Olefination Reactions Using Tetraarylphosphonium (TAP)-Supported Phosphorus Ylides

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Abstract: Tetraarylphosphonium (TAP)-supported phosphorus ylides were prepared and used in copper-catalyzed olefination reactions with diazo compounds to produce conjugated esters, amides, and phosphonates. The TAP-phosphine oxide can easily be separated from the alkene product, recycled, and reused.

Key words: alkenes, diazo compounds, green chemistry, Wittig reaction, ylides

Olefination reactions of carbonyl compounds are among the most commonly used strategies to assemble carboncarbon double bonds.¹ Among these, the Wittig reaction² remains very popular, because of the reliability of this method with a wide range of substrates, as well as good yields and selectivities.³ However, the use of stoichiometric amounts of triphenylphosphine that generates triphenylphosphine oxide as a by-product is still an important drawback associated with this famous reaction.⁴ Although a number of solutions have been disclosed to overcome this problem,⁵ a general method that shows high reactivity combined with the ability to recycle the reagent has not yet been reported. Tetraarylphosphonium (TAP)-supported reagents have recently been reported as an innovative technology to recover and reuse reagents that could potentially be harmful to the environment, while maintaining a high level of reactivity. In particular, tetraarylphosphonium (TAP)-supported triphenylphosphine 1 has successfully been used in the Corey-Fuchs and Mitsunobu reactions.⁶ Herein, we wish to report the use of TAP-phosphorus ylides in olefination reactions, as easily separable and recyclable phosphorus reagents.

At the outset, we decided to investigate the olefination of aldehydes with the TAP-phosphorus ylides generated in situ via the deprotonation of the corresponding TAP-phosphonium salts. TAP-PPh₃ **1** was reacted with two equivalents of ethyl bromoacetate to produce bisphosphonium **2** in 94% yield (Equation 1).

Such a species was found to be highly insoluble in nonpolar solvents, such as toluene or tetrahydrofuran, solvents that are typically used in olefination reactions with bases such as *n*-butyllithium, lithium hexamethyldisilazide, or sodium hexamethyldisilazide. Furthermore, a significant





level of decomposition of the tetraarylphosphonium was observed with potassium tert-butoxide in acetonitrile. Conversely, the use of a milder base such as triethylamine led to the formation of the corresponding TAP-phosphorus ylide, which was not isolated, but directly reacted with aldehydes. The corresponding α,β -unsaturated esters were isolated in excellent yields as pure materials after a precipitation and filtration of the TAP-phosphorus residues (Table 1). As expected with a stabilized ylide, the E-isomer was the major product. However the ratio was slightly lower in comparison to a typical olefination reaction with the triphenylphosphine-derived ester ylide. Aromatic aldehydes produced alkenes 3 and 4 in an 88:12 E/Z ratio, while a modest 78:22 ratio was observed with citronellal. This might be due to a solvent effect (MeCN), as it is known that increasing solvent polarity has a detrimental effect on the E/Z ratio.

Table 1 Olefination of Aldenydes Using TAP-Phosphonium Salt	Salt 2 ª
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^a Reaction was performed on a 1 mmol scale using 1.5 equiv of phosphonium **2** and 1.5 equiv of Et_3N in MeCN (0.2 M) at 60 °C.

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^b Isolated and combined yields of *E*- and *Z*-isomers.

^c Determined by ¹H NMR spectroscopy of the crude mixture.

^d Et₃N (1.2 equiv), **2** (1.2 equiv).

^e Et₃N (1.2 equiv), 2 (1.2 equiv), reflux, sealed tube.

We hypothesized that the corresponding TAP-supported phosphorus ylide might have a better solubility in nonpolar solvents, thus no longer requiring the use of acetonitrile. Thus, the corresponding TAP-stabilized ylide was isolated as follows: after formation of TAP-phosphonium **2**, the reaction mixture was diluted with dichloromethane and washed with a 10% aqueous sodium hydroxide solution to produce the desired TAP-ylide **6** as a stable, slightly yellow solid in 82% yield (Equation 2).



