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Supplementary Material

Direct C-O Bond Activation Mediated by AcOH: A New Metal-free way for α-Functionalization of Ferrocene Alcohols

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Experimental Section

General

Ferrocenyl alcohols were prepared by the known method.[10] Other chemicals were commercially available. Melting points were recorded on an Electrothermal digital melting point apparatus and are uncorrected. IR spectra were recorded on a Varian FT-1000 spectrophotometer using KBr optics. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer using $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal standard. High resolution mass spectra were obtained using Microma GCT-TOF instrument.Optical rotation was measured at 589 nm (Na D line) on a Autopol IV automatic polarimeter. The enantiomeric excesses of the product was determined by HPLC analysis on a Chiralpak AD-H column using 2-propanol/hexane as the eluent.

Typical experimental procedure of C-C bond formation

A mixture of ferrocenyl alcohol (0.6 mmol) and indole or other noleophiles (0.5 mmol) in acetic acid (2 mL) was stirred at room temperature for an appropriate time. Upon completion, monitored by TLC, the mixture was poured into water, then $NaHCO_3$ was added to remove the acetic acid, CH_2Cl_2 was used to extract the product (15 mL×2), the organic layer was dried with anhydrous Na_2SO_4, then the solvent was evaporated under the reduced pressure. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford pure product. This procedure was followed for the synthesis of other ferrocenyl derivatives.

Typical experimental procedure of C-N bond formation

A mixture of ferrocenyl alcohol (0.6 mmol) and aromatic amines (0.5 mmol) in acetic acid (2 mL) was stirred at room temperature for an appropriate time. Upon completion, monitored by TLC, the mixture was poured into water, then $NaHCO_3$ was added to remove the acetic acid, CH_2Cl_2 was used to extract the product (15 mL×2), the organic layer was dried with anhydrous Na_2SO_4, then the solvent was evaporated under the reduced pressure. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford pure product. This procedure was followed for the synthesis of other ferrocenyl derivatives.

Typical experimental procedure of C-O bond formation

A mixture of ferrocenyl alcohol (0.6 mmol) and alcohol (1 mL) in acetic acid (2 mL) was stirred at room temperature for an appropriate time. Upon completion, monitored by TLC, the mixture was poured into water, then $NaHCO_3$ was added to remove the acetic acid, CH_2Cl_2 was used to extract the product (15 mL×2), the organic layer was dried with anhydrous Na_2SO_4, then the solvent was evaporated under the reduced pressure. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford pure product. This procedure was

followed for the synthesis of other ferrocenyl derivatives.

Typical experimental procedure of C-S bond formation

A mixture of ferrocenyl alcohol (0.6 mmol) and naphthalene-2-thiol (0.5 mmol) in acetic acid (2 mL) was stirred at room temperature for an appropriate time. Upon completion, monitored by TLC, the mixture was poured into water, then $NaHCO_3$ was added to remove the acetic acid, CH_2Cl_2 was used to extract the product (15 mL×2), the organic layer was dried with anhydrous Na_2SO_4, then the solvent was evaporated under the reduced pressure. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford pure product. This procedure was followed for the synthesis of other ferrocenyl derivatives.

Screening the effect of volume of EtOH in C-O bond formation procedure

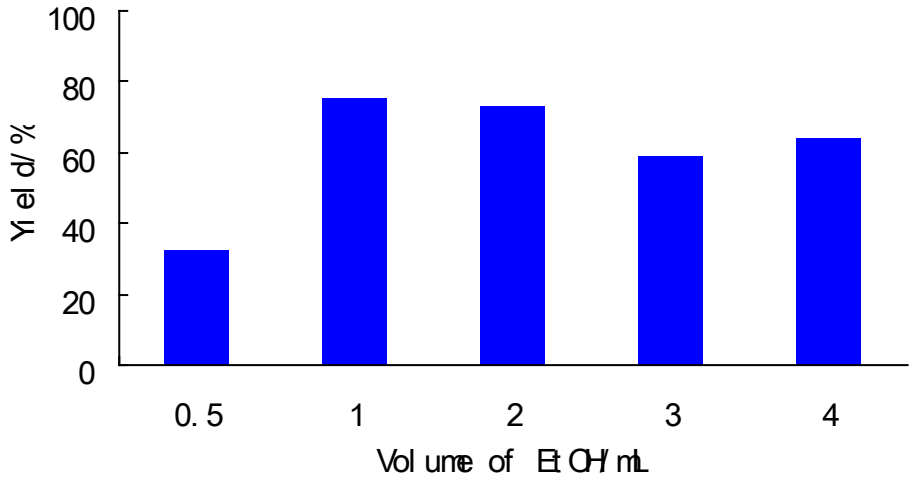


Figure 1

Characterization of compounds of α-Functionalized Ferrocene

*3-(Ferrocenylethyl)-1H-indole (**3a**)* [a]

82% yield; δ_H (400 MHz, $CDCl_3$) 1.70 (d, *J* 5.2, 3H), 4.18 (s, 9H, FcH), 4.28 (s, 1H), 6.74 (s, 1H), 7.10 (d, *J* 2.0, 1H), 7.16 (s, 1H), 7.32 (d, *J* 2.8, 1H), 7.65 (d, *J* 6.0, 1H), 7.83 (s, 1H, NH). *m/z* (HRMS) 329. 0881(M^+), calc. for $C_{20}H_{19}NFe$: 329. 0867.

*4-Methyl-3-(ferrocenylethyl)-1H-indole (**3b**)* [a]

56% yield; δ_H (400 MHz, $CDCl_3$) 1.67 (d, *J* 4.4, 3H), 2.75 (s, 3H), 4.13–4.18 (m, 9H), 4.37 (q, *J* 6.0, 1H), 6.66 (s, 1H), 6.86 (d, *J* 6.4, 1H), 7.05 (t, *J* 7.2, 1H), 7.17 (d, *J* 7.6, 1H), 7.05 (s, 1H, NH). *m/z* (HRMS) 343.1025 (M^+), calc. for $C_{21}H_{21}NFe$: 343.1023.

*4-Benzyloxy-3-(ferrocenylethyl)-1H-indole (**3c**)* [a]

65% yield; δ_H (400 MHz, $CDCl_3$) 1.62 (d, *J* 6.8, 3H), 4.01 (s, 7H), 4.15 (s, 1H), 4.21 (s, 1H), 4.57 (q, *J* 6.8, 1H), 5.23 (s, 2H), 6.45 (s, 1H), 6.60 (d, *J* 8.0, 1H), 6.93 (d, *J* 8.0, 1H), 7.01 (t, *J* 8.0, 1H), 7.34 (t, *J* 7.2, 1H), 7.44 (t, *J* 7.6, 2H), 7.57 (d, *J* 7.6, 2H), 7.76 (br, s, 1H, NH). *m/z* (HRMS) 435.1284 (M^+), calc. for $C_{27}H_{25}NOFe$: 435.1286.

*5-Methyl-3-(ferrocenylethyl)-1H-indole (**3d**)* [a]
66% yield; δ_H (400 MHz, $CDCl_3$) 1.69 (d, *J* 7.2, 3H), 2.46 (s, 3H), 4.07–4.15 (m, 9H), 4.24 (s, 1H), 6.71 (s, 1H), 6.99 (d, *J* 8.4, 1H), 7.22 (d, *J* 8.0, 1H), 7.44 (s, 1H), 7.75 (br s, 1H, NH). *m/z* (HRMS) 343.1029 (M^+), calc. for $C_{21}H_{21}NFe$: 343.1023.

*5-Bromol-3-(ferrocenylethyl)-1H-indole (**3e**)* [a]
61% yield; δ_H (400 MHz, $CDCl_3$) 1.67 (d, *J* 6.8, 3H), 4.05–4.23 (m, 9H), 4.30 (s, 1H), 6.70 (s, 1H), 7.22 (s, 1H), 7.24 (s, 1H), 7.75 (s, 1H), 7.86 (s, 1H, NH). *m/z* (HRMS) 406.9974 (M^+), calc. for $C_{20}H_{18}NBrFe$: 406.9972.

*6-Methyl-3-(ferrocenylethyl)-1H-indole (**3f**)* [a]
67% yield; δ_H (400 MHz, $CDCl_3$) 1.67 (d, *J* 7.2, 3H), 2.44 (s, 3H), 4.06–4.14 (m, 9H), 4.23 (s, 1H), 6.69 (s, 1H), 6.93 (d, *J* 8.4, 1H), 7.12 (s, 1H), 7.53 (d, *J* 8.0, 1H), 7.73 (br s, 1H, NH). *m/z* (HRMS) 343.1021 (M^+), calc. for $C_{21}H_{21}NFe$: 343.1023.

*7-Methyl-3-(ferrocenylethyl)-1H-indole (**3g**)* [a]
76% yield; δ_H (400 MHz, $CDCl_3$) 1.70 (d, *J* 7.2, 3H), 2.45 (s, 3H), 4.07–4.16 (m, 9H), 4.26 (s, 1H), 6.76 (s, 1H), 6.97 (d, *J* 7.2, 1H), 7.03 (t, *J* 7.6, 1H), 7.51 (d, *J* 7.6, 1H), 7.78 (s, 1H, NH). *m/z* (HRMS) 343.1020 (M^+), calc. for $C_{21}H_{21}NFe$: 343.1023.

*2-Phenyl-3-(ferrocenylethyl)-1H-indole (**3h**)* [a]

68% yield; δ_H (300 MHz, $CDCl_3$) 1.70 (d, *J* 7.2, 3H), 3.96–4.16 (m, 9H), 4.48 (q, *J* 7.2, 1H), 6.96 (t, *J* 7.5, 1H), 7.07–7.12 (m, 1H), 7.28–7.41 (m, 2H), 7.46–7.58 (m, 5H), 7.95 (br s, 1H, NH). *m/z* (HRMS) 405.1180 (M^+), calc. for $C_{26}H_{23}FeN$: 405.1180.

*3-(phenyl(ferrocenyl)methyl)-1H-indole (**3i**)* [a]

90% yield; δ_H (400 MHz, $CDCl_3$) 3.98 (m, 9H), 5.32 (s, 1H), 6.82 (s, 1H), 6.93 (t, *J* 7.2, 1H), 7.10 (t, *J* 7.2, 1H), 7.19 (t, *J* 7.6, 1H), 7.25–7.30 (m, 4H), 7.35 (d, *J* 7.6, 2H), 7.86 (br s, 1H, NH). *m/z* (HRMS) 391.1021 (M^+), calc. for $C_{25}H_{21}NFe$: 391.1023.

*4-Benzyloxy-3-(phenyl(ferrocenyl)methyl)-1H-indole (**3j**)* [a]
69% yield; δ_H (400 MHz, $CDCl_3$) 3.80–4.28 (m, 9H), 4.97–5.16 (m, 2H), 5.77 (s, 1H), 6.43 (d, *J* 8.0, 1H), 6.62 (s, 1H), 6.88 (d, *J* 8.0, 1H), 6.98 (t, *J* 8.0, 1H), 7.03 (d, *J* 7.2, 2H), 7.11 (t, *J* 7.6, 3H), 7.32–7.52 (m, 5H), 7.83 (s, 1H, NH). *m/z* (HRMS) 497.1142 (M^+), calc. for $C_{32}H_{27}NOFe$: 497.1442.

*5-Bromo-3-(phenyl(ferrocenyl)methyl)-1H-indole (**3k**)* [a]
72% yield; δ_H (400 MHz, $CDCl_3$) 4.04–4.27 (m, 9H), 5.21 (s, 1H), 6.83 (s, 1H), 7.17 (s, 2H), 7.20–7.23 (m, 1H), 7.27–7.31 (m, 4H), 7.37(s, 1H), 7.93 (br s, 1H, NH). *m/z* (HRMS) 469.0132 (M^+), calc. for $C_{25}H_{20}NBrFe$: 469.0129.

*7-Methyl-3-(phenyl(ferrocenyl)methyl)-1H-indole (**3l**)* [a]
80% yield; δ_H (400 MHz, $CDCl_3$) 2.45 (s, 3H), 4.05–4.29 (m, 9H), 5.28 (s, 1H), 6.85 (d, *J* 7.6, 1H), 6.88 (s, 1H), 6.91 (t, *J* 6.8, 1H), 7.11 (d, *J* 8.0, 1H), 7.18 (t, *J* 7.2, 1H), 7.29 (d, *J* 7.2, 2H), 7.35 (d,

J 7.6, 2H), 7.82 (s, 1H, NH). *m/z* (HRMS) 405.1169 (M^+), calc. for $C_{26}H_{23}NFe$: 405.1180.

*6-Methyl-3-(phenyl(ferrocenyl)methyl)-1H-indole (**3m**)* [a]
94% yield; δ_H (400 MHz, $CDCl_3$) 2.40 (s, 3H), 3.96–4.21 (m, 9H), 5.30 (s, 1H), 6.75 (s, 1H), 6.79 (d, *J* 8.0, 1H), 7.09 (s, 1H), 7.11–7.14 (m, 1H), 7.17–7.21 (m, 1H), 7.26–7.30 (m, 2H), 7.34–7.36 (m, 2H), 7.76 (br s, 1H, NH). *m/z* 405.1180 (HRMS) (M^+), calc. for $C_{26}H_{23}NFe$: 405.1180.

*1-Phenyl-2-[phenyl(ferrocenyl)methyl]butane-1, 3-dione (**3n**)* [b]

38% yield; δ_H (400 MHz, $CDCl_3$) 1.91 (s, 3H), 3.91–3.99 (m, 9H), 4.77 (d, *J* 10.8, 1H), 5.25 (d, *J* 10.8, 1H), 7.28–7.95 (m, 10H). *m/z* 436. 1138 (HRMS) (M^+), calc. for $C_{27}H_{24}O_2Fe$: 436. 1126.

*1, 3-diphenyl-2-[phenyl(ferrocenyl)methyl]propane-1,3-dione (**3o**)* [b]
78% yield; δ_H (400 MHz, $CDCl_3$): δ 3.82–4.01 (m, 9H), 4.95 (d, *J* 10.2, 1H), 6.03 (d, *J* 10.2, 1H), 7.16–7.84 (m, 15H). *m/z* 498.1289 (HRMS) (M^+), calc. for $C_{32}H_{26}O_2Fe$: 498.1282.

*4-[Ferrocenyl(phenyl)methyl]benzene-1,3-diol (**3p**)* [b]

75% yield; δ_H (400 MHz, $CDCl_3$) 3.90 (t, *J* 8.4, 1H), 4.00–4.20 (m, 9H), 5.20-5.21 (d, *J* 6.0, 1H), 5.28 (s, 1H), 6.20–6.38 (m, 2H), 6.68–7.04 (m, 1H), 7.20–7.27 (m, 5H). *m/z* 384.0825 (HRMS) (M^+), calc. for $C_{23}H_{20}O_2Fe$: 384.0813.

*1- [Phenyl(ferrocenyl)methyl]-naphthalen-2-ol (**3q**)* [b]

75% yield; δ_H (400 MHz, $CDCl_3$) 3.98–4.30 (m, 9H), 5.48 (s, 1H), 6.18 (s, 1H), 7.06 (d, *J* 8.4, 1H), 7.22–7.25 (m, 1H), 7.29–7.34 (m, 3H), 7.39–7.41 (m, 2H), 7.43–7.48 (m, 1H), 7.70 (d, *J* 8.8, 1H), 7.77 (d, *J* 8.0, 1H), 8.08 (d, *J* 8.0, 1H). *m/z* 418. 1026 (HRMS) (M^+), calc. for $C_{27}H_{22}OFe$: 418. 1020.

*N-((ferrocenyl)(phenyl)methyl)benzenamine (**5a**)*

94% yield; brown solid. Mp 38–40 ℃. ν_{max}(KBr)/cm^{-1} 3411, 3056, 1605. δ_H (300 MHz, $CDCl_3$)

4.03–4.20 (m, 9H), 4.76 (s, 1H), 5.06 (s, 1H), 6.56 (d, *J* 7.7, 1H), 6.67 (t, *J* 6.9, 1H), 7.12 (t, *J* 7.6, 2H), 7.24 (d, *J* 6.1, 2H), 7.32 (t, *J* 7.2, 2H), 7.45 (d, *J* 7.4, 2H). δ_C (75 MHz, $CDCl_3$) 147.6, 143.1, 129.4, 128.6, 127.2, 126.8, 117.6, 113.5, 94.3, 68.8, 68.1, 67.9, 67.5, 66.8, 57.6. *m/z* 367.1010 (HRMS) (M^+), calc. for $C_{23}H_{21}FeN$: 367.102.

*N-((ferrocenyl)(phenyl)methyl)-4-chlorobenzenamine (**5b**)*

96% yield; orange solid. Mp 85–86 ℃. ν_{max}(KBr)/cm^{-1} 3411, 3025, 1597. δ_H ($CDCl_3$, 400 MHz):

δ 4.07–4.28 (m, 9H) 4.74 (s, 1H), 4.98 (s, 1H), 6.46 (d, *J* 8.0, 2H), 7.04 (d, *J* 8.0, 2H), 7.24–7.42 (m, 5H). δ_C (75 MHz, $CDCl_3$) 146.3, 142.8, 129.4, 128.9, 127.6, 127.1, 122.4, 114.8, 94.1, 69.1, 68.5, 68.3, 67.7, 67.1, 57.9. *m/z* 401.0634 (HRMS) (M^+), calc. for $C_{23}H_{20}ClFeN$: 401.0634.

*N-((ferrocenyl)(phenyl)methyl)-4-bromobenzenamine (**5c**)*

97% yield; yellow solid. Mp 78–79 ℃. ν_{max}(KBr)/cm^{-1} 3372, 3087, 1589. δ_H (300 MHz, $CDCl_3$) 4.02–4.18 (m, 9H), 4.78 (s, 1H), 5.00 (s, 1H), 6.45 (d, *J* 7.9, 2H), 7.18 (d, *J* 7.8, 2H), 7.26 (s, 1H), 7.32 (t, *J* 7.3, 2H), 7.41 (d, *J* 7.7, 2H). δ_C (75 MHz, $CDCl_3$) 146.4, 142.4, 132.0, 128.7, 127.4, 126.8, 115.1, 109.2, 93.8, 68.8, 68.2, 68.0, 67.4, 66.9, 57.52. *m/z* 445.0115 (HRMS) (M^+), calc. for $C_{23}H_{20}BrFeN$: 445.0129.

*N-((ferrocenyl)(phenyl)methyl)-4-methylbenzenamine (**5d**)*

67% yield; yellow solid. Mp 46–48 ℃. ν_{max}(KBr)/cm^{-1} 3411, 3087, 1613. δ_H (300 MHz, $CDCl_3$) 2.20 (s, 3H), 4.05–4.19 (m, 9H), 4.64 (s, 1H), 5.01 (s, 1H), 6.48 (d, *J* 6.6, 2H), 6.59 (d, *J* 6.7, 2H), 7.25-7.31 (m, 3H), 7.43 (d, *J* 6.3, 2H). δ_C (75 MHz, $CDCl_3$) 145.4, 143.4, 129.9, 128.6, 127.2, 126.8, 113.6, 94.5, 68.8, 68.1, 67.8, 67.5, 66.7, 57.9, 20.6. *m/z* 381.1187 (HRMS) (M^+), calc. for $C_{24}H_{23}FeN$: 381.1180.

*N-((ferrocenyl)(phenyl)methyl)-4-methoxybenzenamine (**5e**)*

66% yield; yellow solid. Mp 45–46 ℃. ν_{max}(KBr)/cm^{-1} 3449, 3025, 1636. δ_H (300 MHz, $CDCl_3$) 3.72 (s, 3H), 4.01–4.21 (m, 10H), 5.00 (s, 1H), 6.54 (d, *J* 9.0, 2H), 6.74 (d, *J* 9.0 , 2H), 7.24–7.48 (m, 5H). δ_C (75 MHz, $CDCl_3$) 152.2, 143.6, 142.0, 128.6, 127.2, 126.9, 115.0, 114.7, 94.6, 68.8, 68.1, 67.8, 67.5, 66.6, 58.5, 55.9. *m/z* 397.1127 (HRMS) (M^+), calc. for $C_{24}H_{23}FeNO$: 397.1129.

*N-((ferrocenyl)(phenyl)methyl)-4- nitrobenzenamine (**5f**)*

97% yield; yellow liquid. ν_{max}(KBr)/cm^{-1} 3401, 2986, 1593, 1455, 1307. δ_H (300 MHz, $CDCl_3$) 3.98–4.20 (m, 9H), 5.20 (d, *J* 4.8, 1H), 5.52 (s, 1H), 6.50 (d, *J* 9.1, 2H), 7.29-7.39 (m, 5H), 8.03 (d, *J* 9.1, 2H). δ_C (100 MHz, $CDCl_3$) 152.1, 141.0, 138.5, 128.9, 127.9, 126.8, 126.5, 112.1, 92.5, 69.0, 68.5, 68.5, 67.5, 67.3, 57.0. *m/z* 412.0876 (HRMS) (M^+), calc. for $C_{23}H_{20}FeN_2O_2$: 412.0873.

*N-((Ferrocenyl)(phenyl)methyl)-2- nitro benzenamine (**5g**)*

95% yield; orange solid. IR (KBr) ν_{max}(KBr)/cm^{-1} 3381, 3091, 2840, 1617. δ_H (300 MHz, $CDCl_3$) 3.80-4.28 (m, 9H), 5.33 (d, *J* 4.5, 1H), 6.61 (d, *J* 8.2, 2H), 7.26–7.42 (m, 5H), 8.23 (d, *J* 8.1, 1H), 9.06 (s, 1H). δ_C (100 MHz, $CDCl_3$) 144.2, 142.0, 136.3, 132.4, 128.8, 127.8, 127.0, 126.8, 115.9, 115.5, 92.1, 69.2, 68.5, 68.2, 67.4, 66.2, 56.6. *m/z* 412.0873 (HRMS) (M^+), calc. for $C_{23}H_{20}FeN_2O_2$: 412.0873.

