The synthesis of alkylated or acylated nitroarene cyclopentadienyliron complexes: an alternative approach to the synthesis of arylated alkanoates

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Time-dependent oxidation of η^6-alkylaniline-η^5-cyclopentadienyliron hexafluorophosphates, 17–32, allows for the preparation of nitrobenzene complexes with alkyl 33–48 or keto 49 substituents. Alkylnitroarene complexes are prepared by the oxidation of their corresponding aniline complexes with H_2O_2 in CF_3CO_2H for 20 min. An increase in the reaction time to 24 h gives rise to nitroarene complexes with keto substituents in lower yields. The use of nitroarenes as starting materials in the synthesis of alkanoates is of importance since it allows for the preparation of a large number of this class of compounds with a variety of alkyl substituents. Two different approaches have been utilized to allow for the synthesis of alkanoates. The first approach involves nucleophilic aromatic substitution of alkylnitrobenzene complexes with ethyl alkylacetoacetates followed by demetallation to give the alkanoates. This methodology allows for the preparation of these esters with a variety of alkyl substituents in either the *meta* or *para* positions. Another route outlines the reaction of phenylsulfonylacetonitrile with nitroarene complexes to prepare alkanoic acid precursors with alkyl substituents in the *ortho*, *meta* and *para* positions. The preparation of a larger pool of nitroarene complexes clearly demonstrates the advantage of using the cyclopentadienyliron arene complexes in the synthesis of alkanoates or their precursors, arylated phenylsulfonylacetonitriles, over traditional synthetic routes.

Introduction

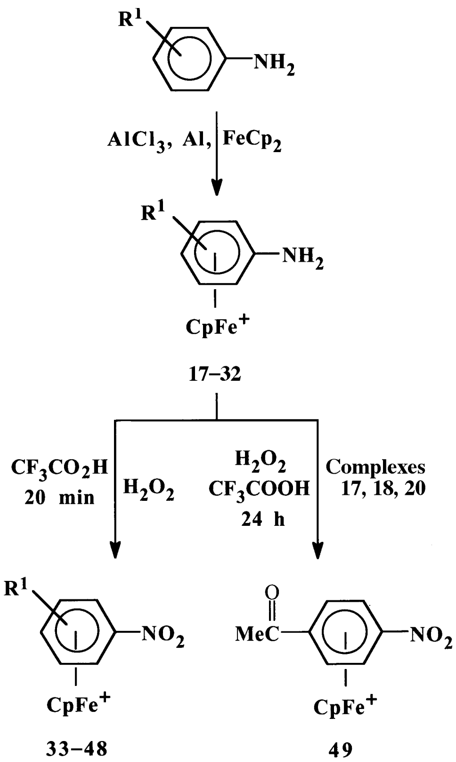
Because of their pharmaceutical importance as anti-inflammatory and antipyretic analgesics,[1–3] we have explored alternative routes to the synthesis of aryl alkanoates by nucleophilic substitution of chloroarene cyclopentadienyliron complexes.[4–7] One of the best known alkanoic acids in this class of compounds is Ibuprofen [2-(4-isobutylphenyl)propanoic acid], which is widely used for the treatment of muscle pain and stiffness, as well as rheumatoid arthritis.[8–10] Previous methods for the synthesis of alkanoic acids have included the conversion of alkyl aryl ketones into esters using a thallium salt,[11] the conversion of alkyl aryl ketones into aldehydes followed by oxidation to give the alkanoic acids,[12] as well as the arylation of phenylsulfonylacetonitriles followed by alkylation, reductive desulfonation and hydrolysis.[13]

The complexation of halogenoarenes with various metallic complexes such as cyclopentadienyliron ($CpFe^+$), cyclopentadienylruthenium ($CpRu^+$), manganese tricarbonyl [$(CO)_3Mn^+$], and chromium tricarbonyl [$(CO)_3Cr$] allows for the activation of the arenes towards nucleophilic aromatic substitution (S_NAr).[14–25] The advantage and flexibility of the $CpFe^+$ moiety as an activating group has been reviewed.[26] Previously, we have used the cyclopentadienyliron chloroarene complexes as starting materials in the synthesis of alkanoates.[4–7] Nevertheless, this strategy is limited by the commercial availability of chloroarenes with alkyl substituents. In light of this observation, we have been searching for alternate arenes which possess good leaving groups in addition to a variety of alkyl substituents. In this article, we report our success in the efficient complexation of a large number of substituted aniline compounds to the cyclopentadienyliron moiety and their oxidation to nitroarene complexes. The synthesis of alkanoates by nucleophilic displacement of the nitro group with phenylsulfonylacetonitrile or ethyl 2-alkylacetoacetate is also presented.

Results and discussion

In a recent communication, we reported initial results on the synthesis of a number of nitroarene cyclopentadienyliron complexes.[27] It has been our intention to prepare a large number of substituted nitroarene complexes because of their potential use as starting materials in the synthesis of various organic compounds.[28,29] There are a limited number of nitroarene cyclopentadienyliron complexes that have been prepared, including nitrobenzene and nitrotoluene.[30] In this study, the reaction of the alkylanilines **1**–**16** with ferrocene in the presence of $AlCl_3$ (anhydrous), Al (powder) and solvent (if needed) led to the formation of the alkylaniline complexes **17**–**32** in very good yields. The identity of these complexes was determined using NMR and IR spectroscopy and elemental analysis.

Earlier, oxidation of aniline- and 4-methylaniline-cyclopentadienyliron complexes with H_2O_2 in CF_3CO_2H for 5 h was reported to give the corresponding nitroarene complexes.[30] Our attempts to oxidize the amino groups of the corresponding 4-ethyl **17**, 4-isopropyl **18**, and 4-butyl **20** complexes under similar conditions gave mixtures of nitroarene complexes. The spectral data of these mixtures indicated that the amino and alkyl groups were oxidized to nitro and keto groups, respectively. After several modifications of the reaction time, it was clear that oxidation of the amino group is quicker than that of the alkyl substituents. Regardless of reaction time, oxidation of the methyl or *tert*-butyl substituted aniline complexes gave their corresponding nitroarene analogues with the alkyl group intact. Reactions of **17**–**32** with H_2O_2 in CF_3CO_2H for 20 min gave the alkylnitrobenzene complexes **33**–**48** in good yields (Scheme 1), while the substituted aniline complexes **17**, **18** and **20** gave 4-nitroacetophenone, **49**, over a 24 h period. It is important to note that an increased reaction time increases the possibility of decomposition and therefore reduces product yields. Nevertheless, this is the first example of multiple oxidation of alkyl-

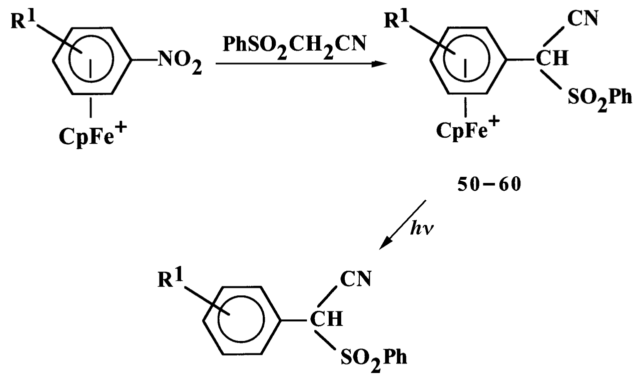


Alkyl substituent(s)	Aniline	Complexed aniline	Complexed nitrobenzene
4-Et	**1**	**17**	**33**
4-Pr^i	**2**	**18**	**34**
2-Pr^i	**3**	**19**	**35**
4-Bu	**4**	**20**	**36**
4-Bu^t	**5**	**21**	**37**
2-Bu^t	**6**	**22**	**38**
4-Bu^s	**7**	**23**	**39**
4-Pentyl	**8**	**24**	**40**
2,3-Me$_2$	**9**	**25**	**41**
2,4-Me$_2$	**10**	**26**	**42**
3,4-Me$_2$	**11**	**27**	**43**
3,5-Me$_2$	**12**	**28**	**44**
2,6-Et$_2$	**13**	**29**	**45**
2,6-Pr$^i_2$	**14**	**30**	**46**
2,5-Pr$^i_2$	**15**	**31**	**47**
2,4,6-Me$_3$	**16**	**32**	**48**

Scheme 1

aniline complexes which allows for the synthesis of arene complexes with two strong electron-withdrawing substituents (keto and nitro groups). The X-ray structure of 4-isopropylnitrobenzene(cyclopentadienyl)iron trifluoroacetate was previously reported but no analytical or spectroscopic data were provided.[31]

Two synthetic routes were used in the preparation of the substituted alkanoic acid precursors. Based on the structure of the desired precursors, substitution of alkylnitrobenzene complexes with ethyl alkylacetoacetates or phenylsulfonylacetonitrile allowed for the preparation of a large number of these compounds with a wide range of alkyl substituents. Reactions with ethyl alkylacetoacetates allow for the introduction of a variety of alkyl substituents at either the *meta* or *para* positions while reactions of phenylsulfonylacetonitrile could lead to alkanoic acid precursors with alkyl substituents in the *ortho*, *meta* and *para* positions. Nitroarene complexes were allowed to react with phenylsulfonylacetonitrile in the presence of K_2CO_3 in DMF for 5 h under a nitrogen atmosphere, after which work-up (see Experimental section) gave the arylated phenylsulfonylacetonitriles **50**–**60** as yellow solids (68–89%; see Scheme 2). The presence of alkyl groups (other than methyl) at the *ortho* positions of the nitroarene complex precluded nucleophilic displacement and resulted in recovery of the starting materials



61–71

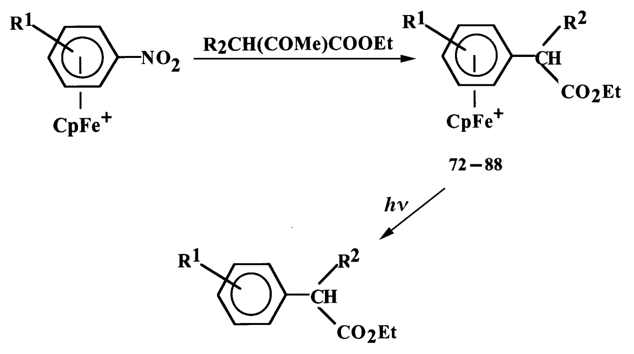
Alkyl substituent(s) (R^1)	Complexed nitrobenzene	Complexed arylphenylsulfonylacetonitrile	Arylphenylsulfonylacetonitrile
4-Et	**33**	**50**	**61**
4-Pr^i	**34**	**51**	**62**
2-Pr^i	**35**	**52**	**63**
4-Bu^t	**37**	**53**	**64**
4-Bu^s	**39**	**54**	**65**
4-Pentyl	**40**	**55**	**66**
2,3-Me$_2$	**41**	**56**	**67**
2,4-Me$_2$	**42**	**57**	**68**
3,4-Me$_2$	**43**	**58**	**69**
3,5-Me$_2$	**44**	**59**	**70**
2,4,6-Me$_3$	**48**	**60**	**71**

Scheme 2

(2-*tert*-butyl-, 2,6-diethyl- or 2,6-diisopropyl-nitrobenzene complexes). Conversely, a methyl or isopropyl substituent at one of the *ortho* positions caused no steric hindrance, and nucleophilic substitution occurred. ^{1}H, ^{13}C NMR and IR spectroscopy and elemental analysis were used to determine the structure of the resulting complexes (see Experimental section). Photolytic demetallation by dissolution of these complexes in CH_2Cl_2–MeCN followed by irradiation of the solution with a xenon lamp for 2 h gave, after purification using column chromatography, the pure arylated phenylsulfonylacetonitriles, **61**–**71**, in high yields (71–91%). Product identification is described in the Experimental section.

Arylated phenylsulfonylacetonitriles are valuable precursors in the synthesis of alkanoic acids. A more direct approach to the synthesis of alkanoates is achieved by the reaction of the nitroarene complexes with ethyl 2-alkylacetoacetates. Reaction of ethyl 2-methyl-, 2-ethyl-, or 2-butylacetoacetates with nitroarene complexes in the presence of K_2CO_3 in DMF for 18 h under a nitrogen atmosphere at 60 °C gave the alkanoate complexes **72**–**88** (Scheme 3). This reaction gave a mixture of products with *o*-alkyl substituted nitrobenzene complexes. Therefore to prepare *o*-methyl substituted alkanoic acids the synthetic method of choice is *via* the arylated phenylsulfonylacetonitriles (see above), followed by alkylation, hydrogenation and hydrolysis.[13] The spectroscopic and analytical data for these complexes are listed in the Experimental section. Photolytic demetallation of the cyclopentadienyliron complexes gave the esters **89**–**105** in very good yields.

In conclusion, the use of chloroarene complexes as starting materials for the synthesis of alkanoates is limited by the difficulty of obtaining suitably alkylated chlorobenzenes from commercial sources. The introduction of various alkyl substituents into the chloroarene complexes, as well as the development of different starting materials that contain alkyl substituents and a good leaving group, are two approaches to overcome this limitation. The synthesis of alkylnitrobenzene complexes has addressed this demand by developing starting materials with both alkyl substituents and a good leaving group. The import-



89 – 105

Complexed nitrobenzene	Complexed alkanoates	(R^1)	(R^2)	Alkanoates
33	**72**	4-Et	Me	**89**
33	**73**	4-Et	Et	**90**
34	**74**	4-Pr^i	Me	**91**
34	**75**	4-Pr^i	Et	**92**
34	**76**	4-Pr^i	Bu	**93**
36	**77**	4-Bu	Me	**94**
37	**78**	4-Bu^t	Me	**95**
37	**79**	4-Bu^t	Et	**96**
37	**80**	4-Bu^t	Bu	**97**
39	**81**	4-Bu^s	Me	**98**
39	**82**	4-Bu^s	Et	**99**
39	**83**	4-Bu^s	Bu	**100**
43	**84**	3,4-Me_2	Me	**101**
43	**85**	3,4-Me_2	Et	**102**
44	**86**	3,5-Me_2	Me	**103**
44	**87**	3,5-Me_2	Et	**104**
44	**88**	3,5-Me_2	Bu	**105**

Scheme 3

ance of these complexes is best demonstrated by their use as starting materials in the synthesis of organic compounds with potential pharmaceutical interest such as alkanoates.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Varian Gemini 200 NMR spectrometer, with chemical shifts (ppm) being calculated from the solvent signals. Deuterioacetone was used as a solvent for all complexes and deuteriochloroform for all organic compounds. Coupling constants are recorded in Hz. Mass spectra were obtained on a Hewlett-Packard 5970 Series Mass Selective Detector, by electron-impact (70 eV); signal positions are given in *m/z*. IR spectra were recorded on a Perkin-Elmer model 781 spectrophotometer. Mps were measured in a capillary using a Mel-Temp II and are uncorrected.

Anhydrous aluminium chloride, aluminium powder, ferrocene, alkylanilines, reagent grade solvents, and ammonium hexafluorophosphate are commercially available and were used without further purification. Silica gel 60–100 mesh was used in the column chromatographic purification of the liberated arenes.

Synthesis of alkylaniline cyclopentadienyliron complexes

A 250 ml 3-necked round-bottomed flask was charged with ferrocene (25 mmol), $AlCl_3$ (anhydrous; 50 mmol), Al (powder; 25 mmol) and the substituted aniline (60 mmol); decalin (30 ml) was used as a solvent if the substituted aniline was a solid. After the mixture had been heated at 145–160 °C under a nitrogen atmosphere for 5 h, it was cooled to 60 °C, poured into ice-water (400 ml) and stirred for 10 min. The yellowish orange solution was then suction filtered through sand. The filtrate was washed with Et_2O (3 × 50 ml) after which it was treated with NH_4PF_6 (25 mmol) to give a yellow precipitate. This was collected and redissolved in CH_2Cl_2 and the solution was dried ($MgSO_4$), filtered and concentrated using a rotary evaporator. Addition of Et_2O to the concentrated solution gave the pure products which were collected by suction filtration as brownish yellow solids.

