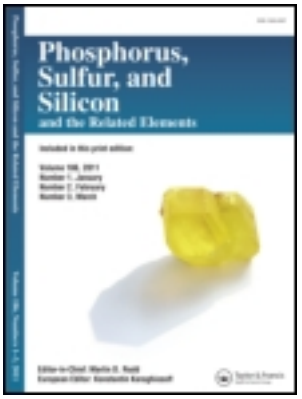

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

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Accepted author version posted online: 10 Aug 2012.

To cite this article: Jarosaw Lewkowski & Marek Dzigielewski (2013) Stereochemistry of Phosphite Addition to Azomethine Bond of Achiral 2,6-Pyridinedicarbaldimines and Isophthalaldimines—A Comparative Study, Phosphorus, Sulfur, and Silicon and the Related Elements, 188:8, 995-1006, DOI: 10.1080/10426507.2012.718298

To link to this article: http://dx.doi.org/10.1080/10426507.2012.718298

Phosphorus, Sulfur, and Silicon, 188:995–1006, 2013

ISSN: 1042-6507 print / 1563-5325 online
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STEREOCHEMISTRY OF PHOSPHITE ADDITION TO AZOMETHINE BOND OF ACHIRAL 2,6-PYRIDINEDICARBALDIMINES AND ISOPHTHALALDIMINES—A COMPARATIVE STUDY

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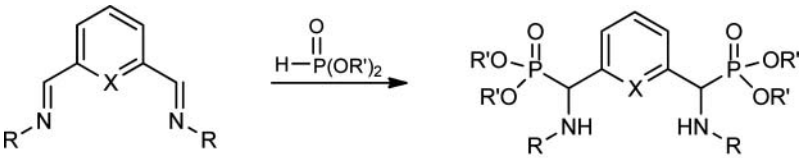
GRAPHICAL ABSTRACT



Abstract *The addition of dialkyl H-phosphonates to isophthalaldimines **1a–d** and pyridine-2,6-dicarboxaldimines **2a–d** was investigated and led to the corresponding aminophosphonates. Diastereoselectivity of the addition to pyridine-2,6-dicarboxaldimines was lower than to isophthalaldimines. In contrast, addition of bis(trimethylsilyl) H-phosphonate to both groups of aldimines demonstrated that the diastereoselectivity in case of pyridine-2,6-dicarboxaldimines is comparable or even better than that for the isophthalic derivatives.*

Keywords Addition; azomethine bond; dialkyl *H*-phosphonates; diastereoselectivity; isophthalaldimines; pyridine-2,6-dicarboxaldimines

INTRODUCTION

Extensive investigations over last twenty years have shown that the addition of various phosphorus nucleophiles to azomethine bond of achiral terephthalic and isophthalic Schiff bases is in a majority of cases diastereoselective and, what is of great importance, a large number of additions occurred with 100% diastereoselectivity.

Received 8 June 2012; accepted 31 July 2012.
Marek Dzięgielewski was the participant of the project entitled Doktoranci—Regionalna Inwestycja w Młodych naukowców—Akronim D-RIM, which is co-financed by the EU from the European Social Fund in the framework of the Operational Programme Human Capital, Priority VIII, Subaction 8.2.1. and is thankful for the scholarship.
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For example, the addition of hypophosphorous acid to achiral *N*-alkyl terephthalic and isophthalic imines has been reported[1,2] to be diastereoselective to 100% and leads to a *meso*-form, whereas the reaction performed with *N*-aryl imines has been noted to depend on the nature of the substituent at the aromatic ring.[2] Similar results have been reported for the addition of dialkyl *H*-phosphonates to achiral *N*-alkyl and *N*-aryl terephthalic and isophthalic Schiff bases.[1,3–8]

Some years ago, we reported that the addition of bis(trimethylsilyl) *H*-phosphonate to *N*,*N*-terephthalylidene-alkyl (or -aryl) amines leads exclusively to the formation of only one diastereomeric form of the corresponding 1,4-phenylene-bis-(*N*-alkylaminomethyl)-phosphonic acid.[9] The investigation of the products identified unexpectedly this diastereomeric form as a pair of enantiomers.

These 1,4-phenylene and 1,3-phenylene-bis(*N*-alkylaminomethyl)-phosphonic derivatives have been found to have coordination abilities toward Cu(II) ions[10] or diaminophosphonate peptide receptor for lysine and arginine.[11] Thus, investigations of these compounds and their synthesis are not only important regarding the respective mechanism but also because of possible applications. It is therefore well visible that the field of terephthalic and isophthalic derivatives has been largely explored.

Contrary to this, stereochemical aspects of the addition of phosphorus nucleophiles to the azomethine bond of achiral Schiff bases, deriving from heteroaromatic di-aldehydes, have not been investigated at all. Recently, we have contributed to this topic reporting on the addition of bis(trimethylsilyl) *H*-phosphonate to achiral 2,5-Diformylfuran Schiff bases.[12] The reaction was not stereoselective except in the case of *N*-benzyl substituted imine.

This encouraged us to study another heteroaromatic ring system, i.e., 2,6-diformylpyridine. The stereochemistry of addition of phosphorus nucleophiles to 2,6-pyridinedicarbaldimines is really unexplored; according to bibliographic databases there is the only one article in which tetraphenyl 2,6-pyridine-bis-(*N*-(*p*-nitrophenylaminomethylphosphonate) was described[13] as the only compound of this type. This prompted us to study the addition of dialkyl *H*-phosphonates and bis(trimethylsilyl) *H*-phosphonate to various *N*-substituted 2,6-diformylpyridine Schiff bases.

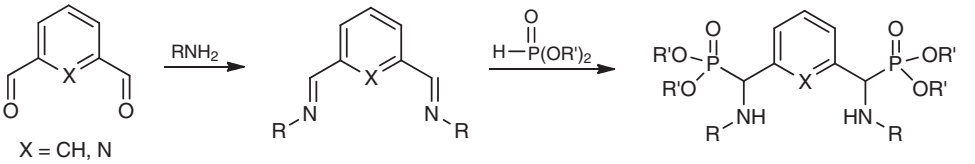
RESULTS AND DISCUSSION

Some literature results of the addition of *H*-phosphonates to isophthalic, achiral Schiff bases demonstrated interesting stereochemical behavior. Barycki et al.[1] reported that addition of diethyl *H*-phosphonate to *N*-benzyl- and *N*-benzhydryl-isophthalaldimines was stereoselective to 100%. According to Failla et al.[4] addition of diethyl *H*-phosphonate to *N*-phenyl-, *N*-(2-pyridylethyl)-, and *N*-(4-phenylazo)phenyl isophthalaldimines was also highly diastereoselective, as *dr* oscillated around 9:1.

