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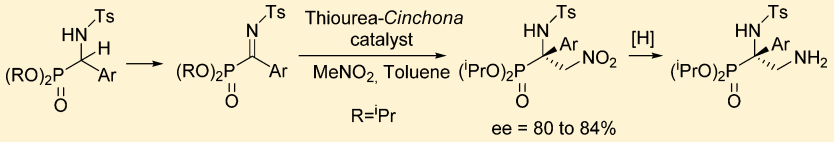
Asymmetric Synthesis of Functionalized Tetrasubstituted α-Aminophosphonates through Enantioselective Aza-Henry Reaction of Phosphorylated Ketimines

Javier Vicario, Pablo Ortiz, José M. Ezpeleta, and Francisco Palacios*

Departamento de Química Orgánica I, Centro de Investigación y Estudios Avanzados "Lucio Lascaray"- Facultad de Farmacia, University of the Basque Country, UPV/EHU Paseo de la Universidad 7, 01006 Vitoria, Spain

Supporting Information



ABSTRACT: Bifunctional *Cinchona* alkaloid thioureas efficiently catalyze asymmetric nucleophilic addition of nitromethane to ketimines derived from α-aminophosphonic acids to afford tetrasubstituted α-amino-β-nitro-phosphonates. Catalytic hydrogenation of (*S*)-α-amino-β-nitro-phosphonate **2d** gives enantiopure (*S*)-α,β-diaminophosphonate **3**.

INTRODUCTION

The stereocontrolled formation of tetrasubstituted carbons is a crucial challenge in chemical synthesis since they are known to be present in many natural products and pharmaceutical agents.[1] The formation of tetrasubstituted centers from ketones and ketimines was unachievable for a long time, due to the poor electrophilic character of the carbonyl or ketimine groups and the additional steric hindrance present on the substrate. In addition, the enantiotopic faces of ketone derivatives are not as easily discriminated as those of aldehyde derivatives when asymmetric synthesis is sought.[2]

Because of their structural analogy to α-amino acids, α-aminophosphonic acid derivatives have found numerous applications[3] in medicinal and pharmaceutical sciences as haptens of catalytic antibodies,[4a] peptide mimetics,[4b] enzyme inhibitors,[4c] antibacterial[4d] and anticancer agents,[4e] as well as agrochemicals.[5] The biological activity of aminophosphonic acids is known to be strongly dependent on their absolute configuration,[6,7] and the stereoselective synthesis of aminophosphonic acid derivatives[8] is a very important task in organic chemistry. Catalytic asymmetric methodologies for the synthesis of α-aminophosphonates[9] have been developed, but remarkably, only a few synthetic protocols are effective for the enantioselective synthesis of tetrasubstituted α-aminophosphonates.[10]

During the past few years, our group has been involved in the development of new strategies for the preparation of simple[11] and vinylic[12] α-aminophosphonates as well as of phosphadepsipeptides[13] and β-aminophosphonates.[14] Continuing with our interest in aminophosphorus chemistry,[7] we reported the asymmetric preparation of α-aminophosphonic acid derivatives,[15] and the preparation of ketimines derived from α-aminophosphonates[10a,16] that have also been successfully exploited as intermediates for the synthesis of enantiopure tetrasubstituted α-cyano α-aminophosphonates.[10a] Because of the proximity of the cyano group to a tetrasubstituted carbon, further derivatization of those substrates proved to be very difficult. Although the hydrolysis of the nitrile to a carboxylic acid group was feasible, those α-cyano α-aminophosphonates failed to provide the corresponding α,β-diaminophosphonates through reduction of the cyano group. The aza-Henry[17] reaction, consisting in the addition of nitronate species to imine electrophiles, is an alternative route to diamines complementary to the cyanation of imine derivatives. Since the first organocatalytic asymmetric aza-Henry reported by Takemoto and co-workers,[18] a number of organocatalysts that are able to catalyze the highly stereoselective addition of nitroalkanes to aldimines have been developed, including Brønsted acids,[19] phase-transfers catalysts,[20] chiral ammonium betaines,[21] and chiral ureas or thioureas.[22] Organocatalytic enantioselective addition of nitroderivatives to cyclic ketimine of heterocycles, such as quinazolin-2(1*H*)-ones[23] and indol-3-ones,[24] have been already described using bifunctional thioureas, and recently, a new bifunctional iminophosphorane organocatalyst has been reported for the catalytic nucleophilic addition of nitromethane to ketimines.[25]

Taking into account all the considerations mentioned above, we thought that a catalytic asymmetric addition of nitromethane to functionalized ketimines derived from α-aminophosphonates would be an excellent method for the access to enantiopure α-aminophosphonate units bearing an all-substituted α-carbon. This synthetic approach can be considered globally as a route for the generation of tetrasubstituted α-aminophosphonates by the substitution of hydrogen in a trisubstituted α-aminophosphonate by a nucleophilic reagent and the complementary process ("umpolung reaction") of the

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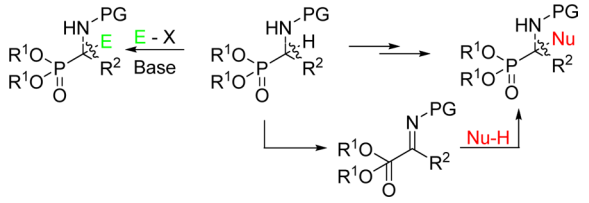
electrophilic substitution of trisubstituted α-aminophosphonate (Scheme 1).

Scheme 1. General Strategies for the Synthesis of Quaternary α-Aminophosphonates

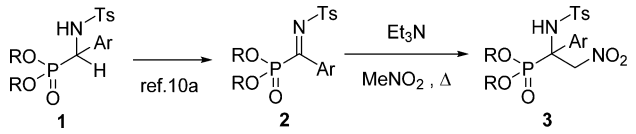


Furthermore, the presence of a β-nitro moiety would confer a great synthetic importance to the proposed methodology (Nu = CH_2NO_2, Scheme 1). Because of the different possible oxidation states of the vicinal nitrogen containing functionalities, they are susceptible to a selective manipulation,[26] most commonly to vicinal diamines,[27] by reduction of the nitro group.

RESULTS AND DISCUSSION

Initially, the construction of the intermediate carbon−nitrogen double bond from *N*-tosyl α-aminophosphonates **1** may be performed by selective *N*-chlorination with an excess of trichloroisocyanuric acid (TCCA) in CH_2Cl_2, followed by treatment with an excess of base to give α-ketiminophosphonates **2** (Scheme 2).[10a] The electrophilic character to its iminic

Scheme 2. Synthesis of Quaternary α-Aminophosphonates



carbon makes them suitable substrates for nucleophilic addition reactions. In a subsequent step, treatment of phosphonates **2a** (R = Me) with triethylamine in boiling nitromethane afforded target racemic α-amino-β-nitro-phosphonates **3a** (R = Me, Scheme 2).

Having demonstrated the effectiveness of our synthetic protocol at a racemic stage, we proceeded to the study of different chiral catalysts in the addition of nitromethane to α-ketiminophosphonates **2**. Bifunctional Bønsted base/H-bond donor organocatalysts have demonstrated their huge potential in the field of organocatalysis. Key features of those catalysts are a basic tertiary amine and a hydrogen bond donor group, both properly located in a chiral atmosphere. In the early 80s, Wynberg and Hiemstra showed that those molecules are able to catalyze organic reactions by activating both the nucleophile and the electrophile substrates, making use of the basic character of the molecule and, simultaneously, establishing hydrogen bond interactions, respectively.[28] Within this class of compounds, the most widely used are *Cinchona* alkaloids **I**−**II** (Figure 1).[29]

In our case, we would expect strong interaction of the H-donor group with the iminic nitrogen and the phosphoryl oxygen while the tertiary amine interacts with the nitromethane nucleophile in a similar manner as in the case of the cyanation reaction of these substrates.[10a] Our preliminary analysis of the aza-Henry reaction of α-iminophosphonate **2a** with nitromethane, without solvent, in the presence of a catalytic amount of a Cinchona alkaloid **I**−**II** leads to a fast formation of α-amino-β-nitro-phosphonates **3a** but, unfortunately, with poor enantioselectivity (Table 1, entries 1−6).

