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Synthesis of some Sulfur-Containing Acylferrocenes

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Summary. Acylferrocenes containing a sulfur atom within their side chain were synthesized in good yields by *Friedel-Crafts* acylation of ferrocene with *in situ* generated acyl halides from the corresponding carboxylic acids (S-protected derivatives of thioglicolic and α- and β-mercaptopropionic acids).

Keywords. Acylferrocenes; *Friedel-Crafts* acylation; α-Mercaptopropionic acid; β-Mercaptopropionic acid; Thioglicolic acid.

Introduction

There is considerable interest in ferrocene derivatives containing two heteroatoms, such as oxygen, nitrogen, sulfur, and phosphorus within the side chains. These compounds are capable of coordinating different transition metal ions, giving complexes that are effective catalysts in many homogenous catalytic processes. Thus, optically active ferrocene diols, aminoalcohols, diamines, mercaptoalcohols, and mercaptoamines are particularly interesting compounds for organic syntheses [1].

Recently, we required a ferrocene derivative containing in its structure a -C*X*-C-S- or -C*X*-C-C-S- fragment ($X = \mathrm{OH}$ or $\mathrm{N}R_2$). A *Friedel-Crafts* acylation of ferrocene with a suitable carboxylic acid chloride was considered appropriate for the syntheses of such compounds. The carbonyl group may then be easily transformed into a hydroxyl or an amino group. The second desired functional group may be introduced either by reaction of the acylferrocene with some sulfur donating reagent, or by employing a sulfur-containing acyl chloride for the acylation of ferrocene. *Toma* and *Kaluz* [2] have reported that sulfur-containing ketones of the type $C_5H_5FeC_5H_4COCH_2CH_2$-S-Ar may be synthesized by *Michael* addition of the corresponding thiophenolols to the double bond of vinyl ferrocenyl ketone. These authors have also mentioned that the *Friedel-Crafts* acylation of ferrocene with the methyl ester chloride of thiodiglycolic acid gives a sulfur

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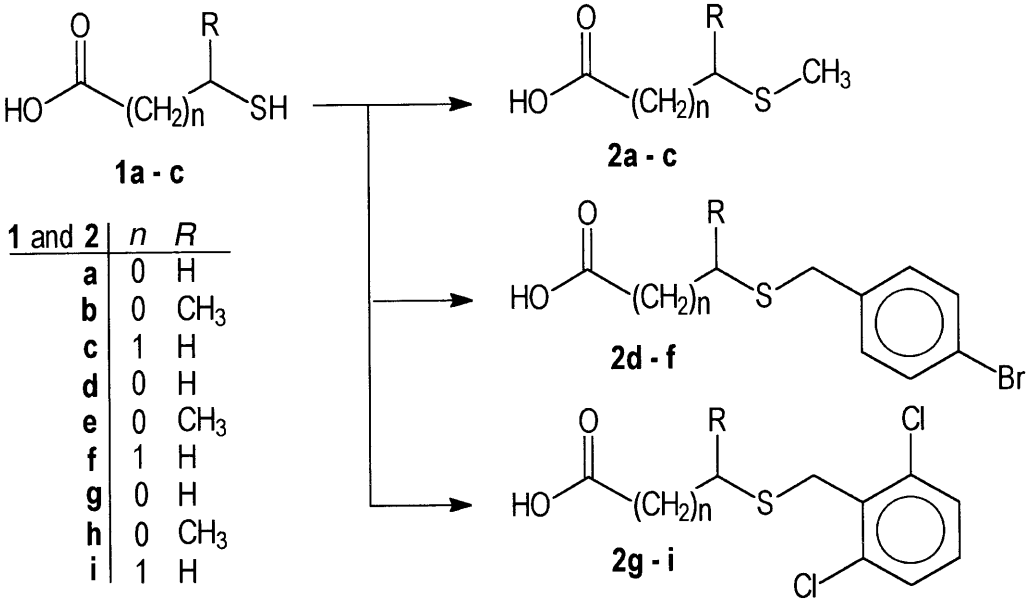
containing oxoester ($C_5H_5FeC_5H_4$-CO-CH_2-S-CH_2COOCH_3) in 30% yield [3]. One more possibility described in literature for introducing a sulfur atom into a ferrocene containing molecule is the condensation of thiols with ferrocenyl carbinols in the presence of trifluoroacetic acid. This has been the method most frequently used in the synthesis of sulfur-containing ferrocene derivatives [4–8].

