Knoevenagel condensation of ferrocenyl substituted carboxaldehydes with methylene active compounds on inorganic supports and the NLO properties of the resulting push–pull alkenes

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Abstract

We report a new method for the condensation of nonamethylferrocenecarboxaldehyde, 3-ferrocenylacrolein, 5-ferrocenylthiophene-2-carboxaldehyde and 5′-ferrocenyl-2,2′-bithienyl-5-carboxaldehyde inorganic supports, with methylene active compounds on the inorganic supports. In this way, conditions leading to very high yield (> 70%) of the product could be achieved. The effect of sonication during the synthesis of nonamethylferrocenecarboxaldehyde is reported and appears to be of great importance. We also report a new method for the synthesis of 3-ferrocenylacrolein. The second-order non-linear optical (NLO) properties of these ferrocenecarboxaldehyde condensation products are measured with the hyper-Rayleigh scattering (HRS) technique. The results of a similar study made for the condensation products of the above-mentioned aldehydes with malononitrile and indan-1,3-indandione are also given. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocenecarboxaldehydes; Knoevenagel condensation; NLO properties; Hyper-Rayleigh scattering

1. Introduction

Inorganic supports have found a wide use in organic synthesis because they allow many reactions to be carried out under very mild conditions (room temperature), either with only a small amount or without any solvent [1–5] and with very simple product isolation. The most frequently used inorganic supports are Al_2O_3, KF/Al_2O_3, SiO_2 and bentonite. Knoevenagel condensation of aldehydes and ketones with methylcyanoacetate on Al_2O_3 was described some time ago [6], just as the condensation of some *o*-benzyloxybenzaldehydes leading to benzofuran derivatives and the condensation of phthalides with azines leading to isoquinoline derivatives on MX/Al_2O_3 [7]. Reactions of malononitrile with

some 1,1-dioxothio-4-pyranones on Al_2O_3 are reported in the literature [8], but as far as we know, no condensations have been reported before for which SiO_2 is used as the support. Until recently, the inorganic support was used very seldom for reactions of ferrocenecarboxaldehyde (Fc–CHO) [9,10]. Condensation of Fc–CHO with *N*-methylrhodanine on KF/Al_2O_3 in a microwave oven was recently described by Villemin et al. [11] and we have reported [12] the condensation of ferrocenecarboxaldehyde (**I**) with the following methylene active compounds: 1,3-indandione, malononitrile, barbituric acid, thiohydantoine, 3-ethylrhodanine, and 3-aminorhodanine. In this condensation reaction, we tested Al_2O_3, KF/Al_2O_3, KOH/Al_2O_3, SiO_2, and KOH/SiO_2 as inorganic supports (Scheme 1).
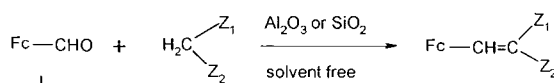
Scheme 1.

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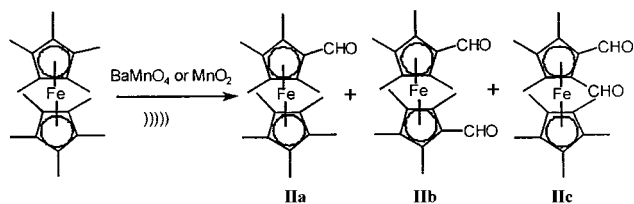
Scheme 2.

Second-order non-linear optical (NLO) properties of ferrocene derivatives were first mentioned by M.L. Green [13]. He found that in 1-ferrocenyl-2-(4-nitro-phenyl)ethene, the *E*-isomer has more enhanced NLO properties than the *Z*-isomer. Since then, a whole range of ferrocene derivatives were examined for their NLO properties. The exploration of NLO properties of different 1-aryl-2-(2-methylferrocenyl)ethenes, having electron-acceptor groups on the aryl moiety, for example, were thoroughly studied by Bunting et al. [14]. Torgi and his co-workers examined the NLO properties of enantiomerically pure 1-(2-vinylferrocenyl)-2-(4-nitro-phenyl)ethene [15]. The 4-nitrophenyl group on the double bond was exchanged either for 4-cyanophenyl- [16], 4-trimethylammoniophenyl- [17] or for 4-pyridyl- or 4-methylpyridinium- groups [16,18] and such stilbene analogs showed very good NLO properties. The first hyperpolarizability β, of 1-ferrocenyl-2-(4-pyridyl)-ethene was enhanced when an electron-acceptor fragment $M(CO)_5$ (M = Cr, Mo, W) was attached to the pyridine nitrogen [19]. The search for new ferrocene derivatives was expanded to the condensation products of ferrocenecarboxaldehyde and 3-ferrocenylacrolein with different methylene active compounds [20–23]. Good NLO properties were described for ferrocene derivatives having inserted *p*-phenylene groups between the ferrocene and double bond, like 1-(4-ferro-cenylphenyl)-2-(4-nitrophenyl)ethene [23]. Even larger hyperpolarizabilities were found for compounds having either 5-(tricyanovinyl)-2-furyl- or 5-(tricyanovinyl)-2-thienyl groups attached to the ferrocenylvinylidene group [24]. Interesting NLO properties were described for different Schiff bases (aldimines) prepared from ferrocenecarboxaldehyde and different aminoarenes [25,26] or 4-ferrocenylazabenzenes [27]. Perepichka described new push–pull ferrocenylethenes having the polynitrofluorenyl group as an acceptor leading to large second-order hyperpolarizabilities [28]. Herrmann et al. combined ferrocene and azulene moieties in NLO materials [29]. Very recently, an important study of the electronic structure of metallocene-based second-order non-linear optical dyes was published by Marder et al. [30]. As metallocenes, they used ferrocene, octamethyl-ferrocene, pentamethylferrocene and ruthenocene as well as osmocene and 4-nitrophenyl-1-methylpyri-dinium-4-yl and different heterocyclic structures were

