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Solvent-free synthesis of ferrocenylimines

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Abstract

The mixing of equimolar quantities of ferrocenylaldehydes and aromatic amines in a solvent-free environment provided excellent yields of ferrocenylimines. After mixing the aldehydes and amines, a melt formed which eventually solidified to the product. An analytically pure sample of the product was obtained by cold recrystallization.

Keywords: Ferrocenylimines; Green chemistry; Solvent-free synthesis

1. Introduction

There has recently been an upsurge of interest in performing chemical transformations in a solvent-free environment. For example, McCluskey et al. [1] have described solvent-free Knoevenagel condensation reactions (Scheme 1). In comparison to methods employing molecular solvents, the solvent-free approach proceeded more cleanly and provided higher yields. Further examples of the solvent-free approach to organic transformations can be found in a recent feature article [2] and a monologue on the subject has recently appeared [3].

One of our current research objectives is to introduce the Green Chemistry Principles [4] into the synthesis of simple ferrocenyl derivatives. In otherwords, our aim is to synthesize ferrocenes using reactions that have a high atom economy, that are conducted under ambient conditions and that use non-toxic recyclable solvents. So far, we have reported on the synthesis of ferrocenoyl esters in [bmim][BF_4] and [bmim][PF_6] [5]. A major concern in using ionic liquids such as imidazolium salts as reaction solvent rests with their possible toxicity and persistence in the environment [6]. In this paper, we describe a highly efficient synthesis of ferrocenylimines by the solvent-free mixing of ferrocenylaldehydes and aromatic amines.

2. Results and discussion

The synthesis of ferrocenylimines by reaction of ferrocenylaldehydes with aromatic amines has been reported by several research groups [7]. The imines are potentially useful ligands for metal complexation and many of the ferrocenylimines have been investigated for non-linear optical properties [8]. In the majority of cases, the ferrocenylimines were prepared by heating a solution of the ferrocenylaldehyde and aromatic amine in solvents such as anhydrous methanol or ethanol. Our research group has also previously utilized this method [9]. One of the problems associated with it is that thermally sensitive ferrocenylimines suffer a degree of decomposition during the heating process. To avoid this problem and to fit in more closely with the principles of green chemistry [4], the reactions have been conducted in a solvent-free environment.

The reactions conducted with ferrocenylaldehydes are shown in Scheme 2. 4-Formylphenylferrocene **1** and 4′-ferrocenyl-biphenyl-4-carbaldehyde **2** were prepared by a modified Suzuki cross-coupling reaction. 4-(4-Ferrocenyl-phenoxy)-benzaldehyde **3** was prepared by the copper(II) acetate coupling of 4-ferrocenylphenol and

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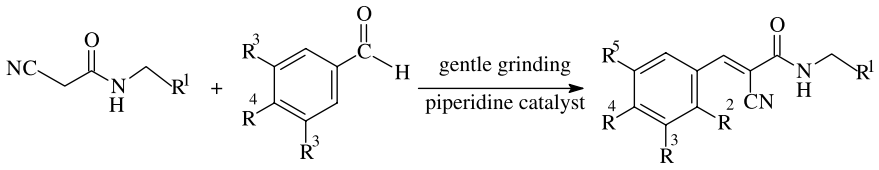
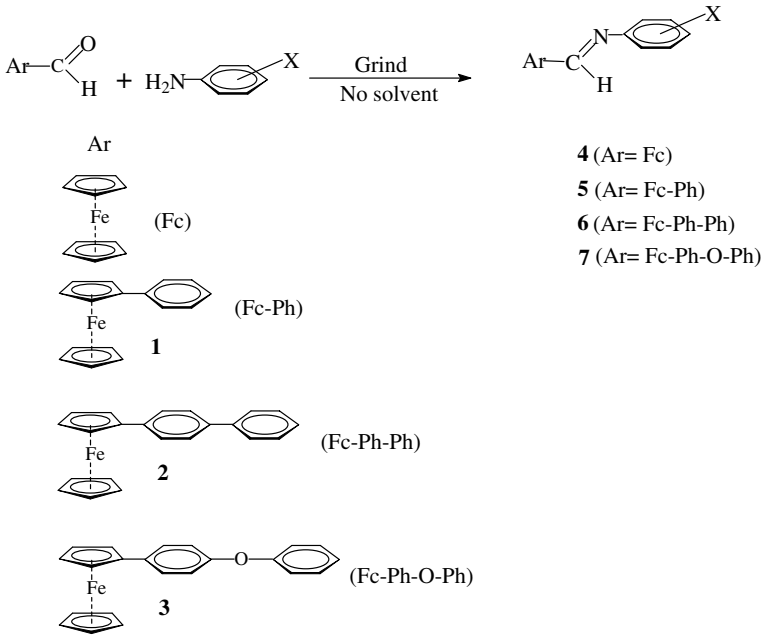


Scheme 1. Solvent-free Knoevenagel reactions.

