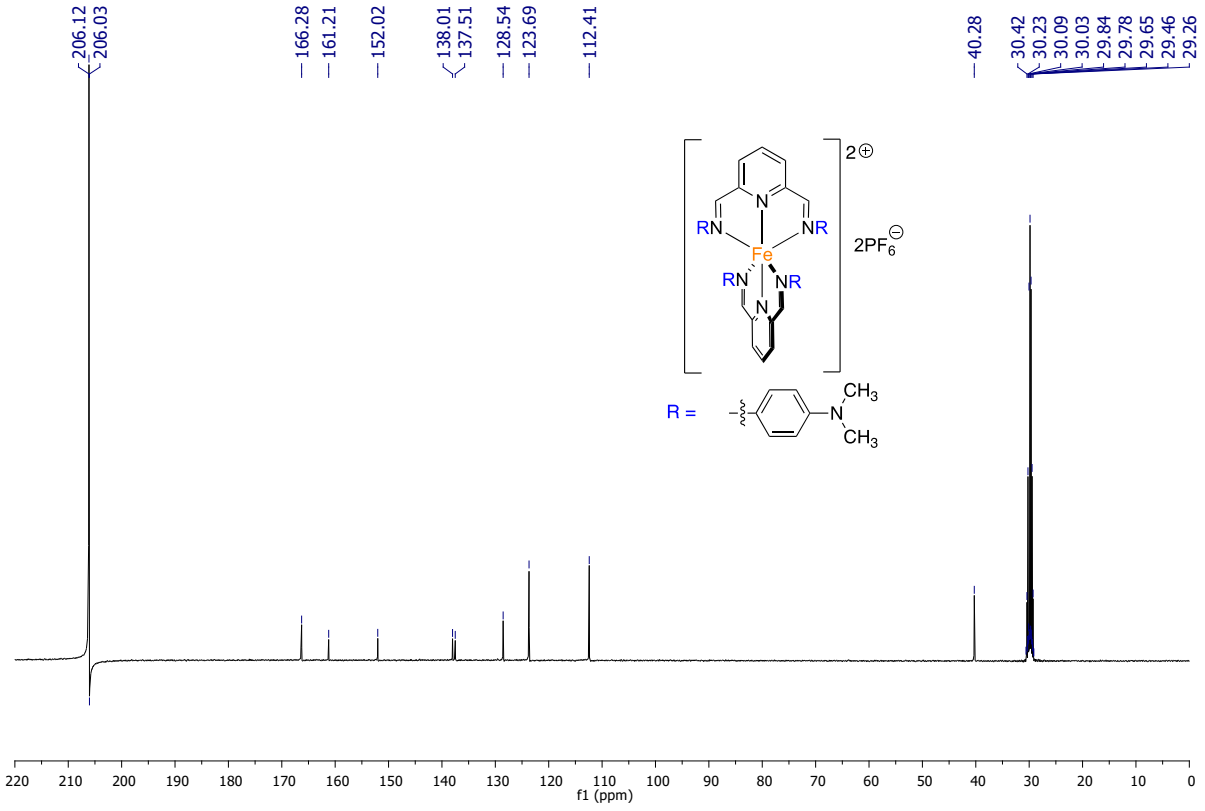
^{13}C NMR for complex **1b** (acetone-d_6, 101 MHz)



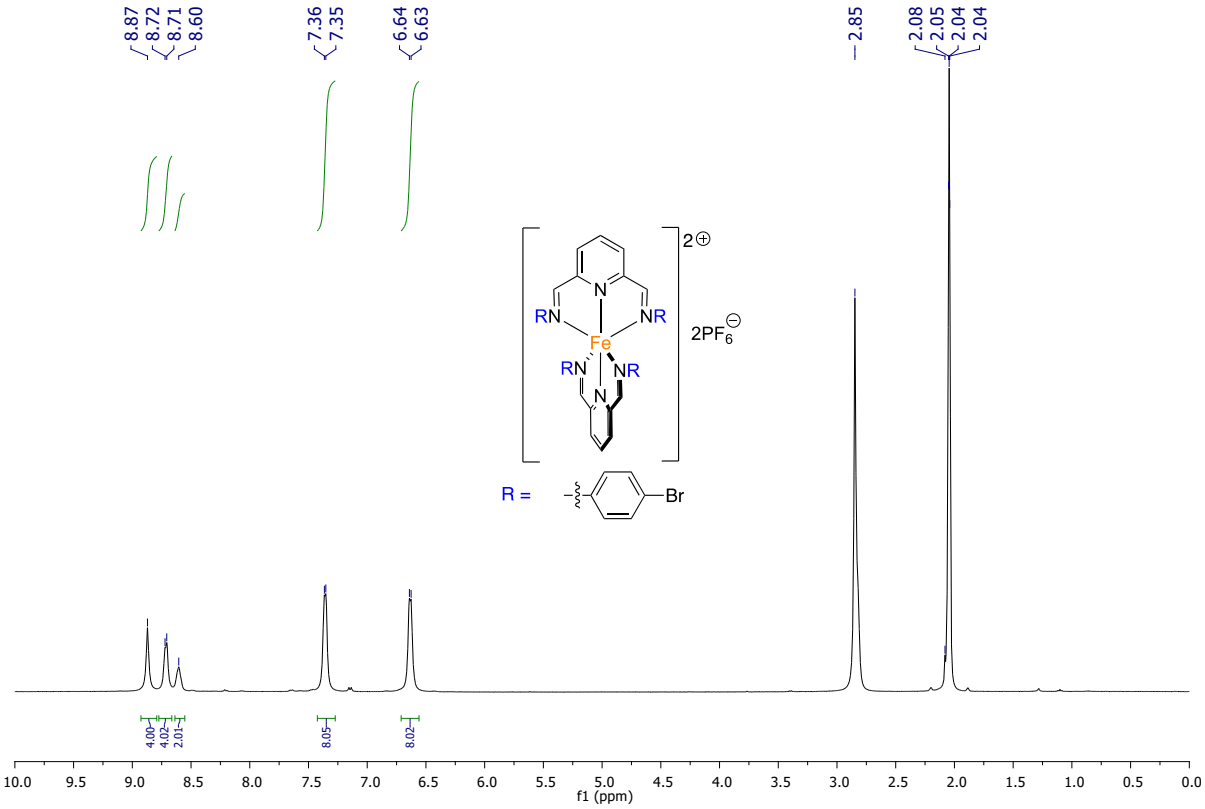
^{1}H NMR for complex **1c** (acetone-d_6, 400 MHz)