used as acceptors. Good NLO properties were also found in $(\eta^5$-cyclopentadienyl)-$(\eta^6$-benzene)iron$(+)$ derivatives, where the organometallic moiety acts as the acceptor group [31]. Two interesting reviews on organometallic NLO materials were published very recently [32,33].The main aim of this work is to examine the synthesis of some structures with potentially good NLO properties based on the condensation products of ferrocenecarboxaldehyde, nonamethylferrocenecarbox-aldehyde and 3-ferrocenylacrolein with methylene active compounds and to extend this synthesis to the condensation products of 5-ferrocenylthiophene-2-car-boxaldehyde and 5′-ferrocenyl-2,2′-bithienyl-5-carbox-aldehyde with the chosen methylene active compounds. A further aim is to use a solvent-free condensation method on inorganic carriers.

2. Results and discussion

To set off the condensation reactions, it is necessary to prepare the starting ferrocene derivatives. De-camethylferrocene is prepared from pentamethylcy-clopentadiene [33], according to the procedure described in [34]. The synthesis of nonamethylfer-rocenecarboxaldehyde (**IIa**) is described elsewhere [35]. Nonamethylferrocenecarboxaldehyde is reportedly iso-lated in 59% yield by the oxidation of decamethylfer-rocene with $BaMnO_4$. Octamethylferrocene-1,1′-dicarboxaldehyde (**IIb**) is reported as a side product in 9% yield. This oxidation takes place in 5–6 h at 50 °C. We have repeated this procedure several times, but could not achieve the same yields and therefore we examined the effect of ultrasound on this reaction. The reaction is found to be much faster and after only 30 min of sonication, 56% of the monoaldehyde **IIa** and 7% of the mixture of dialdehydes **IIb** and **IIc** can be isolated. Prolongation of the reaction time to 60 min results only in a minor improvement (63% of monoaldehyde **IIa** and 9% of the mixture of dialde-hydes **IIb** and **IIc**). We decided, later on, to exchange the expensive $BaMnO_4$ for the much cheaper MnO_2. Sonication of decamethylferrocene for a short period (30 min) with five molar excess of MnO_2 in dry benzene results in 36% nonamethylferrocenecarboxaldehyde (**IIa**) and 7% of the mixture octamethylferrocene-1,1′-dicarboxaldehyde (**IIb**) and octamethyl-1,2-dicarbox-aldehyde (**IIc**) (Scheme 2).

Several methods are described for the synthesis of 3-ferrocenyl-acrolein (**IIIa**) [36–40], but all of them are several-step syntheses and the yields are just around 50%. Therefore, we prepare **IIIa** via a one pot reaction, namely, the metallation of ferrocene by *t*-butyllithium [41] and subsequent quenching of the intermediate by *N,N*-dimethylacrylamide. Using this method, we achieve 63% yield of **IIIa** and 16% of 1,1′-(3-ferro-

cenylene)diacrolein (**IIIb**), calculated on non-recovered ferrocene (Scheme 3). Our attempts for a Vielsmayer–Haack reaction with 3-(*N,N*-dimethylamino)acrolein are unsuccessful in spite of the fact that synthesis of 3-(4-dimethylaminophenyl)acrolein by this method is described in literature [42].

5′-Ferrocenyl-2,2′-bithienyl-5-carboxaldehyde (**IV**) is prepared analogously as is described for 5-ferrocenyl-thiophene-2-carboxaldehyde (**V**) [43] (Scheme 4).

All condensations are carried out at solvent-free conditions just by adsorption of the reagents on the inorganic support. Brockmann II grade alumina or silica gel is used as the solid support at a ratio of 1 g of support to 0.5 mmol of the appropriate carboxaldehyde. The structure of all starting ferrocene carboxaldehydes as well as the reaction products are given in Chart 1.

From the results given in Table 1, it is possible to see that nonamethylferrocenecarboxaldehyde (**IIa**) is much less reactive than 3-ferrocenylacrolein (**IIIa**), which is probably caused by the lowering of the reactivity of the carbonyl group by the electron-donating effect of the nine methyl groups. No reaction of **IIa** with 3-ethyl rhodanine or thiohydantoine is observed, which is caused by the cumulative steric hindrance of the aldehyde and the substrate.

Both 3-ethylrhodanine and thiohydantoic acid are used in the reaction with **IIIa**, but the latter gives poor yields on alumina at room temperature. Raising the reaction temperature to 60–70 °C results in considerably higher yields of the product. It is interesting to note that reactions on silica gel proceeded, in some cases, better than on alumina. We assume that this is caused by the inherent acidity of silica gel, and therefore it can act as a catalyst for the activation of the aldehyde groups.

