

Supporting Information

‘Ferroceneboronic acid and derivatives: synthesis, structure, electronic properties and reactivity in directed C-H bond activation.’

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EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all the reactions were performed under an argon atmosphere. THF was distilled over sodium/benzophenone. For C-H activation reactions, toluene and octane were distilled over CaH₂ and freeze-pump-thaw degassed. Unless otherwise stated, all reagent were used without prior purification. Column chromatography separations were achieved on silica gel (40-63 μ m). All thin layer chromatography was performed on aluminum backed plates pre-coated with silica gel (Merck, Silica Gel 60 F254). TLC were visualized by exposure to UV light. Melting points were measured on a Stuart SMP30 melting point apparatus. IR spectra were taken on a Perkin-Elmer Spectrum 100 spectrometer. ¹H and ¹³C Nuclear Magnetic Resonance (NMR) spectra were recorded either (i) on a Bruker Avance III spectrometer at 300 MHz and 75 MHz, respectively, or/and (ii) on a Bruker Avance III HD at 500 MHz and 125.7 MHz, respectively. ¹¹B and ¹⁹F (NMR) spectra were recorded on a Bruker Avance III spectrometer at 96.2 MHz and 282.3 MHz, respectively. ¹H chemical shifts (δ) are given in ppm relative to the solvent residual peak and ¹³C chemical shifts are relative to the central peak of the solvent signal. Due to their low intensity (resulting from quadrupolar coupling), ¹³C signals arising from the carbon bearing the boronic acid group were not observed.

Safety Considerations. Due to its high pyrophoric character, *t*BuLi need to be use only under inert conditions (anhydrous, nitrogen or argon atmosphere) and by people well trained to the manipulation of reactive organometallics.

Crystallography. For **15**, **16**, **17**, **18**, **19**, **21**, **22** and **25**, the X-ray diffraction data were collected using D8 VENTURE Bruker AXS or APEXII Bruker AXS diffractometers at the temperature given in the crystal data. The samples were studied with monochromatized Mo-K α radiation (λ = 0.71073 Å). The structure was solved by dual-space algorithm using the *SHELXT* program,⁵⁷ and then refined with full-matrix least-square methods based on *F*² (*SHELXL*).⁵⁸ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. The molecular diagrams were generated by MERCURY (version 3.5.1).

Electrochemical measurements. Cyclic voltammetry was performed in anhydrous dimethylformamide (DMF) containing *n*Bu₄PF₆ (0.1 mol.L⁻¹) as supporting electrolyte. An aqueous Ag/AgCl reference electrode, a Pt counter electrode and a glassy carbon working electrode were used.

Ferroceneboronic acid (FcB(OH)₂, 1). To a solution of ferrocene (7.4 g, 40.0 mmol, 1.0 equiv) and *t*BuOK (448.8 mg, 4.0 mmol, 0.1 equiv) in THF (350.0 mL) at -78 °C was added *t*BuLi (1.5 M in pentane, 53.3 mL, 80.0 mmol, 2.0 equiv) dropwise. After addition, the reaction mixture was stirred at -78 °C for 90 min during which lithioferrocene precipitates as an orange solid. The suspension of lithioferrocene was cannulated onto a solution of trimethylborate (17.8 mL, 16.6 g, 160.0 mmol, 4.0 equiv) in THF (100.0 mL) at -78 °C over one hour. After addition, the reaction mixture was stirred 30 min at -78 °C and was warmed to rt. The reaction mixture was concentrated under vacuum and the residue was dissolved into EtOAc (300 mL). The organic layer was extracted with a Na₂CO₃/sorbitol solution (1M, 6 x 100 mL). The combined organic layers were washed with a mixture of Et₂O/pentane (1/1, 100 mL) and cooled to 0 °C. Et₂O (200 mL) was added, and under vigorous stirring, the aqueous layer was acidified with HCl (12 M) until pH 1. The layers were separated and the aqueous layer was extracted with Et₂O (3 x 200 mL). The combined organic layers were washed with water (100 mL),

brine (100 mL), dried over MgSO_4 , filtrated and concentrated under vacuum to give the title product as an orange solid (**1**, 7.86 g, 85%). Mp 145-147 °C. ν_{max} (film)/ cm^{-1} 1462, 1377, 1331, 1304, 1285, 1273, 1223, 1184, 1143, 1127, 1104, 1023, 999, 818, 727, 683. ^1H NMR (500 MHz, $\text{DMSO-d}^6 + \text{D}_2\text{O}$): δ (ppm) 4.38 (t, $J = 1.5$ Hz, 2H, 2 x FcCH), 4.29 (t, $J = 1.5$ Hz, 2H, 2 x FcCH), 4.05 (s, 5H, 5 x FcCH). ^{13}C NMR (125.7 MHz, $\text{DMSO-d}^6 + \text{D}_2\text{O}$): δ (ppm) 74.2 (2 x FcCH), 72.4 (2 x FcCH); 69.2 (5 x FcCH). ^{11}B NMR (96.2 MHz, $\text{DMSO-d}^6 + \text{D}_2\text{O}$): δ (ppm) 31.0 (s).

2-Ferrocenyl-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (FcB(dan), 15). Under air, a suspension of ferroceneboronic acid (**1**, 344.7 mg, 1.5 mmol, 1.0 equiv) in MeCN (15.0 mL) and water (1.0 mL) was stirred at rt for 5 min. Imidazole (306.0 mg, 4.5 mmol, 3.0 equiv), 1,8-diaminonaphthalene (237.3 mg, 1.5 mmol, 1.0 equiv) and a solution of FeCl_3 (12.1 mg, 0.075 mmol, 0.05 mmol) in water (1.5 mL) were added. The reaction mixture was stirred overnight and was concentrated under vacuum to give the crude product. This was purified by column chromatography on silica, eluting with EtOAc/heptane (90/10), to give the title product as an orange solid (**15**, 233.0 mg, 44%). Mp 192-193 °C (decomp.). ν_{max} (film)/ cm^{-1} 1627, 1598, 1513, 1403, 1376, 1231, 1098, 1029, 999, 817, 761, 681. ^1H NMR (500 MHz, DMSO-d^6): δ (ppm) 7.83 (br s, 2H, 2 x NH), 7.08 (t, $J = 7.7$ Hz, 2H, 2x ArCH), 6.88 (d, $J = 7.8$ Hz, 2H, 2 x ArCH), 6.54 (d, $J = 7.6$ Hz, 2H, 2 x ArCH), 4.72 (s, 2H, 2 x FcCH), 4.40 (s, 2H, 2 x FcCH), 4.12 (s, 5H, 5 x FcCH). ^{13}C NMR (125.7 MHz, DMSO-d^6): δ (ppm) 142.6 (ArC), 136.1 (ArC), 127.6 (2 x ArCH), 119.2 (2 x ArC), 115.6 (2 x ArCH), 105.0 (2 x ArCH), 72.1 (2 x FcCH), 71.0 (2 x FcCH), 68.3 (5 x FcCH). ^{11}B NMR (96.2 MHz, DMSO-d^6): δ (ppm) 32.4 (s). Mass: 352 [M^+], 286. Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{BFeN}_2$: C, 68.24; H, 4.87; N, 7.96. Found: C, 68.33; H, 4.95; N, 8.03. **Crystal data for 15.** $\text{C}_{20}\text{H}_{17}\text{BFeN}_2$, $M = 352.01$, $T = 150(2)$ K, monoclinic $P 2_1/n$, $a = 14.2449(15)$, $b = 7.5615(9)$, $c = 14.8752(15)$ Å, $\beta = 96.893(4)^\circ$, $V = 1590.7(3)$ Å³. $Z = 4$, $d = 1.470$ g.cm⁻³, $\mu = 0.950$ mm⁻¹. A final refinement on F^2 with 3636 unique intensities and 223 parameters converged at $\omega R(F^2) = 0.1256$ ($R(F) = 0.0495$) for 3069 observed reflections with $I > 2\sigma(I)$. CCDC 1853256.

2-Ferrocenyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (FcB(aam), 16). Under air, a suspension of ferroceneboronic acid **1** (459.7 mg, 2.0 mmol, 1.0 equiv) in toluene (25.0 mL) and water (2.0 mL) was stirred at rt for 15 min. 2-Aminobenzamide (272.2 mg, 2.0 mmol, 1.0 equiv) was added and the reaction mixture was heated at reflux with azeotropic removal of water using a Dean-Stark trap overnight. The reaction mixture was cooled to rt and concentrated under vacuum to give the crude product. This was purified by column chromatography on silica, eluting with EtOAc/heptane (60/40), to give the title product as an orange solid (**16**, 470.0 mg, 71%). Mp 260-262 °C (decomp.). ν_{max} (film)/ cm^{-1} 3395, 3213 (br), 1643, 1612, 1519, 1488, 1405, 1361, 1316, 1270, 1147, 760. ^1H NMR (500 MHz, DMSO-d^6): δ (ppm) : 9.28 (s, 1H, CONH), 8.79 (s, 1H, NH), 8.00 (d, $J = 7.9$ Hz, 1H, ArCH), 7.53 (t, $J = 7.9$ Hz, 1H, ArCH), 7.33 (t, $J = 7.9$ Hz, 1H, ArCH), 7.05 (t, $J = 7.9$ Hz, 1H, ArCH), 4.86 (s, 2H, 2 x FcCH), 4.45 (s, 2H, 2 x FcCH), 4.07 (s, 5H, 5 x FcCH). ^{13}C NMR (125.7 MHz, DMSO-d^6): δ (ppm) 166.6 (C=O), 146.3 (ArC), 133.7 (ArCH), 128.5 (ArCH), 120.6 (ArCH), 118.9 (ArC), 118.1 (ArCH), 73.1 (2 x FcCH), 72.3 (2 x FcCH), 69.9 (5 x FcCH). ^{11}B NMR (96.2 MHz, DMSO-d^6): δ (ppm) 31.7 (s). Mass: 330 [M^+]. Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{BFeN}_2\text{O}$: C, 61.88; H, 4.58; N, 8.49. Found: C, 61.90; H, 4.61; N, 8.55. **Crystal data for 16.** $\text{C}_{17}\text{H}_{15}\text{BFeN}_2\text{O}$, $M = 329.97$, $T = 150(2)$ K, monoclinic $P 2_1/c$, $a = 11.9718(3)$, $b = 11.0980(3)$, $c = 11.5281(3)$ Å, $\beta = 110.8530(10)^\circ$, $V = 1431.33(7)$ Å³. $Z = 4$, $d = 1.531$ g.cm⁻³, $\mu = 1.054$ mm⁻¹. A final refinement on F^2 with 3262 unique intensities and 205 parameters

converged at $\omega R(F^2) = 0.0820$ ($R(F) = 0.0316$) for 2915 observed reflections with $I > 2\sigma(I)$. CCDC 1853260.

3-Methyl-2-ferrocenyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (FcB(Me-aam), 17).

Under air, a suspension of ferroceneboronic acid (**1**, 459.7 mg, 2.0 mmol, 1.0 equiv), 2-amino-*N*-methylbenzamide (600.7 mg, 4.0 mmol, 2.0 equiv), imidazole (408.4 mg, 6.0 mmol, 3.0 equiv) and FeCl_3 (16.2 mg, 0.1 mmol, 0.05 equiv) in a mixture of toluene (15.0 mL), DMSO (1 mL) and water (2.0 mL) was stirred at rt for 15 min. The reaction mixture was heated at reflux with azeotropic removal of water using a Dean-Stark trap for 1 h. The reaction mixture was cooled to rt. The crude product in solution was purified by column chromatography on silica, eluting with EtOAc/heptane (65:35 to 60:40), to give the crude product after concentration. Diethyl ether (5 mL) was added and the resulting solids were filtrated and washed with diethyl ether (3 x 5 mL) to give the title product as an orange solid (**17**, 125.0 mg, 18%). Mp 242-243 °C (decomp.). ν_{max} (film)/ cm^{-1} 3356, 1615, 1512, 1488, 1417, 1362, 1301, 1106, 1067, 1029, 817, 754, 701. ^1H NMR (300 MHz, DMSO-d_6): δ (ppm): 8.69 (s, 1H, NH), 8.03 (d, $J = 7.6$ Hz, 1H, ArCH), 7.52 (t, $J = 7.6$ Hz, 1H, ArCH), 7.40 (d, $J = 7.6$ Hz, 1H, ArCH), 7.07 (t, $J = 7.6$ Hz, 1H, ArCH), 4.70 (s, 2H, 2 x FcCH), 4.54 (s, 2H, 2 x FcCH), 4.15 (s, 5H, 5 x FcCH), 3.45 (s, 3H, CH_3). ^{13}C NMR (75.4 MHz, DMSO-d_6): δ (ppm) 166.0 (C=O), 144.4 (ArC), 132.9 (ArCH), 128.0 (ArCH), 120.3 (ArCH), 117.6 (ArC), 117.5 (ArCH), 73.9 (2 x FcCH), 71.6 (2 x FcCH), 68.4 (5 x FcCH), 30.8 (CH_3). ^{11}B NMR (96.2 MHz, CDCl_3): δ (ppm) 31.9 (s). Mass: 334 [M^+], 207, 186 (Fc), 121. Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{BFeN}_2\text{O}$: C, 62.85; H, 4.98; N, 8.14. Found: C, 62.83; H, 4.95; N 8.09. **Crystal data for 17.** $\text{C}_{18}\text{H}_{17}\text{BFeN}_2\text{O}$, $M = 343.99$, $T = 150(2)$ K, orthorhombic $P c a 2_1$, $a = 14.2531(8)$, $b = 9.9627(6)$, $c = 10.5709(6)$ Å, $V = 1501.06(15)$ Å³. $Z = 4$, $d = 1.522$ g. cm^{-3} , $\mu = 1.009$ mm⁻¹. A final refinement on F^2 with 3426 unique intensities and 212 parameters converged at $\omega R(F^2) = 0.0609$ ($R(F) = 0.0313$) for 2952 observed reflections with $I > 2\sigma(I)$. CCDC 1853259.

1-Methyl-2-ferrocenyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (FcB(Me-aam), 18).

Under air, a suspension of ferroceneboronic acid (**1**, 459.7 mg, 2.0 mmol, 1.0 equiv), 2-(methylamino)benzamide (600.7 mg, 4.0 mmol, 2.0 equiv), imidazole (408.4 mg, 6.0 mmol, 3.0 equiv) and FeCl_3 (16.2 mg, 0.1 mmol, 0.05 equiv) in a mixture of toluene (15.0 mL), DMSO (1 mL) and water (2.0 mL) was stirred at rt for 15 min. The reaction mixture was heated at reflux with azeotropic removal of water using a Dean-Stark trap for 1 h. The reaction mixture was cooled to rt. The crude product in solution was purified by column chromatography on silica, eluting with EtOAc/heptane (65:35 to 60:40), to give the crude product after concentration. Diethyl ether (5 mL) was added and the resulting solids were filtrated and washed with diethyl ether (4 x 5 mL) to give the title product as an orange solid (**18**, 50.0 mg, 7%). Mp 258-261 °C (decomp.). ν_{max} (film)/ cm^{-1} 3324, 1649, 1604, 1483, 1465, 1392, 1314, 1150, 836, 810, 765. ^1H NMR (500 MHz, DMSO-d_6): δ (ppm) 9.01 (s, 1H, NH), 8.12 (dd, $J = 7.8$, 1.3 Hz, 1H, ArCH), 7.69 (dt, $J = 7.8$, 1.3 Hz, 1H, ArCH), 7.42 (d, $J = 7.8$ Hz, 1H, ArCH), 7.19 (d, $J = 7.8$ Hz, 1H, ArCH), 4.72 (s, 2H, 2 x FcCH), 4.51 (s, 2H, 2 x FcCH), 4.16 (s, 5H, 5 x FcCH), 3.53 (s, 3H, CH_3). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ (ppm) 165.5 (C=O), 147.3 (ArC), 134.2 (ArCH), 128.8 (ArCH), 121.2 (ArCH), 120.0 (ArC), 115.5 (ArCH), 74.7 (2 x FcCH), 72.1 (2 x FcCH), 69.1 (5 x FcCH), 34.8 (CH_3). ^{13}C NMR (125.7 MHz, DMSO-d_6) 146.3 (ArC), 133.7 (ArCH), 128.5 (ArCH), 120.6 (ArCH), 118.9 (ArC), 118.1 (ArCH), 73.1 (2 x FcCH), 72.3 (2 x FcCH), 69.9 (5 x FcCH). ^{11}B NMR (96.2 MHz, CDCl_3): δ (ppm) 31.7 (s). Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{BFeN}_2\text{O}$: C, 62.85; H, 4.98; N, 8.14. Found:

C, 62.90; H, 5.02; N 8.19. **Crystal data for 18.** $C_{18}H_{17}BFeN_2O$, $M = 343.99$, $T = 150(2)$ K, monoclinic $C 2/c$, $a = 28.3010(15)$, $b = 7.1917(5)$, $c = 18.8683(11)$ Å, $\beta = 129.799(2)^\circ$, $V = 2950.5(3)$ Å³. $Z = 8$, $d = 1.549$ g.cm⁻³, $\mu = 1.027$ mm⁻¹. A final refinement on F^2 with 3346 unique intensities and 212 parameters converged at $\omega R(F^2) = 0.0875$ ($R(F) = 0.0390$) for 2620 observed reflections with $I > 2\sigma(I)$. CCDC 1853258.

Potassium ferrocenytrifluoroborate (FcBF₃K, 19). Under air, a suspension of ferroceneboronic acid (**1**, 344.7mg, 1.5 mmol, 1.0 equiv) in MeCN (15.0 mL) and water (2.0 mL) was stirred at rt for 15 min. KF (348.5 mg, 6.0 mmol, 4.0 equiv) in water (1.0 mL) was added and the reaction mixture was stirred for 30 min. A solution of tartaric acid (465.3 mg, 3.1 mmol, 2.1 equiv) in THF (3.0 mL) was added dropwise over 5 min. After addition, the reaction mixture was stirred for 5 min. The reaction mixture was filtrated and the resulting solids were washed with MeCN (3 x 4 mL). The combined filtrates were concentrated under vacuum to give the title product as an orange solid (**19**, 205.1 mg, 47%). Mp 281-282 °C (decomp.). ν_{\max} (film)/cm⁻¹ 1447, 1369, 1237, 1223, 1107, 1053, 973, 948, 910, 883, 853, 825, 812. ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 3.96 (s, 5H, 5x FcCH), 3.87 (s, 4H, 2 x FcCH + 2 x FcCH). ¹³C NMR (125.7 MHz, DMSO-d₆): δ (ppm) 71.1 (2 x FcCH), 67.2 (5 x FcCH), 66.9 (2 x FcCH). ¹¹B NMR (96.2 MHz, DMSO-d₆): δ (ppm) 2.99 (d, $J = 61.3$ Hz). ¹⁹F NMR (282.3 MHz, DMSO-d₆): δ (ppm) -133.1 (d, $J = 61.3$ Hz). Anal. Calcd for C₁₀H₉BF₃FeK: C, 41.14; H, 3.11. Found: C, 41.19; H, 3.21. **Crystal data for 19.** C₁₀H₉BF₃FeK, $M = 291.93$, $T = 150(2)$ K, monoclinic $P 2_1/c$, $a = 13.833(3)$, $b = 7.2083(12)$, $c = 10.5507(17)$ Å, $\beta = 94.868(7)^\circ$, $V = 1048.3(3)$ Å³. $Z = 4$, $d = 1.850$ g.cm⁻³, $\mu = 1.840$ mm⁻¹. A final refinement on F^2 with 2240 unique intensities and 146 parameters converged at $\omega R(F^2) = 0.0688$ ($R(F) = 0.0287$) for 2120 observed reflections with $I > 2\sigma(I)$. CCDC 1853254.

4-Methyl-1-ferrocenyl-2,6,7-trioxa-1-borabicyclo[2.2.2]octan-1-uide (FcB(triolborate), 20). Under air, a suspension of ferroceneboronic acid (**1**, 459.7 mg, 2.0 mmol, 1.0 equiv) in toluene (25.0 mL) and water (2.0 mL) was stirred at rt for 15 min. 1,1,1-Tris(hydroxymethyl)ethane (240.3 mg, 2.0 mmol, 1.0 equiv) was added and the reaction mixture was heated at reflux with azeotropic removal of water using a Dean-Stark trap overnight. The reaction mixture was cooled to rt and concentrated under vacuum to give the crude product **22**. ¹H NMR (300 MHz, DMSO-d₆): δ (ppm) 4.86 (t, $J = 5.1$ Hz, 1H, OH), 4.33 (t, $J = 1.5$ Hz, 2H, 2 x FcCH), 4.27 (t, $J = 1.5$ Hz, 2H, 2 x FcCH), 4.13 (s, 5H, 5 x FcCH), 3.87 (d, $J = 1.8$ Hz, 2H, 2 x CHH), 3.68 (d, $J = 10.8$ Hz, 2H, 2 x CHH), 3.39 (d, $J = 5.1$ Hz, 2H, CH₂), 0.89 (s, 3H, CH₃).

This was dissolved in toluene (10.0 mL) and solid KOH (101.0 mg, 1.8 mmol, 0.9 equiv) was added. The reaction mixture was heated at reflux with azeotropic removal of water using a Dean-Stark trap overnight. The reaction mixture was cooled to rt, and acetone (25 mL) was added dropwise. The resulting solids were filtrated, washed with acetone and dried to give the title product as an orange solid (**20**, 492.6 mg, 70%). Mp 280-285 °C (decomp.). ν_{\max} (film)/cm⁻¹ 3408 (br), 2852, 1451, 1405, 1221, 1181, 1082, 1047, 936, 892, 847, 809. ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 3.98 (s, 5H, 5 x FcCH), 3.85 (s, 2H, 2x FcCH), 3.79 (s, 2H, 2 x FcCH), 3.55(s, 6H, 3 x CH₂), 0.48 (s, 3H, CH₃). ¹³C NMR (125.7 MHz, DMSO-d₆): δ (ppm) 73.2 (3 x CH₂), 71.6 (2 x FcCH), 67.3 (5 x FcCH), 66.5 (2 x FcCH), 34.3 (C), 16.4 (CH₃). ¹¹B NMR (96.2 MHz, DMSO-d₆): δ (ppm) 2.40 (s). Anal. Calcd for C₁₅H₁₈BFeO₃K: C, 51.17; H, 5.15. Found: C, 52.27; H, 5.14.

6-Methyl-2-ferrocenyl-1,3,6,2-dioxazaborocane-4,8-dione (FcB(MIDA), 21). Under air, a suspension of ferroceneboronic acid (**1**, 574.6 mg, 2.5 mmol, 1.0 equiv) in toluene (19.0 mL), DMSO (1.0 mL) and water (1 mL), toluene (25.0 mL) was stirred at rt for 15 min. 2-Methyliminodiacetic acid (367.8 mg, 2.5 mmol, 1.0 equiv) was added and the reaction mixture was heated at reflux with azeotropic removal of water using a Dean-Stark trap overnight. The reaction mixture was cooled to rt and concentrated under vacuum over celite. The residue was purified by column chromatography on silica, eluting with Et₂O/MeCN (100/0 to 70/30), to give the title product as an orange solid (**21**, 553.7 mg, 65%). Mp 280-285 °C (decomp.). ν_{\max} (film)/cm⁻¹ 1759, 1735, 1453, 1341, 1305, 1237, 988, 806. ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 4.27 (s, 2H, 2 x FcCH), 4.23 (d, J = 17.1 Hz, 2H, 2 x CHH), 4.14 (s, 5H, 5 x FcCH), 4.08 (s, 2H, 2 x FcCH), 3.99 (d, J = 17.1 Hz, 2H, 2 x CHH), 2.51 (s, 3H, CH₃). ¹³C NMR (125.7 MHz, DMSO-d₆): δ (ppm) 169.1 (2 x C=O), 71.7 (2 x FcCH), 70.1 (2 x FcCH), 68.2 (5 x FcCH), 61.2 (2 x CH₂), 47.0 (CH₃). ¹¹B NMR (96.2 MHz, DMSO-d₆): δ (ppm) 13.9 (s). Anal. Calcd for C₁₅H₁₆BFeNO₄: C, 52.84; H, 4.73; N, 4.11. Found: C, 52.79; H, 4.69; N 4.03. **Crystal data for 21.** C₁₅H₁₆BFeNO₄, M = 340.95, T = 150(2) K, monoclinic $C2/c$, a = 32.502(3), b = 7.0299(6), c = 12.7697(9) Å, β = 95.460(3) °, V = 2904.4(4) Å³. Z = 8, d = 1.559 g.cm⁻³, μ = 1.055 mm⁻¹. A final refinement on F^2 with 3315 unique intensities and 200 parameters converged at $\omega R(F^2)$ = 0.0799 ($R(F)$ = 0.0311) for 3024 observed reflections with $I > 2\sigma(I)$. CCDC 1853255.

2-(2-(Dimethyl(phenyl)silyl)ferrocenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (FcB(aam)(SiMe₂Ph), 25) and 2-(2,5-bis(dimethyl(phenyl)silyl)ferrocenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (FcB(aam)(SiMe₂Ph)₂, 26). FcB(aam) (**16**, 65.9 mg, 0.2 mmol, 1.0 equiv) and RuH₂(CO)(PPh₃)₃ (22.0 mg, 0.02 mmol, 0.1 equiv) were added to a small vial. This was placed under vacuum and backfilled with argon. Toluene (100.0 µL), dimethylphenylsilane (153.3 µL, 136.3 mg, 1.0 mmol, 5 equiv) and norbornene (100.0 µL, 94.15 mg, 1.0 mmol, 5 equiv) were successively added, the vial was sealed and heated at 145 °C for 21 h. The reaction mixture was cooled to rt and concentrated under vacuum to give the crude product. This was purified by preparative TLC, eluting with heptane/EtOAc (65/35) to give the title mono-silylated product (**25**, 44.0 mg, 47%). Mp 171-172 °C (decomp.). ν_{\max} (film)/cm⁻¹ 3392, 1652, 1609, 1509, 1487, 1397, 1253, 1107, 1044, 810, 793, 753. ¹H NMR (500 MHz, Acetone-d₆): δ (ppm) 8.04 (dd, J = 7.1, 1.3 Hz, 1H, ArCH), 7.71 (br s, 1H, CONH), 7.62-7.60 (m, 2H, 2 x ArCH), 7.46-7.45 (m, 1H, ArCH), 7.43-7.41 (m, 3H, 3 x ArCH), 7.06 (dt, J = 7.7, 0.8 Hz, AH, ArCH), 6.90 (br s, 1H, NH), 6.73 (d, J = 8.1 Hz, 1H, ArCH), 4.99 (dd, J = 2.2, 1.0 Hz, FcCH), 4.74 (t, J = 2.2 Hz, 1H, FcCH), 4.57 (dd, J = 2.2, 1.0 Hz, 1H, FcCH), 4.30 (s, 5H, 5 x FcCH), 0.73 (s, 3H, CH₃), 0.57 (s, 3H, CH₃). ¹³C NMR (125.7 MHz, Acetone-d₆): δ (ppm) 166.0 (C=O), 145.6 (ArC), 141.1 (ArC), 135.0 (2 x ArCH), 134.3 (ArCH), 130.4 (2 x ArCH), 129.3 (ArCH), 129.2 (ArCH), 121.8 (ArCH), 119.9 (ArC), 118.2 (ArCH), 79.7 (FcCH), 79.6 (FcCH), 74.6 (FcCH), 72.9 (FcC), 70.0 (5 x FcCH), -0.4 (CH₃), -0.5 (CH₃). ¹¹B NMR (96.2 MHz, Acetone-d₆): δ (ppm) 31.6 (s). Anal. Calcd for C₂₅H₂₅BFeN₂OSi: C, 64.68; H, 5.43; N, 6.03. Found: C, 64.75; H, 5.49; N 6.08. **Crystal data for 25.** C₂₅H₂₅BFeN₂OSi, M = 464.22, T = 150(2) K, triclinic $P-1$, a = 8.0923(13), b = 11.206(2), c = 12.981(3) Å, α = 96.170(7), β = 97.539(6), γ = 107.556(6) °, V = 1099.1(3) Å³. Z = 2, d = 1.403 g.cm⁻³, μ = 0.761 mm⁻¹. A final refinement on F^2 with 5038 unique intensities and 289 parameters converged at $\omega R(F^2)$ = 0.0766 ($R(F)$ = 0.0298) for 4813 observed reflections with $I > 2\sigma(I)$. CCDC 1853253.

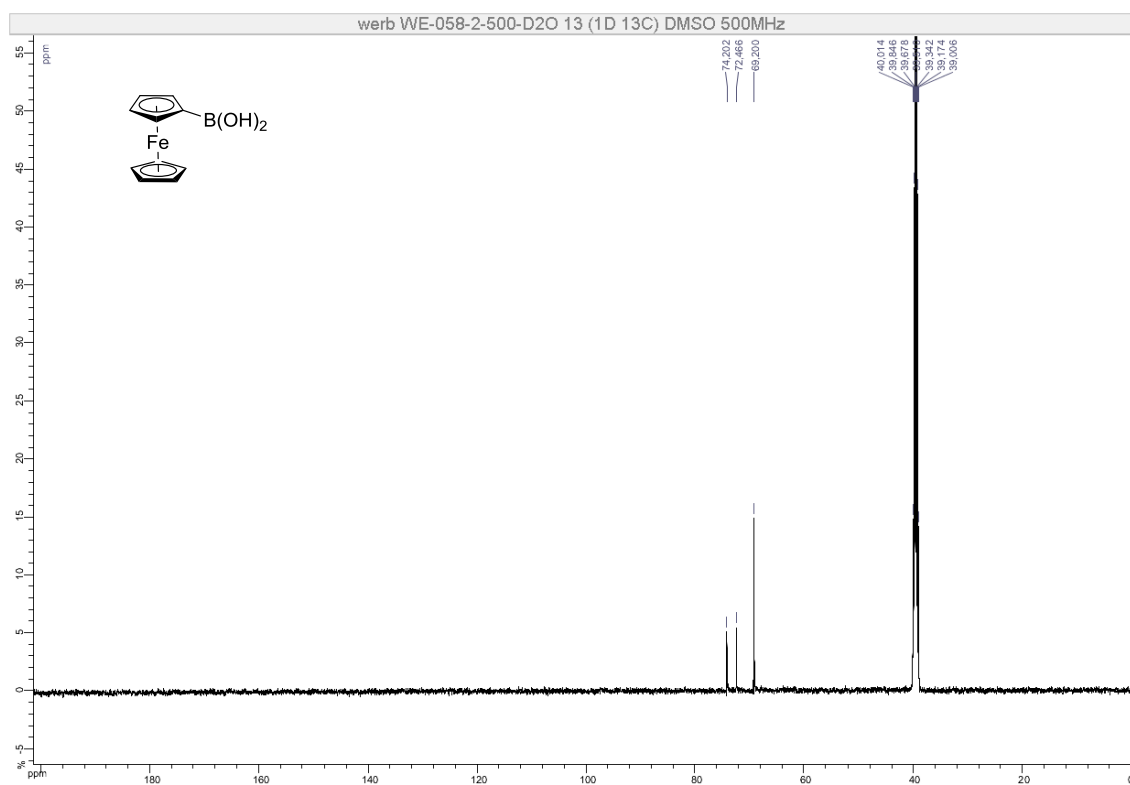
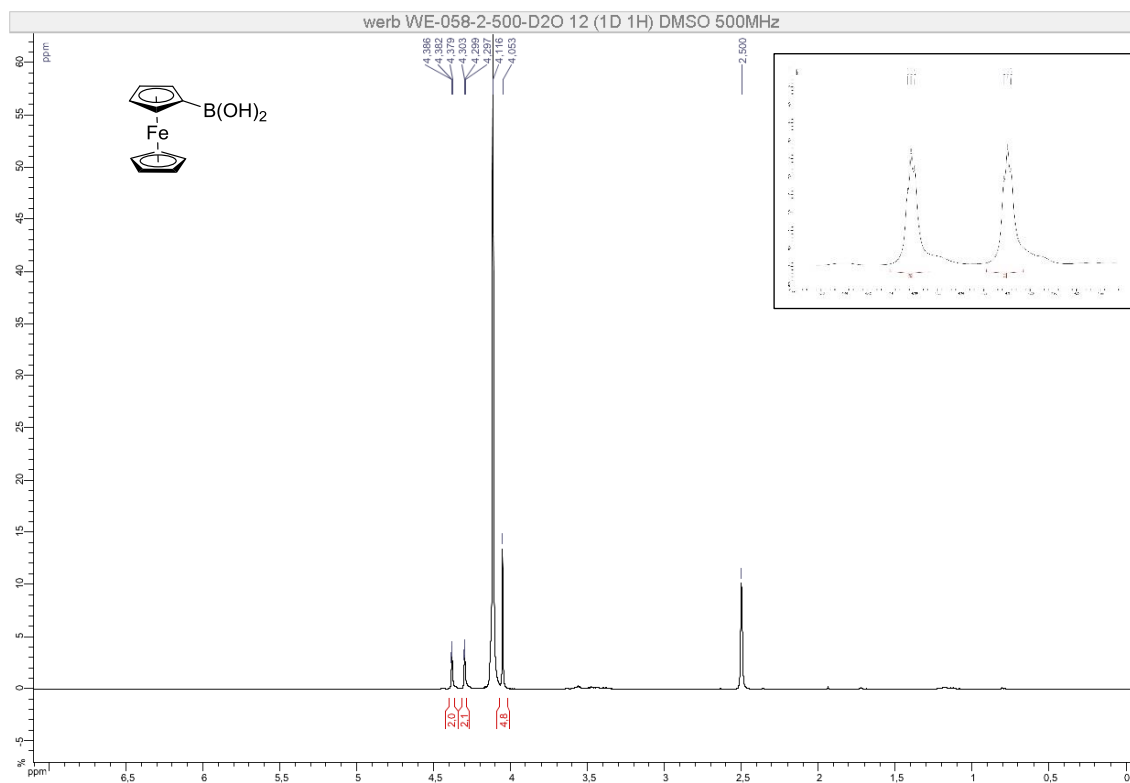
The bis-silylated product was also isolated as a yellow solid (**26**, 44.0 mg, 36%). Mp 181-182 °C (decomp.). ν_{\max} (film)/cm⁻¹ 3319, 1649, 1619, 1520, 1485, 1367, 1318, 1244, 1106, 803, 770, 730. ¹H NMR (500 MHz, CD₃CN): δ (ppm) 8.00 (dd, J = 7.8, 1.5 Hz, 1H, ArCH), 7.50 (m, 1H, ArCH), 7.46-7.42 (m, 4H, 4 x ArCH), 7.28-7.22 (m, 6H, 6 x ArCH), 7.11 (m, 1H, ArCH), 6.91 (br s, 1H, CONH), 6.84 (d, J = 8.0 Hz, 1H, ArCH), 6.57 (br s, 1H, NH), 4.59 (s, 2H, 2 x FcCH), 4.22 (s, 5H, 5 x FcCH); 0.48 (s, 6H, 2 x CH₃), 0.45 (s, 6H, 2 x CH₃). ¹³C NMR (125.7 MHz, CD₃CN): δ (ppm) 165.8 (C=O), 145.2 (ArC), 140.6 (2 x ArC), 134.8 (4 x ArCH), 134.6 (ArCH), 130.0 (2 x ArCH), 129.2 (ArCH), 128.8 (4 x ArCH), 122.4 (ArCH), 119.6 (ArCH), 118.8 (ArCH), 80.0 (2 x FcCH), 79.6 (2 x FcC), 70.1 (5 x FcCH), -0.7 (2 x CH₃), -0.9 (2 x CH₃). ¹¹B NMR (96.2 MHz, CD₃CN): δ (ppm) 32.1 (s). Anal. Calcd for C₃₃H₃₅BF₂N₂OSi₂: C, 66.23; H, 5.89; N, 4.68. Found: C, 66.30; H, 5.95; N 4.77.

