Synthesis and electrochemical properties of N-(ferrocenylmethyl)aminobenzonitrile and N-(ferrocenylmethyl)nitroaniline derivatives

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ABSTRACT

Seven novel ferrocene derivatives containing (methylamino)benzonitrile and N-methylnitroaniline groups (3a-3f and 4) have been synthesized by conventional methods and characterized by FT-IR, NMR and cyclic voltammetry. The electrochemical behavior of these compounds (3a-3f) has been studied by cyclic voltammetry measurements at a platinum electrode in acetonitrile/0.1 M TBAP. The ferrocenyl group in all compounds showed similar reversible one-electron redox process, suggesting that the ferrocene moieties are equivalent and that there are no interactions among them. The formal potential, $E^{0'}$, is shifted to the more positive potential, indicating that the (methylamino)benzonitrile and N-methylnitroaniline introduced to ferrocene moiety exercise an electron-withdrawing effect.

1. INTRODUCTION

In recent years, the design of new ferrocene derivatives has been of considerable interest, because of their utility in organic synthesis[1], catalysis[2], materials science[3,5], asymmetric synthesis[6], medicinal chemistry[7-8] and electrochemistry[9-12]. Our interests in ferrocene derivatives containing (methylamino)benzonitrile and N-methylnitroaniline groups arises from the fact that similar compounds such as N-(ferrocenylmethyl)benzene-carboxamide derivatives possess broad range of biological activities[13]. Moreover, ferrocene derivatives that contain aminobenzonitrile and nitroaniline moieties are capable of undergoing easy transformation into a variety of functionally useful ferrocenes[14-16].

The incorporation of (methylamino)benzonitrile and N-methylnitroaniline in a ferrocene moiety could provide new derivatives with important biological activities since several ferrocene derivatives have already been shown to be active against a number of tumors[17-19]. Herein we report the synthesis, characterization and electrochemical behavior of a series of N-(ferrocenylmethyl)aminobenzonitrile and N-(ferrocenylmethyl)nitroaniline derivatives which combine the ferrocene moiety with (methylamino)benzonitrile and N-methylnitroaniline groups.

2. RESULTS AND DISCUSSION

2.1. Synthesis of compounds (3a-3f and 4)

In this work we describe the synthesis of N-(ferrocenylmethyl)nitroaniline (3a-3c), (ferrocenylmethylamino)benzonitrile (3d-3f), and -3-(diferrocenylmethylamino)benzonitrile (4) from the direct reaction of the quaternary salt (ferrocenylmethyl)trimethylammonium iodide (2) and the corresponding nitroaniline and aminobenzonitrile.

The well-known quaternary salt (ferrocenylmethyl)trimethylammonium iodide (2) was synthesized cleanly and in high yield from ferrocene (1) according to the reported methods of J. M. Osgerby and P. L. Pauson [20] (Scheme 1).

Scheme 1. Synthesis of (ferrocenylmethyl)trimethylammonium iodide

Reaction of this salt (2) with nitroaniline and aminobenzonitrile produced the corresponding N-(ferrocenylmethyl)nitroaniline derivatives (3a-3c) and N-(ferrocenylmethylamino)benzonitrile derivatives (3d-3f), (Scheme 2). All compounds gave analytical and spectroscopic data in accordance with the proposed structures.

Scheme 2. Synthesis of N-(ferrocenylmethyl)nitroaniline and (ferrocenylmethylamino)benzonitrile derivatives, 3a X = 2-NO₂, 3b X = 3-NO₂, 3c X = 4-NO₂, 3d X = 2-CN, 3e X = 3-CN, 3f X = 4-CN,

¹H NMR spectra for all compounds 3a-3f show five protons of the unsubstituted cyclopentadienyl ring (η^5 -C₅H₅) as a strong singlet at δ 4.19-4.27. The protons of the methylene unit adjacent to the ferrocene moiety appear as a doublet (J = 4.72 to 5.13 Hz) at δ 3.96-4.14 often overlapping with the singlet of the (η^5 -C₅H₅) ring. The aromatic protons of the benzene ring appear at δ 6.04-8.23 for all derivatives. In addition, the protons in the ortho-position are shifted downfield compared with those in the meta- and para-positions.

