Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information to

Ferrocenyl-Sulfonium Ionic Liquids - Synthesis, Characterization and Electrochemistry

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Content:

Preparation of Precursors

Preparation of ferrocenyl methyl sulfide.

According to a modified literature known syntheses.[1]

A solution of 3.00 g (16.1 mmol, 1.0 eq.) ferrocene and 0.260 g (2.31 mmol, 0.144 eq.) potassium *tert*-butoxide in 150 mL THF was cooled to −78 °C and 17.5 mL of a solution of *tert*-butyllithium (1.83 mol L^{-1}, 32.0 mmol, 2.0 eq.) in pentane were added within 15 min. After complete addition, the solution was stirred for 1 h at −78 °C. At the same temperature 3.3 mL (3.5 g, 37 mmol, 2.3 eq.) dimethyl disulfide were added during 2 min and the solution was stirred until complete resolving of the solid. The solution was allowed to warm to room temperature and after stirring for 18 h, 30 mL of a sodium hydroxide solution (2 M) in water were added. The organic layer was separated, the aqueous layer was extracted with diethyl ether (3 x 30 mL) and the combined organic layers were washed with 75 mL of brine and water. After removal of the solvent in vacuum the residue was distilled at 50-60 °C at $\leq 1.0 \cdot 10^{-3}$ mbar. 2.88 g (12.4 mmol, 77%) ferrocenyl methyl sulfide were obtained as orange oil. The analytical data correspond to the data reported in literature.[1]

Preparation of bis(p-toluenesulfonyl) sulfide.

According to a literature known syntheses for $(PhSO_2)_2S$.[2]

3.00 g (16.7 mmol, 1.81 eq.) sodium *p*-toluenesulfinate were dissolved in 20 mL diethyl ether and a solution of 950 mg (9.23 mmol, 1.00 eq.) sulfur dichloride in 2 mL diethyl ether were added dropwise. The resulting suspension was stirred for 2 h at 40 °C, then cooled to room temperature. 20 mL water were added and the solid was separated by filtration. After recrystallization from acetone 1.06 g (3.10 mmol, 37%) bis(*p*-toluenesulfonyl) sulfide were obtained as colorless crystals. Elem. Anal. found C, 48.8; H, 4.1; S, 28.8; $C_{14}H_{14}O_4S_3$ (342.45 g·mol^{-1}) requires C 49.1, H 4.1, S 28.1 **^{1}H NMR** ($CDCl_3$): δ = 2.48 (s, 6H, CH_3), 7.36 (d, 4H, $^3J_{HH}$ = 8.2 Hz, $H_{arom.}$), 7.89 (d, 4H, $^3J_{HH}$ = 8.5 Hz, $H_{arom.}$) ppm. **^{13}C NMR** ($CDCl_3$): δ = 21.9 (CH_3), 128.3 ($C_{arom.}$), 130.0 ($C_{arom.}$), 141.8 ($C_{arom.}$), 146.4 ($C_{arom.}$) ppm. **ESI-HRMS(+):** $m \cdot z^{-1}$ calculated for $C_{14}H_{14}O_4S_3Na^+$: 364.9946, found: 364.9948.

Preparation of diferrocenyl sulfide.

According to a modified literature known syntheses with $(PhSO_2)_2S$.[3]

1.45 g (5.47 mmol, 2.0 eq.) bromoferrocene were dissolved in 15 mL diethyl ether and 2.2 ml of 1-butyllithium (2.5 mol L^{-1}, 5.5 mmol, 2.0 eq.) in hexane were added dropwise within 15 min at −15 °C. The resulting suspension was stirred for 45 min at this temperature. Then the solution was cooled to −78 °C and over a period of 2 h, 935 mg (2.73 mmol, 1.0 eq.) bis(*p*-toluenesulfonyl) sulfide in 75 mL diethyl ether were added. The resulting mixture was stirred at −78 °C for 6 h and was allowed to warm slowly to room temperature. 12 mL of water were added and the two-phase-mixture was stirred for 10 min. After separation of the organic layer, the aqueous layer was extracted twice with diethyl ether and the combined organic layers were evaporated to dryness. The product was isolated via flash chromatography with a hexane/dichloromethane (90/10 to 0/100) solvent system. 738 mg (1.84 mmol, 67%) diferrocenyl sulfide were obtained as yellow needles. An analytically clean probe was obtained by recrystallization from a chloroform/hexane mixture. Elem. anal found C, 59.5; H, 4.5; S, 7.8; $C_{20}H_{18}Fe_2S$ (402.11 g·mol^{-1}) requires C 59.7, H 4.5, S 8.0. **^{1}H NMR** (C_6D_6): δ = 3.90 (t, 4H, $^3J_{HH}$ = 1.8 Hz, C*H*), 4.09 (s, 10H, Cp'), 4.30 (t, 4H, $^3J_{HH}$ = 1.8 Hz, C*H*) ppm. **^{13}C NMR** (C_6D_6): δ = 69.0 (Cp), 69.8 (Cp'), 72.8 (Cp), 83.9 (*C*S) ppm. **ESI-HRMS(+):** $m\cdot z^{-1}$ calculated for $C_{20}H_{18}Fe_2S$: 401.9823, found: 401.9826.

Preparation of 1,1'-di(butylthio)ferrocene.

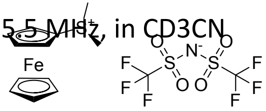
To 790 mg (2.51 mmol, 1.00 eq.) dilithioferrocene · TMEDA in 5 ml THF 912 mg (5.12 mmol, 2.04 eq.) dibutyl disulfide were added within 10 min at −78 °C. The solution was allowed to warm to room temperature and was stirred for 15 h. After adding 5 mL water the organic phase was separated and the aqueous layer was extracted with diethyl ether (3×10 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed at reduced pressure. Purification was performed by flash chromatography with hexane/ether (100:0 to 90:10) with a Büchi Sepacore preparative chromatography system. 460 mg (1.27 mmol, 51%) 1,1'-di(butylthio)ferrocene were obtained as orange red oil. **^{1}H NMR** (CD_3CN): δ = 0.88 (t, 6H, $^3J_{HH}$ = 7.2 Hz, CH_3), 1.39 (tq, 4H, $^3J_{HH}$ = 7.2, 7.2 Hz, CH_2CH_3), 1.44-1.54 (m, 4H, $CH_2CH_2CH_3$), 2.61 (t, 4H, $^3J_{HH}$ = 7.2 Hz, SCH_2), 4.21 (t, 4H, $^3J_{HH}$ = 1.8 Hz, Cp), 4.25 (t, $^3J_{HH}$ = 1.8 Hz, 4H, Cp) ppm. **^{13}C NMR** (CD_3CN): δ = 13.9 (CH_3), 22.4 (CH_2CH_3), 32.6 ($CH_2CH_2CH_3$), 37.2 (SCH_2), 71.2 (Cp), 74.9 (Cp), 83.3 (*C*S) ppm. **ESI-HRMS**(+): $m\cdot z^{-1}$ calculated for $C_{18}H_{27}FeS_2$: 363.0898, found: 363.0869.

Single Crystal X-ray Structures

Crystal Data

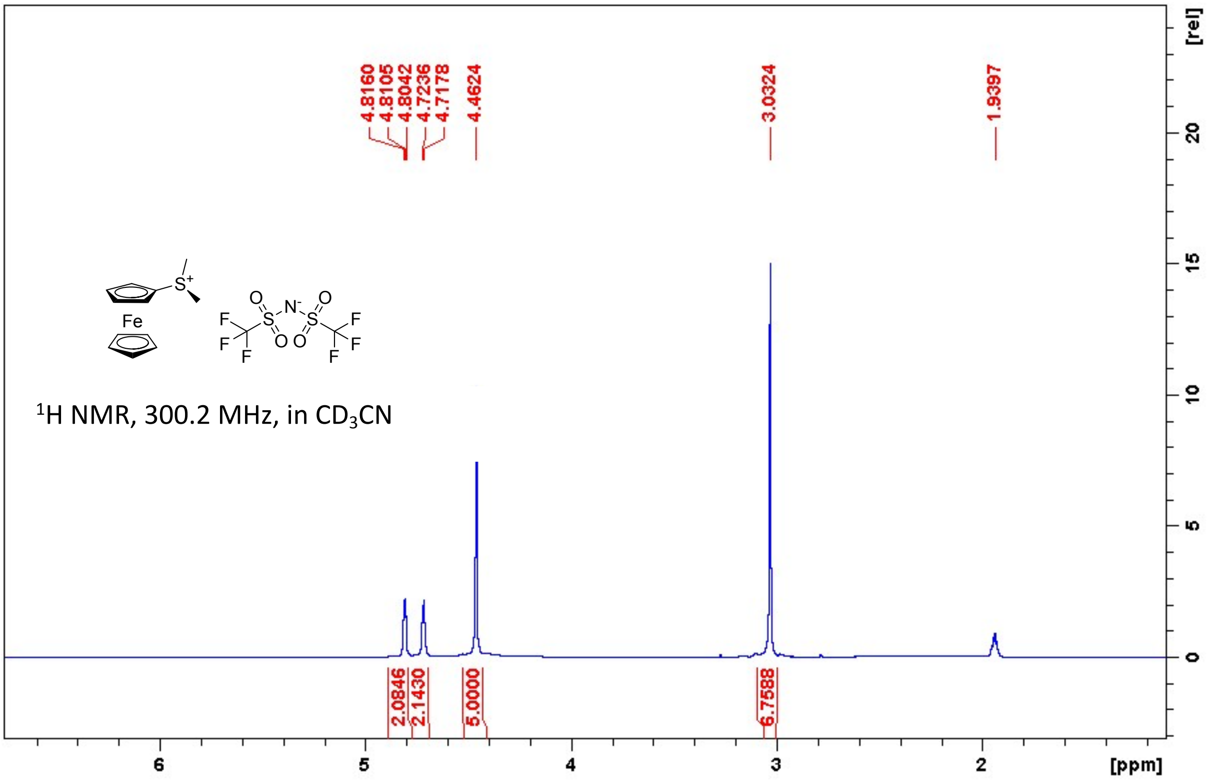
	Dimethylferrocenylsulfonium iodide	Bis(dimethylsulfonium)ferrocene bis(tetraphenylborate) · THF
Formula	C_{12} H_{15} Fe I S	C_{66} H_{68} B_2 Fe O S_2
FW/ g·mol^{-1}	374.05	1018.79
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Color, habit	Yellow, plate	Yellow, orange block
Crystal size/mm^3	0.22 x 0.19 x 0.09	0.30 x 0.27 x 0.24
a/ Å	15.4360(6)	11.0520(5)
b/ Å	9.5323(4)	14.8221(6)
c/ Å	8.8874(3)	18.5056(7)
α/°	90	104.7890(13)
β/°	93.0790(10)	104.0025(14)
γ/°	90	105.4496(14)
V/ Å^3	1305.81(9)	2664.29(19)
Z	4	2
D_{calc}/ g·cm^{-3}	1.903	1.270
Abs. corr.	multi-scan	multi-scan
Max./min. Transm.	0.7455 / 0.6188	0.7455 / 0.7168
μ/ cm^{-1}	36.45	0.405
F(000)	728	1080
T/ K	100(2)	100(2)
θ range/°	2.512 : 27.136	2.24 : 27.19
range h,k,l	−19:19; −12:12; −11:11	−14:14; −19:19; −23:23
Refl. Coll.	25189	76302
Refl. Indep.	2890	11807
Refl. I > 2σ(I)	2523	10384
Data / restr. / param.	2890 / 0 / 138	11807 / 0 / 653
R_{int}	0.0583	0.0325
R_1 (obs)	0.0186	0.0321
wR_2 (all)	0.0376	0.0766
GooF (F_2)	1.045	1.031
Res. e$^-$ dens. (min./ max.)	−0.366 / 0.385	−0.339 / 0.379
CCDC	1583350	1583349

