Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 550–551

Transformations of (ferrocenylmethylidene)malononitrile under the action of molecular sulfur and NaHS

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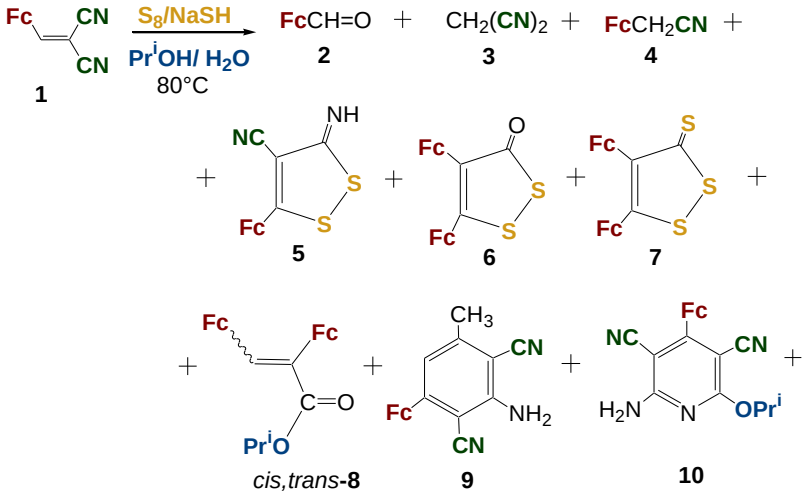
Experimental

Materials and measurements

All the solvents were standardly dried and were freshly distilled before use. Column chromatography was carried out on alumina (Brockmann activity III). Percolated silica gel plates 0.25 mm were employed for analytical TLC. The ^{1}H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (400-MHz and 100 MHz) in $CDCl_3$ with Me_4Si as the internal standard. Chemical shifts (δ in ppm) were reported respect to solvent peaks as internal standard (^{1}H: $CDCl_3$, δ= 7.26 ppm, ^{13}C: $CDCl_3$, δ = 77.2 ppm), δ values were measured with precision 0.01 ppm. The IR spectra were measured on a spectrophotometer FT-IR (Spectrum RXI Perkin Elmer 400 instruments) using KBr pellets. The mass spectra were obtained on a Varian MAT CH-6 instrument (EI MS, 70 eV). An Elementar Analysensysteme LECO CHNS-900 was used for elemental analyses. The following reagents were purchased from Aldrich: ferrocenecarboxaldehyde, 99%; malononitrile, 99%; 2-propanol, 99.9%; sulfur 99%, sodium hydrosulfide hydrate.

2-Cyano-3-ferrocenylacrylonitrile **1** was prepared by condensation of ferrocenecarbaldehyde with malononitrile in benzene in the presence of piperidinium acetate[19] (herein and furtheron the references relate to the main text). The physical and ^{1}H-NMR spectroscopic characteristics of compound **1** were in accordance with the literature data.[20]

Spectral characterization All new compounds were found to be stable at room temperature for a prolonged time and could safely be handled in air. The structures of the products were established based on the data from IR, ^{1}H- and ^{13}C-NMR spectroscopy, mass spectrometry and elemental analysis. The physicochemical characteristics of compounds **2**, **4**[13], **6**,[14] **8a**[15] and **10**[12c] corroborate completely their structures (Scheme S1).



Scheme S1. *Reagents and conditions*: Pr^{i}OH, H_2O, reflux, 6-8 h.

The IR spectra of compounds **3**, **4**, **5**, **9** and **10** contain bands at 2212 – 2225 cm^{-1}, which are characteristic of the cyano groups; the main common feature of the IR spectra of

the compounds **2**, **6**, *cis,trans*-**8** is the strong single band at 1600-1650 cm^{-1} and 1704 cm^{-1}, which is attributed to the C=O and COOR stretching. The 1,2-dithiol-3-one **6** and 1,2-dithiole-3-thione **7** contain bands at 700 - 850 cm^{-1}, 1418 - 1470 cm^{-1}, and 1725 cm^{-1} which are attributed to the fragments C-S-S and C=S.

The ^{1}H NMR spectrum of imino compound **5** contained characteristic resonances for one ferrocene and one imine protons at 4.27 (C_5H_5), 4.72 and 4.98 (C_5H_4), and 8.27 (NH=) ppm, respectively, while their ^{13}C NMR contained signals at 70.50, 71.49, 73.84 ppm, and 157,52 ppm, respectively. The ^{13}C NMR spectra also contained signal for the one carbon of the CN moietie at 118.26 ppm and one signal for $C_{ipso}Fc$ at 74.33 ppm.

Spectral data of the 4,5-diferrocenyl-1,2-dithiol-3-one **6**[14] and relative thione **7** contain two singlets for the two C_5H_5 ferrocenyl fragments (δ = 4.06 and 4.24 ppm) and at (δ = 4.12, 4.19 ppm), respectively. The ^{13}C NMR spectrum of compound **6** shows two signals for two C_5H_5 ferrocenyl groups (δ = 69.57 and 70.55 ppm), one signal for carbonyl group (C=O) (δ = 192.31 ppm), two signals for $C_{ipso}Fc$ (δ = 78.32 and 79.94 ppm). In the ^{13}C-NMR spectra of 1,2-dithiole-3-thione **7**, the signals of ferrocenyl and thiocarbonyl groups are identified in their appropriate regions.

We assigned configuration for *trans*-**8** based on previously reported data, as the signal from one proton of the CH= fragment is observed at higher field (6.43 ppm) than the signal from the proton of the CH= group of the *cis*-**8** (7.23 ppm).[15]

As inferred from the ^{1}H NMR spectrum of compound **9**, it is formed stereo-specifically as single isomer. This spectrum contained singlet and multiplets for the protons of the C_5H_5 and C_5H_4 moieties of the one ferrocene substituent [4.17 (s), 4.49 (m), 4.92 (m) ppm], singlets for the protons of the methyl (2.48 ppm) and amino (5.17 ppm) groups, and one singlet each for low-field protons at δ = 6.77 ppm, which allowed assigning its tentative structure **9**. The ^{13}C NMR spectrum of this compound **9** shows: four signals for one ferrocenyl substituent [70.31 (C_5H_5), 68.75, 70.58 (C_5H_4), 80.55 ($C_{ipso}Fc$) ppm], one signal for methyl group (21.37 ppm), two signals for two CN fragments (115.82, 117.09 ppm). Combining these with the necessary numbers of signals for quaternary carbon atoms (9189, 94.59, 146.40, 149.44, 152.92 ppm), the ^{13}C NMR spectrum corroborates the suggested structure completely.

*Reactions of 2-cyano-3-ferrocenylacrylonitrile **1** with elemental sulfur and sodium hydrosulfide in a $Pr^{i}OH/ H_2O$*

A mixture of compound **1** (5.24 g, 20 mmol), 2-propanol (100 ml), H_2O (10 ml), elemental sulfur (1.6 g) and NaHS (0.56 g) was stirred on reflux for 6-8 h until complete dissolution of compound **1**. The solvent was removed *in vacuo*, and the residue was dissolved in dichloromethane (50 ml). The solution was mixed with Al_2O_3 (30 g), and the solvent was evaporated in air. This material was placed on the top of a column with Al_2O_3 (the height of alumina is *ca*. 20 cm), and the elution was performed first with hexane and then with hexane-ether (4:1), hexane-dichloromethane (5:1) to afford compounds **2-10**. Compounds **5-7** and isomers *cis*-**8** and *trans*-**8** were isolated by thin-layer chromatography (TLC) on Al_2O_3 in a solvent system hexane-ether (4:1).

*Ferrocenecarboxaldehyde **2**:* orange crystals, yield 0.21 g (5%), m.p. 120-121 °C (lit. [Aldrich]: m.p. 122-124°C).

*Ferrocenylacetonitrile **4**:* red crystals, yield 0.06 g (5%), m.p. 82-83°C [lit.[13]: m.p. 81-82°C]. IR (KBr): ν 424, 518, 616, 677, 706, 754, 805, 957, 1069, 1001, 1151, 1187, 1217, 1298, 1317, 1374, 1450, 1491, 1567, 1589, 1687, 2222, 2934, 3032, 3061 cm^{-1}. ^1H NMR: δ 3.55 (2H, s, CH_2), 4.12 (5H, s, C_5H_5), 4.15 (2H, m, C_5H_4), 4.17 (1H, m, C_5H_4), 4.21 (1H, m, C_5H_4). MS: *m/z* 225 $[M]^+$. Anal. Calcd. for $C_{12}H_{11}FeN$: C 64.04, H 4.93, N 6.22. Found: C 63.95, H 4.98, N 6.23.

*4-Cyano-5-ferrocenyl-3-imino-1,2-dithiole **5**:* yellow crystals, yield 0.92 g (14%), m.p. 121°C. IR (KBr): ν 478, 498, 634, 656, 786, 816, 933, 1000, 1031, 1057, 1105, 1206, 1256, 1315, 1348, 1376, 1388, 1401, 1460, 1578, 1666, 2212, 3178, 3351 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.27 (5H, s, C_5H_5), 4.72 (2H, m, C_5H_4), 4.98 (2H, m, C_5H_4), 8.27 (1H, s, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.50 (C_5H_5), 71.49, 73.84 (C_5H_4), 74.33 ($C_{ipso}Fc$), 118.26 (CN), 97.25, 157.52, 162.72 (3C). Anal. calcd. for $C_{14}H_{10}Fe\,N_2S_2$ (326): C, 51.54; H, 3.09; N, 8.58; S, 19.66. Found: C, 51.70; H, 3.12; N, 8.54; S, 19.70 %. MS (El, 70 eV): *m/z* 326 $[M]^+$.

*4,5-Diferrocenyl-1,2-dithiol-3-one **6**:* red crystals, yield 0.58 g (12 %), m.p. 196 °C (lit.[14]: m.p. 195-197°C). IR (KBr): ν 484, 539, 817, 1000, 1026, 1141, 1254, 1296, 1458(S-S), 1506, 1574, 1601, 2837, 2927, 3082 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.06 (5H, s, C_5H_5), 4.24 (5H, s, C_5H_5), 4.17 (2H, m, C_5H_4), 4.22 (2H, m, C_5H_4), 4.40 (4H, m, C_5H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.57, 70.55 ($2C_5H_5$), 67.90, 68.98, 69.49, 70.60 ($2C_5H_4$), 78.32, 79.94 ($2C_{ipso}Fc$),128.28, 161.85 (2C), 192.39 (C=O). Anal. calcd. for $C_{23}H_{18}Fe_2OS_2$ (486): C, 56.83; H, 3.73; S, 13.17. Found: C, 56.80; H, 3.70; S, 13.23 %. MS (El, 70 eV): *m/z* 486 $[M]^+$.