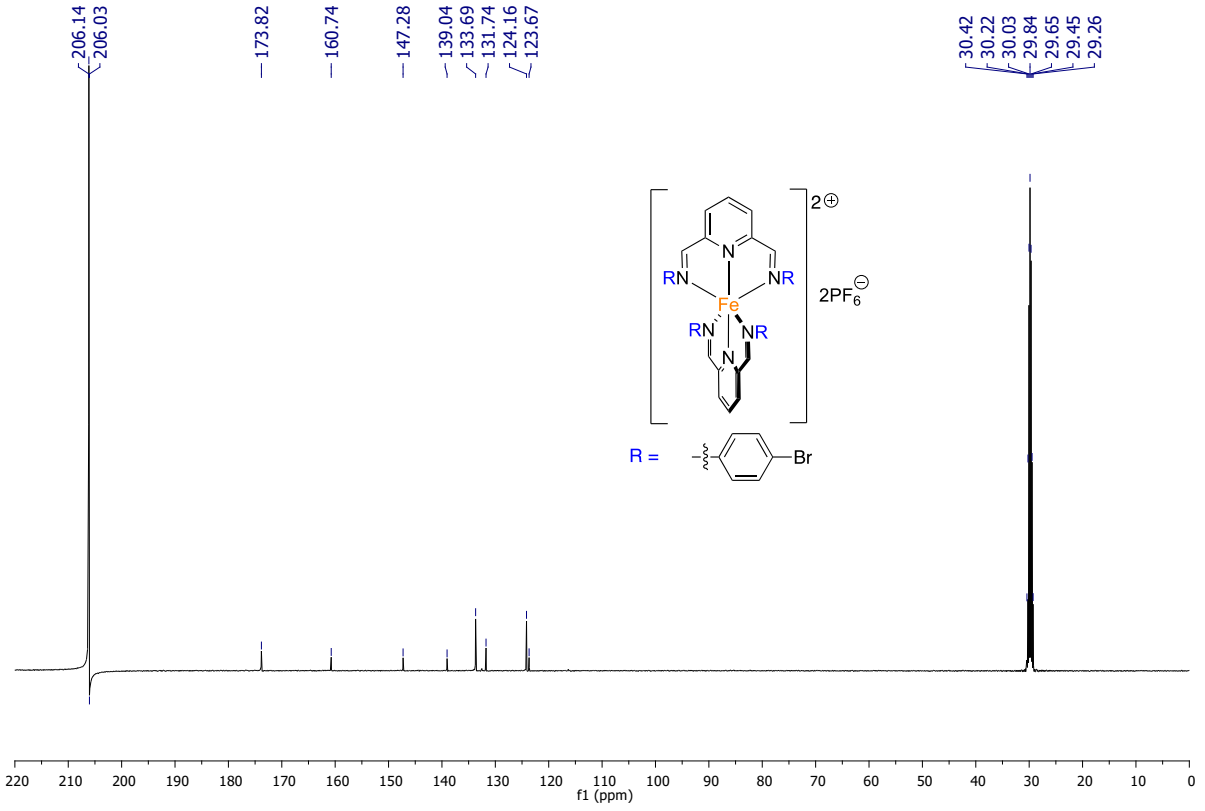
^{13}C NMR for complex **1c** (acetone-d_6, 101 MHz)



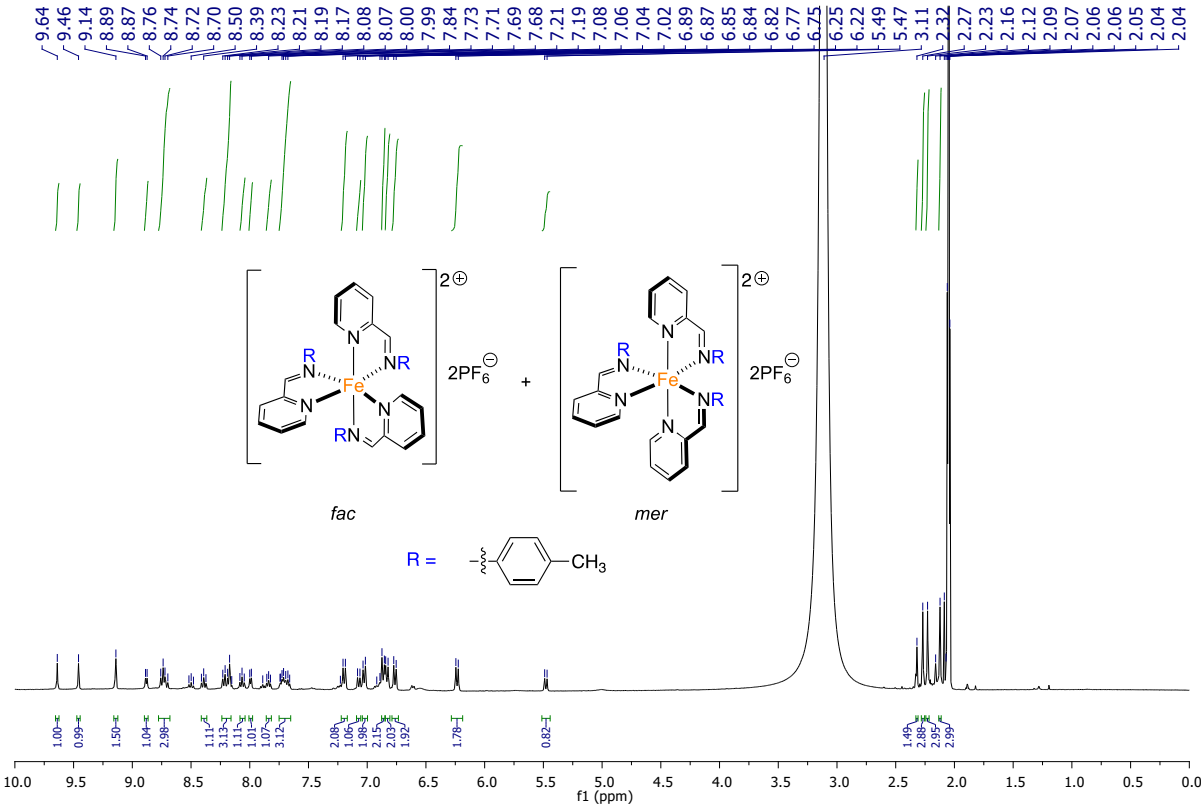
^{1}H NMR for complex **1d** (acetone-d_6, 400 MHz)



