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Nitroanilinomethanephosphonates Derived from Ferrocene and Nitrobenzaldehyde

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ABSTRACT: *A series of new aminophosphonates derived from ferrocene and nitrobenzene were synthesized. They were characterized by means of the ^{1}H and ^{31}P NMR spectroscopy as well as by their elemental analysis. Synthesis of esters was carried out without solvent as refluxing of the reagents in toluene or in acetonitrile gave no results.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:144–148, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10128

INTRODUCTION

The importance of aminophosphonic acids and esters is well known to chemists. After the first preparation [1–3] of various phosphonic analogues of natural amino acids, one could notice the rapid development of their chemistry in the aspect of the synthesis [4–6], the stereochemistry [7–9], biochemical properties [10], and their applications in various fields of agriculture and medicine [11–13].

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 Constable [14]. For the formation of such molecular switches containing ferrocene moiety, it was proposed to use dihydrocholesteryl ester of ferrocenemethanol [14], derivatives of (ferrocenylmethyl)malonate [15], and ferrocene-containing thioethers [16] as well as some derivatives of ferrocenylmethylamines [17] and ferrocenyl ligands containing tetrathiafulvalene molecules [18].

In our search for new phosphonic molecular marking agents, we reached for ferrocenyl-substituted aminophosphonates in hope of their potential activity as biomarkers. Previously, we reported the synthesis of (ferrocenyl)-*N*-alkylaminophosphonates [19], now we continue this study expanding it to *N*-nitroaniline derivatives. But first we wanted to verify how nitroanilines behave in the preparation of aminophosphonates in the reaction with much cheaper reagents. Thus we performed the synthesis of (nitrophenyl)-*N*-nitroanilino methanephosphonates.

To our surprise, the synthetic aspect of (nitrophenyl)-*N*-nitroanilinomethanephosphonates was only partially exploited. Hans Zimmer with his group [20–23] was the unique who synthesized and fully characterized three diphenyl (nitrophenyl)-*N*-nitroanilinomethanephosphonates, using them subsequently for the preparation of various cyclic compounds [24] in the course of the Horner–Wittig reaction. Orlovskii et al. [25] mentioned the synthesis of diethyl [1-(4-nitrophenyl)]-*N*-(4-nitroanilino)-methanephosphonate (**1Aa**), but they did not characterize it by modern techniques.

In this paper we report the first synthesis and the characterization of several new (ferrocenyl)-*N*-nitroanilino methanephosphonates as perspective

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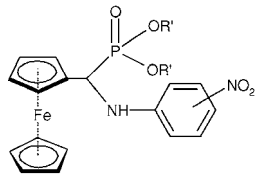
new molecular marking agents. We also report the synthesis of several newly characterized (nitrophenyl)-*N*-nitroanilinomethanephosphonates.

RESULTS AND DISCUSSION

(Ferrocenyl)-*N*-nitroanilinomethanephosphonates **3Aa–3Bc** and (nitrophenyl)-*N*-nitroanilino-methanephosphonates **1Aa–2Bb** were synthesized using Tyka's methodology [4] by the addition of dialkyl phosphites to the azomethine bond of Schiff bases. Diethyl, dibenzyl, and diphenyl phosphites were chosen as the model compounds (Scheme 1).

The phosphite additions were carried out without solvent by simply mixing the Schiff base with the phosphite and subsequent heating for 2 h to 100–120°C. Refluxing of the reagents in toluene or acetonitrile did not give proper results; the 100% recovery of starting materials was noted. Resulting ferrocenyl esters **3Aa–3Bc** were isolated and purified by the column chromatography on cellulose powder as they decomposed on silica gel. Diphenyl ester **3Ac** partially decomposed on cellulose powder, so its purification was performed by shaking with activated charcoal, which gave proper results as shown by elemental analysis. Aminophosphonates deriving from nitrobenzaldehydes were chromatographed on silica gel, but their diphenyl esters **1Bc** and **2Ac** decomposed on silica gel too, so their purification had to be performed on cellulose powder. In this way, we obtained various nitro-substituted diethyl, diphenyl, and dibenzyl (ferrocenyl)-*N*-nitroanilinomethanephosphonates **3Aa–3Bc** and (nitrophenyl)-*N*-nitroanilinomethanephosphonates **1Aa–2Bb** in 65–75% yields (Scheme 1). The ^{1}H and ^{31}P NMR spectroscopy as well as the elemental analysis confirmed their identity and their purity.