η^5-Cyclopentadienyl(η^6-4-ethylaniline)iron(II) hexafluorophosphate 17 (6.99 g, 62%) (Found: C, 40.5; H, 4.1; N, 3.7. $C_{13}H_{16}F_6FeNP$ requires C, 40.3; H, 4.2; N, 3.6%); ν_{max}(neat)/cm^{-1} 3405 and 3495 (NH_2); δ_H(CD_3COCD_3) 1.28 (3 H, t, *J* 7.7, CH_3), 2.71 (2 H, q, *J* 7.5, CH_2), 4.92 (5 H, s, Cp), 5.69 (2 H, br s, NH_2), 5.89 (2 H, d, *J* 6.8, complexed ArH) and 6.10 (2 H, d, *J* 6.8, complexed ArH); δ_C(CD_3COCD_3) 15.55 (CH_3), 27.49 (CH_2), 71.06 (2 C, complexed ArC), 77.54 (5 C, Cp), 86.49 (2 C, complexed ArC), 102.53 (quaternary complexed ArC) and 125.771 (quaternary complexed ArC).

η^5-Cyclopentadienyl(η^6-4-isopropylaniline)iron(II) hexafluorophosphate 18 (5.82 g, 58%) (Found: C, 42.1; H, 4.4; N, 3.6. $C_{14}H_{18}F_6FeNP$ requires C, 41.9; H, 4.5; N, 3.5%); ν_{max}(CH_2Cl_2)/cm^{-1} 3400 and 3495 (NH_2); δ_H(CD_3COCD_3) 1.34 (6 H, d, *J* 6.9, CH_3), 3.01 (1 H, m, *J* 7.0, CH), 4.92 (5 H, s, Cp), 5.71 (2 H, br s, NH_2), 5.89 (2 H, d, *J* 7.0, complexed ArH) and 6.09 (2 H, d, *J* 6.8, complexed ArH); δ_C(CD_3COCD_3) 23.11 (2 C, CH_3), 32.32 (CH), 70.24 (2 C, complexed ArC), 76.79 (5 C, Cp), 84.20 (2 C, complexed ArC), 106.61 (quaternary complexed ArC) and 125.39 (quaternary complexed C).

η^5-Cyclopentadienyl(η^6-2-isopropylaniline)iron(II) hexafluorophosphate 19 (5.90 g, 59%) (Found: C, 41.8; H, 4.65; N, 3.3. $C_{14}H_{18}F_6FeNP$ requires C, 41.9; H, 4.5; N, 3.5%); ν_{max}(neat)/cm^{-1} 3405 and 3500 (NH_2); δ_H(CD_3COCD_3) 1.20 (3 H, d, *J* 6.7, CH_3), 1.58 (3 H, d, *J* 6.8, CH_3), 3.38 (1 H, septet, *J* 6.9, CH), 4.91 (5 H, s, Cp), 5.68 (2 H, br s, NH_2), 5.99 (2 H, m, complexed ArH) and 6.13 (2 H, m, complexed ArH); δ_C(CD_3COCD_3) 20.02 (CH_3), 22.24 (CH_3), 28.10 (CH), 72.03 (complexed ArC), 76.40 (5 C, Cp), 80.49 (complexed ArC), 82.82 (complexed ArC), 85.61 (C, complexed ArC), 94.32 (quaternary complexed ArC) and 122.88 (quaternary complexed ArC).

η^5-Cyclopentadienyl(η^6-4-butylaniline)iron(II) hexafluorophosphate 20 (6.73 g, 65%) (Found: C, 43.4; H, 4.9; N, 3.45. $C_{15}H_{20}F_6FeNP$ requires C, 43.4; H, 4.9; N, 3.4%); ν_{max}(CH_2Cl_2)/cm^{-1} 3400 and 3490 (NH_2); δ_H(CD_3COCD_3) 0.90 (3 H, t, *J* 7.3, CH_3), 1.39–1.43 (2 H, m, CH_2), 1.52–1.60 (2 H, m, CH_2), 2.69 (2 H, t, *J* 7.4, CH_2), 4.89 (5 H, s, Cp), 5.59 (2 H, br s, NH_2), 5.85 (2 H, d, *J* 7.2, complexed ArH) and 6.03 (2 H, d, *J* 6.9, complexed ArH); δ_C(CD_3COCD_3) 13.91 (CH_3), 22.56 (CH_2), 33.80 (CH_2), 34.13 (CH_2), 70.54 (2 C, complexed ArC), 77.01 (5 C, Cp), 86.37 (2 C, complexed ArC), 100.71 (quaternary complexed ArC) and 125.01 (quaternary complexed ArC).

η^5-Cyclopentadienyl(η^6-4-*tert*-butylaniline)iron(II) hexafluorophosphate 21 (6.03 g, 58%) (Found: C, 43.7; H, 4.9; N, 3.55. $C_{15}H_{20}F_6FeNP$ requires C, 43.4; H, 4.9; N, 3.4%); ν_{max}(neat)/cm^{-1} 3400 and 3495 (NH_2); δ_H(CD_3COCD_3) 1.42 (9 H, s, CH_3), 4.94 (5 H, s, Cp), 5.73 (2 H, br s, NH_2), 5.88 (2 H, d, *J* 7.0, complexed ArH) and 6.12 (2 H, d, *J* 7.1, complexed ArH); δ_C(CD_3COCD_3) 30.85 (3 C, CH_3), 34.12 (aliphatic quaternary), 69.92 (2 C, complexed ArC), 76.67 (5 C, Cp), 82.97 (2 C, complexed ArC), 110.66 (quaternary complexed ArC) and 125.56 (quaternary complexed ArC).

η^5-Cyclopentadienyl(η^6-2-*tert*-butylaniline)iron(II) hexafluorophosphate 22 (5.08 g, 49%) (Found: C, 43.2; H, 4.85; N, 3.2. $C_{15}H_{20}F_6FeNP$ requires C, 43.4; H, 4.9; N, 3.4%); ν_{max}(neat)/cm^{-1} 3410 and 3520 (NH_2); δ_H(CD_3COCD_3) 1.54 (9 H, s, CH_3), 4.93 (5 H, s, Cp), 5.70 (2 H, br s, NH_2), 5.92 (2 H, m, complexed ArH), 6.11 (1 H, d, *J* 6.4, complexed ArH) and 6.19 (1 H, d, *J* 6.4, complexed ArH); δ_C(CD_3COCD_3) 26.64 (3 C, CH_3), 27.43 (aliphatic quaternary), 68.49 (complexed ArC), 72.87 (5 C, Cp), 77.27 (complexed ArC), 82.22 (complexed ArC), 82.57 (complexed ArC), 94.03 (quaternary complexed ArC) and 120.45 (quaternary complexed ArC).

η^5-Cyclopentadienyl(η^6-4-*sec*-butylaniline)iron(II) hexafluorophosphate 23 (6.23 g, 60%) (Found: C, 43.5; H, 5.0; N, 3.5.

$C_{15}H_{20}F_6FeNP$ requires C, 43.4; H, 4.9; N, 3.4%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3405 and 3495 (NH_2); $\delta_H(CD_3COCD_3)$ 0.90 (3 H, t, *J* 7.1, CH_3), 1.41 (3 H, d, *J* 6.9, CH_3), 1.68 (2 H, m, CH_2), 2.78 (1 H, m, CH), 4.92 (5 H, s, Cp), 5.71 (2 H, br s, NH_2), 5.89 (2 H, d, *J* 7.1, complexed ArH) and 6.04 (2 H, m, complexed ArH); $\delta_C(CD_3COCD_3)$ 11.66 (CH_3), 19.03 (CH_3), 31.88 (CH_2), 38.91 (CH), 70.16 (complexed ArC), 70.38 (complexed ArC), 76.95 (5 C, Cp), 83.56 (complexed ArC), 85.89 (complexed ArC), 106.18 (quaternary complexed ArC) and 125.77 (quaternary complexed ArC).

η⁵-Cyclopentadienyl(η⁶-4-pentylaniline)iron(II) hexafluorophosphate 24 (6.10 g, 57%) (Found: C, 44.9; H, 4.9; N, 3.4, $C_{16}H_{22}F_6FeNP$ requires C, 44.8; H, 5.2; N, 3.3%); ν_{max}(neat)/cm^{-1} 3395 and 3492 (NH_2); $\delta_H(CD_3COCD_3)$ 0.87 (3 H, t, *J* 6.9, CH_3), 1.36 (2 H, m, CH_2), 1.64 (2 H, m, CH_2), 1.93 (2 H, m, CH_2), 2.71 (2 H, t, *J* 7.4, CH_2), 4.91 (5 H, s, Cp), 5.69 (2 H, br s, NH_2), 5.89 (2 H, d, *J* 6.9, complexed ArH) and 6.10 (2 H, d, *J* 6.8, complexed ArH); $\delta_C(CD_3COCD_3)$ 14.15 (CH_3), 22.45 (CH_2), 22.94 (CH_2), 31.58 (CH_2), 34.66 (CH_2), 70.65 (2 C, complexed ArC), 77.16 (5 C, Cp), 86.61 (2 C, complexed ArC), 100.84 (quaternary complexed ArC) and 125.49 (quaternary complexed ArC).

η⁵-Cyclopentadienyl(η⁶-2,3-dimethylaniline)iron(II) hexafluorophosphate 25 (6.52 g, 67%) (Found: C, 40.6; H, 4.0; N, 3.7. $C_{13}H_{16}F_6FeNP$ requires C, 40.3; H, 4.2; N, 3.6%); ν_{max}(neat)/cm^{-1} 3415 and 3515 (NH_2); $\delta_H(CD_3COCD_3)$ 2.41 (3 H, s, CH_3), 2.54 (3 H, s, CH_3), 4.81 (5 H, s, Cp), 5.67 (2 H, br s, NH_2) and 5.88–5.98 (3 H, m, complexed ArH); $\delta_C(CD_3COCD_3)$ 13.61 (CH_3), 19.77 (CH_3), 70.22 (5 C, Cp), 82.32 (complexed ArC), 84.30 (complexed ArC), 101.37 (quaternary complexed ArC) and 124.20 (quaternary complexed ArC).

η⁵-Cyclopentadienyl(η⁶-2,4-dimethylaniline)iron(II) hexafluorophosphate 26 (6.19 g, 64%) (Found: C, 40.5; H, 4.1; N, 3.7. $C_{13}H_{16}F_6FeNP$ requires C, 40.3; H, 4.2; N, 3.6%); ν_{max}(neat)/cm^{-1} 3400 and 3485 (NH_2); $\delta_H(CD_3COCD_3)$ 2.36 (3 H, s, CH_3), 2.40 (3 H, s, CH_3), 4.82 (5 H, s, Cp), 5.55 (2 H, br s, NH_2), 5.90 (1 H, d, *J* 6.7, complexed ArH), 5.96 (1 H, d, *J* 6.6, complexed ArH) and 6.10 (1 H, s, complexed ArH); $\delta_C(CD_3COCD_3)$ 17.18 (CH_3), 19.46 (CH_3), 70.46 (complexed ArC), 77.50 (5 C, Cp), 85.77 (complexed ArC), 89.33 (complexed ArC), 95.33 (quaternary complexed ArC), 123.52 (quaternary complexed ArC) and 123.59 (quaternary complexed ArC).

η⁵-Cyclopentadienyl(η⁶-3,4-dimethylaniline)iron(II) hexafluorophosphate 27 (5.61 g, 58%) (Found: C, 40.5; H, 4.3; N, 3.6. $C_{13}H_{16}F_6FeNP$ requires C, 40.3; H, 4.2; N, 3.6%); ν_{max}(neat)/cm^{-1} 3405 and 3500 (NH_2); $\delta_H(CD_3COCD_3)$ 2.39 (3 H, s, CH_3), 2.46 (3 H, s, CH_3), 4.83 (5 H, s, Cp), 5.52 (2 H, br s, NH_2), 5.79 (1 H, d, *J* 6.4, complexed ArC), 5.87 (1 H, s, complexed ArH) and 6.03 (1 H, d, *J* 6.5, complexed ArH); $\delta_C(CD_3COCD_3)$ 17.89 (CH_3), 19.02 (CH_3), 69.33 (complexed ArC), 72.95 (complexed ArC), 77.43 (5 C, Cp), 87.30 (complexed ArC), 95.14 (quaternary complexed ArC), 100.52 (quaternary complexed ArC) and 124.57 (quaternary complexed ArC).

η⁵-Cyclopentadienyl(η⁶-3,5-dimethylaniline)iron(II) hexafluorophosphate 28 (5.44 g, 56%) (Found: C, 40.5; H, 4.05; N, 3.7. $C_{13}H_{16}F_6FeNP$ requires C, 40.3; H, 4.2; N, 3.6%); ν_{max}(neat)/cm^{-1} 3395 and 3495 (NH_2); $\delta_H(CD_3COCD_3)$ 2.43 (6 H, s, CH_3), 4.83 (5 H, s, Cp), 5.54 (2 H, br s, NH_2), 5.81 (2 H, s, complexed ArH) and 5.88 (1 H, s, complexed ArH); $\delta_C(CD_3COCD_3)$ 20.34 (2 C, CH_3), 71.05 (2 C, complexed ArC), 77.31 (5 C, Cp), 82.49 (complexed ArC), 101.38 (2 C, quaternary complexed ArC) and 125.02 (quaternary complexed ArC).

η⁵-Cyclopentadienyl(η⁶-2,6-diethylaniline)iron(II) hexafluorophosphate 29 (5.27 g, 51%) (Found: C, 43.7; H, 5.0; N, 3.3. $C_{15}H_{20}F_6FeNP$ requires C, 43.4; H, 4.9; N, 3.4%); ν_{max}(neat)/cm^{-1} 3400 and 3475 (NH_2); $\delta_H(CD_3COCD_3)$ 1.30 (6 H, t, *J* 7.5, CH_3), 2.88 (4 H, q, *J* 7.4, CH_2), 4.80 (5 H, s, Cp), 5.59 (2 H, br s, NH_2), 5.87 (1 H, t, *J* 5.5, complexed ArH) and 6.08 (2 H, d, *J* 5.9, complexed ArH); $\delta_C(CD_3COCD_3)$ 12.98 (2 C, CH_3), 25.03 (2 C, CH_2), 76.82 (5 C, Cp), 80.18 (complexed ArC), 85.63 (2 C, complexed ArC), 89.21 (2 C, quaternary ArC) and 122.16 (quaternary ArC).

η⁵-Cyclopentadienyl(η⁶-2,6-diisopropylaniline)iron(II) hexafluorophosphate 30 (4.92 g, 44%) (Found: C, 45.9; H, 5.5; N, 3.1. $C_{17}H_{24}F_6FeNP$ requires C, 46.1; H, 5.5; N, 3.2%); ν_{max}(neat)/cm^{-1} 3420 and 3510 (NH_2); $\delta_H(CD_3COCD_3)$ 1.21 (6 H, d, *J* 6.9, CH_3), 1.60 (6 H, d, *J* 6.7, CH_3), 3.45 (2 H, m, *J* 6.79, CH), 4.86 (5 H, s, Cp), 5.56 (2 H, br s, NH_2), 5.94 (1 H, t, *J* 6.3, complexed ArH) and 6.15 (2 H, d, *J* 6.2, complexed ArH); $\delta_C(CD_3COCD_3)$ 20.47 (2 C, CH_3), 22.40 (2 C, CH_3), 28.52 (2 C, CH), 76.23 (5 C, Cp), 79.48 (complexed ArC), 81.79 (2 C, complexed ArC), 94.68 (2 C, complexed quaternary ArC) and 119.32 (complexed quaternary ArC).

η⁵-Cyclopentadienyl(η⁶-2,5-diisopropylaniline)iron(II) hexafluorophosphate 31 (5.01 g, 45%) (Found: C, 46.3; H, 5.5; N, 3.0. $C_{17}H_{24}F_6FeNP$ requires C, 46.1; H, 5.5; N, 3.2%); ν_{max}(neat)/cm^{-1} 3410 and 3500 (NH_2); $\delta_H(CD_3COCD_3)$ 1.45 (6 H, br s, 2 CH_3), 1.62 (6 H, br s, 2 CH_3), 2.86 (1 H, m, CH), 3.15 (1 H, m, CH), 4.96 (5 H, s, Cp), 5.49 (2 H, br s, NH_2), 5.97 (1 H, d, *J* 6.7, complexed ArH), 6.08 (1 H, s, complexed ArH) and 6.20 (1 H, d, *J* 6.8, complexed ArH); $\delta_C(CD_3COCD_3)$ 22.04 (2 C, CH_3), 24.40 (2 C, CH_3), 30.42 (2 C, CH), 76.44 (5 C, Cp), 78.55 (complexed ArC), 84.93 (complexed ArC), 87.673 (complexed ArC), 105.10 (complexed quaternary ArC), 116.30 (complexed quaternary ArC) and 123.50 (complexed quaternary ArC).