We decided to perform condensation of 5-ferrocenylthiophene-2-carboxaldehyde (**V**) and 5′-ferrocenyl-2,2′-bithienyl-5-carboxaldehyde (**IV**) just with malononitrile and indan-1,3-dione. Reactions on alumina as well as on SiO_2 proceed smoothly and high yields of the products are isolated.

We begin the study of the NLO properties of our derivatives with the condensates of ferrocenecarboxaldehyde with eight different methylene active compounds. The synthesis of most of them is published in our previous paper [12]. Only a condensation with thiobarbituric acid and 2-methylbenzoimidazole had to be performed.

The NLO properties are determined by the hyper-Rayleigh scattering (HRS) technique using a fundamental wavelength of 1064 nm. Acetone and chloroform are used as solvents. Acetone is the solvent of choice because some of the ferrocene derivatives proved to be unstable on prolonged stay in chloroform, especially if they are not properly protected from light. The UV–vis spectral data exhibit two charge-transfer bands in the visible region. In agreement with previous works and theoretical treatment, we assign the lower energy band to a donor–acceptor charge-transfer transition (DA-CT) and the higher to an inter-ligand $\pi-\pi^*$ transition (LL-CT) [44]. The static hyperpolarizability, β_0, is calculated using the two-level model reported by Oudar and Chemla [45–47]. We are aware of the shortcomings of this model with regard to its applicability to ferrocene-substituted molecules, but chose to use it anyway, because possible alternatives [48,49] are much more difficult to apply. The results are given in Table 2.

In several cases, it is not possible to determine the hyperpolarizability, β, because the HRS signal is too low to detect (LE, lower estimate in Table 2). From the given results, the most promising materials are condensates of ferrocenecarboxaldehyde with malononitrile,
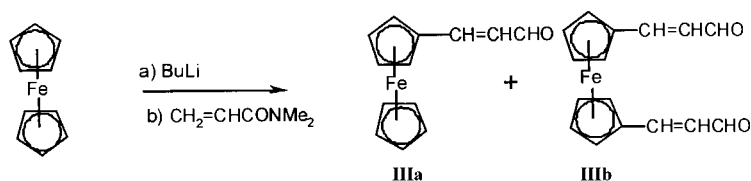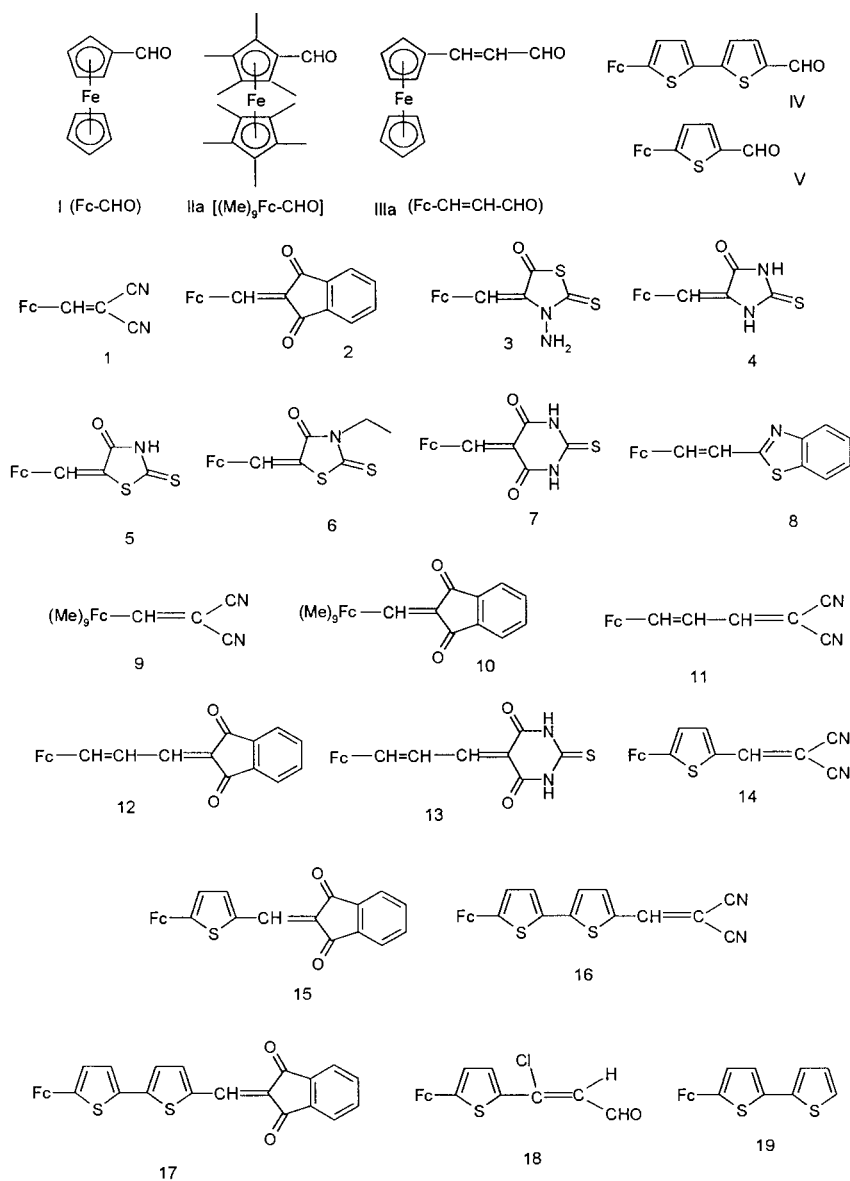