^{13}C NMR, 75.5 MHz, in CD3CN

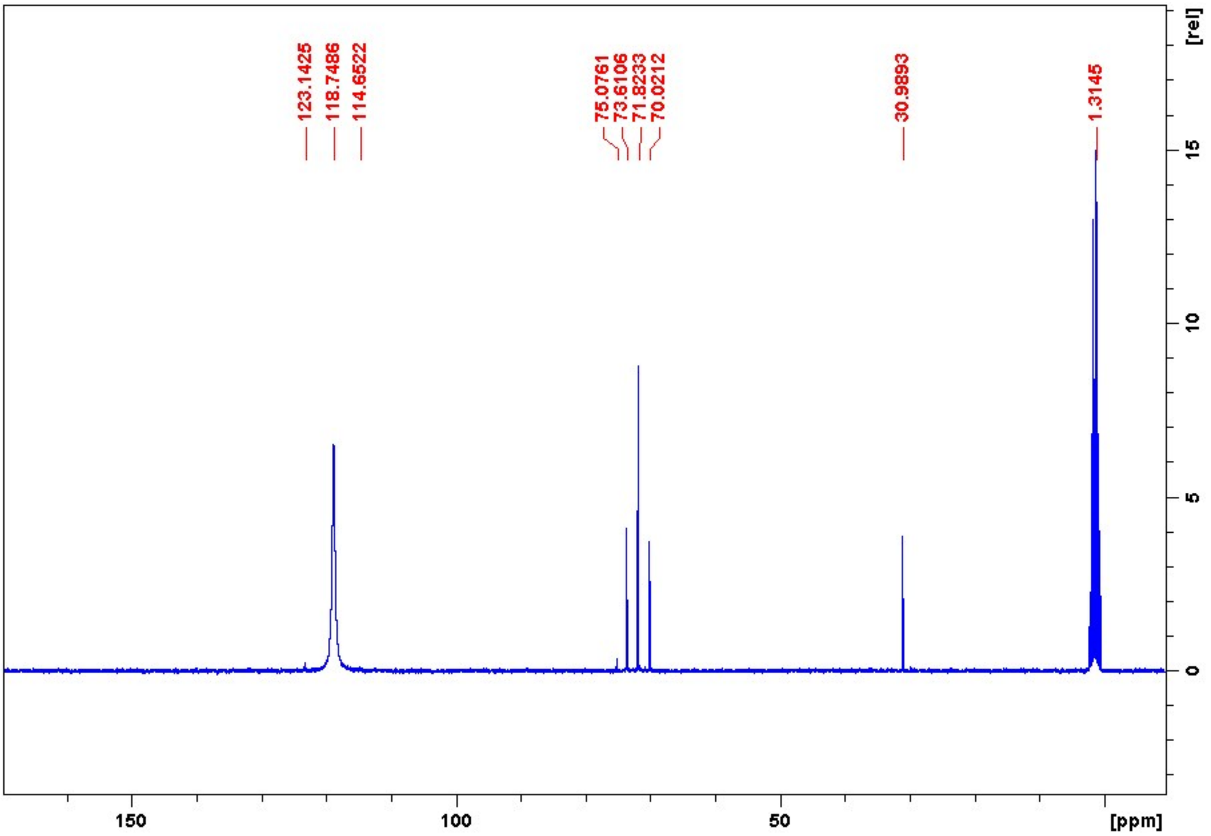


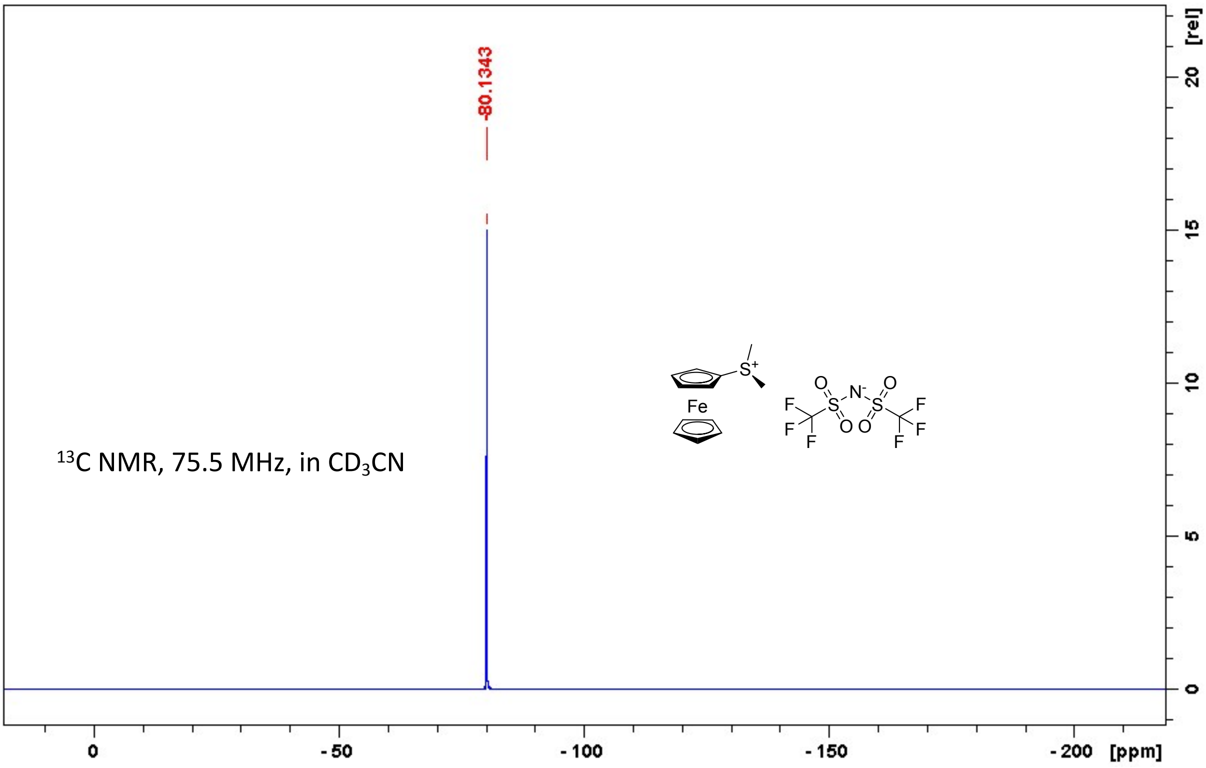
NMR-spectra

Ferrocenyldimethylsulfonium bis(trifluoromethanesulfonyl)imide

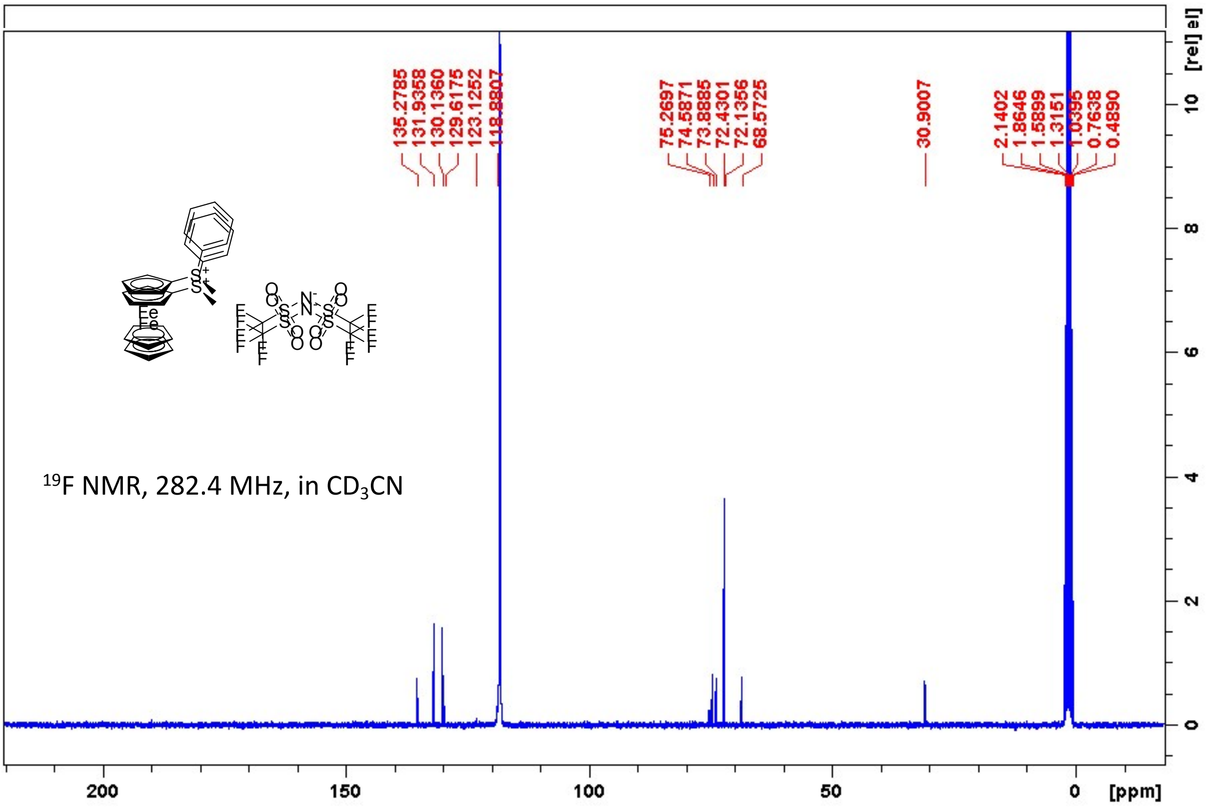


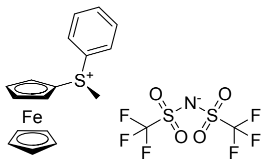
^{1}H NMR, 300.2 MHz, in CD$_3$CN

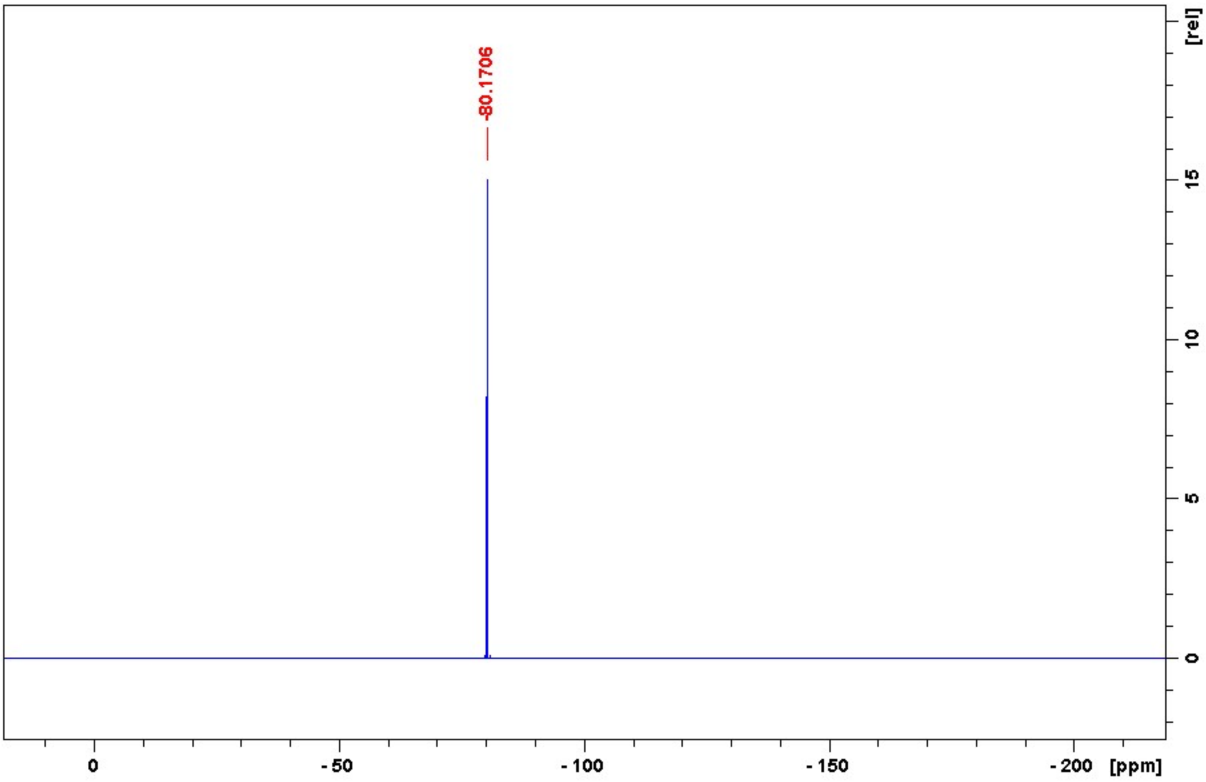




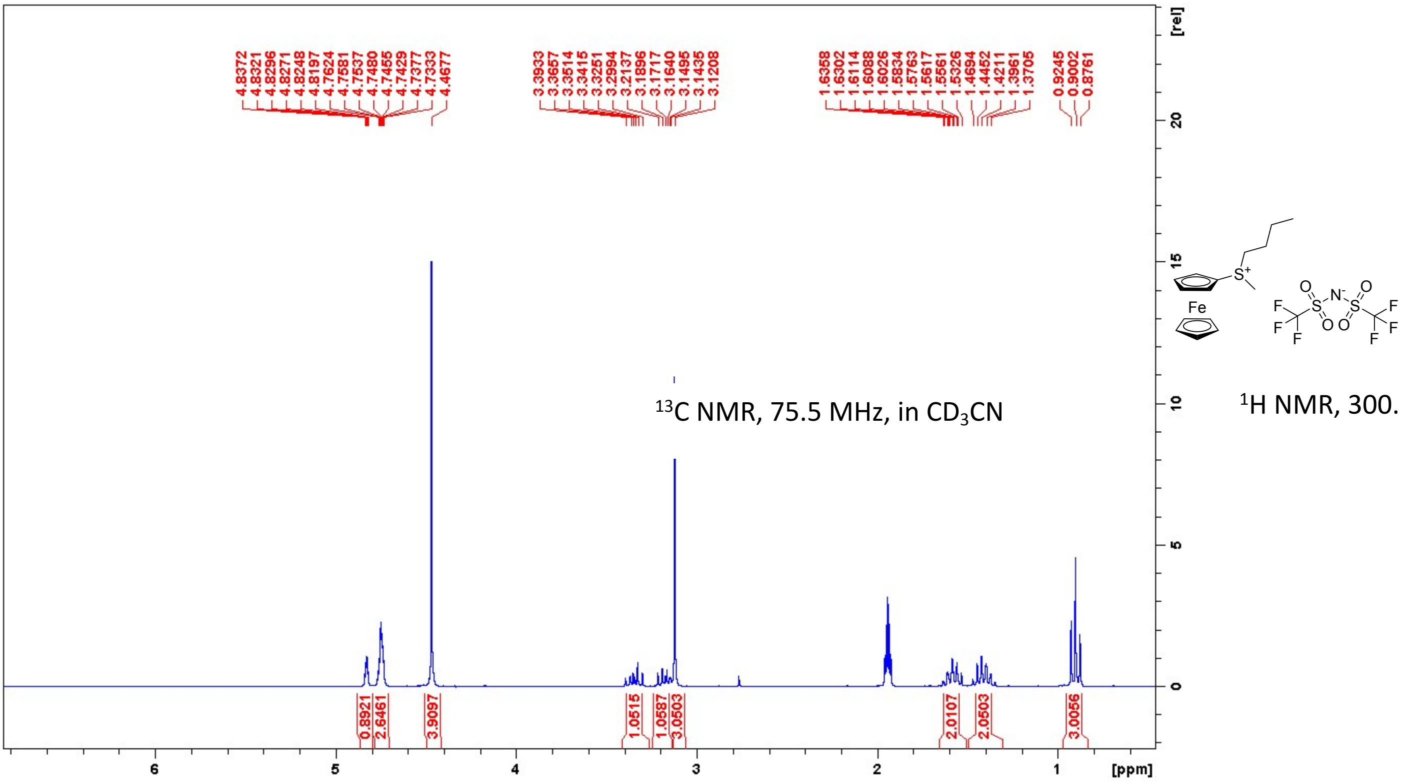
Ferrocenylmethylphenylsulfonium bis(trifluoromethanesulfonyl)imide





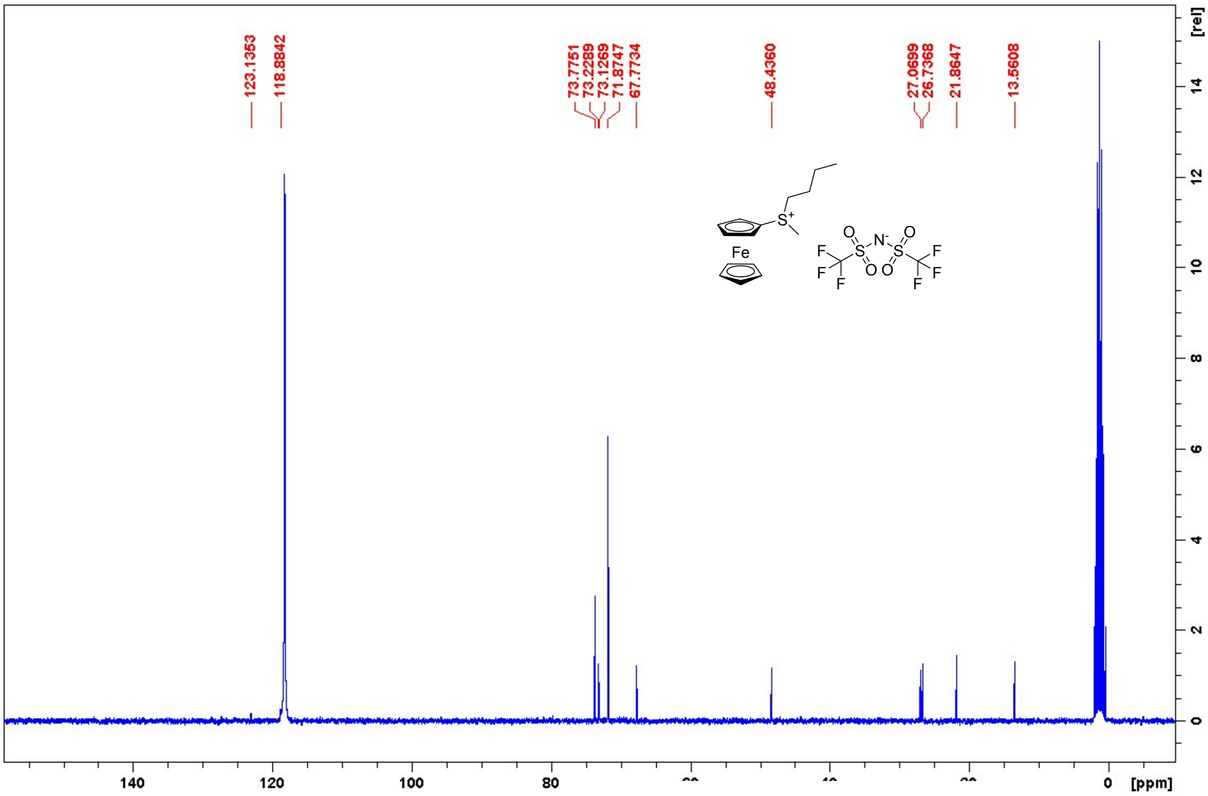


Butylferrocenylmethylsulfonium bis(trifluoromethanesulfonyl)imide

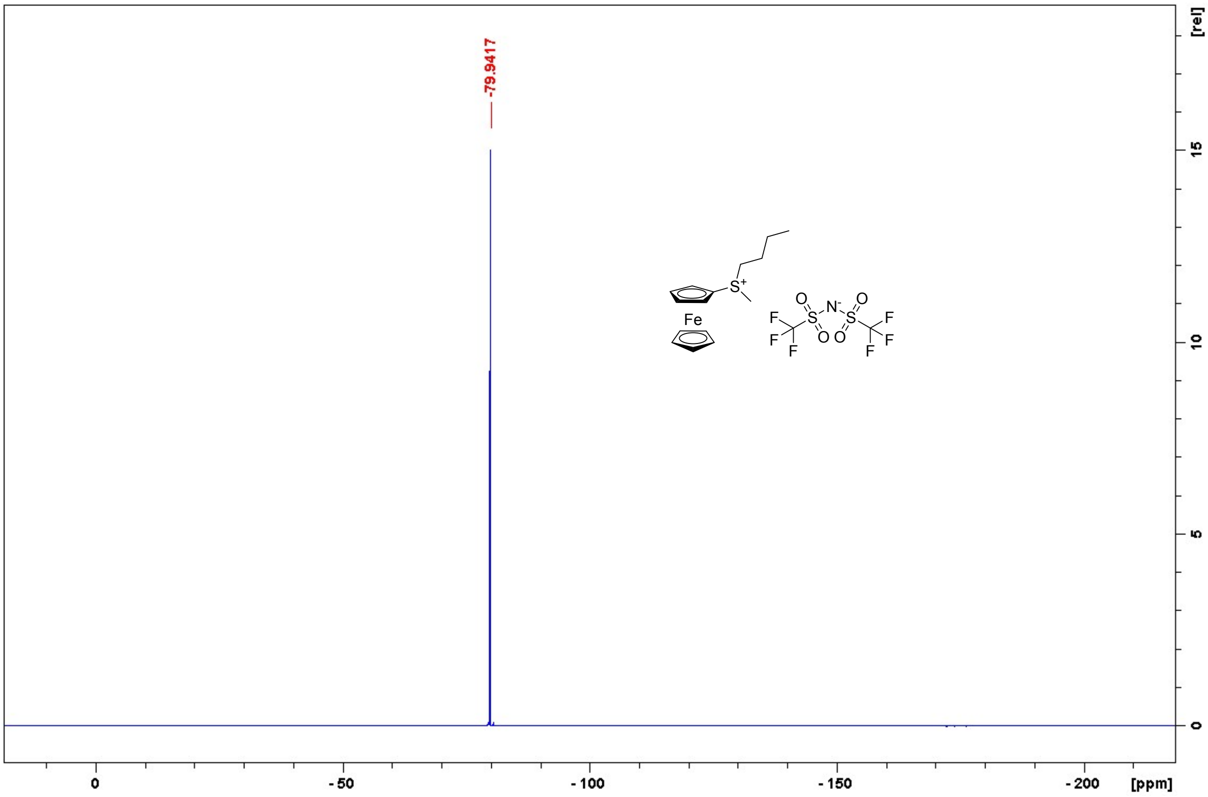


^{13}C NMR, 75.5 MHz, in CD_3CN

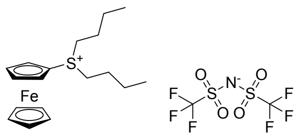
^{1}H NMR, 300.

