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Highly efficient and selective olefination of acyl phosphonates with ethyl diazoacetate catalyzed by a cobalt(II) porphyrin complex

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ABSTRACT

The cobalt(II) porphyrin complex (CoTPP) was found to be an efficient catalyst for the Wittig type olefination of acyl phosphonates with ethyl diazoacetate (EDA) in the presence of triphenylphosphine (Ph_3P). By using this one pot methodology under mild conditions, densely functionalized vinyl phosphonates were obtained in high yields and high *E*/*Z* selectivities in relatively short reaction times. A rather broad substrate spectrum and steric influence on the reaction rate were observed.

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1. Introduction

Vinyl phosphonates constitute a very important class of organic compounds.[1] They have been used as monomers,[2] polymer additives,[3] flame retardants,[4] precursors for drug synthesis,[5] etc. Vinyl phosphonates have also been subjected to a variety of further transformations.[6] Therefore, several methods for the preparation of vinyl phosphonates have been reported in the literature where the metalation of alkynes, hydrophosphynilation of alkynes, Arbusov reactions of vinyl chlorides, Horner–Wadsworth–Emmons (HWE) type olefination of simple alkyl phosphonates via metalation, and radical trapping reactions were all employed.[7] Wittig type olefination is one of the most frequently used methods for the construction of carbon–carbon double bonds in organic synthesis.[8,9] Phosphoranes that are the nucleophilic part of the Wittig reactions were easily prepared by the Arbusov reaction or via the decomposition of diazo compounds in the presence of a transition metal complex.[10,11] Very recently, iron and cobalt porphyrin complexes were successfully utilized for the olefination of aldehydes and for ketones with diazo compounds in the presence of triarylphosphines, wherein metal porphyrins generate stable metal carbene complexes.[12] In conjunction with our ongoing program on acyl phosphonate chemistry,[13] we report here our successful results on the cobalt(II) tetraphenylporphyrin (CoTPP) catalyzed olefination of acyl phosphonates with ethyl diazoacetate (EDA) in the presence of triphenylphosphine (Ph_3P) (Fig. 1). Although several examples on the olefination of acyl phosphonates via a classical stepwise Wittig reaction were shown by Zbiral and Harris in the literature,[7d,14] it has systematically not been investigated so far.

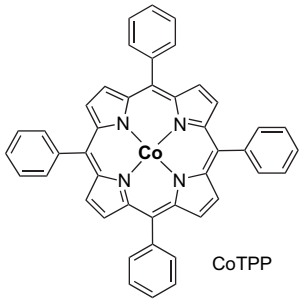

Figure 1. Structure of the cobalt(II) porphyrin (CoTPP) complex.

2. Results and discussion

Although both air-stable CoTPP and the iron(III) tetraphenylporphyrin chloride (FeTPPCl) were able to catalyze the olefination of aldehydes as well as ketones by decomposing the diazo compounds in the presence of Ph_3P,[12e,f] cost-effective CoTPP was the catalyst of choice for our investigation for the acyl phosphonate olefination (Eq. 1). Absolute toluene was used as the solvent because of its relative high boiling point and high solubility of CoTPP in toluene. After the simple optimization of the catalyst loading and the yield using benzoyl phosphonate (**1a**) as the test substrate, 4 mol % of CoTPP was found to be optimum. After stirring at 80 °C for 4 h (TLC) under the standard conditions (CoTPP [4 mol %], EDA [1.20 equiv], Ph_3P [1.20 equiv]), the corresponding olefin product **2a** was obtained in 92% yield and high *E*/*Z* selectivity (97:3) (Table 1, entry 1). Several substituted aroyl phosphonates (**1b**–**g**) were then subjected to the olefination in order to determine the substrate scope of this methodology (Table 1, entries 2–7). The vinyl phosphonates **2b**–**f** were isolated in high yields (72–94%) and *E*/*Z*

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selectivities within 4 h at 80 °C, in which the only exception was the olefin product **2g** bearing a 2-methyl substituted phenyl group. Thus, the sterically hindered aroyl phosphonate **1g** had to be heated at 100 °C for 24 h in order to give the vinyl phosphonate **2g** in good yield (72%) and under *full-stereoselectivity* (*E*/*Z*=100/0, entry 7). The alkoyl phosphonates **1h** and **1i** were the somewhat less reactive substrates for the olefination. However, they could be converted to the corresponding olefin products **2h** and **2i** in 89% and 72% yields and after 6 h and 12 h, respectively (entries 8 and 9). Only *E*-isomers of **2h** and **2i** were obtained. This result of a longer reaction time for the olefination of the alkoyl phosphonate compared to the aroyl phosphonate indicates that alkoyl phosphonates are less reactive toward phosphoranes than aroyl phosphonates. Thus, we attempted to olefinate the sterically hindered and less reactive pivaloyl phosphonate (**1j**) under the standard reaction conditions (entry 10). However, no conversion of **1j** was detected. In spite of all our attempts to convert **1j** by modifying the reaction conditions (e.g., refluxing the reaction mixture for 48 h in the presence of

Table 1
Olefination of acyl phosphonates (**1**) with EDA catalyzed by CoTPP[a]

