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Regioselective synthesis of 1-azinyl-1'-isopropenylferrocenes

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Experimental section

General. The Wittig reactions were carried out under argon using the standard Schlenk techniques. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were recorded on a Bruker AVANCE II NMR spectrometer. Chemical shifts are given in δ values (ppm) using TMS as the internal standard and DMSO-d_6 as the solvent. Electrospray mass spectra were recorded in positive mode with maXis impact high resolution Q-TOF mass spectrometer in 50-2500 Da mass range by direct infusion of sample solutions in methanol using kdScientific syringe pump at 120 ul h^{-1} flow rate. Modified instrument settings of a pre-installed method Direct_Infusion_100-1000 were used. Mass calibration was performed using ES-TOF G1969-85000 tuning mix or lithium acetate in MeOH/ACN/water mixture by HPC or Enhanced Quadratic methods. All data were collected and analyzed with Compass for oTof series 1.7/DataAnalysis 4.2 software package. The IR spectra were recorded using a Perkin Elmer Spectrum One B Fourier-transform infrared spectrometer equipped with a diffuse reflection attachment. The elemental analysis was carried out on automated Perkin Elmer PE 2400 series II CHNS analyzer. The course of the reactions was monitored by TLC on 0.2 mm aluminium oxide plates (Polygram Alox N/UV_{254}). The column chromatography was performed on aluminium oxide (Aluminium oxide 90 netural, Macherey-Nagel).

The solvents were purified according to standard procedures. Acetic anhydride, aluminium chloride, BuLi were purchased from Aldrich. Starting ferrocenylazines [O. N. Chupakhin, I. A. Utepova, I. S. Kovalev, V. L. Rusinov, Z. A. Starikova, *Eur. J. Org. Chem.*, 2007, **5**, 857] and methyl(triphenyl)phosphonium iodide [J. Gao, A. Martin, J. Yatvin, E. White, J. Locklin, *J. Mater. Chem. A*, 2016, **4**, 11719] were prepared according to the published procedures.

Synthesis of 1-acetyl-1'-azinylferrocenes 2a-d (general procedure). Acetic anhydride (0.283 ml, 6 mmol) was added to solution of azinylferrocene **1** (1 mmol) in anhydrous CH_2Cl_2 (20 ml) at 0 °C followed by portionwise addition of $AlCl_3$ (399 mg, 1.1 mmol) for two hours. After stirring at room temperature for 24 h this was poured into cold water and was extracted with CH_2Cl_2. The extract was dried over the sodium sulfate and concentrated under reduced pressure. The residue was purified on Al_2O_3 using hexane-ethyl acetate mixture as eluent. The eluate was concentrated to dryness *in vacuo*.

The following compounds were obtained:

1-acetyl-1'-(pyridin-2-yl)ferrocene **2a**

1-acetyl-1'-(quinolin-2-yl)ferrocene **2b**

1-acetyl-1'-(2",2'"-bipyridin-6-yl)ferrocene **2c**

1-acetyl-1'-(acridin-9-yl)ferrocene **2d**

Synthesis of compounds 3a-d (general procedure). A hexane solution of BuLi (1.6 *M*, 0.71 ml, 1.14 mmol) was added to suspension of methyl triphenylphosphonium iodide (1.25 mmol) in anhydrous diethyl ether (5 ml) under argon at room temperature. After 15 minutes stirring, a solution of the corresponding acetylferrocene **2a-d** (1.0 mmol) in anhydrous diethyl ether (20 ml) was added. After stirring at room temperature for 4 hours, reaction mixture was purified on Al_2O_3 using hexane-ethyl acetate mixture as eluent. The eluate was concentrated to dryness *in vacuo*.

The following compounds were obtained:

1-isopropenyl-1'-(pyridin-2-yl)ferrocene **3a**

1-isopropenyl-1'-(quinolin-2-yl)ferrocene **3b**

1-isopropenyl-1'-(2",2'"-bipyridin-6-yl)ferrocene **3c**

1-isopropenyl-1'-(acridin-9-yl)ferrocene **3d**

Compound **3a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.79 (s, 3H, CH_3); 4.10 (m, 2H, C_5H_4); 4.25 (m, 2H, C_5H_4); 4.35 (m, 2H, C_5H_4); 4.66 (s, 1H, CH_2); 4.89 (m, 2H, C_5H_4); 4.96 (s, 1H, CH_2); 7.13-7.15 (m, 1H, 5'-H); 7.49-7.50 (d, 1H, 3'-H, ^3J = 8.0 Hz); 7.67-7.70 (m, 1H, 4'-H); 8.44-8.45 (d, 1H, 6'-H, ^3J = 4.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.04 (CH_3); 66.89, 67.99, 68.90, 70.67, 84.54, 86.92 (Fc); 109.11, 120.27 (-C=CH_2); 120.69, 135.95, 139.98, 148.95, 157.54 (Py). IR (cm^{-1}): 783.96, 1031.26, 1259.93, 1584.59, 2923.94, 2962.81. HRMS m/z (%):$[M]^+$ = 303.0706 (100%). Found (%): C, 71,28; H, 5.91; N, 4.34. Calc. for $C_{18}H_{17}FeN$ (%): C, 71.29; H, 5.61; N, 4.62.

Table S1 R_f, IR, Elemental Analysis, ESI-MS and Melting Points Data for **2a-d** and **3a-d**

	R_f (eluent)	IR (ν, cm^{-1})	Elemental analysis	HRMS, m/z (%)		M.p., °C
2a	0.15 (hexane:EtOAc, 9:1)	785.52, 1151.81, 1585.44, 1650.51 (CO)	Found: C, 66.98; H, 5.18; N, 4.60. Calc. for $C_{17}H_{15}FeNO$: C, 66.89; H, 4.92; N, 4.59.	$[M+Li]^+$: (100 %)	312.0662	78
2b	0.1 (hexane:EtOAc, 9:1)	823.29, 1273.96, 1597.14, 1666.92 (CO)	Found: C, 71.16; H, 5.03; N, 3.62 Calc. for $C_{21}H_{17}FeNO$: C, 70.99; H, 4.79; N, 3.94	$[M+Li]^+$: (100%)	362.0814	92
2c	0.2 (hexane:EtOAc, 8:2)	779.03, 1274.16, 1427.26, 1563.15, 1667.20 (CO)	Found: C, 69.05; H, 4.80; N, 7.25. Calc. for $C_{22}H_{18}FeN_2O$: C, 69.11; H, 4.71; N, 7.33	$[M+H]^+$: (100%)	383.0841	58
2d	0.15 (hexane:EtOAc, 9:1)	745.54, 1275.43, 1452.25, 1664.31 (CO), 3056.58	Found: C, 73.74; H, 4.74; N, 3.49. Calc. for $C_{25}H_{19}FeNO$: C, 74.07; H, 4.69; N, 3.46	$[M+H]^+$: (100%)	406.0883	112
3a	0.5 (hexane:EtOAc, 9:1)	783.96, 1031.26, 1259.93, 1584.59, 2923.94, 2962.81	Found: C, 71,28; H, 5.91; N, 4.34. Calc. for $C_{18}H_{17}FeN$: C, 71.29; H, 5.61; N, 4.62	$[M]^+$: (100%)	303.0706	84
3b	0.45 (hexane:EtOAc, 9:1)	752.71, 811.54, 1507.78, 1553.45, 1595.00, 2917.94	Found: C, 74.79; H, 5.71; N, 3.60. Calc. for $C_{22}H_{19}FeN$: C, 74.79; H, 5.38; N, 3.97.	$[M+H]^+$: (100%)	354.0930	92
3c	0.6 (hexane:EtOAc, 9:1)	777.48, 1031.07, 1425.18, 1561.10, 3082.63	Found: C, 72.39; H, 5.64; N, 7.06. Calc. for $C_{23}H_{20}FeN_2$: C, 72.63; H, 5.26; N, 7.37	$[M+H]^+$: (100%)	381.1045	76
3d	0.35 (hexane:EtOAc, 10:1)	744.76, 819.68, 1030.39, 1625.37, 1672.24, 2918.86, 3055.59	Found: C, 77.66; H, 5.48; N, 3.62. Calc. for $C_{26}H_{21}FeN$. : C, 77.42; H, 5.21; N, 3.47	$[M+H]^+$: (100%)	404.1097	106