Chiral thioureas have demonstrated their efficiency as organocatalysts, particularly in aza-Henry reactions,[22−25] and for this reason, we tested the nucleophilic addition of nitromethane to α-iminophosphonates **1a** using (thio)ureas **III**−**VIII** as organocatalysts. Although no reaction was observed when (thio)ureas **IIIa,b** and **IV** were used as catalysts, which may be attributable to the absence of the basic partner in the catalytic system, the use of bifunctional thioureas **V**−**VIII** in the aza-Henry reaction of nitromethane with α-iminophosphonate **2a** in the absence of solvent afforded α-amino-β-nitro-phosphonates **3a** with increased enantioselectivities (Table 1, entries 10−13)

Encouraged by these results, we implemented the analysis of the influence of the phosphorus substituent in α-iminophosph-

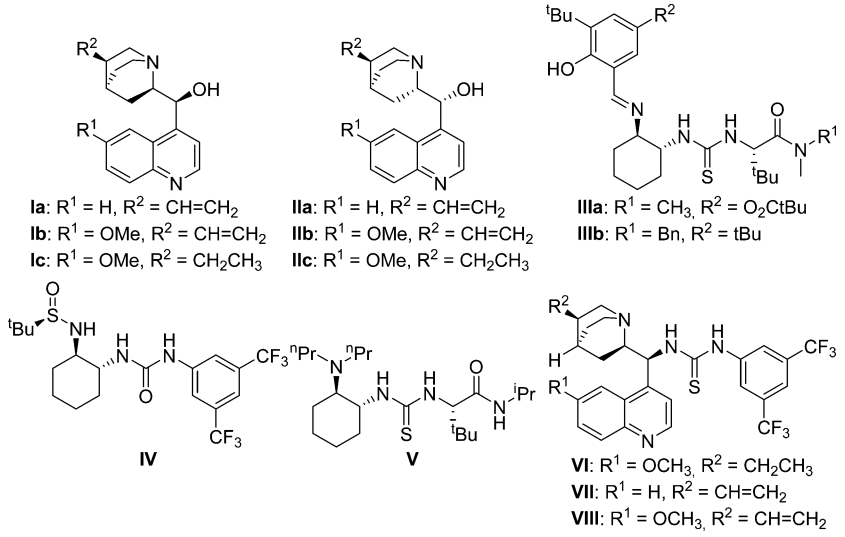


Figure 1. Organocatalysts tested in asymmetric aza-Henry reaction of α-ketiminophosphonates **2**.

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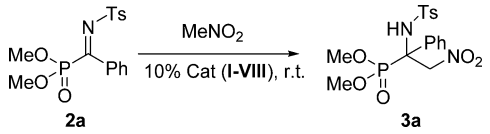
Table 1. Screening of the Catalyst



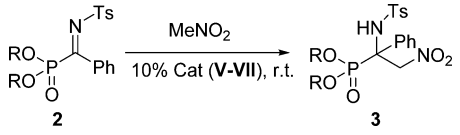
2a **3a**

entry	cat.	t (h)	% conv.[a]	% ee[b]	*major (R/S)*
1	**Ia**	3	75	10	*S*
2	**Ib**	3	100	4	*S*
3	**Ic**	3	100	6	*S*
4	**IIa**	3	95	10	*R*
5	**IIb**	3	95	13	*R*
6	**IIc**	22	60	12	*R*
7	**IIIa**	22	0		
8	**IIIb**	22	0		
9	**IV**	22	0		
10	**V**	3	95	29	*S*
11	**VI**	6	100	22	*R*
12	**VII**	6	95	27	*R*
13	**VIII**	6	95	23	*R*

[a]Determined by ^{31}P NMR. [b]Determined by chiral HPLC.

onate substrates **2** on the enantioselectivity of the aza-Henry reaction using thioureas **V**–**VII**. A correlation between the Winstein–Holness *A*-values[30] of the phosphonate substituents and the enantioselectivity was explored. In the case of the addition of nitromethane to dimethyl phosphonate **2a** using thioureas **V**–**VII** as catalysts (Table 2, entries 1–3, A_{Me} = 1.74

Table 2. Screening of the Phosphorus Substituent



2 **3**

entry	comp	R	cat.	t (h)	% conv.[b]	% ee[c]	*major (R/S)*
1	**3a**	Me	**V**	3	95	29	*R*
2	**3a**	Me	**VI**	6	100	22	*S*
3	**3a**	Me	**VII**	24	95	27	*S*
4	**3b**	Bn	**V**[a]	18	100	10	*R*
5	**3b**	Bn	**VI**[a]	18	100	10	*S*
6	**3c**	Et	**V**	6	100	35	*R*
7	**3c**	Et	**VI**	6	100	31	*S*
8	**3c**	Et	**VII**	6	100	30	*S*
9	**3d**	^{i}Pr	**V**	24	90	37	*R*
10	**3d**	^{i}Pr	**VI**	6	95	42	*S*
11	**3d**	^{i}Pr	**VII**	24	95	45	*S*

[a]Catalyst loading was increased to 20%. [b]Determined by ^{31}P NMR. [c]Determined by chiral HPLC.

kcal·mol^{-1}), a decreased enantiomeric excess was observed toward dimethyl phosphonate **2a** when α-dibenzyphosphonate **2b** (Table 2, entries 4 and 5) with a smaller *A*-value (A_{Bn} = 1.68 kcal·mol^{-1}) was used.

The enantioselectivity can be increased if diethyl phosphonate **2c** is used (Table 2, entries 6–8), where a higher *A*-value is found in the phosphonate substituents (A_{Et} = 1.79 kcal·mol^{-1}). Finally, the best enantiomeric excesses were obtained when di-*iso*-propyl phosphonate **2d** was used as substrate (Table 2, entries 9–11), where a notably higher *A*-value is found ($A_{i\text{-}Pr}$ = 2.21 kcal·mol^{-1}) (Figure 2). A special case is the use of diphenylphosphonate derivatives. In view of the *A*-value

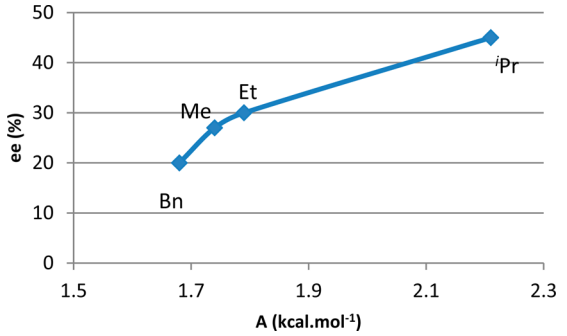
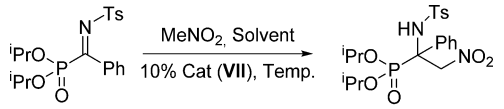


Figure 2. Correlation between the Winstein–Holness *A*-values of the phosphonate substituents and the enantioselectivity of the aza-Henry reaction.

for the phenyl group (A_{Ph} = 2.80 kcal·mol^{-1}), the best enantiomeric excesses would be expected, but on the contrary, a total lack of reactivity is observed in the addition reaction of nitromethane, which may be due to an excessive steric hindrance in the electrophilic imine carbon.

Bearing these results in mind, we thought that better results could be obtained if the aza-Henry reaction was performed under solvation conditions. For this reason, the nucleophilic addition of nitromethane to di-*iso*-propyl α-iminophosphonate **2d** (R = ^{i}Pr) was performed in several solvents, using the thiourea **VII** as a catalyst. To our surprise, the reaction did not proceed at all when coordinating solvents were used (Table 3, entries 1–4). This may be attributable to a stronger interaction of the H-donor module of the thiourea catalyst with the solvent molecules than with the imine substrates **2**.

Table 3. Screening of the Solvent and Temperature



2d **3d**

entry	solvent	T (°C)	t (h)	% conv.[a]	% ee[b]	*major (R/S)*
1	MeOH	20	24	0		
2	THF	20	24	0		
3	AcN	20	24	0		
4	DMF	20	24	0		
5	CH_2Cl_2	20	24	95	68	*S*
6	$CHCl_3$	20	36	90	67	*S*
7	CCl_4	20	48	60	61	*S*
8	$Cl(CH_2)_2Cl$	20	48	95	60	*S*
9	toluene	20	36	100	80	*S*
10	toluene	10	48	81	72	*S*
11	toluene	0	48	64	40	*S*
12	toluene	−10	72	30	24	*S*
13	toluene	−20	72	10	17	*S*
14	toluene	40	24	100	70[c]	*S*

[a]Determined by ^{31}P NMR. [b]Determined by chiral HPLC. [c]β-Elimination of H_2NTs was also detected.

On the other hand, an inverse dependence of the enantioselectivity into the polarity of the solvent is observed if noncoordinating solvents are used (Table 3, entries 5–9). This dependence probably arises from a diminution in the difference of the energy of activation for the formation of the two enantiomers due to a stabilization of both possible

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diastereomeric transition states in a polar solvent, rational for reactions with ionic transition states.

It is well-known that, in most cases, a drop in the temperature of the reaction results in an increase in the enantioselectivity, but in our case, substantial drops in enantioselectivity and conversion were observed when the aza-Henry reaction of α-iminophosphonate **2d** was performed at lower temperatures using toluene as solvent (Table 3, entries 10−13). Such effects may be related to a low solubility of the substrate at low temperature. When the reaction was performed at higher temperature, a drop in the enantioselectivity was observed (Table 3, entry 14). Remarkably, in this case, the formation of a substantial amount of a side product is observed due to a subsequent β-elimination reaction of *p*-toluenesulfonamide. Other attempts at improving the enantioselectivity of the process by increasing the catalyst loading were unsuccessful. An optimal enantiomeric excess of 80% was obtained when the reaction was performed at room temperature using 2 equiv of nitromethane in the presence of a 10% of thiourea catalyst **VII** and using toluene as solvent.

In order to determine the absolute configuration of the stereogenic carbon of the major enantiomer, a pure isomer of α-amino-β-nitro-phosphonate **3d** was isolated by crystallization. The X-ray diffraction spectrum showed an *S* absolute configuration of the stereocenter (see the Supporting Information).