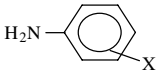


Scheme 2. Reactions of ferrocenylaldehydes with aromatic amines.

4-formylbenzeneboronic acid [9]. The mixing of an equimolar quantity of the ferrocenylaldehyde and aromatic amine provided in most cases a melt after a few minutes. An example of a reaction is that between ferrocenecarboxaldehyde and 4-tetradecyloxyaniline. On mixing the sample of 4-tetradecyloxyaniline with ferrocenecarboxaldehyde, a melt was obtained and this gradually solidified at room temperature under vacuum to give the imine product in high yield (entry 5, Table 1).

The solidified melt was initially analyzed by IR spectroscopy using a KBr pellet in order to substantiate that the reaction was more or less completed under solvent-free conditions. An example of an IR spectrum is provided in Fig. 1 for the solvent-free reaction of 4-formylphenylferrocene and 4-tetradecyloxyaniline. The strong band associated with 4-formylphenylferrocene (CO) which usually resides at approximately 1700 cm^{-1} is absent and is replaced by a strong band at 1631 cm^{-1} (Fig. 1) which is the normal region for an imine bond (C=N). The solidified melt was finally crystallized from cold anhydrous methanol and this provided a product with a high degree of purity as judged by ^{1}H, ^{13}C NMR, high resolution mass spectroscopy and microanalysis. The isolated yields of the imines according to the variation in the aldehyde and the nature of the substituent in the aniline are provided in Table 1 and are generally very good. In some instances, notably

Table 1
Yields of ferrocenylimines from the solvent-free reaction of ferrocenylaldehydes and aromatic amines

Entry	Ferrocenylaldehyde	Aromatic amine  X	Yield of ferrocenylimine[a] (%)
1	FcCHO	4-Cl	94
2	FcCHO	4-CH_3	97
3	FcCHO	4-NO_2	92
4	FcCHO	4-OC_8H_{17}	93
5	FcCHO	4-$OC_{14}H_{29}$	94
6	FcCHO	4-Fc	95
7	FcPhCHO	4-$OC_{14}H_{29}$	96
8	FcPhCHO	4-Fc	92
9	FcPhPhCHO	4-OC_8H_{17}	87
10	FcPhPhCHO	4-$OC_{14}H_{29}$	91
11	FcPhOPhCHO	4-$OC_{14}H_{29}$	90

[a] Yields are based on the starting materials and are isolated ones.

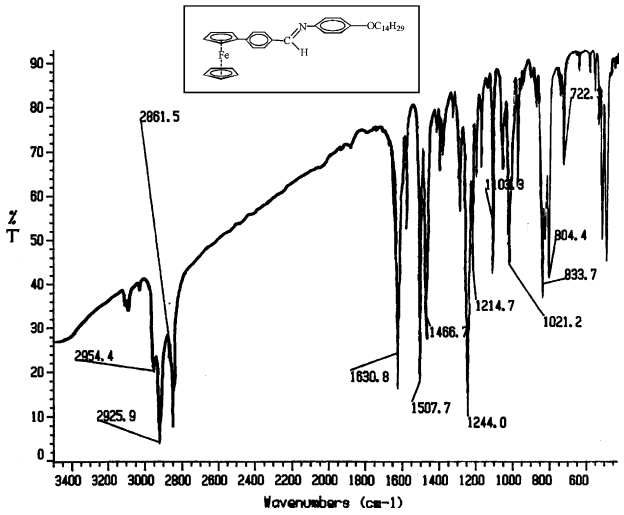


Fig. 1. IR spectrum of 4-tetradecyloxy-N-[4-(4-ferrocenyl)benzylidene]-aniline.

