Asymmetric Michael Additions of a Chiral Phosphite to Nitroalkenes and Knoevenagel Acceptors

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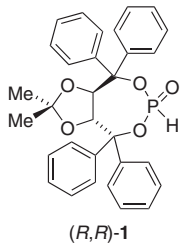
Abstract: The diastereoselective Michael addition of an enantiopure phosphite to nitroalkenes and α,β-unsaturated malonates is described. High asymmetric inductions were obtained using a readily available TADDOL auxiliary. Racemization-free cleavage of the auxiliary led to α-substituted β-nitro phosphonates and β-substituted β-phosphono malonates in good yields and high enantiomeric excesses, respectively. An extension of the method to the synthesis of α,β-disubstituted β-nitrophosphonates with two new neighboring stereogenic centers is also reported.

Key Words: Michael addition, nitroalkenes, phosphonates, P–C bond formation, asymmetric synthesis

Phosphonates are a class of compounds with extraordinary biological properties.[1] Their structural analogy to phosphates, in combination with the hydrolytic stability of the phosphorus–carbon bond enables them to act as enzyme inhibitors in a variety of processes. Phosphonates show significant neurotoxic activity, are used as antibiotics,[2] herbicides,[3] blood pressure regulators[4] and antiviral agents.[5] Recently, phosphonates with antiviral activity such as Viread® or Hepsera™, both inhibitors of reverse transcriptase, have proved to be highly efficient drugs in the treatment of HIV–1 and hepatitis B infections. The main synthetic approaches to phosphonates involve either the Michaelis–Arbusov rearrangement[6] or the addition of phosphites to multiple bonds, a transformation initially reported by the Russian chemist Pudovik[7] in the 1950's and often referred to as the Pudovik reaction.[8] However, despite the importance of enantiomerically pure phosphonates, only a few methods for their asymmetric synthesis have been described. They are generally limited to asymmetric hydrophosphonylation of aldehydes and imines or to a few examples of the asymmetric Michaelis–Arbusov rearrangement.[9]

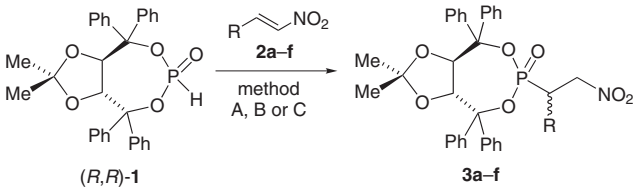
In two recent communications we reported the asymmetric Michael addition[10] of the enantiopure phosphite (3a*R*,8a*R*)-2,2-dimethyl-4,4,8,8-tetraphenylperhydro-6λ^5-[1,3]dioxolo-[4,5-*e*][1,3,2]dioxaphosphepin-6-one, (*R*,*R*)-**1**, to nitroalkenes[11] and α,β-unsaturated malonates[12] as a general method to access enantiomerically enriched bifunctional phosphonates via a P–C bond forming reaction.[13] According to our procedure, the metalated phosphite (*R*,*R*)-**1** was added to the desired Michael acceptors in a highly stereoselective manner. Racemization-free removal of the chiral auxiliary from the addition products provided either β-nitrophosphonic acids or β-phosphonomalonates in good yields and high enantiomeric excesses.



(*R*,*R*)-**1**

Figure 1

We now wish to report in detail our investigations on the reactivity of (*R*,*R*)-**1** and an extension of our protocol. As previously described,[11] the title phosphite was prepared in nearly quantitative yield in a two-step procedure starting from (*R*,*R*)-4,5-bis(diphenylhydroxymethyl)-2,2-dimethyl-1,3-dioxolane (TADDOL).[14] Its reactivity towards the nitroalkenes **2a–f** was tested under different sets of conditions (Scheme 1).



Scheme 1 *Reagents and conditions*: Method A: *n*-BuLi, THF, 0 °C, 40 h. Method B: Et_2Zn, THF, –78 °C to r.t., 12 h. Method C: Et_2Zn, TMEDA, THF, –78 °C, 12 h.

The stereoselectivity of the reaction as well as the absolute configuration of the newly formed stereogenic center turned out to be highly dependent on both the metal base used and the reaction temperature. In the first series of experiments (Scheme 1, Table 1) the phosphite (*R*,*R*)-**1** was metalated in THF at 0 °C using *n*-butyllithium (method A). The resulting P–nucleophile underwent conjugate addition to the nitroalkenes **2a–f** to give the α-substituted β-nitrophosphonates **3a–f**. Although the Michael adducts **3a–f** were obtained in good yields (70–84%), the reactivity of the lithiated phosphite was low. It added sluggishly to the nitroalkenes with reaction times up to 40 hours. Moreover, even though the addition step occurred stereo-

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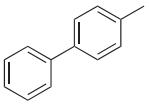
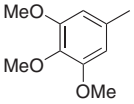
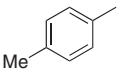
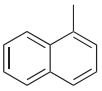
selectively the diastereomeric excesses of the products were only moderate (de = 32–55%). As established by X-ray crystal structure analysis, the absolute configuration of the newly formed stereogenic center for the major diastereoisomer was *S*.

Table 1 *n*-BuLi Mediated Asymmetric Michael Addition of Phosphite (*R*,*R*)-**1** to Nitroalkenes **2a–f** to Afford the β-Nitrophosphonates **3a–f**

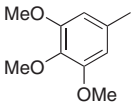
3	R	Method	Yield (%)	de (%)[a]
(*R*,*R*,*S*)-**3a**		A	75	32
(*R*,*R*,*S*)-**3b**		A	70	38
(*R*,*R*,*S*)-**3c**		A	84	47
(*R*,*R*,*S*)-**3d**		A	72	35
(*R*,*R*,*S*)-**3e**		A	77	55
(*R*,*R*,*S*)-**3f**		A	81	35

[a] Determined by ^{31}P NMR and HPLC (Whelk 01, cyclohexane–2-propanol, 9:1).

In order to improve the stereoselectivity of the conjugate addition, the effect of the temperature was investigated using **2c** and **2f** as model substrates. (*R*,*R*)-**1** was metalated with *n*-butyllithium in THF at 0 °C and, after subsequent addition of the nitroalkene, the resulting solution was either cooled to –78 °C or heated to reflux. As shown in Table 2, low temperatures did not have any beneficial effect on the diastereoselectivity. The diastereomeric excesses were comparable with those achieved at 0 °C, but a reversal of facial selectivity was observed for both nitroalkenes, resulting in β-nitrophosphonates **3c** and **3f** with *R*-configurations at the new stereogenic centers. At –78 °C the reactivity of (*R*,*R*)-**1** was significantly lower than at 0 °C, with reaction times of up to one week, while heating the solution to reflux produced a slight increase of diastereomeric excess but led to very poor yields, due to hydrolysis of (*R*,*R*)-**1** at high temperature to recoverable TADDOL.

The conjugate additions were then carried out in the presence of different bases such as sodium or potassium hydride, *n*-butyllithium in the presence of copper salts, dibutylmagnesium or diethylzinc. With alkali metals as counterions, less reactive P–nucleophiles were produced, whereas in the presence of copper or magnesium no reaction could be observed at all. A breakthrough came with

Table 2 Temperature Effect on the *n*-BuLi Mediated Asymmetric *phospha*-Michael Addition to Nitroalkenes **2c** and **2f**

3	R	T (°C)	Method	Yield (%)[a]	de (%)[a]
(*R*,*R*,*S*)-**3c**		0	A	84	47
(*R*,*R*,*R*)-**3c**		–78	A	78	40
(*R*,*R*,*S*)-**3c**		66	A	28	50
(*R*,*R*,*S*)-**3f**		0	A	81	35
(*R*,*R*,*R*)-**3f**		–78	A	77	32
(*R*,*R*,*S*)-**3f**		66	A	22	37

[a] Determined by ^{1}H NMR and HPLC (Whelk 01, cyclohexane–2-propanol, 9:1).

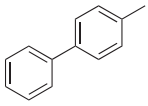
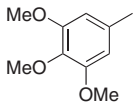
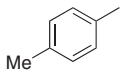
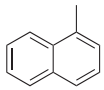
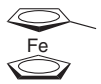
the use of diethylzinc as the metal source. In this case the *phospha*-Michael addition proceeded smoothly even at low temperature (12 h at –78 °C, then 1 h at r.t.) and the *R*-configured β-nitrophosphonates **3a–f** were obtained in high yields and diastereomeric excesses (Scheme 1, Method B, Table 3). The reaction of diethylzinc with (*R*,*R*)-**1** led to the formation of a reactive organozinc phosphorus adduct, which in analogy to previous reports by Noltes et al.[15] turned out to be very reactive, but insoluble. Indeed, after Et_2Zn was added to (*R*,*R*)-**1** at 0 °C and the solution was cooled to –78 °C, the precipitation of a colorless solid was observed. This completely redissolved only when the solution was allowed to warm to 0 °C. Consequently, some of the nucleophiles reacted with the corresponding nitroalkene only at higher temperature.

To enhance the solubility of the reactive intermediate the addition of Et_2Zn was carried out in the presence of a chelating amine such as TMEDA. Under these conditions the conjugate addition of (*R*,*R*)-**1** reached completion at –78 °C and, as a result, improved yields (86–91%) and diastereomeric excesses (de = 84–96%) could be achieved (Scheme 1, Method C, Table 3).

The absolute configuration of the newly formed stereogenic center in **3b** was determined to be *R* by X-ray crystallography (Figure 2).[11] Assuming a uniform reaction mechanism, all examples described should possess the same configuration.

We hoped to extend this methodology to the preparation of β-nitrophosphonates with two new stereogenic centers. The asymmetric conjugate addition of (*R*,*R*)-**1** to α,β-disubstituted nitroalkenes was investigated (Scheme 2, Table 4). In this case, the second stereogenic center is generated through stereoselective protonation of the intermediate nitronate, generated by addition of the phosphorus nucleophile onto the double bond of nitroalkenes **4a–c**. For this reason, besides typical quenching reagents such

Table 3 Et_2Zn-Mediated Asymmetric Michael Addition of Phosphite (*R*,*R*)-**1** to Nitroalkenes **2a–f** to Afford the 1,4-Adducts **3a–f**

3	R	Method	Yield (%)	de (%)[a]
(*R*,*R*,*R*)-**3a**		B	81	84
		C	89	89
(*R*,*R*,*R*)-**3b**		B	84	87
		C	88	92
(*R*,*R*,*R*)-**3c**		B	88	77
		C	91	88
(*R*,*R*,*R*)-**3d**		B	86	82
		C	86	96
(*R*,*R*,*R*)-**3e**		B	95	93
		C	87	93
(*R*,*R*,*R*)-**3f**		B	75	63
		C	86	84

[a] Determined by ^1H NMR and HPLC (Whelk 01, cyclohexane–2-propanol, 9:1).

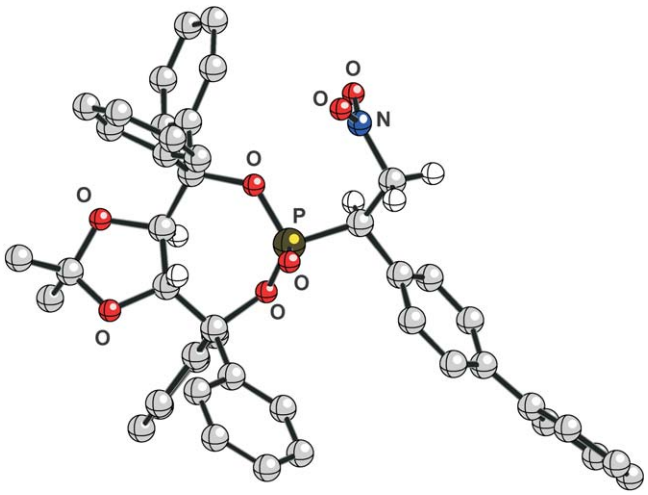
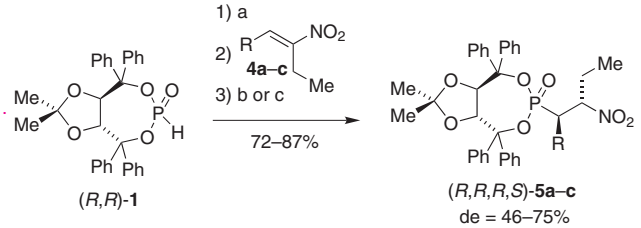


Figure 2 X-ray crystal structure of **3b**

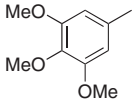
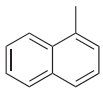
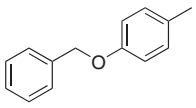
as aqueous ammonium chloride, the use of bulky proton donors such as 4-bromo-2,6-di-*t*-butylphenol at low temperature was employed.

The addition of (*R*,*R*)-**1** to α,β-disubstituted nitroalkenes **4a–c** proceeded smoothly under the optimized conditions described above, affording the corresponding α,β-disubstituted β-nitrophosphonates **5a–c** in good yields (72–87%) and moderate diastereomeric excesses (de = 46–75%, Table 4). The best results were obtained in the case of nitroalkene **4a** when the reaction was quenched at –78 °C with 4-bromo-2,6-di-*tert*-butylphenol and allowed to warm to room temperature. The *anti* relative configuration of the new stereogenic center, as well as the absolute configuration, was established via NOE experiments based on the known configuration of the chiral auxiliary.



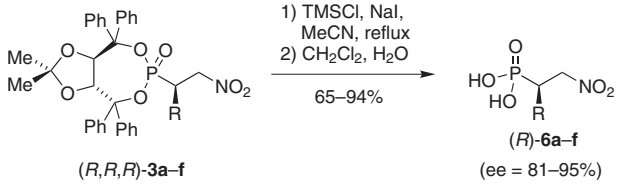
Scheme 2 *Reagents and conditions*: (a) Et_2Zn, TMEDA, THF, –78 °C, 12 h; (b) NH_4Cl (aq); (c) 4-bromo-2,6-di-*tert*-butylphenol.