*4,5-Diferrocenyl-1,2-dithiole-3-thione **7**:* black powder, yield 0.5 g (10%), m.p. 225-226 °C. IR (KBr): ν 467, 482, 705, 749, 813, 887, 1008, 1026, 1071, 1105, 1169, 1195, 1246, 1260, 1295, 1389. 1410, 1457, 1494, 1536, 1650, 1725, 2855, 2922, 2956, 3087 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.12 (s, 5H, C_5H_5), 4.19 (s, 5H, C_5H_5), 4.20 (m, 2H, C_5H_4) 4.35 (m, 2H, C_5H_4) 4.39 (m, 2H, C_5H_4), 4.40 (m, 2H, C_5H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.66, 70.87 ($2C_5H_5$), 67.40, 69.69, 70.09, 71.40 ($2C_5H_4$), 79.58, 80.02 ($2C_{ipso}Fc$), 141.32, 170.59 (2C), 213.95 (C=S). Anal. calcd. for $C_{23}H_{18}Fe_2S_3$ (502): C, 55.02; H, 3.61; S, 19.15; Found: C, 55.10; H, 3.71; S, 19.22%. MS (El, 70 eV): *m/z* 502 $[M]^+$.

*Isopropyl cis-2,3-diferrocenylacrylate cis-**8**:* red crystals, yield 0.37 g (7.8%), m.p. 174°C [lit.[15]: m.p. 173-174°C]. IR (KBr): ν 482, 494, 730, 774, 816, 894, 999, 1027, 1054, 1106, 1187, 1208, 1242, 1256 (Pr^i), 1295, 1371, 1384, 1462, 1550, 1609, 1646, 1703, 2933, 2975, 3094 cm^{-1}. ^1H NMR: δ 1.45 (6H, d, J = 6.3 Hz, $2CH_3$), 4.07 (10H, s, $2C_5H_5$), 4.21 (2H, m, C_5H_4), 4.23 (2H, m, C_5H_4), 4.25 (2H, m, C_5H_4), 4.48 (2H, m, C_5H_4), 5.22 (1H, m, CH), 7.23 (1H, s, CH=). MS: *m/z* 482 $[M]^+$. Anal. Calcd. for $C_{26}H_{26}Fe_2O_2$: C 64.76, H 5.44. Found: C 64.51, H 5.33.

*Isopropyl trans-2,3-diferrocenylacrilate trans-**8**:* red crystals, yield 0.4 g (8.2%), m.p. 186-187°C. IR (KBr): ν 468, 728, 774, 809, 949, 995, 1010, 1072, 1100, 1175, 1210, 1261 (Pr^i), 1292, 1375, 1407, 1463, 1529, 1571, 1647, 1700. 2849, 2917, 3099 cm^{-1}. ^1H NMR: δ 1.40 (6H, d, J = 8.1 Hz, $2CH_3$), 4.15 (5H, s, C_5H_5), 4.19 (5H, s, C_5H_5), 4.26 (2H, m, C_5H_4), 4.27

(2H, m, C_5H_4), 4.31 (2H, m, C_5H_4), 4.42 (2H, m, C_5H_4), 5.26 (1H, m, CH), 6.43 (1H, s, CH=). ^{13}C NMR: δ 21.99 ($2CH_3$), 67.94 (CH), 69.35, 69.54 ($2C_5H_5$), 65.48, 68.51, 69.39 ($2C_5H_4$), 80.34, 83.09 ($2C_{ipso}$Fc), 124.06 (CH=), 129.21, 168.84 (2C), 192.34 (C=O). MS: *m/z* 482 $[M]^+$. Anal. Calcd. for $C_{26}H_{26}Fe_2O_2$: C 64.76, H 5.44. Found: C 64.79, H 5.42.

3-Amino-5-ferrocenyl-1-methylisophthalonitrile ***9****:* yellow crystals, yield 1.36g (20%), m.p. 145-146 °C. IR (KBr): ν 479, 526, 602, 730, 773, 820, 1001, 1019, 1106, 1158, 1243, 1292, 1341, 1383, 1437, 1518, 1552, 1623, 1650, 2215, 2852, 2935, 3093, 3243, 3340 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48(3H, s, CH_3), 4.17 (5H, s, C_5H_5), 4.49 (2H, m, C_5H_4), 4.92 (2H, m, C_5H_4), 5.17 (2H, bs, NH_2), 6.77 (1H, s, CH_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.37 (CH_3), 70.31 (C_5H_5), 68.75, 70.58 (C_5H_4), 80.55 (C_{ipso}Fc), 115.82, 117.09 (2CN), 119.08 (CH=), 91.89, 94.59, 146.40, 149.44, 152.92 (5C). Anal. calcd. for $C_{19}H_{15}FeN_3$ (341): C, 66.89; H, 4.43; N, 12.31. Found: C, 66.83; H, 4.56; N, 12.33 %. MS (El, 70 eV): *m/z* 341 $[M]^+$.

2-Amino-4-ferrocenyl-6-isopropoxypyridine-3,5-dicarbonitrile ***10****:* red crystals, yield 0.8 g (10%), m.p. 175-177 °C [lit.[12c]: m.p. 176-177 °C]. IR (KBr): ν 425, 502, 541, 584, 813, 845, 912, 1003, 1044, 1106, 1185, 1253, 1296, 1322, 1334, 1365, 1383, 1425, 1477, 1483, 1542, 1556, 1612, 2200, 2217, 2325, 2979, 3103, 3224, 3369, 3459 cm^{-1}. ^{1}H NMR: δ 1.39 (6H, d, *J* = 6.3 Hz, $2CH_3$), 4.28 (s, 5H, C_5H_5), 4.57 (m, 2H, C_5H_4), 5.20 (m, 2H, C_5H_4), 5.32 (1H, m, J = 6.3 Hz, CH), 5.53 (2H, bs, NH_2). ^{13}C NMR: δ 21.95 ($2CH_3$), 71.16 (CH), 71.01 (C_5H_5), 70.51, 71.07 (C_5H_4), 82.05 (C_{ipso}Fc), 116.32, 117.77 (2CN), 160.14, 160.21, 161.56, 165.38, 166.86 (5C). MS: *m/z* 386 $[M]^+$. Anal. Calcd. for $C_{20}H_{18}FeN_4O$: C 62.20, H 4.70, N 14.50. Found: C 62.18, H 4.68, N 14.45.

Ferrocenecarboxaldehyde **2**:

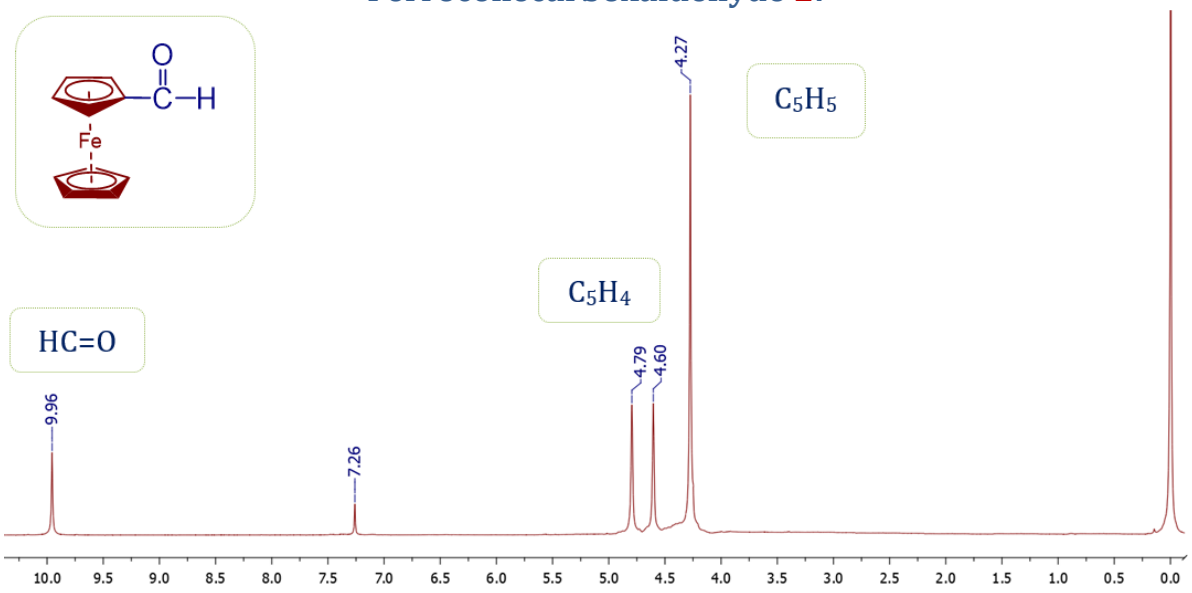


Figure S1: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound **2**

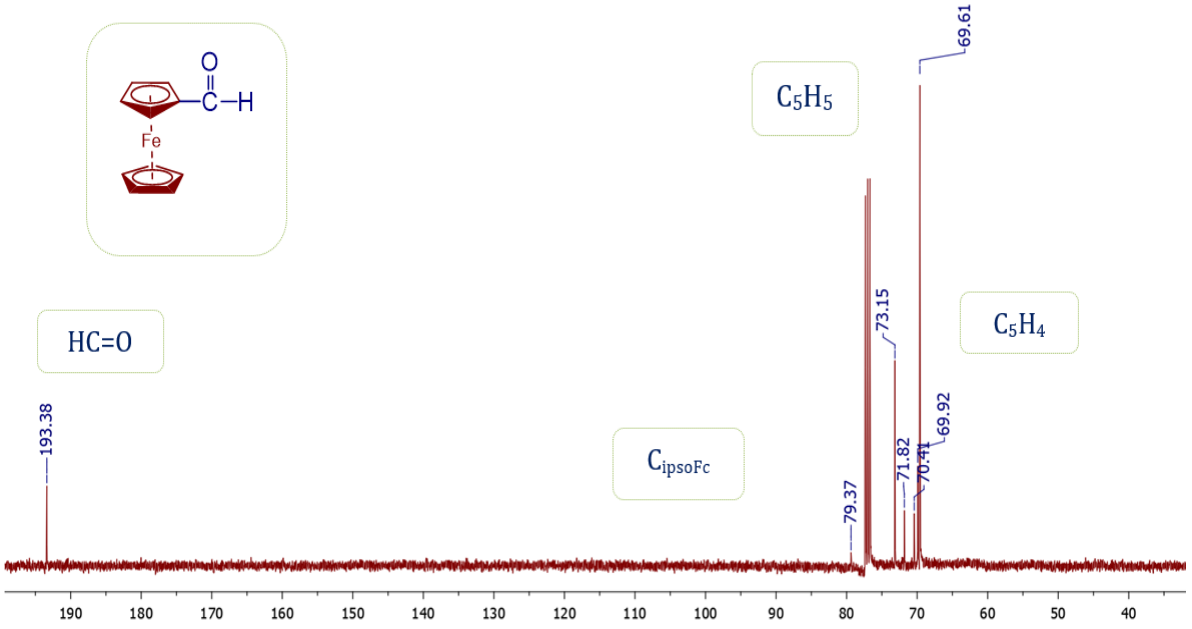


Figure S2: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) spectrum of compound **2**

