RESEARCH ARTICLE

V.O. Nyamori and C. Imrie,
S. Afr. J. Chem., 2009, **62**, 97–101,
<http://journals.sabinet.co.za/sajchem/>.

97

Hydrogenation Reactions in Ionic Liquids. The Efficient Reduction of Nitroarenes, including Nitroferrocenyl Derivatives, to the Corresponding Aminoarenes in [bmim][BF₄]

Vincent O. Nyamori[a*] and Christopher Imrie[b†]

[a]*School of Chemistry, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban 4000, South Africa.*

[b]*Department of Chemistry, Nelson Mandela Metropolitan University, P.O. Box 77000, Port Elizabeth 6031, South Africa.*

ABSTRACT

The catalytic hydrogenation of nitroarenes, including a series of nitroferrocenyl derivatives, to aminoarenes has been successfully achieved in the ionic liquid [bmim][BF₄]. The isolated yields of the aminoarenes are very good and recycling of the solvent and catalyst has been achieved.
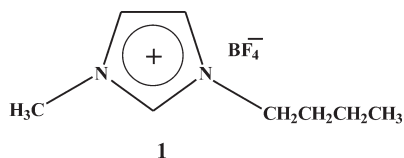
KEYWORDS

Aminoarenes, hydrogenation, ionic liquids, nitroarenes, ferrocenes.
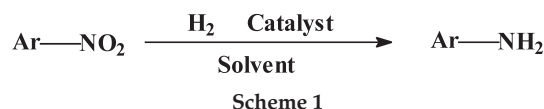
1. Introduction

Aminoarenes are widely used in the chemical industry as intermediates, end-products and in the preparation of a large variety of fine chemicals. They are used in the preparation of dyes,[1] pigments,[2] rubbers,[3] agrochemicals[4] and pharmaceuticals.[5]

Heterogeneous catalytic hydrogenation (Scheme 1) is one of the most useful and widely applied methods for the reduction of nitroarenes to aminoarenes. Many aspects of this type of reaction are appealing in terms of green chemistry. The advantage of this approach is that the reaction can be carried out in a closed system and assuming that there is complete conversion, the major waste of the reaction is solvent and catalyst.

Volatile organic solvents such as ethanol, methanol and THF are often used for the catalytic hydrogenation of nitroarenes.[6] Room temperature ionic liquids have been attracting considerable interest as environmentally benign reaction media for synthetic chemistry.[7] For example, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]][BF₄]) **(1)** and similar dialkylimidazolium salts have been successfully employed as reaction media in a range of reactions including Friedel-Crafts,[8] Diels-Alder,[9] allylation,[10] esterification,[11] Wittig,[12] Heck,[13] Suzuki,[14] oxidation[15] and reduction,[16] including catalytic hydrogenation of dienes[17] and monoalkenes.[18]

1

Apart from our own contribution involving the synthesis of ferrocenoyl esters in [bmim][BF₄] and [bmim][PF₆],[11] there have been few other contributions to date which involve the chemistry of ferrocenes in ionic liquids.[19] Dyson *et al.* have reported on ligand exchange reactions of ferrocene in chloroaluminate (III) ionic liquids.[19a] In a more recent paper, this methodology was

Scheme 1
General catalytic reduction of nitroarenes to aminoarenes.

utilized by the same group to make transition metal-cyclophane complexes.[19b] Stark *et al.*[19c] have investigated the acylation of ferrocene in acidic [emim]I-(AlCl₃)ₓ solutions. Ionic liquids possess a number of desirable properties in terms of green chemistry.

Notably they have low vapour pressures, are non-flammable and can be readily recycled. In this work, we present our results on the catalytic hydrogenation of nitroarenes, including a range of nitroferrocenyl derivatives, to aminoarenes in [bmim][BF₄]. Some of the nitroferrocenyl derivatives and the corresponding ferrocenylanilines are new compounds and to our knowledge they have not been reported in the literature. These compounds could be useful as metal ligands[20] and potential ferrocenomesogens[21] as reported in our earlier papers.
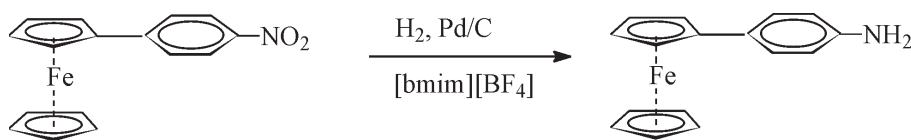
2. Results and Discussion

2.1. Catalytic Hydrogenation of 4-Nitrophenylferrocene

A wide variety of catalysts has been used for the catalytic hydrogenation of nitroarenes to aminoarenes.[2] We began our study by using palladium (10 %) on charcoal. In terms of model reactions, we decided to use the conversion of 4-nitrophenylferrocene to 4-ferrocenylaniline (Scheme 2), since the product is easily identified, is a relatively stable solid and our research group has considerable experience in the field of arylferrocenes.[20–22]