Table S2 ^{1}H and ^{13}C NMR Data for **2a-d** and **3a-d**

	^{1}H NMR data	^{13}C NMR data
2a	2.08 (s, 3H, CH_3); 4.40 (m, 2H, C_5H_4); 4.47 (m, 2H, C_5H_4); 4.59 (m, 2H, C_5H_4); 5.04 (m, 2H, C_5H_4); 7.19-7.22 (m, 1H, 5'-H); 7.54-7.56 (d, ^{3}J = 7.9 Hz, 1H, 3'-H); 7.70-7.74 (m, 1H, 4'-H); 8.47-8.48 (d, ^{3}J = 4.1 Hz, 1H, 6'-H)	27.13 (CH_3); 68.35, 70.51, 71.12, 73.21, 80.28, 85.45 (Fc); 120.43, 121.28, 136.27, 149.11, 156.56 (Py) 200.44 (CO)
2b	2.07 (s, 3H, CH_3); 4.43 (m, 2H, C_5H_4); 4.57 (m, 2H, C_5H_4); 4.61 (m, 2H, C_5H_4); 5.20 (m, 2H, C_5H_4); 7.52-7.55 (m, 1H, 6'-H,); 7.69-7.74 (m, 2H, 5'-H, 7'-H); 7.91-7.95 (m, 2H, 4'-H, 8'-H); 8.27-8.30 (d, ^{3}J = 12 Hz, 1H, 3'-H)	27.12 (CH_3); 69.01, 70.59, 71.67, 73.22, 80.29, 85.08 (Fc); 119.56, 125.60, 126.52, 127.79, 128.30, 129.56, 135.85, 147.47, 157.32 (Quin) 200.45 (CO)
2c	2.03 (s, 3H, CH_3); 4.44 (m, 2H, C_5H_4); 4.52 (m, 2H, C_5H_4); 4.61 (m, 2H, C_5H_4); 5.17 (m, 2H, C_5H_4); 7.46 (m, 1H, 5"-H); 7.61-7.63 (d, ^{3}J= 8.0 Hz, 1H, 5'-H); 7.86-7.89 (t, ^{3}J= 7.6 Hz, 1H, 4'-H); 7.99-8.01 (t, ^{3}J= 7.3 Hz, 1H, 4"-H); 8.20-8.22 (d, ^{3}J= 7.6 Hz, 1H, 3'-H);. 8.51-8.53 (d, ^{3}J= 7.7 Hz, 1H, 3"-H); 8.70 (s, 1H, 6"-H)	27.03 (CH_3); 68.51, 70.53, 71.11, 73.08, 80.27, 85.18 (Fc); 117.74, 120.50, 120.63, 124.04, 137.17, 137.36, 149.08, 154.50, 155.26, 156.13 (biPy); 220.25 (CO)
2d	2.30 (s, 3H, CH_3); 4.59 (m, 2H, C_5H_4); 4.80 (m, 2H, C_5H_4); 4.87 (m, 2H, C_5H_4); 4.98 (m, 2H, C_5H_4); 7.68-7.71 (m, 2H, 2′-H, 7′-H), 7.82-7.86 (m, 2H, 3′-H, 6′-H), 8.15-8.17 (d, 2H, ^{3}J = 8.5 Hz, 1′-H, 8′-H), 8.95-8.97 (d, 2H, ^{3}J = 8.8 Hz, 4′-H, 5′-H)	27.36 (CH_3); 70.99, 71.13, 74.45, 74.83, 79.90, 81.79 (Fc); 124.46, 125.21, 126.95, 129.58, 129.86, 141.89, 148.10 (Acr); 200.94 (CO)
3a	1.79 (s, 3H, CH_3); 4.10 (m, 2H, C_5H_4); 4.25 (m, 2H, C_5H_4); 4.35 (m, 2H, C_5H_4); 4.66 (s, 1H, CH_2); 4.89 (m, 2H, C_5H_4); 4.96 (s, 1H, CH_2); 7.13-7.15 (m, 1H, 5'-H); 7.49-7.50 (d, ^{3}J = 8.0 Hz, 1H, 3'-H); 7.67-7.70 (m, 1H, 4'-H); 8.44-8.45 (d, ^{3}J = 4.0 Hz, 1H, 6'-H)	21.04 (CH_3); 66.89, 67.99, 68.90, 70.67, 84.54, 86.92 (Fc); 109.11, 120.27 (-C=CH_2); 120.69, 135.95, 139.98, 148.95, 157.54 (Py)
3b	1.77 (s, 3H, CH_3); 4.13 (m, 2H, C_5H_4); 4.28 (m, 2H, C_5H_4); 4.45 (m, 2H, C_5H_4); 4.59 (s, 1H, CH_2); 4.95 (m, 2H, C_5H_4); 5.06 (s, 1H, CH_2); 7.49-7.52 (m, 2H, 6'-H, 7'-H); 7.66-7.70 (t, ^{3}J= 7.3 Hz, 1H, 3'-H); 7.88-7.92 (m, 1H, 5'-H); 8.23-8.25 (m, 2H, 8'-H, 4'-H)	20.97 (CH_3); 66.98, 68.68, 69.96, 71.30, 84.25, 87.08 (Fc); 109.19, 119.70 (-C=CH_2); 125.29, 126.36, 127.74, 128.24, 129.40, 135.41,139.90,147.58, 158.34 (Quin);
3c	1.74 (s, 3H, CH_3); 4.15 (m, 2H, C_5H_4); 4.27 (m, 2H, C_5H_4); 4.41 (m, 2H, C_5H_4); 4.59 (s, 1H, CH_2); 4.93 (s, 1H, CH_2); 5.02 (m, 2H, C_5H_4); 7.44-7.47 (m, 1H, 5"-H); 7.54-7.56 (t, ^{3}J= 7.7 Hz, 1H, 4'-H); 7.82-7.86 (m, 1H, 4"-H); 7.97-8.00 (m, 1H, 3'-H); 8.15-8.17 (d, ^{3}J= 7.7 Hz, 1H, 3"-H); 8.50-8.52 (d, ^{3}J = 3.9 Hz, 1H, 5'-H), 8.68-8.69 (d, ^{3}J = 3.9 Hz, 1H, 6"-H)	20.97 (CH_3); 66.96, 68.22, 69.77, 70.61, 84.44, 86.98, (Fc); 109.18, 117.16 (-C=CH_2); 120.45, 120.54, 124.01, 137.05, 137.19, 139.73, 149.13, 154.38, 155.55, 157.11 (biPy);
3d	1.89 (s, 3H, CH_3); 4.30 (m, 2H, C_5H_4); 4.50 (m, 2H, C_5H_4); 4.64 (m, 2H, C_5H_4); 4.84 (m, 3H, C_5H_4, CH_2); 5.12 (s, 1H, CH_2); 7.62-7.66 (m, 2H, 2′-H, 7′-H), 7.79-7.83 (m, 2H, 3′-H, 6′-H), 8.12-8.15 (d, 2H, ^{3}J = 7.0 Hz, 1′-H, 8′-H), 9.03-9.05 (d, 2H, ^{3}J = 8.04 Hz, 4′-H, 5′-H)	21.12 (CH_3); 67.65, 71.19, 71.46, 74.17, 80.47, 87.25 (Fc); 109.79, 124.62 (-C=CH_2); 124.92, 127.26, 129.56, 129.80, 140.16, 143.31, 148.16 (Acr)

^{1}H NMR spectra

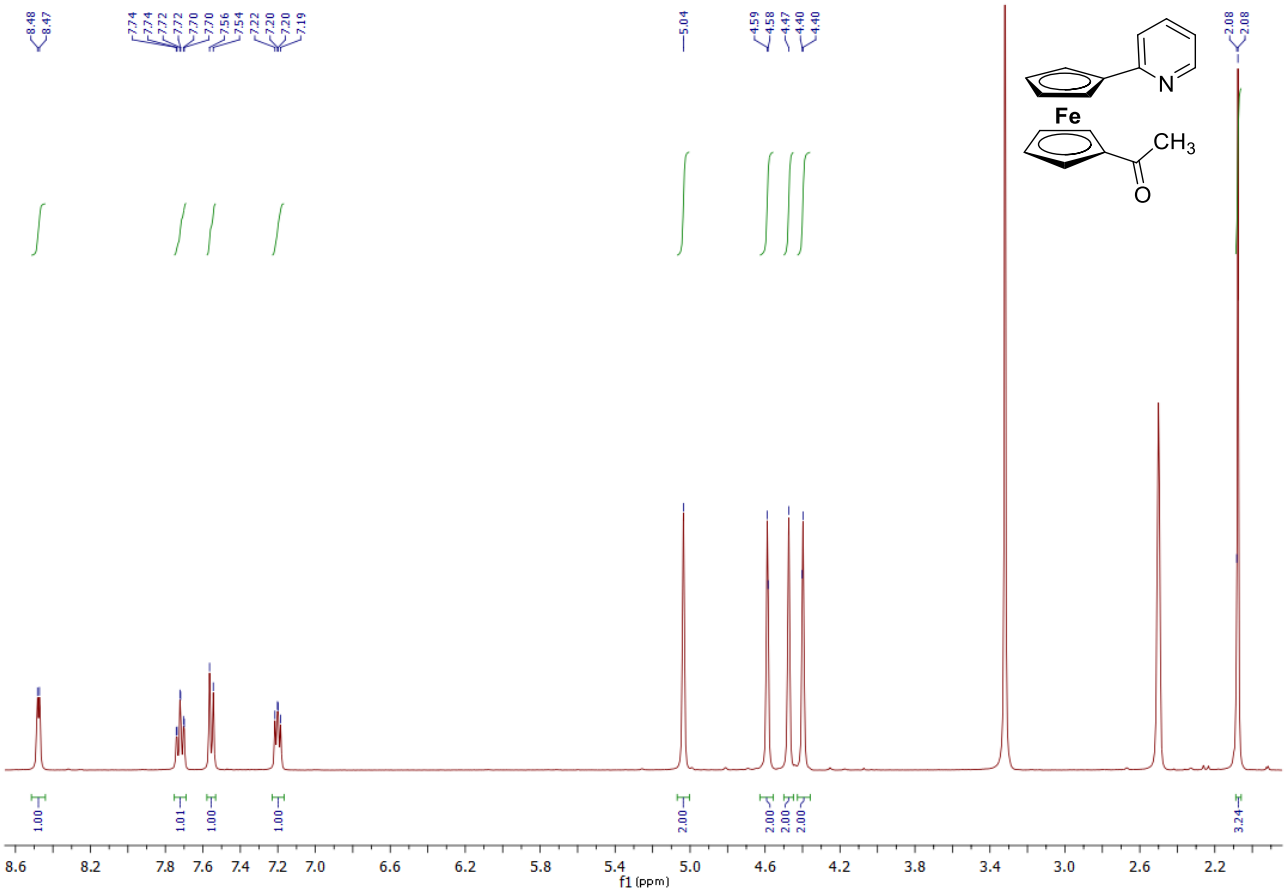

Figure S1 ^{1}H NMR spectrum of 1-acetyl-1'-(pyridin-2-yl)ferrocene **2a**.