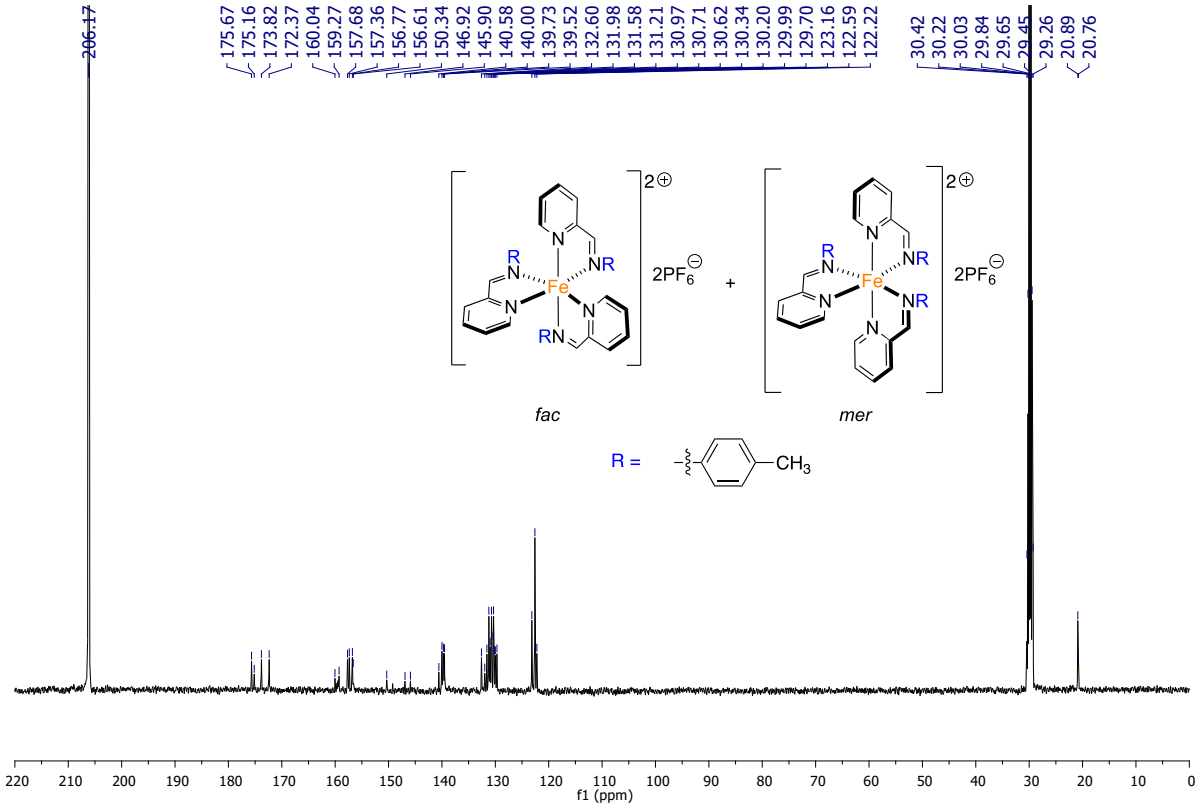
^{13}C NMR for complex **1d** (acetone-d_6, 101 MHz)



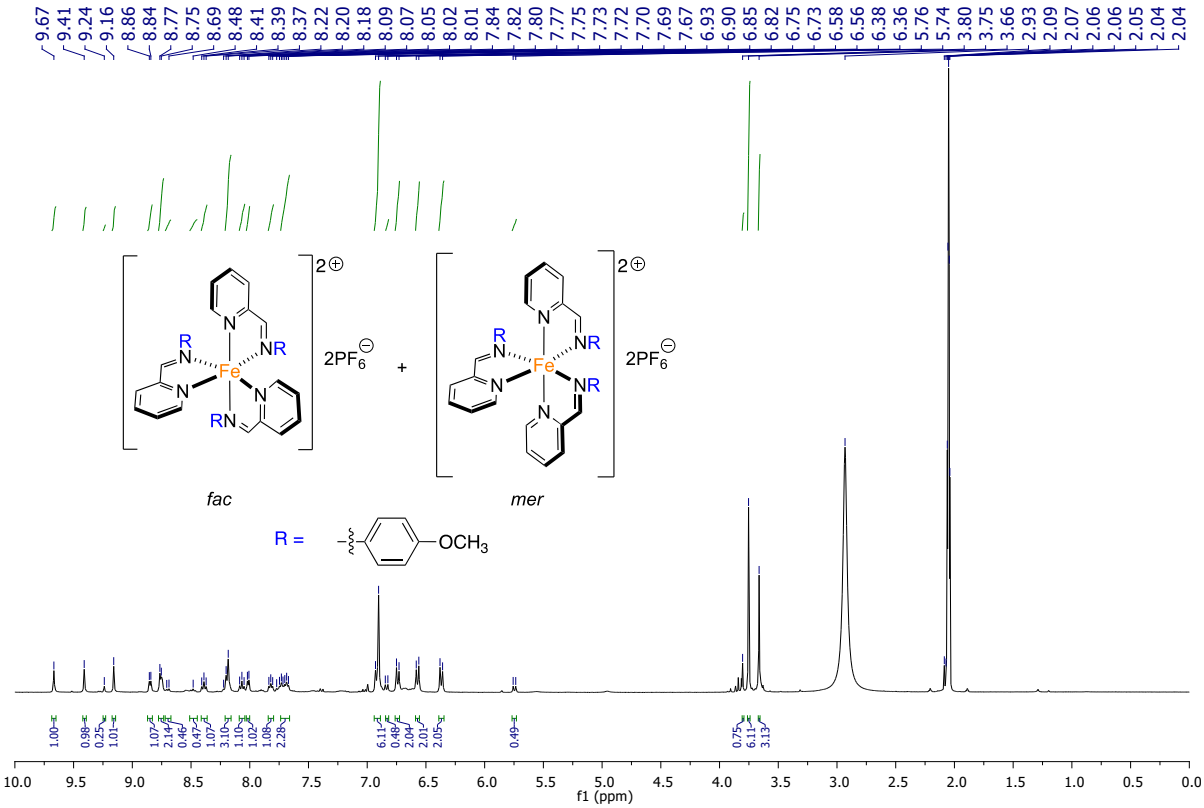
^{1}H NMR for complex **2a** (acetone-d_6, 400 MHz)



