An Efficient Synthesis of Novel α-Aminophosphonates Based on a Mannich-Type Reaction

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Phosphonate-substituted iminium salt **2** was used in Mannich reactions with various nucleophiles to obtain novel α-aminophosphonates. This straightforward and efficient methodology has a broad scope and provides highly functionalized Mannich bases (**4** and **8**). Furthermore, vinylic, aromatic and homoallylic α-aminophosphonates (**5**, **10** and **12**) were synthesized in good yields.

Introduction

α-Aminophosphonic acids and their diesters show a range of diverse biological activities. For example, their use as haptens of catalytic antibodies, potent antibiotics, enzyme inhibitors and herbicides have recently been reported.[1] They also serve as important surrogates for α-amino carboxylic acids yielding peptide isosters with altered isoelectric points and binding properties.[2] Thus, a large number of methods for the preparation of diverse α-aminophosphonates have been published since the first synthesis by Fields[3] in 1952: addition of imines to di- or trialkyl phosphite derivatives,[4] nucleophilic amination of α-hydroxyphosphonate derivatives,[5] electrophilic amination of α-alkylphosphonamides,[6] hydrogenation of dehydroaminophosphonate derivatives,[6c] aldol-type reactions of (isocyanomethyl)phosphonates with aldehydes,[7] hydrogenation of aziridinylphosphonate,[8] addition of phosphites to sulfimines[9] and catalyzed Mannich-type one-pot procedures.[10]

In the course of our studies on modern variants of the Mannich reaction we have disclosed highly diastereoselective methods for the aminoalkylation of activated carbonyl compounds, for example, enamines or imines, with various ternary iminium salts.[11] This strategy has been applied successfully to the direct aminoalkylation of ketones,[12] α-branched aldehydes,[13] electron-rich aromatic compounds[14] and vinylogous nucleophiles.[15]

Some examples of Mannich-type reactions involving phosphanes, phosphinates, phosphorus acids and phosphonates have previously been reported in the literature, but the reaction products are relatively simple and the reaction procedure cannot be employed with a variety of aldehydes and amines.[16] In a major extension of previous work, some efficient, catalyzed, three-component Mannich reactions involving di- or trialkyl phosphites have recently been developed.[10] Gross and Costisella have reported the synthesis of phosphonate-substituted iminium salts which were treated with various OH, NH, SH and PH acidic compounds and acetophenones.[17] In this paper we present a general approach towards the synthesis of highly substituted α-aminophosphonates in which these protocols and the methodologies developed in our group have been combined.

Results and Discussion

Aminoalkylation of Carbonyl Derivatives

The highly diastereoselective aminoalkylation of enamines and imines with ternary iminium salts, which provides *anti*-configured Mannich bases, has been the subject of previous work.[11] To extend this methodology to the synthesis of *C*-phosphoryl Mannich bases, **2** was allowed to react with a variety of enamines **3**.

The *C*-phosphoryl aldiminium salt **2** was synthesized from diethyl phosphonate and DMF dimethyl acetal as readily available starting materials (Scheme 1).[17a]

The aminoalkylation of enamines **3** was carried out under mild conditions[11a] to yield the desired α-aminophosphonates **4** in good yields (Scheme 2, Table 1). The reaction proceeded with very high diastereoselectivity as only one diastereoisomer was observed by NMR spectroscopy in this work. In accordance with our results from the aminoalkylation of enamines and imines with ternary iminium salts the products were assigned the *anti* configuration.[11] Mannich bases **4** easily eliminate the amino group to give substituted vinylphosphonates **5**. Analogous observations on the stability of **4** have also been made by Gross and Costisella in

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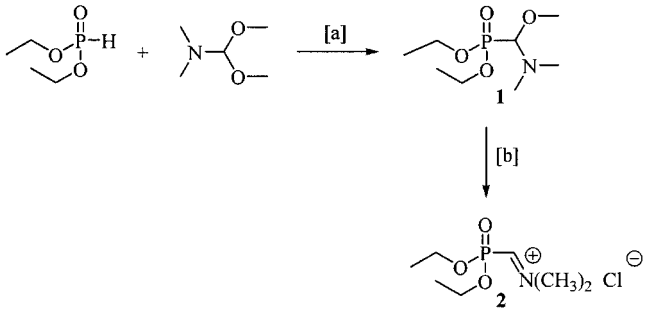
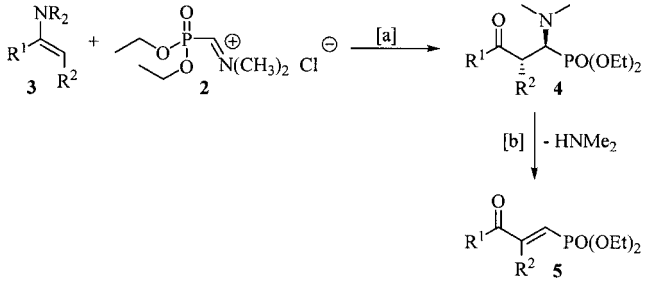
the reactions of **2** with various acetophenones.[17b] Because the amino group is easily eliminated, products **4** could not be purified by column chromatography.



