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Further solvent-free reactions of ferrocenylaldehydes: Synthesis of 1,1′-ferrocenyldiimines and ferrocenylacrylonitriles

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Dedicated to the memory of my Mother, Kathleen Mary Imrie.

Abstract

Grinding of 1,1′-ferrocenedicarboxaldehyde with a 2.2 molar equivalent of an aromatic amine in a solvent-free environment provided excellent yields of 1,1′-ferrocenyldiimines. After mixing the aldehyde and amines, a gum or melt formed which eventually solidified to the product. An analytically pure sample of the product was obtained by cold recrystallization. Grinding of ferrocenecarboxaldehyde and 4-substituted phenylacetonitriles under solvent-free conditions provided good yields of the corresponding ferrocenylacrylonitriles. The yield in this reaction was very low when the substituent group *para* to the acetonitrile group was electron-donating.

Keywords: 1,1′-Ferrocenedicarboxaldehyde; Ferrocenylacrylonitrile compounds; 1,1′-Ferrocenyldiimines; Green chemistry; Solvent-free synthesis

1. Introduction

The solvent-free approach to the synthesis of molecules is an attractive one since the majority of solvents are either toxic or flammable and add considerably to the cost of an overall synthesis. In many instances, the solvent-free approach allows shorter reaction times, improved selectivities and easier separations and purifications than conventional solvents [1]. A monologue has recently appeared on the subject of solvent-free reactions and it provides an up-to-date account of the range of synthetic reactions that have been investigated under solvent-free conditions [2]. One of the current themes in our research is to study the solvent-free synthesis of organometallic molecules, especially ferrocenes and ruthenocenes since this field is relatively undeveloped. The ultimate aim is to use knowledge on simple organometallic molecules to gain an understanding on the molecular parameters required for reactivity in the room temperature grinding of reactants.

Ferrocenecarboxaldehyde (**1**) and acetylferrocene are two important precursors of ferrocene derivatives, and have been shown to be particularly amenable to reaction under solvent-free conditions [3]. For example, it was shown by Imrie et al. that **1** reacts with substituted anilines to provide excellent yields of ferrocenylmonoimines after just a few minutes of grinding [3a]. The reactions took place in most cases at room temperature and the products were isolated by cold recrystallization from a minimal quantity of methanol. This current paper describes our latest results on further reactions of **1** under solvent-free conditions. Furthermore, it reports the first results on the reactivity of 1,1′-ferrocenedicarboxaldehyde under solvent-free conditions.

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2. Results and discussion

2.1. Solvent-free synthesis of ferrocenylimines

Ferrocenylimines have been conventionally prepared by heating a solution of the ferrocenylaldehyde and aromatic amine in solvents such as methanol or ethanol [4]. This approach usually involves heating the reactants for a few hours under reflux; thermally sensitive ferrocenylimines can suffer a degree of decomposition during this time. During our initial study [3a], it became apparent that **1** was extremely reactive under solvent-free conditions. To investigate this further, we decided to look at its reactivity with anilines and amines containing two amino functional groups. The reactions with anilines are summarized in Scheme 1 and the results again demonstrate the reactivity of **1**. The molar ratio of the reactants, **1**:anilines was varied from 1:2, 1:1 and 2:1. In all cases, bisferrocenylimines **2** and **3** were isolated and the excess unreacted starting materials were recovered. The ratio 2:1 (aldehyde:aniline) had the best atom economy and provided excellent yields of the bisimines.

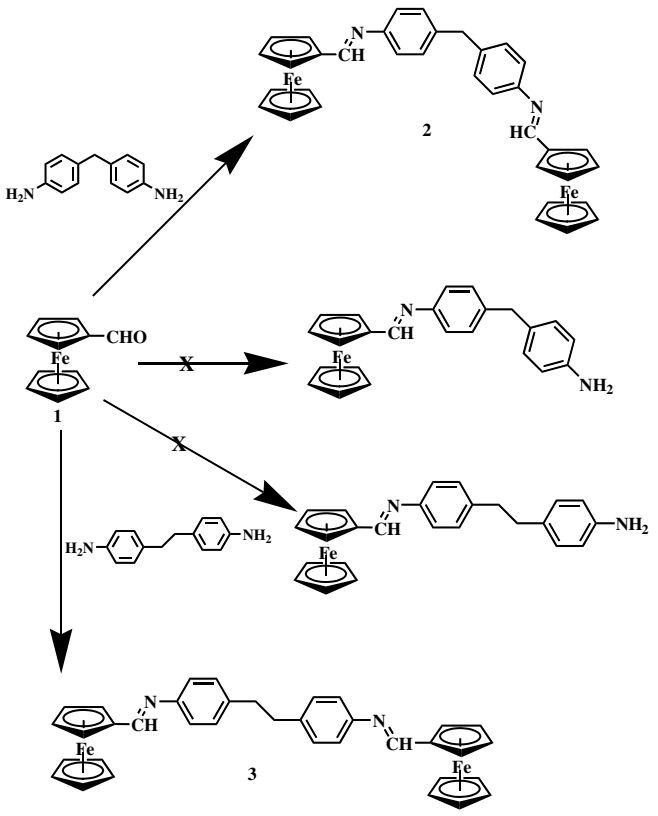
Compound **4** has been previously reported by Lee et al. [5] and was synthesized by the reaction of **1** with ethylenediamine in diethyl ether in the presence of either a drying agent, magnesium sulfate or catalyst, $RuCl_2(PPh_3)_2$. We have found that simple grinding of **1** with ethylenediamine provides **4** (Fig. 1) in quantitative yield in a few minutes. In contrast to the reactions described in Scheme 1, we found that it was necessary to use an excess of the diamine to achieve a high conversion.

Despite the fact that the first synthesis of 1,1′-ferrocenedicarboxaldehyde (**5**) (Scheme 2) was reported many years ago, the synthesis of simple 1,1′-ferrocenyldiimines (Scheme 2) and other derivatives has not been researched in-depth. This could be due in part to the fact that **5** is not commercially available and the difficulties experienced in its synthesis.

The starting materials used in the synthesis of 1,1′-ferrocenyldiimines were all commercially available apart from **5**. The synthesis of **5** according to the available literature methods [6] proved to be very inefficient, giving consistently isolated yields of less than 10% and involved a tedious work-up procedure. However, with the help of modifications communicated separately to us by Loubser and Kamounah [7], it was possible to modify the literature method to give consistently higher yields. Synthesis of 1,1′-ferrocenyldiimines **6**–**12** was achieved by simply mixing and grinding **5** with the aniline under solvent-free conditions in a 1:2.2 mole ratio (Scheme 2).

The reactions occurred readily. In some cases a gum formed and in others the mixture turned into a melt. Upon solidification, ^{13}C NMR was used to analyze the crude product and to gauge the extent of the reaction. This was easily followed by the disappearance of the carbonyl (C=O) resonance peak of **5** and the appearance of a strong resonance for the imine (C=N) functional group in the range 155.00–165.00 ppm. Minimal amounts of anhydrous methanol were used to recrystallize the products. The results are given in Table 1.

In general, under the equivalent solvent-free conditions, **5** was less reactive than **1**, justifying the slight excess of anilines that were used in these reactions. In a few cases, in order to improve the yield, the pyrex reaction tube was immersed in a constant temperature water bath at 50 °C. The reaction did not work very well in cases where the aniline contained an electron-withdrawing group such as nitro; this could be explained by the electrons being inductively pulled from the amino group causing the aniline to be less reactive in this type of reaction. The ^1H NMR spectrum for the 1,1′-ferrocenyldiimines showed a characteristic peak in the region of 8.40–8.20 ppm for the imine protons (CH=N). Its integration represented the two protons that are chemically equivalent.



Scheme 1. Solvent-free reactions of **1** with bis(amino) compounds that provide isolated products.