It was interesting to perform such reactions with Schiff bases of 2,6-diformylpyridine and to compare the results with those obtained for isophthalic derivatives. Therefore, we have chosen four model amines: benzylamine, furfurylamine, *p*-toluidine, and *p*-anisidine and three model *H*-phosphonates: dimethyl and diethyl *H*-phosphonates applied alternately as well as dibenzyl *H*-phosphonate.

Isophthalic aldehyde Schiff bases **1a–d** were synthesized following published procedures.[1–9,14,15] Then, the addition of *H*-phosphonates to their azomethine bond was performed and reactions were carried out in refluxing toluene to obtain bis(aminophosphonates)

3Aa–Ad. In the same way, 2,6-diformylpyridine Schiff bases **2a–d** were synthesized following the published procedures.[1–9,16] Then, the addition of *H*-phosphonates to their azomethine bond was performed and the reactions were carried out in refluxing toluene to obtain bis(aminophosphonates) **4Aa–Bd**. The preparation of **4Bb** from dimethyl *H*-phosphonate and a Schiff base was, however, carried out in dioxane and catalyzed by trifluoroacetic acid. This procedure allowed obtaining the bis(aminophosphonates) **3Aa–Ad** and **4Aa–Bd** in 50–90% yields. (Scheme 1)

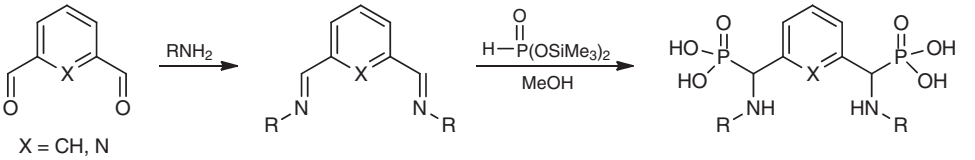


R = 4-MeOC$_6$H$_4$ (**a**), 4-MeC$_6$H$_4$ (**b**), CH$_2$Ph (**c**), CH$_2$(2'-furyl) (**d**)
R' = Me (**A**), Et (**B**), CH$_2$Ph (**C**)

Scheme 1

New bis(aminophosphonates) **3** and **4** were characterized by ^{1}H and ^{31}P NMR spectroscopy as well as by microanalysis, except tetraethyl 2,6-pyridine-bis-(*N*-furfurylaminomethyl)-bis(phosphonate)(**4Bd**). This compound turned out to be too unstable to be purified by chromatography on silica gel and alumina; the routine method of purification suitable for the rest bis(aminophosphonates) **3** and **4** did not allow to purify the product **4Bd** to a degree enough to give satisfactory results of elemental analysis. Therefore tetraethyl 2,6-pyridine-bis-(*N*-furfurylaminomethyl)-bis-phosphonate(**4Bd**) was characterized only by ^{1}H and ^{31}P NMR spectroscopy.

We have also performed the synthesis of 1,3-phenylene-bis(aminomethylphosphonic acids) **5a–d** and 2,6-pyridine-bis(aminomethylphosphonic acids) **6a–d**, which were prepared by the addition of in situ formed bis(trimethylsilyl) *H*-phosphonate to imines **1a–d** and **2a–d**, respectively. The preparation of bis(trimethylsilyl) *H*-phosphonate was performed following the published general procedure[17] by the action of trimethylsilyl bromide on dimethyl *H*-phosphonate. The procedure involving the described methanolysis and precipitation with propylene oxide allowed obtaining aminophosphonic acids **5a–d** in 70–95% yield and acids **6a–d** in 30–75% yield. (Scheme 2)



R = 4-MeOC$_6$H$_4$ (**a**), 4-MeC$_6$H$_4$ (**b**), CH$_2$Ph (**c**), CH$_2$(2'-furyl) (**d**)

Scheme 2

Although Barycki et al.[1] reported that the addition of diethyl *H*-phosphonate to *N,N′*-iso-phthalylidenebenzylamine (**1c**) was highly diastereoselective (de = 95%), which was in accord with Failla's et al.[4] observations, the addition of the investigated *H*-phosphonates to Schiff bases **1a**,**b** and **1d** turned out to be slightly diastereoselective.

The addition of dimethyl *H*-phosphonate to *N*-furfuryl isophthalic Schiff base turned out to be not very diastereoselective (dr = 2:1), which was rather astonishing in the light of studies on terephthalaldehyde-derived aminophosphonates.[6,9] On the other hand, however, such phenomenon has been noticed in the case of addition of hypophosphorous acid to *N*-furfuryl terephthalaldimine,[2] where a complete lack of diastereoselectivity was observed. The addition of dimethyl *H*-phosphonate to *N*-*p*-tolyl imine occurred also with rather low diastereoselectivity (dr = 4:5). Although addition of dibenzyl *H*-phosphonate to *N*-*p*-methoxyphenyl isophthalic Schiff base was almost not selective (dr = 9:11), the addition of dimethyl *H*-phosphonate occurred with dr = 4:1, which undoubtedly confirms that the addition of dibenzyl *H*-phosphonate to isophthalic Schiff bases turns out to be much less diastereoselective than the addition of *H*-phosphonates with typical alkyl chains. It is to remind that the addition of diethyl *H*-phosphonate to *N*-isophthalilidene-bis(1-naphthylamine)[7] leads to the formation of exclusively one diastereomer, while addition of dibenzyl *H*-phosphonate to the same imine was not diastereoselective at all[7] (Table 1).

The additions of *H*-phosphonates to pyridine-2,6-dicarboxaldimines **2a–d** turned out to be slightly less diastereoselective than the addition to the isophthalic derivatives described above. Reactions of dimethyl and dibenzyl *H*-phosphonates with 2,6-bis(*N*-benzylazomethine)-pyridine (**2c**) were characterized by complete lack of diastereoselectivity, as the formation of both possible forms of aminophosphonates **4Ac** and **4Cc** in a 1:1 ratio was observed. In the case of tetramethyl 2,6-pyridine-bis(*N*-benzylaminomethyl)-bis(phosphonate)(**4Ac**),an interesting phenomenon was observed, its ^{31}P NMR spectrum would have indicated the formation of an exclusive diastereomeric form as it displayed only one signal. However, two sets of diagnostic signals in the ^{1}H NMR spectrum demonstrated clearly that two diastereomeric forms occurred in a 1:1 ratio (Table 1).

