

1-Hydroxyalkylphosphonium Salts—Synthesis and Properties

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Abstract: An efficient and convenient method for the synthesis of 1-hydroxyalkylphosphonium salts is described. Reactions were carried out at room temperature, in a short time, and without chromatography for product isolation. The properties of the obtained phosphonium salts were examined and discussed. In this paper, primary attention was paid to the stability of phosphonium salts, depending on the structure of the aldehydes used as substrates in their preparation. Other conditions such as the type of solvent, temperature, and molar ratio of the substrates were also investigated. Finally, the high reactivity of 1-hydroxyalkylphosphonium salts was demonstrated in reactions with amide-type substrates and (hetero)aromatic compounds. The developed step-by-step procedure (with the isolation of 1-hydroxyphosphonium salts) was compared to the one-pot protocol (in situ formation of such phosphonium salts).

Keywords: phosphonium salts; synthesis; stability; alkylation; alkylating agent



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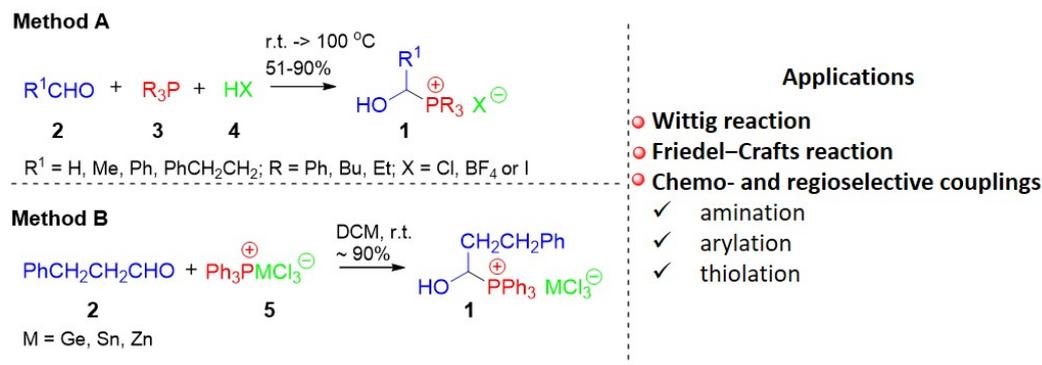


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1. Introduction

Chemical compounds containing a phosphonium moiety play an increasingly important role in organic synthesis. They are already known not only for their use in the Wittig reaction as ylide precursors [1–3], but also as convenient building blocks used in many other reactions, especially various types of couplings [4–8]. Moreover, they are successfully used as solvents and catalysts (PILs—phosphonium ionic liquids are good examples here) [9–13]. Due to some specific properties, the presence of a phosphonium group can also influence the biological properties of the whole molecule (e.g., (TPP⁺)-based mitochondria-targeted compounds) [14].

One of the relatively poorly known classes of phosphonium salts is 1-hydroxyalkylphosphonium salts **1**. Although such phosphonium salts were already described in the 1960s [15–17], their properties (apart from spectroscopic ones [18,19]) have not been studied in detail thus far. However, there have been some references to the synthesis of these compounds based on the three-component reaction of an aldehyde with phosphine in the presence of HX (aqueous or ethereal HBF₄ solution, concentrated hydrochloric acid, etc., Scheme 1/Method A) [15–18,20–22] or the two-component reaction in the presence of complex triphenylphosphonium salts **5** (Scheme 1/Method B) [23]. Each time, they refer to individual examples—most often the synthesis of hydroxymethylphosphonium salts (R¹ = H, from paraformaldehyde or formalin). In many cases, phosphonium salts **1** were further processed without isolation and purification [6,24,25]. They perfectly fulfill the role of building blocks in Wittig reactions (e.g., the Anders-Gassner variant) [20,26,27], Friedel–Crafts reactions, or other couplings characterized by high chemo- and regioselectivity [6,24,25].



Scheme 1. 1-hydroxyalkylphosphonium salts **1**: synthesis and applications.

Therefore, we present our research related to the synthesis and isolation of 1-hydroxyphosphonium salts as well as their properties, with particular emphasis on their stability, and reactivity with selected reagents.

2. Results and Discussion

Our journey to discover the properties of 1-hydroxyalkylphosphonium salts began with the synthesis of a wide range of such salts by slightly modifying the methods already described in the literature [6,24]. To this end, we conducted two-component couplings of an aldehyde (aliphatic, aromatic, simple, and more complex) with triarylphosphonium salts in a molar ratio of 1:1 (see Table 1). We decided to use previously synthesized [24] or commercially available triarylphosphonium salts $\text{Ar}_3\text{P}\cdot\text{HX}$ ($\text{HP}^+\text{Ar}_3\text{X}^-$) in the reaction, rather than generating them in situ from the appropriate phosphines and acids.

Table 1. Synthesis of 1-hydroxyalkylphosphonium salts **1**—optimization of the reaction conditions.

$$\text{CH}_3\text{CH}_2\text{CHO} + \text{Ar}_3\text{P}\cdot\text{HX} \rightleftharpoons \text{HO}-\text{C}(\text{CH}_2\text{CH}_3)-\text{P}^+\text{Ar}_3\text{X}^-$$

2a 6 1

Entry	Phosphonium Salts 1			Time, min	Temp., °C	Solvent	Yield, %
	No.	Ar	X				
1	1a	Ph	BF ₄	30	r.t.	MeCN	99 ^a /92/85 ^b
2	1a	Ph	BF ₄	30	r.t.	CH ₂ Cl ₂	93
3	1a	Ph	BF ₄	30	r.t.	THF	^c
4	1b	Ph	Br	30	r.t.	MeCN	88
5	1c	Ph	TfO	30	r.t.	MeCN	99 ^a /79
6	1d	3-C ₆ H ₄ Cl	BF ₄	30	r.t.	MeCN	^d
7	1e	4-C ₆ H ₄ OMe	BF ₄	30	r.t.	MeCN	99 ^a /66

^a Only after solvent evaporation, no crystallization (crude salt), ^b The reaction of aldehyde **2** and PPh₃ in the presence of HBF₄ (tetrafluoroboric acid diethyl ether complex, molar ratio of 1:1:1), ^c A mixture of products (estimated content of compound **1a** based on ³¹P{¹H} NMR is 76%), ^d A mixture of products (estimated content of compound **1d** based on ¹H and ³¹P{¹H} NMR is 31%), crystallization attempts failed.

In general, the reactions were carried out at room temperature, but in some cases (see paraformaldehyde) raising the temperature was necessary. The type of solvent affects the course of the reaction. Acetonitrile, chloroform, and dichloromethane (DCM) turned out to be the most effective. However, we also noticed that the use of THF leads to a complex reaction mixture (Table 1, entries 1–3). We demonstrated that the described procedure can be applied to a variety of phosphonium salts $\text{Ar}_3\text{P}\cdot\text{HX}$ ($\text{HP}^+\text{Ar}_3\text{X}^-$). The anion (X^-) does not play a significant role, while the triarylphosphonium group is crucial here. So far, we have not been able to obtain phosphonium salt derivatives of triarylphosphines substituted with electron-withdrawing substituents (e.g., P(3-C₆H₄Cl)₃). Triphenylphosphonium

salts and derivatives of triarylphosphines substituted with electron-donating substituents (PPh_3 or $\text{P}(4\text{-C}_6\text{H}_4\text{OMe})_3$) can be synthesized without any problems (compare entries 5–7, Table 1). The reaction in which $\text{Ph}_3\text{P}\cdot\text{HBF}_4$ was generated in situ using PPh_3 and HBF_4 (tetrafluoroboric acid diethyl ether complex) was also performed, but it turned out to be less efficient (92 vs. 86%—Table 1, entry 1).

The structure of the aldehyde appears to be most important to the success of the reaction. The synthesis of pure products from aliphatic aldehydes does not cause any significant problems (see Table 2). Even the use of hydrated chloroacetaldehyde allowed the expected product to be obtained with a high yield (Table 2, entry 8). The reactions can also be scaled up and conducted at a gram-scale. We demonstrated this for the reaction of paraformaldehyde with $\text{Ph}_3\text{P}\cdot\text{HBr}$ (Table 2, entry 5), obtaining 2.6 g of product **1h** with a yield of 87%.

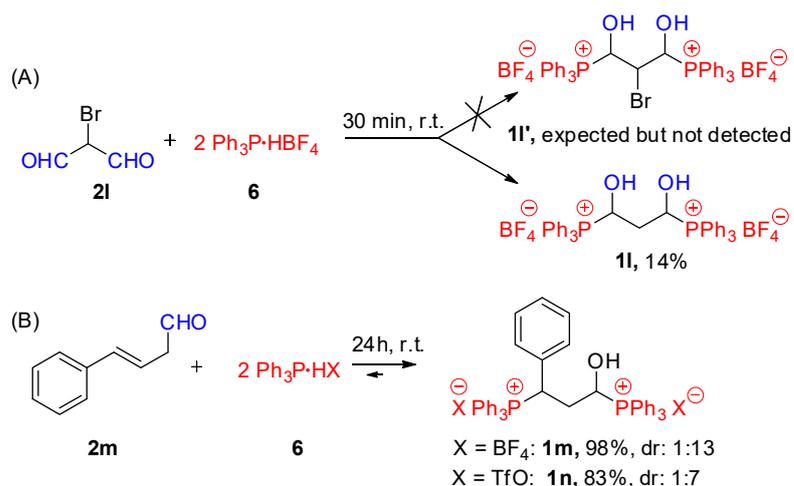
Table 2. Synthesis of 1-hydroxyalkylphosphonium salts **1**—scope of application.

Entry	Phosphonium Salts 1			Time, min	Temp., °C	Solvent	Yield, %
	No.	R ¹	X				
1	1f	H	BF_4	30	r.t.	CHCl_3	n.r.
2	1f	H	BF_4	120	50	CHCl_3	88
3	1f	H	BF_4	120	50	MeCN	95
4	1g	H	TfO	120	50	MeCN	93
5	1h	H	Br	120	50	MeCN	95/87 ^a
6	1i	Me	BF_4	30	r.t.	MeCN	49
7	1i	Me	BF_4	30	r.t.	CH_2Cl_2	99
8	1j	ClCH_2	BF_4	30	r.t.	CHCl_3	89 ^b
9	1k	$n\text{-C}_9\text{H}_{19}$	BF_4	30	r.t.	CHCl_3	99 ^c
10	1k	$n\text{-C}_9\text{H}_{19}$	BF_4	30	r.t.	MeCN	^d

^a A gram-scale synthesis (8 mmol), ^b A 55% wt solution of chloroacetaldehyde in water was used, ^c The salt **1k** was obtained through evaporation of the solvent; crystallization attempts failed, ^d Aldehyde does not dissolve in acetonitrile—the reaction does not occur.

