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A practical synthetic approach to chiral α-aryl substituted ethylphosphonates

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Abstract—A convenient general method is reported for the synthesis of α-aryl substituted ethylphosphonic acids and esters by hydrogenation of α-aryl substituted ethenylphosphonic acids and esters. Racemic α-arylethylphosphonic acids and esters were prepared in 70–88% yield under palladium-assisted transfer hydrogenation conditions using ammonium formate. Asymmetric hydrogenation of α-arylethenylphosphonic acids using chiral Ru(II) catalysts led to α-arylethylphosphonic acids with enantiomeric excesses up to 86%.

1. Introduction

α-Arylethylphosphonates[1] are of interest in the search for new potent drugs such as phosphorus analogues of 2-arylpropionic acids[2] (including naproxen and ibuprofen which are well known non-steroidal anti-inflammatory drugs). α-Arylalkylphosphonates were reported to exhibit negative inotropic and calcium antagonistic activity.[3] They are widely used in electrophotographic materials design[4] and as haptens for reactive immunization.[5] Because of the significant use of α-aryl substituted ethylphosphonates, several methods have been explored for their preparation. The most common method is the Arbuzov reaction of triethyl phosphite with α-arylethyl bromides.[3,6] The reaction of β,β-bis-(methylsulfonyl)styrene with dimethylphosphite followed by catalytic reduction led to α-methylbenzylphosphonate.[7] Cyclic phosphonates were obtained from the corresponding α-phenylethylphosphonic dichlorides.[8] Another approach consisted of the deprotonation of diesters of benzylphosphonic acids followed by alkylation with alkyl halides.[2,9] Dimethyl 1-phenylethylphosphonate was prepared via the intermediate use of a substituted tosyl or nitrophenylsulfonyl hydrazine.[10] Diethyl 1-phenylethylphosphonate was also obtained by the reaction of diethyl 1-lithio-1-chloroethylphosphonate with Ph_2CuLi[11a] or phenyllithium in the presence of a catalytic amount of copper(I) bromide and lithium bromide.[11b,c] Photo-Arbuzov rearrangements of benzylic phosphites were also reported,[12] and the 1,4-addition of an α-lithiated alkylphosphonate to cyclohex-2-enones followed by aromatization yielded a variety of benzylphosphonic esters.[13] The asymmetric alkylation of phosphorus stabilized benzylic carbanions using chiral auxiliaries has also been reported as an efficient method for the preparation of α-arylethylphosphonates with high selectivities.[14]

Hydrogenation of the corresponding α-aryl substituted ethenylphosphonates seems to be a very attractive route to α-aryl substituted ethylphosphonates since the starting materials are very easily prepared. To our knowledge, only a few examples of the hydrogenation of α-substituted ethenylphosphonates may be found in the literature. In one example palladium on carbon at 80 bar pressure of H_2 was used for the hydrogenation of dimethyl ethenylphosphonate bearing a sugar substituent,[15] and Alper and Cho performed the first homogeneous transition metal catalyzed hydrogenation of α,β-unsaturated phosphonates using $[Pd(O_2P^tBu_2)(OP^tBu_2)(HOP^tBu_2)]$.[16]

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The asymmetric synthesis of α-substituted phosphonates is highly desirable for their biological evaluation, and we have previously reported the asymmetric hydrogenation of α-substituted ethenylphosphonates as the method of choice for the synthesis of optically active ethylphosphonates.[17] Herein, we report a convenient procedure for chemoselective palladium-assisted hydrogen transfer reduction of α-aryl substituted ethenylphosphonic acids and diesters by ammonium formate[18] and new developments in the asymmetric hydrogenation of α-aryl substituted ethenylphosphonic acids with chiral Ru(II) catalysts.

2. Results and discussion

2.1. Preparation of α-aryl substituted ethenylphosphonates

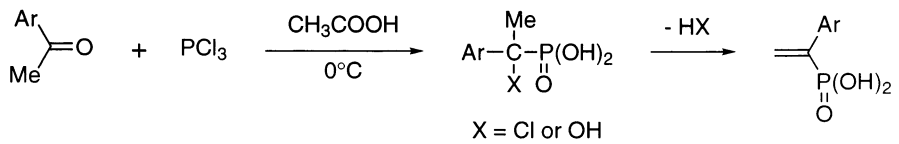
A number of methods for the preparation of starting α-arylethenylphosphonates are presently available, including palladium-catalyzed reactions such as the hydrophosphorylation of alkynes,[19] palladium(0) catalyzed Michaelis–Becker type reaction of dialkyl phosphites with vinyl bromides.[20] Abramov base-catalyzed addition of dialkyl phosphites to acylarenes,[21] the Michaelis–Arbuzov type reaction of copper(I) bromide complexes of trialkyl phosphites with vinylic halides,[22,23] and the addition of alkyl phosphites[24,25] to β-nitrostyrene followed by β-elimination of nitrous acid have also been described.[15] Some processes included the Wittig reaction of 1-oxoalkylphosphonates with methylenetriphenylphosphorane[26] and the reaction of Ivanov-like reagents derived from the reaction between benzylphosphonate and formaldehyde.[27] Other methods using ionic substitution reactions,[28] the thermal elimination of sulfinylphosphonates[29] and the rearrangement of benzyl(dimethoxyphosphoryl)carbene have also been reported,[30] and the reaction between trimethylsilyldiazomethane and functionalized arylketenes afforded the corresponding ethenylphosphonate after decarbonylation.[31]

The Conant reaction[32,33] of acetylarenes with phosphorus trichloride in the presence of glacial acetic acid affords α-arylethenylphosphonic acids, though the mechanism of this reaction is still under discussion.[34] Thus, following a modified literature procedure,[33] acids **1a–d** were prepared in 68–83% yield (Scheme 1).

