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Electronic Supplementary Information (ESI)

Synthesis of ferrocene-containing six-membered cyclic ureas via α-ferrocenyl carbocations

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Figure S1

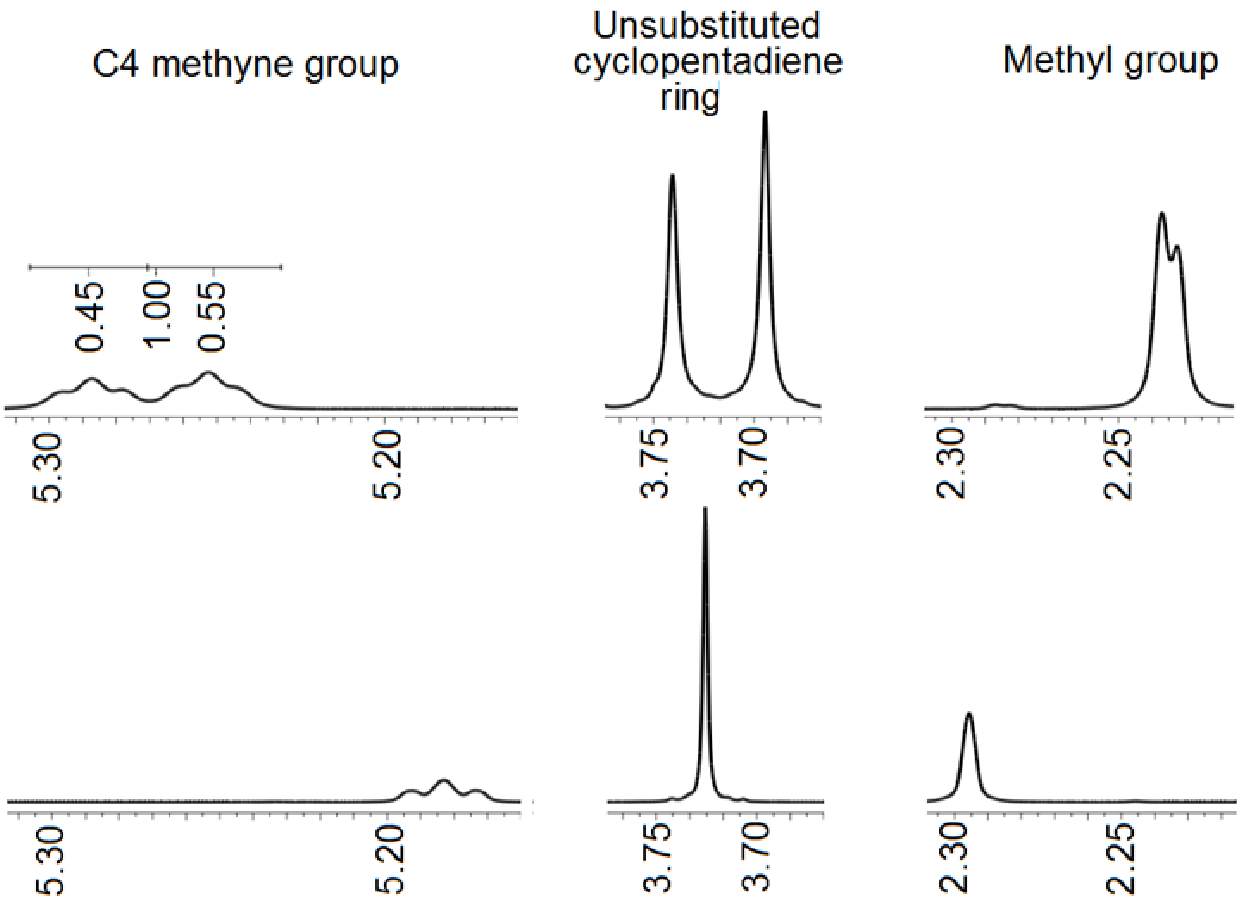


Figure S1 Expansions of 1H NMR spectra of 12b (up) and 12d (down)

Figure S2

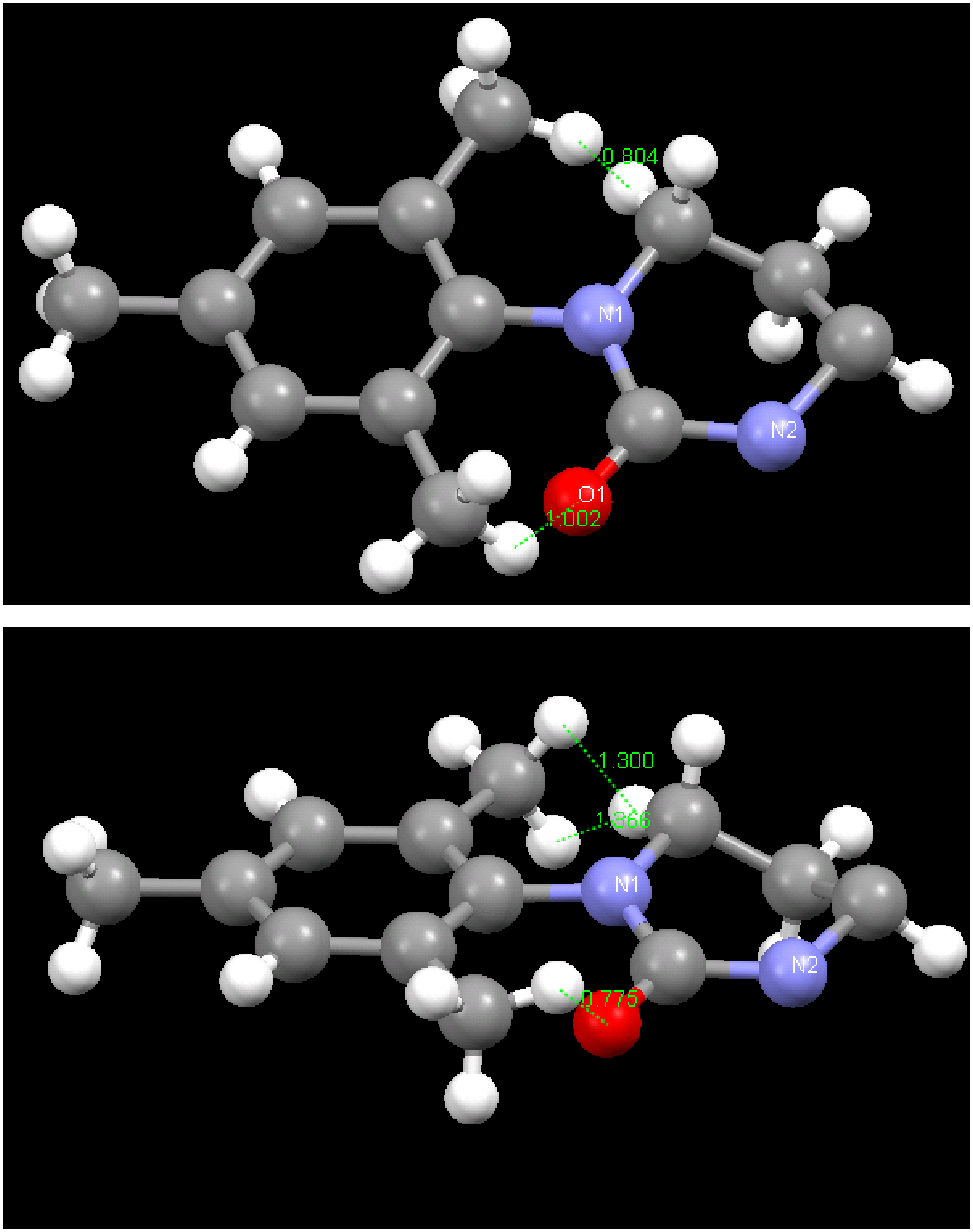


Figure S2 A representation of a part of the structure of compound **12e** (produced using atomic coordinates from the crystal structure of the same compound) illustrating hindered rotation around the C-N bond. The presented conformations were obtained by rotation of two rings around C-N bond. This figure illustrates strong H…H and O…H steric hindrance (distances are given in green color) between the two rings when they adopt an approximately coplanar orientation.

Synthetic procedures

General information

All chemicals were commercially available and used as received, except that the solvents were purified by distillation. Ultrasonic cleaner Elmasonic S 10 (Elma, Germany), 30 W, was used for the ultrasonically supported synthesis. Chromatographic separations were carried out using silica gel 60 (Merck, 230–400 mesh ASTM), whereas silica gel 60 on Al plates, layer thickness 0.2 mm (Merck) was used for TLC. Melting points (uncorrected) were determined on a Mel-Temp capillary melting points apparatus, model 1001. The ^{1}H and ^{13}C NMR spectra of the samples in $CDCl_3$ were recorded on a Varian Gemini (200 MHz) or a Bruker Avance III 400 MHz (^{1}H at 400 MHz, ^{13}C at 101 MHz) NMR spectrometer. Chemical shifts are expressed in ppm (δ) using tetramethylsilane as the internal standard. Coupling constants are reported in Hz. IR measurements were carried out with a Perkin–Elmer FTIR 31725-X spectrophotometer. Microanalyses of carbon, hydrogen and nitrogen were carried out with a Carlo Erba 1106 model microanalyzer.

Acryloylferrocene (6) and 2-ferrocenoylethyl aryl amines (8a-q)

Acryloylferrocene (**6**) and 2-ferrocenoylethyl aryl amines (**8a-q**) were synthesized according to previously described procedures.[1,2] The spectra of compounds **6** and **8a-k** agreed completely with those previously published.[1,2] The spectra of the unknown Mannich bases (**8l-q**) are presented below.

3-((2-Bromophenyl)amino)-1-ferrocenylpropan-1-one (**8l**). Yield (74%), mp. 114 °C; IR (KBr, ν, cm^{-1}): 3409, 3096, 2918, 1674,1599, 1587, 1501, 1452, 1254, 1017, 821, 750; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.8, 1.5 Hz, 1H, H-3'), 7.21 (ddd, *J* = 8.2, 7.4, 1.5 Hz, 1H, H-5'), 6.73 (dd, *J* = 8.2, 1.5 Hz, 1H, H-6'), 6.57 (ddd, *J* = 7.8, 7.4, 1.5 Hz, 1H, H-4'), 4.81 – 4.76 (m, 3H, NH and 2 × CH, C_5H_4), 4.51 (pseudo t, *J* = 2.0 Hz, 2H, 2 × CH, C_5H_4), 4.13 (s, 5H, 5 × CH, C_5H_5), 3.63 (pseudo q, *J* = 5.9 Hz, 2H, -C**H$_2$**NH-), 3.04 (t, *J* = 6.2 Hz, 2H, -COC**H$_2$**-); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7 (C=O), 144.6 (C-1'), 132.7 (C-3'), 128.5 (C-5'), 117.9 (C-4'), 111.1 (C-6'), 110.1 (C-2'), 78.7 (C-1''), 72.5 (C-3'', 4''), 69.8 (C-6''), 69.3 (C-2'', 5''), 38.4 (-**C**H$_2$NH-), 38.2 (-CO**C**H$_2$-). Anal. Calcd for $C_{19}H_{18}BrFeNO$: C, 55.38; H, 4.40; Br, 19.39; Fe, 13.55; N, 3.40; O, 3.88%. Found: C, 55.31, H, 4.39, N, 3.39%.

3-((3-Bromophenyl)amino)-1-ferrocenylpropan-1-one (**8m**). Yield (88%), mp. 121 °C; IR (KBr, ν, cm^{-1}): 3347, 3087, 2928, 1653, 1593, 1482, 1455, 1273, 823, 757; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 – 6.98 (m, 1H, H-5'), 6.83 – 6.76 (m, 2H, H-2', 6'), 6.55 (ddd, *J* = 8.2, 2.1, 1.1 Hz, 1H, H-4'), 4.77 (pseudo t, *J* = 2.0 Hz, 2H, 2 × CH, C_5H_4), 4.51 (pseudo t, *J* = 2.0 Hz, 2H, 2 × CH, C_5H_4), 4.36 – 4.29 (m, 1H, NH), 4.12 (s, 5H, 5 × CH, C_5H_5), 3.54 (pseudo q, *J* = 5.9 Hz, 2H, -C**H$_2$**NH-), 3.00 (t, *J* = 6.0 Hz, 2H, -COC**H$_2$**-); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2 (C=O), 149.1 (C-1'), 130.6 (C-5'), 123.4 (C-3'), 120.2 (C-6'), 115.2 (C-2'), 112.0 (C-4'), 78.7 (C-1''), 72.5 (C-3'',4''), 69.9 (C-6''), 69.2 (C-2'', 5''), 38.5 (-**C**H$_2$NH-), 37.9 (-CO**C**H$_2$-). Anal. Calcd for $C_{19}H_{18}BrFeNO$: C, 55.38; H, 4.40; Br, 19.39; Fe, 13.55; N, 3.40; O, 3.88%. Found: C, 55.40, H, 4.40, N, 3.41%.

3-((4-Bromophenyl)amino)-1-ferrocenylpropan-1-one (**8n**). Yield (82%), mp. 105 °C; IR (KBr, ν, cm^{-1}): 3346, 3090, 2946, 2898, 1654, 1593, 1509, 1486, 1459, 1274, 1065, 821; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, **AA'**MM', 2H, C_6H_4), 6.58 – 6.47 (m, AA'**MM'**, 2H,

C_6H_4), 4.76 (pseudo t, *J* = 2.0 Hz, 2H, 2 × CH, C_5H_4), 4.51 (pseudo t, *J* = 2.0 Hz, 2H, 2 × CH, C_5H_4), 4.26 (s, 1H, -CH_2N**H**-), 4.12 (s, 5H, 5 × CH, C_5H_5), 3.53 (br t, *J* = 5.9 Hz, 2H, -C**H₂**NH-), 2.99 (t, *J* = 6.0 Hz, 2H, -COC**H₂-**); ^{13}C NMR (50 MHz, $CDCl_3$) δ 203.2 (C=O), 146.7 (C_6H_4), 132.0 (C_6H_4), 114.5(C_6H_4), 109.0 (C_6H_4), 78.7 (C_5H_4), 72.5 (C_5H_4), 69.8 (C_5H_5), 69.2 (C_5H_4), 38.8 (-CH_2-), 38.0 (-CH_2-). Anal. Calcd for $C_{19}H_{18}BrFeNO$: C, 55.38; H, 4.40; Br, 19.39; Fe, 13.55; N, 3.40; O, 3.88%. Found: C, 55.42, H, 4.39, N, 3.39%.

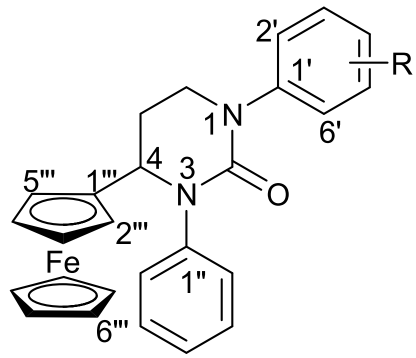
1-Ferrocenyl-3-((2-methoxyphenyl)amino)propan-1-one (**8o**). Yield (76%), mp. 93 °C; IR (KBr, ν, cm^{-1}): 3426, 3067, 2964, 2927, 1665, 1602, 1510, 1454, 1252, 1220, 1025, 820, 735;^{1}H NMR (200 MHz, $CDCl_3$) δ 6.90 (ddd, *J* = 7.8, 7.0, 1.7 Hz, 1H, C_6H_4), 6.79 – 6.61 (m, 3H, C_6H_4), 4.77 (pseudo t, *J* = 2.0 Hz, 2H, 2 × CH, C_5H_4), 4.60 (s, 1H, -CH_2N**H**-), 4.49 (pseudo t, *J* = 2.0 Hz, 2H, 2 × CH, C_5H_4), 4.11 (s, 5H, 5 × CH, C_5H_5), 3.81 (s, 3H, -OCH_3), 3.62 (t, *J* = 6.3 Hz, 2H, -C**H₂**NH-), 3.03 (t, *J* = 6.3 Hz, 2H, -COC**H₂-**); ^{13}C NMR (50 MHz, $CDCl_3$) δ 202.9 (C=O), 147.1 (C_6H_4), 137.6 (C_6H_4), 121.2 (C_6H_4), 116.5 (C_6H_4), 109.6 (2C, C_6H_4), 79.0 (C_5H_4), 72.3 (C_5H_4), 69.8 (C_5H_5), 69.2 (C_5H_4), 55.3 (-OCH_3), 38.5 (-CH_2-), 38.2 (-CH_2-). Anal. Calcd for $C_{20}H_{21}FeNO_2$: C, 66.13; H, 5.83; Fe, 15.37; N, 3.86; O, 8.81%. Found: C, 66.05, H, 5.82, N, 3.87%.

1-Ferrocenyl-3-((3-methoxyphenyl)amino)propan-1-one (**8p**). Yield (76%), mp. 130 °C; IR (KBr, ν, cm^{-1}): 3353, 3091, 2937, 1657, 1614, 1457, 1267, 1161, 825; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.08 (t, *J* = 8.0 Hz, 1H, C_6H_4), 6.31 – 6.19 (m, 3H, C_6H_4), 4.76 (pseudo t, *J* = 1.9 Hz, 2H, 2 × CH, C_5H_4), 4.50 (pseudo t, *J* = 1.9 Hz,, 2H, 2 × CH, C_5H_4), 4.12 (s, 5H, 5 × CH, C_5H_5), 3.76 (s, 3H, -OCH_3), 3.56 (t, *J* = 6.0 Hz, 2H, -C**H₂**NH-), 3.02 (t, *J* = 6.0 Hz, 2H, -COC**H₂-**); ^{13}C NMR (50 MHz, $CDCl_3$) δ 203.4 (C=O), 160.9 (C_6H_4), 149.1 (C_6H_4), 130.0 (C_6H_4), 106.2 (C_6H_4), 102.7 (C_6H_4), 99.0 (C_6H_4), 78.8 (C_5H_4), 72.4 (C_5H_4), 69.8 (C_5H_5), 69.2 (C_5H_4), 55.1 (-OCH_3), 38.7 (-CH_2-), 38.2 (-CH_2-). Anal. Calcd for $C_{20}H_{21}FeNO_2$: C, 66.13; H, 5.83; Fe, 15.37; N, 3.86; O, 8.81%. Found: C, 66.08, H, 5.82, N, 3.85%.

1-Ferrocenyl-3-((4-methoxyphenyl)amino)propan-1-one (**8q**). Yield (66%), mp. 97 °C; IR (KBr, ν, cm^{-1}): 3378, 3084, 2940, 2929, 2832, 1654, 1513, 1451, 1393, 1263, 1236, 1037, 819; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.85 – 6.74 (m, **AA'**MM', 2H, C_6H_4), 6.69 – 6.58 (m, AA'**MM'**, 2H, C_6H_4), 4.76 (pseudo t, *J* = 2.0 Hz, 2H, 2 × CH, C_5H_4), 4.50 (pseudo t, *J* = 2.0 Hz, 2H, 2 × CH, C_5H_4), 4.13 (s, 5H, 5 × CH, C_5H_5), 3.74 (s, 3H, -OCH_3), 3.52 (t, *J* = 6.1 Hz, 2H, -C**H₂**NH-), 3.00 (t, *J* = 6.1 Hz, 2H, -COC**H₂-**); ^{13}C NMR (50 MHz, $CDCl_3$) δ 203.5 (C=O), 152.3 (C_6H_4), 141.9 (C_6H_4), 115.0 (C_6H_4), 114.5 (C_6H_4), 78.9 (C_5H_4), 72.4 (C_5H_4), 69.8 (C_5H_5), 69.2 (C_5H_4), 55.8 (-OCH_3), 39.9 (-CH_2-), 38.3 (-CH_2-). Anal. Calcd for $C_{20}H_{21}FeNO_2$: C, 66.13; H, 5.83; Fe, 15.37; N, 3.86; O, 8.81%. Found: C, 66.17, H, 5.84, N, 3.86%.

1-Aryl-4-ferrocenyl-3-phenyltetrahydropyrimidin-2(1*H*)-ones (12a-q)

To a stirred solution of the corresponding Mannich base **8a-q** (1 mmol) in MeOH (20 mL) at room temperature an excess of $NaBH_4$ was added in several portions (up to 5 mmol) and the progress of the reaction monitored by TLC. After completion of the reaction (*ca.* 2 h), the solvent was distilled off and the residue diluted with water (30 mL). The mixture was extracted with CH_2Cl_2 (two 30 mL portions), the collected organic layers washed with water and brine, and dried overnight (anh. Na_2SO_4). After evaporation of the solvent, the product (the corresponding aminoalcohol **9a-q**) was mixed (without any purification) with phenyl isocyanate (0.12 mL, 1.1 mmol) in a test tube placed in an ultrasonic cleaner and irradiated for 30 min. Afterwards, 1 mL of acetic acid was added and irradiation continued for additional 1.5 h. The reaction mixture was neutralized with $NaHCO_3$ (litmus paper) and extracted with CH_2Cl_2 (two 20 mL portions). The combined organic layers were washed with water and dried over anh. Na_2SO_4. After the solvent was removed by evaporation, the crude product was purified by column chromatography (SiO_2; *n*-hexane-EtOAc, 8:2 (v/v)).



12a-q

Figure S3 Numbering scheme

4-Ferrocenyl-1,3-diphenyltetrahydropyrimidin-2(1*H*)-one (**12a**). Yield (78%), mp. 80 °C; IR (KBr, ν, cm^{-1}): 3089, 2933, 2230, 1639, 1594, 1478, 1427, 130, 1190, 909, 826, 693; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H, H-2''), 7.42 – 7.36 (m, 2H, H-3''), 7.33 – 7.28 (m, 4H, H-2', 3'), 7.23 – 7.18 (m, 1H, H-4''), 7.17 – 7.12 (m, 1H, H-4'), 5.20 (pseudo t, *J* = 3.7 Hz, 1H, H-4eq), 4.23 (dt, *J* = 2.4, 1.3 Hz, 1H, H-5'''), 4.15 (td, *J* = 2.4, 1.3 Hz, 1H, H-3'''), 4.11 (td, *J* = 2.4, 1.3 Hz, 1H, H-4'''), 4.04 (dt, *J* = 2.4, 1.3 Hz, 1H, H-2'''), 3.74 (s, 5H, H-6'''), 3.62 (pseudo td, *J* = 11.7, 3.9 Hz, 1H, H-6ax), 3.52 (dddd, *J* = 11.5, 4.8, 3.2, 1.0 Hz, 1H, H-6eq), 2.60 (pseudo ddt, *J* = 13.0, 12.0, 4.8 Hz, 1H, H-5ax), 2.15 (pseudo dq, *J* = 13.0, 3.5 Hz, 1H, H-5eq); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9 (C-2), 143.9 (C-1'), 143.4 (C-1''), 128.5 (C-3'), 128.4 (C-3''), 128.0 (C-2''), 126.1 (C-4''), 125.8 (C-2'), 125.5 (C-4'), 88.8 (C-1'''), 68.8 (C-6'''), 68.3 (C-3'''), 68.1 (C-5'''), 66.8 (C-4'''), 64.3 (C-2'''), 58.5 (C-4), 45.6 (C-6), 31.0 (C-5). Anal. Calcd for $C_{26}H_{24}FeN_2O$: C, 71.57; H, 5.54; Fe, 12.80; N, 6.42; O, 3.67%. Found: C, 71.49, H, 5.55, N, 6.40%.

4-Ferrocenyl-3-phenyl-1-*o*-tolyltetrahydropyrimidin-2(1*H*)-one (**12b**). Yield (83%), mp. 81 °C; IR (KBr, ν, cm^{-1}): 3087, 2929, 2362, 2238, 1634, 1481, 1434, 1309, 1191, 1105, 909, 721;

Table S1. ^{1}H NMR data for **12b**

Hydrogen	Diastereoisomer **I** (45%)	Diastereoisomer **II** (55%)
H-4eq	5.29 (pseudo t, *J* = 3.5 Hz)	5.25 (pseudo t, *J* = 3.4 Hz)
H-5ax	~ 2.62 (overlapped)	2.57 (pseudo tt , *J* = 12.5, 4.6 Hz)
H-5eq	2.16 (pseudo dq, *J* = 12.7, 3.5 Hz)	2.12 (pseudo dq, *J* = 12.9, 3.4 Hz)
H-6ax	~ 3.46 (overlapped)	
H-6eq	~ 3.42 (overlapped)	3.26-3.19 (m)
H-2'''	4.08-4.06 (m)	4.06-4.03 (m)
H-3'''	~ 4.17 (overlapped)	
H-4'''	4.14-4.10 (m)	4.16-4.13 (m)
H-5'''	4.35-4.32 (m)	4.38-4.35 (m)
H-6'''	3.74 (s)	3.72 (s)
H-3'	~ 7.19 (overlapped)	
H-4'	~ 7.09 (overlapped)	
H-5'	~ 7.18 (overlapped)	
H-6'	~ 7.16 (overlapped)	
H-2''	7.54-7.46 (m)	
H-3''	7.42-7.35 (m)	
H-4''	~ 7.19 (overlapped)	
CH_3	2.23 (s)	2.24 (s)

Table S2. ^{13}C NMR data for **12b**

Carbon	Diastereoisomer **I** (45%)	Diastereoisomer **II** (55%)
C-2	153.4	153.4
C-4	58.7	58.6
C-5	31.0	31.2
C-6	45.7	45.7
C-1'''	88.8	88.8
C-2'''	64.3	64.2
C-3'''	68.3	68.4
C-4'''	66.7	66.8
C-5'''	68.5	67.7
C-6'''	68.8	68.8
C-1'	142.6	142.4
C-2'	136.0	136.4
C-3'	~ 130.7 (overlapped)	
C-4'	127.3	127.5
C-5'	126.8	126.9
C-6'	127.1	128.3
C-1''	143.5	143.4
C-2''	~ 127.7 (overlapped)	
C-3''	~ 128.3 (overlapped)	
C-4''	125.8	125.8
CH_3	18.2	17.6

Anal. Calcd for $C_{27}H_{26}FeN_2O$: C, 72.01; H, 5.82; Fe, 12.40; N, 6.22; O, 3.55%. Found: C, 71.95, H, 5.83, N, 6.21%.

