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TETRAHEDRON: *ASYMMETRY*

A new efficient procedure for asymmetric synthesis of α-aminophosphonic acids via addition of lithiated bis(diethylamino)phosphine borane complex to enantiopure sulfinimines

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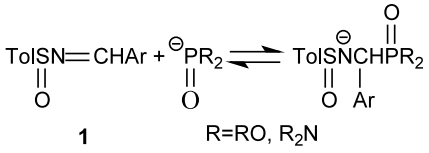
Abstract—The addition of lithiated bis(diethylamino)phosphine borane complex to enantiopure *p*-toluenesulfinimines is highly diastereoselective, affording the corresponding addition products with high efficiency (yields from 72 to 100%). The addition products were readily converted into α-amino-α-arylmethylphosphonic acids with high enantiomeric purities (from 72 to >98%).

1. Introduction

Aminophosphonic and aminophosphinic acids are phosphorus analogues of amino acids in which the planar carboxylic group is replaced by a phosphonic acid, $P(O)(OH)_2$, or phosphinic acid, P(O)(OH)R, moiety.[1] Because of the tetrahedral configuration of phosphorus, these compounds serve as biologically stable analogues of unstable tetrahedral carbon intermediates formed in enzymatic processes and, therefore, act as enzyme inhibitors. In addition to this biological function, aminophosphonic acids exhibit a wide spectrum of biological activities. Thus, many natural and synthetic aminophosphonic acids show antibacterial, anticancer and antiviral properties as well as exhibiting pesticidal, insecticidal and herbicidal activity.[1,2] As such, some of these compounds have found commercial applications in agriculture and medicine.

As in the case of other classes of chiral bioactive compounds, the biological activity of aminophosphonic acids depends strongly on the absolute configuration of the stereogenic carbon atom bearing the amino group. As a consequence, considerable research has been devoted to the asymmetric synthesis of α- and β-aminophosphonic acids during the past decades.[1,3] In the course of our studies on the application of the *p*-toluenesulfinyl group as a chiral auxiliary in asymmetric synthesis,[4–6] we have developed a novel method for the asymmetric synthesis of α- and β-aminophosphonic acids based on the highly diastereoselective addition of phosphite anions and α-phosphonate carbanions, respectively, to enantiomeric sulfinimines **1**.[7,8] However, in contrast to the very efficient addition of α-phosphonate carbanions to **1**, the reaction of **1** with dialkyl phosphite or diamido phosphite anions was found to be reversible, most probably due to the comparable stability of both anions in Eq. (1), i.e. the starting phosphite anion and the amide ion of the adduct formed. The reversibility of the above reaction exerted an influence on the formation of addition products, which were obtained in low yields in the reactions with diamido phosphite anions.



(1)

It was reasonable to expect that the use of more nucleophilic and less stabilized phosphorus anions would suppress the reversibility of this reaction and

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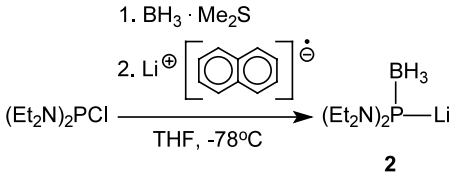
shift it towards the addition products. With this in mind, we turned our attention to the lithiated diaminophosphine borane complex **2** introduced to organic synthesis by Konchel[9] as a useful nucleophilic phosphorus reagent. It is easily prepared from bis(diethylamino)chlorophosphine borane complex and lithium naphthalenide (Eq. (2)) and its high nucleophilicity was demonstrated nicely by the cross-coupling reaction with aryl iodides and bromides which occurs in the absence of palladium or nickel catalyst.

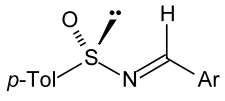


2 (2)

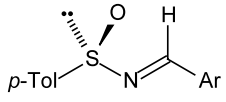
Preliminary experiments revealed that the addition of **2** to sulfinimines **1** occurs efficiently, thus confirming that our reasoning was correct. We wish to describe herein a new procedure for the asymmetric synthesis of α-aminophosphonic acids **3** involving a highly efficient and stereoselective addition of the borane complex **2** to enantiomeric *S*- and *R*-sulfinimines **1** as a key step.[10]

2. Results and discussion

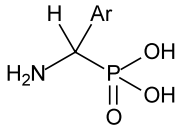
To a freshly prepared solution of the borane complex **2** in THF *S*- and *R*-sulfinimines **1** (dissolved in THF) were added at −78°C. The additions were completed at −78°C and the reactions were allowed to warm to room temperature. After standard work-up and purification by flash chromatography, the corresponding addition products **4** were obtained in very high yields (70–100%) as white solids (see Scheme 1 and Table 1).