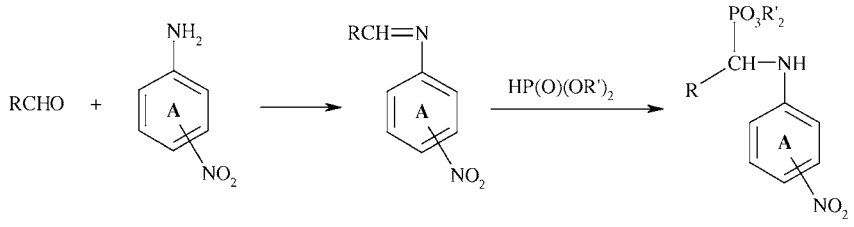


3Aa-3Bc

Attempts to hydrolyze ethyl esters **1Aa, 1Ba, 2Aa, 2Ba, 3Aa**, and **3Ba** failed. We applied acidic cleavage with aqueous hydrochloric acid or in a mixed solvent system (DMSO–water), but in result we recovered starting esters. It is probably due to the hydrophobic character of the molecules bearing nitrophenyl groups. Their dealkylation with bromotrimethylsilane [26] either at room temperature or at boiling temperature did not give positive results either. Complete recovery of starting esters **1Aa, 1Ba, 2Aa**, and **2Ba** was observed. Ferrocenyl esters **3Aa** and **3Ba** decomposed under these conditions, which confirmed our previous observation [19].

EXPERIMENTAL

All solvents (Polish Chemical Reagents—POCh) were routinely distilled and dried prior to use. Nitrobenzaldehydes, ferrocene, and nitroanilines (Aldrich) as well as all phosphites were used as received. Schiff bases were synthesized following published procedures [19,27–29]. Melting points were measured on a Boetius apparatus and are not corrected. NMR spectra were recorded on a Varian Gemini 200BB operating at 200 MHz (^{1}H NMR) and 81 MHz (^{31}P NMR). Elemental analyses were measured in the Laboratory for Microanalysis of the Centre for Molecular and Macromolecular Science (the Polish Academy of Science).



1Aa-3Bc

1Aa: R = *p*-NO_2-C_6H_4, A: *p*-NO_2, R' = CH_2CH_3; **1Ab**: R = *p*-NO_2-C_6H_4, A: *p*-NO_2, R' = CH_2Ph; **1Ba**: R = *p*-NO_2-C_6H_4, A: *m*-NO_2, R' = CH_2CH_3; **1Bb**: R = *p*-NO_2-C_6H_4, A: *m*-NO_2, R' = CH_2Ph; **1Bc**: R = *p*-NO_2-C_6H_4, A: *m*-NO_2, R' = Ph; **2Aa**: R = *m*-NO_2-C_6H_4, A: *p*-NO_2, R' = CH_2CH_3; **2Ab**: R = *m*-NO_2-C_6H_4, A: *p*-NO_2, R' = CH_2Ph; **2Ac**: R = *m*-NO_2-C_6H_4, A: *p*-NO_2, R' = Ph; **2Ba**: R = *m*-NO_2-C_6H_4, A: *m*-NO_2, R' = CH_2CH_3; **2Bb**: R = *m*-NO_2-C_6H_4, A: *m*-NO_2, R' = CH_2Ph; **3Aa**: R = Ferrocenyl, A: *p*-NO_2, R' = CH_2CH_3; **3Ab**: R = Ferrocenyl, A: *p*-NO_2, R' = CH_2Ph; **3Ac**: R = Ferrocenyl, A: *p*-NO_2, R' = Ph; **3Ba**: R = Ferrocenyl, A: *m*-NO_2, R' = CH_2CH_3; **3Bb**: R = Ferrocenyl, A: *m*-NO_2, R' = CH_2Ph; **3Bc**: R = Ferrocenyl, A: *m*-NO_2, R' = Ph.