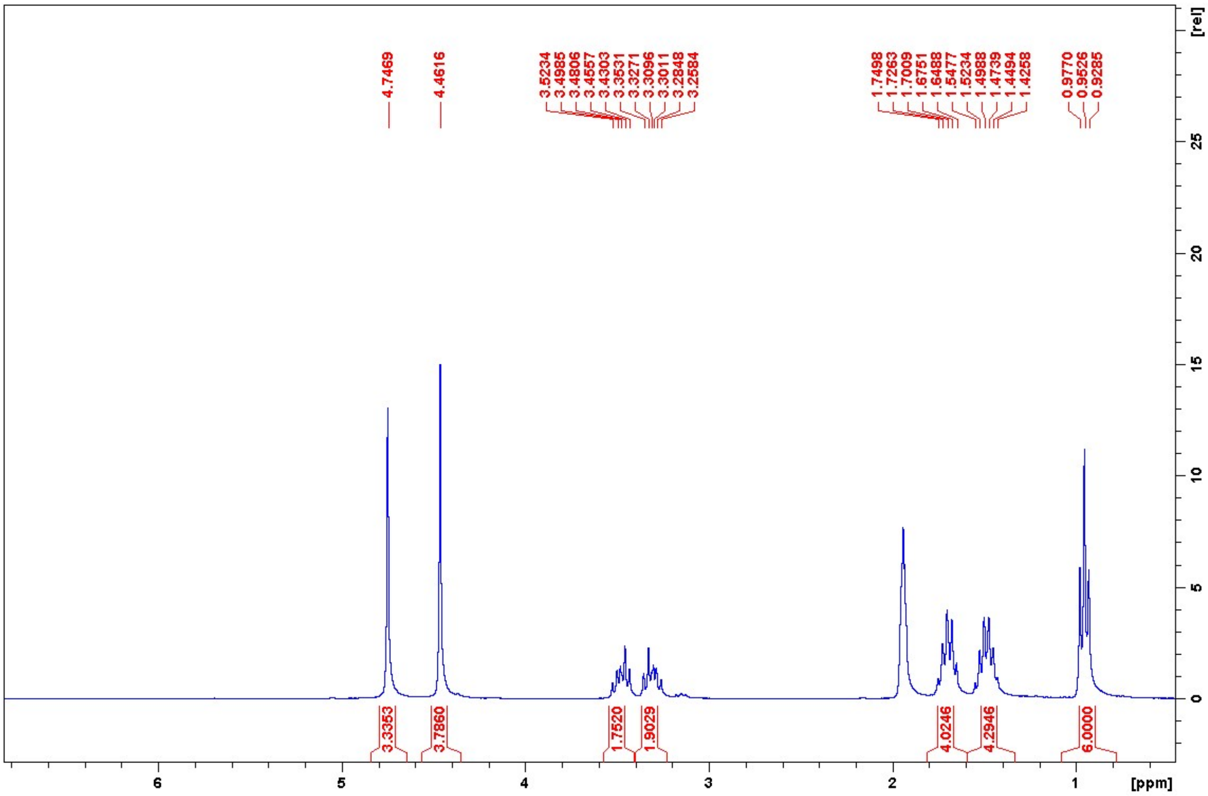


^{19}F NMR, 282.5 MHz, in CD_3CN

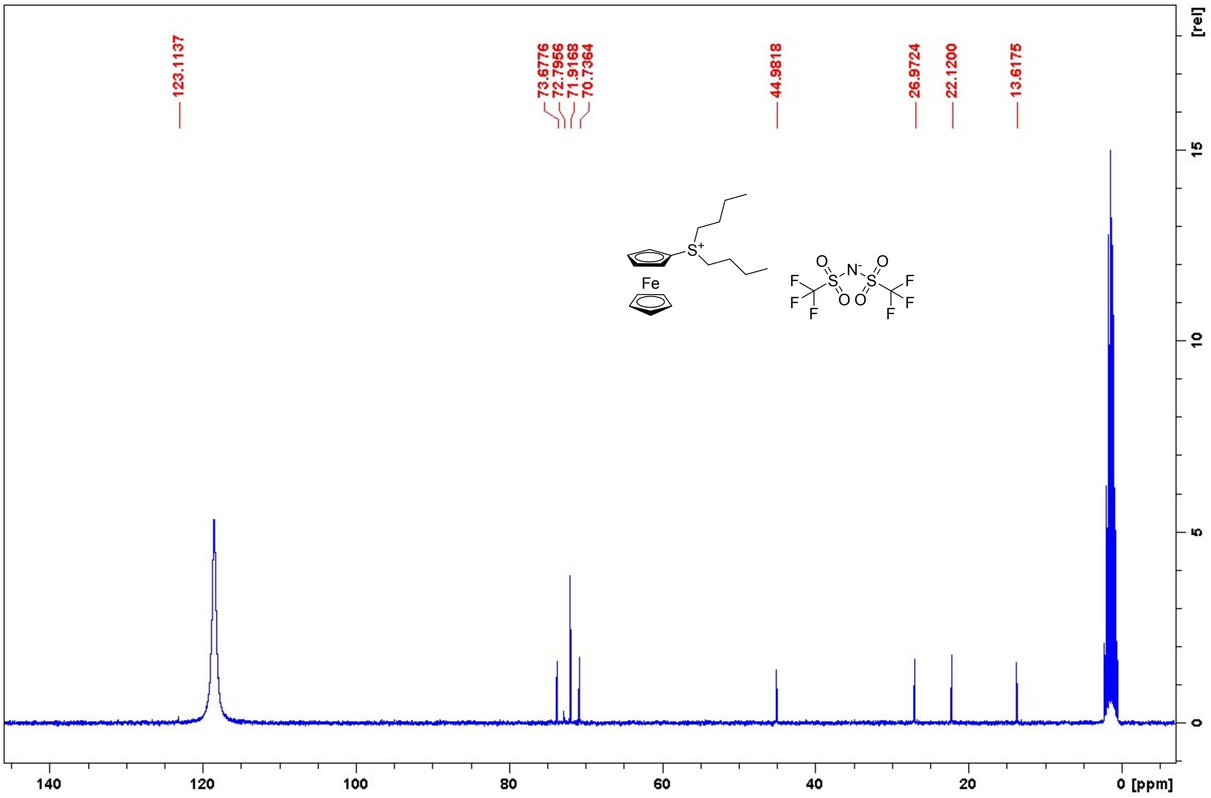


Dibutylferrocenylsulfonium bis(trifluoromethanesulfonyl)imide





^{13}C-NMR, 75.5 MHz, in CD_3CN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71.9168
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S+
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O
N-
O
S
S
F
F
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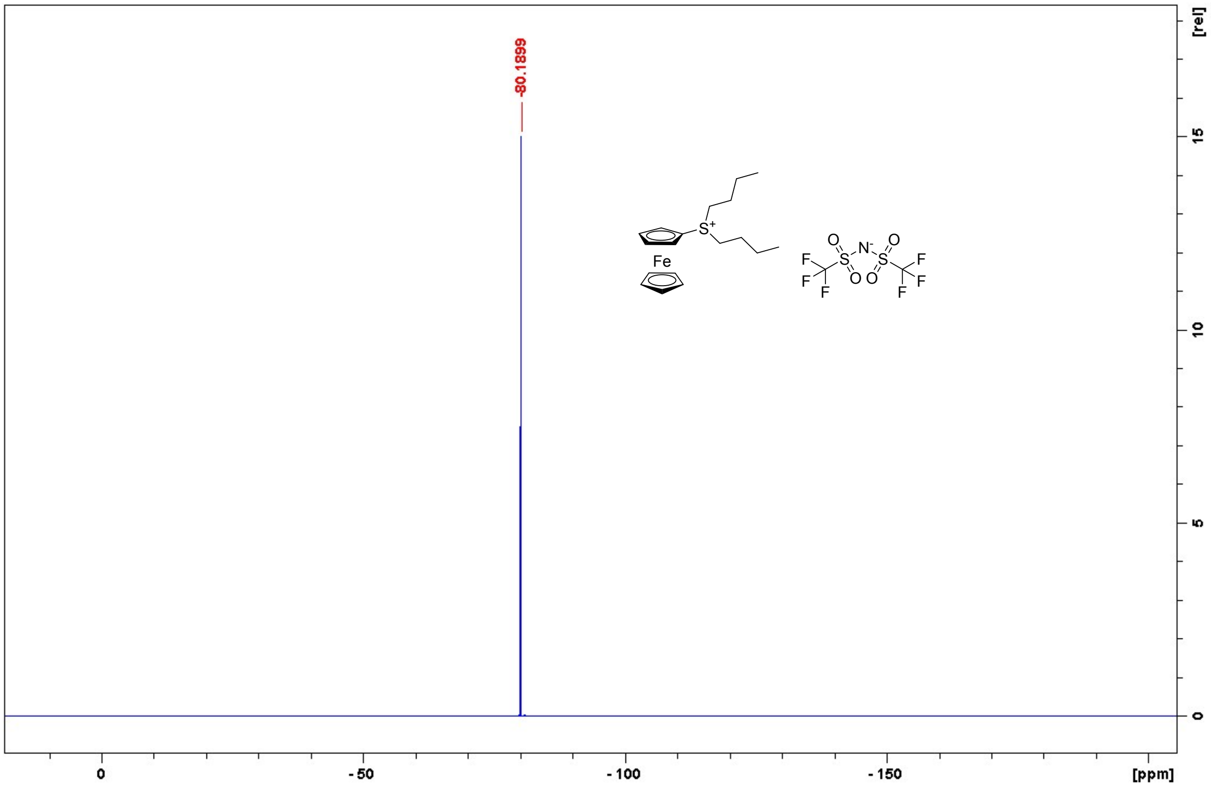
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5
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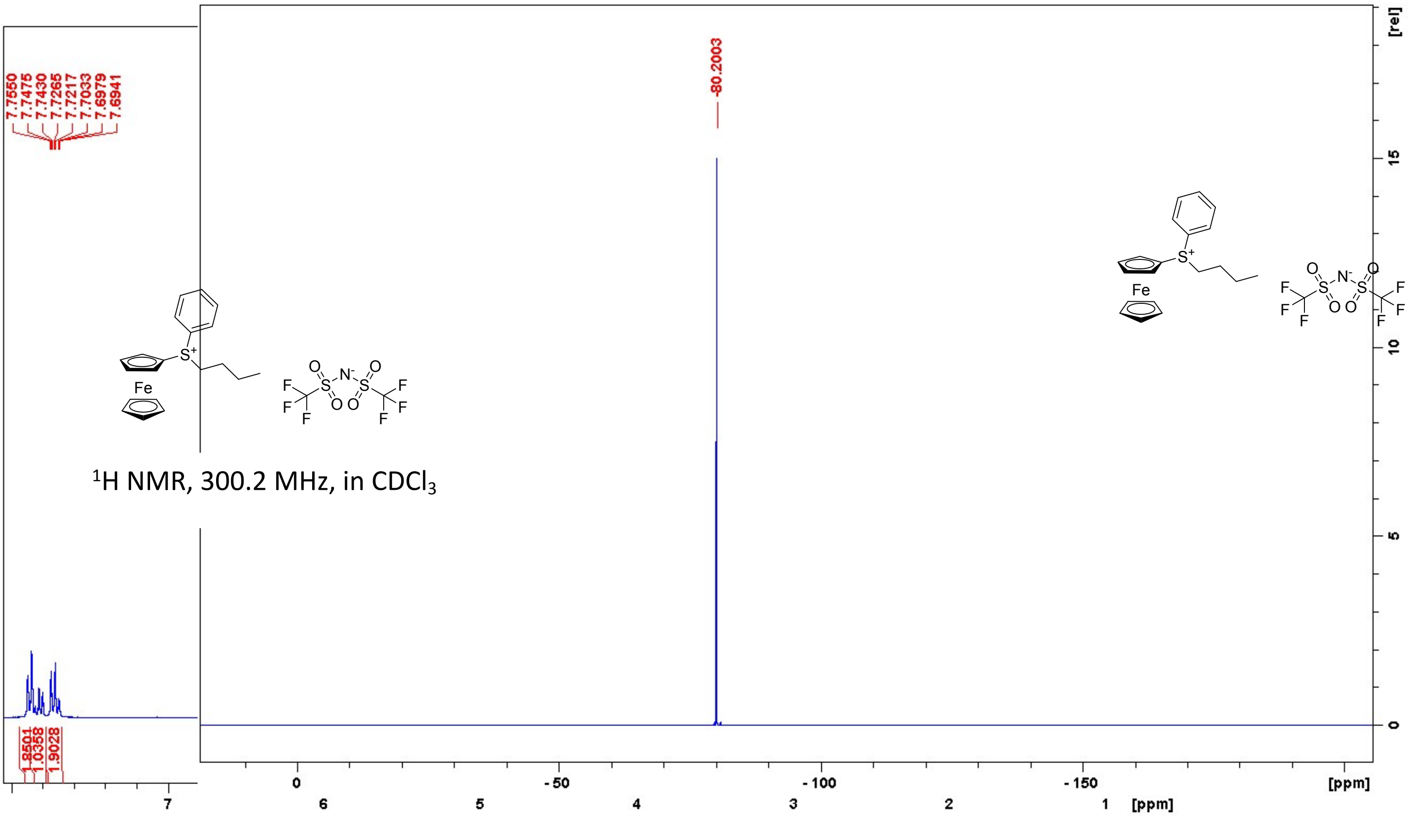
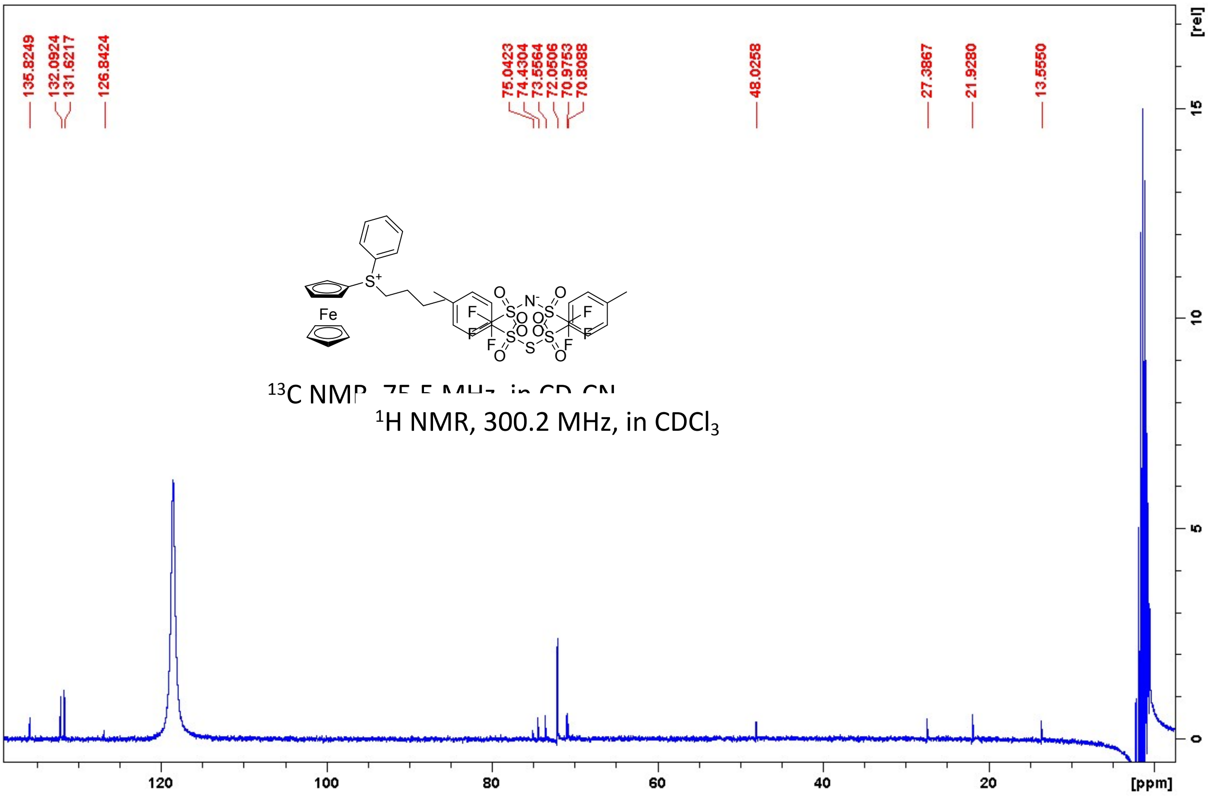
- 50
- 100
- 150
[ppm]