Table 4 Asymmetric *phospha*-Michael Addition of (*R*,*R*)-**1** to Nitroalkenes **4a–c** to Afford α,β-Disubstituted β-Nitrophosphonates **5a–c**

5	R	Method	Yield (%)	de (%)[a]
(*R*,*R*,*R*,*S*)-**5a**		B	81	57
		C	72	75
(*R*,*R*,*R*,*S*)-**5b**		B	87	69
		C	77	46
(*R*,*R*,*R*,*S*)-**5c**		B	81	62
		C	75	67

[a] Determined by ^1H NMR and HPLC (Whelk 01, cyclohexane–2-propanol, 9:1).

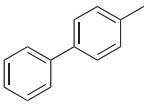
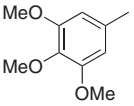
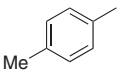
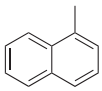
To complete the reaction sequence, the chiral auxiliary was removed from the 1,4-addition products **3a–f**. As previously reported, cleavage of the auxiliary occurred under neutral, racemization-free conditions upon treatment with trimethylsilylchloride and sodium iodide in acetonitrile to yield α-substituted β-nitrophosphonic acids **6a–f** (Scheme 3, Table 5).



Scheme 3

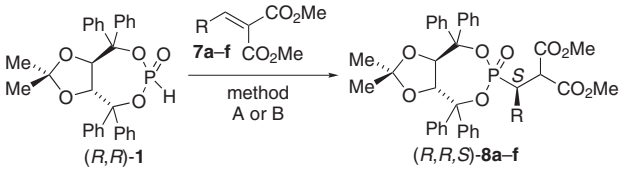
With the purpose of extending the scope of our methodology, we proceeded to investigate the conjugate addition of phosphite (*R*,*R*)-**1** to other Michael acceptors, such as α,β-unsaturated malonates. Since derivatives of β-phosphonomalonic acid have shown promising *in vitro* anti-tumor activity,[16] the synthesis of enantiomerically pure analogues of this type was particularly desirable.

Table 5 Cleavage of the Chiral Auxiliary from β-Nitrophosphonates **3a–f** to Yield β-Nitrophosphonic Acids **6a–f**

6	R	Method	Yield (%)	ee (%)[a]
(*R*)-**6a**		A	87	92
(*R*)-**6b**		A	88	88
(*R*)-**6c**		A	92	86
(*R*)-**6d**		A	94	95
(*R*)-**6e**		A	65	91
(*R*)-**6f**		A	85	81

[a] Measured by chiral HPLC of the dimethylphosphonate derivatives (Daicel OD).

Based on observations by Koenig et al.,[17] that the conjugate addition of diethylphosphite to α,β-unsaturated ketones could be carried out under heterogeneous conditions, using KOH on aluminium oxide as a solid base, we studied the reactivity of (*R*,*R*)-**1** towards Knoevenagel acceptors **7a–f** under both homogeneous and heterogeneous conditions (Scheme 4).

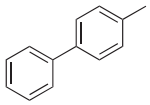


Scheme 4 Method A: Et_2Zn, TMEDA, THF, –78 °C, 12 h. Method B: Al_2O_3–KOH, CH_2Cl_2, r.t., 2 h.

The desired β-substituted β-phosphonomalonates could be obtained under both sets of conditions (Table 6). Comparable results where obtained in the case of aromatic malonates. In contrast, when the aliphatic malonate **7a** was used as a substrate in the heterogeneous system, even if the reaction product was obtained in high yield (93%), only poor stereoselectivity (de = 13%) could be observed.

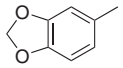
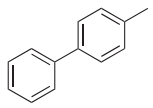
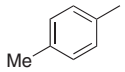
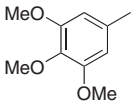
Considering the advantages of heterogeneous asymmetric *phospha*-Michael additions (room temperature, faster reaction times, no dry solvents required), we were interested in developing suitable reaction conditions under which the stereoselectivity of the reaction would be maximized. Our previous investigations showed that the metal oxide on which potassium hydroxide is adsorbed plays a crucial role in the stereochemical course of the addition. After examining a variety of metal oxides, we showed that inexpensive Fe_2O_3–KOH as a solid base in dichloromethane in the presence of small amounts of water provided high diastereomeric excesses (de = 82–94%, Table 7).

Table 6 Asymmetric *phospha*-Michael Addition of (*R*,*R*)-**1** to α,β-Unsaturated Malonates **7a**,**b**,**d** to Afford α,β-Disubstituted β-Nitrophosphonates **8a,b,d** (Preliminary Investigations)

8	R	Method	Yield (%)	de (%)[a]
(*R*,*R*,*S*)-**8a**		A	89	67
(*R*,*R*,*S*)-**8a**		B	93	13
(*R*,*R*,*S*)-**8b**		A	81	75
(*R*,*R*,*S*)-**8b**		B	88	75
(*R*,*R*,*S*)-**8d**		A	79	76
(*R*,*R*,*S*)-**8d**		B	82	69

[a] Determined by ^{31}P NMR and HPLC (Daicel OD, Daicel AD 2, Whelk 01).

Table 7 Michael Addition of Phosphite (*R*,*R*)-**1** to a,b-Unsaturated Malonates **7b–f** Using Fe_2O_3–KOH as Base

8	R	Reaction time (h)	Yield (%)	de (%)[a]
(*R*,*R*,*S*)-**8b**		4	64	86
(*R*,*R*,*S*)-**8c**		5	67	91
(*R*,*R*,*S*)-**8d**		4	63	94
(*R*,*R*,*S*)-**8e**		3	75	82
(*R*,*R*,*S*)-**8f**		4	71	89

[a] Determined by ^{31}P NMR and by HPLC (Daicel OD, AD2).

The absolute configuration of the newly formed stereogenic center was determined to be *S* by X-ray crystal structure analysis in the case of product **8e** (Figure 3).[18] Assuming a uniform reaction mechanism, all cases described should possess the same configuration. This is also supported by the observation that addition of (*R*,*R*)-**1** to Knoevenagel acceptors showed the same relative topicity encountered in the case of nitroalkenes.

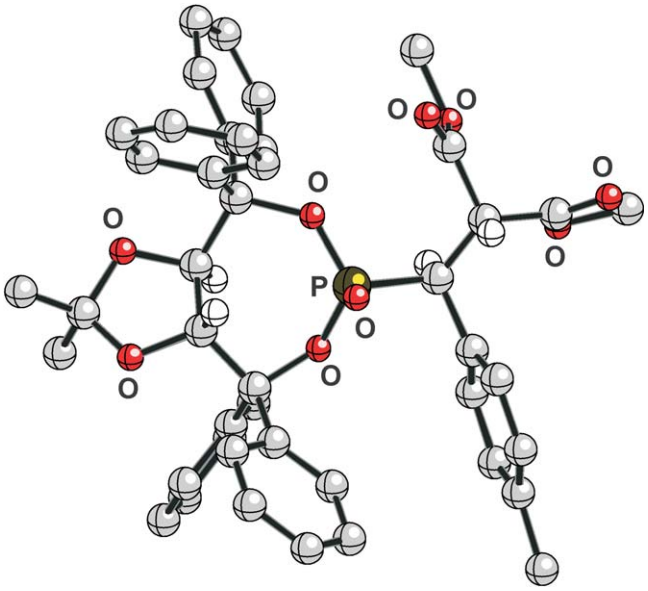


Figure 3 X-ray crystal structure of **8e**

During our preliminary investigations, we noticed that the diastereomeric excess of the Michael adducts **7b–f** was time-dependent; increasing with longer reaction times. In order to quantify this observation we monitored the course of addition of (*R*,*R*)-**1** to alkylidene malonate **7d**. The diastereomeric excess was measured at regular intervals via ^{31}P NMR spectroscopy. The *phospha*-Michael addition was carried out using Fe_2O_3–KOH as a base in either dry dichloromethane or in a dichloromethane–water system. Surprisingly, in the presence of water, the diastereomeric excess increased from the initial value of 62% to >96% after several hours, while it remained constant when the reaction was carried out in dry dichloromethane (Figure 4).

Deuteration experiments seem to suggest that, in the Fe_2O_3–KOH–H_2O system, the reaction product undergoes *retro*-Michael addition. This establishes an equilibrium, which leads to virtually complete conversion of the starting materials into the major diastereoisomer.

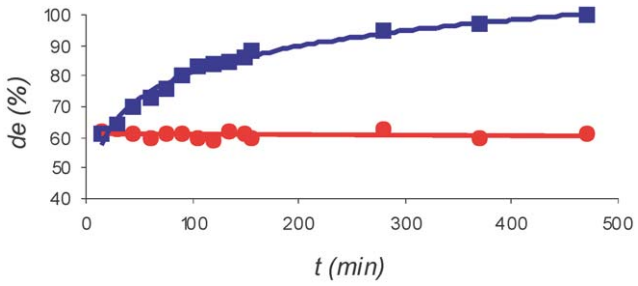


Figure 4 Conjugate addition of (*R*,*R*)-**1** to α,β-unsaturated malonate **7d** using Fe_2O_3–KOH as base in anhydrous (red circles) or wet (blue squares) CH_2Cl_2

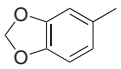
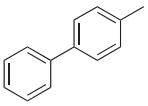
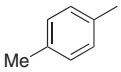
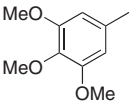
Unfortunately, excessively long reaction times cause partial decomposition of starting materials and products, resulting in poorer yields.

With the desired β-substituted β-phosphonomalonates **8a–f** in the hand, we proceeded to remove the chiral auxiliary, which was accomplished as previously reported upon treatment with trimethylsilyl chloride and sodium iodide in acetonitrile (Scheme 5).

Scheme 5

To facilitate the workup procedure, the resulting free acids were treated with diazomethane and isolated as the corresponding methyl esters. The enantiomeric excesses of the β-substituted β-phosphonomalonates **9b–f** were determined via HPLC over chiral stationary phase and were comparable with the diastereomeric excessesof **8b–f**, indicating that no racemization occurred during the cleavage of the chiral auxiliary.

Table 8 Cleavage of the TADDOL Auxiliary to Yield b-Phosphonomalonates (*S*)-**9b–f**

9	R	^{31}P NMR δ (ppm)	Yield (%)	ee (%)[a]
(*R*,*R*,*S*)-**9b**		27.8	72	84
(*R*,*R*,*S*)-**9c**		27.9	86	92
(*R*,*R*,*S*)-**9d**		27.8	77	94
(*R*,*R*,*S*)-**9e**		28.0	74	84
(*R*,*R*,*S*)-**9f**		27.9	82	90

[a] Determined by chiral HPLC (Daicel OD 2, Daicel AD 2).

In conclusion, we have developed a very efficient asymmetric synthesis of β-functionalised phosphonic acids or phosphonates, with very good diastereomeric and enantiomeric excesses. Our approach constitutes a first broadly applicable method of asymmetric P–C bond formation via conjugate addition. Additionally, a heterogeneous version of the reaction, which occurs under very mild conditions, has been developed. Therefore, considering the importance of functionalized phosphonates as biologically active compounds and synthetic building blocks, our study

may be an important starting point for further developments in this field.

All moisture-sensitive reactions were carried out using standard Schlenk techniques. Reactions involving sensitive phosphorus intermediates were carried out in dried and degassed solvents (N_2). Solvents were dried and purified by conventional methods prior to use. THF was freshly distilled from sodium–lead alloy under argon. Reagents of commercial quality were used from freshly opened containers or purified by common methods. *n*-BuLi (1.6 M in hexane) was purchased from Merck, Darmstadt and Et_2Zn (1.0 M in heptane) was purchased from Fluka. Preparative column chromatography: Merck silica gel 60, particle size 0.040–0.063 mm (230–240 mesh, flash). Analytical TLC: silica gel 60 F_{254} plates from Merck, Darmstadt. Optical rotation values were measured on a Perkin–Elmer P241 polarimeter. Microanalyses were obtained with a Vario EL element analyzer. Mass spectra were acquired on a Finnigan SSQ7000 (CI 100 eV; EI 70 eV) spectrometer. High-resolution mass spectra were recorded on a Finnigan MAT95 spectrometer. IR spectra were taken on a Perkin–Elmer FT/IR 1760. ^1H and ^{13}C NMR spectra were recorded on Gemini 300 or Varian Inova 400 and all measurements were performed with tetramethylsilane as internal standard. Melting points were determined on a Tottoli melting point apparatus and are uncorrected.

Asymmetric *phospha*-Michael Addition to Nitroalkenes; General Procedure (GP 1)

The chiral phosphite **1** (1 equiv) was dissolved in dry THF (2 mL/mmol) and the solution was cooled to –78 °C. Et_2Zn (1 equiv) and TMEDA (1 equiv) were added dropwise, followed by the nitroalkene **2** (1 equiv) dissolved in THF (2 mL/mmol). After stirring for 12 h the mixture was allowed to reach r.t. and was then quenched with sat. aq NH_4Cl (4 mL/mmol). The aqueous layer was extracted with Et_2O (3 × 100 mL). Drying the combined organic layers (Na_2SO_4) and concentration in vacuo gave the crude product, which was purified by column chromatography.

