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Rearrangements of diferrocenylcyclopropenium ions in the reactions with bis-1,4-O,S-nucleophiles

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Experimental

Materials and measurements

All the solvents were dried according to the standard procedures and freshly distilled before use. Column chromatography was carried out on alumina (Brockmann activity III). The ^{1}H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (400-MHz and 100 MHz) for solutions in $CDCl_3$ with Me_4Si as the internal standard. Chemical shifts (δ, ppm) were reported with respect to residual 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: ferrocene, 98%; aluminum chloride, 99.99%; tetrachlorocyclopropene, 98%; triethyloxonium tetrafluoroborate, 1.0 M solution in dichloromethane; Lawesson reagent, 97%; triethylamine, 99.5%; iodomethane, 99.5%; morpholine, 99.5%; 2-mercaptoethanol, 99.0%; 2-mercaptophenol, 99.0%.

The starting 2,3-diferrocenylcyclopropenone was obtained from the ferrocene and tetrachlorocyclopropene in the presence of $AlCl_3$ (Ref. 1, here and further the main text). 2,3-Diferrocenylcyclopropenethione was prepared from 2,3-diferrocenylcyclopropenone and Lawesson reagent[14,16] in benzene. Ethoxy(diferrocenyl)cyclopropenium tetrafluoroborate was obtained by treating 2,3-diferrocenylcyclopropenone in dichloromethane with triethyloxonium tetrafluoroborate. Diferrocenyl(morpholino)cyclopropenium tetrafluoroborate **1a** was obtained from ethoxy(diferrocenyl)-cyclopropenium tetrafluoroborate and morpholine. Diferrocenyl(methylthio)cyclopropenium iodide **1b** was obtained from 2,3-diferrocenylcyclopropenthione and methyl iodide in the benzene[1,15].

*Reactions of diferrocenylcyclopropenium cations **1a,b** with 2-mercaptophenol **2a** and 2-mercaptoethanol **2b**.*

2- Mercaptophenol [or mercaptoethanol] (3.0 mmol) and Et_3N (1.0 mL) was added to a suspension of salt **1a** or **1b** (3.3 mmol) in dry benzene (70 mL) under a nitrogen atmosphere. The reaction mixture was stirred and was heated to refluxing conditions (6-8 h) until complete dissolution of the salts **1a** or **1b** occurred. The solvent was removed *in vacuo*, and the residue was dissolved in dichloromethane (30 mL). The solution was mixed with Al_2O_3 (20 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 **2a**, **2b**, **3a**, **3b** [or *Z*-**4a**, *Z*-**4b,** *E*-**4b,** *Z*-**5a** and *Z*-**5b**]. The geometric isomers *Z*-**4b** and *E*-**4b** were isolated by thin-layer chromatography (TLC) on Al_2O_3 in a solvent system hexane-ether (4:1).

*2-(E-1,2-Diferrocenyl-2-morpholinovinyl)-1,3-benzoxathiole **2a*****:** orange powder, yield 0.96 g (52%), m.p. 138-139 °C. IR (KBr): ν 482, 748, 819, 857, 1028, 1059, 1107, 1156, 1240, 1260, 1356, 1388, 1443, 1566, 1716, 2680, 2854, 2924, 2950, 3057 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.72 (2H, dt, *J* = 4.0, 12.0 Hz, CH_2), 2.98 (2H, dt, *J* = 4.0, 12.0 Hz, CH_2), 3.55 (4H, t, *J* = 4.0 Hz, $2CH_2$), 4.01 (5H, s, C_5H_5), 4.04 (5H, s,

C_5H_5), 4.19 (2H, m, C_5H_4), 4.24 (2H, m, C_5H_4), 4.34 (2H, m, C_5H_4) , 4.39 (1H, m, C_5H_4), 4.43 (1H, m, C_5H_4), 6.18 (1H, s, CH), 6.92 (1H, t, *J* = 7.6 Hz, C_6H_4), 6.92 (1H, d, *J* = 7.6 Hz, C_6H_4), 7.07 (1H, t, *J* = 7.6 Hz, C_6H_4), 7.17 (1H, d, *J* = 7.6 Hz, C_6H_4), ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.77, 67.63 ($4CH_2$), 69.09, 69.10 ($2C_5H_5$), 66.82, 67.27, 68.42, 68.88, 68.92, 69.77, 70.07 70.21 ($2C_5H_4$), 79.76, 94.48 ($2C_{ipso}$Fc), 109.97 (CH), 120.70, 121.23, 121.98, 125.48 (C_6H_4), 103.21, 126.70, 146.43, 156.13 (4C). Anal. calcd. for $C_{33}H_{31}Fe_2NO_2S$ (617.28): C, 64.21; H, 5.06; N, 2.27; S, 5.18. Found: C, 64.32; H, 5.13; N, 2.22; S, 5.20 %. MS (El, 70 eV): *m/z* 617 $[M]^+$.

2-(E-1,2-Diferrocenyl-2-methylthiovinyl)-1,3-benzoxathiole ***2b***: red crystals, yield 0.83 g (48%), m.p. 123-125 °C. IR (KBr): ν 475, 561, 699, 745, 754, 792, 818, 908, 925, 973, 1000, 1027, 1044, 1086, 1106, 1122, 1208, 1237, 1267, 1315, 1389, 1411, 1447, 1462, 1572, 1641, 1722, 2853, 2917, 2957, 3092 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (3H, s, CH_3), 4.09 (5H, s, C_5H_5), 4.13 (5H, s, C_5H_5), 3.82 (1H, m, C_5H_4), 4.13 (1H, m, C_5H_4), 4.19 (1H, m, C_5H_4), 4.20 (2H, m, C_5H_4), 4.40 (1H, m, C_5H_4), 4.43 (1H, m, C_5H_4), 4.48 (1H, m, C_5H_4), 4.68 (1H, m, C_5H_4), 6.60 (1H, s, CH), 6.92 (2H, m, C_6H_4), 7.02 (2H, m, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.20 (CH_3), 69.17, 69.51 ($2C_5H_5$), 67.60, 67.69, 67.88, 68.08, 68.89, 68.98, 69.92, 70.02 ($2C_5H_4$), 81.78, 93.96 ($2C_{ipso}$Fc), 110.02 (CH), 121.21, 122.02, 125.61, 128.01 (C_6H_4), 102.98, 130.86, 132.73, 155.02 (4C). Anal. calcd. for $C_{30}H_{26}Fe_2OS_2$ (578.21): C, 62.31; H, 4.53; S, 11.07. Found: C, 61.95; H, 4.53; N, 11.4 %. MS (El, 70 eV): *m/z* 578 $[M]^+$.

3,4-Diferrocenyl-2-morpholino-2H-1,5-benzoxathiepine ***3a***: red crystals, yield 0.57 g (31%), m.p. 139-141 °C. IR (KBr): ν 480, 588, 632, 705, 739, 814, 967, 1000, 1027, 1067, 1103, 1259, 1381, 1445, 1458, 1569, 1624, 1721, 2872, 2941, 2980, 3091 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.65 (2H, m, CH_2), 2.84 (2H, m, CH_2), 3.59 (4H, t, *J* = 4.0 Hz, $2CH_2$), 4.04 (5H, s, C_5H_5), 4.27 (5H, s, C_5H_5), 4.14 (2H, m, C_5H_4), 4.20 (1H, m, C_5H_4) , 4.25 (1H, m, C_5H_4), 4.31 (1H, m, C_5H_4), 4.70 (2H, m, C_5H_4), 5.09 (2H, m, C_5H_4), 5.48 (1H, s, CH). 7.37 (2H, m, C_6H_4), 7.44 (2H, m, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 53.24, 63.31 ($4CH_2$), 69.22, 69.38 ($2C_5H_5$), 68.60, 69.19, 70.29, 70.31 ($2C_5H_4$), 72.15 (CH), 84.28, 89.43 ($2C_{ipso}$Fc), 121.15, 122.72, 124.72, 125.89 (C_6H_4), 130.21, 135.41, 152.91, 166.26 (4C). Anal. calcd. for $C_{33}H_{31}Fe_2NO_2S$ (617.28): C, 64.21; H, 5.06; N, 2.27; S, 5.18. Found: C, 64.24; H, 5.10; N, 2.24, S, 5.10 %. MS (El, 70 eV): *m/z* 617 $[M]^+$.

3,4-Diferrocenyl-2-methylthio-2H-1,5-benzoxathiepine ***3b*****:** orange powder, yield 0.50 g (29%), m.p. 158-159 °C. IR (KBr): ν 482, 594, 659, 705, 731, 800, 861, 883, 922, 946, 967, 1000, 1025, 1053, 1095, 1105, 1118, 1160, 1196, 1235, 1256, 1302, 1377, 1411, 1450, 1474, 1534,1571, 1589, 1611, 1644, 1721, 2851, 2921, 2961, 3092 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (3H, s, CH_3), 3.95 (5H, s, C_5H_5), 4.21(5H, s, C_5H_5), 4.31 (2H, m, C_5H_4), 4.35 (2H, m, C_5H_4), 4.64 (2H, m, C_5H_4), 4.91 (2H, m, C_5H_4), 5.35 (1H, s, CH),7.20 (1H, m, C_6H_4), 7.31 (2H, t, *J* = 8.0 Hz, C_6H_4), 7.36 (1H, d, *J* = 8.0 Hz, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.80 (CH_3), 69.45, 69.60 ($2C_5H_5$), 67.44, 68.35, 68.37, 68.40, 69.46, 69.55, 69.82, 71.00 ($2C_5H_4$), 72.55 (CH), 79.83, 81.88 ($2C_{ipso}$Fc), 110.38, 124.71, 129.67, 136.85 (C_6H_4), 119.59, 143.11, 148.71, 166.43 (4C). Anal. calcd. for $C_{30}H_{26}Fe_2OS_2$ (578.21): C, 62.31; H, 4.53; S, 11.06. Found: C, 62.23; H, 4.66; S, 11.10 %. MS (El, 70 eV): *m/z* 578 $[M]^+$.