*N-(1-ferrocenylethyl)benzenamine (**5h**)*

61% yield; orange oil. IR (KBr) ν_{max}(KBr)/cm^{-1} 3409, 3092, 2971, 1602, 1504, 1313, 1105, 1000, 819, 748, 692. δ_H (300 MHz, $CDCl_3$) 1.53 (d, *J* 6.6, 3H), 4.16–4.22 (m, 10H), 4.31–4.38 (m, 1H), 6.66–6.75 (m, 3H), 7.19–7.27 (m, 2H). δ_C (100 MHz, $CDCl_3$) 147.9, 129.8, 117.6, 113.7, 94.0, 68.9, 68.2, 68.0, 67.5, 66.6, 47.5, 21.2. *m/z* 305.0876 (HRMS) (M^+), calc. for $C_{18}H_{19}FeN$: 305.0867.

*4-Chloro-N-(1-ferrocenylethyl)benzenamine (**5i**)*

78% yield; orange solid. Mp 96–97°C. ν_{max}(KBr)/cm^{-1} 3403, 3086, 2972, 2870, 1595, 1500, 1398, 1308, 1132, 1028, 998, 815. δ_H (300 MHz, $CDCl_3$) 1.48 (d, *J* 6.0, 3H), 3.90 (br s, 1H), 4.18–4.23 (m, 10H), 6.56 (d, *J* 8.4z, 2H), 7.13 (d, *J* 8.4, 2H). δ_C (100 MHz, $CDCl_3$) 146.5, 129.6, 122.0, 114.7, 93.6, 69.1, 68.9, 68.3, 68.1, 67.5, 66.5, 47.8, 21.2. *m/z* 339.0478 (HRMS) (M^+), calc. for $C_{18}H_{18}ClFeN$: 339.0477.

*N-(1-ferrocenylethyl)-4-methoxybenzenamine (**5j**)*

54% yield; orange oil. ν_{max}(KBr)/cm^{-1} 3405, 3089, 2980, 1597, 1510, 1308, 1100, 819 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 1.49 (d, *J* 6.3, 3H), 3.76–4.27 (m, 10H), 6.23 (s, 3H), 6.23 (d, *J* 8.7, 2H), 6.80 (d, *J* 8.7, 2H). δ_C (100 MHz, $CDCl_3$) 152.4, 142.0, 115.4, 115.3, 93.9, 68.8, 68.1, 67.9, 67.5, 66.5, 56.2, 48.8, 21.5. *m/z* 335.0981 (HRMS) (M^+), calc. for $C_{19}H_{21}FeNO$: 335.0973.

*N-(1-ferrocenylethyl)-4-nitrobenzenamine (**5k**)*

80% yield; orange solid. Mp 110–112°C. ν_{max}(KBr)/cm^{-1} 3400, 3084, 2986, 1593, 1509, 1455, 1307, 1101, 821. δ_H (300 MHz, $CDCl_3$) 1.53 (d, *J* 6.6, 3H), 4.06–4.19 (m, 9H), 4.40–4.44 (m, 1H), 6.54 (d, *J* 6.0, 2H), 8.07 (d, *J* 6.0, 2H). δ_C (75 MHz, $CDCl_3$): δ 152.7, 137.7, 126.9, 111.5, 91.8, 68.9, 68.5, 68.2, 67.4, 66.3, 47.3, 20.7. *m/z* 350.0715 (HRMS) (M^+), calc. for $C_{18}H_{18}FeN_2O_2$: 350.0718.

*2-(1-Ferrocenylethylthio)-naphthalene (**7a**)*

85% yield; orange oil. ν_{max}(KBr)/cm^{-1} 3087, 2971, 1656, 1581, 1364, 1221, 1002, 813. δ_H (300 MHz, $CDCl_3$) 1.67 (d, *J* 6.9, 3H), 4.06–4.29 (m, 10H), 7.42–7.48 (m, 3H), 7.73–7.83 (m, 4H). δ_C (75 MHz, $CDCl_3$) 134.0, 133.2, 132.8, 132.1, 130.9, 128.6, 128.1, 127.9, 126.8, 126.5, 91.2, 69.1, 68.4, 68.2, 68.1, 66.6, 44.0, 21.6. *m/z* 372.0635 (HRMS) (M^+), calc. for $C_{22}H_{20}FeS$: 372.0635.

*2-((Ferrocenyl)(phenzyl)methylthio)-naphthalene (**7b**)*

83% yield; orange solid. Mp 140–141°C. ν_{max}(KBr)/cm^{-1} 3051, 2922, 1581, 1494, 1194, 1028, 815, 742. δ_H (300 MHz, $CDCl_3$): δ 4.11–4.19 (m, 9H), 5.25 (s, 1H), 7.18–7.23 (m, 2H), 7.28–7.32 (m, 2H), 7.40–7.43 (m, 4H), 7.63–7.68 (m, 3H), 7.72–7.76 (m, 1H). δ_C (75 MHz, $CDCl_3$) 142.4, 133.9, 133.6, 132.6, 131.5, 130.2, 128.8, 128.6, 128.4, 128.0, 127.9, 127.7, 126.7, 126.4, 90.0, 69.4, 69.0, 68.6, 68.2, 68.1, 54.7. *m/z* 434.0792 (HRMS) (M^+), calc. for $C_{27}H_{22}FeS$: 434.0792.

*Ferrocenyl (phenyl) (methoxyl)methane (**8a**)* [c]
40% yield; orange solid. Mp 112–113°C. ν_{max}(KBr)/cm^{-1} 3091, 2981, 2870, 1494, 1453, 1397, 1194. δ_H (400 MHz, $CDCl_3$) 3.28 (s, 3H), 3.98-4.30 (m, 9H), 4.98 (s, 1H), 7.30-7.42 (m, 5H). *m/z* 306.0707 (HRMS) (M^+), calc. for $C_{18}H_{18}FeO$: 306.0707.

*Ferrocenyl (phenyl) (ethoxyl)methane (**8b**)*

75% yield; orange solid. Mp 54–55°C. ν_{max}(KBr)/cm^{-1} 3085, 3027, 2869, 2840, 1491, 1452, 1104. δ_H (400 MHz, $CDCl_3$) 1.19 (s, 3H), 3.42 (d, *J* 3.6, 2H), 4.00–4.32 (m, 9H), 5.08 (s, 1H), 7.29–7.41 (m, 5H). δ_C (100 MHz, DMSO-d_6): δ 148.0, 133.7, 132.9, 132.5, 96.3, 85.2, 74.2, 73.0, 73.0, 72.8, 72.4, 69.2, 21.0. *m/z* (HRMS) 320.0864 (M^+), calc. for $C_{19}H_{20}FeO$: 320.0864.

*Ferrocenyl (phenyl) (isopropoxyl)mathan (**8c**)*

40% yield; orange solid. Mp 67–68℃. ν_{max}(KBr)/cm^{-1} 3084, 2965, 2925, 2872, 1490, 1453, 1103, 1062, 809, 726, 701. δ_H (400 MHz, $CDCl_3$) 1.09 (d, *J* 6.0, 3H), 1.21 (d, *J* 6.0, 3H), 3.51–3.60 (m, 1H), 3.94–4.25 (m, 9H), 5.22 (s, 1H), 7.27–7.44 (m, 5H). δ_C (100 MHz, DMSO-d_6) 148.7, 133.6, 132.6, 97.0, 82.1, 74.2, 73.8, 72.9, 72.8, 72.7, 72.3, 28.8, 27.1. *m/z* (HRMS) 334.1018 (M^+), calc. for $C_{20}H_{22}FeO$: 334.1020.

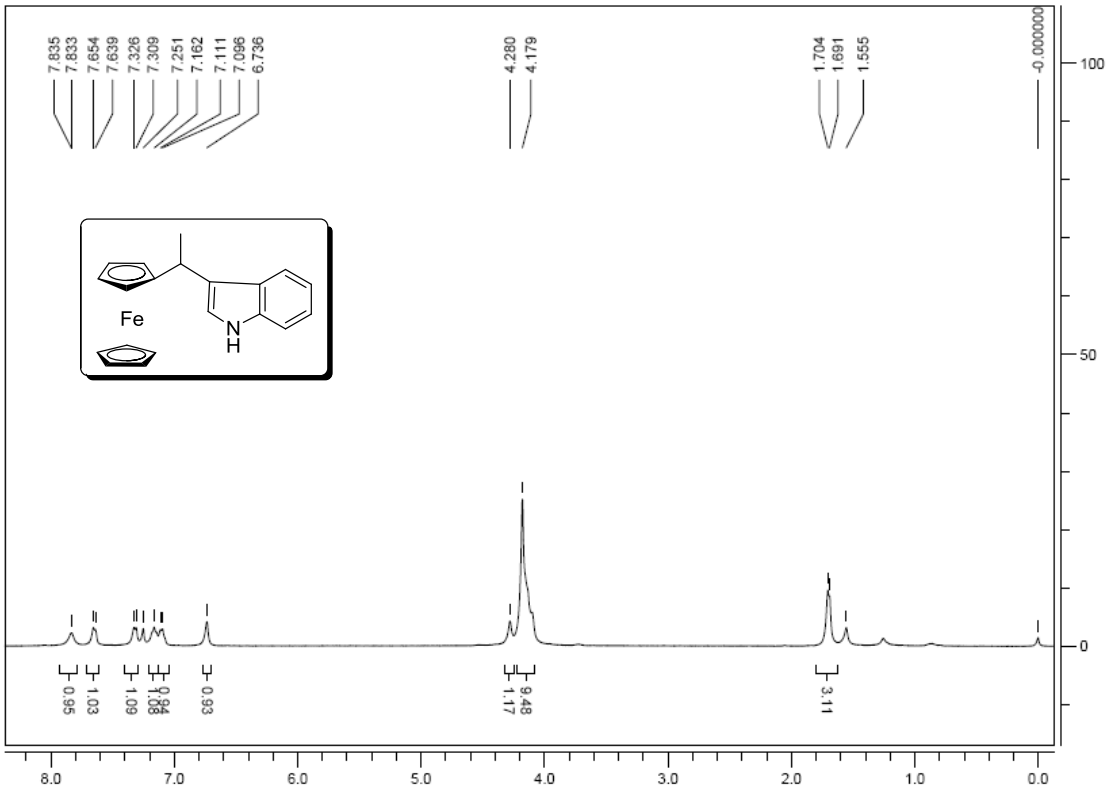
References

(a) R. Jiang, X. P. Xu, T. Chen, H. Y. Li, G. Chen, S. J. Ji, *Synlett* **2009**, 2815. doi: 10.1055/s-0029-1217998

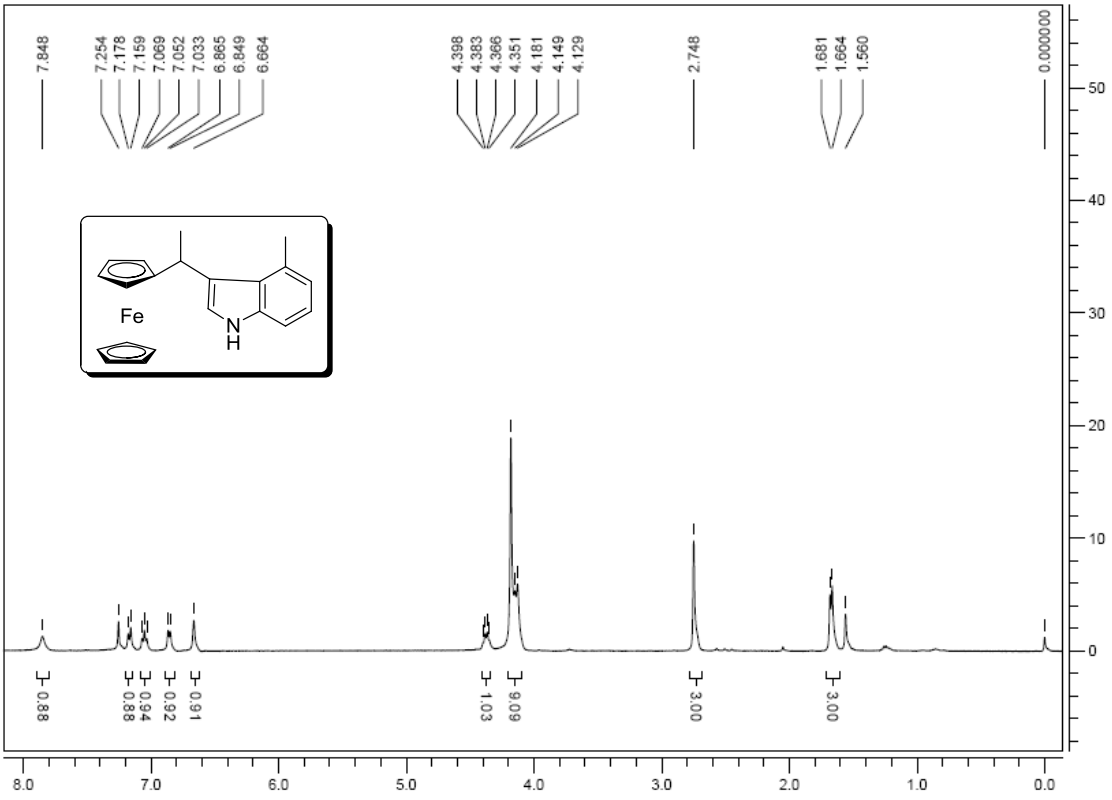
(b) X. P. Xu, R. Jiang, X. G. Zhou, Y. Liu, S. J. Ji, Y. Zhang, *Tetrahedron* **2009**, *65*, 877. doi: 10.1016/j.tet.2008.11.048

(c) M. Cais, A.Eisenstadt, *J. Org. Chem.* **1965**, 30, 1148. doi: 10.1021/jo01015a047

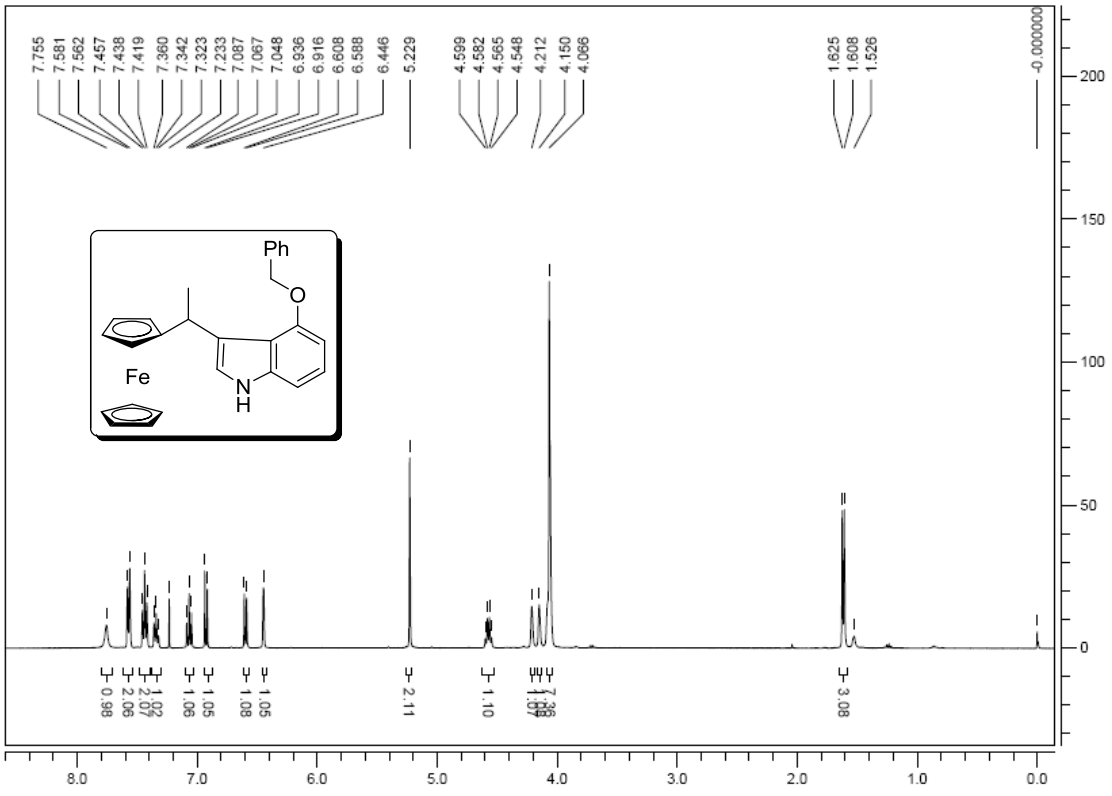
The ^{1}H NMR and ^{13}C NMR charts for compounds of α-Functionalized Ferrocene 3-(ferrocenylethyl)-1H-indole (3a)



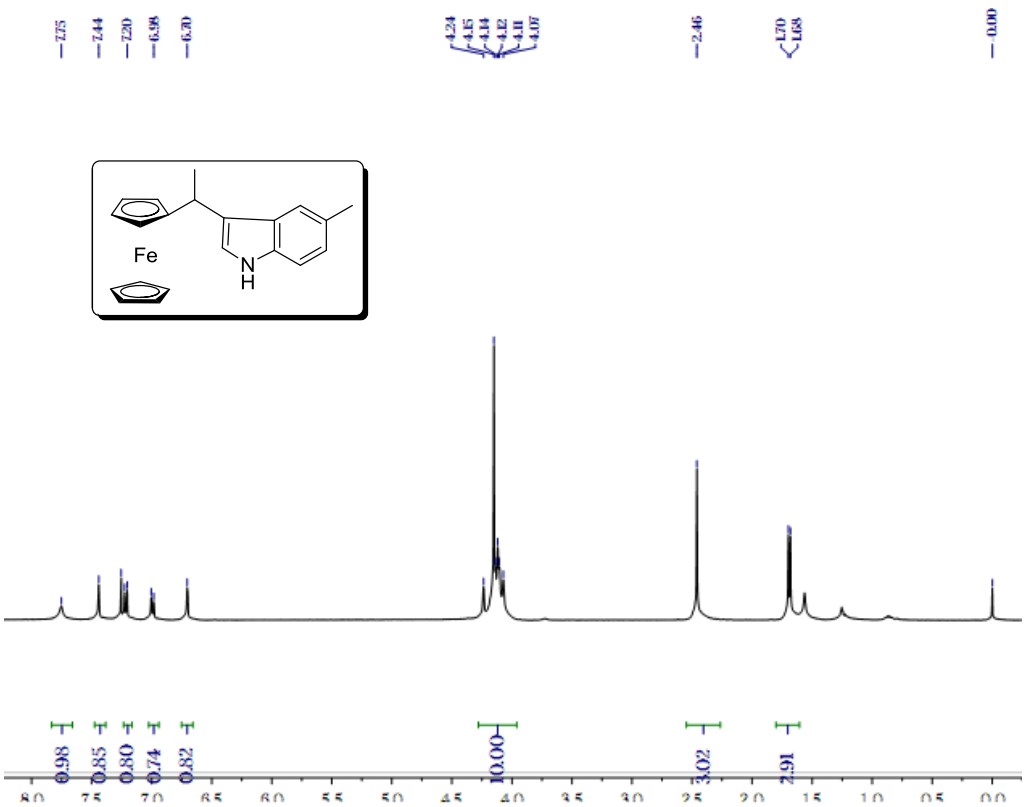
4-methyl-3-(ferrocenylethyl)-1H-indole (3b)



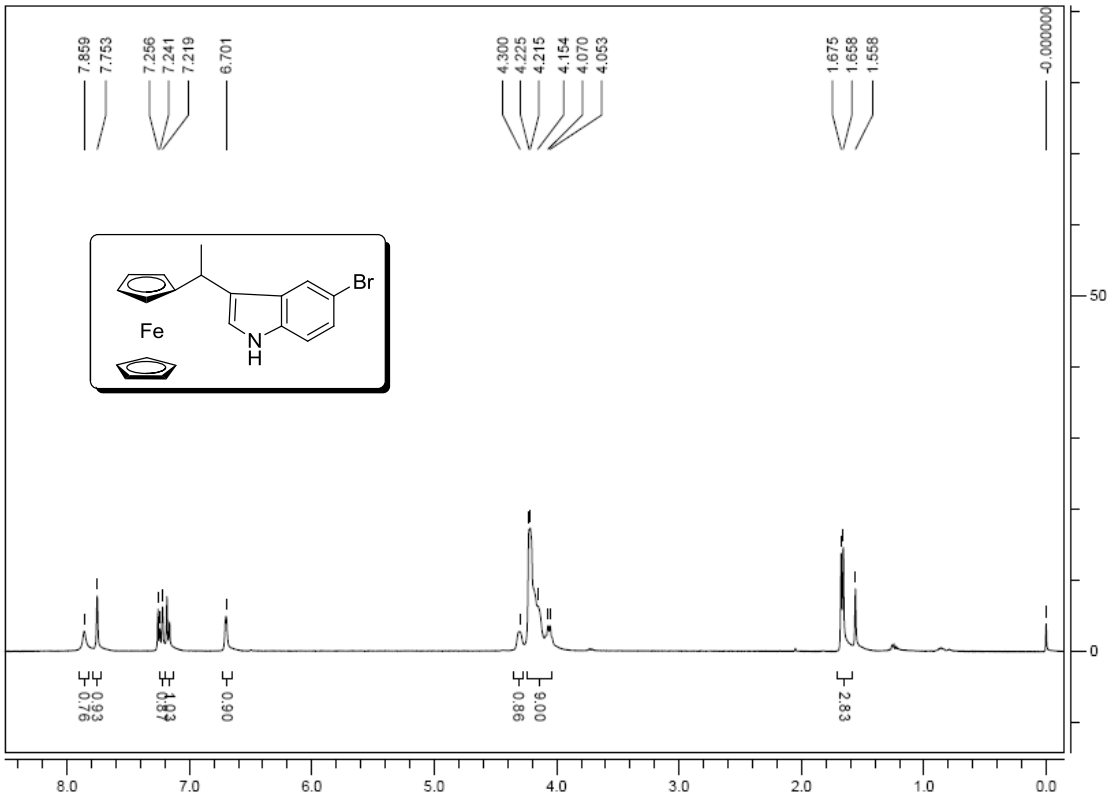
4-benzyloxy-3-(ferrocenylethyl)-1H-indole (3c)