Asymmetric *phospha*-Michael Addition to Knoevenagel Acceptors; General Procedure (GP 2)

The phosphite **1** (1.0 equiv) and the Knoevenagel acceptor **7** (1.0 equiv) were stirred in CH_2Cl_2 (1.0 mL/mmol) in the presence of Fe_2O_3–KOH (5.25 g/g phosphite), prepared by addition of methanolic KOH (0.7 M, 10 mL) to a vigorously stirred suspension of Fe_2O_3 (2.30 g, 14.4 mmol) in MeOH (50 mL), removal of the solvent and drying at 120 °C in high vacuum. After the reaction was complete (TLC, ^{31}P NMR), the suspension was filtered and the residue washed with CH_2Cl_2 (3 × 20 mL). After concentration under reduced pressure, the crude product was purified by column chromatography.

Removal of the Chiral Auxiliary; General Procedure (GP 3)

To a single-neck flask, charged with the β-nitrophosphonate **3** (1.0 equiv) in MeCN (4 mL/mmol) was added a solution of NaI (1.0 equiv) and TMSCl (1.0 equiv). After refluxing for 10 h, the NaCl formed was removed by filtration and the filtrate concentrated under reduced pressure. The crude product was diluted with CH_2Cl_2 (3 mL/mmol) and H_2O (10 mL/mmol) and the solution was stirred at r.t. for 2 h. After separation of the organic phase, the aqueous phase was concentrated to afford the crude nitrophosphonic acid by lyophilization. Purification by recrystallization (MeOH) gave **6** as a colorless solid.

Removal of the Chiral Auxiliary; General Procedure (GP 4)

To a single-neck flask charged with the β-phosphonomalonic acid **8** (1.0 equiv) in MeCN (4 mL/mmol) was added NaI (4.2 equiv) and TMSCl (4.2 equiv). After 8 h reflux, the NaCl formed was removed by filtration and the filtrate concentrated under reduced pressure. The crude product was diluted with CH_2Cl_2 (3 mL/mmol) and H_2O (10 mL/mmol) and stirred at r.t. for 2 h. After separation of the organic phase, the crude β-phosphonomalonic acid was obtained as a colorless solid from the aqueous phase by lyophilisation. The phosphonic acid was dissolved in MeOH–H_2O (10:1, v/v) and treated with a solution of diazomethane in ether at r.t. until a yellow color remained and no further nitrogen was developed. After concentration under reduced pressure, the crude product was purified by column chromatography to yield the phosphonomalonates **9**.

(3a*R*,8a*R*)-2,2-Dimethyl-4,4,8,8-tetraphenylperhydro-6λ^5-[1,3]dioxolo-[4,5-*e*][1,3,2]dioxaphosphepin-6-one [(*R*,*R*)-1]

TADDOL (40.2 g, 86 mmol) was added over 60 min via canula to a solution of PCl_3 (9.7 mL, 111 mmol) and Et_3N (31.1 mL) in THF (345 mL) at 0 °C. After 2 h, the precipitated colorless solid was separated by filtration under argon and a previously degassed mixture of H_2O (1.5 mL), Et_3N (15.5 mL) and THF (5 mL) was added to the filtrate. After 1 h the precipitated colorless solid was separated off by filtration under argon and the crude product was purified by column chromatography (*n*-pentane–Et_2O, 3:2) to give the phosphite (*R*,*R*)-**1** as a colorless solid.

Yield: 95%; mp 225–227 °C; $[\alpha]_D^{26}$ –301.8 (*c* 1.00, $CHCl_3$).

IR (KBr): 3062 (w), 3036 (w), 2987 (w), 2933 (w), 2906 (w), 2441 (w), 1495 (m), 1448 (m), 1383 (w), 1372 (w), 1275 (s), 1241 (m), 1218 (m), 1167 (m), 1113 (m), 1094 (s), 1080 (s), 1053 (m), 1034 (s), 1021 (m), 1002 (m), 952 (s), 902 (m), 859 (w), 747 (s), 727 (m), 700 (s), 673 (w), 654 (w), 641 (w), 584 (w), 497 (w) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.57 (s, 3 H, CCH_3), 0.76 (s, 3 H, CCH_3), 5.21 (d, $^3J_{H-H}$ = 8.2 Hz, 1 H, OCH), 5.36 (d, $^3J_{H-H}$ = 8.0 Hz, 1 H, OCH), 7.08 (d, $^1J_{P-H}$ = 726.8 Hz, 1 H, PH), 7.25–7.43 (m, 12 H, *m*-ArH and *p*-ArH), 7.57–7.61 (m, 8 H, *o*-ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.2, 26.7, 79.8, 80.6, 88.6 (d, $^2J_{C-P}$ = 4.6 Hz, POCH*C*H), 88.7, 114.4, 126.8, 126.9, 127.3, 127.5, 127.9, 128.0, 128.2, 128.3, 128.5, 128.6, 128.7, 128.8, 138.9, 139.1, 143.2, 143.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ = –3.35.

MS (EI, 70 eV): *m*/*z* (%) = 512 (4) [M$^+$], 497 (6), 454 (7), 431 (15), 430 (32), 373 (44), 355 (33), 344 (100), 330 (27), 208.2 (25), 207.2 (83), 183.0 (5), 179.2 (9), 178.2 (9), 165.1 (6).

Anal. Calcd for $C_{31}H_{29}O_5P$: C, 72.65; H, 5.70. Found: C, 72.68; H, 5.99.

(3a*R*,8a*R*)-2,2-Dimethyl-6-[(1*R*)-(2-nitro-1-phenylethyl)]-4,4,8,8-tetra-phenylperhydro-6λ^5-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-one (3a)

Prepared according to GP 1 using phosphite (*R*,*R*)-**1** (2.56 g, 5 mmol), TMEDA (0.75 mL, 5mmol), Et_2Zn (1 N in hexane; 5 mL, 5 mmol) and nitroalkene **2a** (0.745 g, 5 mmol) in THF (20 mL). The crude product was purified by column chromatography (*n*-pentane–Et_2O, 7:3) to give pure **3a** as a colorless solid.

Yield: 89%; mp 202–210 °C; $[\alpha]_D^{26}$ –195.5 (*c* 1.0, $CHCl_3$); de = 89% (^{31}P NMR).

IR (KBr): 3676 (w), 3652 (w), 3432 (m), 3062 (m), 3033 (m), 2989 (m), 2931 (m), 2869 (w), 1736 (w), 1602 (w), 1560 (s), 1496 (s), 1449 (s), 1375 (s), 1326 (w), 1264 (s), 1215 (s), 1167 (s), 1107 (s), 1089 (s), 1054 (s), 1038 (s), 1019 (s), 987 (s), 939 (s), 902 (m), 881 (m), 860 (w), 746 (s), 727 (m), 699 (s), 653 (w), 641 (m), 578 (w), 544 (w), 526 (w), 506 (w) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.43 (s, 3 H, CH_3), 0.80 (s, 3 H, CH_3), 4.13 (dt, $^3J_{H-H}$ = 7.9 Hz, $^2J_{P-H}$ = 26.1 Hz, 1 H, PCH), 5.02 (m, 3 H, CH_2 and CHO), 5.47 (d, $^3J_{H-H}$ = 8.0 Hz, 1 H, CHO), 6.91–7.59 (m, 25 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.7, 27.4, 44.4 (d, $^1J_{C-P}$ = 145.7 Hz, PO*C*H), 74.5 (d, $^2J_{C-P}$ = 6.8 Hz, POCH*C*H), 79.2, 79.2, 79.7, 87.7, 91.6, 114.2, 126.6, 126.9, 127.5, 127.5, 128.0, 128.2, 128.4, 128.5, 128.6, 128.7, 128.8, 129.0, 129.0, 129.1, 129.1, 129.9, 131.8, 139.4, 139.5, 143.4, 144.1.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 16.80 (minor), 17.05 (major).

MS (CI, isobutane): *m*/*z* (%) = 662 (54) [M$^+$], 616 (14), 615 (32), 449 (8), 432 (31), 431 (100), 391 (10), 373 (8), 267 (16), 236 (7), 208 (5), 207 (16), 160 (5), 150 (44), 135 (8), 123 (26), 105 (5), 104 (12), 86 (10).

Anal. Calcd for $C_{39}H_{36}NO_7P$: C, 70.79; H, 5.48; N, 2.12. Found: C, 70.51; H, 5.55; N, 1.94.

(3a*R*,8a*R*)-2,2-Dimethyl-6-[(1*R*)-2-nitro-(4-phenylphenyl)ethyl]-4,4,8,8-tetraphenylperhydro-6λ^5-[1,3]dioxolo[4,5-*e*][1,3,2]-dioxaphosphepin-6-one (3b)

Prepared according to GP 1 using phosphite (*R*,*R*)-**1** (2.56 g, 5 mmol), TMEDA (0.75 mL, 5 mmol), Et_2Zn (1 N in hexane, 5 mL, 5 mmol) and nitroalkene **2b** (1.125 g, 5mmol) in THF (20 mL). The crude product was purified by column chromatography (*n*-pentane–Et_2O, 1:1) to give pure **3b** as a colorless solid.

Yield: 88%; mp 155 °C, $[\alpha]_D^{26}$ –155.5 (*c* 1.0, $CHCl_3$); de = 87% (^{31}P NMR).

IR (KBr): 3433 (m), 3061 (m), 3031 (m), 2990 (m), 2956 (m), 2927 (m), 2879 (m), 2318 (w), 1601 (m), 1561 (vs), 1494 (s), 1448 (s), 1373 (s), 1264 (vs), 1216 (m), 1167 (m), 1106 (m), 1089 (m), 1054 (vs), 1039 (vs), 1020 (vs), 1006 (vs), 985 (vs), 940 (s), 924 (m), 901 (m), 887 (m), 864 (w), 849 (w) 803 (w), 790 (w), 762 (m) 674 (w) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.43 (s, 3 H, CH_3), 0.80 (s, 3 H, CH_3), 4.21 (dt, $^3J_{H-H}$ = 7.1 Hz, $^2J_{P-H}$ = 26.1 Hz, 1 H, PCH), 5.04 (m, 3 H, PCCH_2 and CHO), 5.47 (d, $^3J_{H-H}$ = 8.0 Hz, 1 H, CHO), 6.95–7.61 (m, 29 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.2, 27.9, 43.6 (d, $^1J_{C-P}$ = 145.7 Hz, PO*C*H), 78.7 (d, $^2J_{C-P}$ = 2.3 Hz, POCH*C*H), 79.2, 79.7, 87.3, 114.2, 126.2, 126.8, 127.0, 127.1, 127.1, 127.2, 127.4, 127.6, 127.7, 128.0, 128.0, 128.1, 128.3, 128.3, 128.7, 129.0, 129.0, 129.5, 130.3, 138.9, 139.0, 140.1, 140.9, 142.9, 143.7.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 15.50.

Anal. Calcd for $C_{45}H_{40}NO_7P$: C, 73.26; H, 5.46; N, 1.90. Found: C, 72.93; H, 5.77; N, 1.80.

(3a*R*,8a*R*)-2,2-Dimethyl-6-[(1*R*)-2-nitro-(3,4,5-trimethoxyphenyl)ethyl]-4,4,8,8-tetraphenylperhydro-6λ^5-[1,3]dioxolo[4,5-*e*]-[1,3,2]dioxaphosphepin-6-one (3c)

Prepared according to GP 1 using phosphite (*R*,*R*)-**1** (2.56 g, 5 mmol), TMEDA (0.75 mL, 5mmol), Et_2Zn (1 N in hexane, 5 mL, 5mmol) and nitroalkene **2c** (1.196 g, 5mmol) in THF (20 mL). The crude product was purified by column chromatography (*n*-pentane–Et_2O, 3:7) to give **3c** as a colorless solid.

Yield: 91%; mp 117–127 °C; $[\alpha]_D^{26}$ –203.3 (*c* 1.0, $CHCl_3$); de = 88% (^{31}P NMR).

IR ($CHCl_3$): 3092 (w), 3063 (m), 3011 (s), 2965 (m), 2938 (s), 2840 (m), 1593 (s), 1559 (s), 1510 (s), 1497 (s), 1463 (s), 1449 (s), 1427 (s), 1374 (s), 1335 (s), 1246 (s), 1218 (s), 1188 (s), 1167 (s), 1129 (s), 1107 (s), 1090 (s), 1054 (s), 1039 (s), 1019 (s), 1005 (s), 986 (s), 941 (s), 924 (s), 910 (m), 889 (m), 864 (w), 845 (w), 803 (w), 752 (s), 727 (s), 700 (s), 666 (s), 659 (s), 641 (m) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.49 (s, 3 H, CH_3CCH$_3$), 0.86 (s, 3 H, CH$_3$CCH_3), 3.72 (s, 6 H, *m*-OCH_3), 3,84 (s, 3 H, *p*-OCH_3), 4.17 (ddd, $^3J_{H-H}$ = 4.9 Hz, $^3J_{H-H}$ = 10.7 Hz, $^2J_{P-H}$ = 25.3 Hz, 1 H, CHP), 4.98 (m, 2 H, CH_2), 5.08 (d, $^3J_{H-H}$ = 7.8 Hz, 1 H, CHO), 5.53 (d, $^3J_{H-H}$ = 7.8 Hz, 1 H, CHO), 6.47 (d, 2 H, *J* = 2.2 Hz, C*H*COCH$_3$), 7.03–7.52 (m, 20 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.4, 26.9, 44.2 (d, $^1J_{C-P}$ = 148.8 Hz, PO*C*H), 56.0, 60.8, 75.1, 78.5, 79.61, 87.2 (d, $^2J_{C-P}$ = 8.4 Hz, POCH*C*H), 91.6, 105.8, 113.7, 126.4, 126.8, 127.1, 127.1, 127.7, 127.8, 128.1, 128.2, 128.2, 128.4, 129.4, 137.9, 138.8, 138.9, 139.0, 143.1, 144.2, 144.9, 153.3.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 16.87.

