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# The first synthesis of ferrocenyl aminophosphonic esters

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**Abstract**

The series of aminophosphonates bearing the ferrocenyl moiety was obtained by the addition of dialkyl phosphites to an azomethine bond of Schiff bases. Some successful attempts to perform the asymmetrical synthesis of aminophosphonates were made, but the isolation of diastereomers failed. 

*Keywords:* Ferrocenecarboxaldehyde; Schiff bases; Aminophosphonates; Asymmetrical induction; Ferrocene moiety

## 1. Introduction

The importance of aminophosphonic acids and esters is commonly known. After the first preparation [1–3] of various phosphono-analogues of natural amino acids, one could notice the great development of their chemistry in the aspect of the synthesis [4–6], the stereochemistry [7–9], biochemical properties [10,11] and their applications in various fields of agriculture and medicine [12–14].

Since the last decade ferrocene-derived compounds have been widely employed in the molecular recognition, because they are characterized by their ability to make metal-centred redox systems to generate oxidized or reduced form of different properties, as described by E.C. Constable [15]. For the formation of such molecular switches containing a ferrocene moiety, it was proposed to use dihydrocholesteryl ester of ferrocenemethanol [15], derivatives of (ferrocenylmethyl)malonate [16] and ferrocene-containing thioethers [17] as well as some derivatives of ferrocenylmethylamines [18] and ferrocenyl ligands containing the tetrathiafulvalene molecules [19].

In late 1950s, Schlögl [20] and Osgerby and Pauson [21] reported the first synthesis of the racemic ferrocenylalanine. Much later, Carlström and Frejd [22,23] and Jackson et al. [24] presented the stereoselective synthesis of 1,1′-ferrocenyl-bis-(alanine). Brunner et al. [25] reported the synthesis of the optically active ferrocenylalanine and suggested its application as a possible substitute for phenylalanine in the commercial sweetener aspartame. Kraatz et al. [26] have proposed the synthesis and the structural study on ferrocenoyl amino acids.

Regarding all the above, we wanted to combine properties of mentioned groups of compounds and to synthesize aminophosphonic acids and esters bearing a ferrocenyl moiety. In this paper, we present the first synthesis of variously *N*-substituted ferrocenylaminomethane phosphonic acids and esters using the methodology described by Tyka [4]. These compounds may eventually show potential properties as plant-protection agents or anti-tumour drugs.

## 2. Results and discussion

Ferrocenylaminophosphonates were synthesized by the addition of dialkyl phosphites to the azomethine bond of Schiff bases. As the model compounds, diethyl, dibenzyl and diphenyl phosphites were chosen (Scheme 1).

Schiff bases of ferrocenecarboxaldehyde **2a–e** were prepared following the known methodology [6,27].

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They were characterized by means of elemental analyses and $^1$H-NMR spectroscopy.

The phosphite additions were carried out in toluene or in acetonitrile at a boiling temperature for 5–7 h. Esters were isolated from the post-reaction mixture by the multiple washing with ether of their aqueous acidic solution and by subsequent extraction of the alkaline aqueous mixture with dichloromethane. Resulting crude esters decomposed on silica gel and on neutral aluminium oxide. The esters **3a–k** were purified by the column chromatography on cellulose powder. In this way, we have obtained *N*-substituted diethyl and dibenzyl ferrocenyl aminomethanephosphonates **3a–j** and diphenyl one **3k**. The $^1$H- and $^{31}$P-NMR spectroscopy and the elemental analysis confirmed their identity and their purity.

Diphenyl aminophosphonates **3l–n** decomposed in the above-described conditions. Their isolation was then very troublesome and their formation was confirmed only by spectroscopic measurements of post-reaction mixtures. Their data are quoted in Section 3.

The addition of dialkyl phosphites to the chiral *N*-(*R*)-α-methylbenzyl ferrocenecarbimine **2e** led to the formation of two diastereoisomers of diethyl *N*-(*R*)-α-methylbenzylamino(ferrocenyl)methanephosphonate **3i** in a 1:3 ratio or dibenzyl *N*-(*R*)-α-methylbenzylamino(-ferrocenyl)methanephosphonate **3j** in a 2:5 ratio, which was demonstrated by means of the $^1$H- and $^{31}$P-NMR spectroscopy. Unfortunately, diastereoisomers were not separated due to their fragility to silica gel and cellulose powder was found not efficient enough to provide a good resolution of diastereoisomers.