N-furfuryl and *N*-*p*-methoxyphenyl Schiff bases were stereochemically inactive, as additions of *H*-phosphonates occurred to give the products in 1:1 diastereomeric ratios. The only studied case of 2,6-diformylpyridine derivatives, where diastereoselectivity occurred,

Table 1 Results of addition of dialkyl phosphites to isophthalaldimines **1a–d** and pyridine-2,6-dicarboxaldimines **2a–d**

	R	R′	X	^{31}P NMR	dr
3Aa	4-MeOC$_6$H$_4$	CH_3	CH	24.88; 24.85	7 : 2
3Ca	4-MeOC$_6$H$_4$	CH_2Ph	CH	23.46; 23.36	9 : 11
3Ab	4-MeC$_6$H$_4$	CH_3	CH	24.83; 24.81	4 : 5
3Bc	CH_2Ph	CH_2CH_3	CH	nd	Single diastereoisomer[a]
3Ad	CH_2Fur	CH_3	CH	25.38; 25.33	2 : 1
4Aa	4-MeOC$_6$H$_4$	CH_3	N	22.74; 22.68	1 : 1
4Bb	4-MeC$_6$H$_4$	CH_2CH_3	N	21.42; 21.33	3 : 2
4Cc	CH_2Ph	CH_2Ph	N	22.77; 22.72	1 : 1
4Ac	CH_2Ph	CH_3	N	24.35	1 : 1[b]
4Bd	2-CH_2Fur	CH_2CH_3	N	21.83; 21.81	1 : 1

[a]From Barycki et al.[1]

[b]Diastereoisomeric ratio according to ^{1}H NMR.

Table 2 Results of addition of bis(trimethylsilyl) phosphite to isophthalaldimines **1a–d** and pyridine-2,6-dicarboxaldimines **2a–d**

	R	X	^{31}P NMR	dr
5a	4-$MeOC_6H_4$ 6.0pt1,65.1pt	CH	16.50; 16.21	5 : 2
5b	4-MeC_6H_4	CH	16.61; 16.52	1 : 2
5c	CH_2Ph	CH	9.70; 9.51	2 : 1
5d	CH_2Fur	CH	9.68; 9.48	5 : 4
6a	4-$MeOC_6H_4$	N	15.14; 14.79	9 : 1
6b	4-MeC_6H_4	N	15.21; 14.85	9 : 1
6c	CH_2Ph	N	15.83; 15.73	2 : 1
6d	2-CH_2Fur	N	15.77	Single diastereoisomer

was the addition of diethyl *H*-phosphonate to 2,6-bis(*N*-*p*-methylphenylazomethine)-pyridine (**2b**), where diastereoisomeric forms of **4Bb** were formed in a 3:2 ratio. Therefore, it is to state that stereoselectivity of *H*-phosphonate additions to isophthalic Schiff bases **1a–d** is moderately better than in the case of 2,6-diformylpyridine Schiff bases **2a–d** (Table 1).

Completely different results were observed in the case of addition of bis (trimethylsilyl) *H*-phosphonate to isophthalic Schiff bases **1a–d** and 2,6-diformylpyridine Schiff bases **2a–d**, which led to the formation of aminophosphonic acids **5a–d** and **6a–d**. Addition to isophthalaldimines **1a–d** showed rather limited diastereoselectivity starting from 5:4 for *N*-furfuryl derivative **5d** up to 5:2 for *N*-*p*-methoxyphenyl derivative **5a** (Table 2). In contrast to the previous case, addition of bis(trimethylsilyl) *H*-phosphonate to 2,6-diformylpyridine Schiff bases **2a–d** was highly diastereoselective, and although the *N*-benzyl derivative **6c** occurred in diastereomeric forms in a 2:1 ratio, the formation of 2,6-pyridine-bis(*N*-(*p*-methoxyphenyl)aminomethylphosphonic acid) (**6a**) and 2,6-pyridine-bis(*N*-(*p*-methylphenyl)-aminomethylphosphonic acid) (**6b**) occurred in dr = 9:1 ratio in both cases and 2,6-pyridine-bis(*N*-furfuryl-aminomethylphosphonic acid) (**6d**) formed with 100% diastereoselectivity.

Therefore, it can be concluded that the addition of bis(trimethylsilyl) *H*-phosphonate to 2,6-diformylpyridine Schiff bases **2a–d** is equally or even more diastereoselective as compared to the addition to isophthalic Schiff bases **1a–d** (Table 2).

The difference in diastereoselectivity between the addition of dialkyl *H*-phosphonates to isophthalic and pyridine-2,6-dicarboxaldehyde Schiff bases is surprising because of the similarity of shape and structure of both compounds, and the question arises, why such an important difference occurred. The varying degrees of diastereoselectivity observed appear to result from a complex combination of structural features and further work will be required to elucidate the factors involved.

EXPERIMENTAL

All solvents (POCh-Poland) were routinely distilled and dried prior to use. Amines, *H*-phosphonates, bromotrimethylsilane, isophthalaldehyde, and 2,6-diformylpyridine (Aldrich) were used as received. NMR spectra of imines **1a–d** and **2a–d** as well as of aminophosphonates **3Aa–Ad** and **4Aa–Bd** were recorded with a Bruker Avance III 600 MHz apparatus operating at 600 MHz (^{1}H) and 243 MHz (^{31}P), whereas the NMR

spectra of aminophosphonic acids **5a–d** and **6a–d** were recorded with a Varian Gemini 200 BB apparatus operating at 200 MHz (^{1}H) and 81 MHz (^{31}P). Elemental analyses were performed in the Centre for Molecular and Macromolecular Science of the Polish Academy of Science in Łódź, Poland.

Synthesis of Isophthalic and 2,6-Diformylpyridine Schiff Bases 1a–d and 2a–d: General Procedure

Isophthalaldehyde or 2,6-diformylpyridine (2.5 mmol) was dissolved in methanol (20 mL) and then the corresponding amine (5 mmol) was added. The mixture was stirred overnight and the precipitated solid was filtered, dried, and recrystallized and then collected to obtain the corresponding Schiff bases.

N,N′-Isophthalylidene-*p*-anisidine (1a)

Yield: 88% (0.76 g). Mp: 140–143 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.59$ (s, 2H, CH=N), 8.40 (t, $^4J_{HH} = 1.5$ Hz, 1H, 2-H), 8.04 (dd, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.5$ Hz, 2H, 4-H, 6-H), 7.90 (t, $^3J_{HH} = 7.4$ Hz, 1H, 5-H), 7.30 (A-part of AA'XX', 4H, 4-$MeOC_6H_4$), 6.98 (X-part of AA'XX', 4H, 4-$MeOC_6H_4$), 3.88 (s, 6H, OCH_3). Calcd. for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.63; H, 5.95; N, 8.15%.