η⁵-Cyclopentadienyl(η⁶-2,4,6-trimethylaniline)iron(II) hexafluorophosphate 32 (6.10 g, 61%) (Found: C, 42.0; H, 4.65; N, 3.7. $C_{14}H_{18}F_6FeNP$ requires C, 41.9; H, 4.5; N, 3.5%); ν_{max}(neat)/cm^{-1} 3399 and 3485 (NH_2); $\delta_H(CD_3COCD_3)$ 2.32 (3 H, s, CH_3), 2.44 (6 H, s, CH_3), 4.76 (5 H, s, Cp), 5.42 (2 H, s, NH_2) and 6.02 (2 H, s, complexed ArH); $\delta_C(CD_3COCD_3)$ 17.36 (2 C, CH_3), 19.00 (CH_3), 77.61 (5 C, Cp), 83.27 (2 C, complexed quaternary ArC), 87.27 (2 C, complexed ArC), 94.72 (complexed quaternary ArC) and 122.05 (complexed quaternary ArC).

Oxidation of (alkylaniline)cyclopentadienyliron complexes

The substituted aniline complex (5.0 mmol) was combined with a 1:1 mixture of H_2O_2 and CF_3CO_2H (50 ml) and heated to 60 °C for 20 min after which the mixture was cooled to room temperature and extracted with CH_2Cl_2–CH_3NO_2 (4:1). The organic layer was dried ($MgSO_4$), concentrated using a rotary evaporator, and treated with NH_4PF_6 to give a precipitate which was filtered off and washed with Et_2O (50 ml).

η⁵-Cyclopentadienyl(η⁶-4-ethylnitrobenzene)iron(II) hexafluorophosphate 33 (1.29 g, 63%) (Found: C, 37.6; H, 3.5; N, 3.5. $C_{13}H_{14}F_6FeNO_2P$ requires C, 37.4; H, 3.4; N, 3.4%); $\delta_H(CD_3COCD_3)$ 1.36 (3 H, t, *J* 7.6, CH_3), 3.02 (2 H, q, *J* 7.4, CH_2), 5.40 (5 H, s, Cp), 6.85 (2 H, d, *J* 6.2, complexed ArH) and 7.49 (2 H, d, *J* 6.6, complexed ArH); $\delta_C(CD_3COCD_3)$ 15.07 (CH_3), 30.20 (CH_2), 81.31 (5 C, Cp), 85.00 (2 C, complexed ArC), 88.95 (2 C, complexed ArC), 111.81 (complexed quaternary ArC) and 113.85 (complexed quaternary ArC).

η⁵-Cyclopentadienyl(η⁶-4-isopropylnitrobenzene)iron(II) hexafluorophosphate 34 (1.59 g, 75%) (Found: C, 38.85; H, 3.8; N, 3.3. $C_{14}H_{16}F_6FeNO_2P$ requires C, 39.0; H, 3.7; N, 3.25%); $\delta_H(CD_3COCD_3)$ 1.46 (6 H, d, *J* 7.0, CH_3), 3.32 (1 H, septet, *J* 7.0, CH), 5.44 (5 H, s, Cp), 6.88 (2 H, d, *J* 6.8, complexed ArH) and 7.51 (2 H, d, *J* 7.1, complexed ArH); $\delta_C(CD_3COCD_3)$ 27.42 (2 C, CH_3), 31.42 (CH), 82.66 (5 C, Cp), 85.86 (2 C, complexed ArC), 88.83 (2 C, complexed ArC), 97.10 (complexed quaternary ArC) and 113.68 (complexed quaternary ArC).

η⁵-Cyclopentadienyl(η⁶-2-isopropylnitrobenzene)iron(II) hexafluorophosphate 35 (1.34 g, 62%) (Found: C, 39.1; H, 3.8; N, 3.2. $C_{14}H_{16}F_6FeNO_2P$ requires C, 39.0; H, 3.7; N, 3.25%); $\delta_H(CD_3COCD_3)$ 1.38 (3 H, d, *J* 6.8, CH_3), 1.64 (3 H, d, *J* 6.8, CH_3), 3.43 (1 H, septet, *J* 6.9, CH), 5.40 (5 H, s, Cp), 6.83 (1 H, d, *J* 6.4, complexed ArH), 6.88 (2 H, t, *J* 6.2, complexed ArH) and 7.39 (1 H, d, *J* 6.4, complexed ArH); $\delta_C(CD_3COCD_3)$ 28.24

(CH_3), 29.95 (CH_3), 34.73 (CH), 80.89 (5 C, Cp), 84.73 (2 C, complexed ArC), 86.35 (2 C, complexed ArC), 110.25 (complexed quaternary ArC) and 121.63 (complexed quaternary ArC).

η^5-Cyclopentadienyl(η^6-4-butylnitrobenzene)iron(II) hexafluorophosphate 36 (1.55 g, 70%) (Found: C, 40.0; H, 4.1; N, 3.3. $C_{15}H_{18}F_6FeNO_2P$ requires C, 40.5; H, 4.1; N, 3.15%); δ_H(CD_3COCD_3) 0.93 (3 H, t, *J* 7.3, CH_3), 1.44 (2 H, sextet, *J* 6.2, CH_2), 1.71 (2 H, quintet, *J* 6.4, CH_2), 3.03 (2 H, t, *J* 7.5, CH_2), 5.42 (5 H, s, Cp), 6.87 (2 H, d, *J* 6.0, complexed ArH) and 7.53 (2 H, d, *J* 6.1, complexed ArH); δ_C(CD_3COCD_3) 13.82 (CH_3), 22.56 (CH_2), 33.81 (CH_2), 34.76 (CH_2), 81.12 (5 C, Cp), 84.77 (2 C, complexed ArC), 89.03 (2 C, complexed ArC), 104.30 (complexed quaternary ArC) and 112.40 (complexed quaternary ArC).

η^5-Cyclopentadienyl(η^6-4-*tert*-butylnitrobenzene)iron(II) hexafluorophosphate 37 (1.30 g, 58%) (Found: C, 40.6; H, 3.9; N, 3.1. $C_{15}H_{18}F_6FeNO_2P$ requires C, 40.5; H, 4.1; N, 3.15%); δ_H(CD_3COCD_3) 1.54 (9 H, s, CH_3), 5.46 (5 H, s, Cp), 6.95 (2 H, d, *J* 7.0, complexed ArH) and 7.49 (2 H, d, *J* 7.1, complexed ArH); δ_C(CD_3COCD_3) 31.70 (3 C, CH_3), 35.67 (aliphatic quaternary), 80.71 (5 C, Cp), 84.29 (2 C, complexed ArC), 85.88 (2 C, complexed ArC), 111.23 (complexed quaternary ArC) and 122.50 (complexed quaternary ArC).

η^5-Cyclopentadienyl(η^6-2-*tert*-butylnitrobenzene)iron(II) hexafluorophosphate 38 (1.15 g, 52%) (Found: C, 40.4; H, 3.9; N, 3.2. $C_{15}H_{18}F_6FeNO_2P$ requires C, 40.5; H, 4.1; N, 3.15%); δ_H(CD_3COCD_3) 1.59 (9 H, s, CH_3), 5.56 (5 H, s, Cp), 6.72 (1 H, d, *J* 6.0, complexed ArH), 6.84 (2 H, m, complexed ArH) and 7.13 (1 H, d, *J* 6.3, complexed ArH); δ_C(CD_3COCD_3) 30.75 (3 C, CH_3), 35.84 (aliphatic quaternary), 80.78 (5 C, Cp), 84.38 (2 C, complexed ArC), 85.93 (2 C, complexed ArC), 111.60 (complexed quaternary ArC) and 122.78 (complexed quaternary ArC).

η^5-Cyclopentadienyl(η^6-4-*sec*-butylnitrobenzene)iron(II) hexafluorophosphate 39 (1.57 g, 71%) (Found: C, 40.7; H, 3.95; N, 3.4. $C_{15}H_{18}F_6FeNO_2P$ requires C, 40.5; H, 4.1; N, 3.15%); δ_H(CD_3COCD_3) 0.93 (3 H, t, *J* 6.8, CH_3), 1.51 (3 H, d, *J* 6.9, CH_3), 1.75 (2 H, quintet, *J* 6.9, CH_2), 3.08 (1 H, m, CH), 5.45 (5 H, s, Cp), 6.83 (2 H, m, complexed ArH) and 7.54 (2 H, d, *J* 4.5, complexed ArH); δ_C(CD_3COCD_3) 11.56 (CH_3), 18.65 (CH_3), 31.93 (CH_2), 39.69 (CH), 80.99 (5 C, Cp), 84.52 (complexed ArC), 84.71 (complexed ArC), 86.24 (complexed ArC), 111.82 (quaternary ArC) and 118.08 (quaternary ArC).

η^5-Cyclopentadienyl(η^6-4-pentylnitrobenzene)iron(II) hexafluorophosphate 40 (1.59 g, 69%) (Found: C, 42.2; H, 4.6; N, 3.2. $C_{16}H_{20}F_6FeNO_2P$ requires C, 41.9; H, 4.4; N, 3.05%); δ_H(CD_3COCD_3) 0.87 (3 H, t, *J* 6.2, CH_3), 1.37 (4 H, m, CH_2), 1.72 (2 H, m, CH_2), 2.98 (2 H, t, *J* 7.0, CH_2), 5.42 (5 H, s, Cp), 6.89 (2 H, d, *J* 7.0, complexed ArH) and 7.51 (2 H, d, *J* 7.0, complexed ArH); δ_C(CD_3COCD_3) 14.07 (CH_3), 22.39 (CH_2), 22.78 (CH_2), 31.57 (CH_2), 35.10 (CH_2), 81.25 (5 C, Cp), 84.94 (2 C, complexed ArC), 89.24 (2 C, complexed ArC), 104.43 (complexed quaternary ArC) and 112.56 (complexed quaternary ArC).

η^5-Cyclopentadienyl(η^6-2,3-dimethylnitrobenzene)iron(II) hexafluorophosphate 41 (1.26 g, 60%) (Found: C, 37.4; H, 3.6; N, 3.2. $C_{13}H_{14}F_6FeNO_2P$ requires C, 37.4; H, 3.4; N, 3.4%); δ_H(CD_3COCD_3) 2.71 (3 H, s, CH_3), 2.74 (3 H, s, CH_3), 5.39 (5 H, s, Cp), 6.69 (2 H, m, complexed ArH) and 7.16 (1 H, t, *J* 4.5, complexed ArH); δ_C(CD_3COCD_3) 17.62 (CH_3), 20.96 (CH_3), 81.49 (5C, Cp), 84.09 (complexed ArC), 86.31 (complexed ArC), 91.92 (complexed ArC), 97.96 (complexed quaternary ArC), 103.97 (complexed quaternary ArC) and 111.79 (complexed quaternary ArC).

η^5-Cyclopentadienyl(η^6-2,4-dimethylnitrobenzene)iron(II) hexafluorophosphate 42 (1.18 g, 57%) (Found: C, 37.7; H, 3.2; N, 3.2. $C_{13}H_{14}F_6FeNO_2P$ requires C, 37.4; H, 3.4; N, 3.4%); δ_H(CD_3COCD_3) 2.62 (3 H, s, CH_3), 2.80 (3 H, s, CH_3), 5.39 (5 H, s, Cp), 6.73 (2 H, m, complexed ArH) and 7.26 (1 H, d, *J* 6.5, complexed ArH); δ_C(CD_3COCD_3) 18.67 (CH_3), 20.16 (CH_3), 81.43 (5 C, Cp), 85.18 (complexed ArC), 87.70 (complexed ArC), 91.01 (complexed ArC), 99.09 (complexed quaternary ArC), 107.19 (complexed quaternary ArC) and 117.06 (complexed quaternary ArC).

η^5-Cyclopentadienyl(η^6-3,4-dimethylnitrobenzene)iron(II) hexafluorophosphate 43 (1.10 g, 53%) (Found: C, 37.5; H, 3.5; N, 3.2. $C_{13}H_{14}F_6FeNO_2P$ requires C, 37.4; H, 3.4; N, 3.4%); δ_H(CD_3COCD_3) 2.67 (3 H, s, CH_3), 2.77 (3 H, s, CH_3), 5.35 (5 H, s, Cp), 6.80 (1 H, d, *J* 6.7, complexed ArH), 7.44 (1 H, d, *J* 7.2, complexed ArH) and 7.50 (1 H, s, complexed ArH); δ_C(CD_3COCD_3) 19.06 (CH_3), 29.69 (CH_3), 81.50 (5 C, Cp), 83.34 (complexed ArC), 85.50 (complexed ArC), 89.96 (complexed ArC), 104.61 (complexed quaternary ArC), 107.42 (complexed quaternary ArC) and 107.97 (complexed quaternary ArC).

η^5-Cyclopentadienyl(η^6-3,5-dimethylnitrobenzene)iron(II) hexafluorophosphate 44 (1.19 g, 57%) (Found: C, 37.3; H, 3.5; N, 3.1. $C_{13}H_{14}F_6FeNO_2P$ requires C, 37.4; H, 3.4; N, 3.4%); δ_H(CD_3COCD_3) 2.71 (6 H, s, CH_3), 5.34 (5 H, s, Cp), 6.71 (1 H, s, complexed ArH) and 7.43 (2 H, s, complexed ArH); δ_C(CD_3COCD_3) 20.19 (2 C, CH_3), 81.61 (5 C, Cp), 83.61 (complexed ArC), 93.23 (complexed ArC), 105.37 (complexed quaternary ArC) and 112.10 (complexed quaternary ArC).

η^5-Cyclopentadienyl(η^6-2,6-diethylnitrobenzene)iron(II) hexafluorophosphate 45 (1.35 g, 61%) (Found: C, 40.4; H, 3.9; N, 3.2. $C_{15}H_{18}F_6FeNO_2P$ requires C, 40.5; H, 4.1; N, 3.15%); δ_H(CD_3COCD_3) 1.36 (6 H, t, *J* 7.5, CH_3), 2.81 (2 H, m, CH_2), 3.05 (2 H, m, CH_2), 5.44 (5 H, s, Cp) and 6.70 (3 H, m, complexed ArH); δ_C(CD_3COCD_3) 14.60 (2 C, CH_3), 24.88 (2 C, CH_2), 81.04 (5 C, Cp), 86.24 (2 C, complexed ArC), 89.51 (complexed ArC), 102.15 (2 C, complexed quaternary ArC) and 124.03 (complexed quaternary ArC).

η^5-Cyclopentadienyl(η^6-2,6-diisopropylnitrobenzene)iron(II) hexafluorophosphate 46 (1.14 g, 48%) (Found: C, 43.3; H, 4.7; N, 3.1. $C_{17}H_{22}F_6FeNO_2P$ requires C, 43.15; H, 4.7; N, 3.0%); δ_H(CD_3COCD_3) 1.26 (6 H, d, *J* 6.8, CH_3), 1.69 (6 H, d, *J* 6.8, CH_3), 2.95 (2 H, septet, *J* 6.9, CH), 5.51 (5 H, s, Cp) and 6.72 (3 H, m, complexed ArH); δ_C(CD_3COCD_3) 21.09 (2 C, CH_3), 25.30 (2 C, CH_3), 30.29 (2 C, CH), 80.59 (5 C, Cp), 82.97 (2 C, complexed ArC), 88.86 (complexed ArC), 107.00 (2 C, complexed quaternary ArC) and 124.23 (complexed quaternary ArC).