It is interesting that neither Et_3N, DABCO, pyridine, nor phosphoric acids were able to catalyze the reaction, whereas *Cinchona* alkaloids and thioureas were. It is also interesting that addition of a donor molecule together with a basic reagent does not catalyze the aza-Henry reaction at all. Both *Cinchona* alkaloid derivatives and thioureas share a common structure, having a basic nitrogen at a two carbon distance from a functional group that is able to establish hydrogen bonding (OH in *Cinchona* alkaloids derivatives, NH in thioureas). This might indicate a crucial role for the OH and NH groups in the transition state, which may activate the imino bond by establishing hydrogen bonding.

On the basis of the models for similar processes proposed by other authors,[18,22a] we suggest a tentative transition state where each NH group of the thiourea catalyst establishes hydrogen bonds with the imino nitrogen and phosphoryl oxygen, respectively, while both coordinate with both oxygens of the nitro group, as shown in Figure 3. According to this model, the basic unity of the bifunctional catalyst would capture the acidic proton from the hydroxyl group of the nitromethane tautomer and its nucleophilic carbon would attack the imine carbon. A major steric interaction can be observed between the quinuclidine unity and the thiourea moiety in the transition state proposed for the formation of the *R* isomer.

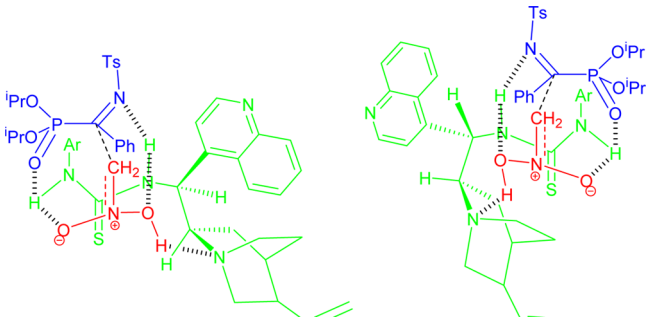

Figure 3. Tentative transition states for the formation of major (left) and minor (right) enantiomers in thiourea (green) catalyzed addition of nitromethane (red) to α-iminophosphonate **2d** (blue).

The generalization of the asymmetric aza-Henry reaction of di-*iso*-propyl α-ketiminophosphonates **2** catalyzed by thiourea **VII** was put into effect using different aromatic α-substituents. Very satisfactory enantioselectivities were obtained relative to the model iminophosphonates **3d**, with a phenyl substituent at the α-carbon, (Table 4, entries 1−6). α-Arylimines with *para*- or *meta*-alkyl substituted aromatic rings showed to be slightly less reactive than the model substrate, but an increase of the reaction times leads to the formation of α-amino-β-nitro-phosphonates **3e−f** in good yields and enantioselectivities (Table 4, entries 2 and 3).

On the contrary, the addition of nitromethane to α-arylimines **3g−i** bearing electron withdrawing *meta*- or *para*-substituents at the aromatic ring proceeded slightly faster than in the case of the model substrate, most likely due to the activation effect of the electron poor aromatic ring into the imine system (Table 4, entries 4−6). Remarkably, when *ortho*-substituted α-arylimines were used as substrates, no reaction at all was observed, even at high temperatures. This fact could be explained by the high steric crowding expected in the resulting structure, especially taking into account that a tetrasubstituted stereogenic carbon is being formed. Unfortunately, the scope of the reaction is not applicable to electron rich aromatic substituents, since imines bearing *O*- or *N*-substituted aromatic rings proved to be totally unreactive in this reaction.

Finally, to show an example of the potential of substrates **3**, an enantiopure fraction of α-amino-β-nitro-phosphonate (*S*)-**3d** was subjected to hydrogenation conditions, affording α,β-diaminophosphonate (*S*)-**4** in excellent yield (Scheme 3). The 1,2-amine moiety occurs in a wide number of natural products and in pharmaceutical agents,[27] while chiral 1,2-diamines are also widely used in catalysis and asymmetric synthesis.[27,31,32] To the best of our knowledge, enantiopure tetrasubstituted α-amino-β-nitro-phosphonates **3** and α,β-diaminophosphonate **4** structures have not been reported so far.

CONCLUSIONS

The first organocatalytic enantioselective aza-Henry reaction using iminophosphonates is reported. The fact that phosphorylated ketimine derivatives are used as substrates allows the asymmetric synthesis of functionalized tetrasubstituted α-aminophosphonates. These α-amino-β-nitrophosphonates are susceptible to a further transformation into enantiopure α,β-diaminophosphonates.

EXPERIMENTAL SECTION

General. Solvents for extraction and chromatography were technical grade. All solvents used in reactions were freshly distilled from appropriate drying agents before use. All other reagents were recrystallized or distilled as necessary. All reactions were performed under an atmosphere of dry nitrogen. Analytical TLC was performed with silica gel 60 F_{254} plates. Visualization was accomplished by UV light. ^{1}H (300 MHz), ^{13}C (75 MHz), and ^{31}P NMR (120 MHz) spectra were performed using $CDCl_3$ solutions with TMS as an internal reference (δ = 0.00 ppm) for ^{1}H and ^{13}C NMR spectra and phosphoric acid (50%) as an external reference (δ = 0.0 ppm) for ^{31}P NMR spectra. Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in hertz. ^{1}H and ^{13}C NMR peak assignments were supported by distortionless enhanced polarization transfer (DEPT), correlation spectroscopy (COSY), or heteronuclear correlation spectroscopy (HETCOR) experiments. Low-resolution

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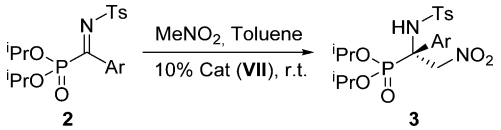
Table 4. Generalization of Organocatalytic Aza-Henry Reaction of Iminophosphonates 2

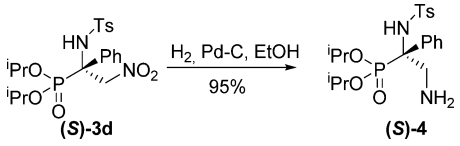


2 3

entry	comp	Ar	t (h)	% yield[a]	% ee[b]	*major (R/S)*
1	**3d**	C_6H_5	36	85, 71[c]	80, >99[c]	*S*
2	**3e**	*p*-CH_3-C_6H_4	48	83	81	*S*
3	**3f**	*m*-CH_3-C_6H_4	48	83	84	*S*
4	**3g**	*p*-CF_3-C_6H_4	24	85	80	*S*
5	**3h**	*p*-NO_2-C_6H_4	24	87	80	*S*
6	**3i**	*m*-NO_2-C_6H_4	24	82	81	*S*

[a]Pure yield after column. [b]Determined by chiral HPLC. [c]After crystallization.

Scheme 3. Synthesis of Enantiopure α,β-Diaminophosphonate 4



(*S*)-3d (*S*)-4

mass spectra (MS) were obtained by electron impact (EI), and high-resolution mass spectra (HRMS) were obtained by positive-ion electrospray ionization (Supporting Information). Data are reported in the form m/z (intensity relative to base = 100). Infrared spectra (IR) were taken as neat solids. Peaks are reported in cm^{-1}. *N*-Tosyl α-ketiminophosphonates **2a–d** and **2g–h**,[10a] tertiary α-aminophosphonates **1a–d** and **1g–h**,[10a] and their tosylimine precursors[33] were synthesized following literature procedures.

Synthesis of *N*-Tosyl α-Aminophosphonates 1. Substrates **1** were synthesized by nucleophilic addition of phosphites to the corresponding tosylimines using the following procedure: To a suspension of the corresponding *N*-tosylimine[33] (25 mmol) and the corresponding dialkylphosphite (30 mmol) in toluene (50 mL) was added triethylamine (0.35 mL, 2.5 mmol). The solution was stirred and refluxed in toluene for 24–48 h until the disappearance of *N*-tosylimine. The solution was allowed to cool to room temperature, and upon cooling to −20 °C, crystals were obtained. The resulting solid was collected by filtration, washed with cold toluene (30 mL) and hexanes (30 mL), and dried under low pressure to afford pure *N*-tosyl α-aminophosphonates. **1a–d** and **1g–h** are known compounds.[10a]

Diisopropyl (((4-Methylphenyl)sulfonamido)(*p*-tolyl)methyl)phosphonate (1e). The procedure was followed, using (*E*)-4-methyl-*N*-(4-methylbenzylidene)-benzenesulfonamide (6.83 g, 25 mmol) and diisopropyl phosphite (4.2 mL, 30 mmol), affording 8.77 g (80%) of **1e** as a white solid. m.p.: 171–172 °C (Toluene). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.81 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 1.21 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 1.35 (d, $^3J_{HH}$ = 6.2 Hz, 6H, 2 × CH_3), 2.25 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 4.36 (m, 1H, CHO), 4.66 (dd, $^3J_{HH}$ = 9.2 Hz, $^2J_{PH}$ = 24.6 Hz, 1H, CHP), 4.78 (m, 1H, CHO), 6.28 (broad s, 1H, NH), 6.87 (d, $^3J_{HH}$ = 8.0 Hz, 2H, 2 × CH_{ar}), 6.97 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}), 7.05 (d, $^3J_{HH}$ = 8.0 Hz, 2H, 2 × CH_{ar}), 7.44 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3 (CH_3), 21.5 (CH_3), 23.1 (d, $^3J_{PC}$ = 6.0 Hz, CH_3), 24.1 (d, $^3J_{PC}$ = 5.7 Hz, CH_3), 24.4 (d, $^3J_{PC}$ = 3.0 Hz, CH_3), 24.7 (d, $^3J_{PC}$ = 2.6 Hz, CH_3), 56.1 (d, $^1J_{PC}$ = 160.0 Hz, CHP), 72.6 (d, $^2J_{PC}$ = 6.8 Hz, CHO), 72.9 (d, $^2J_{PC}$ = 7.2 Hz, CHO), 121.3 (2 × CH_{ar}), 128.4 (2 × CH_{ar}), 128.6 (2 × CH_{ar}), 128.8 (2 × CH_{ar}), 137.2 (C_{quat}), 138.0 (C_{quat}), 138.7 (d, $^2J_{PC}$ = 2.1 Hz, C_{quat}), 142.3 (C_{quat}). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 19.2. FTIR (KBr) ν_{max} (cm^{-1}): 3318 (NH st), 1336 (O═S═O st as), 1229 (P═O st), 1165 (O═S═O st sim). HRMS (Q-TOF) m/z calcd for $C_{21}H_{30}NO_5PS$ $[MH]^+$ 440.1661, found 440.1658.