*2-(E-1,2-Diferrocenyl-2-morpholinovinyl)-1,3-oxathiolane E-****4a***: red oil, yield 0.84 g (49%). IR (KBr): ν 475, 602, 662, 735, 815, 954, 1001, 1280, 1091, 1106, 1261, 1447, 1460, 1492, 1569, 1641, 1722, 2876, 2922, 2968, 3098 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.25 (2H, m, CH_2), 2.89 (2H, m, CH_2), 3.05 (4H, t, *J*= 7.2 Hz, $2CH_2$), 3.91 (4H, t, *J* = 7.2 Hz, $2CH_2$), 4.22 (5H, s, C_5H_5), 4.24 (5H, s, C_5H_5), 4.29 (2H, m, C_5H_4), 4.41 (2H, m, C_5H_4), 4.69 (2H, m, C_5H_4) , 4.77 (2H, m, C_5H_4), 6.92 (1H, s, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.37, 32.02 ($2CH_2$), 40.02, 62.23 ($4CH_2$), 69.49, 70.27 ($2C_5H_5$), 68.24, 68.96, 71.47, 72.37 ($2C_5H_4$), 79.41, 79.55 ($2C_{ipso}$Fc), 129.65 (CH), 138.06, 167.03 (2C). Anal. calcd. for $C_{29}H_{31}Fe_2NO_2S$

(569.24): C, 61.18; H, 5.49; N, 2.46; S, 5.63. Found: C, 61.62; H, 5.40; N, 2.42; S, 5.54 %. MS (El, 70 eV): *m/z* 568 $[M]^+$.

*2-(Z-1,2-Diferrocenyl-2-methylthiovinyl)-1,3-oxathiolane Z-**4b***: red oil, yield 0.5 g (31%). IR (KBr): ν 480, 671, 730, 813, 903, 940, 960, 999, 1028, 1047, 1105, 1185, 1208, 1265, 1380, 1411, 1440, 1462, 1492, 1655, 1718, 2850, 2918, 2957, 3091 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.50 (3H, s, CH_3), 3.15 (1H, m, CH_2), 3.18 (1H, m, CH_2), 3.70 (2H, m, CH_2), 4.10 (5H, s, C_5H_5), 4.26 (5H, s, C_5H_5), 4.30 (2H, m, C_5H_4), 4.65 (2H, m, C_5H_4), 4.83 (2H, m, C_5H_4), 5.15 (2H, m, C_5H_4), 6.81 (1H, s, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.67 (CH_3), 33.87, 66.80 ($2CH_2$), 69.44, 69.74 ($2C_5H_5$), 67.92, 69.30, 69.43, 70.54 ($2C_5H_4$), 83.87, 87.43 ($2C_{ipso}$Fc), 129.46 (CH), 133.76, 164.71 (2C). Anal. calcd. for $C_{26}H_{26}Fe_2OS_2$ (530.17): C, 58.89; H, 4.95; S, 12.07. Found: C, 59.27; H, 4.85; S, 12.15 %. MS (El, 70 eV): *m/z* 530 $[M]^+$.

*2-(E-1,2-Diferrocenyl-2-methylthiovinyl)-1,3-oxathiolane E-**4b**:* red oil, yield 0.37 g (23%). IR (KBr): ν 472, 646, 700, 757, 817, 912, 1000, 1028, 1045, 1106, 1210, 1274, 1310, 1377, 1411, 1451, 1485, 1599, 2867, 2919, 2951, 3086 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.88 (3H, s, CH_3), 3.16 (1H, m, CH_2), 3.21 (1H, m, CH_2), 3.71 (1H, m, CH_2), 4.23 (5H, s, C_5H_5), 4.28 (5H, s, C_5H_5), 4.35 (2H, m, C_5H_4), 4.38 (2H, m, C_5H_4), 4.39 (1H, m, C_5H_4), 4.68 (1H, m, C_5H_4) , 4.87 (1H, m, C_5H_4), 5.16 (1H, m, C_5H_4), 6.58 (1H, s, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.01 (CH_3), 29.67, 67.96 ($2CH_2$), 69.72, 69.80 ($2C_5H_5$), 68.67, 68.70, 69.12, 69.84, 70.61, 71.03, 71.26 71.47 ($2C_5H_4$), 87.88, 89.64 ($2C_{ipso}$Fc), 129.08 (CH), 123.68, 160.65 (2C). Anal. calcd. for $C_{26}H_{26}Fe_2OS_2$ (530.17): C, 58.89; H, 4.95; S, 12.07. Found: C, 58.90; H, 4.90; S, 12.06 %. MS (El, 70 eV): *m/z* 529 $[M]^+$.

*2-Morpholinoethyl (Z)-2,3-diferrocenylprop-2-enethioate **5a**:* orange powder, yield 0.43 g (25%), m.p. 142-144 °C. IR (KBr): ν 470, 594, 612, 673, 749, 817, 962, 1001, 1047, 1080, 1105, 1266, 1442, 1453, 1491, 1562, 1634, 1726, 2856, 2924, 2956, 3094 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.18 (2H, m, CH_2), 2.95 (1H, m, CH_2), 3.07 (4H, m, $2CH_2$), 3.92 (4H, m , $2CH_2$), 4.38 (1H, m, CH_2), 4.20 (5H, s, C_5H_5), 4.24 (5H, s, C_5H_5), 4.19 (2H, m, C_5H_4), 4.30 (1H, m, C_5H_4) , 4.49 (2H, m, C_5H_4), 4.69 (1H, m, C_5H_4) , 4.74 (2H, m, C_5H_4), 7.03 (1H, s, HC=). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.92, 30.33 ($2CH_2$), 38.52, 61.94 ($4CH_2$), 69.07, 70.11 ($2C_5H_5$), 68.25, 69.15, 70.45 70.70 ($2C_5H_4$), 79.35, 79.86 ($2C_{ipso}$Fc), 132.99 (HC=), 136.71 (C), 197.37 (C=O). Anal. calcd. for $C_{29}H_{31}Fe_2NO_2S$ (569.24): C, 61.19; H, 5.49; N, 2.46; S, 5.62. Found: C, 61.40; H, 5.53; N, 2.30; S, 5.44 %. MS (El, 70 eV): *m/z* 569 $[M]^+$.

*2-Methylthioethyl (Z)-2,3-diferrocenylprop-2-enethioate **5b**:* red powder, yield 0.29g (18%), m.p. 127-128 °C. IR (KBr): ν 480, 671, 730, 813, 903, 940, 960, 999, 1028, 1047, 1105, 1185, 1208, 1265, 1380, 1411, 1440, 1462, 1492, 1655, 1718, 2850, 2918, 2957, 3091 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.53 (3H, s, CH_3), 3.12 (1H, m, CH_2), 3.24 (1H, m, CH_2), 3.91 (2H, m, CH_2), 4.18 (5H, s, C_5H_5), 4.22 (5H, s, C_5H_5), 4.24 (2H, m, C_5H_4), 4.38 (2H, m, C_5H_4), 4.47 (2H, m, C_5H_4), 4.91 (2H, m, C_5H_4), 6.91 (1H, s, HC=). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.67 (CH_3), 33.90, 67.58 ($2CH_2$), 69.44, 69.54 ($2C_5H_5$), 67.65, 69.01, 69.30, 69.45, 69.54, 69.61, 69.65, 71.10 ($2C_5H_4$), 83.77, 87.2 ($2C_{ipso}$Fc), 139.46 (HC=), 133.67 (C), 194.80 (C=O). Anal. calcd. for $C_{26}H_{26}Fe_2OS_2$ (530.17): C, 58.89; H, 4.95; S, 12.07. Found: C, 58.80; H, 5.00; S, 12.00 %. MS (El, 70 eV): *m/z* 530 $[M]^+$.

Single-crystal X-ray diffraction data

Suitable single crystals of the compound **2b** were studied by single-crystal X-ray diffraction (Table S1). Each crystal was mounted on a glass fiber and crystallographic data were collected with an Oxford Diffraction Gemini "A" diffractometer with a CCD area detector with λCuKα = 1.54184 Å for **2b**, at 130 K. Unit cell parameters were determined with a set of three runs of 15 frames (1° in ω). The double pass method of scanning was used to exclude any noise.[17,18]

The collected frames were integrated by using an orientation matrix determined from the narrow frame scans. CrysAlisPro and CrysAlis RED software packages[18] were used for data collection and integration. Analysis of the integrated data did not reveal any decay. Final cell parameters were determined by a global refinement of 1955 reflections for **2b**. Collected data were corrected for absorption effects by analytical numeric absorption correction[18] using a multifaceted crystal model based on expressions upon the Laue symmetry using equivalent reflections. Structure solution and refinement were carried with the programs SHELXS-2014.[19-21]

Crystal data and experimental details of the structure determination are listed in Table 1. Select bond lengths and angles are presented in Table 2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary materials CCDC 1980453 **(2b)**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. e-mail: deposit@ccdc.cam.ac.uk.