Interestingly, we also managed to obtain hydroxyalkylphosphonium salts from bis-aldehyde systems (e.g., bromomalonaldehyde; see compound **1l**) or unsaturated aldehydes (e.g., (*E*)-cinnamaldehyde; see compounds **1m** and **1n**). In both cases, we had to use an excess of triphenylphosphonium salt (the molar ratio of substrates **2:6** was 1:2); otherwise, complex reaction mixtures were obtained. Furthermore, in the reaction of bromomalonoaldehyde, we isolated only compound **1l**, most likely due to the reductive dehalogenation that occurred (Scheme 2).

On the other hand, in the case of bulky aldehydes ($\text{R}^1 = i\text{-Pr}$) and especially aromatic aldehydes, we observed the incomplete conversion of substrates (see Figure 1, Tables 3 and 4). We assumed that equilibrium was reached and decided to investigate this phenomenon closely (see also Table S1, Supporting Information). Reactions between 1-naphthaldehyde and triarylphosphonium salts $\text{Ar}_3\text{P}\cdot\text{HX}$ ($\text{HP}^+\text{Ar}_3\text{X}^-$) were chosen as model reactions (see Figure 1 and Table 3). As we checked (^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR), the reaction initially proceeds very quickly (until about 5 min), after which the composition of the reaction mixture does not change at a given temperature (Table 3, entries 1–3).



The proportions of diastereomers in the solution changed over time.

Scheme 2. Hydroxyalkylphosphonium salts from bromomalonaldehyde (A) or (E)-cinnamaldehyde (B): conditions and results.

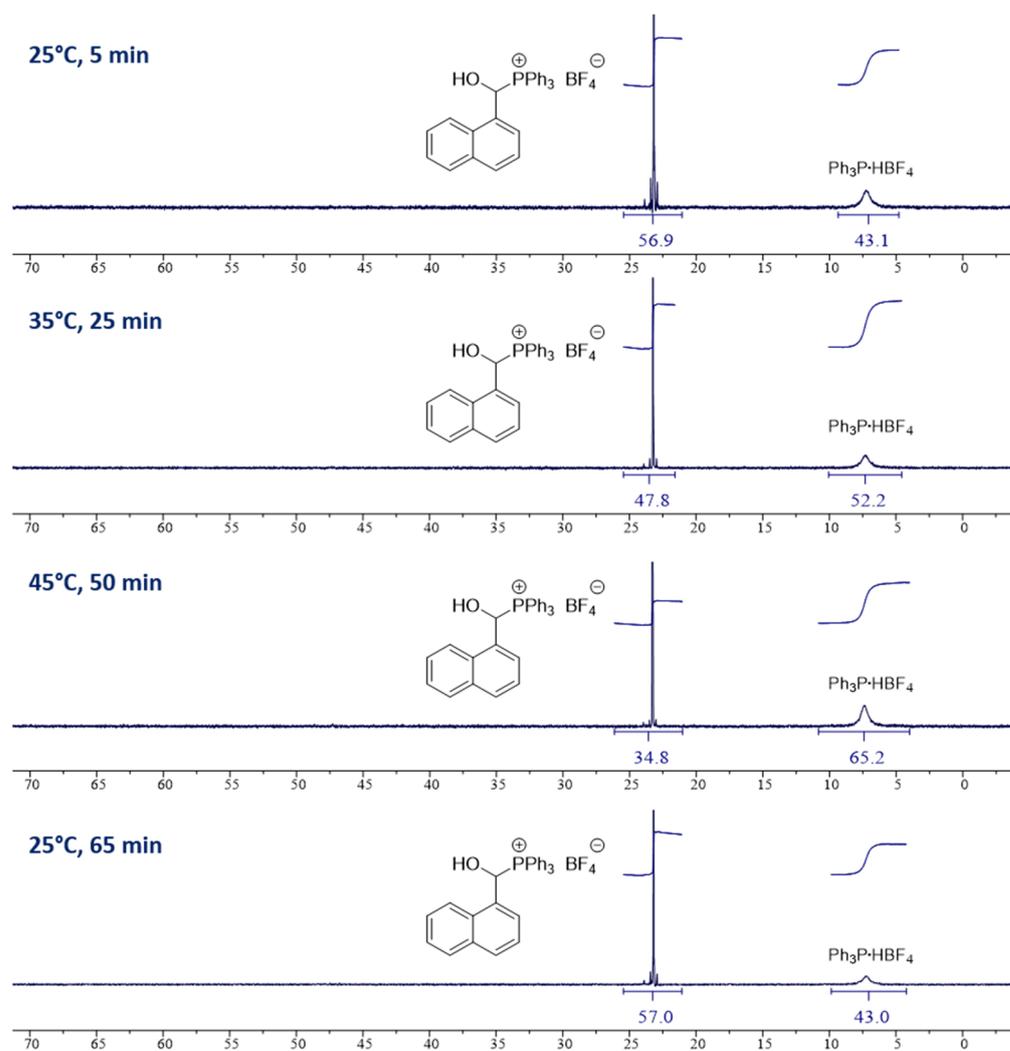


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (162 MHz/ CD_3CN) of reaction mixtures (1-naphthaldehyde with triphenylphosphonium tetrafluoroborate) recorded at 25 °C, 35 °C, 45 °C, and back to 25 °C.

Table 3. Equilibrium in the reaction of naphthaldehyde **2o** and triarylphosphonium salts **6**.

$$\text{2o} + \text{Ar}_3\text{P}^+\text{HX}^- \rightleftharpoons \text{1}$$

Entry	No.	Molar Ratio of 2o:6	Ar	X	Time, min	Temp., °C	Solvent	Molar Ratio of 1:2(6) ^a
1	1o	1:1	Ph	BF ₄	5	25	CD ₃ CN	57:43
2	1o	1:1	Ph	BF ₄	15	25	CD ₃ CN	57:43
3	1o	1:1	Ph	BF ₄	30	25	CD ₃ CN	57:43
4	1o	1:1	Ph	BF ₄	5/65	25	CD ₃ CN	57:43
5	1o	1:1	Ph	BF ₄	25	35	CD ₃ CN	48:52
6	1o	1:1	Ph	BF ₄	50	45	CD ₃ CN	35:65
7	1p	1:1	Ph	TfO	5/65	25	CD ₃ CN	62:38
8	1p	1:1	Ph	TfO	25	35	CD ₃ CN	55:45
9	1p	1:1	Ph	TfO	50	45	CD ₃ CN	44:56
10	1q	1:1	4-C ₆ H ₄ OMe	BF ₄	5/65	25	CD ₃ CN	59:41
11	1q	1:1	4-C ₆ H ₄ OMe	BF ₄	25	35	CD ₃ CN	48:52
12	1q	1:1	4-C ₆ H ₄ OMe	BF ₄	50	45	CD ₃ CN	39:61
13	1o	1:1	Ph	BF ₄	5/65	25	CDCl ₃	45:55
14	1o	1:1	Ph	BF ₄	25	35	CDCl ₃	35:65
15	1o	1:1	Ph	BF ₄	50	45	CDCl ₃	25:75
16	1o	1:1	Ph	BF ₄	5/15/30	25	CD ₃ CN	57:43
17	1o	2:1	Ph	BF ₄	5/15/30	25	CD ₃ CN	75:25
18	1o	3:1	Ph	BF ₄	5/15/30	25	CD ₃ CN	88:12
19	1o	5:1	Ph	BF ₄	5/15/30	25	CD ₃ CN	94:6

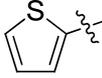
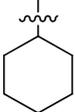
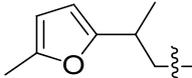
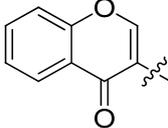
^a The composition of the reaction mixture was estimated based on ¹H and ³¹P{¹H} NMR (see also Table S1, Supporting Information).

Table 4. Equilibrium in the synthesis of 1-hydroxyalkylphosphonium salts **1**.

$$\text{R}^1\text{CHO} + \text{Ph}_3\text{P}^+\text{HBF}_4^- \xrightleftharpoons[\text{30 min.}]{\text{CH}_3\text{CN}} \text{1}$$

Entry	Phosphonium Salts 1		Temp., °C	Solvent	Molar Ratio of 1:2(6) ^a
	No.	R ¹			
1	1r		25	CDCl ₃ CD ₃ CN	57:43 82:18
2	1s		25	CD ₃ CN	67:33
3	1t		25	CD ₃ CN	82:18

Table 4. Cont.

Entry	Phosphonium Salts 1		Temp., °C	Solvent	Molar Ratio of 1:2(6) ^a
	No.	R ¹			
4	1u		25	CD ₃ CN	63:37
5	1v	<i>i</i> -Pr	25	CD ₃ CN	88:12
6	1v	<i>i</i> -Pr	45	CD ₃ CN	72:28
7	1w		25	CDCl ₃	68:32
8	1x		25	CD ₃ CN	84:16 ^b
9	1y		25/50	CD ₃ CN	no reaction

^a The composition of the reaction mixture was estimated by ¹H and ³¹P{¹H} NMR (see also Table S1, Supporting Information), ^b A mixture of two diastereomers is formed at the ratio of 1:1.9.

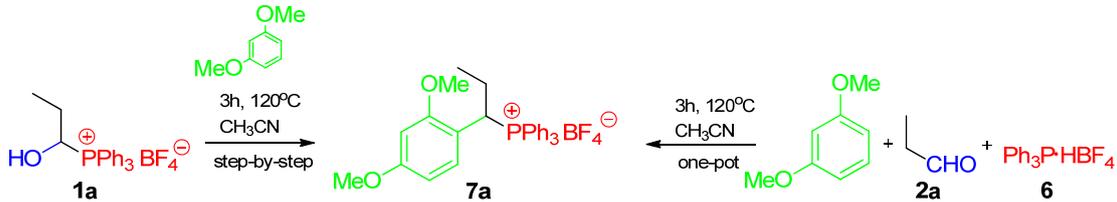
Next, we performed some temperature tests using NMR (VT techniques) and determined the composition of the reaction mixture after increasing the temperature every 10 degrees (from 25 °C to 45 °C and back to 25 °C, see Figure 1 and Table 3). Regardless of the type of phosphonium salt used (anion X or phosphonium moiety Ar₃P), increasing the temperature shifts the equilibrium towards the substrates (see entries 4–15 and Figure 1). Coming back to the initial temperature (25 °C) returns it to the starting composition of the reaction mixture (e.g., compare entries 4–6, Table 3). The equilibrium state itself is slightly affected by the type of solvent used (see CD₃CN vs. CDCl₃, entries 4–6 and 13–15) and the counteranion of the phosphonium salt **6** (compare BF₄ vs. TfO, entries 4–9). We also observed that the use of excess aldehyde **2o** (2:1, 3:1, and 5:1; entries 16–19, Table 3) moves the reaction equilibrium toward product **1**.