MS (EI, 70 eV): *m*/*z* (%) = 751 (19) [M$^+$], 430 (6), 344 (13), 304 (5), 303 (43), 267 (6), 266 (6), 265 (21), 256 (14), 208 (10), 207 (33), 195 (16), 194 (100), 193 (7), 183 (9), 180 (7), 179 (40), 178 (19), 167 (17), 166 (7), 165 (14), 151 (5), 149 (9), 111 (6), 105 (10), 97 (6), 91 (5), 85 (8), 83 (7), 77(5), 73 (7), 71 (10), 69 (6), 60 (12), 59 (5), 57 (22), 56 (6), 55 (14).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{42}H_{42}NO_{10}P$: 751.254; found: 751.254.

(3a*R*,8a*R*)-2,2-Dimethyl-6-[(1*R*)-1-(4-methylphenyl)-2-nitroethyl]-4,4,8,8-tetraphenylperhydro-6λ^5-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-one (3d)

Prepared according to GP 1 using phosphite (*R*,*R*)-**1** (2.56 g, 5 mmol), TMEDA (0.75 mL, 5mmol), Et_2Zn (1 N in hexane, 5 mL, 5 mmol) and nitroalkene **2d** (0.815 g, 5 mmol) in THF (20 mL). The crude product was purified by column chromatography (*n*-pentane–Et_2O, 7:3) to give pure **3d** as a colorless solid.

Yield: 87%; mp 231 °C; $[\alpha]_D^{26}$ –187.3 (*c* 1.00, $CHCl_3$); de = 96% (^{31}P NMR).

IR (KBr): 3435 (w), 3060 (m), 3031 (m), 2989 (m), 2957 (m), 2929 (m), 2869 (w), 1602 (w), 1561 (s), 1516 (m), 1496 (m), 1448 (s), 1374 (s), 1336 (w), 1322 (w), 1261 (s), 1215 (m), 1170 (s), 1115 (m), 1088 (m), 1053 (s), 1038 (s), 1018 (s), 980 (s), 941 (s), 926 (s), 901 (m), 884 (m), 863 (w), 841 (w), 792 (w), 747 (s), 726 (s), 699 (s), 652 (w), 641 (w), 585 (m), 550 (w) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.45 (s, 3 H, CCH_3), 0.82 (s, 3 H, CCH_3), 2.33 (d, $^4J_{H-H}$ = 1.6 Hz, 3 H, ArCH_3), 4.10 (dt, $^3J_{H-H}$ = 8.0 Hz, $^2J_{P-H}$ = 26.1 Hz, 1 H, CHP), 5.00 (m, 3 H, CH_2, CHO), 5.47 (d, $^3J_{H-H}$ = 8.0 Hz, 1 H, CHO), 6.94–7.60 (m, 24 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 26.6, 27.4, 44.1 (d, $^1J_{C-P}$ = 145.7 Hz, PO*C*H), 74.6 (d, $^2J_{C-P}$ = 6.8 Hz, POCH*C*H), 79.3, 79.8, 87.6, 91.4, 114.2, 126.6, 127.4, 127.5, 128.0, 128.1, 128.4, 128.4, 128.5, 128.5, 128.7, 128.8, 129.0, 129.7, 129.9, 138.2, 138.2, 139.4, 139.5, 143.5, 144.2.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 17.22.

MS (CI, isobutane): *m*/*z* (%) = 677 (25) [M + H]$^+$, 676 (57) [M$^+$], 630 (22), 629 (61), 449 (10), 432 (17), 431 (46), 373 (5), 267 (19), 264 (12), 207 (14), 183 (5), 174 (10), 165 (9), 164 (100), 160 (16), 149 (8), 148 (10), 137 (16), 120 (7), 119 (21), 118 (54), 86 (19).

Anal. Calcd for $C_{40}H_{38}NO_7P$: C, 71.10; H, 5.67; N, 2.07. Found: C, 71.13; H, 5.93; N, 1.91.

(3a*R*,8a*R*)-2,2-Dimethyl-6-[(1*R*)-(1-naphthyl)-2-nitroethyl]-4,4,8,8-tetraphenylperhydro-6λ^5-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-one (3e)

Prepared according to GP 1 using phosphite (*R*,*R*)-**1** (2.56 g, 5 mmol), TMEDA (0.75 mL, 5 mmol), Et_2Zn (1 N in hexane, 5 mL, 5 mmol) and nitroalkene **2e** (0.995 g, 5mmol) in THF (20 mL). The crude product was purified by column chromatography (*n*-pentane–Et_2O, 2:3) to give pure **3e** as a colorless solid.

Yield: 87%; mp 131 °C; $[\alpha]_D^{26}$ –219.3 (*c* 1.00, $CHCl_3$); de = 93% (^{31}P NMR).

IR (KBr): 3448 (w), 3060 (m), 3038 (w), 2987 (m), 2934 (w), 2866 (w), 1599 (w), 1560 (s), 1514 (w), 1496 (m), 1448 (s), 1373 (s),

1331 (w), 1269 (s), 1217 (s), 1167 (s), 1112 (m), 1089 (s), 1053 (s), 1037 (s), 1019 (s), 984 (s), 939 (s), 923 (s), 901 (m), 878 (m), 859 (m), 792 (m), 776 (s), 744 (s), 727 (s), 699 (s), 672 (w), 655 (w) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.41 (s, 3 H, CH_3), 0.77 (s, 3 H, CH_3), 4.94 (m, 1 H, C*H*CH_2), 5.06 (m, 1 H, CHO), 5.15 (m, 2 H, CHC*H*$_2$), 5.50 (m, 1 H, CHO), 6.67–7.86 (m, 27 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.2, 26.7, 37.8 (d, $^1J_{C-P}$ = 144.2 Hz, PO*C*H), 75.0 (d, $^2J_{C-P}$ = 5.3 Hz, POCH*C*H), 78.8, 79.6, 87.7, 90.3, 114.0, 122.6, 124.0, 125.5, 125.8, 126.0, 126.7, 126.8, 127.1, 127.2, 127.7, 127.8, 127.9, 128.3, 128.5, 128.7, 128.8, 128.9, 128.9, 129.1, 131.7, 131.7, 133.9, 138.5, 139.2, 142.8, 143.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 15.18.

MS (EI, 70 eV): *m*/*z* (%) = 711 (0.3) [M^+], 471 (5), 445 (6), 265 (18), 234 (7), 233 (46), 208 (27), 207 (100), 191 (19), 183 (13), 180 (6), 179 (39), 178 (27), 168 (6), 167 (28), 166 (7), 165 (12), 155 (6), 154 (36), 153 (22), 152 (10), 105 (16), 102 (5), 77 (5), 57 (8), 55 (6).

HRMS (EI): *m*/*z* [M + 1] $^+$ calcd for $C_{43}H_{38}NO_7P$: 711.23; found: 711.239.

(3a*R*,8a*R*)-2,2-Dimethyl-6-[(1*R*)-2-nitro-1-ferrocenyl-ethyl]-4,4,8,8-tetraphenylperhydro-6λ^5-[1,3]dioxolo [4,5-*e*][1,3,2]dioxaphosphepin-6-one (3f)

Prepared according to GP 1 using phosphite (*R*,*R*)-**1** (2.56 g, 5 mmol), TMEDA (0.75 mL, 5 mmol), Et_2Zn (1 N in hexane, 5 mL, 5 mmol) and nitroalkene **2f** (1.225 g, 5 mmol) in THF (20 mL). The crude product was purified by column chromatography (*n*-pentane–Et_2O, 3:2) to give pure **3f** as a yellow-orange solid.

Yield: 86%; mp 93–95 °C; $[\alpha]_D^{26}$ –84.4 (*c* 1.00, $CHCl_3$); de = 84% (^{31}P NMR).

IR ($CHCl_3$): 3063 (w), 3010 (m), 1561 (s), 1496 (m), 1448 (s), 1374 (m), 1257 (s), 1217 (s), 1167 (m), 1107 (m), 1090 (m), 1053 (s), 1039 (s), 1020 (s), 1004 (s), 982 (s), 940 (m), 925 (m), 902 (m), 880 (w), 820 (w), 804 (w), 756 (s), 727 (s), 700 (s), 668 (m), 642 (w), 576 (w), 484 (m), 465 (w) cm^{-1}.

^1H NMR (400 MHz, C_6D_6): δ = 0.53 (s, 3 H, CCH_3), 0.78 (s, 3 H, CCH_3), 3.78 (m, 1 H), 3.83 (m, 1 H), 3.89 (s, 1 H), 3.92 (m, 1 H), 3.90 (s, 5 H, C_5H_5), 4.10 (dt, $^2J_{H-P}$ = 23.6 Hz, $^3J_{H-H}$ = 6.5 Hz, 1 H, PCH), 4.76 (ddd, $^3J_{H-H}$ = 6.6 Hz, $^2J_{H-H}$ = 13.7 Hz, $^3J_{H-P}$ = 16.5 Hz, 1 H, PCCH), 4.99 (ddd, $^3J_{H-H}$ = 6.3 Hz, $^2J_{H-H}$ = 13.7 Hz, $^3J_{H-P}$ = 13.7 Hz, 1 H, PCCH), 5.37 (d, $^3J_{H-H}$ = 8.1 Hz, 1 H, OCH), 5.89 (d, $^3J_{H-H}$ = 8.1 Hz, 1 H, OCH), 7.05–7.96 (m, 20 H, ArH).

^{13}C NMR (100 MHz, C_6D_6): δ = 26.6, 27.1, 38.9 (d, $^1J_{C-P}$ = 145.7 Hz, PO*C*H), 66.3, 67.9, 68.1, 69.4, 69.3, 74.7, 79.2, 79.8, 81.8, 86.9, 91.8, 113.8, 127.0, 127.2, 127.3, 127.7, 127.9, 128.2, 128.2, 128.3, 128.4, 129.1, 130.4, 139.8, 140.0, 144.0, 144.91.

^{31}P NMR (162 MHz, C_6D_6): δ = 17.69.

MS (EI, 70 eV): *m*/*z* (%) = 770.6 (8), 769.5 (45) [M^+], 722.5 (12), 722.4 (15) [$M^+ - HNO_2$], 431.4 (8), 430.3 (5), 345.4 (8), 344.4 (7), 340.3 (13), 339.1 (92), 337.2 (6), 321.1 (11), 305.2 (5), 293.2 (10), 292.2 (72), 291.4 (6), 290.2 (5), 274.1 (27), 268.4 (7), 267.3 (16), 265.3 (8), 252.2 (5), 237.2 (10), 227.2 (6), 213.1 (14), 212.1 (100) [$FcCHCH_2$]$^+$, 211.1 (10), 210.2 (10), 209.3 (9), 208.2 (19), 207.2 (62), 195.2 (6), 191.2 (6), 184.0 (13), 183.2 (5), 180.2 (12), 179.2 (70), 178.2 (75), 168.2 (11), 167.2 (79), 166.2 (10), 165.1 (28), 152.1 (10), 121.2 (13), 105.2 (30), 102.2 (7), 91.3 (11), 77.2 (6).

Anal. Calcd for $C_{43}H_{40}NO_7P$: C, 67.11; H, 5.24; N, 1.82. Found: C, 67.48; H, 5.53; N, 1.35.

(3a*R*,8a*R*)-2,2-Dimethyl-6-[3-nitro-1-(3,4,5-trimethoxyphenyl)-pentyl]-4,4,8,8-tetraphenylperhydro[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-2-one (5a)

Prepared according to GP 1 using phosphite (*R*,*R*)-**1** (512 mg, 1 mmol), TMEDA (0.15 mL, 5 mmol), Et_2Zn (1 N in hexane,1 mL, 1 mmol) and nitroalkene **4a** (267 mg, 1 mmol) in THF (4 mL). The crude product was purified by column chromatography (*n*-pentane–Et_2O, 1:3) to give **5a** as a colorless solid.

Yield: 66%; mp 126 °C; $[\alpha]_D^{26}$ –194.0 (*c* 0.92, $CHCl_3$); de = 75% (^{31}P NMR).

IR (KBr): 3447 (m), 3062 (m), 3027 (w), 2936 (s), 2839 (m), 1592 (s), 1557 (s), 1509 (s), 1498 (s), 1461 (s), 1449 (s), 1425 (s), 1384 (m), 1373 (s), 1332 (s), 1249 (s), 1217 (s), 1189 (s), 1167 (s), 1129 (s), 1090 (s), 1053 (s), 1037 (s), 1014 (s), 971 (s), 938 (s), 902 (m), 883 (m), 859 (m), 802 (w), 789 (w), 745 (s), 727 (m), 699 (s), 660 (m), 642 (m), 577 (w), 556 (m), 540 (w), 488 (w), 467 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.51 (s, 3 H, CCH_3), 0.83 (s, 3 H, CCH_3), 0.95 (t, $^3J_{H-H}$ = 7.4 Hz, 3 H, CH_2CH_3), 1.98 (m, 1 H, CH_2), 2.5 (m, 1 H, CH_2), 3.74 (s, 6 H, OCH_3), 3.78 (dd, $^3J_{H-H}$ = 6.59 Hz, $^2J_{P-H}$ = 20.2 Hz, 1 H, PCH), 3.82 (s, 3 H, OCH_3), 5.1 (d, $^3J_{H-H}$ = 8.2 Hz, 1 H, OCH), 5.16 (m, 1 H, $CHNO_2$), 5.59 (d, $^3J_{H-H}$ = 8.0 Hz, 1 H, OCH), 6.50 (s, 2 H, ArH), 6.8–7.8 (m, 20 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.0, 26.8, 27.3, 27.3, 44.2 (d, $^1J_{C-P}$ = 148.8 Hz, PO*C*H), 56.0, 60.8, 78.6, 80.2, 87.5 (d, $^2J_{C-P}$ = 8.4 Hz, POCH*C*HNO_2), 91.9, 92.3, 105.8, 113.7, 126.4, 126.8, 127.1, 127.1, 127.7, 127.8, 128.1, 128.2, 128.2, 128.4, 129.4, 129.5, 129.6, 137.9, 138.7, 138.9, 139.0, 143.1, 144.2, 153.3.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 18.93.

