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Solvent-free reactions of *N*,*N*′-thiocarbonyldiimidazole with ferrocenylcarbinols

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This paper is dedicated to the late Prof. Christopher Imrie.

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ABSTRACT

The efficient and simple routes for the synthesis of various ferrocenyl derivatives from ferrocenylcarbinols and *N*,*N*′-thiocarbonyldiimidazole (TCDI) are described. It involves grinding the two substrates in a Pyrex tube with a glass rod at room temperature. The reaction of ferrocenylmethanol (**1a**) provided *S*,*S*-bis(ferrocenylmethyl)dithiocarbonate (**1b**), whose crystal structure and a plausible mechanism for its formation are also reported. The reaction of 1-ferrocenyl-1-phenylmethanol (**2a**) and 1-ferrocenylbutanol (**2b**) gave the products **2c** and **2d**, respectively. The reaction of ω-ferrocenyl alcohols 4-ferrocenylphenol (**3a**) and 6-ferrocenylhexan-1-ol (**3b**) yielded the products **3c** and **3d**, respectively. Reaction of 1,1′-ferrocenedimethanol (**3e**) afforded **3f** in moderate yield, and by contrast, it was not similar to **1b**. Reaction of [4-(trifluoromethyl)phenyl]methanol (**4a**) provided the thiocarbonate **4b** in good yield.

1. Introduction

Thiocarbonylimidazole derivatives of alcohols are useful intermediates in synthetic chemistry. For example, they are used in the Barton–McCombie deoxygenation of alcohols, a method which provides a source of alkyl radicals [1–7]. Thiocarbonylimidazolides have also found wide application in natural product synthesis since they are prepared from alcohol and *N*,*N*′-thiocarbonyldiimidazole (TCDI) under reaction conditions where a variety of functional groups can survive [2,3,5,7]. The classical method for the preparation of thiocarbonylimidazolides is by conventional solution chemistry [2–4]. However, this method has some disadvantages, requiring long reaction times, elevated temperatures, excess use of TCDI and the use of *N*,*N*-dimethylaminopyridine (DMAP) as an activator under an inert atmosphere in sealed tubes [4]. In this account we report on the results of our studies on the synthesis of ferrocenylimidazolides by the solvent-free approach, which surmounts most of the aforementioned difficulties.

2. Results and discussion

The ferrocenylcarbinols used in this study were obtained by the reduction of the corresponding ferrocenylketone or ferrocenylaldehydes with an ethereal solution of lithium aluminium hydride (LAH), with the exception of 4-ferrocenyphenol and 6-ferrocenylhexan-1-ol. 4-Ferrocenylphenol was prepared by the diazonium coupling reaction of ferrocene and 4-aminophenol as described by Zhao et al. [8], while 6-ferrocenylhexan-1-ol was synthesized from 6-ferrocenylhexanylbromide, which in turn was prepared by a literature method [9].

In our hands the reactions of the ferrocenylcarbinols (**1a, 2a, 2b, 3a, 3b and 3e**) and TCDI gave three types of products: ferrocenyldithiocarbonate (**1b**), ferrocenylimidazolides (**2c** and **2d**) and ferrocenylthiocarbonylimidazolides (**3c, 3d** and **3f**) (Scheme 1). The yields of these reactions both under solvent-free and in dichloromethane are shown in Table 1. The yields of entries **1b**, **3c**, **3d**, **3f** and **4d** obtained under solvent-free conditions were higher than those obtained in solvent. On the other hand, yields of entries **2c** and **2d** were slightly lower under solvent-free conditions compared those obtained under solvent conditions. The mixing of equimolar quantities of ferrocenylalcohol with TCDI provided in most cases a paste after a few minutes. An example of a reaction is that between ferrocenylmethanol and TCDI. On mixing the sample of TCDI with ferrocenylmethanol, a paste was formed and this gradually solidified with further grinding at room temperature to give the product.

