Electronic Supplementary Material (ESI) for RSC Advances

Supporting information
For

Functional Ionic liquid [bmim][Sac] Mediated Synthesis of Ferrocenyl Thiopropanones via "Dual Activation of Substrate by Ionic liquid"

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General remarks

All the reactions were carried out in oven-dried glassware. All the reagents and chemicals were purchased from Sigma-Aldrich or Merck chemical Co. and were used directly without any further purification. Progress of reactions was monitored by Thin Layer Chromatography (TLC). NMR spectra were recorded at 300 and 200 MHz (based on availability of instruments) 75 and 50 MHz (for ^{13}C) respectively on Bruker Avance DPX-300 MHz and Bruker Avance DPX-200 MHz. Chemical shifts are reported in δ (ppm) relative to TMS (^{1}H) or $CDCl_3$ (^{13}C) as internal standards. Integrals are in accordance with assignments; coupling constants are given in Hz.

General experimental procedure

Representative experimental procedure for the functional ionic liquid [bmim][Sac]:

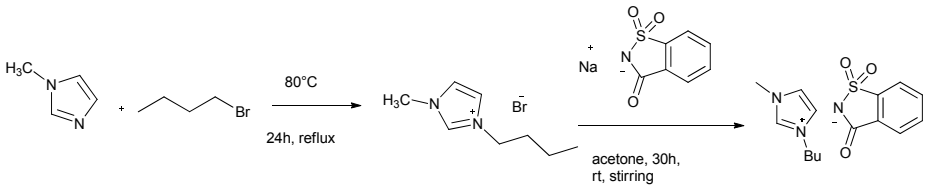


Figure 1 Representative procedure for synthesis of [bmim][Sac].

Experimental procedure for the synthesis of sodium saccharinate:

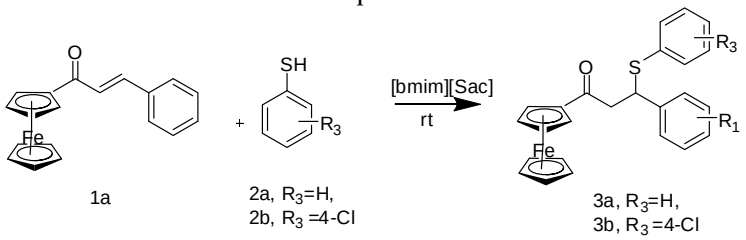
A three-neck 100 ml round bottom flask was fitted with overhead stirrer, condenser and inlet/outlet for nitrogen atmosphere. The flask was charged with 7.32 g saccharin (0.04 mol) and 2.16g (0.04 mol) anhydrous sodium methylate in 50 ml anhydrous methanol. The mixture was stirred and heated to reflux for about 10-20 minutes under nitrogen. Most of the solids went into solution. The system was then set-up for distillation. Methanol was removed under reduced pressure. Colorless solids of sodium saccharin (yield 90%) remained in the flask.

Representative experimental procedure for the [bmim][Sac]

The sodium saccharinate (27.0g, 0.112mol) was added into a solution of 1-*n*-butyl-3-methylimidazolium bromide [bmim][Br] (24.6 g , 0.112mol) in 100mL acetone at room temperature.

After stirring for 30 h, reaction mixture was filtered through a plug of celite. The volatiles were removed under reduced pressure overnight. Viscous oil was yielded with 31.0 g (86%). ^{1}H NMR (DMSOd_6, 300 MHz) δ = 9.17 (s, 1H); 7.89 (d, J = 5.4Hz, 1H), 7.78 (d, J = 2.0Hz, 4H), 7.71 (s, 1H), 4.18 (t, J = 7.2Hz, 2H), 3.85 (s, 1H), 1.80 (m, 2H), 1.28 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR (DMSOd_6, 50 MHz) δ = 164.7, 142.5, 136.5, 133.0, 131.5, 123.5, 122.2, 120.0, 48.4, 35.7, 31.3, 18.7, 13.2.

Table 1: Reaction of **1a** with **2a**/**2b** in the presence of various Bmim based Ionic Liquid[a]



1a

2a, R_3=H,
2b, R_3 =4-Cl

3a, R_3=H,
3b, R_3 =4-Cl

Entry	ILs	Mol[b] (%)	3a[c]	3b[d]
1	[bmim][Br]	10	20	20
2	[bmim][Br]	20	30	35
3	[bmim][BF_4]	10	10	12
4	[bmim][BF_4]	20	25	27
5	[bmim][PF_6]	10	10	11
6	[bmim][PF_6]	20	20	22
7	[bmim][Cl]	10	30	35
8	[bmim][Cl]	20	50	50
9	[bmim][NTf_2]	20	10	10
10	[bmim][OAc]	20	50	59
11	[bmim][$N(CN)_2$]	20	10	10
12	[bmim][N_3]	20	10	5
13	Imidazole	20	0	0
14	Saccharin	20	0	0
15	Na[Sac]	20	0	0
16	[bmim][Sac]	5	50	55
17	[bmim][Sac]	10	78	80
18	[bmim][Sac]	20	90	95

[a]1-Ferrocenyl-3-phenyl-2-propen-1-one (**1a**) (1 mmol) was reacted with thiophenol or 4-chlorothiophenol (**2a**/**2b**) (1.2 mmol) in the presence of the ionic liquid (20 mol %) for 15 min at rt. [b]amount of Ionic Liquid used with respect to **1a**. [c]Isolated yield of **3a**. [d]isolated yield of **3b**. The product was characterized by NMR and MS.

Typical procedure for thia Michael addition for synthesis of 1, 3-ferrocene substituted-3-(phenylthio) propan-1-one in presence of [bmim] [Sac]: A mixture of substituted ferrocenyl-enone (**1a-1p**, 1 mmol, 1 equiv.) and thiophenol / 4-chlorothiophenol (**2a**/**2b**, 1.2 mmol, 1.2 equiv.) was stirred at rt in presence of [bmim][Sac] (20 mol%, with respect to enone) for 15 min. After complete consumption of substituted ferrocenyl-enone (TLC) the mixture was diluted with diethyl ether (3 x

5mL), stirred and decanted. The diethyl ether layer was collected and extracted with water (3 × 5 mL). The combined diethyl ether extracts were dried ($NaSO_4$) and concentrated under vacuum. The crude product on crystallisation with ethanol afforded yellow solid.

Reusability of [bmim] [Sac]:

After completion of reaction (15 min), reaction mixture was diluted with diethyl ether (15 mL) followed by stirring and decantation. The diethyl ether layer was separated, extracted, dried ($NaSO_4$) and concentrated under vacuo to obtain crude product which on crystallisation (EtOAc-Hexane) afforded pure product. After decanting the diethyl ether IL layer was dried which was found to be identical (spectral data) with an authentic sample of [bmim][Sac] (unused ionic liquid), and organic mixture was added to start next run. It is interesting to note that recovered IL was reused for 4-5 succesive batches of reactions at rt to afford pure product after usual work-up and crystallisation (figure 2).

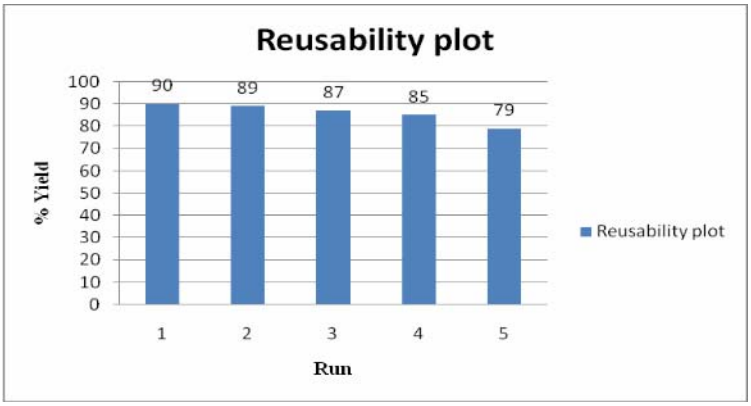


Figure 2 Reusability plot of [bmim][Sac]

Table 2: Reaction of **1a** with **2a/2b** in [bmim] based ionic liquid in the presence of various solvent[a]

Entry	Ionic liquid	Mol[b] (%)	Solvent	3a[c](yield)%	3b[d](Yield)%
1	[bmim][Sac]	20	Ethanol	-	-
2	[bmim][Sac]	20	Methanol	-	-
3	[bmim][Sac]	20	DMSO	-	-
4	[bmim][Sac]	20	Et_2O	-	-
5	[bmim][Sac]	20	MeCN	-	-

[a]1-Ferrocenyl-3-phenyl-2-enone (**1a**) (1 mmol) was reacted with thiophenol or 4-chlorothiophenol (**2a**/**2b**) (1.2mmol) in the presence of the [bmim][Sac] (20 mol %) for 2h at rt. [b]amount of ionic liquid used with respect to **1a**. [c]Isolated yield of **3a**. [d]isolated yield of **3b**.

Electrochemical analysis

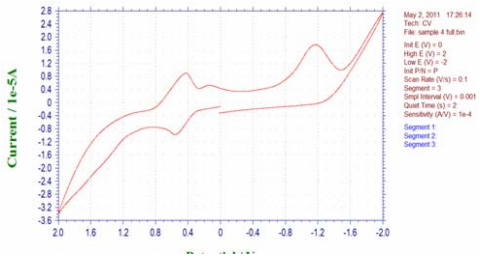


Figure 3. cyclic voltammogram of compound **3a**

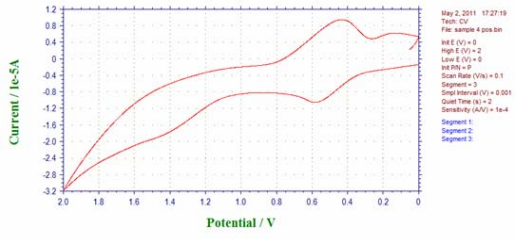


Figure 4. Cyclic voltammogram of compound **3a** showing reversible Fe Cp_2 $^{0/+}$ couple (+ve potential)

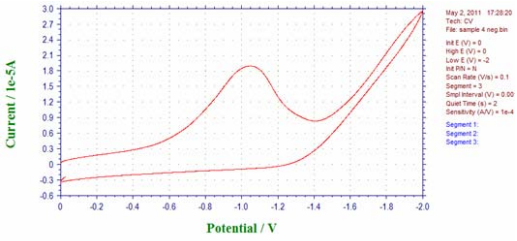


Figure 5. Cyclic voltammogram of compound **3a** showing irreversible reduction wave (-ve potential)

Electrochemical measurements were performed with a CHI 620c electrochemical analyzer. All measurements were carried out in a one-compartment cell under N_2 gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and a Ag/Ag+ reference electrode. The supported electrolyte was a 0.10 mol L^{-1} dichloromethane solution Bu_4NPF_6 at 100 mV/s (fig 3-5).

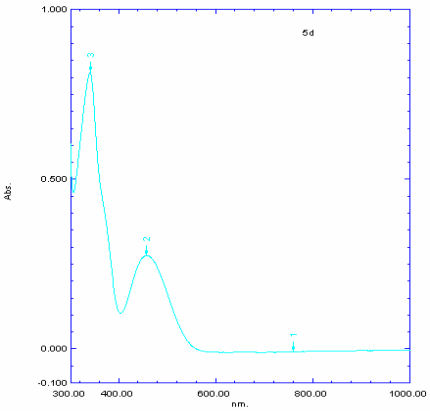


Figure 6. UV visible spectra of 3a

The UV-visible spectrum of **3a** recorded in Dichloromethane is consistent with most ferrocenyl chromophores in that they exhibit two charge-transfer bands in the visible region (figure 6).[1] The prominent band at 300-400 nm, is assigned to a ligand-centred n-π* electronic transition (L-π*), attributed to a charge transfer (CT) from the donor sulphur group to the acceptor carbonyl group and the less energetic and weaker band at 400-500nm (LE), responsible for the bright orange colour of this compound, is attributed to a metal-to-ligand charge-transfer (MLCT) process (d_{π}-π*). This assignment is in accordance with the latest theoretical treatment (model III) reported by *Barlow et. al.*[2]

Mass spectrum of sample after 15 min of treatment/mixing of 1j and 2a with [bmim][Sac]:

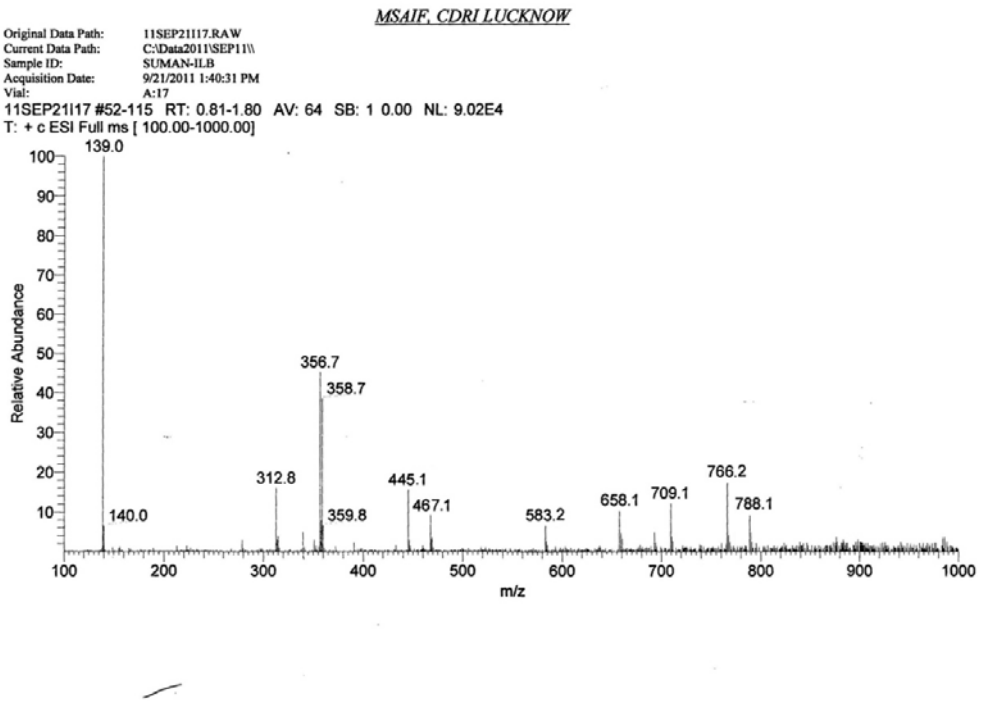


Figure 7. TIC of (+ve) ESI MS of sample withdrawn after 15 min for the reaction of **1j** with **2a** catalyzed by [bmim][Sac].

