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The Unusual Stereochemical Behavior in the Addition of Phosphites to N-1-Naphthyl Terephthalic and Isophthalic Schiff Bases

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ABSTRACT: *The reaction of N-α-naphthylimines of terephthalic and isophthalic aldehydes with dialkyl and diaryl phosphites gave corresponding N-α-naphthylamino-phosphonates in fair yields. An unusual stereochemical behavior was observed and the explanation for such a phenomenon was suggested.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:27–32, 2001

INTRODUCTION

The first preparation of aminoalkanephosphonic acids and their esters [1–3] stimulated the studies on their biochemistry, which confirmed the possibility of the application of such compounds in the field of medicine and agriculture [4]. Since that time some heterocyclic derivatives were prepared starting from furfural [5–9] and also from thiophene and pyrrole by sonochemical activation [10].

In our search to screen for new plant protection agents, we synthesized the series of *N*-1-naphthyl substituted aminophosphonates, which will be published elsewhere. The report of the potential antitumor activity of di-(*β*-chloroethyl)-*N*-1-naphthylaminophosphonates [11] prompted us to choose this class of compounds.

The synthesis of *N*-1-naphthyl-substituted aminophosphonates was first reported by Borisov [12] and Lugovkin [13]. Zoń and Mastalerz [14] synthesized *N*-1-naphthyl-substituted aminophosphonates derived from salicylic aldehyde. Pavlichenko et al. [15] carried out the reaction without solvent, while Krutikov [16] refluxed the reagents in benzene or in a benzene-acetonitrile solvent system.

The addition of dialkyl (-aryl) phosphites to terephthalic and isophthalic imines should lead to the formation of two diastereoisomeric forms: a meso-form and a pair of enantiomers. As it was previously shown [17–20], this addition is stereoselective. In our previous article [21], we recognized the exclusive product as the meso-form, and we proposed the mechanism of the stereochemistry of this reaction. We explained this by the formation of intermolecular hydrogen bonding [21]. In this article, we would like to report the first synthesis of *N*-1-naphthyl substituted phenylene-bis-(aminomethanephosphonates) and by the addition of dialkyl and diaryl phosphites to the azomethine bond of bis-*N*-naphthyl substituted Schiff bases of terephthalic and isophthalic aldehydes and to discuss the unusual stereochemistry of this reaction.

RESULTS AND DISCUSSION

1,4-Phenylene-bis-*N*-1-naphthylamino-bis-phosphonates (**2a–c**) were obtained in fair yields, and the reactions were carried out in refluxing toluene during a relatively short period of time. After the reaction, products were easily isolated from the reaction mixture and purified by crystallization (Scheme 1).

The synthesis of 1,3-phenylene-bis-(*N*-1-naphthylaminomethane)-bis-phosphonates (**4a–c**) was

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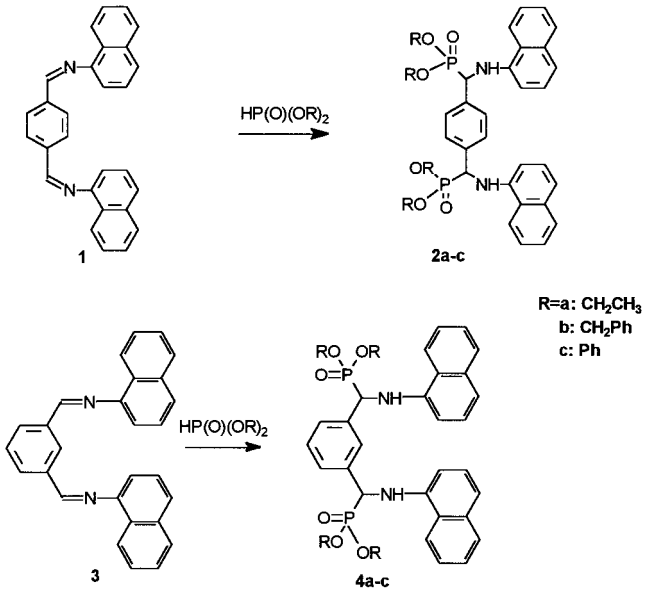
more troublesome. The conversion rates of the formation of these esters were about 40–60%. We succeeded in isolating the tetraethyl ester **4a** by column chromatography on silica gel and the tetraphenyl and tetrabenzyl esters by acidification, washing with ether, making the solutions alkaline, and finally by extraction with dichloromethane. Both derivatives **4b** and **4c** partially decomposed on silica gel, so yields decreased dramatically (Scheme 1).