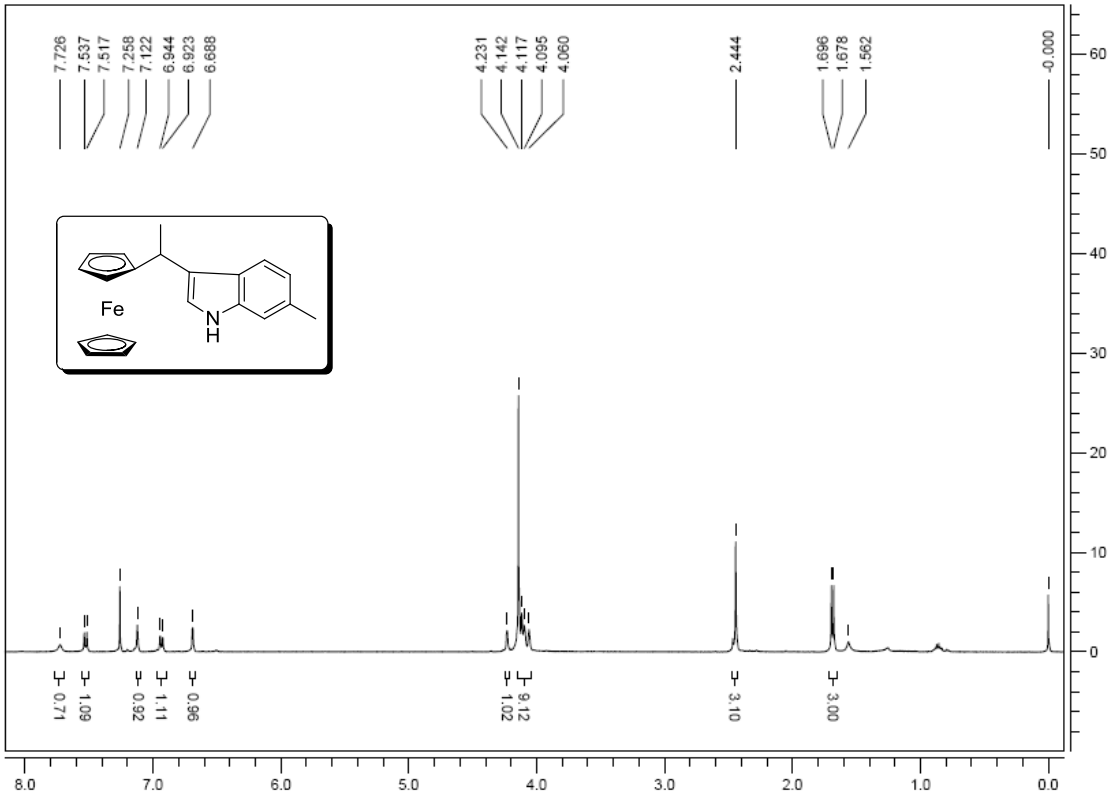
5-methyl-3-(ferrocenylethyl)-1H-indole (3d)



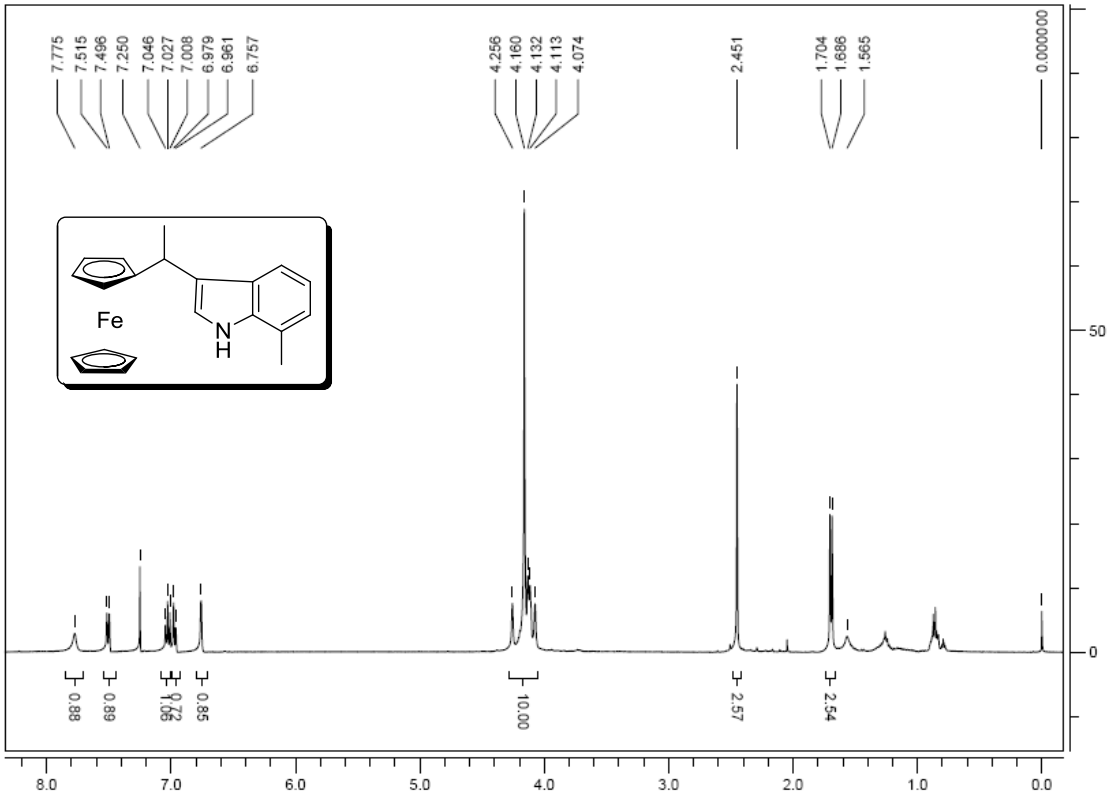
5-bromol-3-(ferrocenylethyl)-1*H*-indole (3e)



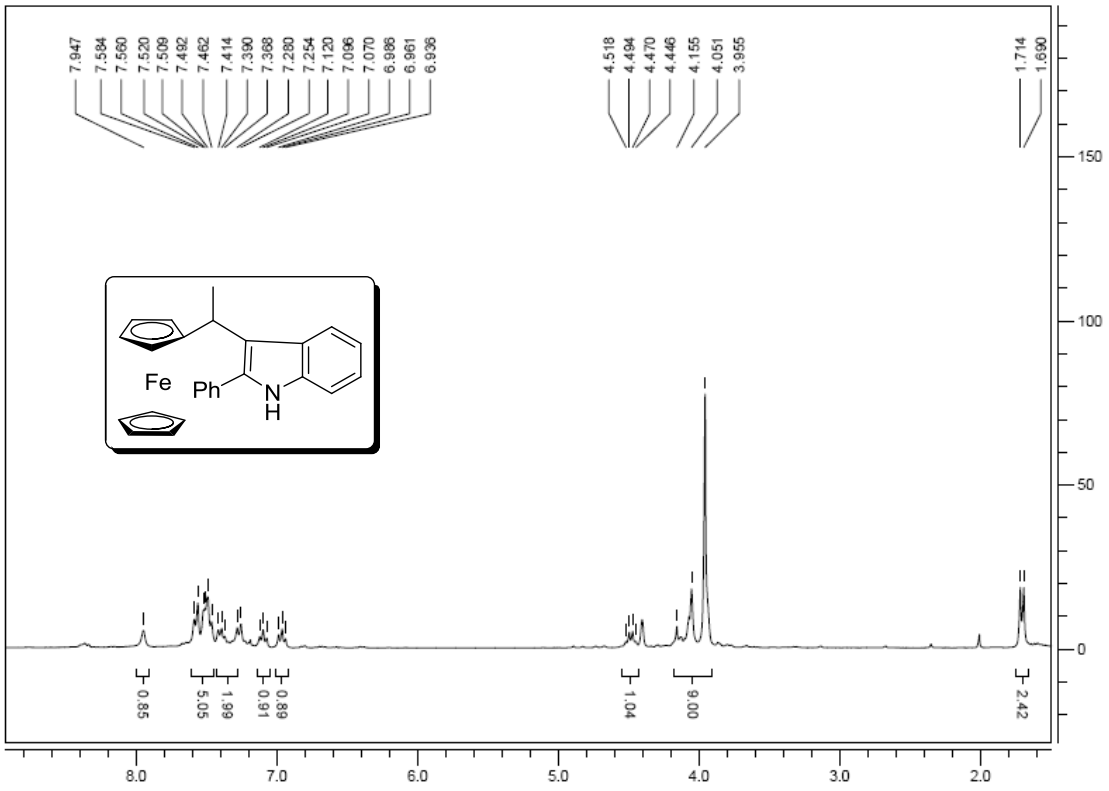
6-methyl-3-(ferrocenylethyl)-1*H*-indole (3f)



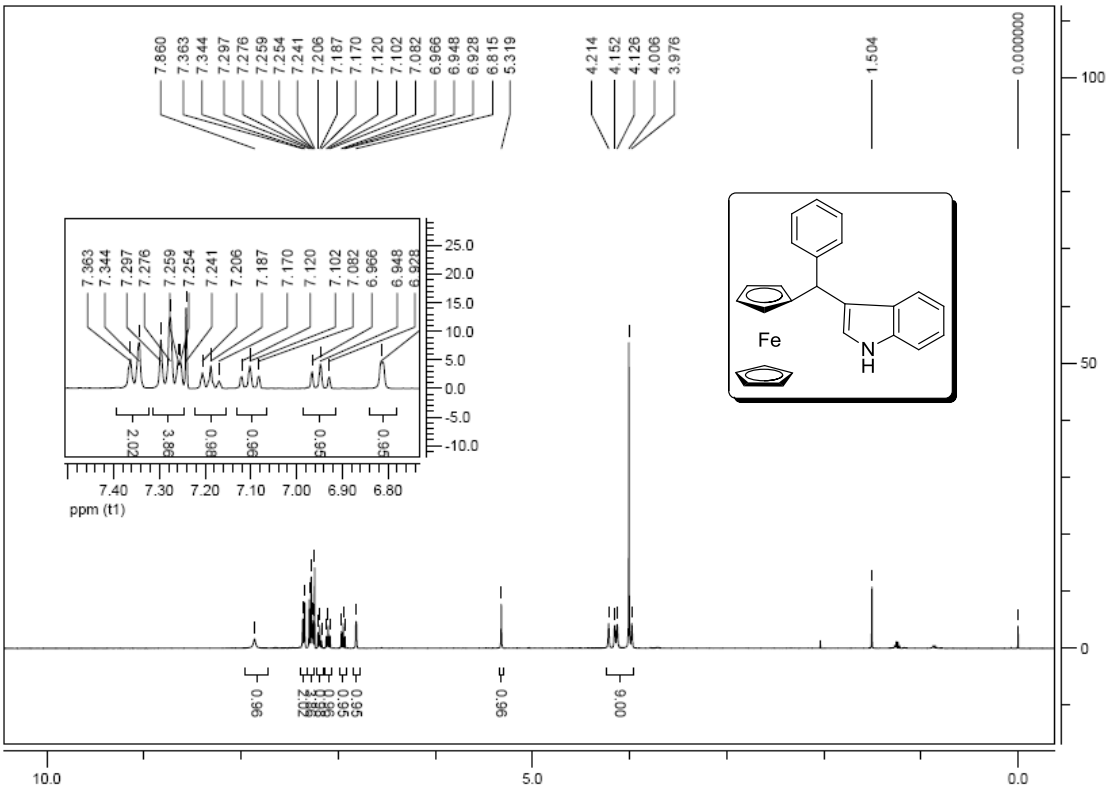
7-methyl-3-(ferrocenylethyl)-1*H*-indole(3g)



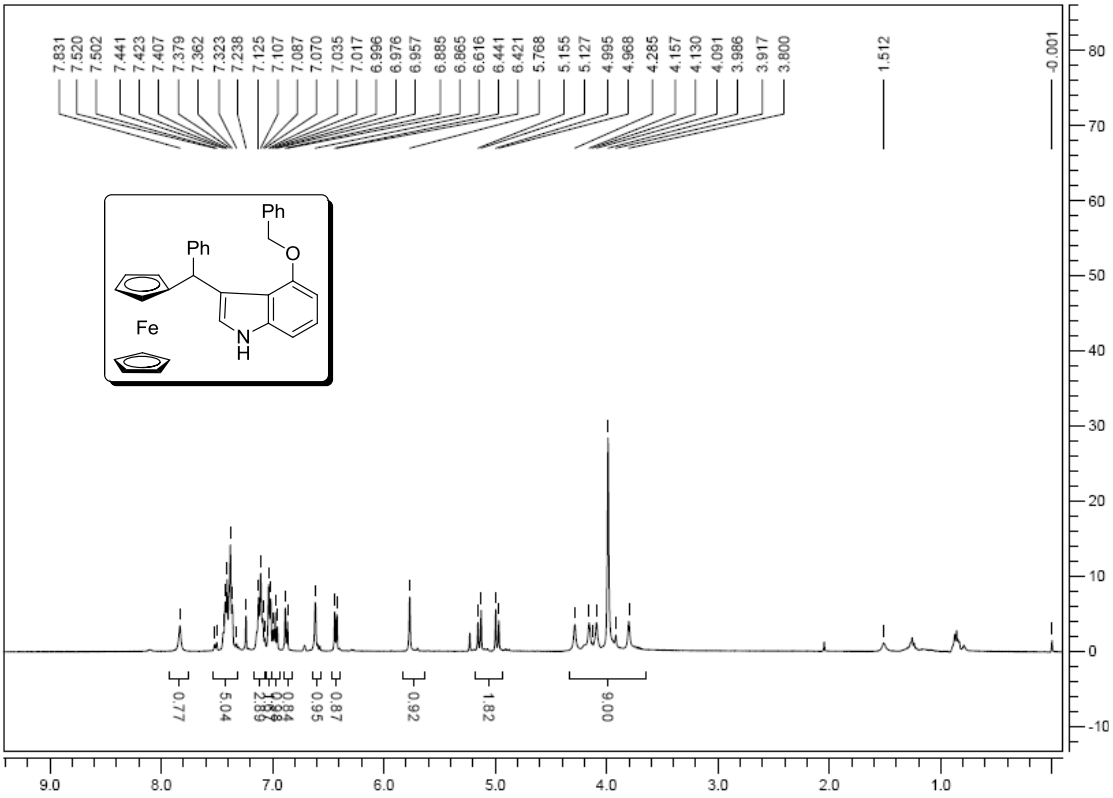
2-phenyl-3-(ferrocenylethyl)-1*H*-indole (3h)



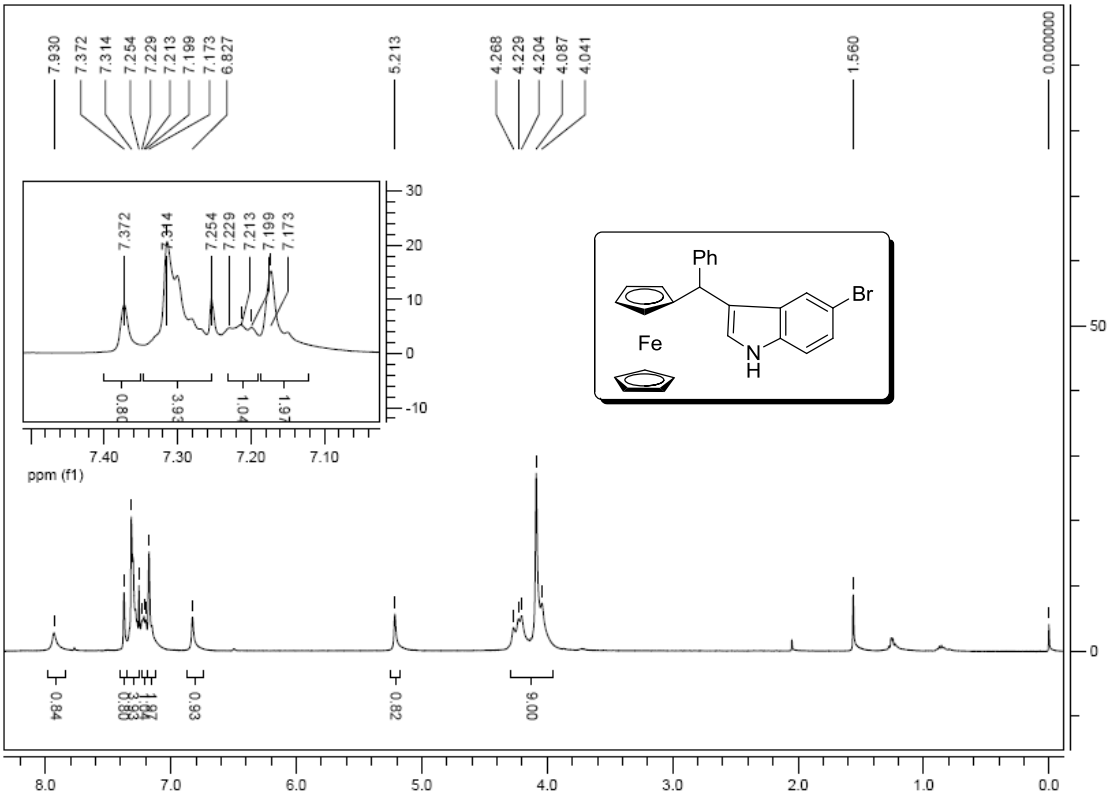
3-(phenyl(ferrocenyl)methyl)-1*H*-indole (3i)



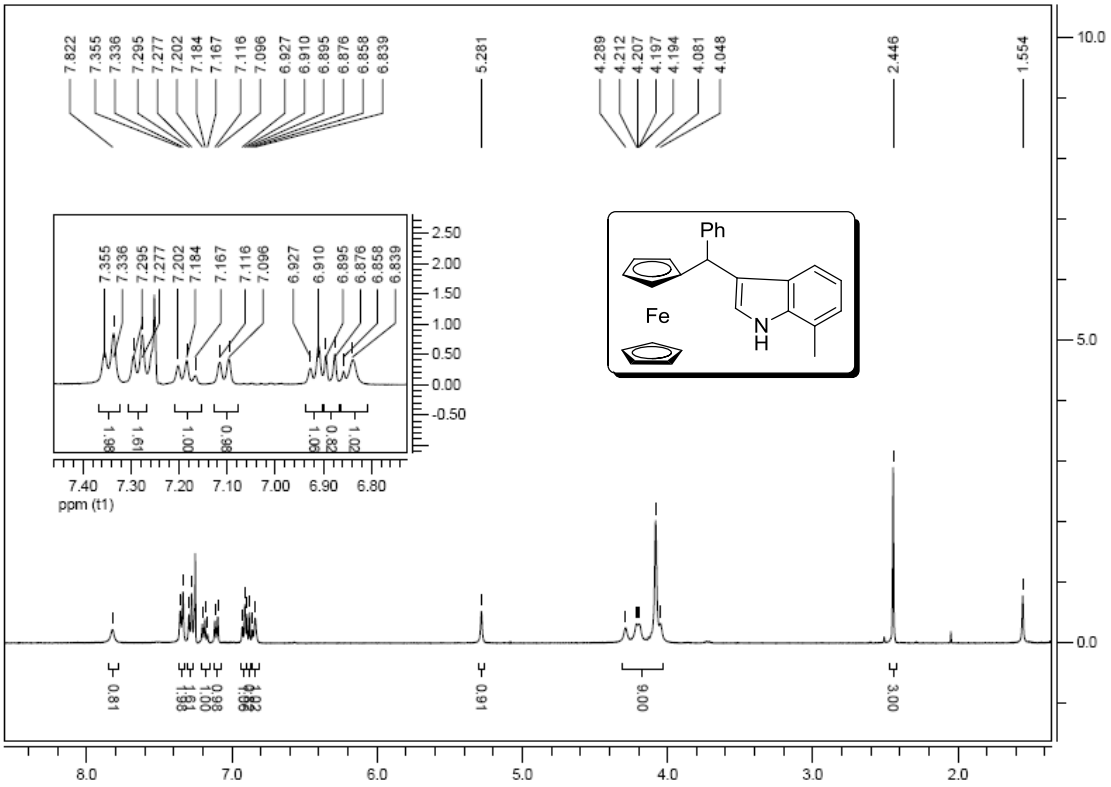
4-benzyloxy-3-(phenyl(ferrocenyl)methyl)-1*H*-indole (3j)



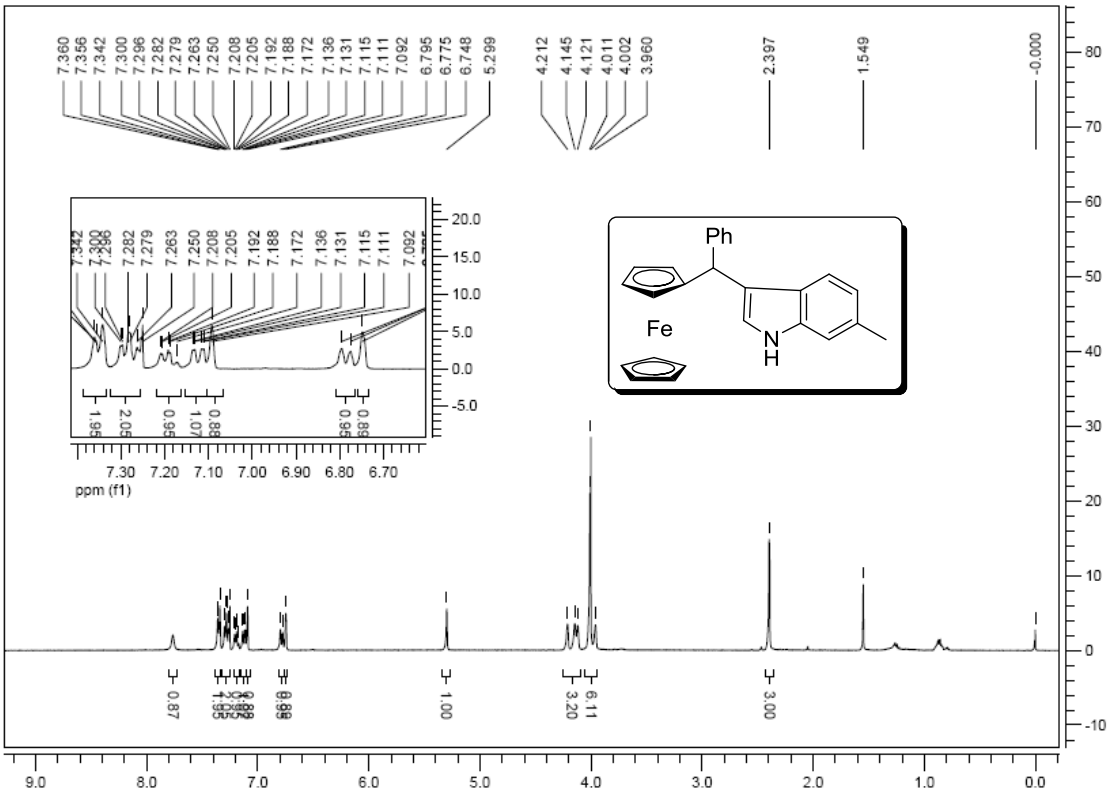
5-bromo-3-(phenyl(ferrocenyl)methyl)-1*H*-indole (3k)