We performed (+ve) ESI MS studies on aliquots of samples withdrawn after 15 min from the [bmim] [Sac] catalyzed reaction of **1j** with **2a.** The total ion chromatogram (TIC) revealed the presence of ions at *m*/*z* 788.1 (m1), 766.2 (m2), 709.1 (m3), 583.2 (m4) 467.1(m5) 445.1(m6), corresponding to [**A/B** + Na+], [**A/B**+H+], [**A/B**+ - Bu], **[A/B+** - Sac], [Product + Na+], [Product + H+], respectively (Fig 7), which supports the formation of supramolecular assembly A/B**.**

Materials and method for *in vitro* antiproliferative screening: The human cancer cell lines- KB (oral squamous cell carcinoma), C33A (cervical carcinoma), MCF-7 (breast adenocarcinoma), A549 (lung carcinoma) and mouse embryo fibroblast (NIH3T3) were obtained from American Type Culture Collection (ATCC), USA. These cells were grown in recommended media supplemented with 10% FBS, 50 µg/mL gentamycin and 2.5 µg/mL amphotericin B in a 5% CO_2 humidified atmosphere at 37ºC. Cells below 15 passage level was used for this study.

Table 3. Results of the *in vitro* antiproliferative activity of compounds belonging to Scheme 1-3

S no	Comp.	IC_{50}(µg/ml)				
		KB	**C-33A**	**MCF-7**	**A549**	**NIH3T3**
1	**3a**	**5.82**	**13.7**	**28.59**	**26.77**	**28.98**
2	**3b**	29.98	NA	35.18	35.01	NA
3	**3c**	NA	43.53	NA	30.28	NA
4	**3d**	24.07	20.08	NA	22.77	NA
5	**3e**	27.26	NA	38.26	46.67	27.88
6	**3f**	23.34	27.26	NA	38.26	46.67
7	**3g**	19.68	15.16	29.73	21.27	39.69
8	**3h**	24.69	13.59	16.25	27.54	11.12
9	**3i**	**5.18**	**14.95**	**10.89**	**8.77**	**9.73**
10	**3j**	36.57	40.48	NA	NA	NA
11	**3k**	**5.22**	**3.77**	**8.59**	**12.77**	**9.98**
12	**3l**	16.56	24.48	26.25	17.54	11.12
13	**3m**	23.8	NA	NA	NA	NA
14	**3n**	27.68	NA	19.73	11.27	9.69
15	**3o**	27.26	32.32	38.26	46.67	27.54
16	**3p**	**6.22**	**7.77**	**5.59**	**8.77**	**8.98**
17	Doxorubicin	0.199	0.28	0.456	0.33	ND

IC_{50} = Compound concentration required to inhibit tumor cell proliferation by 50%. Data are expressed as mean from the dose response curves of at least two independent experiments with three determinations in each. NA = not active, that is, the IC_{50} is greater than 50 µM. ND = not determined.

A colorimetric sulforhodamine B assay was used for the measurement of cell cytotoxicity. 1 x 10^4 cells (in 180 µL) were added to each well of 96-well plate and incubated overnight to allow for cell attachment. Cells were then treated with serial two-fold dilutions of test compounds (100 to 1.6 µg/mL) and untreated cells receiving the same volume of medium served as control. After 48h of

exposure, cells were fixed with ice-cold 50% TCA, stained with 0.4% (w/v) SRB in 1% acetic acid, washed and air dried. Bound dye was dissolved in 150 µL of 10 mM tris base. The plates were read at 540 nm absorbance on plate reader (Polarstar Galaxy, BMG, Germany). The cytotoxic effects of compounds were calculated as percentage inhibition in cell growth as per the formula [100 - (absorbance of compound treated cells/absorbance of untreated cells)] x 100.

Characterisation data of all the synthesized compounds

1-Ferrocenyl-3-phenyl-3-(phenylthio)-propan-1-ones (3a) : 90% as a yellow solid; mp 112-115°C; IR (KBr) 1689 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ = 7.43 (d, J = 7.2Hz, 2H, ArH), 7.37 (d, J = 6.5Hz, 2H, ArH), 7.30 (m, 6H, ArH), 5.01 (q, J = 5.2Hz, 1H, CH), 4.72 (d, J = 7.4Hz, 2H, FcH), 4.46 (s, 2H, FcH), 3.96 (s, 5H, FcH), 3.44 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75MHz) δ = 200.7, 141.6, 134.9, 132.2, 129.0, 128.6, 128.1, 127.6, 127.4, 78.8, 72.5, 69.8, 69.4, 69.2, 47.7, 46.3; MS (ESI^+) *m/z*: = 427.1 $(M+H)^+$ ESI-HR-MS: *m/z*: = 427.0813. calcd. for $C_{25}H_{22}FeOS$ $[MH]^+$: = 427.0819.

3-(4-Chlorophenylthio)-1-Ferrocenyl-3-phenylpropan-1-one (3b): 95% as a yellow solid; mp 115-122°C; IR (KBr) 1680 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.40 (d, J = 7.1Hz, 2H, ArH), 7.30 (m, 7H, Ar-H), 4.96 (q, J = 5.6Hz, 1H, CH), 4.73 (d, J = 8.3Hz, 2H, Fc-H), 4.47 (s, 2H, Fc-H), 3.98 (s, 5H, Fc-H), 3.41-3.18 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75MHz) δ = 200.4, 141.5, 133.6, 133.5, 133.3, 129.1, 128.7, 128.1, 127.7, 78.7, 72.6, 72.5, 69.8, 69.4, 69.2, 48.1, 46.1; MS (ESI^+) *m/z*: = 461.1 $(M+H)^+$. ESI-HR-MS: *m/z*: = 461.0432. calcd. for $C_{25}H_{21}ClFeOS$ $[MH]^+$: = 461.0429.

3-(4-Chlorophenylthio)-3-(4-chlorophenyl)-Ferrocenylpropan-1-one (3c): 87% as a yellow solid; mp 122-125°C; IR (KBr) 1696 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ = 7.41 (d, J = 8.6Hz, 2H, ArH), 7.32 (m, 6H, ArH), 4.91 (t, J = 6.2Hz, 1H, CH), 4.72 (s, 2H, Fc-H), 4.50 (d, J = 1.8Hz, 2H, Fc-H), 4.03 (s, 5H, Fc-H), 3.35-3.18 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 50MHz) δ = 200.2, 140.2, 135.2, 133.9, 133.3, 132.7, 129.4, 129.2, 128.8, 78.5, 72.7, 69.9, 69.4, 69.2, 47.7, 45.9; MS (ESI^+) *m/z*: = 496.1 $(M+H)^+$. ESI-HR-MS: *m/z*: = 495.0143.calcd. for $C_{25}H_{20}Cl_2FeOS$ $[MH]^+$: = 495.0040.

3-(4-Chlorophenyl)-1-Ferrocenyl-3-(phenylthio)-propan-1-one (3d): 80% as a yellow solid; mp 120-122°C; IR (KBr) 1695 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.51 (d, J = 7.3Hz, 2H, ArH), 7.35 (t, J = 7.8Hz, 6H, Ar-H), 7.22 (m, 1H, ArH), 4.95 (t, J = 6.4Hz, 1H, CH), 4.71 (s, 2H, Fc-H), 4.48 (s, 2H, Fc-H), 4.01 (s, 5H, Fc-H), 3.31 (t, J = 7.56Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 50MHz) δ = 200.5, 140.4, 134.3, 133.2, 132.6, 129.5, 129.2, 129.1, 128.7, 127.6, 127.3, 78.6, 72.6, 69.9, 69.3, 47.3, 46.0; MS (ESI^+) *m/z*: = 461.1 $(M+H)^+$. ESI-HR-MS: *m/z*: = 461.0423, calcd. for $C_{25}H_{21}ClFeOS$ $[MH]^+$: = 461.0429.

1-Ferrocenyl-3-(4-nitrophenyl)-3-(phenylthio)propan-1-one (3e): 85% as a yellow solid; mp 112-120°C; IR (KBr) 1694 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ = 8.27 (s, 1H, ArH), 8.06 (d, J =

7.2Hz, 1H, ArH), 7.67 (d, *J* = 7.7Hz, 1H, ArH), 7.44 (t, *J* = 8.0Hz, 1H, ArH), 7.34 (d, *J* = 3.2Hz, 2H, ArH), 7.24 (s, 3H, ArH), 5.04 (t, *J* = 6.7Hz, 1H, CH), 4.74 (d, *J* = 1.2Hz, 2H, Fc-H), 4.50 (s, 2H, Fc-H), 4.01 (s, 5H, Fc-H), 3.39 (m, 2H, CH_2); MS (ESI^+) *m/z*: = 472.1 $(M+H)^+$. ESI-HR-MS: *m/z*: = 472.0772. calcd. for $C_{25}H_{21}FeNO_3S$ $[MH]^+$: = 472.0670.

3-(2-Bromophenyl)-3-(4-chlorophenylthio)-1-Ferrocenyl propan-1-one (3f): 79% as a yellow solid; mp 105-110°C; IR (KBr) 1681 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ = 7.55 (d, *J* = 7.6Hz, 2H, ArH), 7.29 (m, 5H, ArH), 7.10 (t, *J* = 7.2Hz, 1H, ArH), 5.42(t, *J* = 6.8Hz, 1H, CH), 4.76 (s, 2H, Fc-H), 4.49 (s, 2H, Fc-H), 4.11 (s, 5H, Fc-H), 3.43-3.23 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75MHz) δ = 200.1, 144.0, 135.3, 134.0, 133.8, 132.6, 130.9, 130.8, 130.1, 129.5, 129.4, 129.2, 127.1, 122.8, 78.5, 72.7, 72.6, 69.9, 69.4, 69.2, 47.7, 45.9; MS (ESI^+) *m/z*: = 539.1 $(M+H)^+$. ESI-HR-MS: *m/z*: =538.9597. calcd. for $C_{25}H_{20}BrClFeOS$ $[MH]^+$: = 538.9534.

3-(4-Chlorophenylthio)-3-(4-methoxyphenyl)-Ferrocenylpropan-1-one (3g): 85% as a yellow solid; mp 142-145°C; IR (KBr) 1680 (C=O) cm^{-1}; ^1H NMR($CDCl_3$, 300MHz) δ = 7.31 (m, 6H, ArH), 6.82 (d, *J* = 8.6Hz, 2H, Ar-H), 4.93 (q, *J* = 5.4Hz, 1H, CH), 4.72 (d, *J* = 5.7Hz, 2H, FcH), 4.47 (s, 2H, FcH), 4.00 (s, 5H, FcH), 3.74 (s, 3H, OCH_3), 3.37-3.15 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75MHz) δ = 200.6, 159.1, 133.6, 133.5, 133.5, 133.4, 129.2, 129.1, 114.1, 78.8, 72.6, 72.5, 69.9, 69.4, 69.2, 55.4, 47.6, 46.2; MS (ESI^+) *m/z*: = 491.1 $(M+H)^+$. ESI-HR-MS: *m/z*: = 491.0531. calcd. for $C_{26}H_{23}ClFeO_2S$ $[MH]^+$: = 491.0535.