All attempts to hydrolyse ethyl esters **3a**, **3c**, **3e**, **3g** and **3i** failed. We tried to use acidic cleavage with aqueous hydrochloric acid as well as the known [6] method with trimethylsilyl bromide. Both methods led to a variety of products, among which, we identified phosphoric acid derivatives. The rest remained unidentified.

Attempts were made to cleave diethyl esters with aqueous sodium hydroxide but instead of this, the retro-addition reaction was observed. The main products of the reaction were the starting ferrocenecarboxaldehyde **1** and the corresponding amine.

We are searching for a more suitable method for the synthesis of ferrocene-derived aminophosphonic acids, as they are of interest as the starting material for the synthesis of their derivatives bearing such biomolecules as steroids or nucleosides. This is why the problem is still under study.

## 3. Experimental

All solvents were routinely distilled and dried prior to use. Amines (Aldrich), phosphites (Aldrich) and ferrocenecarboxaldehyde (Aldrich) were used as received. Cellulose powder was provided by Aldrich. All NMR spectra were recorded on a Brucker Gemini 200 BB spectrometer operating at 200 MHz for $^1$H-NMR and at 81 MHz for $^{31}$P-NMR. Elemental analyses were performed in the Laboratory of Microanalysis at the Centre of Molecular and Macromolecular Studies in Łódź.

### 3.1. Schiff bases of ferrocenecarboxaldehyde

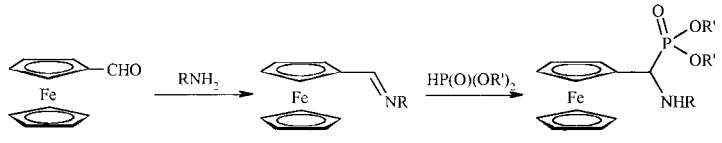
To a solution of ferrocenecarboxaldehyde (1.07 g, 5 mmol) in methanol (30 ml), an amine (5 mmol) was added. The mixture was then stirred for 20 h at a room temperature (r.t.), then the mixture was evaporated, the solid residue dissolved in benzene and precipitated with hexane to give a pure product as red–brown crystals.

#### 3.1.1. *N*-Ferrocenylidenebenzylamine (**2a**)

Y = 1.46 g (96%); m.p: 99–102 °C (benzene–hexane, 1:1).

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 8.24 (s, CH=N, 1H); 7.3–7.2 (m, ArH, 5H); 4.68 (m, $H_{fer}$, 2H); 4.67 (s, $CH_2Ph$, 2H); 4.38 (m, $H_{fer}$, 2H); 4.17 (s, $C_5H_5$, 5H).

Elemental analysis: Anal. Found: C, 71.27; H, 5.54; N, 4.61. Calc. for $C_{18}H_{17}FeN$: C, 71.31; H, 5.65; N, 4.62%.




**1** **2a-e** **3a-n**

**2a**: R=$CH_2Ph$; **2b**: R=$CH_2$(2-Fur); **2c**: R=$C(CH_3)_3$; **2d**: R=$CHPh_2$; **2e**: R=(*R*)-$CH(CH_3)Ph$

**3a**: R=$CH_2Ph$, R'=Et; **3b**: R=$CH_2Ph$, R'=$CH_2Ph$; **3c**: R=$CH_2$(2-Fur), R'=Et;
**3d**: R=$CH_2$(2-Fur), R'=$CH_2Ph$;**3e**: R=$C(CH_3)_3$, R'=Et; **3f**: R=$C(CH_3)_3$, R'=$CH_2Ph$;
**3g**: R=$CHPh_2$, R'=Et; **3h**: R=$CHPh_2$, R'=$CH_2Ph$; **3i**: R=(*R*)-$CH(CH_3)Ph$, R'=Et;
**3j**: R=(*R*)-$CH(CH_3)Ph$, R'=$CH_2Ph$; **3k**: R=$CHPh_2$, R'=Ph;**3l**: R=$CH_2Ph$, R'=Ph;
**3m**: R=$CH_2$(2-Fur), R'=Ph; **3n**: R=$C(CH_3)_3$, R'=Ph