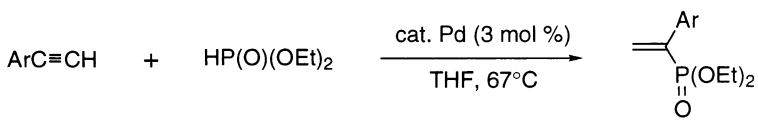
However, the presence of strongly electron donating substituents on the aromatic ring such as a methoxy group led to a mixture of unidentified products. Consequently, the Tanaka procedure[19] involving palladium-catalyzed hydrophosphorylation of terminal alkynes was modified (as shown in Scheme 2): commercially available $Pd_2(dba)_3{\cdot}CHCl_3$ (1.5 mol%) in the presence of triphenylphosphine (6–12 mol%) was used instead of the air-sensitive $Pd(PPh_3)_4$ or *cis*-$PdMe_2(PPh_2Me)_2$ complexes (Table 1).

2.2. Palladium-assisted hydrogen transfer reduction of α-aryl substituted ethenylphosphonates

In the search for a convenient and practical procedure for a large scale preparation of racemic α-aryl substituted ethylphosphonic acids and esters, the hydrogenation was carried out with several reducing agents using the model substrate **2a** (Table 2).



Scheme 1.



Scheme 2.

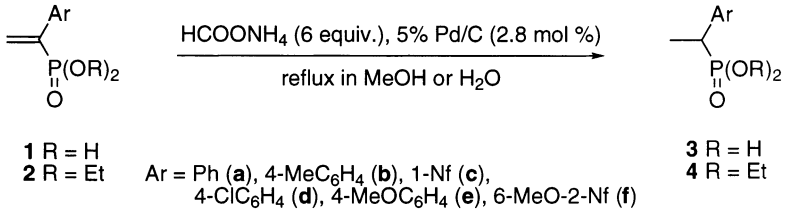
Table 1. Palladium-catalyzed hydrophosphorylation of terminal alkynes

Entry	Substrate	Catalyst	Time (h)	% Yield	
				Determined by ^{31}P NMR	Isolated
1	**2a**	$Pd(PPh_3)_4$	15	84	75
2	**2a**	$1/2Pd_2(dba)_3{\cdot}CHCl_3 + 2PPh_3$	12	86	–
3	**2e**	$1/2Pd_2(dba)_3{\cdot}CHCl_3 + 4PPh_3$	14	85	65
4	**2f**	$1/2Pd_2(dba)_3{\cdot}CHCl_3 + 4PPh_3$	27	90	74

Table 2. Hydrogenation of **2a** using various reducing agents

Entry	Reducing agent (amount)	Solvent	Temp. (°C)	Reaction time (h)	Yield (%), ^{31}P NMR
1	$HCOONH_4$/Pd/C (6 equiv.)/(2.8 mol%)	MeOH	65	3	100
2	$HCOONH_4$/Pd/C (6 equiv.)/(4.7 mol%)	MeOH	65	0.3	97
3	$HCOONH_4$/Pd/C (6 equiv.)/(4.7 mol%)[a]	MeOH	65	0.3	70
4	$HCOONH_4$/Ni (6 equiv.)/(30 mol%)	MeOH	65	1.75	40
5	$NaBH_4/CoCl_2{\cdot}6H_2O$ (2 equiv.)/(1 mol%)	EtOH	78	2	20

[a] Re-used catalyst of entry 2.



Scheme 3.

Table 3. Hydrogenation of α-arylethenylphosphonic acids and esters by ammonium formate/Pd/C

Entry	Substrate	Solvent	Time (h)	Product	% Yield	
					Determined by ^{31}P NMR	Isolated
1	**1a**	H_2O	2.5	**3a**	100	–
2	**1a**	MeOH	4	**3a**	100	70
3	**2a**	MeOH	3	**4a**	100	87
4	**1b**	MeOH	4	**3b**	100	87
5	**1c**	MeOH	5	**3c**	60	–
6	**1c**	H_2O	4	**3c**	100	74
7[a]	**2e**	MeOH	10	**4e**	100	88
8[a]	**2f**	MeOH	10	**4f**	100	88
9	**1d**	MeOH	4	**3d** + **3a**	50 + 50	–

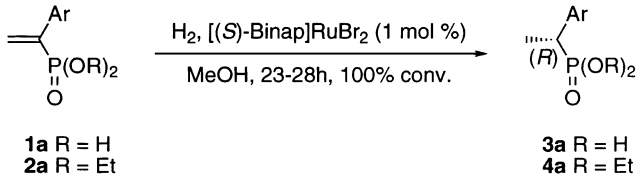
[a] 5% Pd/C (5 mol%), $HCOONH_4$ (7.5 equiv.).

Ammonium formate (6 equiv.) in the presence of 5% palladium on charcoal (2.8 or 4.7 mol%) readily reduced diethyl phenylethenylphosphonate **2a** under reflux in methanol affording the corresponding saturated phosphonate **4a** in high yields (entries 1, 2). The palladium catalyst may be filtered off and reused however, with some loss of activity (entries 2 and 3). Replacement of Pd/C by Raney nickel or reduction using $NaBH_4/CoCl_2{\cdot}6H_2O$[35] was found to be less effective (entries 4, 5). The best reaction conditions were applied to the synthesis of other α-arylethylphosphonic acids **3** and diethyl esters **4**, which were not readily accessible by conventional methods (Scheme 3). The results obtained are presented in Table 3.