Ferrocenylacetonitrile **4**

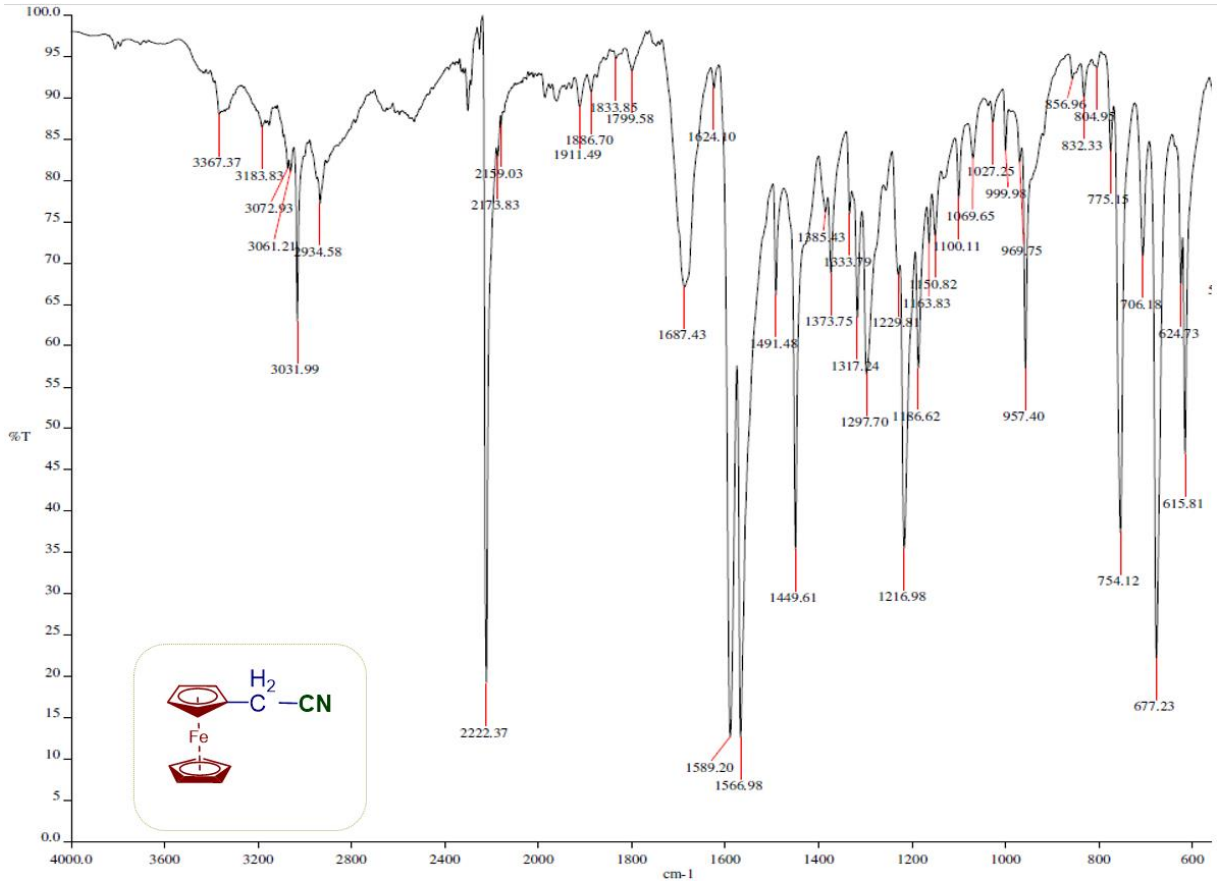


Figure S4: IR (KBr) spectrum of compound **4**

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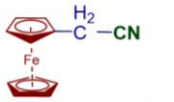
User ID	M en I. Victor Lemus
Comments	Muestra: KE300220B-350

Run	Weight	Carbon	Hydrogen	Nitrogen
53159A	1.02	64.10	4.95	6.29
53159B	1.08	63.90	4.98	6.19
53159C	1.12	63.85	5.01	6.20

	Weight	Carbon	Hydrogen	Nitrogen
Average	1.07	63.95	4.98	6.23
Variance	0.00	0.02	0.00	0.00
Standard Deviation	0.05	0.13	0.03	0.06



$C_{12}H_{11}FeN$

C: 64.04 %
H: 4.93 %
N: 6.22 %

Figure S5: Elemental analysis of compound **4**

4- Cyano-5-ferrocenyl-1,2- dithiol-3-imine **5**

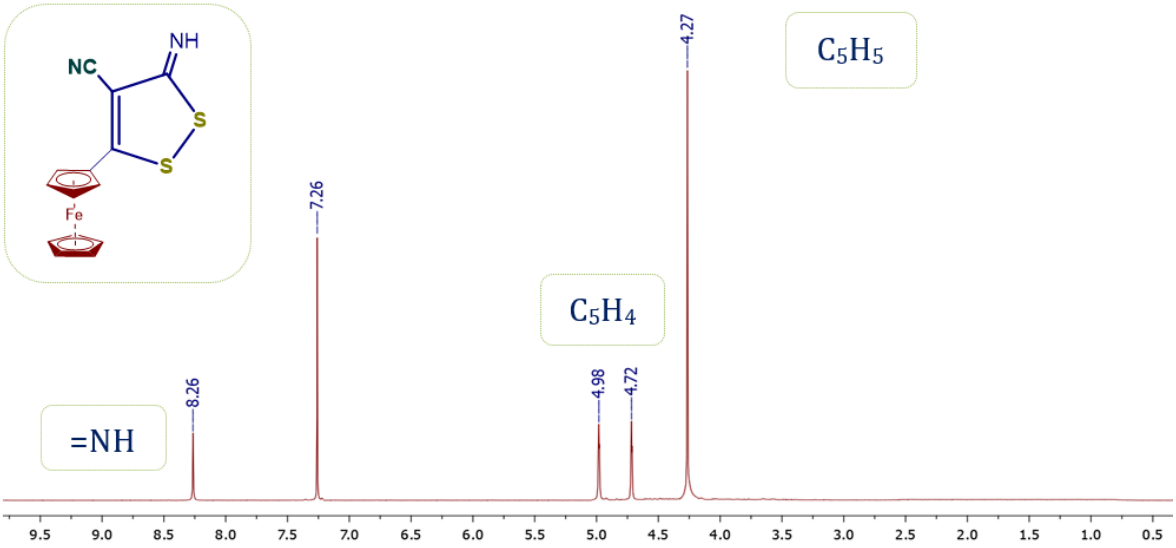


Figure S6: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound **5**

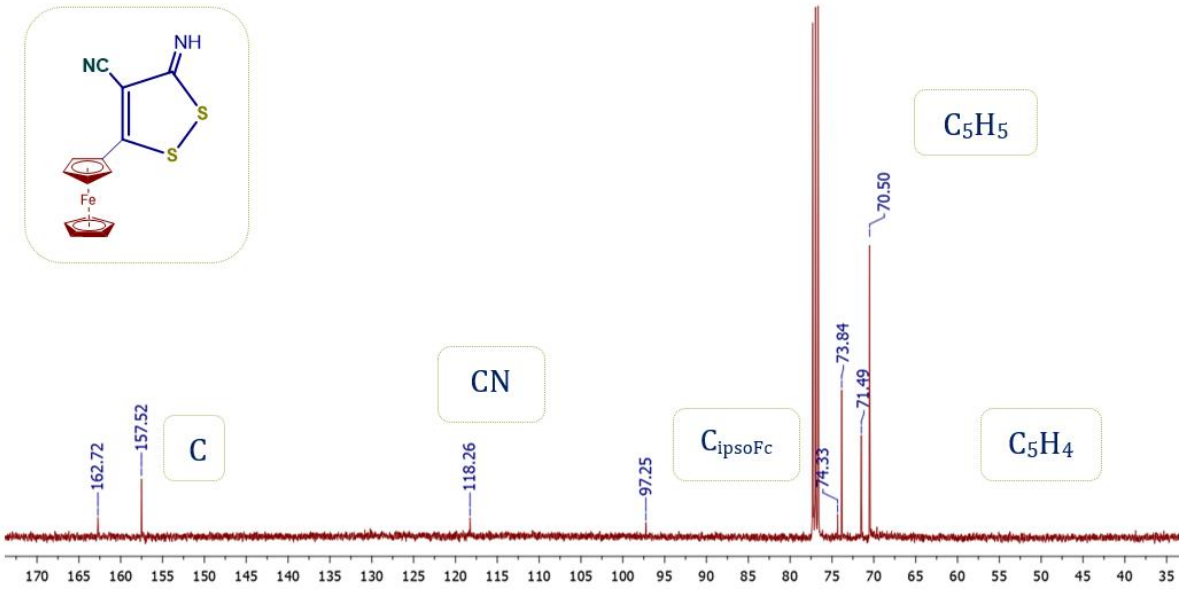


Figure S7: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) spectrum of compound **5**

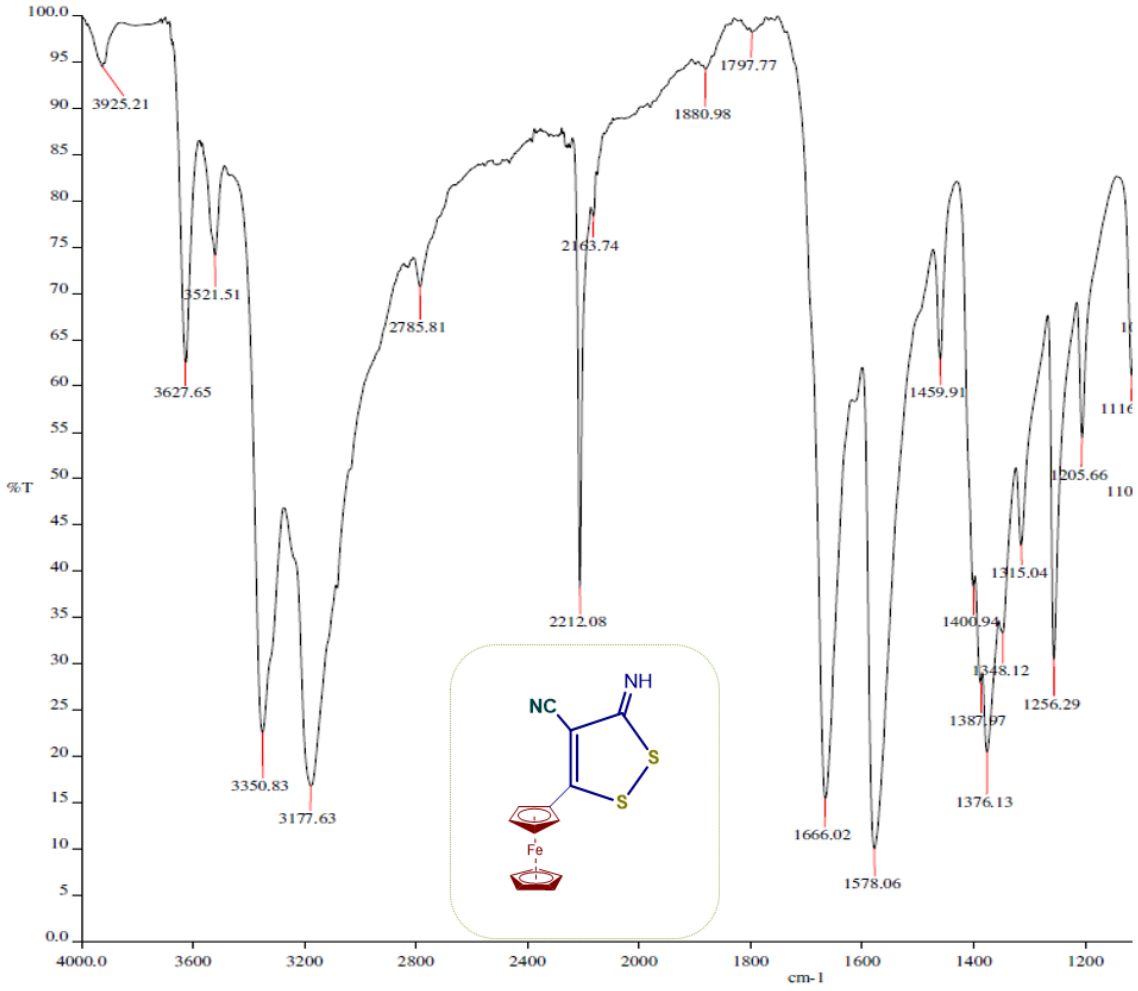


Figure S8: IR (KBr) spectrum of compound **5**

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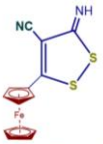
User ID	M en I. Victor Lemus
Comments	Muestra: KE0119R