Butylferrocenylphenylsulfonium bis(trifluoromethanesulfonyl)imide



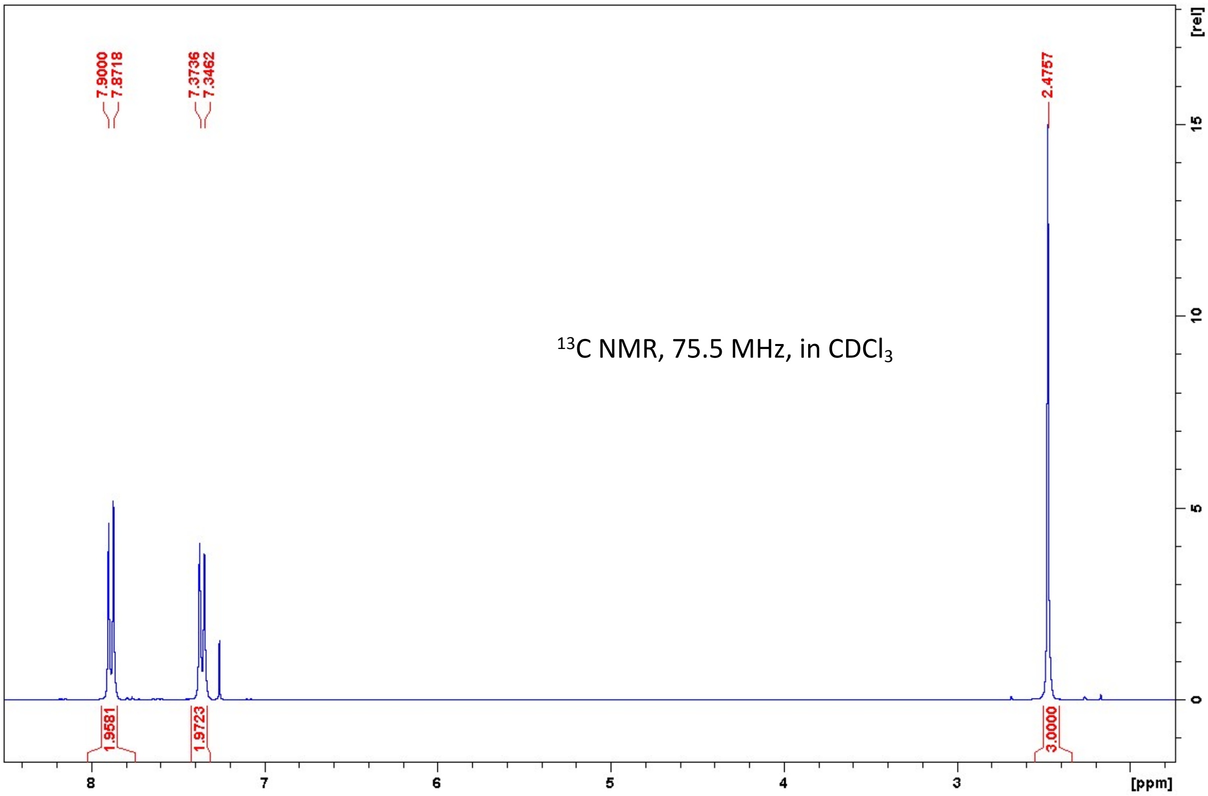
^{1}H NMR, 300.2 MHz, in CDCl$_3$



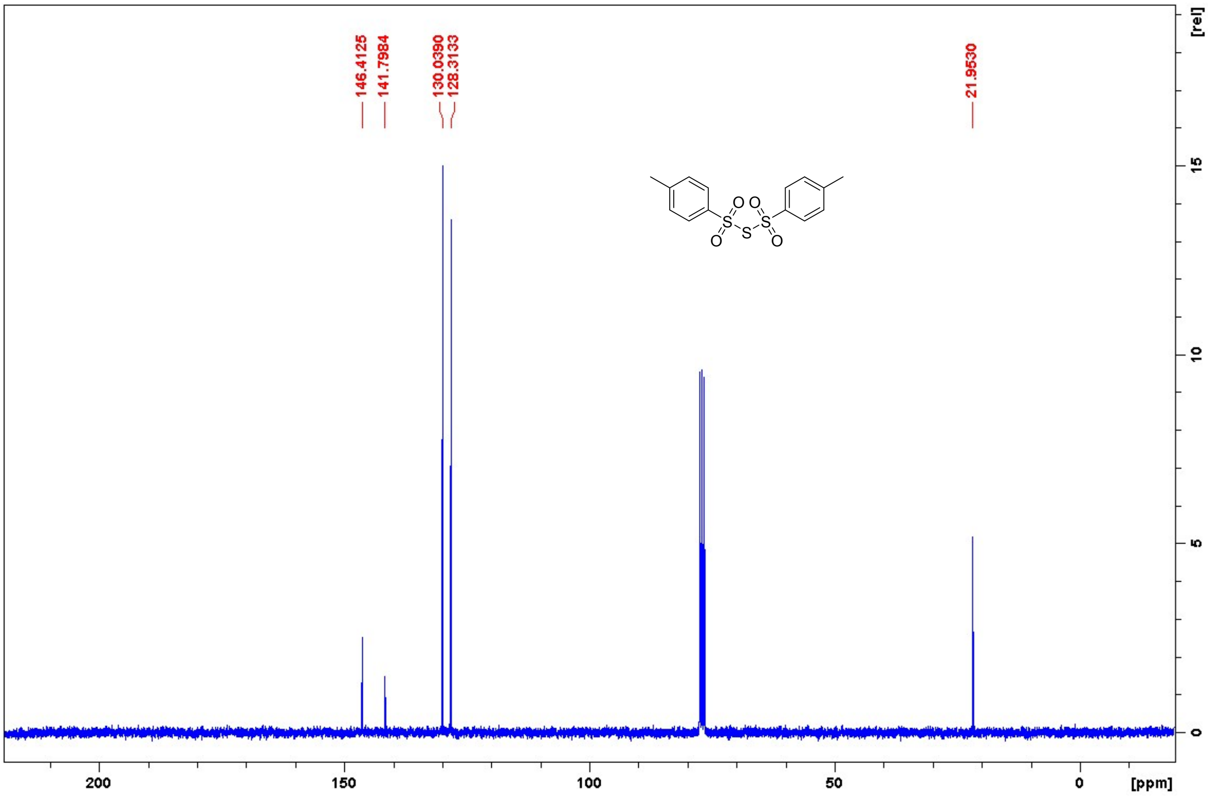
^{13}C NMR, 75.5 MHz, in CD$_3$CN

^{1}H NMR, 300.2 MHz, in CDCl$_3$

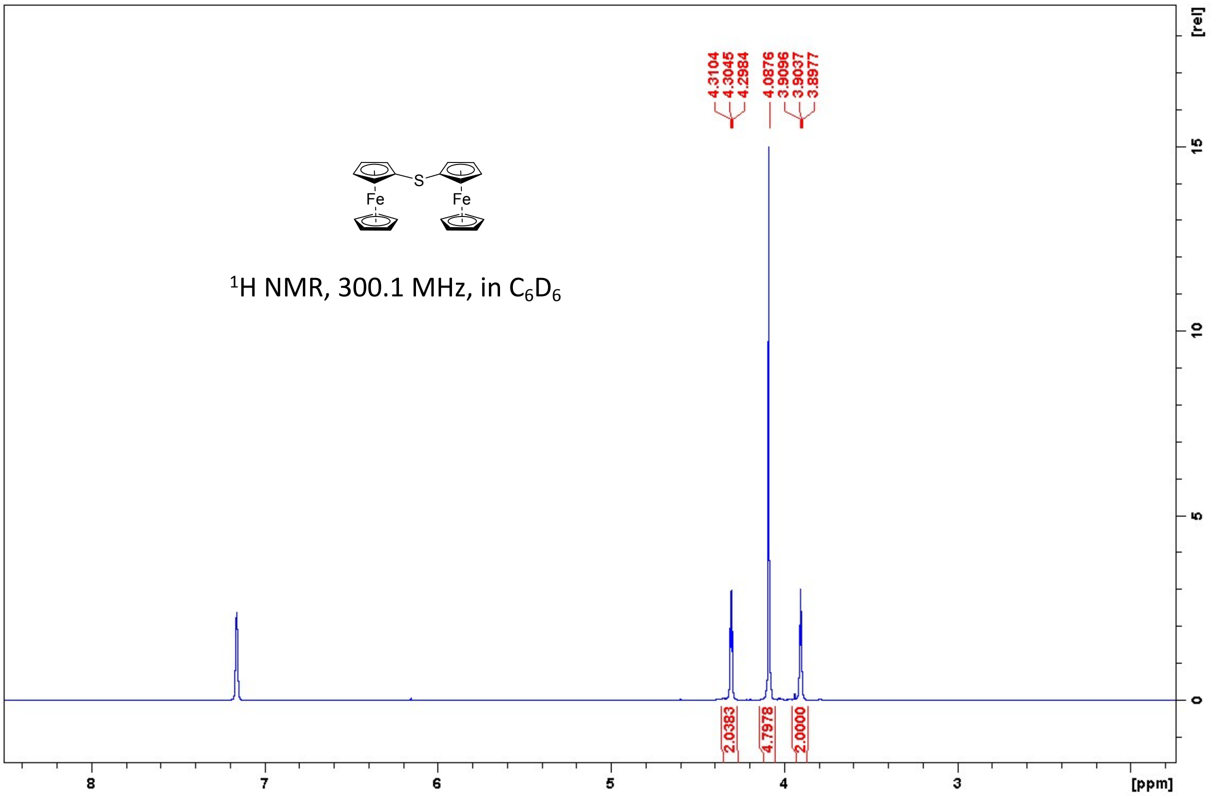
Bis(-p-toluenesulfonyl) sulfide

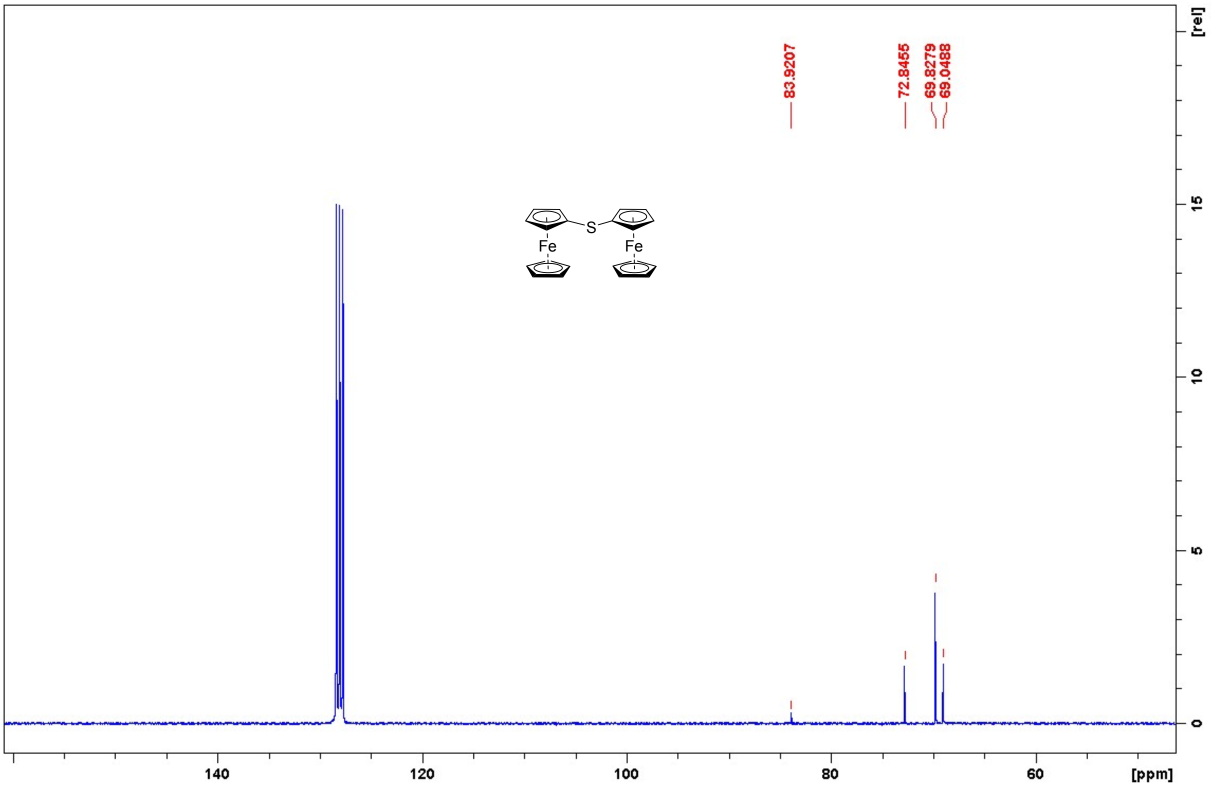


^{13}C NMR, 75.5 MHz, in CDCl$_3$