The presence of equilibria was confirmed for the reactions of structurally diverse aldehydes, mostly aromatic but sometimes also aliphatic (e.g., isobutyraldehyde, cyclohexanecarbaldehyde; see Table 4). Generally, in CD₃CN the equilibrium is clearly shifted toward the 1-hydroxyalkylphosphonium salts. In CDCl₃, it looks less favorable, most likely due to the acidic nature of this solvent. Furthermore, the (hetero)aromatic systems react less willingly, giving reaction mixtures with lower contents of 1-hydroxyalkylphosphonium salts **1**.

Attempts to isolate pure 1-aryl-1-hydroxyalkylphosphonium salts, e.g., by crystallization from the CH₂Cl₂/Et₂O or CD₃CN/Et₂O, failed (the crystallization leads to the precipitation of Ar₃P·HX rather than to 1-aryl-1-hydroxyalkylphosphonium salts).

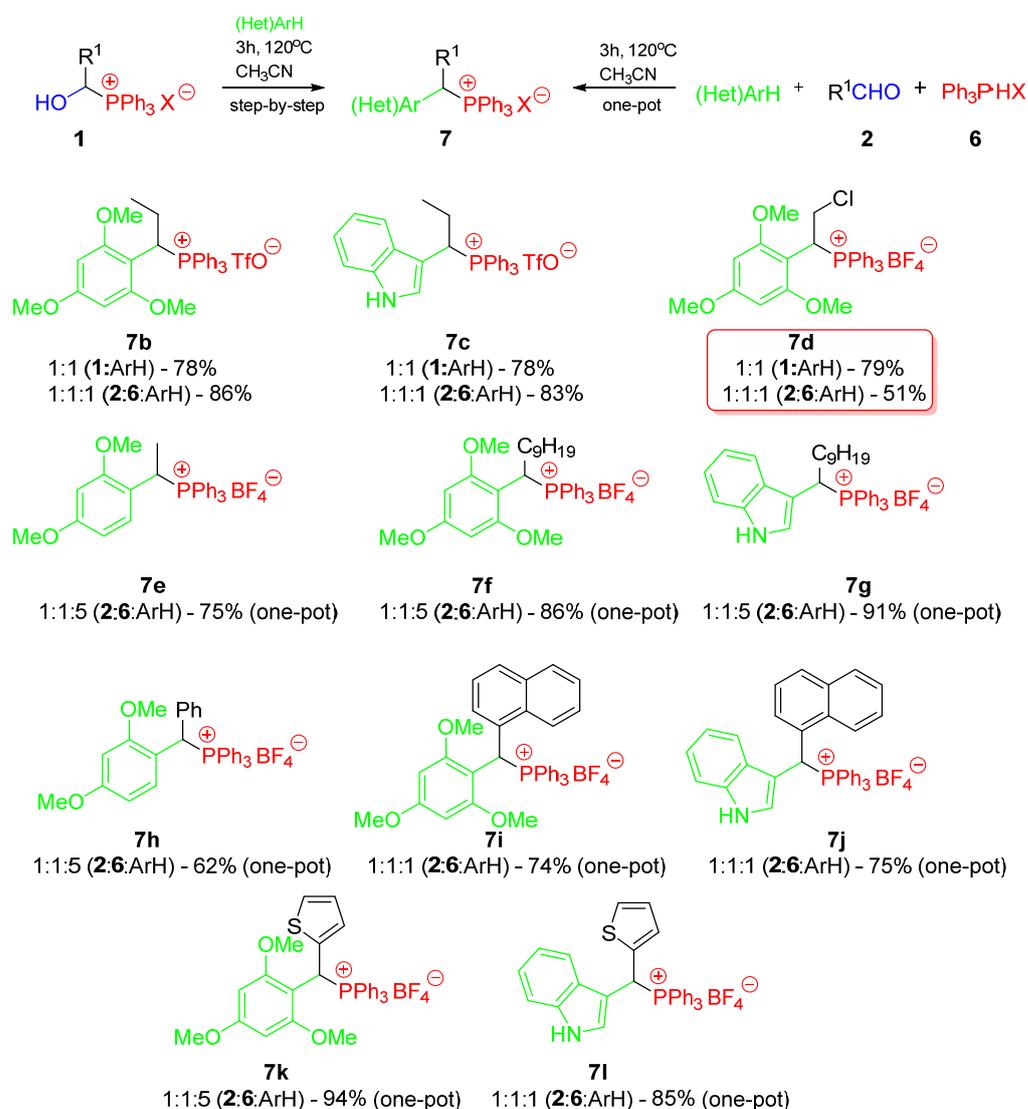
Masarwa et al. reported similar observations for many aromatic aldehydes. They were also unable to isolate 1-hydroxyalkylphosphonium salts either through crystallization or flash chromatography, but they did not provide any explanation for this problem [6].

The high reactivity of the 1-hydroxyalkylphosphonium salts generated in situ (one-pot method) toward aromatic compounds or heteronucleophiles is well documented [6,24]. Therefore, we decided to examine the reactivity of the isolated 1-hydroxyalkylphosphonium salts (step-by-step procedure); however, some in-house results for one-pot reactions are also presented for comparison (see Table 5, Scheme 3, and Table S2, Supporting Information). To this end, we used the reaction with (hetero)aromatic systems or amide-type substrates (amides/carbamates/lactams).

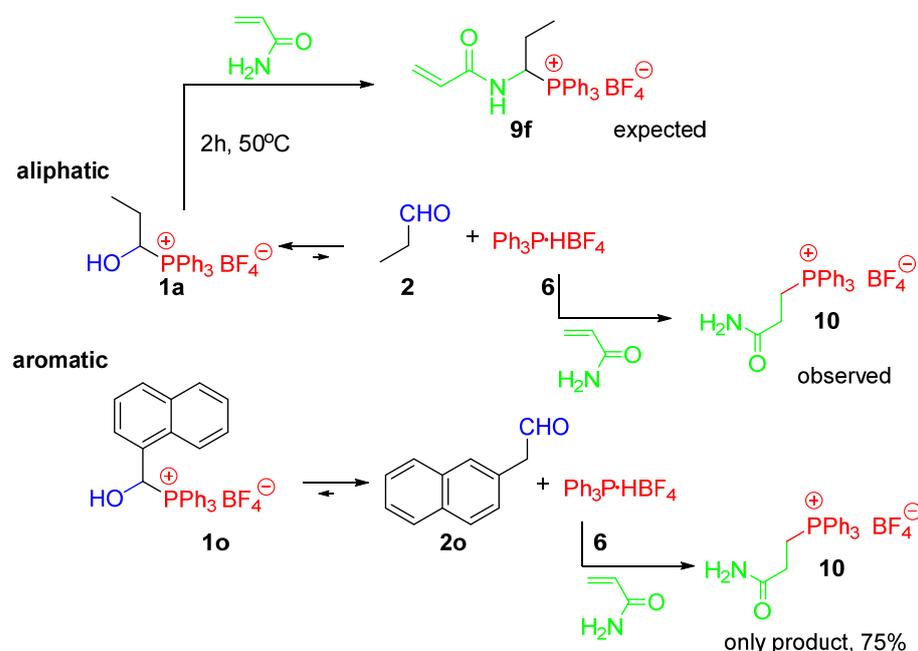
Table 5. The reaction of 1-hydroxyalkylphosphonium salts **1** with aromatic compounds—optimization of the conditions (step-by-step vs. one-pot protocol).


Entry	Molar Ratio	Procedure	Solvent	Yield, %
1	1:5 (1a:ArH)	step-by-step	CD ₃ CN	89 ^a / 76 ^b
2	1:2 (1a:ArH)	step-by-step	CD ₃ CN	83 ^a / 82 ^b
3	1:5 (1a:ArH)	step-by-step	no solvent	57 ^b
4	1:1:5 (2a:6:ArH)	one-pot	CD ₃ CN	77 ^b
5	1:1:1:5 (2a:PPh ₃ :HBF ₄ :ArH) ^c	one-pot	CD ₃ CN	78 ^b

^a The yield was estimated based on ¹H and ³¹P{¹H} NMR, ^b The isolated yields, ^c The reaction of aldehyde **2a**, 1,3-dimethoxybenzene, and PPh₃ in the presence of HBF₄ (tetrafluoroboric acid diethyl ether complex).

**Scheme 3.** Conditions and results for the reaction of 1-hydroxyalkylphosphonium salts **1** with (hetero)aromatic compounds (step-by-step vs. one-pot protocol).

the course of the reaction proposed in Scheme 5. The addition to the double bond appears to occur more readily, causing the equilibrium to be shifted, limiting the formation of the desired product **9f**. The 1-aryl-1-hydroxyalkylphosphonium salts (e.g., **1o**) are much less stable, which means that there is more $\text{Ph}_3\text{P}\cdot\text{HBF}_4$ in the system and thus the addition to the double bond is even more privileged.



Scheme 5. The reaction of 1-hydroxyalkylphosphonium salts **1a** and **1o** with acrylamide—possible pathways.

3. Materials and Methods

3.1. General Methods

Melting points were determined in capillaries and were uncorrected. The ^1H - and ^{13}C -NMR spectra were recorded at operating frequencies of 400 and 100 MHz, respectively, using TMS (tetramethylsilane) as the internal resonance shift standard. The ^{31}P -NMR spectra were recorded at an operating frequency of 161.9 MHz, with respect to H_3PO_4 at zero ppm. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. Infrared (IR) spectra were measured on a Fourier transform (FT)-IR spectrophotometer (Attenuated Total Reflectance—ATR method). High-resolution mass spectrometry (HR-MS) analyses were performed using a Waters Xevo G2 Q-TOF mass spectrometer equipped with an ESI source operating in positive ion mode. The accurate mass and composition of the molecular ion adducts were calculated using the MassLynx 4.1 software incorporated within the instrument. Solvents (ACS grade) were stored over molecular sieves prior to use. All other commercially available reagents were used as received, without further purification or modifications.