Equation 2

The reaction of aldehydes with TAP-ylide **6** in tetrahydrofuran produced the corresponding α , β -unsaturated esters in high yields and *E*/*Z* ratios (Table 2). A simple precipitation and filtration of the TAP-phosphorus residues afforded pure alkene products.

Table 2Olefination of Aldehydes Using TAP-Ylide 6^a



^a Reaction was performed on a 1 mmol scale using 1.5 equiv of TAPylide **6** in THF at r.t.

^b Isolated and combined yields of *E*- and *Z*-isomers.

^c Determined by ¹H NMR of the crude mixture.

The additional step to prepare reagent **6**, combined with the fact that the E/Z ratios were still lower than those observed in the normal Wittig reaction, prompted us to study alternative methods to produce the phosphorus ylide. Recently, a number of methods based on the transitionmetal-catalyzed decomposition of diazo compounds in the presence of phosphorus reagents to produce alkenes from aldehydes have been disclosed.⁷ In particular, copper salts appear to be general, cost-effective and efficient catalysts for such a reaction.⁸ As copper-catalyzed olefination reactions with diazo compounds proceeded under mild nonbasic reaction conditions, these were particularly appropriate for sensitive carbonyl substrates that decomposed under typical Wittig reaction conditions.^{8a,c} The olefination of hydrocinnamaldehyde in the presence of ethyl diazoacetate (EDA), TAP-PPh₃ 1 and 5–10 mol% of copper(I) iodide was thus investigated in various nonpolar solvents (Table 3). The desired α , β -unsaturated ester 7 was produced in an excellent E/Z ratio (95:5) albeit in moderate yields with tetrahydrofuran, 1,4-dioxane, and toluene (Table 3, entries 1-5) as solvents. Conversely, the yield was improved using 1,2-dichloroethane (DCE) at 80 °C, while maintaining a high level of diastereoselectivity (entry 7). Decreasing the catalyst loading led to lower yields, whereas the use of 10 mol% copper(I) iodide gave slightly better results (entries 7-9), although this had no impact on the isolated yield (entries 10, 11). The amount of ethyl diazoacetate can be decreased to 1.2 equivalents if added dropwise (entries 7 vs. 10). Using such a procedure, it was found that excess ethyl diazoacetate was deleterious to the olefination reactions as the yield was lower when using 2 equivalents versus 1.2 equivalents (entries 11-13). The use of an excess of TAP-PPh₃ 1 was not beneficial to the reaction either (entries 14, 15).

Table 3 Copper-Catalyzed Olefination of Hydrocinnamaldehydewith Ethyl Diazoacetate and TAP-PPh3 1 Producing Alkene 7^a

Entry	CuI (mol%	EDA 6) (equiv)	Conditions	Yield (%) ^{b,c}	E/Z^d
1	5	2	THF (0.22 M), 60 °C	48	95:5
2	5	2	1,4-dioxane (0.22 M), 60 °C	35	95:5
3	5	1.5	1,4-dioxane (0.16 M), 80 °C	43	95:5
4	5	2	toluene (0.22 M), 60 °C	52	95:5
5	5	1.5	toluene (0.16 M), 80 °C	46	95:5
6	5	2	DCE (0.22 M), 60 °C	62	95:5
7	5	1.5	DCE (0.16 M), 80 °C	69	95:5
8	2.5	1.5	DCE (0.16 M), 80 °C	58	95:5
9	10	1.5	DCE (0.16 M), 80 °C	77	95:5
10	5	1.2 ^e	DCE (0.16 M), 80 °C	73 (68)	95:5
11	10	1.2 ^e	DCE (0.16 M), 80 °C	80 (66)	95:5
12	10	1.5 ^e	DCE (0.16 M), 80 °C	74	95:5
13	10	2.0 ^e	DCE (0.16 M), 80 °C	71	95:5
$14^{\rm f}$	10	1.2 ^e	DCE (0.16 M), 80 °C	75	95:5
15 ^g	10	1.2 ^e	DCE (0.16 M), 80 °C	71	95:5

^a Performed on a 0.25 mmol scale.