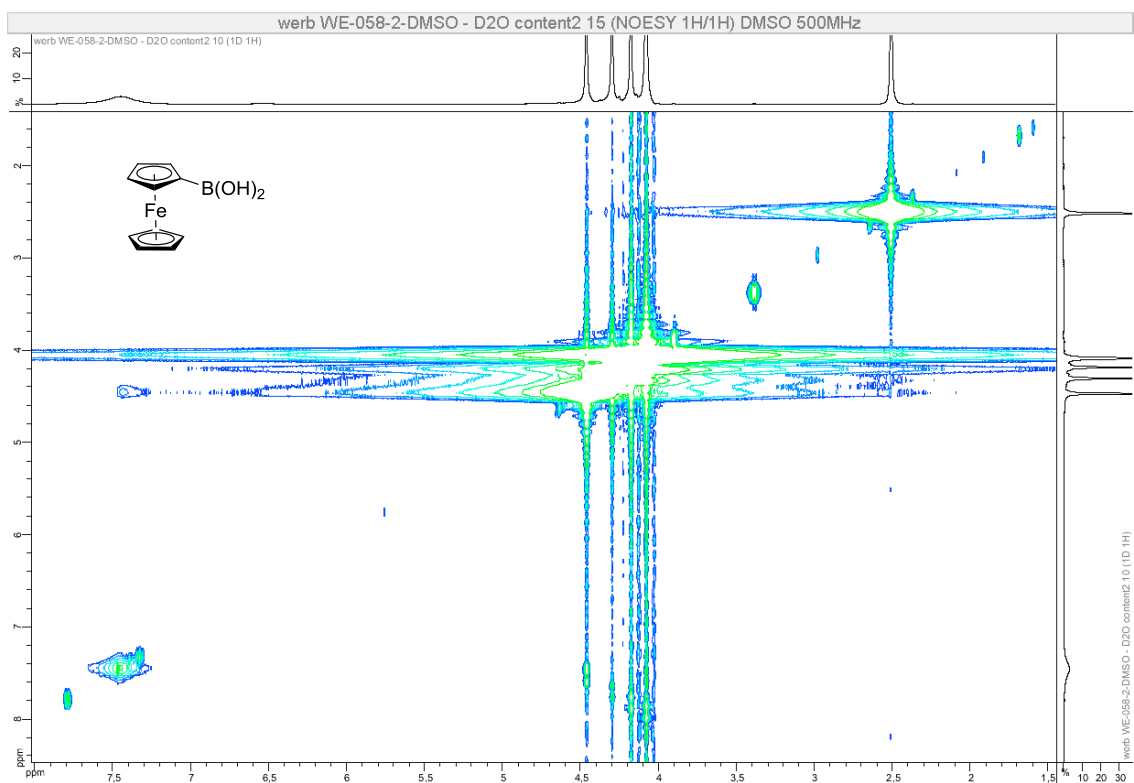
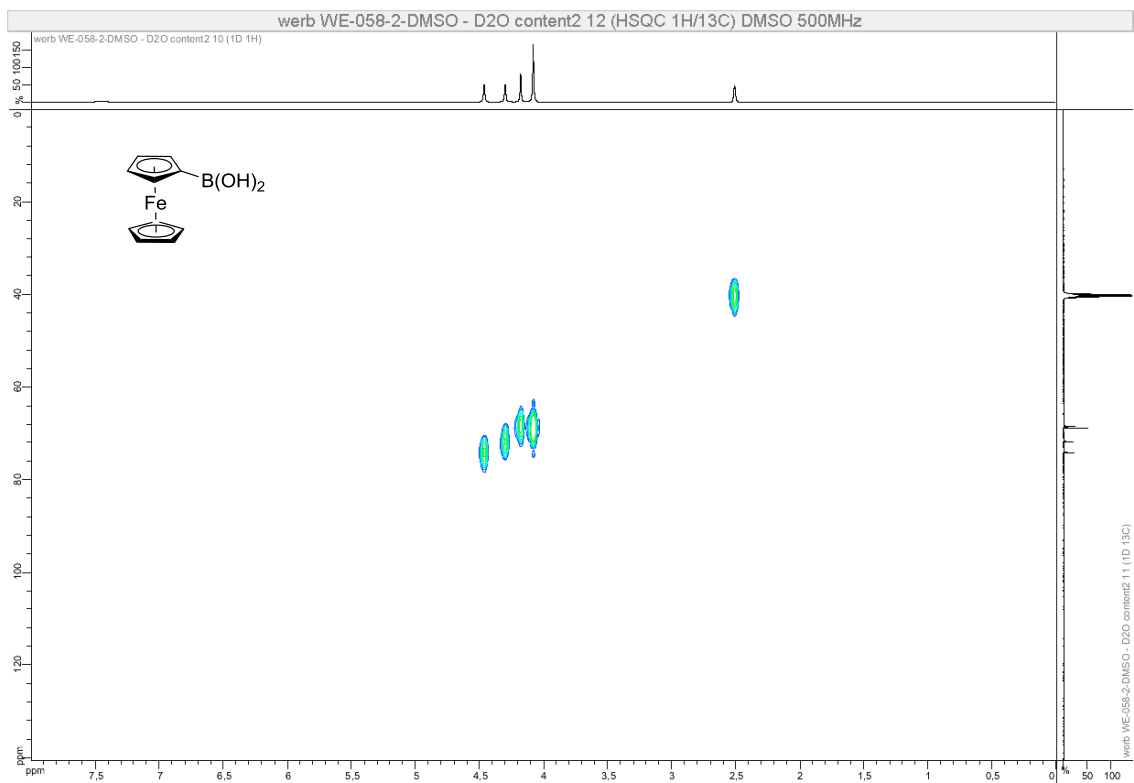
2-Ferrocenyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-

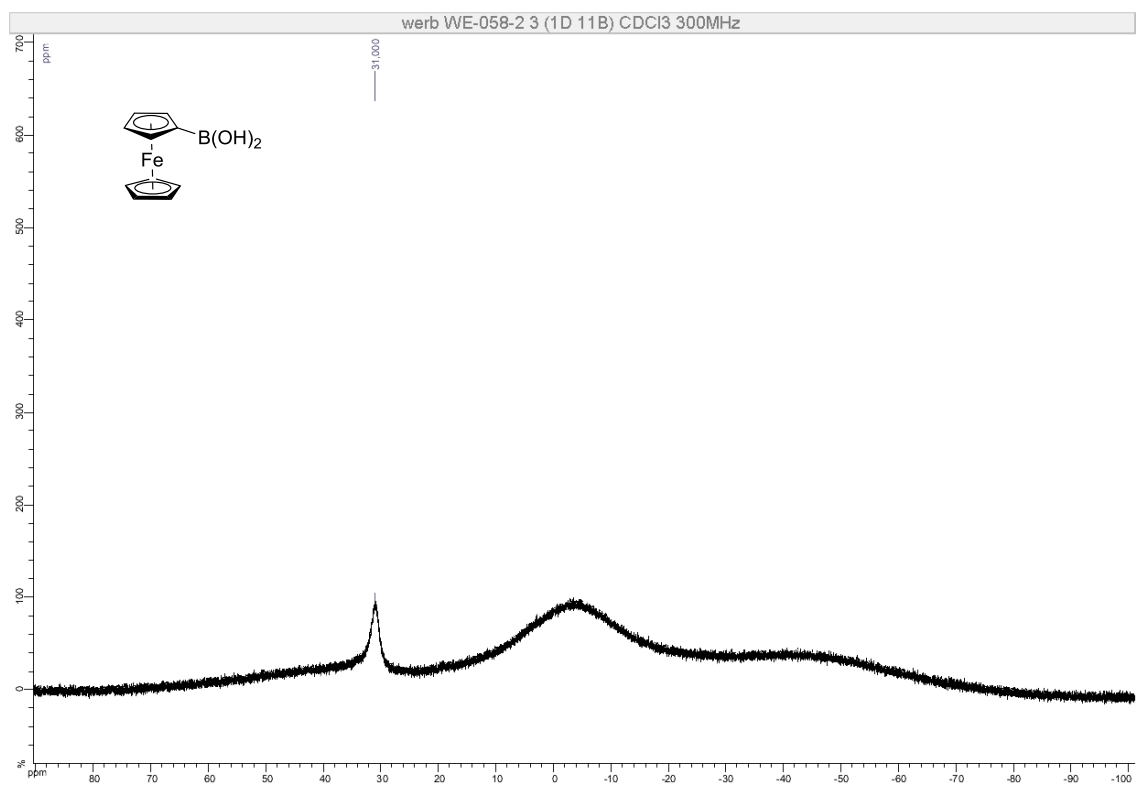
dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (FcB(aam)BPIn, **28). FcB(aam) (**16**, 82.4 mg, 0.25 mmol, 1.0 equiv), [Ir(OMe)(COD)]₂ (2.5 mg, 0.0038 mmol, 1.5 mol%), 4,4'-di-*tert*-butyl-[2,2']bipyridinyl (2.0 mg, 0.0075 mmol, 3.0 mol%), B₂pin₂ (63.5 mg, 0.25 mmol, 1.0 equiv) and octane (0.9 mL) were added into a sealed tube, evacuated and backfilled with argon three times and the reaction mixture was stirred at 126 °C for 20 h. The reaction mixture was cooled to rt and purified by preparative TLC, eluting with heptane/EtOAc (65/35) to give the title product as a yellow solid (35 mg, 30.5%). Mp 268 °C (decomp.). ν_{\max} (film)/cm⁻¹ 3385, 1652, 1596, 1520, 1447, 1371, 1349, 1303, 1266, 1141, 1103, 966, 887, 861, 840, 821, 766, 747, 698. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.66 (s, 1H, NH), 8.34 (dd, J = 7.9, 1.2 Hz, 1H, ArCH), 8.00 (dd, J = 7.2, 1.5 Hz, 1H, ArCH), 7.28 (s, 1H, CONH), 7.09 (t, J = 7.3 Hz, 1H, ArCH), 4.49 (t, J = 1.5 Hz, 2H, 2 x FcCH), 4.39 (t, J = 1.5 Hz, 2H, 2 x FcCH), 4.11 (s, 5H, 5 x FcCH), 1.44 (s, 12H, 4 x CH₃). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 167.1 (C=O), 150.9 (ArC), 142.0 (ArCH), 133.3 (ArCH), 120.6 (ArCH), 118.6 (ArC), 84.5 (4 x Cq), 72.5 (2 x FcCH), 71.7 (2 x FcCH), 69.1 (5 x FcCH), 25.3 (4 x CH₃). ¹¹B NMR (96.2 MHz, CDCl₃): δ (ppm) 31.5 (s). Anal. Calcd for C₂₃H₂₆B₂FeN₂O₃: C, 60.59; H, 5.75; N, 6.14. Found: C, 60.72; H, 5.79; N 6.21. **Crystal data for **25**.** C₂₃H₂₆B₂FeN₂O₃, M = 455.93, T = 150(2) K, orthorhombic P 2₁ 2₁ 2₁, a = 10.7306(3), b = 17.6119(4), c = 23.2767(7) Å, V = 4399.0(2) Å³. Z = 8, d = 1.377 g.cm⁻³, μ = 0.713 mm⁻¹. A final refinement on F^2 with 9999 unique intensities and 567 parameters converged at $\omega R(F^2)$ = 0.0907 ($R(F)$ = 0.0388) for 8726 observed reflections with $I > 2\sigma(I)$. CCDC 1853257.**

(1) NMR Spectra

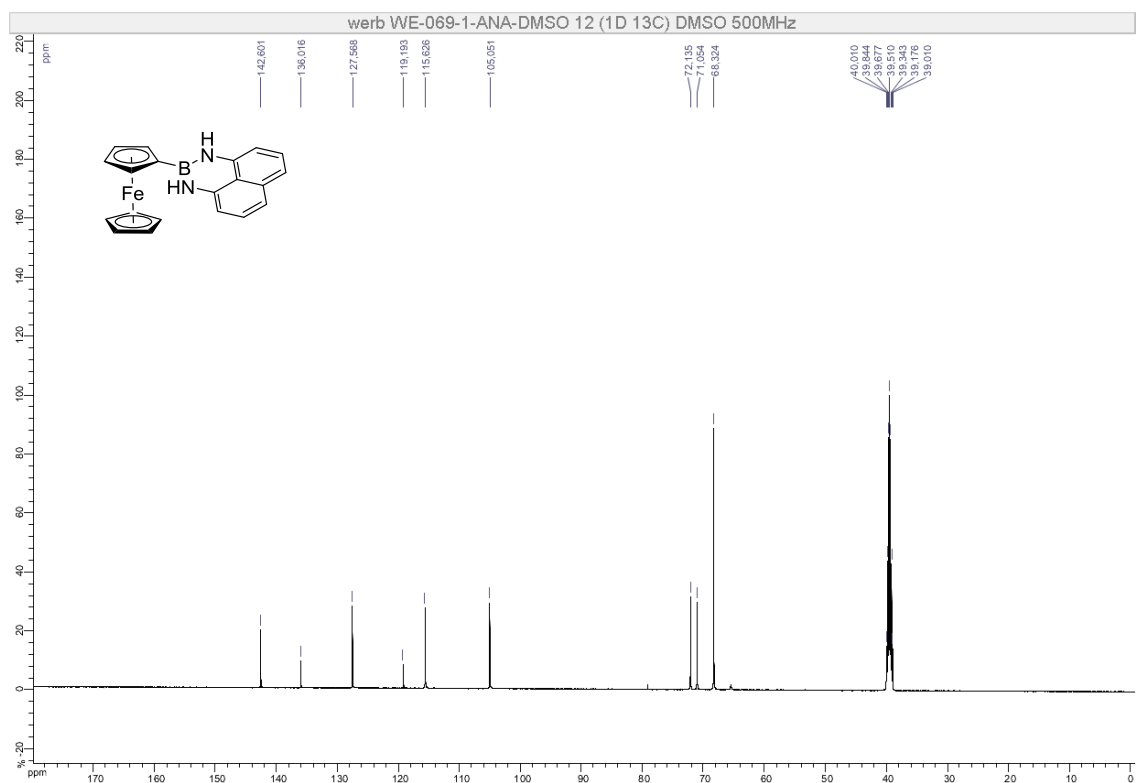
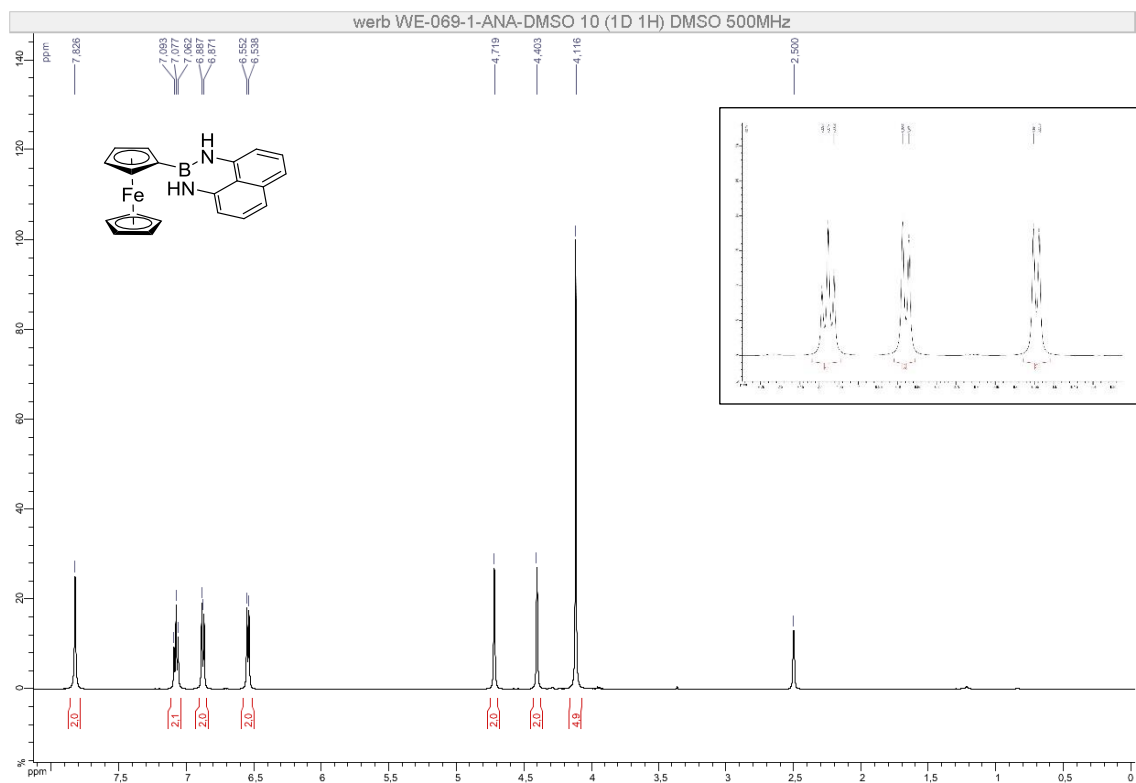
Ferroceneboronic acid (FcB(OH)₂ - 1)

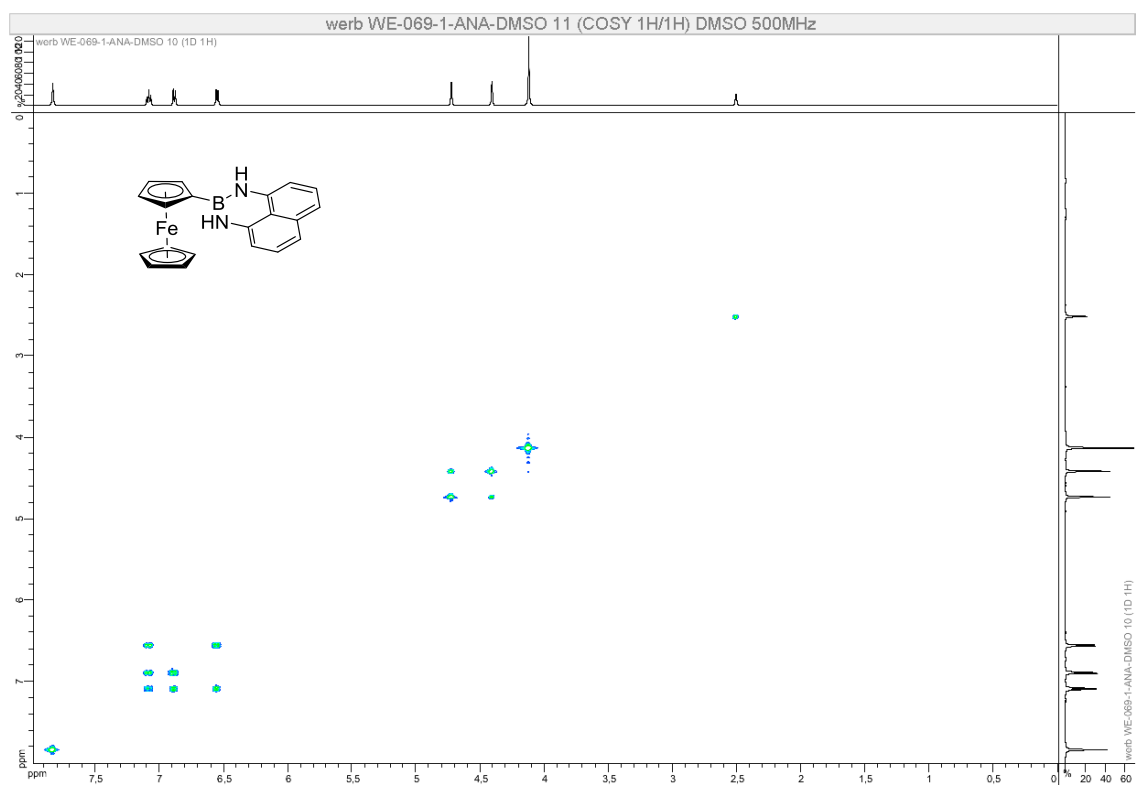
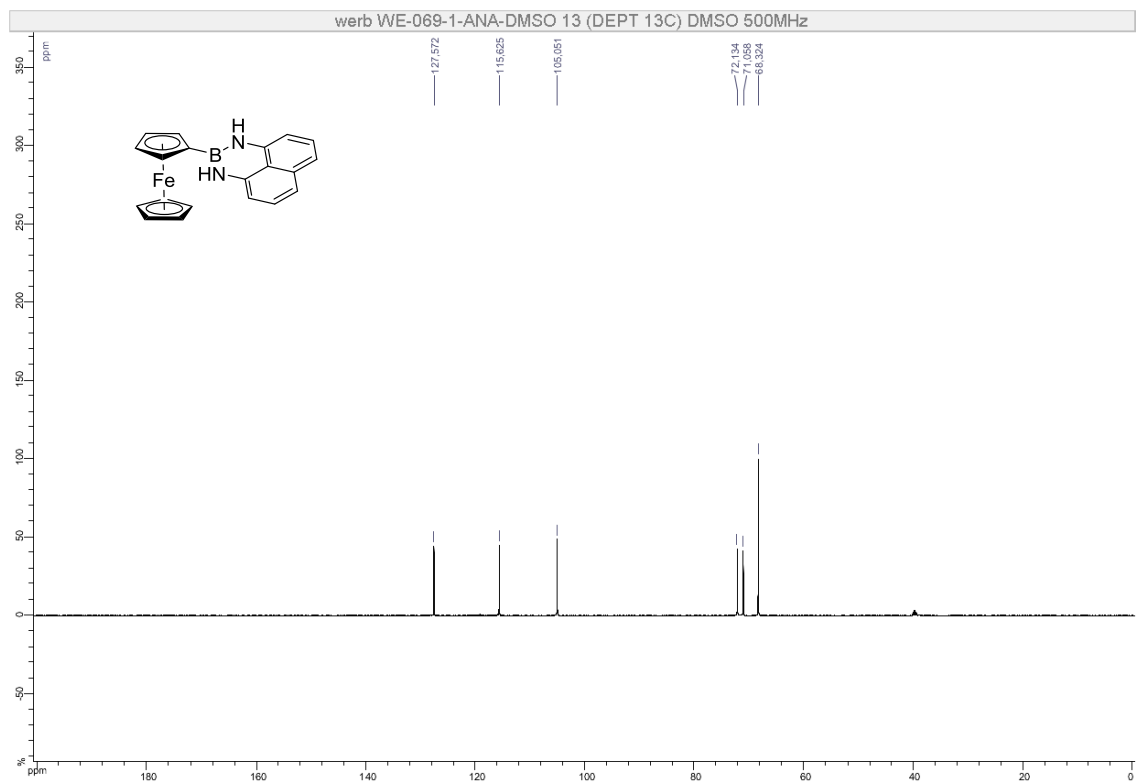


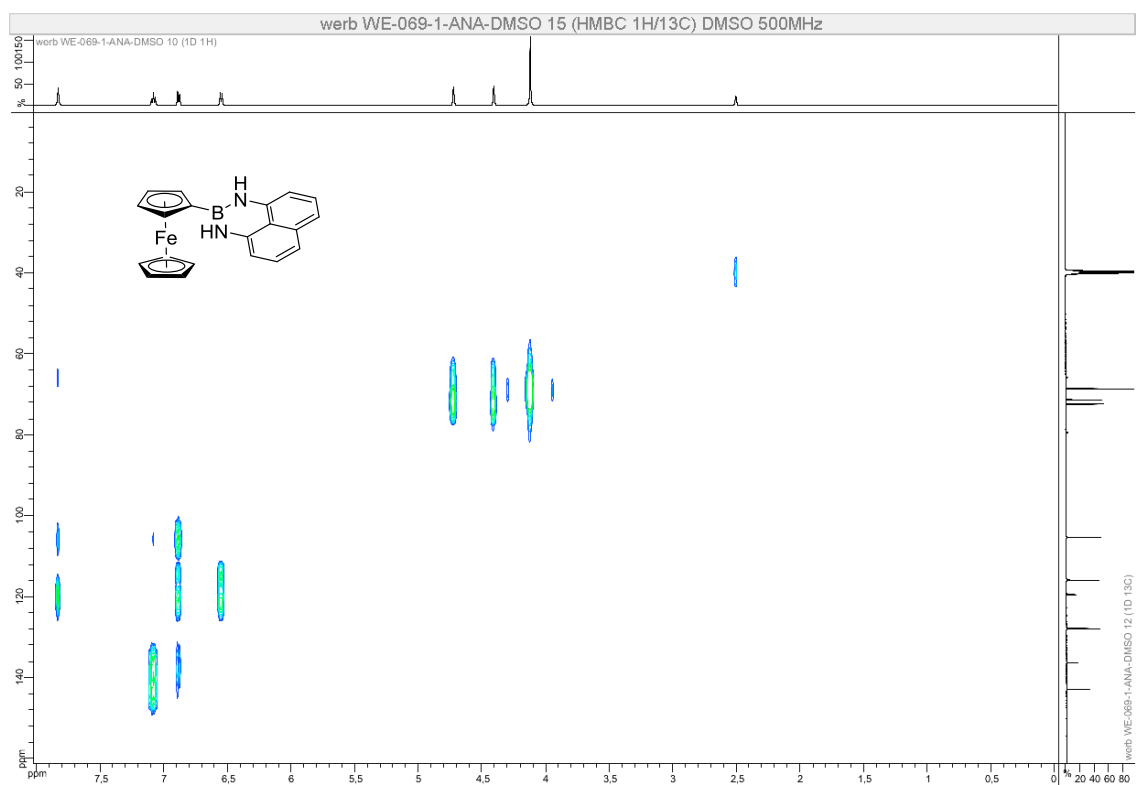
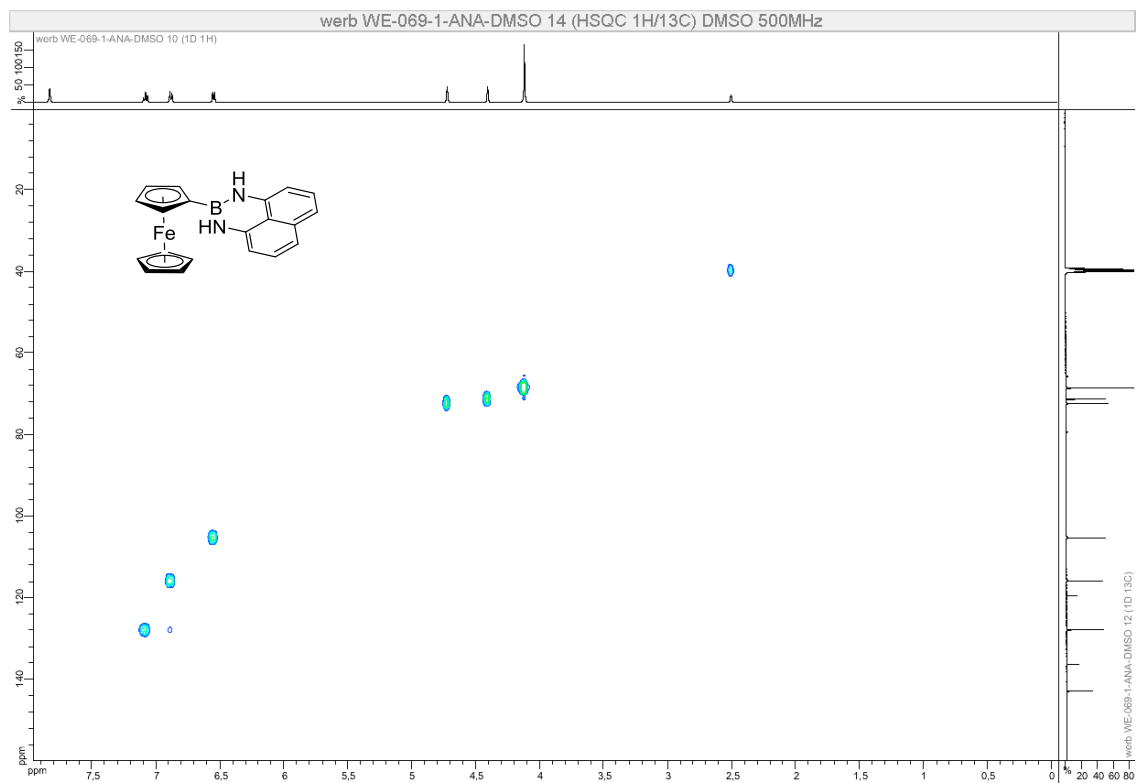


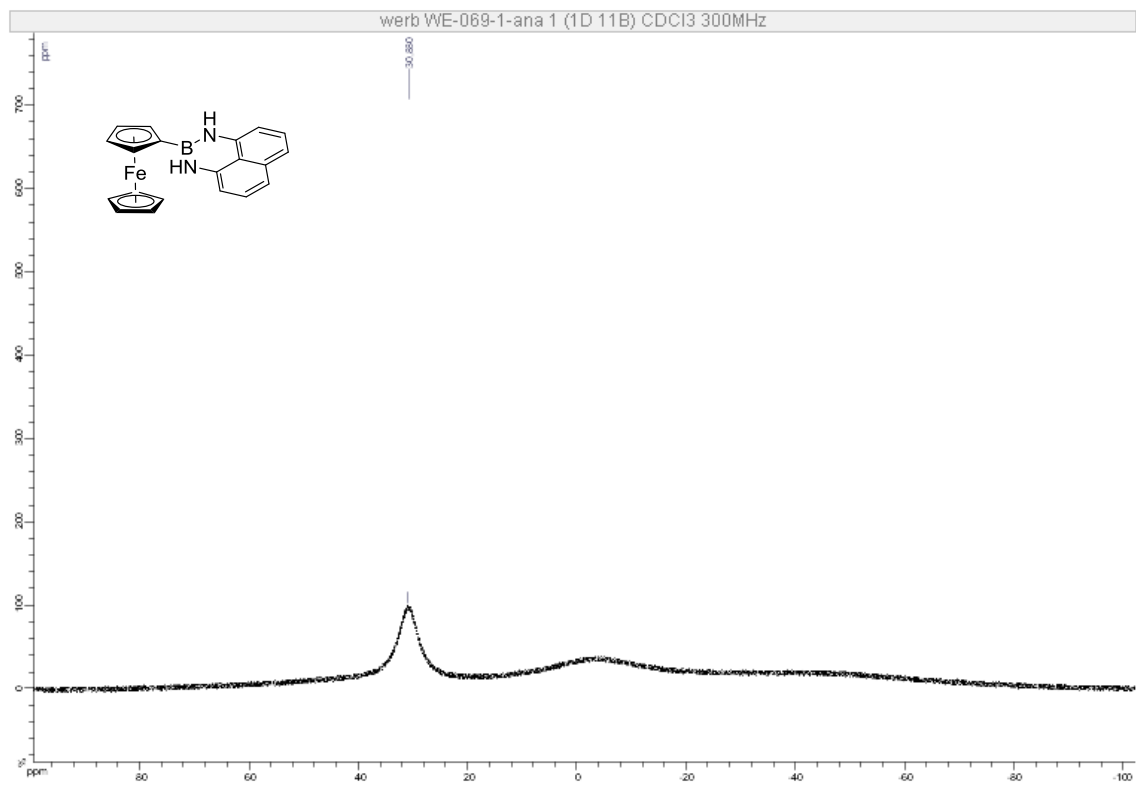
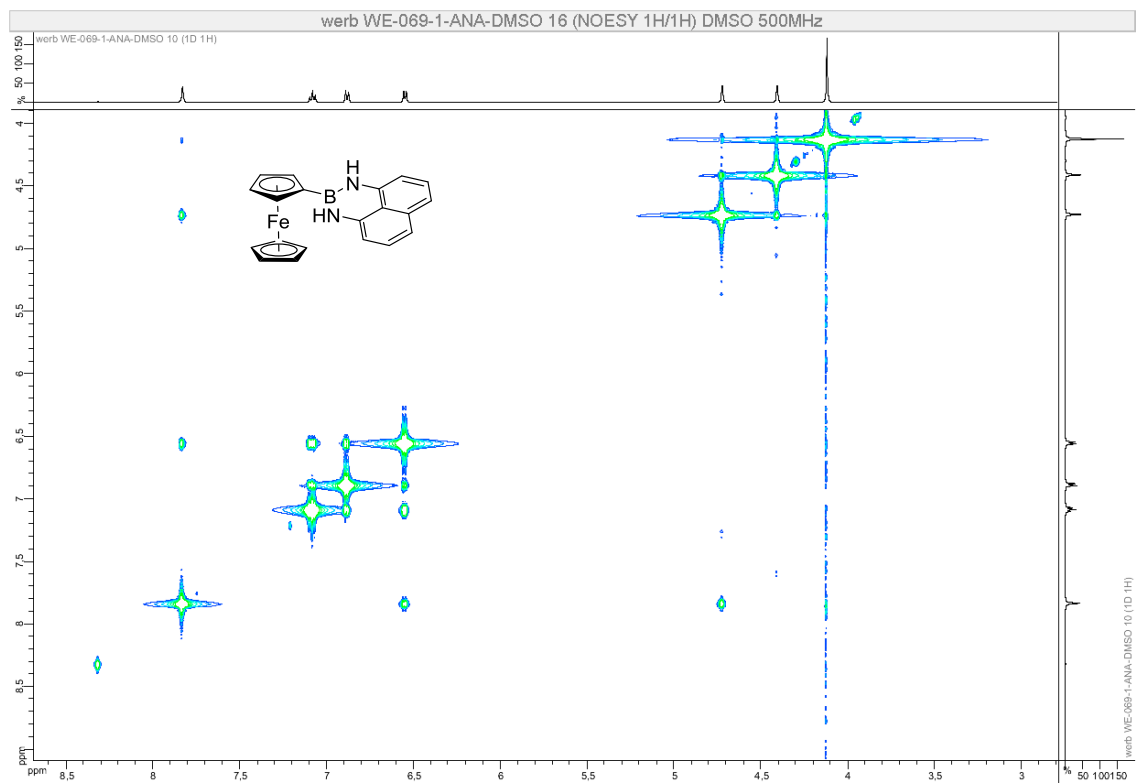