As we previously mentioned, the addition of phosphites to terephthalic and isophthalic Schiff bases leads exclusively to the formation of a meso-form. The addition of phosphites to *N*-terephthalilidene-1-naphthylamine **1** and its isophthalilidene isomer **3** demonstrated unusual stereochemical behaviour. The addition of dibenzyl and diphenyl phosphites to terephthalic imine **1** was stereoselective and led exclusively to the formation of one isomer, while its reaction with diethyl phosphite resulted in the racemic product. It was demonstrated by means of NMR spectroscopy, as the spectra of **2b** and **2c** showed one set of ^{1}H and ^{31}P NMR signals. The ^{1}H and ^{31}P NMR spectra of the diethyl ester **2a** demonstrated the occurrence of two sets of signals in a 1:1 ratio. In order to exclude the existence of the second diastereoisomeric form, we analyzed the postreaction mixture by means of NMR spectroscopy in each case. As this analysis showed no appearance of the other diastereoisomeric form, we can state that the stereoselectivity could not arise from preferential crystallisation of one of the isomers. Analogously to the previous case [21], we supposed that aminophosphonates **2b** and **2c** are meso-forms. To confirm this, we performed another experiment. The starting bis-phosphonate **2b** was converted into its chiral salt (**6**) with (*S*)-mandelic acid (Scheme 2). NMR studies showed the clear formation of a salt: the ^{31}P chemical shift occurred at 22.58 ppm, at about 0.1 ppm downfield of the starting bis-aminophosphonate. ^{1}H and ^{13}C NMR signals shifted downfield about 0.05 and 0.1 ppm, respectively. However, the most significant change was the shift of the ^{1}H NMR signal corresponding to the NH group: a broad singlet occurred at 5.49 ppm about 3 ppm downfield of the NH signal in the starting ester **2b** (δ_H = 2.46 ppm). Only one set of NMR signals was observed, which demonstrates clearly the initial formation of the meso-form.

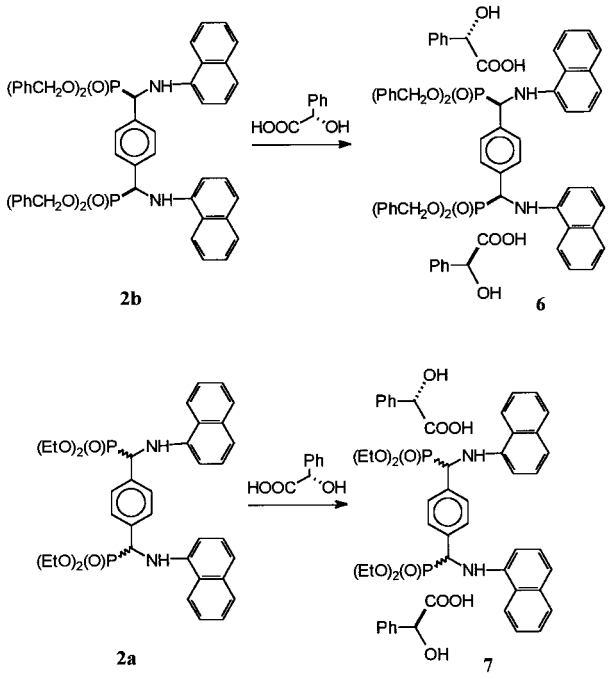
A similar experiment was performed with tetraethyl bis-aminophosphonate **2a** (Scheme 2). The conversion into its salt **7** with (*S*)-mandelic acid showed the formation of three diastereoisomers in a 2:1:1 ratio, which was visible in the ^{31}P NMR spectrum (δ_P = 21.83, 21.65, and 21.58).

The addition of phosphites to the bis-imine **3** showed a different orientation. The addition of diethyl phosphite was stereoselective, leading to the exclusive diastereoisomeric form of **4a**. The addition of dibenzyl and diphenyl phosphites led to the formation of both diastereoisomeric forms of **4b** and **4c** in a 1:1 ratio, which was demonstrated as aforementioned by ^{1}H and ^{31}P NMR spectroscopy.