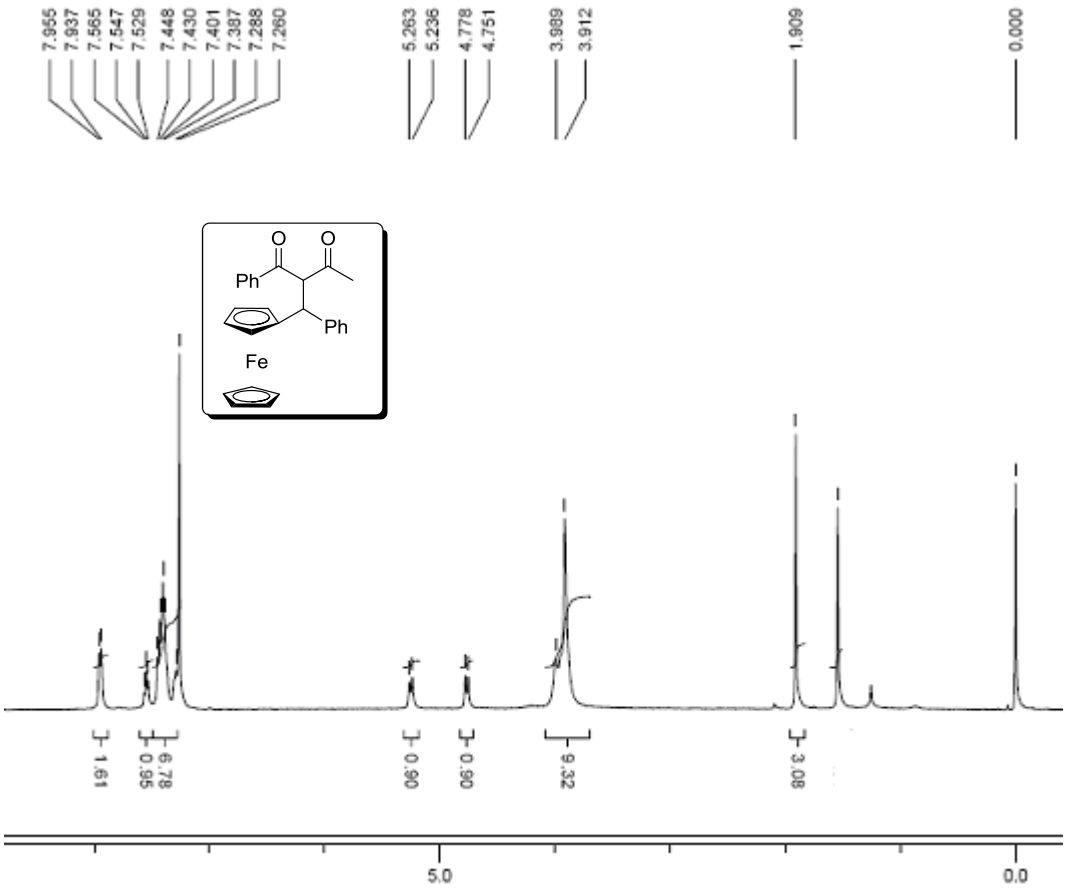
7-methyl-3-(phenyl(ferrocenyl)methyl)-1*H*-indole (3l)



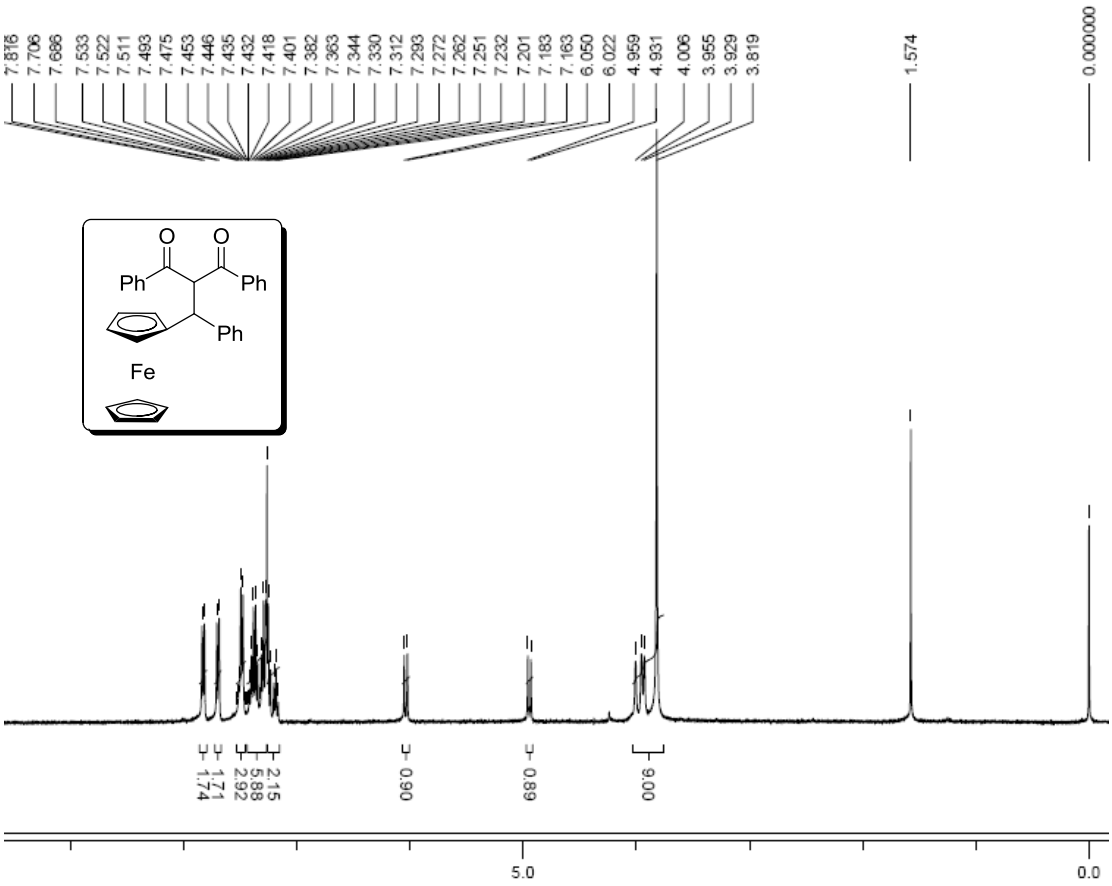
6-methyl-3-(phenyl(ferrocenyl)methyl)-1*H*-indole (3m)



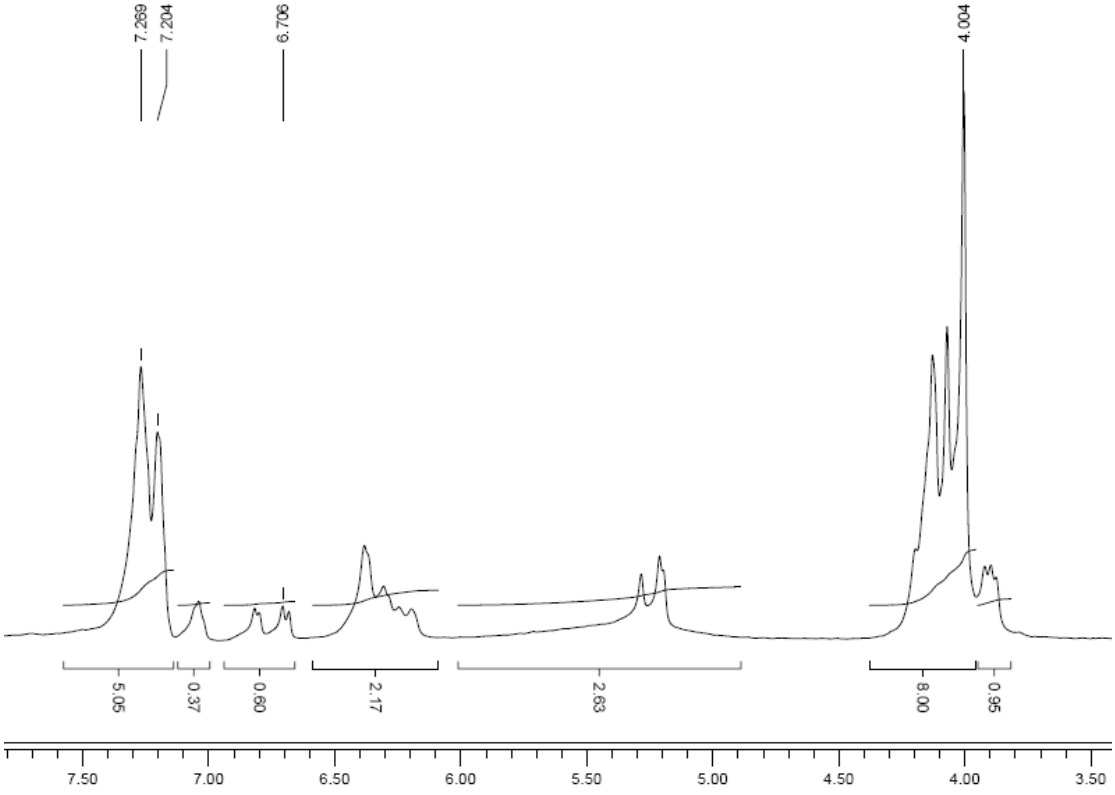
1- phenyl-2-[phenyl(ferrocenyl)methyl]butane-1, 3-dione (3n)



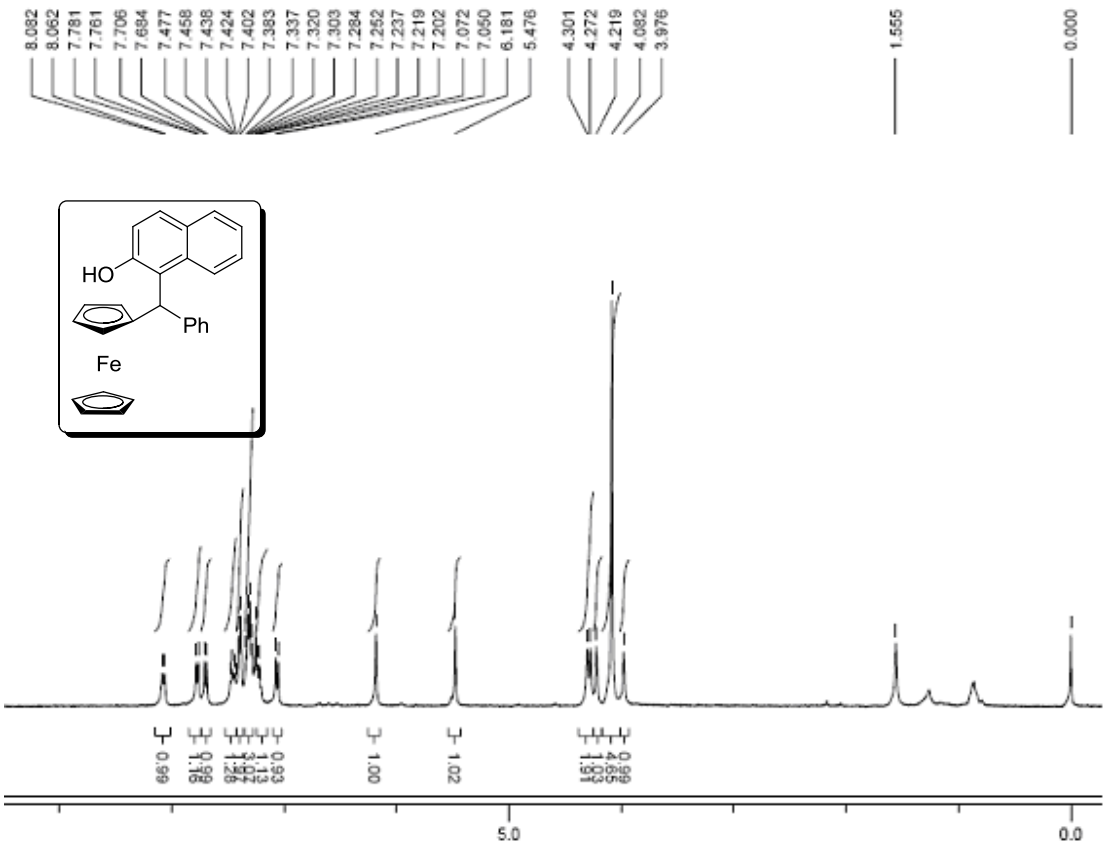
1, 3-diphenyl-2-[phenyl(ferrocenyl)methyl]propane-1,3-dione (3o)



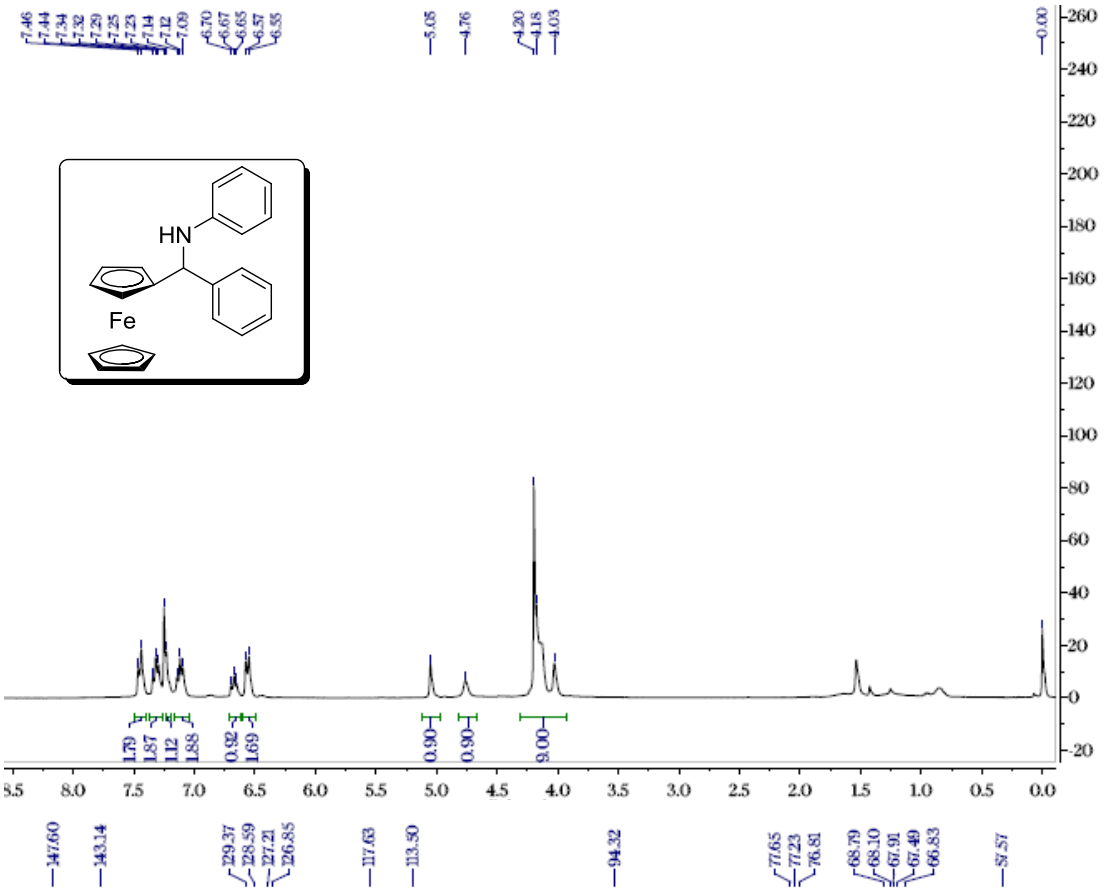
4-[ferrocenyl(phenyl)methyl]benzene-1, 3-diol (3p)

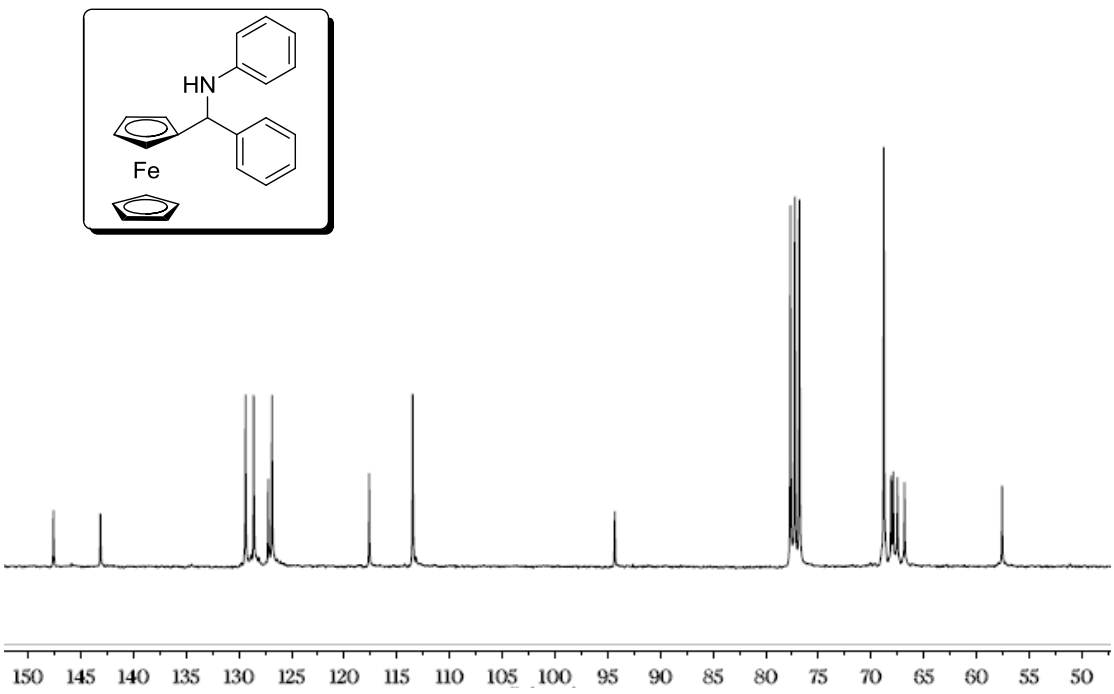


1- [phenyl(ferrocenyl)methyl]-naphthalen-2-ol (3q)



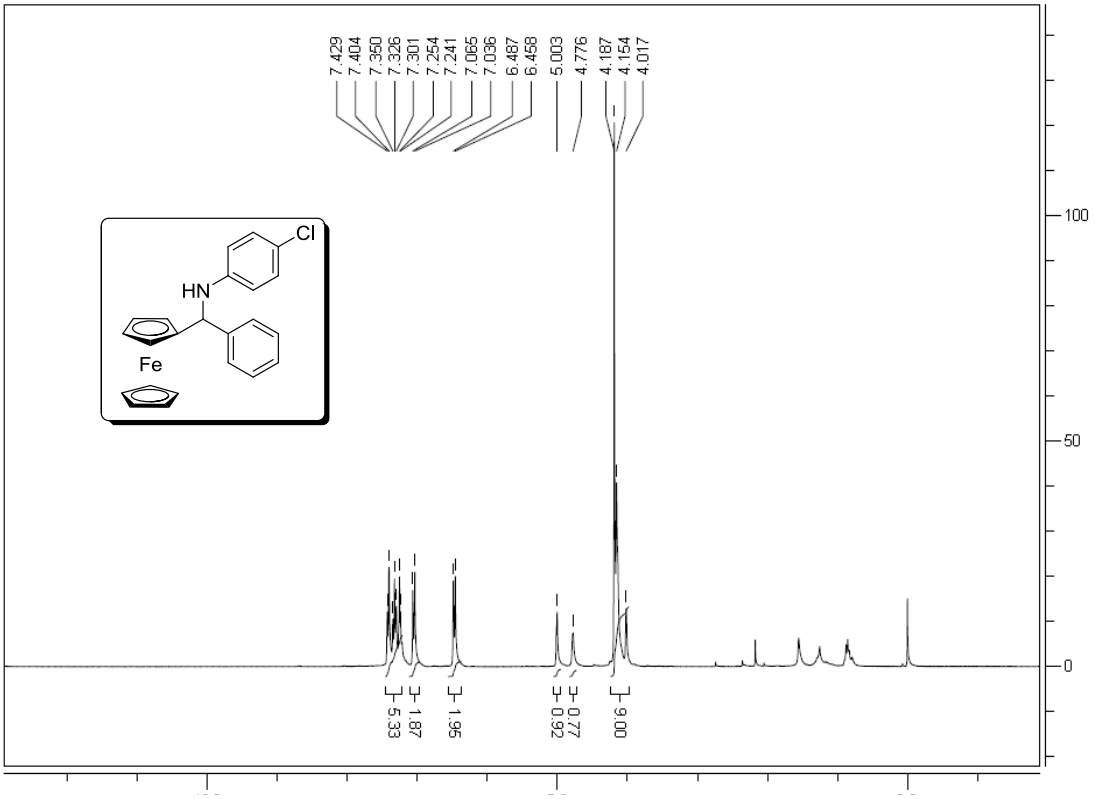
***N*-((Ferrocenyl)(phenyl)methyl)benzenamine (5a)**