2-Ferrocenyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (FcB(dan)) - 15

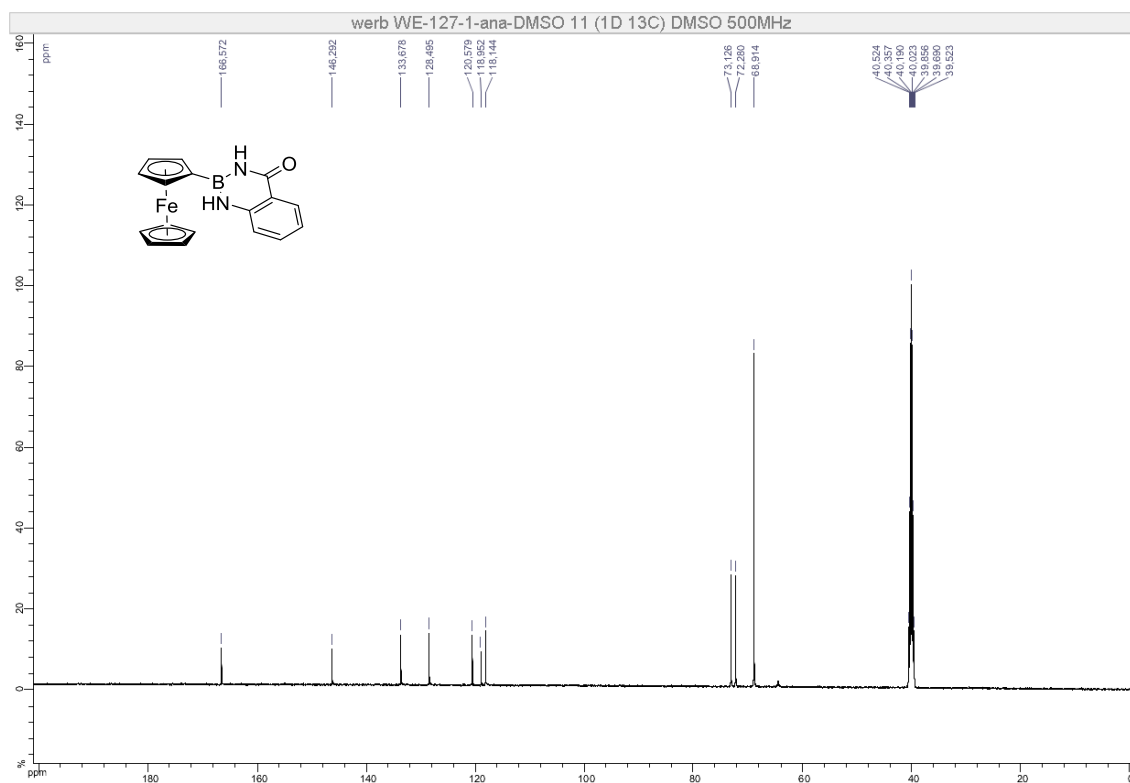
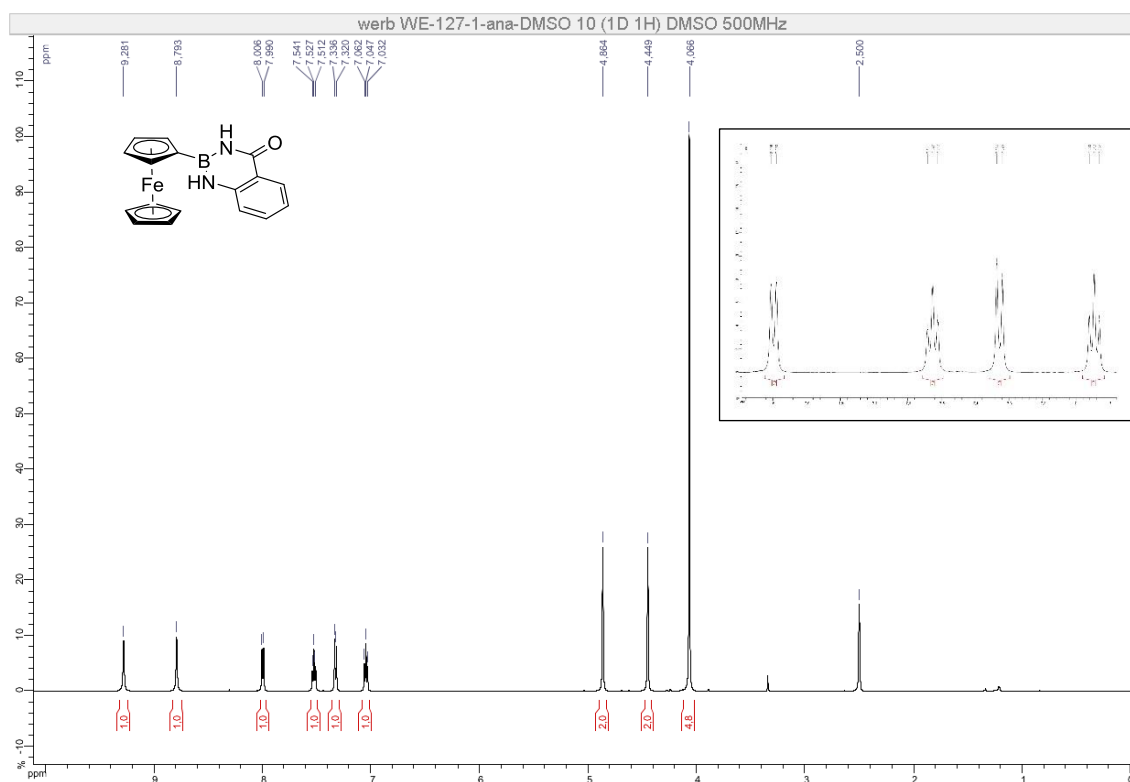


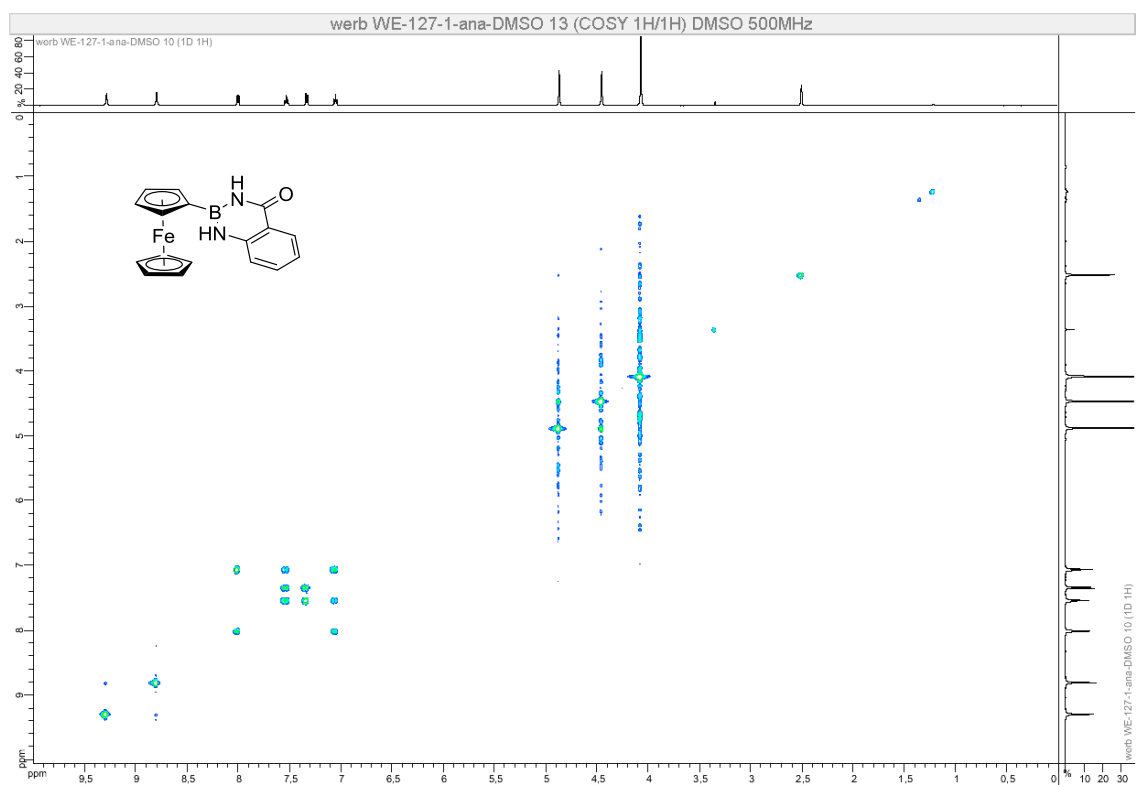
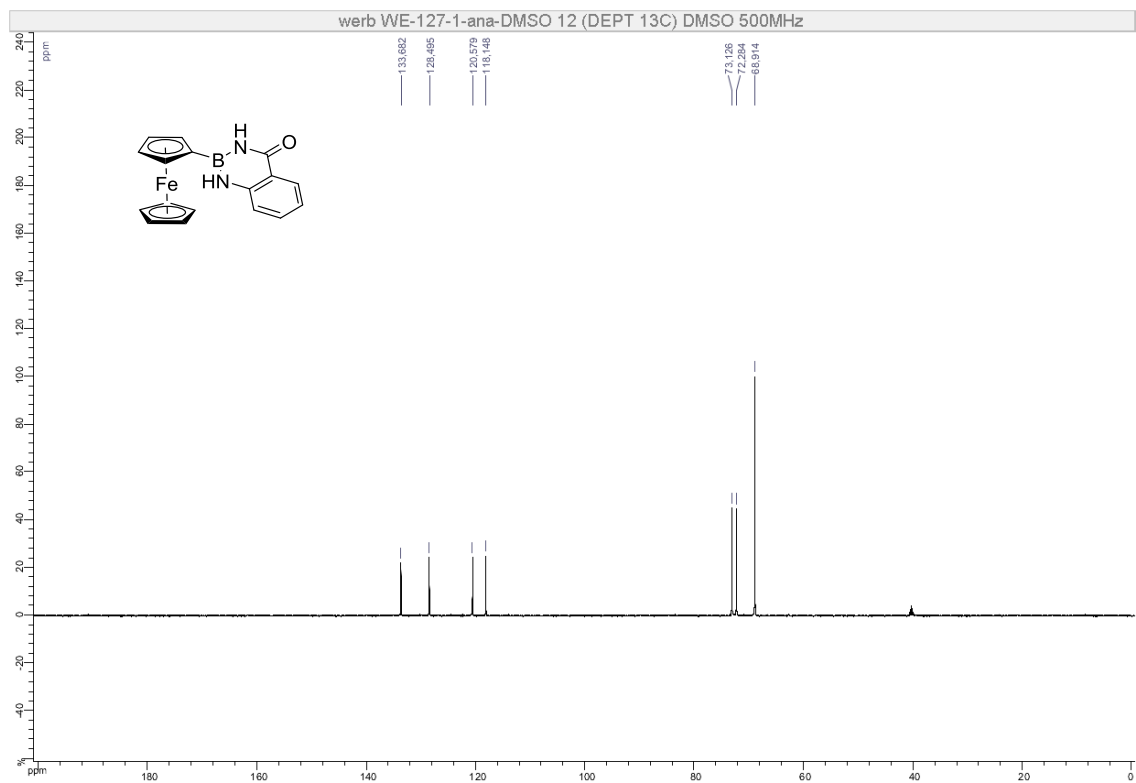


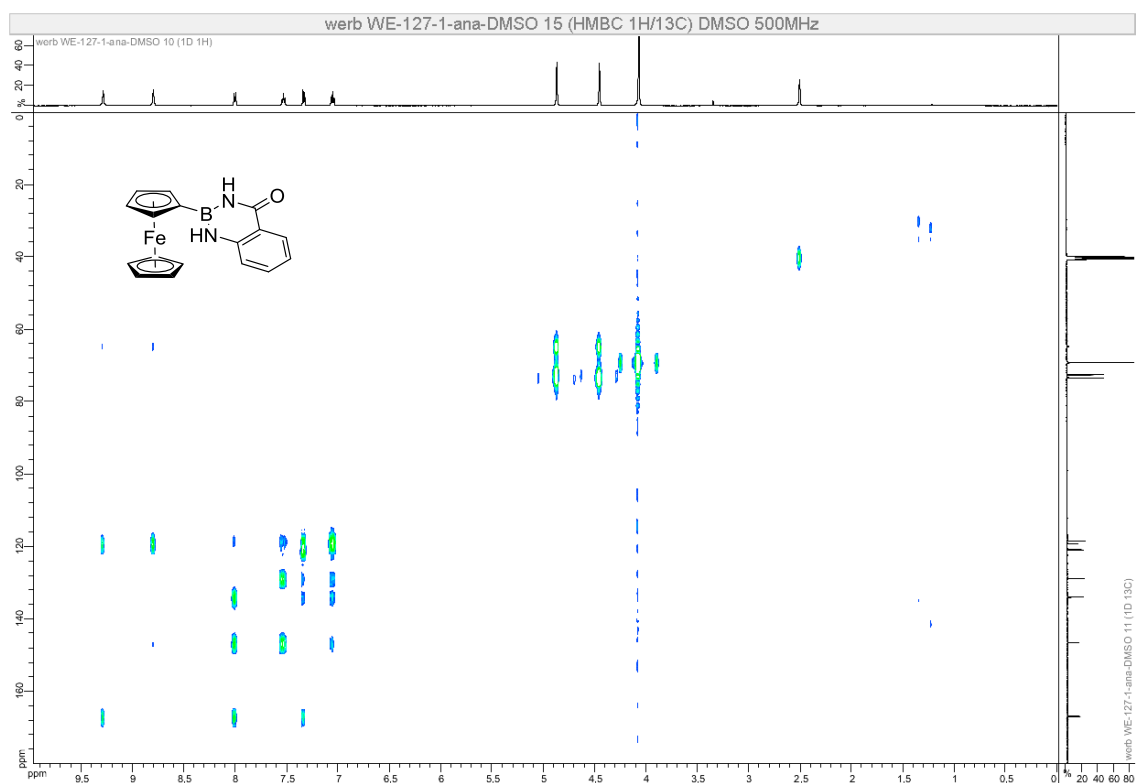
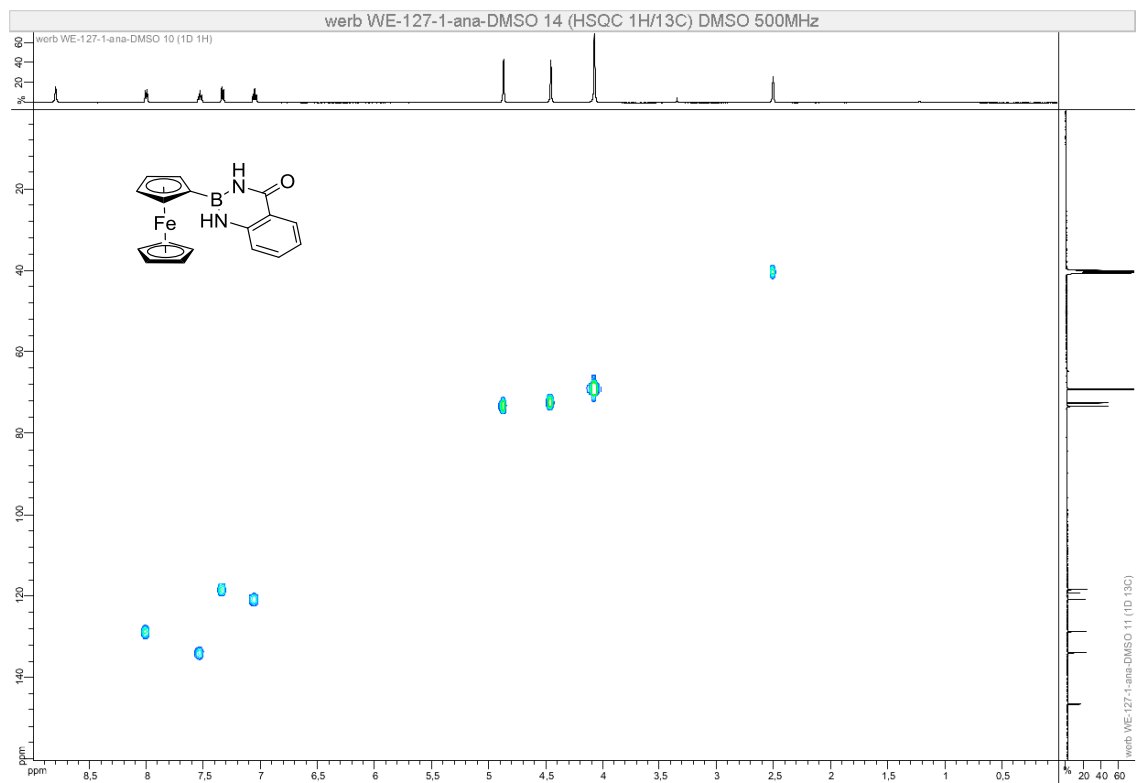


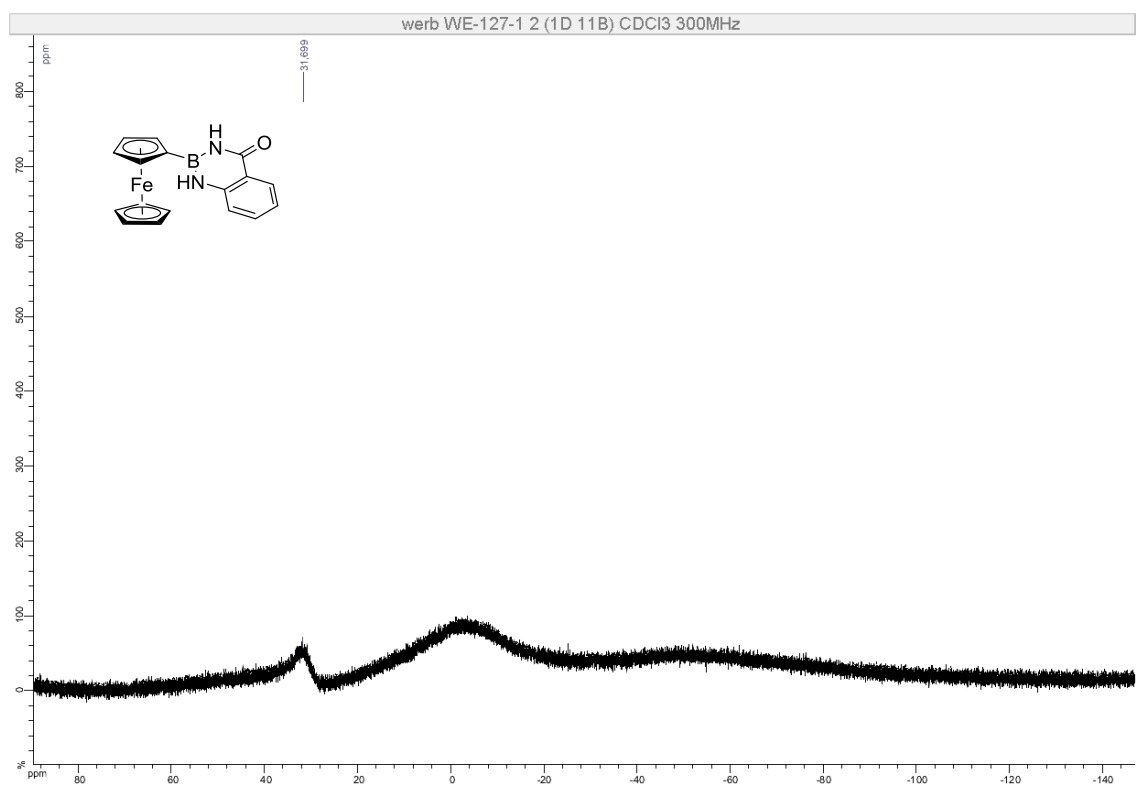
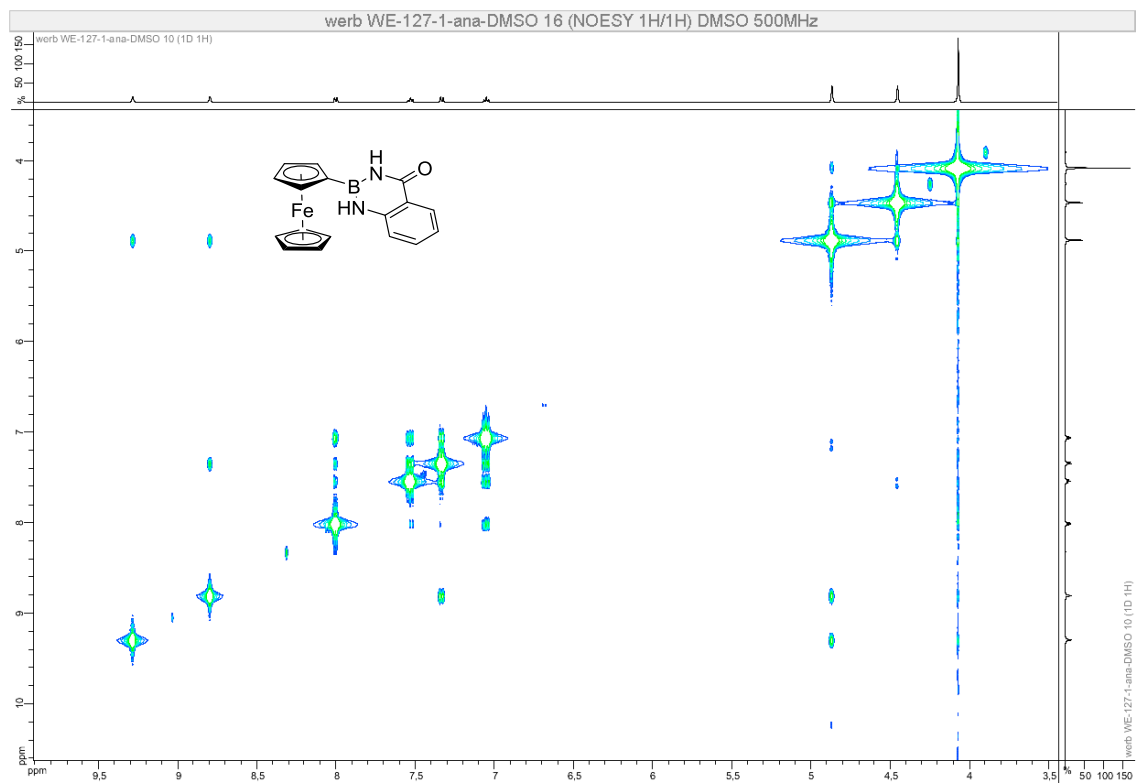


2-Ferrocenyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (FcB(aam) - 16)

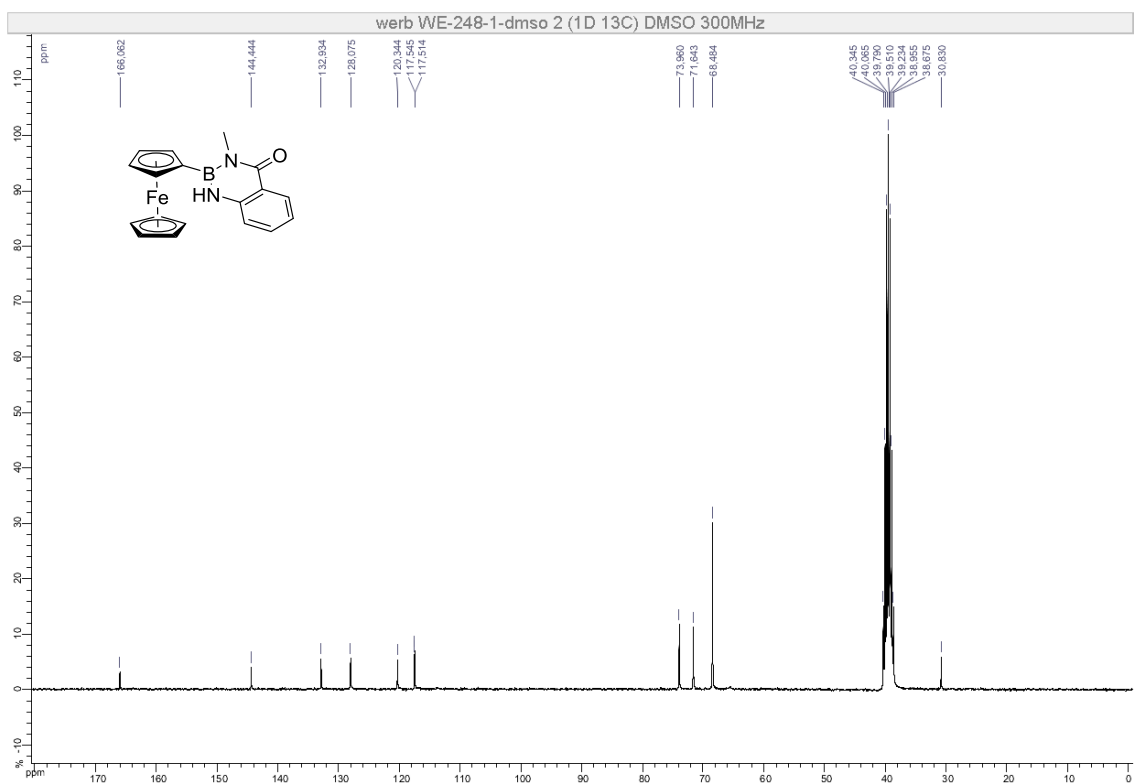
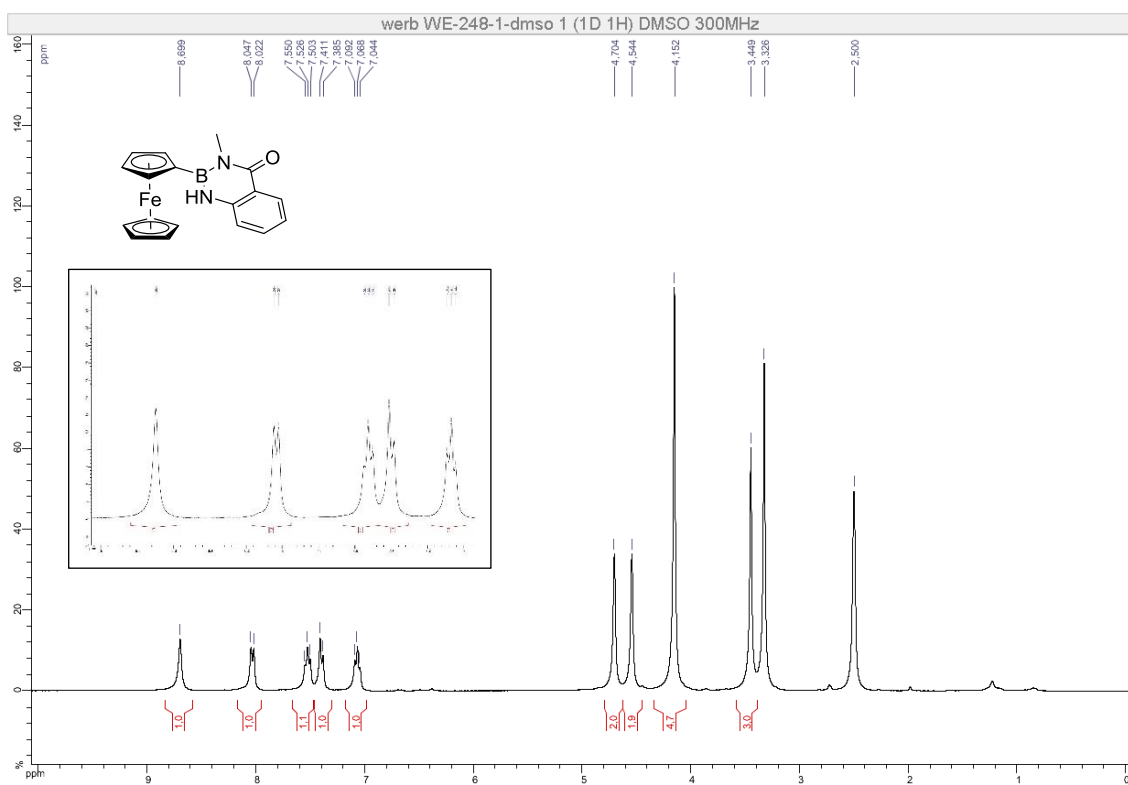


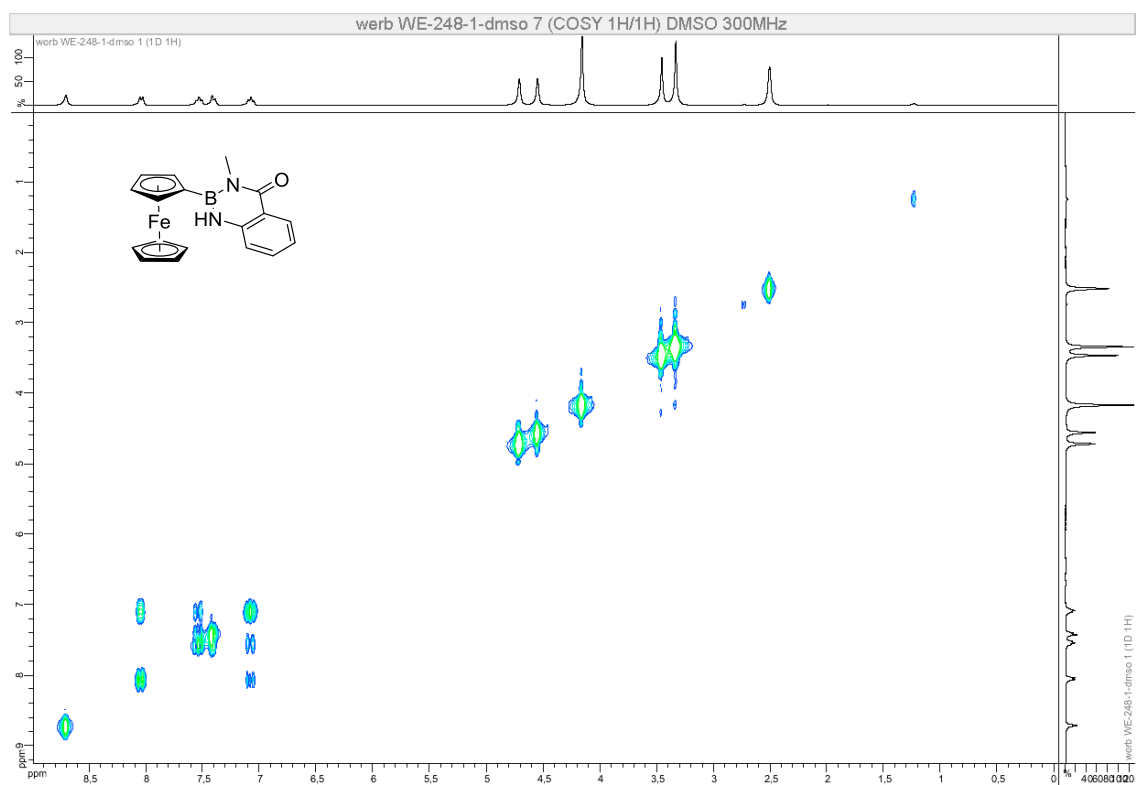
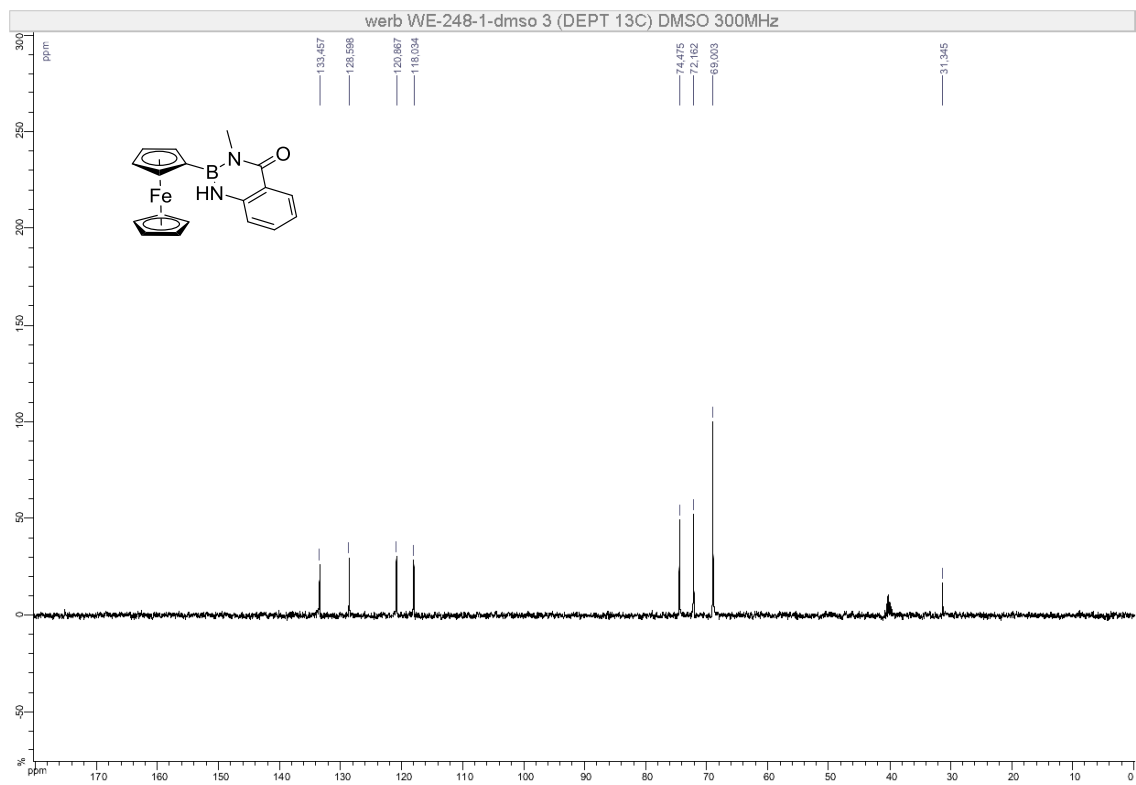