^b Combined yields of *E*- and *Z*-isomers determined by ¹H NMR spectroscopy with bibenzyl as standard.

^c Isolated yields in parentheses.

^d Determined by ¹H NMR of the crude mixture.

^e EDA was added over 2 hours.

^f Using 1.5 equiv of TAP-PPh₃ 1.

^g Using 2.0 equiv of TAP-PPh₃ 1.

Finally, alkene **7** was isolated in 68% yield in an *E/Z* ratio of 95:5 in the presence of 1.2 equivalents of ethyl diazoacetate and TAP-PPh₃ **1** in 1,2-dichloroethane at 80 °C using 5 mol% copper(I) iodide (Table 4, entry 7). It is assumed that ylide **6** is produced under these reaction conditions according to precedent mechanistic investigations for copper-catalyzed olefination with diazo compounds (Scheme 1).^{8a} The purification procedure was simplified to a precipitation of the phosphorus residue using diethyl ether. Whereas the crude ¹H NMR sprectrum of the reaction with triphenylphosphine showed aromatic impurities (spectrum A), all tetraarylphosphonium residues could be precipitated with diethyl ether from the reaction mixture and collected by filtration (spectrum B)⁹ (Figure 1).



Scheme 1 Green cycle using TAP-PPh₃ 1

Moreover, TAP-PPh₃ **1** can be easily recycled from TAP-Ph₃P=O by reduction using trichlorosilane^{6a} and reused in subsequent reactions with the same efficiency (Scheme 1). Overall we have developed an efficient green cycle for olefination reaction that allowed for the easy recovery and recycle of the phosphine derivative, while maintaining a good reactivity.

The optimal reaction conditions were tested with various aldehydes using diazo carbonyl and phosphonate reagents with TAP-PPh₃ 1 (Table 4). Good yields and high selectivities were obtained with aromatic aldehydes containing either electron-withdrawing or -donating groups (Table 4, entries 1-5). The desired alkenes were produced not only with ethyl diazoacetate, but also with dimethyl diazoacetamide and Seyferth-Gilbert reagent (entries 1 and 4 compared to 5 and 2). Heterocycles such as pyridine are also compatible under these reaction conditions, and the corresponding conjugated ester was recovered with 55% yield in an E/Z ratio of 93:7 (entry 6). Aliphatic aldehydes also produced the desired alkenes in good yields and high selectivities with ethyl diazoacetate (entries 7 and 9). Conversely, moderate yields and slightly lower diastereoselectivities were observed with dimethyl (diazomethyl)phosphonate as the reagent (entries 8 and 10). There is a good functional group tolerance for Boc-protected amines (entries 4, 5) and acetal-derived substrates (entry 10).



Figure 1 Crude ¹H NMR spectrum of alkene **7** prepared from hydrocinnamaldehyde, after precipitation with Et₂O. Reaction conditions: Method A: EDA (1.2 equiv), Ph₃P (1.2 equiv), CuI (5 mol%) in THF (0.25 M) at 60 °C; Method B: EDA (1.2 equiv), TAP-PPh₃ (1.2 equiv), CuI (5 mol%) in DCE (0.15 M) at 80 °C.

Finally, trifluoromethylketone **16** was also reacted under these reaction conditions leading to the formation of conjugated ester **17** and amide **18** in good yields and selectivities (Equation 3).



Equation 3

In conclusion, we have shown that TAP-PPh₃ **1** can be used to prepare phosphorus ylides that can be isolated or in situ generated from diazo reagents. Subsequent olefination reactions were performed with various carbonyl compounds to produce the desired alkenes. Finally, the separation and the recovery of TAP-PPh₃ **1** are straightforward, allowing an efficient recycling of the phosphorus reagent.