4-Ferrocenyl-3-phenyl-1-*m*-tolyltetrahydropyrimidin-2(1*H*)-one (**12c**). Yield (86%), mp. 131 °C; IR (KBr, ν, cm^{-1}): 3042, 2971, 2857, 1646, 1480, 1437, 1313, 1198, 766, 706; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H, H-2''), 7.41 – 7.34 (m, 2H, H-3''), 7.22 – 7.16 (m, 2H, H-5' and H-4''), 7.16 – 7.13 (m, 1H, H-2'),7.08 – 7.04 (m, 1H, H-6'), 6.99 – 6.94 (m, 1H, H-4'), 5.19 (pseudo t, *J* = 3.8 Hz, 1H, H-4eq), 4.23 (dt, *J* = 2.4, 1.2 Hz, 1H, H-5'''), 4.15 (td, *J* = 2.4, 1.2 Hz, 1H, H-3'''), 4.12 (td, *J* = 2.4, 1.2 Hz, 1H, H-4'''), 4.04 (dt, *J* = 2.4, 1.2 Hz, 1H, H-2'''), 3.74 (s, 5H, H-6'''), 3.61 (pseudo td, *J* = 11.8, 3.9 Hz, 1H, H-6ax), 3.51 (dddd, *J* = 11.9, 11.8, 4.8, 3.3, 1.0 Hz, 1H, H-6eq), 2.59 (dddd, *J* = 13.0, 11.9, 4.8, 3.8 Hz, 1H, H-5ax), 2.30 (s, 3H, CH_3), 2.15 (pseudo dq, *J* = 13.0, 3.5 Hz, 1H, H-5eq); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9 (C-2), 143.8 (C-1'), 143.5 (C-1''), 138.3 (C-3'), 128.4 (C-5'), 128.3 (C-3''), 128.0 (C-2''), 126.8 (C-2'), 126.3 (C-4'), 126.0 (C-4''), 122.7 (C-6'), 88.9 (C-1'''), 68.8 (C-6'''), 68.3 (C-3'''), 68.2 (C-5'''), 66.8 (C-4'''), 64.4 (C-2'''), 58.6 (C-4), 45.7 (C-6), 31.0 (C-5), 21.3 (CH_3). Anal. Calcd for $C_{27}H_{26}FeN_2O$: C, 72.01; H, 5.82; Fe, 12.40; N, 6.22; O, 3.55%. Found: C, 72.07, H, 5.81, N, 6.21%.

4-Ferrocenyl-3-phenyl-1-*p*-tolyltetrahydropyrimidin-2(1*H*)-one (**12d**). Yield (80%), mp. 70 °C; IR (KBr, ν, cm^{-1}): 3090, 3029, 2923, 2855, 1649, 1513, 1481, 1433, 1303, 1195, 813, 705; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 2H, H-2''), 7.41 – 7.34 (m, 2H, H-3''), 7.21 – 7.14 (m, 3H, H-2' and H-4''), 7.13 – 7.08 (m, 2H, H-3'), 5.18 (pseudo t, *J* = 3.8 Hz, 1H, H-4eq), 4.23 (dt, *J* = 2.4, 1.3 Hz, 1H, H-5'''), 4.14 (td, *J* = 2.4, 1.3 Hz, 1H, H-3'''), 4.11 (td, *J* = 2.4, 1.3 Hz, 1H, H-4'''), 4.04 (dt, *J* = 2.4, 1.3 Hz, 1H, H-2'''), 3.74 (s, 5H, H-6'''), 3.58 (pseudo td, *J* = 11.8, 3.9 Hz, 1H, H-6ax), 3.49 (dddd, *J* = 11.5, 4.9, 3.0, 1.0 Hz, 1H, H-6eq), 2.59 (pseudo ddt, *J* = 12.9, 11.9, 4.8 Hz, 1H, H-5ax), 2.30 (s, 3H, CH_3), 2.14 (pseudo dq, *J* = 12.9, 3.5 Hz, 1H, H-5eq); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0 (C-2), 143.6 (C-1''), 141.4 (C-1'), 135.2 (C-4'), 129.2 (C-3'), 128.3 (C-3''), 128.0 (C-2''), 126.0 (C-4''), 125.8 (C-2'), 88.9 (C-1'''), 68.8 (C-6'''), 68.3 (C-3'''), 68.2 (C-5'''), 66.8 (C-4'''), 64.4 (C-2'''), 58.6 (C-4), 45.8 (C-6), 31.0 (C-5), 20.9 (CH_3). Anal. Calcd for $C_{27}H_{26}FeN_2O$: C, 72.01; H, 5.82; Fe, 12.40; N, 6.22; O, 3.55%. Found: C, 71.94, H, 5.82, N, 6.23%.

4-Ferrocenyl-3-phenyl-1-(2,4,6-trimethylphenyl)tetrahydropyrimidin-2(1*H*)-one (**12e**). Yield (78%), mp. 188 °C; IR (KBr, ν, cm^{-1}): 3090, 2920, 2857, 1640, 1481, 1436, 1315, 1302, 1194, 703; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H, H-2''), 7.42 – 7.35 (m, 2H, H-3''), 7.20 – 7.14 (m, 1H, H-4''), 6.89 – 6.81 (m, 2H, H-3'), 5.35 (pseudo t, *J* = 3.0 Hz, 1H, H-4eq), 4.39 (dt, *J* = 2.3, 1.2 Hz, 1H, H-5'''), 4.15 (td, *J* = 2.3, 1.2 Hz, 1H, H-3'''), 4.13 (td, *J* = 2.3, 1.2 Hz, 1H, H-4'''), 4.06 (dt, *J* = 2.3, 1.2 Hz, 1H, H-2'''), 3.71 (s, 5H, H-6'''), 3.38 (pseudo td, *J* = 12.2, 3.8 Hz, 1H, H-6ax), 3.49 (dddd, *J* = 12.0, 4.8, 3.3, 1.0 Hz, 1H, H-6eq), 2.56 (pseudo tt, *J* = 12.7, 4.9 Hz, 1H, H-5ax), 2.23 (s, 3H, *p*-CH_3), 2.17 (s, 3H, *o*-CH_3), 2.16 (s, 3H, *o*-CH_3), 2.13 (pseudo dq, *J* = 12.9, 3.5 Hz, 1H, H-5eq); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1 (C-2), 143.7 (C-1''), 138.5 (C-1'), 136.7 (C-4'), 135.70 and 135.67 (2C, C-2' and C-6'), 129.11 and 129.10 (2C, C-3' and C-5'), 128.3 (C-3''), 127.7 (C-2''), 125.7 (C-4''), 89.0 (C-1'''), 68.9 (C-6'''), 68.6 (C-3'''), 68.4 (C-5'''), 66.6 (C-4'''), 64.2 (C-2'''), 58.6 (C-4), 44.0 (C-6), 31.1 (C-5), 20.9 (*p*-CH_3), 18.2 (*o*-CH_3), 17.7 (*o*-CH_3). Anal. Calcd for $C_{29}H_{30}FeN_2O$: C, 72.81; H, 6.32; Fe, 11.67; N, 5.86; O, 3.34%. Found: C, 72.74, H, 6.33, N, 5.87%.

4-Ferrocenyl-1-(2-fluorophenyl)-3-phenyltetrahydropyrimidin-2(1*H*)-one (**12f**). Yield (84%), mp. 104 °C; IR (KBr, ν, cm^{-1}): 3090, 2932, 2235, 1643, 1498, 1480, 1434, 1314, 1195, 908, 756; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.44 (m, 2H, H-2'' and H-6''), 7.40 – 7.34 (m, 2H, H-3'' and H-5''), 7.31-7.26 (m, 1H, H-2'), 7.22 – 7.16 (m, 2H, H-4' and H-4''), 7.11 – 7.05 (m, 2H, H-3' and H-5'), 5.19 (pseudo t, *J* = 3.8 Hz, 1H, C-4eq), 4.32 – 4.29 (m, 1H, H-5'''), 4.15 (td, *J* =

2.4, 1.3 Hz, 1H, H-3'''), 4.12 (td, *J* = 2.4, 1.3 Hz, 1H, H-4'''), 4.04 (dt, *J* = 2.4, 1.3 Hz, 1H, H-2'''), 3.73 (s, 5H, H-6'''), 3.53 (pseudo td, *J* = 11.7, 3.9 Hz, 1H, H-6ax), 3.46 (dddd, *J* = 11.5, 5.0, 2.9, 1.0 Hz, 1H, H-6eq), 2.63 (pseudo ddt, *J* = 12.9, 11.8, 5.0 Hz, 1H, H-5ax), 2.15 (dq, *J* = 13.0, 3.5 Hz, 1H, H-5eq); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4 (d, $^1J_{C-F}$ = 249.4 Hz, C-2'), 153.7 (C=O), 143.3 (C-1''), 131.1 (d, $^2J_{C-F}$ = 12.5 Hz, C-1'), 129.8 (d, $^3J_{C-F}$ = 1.5 Hz, C-6'), 128.4 (C-3''), 128.2 (d, $^3J_{C-F}$ = 7.9 Hz, C-4'), 127.9 (C-2''), 126.2 (C-4''), 124.3 (d, $^4J_{C-F}$ = 3.7 Hz, C-5'), 116.4 (d, $^2J_{C-F}$ = 20.3 Hz, C-3'), 88.5 (C-1'''), 68.8 (C-6'''), 68.4 (C-4'''), 68.3 (C-2'''), 66.8 (C-3'''), 64.4 (C-5'''), 58.8 (C-4), 45.9 (d, $^4J_{C-F}$ = 2.0 Hz, C-6), 31.1 (C-5). Anal. Calcd for $C_{26}H_{23}FFeN_2O$: C, 68.74; H, 5.10; F, 4.18; Fe, 12.29; N, 6.17; O, 3.52%. . Found: C, 68.67, H, 5.11, N, 6.16%.

4-Ferrocenyl-1-(3-fluorophenyl)-3-phenyltetrahydropyrimidin-2(1*H*)-one (**12g**). Yield (91%), mp. 62 °C; IR (KBr, ν, cm^{-1}): 3089, 2925, 1651, 1609, 1589, 1481, 1428, 1316, 1301, 1198, 707, 691; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H, H-2''), 7.42 – 7.36 (m, 2H, H-3''), 7.26 – 7.18 (m, 2H, H-5' and H-4''), 7.13 – 7.06 (m, 2H, H-2' and H-6'), 6.87-6.80 (m, 1H, H-4'), 5.17 (pseudo t, *J* = 3.9 Hz, 1H, H-4eq), 4.17 (dt, *J* = 2.3, 1.2 Hz, 1H, H-5'''), 4.16 (td, *J* = 2.3, 1.2 Hz, 1H, H-3'''), 4.11 (td, *J* = 2.3, 1.2 Hz, 1H, H-4'''), 4.05 (dt, *J* = 2.3, 1.2 Hz, 1H, H-2'''), 3.75 (s, 5H, H-6'''), 3.62 (pseudo td, *J* = 11.6, 3.9 Hz, 1H, H-6ax), 3.53 (dddd, *J* = 11.4, 4.6, 3.4, 1.0 Hz, 1H, H-6eq), 2.60 (pseudo ddt, *J* = 13.0, 11.7, 4.8 Hz, 1H, H-5ax), 2.18 (pseudo dq, *J* = 13.0, 3.6 Hz, 1H, H-5eq); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, $^1J_{C-F}$= 245.1 Hz, C-3'), 153.7 (C-2), 145.4 (d, $^3J_{C-F}$= 10.1 Hz, C-1'), 143.2 (C-1''), 129.4 (d, $^3J_{C-F}$= 9.3 Hz, C-5'), 128.5 (C-3''), 128.0 (C-2''), 126.3 (C-4''), 120.9 (d, $^4J_{C-F}$= 3.0 Hz, C-6'), 113.0 (d, $^2J_{C-F}$= 23.5 Hz, C-2'), 112.1 (d, $^2J_{C-F}$= 21.0 Hz, C-4'), 88.6 (C-1'''), 68.8 (C-6'''), 68.4 (C-3'''), 68.2 (C-5'''), 67.0 (C-4'''), 64.4 (C-2'''), 58.6 (C-4), 45.5 (C-6), 31.0 (C-5). Anal. Calcd for $C_{26}H_{23}FFeN_2O$: C, 68.74; H, 5.10; F, 4.18; Fe, 12.29; N, 6.17; O, 3.52%. . Found: C, 68.78, H, 5.09, N, 6.18%.

4-Ferrocenyl-1-(4-fluorophenyl)-3-phenyltetrahydropyrimidin-2(1*H*)-one (**12h**). Yield (80%), mp. 151 °C; IR (KBr, ν, cm^{-1}): 3076, 2922, 2232, 1628, 1593, 1478, 1437, 1309, 1205, 1197, 828, 716; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H, H-2''), 7.42 – 7.36 (m, 2H, H-3''), 7.27 – 7.23 (m, 2H, H-2'), 7.23 – 7.20 (m, 1H, H-4''), 7.02 – 6.94 (m, 2H, H-3'), 5.19 (pseudo t, *J* = 3.8 Hz, 1H, H-4eq), 4.21 (dt, *J* = 2.4, 1.3 Hz, 1H, H-5'''), 4.16 (td, *J* = 2.4, 1.3 Hz, 1H, H-3'''), 4.12 (td, *J* = 2.4, 1.3 Hz, 1H, H-4'''), 4.04 (dt, *J* = 2.4, 1.3 Hz, 1H, H-2'''), 3.74 (s, 5H, H-6'''), 3.58 (pseudo td, *J* = 11.7, 4.0 Hz, 1H, H-6ax), 3.47 (dddd, *J* = 11.5, 4.8, 3.1, 1.0 Hz, 1H, H-6eq), 2.60 (pseudo ddt, *J* = 13.0, 11.9, 4.9 Hz, 1H, H-5ax), 2.16 (pseudo dq, *J* = 13.0, 3.6 Hz, 1H, H-5eq); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4 (d, $^1J_{C-F}$= 244.7 Hz, C-4'), 154.0 (C-2), 143.3 (C-1''), 139.9 (d, $^4J_{C-F}$= 3.0 Hz, C-1'),128.4 (C-3''), 128.0 (C-2''), 127.7 (d, $^3J_{C-F}$= 8.4 Hz, C-2'), 126.2 (C-4''), 115.3 (d, $^2J_{C-F}$= 22.5 Hz, C-3'), 88.7 (C-1'''), 68.8 (C-6'''), 68.4 (C-3'''), 68.1 (C-5'''), 66.9 (C-4'''), 64.4 (C-2'''), 58.7 (C-4), 46.0 (C-6), 31.0 (C-5). Anal. Calcd for $C_{26}H_{23}FFeN_2O$: C, 68.74; H, 5.10; F, 4.18; Fe, 12.29; N, 6.17; O, 3.52%. . Found: C, 68.65, H, 5.11, N, 6.17%.

1-(2-Chlorophenyl)-4-ferrocenyl-3-phenyltetrahydropyrimidin-2(1*H*)-one (**12i**). Yield (80%), mp. 142 °C; IR (KBr, ν, cm^{-1}): 3086, 3067, 2970, 2938, 2859, 1647, 1481, 1438, 1313, 1200, 761;

Table S3. ^{1}H NMR data for **12i**

Hydrogen	Diastereoisomer **I** (45%)	Diastereoisomer **II** (55%)
H-4eq	~ 5.16 (overlapped m)	
H-5ax	2.73-2.55 (overlapped m)	
H-5eq	~ 2.23 (overlapped m)	~ 2.16 (overlapped m)
H-6ax	~ 3.81 (overlapped m)	3.57-3.28 (overlapped m)
H-6eq	3.57-3.28 (overlapped m)	
H-2'''	4.14-4.04 (3.57-3.28 (overlapped m)	
H-3'''	4.23-4.14 (3.57-3.28 (overlapped m)	
H-4'''		
H-5'''	~ 4.51 (3.57-3.28 (overlapped m)	~ 4.37 (3.57-3.28 (overlapped m)
H-6'''	~ 3.77 (3.57-3.28 (overlapped s)	
H-3'		
H-4'		
H-5'	7.51-7.33 (3.57-3.28 (overlapped m, 5H)	
H-6'	7.32-7.23 (3.57-3.28 (overlapped m, 2H)	
H-2''	7.22-7.12 (3.57-3.28 (overlapped m, 2H)	
H-3''		
H-4''		

Table S4. ^{13}C NMR data for **12i**

Carbon	Diastereoisomer **I** (45%)	Diastereoisomer **II** (55%)
C-2	153.5	
C-4	~ 58.9	
C-5	31.4	30.9
C-6	~ 45.6	
C-1'''	89.7	89.1
C-2'''	65.2	64.8
C-3'''	~ 68.9	
C-4'''	67.4	67.1
C-5'''	69.8	68.5
C-6'''	~ 69.3	
C-1'	140.9	
C-2'	133.3	
C-3'		
C-4'	130.1, 128.5, 128.1, 127.8	
C-5'		
C-6'		
C-1''	~ 143.2	
C-2''	127.6	
C-3''	128.4	
C-4''	126.0	

Anal. Calcd for $C_{26}H_{23}ClFeN_2O$: C, 66.33; H, 4.92; Cl, 7.53; Fe, 11.86; N, 5.95; O, 3.40%. Found: C, 66.28, H, 4.93, N, 5.94%.

1-(3-Chlorophenyl)-4-ferrocenyl-3-phenyltetrahydropyrimidin-2(1*H*)-one (**12j**). Yield (88%), mp. 74 °C; IR (KBr, ν, cm^{-1}): 2924, 2853, 1652, 1593, 1480, 1436, 1312, 1196, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H, H-2''), 7.42 – 7.37 (m, 2H, H-3''), 7.37 – 7.34 (m, 1H, H-2'), 7.25 – 7.19 (m, 3H, H-2', H-4' and H-4''), 7.14 – 7.08 (m, 1H, H-5'), 5.17 (pseudo t, *J* = 3.9 Hz, 1H, H-4eq), 4.17 (dt, *J* = 2.4, 1.3 Hz, 1H, H-5'''), 4.16 (td, *J* = 2.4, 1.3 Hz, 1H, H-3'''), 4.11 (td, *J* = 2.4, 1.3 Hz, 1H, H-4'''), 4.04 (dt, *J* = 2.4, 1.3 Hz, 1H, H-2'''), 3.74 (s, 5H, H-6'''), 3.62 (pseudo td, *J* = 11.6, 3.9 Hz, 1H, H-6ax), 3.52 (dddd, *J* = 11.4, 4.6, 3.3, 1.0 Hz, 1H, H-6eq), 2.60 (pseudo ddt, *J* = 13.0, 11.7, 4.8, 3.3 Hz, 1H, H-5ax), 2.18 (pseudo dq, *J* = 13.0, 3.6 Hz, 1H, H-5eq); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6 (C-2), 145.0 (C-1'), 143.2 (C-1''), 133.9 (C-3'), 129.4 (C-6'), 128.5 (C-3''), 128.0 (C-2''), 126.4 (C-4''), 125.9 (C-2'), 125.4 (C-5'), 123.7 (C-4'), 88.6 (C-1'''), 68.8 (C-6'''), 68.4 (C-3'''), 68.2 (C-5'''), 67.0 (C-4'''), 64.4 (C-2'''), 58.6 (C-4), 45.5 (C-6), 31.0 (C-5). Anal. Calcd for $C_{26}H_{23}ClFeN_2O$: C, 66.33; H, 4.92; Cl, 7.53; Fe, 11.86; N, 5.95; O, 3.40%. Found: C, 66.35, H, 4.91, N, 5.95%.

1-(4-Chlorophenyl)-4-ferrocenyl-3-phenyltetrahydropyrimidin-2(1*H*)-one (**12k**). Yield (83%), mp. 130 °C; IR (KBr, ν, cm^{-1}): 3095, 2924, 1644, 1495, 1479, 1316, 1297, 1198, 759, 697; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H, H-2''), 7.41 – 7.36 (m, 2H, H-3''), 7.28 – 7.18 (m, 5H, H-2', H-3' and H-4''), 5.17 (pseudo t, *J* = 3.9 Hz, 1H, H-4eq), 4.18 (dt, *J* = 2.4, 1.3 Hz, 1H, H-5'''), 4.15 (td, *J* = 2.4, 1.3 Hz, 1H, H-3'''), 4.10 (td, *J* = 2.4, 1.3 Hz, 1H, H-4'''), 4.04 (dt, *J* = 2.4, 1.3 Hz, 1H, H-2'''), 3.74 (s, 5H, H-6'''), 3.60 (pseudo td, *J* = 11.6, 3.9 Hz, 1H, H-6ax), 3.49 (dddd, *J* = 11.5, 4.9, 3.2, 1.0 Hz, 1H, H-6eq), 2.59 (pseudo ddt, *J* = 13.0, 11.8, 4.8 Hz, 1H, H-5ax), 2.16 (pseudo dq, *J* = 13.0, 3.6 Hz, 1H, H-5eq); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7 (C-2), 143.2 (C-1''), 142.4 (C-1'), 130.7 (C-4'), 128.6 (C-2'), 128.4 (C-3''), 128.0 (C-2''), 127.0 (C-3'), 126.3 (C-4''), 88.6 (C-1'''), 68.8 (C-6'''), 68.4 (C-3'''), 68.1 (C-5'''), 66.9 (C-4'''), 64.4 (C-2'''), 58.6 (C-4), 45.6 (C-6), 31.0 (C-5). Anal. Calcd for $C_{26}H_{23}ClFeN_2O$: C, 66.33; H, 4.92; Cl, 7.53; Fe, 11.86; N, 5.95; O, 3.40%. Found: C, 66.39, H, 4.93, N, 5.96%.

1-(2-Bromophenyl)-4-ferrocenyl-3-phenyltetrahydropyrimidin-2(1*H*)-one (**12l**). Yield (62%), mp. 88 °C; IR (KBr, ν, cm^{-1}): 3269, 3083, 2930, 1645, 1477, 1433, 1312, 1298, 1192, 1026, 757;

Table S5. ^{1}H NMR data for **12l**

Hydrogen	Diastereoisomer **I** (43%)	Diastereoisomer **II** (57%)
H-4eq	5.27 (pseudo t, *J* = 3.7 Hz)	5.25 (pseudo t, *J* = 3.5 Hz)
H-5ax	2.63 (pseudo tt, *J* = 12.3, 4.8 Hz)	2.69 (pseudo tt, *J* = 12.4, 4.9 Hz)
H-5eq	2.21 (pseudo dq, *J* = 12.9, 3.4 Hz)	2.14 (pseudo dq, *J* = 12.9, 3.5 Hz)
H-6ax	~ 3.79 (overlapped)	3.35 (pseudo td, *J* = 11.8, 4.0 Hz)
H-6eq	3.34-3.27 (m)	3.42 (dddd, *J* = 11.3, 4.4, 2.9, 1.0 Hz)
H-2'''	~ 4.08 (overlapped)	~ 4.06 (overlapped)
H-3'''	~ 4.13 (overlapped)	~ 4.17 (overlapped)
H-4'''	~ 4.09 (overlapped)	~ 4.15 (overlapped)
H-5'''	4.47-4.44 (m)	4.34-4.31 (m)
H-6'''	3.72 (s)	3.74 (s)
H-3'	~ 7.28 (overlapped)	
H-4'	7.16-7.09 (m)	
H-5'	7.63-7.56 (m)	
H-6'	~ 7.29 (overlapped)	
H-2''	7.53-7.45 (m)	
H-3''	7.41-7.35 (m)	
H-4''	7.23-7.16 (m)	

Table S6. ^{13}C NMR data for **12l**

Carbon	Diastereoisomer **I** (43%)	Diastereoisomer **II** (57%)
C-2	153.4	153.4
C-4	~ 58.7 (overlapped)	
C-5	31.2	30.9
C-6	45.5	45.7
C-1'''	88.6	88.8
C-2'''	64.3	64.4
C-3'''	68.3	68.5
C-4'''	66.6	66.8
C-5'''	69.4	68.0
C-6'''	68.8	68.9
C-1'	142.7	142.4
C-2'	123.7	123.8
C-3'	130.6	130.2
C-4'	128.6	128.8
C-5'	133.2	133.3
C-6'	~ 128.4 (overlapped)	
C-1"	143.2	143.3
C-2"	128.1	127.8
C-3"	~ 128.3 (overlapped)	
C-4"	126.1	126.0

Anal. Calcd for $C_{26}H_{23}BrFeN_2O$: C, 60.61; H, 4.50; Br, 15.51; Fe, 10.84; N, 5.44; O, 3.11%. Found: C, 60.55, H, 4.49, N, 5.45%.