Scheme 1. Synthesis of *C*-phosphoryl aldiminium salt **2**. Reagents and conditions: a. neat, room temperature; b. $SOCl_2$ in Et_2O, 0 °C, 30 min



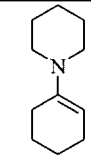
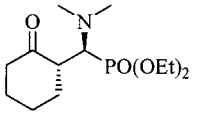
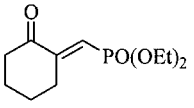
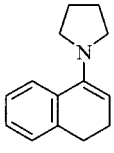
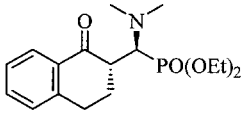
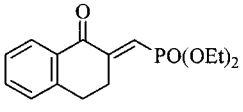
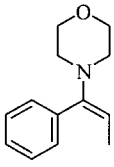
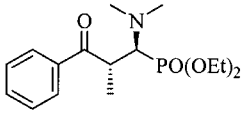
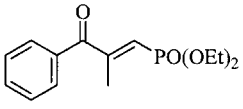
Scheme 2. Synthesis of α-aminophosphonates **4** and vinylphosphonates **5**. Reagents and conditions. a. i) CH_2Cl_2, −80 to −30 °C, 15 h; ii) aq. HCl; b. SiO_2, CH_2Cl_2, room temperature, 15 h

However, the systematic synthesis of novel substituted vinylphosphonates **5** could easily be performed under mild conditions by simply stirring a solution of **4** in dichloromethane in the presence of silica gel. Our studies on the SiO_2-catalyzed β-elimination of the amino group from various of Mannich bases have shown that *E*-configured double bonds are formed selectively starting from *anti*-configured Mannich bases.[18] By comparison of the spectroscopic data of the single isomer of **5** isolated after the elimination reaction with those of analogous Michael acceptors derived by the elimination reaction of Mannich bases[18] we can deduce that the double bond of **5** is *E*-configured. Furthermore, our assignment is supported by the $^3J_{C,P}$ coupling constants (20−25 Hz) which are characteristic of *trans*-configured structures. In general, the $^3J_{C,P}$ values of *trans* structures (18−30 Hz) are significantly larger than those of *cis* structures (6−13 Hz).[19]

The direct aminoalkylation of ketones was performed with highly reactive carboxylic-ester-substituted iminium salts as arylidene iminium salts do not react with ketones.[12] In order to explore the reactivity of the *C*-phosphoryl aldiminium salt, **2** was treated with ketones **6** at room temperature. Although the yields of the direct aminoalkylation of ketones **6** are comparable to the results of the aminoalkylation of enamines **3**, the diastereoselectivity of the reaction is significantly lower (*anti*/*syn* = 2:1).

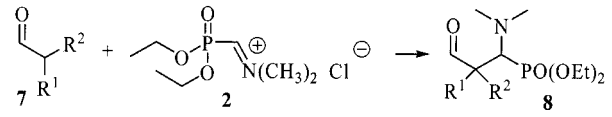
Recently, we disclosed that α-branched aldehydes **7** can also be aminoalkylated directly with carboxylic-ester-substituted iminium salts in good yields.[13] In contrast to Mannich bases derived from ketones, these products are not sensitive to β-elimination of the amino group. This strategy has been successfully employed in the synthesis of stable β-formyl-α-aminophosphonates **8** which have not been described in the literature before. By reacting iminium salt **2** with α-branched aldehydes **7** at room temperature products **8** have been isolated in good yields (Scheme 3, Table 2). However, the diastereoselectivity of this reaction is very low. If unsymmetrically substituted aldehydes **7** were used, a

Table 1. Synthesis of α-aminophosphonates **4** and vinylphosphonates **5**

Entry	Enamine **3**	Mannich base **4**	Vinylphosphonate **5**	Yield [%][a]
a				**4a**: 55 **5a**: 99
b				**4b**: 49 **5b**: 75
c				**4c**: 53 **5c**: 35[b]

[a] Yield of crude product. [b] SiO_2, CH_2Cl_2, reflux, 15 h.

mixture of the two diastereoisomers (*anti*/*syn* = 1:1) was obtained.