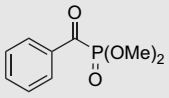
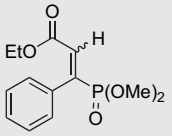
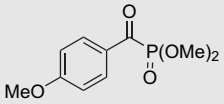
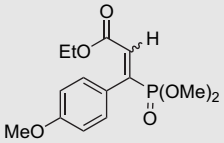
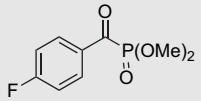
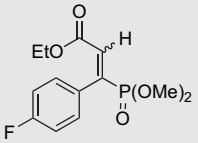
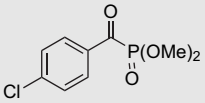
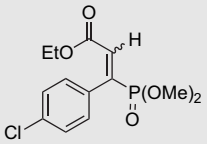
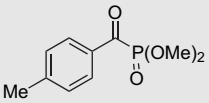
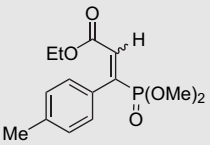
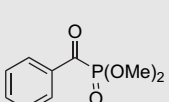
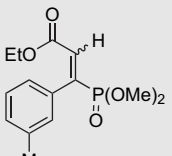
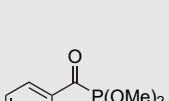
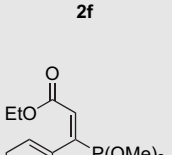
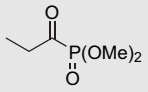
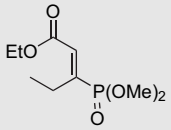
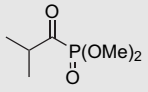
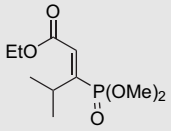
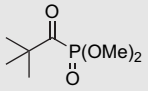
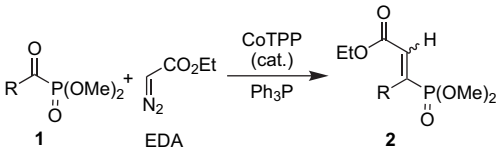
Entry	Substrate	Product	Time (h)	Yield[b] (%)	*E*/*Z*[c]
1	 **1a**	 **2a**	4	92	97/3
2	 **1b**	 **2b**	4	80	95/5
3	 **1c**	 **2c**	4	81	97/3
4	 **1d**	 **2d**	4	83	97/3
5	 **1e**	 **2e**	4	94	97/3
6	 **1f**	 **2f**	4	90	97/3
7	 **1g**	 **2g**	24[d]	72	100/0

Table 1 (*continued*)

Entry	Substrate	Product	Time (h)	Yield[b] (%)	*E*/*Z*[c]
8	 **1h**	 **2h**	6	89	100/0
9	 **1i**	 **2i**	12	72	100/0
10	 **1j**	—	48	—	—

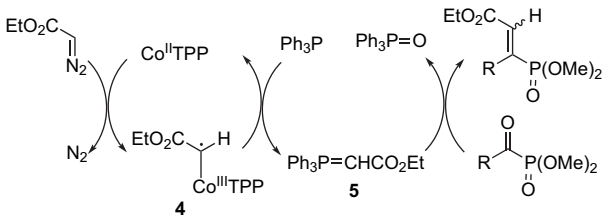
[a] Reactions were carried out at 80 °C in toluene under argon, using 1.00 equiv of acyl phosphonate, 1.20 equiv of EDA, 1.20 equiv of Ph_3P, and 4.0 mol % of CoTPP.
[b] Isolated yield.
[c] Determined by ^1H NMR.
[d] Reaction was run at 100 °C.

1.00 equiv of benzoic acid as the Brønsted acid catalyst),[12e,f] no conversion of **1j** could be achieved. Then, the olefination of pivaloyl phosphonate (**1j**) was attempted by employing trimethyl phosphite ($(MeO)_3P$) and lithium bromide for the generation of less hindered ylide compared to what is formed from Ph_3P, as reported by Aggarwal et al.[12b] (Scheme 1). Thus, we were able to minimize sterical influences on the reaction. However, all experiments using toluene or dioxane as the solvents at 80 °C or at reflux temperature for 48 h failed. While no conversion of **1j** was observed, the sole product isolated was the phosphonate **3**, which demonstrated that CoTPP is also able to transfer carbene to trimethyl phosphite forming the desired ylide for further transformations (Scheme 1).



(1)

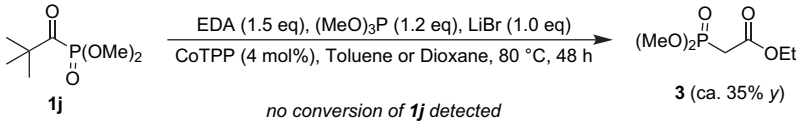
E/*Z* ratios of the olefin products (**2a**–**i**) were determined by means of ^1H NMR by proportioning the integration areas of the *E*- and *Z*-olefin protons to each other. The *E*-configuration for the major products was assigned because of the vicinal cis H,P coupling ($^3J_{H-P}$=24.0 Hz).[7d,14] The vicinal *trans* H,P coupling has a value of 44.0 Hz ($^3J_{H-P}$). Due to hindered rotation about the C(aryl)–C(olefin) bond, the molecule **2g** has axial chirality, which in turn causes the two OMe groups of the phosphoryl moiety to be diastereotopic. The CH_2 protons of the ethoxy group are also diastereotopic, but they may be too far from the chiral axis to cause different chemical shifts in the NMR spectra. The possible reaction mechanism can be derived from what is proposed for the metalloporphyrin catalyzed olefination of aldehydes and ketones,[12] which includes the radical metallocarbene (**4**) formation from CoTPP and EDA followed by phosphorane (**5**) formation and olefination as depicted in Scheme 2.