1-(3-Bromophenyl)-4-ferrocenyl-3-phenyltetrahydropyrimidin-2(1*H*)-one (**12m**). Yield (68%), mp. 81 °C; IR (KBr, ν, cm^{-1}): 3077, 2938, 1645, 1587, 1472, 1417, 1296, 1187, 997, 774, 689; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 1H, H-2'), 7.45 – 7.37 (m, 4H, H-2", H-3"), 7.28 – 7.20 (m, 3H, H-4', H-6' and H-4"), 7.19 – 7.12 (m, 1H, H-5'), 5.17 (pseudo t, *J* = 3.9 Hz, 1H, H-4eq), 4.17 (dt, *J* = 2.4, 1.3 Hz, 1H, H-5'''), 4.16 (dt, *J* = 2.4, 1.3 Hz, 1H,H-3'''), 4.11 (td, *J* = 2.4, 1.3 Hz, 1H, H-4'''), 4.04 (dt, *J* = 2.5, 1.3 Hz, 1H, H-2'''), 3.74 (s, 5H, H-6'''), 3.62 (pseudo td, *J* = 11.6, 3.9 Hz, 1H, H-6ax), 3.51 (dddd, *J* = 11.5, 4.6, 3.3, 1.0 Hz, 1H, H-6eq), 2.60 (pseudo ddt, *J* = 13.0, 11.8, 4.8 Hz, 1H, H-5ax), 2.18 (pseudo dq, *J* = 13.0, 3.6 Hz, 1H, H-5eq); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6 (C-2), 145.1 (C-1'), 143.2 (C-1"), 129.7 (C-5'), 128.8 (C-2'), 128.5 (C-3"), 128.3 (C-6'), 128.0 (C-2"), 126.4 (C-4"), 124.1 (C-4'), 121.9 (C-3'), 88.6 (C-1'''), 68.8 (C-6'''), 68.4 (C-3'''), 68.2 (C-5'''), 67.0 (C-4'''), 64.4 (C-2'''), 58.6 (C-4), 45.5 (C-6), 31.0 (C-5). Anal. Calcd for $C_{26}H_{23}BrFeN_2O$: C, 60.61; H, 4.50; Br, 15.51; Fe, 10.84; N, 5.44; O, 3.11%. Found: C, 60.67, H, 4.49, N, 5.44%.

1-(4-Bromophenyl)-4-ferrocenyl-3-phenyltetrahydropyrimidin-2(1*H*)-one (**12n**). Yield (89%), mp. 90 °C; IR (KBr, ν, cm^{-1}): 3083, 2930, 1645, 1477, 1431, 1313, 1297, 1195, 1001, 809, 716; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 6H, H-3' and H-2" and H-3"), 7.24–7.21 (m, 1H, H-4"), 7.21 – 7.17 (m, 2H, H-2'), 5.17 (pseudo t, *J* = 3.9 Hz, 1H, H-4eq), 4.17 (dt, *J* = 2.4, 1.3 Hz, 1H, H-5'''), 4.15 (dt, *J* = 2.4, 1.3 Hz, 1H, H-3'''), 4.10 (td, *J* = 2.4, 1.3 Hz, 1H, H-4'''), 4.04 (dt, *J* = 2.5, 1.3 Hz, 1H, H-2'''), 3.74 (s, 5H, H-6'''), 3.60 (pseudo td, *J* = 11.6, 3.9 Hz, 1H, H-6ax), 3.50 (dddd, *J* = 11.5, 4.6, 3.2, 1.0 Hz, 1H, H-6eq), 2.60 (pseudo ddt, *J* = 13.0, 11.8, 4.8 Hz, 1H, H-5ax), 2.17 (pseudo dq, *J* = 13.0, 3.6 Hz, 1H, H-5eq); ^{13}C NMR (101 MHz, $CDCl_3$)

δ 153.7 (C-2), 143.2 (C-1''), 142.9 (C-1'), 131.5 (C-3'), 128.5 (C-3''), 128.0 (C-2''), 127.3 (C-2'), 126.3 (C-4''), 118.6 (C-4'), 88.6 (C-1'''), 68.8 (C-6'''), 68.4 (C-3'''), 68.2 (C-5'''), 66.9 (C-4'''), 64.4 (C-2'''), 58.6 (C-4), 45.5 (C-6), 31.0 (C-5). Anal. Calcd for $C_{26}H_{23}BrFeN_2O$: C, 60.61; H, 4.50; Br, 15.51; Fe, 10.84; N, 5.44; O, 3.11%. Found: C, 60.58, H, 4.51, N, 5.43%.

4-Ferrocenyl-1-(2-methoxyphenyl)-3-phenyltetrahydropyrimidin-2(1*H*)-one (**12o**). Yield (99%), mp. 143 °C; IR (KBr, ν, cm^{-1}): 2932, 1641, 1499, 1440, 1339, 1308, 1190, 1106, 1030, 760; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H, H-2''), 7.41 – 7.32 (m, 2H, H-3''), 7.24 – 7.18 (m, 2H, H-4' and H-6'), 7.18-7.14 (m, 1H, H-4''), 6.95 – 6.87 (m, 2H, H-3' and H-5'), 5.21 (pseudo t, *J* = 3.6 Hz, 1H, H-4eq), 4.47-4.35 (m, 1H, H-5'''), 4.16 – 4.13 (m, 1H, H-3'''), 4.13-4.11 (m, 1H, H-4'''), 4.07 – 4.04 (m, 1H, H-2'''), 3.81 (s, 3H, OCH_3), 3.73 (s, 5H, H-6'''), 3.56-3.40 (m, 1H, H-6ax), 3.39-3.27 (m, 1H, H-6eq), 2.62 (pseudo tt, *J* = 12.8, 4.6 Hz, 1H, H-5ax), 2.09 (pseudo dq, *J* = 12.9, 3.3 Hz, 1H, H-5eq); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6 (C-2'), 154.1 (C-2), 143.7 (C-1''), 132.4 (C-1'), 129.9 (C-4'), 128.2 (C-3''), 128.2 (C-6'), 127.9 (C-2''), 125.8 (C-4''), 120.7 (C-5'), 111.9 (C-3'), 89.1 (C-1'''), 68.8 (C-6'''), 68.6 (C-5'''), 68.2 (C-3'''), 66.5 (C-4'''), 64.4 (C-2'''), 58.7 (C-4), 55.5 (OCH_3), 45.4 (C-6), 31.2 (C-5). Anal. Calcd for $C_{27}H_{26}FeN_2O_2$: C, 69.54; H, 5.62; Fe, 11.97; N, 6.01; O, 6.86%. Found: C, 69.46, H, 5.61, N, 5.99%.

4-Ferrocenyl-1-(3-methoxyphenyl)-3-phenyltetrahydropyrimidin-2(1*H*)-one (**12p**). Yield (58%), mp. 138 °C; IR (KBr, ν, cm^{-1}): 3072, 2974, 2933, 2861, 2832, 1633, 1594, 1432, 1300, 1197, 1038, 764; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H, H-2''), 7.42 – 7.35 (m, 2H, H-3''), 7.23 – 7.17 (m, 2H, H-5' and H-4''), 6.91 – 6.89 (m, 1H, H-2'), 6.89 – 6.85 (m, 1H, H-6'), 6.74 – 6.68 (m, 1H, H-4'), 5.18 (pseudo t, *J* = 3.8 Hz, 1H, H-4eq), 4.21 (dt, *J* = 2.4, 1.3 Hz, 1H, H-5'''), 4.15 (td, *J* = 2.4, 1.3 Hz, 1H, H-3'''), 4.11 (td, *J* = 2.4, 1.3 Hz, 1H, H-4'''), 4.04 (dt, *J* = 2.4, 1.3 Hz, 1H, H-2'''), 3.76 (s, 3H, OCH_3),3.74 (s, 5H, H-6'''), 3.61 (pseudo td, *J* = 11.7, 3.9 Hz, 1H, H-6ax), 3.54 (dddd, *J* = 11.5, 4.6, 3.1, 1.0 Hz, 1H, H-6eq), 2.60 (pseudo ddt, *J* = 13.0, 11.9, 4.8 Hz, 1H, H-5ax), 2.16 (pseudo dq, *J* = 13.0, 3.6 Hz, 1H, H-5eq); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (C-3'), 153.8 (C-2), 145.1 (C-1'), 143.4 (C-1''),129.2 (C-5'), 128.4 (C-3''), 128.0 (C-2''), 126.2 (C-4''), 118.0 (C-6'), 111.9 (C-2'), 111.5 (C-4'), 88.8 (C-1'''), 68.8 (C-6'''), 68.4 (C-3'''), 68.2 (C-5'''), 66.9 (C-4'''), 64.4 (C-2'''), 58.6 (C-4), 55.4 (OCH_3), 45.8 (C-6), 31.0 (C-5). Anal. Calcd for $C_{27}H_{26}FeN_2O_2$: C, 69.54; H, 5.62; Fe, 11.97; N, 6.01; O, 6.86%. Found: C,69.57, H, 5.62, N, 6.02%.

4-Ferrocenyl-1-(4-methoxyphenyl)-3-phenyltetrahydropyrimidin-2(1*H*)-one (**12p**). Yield (64%), mp. 140 °C; IR (KBr, ν, cm^{-1}): 1644, 1514, 1475, 1433, 1296, 1246, 1188, 1175, 1029, 831, 705; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H, H-2''), 7.41 – 7.34 (m, 2H, H-3''), 7.23 – 7.13 (m, 3H, H-2' and H-4''), 6.87 – 6.80 (m, 2H, H-3'), 5.19 (pseudo t, *J* = 3.7 Hz, 1H, H-4eq), 4.25 (dt, *J* = 2.4, 1.3 Hz, 1H, H-5'''), 4.15 (td, *J* = 2.4, 1.3 Hz, 1H, H-3'''), 4.12 (td, *J* = 2.4, 1.3 Hz, 1H, H-4'''), 4.04 (dt, *J* = 2.4, 1.3 Hz, 1H, H-2'''), 3.76 (s, 3H, OCH_3), 3.73 (s, 5H, H-6'''), 3.55 (pseudo td, *J* = 11.8, 4.0 Hz, 1H, H-6ax), 3.46 (dddd, *J* = 11.6, 5.0, 3.0, 1.1 Hz, 1H, H-6eq), 2.59 (pseudo ddt, *J* = 12.9, 12.1, 4.8 Hz, 1H, H-5ax), 2.13 (pseudo dq, *J* = 12.9, 3.4 Hz, 1H, H-5eq); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4 (C-4'), 154.1 (C-2), 143.6 (C-1''), 137.0 (C-1'), 128.3 (C-3''), 127.9 (C-2''), 127.4 (C-2'), 125.9 (C-4''), 113.9 (C-3'), 88.9 (C-1'''), 68.8 (C-6'''), 68.3 (C-3'''), 68.1 (C-5'''), 66.8 (C-4'''), 64.4 (C-2'''), 58.6 (C-4), 55.5 (OCH_3), 46.1 (C-6), 31.0 (C-5). Anal. Calcd for $C_{27}H_{26}FeN_2O_2$: C, 69.54; H, 5.62; Fe, 11.97; N, 6.01; O, 6.86%. Found: C, 69.49, H, 5.61, N, 6.00%.

4-Ferrocenyl-1,2,3,4-tetrahydroquinoline (10)

A mixture of the aminoalcohol **9a** (obtained from 1 mmol of **8a**, as described above for the synthesis of **12a-q**), aniline (2 mmol) and acetic acid (1 mL) was placed in an ultrasonic cleaner and irradiated for 2 h. The reaction mixture was neutralized with $NaHCO_3$ and extracted with CH_2Cl_2 (two 20 mL portions). The combined organic layers were washed with water and dried over anh. Na_2SO_4. After the evaporation of the solvent, the crude product was purified by column chromatography (SiO_2; *n*-hexane-EtOAc, 8:2 (v/v)).

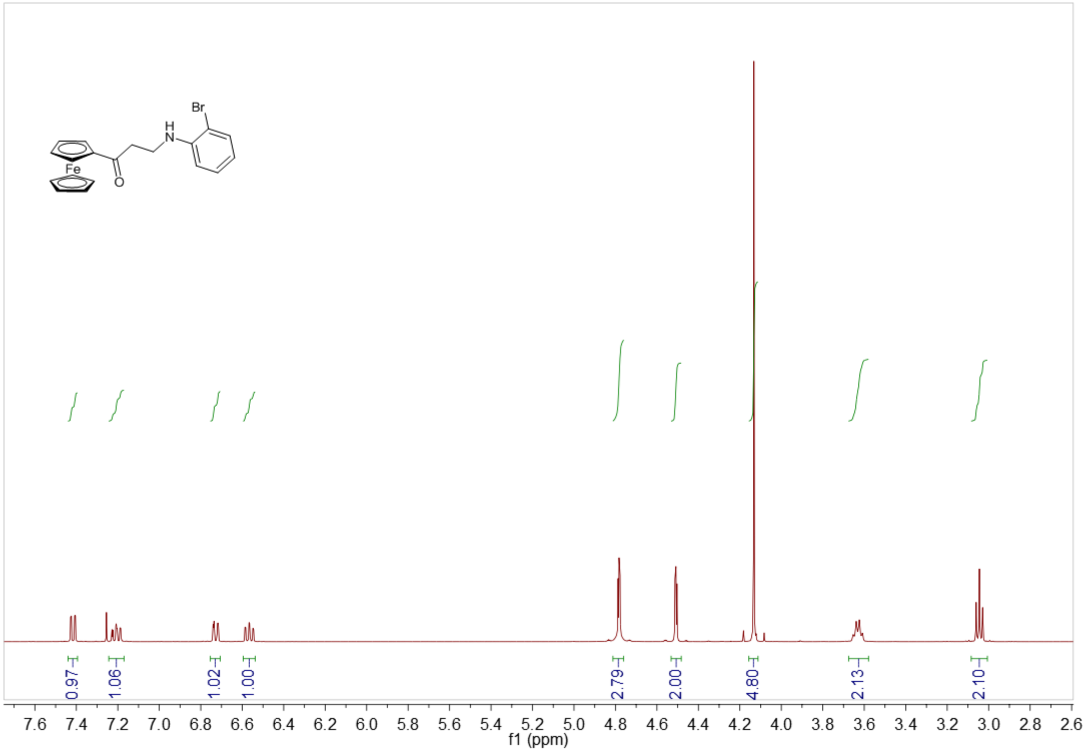
4-Ferrocenyl-1,2,3,4-tetrahydroquinoline (**10**). Yield (90%), mp. 120 °C; IR (KBr, ν, cm^{-1}): 3425, 3082, 2978, 2927, 2860, 2835, 1601, 1494, 1313, 1283, 1103, 810, 748; ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (pseudo d, *J* = 7.5 Hz, 1H, H-5), 7.00 – 6.95 (m, 1H, H-7), 6.59 (td, *J* = 7.4, 1.2 Hz, 1H, H-6), 6.45 (dd, *J* = 8.0, 1.2 Hz, 1H, H-8), 4.16 (s, 5H, H-6'), 4.11 (td, *J* = 2.4, 1.3 Hz, 1H, H-4'), 4.10 – 4.06 (m, 2H, H-3' and H-4'), 3.89 (dt, *J* = 2.5, 1.3 Hz, 1H, H-2'), 3.85-3.81 (overlapped m, 2H, H-4 and N-H), 3.29 – 3.16 (m, 2H, H-2a and H-2b), 2.23 (ddt, *J* = 13.0, 8.8, 4.5 Hz, 1H, H-3a), 1.98 (dddd, *J* = 13.0, 10.1, 6.3, 3.8 Hz, 1H, H-3b); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0 (C-8a), 129.5 (C-5), 127.1 (C-7), 123.7 (C-4a), 116.3 (C-6), 113.8 (C-8), 94.1 (C-1'), 69.8 (C-2'), 68.6 (5C, C-6'), 67.6 (C-4'), 66.5, 65.8 (C-3', 5'), 39.3 (C-2), 36.3 (C-4), 29.6 (C-3). Anal. Calcd for $C_{19}H_{19}FeN$: C, 71.94; H, 6.04; Fe, 17.61; N, 4.42%. Found: C, 71.89, H, 6.05, N, 4.41%.

1-(4-Chlorophenyl)-1-(3-ferrocenyl-3-hydroxypropyl)-3-phenylurea (11k). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H, H-2'), 7.33 – 7.27 (m, 2H, H-3'), 7.27 – 7.20 (m, 4H, H-2'' and H-3''), 7.04 – 6.98 (m, 1H, H-4'), 6.41 (br s, 1H, NH), 4.54 – 4.49 (m, 1H, H-6), 4.24 – 4.20 (m, 1H, C_5H_4), 4.19 – 4.16 (m, 1H, H-4a), 4.13 (s, 5H, C_5H_5), 4.13 – 4.10 (m, 3H, C_5H_4), 3.66 (ddd, *J* = 14.4, 6.8, 4.4 Hz, 1H, H-4b), 3.40 (d, *J* = 4.1 Hz, 1H, OH), 2.02 – 1.90 (m, 1H, H-5a), 1.80 (ddt, *J* = 14.0, 6.0, 4.4 Hz, 1H, H-5b); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8 (C=O), 139.7 (C-1'), 138.5 (C-4''), 133.8 (C-1''), 130.5 (C-2'), 129.6, 128.9 (C-2'', 3''), 123.3 (C-4'), 119.5 (C-3'), 92.5 (C_5H_4), 68.6 (C_5H_4), 68.4 (C_5H_5), 67.9 (C_5H_4), 67.7(C_5H_4), 66.5 (C-6), 66.1 (C_5H_4), 46.7 (C-4), 36.3 (C-5).

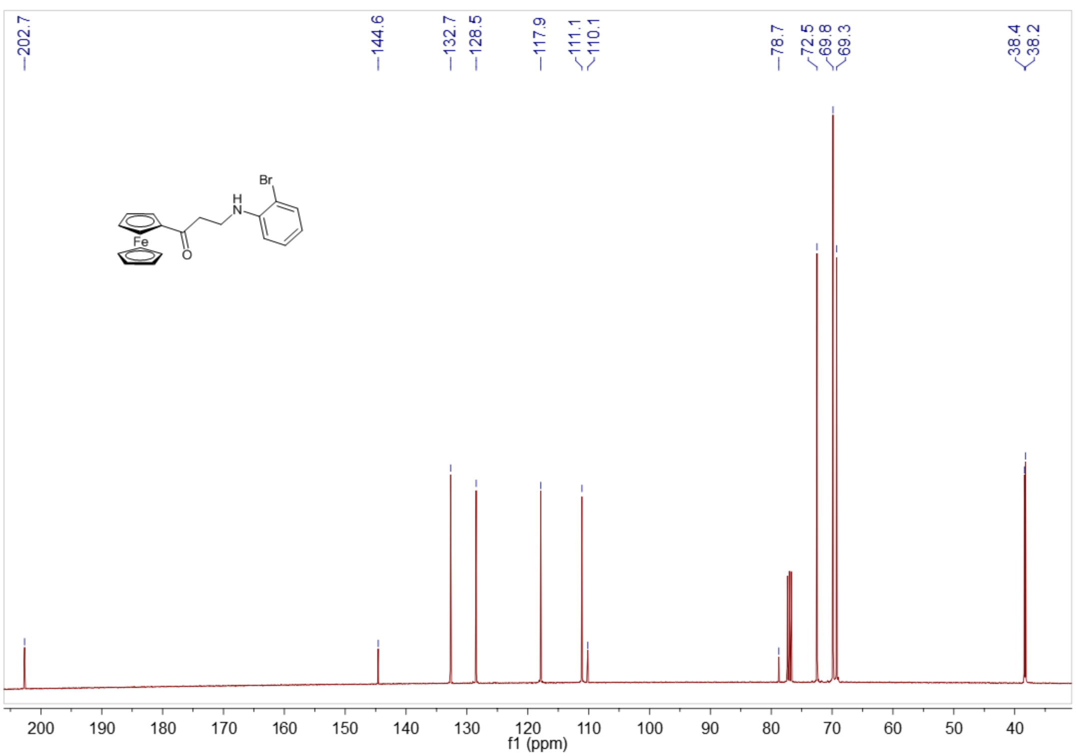
References

1. I. Damljanović, D. Stevanović, A. Pejović, M. Vukićević, S. B. Novaković, G. A. Bogdanović, T. Mihajilov-Krstev, N. Radulović, R. D. Vukićević, *J. Organomet. Chem.* 2011, **696**, 3703
2. A. Pejović, D. Stevanović, I. Damljanović, M. Vukićević, S. B. Novaković, G. A. Bogdanović, T. Mihajilov-Krstev, N. Radulović, R. D. Vukićević, *Helv. Chim. Acta*, 2012, **95**, 1425

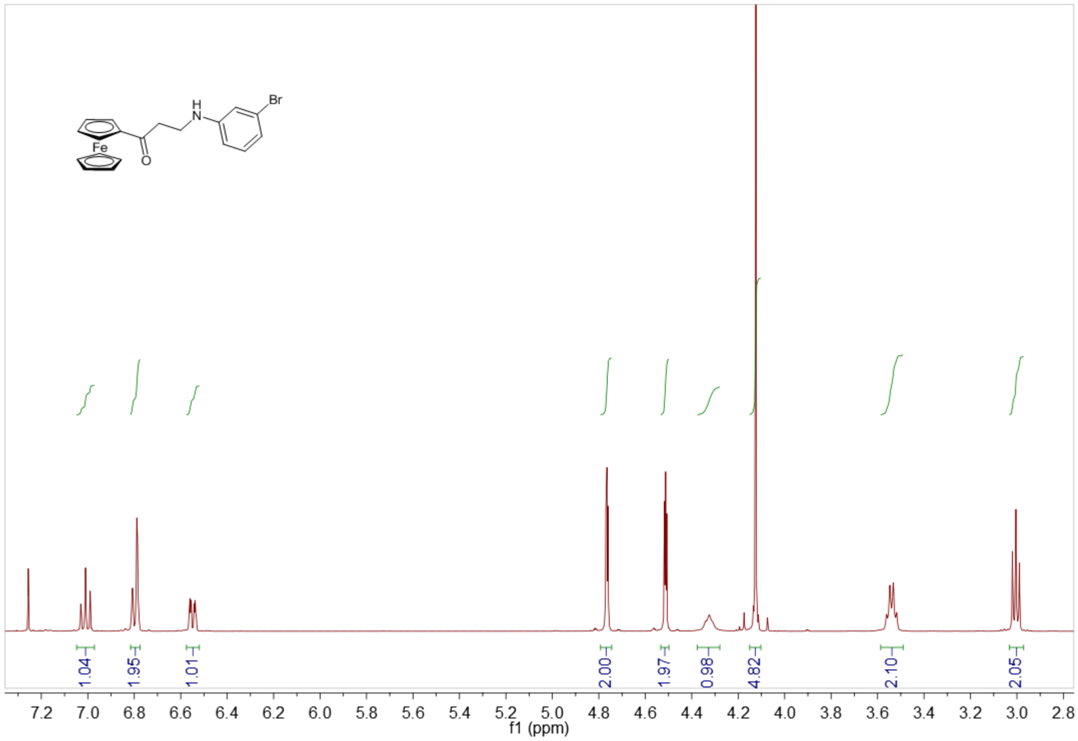
^{1}H and ^{13}C NMR spectra



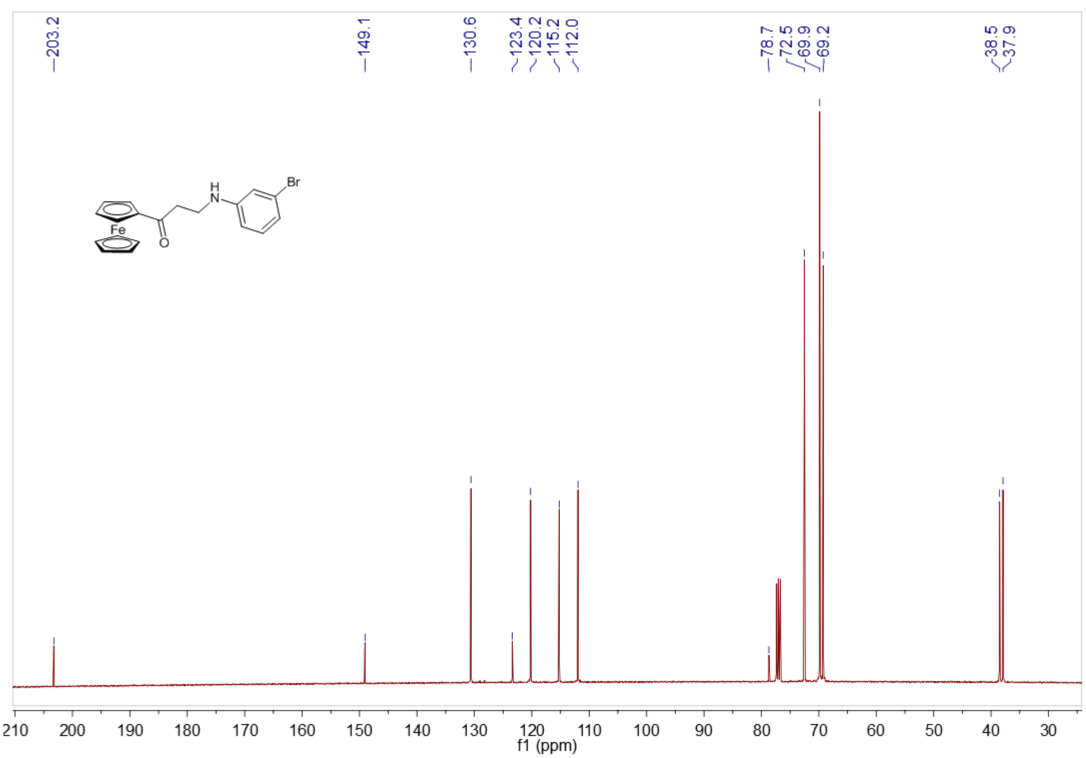
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8l**