Scheme 3.
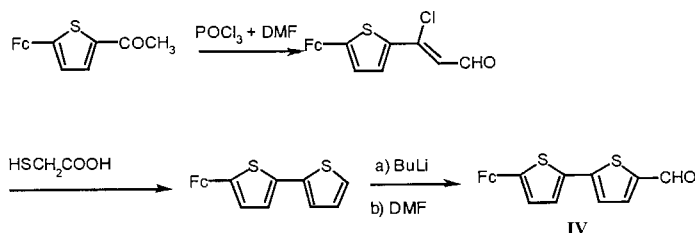
Scheme 4.

Chart 1.

indan-1,3-dione, 2-thiobarbituric acid and 2-methylbenzothiazole. We decided to further investigate the hyperpolarizabilities of the condensation products with malononitrile and indan-1,3-dione which allows us to compare the effects of different ferrocenyl substituted carboxaldehydes (a 'push' group). The results in Table 1 show that substitution of all hydrogen atoms with methyl groups in ferrocenecarboxaldehyde caused no remarkable increase in the NLO response. This is in contrast with the electron-donating effect of the methyl groups and can only be explained by their bulkiness, which hinders the coplanarity of the permethylated cyclopentadienyl ring with the C=C double bond. However, insertion of the C=C double bond between the ferrocenyl and carboxaldehyde group results in an increase of the observed β-values. Even greater effects are

observed when one or two thiophenyl moieties are inserted between the ferrocenyl and carboxaldehyde group. It should be noted that the octamethylferrocene/octamethylferrocenium redox couple provides for redox-based switching of the hyperpolarizability at modest potential [50].

From our results, it follows that most of our samples have higher first hyperpolarizabilities than metal–carbonyl complexes of 1-ferrocenyl-2-(4-pyridyl)ethenes [19] and much higher than 1-metallocenyl-2-(4-nitro-, respectively 4-cyanophenyl)ethenes described by Marder [51]. The β values of our compounds are close to the ones reported for bimetallic sesquifulvalene complexes [52]. Derivatives having two thiophene rings inserted between the ferrocene unit and the double bond have even higher β values than have been de-

Table 1
Results of the Knoevenagel condensations of ferrocenyl substituted carboxaldehydes with methylene active compounds

Carboxaldehyde	$CH_2Z^1Z^2$	Yield (%)/Time	
		Support Al_2O_3	Support SiO_2
IIa	Indan-1,3-dione	0/48 h	75/48 h
IIa	Malononitrile	96/24 h	94/36 h
IIa	Thiobarbituric acid	0/48 h	0/48 h
IIa	3-Ethylrhodanine	0/48 h	0/48 h
IIIa	Indan-1,3-dione	92/10 min	–
IIIa	Malononitrile	95/5 min	–
IIIa	Thiobarbituric acid	8/96 h [a]	68/24 h
IIIa	3-Ethylrhodanine	89/4 h	–
IV	Indan-1,3-dione	92/3 h	76/12 h
IV	Malononitrile	90/1 h	70/48 h
V	Indan-1,3-dione	87/24 h	73/48 h
V	Malononitrile	98/1 h	83/4 h

[a] 67/6 h at 60 °C.

scribed for 1-(4-diethylamino)-2-(5-(2,2-dicyanovinyl)-thienyl)ethenes [53].

3. Experimental

Pentamethylcyclopentadiene, decamethylferrocene, 5-ferrocenylthiophene and 5-ferrocenylthiophene-2-carboxaldehyde (**V**) and 2-acetyl-5-ferrocenylthiophene were prepared according to [33,34,43,54,43], respectively. All other reagents were used as purchased from Aldrich. Melting points (m.p.) were measured on a Koffler instrument. ^{1}H-NMR spectra were measured on a Varian GEMINI 2000, 300 MHz instrument with the solution in $CDCl_3$, if not indicated otherwise; Me_4Si was used as the internal standard. Sonochemical experiments were performed in an ultrasonic horn reactor UUA 001 ULTRAGEN (20 kHz, 300 W) that worked in a 50% cycle. The efficiency of sonication was characterized by the KI–KI_3 test [55]. Sonication of 50 cm^3 of KI (1 M) for 3 min gave 4.7×10^{-6} mol dm^{-3} of KI_3. All inorganic supports were activated in a microwave oven (2 min, 1000 W) just before the reaction.

The hyperpolarizabilities, β, of the compounds are measured by the HRS technique reported before [56,57]. All measurements are performed in $CHCl_3$ or acetone and the hyperpolarizability of p-nitroaniline (p-NA), known in both solvents, is used as an external reference ($\beta_{p\text{-}NA}$ $(CHCl_3) = 23 \times 10^{-30}$ esu and $\beta_{p\text{-}NA}$ (acetone) $= 25.9 \times 10^{-30}$ esu [58]. The fundamental light is generated with an injection seeded, Q-switched Nd:YAG laser (Quanta-Ray, GCR-5, 10 ns pulses, 10 Hz).