Table 4Copper-Catalyzed Olefination of Aldehydes with TAP- $PPh_3 1^a$

Entry	Produc	t	Yield (%) ^b	E/Z^{c}
1	3	OEt	78	96:4
2	8	OMe OMe	60	95:5
3	9	O ₂ N OEt	83	93:7
4	10	BocHN	69	98:2
5	11	BocHN NMe2	70	97:3
6	12	OEt OEt	55	93:7
7	7	OEt	68	95:5
8	13	O II_OMe OMe	53	90:10
9	14	OEt	57 ^d	92:8
10	15	MeO,,,,,O,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	57	92:8

^a Reaction was performed on a 1 mmol scale using 1.2 equiv of TAP-PPh₃ 1, 1.2 equiv of diazo reagent, 5 mol% of CuI in DCE at 80 °C.

^b Isolated and combined yields of *E*- and *Z*-isomers. ^c Determined by GC-MS of the crude mixture.

^d Using 10 mol% CuI.

Unless otherwise noted, all the nonaqueous reactions were performed under an oxygen-free atmosphere of argon with rigid exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds.¹⁰ All glassware were stored in the oven and/or was flame dried prior to use under an inert atmosphere of gas. The solvents were dried using standard methods prior to use. The commercially available aldehydes were purified using standard methods prior to use. (TAP)-

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PPh₃ **1** was prepared according to literature.^{6a} CAUTION: Although no explosions occurred in any of our experiments, diazo compounds are toxic and potentially explosive. They should be stored in refrigerator and handled with caution in a fume hood. Ethyl diazoacetate is commercially available, but was prepared from ethyl glycinate hydrochloride according to the literature.¹¹ N,Ndiazoacetamide¹² Dimethyl and dimethyl (diazomethyl)phosphonate¹³ were prepared according to published procedures. Analytical TLC was performed using 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ethanolic phosphomolybdic acid, I₂, or aq KMnO₄. Flash chromatography was performed using silica gel 60 (230-400 mesh) with the indicated solvent system according to standard technique.14 Melting points are uncorrected. IR spectra are reported in cm⁻¹ and recorded neat with a Golden Gate Diamond ATR. Chemical shifts for ¹H NMR spectra were recorded in parts per million (ppm) on the δ scale relative to an internal standard of residual solvent (chloroform, $\delta =$ 7.27). Data are reported as follows: chemical shift, multiplicity (using standard abbreviations), coupling constant in Hz, integration, and assignment. Chemical shifts for ¹³C NMR spectra were recorded in parts per million from TMS using the central peak of CDCl₃ (77.23 ppm) as the internal standard. All spectra were obtained with complete proton decoupling. When ambiguous, proton and carbon assignments were established using COSY, HMQC or HSQC, and DEPT experiments. High-resolution mass spectra were recorded by the Centre régional de spectroscopie de masse de l'Université de Montréal. Accurate mass measurements were performed on a LC-MSD-TOF instrument from Agilent Technologies in positive electrospray. Either protonated molecular ions [M + H]⁺ or sodium adducts $[M + Na]^+$ were used for empirical formula confirmation. Combustion analyses were performed by the Laboratoire d'analyse élémentaire de l'Université de Montréal.

(2-Ethoxy-2-oxoethyl)(diphenyl)[3-triphenyl(phosphonio)phenyl]phosphonium Bromide Perchlorate (2)

To a solution of TAP-PPh₃ 1^{6a} (10.0 g, 16.0 mmol, 1.00 equiv) in MeCN (40 mL, 0.4 M) was added ethyl bromoacetate (3.42 mL, 32.0 mmol, 2.00 equiv). The solution was stirred at r.t. and a precipitate formed as the reaction proceeded. After stirring for 16 h, Et₂O (200 mL) was added to precipitate the bisphosphonium salt **2** and the mixture was vigorously stirred for an additional 20 min. The solid was collected by filtration and further washed with Et₂O (50 mL) to afford the bisphosphonium salt **2** as a white solid; yield: 11.95 g (94%); mp 190 °C (dec.), 205 °C (melt).

IR (neat): 3422, 2169, 1721, 1585, 1438, 1311, 1188, 1085, 954, 687, 622 cm⁻¹.