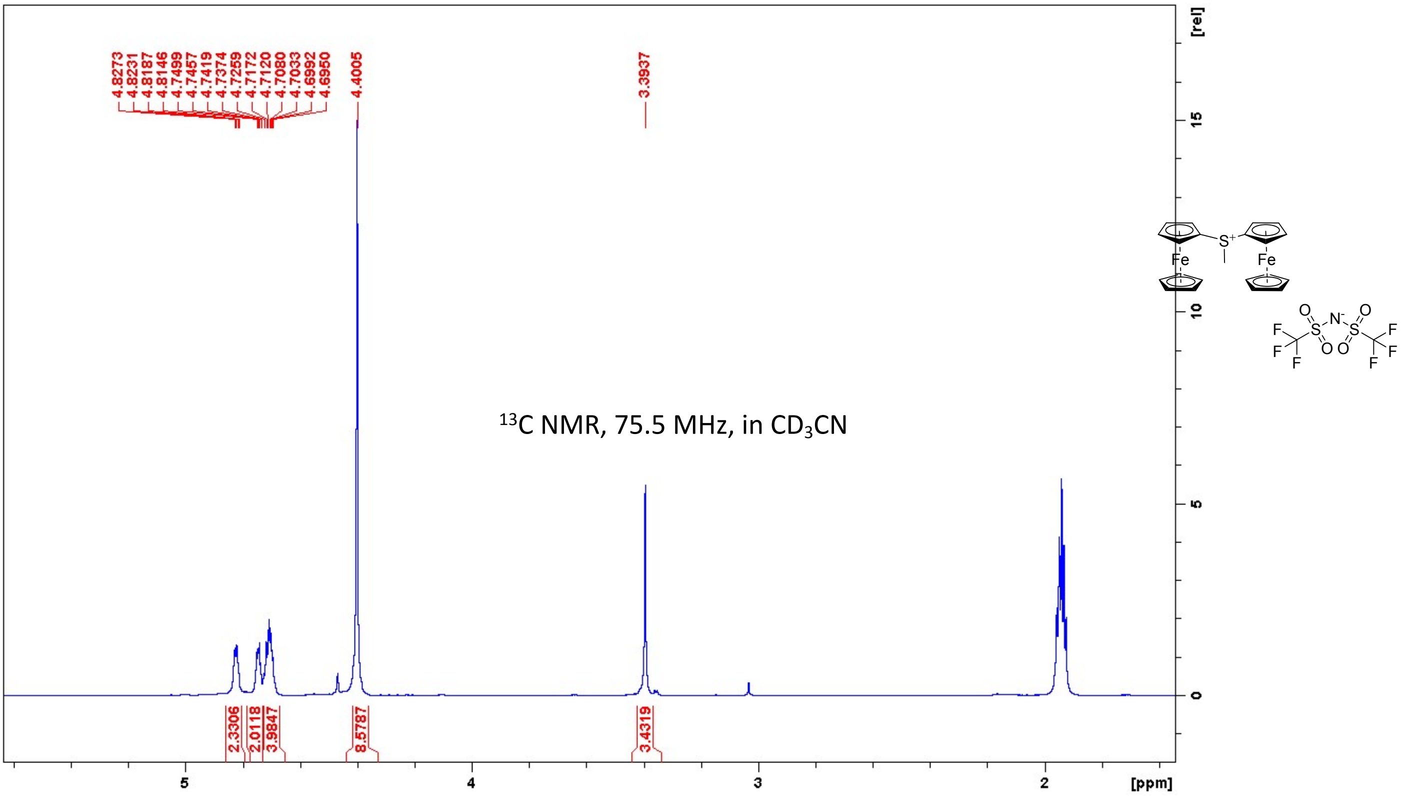


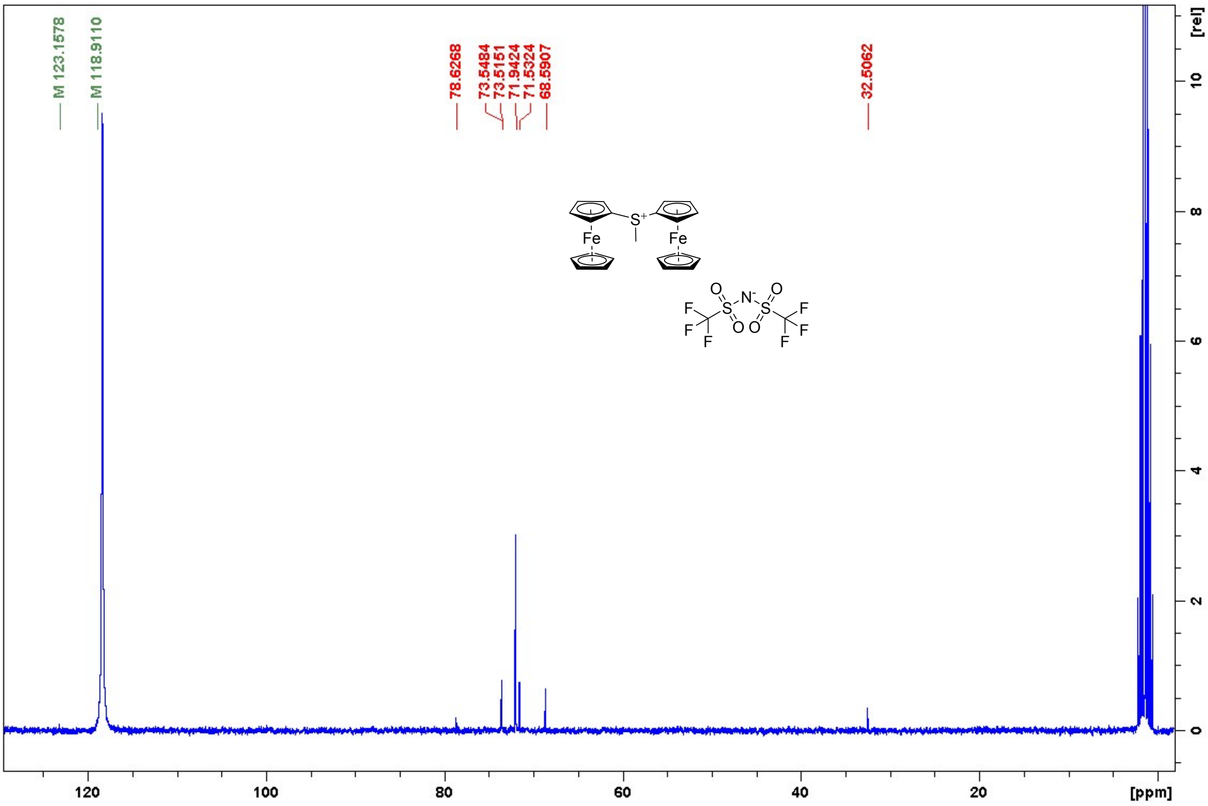
Diferrocenyl sulfide

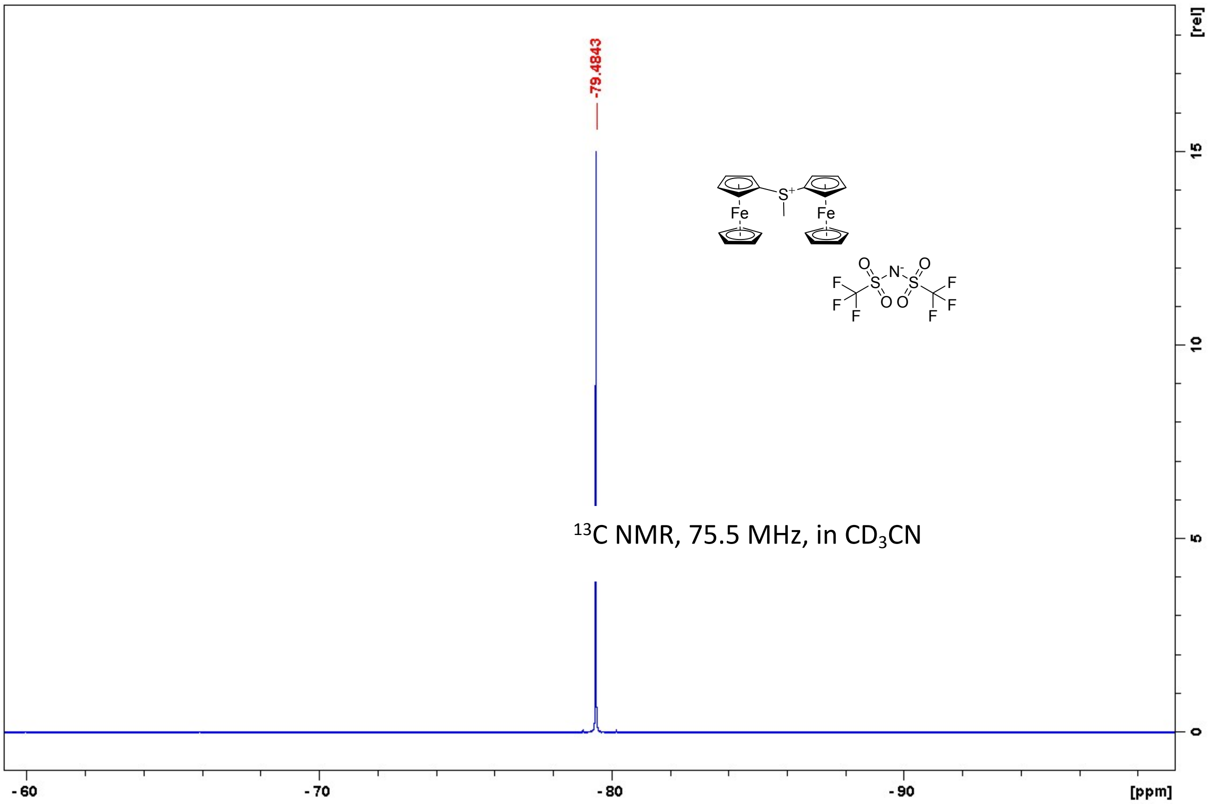




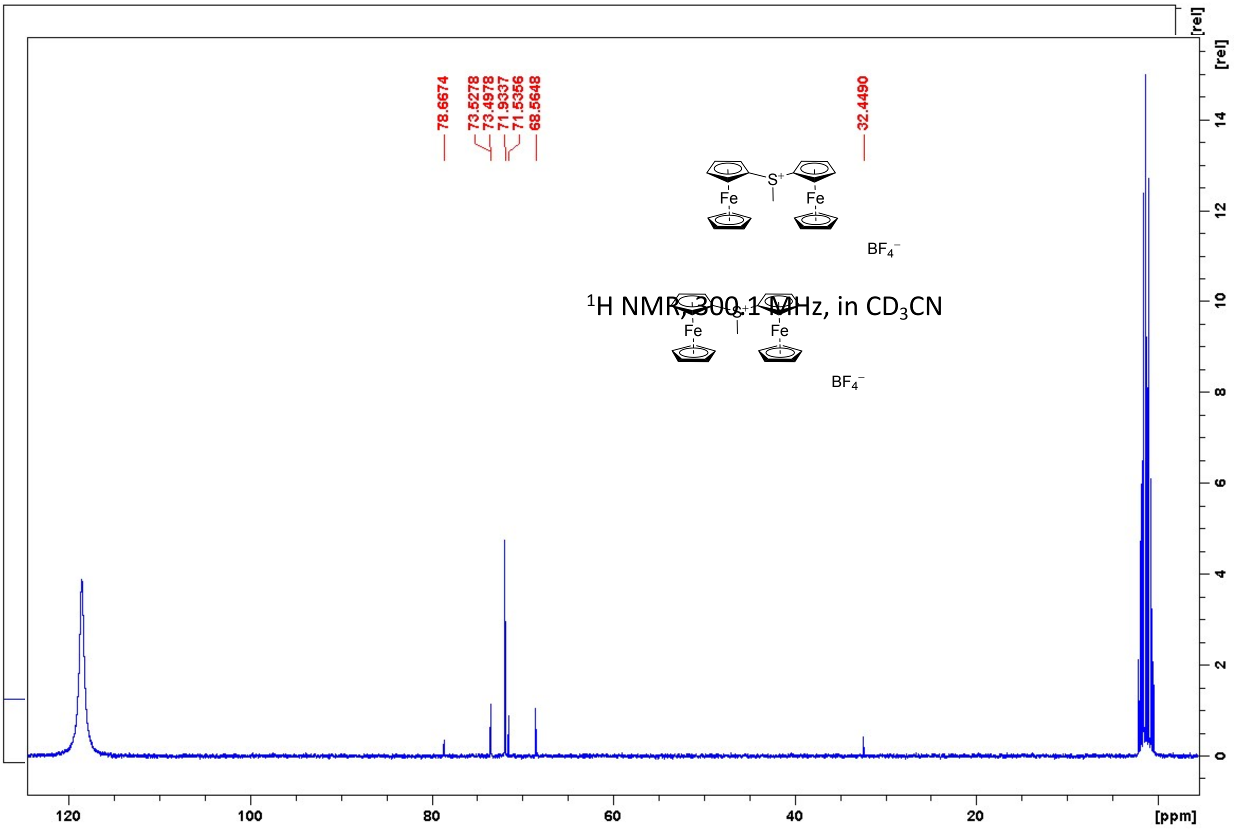
Diferrocenylmethylsulfonium bis(trifluoromethanesulfonyl)imide

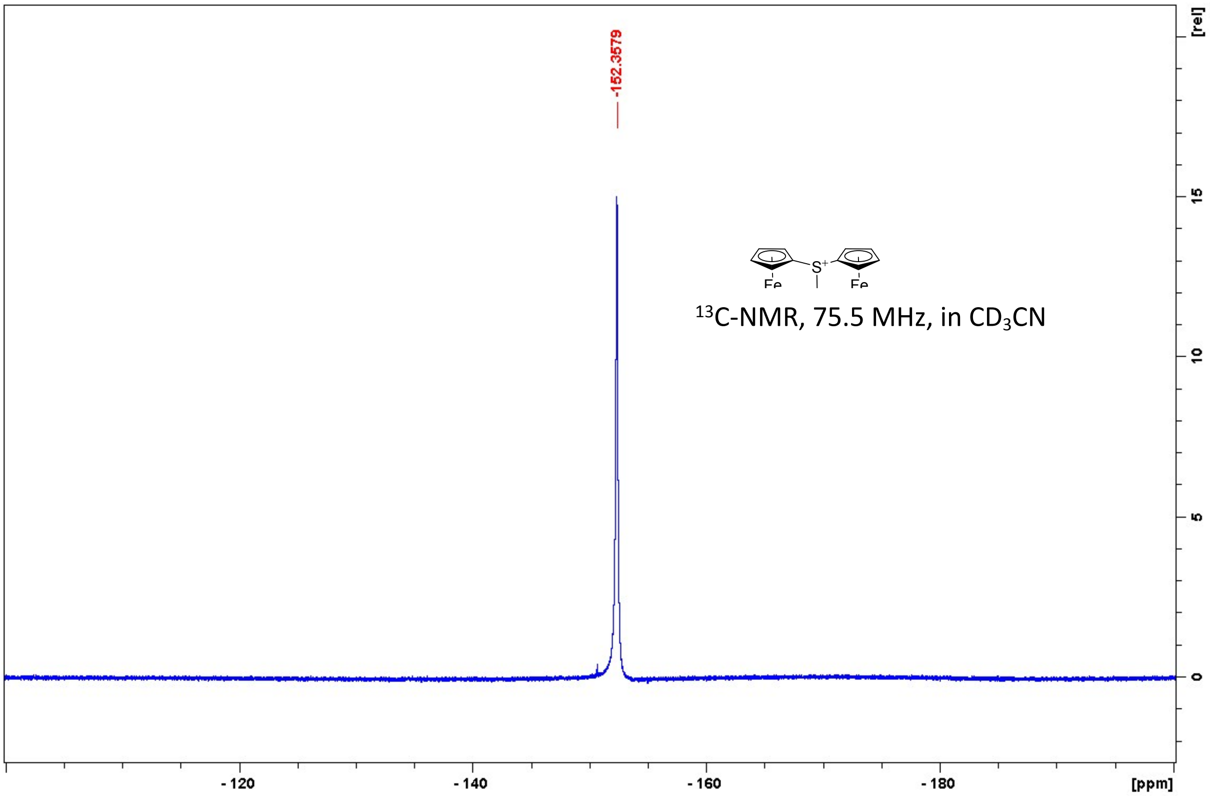




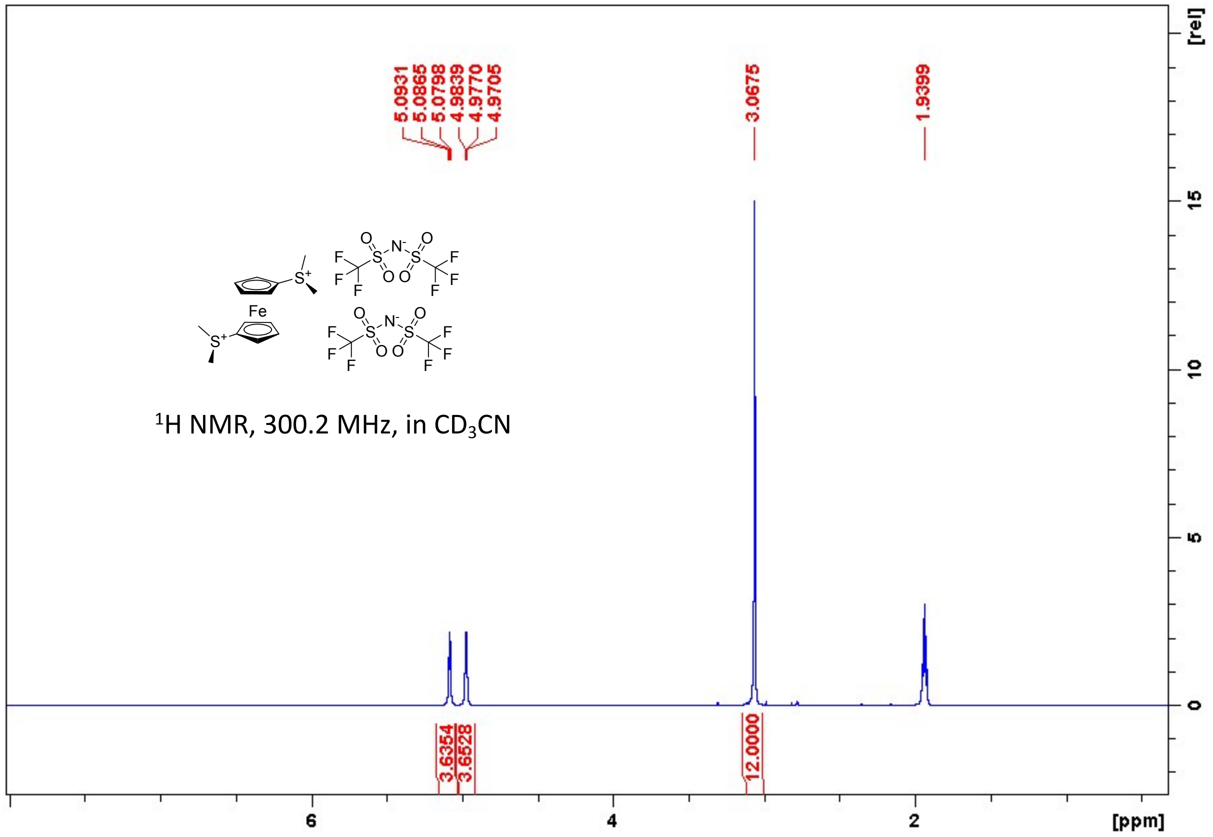


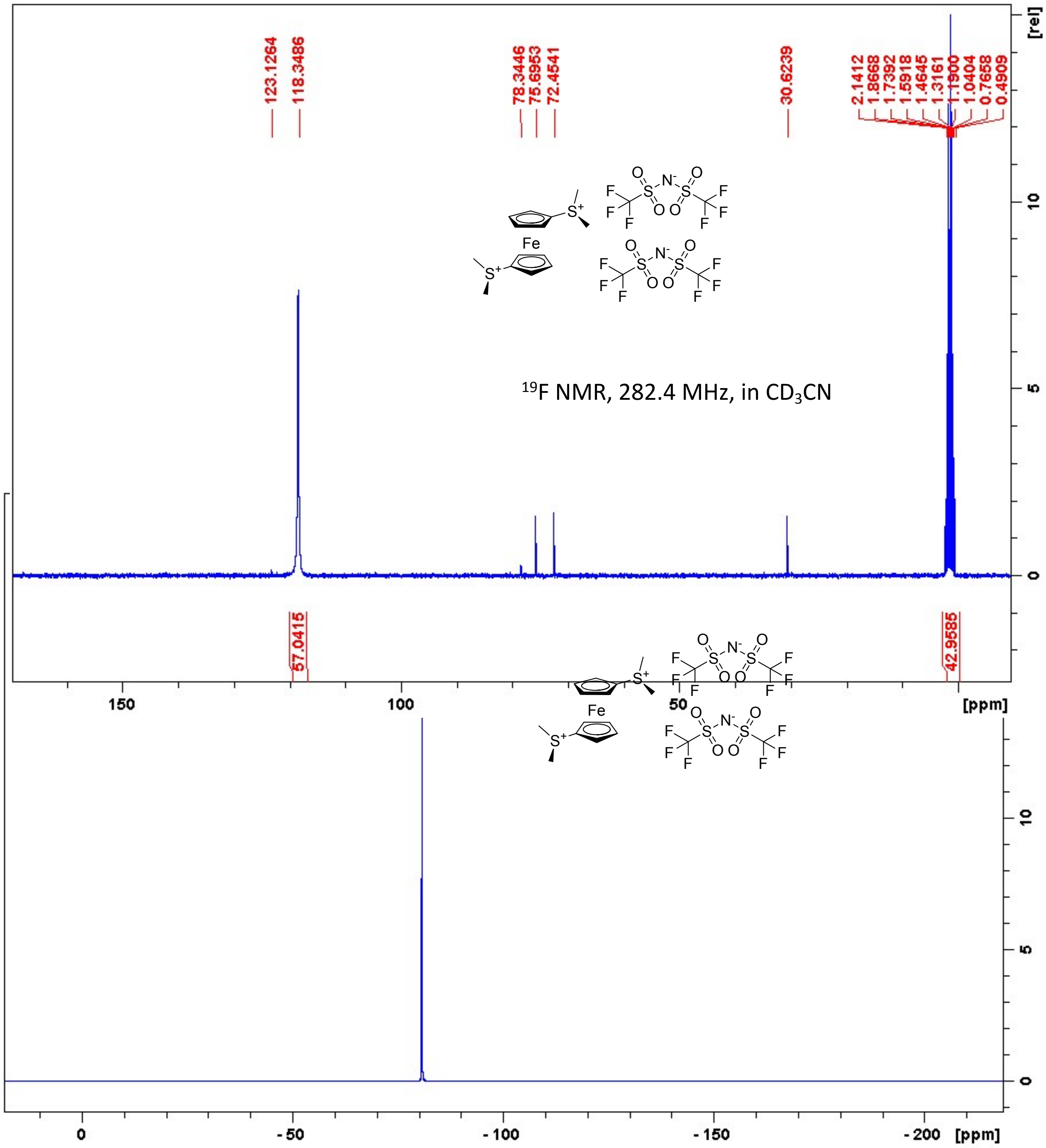
Diferrocenylmethylsulfonium tetrafluoroborate