The results for the hydrogenation of 4-nitrophenylferrocene in [bmim][BF₄] using a palladium (10 %) on charcoal catalyst are shown graphically in Fig. 1. The yields are isolated ones based on 4-nitrophenylferrocene starting material. The reactions were performed over two different time periods, *viz.* 24 h and 72 h. After the 72 h reaction time, no further significant reduction was noted. However, in the comparative analysis of 24 h *vs.* 72 h, a

Scheme 2
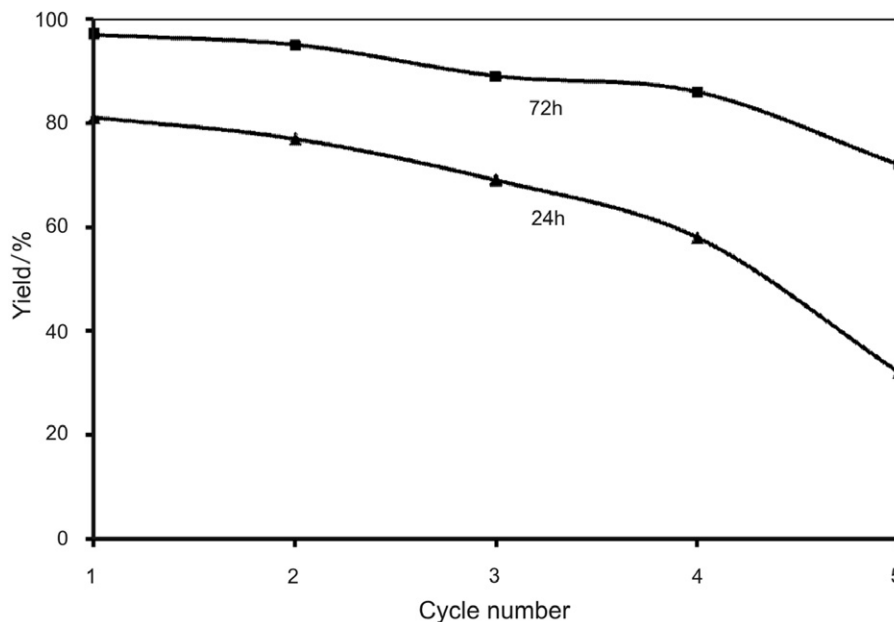Reduction of 4-nitrophenylferrocene to 4-ferrocenylaniline.

Figure 1 Results for the catalytic hydrogenation of 4-nitrophenylferrocene over 5 cycles for 24 h and 72 h reaction periods in [bmim][BF$_4$].

considerable time effect was noted. The results clearly indicate that the reaction proceeds more efficiently over the 72 h period. For example, in the first cycle, the overall isolated yield of the product after 72 h was 97 %, compared with 81 % after 24 h.

The catalyst stability was also investigated. This was achieved by recycling the ionic liquid and catalyst four times and repeating the reaction. For the 72 h period, the isolated yields of product remained consistently high and only declined markedly on the fifth cycle. Analysis of the ionic liquid at the end of the series of reactions by means of ^{1}H and ^{13}C NMR spectroscopy showed that it had remained relatively uncontaminated and intact. This suggested that the decline in the yield was due to a decrease in the activity of the catalyst. A small percentage of the ionic liquid was lost after each reaction cycle due to inefficiencies in the transferral of the viscous liquid from the hydrogenation reactor to the extractor. However, the loss of ionic liquid should not have any effect on the catalyst activity.

The same reaction was reinvestigated by using different transition metal catalysts, namely, PtO$_2$, Rh/Al$_2$O$_3$ (5 %) and Ru/Al$_2$O$_3$ (5 %). The results are reported in Table 1. It is clear that with the current reaction conditions, palladium (10 %) on charcoal was the best catalyst whilst Ru/Al$_2$O$_3$ (5 %) was very inefficient. This trend correlates well with previous work in which palladium catalysts, in particular in the form supported on carbon, have frequently been employed for the hydrogenation of aromatic nitro compounds and have been preferred to PtO$_2$ because of their high activity, as well as a lower tendency towards hydrogenation of the aromatic ring.[23] The reduction of several other nitroferrocenyl derivatives (**2–6**) was efficiently undertaken in [bmim][BF$_4$].

The major impetus behind research into ionic liquid chemistry stems from the desire to introduce it into important industrial processes. With this in mind, we turned our attention to the catalytic reduction of various substituted nitroarenes, many of which are important intermediates in the chemical industry. Reactions were carried out in [bmim][BF$_4$] with a palladium (10 %) on charcoal catalyst and a 72 h reaction time period, and the results are shown in Fig. 2.