(*S*)-**1**



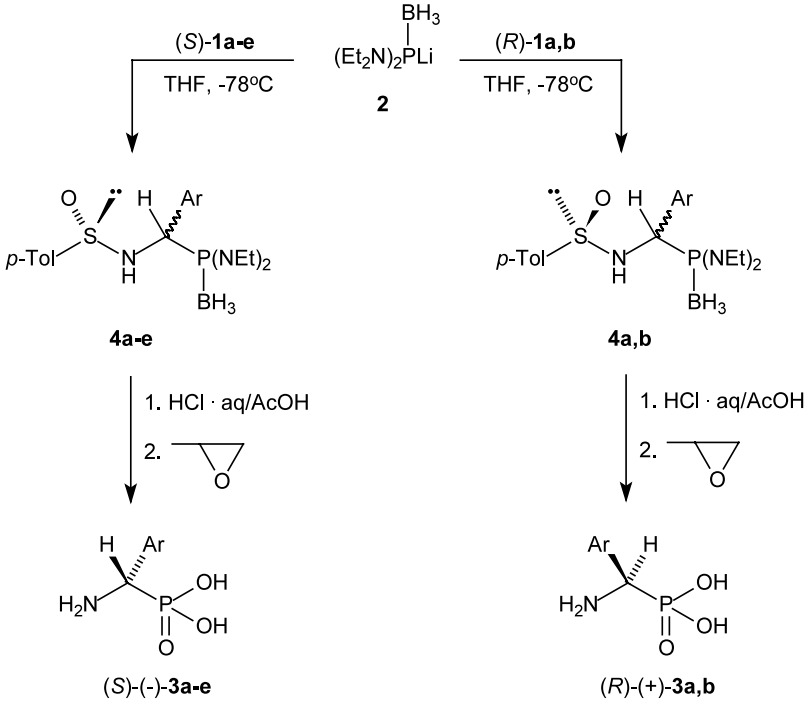
(*R*)-**1**



3

a, Ar=Ph
b, Ar=2-thienyl
c, Ar=4-C_6H_4F
d, Ar=4-C_6H_4Br
e, Ar=4-$C_6H_4NMe_2$

To further characterize the adducts **4** obtained and to determine the diastereoselectivity of the addition, the ^1H and ^{31}P NMR spectra of **4** were recorded. It turned out, however, that they were not indicative of the presence of the diastereomers of **4**, which could be formed in the addition reaction. Thus, the ^1H NMR spectrum of each adduct showed only one singlet of the *p*-toluenesulfinyl methyl protons at 2.20 ppm, and a multiplet due to the CH and NH protons at 5.13–5.30 ppm. In the phosphorus spectra only one multiplet at 91.4–93.5 ppm characteristic of the P-BH_3 group was observed. Therefore, the isolated addition products were converted into the corresponding free α-aminophosphonic acids **3** by heating for 4 h in a refluxing mixture of glacial acetic acid and hydrochloric acid (36% aq). The yields, specific rotation values and enantiomeric purities of **3** prepared in this way are collected in Table 1. The latter values were determined

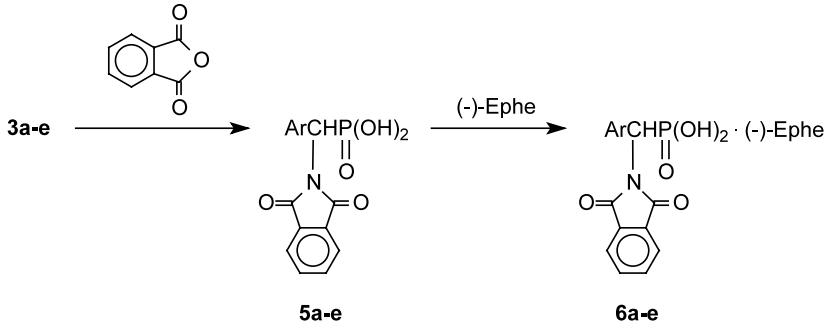


Scheme 1.