Diisopropyl (((4-Methylphenyl)sulfonamido)(*m*-tolyl)methyl)phosphonate (1f). The procedure was followed, using (*E*)-4-methyl-*N*-(3-methylbenzylidene)-benzenesulfonamide (6.83 g, 25 mmol) and diisopropyl phosphite (4.2 mL, 30 mmol), affording 9.22 g (84%) of **1f** as a white solid. m.p.: 169–170 °C (Toluene). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.81 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 1.23 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 1.38 (d, $^3J_{HH}$ = 6.0 Hz, 3H, CH_3), 1.39 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 4.35 (m, 1H, CH), 4.69 (dd, $^3J_{HH}$ = 9.4 Hz, $^2J_{PH}$ = 24.6 Hz, 1H, CHP), 4.86 (m, 1H, CH), 6.74 (broad s, 1H, NH), 6.89–6.97 (m, 6H, 6 CH_{ar}), 7.42 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.0 (CH_3), 21.4 (CH_3), 23.1 (d, $^3J_{PC}$ = 6.2 Hz, CH_3), 24.0 (d, $^3J_{PC}$ = 5.6 Hz, CH_3), 24.4 (d, $^3J_{PC}$ = 2.9 Hz, CH_3), 24.7 (d, $^3J_{PC}$ = 3.1 Hz, CH_3), 53.6 (d, $^1J_{PC}$ = 160.6 Hz, CHP), 72.4 (d, $^2J_{PC}$ = 7.4 Hz, CHO), 73.1 (d, $^2J_{PC}$ = 7.4 Hz, CHO), 126.1 (d, $^3J_{PC}$ = 5.8 Hz, CH_{ar}), 127.2 (2 × CH_{ar}), 127.8 (CH_{ar}), 128.1 (d, $^4J_{PC}$ = 1.9 Hz, CH_{ar}), 129.3 (d, $^3J_{PC}$ = 5.9 Hz, CH_{ar}), 133.6 (C_{quat}), 137.4 (C_{quat}), 138.6 (C_{quat}), 142.3 (C_{quat}). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 19.2. FTIR (KBr) ν_{max} (cm^{-1}): 3321 (NH st), 1333 (O═S═O st as), 1235 (P═O st), 1170 (O═S═O st sim). HRMS (Q-TOF) m/z calcd for $C_{21}H_{30}NO_5PS$ $[MH]^+$ 440.1661, found 440.1657.

Diisopropyl (((4-Methylphenyl)sulfonamido)(3-nitrophenyl)-methyl)phosphonate (1i). The procedure was followed, using (*E*)-4-methyl-*N*-(3-nitrobenzylidene)-benzenesulfonamide (7.65 g, 25 mmol) and diisopropyl phosphite (4.2 mL, 30 mmol), affording 10.34 g (88%) of **1i** as a white solid. m.p.: 192–193 °C (Toluene). ^{1}H NMR (300 MHz, $CDCl_3$): 0.98 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 1.34 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 1.47 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH_3), 1.52 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 2.13 (s, 3H, CH_3), 4.58 (m, 1H, CH), 4.91 (dd, $^3J_{HH}$ = 10.3 Hz, $^2J_{PH}$ = 25.8 Hz, 1H, CHP), 5.06 (m, 1H, CH), 6.78 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}), 7.22 (t, $^3J_{HH}$ = 7.8 Hz, 1H, CH_{ar}), 7.39 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}), 7.49 (d, $^3J_{HH}$ = 7.3 Hz, 1H, CH_{ar}), 7.84 (d, $^3J_{HH}$ = 8.2 Hz, 1H, CH_{ar}), 7.95 (d, $^4J_{PH}$ = 1.8 Hz, 1H, CH_{ar}), 8.19 (broad d, $^2J_{PH}$ = 9.3 Hz, 1H, NH),). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3 (CH_3), 23.4 (d, $^3J_{PC}$ = 6.2 Hz, CH_3), 24.0 (d, $^3J_{PC}$ = 5.7 Hz, CH_3), 24.4 (d, $^3J_{PC}$ = 3.0 Hz, CH_3), 24.8 (d, $^3J_{PC}$ = 3.1 Hz, CH_3), 55.8 (d, $^1J_{PC}$ = 161.9 Hz, CHP), 72.9 (d, $^2J_{PC}$ = 7.6 Hz, CHO), 74.3 (d, $^2J_{PC}$ = 7.4 Hz, CHO), 122.3 (d, $^3J_{PC}$ = 2.8 Hz, CH_{ar}), 123.4 (d, $^5J_{PC}$ = 4.8 Hz, CH_{ar}), 127.1 (2 × CH_{ar}), 128.7 (d, $^4J_{PC}$ = 2.0 Hz, CH_{ar}), 130.9 (2 × CH_{ar}), 135.1 (d, $^2J_{PC}$ = 5.7 Hz, C_{quat}), 135.9 (C_{quat}), 138.3 (d, $^2J_{PC}$ = 2.2 Hz, C_{quat}), 142.9 (C_{quat}). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 17.5. FTIR (KBr) ν_{max} (cm^{-1}): 3311 (NH st), 1331 (O═S═O st as), 1228 (P═O st), 1160 (O═S═O st sim). HRMS (Q-TOF) m/z calcd for $C_{20}H_{28}N_2O_7PS$ $[MH]^+$ 471.1355, found 471.1358.

Synthesis of *N*-Tosyl α-Ketiminophosphonates 2. Procedure: To a solution of *N*-tosyl α-aminophosphonate **1** (10 mmol) in CH_2Cl_2 (30 mL) was added trichloroisocyanuric acid (30 mmol). The resulting suspension was stirred until the disappearance of the starting *N*-tosyl α-aminophosphonate, which was monitored by ^{31}P NMR. Then, the solid residue was removed by filtration to afford a clear solution of the intermediate *N*-chloro α-aminophosphonate and

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poly(4-vinylpyridine) (3 g), previously dried at 100 °C overnight, was added. The resulting suspension was stirred under reflux overnight, and the reaction was then filtered and concentrated under reduced pressure. The resulting yellow oily crude was purified by crystallization from diethyl ether.

Diisopropyl (*p*-Tolyl(tosylimino)methyl)phosphonate (2e). The procedure was followed, using diisopropyl (*p*-tolyl(tosylamino)-methyl)phosphonate **1e** (4.39 g, 10 mmol), affording 3.19 g (73%) of **2e** as a white solid. The formation of the intermediate *N*-chloro α-aminophosphonate was ensured by ^{31}P NMR (δ = 16.1 ppm). m.p.: 114−115 °C (Et_2O). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.08 (d, $^3J_{HH}$ = 6.1 Hz, 6H, 2 × CH_3), 1.25 (d, $^3J_{HH}$ = 6.1 Hz, 6H, 2 × CH_3), 2.41 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 4.66 (m, 2H, 2 × CHO), 7.26 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}),.7.29 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}),.7.73 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}),.7.80 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8 (CH_3), 21.9 (CH_3), 23.5 (d, $^3J_{PC}$ = 5.7 Hz, 2 × CH_3), 24.2 (d, $^3J_{PC}$ = 3.4 Hz, 2 × CH_3), 73.9 (d, $^2J_{PC}$ = 7.3 Hz, 2 × CHO), 127.8 (d, $^3J_{PC}$ = 1.9 Hz 2 × CH_{ar}), 128.9 (2 × CH_{ar}), 129.0 (2 × CH_{ar}), 129.7 (2 × CH_{ar}), 131.5 (d, $^2J_{PC}$ = 24.1 Hz, C_{quat}), 137.5(d, $^5J_{PC}$ = 1.4 Hz C_{quat}), 142.7 (C_{quat}), 144.4 (C_{quat}), 178.9 (d, $^1J_{PC}$ = 197.4 Hz, C═N). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 3.4. FTIR (KBr) ν_{max} (cm^{-1}): 1609 (C═N st), 1335 (O═S═O st as), 1261 (P═O st), 1168 (O═S═O st sim). HRMS (Q-TOF) *m*/*z* calcd for $C_{21}H_{28}NO_5PS$ $[MH]^+$ 438.1504, found 438.1599.