3.1. Oxidation of decamethylferrocene: (a) with BaMnO$_4$

Barium manganate (2.56 g, 10 mmol) was added to the solution of decamethylferrocene (0.65 g, 2 mmol) in 15 ml of dry benzene. The reaction mixture was then

Table 2
Comparison of linear and non-linear optical data of several condensates of different ferrocenyl substituted carboxaldehydes with methylene active compounds

Compound	λ_{max} (nm) (ε (M^{-1} cm^{-1}))				β (10^{-30} esu)			
	Acetone		Chloroform		Acetone		Chloroform	
	DA–CT	LL–CT	DA–CT	DA–CT				
1	525 (2900)	385 (16 200)	536 (2800)	330 (15 600)	–	–	90	0.5
2	565 (5100)	355 (23 300)	574 (5000)	362 (21 400)	–	–	224	26
3	537 (4300)	376 (25 100)	553 (5500)	383 (24 000)	–	–	–	
4	508 (2000)	366 (18 100)	523 (3000)	370 (18 200)	72	49	–	–
5	530 (7000)	374 (37 000)	542 (3200)	380 (15 100)			173	5
6	538 (5100)	377 (25 600)	545 (5200)	383 (24 000)	–	–	135	4
7	601 (2600)	416 (8600)	586 (5900)	378 (2700)	181	34		
8	480 (3400)	336 (26 300)	488 (2600)	340 (23 200)	65	10		
9	581 (3700)	359 (18 400)	582 (3400)	363 (16 000)	–	–	55	8
10	639 (6400)	410 (22 500)	650 (6200)	415 (24 000)	84	24		
11	558 (6300)	370 (26 900)	570 (6700)	379 (26 600)	140	10		
12	581 (10 000)	401 (32 400)	593 (10 700)	407 (30 200)	182	25		
13	602 (22 300)	418 (72 400)	636 (5500)	431 (16 000)	214	40		
14	555 (6500)	407 (24 300)	570 (7300)	411 (25 600)	217	14		
15	563 (9000)	426 (24 200)	582 (6800)	438 (17 300)	336	29	305	42
16	555 (10 800)	453 (23 500)	554 (13 400)	463 (26 300)	558	35		
17	568 (5600)	480 (18 000)	562 (22 000)	490 (30 900)	672	67		

sonicated for 30 min in the ultrasonic horn reactor. The solid material was filtered off and washed with dry benzene. Benzene was evaporated and the residue chromatographed on a silica gel column; an EtOAc–isohexane 1:3 mixture was used as the eluent. Some decamethylferrocene was recovered from the first band, nonamethylferrocenecarboxaldehyde (**IIa**) (0.38 g, 56%, subl. at 125 °C, dec. at 250–260 °C) was isolated from the second band and from the third band was isolated 0.04 g (6%) of a 10:1 mixture of octamethylferrocene-1,2-dicarboxaldehyde (**IIb**) and octamethylferrocene-1,1′-dicarboxaldehyde (**IIc**) (m.p. dec. > 360 °C). ^{1}H-NMR (CDCl$_3$, δ ppm) for **IIb**: 1.63 (s, 15H, 1′-CH$_3$); 1.85 (s, 6H, β-CH$_3$); 2.10 (s, 6H, α-CH$_3$); 10.29 (s, 2H, CHO). ^{1}H-NMR for **IIc**: 1.63 (s, 12H, β-CH$_3$); 1.98 (s, 12H, α-CH$_3$); 10.00 (s, 2H, CHO).

The sonication of the reaction mixture was prolonged to 60 min in the next experiment, but just minor improvement of the yields was observed (63% of **IIa** and 9% of the mixture of **IIb** and **IIc**).

3.2. Oxidation of decamethylferrocene: (b) with MnO$_2$

Oxidation was carried out as described above; just 0.43 g of MnO$_2$ was used as the oxidant. Chromatography afforded 56% of **IIa** and 7% of the mixture of **IIb** and **IIc**.

3.3. Synthesis of 3-ferrocenylacrolein (IIIa)

A solution of 10.74 mmol (2 g) of ferrocene in 30 ml of dry THF (under Ar atmosphere) was cooled down to −20 °C. A pentane solution of t-butyllithium (10 ml of 1.7 M sol.) was then added dropwise for 30 min to the stirred reaction mixture at the same temperature. The temperature was than raised to −10 °C and 21.5 mmol of 3-(dimethylamino)acrolein was then added dropwise to the reaction mixture. The reaction mixture was then stirred at room temperature (r.t.) for 30 min, and dilute (10%) HCl was added till the color of the reaction mixture did not change from orange to purple. The mixture was then poured onto crushed ice and the organic material was extracted into CH$_2$Cl$_2$. Extracts were washed with water, dried and the solvent was evaporated. Flash chromatography on a silica gel column using an EtOAc–isohexane 2:5 mixture as the eluent. Ferrocene (1 g, 52%) was eluted from the first band; 3-ferrocenylacrolein (**IIIa**) (1.63 g, 63% based on non-recovered ferrocene), purple crystals (m.p. 90–92 °C) were isolated from the second band; and 3-(1,1′-ferrocenylene)diacrolein (**IIIb**) (0.53 g, 17% based on non-recovered ferrocene), deep-purple crystals (m.p. 144–146 °C) were isolated from the third band. The melting points of **IIIa** and **IIIb** are in accord with [41].