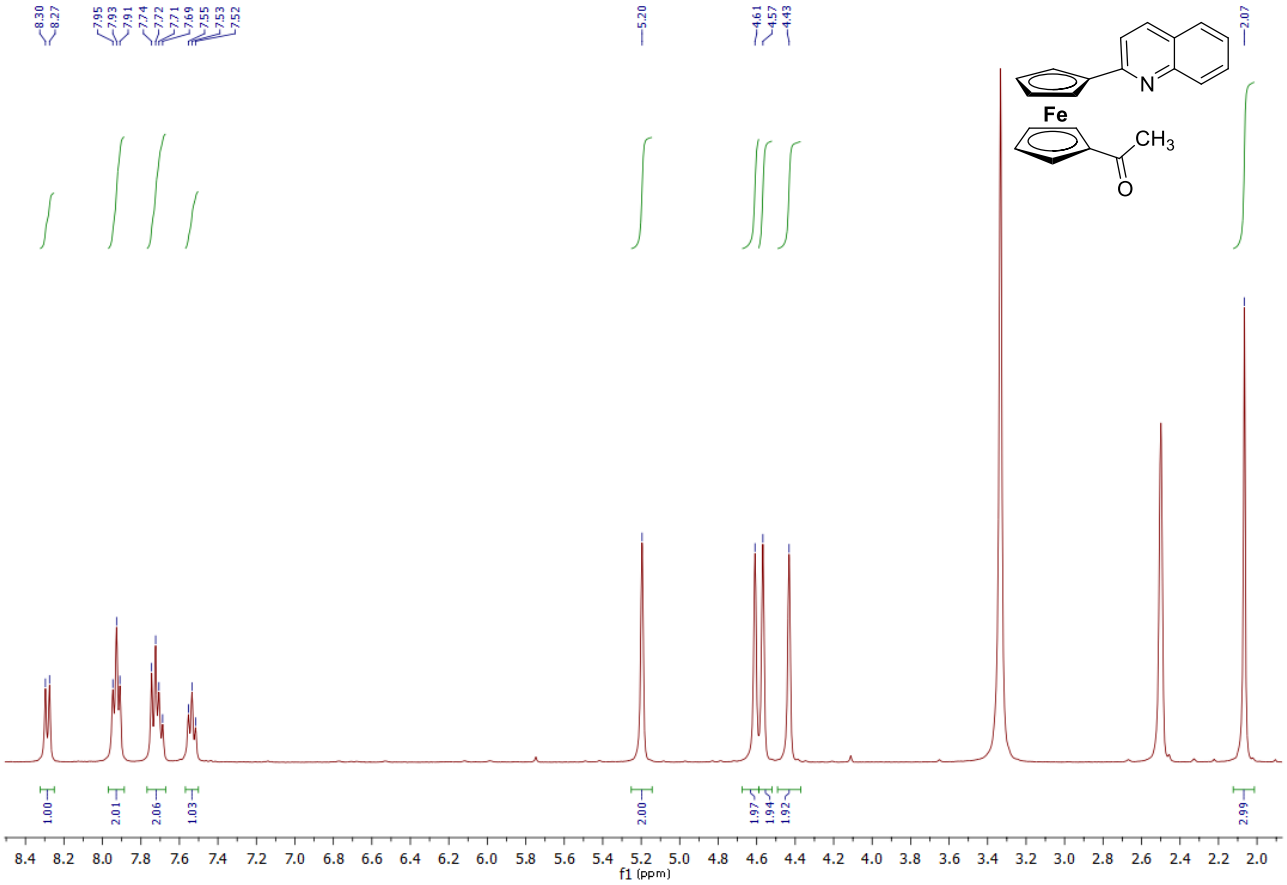

Figure S2 ^{1}H NMR spectrum of 1-acetyl-1'-(quinolin-2-yl)ferrocene **2b**.

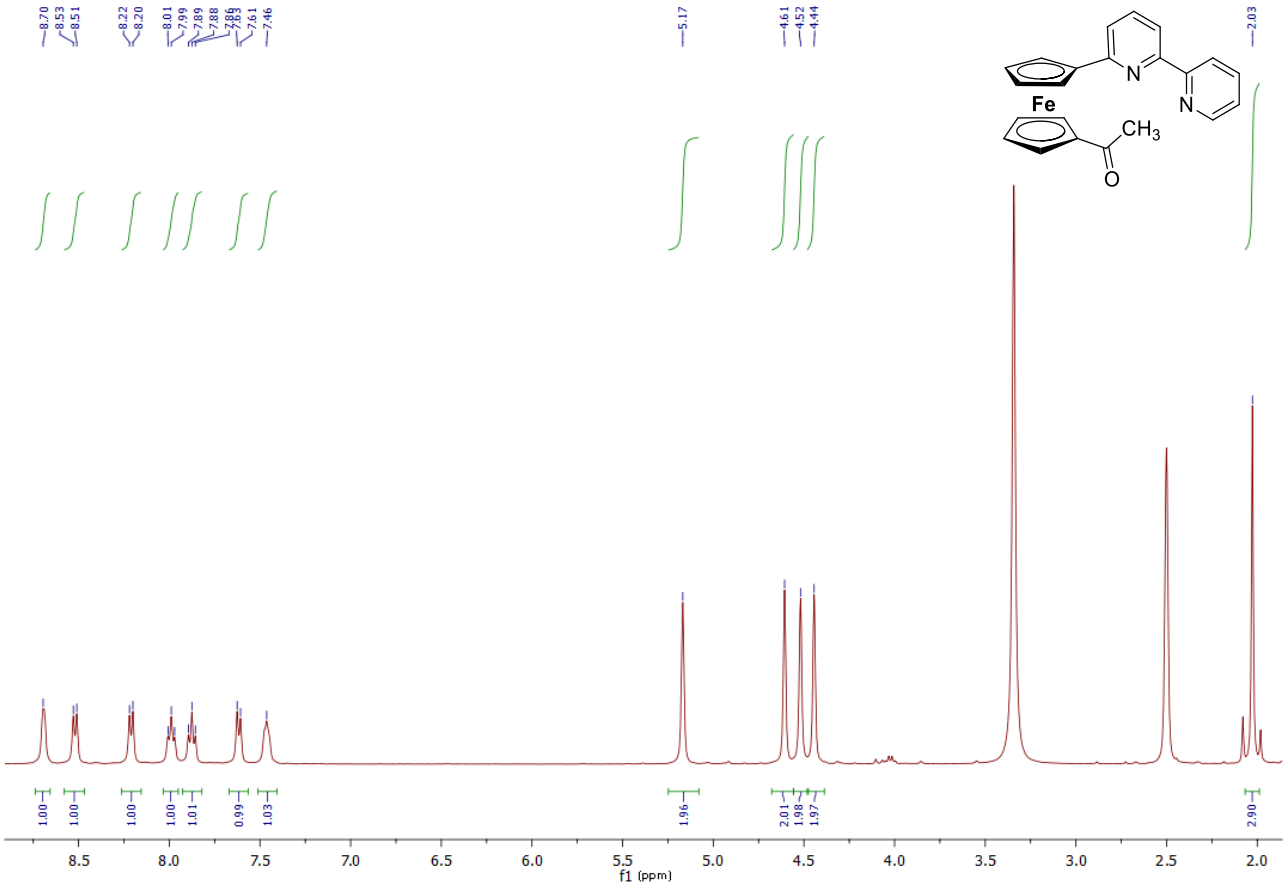

Figure S3 [1]H NMR spectrum of 1-acetyl-1'-(2",2"'-bipyridin-6-yl)ferrocene **2c**.