Scheme 1. Synthesis of aminophosphonates 3a–n

*3.1.2. N-Ferrocenylidenefurfurylamine (**2b**)*

Y = 1.13 g (77%); m.p.: 86–91 °C (benzene–hexane, 1:1).

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 8.20 (s, CH=N, 1H); 7.39 (m, $H^5_{fur}$, 1H); 6.34 (m, $H^3_{fur}$, 1H); 6.27 (m, $H^4_{fur}$, 1H); 4.69 (m, $H_{fer}$, 2H); 4.61 (s, $CH_2$Fur, 2H); 4.39 (m, $H_{fer}$, 2H); 4.18 (s, $C_5H_5$, 5H).

Elemental analysis: Anal. Found: C, 65.63; H, 5.13; N, 4.63. Calc. for $C_{16}H_{15}FeNO$: C, 65.55; H, ,5.16; N, 4.78%.

*3.1.3. N-Ferrocenylidene tert-butylamine (**2c**)*

Y = 2.45 g (91%); m.p.: 65–69 °C (benzene–hexane, 1:1).

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 8.12 (s, CH=N, 1H); 4.80 (m, $H_{fer}$, 2H); 4.44 (m, $H_{fer}$, 2H); 4.18 (s, $C_5H_5$, 5H); 1.32 (s, $CH_3$, 9H).

Elemental analysis: Anal. Found: C, 66.53; H, 7.06; N, 4.95. Calc. for $C_{15}H_{19}FeN$: C, 66.93; H, 7.12; N, 5.20%.

*3.1.4. N-ferrocenylidenediphenylmethylamine (**2d**)*

Y = 90% (1.7 g); m.p.: 143–144 °C (benzene–hexane, 1:1).

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 8.26 (s, CH=N, 1H); 7.31 (m, ArH, 10 H); 5.49 (s, CH, 1H); 4.73 (dd, $J$ = 1.8 and 1.9 Hz, $CH_2$, 2H); 4.37 (dd, $J$ = 1.8 and 1.9 Hz, $CH_2$, 2H); 4.08 (s, $C_5H_5$, 5H).

Elemental analysis: Anal. Found: C, 75.96; H, 5.54; N, 3.68. Calc. for $C_{24}H_{21}FeN$: C, 76.00; H, 5.58; N, 3.69%.

*3.1.5. N-Ferrocenylidene-(R)-α-methylbenzylamine (**2e**)*

Y = 1.70 g (90%); m.p.: 48–50 °C (benzene–hexane, 1:1).

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 8.21 (s, CH=N, 1H); 7.37–7.25 (m, ArH, 5H); 4.73 (m, $CH_{fer}$, 1H); 4.65 (m, $CH_{fer}$, 1H); 4.43 (quart, $J$ = 6.8 Hz, CHPh, 1H); 4.36 (m, $CH_{fer}$, 2H); 4.12 (s, $C_5H_5$, 5H); 1.58 (d, $J$ = 6.8 Hz, $CH_3$, 3H).

Elemental analysis: Anal. Found: C, 71.75; H, ,6.18; N, 4.51. Calc. for $C_{19}H_{19}FeN$: C, 71.94; H, 6.04; N, 4.42%.

*3.2. Dialkyl N-alkylaminoferrocenemethane-phosphonates (**3a–n**)*

To a solution of an imine (5 mmol) in toluene (or in acetonitrile, in the case of **2e**) (50 ml), dialkyl phosphite (5 mmol) was added. The solution was refluxed for 7 h, then stirred at a r.t. for 12 h. The solvent was evaporated, the residue was dissolved in the 10% aqueous HCl–ethanol (4:1), washed with ether (3 × 20 ml), the aqueous layer extracted with dichloromethane (3 × 25 ml), the organic layers dried and evaporated to give an appropriate product. The product was purified by means of column chromatography on cellulose powder.