The solvent-free synthesis of thiocarbonylimidazolides by the reaction of alcohols with TCDI has been reported by Hagiwara et al. [7]. In our work, the reaction of ferrocenylmethanol (**1a**) with TCDI did not form a similar product, but instead the dimeric

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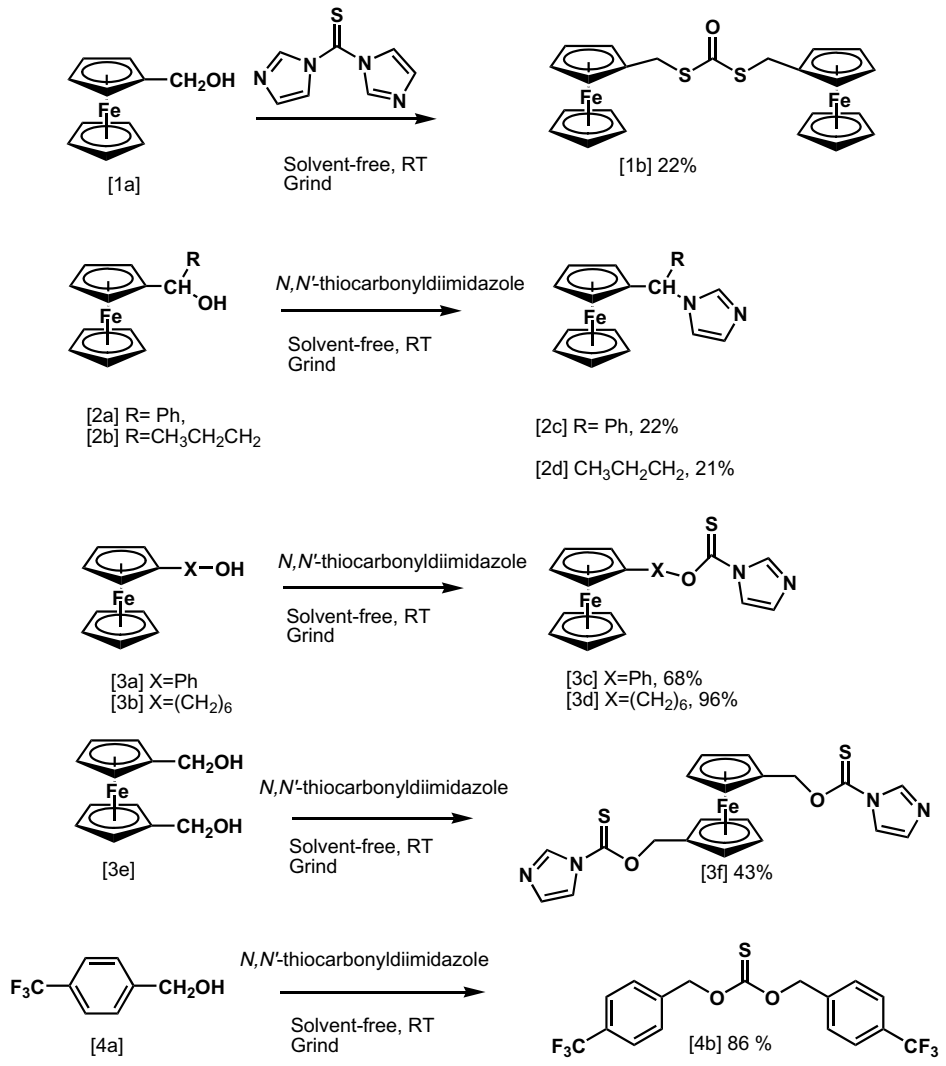


Scheme 1. Reactions of ferrocenylcarbinols with *N,N′*-thiocarbonyldiimidazole.