SCHEME 1

Synthesis of Aminophosphonic Esters, General Method

Aldehyde (10 mmol) was dissolved in methanol (50 ml) and nitroaniline (1.38 g, 10 mmol) was added. The solution was stirred for 3 h at 50°C (nitrobenzaldehyde) and then for about 24 h at room temperature or melted together and heated for 1/2 h (ferrocene). The precipitate was collected by filtration and used without further purification. In case of the reaction in melt, residue was dissolved in dichloromethane, dried over magnesium sulfate, evaporated, and used without further purification.

A Schiff base (4 mmol) and dialkyl phosphite (4 mmol) were mixed together and heated for 2 h at 100–120°C, then the mixture was cooled and the solid residue was purified by the column chromatography on silica gel or on cellulose powder.

*Diethyl [1-(4-Nitrophenyl)]-N-(4-nitroanilino) Methanephosphonate (***1Aa***).* mp = 65–67°C; lit [25] 70–71°C (hexane–AcOEt; 1:2); 0.89 g (55%). ^{1}H NMR ($CDCl_3$): δ 8.24 and 7.66 (2d, $J = 8.6$ Hz, C_6H_4, 2 × 2H); 8.02 and 6.56 (2d, $J = 8.8$ Hz, C_6H_4, 2 × 2H); 5.92 (dd, $^3J_{PH} = 7.8$ Hz and $J = 10.9$ Hz, NH, 1H); 4.94 (dd, $^2J_{PH} = 25.2$ Hz and $J = 10.9$ Hz, CHP, 1H); 4.21–3.20 (m, CH_2, 4H); 1.32 and 1.19 (2t, $J = 6.8$ Hz, CH_3, 6H). ^{31}P NMR ($CDCl_3$): δ 20.19. Anal. Calcd for $C_{17}H_{20}N_3O_7P$: C-49.88; H-4.92; N-10.27. Found: C-49.55; H-5.18; N-10.21.

*Dibenzyl [1-(4-Nitrophenyl)]-N-(4-nitroanilino) Methanephosphonate (***1Ab***).* mp = 146–147°C (hexane–AcOEt; 1:1); 1.34 g (63%). ^{1}H NMR ($CDCl_3$): δ 8.08 and 7.45 (2d, $J = 8.8$ Hz, C_6H_4, 2 × 2H); 7.97 and 6.36 (2d, $J = 9.2$ Hz, C_6H_4, 2 × 2H); 7.49–7.14 (m, ArH, C_6H_4, 12H); 5.04 (m, CH_2Ph, 2H); 4.88 (m, CH_2Ph, 2H); 4.78 (d, $^2J_{PH} = 24.0$ Hz, CHP, 1H). ^{31}P NMR ($CDCl_3$): δ 21.20. Anal. Calcd for $C_{27}H_{24}N_3O_7P$: C-60.79; H-4.53; N-7.88. Found: C-60.62; H-4.58; N-7.81.

*Diethyl [1-(4-Nitrophenyl)]-N-(3-nitroanilino) Methanephosphonate (***1Ba***).* mp = 128–130°C (hexane–AcOEt; 1:1); 0.95 g (58%). ^{1}H NMR ($CDCl_3$): δ 8.23 and 7.68 (2d, $J = 8.2$ Hz, C_6H_4, 2 × 2H); 7.56 (d, $J = 8.0$ Hz, *m*-C_6H_4, 1H); 7.40 (s, *m*-C_6H_4, 1H); 7.26 (m, *m*-C_6H_4, 1H); 6.86 (d, $J = 8.0$ Hz, *m*-C_6H_4, 1H); 5.52 (dd, $^3J_{PH} = 9.7$ Hz and $J = 7.4$ Hz, NH, 1H); 4.91 (dd, $^2J_{PH} = 25.4$ Hz and $J = 7.4$ Hz, CHP, 1H); 4.22–3.88 (m, $\underline{CH_2}CH_3$, 4H); 1.33 and 1.19 (2t, $J = 6.8$ Hz, CH_3, 6H). ^{31}P NMR ($CDCl_3$): δ 20.66. Anal. Calcd for $C_{17}H_{20}N_3O_7P$: C-49.88; H-4.92; N-10.27. Found: C-49.73; H-5.02; N-9.90.

