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Asymmetric Michael additions of a β-oxophosphonate to nitroalkenes in the presence of chiral diamine complexes

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ABSTRACT

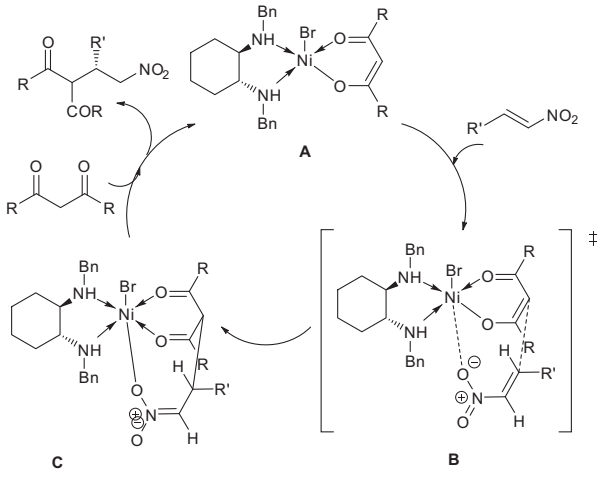
Transition metal catalyzed asymmetric Michael additions of dimethyl (2-oxo-2-phenylethyl)phosphonate to a variety of aromatic nitroalkenes have been developed. The effects of ligand structure, metal ions, and solvent on the reaction are described. Ni(II)–bis[(1*R*,2*R*)-*N*,*N*′-dibenzylcyclohexane-1,2-diamine]Br_2 was found to be an effective catalyst for this reaction. The corresponding adducts were obtained in the presence of this complex in good yields and with excellent enantioselectivity (up to 99% ee). The absolute configurations of the reaction products were determined by X-ray diffraction.

1. Introduction

Chiral γ-nitro phosphonates are valuable building blocks for the synthesis of γ-amino phosphonates—GABA and GABOB analogs because many of them exhibit neurotropic activity.[1] Therefore the development of a highly efficient method for the synthesis of these molecules is of great interest.[2] Asymmetric conjugate additions of phosphorus containing Michael donors to nitroalkenes are considered as a possible route for the synthesis of the precursors of these compounds.[3]

Transition metal catalyzed nucleophilic addition to electron-deficient unsaturated compounds is a powerful and environmentally friendly strategy for the stereoselective synthesis of highly valuable chiral building blocks.[4] The most practical process is the enantioselective addition of 1,3-dicarbonyl compounds to nitroalkenes, which provide access to synthetically useful enantioenriched nitro derivatives under mild conditions. High yields and enantioselectivities have been obtained for the conjugate addition of activated methylene compounds, such as 1,3-diketones, ketoesters, and malonates, to nitrostyrenes in the presence of magnesium,[5] nickel,[6] cobalt,[7] manganese[7], and ruthenium[8] complexes.

The most remarkable results were obtained with Ni(II)–bis[(*R*,*R*)-*N*,*N*′-dibenzylcyclohexane-1,2-diamine]Br_2 as the catalyst for the Michael additions of 1,3-dicarbonyl compounds to nitroalkenes at room temperature in good yields and with high enantioselectivities.[6a,b,g–i] The two diamine ligands in this catalytic system play a distinct role: one serves as a chiral ligand to provide stereoinduction in the addition step, while the other functions as a base for substrate enolization.[6a,b] Evans et al.[6a,b] proposed the formation of the nickel enolate **A** with simultaneous coordination of the nitroalkene on the apical position **B**. Further nucleophilic attack of the enolate to the activated bond of nitroalkene results in the formation of the product. The displacement of the product in the Ni intermediate **C** with a dicarbonyl substrate occurs with concurrent deprotonation, which regenerates enolate **A** in the catalytic cycle (Scheme 1).



Scheme 1. Proposed mechanism for the Michael addition of 1,3-dicarbonyl compounds to nitroalkenes catalyzed by nickel complexes.[6b]

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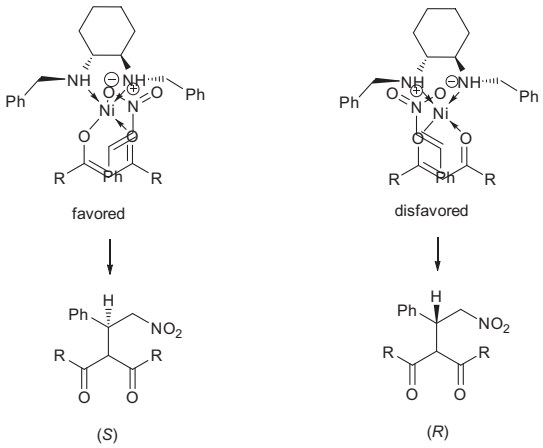


Scheme 2. Proposed transition state for the Ni-catalyzed Michael addition of 1,3-dicarbonyl compounds to nitrostyrene.[6b]

As reported by Evans et al.,[6b] the observed stereoinduction in the reaction can be explained on the basis of the transition state **B**. In the disfavored transition state (pro *S* addition), the nitro moiety of the nitroalkene faces steric interacts with the *N*-benzyl group of the ligand. On the other hand, in the favored transition state (pro *R* addition), the *N*-benzyl group of the ligand is orientated away from the nitroalkene (Scheme 2).

Due to the relatively high acidity of β-oxo phosphonates (pK_a = 13.5 for $(EtO)_2P(O)CH_2C(O)Ph$[9]) and their ability to form chelates with metal ions,[10] these compounds are good candidates for the development of numerous asymmetric transformations catalyzed by chiral Lewis acids, such as alkylations,[11] fluorinations,[12] Mannich type reactions[13], and Michael additions to azodicarboxylates.[14]

The first example of an organocatalytic asymmetric Michael addition of β-oxo phosphonates to nitroalkenes has been previously described.[3] However, a thiourea catalyzed reaction leads to a mixture of diastereomers and is sensitive to the nature of the substituents at the phosphoryl group. While diethyl (2-oxo-2-phenylethyl)phosphonate gives adducts with nitroalkenes with satisfactory enantiomeric excess (50–98%), the reaction with the dimethyl ester leads to a dramatic decrease in the enantioselectivity of the reaction.[3] Furthermore, it requires a high ratio of catalyst–substrate (20 mol %).