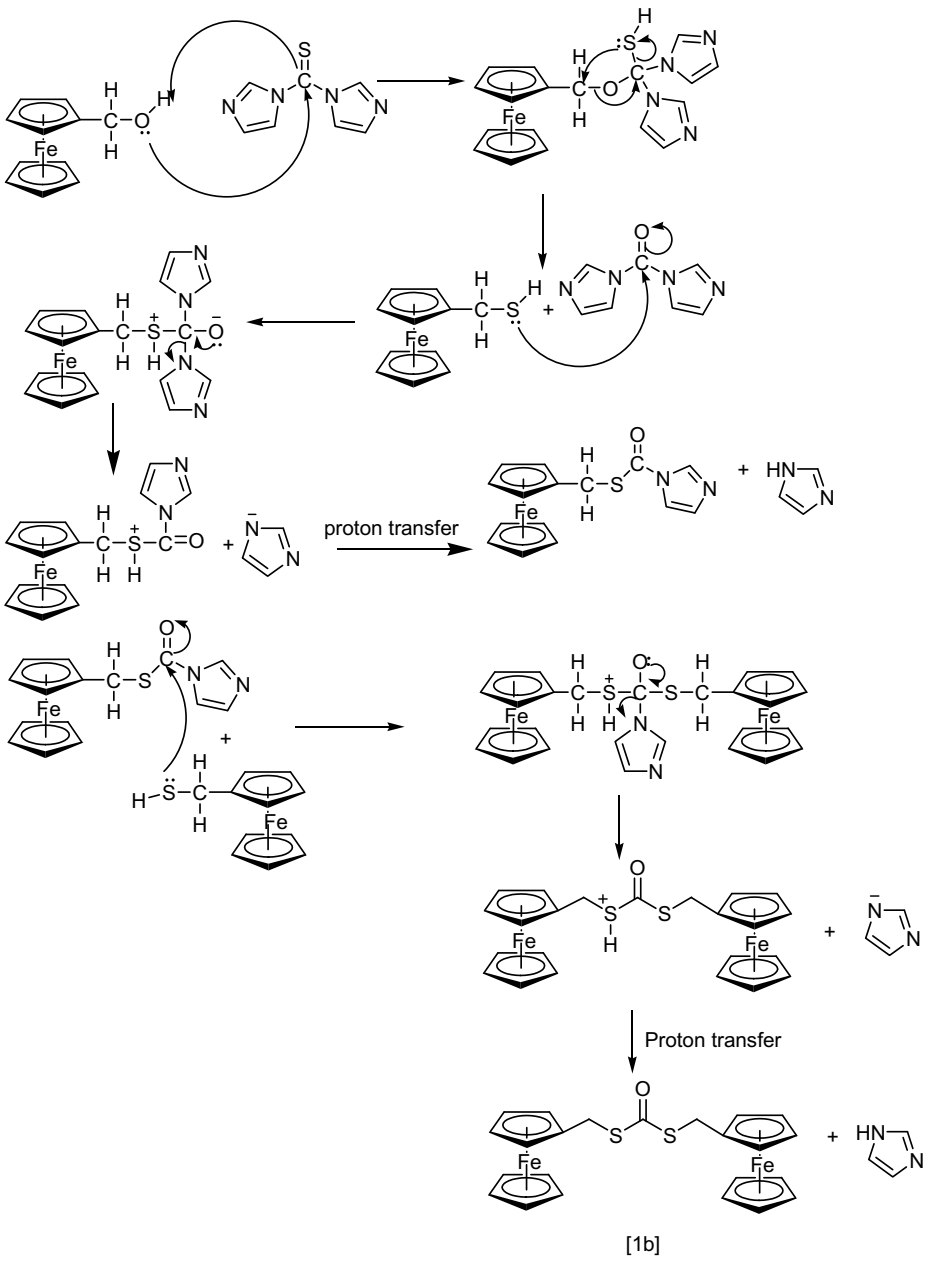
Table 1
Yields (%) of reactions of ferrocenylcarbinols with TCDI.

Entry	Solvent-free	Solvent (CH_2Cl_2)
1b	22	11
2c	21	23
2d	22	25
3c	68	60
3d	96	80
3f	43	38
4b	86	75

product *S,S*-bis(ferrocenylmethy)dithiocarbonate (**1b**) was isolated both in the solvent-free approach and in dichloromethane. This rearrangement product **1b** may be attributed to the fact that ferrocene is more aromatic than benzene. The thiocarbamate group Im-C=SO– at α-position to the ferrocene fragment is very labile and readily undergoes rearrangement. The structure of this compound was confirmed by IR, NMR, mass spectroscopy and X-ray diffraction analysis. The chemical shift of the carbon (SCOS) of the dithiocarbonate (**1b**) is 189 ppm, which is consistent with the chemical shifts that have been reported previously [11]. The IR spectrum displayed a sharp peak at 1635 cm^{-1}, corresponding to ν(C=O). A plausible mechanism for the formation of **1b** is given in Scheme 2.