The main goal of the work presented in this paper was to study possibilities of the second approach, *i.e.* the direct synthesis of sulfur-containing acylferrocenes by the *Friedel-Crafts* reaction. Since we have reported recently that ferrocene can be successfully acylated by an acyl chloride generated *in situ* from the corresponding carboxylic acid and phosphorus trichloride [4], we now decided to apply this method to synthesize the above mentioned sulfur-containing acyl ferrocenes. As the sulfur donating acylating agents, α- and β-sulfur-substituted carboxylic acids (thioglicolic (**1a**), α-mercaptopropionic (**1b**), β-mercaptopropionic acids (**1c**) were chosen.

Results and Discussion

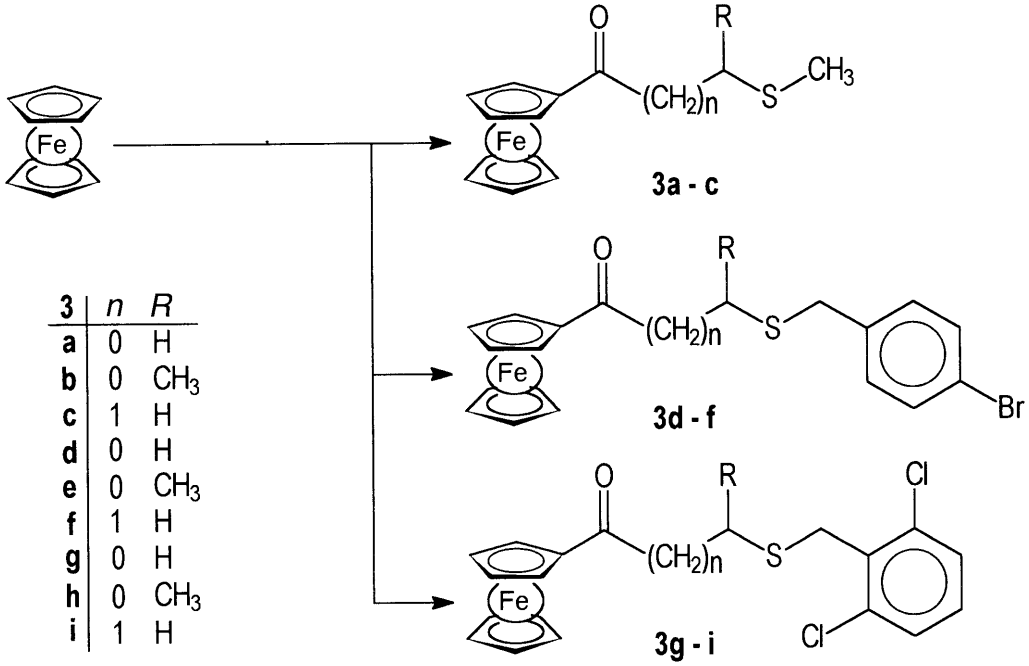
We started the acylation reaction by stirring a mixture of ferrocene, the corresponding mercaptocarboxylic acid, phosphorus trichloride, and aluminum trichloride in dichloromethane at room temperature [9, 10]. As expected, we failed to obtain the desired ketones; evidently, the free SH group of the starting acids prevents the reaction. Therefore, the acids **1a–c** were treated with methyl iodide, 4-bromobenzylbromide, and 2,6-dichlorobenzyl bromide according to literature [11–13] in order to protect the SH group, thus affording acids **2a–i** (Scheme 1).