Scheme 2. Possible olefination mechanism catalyzed by CoTPP is in agreement with what is proposed in the literature.[12f]

3. Conclusions

In conclusion, we have presented a very practical route toward the synthesis of alkoxycarbonylmethylidene phosphonates by reacting the acyl phosphonates with EDA in the presence of Ph_3P and a catalytic amount of commercially available CoTPP. Easily accessible aroyl and alkoyl phosphonates could be olefinated in very high yields, in excellent *E*/*Z* ratios, and in short reaction times by using this one pot protocol under neutral and mild conditions, which made this methodology very practical for synthesis. Moreover, this methodology could also excellently extend the application area of the metalloporphyrin catalyzed olefination reactions for the synthesis of potentially useful unsaturated trisubstituted systems bearing carboxylic- and phosphonic-ester functionalities. Further investigations on the use of these trisubstituted vinyl phosphonates are in progress at our laboratory.



Scheme 1. Search for the olefination of **1j** as the sterically hindered acyl phosphonate.

4. Experimental

4.1. General

All reactions were carried out in oven-dried Schlenk tubes with magnetic stirring under a positive pressure of argon. Toluene and dioxane were freshly distilled from sodium/benzophenone prior to use under an argon atmosphere. Ethyl diazoacetate (EDA) and triphenylphosphine (Ph_3P) were purchased from Aldrich and used as-received. Cobalt(II) tetraphenylporphyrin complex (CoTPP) was synthesized from the reaction of tetraphenylporphyrin ($TPPH_2$) with excessive anhydrous cobalt(II) chloride in the presence of 2,6-lutidine (2.00 equiv) in boiling dimethylformamide (DMF) and it was purified by recrystallization from dichloromethane (DCM)/acetonitrile (MeCN) mixture.[15] Acyl phosphonates were prepared according to the literature procedures and purified by vacuum distillation.[16] Thin layer chromatography (TLC) was conducted on aluminum sheets that were pre-coated with silica gel SIL G/UV_{254} from MN GmbH & Co., in which the spots were visualized in UV light (λ=254 nm) and/or by staining with ninhydrin. Chromatographic separations were performed using silica gel (MN-silica gel 60, 230–400 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX400 NMR spectrometer. Chemical shifts δ are reported in parts per million (ppm) relative to the residual protons in the NMR solvent ($CHCl_3$: δ 7.24) and carbon resonance of the solvent ($CDCl_3$: δ 77.0). NMR peak multiplicities were given as follows: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad. ^{13}C atoms were assigned by means of DEPT-135 experiments. The IR measurements were performed on a Varian 1000 FTIR spectrometer. High resolution CI mass spectra were recorded on a Finnigan MAT. Elemental analyses (EA) were performed using a LECO, CHNS-932 instrument.