The crystal structure of compound **1b** was obtained with single crystals grown from a mixture of dichloromethane and hexane. An ORTEP drawing of this molecule, with thermal ellipsoids drawn at 30% probability and showing the atomic numbering, is given in Fig. 1, while the packing diagram is shown in Fig. 2. Some selected bond lengths and bond angles are listed in Table 2. The parameters for crystal data collection and structure refinements are given in Table 3.

The molecule exhibits a plane of symmetry along the O1–C12 axis. The ferrocenyl rings have an eclipsed conformation with a 3.18° staggering angle. The cyclopentadienyl rings are coplanar with a dihedral angle of 0.44° between them, and the average Fe–C bond distance is 2.025(6) Å for the C1–C5 ring and 2.01(1) Å for the C6–C10 ring. The Fe atom is on average 1.65 Å from the ring centroids. As expected, the O1–C12 bond is a double bond at 1.25(1) Å, with the S1–C12 and S1–C11 bonds being single with distances of 1.739(6) and 1.824(8) Å, respectively. The larger than expected O1–C12–S1 bond angle (around a sp^2-hybridized carbon atom) of 126.6(3)° and smaller (than the expected 120°) S1–C12–S1a angle of 106.9(5)° illustrate the angular strain and interatomic repulsion in the S1–CO–S1a bridge between the two ferrocenyl moieties. The coplanarity of C11 with the C1–C5 ring is illustrated by the torsion angles C11–C1–C2–C3 [180.0(5)°] and C11–C1–C5–C4 [−179.2(6)°]. The C11–S1–C12–O1 torsion angle equals



Scheme 2. Plausible mechanism for the formation *S*,*S*-bis(ferrocenylmethyl)dithiocarbonate.

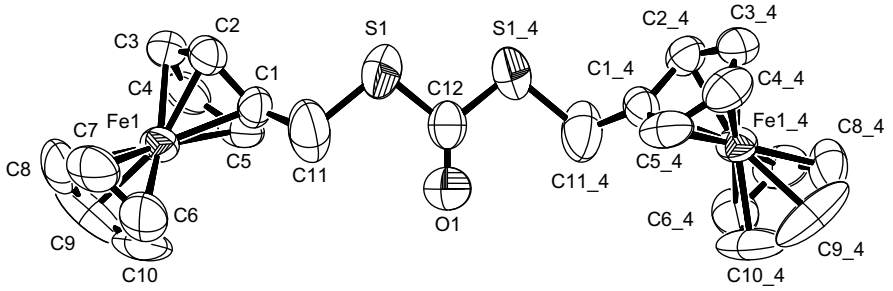


Fig. 1. An ORTEP view of the molecular structure of *S*,*S*-bis(ferrocenylmethyl)dithiocarbonate (**1b**). Hydrogen atoms were omitted for clarity.

−15.1(3)°. An intramolecular hydrogen bond of 2.989(8) Å exists between C11H11a and O1.

The reaction of the α-ferrocenylcarbinols, i.e. 1-ferrocenyl-1-phenylmethanol (**2a**) and 1-ferrocenylbutanol (**2b**) with TCDI under solvent-free conditions and in dichloromethane led to the formation of the ferrocenylimidazolides **2c** and **2d**, respectively in moderate yields. With ferrocenylmethanol this type of product was not obtained, nor did we isolate the kind of products reported

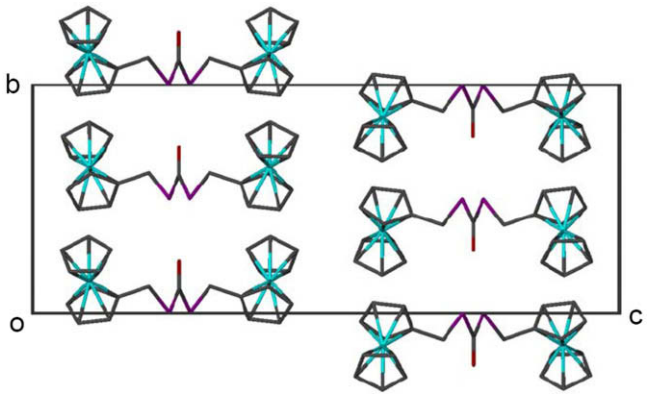


Fig. 2. Packing diagram for compound **1b** viewed along the *a* axis.