3.2. Synthesis of 1-Hydroxyalkylphosphonium Salts

To an aldehyde (1.0 mmol) and a solvent (1 cm^3) placed in a glass vial sealed with a screw-cap, triarylphosphonium salt $\text{HP}^+\text{Ar}_3\text{X}^-$ (1 mmol) was added. The reaction was carried out under the conditions given in Table 1 and 2. Then, 1-hydroxyalkylphosphonium salts **1** were precipitated using Et_2O . The crude 1-hydroxyalkylphosphonium salts **1** can also be obtained only via the evaporation of volatile components.

3.3. Synthesis of 1-Hydroxyalkylphosphonium Salts on a Gram-Scale

The reaction was carried out in a 25 cm^3 round-bottom flask equipped with a reflux condenser. Triphenylphosphonium bromide (2.74 g, 8 mmol) was added to a solution

of paraformaldehyde (0.24 g, 8 mmol) in CH₃CN (8 cm³). Then, the obtained mixture was stirred vigorously and heated at 50 °C for 2 h using an oil bath. After cooling to room temperature, the product was precipitated with diethyl ether (10 cm³), separated via vacuum filtration, washed on a Büchner funnel with CH₃CN/Et₂O (10 cm³, 1:3 [v/v]), and dried to afford pure hydroxymethyltriphenylphosphonium bromide **1h** at an 87% yield.

3.4. Synthesis of 1-Hydroxyalkylphosphonium Salts in the Presence of PPh₃ and HBF₄·Et₂O

To a solution of propionaldehyde (67 µL, 58.1 mg, 1.0 mmol) in CH₃CN (1 cm³) placed in a glass vial sealed with a screw-cap, PPh₃ (262.2 mg, 1.0 mmol) and HBF₄·Et₂O (136 µL, 161.9 mg, 1.0 mmol) were added. The reaction was carried out under the conditions given in Table 1. Then, 1-hydroxyalkylphosphonium salt **1a** was precipitated using Et₂O.

1-hydroxypropyltriphenylphosphonium tetrafluoroborate (1a). White crystals (379.6 mg, 93% yield), mp 125–127 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.83–7.62 (m, 15H, 3×Ph), 5.64 (dd, *J* = 10.2, 3.0 Hz, 1H, C_αH), 5.31 (br s, 1H, OH), 1.91–1.80 (m, 2H, CH₂), and 1.20 (td, *J* = 7.2, 0.9 Hz, 3H, CH₃); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ aromatic carbons: 135.2, 134.3 (d, *J* = 8.5 Hz), 130.5 (d, *J* = 12.0 Hz), 117.2 (d, *J* = 81.1 Hz), 69.9 (d, *J* = 60.9 Hz, C_αH), 25.7 (d, *J* = 4.9 Hz, CH₂), and 10.3 (d, *J* = 14.4 Hz, CH₃); ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ 21.5 ppm; IR (ATR) 3407, 1438, 1110, 1088, 1066, 996, and 976 cm⁻¹. HRMS (TOF-ESI) calcd. for C₂₁H₂₂OP⁺ [M⁺] 321.1408, found 321.1422.

1-hydroxypropyltriphenylphosphonium bromide (1b) [24]. White crystals (353.1 mg, 88% yield), mp 150–152 °C (lit.: mp 157–159 °C [24]). ¹H NMR (400 MHz, CDCl₃) δ 7.95–7.71 (m, 9H, Ph), 7.70–7.58 (m, 6H, Ph), 5.96–5.88 (m, 1H, C_αH), 1.91–1.77 (m, 2H, CH₂), and 1.24 (td, *J* = 7.2, 1.1 Hz, 3H, CH₃); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ aromatic carbons: 134.9 (d, *J* = 3.0 Hz), 134.4 (d, *J* = 9.0 Hz), 130.3 (d, *J* = 12.1 Hz), 117.7 (d, *J* = 80.6 Hz), 68.4 (d, *J* = 60.4 Hz, C_αH), 25.7 (d, *J* = 6.2 Hz, CH₂), and 10.7 (d, *J* = 14.5 Hz, CH₃); ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ 20.9 ppm; IR (ATR) 3072, 1438, 1111, 754 cm⁻¹.

1-hydroxypropyltriphenylphosphonium triflate (1c). White crystals (371.6 mg, 79% yield), mp 132–134 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.84–7.70 (m, 9H, Ph), 7.70–7.62 (m, 6H, Ph), 5.76–5.67 (m, 1H, C_αH), 1.91–1.76 (m, 2H, CH₂), and 1.21 (td, *J* = 7.4, 1.2 Hz, 3H, CH₃); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ aromatic carbons: 135.1 (d, *J* = 3.0 Hz), 134.4 (d, *J* = 8.9 Hz), 130.5 (d, *J* = 12.0 Hz), 120.7 (q, *J* = 319.6 Hz, CF₃), 117.5 (d, *J* = 80.7 Hz), 69.7 (d, *J* = 60.4 Hz, C_αH), 25.8 (d, *J* = 5.4 Hz, CH₂), and 10.4 (d, *J* = 14.7 Hz, CH₃); ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ 21.0 ppm; IR (ATR) 3266, 1438, 1292, 1244, 1224, 1155, 1109, and 1028 cm⁻¹. HRMS (TOF-ESI) calcd. For C₂₁H₂₂OP⁺ [M⁺] 321.1408, found 321.1407.

1-hydroxypropyltris(4-methoxyphenyl)phosphonium tetrafluoroborate (1d). Resin (328.8 mg, 66% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.70–7.53 (m, 6H, aromatic), 7.20–7.07 (m, 6H, aromatic), 5.42 (dd, *J* = 10.5, 3.0 Hz, 1H, C_αH), 3.90 (s, 9H, 3×OCH₃), 1.87–1.68 (m, 2H, CH₂), and 1.17 (td, *J* = 7.2, 0.4 Hz, 3H, CH₃); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ aromatic carbons: 164.7 (d, *J* = 3.0 Hz), 136.1 (d, *J* = 10.5 Hz), 116.1 (d, *J* = 13.2 Hz), 108.0 (d, *J* = 89.2 Hz), 70.1 (d, *J* = 65.2 Hz, C_αH), 55.9 (OCH₃), 25.4 (CH₂), and 10.3 (d, *J* = 14.3 Hz, CH₃); ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ 19.9 ppm; IR (ATR) 3442, 1593, 1503, 1263, 1110, 1055, and 1016 cm⁻¹. HRMS (TOF-ESI) calcd. for C₂₄H₂₈O₄P⁺ [M⁺] 411.1725, found 411.1721.

hydroxymethyltriphenylphosphonium tetrafluoroborate (1f) [16,17]. White crystals (361.1 mg, 95% yield), mp 132–134 °C (lit.: mp 128–130 °C [16], 130–131 °C [17]). ¹H NMR (400 MHz, CDCl₃) δ 7.85–7.64 (m, 15H, 3×Ph), 5.47 (s, 2H, CH₂); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ aromatic carbons: 135.4 (d, *J* = 3.0 Hz), 134.1 (d, *J* = 9.5 Hz), 130.5 (d, *J* = 12.3 Hz), 117.3 (d, *J* = 83.9 Hz), and 57.5 (d, *J* = 65.2 Hz, CH₂); ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ 17.1 ppm; IR (ATR) 3073, 1439, 1076, 1025, and 998 cm⁻¹. HRMS (TOF-ESI) calcd. for C₁₉H₁₈OP⁺ [M⁺] 293.1095, found 293.1085.

hydroxymethyltriphenylphosphonium triflate (1g) [28]. White crystals (411.4 mg, 93% yield), mp 134–135 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.89–7.78 (m, 3H, Ph), 7.75–7.63 (m, 12H, Ph), 5.41 (s, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ aromatic carbons: 135.5 (d, $J = 3.0$ Hz), 134.0 (d, $J = 9.5$ Hz), 130.6 (d, $J = 12.4$ Hz), 120.6 (q, $J = 319.6$ Hz, CF_3), 116.7 (d, $J = 84.0$ Hz), and 58.1 (d, $J = 65.1$ Hz, CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3) δ 17.2 ppm; IR (ATR) 3313, 1438, 1281, 1249, 1228, 1158, 1113, and 1027 cm^{-1} . HRMS (TOF-ESI) calcd. for $\text{C}_{19}\text{H}_{18}\text{OP}^+$ [M^+] 293.1095, found 293.1096.

hydroxymethyltriphenylphosphonium bromide (1h) [29]. White crystals (354.5 mg, 95% yield), mp 191–193 °C (lit.: mp 203 °C [29]). ^1H NMR (400 MHz, CDCl_3) δ 7.85–7.61 (m, 15H, 3xPh), 5.47 (s, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ aromatic carbons: 135.4 (d, $J = 3.0$ Hz), 134.1 (d, $J = 9.5$ Hz), 130.5 (d, $J = 12.3$ Hz), 117.3 (d, $J = 83.6$ Hz), and 57.6 (d, $J = 65.1$ Hz, CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3) δ 17.1 ppm; IR (ATR) 3087, 1435, 1115, and 1051 cm^{-1} . HRMS (TOF-ESI) calcd. For $\text{C}_{19}\text{H}_{18}\text{OP}^+$ [M^+] 293.1095, found 293.1096.

1-hydroxyethyltriphenylphosphonium tetrafluoroborate (1i). White crystals (390.3 mg, 99% yield), mp 114–116 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.90–7.55 (m, 15H, 3xPh), 5.96–5.86 (m, 1H, C_αH), 5.29 (dd, $J = 13.1, 6.8$ Hz, 1H, OH), and 1.70 (dd, $J = 18.2, 6.8$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ aromatic carbons: 135.3 (br s), 134.2 (d, $J = 8.9$ Hz), 130.5 (d, $J = 12.1$ Hz), 116.8 (d, $J = 82.1$ Hz), 65.4 (d, $J = 65.1$ Hz, C_αH), and 18.5 (br s, CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3) δ 17.5 ppm; IR (ATR) 3451, 1488, 1439, 1108, 1060, 996, and 976 cm^{-1} . HRMS (TOF-ESI) calcd. for $\text{C}_{20}\text{H}_{20}\text{OP}^+$ [M^+] 307.1252, found 307.1251.