where the aromatic amine contained an electron-withdrawing group (Table 1, entry 3) or where the aldehyde was less reactive (Table 1, entry 11), gentle heating (50 °C) of the solid reaction mixture was required to obtain a good conversion. Analysis of the reaction between ferrocenecarboxaldehyde and 4-nitroaniline was carried out by DSC and the results are shown in Fig. 2. First of all, the starting materials and the product were analyzed individually. Ferrocenecarboxaldehyde (Fig. 2(a)) shows a phase transition at 48 °C representing the formation of a so-called plastic crystal phase [10] and this runs to its melting point at 121 °C. The 4-tetradecyloxyaniline and imine product exhibited sharp melting points (57° and 78°, respectively). The DSC analysis of the solvent-free reaction is shown in Fig. 2(b) and it indicates that the reaction began at the point where ferrocenecarboxaldehyde entered the plastic crystal phase. This suggests that the reaction could be promoted by the phase change and this warrants future investigations.

The melting behaviors of the imine products are in accordance with the guidelines provided by Imrie and Loubser [11]. Compounds containing one ferrocenyl group plus one phenyl ring have sharp melting points; those with one ferrocenyl group plus two phenyl rings show some crystal–crystal phase transitions and finally those with one ferrocenyl group and three phenyl rings exhibit liquid crystal behavior.

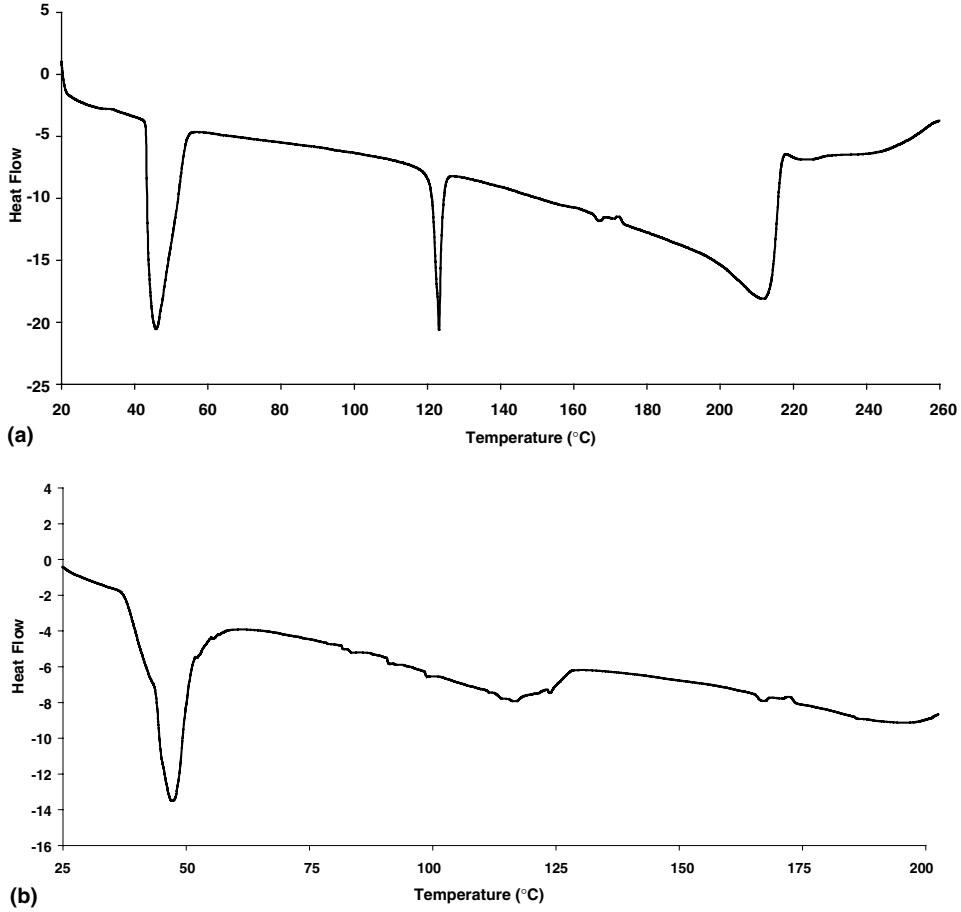


Fig. 2. DSC analysis of (a) ferrocenecarboxaldehyde and (b) the reaction between ferrocenecarboxaldehyde and 4-tetradecyloxyaniline.

3. Conclusion

A simple, convenient and more environmentally friendly route for the synthesis of ferrocenylimines has been described. This involved the solvent-free mixing of substituted anilines and ferrocenylaldehydes. The yields of ferrocenylimines were very high and purification was achieved simply by cold recrystallization from methanol.