The reactions were monitored using ^{31}P NMR. The signals of arylethylphosphonates **4** ranged between 30 and 31 ppm, but the signals of the reaction mixtures of phosphonic acids **3** were broader so, in this case, the ^{31}P NMR analysis was performed after the work-up. The reactions of both α-arylated ethenylphosphonic acids and esters are very clear (except the case of 1-(4-chlorophenyl)ethenylphosphonic acid **1d** which is discussed below); no side products were detected.

Water was more appropriate for the hydrogenation of α-arylated ethenylphosphonic acids (entries 1 and 6) due in part to their better solubility in this solvent. α-Arylethenylphosphonates **2e** and **2f** bearing strong electron donating substituents on the aromatic ring are less reactive (entries 7 and 8) and the reaction was carried out with an increased amount of ammonium formate (7.5 equiv.), palladium catalyst (5 mol%), and prolongation of the reaction time up to 10 h.

Chemoselective hydrogenation of 1-(4-chlorophenyl)-ethenylphosphonic acid **1d** using a $HCOONH_4$/Pd/C system failed and dehalogenation of the aromatic ring was observed. When the solution of **1d** in methanol was heated under reflux with $HCOONH_4$ (6 equiv.) and 5% Pd/C (2.8 mol%) a 1:1 mixture of **3d** and **3a** was isolated (entry 9). Carrying out the reaction at room temperature failed to prevent the dehalogenation. Except for the diethyl 2-(4-chlorophenyl)ethenyl-



1a R = H
2a R = Et

3a R = H
4a R = Et

Scheme 4.

Table 4. Optimization of the asymmetric hydrogenation reaction conditions

Entry	Substrate	Pressure (bar)	Temperature (°C)	E.e. (%)
1	**1a**	1	20	54
2	**1a**	1	80	68
3	**1a**	10	80	73
4	**1a**	100	80	63
5	**2a**	80	80	66[a]

[a] E.e. was measured by GC analysis (Megadex 5 column).

phosphonate,[18b] the results are consistent with literature data.[36]

2.3. Asymmetric hydrogenation of α-aryl substituted ethenylphosphonic acids and esters with chiral Ru(II) catalysts

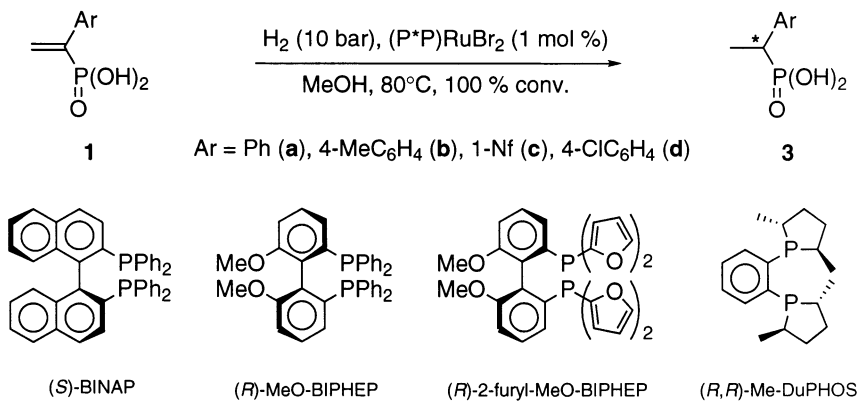
We have previously reported[17] the first asymmetric hydrogenation of α-aryl substituted ethenylphosphonic acids **1a–d** and the diethyl ester **2a** to the corresponding α-arylethylphosphonic acids **3a–d** and ester **4a** with chiral Ru(II) catalysts (Scheme 4).

Preliminary optimization of the experimental conditions was performed using **1a** and [(*S*)-Binap]$RuBr_2$ (1 mol%) in methanol as a representative example (Table 4). The enantioselectivity of this reaction was found to improve at elevated temperatures. A reaction completed at 20°C gave an e.e. of 54%, whilst an e.e. of 68% was achieved by raising the reaction temperature to 80°C (entries 1 and 2). An effect of the reaction pressure on enantioselectivity was also noticed, and the best selectivity (e.e. of 73%, entry 3) was observed under a hydrogen pressure of 10 bar (the pressure was varied in reactions from 1 to 100 bar, as shown in entries 2–4). The reactivity of phosphonic acid **1a** was superior to that of the corresponding diethyl ester **2a**. For example, phosphonate **2a** did not react at low pressure and temperature, but under a pressure of 80 bar at a temperature of 80°C it was converted to **4a** in quantitative yield with an e.e. of 66% (entry 5).

Table 5. Asymmetric hydrogenation of α-arylethenylphosphonic acids using Ru(II) catalysts

Entry	Substrate	(P*P)	Product	E.e. (%)
1	**1a**	(*S*)-BINAP	(*R*)-**3a**	73
2	**1a**	(*R*)-MeO-BIPHEP	(*S*)-**3a**	77
3	**1a**	(*R*)-2-Furyl-MeO-BIPHEP	(*S*)-**3a**	24
4	**1a**	(*R,R*)-Me-DuPHOS	(*R*)-**3a**	21
5	**1b**	(*S*)-BINAP	(*R*)-**3b**	71
6	**1b**	(*R*)-MeO-BIPHEP	(*S*)-**3b**	78
7	**1b**	(*R*)-2-Furyl-MeO-BIPHEP	(*S*)-**3b**	25
8	**1b**	(*R,R*)-Me-DuPHOS	(*R*)-**3b**	16
9	**1c**	(*S*)-BINAP	(*R*)-**3c**	73
10	**1c**	(*R*)-MeO-BIPHEP	(*S*)-**3c**	86
11	**1c**	(*R*)-2-Furyl-MeO-BIPHEP	(*S*)-**3c**	32
12	**1c**	(*R,R*)-Me-DuPHOS	(*R*)-**3c**	37
13	**1d**	(*S*)-BINAP	(*R*)-**3d**	74
14	**1d**	(*R*)-MeO-BIPHEP	(*S*)-**3d**	80
15	**1d**	(*R*)-2-Furyl-MeO-BIPHEP	(*S*)-**3d**	19
16	**1d**	(*R,R*)-Me-DuPHOS	(*R*)-**3d**	25