3-(4-Chlorophenylthio)-3-(4-fluorophenyl)-Ferrocenylpropan-1-one (3h): 89% as a yellow solid; mp 125-130°C; IR (KBr) 1687 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ = 7.37 (q, *J* = 5.5Hz, 2H, ArH), 7.22 (m, 3H, ArH), 6.99 (t, *J* = 8.6Hz, 2H, ArH), 4.93 (q, *J* = 5.8Hz, 1H, CH), 4.72 (s, 2H, FcH), 4.49 (s, 2H, Fc-H), 4.01 (s, 5H, Fc-H), 3.36-3.18 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 50MHz) δ = 200.4, 137.3, 133.9, 132.9, 129.8, 129.2, 115.8, 115.3, 78.6, 72.7, 69.9, 69.4, 69.3, 47.5, 46.1; MS (ESI^+) *m/z*: = 479.3 $(M+H)^+$. ESI-HR-MS: *m/z*: = 479.0332. calcd. for $C_{25}H_{20}ClFFeOS$ $[MH]^+$: = 479.0335.

1-Ferrocenyl-3-(4-methoxyphenyl)-3-(phenylthio)-propan-1-one (3i): 87% as a yellow solid; mp 120-128°C; IR (KBr) 1686 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ = 7.35 (m, 7H, ArH), 6.83 (d, *J* = 8.1Hz, 2H, Ar-H), 4.97 (t, *J* = 4.8Hz, 1H, CH), 4.71 (d, *J* = 7.1Hz, 2H, FcH), 4.45 (s, 2H, FcH), 3.98 (s, 5H, FcH), 3.74 (s, 3H, OCH_3), 3.40-3.17 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75MHz) δ = 200.9, 159.0, 135.0, 133.5, 132.2, 129.2, 129.0, 127.3, 114.0, 78.8, 72.5, 69.8, 69.4, 69.2, 55.4, 47.2, 46.4; MS (ESI^+) *m/z*: = 457.1 $(M+H)^+$. ESI-HR-MS: *m/z*: = 457.0992. calcd. for $C_{26}H_{24}FeO_2S$ $[MH]^+$: = 457.0925.

1-Ferrocenyl-3-(4-Fluorophenyl)-3-(phenylthio)propan-1-one (3j): 88% as a yellow solid; mp 140-142°C; IR (KBr) 1679 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.37 (m, 7H, ArH), 7.00 (t,

J = 8.0Hz, 2H, Ar-H), 4.98 (s, 1H, CH), 4.73 (s, 2H, Fc-H), 4.49 (s, 2H, Fc-H), 4.00 (s, 5H, Fc-H), 3.41-3.24 (m, 2H, CH_2); MS (ESI^+) m/z: = 445.1 $(M+H)^+$. ESI-HR-MS: *m/z*: = 445.0788. calcd. for $C_{25}H_{21}FFeOS$ $[MH]^+$:= 445.0725.

1-Ferrocenyl-3-(2-methylphenyl)-3-(phenylthio)-propan-1-one (3k): 89% as a yellow solid; mp 132-138°C; IR (KBr) 1702 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ = 7.38 (m, 7H, ArH), 7.10 (d, *J* = 7.6Hz, 2H, ArH), 4.99 (q, *J* = 5.4Hz, 1H, CH), 4.71 (d, *J* = 6.4Hz, 2H, Fc-H), 4.45 (s, 2H, Fc-H), 3.97 (s, 5H, Fc-H), 3.41-3.12 (m, 2H, CH_2), 2.27 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75MHz) δ = 200.8, 138.4, 137.2, 135.0, 132.0, 129.1, 128.9, 127.9, 127.2, 78.7, 72.3, 69.8, 69.3, 69.1, 47.3, 46.3, 21.1; MS (ESI^+) *m/z*: = 441.3 $(M+H)^+$. ESI-HR-MS: *m/z*: = 441.0974, calcd. for $C_{26}H_{24}FeOS$ $[MH]^+$:= 441.0976.

3-(4-Chloro-phenylthio)-1-ferrocenyl-3-(2-methylphenyl)-propan-1-one (3l): 83% as a yellow solid; mp 132-138°C IR (KBr) 1700 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ = 7.29 (m, 6H, ArH), 7.10 (d, *J* = 7.7Hz, 2H, ArH), 4.94 (t, *J* = 5.3Hz, 1H, CH), 4.72 (d, *J* = 6.2Hz, 2H, Fc-H), 4.47 (s, 2H, Fc-H), 3.99 (s, 5H, Fc-H), 3.38-3.16 (m, 2H, CH_2), 2.27 (s, 3H, CH_3); MS (ESI^+) *m/z*: = 475.2 $(M+H)^+$. ESI-HR-MS: *m/z*: = 475.0551. calcd. for $C_{26}H_{23}ClFeOS$ $[MH]^+$:= 475.0586.

3-Ferrocenyl-(3-phenylthio)-1-phenyl-propan-1-one (3m): 86% as a yellow solid; mp 110-115°C; IR (KBr) 1689 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ = 7.95 (d, *J* = 7.3Hz, 2H, ArH), 7.60 (t, *J* = 7.3Hz, 1H, ArH), 7.49 (t, *J* = 7.6Hz, 2H, ArH), 7.34 (d, *J* = 3.3Hz, 2H, ArH), 7.26 (t, *J* = 3.9Hz, 3H, ArH), 4.85 (t, *J* = 6.2Hz, 1H, CH), 4.13 (m, 9H, Fc-H), 3.57 (d, *J* = 5.6Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 50MHz) δ = 197.8, 137.1, 134.4, 133.6, 133.4, 128.9, 128.8, 128.3, 127.7, 90.1, 68.9, 68.0, 67.8, 67.0, 44.6, 44.0; MS (ESI^+) *m/z*: = 427.2 $(M+H)^+$. ESI-HR-MS: *m/z*: = 427.0872, calcd. for $C_{25}H_{22}FeOS$ $[MH]^+$: = 427.0819.

3-Ferrocenyl-1-(4-fluorophenyl)(3-phenylthio)-propan-1-one (3n): 76% as a yellow solid; mp 118-125C IR (KBr) 1680 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ = 7.97 (q, *J* = 5.5Hz, 2H, ArH), 7.34 (d, *J* = 3.4Hz, 2H, ArH), 7.25 (t, *J* = 3.2Hz, 3H, ArH), 7.15 (t, *J* = 8.5Hz, 2H, ArH), 4.82(t, *J* = 6.3Hz, 1H, CH), 4.13 (m, 9H, Fc-H), 3.53 (d, *J* = 6.4Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 50MHz) δ = 196.3, 134.3, 133.6, 131.1, 130.9, 128.9, 127.8, 116.1, 115.7, 90.0, 69.0, 68.1, 67.9, 67.1, 44.5, 44.2; MS (ESI^+) *m/z*: = 445.1 $(M+H)^+$. ESI-HR-MS: *m/z*: = 445.0721.calcd. for $C_{25}H_{21}FFeOS$ $[MH]^+$: = 445.0725.

3-(4-Chlorophenylthio)-3-ferrocenyl-1-(4-fluorophenyl)-propan-1-one (3o): 87% as a yellow solid; mp 125-130°C IR (KBr) 1692 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ = 7.99 (q, *J* = 5.3Hz, 2H, ArH), 7.26 (m, 6H, ArH), 4.74 (s, 1H, CH), 4.15 (m, 9H, Fc-H), 3.51 (d, *J* = 5.9Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 50MHz) δ = 196.0, 135.2, 134.1, 133.5, 132.6, 131.0, 130.9, 129.0, 116.2, 115.7, 89.8, 69.0, 68.2, 68.0, 66.9, 44.5, 44.2; MS (ESI^+) *m/z:* = 479.1 $(M+H)^+$. ESI-HR-MS: *m/z*: = 479.0338. calcd. for $C_{25}H_{20}ClFFeOS$ $[MH]^+$: = 479.0335.

1,3-Bisferrocenyl-3-(phenylthio)-propan-1-one (3p): 67% as a yellow solid, mp 130-135°C; IR (KBr) 1699 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300MHz) δ = 7.45 (d, J = 6.7Hz, 2H, ArH), 7.29 (d, J = 7.9Hz, 4H, ArH), 4.85 (m, 3H, CH and Fc-H), 4.50 (s, 2H, Fc-H), 4.15 (m, 14H, Fc-H), 3.29 (d, J = 5.5Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 50MHz) δ = 200.5, 139.4, 135.2, 133.0, 129.0, 127.5, 114.2, 90.3, 79.1, 72.5, 70.0, 69.5, 69.0, 68.0, 67.7, 67.6, 46.3, 43.5; MS (ESI^+) *m/z:* = 535.2 $(M+H)^+$. ESI-HR-MS: *m/z*: = 535.0463, calcd. for $C_{29}H_{26}Fe_2OS$ $[MH]^+$: = 535.0481.

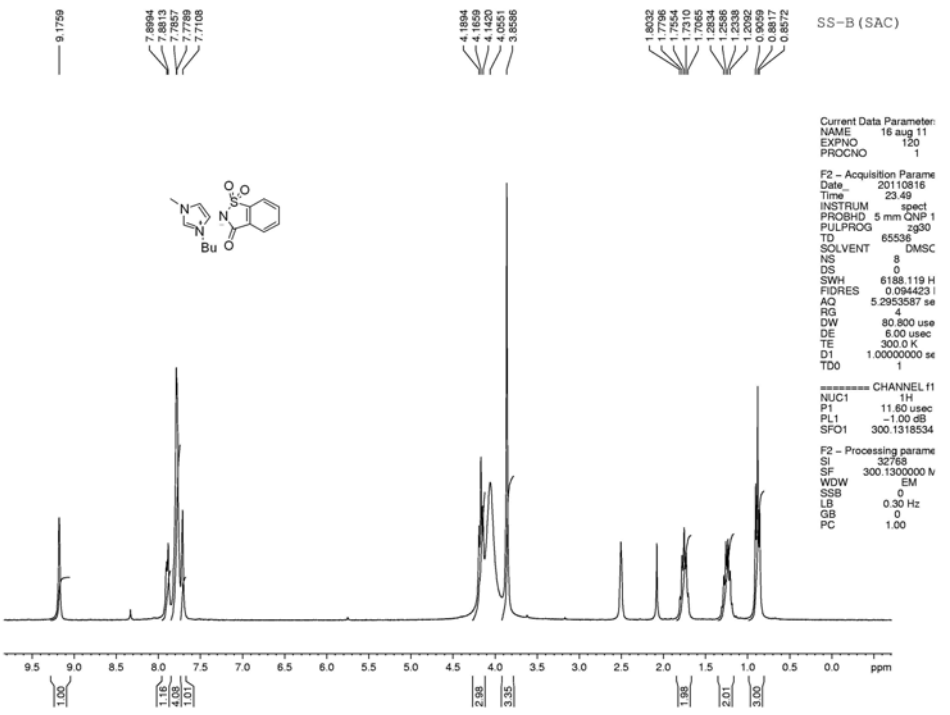


Fig 8. ^{1}H-NMR spectrum of [Bmim][Sac] in DMSO-d_6($CDCl_3$, 300MHz).

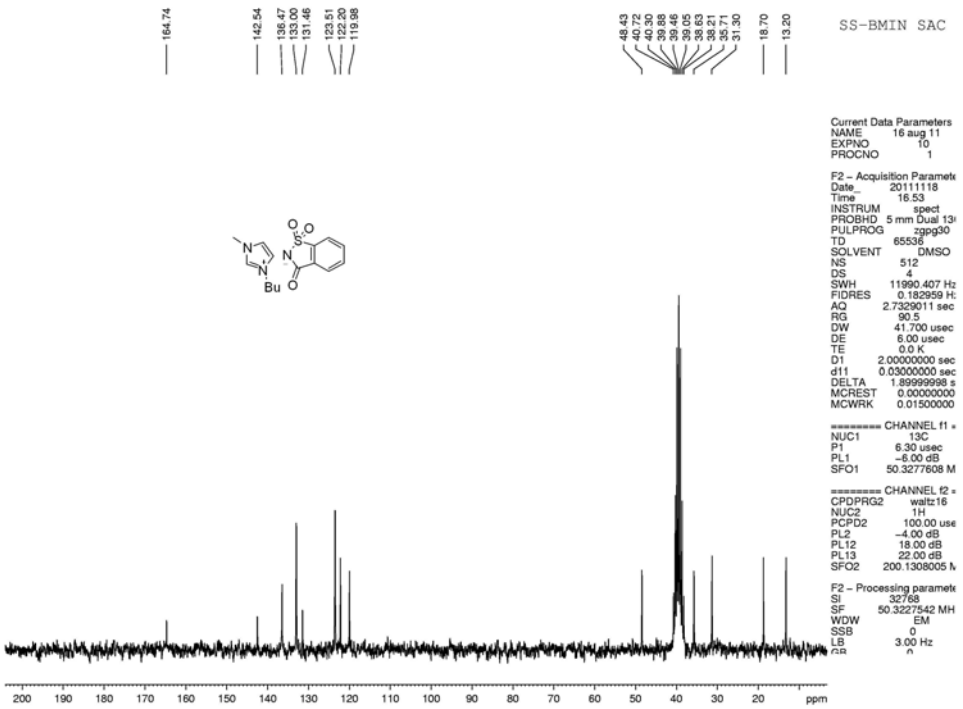


Fig 9. ^{13}C-NMR spectrum of [Bmim][Sac] in DMSO-d_6 ($CDCl_3$, 50MHz).