¹H NMR (400 MHz, CD_2Cl_2): $\delta = 8.29-8.24$ (m, 1 H), 8.02-7.96 (m, 2 H), 7.92-7.77 (m, 16 H), 7.73-7.63 (m, 10 H), 5.43 (d, J = 14.1 Hz, 2 H), 4.01 (q, J = 7.1 Hz, 2 H), 1.07 (t, J = 7.1 Hz, 3 H).

¹³C NMR (100 MHz, CD₂Cl₂): δ = 165.0 (d, J = 3.2 Hz, 1 C), 141.6 (t, J = 12.6 Hz, 1 C), 141.2 (dd, J = 2.8, 10.5 Hz, 1 C), 140.5 (dd, J = 2.9, 9.9 Hz, 1 C) 136.1 (d, J = 3.0 Hz, 3 C), 136.0 (d, J = 3.1 Hz, 2 C), 135.5 (d, J = 10.7 Hz, 6 C), 134.5 (d, J = 10.7 Hz, 4 C), 131.8 (t, J = 12.3 Hz, 1 C), 131.0 (d, J = 13.0 Hz, 6 C), 130.9 (d, J = 13.0 Hz, 4 C), 122.0 (dd, J = 13.4, 90.3 Hz, 1 C), 121.5 (dd, J = 13.5, 90.2 Hz, 1 C), 117.0 (d, J = 89.3 Hz, 2 C), 117.0 (d, J = 89.8 Hz, 3 C), 63.6 (1 C), 32.9 (d, J = 13.0 Hz, 1 C), 14.0 (1 C).

³¹P NMR (162 MHz, CD₂Cl₂): δ = 23.8 (d, *J* = 3.6 Hz, 1 P), 21.6 (d, *J* = 3.4 Hz, 1 P).

HRMS (API-ES+): m/z calcd for $C_{40}H_{36}O_2P_2$ [M]²⁺: 305.1089; found: 305.1100.

HRMS (ESI–): *m*/*z* calcd for ClO₄ [M]⁻: 98.9490; found: 98.9490. *m*/*z* calcd for Br [M]⁻: 78.9188; found: 78.9187.

Wittig Olefination with TAP-Supported Phosphonium Salt 2; General Procedure

To a suspension of TAP-phosphonium salt **2** (1.19 g, 1.50 mmol, 1.50 equiv) in MeCN (5 mL, 0.2 M), under argon was added Et₃N (210 μ L, 1.50 mmol, 1.50 equiv) at r.t. After 15 min, the aldehyde (1.00 mmol, 1.00 equiv) was added, the mixture stirred for 16 h, and diluted with CH₂Cl₂ (40 mL). The CH₂Cl₂ layer was washed with aq 10% (w/w) HCl (5 mL), H₂O (5 mL), brine (5 mL), dried (MgSO₄), and concentrated under reduced pressure to a minimum volume (1–2 mL). Et₂O (10 mL) was slowly added to the residue to induce the complete precipitation of the TAP-supported phosphine oxide and the mixture was filtered on Celite, further washed with Et₂O (20 mL) and the filtrate was concentrated under reduce pressure to a flord pure mixture of *E*- and *Z*-olefin isomers.¹⁵

Ethyl (E)-Cinnamate (3)

Yield: 99%; colorless oil (88:12 dr).

All physical and spectroscopic data were identical to those previously reported. $^{\rm 8d}$

Ethyl (E)-3-(Thiophen-2-yl)acrylate (4)

Yield: 98%; yellow oil (88:12 dr).

All physical and spectroscopic data were identical to those previously reported. $^{\rm 8d}$

Ethyl (E)-5,9-Dimethyldeca-2,8-dienoate (5)

Yield: 98%; colorless oil (78:22 dr).