3.4. Synthesis of 3-chloro-3-(5-ferrocenyl-thienyl)acrolein (18)

N,N-Dimethylformamide (22 ml) was cooled down to 0° C and phosphorus oxychloride (5.8 ml) was then added dropwise. The reaction mixture was stirred at 0° C for 30 min and the solution of 2-acetyl-5-ferrocenylthiophene (6.33 g, 20 mmol) in 10 ml of DMF was added at such a rate that the reaction temperature did not exceed 1 °C (the color of the reaction mixture changed from deep-red to dirty-green). The reaction mixture was stirred for 30 min at 0 °C and for 3 h at r.t., poured into 100 ml of a 20% solution of ice-cooled AcONa and stirred overnight. The product was extracted into CHCl$_3$, the chloroform solution was dried over anhydrous Na$_2$SO$_4$, the solvent was evaporated and the residue chromatographed on a silica gel column, using an isohexane–EtOAc 3:1 mixture as the eluent. Chromatography afforded 5.34 g (75%) of 3-chloro-3-(5-ferrocenylthienyl)acrolein (**18**) (red crystals, m.p. 97–101 °C). Anal. Found: C, 57.72; H, 3.81. Calc. for C$_{17}$H$_{13}$ClFeOS (MW 356.65): C, 57.25; H, 3.67%. ^{1}H-NMR (CDCl$_3$, δ ppm): 4.13 (s, 5H, C$_5$H$_5$); 4.14 (t, 2H, H$_\beta$); 4.64 (t, 2H, H$_\alpha$); 6.53 (d, 1H, [$^3J_{H-H}$ = 6.9 Hz], C=CH); 7.01 (d, 1H, [$^3J_{H-H}$ = 3.9 Hz], Th); 7.51 (d, 1H, [$^3J_{H-H}$ = 3.9 Hz], Th); 10.13 (d, 1H, [$^3J_{H-H}$ = 6.9 Hz], CHO).

3.5. Synthesis of 5′-ferrocenyl-2,2′-bithienyl (19)

Thioglycolic acid (2 g, 2.2 mmol) and Et$_3$N (2.2 g, 2.2 mmol) were added to the stirred solution of 3-chloro-3-(5-ferrocenylthienyl)acrolein (5.5 g, 1.6 mmol) in 25 ml of dry DMF cooled to 1 °C. The reaction mixture was stirred for 4 h at 80 °C. The mixture was then cooled to r.t. and poured into 40 ml of 20% aqueous solution of NaOH. The product was extracted into Et$_2$O and the solution was dried over anhydrous Na$_2$SO$_4$. The residue left after vacuum evaporation of the solvent was chromatographed on silica gel using an isohexane–EtOAc (3:1) mixture as the eluent. Chromatography afforded 5′-ferrocenyl-2,2′-bithienyl (**19**) (67 mg, 12%) as orange crystals (m.p.101–103 °C). Anal. Found: C, 62.1; H, 4.1. Calc. for C$_{18}$H$_{14}$FeS$_2$ (MW 350.3): C, 61.8; H, 4%. ^{1}H-NMR (CDCl$_3$, δ ppm): 4.13 (s, 5H, C$_5$H$_5$); 4.38 (s, 2H, H$_\beta$); 4.58 (s, 2H, H$_\alpha$); 6.90 (dd, 1H, α-Th);7.03 (m, 2H, Th); 7.17 (m, 2H, Th).

3.6. Synthesis of 5′-ferrocenyl-2,2′-bithienyl-5-carboxaldehyde (IV)

A stirred solution of 3-chloro-3-(5-ferrocenylthienyl)acrolein (0.66 g, 1.9 mmol) in 10 ml of dry THF was cooled to −65 °C, ‰ drops of TMEDA were then added followed by 1.25 ml (3.8 mmol) of 2.5 M hexane solution of t-BuLi. The reaction mixture was stirred at

-40 °C for 1.5 h and DMF (0.56 g, 7.6 mmol) was then added dropwise. The reaction mixture was allowed to warm to r.t. and then poured onto crushed ice. The product was extracted into Et_2O and the solution was dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was chromatographed on a silica gel column using an isohexane–EtOAc (3:1) mixture as the eluent. Chromatography afforded 5′-ferrocenyl-2,2′-bithienyl-5-carboxaldehyde (0.52 g, 76%) as red crystals (m.p.173–175 °C). Anal. Found: C, 60.45; H, 3.91. Calc. for $C_{19}H_{14}FeOS_2$ (MW 378.3): C, 60.4; H, 1.0%. ^{1}H-NMR (CDCl$_3$, δ ppm): 4.13 (s, 5H, C$_5$H$_5$); 4.35 (s, 2H, H$_\beta$); 4.61 (s, 2H, H$_\alpha$); 6.96 (d, 1H, [$^3J_{H-H} = 3.9$ Hz, Th]); 7.23 (m, 2H, Th); 7.67 (d, 1H, [$^3J_{H-H} = 3.9$ Hz, Th]); 9.87 (s, 1H, CHO).