*3.2.1. Diethyl N-benzylaminoferrocenylo-methanephosphonate (**3a**)*

Y = 1.65 g (75%).

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 7.47–7.21 (m, ArH, 5H); 4.67 (m, $CH_{fer}$, 2H); 4.38–3.97 (m, $OCH_2CH_3$, $CH_{fer}$, $CH_2$Ph, 8H); 4.06 (s, $C_5H_5$, 5H); 3.74 (d, $^2J_{PH}$ = 10.1 Hz, CHP, 1H); 1.28 and 1.25 (2t, $J$ = 6.8 Hz, 6H, $OCH_2CH_3$). $^{31}$P-NMR (81 MHz, $CDCl_3$): $\delta$ 22.08.

EI-MS: $m/z$ = 441.1 [$M^+$]; 303.1 [$M^+$–HOP$(OEt)_2$]; 212.0 [Fc-CH=$N^+$]; 121.1 [$CpFe^+$]; 109.3 [$^+$P(O)-(OH)(OEt)]; 91.1 [$^+CH_2$Ph]; 65.1 [$Cp^+$]; 28.1 [$CH_2$=$CH_2$].

Elemental analysis: Anal. Found: C, 60.03; H, 6.31; N, 3.43. Calc. for $C_{22}H_{28}FeNO_3P$: C, 59.88; H, 6.40; N, 3.17%.

*3.2.2. Dibenzyl N-benzylaminoferrocenylo-methanephosphonate (**3b**)*

Y = 1.76 g (62%).

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 7.36–7.23 (m, ArH, 15H); 4.95 (m, $OCH_2$Ph, 2H); 4.26 (m, $CH_{fer}$, 2H); 4.22 (d, $J$ = 12.6 Hz, $CH_2$Ph, 1H); 4.15 (m, $CH_{fer}$, 2H); 4.05 (d, $J$ = 12.6 Hz, $CH_2$Ph, 1H); 4.04 (s, $C_5H_5$, 5H); 3.95 (m, $OCH_2$Ph, 2H); 3.81 (d, $^2J_{PH}$ = 10.0 Hz, 1H); 1.25 (s, NH, 1H). $^{31}$P-NMR (81 MHz, $CDCl_3$): $\delta$ 22.67.

EI-MS: $m/z$ = 565.2 [$M^+$]; 303.1 [$M^+$–HOP-$(OCH_2Ph)_2$]; 212.0 [Fc-CH=$N^+$]; 171.0 [$^+$P(O)(OH)-$(OCH_2Ph)$]; 121.1 [$CpFe^+$]; 107.1 [$^+OCH_2$Ph]; 91.1 [$^+CH_2$Ph]; 65.1 [$Cp^+$].

Elemental analysis: Anal. Found: C, 68.21; H, 5.80; N, 2.84. Calc. for $C_{32}H_{32}FeNO_3P$: C, 7.95; H, 5.71; N, 2.48%.

*3.2.3. Diethyl N-furfurylaminoferrocenylo-methanephosphonate (**3c**)*

Y = 1.1 g (51%).

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 7.42 (m, $H^{fur}_5$, 1H); 6.37 (m, $H^{fur}_3$, 1H); 6.32 (m, $H^{fur}_4$, 1H); 4.25 (m, $CH_{fer}$, 2H); 4.18 (s, $CH_2$Fur, 2H); 4.14 (m, $CH_{fer}$, 2H); 4.10 (s, $C_5H_5$, 5H); 4.00 (m, $OCH_2CH_3$, 4H); 3.68 (d, $^2J_{PH}$ = 7.54 Hz, CHP, 1H); 1.26 and 1.24 (2t, $J$ = 7.0 Hz, 6H, $OCH_2CH_3$). $^{31}$P-NMR (81 MHz, $CDCl_3$): $\delta$ 22.13.

