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PAPER

Probing the reactivity of *H*-phosphonate derivatives for the hydrophosphonylation of various alkenes and alkynes under free-radical conditions

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Hydrophosphonylation is an efficient process to create carbon-phosphorus bonds from unsaturated C-C bonds and to give rise to alkylphosphonate or vinylphosphonate derivatives. In this work, we report on the reactivity of *H*-phosphonate derivatives for the hydrophosphonylation of various alkenes and alkynes under photoinduced free-radical conditions. The reaction was carried on activated, unactivated and/or disubstituted alkenes or alkynes with 2,2-dimethoxy-2-phenylacetophenone as photoinitiator under UV irradiation.

1. Introduction

Phosphonic acids and their phosphonate derivatives[1] represent an important class of compounds owing to their analogy with naturally occurring phosphates. In this regards, their incorporation into numerous compounds have been extensively studied.[2,3] Thus, a large number of synthetic strategies have been proposed[4-19] as alternatives to traditional methods, *i.e*. Michaelis-Arbuzov[20-23] or Michaelis-Becker approach.[24,25] Among them, the addition of compounds containing phosphorus-hydrogen bonds to C-C double or triple bonds has been developed over the last years[26-29] as it provides an atom-economical approach.[6,11,26,30-34] The most common is the hydrophosphonylation of alkenes or alkynes by *H*-phosphonates[35] involving radical addition, based-promoted or transition-metal catalysis.[26,32,36-38] Recently, Dondoni[5,6,16] and co-workers reported an efficient free-radical hydrophosphonylation of alkenes by *H*-phosphonate under neutral conditions, at room temperature and using UV/Vis light irradiation. These latter also described the first example of alkyne hydrophosphonylation under free-radical conditions to afford *Z*- and *E*-vinylphosphonates in a 1:1 ratio. This new methodology is of considerable interest in comparison to radical reactions promoted by organic peroxides,[39] AIBN,[40,41] $Mn(OAc)_2$ in the presence of air[33] and titanocene/epoxide,[11] which cannot be used with sensitive compounds due to a preliminary thermic activation. Surprisingly, the scope of this methodology has not yet been explored and it prompted us to probe the reactivity of various *H*-phosphonate derivatives, including bis(S-acyl-2-thioethyl) (SATE) *H*-phosphonate, for the hydrophosphonylation of a wide range of substrates such as activated, unactivated and/or disubstituted alkenes and/or alkynes catalyzed by 2,2-dimethoxy-2-phenylacetophenone (DPAP) under photoinduced free-radical conditions.

2. Results and discussion

In a first set of assays, hydrophosphonylation reaction was studied with several alkenes and the common dimethyl *H*-phosphonate. Experiments were carried out, according to literature,[6] with 100 eq. of *H*-phosphonate used as reagent and solvent and 0.5 eq. of DPAP as photoinitiator under UV-A irradiation (Table 1). The reaction proceeded efficiently with all substrates, giving rise to the corresponding phosphonates in good to excellent yields and anti-Markovnikov selectivity was exclusively observed for terminal alkenes. Entries 1, 4, and 6 gave the desired phosphonates, respectively with 99%, 81% and 83% yield. Under these conditions, allylsilane (entry 9) also led to the corresponding phosphonate in high yield (96%). Then, endo and exo-cyclic double bonds were examined (entry 7 and 8) and the best reactivity was obtained for the compound with endo-cyclic double bond (86% versus 75%). Internal alkene has been also investigated using oct-2-ene (entry 10). In this case, formation of regioisomers was observed in excellent yield (99%, ratio 57/43). No reaction proceeded in the case of styrene, probably due to polymerization reaction under these conditions. The reaction can also be achieved with reduced *H*-phosphonate loading (entry 2, 10 eq.), albeit with lower yield (79% vs 99%).

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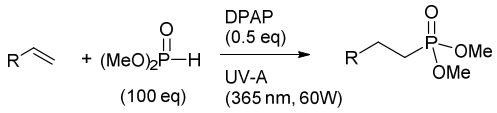
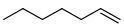
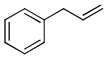
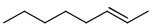
Alternatively, it can be carried out under sunlight irradiation (entry 3). However, a prolonged reaction time was required (480 min. vs 30 min.).

Table 1: Hydrophosphonylation of various alkenes with dimethyl H-phosphonate.