¹³C NMR spectra of compounds 3a-3f show signals typical of the unsubstituted ferrocene ring (η^5 -C₅H₅) at δ 68.78-69.09. The signals of the substituted ring (η^5 -C₅H₄) appear between δ 67.29 and 85.60. The signals corresponding to the quaternary carbon are absent in the DEPT spectra.

The bisferrocenyl compound (4) was also isolated from the reaction of (ferrocenylmethyl)trimethylammonium iodide (2) and 3-aminobenzonitrile, (Scheme 3). This unexpected formation of the complex (4) is probably due to the attack of the nitrogen atom of the formed compound 3-(ferrocenylmethylamino)benzonitrile (3e) on (ferrocenylmethyl)trimethylammonium iodide (2).

Scheme 3. 3-(diferrocenylmethylamino)benzonitrile

The ten protons of the two unsubstituted cyclopentadienyl rings of compound 4 appear as a strong singlet at δ 4.17, whereas the protons of the methylene group appear as a singlet at δ 4.26. The

aromatic protons of the benzene ring are shifted downfield compared with the corresponding protons in compounds (3a-3f).

^{13}C NMR spectra of compound 4 show the signal of the two unsubstituted cyclopentadienyl rings at δ 69.12 and the signals of the two substituted rings between δ 68.37 and 69.33.

2.2. Cyclic voltammetry study

Cyclic voltammetry measurements were performed in an electrochemical cell with a volumetric capacity of 50 mL containing a platinum working electrode of surface area 2 mm^2 , a platinum wire counter electrode of surface area 5 mm^2 , and an $\text{Hg}/\text{Hg}_2\text{Cl}_2$ reference electrode (saturated with KCl). The potential was swept starting from 0 to +650 mV with a scanning rate of $100\text{ mV}\cdot\text{s}^{-1}$. All electrochemical experiments were carried out in acetonitrile under a moisture-free nitrogen atmosphere. Tetrabutylammonium perchlorate (TBAP) was used as a supporting electrolyte.

The voltammograms of new synthesized (ferrocenylmethylamino)benzonitrile (3a-3c) and N-(ferrocenylmethyl)nitroaniline derivatives (3d-3f) in acetonitrile (10^{-3} M) are shown in Fig. 1. Electrochemical studies showed shift of the ferrocene oxidation wave to more positive potentials with maximum shifts for compound 3d. All studied compounds showed one pair of redox waves corresponding to one electron transfer process. The electrochemical results of the investigated compounds were compared to that of ferrocene and summarized in Table 1.

The electrochemical parameters in Table 1 indicate that there is a significant difference between the electrochemical behaviors of compounds (3a-3f) and ferrocene. The results also indicate that the oxidation/reduction couple appears to be reversible with a separation peak of almost 71 mV (similar to that found for ferrocene under similar conditions). This value of the separation peak are, however, significantly greater than the ideal value of 60 mV for a fully reversible one-electron processes. This may be due to a combination of uncompensated solution resistance and slightly slow electron-transfer kinetics. The anodic and cathodic current intensities ratios are close to the unity which indicates the reversibility of the systems. These results also indicate a small positive shift in the formal potential values $E^{0'}$ of all studied compounds. This shift can be attributed to the replacement of hydrogen atom in ferrocene by the electron withdrawing N-methylnitroaniline groups in compounds 3a-3c and (methylamino)benzonitrile groups in compounds 3d-3f, which facilitate the redox process of compounds (3a-3f).

These results further show that the separation of the anodic and the cathodic peak potentials, ΔE_p values, are almost the same for compounds (3a) and (3b), while, a small positive shift in the formal potential $E^{0'}$ (33.7 mV) for compound 3a was observed compared to compound (3b). This finding confirms that the introduction of N-methylnitroaniline group in the ortho-position in compound 3a enhances the electron transfer process compared to the meta-position.