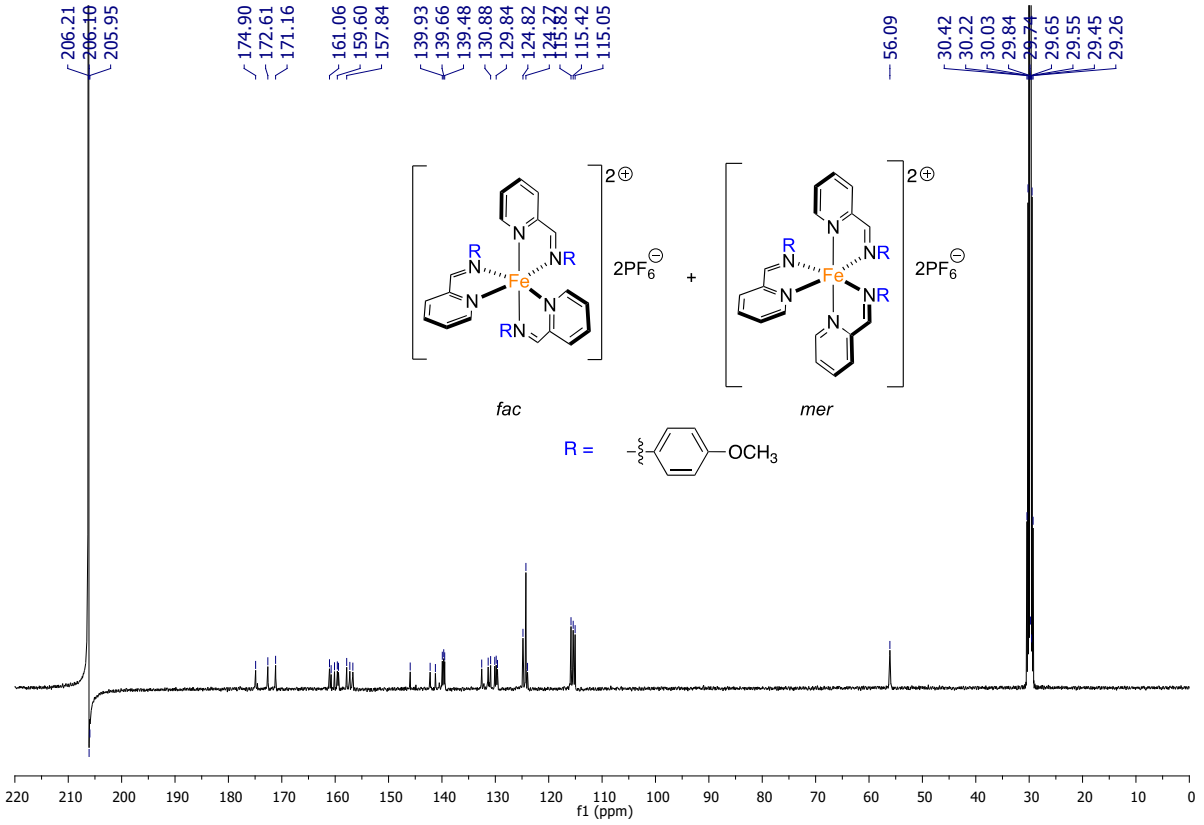
^{13}C NMR for complex **2a** (acetone-d_6, 101 MHz)



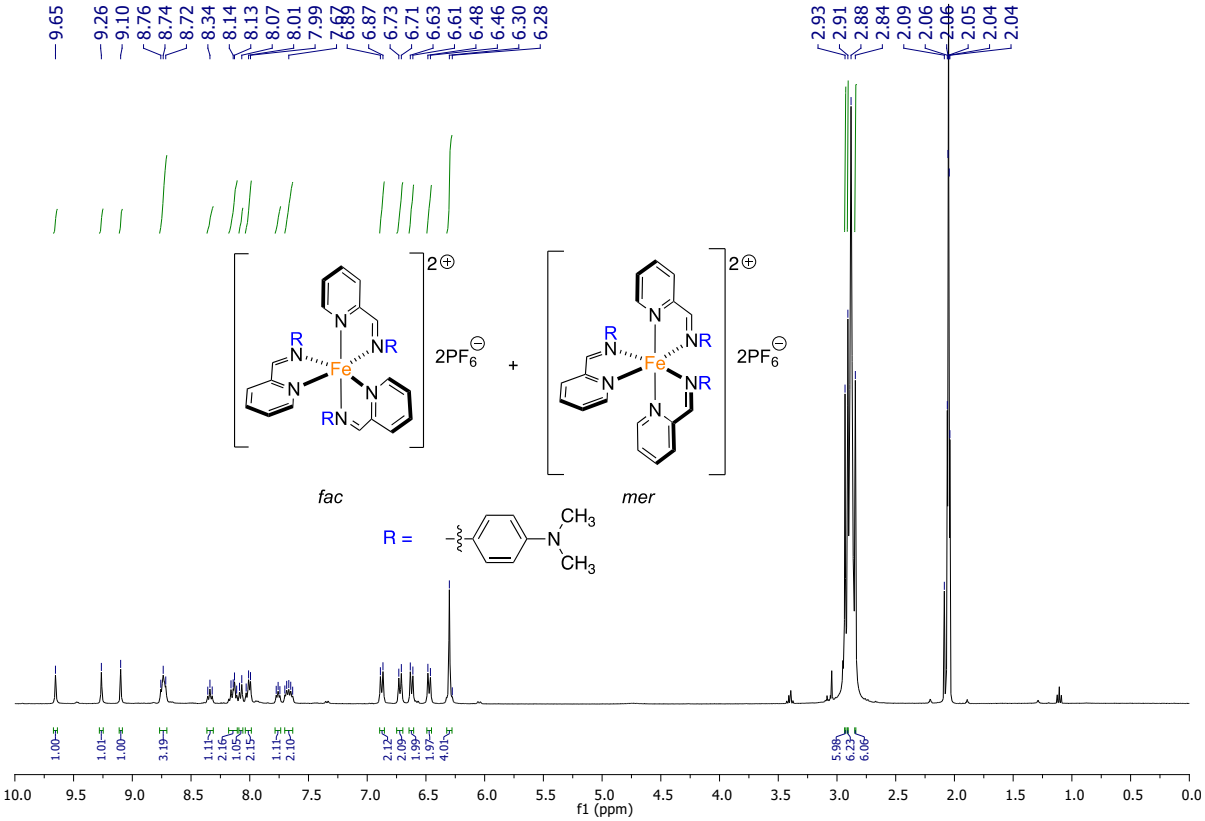
^{1}H NMR for complex **2b** (acetone-d_6, 400 MHz)