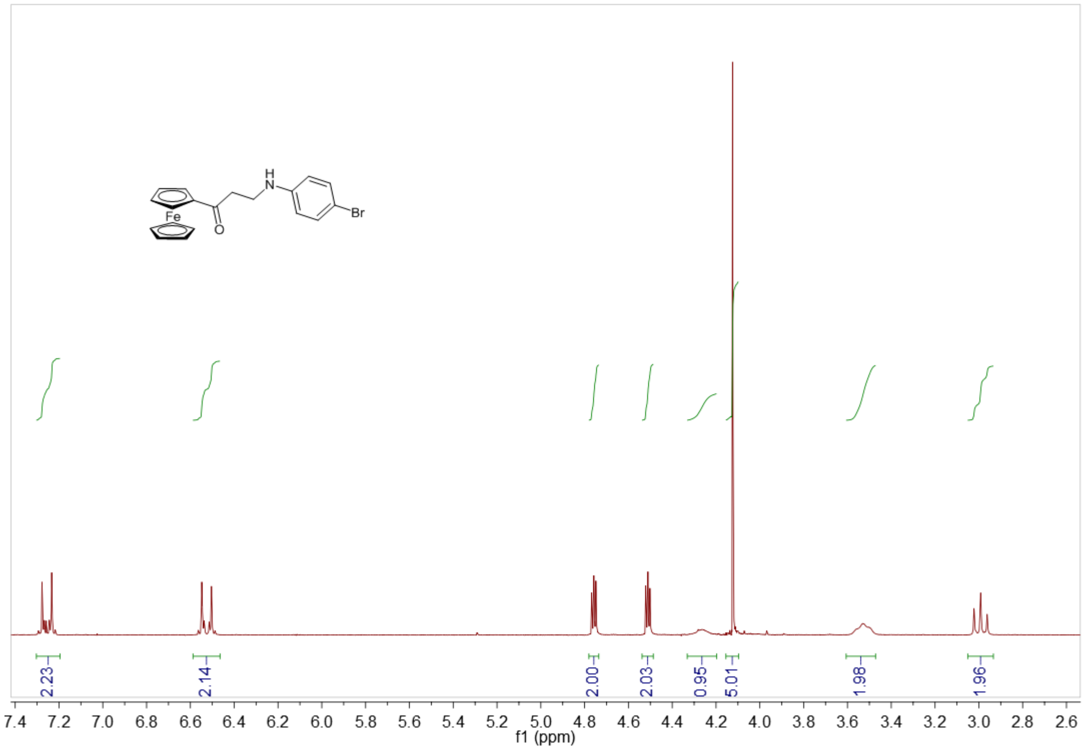
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **8l**



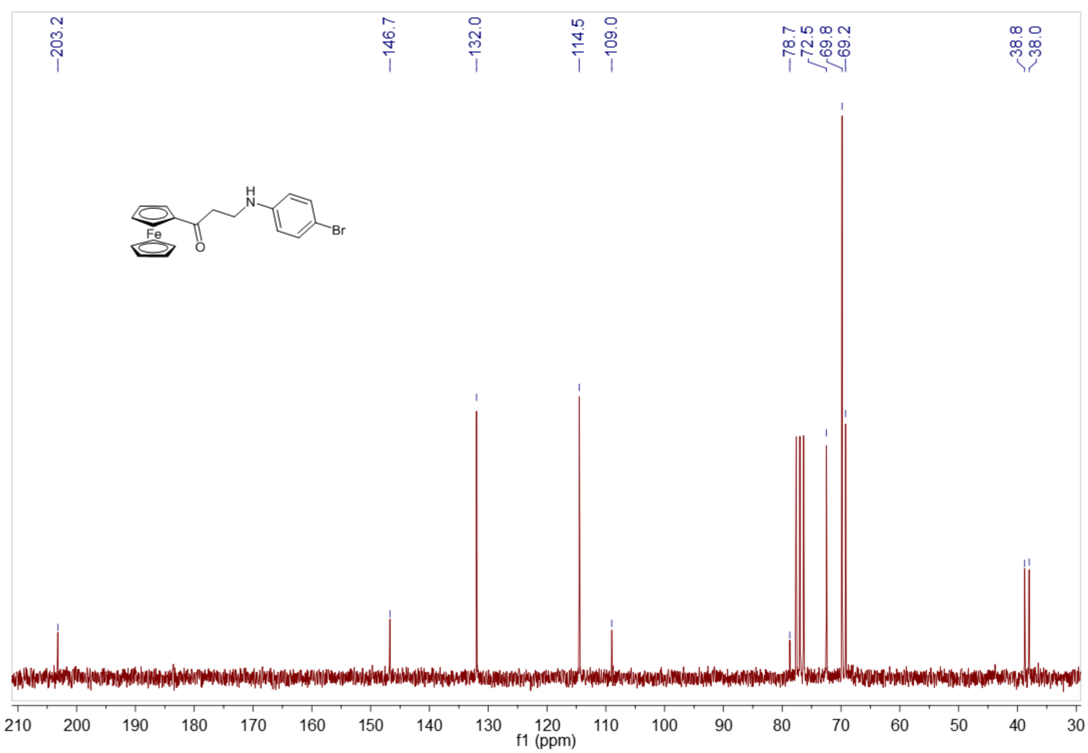
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8m**



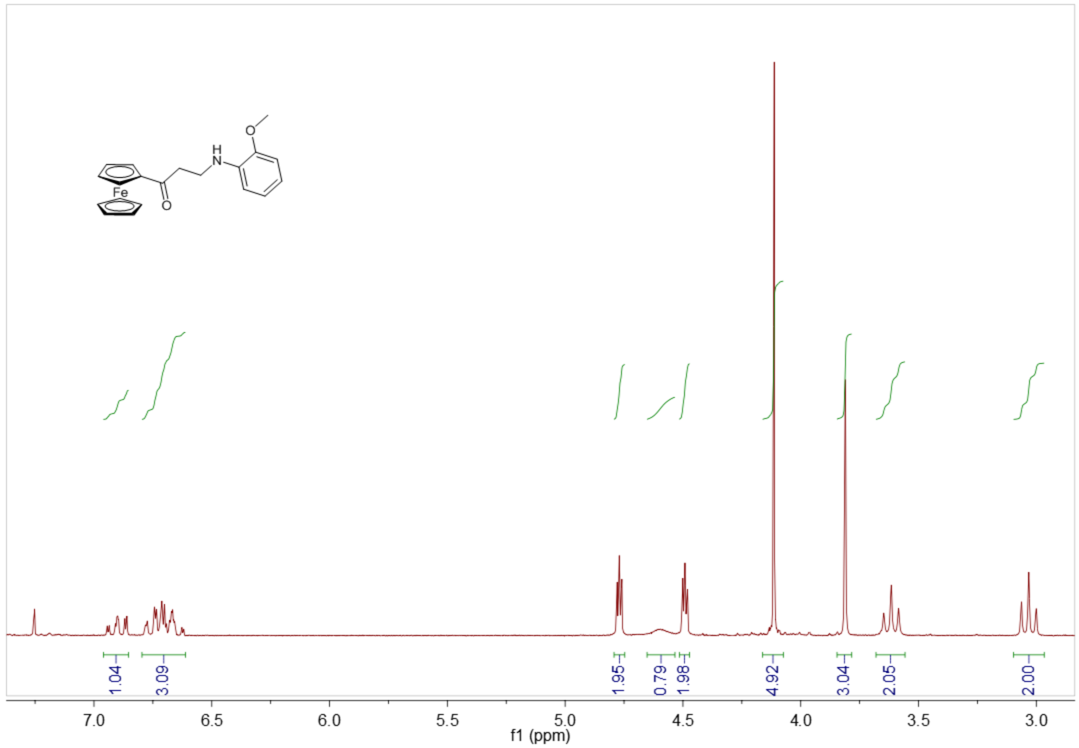
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **8m**



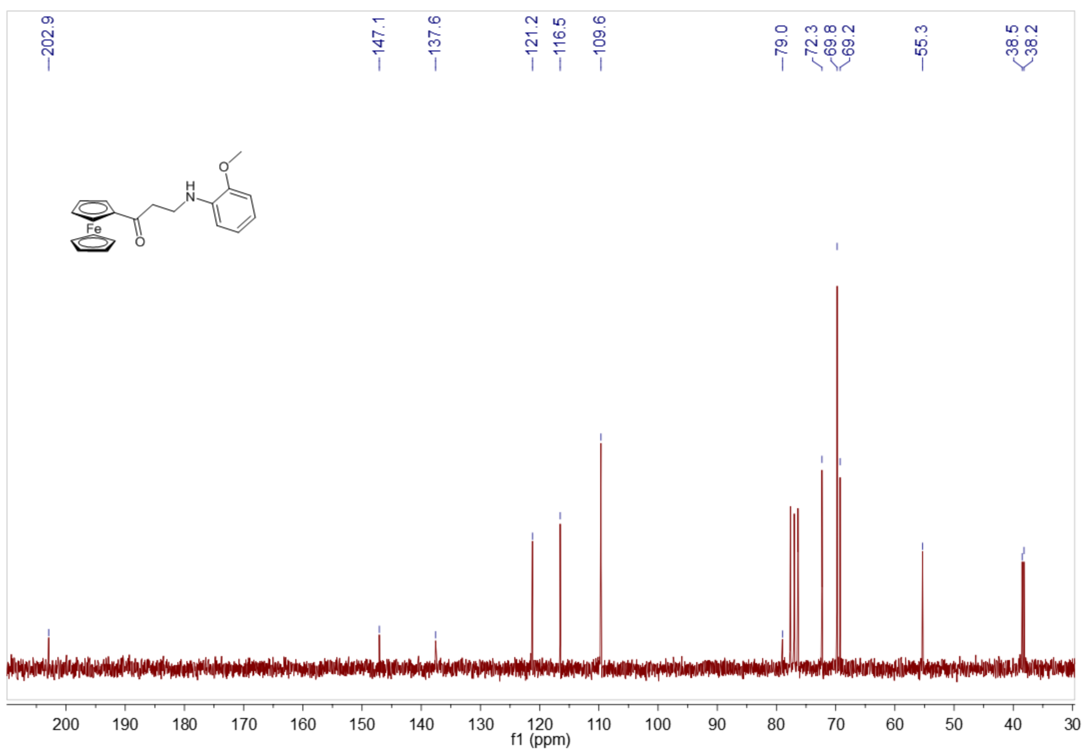
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **8n**



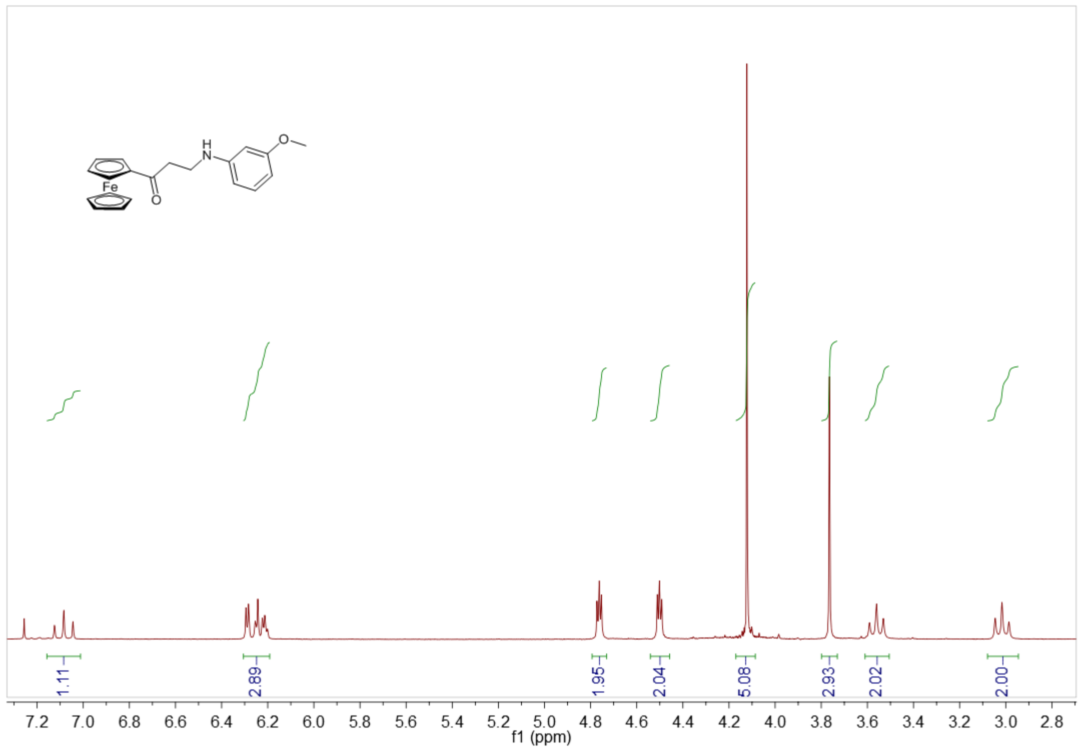
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **8n**



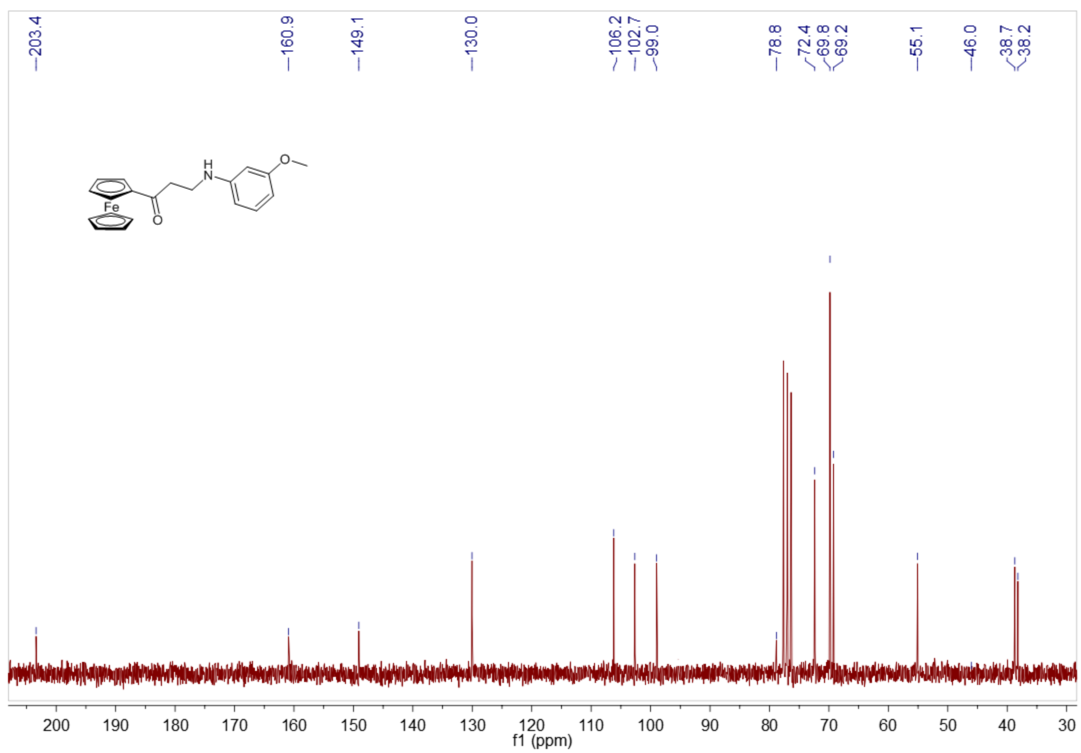
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **8o**



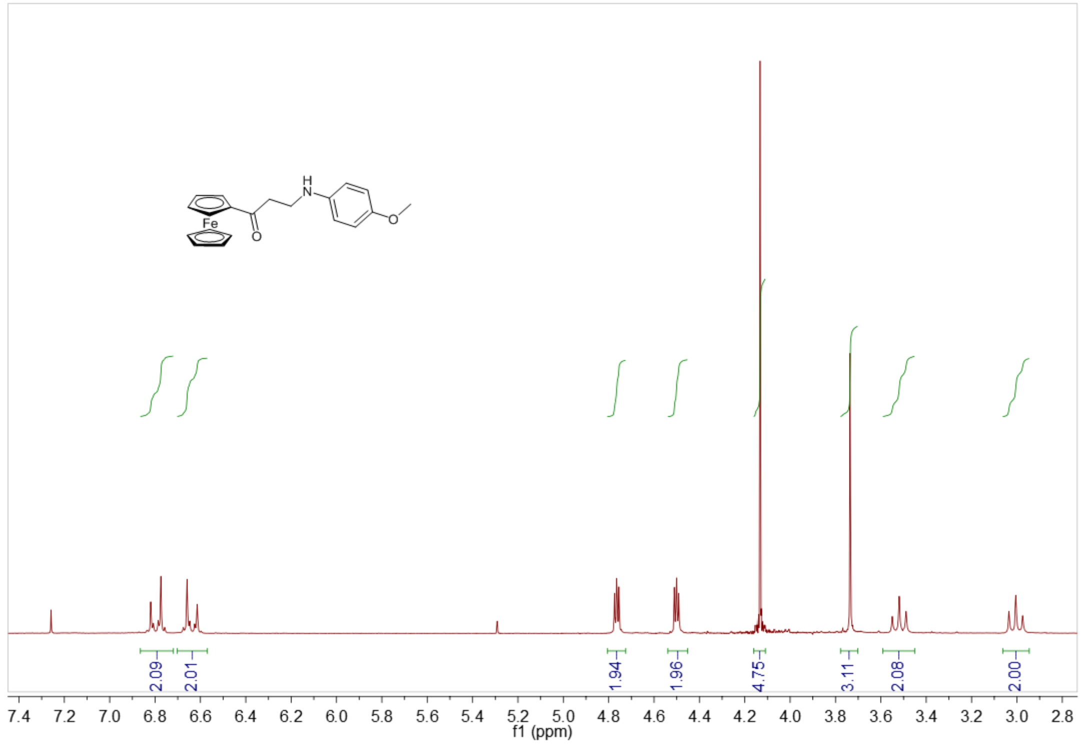
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **8o**



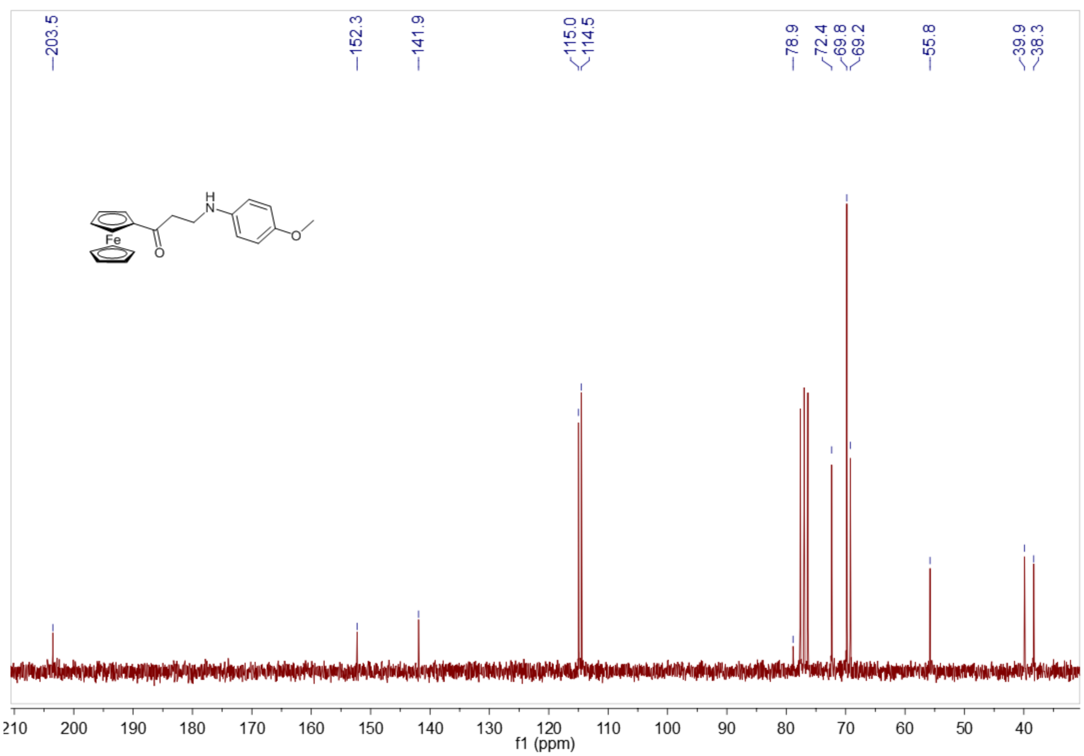
[1]H NMR (200 MHz, $CDCl_3$) spectrum of **8p**



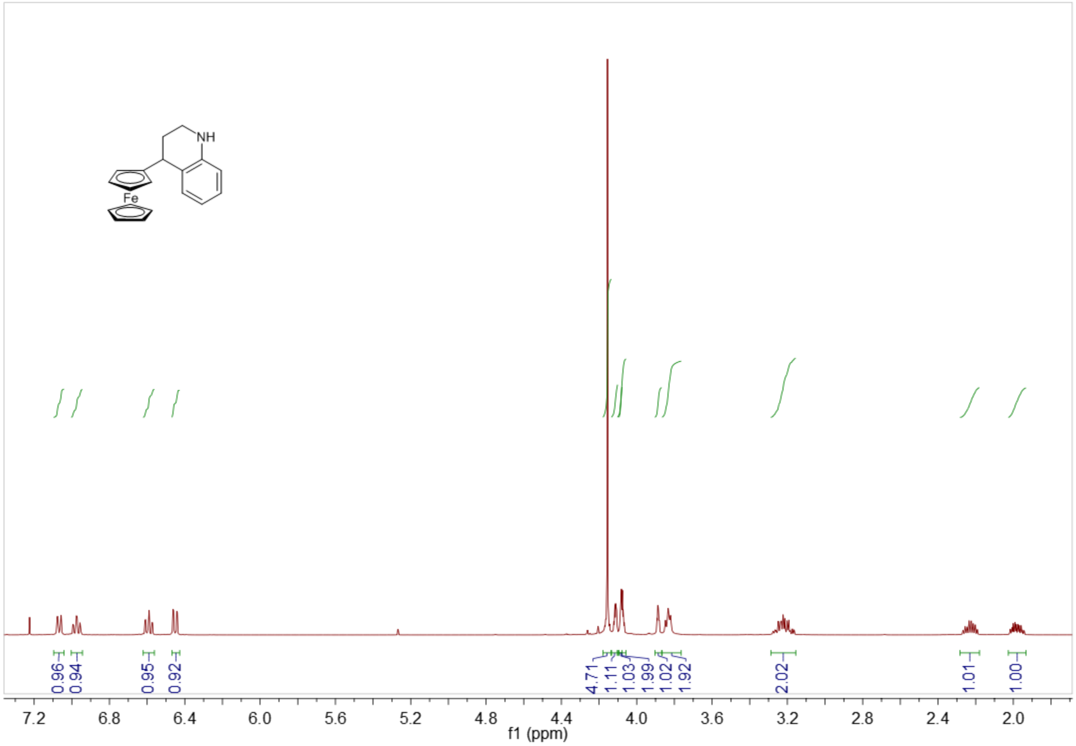
[13]C NMR (50 MHz, $CDCl_3$) spectrum of **8p**



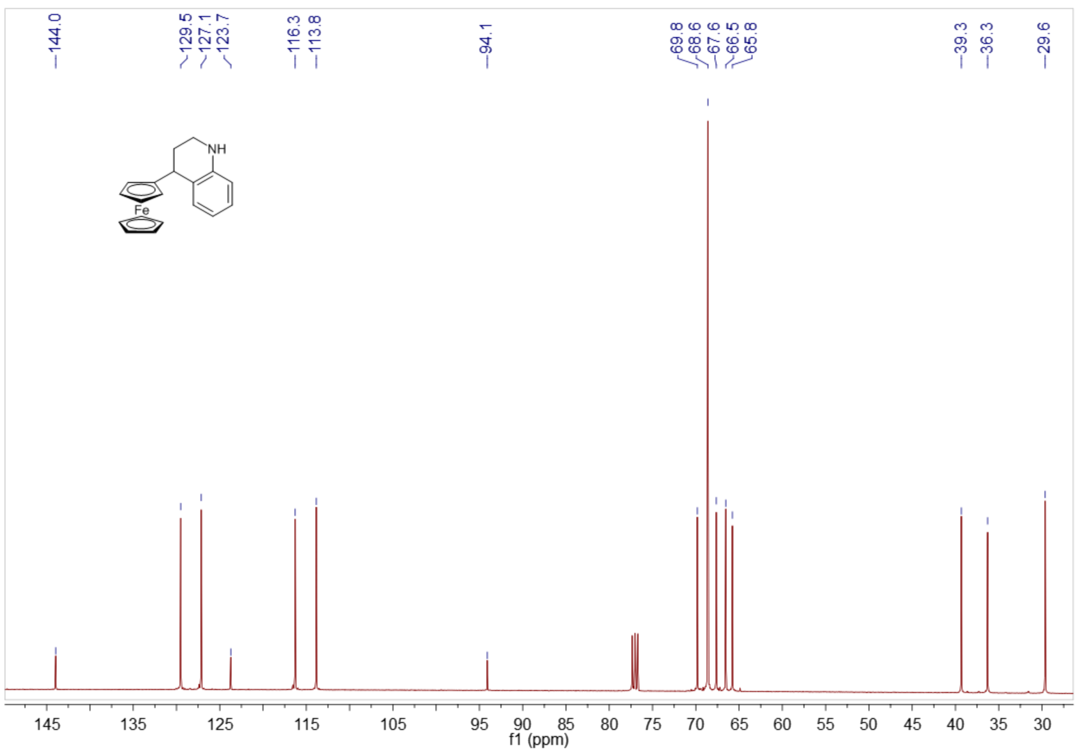
[1]H NMR (200 MHz, $CDCl_3$) spectrum of **8q**