Acylation of ferrocene with **2a** was performed as described above. Column chromatography of the reaction mixture gave – besides some unchanged ferrocene – only one product. On the basis of its spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR) it



1 and 2	*n*	*R*
a	0	H
b	0	CH_3
c	1	H
d	0	H
e	0	CH_3
f	1	H
g	0	H
h	0	CH_3
i	1	H

Scheme 1



3	*n*	*R*
a	0	H
b	0	CH_3
c	1	H
d	0	H
e	0	CH_3
f	1	H
g	0	H
h	0	CH_3
i	1	H

Scheme 2

was identified as the ketone **3a**. Acylation of ferrocene with the other two acids containing the S-CH_3 group (**2b** and **2c**) under the same reaction conditions afforded the corresponding ketones **3b** and **3c**. A slightly different behaviour was observed in the case of the acids **2d–i** containing 4-bromobenzyl and 2,6-dichlorobenzyl groups instead of the methyl group. The acids **2d**, **2f**, **2g**, and **2i** reacted in a similar manner as acids **2a–c**, yielding the corresponding ketones **3d**, **3f**, **3g**, and **3i** in good to very good yields. Surprisingly, acylation of ferrocene with the acids **2e** and **2h** resulted in considerable lower yields of the corresponding ketones **3e** and **3h**.

In order to optimize the yields of the corresponding ketones in the acylation of ferrocene with S-protected derivatives of α-mercaptopropionic acid (**2e** and **2h**), this reaction was performed at approximately 0°C as well as at reflux temperature of dichloromethane; however, **3e** and **3h** were obtained in almost the same yield as at room temperature. Also, elongated reaction times did not increase the yield. In this case, however, almost complete consumption of the starting ferrocene was observed leading to the formation of considerable amounts of unknown polar products which could not separated and identified.

Other solvents were also applied at different temperatures. Thus, reaction in carbon disulfide (ice bath, room temperature, reflux) gave the desired ketones in only 5–8% yield. Reaction in benzene provided a somewhat higher yield, but still considerably lower than that in dichloromethane. Neither nitrobenzene nor 1,2-dichlorobenzene (ice bath, room temperature, 80°C) gave any useful results. In all solvents used, acids **2a**, **2b**, **2c**, **2d**, **2f**, **2g**, and **2i** gave higher yields than acids **2e** and **2h**.

As our results show, *in situ* generated acyl chlorides from phosphorus trichloride and α- and β-sulfur-containing carboxylic acids can be successfully used (without isolation and purification) for the acylation of ferrocene. The phosphorus species, whatever they are (phosphorous acid or, more probably, phosphorus trioxide), do not hinder the catalytic action, thus rendering this procedure superior to the classical acylation with acyl chlorides or carboxylic acid anhydrides.

Experimental

All chemicals used were commercially available and were used as received. CH_2Cl_2 was dried over P_2O_5 and distilled before use; the other solvents were purified by distillation. Thioglicolic, α- and β-mercaptopropionic acids were purchased from Merck. Methylthiocarboxylic acids **2a** and **2c**, although also known and commercially available, as well as acids **2b** and **2d–i**, were synthesized according to a modified literature procedure as given below [11–13]. Methyl iodide, 4-bromobenzyl bromide, and 2,6-dichlorobenzyl bromide were obtained from Fluka. IR measurements were carried out with a Perkin-Elmer 457 grating FT instrument. NMR spectra were recorded on a Varian Gemini 200 or a Bruker AC 250 spectrometer using $CDCl_3$ as the solvent. Chemical shifts are expressed in ppm relative to internal *TMS*.