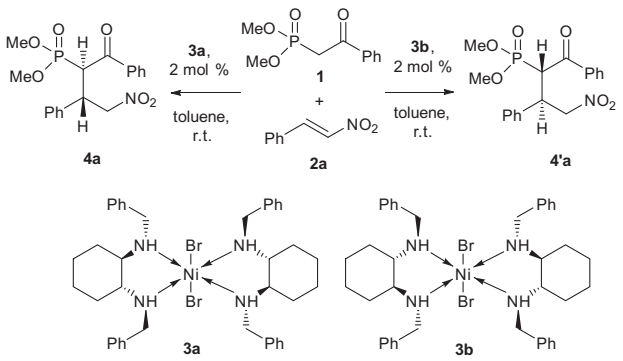
Previously, we reported one example of an asymmetric addition of dimethyl [2-(1-adamantyl)-2-oxoethyl]phosphonate to nitrostyrene in the presence of Ni(II) complex with (*R*,*R*)-*N*,*N*′-dibenzylcyclohexane-1,2-diamine.[15] Herein, we report the highly enantioselective conjugate addition of dimethyl (2-oxo-2-phenylethyl)phosphonate to various nitroalkenes, catalyzed by chiral Ni(II) complexes.

2. Results and discussion

Initially, we studied the addition of β-oxo phosphonate **1** to nitrostyrene **2a** in the presence of chiral Ni(II) catalysts **3a** and **3b** (Scheme 3).

When carrying out the reaction in toluene in the presence of (*S*,*S*)-**3b**, one diastereomer (+)-**4′a** crystallizes from the reaction mixture. The enantiomeric excess of the Michael adducts **4a** and **4′a** was found to be >99% as determined by chiral HPLC.

Compounds (+)-**4′a** were recrystallized from methanol to obtain a single crystal suitable for analysis. The (2*S*,3*R*)-configuration of the (+)-enantiomer **4′a** was determined by X-ray analysis (Fig. 1) (Flack parameter[16] $x = -0.08(3)$). Similarly, the absolute



Scheme 3. Asymmetric addition of β-oxo phosphonate **1** to nitrostyrene **2a** in the presence of Ni(II) complexes with (*R*,*R*)- and (*S*,*S*)-*N*,*N*′-dibenzylcyclohexane-1,2-diamine.

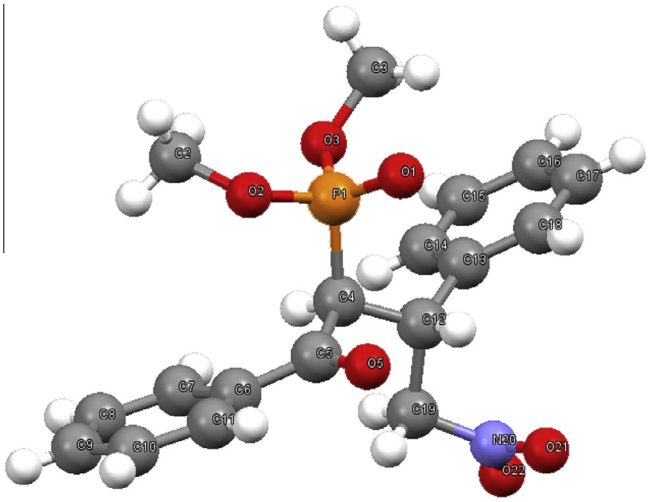


Figure 1. The ORTEP diagram of Michael adduct (2*S*,3*R*)-**4′a**.

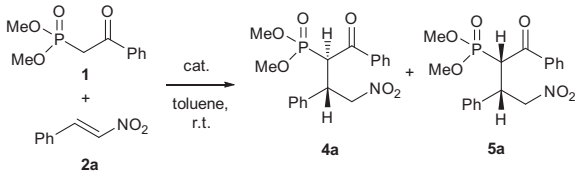
configuration of (−)-enantiomer **4a**, obtained in the presence of the optical antipode of catalyst (*S*,*S*)-**3b**—catalyst (*R*,*R*)-**3a**, was assigned as (2*R*,3*S*).

We screened various ligand–metal combinations for the asymmetric Michael addition of β-oxo phosphonate **1** to nitrostyrene **2a**. As shown in Table 1, the nickel complexes exhibit catalytic activity in the model reaction (entries 1–5), while cobalt, manganese, and copper complexes obtained in situ are not active in these reaction (entries 7–9).

The reaction led to predominantly one diastereomer (see Table 1), which is very slightly soluble in toluene and crystallized over the course of reaction. The enantiomeric excess of (2*R*,3*S*)-**4a** was determined by chiral HPLC by the assignment of the retention times of (2*R*,3*S*)-**4a** and its optical antipode (2*S*,3*R*)-**4′a**.

The type of ligand (Fig. 2) had an important influence on the enantioselectivity of the Michael addition. In entries 1 and 2, $[NiBr_2(\mathbf{L1})_2]$ promoted the asymmetric reaction with high yield and excellent enantioselectivity. The complex with one diamine ligand $[NiBr_2(\mathbf{L1})]$ proved less active in this reaction (entry 3). $[NiCl_2(\mathbf{L2})]$ did not exhibit any catalytic activity (entry 6). Using one equivalent of achiral base (triethylamine) led to an increase in the catalytic activity of $[NiBr_2(\mathbf{L1})]$, while maintaining a high enantioselectivity (entry 4). We suggest that the 2-oxo phosphonate is deprotonated by triethylamine, thus promoting the formation of enolate complex **D** in accordance with the mechanism proposed for 1,3-dicarbonyl compounds.[6b] Further coordination

Table 1
Screening of chiral catalysts for the synthesis of nitrophosphonates **4a**–**5a**



Entry	Salt or complex	mol %	Ligand	mol %	Time (day)	Yield[a] (%) of **3a**	dr[b], **4a**/**5a**	% ee[c], **3a**
1	[$NiBr_2$(**L1**)$_2$]	**2.0**	—	—	**0.5**	**100**	37:1	**>99**
2	[$NiBr_2$(**L1**)$_2$]	0.2	—	—	15	94.0	35:1	**>99**
3	[$NiBr_2$(**L1**)]	2.0	—	—	29	53.7	37:1	—
4	[$NiBr_2$(**L1**)]	2.0	Et_3N	2.0	2	100	1:0	>99
5	$NiCl_2{\cdot}6H_2O$	0.2	**L1**	0.4	15	100	1:0	>99
6	[$NiCl_2$(**L2**)]	2.0	—	—	30	0	—	—
7	$CoCl_2{\cdot}6H_2O$	0.2	**L1**	0.4	29	0	—	—
8	$MnCl_2{\cdot}4H_2O$	0.2	**L1**	0.4	29	0	—	—
9	$CuCl_2$	0.2	**L1**	0.4	29	0	—	—