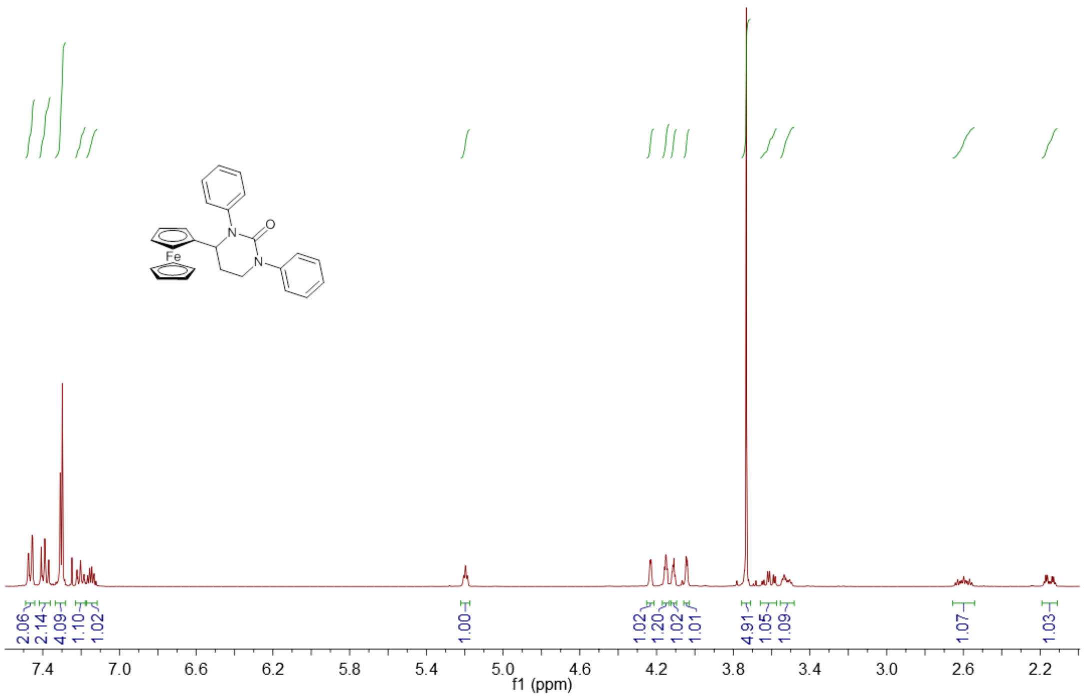
[13]C NMR (50 MHz, $CDCl_3$) spectrum of **8q**



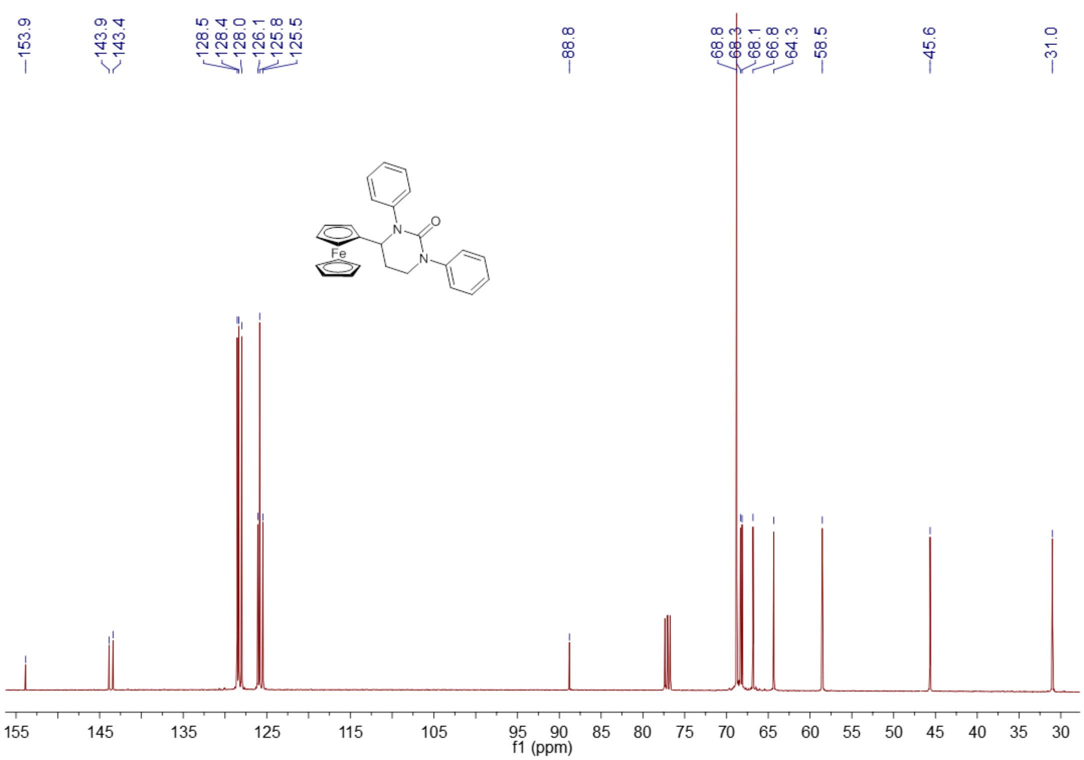
[1]H NMR (400 MHz, $CDCl_3$) spectrum of **10**



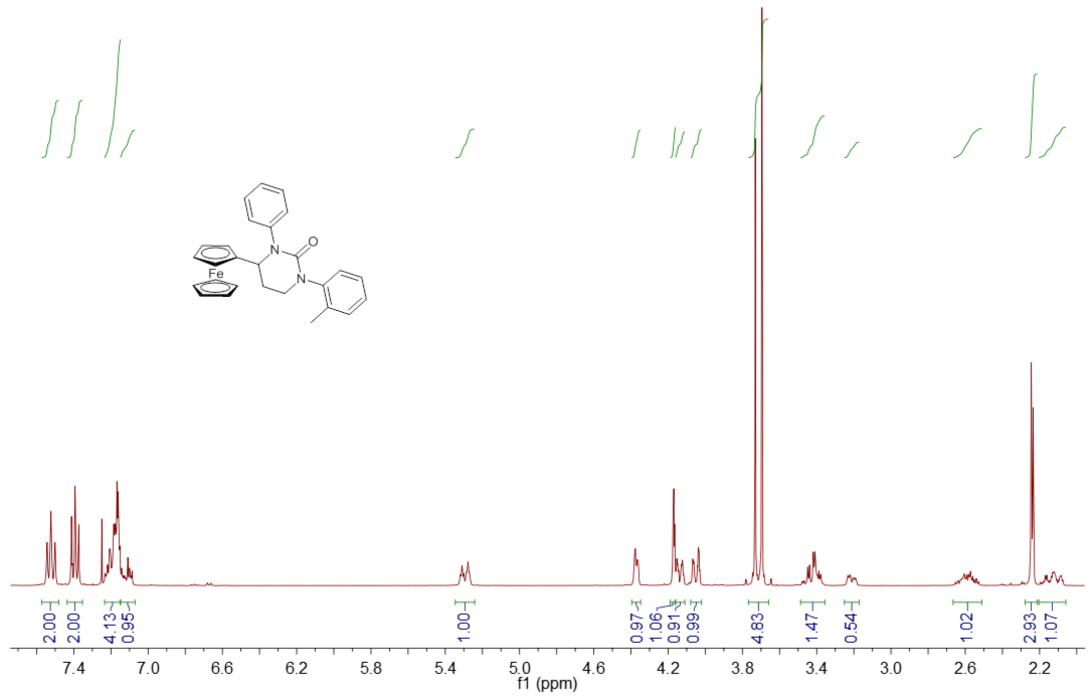
[13]C NMR (101 MHz, $CDCl_3$) spectrum of **10**



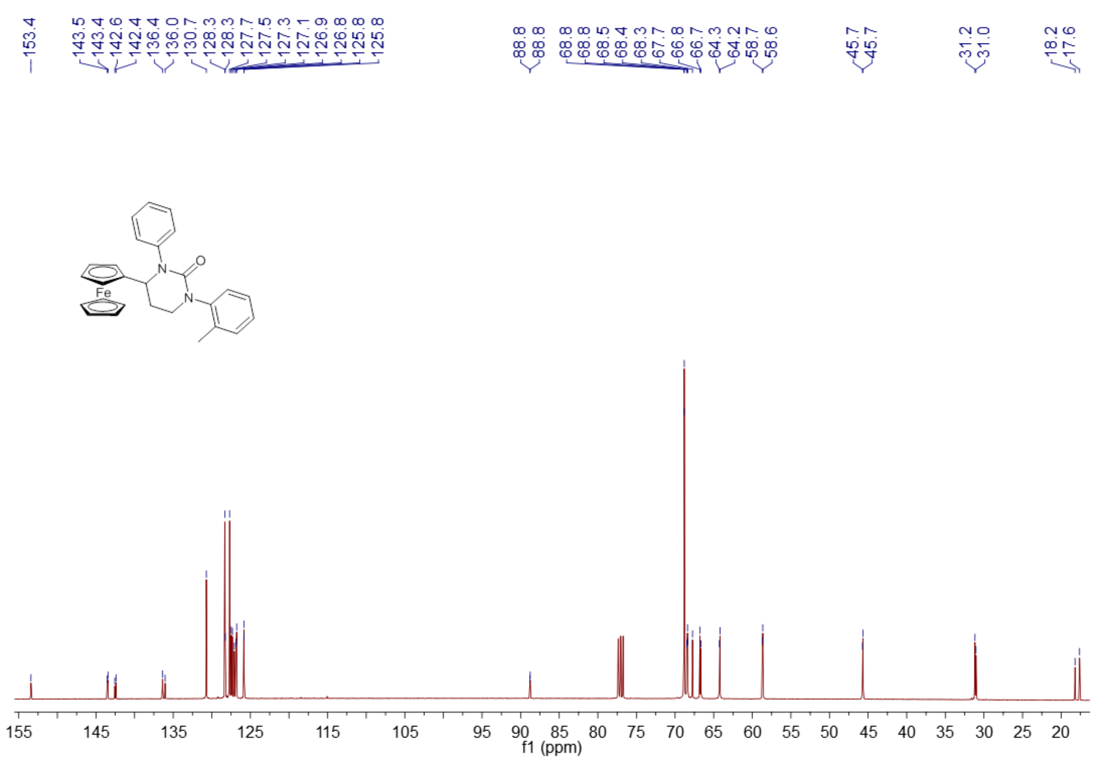
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12a**



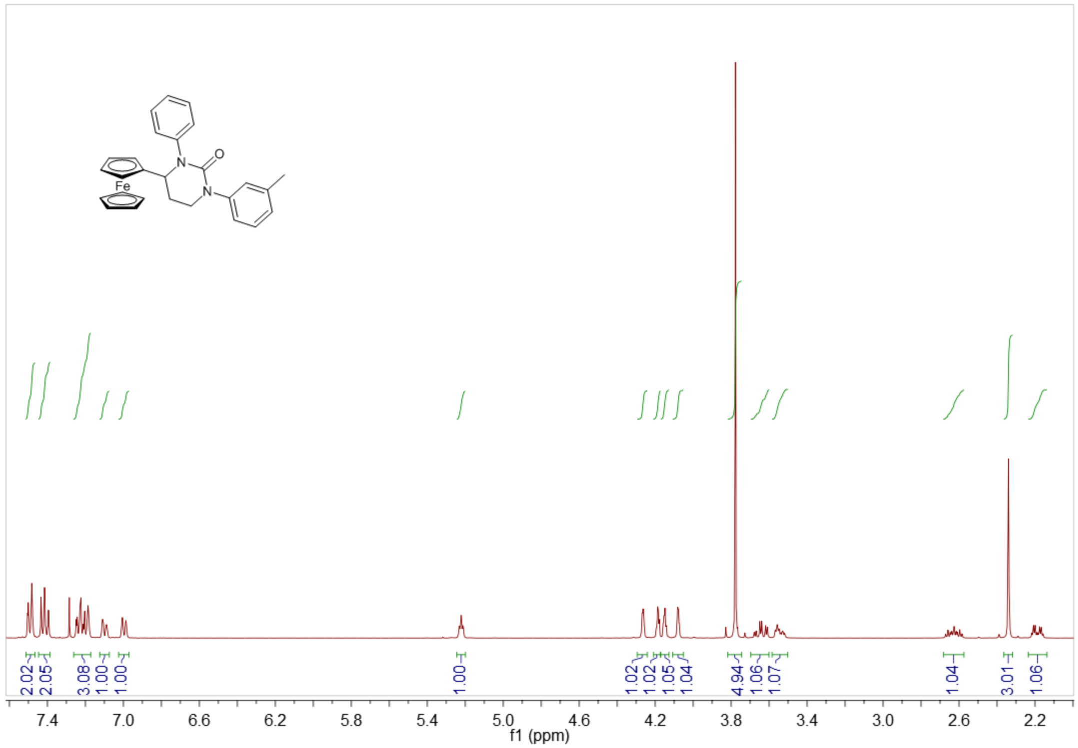
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12a**



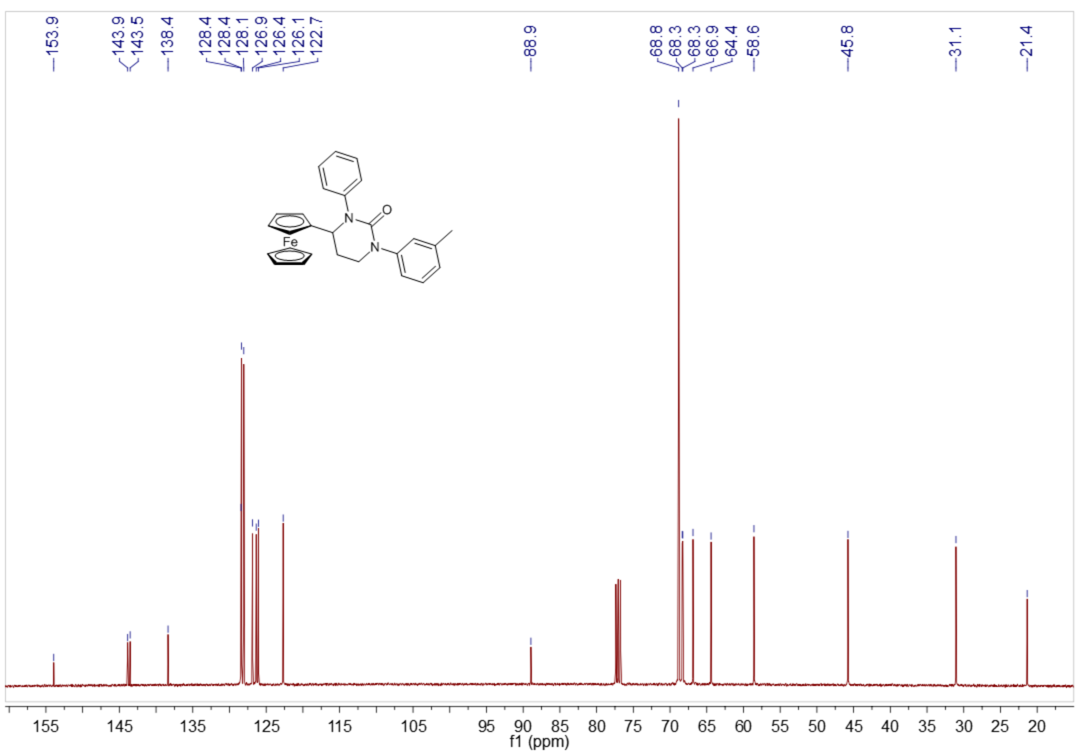
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12b**



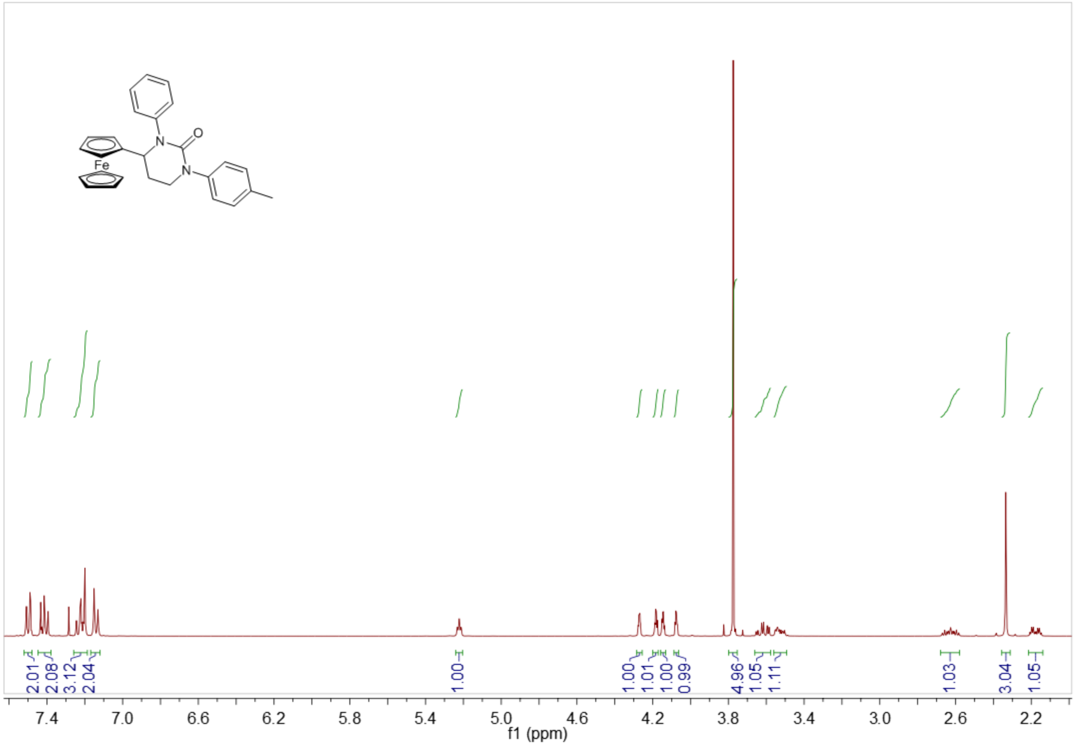
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12b**



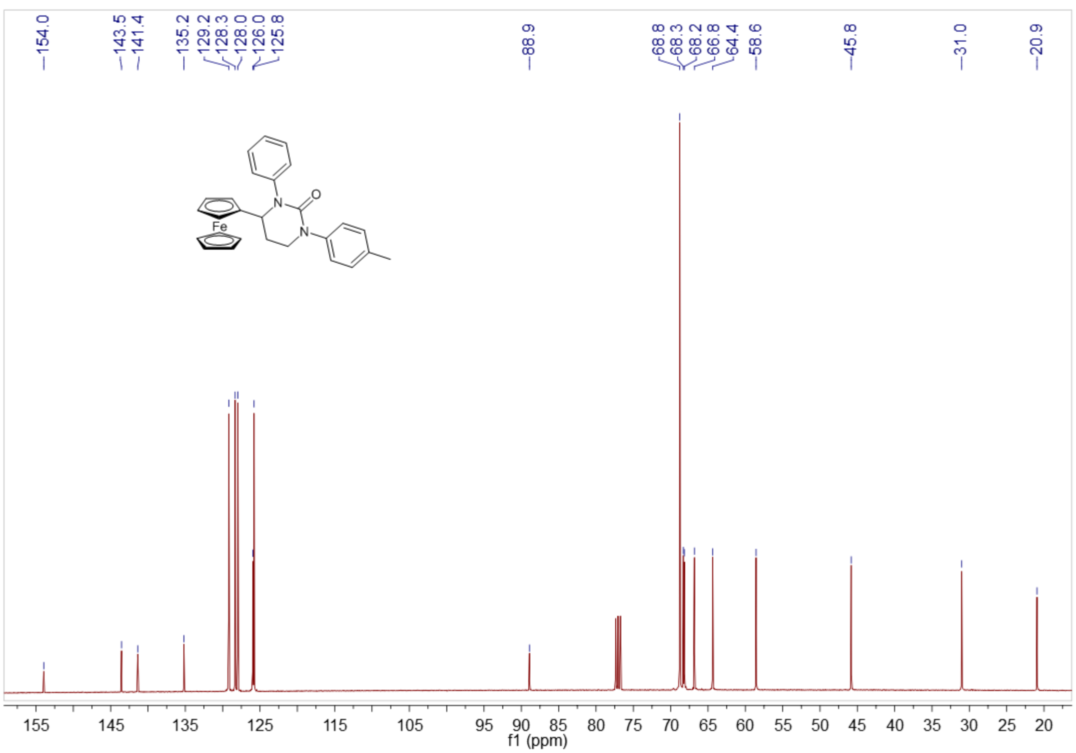
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12c**



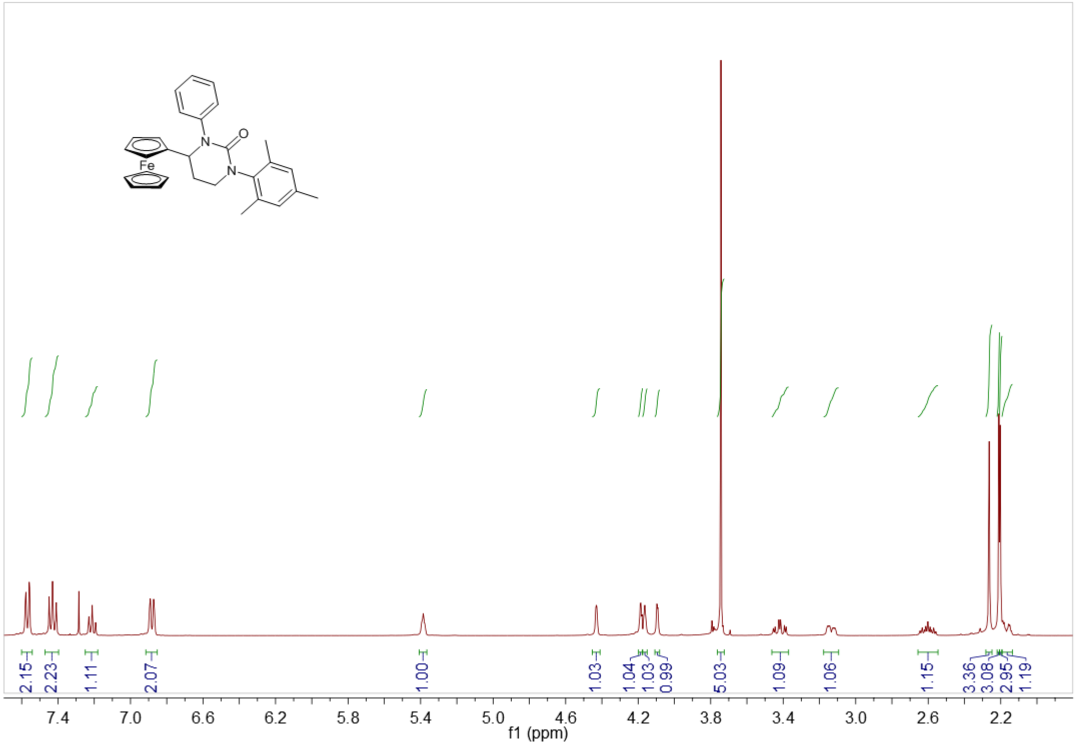
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12c**



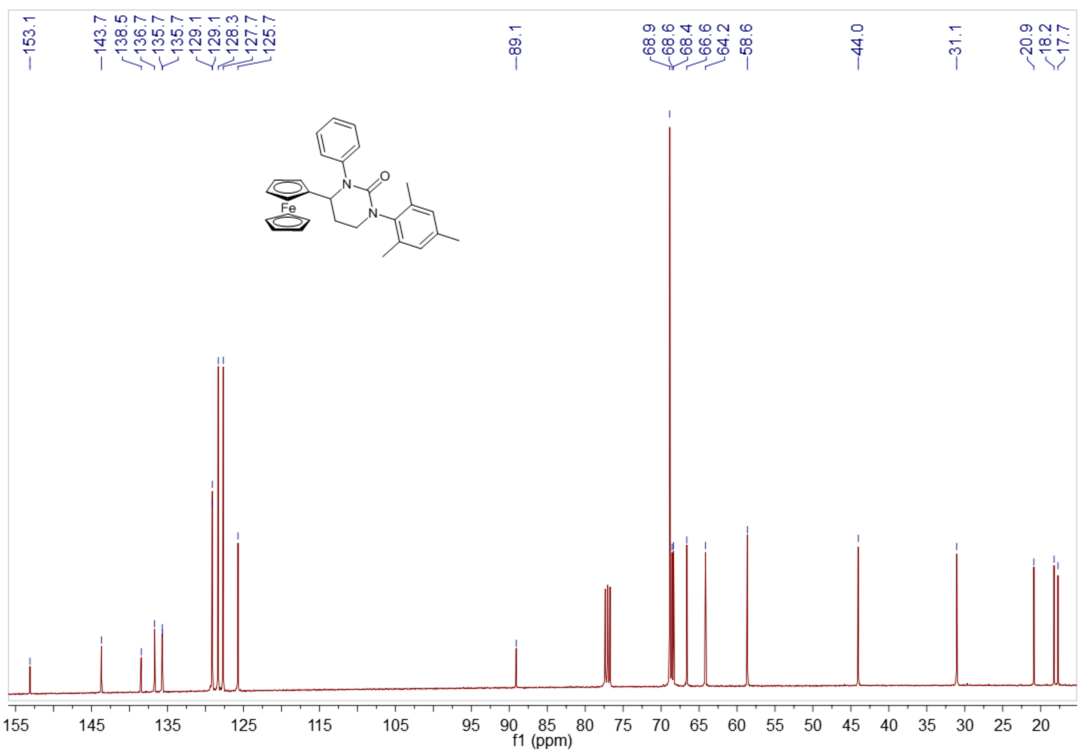
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12d**