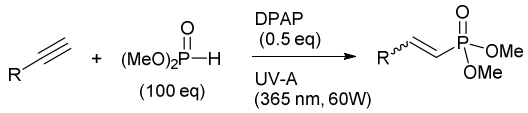


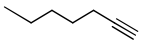
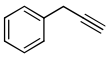
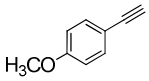
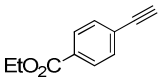
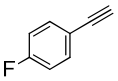
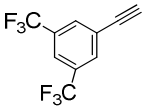
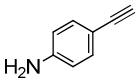
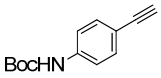
Entry[a]	Alkene	Time (min)	Yield [b] (%)
1		30	99
2[c]		60	79
3[d]		480	84
4		30	81
5		90	-
6		60	83
7		30	75
8		30	86
9		30	96
10		30	99 *(57/43 ratio)*

[a] Procedure A (see experimental part)
[b] After purification by column chromatography
[c] 10 eq. of dimethyl H-phosphonate were used
[d] Reaction under sunlight irradiation

In second attempt, a range of terminal alkynes were investigated as reactional partners with dimethyl *H*-phosphonate using the same conditions (Table 2). Aliphatic and aromatic compounds were tested in our study. The reaction proceeded efficiently, giving rise to the corresponding vinylphosphonates in moderate to excellent yields. In each case, formation of Z/E isomers occurred and the ratio was determined by ^{1}H-NMR analysis. Within the aromatic series (entry 3 to 7), differences were observed depending on the nature of the substituent present on the aromatic ring. The derivatives bearing electron-donating substituents provided the desired products in good yields (entry 5), whereas lower yield was observed when the substrate incorporated an electron-withdrawing group (entry 6, 7). No reaction occurred for the bis-trifluoromethylated compound and also for ethynylphenyl amine (entry 8 and 9). However, reactivity was recovered after protection of the amino group with the electro-attractive Boc protective group (entry 10).

Table 2: Hydrophosphonylation of various alkynes with dimethyl H-phosphonate.



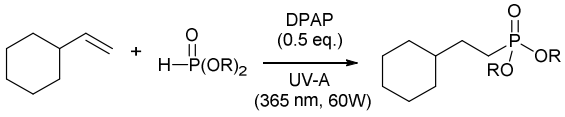
Entry[a]	Alkyne	Time (min)	Z/E ratio [b]	Yield [c] (%)
1		30	48/52	78
2		60	40/60	42
3		30	58/42	40
4		30	47/53	89
5		90	60/40	57
6		10h	45/55	30
7		30	25/75	31
8		60	-	-
9		60	-	-
10		14h	50/50	30

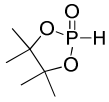
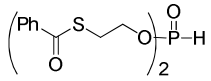
[a] Procedure B (see experimental part)
[b] Determined by ^{1}H-NMR of the crude reaction mixture
[c] After purification by column chromatography

Finally, having identified the most reactive vinylcyclohexane (table 1, entry 1), the scope of the reaction was extended to various *H*-phosphonate derivatives (table 3), thus allowing to proceed removal of the phosphonic acid protecting group in various conditions. Indeed, trimethylsilyl halides are commonly

used for the deprotection of dimethyl and diethyl phosphonate functionalities and these reaction conditions are not always suitable for sensitive molecules.

Table 3: Hydrophosphonylation of vinylcyclohexene with various H-phosphonates.



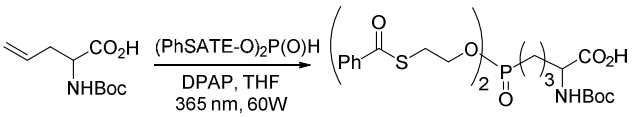
Entry	*H*-Phosphonate	Time (min)	Yield [c] (%)
1 [a]	$(MeO)_2P(O)H$	30	99
2 [a]	$(EtO)_2P(O)H$	30	93
3 [b]	$(PhO)_2P(O)H$	60	-
4 [b]	$(BnO)_2P(O)H$	120	44
5 [b]		120	72
6 [b]		120	32

[a] Procedure A (see experimental part)

[b] Procedure C (see experimental part)

[c] After purification by column chromatography

Dimethyl and diethyl *H*-phosphonates were used as reagent and solvent owing to their low cost (entry 1 and 2) and afforded, after 30 min., the expected products in excellent yields (99% and 93% respectively). The reaction, as defined in procedure A, could not be performed in the case of expensive dibenzyl- or pinacol-derived *H*-phosphonate. Therefore, the number of equivalents of *H*-phosphonate was decreased from 100 eq. to 2 eq. (Procedure C) but requiring the use of solvent. Several organic solvents were screened (see Table in supporting information) and THF was selected. However, diphenyl *H*-phosphonate was unsuccessful (entry 3). In the case of dibenzyl *H*-phosphonate (entry 4), a longer reaction time was required to give a moderate yield (44%). Pinacol-derived *H*-phosphonate (entry 5) afforded phosphonate adduct in good yield (72%). Moreover, we decided to test the hydrophosphonylation reaction with bis(phenyl)*S*-acyl-2-thioethyl (SATE) *H*-phosphonate.[42] This latter has been recently used for the synthesis of prodrugs of ribonucleoside β-hydroxyphosphonate analogs. Our group has extensively developed the corresponding approach using the SATE group as esterase-labile phosphate or phosphonate protection for the intracellular delivery of nucleos(t)ide analogs[43] as well as with phosphopeptides.[44,45] Thus, the attempt was performed following procedure C (entry 6), and the expected bis(phenyl)SATE *H*-phosphonate was obtained with 32% yield. Encouraged by this result, we exemplified the reaction for hydrophosphonylation of racemic N-Boc-allylglycine (scheme) as potential substrate of biological interest.