The origin of this anomalous stereochemical be-



SCHEME 1



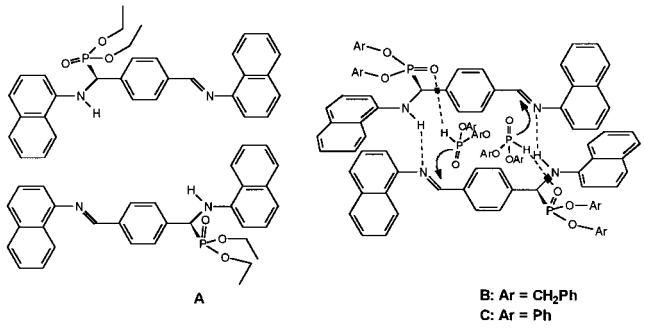
SCHEME 2

havior is unclear. Considering the postulated mechanism [21], we suppose that steric reasons are the factors determining the stereochemistry of this reaction. If we consider that the mono-addition intermediate adopts the conformation **A,** which seems to be sterically convenient, the hydrogen bonding cannot occur due to the distance between N–H and C = N groups. Also, the formation of these hydrogen bonds is the condition sine qua non for the asymmetric induction (Scheme 3). That is why the addition of diethyl phosphite is not stereoselective.

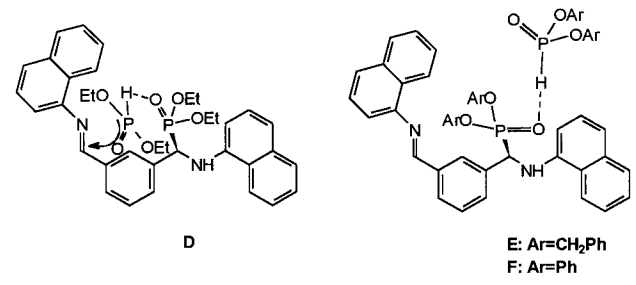
Mono-addition intermediates of the diphenyl or dibenzyl phosphites have bulkier dialkoxyphosphono groups and they probably adopt the conformations **B** and **C.** Thus, they can form hydrogen bonds between C = N and N–H as well as between P = O and H–P groups, which can force the attack at the one face (Scheme 3).

The stereochemistry of the addition of phosphites to *N*-isophthalilidene-1-naphtylamine is complex, and perhaps it can be explained as follows. In the case of the diethyl phosphite addition, the probable adopted conformation of the mono-addition product (the intermediate **D**) allows the formation of hydrogen bonding with the molecule of diethyl phosphite; thus, the addition is oriented and, consequently, stereoselective (Scheme 4). In the case of dibenzyl and diphenyl phosphonic groups, the mono-addition product will adopt conformations such as **E** and **F** due to the repulsion between phenyl and naphthyl rings. The hydrogen bonding between P = O and H–P cannot force the asymmetric induction and that is why the reactions are not stereoselective.

The above explanation of the stereochemistry of this reaction is rather hypothetical and the study will be continued.



SCHEME 3



SCHEME 4

EXPERIMENTAL

All solvents were routinely dried and distilled prior to use. 1-Naphthylamine as well as all three phosphites (Aldrich) were used as received. Imines were prepared following the published [7,10,22] or slightly modified procedures. NMR measurements were recorded on a Varian Gemini 200 BB (200 MHz) apparatus. Melting points were measured on a MeltTemp II apparatus.

*N-Terephthalilidene-bis-1-naphthylamine (***1***)*

m.p. 175–177°C (ethyl acetate), lit. [22] 223–225°C. *Y* = 13.22 g (72%)

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.63 (s, CH = N, 2H); 8.40 (dd, J = 6.0 and 3.4 Hz, H3, 2H); 8.16 (s, C_6H_4, 4H); 7.87 (dd, J = 3.0 and 6.2 Hz, H6, 2H); 7.75 (d, J = 8.4 Hz, H8, 2H); 7.60–7.41 (m, H7, H5, H2, 6H); 7.10 (d, J = 7.4 Hz, H4, 2H).

Anal: Calctd. for ($C_{28}H_{20}N_2$): C, 87.47; H, 5.24; N, 7.29. Found: C, 87.75; H, 5.21; N, 7.27.