4.1.1. Ethyl (E)-3-(dimethoxyphosphinyl)-3-phenyl-2-propenoate (E-**2a**) (representative procedure)

CoTPP (40.0 μmol, 4 mol %) and Ph_3P (1.2 mmol, 1.20 equiv) were placed in an oven-dried Schlenk tube and then the tube was capped with a glass stopper. The tube was evacuated for 15 min and back-filled with argon. The glass stopper was replaced with a rubber septum under positive pressure of argon. After addition of absolute toluene (2 mL) as the solvent, dimethyl benzoyl phosphonate (1.0 mmol, 1.00 equiv) was added in one portion succeeded by the addition of EDA (1.2 mmol, 1.20 equiv) in one portion at room temperature. After stirring the homogenous mixture at room temperature for several minutes, the mixture was stirred at 80 °C (oil-bath temperature) under argon. The reaction progress was monitored by TLC. Upon completion of the reaction (80 °C, 4 h, as indicated in Table 1), the mixture was cooled to room temperature and evaporated. By the addition of diethyl ether (ca. 10–15 mL), triphenylphosphine oxide was precipitated and it was removed from the reaction mixture by decanting the solution phase. After removing all volatile components of the solution by rotary evaporation, the olefin product **2a** was obtained as a light yellow oil (260 mg, 0.92 mmol, 92% yield) after column chromatography on silica gel. R_f=0.47 (silica gel, DCM/EtOAc 1:1). FTIR (film): ν_{max} (cm^{-1})=3068 (w), 2984 (m), 2957 (m), 2853 (w), 1729 (s), 1446 (m), 1369 (m), 1255 (s), 1205 (s),1027 (s), 832 (m), 781 (m), 700 (m), 577 (m), 542 (m). ^1H NMR (400 MHz, $CDCl_3$): δ=0.96 (t, $^3J_{H-H}$=8.0 Hz, 3H, CH_3CH_2), 3.65 (d, $^3J_{H-P}$=12.0 Hz, 6H, $P(O)(OCH_3)_2$), 3.95 (q, $^3J_{H-H}$=8.0 Hz, 2H, CH_3CH_2), 6.81 (d, $^3J_{H-P}$=24.0 Hz, 1H, CH_{olefin}), 7.19–7.22 (m, 2H, H_{aryl}), 7.22–7.35 (m, 3H, H_{aryl}). ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.6 (q, CH_3CH_2), {53.06, 53.12} (q, $^2J_{C-P}$=6.0 Hz, $P(O)(OCH_3)_2$), 60.7 (t, CH_3CH_2), 127.89 (d, *meta*-C_{aryl}), 127.94 (d, *para*-C_{aryl}), {128.26, 128.28} (d, $^3J_{C-P}$=2.0 Hz, *ortho*-C_{aryl}), {133.12, 133.23} (d, $^2J_{C-P}$=11.0 Hz, CH_{olefin}), {133.81, 133.88} (s, $^2J_{C-P}$=7.0 Hz, C_{aryl}), {142.23, 143.96} (s, $^1J_{C-P}$=173.0 Hz, C_{olefin}), {164.19, 164. 48} (s, $^3J_{C-P}$=29.0 Hz, EtO(O)*C*). ^{31}P NMR (161 MHz, $CDCl_3$): δ=17.0. EA: Anal. Calcd for $C_{13}H_{17}O_5P$: C, 54.93; H, 6.03. Found: C, 54.89; H, 6.29. Several well resolved NMR signals for the minor diastereomer (*Z*-**2a**) could also be obtained and assigned as follows: ^1H NMR (400 MHz, $CDCl_3$): δ=1.29 (t, $^3J_{H-H}$=8.0 Hz, 3H, CH_3CH_2), 4.25 (q, $^3J_{H-H}$=8.0 Hz, 2H, CH_3CH_2), 6.55 (d, $^3J_{H-P}$=44.0 Hz, 1H, CH_{olefin}). ^{31}P NMR (161 MHz, $CDCl_3$): δ=15.3.

4.1.2. Ethyl (E)-3-(dimethoxyphosphinyl)-3-(4-methoxyphenyl)-2-propenoate (E-**2b**)

After stirring the reaction mixture at 80 °C for 4 h under argon, the olefin product **2b** was obtained as a light yellow oil (250 mg, 0.80 mmol, 80%) via column chromatographic purification. R_f=0.41 (silica gel, DCM/EtOAc 1:1). FTIR (film): ν_{max} (cm^{-1})=2957 (w), 1728 (s), 1606 (s), 1511 (s), 1462 (m), 1369 (w), 1291 (s), 1251 (s), 1205 (s), 1179 (s), 1029 (s), 836 (s), 773 (m), 571 (m), 531 (m). ^1H NMR (400 MHz, $CDCl_3$): δ=1.12 (t, $^3J_{H-H}$=8.0 Hz, 3H, CH_3CH_2), 3.74 (d, $^3J_{H-P}$=8.0 Hz, 6H, $P(O)(OCH_3)_2$), 3.82 (s, 3H, OCH_3), 4.08 (q, $^3J_{H-H}$=8.0 Hz, 2H, CH_3CH_2), 6.86 (d, $^3J_{H-P}$=24.0 Hz, 1H, CH_{olefin}), 6.89 (d, $^3J_{H-H}$=10.0 Hz, 2H, *meta*-H_{aryl}), 7.24 (d, $^3J_{H-H}$=10.0 Hz, 2H, *ortho*-H_{aryl}). ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.8 (q, CH_3CH_2), {53.11, 53.17} (q, $^2J_{C-P}$=6.0 Hz, $P(O)(OCH_3)_2$), 51.2 (q, OCH_3), 60.8 (t, CH_3CH_2), 113.6 (d, *meta*-C_{aryl}), {125.80, 125.87} (s, $^2J_{C-P}$=7.0 Hz, C_{aryl}), {129.55, 129.61} (d, $^3J_{C-P}$=6.0 Hz, *ortho*-C_{aryl}), {132.56, 132.67} (d, $^2J_{C-P}$=11.0 Hz, CH_{olefin}), {141.88, 143.66} (s, $^1J_{C-P}$=173.0 Hz, C_{olefin}), 159.8 (s, MeO–C_{aryl}), {164.53, 164.82} (s, $^3J_{C-P}$=29.0 Hz, EtO(O)*C*). ^{31}P NMR (161 MHz, $CDCl_3$): δ=17.0. EA: Anal. Calcd for $C_{13}H_{17}O_5P$: C, 53.50; H, 6.09. Found: C, 53.73; H, 6.21. Several well resolved NMR signals for the minor diastereomer (*Z*-**2b**) could also be obtained and assigned as follows: ^1H NMR (400 MHz, $CDCl_3$): δ=1.38 (t, $^3J_{H-H}$=8.0 Hz, 3H, CH_3CH_2), 4.33 (q, $^3J_{H-H}$=8.0 Hz, 2H, CH_3CH_2), 6.61 (d, $^3J_{H-P}$=44.0 Hz, 1H, CH_{olefin}). ^{31}P NMR (161 MHz, $CDCl_3$): δ=15.3.