Scheme: Hydrophosphonylation of *N*-Boc-allylglycine (Procedure C).

Thus, the treatment of *N*-Boc-allylglycine with bis(phenyl)SATE *H*-phosphonate (2 eq.) and DPAP (0.5 eq) as photoinitiator under UV-A irradiation gave the corresponding bis(phenylSATE) phosphonate in 22% yield. No reaction was observed with unprotected allylglycine or with the corresponding methyl ester.

3. Conclusions

In conclusion, hydrophosphonylation of various unsaturated compounds, including activated, unactivated, disubstituted alkenes and/or alkynes, with diverse *H*-phosphonates under photoinduced free-radical conditions has been described with moderate to excellent yield. Additionally, we have shown that bis(*S*-acyl-2-thioethyl) (SATE) *H*-phosphonate can be used in these conditions to give corresponding bis (SATE) phosphonate analog of aminoacids and therefore expanding the scope of this approach towards compounds of interest.[46,47]

4. Experimental section

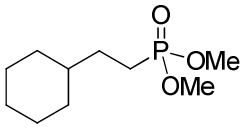
4.1. General conditions

^1H, ^{31}P and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker Avance III HD 400 MHz. Chemical shifts (δ) are quoted in parts per million (ppm) referenced to the residual solvent peak, ($CDCl_3$ fixed at 7.26 ppm and 77.16 ppm) relative to tetramethylsilane (TMS). Coupling constants, J, are reported in Hertz. ESI Mass and High Resolution Mass spectra were recorded in the positive or negative-ion mode on a Micromass Q-TOF. Thin-layer chromatography was performed on pre-coated aluminum sheets of Silica 60 F254 (Merck, Art. 5554), visualization of products being accomplished by UV absorbance and by charring with anisaldehyde solution, Dittmer reagent or $KMnO_4$ (solution in ethanol) and heating. Chromatography was performed on Merck Silica gel 60 (230-400 mesh ASTM).

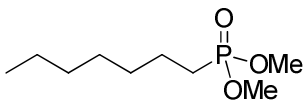
4.1.1. General procedure A: The alkene (0.25 mmol, 1 eq) and the phosphite (25 mmol, 100 eq) were placed in a glass vial (diameter: 1 cm; wall thickness: 0.65 mm). DPAP (0.125 mmol, 0.5 eq) was added and the reaction mixture was stirred under UV activation (UV-A lamp, λmax = 365 nm, 4 x 15W tubes; vial located 2.5 cm away from the lamp) for the indicated time. The solution was diluted with EtOAc and washed with aqueous saturated $NaHCO_3$. The organic phase was dried ($MgSO_4$) and concentrated in vacuo and purification by flash chromatography on silica gel (CH_2Cl_2/MeOH) afforded the corresponding phosphonate.

4.1.2. General procedure B: The alkyne (0.25 mmol, 1 eq) and dimethylphosphite (25 mmol, 100 eq) were placed in a glass vial (diameter: 1 cm; wall thickness: 0.65 mm). DPAP (0.125 mmol, 0.5 eq) was added and the reaction mixture was stirred under UV activation (UV-A lamp, λmax = 365 nm, 4 x 15W tubes; vial located 2.5 cm away from the lamp) for the indicated time. The solution was diluted with EtOAc and washed with aqueous saturated $NaHCO_3$. The organic phase was dried ($MgSO_4$) and concentrated in vacuo and purification by flash chromatography on silica gel (CH_2Cl_2/MeOH) afforded the corresponding vinylphosphonate.

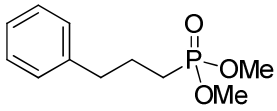
4.1.3. General procedure C: The alkene (0.25 mmol, 1 eq) and the phosphite (0.5 mmol, 2 eq) were dissolved in THF (2 mL) in a glass vial (diameter: 1 cm; wall thickness: 0.65 mm). DPAP (0.125 mmol, 0.5 eq) was added and the reaction mixture was stirred under UV activation (UV-A lamp, λmax = 365 nm, 4 x 15W tubes; vial located 2.5 cm away from the lamp) for the indicated time. The mixture was concentrated and treated by I_2 (2 eq) in pyridine/H_2O (98/2, v/v, 10 mL/mmol) for 15 min. Excess I_2 was neutralized (aq. sat. $Na_2S_2O_3$), the mixture was diluted (CH_2Cl_2), washed with water, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (CH_2Cl_2/MeOH) afforded the corresponding phosphonate.