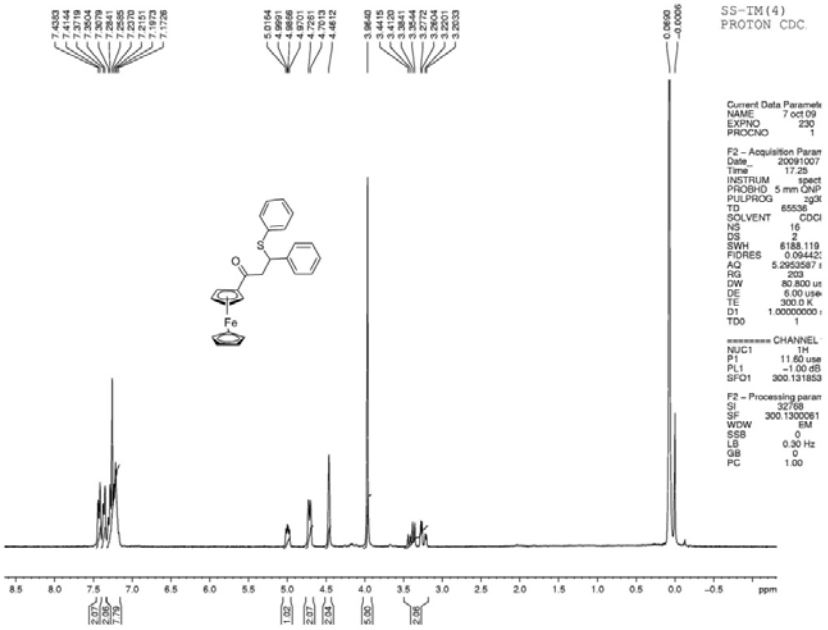


Fig 10. ^{1}H NMR spectrum of 3a ($CDCl_3$, 300MHz)

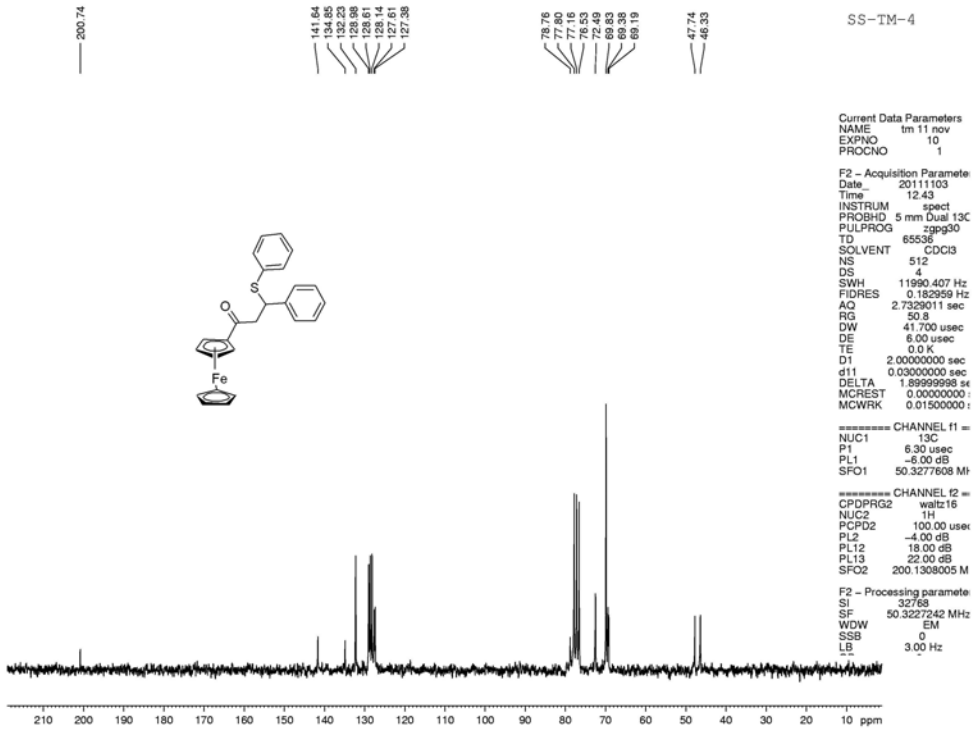


Fig 11. ^{13}C NMR spectrum of 3a ($CDCl_3$, 50MHz)

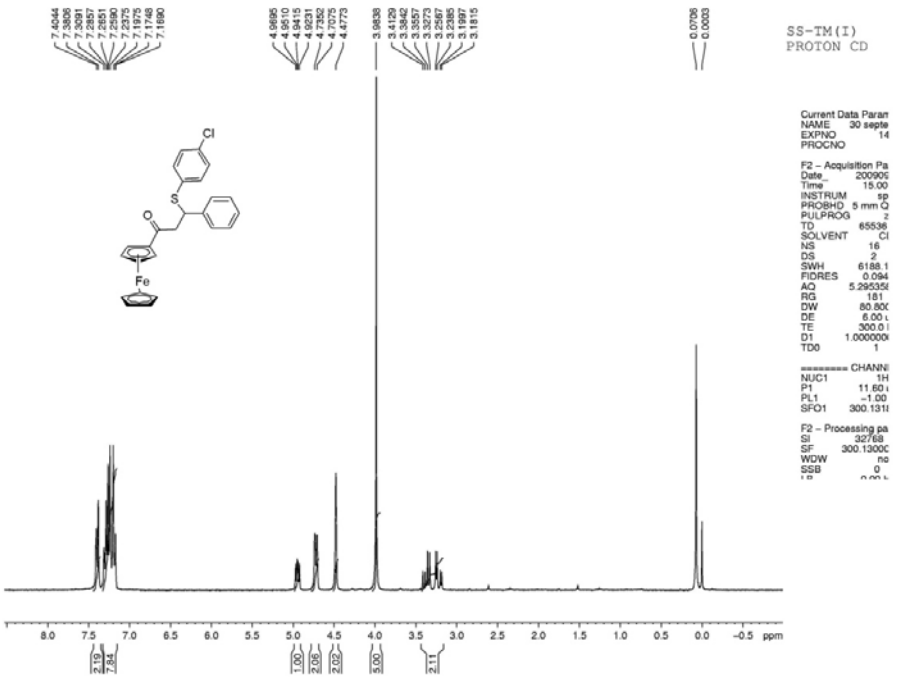


Fig 12. ^{1}H NMR spectrum of 3b ($CDCl_3$, 300MHz)

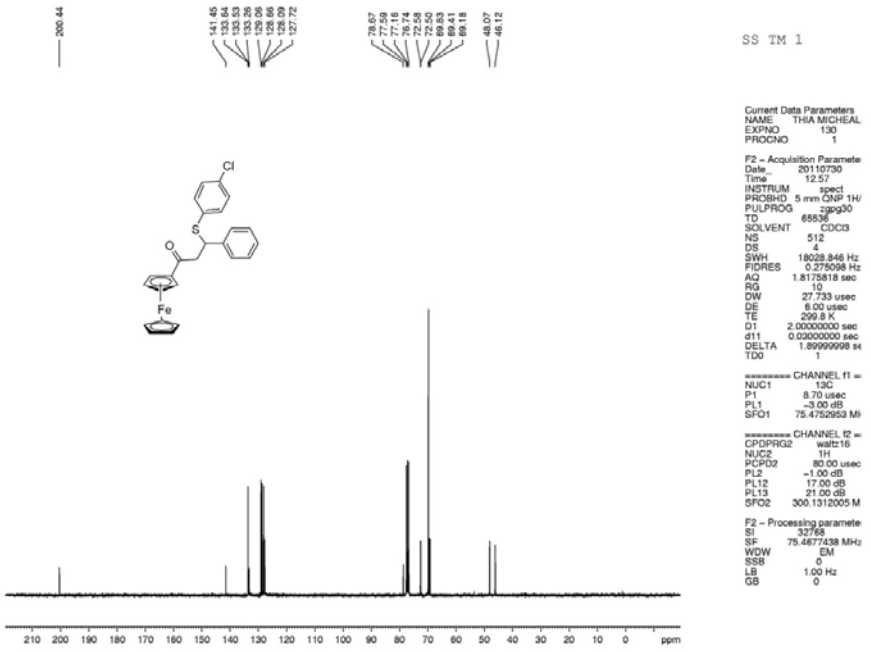


Fig 13. ^{13}C NMR spectrum of 3b ($CDCl_3$, 75MHz)

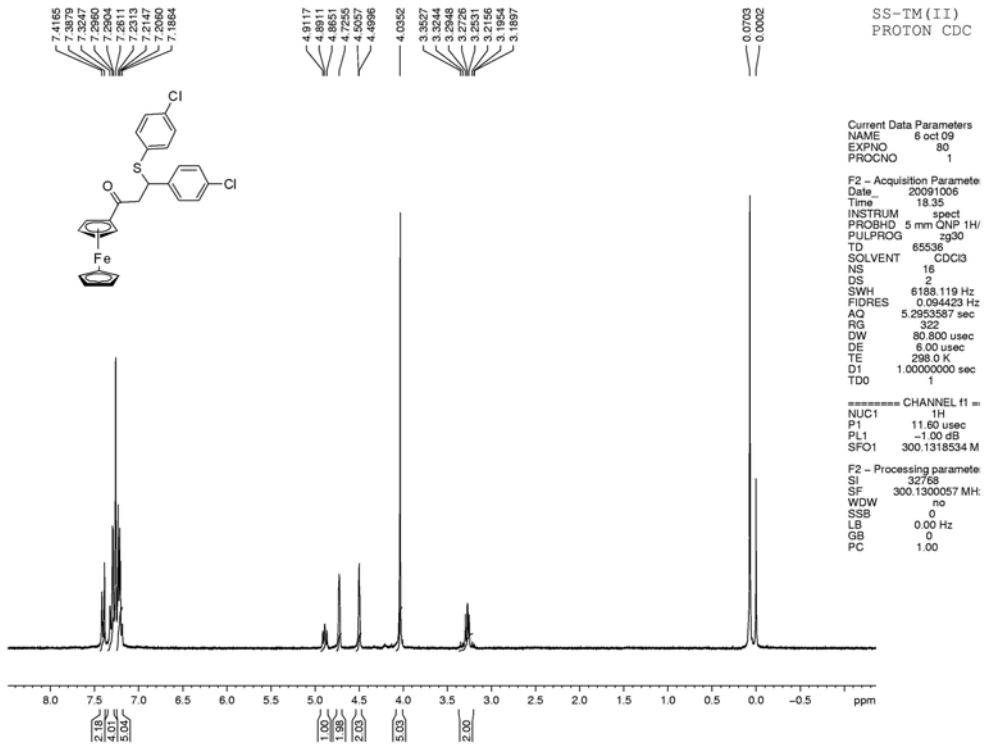


Fig 14. ^{1}H NMR spectrum of 3c ($CDCl_3$, 300MHz)

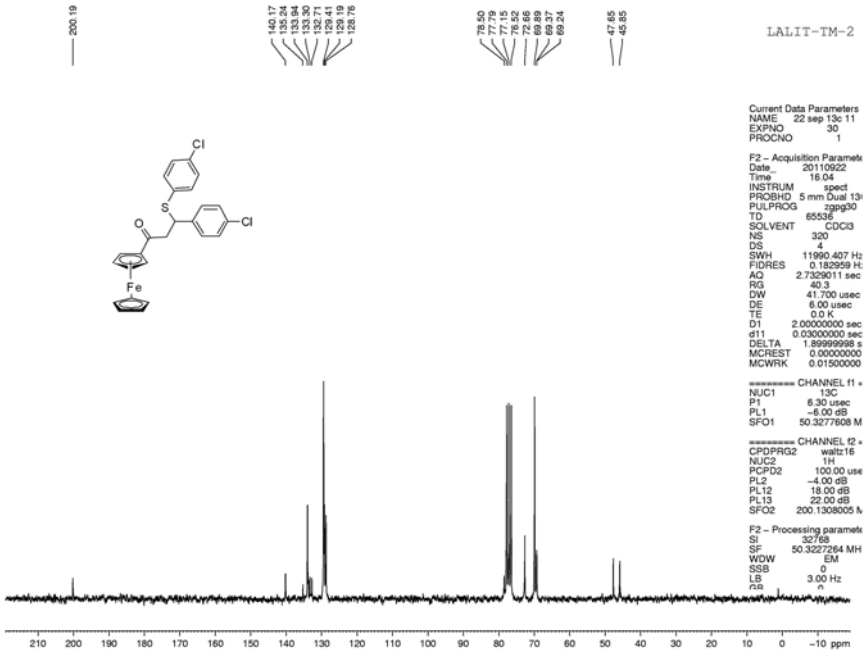


Fig 15. ^{13}C NMR spectrum of 3c ($CDCl_3$, 50MHz)