Diisopropyl (*m*-Tolyl(tosylimino)methyl)phosphonate (2f). The procedure was followed, using diisopropyl (*m*-tolyl(tosylamino)-methyl)phosphonate **1f** (4.39 g, 10 mmol), affording 3.10 g (71%) of **2f** as a white solid. The formation of the intermediate *N*-chloro α-aminophosphonate was ensured by ^{31}P NMR (δ = 16.2 ppm). m.p.: 118−119 °C (Et_2O). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.09 (d, $^3J_{HH}$ = 6.2 Hz, 6H, 2 × CH_3), 1.26 (d, $^3J_{HH}$ = 6.2 Hz, 6H, 2 × CH_3), 2.39 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 4.74 (m, 2H, 2 × CHO), 7.25−7.33 (m, 5H, 5 × CH_{ar}), 7.75 (m, 1H, CH_{ar}), 7.76 (d, $^3J_{HH}$ = 8.3 Hz, 2H, 2 × CH_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6 (CH_3), 21.8 (CH_3), 23.3 (d, $^3J_{PC}$ = 5.8 Hz, 2 × CH_3), 23.4 (d, $^3J_{PC}$ = 3.5 Hz, 2 × CH_3), 74.0 (d, $^2J_{PC}$ = 7.2 Hz, 2 × CHO), 125.7 (d, $^3J_{PC}$ = 4.4 Hz CH_{ar}), 127.9 (2 × CH_{ar}), 128.1 (CH_{ar}), 128.7 (d, $^3J_{PC}$ = 3.8 Hz CH_{ar}), 129.7 (2 × CH_{ar}), 132.4 (d, $^4J_{PC}$ = 1.1 Hz CH_{ar}), 134.2 (d, $^2J_{PC}$ = 24.5 Hz, C_{quat}), 137.3 (d, $^4J_{PC}$ = 2.3 Hz, C_{quat}), 137.9 (C_{quat}), 144.0 (C_{quat}), 179.3 (d, $^1J_{PC}$ = 197.8 Hz, C═N). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 3.2. FTIR (KBr) ν_{max} (cm^{-1}): 1611 (C═N st), 1331 (O═S═O st as), 1267 (P═O st), 1163 (O═S═O st sim). HRMS (Q-TOF) *m*/*z* calcd for $C_{21}H_{28}NO_5PS$ $[MH]^+$ 438.1504, found 438.1598.

Diisopropyl ((3-Nitrophenyl)(tosylimino)methyl)phosphonate (2i). The procedure was followed, using diisopropyl (*m*-nitrophenyl(tosylamino)methyl)-phosphonate **1i** (4.70 g, 10 mmol), affording 3.65 g (78%) of **2i** as a white solid. The formation of intermediate *N*-chloro α-aminophosphonate was ensured by ^{31}P NMR (δ = 15.1 ppm). m.p.: 121−122 °C (Et_2O). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.14 (d, $^3J_{HH}$ = 6.2 Hz, 6H, 2 × CH_3), 1.30 (d, $^3J_{HH}$ = 6.2 Hz, 6H, 2 × CH_3), 2.43 (s, 3H, CH_3), 4.72 (m, 2H, 2 × CHO), 7.31 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 2 × CH_{ar}), 7.66 (t, $^3J_{HH}$ = 8.0 Hz, 1H, CH_{ar}), 7.77 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 2 × CH_{ar}), 8.01 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.6 Hz, H, CH_{ar}), 8.35 (m, 1H, CH_{ar}), 8.48 (s, 1H, CH_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7 (CH_3), 23.4 (d, $^3J_{PC}$ = 5.7 Hz, 2 × CH_3), 24.1 (d, $^3J_{PC}$ = 3.6 Hz, 2 × CH_3), 74.7 (d, $^2J_{PC}$ = 7.2 Hz, 2 × CHO), 123.0 (d, $^3J_{PC}$ = 3.2 Hz CH_{ar}), 125.7 (CH_{ar}), 127.9 (2 × CH_{ar}), 129.7 (2 × CH_{ar}), 129.9 (CH_{ar}), 134.0 (d, $^3J_{PC}$ = 3.8 Hz CH_{ar}), 135.4 (d, $^2J_{PC}$ = 25.3 Hz, C_{quat}), 136.2 (d, $^4J_{PC}$ = 2.2 Hz, C_{quat}), 145.3 (C_{quat}), 147.6 (C_{quat}), 176.2 (d, $^1J_{PC}$ = 202.0 Hz, C═N). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 2.4. FTIR (KBr) ν_{max} (cm^{-1}): 1608 (C═N st), 1327 (O═S═O st as), 1261 (P═O st), 1160 (O═S═O st sim). HRMS (Q-TOF) *m*/*z* calcd for $C_{29}H_{25}N_2O_7PS$ $[MH]^+$ 469.1198, found 469.1111.

Asymmetric Aza-Henry of *N*-Tosyl α-Ketiminophosphonates 2. *Procedure A.* A solution of α-ketiminophosphonate **2a−c** (0.5 mmol) and thiourea **VII** (10%) in nitromethane (2 mLwas stirred at rt for 3−24 h. (see Table 2). The resulting solution was concentrated under vacuum, and the crude residue was purified by column chromatography (AcOEt/Hexanes).

Procedure B. A solution of α-ketiminophosphonate **2d−i** (0.5 mmol), nitromethane (1 mmol), and thiourea **VII** (10%) in toluene (2 mL) was stirred at rt for 24−48 h. (see Table 4). The resulting solution was concentrated under vacuum, and the crude residue was purified by column chromatography (AcOEt/Hexanes).

Dimethyl (1-((4-Methylphenyl)sulfonamido)-2-nitro-1-phenylethyl)phosphonate (3a). Procedure A was followed, using (*E*)-diethyl(phenyl(tosylimino)methyl)phosphonate **2a** (184 mg, 0.5 mmol), affording 139 mg (76%) of **3a** as a white solid (ee = 27%). m.p.: 167−168 °C (Et_2O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H, CH_3), 3.44 (d, $^3J_{PH}$ = 11.1 Hz, 3H, CH_3O), 3.48 (d, $^3J_{PH}$ = 11.1 Hz, 3H, CH_3O), 5.58 (d, $^3J_{PH}$ = 8.6 Hz, 1H, CH_2NO_2), 5.62 (s, 1H, CH_2NO_2), 5.82 (d, $^3J_{PH}$ = 11.6 Hz, 1H, NH), 7.19 (d, $^3J_{HH}$ = 8.3 Hz, 2 × CH_{ar}), 7.20 (d, $^3J_{HH}$ = 6.6 Hz, 2 × CH_{ar}), 7.26−7.30 (m, 3H, 3 × CH_{ar}), 7.52 (d, $^3J_{HH}$ = 8.3 Hz, 2 × CH_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7 (CH_3), 54.7 (d, $^2J_{PC}$ = 7.8 Hz, CH_3O), 55.0 (d, $^2J_{PC}$ = 7.5 Hz, CH_3O), 62.8 (d, $^1J_{PC}$ = 152.2 Hz, C_{quat}), 76.0 (CH_2), 127.4 (2 × CH_{ar}) 127.6 (d, $^3J_{PC}$ = 4.8 Hz, 2 × CH_{ar}), 128.6 (d, $^4J_{PC}$ = 2.6 Hz, 2 × CH_{ar}), 129.1 (d, $^5J_{PC}$ = 2.6 Hz, CH_{ar}), 129.4 (2 × CH_{ar}), 132.0 (d, $^2J_{PC}$ = 7.8 Hz, C_{quat}) 138.7 (C_{quat}),143.8 (C_{quat}). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 20.1. FTIR (neat) ν_{max} (cm^{-1}): 3313(NH st), 1559 (N═O st as), 1369 (N═O st sim), 1321(O═S═O st sim), 1150 (O═S═O st as), 1022 (P═O st), HRMS (Q-TOF) *m*/*z* calcd for $C_{17}H_{21}N_2O_7PS$ $[MH]^+$ 429.0885, found 429.0882. $[\alpha]_D^{20}$ = −9.5° (*c* = 0.41, CH_2Cl_2). ee was determined by HPLC analysis (Chiracel-IA, Heptane/Ethanol 90:10, 1 mL/min). Retention time (min): 25.90 (minor) and 34.37 (major).