4.1.3. Ethyl (E)-3-(dimethoxyphosphinyl)-3-(4-fluorophenyl)-2-propenoate (E-**2c**)

After stirring the reaction mixture at 80 °C for 4 h under argon, the olefin product **2c** was obtained as a light yellow oil (245 mg, 0.81 mmol, 81%) via column chromatographic purification. R_f=0.44 (silica gel, DCM/EtOAc 1:1). FTIR (film): ν_{max} (cm^{-1})=2985 (w), 2958 (m), 1728 (s), 1600 (m), 1508 (s), 1464 (m), 1369 (w), 1256 (s), 1222 (s), 1205 (s), 1027 (s), 837 (s), 774 (m), 569 (m), 509 (m). ^1H NMR (400 MHz, $CDCl_3$): δ=1.10 (t, $^3J_{H-H}$=8.0 Hz, 3H, CH_3CH_2), 3.75 (d, $^3J_{H-P}$=12.0 Hz, 6H, $P(O)(OCH_3)_2$), 4.07 (q, $^3J_{H-H}$=8.0 Hz, 2H, CH_3CH_2), 6.88 (d, $^3J_{H-P}$=24.0 Hz, 1H, CH_{olefin}), 7.06 (t, J=8.0 Hz, 2H, *meta*-H_{aryl}), 7.24–7.28 (m, 2H, *ortho*-H_{aryl}). ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.8 (q, CH_3CH_2), {53.19, 53.25} (q, $^2J_{C-P}$=6.0 Hz, $P(O)(OCH_3)_2$), 60.9 (t, CH_3CH_2), {115.07, 115.08, 115.28, 115.29} (d, $^4J_{C-P}$=4.0 Hz, $^2J_{C-F}$=21.0 Hz, *meta*-C_{aryl}), {129.63, 129.67, 129.70, 129.74} (s, $^4J_{C-F}$=4.0 Hz, $^2J_{C-P}$=7.0 Hz, C_{aryl}), {129.95, 130.01, 130.04, 130.09} (d, $^3J_{C-P}$=6.0 Hz, $^3J_{C-F}$=9.0 Hz, *ortho*-C_{aryl}), {133.35, 133.46} (d, $^2J_{C-P}$=11.0 Hz, CH_{olefin}), {141.50, 143.24} (s, $^1J_{C-P}$=174.0 Hz, C_{olefin}), {161.55, 161.58, 164.02, 164.05} (s, $^5J_{C-P}$=3.0 Hz, $^1J_{C-F}$=247.0 Hz, F–C_{aryl}), {164.14, 164.42} (s, $^3J_{C-P}$=28.0 Hz, EtO(O)*C*). ^{31}P NMR (161 MHz, $CDCl_3$): δ=16.8. EA: Anal. Calcd for $C_{13}H_{16}FO_5P$: C, 51.66; H, 5.34. Found: C, 51.72; H, 5.62. Several well resolved NMR signals for the minor diastereomer (*Z*-**2c**) could also be obtained and assigned as follows: ^1H NMR (400 MHz, $CDCl_3$): δ=1.37 (t, $^3J_{H-H}$=8.0 Hz, 3H, CH_3CH_2), 4.33 (q, $^3J_{H-H}$=8.0 Hz, 2H, CH_3CH_2), 6.61 (d, $^3J_{H-P}$=44.0 Hz, 1H, CH_{olefin}). ^{31}P NMR (161 MHz, $CDCl_3$): δ=15.1.

4.1.4. Ethyl (E)-3-(dimethoxyphosphinyl)-3-(4-chlorophenyl)-2-propenoate (E-**2d**)

After stirring the reaction mixture at 80 °C for 4 h under argon, the olefin product **2d** was obtained as a light yellow oil (265 mg, 0.83 mmol, 83%) via column chromatographic purification. R_f=0.47