η^5-Cyclopentadienyl(η^6-2,5-diisopropylnitrobenzene)iron(II) hexafluorophosphate 47 (1.22 g, 52%) (Found: C, 43.1; H, 4.5; N, 3.0. $C_{17}H_{22}F_6FeNO_2P$ requires C, 43.15; H, 4.7; N, 3.0%); δ_H(CD_3COCD_3) 1.58 (12 H, d, *J* 5.4, CH_3), 2.88 (1 H, septet, *J* 5.5, CH), 3.08 (1 H, septet, *J* 5.7, CH), 5.54 (5 H, s, Cp), 6.66 (1 H, d, *J* 6.0, complexed ArH), 6.75 (1 H, d, *J* 5.7, complexed ArH) and 7.09 (1 H, s, complexed ArH); δ_C(CD_3COCD_3) 22.41 (2 C, CH_3), 24.24 (2 C, CH_3), 30.51 (2 C, CH), 80.17 (5 C, Cp), 84.36 (complexed ArC), 86.20 (complexed ArC), 87.76 (complexed ArC), 104.47 (complexed quaternary ArC), 108.79 (complexed quaternary ArC) and 117.93 (complexed quaternary ArC).

η^5-Cyclopentadienyl(η^6-2,4,6-trimethylnitrobenzene)iron(II) hexafluorophosphate 48 (1.24 g, 58%) (Found: C, 39.3; H, 3.8; N, 3.5. $C_{14}H_{16}F_6FeNO_2P$ requires C, 39.0; H, 3.7; N, 3.25%); δ_H(CD_3COCD_3) 2.56 (3 H, s, CH_3), 2.61 (6 H, s, CH_3), 5.36 (5 H, s, Cp) and 6.61 (2 H, s, complexed ArH); δ_C(CD_3COCD_3) 16.84 (CH_3), 20.05 (2 C, CH_3), 81.61 (5 C, Cp), 88.12 (2 C, complexed ArC), 96.64 (2 C, complexed quaternary ArC), 105.33 (complexed quaternary ArC) and 123.61 (complexed quaternary ArC).

η^5-Cyclopentadienyl(η^6-4-acetylnitrobenzene)iron(II) hexafluorophosphate 49 (28–37%, based on the nature of the starting aniline complex; 24 h reaction time) (Found: C, 36.3; H, 2.7; N, 3.0. $C_{13}H_{12}F_6FeNO_3P$ requires C, 36.2; H, 2.8; N, 3.25%); ν_{max}(neat)/cm^{-1} 1725 (CO); δ_H(CD_3COCD_3) 2.89 (3 H, s, CH_3), 5.56 (5 H, s, Cp), 7.45 (2 H, d, *J* 7.2, complexed ArH) and 7.75 (2 H, d, *J* 7.3, complexed ArH); δ_C(CD_3COCD_3) 27.36 (CH_3), 82.60 (5 C, Cp), 85.86 (2 C, complexed ArC), 88.79 (2 C, complexed ArC), 97.02 (complexed quaternary ArC), 113.45 (complexed quaternary ArC) and 197.852 (CO).

Nucleophilic substitutions

A mixture of the substituted nitroarene complex (1.0 mmol) was combined with phenylsulfonylacetonitrile (1.2 mmol) or an ethyl alkylacetoacetate (1.2 mmol) and K_2CO_3 (2.5 mmol) in DMF (6 ml). The mixture was then stirred under N_2 for 5 h at room temperature (in the case of the ethyl alkylacetoacetate, it was heated to 60 °C for 18 h) after which, as a red reaction mixture, it was filtered into 10% aqueous HCl. Concentrated aqueous NH_4PF_6 was added to the mixture to give a precipitate which was filtered off and washed three times with Et_2O (25 ml). Alternatively, the mixture was extracted with CH_2Cl_2, and the extract washed four times with water, dried ($MgSO_4$) and concentrated using a rotary evaporator. Addition of Et_2O to the concentrates precipitated the products. The following are the spectroscopic and analytical data for complexes **50**–**60** and **72**–**88**.

η^5-Cyclopentadienyl[η^6-4-ethylphenyl(phenylsulfonyl)acetonitrile]iron(II) hexafluorophosphate 50 (0.413 g, 75%) (Found: C, 45.9; H, 3.8; N, 2.4. $C_{21}H_{20}F_6FeNO_2PS$ requires C, 45.75; H, 3.7; N, 2.5%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2305 (CN) and 1162 and 1348 (SO_2); $\delta_H(CD_3COCD_3)$ 1.37 (3 H, t, *J* 7.3, CH_3), 3.00 (2 H, q, *J* 7.3, CH_2), 5.29 (5 H, s, Cp), 6.42 (2 H, d, *J* 6.41, complexed ArH), 6.57–6.61 (3 H, m, complexed ArH and CH), 7.77–7.80 (2 H, m, SO_2Ph) and 7.88–7.92 (3 H, m, SO_2Ph); $\delta_C(CD_3COCD_3)$ 15.01 (CH_3), 31.11 (CH_2), 61.89 (CH), 79.67 (5 C, Cp), 87.23 (complexed ArC), 89.03 (complexed ArC), 89.21 (complexed ArC), 91.01 (complexed ArC), 90.87 (complexed quaternary ArC), 111.80 (complexed quaternary ArC), 113.34 (CN), 130.96 (2 C, SO_2Ph), 131.05 (2 C, SO_2Ph), 135.22 (quaternary SO_2Ph) and 137.41 (SO_2Ph).

η^5-Cyclopentadienyl[η^6-4-isopropylphenyl(phenylsulfonyl)acetonitrile]iron(II) hexafluorophosphate 51 (0.483 g, 85%) (Found: C, 46.4; H, 3.7; N, 2.6. $C_{22}H_{22}F_6FeNO_2PS$ requires C, 46.7; H, 3.9; N, 2.5%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2341 (CN) and 1136 and 1332 (SO_2); $\delta_H(CD_3COCD_3)$ 1.44 (6 H, d, *J* 7.0, CH_3), 3.29 (1 H, septet, *J* 6.9, CH), 5.32 (5 H, s, Cp), 6.41 (2 H, d, *J* 6.8, complexed ArH), 6.64 (2 H, m, SO_2Ph) and 7.81–7.96 (3 H, m, SO_2Ph); $\delta_C(CD_3COCD_3)$ 22.86 (CH_3), 23.07 (CH_3), 33.38 (CH), 61.69 (CH), 79.30 (5 C, Cp), 86.85 (complexed ArC), 87.13 (complexed ArC), 87.43 (complexed ArC), 90.88 (complexed quaternary ArC), 90.89 (complexed ArC), 113.16 (CN), 116.23 (complexed quaternary ArC), 130.79 (2 C, SO_2Ph), 130.87 (2 C, SO_2Ph), 135.87 (SO_2Ph) and 137.26 (C, SO_2Ph).

η^5-Cyclopentadienyl[η^6-2-isopropylphenyl(phenylsulfonyl)acetonitrile]iron(II) hexafluorophosphate 52 (0.382 g, 68%) (Found: C, 46.9; H, 3.7; N, 2.6. $C_{22}H_{22}F_6FeNO_2PS$ requires C, 46.7; H, 3.9; N, 2.5%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2305 (CN) and 1135 and 1337 (SO_2); $\delta_H(CD_3COCD_3)$ 1.35 (3 H, d, *J* 6.5, CH_3), 1.69 (3 H, d, *J* 6.6, CH_3), 3.34 (1 H, m, CH), 5.34 (5 H, s, Cp), 6.49 (1 H, d, *J* 6.4, complexed ArH), 6.69–6.81 (4 H, m, complexed ArH and CH), 7.76–7.88 (2 H, m, SO_2Ph) and 7.91–8.06 (3 H, m, SO_2Ph); $\delta_C(CD_3COCD_3)$ 23.91 (CH_3), 25.31 (CH_3), 58.18 (CH), 59.21 (CH), 79.20 (5 C, Cp), 81.08 (complexed ArC), 86.29 (complexed ArC), 87.01 (complexed ArC), 89.62 (complexed ArC), 90.94 (complexed quaternary ArC), 114.38 (CN), 118.79 (complexed quaternary ArC), 130.82 (2 C, SO_2Ph), 130.98 (2 C, SO_2Ph), 135.36 (quaternary, SO_2Ph) and 137.33 (C, SO_2Ph).

η^5-Cyclopentadienyl[η^6-4-*tert*-butylphenyl(phenylsulfonyl)acetonitrile]iron(II) hexafluorophosphate 53 (0.459 g, 79%) (Found: C, 47.8; H, 4.0; N, 2.7. $C_{23}H_{24}F_6FeNO_2PS$ requires C, 47.7; H, 4.2; N, 2.4%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2306 (CN) and 1160 and 1343 (SO_2); $\delta_H(CD_3COCD_3)$ 1.53 (9 H, s, CH_3), 5.33 (5 H, s, Cp), 6.43 (2 H, m, complexed ArH), 6.65–6.69 (3 H, m, complexed ArH and CH), 7.77–7.80 (2 H, m, SO_2Ph) and 7.86–7.88 (3 H, m, SO_2Ph); $\delta_C(CD_3COCD_3)$ 31.10 (3 C, CH_3), 35.92 (aliphatic quaternary), 62.06 (CH), 79.33 (5 C, Cp), 86.18 (complexed ArC), 86.34 (complexed ArC), 86.83 (complexed ArC), 90.61 (complexed ArC), 91.13 (complexed quaternary ArC), 113.56 (CN), 121.03 (complexed quaternary ArC), 131.20 (2 C, SO_2Ph), 131.26 (2 C, SO_2Ph), 135.45 (quaternary SO_2Ph) and 137.68 (SO_2Ph).

η^5-Cyclopentadienyl[η^6-4-*sec*-butylphenyl(phenylsulfonyl)acetonitrile]iron(II) hexafluorophosphate 54 (0.451 g, 78%) (Found: C, 47.7; H, 3.6; N, 2.5. $C_{23}H_{24}F_6FeNO_2PS$ requires C, 47.7; H, 4.2; N, 2.4%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2310 (CN) and 1162 and 1347 (SO_2); $\delta_H(CD_3COCD_3)$ 0.94 (3 H, t, *J* 7.0, CH_3), 1.50 (3 H, d, *J* 6.7, CH_3), 1.70–1.78 (2 H, m, CH_2), 2.93–3.06 (1 H, m, CH), 5.32 (5 H, s, Cp), 6.38–6.41 (2 H, m, complexed ArH), 6.57–6.60 (3 H, m, complexed ArH and CH), 7.72–7.79 (2 H, m, SO_2Ph) and 7.86–7.99 (3 H, m, SO_2Ph); $\delta_C(CD_3COCD_3)$ 11.61 (CH_3), 18.58 (CH_3), 31.87 (CH_2), 39.58 (CH), 61.66 (CH), 79.27 (5 C, Cp), 86.49 (complexed ArC), 86.74 (complexed ArC), 88.37 (complexed ArC), 90.63 (complexed ArC), 91.05 (complexed quaternary ArC), 113.15 (CN), 115.86 (complexed quaternary ArC), 130.75 (2 C, SO_2Ph), 130.81 (2 C, SO_2Ph), 134.96 (quaternary SO_2Ph) and 137.26 (SO_2Ph).

η^5-Cyclopentadienyl[η^6-4-pentylphenyl(phenylsulfonyl)acetonitrile]iron(II) hexafluorophosphate 55 (0.476 g, 80%) (Found: C, 48.8; H, 4.4; N, 2.2. $C_{24}H_{26}F_6FeNO_2PS$ requires C, 48.6; H, 4.4; N, 2.4%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2304 (CN) and 1162 and 1348 (SO_2); $\delta_H(CD_3COCD_3)$ 0.90 (3 H, t, *J* 5.6, CH_3), 1.35–1.40 (4 H, m, CH_2), 1.71–1.75 (2 H, m, CH_2), 2.88 (2 H, t, *J* 6.2, CH_2), 5.31 (5 H, s, Cp), 6.41 (2 H, m, complexed ArH), 6.64 (3 H, m, complexed ArH and CH), 7.77–7.80 (2 H, m, SO_2Ph) and 7.87–7.90 (3 H, m, SO_2Ph); $\delta_C(CD_3COCD_3)$ 14.08 (CH_3), 22.81 (CH_2), 31.40 (CH_2), 31.82 (CH_2), 35.33 (CH_2), 61.69 (CH), 79.63 (5 C, Cp), 87.07 (complexed ArC), 89.36 (complexed ArC), 89.58 (complexed ArC), 90.59 (complexed quaternary ArC), 90.90 (complexed ArC), 110.304 (complexed quaternary ArC), 113.01 (CN), 130.70 (2 C, SO_2Ph), 130.79 (2 C, SO_2Ph), 134.89 (quaternary SO_2Ph) and 137.18 (SO_2Ph).

η^5-Cyclopentadienyl[η^6-2,3-dimethylphenyl(phenylsulfonyl)acetonitrile]iron(II) hexafluorophosphate 56 (0.441 g, 80%) (Found: C, 45.9; H, 3.6; N, 2.65. $C_{21}H_{20}F_6FeNO_2PS$ requires C, 45.75; H, 3.7; N, 2.5%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2319 (CN) and 1160 and 1345 (SO_2); $\delta_H(CD_3COCD_3)$ 2.61 (3 H, s, CH_3), 2.66 (3 H, s, CH_3), 5.21 (5 H, s, Cp), 6.33 (1 H, d, *J* 6.6, complexed ArH), 6.55 (1 H, t, *J* 6.3, complexed ArH), 6.65–6.69 (2 H, m, complexed ArH and CH), 7.76–7.83 (2 H, m, SO_2Ph) and 7.93–7.98 (3 H, m, SO_2Ph); $\delta_C(CD_3COCD_3)$ 15.71 (CH_3), 20.13 (CH_3), 60.15 (CH), 79.62 (5 C, Cp), 86.53 (complexed ArC), 87.57 (complexed ArC), 91.51 (complexed ArC), 90.46 (complexed quaternary ArC), 104.25 (complexed quaternary ArC), 104.41 (quaternary complexed ArC), 113.93 (CN), 130.74 (2 C, SO_2Ph), 130.91 (2 C, SO_2Ph), 135.05 (quaternary SO_2Ph) and 137.30 (SO_2Ph).

η^5-Cyclopentadienyl[η^6-2,4-dimethylphenyl(phenylsulfonyl)acetonitrile]iron(II) hexafluorophosphate 57 (0.438 g, 79%) (Found: C, 45.6; H, 3.5; N, 2.5. $C_{21}H_{20}F_6FeNO_2PS$ requires C, 45.7; H, 3.7; N, 2.5%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2320 (CN) and 1160 and 1334 (SO_2); $\delta_H(CD_3COCD_3)$ 2.62 (3 H, s, CH_3), 2.63 (3 H, s, CH_3), 5.22 (5 H, s, Cp), 6.34 (1 H, d, *J* 6.9, complexed ArH), 6.55–6.58 (3 H, m, complexed ArH and CH), 7.76–7.80 (2 H, m, SO_2Ph) and 7.83–7.98 (3 H, m, SO_2Ph); $\delta_C(CD_3COCD_3)$ 18.76 (CH_3), 20.32 (CH_3), 59.64 (CH), 79.71 (5 C, Cp), 86.97 (complexed ArC), 88.65 (complexed ArC), 89.25 (complexed quaternary ArC), 91.69 (complexed ArC), 104.62 (complexed quaternary ArC), 106.16 (complexed quaternary ArC), 113.64 (CN), 130.70 (2 C, SO_2Ph), 130.93 (SO_2Ph), 135.00 (quaternary SO_2Ph) and 137.29 (SO_2Ph).

η^5-Cyclopentadienyl[η^6-3,4-dimethylphenyl(phenylsulfonyl)acetonitrile]iron(II) hexafluorophosphate 58 (0.401 g, 73%) (Found: C, 45.9; H, 3.8; N, 2.7. $C_{21}H_{20}F_6FeNO_2PS$ requires C, 45.7; H, 3.7; N, 2.5%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2317 (CN) and 1160 and 1341 (SO_2); δ_H(CD_3COCD_3) 2.60 (3 H, s, CH_3), 2.64 (3 H, s, CH_3), 5.22 (5 H, s, Cp), 6.30–6.56 (4 H, m, complexed ArH and CH), 7.77–7.87 (2 H, m, SO_2Ph) and 7.90–7.96 (3 H, m, SO_2Ph); δ_C(CD_3COCD_3) 18.95 (CH_3), 19.18 (CH_3), 61.64 (CH), 79.80 (5 C, Cp), 85.61 (complexed ArC), 90.21 (complexed ArC), 91.703 (complexed ArC), 104.51 (complexed quaternary ArC), 105.21 (complexed quaternary ArC), 105.29 (complexed quaternary ArC), 113.22 (CN), 130.87 (4 C, SO_2Ph), 135.00 (complexed quaternary ArC) and137.23 (SO_2Ph).