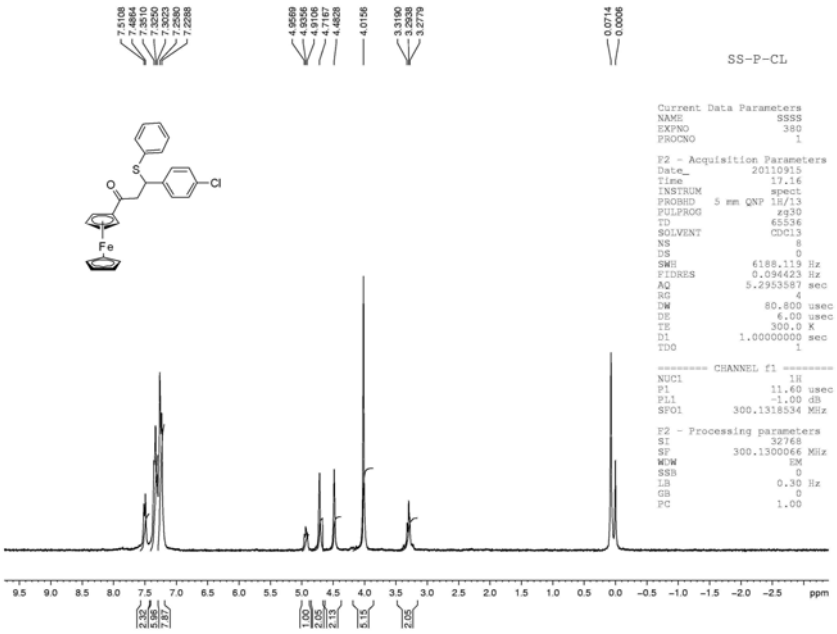


Fig 16. ^{1}H NMR spectrum of 3d ($CDCl_3$, 300MHz)

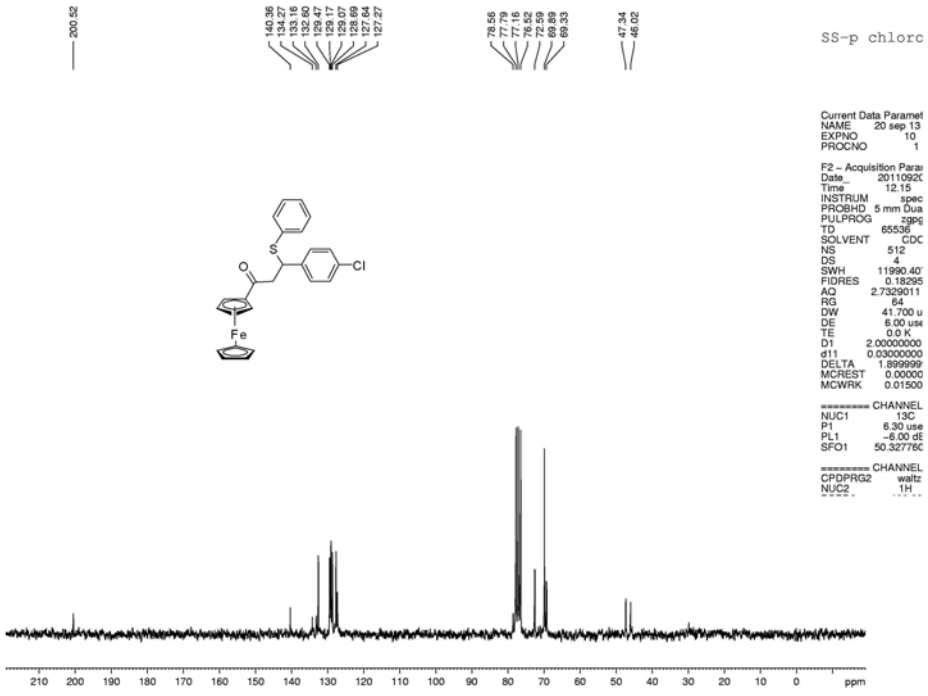


Fig 17. ^{13}C NMR spectrum of 3d ($CDCl_3$, 50MHz)

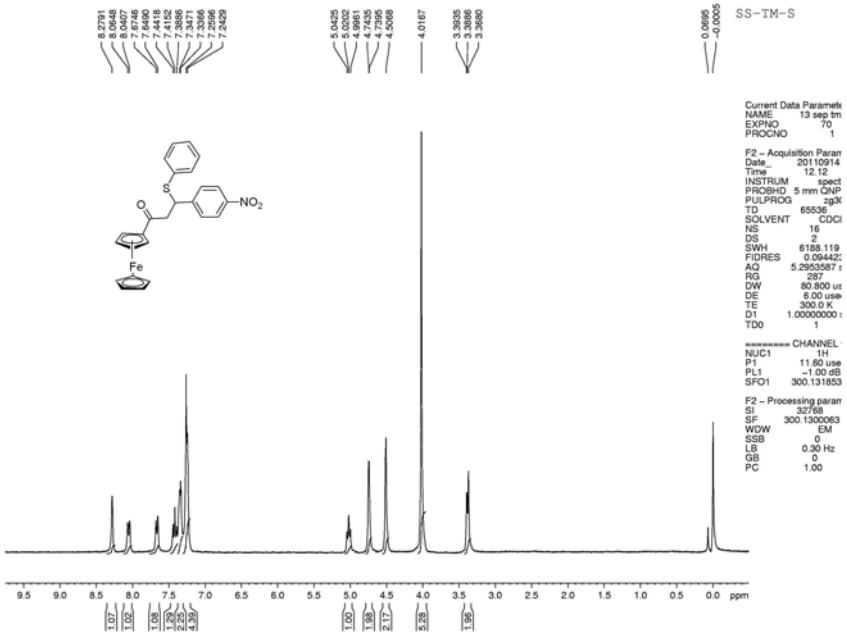


Fig 18. ^{1}H NMR spectrum of 3e ($CDCl_3$, 300MHz)

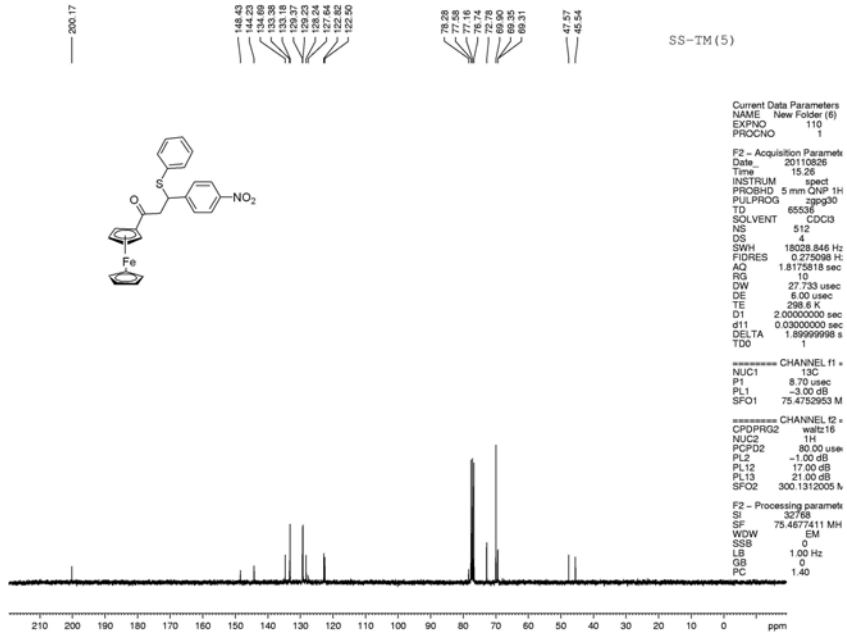


Fig 19. ^{13}C NMR spectrum of 3e ($CDCl_3$, 75MHz)

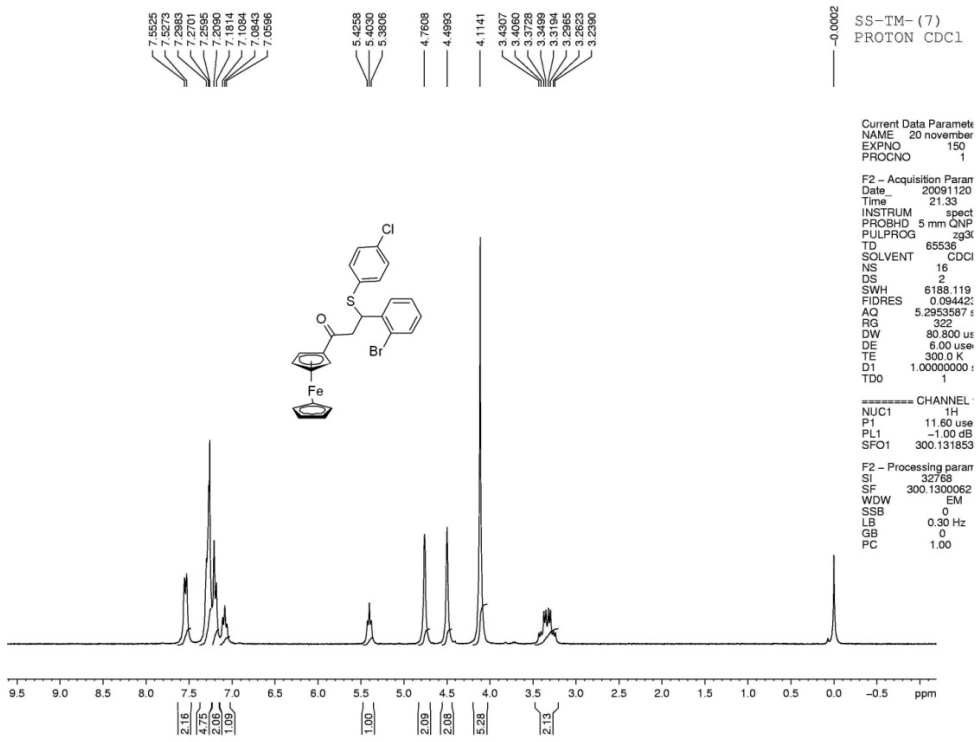


Fig 20. ^{1}H NMR spectrum of 3f ($CDCl_3$, 300MHz)

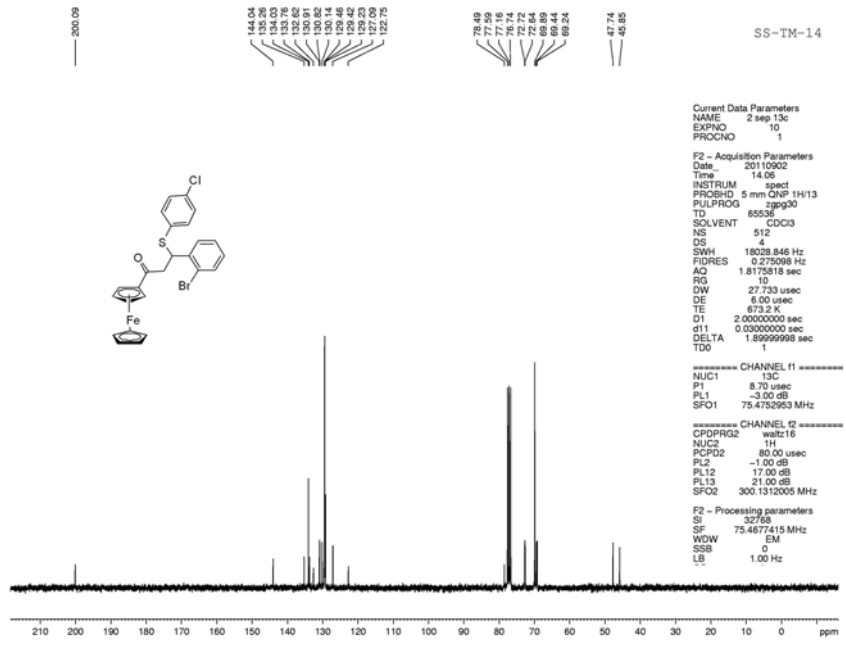


Fig 21. ^{13}C NMR spectrum of 3f ($CDCl_3$, 75MHz)