2-(*E*-1,2-Diferrocenyl-2-morpholinovinyl)-1,3-benzoxathiole 2a

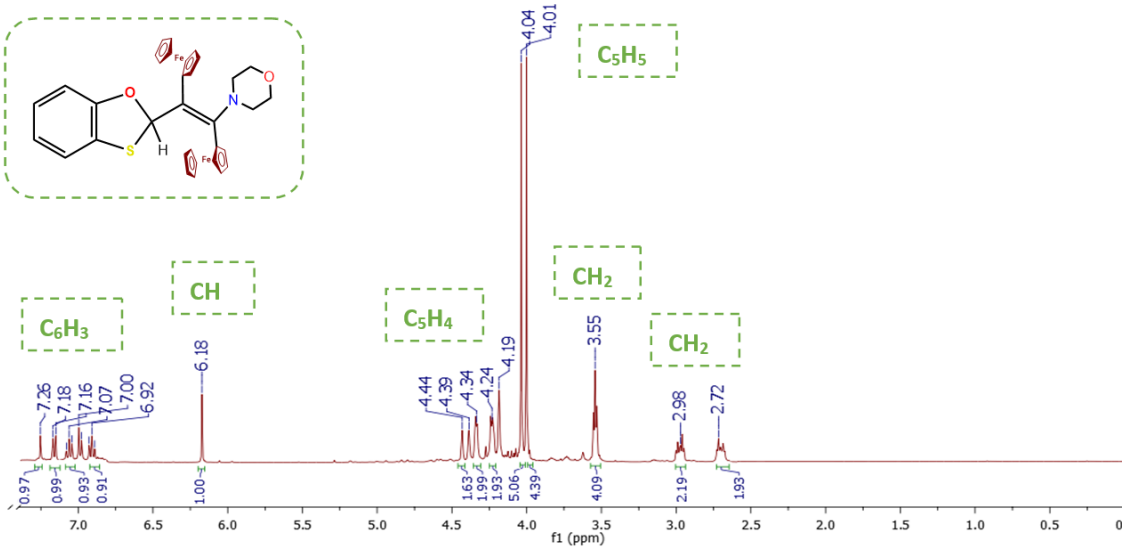

Fig. S1: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound **2a**

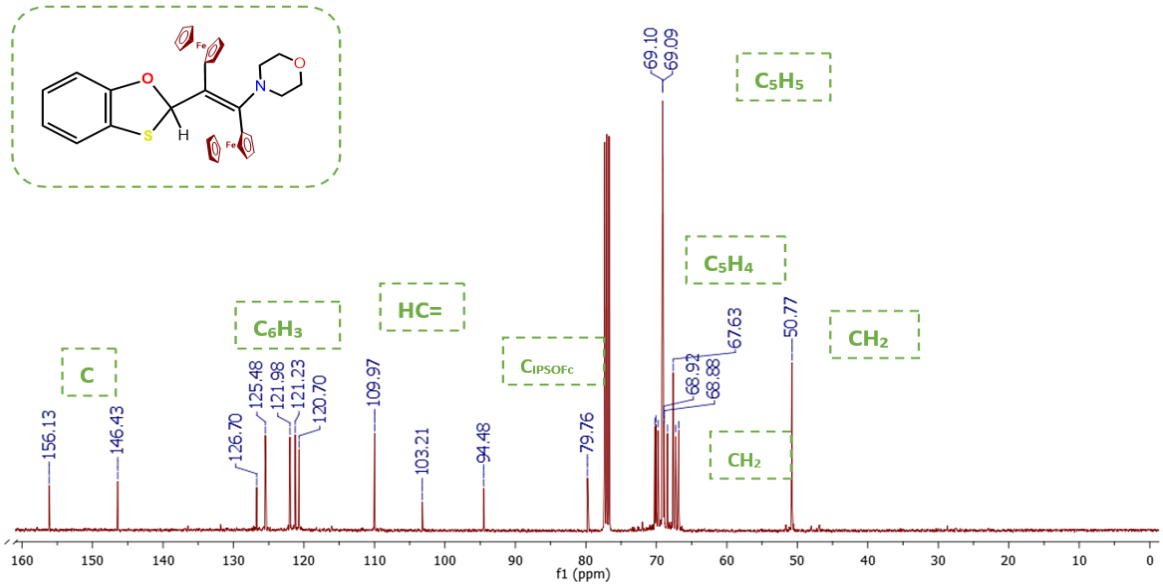

Fig. S-2: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) Spectrum of compound **2a**

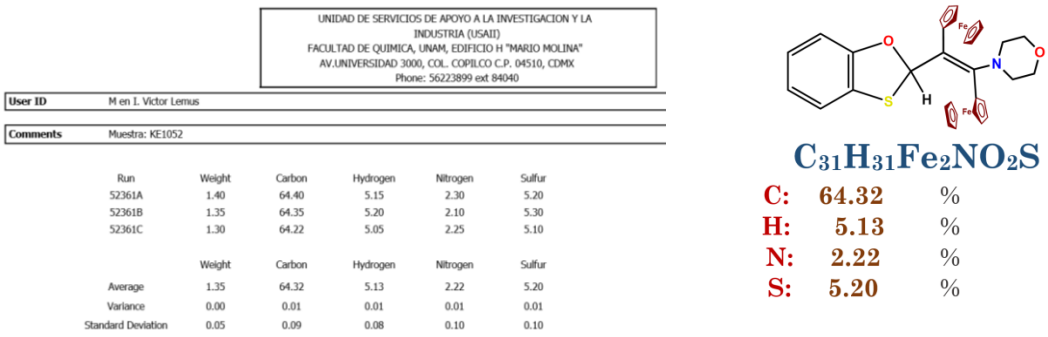

Fig. S-3: Elemental Analysis of compound 2**a**

2-(*E*-1,2-Diferrocenyl-2-methylthiovinyl)-1,3-benzoxathiole 2b

Single crystal X-ray structure determination of 2**b**
Crystals of **2b** were obtained by crystallization from dichloromethane

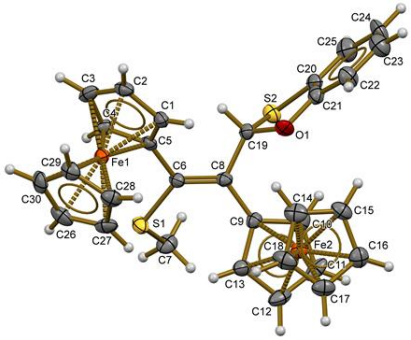

Fig. S4: Crystal structure of 2b

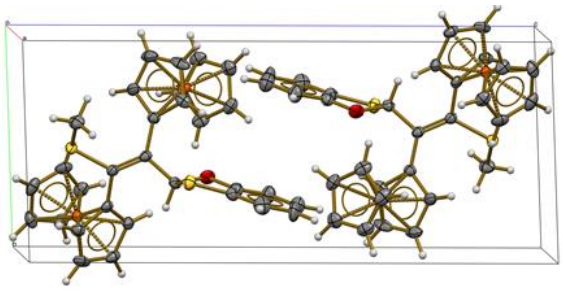

Fig. S5: Cristal Packing of 2b

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary materials CCDC 1980452 **(2b)**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. e-mail: deposit@ccdc.cam.ac.uk.

Table S1: Selected bond lengths and bond angles for compounds 2b

Selected bond lengths (Å)		Selected bond angles (°)	
C(6)-C(5)	1.486 (4)	C(13)-C(9)-C(8)	125.7(3)
C(8)-C(9)	1.475 (4)	C(10)-C(9)-C(8)	128.1(3)
C(7)-S(1)	1.803 (4)	C(1)-C(5)-C(6)	126.0(3)
S(1)-C(6)	1.774 (3)	C(4)-C(5)-C(6)	126.6(3)
C(6)-C(8)	1.359 (4)	C(8)-C(6)-S(1)	126.0(2)
C(8)-C(19)	1.508 (4)	C(5)-C(6)-S(1)	110.7(2)
C(19)-O(1)	1.466 (4)	C(6)-C(8)-C(19)	116.4(3)
C(19)-S(2)	1.857 (3)	O(1)-C(19)-C(8)	114.2(2)
O(1)-C(21)	1.377 (4)	O(1)-C(19)-S(2)	106.85(19)
S(2)-C(20)	1.740 (3)	C(8)-C(19)-S(2)	112.3(2)
C(21)-C(22)	1.378 (5)	O(1)-C(21)-C(20)	116.9(3)
C(22)-C(23)	1.374 (5)	C(23)-C(22)-C(21)	117.0(4)
C(23)-C(24)	1.380 (5)	C(22)-C(23)-C(24)	122.0(4)
C(24)-C(25)	1.394 (5)	C(24)-C(25)-C(20)	118.6(4)
C(25)-C(20)	1.403 (5)		