η5-Cyclopentadienyl[η6-3,5-dimethylphenyl(phenylsulfonyl)-acetonitrile]iron(II) hexafluorophosphate 59 (0.489 g, 89%) (Found: C, 45.95; H, 3.5; N, 2.6. $C_{21}H_{20}F_6FeNO_2PS$ requires C, 45.7; H, 3.7; N, 2.5%); ν_{max}(CH_2Cl_2)/cm^{-1} 2315 (CN) and 1162 and 1347 (SO_2); δ_H(CD_3COCD_3) 2.56 (3 H, s, CH_3), 2.61 (3 H, s, CH_3), 5.24 (5 H, s, Cp), 6.24 (1 H, s, CH), 6.29 (1 H, s, complexed ArH), 6.44 (1 H, s, complexed ArH), 6.62 (1 H, s, complexed ArH), 7.77–7.87 (2 H, m, SO_2Ph) and 7.90–7.97 (3 H, m, SO_2Ph); δ_C(CD_3COCD_3) 20.06 (2 C, CH_3), 61.66 (CH), 79.70 (5 C, Cp), 85.42 (complexed ArH), 89.47 (complexed ArH), 90.63 (complexed quaternary ArC), 91.16 (complexed ArC), 104.59 (complexed quaternary ArC), 104.90 (complexed quaternary ArC), 112.76 (CN), 130.63 (4 C, SO_2Ph), 134.49 (quaternary SO_2Ph) and 137.04 (SO_2Ph).

η5-Cyclopentadienyl[η6-2,4,6-trimethylphenyl(phenylsulfonyl)acetonitrile]iron(II) hexafluorophosphate 60 (0.404 g, 72%) (Found: C, 46.5; H, 3.8; N, 2.7. $C_{22}H_{22}F_6FeNO_2PS$ requires C, 46.7; H, 3.9; N, 2.5%); ν_{max}(CH_2Cl_2)/cm^{-1} 2305 (CN) and 1162 and 1356 (SO_2); δ_H(CD_3COCD_3) 2.61 (3 H, s, CH_3), 2.62 (3 H, s, CH_3), 2.71 (3 H, s, CH_3), 5.21 (5 H, s, Cp), 6.55 (1 H, s, CH), 6.57 (1 H, s, complexed ArH), 6.64 (1 H, s, complexed ArH), 7.82–7.99 (2 H, m, SO_2Ph), 8.02–8.13 (3 H, m, SO_2Ph); δ_C(CD_3COCD_3) 20.08 (CH_3), 20.10 (CH_3), 20.17 (CH_3), 58.45 (CH), 80.04 (5 C, Cp), 91.12 (complexed ArC), 91.65 (complexed ArC), 96.84 (quaternary complexed ArC), 103.42 (quaternary complexed ArC), 104.73 (quaternary complexed ArC), 105.44 (quaternary complexed ArC), 113.85 (CN), 130.45 (2 C, SO_2Ph), 130.52 (2 C, SO_2Ph), 136.72 (quaternary SO_2Ph) and 137.34 (SO_2Ph).

η5-Cyclopentadienyl[η6-ethyl 2-(4-ethylphenyl)propanoate]-iron(II) hexafluorophosphate 72 (0.239 g, 51%) (Found: C, 46.1; H, 4.8. $C_{18}H_{23}F_6FeO_2P$ requires C, 45.8; H, 4.9%); ν_{max}-(CH_2Cl_2)/cm^{-1} 1732 (CO_2Et); δ_H(CD_3COCD_3) 1.23–1.34 (6 H, m, 2 CH_3), 1.61 (3 H, d, *J* 6.8, CH_3), 2.87 (2 H, q, *J* 7.3, CH_2), 4.07 (1 H, q, *J* 6.9, CH), 4.24 (2 H, q, *J* 7.0, CH_2), 5.13 (5 H, s, Cp) and 6.41 (4 H, br s, complexed ArH); δ_C(CD_3COCD_3) 14.24 (CH_3), 14.97 (CH_3), 18.25 (CH_3), 29.80 (CH_2), 43.91 (CH), 62.07 (CH_2), 78.04 (5 C, Cp), 86.63 (complexed ArC), 87.37 (complexed ArC), 87.76 (complexed ArC), 87.82 (complexed ArC), 105.16 (quaternary complexed ArC), 109.29 (quaternary complexed ArC) and 172.61 (CO_2Et).

η5-Cyclopentadienyl[η6-ethyl 2-(4-ethylphenyl)butanoate]-iron(II) hexafluorophosphate 73 (0.276 g, 57%) (Found: C, 47.1; H, 5.0. $C_{19}H_{25}F_6FeO_2P$ requires C, 46.9; H, 5.2%); ν_{max}(CH_2Cl_2)/cm^{-1} 1731 (CO_2Et); δ_H(CD_3COCD_3) 0.98 (3 H, t, *J* 7.2, CH_3), 1.26–1.38 (6 H, m, 2 CH_3), 1.88–1.92 (2 H, m, CH_2), 2.92 (2 H, q, *J* 7.4, CH_2), 3.82 (1 H, t, *J* 7.1, CH), 4.37 (2 H, q, *J* 7.1, CH_2), 5.11 (5 H, s, Cp) and 6.40–6.52 (4 H, m, complexed ArH); δ_C(CD_3COCD_3) 12.04 (CH_3), 14.31 (CH_3), 14.85 (CH_3), 22.29 (CH_2), 30.97 (CH_2), 51.38 (CH), 62.02 (CH_2), 77.90 (5 C, Cp), 86.16 (complexed ArC), 87.66 (complexed ArC), 87.68 (complexed ArC), 88.08 (complexed ArC), 103.99 (quaternary complexed ArC), 109.28 (quaternary complexed ArC) and 172.21 (CO_2Et).

η5-Cyclopentadienyl[η6-ethyl 2-(4-isopropylphenyl)propanoate]iron(II) hexafluorophosphate 74 (0.247 g, 51%) (Found: C, 46.8; H, 5.4. $C_{19}H_{25}F_6FeO_2P$ requires C, 46.9; H, 5.2%); ν_{max}(CH_2Cl_2)/cm^{-1} 1730 (CO_2Et); δ_H(CD_3COCD_3) 1.27 (3 H, t, *J* 7.1, CH_3), 1.37 (6 H, d, *J* 6.9, 2 CH_3), 1.62 (3 H, d, *J* 7.2, CH_3), 3.20 (1 H, septet, *J* 6.9, CH), 4.10 (1 H, q, *J* 7.2, CH), 4.25 (2 H, q, *J* 7.1, CH_2), 5.15 (5 H, s, Cp) and 6.41–6.50 (4 H, m, complexed ArH); δ_C(CD_3COCD_3) 14.28 (CH_3), 18.33 (CH_3), 22.84 (CH_3), 23.01 (CH_3), 33.04 (CH), 43.97 (CH), 62.12 (CH_2), 77.85 (5 C, Cp), 86.03 (complexed ArC), 86.14 (complexed ArC), 86.50 (complexed ArC), 87.15 (complexed ArC), 105.43 (quaternary complexed ArC), 113.92 (quaternary complexed ArC) and 172.65 (CO_2Et).

η5-Cyclopentadienyl[η6-ethyl 2-(4-isopropylphenyl)butanoate]iron(II) hexafluorophosphate 75 (0.278 g, 56%) (Found: C, 48.1; H, 5.3. $C_{20}H_{27}F_6FeO_2P$ requires C, 48.0; H, 5.4%); ν_{max}(CH_2Cl_2)/cm^{-1} 1731 (CO_2Et); δ_H(CD_3COCD_3) 0.98 (3 H, t, *J* 7.3, CH_3), 1.29–1.41 (9 H, m, 3 CH_3), 1.95–1.98 (2 H, m, CH_2), 3.21 (1 H, septet, *J* 7.0, CH), 3.85 (2 H, t, *J* 5.5, CH_2), 4.36 (2 H, q, *J* 7.0, CH_2), 5.12 (5 H, s, Cp) and 6.40–6.56 (4 H, m, complexed ArH); δ_C(CD_3COCD_3) 12.07 (CH_3), 14.31 (CH_3), 22.66 (CH_3), 22.69 (CH_3), 32.94 (CH), 41.27 (CH_2), 51.39 (CH), 62.03 (CH_2), 77.74 (5 C, Cp), 85.82 (complexed ArC), 85.89 (complexed ArC), 86.43 (complexed ArC), 87.80 (complexed ArC), 104.18 (quaternary complexed ArC), 113.82 (quaternary complexed ArC) and 172.18 (CO_2Et).

η5-Cyclopentadienyl[η6-ethyl 2-(4-isopropylphenyl)hexanoate]iron(II) hexafluorophosphate 76 (0.277 g, 53%) (Found: C, 50.3; H, 6.1. $C_{22}H_{31}F_6FeO_2P$ requires C, 50.0; H, 5.9%); ν_{max}(CH_2Cl_2)/cm^{-1} 1731 (CO_2Et); δ_H(CD_3COCD_3) 0.90 (3 H, t, *J* 7.0, CH_3), 1.29–1.42 (11 H, m, 3 CH_3 and CH_2), 1.72–1.89 (4 H, m, 2 CH_2), 3.25 (1 H, septet, *J* 7.1, CH), 3.92 (1 H, t, *J* 4.9, CH), 4.35 (2 H, q, *J* 7.2, CH_2), 5.13 (5 H, s, Cp) and 6.41–6.58 (4 H, m, complexed ArH); δ_C(CD_3COCD_3) 13.85 (CH_3), 14.32 (CH_3), 22.66 (CH_3), 22.69 (CH_3), 22.73 (CH_2), 33.04 (CH), 35.83 (2 C, CH_2), 49.89 (CH), 62.08 (CH_2), 77.77 (5 C, Cp), 85.67 (complexed ArC), 85.90 (complexed ArC), 86.54 (complexed ArC), 87.98 (complexed ArC), 104.43 (quaternary complexed ArC), 113.87 (quaternary complexed ArC) and 172.36 (CO_2Et).

η5-Cyclopentadienyl[η6-ethyl 2-(4-butylphenyl)propanoate]-iron(II) hexafluorophosphate 77 (0.290 g, 58%) (Found: C, 48.2; H, 5.4. $C_{20}H_{27}F_6FeO_2P$ requires C, 48.0; H, 5.4%); ν_{max}(CH_2Cl_2)/cm^{-1} 1729 (CO_2Et); δ_H(CD_3COCD_3) 0.92 (3 H, t, *J* 7.0, CH_3), 1.27 (3 H, t, *J* 7.0, CH_3), 1.34–1.45 (4 H, m, 2 CH_2), 1.65 (3 H, d, *J* 7.2, CH_3), 2.88 (2 H, t, *J* 7.3, CH_2), 4.07 (1 H, q, *J* 7.0, CH), 4.21 (2 H, q, *J* 7.0, CH_2), 5.14 (5 H, s, Cp) and 6.41 (4 H, s, complexed ArH); δ_C(CD_3COCD_3) 13.77 (CH_3), 14.11 (CH_3), 18.10 (CH_3), 22.52 (CH_2), 33.71 (CH_2), 34.63 (CH_2), 43.76 (CH), 61.94 (CH_2), 77.96 (5 C, Cp), 86.52 (complexed ArC), 87.23 (complexed ArC), 88.04 (complexed ArC), 88.11 (complexed ArC), 104.98 (quaternary complexed ArC), 107.48 (quaternary complexed ArC) and 172.48 (CO_2Et).

η5-Cyclopentadienyl[η6-ethyl 2-(4-*tert*-butylphenyl)propanoate]iron(II) hexafluorophosphate 78 (0.261 g, 52%) (Found: C, 47.8; H, 5.5. $C_{20}H_{27}F_6FeO_2P$ requires C, 48.0; H, 5.4%); ν_{max}(CH_2Cl_2)/cm^{-1} 1731 (CO_2Et); δ_H(CD_3COCD_3) 1.28 (3 H, t, *J* 7.1, CH_3), 1.49 (9 H, s, 3 CH_3), 1.66 (3 H, d, *J* 7.2, CH_3), 4.12 (1 H, q, *J* 7.2, CH), 4.23 (2 H, q, *J* 7.2, CH_2), 5.19 (5 H, s, Cp) and 6.45–6.52 (4 H, m, complexed ArH); δ_C(CD_3COCD_3) 14.36 (CH_3), 18.54 (CH_3), 30.43 (3 C, CH_3), 34.83 (aliphatic quaternary), 43.68 (CH), 62.26 (CH_2), 77.63 (5 C, Cp), 84.78 (ArC), 84.84 (ArC), 86.29 (ArC), 86.86 (ArC), 105.00 (quaternary complexed ArC), 118.10 (quaternary complexed ArC) and 173.2 (CO_2Et).

η5-Cyclopentadienyl[η6-ethyl 2-(4-*tert*-butylphenyl)butanoate]iron(II) hexafluorophosphate 79 (0.297 g, 58%) (Found: C, 49.2; H, 5.8. $C_{21}H_{29}F_6FeO_2P$ requires C, 49.05; H, 5.6%); ν_{max}(CH_2Cl_2)/cm^{-1} 1729 (CO_2Et); δ_H(CD_3COCD_3) 0.99 (3 H, t, *J* 7.4, CH_3), 1.36 (3 H, t, *J* 7.1, CH_3), 1.49 (9 H, s, 3 CH_3), 1.85–1.99 (2 H, m, CH_2), 3.89 (1 H, t, *J* 6.3, CH), 4.37 (2 H, q, *J* 7.1, CH_2), 5.15 (5 H, s, Cp) and 6.45–6.51 (4 H, m, complexed ArH); δ_C(CD_3COCD_3) 12.55 (CH_3), 14.83 (CH_3), 30.96 (CH_2), 31.11 (3 C, CH_3), 34.35 (aliphatic quaternary), 51.88 (CH), 62.61 (CH_2), 77.94 (5 C, Cp), 85.14 (complexed ArC), 85.43 (complexed ArC), 86.12 (complexed ArC), 87.95 (complexed ArC), 104.11 (quaternary complexed ArC), 118.25 (quaternary complexed ArC) and 172.29 (CO_2Et).

η^5-Cyclopentadienyl[η^6-ethyl 2-(4-*tert*-butylphenyl)hexanoate]iron(II) hexafluorophosphate 80 (0.278 g, 51%) (Found: C, 51.0; H, 5.9. $C_{23}H_{33}F_6FeO_2P$ requires C, 50.9; H, 6.1%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1730 (CO_2Et); $\delta_H(CD_3COCD_3)$ 0.87 (3 H, t, *J* 7.0, CH_3), 1.26–1.44 (7 H, m, CH_3 and 2 CH_2), 1.48 (9 H, s, 3 CH_3), 1.76–1.96 (2 H, m, CH_2), 3.94 (1 H, t, *J* 7.2, CH), 4.35 (2 H, q, *J* 6.9, CH_2), 5.14 (5 H, s, Cp) and 6.43–6.51 (4 H, m, complexed ArH); $\delta_C(CD_3COCD_3)$ 13.98 (CH_3), 14.50 (CH_3), 22.82 (CH_2), 30.80 (3 C, CH_3), 35.10 (aliphatic quaternary), 36.04 (2 C, CH_2), 50.07 (CH), 62.27 (CH_2), 77.63 (5 C, Cp), 84.83 (complexed ArC), 85.15 (complexed ArC), 85.71 (complexed ArC), 87.72 (complexed ArC), 104.33 (quaternary complexed ArC), 118.29 (quaternary complexed ArC) and 172.40 (CO_2Et).