*N-Isophthalilidene-bis-1-naphthylamine (***3***)*

Y = 13.22 g (72%)

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.47 (s, CH = N, 2H); 8.38 (m, H3, 2H); 8.06 (d, J = 7.4 Hz, H8, 2H); 7.82–7.65 (m, CH_{arom}, 4H); 7.49–7.32 (m, H5, H6, H7, 6H); 7.21 (d, J = 7.1 Hz, H2, 2H); 6.98 (d, J = 7.3 Hz, H4, 2H); 6.62 (dd, J = 7.6 and 6.4 Hz, ArH_{isol}, 1H).

Anal: Calctd. for ($C_{28}H_{20}N_2$): C, 87.47; H, 5.24; N, 7.29. Found: C, 87.70, H, 5.14; N, 7.23.

Tetraalkyl (or -aryl) 1,4-phenylene-bis-(N-naphthylaminomethane)-bis-phosphonates **2**

N-Terephalilideno-bis-1-naphthylamine (1.9 g, 5 mmol) was dissolved in toluene (30 mL) and slightly heated. To this solution, dialkyl (or -aryl) phosphite (10 mmol) was added. The mixture was refluxed for 7 hours and then stirred for 12 hours at room temperature. The solid product was collected by filtration, dissolved in ethyl acetate, and precipitated with hexane.

Tetraalkyl (or -aryl) 1,3-phenylene-bis-(N-naphthylaminomethane)-bis-phosphonates **4**

N-Isophthalilideno-bis-1-naphthylamine (1.9 g, 5 mmol) was dissolved in toluene (30 mL) and slightly heated. To this solution, dialkyl (or -aryl) phosphite (10 mmol) was added. The mixture was then refluxed for 7 hours and stirred for 12 hours at room temperature. Then the mixture was dissolved in 10% HCl_{aq}:ethanol 4:1 (100 mL) and the solution was washed with ether. The aqueous solution was then made alkaline, extracted with dichloromethane (3 × 50 mL), dried, and evaporated.

*Tetraethyl 1,4-phenylene-bis-(N-naphthylaminomethane)-bis-phosphonate (***2a***)*

m.p. 92–94°C. Yield: 58% (1.9 g)

^{1}H NMR (200 MHz, $CD_3C(O)CD_3$): δ 8.01 (m, H3, 2H); 7.78 (m, H6, 2H); 7.49 (m, H8 and C_6H_4, 6H); 7.26–7.05 (m, H7, H5, H2, 6H); 6.33 (d, J = 7.6 Hz, H4, 2H); 4.91 and 4.89 (2d, $^2J_{PH}$ = 24.0 Hz, CHP, 2H); 4.20–4.02 and 3.98–3.42 (2m, $\underline{CH_2}CH_3$, 8H); 2.36 (s, NH, 2H); 1.25 and 1.22 (2t, J = 6.9 Hz, CH_3, 12H); 1.09 and 0.93 (2t, J = 7.14 Hz, CH_3, 12H). ^{31}P NMR (81 MHz, $CD_3C(O)CD_3$): δ 21.73; 21.64 (in 1:1 ratio). ^{13}C NMR (50 MHz, $CD_3C(O)CD_3$): δ 141.15 (d, $^2J_{PC}$ = 15.8 Hz, C_{ipso}); 135.48 ($C1_{napht}$); 134.28 ($C10_{napht}$); 128.38 ($C3_{napht}$); 127.88 ($C_{phenylene}$); 126.08 ($C6_{napht}$); 125.89 ($C8_{napht}$); 125.13 ($C7_{napht}$); 123.89 ($C9_{napht}$); 120.16 ($C2_{napht}$); 118.75 ($C5_{napht}$); 106.63 ($C4_{napht}$); 62.80 and 62.84 (2d, $^2J_{PC}$ = 18.9 Hz, Et); 62.68 and 62.62 (2d, $^2J_{PC}$ = 19.2 Hz, Et); 59.45 and 58.96 (2d, $^1J_{PC}$ = 152.6 Hz, CHP); 16.65 and 16.59 (2d, $^2J_{PC}$ = 13.9 Hz, Et); 16.39 and 16.35 (2d, $^2J_{PC}$ = 14.3 Hz, Et).