All physical and spectroscopic data were identical to those previously reported. $^{\rm 8d}$

(2-Ethoxy-2-oxoethyl)(diphenyl)[3-triphenyl(phosphonio)phenyl]phosphorane Perchlorate (6)

To a solution of TAP-PPh₃ 1^{6a} (5.00 g, 8.00 mmol, 1.00 equiv) in MeCN (20 mL, 0.40 M) was added ethyl bromoacetate (1.70 mL, 16.0 mmol, 2.00 equiv). The solution was stirred at r.t. and a white precipitate formed as the reaction proceeded. After stirring for 16 h, Et₂O (100 mL) was added to the solution, and the mixture was stirred vigorously for an additional 20 min. The solid was collected by filtration and washed with $Et_2O(2 \times 20 \text{ mL})$. The solid was then dissolved in CH₂Cl₂ (100 mL) and the CH₂Cl₂ layer was transferred to a separatory funnel. Aq 10% NaOH (100 mL) was added and the separatory funnel was shaken vigorously. The yellow organic layer was dried (MgSO₄) and concentrated under vacuum to a volume of 20 mL. This solution was added dropwise to Et₂O (300 mL) and vigorously stirred for 20 min. The slightly yellow solid was collected by filtration and washed with Et₂O (50 mL) to give the TAPylide 6; yield: 4.66 g (82%); mp 101-105 °C (dec.), 182-186 °C (melt).

IR (neat): 2971, 1606, 1437, 1326, 1081, 996, 893, 725, 686, 621 $\rm cm^{-1}.$

¹H NMR (500 MHz, CD₂Cl₂, 25 °C): δ = 8.13–7.47 (m, 29 H), 3.88 (br s, 2 H), 2.87 (br s, 1 H), 1.14 (br s, 3 H)

¹H NMR (500 MHz, CD₂Cl₂, -30 °C): δ (two isomers in a ratio of 1:0.14 were visible): 8.14–7.46 (m, 33 H, major + minor), 3.88 (q, J = 6.9 Hz, 2 H, major), 3.56 (br s, 2 H, minor), 2.90 (d, J = 23.9 Hz, 1 H, major), 2.53 (br d, J = 23.2 Hz, 1 H, minor), 1.15 (t, J = 7.1 Hz, 3 H, major), 0.42 (br s, 3 H, minor).

¹³C NMR (126 MHz, CD₂Cl₂, -30 °C): δ (major isomer) = 171.2 (d, J = 14.3 Hz, 1 C), 139.2 (t, J = 11.5 Hz, 1 C), 139.1 (d, J = 11.0 Hz, 1 C), 137.1 (d, J = 10.3 Hz, 1 C), 135.8 (d, J = 3.1 Hz, 1 C), 135.7 (s, 3 C), 134.5 (d, J = 10.6 Hz, 6 C), 132.9 (s, 2 C), 132.6 (d, J = 10.1 Hz, 4 C), 131.6 (dd, J = 88.6, 12.2 Hz, 1 C), 130.4 (d,

J = 13.0 Hz, 6 C), 129.2 (d, J = 12.3 Hz, 4 C), 124.6 (d, J = 93.2 Hz, 2 C), 118.2 (dd, J = 89.4, 12.7 Hz, 1 C), 116.5 (d, J = 89.6 Hz, 3 C), 58.0 (s, 1 C), 28.3 (d, J = 130.4 Hz, 1 C), 14.7 (s, 1 C).

³¹P NMR (162 MHz, CD_2Cl_2 , 25 °C): δ = 24.32, 19.44.

HRMS (ESI+): m/z calcd for $C_{40}H_{35}O_2P_2$ [M]⁺: 609.2106; found: 609.2128.

HRMS (ESI-): *m*/*z* calcd for ClO₄ [M]⁻: 98.9490; found: 98.9493.

Wittig Olefination with TAP-Supported Ylide 6; General Procedure

To a suspension of the TAP-ylide **6** (1.06 g, 1.50 mmol, 1.50 equiv) in THF (20 mL, 0.05 M) was added the aldehyde (1.00 mmol, 1.00 equiv) at r.t. under argon and the solution was stirred for 16 h. After removing the solvent under vacuum, the resulting solid was solubilized in CH₂Cl₂ (2 mL) and added dropwise to Et₂O (20 mL) to induce the complete precipitation of the TAP-supported phosphine oxide. The mixture was vigorously stirred for an additional 20 min. The mixture was then filtered and further washed with Et₂O (2 × 5 mL). The filtrate was concentrated under vacuum to a volume of 5 mL and the solution was filtered again on a small pad of silica gel. After removing the solvent under vacuum a pure mixture of *E*- and *Z*-olefin isomers was obtained.¹⁵

Ethyl (E)-Cinnamate (3)

Yield: 91%; colorless oil (93:7 dr).