N,N′-Isophthalylidene-*p*-toluidine (1b)

Yield: 76% (0.59 g). Mp: 135–138 °C, ref [18]: 128.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.58$ (s, 2H, CH=N), 8.42 (m, 1H, 2-H), 8.06 (dd, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.8$ Hz, 2H, 4-H, 6-H), 7.90 (t, $^3J_{HH} = 7.8$ Hz, 1H, 5-H), 7.25 (A-part of AA'BB', 4H, 4-MeC_6H_4), 7.20 (B-part of AA'BB', 4H, 4-MeC_6H_4), 2.42 (s, 6H, CH_3).

N,N′-Iso-phthalylidenebenzylamine (1c)[1]

Yield: 97% (0.76 g), dark yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.47$–8.46 (m, 2H, CH=N), 8.20–8.19 (m, 1H, H_2), 7.92 (dd, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 1.8$ Hz, 2H, 4-H, 6-H), 7.51 (t, $^3J_{HH} = 7.2$ Hz, 1H, 5-H), 7.41–7.38 (m, 8H, C_6H_5), 7.33–7.30 (m, 2H, C_6H_5), 4.88 (d, $^4J_{HH} = 1.2$ Hz, 4H, CH_2Ph).

N,N′-Iso-phthalylidenefurfurylamine (1d)

Yield: 81% (0.59 g). Mp: 53–54 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.38$ (s, 2H, CH=N), 8.13–8.12 (m, 1H, 2-H), 7.87 (dd, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.8$ Hz, 2H, 4-H, 6-H), 7.48 (t, $^3J_{HH} = 7.8$ Hz, 1H, 5-H), 7.42–7.41 (m, 2H, 5-H of 2′-furyl), 6.38–6.37 (m, 2H, 4-H of 2′-furyl), 6.30–6.29 (m, 2H, 3-H of 2′-furyl), 4.81 (s, 4H, CH_2). Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.84; H, 5.67; N, 9.54%.

2,6-bis(*N-p*-methoxyphenyliminomethyl)-pyridine (2a)

Yield: 92% (0.72 g). Mp: 165–166 °C, ref [14]: 159 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.70$ (s, 2H, CH=N), 8.24 (d, $^3J_{HH} = 7.8$ Hz, 2H, H-pyridyl), 7.90 (t, $^3J_{HH} = 7.8$ Hz,

1H, H-pyridyl), 6.35 (A-part of AA'BB', 4H, 4-$MeOC_6H_4$), 6.95 (B-part of AA'BB', 4H, 4-$MeOC_6H_4$), 3.84 (s, 6H, OCH_3).

2,6-bis(*N*-*p*-methylphenyliminomethyl)-pyridine (2b)[15]

Yield: 86% (0.90 g). Mp: 180–182 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.72$ (s, 2H, CH=N), 8.30 (d, $^3J_{HH} = 7.8$ Hz, 2H, H-pyridyl), 7.95 (t, $^3J_{HH} = 7.8$ Hz, 1H, H-pyridyl), 7.29 (A-part of AA'BB', 4H, 4-MeC_6H_4); 7.26 (B-part of AA'BB', 4H, 4-MeC_6H_4); 2.42 (s, 6H, CH_3).

2,6-bis(*N*-benzyliminomethyl)-pyridine (2c)

Yield: 82% (0.70 g). Mp: 78–79 °C, ref [16]: 80 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta =$ 8.56 (s, 2H, CH=N), 8.12 (d, $^3J_{HH} = 7.8$ Hz, 2H, H-pyridyl), 7.83 (t, $^3J_{HH} = 7.8$ Hz, 1H, H-pyridyl), 7,39 (m, 8H, C_6H_5), 7.32 (m, 2H, C_6H_5), 4.93 (s, 4H, CH_2).

2,6-bis(*N*-furfuryliminomethyl)-pyridine (2d)

Yield: 83% (0.81 g), light-brown crystals. Mp: 82–84 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.49$ (t, $^4J_{HH} = 1.2$ Hz, 2H, CH=N), 8.08 (d, $^3J_{HH} = 7.8$ Hz, 2H, H-pyridyl), 7.82 (t, $^3J_{HH} = 7.8$ Hz, 1H, H-pyridyl), 7.42 (dd, $^3J_{HH} = 1.8$ Hz, $^4J_{HH} = 0.6$ Hz, 2H, 5′-H of 2′-furyl), 6.38 (dd, $^3J_{HH} = 1.8$ Hz, $^3J_{HH} = 3.3$ Hz, 2H, 4′-H of 2′-furyl), 7.32 (dd, $^3J_{HH} =$ 3.3 Hz, $^4J_{HH} = 0.6$ Hz, 2H, 3′-H of 2′-furyl), 4.88 (d, $^4J_{HH} = 1.2$ Hz, 4H, CH_2). Calcd. for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33. Found: C, 69.63; H, 5.21; N, 14.13%.

Tetraalkyl 1,3-Phenylene-bis(*N*-alkylaminomethane)-bis (phosphonates) (3Aa–3Cd) and Tetraalkyl 2,6-Pyridine-bis (*N*-alkylaminomethane)-bis(phosphonates) (4Aa–4Cd): General Procedure

Schiff base (**1a–d**) or (**2a–d**) (0.5 mmol) was dissolved in toluene (15 mL) and the respective dialkyl *H*-phosphonate (1 mmol) was added. For the addition of dimethyl *H*-phosphonate to **2b** the reaction was carried out in dioxane (15 mL) with 2–3 drops of trifluoroacetic acid. The mixture was refluxed for 3–5 h. After cooling to r.t. the solids precipitated were collected by filtration, washed, and dried; oils were isolated by evaporating solvent in vacuo. Products were purified first by washing their solutions in dichloromethane with saturated aqueous $NaHCO_3$ (3×15 mL) and then, if solids, by crystallization.

Tetramethyl 1,3-Phenylene-bis(*N*-*p*-methoxyphenylaminomethyl)-bis (phospho-nate) (3Aa)

Overall yield: 54% (0.15 g); 4:1 mixture of diastereoisomers. The predominant diastereoisomer spontaneously crystallized from the postreaction mixture.