2-chloro-1-hydroxyethyltriphenylphosphonium tetrafluoroborate (1j). White crystals (369.0 mg, 89% yield), mp 111.5–113.5 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.90–7.74 (m, 9H, Ph), 7.70–7.59 (m, 6H, Ph), 6.11 (br s, 1H, OH), 5.73 (dd, $J = 13.2, 6.2$ Hz, 1H, C_αH), 4.03 (ddd, $J = 19.9, 12.8, 4.3$ Hz, 1H, CHH), and 3.88 (ddd, $J = 12.9, 8.2, 5.0$ Hz, 1H, CHH); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ aromatic carbons: 135.6 (d, $J = 3.1$ Hz), 134.3 (d, $J = 9.5$ Hz), 130.6 (d, $J = 12.5$ Hz), 116.5 (d, $J = 82.7$ Hz), 69.8 (d, $J = 67.3$ Hz, C_αH), and 44.4 (d, $J = 7.3$ Hz, CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3) δ 20.8 ppm; IR (ATR) 3337, 1586, 1483, 1436, 1061, 1023, 995, and 973 cm^{-1} . HRMS (TOF-ESI) calcd. for $\text{C}_{20}\text{H}_{19}\text{ClOP}^+$ [M^+] 341.0862, found 341.0861.

1-hydroxydecyltriphenylphosphonium tetrafluoroborate (1k). Resin (501.3 mg, 99% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.87–7.60 (m, 15H, 3xPh), 5.73–5.66 (m, 1H, C_αH), 5.29 (br s, 1H, OH), aliphatics (8x CH_2): 1.90–1.66 (m, 3H), 1.66–1.46 (m, 1H), 1.35–1.11 (m, 12H), and 0.85 (t, $J = 6.9$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ aromatic carbons: 135.2 (d, $J = 3.0$ Hz), 134.3 (d, $J = 8.9$ Hz), 130.5 (d, $J = 12.0$ Hz), 117.2 (d, $J = 80.9$ Hz), 68.9 (d, $J = 60.1$ Hz, C_αH), 32.3 (d, $J = 4.3$ Hz, CH_2), 31.9 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 25.7 (d, $J = 13.4$ Hz, CH_2), 22.7 (br s, CH_2), and 14.2 (CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3) δ 21.4 ppm; IR (ATR) 2923, 2854, 1439, 1109, 1056, and 996 cm^{-1} . HRMS (TOF-ESI) calcd. for $\text{C}_{28}\text{H}_{36}\text{OP}^+$ [M^+] 419.2504, found 419.2499.

1,3-dihydroxypropane-1,3-bis(triphenylphosphonium) bis(tetrafluoroborate) (1l). White crystals (108.1 mg, 14% yield), mp 150–151 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.90–7.50 (m, 30H, 6xPh), 6.64 (br s, 2H, OH), 5.94 (br s, 2H, C_αH), and 2.18–2.05 (m, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ aromatic carbons: 135.4 (br s), 134.7–134.3 (m), 130.9–130.5 (m), 116.1 (d, $J = 84.2$ Hz), 62.7 (dd, $J = 73.2, 13.8$ Hz, C_αH), and 33.5 (t, $J = 8.7$ Hz, CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3) δ 22.7 ppm; IR (ATR) 2989, 1586, 1483, 1437, 1109, 1045, and 995 cm^{-1} . HRMS (TOF-ESI) calcd. for $\text{C}_{39}\text{H}_{36}\text{O}_2\text{P}_2^{2+}$ [M^{2+}] 299.1090, found 299.1087.

1-hydroxy-3-phenylpropane-1,3-bis(triphenylphosphonium) bis(tetrafluoroborate) (1m). White crystals (815.8 mg, 98% yield), mp 205–207 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.83–7.71 (m, 6H, Ph), 7.69–7.54 (m, 18H, Ph), 7.47–7.39 (m, 6H, Ph), 7.39–7.30 (m, 1H, Ph), 7.27–7.21 (m, 2H, Ph), 7.06–7.00 (m, 2H, Ph), 6.16 (t, $J = 7.1$ Hz, 1H, OH), 5.24–5.16 (m, 1H, CH-Ph or C_αH),

5.04 (dd, $J = 17.1, 10.8$ Hz, 1H, CH-Ph or $C_{\alpha}H$), 2.81–2.69 (m, 1H, CHH), and 2.59–2.50 (m, 1H, CHH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ aromatic carbons: 135.6 (d, $J = 3.0$ Hz), 135.5 (d, $J = 3.1$ Hz), 134.4 (d, $J = 9.4$ Hz), 134.1 (d, $J = 9.3$ Hz), 131.3 (d, $J = 5.8$ Hz), 130.7 (d, $J = 12.4$ Hz), 130.6 (d, $J = 12.5$ Hz), 130.1 (d, $J = 3.0$ Hz), 129.9 (d, $J = 2.2$ Hz), 129.4 (d, $J = 5.1$ Hz), 116.1 (d, $J = 83.9$ Hz), 115.4 (d, $J = 82.6$ Hz), 66.5 (dd, $J = 66.2, 14.8$ Hz, $C_{\alpha}H$), 40.2 (dd, $J = 47.7, 15.6$ Hz, CH-Ph), and 35.2 (br d, $J = 10.2$ Hz, CH_2); $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 26.9 (d, $J = 9.1$ Hz), 21.8 (d, $J = 9.1$ Hz) ppm; IR (ATR) 3410, 1439, 1108, 1050, and 996 cm^{-1} . HRMS (TOF-ESI) calcd. for $C_{39}H_{36}O_2P_2^{2+}$ [M^{2+}] 329.1277, found 329.1265.

1-hydroxy-3-phenylpropane-1,3-bis(triphenylphosphonium) bis(triflate) (1n). White crystals (108.1 mg, 14% yield), mp 190–192 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.84–7.70 (m, 6H, Ph), 7.69–7.56 (m, 18H, Ph), 7.49–7.41 (m, 6H, Ph), 7.39–7.33 (m, 1H, Ph), 7.27–7.22 (m, 2H, Ph), 7.05–6.99 (m, 2H, Ph), 5.18–5.02 (m, 2H, CH-Ph and $C_{\alpha}H$), 2.76–2.64 (m, 1H, CHH), 2.59–and 2.46 (m, 1H, CHH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ aromatic carbons: 135.6 (d, $J = 3.0$ Hz), 135.4 (d, $J = 3.1$ Hz), 134.6 (d, $J = 9.4$ Hz), 134.3 (d, $J = 9.3$ Hz), 131.4 (d, $J = 5.8$ Hz), 130.7 (d, $J = 12.4$ Hz), 130.7 (d, $J = 12.4$ Hz), 130.2 (d, $J = 3.0$ Hz), 129.9 (d, $J = 2.3$ Hz), 129.5 (d, $J = 5.1$ Hz), 120.6 (q, $J = 320.2$ Hz, CF_3), 116.3 (d, $J = 83.9$ Hz), 115.8 (d, $J = 82.5$ Hz), 66.3 (dd, $J = 66.8, 14.8$ Hz, $C_{\alpha}H$), 40.0 (dd, $J = 47.7, 15.7$ Hz, CH-Ph), and 35.2 (dd, $J = 9.8, 1.0$ Hz, CH_2); $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 26.4 (d, $J = 8.7$ Hz), 21.4 (d, $J = 8.7$ Hz) ppm; IR (ATR) 3062, 1439, 1262, 1107, 1025, and 997 cm^{-1} . HRMS (TOF-ESI) calcd. For $C_{39}H_{36}O_2P_2^{2+}$ [M^{2+}] 329.1277, found 329.1270.

3.5. NMR Experiments (Studies of Equilibria)

A mixture of an aldehyde (0.1 mmol), a triarylphosphonium salt $Ar_3P \cdot HX$ (0.1 mmol), and a deuterated solvent (0.65 cm^3) was placed in an NMR tube. The reaction was carried out under the conditions given in Tables 3 and 4. Changes in substrate and/or product concentrations were monitored via 1H NMR and confirmed via $^{31}P\{^1H\}$ NMR spectroscopy (for $^{31}P\{^1H\}$ NMR: seqfil = s2pul, sw = 249 ppm, at = 0.813 s, np = 65,536, pw = 3.356 μs , d1 = 1 s, and offset = 16,377.3 Hz).

3.6. Reactions of 1-Hydroxyalkylphosphonium Salts with (hetero)arenes (Step-by-Step)

To a solution of 1-hydroxyalkylphosphonium salt (1.0 mmol) in CH_3CN (1 cm^3) placed in a glass vial sealed with a screw-cap, a (hetero)aromatic compound (5, 2, or 1 mmol) was added. The reaction was carried out under the conditions given in Scheme 3. Then, the 1-arylalkylphosphonium salts 7 were precipitated using Et_2O .

3.7. Reactions of Aldehydes with (hetero)arenes in the Presence of $Ar_3P \cdot HX$ (One-Pot)

To a solution of aldehydes (1.0 mmol) in CH_3CN (1.0 cm^3) placed in a glass vial sealed with a screw-cap, the $Ar_3P \cdot HX$ (1.0 mmol) and a (hetero)aromatic compound (5.0 mmol or 1.0 mmol) were added. The reaction was carried out under the conditions given in Table 5 and Scheme 3. Then, the 1-arylalkylphosphonium salts 7 were precipitated using Et_2O .

3.8. Reactions of Aldehydes with (hetero)arenes in the Presence of PPh_3 and $HBF_4 \cdot Et_2O$ (One-Pot)

To a solution of propionaldehyde (67 μL , 58.1 mg, 1.0 mmol) in CH_3CN (1.0 cm^3) placed in a glass vial sealed with a screw-cap, PPh_3 (262.2 mg, 1.0 mmol), $HBF_4 \cdot Et_2O$ (136 μL , 161.9 mg, 1.0 mmol), and 1,3-dimethoxybenzene (648.6 μL , 690.8 mg, 5 mmol) were added. The reaction was carried out under the conditions given in Table 5. Then, the 1-arylalkylphosphonium salt 7a was precipitated using Et_2O .