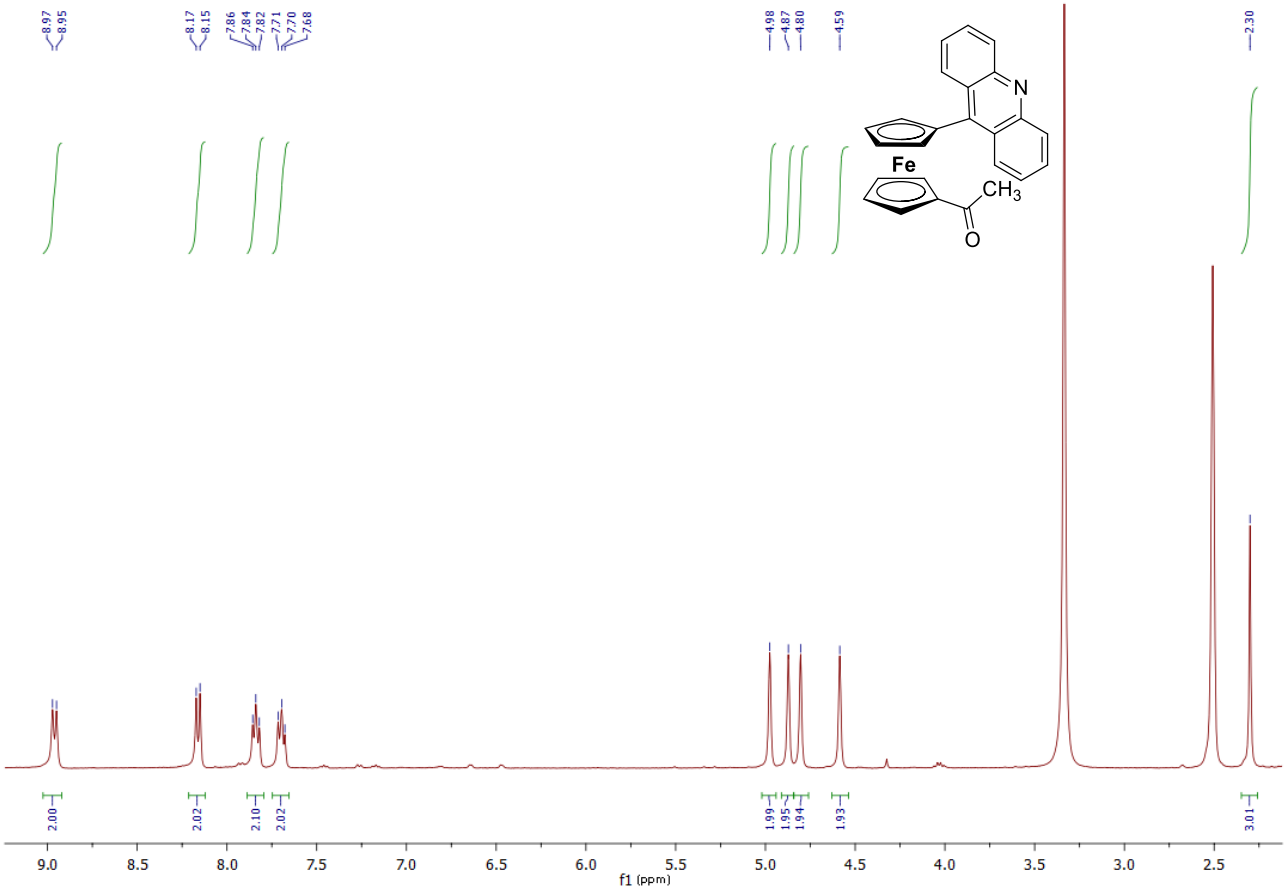

Figure S4 [1]H NMR spectrum of 1-acetyl-1'-(acridin-9-yl)ferrocene **2d**.

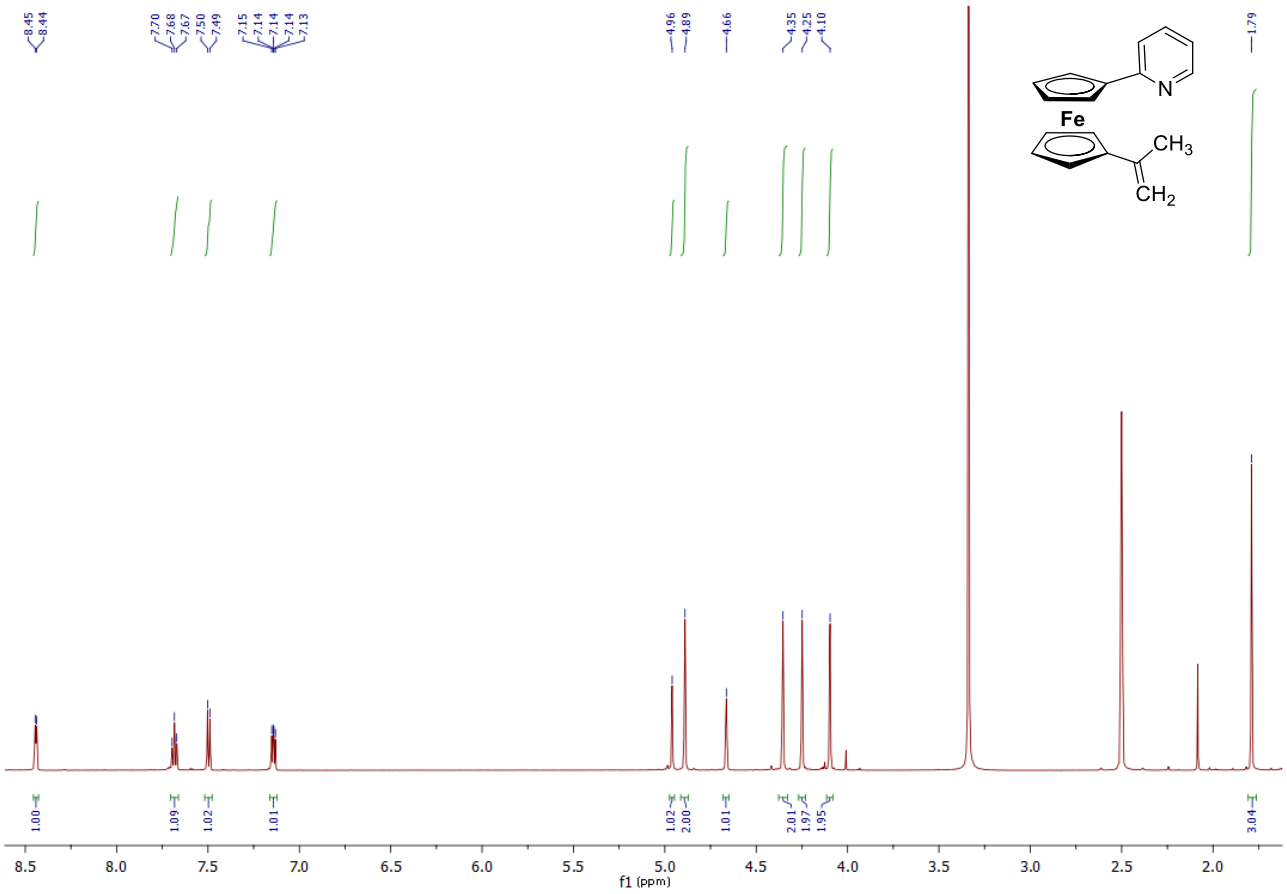

Figure S5 ^{1}H NMR spectrum of 1-isopropenyl-1'-(pyridin-2-yl)ferrocene **3a**.

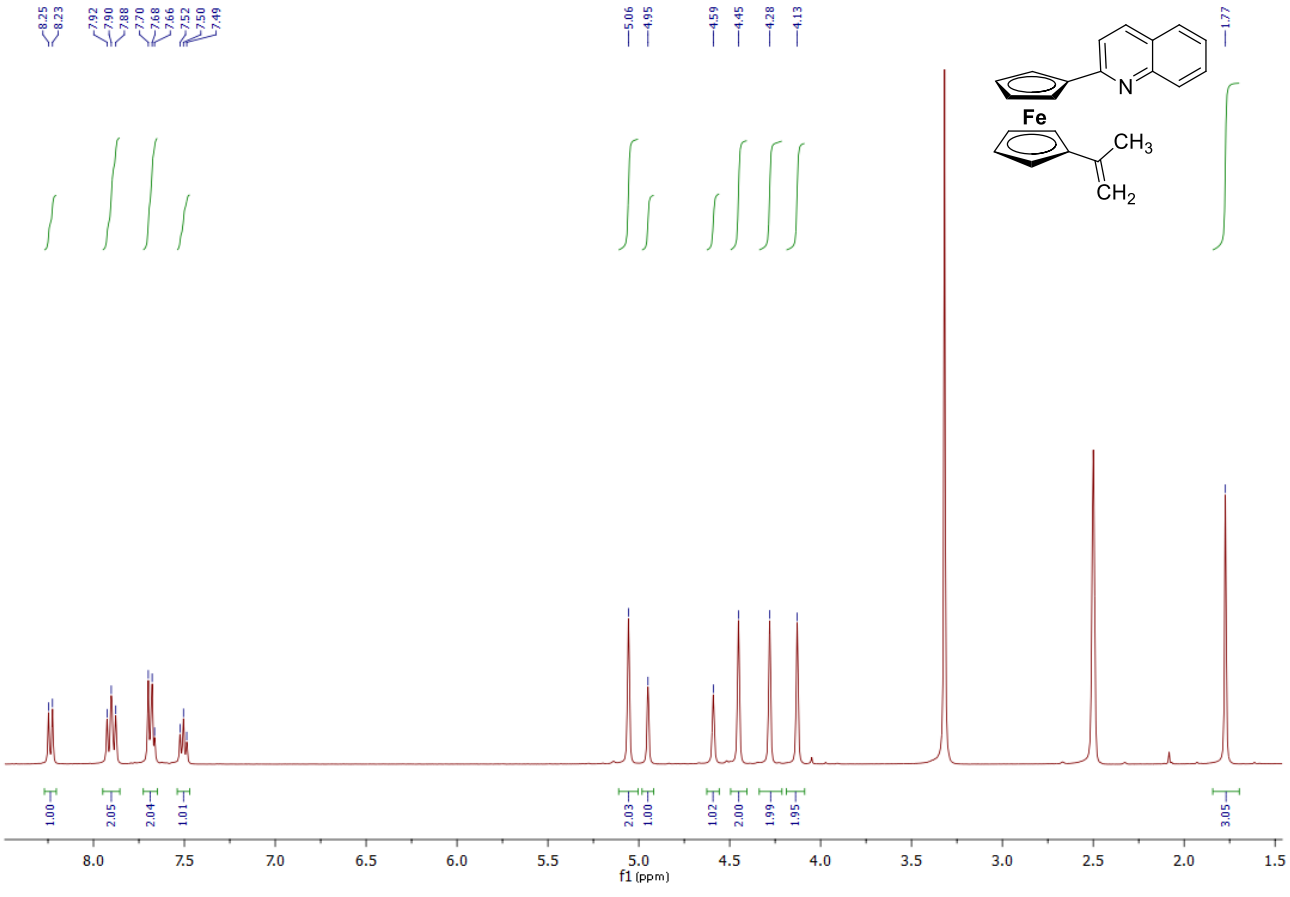

Figure S6 ^{1}H NMR spectrum of 1-isopropenyl-1'-(quinolin-2-yl)ferrocene **3b**.