All physical and spectroscopic data were identical to those previously reported. $^{\rm 8d}$

Ethyl (E)-3-(Thiophen-2-yl)acrylate (4)

Yield: 95%; yellow oil (89:11 dr).

All physical and spectroscopic data were identical to those previously reported.^{8d}

Ethyl (E)-5-Phenylpent-2-enoate (7)

Yield: 89%; colorless oil (89:11 dr).

All physical and spectroscopic data were identical to those previously reported.^{8d}

Copper-Catalyzed Olefination with TAP-PPh₃ 1; General Procedure

To a solution of CuI (10 mg, 0.050 mmol) and phosphonium salt **1** (748 mg, 1.20 mmol) in DCE (6.5 mL), under an argon atmosphere, was added the aldehyde (1.00 mmol). The mixture was stirred for 5 min and then heated to 80 °C. The diazo compound (1.20 mmol) was added dropwise over a period of 2 h. The solution was stirred until the reaction was complete (GC or TLC analysis). The resulting mixture was cooled to r.t. and the solution was poured dropwise into Et₂O (65 mL) under strong stirring (rpm >1000). The suspension was removed by filtration and the solution was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc–hexanes, 1:19 or 1:9, depending on the product) (Table 4).

Ethyl (*E*)-Cinnamate (3)

Yield: 78%; colorless oil (96:4 dr).

All physical and spectroscopic data were identical to those previously reported. $^{\rm 8d}$

Dimethyl (E)-Styrylphosphonate (8)

Yield: 60%; yellow oil (95:5 dr).

All physical and spectroscopic data were identical to those previously reported. $^{\rm 8d}$

Ethyl (E)-3-(4-Nitrophenyl)acrylate (9)

Yield: 83%; yellow solid (93:7 dr); mp 135 °C (Lit.¹⁶ mp 138–139 °C).

All physical and spectroscopic data were identical to those previously reported. $^{\rm 8d}$

tert-Butyl 4-[(*E*)-2-(Ethoxycarbonyl)vinyl]phenylcarbamate (10)

Yield: 69%; yellow solid (98:2 dr); mp 95 °C (Lit.17 mp 92–94 °C).

All physical and spectroscopic data were identical to those previously reported. $^{\rm 8d}$

tert-Butyl 4-[(*E*)-2-(Dimethylcarbamoyl)vinyl]phenylcarbamate (11)

Yield: 70%; light yellow oil (97:3 dr).

All physical and spectroscopic data were identical to those previously reported.^{8d}

Ethyl (E)-3-(Pyridin-2-yl)acrylate (12)

Yield: 55%; yellow oil (93:7 dr).

All physical and spectroscopic data were identical to those previously reported. $^{\mbox{\scriptsize 8d}}$

Ethyl (E)-5-Phenylpent-2-enoate (7)

Yield: 68%; colorless oil (95:5 dr).

All physical and spectroscopic data were identical to those previously reported. $^{\rm 8d}$

Dimethyl (E)-4-Phenylbut-1-enylphosphonate (13)

Yield: 53%; yellow oil (90:10 dr).

All physical and spectroscopic data were identical to those previously reported. $^{\rm 8d}$

Ethyl (E)-Oct-2-enoate (14)

Yield: 57%; colorless oil (92:10 dr) using 10 mol% of CuI.

All physical and spectroscopic data were identical to those previously reported. $^{\rm 18}$

Dimethyl (*E*)-2-[(3a*R*,4*R*,6*R*,6a*R*)-Tetrahydro-4-methoxy-2,2dimethylfuro[3,4-*d*][1,3]dioxol-6-yl]vinylphosphonate (15) Yield: 57%; yellow oil (92:8 dr).

All physical and spectroscopic data were identical to those previously reported.^{8d}

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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