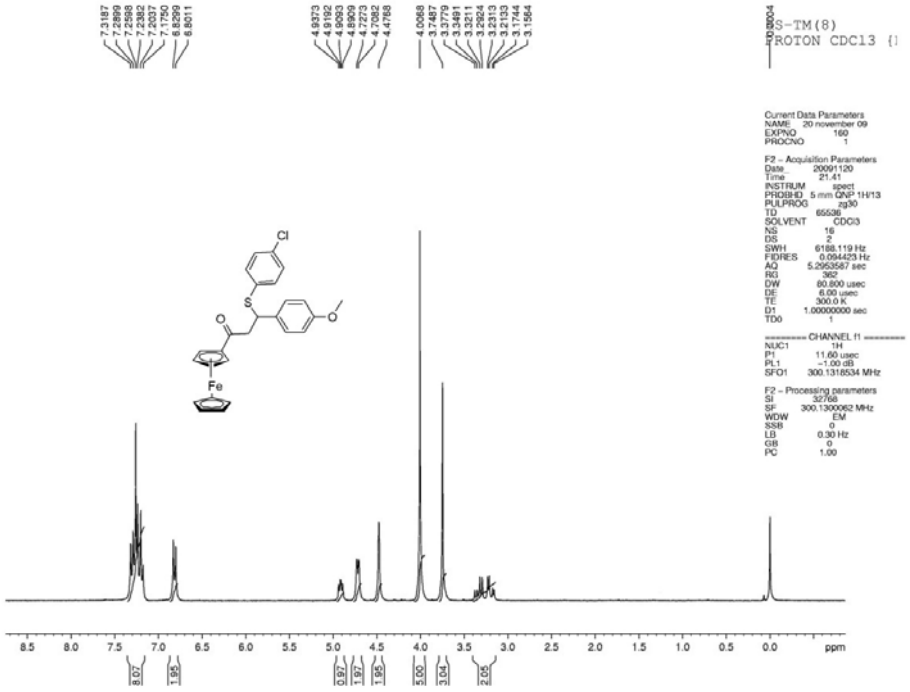


Fig 22. ^{1}H NMR spectrum of 3g ($CDCl_3$, 300MHz)

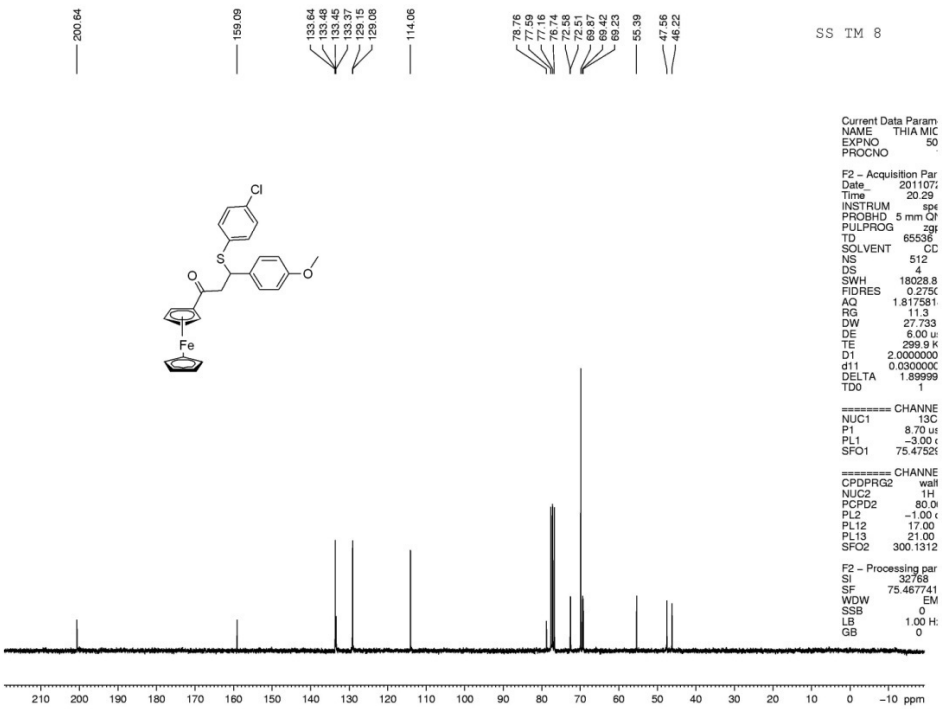


Fig 23. ^{13}C NMR spectrum of 3g ($CDCl_3$, 75MHz)

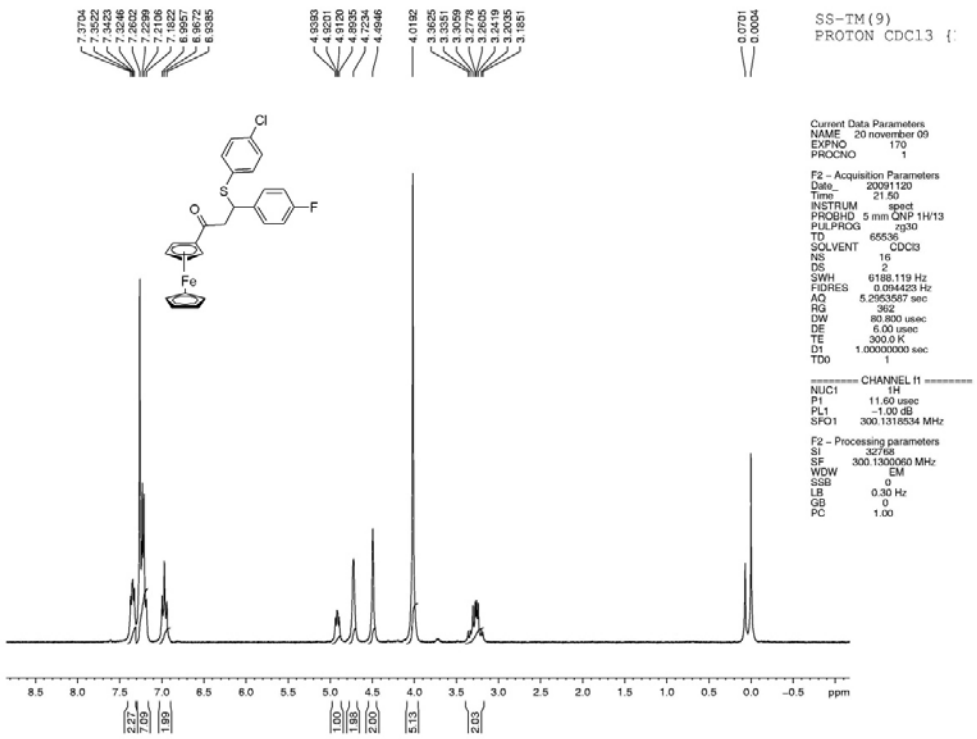


Fig 24. ^{1}H NMR spectrum of 3h ($CDCl_3$, 300MHz)

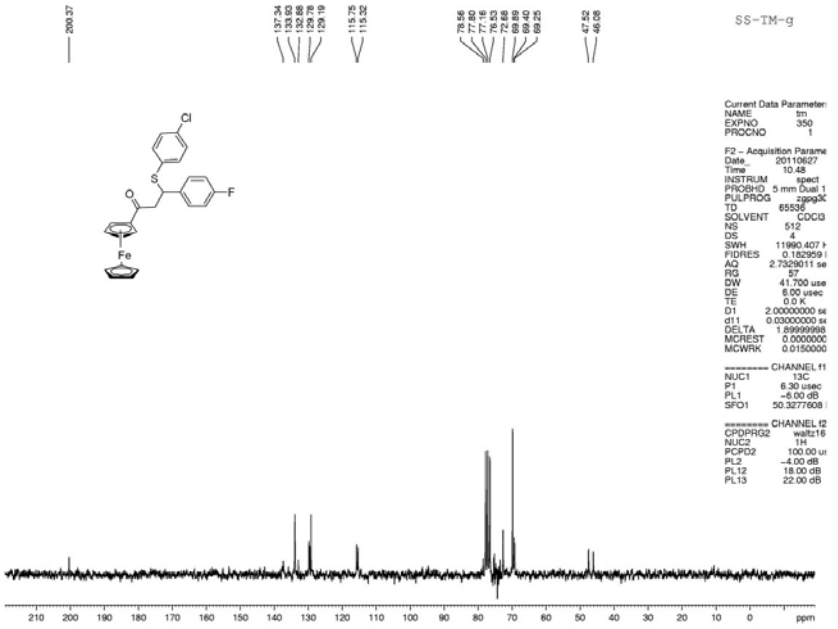


Fig 25. ^{13}C NMR spectrum of 3h ($CDCl_3$, 50MHz)

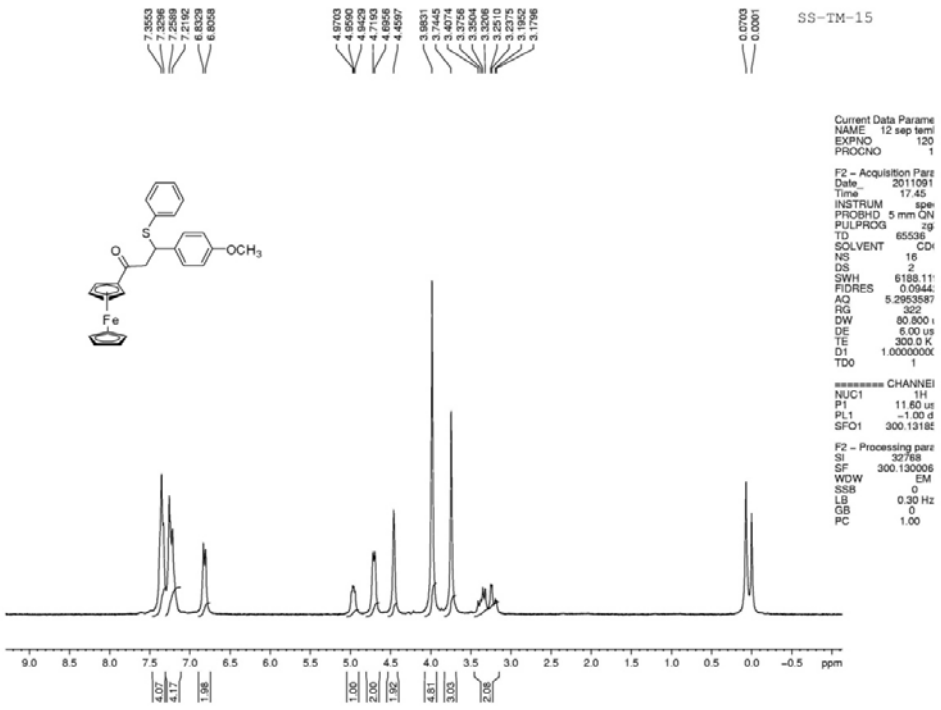


Fig 26. ^{1}H NMR spectrum of 3i ($CDCl_3$, 300MHz)

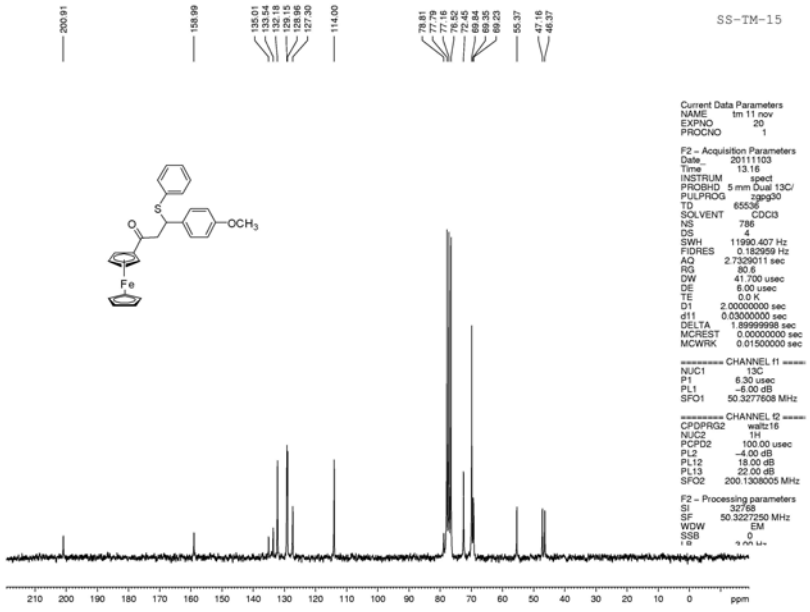


Fig 27. ^{13}C NMR spectrum of 3i ($CDCl_3$, 50MHz)