We then investigated the asymmetric hydrogenation of α-aryl substituted ethenylphosphonic acids **1a–d** using the optimized conditions (hydrogen pressure of 10 bar, temperature of 80°C) with Ru(II) catalysts prepared in situ[37] with various optically active diphosphine ligands (Scheme 5). The results obtained are given in Table 5. For all α-arylethenylphosphonic acids **1** examined, only moderate enantioselectivities were attained by use of (*R,R*)-Me-DuPHOS (e.e.s of 16–37%, entries 4, 8, 12, 16) when the α-arylethenylphosphonic acids **1** were hydrogenated under optimized reaction conditions (10 bar, 80°C, MeOH). (*S*)-BINAP provided good enantioselectivities (e.e.s of 71–74%, entries 1, 5, 9, 13). The



Scheme 5.

best results were obtained using (*R*)-MeO-BIPHEP (77–86% e.e., entries 2, 6, 10, 14) although moderate enantioselectivities were obtained when (*R*)-2-furyl-MeO-BIPHEP was used as the ligand (entries 3, 7, 11, 15). Atropoisomeric ligands with (*R*) absolute configuration afforded the (*S*)-enantiomers of α-arylethylphosphonic acids **3**. This result was opposite to earlier obtained for enantioselective hydrogenation of 2-aryl substituted acrylic acids.[38]

The determination of the enantiomeric purity of the phosphonic acids was performed by treating **3a**–**d** with various chiral diamines, such as (*S*)-2-phenylethylamine **5**, (1*R*,2*R*)-(−)-1,2-cyclohexyldiamine **6**, (1*S*,2*S*)-(−)-1,2-diphenylethylene-1,2-diamine **7**, and (1*S*,2*S*)-(−)-*N*,*N*′-dimethyl-1,2-diphenylethylene-1,2-diamine **8** in $CDCl_3$ doped with CD_3OD (ca. 4%). In all cases, inseparable signals of diastereomeric mixtures of ammonium salts were observed by ^{31}P NMR, except for (1*S*,2*S*)-**8** ($\Delta\delta = 0.4$ ppm) (Scheme 6).

The (*R*) absolute configuration of 1-phenylethylphosphonic acid **3a** (entry 1) was assigned by comparing the specific rotation of the corresponding dimethylphosphonate (obtained by treatment of **3a** with diazomethane) with the literature data.[14a] The absolute configuration of (*S*)-**3b** (entry 6) was assigned by comparison of the specific rotation of the corresponding dimethyl ester with that of an authentic sample of the (*S*)-enantiomer, prepared according to the procedure of Hanessian[14a] (Scheme 7).

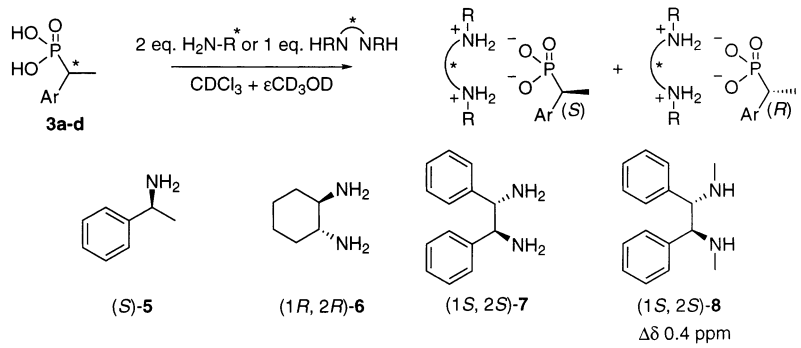
3. Conclusion

In conclusion, the hydrogenation of the carbon–carbon double bond of α-aryl substituted ethenylphosphonic acids and diesters readily available from the corresponding acetylarenes or arylacetylenes provides a general method for the synthesis of 1-arylethylphosphonates. The use of ammonium formate in the presence of palladium on carbon as a reducing agent makes the operation simple. Optically active α-aryl substituted ethylphosphonic acids are obtained with good enantiofacial discrimination by the homogeneous enantioselective ruthenium mediated hydrogenation of the corresponding α,β-unsaturated phosphonic acids.

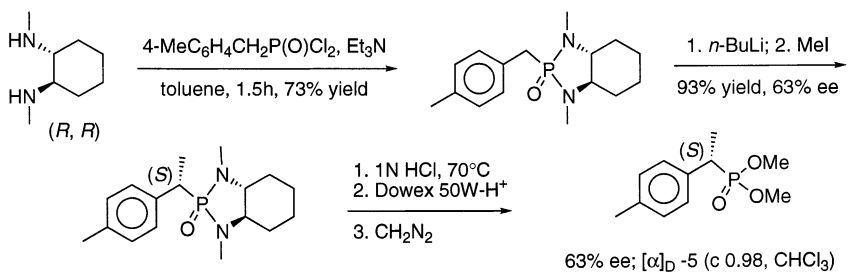
4. Experimental

4.1. Physical measurements

^1H NMR spectra were recorded on a Varian VXR-400 spectrometer. ^{31}P NMR spectra were recorded with a Varian FT-80A or a Bruker 80-WP (32.4 MHz). Chemical shift values (δ) are denoted in ppm and are referenced to residue protons in deuterated solvents for ^1H NMR ($CDCl_3$: 7.27 ppm; CD_3OD: 3.34 ppm) and to external H_3PO_4 (85% solution in D_2O, 0 ppm) for ^{31}P NMR. The IR spectra were obtained using a UR-20 spectrophotometer (Carl Zeiss Jena). HRMS were recorded with a Varian MAT-212 instrument in the range 35–600 Daltons using EI ionization; $R = 25.000$.