3.7. Knoevenagel condensation of ferrocenyl substituted carboxaldehydes with methylene active compounds on inorganic supports

Reagents with an active methylene group (0.5 mmol) was dissolved in 0.5–1 cm^3 of dry CH_2Cl_2, or CHCl$_3$ was added to the inorganic support and the solvent was evaporated. The solution of 0.4 mmol of the appropriate carboxaldehyde in the minimal amount of CH_2Cl_2 was added to this solid material and the solvent was evaporated. The reaction mixture was left to stand at r.t. for the appropriate time. The course of the reaction was checked by TLC. When the reaction was over, the mixture (a powder) was transferred on a SiO$_2$ (100–160 μm) column, and the product was separated by chromatography using an isohexane–EtOAc (5:1–3:1) mixture as the eluent. The products were crystallized from an EtOAc–isohexane mixture. The results are given in Table 2.

3.7.1. 5-Ferrocenylmethylenethiobarbituric acid (7)
Dark green crystals, m.p. dec. > 260 °C. Anal. Found: C, 53.21; H, 4.01; N, 7.91. Calc. for $C_{15}H_{12}FeN_2O_2S$ (MW 340.8): C, 52.92; H, 3.59; N, 8.23%. ^{1}H-NMR (CDCl$_3$, δ ppm): 4.33 (s, 5H, Cp); 5.09 (t, 2H, H$_\beta$); 5.36 (t, 2H, H$_\alpha$); 8.48 (s, 1H, –CH=); 8.70 (bs, 1H, NH); 8.78 (bs, 1H, NH).

3.7.2. 1-Ferrocenyl-2-(2-benzothiazolyl)ethene (8)
Red crystals, m.p. 145–147 °C. Anal. Found: C, 66.07; H, 4.50; N, 4.10. Calc. for $C_{19}H_{15}FeNS$ (MW 345.2): C, 66.09; H, 4.92; N, 4.05%. ^{1}H-NMR (CDCl$_3$, δ ppm): 4.18 (s, 5H, Cp); 4.42 (t, 2H, H$_\beta$); 4.56 (t, 2H, H$_\alpha$); 7.00 (d, 1H, [$^3J_{H-H} = 16.2$ Hz], –CH=); 7.35 (d, 1H, [$^3J_{H-H} = 16.2$ Hz], –CH=); 7.42 (m, 2H, Ar H 5 and 6); 7.83 (d, 1H, [$^3J_{H-H} = 7.1$ Hz], Ar H 4); 7.95 (d, 1H, [$^3J_{H-H} = 7.1$ Hz], Ar H 7).

3.7.3. Nonamethylferrocenylmethylenemalondinitrile (9)
Deep-blue crystals, m.p. 165–168 °C. Anal. Found: C, 71.19; H, 7.24; N, 7.31. Calc. for $C_{23}H_{28}FeN_2$ (MW 388.34): C, 71.14; H, 7.27; N, 7.21%. ^{1}H-NMR (CDCl$_3$, δ ppm): 1.63 (s, 15H, CH$_3$ of C$_5$Me$_5$); 1.82 (s, 6H, β-CH$_3$); 1.90 (s, 6H, α-CH$_3$); 7.43 (s, 1H, –CH=).

3.7.4. 2-(Nonamethylferrocenylmethylene)indane-1,3-dione (10)
Violet crystals, m.p. 208–213 °C. Anal. Found: C, 74.25; H, 6.99. Calc. for $C_{29}H_{32}FeO_2$ (MW 468.4) : C, 74.36; H, 6.89%. ^{1}H-NMR (CDCl$_3$, δ ppm): 1.64 (s, 15H, CH$_3$ of C$_5$Me$_5$); 1.83 (s, 6H, β-CH$_3$); 1.86 (s, 6H, α-CH$_3$); 7.93 (dd, 1H$_4$ of indandione, [$J = 2$ Hz and 3 Hz]); 7.85 (dd, 1H, H$_7$ of indandione, [$J = 2$ Hz and 3 Hz)]; 7.84 (s,1H, CH=); 7.71 (dd, 2H, H$_{5,6}$ of indandione, [$J = 2$ Hz]).

3.7.5. 3-Ferrocenylpropenylidenemalondinitrile (11)
Deep-violet crystals, m.p. 157–159 °C. Anal. Found: C, 66.65; H, 4.21; N, 9.65. Calc. for $C_{16}H_{12}FeN_2$ (MW 288.13): C, 66.70; H, 4.20; N, 9.72%. ^{1}H-NMR (δ ppm): 4.22 (s, 5H, Cp); 4.63 (s, 2H, H$_\beta$); 4.76 (s, 2H, H$_\alpha$); 6.80 (d, 1H, [$^3J_{H-H} = 11.7$ Hz and 14.7 Hz], –CH=); 7.26 (d, 1H, [$^3J_{H-H} = 14.7$ Hz], =CH–); 7.44 (d, 1H, [$^3J_{H-H} = 11.7$ Hz], –CH=C(CN)$_2$).

3.7.6. 3-Ferrocenylpropenylideneindane-1,3-dione (12)
Dark-green crystals, m.p. 176.5–178.5 °C. Anal. Found: C, 66.65; H, 4.38. Calc. for $C_{22}H_{16}FeO_2$ (MW 288.13): C, 71.76; H, 4.40%. ^{1}H-NMR (δ ppm): 4.20 (s, 5H, Cp); 4.62 (dd, 2H, H$_\beta$); 4.70 (dd, 2H, H$_\alpha$); 7.33 (d, 1H, [$^3J_{H-H} = 15.3$ Hz], =CH–); 7.54 (d, 1H, [$^3J_{H-H} = 12$ Hz], –CH=); 7.75 (dd 2H, 4,7H of indandione); 7.95 (dd, 2H, 5,6H of indandione); 8.00 (d, 1H, [$^3J_{H-H} = 15.3$ Hz], –CH=).