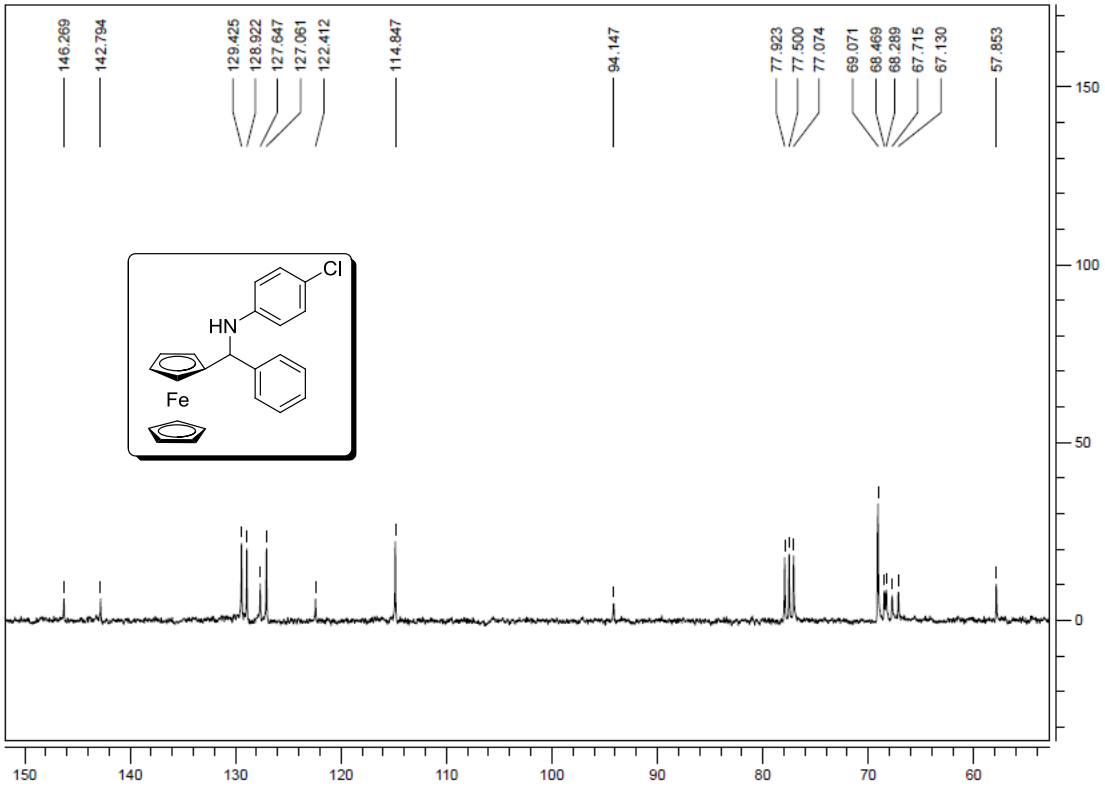


_N_-((Ferrocenyl)(phenyl)methyl)-4-chlorobenzenamine (5b)

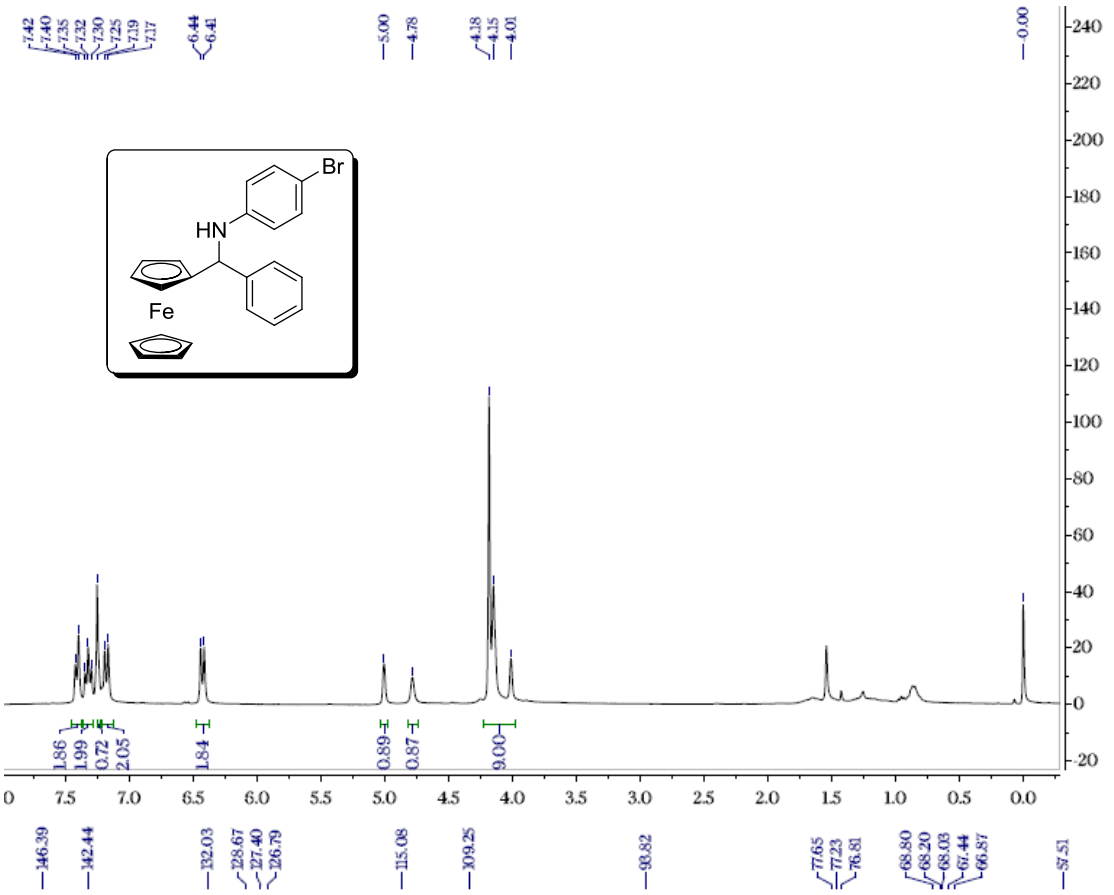
^{1}H NMR

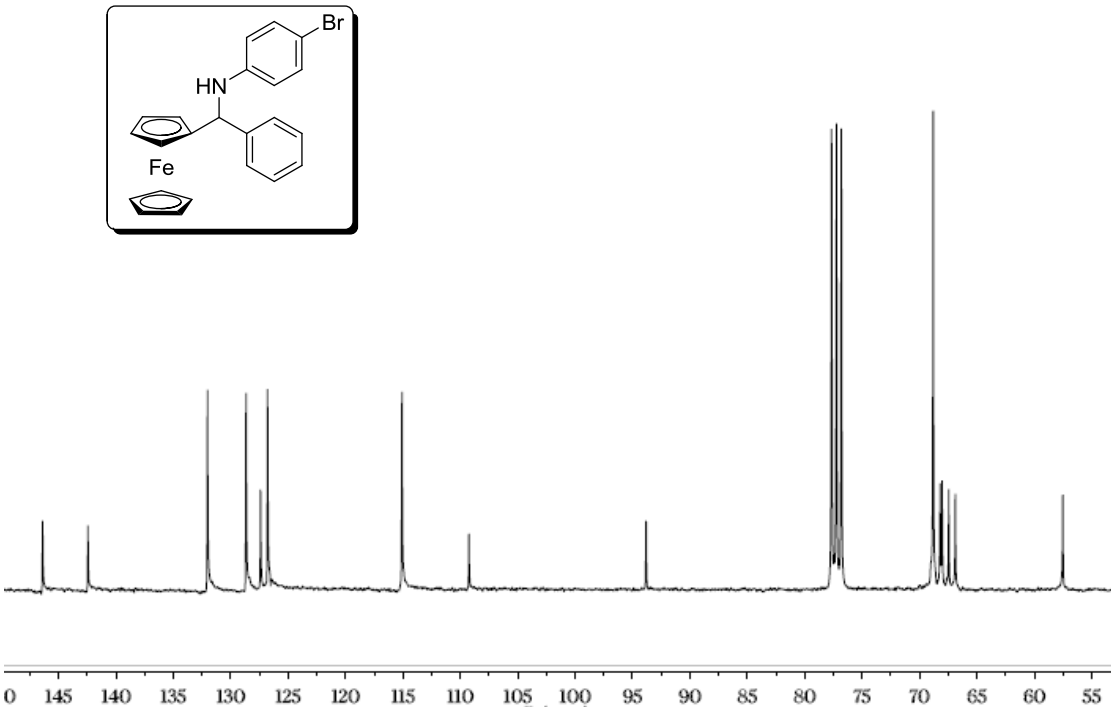


^{13}C NMR

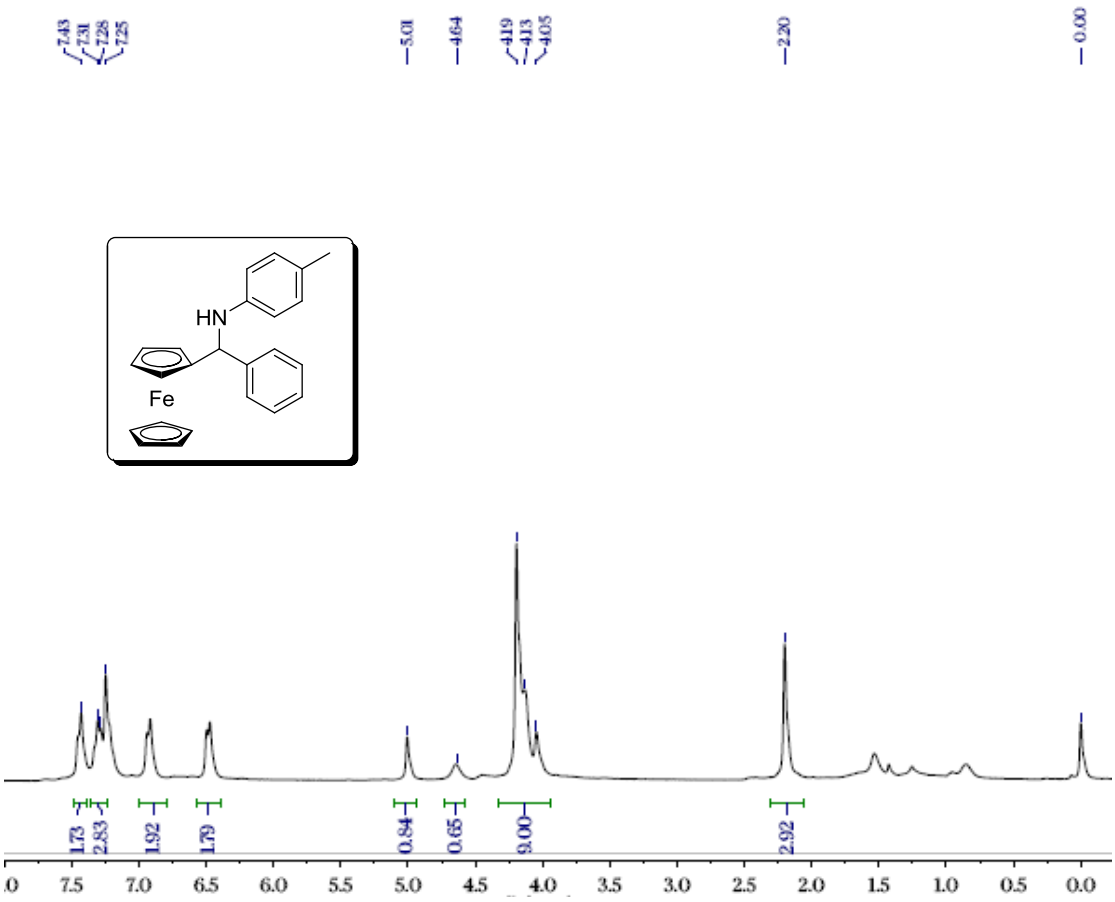


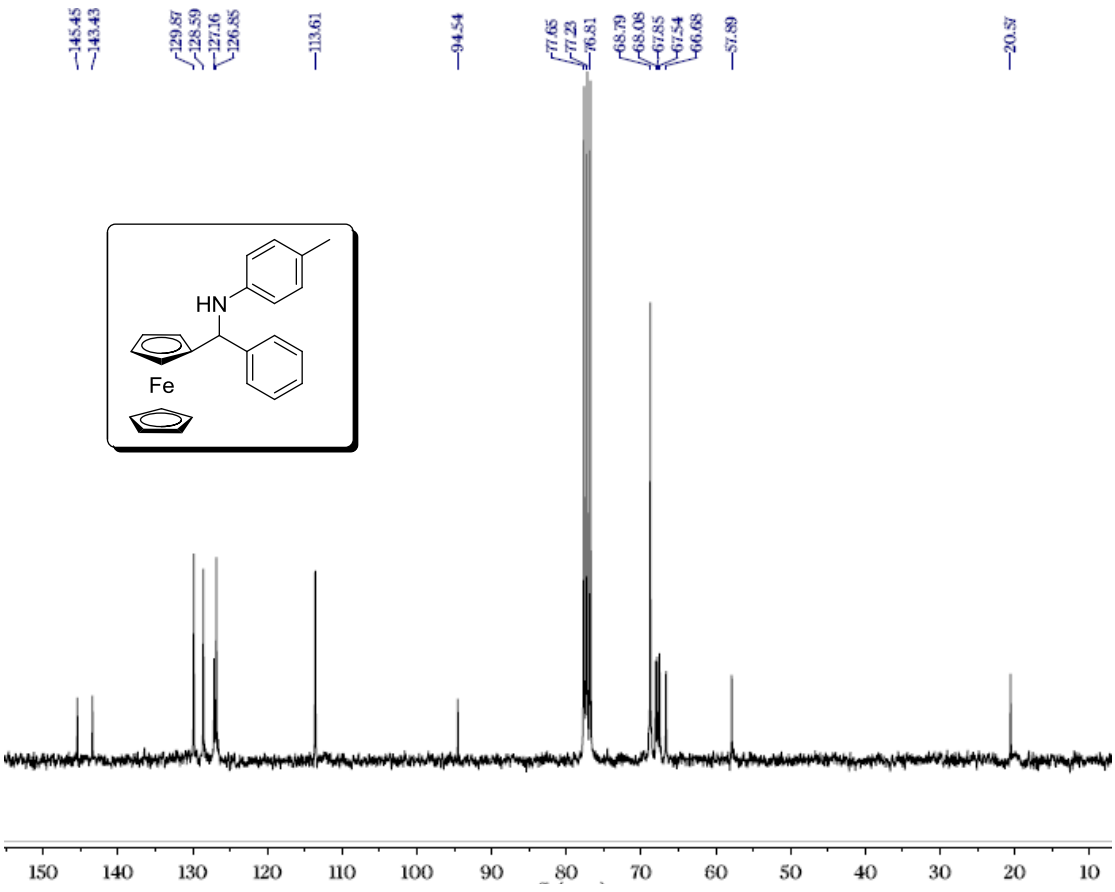
N-((Ferrocenyl)(phenyl)methyl)-4-bromobenzenamine (5c)



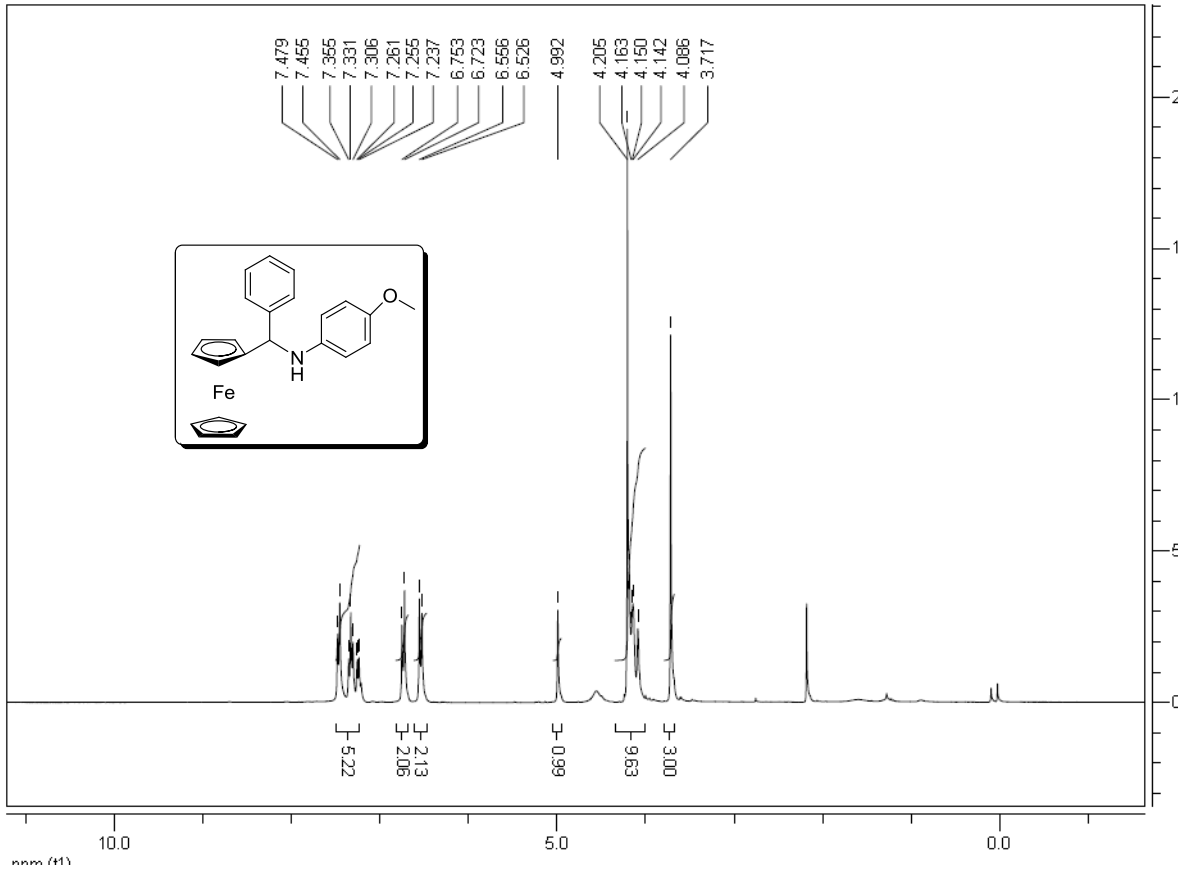


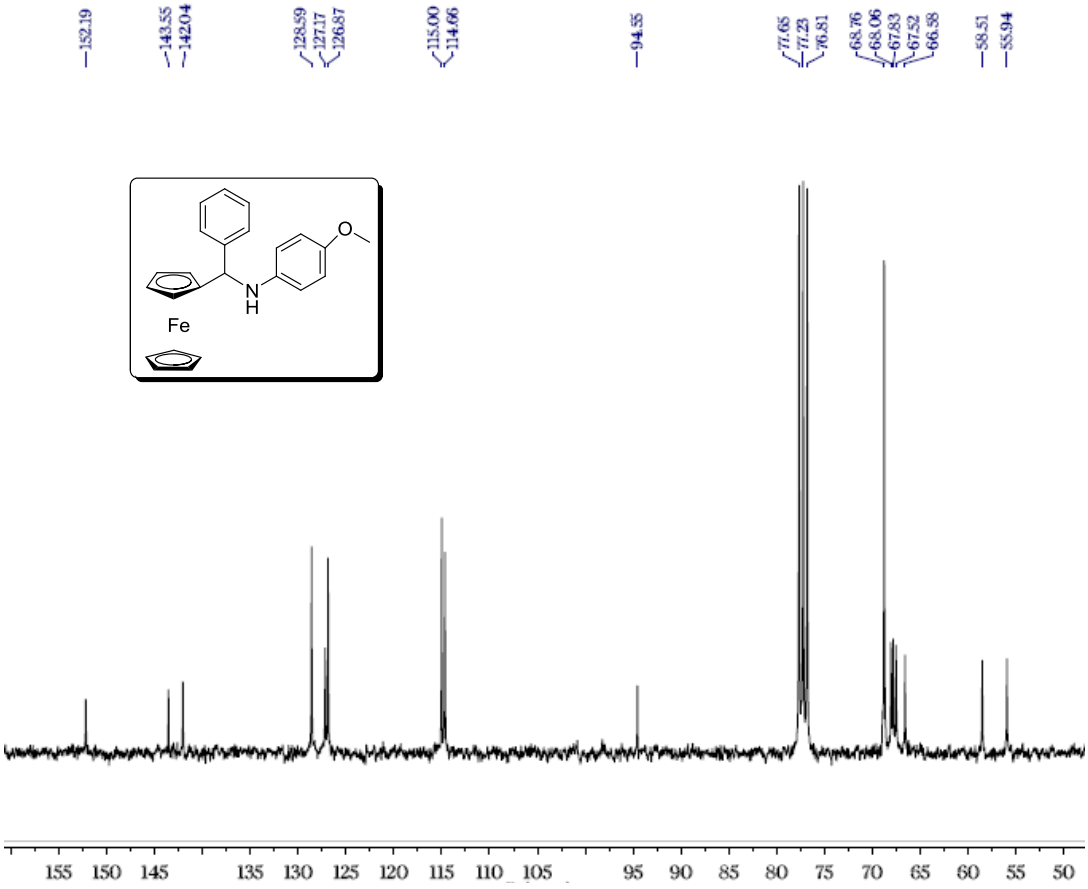
***N*-((Ferrocenyl)(phenyl)methyl)-4-methylbenzenamine (5d)**