Run	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
54162A	1.15	51.60	3.15	8.52	19.70
54162B	1.12	51.49	3.12	8.49	19.65
54162C	1.10	52.00	3.09	8.60	19.75
	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
Average	1.12	51.70	3.12	8.54	19.70
Variance	0.00	0.07	0.00	0.00	0.00
Standard Deviation	0.03	0.27	0.03	0.06	0.05



$C_{14}H_{10}FeN_2S_2$

C: 51.54 %
H: 3.09 %
N: 8.58 %
S: 19.66 %

Figure S9: Elemental analysis of compound **5**

4,5-Diferrocenyl-1,2-dithiol-3-one 6

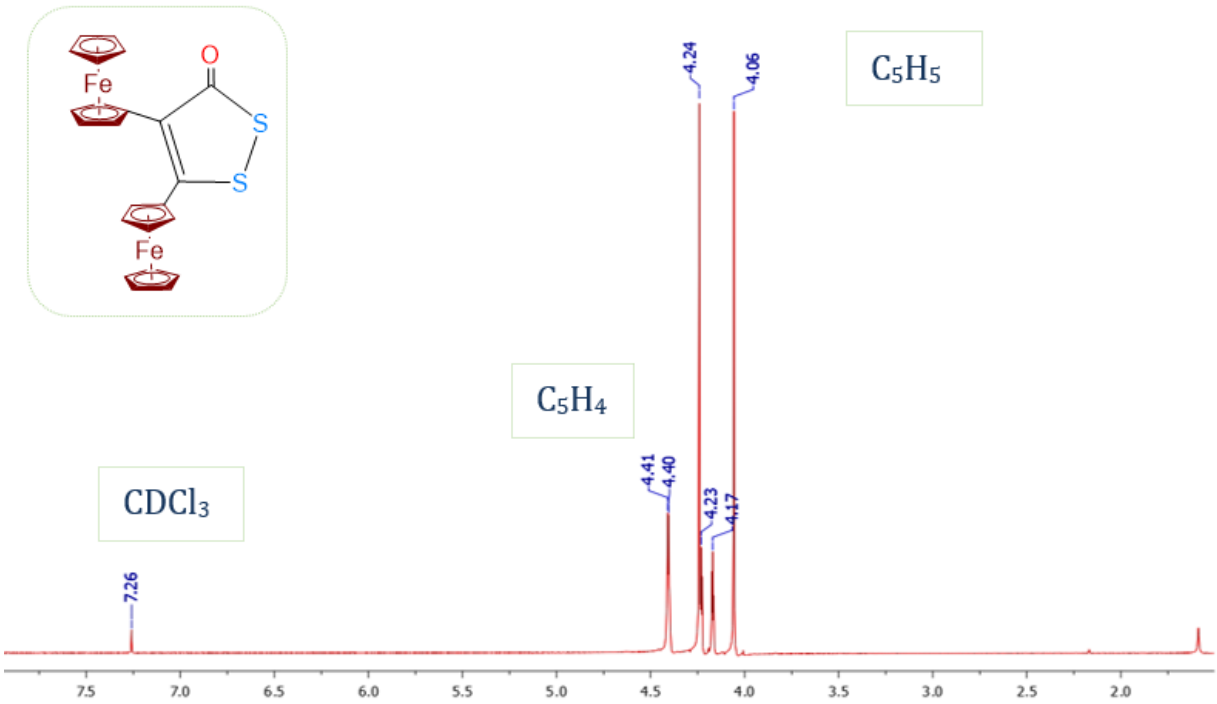


Figure S10: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound **6**

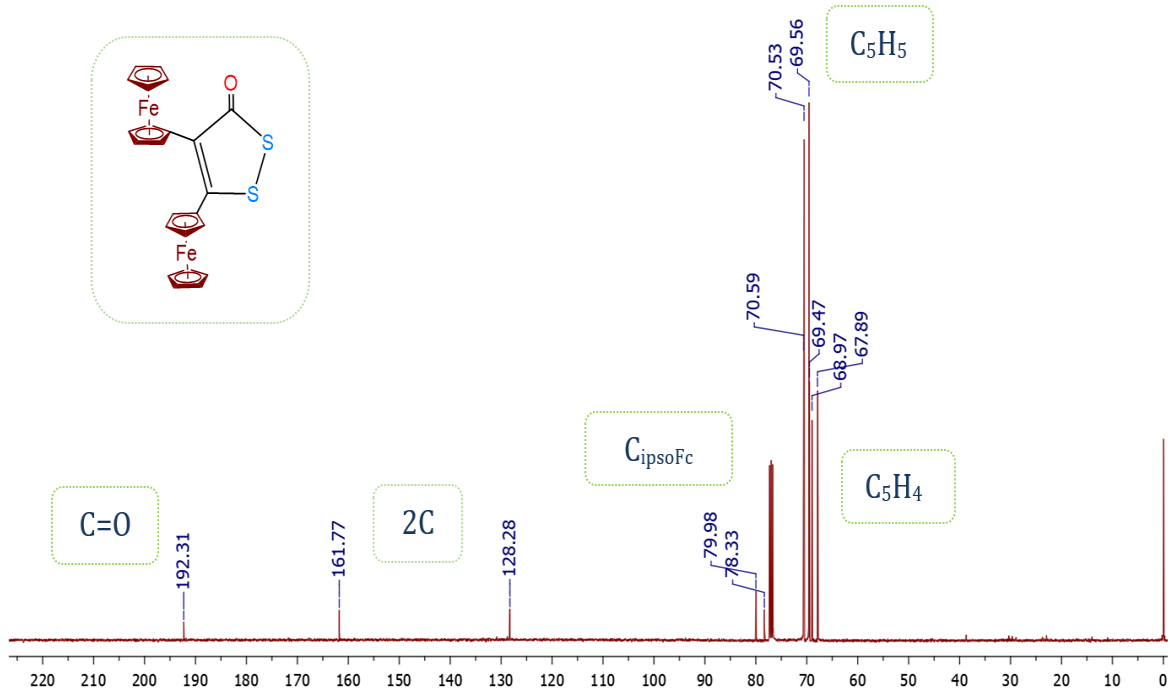


Figure S11: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) spectrum of compound **6**

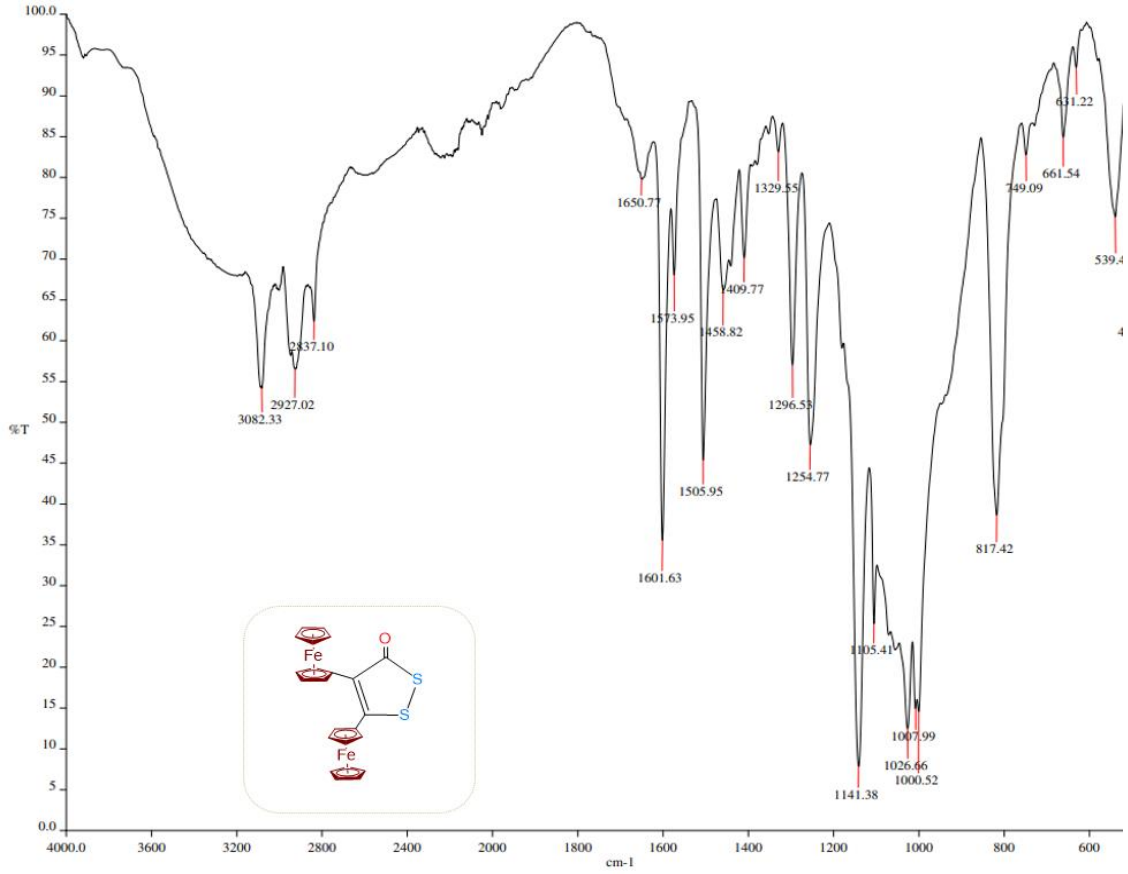


Figure S12: IR (KBr) spectrum of compound **6**

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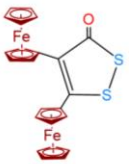
Phone: 56223899 ext 84040

User ID	M en I. Victor Lemus
Comments	Muestra: KE102

Run	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
52369A	1.40	56.60	3.80	0.10	13.20
52369B	1.45	56.80	3.70	0.05	13.10
52369C	1.35	57.00	3.60	0.20	13.40

	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
Average	1.40	56.80	3.70	0.12	13.23
Variance	0.00	0.04	0.01	0.01	0.02
Standard Deviation	0.05	0.20	0.10	0.08	0.15