Scheme 3. Synthesis of α-amino-β-formylphosphonates **8**. Reagents and conditions: CH_2Cl_2, room temperature, 15 h

Table 2. Synthesis of α-amino-β-formylphosphonates **8**

Entry	R^1	R^2	Yield [%][a]
8a	Me	Me	49
8b	Me	Et	48
8c	Me	Ph	61
8d	Et	Bu	35
8e		$-(CH_2)_5-$	46

[a] Isolated yield after flash column chromatography on silica.

The results obtained have allowed us to conclude that the iminium salt **2** is much more reactive than ternary iminium salts since ketones **6** and aldehydes **7** have been aminoalkylated directly. On the other hand, the yields in these cases have been found to be significantly lower than those of Mannich reactions in which highly reactive carboxylic-ester-substituted iminium salts were used.[12,13] The results also clearly indicate that the direct aminoalkylation of ketones **6** and aldehydes **7** with *C*-phosphoryl aldiminium salt **2** occurs by a different mechanism to the highly diastereoselective polar [2s + 2s] cycloaddition mechanism which has been proposed for the aminoalkylation of enamines and imines.[11]

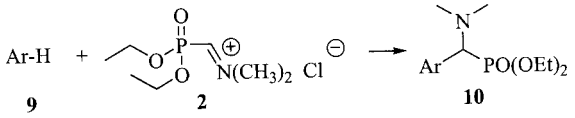
Our results from the aminoalkylation of β-enaminonitriles with **2**, as a part of our investigations into the vinylogous Mannich reaction that yields highly substituted nicotinonitriles, have already been published elsewhere.[15b]

Aminoalkylation of Electron-Rich Aromatic Compounds

Non-proteinogenic α-aryl-α-amino acids are interesting building blocks in the synthesis of biologically active compounds and therefore various synthetic routes to this attractive class of substance have been published.[20]

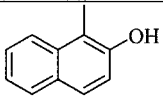
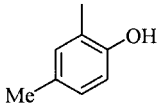
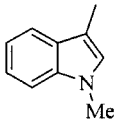
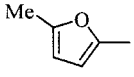
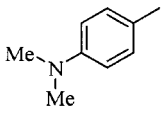
As a part of our investigations into modern variants of the Mannich reaction we have developed an efficient and inexpensive synthetic route that yields aromatic α-amino acids in a one-pot reaction sequence.[12b] It has been our goal to apply the knowledge we gained from the aminoalkylation of carbonyl derivatives with **2** to the aminoalkylation of aromatic compounds as aromatic α-aminophosphonates have been reported to have potent biological activities (e.g. the protection of endothelium, anti-atherosclerosis and anti-thrombosis).[1k] The auto-catalyzed Mannich reaction published by Yang et al. yields a variety of highly substituted aromatic α-aminophosphonates in moderate-to-excellent yields.[10b] However, this method is of limited scope as only phenolic benzaldehyde derivatives can be employed. In a major extension to previous work,[12,14] we describe herein the direct aminoalkylation of electron-rich aromatic compounds **9** with iminium salt **2** under mild conditions.

We started our studies by using β-naphthol (**9a**) and *N*-methylindole (**9c**) as these nucleophilic aromatic compounds are known to be standards in aminoalkylation reactions.[21] The optimized reaction conditions involved refluxing the reagents in THF to give the highest yields of novel α-amino-α-arylphosphonates **10** (Scheme 4). This procedure was also employed successfully in the aminoalkylation of other less nucleophilic aromatic compounds **10**. The results are summarized in Table 3.



Scheme 4. Synthesis of aromatic α-aminophosphonates **10**. Reagents and conditions: THF, reflux, 3 h

Table 3. Synthesis of aromatic α-aminophosphonates **10**

Entry	Ar-	Yield [%][a]
10a		51
10b		57
10c		43
10d		59
10e		63
10f		55[b]

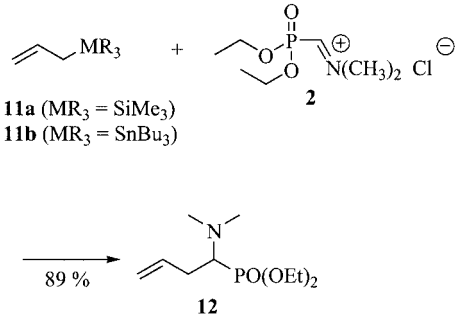
[a] Isolated yield after flash column chromatography on silica. [b] Obtained as the hydrochloride.