MS (EI, 70 eV): *m*/*z* (%) = 780 (10) [M^+], 779 (21), 331 (8), 302 (5), 265 (15), 223 (14), 222 (100), 208 (7), 207 (33), 191 (5), 179 (19), 178 (11), 167 (12), 105 (5).

HRMS (EI): *m*/*z* [M + 1] $^+$ calcd for $C_{44}H_{46}NO_{10}P$: 779.285; found: 779.283.

Anal. Calcd for $C_{44}H_{46}NO_{10}P$: C, 67.78; H, 5.95; N, 1.80. Found: C, 68.19; H, 6.25; N, 1.59.

(3a*R*,8a*R*)-2,2-Dimethyl-6-[1-(1-naphthyl)-3-nitropropentyl]-4,4,8,8-tetraphenylperhydro[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-2-one (5b)

Prepared according to GP 1 using phosphite (*R*,*R*)-**1** (512 mg, 1 mmol), TMEDA (0.15 mL, 5 mmol), Et_2Zn (1 N in hexane, 1 mL, 1 mmol) and nitroalkene **4b** (227 mg, 1 mmol) in THF (4 mL). The crude product was purified by column chromatography (*n*-pentane–Et_2O, 4:3) to give **5b** as a colorless solid.

Yield: 87%; mp 138 °C; $[\alpha]_D^{26}$ –183.0 (*c* 0.71, $CHCl_3$); de = 69% (^{31}P NMR).

IR (KBr): 3651 (w), 3449 (m), 3061 (m), 2986 (m), 2933 (m), 1599 (m), 1558 (s), 1496 (m), 1448 (s), 1372 (s), 1260 (s), 1216 (s), 1167 (s), 1105 (m), 1088 (s), 1053 (s), 1037 (s), 1018 (s), 979 (s), 938 (s), 923 (s), 882 (m), 810 (m), 790 (m), 776 (m), 744 (s), 728 (s), 699 (s), 673 (w), 657 (m), 641 (m), 583 (m), 557 (w), 541 (m), 522 (w), 505 (w), 489 (w) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.54 (s, 3 H, CCH_3), 0.83 (s, 3 H, CCH_3), 1.02 (t, $^3J_{H-H}$ = 7.4 Hz, 3 H, CH_2CH_3), 1.98 (m, 2 H, CH_2), 4.98 (m, 2 H, PCH and OCH), 5.13 (m, 1 H, $CHNO_2$), 5.59 (d, $^3J_{H-H}$ = 8.0 Hz, 1 H, OCH), 6.81–8.02 (m, 27 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.2, 26.0, 28.1, 28.3, 44.2 (d, $^1J_{C-P}$ = 147.2 Hz, PO*C*H), 78.6, 80.2, 86.5 (d, $^2J_{C-P}$ = 8.1 Hz, POCH*C*HNO_2), 91.7, 105.4, 113.7, 126.4, 126.8, 127.1, 127.1, 127.7, 127.8, 128.1, 128.2, 128.2, 128.4, 129.4, 129.5, 129.6, 137.9, 138.8, 138.9, 139.0, 143.1, 144.2, 153.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.93.

MS (EI, 70 eV): *m*/*z* (%) = 739 (0.2) [M$^+$], 499 (6), 473 (7), 274 (12), 265 (17), 262 (6), 261 (15), 219 (13), 208 (21), 207 (100), 191 (7), 183 (7), 182 (26), 181 (8), 180 (6), 179 (26), 178 (18), 167 (20), 166 (5), 165 (9), 155 (7), 153 (13), 105 (8).

Anal. Calcd for $C_{45}H_{42}NO_7P$: C, 73.06; H, 5.72; N, 1.89. Found: C, 72.89; H, 5.41; N, 1.66.

(3a*R*,8a*R*)-6-[1-(4-Benzyloxyphenyl)-3-nitropenthyl]-2,2-dimethyl-4,4,8,8-tetraphenylperhydro[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-2-one (5c)

Prepared according to GP 1 using phosphite (*R*,*R*)-**1** (1.024 g, 2 mmol), TMEDA (0.30 mL, 2 mmol), Et_2Zn (1 N in hexane, 2 mL, 2 mmol) and nitroalkene **4c** (0.566 mg, 2 mmol) in THF (8 mL). The crude product was purified by column chromatography (*n*-pentane–Et_2O, 1:1) to give **5c** as a colorless solid.

Yield: 81%; mp 163 °C; $[\alpha]_D^{26}$ –198.2 (*c* 1.31, $CHCl_3$); de = 61% (^{31}P NMR).

IR (KBr): 3463 (w), 3062 (m), 3034 (m), 2985 (m), 2934 (m), 1736 (w), 1610 (m), 1584 (m), 1556 (s), 1511 (s), 1496 (s), 1449 (s), 1373 (s), 1354 (m), 1303 (m), 1251 (s), 1222 (s), 1181 (s), 1167 (s), 1107 (s), 1089 (s), 1053 (s), 1038 (s), 1017 (s), 979 (s), 938 (s), 921 (s), 902 (m), 883 (m), 861 (m), 840 (m), 801 (w), 744 (s), 727 (s), 698 (s), 672 (w), 641 (m), 583 (m), 548 (m), 507 (w), 488 (w) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.43 (s, 3 H, CH_3), 0.86 (s, 3 H, CH_3), 0.92 (t, $^3J_{H-H}$ = 7.4 Hz, 3 H, CH_3), 1.98 (m, 2 H, CH_2), 2.48 (m, 2 H, CH_2), 3.74 (dd, $^3J_{H-H}$ = 12.1 Hz, $^3J_{P-H}$ = 20.1 Hz, 1 H, PCH), 5.01 (s, 2 H, CH_2), 5.02 (d, $^3J_{H-H}$ = 6.32 Hz, 1 H, OC*H*), 5.12 (m, 1 H, C*H*NO_2), 5.57 (d, $^3J_{H-H}$ = 7.97 Hz, 2 H, OCH), 6.84–7.61 (m, 29 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.5, 26.1, 26.7, 26.9, 48.1, 69.8, 78.4, 79.4, 87.2, 91.0, 91.5, 113.6, 114.7, 124.7, 127.0, 127.2, 127.6, 127.6, 127.7, 127.8, 127.9, 128.0, 128.4, 128.5, 129.5, 130.3, 136.5, 139.2, 139.3, 139.5, 139.8, 143.1, 143.7.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.34.

MS (EI, 70 eV): *m*/*z* (%) = 795 (0.01) [M$^+$], 432 (16), 431 (50), 373 (20), 348 (14), 347 (65), 345 (26), 318 (23), 317 (18), 286 (14), 284 (13), 271 (24), 269 (25), 265 (70), 238 (24), 220 (32), 208 (8), 207 (61), 205 (100), 177 (10), 150 (7), 149 (72), 147 (8), 145 (13), 141 (14), 131 (16), 128 (13), 127 (10), 119 (14), 115 (14), 111 (17), 105 (23), 102 (10), 98 (10), 97 (28), 95 (15), 91 (12), 85 (29), 83 (29), 81 (16), 71 (30), 70 (13), 69 (22), 59 (13), 57 (62), 56 (12), 55 (22), 49 (21).

Anal. Calcd for $C_{48}H_{46}NO_8P$: C, 72.44; H, 5.83; N, 1.76. Found: C, 72.27; H, 6.11; N, 1.95.

2-Nitro-1-phenylethylphosphonic Acid (6a)

Prepared according to GP 3 using nitrophosphonate **3a** (1.877 g, 2.8 mmol), NaI (0.851 g, 5.7 mmol) and TMSCl (0.71 mL, 5.7 mmol) in MeCN (10 mL). The crude product was purified by recrystallization (MeOH) to give **6a** as a colorless solid.

Yield: 86%; mp 77 °C; $[\alpha]_D^{26}$ +9.2 (*c* 0.83, MeOH); ee = 92% (HPLC; Daicel OD; *n*-heptane–*i*-PrOH, 9.5:0.5).

IR (KBr): 3418 (s), 3034 (m), 2923 (m), 2323 (w), 1656 (s), 1556 (s), 1496 (m), 1455 (m), 1435 (m), 1377 (s), 1327 (w), 1158 (s), 1084 (m), 989 (s), 941 (s), 838 (m), 776 (m), 751 (m), 701 (s), 596 (w), 545 (m) cm^{-1}.

^{1}H NMR (400 MHz, CD_3OD): δ = 3.92 (ddd, $^3J_{H-H}$ = 4.4 Hz, $^3J_{H-H}$ = 11.3 Hz, $^2J_{P-H}$ 23.9 Hz, 1 H, CHP), 4.95–5.09 (m, 2 H, CH_2), 7.22–7.37 (m, 5 H, ArH).

^{13}C NMR (100 MHz, CD_3OD): δ = 44.9 (d, $^1J_{P-C}$ = 133.5 Hz, POCH), 76.0 (d, $^2J_{P-C}$ = 4.5 Hz, POCH*C*HNO_2), 127.5, 128.5, 128.9, 134.2.

^{31}P NMR (160 MHz, CD_3OD): δ = 19.75.

MS (FAB, negative ions): *m*/*z* (%) = 229 (38), 180 (15), 126 (5), 94 (5), 78 (100), 62 (8).

Anal. Calcd for $C_8H_{10}NO_5P$: C, 41.57; H, 4.67; N, 6.06. Found: C, 41.34; H, 4.95; N, 6.11.

2-Nitro-1-(4-phenylphenyl)ethylphosphonic Acid (6b)

Prepared according to GP 3 using nitrophosphonate **3b** (2.065 g, 2.8 mmol), NaI (0.851 g, 5.7 mmol) and TMSCl (0.71 mL, 5.7 mmol) in MeCN (10 mL). The crude product was purified by recrystallization (MeOH) to give **6b** as a colorless solid.

Yield: 88%; mp 102 °C; $[\alpha]_D^{26}$ +11.2 (*c* 0.91, MeOH); ee = 88% (HPLC; Daicel OD; *n*-heptane–*i*-PrOH, 9.5:0.5).

IR (KBr): 3501 (s), 3029 (m), 2915 (m), 2311 (w), 1667 (s), 1543 (s), 1521 (s), 1496 (s), 1455 (m), 1435 (m), 1377 (s), 1327 (w), 1158 (s), 1084 (m), 989 (s), 941 (s), 844 (m), 786 (m), 733 (m), 710 (s), 575 (w), 545 (m) cm^{-1}.

^{1}H NMR (400 MHz, CD_3OD): δ = 3.81 (ddd, $^3J_{H-H}$ = 5.0 Hz, $^3J_{H-H}$ = 11.8 Hz, $^2J_{P-H}$ 23.2 Hz, 1 H, CHP), 4.88 (m, 2 H, CH_2), 7.31–7.56 (m, 9 H, ArH).

^{13}C NMR (100 MHz, CD_3OD): δ = 44.9 (d, $^1J_{P-C}$ = 133.5 Hz, POCH), 76.0 (d, $^2J_{P-C}$ = 4.5 Hz, POCH*C*H), 127.2, 127.5, 128.5, 128.9, 131.1, 134.2, 135.2.

^{31}P NMR (162 MHz, CD_3OD): δ = 20.1.

MS (FAB, negative ions): *m*/*z* (%) = 305 (43), 272 (27), 2.01 (23), 145 (15), 126 (5), 94 (5), 69 (100), 62 (8).

Anal. Calcd for $C_{14}H_{14}NO_5P$: C, 54.73; H, 4.59; N, 4.56. Found: C, 54.40; H, 4.91; N, 4.20.

2-Nitro-1-(3,4,5-trimethoxyphenyl)ethylphosphonic Acid (6c)

Prepared according to GP 3 using nitrophosphonate **3c** (2.253 g, 2.8 mmol), NaI (0.851 g, 5.7 mmol) and TMSCl (0.71 mL, 5.7 mmol) in MeCN (10 mL). The crude product was purified by recrystallization (MeOH) to give **6c** as a colorless solid.

Yield: 92%; mp 89 °C; $[\alpha]_D^{26}$ +9.8 (*c* 2.5, MeOH); ee = 86% (HPLC; Daicel OD; *n*-heptane–*i*-PrOH, 9.8:0.2).

IR (KBr): 3508 (m), 3011 (w), 2946 (w), 2846 (w), 1595 (s), 1548 (s), 1511 (m), 1459 (m), 1431 (s), 1374 (m), 1336 (m), 1318 (w), 1291 (w), 1252 (s), 1236 (s), 1186 (m), 1154 (m), 1124 (s), 1034 (s), 1015 (s), 988 (s), 941 (s), 909 (m), 857 (m), 814 (w), 776 (w), 651 (m), 537 (m), 455 (m) cm^{-1}.

^{1}H NMR (400 MHz, CD_3OD): δ = 3.72 (s, 3 H, *p*-ArCH_3), 3.81 (s, 6 H, *m*-ArCH_3), 3.92 (ddd, *J* = 5.2 Hz, *J* = 10.7 Hz, *J* = 23.9 Hz, 1 H, CH), 4.96–5.05 (m, 2 H, CH_2), 6.67 (d, *J* = 2.5 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, CD_3OD): δ = 44.7 (d, $^1J_{P-C}$ = 135.2 Hz, PO*C*H), 55.5, 59.9, 75.7 (d, $^2J_{P-C}$ = 4.6 Hz, POCH*C*H), 106.3, 129.7, 133.0, 134.4.