$C_{23}H_{18}Fe_2OS_2$

C:	**56.81**	%
H:	**3.73**	%
S:	**13.19**	%

Figure S13: Elemental analysis of compound **6**

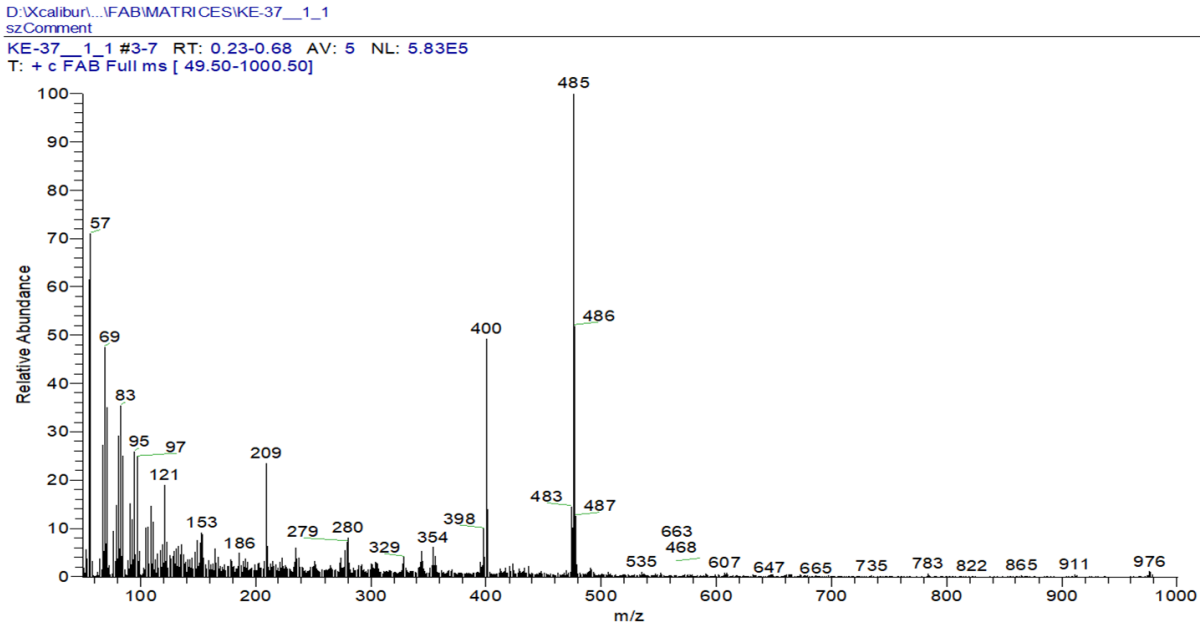


Figure S14: MS (EI, 70 Ev): m/z [M]+ of compound **6**

4,5-Diferrocenyl-1,2-dithiole-3-thione **7**

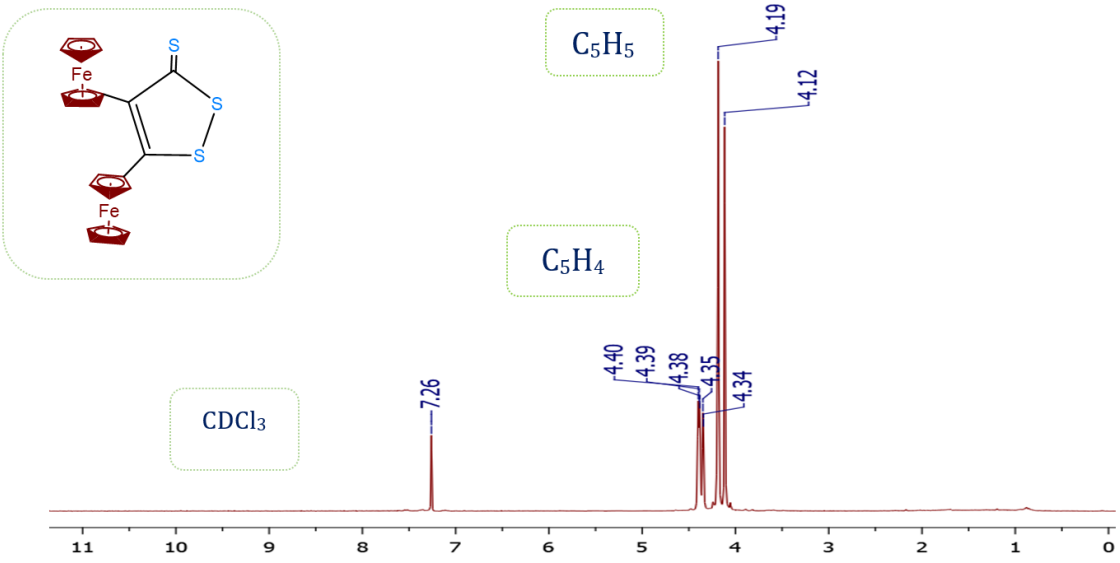


Figure S15: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound **7**

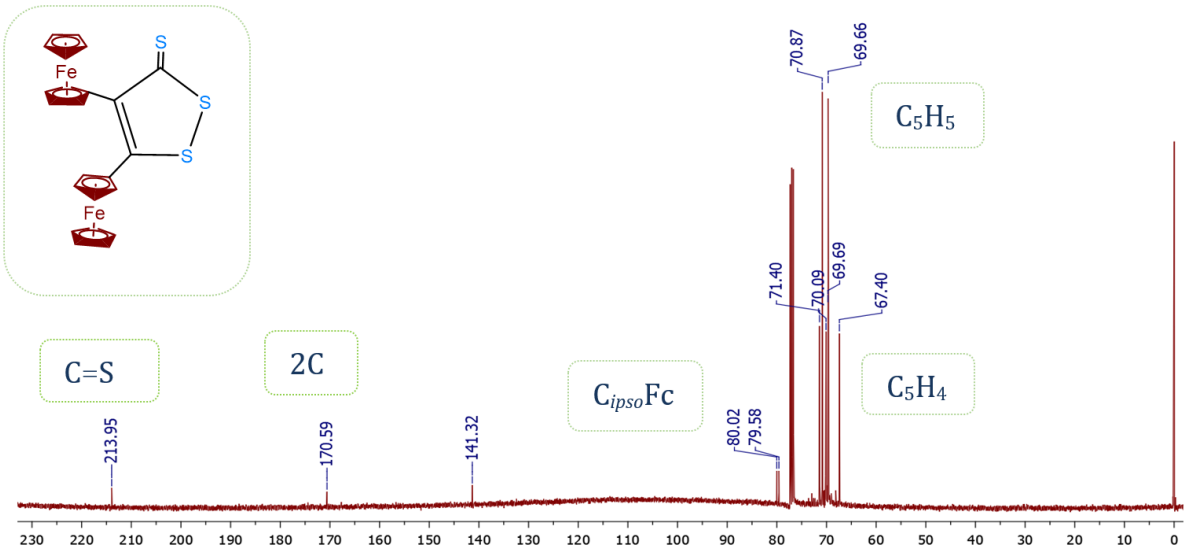


Figure S16: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) spectrum of compound **7**

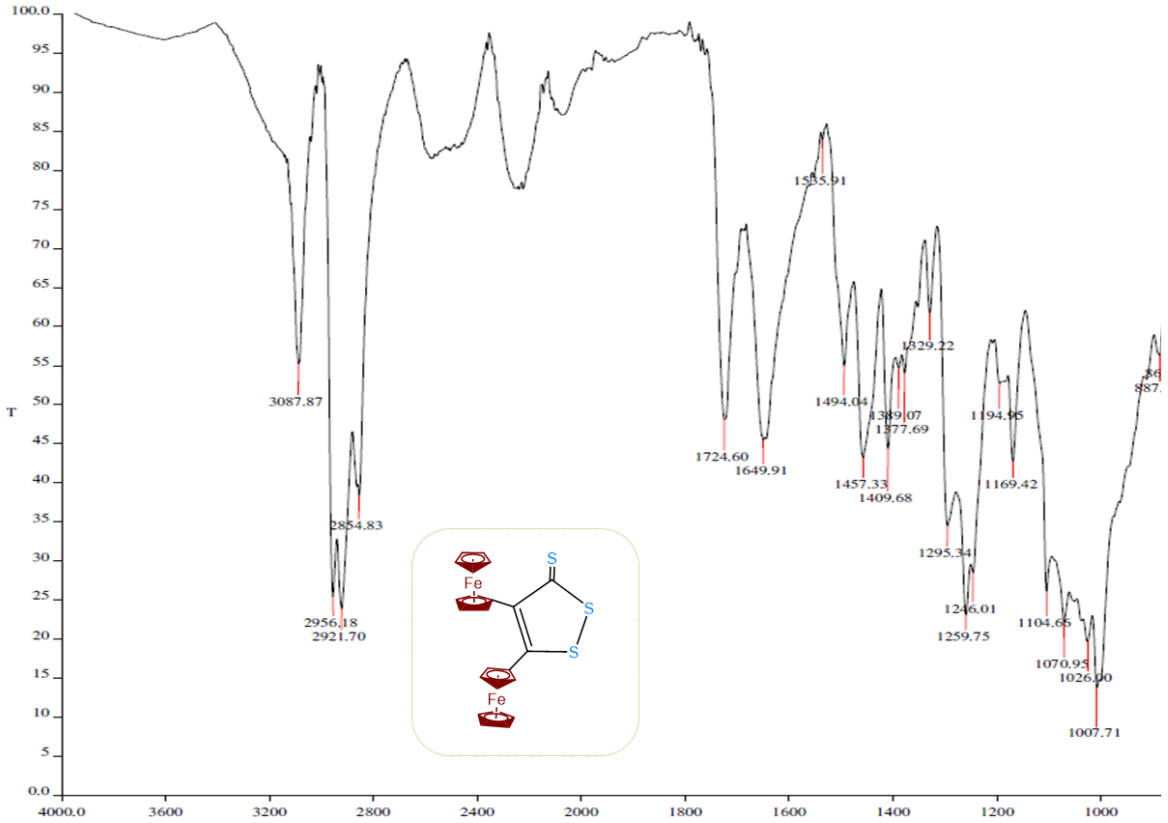


Figure S17: IR (KBr) spectrum of compound **7**

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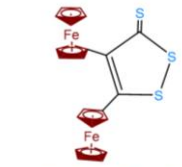
Phone: 56223899 ext 84040

User ID	M en I. Victor Lemus
Comments	Muestra: KE056

Run	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
12358A	1.60	55.10	3.80	0.05	19.25
12358B	1.62	55.00	3.72	0.20	19.30
12358C	1.50	55.20	3.60	0.10	19.10

	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
Average	1.57	55.10	3.71	0.12	19.22
Variance	0.00	0.01	0.01	0.01	0.01
Standard Deviation	0.06	0.10	0.10	0.08	0.10