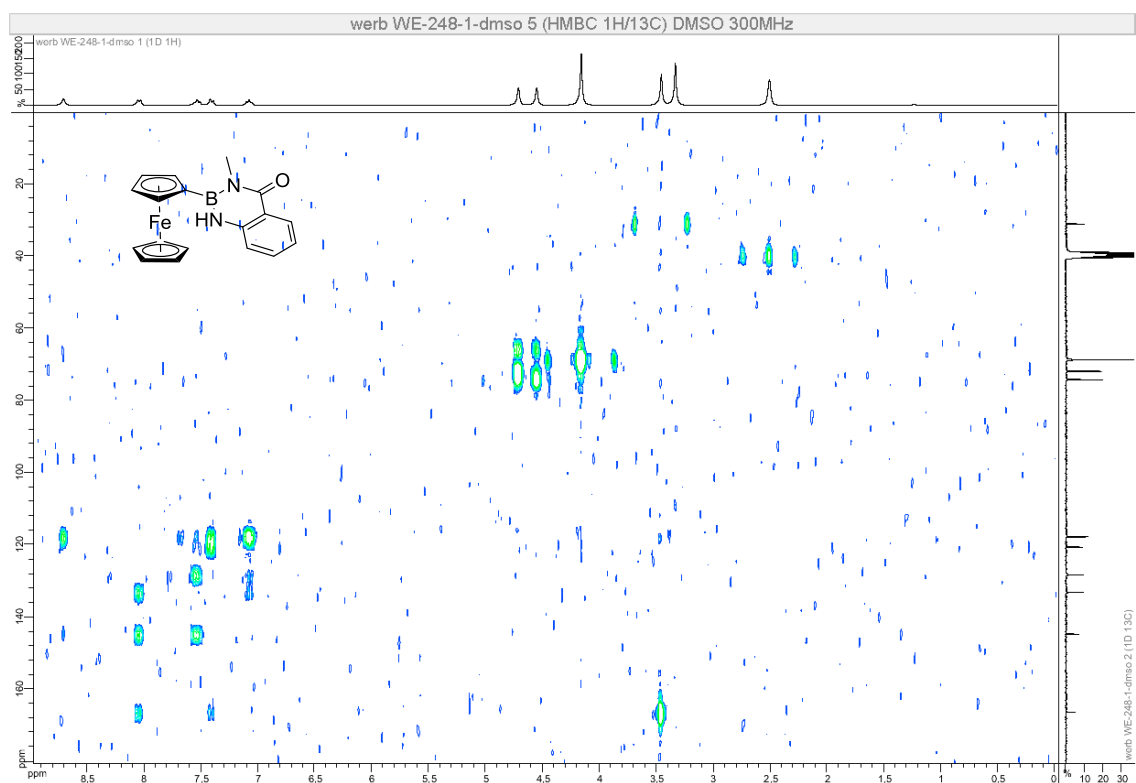
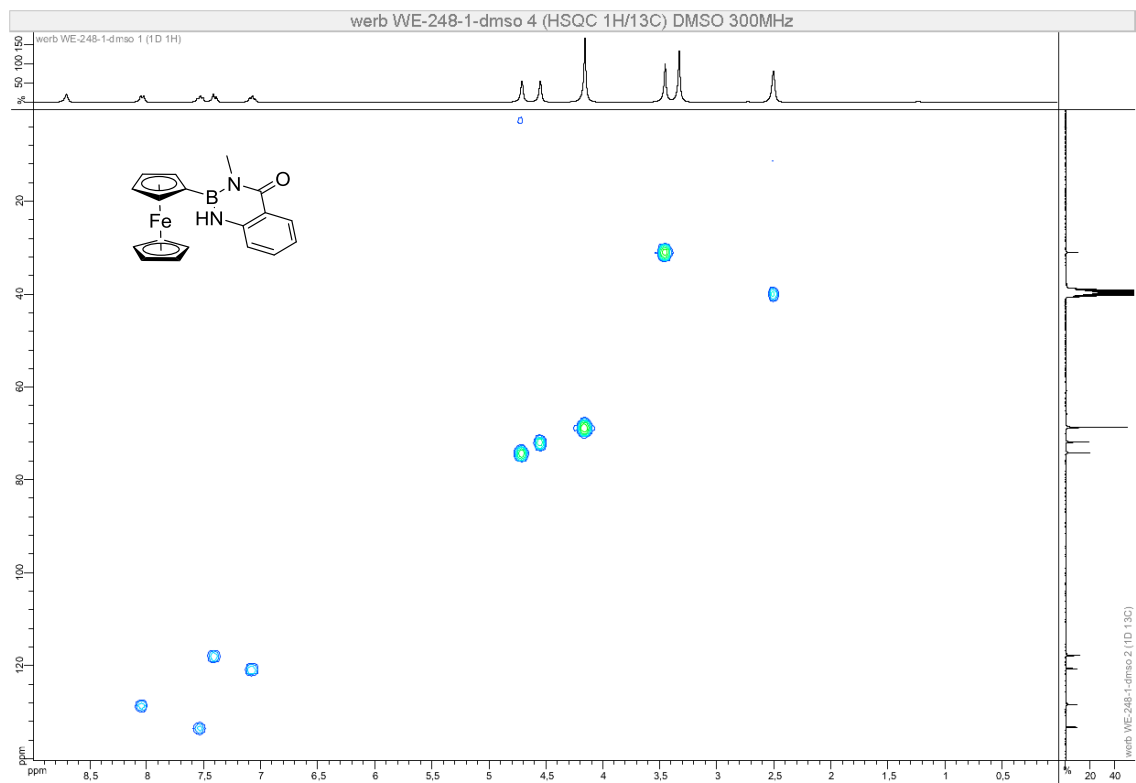


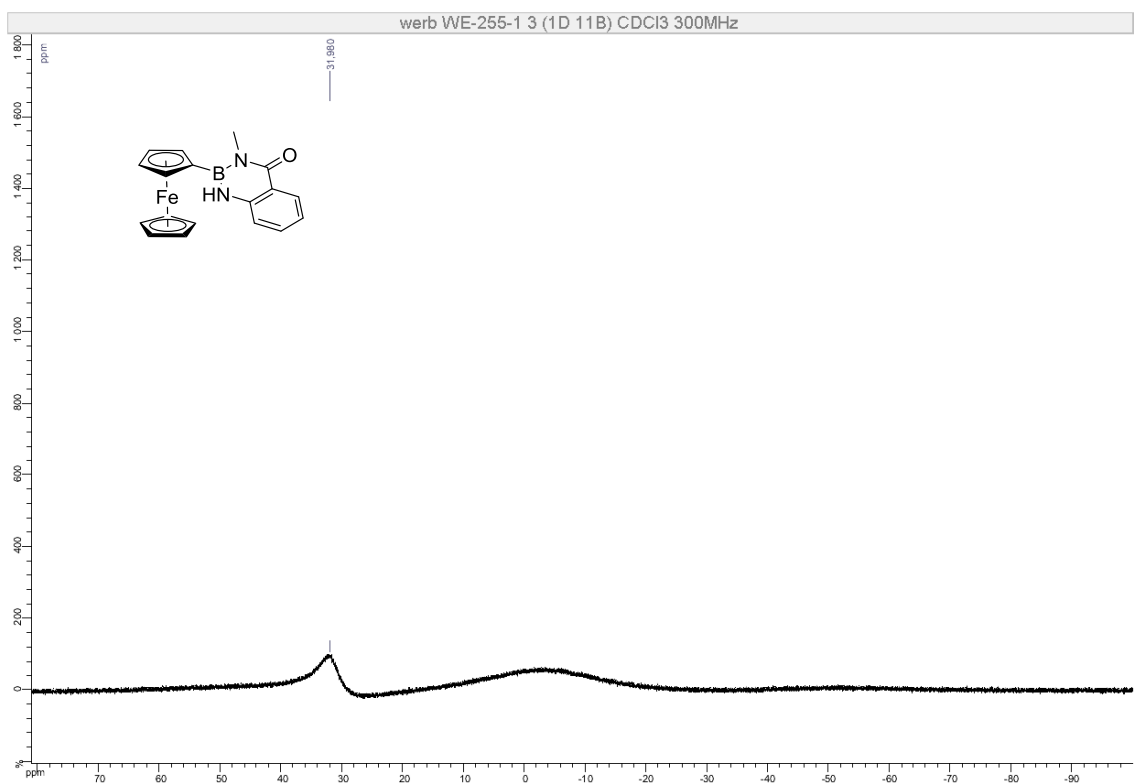
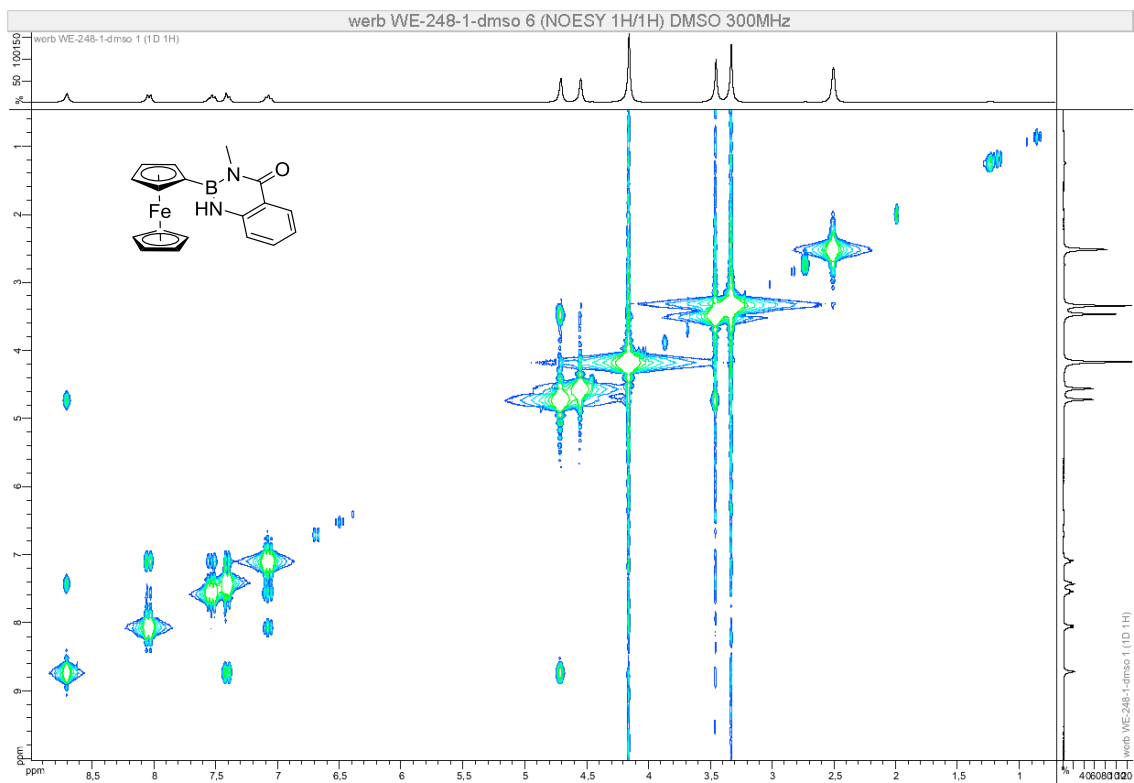


3-Methyl-2-ferrocenyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (FcB(Me-aam) - 17)

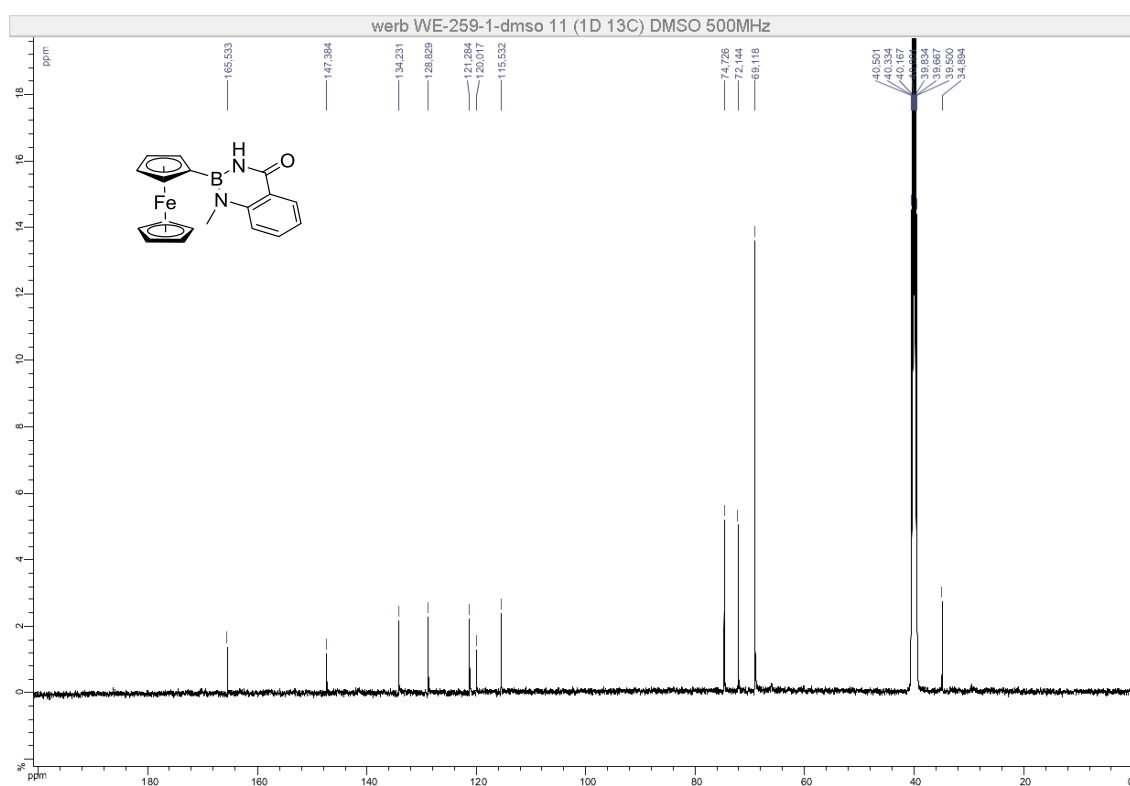
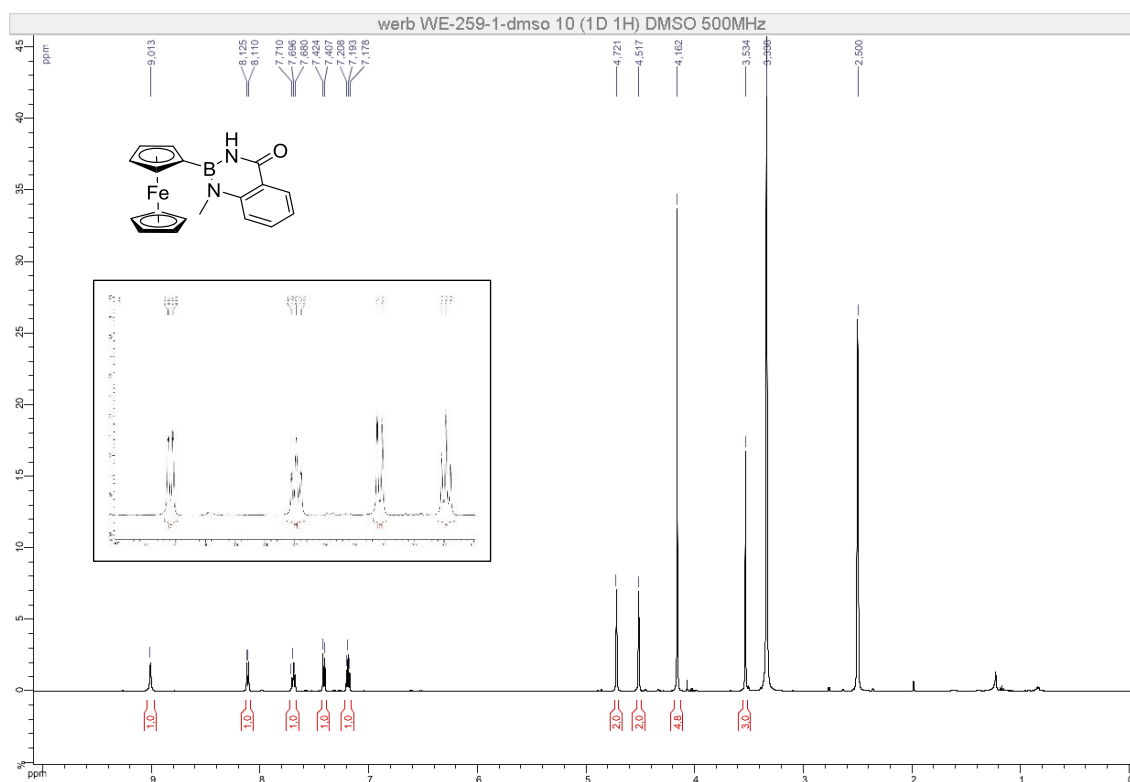


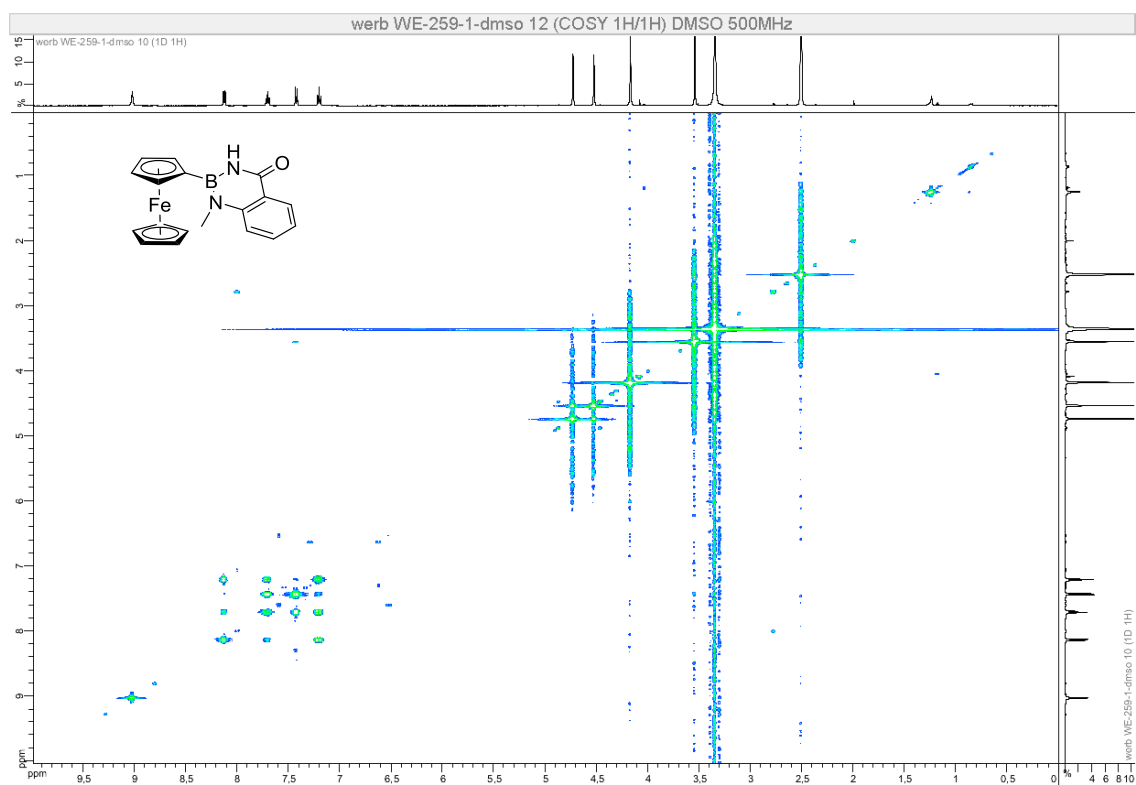
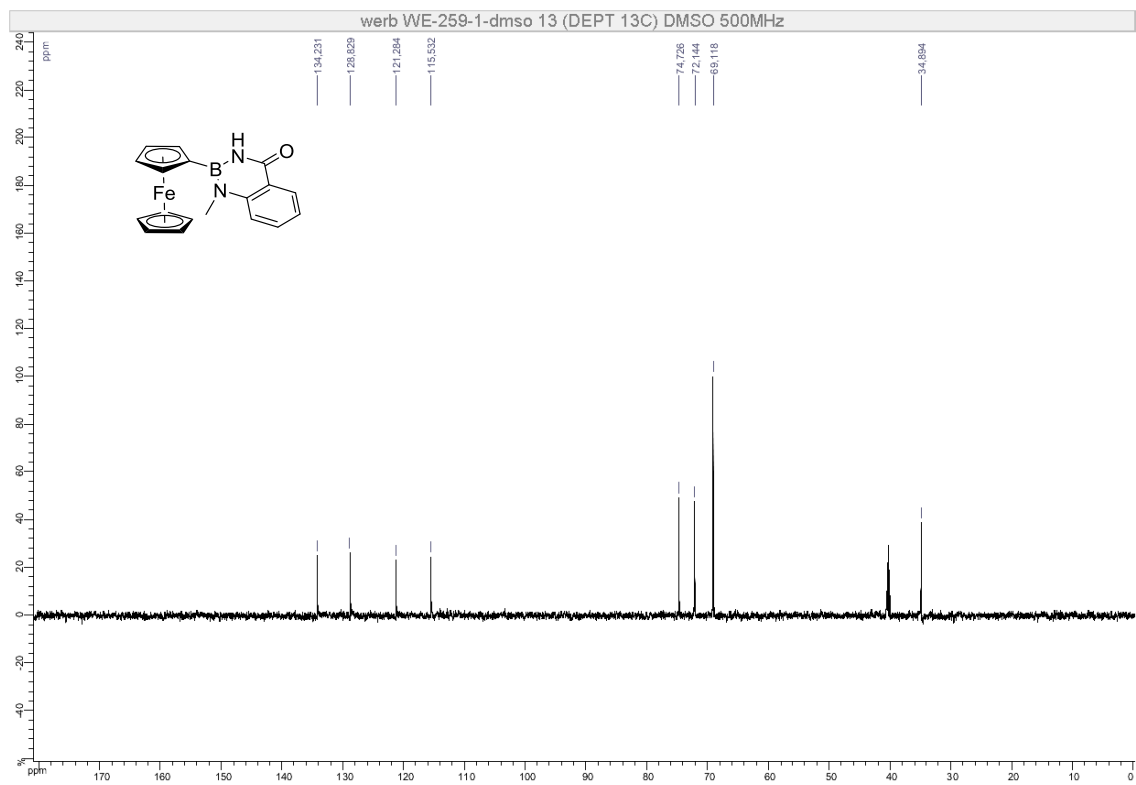


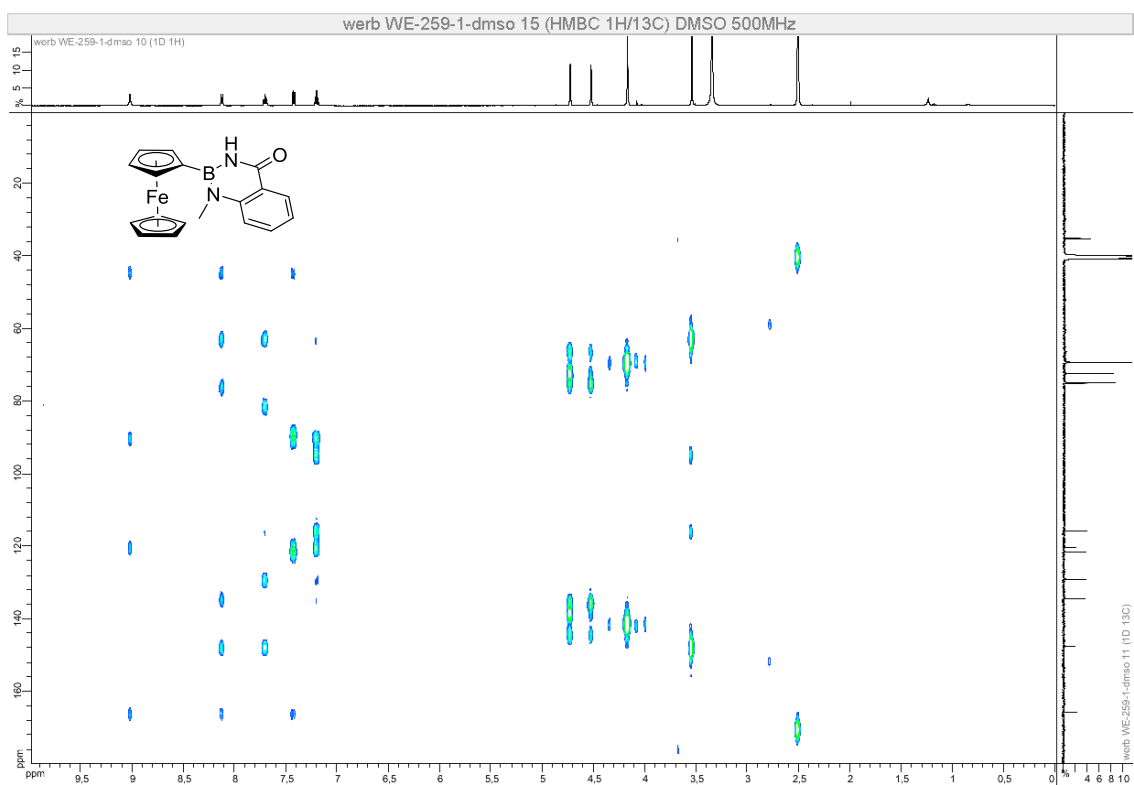
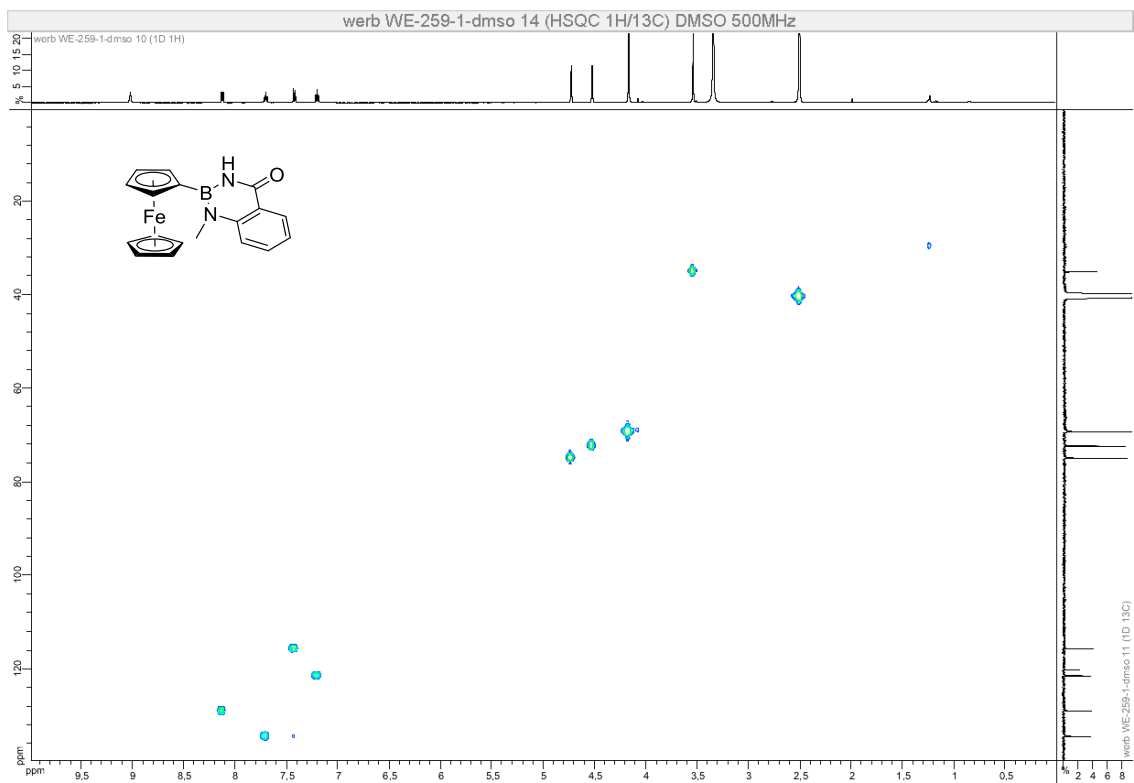


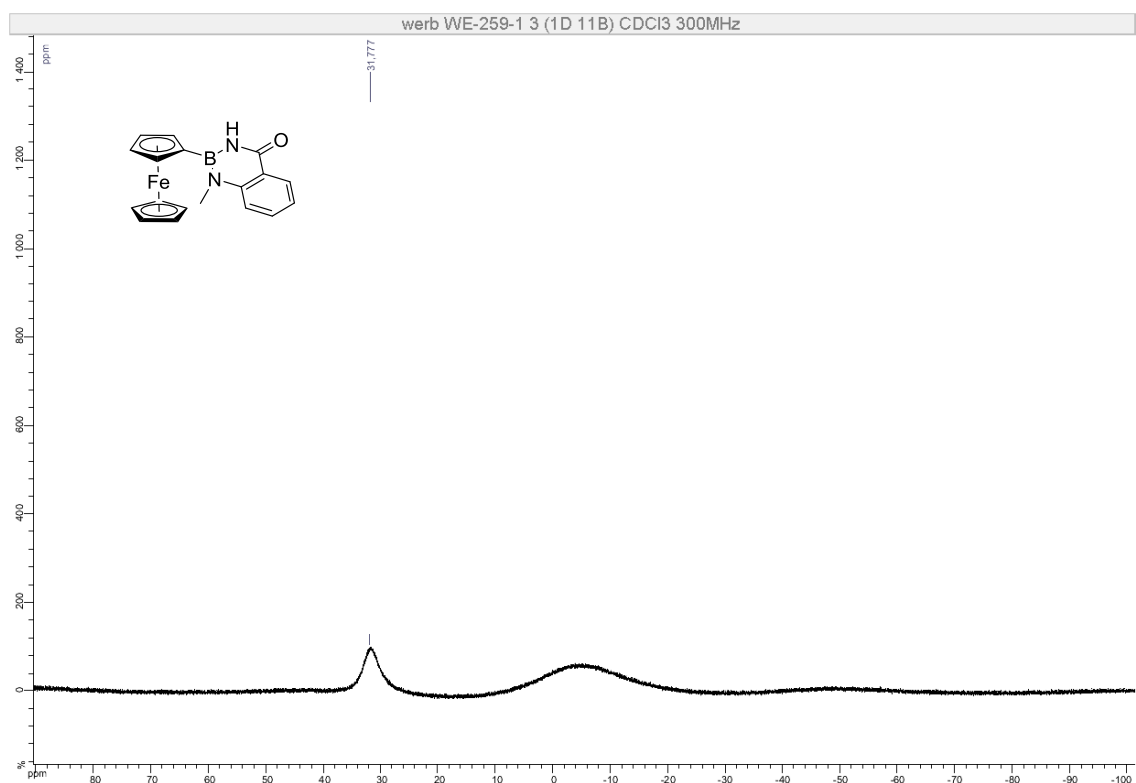
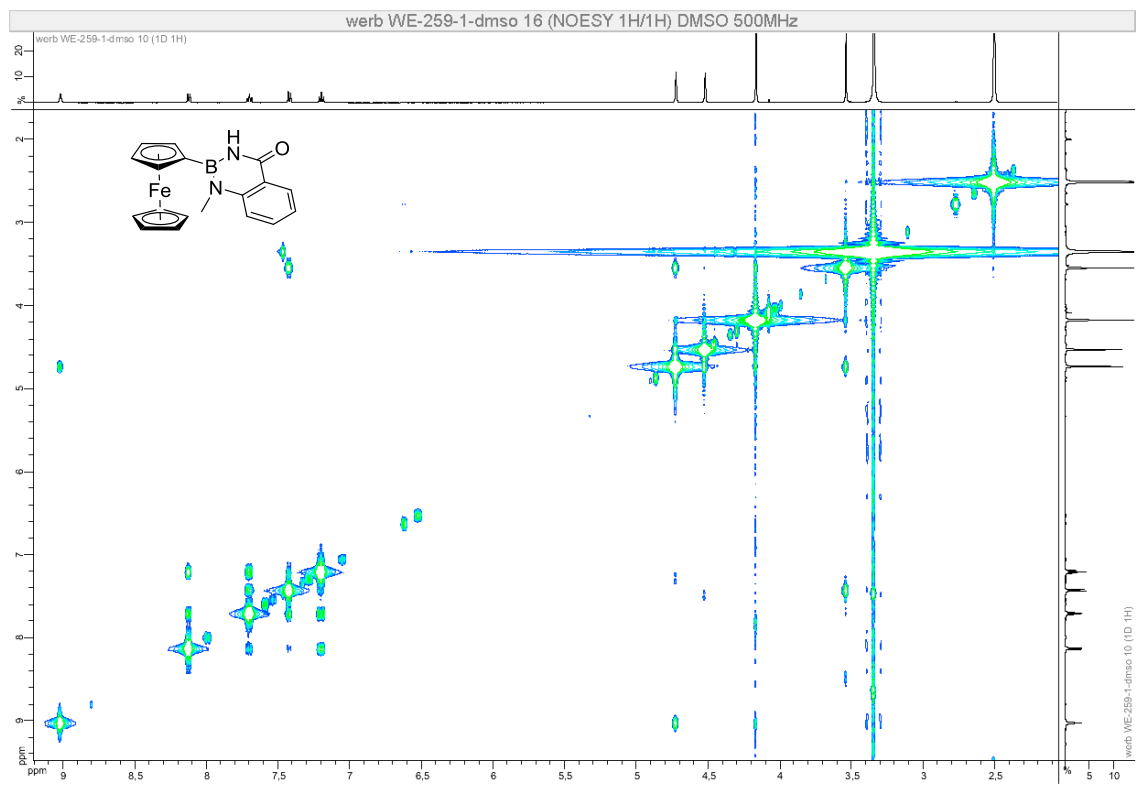


1-Methyl-2-ferrocenyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (FcB(Me-aam) – 18)

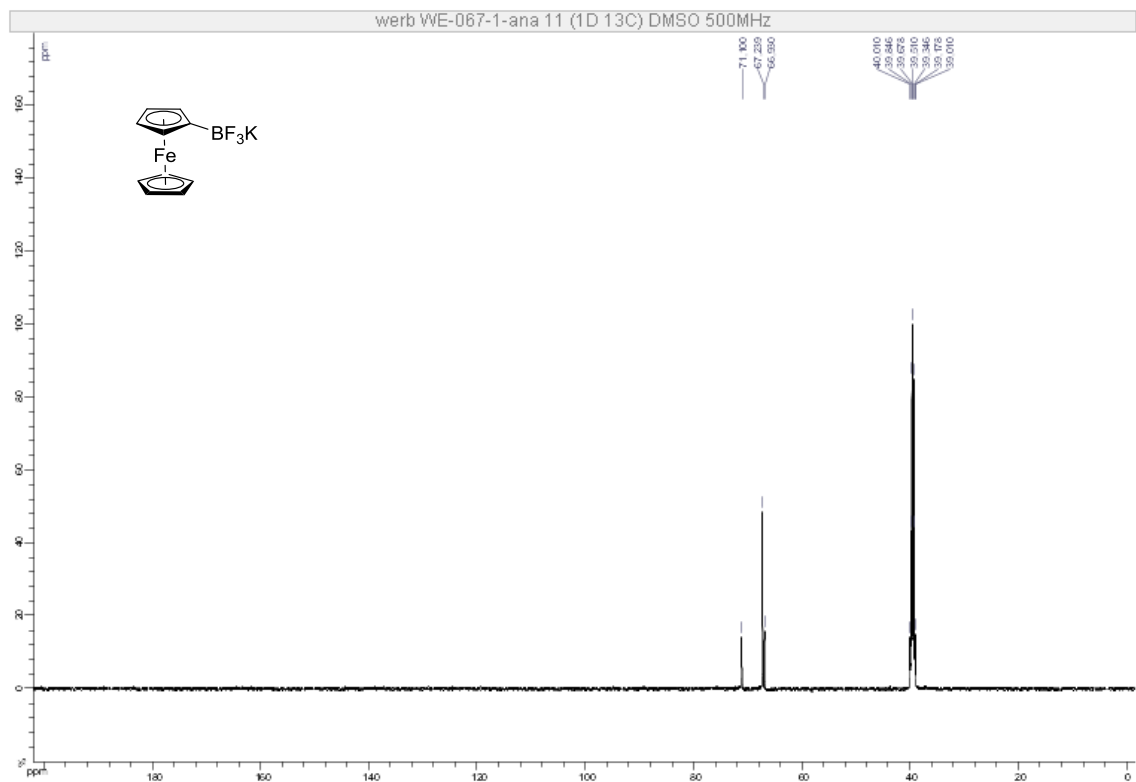
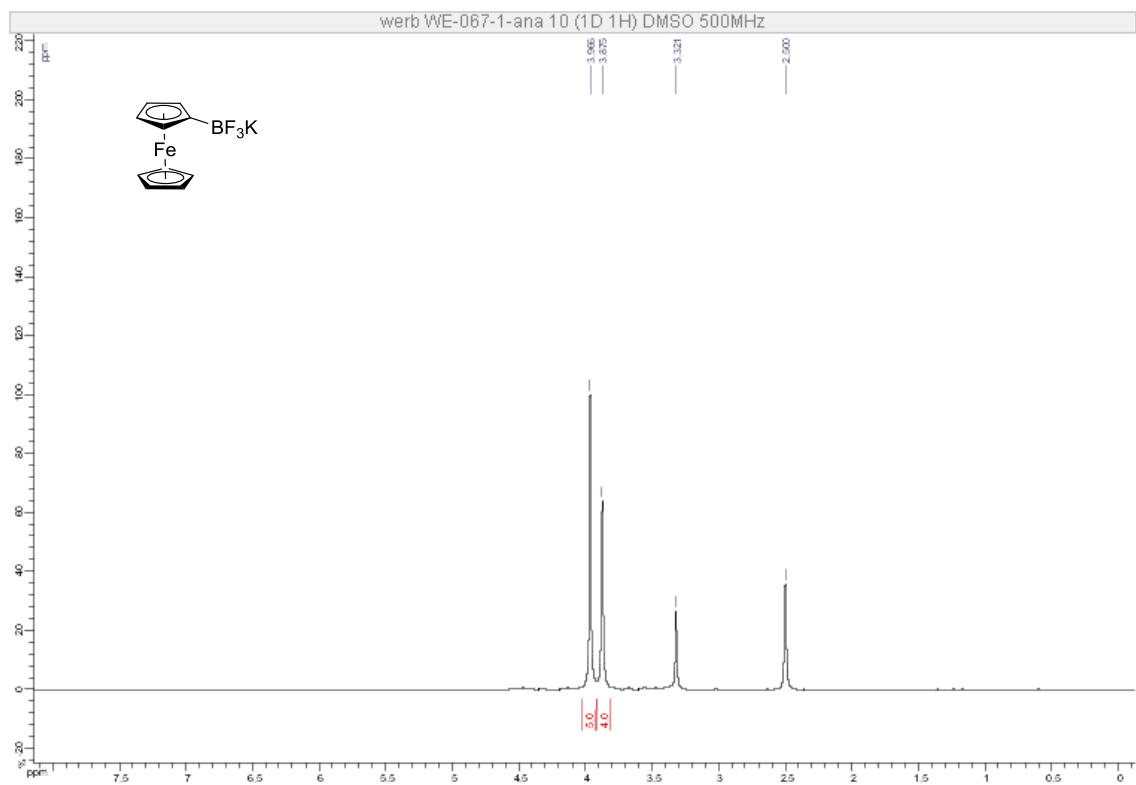