Table S2: Crystallographic data and structure refinement detail for compound 2b

Empirial formula	$C_{30}H_{26}FeOS_2$
Formula weight	578.33
Temperature (K)	130(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	P-1
a (Å)	7.6795(6)
b (Å)	8.5130(4)
c (Å)	19.7792(14)
α (º)	88.655(4)
β (º)	87.639(6)
γ (º)	71.950(5)
V (Å^3)	1228.32(15)
Z	2
$D_{Calc.}$ (mg/m^3)	1.564
Absorption coefficient	1.374mm^{-1}
F (000)	596
θ range for data collection	3.411 - 29.54º
Reflections collected	16637
Independent reflections	5923 [Rint = 0.0485]
Goodness-of-fit on F^2	1.043
Final *R* indices [$I > 2\sigma(I)$]	R1=0.0500, wR2=0.0978
R indices (all data)	R1=0.0788, wR2=0.1109
Data/restraints/paramaters	5923 / 0 / 317
Largest diff. peak and hole (e Å^{-3})	1.374 and -0.682

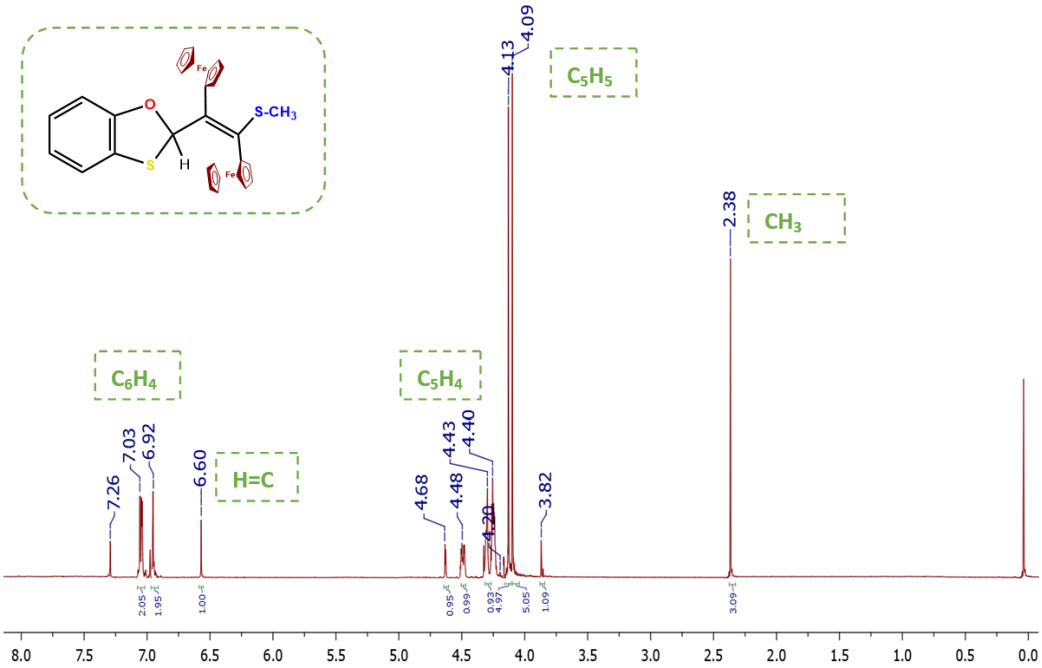

Fig. S6: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound **2b**

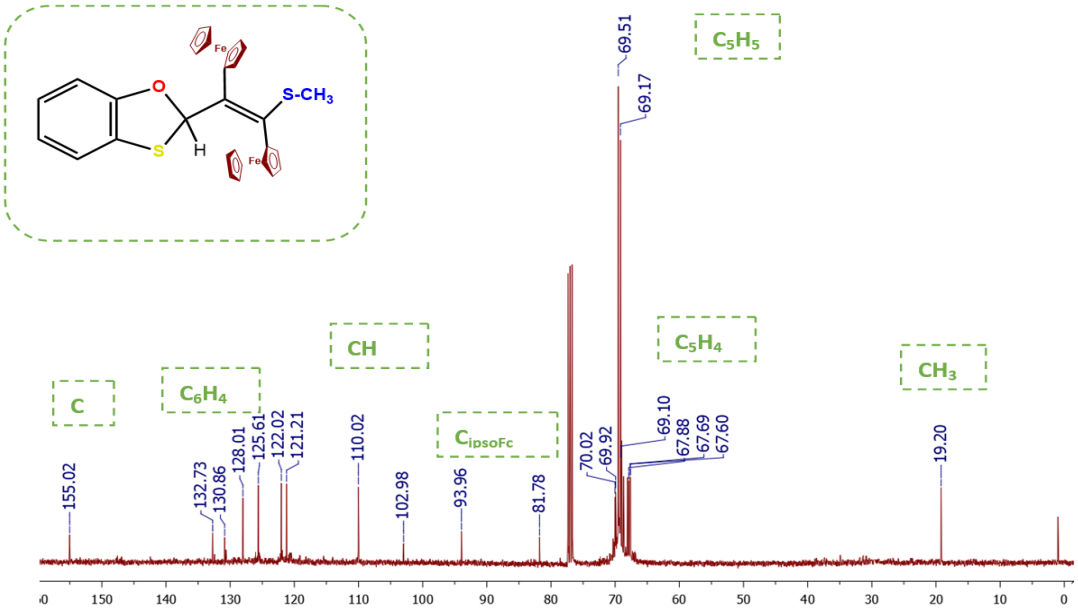

Fig. S7: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) spectrum of compound **2b**

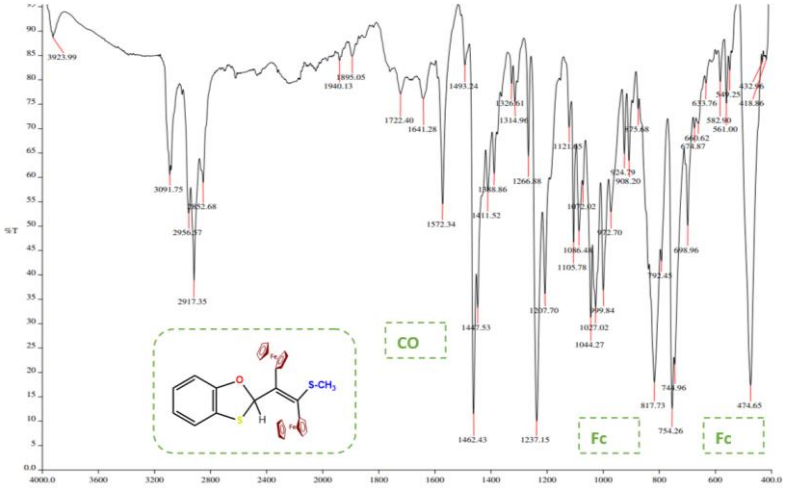

Fig. S8: IR (KBr) spectrum of compound **2b**

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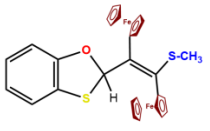
User ID M en I. Victor Lemus

Comments Muestra: KE0180

Run	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
623511A	1.35	62.15	4.68	0.05	11.50
623511B	1.42	61.76	4.28	0.10	11.35
623511C	1.55	61.95	4.58	0.04	11.35

	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
Average	1.44	61.95	4.51	0.06	11.40
Variance	0.01	0.04	0.04	0.00	0.01
Standard Deviation	0.10	0.20	0.21	0.03	0.09