Scheme 6.



Scheme 7.

4.2. Materials

4-Methoxyphenylacetylene,[39] 2-ethynyl-6-methoxynaphthalene,[40] and $Pd_2(dba)_3{\cdot}CHCl_3$[41] were prepared by the reported methods. Other reagents are commercial ones and were purified by distillation under argon or recrystallization. Methanol was dried over magnesium and distilled before use. THF was refluxed and then distilled from KOH and sodium/benzophenone ketyl. Before use it was freeze-pump-thawed (10^{-2} mmHg) and vacuum-transferred into reaction vessel.

4.3. Palladium on charcoal catalyst (5% Pd)

A mixture of palladium(II) chloride (0.167 g), concentrated hydrochloric acid (0.4 mL) and water (1 mL) was heated on a steam bath for about 30 min until complete dissolution. The solution obtained was added to a rapidly stirred, hot (80°C) suspension of charcoal (1.9 g) in water (24.5 mL) and 37% formaldehyde solution (0.5 mL) was added dropwise. The suspension was stirred for 30 min and cooled on ice. The reaction mixture was treated with 30% potassium hydroxide solution until slightly alkaline to litmus and the resultant mixture was stirred for 30 min at 60°C and then for 2 h at room temperature. The catalyst was collected on a filter, washed with water until negative reaction to phenolphthalein, and dried first in air, and then in a vacuum desiccator over KOH.

1-Phenylethenylphosphonic acid **1a**. Phosphorus trichloride (24.0 mL, 0.275 mol) was added dropwise to acetophenone (23.3 mL, 0.20 mol) under ice cooling (0–5°C). The mixture was stirred at room temperature for a further 1 h. Glacial acetic acid (28.8 mL, 0.50 mol) was then added over 0.5 h, while the temperature was kept below 10°C. The reaction mixture was stirred overnight, then poured onto ice (700 g), and allowed to stand for 12 h. The solution was evaporated at 90–92°C, and the residue became almost solid while standing in a vacuum desiccator over potassium hydroxide. The crystals were dissolved in 50 mL of boiling concentrated hydrochloric acid and the mixture was refluxed for 3.5 h. The solution was cooled and the product was collected as a white crystalline solid (30.6 g, 83% yield). Mp 100–101°C; raised after recrystallization from benzene–dichloromethane mixture to mp 112–113°C.[32] ^{31}P NMR (CH_3OH): δ 17.0. ^{1}H NMR (CD_3OD): δ 5.32 (s, O*H*), 6.05 (dd, $^2J_{HH}=1.6$ Hz, $^3J_{PH}=44.4$ Hz, 1H, *trans*-PC=C*H*), 6.23 (dd, $^2J_{HH}=1.6$ Hz, $^3J_{PH}=21.6$ Hz, 1H, *cis*-PC=C*H*), 7.31–7.41 (m, 3H, arom.), 7.61 (m, 2H, arom.). IR (Nujol): $\nu=2700$ v.br., 2230 v.br., 1500, 1210, 1030, 945, 785, 720, 700 cm^{-1}.

1-(4-Methylphenyl)ethenylphosphonic acid **1b** was prepared analogously to **1a** in 71% yield from *p*-methylacetophenone (7.3 mL, 55 mmol), PCl_3 (6.5 mL, 74 mmol) and CH_3COOH (9.4 mL, 164 mmol). White crystalline solid, mp 120–121°C.[33a] ^{31}P NMR (CH_3OH): δ 13.2. ^{1}H NMR (CD_3OD): δ 2.37 (s, 1H, C*H*$_3$), 4.94 (s, O*H*), 6.02 (dd, $^2J_{HH}=1.8$ Hz, $^3J_{PH}=44.4$ Hz, 1H, *trans*-PC=C*H*), 6.17 (dd, $^2J_{HH}=1.8$ Hz, $^3J_{PH}=22.0$ Hz, 1H, *cis*-PC=C*H*), 7.19 (d, $^3J_{AB}=8.1$ Hz, 2H, arom.), 7.50 (dd, $^3J_{AB}=8.1$ Hz, 2H, arom.). IR (Nujol): $\nu=$ 2700 v.br., 2300 v.br., 1520, 1145, 1020, 960, 830, 745 cm^{-1}. Anal. calcd for $C_9H_{11}O_3P$: C, 54.55; H, 5.59. Found: C, 54.25; H, 5.54%.

1-(1-Naphthyl)ethenylphosphonic acid **1c** was prepared analogously to **1a** in 68% yield from 1-acetylnaphthalene (9.16 g, 54 mmol), PCl_3 (6.4 mL, 73 mmol) and CH_3COOH (9.7 mL, 169 mmol). White crystalline solid, mp 133–134°C (water). ^{31}P NMR (CH_3OH): δ 13.8. ^{1}H NMR (CD_3OD): δ 5.08 (s, O*H*), 5.88 (dd, $^2J_{HH}=2.2$ Hz, $^3J_{PH}=45.1$ Hz, 1H, *trans*-PC=C*H*), 6.57 (dd, $^2J_{HH}=2.2$ Hz, $^3J_{PH}=21.9$ Hz, 1H, *cis*-PC=C*H*), 7.50 (m, 4H, arom.), 7.88 (m, 2H, arom.). 8.07 (m, 1H, arom.). IR (Nujol): $\nu=2700$ v.br., 2320 v.br., 1160, 1040, 940, 805, 785, 730 cm^{-1}. Anal. calcd for $C_{12}H_{11}O_3P$: C, 61.54; H, 4.73. Found: C, 61.73; H, 4.72%.