In the case of phenolic derivatives **9a**,**b**, equimolecular amounts of NEt_3 were added to increase the concentration of phenolate ions.[14] A regioselective *ortho*-aminoalkylation of phenols with respect to the hydroxy group was also observed. In contrast to earlier studies on Friedel–Crafts reactions of electron-rich aromatic compounds by Heaney

and co-workers,[22] *N*-methylindole **9c** was selectively monoaminoalkylated by **2** at the C-3 position. Both observations are in accordance with our results on analogous Mannich-type reactions with ternary iminium salts.[12,14]

Aminoalkylation of Allylic Derivatives

In the course of our studies on the aminoalkylation of various types of nucleophiles, organoallylic compounds **11** were also treated with *C*-phosphoryl aldiminium salt **2**. We found both silicon (**11a**) and tin derivatives (**11b**) to be versatile building blocks in the synthesis of novel homoallylic α-aminophosphonates **12** (Scheme 5).



Scheme 5. Synthesis of homoallylic α-aminophosphonate **12**. Reagents and conditions: CH_2Cl_2, room temperature, 15 h

This new type of α-aminophosphonate **12** has not been described in the literature before. The development of new synthetic strategies towards non-proteinogenic unsaturated α-amino acids remains active since they are important building blocks in the synthesis of biologically active compounds.[19] Our first examples of these α-amino acid surrogates **12** show that our protocol facilitates a general and straightforward access to this promising class of homoallylic derivative.

Conclusions

In summary, the aminoalkylation of ketones **6** and α-branched aldehydes **7** with iminium salt **2** gives phosphonate-substituted Mannich bases **4** and **8** which have not been described in the literature before. In addition, the reaction can be carried out with high diastereoselectivity if enamines **3** are used instead of ketones **6**. SiO_2-catalyzed elimination of the amino group selectively yields *E*-configured vinylphosphonates **5**. The reaction of phenols and *N*- and *O*-heteroaromatics with **2** provides a simple and straightforward route to novel aromatic α-aminophosphonates **10**. These Mannich-type reactions with preformed iminium salt **2** can also be successfully applied to the synthesis of homoallyl aminophosphonates **12** by aminoalkylation of allylsilanes (**11a**) and -stannanes (**11b**). Furthermore, this strategy has good prospects as it can be extended to other nucleophiles, such as organometallic compounds, nitro or nitrile derivatives. Based on our results, in particular, on the formation of racemic α-aminophosphonates, we also expect our method to be suitable for enantioselective syntheses by employing chiral-modified *C*-phosphoryl aldiminium salts.

Experimental Section

General Remarks: All reagents were purchased from commercial sources and used without further purification unless specified. All solvents were dried and distilled according to standard procedures and stored under argon. All reactions were conducted under argon. Enamines **3** were prepared according to literature procedures.[23] Chromatographic separation was performed on silica gel 60 (Merck, 0.040−0.063 mm). Melting points were obtained on a Büchi SMP-20 melting point apparatus and are uncorrected. IR spectra were measured on a Nicolet 510 P FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker ARX 200 spectrometer (200 MHz and 50 MHz, for ^1H and ^{13}C, respectively); chemical shifts are reported relative to TMS as the internal reference. ^{31}P NMR spectra were measured with a Bruker AMX 300 instrument with H_3PO_4 as the internal reference. Mass spectra were recorded using a Finnigan MAT 8230 apparatus; GC/MS spectra were recorded with a Finnigan MAT Magnum System 240 instrument. Elemental analyses were obtained with a Perkin−Elmer M240 analyzer.

Diethyl (Dimethylamino)(methoxy)methylphosphonate (1): A stirred mixture of DMF dimethyl acetal (11.9 g, 0.1 mol) and diethyl phosphonate (13.8 g, 0.1 mol) was cooled occasionally in a water bath to keep the temperature below 30 °C. The reaction was finished when a constant refraction index was observed (n_D^{22} = 1.4181). The crude product was then purified by kugelrohr distillation to give 16.4 g (73%) of **1** as a colorless liquid, b.p. 86−88 °C/0.5 mbar (ref.[17a] 66%, b.p. 65 °C/0.02 Torr). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.18−1.29 (m, 6 H), 2.48 (s, 6 H), 3.33 (s, 3 H), 3.96−4.12 (m, 5 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.8 (q, $^3J_{C,P}$ = 5 Hz), 41.0 (q, $^3J_{C,P}$ = 6 Hz), 59.3 (q, $^3J_{C,P}$ = 13 Hz), 62.6 (t, $^2J_{C,P}$ = 17 Hz), 94.1 (d, $^1J_{C,P}$ = 195 Hz) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 3.67 (s) ppm.