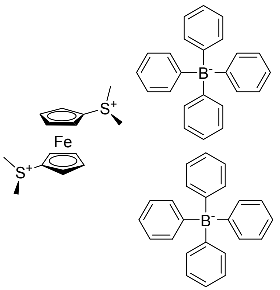


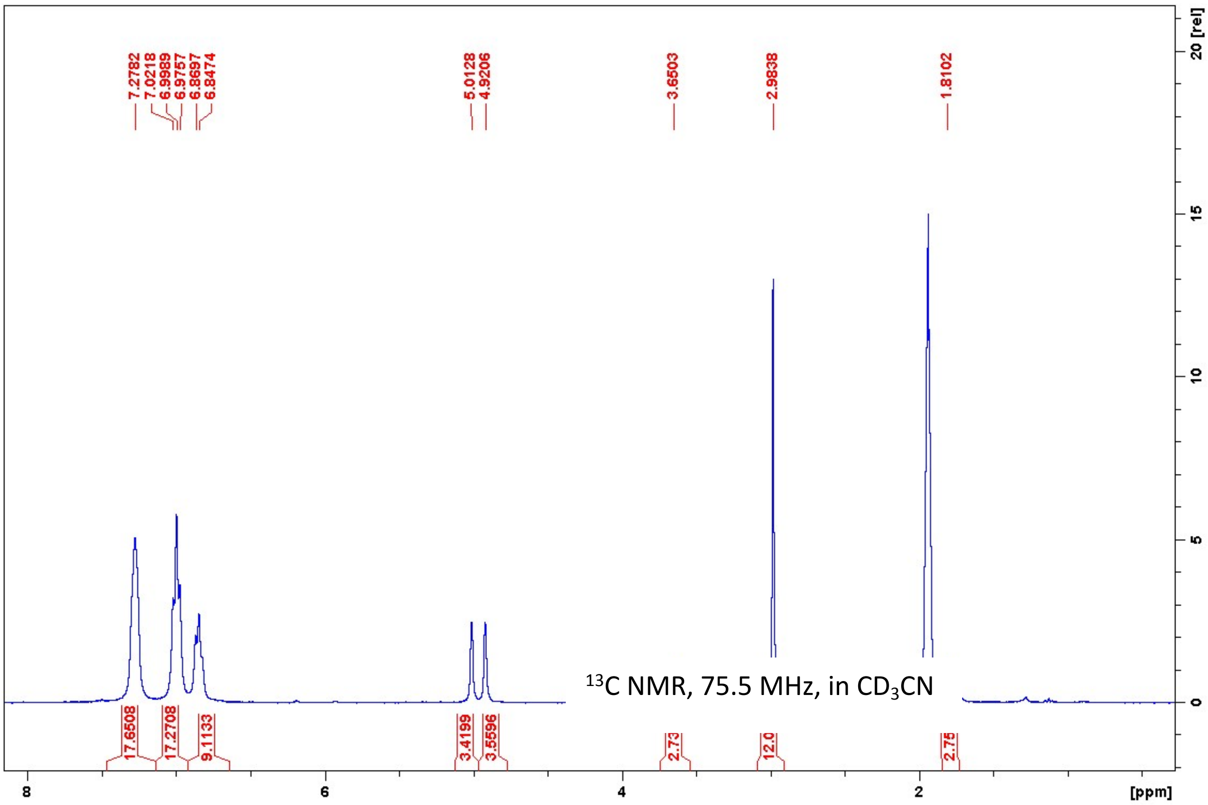
Bis(dimethylsulfonium)ferrocene di{bis(trifluoromethanesulfonyl)imide}