*Dibenzyl [1-(4-Nitrophenyl)]-N-(3-nitroanilino) Methanephosphonate (***1Bb***).* mp = 108–110°C (hexane–AcOEt; 1:1); 1.23 g (58%). ^{1}H NMR ($CDCl_3$): δ 8.05 and 7.52 (2d, $J = 8.4$ Hz, C_6H_4, 2 × 2H); 7.51 (d, $J = 8.0$ Hz, *m*-C_6H_4, 1H); 7.30–7.14 (m, ArH, *m*-C_6H_4, 12H); 6.68 (d, $J = 8.0$ Hz, *m*-C_6H_4, 1H); 5.45 (dd, $^3J_{PH} = 9.6$ Hz and $J = 7.4$ Hz, NH, 1H); 5.07 (m, CH_2Ph, 2H); 4.90 (m, CH_2Ph, 2H); 4.76 (dd, $^2J_{PH} = 24.5$ Hz and $J = 7.4$ Hz, CHP, 1H). ^{31}P NMR ($CDCl_3$): δ 21.64. Anal. Calcd for $C_{27}H_{24}N_3O_7P$: C-60.79; H-4.53; N-7.88. Found: C-60.77; H-4.61; N-7.64.

*Diphenyl [1-(4-Nitrophenyl)]-N-(3-nitroanilino) Methanephosphonate (***1Bc***).* mp = 122–124°C; 1.29 g (64%). ^{1}H NMR ($CDCl_3$): δ 8.18 and 7.76 (2d, $J = 8.7$ Hz, p-C_6H_4, 2 × 2H); 7.59 (d, $J = 8.0$ Hz, *m*-C_6H_4, 1H); 7.41 (s, *m*-C_6H_4, 1H); 7.29–7.19 (m, ArH, 6H); 7.11 (m, ArH, 2H); 6.91 (m, ArH, *m*-C_6H_4, 3H); 6.84 (dd, $J = 8.0$ and 8.5 Hz, *m*-C_6H_4, 1H); 5.86 (large s, NH, 1H); 5.30 (d, $^2J_{PH} = 25.3$ Hz, CHP, 1H). ^{31}P NMR ($CDCl_3$): δ 11.87. Anal. Calcd for $C_{25}H_{20}N_3O_7P$: C-59.41; H-3.99; N-8.31. Found: C-59.11; H-4.17; N-8.44.

*Diethyl [1-(3-Nitrophenyl)]-N-(4-nitroanilino) Methanephosphonate (***2Aa***).* mp = 143–145°C (hexane–AcOEt; 1:1); 0.85 g (56%). ^{1}H NMR ($CDCl_3$): δ 8.37 (s, C_6H_4, 1H); 8.18 (d, $J = 8.0$ Hz, C_6H_4, 1H); 8.02 (d, $J = 9.0$ Hz, *p*-C_6H_4, 2H); 7.83 (d, $J = 7.4$ Hz, C_6H_4, 1H); 7.57 (t, $J = 8.0$ Hz, C_6H_4, 1H); 6.62 (d, $J = 9.0$ Hz, *p*-C_6H_4, 2H); 5.40 (large s, NH, 1H); 4.94 (d, $^2J_{PH} = 24.9$ Hz, CHP, 1H); 4.31–3.87 (m, $\underline{CH_2}CH_3$, 4H); 1.33 and 1.20 (2t, $J = 7.1$ Hz, CH_3, 6H). ^{31}P NMR ($CDCl_3$): δ 19.40. Anal. Calcd for $C_{17}H_{20}N_3O_7P$: C-49.88; H-4.92; N-10.27. Found: C-49.71; H-4.95; N-10.16.