The reduction of nitrobenzene was very efficient, providing aniline in a yield of 98 %. Nitrobenzene was used as a reference with which other substituted benzenes were compared. In the case of the chloronitrobenzenes, the yields of product were slightly lower, and this could be due to a competitive dehalogenation reaction, which has been observed for these substrates in volatile organic solvents.[24] However, substituents on the *para*, *ortho* and *meta* positions of the substituted nitrobenzenes did not show much steric effect. The *meta*-substituted derivatives had slightly lower yields but this cannot necessarily be attributed to the steric factors (Fig. 2). The reduction of nitrophenols and nitrobenzoic acids under the same conditions was also attempted but ran into problems due to solubility issues in terms of extracting the product out of the ionic liquid. The yields of isolated product from these reactions were consistently low and we are currently investigating the extraction process with supercritical CO$_2$, since this could prove to be more efficient and more environmen-

Table 1 Yield of 4-ferrocenylaniline from the catalytic hydrogenation of 4-nitrophenylferrocene in [bmim][BF$_4$] using different catalysts.
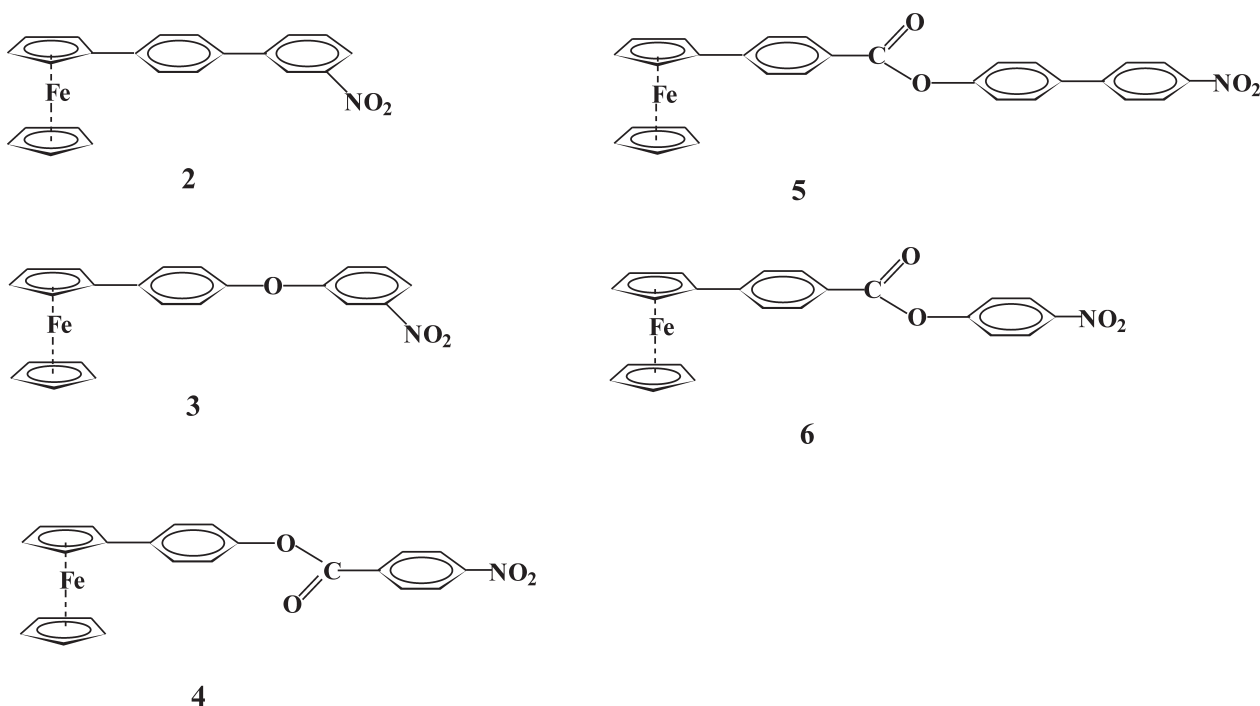
Catalyst	Yield/%[a]
Pd/C (10 %)	96
PtO$_2$	69
Rh/Al$_2$O$_3$ (5 %)	60
Ru/Al$_2$O$_3$ (5 %)	31

[a] Yields are isolated ones based on 4-nitrophenylferrocene starting material.

RESEARCH ARTICLE

V.O. Nyamori and C. Imrie,
S. Afr. J. Chem., 2009, **62**, 97–101,
<http://journals.sabinet.co.za/sajchem/>.