η^5-Cyclopentadienyl[η^6-ethyl 2-(4-*sec*-butylphenyl)propanoate]iron(II) hexafluorophosphate 81 (0.271 g, 54%) (Found: C, 47.9; H, 5.5. $C_{20}H_{27}F_6FeO_2P$ requires C, 48.0; H, 5.4%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1730 (CO_2Et); $\delta_H(CD_3COCD_3)$ 0.92 (3 H, t, *J* 7.4, CH_3), 1.32 (3 H, t, *J* 7.0, CH_3), 1.47 (3 H, d, *J* 6.9, CH_3), 1.54–1.74 (5 H, m, CH_3 and CH_2), 2.83–3.03 (1 H, m, CH), 4.18 (1 H, q, *J* 7.3, CH), 4.23 (2 H, q, *J* 7.2, CH_2), 5.18 (5 H, s, Cp) and 6.40–6.48 (4 H, m, complexed ArH); $\delta_C(CD_3COCD_3)$ 11.48 (CH_3), 14.18 (2 C, 2 CH_3), 18.43 (CH_3), 31.70 (CH_2), 39.27 (CH), 43.87 (CH), 62.03 (CH_2), 77.77 (5 C, Cp), 85.23 (complexed ArC), 86.76 (complexed ArC), 87.33 (complexed ArC), 87.47 (complexed ArC), 105.40 (quaternary complexed ArC), 113.42 (quaternary complexed ArC) and 172.56 (CO_2Et).

η^5-Cyclopentadienyl[η^6-ethyl 2-(4-*sec*-butylphenyl)butanoate]iron(II) hexafluorophosphate 82 (0.251 g, 49%) (Found: C, 49.2; H, 5.8. $C_{21}H_{29}F_6FeO_2P$ requires C, 49.0; H, 5.7%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1731 (CO_2Et); $\delta_H(CD_3COCD_3)$ 0.85–1.01 (6 H, m, 2 CH_3), 1.30–1.47 (6 H, m, 2 CH_3), 1.57–1.69 (2 H, m, CH_2), 1.70–1.99 (2 H, m, CH_2), 2.95–2.98 (1 H, m, CH), 3.84 (1 H, t, *J* 7.2, CH), 4.35 (2 H, q, *J* 7.0, CH_2), 5.13 (5 H, s, Cp) and 6.35–6.52 (4 H, m, complexed ArH); $\delta_C(CD_3COCD_3)$ 11.55 (CH_3), 12.11 (CH_3), 14.39 (CH_3), 18.11 (CH_3), 31.58 (CH_2), 31.90 (CH_2), 39.40 (CH), 51.52 (CH), 62.13 (CH_2), 77.86 (5 C, Cp), 85.75 (complexed ArC), 85.82 (complexed ArC), 87.31 (complexed ArC), 89.97 (complexed ArC), 104.44 (quaternary complexed ArC), 113.62 (quaternary complexed ArC) and 172.33 (CO_2Et).

η^5-Cyclopentadienyl[η^6-ethyl 2-(4-*sec*-butylphenyl)hexanoate]iron(II) hexafluorophosphate 83 (0.261 g, 48%) (Found: C, 50.8; H, 6.1. $C_{23}H_{33}F_6FeO_2P$ requires C, 50.9; H, 6.1%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1730 (CO_2Et); $\delta_H(CD_3COCD_3)$ 0.79–1.05 (6 H, m, 2 CH_3), 1.22–1.46 (8 H, m, 2 CH_3 and CH_2), 1.54–1.85 (4 H, m, 2 CH_2), 2.77–3.04 (2 H, m, CH_2), 3.34–3.44 (1 H, m, CH), 3.85–3.95 (1 H, t, *J* 7.0, CH), 4.30–4.45 (2 H, q, *J* 7.1, CH_2), 5.12 (5 H, s, Cp) and 6.24–6.63 (4 H, m, complexed ArH); $\delta_C(CD_3COCD_3)$ 11.55 (CH_3), 13.92 (CH_3), 14.37 (CH_3), 18.61 (CH_3), 22.75 (CH_2), 31.54 (CH_2), 35.72 (CH_2), 35.94 (CH_2), 39.13 (CH), 50.07 (CH), 62.22 (CH_2), 77.81 (5 C, Cp), 85.67 (complexed ArC), 85.71 (complexed ArC), 87.24 (complexed ArC), 87.68 (complexed ArC), 104.43 (quaternary complexed ArC), 113.39 (quaternary complexed ArC) and 172.38 (CO_2Et).

η^5-Cyclopentadienyl[η^6-ethyl 2-(3,4-dimethylphenyl)propanoate]iron(II) hexafluorophosphate 84 (0.249 g, 53%) (Found: C, 45.6; H, 5.0. $C_{18}H_{23}F_6FeO_2P$ requires C, 45.8; H, 4.9%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1731 (CO_2Et); $\delta_H(CD_3COCD_3)$ 1.30 (3 H, t, *J* 7.0, CH_3), 1.64 (3 H, d, *J* 7.2, CH_3), 2.56 (6 H, s, 2 CH_3), 4.02 (1 H, q, *J* 7.1, CH), 4.24 (2 H, q, *J* 7.1, CH_2), 5.07 (5 H, s, Cp) and 6.32–6.38 (3 H, m, complexed Ar); $\delta_C(CD_3COCD_3)$ 14.77 (CH_3), 18.16 (CH_3), 18.41 (CH_3), 30.16 (CH_3), 44.38 (CH), 62.57 (CH_2), 78.93 (5 C, Cp), 85.6 (complexed ArC), 86.32 (complexed ArC), 89.56 (complexed ArC), 103.41 (quaternary complexed ArC), 105.25 (2 C, quaternary complexed ArC) and 173.50 (CO_2Et).

η^5-Cyclopentadienyl[η^6-ethyl 2-(3,4-dimethylphenyl)butanoate]iron(II) hexafluorophosphate 85 (0.288 g, 59%) (Found: C, 47.0; H, 5.2. $C_{19}H_{25}F_6FeO_2P$ requires C, 46.9; H, 5.2%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1732 (CO_2Et); $\delta_H(CD_3COCD_3)$ 0.97 (3 H, t, *J* 7.3, CH_3), 1.34 (3 H, t, *J* 7.2, CH_3), 1.80–1.95 (2 H, m, CH_2), 2.56 (3 H, s, CH_3), 2.57 (3 H, s, CH_3), 3.73 (1 H, t, *J* 7.2, CH), 4.34 (2 H, q, *J* 7.1, CH_2), 5.04 (5 H, s, Cp) and 6.32–6.42 (3 H, m, complexed ArH); $\delta_C(CD_3COCD_3)$ 12.25 (CH_3), 14.51 (CH_3), 20.25 (CH_3), 20.56 (CH_3), 32.60 (CH_2), 51.50 (CH), 62.23 (CH_2), 77.93 (5 C, Cp), 85.16 (complexed ArC), 87.69 (complexed ArC), 88.90 (complexed ArC), 103.60 (quaternary complexed ArC), 103.93 (quaternary complexed ArC), 105.63 (quaternary complexed ArC) and 173.21 (CO_2Et).

η^5-Cyclopentadienyl[η^6-ethyl 2-(3,5-dimethylphenyl)propanoate]iron(II) hexafluorophosphate 86 (0.267 g, 56%) (Found: C, 45.9; H, 5.1. $C_{18}H_{23}F_6FeO_2P$ requires C, 45.8; H, 4.9%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1732 (CO_2Et); $\delta_H(CD_3COCD_3)$ 1.28 (3 H, t, *J* 7.1, CH_3), 1.66 (3 H, d, *J* 7.2, CH_3), 2.55 (6 H, s, 2 CH_3), 4.02 (1 H, q, *J* 7.1, CH), 4.24 (2 H, q, *J* 7.0, CH_2), 5.10 (5 H, s, Cp), 6.33 (2 H, s, complexed ArH) and 6.4 (1 H, s, complexed ArH); $\delta_C(CD_3COCD_3)$ 14.22 (CH_3), 18.21 (CH_3), 20.20 (2 C, CH_3), 44.02 (CH), 62.02 (CH_2), 78.43 (5 C, Cp), 85.93 (complexed ArC), 86.61 (complexed ArC), 89.45 (complexed ArC), 103.38 (quaternary complexed ArC), 103.53 (quaternary complexed ArC) and 172.66 (CO_2Et).

η^5-Cyclopentadienyl[η^6-ethyl 2-(3,5-dimethylphenyl)butanoate]iron(II) hexafluorophosphate 87 (0.291 g, 60%) (Found: C, 46.7; H, 5.3. $C_{19}H_{25}F_6FeO_2P$ requires C, 46.9; H, 5.2%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1731 (CO_2Et); $\delta_H(CD_3COCD_3)$ 0.97 (3 H, t, *J* 7.3, CH_3), 1.35 (3 H, t, *J* 7.1, CH_3), 1.88–1.99 (2 H, m, CH_2), 2.54 (3 H, s, CH_3), 2.55 (3 H, s, CH_3), 3.77 (1 H, q, *J* 5.4, CH), 4.39 (2 H, q, *J* 7.2, CH_2), 5.06 (5 H, s, Cp), 6.34 (1 H, s, complexed ArH), 6.37 (1 H, s, complexed ArH) and 6.40 (1 H, s, complexed ArH); $\delta_C(CD_3COCD_3)$ 12.05 (CH_3), 14.50 (CH_3), 20.22 (CH_3), 20.50 (CH_3), 31.56 (CH_2), 51.65 (CH), 62.20 (CH_2), 78.53 (5 C, Cp), 85.53 (complexed ArC), 87.59 (complexed ArC), 89.60 (complexed ArC), 103.50 (quaternary complexed ArC), 103.80 (quaternary complexed ArC), 104.52 (quaternary complexed ArC) and 172.20 (CO_2Et).

η^5-Cyclopentadienyl[η^6-ethyl 2-(3,5-dimethylphenyl)hexanoate]iron(II) hexafluorophosphate 88 (0.276 g, 54%) (Found: C, 49.1; H, 5.8. $C_{21}H_{29}F_6FeO_2P$ requires C, 49.05; H, 5.7%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1730 (CO_2Et); $\delta_H(CD_3COCD_3)$ 0.87 (3 H, t, *J* 7.1, CH_3), 1.22–1.41 (7 H, m, CH_3 and 2 CH_2), 1.70–1.89 (2 H, m, CH_2), 2.54 (3 H, s, CH_3), 2.55 (3 H, s, CH_3), 3.82 (1 H, t, *J* 7.2, CH), 4.40 (2 H, q, *J* 7.1, CH_2), 5.05 (5 H, s, Cp), 6.32 (1 H, s, complexed ArH), 6.35 (1 H, s, complexed ArH) and 6.38 (1 H, s, complexed ArH); $\delta_C(CD_3COCD_3)$ 14.45 (CH_3), 20.35 (CH_3), 20.52 (CH_3), 22.86 (CH_2), 29.67 (CH_3), 30.57 (CH_2), 35.81 (CH_2), 50.23 (CH), 62.14 (CH_2), 78.53 (5 C, Cp), 85.47 (complexed ArC), 87.65 (complexed ArC), 89.60 (complexed ArC), 103.60 (quaternary complexed ArC), 103.87 (quaternary complexed ArC), 104.60 (quaternary complexed ArC) and 172.37 (CO_2Et).

Photolytic demetallation: general procedure for photolysis

Each of the complexes **50**–**60**, **72**–**88** (0.5 mmol) was separately dissolved in a mixture of dichloromethane–acetonitrile (15 ml/5 ml) in a Pyrex tube and the solution was deoxygenated under a stream of nitrogen. The reaction tube was then fitted into a photochemical apparatus equipped with a Xenon lamp and irradiated at room temperature for 4 h. After the reaction mixture had been concentrated to a volume of 1–2 ml by rotary evaporation, the residue was applied to a silica gel column which was then washed with hexane and eluted with chloroform. Removal of the solvent from the eluate gave the expected liberated arenes **61**–**71**, **89**–**105** with the following yields and spectral data.

4-Ethylphenyl(phenylsulfonyl)acetonitrile 61. A yellowish solid (0.128 g, 90%) (Found: C, 67.5; H, 5.3; N, 4.8.

$C_{16}H_{15}NO_2S$ requires C, 67.3; H, 5.3; N, 4.9%); mp 125–127 °C; ν_{max}(CHCl$_3$)/cm^{-1} 2253 (CN) and 1158 and 1333 (SO$_2$); δ_H(CDCl$_3$) 1.21 (3 H, t, *J* 7.7, CH$_3$), 2.67 (2 H, q, *J* 7.6, CH$_2$), 5.07 (1 H, s, CH), 7.18 (4 H, s, ArH), 7.44–7.55 (2 H, m, SO$_2$Ph) and 7.67–7.74 (3 H, m, SO$_2$Ph); δ_C(CDCl$_3$) 15.31 (CH$_3$), 28.59 (CH$_2$), 62.87 (CH), 113.5 (CN), 122.32 (quaternary ArC), 128.56 (2 C, SO$_2$Ph), 129.15 (2 C, ArC), 129.70 (2 C, ArC), 130.08 (2 C, SO$_2$Ph), 134.44 (quaternary ArC), 135.16 (SO$_2$Ph) and 147.14 (C, quaternary SO$_2$Ph); *m/z* 285 (M$^+$, 2%), 144 (100), 117 (22) and 77 (47).

4-Isopropylphenyl(phenylsulfonyl)acetonitrile 62. A yellowish solid (0.112 g, 75%) (Found: C, 68.0; H, 5.6; N, 4.9. $C_{17}H_{17}NO_2S$ requires C, 68.2; H, 5.7; N, 4.7%); mp 94–96 °C; ν_{max}(CHCl$_3$)/cm^{-1} 2253 (CN) and 1159 and 1334 (SO$_2$); δ_H(CDCl$_3$) 1.24 (6 H, d, *J* 7.0, 2 CH$_3$), 2.91 (1 H, septet, *J* 6.4, CH), 5.07 (1 H, s, CH), 7.20 (4 H, s, ArH), 7.47–7.55 (2 H, m, SO$_2$Ph) and 7.67–7.74 (3 H, m, SO$_2$Ph); δ_C(CDCl$_3$) 23.70 (2 C, 2 CH$_3$), 33.83 (CH), 62.78 (CH), 113.44 (CN), 122.32 (quaternary ArC), 127.11 (2 C, ArC), 129.09 (2 C, SO$_2$Ph), 129.68 (2 C, SO$_2$Ph), 129.98 (2 C, ArC), 134.42 (quaternary ArC), 135.11 (SO$_2$Ph) and 151.68 (quaternary SO$_2$Ph); *m/z* 299 (M$^+$, 2%), 158 (100), 116 (26) and 77 (54).

2-Isopropylphenyl(phenylsulfonyl)acetonitrile 63. A yellowish solid (0.105 g, 71%) (Found: C, 68.4; H, 5.6; N, 4.7. $C_{17}H_{17}NO_2S$ requires C, 68.2; H, 5.7; N, 4.7%); mp 68–70 °C; ν_{max}(CHCl$_3$)/cm^{-1} 2258 (CN) and 1162 and 1345 (SO$_2$); δ_H(CDCl$_3$) 1.17 (3 H, d, *J* 6.9, CH$_3$), 1.31 (3 H, d, *J* 6.7, CH$_3$), 3.10 (1 H, septet, *J* 6.9, CH), 5.52 (1 H, s, CH), 7.14–7.15 (2 H, m, ArH), 7.37–7.41 (2 H, m, ArH), 7.51–7.68 (2 H, m, SO$_2$Ph) and 7.69–7.87 (3 H, m, SO$_2$Ph); δ_C(CDCl$_3$) 22.39 (CH$_3$), 25.06 (CH$_3$), 29.39 (CH), 58.76 (CH), 114.34 (CN), 122.45 (quaternary ArC), 126.25 (2 C, ArC), 126.46 (2 C, ArC), 129.29 (2 C, SO$_2$Ph), 130.15 (2 C, SO$_2$Ph), 134.88 (quaternary ArC), 135.26 (SO$_2$Ph) and 148.67 (quaternary SO$_2$Ph); *m/z* 299 (M$^+$, 2%), 158 (100), 143 (30) and 77 (46).