(silica gel, DCM/EtOAc 1:1). FTIR (film): ν_{max} (cm^{-1})=2985 (w), 2957 (m), 1729 (s), 1489 (m), 1463 (w), 1369 (w), 1258 (s), 1207 (s), 1092 (m), 1028 (s), 837 (m), 775 (m), 710 (w), 565 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.11 (t, $^3J_{H-H}$=8.0 Hz, 3H, CH_3CH_2), 3.75 (d, $^3J_{H-P}$=12.0 Hz, 6H, P(O)(OCH_3)$_2$), 4.07 (q, $^3J_{H-H}$=8.0 Hz, 2H, CH_3CH_2), 6.89 (d, $^3J_{H-P}$=24.0 Hz, 1H, CH_{olefin}), 7.22 (dd, $^4J_{H-P}$=2.0 Hz, $^3J_{H-H}$=8.0 Hz, 2H, *ortho*-H_{aryl}), 7.35 (d, $^3J_{H-H}$=8.0 Hz, 2H, *meta*-H_{aryl}). ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.8 (q, CH_3CH_2), {53.23, 53.29} (q, $^2J_{C-P}$=6.0 Hz, P(O)(OCH_3)$_2$), 70.0 (t, CH_3CH_2), {128.34, 128.35} (d, $^4J_{C-P}$=1.0 Hz, *meta*-C_{aryl}), {129.47, 129.52} (d, $^3J_{C-P}$=5.0 Hz, *ortho*-C_{aryl}), {132.28, 132.35} (s, $^2J_{C-P}$=70 Hz, C_{aryl}), {133.42, 133.53} (d, $^2J_{C-P}$=11.0 Hz, CH_{olefin}), 134.6 (s, *para*-C_{aryl}), {141.54, 143.28} (s, $^1J_{C-P}$=174.0 Hz, C_{olefin}), {164.01, 164.29} (s, $^3J_{C-P}$=28.0 Hz, EtO(O)*C*). ^{31}P NMR (161 MHz, $CDCl_3$): δ=16.5. EA: Anal. Calcd for $C_{13}H_{16}ClO_5P$: C, 48.99; H, 5.06. Found: C, 49.22; H, 5.34. Several well resolved NMR signals for the minor diastereomer (*Z*-**2d**) could also be obtained and assigned as follows: ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.37 (t, $^3J_{H-H}$=8.0 Hz, 3H, CH_3CH_2), 4.34 (q, $^3J_{H-H}$=8.0 Hz, 2H, CH_3CH_2), 6.63 (d, $^3J_{H-P}$=44.0 Hz, 1H, CH_{olefin}). ^{31}P NMR (161 MHz, $CDCl_3$): δ=15.9.

4.1.5. Ethyl (E)-3-(dimethoxyphosphinyl)-3-(4-methylphenyl)-2-propenoate (E-**2e**)

After stirring the reaction mixture at 80 °C for 4 h under argon, the olefin product **2e** was obtained as a light yellow oil (280 mg, 0.94 mmol, 94%) via column chromatographic purification. R_f=0.57 (silica gel, DCM/EtOAc 1:1). FTIR (film): ν_{max} (cm^{-1})=2984 (w), 2956 (m), 1730 (s), 1510 (w), 1460 (w), 1256 (s), 1202 (s), 1027 (s), 833 (m), 773 (w), 570 (m), 510 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.10 (t, $^3J_{H-H}$=8.0 Hz, 3H, CH_3CH_2), 2.36 (s, 3H, H_3C-C_{aryl}), 3.74 (d, $^3J_{H-P}$=12.0 Hz, 6H, P(O)(OCH_3)$_2$), 4.07 (q, $^3J_{H-H}$=8.0 Hz, 2H, CH_3CH_2), 6.88 (d, $^3J_{H-P}$=24.0 Hz, 1H, CH_{olefin}), 7.17 (br s, 4H, H_{aryl}). ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.8 (q, CH_3CH_2), 21.3 (q, H_3C-C_{aryl}), {53.12, 53.18} (q, $^2J_{C-P}$=6.0 Hz, P(O)(OCH_3)$_2$), 60.8 (t, CH_3CH_2), {127.80, 127.85} (d, $^3J_{C-P}$=5.0 Hz, *ortho*-C_{aryl}), 128.8 (d, *meta*-C_{aryl}), {130.68, 130.75} (s, $^2J_{C-P}$=7.0 Hz, C_{aryl}), {132.87, 132.99} (d, $^2J_{C-P}$=12.0 Hz, CH_{olefin}), {138.30, 138.33} (s, $^5J_{C-P}$=3.0 Hz, H_3C-C_{aryl}), {142.45, 144.17} (s, $^1J_{C-P}$=172.0 Hz, C_{olefin}), {164.33, 164.61} (s, $^3J_{C-P}$=28.0 Hz, EtO(O)*C*). ^{31}P NMR (161 MHz, $CDCl_3$): δ=17.4. EA: Anal. Calcd for $C_{14}H_{19}O_5P$: C, 56.37; H, 6.42. Found: C, 56.65; H, 6.58. Several well resolved NMR signals for the minor diastereomer (*Z*-**2e**) could also be obtained and assigned as follows: ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.38 (t, $^3J_{H-H}$=8.0 Hz, 3H, CH_3CH_2), 4.34 (q, $^3J_{H-H}$=8.0 Hz, 2H, CH_3CH_2), 6.63 (d, $^3J_{H-P}$=44.0 Hz, 1H, CH_{olefin}). ^{31}P NMR (161 MHz, $CDCl_3$): δ=15.8.