1-(4-Chlorophenyl)ethenylphosphonic acid **1d** was prepared in 76% yield analogously to **1a** from *p*-chloroacetophenone (10.4 mL, 0.08 mol), PCl_3 (9.6 mL, 0.11 mol) and CH_3COOH (13.6 mL, 0.24 mol). White crystalline solid, mp 137–139°C (conc. aq. HCl).[33b] ^{31}P NMR (CH_3OH): δ 12.7. ^{1}H NMR (CD_3OD): δ 5.14 (s, O*H*), 6.07 (dd, $^2J_{HH}=1.5$ Hz, $^3J_{PH}=43.8$ Hz, 1H, *trans*-PC=C*H*), 6.24 (dd, $^2J_{HH}=1.5$ Hz, $^3J_{PH}=21.6$ Hz, 1H, *cis*-PC=C*H*), 7.38 (d, $^3J_{AB}=8.3$ Hz, 2H, arom.), 7.60 (dd, $^3J_{AB}=8.3$ Hz, 2H, arom.). IR (Nujol): $\nu=2700$ v.br., 2270 v.br., 1500, 1140, 1075, 1010, 935, 850, 835, 720 cm^{-1}. Anal. calcd for $C_8H_8O_3PCl$: C, 43.96; H, 3.69. Found: C, 44.29; H, 3.67%.

4.4. Hydrophosphorylation of phenylacetylene. Typical procedure

A solution of phenylacetylene (1.14 g, 11 mmol), diethyl phosphite (1.38 g, 10 mmol) and $Pd(PPh_3)_4$ (0.34 g, 0.3 mmol) in THF (10 mL) was heated in a sealed glass ampoule at 67°C for 15 h. The ampoule was opened; the reaction mixture was filtered to remove palladium black, volatiles were evaporated under reduced pressure and the residue was distilled in vacuo to give diethyl 1-phenylethenylphosphonate **2a** as a yellowish viscous liquid (1.8 g, 75%), bp 112–115°C/10^{-1} mmHg.[23,24,26,27] ^{31}P NMR (CH_3OH): δ 17.1. ^{1}H NMR ($CDCl_3$): δ 1.20 (t, $^3J_{HH}=6.8$ Hz, 6H, CH_2CH_3), 4.07 (m, 4H, CH_2CH_3), 6.13 (dd, $^2J_{HH}=1.6$ Hz, $^3J_{PH}=$ 45.7 Hz, 1H, *trans*-PC=C*H*), 6.31 (dd, $^2J_{HH}=1.6$ Hz, $^3J_{PH}=21.9$ Hz, 1H, *cis*-PC=C*H*), 7.31 (m, 3H, arom.), 7.50 (m, 2H, arom.). IR (Nujol): $\nu=2985$, 1500, 1395, 1235, 1165, 1020, 960, 850, 780, 715 cm^{-1}.

Diethyl 1-(4-methoxyphenyl)ethenylphosphonate **2e** was prepared in 65% yield analogously to **2a** from 4-methoxyphenylacetylene (1.01 g, 7.6 mmol), $HP(O)(OEt)_2$ (0.98 mL, 7.6 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (117 mg, 113 μmol) and PPh_3 (246 mg, 0.94 mmol) in THF (7.6 mL). **2a** was isolated as a yellowish viscous liquid, bp 133–135°C/10^{-1} mmHg, R_f 0.5 (Silufol, EtOAc). ^{31}P NMR (CH_3OH): δ 18.0. ^{1}H NMR ($CDCl_3$): δ 1.25 (t, $^3J_{HH}=7.0$ Hz, 6H, CH_2CH_3), 3.77 (s, 3H, OCH_3), 4.10 (m, 4H, CH_2CH_3), 6.07 (dd, $^2J_{HH}=1.3$ Hz, $^3J_{PH}=45.8$ Hz, 1H, *trans*-PC=C*H*), 6.21

(dd, $^2J_{HH}$=1.3 Hz, $^3J_{PH}$=21.6 Hz, 1H, *cis*-PC=C*H*), 6.84 (d, $^3J_{AB}$=8.8 Hz, 2H, arom.), 7.45 (dd, $^3J_{AB}$=8.8 Hz, 2H, arom.). IR (film): ν=2985, 1610, 1520, 1300, 1260, 1185, 1040, 970, 845, 800 cm^{-1}.

1-(6-Methoxy-2-naphthyl)ethenylphosphonate **2f** was prepared in 74% yield analogously to **2a** from 2-ethynyl-6-methoxynaphthalene (0.64 g, 3.5 mmol), HP(O)(OEt)$_2$ (0.45 mL, 3.5 mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (54.4 mg, 53 μmol) and PPh$_3$ (110 mg, 0.42 mmol) in THF (3.5 mL). After evaporation of the solvent, the residue was purified by chromatography on silica gel (Chemapol, L 5/40). PPh$_3$ and dibenzylideneacetone were eluted with benzene and diethyl ether then **2e** was eluted with ethyl acetate. Evaporation of the product fractions afforded a reddish oil, R_f 0.2 (Silufol, Et$_2$O). ^{31}P NMR (CH$_3$OH): δ 17.0. ^{1}H NMR (CDCl$_3$): δ 1.28 (t, $^3J_{HH}$=7.2 Hz, 6H, CH$_2$C*H*$_3$), 3.92 (s, 3H, OC*H*$_3$), 4.12 (m, 4H, C*H*$_2$CH$_3$), 6.25 (dd, $^2J_{HH}$=1.5 Hz, $^3J_{PH}$=45.8 Hz, 1H, *trans*-PC=C*H*), 6.37 (dd, $^2J_{HH}$=1.5 Hz, $^3J_{PH}$=21.9 Hz, 1H, *cis*-PC=C*H*), 7.1–7.2 (m, 2H, arom.), 7.6–7.8 (m, 3H, arom.), 7.98 (s, 1H, arom.). IR (film): ν=2990, 1635, 1610, 1490, 1395, 1265, 1170, 1040, 970, 860, 810, 760 cm^{-1}.