General procedure for the synthesis of acids **2a–i**

The corresponding mercaptoacids **1a–c** (10 mmol) and sodium hydroxide (20 mmol) were dissolved in 50 cm^3 H_2O. To this solution, 11 mmol of the corresponding halide (methyl iodide in the case of acids **2a–c** and 4-bromobenzyl bromide in the case of **2d–f**) dissolved in 30 cm^3 methanol were added, and the mixture was stirred for 3 h. In the case of **2g–i**, 2,6-dichlorobenzyl bromide (11 mmol) was dissolved in 30 cm^3 ether and added to the aqueous solution of the disodium salt of the corresponding mercaptocarboxylic acid. To the resulting two-phase solution methanol was added until the mixture became homogenous (about 40 cm^3); After stirring for 3 h, the organic solvents (methanol, *i.e.* methanol and ether) were evaporated, and the residue (the aqueous solution) was extracted twice with 30 cm^3 portions of ether and then acidified with a 10% HCl solution. The liberated carboxylic acids were extracted with three 30 cm^3 portions of ether, and the combined organic layers were washed with H_2O and brine and dried over anhydrous sodium sulfate. After filtration, the solvent was distilled off, and the remaining S-protected acids (60–85%) were pure enough (IR, ^{1}H NMR, ^{13}C NMR) to be used in the further studies.

2-Methylthio-propanoic acid (**2b**; $C_4H_8O_2S$)

Yield: 60%; IR (film): $\nu_{max} = 2986, 2928, 1708, 1455, 1421, 1379, 1323, 1287, 1241, 1197, 1072, 1000, 957\,cm^{-1}$; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.46$ (d, $J = 7.1$ Hz, 3H), 2.21 (s, 3H), 3.36 (q, $J = 7.1$, 1H), 10.33 (br s, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.0, 18.1, 41.7, 179.0$ ppm.

4-Bromobenzylthio-acetic acid (**2d**; $C_9H_9BrO_2S$)

Yield: 79%; IR (KBr): $\nu_{max} = 3445$ (br), 3076, 2998, 2899, 2657, 2543, 1694, 1484, 1432, 1408, 1292, 1160, 1126, 1099, 1069, 1009, 917, 835, 727, 671, 611, 586, 495, $471\,cm^{-1}$; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.08$ (s, 2H), 3.81 (s, 2H), 7.21–7.26 (m, 2H), 7.43–7.47 (m, 2H), 10.20 (br s, 1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 31.9, 35.7, 121.4, 130.9, 131.7, 135.9, 176.7$ ppm.

2-(4-Bromobenzylthio)-propanoic acid (**2e**; $C_{10}H_{11}BrO_2S$)

Yield: 82%; IR (KBr): $\nu_{max} = 3026, 2982, 2931, 2721, 2636, 2549, 2363, 1902, 1707, 1591, 11487, 1453, 1416, 1379, 1323, 1286, 1240, 1196, 1071, 1011, 935, 882, 827, 729\,cm^{-1}$; ^{1}H NMR

(250 MHz, $CDCl_3$): $\delta = 1.40$ (d, $J = 7.1$, 3H), 3.25 (q, $J = 7.1$, 1H), 3.77 and 3.88 (AB system, $J_{AB} = 10,9$ Hz, 2H), 7.21–7.26 (m, 2H), 7.42–7.47 (m, 2H), 10.50 (br s, 1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 16.3$, 35.4, 39.6, 121.1, 130.8, 131.6, 136.3, 179.6 ppm.

3-(4-Bromobenzylthio)-propanoic acid (**2f**; $C_{10}H_{11}BrO_2S$)

Yield: 85%; IR (KBr): $\nu_{max} = 3444$ (br), 3064, 2961, 2922, 2746, 2669, 2585, 1907, 1696, 1485, 1424, 1400, 1344, 1267, 1244, 1199, 1157, 1099, 1068, 1007, 948, 865, 823, 772, 743, 721, 683, 655, 609, 494 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.62$ (m, 4H), 3.67 (s, 2H), 7.16–7.20 (m, 2H), 7.40–7.45 (m, 2H), 11.50 (br s, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.7$, 43.2, 35.6, 120.9, 130.4, 131.6, 136.9, 178.2 ppm.