Figure 1. Cyclic voltammograms of compounds (3a-3f) (1 mM) in 0.1 M TBAP/MeCN at scan rate of 100 mV/s

Table 1. Electrochemical data for 3a-3f and ferrocene in acetonitrile/0.1 M TBAP

COMPOUND	E_{p_a}	E_{p_c}	$E^{0'}$	ΔE_p	i_{p_a}	i_{p_a}/i_{p_c}
1	452.2	380.4	416.3	71.8	17.7	0.99
3A	497.7	425.9	461.8	71.8	9.66	0.99
3B	463.8	392.4	428.1	71.4	6.08	1.04
3C	474.9	402.5	438.7	72.4	5.84	1.04
3D	507.7	436.9	472.3	70.8	12.35	1.04
3E	492.1	404.3	448.2	87.8	4.66	1
3F	493.6	405.4	449.5	88.2	16.38	1.01

E_{p_a} and E_{p_c} are the oxidation and reduction wave potential; $E^{0'}$ formal potential, ΔE_p separation peak, i_{p_a} and i_{p_c} are the oxidation and reduction peak currents. The potentials are listed versus SCE.

The peak current of all studied compounds (3a-3f) are markedly affected by the scan rate. The plots of i_p versus $v^{1/2}$ (i_p = anodic peak intensity and v = scan rate) for all derivatives were linear which indicates that the oxidation is Nernstian and is controlled by diffusion.

3. EXPERIMENTAL

3.1. Equipment and materials

2-nitroaniline (98%), 3-nitroaniline (98%), 4-nitroaniline (98%), 4-aminobenzonitrile (98%), ferrocene (99%), Orthophosphoric acid (85%), acetone (99.5%), hexane (99%) were purchased from Alfa Aesar. 2-Aminobenzonitrile (Antranilotrile) (98%), 3-aminobenzonitrile (98%), magnesium sulfate anhydrous (97%), and iodomethane were purchased from Acros Organics. Ethanol (95%), toluene p.a. and acetic acid (99-100%) were purchased from Biochem Chemopharma Co (Canada). Formaldehyde (37%) was obtained from Merck Co. All other reagents used were of analytical grade.

3.2. Methods

All reactions were conducted under nitrogen. Solutions were dried over anhydrous magnesium sulphate and evaporated under reduced pressure using a rotary evaporator (rotary

evaporator (IKA Evaporator RV 06-ML). Solvents were purified according to standard methods [30]. Dry acetonitrile was obtained by refluxing under nitrogen over CaH_2 .

3.3. Physical measurements

Voltammograms were obtained using a PGZ301 potentiostat with voltamaster 4 version 7.08 soft ware (radiometer analytical SAS).

^1H NMR spectra were recorded on BRUCKER AC 300 MHz spectrometer at 0°C , and the chemical shifts are reported in ppm relative to the central line of the triplet for CDCl_3 at 7.26 ppm. Coupling constants (J values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

^{13}C NMR and DEPT were recorded on BRUCKER AC 75 MHz spectrometer at 0°C and all are reported in ppm relative to the central line of the triplet for CDCl_3 at 77.16 ppm. The spectra reported are proton decoupled

IR spectra were recorded on SHIMADZU 830-FTIR spectrometer using KBr pellets.

Melting points were obtained on a Gallenkamp melting point apparatus, and are uncorrected.

Column chromatography was performed using silica gel (Merck 230-400 mesh). Thin layer chromatography was performed on precoated 0.25 mm silica gel plates 60F₂₅₄ purchased from Merck.

3.4. Synthesis

(Ferrocenylmethyl)trimethylammonium iodide (2)

This salt was obtained according to literature procedures [26].

General procedure for the synthesis of N-(ferrocenylmethyl)nitroaniline (3a-3c) and (ferrocenylmethylamino)benzonitrile derivatives (3d-3f)

The corresponding aminobenzonitrile (1.83g, 15.48 mmol) or nitroaniline (2.14g, 15.48 mmol) was added in small portions to well-stirred solution of (ferrocenylmethyl)trimethylammonium iodide (6g, 15.48 mmol) in water (120 cm³). The resulting mixture was then heated at $110\text{--}115^\circ\text{C}$ for 6 hours. It was then allowed to cool to room temperature. The resulting precipitate was separated by filtration, washed with water to remove any trace of unchanged quaternary ammonium salt and finally recrystallized to produce the target compound.

N-(ferrocenylmethyl)-2-nitroaniline (3a)

N-(ferrocenylmethyl)-2-nitroaniline (4.85g, 92%) was obtained, as described above, from (ferrocenylmethyl)trimethylammonium iodide and 2-nitroaniline. The product was recrystallized from ethanol 95% to furnish compound (3a) as cinnabar-red needles, m.p. $110\text{--}112^\circ\text{C}$.