4.5. Reduction of 1-phenylethenylphosphonic acid 1a. Typical procedure

A mixture of **1a** (0.92 g, 5 mmol), ammonium formate (1.90 g, 30 mmol) and palladium on carbon (5%, 0.30 g) in MeOH (70 mL) was heated under reflux for 4 h under argon. The mixture was filtered through a short pad of silica gel. Methanol was removed from the filtrate in vacuo. The residue was acidified with conc. HCl (ca. 1 mL) and extracted with AcOEt. The combined organic layers were dried (MgSO$_4$), filtered and evaporated in vacuo to furnish a pale yellow oil. Recrystallization from benzene/petroleum ether afforded 1-phenylethylphosphonic acid **3a** as a white solid (0.65 g, 70%), mp 151°C.[6a] ^{31}P NMR (EtOAc): δ 31.0. ^{1}H NMR (CD$_3$OD): δ 1.59 (dd, $^3J_{HH}$=7.6 Hz, $^3J_{PH}$=18.0 Hz, 3H, C*H*$_3$), 3.18 (dq, $^3J_{HH}$=7.6 Hz, $^2J_{PH}$=22.6 Hz, 1H, C*H*), 4.95 (s, O*H*), 7.20–7.40 (m, 1+2+2H, arom.). IR (Nujol): ν=2700 v.br., 2350 v.br., 1500, 1175, 1005, 940, 775, 700 cm^{-1}.

1-(4-Methylphenyl)ethylphosphonic acid **3b** was prepared in 87% yield analogously to **3a** from 1-(4-methylphenyl)ethenylphosphonic acid **1b** (0.99 g, 5 mmol), HCOONH$_4$ (1.90 g, 30 mmol) and Pd/C (5%, 0.30 g) in MeOH (70 mL). Pale cream solid, mp 129–130°C. ^{31}P NMR (CD$_3$OD): δ 27.9. ^{1}H NMR (CD$_3$OD): δ 1.52 (dd, $^3J_{HH}$=7.0 Hz, $^3J_{PH}$=17.9 Hz, 3H, CHC*H*$_3$), 2.28 (s, 3H, C*H*$_3$C$_6$H$_4$), 3.08 (dq, $^3J_{HH}$=7.0 Hz, $^2J_{PH}$=22.1 Hz, 1H, C*H*), 5.13 (s, O*H*), 7.09 (d, $^3J_{AB}$=7.6 Hz, 2H, arom.), 7.21 (d, $^3J_{AB}$=7.6 Hz, 2H, arom.). IR (Nujol): ν=2700 v.br., 2270 v.br., 1520, 1205, 1005, 950, 825, 730 cm^{-1}. Anal. calcd for C$_9$H$_{13}$O$_3$P: C, 54.00; H, 6.55; P, 15.47. Found: C, 53.81; H, 6.64; P, 15.24%.

1-(1-Naphthyl)ethylphosphonic acid **3c** was prepared in 74% yield analogously to **3a** from 1-naphthylethenylphosphonic acid **1c** (1.22 g, 5.2 mmol), HCOONH$_4$ (1.98 g, 31 mmol) and Pd/C (5%, 0.31 g) in water (40 mL). Pale cream solid, mp 181–182°C. ^{31}P NMR (CD$_3$OD): δ 28.6. ^{1}H NMR (CD$_3$OD): δ 1.71 (dd, $^3J_{HH}$=7.4 Hz, $^3J_{PH}$=17.8 Hz, 3H, C*H*$_3$), 4.14 (dq, $^3J_{HH}$=7.4 Hz, $^2J_{PH}$=22.8 Hz, 1H, C*H*), 5.48 (s, O*H*), 7.4–7.6 (m, 3H, arom.), 7.7–7.8 (m, 2H, arom.), 7.86 (d, $^3J_{HH}$=8.0 Hz, 1H, arom.), 8.19 (d, $^3J_{HH}$=8.0 Hz, 1H, arom.). IR (Nujol): ν=2700 v.br., 2230 v.br., 1520, 1130, 990, 935, 800, 780 cm^{-1}. Anal. calcd for C$_{12}$H$_{13}$O$_3$P: C, 61.02; H, 5.55; P, 13.11. Found: C, 60.96; H, 5.42; P, 13.00%.