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

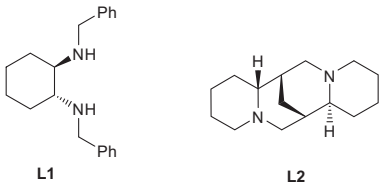
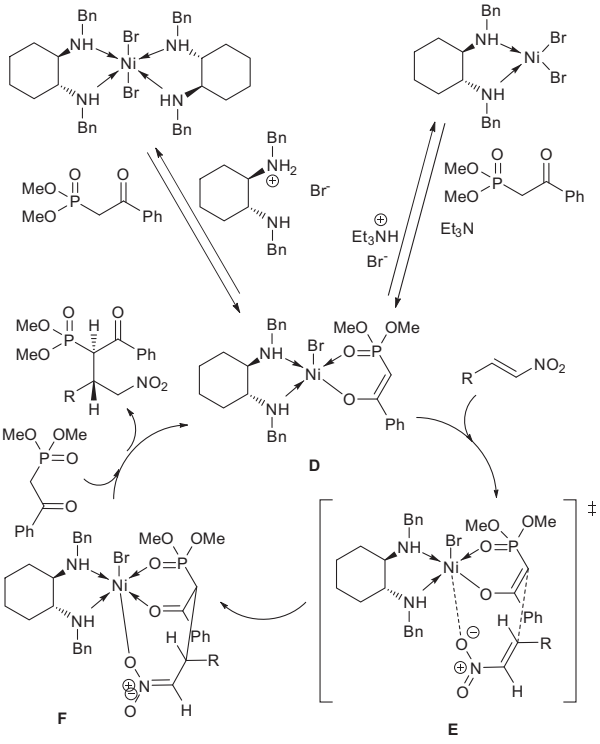
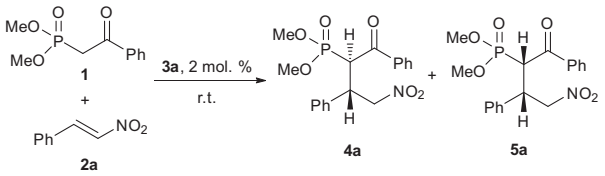


Figure 2. Ligands screened.



Scheme 4. Proposed mechanism of the Michael addition of β-oxo phosphonate **1** to nitroalkenes catalyzed by Ni complexes.

Table 2
Dependence on the solvent and catalyst loading in the Michael addition of phosphonate **1** to nitrostyrene **2a** at rt in the presence of catalyst **3a**



Entry	Solvent	Time (day)	Conversion[a] (%)	dr[a], **4a**/**5a**
1	Toluene	0.5	100	37:1
2	EtOAc	12	100	1.3:1
3	$CHCl_3$	12	60	1:1
4	CCl_4	12	100	2.4:1
5	THF	12	98	9:1
6	1,4-Dioxane	12	100	0.8:1
7	Nitromethane	12	100	1.3:1
8	Et_2O	12	100	1:0

[a] Determined by ^{31}P NMR analysis of reaction mixture.

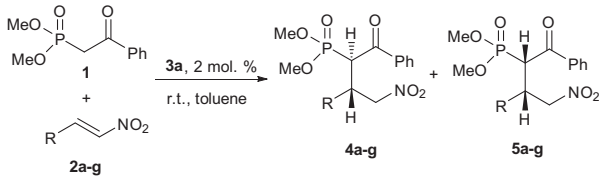
of nitroalkene to nickel atom and the nucleophilic addition of β-oxo phosphonate to the activated double bond of nitroalkene gave the reaction product (Scheme 4).

The asymmetric addition of phosphonate **1** to nitrostyrene **2a** can be carried out in the presence of a catalyst obtained in situ from nickel chloride hexahydrate and ligand **L1** (Table 1, entry 5). Thus, we chose [$NiBr_2$(**L1**)$_2$] **3a** as the catalyst for optimization of the reaction conditions. The results are listed in Table 2.

A survey of solvents revealed that all of the reactions proceeded smoothly to give the desired adduct with satisfactory results. A substantial change in diastereomeric ratio (2*R*,3*S*)-**4a**/(2*S*,3*S*)-**5a** was observed in the cases of toluene against other solvents. The diastereomeric excess was small when solvents were used in which **4a** was sufficiently soluble (entries 2–7). When carrying out the reaction in toluene, pure diastereomer **4a** crystallizes (dr 37:1, Table 2, entry 1). Considering both the diastereoselectivity and reaction time, toluene seems to be the optimal solvent for the reaction. The scope of the addition of β-oxo phosphonate **1** to various nitroalkenes **2a**–**g** under the optimized reaction conditions is summarized in Table 3.

The reaction gave a mixture of diastereomers **4** and **5** in various ratios. High diastereomeric excess was observed when the reaction

Table 3
Michael addition of phosphonate **1** to various nitroalkenes **2a–g**[a]



Entry	**2**, R	Conversion[b] (%)	dr[b] **4**/**5**	ee[c](%) **4**	Yield[d] (%) of **4**	dr[d] **4**/**5**	ee[d](%) **4**
1	**2a**, Ph	100	37:1	>99	45	37:1	>99
2	**2b**, 4-ClC_6H_4	100	21:1	>99	43	21:1	>99
3	**2c**, 2-ClC_6H_4	100	1.3:1	91.4	73[e]	1.3:1[e]	91.4[e]
4	**2d**, 4-$MeOC_6H_4$	100	3.8:1	>99	55	100:0	>99
5	**2e**, 3-$MeOC_6H_4$	100	1.3:1	84.5	40	22:1	98.2
6	**2f**, 2-$MeOC_6H_4$	100	7:1	79.9	36	34:1	96.3
7	**2g**, 2,4,6-$(MeO)_3C_6H_2$	100	9.3:1	96.0	46	34:1	>99

[a] The absolute configuration of **4a** was determined by X-ray crystallography, and the absolute configurations of **4b–g** were assumed by analogy.
[b] Determined by ^{31}P NMR analysis of reaction mixture.
[c] Determined by HPLC.
[d] Isolated yield, dr and ee after purification by recrystallization.
[e] Isolated yield, dr and ee after purification by silica gel column chromatography.

product was poorly soluble in toluene. The formed crystalline products were recrystallized from methanol to give individual diastereomers (−)-**4**. In the cases of **4–5c** and **4–5e**, the products do not crystallize from the reaction mixture and were isolated by chromatography. Following crystallization of **4–5e** from methanol gave (−)-**4e** as an individual diastereomer. Compounds **4–5c** were obtained as a mixture of diastereomers.