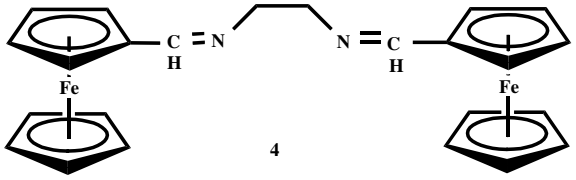
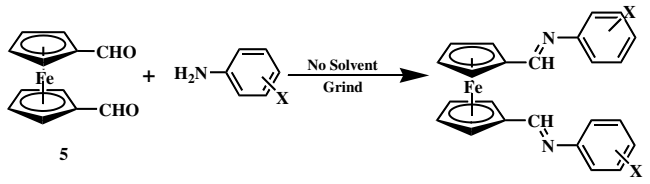


Fig. 1. Structure of *N*,*N*′-ethylenebis[(ferrocenylmethylidene)amine].



X= 4-OCH_3 (6), 4-CH_3 (7), 4-F (8), 4-Cl (9), 4-Br (10), 3,4,5-$(Cl)_3$ (11), 4-Fc (12)

Scheme 2. Synthesis of 1,1′-ferrocenyldiimines under solvent-free conditions.

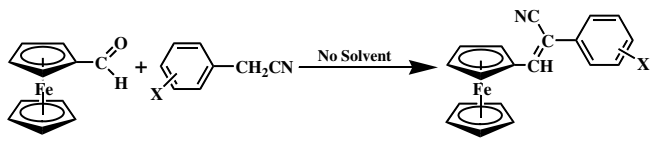
Table 1
Yields of 1,1′-ferrocenyldiimines from the reaction of 1,1′-ferrocenedicarboxaldehyde and substituted anilines under solvent-free conditions

Compound	Substituent X (Scheme 2)	Yield (%)[a,b]
6	4-OCH_3	98
7	4-CH_3	98
8	4-F	82
9	4-Cl	96
10	4-Br	95
11	3,4,5-$(Cl)_3$	74
12	4-Fc	91

[a] Yields are based on isolated products.
[b] Imines were isolated and characterized by IR, NMR (^1H, ^{13}C), high resolution mass spectroscopy and elemental analysis.

2.2. Solvent-free synthesis of ferrocenylacrylonitriles

Ferrocenecarboxaldehyde (**1**) is known to undergo Knoevenagel condensations under classical homogeneous conditions in ethanol with occasional necessary use of Schlenk techniques or Dean-Stark trap apparatus [8]. Use of inorganic supports such as aluminium oxide or silica gel under solvent-free conditions has also been investigated by Cooke et al. [9] and Stankovic et al. [10], respectively. In their work they used either Al_2O_3 or SiO_2 to catalyze the condensation of ferrocenecarboxaldehyde with active methylene compounds to provide good-to-excellent yields of the ferrocenylmethylene in the range of 58–100%. However, the reactions involved 2–5 h of stirring the mixture (solution or molten, depending on the active methylene compound) and in some cases heat was required to improve the efficiency. The extraction of the product from the inorganic support using dichloromethane also makes this approach less favourable in terms of its green chemistry credentials. Following a recent report by McClusky et al. on the Knoevenagel reaction [11], it was decided to attempt the synthesis of ferrocenylacrylonitriles by simply grinding **1** with phenylacetonitriles in the presence of a catalytic amount of piperidine (Scheme 3).



X= 4-OCH_3 (**13**), 4-Cl (**14**), 4-F (**15**), 4-CN (**16**), 4-CF_3 (**17**), 4-NO_2 (**18**)

Scheme 3. Solvent-free synthesis of ferrocenylacrylonitriles.

The starting compounds were thoroughly ground together and the resultant solids were allowed to dry in the open air before being analysed by IR, ^1H NMR and ^{13}C NMR spectrometry to determine the reaction progress. In most cases the reactions occurred readily and this was characterized by the formation of a dark purple melt. The reaction proved to be very favourable, especially when electron withdrawing-groups such as nitro and trifluoromethyl were attached to the *para* position of the phenylacetonitrile (see Table 2). In these cases, the reaction was observed to be instantaneous. The strong inductive effect of the electron-withdrawing group would contribute to the activation of the methylene group taking part in the reaction. In the case of an electron-donating group such as methoxy on the *para*-position of the phenylacetonitrile, the efficiency of the reaction dropped drastically. An attempt to change the reaction conditions in this instance, for example by heating, did not prove to be very successful.

2.3. Electronic spectroscopy of ferrocenylacrylonitriles

The UV–Vis spectra of selected ferrocenylacrylonitriles were recorded in acetonitrile (Fig. 2). Spectral comparisons were made with unsubstituted ferrocene. Ferrocene exhibits two major bands at 327 and 445 nm, which have been assigned to $^1A_{2g} \rightarrow {}^1E_{2g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$ ligand field d–d transitions [12].

In most cases, on substitution of the cyclopentadienyl ring of ferrocene with conjugated substituents, a shift to lower energy for the absorption would be anticipated. Increased mixing of ligand orbitals with metal d-orbitals is anticipated. There is a marked bathochromic shift of the longer wavelength absorption as a result of conjugation of the ferrocenyl group with a phenyl substituent. This is evident on comparative analysis on the λ_{max} of the unsubstituted ferrocene and those of ferrocenylacrylonitrile compounds. Compound **18** exhibits the largest bathochromic shift while **13** shows the smallest effect. The molar extinction coefficients were also determined and are listed in Table 3.

Table 2
Yields of ferrocenylacrylonitriles from the reactions of ferrocenecarboxaldehyde and substituted phenylacetonitriles under solvent-free conditions

Compound	Substituent X (Scheme 3)	Yield (%)[a,b]
13	4-OCH_3	6
14	4-Cl	89
15	4-F	91
16	4-CN	95
17	4-CF_3	93
18	4-NO_2	99

[a] Yields are based on isolated products.
[b] Ferrocenylacrylonitriles were characterized by IR, NMR (^1H, ^{13}C), high resolution mass spectroscopy and elemental analysis.

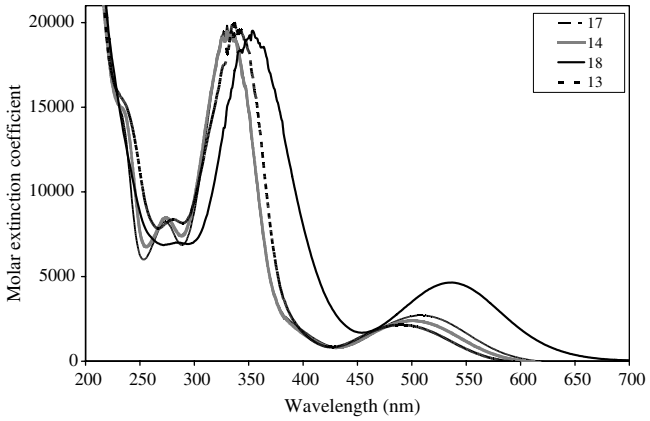


Fig. 2. UV–Vis spectra of ferrocenylacrylonitriles in acetonitrile.