*Dibenzyl [1-(3-Nitrophenyl)]-N-(4-nitroanilino) Methanephosphonate (***2Ab***).* mp = 142–144°C (hexane–AcOEt; 1:1); 0.54 g (27%). ^{1}H NMR ($CDCl_3$): δ 8.11 (m, *m*-C_6H_4, 1H); 7.97 (d, $J = 9.1$ Hz, *p*-C_6H_4, 2H); 7.65 (d, $J = 8.4$ Hz, *m*-C_6H_4, 1H); 7.45 (dd, $J = 8.4$ and 8.0 Hz, *m*-C_6H_4, 1H); 7.36–7.23 (m, Ph, 10H); 7.17 (d, $J = 8.0$ Hz, *m*-C_6H_4, 1H); 6.40 (d, $J = 9.1$ Hz, *p*-C_6H_4, 2H); 5.41 (dd, $^3J_{PH} = 10.1$ Hz and $^3J_{HH} = 6.7$ Hz, NH, 1H); 5.04 (dd, $J = 10.2$ Hz and 6.0 Hz, CH_2Ph, 2H); 4.90 (d, $J = 9.7$ Hz, CH_2Ph, 2H); 4.74 (dd, $^2J_{PH} = 25.0$ Hz and $^3J_{HH} = 6.7$ Hz, CHP, 1H). ^{31}P NMR ($CDCl_3$): δ 20.03. Anal. Calcd for $C_{27}H_{24}N_3O_7P$: C-60.79; H-4.53; N-7.88. Found: C-60.52; H-4.58; N-7.62.

Diphenyl [1-(3-Nitrophenyl)]-N-(4-nitroanilino) Methanephosphonate (**2Ac**). mp = 55–57°C (hexane–AcOEt; 1:1); 1.09 g (56%) (*finally purified by shaking with activated charcoal*). ^{1}H NMR ($CDCl_3$): δ 8.45 (s, *m*-C_6H_4, 1H); 8.16 (d, $J = 7.7$ Hz, *m*-C_6H_4, 1H); 7.96 (d, $J = 9.2$ Hz, *p*-C_6H_4, 2H); 7.89 (d, $J = 7.5$ Hz, *m*-C_6H_4, 1H); 7.51 (t, $J = 7.8$ Hz, *m*-C_6H_4, 1H); 7.23 (m, *m*-H from Ph—O—P, 4H); 7.07 (m, *o*-H from Ph—O—P, 2H); 6.93 (m, *o*-H from Ph—O—P, 2H); 6.77 (m, *p*-H from Ph—O—P, 2H); 5.35 (d, $^2J_{PH} = 25.4$ Hz, CHP, 1H); 4.80 (large s, NH, 1H). ^{31}P NMR ($CDCl_3$): δ 11.55. Anal. Calcd for $C_{25}H_{20}N_3O_7P$: C-59.41; H-3.99; N-8.31. Found: C-59.20; H-4.09; N-8.11.

Diethyl [1-(3-Nitrophenyl)]-N-(3-nitroanilino) Methanephosphonate (**2Ba**). mp = 158–160°C (hexane–AcOEt; 1:1); 0.83 g (55%). ^{1}H NMR ($CDCl_3$): δ 8.39 (s, C_6H_4, 1H); 8.16 (d, $J = 8.0$ Hz, C_6H_4, 1H); 7.86 (d, $J = 7.5$ Hz, C_6H_4, 1H); 7.59–7.48 (m, C_6H_4, 3H); 7.24 (t, $J = 8.2$ Hz, C_6H_4, 1H); 6.86 (d, $J = 8.0$ Hz, C_6H_4, 1H); 5.95 (t, $J = 7.0$ Hz and $^3J_{PH} = 9.9$ Hz, NH, 1H); 4.94 (dd, $^2J_{PH} = 24.7$ Hz and $J = 7.0$ Hz, CHP, 1H); 4.31–3.87 (m, $\underline{CH_2}CH_3$, 4H); 1.34 and 1.21 (2t, $J = 7.1$ Hz, CH_3, 6H). ^{31}P NMR ($CDCl_3$): δ 19.39. Anal. Calcd for $C_{17}H_{20}N_3O_7P$: C-49.88; H-4.92; N-10.27. Found: C-49.92; H-4.95; N-10.20.