Table 1. Asymmetric addition of the aminophosphine borane complex **2** to (*S*)- and (*R*)-sulfinimines **1** and hydrolysis of the adducts **4** to α-aminophosphonic acids **3**

Sulfinimine **1**[a]	Adduct **4**			α-Aminophosphonic acid (*S*)-(−)- and (*R*)-(+)-**3**			
		Yield (%)[b]	$[\alpha]_D$ (*c*)[c]		Yield (%)[b]	$[\alpha]_D$ (*c*)[d]	ee (%)
(*S*)-(+)-**1a**	**4a**	100	+78.4 (1.0)	**3a**	92	−19.3 (1.29)	98
(*R*)-(−)-**1a**	**4a**	100	−78.0 (1.1)	**3a**	95	+19.9 (1.16)	>98
(*S*)-(−)-**1b**	**4b**	75	+96.4 (1.12)	**3b**	70	−4.2 (0.85)	77
(*R*)-(+)-**1b**	**4b**	72	−97.9 (1.05)	**3b**	75	+4.8 (0.35)	89
(*S*)-(+)-**1c**	**4c**	96	+83.2 (1.2)	**3c**	93	−19.3 (0.54)	>98
(*S*)-(+)-**1d**	**4d**	86	+30.6 (1.41)	**3d**	75	−20.5 (0.81)	>98
(*S*)-(−)-**1e**	**4e**	72	+25.2 (1.12)	**3e**	89	−17.1 (0.23)	76

[a] Sulfinimines **1** were prepared from (*S*)-(−)- or (*R*)-(+)-menthyl *p*-toluenesulfinate according to the procedure described by Davis at al.[11]
[b] Isolated yields.
[c] Measured in $CHCl_3$.
[d] Measured in 1N NaOH.



Scheme 2.

by the method elaborated by Glowacki et al.[12] and based on the ^{31}P NMR nonequivalence of diastereomeric salts of *N*-phthaloyl protected α-aminophosphonic acids with optically active amines. Hence, all the α-aminophosphonic acids **3** synthesized in this work were converted into *N*-phthaloyl derivatives **5** and then treated with equimolar amounts of (−)-ephedrine (Ephe) to form the corresponding salts **6** (Scheme 2). As expected, the diastereomeric salts **6** showed the nonequivalent ^{31}P NMR signals integration of which allowed determination of the enantiomeric purity of the acids **3**. The ^{31}P NMR chemical shifts of the acids **5** and their salts **6** are collected in Table 2.

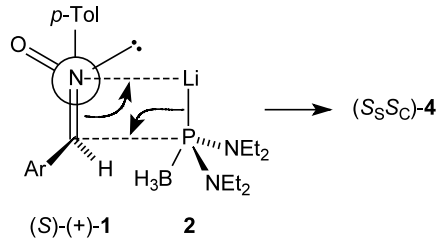
It was gratifying to find that the α-aminophosphonic acids (−)- and (+)-**3a**, (−)-**3c** and (−)-**3d** were obtained as practically pure enantiomers (ee ≥ 98%). For the acids (+)- and (−)-**3b** as well as for (−)-**3e** the ee values were in the range between 76 and 89%.

Taking into account the fact that the absolute configuration of α-amino-α-phenylmethylphosphonic acid **3a** is known to be (*S*)-(−) and (*R*)-(+)[13] as well as the fact that the bonds around the stereogenic α-carbon atom are not broken during the conversion of **4a**→**3a**, it is possible to assign S_S,S_C stereochemistry for the adduct (+)-**4a**. The reasonable assumption is that the dextrorotatory adducts **4b–e** formed by the addition of **2** to (*S*)-**1** all have the same stereochemistry. It is interesting to point out that the steric course of the above additions is analogous to that of the addition of lithium diamido phosphites. However, it is opposite to that observed with lithium dialkyl phosphites.[8] In the latter case the stereoselectivity of additions to (*S*)-(+)-**1a** was rationalized by Davis[14] by proposing a six-membered chelating transition state model in which the lithium cation is coordinated to the sulfinyl and phosphite oxygens. A reversal of diastereoselectivity observed by us in the addition of **2** may reasonably be explained in terms of the transition state model shown below where

Table 2. ^{31}P NMR chemical shifts and chemical shift differences of *N*-phthaloyl-1-aminophosphonic acids **5** and their salts **6** with (−)-ephedrine

Acid **3**	Acid **5**	Salt **6**
	δ (ppm)[a]	δ (ppm)[b] (Δδ)
(−)-**3a**	15.9	<u>12.43</u>[d], 10.65 (1.78)
(+)-**3a**	15.10	10.71[c]
(−)-**3b**	18.22	<u>11.33</u>[d], 11.81 (0.48)
(+)-**3b**	17.00	11.98, <u>12.43</u>[d] (0.45)
(−)-**3c**	16.80	12.76[c]
(−)-**3d**	19.57	12.09[c]
(−)-**3e**	18.61	<u>11.98</u>[d], 12.41 (0.43)

[a] In $CDCl_3$ and DMSO-d_6.
[b] In $CDCl_3$.
[c] Only one signal visible.
[d] Chemical shift of major diastereomer is underlined.