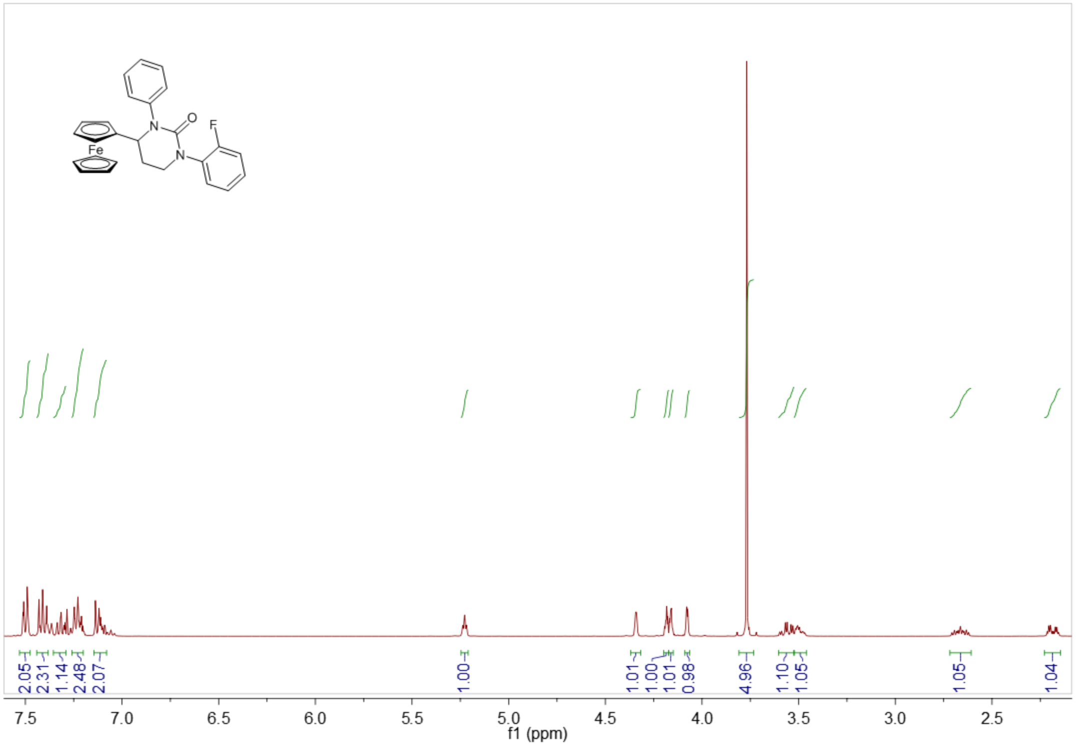
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12d**



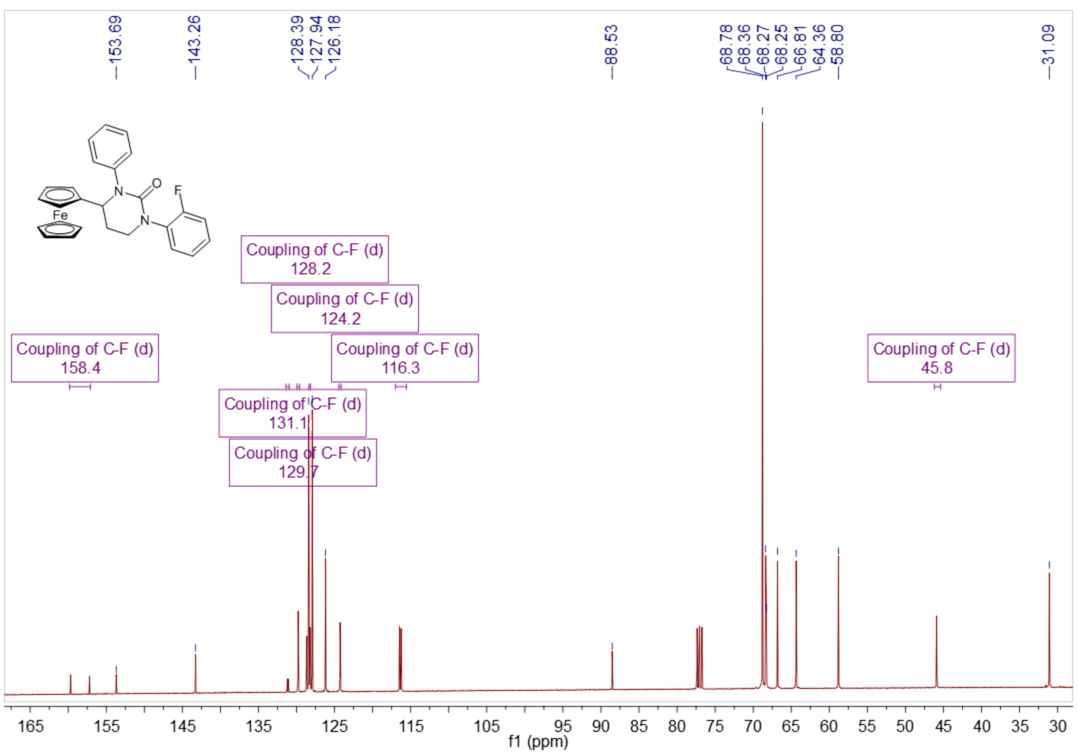
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12e**



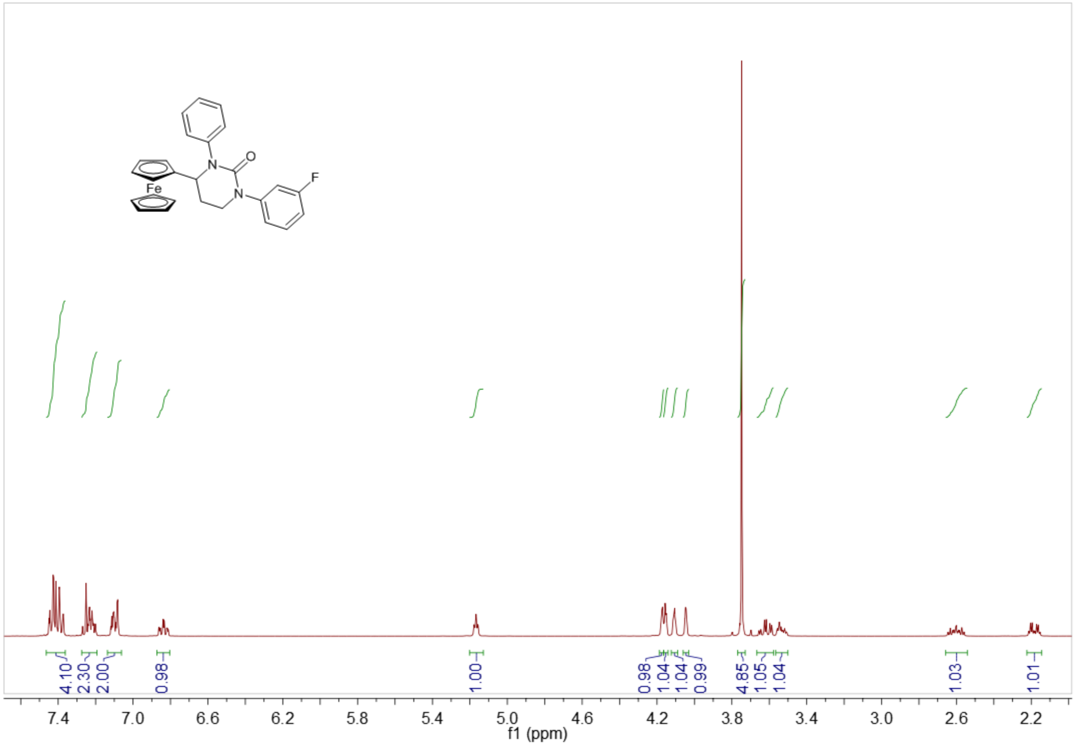
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12e**



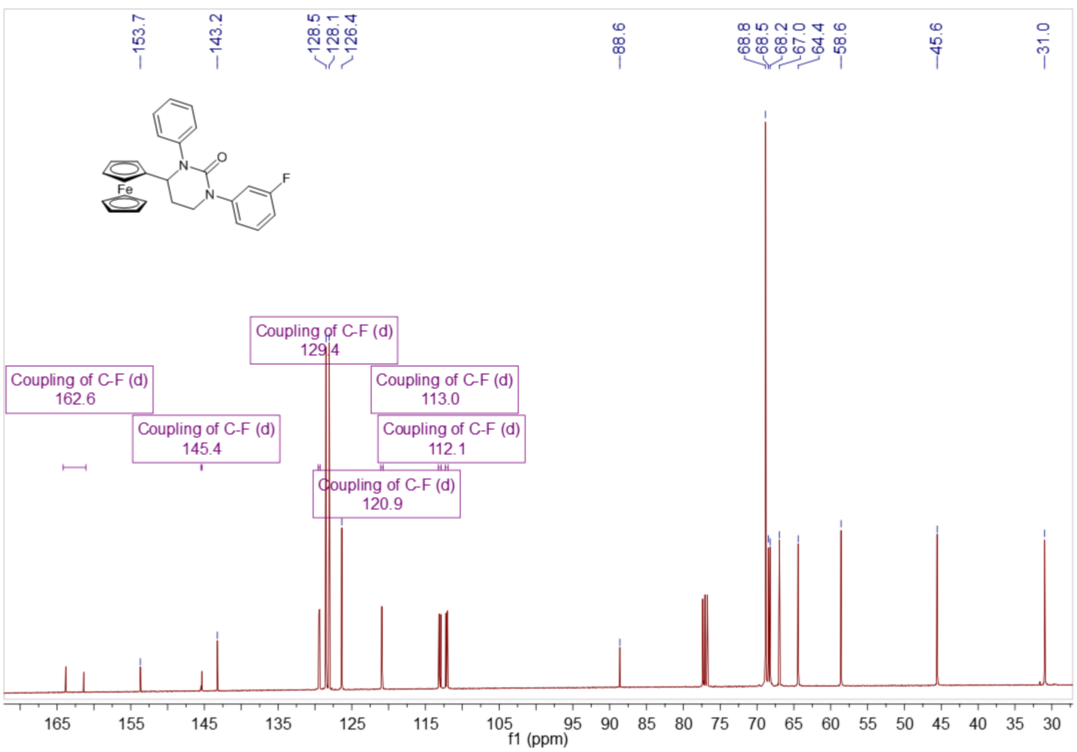
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12f**



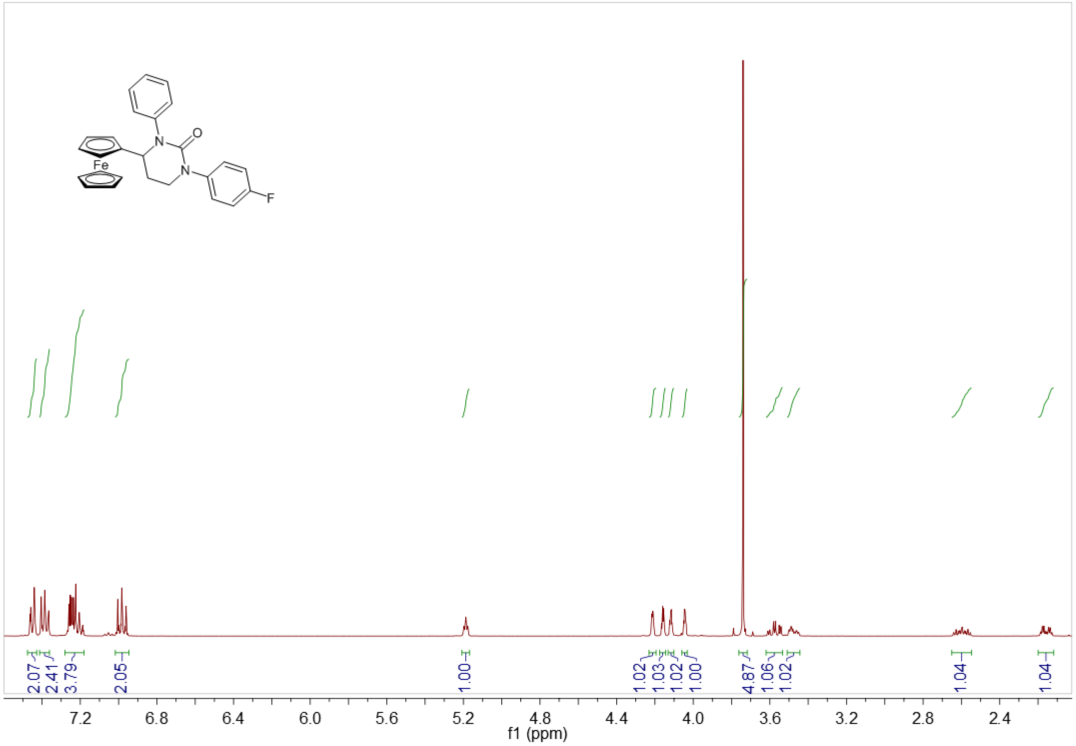
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12f**



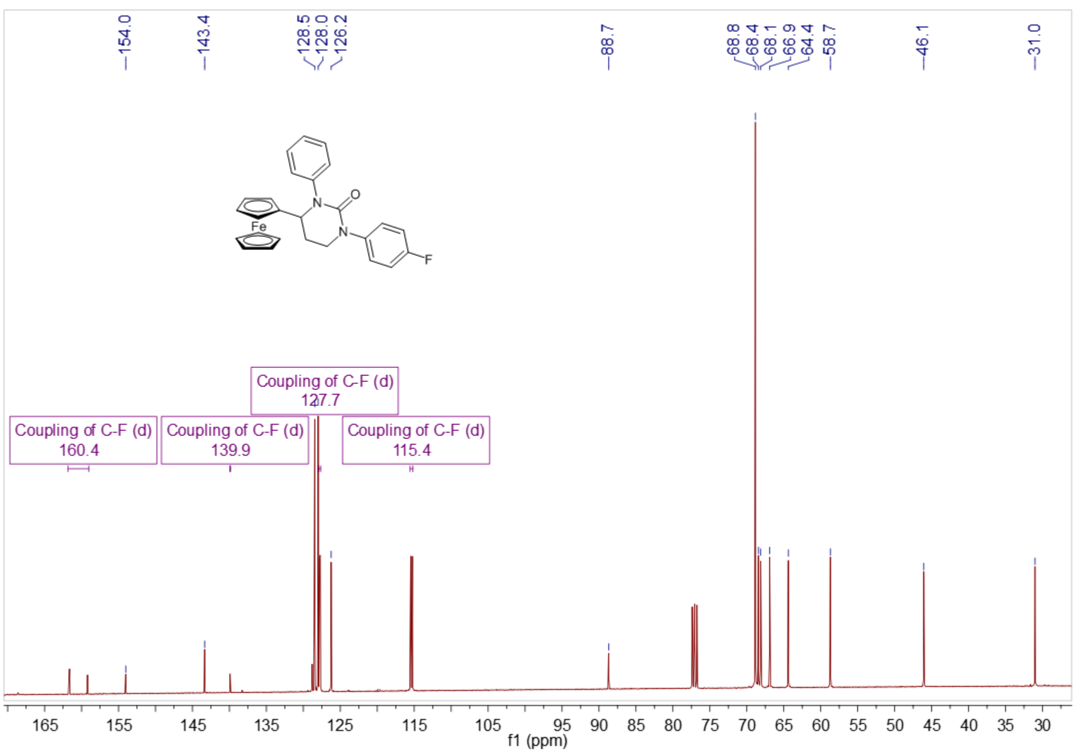
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12g**



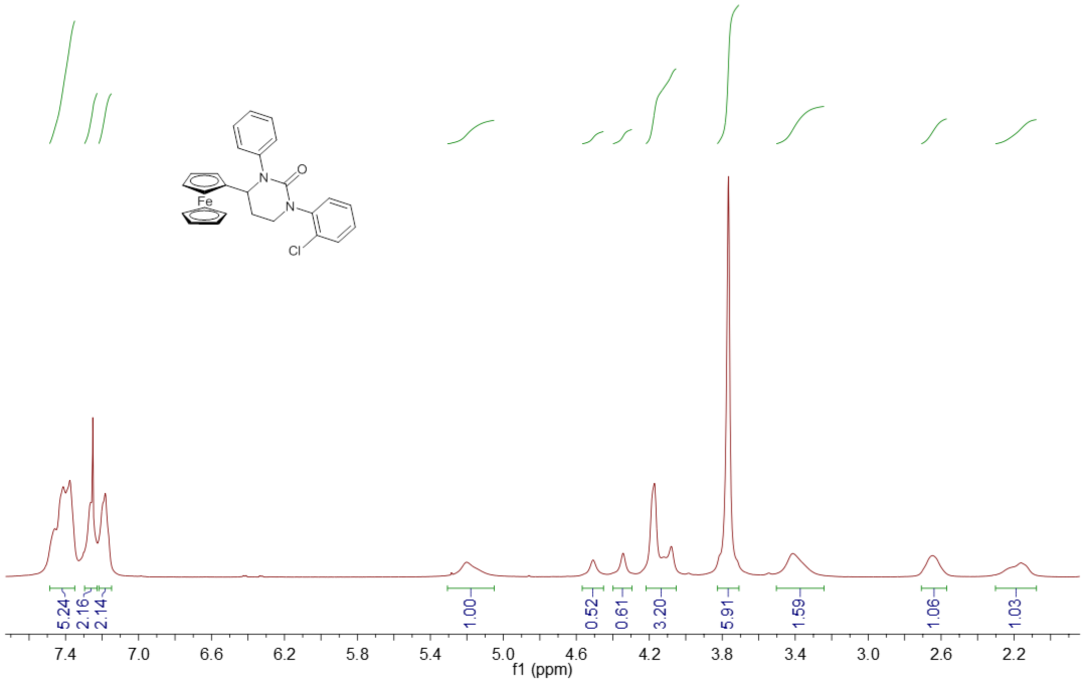
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12g**



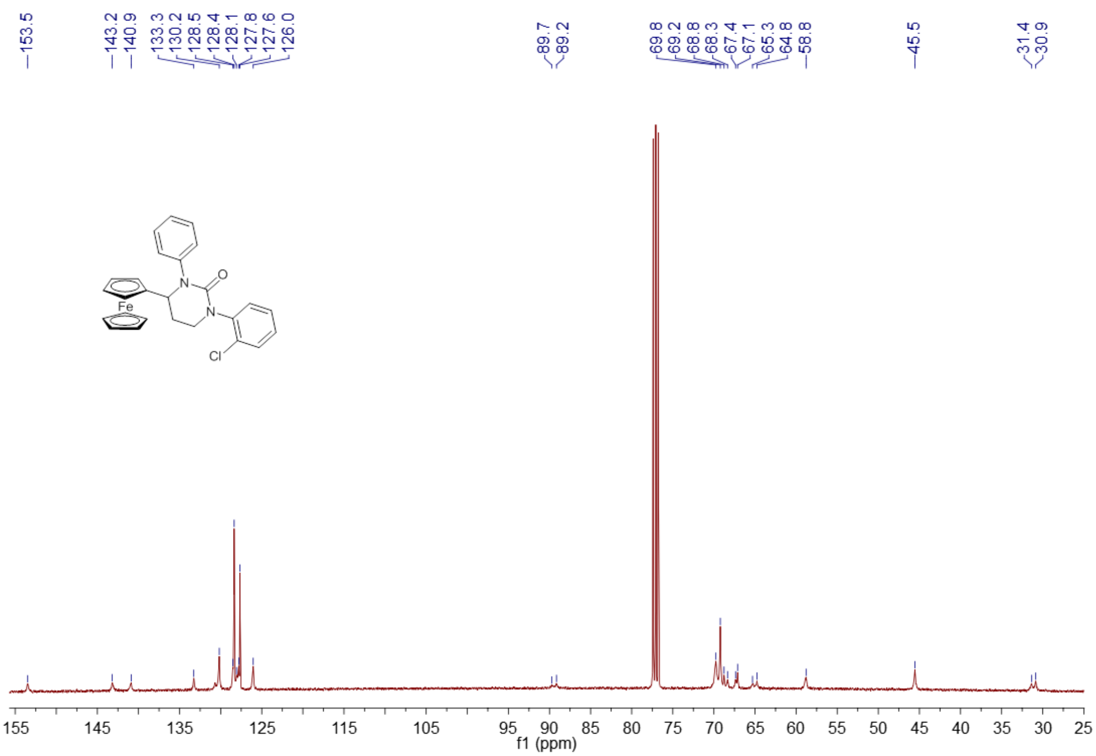
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12h**



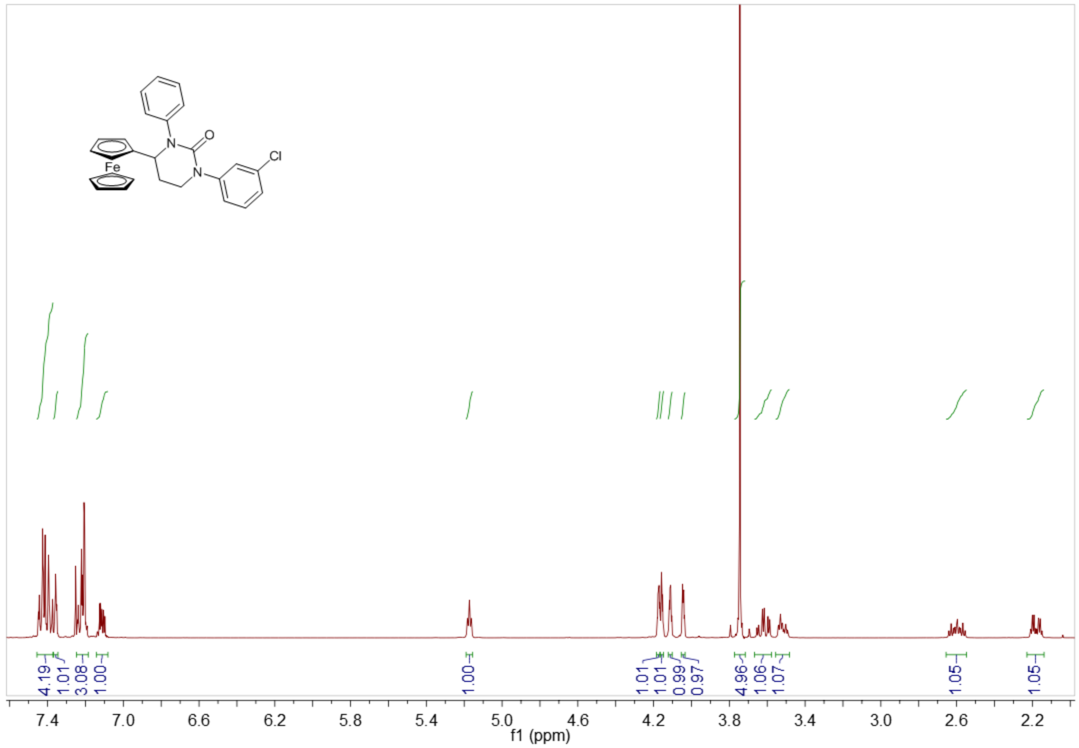
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12h**



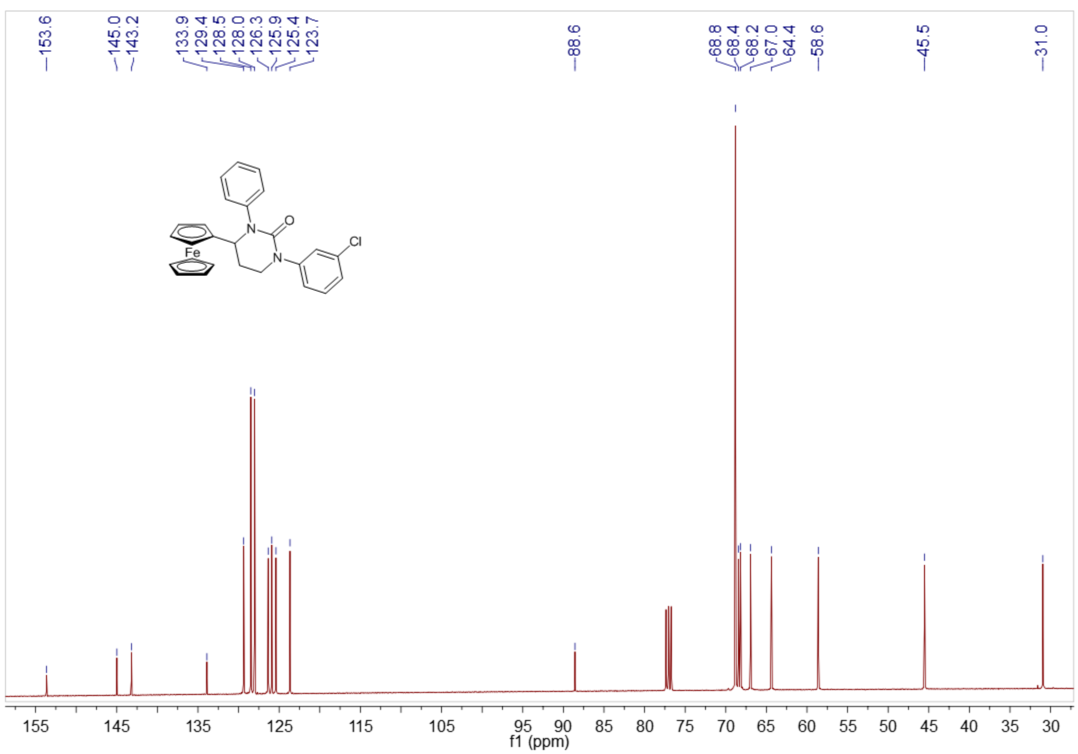
[1]H NMR (400 MHz, $CDCl_3$) spectrum of **12i**