1-(2,4-dimethoxyphenyl)propyltriphenylphosphonium tetrafluoroborate (7a). White crystals (433.2 mg, 82%), mp 174–176 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.88–7.79 (m, 3H, Ph), 7.73–7.63 (m, 6H, Ph), 7.51–7.40 (m, 6H, Ph), 6.58 (dd, $J = 9.3, 2.4$ Hz, 1H, aromatic), 6.44–6.33 (m, 2H, aromatic), 4.90 (ddd, $J = 15.1, 12.2, 2.6$ Hz, 1H, $C_{\alpha}H$), 3.82 (s, 3H, OCH_3), 3.43 (s, 3H, OCH_3), 2.35–2.20 (m, 1H, CHH), 2.19–2.08 (m, 1H, CHH), and 0.95 (td, $J = 7.1, 1.2$ Hz, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ aromatic carbons: 161.9 (d, $J = 3.0$ Hz), 159.4

(d, $J = 5.9$ Hz), 135.4 (d, $J = 3.0$ Hz), 134.3 (d, $J = 9.0$ Hz), 130.5 (d, $J = 12.1$ Hz), 117.7 (d, $J = 82.4$ Hz), 110.5 (d, $J = 5.2$ Hz), 105.8 (d, $J = 2.6$ Hz), 98.9 (d, $J = 2.4$ Hz), 55.7 (OCH₃), 55.5 (OCH₃), 36.7 (d, $J = 41.6$ Hz, C_αH), 24.2 (CH₂), and 12.5 (d, $J = 15.3$ Hz, CH₃) ppm; ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ 23.2 ppm; IR (ATR) 2971, 1608, 1585, 1508, 1438, 1107, 1050, 1027, and 997 cm⁻¹. HRMS (TOF-ESI) calcd. for C₂₉H₃₀O₂P⁺ [M⁺] 441.1983 found 441.1982.

1-(2,4,6-trimethoxyphenyl)propyltriphenylphosphonium triflate (7b). Resin (533.7 mg, 86%). ¹H NMR (400 MHz, CDCl₃) 7.88–7.75 (m, 3H, Ph), 7.71–7.59 (m, 6H, Ph), 7.44–7.31 (m, 6H, Ph), 6.03 (s, 2H, aromatic), 5.00 (ddd, $J = 17.5, 11.9, 3.2$ Hz, 1H, C_αH), 3.84 (s, 3H, OCH₃), 3.46 (s, 3H, OCH₃), 3.15 (s, 3H, OCH₃), 2.77–2.62 (m, 1H, CHH), 2.13–2.00 (m, 1H, CHH), and 0.91 (td, $J = 7.2, 1.1$ Hz, 3H, CH₃) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ aromatic carbons: 162.7 (d, $J = 2.8$ Hz), 160.0 (d, $J = 7.5$ Hz), 135.0 (d, $J = 3.0$ Hz), 134.0 (d, $J = 8.9$ Hz), 130.1 (d, $J = 12.0$ Hz), 121.0 (q, $J = 320.7$ Hz, CF₃), 118.8 (d, $J = 82.4$ Hz), 98.6 (d, $J = 5.3$ Hz), 91.0, 56.1 (OCH₃), 55.7 (OCH₃), 54.7 (OCH₃), 36.4 (d, $J = 45.5$ Hz, C_αH), and 21.6 (CH₂), 13.0 (d, $J = 15.1$ Hz, CH₃) ppm; ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ 21.7 ppm; IR (ATR) 2940, 1609, 1586, 1438, 1266, 1222, 1141, 1119, 1103, and 1030 cm⁻¹. HRMS (TOF-ESI) calcd. for C₃₀H₃₂O₃P⁺ [M⁺] 471.2089 found 471.2093.

1-(H-indol-3-yl)propyltriphenylphosphonium triflate (7c). White crystals (472.8 mg, 83%), mp 191–193 °C. ¹H NMR (400 MHz, CDCl₃) 10.22 (s, 1H, NH), 7.77–7.69 (m, 3H, Ph), 7.61–7.53 (m, 6H, Ph), 7.51–7.43 (m, 7H, aromatic), 7.07–6.99 (m, 1H, aromatic), 6.97–6.91 (m, 1H, aromatic), 6.81 (br t, $J = 7.5$ Hz, 1H, aromatic), 6.65 (br t, $J = 3.0$ Hz, 1H, aromatic), 4.73 (ddd, $J = 14.4, 12.2, 2.4$ Hz, 1H, C_αH), 2.40–2.21 (m, 1H, CHH), 2.15–2.01 (m, 1H, CHH), and 0.91 (td, $J = 7.1, 1.3$ Hz, 3H, CH₃) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ aromatic carbons: 136.2, 135.2 (d, $J = 2.0$ Hz), 134.3 (d, $J = 8.9$ Hz), 130.3 (d, $J = 12.0$ Hz), 127.4 (d, $J = 4.6$ Hz), 126.3 (d, $J = 7.8$ Hz), 122.4, 121.0 (q, $J = 318.8$ Hz, CF₃), 119.9, 117.8 (d, $J = 80.9$ Hz), 117.7, 112.9, 103.0 (d, $J = 5.8$ Hz), 36.8 (d, $J = 45.2$ Hz, C_αH), 25.6 (CH₂), and 12.4 (d, $J = 14.9$ Hz, CH₃) ppm; ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ 21.9 ppm; IR (ATR) 3329, 1438, 1277, 1266, 1248, 1225, 1158, 1109, and 1030 cm⁻¹. HRMS (TOF-ESI) calcd. for C₂₉H₂₇NP⁺ [M⁺] 420.1881 found 420.1882.

2-chloro-1-(2,4,6-trimethoxyphenyl)ethyltriphenylphosphonium tetrafluoroborate (7d). White crystals (457.3 mg, 79%), mp 159–160 °C. ¹H NMR (400 MHz, CDCl₃) 7.86–7.79 (m, 3H, Ph), 7.72–7.64 (m, 6H, Ph), 7.49–7.41 (m, 6H, Ph), 6.03 (s, 2H, aromatic), 5.50 (ddd, $J = 16.4, 7.8, 7.1$ Hz, 1H, C_αH), 4.45–4.27 (m, 2H, CH₂Cl), 3.83 (s, 3H, OCH₃), and 3.42 (s, 6H, OCH₃) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ aromatic carbons: 163.5 (d, $J = 2.7$ Hz), 159.5 (br s), 135.4 (d, $J = 3.1$ Hz), 134.2 (d, $J = 9.4$ Hz), 130.3 (d, $J = 12.4$ Hz), 117.8 (d, $J = 83.1$ Hz), 98.3 (d, $J = 5.1$ Hz), 91.2, 55.9 (OCH₃), 55.5 (OCH₃), 41.7 (d, $J = 5.0$ Hz, CH₂Cl), and 38.5 (d, $J = 45.6$ Hz, C_αH) ppm; ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ 22.1 ppm; IR (ATR) 3354, 2843, 1608, 1590, 1438, 1340, 1209, 1157, 1142, 1118, 1103, 1032, and 997 cm⁻¹. HRMS (TOF-ESI) calcd. for C₂₉H₂₉ClO₃P⁺ [M⁺] 491.1543 found 491.1546.

1-(2,4-dimethoxyphenyl)ethyltriphenylphosphonium tetrafluoroborate (7e) [30]. Resin (385.7 mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ 7.93–7.80 (m, 3H, Ph), 7.73–7.60 (m, 6H, Ph), 7.53–7.42 (m, 6H, Ph), 6.69–6.58 (m, 1H, aromatic), 6.42–6.32 (m, 2H, aromatic), 5.27–5.14 (m, 1H, C_αH), 3.81 (s, 3H, OCH₃), 3.41 (s, 3H, OCH₃), and 1.82 (dd, $J = 18.5, 7.4$ Hz, 3H, CH₃) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ aromatic carbons: 161.8 (d, $J = 3.0$ Hz), 158.1 (d, $J = 5.6$ Hz), 135.2 (d, $J = 3.0$ Hz), 134.2 (d, $J = 8.9$ Hz), 130.3 (d, $J = 12.1$ Hz), 130.1 (d, $J = 5.0$ Hz), 117.3 (d, $J = 82.4$ Hz), 112.6 (d, $J = 5.4$ Hz), 105.5 (d, $J = 2.6$ Hz), 98.7 (d, $J = 2.5$ Hz), 55.6 (OCH₃), 55.2 (OCH₃), 29.7 (d, $J = 45.7$ Hz, C_αH), and 16.5 (CH₃) ppm; δ ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ 24.2 ppm; IR (ATR) 2936, 1608, 1506, 1486, 1438, 1301, 1209, 1107, 1049, 1023, and 996 cm⁻¹. The spectra reported here are in agreement with previously published data [30].

1-(2,4,6-trimethoxyphenyl)decyltriphenylphosphonium tetrafluoroborate (7f). White crystals (564.6 mg, 86%), mp 110–112 °C. ^1H NMR (400 MHz, CDCl_3) 7.88–7.76 (m, 3H, Ph), 7.70–7.60 (m, 6H, Ph), 7.44–7.31 (m, 6H, Ph), 6.06 (s, 1H, aromatic), 6.03 (s, 1H, aromatic), 5.08 (ddd, $J = 17.7, 12.0, 3.0$ Hz, 1H, C_αH), 3.85 (s, 3H, OCH_3), 3.45 (s, 3H, OCH_3), 3.16 (s, 3H, OCH_3), and aliphatics ($8\times\text{CH}_2$): 2.81–2.64 (m, 1H), 1.99–1.81 (m, 1H), 1.32–1.09 (m, 14H), and 0.85 (t, $J = 7.0$ Hz, 3H, CH_3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ aromatic carbons: 162.7 (d, $J = 2.9$ Hz), 160.1 (d, $J = 3.6$ Hz), 159.8 (d, $J = 6.5$ Hz), 135.0 (d, $J = 3.0$ Hz), 134.1 (d, $J = 8.9$ Hz), 130.2 (d, $J = 12.1$ Hz), 118.8 (d, $J = 82.3$ Hz), 98.8 (d, $J = 5.4$ Hz), 91.1 (br s), 56.1 (OCH_3), 55.8 (OCH_3), 54.7 (OCH_3), 34.8 (d, $J = 45.3$ Hz, C_αH), 31.9 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 28.8 (CH_2), 28.1 (d, $J = 13.6$ Hz), 27.7 (CH_2), 22.7 (CH_2), and 14.2 (CH_3) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3) δ 21.7 ppm; IR (ATR) 2925, 2853, 1607, 1589, 1456, 1437, 1206, 1147, 1127, 1101, 1046, 1033, and 996 cm^{-1} . HRMS (TOF-ESI) calcd. for $\text{C}_{37}\text{H}_{46}\text{O}_3\text{P}^+$ [M^+] 569.3185 found 569.3185.