$C_{23}H_{18}Fe_2S_3$

C: 55.0 %
H: 3.61 %
S: 19.15 %

Figure S18: Elemental analysis of compound 7

Isopropyl *cis*-2,3-diferrocenylacrilate *cis*-8

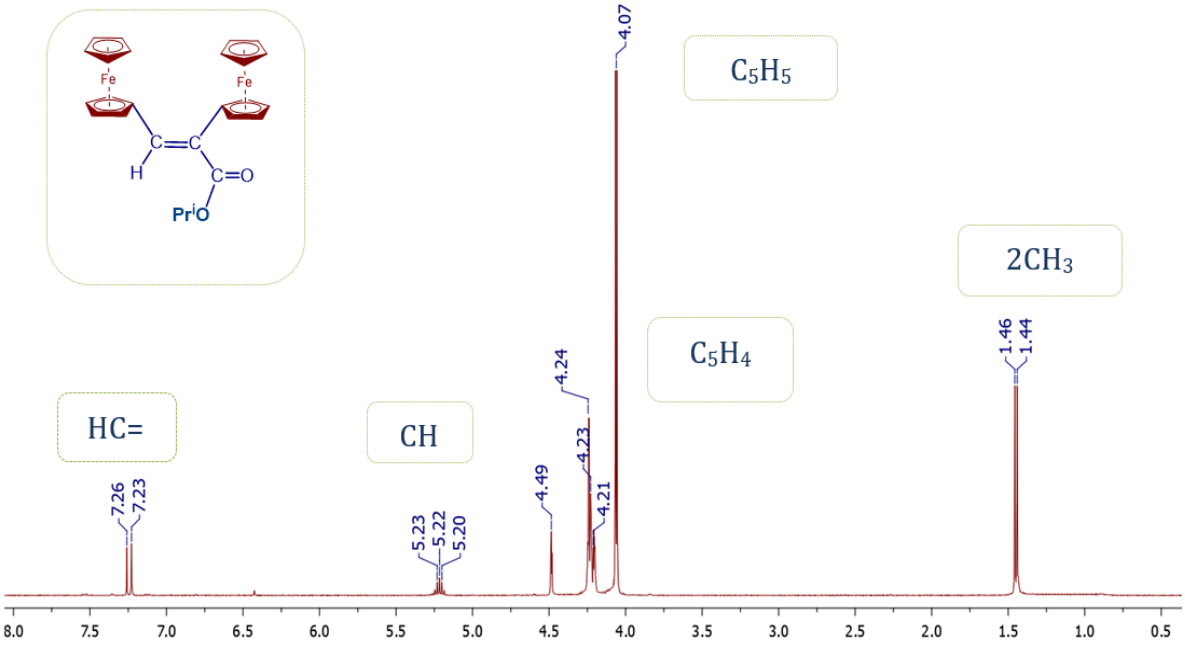


Figure S19: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound *cis*-8

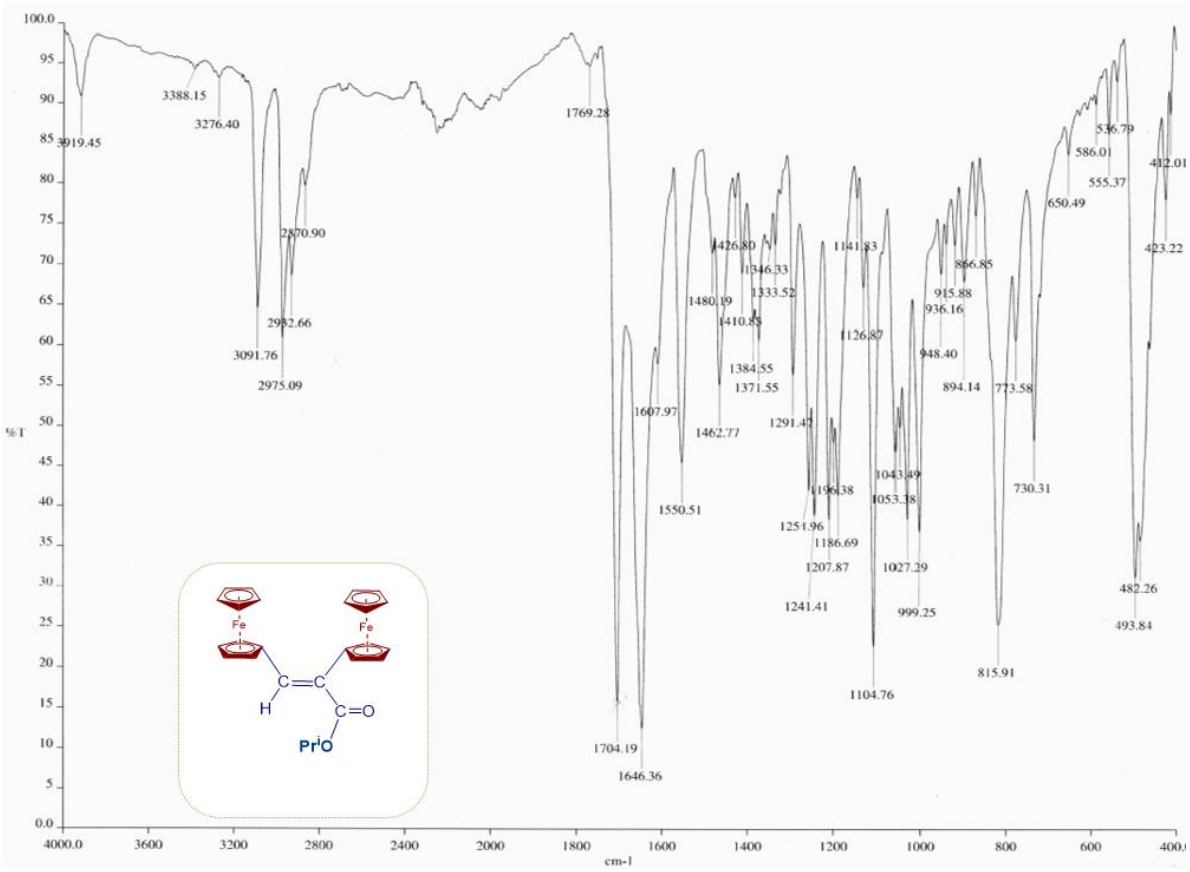


Figure S20: IR (KBr) spectrum of compound *cis*-**8**

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User ID	M en I. Victor Lemus
Comments	Muestra: KE652_1853

Run	Weight	Carbon	Hydrogen	Nitrogen
54165A	1.25	64.85	5.40	0.05
54165B	1.35	64.80	5.30	0.10
54165C	1.20	64.70	5.50	0.08

	Weight	Carbon	Hydrogen	Nitrogen
Average	1.27	64.78	5.40	0.08
Variance	0.01	0.01	0.01	0.00
Standard Deviation	0.08	0.08	0.10	0.03

$C_{26}H_{26}Fe_2O_2$

C: 64.76 %

H: 5.44 %

Figure S21: Elemental analysis of compound *cis*-**8**

Isopropyl *trans*-2,3-diferrocenylacrilate *trans*-**8**

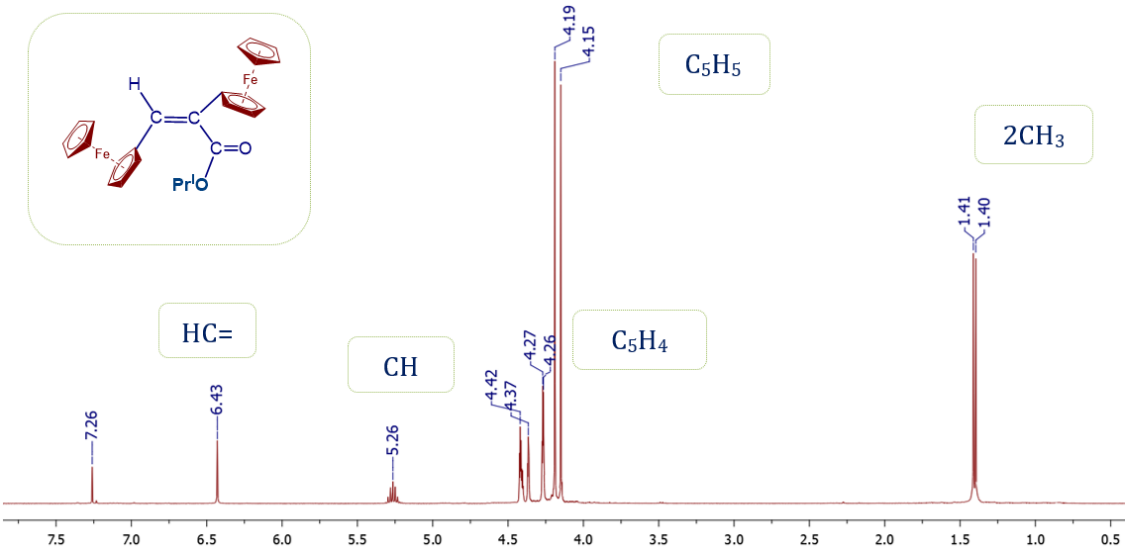

Figure S22: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound *trans*-**8**

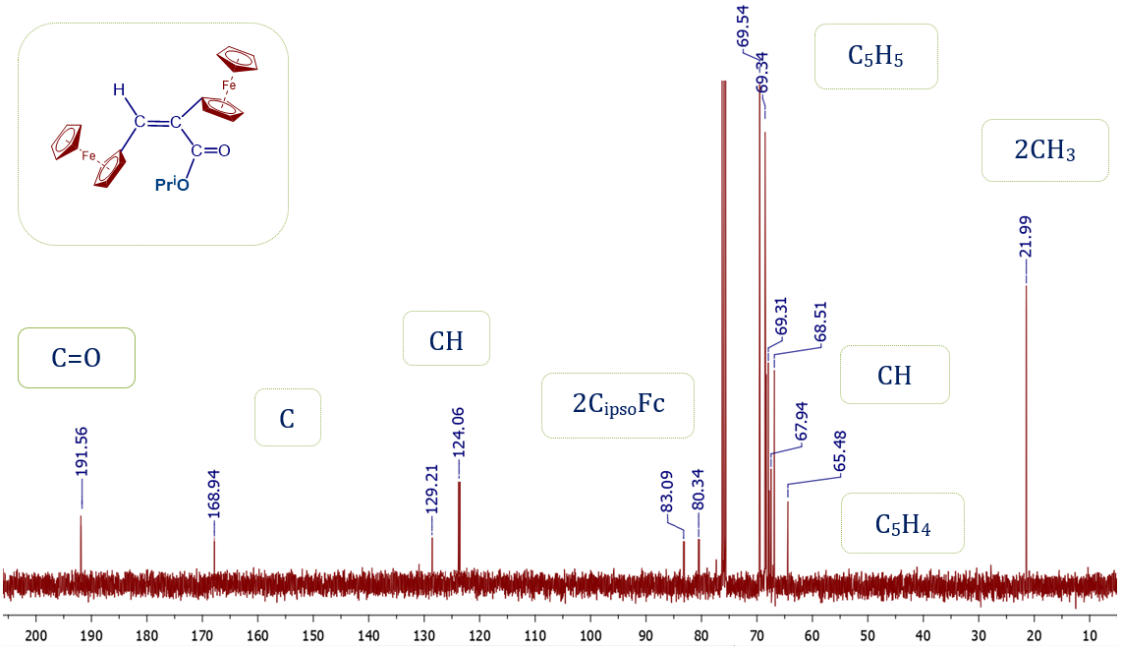

Figure S23: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) spectrum of compound *trans*-**8**

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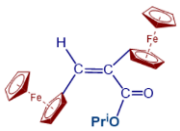
User ID	M en I. Victor Lemus
Comments	Muestra: KE12219-1191

Run	Weight	Carbon	Hydrogen	Nitrogen
54175A	1.15	64.80	5.40	0.10
54175B	1.05	64.82	5.35	0.08
54175C	1.08	64.74	5.50	0.09

	Weight	Carbon	Hydrogen	Nitrogen
Average	1.09	64.79	5.42	0.09
Variance	0.00	0.00	0.01	0.00
Standard Deviation	0.05	0.04	0.08	0.01