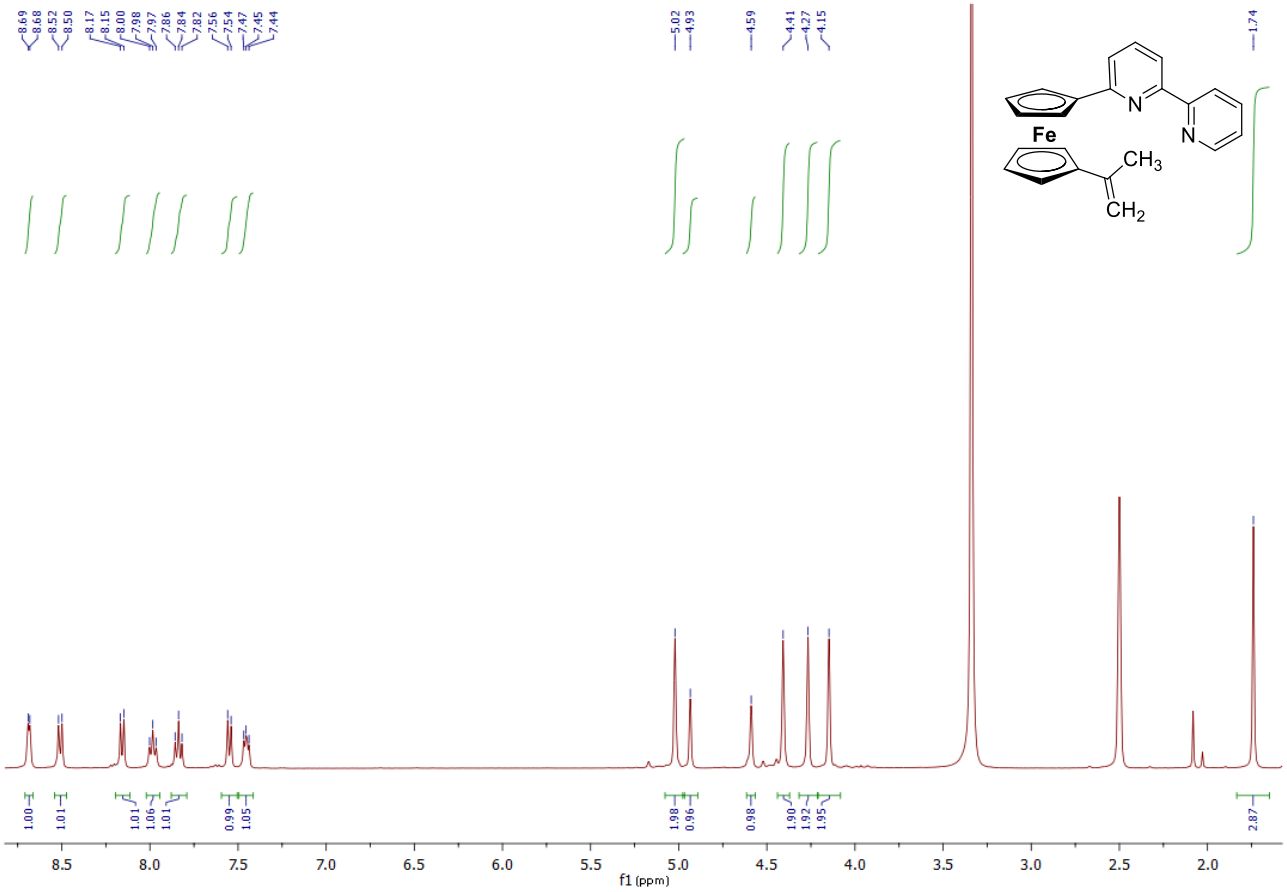

Figure S7 ^{1}H NMR spectrum of 1-isopropenyl-1'-(2",2'"-bipyridin-6-yl)ferrocene **3c**.

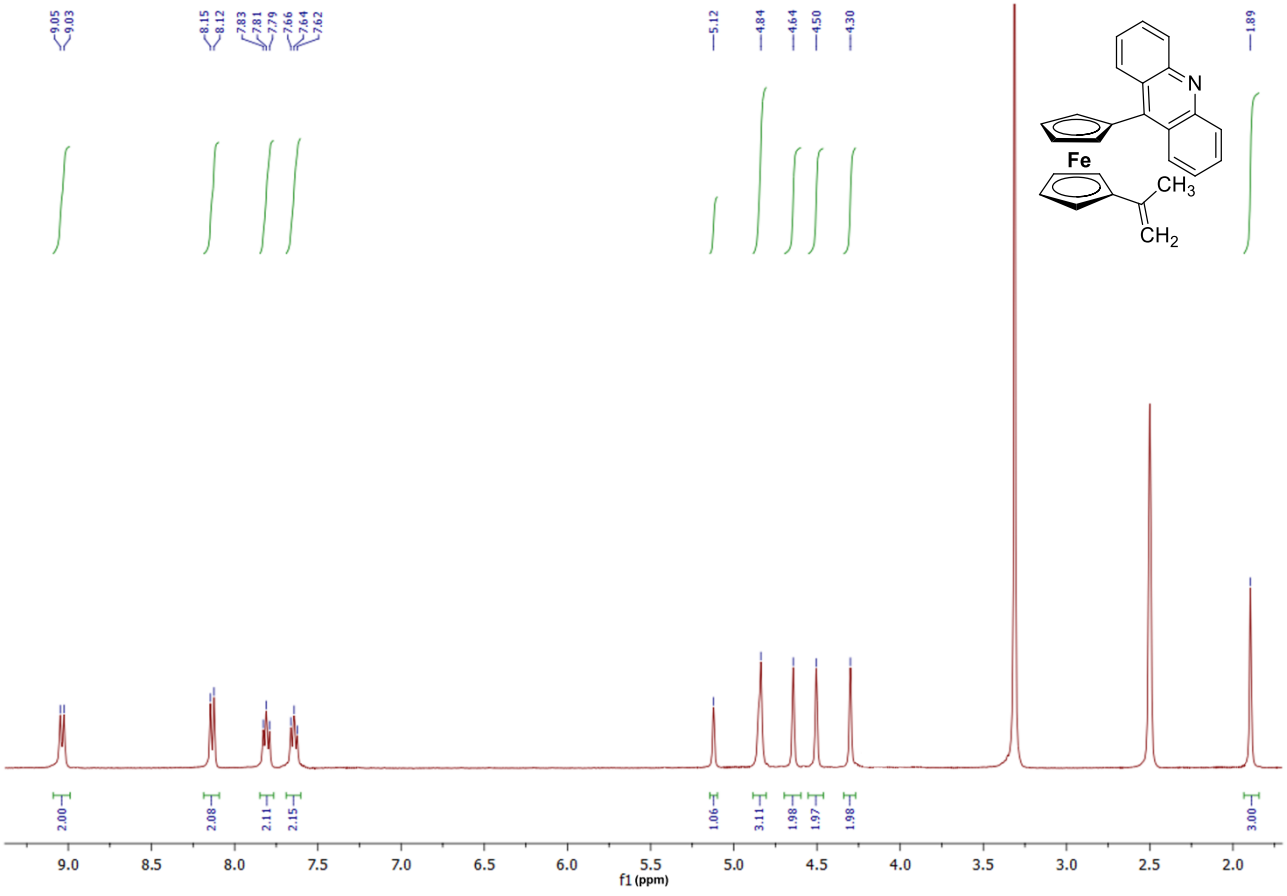

Figure S8 ^{1}H NMR spectrum of 1-isopropenyl-1'-(acridin-9-yl)ferrocene **3d**.