(2,6-Dichlorobenzylthio)-acetic acid (**2g**; $C_9H_8Cl_2O_2S$)

Yield: 76%; IR (KBr): $\nu_{max} = 3470$ (br), 2983, 2926, 2706, 2580, 2362, 1950, 1804, 1699, 1576, 1557, 1432, 1377, 1305, 1239, 1209, 1175, 1124, 1086, 977, 919, 897, 841, 787, 761, 670, 537, 509 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.40$ (s, 2H), 4.19 (s, 2H), 7.10–7.17 (m, 2H), 7.27–7.33 (m, 2H); 11.10 (br s, 1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 32.1$, 34.0, 128.5, 129.0, 134.2, 135.6, 176.6 ppm.

2-(2,6-Dichlorobenzylthio)-propanoic acid (**2h**; $C_{10}H_{10}Cl_2O_2S$)

Yield: 77%; IR (KBr): $\nu_{max} = 3443$ (br), 2977, 2930, 2726, 2632, 2554, 1697, 1580, 1560, 1438, 1419, 1379, 1324, 1292, 1244, 1194, 1121, 1073, 1001, 977, 925, 897, 826, 767, 681, 606, 516 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.51$ (d, $J = 7.2$ Hz, 3H), 3.65 (q, $J = 7.2$ Hz, 1H), 4.23 (s, 2H), 7.09–7.16 (m, 2H), 7.26–7.32 (m, 2H), 10.57 (br s, 1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 17.0$, 31.6, 42.0, 128.4, 128.9, 134.0, 135.7, 179.3 ppm.

3-(2,6-Dichlorobenzylthio)-propanoic acid (**2i**; $C_{10}H_{10}Cl_2O_2S$)

Yield: 75%; IR (KBr): $\nu_{max} = 3462$ (br), 3045, 2941, 2753, 2658, 1692, 1579, 1560, 1436, 1419, 1332, 1263, 1197, 1088, 987, 913, 893, 870, 782, 760, 684, 655, 489 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.79$ (m, 4H), 4.05 (s, 2H), 7.09–7.15 (m, 1H), 7.29–7.32 (m, 2H), 1060 (br s, 1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): 26.8, 31.5, 34.9, 128.5, 128.7, 135.0, 135.4, 178.1 ppm.

General procedure for the acylation of ferrocene

To a solution of 1.2 mmol of the corresponding carboxylic acid in 20 cm^3 of the appropriate solvent placed in a two-necked round bottom flask supplied with a magnetic stirrer and a reflux condenser, 0.1 cm^3 ($\sim$1 mmol) PCl_3 were added under an argon atmosphere and the resulting mixture was stirred overnight. 186 mg of ferrocene (1 mmol) and 200 mg of $AlCl_3$ were added, and the mixture was stirred for 3 h under cooling in an ice-water bath, at room temperature, under reflux, or at 80°C (cf. Results and Discussion). Subsequently, the reaction mixture was poured into 40 cm^3 of a cold solution of KOH (1 mol/dm^3) in order to remove the remaining carboxylic acid as well as aluminum and phosphorus species. The organic layer was separated, and the aqueous phase was extracted with 30 cm^3 of diethyl ether. The organic layers were collected and washed with H_2O, brine, and again H_2O and dried over anhydrous Na_2SO_4. After evaporation of the solvents, the crude reaction mixture was separated by column chromatography (SiO_2/toluene, then toluene: ethyl acetate = 9:1). In all experiments, the toluene fractions contained unchanged ferrocene, whereas the second fractions contained the acylated products **3a–i**. When nitrobenzene and 2,6-dichlorobenzene were used as solvents, they were removed from the reaction mixture prior to work-up by steam distillation.