ν_{max} (KBr disc) 1614 cm^{-1} ;

^1H NMR: δ 4.14(d, 2H, $J = 4.73\text{ Hz}$, CH_2Fc); 4.21(t, 2H, $J = 1.88\text{ Hz}$, $\eta^5\text{-C}_5\text{H}_4$ ortho); 4.27(s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 4.28(d, 2H, $\eta^5\text{-C}_5\text{H}_4$ meta); 6.68(t, 1H, $J = 7.18\text{ Hz}$, ArH); 6.90(d, 1H, $J = 8.49\text{ Hz}$, ArH); 7.47(t, 1H, $J = 8.12\text{ Hz}$, ArH); 8.23(dd, 1H, $J = 8.12\text{ Hz}$, ArH); 8.37(s, 1H, NH);

^{13}C NMR: δ 42.3 (-ve DEPT) (1C, CH_2Fc); 67.3(2C, $\eta^5\text{-C}_5\text{H}_4$ meta); 68.1(2C, $\eta^5\text{-C}_5\text{H}_4$); 68.8(5C, $\eta^5\text{-C}_5\text{H}_5$); 84.5(1C, $\eta^5\text{-C}_5\text{H}_4$); 113.8(1C, C_6H_4); 115.3(1C, C_6H_4); 126.9(1C, C_6H_4); 131.8(1C, C_6H_4); 136.3(1C, C_6H_4); 144.9(1C, C_6H_4).

N-(ferrocenylmethyl)-3-nitroaniline (3b)

N-(ferrocenylmethyl)-3-nitroaniline (4.98g, 95%) was obtained from (ferrocenylmethyl)trimethylammonium iodide and 3-nitroaniline. The product was recrystallized from ethanol 95% to give alizarin-red crystals, m.p. 118°C .

ν_{max} (KBr disc) 1616.2 cm^{-1} ;

^1H NMR: δ 4.03(d, 2H, $J = 5.13\text{ Hz}$, CH_2Fc); 4.18(t, 2H, $J = 1.83\text{ Hz}$, $\eta^5\text{-C}_5\text{H}_4$ ORTHO); 4.19(s, 1H, NH); 4.21(s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 4.25(t, 2H, $J = 1.83\text{ Hz}$, $\eta^5\text{-C}_5\text{H}_4$ META); 6.86-6.90(dd, 1H, $J = 5.49\text{ Hz}$, ArH); 7.29(t, 1H, $J = 8.05\text{ Hz}$, ArH); 7.45(t, 1H, $J = 2.20\text{ Hz}$, ArH); 7.52(dd, 1H, $J = 8.05\text{ Hz}$, ArH);

^{13}C NMR: δ 43.7(-ve DEPT)(1C, CH_2Fc); 68.7(4C, $\eta^5\text{-C}_5\text{H}_4$ ortho and meta); 69.0(5C, $\eta^5\text{-C}_5\text{H}_5$); 85.5(1C, $\eta^5\text{-C}_5\text{H}_4$); 107.1(1C, C_6H_4); 116.3(1C, C_6H_4); 126.4(1C, C_6H_4); 131.7 and 149.2 (2C, C_6H_4); 149.2 (1C, C_6H_4).

N-(ferrocenylmethyl)-4-nitroaniline (3c)

N-(ferrocenylmethyl)-4-nitroaniline (4.93g, 94%) was obtained from (ferrocenylmethyl)trimethylammonium iodide and 4-nitroaniline. The product was recrystallized from ethanol 95% to afford compound (3c) as pumpkin-orange crystals, m.p. 115°C.