Table 3
Wavelength maxima and extinction coefficients of ferrocenylacrylonitriles in acetonitrile

Compound	λ_{max}/nm (ε_{max}/mol^{-1} dm^3 cm^{-1})
Ferrocene	445 (97), 327 (57)
18	537 (4646), 353 (19541)
17	509 (2705), 330 (19852), 274 (8259)
14	501 (2380), 330 (19394), 274 (8443)
13	492 (2145), 337 (20018)

Ferrocenylacrylonitriles were also investigated for solvatochromic behaviour. Compounds that exhibit solvatochromic behaviour are known to exhibit NLO properties [13]. The UV–Vis spectrum of each compound was recorded in a range of solvents of differing polarity. The solvents used were chloroform, acetonitrile, toluene and dimethylformamide (DMF). Results are shown graphically in Fig. 3 for compound **18** in toluene and DMF. The comparative λ_{max} for each compound in all solvents are listed in Table 4.

cis-[1-Ferrocenyl-2-(4-nitrophenyl)ethylene] synthesized by Green et al. was one of the first examples of ferrocenyl derivatives that exhibited solvatochromic behaviour and was found to have second-order nonlinear optical properties [14]. Cooke et al. have also reported λ_{max} values of similar ferrocenyl derivatives. In their results toluene, dichloromethane and DMF were used as solvents for determining the solvatochromic behaviour [9]. In our results, compound **18** (Fig. 3) exhibited a significant bathochromic shift when the solvent was changed from toluene to DMF whereas compound **14** and **17** showed a hypsochromic shift (Table 4). This warrants further examination with regards to their NLO properties. 3-Ferrocenyl-2-(4-methoxyphenyl)acrylonitrile **13** did not show much behavioural difference in the different solvents.

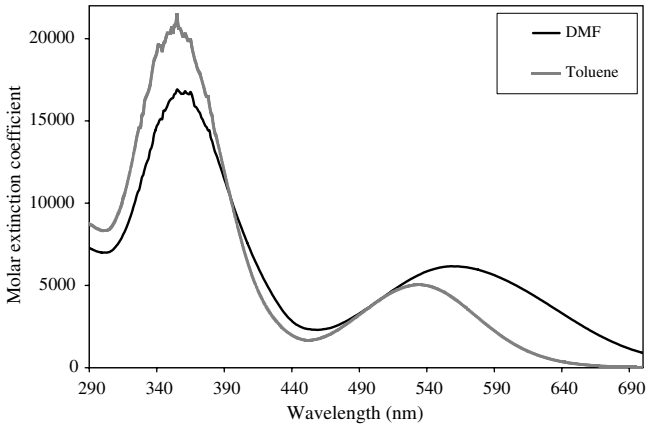


Fig. 3. Electronic spectra of compound **18** in toluene and DMF.

Table 4
Comparative λ_{max} values for ferrocenylacrylonitriles in different solvents

Compound	λ_{max} (nm)			
	Chloroform	Acetonitrile	Toluene	DMF
17	512	509	510	476
	337	330	330	335
14	502	501	501	469
	337	330	338	330
18	542	537	533	558
	359	353	355	355
13	498	492	491	482
	344	337	340	343

2.4. Cyclic voltammetry of ferrocenylacrylonitriles

The redox behaviour of selected ferrocenylacrylonitriles prepared in this study was evaluated using cyclic voltammetry. The observed redox behaviour of the respective complexes are all reported with regard to the reversible redox wave of unsubstituted ferrocene, which showed an $E_{1/2}$ at 429.5 mV under the given conditions in acetonitrile with tetrabutylammonium perchlorate (TBAP) as background electrolyte. The observed couples were all reversible, where reversibility in this case is taken to imply that the difference between anodic and cathodic peak potentials is less than 80 mV, as well as the peak current ratios (i_{pa}/i_{pc}) being approximately equal to unity (0.91–1.02). Derivatization of ferrocene gave a positive shift for all compounds studied, indicating that placing a substituent on the cyclopentadienyl ring of ferrocene made the ferrocene group harder to oxidise. The extent of shift, however, was dependant on the nature of the substituent. The *p*-nitro substituent on the phenyl ring (compound **18**) showed the most positive shift while the *p*-methoxy substituent on the phenyl ring (compound **13**) showed the least. Half-wave potentials of ferrocene and selected ferrocenylacrylonitriles are listed in Table 5 with corresponding anodic E_{pa} and cathodic E_{pc} peak potentials.

2.5. X-ray crystallography

The crystal and molecular structures of **16** and **17** were determined by single crystal X-ray crystallography. The ORTEP diagrams of the two molecules showing their num-

Table 5
Electrochemical data of ferrocene and ferrocenylacrylonitriles in acetonitrile

Compound	E_{pa} (mV)	E_{pc} (mV)	$E_{1/2}$ (mV)
Ferrocene	465	394	429.5
17	670	597	633.5
14	659	582	620.5
18	690	624	657
13	629	560	594.5

bering schemes are shown in Fig. 4. Selected bond lengths and angles for **16** and **17** are provided in Tables 6 and 7, respectively.

In compound **16**, the nitrile-ethylene and cyano-phenyl moieties are almost coplanar with the ferrocenyl C_p ring. The torsion angles of C(6)–C(10)–C(11)–C(12), C(10)–C(11)–C(12)–C(13) and C(13)–C(12)–C(14)–C(19) are −2.7(3)°, 2.3(3)° and −7.4(2)°, respectively. The ferrocenyl rings have an eclipsed conformation with a 1.9° staggering angle. The single C–C bond length C10–C11, 1.448(2) Å, is shorter than C12–C14, 1.488(2) Å. This difference in bond lengths is not observed in the comparable molecules 1-ferrocenyl-1-phenyl-2-(4-cyanophenyl)ethylene [15] and 2-ferrocenyl-1-(4-(trifluoromethyl)phenyl)propene [15], where the substituent on the ethylene group is not nitrile. A similar difference was observed in the molecule, 2,5-dicyano-3-diferrocenylhexa-2,4-dienedinitrile [16]. In contrast to **16**, molecules of compound **17** have the nitrile-ethylene and cyano-phenyl moieties twisted out of the plane of the ferrocenyl C_p ring. The torsion angles of C(9)–C(10)–C(11)–C(12), C(10)–C(11)–C(12)–C(13) and C(19)–C(14)–C(15)–C(16) are 32.9(4)°, 6.8(4)° and −2.5(4)°, respectively. The ferrocenyl rings are again eclipsed, with a 3.3° staggering angle. The single C–C bond lengths around the ethylene are similar to **16**: C10–C11, 1.438(3) Å and C12–C14, 1.474(3) Å. The only noteworthy intermolecular interactions is that between two fluorine atoms, F2′···F2′ related by a centre of inversion. However, since CF_3 is disordered, this distance may not really be significant.

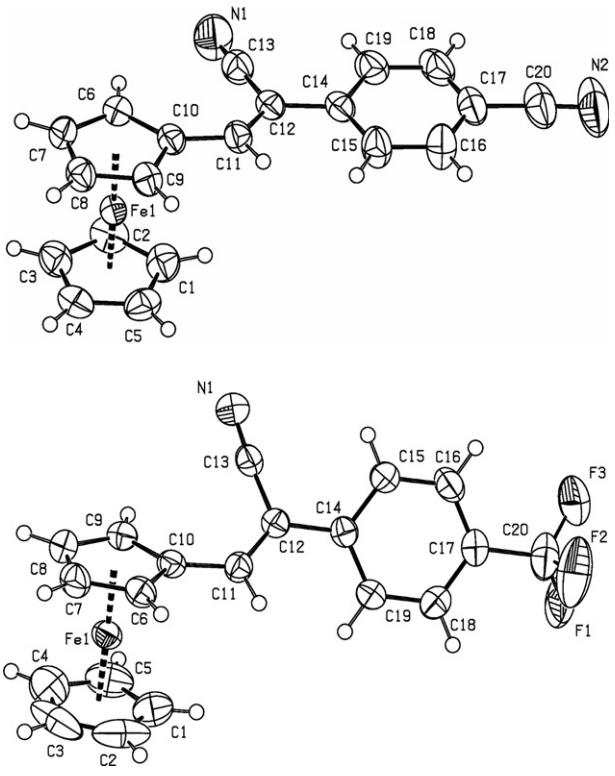


Fig. 4. Molecular structures of compounds **16** and **17** showing the atom numbering scheme.