1-Ferrocenyl-3-thiabutan-1-one (**3a**; $C_{13}H_{14}FeOS$)

Yield: 60%; IR (KBr): $\nu_{max} = 1635, 1450, 1410, 1370, 1290, 1170, 1105, 1070, 995, 820\,cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.17$ (s, 3H), 3.52 (s, 2H), 4.22 (s, 5H), 4.53 (t, $J = 1.6$ Hz, 2H), 4.79 (t, $J = 1.6$ Hz, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 16.1$, 40.2, 69.7, 69.9, 72.5, 77.2, 198.4 ppm.

1-Ferrocenyl-2-methyl-3-thiabutan-1-one (**3b**; $C_{14}H_{16}FeOS$)

Yield: 70%; IR (KBr): $\nu_{max} = 3080, 2940, 2915, 1650, 1450, 1375, 1255, 1200, 1110, 1050, 1025, 100, 825, 490\,cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.53$ (d, $J = 6.9$ Hz, 3H), 1.99 (s, 3H), 3.87 (q, $J = 6.9$ Hz, 1H), 4.20 (s, 5H), 4.49 (t, $J = 1.4$, 1H), 4.54 (t, $J = 1.4$, 1H), 4.73 (t, $J = 1.4$, 1H), 4.88 (t, $J = 1.4$, 1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 11.1, 15.2, 42.5, 69.2, 69.7, 70.1, 72.3, 77.3, 199.3$ ppm.

1-Ferrocenyl-4-thiapentan-1-one (**3c**; $C_{14}H_{16}FeOS$)

Yield: 66%; IR (KBr): $\nu_{max} = 1655, 1450, 1405, 1370, 1330, 1260, 1210, 1105, 1080, 1025, 1000, 890, 820\,cm^{-1}$; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.19$ (s, 3H), 2.86–3.02 (m, 4H), 4.23 (s, 5H), 4.52 (t, $J = 2.0$ Hz, 2H), 4.80 (t, $J = 2.0$ Hz, 2H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 16.0, 28.6, 38.4, 69.2, 69.8, 72.3, 78.6, 202.3$ ppm.

4-(4-Bromophenyl)-1-ferrocenyl-3-thiabutan-1-one (**3d**; $C_{19}H_{17}BrFeOS$)

Yield: 60%; IR (KBr): $\nu_{max} = 3094, 2921, 1730, 1657, 1590, 1486, 1452, 1406, 1377, 1289, 1105, 1069, 1030, 1009, 893, 826, 730\,cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 3.38$ (s, 2H), 3.74 (s, 2H), 4.19 (s, 5H), 4.53 (t, $J = 1.8$ Hz, 2H), 4.75 (t, $J = 1.8$ Hz, 2H), 7.24–7.28 (m, 2H), 7.43–7.46 (m, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 35.4, 36.4, 69.7, 69.9, 72.7, 77.3, 121.0, 131.0, 131.5, 136.5, 198.7$ ppm.

4-(4-Bromophenyl)-1-ferrocenyl-2-methyl-3-thiabutan-1-one (**3e**; $C_{20}H_{19}BrFeOS$)

Yield: 50%; IR (KBr): $\nu_{max} = 3096, 2972, 2925, 1728, 1659, 1589, 1486, 1450, 1406, 1376, 1320, 1257, 1195, 1104, 1069, 1052, 1009, 964, 879, 826, 778, 723\,cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.58$ (d, $J = 6.9$ Hz, 3H), 3.64 and 3.73 (AB system, $J_{AB} = 9.5$ Hz, 2H), 3.87 (q, $J = 6.9$ Hz, 1H), 4.18 (s, 5H), 4.50 (m, 1H), 4.56 (m, 1H), 4.64 (m, 1H), 4.83 (m, 1H), 7.17–7.20 (m, 2H), 7.41–7.44 (m, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 16.9, 33.1, 43.8, 69.4, 69.8, 70.0, 72.5, 77.1, 120.9, 130.8, 131.5, 136.7, 200.3$ ppm.