Dibenzyl (1-((4-Methylphenyl)sulfonamido)-2-nitro-1-phenylethyl)phosphonate (3b). Procedure A was followed (in this case, 20% catalyst loading was used), using α-dibenzyl(phenyl(tosylimino)-methyl)phosphonate **2b** (260 mg, 0.5 mmol), affording 185 mg (71%) of **3b** as a white solid (ee = 10%). m.p.: 128−129 °C (Et_2O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.29 (s, 3H, CH_3), 4.35−4.70 (m, 4H, 2 × CH_2O), 5.46 (dd, $^2J_{HH}$ = 10.2, $^3J_{PH}$ = 41.8 Hz, 1H, CH_2NO_2), 5.52 (dd, $^2J_{HH}$ = 10.3, $^3J_{PH}$ = 24.6 Hz, 1H, CH_2NO_2), 5.96 (d, $^3J_{PH}$ = 11.6 Hz, 1H, NH), 6.96 (d, $^3J_{HH}$ = 7.0 Hz, 2H, 2 × CH_{ar}), 7.01−7.07 (m, 6H, 6 × CH_{ar}), 7.13−7.22 (m, 9H, 9 × CH_{ar}), 7.38 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3 (CH_3), 62.7 (d, $^1J_{PC}$ = 151.9 Hz, C_{quat}), 69.8 (d, $^2J_{PC}$ = 7.9 Hz, CH_2O), 69.9 (d, $^2J_{PC}$ = 8.0 Hz, CH_2O), 75.7 (CH_2NO_2), 126.4 (CH_{ar}), 127.3 (2 × CH_{ar}),127.6 (d, $^4J_{PC}$ = 4.8 Hz, 2 × CH_{ar}), 128.2(2 × CH_{ar}), 128.3(2 × CH_{ar}), 128.4 (d, $^4J_{PC}$ = 2.6 Hz, 2 × CH_{ar}),128.6 (d, $^4J_{PC}$ = 4.6 Hz, 2 × CH_{ar}), 128.8 (d, $^3J_{PC}$ = 7.0 Hz, 2 × CH_{ar}), 128.9 (CH_{ar}), 129.3 (2 × CH_{ar}), 129.6 (CH_{ar}), 132.1 (d, $^2J_{PC}$ = 7.6 Hz, C_{quat}) 135.1 (d, $^2J_{PC}$ = 5.5 Hz, C_{quat}), 135.1 (d, $^2J_{PC}$ = 5.3 Hz, C_{quat}), 138.7 (C_{quat}),143.6 (C_{quat}). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 18.7. FTIR (KBr) ν_{max} (cm^{-1}): 3297 (NH st), 1557 (N═O st as), 1330 (N═O st sim), 1370 (O═S═O st sim), 1156 (O═S═O st as), 987 (P═O st). HRMS (Q-TOF) *m*/*z* calcd for $C_{29}H_{29}N_2O_7PS$ $[MH]^+$ 581.1511, found 581.1525. $[\alpha]_D^{20}$ = −3.2° (*c* = 0.26, CH_2Cl_2). ee was determined by HPLC analysis (Chiracel-IA, Heptane/Ethanol 90:10, 1 mL/min). Retention time (min): 29.67 (minor) and 32.11 (major).

Diethyl (1-((4-Methylphenyl)sulfonamido)-2-nitro-1-phenylethyl)phosphonate (3c). Procedure A was followed, using diethyl-(phenyl(tosylimino)methyl)phosphonate **2c** (198 mg, 0.5 mmol), affording 166 mg (73%) of **3c** as a white solid (ee = 30%). m.p.: 143−144 °C (Et_2O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.02 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 1.14 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3), 2.33 (s, 3H, CH_3), 3.51−3.93 (m, 4H, 2 × CH_2O), 5.51 (s, 1H, CH_2NO_2), 5.55 (d, $^3J_{PH}$ = 3.5 Hz, 1H, CH_2NO_2), 5.83 (broad d, $^3J_{PH}$ = 10.5 Hz, 1H, NH), 7.08 (d, $^3J_{HH}$ = 8.2 Hz, 4 × CH_{ar}), 7.14−7.21 (m, 3H, 3 × CH_{ar}), 7.40 (d, $^3J_{HH}$ = 8.2 Hz, 2 × CH_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.1 (d, $^3J_{PC}$ = 5.7 Hz, 2 × CH_3), 21.6 (CH_3), 62.5 (d, $^2J_{PC}$ = 151.5 Hz, C_{quat}), 64.5 (d, $^2J_{PC}$ = 7.8 Hz, CH_2O), 64.9 (d, $^2J_{PC}$ = 7.5 Hz, CH_2O), 76.1 (CH_2NO_2), 127.4 (2 × CH_{ar}) 127.7 (d, $^3J_{PC}$ = 4.8 Hz, 2 × CH_{ar}), 128.3 (d, $^4J_{PC}$ = 2.5 Hz, 2 × CH_{ar}), 128.9 (d, $^5J_{PC}$ = 2.7 Hz, CH_{ar}), 129.3 (2 × CH_{ar}), 132.0 (d, $^2J_{PC}$ = 7.4 Hz, C_{quat}) 138.8 (C_{quat}),143.6 (C_{quat}). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 17.9. FTIR (KBr) ν_{max}

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(cm^{-1}): 3298 (NH st), 1556 (N═O st as), 1331 (N ═O st sim), 1245 (O═S═O st sim), 1152 (O═S═O st as), 1023 (P═O st). HRMS (Q-TOF) m/z calcd for $C_{29}H_{25}N_2O_7PS$ $[MH]^+$ 457,1198, found 457.1201. $[\alpha]_D^{20} = -8.3°$ (c = 0.29, CH_2Cl_2). ee was determined by HPLC analysis (Chiracel-IA, Heptane/Ethanol 90:10, 1 mL/min). Retention time (min): 16.69 (minor) and 19.31 (major).

Diisopropyl (1-((4-Methylphenyl)sulfonamido)-2-nitro-1-phenylethyl)phosphonate (3d). Procedure B was followed, using diisopropyl(phenyl(tosylimino)methyl)phosphonate **2d** (212 mg, 0.5 mmol), affording 205 mg (85%) of **3d** as a white solid (ee = 80%, >99% after crystallization from Et_2O). m.p.: 161−162 °C (Et_2O). ^1H NMR (300 MHz, $CDCl_3$): δ 0.76 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 1.16 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 1.19 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 1.20 (d, $^3J_{HH}$ = 6.0 Hz, 3H, CH_3), 2.31 (s, 3H, CH_3), 4.21 (m, 1H, CHO), 4.50 (m, 1H, CHO), 5.44 (dd, $^2J_{HH}$ = 13.8, $^3J_{PH}$ = 7.8 Hz, 1H, CH_2NO_2), 5.56 (dd, $^2J_{HH}$ = 13.8, $^3J_{PH}$ = 20.3 Hz, 1H, CH_2NO_2), 5.83 (broad d, $^3J_{PH}$ = 8.3 Hz, 1H, NH), 7.01 (d, $^3J_{HH}$ = 7.6 Hz, 2H, 2 × CH_{ar}),7.02 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 2 × CH_{ar}), 7.10−7.20 (m, 3H, 3 × CH_{ar}), 7.31 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 2 × CH_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5 (CH_3), 22.9 (d, $^3J_{PC}$ = 6.3 Hz, CH_3), 23.6 (d, $^3J_{PC}$ = 5.5 Hz, CH_3), 23.7 (d, $^3J_{PC}$ = 3.8 Hz, CH_3), 24.2 (d, $^3J_{PC}$ = 2.7 Hz, CH_3), 62.1 (d, $^1J_{PC}$ = 153.4 Hz, C_{quat}), 74.1 (d, $^2J_{PC}$ = 8.2 Hz, CHO), 74.5 (d, $^2J_{PC}$ = 7.8 Hz, CHO), 76.3 (d, $^2J_{PC}$ = 1.4 Hz CH_2), 127.2 (2 × CH_{ar}), 127.8 (2 × CH_{ar}), 127.9 (d, $^4J_{PC}$ = 3.3 Hz, 2 × CH_{ar}), 128.6 (d, $^5J_{PC}$ = 3.3 Hz, CH_{ar}), 129.0 (2 × CH_{ar}),, 131.6 (d, $^2J_{PC}$ = 6.8 Hz, C_{quat}) 138.9 (C_{quat}),143.4 (C_{quat}). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 16.3. FTIR (KBr) ν_{max} (cm^{-1}): 3266 (NH st), 1548 (N═O st as), 1370 (N═O st sim), 1321 (O═S═O st sim), 1156 (O═S═O st as), 979 (P ═O st) HRMS (Q-TOF) m/z calcd for $C_{21}H_{30}N_2O_7PS$ $[MH]^+$ 485,1511, found 485.1518. $[\alpha]_D^{20} = -33.0°$ (c = 0.91, CH_2Cl_2). ee was determined by HPLC analysis (Chiracel-IA, Heptane/Ethanol 90:10, 1 mL/min). Retention time (min): 49.51 (minor) and 51.23 (major).