Table 6
Selected bond lengths (Å) and angles (°) for **16**

Bond length (Å)		Bond angles (°)	
C11–C12	1.351(2)	C11–C12–C13	120.4(2)
C10–C11	1.447(3)	C11–C12–C14	123.7(2)
C12–C13	1.436(2)	C12–C11–C10	131.2(2)
C12–C14	1.488(3)	C13–C12–C14	115.9(2)
C13–N1	1.144(2)	C12–C11–H11	114.4
C17–C20	1.44(3)	C10–C11–H11	114.4
C20–N2	1.136(3)	C16–C17–C20	118.4(2)
C6–C7	1.413(2)	N1–C13–C12	177.4(2)
C7–C8	1.414(3)	N2–C20–C17	176.8(3)

Table 7
Selected bond lengths (Å) and angles (°) for **17**

Bond length (Å)		Bond angles (°)	
C11–C12	1.354(3)	C11–C12–C13	120.1(2)
C10–C11	1.438(3)	C11–C12–C14	124.0(2)
C12–C13	1.448(3)	C12–C11–C10	128.3(2)
C12–C14	1.474(3)	C13–C12–C14	115.6(2)
C13–N1	1.139(3)	C12–C11–H11	116(2)
C17–C20	1.487(4)	C10–C11–H11	116(2)
C6–C7	1.402(4)	C16–C17–C20	120.2(3)
C7–C8	1.407(3)	N1–C13–C12	175.2(3)

3. Conclusion

Solvent-free reaction of ferrocenecarboxaldehyde with diamines provided excellent yields of the corresponding diimines. The solvent-free method was also successfully applied in the synthesis of 1,1′-ferrocenyldiimines by the reaction of 1,1′-ferrocenedicarboxaldehyde and a range of substituted anilines. The products were isolated in good yield with minimum work-up. Solvent-free synthesis of ferrocenylacrylonitriles using the Knoevenagel reaction was successful. The synthetic procedure was very simple and the products were generally obtained in very good yield.

4. Experimental

4.1. Purification and characterization of the materials

All reactions, unless otherwise stated, were performed under an inert atmosphere of dry nitrogen. For more sensitive manipulations, standard Schlenk techniques were applied and pure argon was used. *n*-Butyllithium (1.6 M and 10.0 M in hexanes), *N*,*N*,*N*′,*N*′-tetramethylethylenedi-

amine (packaged under nitrogen in sealed bottles), ferrocene, ferrocenecarboxaldehyde and the phenylacetonitriles were obtained from the Sigma–Aldrich Chemical Company, Milwaukee, USA. Thin layer chromatography was performed on aluminium-backed silica gel or Merck silica gel 60 F_{254} (1.5 mm) as adsorbent in a variety of solvent systems using the ascending technique. Plates were analysed under ultraviolet light. Column chromatography was conducted either on silica gel 60, particle size 0.063–0.200 mm (70–230 mesh ASTM) or neutral alumina, particle size 0.063–0.200 mm (70–230 mesh ASTM). Unless otherwise stated, all recrystallizations were performed at room temperature. If more than one solvent was used to perform the recrystallization, two different annotations are used, e.g., dichloromethane/ethanol or dichloromethane/hexane denotes that a mixture of two solvents was used, whereas dichloromethane-ethanol denotes that dichloromethane was used to dissolve the solid and the slow addition of ethanol resulted in crystallization.

Melting points were determined on an Electrothermal IA 900 series digital melting point apparatus and are uncorrected. Infrared spectra were recorded on either, a Perkin–Elmer 1600 series instrument, a Nicolet Magna 550 Fourier Transform spectrophotometer or on a DigiLab FTS 3100 Excalibur HE Series, packaged to DigiLab Resolution 4.0 software with solid samples prepared as potassium bromide disks and solution samples in sodium chloride solution cells. Microanalyses were obtained on a Carlo Erba EA 1108 elemental analyser. Fast atomic bombardment (FAB) and high resolution (EI) mass spectra were recorded on a micromass autospec-Tof mass spectrometer at the University of the North West in South Africa. NMR spectra were recorded on a Bruker AX (300 MHz) spectrometer at ambient temperatures. ^{1}H NMR spectra were referenced internally using residual protons in the deuterated solvent and values reported relative to tetramethylsilane (δ 0.00). ^{13}C NMR spectra were similarly referenced internally to the solvent resonance with values reported relative to tetramethylsilane (δ 0.00). Electrochemical data were obtained by cyclic voltammetry with a BASi Epsilon-EC instrument using version 1.50.69_XP software. A platinum working electrode, platinum-wire auxiliary electrode and silver/silver chloride reference electrode were used with 3 M sodium chloride filling in a single-compartment-cell configuration. Solution volumes of ca. 10 cm^3 were used that were ca. 10^{-3} M in compound. Anhydrous acetonitrile was used with the supporting electrolyte, TBAP which was present in 0.1 M concentration. Solutions were deaerated by nitrogen bubbling for ca. 15 min and were maintained under a nitrogen stream at ambient temperatures (25 ± 2 °C). Calculation of $E_{1/2}$ values was by averaging the anodic and cathodic peak potentials. Scans were carried out at a scan rate of 100 mV/s. Electronic spectra were obtained with a Perkin–Elmer 330 spectrophotometer. The sample path length or cell width was 0.1 cm and the sample holder tube was quartz for all samples. Solution concentrations of the ferrocenylacrylonitriles were in the range 5×10^{-3} M.

4.2. Solvent-free synthesis of ferrocenylimines: general procedure for the reaction of ferrocenylmonocarboxaldehydes and aromatic amines

The ferrocenylmonocarboxaldehyde and aniline (equimolar quantities) were added to a pyrex tube fitted with a ground glass joint. The two compounds were ground together using a glass rod at room temperature (ca. 25 °C). In some cases, a gum formed and in others the mixture turned into a melt. The pyrex tube was sealed and then placed on a shaker for approximately 30 min at room temperature. In cases where the starting materials were less reactive, the pyrex tube was immersed in a constant temperature water bath at 50 °C. The samples were then placed under a high vacuum overnight. Initial characterization of the ferrocenylimine was carried out by IR spectroscopy (KBr disc). This showed the disappearance of the carbonyl absorption of the aldehyde at approximately 1680 cm^{-1} and the appearance of a strong band between 1615 and 1635 cm^{-1} for the imine. The ferrocenylimines were characterized by ^{1}H, ^{13}C, mass spectroscopy and microanalysis.

4.2.1. 3,4,5-Trichloro-N-(ferrocenylmethylidene)aniline

The general procedure in Section 4.2 was followed using ferrocenecarboxaldehyde (**1**) (100 mg, 0.47 mmol) and 3,4,5-trichloroaniline (93 mg, 0.47 mmol). The product was isolated as a red crystalline solid and was recrystallized from cold anhydrous methanol (167 mg, 91%); m.p. 97 °C; IR (KBr, cm^{-1}) 3079, 2888, 1619, 1571, 1541, 1426, 1374, 1253, 1226, 1188, 1143, 1105, 1040, 1004, 947, 861, 819, 803, 780, 492, 477; ^{1}H NMR ($CDCl_3$) 8.34 (1H, s, CHN), 7.19 (2H, s, ArH), 4.81 (2H, s, C_5H_4), 4.57 (2H, s, C_5H_4), 4.27 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) 164.14, 152.23, 134.68, 127.76, 121.50, 79.74, 72.45, 69.88, 69.80; *m/z* (EI) 393 (M^++2, 93%), 392 (M^++1, 21%), 391 (M^+, 100%), 272 (10), 270 (10), 237 (10), 235 (20), 228 (12), 202 (15), 200 (35), 199 (13), 186 (11), 181 (13), 164 (30), 121 (99). Anal. Calc. for $C_{17}H_{12}Cl_3FeN$: C, 52.0; H, 3.1; N, 3.6; [M^+], 390.938472. Found: C, 51.9; H, 3.1; N, 3.3%; [M^+], 390.938479.