The assignment of the signals in the NMR spectra of diastereomers was made based on epimerization experiments. For example, the epimerization of compound **4f** results in a new signal of the second diastereomer **5f** in the ^{31}P NMR at 23.90 ppm and differs from the first diastereomer **4f** by 0.55 ppm. Two doublets [3.69 and 3.81 ppm ($^3J_{HP}$ 11 Hz)] of two nonequivalent methoxy groups at the phosphorus atom were observed in the ^1H NMR spectrum of the first diastereomer **4f**. The corresponding resonance signals of the second diastereomer **5f** were shifted upfield (3.52 and 3.56 ppm, $^3J_{HP}$ 11 Hz).

The observed correlation between the solubility and dr (Table 2, entries 2–7, Table 3, entries 3 and 5) suggests that the direct stereochemical result of the reaction is a mixture of two diastereomers, which are in equilibrium in solution. In the case of the low solubility of the (2*R*,3*S*)-isomer, the equilibrium shifts due to its crystallization from solution.

This hypothesis is also confirmed by the following experiment. The epimerization of compound **4a** in THF in the presence of 5% of *t*-BuOK leads to a mixture of diastereomers (2*R*,3*S*)-**4a** (δ_P 22.48 ppm) and (2*S*,3*S*)-**5a** (δ_P 22.67 ppm) in a 2:1 ratio. Treatment of the thus obtained diastereomeric mixture by toluene leads to the crystallization of one diastereomer **4a**. It is noteworthy that a similar reaction of ethyl acetoacetate with nitrostyrenes in the presence of **3a** as catalyst leads to a mixture of (2*S*,3*S*)- and (2*R*,3*S*)-diastereomers,[6b] but recrystallization leads to a single (2*R*,3*S*)-diastereomer. This fact is also evidence in favor of this formation of diastereomers **4a–g**.

The (2*R*,3*S*)-configuration of (−)-**4b–g** was assigned by correlating the sign and value of the specific rotation of these compounds with that of (−)-(2*R*,3*S*)-**4a**.

The enantiomers of compounds **4a–g** were obtained using (*R*,*R*)-**3b** as a catalyst for reliable determination of the enantiomeric excess of these compounds by HPLC.

Good yields and excellent enantioselectivities at the β-position to the nitro group were obtained for 4-substituted nitrostyrenes (Table 3, entries 2 and 4). The enantioselectivity of the reaction is reduced in the case of 2- and 3-substituted nitrostyrenes (Table 3, entries 3, 5 and 6).

It should be noted that the enantioselectivity of the addition of β-oxo phosphonates to nitroalkenes is higher in some cases than similar reactions with 1,3-dicarbonyl compounds.[6a,b] Moreover a similar trend was observed in the asymmetric fluorination of β-oxo phosphonates and 1,3-dicarbonyl compounds.[12c] The formation of enolates as key intermediates is also postulated for these reactions. It is clear from the obtained results that there is a strong preference for the (*R*,*R*)-**3a** ligand to give Michael adducts **4** with a (3*S*)-configuration in the reaction of β-oxo phosphonate **1** with nitroalkenes **2a–g**. This stipulates that the attack by the β-oxo phosphonate **1** occurs predominantly at the *Re* face of the nitroalkenes; a transition state rationalizing this outcome is proposed in Scheme 5. Based on Evans' model (Scheme 2),[6b] we assume that the β-oxo phosphonate is coordinated to the nickel atom in two equatorial position, while nitroalkene is coordinated in an apical position. One of the quadrants in the proposed transition state is blocked by the benzyl moiety of the diamine ligand. Thus, the β-oxo phosphonate attacks the nitroalkene from the *Re* face, and the corresponding Michael adduct is obtained with a (3*S*)-configuration [as a mixture of (2*R*,3*S*)- and (2*S*,3*S*)-diastereomers] (Scheme 5). In the case of toluene as a solvent, (2*R*,3*S*)-**4** predominantly crystallizes.

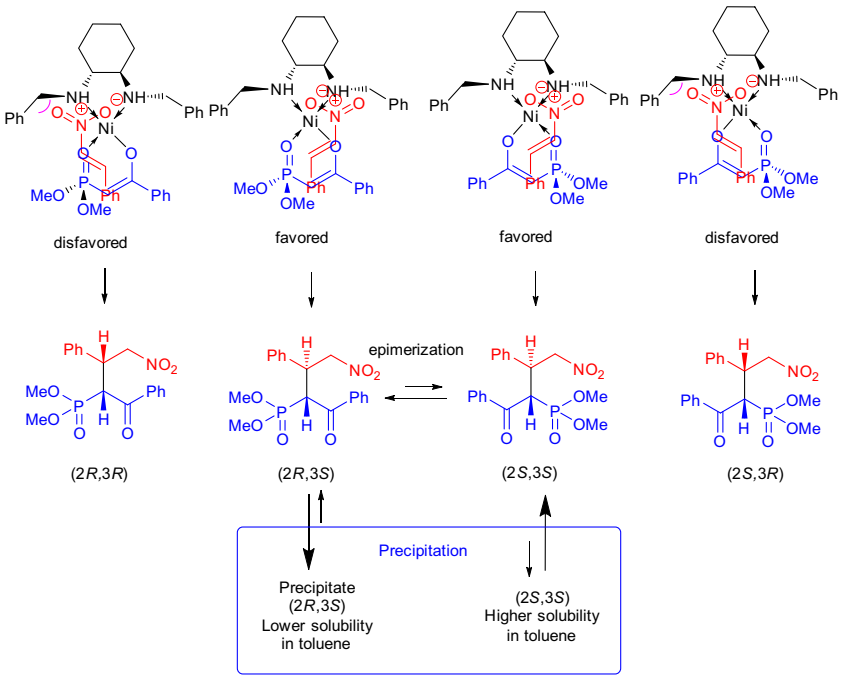
3. Conclusions

The asymmetric synthesis of α-nitroalkyl substituted β-oxo phosphonates, valuable synthetic intermediates, has been developed via transition metal catalyzed Michael addition. In the presence of (1*R*,2*R*)-*N*,*N*′-dibenzylcyclohexane-1,2-diamine–Ni complex **3a**, dimethyl (2-oxo-2-phenylethyl)phosphonate **1** reacted with a variety of aromatic nitroalkenes **2a–g** to give adducts **4a–g** in high yields and with excellent enantioselectivities. This method provides access to various chiral phosphonates from readily available starting materials.

4. Experimental

4.1. General

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on JEOL JNM-ECX400 (^1H NMR—399.78 MHz, ^{13}C NMR 100.53 MHz, ^{31}P NMR



Scheme 5. Proposed transition state for the asymmetric addition of β-oxo phosphonate to nitrostyrene.