ν_{max} (KBr disc) 1601 cm^{-1} ;

^1H NMR: δ 4.06(d, 2H, $J = 5.13$ Hz, CH_2Fc); 4.19(d, 2H, $J = 1.83$ Hz, $\eta^5\text{-C}_5\text{H}_4$ ortho); 4.21(s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 4.23(s, 1H, NH); 4.24(t, 2H, $J = 1.83$ Hz, $\eta^5\text{-C}_5\text{H}_4$ meta); 6.55(t, 1H, $J = 3.30$ Hz, C_6H_4 ArH); 6.59(t, 1H, $J = 3.29$ Hz, ArH); 8.09(d, 1H, $J = 3.29$ Hz, ArH) 8.14(s, 1H, ArH);

^{13}C NMR: δ 43.3(-ve DEPT)(1C, CH_2Fc); 68.7 (2C, $\eta^5\text{-C}_5\text{H}_4$ meta); 69.1(5C, $\eta^5\text{-C}_5\text{H}_5$); 85.5(1C, $\eta^5\text{-C}_5\text{H}_4$); 70.0(2C, $\eta^5\text{-C}_5\text{H}_4$ ortho); 111.4(2C, C_6H_4); 116.3(2C, C_6H_4); 126.9(1C, C_6H_4); 153.2(1C, C_6H_4).

2-(ferrocenylmethylamino)benzonitrile (3d)

2-(ferrocenylmethylamino)benzonitrile (4.68g, 95.5%) was obtained from (ferrocenylmethyl)trimethylammonium iodide and 2-aminobenzonitrile. The product was recrystallized from aqueous ethanol 95% (1: 2) to give buttercup yellow pellets, m.p. 128°C.

ν_{max} (KBr disc) 1605; 2208 cm^{-1} ;

^1H NMR: δ 4.02(d, 2H, $J = 4.72$ Hz, CH_2Fc); 4.20(t, 2H, $J = 1.70$ Hz, $\eta^5\text{-C}_5\text{H}_4$ ortho); 4.27(s, 2H, $\eta^5\text{-C}_5\text{H}_4$ meta); 4.27(s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 4.99(s, 1H, NH); 6.70(t, 1H, $J = 7.75$ Hz, ArH); 6.74(d, 1H, ArH); 7.42(d, 1H, ArH); 7.44(t, 1H, ArH);

^{13}C NMR: δ 42.6(-ve DEPT)(1C, CH_2Fc); 67.9(2C, $\eta^5\text{-C}_5\text{H}_4$ meta); 68.5(2C, $\eta^5\text{-C}_5\text{H}_4$ ortho); 69.1(5C, $\eta^5\text{-C}_5\text{H}_5$); 85.6(1C, $\eta^5\text{-C}_5\text{H}_4$); 96.0(1C, C_6H_4); 111.0(1C, C_6H_4); 116.9(1C, C_6H_4); 118.4(1C, CN); 133.1(1C, C_6H_4); 134.7(1C, C_6H_4); 150.4(1C, C_6H_4).

4-(ferrocenylmethylamino)benzonitrile (3f)

4-(ferrocenylmethylamino)benzonitrile (4.54g, 92.7%) was obtained from (ferrocenylmethyl)trimethylammonium iodide and 4-aminobenzonitrile. The product was recrystallized from aqueous ethanol 95%-acetone (1:1:1) to furnish golden yellow crystals, m.p. 132°C.

ν_{max} (KBr disc) 2208; 1603 cm^{-1} ;

^1H NMR: δ 4.00(d, 2H, $J = 5.09$ Hz, CH_2Fc); 4.18(t, 2H, $J = 1.70$ Hz, $\eta^5\text{-C}_5\text{H}_4$ ortho); 4.19(s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 4.23(t, 2H, $J = 1.70$ Hz, $\eta^5\text{-C}_5\text{H}_4$ meta); 4.45(s, 1H, NH); 6.58-6.61(d, 2H, ArH); 7.42-7.45(d, 2H, ArH);

^{13}C NMR: δ 43.0(-ve DEPT)(1C, CH_2Fc); 68.5(2C, $\eta^5\text{-C}_5\text{H}_4$ meta); 68.6(2C, $\eta^5\text{-C}_5\text{H}_4$ ortho); 70.0(5C, $\eta^5\text{-C}_5\text{H}_5$); 85.2(1C, $\eta^5\text{-C}_5\text{H}_4$); 99.1(1C, C_6H_4); 112.5(2C, C_6H_4); 120.8(1C, CN); 134.1(2C, C_6H_4 and $\eta^5\text{-C}_5\text{H}_4$); 151.3(1C, C_6H_4).