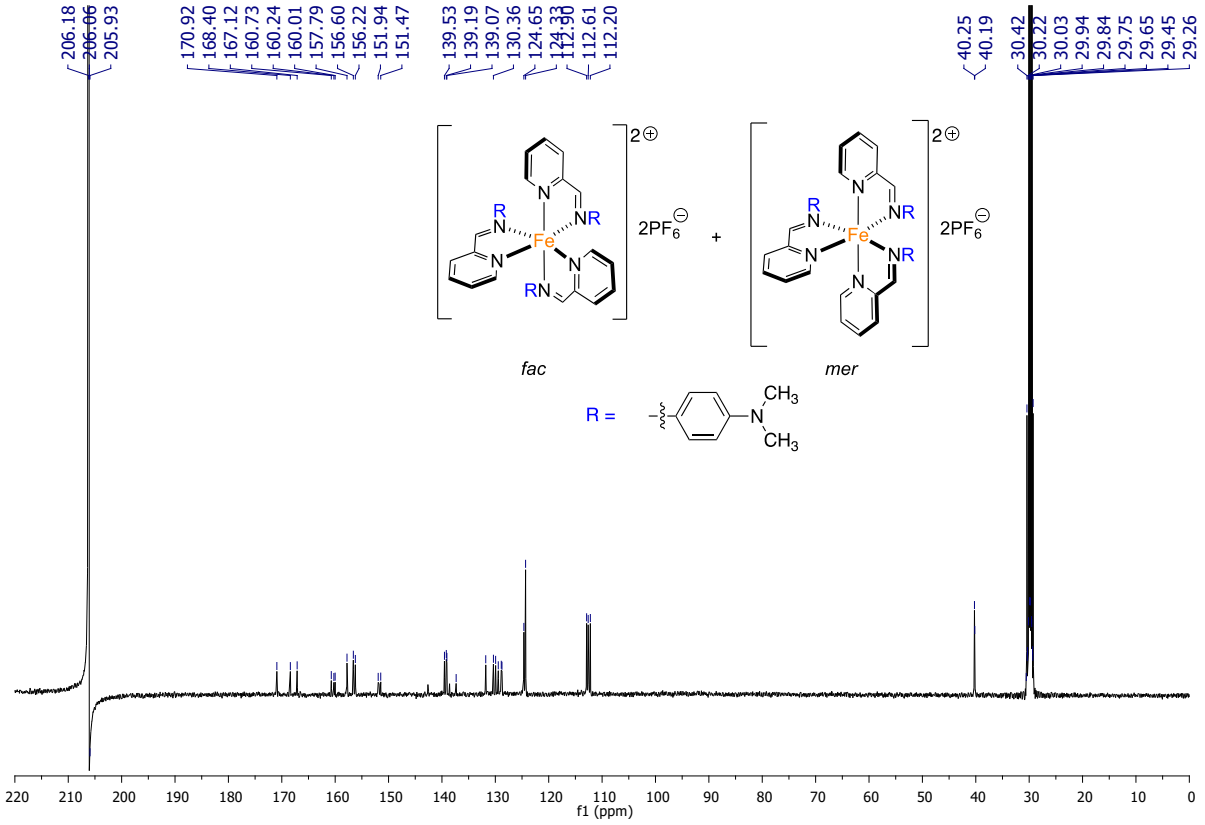
^{13}C NMR for complex **2b** (acetone-d_6, 101 MHz)



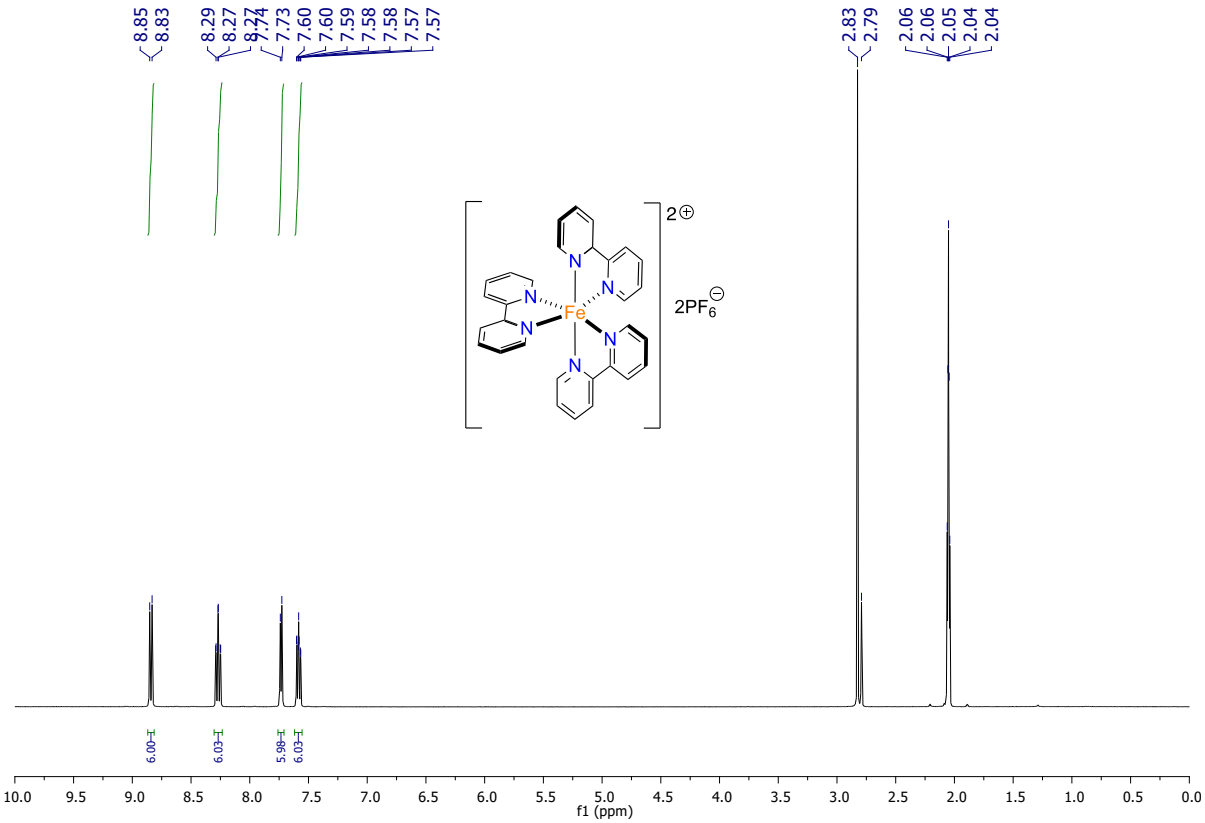
^{1}H NMR for complex **2c** (acetone-d_6, 400 MHz)