4.2.2. 4-[4-(Ferrocenylmethyleneamino)benzyl]-N-(ferrocenylmethylene)benzenamine (2)

The general procedure in Section 4.2 was followed except that 2 molar equivalents of ferrocenecarboxaldehyde (200 mg, 0.93 mmol) and 1 molar equivalent of 4,4′-methylenedianiline (93 mg, 0.47 mmol) was used. The product was isolated as a orange solid and was recrystallized from cold anhydrous $CHCl_3$–MeOH (225 mg, 81%); m.p. 128 °C; IR (KBr, cm^{-1}) 3083, 2923, 1628, 1596, 1503, 1467, 1412, 1370, 1327, 1251, 1219, 1192, 1169, 1105, 1043, 1002, 966, 823, 748, 703, 638, 596, 483; ^{1}H NMR ($CDCl_3$) 8.36 (2H, s, CHN), 7.22 (4H, d, *J* 8.3, ArH), 7.13 (4H, d, *J* 8.0, ArH), 4.82 (4H, s, C_5H_4), 4.51

(4H, s, C_5H_4), 4.26 (10H, s, C_5H_5), 4.01 (2H, s, CH_2); ^{13}C NMR ($CDCl_3$) 161.36, 151.20 138.71, 130.04, 121.17, 80.83, 71.71, 69.69, 69.45, 41.36; *m/z* (FAB) 590 (M^+, 98%), 525 (10), 487 (8), 394 (15), 302 (20), 289 (15), 274 (8), 224 (5), 212 (8), 179 (12), 154 (100), 136 (86), 121 (36). Anal. Calc. for $C_{35}H_{30}Fe_2N_2$: C, 71.2; H, 5.1; N, 4.7; [M^+], 590.110803. Found: C, 70.6; H, 5.2; N, 4.7%; [M^+], 590.110778.

4.2.3. 4-[4-(Ferrocenylmethyleneamino)phenethyl]-N-(ferrocenylmethylene)benzenamine (3)

The general procedure in Section 4.2 was followed except that 2 molar equivalents of ferrocenecarboxaldehyde (200 mg, 0.93 mmol) and 1 molar equivalent 4,4′-diaminobibenzyl (103 mg, 0.47 mmol) was used. The product was isolated as an orange solid and was recrystallized from cold anhydrous $CHCl_3$–MeOH (245 mg, 86%); m.p. 191 °C; IR (KBr, cm^{-1}) 3025, 2913, 2886, 1622, 1595, 1506, 1465, 1411, 1369, 1325, 1250, 1220, 1192, 1169, 1105, 1045, 1002, 839; 820, 639, 479; ^1H NMR ($CDCl_3$) 8.36 (2H, s, CHN), 7.19 (4H, d, *J* 8.4, ArH), 7.10 (4H, d, *J* 8.4, ArH), 4.82 (4H, t, *J* 1.9, C_5H_4), 4.50 (4H, t, *J* 1.8, C_5H_4), 4.27 (10H, s, C_5H_5), 2.96 (4H, s, $2\times CH_2$); ^{13}C NMR ($CDCl_3$) 161.30, 151.10, 139.20, 129.65, 121.01, 80.91, 71.66, 69.69, 69.41, 37.93; *m/z* (FAB) 604 (M^+, 55%), 307 (45), 289 (28), 273 (8), 212 (15), 180 (8), 154 (100), 136 (85), 121 (15). Anal. Calc. for $C_{36}H_{32}Fe_2N_2$: [M^+], 604.126874. Found: [M^+], 604.126874.

4.2.4. N,N′-Ethylenebis[(ferrocenylmethylidene)amine] (4) [17]

Ferrocenecarboxaldehyde (400 mg, 1.87 mmol) and ethylenediamine (100 mg, 1.66 mmol) were added together and ground using a mortar and pestle. The yellow paste was placed into a glass tube fitted with a ground glass joint and the solid was placed on a vacuum pump overnight. The product was obtained as a yellow solid and identified as *N*,*N*-ethylenebis(ferrocenylmethylidene)amine (**4**) (380 mg, 83%).

4.3. General procedure for the synthesis of ferrocenyldiimines from 1,1′-ferrocenedicarboxaldehyde and anilines

1,1′-Ferrocenedicarboxaldehyde (**5**) (1 molar equivalent) and a substituted aniline (2.2 molar equivalent) were added to a pyrex tube fitted with a ground glass joint. The two compounds were ground together using a glass rod at room temperature (ca. 25 °C). In some cases, a gum formed and in others the mixture turned into a melt. The pyrex tube was sealed and then placed on a shaker for approximately 30 min at room temperature (25 °C). The samples were then placed under a high vacuum overnight. Initial characterization of the ferrocenylimine was carried out by ^{13}C NMR spectroscopy ($CDCl_3$). This indicated a disappearance of the carbonyl (C=O) resonance peak of the 1,1′-ferrocenedicarboxaldehyde and showed a strong resonance for the imine (C=N) functional group (range 155.00–165.00 ppm). Further purification was achieved by minimal washing using cold anhydrous methanol. Sample purity was confirmed by ^1H NMR, IR spectroscopy, mass spectroscopy and microanalysis.

4.3.1. N,N′-(Ferrocene-1,1′-diyldimethylylidene)di-(4-methoxyaniline) (6)

The general procedure was followed as in Section 4.3 using 1,1′-ferrocenedicarboxaldehyde (150 mg, 0.62 mmol) and 4-methoxyaniline (170 mg, 1.38 mmol). The product was isolated as a red solid and was recrystallized from cold anhydrous methanol (275 mg, 98%); m.p. 150 °C; IR (KBr, cm^{-1}) 3064, 2999, 2958, 2833, 1622, 1579, 1505, 1470, 1290, 1244, 1216, 1033, 827, 784, 722, 638; ^1H NMR ($CDCl_3$) 8.29 (2H, s, CHN), 7.10 (4H, d, *J* 8.8, ArH), 6.85 (4H, d, *J* 8.8, ArH), 4.87 (4H, t, *J* 1.7, C_5H_4), 4.52 (4H, t, *J* 1.7, C_5H_4), 3.83 (6H, s, $2\times OCH_3$); ^{13}C NMR ($CDCl_3$) 158.89, 158.19, 145.76, 122.24, 114.71, 82.45, 72.38, 70.29, 55.86; *m/z* (EI) 453 (M^++1, 8%), 452 (M^+, 26%), 358 (100), 356 (6), 328 (8), 312 (11), 254 (7), 191 (12), 190 (26), 165 (11), 163 (10), 152 (7), 122 (7), 121 (70), 56 (15), 32 (18). Anal. Calc. for $C_{26}H_{24}FeN_2O_2$: [M^+], 452.118717. Found: [M^+], 452.118698.