1-(H-indol-3-yl)decyltriphenylphosphonium tetrafluoroborate (7g). Creamy crystals (551.0 mg, 91%), mp 195–197 °C. ^1H NMR (400 MHz, CDCl_3) 9.70 (s, 1H, NH), 7.82–7.70 (m, 3H, Ph), 7.65–7.53 (m, 6H, Ph), 7.52–7.40 (m, 7H, aromatic), 7.12–7.01 (m, 1H, aromatic), 6.91–6.78 (m, 2H, aromatic), 6.77–6.68 (m, 1H, aromatic), 4.81–4.66 (m, 1H, C_αH), and aliphatics ($8\times\text{CH}_2$): 2.27–2.01 (m, 2H), 1.42–0.98 (m, 14H), and 0.82 (t, $J = 7.1$ Hz, 3H, CH_3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ aromatic carbons: 136.2, 135.3 (d, $J = 2.9$ Hz), 134.3 (d, $J = 8.9$ Hz), 130.4 (d, $J = 12.0$ Hz), 127.2 (d, $J = 4.4$ Hz), 126.6 (d, $J = 6.9$ Hz), 122.6, 120.1, 117.9 (d, $J = 82.0$ Hz), 117.5, 113.0, 103.4 (d, $J = 5.9$ Hz), 35.4 (d, $J = 44.8$ Hz, C_αH), 32.0 (br s, CH_2), 31.9 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 27.6 (d, $J = 13.6$ Hz), 22.7 (CH_2), and 14.2 (CH_3) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3) δ 21.9 ppm; IR (ATR) 3357, 2927, 2854, 1484, 1459, 1436, 1340, 1106, 1055, 1020, 995, 744, 720, and 691 cm^{-1} . HRMS (TOF-ESI) calcd. for $\text{C}_{36}\text{H}_{41}\text{NP}^+$ [M^+] 518.2977 found 518.2982.

1-(2,4-dimethoxyphenyl)phenylmethyltriphenylphosphonium tetrafluoroborate (7h) [30]. White crystals (357.4 mg, 62%), mp 209–211 °C (lit.: mp 199.5–200.5 °C [30]). ^1H NMR (400 MHz, CDCl_3) δ 7.84–7.75 (m, 3H), 7.67–7.58 (m, 8H), 7.51–7.40 (m, 6H), 7.32–7.19 (m, 1H), 7.14–7.07 (m, 2H), 7.02–6.95 (m, 1H), 6.52 (d, $J = 18.2$ Hz, 1H, C_αH), 6.44–6.40 (m, 2H), 3.80 (s, 3H, OCH_3), and 3.62 (s, 3H, OCH_3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ aromatic carbons: 161.8 (d, $J = 2.1$ Hz), 157.7 (d, $J = 6.5$ Hz), 135.1 (d, $J = 3.0$ Hz), 134.5 (d, $J = 9.0$ Hz), 132.5 (d, $J = 3.1$ Hz), 131.6 (d, $J = 6.1$ Hz), 130.4 (d, $J = 6.2$ Hz), 130.1 (d, $J = 12.2$ Hz), 129.2 (d, $J = 1.9$ Hz), 129.0 (d, $J = 2.8$ Hz), 118.3 (d, $J = 82.4$ Hz), 112.8 (d, $J = 3.5$ Hz), 105.5 (d, $J = 1.6$ Hz), 99.1 (d, $J = 1.6$ Hz), 55.6 (OCH_3), 55.5 (OCH_3), and 41.8 (d, $J = 45.5$ Hz, C_αH) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3) δ 22.0 ppm; IR (ATR) 3058, 1614, 1582, 1505, 1438, 1215, and 1035 cm^{-1} . The spectra reported here are in agreement with previously published data [30].

1-(naphthalen-1-yl)-1-(2,4,6-trimethoxyphenyl)methyltriphenylphosphonium tetrafluoroborate (7i). Resin (485.8 mg, 74%). ^1H NMR (400 MHz, CDCl_3) 7.90–7.76 (m, 3H, aromatic), 7.75–7.62 (m, 4H, aromatic), 7.60–7.39 (m, 13H, aromatic), 7.40–7.27 (m, 2H, aromatic), 7.19 (d, $J = 19.4$ Hz, 1H, C_αH), 6.08 (s, 2H, aromatic), 3.81 (s, 3H, OCH_3), and 3.44 (s, 6H, OCH_3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ aromatic carbons: 162.8 (d, $J = 1.8$ Hz), 158.6 (d, $J = 5.5$ Hz), 134.7 (d, $J = 3.1$ Hz), 134.5 (d, $J = 8.9$ Hz), 134.0, 131.4 (d, $J = 8.1$ Hz), 130.8 (d, $J = 6.4$ Hz), 129.9 (d, $J = 12.1$ Hz), 129.8, 129.3 (d, $J = 1.9$ Hz), 129.3, 127.1, 126.1, 124.8 (d, $J = 2.1$ Hz), 122.7, 120.3 (d, $J = 82.5$ Hz), 102.1 (d, $J = 3.6$ Hz), 91.5 (d, $J = 1.3$ Hz), 55.8 (OCH_3), 55.4 (OCH_3), and 37.7 (d, $J = 49.6$ Hz, C_αH) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3) δ 22.4 ppm; IR (ATR) 2940, 1604, 1587, 1458, 1207, 1149, 1097, 1049, 996, and 690 cm^{-1} . HRMS (TOF-ESI) calcd. for $\text{C}_{38}\text{H}_{34}\text{O}_3\text{P}^+$ [M^+] 569.2246 found 569.2252.

1-(H-indol-3-yl)-1-(naphthalen-1-yl)methyltriphenylphosphonium tetrafluoroborate (7j). Pink crystals (454.1 mg, 75%), mp 115–117 °C. ^1H NMR (400 MHz, CDCl_3) 9.81 (s, 1H, NH), 8.07–7.99

(m, 1H, aromatic), 7.87–7.75 (m, 2H, aromatic), 7.73–7.58 (m, 3H, aromatic), 7.54–7.35 (m, 15H, aromatic), 7.33–7.19 (m, 2H, aromatic), 7.07–6.95 (m, 3H, aromatic), 6.96 (d, $J = 17.2$ Hz, 1H, $C_{\alpha}H$), and 6.87–6.73 (m, 1H, aromatic) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ aromatic carbons: 136.1, 135.3 (d, $J = 3.0$ Hz), 134.8 (d, $J = 8.9$ Hz), 134.2, 131.2 (d, $J = 8.1$ Hz), 130.3 (d, $J = 12.0$ Hz), 130.1 (d, $J = 2.1$ Hz), 130.0 (d, $J = 1.8$ Hz), 129.5, 128.5 (d, $J = 7.1$ Hz), 128.4 (d, $J = 5.5$ Hz), 127.8, 126.7, 126.0 (d, $J = 6.4$ Hz), 125.1 (d, $J = 1.9$ Hz), 122.6, 122.2, 120.2, 118.5 (d, $J = 80.9$ Hz), 117.5, 113.0, 104.9 (d, $J = 4.8$ Hz), and 38.4 (d, $J = 47.1$ Hz, $C_{\alpha}H$) ppm; $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 19.6 ppm; IR (ATR) 3356, 3059, 1461, 1023, 997, 738, 719, and 690 cm^{-1} . HRMS (TOF-ESI) calcd. for $C_{37}H_{29}NP^+$ [M^+] 518.2038 found 518.2036.

1-(tiophen-2-yl)-1-(2,4,6-trimethoxyphenyl)methyltriphenylphosphonium (7k). White crystals (575.7 mg, 94%), mp 195–197 °C (decomposition). 1H NMR (400 MHz, $CDCl_3$) 7.83–7.76 (m, 3H, Ph), 7.66–7.58 (m, 6H, Ph), 7.39–7.29 (m, 6H, Ph), 7.24–7.19 (m, 1H, aromatic), 6.90–6.84 (m, 1H, aromatic), 6.84 (d, $J = 18.7$ Hz, 1H, $C_{\alpha}H$), 6.70 (br t, $J = 3.5$ Hz, 1H), 6.13 (s, 2H, aromatic), 3.86 (s, 3H, OCH_3), and 3.48 (br s, 6H, OCH_3) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ aromatic carbons: 163.2 (d, $J = 2.1$ Hz), 158.9 (br s), 135.1 (d, $J = 3.0$ Hz), 134.3 (d, $J = 8.8$ Hz), 134.1 (d, $J = 8.8$ Hz), 130.2 (d, $J = 12.2$ Hz), 129.8 (d, $J = 6.7$ Hz), 127.4 (d, $J = 4.1$ Hz), 127.1 (d, $J = 3.2$ Hz), 119.0 (d, $J = 82.5$ Hz), 101.8 (d, $J = 3.7$ Hz), 91.2, 55.9 (OCH_3), 55.5 (OCH_3), and 37.8 (d, $J = 49.2$ Hz, $C_{\alpha}H$) ppm; $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 21.9 ppm; IR (ATR) 3111, 2947, 1608, 1596, 1435, 1421, 1220, 1158, 1100, 1049, and 997 cm^{-1} . HRMS (TOF-ESI) calcd. for $C_{32}H_{30}O_3PS^+$ [M^+] 525.1653 found 525.1655.

1-(H-indol-3-yl)-1-(tiophen-2-yl)methyltriphenylphosphonium tetrafluoroborate (7l). Pink crystals (477.2 mg, 85%), mp 185–187 °C. 1H NMR (400 MHz, $CDCl_3$) 9.87 (s, 1H, NH), 7.81–7.71 (m, 3H, Ph), 7.60–7.51 (m, 7H, aromatic), 7.40–7.30 (m, 6H, Ph), 7.21–7.15 (m, 2H, aromatic), 7.15–7.08 (m, 1H, aromatic), 6.95–6.87 (m, 2H, aromatic), 6.86–6.82 (m, 1H, aromatic), 6.78–6.72 (m, 1H, aromatic), and 6.45 (d, $J = 16.4$ Hz, 1H, $C_{\alpha}H$) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ aromatic carbons: 135.9, 135.6 (d, $J = 2.9$ Hz), 134.8 (d, $J = 8.9$ Hz), 130.4 (d, $J = 12.1$ Hz), 127.8 (d, $J = 4.0$ Hz), 127.7 (d, $J = 3.2$ Hz), 127.5 (d, $J = 2.9$ Hz), 127.4 (d, $J = 2.7$ Hz), 126.4 (d, $J = 6.4$ Hz), 123.1, 120.5, 117.5 (d, $J = 82.0$ Hz), 117.5, 113.2, 104.4 (d, $J = 0.9$ Hz), 104.4 (d, $J = 1.7$ Hz), and 38.4 (d, $J = 47.5$ Hz, $C_{\alpha}H$) ppm; $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 19.9 ppm; IR (ATR) 3362, 3060, 1437, 1343, 1107, 1055, 996, and 688 cm^{-1} . HRMS (TOF-ESI) calcd. for $C_{31}H_{25}NPS^+$ [M^+] 474.1445 found 474.1437.