Dibenzyl [1-(3-Nitrophenyl)]-N-(3-nitroanilino) Methanephosphonate (**2Bb**). mp = 147–148°C (hexane–AcOEt; 1:1); 1.07 g (53%). ^{1}H NMR ($CDCl_3$): δ 8.21 (m, C_6H_4, 1H); 8.09 (d, $J = 8.2$ Hz, C_6H_4, 1H); 7.71 (d, $J = 7.4$ Hz, C_6H_4, 1H); 7.52 (dd, $J = 8.4$ Hz and $J = 1.8$ Hz, C_6H_4, 1H); 7.44 (t, $J = 7.6$ Hz, C_6H_4, 1H); 7.34–7.26 (m, Ph, 10H); 7.18 (m, C_6H_4, 1H); 6.70 (dd, $J = 8.2$ Hz and $J = 2.2$ Hz, C_6H_4, 1H); 5.46 (large s, NH, 1H); 5.07 (dd, $J = 10.0$ Hz and 4.8 Hz, CH_2Ph, 2H); 4.90 (d, $J = 9.6$ Hz, CH_2Ph, 2H); 4.76 (d, $^2J_{PH} = 24.6$ Hz, CHP, 1H). ^{31}P NMR ($CDCl_3$): δ 20.37. Anal. Calcd for $C_{27}H_{24}N_3O_7P$: C-60.79; H-4.53; N-7.88. Found: C-60.58; H-4.47; N-7.82.

Diethyl N-p-Nitrophenyl-(ferrocenyl)-methanephosphonate (**3Aa**). mp = 235–236°C (hexane–AcOEt; 1:1); 0.97 g (52%). ^{1}H NMR ($CDCl_3$): δ 8.16 (d, $J = 8.2$ Hz, CH_{arom}, 2H); 6.80 (d, $J = 8.2$ Hz, 2H); 4.60 (d, $^2J_{PH} = 16.2$ Hz, CHP, 1H); 4.3–3.7 (m, CH_2, 4 H); 4.36 (m, CH_{fer}, 2H); 4.20 (s, CH_{fer}, 2H); 4.07 (s, CH_{fer}, 5H). ^{31}P NMR ($CDCl_3$): δ 19.50. Anal. Calcd for $C_{21}H_{25}FeN_2O_5P$: C-53.41; H-5.34; N-5.93. Found: C-53.20; H-5.30; N-5.98.

Dibenzyl N-p-Nitrophenyl-(ferrocenyl)-methanephosphonate (**3Ab**). mp = 167–168°C (hexane–AcOEt; 1:1); 1.56 g (65%). ^{1}H NMR ($CDCl_3$): δ 8.07 (d, $J = 9.2$ Hz, CH_{arom}, 2H); 7.31–7.18 (m, CH_{arom}, 10H); 6.67 (d, $J = 9.2$ Hz, CH_{arom}, 2H); 4.90 (m, CH_2Ph, 2H); 4.85 and 4.61 (Part of AMX system, $^2J_{HH} = 15.3$ Hz and $^3J_{PH} = 8.7$ Hz, CH_2Ph, 2H); 4.58 (d, $^2J_{PH} = 16.0$ Hz, CHP, 1H); 4.30 (m, CH_{fer}, 2H); 4.21 (s, CH_{fer}, 2H); 4.04 (s, CH_{fer}, 5H). ^{31}P NMR ($CDCl_3$): δ 20.27. Anal. Calcd for $C_{31}H_{29}FeN_2O_5P$: C-62.43; H-4.90; N-4.70. Found: C-62.17; H-4.92; N-5.07.

Diphenyl N-p-Nitrophenyl-(ferrocenyl)-methanephosphonate (**3Ac**). mp = 203–204°C (hexane–AcOEt; 1:1); 1.22 g (54%) (*finally purified by shaking with activated charcoal*). ^{1}H NMR ($CDCl_3$): δ 8.06 (d, $J = 9.2$ Hz, CH_{arom}, 2H); 7.39–7.12 (m, CH_{arom}, 10H); 6.69 (d, $J = 9.2$ Hz, CH_{arom}, 2H); 4.52 (d, $^2J_{PH} = 26.7$ Hz, CHP, 1H); 4.36 (m, CH_{fer}, 1H); 4.28 (m, CH_{fer}, 1H); 4.20 (m, CH_{fer}, 2H); 4.04 (s, CH_{fer}, 5H); 2.39 (large s, NH, 1H). ^{31}P NMR ($CDCl_3$): δ 12.95. Anal. Calcd for $C_{29}H_{25}FeN_2O_5P$: C-61.29; H-4.43; N-4.93. Found: C-61.45; H-4.31; N-5.11.