3.7.7. 3-Ethyl-5-ferrocenylpropenylidenerhodanine (20)
Dark-blue crystals, m.p. 190–192 °C. Anal. Found: C, 56.31; H, 4.39; N, 3.51. Calc. for $C_{18}H_{17}FeNOS_2$ (MW 383.32): C, 56.40; H, 4.47; N, 3.65%. ^{1}H-NMR (δ ppm): 1.27 (t, 3H, CH$_3$); 4.15 (qv, 2H, CH$_2$); 4.17 (s, 5H, Cp); 4.51 (dd, 2H, H$_\beta$); 4.53 (dd, 2H, H$_\alpha$); 6.30 (dd, 1H, [$^3J_{H-H} = 12$ and 17 Hz], –CH=); 6.98 (d, 1H, [$^3J_{H-H} = 15$ Hz], =CH–); 7.30 (d, 1H, [$^3J_{H-H} = 11.4$ Hz], –CH=).

3.7.8. 5-Ferrocenylpropenylidenethiobarbituric acid (13)
Dark-green crystals, m.p. dec. > 310 °C. Anal. Found: C, 55.83; H, 3.91; N, 7.59. Calc. for $C_{17}H_{14}FeN_2O_2S$ (MW 366.22): C, 55.76; H, 3.85; N, 7.65%. ^{1}H-NMR (DMSO-d_6, δ ppm): 4.27 (s, 5H, Cp); 4.76 (dd, 2H, H$_\beta$); 4.80 (dd, 2H, H$_\alpha$); 7.79 (d, 1H, –CH=); 7.96 (m, 1H, =CH–); 7.98 (sd, 2H, –CH=); 12.16 (bs, 1H, NH); 12.21 (bs, 1H, NH).

3.7.9. 5-Ferrocenyl-2-(2,2-dicyanovinyl)thiophene (14)

Deep-red crystals, m.p. 173–175 °C. Anal. Found: C, 62.22; H, 3.63; N, 8.08. Calc. for $C_{18}H_{12}FeN_2S$ (MW 344.2): C, 62.81; H, 3.51; N, 8.14%. ^{1}H-NMR (δ ppm): 4.13 (s, 5H, Cp); 4.54 (t, 2H, H_β); 4.75 (t, 2H, H_α); 7.06 (d, 1H, [$^3J_{H-H} = 4.2$ Hz], Th); 7.55(d, 1H, [$^3J_{H-H} = 4.2$ Hz], Th); 7.18 (s, 1H, –CH=).

3.7.10. 2-[(5-Ferrocenylthien-2-yl)methylene]indan-1,3-dione (15)

Violet crystals, m.p. 171–175 °C. Anal. Found: C, 68.42; H, 3.87. Calc. for $C_{24}H_{16}FeO_2S$ (MW 424.3): C, 68.59; H, 3.84%. ^{1}H-NMR (δ ppm): 4.13 (s, 5H, Cp); 4.51 (t, 2H, H_β); 4.81 (t, 2H, H_α); 7.15 (s, 1H, –CH=); 7.76 (m, 3H, Ar); 7.93 (m, 3H, Ar).

3.7.11. 5′-Ferrocenyl-5-(2,2-dicyanovinyl)-2,2′-bithienyl (16)

Deep-purple crystals, m.p. dec. > 300 °C. Anal. Found: C, 61.91; H, 3.35; N, 6.54. Calc. for $C_{22}H_{14}FeN_2S_2$ (MW 426.3): C, 61.98; H, 3.31; N, 6.57%. ^{1}H-NMR (δ ppm): 4.12 (s, 5H, Cp); 4.38 (t, 2H, H_β); 4.62 (t, 2H, H_α); 6.98 (d, 1H, [$^3J_{H-H} = 4.2$ Hz], Th); 7.22 (d, 1H, [$^3J_{H-H} = 4.2$ Hz], Th); 7.60 (d, 1H, [$^3J_{H-H} = 4.2$ Hz], Th); 7.69 (s, 1H, –CH=).

3.7.12. 2-[(5′-Ferrocenyl-2,2′ bithien-5-yl)methylene]-indan-1,3-dione (17)

Purple crystals, m.p. dec. 240 °C. Anal. Found: C, 66.37; H, 3.59. Calc. for $C_{28}H_{18}FeO_2S_2$ (MW 506.4): C, 66.41; H, 3.58%. ^{1}H-NMR (δ ppm): 4.14 (s, 5H, Cp); 4.38 (t, 2H, H_β); 4.64 (t, 2H, H_α); 7.00 (s, 1H, –CH=); 7.01 (d, 1H, [$^3J_{H-H} = 4.2$ Hz], Th); 7.28 (d, 1H, [$^3J_{H-H} = 4.2$ Hz], Th); 7.33 (d, 1H, [$^3J_{H-H} = 4.2$ Hz], Th); 7.85 (d, 1H, [$^3J_{H-H} = 4.2$ Hz], Th); 7.80 (m, 2H, Ar); 7.95 (m, 2H, Ar).

Acknowledgements

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