$C_{26}H_{26}Fe_2O_2$

C: 64.76 %
H: 5.44 %

Figure S24: Elemental analysis of compound *trans*-**8**

3-Amino-5-ferrocenyl-1-methylisophthalonitrile **9**

Single crystal X-ray structure determination of **9**

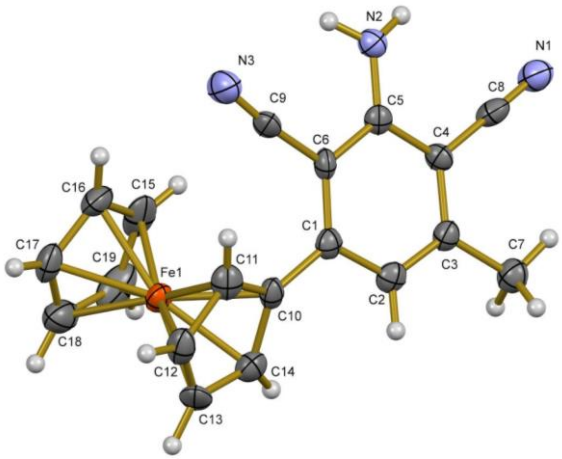


Figure S-25: Crystal structure of **9**
With the atomic labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

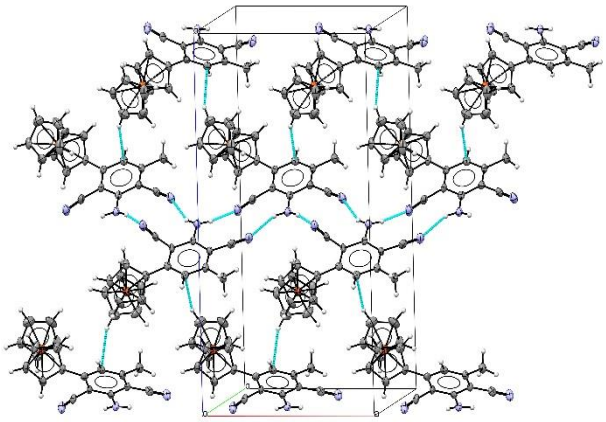


Figure S26: Crystal packing of **9**
View along the b-axis and with perspective to plane formed by *a-c axes*.

Crystal data for **9**. Crystals **9** were obtained by crystallization from dichloromethane $C_{19}H_{15}FeN_3$ (M = 341.19), orthorhombic, space group *Pbca*, at 130(2) K: a = 10.9523(10), b = 12.5542(12), c = 22.231(2) Å, α = 90°, β = 90°, γ = 90°, Z = 8, d_{calc} = 1.483 g cm^{-3}, V = 3056.7(5) Å^3, μ(MoKα =0.988 mm^{-1}, F(000) = 1408. A total of 21447 reflections were collected (3878 independent reflections, R_{int} = 0.3216), GOOF 1.243, final R indices [$I > 2\sigma(I)$] R_1 = 0.1754 and wR_2 = 0.3558, R indices (all data) R_1 = 0.2740 and wR_2 = 0.3839, 210 refined parameters. Crystallographic data were collected on an Oxford Diffraction Gemini "A" diffractometer with a CCD area detector with λMoKα = 1.71073 Å at 130 K. Structure solution and refinement were carried out using the programs SHELXS-2014[19] and SHELXL-2014[19], respectively, WinGX v2018.3[20] and Mercury CSD 4.1.0[21] were used to prepare the material for publication. Full-matrix least-squares refinement was carried out by minimizing (Fo^2 - Fc^2)^2. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon atoms were placed in geometrically idealized positions and refined as riding on their parent atoms, with C-H = 0.95 – 1.00 Å with Uiso (H) = 1.2 Ueq(C) for aromatic and methyne groups, and Uiso (H) = 1.5 Ueq(C) for methyl group. CCDC 2065188. contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk

Table S1: Crystallographic data and structure refinement detail for compound **9**

Empirical formula	$C_{19}H_{15}FeN_3$
Formula weight	341.19
Temperature (K)	130(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	P b c a
a (Å)	10.9523(10)
b (Å)	12.5542(12)
c (Å)	22.231(2)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3056.7(5)
Z	8
$D_{Calc.}$ (Mg/m^3)	1.483
Absorption coefficient (mm^{-1})	0.988
F(000)	1408
θ range for data collection (°)	3.666 – 29.472
Reflections collected	21447
Independent reflections	3878 [$R_{(int)}$ = 0.3216]
Goodness-of-fit on F^2	1.243
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.1754, wR_2 = 0.3558
R indices (all data)	R_1 = 0.2740, wR_2 = 0.3839
Data/restraints/parameters	3878/0/210
Largest diff. peak and hole (eÅ^{-3})	1.254 and -0.840

Table S-2: Selected bond lengths and bond angles for compound **9**.

Selected bond	lengths (Å)	Selected bond	angles (°)
C(6) – C(13)	1.397(11)	C(6) – C(13) -C(12)	121.8(7)
C(13 – C(12)	1.381(11)	C(13) – C(12) -C(10)	119.4(7)
C(12) – C(10)	1.393(11)	C(9) – C(10) -C(12)	121.1(7)
C(10) – C(9)	1.421(11)	C(10) – C(9) -C(7)	117.8(7)
C(9) – C(7)	1.404(11)	C(9) – C(7) -C(6)	121.4(7)
C(6) – C(7)	1.407(11)	C(7) – C(6) -C(13)	118.4(7)
N(1) – C(8)	1.149(10)	C(7) – C(8) -N(1)	174.6(9)
N(2) – C(9)	1.354(10)	C(10) – C(9) -N(2)	120.4(7)
N(3) – C(11)	1.147(10)	C(1) – C(6) -C(7)	123.7(7)
C(10) – C(11)	1.444(12)	C(10) – C(12) -C(14)	121.8(7)
C(12) – C(14)	1.504(11)	C(7) – C(9) -N(2)	121.9(7)

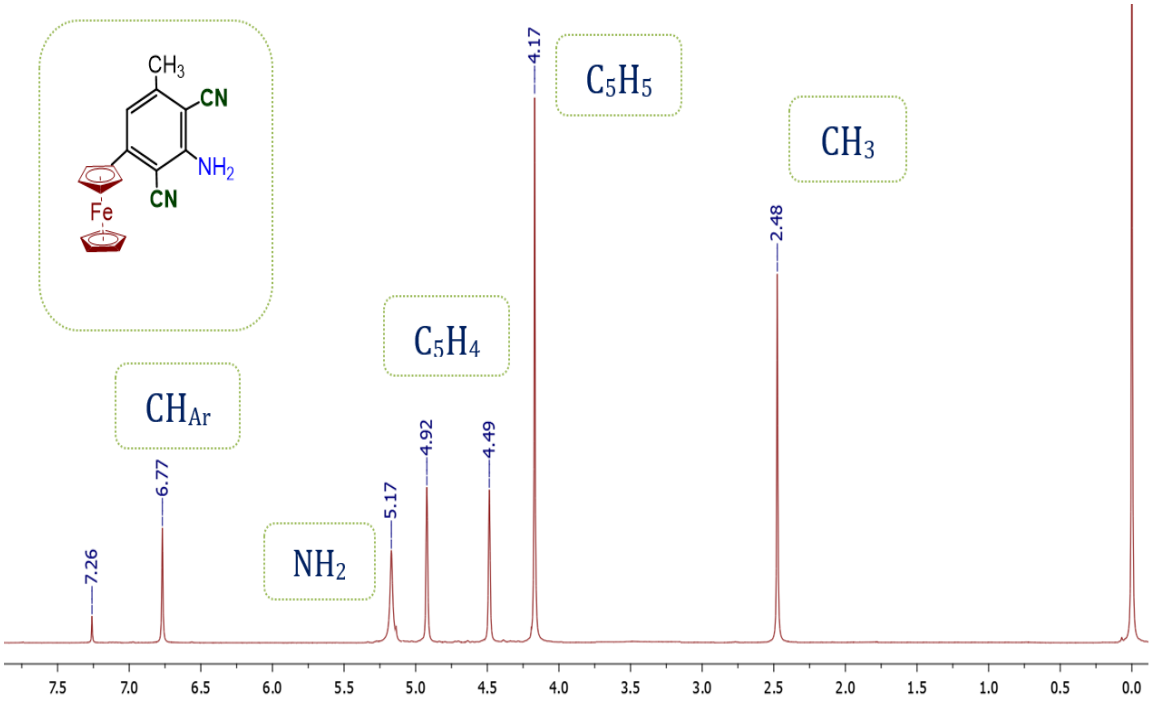


Figure S27: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound **9**

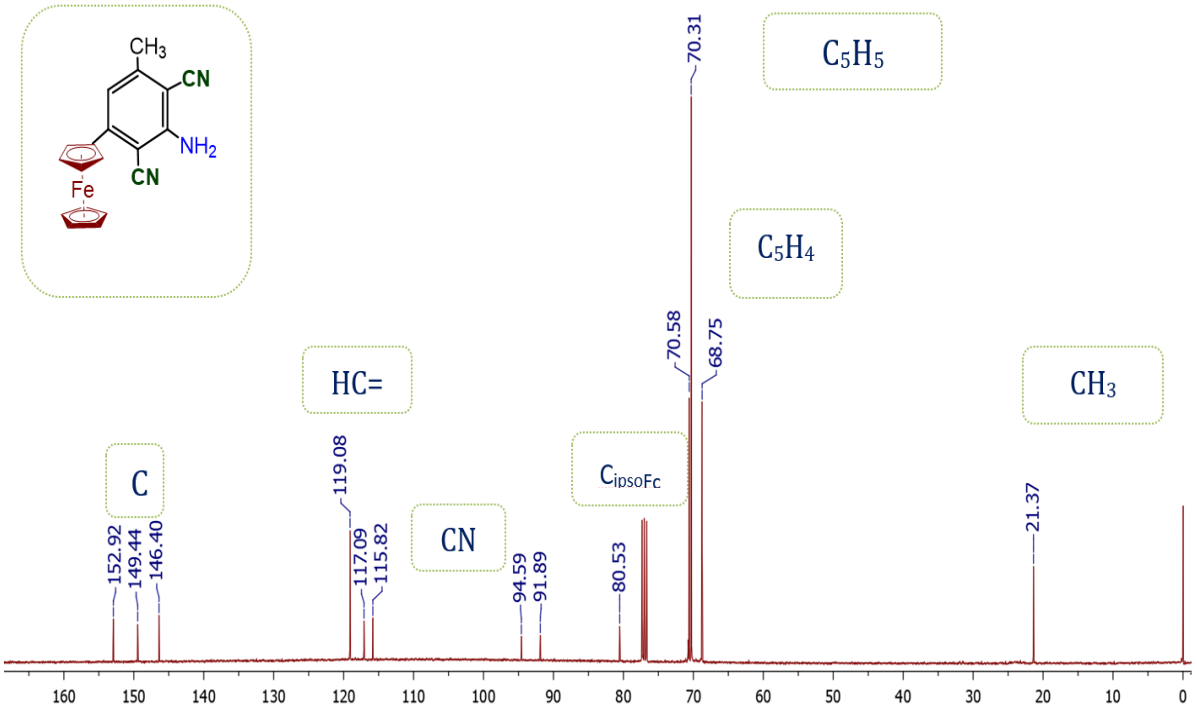


Figure S28: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) spectrum of compound **9**