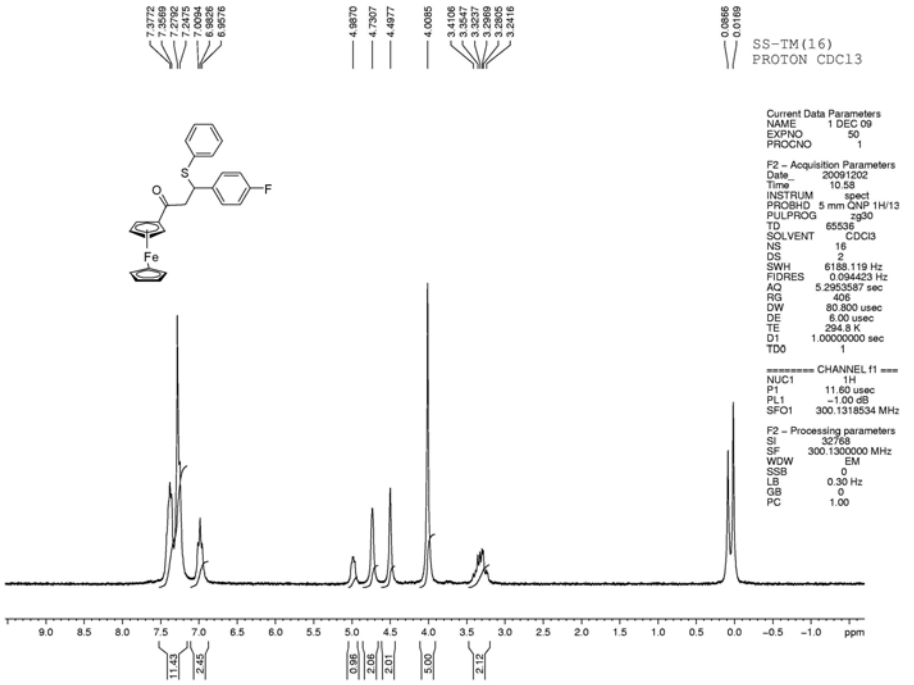


Fig 28. ^{1}H NMR spectrum of 3j ($CDCl_3$, 300MHz)

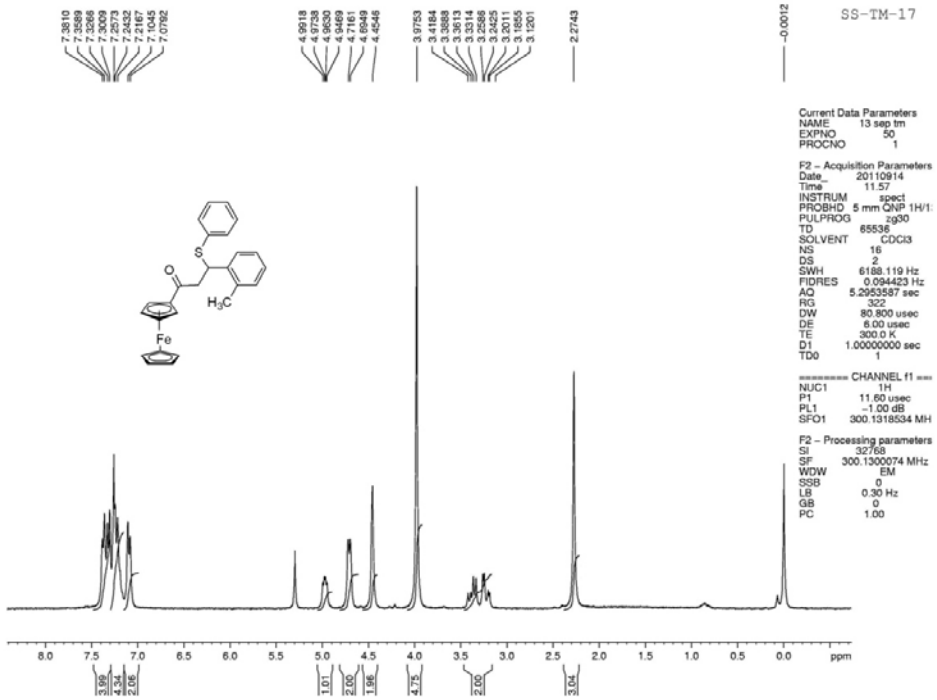


Fig 29. ^{1}H NMR spectrum of 3k ($CDCl_3$, 300MHz)

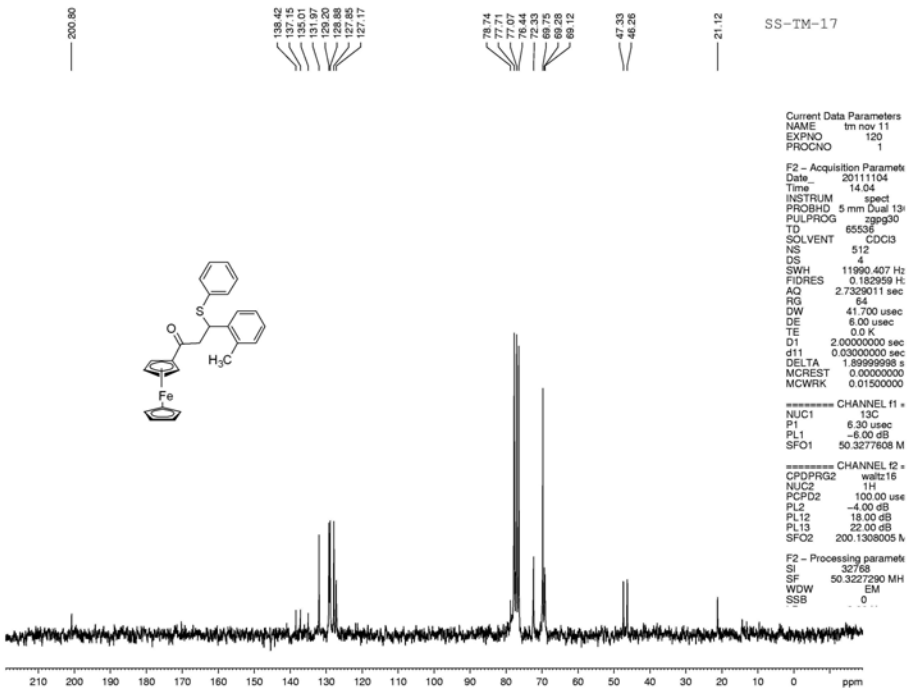


Fig 30. ^{13}C NMR spectrum of 3k ($CDCl_3$, 50MHz)

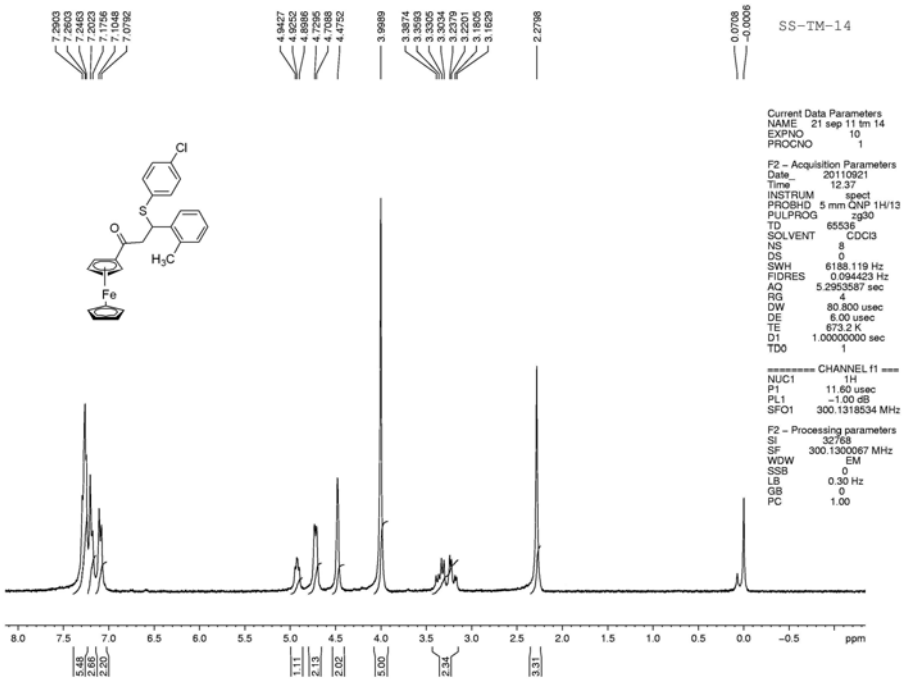


Fig 31. ^{1}H NMR spectrum of 3l ($CDCl_3$, 300MHz)

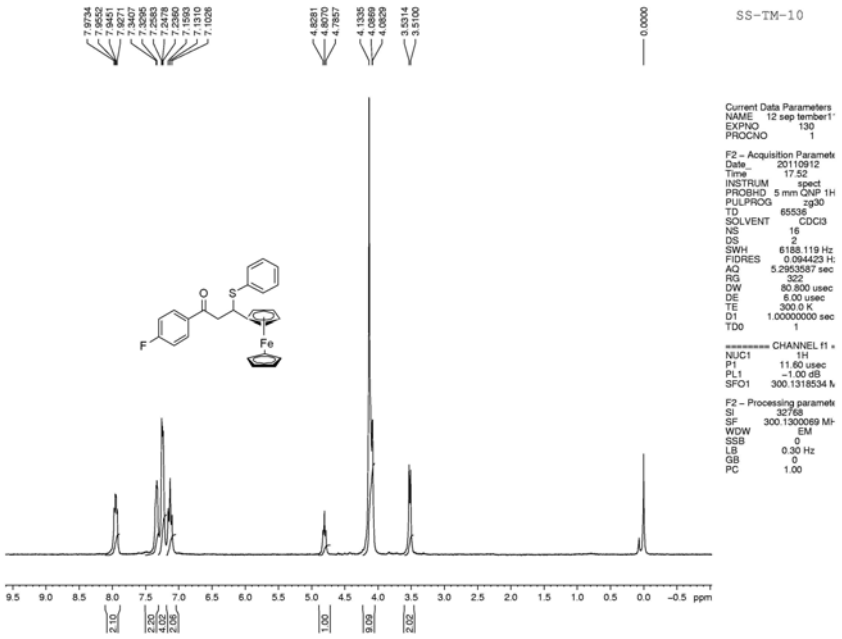


Fig 32. ^{1}H NMR spectrum of 3m ($CDCl_3$, 300MHz)

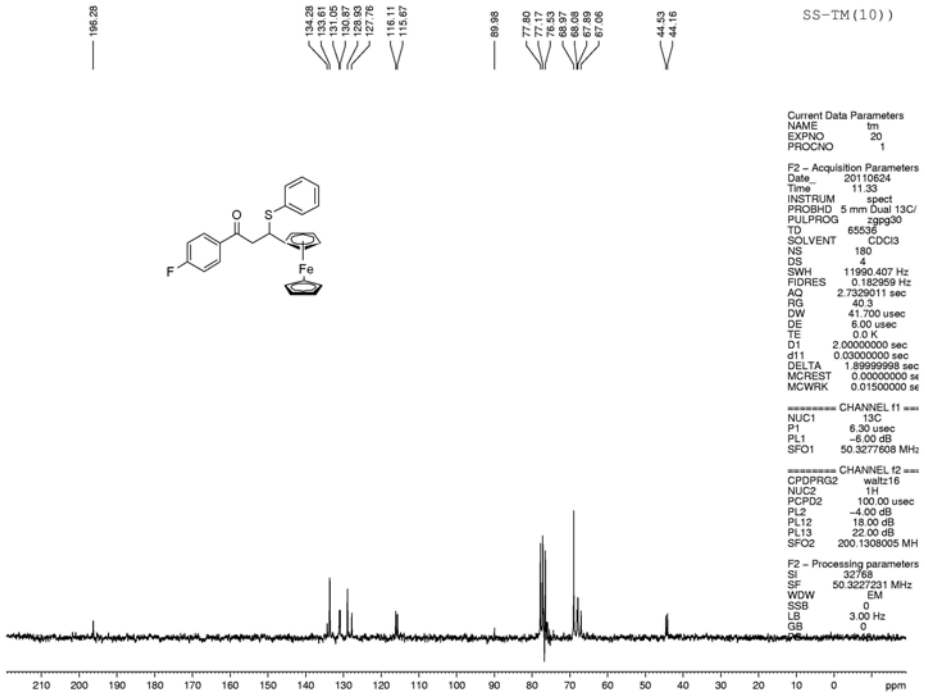


Fig 33. ^{13}C NMR spectrum of 3m ($CDCl_3$, 50MHz)