Scheme 3.

steric hindrance factors determine the stereoselectivity. It is not excluded that the lithium atom of **2** is coordinated to the nitrogen lone pair, facilitating the delivery of the phosphorus atom to the prochiral trigonal carbon center from the less hindered face occupied by the lone pair of electrons on sulfur (Scheme 3).

3. Conclusion

We have described herein a new procedure for the asymmetric synthesis of α-aminophosphonic acids which involves a very effective and highly diastereoselective addition of the lithiated bis(diethylamino)phosphine borane complex to enantiopure *p*-toluenesulfinimines derived from aldehydes. The stereoselectivity of the addition was explained by proposing a transition state model where steric approach control is a decisive factor.

4. Experimental

4.1. General

NMR spectra were recorded on a Bruker 1C 200 spectrometer at 200 MHz. All optical rotation measurements were carried out on a Perkin–Elmer MC 241 photopolarimeter at room temperature. Reactions were monitored by TLC chromatography (Merck Kieselgel 60_{254}). Column chromatography was conducted on Merck silica gel (70–230 mesh).

4.2. General procedure for the addition of lithiated bis-(diethylamino)phosphine borane complex 2 to sulfinimines 1

Bis(diethylamino)chlorophosphine (0.01 mol) in THF (10 mL) was cooled to 0°C and borane·methyl sulfide complex (5 mL) was added. The reaction mixture was stirred for 4 h at rt and the solvent was removed under vacuum affording the pure bis(diethylamino)-chlorophosphine borane complex. This complex was dissolved in THF (10 mL) and added slowly to lithium naphthalenide prepared from naphthalene (0.02 mol) and cut lithium wire (0.02 mol) at −78°C. After stirring for 30 min, the solution of appropriate sulfinimine **1a–e** (0.023 mol) in THF (5 mL) was dropped. The reaction mixture was stirred for 4 h at −78°C. Then, after warming to room temperature and quenching with a water solution of NH_4Cl, the organic layer was separated. The aqueous layer was extracted with ethyl ether and combined organic layers were dried over $MgSO_4$ and evaporated. Purification by flash chromatography (silica gel, hexane:ether 2:1 or 1:1) afforded the desired *N*-*p*-toluenesulfinyl-1-amino-1-arylmethylphosphine borane complex **4**.

4.2.1. Data for (+)-*N*-*p*-toluenesulfinyl-1-amino-1-phenylmethyl-bis(diethylamino)phosphine borane, 4a (prepared from (+)-1a). Obtained in ∼100% yield as a white solid, mp = 144–145°C, $[\alpha]_D = +78.4$ (*c* 1.0; $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.612 (t, 6H, $J = 7.03$ Hz), 1.19 (t, 6H, $J = 7.02$ Hz), 2.20 (s, 3H), 2.67–2.83 (m, 4H), 2.86–3.45 (m, 4H), 5.13–5.30 (m, 2H), 6.85–7.30 (m, 9H). ^{31}P NMR ($CDCl_3$) δ 92.32–93.59. HRMS calcd for $C_{22}H_{37}BN_3OPS$ (M+H), 434.2570; found 434.2565.

4.2.2. Data for (−)-*N*-*p*-toluenesulfinyl-1-amino-1-phenylmethyl-bis(diethylamino)phosphine borane, 4a (prepared from (−)-1a). Obtained in ca. 100% yield as a white solid, mp = 145–146°C, $[\alpha]_D = -78.0$ (*c* 1.1; $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.611 (t, 6H, $J = 7.05$ Hz), 1.19 (t, 6H, $J = 7.02$ Hz), 2.20 (s, 3H), 2.67–2.80 (m, 4H), 2.86–3.44 (m, 4H), 5.13–5.30 (m, 2H), 6.85–7.20 (m, 9H). ^{31}P NMR ($CDCl_3$) δ 92.13–93.37. HRMS calcd for $C_{22}H_{37}BN_3OPS$ (M+H), 434.2570; found 434.2562.