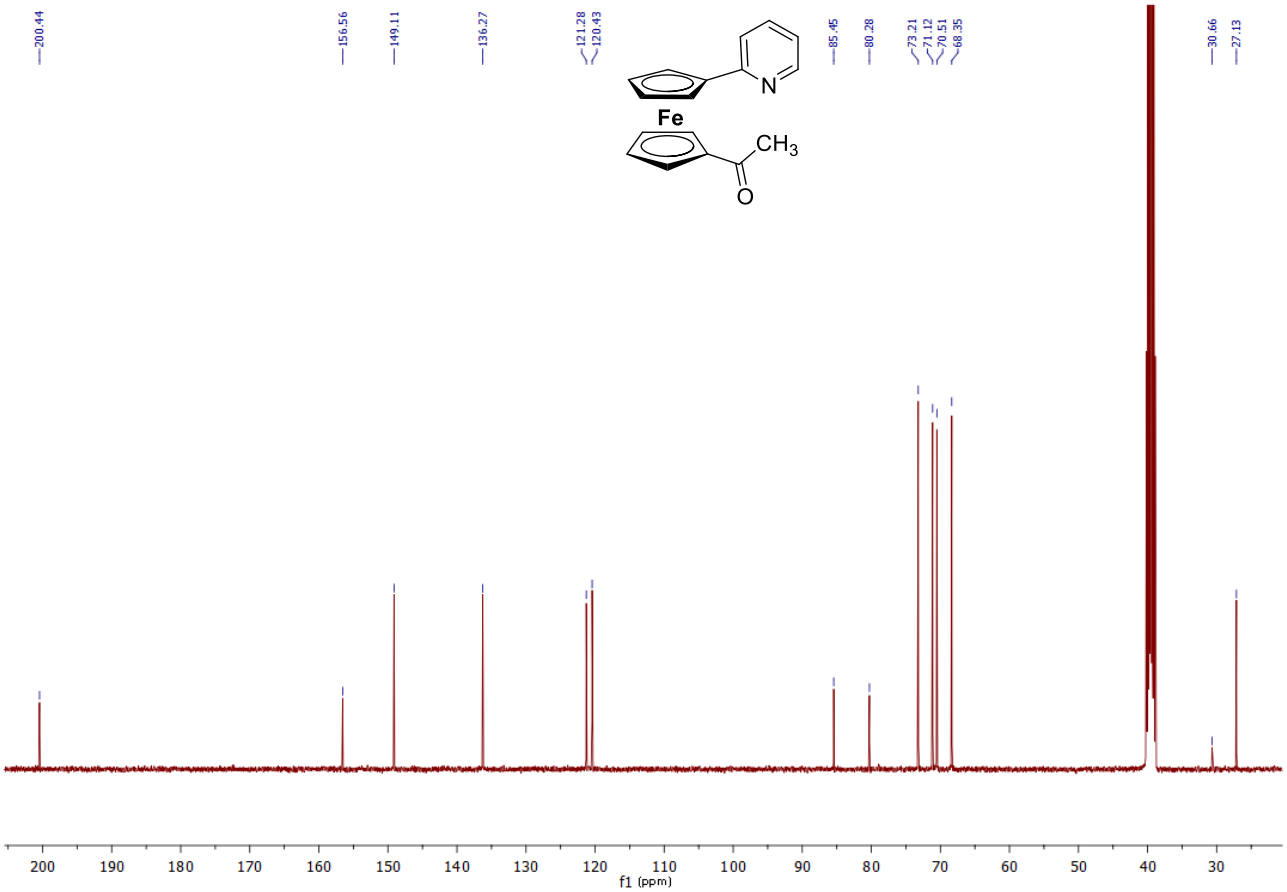

Figure S9 ^{13}C NMR spectrum of 1-acetyl-1'-(pyridin-2-yl)ferrocene **2a**.

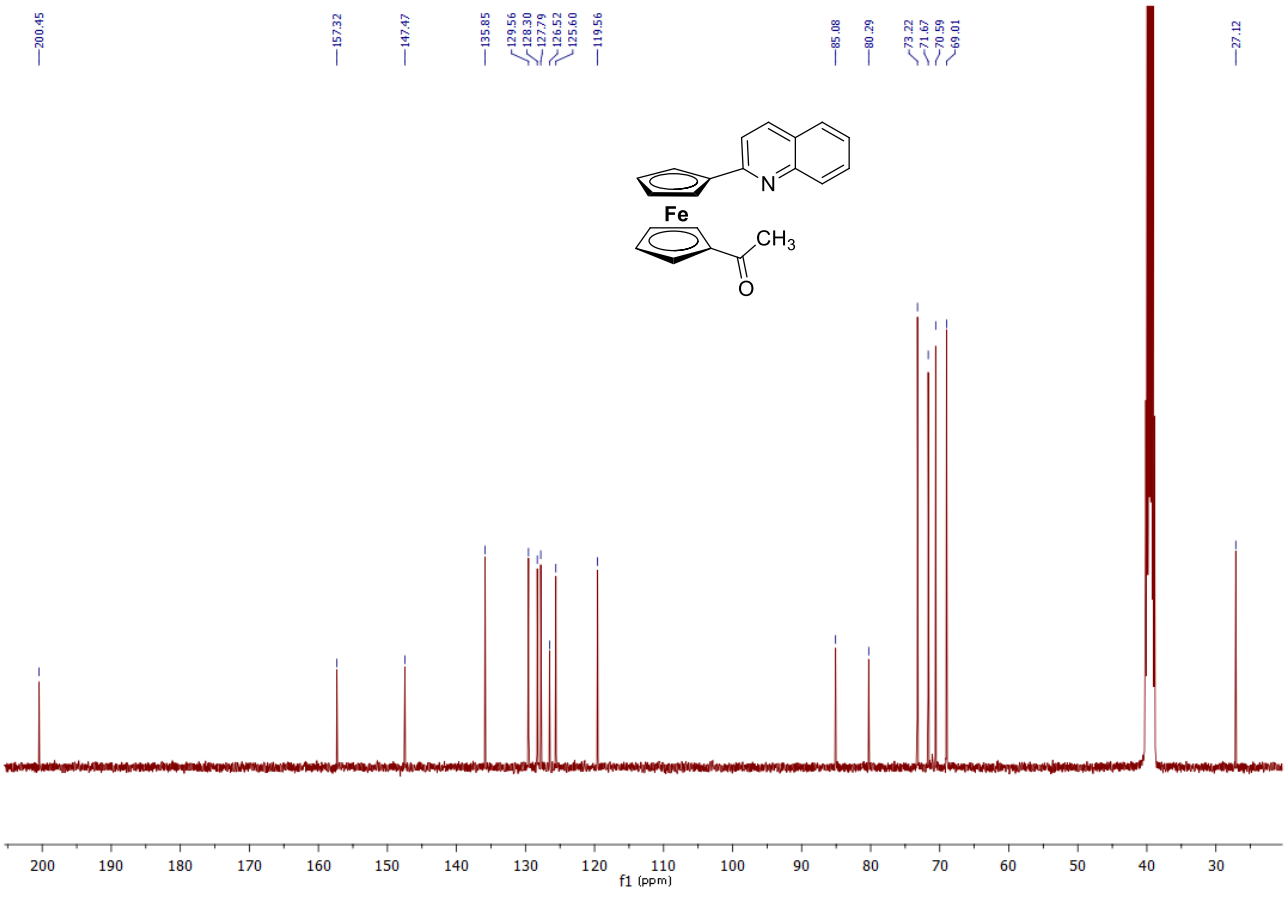

Figure S10 ^{13}C NMR spectrum of 1-acetyl-1'-(quinolin-2-yl)ferrocene **2b**.

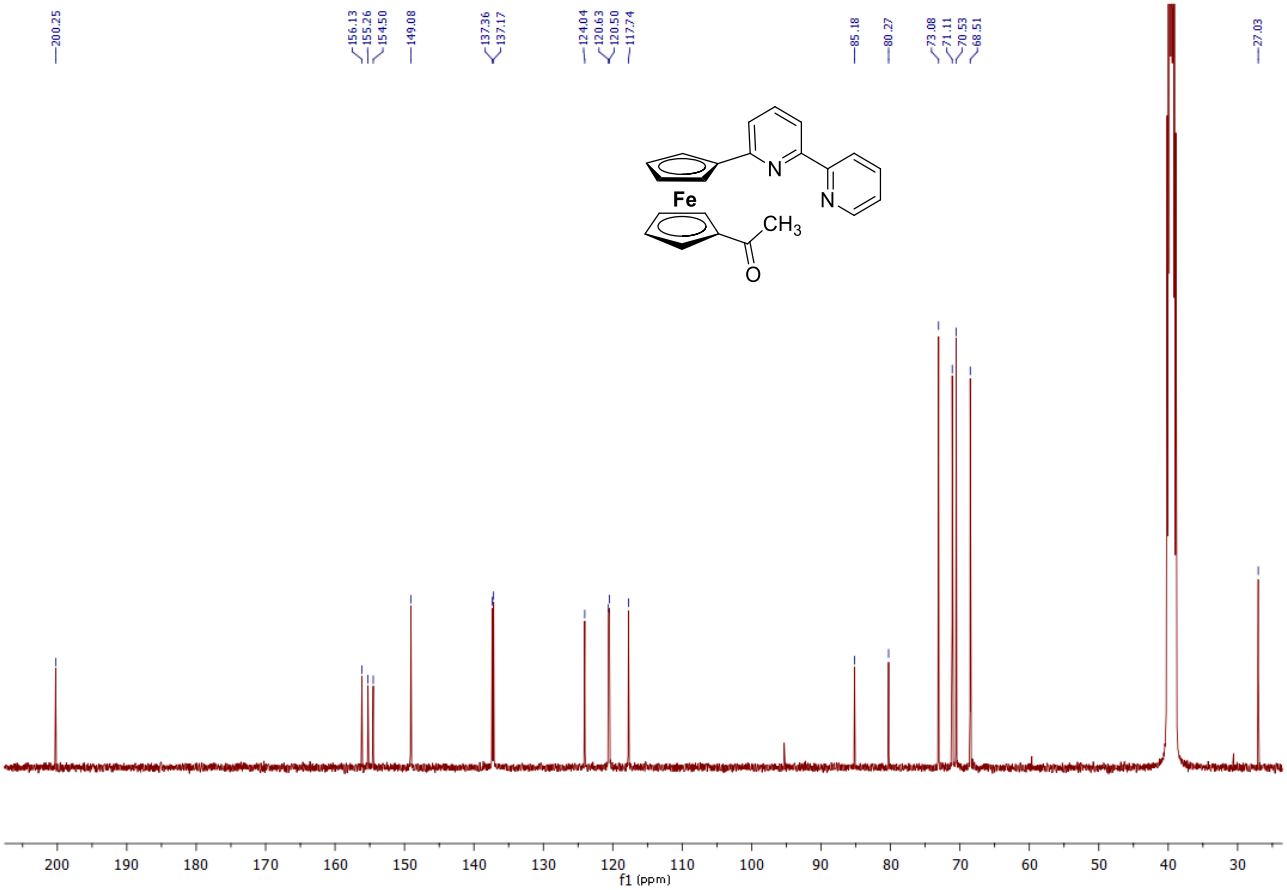

Figure S11 ^{13}C NMR spectrum of 1-acetyl-1'-(2",2"'-bipyridin-6-yl)ferrocene **2c**.