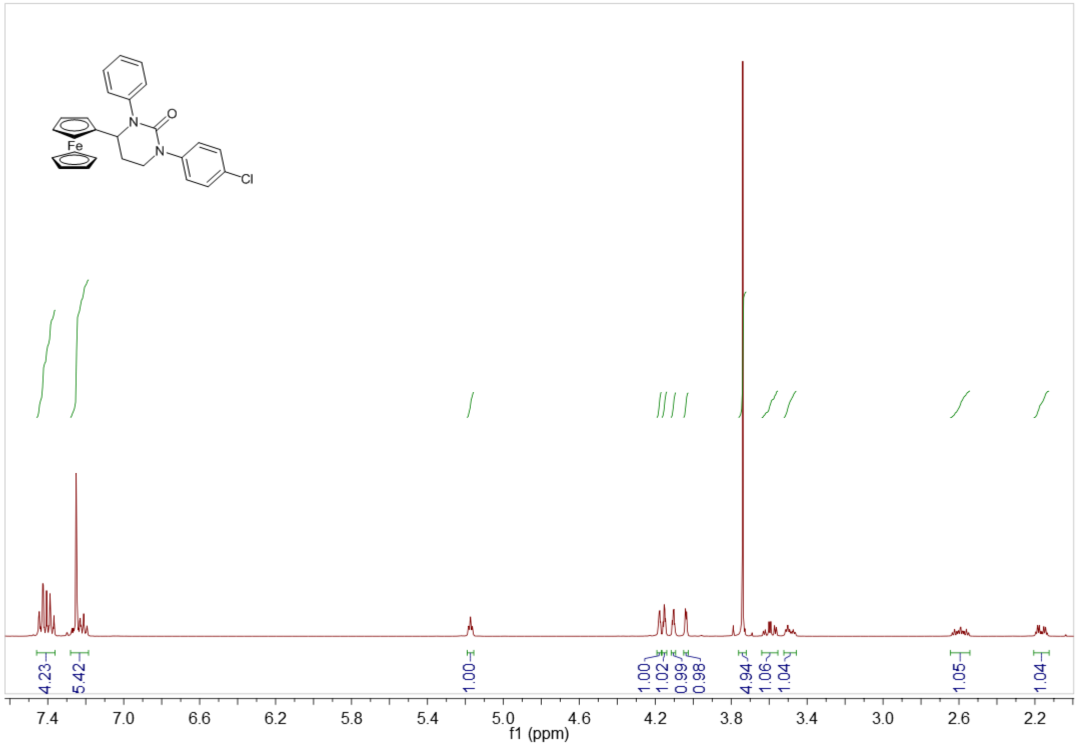
[13]C NMR (101 MHz, $CDCl_3$) spectrum of **12i**



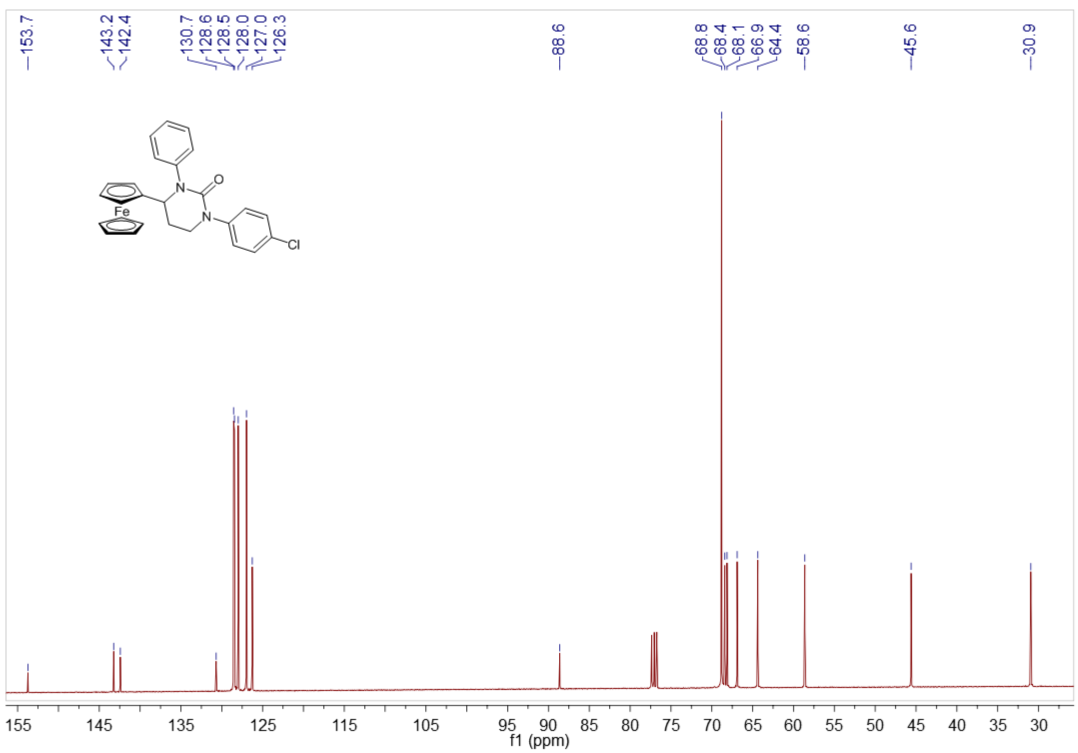
[1]H NMR (400 MHz, $CDCl_3$) spectrum of **12j**



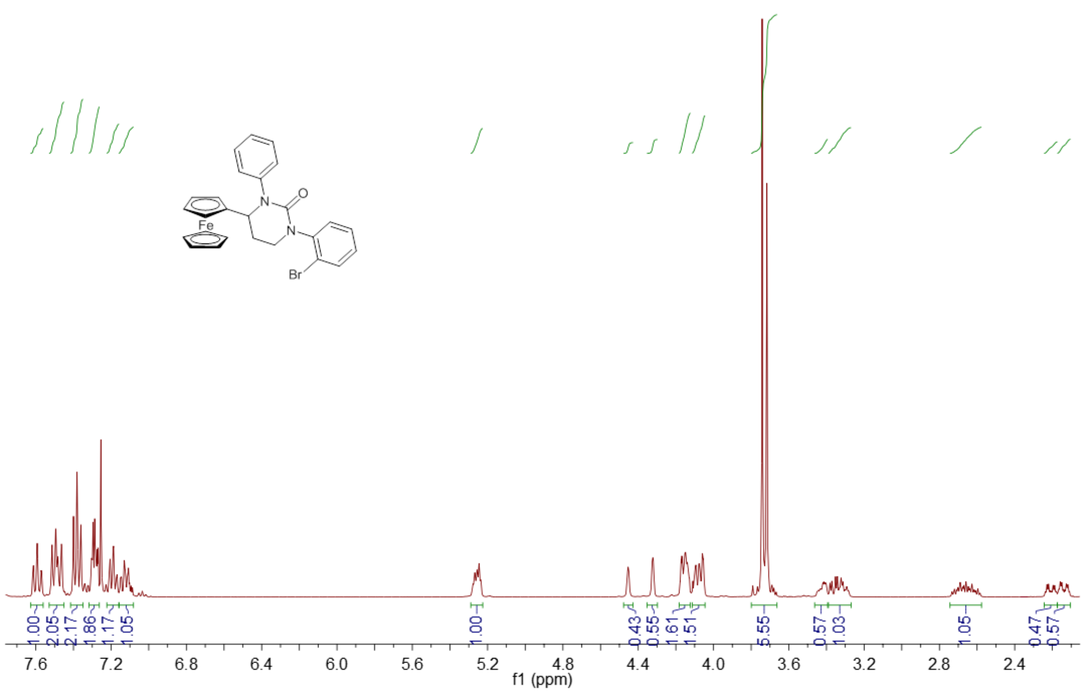
[13]C NMR (101 MHz, $CDCl_3$) spectrum of **12j**



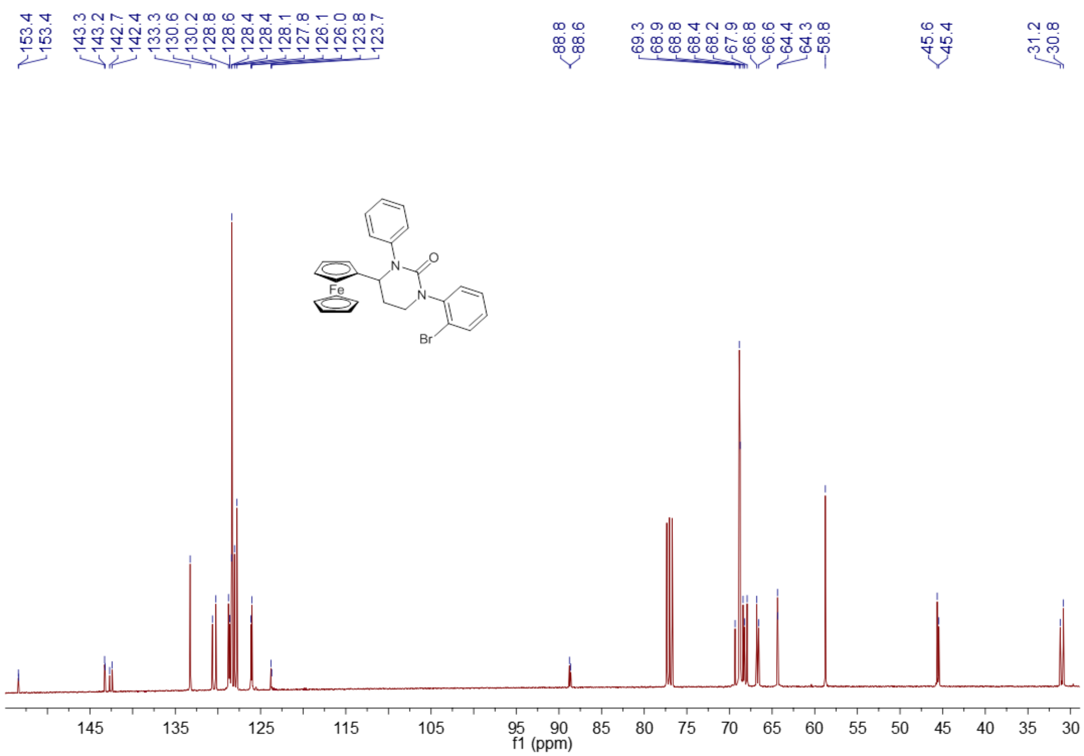
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12k**



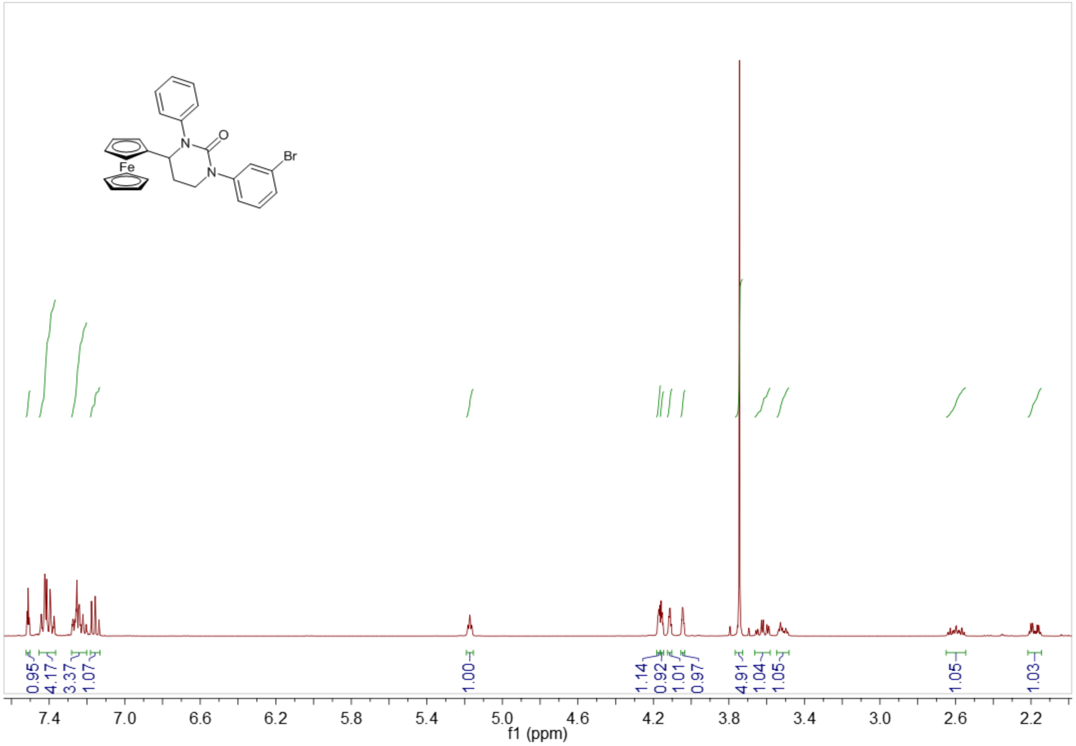
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12k**



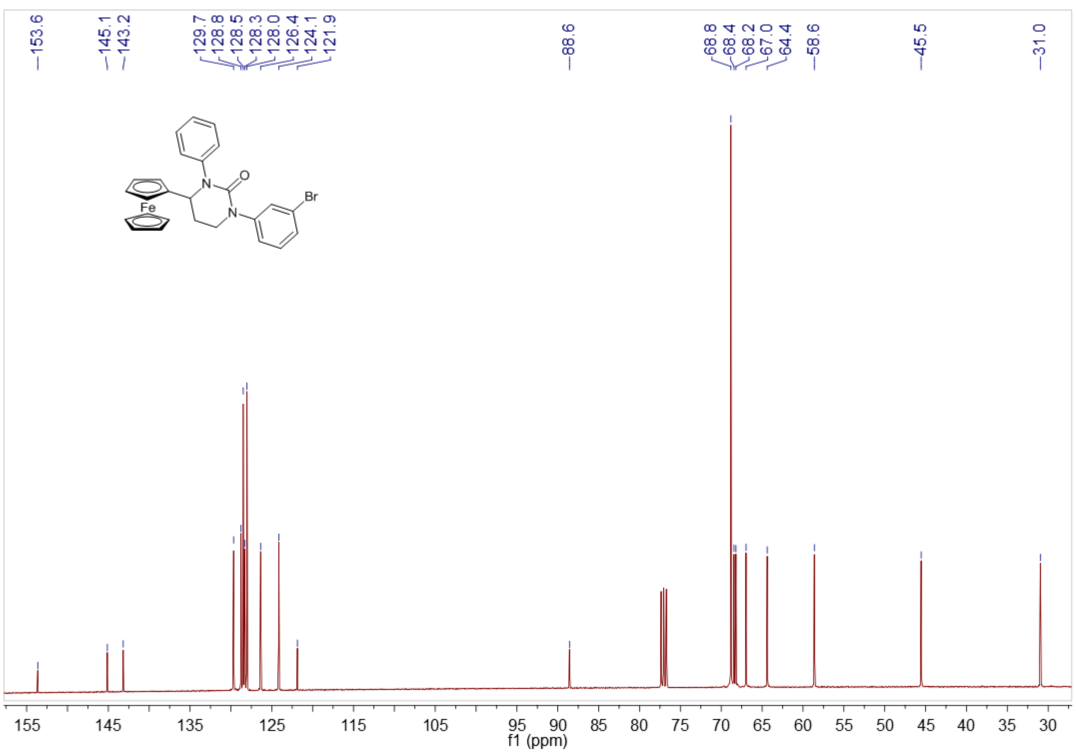
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12l**



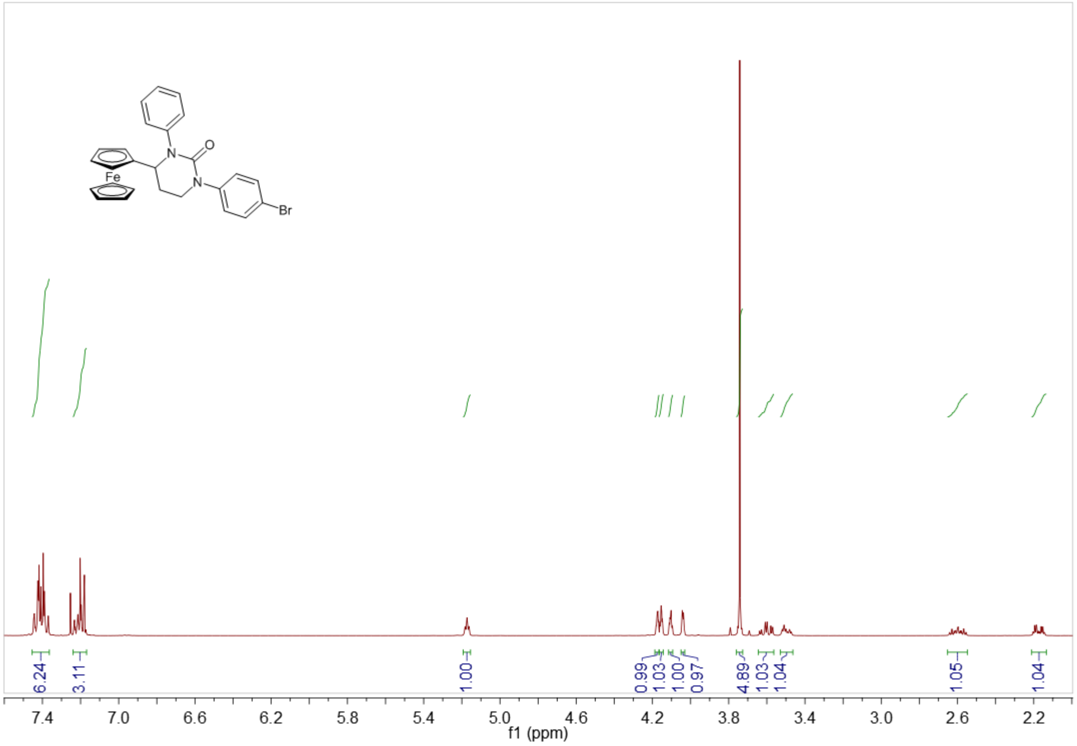
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12l**



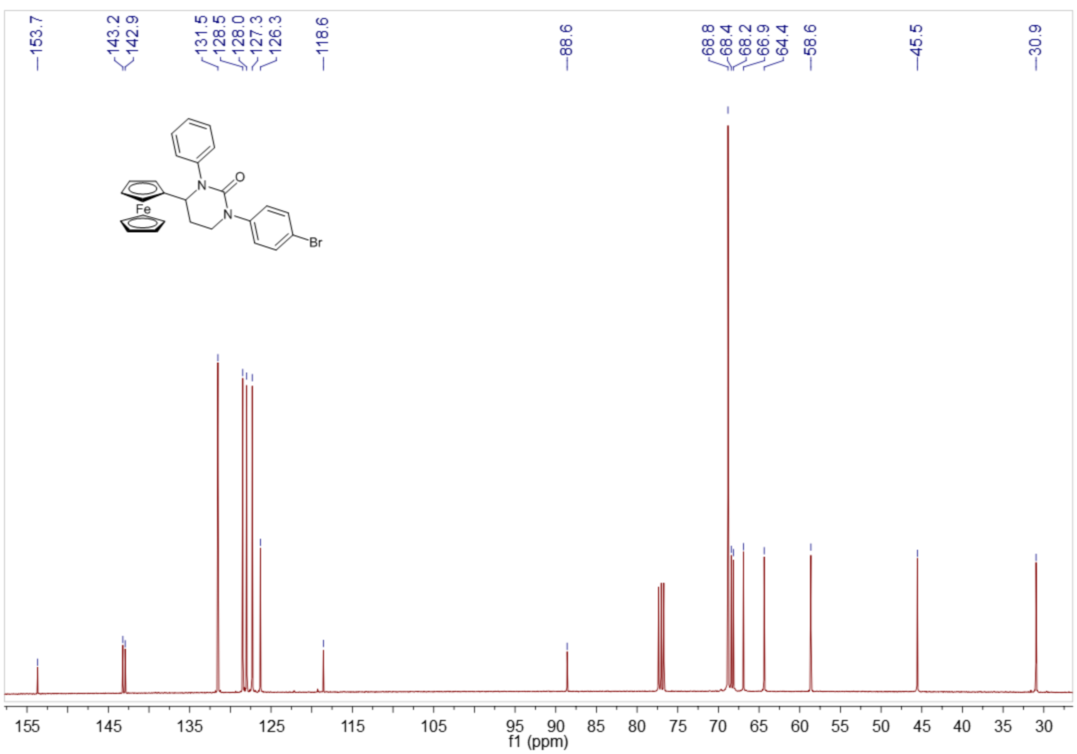
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12m**



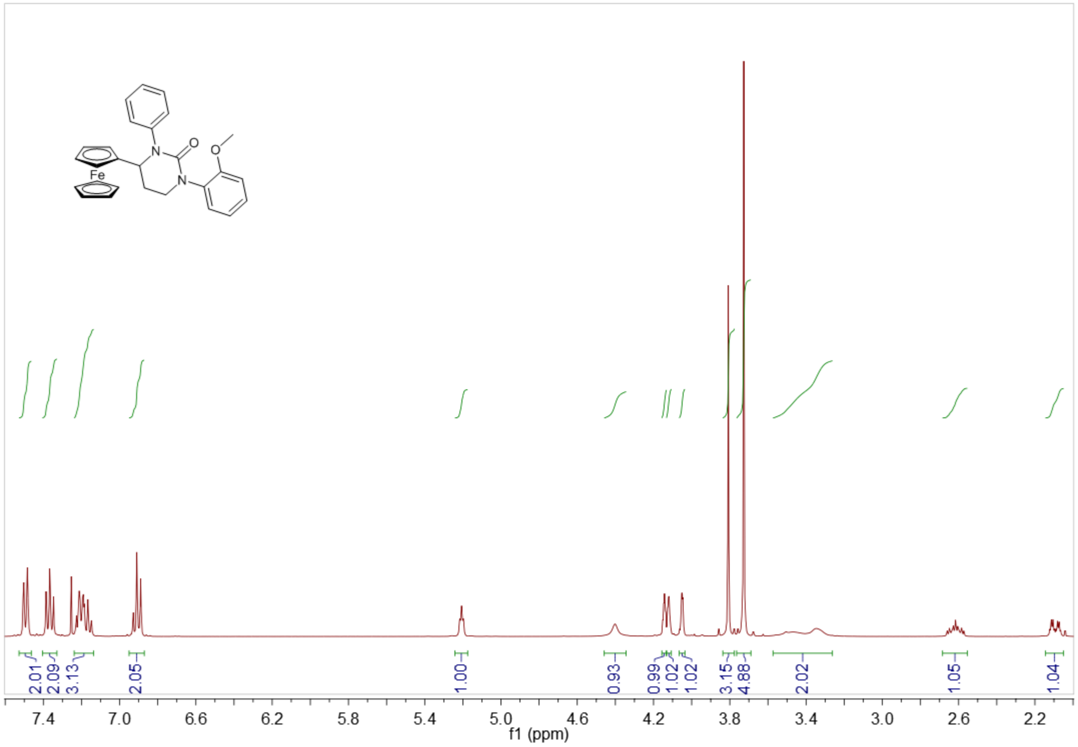
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12m**



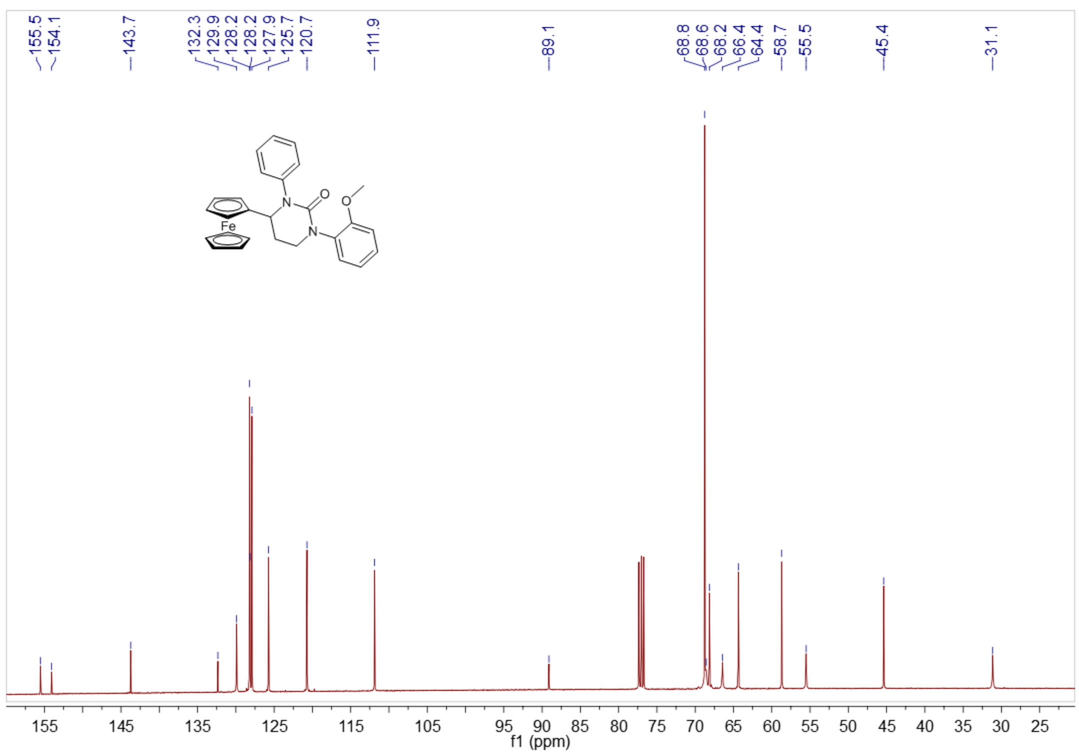
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12n**