EI-MS: $m/z$ = 431.2 [$M^+$]; 293.0 [$M^+$–HOP$(OEt)_2$]; 212.0 [Fc-CH=$N^+$]; 121.1 [$CpFe^+$]; 109.3 [$^+$P(O)-(OH)(OEt)]; 81.2 [$^+CH_2$Fur]; 65.1 [$Cp^+$]; 28.1 [$CH_2$=$CH_2$].

Elemental analysis: Anal. Found: C, 55.28; H, 5.79; N, 3.28. Calc. for $C_{20}H_{26}FeNO_4P$: C, 55.67; H, 6.08; N, 3.25%.

*3.2.4. Dibenzyl N-furfurylaminoferrocenylomethane-phosphonate (**3d**)*

Y = 2.44 g (88%); m.p.: 93–95 °C.

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 7.40–7.16 (m, ArH, $H^{fur}_5$, 11H); 6.34 (m, $H^{fur}_4$, 1H); 6.21 (m, $H^{fur}_4$, 1H); 4.92 (the AB part of ABX system, $^3J_{PH}$ = 4.6 Hz, $^2J_{HH}$ =

11.3 Hz, $OCH_2Ph$, 2H); 4.27 (m, $CH_2Ph$, 2H); 4.25 (m, $CH_{fer}$, 2H); 4.19 (m, $CH_{fer}$, 2H); 4.15 (s, $CH_2Fur$, 2H); 4.09 (s, $C_5H_5$, 5H); 3.74 (d, $^2J_{PH} = 7.2$ Hz, 1H). $^{31}$P-NMR (81 MHz, $CDCl_3$): $\delta$ 22.62.

EI-MS: $m/z = 555.2$ [$M^+$]; 293.0 [$M^+$–$HOP(OCH_2Ph)_2$]; 212.0 [Fc-CH=$N^+$]; 171.0 [$^+$P(O)(OH)($OCH_2Ph$)]; 121.1 [$CpFe^+$]; 107.1 [$^+OCH_2Ph$]; 91.1 [$^+CH_2Ph$]; 81.2 [$^+CH_2Fur$]; 65.1 [$Cp^+$].

Elemental analysis: Anal. Found: C, 64.96; H, 5.32; N, 2.45. Calc. for $C_{30}H_{30}FeNO_4P$: C, 64.85; H, 5.45; N, 2.52.

### 3.2.5. Diethyl N-tert-butylaminoferrocenylomethanephosphonate (3e)

Y = 1.2 g (59%).

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 4.36–4.04 (m, $2H^a_{fer}$, $2H^b_{fer}$, $OCH_2CH_3$, 8H); 4.21 (s, $C_5H_5$, 5H); 3.82 (d, $^2J_{PH} = 17.1$ Hz, CHP, 1H); 1.34 and 1.31 (2t, $J = 7.1$ Hz, 6H, $OCH_2CH_3$); 1.18 (s, $CH_3$, 9H). $^{31}$P-NMR (81 MHz, $CDCl_3$): $\delta$ 23.59.

EI-MS: $m/z = 431.2$ [$M^+$]; 269.1 [$M^+$–$HOP(OEt)_2$]; 213.0 [Fc-CH=$HN^+$]; 121.1 [$CpFe^+$]; 109.3 [$^+$P(O)(OH)(OEt)]; 65.1 [$Cp^+$]; 55.9 [$Me_2C{=}CH_2$]; 28.1 [$CH_2{=}CH_2$].

Elemental analysis: Anal. Found: C, 56.07; H, 7.38; N, 3.51. Calc. for $C_{19}H_{30}FeNO_3P$: C, 56.00; H, 7.43; N, 3.44%.

### 3.2.6. Dibenzyl N-tert-butylaminoferrocenylomethanephosphonate (3f)

Y = 1.77 g (70%); m.p.: 95–98 °C.