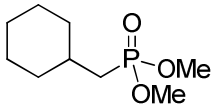
4.2. Dimethyl (2-cyclohexylethyl)phosphonate (Table 1, Entry 1). Procedure A, 73 mg (99%), colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.73 (d, *J* = 10.7 Hz, 6H), 1.78-1.66 (m, 7H), 1.51-1.43 (m, 2H), 1.26-1.10 (m, 4H), 0.91-0.83 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 52.4 (d, *J* = 6.5 Hz), 38.4 (d, *J* = 17 Hz), 32.8, 29.6 (d, *J* = 5 Hz), 26.6, 26.2, 22.3 (d, *J* = 140 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 35.9. HRMS (ESI$^+$) calcd for $C_{10}H_{21}O_3P$: 221.1307 found: 221.1306



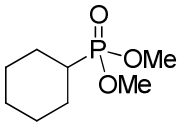
4.3. Dimethyl heptylphosphonate (Table 1, Entry 2).[48] Procedure A, 68 mg (81%), colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.72 (d, *J* = 12 .0 Hz, 6H), 1.73-1.68 (m, 2H), 1.61-1.54 (m, 2H), 1.37-1.24 (m, 8H), 0.88-0.85 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 52.4 (d, *J* = 6.5 Hz), 31.7, 30.7 (d, *J* = 16.9 Hz), 28.9, 24.8 (d, *J* = 140.2 Hz), 22.7, 22.4 (d, *J* = 5.3 Hz), 14.2. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 35.3. HRMS (ESI$^+$) calcd for $C_9H_{22}O_3P$: 209.1307, found: 209.1309.



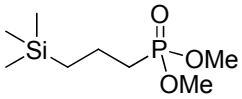
4.4. Dimethyl (3-phenylpropyl)phosphonate (Table 1, Entry 4).[49] Procedure A, 56 mg (83%), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.24 (m, 5H), 3.79 (d, *J* = 10.7 Hz, 6H), 2.78 (t, *J* = 7.4 Hz, 2H), 2.07-1.96 (m, 2H), 1.87-1.79 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.0, 128.6, 128.6, 126.3, 52.4 (d, *J* = 6.5 Hz), 36.5 (d, *J* = 17.1 Hz), 24.2 (d, *J* = 141.1 Hz), 24.1 (d, *J* = 4.8 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 34.7. HRMS (ESI+) calcd for $C_{11}H_{18}O_3P$: 229.0994, found: 229.0994



4.5. Dimethyl (cyclohexylmethyl)phosphonate (Table 1, Entry 5).[50] Procedure A, 52 mg (75%), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.71 (d, *J* = 10.8 Hz, 6H), 1.87-1.83 (m, 2 H), 1.70-1.60 (m, 5H), 1.32-0.94 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 52.2 (d, *J* = 6.6 Hz), 34.6 (d, *J* = 10.9 Hz), 32.6 (d, *J* = 4.2 Hz), 32.3 (d, *J* = 138.0 Hz), 26.1 (d, *J* = 10.2 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 34.6. HRMS (ESI$^+$) calcd for $C_9H_{20}O_3P$: 207.1150, found: 207.1152.

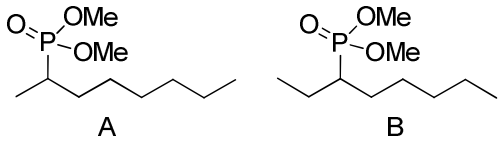


4.6. Dimethyl cyclohexylphosphonate (Table 1, Entry 6).[51] Procedure A, 45 mg (86%), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.73 (d, *J* = 10.5 Hz, 6H), 1.96-1.92 (m, 2H), 1.82-1.68 (m, 4H), 1.42-1.32 (m, 2H), 1.28-1.22 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 52.6 (d, *J* = 6.8 Hz), 35.4 (d, *J* = 142.1 Hz), 26.2 (d, *J* = 16.2 Hz), 26.0 (d, *J* = 6.4 Hz), 25.8. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 35.3. HRMS (ESI$^+$) calcd for $C_8H_{17}O_3P$: 193.0994 found: 193.0997.

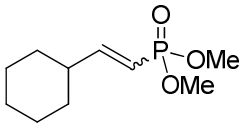


4.7. Dimethyl (3-(trimethylsilyl)propyl)phosphonate (Table 1, Entry 7). 60 mg (96%), colorless oil. Procedure A. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.72 (d, *J* = 10.7 Hz, 6H), 1.81-1.73 (m, 2H),

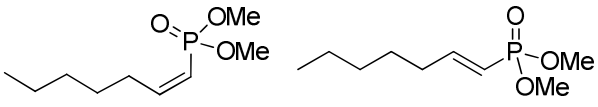
1.65-1.56 (m, 2H), 0.61-0.56 (m, 2H), 0.02 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 52.3 (d, *J* = 6.6 Hz), 28.7 (d, *J* = 137.1 Hz), 18.6 (d, *J* = 15 Hz), 17.4 (d, *J* = 5.4 Hz), -1.6. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 34.5. HRMS (ESI$^+$) calcd for $C_8H_{21}O_3P$: 225.1076 found: 225.1077.