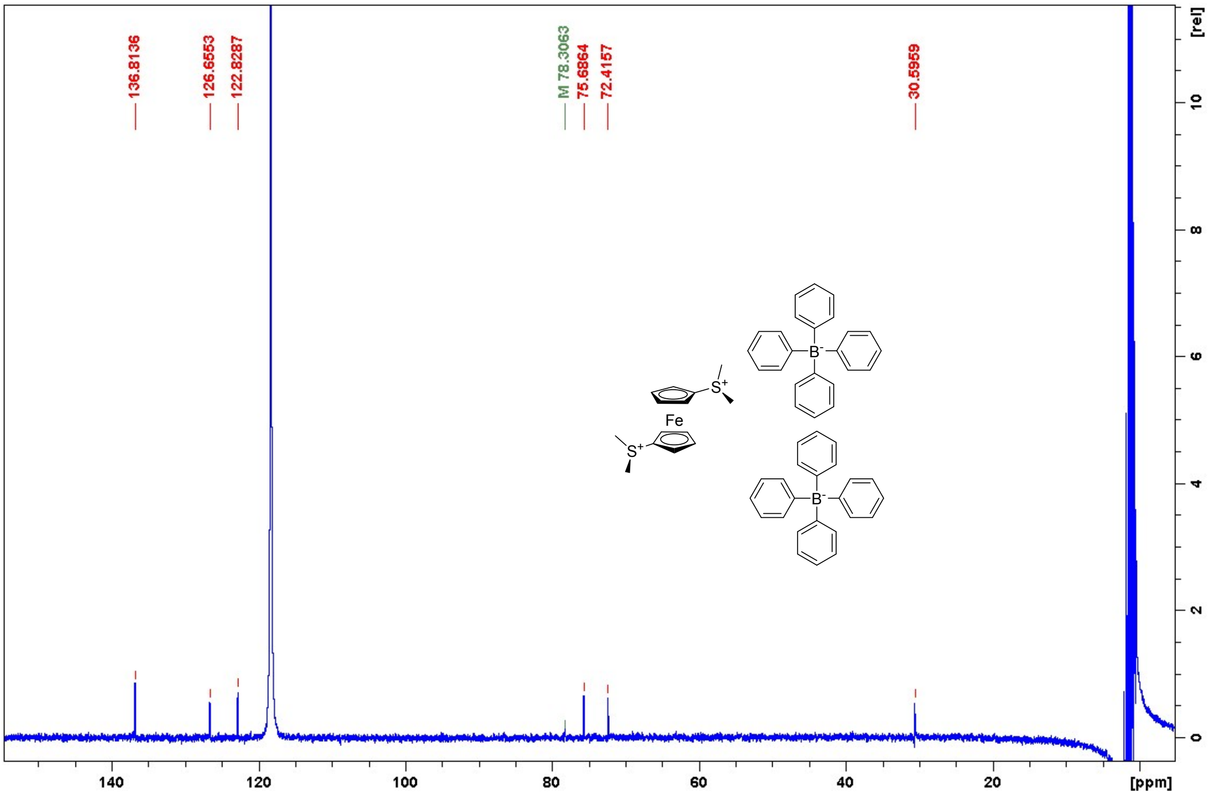

^{19}F NMR, 282.4 MHz, in CD$_3$CN

Bis(dimethylsulfonium)ferrocene di(tetraphenylborate) · THF

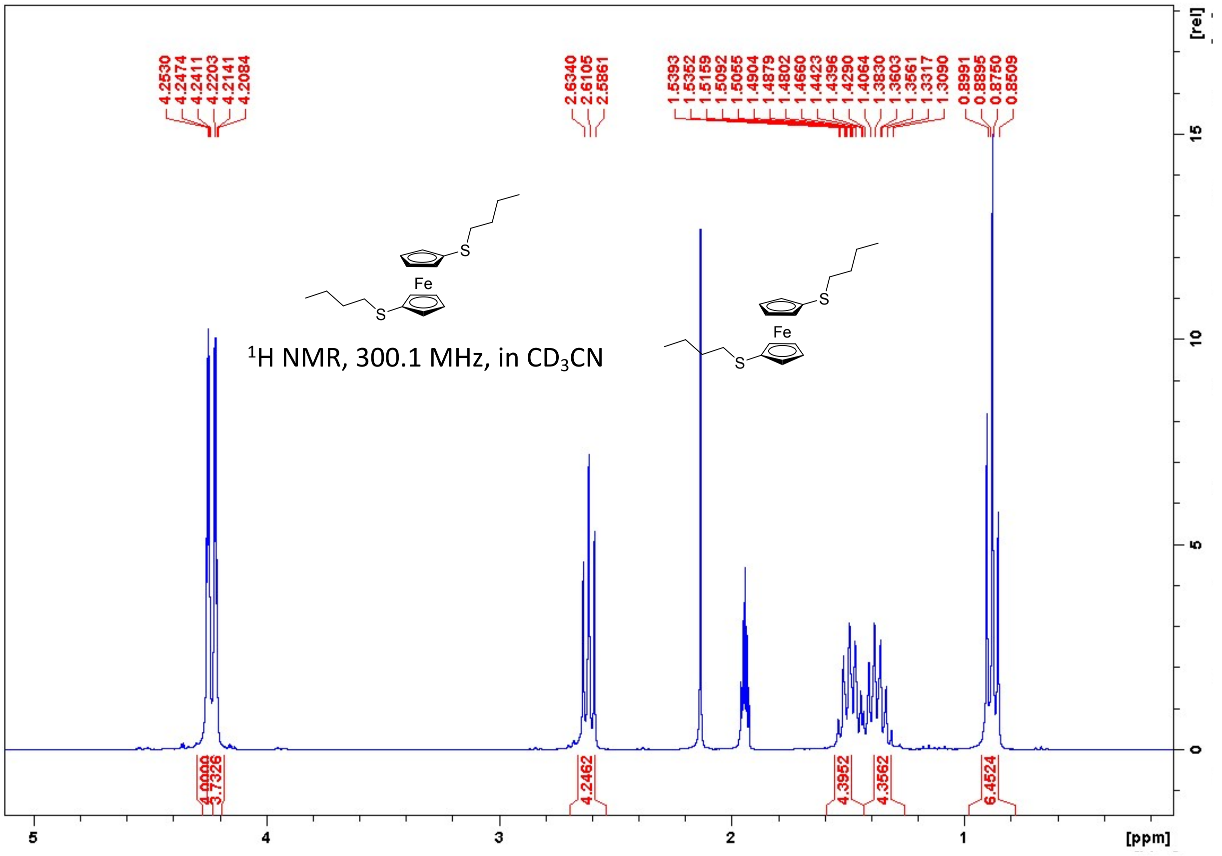




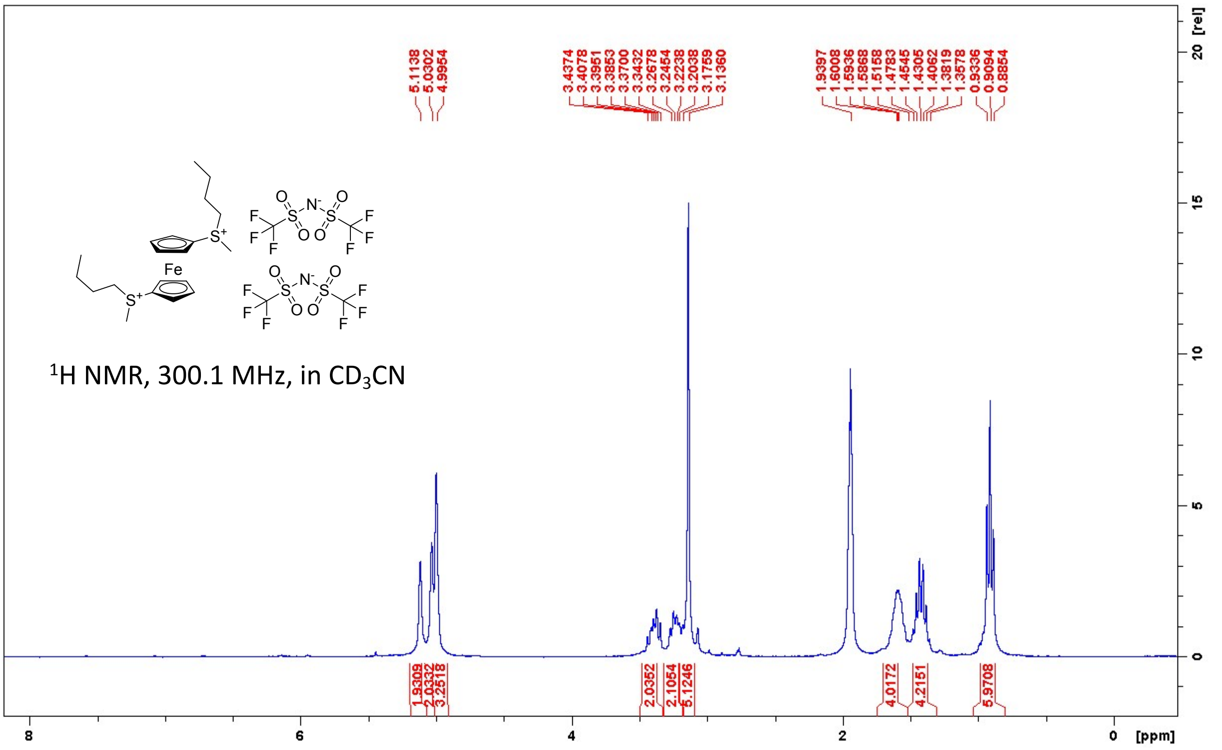
^{13}C NMR, 75.5 MHz, in CD$_3$CN

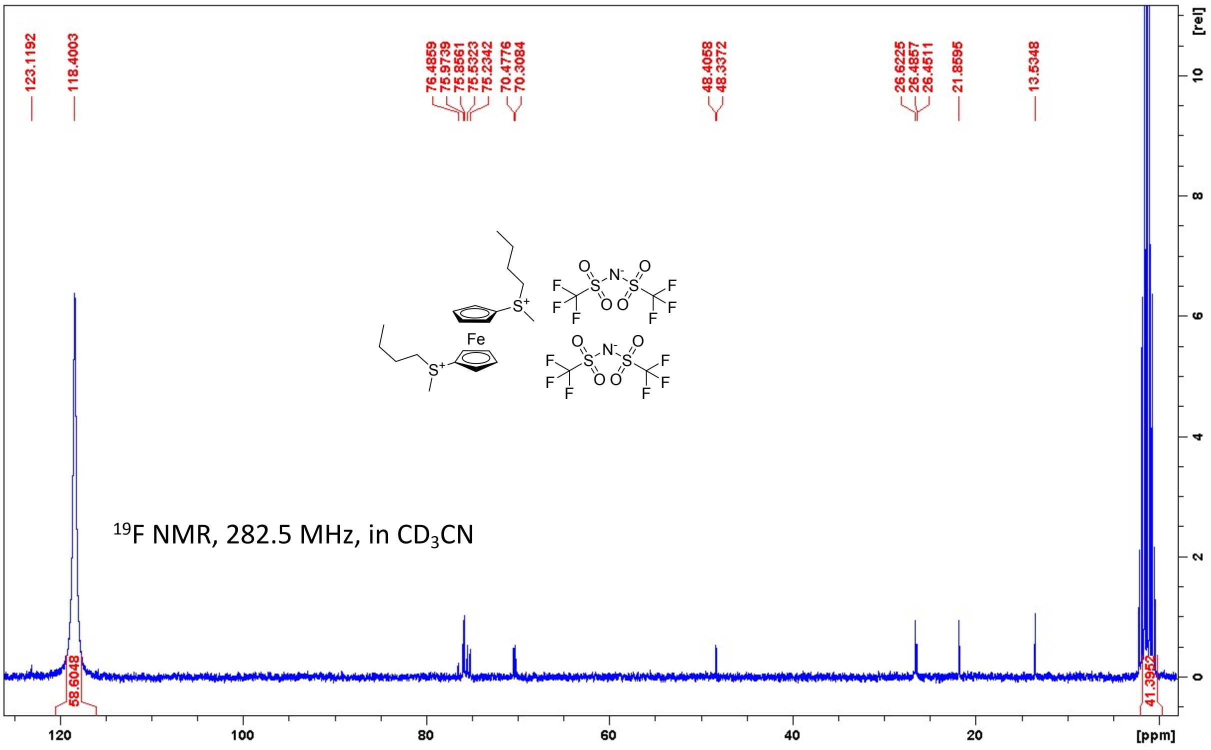


1,1‘-Di(butylthio)ferrocene

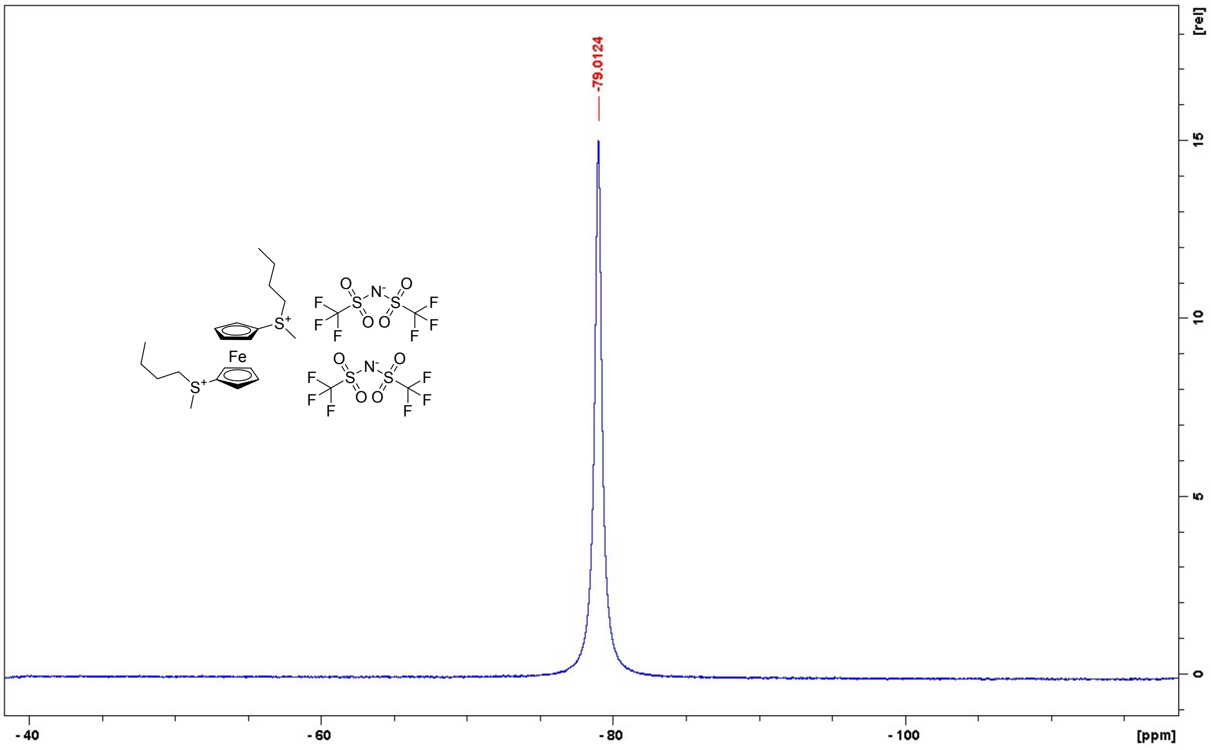


1,1‘-Di(butylmethylsulfonium)ferrocene di{bis(trifluoromethanesulfonyl)imide}



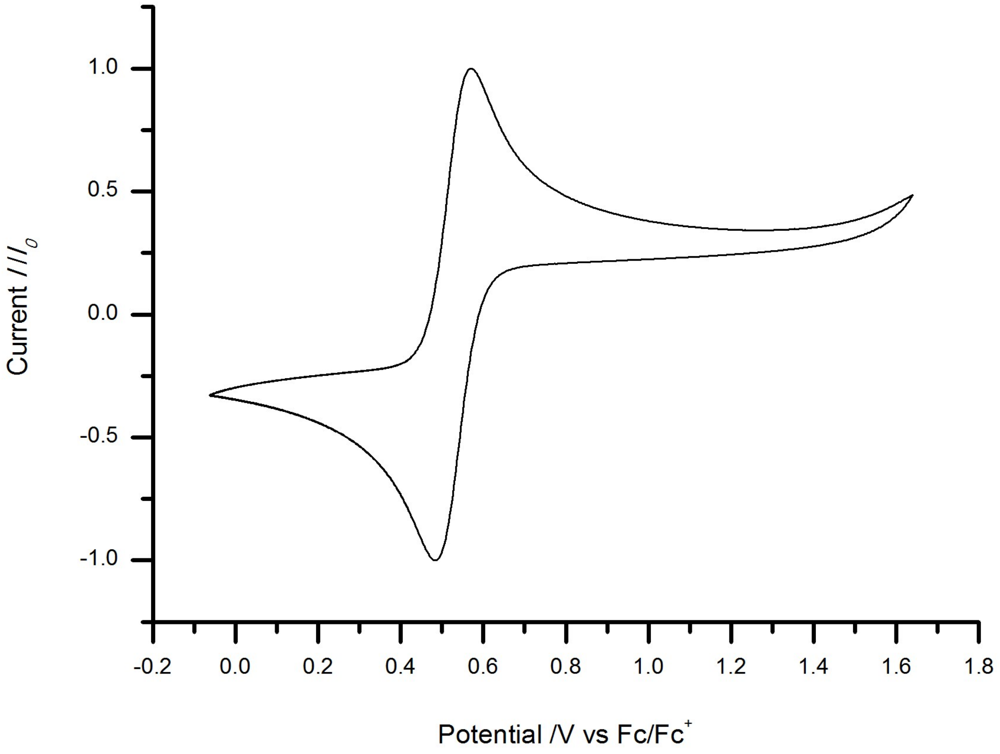


^{19}F NMR, 282.5 MHz, in CD_3CN

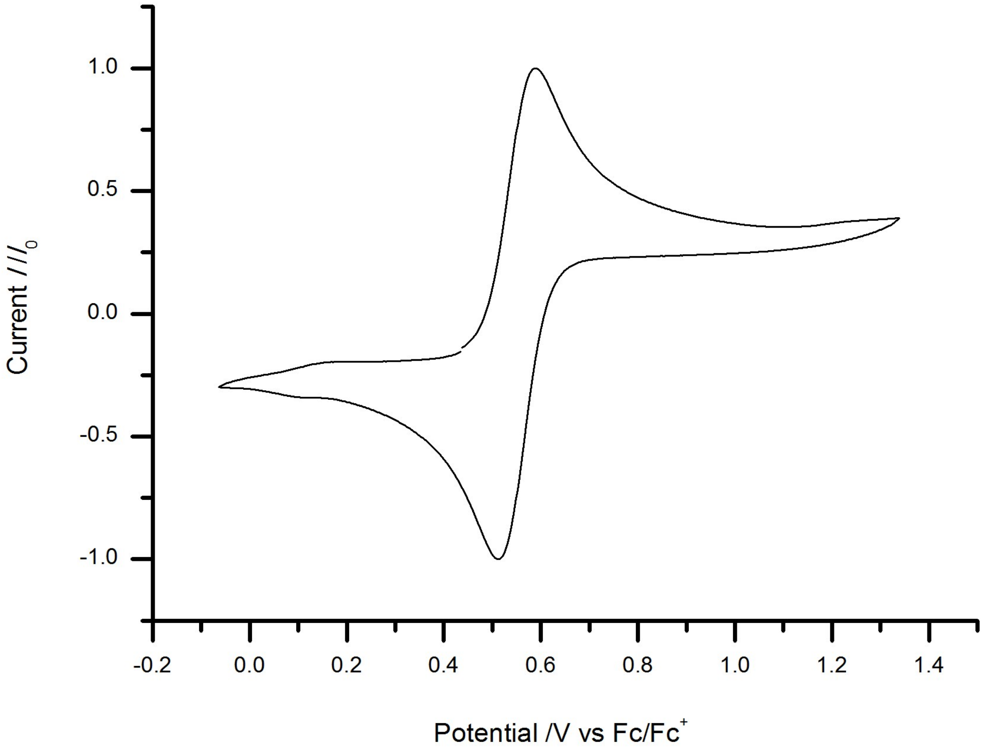


Cyclic voltammetry

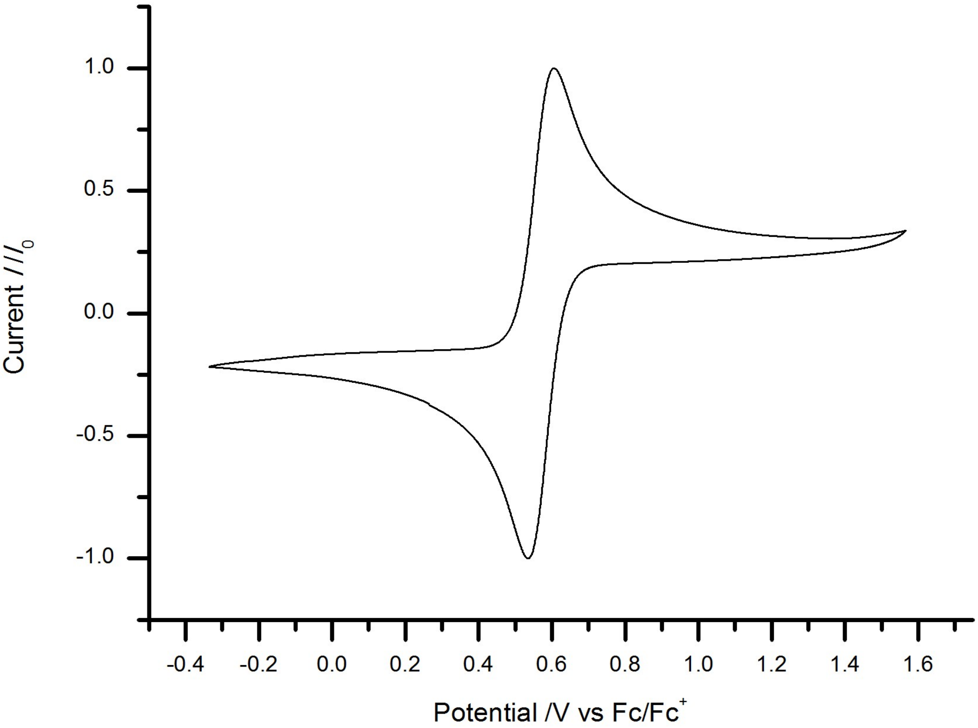
Ferrocenyldimethylsulfonium bis(trifluoromethanesulfonyl)imide (**10 mV s^{-1} in [EMIM]TFSI**)



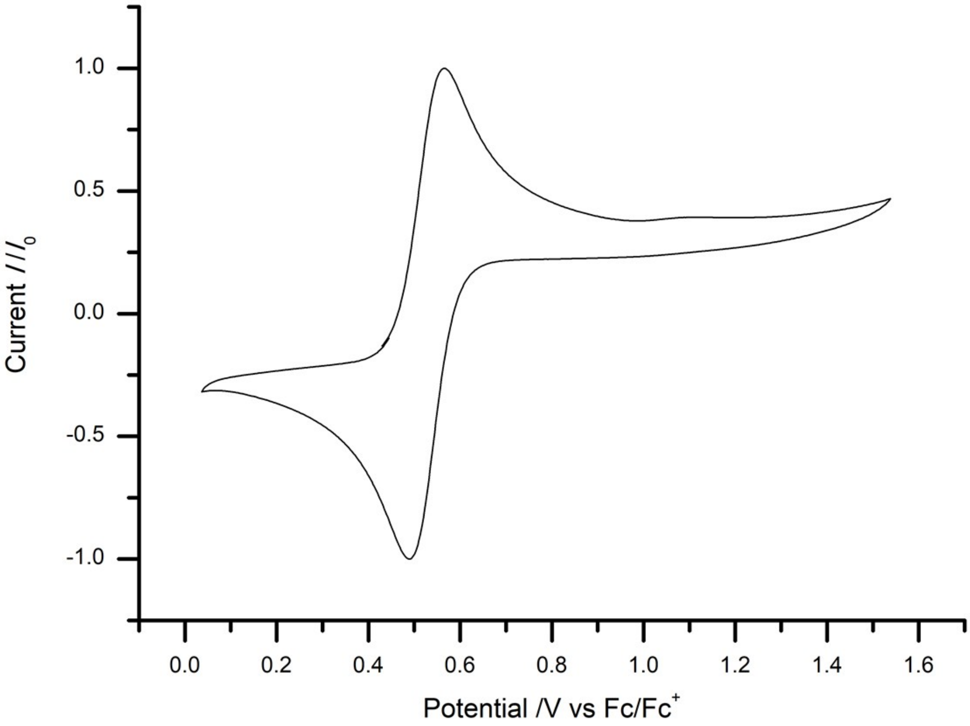
Ferrocenylmethylphenylsulfonium bis(trifluoromethanesulfonyl)imide (**10 mV s^{-1} in [EMIM]TFSI**)



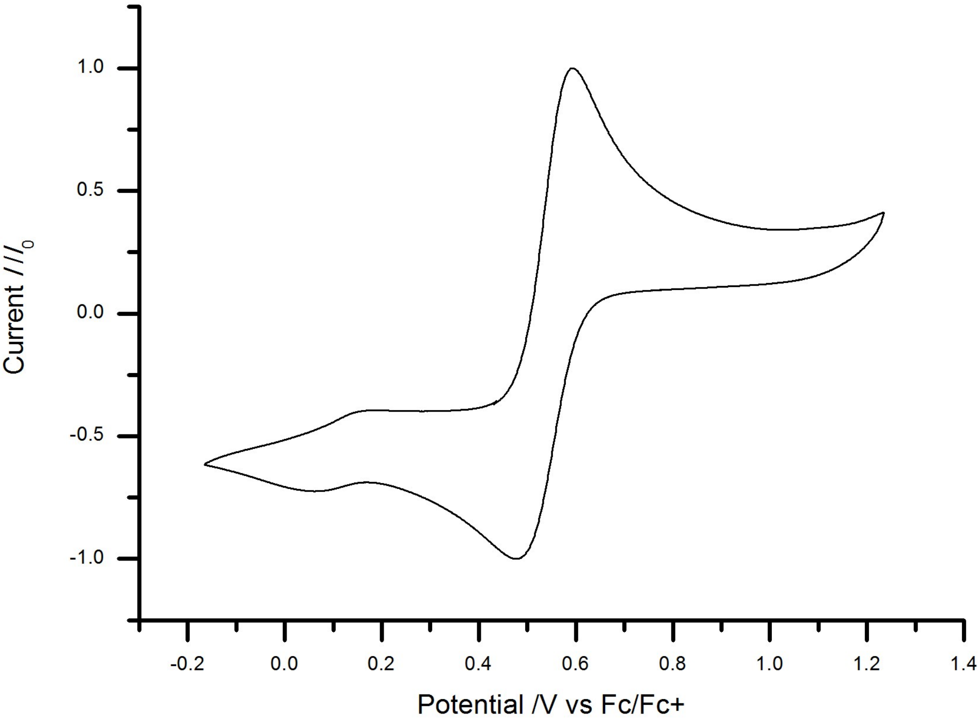
Butylferrocenylmethylsulfonium bis(trifluoromethanesulfonyl)imide *(10 mV s^{-1} in [EMIM]TFSI)*



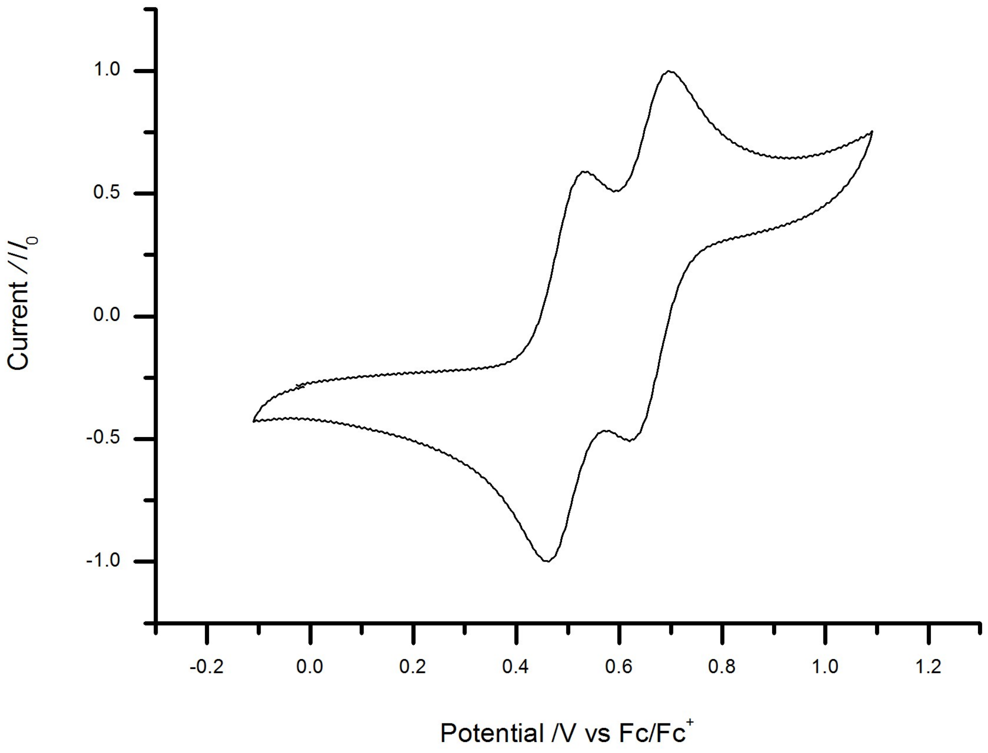
Dibutylferrocenylsulfonium bis(trifluoromethanesulfonyl)imide *(10 mV s^{-1} in [EMIM]TFSI)*



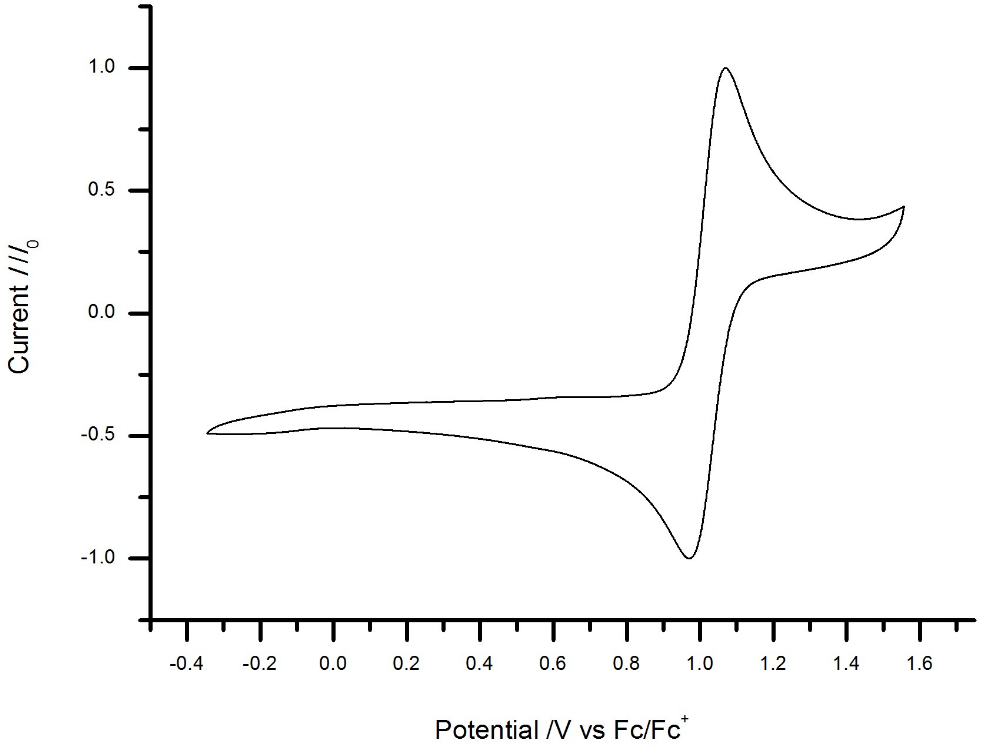
***Butylferrocenylphenylsulfonium bis(trifluoromethanesulfonyl)imide** (10 mV s^{-1} in [EMIM]TFSI)*