^{31}P NMR (162 MHz, CD_3OD): δ = 20.48.

MS (FAB, negative ions): *m*/*z* (%) = 320 (96), 306 (5), 181 (6), 79 (100).

Anal. Calcd for $C_{11}H_{16}NO_8P$: C, 41.13; H, 5.02; N, 4.36. Found: C, 41.26; H, 5.37; N, 4.01.

1-(4-Methylphenyl)-2-nitroethylphosphonic Acid (6d)

Prepared according to GP 3 using nitrophosphonate **3d** (2.298 g, 3.4 mmol), NaI (1.020 g, 6.8 mmol) and TMSCl (0.85 mL, 6.8 mmol) in MeCN (10 mL). The crude product was purified by recrystallization (MeOH) to give **6d** as a colorless solid.

Yield: 94%; mp 83 °C; $[\alpha]_D^{26}$ +15.3 (*c* 2.5, MeOH); ee = 95% (HPLC; Daicel OD; *n*-heptane–*i*-PrOH, 9.5:0.5).

IR (KBr): 3433 (m), 3033 (m), 2924 (s), 2312 (w), 1637 (m), 1558 (s), 1515 (m), 1479 (w), 1437 (m), 1377 (s), 1158 (s), 1000 (s), 939 (s), 849 (m), 822 (m), 737 (w), 717 (w), 681 (m), 561 (s), 500 (m) cm^{-1}.

^1H NMR (400 MHz, CD_3OD): δ = 2.27 (s, 3 H, CH_3), 3.88 (ddd, $^3J_{H-H}$ = 4.4 Hz, $^3J_{H-H}$ = 11.5 Hz, $^2J_{P-H}$ 23.9 Hz, 1 H, CHP), 4.90–5.03 (m, 2 H, CH_2), 7.12 (d, $^3J_{H-H}$ = 8.0 Hz, 2 H, *o*-ArH), 7.23 (dd, $^3J_{H-H}$ = 1.6 Hz, *J* = 8.0 Hz, 2 H, *m*-ArH).

^{13}C NMR (100 MHz, CD_3OD): δ = 20.1, 44.4 (d, $^1J_{P-H}$ = 135.0 Hz, PO*C*H), 75.9 (d, $^2J_{P-H}$ = 4.6 Hz, POCH*C*H), 128.7, 129.1, 130.8, 137.4.

^{31}P NMR (160 MHz, CD_3OD): δ = 20.38.

MS (FAB, negative ions): *m*/*z* (%) = 243 (80), 209 (6), 180 (11), 158 (6), 78 (100), 62 (6).

Anal. Calcd for $C_9H_{12}NO_5P$: C, 44.09; H, 4.93; N, 5.71. Found: C, 44.32; H, 5.30; N, 5.55.

1-(1-Naphthyl)-2-nitroethylphosphonic Acid (6e)

Prepared according to GP 3 using nitrophosphonate **3e** (2.133 g, 3.0 mmol), NaI (0.899 g, 6.0 mmol) and TMSCl (0.75 mL, 6.0 mmol) in MeCN (10 mL). The crude product was purified by recrystallization (MeOH) to give **6e** as a colorless solid.

Yield: 65%; mp 105 °C; $[\alpha]_D^{26}$ +8.7 (*c* 0.93, MeOH); ee = 91% (HPLC; Daicel OD; *n*-heptane–*i*-PrOH, 9.5:0.5).

IR (KBr): 3551 (s), 3474 (s), 3415 (s), 3050 (w), 2924 (w), 2290 (w), 1637 (m), 1619 (s), 1598 (m), 1556 (s), 1512 (m), 1479 (w), 1435 (w), 1397 (w), 1377 (s), 1334 (w), 1258 (m), 1164 (m), 980 (s), 943 (s), 825 (w), 798 (m), 777 (s), 728 (w), 682 (w), 639 (w), 614 (w), 560 (w), 504 (m) cm^{-1}.

^1H NMR (400 MHz, CD_3OD): δ = 4.96–5.33 (m, 3 H, CH_2CHP), 7.30–8.23 (m, 7 H, ArH).

^{13}C NMR (100 MHz, CD_3OD): δ = 44.9 (d, $^1J_{P-C}$ = 133.5 Hz, PO*C*H), 76.0 (d, $^2J_{P-C}$ = 4.5 Hz, POCH*C*H), 124.9, 125.7, 126.0, 127.5, 128.5, 128.6, 128.9, 134.2, 134.6, 138.9.

^{31}P NMR (160 MHz, CD_3OD): δ = 20.17.

MS (FAB, negative ions): *m*/*z* (%) = 281 (4), 280 (40), 277 (5), 199 (5), 181 (17), 159 (6), 127 (11), 95 (5), 79 (100), 63 (9).

Anal. Calcd for $C_{12}H_{12}NO_5P$: C, 51.26; H, 4.30; N, 4.98. Found: C, 51.45; H, 4.11; N, 5.28.

2-{(*S*)-1-[(3a*R*,8a*R*)-2,2-Dimethyl-6-oxo-4,4,8,8-tetraphenylperhydro-6λ^5-phosphepino[4,5-*d*][1,3]dioxol-6-yl]-2-methylpropyl}malonic Acid Dimethyl Ester (8a)

Prepared according to GP 1 using phosphite (*R*,*R*)-**1** (512 mg, 1 mmol), TMEDA (0.15 mL, 1 mmol), Et_2Zn (1 N in hexane, 1 mL, 1 mmol) and the α,β-unsaturated malonate **7a** (186 mg, 1 mmol) in THF (4 mL). The crude product was purified by column chromatography (*n*-pentane–Et_2O, 2:3) to give **8a** as a colorless oil.

Yield: 89%; $[\alpha]_D^{26}$ –192.2 (*c* 1.00, $CHCl_3$); de = 67% (^{31}P NMR).

IR (KBr): 3458 (m), 3059 (m), 3026 (m), 2989 (m), 2935 (m), 2879 (m), 2340 (w), 2199 (w), 1763 (vs), 1742 (vs), 1688 (m), 1676 (w), 1602 (m), 1497 (s), 1449 (s), 1435 (s), 1383 (m), 1372 (m), 1305 (s), 1263 (vs), 1225 (vs), 1169 (vs), 1137 (s), 1112 (s), 1089 (s), 1054 (s), 1039 (vs), 1017 (vs), 975 (vs), 937 (vs), 917 (vs), 901 (s), 877 (s), 804 (m), 787 (m), 745 (vs), 726 (s), 700 (vs), 675 (m), 652 (m), 641 (m), 617 (w), 591 (m), 581 (m), 560 (m), 535 (m), 519 (m), 487 (m), 464 (w) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.52 (s, 3 H, CCH_3), 0.83 (s, 3 H, CCH_3), 1.09 [d, $^3J_{H-H}$ = 6.6 Hz, 3 H, $CH(CH_3)_2$], 1.11 [d, $^3J_{H-H}$ = 6.9 Hz, 3 H, $CH(CH_3)_2$], 2.20 (m, 1 H, PCH), 2.96 [dt, $^3J_{H-H}$ = 5.8 Hz, 1 H, $(CH_3)_2CH$], 3.38 (s, 3 H, CO_2CH_3), 3.54 (s, 3 H, CO_2CH_3), 3.89 (dd, $^3J_{H-H}$ = 6.9 Hz, $^3J_{P-H}$ = 18.3 Hz, 1 H, PCC*H*CO_2CH_3), 5.30 (d, $^3J_{H-H}$ = 8.0 Hz, 1 H, OCH), 5.61 (d, $^3J_{H-H}$ = 8.0 Hz, 1 H, OCH), 7.20–7.77 (m, 20 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 21.5, 26.9, 27.0, 28.0, 44.7 (d, $^1J_{P-C}$ = 145.7 Hz, PO*C*H), 52.6 (d, $^2J_{P-C}$ = 29.1 Hz, POCH*C*H), 52.6, 78.5, 79.3, 86.9, 91.1, 113.3, 126.8, 126.9, 127.1, 127.2, 127.3, 127.6, 127.6, 127.7, 127.7, 128.8, 128.9, 129.9, 139.7, 139.9, 143.9, 144.80, 167.9, 168.0.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.53.

MS (EI, 70 eV): *m*/*z* (%) = 252 (10), 251 (100), 219 (17), 207 (16), 179 (11), 178 (8), 123 (5), 105 (7).

MS (CI, 100 eV): *m*/*z* (%) = 699 (100), 471 (6), 463 (14), 460 (6), 459 (21), 447 (10), 432 (18), 431 (60), 269 (58), 251 (28), 155 (7).

Anal. Calcd for $C_{40}H_{43}O_9P$: C, 68.76; H, 6.20. Found: C, 68.60; H, 6.29.

2-{(*S*)-1-[(3a*R*,8a*R*)-2,2-Dimethyl-6-oxo-4,4,8,8-tetraphenylperhydro-6λ^5-phosphepino[4,5-*d*][1,3]dioxol-6-yl]-1-phenylmethyl}malonic Acid Dimethyl Ester (8b)

Prepared according to GP 2 using 2-benzylidene malonic acid dimethylester **7b** (220 mg, 1.0 mmol), phosphite (*R*,*R*)-**1** (512 mg, 1.0 mmol) and Fe_2O_3/KOH (2.698 g, 2.5 equiv KOH) in H_2O (92 μL). The crude product was purified by column chromatography (*n*-pentane–Et_2O, 1:1) to give **8b** as a colorless solid.

Yield: 64%; mp 210 °C; $[\alpha]_D^{26}$ –147.3 (*c* 1.00, $CHCl_3$); de = 86% (^{31}P NMR).

IR (KBr): 3445 (m), 362 (m), 3028 (m), 2986 (m), 2960 (m), 2922 (m), 2195 (w), 1742 (vs), 1705 (m), 1658 (m), 1639 (m), 1602 (m), 1561 (m), 1543 (m), 1525 (m), 1497 (s), 1458 (s), 1431 (m), 1380 (m), 1328 (m), 1290 (s), 1261 (vs), 1229 (vs), 1205(s), 1170 (s), 1155 (s), 1116 (s), 1088 (s), 1055 (s), 1036 (vs), 1010 (vs), 962 (vs), 940 (vs), 920 (s), 901 (s), 883 (s), 806 (m), 791 (s), 745 (s), 726 (s), 699 (vs), 673 (m), 641 (m), 616 (w), 581 (m), 562 (m), 540 (m), 518 (m), 499 (m), 483 (w), 465 (w) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.32 (s, 3 H, CCH_3), 0.76 (s, 3 H, CCH_3), 3.36 (s, 3 H, CO_2CH_3), 3.52 (s, 3 H, CO_2CH_3), 4.09–4.37 (m, 2 H, PC*HCH*), 4.87 (d, $^3J_{H-H}$ = 8.0 Hz, 1 H, OCH), 5.46 (d, $^3J_{H-H}$ = 8.0 Hz, 1 H, OCH), 6.90–7.46 (m, 25 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.8, 26.3, 44.9 (d, $^1J_{C-P}$ = 122.1 Hz, PO*C*H), 52.7 (d, $^2J_{C-P}$ = 23.7 Hz, POCH*C*H), 52.9, 86.5, 86.6, 88.6, 89.9, 113.0, 126.2, 126.4, 126.7, 126.8, 127.0, 127.0, 127.1, 127.3, 127.4, 127.5, 127.7, 127.7, 127.8, 128.0, 128.0, 128.3, 128.5, 129.2, 133.1, 139.5, 143.1, 143.2, 166.6, 166.9.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 20.06.

MS (EI, 70 eV): *m*/*z* (%) = 467 (7), 286 (13), 285 (100), 265 (6), 253 (12), 208 (6), 207 (23), 179 (12), 178 (9), 167 (6), 165 (5), 131 (5), 105 (6).

MS (CI, 100 eV): *m*/*z* (%) = 163 (6), 119 (7), 117 (14), 93 (10), 89 (100), 75 (50), 73 (54), 61 (17).

Anal. Calcd for $C_{43}H_{41}O_9P$: C, 70.48; H, 5.64. Found: C, 70.88; H, 5.21.

2-{(*S*)-1-[(3a*R*,8a*R*)-2,2-Dimethyl-6-oxo-4,4,8,8-tetraphenylperhydro-6λ^5-phosphepino[4,5-*d*][1,3]dioxol-6-yl]-1-(1,3-benzodioxol-5-yl)methyl}malonic Acid Dimethyl Ester (8c)

Prepared according to GP 2 using **7c** (264 mg, 1.0 mmol), phosphite (*R*,*R*)-**1** (512 mg, 1.0 mmol) and Fe_2O_3/KOH (2.698 g, 2.5 equiv KOH) in H_2O (92 μL). The crude product was purified by column chromatography (*n*-pentane–Et_2O, 2:3) to give **8c** as a colorless solid.

Yield: 67%; mp 110 °C; $[\alpha]_D^{26}$ –130.3 (*c* 1.00, $CHCl_3$); de = 91% (^{31}P NMR).