4.2.3. Data for (+)-*N*-*p*-toluenesulfinyl-1-amino-1-(2-thienyl)methyl-bis(diethylamino)phosphine borane, 4b (prepared from (−)-1b). Obtained in 75% yield as a white solid, mp = 126–127°C, $[\alpha]_D = +96.4$ (*c* 1.12; $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.73 (t, 6H, $J = 7.04$ Hz), 1.18 (t, 6H, $J = 7.05$ Hz), 2.29 (s, 3H), 2.83–3.11 (m, 4H), 3.11–3.42 (m, 4H), 5.22 (t, 1H, $J = 6.22$ Hz), 5.51 (dd, 1H, $J = 5.86$ Hz, $J = 10.64$ Hz), 6.58–6.69 (m, 2H), 6.69–7.00 (m, 1H), 7.01–7.41 (like AB system, 4H, $J = 7.99$ Hz). ^{31}P NMR ($CDCl_3$) δ 91.37–92.61. Anal. calcd for $C_{19}H_{35}BN_3OPS_2$: C, 54.66; H, 8.03; N, 9.56; P, 7.05; S, 14.59; found: C, 54.59; H, 8.20; N, 9.32; P, 7.33; S, 14.49%.

4.2.4. Data for (−)-*N*-*p*-toluenesulfinyl-1-amino-1-(2-thienyl)methyl-bis(diethylamino)phosphine borane, 4b (prepared from (+)-1b). Obtained in 72% yield as a white solid, mp = 132–133°C, $[\alpha]_D = -97.9$ (*c* 1.05; $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.727 (t, 6H, $J = 7.06$ Hz), 1.18 (t, 6H, $J = 7.06$ Hz), 2.29 (s, 3H), 2.61–3.03 (m, 4H), 3.03–3.46 (m, 4H), 5.23 (t, 1H, $J = 6.30$ Hz), 5.51 (dd, 1H, $J = 5.9$ Hz, $J = 10.62$ Hz), 6.54–6.76 (m, 2H), 6.98–7.00 (m, 1H), 7.01–7.40 (AB, 4H, $J = 7.9$ Hz). ^{31}P NMR ($CDCl_3$) δ 91.38–92.59. Anal. calcd for $C_{19}H_{35}BN_3OPS_2$: C, 54.66; H, 8.03; N, 9.56; P, 730; S, 14.95; found: C, 54.63; H, 8.19; N, 9.49, P, 7.30; S, 14.42%.

4.2.5. Data for (+)-*N*-*p*-toluenesulfinyl-1-amino-1-(*p*-fluorophenyl)methyl-bis(diethylamino)phosphine borane, 4c (prepared from (+)-1c). Obtained in 96% yield as a white solid, mp = 138–139°C, $[\alpha]_D = +83.2$ (*c* 1.12; $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.65 (t, 6H, $J = 7.04$ Hz), 1.19 (t, 6H, $J = 7.04$ Hz), 2.23 (s, 3H), 2.64–2.88 (m,

4H), 2.88–3.44 (m, 4H), 5.16–5.27 (m, 2H), 7.01–7.28 (m, 8H). ^{31}P NMR ($CDCl_3$) δ 91.90–93.05. HRMS calcd for $C_{22}H_{36}BFN_3OPS$ (M+H), 452.2471; found 452.2463.

4.2.6. Data for (+)-*N*-*p*-toluenesulfinyl-1-amino-1-(*p*-bromophenyl)methyl-bis(diethylamino)phosphine borane, 4d (prepared from (+)-1d). Obtained in 86% yield as white solid, mp = 154–155°C, $[\alpha]_D$ = +30.6 (*c* 1.41; $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 0.67 (t, 6H, *J* = 6.93 Hz), 1.18 (t, 6H, *J* = 6.93 Hz), 2.27 (s, 3H), 2.72–2.81 (m, 2H), 2.88–2.97 (m, 2H), 3.15–3.24 (m, 2H), 3.31–3.40 (m, 2H), 5.18–5.21 (m, 2H), 6.89–6.91 (m, 4H), 7.04–7.06 (m, 2H), 7.22–7.25 (m, 2H). ^{31}P NMR ($CDCl_3$) δ 92.81–93.33. HRMS calcd for $C_{22}H_{36}BBrN_3OPS$ (M+H), 512.1676; found 512.1640.