4. Experimental

4.1. Purification and characterization of the materials

Silica gel 50 was used for column chromatography. Thin layer preparative chromatography was carried out on plates using Merck silica gel 60 F_{254} (1.5 mm) as adsorbent. M.p.s were recorded on an Electrothermal IA 900 series digital m.p. apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 1600 series Fourier Transform IR spectrometer as KBr discs or as solutions in chloroform. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer as solutions in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Mass spectra were recorded on a micromass autospec-Tof mass spectrometer at the University of Potchefstroom in South Africa. Microanalyzes of the compounds were obtained on a Carlo Erba EA 1108 elemental analyzer. Transition temperatures of the liquid crystal molecules were investigated by differential scanning calorimetry (DSC) utilizing a DSC Q100 cell, connected to a Universal Analysis thermal analyzer. Compounds were studied at various scanning rates (2.5, 5 or 10 °C min^{-1}) for both the heating and cooling cycles, after being encapsulated in aluminium pans. An empty aluminium pan served as the reference. The calorimeter was calibrated with an indium standard. The textures of the mesophases were studied with a Nikon Eclipse E 600 optical polarizing microscope equipped with a Linkam heating-freezing stage linked to a Linkam range TMS 93 precision temperature control at Rhodes University, Grahamstown. Ferrocenecarboxaldehyde was purchased from the Strem chemical company (USA) and was used without further purification. 4-Formylphenylferrocene and 4′-ferrocenyl-biphenyl-4-carbaldehyde were prepared by a modified Suzuki cross-coupling reaction as described previously [9]. 4-(4-ferrocenyl-phenoxy)-benzaldehyde was prepared by the copper(II) acetate-promoted coupling of 4-ferrocenylphenol and 4-formylbenzeneboronic acid [9]. 4-Ferrocenylphenol and 4-ferrocenylaniline were prepared by the diazonium salt method.

4.2. General procedure for the reaction of ferrocenylaldehydes and aromatic amines

The ferrocenylaldehyde 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. 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 indicated a disappearance of the carbonyl absorption of the aldehyde and showed a strong absorption for the imine functional group. The ferrocenylimines were finally characterized by ^{1}H, ^{13}C, mass spectroscopy and microanalysis.

4.3. Preparation of ferrocenylimines derived from ferrocenecarboxaldehyde

4.3.1. 4-Chloro-N-(ferrocenylmethylidene)aniline **4** (X = 4-Cl)

The general procedure was followed using ferrocenecarboxaldehyde (200 mg, 0.93 mmol) and 4-chloroaniline (119 mg, 0.93 mmol). The product was isolated as a red solid and was recrystallized from cold anhydrous methanol (283 mg, 94%); m.p. 108–110 °C; IR (KBr cm^{-1}) 3097, 3015, 2967, 2866, 1619, 1586, 1489, 1464, 1370, 1228, 1186, 1167, 1099, 1040, 1010, 967, 904, 861, 826, 746, 716, 664; ^{1}H NMR ($CDCl_3$) 8.36 (1H, s, CHN), 7.34 (2H, d, *J* 7.5, ArH), 7.12 (2H, d, *J* 7.4, ArH), 4.83 (2H, t, *J* 1.8, C_5H_4), 4.54 ((2H, t, *J* 1.8, C_5H_4), 4.27 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) 161.31, 151.30, 131.16, 129.61, 122.31, 80.22, 72.14, 70.06, 69.74; *m/z* 326, 325, 323 (M^+, 100), 258, 186, 167, 139, 121, 56. Anal. Calc. for $C_{17}H_{14}FeNCl$: [M^+], 323.016417. Found: [M^+], 323.016487.