IR (KBr): 3466 (w), 3061 (m), 3028 (m), 2991 (m), 2952 (m), 2902 (m), 1763 (s), 1743 (vs), 1608 (w), 1490 (s), 1447 (s), 1384 (m), 1373 (m), 1348 (m), 1249 (vs), 1219 (s), 1166 (s), 1105 (m), 1089 (s), 1052 (vs), 1038 (vs), 1019 (vs), 984 (s), 936 (s), 884 (m), 819 (w), 804 (w), 744 (s), 728 (s), 700 (s), 672 (w), 655 (m), 642 (m), 574 (w), 548 (w), 510 (w), 454 (w) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.35 (s, 3 H, CCH_3), 0.92 (s, 3 H, CCH_3), 3.47 (s, 3 H, CO_2CH_3), 3.52 (s, 3 H, CO_2CH_3), 4.16 (dd, $^3J_{H-H}$ = 12.1 Hz, $^2J_{P-H}$ = 20.6 Hz, 1 H, PCH), 4.87 (dd, $^3J_{H-H}$ = 9.7 Hz, $^2J_{P-H}$ = 10.3 Hz, 1 H, PCCH), 4.94 (d, $^3J_{H-H}$ = 8.2 Hz, 1 H, OCH), 5.47 (d, $^3J_{H-H}$ = 7.8 Hz, 1 H, OCH), 5.89 (d, $^3J_{H-H}$ = 1.4 Hz, 1 H), 5.93 (d, $^2J_{H-H}$ = 1.6 Hz, 1 H, OCH_2), 6.57–7.35 (m, 23 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.9, 27.0, 44.7 (d, $^1J_{C-P}$ = 147.2 Hz, POCH), 52.6, 52.7 (d, $^2J_{C-P}$ = 25.9 Hz, POCH*C*H), 86.5, 86.6, 88.6, 89.9, 100.9, 110.2, 110.1, 113.2, 126.6, 126.4, 126.9, 127.0, 127.4, 127.4, 127.6, 127.6, 127.7, 127.9, 128.6, 129.3, 139.1, 139.6, 143.3, 143.7, 146.7, 147.2, 166.6, 166.8.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 20.09.

MS (EI, 70 eV): *m*/*z* (%) = 330 (7), 329 (45), 328 (100), 297 (8), 283 (6), 269 (12), 268 (9), 265 (11), 237 (6), 207 (19), 201 (9), 196 (5), 179 (31), 175 (11), 165 (40), 146 (5), 145 (6), 131 (6), 125 (6), 119 (6), 109 (6), 105 (20), 97 (12), 91 (8), 85 (18), 83 (19), 73 (10), 69 (24), 57 (41), 51 (8), 45 (27).

MS (CI, 100 eV): *m*/*z* (%) = 779 (12), 778 (17), 777(100), 265 (15), 207 (27).

Anal. Calcd for $C_{44}H_{41}O_{11}P$: C, 68.04; H, 5.32. Found: C, 67.83; H, 5.54.

2-{(*S*)-1-[(3a*R*,8a*R*)-2,2-Dimethyl-6-oxo-4,4,8,8-tetraphenylperhydro-6λ^5-phosphepino[4,5-*d*] [1,3]dioxol-6-yl]-1-(4-phenylphenyl)methyl}malonic Acid Dimethyl Ester (8d)

Prepared according to GP 2 using **7d** (296 mg, 1.0 mmol), phosphite (*R*,*R*)-**1** (512 mg, 1.0 mmol) and Fe_2O_3/KOH (2.698 g, 2.5 equiv KOH) in H_2O (92 μL). The crude product was purified by column chromatography (*n*-pentane–Et_2O, 2:3) to give **8d** as a colorless solid.

Yield: 63%; mp 154 °C; $[\alpha]_D^{26}$ –138.9 (*c* 1.00, $CHCl_3$); de = 94% (^{31}P NMR).

IR (KBr): 3448 (m), 3060 (m), 3030 (m), 2990 (m), 2951 (s), 2935 (m), 2866 (m), 2340 (m), 2191 (m), 1763 (vs), 1743 (vs), 1687 (m), 1676 (w), 1655 (m), 1638 (m), 1618 (m), 1601 (m), 1585 (m), 1495 (s), 1449 (s), 1435 (s), 1384 (m), 1374 (m), 1352 (s), 1321 (s), 1264 (vs), 1217 (vs), 1166 (vs), 1107 (s), 1089 (s), 1053 (vs), 1038 (vs), 1018 (vs), 982 (vs), 938 (s), 902 (s), 883 (s), 862 (m), 844 (m), 762 (m), 744 (s), 728 (s), 699 (vs), 672 (m), 641 (m), 581 (m), 561 (m), 521 (m), 504 (m), 457 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.32 (s, 3 H, CCH_3), 0.91 (s, 3 H, CCH_3), 3.42 (s, 3 H, CO_2CH_3), 3.53 (s, 3 H, CO_2CH_3), 4.32 (dd, $^3J_{H-H}$ = 11.8 Hz, $^2J_{P-H}$ = 18.9 Hz, 1 H, PCH), 4.40 (dd, $^3J_{H-H}$ = 1.1 Hz, $^2J_{P-H}$ = 12.1 Hz, 1 H), 4.92 (d, $^3J_{H-H}$ = 7.8 Hz, 1 H, OCH), 5.47 (d, $^3J_{H-H}$ = 7.8 Hz, 1 H, OCH), 6.57–7.35 (m, 29 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.8, 27.0, 44.3 (d, $^1J_{C-P}$ = 146.5 Hz, POCH), 52.4, 52.9 (d, $^2J_{C-P}$ = 29.9 Hz, POCH*C*H), 79.0, 80.1, 86.7, 90.0, 113.2, 126.6, 126.3, 126.6, 126.6, 127.7, 127.0, 127.2, 127.4, 127.5, 127.6, 127.6, 127.8, 127.9, 127.5, 128.6, 129.3, 132.3, 139.0, 139.9, 140.1, 143.2, 143.7, 166.6, 166.8.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.98.

MS (EI, 70 eV): *m*/*z* (%) = 362 (19), 361 (100), 360 (33), 329 (8), 315 (6), 301 (14), 300 (5), 265 (11), 238 (8), 233 (5), 208 (6), 207 (23), 197 (15), 179 (18), 178 (16), 167 (8), 165 (8), 105 (8).

MS (CI, 100 eV): *m*/*z* (%) = 809 (100), 459 (9), 432 (8), 431 (24), 380 (9), 379 (49), 361 (24), 325 (5), 297 (17), 265 (28), 239 (14).

Anal. Calcd for $C_{49}H_{45}O_9P$: C, 72.76; H, 5.61. Found: C, 72.38; H, 6.01.

2-{(*S*)-1-[(3a*R*,8a*R*)-2,2-Dimethyl-6-oxo-4,4,8,8-tetraphenylperhydro-6λ^5-phosphepino[4,5-*d*] [1,3]dioxol-6-yl]-1-(4-phenylmethyl)methyl}malonic Acid Dimethyl Ester (8e)

Prepared according to GP 2 using **7e** (234 mg, 1.0 mmol), phosphite (*R*,*R*)-**1** (512 mg, 1.0 mmol) and Fe_2O_3/KOH (2.698 g, 2.5 equiv KOH) in H_2O (92 μL). The crude product was purified by column chromatography (*n*-pentane–Et_2O, 1:1) to give **8e** as a colorless solid.

Yield: 75%; mp 205–206 °C; $[\alpha]_D^{26}$ –136.9 (*c* 1.00, $CHCl_3$); de = 82% (^{31}P NMR).

IR (KBr): 3454 (m), 3061 (m), 3027 (m), 2988 (m), 2954 (m), 2930 (m), 1747 (vs), 1602 (w), 1515 (m), 1496 (m), 1449 (s), 1433 (m), 1383 (m), 1373 (m), 1321 (m), 1266 (vs), 1222 (vs), 1168 (s), 1107 (s), 1090 (s), 1053 (s), 1037 (vs), 1015 (vs), 980 (s), 964 (s), 939 (s), 922 (s), 900 (m), 645 (m), 616 (w), 585 (m), 565 (m), 532 (m), 504 (w), 485 (w), 467 (w) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.33 (s, 3 H, CCH_3), 0.93 (s, 3 H, CCH_3), 2.32 (s, 3 H, $ArCH_3$), 3.42 (s, 3 H, CO_2CH_3), 3.53 (s, 3 H, CO_2CH_3), 4.23 (dd, $^3J_{H-H}$ = 11.9 Hz, $^2J_{P-H}$ = 21.8 Hz, 1 H, PCH), 4.40 (dd, $^3J_{H-H}$ = 10.7 Hz, $^3J_{P-H}$ = 11.9 Hz, 1 H), 4.92 (d, $^3J_{H-H}$ = 7.8 Hz, 1 H, OCH), 5.47 (d, $^3J_{H-H}$ = 7.8 Hz, 1 H, OCH), 6.57–7.35 (m, 24 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 25.8, 27.0, 44.6 (d, $^1J_{C-P}$ = 146.8 Hz, POCH), 52.6, 52.8 (d, $^2J_{C-P}$ = 29.0 Hz, POCH*C*H), 78.1, 80.2, 86.7, 90.0, 113.1, 126.3, 126.8, 127.0, 127.3, 127.5, 127.5, 127.7, 127.7, 127.8, 128.6, 128.7, 129.3, 130.1, 136.8, 139.4, 143.4, 143.9, 166.8, 167.0.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 20.24.

MS (EI, 70 eV): *m*/*z* (%) = 300 (15), 299 (100), 267 (15), 207 (19), 203 (6), 179 (14), 178 (12), 171 (7), 167 (6), 145 (7), 135 (12), 105 (7), 57 (6).

MS (CI, 100 eV): *m*/*z* (%) = 749 (17), 748 (32), 299 (6), 236 (14), 235 (100), 177 (59).

Anal. Calcd for $C_{44}H_{43}O_9P$: C, 70.77; H, 5.80. Found: C, 70.93; H, 6.18.

2-{(*S*)-1-[(3a*R*,8a*R*)-2,2-Dimethyl-6-oxo-4,4,8,8-tetraphenylperhydro-6λ^5-phosphepino[4,5-*d*] [1,3]dioxol-6-yl]-1-(3,4,5-trimethoxyphenyl)methyl}malonic Acid Dimethyl Ester (8f)

Prepared according to GP 2 using phosphite (*R*,*R*)-**1** (512 mg, 1 mmol), **7f** (0.31 g, 1 mmol) and Fe_2O_3/KOH (2.698 g, 2.5 equiv KOH) in H_2O (92 μL). The crude product was purified by column chromatography (*n*-pentane–Et_2O, 3:7) to give **8f** as a colorless solid.

Yield: 71%; mp 162 °C; $[\alpha]_D^{26}$ –126.3 (*c* 1.00, $CHCl_3$); de = 89% (^{31}P NMR).

IR (KBr): 3449 (m), 3061 (m), 2992 (m), 2938 (m), 2839 (m), 1763 (s), 1743 (vs), 1591 (s), 1509 (s), 1498 (s), 1449 (s), 1431 (s), 1384 (m), 1374 (m), 1332 (s), 1257 (vs), 1216 (s), 1165 (s), 1128 (vs), 1090 (s), 1053 (s), 1036 (vs), 1017 (vs), 938 (s), 884 (m), 744 (s), 728 (m), 700 (s), 659 (m), 641 (m), 557 (w), 536 (w), 488 (w), 466 (w) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.38 (s, 3 H, CCH_3), 1.02 (s, 3 H, CCH_3), 3.46 (s, 3 H, CO_2CH_3), 3.50 (s, 3 H, CO_2CH_3), 4.25 (dd, $^3J_{H-H}$ = 11.2 Hz, $^2J_{P-H}$ = 21.6 Hz, 1 H, PCH), 4.41 (dd, $^3J_{H-H}$ = 10.7 Hz, $^3J_{P-H}$ = 11.9 Hz, 1 H), 4.97 (d, $^3J_{H-H}$ = 8.2 Hz, 1 H, OCH), 5.55 (d, $^3J_{H-H}$ = 7.8 Hz, 1 H, OCH), 6.48 (d, $^4J_{H-H}$ = 2.2 Hz, 2 H, ArH), 6.57–7.35 (m, 20 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.4, 26.7, 44.2 (d, $^1J_{C-P}$ = 148.8 Hz, POCH), 56.0, 60.8, 75.1, 78.5, 79.6, 87.2, 91.6, 105.8 (d, $^2J_{C-P}$ = 6.1 Hz, POCH*C*H), 113.7, 126.4, 126.8, 127.1, 127.1, 127.7, 127.8, 128.1, 128.2, 128.2, 128.4, 129.4, 137.9, 138.8, 138.9, 139.0, 143.0, 144.2, 144.9, 153.3.

MS (EI, 70 eV): *m/z* (%) = 824 (18), 823 (32), 391 (5), 375 (32), 374 (100), 346 (33), 343 (16), 315 (9), 314 (6), 311 (9), 279 (6), 265 (13), 252 (16), 247 (10), 237 (19), 211 (24), 208 (9), 207 (28), 205 (5), 196 (9), 195 (8), 191 (6), 179 (38), 167 (27), 155 (5), 152 (8), 149 (9), 141 (7), 139 (8), 137 (6), 135 (6), 133 (6), 131 (5), 129 (7), 125 (13), 119 (12), 115 (8), 111 (24), 107 (5), 105 (27), 104 (7), 97 (34), 91 (11), 87 (8), 83 (39), 79 (8), 77 (15), 73 (21), 71 (44), 69 (44), 64 (16), 60 (40), 57 (88), 55 (66), 46 (20), 45 (55).

MS (CI, 100 eV): *m/z* (%) = 825 (7), 824 (16), 312 (16), 311 (100), 310 (7), 279 (9), 253 (8), 237 (11).

Anal. Calcd for $C_{46}H_{47}O_{12}P$: C, 67.15; H, 5.76. Found: C, 66.78; H, 5.81.