4.6. Reduction of diethyl 1-phenylethenylphosphonate 2a. Typical procedure

A mixture of **2a** (1.20 g, 5 mmol), ammonium formate (1.91 g, 30 mmol) and palladium on carbon (5%, 0.29 g) in 70 mL of MeOH was heated to reflux for 3 h under argon atmosphere. The catalyst was filtered off using a short pad of silica gel. The reaction mixture was evaporated to dryness in vacuo. The residue was extracted with Et$_2$O and the combined organic layers were washed with water, dried (MgSO$_4$), filtered and evaporated. The pale yellow oil thus obtained was distilled to give diethyl 1-phenylethylphosphonate **4a** as a colorless viscous liquid (1.05 g, 87%), bp 90–92°/10^{-1} mmHg.[6b,c,11c] ^{31}P NMR (CH$_3$OH): δ 30.2. ^{1}H NMR (CDCl$_3$): δ 1.13 (t, $^3J_{HH}$=7.1 Hz, 3H, CH$_2$C*H*$_3$), 1.26 (t, $^3J_{HH}$=7.1 Hz, 3H, CH$_2$C*H*$_3$), 1.57 (dd, $^3J_{HH}$=7.4 Hz, $^3J_{PH}$=18.5 Hz, 3H, CHC*H*$_3$), 3.17 (dq, $^3J_{HH}$=7.4 Hz, $^2J_{PH}$=22.6 Hz, 1H, C*H*), 3.78 (m, 1H, C*H*$_2$CH$_3$), 3.92 (m, 1H, C*H*$_2$CH$_3$), 4.02 (m, 2H, C*H*$_2$CH$_3$), 7.20–7.35 (m, 5H, arom.). IR (film): ν=2985, 2935, 1500, 1460, 1395, 1250, 1165, 1030, 965, 810, 770, 705 cm^{-1}.

Diethyl 1-(4-methoxyphenyl)ethylphosphonate **4e** was prepared in 88% yield analogously to **4a** from diethyl 1-(4-methoxyphenyl)ethenylphosphonate **2e** (0.72 g, 2.7 mmol), HCOONH$_4$ (1.27 g, 20 mmol) and Pd/C (5%, 0.28g) in MeOH (40 mL). Reaction time was 10 h. Compound **4e** was isolated as a colorless viscous liquid, bp 137–141°C/10^{-1} mmHg. ^{31}P NMR (CH$_3$OH): δ 30.6. ^{1}H NMR (CDCl$_3$): δ 1.14 (t, $^3J_{HH}$=7.0 Hz, 3H, CH$_2$C*H*$_3$), 1.26 (t, $^3J_{HH}$=7.0 Hz, 3H, CH$_2$C*H*$_3$), 1.53 (dd, $^3J_{HH}$=7.4 Hz, $^3J_{PH}$=18.5 Hz, 3H, CHC*H*$_3$), 3.11 (dq, $^3J_{HH}$=7.4 Hz, $^2J_{PH}$=22.5 Hz, 1H, C*H*), 3.78 (s, 3H, OC*H*$_3$), 3.79 (m, 1H, C*H*$_2$CH$_3$), 3.90 (m, 1H, C*H*$_2$CH$_3$), 4.01 (m, 2H, C*H*$_2$CH$_3$), 6.85 (d, $^3J_{AB}$=8.7 Hz, 2H, arom.), 7.10 (d, $^3J_{AB}$=8.7 Hz, 2H, arom.). IR (film): ν=2990, 2940, 1520, 1470, 1300, 1250, 1180, 1030, 960, 840, 785 cm^{-1}. Anal. calcd for C$_{13}$H$_{21}$O$_4$P: C, 57.35; H, 7.77; P, 11.38. Found: C, 57.26; H, 8.05; P, 11.12%.

Diethyl 1-(6-methoxy-2-naphthyl)ethylphosphonate **4f** was prepared in 88% yield analogously to **4a** from 1-(6-methoxyl-2-naphthyl)ethenylphosphonate **2f** (0.72 g, 2.3 mmol), HCOONH$_4$ (1.06 g, 16.9 mmol) and Pd/C (5%, 0.24g) in 34 mL of MeOH. Reaction time 10 h. Pale yellow oil. ^{31}P NMR (CH$_3$OH): δ 30.0. ^{1}H NMR (CDCl$_3$): δ 1.06 (t, $^3J_{HH}$=7.0 Hz, 3H, CH$_2$C*H*$_3$), 1.22 (t, $^3J_{HH}$=7.0 Hz, 3H, CH$_2$C*H*$_3$), 1.61 (dd, $^3J_{HH}$=7.2

Hz, $^3J_{PH}$=18.4 Hz, 3H, CHCH_3),), 3.30 (dq, $^3J_{HH}$=7.2 Hz, $^2J_{PH}$=22.5 Hz, 1H, CH), 3.76 (m, 1H, CH_2CH$_3$), 3.80 (s, 3H, OCH_3), 3.93 (m, 1H, CH_2CH$_3$), 4.04 (m, 2H, CH_2CH$_3$), 7.0–7.7 (m, 6H, arom.). IR (film): ν= 2990, 2930, 1610, 1490, 1395, 1230, 1165, 1030, 965, 860, 815, 790 cm^{-1}. HRMS: calcd for $C_{17}H_{23}O_4P$ 322.1334; found 322.1330.

4.7. General procedure for asymmetric hydrogenation

(*R*)-MeO-BIPHEP (7 mg, 0.012 mmol) and (COD)Ru(η^3-(CH$_2$)$_2$CCH$_3$) (3.2 mg, 0.01 mmol) were placed in a 50 mL flask and anhydrous acetone (5 mL) was added dropwise. A methanolic solution of HBr (122 μL, 0.18 M) was added dropwise to the suspension. The reaction mixture was stirred at room temperature for about 30 min and a resulting yellow suspension was observed. The solvent was removed under vacuum. The orange solid residue was used as catalyst for the hydrogenation reaction. Methanol (2 mL) and the appropriate substrate (1 mmol) were added and the reaction vessel was then placed in a 500 mL stainless steel autoclave under argon. The autoclave was pressurized to the desired hydrogen pressure and the reaction was allowed to proceed until complete conversion.

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