99

2

5

3

6

4

tally friendly.[25] Moreover, the hydrogenation of nitro compounds in green solvents (such as supercritical CO_2 and H_2O) has been studied previously.[26]
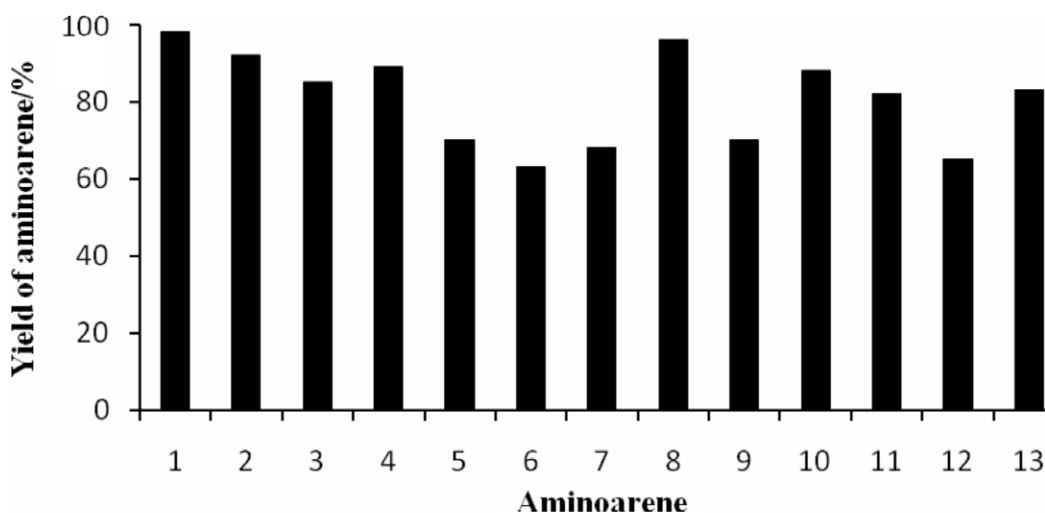
3. Conclusion

The catalytic reduction of a range of aromatic nitroarenes in [bmim][BF$_4$] by using palladium (10 %) on charcoal as catalyst was very successful. The overall isolated yields of product were excellent and efficient recovery and reuse of the ionic liquid and catalyst were achieved. The quality of the ionic liquid after a series of cycles remained high and loss was mainly due to inefficient transfer between the hydrogenation reactor and extractor.

4. Experimental

4.1. Purification and Characterization of the Materials

Infrared spectra were recorded on either a Perkin Elmer 1600 series instrument (Downers Grove, IL, USA) or a Nicolet Magna 550 Fourier transform spectrometer (Madison, WI, USA) as KBr discs or as solutions in chloroform. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AX 300 MHz spectrometer (Rheinstetten, Germany) at room temperature. Mass spectra were recorded on a high resolution VG70-SEQ spectrometer (Manchester, UK) with a 70 eV direct insertion probe or FAB. The Parr hydrogenation reactor (Moline, IL, USA) used for catalytic reduction was a Parr

1 = aniline
2 = 4-methylaniline
3 = 3-methylaniline
4 = 2-methylaniline
5 = 4-chloroaniline
6 = 3-chloroaniline
7 = 2-chloroaniline

8 = 4-ferrocenylaniline
9 = 4-ferrocenyl-biphenyl-3-ylamine
10 = 3-(4-ferrocenyl-phenoxy)-phenylamine
11 = 4-amino-benzoic acid 4'-ferrocenylphenyl ester
12 = 4-ferrocenyl-benzoic acid 4'-amino-biphenyl-4-yl ester
13 = 4-ferrocenyl-benzoic acid 4-amino-phenyl ester

Figure 2 Results of the reduction of various nitroarenes to corresponding aminoarenes with Pd/C (10 %), 72 h reaction time, in [bmim][BF$_4$].

RESEARCH ARTICLE

V.O. Nyamori and C. Imrie,
S. Afr. J. Chem., 2009, **62**, 97–101,
<http://journals.sabinet.co.za/sajchem/>.

100

4522 reactor with a 482 controller. Rhodium (5 %) on alumina and ruthenium (5 %) on alumina were obtained from Lancaster Chemicals, Morecambe, UK. Platinum (IV) oxide was supplied by the Aldrich Chemical Company, Milwaukee, WI, USA. Palladium (10 %) on charcoal was obtained from BDH Laboratory, Poole, UK. All other common laboratory chemicals were of analytical grade and were used without further purification. [Bmim][Cl][27] was used as the precursor for the synthesis of [bmim][BF$_4$].[28]