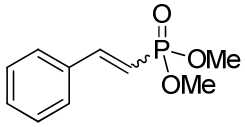
4.8. Dimethyl 1-methyl-heptylphosphonate (A) and dimethyl 1-ethyl-hexylphosphonate (B) Table 1, Entry 8). Procedure A, 60 mg (99%), colorless oil (inseparable isomers). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.73 (d, *J* = 10.5 Hz, 3H, *isomer A*), 3.73 (d, 3H, *J* = 10.5 Hz, *isomer A*), 3.72 (d, *J* = 10.5 Hz, 6H, *isomer B*), 1.88-1.24 (m, 23H), 1.15 (dd, *J* = 7.2, 18.8 Hz, 3H, *isomer B*), 0.99 (t, *J* = 7.4 Hz, 3H, *isomer A*), 0.89-0.85 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 52.6-52.3 (m), 37.1 (d, *J* = 137.2 Hz), 32.0, 31.8, 31.2, 30.0, 29.9, 29.7, 29.2, 27.6-27.2 (m), 22.7, 22.6, 21.2 (d, *J* = 3.5 Hz), 14.2, 13.2 (d, *J* = 5 Hz), 12.2 (d, *J* = 8.9 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 37.7 (*isomer A*), 37.5 (*isomer B*). HRMS (ESI$^+$) calcd for $C_{10}H_{23}O_3P$: 223.1463 found: 223.1467.



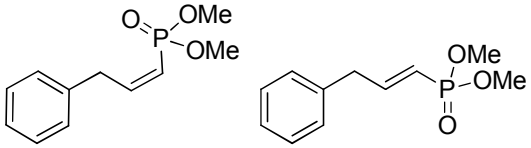
4.9. Dimethyl (2-cyclohexylvinyl)phosphonate (Table 2, Entry 1).[16] Procedure B, 46 mg (78%), colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.76 (ddd, *J* = 6.3, 17.3, 22.7 Hz, 1H, *E isomer*), 6.32 (ddd, *J* = 10.4, 13.0, 53.5 Hz, 1H), 5.54 (ddd, *J* = 1.5, 17.3, 21.1 Hz, 1H, *E isomer*), 5.42 (ddd, *J* = 0.7, 13.0, 19.8 Hz, 1H, *Z isomer*), 3.71 (d, *J* = 11.1 Hz, 6H, *Z isomer*), 3.70 (d, *J* = 11.0 Hz, 6H, *E isomer*), 1.79-1.64 (m, 11H), 1.39-1.06 (m, 11H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.2 (d, *J* = 5.3 Hz, *E isomer*), 160.0 (d, *J* = 3.5 Hz, *Z isomer*), 112.8 (d, *J* = 184.7 Hz, *E isomer*), 112.7 (d, *J* = 188.7 Hz, *Z isomer*), 52.4 (d, *J* = 5.7 Hz, *Z isomer*), 52.1 (d, *J* = 5.6 Hz, *E isomer*), 42.1 (d, *J* = 20.5 Hz, *E isomer*), 39.6 (d, *J* = 7.6 Hz, *Z isomer*), 32.5, 31.6, 26.0, 25.9, 25.8, 25.3. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 22.6 (*E isomer*), 20.3 (*Z isomer*). HRMS (ESI$^+$) calcd for $C_{10}H_{19}O_3P$: 219.1150, found: 219.1153.



4.10. (*Z*)- and (*E*)-Dimethyl hept-1-en-1-ylphosphonate (Table 2, Entry 2). Procedure B, 22 mg (42%), colorless oil. Further purification by flash chromatography on silica gel (cyclohexane/ethyl acetate, 6/4, v/v) gave pure analytical samples of (Z) and (E) isomers. For (Z) isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.53 (ddt, *J* = 53.5, 13.0, 7.7 Hz, 1H), 5.55 (ddt, *J* = 20.0, 13.0, 1.5 Hz, 1H), 3.72 (d, *J* = 11.1 Hz, 6H), 2.51 (m, 2H), 1.48-1.41 (m, 2H), 1.34-1.30 (m, 4H), 0.91-0.87 (m, 3H). 13C NMR (CDCl3, 100 MHz): δ 155.5 (d, *J* = 4.7 Hz), 115.0 (d, *J* = 184.6 Hz), 52.1 (d, *J* = 5.7 Hz), 31.5, 31.0 (d, *J* = 8.2 Hz), 28.7, 22.6, 14.10. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 20.2. HRMS (ESI+) calcd for $C_9H_{20}O_3P$: 207.1150, found: 207.1152. For (E) isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.80 (ddt, *J* = 22.1, 17.2, 6.6 Hz, 1H), 5.60 (ddt, *J* = 21.4, 17.2, 1.6 Hz, 1H), 3.70 (d, *J* = 11.0 Hz, 6H), 2.30-2.15 (m, 2H), 1.51-1.39 (m, 2H), 1.35-1.24 (m, 4H), 0.94-0.83 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.3 (d, *J* = 4.3 Hz), 115.3 (d, *J* = 188.5 Hz), 52.4 (d, *J* = 5.7 Hz), 34.3 (d, *J* = 22.2 Hz), 31.4, 28.5, 22.5, 14.1. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 21.7. HRMS (ESI+) calcd for $C_9H_{20}O_3P$: 207.1150, found: 207.1151.