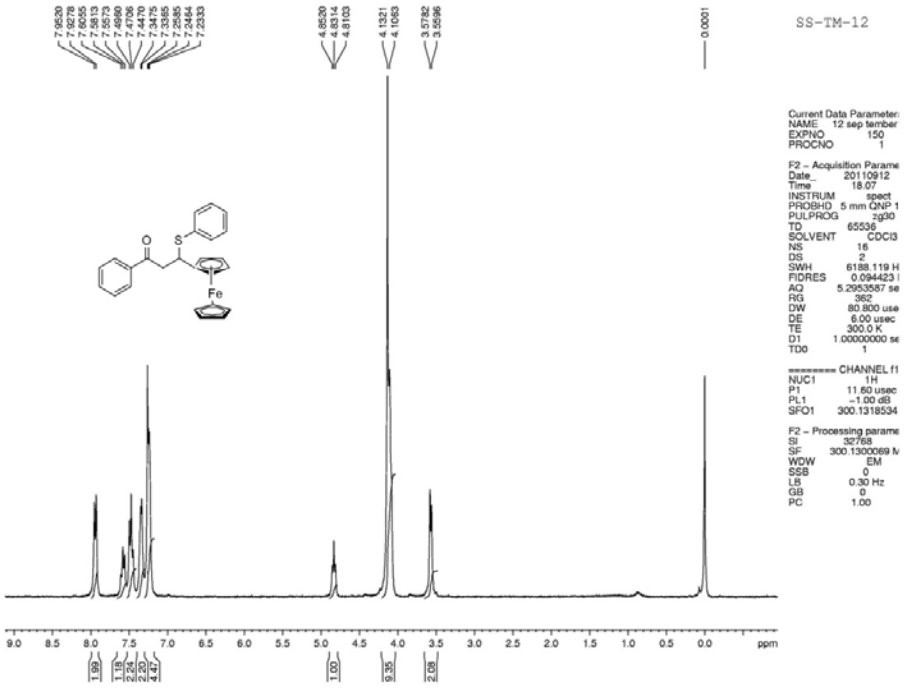


Fig 34. ^{1}H NMR spectrum of 3n ($CDCl_3$, 300MHz)

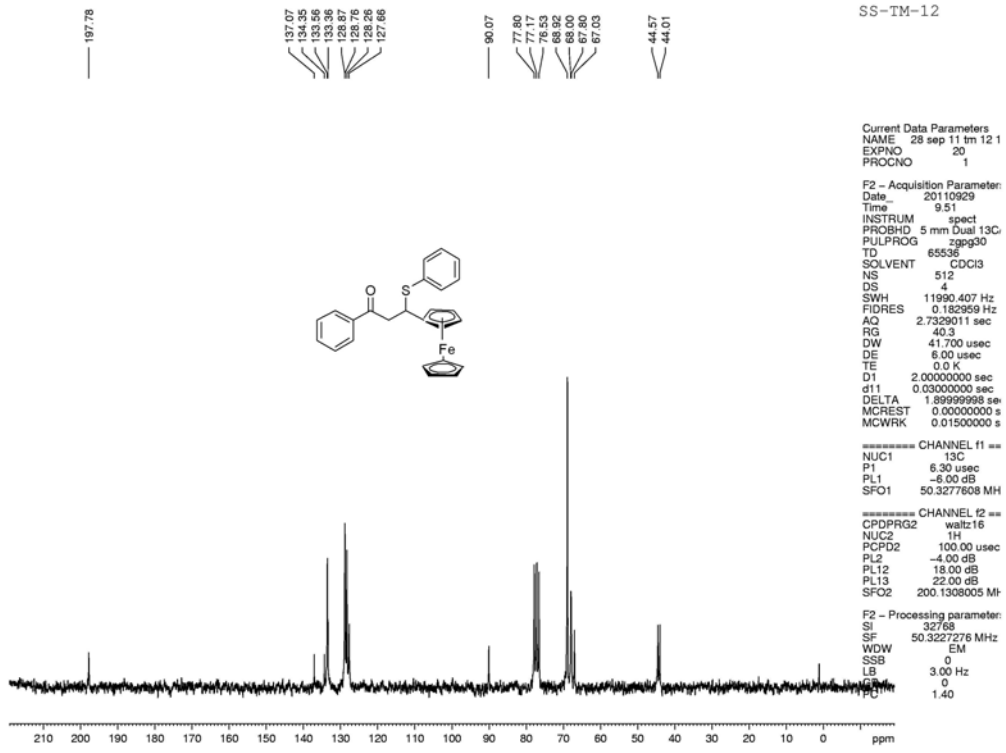


Fig 35. ^{13}C NMR spectrum of 3n ($CDCl_3$, 50MHz)

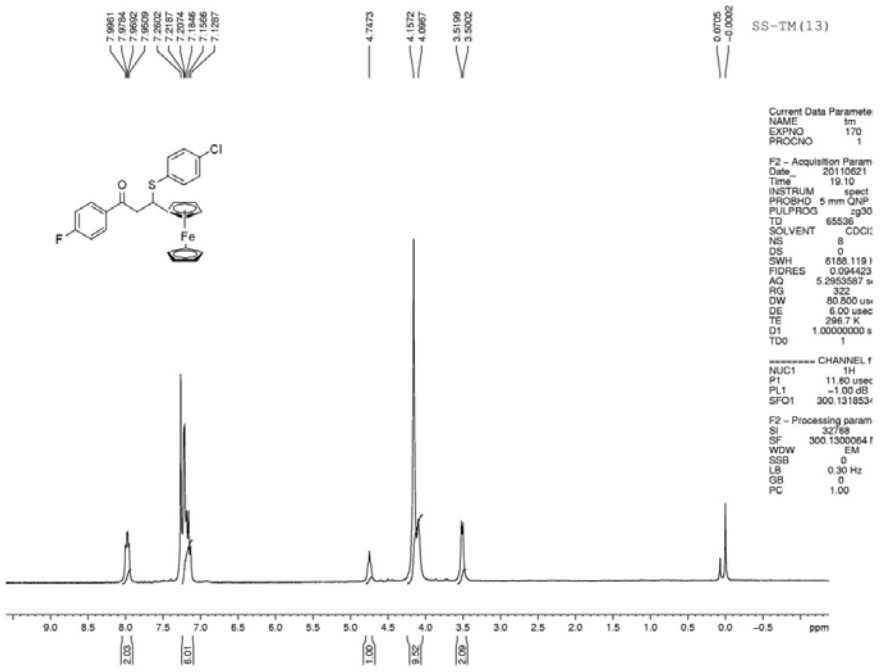


Fig 36. ^{1}H NMR spectrum of 3o ($CDCl_3$, 300MHz)

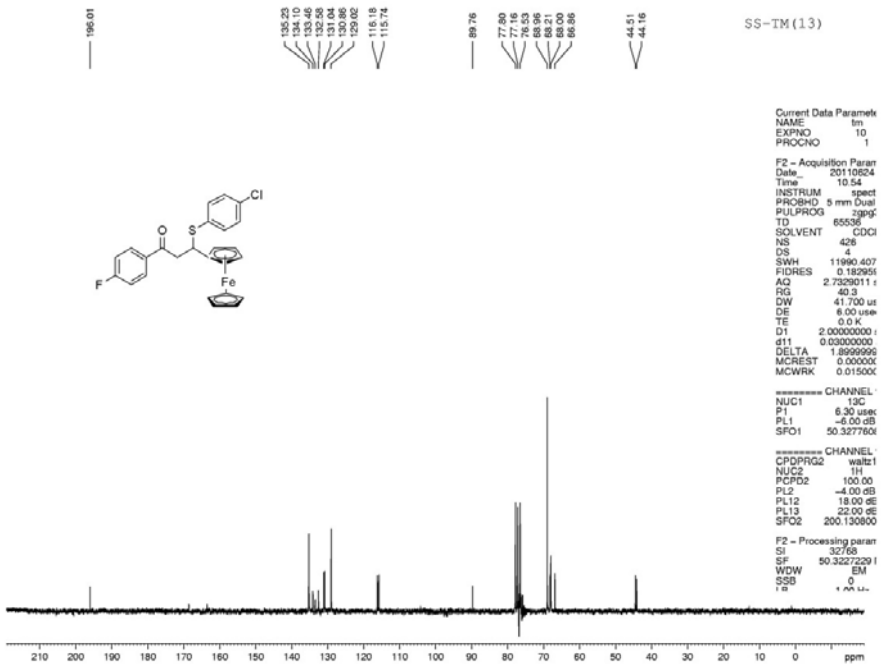


Fig 37. ^{13}C NMR spectrum of 3o ($CDCl_3$, 50MHz)

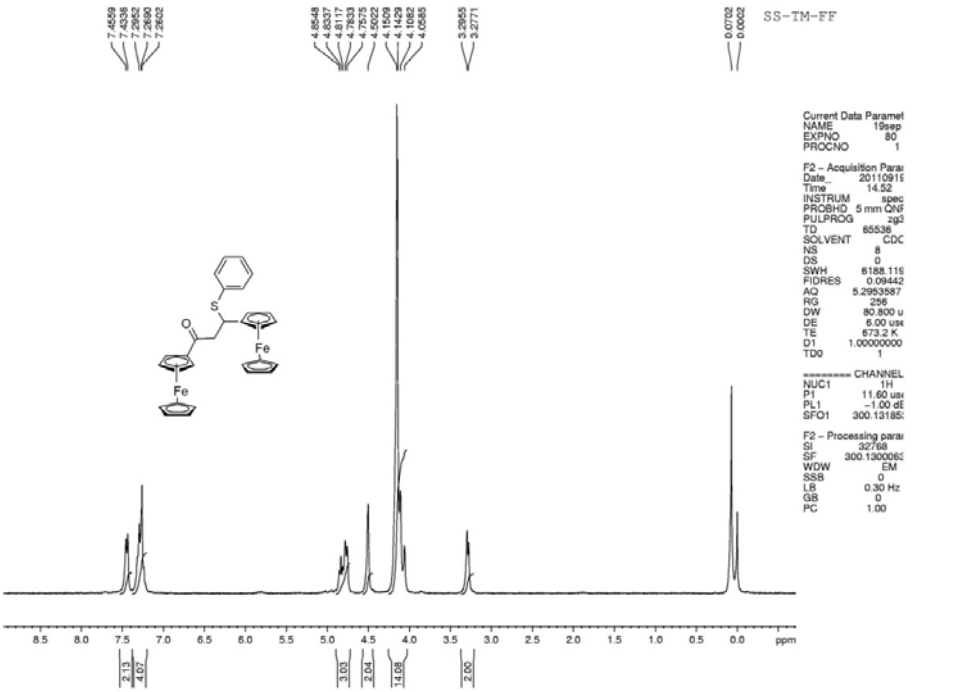


Fig 38. ^{1}H-NMR spectrum of 3p ($CDCl_3$, 300MHz)

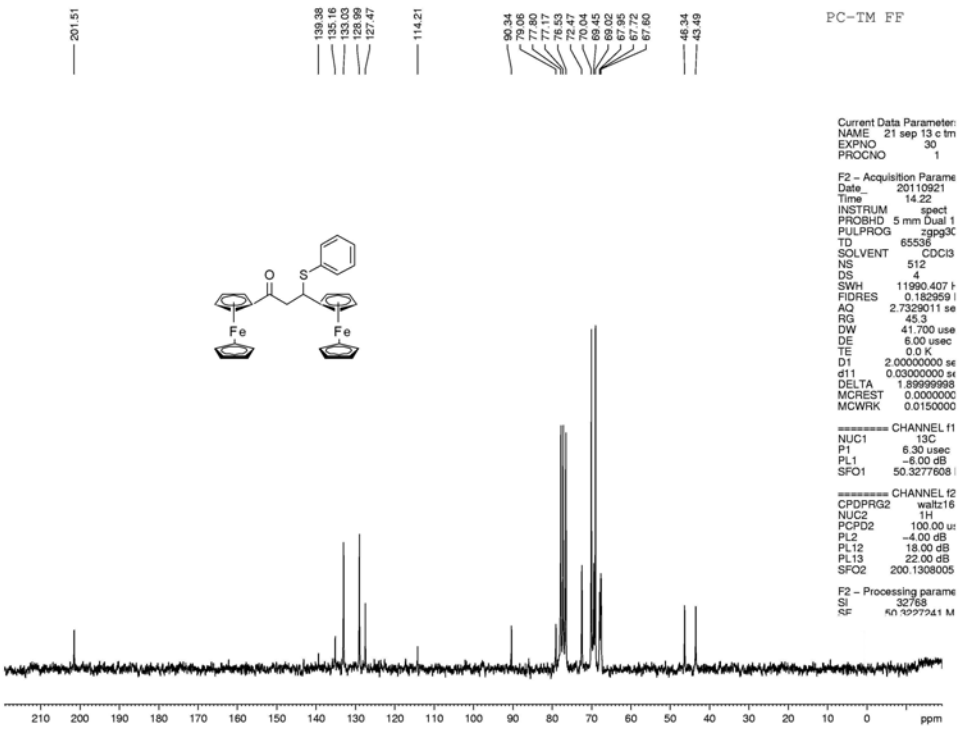


Fig 39. ^{13}C-NMR spectrum of 3p ($CDCl_3$, 50MHz)

References:

1. T. Farrel, T. Meyer-Friedrichsen, M. Malessa, D. Haase, W. Saak, I. Asselberghs, K. Wostyn, K. Clays, A. Persoons, J. Heck, A. R. Manning, *J. Chem. Soc. Dalton Trans*. 2001, 29-36, and references therein.
2. S. Barlow, H. E. Bunting, C. Ringham, J. C. Green, G. U. Bublitz, S. G. Boxer, J.W. Perry, S. R. Marder, *J. Am. Chem. Soc***.** 1999, **121,** 3715- 3723.