5-(4-Bromophenyl)-1-ferrocenyl-4-thiapentan-1-one (**3f**; $C_{20}H_{19}BrFeOS$)

Yield: 70%; IR (KBr): $\nu_{max} = 3093, 2922, 2853, 1732, 1665, 1590, 1486, 1454, 1406, 1379, 1343, 1258, 1209, 1105, 1075, 1030, 1008, 882, 826, 734, 698\,cm^{-1}$; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.83$ (m, 4H), 3.70 (s, 2H), 4.17 (s, 5H), 4.47 (t, $J = 1.9$ Hz, 2H 1.9 Hz, 2H), 4.71 (t, $J = 1.9$ Hz, 2H), 7.19–7.24 (m, 2H), 7.41–7.45 (m, 2H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.6, 36.1, 39.3, 69.0, 69.6, 72.1, 78.2, 120.6, 130.4, 131.4, 137.4, 201.7$ ppm.

4-(2,6-Dichlorophenyl)-1-ferrocenyl-3-thiabutan-1-one (**3g**; $C_{19}H_{16}Cl_2FeOS$)

Yield: 67%; IR (KBr): $\nu_{max} = 3092, 2926, 1737, 1661, 1580, 1562, 1514, 1440, 1413, 1377, 1347, 1289, 1220, 1153, 1126, 1109, 1088, 1067, 1028, 1001, 893, 824, 781, 761, 721, 689\,cm^{-1}$; ^1H NMR

(200 MHz, $CDCl_3$): $\delta = 3.77$ (s, 2H), 4.16 (s, 2H), 4.19 (s, 5H), 4.52 (s, 2H), 4.76 (s, 2H), 7.08–7.15 (m, 1H), 7.28–7.31 (m, 2H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 32.0$, 39.2, 69.5, 69.8, 72.5, 77.4, 128.3, 128.7, 134.5, 135.5, 198.6 ppm.

4-(2,6-Dichlorophenyl)-1-ferrocenyl-2-methyl-3-thiabutan-1-one (**3h**; $C_{20}H_{18}Cl_2FeOS$)

Yield: 51%; IR (KBr): $\nu_{max} = 3098$, 2972, 2925, 1786, 1655, 1579, 1559, 1438, 1376, 1321, 1256, 1213, 1192, 1156, 1104, 1053, 1001, 961, 887, 830, 782, 759, 721, 687, 527, 497, 460, 425 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.7$ (d, $J = 6.9$ Hz, 3H), 3.94 and 4.17 (AB system, $J_{AB} = 12.3$ Hz, 2H), 4.06 (q, $J = 6.8$ Hz, 1H), 4.15 (s, 5H), 4.46 (s, 1H), 4.51 (s, 1H), 4.66 (s, 1H), 4.78 (s, 1H), 7.06–7.13 (m, 1H), 7.25–7.29 (m, 2H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 17.5$, 29.5, 44.4, 69.2, 69.6, 72.3, 77.0, 128.3, 128.7, 134.0, 135.5, 200.2 ppm.

5-(2,6-Dichlorophenyl)-1-ferrocenyl-4-thiapentan-1-one (**3i**; $C_{20}H_{18}Cl_2FeOS$)

Yield: 83%; IR (KBr): $\nu_{max} = 3332$, 3089, 1733, 1667, 1580, 1561, 1454, 1436, 1413, 1379, 1340, 1256, 1213, 1159, 1107, 1083, 1029, 1001, 977, 877, 825, 781, 762, 695 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 3.01$ (s, 4H), 4.10 (s, 2H), 4.20 (s, 5H), 4.49 (s, 2H), 4.76 (s, 2H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 26.7$, 32.0, 39.9, 69.1, 59.7, 72.2, 78.4, 128.4, 128.5, 135.3, 202.0 ppm.

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