4.3.2. N,N′-(Ferrocene-1,1′-diyldimethylylidene)di-(4-methylaniline) (7)

The general procedure was followed as in Section 4.3 using 1,1′-ferrocenedicarboxaldehyde (150 mg, 0.62 mmol) and 4-aminotoluene (146 mg, 1.36 mmol). The product was isolated as a red solid and was recrystallized from cold anhydrous methanol (255 mg, 98%); m.p. 107 °C; IR (KBr, cm^{-1}) 3022, 2915, 2855, 1622, 1595, 1508, 1466, 1373, 1329, 1250, 1216, 1189, 1169, 1042, 1021, 968, 820, 786, 535; ^1H NMR ($CDCl_3$) 8.31 (2H, s, CHN), 7.13 (4H, d, *J* 8.2, ArH), 7.04 (4H, d, *J* 8.3, ArH), 4.87 (4H, t, *J* 1.8, C_5H_4), 4.54 (4H, t, *J* 1.8, C_5H_4), 2.36 (6H, s, $2\times CH_3$); ^{13}C NMR ($CDCl_3$) 160.02, 150.14, 135.65, 130.15, 120.99, 82.20, 72.58, 70.47, 21.41; *m/z* (EI) 421 (M^++1, 10), 420 (M^+, 31%), 329 (6), 238 (8), 182 (4), 91 (5) 32 (22), 28 (100). Anal. Calc. for $C_{26}H_{24}FeN_2$: C, 74.3; H, 5.8; N, 6.7 [M^+], 420.12889. Found: C, 73.7; H, 5.7; N, 6.5%; [M^+], 420.128903.

4.3.3. N,N′-(Ferrocene-1,1′-diyldimethylylidene)di-(4-fluoroaniline) (8)

The general procedure was followed as in Section 4.3 using 1,1′-ferrocenedicarboxaldehyde (150 mg, 0.62 mmol) and 4-fluoroaniline (151 mg, 1.36 mmol) except that reaction mixture in the pyrex tube was initially immersed in a constant temperature water bath at 50 °C for 1 h. The product was isolated as a maroon solid and was recrystallized from cold anhydrous methanol (217 mg, 82%); m.p. 112 °C; IR (KBr, cm^{-1}) 3090, 2862, 1621, 1593, 1503, 1467, 1372, 1328, 1251, 1225, 1212, 1182, 1095, 1028, 939, 829, 797, 728, 642, 531, 480, 348; ^1H NMR ($CDCl_3$) 8.27 (2H, s, CHN), 7.02 (8H, m, ArH), 4.88 (4H, s, C_5H_4), 4.55 (4H, s, C_5H_4); ^{13}C NMR ($CDCl_3$) 161.72,

(1C, d, J_{CaF} 183.4, C_a), 159.70, 148.74, 122.35 (2C, d, J_{CcF} 8.3, C_c) 116.19 (2C, d, J_{CbF} 22.4, C_b), 82.00, 72.63, 70.51; *m/z* (EI) 429 (M^++1, 57%), 428 (M^+, 100), 426 (13), 333 (33), 242 (28), 186 (23), 95 (11). Anal. Calc. for $C_{24}H_{18}F_2FeN_2$: C, 67.3; H, 4.2; N, 6.5; [M^+], 428.078744. Found: C, 67.6; H, 4.1; N, 6.0%; [M^+], 428.078711.

4.3.4. N,N′-(Ferrocene-1,1′-diyldimethylylidene)di-(4-chloroaniline) (**9**)

The general procedure was followed as in Section 4.3 using 1,1′-ferrocenedicarboxaldehyde (150 mg, 0.62 mmol) and 4-chloroaniline (174 mg, 1.36 mmol). The product was isolated as a red solid and was recrystallized from cold anhydrous methanol (275 mg, 96%); m.p. 144 °C; IR (KBr, cm^{-1}) 3101, 3081, 2861, 1624, 1580, 1489, 1470, 1372, 1329, 1252, 1220, 1188, 1169, 1093, 1043, 1031, 1011, 940, 875, 824, 763, 657; ^1H NMR ($CDCl_3$) 8.26 (2H, s, CHN), 7.27 (4H, d, *J* 8.3, ArH), 7.01 (4H, d, *J* 8.6, ArH), 4.89 (4H, t, *J* 1.7, C_5H_4), 4.56 (4H, t, *J* 1.7, C_5H_4); ^{13}C NMR ($CDCl_3$) 161.06, 151.09, 131.44, 129.59, 122.29, 81.86, 72.77, 70.63; *m/z* (EI) 460 (M^+, 17%), 308 (6), 258 (4), 242 (13), 186 (3), 178 (11), 121 (5), 32 (17), 28 (100). Anal. Calc. for $C_{24}H_{18}Cl_2FeN_2$: C, 62.5; H, 3.9; N, 6.1; [M^+], 460.019643. Found: C, 62.2; H, 3.9; N, 5.5%; [M^+], 460.019598.

4.3.5. N,N′-(Ferrocene-1,1′-diyldimethylylidene)di-(4-bromoaniline) (**10**)

The general procedure was followed as in Section 4.3 using 1,1′-ferrocenedicarboxaldehyde (150 mg, 0.62 mmol) and 4-bromoaniline (234 mg, 1.36 mmol). The product was isolated as a red solid and was recrystallized from cold anhydrous methanol (324 mg, 95%); m.p. 137 °C; IR (KBr, cm^{-1}) 3082, 2863, 1624, 1577, 1488, 1469, 1329, 1252, 1219, 1189, 1169, 1102, 1072, 1032, 1006, 824, 758; ^1H NMR ($CDCl_3$) 8.26 (2H, s, CHN), 7.42 (4H, d, *J* 8.6, ArH), 6.95 (4H, d, *J* 8.6, ArH), 4.89 (4H, t, *J* 1.7, C_5H_4), 4.56 (4H, t, *J* 1.8, C_5H_4); ^{13}C NMR ($CDCl_3$) 161.15, 151.54, 132.56, 122.70, 119.29, 81.81, 72.82, 70.65; *m/z* (FAB) 550 (M^++2, 100%), 548 (M^+, 51), 395 (8), 308 (29), 290 (9), 249 (7), 222 (9), 211 (6), 167 (33), 154 (89), 136 (82), 120 (17). Anal. Calc. for $C_{24}H_{18}Br_2FeN_2$: C, 52.4; H, 3.3; N, 5.1; [M^+], 547.918610. Found: C, 52.0; H, 3.3; N, 4.8%; [M^+], 547.918244.

4.3.6. N,N′-(Ferrocene-1,1′-diyldimethylylidene)di-(3,4,5-trichloroaniline) (**11**)

The general procedure was followed as in Section 4.3 using 1,1′-ferrocenedicarboxaldehyde (150 mg, 0.62 mmol) and 3,4,5-trichloroaniline (270 mg, 1.37 mmol) except that the reaction mixture in the pyrex tube was initially immersed in a constant temperature water bath at 50 °C for 1 h. The product was isolated as an orange solid and was recrystallized from cold anhydrous methanol (275 mg, 74%); m.p. 180 °C; IR (KBr, cm^{-1}) 3070, 2887, 1626, 1572, 1541, 1473, 1426, 1374, 1254, 1226, 1188, 1142, 1027, 938, 874, 859, 807, 782, 690, 661; ^1H NMR ($CDCl_3$) 8.22 (2H, s, CHN), 7.06 (4H, s, ArH), 4.92 (4H, t, *J* 1.8, C_5H_4), 4.60 (4H, t, *J* 1.8, C_5H_4); ^{13}C NMR ($CDCl_3$) 162.42, 151.12, 134.80, 128.39, 121.31, 81.26, 73.21, 70.98; *m/z* (EI) 598 (M^+, 16%), 307 (18), 289 (10), 200 (5), 180 (7), 154 (100), 136 (84), 120 (15). Anal. Calc. for $C_{24}H_{14}Cl_6FeN_2$: C, 48.1; H, 2.4; N, 4.7; [M^+], 595.863754. Found: C, 47.6; H, 2.3; N, 4.0%; [M^+], 595.863804.