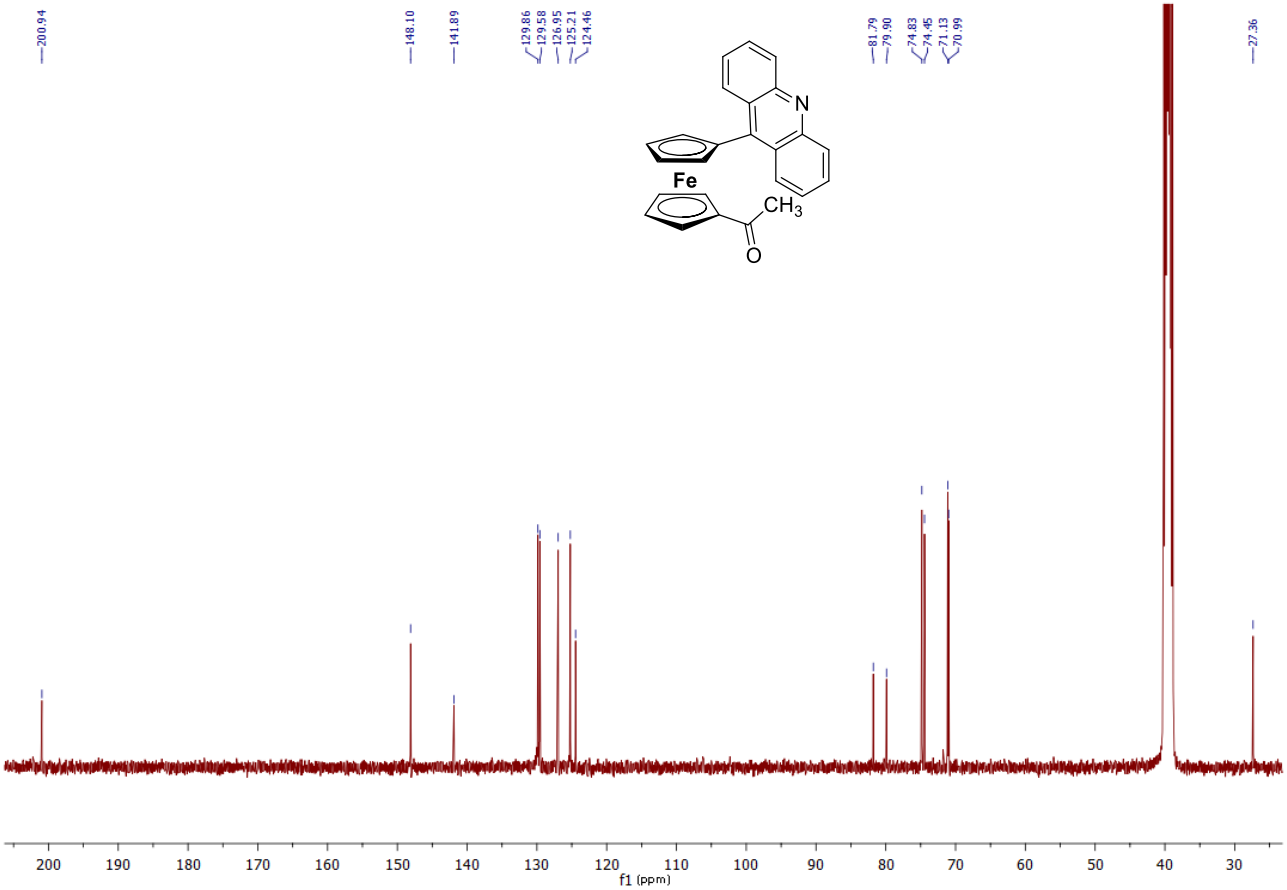

Figure S12 ^{13}C NMR spectrum of 1-acetyl-1'-(acridin-9-yl)ferrocene **2d**.

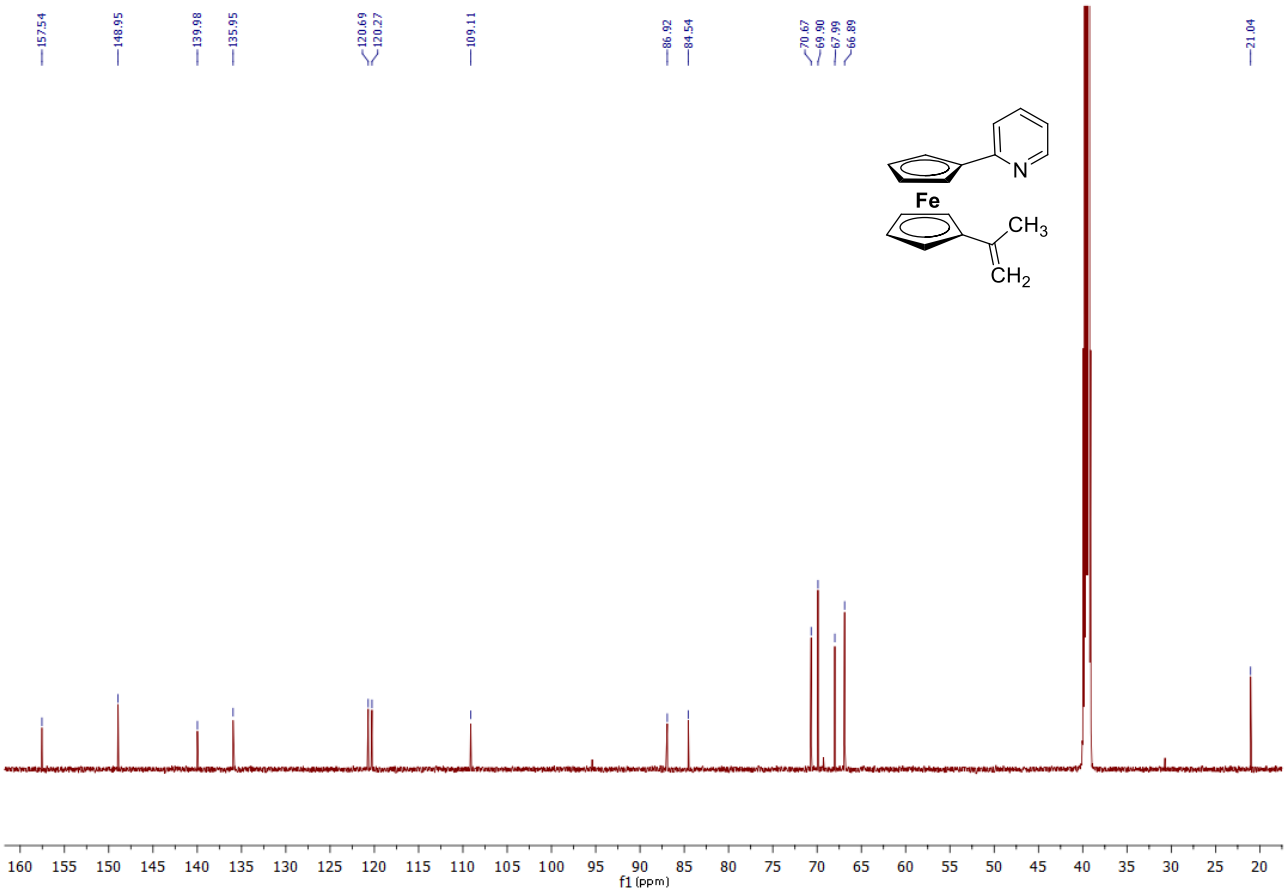

Figure S13 ^{13}C NMR spectrum of 1-isopropenyl-1'-(pyridin-2-yl)ferrocene **3a**.