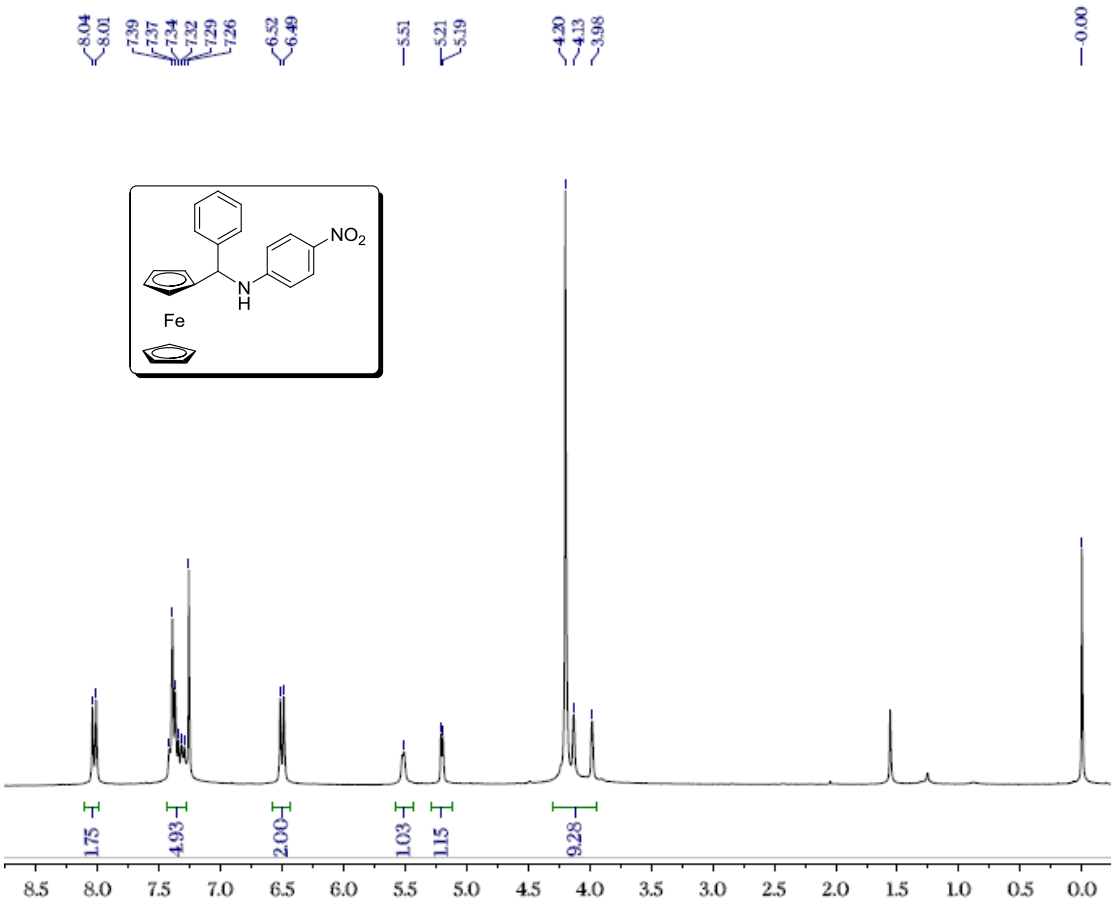


N-((Ferrocenyl)(phenyl)methyl)-4-methoxybenzenamine (5e)





***N*-((Ferrocenyl)(phenyl)methyl)-4- nitrobenzenamine (5f)**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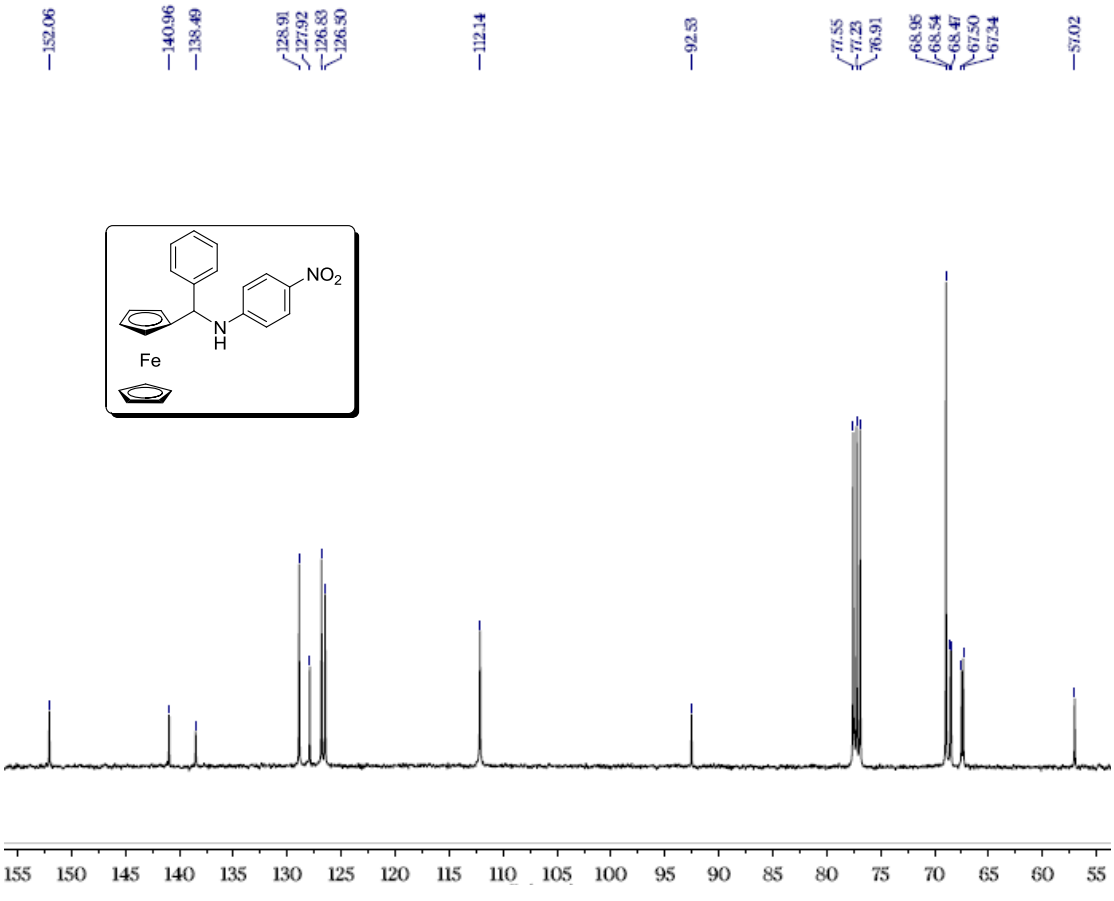
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H
Fe
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150
145
140
135
130
125
120
115
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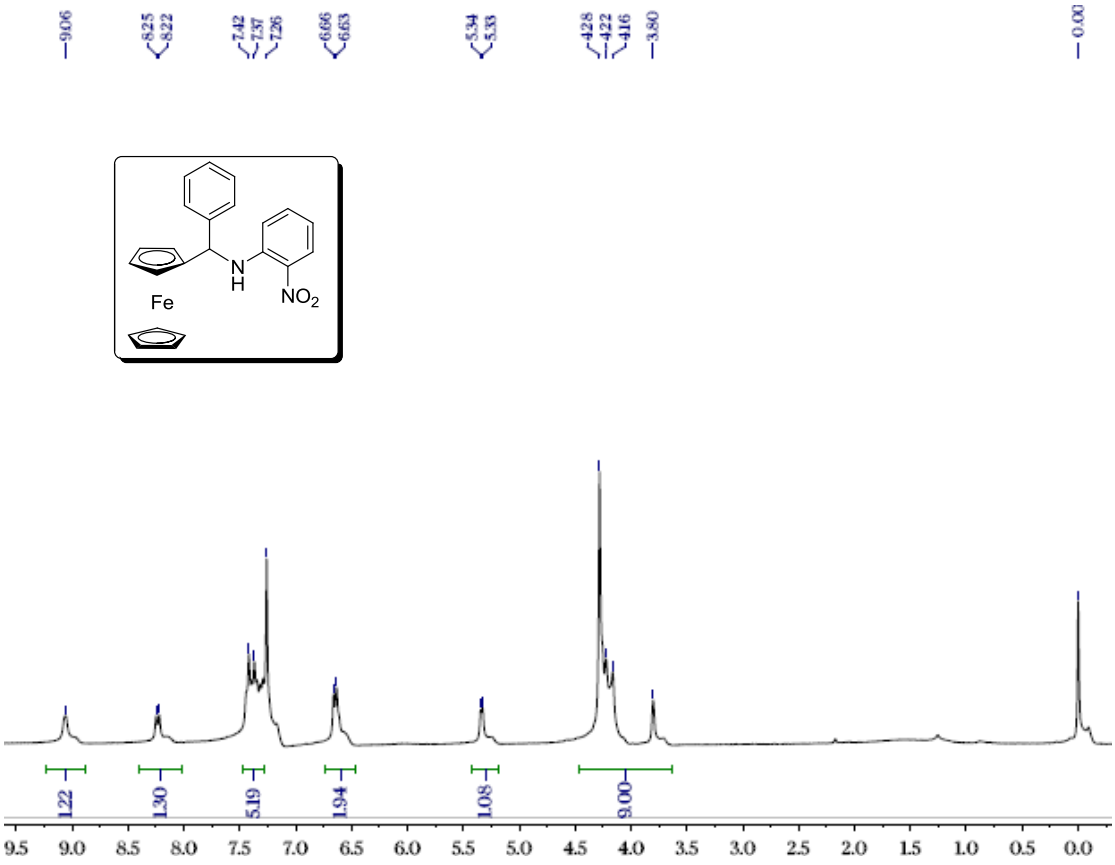
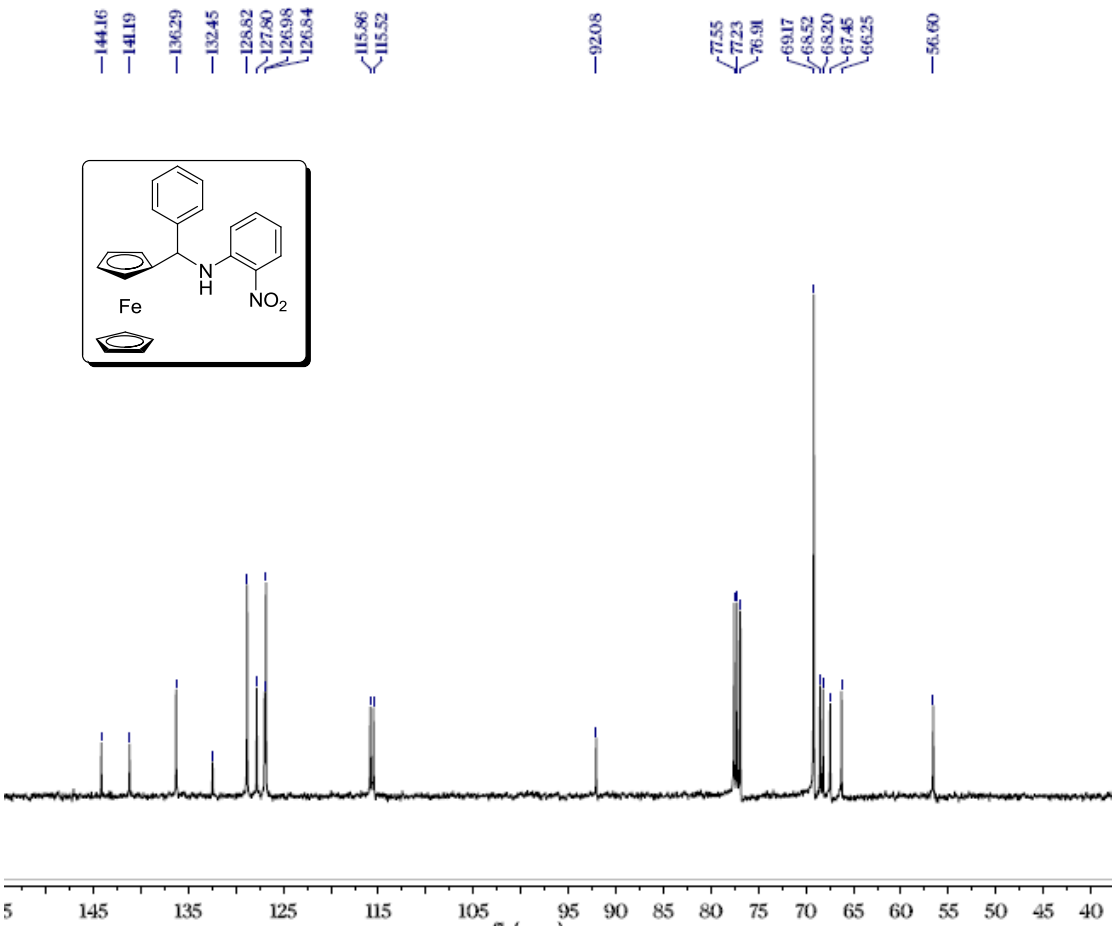
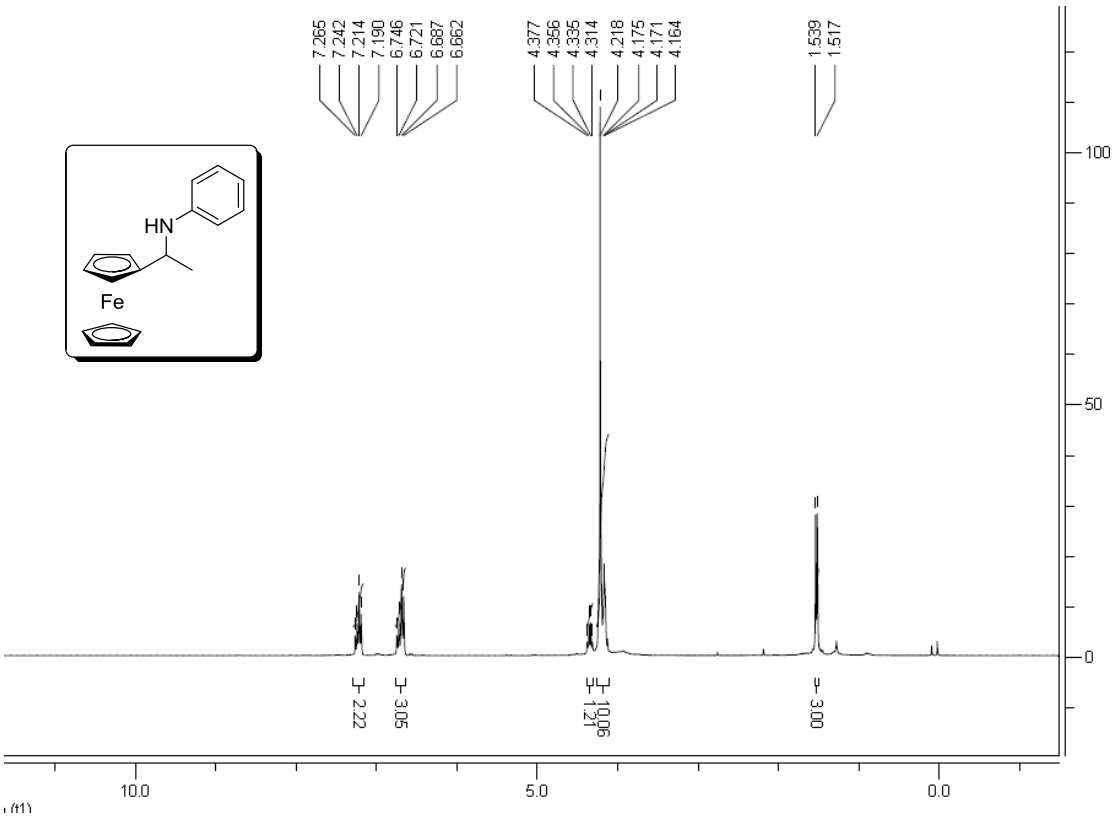
***N*-((Ferrocenyl)(phenyl)methyl)-2- nitro benzenamine (5g)**



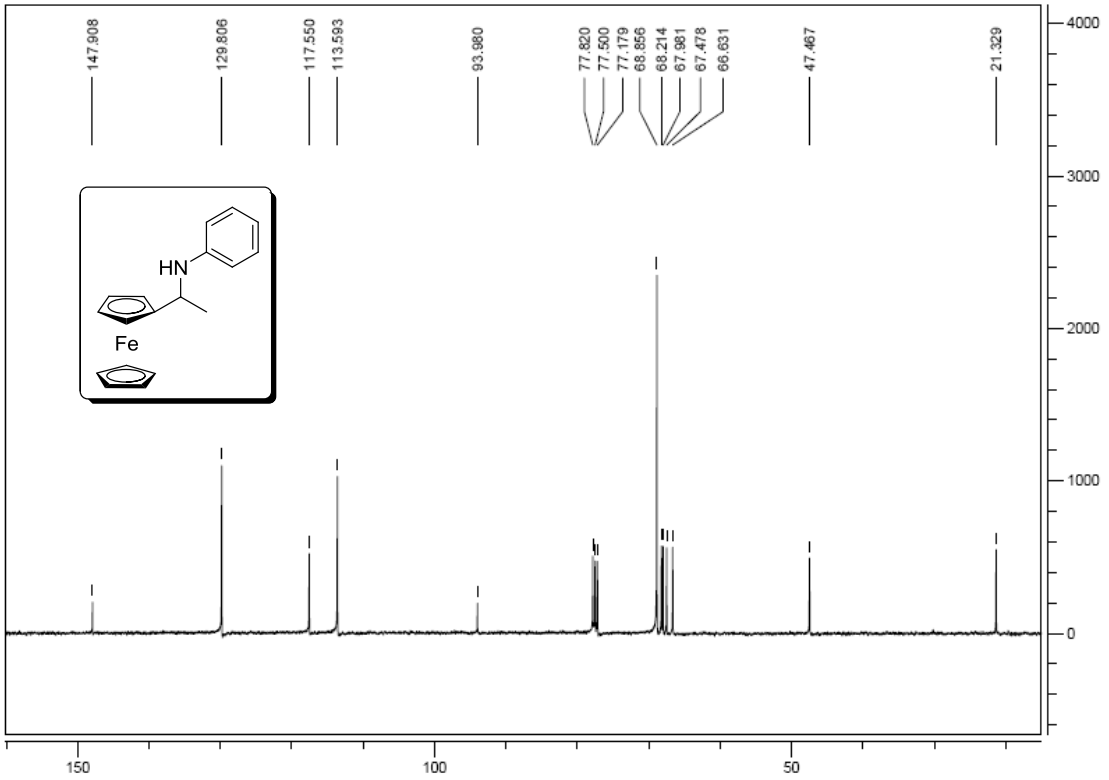


***N*-(1-ferrocenylethyl)benzenamine (5h)**

^{1}H NMR

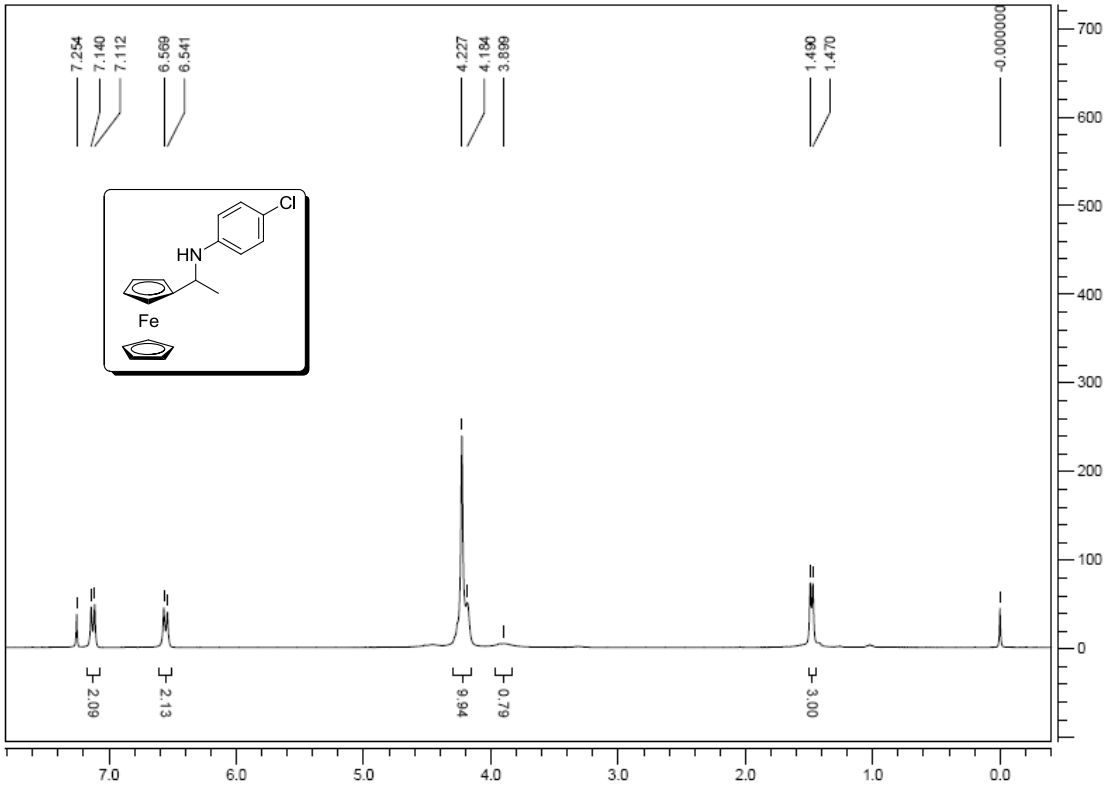


^{13}C NMR

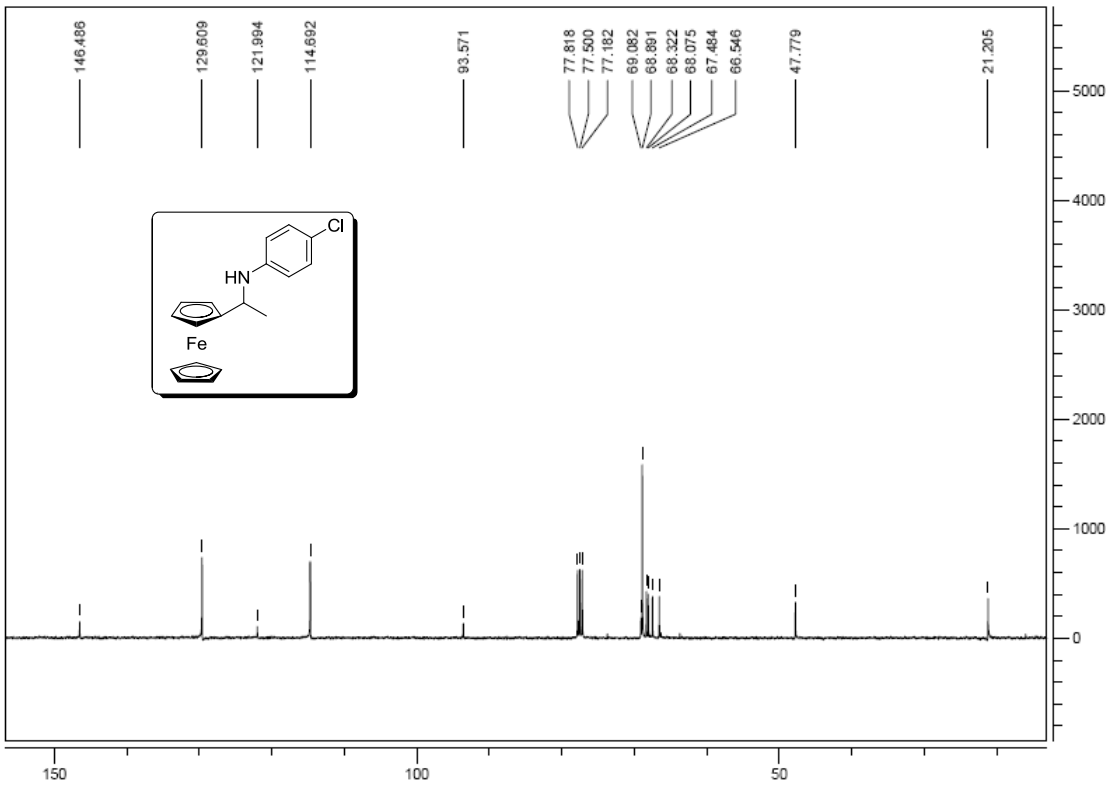


4-chloro-N-(1-ferrocenylethyl)benzenamine (5i)