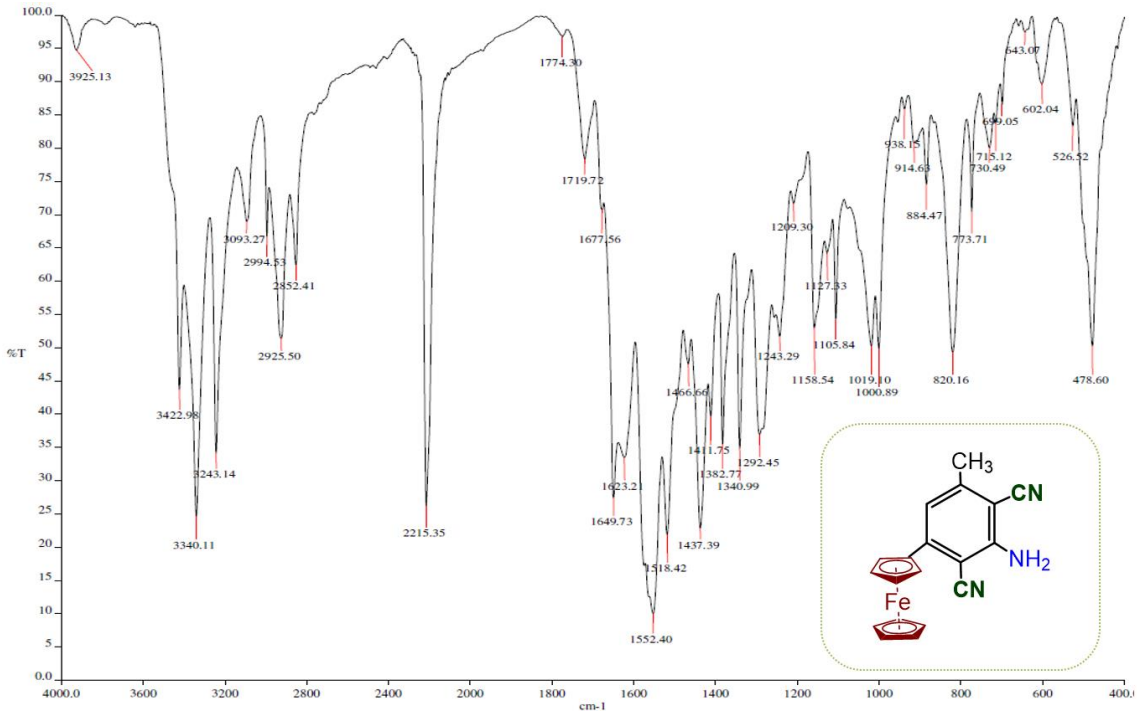
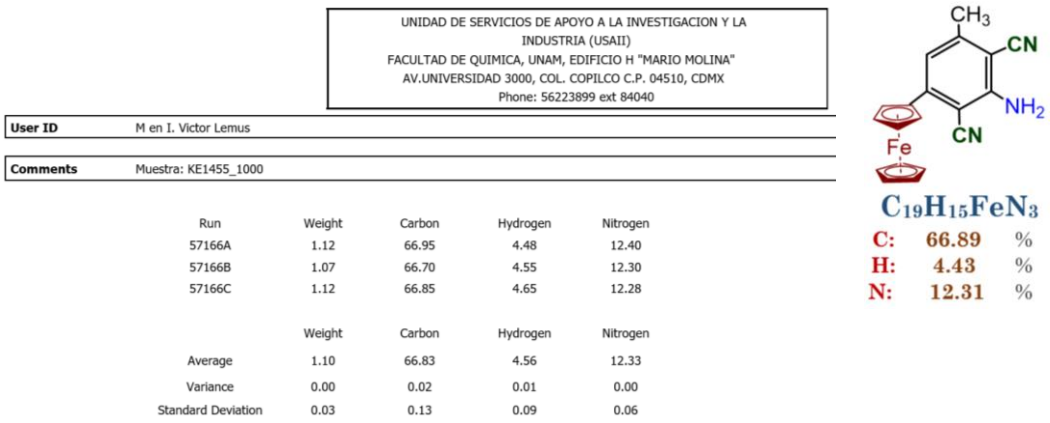


Figure S29: IR (KBr) spectrum of compound **9**



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User ID	M en I. Victor Lemus
Comments	Muestra: KE1455_1000

Run	Weight	Carbon	Hydrogen	Nitrogen
57166A	1.12	66.95	4.48	12.40
57166B	1.07	66.70	4.55	12.30
57166C	1.12	66.85	4.65	12.28

	Weight	Carbon	Hydrogen	Nitrogen
Average	1.10	66.83	4.56	12.33
Variance	0.00	0.02	0.01	0.00
Standard Deviation	0.03	0.13	0.09	0.06

$C_{19}H_{15}FeN_3$

C: 66.89 %
H: 4.43 %
N: 12.31 %

Figure S30: Elemental analysis of compound **9**

2-Amino-4-ferrocenyl-6-isopropoxypyridine-3,5-dicarbonitrile **10**

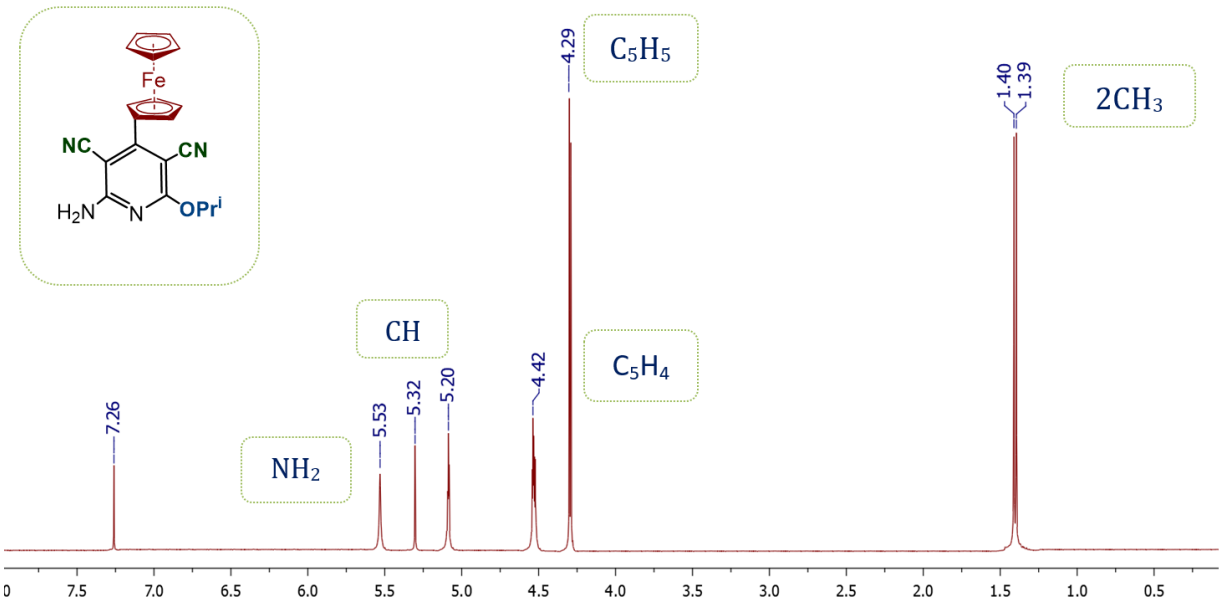


Figure S31: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound **10**

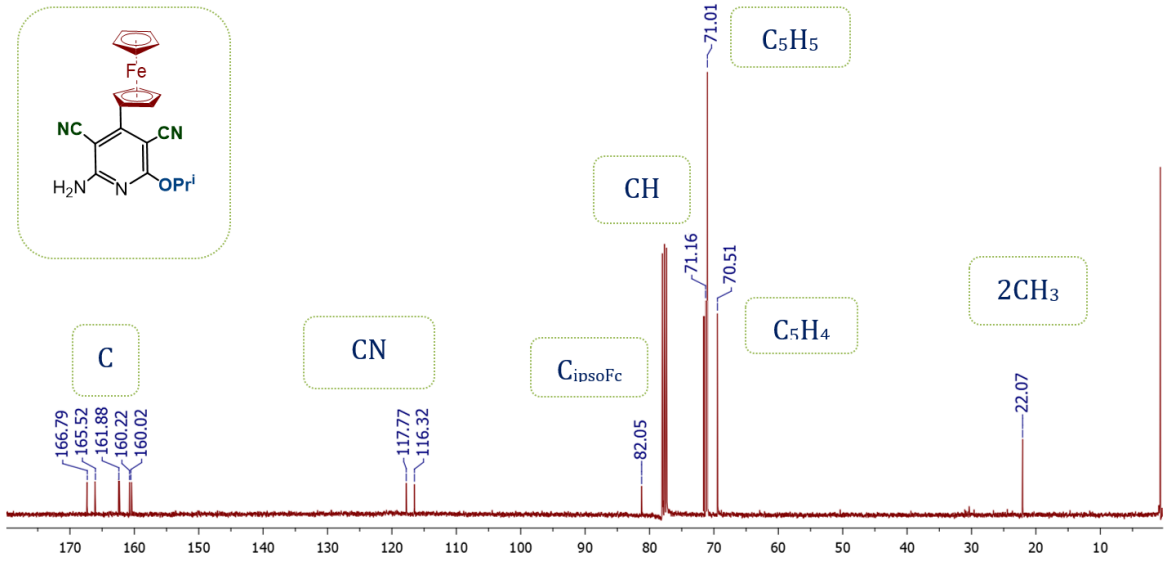
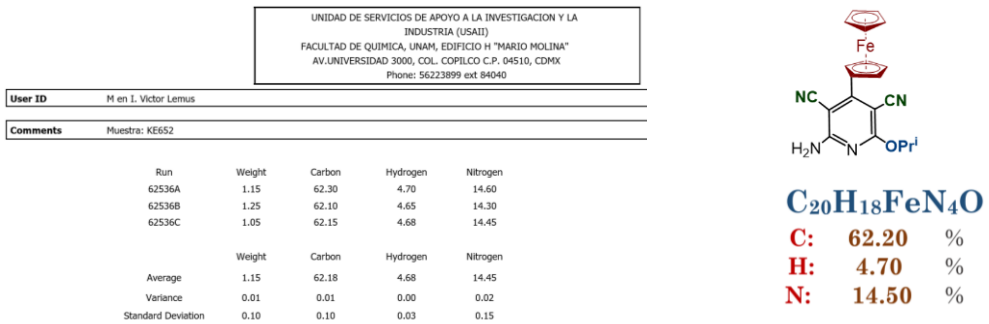


Figure S32: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) spectrum of compound **10**



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User ID	M en I. Victor Lemus
Comments	Muestra: KE652

Run	Weight	Carbon	Hydrogen	Nitrogen
62536A	1.15	62.30	4.70	14.60
62536B	1.25	62.10	4.65	14.30
62536C	1.05	62.15	4.68	14.45

	Weight	Carbon	Hydrogen	Nitrogen
Average	1.15	62.18	4.68	14.45
Variance	0.01	0.01	0.00	0.02
Standard Deviation	0.10	0.10	0.03	0.15

$C_{20}H_{18}FeN_4O$

C: 62.20 %
H: 4.70 %
N: 14.50 %

Figure S33: Elemental analysis of compound **10**