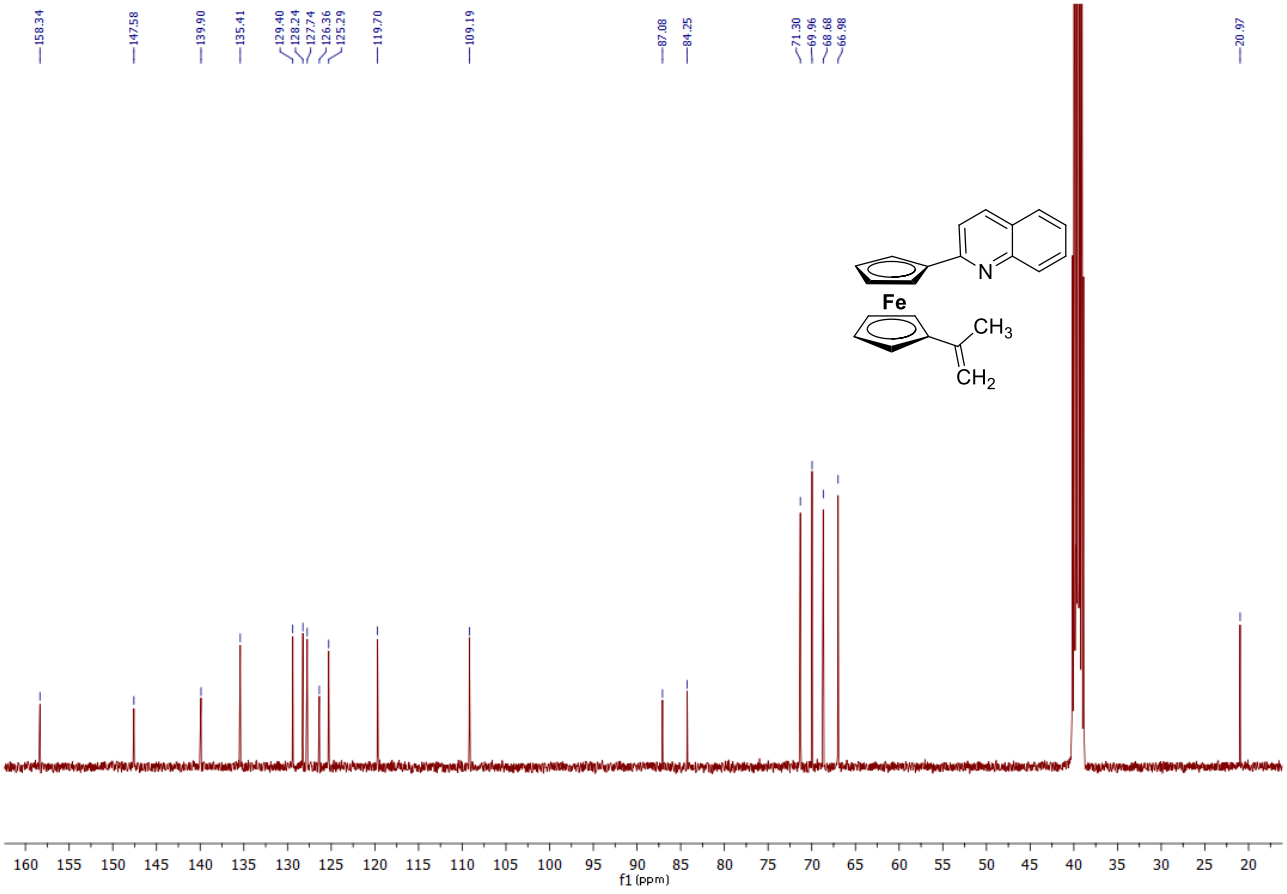

Figure S14 ^{13}C NMR spectrum of 1-isopropenyl-1'-(quinolin-2-yl)ferrocene **3b**.

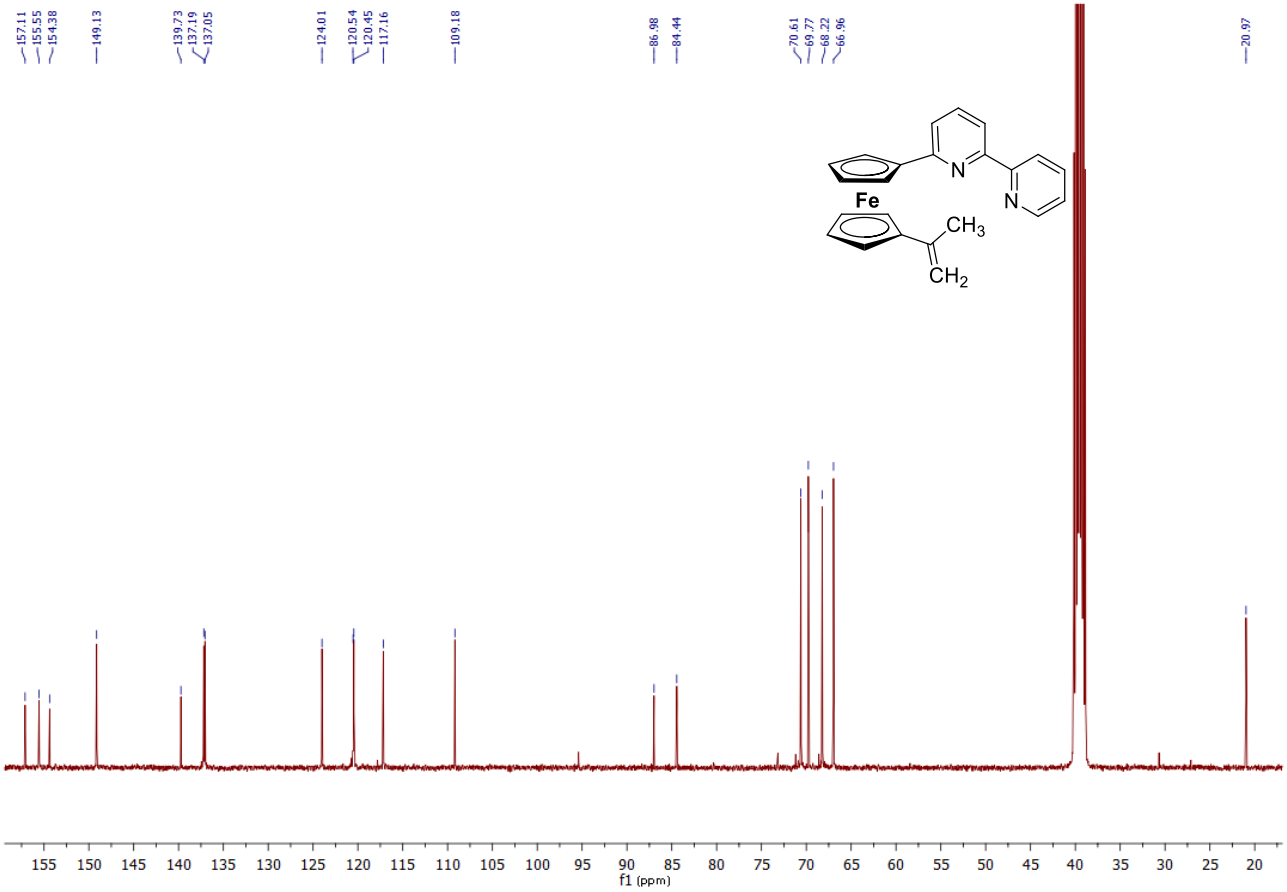

Figure S15 ^{13}C NMR spectrum of 1-isopropenyl-1'-(2",2"'-bipyridin-6-yl)ferrocene **3c**.

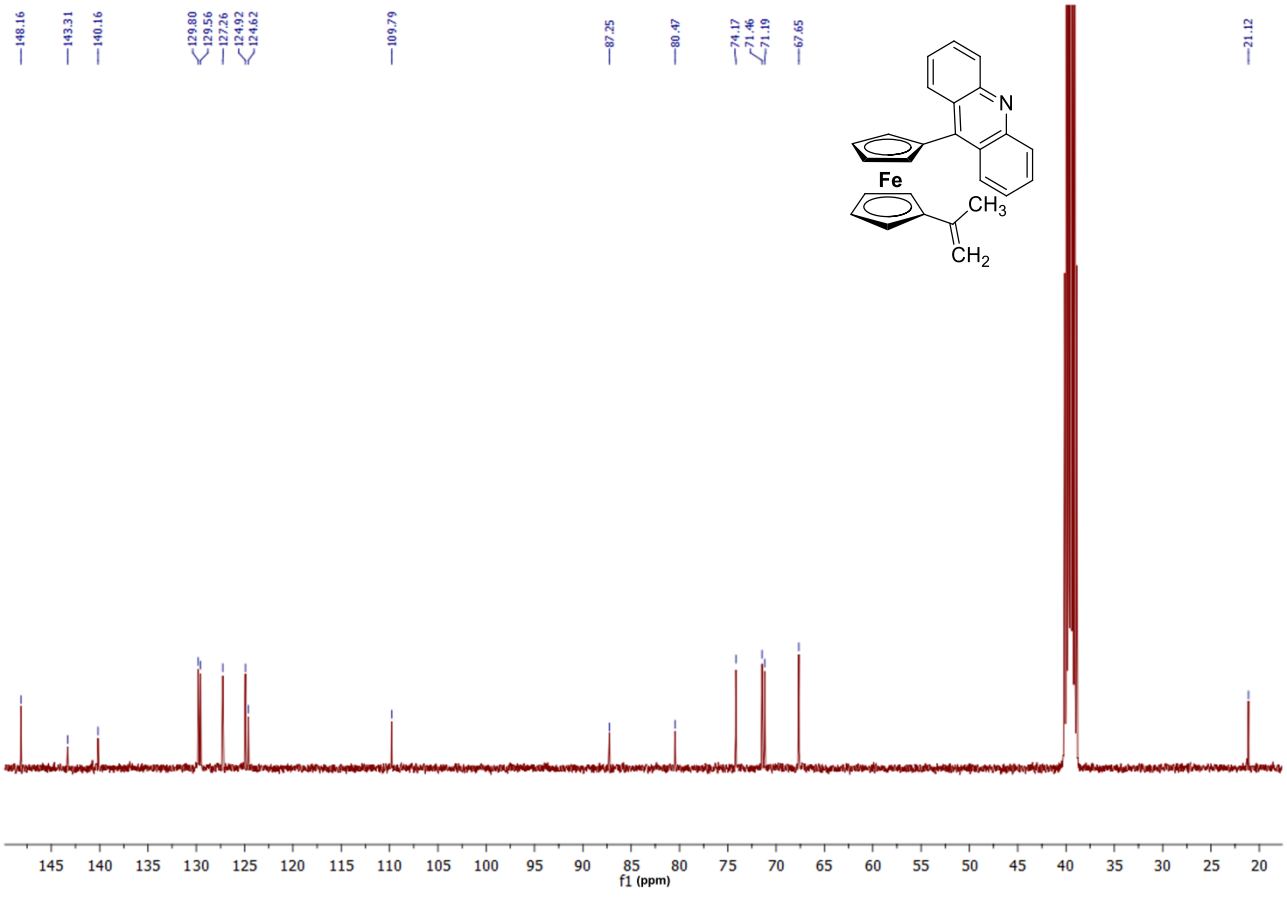

Figure S16 ^{13}C NMR spectrum of 1-isopropenyl-1'-(acridin-9-yl)ferrocene **3d**.