Table 2
Selected bond lengths (Å) and angles (°) of compound **1b**.

Fe–C1	2.016(5)	Fe–C2	2.028(5)
Fe–C6	2.02(1)	Fe–C7	2.012(7)
C12–O1	1.25(1)	S1–C11	1.824(8)
C1–C11	1.468(9)	S1–C12	1.739(6)
C1–C2	1.404(7)	C1–C5	1.429(9)
C6–C7	1.33(1)	C10–C9	1.41(2)
S1–C12–O1	126.6(3)	S1–C11–C1	110.7(5)
C11–S1–C12	102.1(3)	C1–C11	126.1(5)
S1–C12–S1a	109.0(5)	S1a–C12–O1	126.6(3)
C1–C2–C3	40.6(2)	C1–Fe–C6	108.7(3)
C1–Fe–C2	106.9(5)	C6–Fe–C7	38.6(4)

Table 3
Crystal data and structure refinement for compound **1b**.

Empirical formula	$C_{23}H_{22}Fe_2OS_2$
Formula weight	490.25
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pbcn*
Unit cell dimensions	
a (Å)	7.9002(2)
b (Å)	10.1930(3)
c (Å)	26.0104(8)
Volume (Å^3)	2094.53(10)
Z	4
Density (calculated) (mg/m^3)	1.555
Absorption coefficient (mm^{-1})	1.596
F(000) 1008	
Crystal size (mm^3)	0.12 × 0.08 × 0.04
Theta range for data collection (°)	4.02–25.41
Index ranges	$-9 \leqslant h \leqslant 9$ $-12 \leqslant k \leqslant 12$ $-31 \leqslant l \leqslant 31$
Reflections collected	36511
Independent reflections [$R_{(int)}$]	1920 [0.0976]
Completeness to theta (%)	99.1
Maximum and minimum transmission	0.9389 and 0.8316
Data/restraints/parameters	1920/0/128
Goodness-of-fit (GOF) on F^2	1.083
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0579$ $wR_2 = 0.0973$
R indices (all data)	$R_1 = 0.1149$ $wR_2 = 0.1168$
Largest difference peak and hole (e Å^{-3})	0.323 and −0.307

by Hagiwara et al. [7]. However, products of type **2** have been reported by Simenel et al., who synthesized the ferrocenylimidazolides in excellent yields by heating equimolar quantities of ferrocenylcarbinols and *N*,*N*′-carbonyldiimidazole (CDI) in anhydrous dichloromethane [10]. In our hands the reaction of 1-diphenyl-1-ferrocenylmethanol with TCDI did not form any products, and only the starting material was recovered.

The results above motivated us to investigate the ω-ferrocenylcarbinols, using 4-ferrocenylphenol (**3a**) and 6-ferrocenylhexan-1-ol (**3b**). The corresponding ferrocenylthiocarbonylimidazolides **3c** and **3d** were isolated in good yields, both under solvent-free conditions and in dichloromethane. A similar product was also formed when 1,1′-ferrocenedimethanol (**3e**) was reacted with TCDI to form **3f.** Surprisingly, 1,1′-ferrocenedimethanol did not form the dimeric product of type **1b.** This may be attributable to steric hindrance caused by the presence of the two methanol groups.

In order to synthesis organic compounds of the type **1b,** we investigated the use of benzylic alcohol as reagent. The reaction of [4-(trifluoromethyl)phenyl]methanol (**4a**) with TCDI led to the formation of *O*,*O*-bis[4-(trifluoromethyl)benzyl]thiocarbonate (**4b**) in excellent yield (Scheme 1). We therefore conclude that the formation of **1b** is influenced by the presence of α-ferrocene in the methylene alcohol. As the chain is lengthened, the influence of the ferrocenyl moiety on the alcohol became less pronounced and the formation of the thiocarbonylimidazolides **3c** and **3d** is favoured. This phenomenon was observed previously, when 2-ferrocenylethanol and 4-ferrocenylethanol were used to produce 2-ferrocenylethyl-1*H*-imidazole-1-carboxylate and 4-ferrocenylbutyl-1*H*-imidazole-1-carboxylate, respectively [10].