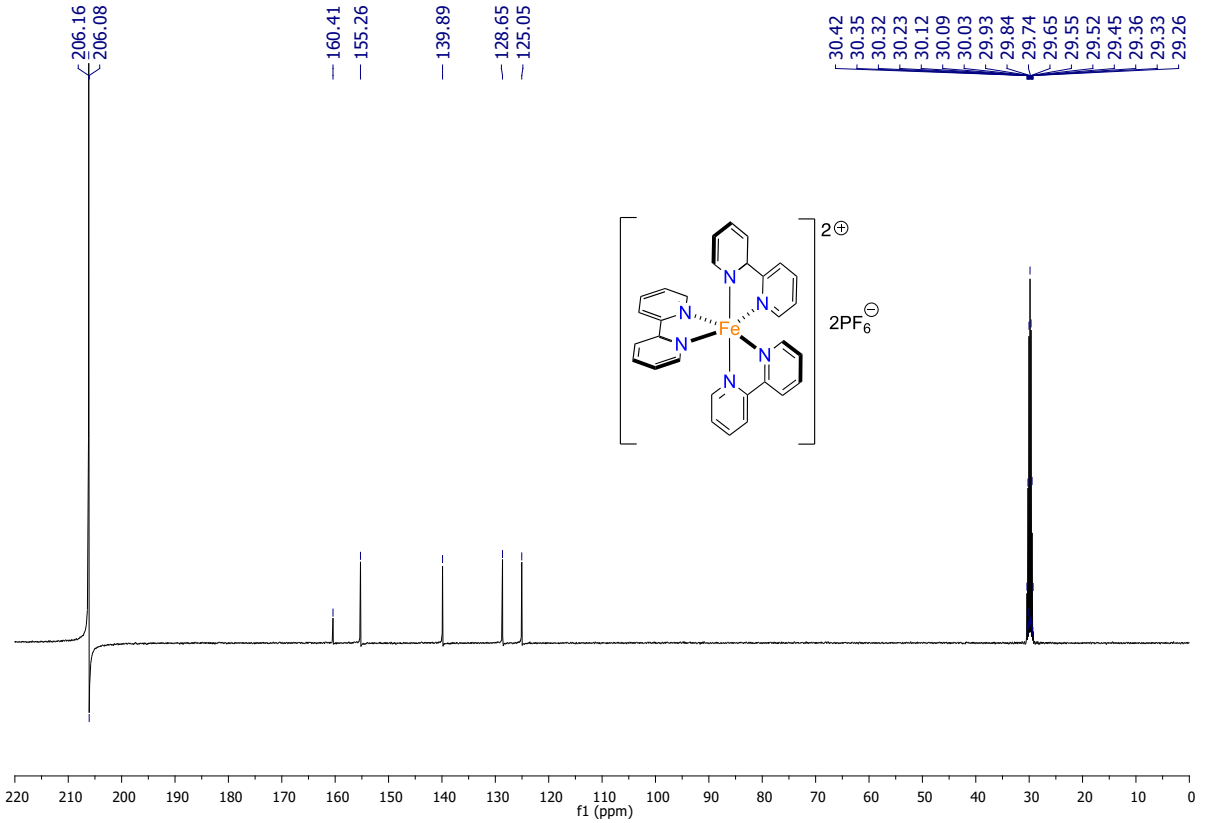
^{13}C NMR for complex **2c** (acetone-d_6, 101 MHz)