4.1.6. Ethyl (E)-3-(dimethoxyphosphinyl)-3-(3-methylphenyl)-2-propenoate (E-**2f**)

After stirring the reaction mixture at 80 °C for 4 h under argon, the olefin product **2f** was obtained as a light yellow oil (268 mg, 0.90 mmol, 90%) via column chromatographic purification. R_f=0.44 (silica gel, DCM/EtOAc 1:1). FTIR (film): ν_{max} (cm^{-1})=2984 (m), 2966 (m), 1729 (s), 1603 (w), 1461 (m), 1369 (m), 1254 (s), 1188 (s), 1027 (s), 833 (m), 775 (m), 705 (m), 625 (w), 588 (w), 547 (m), 520 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.06 (t, $^3J_{H-H}$=8.0 Hz, 3H, CH_3CH_2), 2.36 (s, 3H, H_3C-C_{aryl}), 3.74 (d, $^3J_{H-P}$=12.0 Hz, 6H, P(O)(OCH_3)$_2$), 4.05 (q, $^3J_{H-H}$=8.0 Hz, 2H, CH_3CH_2), 6.87 (d, $^3J_{H-P}$=24.0 Hz, 1H, H_{olefin}), 7.05–7.28 (m, 4H, H_{aryl}). ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.7 (q, CH_3CH_2), 21.4 (q, H_3C-C_{aryl}), {53.15, 53.21} (q, $^2J_{C-P}$=6.0 Hz, P(O)(OCH_3)$_2$), 60.8 (t, CH_3CH_2), {124.95, 125.01} (d, $^3J_{C-P}$=6.0 Hz, *ortho*-C_{aryl}), {127.91, 127.92} (d, $^5J_{C-P}$=1.0 Hz, *para*-C_{aryl}), {128.37, 128.42} (d, $^3J_{C-P}$=5.0 Hz, *ortho*-C_{aryl}), {129.17, 129.19} (d, $^4J_{C-P}$=2.0 Hz, *meta*-C_{aryl}), {133.08, 133.19} (d, $^2J_{C-P}$=11.0 Hz, CH_{olefin}), {133.65, 133.72} (s, $^2J_{C-P}$=7.0 Hz, C_{aryl}), {137.61, 137.62} (s, $^4J_{C-P}$=1.0 Hz, H_3C-C_{aryl}), {142.30, 144.02} (s, $^1J_{C-P}$=172.0 Hz, C_{olefin}), {164.34, 164.63} (s, $^3J_{C-P}$=29.0 Hz, EtO(O)*C*). ^{31}P NMR (161 MHz, $CDCl_3$): δ=17.2. EA: Anal. Calcd for $C_{14}H_{19}O_5P$: C, 56.37; H, 6.42. Found: C, 56.65; H, 6.58. Several well resolved NMR signals for the minor diastereomer (*Z*-**2f**) could also be obtained and assigned as follows: ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.37 (t, $^3J_{H-H}$=8.0 Hz, 3H, CH_3CH_2), 4.33 (q, $^3J_{H-H}$=8.0 Hz, 2H, CH_3CH_2), 6.62 (d, $^3J_{H-P}$=44.0 Hz, 1H, H_2). ^{31}P NMR (161 MHz, $CDCl_3$): δ=15.5.

4.1.7. Ethyl (E)-3-(dimethoxyphosphinyl)-3-(2-methylphenyl)-2-propenoate (E-**2g**)

After stirring the reaction mixture at 100 °C for 24 h under argon, the olefin product **2g** was obtained as a light yellow oil (215 mg, 0.72 mmol, 72%) via column chromatography purification. R_f=0.50 (silica gel, DCM/EtOAc 1:1). FTIR (film): ν_{max} (cm^{-1})=2984 (w), 2957 (m), 1731 (s), 1627 (w), 1459 (w), 1255 (s), 1199 (s), 1028 (s), 832 (m), 756 (w), 726 (w), 562 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.94 (t, $^3J_{H-H}$=8.0 Hz, 3H, CH_3CH_2), 2.17 (s, 3H, H_3C-C_{aryl}), 3.63 (d, $^3J_{H-P}$=8.0 Hz, 3H, P(O)(OCH_3)), 3.66 (d, $^3J_{H-P}$=8.0 Hz, 3H, P(O)(OCH_3)), 3.92 (q, $^3J_{H-H}$=8.0 Hz, 2H, CH_3CH_2), 6.83 (d, $^3J_{H-P}$=24.0 Hz, 1H, CH_{olefin}), 6.97 (d, *J*=8.0 Hz, 1H, *meta*-H_{aryl}), 7.08–7.17 (m, 3H, H_{aryl}). ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.6 (q, CH_3CH_2), 19.6 (q, H_3C-C_{aryl}), {53.20, 53.26} (q, $^2J_{C-P}$=6.0 Hz, P(O)(OCH_3)), {53.35, 53.42} (q, $^2J_{C-P}$=7.0 Hz, P(O)(OCH_3)), 60.7 (t, CH_3CH_2), {125.25, 125.27} (d, $^4J_{C-P}$=2.0 Hz, *meta*-C_{aryl}), {127.58, 127.63} (d, $^3J_{C-P}$=5.0 Hz, *ortho*-C_{aryl}), {128.07, 128.09} (d, $^4J_{C-P}$=2.0 Hz, *meta*-C_{aryl}), {129.75, 129.77} (d, $^7J_{C-P}$=2.0 Hz, *para*-C_{aryl}), {133.05, 133.16} (d, $^2J_{C-P}$=11.0 Hz, CH_{olefin}), {133.27, 133.32} (s, $^3J_{C-P}$=5.0 Hz, H_3C-C_{aryl}), {135.82, 135.88} (s, $^2J_{C-P}$=6.0 Hz, C_{aryl}), {143.17, 144.90} (s, $^1J_{C-P}$=173.0 Hz, C_{olefin}), {163.81, 164.10} (s, $^3J_{C-P}$=29.0 Hz, EtO(O)*C*). ^{31}P NMR (161 MHz, $CDCl_3$): δ=15.9. EA: Anal. Calcd for $C_{14}H_{19}O_5P$: C, 56.37; H, 6.42. Found: C, 56.65; H, 6.58.