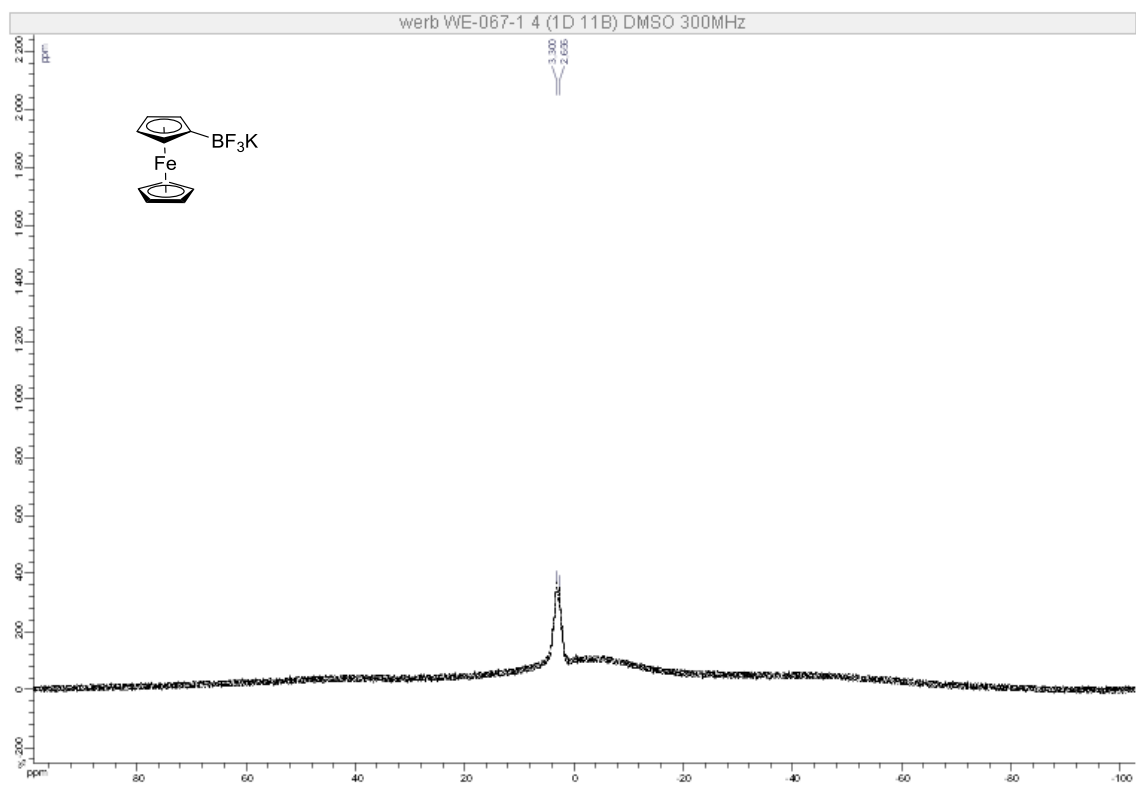
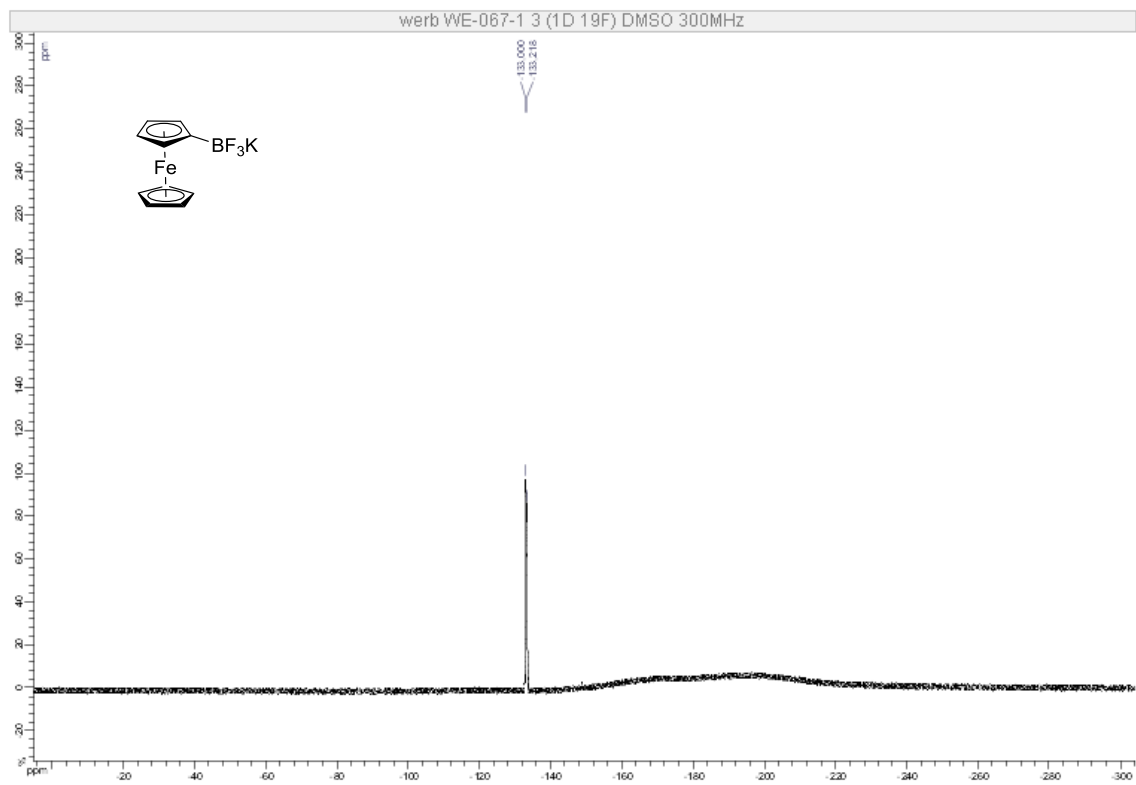




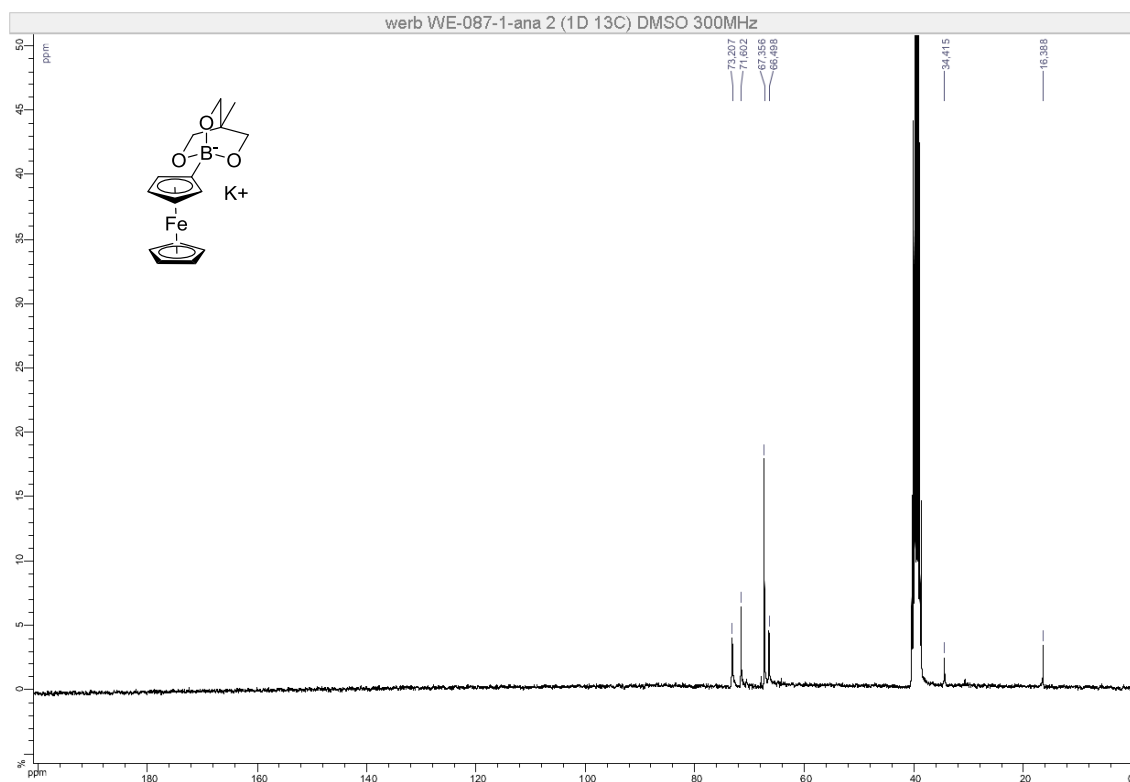
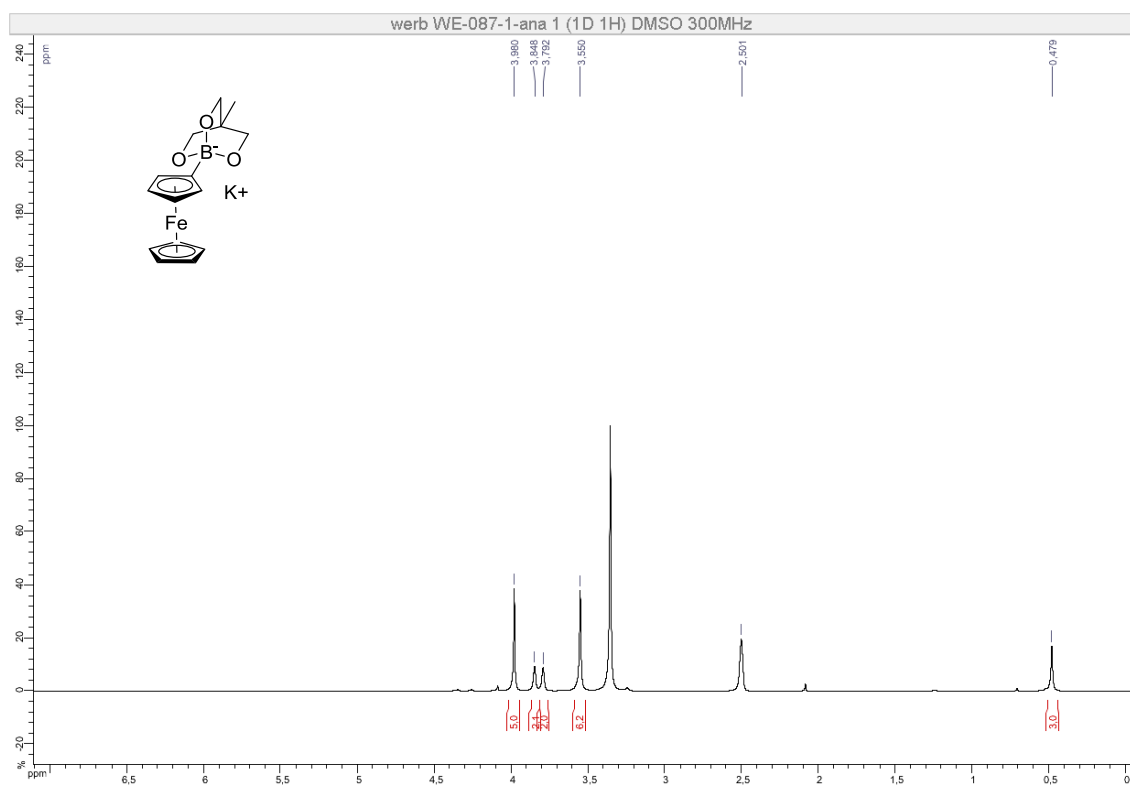


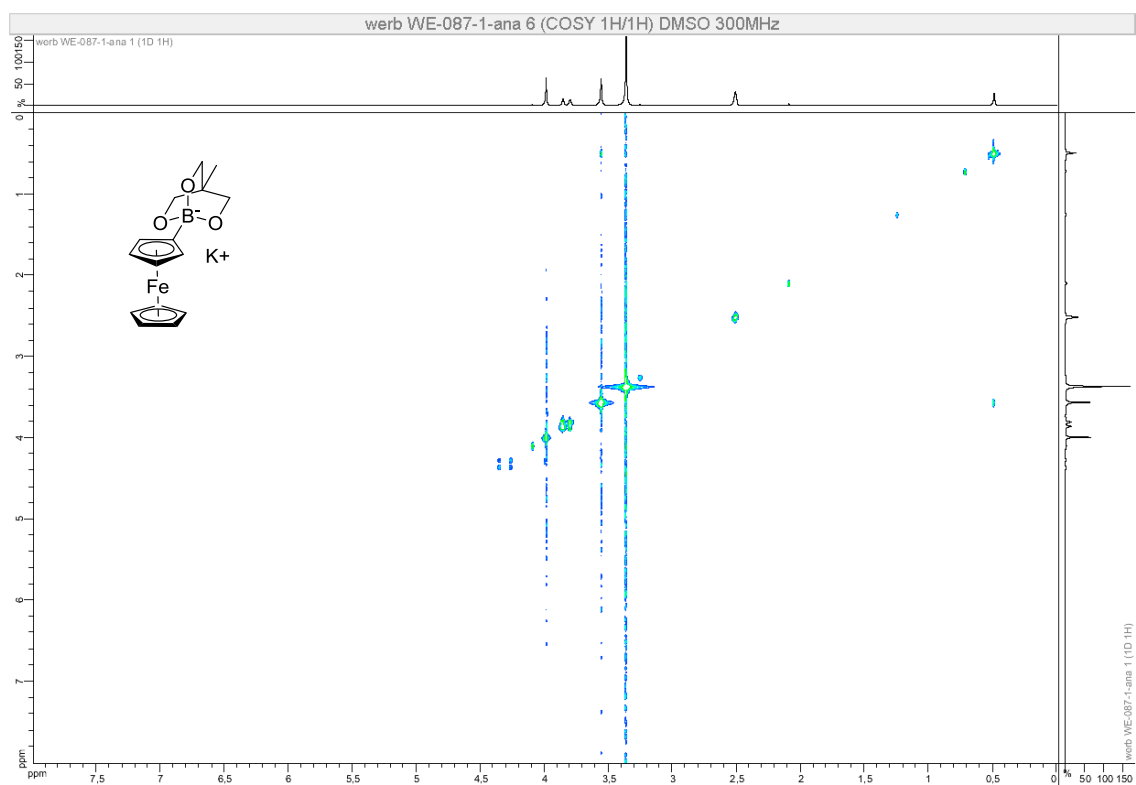
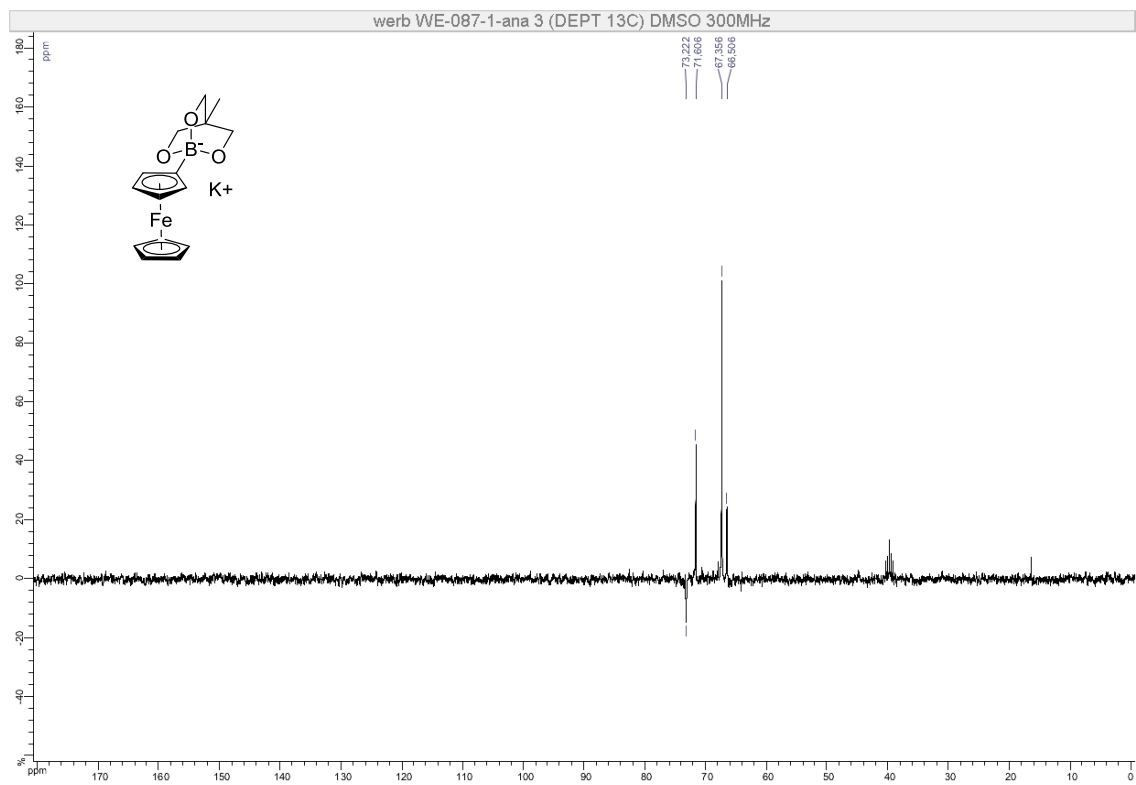
Potassium ferrocenyltrifluoroborate (FcBF₃K - 19).

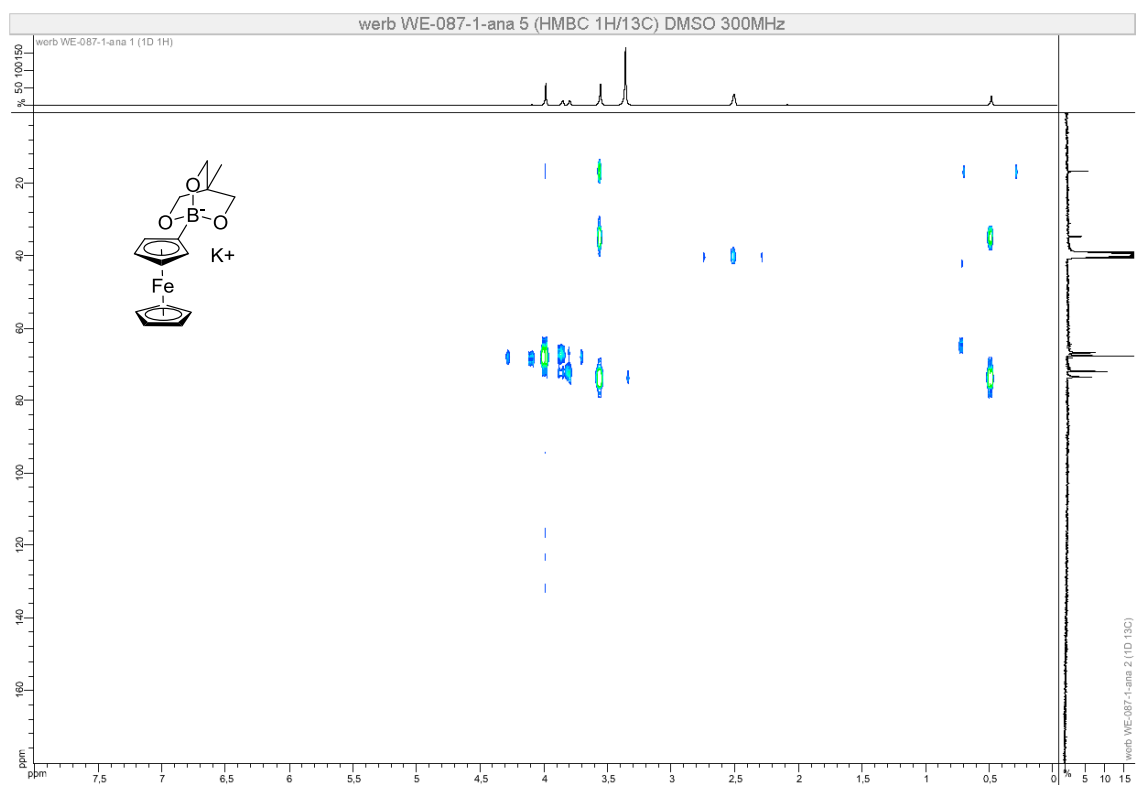
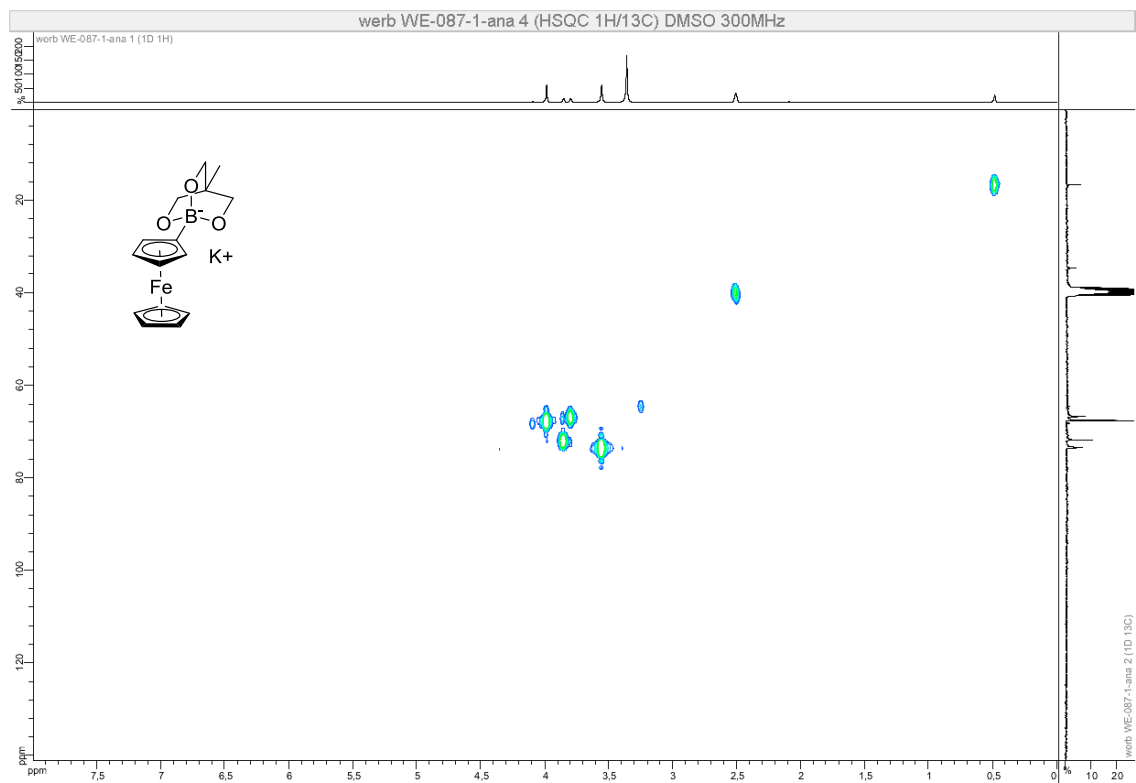


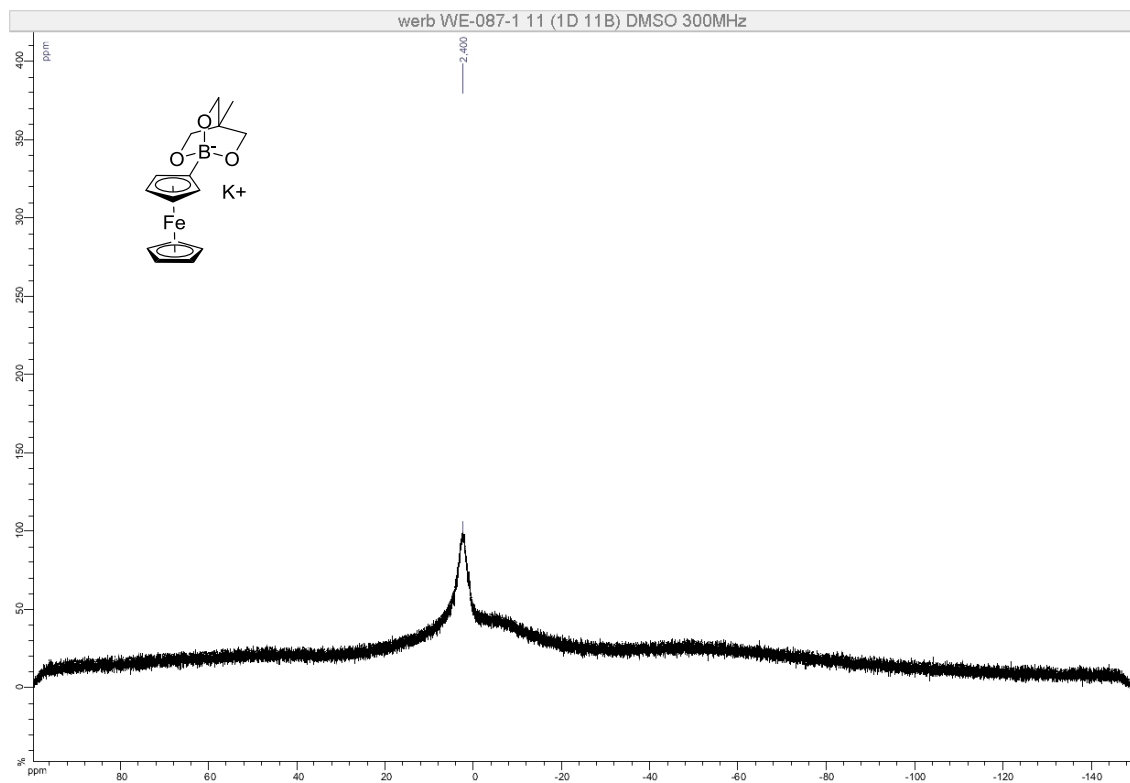


4-Methyl-1-ferrocenyl-2,6,7-trioxa-1-borabicyclo[2.2.2]octan-1-uide (FcB(triolborate) - 20)

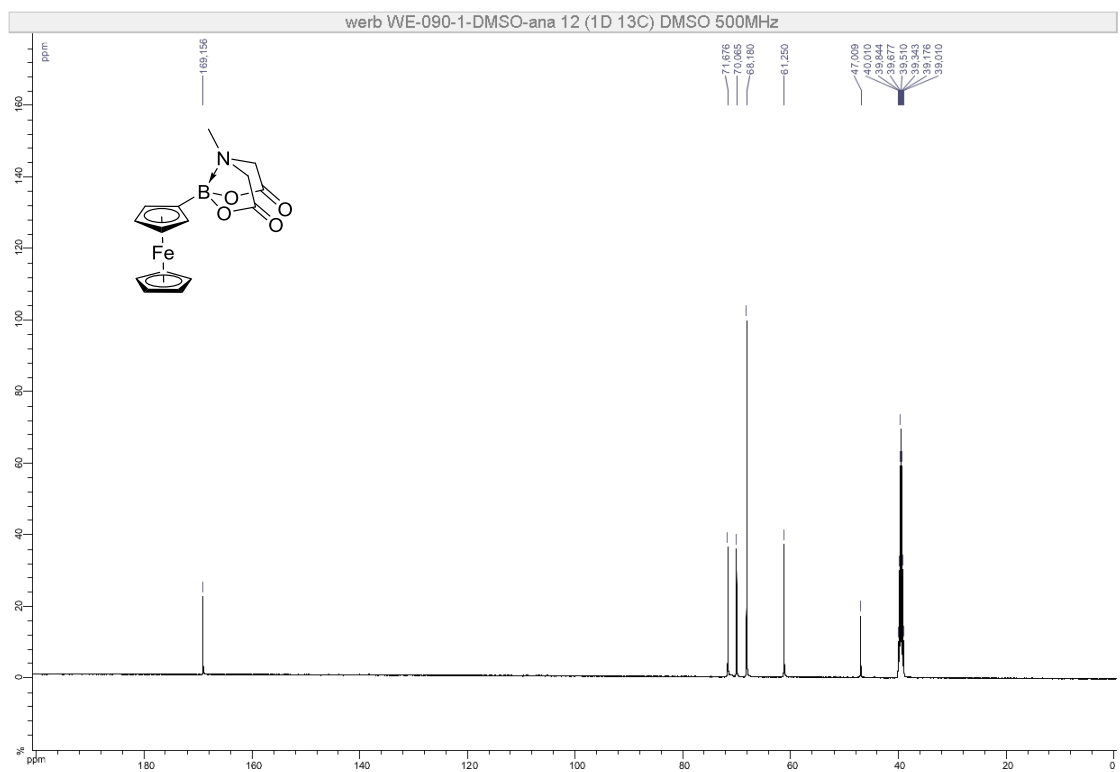
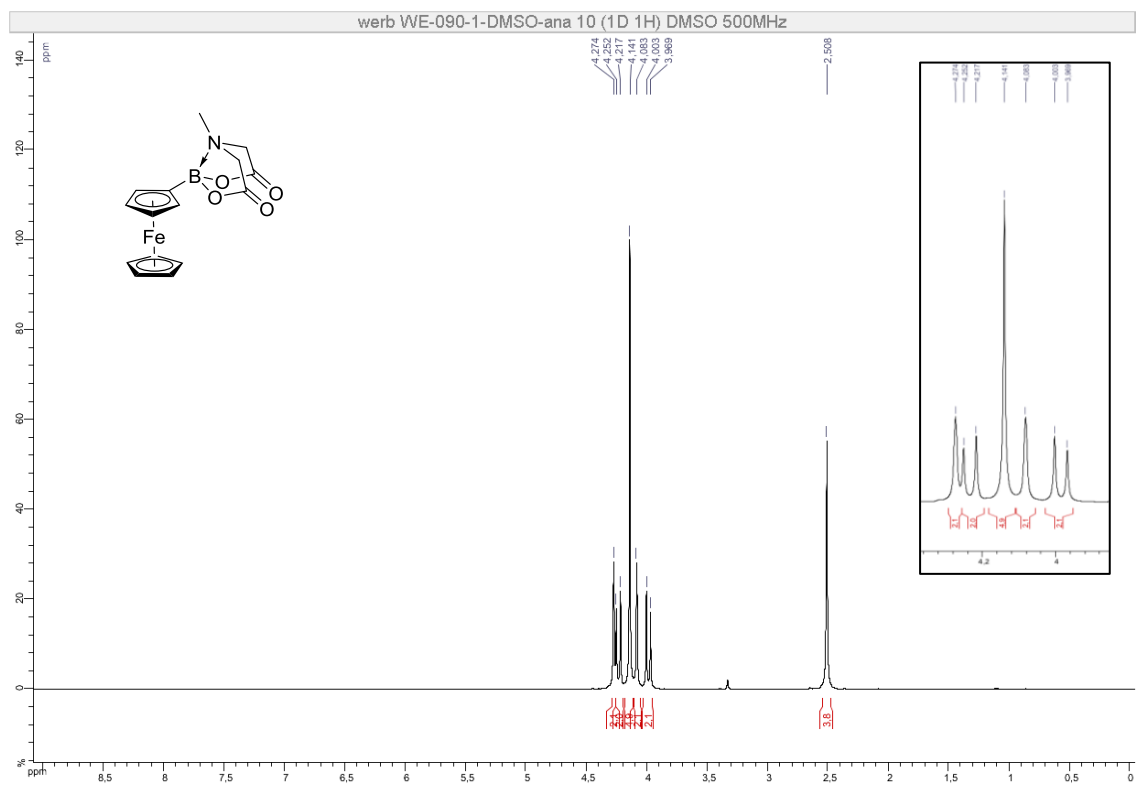