4.3.7. N,N′-(Ferrocene-1,1′-diyldimethylylidene)di-(4-ferrocenylaniline) (**12**)

The general procedure was followed as in Section 4.3 using 1,1′-ferrocenedicarboxaldehyde (100 mg, 0.41 mmol) and 4-ferrocenylaniline (230 mg, 0.83 mmol). The product was isolated as an orange solid and was recrystallized from cold anhydrous $CHCl_3$–MeOH (284 mg, 91%); m.p. 120–121 °C; IR (KBr, cm^{-1}) 3089, 2863, 1621, 1593, 1521, 1452, 1219, 1105, 1001, 889, 821, 504; ^1H NMR ($CDCl_3$) 8.40 (2H, s, CHN), 7.46 (4H, d, *J* 8.5, ArH), 7.12 (4H, d, *J* 8.4, ArH), 4.93 (4H, t, *J* 1.7, C_5H_4), 4.65 (4H, t, *J* 1.8, C_5H_4), 4.58 (4H, t, *J* 1.8, C_5H_4), 4.33 (4H, t, *J* 1.8, C_5H_4), 4.06 (10H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) 169.99, 159.78, 137.23, 127.19, 121.28, 85.47, 82.24, 72.75, 70.59, 70.03, 69.35, 66.80; *m/z* (FAB) 757 (M^+, 31%), 407 (8), 307 (15), 288 (10), 276 (8), 260 (5), 180 (6), 154 (100), 136 (33), 120 (16). Anal. Calc. for $C_{44}H_{36}Fe_3N_2$: [M^+], 757.069192. Found: [M^+], 757.069439.

4.4. General procedure for the solvent-free synthesis of ferrocenylacrylonitrile compounds

Into a pyrex tube fitted with a ground glass joint, was added an equimolar quantity of ferrocenemonocarboxaldehyde and a substituted phenylacetonitrile. The compounds were thoroughly mixed (ground in case of two solids). One or two drops of piperidine was introduced and allowed to mix thoroughly using a glass rod at room temperature (ca. 25 °C). The pyrex tube was sealed and then placed on a shaker for approximately 30 min at room temperature. The samples were then allowed to dry in open air before being placed on a pump. Initial characterization of the ferrocenylacrylonitrile was by NMR (^1H and ^{13}C) and IR spectroscopy (KBr disc). In a typical case, the ^{13}C NMR spectrum showed the disappearance of the carbonyl resonance and the appearance of resonance peaks for the alkene. The carbonyl absorption band in the IR spectrum disappeared and the intense band for the nitrile group appeared at approximately 2200 cm^{-1}. The products were purified for microanalysis and mass spectrometry using preparative TLC plates or column chromatography on silica gel.

4.4.1. 3-Ferrocenyl-2-(4-methoxyphenyl)acrylonitrile (**13**)

The general procedure was followed as in Section 4.4 using ferrocenecarboxaldehyde (200 mg, 0.93 mmol) and 4-methoxyphenylacetonitrile (138 mg, 0.94 mmol) except that the reaction mixture was heated to 80 °C in a constant

temperature water bath. The mixture formed a melt that was placed on a shaker for 1 h and was then allowed to dry in air overnight to form a red solid. The product was further subjected to column chromatography using hexane/diethyl ether (6:1) as the eluting solvent to achieve red crystals (18 mg, 6%); m.p. 92 °C; IR (KBr, cm^{-1}) 3010, 2968, 2935, 2841, 2214, 1605, 1515, 1457, 1424, 1252, 1184, 1107, 1041, 1001, 831, 821, 499, 481; ^1H NMR ($CDCl_3$) 7.55 (2H, d, *J* 8.9, ArH), 7.27 (1H, s, CH), 6.96 (2H, d, *J* 8.9, ArH), 4.96 (2H, t, *J* 1.9, C_5H_4), 4.52 (2H, t, *J* 1.9, C_5H_4), 4.25 (5H, s, C_5H_5), 3.87 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$) 160.11, 141.51, 127.74, 126.86, 119.68, 114.86, 106.85, 78.20, 71.65, 70.28, 70.16, 55.86; *m/z* (EI) 344 (M^++1, 47%), 343 (M^+, 100), 340 (13), 278 (19), 251 (23), 195 (18), 152 (16), 121 (25), 56 (10). Anal. Calc. for $C_{20}H_{17}FeNO$: [M^+], 343.065954. Found: [M^+], 343.065902.

4.4.2. 3-Ferrocenyl-2-(4-chlorophenyl)acrylonitrile (**14**)

The general procedure was followed as in Section 4.4 using ferrocenecarboxaldehyde (200 mg, 0.93 mmol) and 4-chlorophenylacetonitrile (141 mg, 0.93 mmol). An initial yellow melt was obtained and on mixing with 2 drops of piperidine, it turned into a red solution. The product was isolated as a red solid which was further subjected to column chromatography using hexane/diethyl ether (5:1) as the eluting solvent to achieve red crystals (287 mg, 89%); m.p. 133 °C; IR (KBr, cm^{-1}) 3094, 3033, 2208, 1644, 1597, 1492, 1458, 1408, 1363, 1271, 1252, 1184, 1096, 1052, 999, 923, 898, 827, 505, 482, 424; ^1H NMR ($CDCl_3$) 7.55 (2H, d, *J* 8.6, ArH), 7.41 (1H, s, CH), 7.38 (2H, s, ArH), 4.99 (2H, t, *J* 1.7, C_5H_4), 4.58 (2H, t, *J* 1.7, C_5H_4), 4.26 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) 144.20, 134.45, 133.66, 129.62, 126.74, 119.25, 105.82, 77.55, 72.22, 70.64, 70.32; *m/z* (EI) 350 (M^++3, 22%), 349 (M^++2, 73), 347 (M^+, 100), 282 (41), 257 (13), 255 (39), 199 (16), 191 (14), 190 (35), 165 (17), 164 (25), 163 (28), 121 (31), 56 (18), 45 (17), 44 (13), 28 (11). Anal. Calc. for $C_{19}H_{14}ClFeN$: C, 65.7; H, 4.1; N, 4.0; [M^+], 347.016417. Found: C, 66.1; H, 4.3; N, 3.8%; [M^+], 347.016398.

4.4.3. 3-Ferrocenyl-2-(4-fluorophenyl)acrylonitrile (**15**)

The general procedure was followed as in Section 4.4 using ferrocenecarboxaldehyde (200 mg, 0.93 mmol) and 4-fluorophenylacetonitrile (126 mg, 0.93 mmol). An initial yellow paste was obtained on grinding with piperidine and this eventually turned red. The product was isolated as a red solid which was further subjected to column chromatography using hexane/diethyl ether (5:1) as the eluting solvent to achieve red crystals (281 mg, 91%); m.p. 95–96 °C; IR (KBr, cm^{-1}) 3054, 2921, 2851, 2214, 1602, 1590, 1511, 1454, 1415, 1366, 1308, 1279, 1251, 1233, 1164, 1105, 923, 831, 722, 614, 595, 494, 450, 431, 331; ^1H NMR ($CDCl_3$) 7.59 (2H, dd, J_{bc} 8.9, J_{bF} 5.1, ArH), 7.33 (1H, s, CH), 7.12 (2H, t, J_{CbF} 8.6, ArH), 4.97 (2H, t, *J* 1.9, C_5H_4), 4.56 (2H, t, *J* 1.9, C_5H_4), 4.26 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) 162.99 (1C, d, J_{CaF} 248.9, C_a), 143.61, 131.36, 127.32 (2C, d, J_{CcF} 8.2, C_c), 119.42, 116.46 (2C, d, J_{CbF} 22.0, C_b), 106.03, 77.66, 71.99, 70.49, 70.24; *m/z* (EI) 333 (M^++1, 18%), 332 (M^+, 100), 331 (55), 266 (85), 240 (25), 239 (94), 190 (24), 184 (26), 183 (94), 182 (10), 164 (14), 163 (25), 157 (16), 121 (73), 95 (12), 56 (56), 43 (16), 39 (24). Anal. Calc. for $C_{19}H_{14}FFeN$: C, 68.9; H, 4.3; N, 4.2; [M^+], 332.053792. Found: C, 68.3; H, 4.3; N, 3.7%; [M^+], 332.053805.