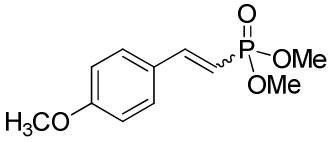


4.11. Dimethyl styrylphosphonate (Table 2, Entry 3).[52] Procedure B, 22 mg (40%), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69-7.36 (m, 11H), 7.26 (d, *J* = 14.2 Hz, 1H, *E isomer*), 6.22 (t, *J* = 17.7 Hz, 1H, *E isomer*), 5.78 (dd, *J* = 15.6, 14.2 Hz, 1H, *Z isomer*), 3.78 (d, *J* = 11.1 Hz, 6H, *E isomer*), 3.62 (d, *J* = 11.2 Hz, 6H, *Z isomer*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.5 (d, *J* = 6.6 H, *E isomer*), 149.0 (*Z isomer*), 135.0 (d, *J* = 8.8 Hz, *Z isomer*), 134.5 (d, *J* = 23.4 Hz, *E isomer*), 130.2 (*E isomer*), 129.4 (*Z isomer*), 129.3 (*Z isomer*), 128.7 (*E isomer*), 128.1 (*Z isomer*), 127.6 (*E isomer*), 114.9 (d, *J* = 186.4 Hz, *Z isomer*), 112.2 (d, *J* = 192.4 Hz, *E isomer*), 52.3 (d, *J* = 5.6 Hz, *E isomer*), 52.1 (d, *J* = 6.0 Hz, *Z isomer*). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 22.4 (*E isomer*), 18.9 (*Z isomer*). HRMS (ESI$^+$) calcd for $C_{10}H_{14}O_3P$: 213.0681, found: 213.0682.

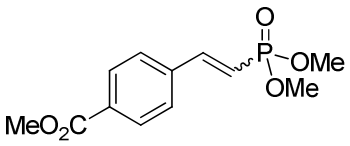


4.12. (*Z*)- and (*E*)-Dimethyl (3-phenylprop-1-en-1-yl)phosphonate (Table 2, Entry 4). Procedure B, 55 mg (89%), colorless oil. Further purification by flash chromatography on silica gel (cyclohexane/ethyl acetate/ NEt_3, 25/75/0.5, v/v/v) gave pure analytical samples of (*Z*) and (*E*) isomers. *For (Z) isomer:* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32-7.28 (m, 2H), 7.24-7.19 (m, 3H), 6.65 (ddt, *J* = 7.8, 12.9, 52.5 Hz, 1H), 5.64 (ddt, *J* = 1.5, 12.9, 18.9 Hz, 1H), 3.89 (ddd, *J* = 1.4, 2.9, 7.7 Hz, 2H), 3.68 (d, *J* = 11.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.8 (d, *J* = 3.7 Hz), 138.7 (d, *J* = 1.7 Hz), 128.8, 128.7, 126.6, 115.6 (d, *J* = 184.4 Hz), 52.2 (d, *J* = 5.8 Hz), 47.0 (d, *J* = 8.4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 19.5. HRMS (ESI$^+$) calcd for $C_{11}H_{15}O_3P$: 227.0837, found: 227.0839. *For (E) isomer:* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27-7.23 (m, 2H), 7.19-7.16 (m, 1H), 7.10-7.08 (m, 2H), 6.95-682 (m, 1H), 5.58-5.47 (m, 1H), 3.63 (d, *J* = 11.1 Hz, 6H), 3.50-3.56 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.9 (d, *J* = 5.3 Hz), 137.3, 129.0, 128.9, 126.9, 116.8 (d, *J* = 188.4 Hz), 52.4 (d, *J* = 5.7 Hz), 40.5 (d, *J* = 22.9 Hz). ^{31}P NMR ($CDCl_3$, 162

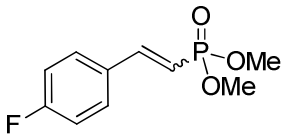
MHz): δ 21.1. HRMS (ESI$^+$) calcd for $C_{11}H_{15}O_3P$: 227.0837, found: 227.0840.



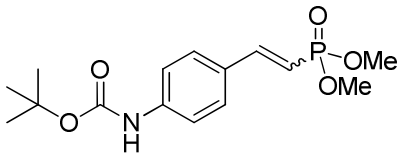
4.13. Dimethyl 4-methoxystyrylphosphonate (Table 2, Entry 5). Procedure B, 34 mg (57%), orange oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70-6.89 (m, 10H), 6.05 (t, *J* = 17.7 Hz, 1H, *E isomer*), 5.61 (dd, *J* = 15.3, 14.3 Hz, 1H, *Z isomer*), 3.84 (s, 3H, *E isomer*), 3.83 (s, 3H, *Z isomer*), 3.76 (d, *J* = 11.1 Hz, 6H, *E isomer*), 3.65 (d, *J* = 11.2 Hz, 6H, *Z isomer*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.6 (*E isomer*), 160.9 (*Z isomer*), 149.5 (*E isomer*), 149.0 (*Z isomer*), 131.7 (*Z isomer*), 129.5 (*E isomer*), 114.4 (*E isomer*), 113.8 (*Z isomer*), 111.6 (d, *J* = 184.8 Hz, *Z isomer*), 109.4 (d, *J* = 192.1 Hz, *E isomer*), 55.5 (*E isomer*), 55.4 (*Z isomer*), 52.6-52.4 (m). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 23.3 (*E isomer*), 19.8 (*Z isomer*). HRMS (ESI$^+$) calcd for $C_{11}H_{16}O_4P$: 243.0786, found: 243.0789.