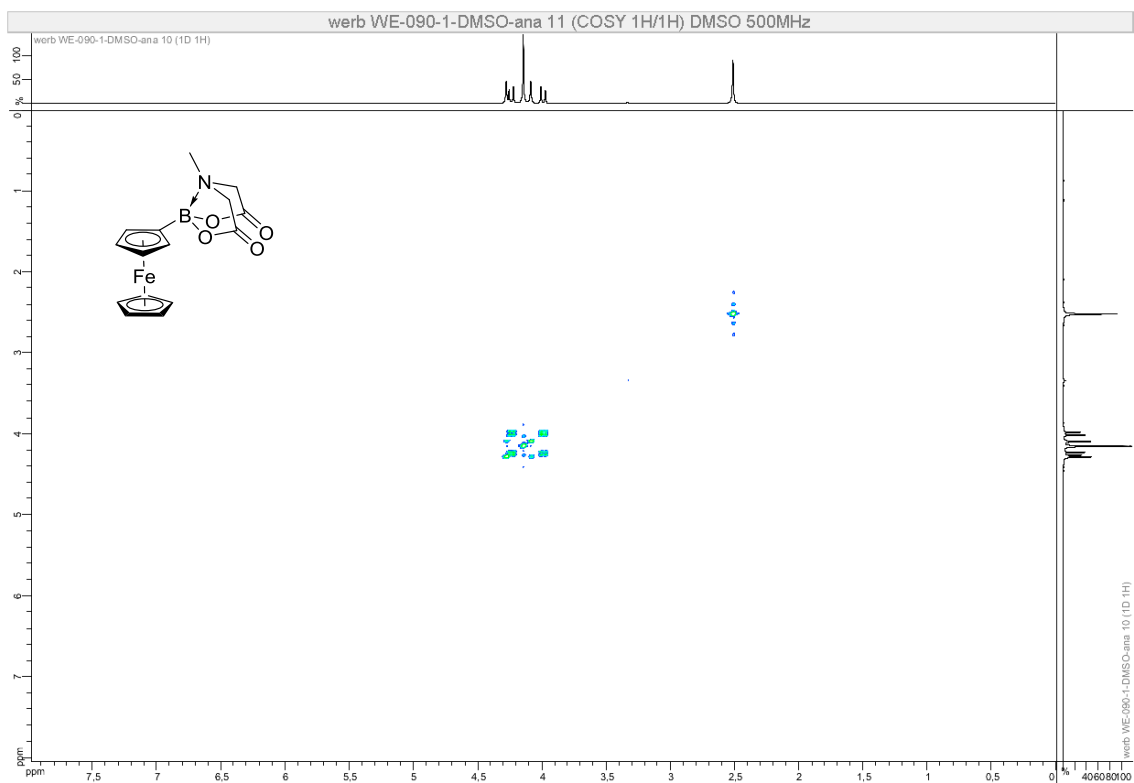
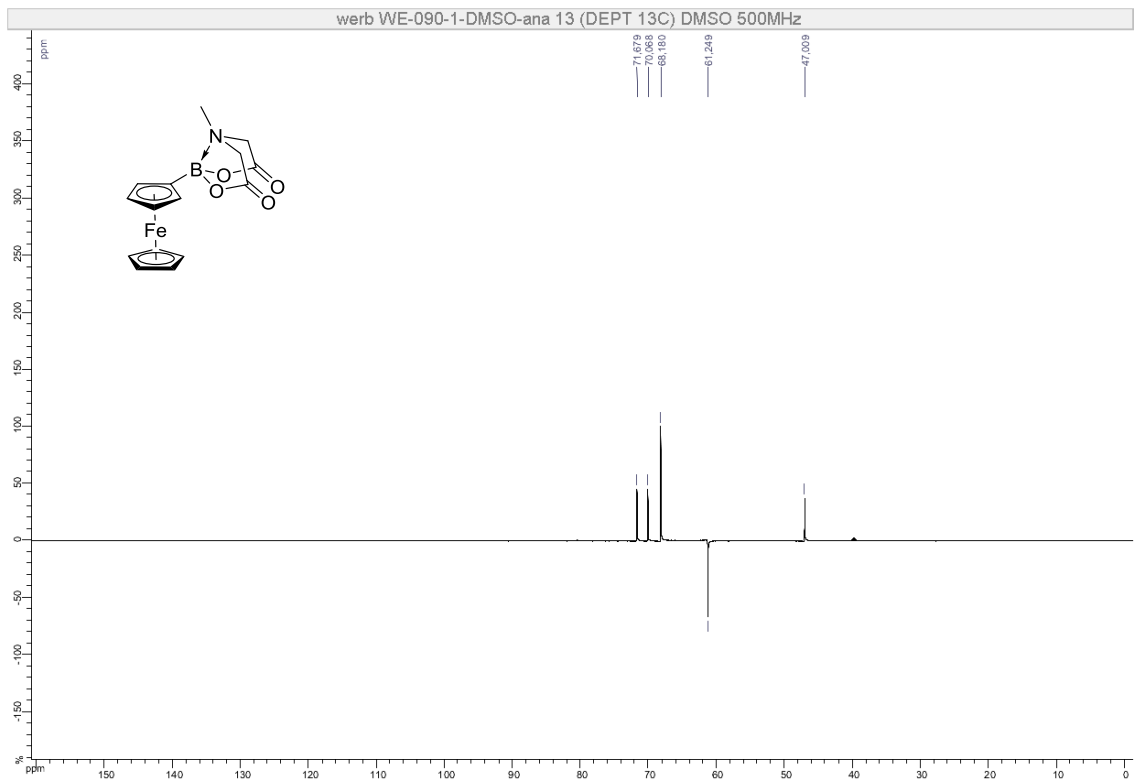


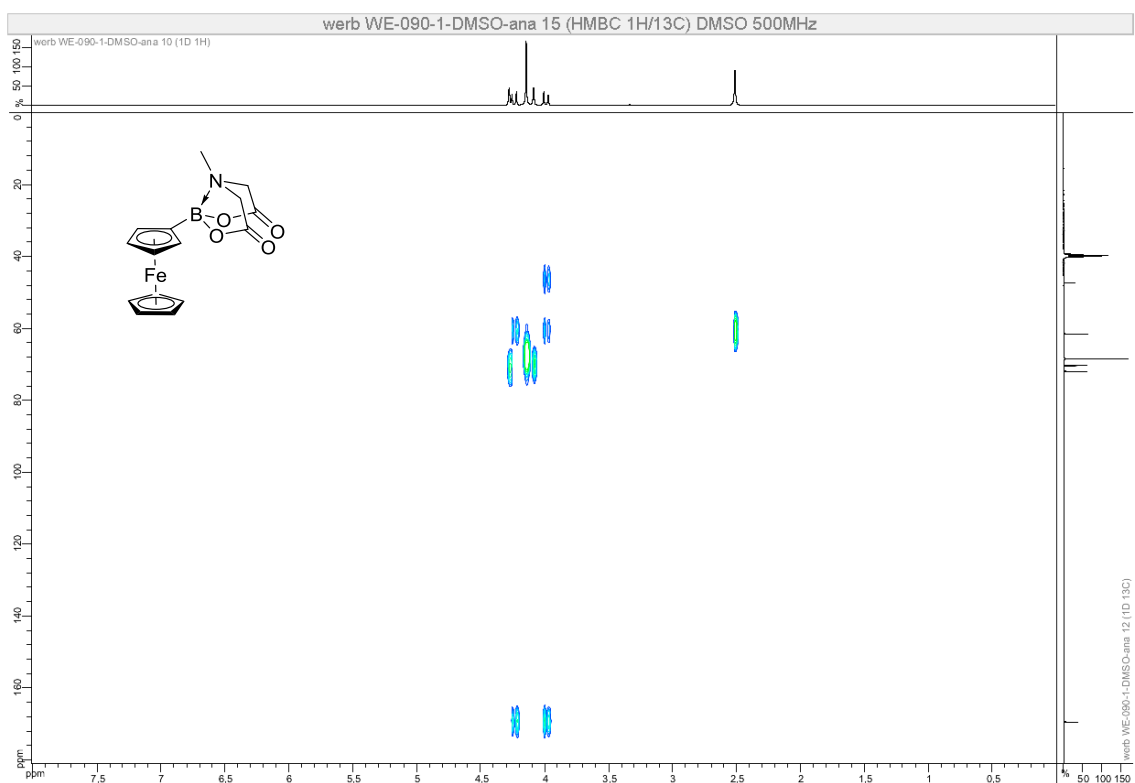
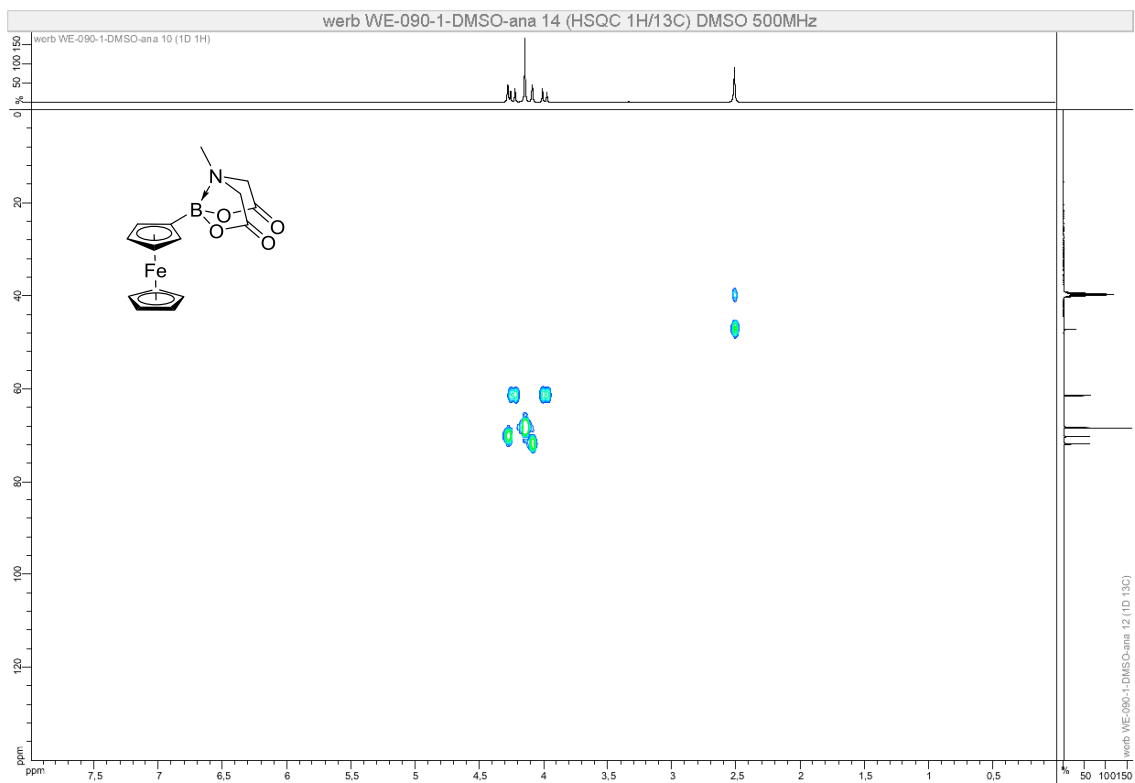


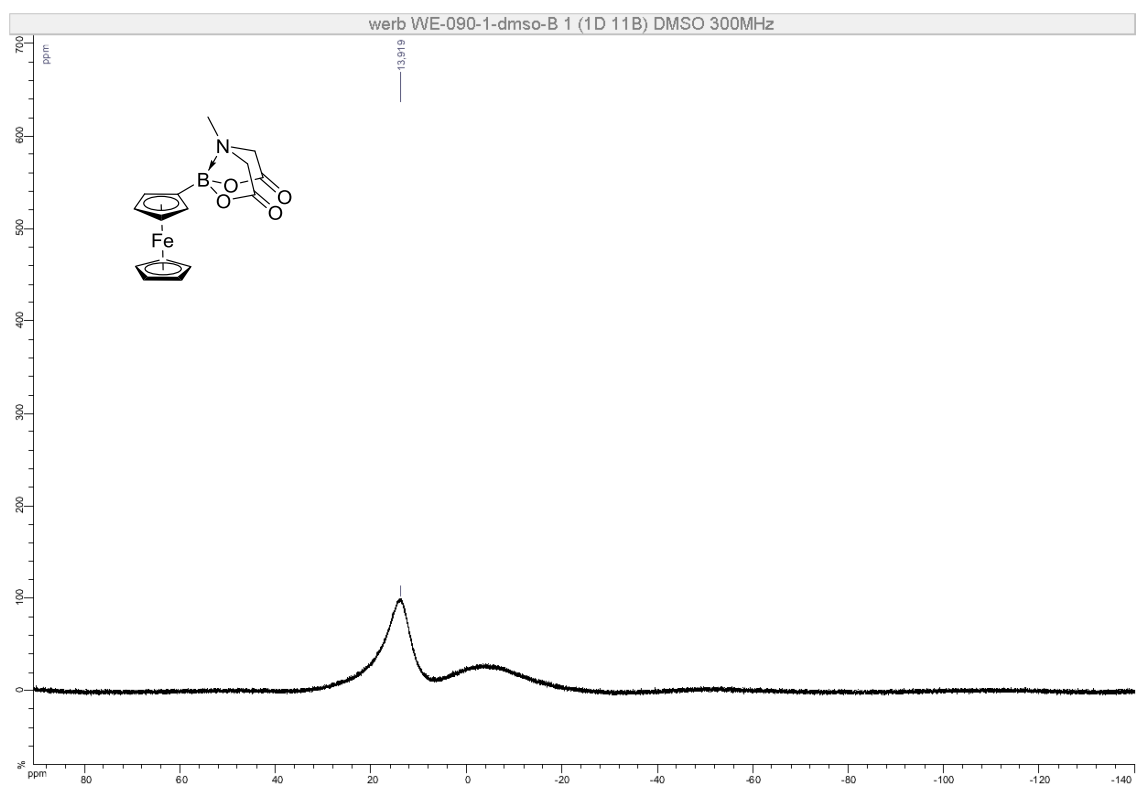
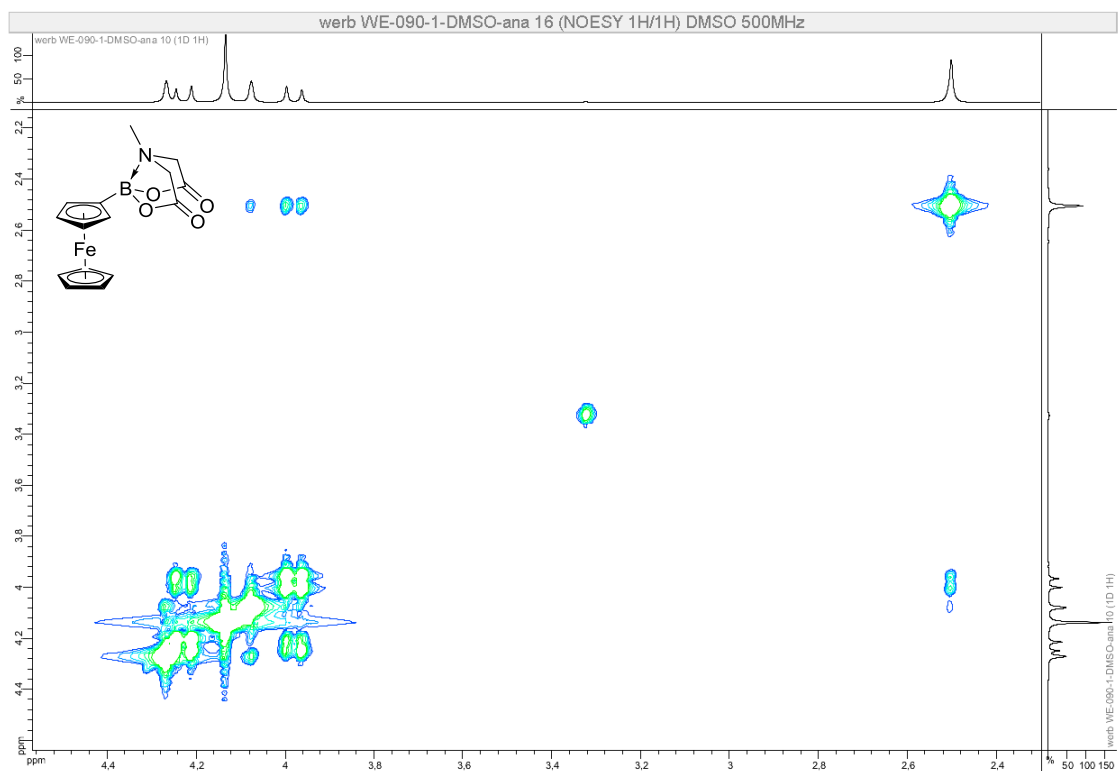


6-Methyl-2-ferrocenyl-1,3,6,2-dioxazaborocane-4,8-dione (FcB(MIDA) - 21)

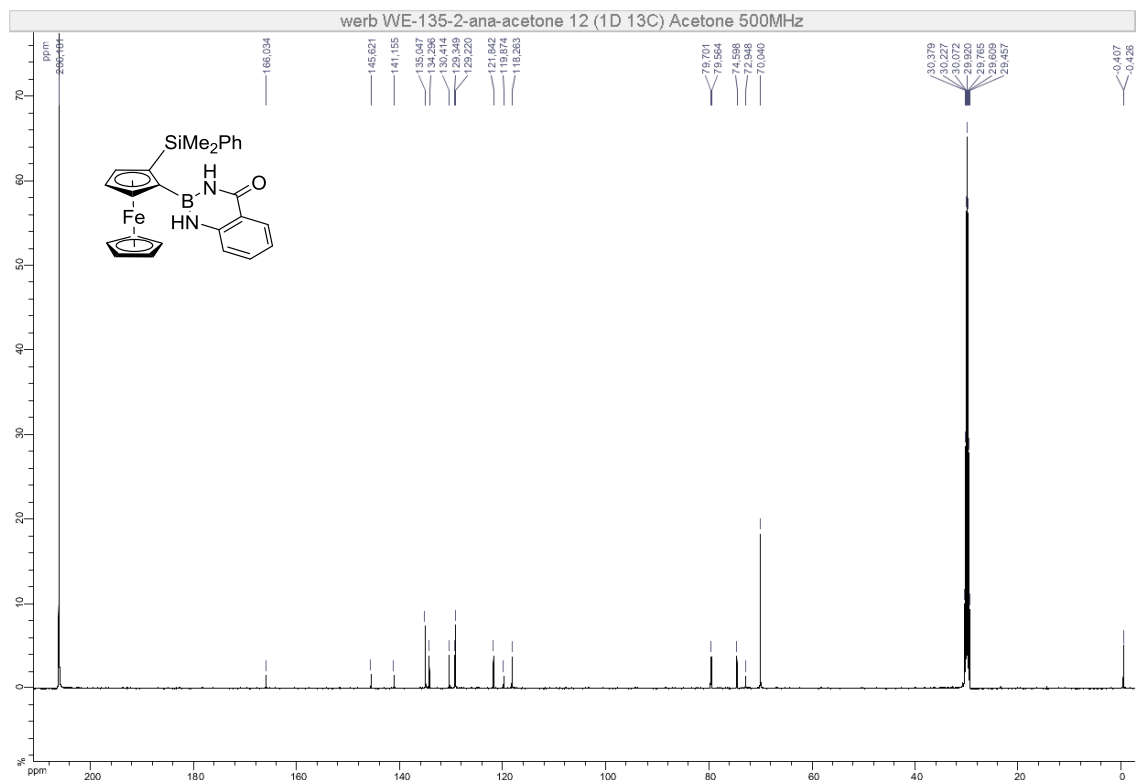
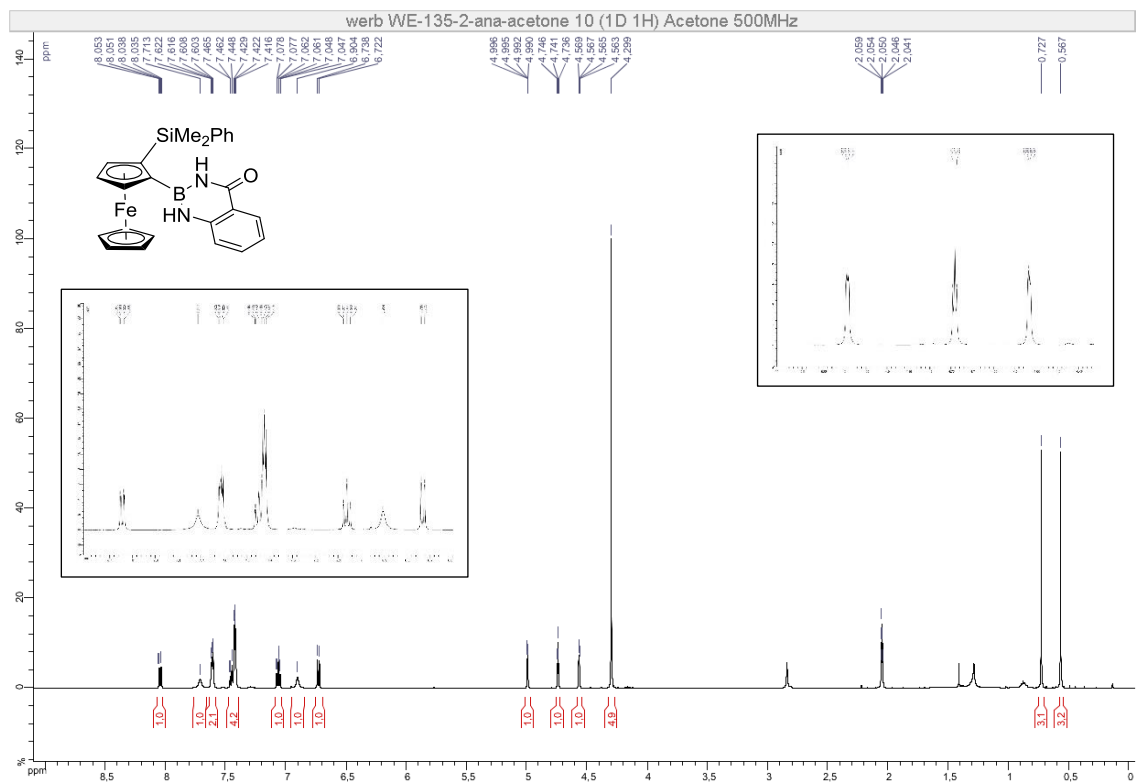


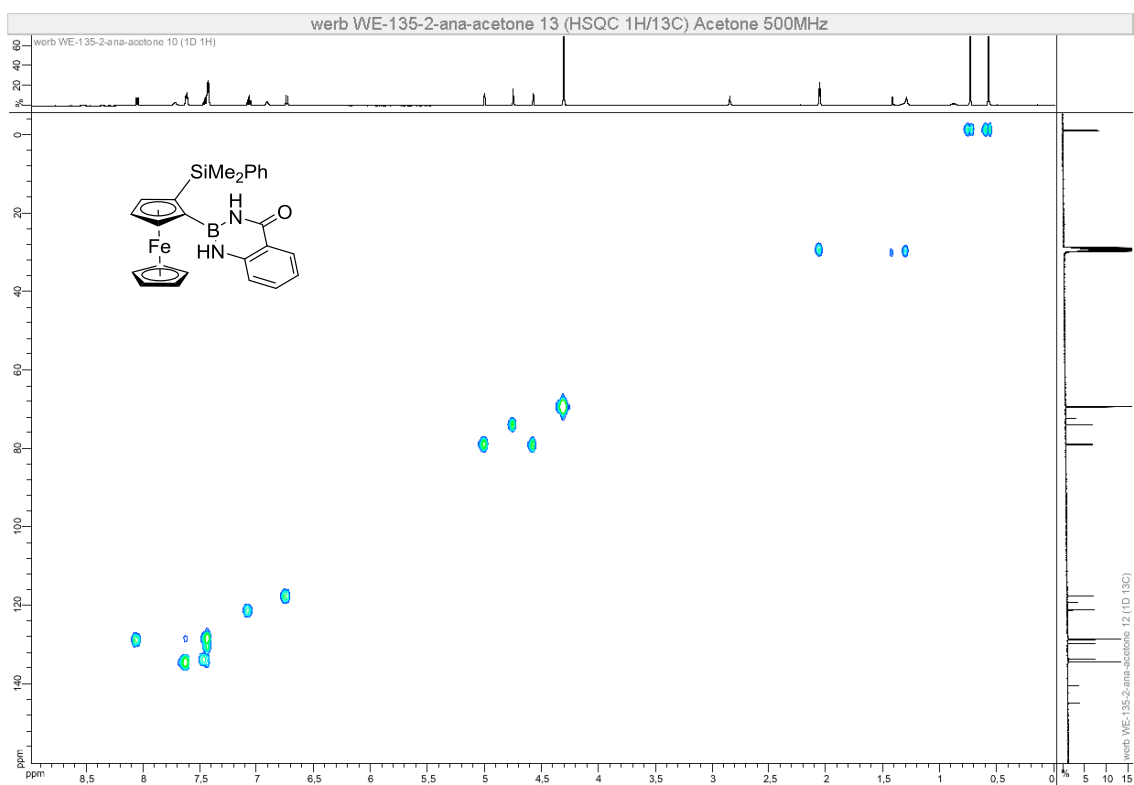
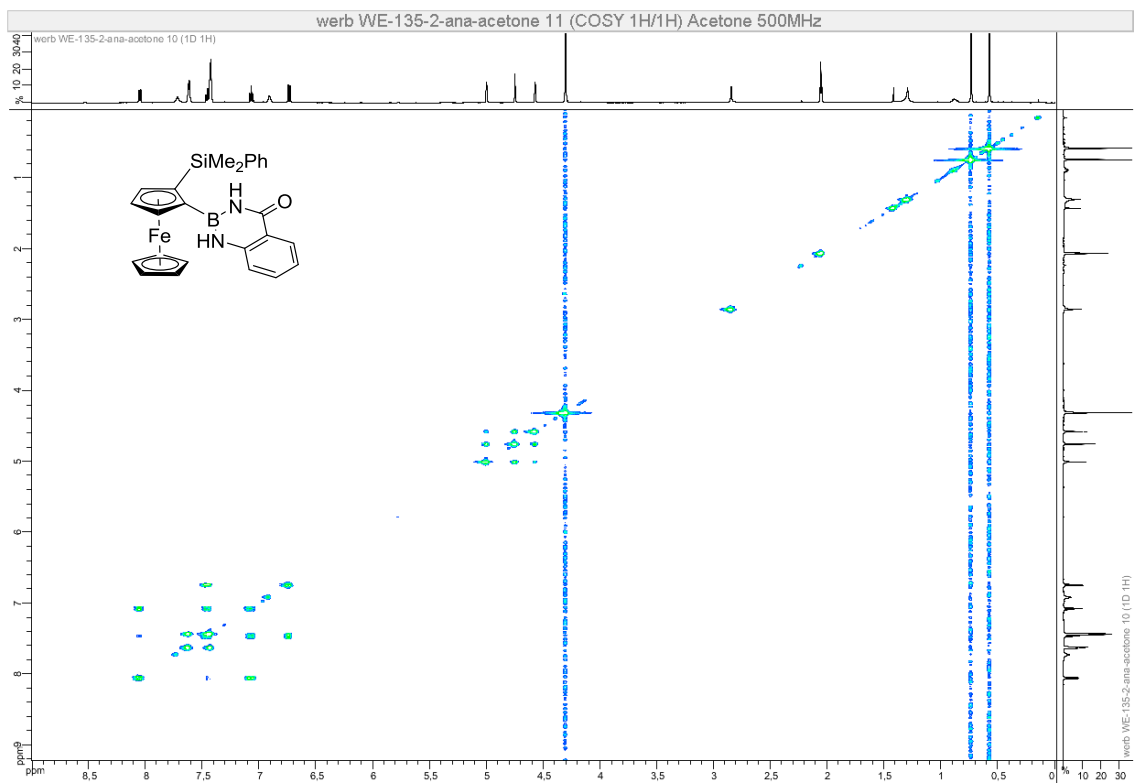


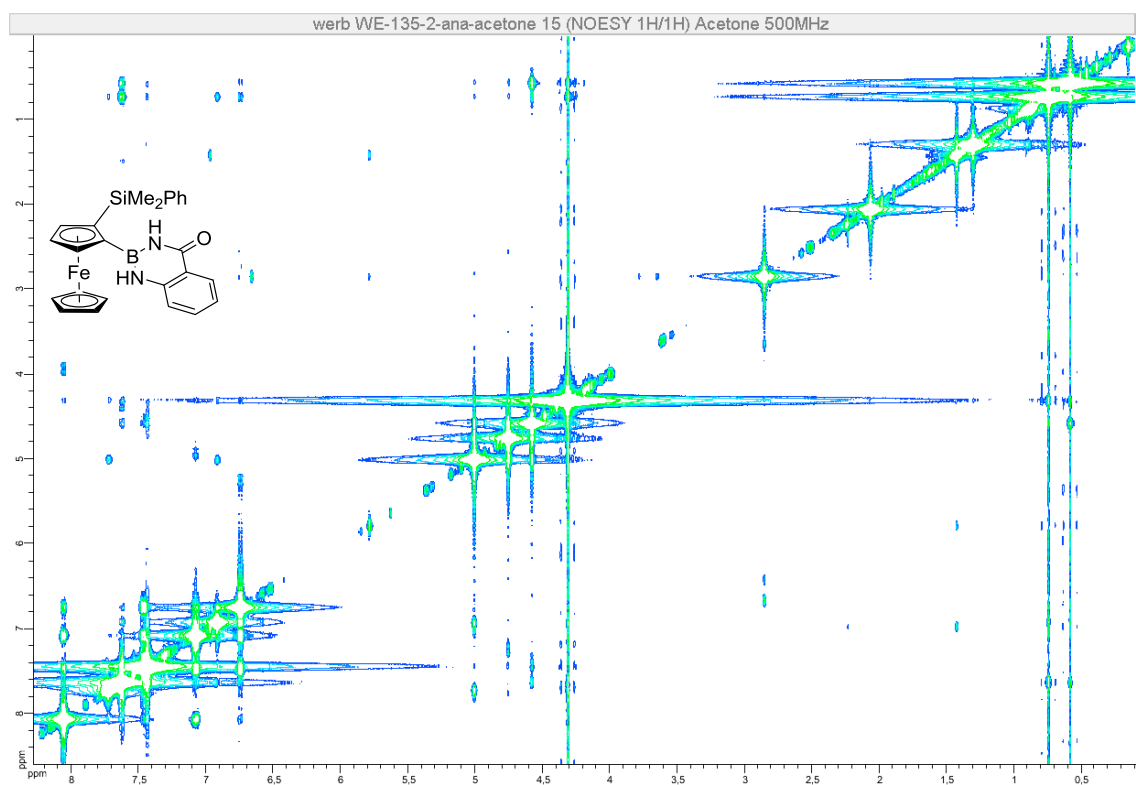
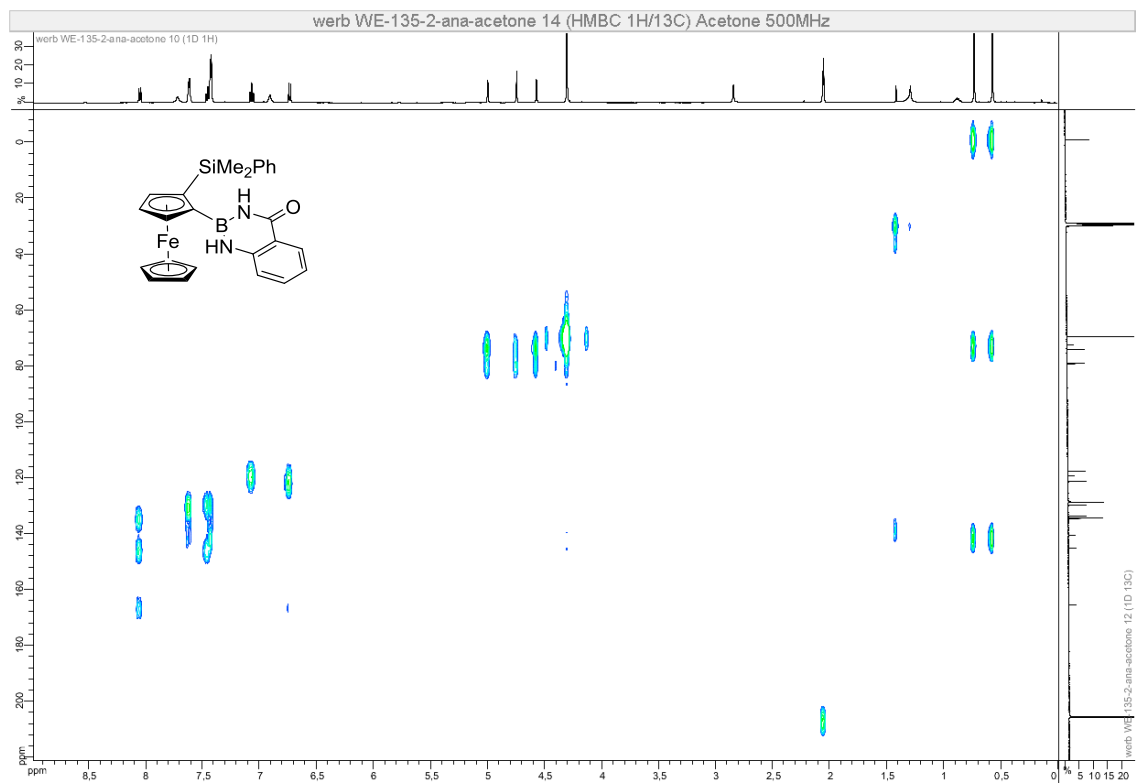


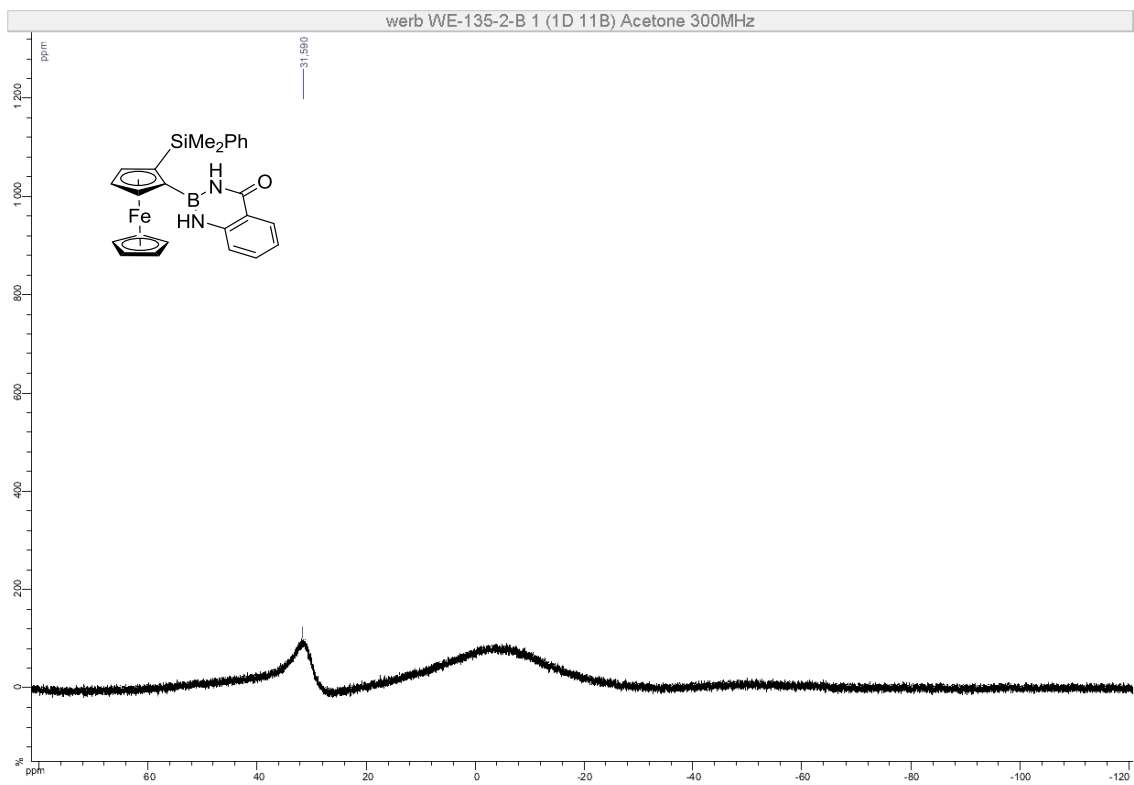


2-(2-(Dimethyl(phenyl)silyl)ferrocenyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (FcB(aam)(SiMe₂Ph) - 25).