161.83 MHz). All signals are expressed as ppm using a residual solvent peak as an internal standard ($CDCl_3$: 7.25 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR). FTIR spectra were recorded on a Shimadzu IRAffinity-1 spectrophotometer in KBr pellets or thin-layer (KBr prisms). Melting points were determined on an electrothermal melting point apparatus and are uncorrected. Elemental analysis was performed on an EuroVector EA-3000 analyzer. Optical rotations were measured on Rudolph Research Analytical (Autopol V Plus Automatic Polarimeter) with a sodium lamp at 589 nm. The enantiomeric purity of the products was determined by HPLC analysis on Waters LC equipped with a chiral stationary phase column Chiralpak AD-3 with hexane/2-propanol 80:20 as eluent. HPLC analysis of the individual enantiomers (2*R*,3*S*)-(−)- and (2*S*,3*R*)-(+)-**4a**–**g** and the samples with the addition of optical antipodes was performed for the reliable determination of ee. Column chromatography was performed on Silica gel 60, Merck (230–400 mesh). X-ray crystallographic data were collected using a Stoe STADI-VARI Pilatus-100 K diffractometer.

4.2. Synthesis of initial compounds

Nitroalkenes **2a**–**g** was prepared from the corresponding aldehydes and nitromethane according to the literature.[17] The synthesis of dimethyl (2-oxo-2-phenylethyl)phosphonate **1** was carried out by the Michaelis–Arbuzov reaction of phenacyl bromide methoxycarbonylhydrazone with trimethylphosphite followed by deprotection of the carbonyl group.[18] The synthesis of complexes Ni(II)–bis[(1*R*,2*R*)-*N*,*N*′-dibenzylcyclohexane-1,2-diamine]Br_2 **3a** and [$NiCl_2$((−)-sparteine)] is described in the literature,[6b,19] respectively.

4.3. General procedure for Ni(II) catalyzed enantioselective Michael addition of phosphonate 1 to nitroalkenes 2a–g

Method A: A mixture of phosphonate **1** (2.80 mmol), nitroalkene **2a**–**g** (2.50 mmol) and Ni(II)–bis[(*R*,*R*)-*N*,*N*′-dibenzylcyclohexane-1,2-diamine]Br_2 (0.05 mmol) **3a** in 3.0 mL of toluene was stirred at rt for 12 h. The formed crystalline product was filtered and recrystallized from methanol, to give an individual diastereomer. In the case of nitroalkenes **2c** and **2e**, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica column chromatography ($CHCl_3$) to give the product as a yellow oil (mixture of diastereomers).

Method B: To a mixture of phosphonate **1** (2.80 mmol) and nitrostyrene **2** (2.50 mmol) in 3.0 mL of toluene were added the complex [$NiBr_2$(**L1**)] (0.05 mmol) and then Et_3N (7.0 μL, 0.05 mmol). The mixture was then stirred at rt for 2 days. The formed crystalline product was filtered and recrystallized from methanol, to give an individual diastereomer.

4.4. General procedure for Michael addition of phosphonate 1 to nitrostyrene 2a in the presence of the catalyst obtained in situ

Metal salt (1.12 mmol, 1 equiv) and ligand **L1** (2.24 mmol, 2 equiv) are combined in the reaction flask. Next, 2.24 mL of MeOH was added and the mixture was stirred for 3 h, after which 50 μL of the obtained 0.5 M solution of catalyst was added to a mixture of phosphonate **1** (2.80 mmol) and nitrostyrene **2** (2.50 mmol) in 3.0 mL of toluene. The conversion was determined by NMR analysis.

4.5. Epimerization of dimethyl [(2*R*,3*S*)-4-nitro-1-oxo-1,3-diphenylbut-2-yl]phosphonate 4a

To a solution of the phosphonate **4a** (0.60 g, 1.59 mmol) in THF (10 mL) was added potassium *tert*-butoxide (18 mg, 0.160 mmol) and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was then washed with a saturated aqueous sodium hydrogen carbonate solution. The organic phase was separated. The aqueous phase was extracted twice with dichloromethane. The combined organic phases were dried over sodium sulfate. The solvent was removed under vacuum. Yield: 0.60 g (quantitative). ^{31}P NMR ($CDCl_3$): δ = 22.48 (2*R*,3*S*), 22.67 (2*S*,3*S*). dr 2:1.

To the resulting mixture of diastereomers, toluene (3 mL) was added and stirred at room temperature for 24 h. The formed crystalline precipitate was filtered off, washed with 2 mL of toluene and dried in vacuo. Yield: 150 mg (25%) of (2*R*,3*S*)-diastereomer. ^{31}P NMR ($CDCl_3$): δ = 22.48.

The filtrate was evaporated in vacuo and the residue was analyzed by NMR ^{31}P spectroscopy. According to NMR, the residue was a mixture of diastereomers in a ratio of 1.8:1. Yield: 450 mg (75%). ^{31}P NMR ($CDCl_3$): δ = 22.48 (2*R*,3*S*), 22.67 (2*S*,3*S*).

4.6. Characterization data of the phosphonates

4.6.1. Dimethyl [(2*R*,3*S*)-4-nitro-1-oxo-1,3-diphenylbut-2-yl]phosphonate 4a

Yield: 45%; >99% ee; colorless crystals; mp 162–166 °C (methanol); $[\alpha]_D^{20}$ = −38.4 (*c* 5.0, CH_2Cl_2); IR (KBr, cm^{-1}): ν = 3063 (w), 2949 (w), 2853 (w), 1674 (s), 1597 (w), 1545 (s), 1449 (w), 1383 (w), 1250 (s), 1045 (s), 968 (m), 858 (w), 849 (w), 783 (m), 706 (m), 519 (m); ^1H NMR ($CDCl_3$): δ = 3.52 (d, $^3J_{HP}$ = 10.1 Hz, 3H), 3.55 (d, $^3J_{HP}$ = 10.1 Hz, 3H), 4.30–4.42 (m, 1H), 4.63 (dd, $^3J_{HH}$ = 6.9 Hz, $^2J_{HP}$ = 23.4 Hz, 1H), 5.00–5.15 (m, 2H), 7.18–7.27 (m, 5H), 7.38–7.42 (m, 2H), 7.52–7.56 (m, 1H), 7.77–7.79 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 43.0 (d, $^2J_{CP}$ = 2.9 Hz), 50.3 (d, $^1J_{CP}$ = 128.4 Hz), 53.7 (d, $^2J_{CP}$ = 6.7 Hz), 77.4 (d, $^3J_{CP}$ = 9.6 Hz), 128.0, 128.4, 128.7, 128.9, 129.1, 134.0, 137.3, 137.4 (d, $^3J_{CP}$ = 9.6 Hz), 195.54 (d, $^2J_{CP}$ = 4.8 Hz). Multiplicities and *J* values indicated are only for C–P coupling; ^{31}P NMR ($CDCl_3$): δ = 22.48 (2*R*,3*S*), 22.67 (2*S*,3*S*). Anal. Calcd for $C_{18}H_{20}NO_6P$: C, 57.30; H, 5.34; N, 3.71. Found: C, 57.35; H, 5.31; N, 3.73.