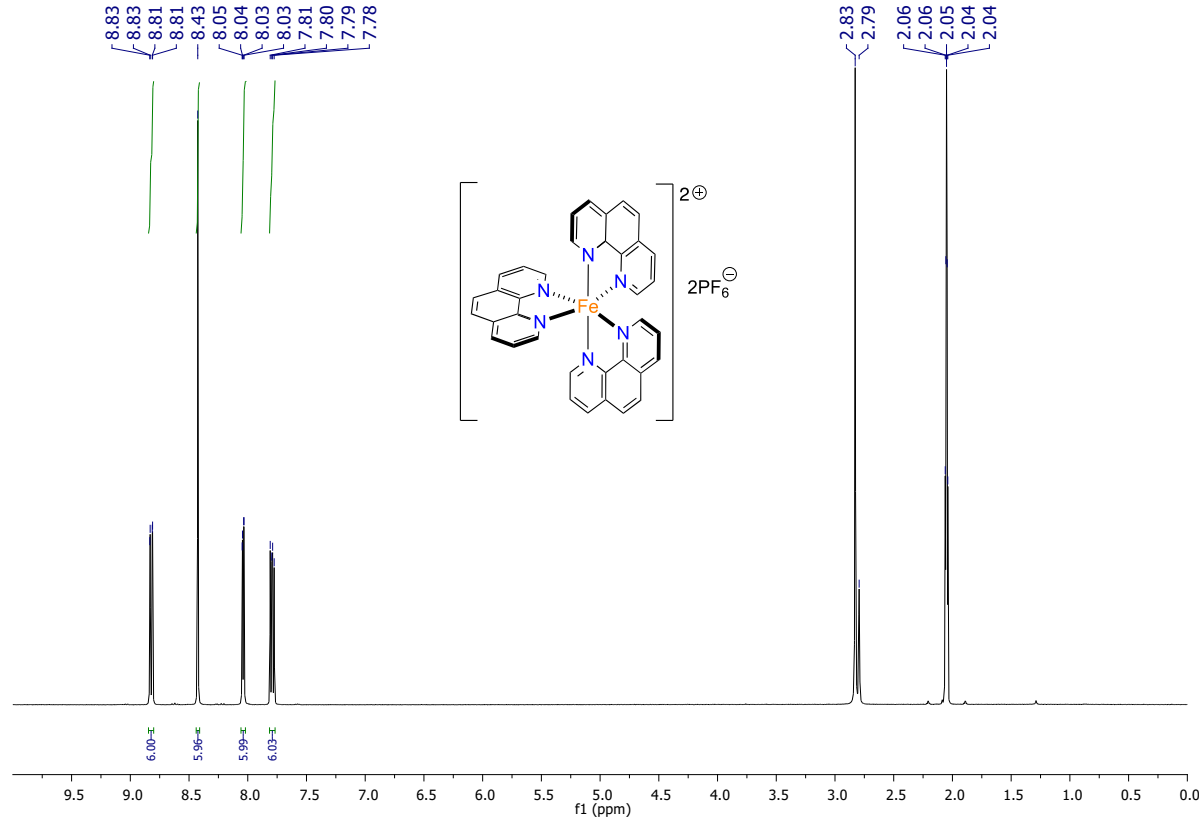
^{1}H NMR for complex **3a** (acetone-d_6, 400 MHz)



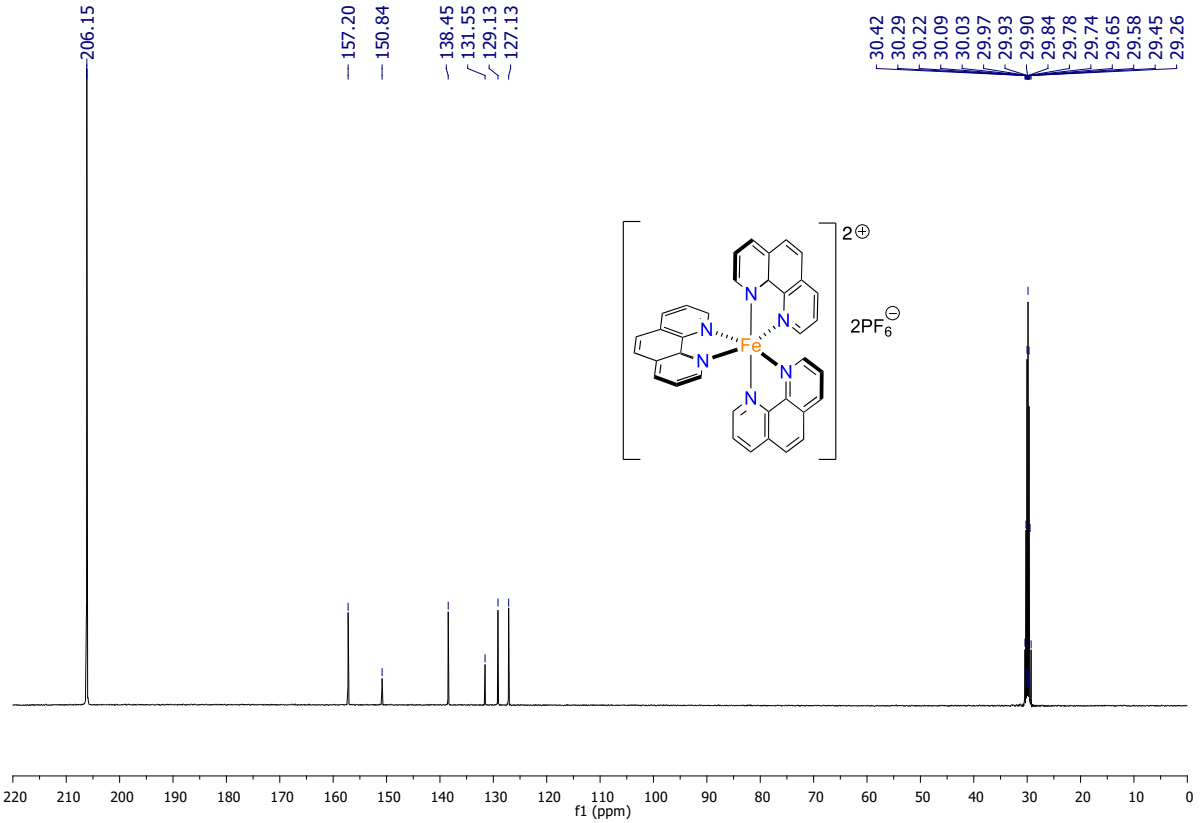
^{13}C NMR for complex **3a** (acetone-d_6, 101 MHz)