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 7.36–7.29 (m, ArH, 10H); 5.09 (dd, $^2J_{HH} = 12.3$ Hz, $^2J_{PH} = 7.4$ Hz, $OCH_2Ph$, 2H); 4.94 (dd, $^2J_{HH} = 12.3$ Hz, $^2J_{PH} = 8.7$ Hz, $OCH_2Ph$, 2H); 4.27 (m, $CH_{fer}$, 2H); 4.21 (m, $CH_{fer}$, 2H); 4.15 (s, $C_5H_5$, 5H); 3.89 (d, $^2J_{PH} = 16.6$ Hz, 1H); 1.16 (s, NH, 1H). $^{31}$P-NMR (81 MHz, $CDCl_3$): $\delta$ 24.08.

EI-MS: $m/z = 531.3$ [$M^+$]; 269.1 [$M^+$–HOP-($OCH_2Ph)_2$]; 213.0 [Fc-CH=$NH^+$]; 171.0 [$^+$P(O)(OH)-($OCH_2Ph$)]; 121.1 [$CpFe^+$]; 107.1 [$^+OCH_2Ph$]; 91.1 [$^+CH_2Ph$]; 65.1 [$Cp^+$]; 55.9 [$Me_2C{=}CH_2$].

Elemental analysis: Anal. Found: C, 65.41; H, 6.40; N, 2.35. Calc. for $C_{29}H_{34}FeNO_3P$: C, 65.55; H, 6.45; N, 2.64%.

### 3.2.7. Diethyl N-diphenylmethylamino(ferrocenyl)-methane phosphonate (3g)

Y = 1.9 g (75%); m.p.: 138–140°C.

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 7.56–7.25 (m, ArH, 10H); 5.60 (s, CH, 1H); 4.33 (m, $CH_{fer}$, 1H); 4.27 (m, $CH_{fer}$, 1H); 4.24–3.97 (m, $CH_2CH_3$, 4H); 4.15 (m, $CH_{fer}$, 2H); 4.06 (s, $C_5H_5$, 5H); 3.82 (d, $^2J_{HH} = 15.0$ Hz, CHP, 1H); 2.04 (large s, NH, 1H); 1.27 and 1.26 (2t, $J = 7.1$ Hz, $CH_2CH_3$, 6H). $^{31}$P-NMR (81 MHz, $CDCl_3$): $\delta$ 22.41.

EI-MS: $m/z = 517.2$ [$M^+$]; 379.1 [$M^+$–$HOP(OEt)_2$]; 212.0 [Fc-CH=$N^+$]; 167.1 [$^+CHPh_2$]; 121.1 [$CpFe^+$]; 109.3 [$^+$P(O)(OH)(OEt)]; 77.2 [$^+$Ph]; 65.1 [$Cp^+$]; 28.1 [$CH_2{=}CH_2$].

Elemental analysis: Anal. Found: C, 64.73; H, 6.43; N, 2.78. Calc. for $C_{28}H_{32}FeNO_3P$: C, 65.00; H, 6.23; N, 2.71%.

### 3.2.8. Dibenzyl N-diphenylmethylamino(ferrocenyl)-methane phosphonate (3h)

Y = 2.3 g (72%); m.p.: 103–105 °C.

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 7.48–7.25 (m, ArH, 20H); 5.58 (s, CH, 1H); 4.93 (m, $CH_2Ph$, 4H); 4.31 (m, $CH_{fer}$, 1H); 4.24 (m, $CH_{fer}$, 1H); 4.16 (m, $CH_{fer}$, 2H); 4.03 (s, $C_5H_5$, 5H); 3.90 (d, $^2J_{HH} = 14.1$ Hz, CHP, 1H); 2.17 (large s, NH, 1H). $^{31}$P-NMR (81 MHz, $CDCl_3$): $\delta$ 22.96.

EI-MS: $m/z = 641.3$ [$M^+$]; 379.1 [$M^+$–HOP-($OCH_2Ph)_2$]; 212.0 [Fc-CH=$N^+$]; 171.0 [$^+$P(O)(OH)-($OCH_2Ph$)]; 167.1 [$^+CHPh_2$]; 121.1 [$CpFe^+$]; 107.1 [$^+OCH_2Ph$]; 91.1 [$^+CH_2Ph$]; 77.2 [$^+$Ph]; 65.1 [$Cp^+$].