For (2*S*,3*R*)-**4′a**: Yield: 47%; $[\alpha]_D^{20}$ = +38.5 (*c* 5.0, CH_2Cl_2); all spectroscopic characteristics identical to (2*R*,3*S*)-enantiomer. Selected X-ray crystallographic data for (2*S*,3*R*)-**4′a**: $C_{18}H_{20}NO_6P$, *M* = 377.33, monoclinic, space group $P2_1$, *a* = 5.7582(9) Å, *b* = 20.206(3) Å, *c* = 8.4373(10) Å, β = 102.828(11)°; *V* = 957.2(2) Å^3, D_c = 1.309 Mg/m^3, *Z* = 2, *F*(000) = 396, λ = 1.54186 Å, μ = 1.569 mm^{-1}, total/unique reflections = 2979/1742 [R_{int} = 0.0358], *T* = 295(1) K, Θ range = 4.38–72.05°, Final *R* indices [$I > 2\sigma(I)$] R_1 = 0.0763, wR_2 = 0.0879, *R* indices (all data) R_1 = 0.0445, wR_2 = 0.0785, Flack *x* parameter = −0.08(3). Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as Private communication Number CCDC 935781. Copies of the data can be obtained free of charge on application to CCDC (http://www.ccdc.cam.ac.uk).

HPLC analysis (Chiralpak AD-3 column; hexane/2-propanol, 80:20; flow rate 1.0 mL/min; wavelength 230 nm): t_r = 9.7 (2*R*,3*S*), 22.3 (2*S*,3*R*) min.

4.6.2. Dimethyl [(2*R*,3*S*)-3-(4-chlorophenyl)-4-nitro-1-oxo-1-phenylbut-2-yl]phosphonate 4b

Yield: 43%; >99% ee; colorless crystals; mp 156–158 °C (methanol); $[\alpha]_D^{20}$ = −34.7 (*c* 2.5, CH_2Cl_2); IR (KBr, cm^{-1}): ν = 3055 (w), 2951 (w), 2924 (w), 2853 (w), 1668 (s), 1597 (m), 1553 (s), 1497 (m), 1450 (m), 1379 (m), 1246 (s), 1039 (s), 1024 (s), 1014 (s), 972 (m), 850 (m), 783 (m), 772 (m), 685 (w), 667 (w), 527 (m); ^1H NMR ($CDCl_3$): δ = 3.54 (d, $^3J_{HP}$ = 11.0 Hz, 3H), 3.58 (d, $^3J_{HP}$ = 11.0 Hz, 3H), 4.30–4.40 (m, 1H), 4.61 (dd, $^3J_{HH}$ = 6.9 Hz, $^2J_{HP}$ = 23.8 Hz, 1H), 4.99–5.10 (m, 2H), 7.19 (d, $^3J_{HH}$ = 8.72 Hz, 2H), 7.24 (d, $^3J_{HH}$ = 8.72 Hz, 2H), 7.40–7.46 (m, 2H), 7.56–7.60 (m, 1H), 7.81–7.83 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 42.4 (d, $^2J_{CP}$ = 2.9 Hz), 50.1 (d, $^1J_{CP}$ = 128.4 Hz), 53.6 (d, $^2J_{CP}$ = 6.7 Hz), 77.3 (d, $^3J_{CP}$ = 8.6 Hz), 128.8, 129.0, 129.2, 129.4, 134.3, 135.9 (d, $^3J_{CP}$ = 10.6 Hz), 137.1, 195.2 (d, $^2J_{CP}$ = 4.8 Hz). Multiplicities and *J* values indicated are only for C–P coupling; ^{31}P NMR ($CDCl_3$): δ = 22.07 (2*R*,3*S*), 22.22 (2*S*,3*S*). Anal. Calcd for $C_{18}H_{19}ClNO_6P$: C, 52.50; H, 4.65; N, 3.40. Found: C, 52.56; H, 4.60; N, 3.43.

For the (2*S*,3*R*)-isomer: Yield: 41%; $[\alpha]_D^{20}$ = +34.3 (*c* 2.5, CH_2Cl_2); all spectroscopic characteristics identical to the (2*R*,3*S*)-enantiomer. HPLC analysis (Chiralpak AD-3 column; hexane/2-propanol, 80:20; flow rate 1.0 mL/min; wavelength 230 nm): t_r = 13.1 (2*R*,3*S*), 29.8 (2*S*,3*R*) min.

4.6.3. Dimethyl [(3*S*)-3-(2-chlorophenyl)-4-nitro-1-oxo-1-phenylbut-2-yl]phosphonate 4c

Yield: 73%; yellow oil [mixture of diastereomers, dr 1.3:1, 91.4% ee of (3*S*)-enantiomers]; $[\alpha]_D^{20}$ = −47.3 (*c* 2.5, $CHCl_3$); IR (film, cm^{-1}): ν = 3063 (m), 3009 (m), 2955 (m), 2855 (m), 1682 (s), 1597 (m), 1558 (s), 1450 (m), 1381 (m), 1258 (s), 1188 (m), 1034 (s), 988 (m), 841 (m), 756 (s), 694 (m), 602 (m), 540 (m), 509 (m); ^1H NMR ($CDCl_3$) δ = 3.61 (d, $^3J_{HP}$ = 11.2 Hz, 3H—first diastereomer), 3.70 (d, $^3J_{HP}$ = 11.2 Hz, 3H—first diastereomer), 3.73 (d, $^3J_{HP}$ = 10.8 Hz, 3H—second diastereomer), 3.77 (d, $^3J_{HP}$ = 11.0 Hz, 3H—second diastereomer), 4.76–4.78 (m, 1H—first diastereomer), 4.83–4.91 (m, 1H—first diastereomer), 5.08–5.16 (m, 1H—second diastereomer), 5.20–5.40 (m, 1H—second diastereomer, 2H—first and second diastereomer), 7.06–7.14 (m, 2H), 7.20–7.42 (m, 1H), 7.37–7.42 (m, 3H), 7.50–7.54 (m, 1H), 7.71–7.54 (m, 1H), 7.81 (d, $^3J_{HH}$ = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 39.2, 48.0 (d, $^1J_{CP}$ = 125.5 Hz—second diastereomer), 48.3 (d, $^1J_{CP}$ = 127.4 Hz—first diastereomer), 53.6 (d, $^2J_{CP}$ = 5.7 Hz), 53.9 (d, $^2J_{CP}$ = 5.7 Hz), 75.4 (d, $^3J_{CP}$ = 6.7 Hz), 127.3, 127.4, 128.5, 128.6, 128.8, 128.9, 129.5, 130.5, 130.7, 133.8, 134.0 (d, $^3J_{CP}$ = 21.0 Hz), 134.4 (d, $^3J_{CP}$ = 11.5 Hz), 136.9 (first diastereomer), 137.2 (second diastereomer), 194.2 (d, $^2J_{CP}$ = 5.8 Hz—second diastereomer), 195.3 (d, $^2J_{CP}$ = 4.8 Hz—first diastereomer). Multiplicities and *J* values indicated are only for C–P coupling; ^{31}P NMR ($CDCl_3$): δ = 22.08 (first diastereomer), 22.72 (second diastereomer). Anal. Calcd for $C_{18}H_{19}ClNO_6P$: C, 52.50; H, 4.65; N, 3.40. Found: C, 52.58; H, 4.62; N, 3.44.