4-*tert*-Butylphenyl(phenylsulfonyl)acetonitrile 64. A yellowish solid (0.142 g, 91%) (Found: C, 69.1; H, 5.9; N, 4.7. $C_{18}H_{19}NO_2S$ requires C, 69.0; H, 6.1; N, 4.5%); mp 132–133 °C; ν_{max}(CHCl$_3$)/cm^{-1} 2254 (CN) and 1159 and 1334 (SO$_2$); δ_H(CDCl$_3$) 1.31 (9 H, s, 3 CH$_3$), 5.09 (1 H, s, CH), 7.20 (2 H, d, *J* 8.1, ArH), 7.37 (2 H, d, *J* 8.1, ArH), 7.53–7.56 (2 H, m, SO$_2$Ph) and 7.73–7.76 (3 H, m, SO$_2$Ph); δ_C(CDCl$_3$) 31.09 (3 C, CH$_3$), 34.75 (aliphatic quaternary C), 62.64 (CH), 113.48 (CN), 122.02 (quaternary ArC), 126.00 (2 C, ArC), 129.10 (2 C, SO$_2$Ph), 129.44 (2 C, ArC), 129.66 (2 C, SO$_2$Ph), 134.52 (quaternary ArC), 135.12 (SO$_2$Ph) and 153.97 (quaternary SO$_2$Ph); *m/z* 313 (M$^+$, 2%), 172 (100), 145 (21), 129 (30) and 77 (79).

4-*sec*-Butylphenyl(phenylsulfonyl)acetonitrile 65. A yellow oil (0.126 g, 81%) (Found: C, 69.2; H, 6.0; N, 4.6. $C_{18}H_{19}NO_2S$ requires C, 69.0; H, 6.1; N, 4.5%); ν_{max}(CHCl$_3$)/cm^{-1} 2258 (CN) and 1160 and 1334 (SO$_2$); δ_H(CDCl$_3$) 0.78 (3 H, t, *J* 7.3, CH$_3$), 1.19 (3 H, d, *J* 6.7, CH$_3$), 1.55 (2 H, quintet, *J* 7.0, CH$_2$), 2.59 (1 H, m, CH), 5.08 (1 H, s, CH), 7.16 (4 H, br s, ArH), 7.44–7.52 (2 H, m, SO$_2$Ph) and 7.66–7.69 (3 H, m, SO$_2$Ph); δ_C(CDCl$_3$) 12.03 (CH$_3$), 21.62 (CH$_3$), 30.85 (CH$_2$), 41.38 (CH), 62.86 (CH), 113.44 (CN), 122.48 (quaternary ArC), 127.74 (2 C, ArC), 129.07 (2 C, SO$_2$Ph), 129.60 (2 C, SO$_2$Ph), 130.02 (2 C, ArC), 134.34 (quaternary ArC), 135.12 (SO$_2$Ph) and 150.49 (quaternary SO$_2$Ph); *m/z* 313 (M$^+$, 2%), 172 (100), 130 (32), 116 (82) and 77 (73).

4-Pentylphenyl(phenylsulfonyl)acetonitrile 66. A yellowish solid (0.135 g, 83%) (Found: C, 69.9; H, 6.7; N, 4.1. $C_{19}H_{21}NO_2S$ requires C, 69.7; H, 6.5; N, 4.3%); mp 78–79 °C; ν_{max}(CHCl$_3$)/cm^{-1} 2280 (CN) and 1160 and 1337 (SO$_2$); δ_H(CDCl$_3$) 0.88 (3 H, t, *J* 6.6, CH$_3$), 1.23–1.30 (4 H, m, 2 CH$_2$), 1.54–1.61 (2 H, m, CH$_2$), 2.60 (2 H, t, *J* 7.4, CH$_2$), 5.07 (1 H, s, CH), 7.15 (4 H, s, ArH), 7.46–7.54 (2 H, m, SO$_2$Ph) and 7.66–7.73 (2 H, m, SO$_2$Ph); δ_C(CDCl$_3$) 13.99 (CH$_3$), 22.45 (CH$_2$), 30.81 (CH$_2$), 31.29 (CH$_2$), 35.55 (CH$_2$), 62.86 (CH), 113.51 (CN), 122.35 (quaternary ArC), 129.11 (4 C, ArC), 129.59 (2 C, SO$_2$Ph), 130.07 (2 C, SO$_2$Ph), 134.40 (quaternary ArC), 135.15 (SO$_2$Ph) and 145.84 (quaternary SO$_2$Ph); *m/z* 327 (M$^+$, 2%), 186 (100), 130 (28), 116 (50) and 77 (31).

2,3-Dimethylphenyl(phenylsulfonyl)acetonitrile 67. A white solid (0.119 g, 84%) (Found: C, 67.5; H, 5.5; N, 5.0. $C_{16}H_{15}NO_2S$ requires C, 67.3; H, 5.3; N, 4.9%); mp 140–142 °C; ν_{max}(CHCl$_3$)/cm^{-1} 2250 (CN) and 1160 and 1334 (SO$_2$); δ_H(CDCl$_3$) 2.25 (3 H, s, CH$_3$), 2.30 (3 H, s, CH$_3$), 5.50 (1 H, s, CH), 7.00–7.04 (2 H, m, ArH), 7.19–7.23 (1 H, m, ArH), 7.50–7.58 (2 H, m, SO$_2$Ph) and 7.69–7.80 (3 H, m, SO$_2$Ph); δ_C(CDCl$_3$) 16.26 (CH$_3$), 21.44 (CH$_3$), 60.46 (CH), 114.84 (CN), 123.84 (quaternary ArC), 125.83 (ArC), 127.77 (ArC), 129.15 (2 C, SO$_2$Ph), 130.01 (2 C, SO$_2$Ph), 132.14 (ArC), 134.73 (quaternary ArC), 135.16 (SO$_2$Ph), 136.77 (quaternary ArC) and 138.06 (quaternary SO$_2$Ph); *m/z* 285 (M$^+$, 4%), 144 (100), 117 (26), 91 (8) and 77 (17).

2,4-Dimethylphenyl(phenylsulfonyl)acetonitrile 68. A white solid (0.102 g, 72%) (Found: C, 67.2; H, 5.4; N, 5.1. $C_{16}H_{15}NO_2S$ requires C, 67.3; H, 5.3; N, 4.9%); mp 144–145 °C; ν_{max}(CHCl$_3$)/cm^{-1} 2252 (CN) and 1162 and 1338 (SO$_2$); δ_H(CDCl$_3$) 2.31 (3 H, s, CH$_3$), 2.34 (3 H, s, CH$_3$), 5.34 (1 H, s, CH), 6.97 (1 H, s, ArH), 7.04 (2 H, d, *J* 7.9, ArH), 7.52–7.59 (2 H, m, SO$_2$Ph) and 7.69–7.82 (3 H, m, SO$_2$Ph); δ_C(CDCl$_3$) 19.28 (CH$_3$), 21.11 (CH$_3$), 59.40 (CH), 114.12 (CN), 120.91 (quaternary ArC), 127.31 (ArC), 129.22 (2 C, SO$_2$Ph), 129.85 (ArC), 130.05 (2 C, SO$_2$Ph), 132.01 (ArC), 134.83 (quaternary ArC), 135.19 (SO$_2$Ph), 137.90 (quaternary ArC) and 140.85 (quaternary SO$_2$Ph); *m/z* 285 (M$^+$, 2%), 144 (100), 117 (23), 91 (8) and 77 (15).

3,4-Dimethylphenyl(phenylsulfonyl)acetonitrile 69. A yellowish solid (0.123 g, 87%) (Found: C, 67.4; H, 5.1; N, 5.0. $C_{16}H_{15}NO_2S$ requires C, 67.3; H, 5.3; N, 4.9%); mp 81–83 °C; ν_{max}(CHCl$_3$)/cm^{-1} 2251 (CN) and 1158 and 1333 (SO$_2$); δ_H(CDCl$_3$) 2.21 (3 H, s, CH$_3$), 2.25 (3 H, s, CH$_3$), 5.02 (1 H, s, CH), 6.99 (1 H, s, ArH), 7.08 (1 H, d, *J* 7.8, ArH), 7.12 (1 H, d, *J* 7.8, ArH), 7.49–7.68 (2 H, m, SO$_2$Ph) and 7.71–7.76 (3 H, m, SO$_2$Ph); δ_C(CDCl$_3$) 19.56 (CH$_3$), 20.63 (CH$_3$), 62.74 (CH), 113.57 (CN), 122.28 (quaternary ArC), 127.11 (ArC), 129.05 (ArC), 130.03 (2 C, SO$_2$Ph), 130.05 (ArC), 130.12 (SO$_2$Ph), 130.67 (SO$_2$Ph), 134.45 (quaternary ArC), 135.06 (SO$_2$Ph), 137.56 (quaternary ArC) and 139.46 (quaternary SO$_2$Ph); *m/z* 285 (M$^+$, 2%), 144 (100), 117 (11), 91 (9) and 77 (42).

3,5-Dimethylphenyl(phenylsulfonyl)acetonitrile 70. A yellowish solid (0.116 g, 82%) (Found: C, 67.5; H, 5.3; N, 4.8. $C_{16}H_{15}NO_2S$ requires C, 67.3; H, 5.3; N, 4.9%); mp 107–109 °C; ν_{max}(CHCl$_3$)/cm^{-1} 2305 (CN) and 1160 and 1335 (SO$_2$); δ_H(CDCl$_3$) 2.25 (6 H, s, 2 CH$_3$), 5.00 (1 H, s, CH), 6.83 (2 H, s, ArH), 7.04 (1 H, s, ArH), 7.48–7.56 (2 H, m, SO$_2$Ph) and 7.67–7.74 (3 H, m, SO$_2$Ph); δ_C(CDCl$_3$) 21.05 (2 C, CH$_3$), 62.98 (CH), 113.53 (CN), 124.85 (quaternary ArC), 127.44 (2 C, ArC), 129.00 (2 C, SO$_2$Ph), 130.06 (2 C, SO$_2$Ph), 132.07 (ArC), 134.35 (2 C, quaternary AC), 135.07 (SO$_2$Ph) and 138.00 (quaternary SO$_2$Ph); *m/z* 285 (M$^+$, 4%), 144 (100), 117 (13), 91 (14) and 77 (48).

2,4,6-Trimethylphenyl(phenylsulfonyl)acetonitrile 71. A white crystalline solid (0.107 g, 72%) (Found: C, 68.3; H, 5.7; N, 4.9. $C_{17}H_{17}NO_2S$ requires C, 68.2; H, 5.7; N, 4.7%); mp 169–170 °C; ν_{max}(CHCl$_3$)/cm^{-1} 2260 (CN) and 1160 and 1342 (SO$_2$); δ_H(CDCl$_3$) 2.27 (3 H, s, CH$_3$), 2.30 (3 H, s, CH$_3$), 2.51 (3 H, s, CH$_3$), 5.47 (1 H, s, CH), 6.91 (2 H, s, ArH), 7.57–7.65 (2 H, m, SO$_2$Ph), 7.72–7.75 (1 H, m, SO$_2$Ph) and 7.93–7.97 (2 H, m, SO$_2$Ph); δ_C(CDCl$_3$) 20.81 (3 C, CH$_3$), 57.86 (CH), 113.19 (CN), 118.92 (quaternary ArC), 129.46 (ArC), 129.64 (ArC), 130.04 (2 C, SO$_2$Ph), 131.57 (2 C, SO$_2$Ph), 135.17 (SO$_2$Ph), 136.93 (quaternary ArC), 139.02 (quaternary ArC), 139.66 (quaternary ArC) and 140.44 (quaternary SO$_2$Ph); *m/z* 299 (M$^+$, 2%), 158 (100), 131 (25), 91 (14) and 77 (15).

Ethyl 2-(4-ethylphenyl)propanoate 89. A yellow oil (0.078 g, 76%) (Found: C, 75.5; H, 8.9. $C_{13}H_{18}O_2$ requires C, 75.7; H, 8.8%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1717 (CO_2Et); $\delta_H(CDCl_3)$ 1.14–1.24 (6 H, m, 2 CH_3), 1.47 (3 H, d, *J* 7.2, CH_3), 2.58 (2 H, q, *J* 7.4, CH_2), 3.64 (1 H, q, *J* 7.0, CH), 4.11 (2 H, q, *J* 7.0, CH_2) and 7.10–7.23 (4 H, m, ArH); $\delta_C(CDCl_3)$ 14.12 (CH_3), 15.45 (CH_3), 18.43 (CH_3), 28.43 (CH_2), 45.14 (CH), 60.65 (CH_2), 127.34 (2 C, ArC), 128.03 (2 C, ArC), 137.66 (quaternary ArC), 142.95 (quaternary ArC) and 175.61 (CO_2Et); *m/z* 206 (M^+, 10%), 133 (100), 105 (60), 91 (30), 77 (25) and 29 (40).

Ethyl 2-(4-ethylphenyl)butanoate 90. A yellow oil (0.094 g, 86%) (Found: C, 76.5; H, 9.3. $C_{14}H_{20}O_2$ requires C, 76.3; H, 9.15%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1728 (CO_2Et); $\delta_H(CDCl_3)$ 0.88 (3 H, t, *J* 7.3, CH_3), 1.16–1.36 (6 H, m, 2 CH_3), 1.94–2.12 (2 H, m, CH_2), 2.59 (2 H, q, *J* 7.3, CH_2), 3.38 (1 H, t, *J* 7.3, CH), 4.15 (2 H, q, *J* 7.2, CH_2) and 7.10–7.23 (4 H, m, ArH); $\delta_C(CDCl_3)$ 12.17 (CH_3), 14.01 (CH_3), 14.14 (CH_3), 24.45 (CH_2), 33.97 (CH_2), 53.13 (CH), 60.50 (CH_2), 127.78 (2 C, ArC), 127.93 (2 C, ArC), 136.42 (quaternary ArC), 142.95 (quaternary ArC) and 174.22 (CO_2Et); *m/z* 220 (M^+, 15%), 147 (100), 119 (85), 91 (37), 77 (18) and 29 (48).

Ethyl 2-(4-isopropylphenyl)propanoate 91. A yellow oil (0.085 g, 77%) (Found: C, 76.2; H, 9.1. $C_{14}H_{20}O_2$ requires C, 76.3; H, 9.15%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 (CO_2Et); $\delta_H(CDCl_3)$ 1.22 (3 H, t, *J* 7.1, CH_3), 1.26 (6 H, d, *J* 7.0, 2 CH_3), 1.51 (3 H, d, *J* 7.2, CH_3), 2.89 (1 H, septet, *J* 7.0, CH), 3.67 (1 H, q, *J* 7.2, CH), 4.17 (2 H, q, *J* 7.0, CH_2) and 7.11–7.15 (4 H, m, ArH); $\delta_C(CDCl_3)$ 14.12 (CH_3), 18.64 (CH_3), 18.67 (CH_3), 23.95 (CH_3), 33.68 (CH), 45.12 (CH), 60.63 (CH_2), 126.60 (2 C, ArC), 127.32 (2 C, ArC), 137.96 (quaternary ArC), 147.55 (quaternary ArC) and 174.40 (CO_2Et); *m/z* 220 (M^+, 26%), 147 (100), 119 (81), 77 (15) and 29 (17).

Ethyl 2-(4-isopropylphenyl)butanoate 92. A yellow oil (0.096 g, 82%) (Found: C, 77.0; H, 9.5. $C_{15}H_{22}O_2$ requires C, 76.9; H, 9.5%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1728 (CO_2Et); $\delta_H(CDCl_3)$ 0.88 (3 H, t, *J* 7.2, CH_3), 1.16–1.23 (9 H, m, 3 CH_3), 1.74–2.06 (2 H, m, CH_2), 2.86 (1 H, septet, *J* 7.1, CH), 3.39 (1 H, t, *J* 7.6, CH), 4.12 (2 H, q, *J* 7.0, CH_2) and 7.10–7.24 (4 H, m, ArH); $\delta_C(CDCl_3)$ 12.21 (CH_3), 14.15 (CH_3), 23.92 (2 C, CH_3), 26.69 (CH_2), 33.66 (CH), 53.12 (CH), 60.47 (CH_2), 126.49 (2 C, ArC), 127.74 (2 C, ArC), 136.51 (quaternary ArC), 147.53 (quaternary ArC) and 174.23 (CO_2Et); *m/z* 234 (M^+, 5%), 161 (100), 133 (11), 118 (29), 91 (47), 77 (14) and 29 (81).