Elemental analysis: Anal. Found: C, 71.00; H, 5.89; N, 2.36. Calc. for $C_{38}H_{36}FeNO_3P$: C, 71.15; H, .66; N, 2.18%.

### 3.2.9. Diethyl N-(R)-α-methylbenzylaminoferrocenylomethanephosphonate (3i)

Y = 1.4 g (62%).

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 7.47–7.27 (m, ArH, 5H); 4.41 and *4.34* (quart, $J = 6.4$ Hz, CHN, 1H); 4.23–4.00 (m, $OCH_2CH_3$, $CH_{fer}$, 8H); 3.97 (s, $C_5H_5$, 5H); 3.74 (d, $^2J_{PH} = 19.0$ Hz, CHP, 1H); 3.62 (d, $^2J_{PH} = 10.1$ Hz, CHP, 1H); 1.48 and *1.40* (d, $J = 6.7$ Hz, $CH_3$, 3H); 1.27 and *1.26* (2t, $J = 7.0$ Hz, 6H, $OCH_2CH_3$). $^{31}$P-NMR (81 MHz, $CDCl_3$): $\delta$ 18.36 and *17.84*.

EI-MS: $m/z = 455.2$ [$M^+$]; 317.2 [$M^+$–$HOP(OEt)_2$]; 213.0 [Fc-CH=$NH^+$]; 121.1 [$CpFe^+$]; 109.3 [$^+$P(O)(OH)(OEt)]; 104.0[PhCH=$CH_2$]; 77.2[$^+$Ph]; 65.1[$Cp^+$]; 28.1[$CH_2{=}CH_2$].

Elemental analysis: Anal. Found: C, 60.64; H, 6.66; N, 3.40. Calc. for $C_{23}H_{30}FeNO_3P$: C, 60.67; H, 6.64; N, 3.08%.

### 3.2.10. Dibenzyl N-(R)-α-methylbenzylaminoferrocenylomethanephosphonate (3j)

Y = 1.8 g (65%).

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 7.35–7.24 (m, ArH, 15H); 5.01–4.84 (m, CHMe, $CH_2Ph$, 3H); 4.41 (m, $CH_2Ph$, 1H); 4.28–4.19 (m, $CH_2Ph$, $CH_{fer}$, 5H); 4.11 and *3.94* (2s, $C_5H_5$, 5H); 3.83 (d, $^2J_{PH} = 18.4$ Hz, CHP, 1H); 3.68 (d, $^2J_{PH} = 9.6$ Hz, CHP, 1H); 1.41 and *1.38* (d, $J = 6.8$ Hz, $CH_3$, 3H). $^{31}$P-NMR (81 MHz, $CDCl_3$): $\delta$ 23.49 and *22.94*.

EI-MS: $m/z = 565.3$ [$M^+$]; 317.1 [$M^+$–$HOP(OCH_2Ph)_2$]; 213.0 [Fc-CH=$NH^+$]; 171.0 [$^+$P(O)(OH)($OCH_2$-

Ph)]; 121.1 [CpFe$^+$]; 107.1 [$^+$OCH$_2$Ph]; 104.0 [PhCH=CH$_2$]; 91.1 [$^+$CH$_2$Ph]; 77.2 [$^+$Ph]; 65.1 [Cp$^+$].

Elemental analysis: Anal. Found: C, 68.49; H, 6.03; N, 2.46. Calc. for $C_{23}H_{30}FeNO_3P$: C, 68.40; H, 5.91; N, 2.42%.

### 3.2.11. Diphenyl N-diphenylmethylamino(ferrocenyl)-methane phosphonate (**3k**)

Y = 2.2 g (72%); m.p.: 128–130 °C.

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 7.49–6.83 (m, ArH, 20H); 5.62 (s, CH, 1H); 4.37 (m, $CH_{fer}$, 2H); 4.20 (d, $^2J_{HH}$ = 22.0 Hz, CHP, 1H); 4.19 (m, $CH_{fer}$, 2H); 4.07 (s, $C_5H_5$, 5H); 3.90 (d, $^2J_{HH}$ = 14.1 Hz, CHP, 1H); 2.14 (large s, NH, 1H). $^{31}$P-NMR (81 MHz, $CDCl_3$): $\delta$ 15.83.