Major diastereoisomer: Yield: 0.12 g. Mp: 170–173 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.56$ (m, 1H, arom-H), 7.40–7.38 (m, 2H, arom-H), 7.36–7.33(m, 1H, arom-H), 6.66 (A-part of AA'BB', 4H, 4-$MeOC_6H_4$), 6.52 (B-part of AA'BB', 4H, 4-$MeOC_6H_4$), 4.74 (d, $^2J_{PH} = 24.0$ Hz, 2H, CHP), 3.70 (s, 6H, OCH_3), 3.76 (d, $^3J_{PH} = 10.8$ Hz, 3H, $POCH_3$), 3.30 (d, $^3J_{PH} = 10.8$ Hz, 3H, $POCH_3$). ^{31}P NMR (243 MHz, $CDCl_3$):

$\delta = 24.88$. Calcd. for $C_{26}H_{34}N_2O_8P_2$: C, 55.32; H, 6.07; N, 4.96. Found: C, 55.45; H, 6.01; N, 4.97%.

Minor diastereoisomer: Yield: 0.03 g. Mp: 162–165 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.28$–7.26 (m, 2H, arom-H), 7.20–7.17 (m, 2H, arom-H), 6.66 (A-part of AA'BB', 4H, 4-$MeOC_6H_4$), 6.52 (B-part of AA'BB', 4H, 4-$MeOC_6H_4$), 4.86 (d, $^2J_{PH} = 24.0$ Hz, 1H, CHP), 4.72 (d, $^2J_{PH} = 24.0$ Hz, 1H, CHP), 3.69 (s, 6H, OCH_3), 3.70 (d, $^3J_{PH} = 10.2$ Hz, 3H, $POCH_3$), 3.41 (d, $^3J_{PH} = 10.2$ Hz, 3H, $POCH_3$). ^{31}P NMR (243 MHz, $CDCl_3$): $\delta = 24.85$.

Tetrabenzyl 1,3-Phenylene-bis(*N*-*p*-methoxyphenylaminomethyl)-bis (phosphonate) (3Ca)

Yield: 55% (0.24 g), dark yellow oil. Signals of the major isomer are marked by (*). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.38$–7.35 (m, 2H, C_6H_5), 7.31–7.28 (m, 8H, C_6H_5), 7.26–7.21 (m, 10H, C_6H_5), 7.07–7.06 (m, 2H, arom-H), 7.04–7.03 (m, 2H, arom-H), 6.58–6.56 (m, 4H, 4-$MeOC_6H_4$); 6.48–6.46 (m, 4H, 4-$MeOC_6H_4$), 4.97 (d, $^2J_{PH} = 8.4$ Hz, 2H, CHP), 4.92* (part of AMX spin system, $^3J_{PH} = 7.8$ Hz, $^3J_{PH} = 9.0$ Hz, $^2J_{HH} = 12.0$ Hz, 2H, CH_2Ph), 4.78–4.69 (m, 4H, CH_2Ph), 4.38 (part of AMX system, $^3J_{PH} = 8.4$ Hz, $^3J_{PH} = 9.6$ Hz, $^2J_{HH} = 11.4$ Hz, 2H, CH_2Ph), 3.58 (s, 6H, OCH_3), 3.57 (s, 6H, OCH_3). ^{31}P NMR (243 MHz, $CDCl_3$): $\delta = 23.46$, 23.36* (9:11). Calcd. for $C_{50}H_{50}N_2O_8P_2 \cdot CH_3OH$: C, 67.99; H, 6.04; N, 3.11. Found: C, 67.92; H, 6.04; N, 4.35%.

Tetramethyl 1,3-Phenylene-bis(*N*-*p*-methylphenylaminomethane)-bis (phospho-nate) (3Ab)

Yield: 67% (0.19 g). Mp: 61–65 °C. Signals of the major isomer are marked by (*). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.57$–7.56 (m, 1H, arom-H), 7.40–7.39 (m, 2H, arom-H), 7.36–7.33 (m, 1H, arom-H), 6.89–6.87 (m, 8H, 4-MeC_6H_4), 6.50–6.46* (m, 8H, 4-MeC_6H_4), 4.79* (d, $^2J_{PH} = 24.0$ Hz, 2H, CHP), 4.77 (d, $^2J_{PH} = 24.0$ Hz, 2H, CHP), 3.76* (d, $^3J_{PH} = 10.8$ Hz, 3H, $POCH_3$), 3.27* (d, $^3J_{PH} = 10.8$ Hz, 3H, $POCH_3$), 3.69 (d, $^3J_{PH} = 10.8$ Hz, 3H, $POCH_3$), 3.41 (d, $^3J_{PH} = 10.8$ Hz, 3H, $POCH_3$), 2.20 (s, 6H, CH_3), 2.19* (s, 6H, CH_3). ^{31}P NMR (243 MHz, $CDCl_3$): $\delta = 24.83$, 24.81* (4:5). Calcd. for $C_{26}H_{34}N_2O_6P_2$: C, 58.64; H, 6.44; N, 5.26. Found: C, 58.78; H, 6.79; N, 5.14%.

Tetramethyl 1,3-Phenylene-bis(*N*-furfurylaminomethyl)-bis (phosphonate) (3Ad)

Yield: 68% (0.17 g). Signals of the major isomer are marked by (*). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.51$–7.50 (m, 1H, arom-H), 7.44–7.42 (m, 3H, 5′-H of 2′-furyl, arom-H), 7.40–7.39 (m, 2H, arom-H), 6.32–7.30 (m, 1H, 3′-H of 2′-furyl), 6.13–7.12 (m, 1H, 4′-H of 2′-furyl), 4.15 (d, $^2J_{PH} = 25.2$ Hz, 2H, CHP), 4.14* (d, $^2J_{PH} = 25.2$ Hz, 2H, CHP), 3.84 (d, $J = 15.0$ Hz, 4H, CH_2), 3.83 (d, $J = 15.0$ Hz, 4H, CH_2), 3.73* (d, $^3J_{PH} = 10.8$ Hz, 6H, $POCH_3$), 3.62* (d, $^3J_{PH} = 10.8$ Hz, 6H, $POCH_3$), 3.74 (d, $^3J_{PH} = 10.8$ Hz, 6H, $POCH_3$), 3.66 (d, $^3J_{PH} = 10.8$ Hz, 6H, $POCH_3$), 3.61* (d, $J = 15.0$ Hz, 4H, CH_2), 3.62* (d, $J = 15.0$ Hz, 4H, CH_2). ^{31}P NMR (243 MHz, $CDCl_3$): $\delta = 25.38$*, 25.33

(2:1). Calcd. for $C_{22}H_{30}N_2O_8P_2$: C, 51.57; H, 5.90; N, 5.47. Found: C, 51.33; H, 6.03; N, 5.30%.