Diethyl N-m-Nitrophenyl-(ferrocenyl)-methanephosphonate (**3Ba**). mp = 165–166°C (hexane–AcOEt; 1:1); 1.30 g (69%). ^{1}H NMR ($CDCl_3$): δ 7.69 (s, CH_{arom}, 1H); 7.58 (d, $J = 7.8$ Hz, CH_{arom}, 1H); 7.34 (t, $J = 8.0$ Hz, CH_{arom}, 1H); 7.10 (d, $J = 8.0$ Hz, CH_{arom}, 1H); 4.55 (d, $^2J_{PH} = 16.2$ Hz, CHP, 1H); 4.36 (m, CH_{fer}, 2H); 4.19 (s, CH_{fer}, 2H); 4.07 (s, CH_{fer}, 5H); 4.10–3.80 (m, $\underline{CH_2}CH_3$, 4H); 1.22 and 1.18 (2t, $J = 6.9$ Hz, $CH_2\underline{CH_3}$, 6H). ^{31}P NMR ($CDCl_3$): δ 20.32. Anal. Calcd for $C_{21}H_{25}FeN_2O_5P$: C-53.41; H-5.34; N-5.93. Found: C-53.48; H-5.21; N-5.98.

Dibenzyl N-m-Mitrophenyl-(ferrocenyl)-methanephosphonate (**3Bb**). mp = 145–146°C (hexane–AcOEt; 1:1); 1.61 g (67%). ^{1}H NMR ($CDCl_3$): δ 7.57 (s, CH_{arom}, 1H); 7.54 (d, $J = 7.6$ Hz, CH_{arom}, 1H); 7.31–7.18 (m, CH_{arom}, 11H); 7.01 (d, $J = 7.8$ Hz, CH_{arom}, 1H); 4.95 and 4.91 (Part of ABX system, CH_2Ph, 2H); 4.81 and 4.57 (Part of AMX system, $^2J_{HH} = 16.3$ Hz and $^3J_{PH} = 8.8$ Hz, CH_2Ph, 2H); 4.58 (d, $^2J_{PH} = 16.2$ Hz, CHP, 1H); 4.32 (d, $^4J_{PH} = 8.8$ Hz; CH_{fer}, 2H); 4.18 (s, CH_{fer}, 2H); 4.03 (s, CH_{fer}, 5H). ^{31}P NMR ($CDCl_3$): δ 20.80. Anal. Calcd for $C_{31}H_{29}FeN_2O_5P$: C-62.43; H-4.90; N-4.70. Found: C-62.20; H-4.84; N-4.79.

Diphenyl N-m-Nitrophenyl-(ferrocenyl)-methanephosphonate (**3Bc**). mp = 194–195°C (hexane–AcOEt; 1:1); 0.97 g (43%). ^{1}H NMR ($CDCl_3$): δ 7.69 (s, CH_{arom}, 1H); 7.62 (d, $J = 8.2$ Hz, CH_{arom}, 1H);

7.36–7.05 (m, CH_{arom}, 10H); 7.00–6.95 (m, CH_{arom}, 2H); 5.04 (d, $^2J_{PH} = 17.0$ Hz, CHP, 1H); 4.42 (s, CH_{fer}, 2H); 4.20 (m, CH_{fer}, 2H); 4.06 (s, CH_{fer}, 5H). ^{31}P NMR ($CDCl_3$): δ 12.57. Anal. Calcd for $C_{29}H_{25}FeN_2O_5P$: C-61.29; H-4.43; N-4.93. Found: C-61.49; H-4.33; N-5.32.

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