For the (3*R*)-isomer: yield: 72%; $[\alpha]_D^{20}$ = +46.2 (*c* 2.5, $CHCl_3$); all spectroscopic characteristics identical to the (3*S*)-enantiomer. HPLC analysis (Chiralpak AD-3 column; hexane/2-propanol, 80:20; flow rate 1.0 mL/min; wavelength 230 nm): t_r = 9.6 min (3*R*)-second diastereomer, 9.8 min (3*S*)-first diastereomer, 11.1 min (3*S*)-second diastereomer, 13.4 min (3*R*)-first diastereomer.

4.6.4. Dimethyl [(2*R*,3*S*)-3-(4-methoxyphenyl)-4-nitro-1-oxo-1-phenylbut-2-yl]phosphonate 4d

Yield: 55%; >99% ee; colorless crystals; mp 140–143 °C (methanol); $[\alpha]_D^{20}$ = −42.4 (*c* 2.5, CH_2Cl_2); IR (KBr, cm^{-1}): ν = 3068 (w), 2949 (w), 2847 (w), 1672 (s), 1614 (m), 1597 (m), 1551 (s), 1518 (m), 1449 (m), 1383 (m), 1273 (s), 1258 (s), 1238 (s), 1185 (s), 1039 (s), 1020 (s), 970 (m), 853 (m), 802 (w), 781 (m), 692 (m), 538 (s); ^1H NMR ($CDCl_3$): δ = 3.54 (d, $^3J_{HP}$ = 6.2 Hz, 3H), 3.57 (d, $^3J_{HP}$ = 6.2 Hz, 3H), 3.73 (s, 3H), 4.25–4.37 (m, 1H), 4.61 (dd, $^3J_{HH}$ = 6.9 Hz, $^2J_{HP}$ = 23.6 Hz, 1H), 4.95–5.10 (m, 2H), 6.78 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.16 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.41–7.45 (m, 2H), 7.55–7.58 (m, 1H), 7.80–7.82 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 42.4 (d, $^2J_{CP}$ = 2.9 Hz), 50.5 (d, $^1J_{CP}$ = 128.4 Hz), 53.5 (d, $^2J_{CP}$ = 6.7 Hz), 53.7 (d, $^2J_{CP}$ = 6.7 Hz), 55.3, 77.8 (d, $^3J_{CP}$ = 8.6 Hz), 114.4, 128.8, 129.0, 129.3, 129.4, 134.3, 135.9 (d, $^3J_{CP}$ = 10.6 Hz), 137.1, 195.2 (d, $^2J_{CP}$ = 4.8 Hz). Multiplicities and *J* values indicated are only for C–P coupling; ^{31}P NMR ($CDCl_3$): δ = 22.58. Anal. Calcd for $C_{19}H_{22}NO_7P$: C, 56.02; H, 5.44; N, 3.44. Found: C, 56.06; H, 5.38; N, 3.48.

For the (2*S*,3*R*)-isomer: Yield: 52%; $[\alpha]_D^{20}$ = +42.4 (*c* 2.5, CH_2Cl_2); all spectroscopic characteristics identical to the (2*R*,3*S*)-enantiomer. HPLC analysis (Chiralpak AD-3 column; hexane/2-propanol, 80:20; flow rate 1.0 mL/min; wavelength 230 nm): t_r = 11.7 (2*R*,3*S*), 23.0 (2*S*,3*R*) min.

4.6.5. Dimethyl [(2*R*,3*S*)-3-(3-methoxyphenyl)-4-nitro-1-oxo-1-phenylbut-2-yl]phosphonate 4e

Yield: 40%; 98.2% ee; colorless crystals; mp 142–145 °C (methanol); $[\alpha]_D^{20}$ = −42.3 (*c* 2.5, CH_2Cl_2); IR (KBr, cm^{-1}): ν = 3055 (w), 2961 (m), 2837 (w), 1680 (s), 1609 (m), 1582 (m), 1560 (s), 1489 (m), 1448 (m), 1437 (m), 1383 (m), 1333 (m), 1292 (m), 1261 (s), 1215 (m), 1198 (m), 1159 (w), 1053 (s), 1018 (s), 872 (m), 833

(m), 779 (s), 704 (m), 689 (m); ^{1}H NMR ($CDCl_3$): δ = 3.62 (s, 3H), 3.70 (d, $^3J_{HP}$ = 11.0 Hz, 3H), 3.80 (d, $^3J_{HP}$ = 11.0 Hz, 3H), 4.32–4.44 (m, 1H), 4.68 (dd, $^3J_{HH}$ = 8.7 Hz, $^2J_{HP}$ = 20.2 Hz, 1H), 4.88–4.94 (m, 2H), 5.21–5.25 (m, 1H), 6.60–6.63 (m, 1H), 6.65–6.68 (m, 1H), 6.73–6.75 (m, 1H), 7.00–7.07 (m, 1H), 7.30–7.40 (m, 2H), 7.48–7.51 (m, 1H), 7.62–7.74 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 43.3 (d, $^2J_{CP}$ = 3.8 Hz), 49.2 (d, $^1J_{CP}$ = 126.5 Hz), 53.8 (d, $^2J_{CP}$ = 6.7 Hz), 54.0 (d, $^2J_{CP}$ = 6.7 Hz), 55.2, 78.8 (d, $^3J_{CP}$ = 9.6 Hz), 113.7, 114.0, 119.9, 128.3, 128.7, 130.0, 133.6, 137.2, 138.5 (d, $^3J_{CP}$ = 15.3 Hz), 159.8 (d, $^3J_{CP}$ = 24.1 Hz), 194.1 (d, $^2J_{CP}$ = 5.8 Hz). Multiplicities and J values indicated are only for C–P coupling; ^{31}P NMR ($CDCl_3$): δ = 22.70 (2*R*,3*S*), 22.52 (2*S*,3*S*). Anal. Calcd for $C_{19}H_{22}NO_7P$: C, 56.02; H, 5.44; N, 3.44. Found: C, 56.08; H, 5.39; N, 3.46.