2-[(Dimethoxyphosphoryl)phenylmethyl]malonic Acid Dimethyl Ester (9b)

Prepared according to GP 4 using β-phosphonomalonate **8b** (732 mg, 1.0 mmol), NaI (601 mg, 4.0 mmol) and TMSCl (0.5 mL, 4.0 mmol) in MeCN (4 mL). The crude product was purified by column chromatography (*n*-heptane–*i*-propanol, 4:1) to give **9b** as a colorless solid.

Yield: 72%; mp 78 °C; $[\alpha]_D^{26}$ +7.2 (*c* 0.94, MeOH); ee = 84% (HPLC; Daicel OD; *n*-heptane–*i*-PrOH, 9.5:0.5).

IR (KBr): 3469 (br w), 3032 (w), 2960 (m), 2858 (w), 1738 (vs), 1497 (m), 1455 (m), 1434 (m), 1326 (m), 1301 (m), 1253 (vs), 1214 (s), 1185 (m), 1153 (s), 1091 (m), 1065 (s), 1024 (s), 980 (w), 855 (m), 841 (m), 803 (m), 764 (w), 699 (m), 559 (m) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.42 (s, 3 H, CO_2CH_3), 3.49 (d, $^2J_{C-P}$ = 10.4 Hz, 3 H, $POCH_3$), 3.68 (d, $^2J_{C-P}$ = 11.0 Hz, 3 H, CO_2CH_3), 3.82 (s, 3 H, CO_2CH_3), 4.01 (dd, $^3J_{H-H}$ = 11.8 Hz, $^2J_{P-H}$ = 20.3 Hz, 1 H, PCH), 4.24 (dd, $^3J_{H-H}$ = 11.8 Hz, $^3J_{P-H}$ = 10.2 Hz, 1 H, PCCH), 7.25–7.36 (m, 5 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.6 (d, $^1J_{C-P}$ = 138.9 Hz, POCH), 52.5, 52.9, 53.0, 53.7 (d, $^2J_{C-P}$ = 6.1 Hz, POCH*C*H), 127.7, 128.4, 129.4, 132.9, 166.6, 167.4.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 27.82.

MS (EI, 70 eV): *m/z* (%) = 331 (6), 330 (34) [M$^+$], 299 (10), 298 (9), 297 (7), 272 (8), 271 (61), 267 (14), 266 (26), 240 (14), 239 (100), 211 (6), 189 (35), 162 (7), 161 (13), 157 (10), 145 (19), 135 (5), 131 (51), 121 (56), 117 (5), 115 (6), 109 (15), 103 (25), 102 (7), 93 (14), 91 (11), 79 (7), 77 (14), 63 (5), 59 (11).

Anal. Calcd for $C_{14}H_{19}O_7P$: C, 50.91; H, 5.80. Found: C, 50.96; H, 5.96.

2-[(1,3-Benzodioxol-5-yl)(dimethoxyphosphoryl)methyl]malonic Acid Dimethyl Ester (9c)

Prepared according to GP 4 using β-phosphonomalonate **8c** (777 mg, 1.0 mmol), NaI (601 mg, 4.0 mmol) and TMSCl (0.5 mL, 4.0 mmol) in MeCN (4 mL). The crude product was purified by column chromatography (*n*-heptane–*i*-propanol, 4:1) to give **9c** as a colorless solid.

Yield: 86%; mp 94 °C; $[\alpha]_D^{26}$ +5.2 (*c* 1.32, MeOH); ee = 92% (HPLC; Daicel AD2; *n*-heptane–*i*-PrOH, 9.5:0.5).

IR (KBr): 3005 (w), 2957 (m), 2889 (m), 2853 (w), 1736 (vs), 1510 (s), 1491 (s), 1442 (s), 1346 (m), 1313 (m), 1252 (vs), 1214 (s), 1155 (vs), 1105 (m), 1057 (vs), 1034 (vs), 931 (m), 878 (m), 840 (s), 762 (s), 627 (s), 526 (m), 479 (w) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.50 (s, 3 H, CO_2CH_3), 3.55 (d, $^3J_{P-H}$ = 10.7 Hz, 3 H, $POCH_3$), 3.69 (d, $^3J_{P-H}$ = 11.3 Hz, 3 H, $POCH_3$), 3.80 (s, 3 H, CO_2CH_3), 3.91 (dd, $^3J_{H-H}$ = 11.8 Hz, $^2J_{P-H}$ = 20.3 Hz, 1 H, PCH), 4.14 (dd, $^3J_{P-H}$ = 10.4 Hz, $^3J_{H-H}$ = 11.5 Hz, 1 H, PCCH), 6.74–6.86 (m, 3 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.2 (d, $^1J_{C-P}$ = 139.6 Hz, PO*C*H), 52.6, 53.0, 53.2, 53.8 (d, $^2J_{C-P}$ = 6.9 Hz, POCH*C*H), 101.1, 108.2, 109.8, 122.9, 126.4, 147.1, 147.5, 166.6, 167.3.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 27.86.

MS (EI, 70 eV): *m/z* (%) = 375 (6), 374 (42) [M$^+$], 342 (11), 315 (18), 314 (10), 311 (18), 310 (46), 284 (13), 283 (100), 282 (7), 233 (9), 206 (21), 201 (12), 175 (21), 173 (6), 166 (6), 165 (55), 147 (5), 146 (8), 145 (20), 135 (7), 117 (11), 109 (10), 93 (30), 89 (18), 79 (7), 63 (8), 59 (10).

Anal. Calcd for $C_{15}H_{19}O_9P$: C, 48.14; H, 5.12. Found: C, 48.25; H, 5.07.

2-[(Dimethoxyphosphoryl)(4-phenylphenyl)methyl]malonic Acid Dimethyl Ester (9d)

Prepared according to GP 4 using β-phosphonomalonate **8d** (809 mg, 1.0 mmol), NaI (601 mg, 4.0 mmol) and TMSCl (0.5 mL, 4.0 mmol) in MeCN (4 mL). The crude product was purified by column chromatography (*n*-heptane–*i*-propanol, 4:1) to give **9d** as a colorless solid.

Yield: 77%; mp 70–75 °C; $[\alpha]_D^{26}$ +12.1 (*c* 0.82, MeOH).

IR (KBr): 3464 (m), 3032 (m), 3002 (m), 2954 (s), 2872 (m), 2849 (m), 1735 (vs), 1601 (w), 1522 (m), 1489 (s), 1436 (s), 1413 (m), 1344 (m), 1307 (s), 1254 (vs), 1215(s), 1183 (s), 1156 (s), 1053 (vs), 1024 (vs), 936 (m), 855 (s), 826 (s), 804 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3,45 (s, 3 H, CO_2CH_3), 3.54 (d, $^3J_{P-H}$ = 10.7 Hz, 3 H, $POCH_3$), 3.70 (d, $^3J_{P-H}$ = 11.0 Hz, 3 H, $POCH_3$), 3.82 (s, 3 H, CO_2CH_3), 4.06 (dd, $^2J_{P-H}$ = 20.3 Hz, $^3J_{H-H}$ = 11.8 Hz, 1 H, PCH), 4.27 (dd, $^3J_{H-H}$ = 11.8 Hz, $^3J_{P-H}$ = 9.9 Hz, 1 H, PCCH), 7.30–7.59 (m, 9 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.2 (d, $^1J_{C-P}$ = 139.6 Hz, POCH), 52.6, 53.0, 53.0, 53.8 (d, $^2J_{C-P}$ = 6.1 Hz, POCH*C*H), 126.8, 127.0, 127.3, 128.6, 129.7, 131.9, 140.1, 140.4, 166.7, 167.4.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 27.86.

MS (EI, 70 eV): *m/z* (%) = 407 (10), 406 (43) [M$^+$], 374 (12), 347 (34), 343 (12), 342 (36), 316 (19), 315 (100), 265 (11), 238 (9), 233 (6), 221 (6), 207 (16), 205 (6), 198 (7), 197 (49), 179 (12), 178 (35), 176 (5), 172 (7), 167 (5), 165 (15), 152 (7), 109 (7), 93 (16), 59 (7).

Anal. Calcd for $C_{20}H_{23}O_7P$: C, 59.11; H, 5.70. Found: C, 58.83; H, 5.92.

2-[(Dimethoxyphosphoryl)(4-methylphenyl)methyl]malonic Acid Dimethyl Ester (9e)

Prepared according to GP 4 using β-phosphonomalonate **8e** (747 mg, 1.0 mmol), NaI (601 mg, 4.0 mmol) and TMSCl (0.5 mL, 4.0 mmol) in MeCN (4 mL). The crude product was purified by column chromatography (*n*-heptane–*i*-propanol, 4:1) to give **9e** as a colorless solid.

Yield: 74%; mp 103 °C; $[\alpha]_D^{26}$ +6.7 (*c* 0.63, MeOH); ee = 84% (HPLC; Daicel OD2; *n*-heptane–*i*-PrOH, 9:1).

IR (KBr): 2957 (m), 2857 (w), 1768 (vs), 1735 (m), 1514 (m), 1439 (m), 1354 (m), 1311 (s), 1250 (vs), 1225 (m), 1210 (m), 1179 (m), 1140 (s), 1056 (vs), 1025 (vs), 966 (m), 936 (w), 851 (s), 828 (m), 816 (m), 767 (s), 719 (w), 563 (s), 524 (w) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3 H, $ArCH_3$), 3.43 (s, 3 H, CO_2CH_3), 3.50 (d, $^3J_{P-H}$ = 10.7 Hz, 2 H, $POCH_3$), 3.67 (d, $^3J_{P-H}$ = 10.7 Hz, 3 H, $POCH_3$), 3.80 (s, 3 H, CO_2CH_3), 3.97 (dd, $^3J_{H-H}$ = 11.9 Hz, $^2J_{P-H}$ = 20.2 Hz, 1 H, PCH), 4.18 (dd, $^3J_{P-H}$ = 9.9

Hz, $^3J_{H-H}$ = 11.8 Hz, 1 H), 7.11 (d, *J* = 8.2 Hz, 2 H, ArH), 7.22 (dd, *J* = 2.2 Hz, *J* = 8.2 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 43.2 (d, $^1J_{P-C}$ = 138.9 Hz, POCH), 52.5, 53.0, 53.1, 53.7 (d, $^2J_{P-C}$ = 6.1 Hz, POCH*C*H), 129.1, 129.3, 129.8, 137.4, 166.7, 167.5.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.07.

MS (EI, 70 eV): *m*/*z* (%) = 345 (7), 344 (40) [M$^+$], 313 (8), 312 (7), 286 (6), 285 (45), 281 (12), 280 (35), 254 (13), 253 (100), 225 (8), 203 (13), 175 (5), 171 (6), 159 (10), 145 (23), 136 (5), 135 (53), 117 (9), 116 (7), 115 (16), 109 (8), 93 (16), 91 (10), 59 (7).

Anal. Calcd for $C_{15}H_{21}O_7P$: C, 52.33; H, 6.15. Found: C, 52.64; H, 6.40.

2-[(Dimethoxyphosphoryl)(3,4,5-trimethoxyphenyl)methyl]malonic Acid Dimethyl Ester (9f)

Prepared according to GP 4 using β-phosphonomalonate **8f** (822 mg, 1.0 mmol), NaI (601 mg, 4.0 mmol) and TMSCl (0.5 mL, 4.0 mmol) in MeCN (4 mL). The crude product was purified by column chromatography (*n*-heptane–*i*-propanol, 4:1) to give **9f** as a colorless solid.

Yield: 82%; mp 95 °C; $[\alpha]_D^{26}$ +9.8 (*c* 1.02, MeOH); ee = 90% (HPLC; Daicel AD2; *n*-heptane–*i*-PrOH, 9:1).

IR (KBr): 3001 (m), 2954 (m), 2849 (m), 1757 (vs), 1590 (s), 1510 (m), 1462 (s), 1428 (s), 1331 (m), 1299 (s), 1259 (vs), 1177 (s), 1125 (vs), 1061 (s), 1038 (vs), 1006 (s), 915 (m), 874 (m), 827 (m), 652 (m), 613 (w), 532 (m) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.48 (s, 3 H, *p*-$ArOCH_3$), 3.54 (d, $^3J_{P-H}$ = 10.7 Hz, 3 H, $POCH_3$), 3.70 (d, $^3J_{P-H}$ = 10.7 Hz, 3 H, $POCH_3$), 3.81 (s, 3 H, CO_2CH_3), 3.82 (s, 3 H, CO_2CH_3), 3.85 (s, 6 H, *m*-$ArOCH_3$), 3.93 (dd, $^3J_{H-H}$ = 11.8 Hz, $^2J_{P-H}$ = 20.3 Hz, 1 H, PCH), 4.21 (dd, $^3J_{P-H}$ = 10.4 Hz, $^3J_{H-H}$ = 11.7 Hz, 1 H, PCHCH), 6.58 (s, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.7 (d, $^1J_{P-C}$ = 139.6 Hz, POCH), 52.7, 52.9, 53.0, 53.9 (d, $^2J_{P-C}$ = 6.9 Hz, POCH*C*H), 56.1, 60.8, 106.9, 128.3, 138.8, 152.9, 166.6, 167.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 27.9.

MS (EI, 70 eV): *m*/*z* (%) = 421 (14), 420 (77) [M$^+$], 361 (11), 360 (14), 357 (20), 356 (45), 341 (8), 330 (15), 329 (100), 328 (6), 313 (7), 311 (14), 310 (8), 289 (12), 279 (14), 252 (17), 247 (14), 237 (15), 235 (7), 212 (6), 211 (50), 205 (5), 181 (10), 178 (5), 177 (10), 163 (6), 151 (5), 149 (8), 135 (6), 119 (5), 109 (16), 93 (35), 79 (8), 59 (9).

Anal. Calcd for $C_{17}H_{25}O_{10}P$: C, 48.58; H, 5.99. Found: C, 48.72; H, 5.99.

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