Diisopropyl (1-((4-Methylphenyl)sulfonamido)-2-nitro-1-(*p*-tolyl)ethyl)phosphonate 3e. Procedure B was followed, using diisopropyl (*p*-tolyl(tosylimino)methyl)phosphonate **2e** (219 mg, 0.5 mmol), affording 207 mg (83%) of **3e** as a white solid (ee = 81%). m.p.: 131−132 °C (Et_2O). ^1H NMR (300 MHz, $CDCl_3$): δ 0.82 (d, $^3J_{HH}$ = 6.0 Hz, 3H, CH_3), 1.20 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH_3), 1.22 (d, $^3J_{HH}$ = 6.1 Hz, 6H, 2 × CH_3), 2.23 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 4.26 (m, 1H, CHO), 4.58 (m, 1H, CHO), 5.46 (dd, $^2J_{HH}$ = 13.7, $^3J_{PH}$ = 7.6 Hz, 1H, CH_2NO_2), 5.59 (dd, $^2J_{HH}$ = 13.7, $^3J_{PH}$ = 20.5 Hz, 1H, CH_2NO_2), 6.82 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}), 7.06 (d, $^3J_{HH}$ = 8.3 Hz, 1H, CH_{ar}), 7.09 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{PH}$ = 2.1 Hz, 2H, 2 × CH_{ar}), 7.35 (d, $^3J_{HH}$ = 8.3 Hz, 2H, 2 × CH_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.5 (CH_3), 21.0 (CH_3), 22.4 (d, $^3J_{PC}$ = 6.2 Hz, CH_3), 23.0 (d, $^3J_{PC}$ = 5.4 Hz, CH_3), 23.2 (d, $^3J_{PC}$ = 3.0 Hz, CH_3), 24.0 (d, $^3J_{PC}$ = 2.4 Hz, CH_3), 61.4 (d, $^1J_{PC}$ = 154.7 Hz, C_{quat}), 73.5 (d, $^2J_{PC}$ = 8.2 Hz, CHO), 73.9 (d, $^2J_{PC}$ = 7.3 Hz, CHO), 75.5 (CH_2), 126.7 (2 × CH_{ar}), 128.1 (2 × CH_{ar}), 128.5 (2 × CH_{ar}), 128.9 (2 × CH_{ar}),, 138.0 (d, $^2J_{PC}$ = 2.8 Hz, C_{quat}) 138.3 (C_{quat}), 138.4 (C_{quat}), 142.7 (C_{quat}). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 16.1. FTIR (KBr) ν_{max} (cm^{-1}): 3285 (NH st), 1561 (N═O st as), 1323 (N═O st sim), 1367 (O═S═O st sim), 1158 (O═S═O st as), 988 (P═O st). $[\alpha]_D^{20} = -21.2°$ (c = 0.21, CH_2Cl_2). HRMS (Q-TOF) m/z calcd for $C_{22}H_{31}N_2O_7PS$ $[MH]^+$ 499.1668, found 499.1671. ee was determined by HPLC analysis (Chiracel-IA, Heptane/Ethanol 99:1, 1 mL/min). Retention time (min): 21.84 (minor) and 55.53 (major).

Diisopropyl (1-((4-Methylphenyl)sulfonamido)-2-nitro-1-(*m*-tolyl)ethyl)phosphonate (3f). Procedure B was followed, using diisopropyl (*m*-tolyl(tosylimino)methyl)phosphonate **2f** (219 mg, 0.5 mmol), affording 207 mg (83%) of **3f** as a white solid (ee = 84%). m.p.: 133−134 °C (Et_2O). ^1H NMR (300 MHz, $CDCl_3$): δ 0.82 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 1.20 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 1.22 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH_3), 1.24 (d, $^3J_{HH}$ = 6.0 Hz, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 4.28 (m, 1H, CHO), 4.53 (m, 1H, CHO), 5.48 (dd, $^2J_{HH}$ = 13.6, $^3J_{PH}$ = 7.3 Hz, 1H, CH_2NO_2), 5.63 (dd, $^2J_{HH}$ = 13.6, $^3J_{PH}$ = 21.6 Hz, 1H, CH_2NO_2), 7.00 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}),7.08 (d, $^3J_{HH}$ = 8.2 Hz, 1H, CH_{ar}), 7.22−7.28 (m, 3H, 3 × CH_{ar}), 7.35 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}), 7.80 (d, $^3J_{HH}$ = 8.2 Hz, 1H, CH_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.2 (CH_3), 21.6 (CH_3), 22.9 (d, $^3J_{PC}$ = 6.2 Hz, CH_3), 23.5 (d, $^3J_{PC}$ = 5.7 Hz, CH_3), 23.8 (d, $^3J_{PC}$ = 3.0 Hz, CH_3), 24.2 (d, $^3J_{PC}$ = 2.5 Hz, CH_3), 62.2 (d, $^1J_{PC}$ = 153.7 Hz, C_{quat}), 74.3 (d, $^2J_{PC}$ = 8.0 Hz, CHO), 74.5 (d, $^2J_{PC}$ = 7.7 Hz, CHO), 76.3 (CH_2), 125.1 (d, $^3J_{PC}$ = 5.1 Hz, CH_{ar}), 127.3 (2 × CH_{ar}), 128.1 (d, $^4J_{PC}$ = 2.0 Hz, CH_{ar}), 128.8 (d, $^3J_{PC}$ = 2.2 Hz, CH_{ar}), 129.2 (2 × CH_{ar}), 131.3 (d, $^3J_{PC}$ = 5.9 Hz, CH_{ar}), 135.6 (C_{quat}), 137.4 (d, $^2J_{PC}$ = 2.6 Hz, C_{quat}), 139.2 (d, $^5J_{PC}$ = 1.4 Hz, C_{quat}), 140.3 (C_{quat}). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 16.1. FTIR (KBr) ν_{max} (cm^{-1}): 3289 (NH st), 1562 (N═O st as), 1335 (N═O st sim), 1362 (O═S═O st sim), 1160 (O═S═O st as), 988 (P═O st). HRMS (Q-TOF) m/z calcd for $C_{22}H_{31}N_2O_7PS$ $[MH]^+$ 499.1668, found 499,1672. $[\alpha]_D^{20} = -26.7°$ (c = 0.31, CH_2Cl_2). ee was determined by HPLC analysis (Chiracel-IA, Heptane/Ethanol 99:1, 1 mL/min). Retention time (min): 22.66 (minor) and 49.15 (major).

Diisopropyl (1-((4-Methylphenyl)sulfonamido)-2-nitro-1-(4-(trifluoromethyl)phenyl)ethyl)phosphonate (3g). The procedure was followed, using diisopropyl ((tosylimino)(4-(trifluoromethyl)-phenyl)methyl)phosphonate **2g** (246 mg, 0.5 mmol), affording 325 mg (85%) of **3g** as a white solid (ee = 80%). m.p.: 177−178 °C (Et_2O). ^1H NMR (300 MHz, $CDCl_3$): δ 0.85 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 1.23 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 1.27 (d, $^3J_{HH}$ = 2.2 Hz, 3H, CH_3), 1.29 (d, $^3J_{HH}$ = 2.2 Hz, 3H, CH_3), 2.37 (s, 3H, CH_3), 4.38 (m, 1H, CH), 4.66 (m, 1H, CH), 5.57 (dd, $^2J_{HH}$ = 13.9, $^3J_{PH}$ = 21.6 Hz, 1H, CH_2NO_2), 5.61 (dd, $^2J_{HH}$ = 13.9, $^3J_{PH}$ = 30.6 Hz, 1H, CH_2NO_2), 6.10 (broad d, $^3J_{PH}$ = 8.9 Hz, 1H, NH), 7.08 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}), 7.27−7.35 (m, 4H, 4 × CH_{ar}), 7.40 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.2 (CH_3), 22.7 (d, $^3J_{PC}$ = 6.0 Hz, CH_3), 23.3 (d, $^3J_{PC}$ = 5.5 Hz, CH_3), 23.5 (d, $^3J_{PC}$ = 3.7 Hz, CH_3), 23.9 (d, $^3J_{PC}$ = 2.9 Hz, CH_3), 61.7 (d, $^1J_{PC}$ = 151.7 Hz, C_{quat}), 74.5 (d, $^2J_{PC}$ = 5.8 Hz, CHO), 74.6 (d, $^2J_{PC}$ = 6.1 Hz, CHO), 75.1 (d, $^2J_{PC}$ = 1.8 Hz, CH_2NO_2), 123.5 (d, $^1J_{FC}$ = 271.9 Hz, CF_3), 124.4 (d, $^3J_{FC}$ = 3.2 Hz, 2 × CH_{ar}), 126.2 (2 × CH_{ar}), 128.4 (d, $^3J_{PH}$ = 5.0 Hz, 2 × CH_{ar}), 129.4 (2 × CH_{ar}), 135.8 (dq, $^2J_{PC}$ = 5.2 Hz, $^5J_{FC}$ = 1.8 Hz, C_{quat}), 138.3 (C_{quat}), 139.5 (C_{quat}), 143.1 (C_{quat}). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 14.8 (q, $^7J_{PF}$ = 1.8 Hz). FTIR (KBr) ν_{max} (cm^{-1}): 3301 (NH st), 1560 (N═O st as), 1334 (N═O st sim), 1366 (O═S═O st sim), 1151 (O═S═O st as), 995 (P═O st). HRMS (Q-TOF) m/z calcd for $C_{22}H_{28}F_{32}O_7PS$ $[MH]^+$ 553,1385, found 553,1382. $[\alpha]_D^{20} = -28.2°$ (c = 0.33, CH_2Cl_2). ee was determined by HPLC analysis (Chiracel-IA, Heptane/Ethanol 90:10, 1 mL/min). Retention time (min): 25.62 (minor) and 28.12 (major).