^{1}H NMR

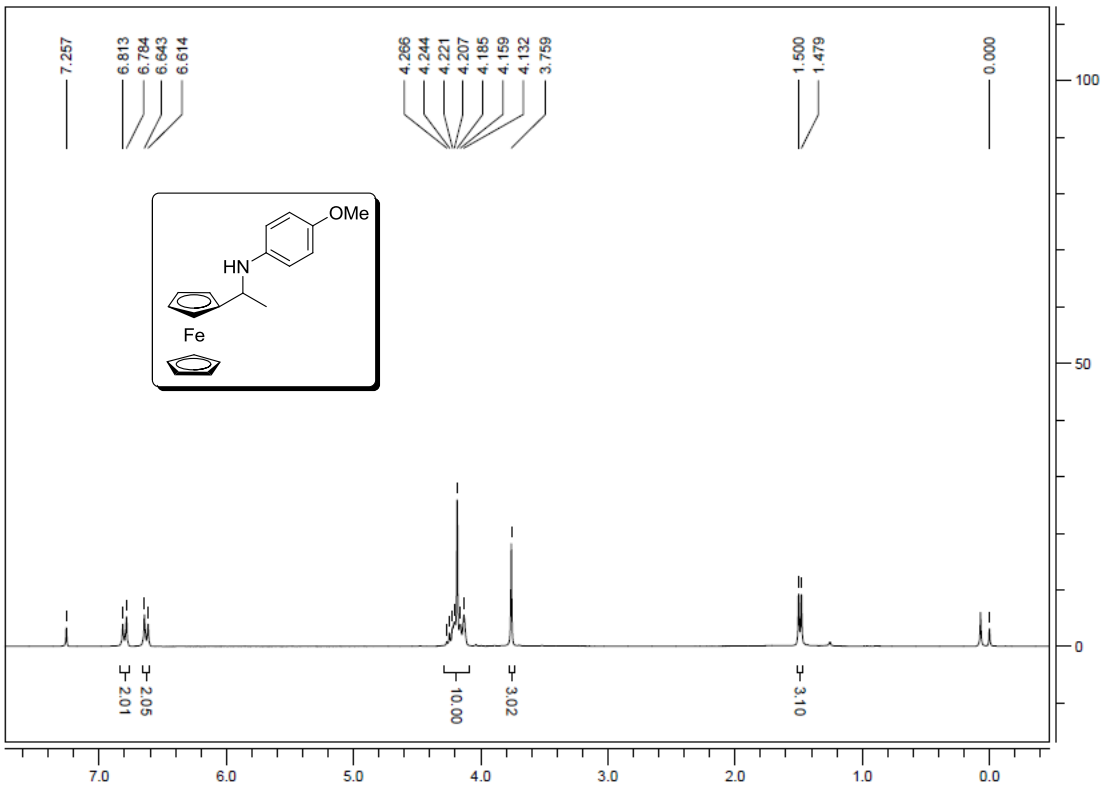


^{13}C NMR

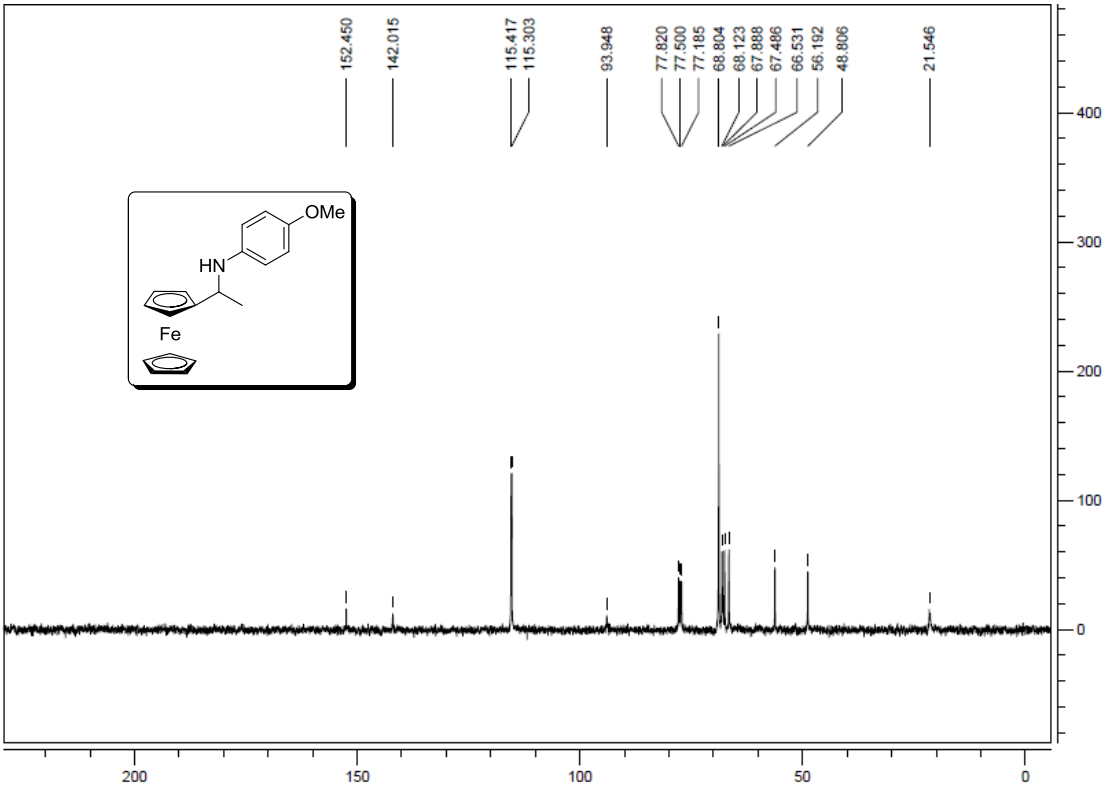


***N*-(1-ferrocenylethyl)-4-methoxybenzenamine (5j)**

^{1}H NMR

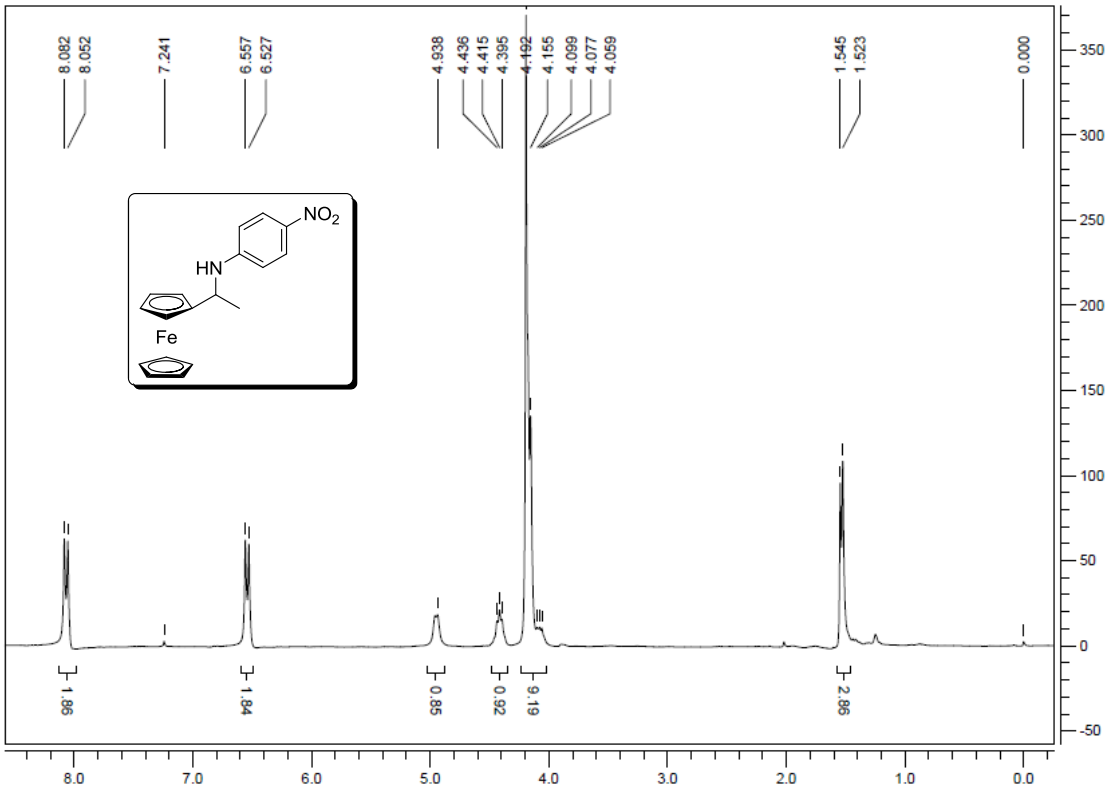


^{13}C NMR

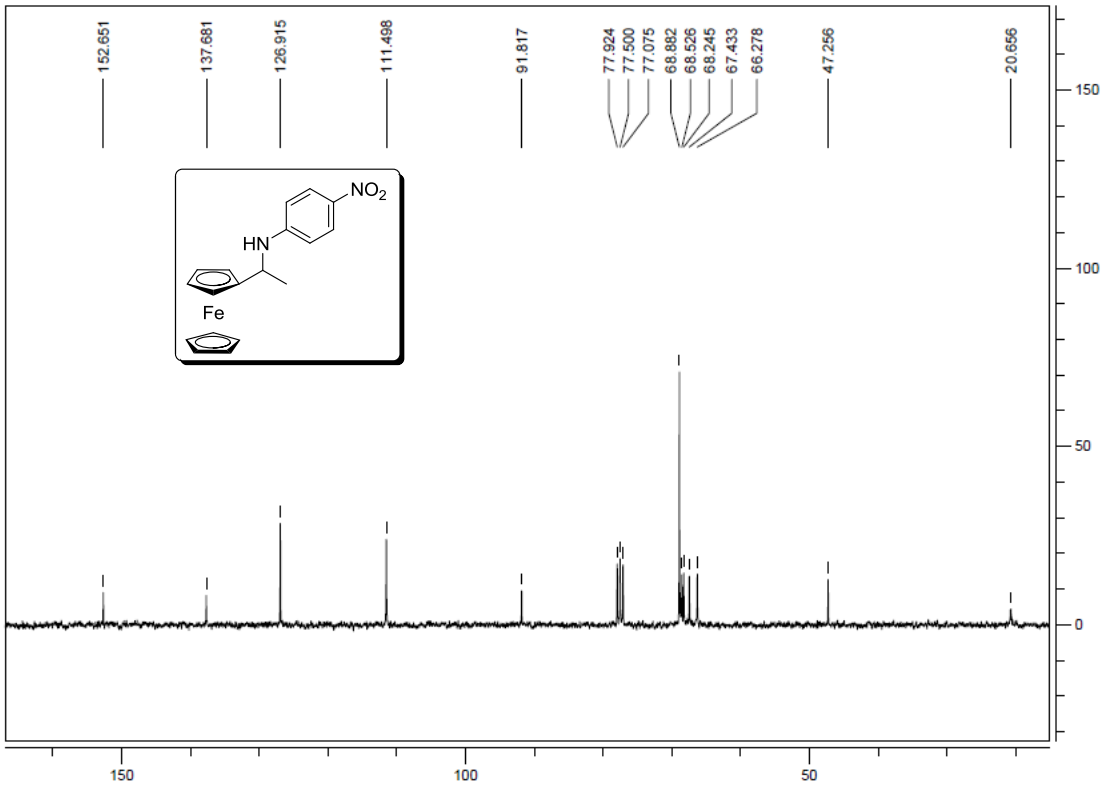


***N*-(1-ferrocenylethyl)-4-nitrobenzenamine (5k)**

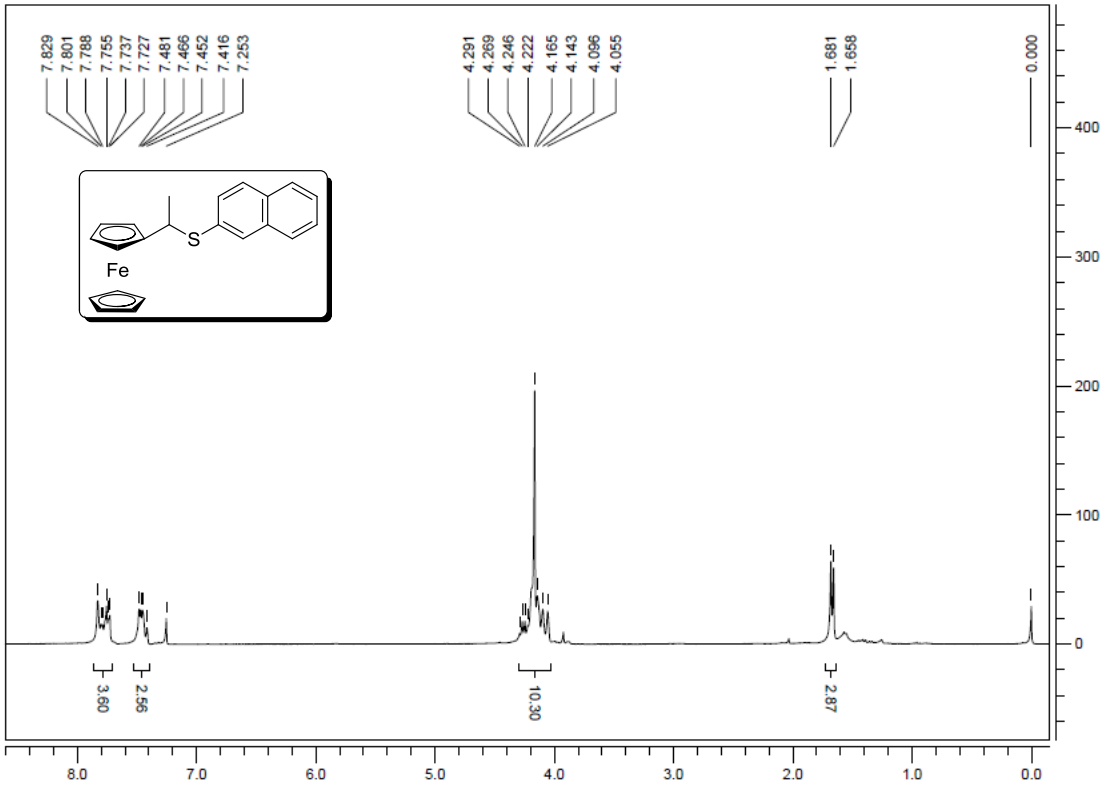
^{1}H NMR



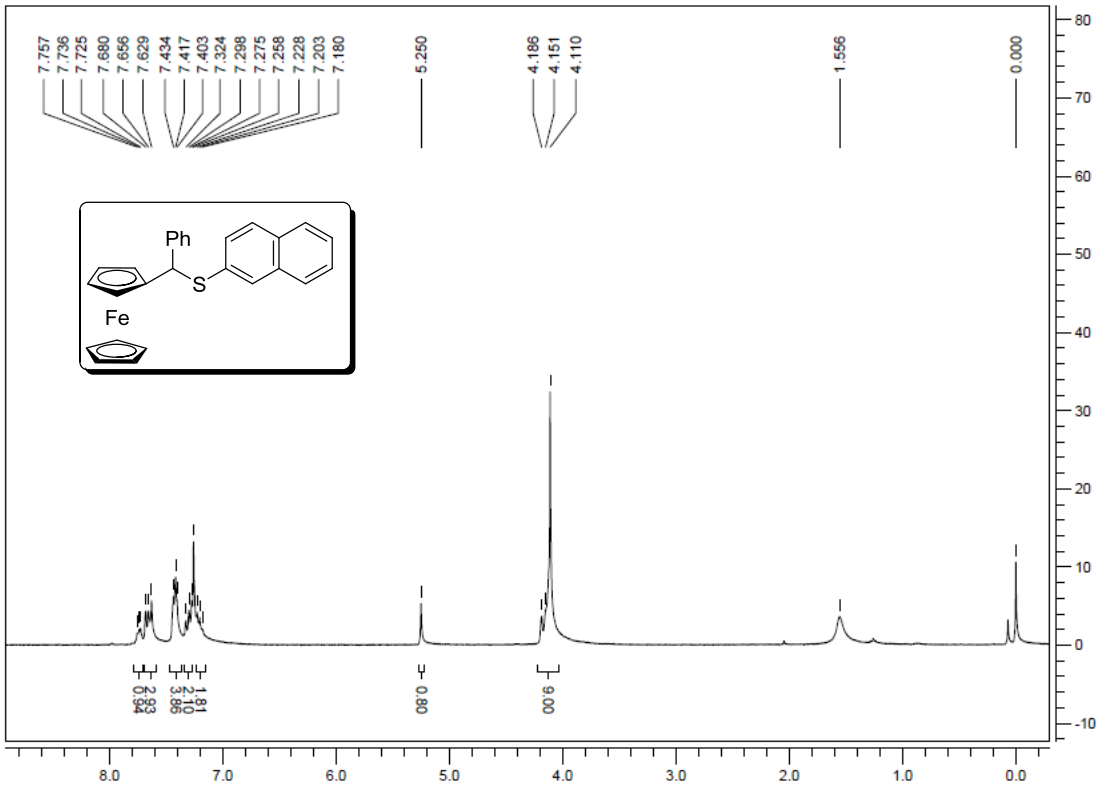
^{13}C NMR



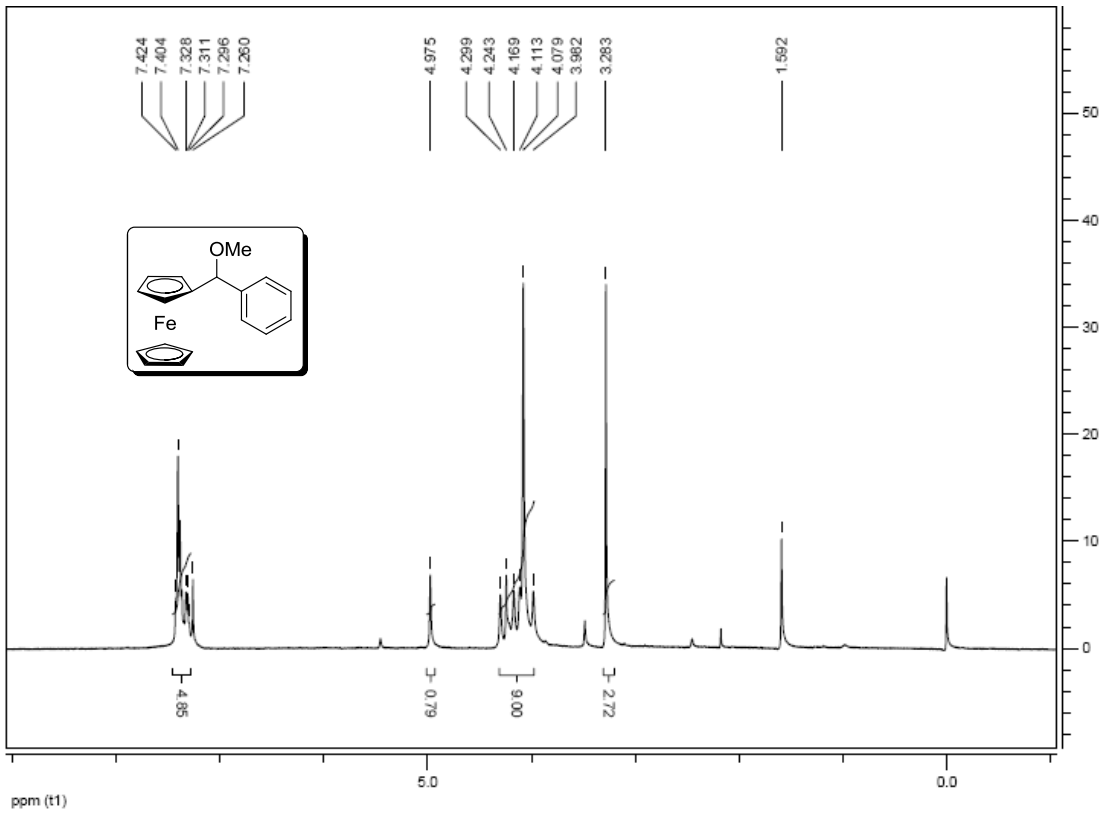
2-(1-ferrocenylethylthio)-naphthalene (7a)