$C_{30}H_{26}Fe_2OS_2$

C: 62.31 %
H: 4.53 %
S: 11.07 %

Fig. S9: Elemental Analysis of compound **2b**

3,4-Diferrocenyl-2-morpholino-2*H*-1,5-benzoxathiepine **3a**

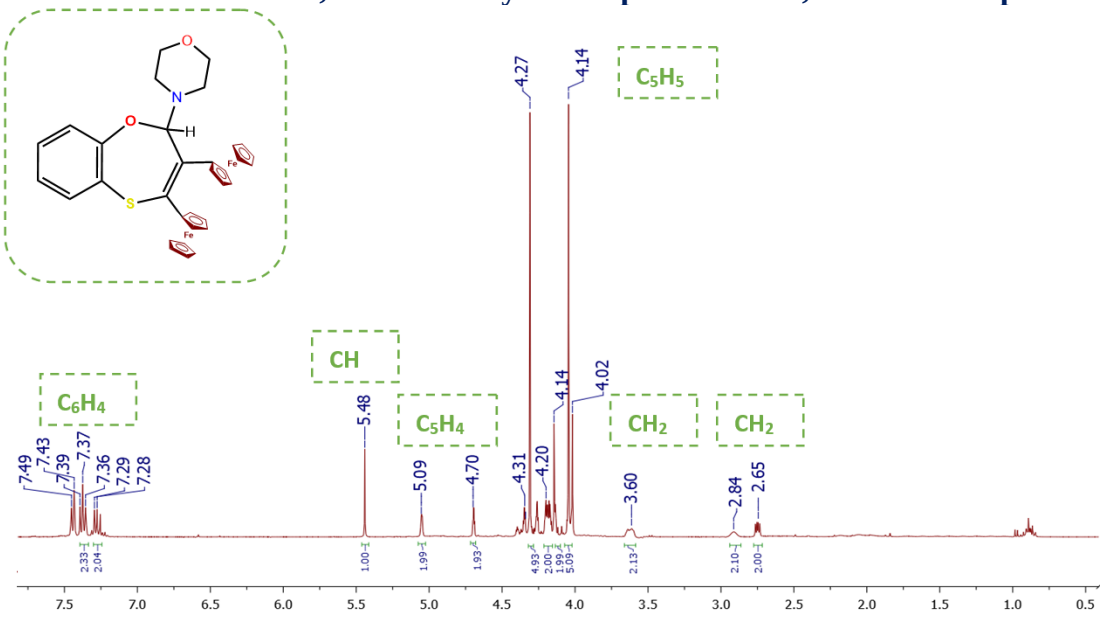


Fig. S10: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound **3a**

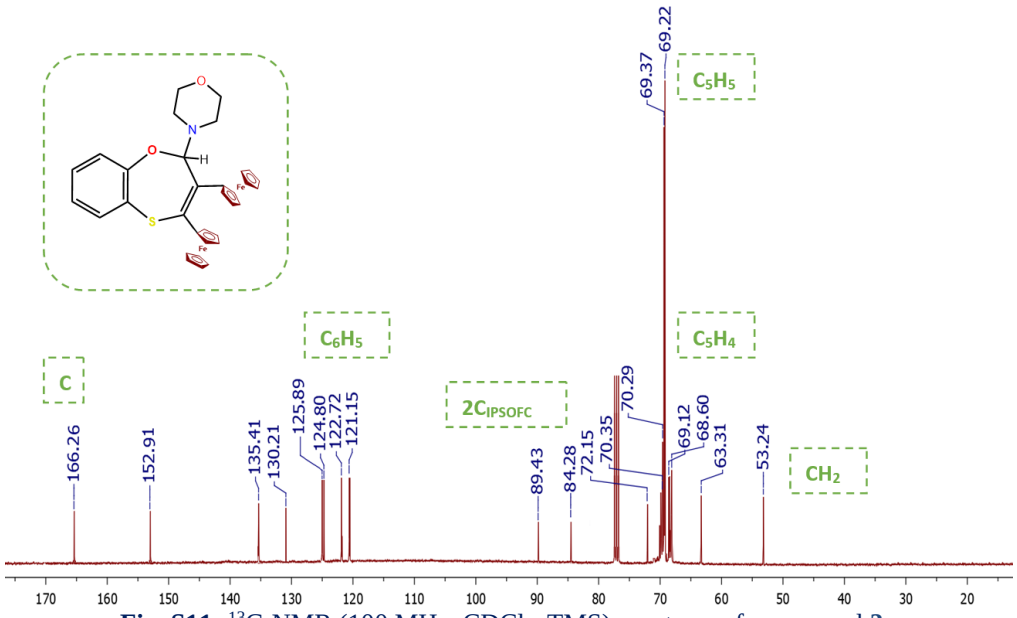


Fig. S11: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) spectrum of compound **3a**

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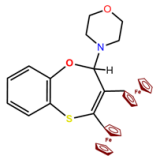
User ID	M en I. Victor Lemus
Comments	Muestra: KE5263

Run	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
65305A	1.52	64.20	5.10	2.30	5.05
65305B	1.45	64.30	5.15	2.18	5.15
65305C	1.60	64.22	5.05	2.25	5.10

	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
Average	1.52	64.24	5.10	2.24	5.10
Variance	0.01	0.00	0.00	0.00	0.00
Standard Deviation	0.08	0.05	0.05	0.06	0.05



$C_{33}H_{31}Fe_2NO_2S$

C: 64.20 %
H: 5.06 %
N: 2.27 %
S: 5.19 %

Fig. S12: Elemental Analysis of compound **3a**

3,4-Diferrocenyl-3-methylthio-2*H*-1,5-benzoxathiepine **3b**

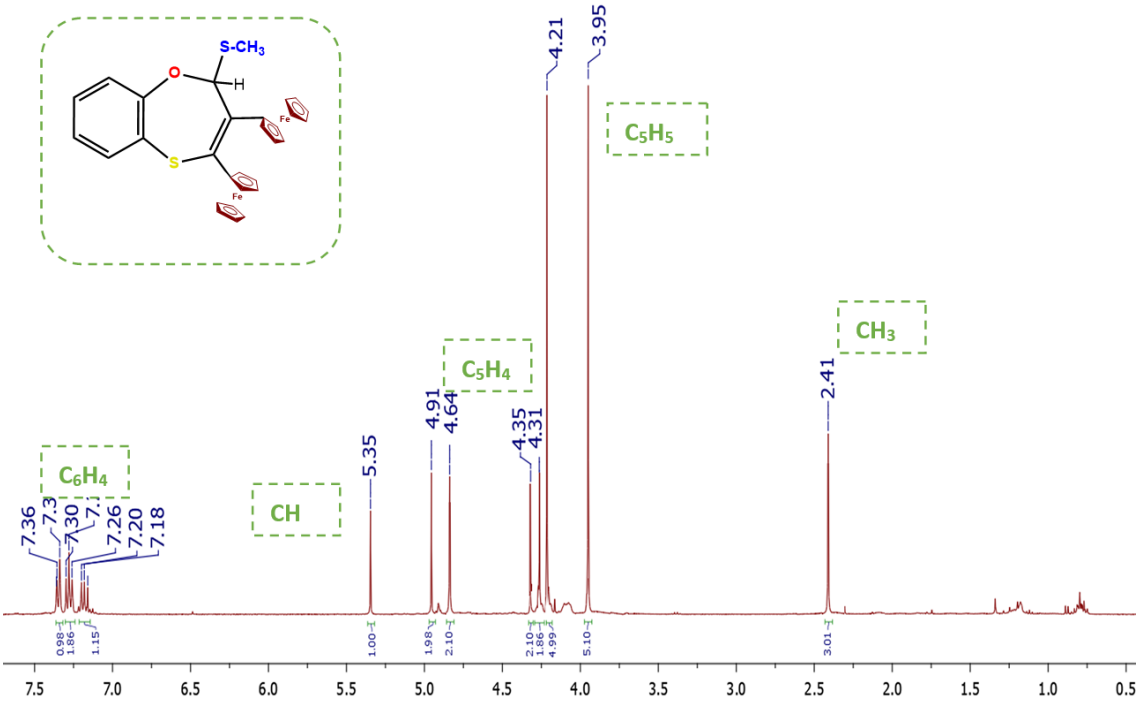


Fig. S13: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound **3b**

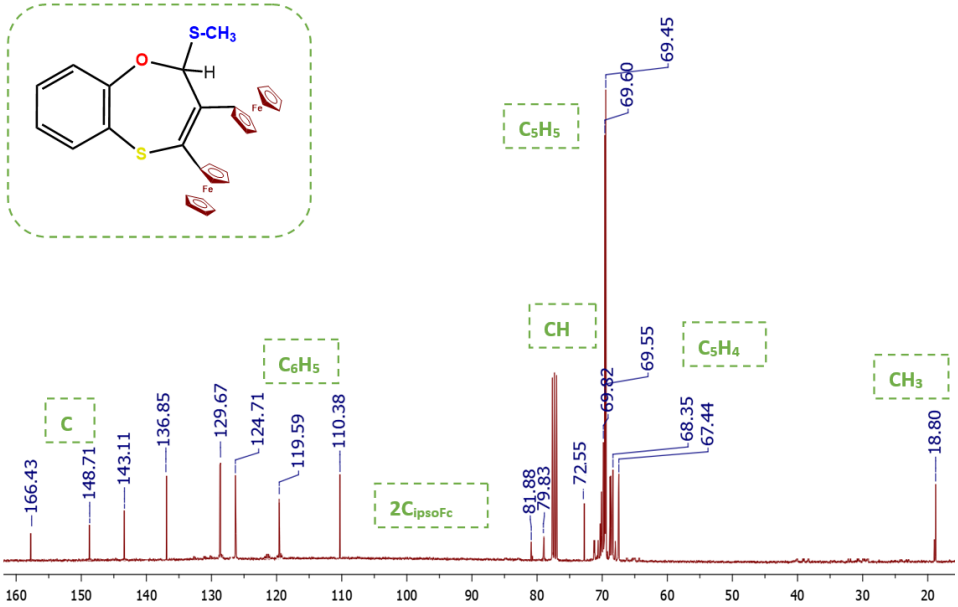


Fig. S14: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) spectrum of compound **3b**

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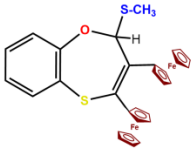
User ID	M en I. Victor Lemus
Comments	Muestra: KE6523

Run	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
68523A	1.60	62.35	4.80	0.30	11.05
68523B	1.65	62.33	4.68	0.10	11.15
68523C	1.50	62.00	4.50	0.15	11.10
	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
Average	1.58	62.23	4.66	0.18	11.10
Variance	0.01	0.04	0.02	0.01	0.00
Standard Deviation	0.08	0.20	0.15	0.10	0.05