4.4.4. 3-Ferrocenyl-2-(4-cyanophenyl)acrylonitrile (**16**)

The general procedure was followed as in Section 4.4 using ferrocenecarboxaldehyde (200 mg, 0.93 mmol) and 4-cyanophenylacetonitrile (132 mg, 0.93 mmol). A maroon paste was obtained upon grinding. Upon drying, the product was isolated as a dark red solid which was further subjected to TLC preparative plates using hexane/diethyl ether (1:1) to achieve maroon crystals (300 mg, 95%); m.p. 140 °C; IR (KBr, cm^{-1}) 3100, 3024, 2933, 2226, 2213, 1605, 1581, 1458, 1411, 1380, 1308, 1255, 1176, 1104, 1053, 1040, 1001, 923, 836, 821, 545, 504, 481, 434; ^1H NMR ($CDCl_3$) 7.72 (4H, s, ArH), 7.55 (1H, s, CH), 5.03 (2H, t, *J* 1.7, C_5H_4), 4.65 (2H, t, *J* 1.7, C_5H_4), 4.28 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) 147.04, 139.49, 133.26, 125.84, 119.01, 118.77, 111.70, 104.86, 77.64, 72.98, 71.07, 70.51; *m/z* (EI), 339 (M^++1, 10%), 338 (M^+, 44%), 273 (8), 246 (8) 215 (7), 190 (24), 121 (31), 56 (11), 32 (19), 28 (100). Anal. Calc. for $C_{20}H_{14}FeN_2$: C, 71.0; H, 4.2; N, 8.3; [M^+], 338.050638. Found: C, 70.8; H, 4.2; N, 7.9%; [M^+], 338.050578.

4.4.5. 3-Ferrocenyl-2-[4-(trifluoromethyl)phenyl]acrylonitrile (**17**)

The general procedure was followed as in Section 4.4 using ferrocenecarboxaldehyde (200 mg, 0.93 mmol) and 4-(trifluoromethyl)phenylacetonitrile (172 mg, 0.93 mmol). An orange/red paste was obtained on grinding. The product was isolated as a red solid which was further subjected to column chromatography using hexane/diethyl ether (5:1) as the eluting solvent to achieve dark red crystals (331 mg, 93%); m.p. 125 °C; IR (KBr, cm^{-1}) 3056, 2936, 2217, 1615, 1593, 1454, 1417, 1334, 1251, 1169, 1110, 1073, 1000, 837, 733, 617, 492; ^1H NMR ($CDCl_3$) 7.71 (4H, m, ArH), 7.51 (1H, s, CH), 5.02 (2H, t, *J* 1.8, C_5H_4), 4.62 (2H, t, *J* 1.8, C_5H_4), 4.27 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) 146.03, 138.55, 130.53, 130.10, 126.43, 125.67, 119.09, 105.36, 77.17, 72.60, 70.89, 70.41; *m/z* (EI) 382 (M^++1, 9%), 381 (M^+, 38%), 240 (6), 191 (9), 190 (13), 121 (10), 32 (19), 28 (100). Anal. Calc. for $C_{20}H_{14}F_3FeN$: C, 63.0; H, 3.7; N, 3.7; [M^+], 381.042774. Found: C, 62.9; H, 3.7; N, 3.5%; [M^+], 381.042792.

4.4.6. 3-Ferrocenyl-2-(4-nitrophenyl)acrylonitrile (**18**)

The general procedure was followed as in Section 4.4 using ferrocenecarboxaldehyde (200 mg, 0.93 mmol) and 4-nitrophenylacetonitrile (151 mg, 0.93 mmol). Upon addition of two drops of piperidine the solid mixture changed rapidly into a purple melt. The product was isolated as a

dark purple solid. The product was further subjected to column chromatography using hexane/diethyl ether (4:1) as the eluting solvent to achieve purple crystals (331 mg, 99%); m.p. 195 °C; IR (KBr, cm^{-1}) 3094, 3054, 2219, 1603, 1582, 1514, 1457, 1372, 1340, 1254, 1199, 1113, 1050, 1032, 1002, 849, 825, 753, 690; ^1H NMR ($CDCl_3$) 8.29 (2H, d, *J* 8.9, ArH), 7.77 (2H, d, J, 8.9, ArH), 7.61 (1H, s, CH), 5.05 (2H, t, *J* 1.8, C_5H_4), 4.68 (2H, t, *J* 1.8, C_5H_4), 4.29 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) 147.87, 147.31, 141.35, 125.89, 124.87, 118.77, 104.41, 76.90, 73.21, 71.21, 70.59; *m/z* (EI) 359 (M^++1, 12%), 358 (M^+, 55%), 312 (7), 191 (6), 190 (12), 165 (6), 121 (25), 56 (6), 32 (19), 28 (100). Anal. Calc. for $C_{19}H_{14}FeN_2O_2$: C, 63.7; H, 3.9; N, 7.8; [M^+], 358.040467. Found: C, 64.2; H, 4.3; N, 7.5%; [M^+], 358.040422.

5. X-ray crystallography

5.1. Structural analysis of 3-ferrocenyl-2-(4-cyanophenyl)-acrylonitrile (*16*)

X-ray diffraction data for **16** and **17** were collected on a Bruker SMART 1K CCD area detector diffractometer with graphite-monochromated Mo Kα radiation (50 kV, 30 mA). The collection method involved ω-scan of width 0.3°. Data reduction was carried out using the program SAINT+, Version 6.02 [18]. Multi-scan absorption corrections were made using the program SADABS [19]. The crystal structures were solved by direct methods using SHELXS-97 [20]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculation based on F^2 using SHELXL-97 [20]. Hydrogen atoms were first located in the different map then positioned geometrically and allowed to ride on their respective parent atoms. Diagrams and publication materials were generated using SHELXTL, PLATON [21] and ORTEP3 [22]. The general-purpose crystallographic tool PLATON was used for structure analysis.

Crystal data for **16**: $M_r = 338.18\ g\ mol^{-1}$, crystal size $0.42 \times 0.38 \times 0.22\ mm^3$, monoclinic, space group *C*2/*c*, $a = 26.4576(15)$ Å, $b = 11.2470(6)$ Å, $c = 11.6638(6)$ Å, $V = 3159.8(3)$ Å^3, $T = 293$ K, $Z = 8$, μ(Mo Kα) = 0.954 mm^{-1}, 3107 independent reflections, $R_{int} = 0.0279$, $R_{1obs} = 0.0254$, $wR_{2obs} = 0.0704$, $R_{1all} = 0.0330$, $wR_{2all} = 0.0737$, goodness-of-fit = 1.102.

5.2. Structural analysis of 3-ferrocenyl-2-(4-trifluoromethyl)acrylonitrile (*17*)

X-ray diffraction data were collected as in Section 5.1. Crystal data for 3-ferrocenyl-2-(4-trifluoromethyl)acrylonitrile **17**: $M_r = 381.17\ g\ mol^{-1}$, crystal size $0.48 \times 0.17 \times 0.11\ mm^3$, monoclinic, space group $P2_1/c$, $a = 14.167(3)$ Å, $b = 16.063(3)$ Å, $c = 7.6065(15)$ Å, $V = 1682.4(6)$ Å^3, $T = 293$ K, $Z = 4$, $\mu(M_o - K_\alpha) = 0.928$ mm^{-1}, 4051 independent reflections, $R_{int} = 0.0982$, $R_{1obs} = 0.0389$, $wR_{2obs} = 0.0898$, $R_{1all} = 0.0790$, $wR_{2all} = 0.1001$, goodness-of-fit = 0.920.

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Appendix A. Supplementary material

CCDC 286626 and 286627 contain the supplementary crystallographic data for **16** and **17**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.04.011.

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