EI-MS: $m/z$ = 613.3 [M$^+$]; 379.1 [M$^+$–HOP(OPh)$_2$]; 234.0 [$^+$P(O)(OPh)$_2$]; 212.0 [Fc-CH=N$^+$]; 167.1 [$^+$CHPh$_2$]; 121.1 [CpFe$^+$]; 94.1 [$^+$OPh]; 77.2 [$^+$Ph]; 65.1 [Cp$^+$].

Elemental analysis: Anal. Found: C, 70.49; H, 5.76; N, 2.35. Calc. for $C_{38}H_{36}FeNO_3P$: C, 70.48; H, 5.26; N, 2.28%.

### 3.2.12. Diphenyl N-benzylaminoferrocenylo-methanephosphonate (**3l**) (identified by means of NMR spectroscopy)

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 7.36–6.85 (m, ArH, 15H); 4.37 (d, $^2J_{PH}$ = 12.8 Hz, 1H); 4.27 (m, $CH_{fer}$, 2H); 4.15 (m, $CH_{fer}$, 2H); 4.11 (s, $C_5H_5$, 5H). $^{31}$P-NMR (81 MHz, $CDCl_3$): $\delta$ 14.49.

EI-MS: $m/z$ = 537.3 [M$^+$]; 303.1 [M$^+$–HOP(OPh)$_2$]; 234.0 [$^+$P(O)(OPh)$_2$]; 212.0 [Fc-CH=N$^+$]; 121.1 [CpFe$^+$]; 94.1 [$^+$OPh]; 91.1 [$^+$CH$_2$Ph]; 77.2 [$^+$Ph]; 65.1 [Cp$^+$].

### 3.2.13. Diphenyl N-Furfurylaminoferrocenylo-methanephosphonate (**3m**) (identified by means of NMR spectroscopy)

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 7.43–7.04 (m, ArH, $H_5^{fur}$, 11H); 6.77 (m, $H_4^{fur}$, 1H); 6.37 (m, $H_4^{fur}$, 1H); 4.61 (d, $^2J_{PH}$ = 12.1 Hz, CHP, 1H); 4.34 (m, $CH_{fer}$, 2H); 4.27 (s, $CH_2$Fur, 2H); 4.18 (m, $CH_{fer}$, 2H); 4.14 (s, $C_5H_5$, 5H). $^{31}$P-NMR (81 MHz, $CDCl_3$): $\delta$ 14.41.

EI-MS: $m/z$ = 527.3 [M$^+$]; 293.0 [M$^+$–HOP(OPh)$_2$]; 234.0 [$^+$P(O)(OPh)$_2$]; 212.0 [Fc-CH=N$^+$]; 121.1 [CpFe$^+$]; 94.1 [$^+$OPh]; 81.1 [$^+$CH$_2$Fur]; 77.2 [$^+$Ph]; 65.1 [Cp$^+$].

### 3.2.14. Diphenyl N-tert-butylaminoferrocenylo-methanephosphonate (**3n**) (identified by means of NMR spectroscopy)

$^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 7.24–6.62 (m, ArH, 15H); 4.52 (d, $^2J_{PH}$ = 12.8 Hz, 1H); 4.79 (m, $CH_{fer}$, 2H); 4.41 (m, $CH_{fer}$, 2H); 4.17 (s, $C_5H_5$, 5H); 1.32 (s, $CH_3$, 9H). $^{31}$P-NMR (81 MHz, $CDCl_3$): $\delta$ 15.53.

EI-MS: $m/z$ = 503.3 [M$^+$]; 269.1 [M$^+$–HOP(OPh)$_2$]; 234.0 [$^+$P(O)(OPh)$_2$]; 213.0 [Fc-CH=NH$^+$]; 121.1 [CpFe$^+$]; 94.1 [$^+$OPh]; 77.2 [$^+$Ph]; 65.1 [Cp$^+$]; 55.9 [Me$_2$C=CH$_2$].

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