$C_{30}H_{26}Fe_2OS_2$

C: 62.31 %
H: 4.53 %
S: 11.07 %

Fig. S15: Elemental Analysis of compound **3b**

2-(*E*-1,2-Diferrocenyl-2-morpholinovinyl)-1,3-oxathiolane *E*-4a

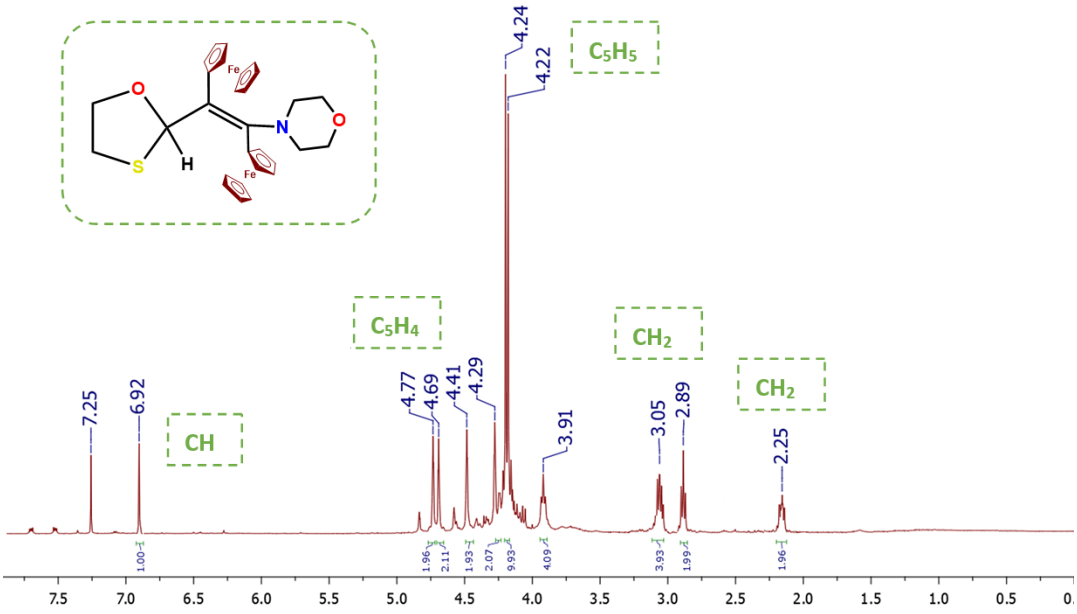


Fig. S16: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound **4a**

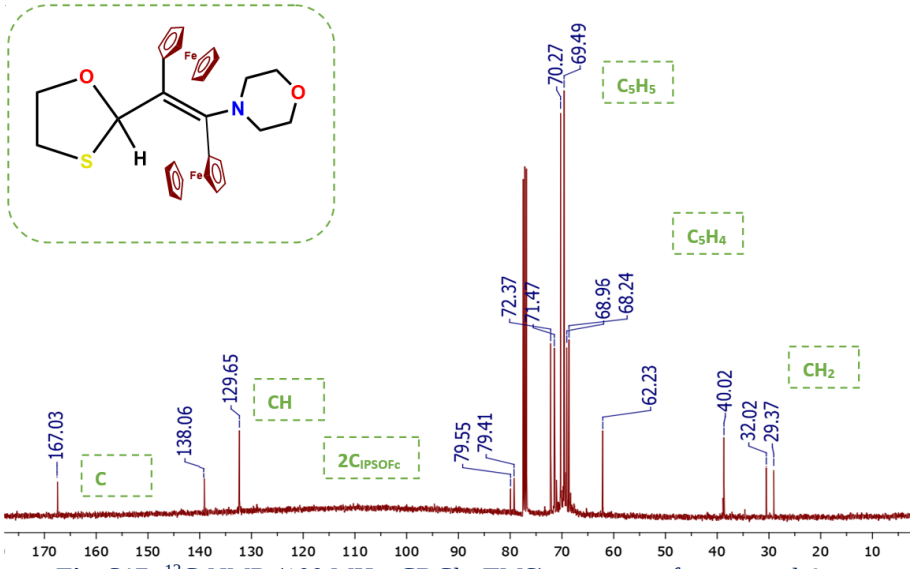


Fig. S17: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) spectrum of compound **4a**

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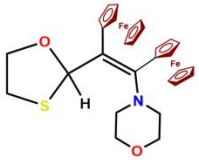
User ID	M en I. Victor Lemus
Comments	Muestra: KE0010

Run	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
523550A	1.40	61.20	5.40	2.45	5.63
523550B	1.45	62.25	5.30	2.50	5.20
523550C	1.80	61.40	5.50	2.30	5.80

	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
Average	1.55	61.62	5.40	2.42	5.54
Variance	0.05	0.31	0.01	0.01	0.10
Standard Deviation	0.22	0.56	0.10	0.10	0.31



$C_{29}H_{31}Fe_2NO_2S$

C: 61.18 %
H: 5.49 %
N: 2.46 %
S: 5.63 %

Fig. S18: Elemental Analysis of compound **4a**

2-(*Z*-1,2-Diferrocenyl-2-methylthiovinyl)-1,3-oxathiolane *Z*-4b

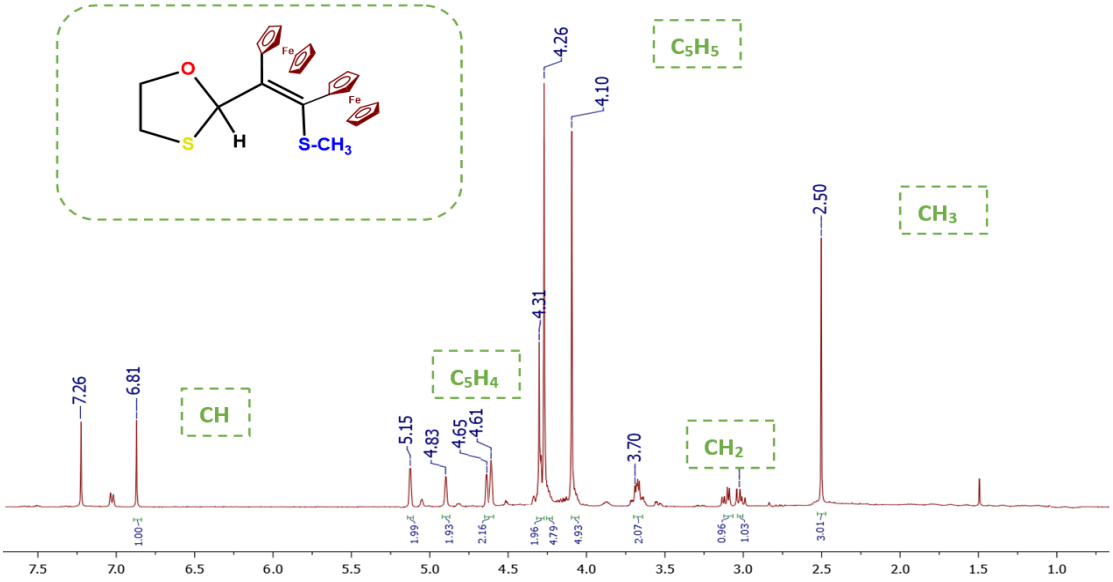


Fig. S19: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound ***Z*-4b**

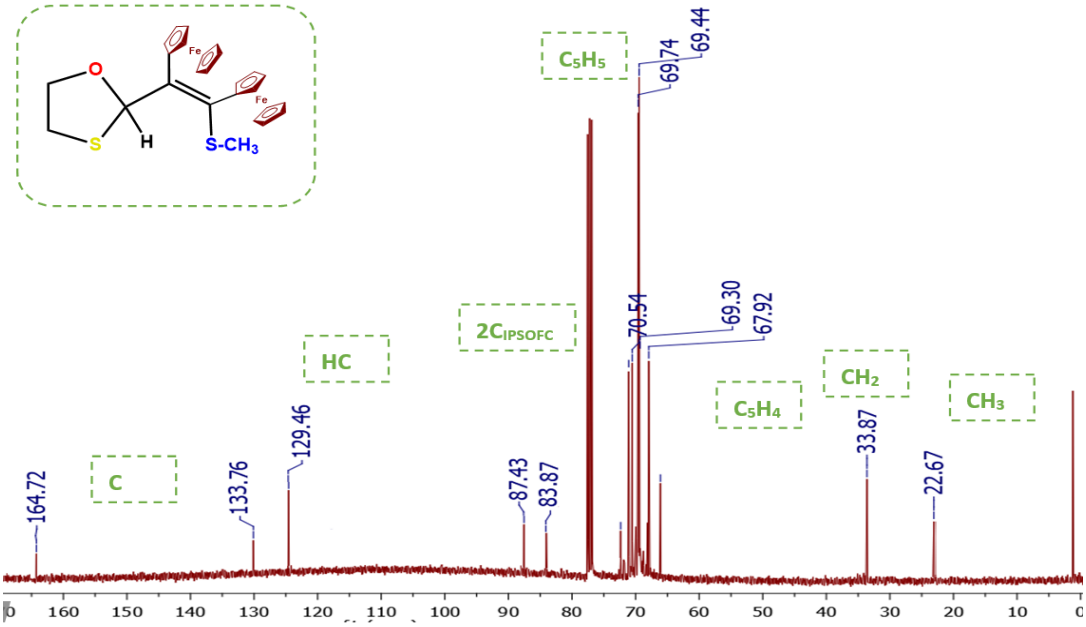


Fig. S20: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) spectrum of compound ***Z*-4b**