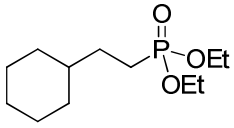
4.14. Methyl 4-(2-(dimethoxyphosphoryl)vinyl)benzoate (Table 2, Entry 6). Procedure B, 20 mg (30%), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07-8.04 (m, 4H), 7.72 (d, *J* = 8.2 Hz, 2H, *Z isomer*), 7.57-7.43 (m, 4H), 6.35 (t, *J* = 17.4 Hz, 1H, *E isomer*), 5.91 (dd, *J* = 15.3, 14.2 Hz, 1H, *Z isomer*), 3.94 (s, 3H, *Z isomer*), 3.93 (s, 3H, *E isomer*), 3.79 (d, *J* = 11.1 Hz, 6H, *Z isomer*), 3.63 (d, *J* = 11.2 Hz, 6H, *E isomer*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.6, 166.4, 148.10 (d, *J* = 6.7 Hz), 147.7, 138.9, 138.8 (d, *J* = 23.3 Hz), 131.5, 130.7, 130.1, 129.3, 128.8, 127.6, 117.8 (d, *J* = 186.0 Hz, *Z isomer*), 115.5 (d, *J* = 191.6 Hz, *E isomer*), 52.6-52.3 (m). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 21.2 (*E isomer*), 17.9 (*Z isomer*). HRMS (ESI$^+$) calcd for $C_{12}H_{16}O_5P$: 271.0735, found: 271.0737.



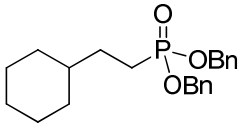
4.15. Dimethyl 4-fluorostyrylphosphonate (Table 2, Entry 7).[52] Procedure B, 20 mg (31%), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72-7.69 (m, 2H, *Z isomer*), 7.54-7.44 (m, 3H, *E isomer*), 7.27 (dd, *J* = 14.3, 51.4 Hz, 1H, *Z isomer*), 7.10-7.05 (m, 4H, *Z and E isomer*), 6.14 (m, 1H, H1, *isomer*), 5.75 (t, *J* = 14.7, Hz, 1H, *Z isomer*), 3.78 (d, *J* = 11.1 Hz, 6H, *E isomer*), 3.65 (d, *J* = 11.2 Hz, 6H, *Z isomer*). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 22.1 (*E isomer*), 18.7 (Z). ^{19}F NMR ($CDCl_3$, 375 MHz): δ -109.5 (*E isomer*), -110.7 (Z *isomer*). HRMS (ESI$^+$) calcd for $C_{10}H_{13}O_3FP$: 231.0586, found: 231.0584.



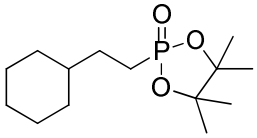
4.16. *tert*-Butyl (4-(2-(dimethoxyphosphoryl)vinyl)phenyl)carbamate (Table 2, Entry 10). Procedure B, 26 mg (30%), brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, *J* = 8.6 Hz, 2H, *Z isomer*), 7.50-7.38 (m, 7H), 7.22 (dd, *J* = 14.3, 51.9 Hz, 1H, *Z isomer*), 6.74 (s, 1H, *Z isomer*), 6.71 (s, 1H, *E isomer*), 6.09 (t, *J* = 17.7 Hz, 1H, *E isomer*), 5.75 (t, *J* = 16.0 Hz, 1H, *Z isomer*), 3.76 (d, *J* = 11.1 Hz, 6H, *E isomer*), 3.64 (d, *J* = 11.2 Hz, 6H, *Z isomer*), 1.52 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.5, 149.2 (d, *J* = 6.8 Hz, *E isomer*), 148.8 (*Z isomer*), 140.7 (*E isomer*), 140.0 (*Z isomer*), 139.2 (d, *J* = 32.5 Hz, *Z isomer),* 131.0 (*Z isomer*), 129.5 (d, *J* = 23.6 Hz, *E isomer*), 128.9 (*E isomer*), 118.4 (*E isomer*), 117.9 (*Z isomer*), 112.7 (d, *J* = 186.4 Hz, *Z isomer*), 110.3 (d, *J* = 193.4 Hz, *E isomer*), 81.2, 52.5 (d, *J* = 5.6 Hz, *E isomer*), 52.4 (d, *J* = 6.1 Hz, *Z isomer*), 28.4 ppm. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 23.0 (*E isomer*), 19.8 (*Z isomer*). HRMS (ESI$^+$) calcd for $C_{15}H_{23}NO_5P$: 328.1314, found: 328.1314.