Diethyl Dimethyliminiomethylphosphonate Chloride (2): Freshly distilled thionyl chloride (2.38 g, 20 mmol) was added dropwise at 0 °C to a solution of **1** (4.50 g, 20 mmol) in abs. diethyl ether (25 mL). After 30 min the solvent was decanted and the oily precipitate was washed with abs. diethyl ether (3 × 10 mL). The product was dried in vacuo to give 4.36 g (95%) of **2** as a yellow oil (ref.[17a] 92%). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.21−1.27 (m, 6 H), 2.79 (br, 6 H), 4.21−4.28 (m, 4 H), 6.48 (br, 1 H) ppm.

General Procedure for the Aminoalkylation of Enamines (3): A solution of **2** (0.57 g, 2.5 mmol) in abs. CH_2Cl_2 (10 mL) was cooled to −80 °C. Enamine **3** (2.5 mmol) was added dropwise whilst stirring. The temperature was then allowed to rise slowly to −30 °C over a period of 2−3 h. The reaction mixture was stored at this temperature in a refrigerator for 15 h. Then the mixture was quenched with 6 M HCl (5 mL) and the aqueous layer was washed with Et_2O (3 × 50 mL). The aqueous layer was basified by the addition of aqueous saturated $NaHCO_3$ solution and 2 M NaOH to pH 8−9. The product was extracted with CH_2Cl_2 (3 × 50 mL), the combined organic layers were dried (Na_2SO_4) and the solvent was removed in vacuo.

Diethyl (Dimethylamino)(2-oxocyclohexyl)methylphosphonate (4a): Yield: 306 mg (42%); yellow-brown oil. IR (film): $\tilde{\nu}$ = 2933, 2868, 2796, 1712, 1452, 1390, 1246, 1163, 1053, 1026, 960, 795, 733 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.24 (dt, ^3J = 7.0, $^4J_{H,P}$ =

2.3 Hz, 6 H), 1.46−2.02 (m, 8 H), 2.40 (d, $^4J_{H,P}$ = 2.3 Hz, 6 H), 3.48 (dd, ^3J = 9.8, $^2J_{H,P}$ = 15.9 Hz, 1 H), 3.62−3.79 (m, 1 H), 3.91−4.19 (m, 4 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.8 (q, $^3J_{C,P}$ = 4.7 Hz), 22.7, 28.3, 30.4, 40.5 (q), 42.5 (q, $^3J_{C,P}$ = 2.8 Hz), 50.5 (d, $^2J_{C,P}$ = 9.0 Hz), 60.7 (d, $^1J_{C,P}$ = 136.3 Hz), 61.3 (t, $^2J_{C,P}$ = 7.5 Hz), 211.4 (s, $^3J_{C,P}$ = 13.5 Hz) ppm.

Diethyl (Dimethylamino)(1,2,3,4-tetrahydro-1-oxonaphthalen-2-yl)-methylphosphonate (4b): Yield: 568 mg (67%); yellow oil. IR (film): $\tilde{\nu}$ = 2983, 2939, 2871, 2796, 1680, 1599, 1456, 1392, 1284, 1238, 1163, 1024, 966, 796, 741 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.04−1.15 (m, 2 H), 1.29 (dt, ^3J = 7.1, $^4J_{H,P}$ = 1.5 Hz, 6 H), 2.43 (s, 6 H), 2.78−3.00 (m, 2 H), 3.92−4.02 (m, 2 H), 4.03−4.22 (m, 4 H), 7.13−7.28 (m, 2 H), 7.34−7.45 (m, 1 H), 7.88−7.96 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.7 (q, $^3J_{C,P}$ = 5.9 Hz), 27.4 (t, $^3J_{C,P}$ = 3.9 Hz), 28.6 (t), 43.6 (q, $^3J_{C,P}$ = 6.9 Hz), 45.3 (d, $^2J_{C,P}$ = 9.4 Hz), 60.3 (d, $^1J_{C,P}$ = 154.6 Hz), 61.3 (t, $^2J_{C,P}$ = 7.4 Hz), 126.9, 128.0, 129.0 (d), 132.6 (s), 133.5 (d), 143.8 (s), 198.0 (s, $^3J_{C,P}$ = 5.9 Hz) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 23.6 (s) ppm. MS (EI, 80 eV): *m/z* (%) = 340 (7) [M$^+$ + 1], 295 (9), 266 (2), 249 (2), 220 (2), 202 (100), 194 (7), 157 (3), 128 (10), 115 (5), 84 (13), 74 (4). $C_{17}H_{26}NO_4P$ (339.37): calcd. C 60.17, H 7.72, N 4.13; found C 60.26, H 7.81, N 4.04.