4.2. Catalytic Hydrogenation of 4-Nitrophenylferrocene to 4-Ferrocenylaniline in [bmim][BF$_4$]

4.2.1. *General Procedure*

A mixture of 4-nitrophenylferrocene (0.5 g, 1.63 mmol), palladium (10 %) on charcoal (0.5 g) and [bmim][BF$_4$] (200 mL) was stirred under H$_2$ in a Parr hydrogenation reactor for 72 h at room temperature. The colour of the mixture changed from deep red to black. The reaction mixture was then placed in a liquid–liquid extractor and extracted continuously for 72 h with diethyl ether. The extract was then concentrated to give a crude product which was subjected to chromatography on silica gel with hexane/diethyl ether as the eluent. The orange band was collected and concentrated to give yellow crystals of 4-ferrocenylaniline (0.44 g, 97 %), m.p. 159 °C (lit.[29] 159–160 °C); ν_{max} (KBr): 3475, 3382, 3102, 1619, 1529, 1455, 1280, 1102, 1012, 817, 640, 531, 507 cm^{-1}; δ_H (300 MHz, CDCl$_3$): 7.28 (2H, d, J 8.5 Hz, ArH), 6.63 (2H, d, J 8.5 Hz, ArH), 4.53 (2H, t, J 1.8 Hz, C$_5$H$_4$), 4.23 (2H, t, J 1.8 Hz, C$_5$H$_4$), 4.04 (5H, s, C$_5$H$_5$), 3.61 ppm (2H, s, NH$_2$); δ_C (300 MHz, CDCl$_3$): 144.94, 129.40, 127.54, 115.59, 96.51, 86.95, 68.58, 66.20 ppm; *m/z*: 278 (M+1, 20 %), 277 (M$^+$, 100 %), 156 (13 %), 121 (4 %); (found: M$^+$, 277.0563, C$_{16}$H$_{15}$FeN requires 277.0551).

4.2.2. *General Procedure for the Recycling Reaction*

A mixture of 4-nitrophenylferrocene (100 mg, 0.33 mmol), palladium (10 %) on charcoal (100 mg) and [bmim][BF$_4$] (200 mL) was stirred under H$_2$ in a Parr hydrogenation reactor for either 24 h or 72 h at room temperature. The rest of the procedure was as given above, except that after extraction and removal of residual ether from the ionic liquid, the remaining ionic liquid/catalyst mixture was reused. Before reuse, the ionic liquid/catalyst mixture was washed with anhydrous diethyl ether and dried under reduced pressure. The recycling experiment was repeated four times and the product was in each case characterized as in the general procedure.

4.2.3. *General Procedure for Usage of Different Catalysts*

A mixture of 4-nitrophenylferrocene (200 mg, 0.65 mmol), the catalyst (200 mg) and [bmim][BF$_4$] (50 mL) was stirred under H$_2$ in a Parr hydrogenation reactor for 72 h at room temperature. The rest of the experiment was carried out as in the general procedure. The product 4-ferrocenylaniline was obtained and characterized as before. Yields: palladium (10 %) on charcoal (172 mg, 96 %); platinum (IV) oxide (124 mg, 69 %); rhodium (5 %) on alumina (107 mg, 60 %); ruthenium (5 %) on alumina (56 mg, 31 %).

4.2.4. *Catalytic Hydrogenation of Nitroarenes to Aminoarenes in [bmim][BF$_4$]*

Experimental procedure was as in the general procedure for the catalytic hydrogenation of 4-ferrocenylaniline. In all reactions, the nitroarene (0.50 g) was used except in the case of nitrobenzene (1.00 g). Yields: aniline (0.74 g, 98 %); 4-methylaniline (360 mg, 92 %); 3-methylaniline (332 mg, 85 %); 2-methylaniline (348 mg, 89 %); 4-chloroaniline (248 mg, 70 %); 3-chloroaniline (256 mg, 63 %); 2-chloroaniline (276 mg, 68 %).

4.2.5. *Catalytic Hydrogenation of Elongated Nitroferrocenyl Derivatives in [bmim][BF$_4$]*

4-Ferrocenyl-biphenyl-3-ylamine

A mixture of 4-ferrocenyl-3-nitro-biphenyl (150 mg, 0.39 mmol) (**2**), palladium (10 %) on charcoal (150 mg) and [bmim][BF$_4$] (50 mL) was stirred under H$_2$ in a Parr hydrogenation reactor for 72 h at room temperature. The rest of the experiment was carried out as in the general procedure. Yellow crystals of 4-ferrocenyl-biphenyl-3-ylamine were obtained (101 mg, 70 %), m.p. 125–126 °C; ν_{max} (KBr): 3689, 3015, 2362, 1649, 1602, 1531,1492, 1457, 1410, 1318, 1231, 1200 cm^{-1}; δ_H (300 MHz, CDCl$_3$): 7.52–7.43 (4H, m, ArH), 7.22 (1H, d, J 7.8 Hz, ArH), 7.02 (1H, m, ArH), 6.93 (1H, m, ArH), 6.67 (1H, m, ArH), 4.67 (2H, t, J 1.8 Hz, C$_5$H$_4$), 4.33 (2H, t, J 1.8 Hz, C$_5$H$_4$), 4.06 ppm (5H, s, C$_5$H$_5$); δ_C (300 MHz, CDCl$_3$): 147.10, 142.54, 139.16, 138.74, 130.09, 127.35, 126.76,117.77, 114.36, 113.94, 85.47, 70.18, 69.37, 66.89 ppm; *m/z* 353 (M$^+$, 100 %), 352 (5 %), 351 (M-[C$_{23}$H$_{19}$Fe], 8 %), 232 (M-[C$_{17}$H$_{14}$N], 9 %), 176 (11 %); (found: C, 75.1; H, 3.5; N, 6.6; M$^+$, 353.08572. C$_{23}$H$_{19}$FeN requires C, 74.8; H, 3.9; N, 5.4 %; M$^+$, 353.08669).