The IR spectra of **3c, 3d, 3f** and **4b** displayed sharp peaks in the range 1101–1116 cm^{-1}, corresponding to ν(C=S), which is in good agreement with the literature values [2,7]. The replacement of oxygen by sulfur shifts the IR peak from about 1750–1600 cm^{-1} to about 1100–1060 cm^{-1}. The chemical shift of the OCSO carbon of the thiocarbonate **4b** is 195 ppm and this is consistent with the values reported in the literature [11]. The chemical shifts of the (OCSN) carbons of **3c** and **3d** are 184 and 185 ppm, respectively. These values are also in good agreement with those reported in the literature [2,3]. The carbon chemical shift of (OCSN) for **3f** is 166 ppm, which falls outside the above ranges.

In summary, we have described the reactions of ferrocenylcarbinols with TCDI under both solvent-free conditions and in dichloromethane. It is worthy to note that various products were obtained in this study depending on the nature of groups in the vicinity of the alcohols. The simplicity, efficiency and milder conditions of the solvent-free operation makes it the synthetic method of choice for these reactions.

3. Experimental

Infra-red spectra were recorded on a DigiLab FTS 3100 Excalibur HE spectrophotometer as KBr disks (for solids) or NaCl neat films (for oils). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer as solutions in $CDCl_3$, or d_6-acetone using tetramethylsilane as an internal standard. Melting points were measured on an Electrothermal IA 900 series digital apparatus and are uncorrected. Mass spectra were recorded at the University of Witwatersrand in Johannesburg.

3.1. General synthetic procedure

The reaction of ferrocenylmethanol and TCDI as general example.

a. *Solvent-free conditions.* A mixture of ferrocenylmethanol (**1a**) (200 mg, 0.93 mmol) and TCDI (170 mg, 0.95 mmol) was ground together with a glass rod at room temperature in a Pyrex tube fitted with a glass joint. After grinding the substrates for a few

minutes (~5–10 min), a paste was formed, and in some cases it solidified after further grinding. The progress of the reaction was monitored by TLC, and in most cases it was complete within an hour. However, some reactions took longer (~3 h) before maximum conversion was obtained. After grinding for 3 h, the resulting residue was dissolved in dichloromethane. The reaction mixture was then purified by column chromatography using silica gel. Elution with hexane/ether (1:1) and removal of the solvent and drying under *vacuo* provided the product *S,S*-bis(ferrocenylmethyl) dithiocarbonate.

b. *Solvent conditions*. Ferrocenylmethanol (**1a**) (200 mg, 0.93 mmol) and TCDI (170 mg, 0.95 mmol) were added to anhydrous dichloromethane (50 cm^3) and heated under reflux for 3 h under nitrogen. The reaction mixture was then concentrated and purified by column chromatography using silica gel. Elution with hexane/ether (1:1) and removal of the solvent and drying under *vacuo* provided the product *S,S*-bis(ferrocenylmethyl)dithiocarbonate.

3.1.1. Product with ferrocenyldithiocarbonate

*3.1.1.1. S,S-bis(ferrocenylmethyl)dithiocarbonate (**1b**).* Ferrocenylmethanol (**1a**) (200 mg, 0.93 mmol) and TCDI (170 mg, 0.95 mmol). The product was isolated as a yellow solid (51 mg, 22%), (26 mg, 11%*); m.p. 159–160 °C; IR (KBr, cm^{-1}): 3470, 3108, 2927, 2340, 2361, 1635, 1559, 1539,1104, 999, 879, 852, 864; ^{1}H NMR ($CDCl_3$): 4.21 (4H, t, *J* 2.1, 2 × C_5H_4), 4.18 (10H, s, 2 × C_5H_5), 4.14 (4H, t, *J* 1.8, 2 × C_5H_4), 4.07 (4H, s, 2 × C_2H_2); ^{13}C NMR ($CDCl_3$): 189.65, 83.88, 69.24, 69.15, 68.66, 31. 31; MS: *m*/*z* (EI) 490 (M^+, 38%). * represents yield obtained under solvent conditions.