4.1.8. Ethyl (E)-3-(dimethoxyphosphinyl)-2-pentenoate (E-**2h**)

After stirring the reaction mixture at 80 °C for 6 h under argon, the olefin product **2h** was obtained as a light yellow oil (210 mg, 0.89 mmol, 89%) via column chromatographic purification. R_f=0.44 (silica gel, EtOAc 100%). FTIR (film): ν_{max} (cm^{-1})=2982 (m), 2957 (m), 1723 (s), 1630 (w), 1462 (m), 1371 (w), 1255 (s), 1196 (s), 1029 (s), 831 (m), 782 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.09 (t, $^3J_{H-H}$=6.0 Hz, 3H, $CH_3CH_2C_{olefin}$), 1.24 (t, $^3J_{H-H}$=6.0 Hz, 3H, CH_3CH_2O), 2.58–2.67 (m, 2H, $CH_3CH_2C_{olefin}$), 3.70 (d, $^3J_{H-P}$=12.0 Hz, 6H, P(O)(OCH_3)$_2$), 4.15 (q, $^3J_{H-H}$=8.0 Hz, 2H, CH_3CH_2O), 6.53 (d, $^3J_{H-P}$=24.0 Hz, 1H, CH_{olefin}). ^{13}C NMR (100 MHz, $CDCl_3$): δ={13.43, 13.44} (q, $^3J_{C-P}$=1.0 Hz, $CH_3CH_2C_{olefin}$), 14.0 (q, CH_3CH_2O), {21.94, 22.01} (t, $^2J_{C-P}$=7.0 Hz, $CH_3CH_2C_{olefin}$), {52.57, 52.62} (q, $^2J_{C-P}$=5.0 Hz, P(O)(OCH_3)$_2$), 60.5 (t, CH_3CH_2O), {130.81, 130.93} (d, $^2J_{C-P}$=12.0 Hz, CH_{olefin}), {147.35, 149.01} (s, $^1J_{C-P}$=166.0 Hz, C_{olefin}), {164.19, 164.51} (s, $^3J_{C-P}$=32.0 Hz, EtO(O)*C*). ^{31}P NMR (161 MHz, $CDCl_3$): δ=20.6. HRMS (ApCI$^+$): Calcd for [$C_9H_{18}O_5P$] ([M+H]$^+$): 237.0892, found: 237.0890.

4.1.9. Ethyl (E)-3-(dimethoxyphosphinyl)-4-methyl-2-pentenoate (E-**2i**)

After stirring the reaction mixture at 80 °C for 12 h under argon, the olefin product **2i** was obtained as a light yellow oil (180 mg, 0.72 mmol, 72%) via column chromatographic purification. R_f=0.48 (silica gel, EtOAc 100%). FTIR (film): ν_{max} (cm^{-1})=2956 (m), 1724 (s), 1465 (w), 1369 (w), 1254 (s), 1204 (s), 1028 (s), 829 (m), 775 (w), 579 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.14 (d, $^3J_{H-H}$=8.0 Hz, 6H, $CH(CH_3)_2$), 1.24 (t, $^3J_{H-H}$=6.0 Hz, 3H, CH_3CH_2), 3.53–3.65 (m, 1H, $CH(CH_3)_3$), 3.69 (d, $^3J_{H-P}$=8.0 Hz, 6H, P(O)(OCH_3)$_2$), 4.15 (q, $^3J_{H-H}$=8.0 Hz, 2H, CH_3CH_2), 6.52 (d, $^3J_{H-P}$=24.0 Hz, 1H, CH_{olefin}). ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.0 (q, CH_3CH_2), {21.05, 21.08} (q, $^3J_{C-P}$=3.0 Hz, $CH(CH_3)_2$), {28.83, 28.91} (d, $^2J_{C-P}$=8.0 Hz, $CH(CH_3)_2$), {52.38, 52.44} (q, $^2J_{C-P}$=6.0 Hz, P(O)(OCH_3)$_2$), 60.7 (t, CH_3CH_2), {131.03, 131.14} (d, $^2J_{C-P}$=11.0 Hz, CH_{olefin}), {150.17, 151.78} (s, $^1J_{C-P}$=161.0 Hz, C_{olefin}), {164.64, 164.95} (s, $^3J_{C-P}$=31.0 Hz, EtO(O)*C*). ^{31}P

NMR (161 MHz, $CDCl_3$): δ=20.4. HRMS ($ApCl^+$): calcd for $[C_{10}H_{20}O_5P]$ ($[M+H]^+$): 251.1048, found: 251.1045.

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