3-(4-Ferrocenyl-phenoxy)-phenylamine

A mixture of 4-(3-nitro)phenoxyphenylferrocene (220 mg, 0.55 mmol) (**3**), palladium (10 %) on charcoal (150 mg) and [bmim][BF$_4$] (50 mL) was stirred under H$_2$ in a Parr hydrogenation reactor for 72 h at room temperature. The rest of the experiment was carried out as in the general procedure. The product 3-(4-ferrocenyl-phenoxy)-phenylamine was obtained as orange crystals (179 mg, 88 %), m.p. 139–140 °C; ν_{max} (KBr): 3483, 3389, 1610, 1519, 1489, 1451, 1287, 1224, 1173, 1146, 1105, 841 cm^{-1}; δ_H (300 MHz, CDCl$_3$): 7.41–7.28 (2H, m, ArH), 7.19 (1H, t, J 7.9 Hz, ArH), 6.94 (1H, d, J 5.8 Hz, ArH), 6.58 (2H, d, J 7.5 Hz, ArH), 6.53 (2H, d, J 7.5 Hz, ArH), 4.80 (2H, t, J 1.8 Hz, C$_5$H$_4$), 4.49 (2H, t, J 1.8 Hz, C$_5$H$_4$), 4.21 (5H, s, C$_5$H$_5$), 3.80–3.50 ppm (2H, broad, NH$_2$); δ_C (300 MHz, CDCl$_3$): 158.99, 155.60, 134.66, 130.81, 127.72, 119.53, 119.53, 119.30, 111.10, 109. 96, 106.48, 86.13, 70.18, 69.35, 66.86 ppm; *m/z* 369 (M$^+$, 100 %), 277 (2 %), 261 (3 %), 185 (5 %), 121 (7 %); (found M$^+$, 369.08109. C$_{22}$H$_{19}$OFeN requires M$^+$, 369.08160).

4-Amino-benzoic Acid 4-Ferrocenylphenyl Ester

A mixture of 4-nitro-benzoic acid 4-ferrocenylphenyl ester (40 mg, 0.094 mmol) (**4**), palladium (10 %) on charcoal (50 mg) and [bmim][BF$_4$] (50 mL) was stirred under H$_2$ in a Parr hydrogenation reactor for 72 h at room temperature. The rest of the experiment was carried out as in the general procedure. 4-Amino-benzoic acid 4'-ferrocenylphenyl ester was obtained as orange crystals (31 mg, 82 %), m.p. 211–213 °C; ν_{max} (KBr): 3433, 3558, 3233, 3091, 2966, 2892, 1708, 1633, 1616, 1533, 1458, 1316, 1275, 1216, 1158, 1083, 1008, 875, 858 cm^{-1}; δ_H (300 MHz, CDCl$_3$): 8.02 (2H, d, J 7.9 Hz, ArH), 7.50 (2H, d, J 8.6 Hz, ArH), 7.12 (2H, d, J 8.6 Hz, ArH), 6.70 (2H, d, J 8.6 Hz, ArH), 4.62 (2H, t, J 1.8 Hz, C$_5$H$_4$), 4.31 (2H, t, J 1.8 Hz, C$_5$H$_4$), 4.16 (2H, s, NH$_2$), 4.06 ppm (5H, s, C$_5$H$_5$); δ_C (300 MHz, CDCl$_3$): 165.6, 151.8, 149.7, 137.0, 132.7, 127.4, 122.1, 119.2, 114.3, 85.4, 70.0, 69.3, 67.0 ppm; *m/z*: 398 (M+1, 12 %), 397 (M$^+$, 44 %), 279 (19 %), 278 (100 %), 277 (7 %), 276 (7 %), 121 (11 %), 120 (37 %); (found: M$^+$, 397.0764; C$_{23}$H$_{19}$FeNO$_2$ requires M$^+$, 397.0762).