Anal: Calctd. for ($C_{36}H_{42}N_2O_6P_2$): C, 65.45; H, 6.41; N, 4.24; P, 9.38. Found: C, 65.12; H, 6.44; N, 4.03; P, 9.26.

*Tetrabenzyl 1,4-phenylene-bis-(N-naphthylaminomethane)-bis-phosphonate (***2b***)*

m.p. 169–171°C. Yield: 55% (2.5 g)

^{1}H NMR (200 MHz, $CD_3C(O)CD_3$): δ 7.92 (dd, J = 6.0 and 3.2 Hz, H3, 2H); 7.76 (dd, J = 6.4 and 3.4 Hz, H6, 2H); 7.48 (d, J = 3.4 Hz, H8, 2H); 7.46 (m, C_6H_4 and PhH, 6H); 7.25–7.22 (m, PhH, 18H); 7.13, 7.02, 6.92 (3m, H7, H5, H2, 6H); 6.31 (d, J = 7.4 Hz, H4, 2H); 5.01 (AB part of ABX system, $O\underline{CH_2}Ph$, 4H); 4.78 (dd, $^2J_{HH}$ = 11.8 Hz and $^3J_{PH}$ = 9.2 Hz, $O\underline{CH_2}Ph$, 2H); 4.72 (d, $^2J_{PH}$ = 20.9 Hz, CHP, 2H); 4.32 (dd, $^2J_{HH}$ = 11.6 Hz and $^3J_{PH}$ = 8.0 Hz, $O\underline{CH_2}Ph$, 2H); 2.46 (s, NH, 2H). ^{31}P NMR (81 MHz, $CD_3C(O)CD_3$): δ 22.48. ^{13}C NMR (50 MHz, $CD_3C(O)CD_3$): δ 141.05 (d, $^2J_{PC}$ = 15.0 Hz, C_{ipso}); 135.80 (C_{ipso}); 135.45 ($C1_{napht}$); 134.22 ($C10_{napht}$); 128.62 (C_m); 128.53 (C_o); 128.46 (C_m); 128.36 (C3); 128.31 (C_o, C_p); 128.00 (C_p); 127.87 ($C_{phenylene}$); 126.03 ($C6_{napht}$); 125.87 ($C8_{napht}$); 125.13 ($C7_{napht}$); 123.86 ($C9_{napht}$); 120.04 ($C2_{napht}$); 118.77 ($C5_{napht}$); 106.52 ($C4_{napht}$); 68.76 and 68.64 (2d, $^2J_{PC}$ = 6.5 Hz, CH_2); 56.13 (d, $^1J_{PC}$ = 149.9 Hz, CHP).

Anal: Calcd. for ($C_{56}H_{50}N_2O_6P_2$): C, 74.00; H, 5.54; N, 3.08; P, 6.82. Found: C, 74.36; H, 5.47; N, 3.26; P, 6.82.

*Tetraphenyl 1,4-phenylene-bis-(N-naphthylaminomethane)-bis-phosphonate (***2c***)*

m.p. 178–180°C. Yield: 59% (2.5 g)

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.90 (m, H3, 2H); 7.80 (m, H6, 2H); 7.62 (s, C_6H_4, 4H); 7.47 (m, PhH, 4H); 7.31–7.03 (m, PhH, H7, H5, H8, 19H); 6.78 (d, J = 7.7 Hz, H2, 2H); 6.48 (d, J = 7.2 Hz, H4, 2H); 5.29 (d, $^2J_{PH}$ = 23.3 Hz, CHP, 2H); 1.78 (s, NH, 2H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 12.51

Anal: Calcd. for ($C_{52}H_{42}N_2O_6P_2$): C, 73.23; H, 4.96; N, 3.28; P, 7.26. Found: C, 73.42; H, 4.85; N, 3.40; P, 7.29.

*Tetraethyl 1,3-phenylene-bis-(N-naphthylaminomethane)-bis-phosphonate (***4a***)*

Yield: 19% (0.6 g) eluted with AcOEt-hexane (2:1)

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.80 (m, H3, H6, 4H); 8.01–7.25 (m, C_6H_4 and H8, H7, H5, H2, 12H); 6.58 (m, H4, 2H); 5.08 (d, $^2J_{PH}$ = 23.5 Hz, CHP, 2H); 4.27–3.95 (m, $\underline{CH_2}CH_3$, 8H); 2.36 (s, NH, 2H); 1.31 and 1.26 (2t, J = 7.1 Hz, CH_3, 12H). ^{31}P NMR (81 MHz, $CDCl_3$); δ 21.93.