Diethyl 1-(Dimethylamino)-2-methyl-3-oxo-3-phenylpropylphosphonate (4c): Yield: 565 mg (69%); yellow oil. IR (film): $\tilde{\nu}$ = 2981, 2935, 2873, 2840, 2798, 2233, 1681, 1645, 1597, 1448, 1392, 1238, 1163, 1045, 1022, 970, 793, 706, 582 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.20 (d, $^4J_{H,P}$ = 6.5 Hz, 3 H), 1.31 (dt, ^3J = 6.8, $^4J_{H,P}$ = 1.2 Hz, 6 H), 2.34 (d, $^4J_{H,P}$ = 2.3 Hz, 6 H), 3.45 (dd, ^3J = 10.4, $^4J_{H,P}$ = 13.1 Hz, 1 H), 3.56−4.01 (m, 1 H), 4.02−4.24 (m, 4 H), 7.28−7.55 (m, 3 H), 7.86−7.98 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.8 (q), 16.8 (q, $^3J_{C,P}$ = 6.4 Hz), 40.9 (d, $^2J_{C,P}$ = 11.3 Hz), 42.6 (q, $^3J_{C,P}$ = 2.0 Hz), 61.3 (t, $^2J_{C,P}$ = 7.9 Hz), 64.9 (d, $^1J_{C,P}$ = 133.9 Hz), 128.4, 129.0, 133.2 (d), 137.3 (s, $^4J_{C,P}$ = 3.5 Hz), 203.4 (s, $^3J_{C,P}$ = 16.2 Hz) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 27.6 (s) ppm. MS (EI, 80 eV): *m/z* (%) = 327 (2) [M$^+$], 190 (100), 166 (2), 138 (4), 105 (54), 84 (11), 77 (12), 70 (6). $C_{16}H_{26}NO_4P$ (327.36): calcd.: C 58.70, H 8.01, N 4.28; found: C 58.62, H 8.09, N 4.36.

General Procedure for the Aminoalkylation of Ketones 6 and α-Branched Aldehydes 7: Ketones **6** or aldehydes **7** (2.5 mmol) were added to a solution of **2** (0.57 g, 2.5 mmol) in abs. CH_2Cl_2 (10 mL) at ambient temperature. After a reaction time of 15 h the mixture was quenched with 6 M HCl (5 mL) and the aqueous layer was washed with Et_2O several times. The aqueous layer was basified by the addition of aqueous saturated $NaHCO_3$ solution and 2 M NaOH to pH 8−9. The product was extracted with CH_2Cl_2, the combined organic layers were dried (Na_2SO_4) and the solvent was removed in vacuo.

Diethyl 1-(Dimethylamino)-2-formyl-2-methylpropylphosphonate (8a): Yield: 325 mg (49%); yellow oil. IR (film): $\tilde{\nu}$ = 2978, 2933, 2873, 2840, 2800, 1728, 1454, 1390, 1242, 1163, 1047, 962, 800, 582 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.12 (s, 3 H), 1.20 (s, 3 H), 1.26 (dt, ^3J = 6.9, $^4J_{H,P}$ = 2.7 Hz, 6 H), 2.46 (d, $^4J_{H,P}$ = 2.1 Hz, 6 H), 3.12 (d, $^2J_{H,P}$ = 21.9 Hz, 1 H), 3.97−4.13 (m, 4 H), 9.38 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.8 (q, $^3J_{C,P}$ = 6.0 Hz), 20.1, 21.5 (q, $^3J_{C,P}$ = 4.9 Hz), 45.0 (q, $^3J_{C,P}$ = 2.8 Hz), 50.9 (q, $^2J_{C,P}$ = 12.1 Hz), 61.6 (t, $^2J_{C,P}$ = 7.3 Hz), 66.8 (d, $^1J_{C,P}$ = 134.0 Hz), 203.8 (d, $^3J_{C,P}$ = 11.1 Hz) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 25.9 (s) ppm. MS (EI, 80 eV): *m/z* (%) = 265 (12) [M$^+$], 194 (34), 128 (100), 100 (18), 84 (8), 58 (3), 42 (4). $C_{11}H_{24}NO_4P$ (265.29): calcd.: C 49.80, H 9.12, N 5.28; found: C 49.76, H 9.15, N 5.33.