For the (2*S*,3*R*)-isomer: Yield: 37%; $[\alpha]_D^{20}$ = +42.4 (*c* 2.5, CH_2Cl_2); all spectroscopic characteristics identical to the (2*R*,3*S*)-enantiomer. HPLC analysis (Chiralpak AD-3 column; hexane/2-propanol, 80:20; flow rate 1.0 mL/min; wavelength 230 nm): t_r = 8.9 (2*R*,3*S*), 10.9 (2*S*,3*R*) min.

4.6.6. Dimethyl [(2*R*,3*S*)-3-(2-methoxyphenyl)-4-nitro-1-oxo-1-phenylbut-2-yl]phosphonate 4f

Yield: 36%; 96.3% ee; colorless crystals; mp 140–143 °C (methanol); $[\alpha]_D^{20}$ = −44.7 (*c* 2.5, $CHCl_3$); IR (KBr, cm^{-1}): ν = 3069 (w), 3015 (w), 2949 (m), 2847 (w), 1672 (s), 1614 (m), 1597 (m), 1551 (s), 1518 (m), 1449 (m), 1440 (m), 1383 (m), 1315 (m), 1302 (m), 1273 (s), 1258 (s), 1238 (s), 1207 (m), 1184 (s), 1117 (w), 1040 (s), 1020 (s), 970 (m), 853 (m), 839 (m), 802 (m), 781 (m), 692 (m), 538 (s); ^{1}H NMR ($CDCl_3$): δ = 3.69 (s, 3H), 3.69 (d, $^3J_{HP}$ = 11.0 Hz, 3H), 3.81 (d, $^3J_{HP}$ = 11.0 Hz, 3H), 4.38–4.47 (m, 1H), 5.10 (dd, $^3J_{HH}$ = 11.0 Hz, $^2J_{HP}$ = 19.6 Hz, 1H), 5.08–5.18 (m, 2H), 6.60–6.62 (m, 1H), 6.72–6.76 (m, 1H), 7.05–7.09 (m, 2H), 7.32–7.35 (m, 2H), 7.45–7.50 (m, 1H), 7.65–7.70 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 42.1, 46.9 (d, $^1J_{CP}$ = 127.4 Hz), 53.6 (d, $^2J_{CP}$ = 5.8 Hz), 53.9 (d, $^2J_{CP}$ = 5.8 Hz), 55.2, 76.8, 111.0, 121.0, 123.6, 123.8, 128.2, 128.5, 129.6, 132.3, 137.4, 156.9, 194.9 (d, $^2J_{CP}$ = 5.8 Hz). Multiplicities and J values indicated are only for C–P coupling; ^{31}P NMR ($CDCl_3$): δ = 23.90 (2*R*,3*S*), 23.35 (2*S*,3*S*). Anal. Calcd for $C_{19}H_{22}NO_7P$: C, 56.02; H, 5.44; N, 3.44. Found: C, 56.06; H, 5.40; N, 3.47.

For the (2*S*,3*R*)-isomer: Yield: 33%; $[\alpha]_D^{20}$ = +44.3 (*c* 2.5, $CHCl_3$); all spectroscopic characteristics identical to the (2*R*,3*S*)-enantiomer. HPLC analysis (Chiralpak AD-3 column; hexane/2-propanol, 80:20; flow rate 1.0 mL/min; wavelength 230 nm): t_r = 9.2 (2*R*,3*S*), 20.7 (2*S*,3*R*) min.

4.6.7. Dimethyl [(2*R*,3*S*)-3-(3,4,5-trimethoxyphenyl)-4-nitro-1-oxo-1-phenylbut-2-yl]phosphonate 4g

Yield: 46%; >99% ee; colorless crystals; mp 152–154 °C (methanol); $[\alpha]_D^{20}$ = −35.6 (*c* 2.5, $CHCl_3$); IR (KBr, cm^{-1}): ν = 3005 (w), 2959 (w), 2938 (w), 2839 (w), 1674 (s), 1595 (s), 1553 (s), 1512 (m), 1466 (m), 1450 (m), 1429 (m), 1381 (w), 1341 (m), 1327 (m), 1254 (s), 1188 (m), 1159 (w), 1130 (s), 1049 (s), 775 (m); ^{1}H NMR ($CDCl_3$): δ = 3.61 (s, 6H), 3.66 (s, 3H), 3.72 (d, $^3J_{HP}$ = 11.0 Hz, 3H), 3.81 (d, $^3J_{HP}$ = 11.0 Hz, 3H), 4.25–4.35 (m, 1H), 4.67–4.75 (m, 1H), 4.85–4.92 (m, 1H), 5.18–5.22 (m, 1H), 6.29 (s, 2H), 7.34–7.38 (m, 2H), 7.48–7.52 (m, 1H), 7.70–7.72 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 43.7, 49.0 (d, $^1J_{CP}$ = 126.5 Hz), 53.7 (d, $^2J_{CP}$ = 5.8 Hz), 54.1 (d, $^2J_{CP}$ = 5.8 Hz), 56.1, 60.8, 78.9, 105.2, 128.2, 128.7, 132.4, 133.7, 137.7, 153.3, 194.2 (d, $^2J_{CP}$ = 5.8 - Hz). Multiplicities and J values indicated are only for C–P coupling; ^{31}P NMR ($CDCl_3$): δ = 22.83 (2*R*,3*S*), 22.64 (2*S*,3*S*). Anal. Calcd for $C_{21}H_{26}NO_9P$: C, 53.96; H, 5.61; N, 3.00. Found: C, 53.99; H, 5.56; N, 3.05.

For the (2*S*,3*R*)-isomer: Yield: 42%. $[\alpha]_D^{20}$ = +35.2 (*c* 2.5, $CHCl_3$); all spectroscopic characteristics identical to the (2*R*,3*S*)-enantiomer. HPLC analysis (Chiralpak AD-3 column; hexane/2-propanol, 80:20; flow rate 1.0 mL/min; wavelength 230 nm): t_r = 11.7 (2*R*,3*S*), 13.2 (2*S*,3*R*) min.

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