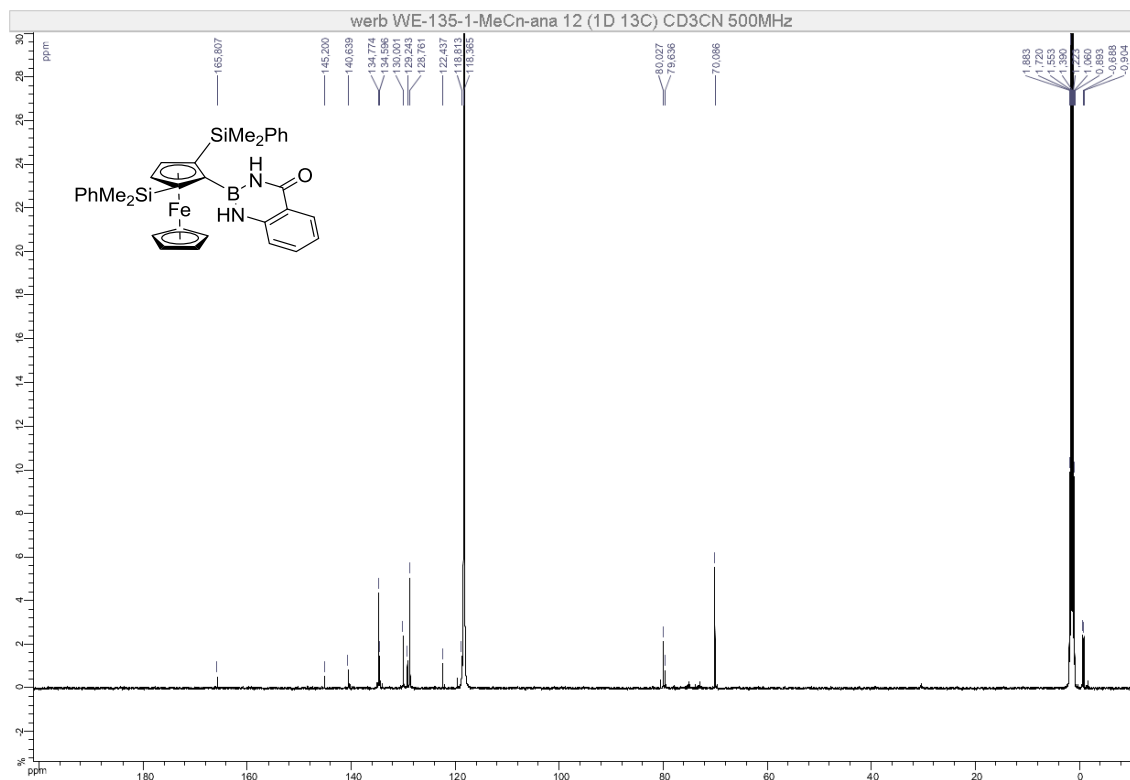
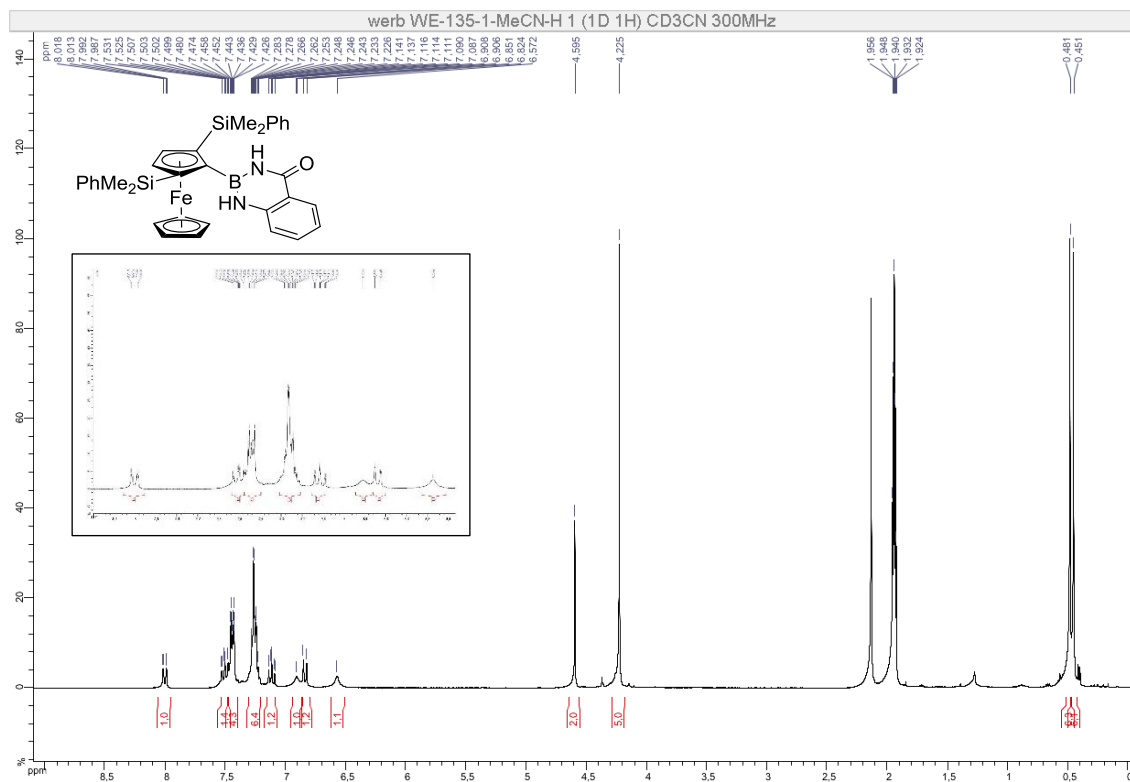


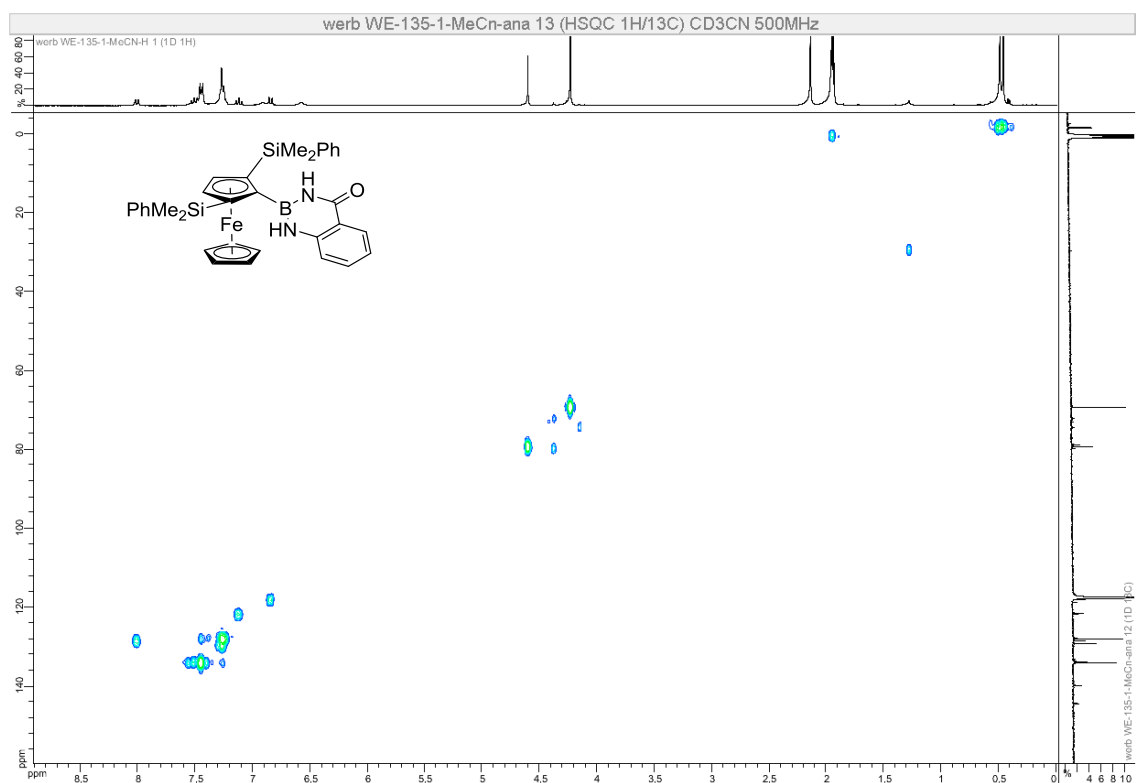
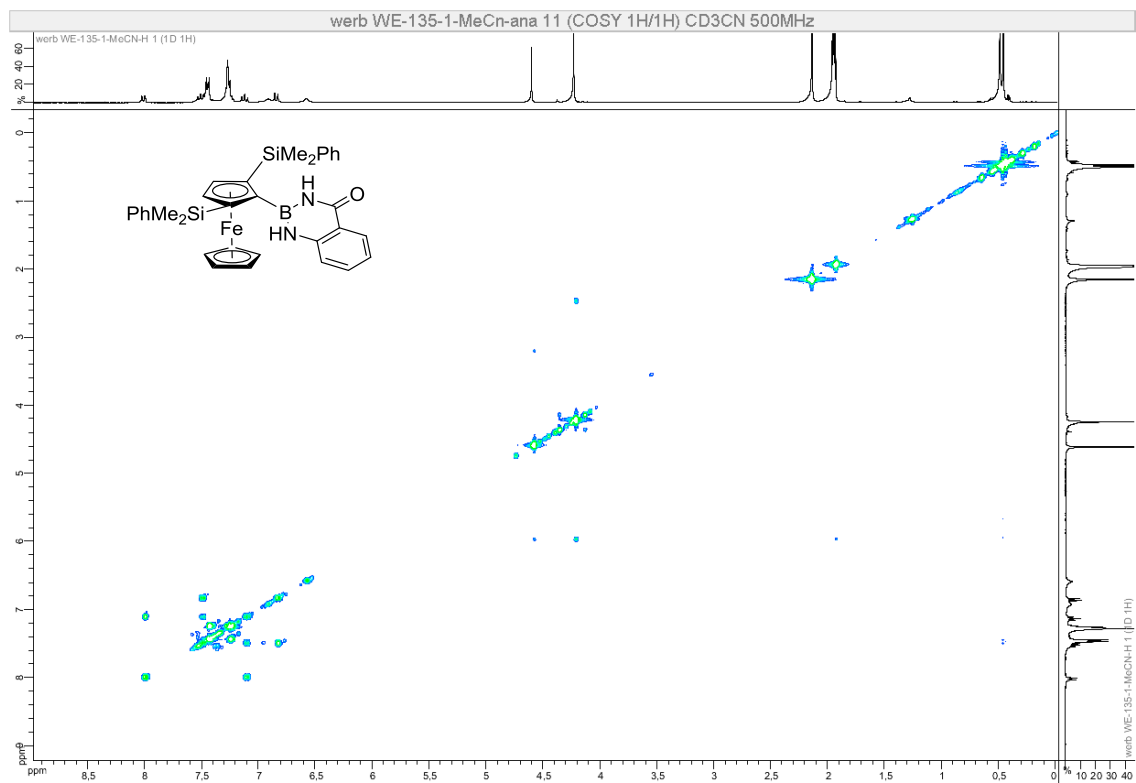


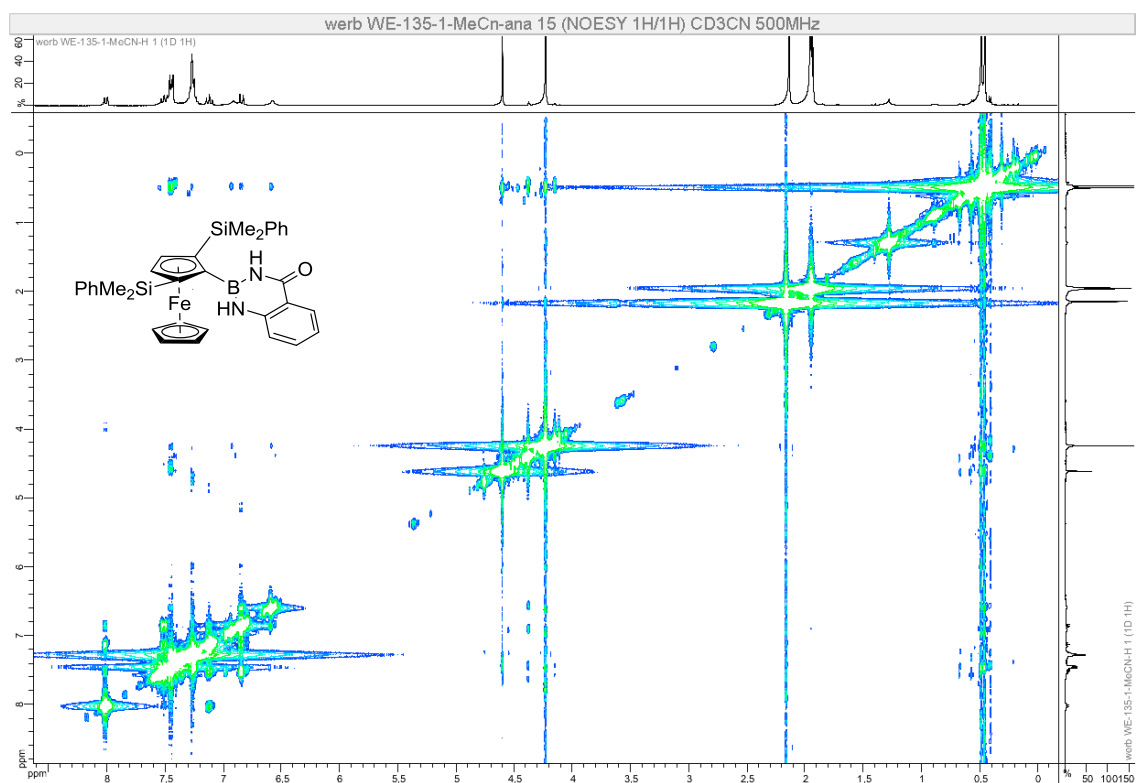
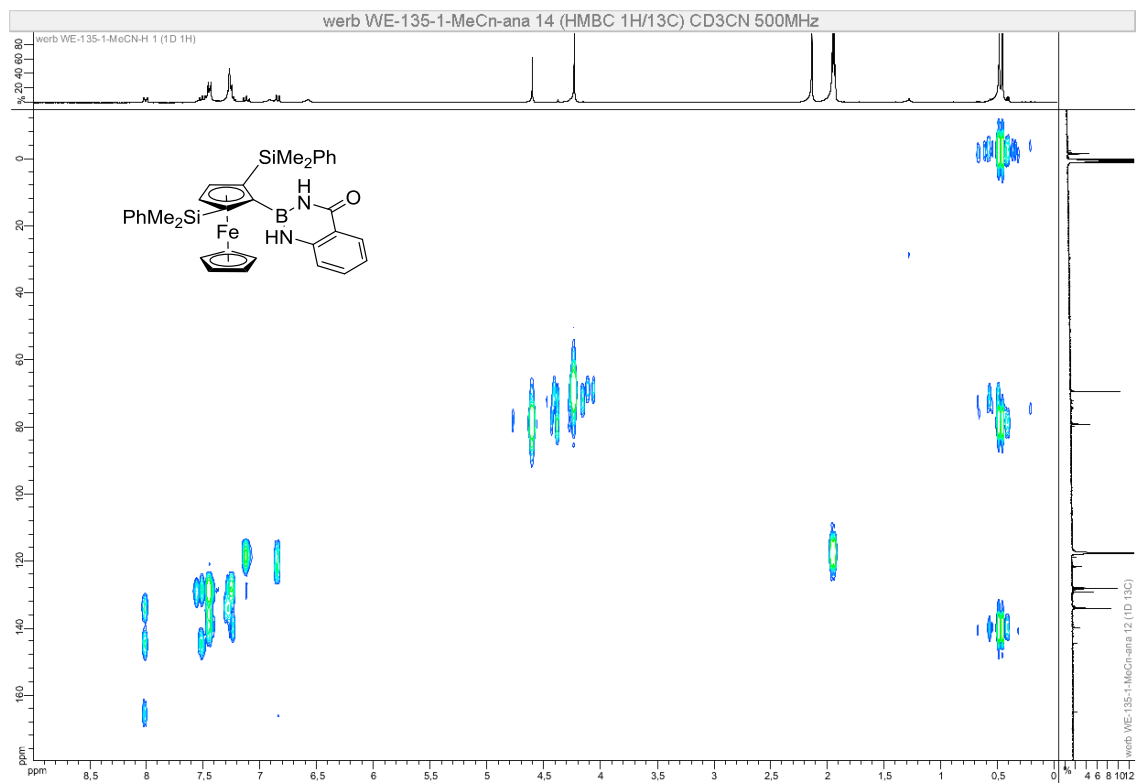


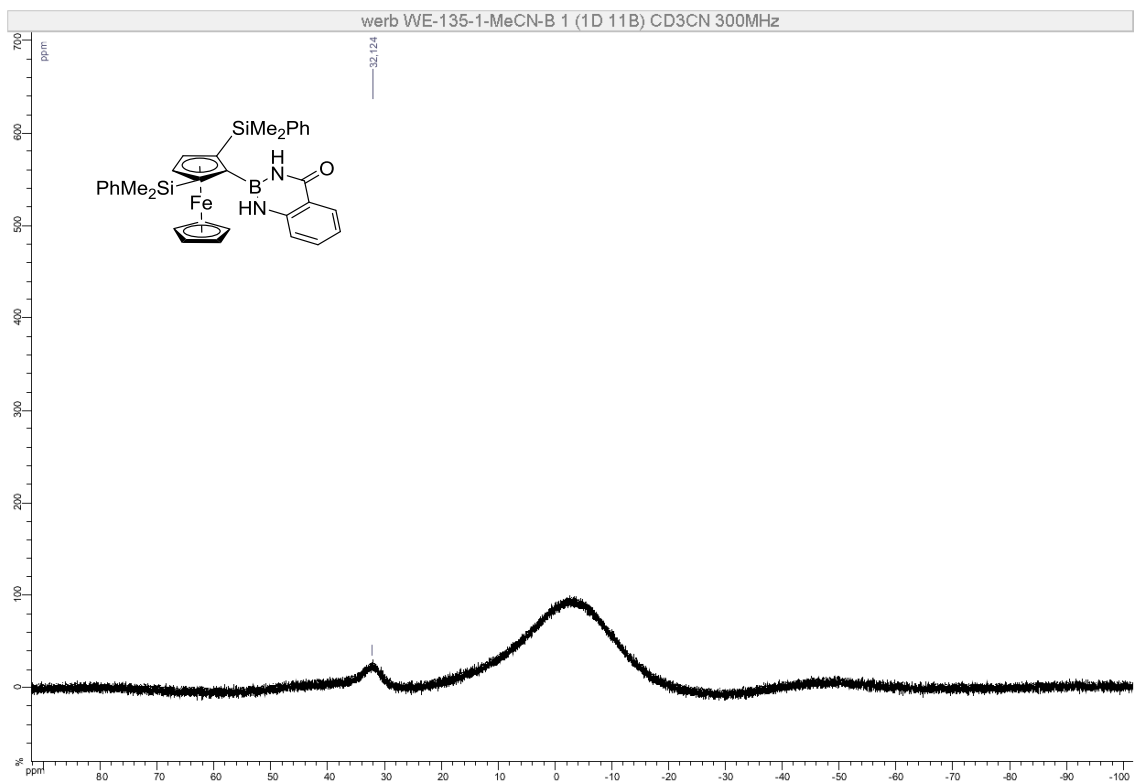


2-(2,5-bis(dimethyl(phenyl)silyl)ferrocenyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (FcB(aam)(SiMe₂Ph)₂ - 26).

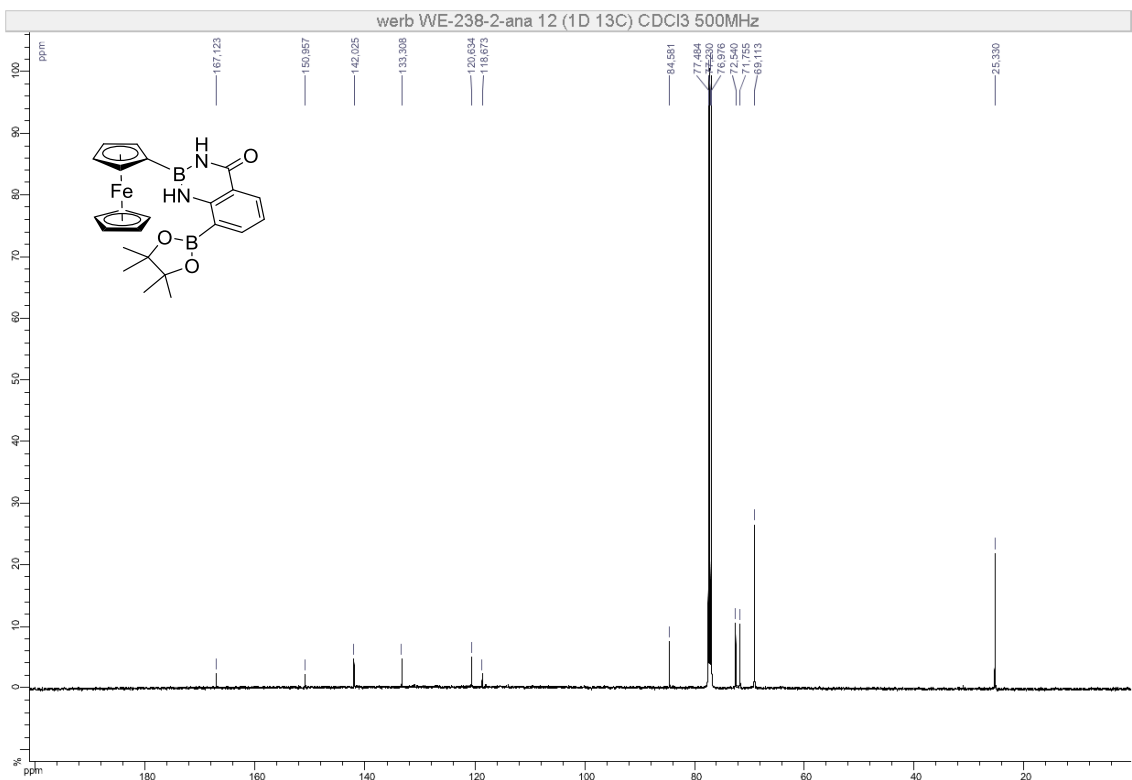
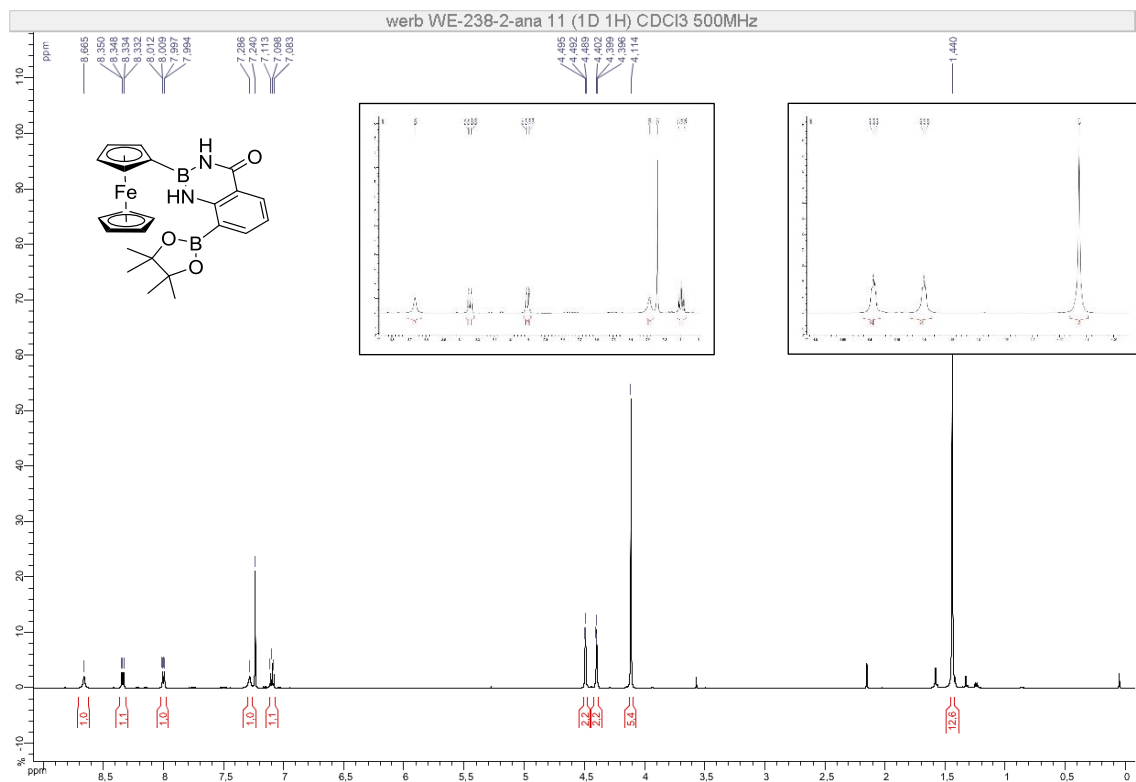


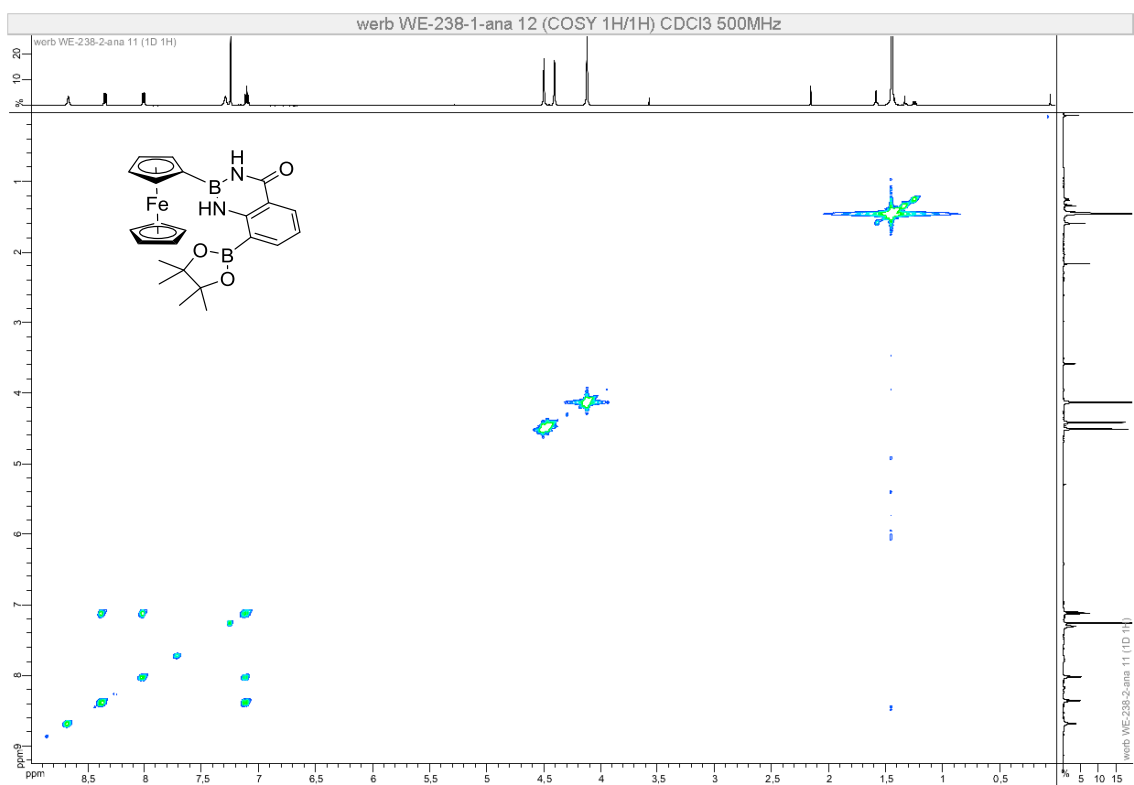
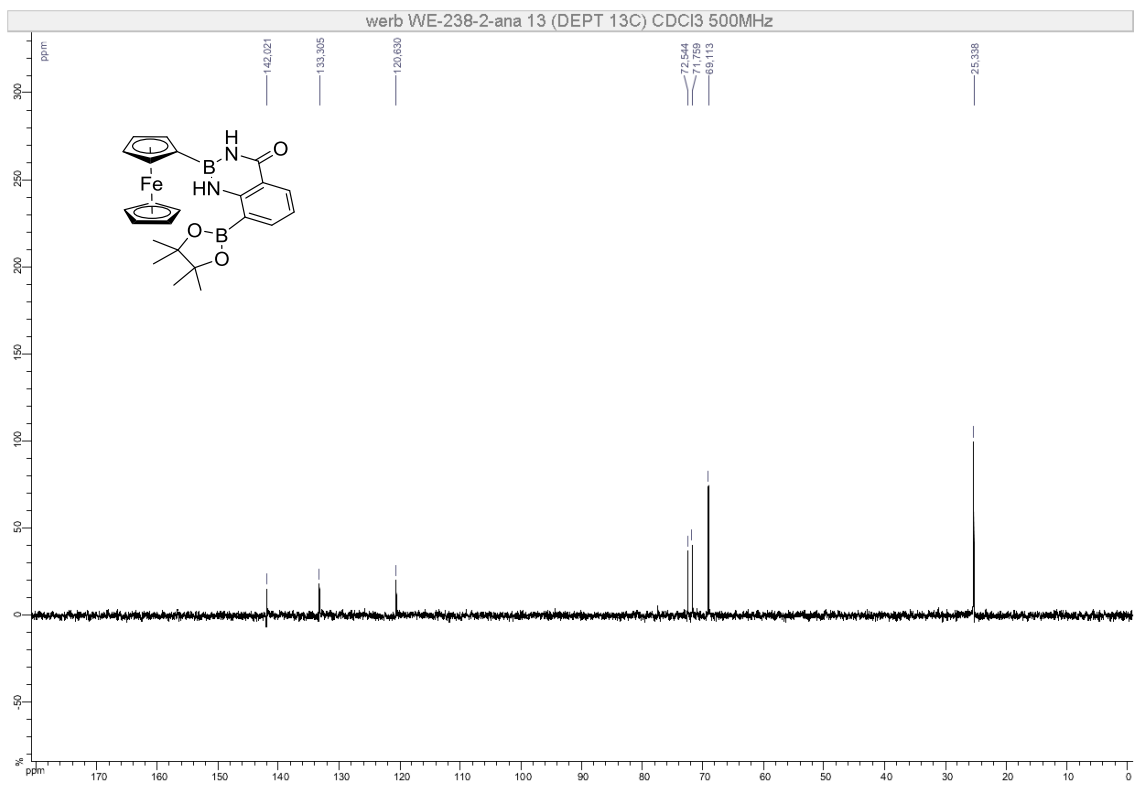


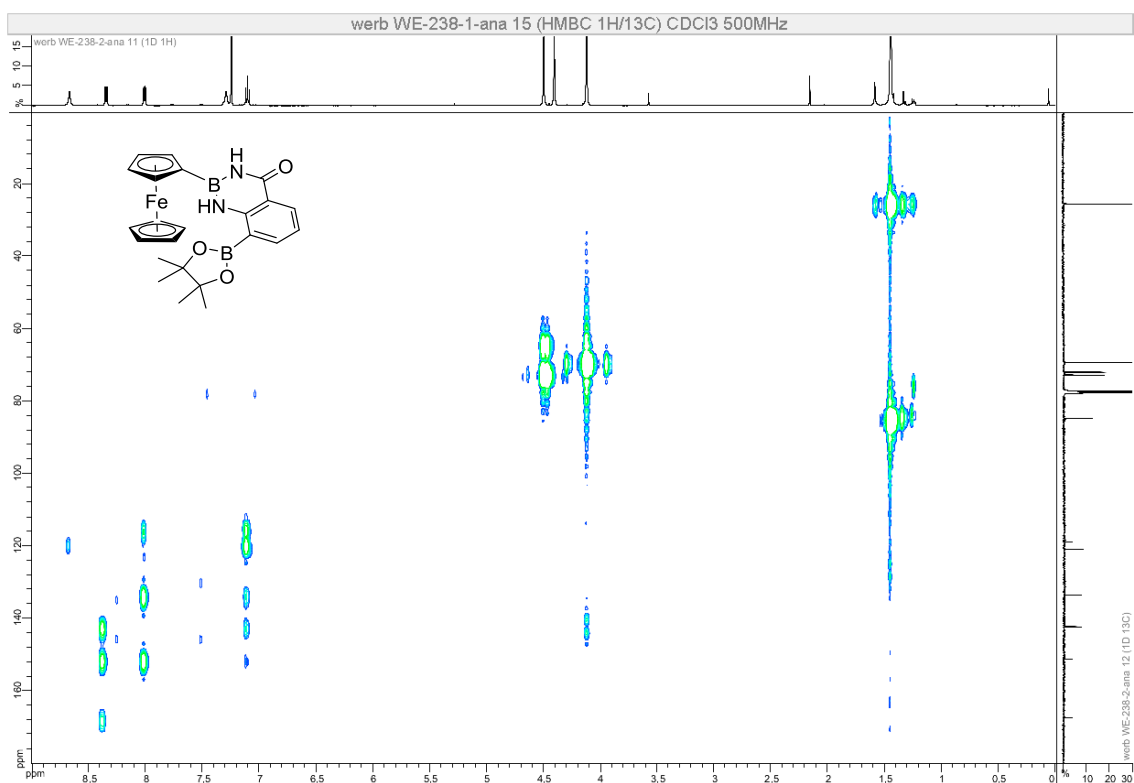
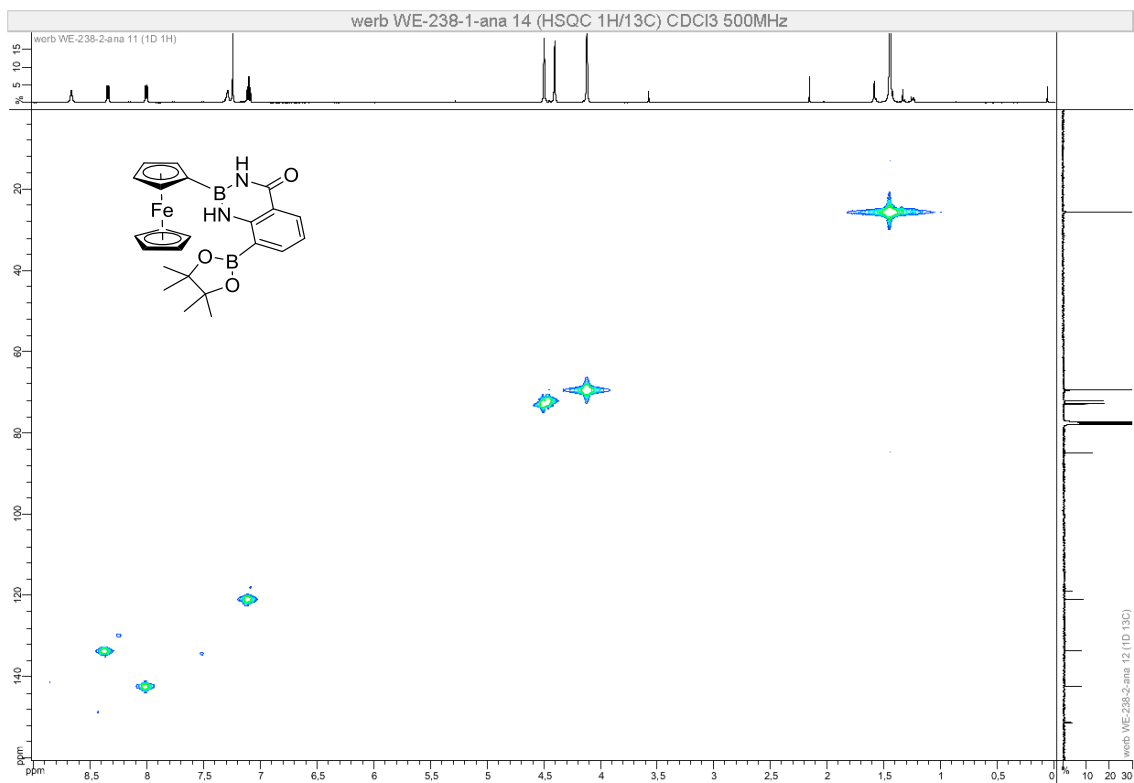