Tetramethyl 2,6-Pyridine-bis(*N*-*p*-methoxyphenylaminomethane)-bis(phosphonate) (4Aa)

Yield: 85% (0.24 g). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.65$ (t, $^3J_{HH} = 7.8$ Hz, 1H, H-pyridyl), 7.64 (t, $^3J_{HH} = 7.8$ Hz, 1H, H-pyridyl), 7.26 (dd, $^3J_{HH} = 7.8$ Hz, $^4J_{PH} = 4.2$ Hz, 2H, H-pyridyl), 7.25 (dd, $^3J_{HH} = 7.8$ Hz, $^4J_{PH} = 4.2$ Hz, 2H, H-pyridyl), 6.71 (A-part of AA'BB', 2H, 4-$MeOC_6H_4$), 6.70 (A-part of AA'BB', 2H, 4-$MeOC_6H_4$), 6.64 (B-part of AA'BB', 4H, 4-$MeOC_6H_4$), 4.98 (d, $^2J_{PH} = 22.8$ Hz, 2H, CHP), 4.96 (d, $^2J_{PH} = 22.8$ Hz, 2H, CHP), 3.72 (s, 6H, OCH_3), 3.71 (s, 6H, OCH_3), 3.83 (d, $^3J_{PH} = 10.2$ Hz, 6H, $POCH_3$), 3.81 (d, $^3J_{PH} = 10.2$ Hz, 6H, $POCH_3$), 3.61 (d, $^3J_{PH} = 10.2$ Hz, 6H, $POCH_3$), 3.56 (d, $^3J_{PH} = 10.2$ Hz, 6H, $POCH_3$). ^{31}P NMR (243 MHz, $CDCl_3$): $\delta = 22.74$, 22.68 (1:1). Calcd. for $C_{25}H_{33}N_3O_8P_2$: C, 53.10; H, 5.88; N, 7.47. Found: C, 53.84; H, 5.97; N, 7.18%.

Tetraethyl 2,6-Pyridine-bis(*N*-*p*-methylphenylaminomethane)-bis (phosphonate) (4Bb)

Yield: 73% (0.22 g). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.62$ (t, $^3J_{HH} = 7.6$ Hz, 1H, H-pyridyl), 7.61 (t, $^3J_{HH} = 7.6$ Hz, 1H, H-pyridyl), 7.16 (m, 2H, H-pyridyl), 6.93 (A-part of AA'BB', 4H, 4-MeC_6H_4), 6.61 (B-part of AA'BB', 4H, 4-MeC_6H_4), 6.90 (A-Part of AA'BB', 4H, 4-MeC_6H_4), 6.59 (B-part of AA'BB', 4H, 4MeC_6H_4), 5.00 (d, $^2J_{PH} = 22.8$ Hz, 2H, CHP), 4.98 (d, $^2J_{PH} = 22.8$ Hz, 2H, CHP), 4.21–4.13 (m, 4H, O$\underline{CH_2}CH_3$), 4.02–3.95 (m, 2H, O$\underline{CH_2}CH_3$), 3.87–3.81 (m, 2H, O$\underline{CH_2}CH_3$), 2.22 (s, 6H, CH_3), 2.21 (s, 6H, CH_3), 1.32 (t, $^3J_{HH} = 7.2$ Hz, 6H, $OCH_2\underline{CH_3}$), 1.31 (t, $^3J_{HH} = 7.2$ Hz, 6H, $OCH_2\underline{CH_3}$), 1.16 (t, $^3J_{HH} = 7.2$ Hz, 6H, $OCH_2\underline{CH_3}$), 1.12 (t, $^3J_{HH} = 7.2$ Hz, 6H, $OCH_2\underline{CH_3}$). ^{31}P NMR (81 MHz, NaOD/D_2O): $\delta = 21.42$, 21.33 (3:2). Calcd. for $C_{29}H_{41}N_3O_6P_2$: C, 59.08; H, 7.01; N, 7.13. Found: C, 59.41; H, 7.14; N, 7.35%.

Tetramethyl 2,6-Pyridine-bis(*N*-benzylaminomethyl)-bis(phosphonate) (4Ac)

Yield: 78% (0.21 g). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.42$ (ddd, $^3J_{HH} = 7.5$ Hz, $^4J_{PH} = 2.4$ Hz, $^4J_{HH} = 1.8$ Hz, 2H, H-pyridyl), 7.39 (ddd, $^3J_{HH} = 7.5$ Hz, $^4J_{PH} = 2.4$ Hz, $^4J_{HH} = 1.8$ Hz, 2H, H-pyridyl), 7.32–7.29 (m, 10H, C_6H_5), 7.26 (m, 1H, H-pyridyl), 4.31 (d, $^2J_{PH} = 21.9$ Hz, 2H, CHP), 4.28 (d, $^2J_{PH} = 21.9$ Hz, 2H, CHP), 3.86 (d, $J = 13.2$ Hz, 2H, CH_2Ph), 3.84 (d, $J = 13.2$ Hz, 2H, CH_2Ph), 3.79 (d, $^3J_{PH} = 10.2$ Hz, 6H, OCH_3), 3.77 (d, $^3J_{PH} = 10.2$ Hz, 6H, OCH_3), 3.67 (d, $^3J_{PH} = 10.2$ Hz, 6H, OCH_3), 3.65 (2d, $^3J_{PH} = 10.2$ Hz, 6H, OCH_3). ^{31}P NMR (243 MHz, $CDCl_3$): $\delta = 24.35$. Calcd. for $C_{25}H_{33}N_3O_6P_2$: C, 56.28; H, 6.23; N, 7.88. Found: C, 56.12; H, 6.37; N, 7.73%.