Diethyl 1-(Dimethylamino)-2-formyl-2-methylbutylphosphonate (8b): Yield: 353 mg (48%); yellow oil. Two diastereoisomers (71:29, * minor diastereoisomer). IR (film): $\tilde{\nu}$ = 2983, 2939, 2802, 1722, 1641, 1444, 1392, 1230, 1163, 1039, 970, 750, 539 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.54−0.71 (m, 3 H), 1.05−1.32 (m, 9 H), 1.49−1.73 (m, 2 H), 2.35 (s, 6 H), 3.01−3.24 (m, 1 H), 3.90−4.17 (m, 4 H), 9.27, 9.34* (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.5 (q), 15.4 (q), 16.8 (q, $^3J_{C,P}$ = 6.4 Hz), 28.2 (t, $^3J_{C,P}$ = 2.0 Hz), 44.8 (q, $^3J_{C,P}$ = 1.5 Hz), 45.0* (q, $^3J_{C,P}$ = 2.9 Hz), 54.1 (s, $^2J_{C,P}$ = 11.8 Hz), 61.50 (t, $^2J_{C,P}$ = 7.9 Hz), 66.8* (d, $^1J_{C,P}$ = 135.4 Hz), 67.0 (d, $^1J_{C,P}$ = 130.9 Hz), 203.4* (d, $^3J_{C,P}$ = 15.8 Hz), 203.5 (d, $^3J_{C,P}$ = 14.8 Hz) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 19.1 (s) ppm. MS (EI, 80 eV): *m/z* (%) = 279 (8) [M$^+$], 194 (47), 166 (2), 142 (100), 114 (21), 98 (13), 84 (4), 68 (2). $C_{12}H_{26}NO_4P$ (279.31): calcd.: C 51.60, H 9.38, N 5.01; found: C 51.68, H 9.31, N 4.96.

Diethyl 1-(Dimethylamino)-2-formyl-2-phenylpropylphosphonate (8c): Yield: 498 mg (61%); yellow oil. IR (film): $\tilde{\nu}$ = 2987, 2939, 1655, 1637, 1629, 1446, 1392, 1230, 1028, 977, 762, 702 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.24−1.42 (m, 6 H), 1.79 (d, $^4J_{H,P}$ = 2.3 Hz, 3 H), 2.57 (d, $^4J_{H,P}$ = 1.8 Hz, 6 H), 3.74−3.93 (m, 1 H), 3.95−4.25 (m, 4 H), 7.09−7.53 (m, 5 H), 9.45 (d, $^4J_{H,P}$ = 3.3 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.4 (q, $^3J_{C,P}$ = 5.9 Hz), 16.7 (q, $^3J_{C,P}$ = 5.4 Hz), 45.5 (q, $^3J_{C,P}$ = 3.0 Hz), 57.7 (s, $^2J_{C,P}$ = 13.8 Hz), 62.9 (t, $^2J_{C,P}$ = 15.3 Hz), 67.3 (d, $^1J_{C,P}$ = 134.9 Hz), 127.7, 127.8, 128.3, 128.6, 128.8, 129.2, 129.4 (d), 137.9 (s), 199.9 (d, $^3J_{C,P}$ = 18.2 Hz) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 19.1 (s) ppm. MS (EI, 80 eV): *m/z* (%) = 327 (4) [M$^+$], 300 (100), 288 (39), 261 (28), 233 (10), 208 (13), 180 (26), 152 (30), 136 (18), 124 (20), 109 (11), 91 (9), 81 (19), 65 (30), 60 (21). $C_{16}H_{26}NO_4P$ (327.36): calcd.: C 58.70, H 8.01, N 4.28; found: C 58.59, H 7.89, N 4.18.