4.2.7. Data for (+)-*N*-*p*-toluenesulfinyl-1-amino-1-(*p*-*N*,*N* - dimethylaminophenyl)methyl - bis(diethylamino)-phosphine borane, 4e (prepared from (−)-1e). Obtained in 72% yield as a white solid, mp = 129–130°C, $[\alpha]_D$ = +25.2 (*c* 1.12; $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 0.66 (t, 6H, *J* = 7.05 Hz), 1.18 (t, 6H, *J* = 7.04 Hz), 2.24 (s, 3H), 2.83 (s, 6H), 2.71–2.99 (m, 4H), 2.99–3.42 (m, 4H), 5.03–5.15 (m, 2H), 6.34–7.34 (AB, 4H, *J* = 8.2 Hz), 6.92–6.98 (m, 4H). ^{31}P NMR ($CDCl_3$) δ 91.44–92.77. HRMS calcd for $C_{24}H_{42}BHN_4OPS$ (M+H), 477.2992; found 477.3000.

4.3. General procedure for hydrolysis of *N*-*p*-toluenesulfinyl-1-amino-1-arylmethyl-bis(diethylamino)phosphine borane 4

The phosphine borane complexes **4** (0.001 mol) were heated under reflux in a mixture of glacial acetic acid (4.4 mL) and hydrochloric acid (36% water solution) (12.1 mL) for 4 h. Then, the solvents were evaporated and the residue dissolved in absolute EtOH (3 mL) and alkalized with propylene oxide to pH 6. The precipitate formed was filtered off and washed with EtOH and diethyl ether affording the pure 1-amino-1-arylmethylphosphonic acids **3**.

4.3.1. Data for (−)-1-amino-1-phenylmethylphosphonic acid, 3a (prepared from (+)-4a). Obtained in 92% yield, mp = 285–288°C, $[\alpha]_D$ = −19.3 (*c* 1.29; 1N NaOH). ^{31}P NMR (D_2O) δ 10.97.

4.3.2. Data for (+)-1-amino-1-phenylmethylphosphonic acid, 3a (prepared from (−)-4a). Obtained in 95% yield, mp = 286–288°C, $[\alpha]_D$ = +19.9 (*c* 1.16; 1N NaOH). ^{31}P NMR (D_2O) δ 10.90.

4.3.3. Data for (−)-1-amino-1-(2-thienyl)methylphosphonic acid, 3b (prepared from (+)-4b). Obtained in 70% yield, mp = 256–258°C, $[\alpha]_D$ = −4.2 (*c* 0.85; 1N NaOH). ^{31}P NMR (D_2O) δ 9.96. HRMS calcd for $C_5H_8NO_3PS$ (M+H) 194.0041; found 194.0035.

4.3.4. Data for (+)-1-amino-1-(2-thienyl)methylphosphonic acid, 3b (prepared from (−)-4b). Obtained in 75% yield, mp = 257–259°C, $[\alpha]_D$ = +4.8 (*c* 0.35; 1N NaOH). ^{31}P NMR (D_2O) δ 9.96. HRMS calcd for $C_5H_8NO_3PS$ (M+H) 194.0041; found 194.0040.

4.3.5. Data for (−)-1-amino-1-(*p*-fluorophenyl)methylphosphonic acid, 3c (prepared from (+)-4c). Obtained in 93% yield, mp = 284–287°C, $[\alpha]_D$ = −19.3 (*c* 0.54; 1N NaOH). ^{31}P NMR (D_2O) δ 10.72. HRMS calcd for $C_7H_9NO_3FP$ (M+H) 206.0382; found 206.0388.

4.3.6. (−)-1-Amino-1-(*p*-bromophenyl)methylphosphonic acid, 3d (prepared from (+)-4d). Obtained in 75% yield, mp = 281–283°C, $[\alpha]_D$ = −20.5 (*c* 0.81; 1N NaOH). ^{31}P NMR (D_2O) δ 10.7. HRMS calcd for $C_7H_9NO_3BrP$ (M+H) 265.9581; found 265.9586.

4.3.7. (−)-1-Amino-1-(*p*-*N*,*N*-dimethylphenyl)methylphosphonic acid, 3e (prepared from (+)-4e). Obtained in 89% yield, mp = 219–222°C, $[\alpha]_D$ = −17.1 (*c* 0.23; 1N NaOH). ^{31}P NMR (D_2O) δ 10.91. HRMS calcd for $C_9H_{15}N_2O_3P$ (M+H) 231.0898; found 321.0901.

Acknowledgements

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