Anal: Calctd. for ($C_{36}H_{42}N_2O_6P_2$): C, 65.45; H, 6.41; N, 4.24; P, 9.38. Found: C, 65.08; H, 6.16; N, 4.03; P, 9.08.

*Tetrabenzyl 1,3-phenylene-bis-(N-naphthylaminomethane)-bis-phosphonate (***4b***)*

Yield: 44% (2.0 g)

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.88 (m, H3, 2H); 7.78 (m, H6, 2H); 7.44 (m, H8, 2H); 7.27–7.11 (m, PhH, 23H); 7.13, 7.02, 6.92 (2m, H7, H5, 6H); 6.33 (d, J = 7.0 Hz, H2, 2H); 6.20 (d, J = 7.4 Hz, H4, 2H); 4.88 (AB part of ABX system, $O\underline{CH_2}Ph$, 4H); 4.78 (dd, $^2J_{HH}$ = 11.8 Hz and $^3J_{PH}$ = 9.2 Hz, $O\underline{CH_2}Ph$, 2H); 4.78 (d, $^2J_{PH}$ = 20.9 Hz, CHP, 2H); 4.25 (dd, $^2J_{HH}$ = 11.6 Hz and $^3J_{PH}$ = 8.0 Hz, $O\underline{CH_2}Ph$, 2H); 1.71 (s, NH, 2H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 22.51 and 22.22 (1:1 ratio)

Anal: Calcd. for ($C_{56}H_{50}N_2O_6P_2$): C, 74.00; H, 5.54;

N, 3.08; P, 6.82. Found: C, 74.56; H, 5.14; N, 3.46; P, 6.98.

*Tetraphenyl 1,3-phenylene-bis-(N-naphthyl-aminomethane)-bis-phosphonate (**4c**)*

Yield: 52% (2.2 g)

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.94–7.74 (m, H3, H6, 4H); 7.50 (m, C_6H_4, 1H); 7.49–7.33 (m, C_6H_4, 3H); 7.25–7.33 (m, ArH, 20 H); 6.94–6.77 (m, H5, H7, H8, 6H); 6.68 (m, H4, 2H); 6.46 and 6.34 (2d, J = 7.4 Hz, H2, 2H); 5.32 and 5.30 (2d, $^2J_{PH}$ = 24.9 Hz, CHP, 2H); 1.78 (s, NH, 2H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 14.55 and 14.49 (1:1 ratio)

Anal: Calcd. for ($C_{52}H_{42}N_2O_6P_2$): C, 73.23; H, 4.96; N, 3.28; P, 7.26. Found: C, 73.44; H, 5.38; N, 3.23; P, 7.35.

Preparation of Chiral Salts **6** *and* **7**

Aminophosphonic esters **2a** or **2b** were packed into an NMR tube and dissolved in 0.5 mL of acetone-D6. Spectra were recorded and then a solution of S-mandelic acid in acetone D6 was added. Spectra were immediately recorded, showing the formation of salts.