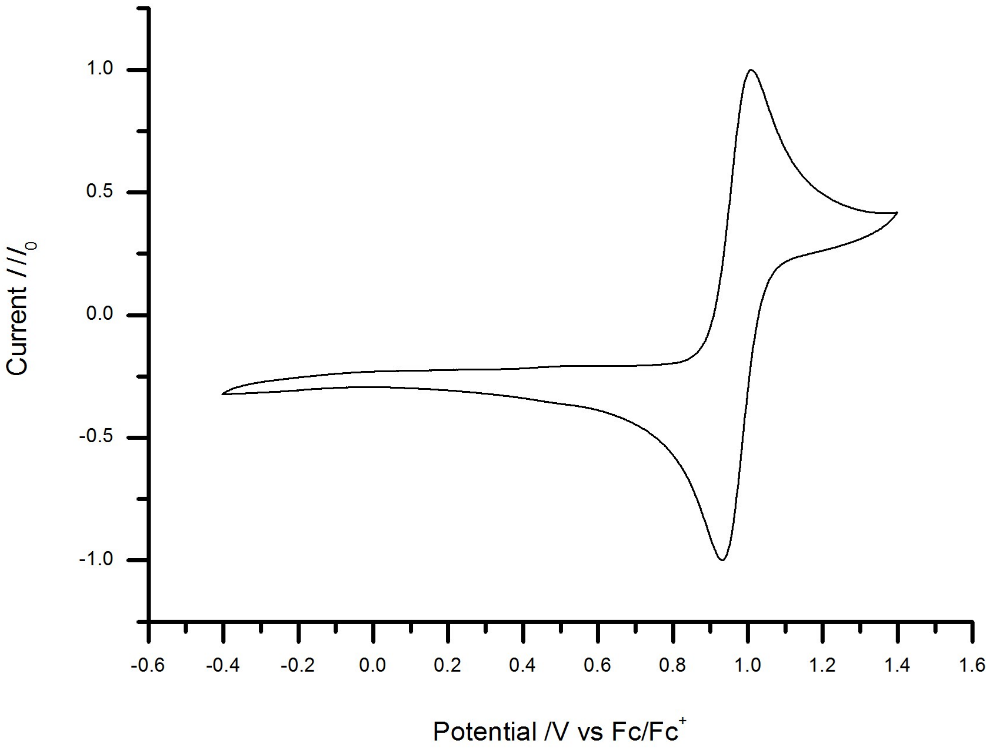
***Diferrocenylmethylsulfonium tetrafluoroborate** (50 mV s^{-1} in [EMIM]TFSI)*



Bis(dimethylsulfonium)ferrocene di{bis(trifluoromethanesulfonyl)imide} *(10 mV s^{-1} in [EMIM]TFSI**)***

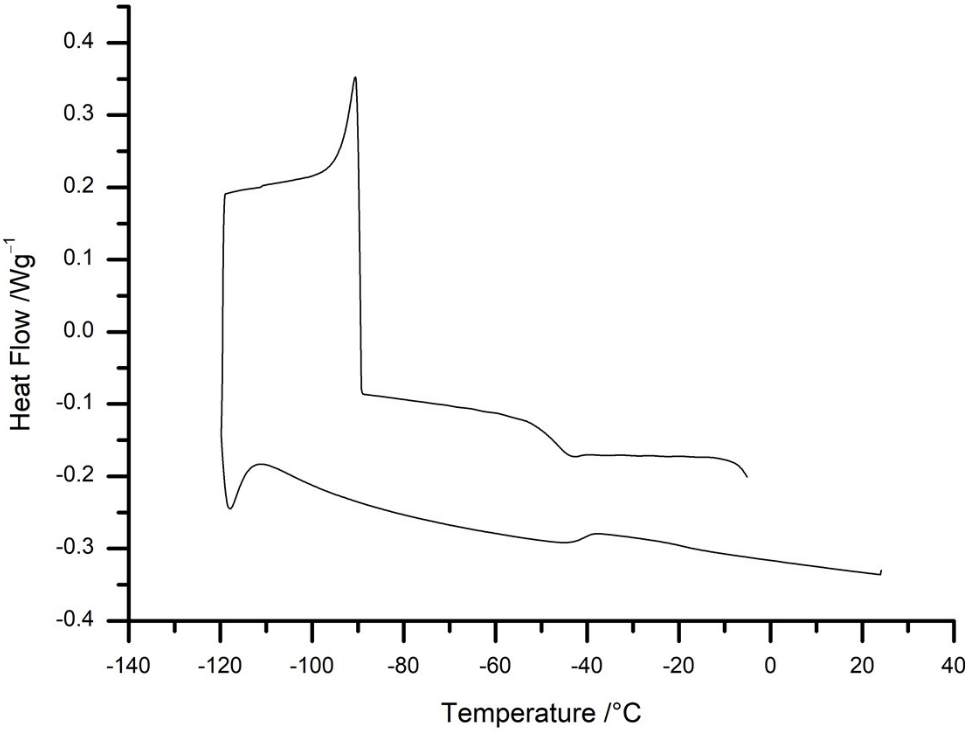


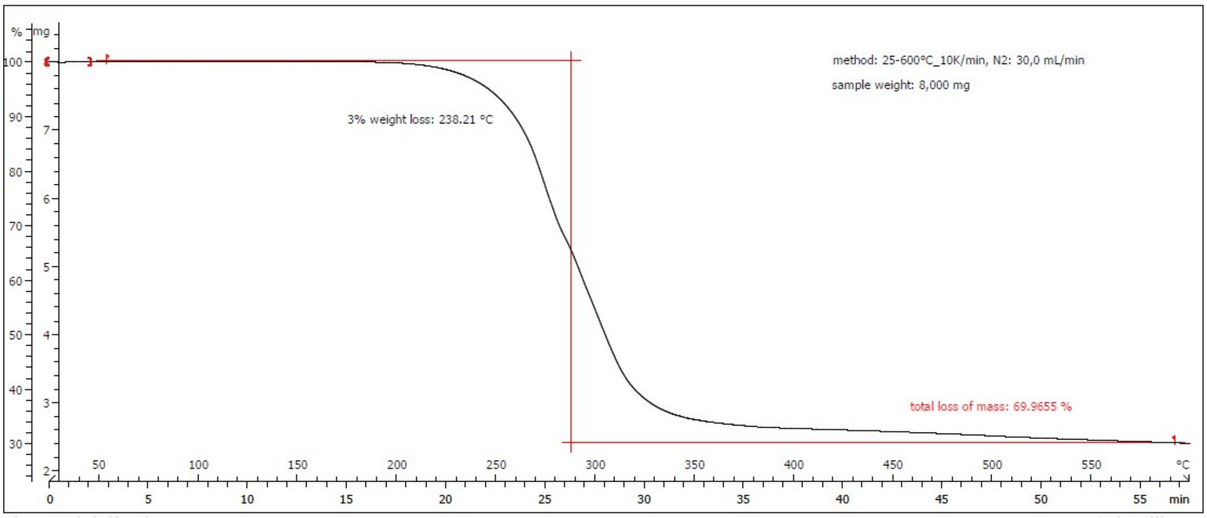
1,1'-Di(butylmethylsulfonium)ferrocene di{bis(trifluoromethanesulfonyl)imide} *(10 mV s^{-1} in [EMIM]TFSI**)***



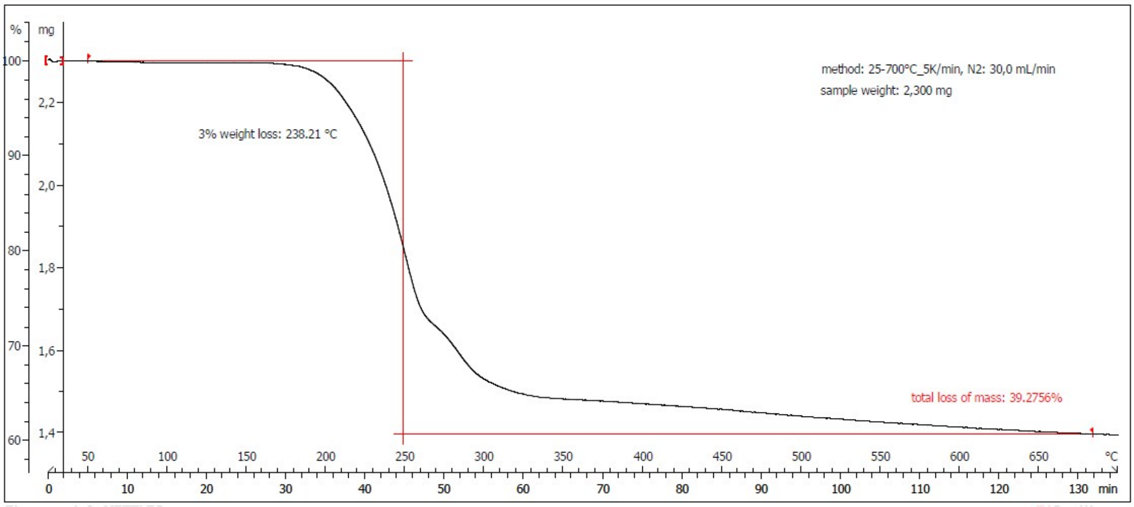
Differential Scanning Calorimetry and Thermal Gravimetric Analysis

Ferrocenyldimethylsulfonium bis(trifluoromethanesulfonyl)imide *(DSC above, TGA below, each 10 K min^{-1})*



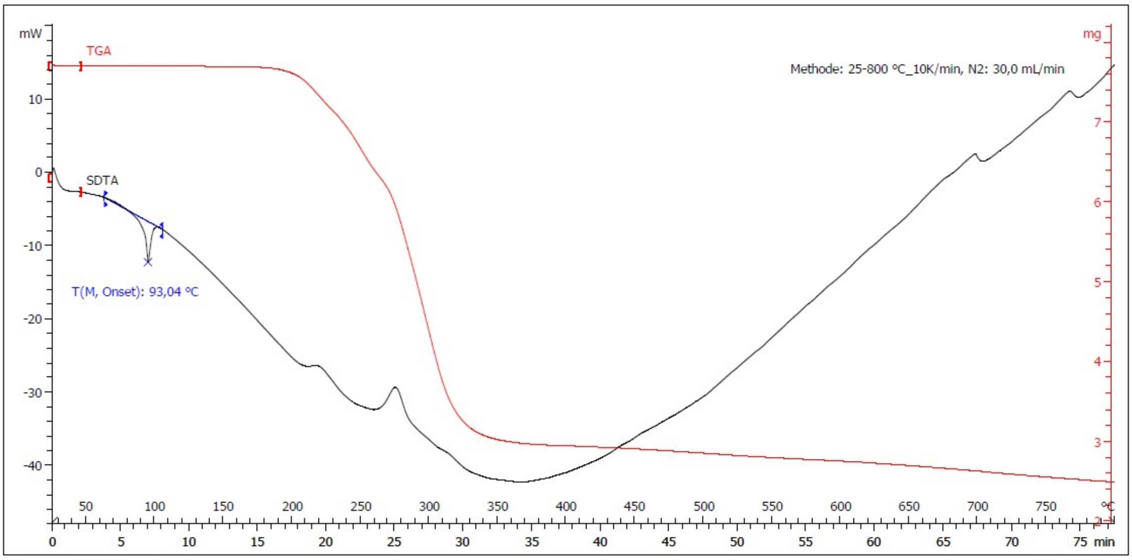


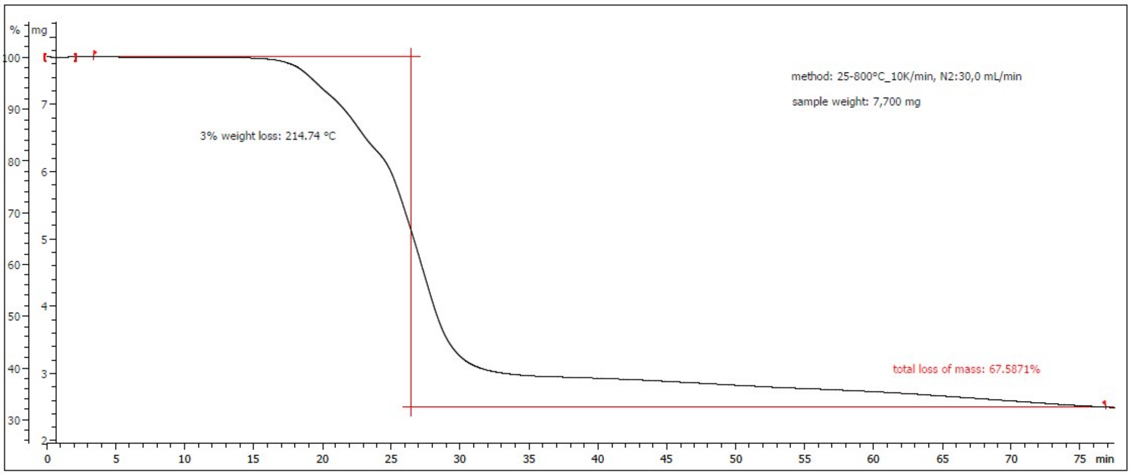
Bis(dimethylsulfonium)ferrocene di{bis(trifluoromethanesulfonyl)imide} *(TGA, 10 K min^{-1})*



1,1‘-Di(butylmethylsulfonium)ferrocene di{bis(trifluoromethanesulfonyl)imide} *(sDTA above, TGA below, each 10 K min^{-1})*

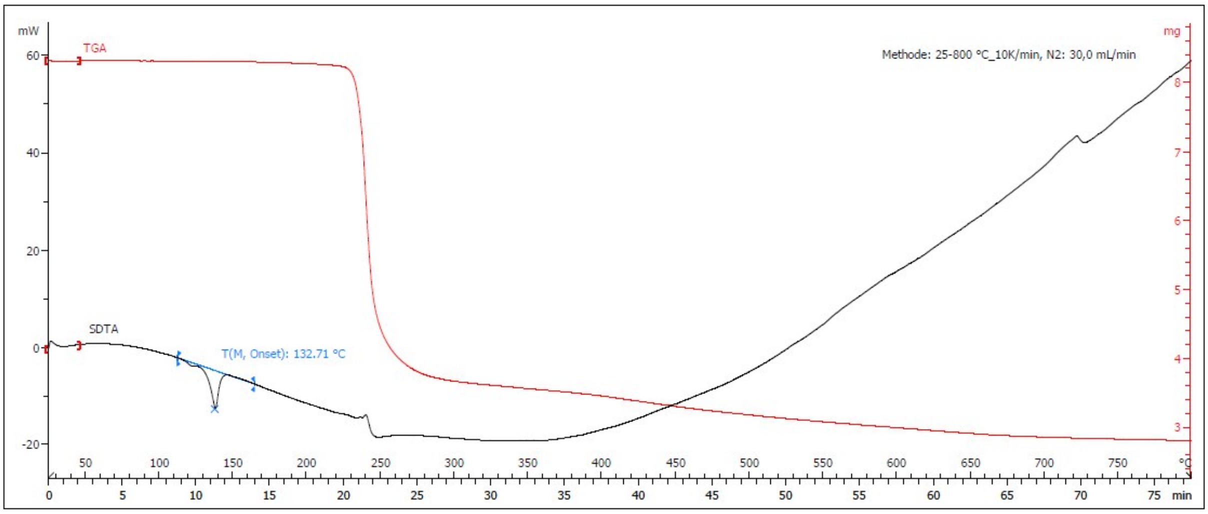
exo ↑

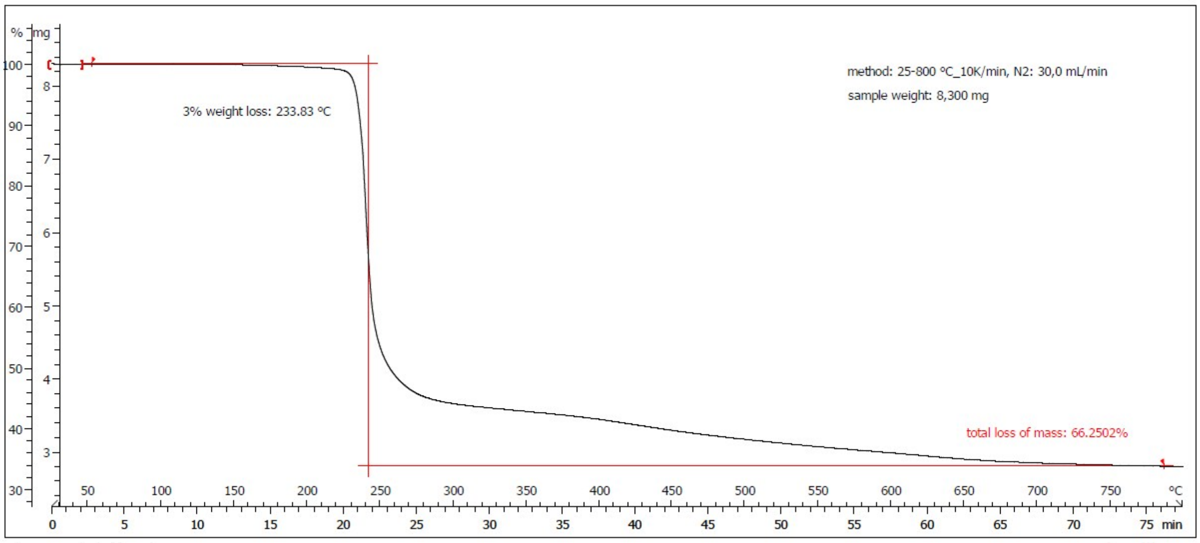




Diferrocenylmethylsulfonium tetrafluoroborate (sDTA above, *TGA below, each 10 K min^{-1}*)

exo ↑





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