3.1.2. Products with ferrocenyl (alkyl)imidazolides

*3.1.2.1. 1-(1-Ferrocenylbutyl)-1H-imidazole (**2c**).* 1-Ferrocenylbutan-1-ol (**2b**) (340 mg, 1.30 mmol) and TCDI (278 mg, 1.56 mmol). The product was isolated as a yellow oil (100 mg, 21%), (110 mg, 23%*); IR (NaCl, cm^{-1}): 3470, 3108, 2927, 2340, 2361, 1635, 1559, 1539, 1104, 999, 879, 852, 864; ^{1}H NMR ($CDCl_3$): 7.61 (1H, s, ArH), 7.09 (1H, s, ArH), 6.97(1H, s, ArH), 4.94 (1H, t, *J* 6, CH), 4.21 (2H, t, *J* 2.1, C_5H_4), 4.18 (5H, s, C_5H_5), 4.14 (2H, t, *J* 1.8, C_5H_4), 2.06 (2H, m, CH_2), 1.20 (2H, m, CH_2), 0.95 (3H, t, *J* 7.2, CH_3); ^{13}C NMR ($CDCl_3$): 136.76, 129.32, 117.74, 89.88, 68.26, 68.78, 67.30, 57.98, 38.88, 20.00, 14.03; MS: *m*/*z* (EI) 308 (M^+, 100%).

*3.1.2.2. 1-[Ferrocenyl(phenyl)methyl]-1H-imidazole (**2d**).* 1-Ferrocenyl-1-phenylmethanol (**2a**) (200 mg, 6.50 mmol) and TCDI (170 mg, 7.80 mmol). The product was isolated as a yellow oil (51 mg, 22%), (58 mg, 25%*), IR (NaCl, cm^{-1}): 2929, 2856, 1544, 1423, 1225, 1108, 1073, 929. ^{1}H NMR ($CDCl_3$): 7.79 (1H, s, ArH), 7.38 (3H, m, ArH), 7.23 (2H, m, ArH), 7.20 (1H, s, ArH), 6.90 (1H, s, ArH), 4.00 (9H, m, 2 × C_5H_4); ^{13}C NMR ($CDCl_3$): 140.29, 137.15, 129.00, 128.70, 127.79, 119.49, 96.52, 87.08, 69.52, 69.28, 68.82; MS: *m*/*z* (EI) 342 (M^+, 100%).

3.1.3. Products with ferrocenylthiocarbonylimidazolides

*3.1.3.1. O-4-Ferrocenylphenyl-1H-imidazole-1-carbothioate (**3c**).* 4-Ferrocenylphenol (**3a**) (200 mg, 0.72 mmol) and TCDI (308 mg, 1.7 mmol). The product was isolated as a yellow solid (177 mg, 68%), (156 mg, 60%*) m.p. 128–129 °C; IR (KBr, cm^{-1}): 3154, 2925, 2856, 1637, 1518, 1404, 1403, 1325, 1293, 1238, 1212, 1158, 1040, 957, 885; ^{1}H NMR (d_6-acetone): 8.60 (1H, s, 1 × $C_3N_2H_3$), 7.90 (1H, s, $C_3N_2H_3$), 7.70 (2H, d, *J* 8.0 2 × ArH), 7.31 (2H, d, *J* 9.0, 2 × ArH), 7.12 (1H, s, $C_3N_2H_3$), 4.85 (2H, s, C_5H_4), 4.40 (2H, s, C_5H_4) 4.10 (5H, s, C_5H_5); ^{13}C NMR (d_6-acetone): 184.84, 151.54, 139.26, 137.63, 131.50, 127.42, 122.25, 119.173, 84.37, 69.914, 69.58, 66.95; MS: *m*/*z* (EI) 388 (M^+, 100%).