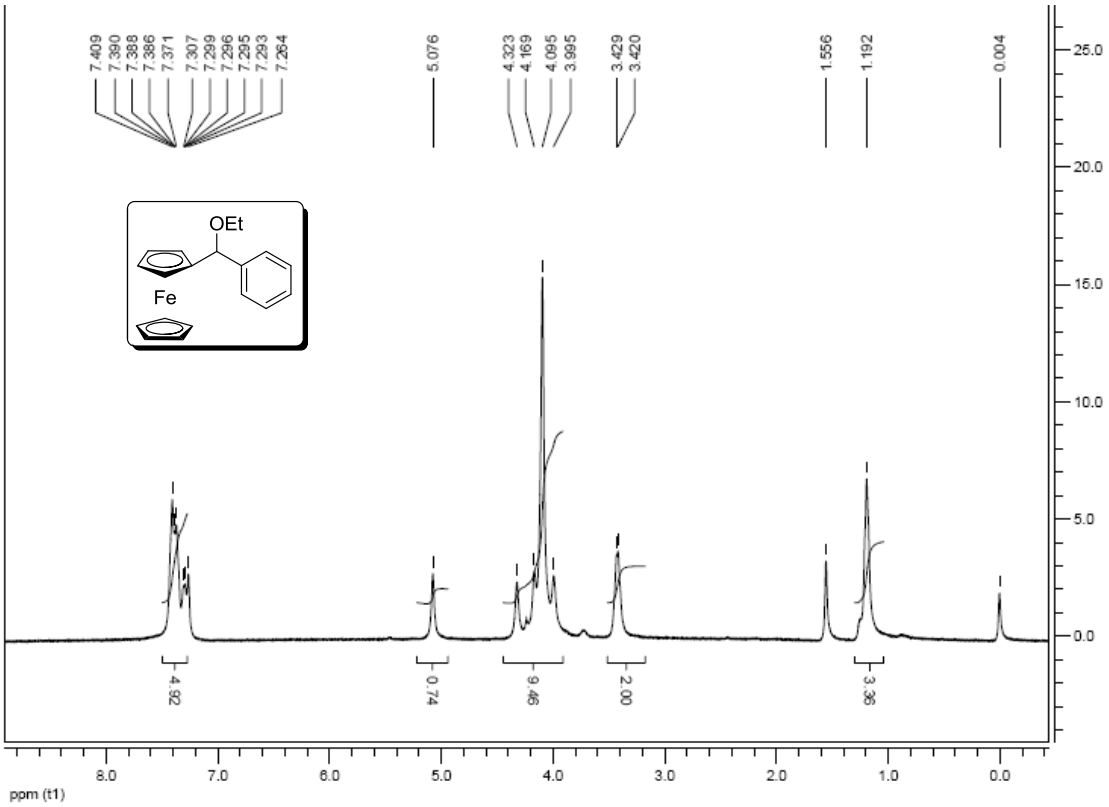
2-((ferrocenyl)(phenzyl)methylthio)-naphthalene (7b)

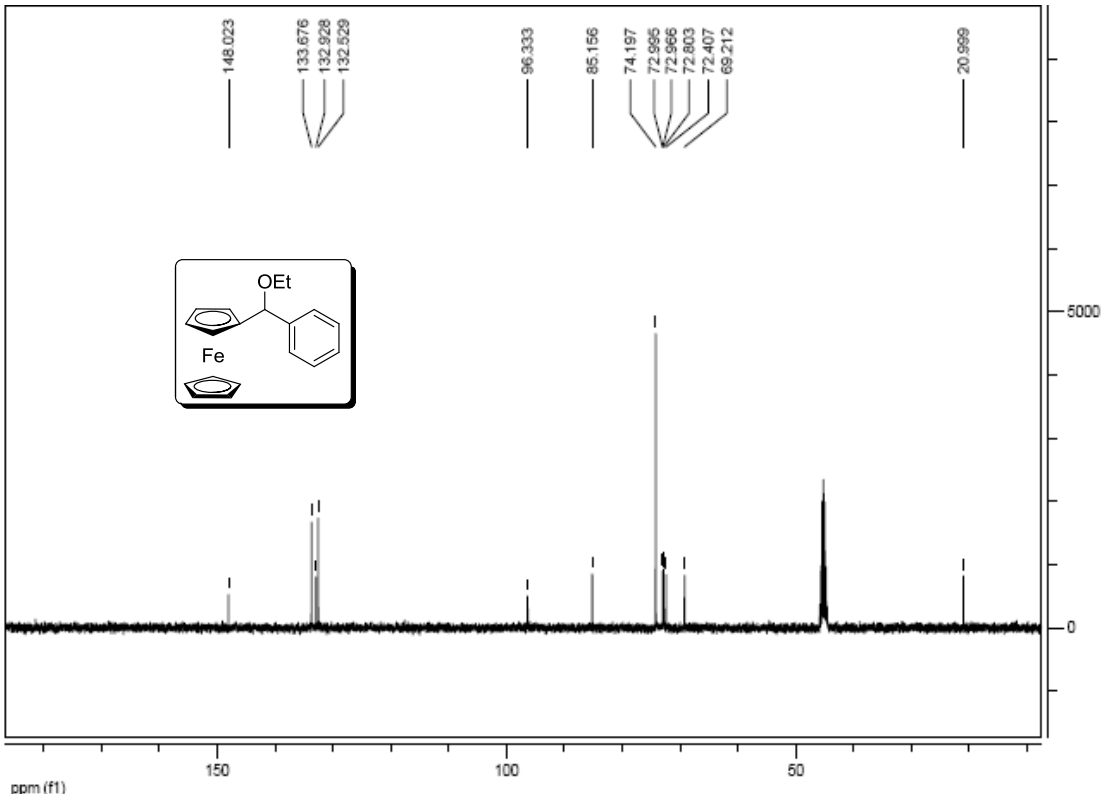


Ferrocenyl (phenyl) (methoxyl)methane (8a)

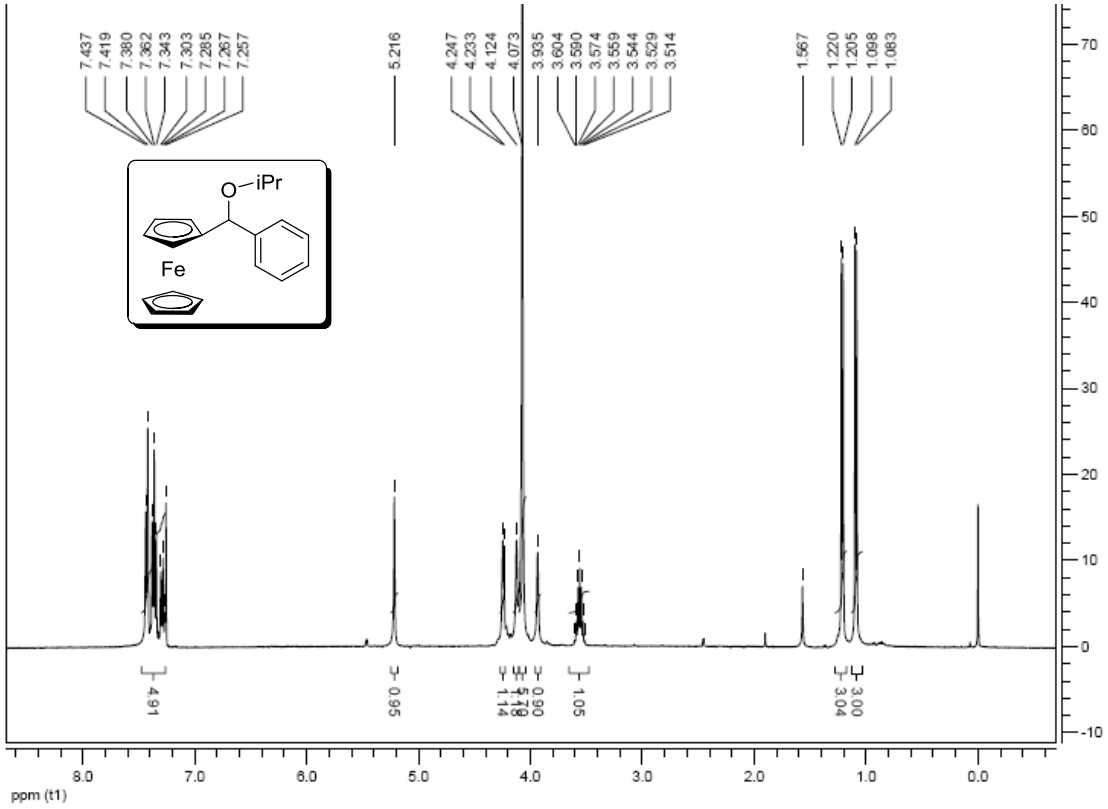


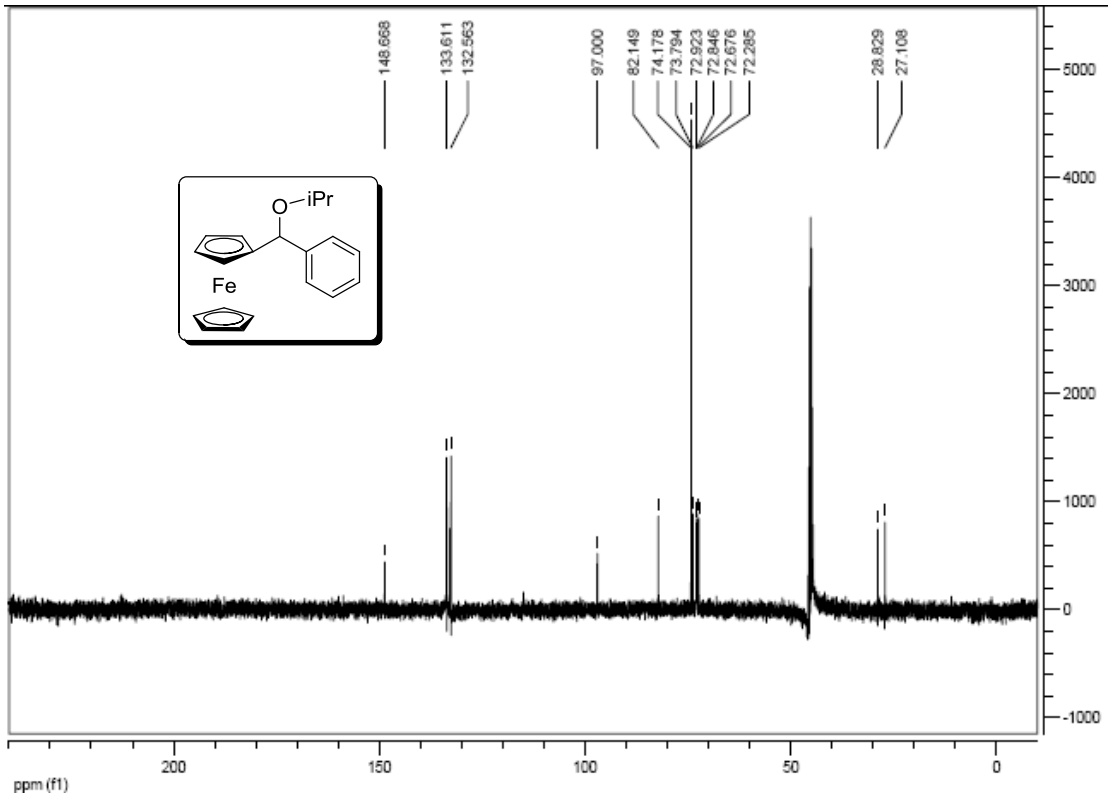
Ferrocenyl (phenyl) (ethoxyl)methane (8b)





Ferrocenyl (phenyl) (isopropoxyl)mathan (8c)





Information of HPLC analysis of (*R*)-5b'

HPLC analysis of **(*R*)-5b'**

$[\alpha]_D$ = -50.0 (c 0.1, THF)

HPLC analysis AD-H: flux 1mL/m (hexane: i-PrOH) 99:1. tm: “10.29 min”, TM: “12.76 min”. ee 98.5%.

Copies of HPLC analysis of **race-2ad** and **(*R*)-5b’**

race-5b

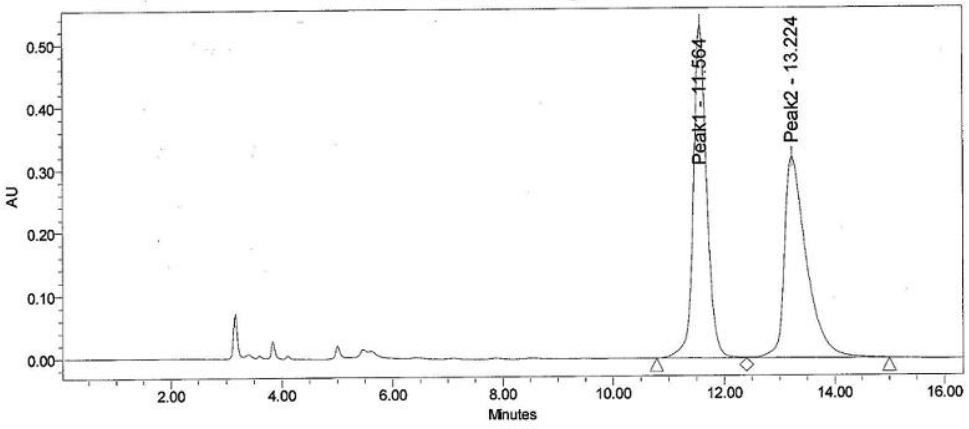
Empower 2 software

zyw

SAMPLE INFORMATION

Sample Name:	jr-rac	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	Untitled
Injection #:	2	Processing Method:	895
Injection Volume:	5.00 ul	Channel Name:	210.5nm
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.5 nm
Date Acquired:	2010-3-18 17:55:52 CST		
Date Processed:	2010-3-18 18:14:24 CST		

Auto-Scaled Chromatogram

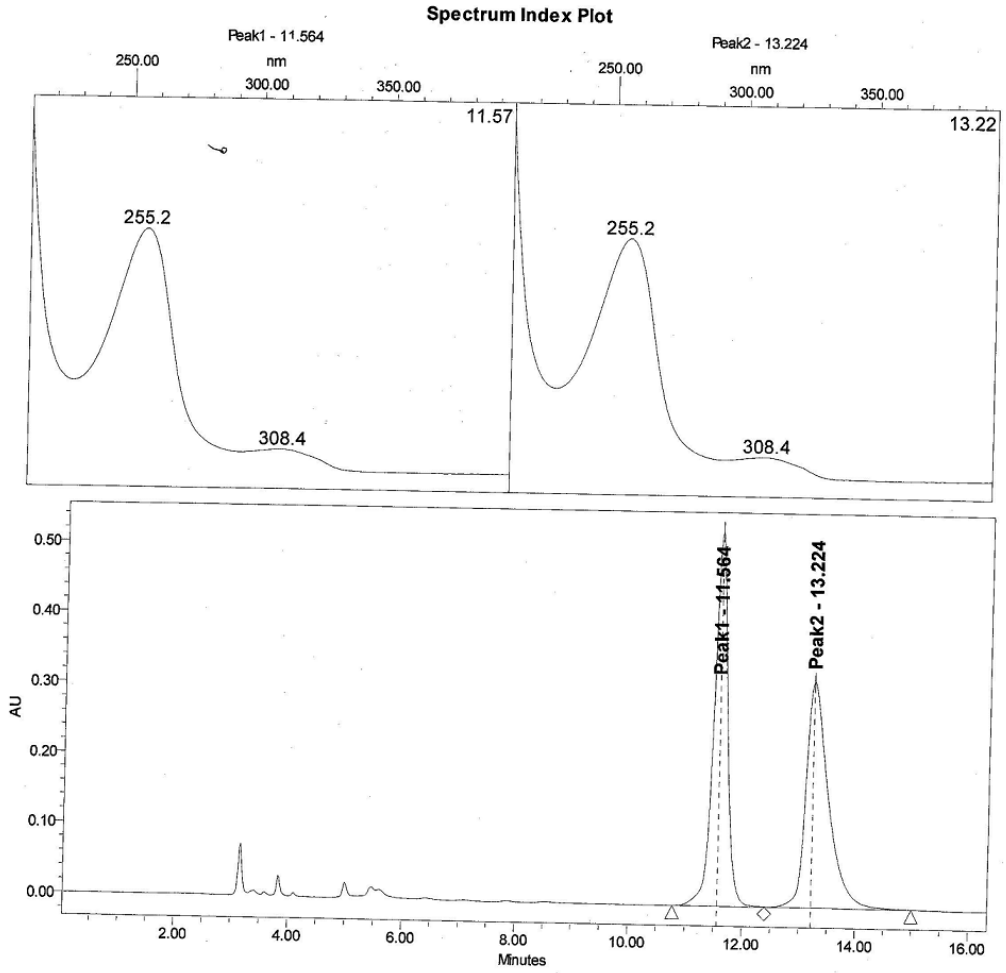


Peak Results

	Name	RT	Area	% Area	Height	Amount	Units
1	Peak1	11.564	8784961	49.78	530782		
2	Peak2	13.224	8861442	50.22	320093		

Reported by User: System
Report Method: zyw
Report Method ID 1398
Page: 1 of 2

Project Name: zyw
Date Printed:
2010-3-18
18:15:02 PRC



Reported by User: System
Report Method: zyw
Report Method ID 1398
Page: 2 of 2

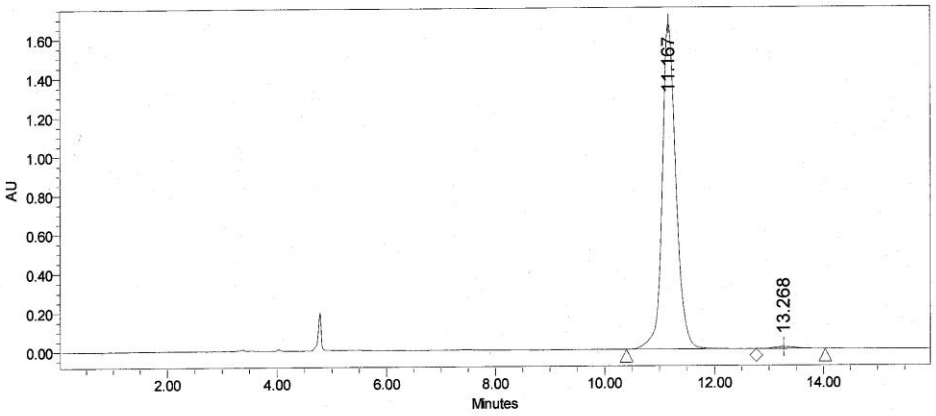
Project Name: zyw
Date Printed:
2010-3-18
18:15:02 PRC

(*R*)-5b'

SAMPLE INFORMATION

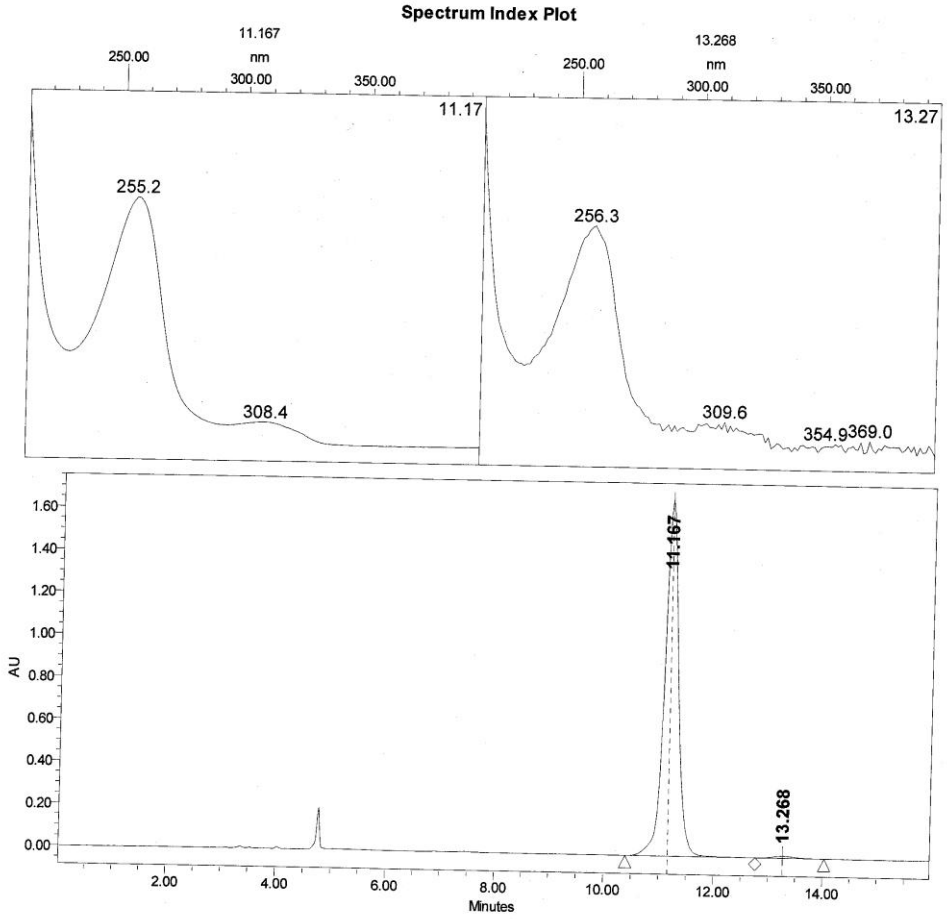
Sample Name:	jr-AcOH	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	Untitled
Injection #:	3	Processing Method:	2258
Injection Volume:	5.00 ul	Channel Name:	210.5nm
Run Time:	16.0 Minutes	Proc. Chnl. Descr.:	PDA 210.5 nm
Date Acquired:	2010-3-18 18:13:04 CST		
Date Processed:	2010-3-18 18:34:25 CST		

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	% Area	Height	Amount	Units
1		11.167	29032248	99.02	1670298		
2		13.268	286596	0.98	10250		


Spectrum Index Plot
11.167
nm
250.00
300.00
350.00
13.268
nm
250.00
300.00
350.00
11.17
13.27
255.2
256.3
308.4
309.6
354.9
369.0
11.167
13.268
AU
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
Minutes