Ethyl 2-(4-isopropylphenyl)hexanoate 93. A yellow oil (0.110 g, 84%) (Found: C, 78.0; H, 10.1. $C_{17}H_{26}O_2$ requires C, 77.8; H, 10.0%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1725 (CO_2Et); $\delta_H(CDCl_3)$ 0.85 (3 H, t, *J* 7.2, CH_3), 1.14–1.31 (13 H, m, 3 CH_3 and 2 CH_2), 1.99–2.04 (2 H, m, CH_2), 2.86 (1 H, septet, *J* 7.0, CH), 3.46 (1 H, t, *J* 7.7, CH), 4.09 (2 H, q, *J* 7.2, CH_2) and 7.10–7.19 (4 H, m, ArH); $\delta_C(CDCl_3)$ 13.86 (CH_3), 14.13 (CH_3), 22.42 (CH_2), 23.90 (2 C, CH_3), 33.39 (2 C, CH_2), 33.63 (CH), 51.35 (CH), 60.49 (CH_2), 126.48 (2 C, ArC), 127.67 (2 C, ArC), 136.68 (quaternary ArC), 147.48 (quaternary ArC) and 174.33 (CO_2Et); *m/z* 262 (M^+, 7%), 206 (19), 133 (100), 91 (46), 77 (6) and 29 (32).

Ethyl 2-(4-butylphenyl)propanoate 94. A yellow oil (0.091 g, 78%) (Found: C, 76.7; H, 9.4. $C_{15}H_{22}O_2$ requires C, 76.9; H, 9.5%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1727 (CO_2Et); $\delta_H(CDCl_3)$ 0.92 (3 H, t, *J* 7.3, CH_3), 1.21 (3 H, t, *J* 7.1, CH_3), 1.26–1.41 (2 H, m, CH_2), 1.51–1.66 (2 H, m, CH_2), 2.59 (2 H, t, *J* 7.3, CH), 3.66 (1 H, q, *J* 7.3, CH), 4.15 (2 H, q, *J* 7.2, CH_2) and 7.11–7.16 (4 H, m, ArH); $\delta_C(CDCl_3)$ 13.90 (CH_3), 14.07 (CH_3), 18.58 (CH_3), 22.35 (CH_2), 33.52 (CH_2), 35.20 (CH_2), 45.11 (CH), 60.59 (CH_2), 127.22 (2 C, ArC), 128.53 (2 C, ArC), 137.79 (quaternary ArC), 141.59 (quaternary ArC) and 174.70 (CO_2Et); *m/z* 234 (M^+, 10%), 161 (100), 117 (41), 91 (37), 77 (12) and 29 (47).

Ethyl 2-(4-*tert*-butylphenyl)propanoate 95. A yellow oil (0.079 g, 68%) (Found: C, 77.1; H, 9.5. $C_{15}H_{22}O_2$ requires C, 76.9; H, 9.5%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1727 (CO_2Et); $\delta_H(CDCl_3)$ 1.21 (3 H, t, *J* 7.2, CH_3), 1.30 (9 H, s, 3 CH_3), 1.49 (3 H, d, *J* 7.2, CH_3), 3.65 (1 H, q, *J* 7.0, CH), 4.11 (2 H, q, *J* 7.1, CH_2) and 7.20–7.35 (4 H, m, ArH); $\delta_C(CDCl_3)$ 14.07 (CH_3), 18.55 (CH_3), 31.27 (3 C, 3 CH_3), 34.35 (aliphatic quaternary C), 44.95 (CH), 60.56 (CH_2), 125.39 (2 C, ArC), 126.99 (2 C, ArC), 137.50 (quaternary ArC), 149.72 (quaternary ArC) and 174.75 (CO_2Et); *m/z* 234 (M^+, 10%), 219 (55), 161 (100), 146 (29), 131 (32), 91 (33) and 57 (67).

Ethyl 2-(4-*tert*-butylphenyl)butanoate 96. A yellow oil (0.085 g, 69%) (Found: C, 77.6; H, 9.8. $C_{16}H_{24}O_2$ requires C, 77.4; H, 9.7%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1732 (CO_2Et); $\delta_H(CDCl_3)$ 0.86 (3 H, t, *J* 7.3, CH_3), 1.19 (3 H, t, *J* 7.0, CH_3), 1.27 (9 H, s, 3 CH_3), 1.73–2.02 (2 H, m, CH_2), 3.38 (1 H, t, *J* 7.3, CH), 4.08 (2 H, q, *J* 7.3, CH_2) and 7.17–7.31 (4 H, m, ArH); $\delta_C(CDCl_3)$ 12.25 (CH_3), 14.18 (CH_3), 26.88 (CH_2), 31.34 (3 C, 3 CH_3), 34.50 (aliphatic quaternary), 53.07 (CH), 60.52 (CH_2), 125.38 (2 C, ArC), 127.49 (2 C, ArC), 136.16 (quaternary ArC), 148.45 (quaternary ArC) and 173.25 (CO_2Et); *m/z* 248 (M^+, 20%), 233 (79), 175 (100), 147 (31), 91 (31), 77 (10), 57 (52) and 29 (60).

Ethyl 2-(4-*tert*-butylphenyl)hexanoate 97. A yellow oil (0.103 g, 75%) (Found: C, 78.3; H, 10.3. $C_{18}H_{28}O_2$ requires C, 78.2; H, 10.2%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1725 (CO_2Et); $\delta_H(CDCl_3)$ 0.86 (3 H, t, *J* 7.0, CH_3), 1.17–1.39 (5 H, m, CH_3 and CH_2), 1.45 (9 H, s, 3 CH_3), 1.64–1.78 (2 H, m, CH_2), 1.98–2.00 (2 H, m, CH_2), 3.47 (1 H, t, *J* 7.3, CH), 4.13 (2 H, q, *J* 7.3, CH_2) and 7.17–7.33 (4 H, m, ArH); $\delta_C(CDCl_3)$ 14.16 (CH_3), 22.46 (CH_2), 28.81 (CH_2), 31.33 (3 C, 3 CH_3), 33.43 (CH_2), 34.40 (aliphatic quaternary), 51.30 (CH), 60.54 (CH_2), 125.37 (2 C, ArC), 127.43 (2 C, ArC), 136.36 (quaternary ArC), 148.79 (quaternary ArC) and 174.00 (CO_2Et); *m/z* 276 (M^+, 12%), 261 (66), 220 (21), 147 (100), 117 (24), 91 (20), 57 (60) and 29 (55).

Ethyl 2-(4-*sec*-butylphenyl)propanoate 98. A yellow oil (0.085 g, 73%) (Found: C, 77.1; H, 9.4. $C_{15}H_{22}O_2$ requires C, 76.9; H, 9.5%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1729 (CO_2Et); $\delta_H(CDCl_3)$ 0.79 (3 H, t, *J* 7.5, CH_3), 1.15–1.22 (6 H, m, 2 CH_3), 1.47 (3 H, d, *J* 7.2, CH_3), 1.51–1.58 (2 H, quintet, *J* 7.3, CH_2), 2.56 (1 H, m, CH), 3.63 (1 H, q, *J* 7.3, CH), 4.12 (2 H, q, *J* 7.3, CH_2) and 7.07–7.23 (4 H, m, ArH); $\delta_C(CDCl_3)$ 12.25 (CH_3), 14.14 (CH_3), 18.62 (CH_3), 21.69 (CH_3), 31.16 (CH_2), 41.25 (CH), 45.13 (CH), 60.64 (CH_2), 127.21 (2 C, ArC), 127.26 (2 C, ArC), 137.92 (quaternary ArC), 146.42 (quaternary ArC) and 174.00 (CO_2Et); *m/z* 234 (M^+, 22%), 205 (82), 161 (100), 117 (44), 91 (31), 77 (14) and 29 (59).

Ethyl 2-(4-*sec*-butylphenyl)butanoate 99. A yellow oil (0.083 g, 67%) (Found: C, 77.5; H, 9.6. $C_{16}H_{24}O_2$ requires C, 77.4; H, 9.7%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1733 (CO_2Et); $\delta_H(CDCl_3)$ 0.82–1.03 (6 H, m, 2 CH_3), 1.22–1.39 (6 H, m, 2 CH_3), 1.57–1.77 (2 H, m, CH_2), 1.81–2.23 (2 H, m, CH_2), 2.59–2.66 (1 H, m, CH), 3.45 (1 H, t, *J* 7.3, CH), 4.20 (2 H, q, *J* 7.2, CH_2) and 7.13–7.34 (4 H, m, ArH); $\delta_C(CDCl_3)$ 12.23 (2 C, 2 CH_3), 14.18 (CH_3), 21.67 (CH_3), 26.88 (CH_2), 31.17 (CH_2), 41.25 (CH), 53.19 (CH), 60.52 (CH_2), 127.44 (2 C, ArC), 127.71 (2 C, ArC), 136.54 (quaternary ArC), 145.45 (quaternary ArC) and 174.29 (CO_2Et); *m/z* 248 (M^+, 23%), 219 (80), 175 (100), 147 (31), 91 (58), 77 (11) and 29 (70).

Ethyl 2-(4-*sec*-butylphenyl)hexanoate 100. A yellow oil (0.098 g, 71%) (Found: C, 78.4; H, 10.3. $C_{18}H_{28}O_2$ requires C, 78.2; H, 10.2%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1725 (CO_2Et); $\delta_H(CDCl_3)$ 0.69–0.88 (6 H, m, 2 CH_3), 1.16–1.48 (7 H, m, CH_3 and 2 CH_2), 1.55 (3 H, t, *J* 7.3, CH_3), 2.00–2.16 (4 H, m, 2 CH_2), 2.53–2.56 (1 H, m, CH), 3.43 (1 H, t, *J* 7.2, CH), 4.09 (2 H, q, *J* 7.1, CH_2) and 7.04–7.24 (4 H, m, ArH); $\delta_C(CDCl_3)$ 12.20 (CH_3), 13.88 (CH_3), 14.12 (CH_3), 21.63 (CH_3), 22.44 (CH_2), 29.80 (CH_2), 31.14 (CH_2), 33.39 (CH_2), 41.21 (CH), 51.39 (CH), 60.50 (CH_2), 127.12 (2 C, ArC), 127.63 (2 C, ArC), 136.71 (quaternary ArC), 146.38 (quaternary ArC) and 174.50 (CO_2Et); *m/z* 276 (M^+, 7%), 247 (40), 147 (100), 91 (55), 77 (32) and 29 (76).

Ethyl 2-(3,4-dimethylphenyl)propanoate 101. A yellow oil (0.068 g, 66%) (Found: C, 75.8; H, 8.8. $C_{13}H_{18}O_2$ requires C, 75.7; H, 8.8%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1726 (CO_2Et); $\delta_H(CDCl_3)$ 1.38 (3 H, t, *J* 7.0, CH_3), 1.65 (3 H, d, *J* 7.2, CH_3), 2.40 (3 H, s, CH_3), 2.43 (3 H, s, CH_3), 3.80 (1 H, q, *J* 7.2, CH), 4.32 (2 H, q, *J* 7.0, CH_2) and 7.22–7.27 (3 H, m, ArH); $\delta_C(CDCl_3)$ 14.10

(CH_3), 18.71 (2 C, 2 CH_3), 18.73 (CH_3), 45.09 (CH), 60.62 (CH_2), 124.73 (ArC), 128.69 (ArC), 129.79 (ArC), 135.28 (quaternary ArC), 136.00 (quaternary ArC), 138.14 (quaternary ArC) and 174.79 (CO_2Et); *m/z* 206 (M^+, 11%), 133 (100), 105 (11), 91 (14), 77 (10) and 29 (24).

Ethyl 2-(3,4-dimethylphenyl)butanoate 102. A yellow oil (0.081 g, 74%) (Found: C, 76.4; H, 9.3. $C_{14}H_{20}O_2$ requires C, 76.3; H, 9.15%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1725 (CO_2Et); $\delta_H(CDCl_3)$ 0.87 (3 H, t, *J* 7.3, CH_3), 1.19 (3 H, t, *J* 7.3, CH_3), 1.73–2.18 (2 H, m, CH_2), 2.21 (3 H, s, CH_3), 2.25 (3 H, s, CH_3), 3.35 (1 H, t, *J* 7.7, CH), 4.09 (2 H, q, *J* 7.2, CH_2) and 7.03–7.07 (3 H, m, ArH); $\delta_C(CDCl_3)$ 12.20 (2 C, 2 CH_3), 14.15 (2 C, 2 CH_3), 26.80 (CH_2), 53.11 (CH), 60.51 (CH_2), 125.21 (quaternary ArC), 125.25 (ArC), 129.13 (ArC), 129.50 (quaternary ArC), 129.73 (ArC), 137.20 (quaternary ArC) and 174.25 (CO_2Et); *m/z* 220 (M^+, 18%), 147 (100), 119 (91), 91 (23), 77 (11) and 29 (39).

Ethyl 2-(3,5-dimethylphenyl)propanoate 103. A yellow oil (0.075 g, 73%) (Found: C, 75.9; H, 8.7. $C_{13}H_{18}O_2$ requires C, 75.7; H, 8.8%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1726 (CO_2Et); $\delta_H(CDCl_3)$ 1.20 (3 H, t, *J* 7.1, CH_3), 1.43 (3 H, t, *J* 7.2, CH_3), 2.29 (6 H, s, 2 CH_3), 3.59 (1 H, q, *J* 7.1, CH), 4.11 (2 H, q, *J* 7.1, CH_2), 6.88 (1 H, s, ArH) and 6.89 (2 H, s, ArH); $\delta_C(CDCl_3)$ 14.05 (CH_3), 18.65 (2 C, CH_3), 21.60 (CH_3), 45.31 (CH), 60.56 (CH_2), 125.15 (2 C, ArC), 128.66 (ArC), 137.99 (2 C, quaternary ArC), 140.65 (quaternary ArC) and 174.80 (CO_2Et); *m/z* 206 (M^+, 12%), 133 (100), 105 (11), 91 (14), 77 (10) and 29 (24).

Ethyl 2-(3,5-dimethylphenyl)butanoate 104. A yellow oil (0.067 g, 61%) (Found: C, 76.2; H, 9.1. $C_{14}H_{20}O_2$ requires C, 76.3; H, 9.15%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1727 (CO_2Et); $\delta_H(CDCl_3)$ 0.87 (3 H, t, *J* 7.4, CH_3), 1.20 (3 H, t, *J* 7.1, CH_3), 1.72–2.21 (2 H, m, CH_2), 2.28 (3 H, s, CH_3), 2.28 (3 H, s, CH_3), 3.33 (1 H, t, *J* 7.0, CH), 4.14 (2 H, q, *J* 7.1, CH_2), 6.87 (1 H, s, ArH) and 6.89 (2 H, s, ArH); $\delta_C(CDCl_3)$ 12.22 (2 C, CH_3), 14.15 (CH_3), 21.20 (CH_3), 26.82 (CH_2), 53.39 (CH), 60.50 (CH_2), 125.65 (2 C, ArC), 128.74 (ArC), 137.91 (2 C, quaternary ArC), 139.70 (quaternary ArC), and 174.20 (CO_2Et); *m/z* 220 (M^+, 17%), 147 (69), 119 (100), 91 (22), 77 (10) and 29 (38).

Ethyl 2-(3,5-dimethylphenyl)hexanoate 105. A yellow oil (0.104 g, 84%) (Found: C, 77.6; H, 9.8. $C_{16}H_{24}O_2$ requires C, 77.4; H, 9.7%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 (CO_2Et); $\delta_H(CDCl_3)$ 0.85 (3 H, t, *J* 7.3, CH_3), 1.13–1.32 (7 H, m, CH_3 and 2 CH_2), 1.67–1.99 (2 H, m, CH_2), 2.27 (3 H, s, CH_3), 2.70 (3 H, s, CH_3), 3.44 (1 H, t, *J* 7.1, CH), 4.16 (2 H, q, *J* 7.1, CH_2), 6.86 (1 H, s, ArH) and 6.89 (2 H, s, ArH); $\delta_C(CDCl_3)$ 13.88 (2 C, CH_3), 14.13 (CH_3), 15.23 (CH_3), 22.47 (CH_2), 29.82 (CH_2), 33.39 (CH_2), 51.64 (CH), 60.52 (CH_2), 125.60 (2 C, ArC), 128.48 (2 C, ArC), 137.93 (2 C, quaternary ArC), 139.33 (quaternary ArC) and 173.25 (CO_2Et); *m/z* 248 (M^+, 9%), 192 (20), 175 (11), 119 (100), 91 (14), 77 (9) and 29 (17).

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