Diisopropyl (1-((4-Methylphenyl)sulfonamido)-2-nitro-1-(4-nitrophenyl)ethyl)phosphonate (3h). The procedure was followed, using diisopropyl ((4-nitrophenyl)(tosylimino)methyl)-phosphonate **2h** (234 mg, 0.5 mmol), affording 230 mg (87%) of **3h** as a white solid (ee = 80%). m.p.: 166−167 °C (Et_2O). ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH_3), 1.19 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH_3), 1.24 (d, $^3J_{HH}$ = 6.1 Hz, 6H, 2 × CH_3), 2.34 (s, 3H, CH_3), 4.39 (m, 1H, CH), 4.63 (m, 1H, CH), 5.51 (d, $^3J_{PH}$ = 2.5 Hz, 1H, CH_2NO_2), 5.55 (s, 1H, CH_2NO_2), 6.06 (broad d, $^3J_{PH}$ = 9.1 Hz, 1H, NH), 7.05 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 2 × CH_{ar}), 7.33 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 2 × CH_{ar}), 7.40 (dd, $^3J_{HH}$ = 9.0, $^4J_{PH}$ = 2.2 Hz, 2H, 2 × CH_{ar}), 7.83 (d, $^3J_{HH}$ = 9.0 Hz, 2H, 2 × CH_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8 (CH_3), 23.3 (d, $^3J_{PC}$ = 5.9 Hz, CH_3), 23.8 (d, $^3J_{PC}$ = 5.4 Hz, CH_3), 24.0 (d, $^3J_{PC}$ = 3.7 Hz, CH_3), 24.2 (d, $^3J_{PC}$ = 3.2 Hz, CH_3), 62.4 (d, $^1J_{PC}$ = 149.9 Hz, C_{quat}), 75.1 (d, $^2J_{PC}$ = 7.9 Hz, CHO), 75.2 (d, $^2J_{PC}$ = 8.2 Hz, CHO), 76.1 (d, $^2J_{PC}$ = 2.2 Hz CH_2NO_2), 122.9 (d, $^4J_{PC}$ = 2.3 Hz, 2 × CH_{ar}), 127.3 (2 × CH_{ar}) 129.3 (d, $^3J_{PC}$ = 4.8 Hz, 2 × CH_{ar}), 129.6 (2 × CH_{ar}), 138.5 d, $^5J_{PC}$ = 1.4 Hz, C_{quat}), 139.7 (d, $^2J_{PC}$ = 6.1 Hz, C_{quat}), 144.5 (C_{quat}), 147.7 (d, $^4J_{PC}$ = 3.0 Hz, C_{quat}). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 15.3. FTIR (KBr) ν_{max} (cm^{-1}): 3324 (NH st), 1552 (N═O st as), 1352 (N═O st sim), 1348 (O═S═O st sim), 1152 (O═S═O st as), 969 (P ═O st). HRMS (Q-TOF) m/z calcd for $C_{21}H_{28}N_3O_9PS$ $[MH]^+$ 530.1362, found 530.1359. $[\alpha]_D^{20} = -27.3°$ (c = 0.34, CH_2Cl_2). ee was determined by HPLC analysis (Chiracel-IB, Heptane/Ethanol 99:1, 1 mL/min). Retention time (min): 45.72 (minor) and 50.88 (major).

Diisopropyl (1-((4-Methylphenyl)sulfonamido)-2-nitro-1-(3-nitrophenyl)ethyl)phosphonate (3i). Procedure B was followed,

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using diisopropyl ((3-nitrophenyl)(tosylimino)methyl)phosphonate **2i** (230 mg, 0.5 mmol), affording 217 mg (82%) of **3i** as a white solid (ee = 81%). m.p.: 161−162 °C (Et_2O). ^1H NMR (300 MHz, $CDCl_3$): δ 1.25 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH_3), 1.30 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH_3), 1.31 (d, $^3J_{HH}$ = 6.1 Hz, 6H, 2 × CH_3), 2.41 (s, 3H, CH_3), 4.69 (m, 1H, CHO), 4.78 (m, 1H, CHO), 5.01 (dd, $^2J_{HH}$ = 13.0, $^3J_{PH}$ = 5.2 Hz, 1H, CH_2NO_2), 5.63 (dd, $^2J_{HH}$ = 13.0, $^3J_{PH}$ = 5.0 Hz, 1H, CH_2NO_2), 5.58 (broad s, 1H, NH), 7.03 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 2 × CH_{ar}), 7.56 (t, $^3J_{HH}$ = 8.0 Hz, 1H, CH_{ar}), 7.80 (d, $^3J_{HH}$ = 8.0 Hz, 1H, CH_{ar}), 7.95 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 2 × CH_{ar}), 8.20 (d, $^3J_{HH}$ = 8.0 Hz, 1H, CH_{ar}), 8.52 (d, $^4J_{PH}$ = 1.9 Hz, 1H, CH_{ar}) ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6 (CH_3), 23.6 (d, $^3J_{PC}$ = 5.5 Hz, CH_3), 23.9 (d, $^3J_{PC}$ = 5.0 Hz, CH_3), 24.1 (d, $^3J_{PC}$ = 3.5 Hz, CH_3), 24.2 (d, $^3J_{PC}$ = 3.0 Hz, CH_3), 64.4 (d, $^1J_{PC}$ = 157.9 Hz, C_{quat}), 74.4 (d, $^2J_{PC}$ = 8.1 Hz, CHO), 74.7 (d, $^2J_{PC}$ = 7.5 Hz, CHO), 76.0 (CH_2NO_2), 122.0 (d, $^3J_{PC}$ = 3.9 Hz, CH_{ar}), 123.9 (CH_{ar}), 126.5 (2 × CH_{ar}), 129.3 (d, $^4J_{PC}$ = 3.0 Hz, CH_{ar}), 129.8 (2 × CH_{ar}), 132.7 (d, $^2J_{PC}$ = 4.0 Hz, C_{quat}), 135.7 (C_{quat}), 138.7 (d, $^2J_{PC}$ = 1.2 Hz, C_{quat}), 143.5 (C_{quat}). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 15.5. FTIR (KBr) ν_{max} (cm^{-1}): 3287 (NH st), 1560 (N═O st as), 1336 (N═O st sim), 1367 (O═S═O st sim), 1157 (O═S═O st as), 991 (P═O st). HRMS (Q-TOF) m/z calcd for $C_{21}H_{28}N_3O_9PS$ $[MH]^+$ 530.1362, found 530.1360. $[\alpha]_D^{20}$ = −27.8° (c = 0.35, CH_2Cl_2). ee was determined by HPLC analysis (Chiracel-IB, Heptane/Ethanol 99:1, 1 mL/min). Retention time (min): 28.99 (minor) and 33.56 (major).

Synthesis of Diisopropyl (2-Amino-1-((4-methylphenyl)-sulfonamido)-1-(3-nitrophenyl)ethyl)phosphonate ((*S*)-4). Procedure: A solution of diisopropyl (1-((4-methylphenyl)sulfonamido)-2-nitro-1-phenylethyl)phosphonate (*S*)-**3d** (97 mg, 0.2 mmol) in methanol (1 mL) was stirred for 3 days in the presence of Pd-C (10%) under a hydrogen atmosphere (80 psi). The resulting suspension was filtered through Celite in order to remove Pd-C, and the resulting clear solution was evaporated under reduced pressure. The crude residue was purified by column chromatography (AcOEt/MeOH 3:1), affording 88 mg (95%) of (*S*)-**4** as a white solid. m.p.: 133−134 °C (Hexanes/CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ: 0.79 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH_3), 1.12 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH_3), 1.15 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH_3), 1.16 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH_3), 2.29 (s, 3H, CH_3), 3.24 (broad s, 3H, NH + NH_2), 3.63 (s, 1H, CH_2NH_2), 3.70 (d, $^3J_{PH}$ = 13.8, 1H, CH_2NH_2), 4.23 (m, 1H, CH), 4.50 (m, 1H, CH), 7.00 (d, $^3J_{HH}$ = 8.2 Hz, 4H, 4 × CH_{ar}),7.06 (dd, $^3J_{HH}$ = 6.9, $^4J_{HH}$ = 1.4 Hz, 1H, CH_{ar}), 7.19−7.22 (m, 2H, 2 × CH_{ar}), 7.37 (d, $^3J_{HH}$ = 8.2 Hz, 2H, 2 × CH_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6 (CH_3), 23.1 (d, $^3J_{PC}$ = 6.3 Hz, CH_3), 23.8 (d, $^3J_{PC}$ = 5.4 Hz, CH_3), 24.2 (d, $^3J_{PC}$ = 3.4 Hz, CH_3), 24.3 (d, $^3J_{PC}$ = 2.5 Hz, CH_3), 45.3 (d, $^2J_{PC}$ = 3.9 Hz, CH_2), 65.1 (d, $^1J_{PC}$ = 149.3 Hz, C_{quat}), 73.2 (d, $^2J_{PC}$ = 8.0 Hz, CHO), 73.5 (d, $^2J_{PC}$ = 7.8 Hz, CHO), 127.2 (2 × CH_{ar}), 127.7 (d, $^5J_{PC}$ = 2.9 Hz, CH_{ar}), 127.9 (d, $^4J_{PC}$ = 2.5 Hz, 2 × CH_{ar}), 128.3 (d, $^3J_{PC}$ = 5.0 Hz, 2 × CH_{ar}), 129.2 (2 × CH_{ar}), 134.7 (d, $^2J_{PC}$ = 4.4 Hz, C_{quat}) 139.0 (C_{quat}),143.3 (C_{quat}). ^{31}P NMR (120 MHz, $CDCl_3$): δ (ppm) 21.6. FTIR (KBr) ν_{max} (cm^{-1}): 3399 (NH st), 3132 (NH st), 1321 (O═S═O st sim), 1156 (O═S═O st as), 969 (P═O st). HRMS (Q-TOF) m/z calcd for $C_{21}H_{31}N_2O_5PS$ $[MH]^+$ 455.1770, found 455.1776. $[\alpha]_D^{20}$ = −19.2° (c = 0.88, CH_2Cl_2).

■ ASSOCIATED CONTENT

Supporting Information

CIF file and thermal ellipsoid plot for **3d** and copies of ^1H and ^{13}C NMR spectra for compounds **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: francisco.palacios@ehu.es.

Notes

The authors declare no competing financial interest.

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