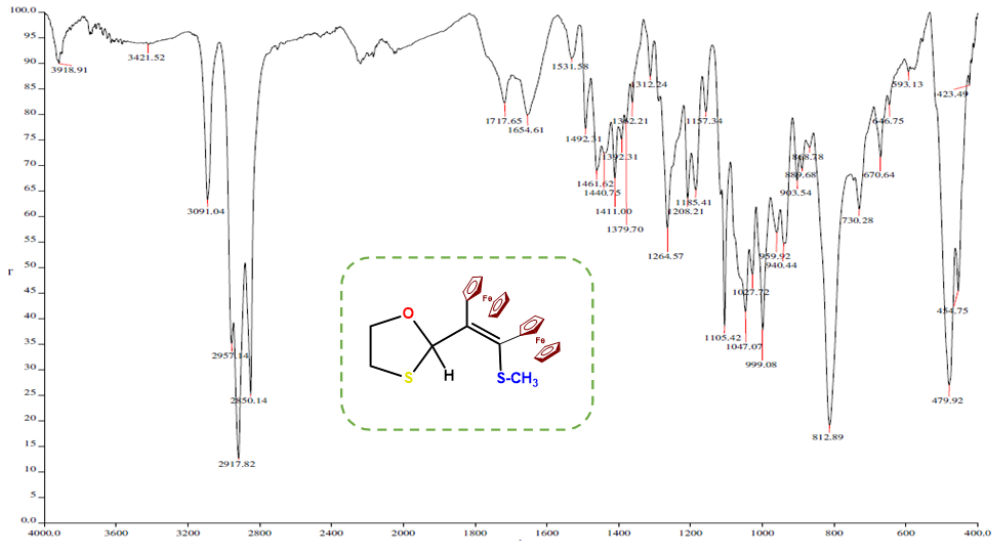


Fig. S21: IR (KBr) spectrum of compound ***Z*-4b**

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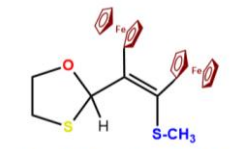
Phone: 5622899 ext 84040

User ID	M en I. Victor Lemus
Comments	Muestra: KE859

Run	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
58632A	1.40	58.80	4.90	0.10	12.15
58632B	1.60	59.00	4.80	0.35	12.00
58632C	1.58	60.00	4.86	0.25	12.30
	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
Average	1.53	59.27	4.85	0.23	12.15
Variance	0.01	0.41	0.00	0.02	0.02
Standard Deviation	0.11	0.64	0.05	0.13	0.15



$C_{26}H_{26}Fe_2OS_2$

C: 58.89 %
H: 4.95 %
S: 12.07 %

Fig. S22: Elemental Analysis of compound ***Z*-4b**

2-(*E*-1,2-Diferrocenyl-2-methylthiovinyl)-1,3-oxathiolane *E*-4b

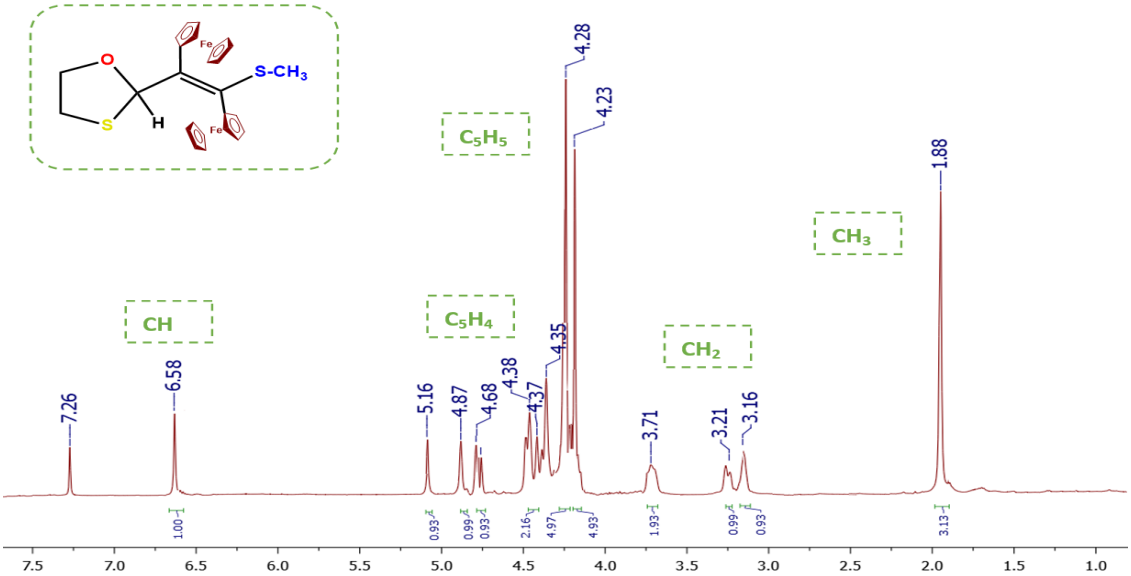


Fig. S23: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound ***E*-4b**

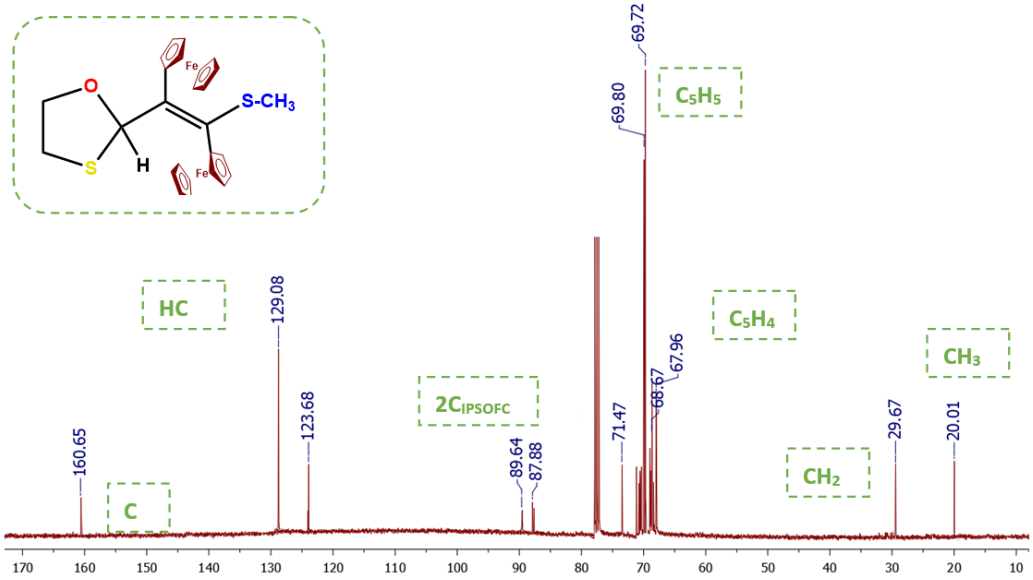


Fig. S24: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) spectrum of compound ***E*-4b**

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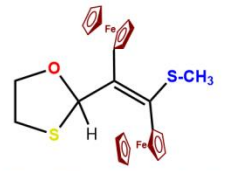
User ID	M en I. Victor Lemus
Comments	Muestra: KE05236

Run	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
58658A	1.15	58.75	4.90	0.05	12.05
58658B	1.35	59.15	4.85	0.30	12.10
58658C	1.40	58.80	4.95	0.10	12.05
	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
Average	1.30	58.90	4.90	0.15	12.07
Variance	0.02	0.05	0.00	0.02	0.00
Standard Deviation	0.13	0.22	0.05	0.13	0.03