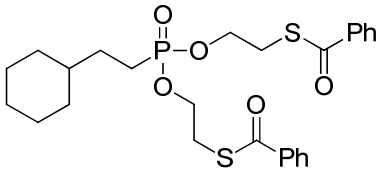
4.17. Diethyl (2-cyclohexylethyl)phosphonate (Table 3, Entry 2).[53] Procedure A, 58 mg (93%), colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.15-4.01 (m, 4H), 1.76-1.62 (m, 7H), 1.51-1.43 (m, 2H), 1.31 (t, *J* = 7.0 Hz, 6H), 1.21-1.11 (m, 4H), 0.91-0.83 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 61.5 (d, *J* = 6.5 Hz), 38.4 (d, *J* = 16.8 Hz), 32.9, 29.7 (d, *J* = 5.2 Hz), 26.7, 26.3, 23.3 (d, *J* = 141 Hz), 16.6 (d, *J* = 6.1 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 33.4. HRMS (ESI$^+$) calcd for $C_{12}H_{26}O_3P$: 249.1620, found: 249.1619.



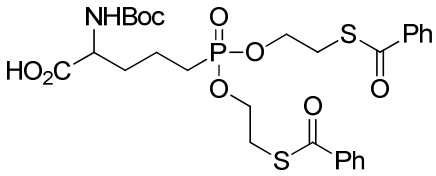
4.18. Dibenzyl (2-cyclohexylethyl)phosphonate (Table 3, Entry 4). Procedure C, 41 mg (44%), colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.31 (m, 10H), 5.01 (ddd, *J* = 36.1, 11.9, 8.4 Hz, 4H), 1.79-1.61 (m, 7H), 1.49-1.40 (m, 2H), 1.21-1.08 (m, 4H), 0.85-0.76 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.7 (d, *J* = 5.9 Hz), 128.7, 128.5, 128.0, 67.2 (d, *J* = 6.4 Hz), 38.3 (d, *J* = 16.9 Hz), 32.8, 29.5 (d, *J* = 5.2 Hz), 26.6, 26.3, 23.7 (d, *J* = 140 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 34.5. HRMS (ESI$^+$) calcd for $C_{22}H_{30}O_3P$: 373.1933, found: 373.1939.



4.19. 2-(2'-cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-oxide (Table 3, Entry 5). Procedure C, 49 mg (72%), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.88-1.80 (m, 2H), 1.72-1.55 (m, 6H), 1.48 (s, 6H), 1.34 (s, 6H), 1.31-1.11 (m, 5H), 0.93-0.84 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 87.9, 38.4 (d, *J* = 16.1 Hz), 32.8, 30.1 (d, *J* = 5.1 Hz), 26.6, 26.3, 25.8 (d, *J* = 130 Hz), 24.9, 24.9, 24.2, 24.2. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 45.1. HRMS (ESI^+) calcd for $C_{14}H_{28}O_3P$: 275.1776, found: 275.1776.



4.20. *S,S'*-((((2'-cyclohexylethyl)phosphoryl)bis(oxy))bis-(ethane-2,1-diyl)) dibenzothioate (Table 3, Entry 6). Procedure C, 42 mg (32%), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96-7.94 (m, 4H), 7.59-7.55 (m, 2H), 7.46-7.42 (m, 4H), 4.27-4.20 (m, 4H), 3.37 (t, *J* = 6.5 Hz, 4H), 1.83-1.74 (m, 2H), 1.67-1.60 (m, 7H), 1.25-1.07 (m, 4H), 0.87-0.78 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.0, 136.8, 133.8, 128.8, 127.5, 64.0 (d, *J* = 6.5 Hz), 38.3 (d, *J* = 17.2 Hz), 32.8, 29.6, 26.6, 26.3, 23.2 (d, *J* = 8 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 34.2. HRMS (ESI^+) calcd for $C_{26}H_{34}O_5PS_2$: 521.1585, found: 521.1584.



4.21. *5*-(bis(2-(benzoylthio)ethoxy)phosphoryl)-2-((*tert*-butoxycarbonyl)amino)pentanoic acid. Procedure C, 34 mg (22%), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95-7.93 (m, 4H), 7.58-7.55 (m, 2H), 7.45-7.42 (m, 4H), 5.33 (d, *J* = 7.6 Hz, 1H), 4.30-4.20 (m, 5H), 3.35 (t, *J* = 6.5 Hz, 4H), 1.92-1.71 (m, 6H), 1.42 (s, 9H). 13C NMR (CDCl3, 100 MHz): δ 191.0, 174.2, 155.8, 136.7, 133.8, 128.8, 127.5, 80.1, 64.5 (d, *J* = 6.5 Hz), 52.8, 33.2 (d, *J* = 15.8 Hz), 29.4 (d, *J* = 5.8 Hz), 28.5, 24.8 (d, *J* = 141 Hz), 18.2. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 33.2. HRMS (ESI+) calcd for $C_{28}H_{37}NO_9PS_2$: 626.1647, found: 626.1652.

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Probing the reactivity of H-phosphonate derivatives for the hydrophosphonylation of various alkenes and alkynes under free-radical conditions

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Graphical Abstract

Text

Hydrophosphonylation of various alkenes and alkynes is reported using DPAP as photoinitiator under UV irradiation.