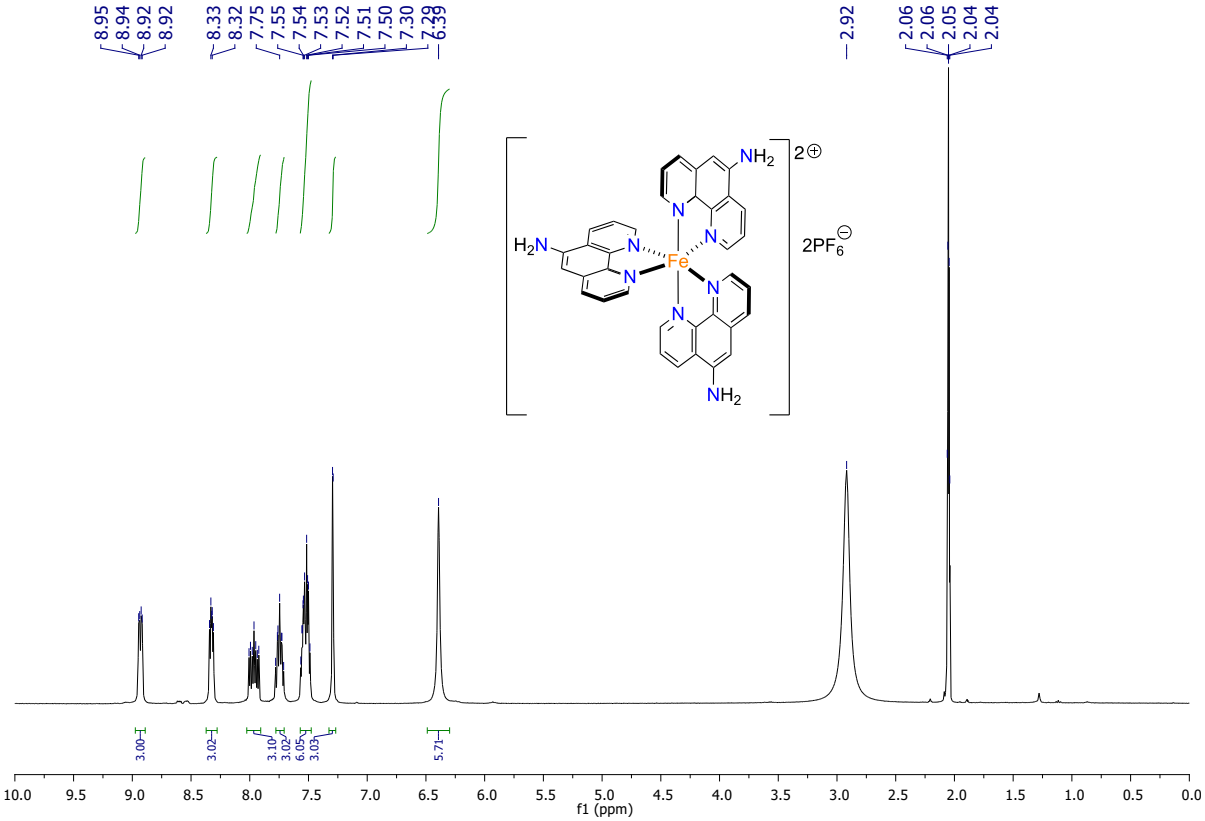
^{1}H NMR for complex **3b** (acetone-d_6, 400 MHz)



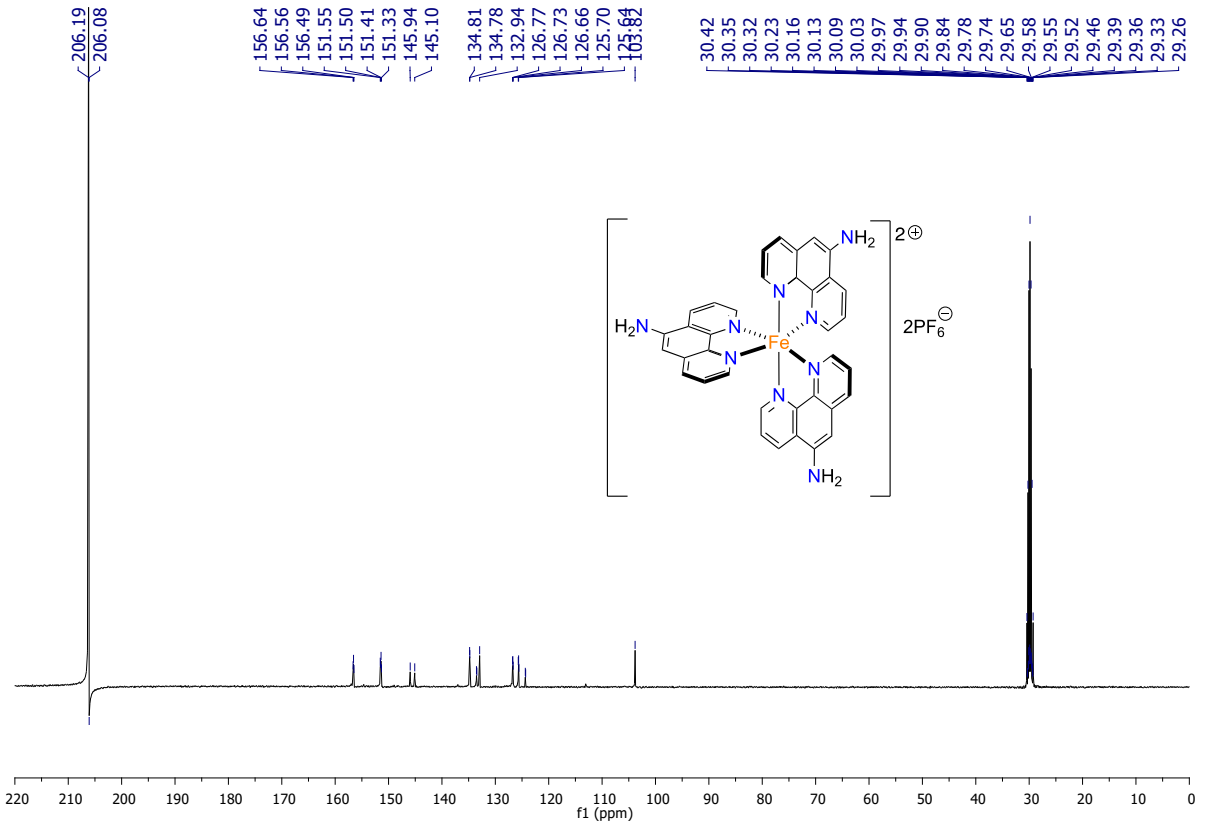
^{13}C NMR for complex **3b** (acetone-d_6, 101 MHz)



^{1}H NMR for complex **3c** (acetone-d_6, 400 MHz)



^{13}C NMR for complex **3c** (acetone-d_6, 101 MHz)



4 References

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(2) Zhang, J.; Campolo, D.; Dumur, F.; Xiao, P.; Fouassier, J. P.; Gigmes, D.; Lalevée, J. Iron complexes as photoinitiators for radical and cationic polymerization through photoredox catalysis processes. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 42-49.
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