4.3.2. 4-Methyl-N-(ferrocenylmethylidene)aniline **4** (X = 4-CH_3)

The general procedure was followed using ferrocenecarboxaldehyde (200 mg, 0.93 mmol) and 4-methylaniline (100 mg, 0.93 mmol). The product was isolated as a red solid and was recrystallized from cold anhydrous methanol (263 mg, 97%); m.p. 89–90 °C; IR (KBr cm^{-1}) 3099, 3010, 2959, 2867, 1624, 1598, 1507, 1466, 1371, 1252, 1214, 1188, 1106, 1040, 1001, 909, 867, 822, 791, 738, 666; ^{1}H NMR ($CDCl_3$) 8.35 (1H, s, CHN), 7.19 (2H, d, *J* 7.5, ArH), 7.09 (2H, d, *J* 7.5, ArH), 4.81 (2H, s, C_5H_4), 4.55 (2H, s, C_5H_4), 4.26 (5H, s, C_5H_5), 2.38 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$) 161.11, 150.69, 135.35, 130.13, 120.92, 80.95, 71.60, 69.66, 69.39, 21.39; *m/z*

304, 303 (M^+, 100), 302, 238, 182, 121, 91, 56. Anal. Calc. for $C_{18}H_{17}FeN$: C, 71.4; H, 5.6; N, 4.6; [M^+], 303.071039. Found: C, 70.9; H, 5.3; N, 4.6%; [M^+], 303.071989.

4.3.3. 4-Nitro-N-(ferrocenylmethylidene)aniline **4** (X = 4-NO_2)

The general procedure was followed using ferrocenecarboxaldehyde (200 mg, 0.93 mmol) and 4-nitroaniline (129 mg, 0.93 mmol) except that the reaction mixture was warmed to 50 °C in a water bath. The product was isolated as a red solid and was recrystallized from cold anhydrous methanol (286 mg, 92%); m.p. 183–185 °C; IR (KBr cm^{-1}) 3102, 2914, 1631, 1593, 1578, 1506, 1341, 1223, 1111, 1052, 867, 828, 742, 703, 650, 492; ^1H NMR ($CDCl_3$) 8.37 (1H, s, CHN), 8.26 (2H, d, *J* 7.7, ArH), 7.20 (2H, d, *J* 7.6, ArH), 4.84 (2H, s, C_5H_4), 4.60 (2H, s, C_5H_4), 4.29 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) 164.51, 158.98, 145.32, 125.51, 121.48, 79.79, 72.62, 70.07, 69.93; *m/z* 335, 334 (M^+, 100), 323, 288, 222, 214, 186, 167, 139, 121, 56. Anal. Calc. for $C_{17}H_{14}FeN_2O_2$: [M^+], 334.040467. Found: [M^+], 334.040503.

4.3.4. 4-Octyloxy-N-(ferrocenylmethylidene)aniline **4** (X = 4-OC_8H_{17})

The general procedure was followed using ferrocenecarboxaldehyde (100 mg, 0.47 mmol) and 4-octyloxyaniline (104 mg, 0.47 mmol). The product was isolated as a red solid and was recrystallized from cold anhydrous methanol (182 mg, 93%); m.p. 71–72 °C; IR (KBr cm^{-1}) 2921, 2861, 1631, 1512, 1473, 1302, 1249, 1190, 1117, 1038, 1005, 834, 736, 532, 505, 479; ^1H NMR ($CDCl_3$) 8.35 (1H, s, CHN), 7.15 (2H, d, *J* 8.6, ArH), 6.92 (2H, d, *J* 8.6, ArH), 4.80 (2H, s, C_5H_4), 4.48 (2H, s, C_5H_4), 4.26 (5H, s, C_5H_5), 3.99 (2H, t, OCH_2), 1.80 (2H, m, CH_2), 1.47–1.29 (10H, m, $CH_2 \times 5$), 0.92 (3H, t, CH_3); ^{13}C NMR ($CDCl_3$) 159.92, 157.64, 146.10, 122.07, 115.38, 81.17, 70.06, 69.62, 69.27, 68.72, 32.23, 29.79, 29.73, 29.66, 26.47, 23.07, 14.52; *m/z* 418, 417 (M^+, 100), 415, 305, 304, 221, 186, 121, 109, 43. Anal. Calc. for $C_{25}H_{31}FeNO$: C, 72.0; H, 7.5; N, 3.3; [M^+], 417.175504. Found: C, 72.3; H, 7.3; N, 3.6; [M^+], 417.175484.