Tetrabenzyl 2,6-Pyridine-bis(*N*-benzylaminomethyl)-bis(phosphonate) (4Cc)

Yield: 55% (0.23 g). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.62$ (m, 1H, H-pyridyl), 7.39–7.20 (m, 32H, C_6H_5, H-pyridyl), 5.13–5.11 (part of AMX spectrum, $^3J_{PH} = 8.4$ Hz,

$^2J_{HH}$ = 13.2 Hz, 4H, OCH_2Ph), 5.07–5.03 (part of AMX spectrum, $^3J_{PH}$ = 8.4 Hz, $^2J_{HH}$ = 13.2 Hz, 4H, OCH_2Ph); 5.00–4.96 (part of AMX spectrum, $^3J_{PH}$ = 9.0 Hz, $^2J_{HH}$ = 12.0 Hz, 4H, OCH_2Ph), 4.92–4.88 (part of AMX spectrum, $^3J_{PH}$ = 9.0 Hz, $^2J_{HH}$ = 12.0 Hz, 4H, OCH_2Ph), 4.34 (d, $^2J_{PH}$ = 20.4 Hz, 2H, CHP), 4.31 (d, $^2J_{PH}$ = 20.4 Hz, 2H, CHP), 3.78 (d, J = 9.6 Hz, 2H, CH_2Ph), 3.76 (d, J = 9.6 Hz, 2H, CH_2Ph), 3.56 (d, J = 13.2 Hz, 2H, CH_2Ph), 3.55 (d, J = 13.2 Hz, 2H, CH_2Ph). ^{31}P NMR (243 MHz, $CDCl_3$): δ = 22.77, 22.72 (1:1). Calcd. for $C_{49}H_{49}N_3O_6P_2$: C, 70.24; H, 5.89; N, 5.02. Found: C, 70.00; H, 6.03; N, 5.01%.

Tetraethyl 2,6-Pyridine-bis(*N*-furfurylaminomethyl)-bis(phosphonate) (4Bd)

The compound turned out to be too unstable to be purified by chromatography on silica gel or alumina and the routine method of purification did not allow purifying the product to a degree enough to give satisfactory results of elemental analysis.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 (t, $^3J_{HH}$ = 7.8 Hz, 1H, H-pyridyl), 7.67 (t, $^3J_{HH}$ = 7.8 Hz, 1H, H-pyridyl), 7.41–7.37 (m, 2H, H-pyridyl), 7.31 (m, 1H, 5′-H of 2′-furyl), 6.28 (dd, $^3J_{HH}$ = 2.4 Hz, $^3J_{HH}$ = 4.8 Hz, 2H, 3′-H of 2′-furyl), 6.16–6.15 (m, 2H, 3′-H of 2′-furyl), 4.28 (d, $^2J_{PH}$ = 21.0 Hz, 2H, CHP), 4.26 (d, $^2J_{PH}$ = 21.0 Hz, 2H, CHP), 4.20–4.05 (m, 6H, $O\underline{CH_2}CH_3$), 4.03–3.95 (m, 3H, $O\underline{CH_2}CH_3$), 3.85 (d, $^2J_{HH}$ = 14.4 Hz, 2H, CH_2-furyl), 3.83 (d, $^2J_{HH}$ = 14.4 Hz, 2H, CH_2-furyl), 3.66 (d, $^2J_{HH}$ = 14.4 Hz, 2H, CH_2-furyl), 3.65 (d, $^2J_{HH}$ = 14.4 Hz, 2H, CH_2-furyl), 1.29 (t, $^3J_{HH}$ = 7.2 Hz, 6H, $OCH_2\underline{CH_3}$), 1.24 (t, $^3J_{HH}$ = 7.2 Hz, 6H, $OCH_2\underline{CH_3}$), 1.23 (t, $^3J_{HH}$ = 7.2 Hz, 6H, $OCH_2\underline{CH_3}$). ^{31}P NMR (243 MHz, $CDCl_3$): δ = 21.83, 21.81 (1:1).

1,3-Phenylene-bis(aminomethylphosphonic Acids) (5a–d) and 2,6-Pyridine-bis-(aminomethylphosphonic Acids) (6a–d): General Procedure

Diethyl *H*-phosphonate(1 mmol, 0.11 g) was dissolved in dry dichloromethane; to this solution, bromotrimethylsilane (4.2 mmol, 0.65 g) was added dropwise during 15 min. The mixturewas stirred for 1 h at r.t. Then, a solution of the respective Schiff base (0.5 mmol) in dry dichloromethane was added and the mixture was refluxed for 4 h. The solution wasevaporated in vacuo and the residue was dissolvedin dry methanol. It was stirred for 30–45 min until precipitation of a solid occurred, which was filtered off andcollected. In the cases, in which no precipitate was formed, 10–20 mL of propylene oxide was added andthe mixture was refrigerated for 3–7 days. Thenthe solid was filtered off and collected. Products were purified by dissolution in 10% aqueous NaOH followed by precipitation on acidification with 1 MHCl.

1,3-Phenylene-bis(*N*-(*p*-methoxyphenyl)aminomethylphosphonic Acid) (5a)

Yield: 70% (0.18 g). Mp: 210–215 °C. Signals of the major isomer are marked by (*). ^{1}H NMR (200 MHz, NaOD/D_2O): δ = 7.56 (m, 1H, arom-H), 7.28–7.23 (m, 1H, arom-H), 7.12–7.05 (m, 2H, arom-H), 6.50 (A-part of AA'BB', 8H, 4-$MeOC_6H_4$), 6.36 (B-part of AA'BB', 8H, 4-$MeOC_6H_4$), 4.25* (d, $^2J_{PH}$ = 21.8 Hz, 2H, CHP), 4.20 (d, $^2J_{PH}$ = 21.2 Hz, 2H, CHP), 3.56 (s, 6H, OCH_3), 3.55* (s, 6H, OCH_3). ^{31}P NMR (81 MHz, NaOD/D_2O):

δ = 16.50, 16.21 (5:2). Calcd. for $C_{22}H_{26}N_2O_8P_2 \cdot {}^3/_2\ H_2O$: C, 49.35; H, 5.46; N, 5.23. Found: C, 49.54; H, 5.34; N, 5.02%.

1,3-Phenylene-bis(*N*-(*p*-methylphenyl)aminomethylphosphonic Acid) (5b)

Yield: 79% (0.19 g). Mp: 179–184 °C. Signals of the major isomer are marked by (*). ^{1}H NMR (200 MHz, NaOD/D_2O): δ 7.29 (m, 1H, arom-H), 7.06–7.09 (m, 3H, arom-H), 6.78 (A-part of AA'BB', 4H, 4-MeC_6H_4), 6.72* (A-part of AA'BB', 4H, 4-MeC_6H_4), 6.41 (B-part of AA'BB', 4H, 4-MeC_6H_4), 6.34* (B-part of AA'BB', 4H, 4-MeC_6H_4), 4.32 (d, $^2J_{PH}$ = 22.0 Hz, 2H, CHP), 4.25* (d, $^2J_{PH}$ = 22.0 Hz, 2H, CHP), 2.08* (s, 6H, CH_3), 2.06 (s, 6H, CH_3). ^{31}P NMR (81 MHz, NaOD/D_2O): δ = 16.61, 16.52 (1:2). Calcd. for $C_{22}H_{26}N_2O_6P_2 \cdot {}^3/_2\ H_2O$: C, 52.18; H, 5.84; N, 5.53. Found: C, 52.40; H, 6.09; N, 5.31%.