3.9. Reactions of 1-Hydroxyalkylphosphonium Salts with Amide-Type Substrates

To a solution of 1-hydroxyalkylphosphonium salt (1.0 mmol) in CH_3CN (1 cm^3) placed in a glass vial sealed with a screw-cap, an amide-type substrate (1 mmol) was added. The reaction was carried out under the conditions given in Scheme 4. Then, 1-(*N*-acylamino)alkylphosphonium salts **9** were precipitated using Et_2O .

1-(N-acetylamino)propyltriphenylphosphonium tetrafluoroborate (9a) [24]. White crystals (386.3 mg, 86%), mp 199–201 °C (lit.: mp 185–186 °C [24]). 1H NMR (400 MHz, $CDCl_3$) δ 7.87–7.76 (m, 4H, Ph + NH), 7.74–7.66 (m, 12H, Ph), 5.67 (dddd, $J = 12.0, 9.2, 7.7, 2.7$ Hz, 1H, $C_{\alpha}H$), 2.13–1.97 (m, 1H, CHH), 1.91 (d, $J = 1.2$ Hz, 3H, $CH_3C=O$), 1.86–1.70 (m, 1H, CHH), and 1.12 (td, $J = 7.2, 1.3$ Hz, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.6 (d, $J = 3.0$ Hz, $C=O$), aromatic carbons: 135.4 (d, $J = 3.0$ Hz), 134.3 (d, $J = 9.3$ Hz), 130.6 (d, $J = 12.3$ Hz), 117.2 (d, $J = 81.7$ Hz), 49.6 (d, $J = 53.4$ Hz, $C_{\alpha}H$), 25.2 (d, $J = 5.4$ Hz, CH_2), 22.3 ($CH_3C=O$), and 11.5 (d, $J = 14.1$ Hz, CH_3) ppm; $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ 26.3 ppm; IR (ATR) 3330, 1683, 1522, 1440, 1286, 1109, 1062, 1020, and 996 cm^{-1} . The spectra reported here are in agreement with previously published data [24].

1-(N-benzoylamino)propyltriphenylphosphonium tetrafluoroborate (9b) [24]. White crystals (383.5 mg, 75%), mp 197–198 °C (lit.: mp 198–199 °C [24]). 1H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, $J = 8.2, 2.5$ Hz, 1H, NH), 7.83–7.73 (m, 8H, Ph), 7.72–7.68 (m, 3H, Ph), 7.68–7.59 (m, 6H, Ph), 7.48–7.42 (m, 1H, Ph), 7.39–7.33 (m, 2H, Ph), 5.81 (dtd, $J = 11.5, 8.3, 3.0$ Hz,

1H, C α H), 2.54–2.37 (m, 1H, CHH), 1.89–1.77 (m, 1H, CHH), and 1.17 (td, $J = 7.2, 1.2$ Hz, 3H, CH₃) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 168.5 (d, $J = 2.3$ Hz, C=O), aromatic carbons: 134.9 (d, $J = 3.0$ Hz), 134.4 (d, $J = 9.4$ Hz), 132.3, 131.7, 130.1 (d, $J = 12.3$ Hz), 128.6, 127.4, 117.9 (d, $J = 81.7$ Hz), 51.4 (d, $J = 51.7$ Hz, C α H), 24.9 (d, $J = 5.2$ Hz, CH₂), and 11.7 (d, $J = 13.9$ Hz, CH₃) ppm; ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ 27.0 ppm; IR (ATR) 3357, 1670, 1508, 1483, 1438, 1111, 1070, 1030, and 996 cm⁻¹. The spectra reported here are in agreement with previously published data [24].

1-(*N*-benzyloxycarbonylamino)propyltriphenylphosphonium tetrafluoroborate (**9c**) [24]. White crystals (465.5 mg, 86%), mp 176–177 °C (lit.: mp 161–162 °C [24]). ¹H NMR (400 MHz, CDCl₃) δ 7.81–7.71 (m, 3H, Ph), 7.70–7.56 (m, 12H, Ph), 7.33–7.24 (m, 3H, Ph), 7.24–7.17 (m, 2H, Ph), 6.93 (d, $J = 9.1$ Hz, 1H, NH), 5.45–5.33 (m, 1H, C α H), 4.98, 4.89 (ABq, $J = 12.5$ Hz, 2H, CH₂), 2.28–2.14 (m, 1H, CHH), 1.83–1.70 (m, 1H, CHH), and 1.15 (td, $J = 7.2, 1.3$ Hz, 3H, CH₃) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 156.9 (d, $J = 2.9$ Hz, C=O), aromatic carbons: 136.1, 135.3 (d, $J = 2.9$ Hz), 134.3 (d, $J = 9.3$ Hz), 130.5 (d, $J = 12.3$ Hz), 128.6, 128.1, 128.0, 117.1 (d, $J = 81.2$ Hz), 67.4 (C_{CH₂}Ph), 52.7 (d, $J = 52.9$ Hz, C α H), 25.0 (d, $J = 6.2$ Hz, C_{CH₂}), and 11.5 (d, $J = 13.9$ Hz, CH₃) ppm; ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ 25.6 ppm; IR (ATR) 3334, 1712, 1519, 1439, 1227, 1110, 1063, 1035, 1009, and 995 cm⁻¹. The spectra reported here are in agreement with previously published data [24].

1-(2-Oxopyrrolidin-1-yl)propyltriphenylphosphonium tetrafluoroborate (**9d**) [24]. White crystals (366.0 mg, 77%), mp 189–191 °C (lit.: mp 186–188 °C [24]). ¹H NMR (400 MHz, CDCl₃) δ 7.91–7.80 (m, 3H, Ph), 7.79–7.65 (m, 12H, Ph), and 5.72 (ddd, $J = 12.4, 10.5, 3.1$ Hz, 1H, C α H), CH₂ groups: 3.57–3.42 (m, 1H), 3.32–3.17 (m, 1H), 2.48–2.28 (m, 1H), 2.27–2.09 (m, 2H), 1.98–1.80 (m, 3H), and 1.07 (td, $J = 7.2, 1.3$ Hz, 3H, CH₃) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 177.0 (d, $J = 2.3$ Hz, C=O), aromatic carbons: 135.6 (d, $J = 3.1$ Hz), 134.3 (d, $J = 9.7$ Hz), 130.8 (d, $J = 12.4$ Hz), 117.1 (d, $J = 81.4$ Hz), 53.3 (d, $J = 51.4$ Hz, C α H), 46.9 (CH₂N), 30.3 (CH₂), 22.8 (d, $J = 5.0$ Hz, CH₂), 18.6 (CH₂), and 11.5 (d, $J = 14.1$ Hz, CH₃) ppm; ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ 24.7 ppm; IR (ATR) 2880, 1692, 1509, 1438, 1405, 1271, 1109, 1047, 1035, and 997 cm⁻¹. The spectra reported here are in agreement with previously published data [24].

(*N*-Acetylamino)methyltriphenylphosphonium tetrafluoroborate (**9e**) [24,31]. White crystals (383.3 mg, 91%), mp 191–193 °C (lit.: mp 191–193 °C [24]). ¹H NMR (400 MHz, CDCl₃) δ 9.67 (t, $J = 6.2$ Hz, 1H, NH), 7.86–7.76 (m, 9H, Ph), 7.74–7.63 (m, 6H, Ph), 5.13 (dd, $J = 6.3, 2.9$ Hz, 2H, CH₂), and 1.89 (d, $J = 1.4$ Hz, 3H, CH₃) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 172.2 (d, $J = 1.4$ Hz, C=O), aromatic carbons: 135.3 (d, $J = 3.1$ Hz), 134.2 (d, $J = 9.8$ Hz), 130.3 (d, $J = 12.6$ Hz), 117.5 (d, $J = 83.9$ Hz), 37.6 (d, $J = 56.8$ Hz, CH₂), and 22.6 (CH₃) ppm; ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ 20.7 ppm; IR (ATR) 3356, 1671, 1508, 1483, 1437, 1111, 1071, 1030, and 996 cm⁻¹. The spectra reported here are in agreement with previously published data [24,31].

2-Carbamoyletyltriphenylphosphonium tetrafluoroborate (**10**) [24]. White crystals (315.9 mg, 75%), mp 145–147 °C (lit.: mp 146–148 °C [24]). ¹H NMR (400 MHz, CDCl₃) δ 7.85–7.64 (m, 15H, Ph), 6.98 (br s, 1H, NH), 5.33 (br s, 1H, NH), 3.49–3.41 (m, 2H, CH₂), and 2.85–2.78 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 171.3 (d, $J = 14.2$ Hz), 135.4 (d, $J = 3.0$ Hz), 133.5 (d, $J = 10.0$ Hz), 130.7 (d, $J = 12.7$ Hz), 117.5 (d, $J = 86.7$ Hz), 27.3 (d, $J = 2.9$ Hz), and 19.1 (d, $J = 56.0$ Hz); ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ 24.6; IR (ATR) 3422, 3198, 1669, 1441, 1025, and 996 cm⁻¹. The spectra reported here are in agreement with previously published data [24].

4. Conclusions

An efficient and convenient method for the preparation of 1-hydroxyalkylphosphonium salts was optimized and improved. This synthesis is based on the reaction of aldehydes

with triarylphosphonium salts in a stoichiometric ratio under mild conditions: r.t., 30 min, without chromatography. The properties of the compounds obtained were determined on the basis of almost 50 examples, which also helped identify factors affecting their stability in solutions. The selected products were isolated and purified by crystallization from CH₃CN/Et₂O or CH₂Cl₂/Et₂O and then reacted with aromatic systems (120 °C, 2 h) or amide-type substrates (amide/carbamate/lactam; 50 °C, 2 h). The two protocols, ‘step-by-step’ and ‘one-pot’, have been described and compared with each other. New products such as 1-arylalkylphosphonium salts and 1-(*N*-acylamino)alkylphosphonium salts were formed with good or very good yields.

This confirms the high reactivity of 1-hydroxyalkylphosphonium salts, which are not necessarily generated in situ.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules29010018/s1>, Supporting information includes apparatus for the synthesis; ¹H-, ¹³C-, ³¹P-NMR, IR, and MS spectra of all new compounds; comparison of in-house results with available literature data [24]; Table S1. Characteristic signals (¹H and ³¹P{¹H} NMR) for the identification of compounds 1o-x; Table S2. Comparison of yields in one-pot and step-by-step methodology for the reactions of 1-hydroxyalkylphosphonium salts 1 with the amide-type substrates.

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