$C_{26}H_{26}Fe_2OS_2$

C: 58.89 %
H: 4.95 %
S: 12.07 %

Fig. S25: Elemental Analysis of compound ***E*-4b**

2-Morpholinoethyl (*Z*)-2,3-diferrocenylprop-2-enethioate 5a

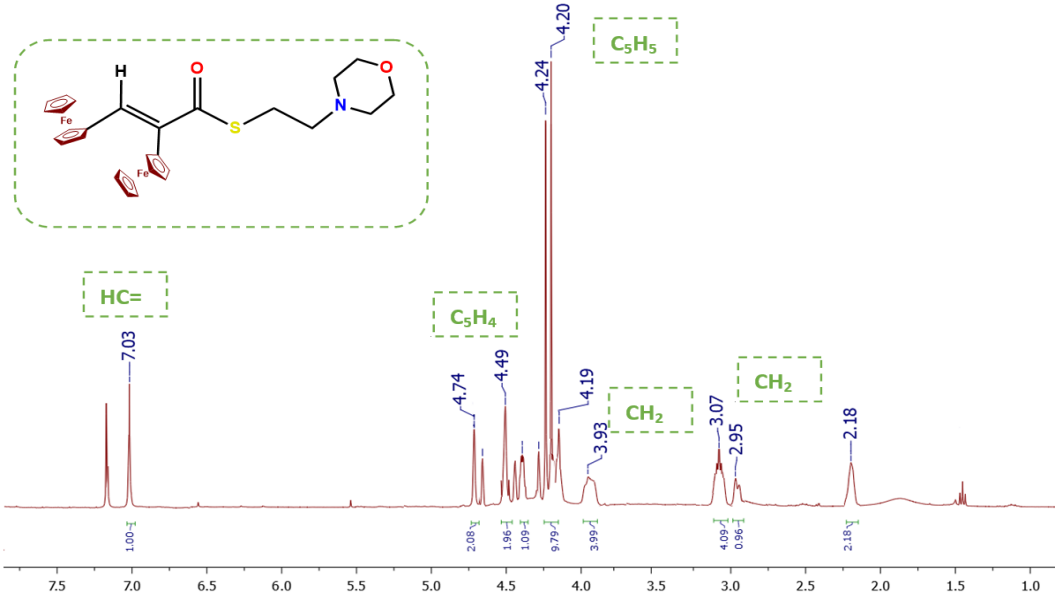


Fig. S26: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound **5a**

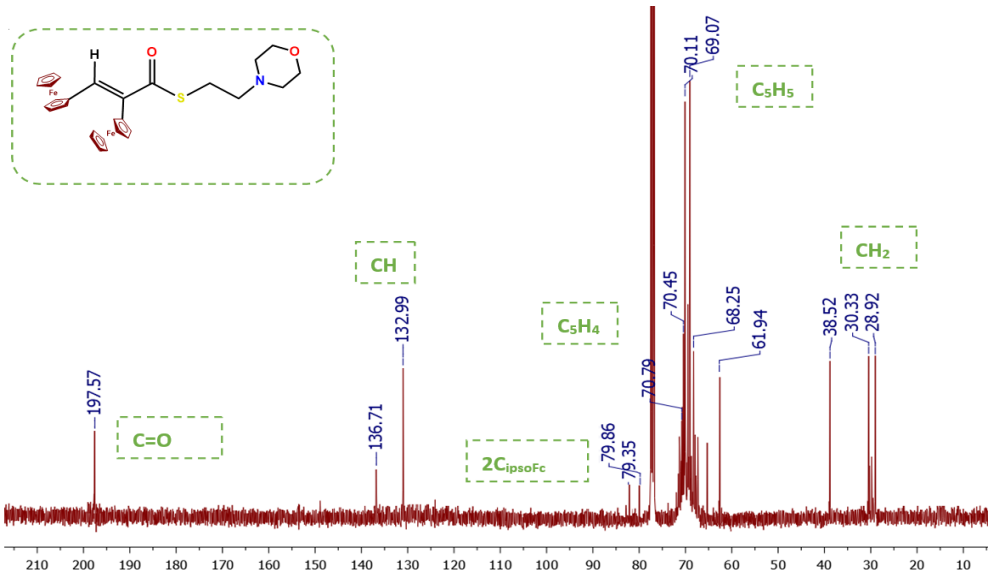
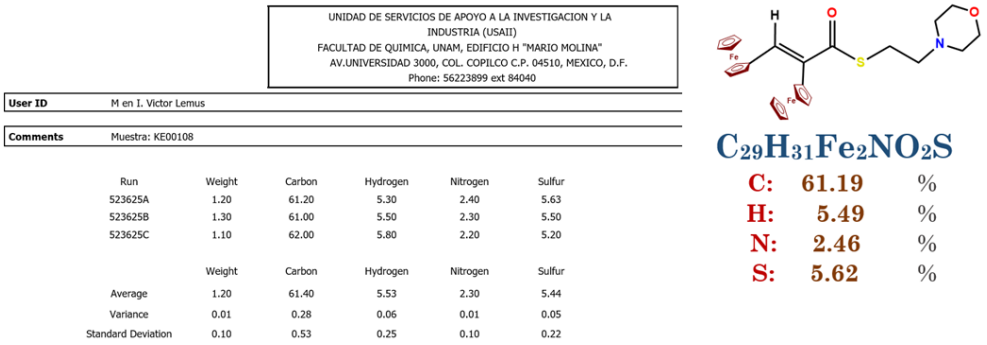


Fig. S27: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) spectrum of compound **5a**



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User ID	M en I. Victor Lemus
Comments	Muestra: KE00108

Run	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
523625A	1.20	61.20	5.30	2.40	5.63
523625B	1.30	61.00	5.50	2.30	5.50
523625C	1.10	62.00	5.80	2.20	5.20

	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
Average	1.20	61.40	5.53	2.30	5.44
Variance	0.01	0.28	0.06	0.01	0.05
Standard Deviation	0.10	0.53	0.25	0.10	0.22

$C_{29}H_{31}Fe_2NO_2S$

C:	61.19	%
H:	5.49	%
N:	2.46	%
S:	5.62	%

Fig. S28: Elemental analysis of compound **5a**

2-Methylthioethyl (*Z*)-2,3-Diferrocenylprop-2-enethioate 5b

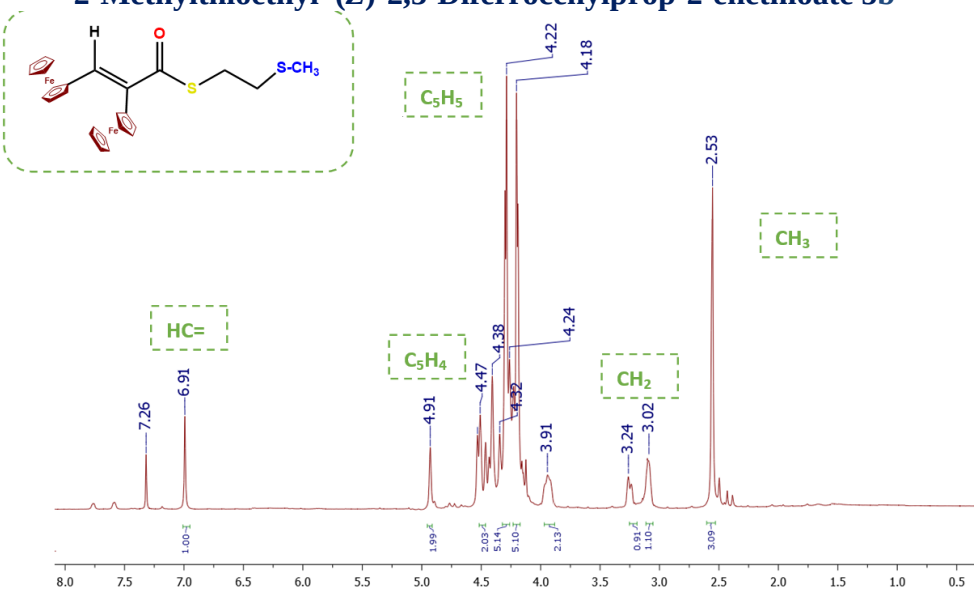

Fig. S29: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) spectrum of compound **5b**

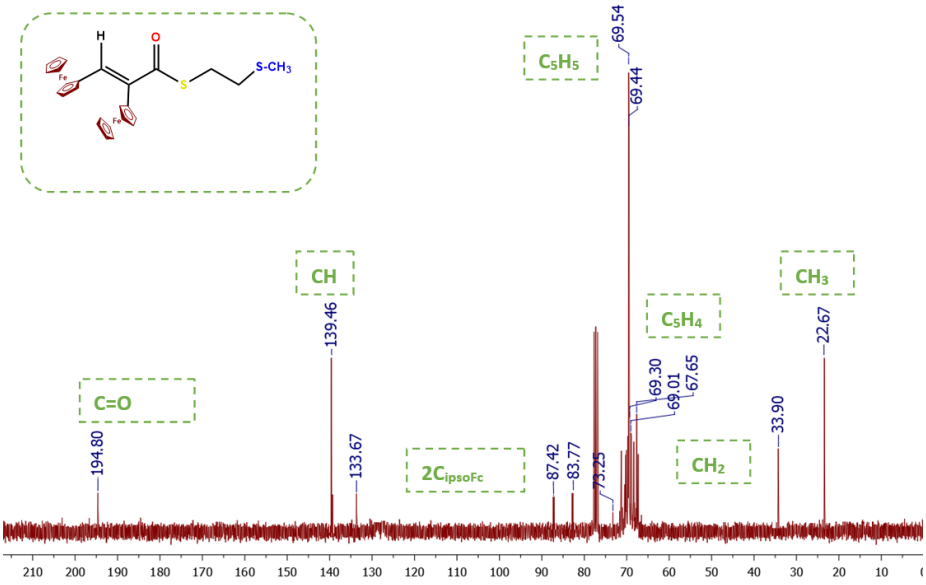

Fig. S30: ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) spectrum of compound **5b**

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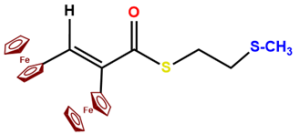
Phone: 56223899 ext 84040

User ID	M en I. Victor Lemus
Comments	Muestra: KE001051

Run	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
523681A	1.50	58.90	4.90	0.00	12.10
523681B	1.60	59.00	5.10	0.30	12.00
523681C	1.40	58.50	5.00	0.20	11.90
	Weight	Carbon	Hydrogen	Nitrogen	Sulfur
Average	1.50	58.80	5.00	0.17	12.00
Variance	0.01	0.07	0.01	0.02	0.01
Standard Deviation	0.10	0.26	0.10	0.15	0.10



$C_{26}H_{26}Fe_2S_2O$

C: 58.89 %
H: 4.95 %
N: 0.00 %
S: 12.07 %

Fig. S31: Elemental Analysis of compound **5b**