4.3.5. 4-Tetradecyloxy-N-(ferrocenylmethylidene)aniline **4** (X = 4-$OC_{14}H_{29}$)

The general procedure was followed using ferrocenecarboxaldehyde (100 mg, 0.47 mmol) and 4-tetradecyloxyaniline (143 mg, 0.47 mmol). The product was isolated as a yellow crystalline solid and was recrystallized from cold anhydrous methanol (221 mg, 94%); m.p. 77–78 °C; IR (KBr cm^{-1}) 3097, 2923, 2872, 1631, 1502, 1472, 1244, 1103, 1015, 840, 798, 728, 505, 488; ^1H NMR ($CDCl_3$) 8.35 (1H, s, CHN), 7.15 (2H, d, *J* 8.6, ArH), 6.92 (2H, d, *J* 8.6, ArH), 4.80 (2H, s, C_5H_4), 4.48 (2H, s, C_5H_4), 4.25 (5H, s, C_5H_5), 3.98 (2H, t, OCH_2), 1.82 (2H, m, CH_2), 1.48–1.29 (22H, m, $CH_2 \times 11$), 0.91 (3H, t, CH_3); ^{13}C NMR ($CDCl_3$) 159.91, 157.64, 146.12, 122.08, 115.37, 81.20, 71.48, 69.62, 69.27, 68.71, 32.35, 30.09, 30.03, 29.85, 29.79, 29.75, 26.48, 23.12, 14.56; *m/z* 503, 502, 501 (M^+, 100), 417, 305, 304, 221, 214, 186, 121, 109, 69, 57, 43. Anal. Calc. for $C_{31}H_{43}FeNO$: C, 74.3; H, 8.6; N, 2.8; [M^+], 501.269405. Found: C, 74.6; H, 9.0; N, 2.6; [M^+], 501.269387.

4.3.6. 4-Ferrocenyl-N-(ferrocenylmethylidene)aniline **4** (X = 4-Fc)

The general procedure was followed using ferrocenecarboxaldehyde (100 mg, 0.47 mmol) and 4-ferrocenylaniline (130 mg, 0.47 mmol). The product was isolated as a red solid and was recrystallized from cold anhydrous methanol (211 mg, 95%); m.p. 211–212 °C; IR (KBr cm^{-1}) 3050, 1619, 1598, 1525, 1460, 1103, 1052, 1012, 894, 834, 512, 492; ^1H NMR ($CDCl_3$) 8.41 (lH, s, CHN), 7.50 (2H, d, *J* 7.7, ArH), 7.13 (2H, d, *J* 7.8, ArH), 4.83 (2H, s, C_5H_4), 4.67 (2H, s, C_5H_4), 4.52 (2H, s, C_5H_4), 4.34 (2H, s, C_5H_4), 4.28 (5H, s, C_5H_5), 4.07 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) 160.85, 150.91, 136.80, 127.18, 121.18, 85.66, 81.03, 71.71, 70.02, 69.71, 69.44, 69.30, 66.75; *m/z* 474, 473 (M^+), 471, 278, 277 (100), 275, 156, 121, 49. Anal. Calc. for $C_{27}H_{23}Fe_2N$: C, 68.6; H, 4.9; N, 3.1; [M^+], 473.052928. Found: C, 67.9; H, 4.5; N, 3.1; [M^+], 473.052125.

4.4. Preparation of ferrocenylimines derived from 4-formylphenylferrocene

4.4.1. 4-Tetradecyloxy-N-[4-(4-ferrocenyl)benzylidene]aniline **5** (X = 4-$OC_{14}H_{29}$)

The general procedure was followed as in 4.2 using 4-formylphenylferrocene (100 mg, 0.34 mmol) and 4-tetradecyloxyaniline (104 mg, 0.34 mmol). The product was isolated as an orange solid and was recrystallized from cold anhydrous methanol (188 mg, 96%); m.p. 110–112 °C; IR (KBr cm^{-1}) 2933, 2861, 1625, 1607, 1508, 1473, 1297, 1256, 1174, 1027, 845, 722, 546; ^1H NMR ($CDCl_3$) 8.47 (lH, s, CHN), 7.82 (2H, d, *J* 8.3, ArH), 7.58 (2H, d, *J* 8.2, ArH), 7.25 (2H, d, *J* 8.8, ArH), 6.94 (2H, d, *J* 8.8, ArH), 4.75 (2H, t, *J* 1.8, C_5H_4), 4.41 (2H, t, *J* 1.8, C_5H_4), 4.07 (5H, s, C_5H_5), 4.01 (2H, t, *J* 5.6, OCH_2), 1.80 (2H, m, CH_2), 1.59–1.28 (22H, m, $CH_2 \times 11$), 0.90 (3H, t, CH_3); ^{13}C NMR ($CDCl_3$) 158.55, 158.15, 145.36, 143.37, 134.46, 129.07, 126.50, 122.53, 115.37, 84.36, 70.18, 69.97, 68.69, 67.11, 32.34, 30.08, 30.01, 29.83, 29.78, 29.72, 26.47, 23.11, 14.55; *m/z* 578, 577 (M^+), 418, 417, 305, 290, 109 (100), 108, 69, 43. Anal. Calc. for $C_{37}H_{47}FeNO$: C, 77.0; H, 8.2; N, 2.4; [M^+], 577.300705. Found: C, 77.3; H, 8.2; N, 2.2; [M^+], 577.300679.