3-(diferrocenylmethylamino)benzonitrile (4)

Following the same general procedure as described for the synthesis of compounds (3a-3f), two products were obtained from the reaction of (ferrocenylmethyl)trimethylammonium iodide (6g, 15.48 mmol) and 3-aminobenzonitrile (1.83g, 15.48mmol). They were separated by column chromatography using a mixture of hexane/toluene as eluent.

The first red/orange fraction ($R_f = 0.56$ in 3:7 hexane/toluene) was collected to give 3-(diferrocenylmethylamino)benzonitrile (4) which was recrystallized from acetone to yield (2.25g, 28%) of pumpkin-orange crystals, m.p. 171°C.

ν_{max} (KBr disc) 2224; 1602 cm^{-1} ;

^1H NMR: δ 4.09-4.14(d, 4H, $2\eta^5\text{-C}_5\text{H}_4$ ortho); 4.17(s, 10H, $2\eta^5\text{-C}_5\text{H}_5$); 4.23(s, 4H, $2\eta^5\text{-C}_5\text{H}_4$ meta); 4.26(s, 4H, $(\text{CH}_2\text{Fc})_2$); 6.93(d, 1H, ArH); 7.22(d, 1H, ArH); 7.03(s, 1H, ArH); 6.98(q, 1H, ArH);

^{13}C NMR: δ 49.1(-ve DEPT)(2C, $(\text{CH}_2\text{Fc})_2$); 68.3(4C, $2\eta^5\text{-C}_5\text{H}_4$ meta); 69.1(10C, $2\eta^5\text{-C}_5\text{H}_5$); 69.3(4C, $2\eta^5\text{-C}_5\text{H}_4$ ortho); 84.2(2C, $2\eta^5\text{-C}_5\text{H}_4$); 113.1(1C, C_6H_4); 120.1 (1C, CN); 130.1(1C, C_6H_4); 149.1(1C, C_6H_4); 116.1-117.5 (2C, C_6H_4).

3-(ferrocenylmethylamino)benzonitrile (3e)

Further elution of the second fraction ($R_f = 0.4$ in 3:7 hexane/toluene) with the same mixture of solvents gave 3-(ferrocenylmethylamino)benzonitrile which was recrystallized from acetone to yield (2.30 g, 47%) of red orange crystals, m.p. 126°C .

ν_{max} (KBr disc) 2224; 1599 cm^{-1} ;

^1H NMR: δ 4.14(d, 2H, $\eta^5\text{-C}_5\text{H}_4$ ortho); 4.17(s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 4.22(s, 2H, $\eta^5\text{-C}_5\text{H}_4$ meta); 4.26(s, 2H, CH_2Fc); 5.00(s, 1H, NH); 6.93(d, 1H, $J = 7.36\text{ Hz}$, ArH); 6.98(dd, 1H, $J = 8.5\text{ Hz}$ ArH); 7.03(s, 1H, ArH); 7.22(d, 1H, $J = 7.93\text{ Hz}$, ArH);

^{13}C NMR: δ 49.1(-ve DEPT)(1C, CH_2Fc); 68.4(2C, $\eta^5\text{-C}_5\text{H}_4$ meta); 69.1(5C, $\eta^5\text{-C}_5\text{H}_5$); 69.3(2C, $\eta^5\text{-C}_5\text{H}_4$ ortho); 84.2(1C, $\eta^5\text{-C}_5\text{H}_4$); 113.1(1C, C_6H_4); 120.1(1C, CN); 130.1(1C, C_6H_4); 119.8(1C, CN); 121.0(1C, C_6H_4); 130.2(1C, C_6H_4); 149.1(1C, C_6H_4).

4. CONCLUSION

In summary, we have successfully synthesized and characterized seven ferrocene derivatives containing N-methylnitroaniline and (methylamino)benzonitrile groups. Electrochemical studies show that the electron-withdrawing N-methylnitroaniline and (methylamino)benzonitrile groups introduced to ferrocene influence the redox potential of the iron centre. This may be due to the non-insulating effect of the methylene between the nitroaniline or aminobenzonitrile group and the cyclopentadienyl ring of the ferrocene. The electron-withdrawing character of N-methylnitroaniline decreases in the order $3a > 3c > 3b$, whereas the electron-withdrawing character of (methylamino)benzonitrile decreases in the order $3d > 3f \approx 3e$.

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