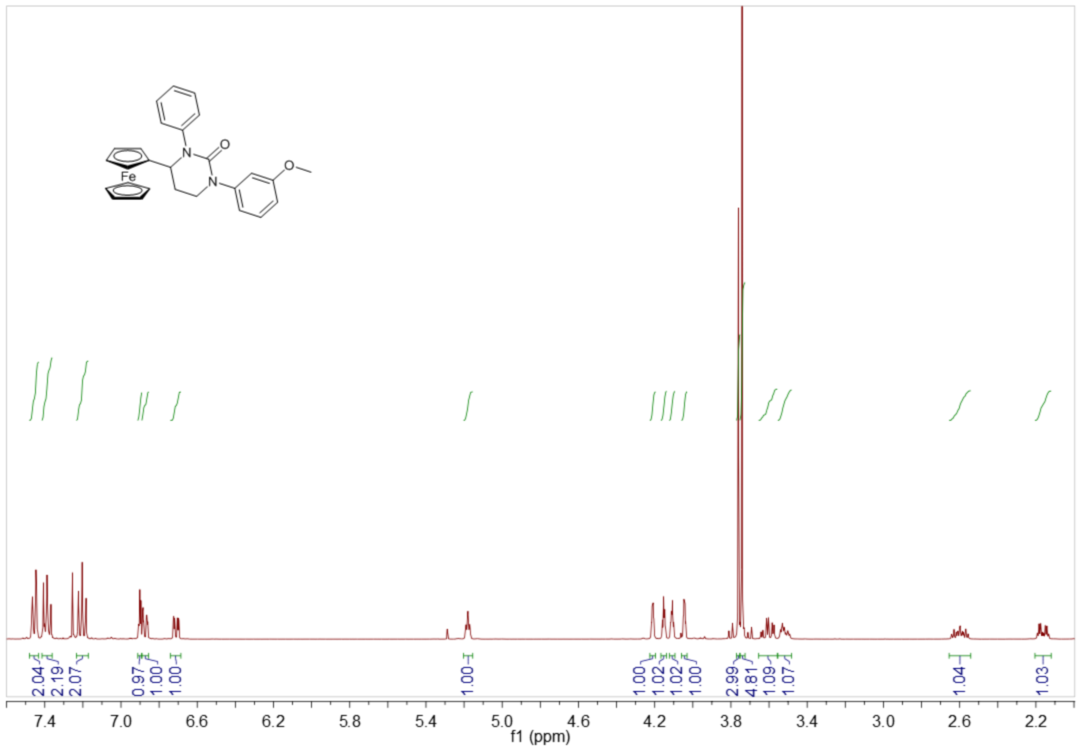
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12n**



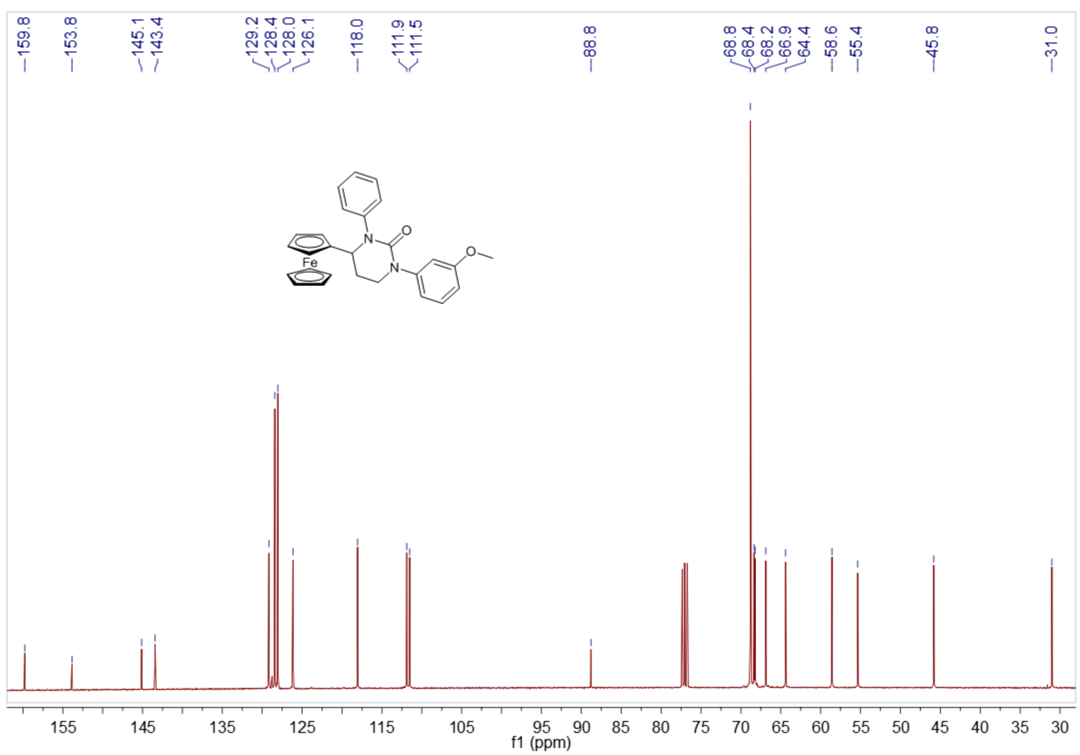
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12o**



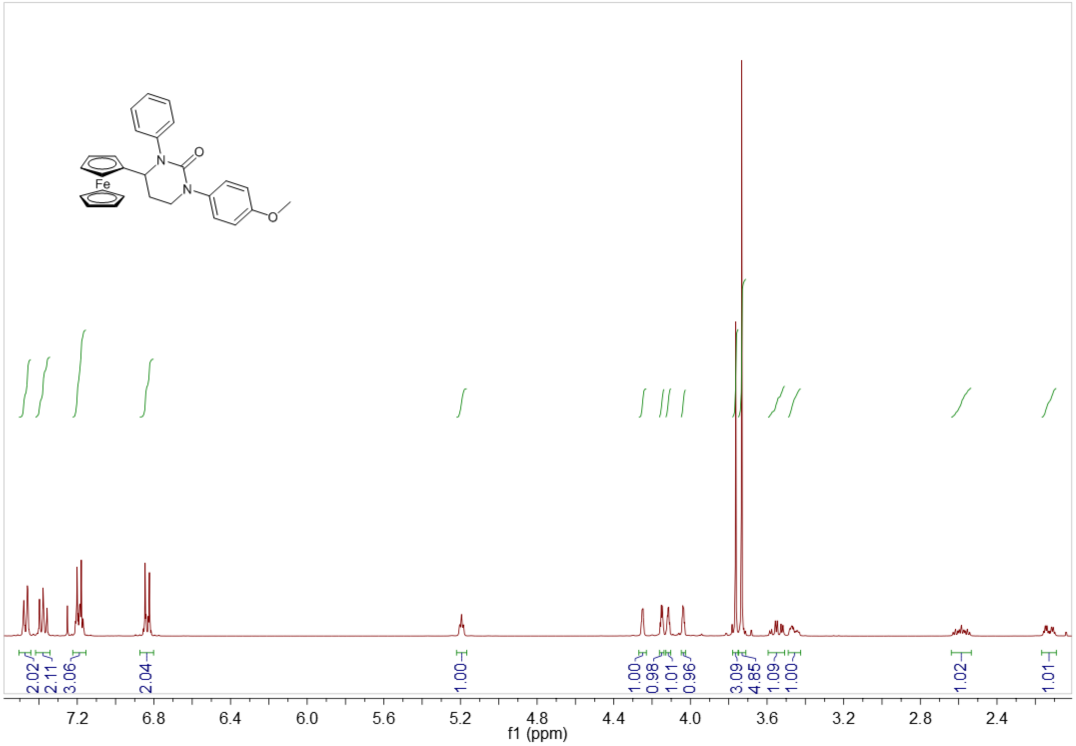
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12o**



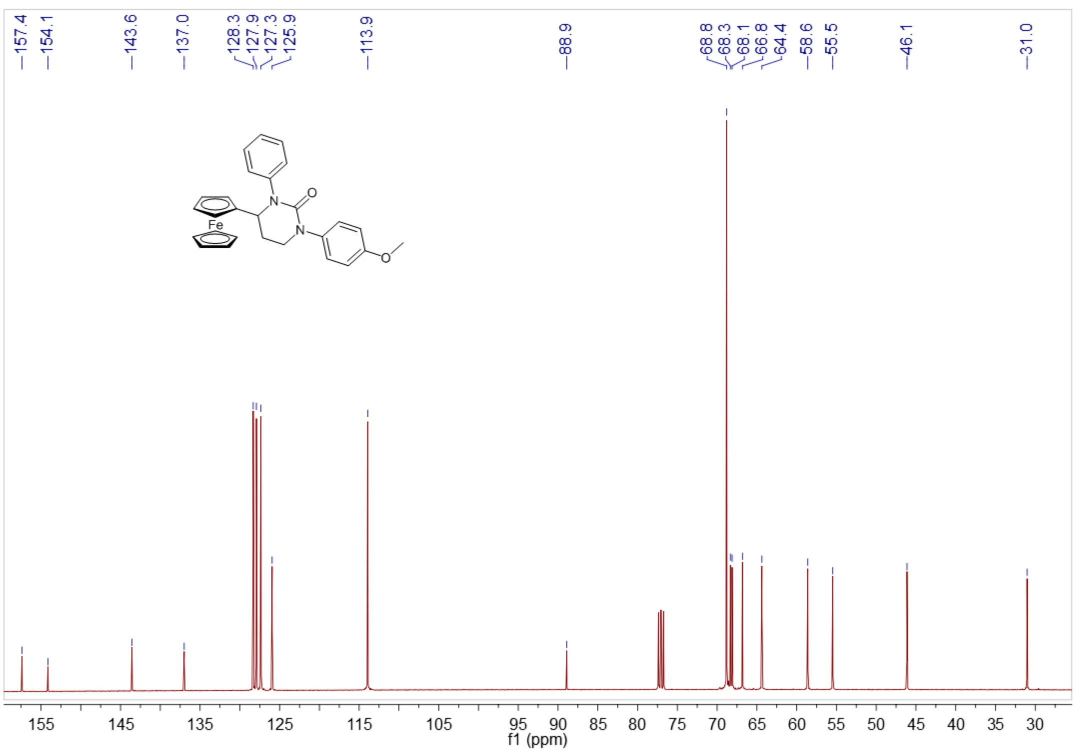
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12p**



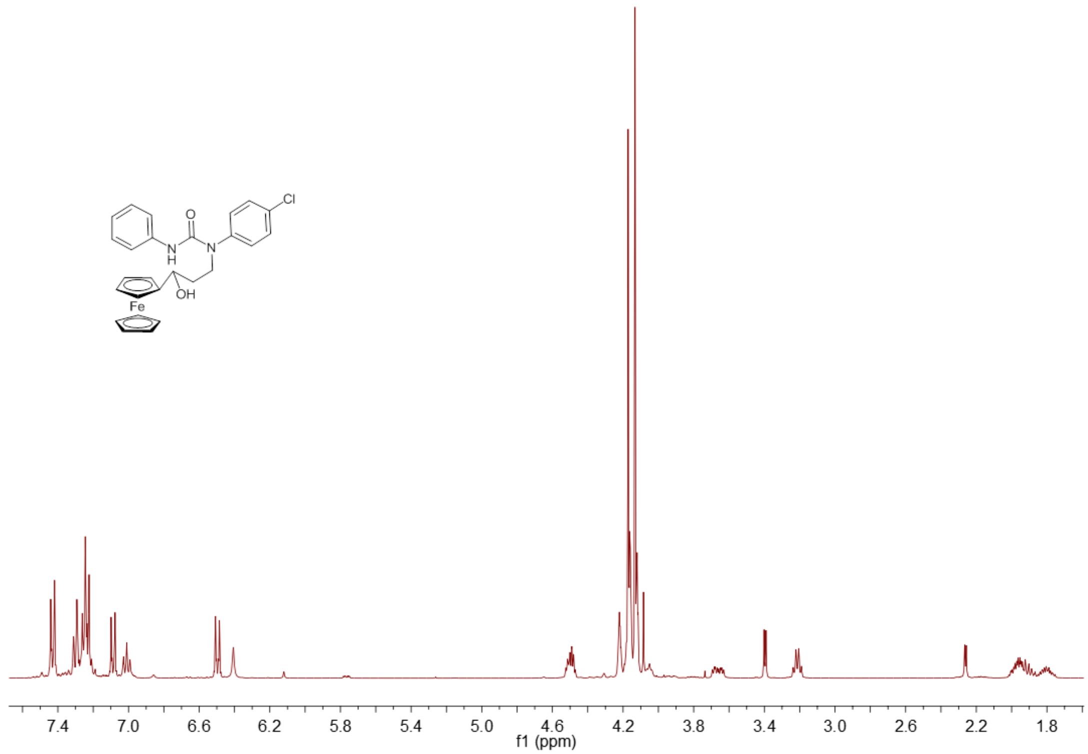
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12p**



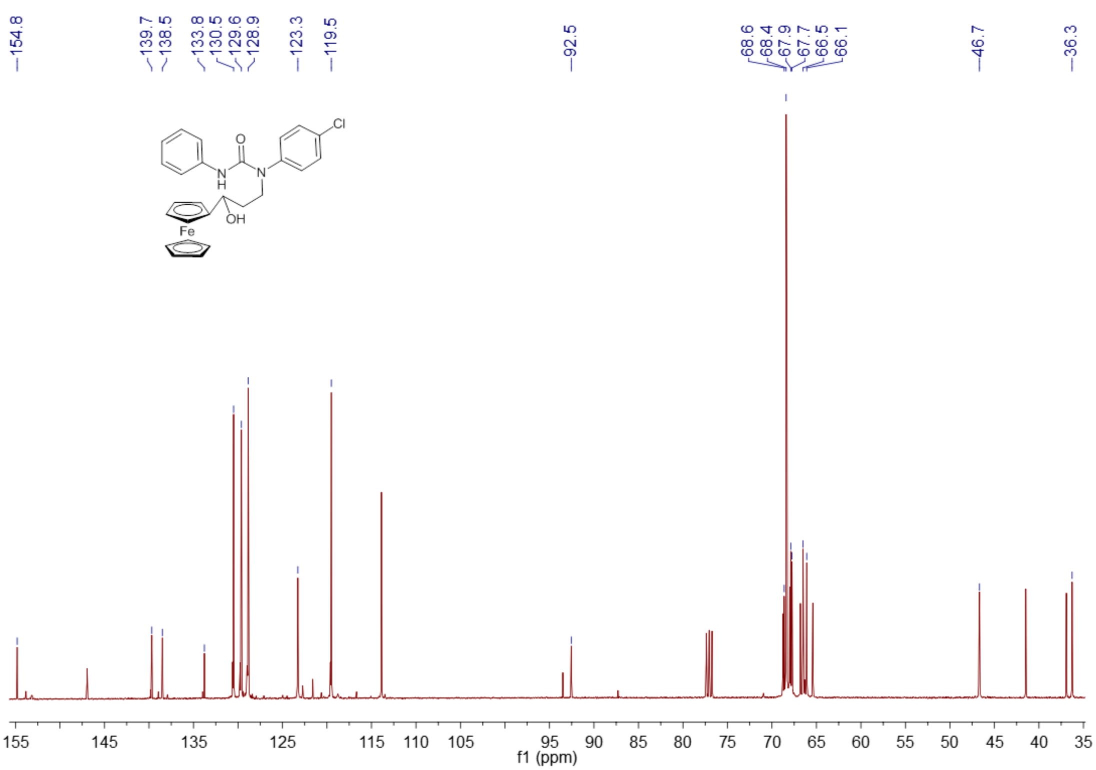
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12q**



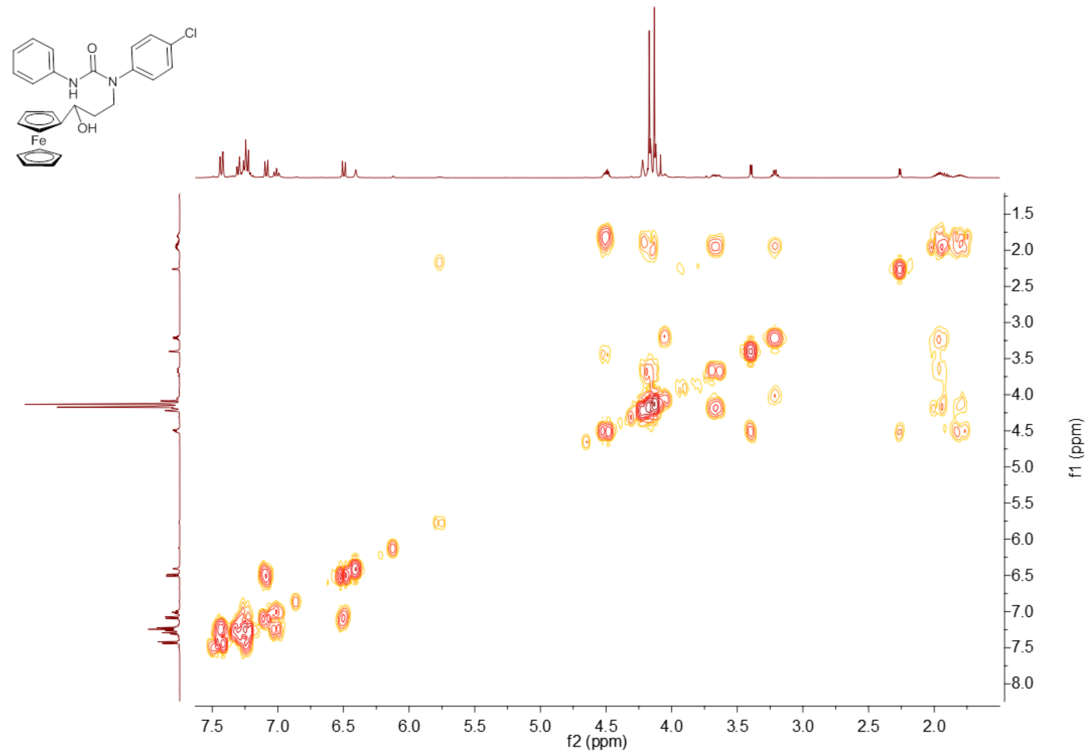
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12q**



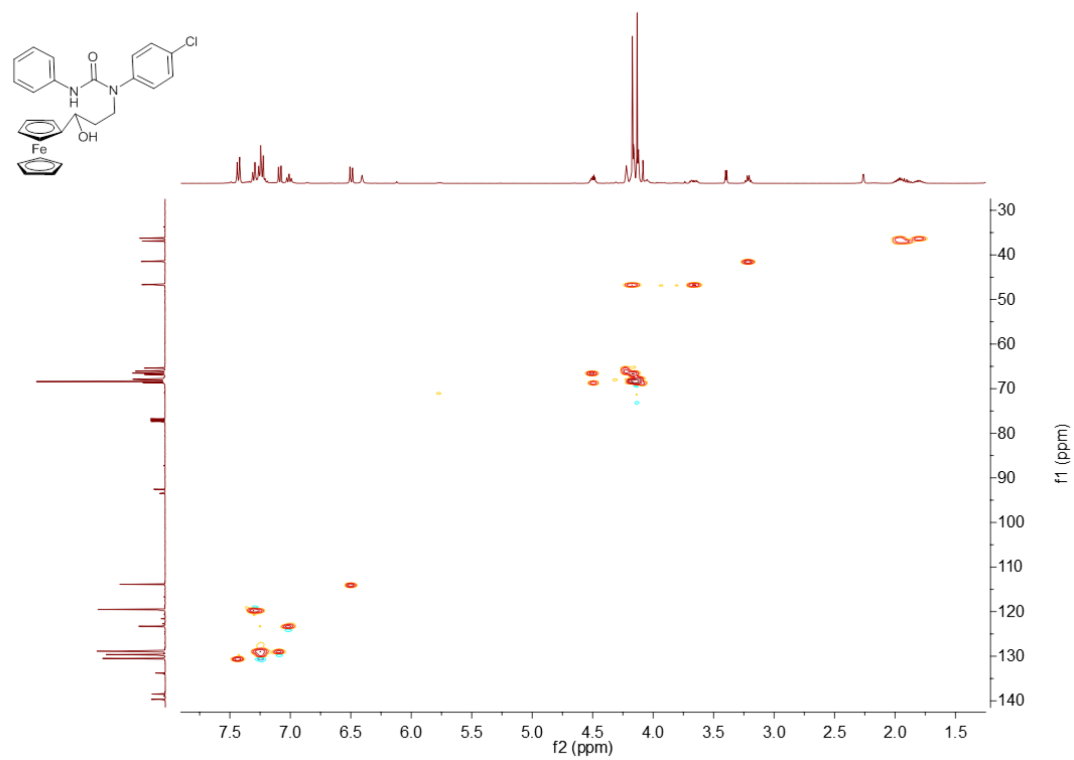
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of mixture **9k** and **11k**



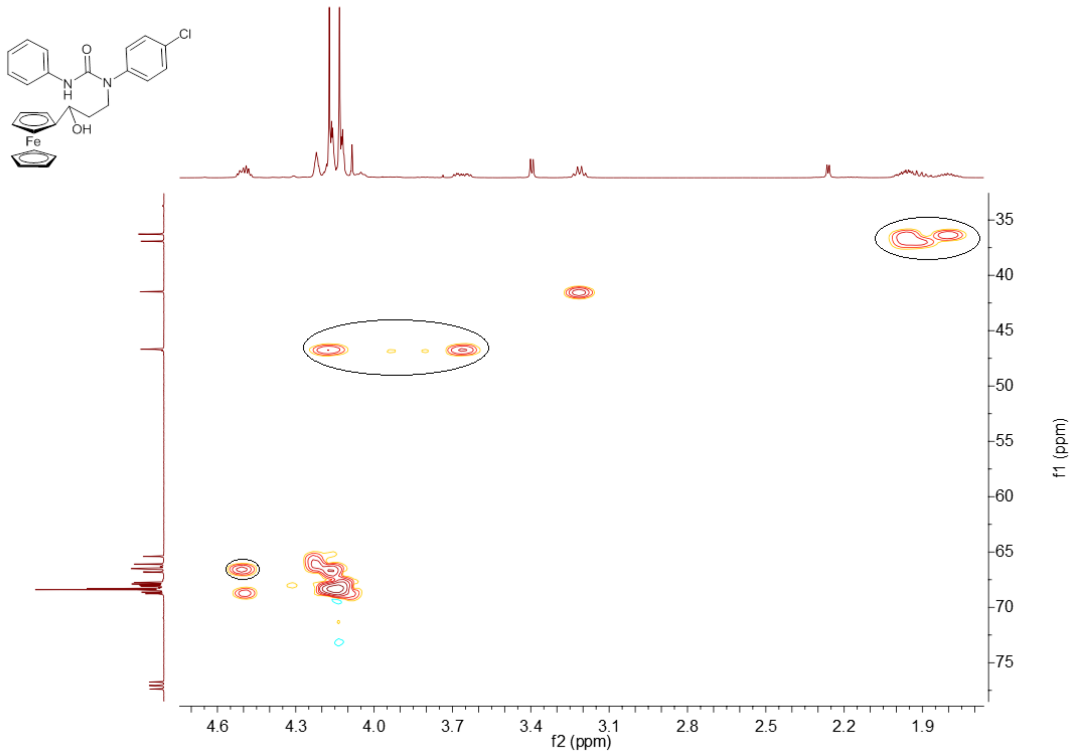
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of mixture **9k** and **11k**



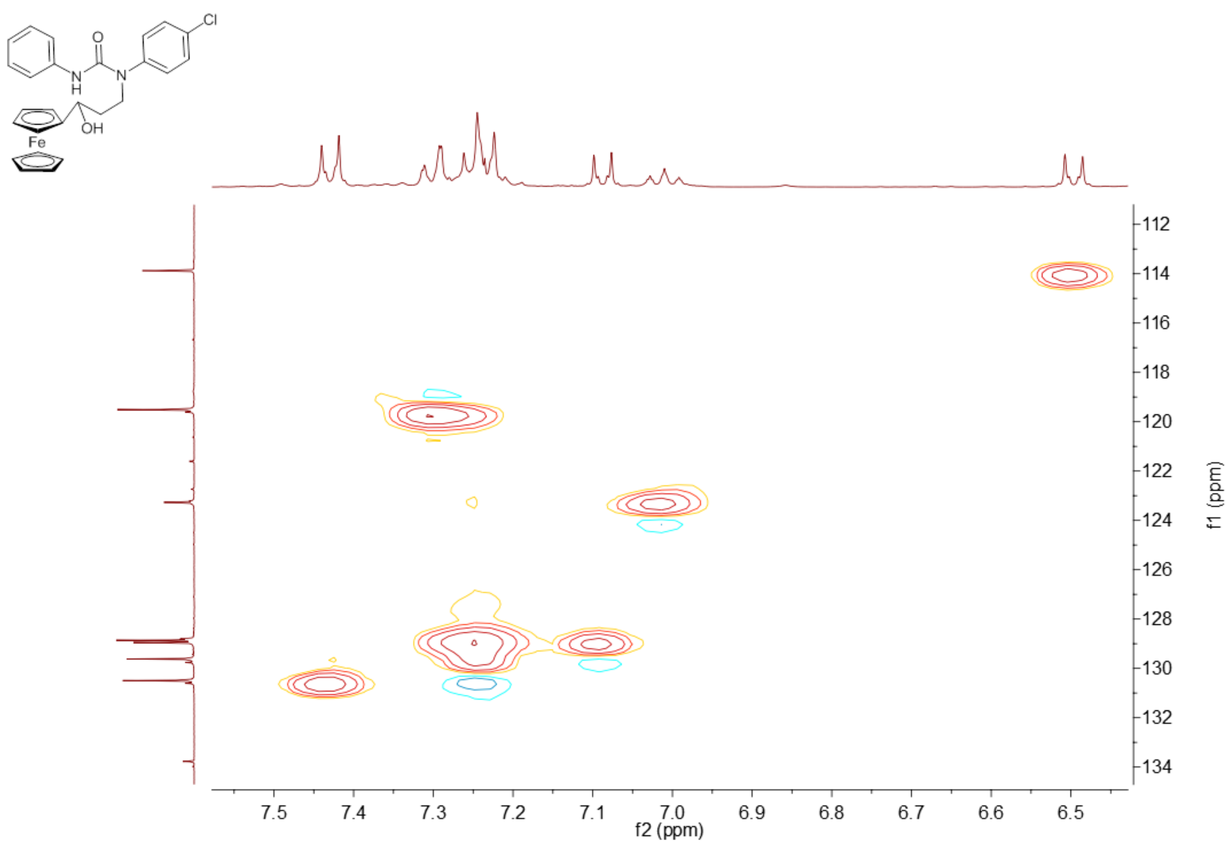
COSY spectrum of mixture **9k** and **11k**



HSQC spectrum of mixture **9k** and **11k**



Fragment of HSQC spectrum of mixture **9k** and **11k**



Fragment of HSQC spectrum of mixture **9k** and **11k**