4.4.2. 4-Ferrocenyl-N-[4-(4-ferrocenyl)benzylidene]aniline **5** (X = 4-Fc)

The general procedure was followed as in 4.2 using 4-formylphenylferrocene (100 mg, 0.34 mmol) and

4-ferrocenylaniline (95 mg, 0.34 mmol). The pyrex tube was warmed to 50 °C during the reaction. The product was isolated as a red solid and was recrystallized from cold anhydrous methanol (172 mg, 92%); m.p. 260 °C dec; IR (KBr cm^{-1}) 3090, 2358, 2336, 1629, 1612, 1563, 1530, 1179, 1108, 1009, 822, 532, 510; ^1H NMR ($CDCl_3$) 8.52 (lH, s, CHN), 7.85 (2H, d, *J* 7.9, ArH), 7.59 (2H, d, *J* 7.9, ArH), 7.53 (2H, d, *J* 8.2, ArH), 7.22 (2H, d, *J* 8.0, ArH), 4.75 (2H, s, C_5H_4), 4.68 (2H, s, C_5H_4), 4.41 (2H, s, C_5H_4), 4.35 (2H, s, C_5H_4), 4.08 (10H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) 159.53, 150.31, 143.72, 137.52, 134.36, 129.26, 127.16, 126.55, 121.48, 85.49, 84.30, 70.31, 70.20, 70.03, 69.36, 67.15, 66.78; *m/z* 549 (M^+), 547, 501, 473, 417, 304, 290, 277, 274, 236, 186, 156, 139, 121, 109, 98, 83, 69, 57, 44, 39. Anal. Calc. for $C_{33}H_{27}Fe_2N$: C, 72.2; H, 5.0; N, 2.5; [M^+], 549.084229. Found: C, 72.3; H, 4.8; N, 2.7; [M^+], 549.084302.

4.5. Preparation of ferrocenylimines derived from 4′-ferrocenyl-biphenyl-4-carbaldehyde

4.5.1. 4-Octyloxy-N-[4-(4-ferrocenylphenyl)benzylidene]-aniline **6** *(X = 4-OC_8H_{17})*

The general procedure was followed as in 4.2 using 4′-ferrocenyl-biphenyl-4-carbaldehyde (50 mg, 0.14 mmol) and 4-octyloxyaniline (31 mg, 0.14 mmol). The pyrex tube was warmed to 50 °C during the reaction. The product was isolated as an orange solid and was recrystallized from CH_2Cl_2–MeOH (69 mg, 87%). The product was found to have an identical characterization to that reported previously [9].

4.5.2. 4-Tetradecyloxy-N-[4-ferrocenylphenyl)benzylidene]-aniline **6** *(X = 4-$OC_{14}H_{29}$)*

The general procedure was followed as in 4.2 using 4′-ferrocenyl-biphenyl-4-carbaldehyde (50 mg, 0.14 mmol) and 4-tetradecyloxyaniline (43 mg, 0.14 mmol). The product was isolated as a yellow solid and was recrystallized from CH_2Cl_2–MeOH (83 mg, 91%). The product was found to have an identical characterization to that reported previously [9].

4.6. Preparation of a ferrocenylimine derived from 4-(4-ferrocenyl-phenoxy)-benzaldehyde

4.6.1. 4-Tetradecyloxy-N-{1-[4-(ferrocenylphenoxy)-phenyl]-methylidene}aniline **7** *(X = 4-$OC_{14}H_{29}$)*

The general procedure was followed as in 4.2 using 4-(4-ferrocenyl-phenoxy)-benzaldehyde (50 mg, 0.13 mmol) and 4-tetradecyloxyaniline (40 mg, 0.13 mmol). The pyrex tube was warmed to 50 °C during the reaction. The product was isolated as a yellow solid and was recrystallized from cold CH_2Cl_2–MeOH (78 mg, 90%). The product was found to have an identical characterization to that reported previously [9].