4-Ferrocenyl-benzoic Acid 4-Amino-biphenyl-4-yl Ester

A mixture of 4-ferrocenyl-benzoic acid 4-nitrobiphenyl-4-yl ester (160 mg, 0.32 mmol) (**5**), palladium (10 %) on charcoal (125 mg) and [bmim][BF$_4$] (50 mL) was stirred under H$_2$ in a Parr hydrogenation reactor for 72 h at room temperature. The rest of

the experiment was carried out as in the general procedure. Orange crystals of 4-ferrocenyl-benzoic acid 4-amino-biphenyl-4-yl ester were obtained (98 mg, 65 %), m.p. 228–230 °C; ν_{max} (KBr): 3446, 3365, 3089, 2922, 1618, 1530, 1492, 1455, 1406, 1313, 1227, 1104, 1000, 834, 780, 698, 497 cm^{-1}; δ_H (300 MHz, CDCl$_3$): 8.13 (2H, d, *J* 8.4 Hz, ArH), 7.59 (2H, d, *J* 8.5 Hz, ArH), 7.58 (2H, d, *J* 8.7 Hz, ArH), 7.25 (2H, d, *J* 8.6 Hz, ArH), 6.77 (2H, d, *J* 8.4 Hz, ArH), 4.75 (2H, t, *J* 1.8 Hz, C$_5$H$_4$), 4.42 (2H, t, *J* 1.8 Hz, C$_5$H$_4$), 4.06 (5H, s, C$_5$H$_5$), 3.76 ppm (2H, s (broad), NH$_2$); δ_C (300 MHz, CDCl$_3$): 165.74, 150.11, 146.45, 146.28, 139.34, 131.25, 130.75, 128.42, 127.79, 127.05, 126.16, 122.28, 115.81, 83.51, 70.35, 70.29, 67.38 ppm; *m/z*: 475 (M+3, 5 %), 474 (M+2, 26 %), 473 (M$^+$, 76 %), 290 (7 %), 289 (36 %), 262 (19 %), 261 (100 %), 260 (6 %), 259 (7 %), 205 (8 %), 185 (5 %), 184 (6 %), 139 (11 %); (found: C, 73.6; H, 5.1; N, 2.8 ; M$^+$, 473.10750. C$_{29}$H$_{23}$FeNO$_2$ requires C, 73.6; H, 4.9; N, 2.9 %; M$^+$, 473.10782).

4-Ferrocenyl-benzoic Acid 4-Amino-phenyl Ester

A mixture of 4-ferrocenyl-benzoic acid 4-nitro-phenyl ester (200 mg, 0.5 mmol) (**6**), palladium (10 %) on charcoal (125 mg) and [bmim][BF$_4$] (50 mL) was stirred under H$_2$ in a Parr hydrogenation reactor for 72 h at room temperature. The rest of the experiment was carried out as in the general procedure. Orange crystals of 4-ferrocenyl-benzoic acid 4-amino-phenyl ester were obtained (165 mg, 83 %), m.p. 199 °C; ν_{max} (KBr): 3443, 1720, 1617, 1511, 1429, 1275, 1229, 1203, 1021, 864, 826, 776, 707, 650, 525 cm^{-1}; δ_H (300 MHz, CDCl$_3$): 8.09 (2H, d, *J* 8.5 Hz, ArH), 7.57 (2H, d, *J* 8.5 Hz, ArH), 7.01 (2H, d, *J* 8.7 Hz, ArH), 6.72 (2H, d, *J* 8.7 Hz, ArH), 4.74 (2H, t, *J* 1.8 Hz, C$_5$H$_4$), 4.41 (2H, t, *J* 1.8 Hz, C$_5$H$_4$), 4.05 ppm (5H, s, C$_5$H$_5$); δ_C (300 MHz, CDCl$_3$): 165.7, 145.8, 144.1, 143.2, 130.2, 126.9, 125.7, 122.3, 115.7, 96.1, 83.2, 69.9, 66.9 ppm; *m/z*: 398 (M$^+$, 16 %), 289 (41 %), 262 (20 %), 261 (100 %), 139 (13 %); (found: C, 69.4; H, 4.6; N, 3.5; M$^+$, 397.07699; C$_{23}$H$_{19}$NO$_2$Fe requires C, 69.6; H, 4.8; N, 3.5 %; M$^+$, 397.07652).

Acknowledgements

References

1 S. Suwanprasop, T. Nhujak, S. Roengsumran and A. Petsom, *Ind. Eng. Chem. Res.*, 2004, **43**, 4973–4978.

2 M.A. Hanna, *Pigm. Resin Technol.*, 1991, **20**, 4–7.

3 P.W. Sherwood, *Ind. Eng. Chem.*, 1963, **55**, 29–31.

4 H.U. Blaser, A. Baiker and R. Prins (eds.), *Heterogeneous Catalysis and Fine Chemicals IV*, Elsevier, Amsterdam, the Netherlands, 1997, pp. 17–30.

5 J.M. Fevig, J. Cacciola, R.S. Alexander, R.M. Knabb, G.N. Lam, P.C. Wong and R.R. Wexler, *Bioorg. Med. Chem. Lett.*, 1998, **8**, 3143–3148.

6 S. Nishimura (ed.), *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, John Wiley and Sons, New York, NY, USA, 2001.

7 R.D. Rogers and K.R. Seddon (eds.), *Ionic Liquids: Industrial Applications to Green Chemistry*, American Chemical Society, Washington, DC, USA, 2002.