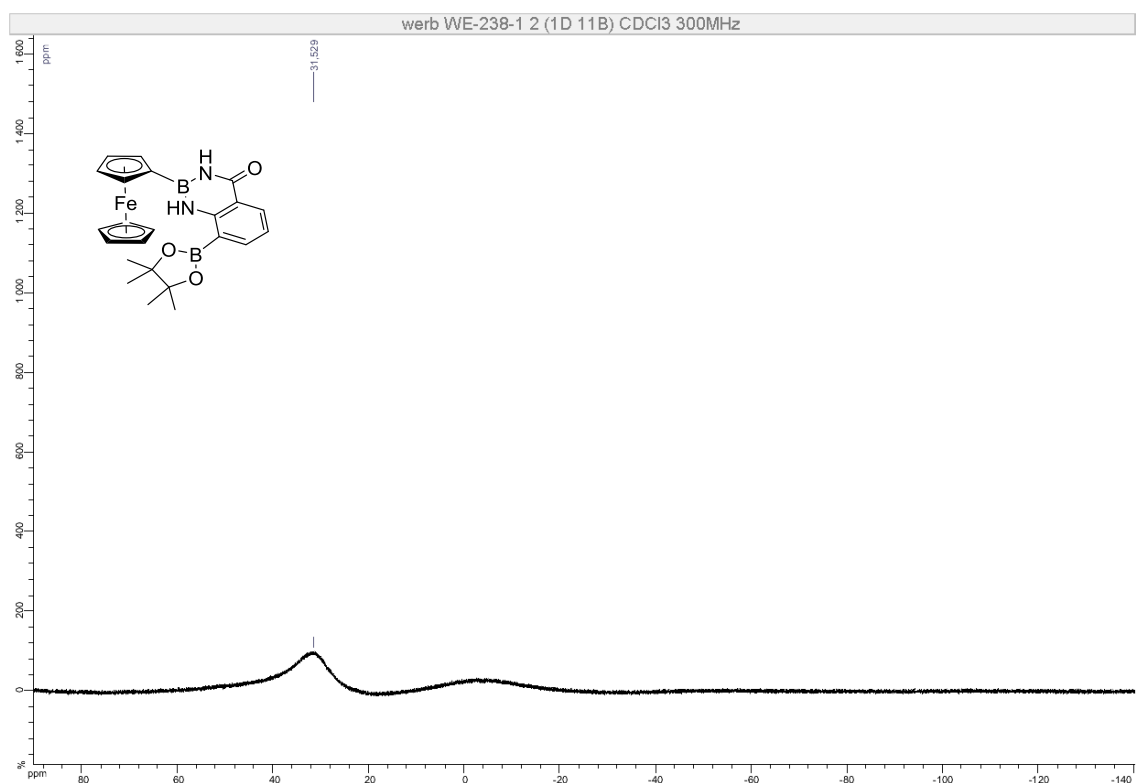
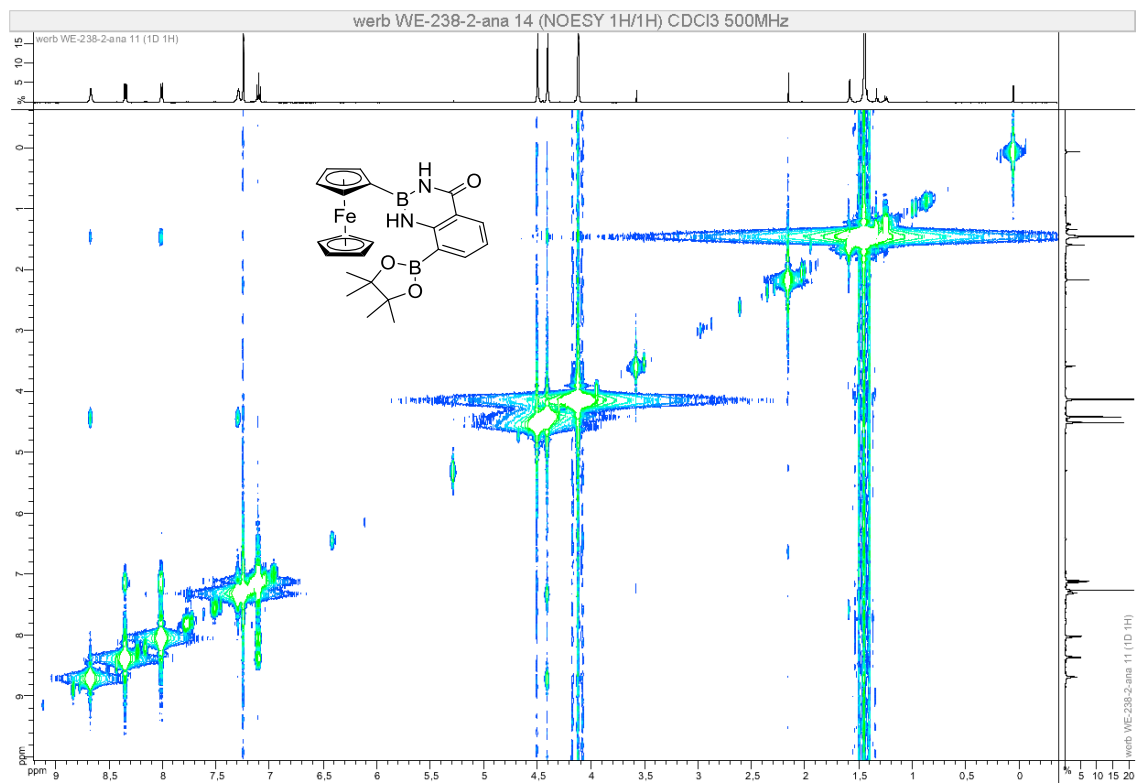


2-Ferrocenyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (FcBaamBpin – 28)



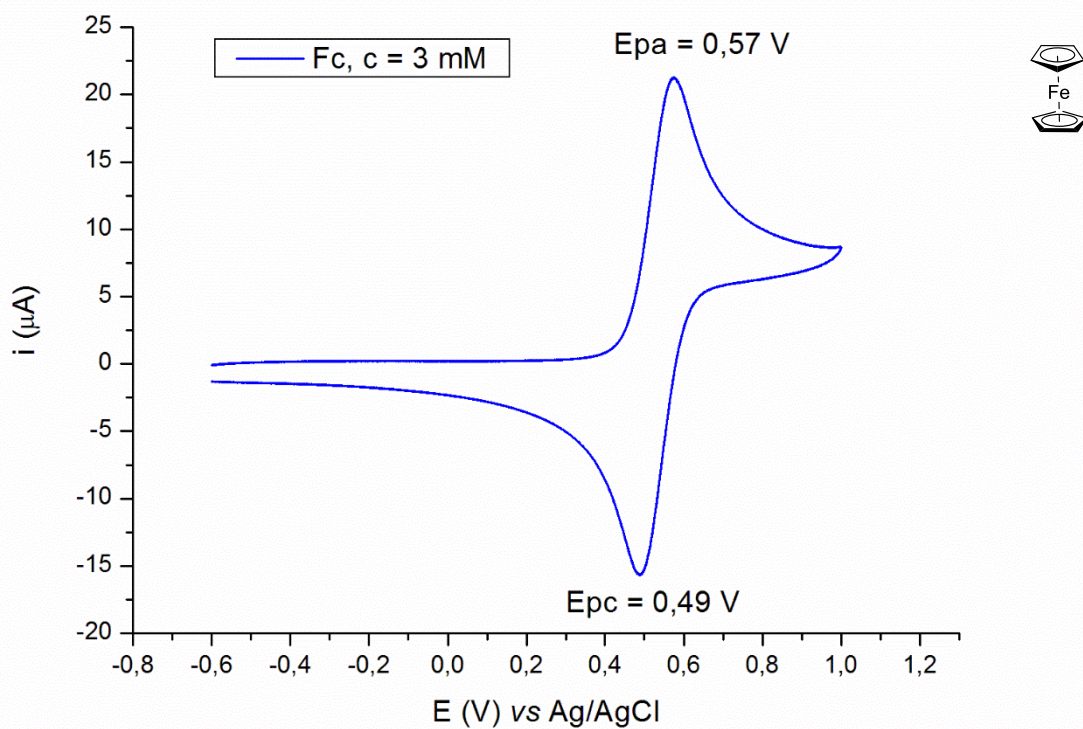




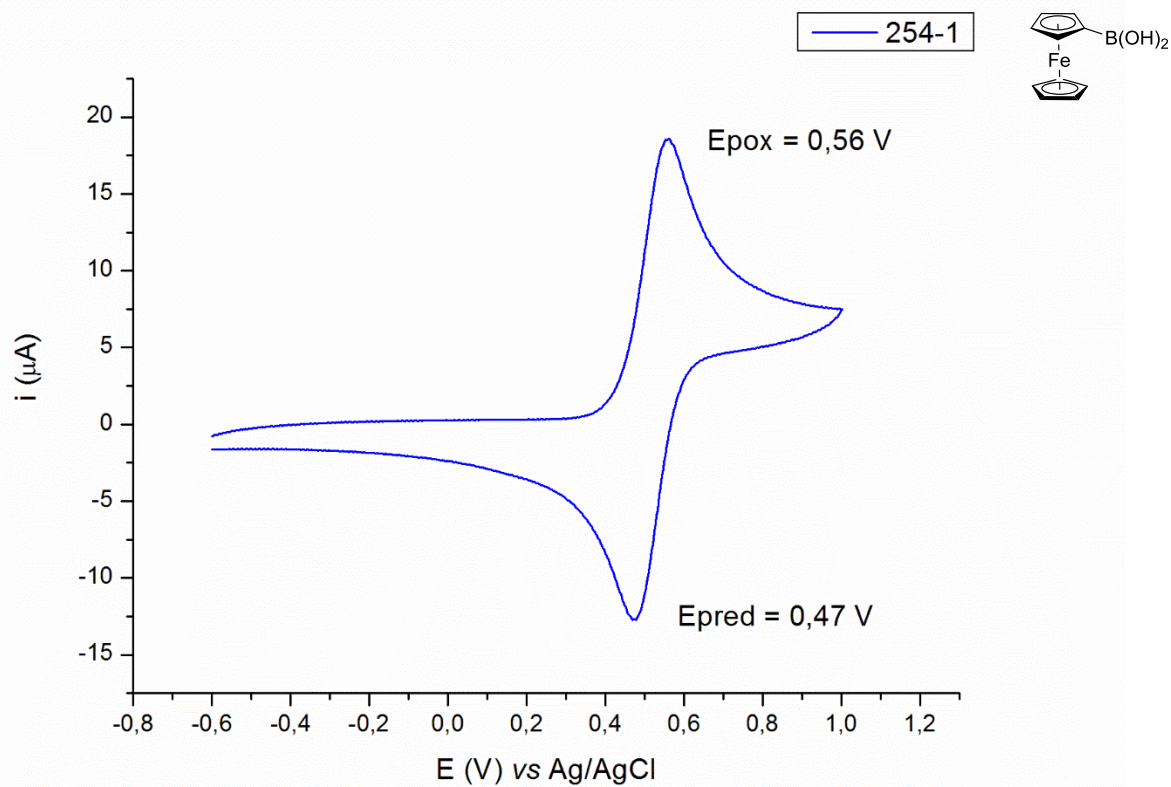


(2) Cyclic voltammograms

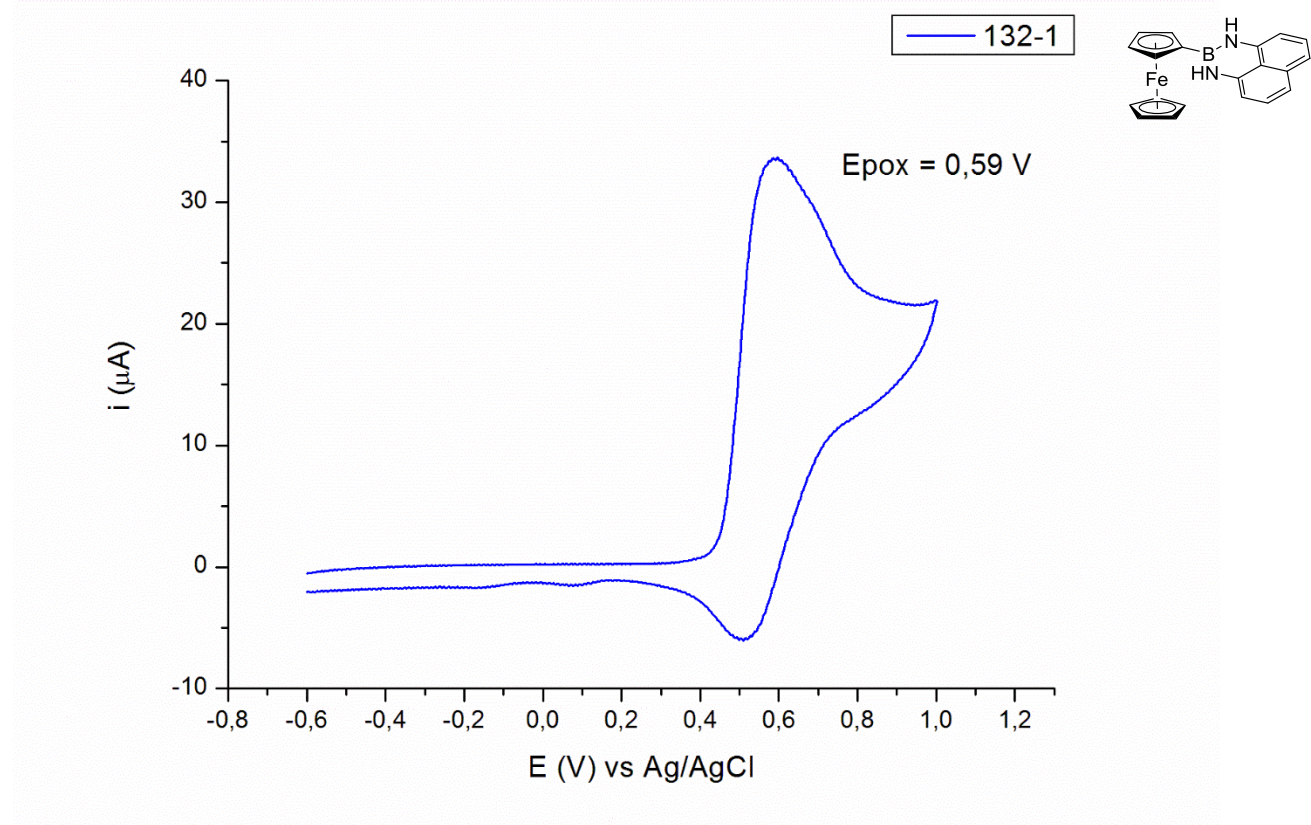
Ferrocene



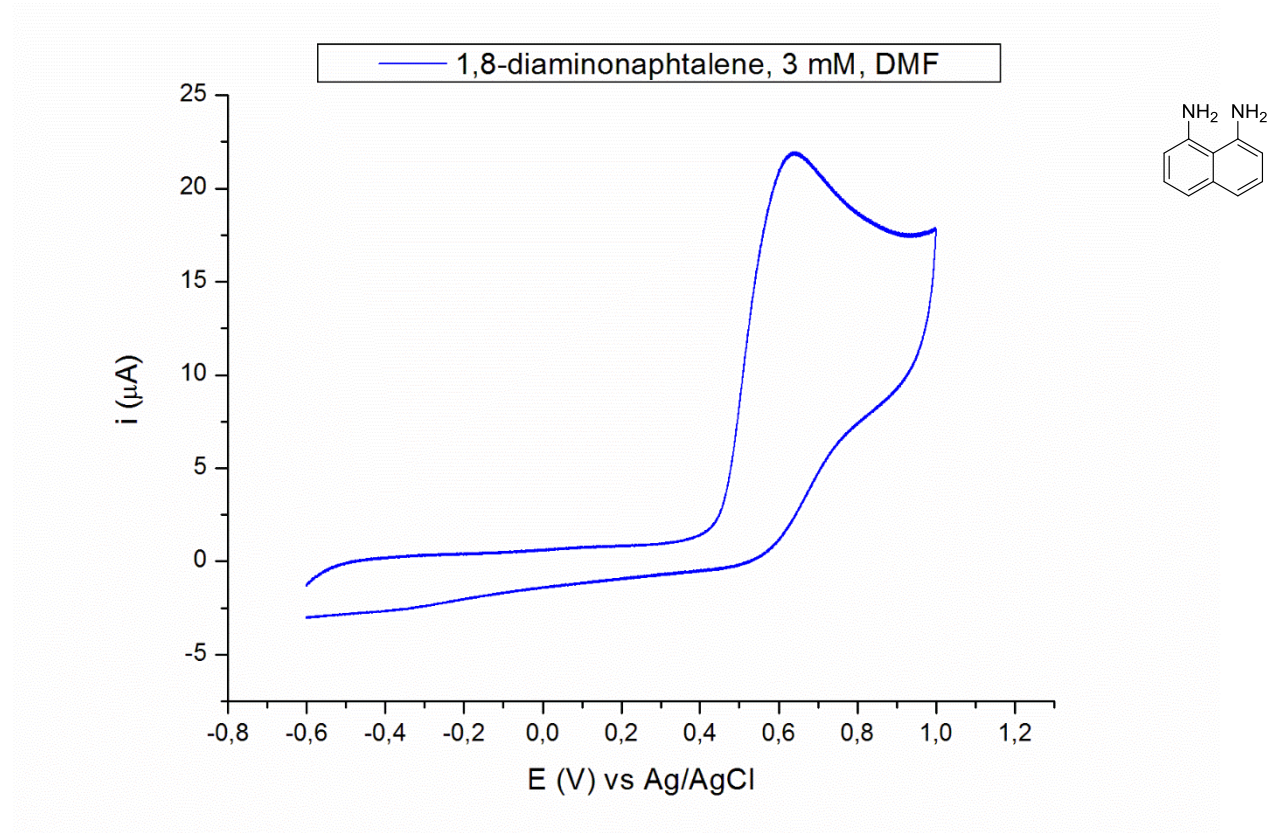
Ferroceneboronic acid (FcB(OH)₂ - 1)



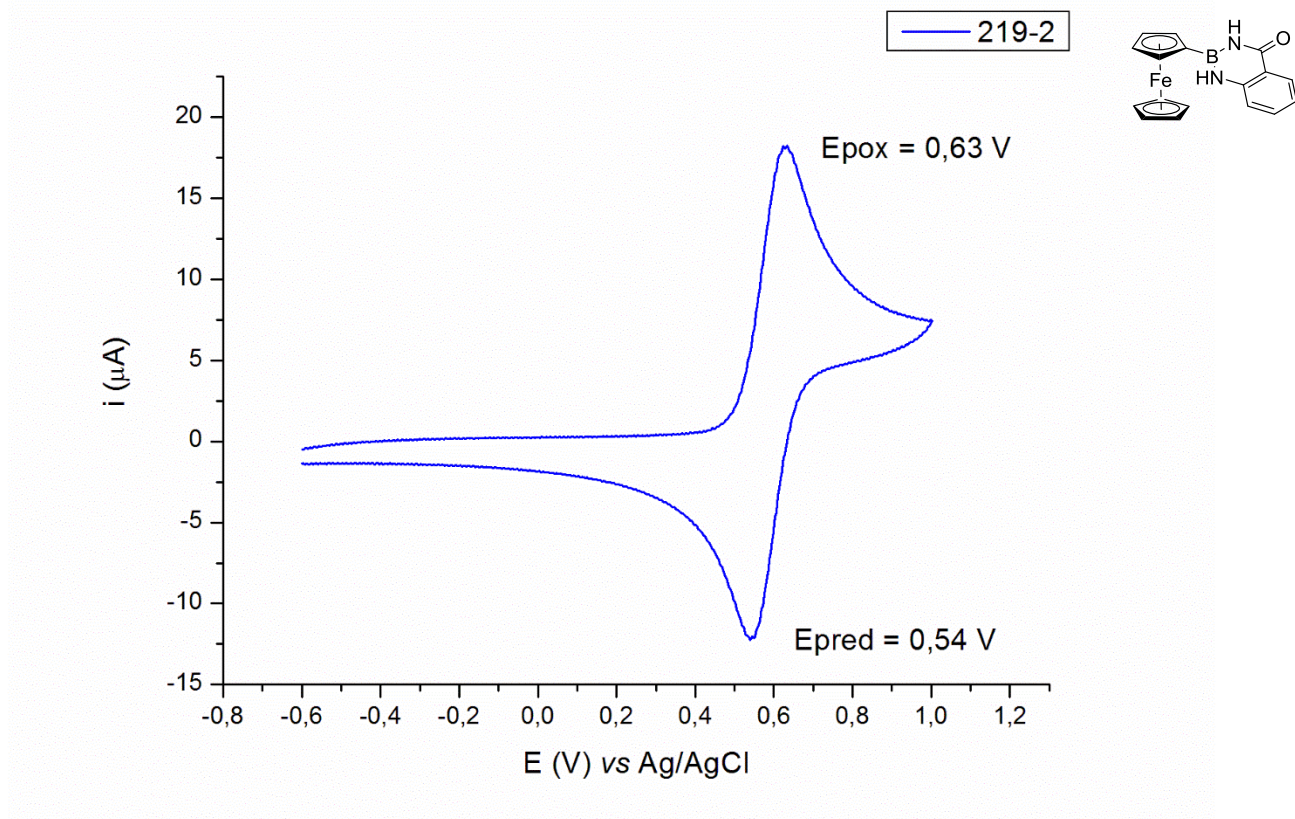
2-Ferrocenyl-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (FcB(dan) - 15)



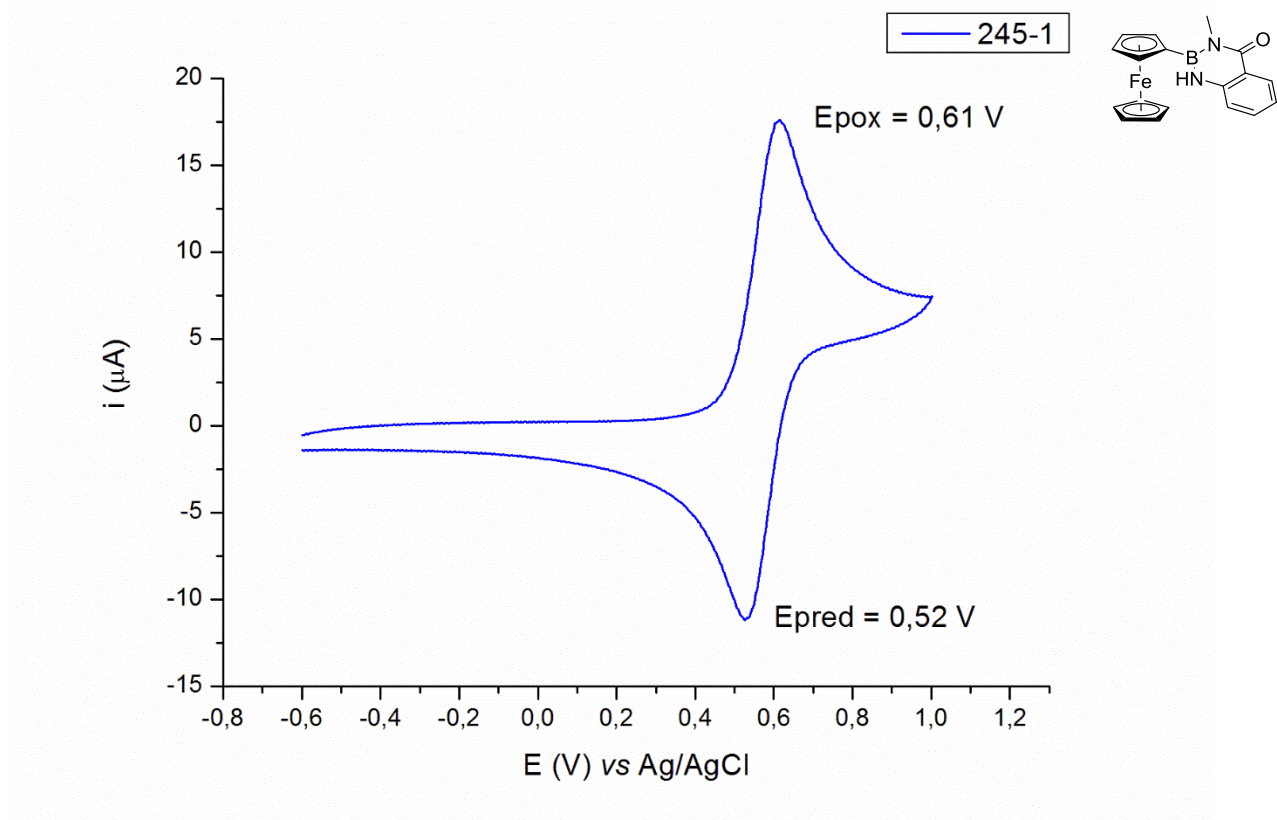
1,8-Diaminonaphtlene



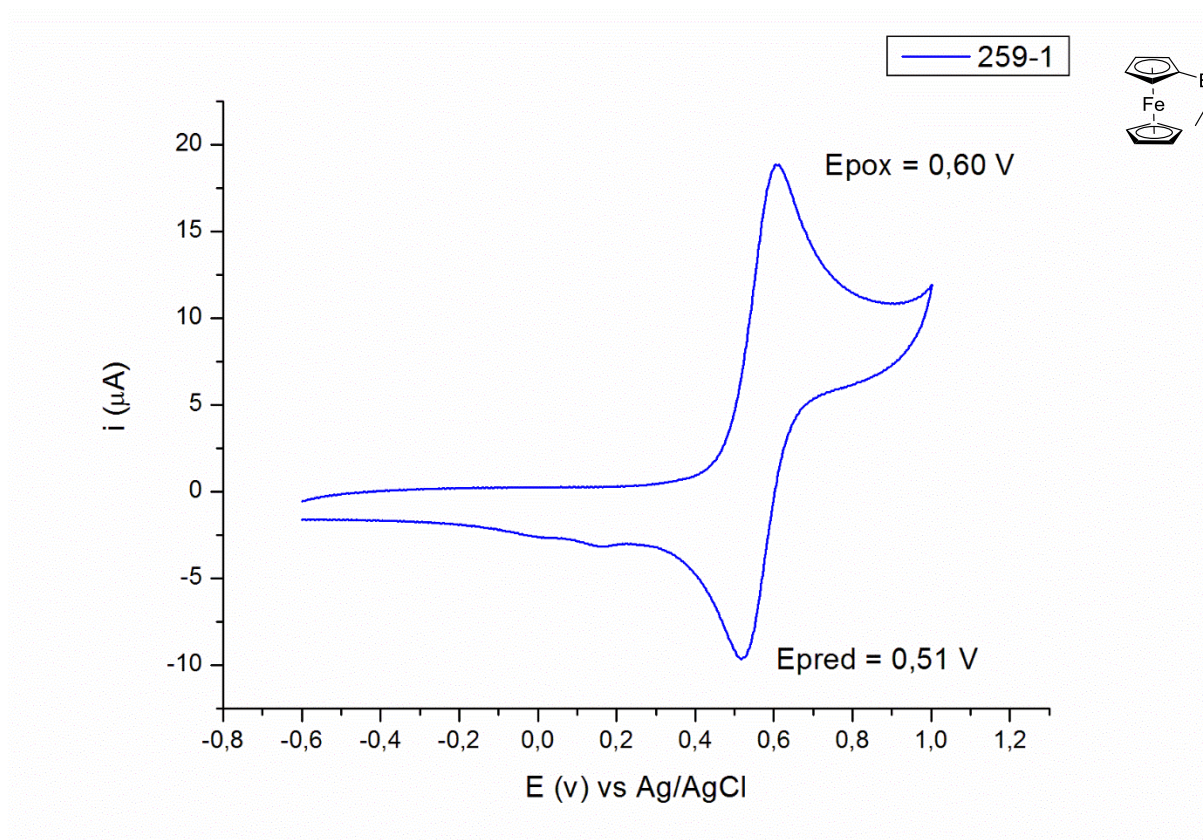
2-Ferrocenyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (FcB(aam) - 16)



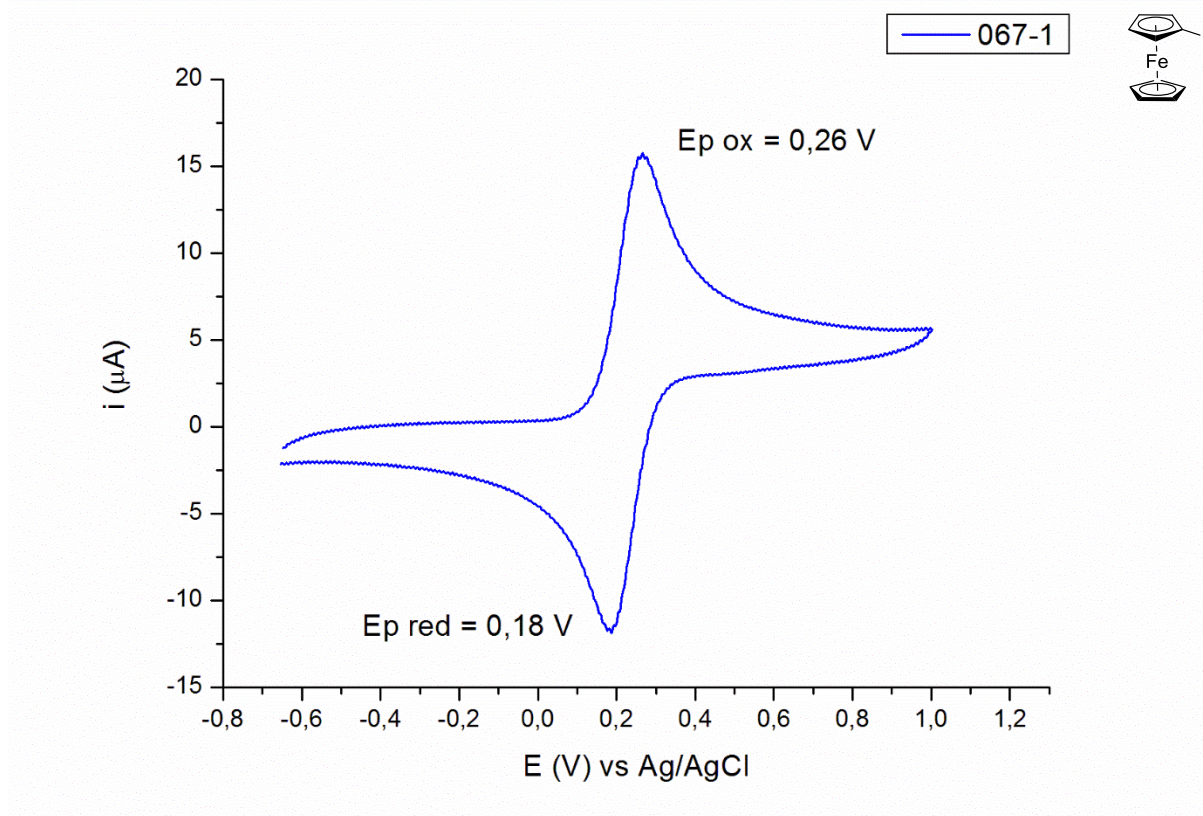
3-Methyl-2-ferrocenyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (FcB(Me-aam) - 17)



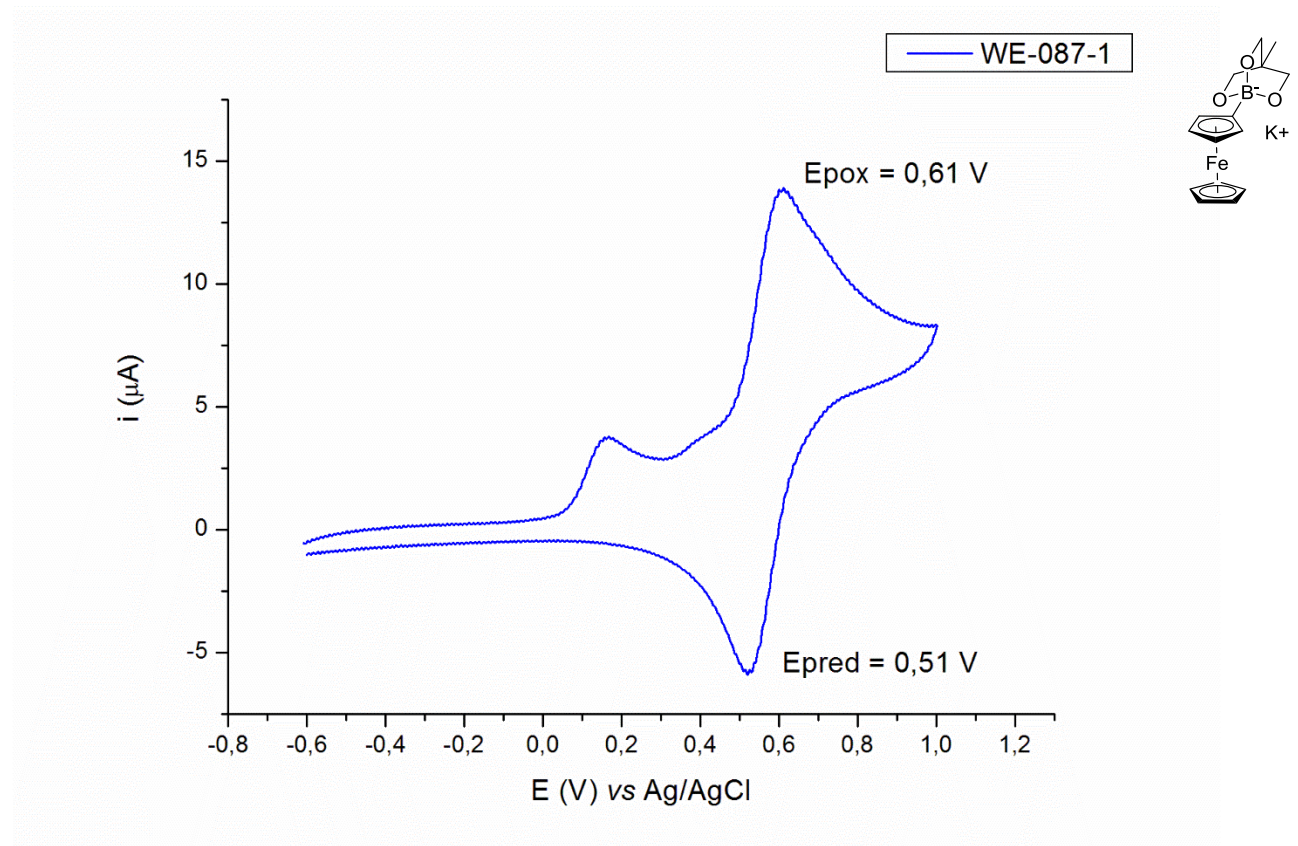
Methyl-2- ferrocenyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1*H*)-one (FcB(Me-aam) – 18)



Potassium ferrocenyltrifluoroborate (FcBF₃K - 19)



4-Methyl-1-ferrocenyl-2,6,7-trioxa-1-borabicyclo[2.2.2]octan-1-uide (FcB(triolborate) - 20)



6-Methyl-2-ferrocenyl-1,3,6,2-dioxazaborocane-4,8-dione (FcB(MIDA) - 21)