4.7. Preparation of a ferrocenylimine derived from the reaction of 4-ferrocenylaniline and 3,4,5-trimethoxybenzaldehyde

4.7.1. 4-Ferrocenyl-[3,4,5-(trimethoxybenzylidene)]aniline

The general procedure was followed using 3,4,5-trimethoxybenzaldehyde (100 mg, 0.51 mmol) and 4-ferrocenylaniline (142 mg, 0.51 mmol). The product was isolated as a red solid and was recrystallized from cold methanol (202 mg, 87%), m.p. 132–134 °C; IR (KBr cm^{-1}) 3006, 1625, 1581, 1520, 1504, 1463, 1417, 1370, 1329, 1236, 1202, 1129, 999, 889, 860, 813, 750, 674, 624; ^1H NMR ($CDCl_3$) 8.45 (1H, s, CHN), 7.51 (2H, s, ArH), 7.28 (1H, s, ArH), 7.21 (3H, s, ArH), 4.70 (2H, s, C_5H_4), 4.37 (2H, s, C_5H_4), 4.09 (5H, s, C_5H_5), 3.98 (6H, s, $2 \times OCH_3$), 3.95 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$) 159.26, 153.94, 127.15, 121.46, 106.19, 85.37, 70.08, 69.47, 66.81, 61.42, 56.69; *m/z* 457, 456, 455 (M^+, 100), 363, 287, 277, 274, 261, 139, 121, 56, 43, 39. Anal. Calc. for $C_{26}H_{25}FeNO_3$: C, 68.6; H, 5.5; N, 3.1; [M^+], 455.118416. Found: C, 68.5; H, 5.4; N, 3.1; [M^+], 455.118383.

References

[1] A. McCluskey, P.J. Robinson, T. Hill, J.L. Scott, J.K. Edwards, Tetrahedron Lett. 43 (2002) 3117.
[2] G.W.V. Cave, C.L. Raston, J.L. Scott, Chem. Commun. (2001) 2159.
[3] K. Tanaka, F. Toda, Solvent-free Organic Synthesis, Wiley-VCH, New York, 2003.
[4] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practise, Oxford Science Publications, New York, 1998.
[5] C. Imrie, E.R.T. Elago, C.W. McCleland, N. Williams, Green Chem. 4 (2002) 159.
[6] M. Lancaster, Green Chemistry: An Introductory Text, RSC Paperbacks, Cambridge, 2002.
[7] (a) E. Bullita, U. Casellato, F. Ossola, P. Tomasin, P.A. Vigato, U. Russo, Inorg. Chim. Acta. 287 (1999) 117;
(b) S.K. Pal, K. Alagesan, A.G. Samuelson, J. Pebler, J. Organomet. Chem. 575 (1999) 108;
(c) R. Krieg, R. Wyrwa, U. Möllmann, H. Görls, B. Schönecker, Steroids 63 (1998) 531;
(d) R. Bosque, C. López, J. Sales, X. Solans, M. Font-Bardia, J. Chem. Soc., Dalton Trans. (1994) 735;
(e) H. Kersten, P. Boldt, J. Chem. Res. (S) (1994) 366;
(f) A. Houlton, N. Jasim, R.M.G. Roberts, J. Silver, D. Cunningham, P. McArdle, T. Higgins, J. Chem. Soc., Dalton Trans. (1992) 2235.
[8] I. Ratera, D. Ruiz-Molina, C. Sánchez, R. Alcalá, C. Rovira, J. Veciana, Synthetic Met. 121 (2001) 1834.
[9] C. Imrie, P. Engelbrecht, C. Loubser, C.W. McCleland, V.O. Nyamori, R. Bogardi, D.C. Levendis, N. Tolom, J.L. van Rooyen, N. Williams, J. Organomet. Chem. 645 (2002) 65.
[10] L. Verbit, T.R. Halbert, Mol. Cryst. Liq. Cryst. 30 (1975) 209.
[11] C. Loubser, C. Imrie, J. Chem. Soc., Perkin Trans. 2 (1997) 399;
C. Imrie, P. Engelbrecht, C. Loubser, C.W. McCleland, Appl. Organomet. Chem. 15 (2001) 1;
C. Imrie, C. Loubser, P. Engelbrecht, C.W. McCleland, Y. Zheng, J. Organomet. Chem. 665 (2003) 48.