*3.1.3.2. O-(6-Ferrocenylhexyl)-1H-imidazole-1-carbothioate (**3d**).* 6-Ferrocenylhexan-1-ol (**3b**) (310 mg, 1.10 mmol) and *N,N′*-thiocarbonyldiimidazole (360 mg, 1.30 mmol). The product was isolated as a yellow oil (410 mg, 96%), (341 mg, 80%*); IR (NaCl, cm^{-1}): 3092, 2931, 2855, 1762, 1709, 1530, 1461, 1385, 1329, 1286, 1232, 1105, 1040, 986, 891, 820; ^{1}H NMR ($CDCl_3$): 8.37 (1H, s, ArH) 7.67(1H, s, ArH), 7.08 (1H, s, ArH), 4.66 (2H, t, *J*, 6.57 C_2H_2), 4.12 (5H, s, C_5H_5), 4.08 (4H, 2 × C_5H_4), 2.34 (2H, t, *J* 7.1, CH_2), 1.91 (2H, q, *J* CH_2) 1.46 (6H, m, 3 × CH_2); ^{13}C NMR ($CDCl_3$): 185.58, 139.12, 131.54, 120.08, 89.46, 74.29, 68.87, 68.47, 67. 50, 31.45, 29.94, 29.48, 28.41, 26.24; MS: *m*/*z* (EI) 396 (M^+, 100%).

*3.1.3.3. O,O′-[1,1′-Ferrocenyl bis(methylene)] bis(1H-imidazole-1-carbothioate) (**3f**).* 1,1′-Ferrocenedimethanol (**3e**) (100 mg, 0.46 mmol) and TCDI (200 mg, 1.10 mmol). The product was isolated as a yellow solid (93 mg, 43%), (82 mg, 38%*); m.p. 123–125 °C; IR (KBr, cm^{-1}): 3097, 2924, 2854, 1694, 1527, 1474, 1403, 1362, 1293, 1217, 1101, 884, 668; ^{1}H NMR ($CDCl_3$): 8.29 (2H, s, $C_3N_2H_3$), 7.55 (2H, s, 2 × $C_3N_2H_3$), 7.17 (2H, s, 2 × $C_3N_2H_3$), 4.32 (4H, s, 2 × CH_2), 4.24 (4H, s, 2 × C_5H_4), 4.22 (4H, s, 2 × C_5H_4); ^{13}C NMR ($CDCl_3$); 166.32, 135.97, 131.45, 116.44, 83. 52, 70.19, 70.08, 31.39; MS: *m*/*z* (EI) 466 (M^+, 100%).

3.1.4. Benzylthiocarbonates

*3.1.4.1. O,O-Bis[(4-trifluoromethyl)benzyl]thiocarbonate (**4b**).* 4-(Trifluoromethyl)benzyl alcohol (**4a**) (200 mg, 0.93 mmol) and TCDI (170 mg, 0.95 mmol). The product was isolated as a white solid (220 mg, 86%), (192 mg, 75%*); m.p. 75–76 °C; IR (KBr, cm^{-1}): 2951, 2294, 1626,1422, 1391, 1336, 1266, 1251, 1165, 1116, 1069, 1019, 947, 866, 829; ^{1}H NMR ($CDCl_3$): 7.66 (4H, d, *J* 8.2, 4 × ArH), 7.50 (4H, d, J, 10.9, 4 × ArH), 5.57 (4H, s, 2 × CH_2); ^{13}C NMR ($CDCl_3$): 195.14, 138.73, 131.46, 128.77, 126.04, 122.50, 74.01; MS: *m*/*z* (EI) 394 (M^+, 100%).

3.2. X-ray crystallography

X-ray diffraction data for *S,S′*-bis(ferrocenylmethyl)dithiocarbonate (**1b**) were collected on a Bruker Smart 1K CCD diffractometer with graphite-monochromated Mo Kα radiation. The collection method involved ω-scan of width 0.3°. Data reduction was carried out by the program SAINT +, Version 6.02 [12]. Multiscan absorption corrections were made with the program SADABS [13]. The structure was solved by direct methods using SHELXS-97 [14]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculation based on F^2 using SHELXL-97 [14]. Hydrogen atoms were first located in the difference map, then positioned geometrically and allowed to ride on their respective parent atoms. The general purpose crystallographic tool PLATON [15] was used for structure analysis, and ORTEP3 [16] was used for diagram generation.

Appendix A. Supplementary material

CCDC 697541 contains the supplementary crystallographic data for **1b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.10.023.

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