8 C.J. Adams, M.J. Earle, G. Roberts and K.R. Seddon, *Chem. Commun.*, 1998, 2097–2098.

9 (a) T. Fischer, A. Sethi, T. Welton and J. Woolf, *Tetrahedron Lett.*, 1999, **40**, 793–796; (b) M.J. Earle, P.B. McCormac and K.R.Seddon, *Green Chem.*, 1999, **1**, 23–25.

10 C.M. Gordon and A. McCluskey, *Chem. Commun.*, 1999, 1431–1432.

11 C. Imrie, E.R.T. Elago, C.W. McCleland and N. Williams, *Green Chem.*, 2002, **4**, 159–160.

12 V. Le Boulaire and R. Greé, *Chem. Commun.*, 2000, 2195–2196.

13 R.R. Deshmukh, R. Rajagopal and K.V. Srinivasan, *Chem. Commun.*, 2001, 1544–1545.

14 C.J. Mathews, P.J. Smith and T. Welton, *Chem. Commun.*, 2000, 1249–1250.

15 (a) J. Howarth, *Tetrahedron Lett.*, 2000, **41**, 6627–6629; (b) C.E. Song and E.J. Roh, *Chem. Commun.*, 2000, 837–838; (c) G.S. Owens and M.M. Abu-Omar, *Chem. Commun.*, 2000, 1165–1166.

16 G.W. Kabalka and R.R. Malladi, *Chem. Commun.*, 2000, 2191.

17 J. Dupont, P.A.Z. Suarez, A.P. Umpierre and R.F. de Souza, *J. Braz. Chem. Soc.*, 2000, **11**, 293–297.

18 (a) Y. Chauvin, L. Mussmann and H. Olivier, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 2698–2700; (b) P.J. Dyson, D.J. Ellis, D.G. Parker and T. Welton, *Chem. Commun.*, 1999, 25–26.

19 (a) P.J. Dyson, M.C. Grossel, N. Srinivasan, T. Vine, T. Welton, D.J. Williams, A.J.P. White and T. Zigras, *J. Chem. Soc., Dalton Trans.*, 1997, 3465–3469; (b) D. Crofts, P.J. Dyson, K.M. Sanderson, N. Srinivasan and T. Welton, *J. Organomet. Chem.*, 1999, **573**, 292–298; (c) A. Stark, B.L. MacLean and R.D. Singer, *J. Chem. Soc., Dalton Trans.*, 1999, 63–66.

20 C. Imrie, J.R. Dilworth, Y. Zheng, A. Abrahams, T.I.A. Gerber and V.O. Nyamori, *J. Chem. Soc., Dalton Trans.*, 2001, 2624–2633.

21 C. Imrie, P. Engelbrecht, C. Loubser, C.W. McCleland, V.O. Nyamori, R. Bogardi, D.C. Levendis, N. Tolom and J.L. van Rooyen, *J. Organomet. Chem.*, 2002, **645**, 65–81.

22 (a) C. Imrie and C. Loubser, *J. Chem. Soc., Perkin Trans. 2*, 1997, 399–409; (b) C. Imrie, C. Loubser, P. Engelbrecht and C.W. McCleland, *J. Chem. Soc., Perkin Trans. 1*, 1999, 2513–2523.

23 (a) L.H. Klemm, J.W. Sprague and E.Y.K. Mak, *J. Org. Chem.*, 1957, **22**, 161–166; (b) M. Freifelder, *Catalytic Hydrogenation in Organic Synthesis. Procedures and Commentary*, Wiley-Interscience, New York, NY, USA, 1978, p. 27.

24 (a) R. Baltzly and A.P. Phillips, *J. Am. Chem. Soc.*, 1946, **68**, 261–265; (b) R. Baltzly, *J. Am. Chem. Soc.*, 1952, **74**, 4586–4589.

25 L.A. Blanchard and J.F. Brennecke, *Ind. Eng. Chem. Res.*, 2001, **40**, 287–292.

26 (a) D.-Q. Xu, Z.-Y. Hu, W.-W. Li, S.-P. Luo and Z.-Y. Xu, *J. Mol. Catal. Chem. A*, 2005, **235**, 137–142; (b) P. Maity, S. Basu, S. Bhaduri and G.K. Lahiri, *Adv. Synth. Catal.*, 2007, **349**, 1955–1962.

27 J.S. Wilkes, J.A. Levisky, R.A. Wilson and C.L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263–1264.

28 P.A.Z. Suarez, J.E.L. Dullius, S. Einloft, R.F. De Sousa and J. Dupont, *Polyhedron*, 1996, **15**, 1217–1219.

29 A.N. Nesmeyanov, E.G. Perevalova, R.V. Golovnya and L. Shilov-tsera, *Dokl. Akad. Nauk SSSR*, 1955, **102**, 535–538.