Chiral Salt **6**

^{1}H NMR (200 MHz, $CD_3C(O)CD_3$): δ 7.92 (dd, J = 6.0 and 3.2 Hz, H3, 2H); 7.76 (dd, J = 6.4 and 3.4 Hz, H6, 2H); 7.54–7.48 (m, ArH, H8, 12H); 7.46 (m, C_6H_4 and PhH, 6H); 7.25–7.22 (m, PhH, 18H); 7.13, 7.02, 6.92 (3m, H7, H5, H2, 6H); 6.31 (d, J = 7.4 Hz, H4, 2H); 5.49 broad s, NH_2^+, OH, 6H); 5.21 (s, CH, 2H); 5.01 (AB part of ABX system, O$\underline{CH_2}$Ph, 4H); 4.78 (dd, $^2J_{HH}$ = 11.8 Hz and $^3J_{PH}$ = 9.2 Hz, O$\underline{CH_2}$Ph, 2H); 4.72 (d, $^2J_{PH}$ = 20.9 Hz, CHP, 2H); 4.32 (dd, $^2J_{HH}$ = 11.6 Hz and $^3J_{PH}$ = 8.0 Hz, O$\underline{CH_2}$Ph, 2H). ^{31}P NMR (81 MHz, $CD_3C(O)CD_3$): δ 22.58. ^{13}C NMR (50 MHz, $CD_3C(O)CD_3$): δ 174.65 (C=O); 141.15 (d, $^2J_{PC}$ = 15.0 Hz, C_{ipso}); 140.88 (C_{ipso}); 135.80 (C_{ipso}); 135.55 (Cl_{napht}); 134.33 ($C10_{napht}$); 129.21 (C_m); 128.84 (C_o); 128.73 (C_m); 128.63 (C_o); 128.56 (C_m); 128.46 ($C3_{napht}$); 128.41 (C_o, C_p); 128.12 (C_p); 127.98 ($C_{phenylene}$); 127.81 (C_p); 126.13 ($C6_{napht}$); 125.95 ($C8_{napht}$); 125.23 ($C7_{napht}$); 123.96 ($C9_{napht}$); 120.14 ($C2_{napht}$); 118.87 ($C5_{napht}$); 106.63 ($C4_{napht}$); 73.50 (CH); 68.76 and 68.64 (2d, $^2J_{PC}$ = 6.5 Hz, CH_2); 56.13 (d, $^1J_{PC}$ = 149.9 Hz, CHP).

Chiral Salt **7**

(Signals of the products in minority are presented in italics.)

^{1}H NMR (200 MHz, $CD_3C(O)CD_3$): δ 8.01 (m, H3, 2H); 7.78 (m, H6, 2H); 7.54–7.51 (m, ArH, 10H); 7.49 (m, H8 and C_6H_4, 6H); 7.26–7.05 (m, H7, H5, H2, 6H); 6.33 (d, J = 7.6 Hz, H4, 2H); 5.46 (broad s, NH_2^+, OH, 6H); 5.24, *5.21* and *5.18* (s, CH, 2H); 4.91 *4.89* and *4.86* (3d, $^2J_{PH}$ = 24.0 Hz, CHP, 2H); 4.20–3.38 (3m, $\underline{CH_2}CH_3$, 8H); 2.36 (s, NH, 2H); 1.25 and 1.22 (2t, J = 6.9 Hz, CH_3, 12H); *1.11, 1.08, 1.02*, and *0.93* (2t, J = 7.14 Hz, CH_3, 12H). ^{31}P NMR (81 MHz, $CD_3C(O)CD_3$): δ 21.83; *21.65* and *21.58* (in 2:1:1 ratio). ^{13}C NMR (50 MHz, $CD_3C(O)CD_3$): δ 174.65 (C=O); 141.25 (d, $^2J_{PC}$ = 15.8 Hz, C_{ipso}); 140.87 (C_{ipso}); 135.54 ($C1_{napht}$); 134.37 ($C10_{napht}$); 128.84 (C_o); 128.49 ($C3_{napht}$); 127.98 ($C_{phenylene}$); 127.81 (C_p); 127.72 (C_m); 126.19 ($C6_{napht}$); 125.93 ($C8_{napht}$); 125.24 ($C7_{napht}$); 123.94 ($C9_{napht}$); 120.24 ($C2_{napht}$); 118.84 ($C5_{napht}$); 106.75 ($C4_{napht}$); 73.60, 73.58 and 73.52 (CH); 62.94 and 62.90 (2d, $^2J_{PC}$ = 18.9 Hz, Et); 62.79 and 62.74 (2d, $^2J_{PC}$ = 19.2 Hz, Et); 62.69 and 62.65 (2d, $^2J_{PC}$ = 19.2 Hz, Et); 59.52, 59.39 and 59.02 (3d, $^1J_{PC}$ = 152.6 Hz, CHP); 16.72 and 16.68 (2d, $^2J_{PC}$ = 13.9 Hz, Et); 16.43 and 16.39 (2d, $^2J_{PC}$ = 14.3 Hz, Et); 16.36 and 16.33 (2d, $^2J_{PC}$ = 14.3 Hz, Et).

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