1,3-Phenylene-bis(*N*-benzylaminomethylphosphonic Acid) (5c)

Yield: 87% (0.21 g). Mp: 245–248 °C, ref [1]: 267–272 °C. Signals of the major isomer are marked by (*). ^{1}H NMR (200 MHz, D_2O): δ = 7.56–7.49 (m, 3H, C_6H_5, arom-H), 7.45–7.36 (m, 11H, C_6H_5, arom-H), 4.34 (d, $^2J_{PH}$ = 15.7 Hz, 2H, CHP), 4.31* (d, $^2J_{PH}$ = 16.2 Hz, 2H, CHP), 4.29* (d, J = 13.4 Hz, 2H, CH_2Ph), 4.19 (d, J = 13.4 Hz, 2H, CH_2Ph). ^{31}P NMR (81 MHz, D_2O): δ = 9.70*, 9.51 (2:1).

1,3-Phenylene-bis(*N*-furfurylaminomethylphosphonic Acid) (5d)

Yield: 95% (0.21 g). Mp: 215–218 °C. Signals of the major isomer are marked by (*). ^{1}H NMR (200 MHz, D_2O): δ = 7.62–7.51 (m, 6H, arom-H, 5′-H of 2′-furyl), 6.54–6.52 (m, 2H, 3′-H of 2′-furyl), 6.46–6.44 (m, 2H, 4′-H of 2′-furyl); 4.36–4.19 (m, 6H, CHP, CH_2Ph). ^{31}P NMR (81 MHz, D_2O): δ = 9.68*, 9.48 (5:4). Calcd. for $C_{18}H_{22}N_2O_8P_2 \cdot {}^5/_2\ H_2O$: C, 43.12; H, 5.43; N, 5.59. Found: C, 42.89; H, 5.17; N, 5.31%.

2,6-Pyridine-bis(*N*-(*p*-methoxyphenylaminomethylphosphonic Acid) (6a)

Yield: 74% (0.19 g). Mp: 181–183 °C. Signals of the major isomer are marked by (*). ^{1}H NMR (200 MHz, NaOD/D_2O): δ = 7.40 (t, $^3J_{HH}$ = 7.7 Hz, 1H, H-pyridyl), 7.26 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H-pyridyl), 6.62 (A-part of AA'BB', 4H, 4-MeOC_6H_4), 6.48 (B-part of AA'BB', 4H, 4-MeOC_6H_4), 4.47* (d, $^2J_{PH}$ = 20.6 Hz, 2H, CHP), 4.41 (d, $^2J_{PH}$ = 21.4 Hz, 2H, CHP), 3.54 (s, 6H, OCH_3). ^{31}P NMR (81 MHz, NaOD/D_2O): δ = 15.14*, 14.79 (9:1). Calcd. for $C_{21}H_{25}N_3O_8P_2 \cdot {}^3/_2\ H_2O$: C, 47.02; H, 5.26; N, 7.83. Found: C, 46.79; H, 5.42; N, 7.66%.

2,6-Pyridine-bis(*N*-(*p*-methylphenylaminomethylphosphonic Acid) (6b)

Yield: 62% (0.15 g). Mp: 175–177 °C. Signals of the major isomer are marked by (*). ^{1}H NMR (200 MHz, NaOD/D_2O): δ = 7.38 (t, $^3J_{HH}$ = 7.6 Hz, 1H, H-pyridyl), 7.16 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H-pyridyl), 6.93 (A-part of AA'BB', 4H, 4-MeC_6H_4), 6.84* (A-part

of AA'BB', 4H, 4-MeC_6H_4), 6.62 (B-part of AA'BB', 4H, 4-MeC_6H_4), 6.46* (B-part of AA'BB', 4H, 4-MeC_6H_4), 4.52 (d, $^2J_{PH}$ = 23.6 Hz, 2H, CHP), 4.51* (d, $^2J_{PH}$ = 20.6 Hz, 2H, CHP), 2.07 (s, 6H, CH_3), 2.01* (s, 6H, CH_3). ^{31}P NMR (81 MHz, NaOD/D_2O): δ = 15.21*, 14.85 (9:1). Calcd. for $C_{21}H_{25}N_3O_6P_2 \cdot {}^5/_2\ H_2O$: C, 48.28; H, 5.79; N, 8.04. Found: C, 48.11; H, 5.81; N, 8.32%.

2,6-Pyridine-bis(*N*-benzylaminomethylphosphonic Acid) (6c)

Yield: 65% (0.16 g). Mp: 244–246 °C. ^{1}H NMR (200 MHz, NaOD/D_2O): δ = 7.56 (t, $^3J_{HH}$ = 7.8 Hz, 1H, H-pyridyl), 7.20–7.08 (m, 12H, C_6H_5, H-pyridyl), 3.75 (d, $^2J_{PH}$ = 17.8 Hz, 2H, CHP), 3.86 (d, J = 13.4 Hz, 2H, CH_2Ph), 3.84 (d, J = 13.4 Hz, 2H, CH_2Ph). ^{31}P NMR (81 MHz, $CDCl_3$): δ = 15.83, 15.73 (2:1). Calcd. for $C_{21}H_{25}N_3O_6P_2 \cdot {}^3/_2\ H_2O$: C, 50.00; H, 5.60; N, 8.33. Found: C, 50.06; H, 5.84; N, 8.11%.

2,6-Pyridine-bis(*N*-furfurylaminomethylphosphonic Acid) (6d)

Yield: 32% (0.08 g). Mp: 250–251 °C. ^{1}H NMR (200 MHz, NaOD/D_2O): δ = 7.44 (t, $^3J_{HH}$ = 7.8 Hz, 1H, H-pyridyl), 7.21 (m, 2H, 5′-H of 2′-furyl), 7.05 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H-pyridyl), 6.11 (m, 2H, 3′-H of 2′-furyl), 5.92 (m, 2H, 4′-H of 2′-furyl), 3.64 (d, $^2J_{PH}$ = 17.8 Hz, 2H, CHP), 3.47 (d, J = 14.4 Hz, 4H, CH_2-furyl), 3.38 (d, J = 14.4 Hz, 4H, CH_2-furyl). ^{31}P NMR (81 MHz, NaOD/D_2O): δ = 15.77. Calcd. for $C_{17}H_{21}N_3O_8P_2 \cdot 4\ CH_3OH$: C, 43.08; H, 6.37; N, 7.18. Found: C, 42.87; H, 6.14; N, 7.02%.

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