Diethyl 1-(Dimethylamino)-2-ethyl-2-formylhexylphosphonate (8d): Yield: 282 mg (35%); yellow oil. Two diastereoisomers (54:46, *minor diastereoisomer). IR (film): $\tilde{\nu}$ = 2985, 2937, 2875, 2802, 1711, 1643, 1477, 1444, 1392, 1230, 1163, 1038, 1163, 1038, 975, 731 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.63−0.90 (m, 8 H), 1.02−1.39 (m, 8 H), 1.47−2.05 (m, 4 H), 2.38 (s, 6 H), 2.95 (d, $^2J_{H,P}$ = 22.2 Hz, 1 H), 2.96* (d, $^2J_{H,P}$ = 24.0 Hz, 1 H), 3.98−4.22 (m, 4 H), 9.78*, 9.81 (d, $^4J_{H,P}$ = 2.3 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 7.9*, 8.6, 14.2*, 14.4 (q), 16.7 (q, $^3J_{C,P}$ = 3.0 Hz), 21.3, 22.8*, 23.6*, 23.7, 25.5*, 26.1, 29.4 (t), 44.5 (q, $^3J_{C,P}$ = 4.9 Hz), 57.8, 57.9* (s, $^2J_{C,P}$ = 12.3 Hz), 61.5 (t, $^2J_{C,P}$ = 7.4 Hz), 66.6, 66.9* (d, $^1J_{C,P}$ = 130.4 Hz), 206.2 (d, $^3J_{C,P}$ = 6.4 Hz), 206.3* (d, $^3J_{C,P}$ = 7.4 Hz) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 19.1 (s) ppm. MS (EI, 80 eV): *m/z* (%) = 322 (3) [M$^+$ + 1], 249 (3), 194 (71), 184 (100), 166 (10), 156 (26), 138 (13), 120 (5), 112 (14), 98 (8), 84 (7). $C_{15}H_{32}NO_4P$ (321.39): calcd.: C 56.06, H 10.04, N 4.36; found: C 55.98, H 10.14, N 4.29.

Diethyl (Dimethylamino)(1-formylcyclohexyl)methylphosphonate (8e): Yield: 351 mg (46%); yellow oil. IR (film): $\tilde{\nu}$ = 2933, 2868, 2796, 1712, 1452, 1390, 1246, 1163, 1053, 1026, 960, 795, 733 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.29 (dt, ^3J = 7.1, $^4J_{H,P}$ = 2.5 Hz, 6 H), 1.45−1.91 (m, 6 H), 1.92−2.20 (m, 4 H), 2.46 (s, 6 H), 2.96 (d, $^2J_{H,P}$ = 21.9 Hz, 1 H), 3.99−4.28 (m, 4 H), 9.55 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.8 (q), 23.0, 23.2, 25.6 (t), 29.5 (t, $^3J_{C,P}$ = 3.9 Hz), 30.0 (t, $^3J_{C,P}$ = 3.4 Hz), 44.5 (q, $^3J_{C,P}$ = 4.4 Hz), 54.6 (s, $^2J_{C,P}$ = 12.3 Hz), 61.7 (t), 68.8 (d, $^1J_{C,P}$ = 128.0 Hz), 205.6 (d, $^3J_{C,P}$ = 7.9 Hz) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 19.2 (s) ppm. MS (EI, 80 eV): *m/z* (%) = 306 (5) [M$^+$ + 1], 194 (77), 168 (100), 140 (10), 125 (5), 110 (5), 84 (3).

$C_{14}H_{28}NO_4P$ (305.35): calcd.: C 55.07, H 9.24, N 4.59; found: C 55.01, H 9.32, N 4.68.

General Procedure for the SiO_2-Catalyzed β-Elimination in Mannich Bases (4): Silica gel (0.5 g) was added to a solution of **4** (2.5 mmol) in abs. CH_2Cl_2 (20 mL) which was then stirred for 15 h at room temperature. The silica gel was filtered off and washed with CH_2Cl_2 (2 × 15 mL) and methanol (10 mL). The combined organic phases were evaporated to give vinylphosphonates **5** which could be purified by flash column chromatography (SiO_2) by using CH_2Cl_2 as eluent.

Diethyl (*E*)-(2-Oxocyclohexylidene)methylphosphonate (5a): Yield: 609 mg (99%); yellow oil, after flash column chromatography. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.09−1.22 (m, 6 H), 1.71−2.01 (m, 4 H), 2.40−2.70 (m, 4 H), 3.86−4.26 (m, 4 H), 6.32 (d, $^2J_{H,P}$ = 19.5 Hz, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.7 (q, $^3J_{C,P}$ = 6 Hz), 24.0 (t), 30.5 (t, $^4J_{C,P}$ = 6 Hz), 34.3 (t), 41.2 (t, $^4J_{C,P}$ = 3 Hz), 62.2 (t, $^2J_{C,P}$ = 6 Hz), 120.2 (d, $^1J_{C,P}$ = 185 Hz), 155.4 (s, $^2J_{C,P}$ = 8 Hz), 200.5 (s, $^3J_{C,P}$ = 22 Hz) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 16.36 ppm. $C_{11}H_{19}O_4P$ (246.24): calcd.: C 53.65, H 7.78; found: C 54.01, H 7.66.

Diethyl (*E*)-(3,4-Dihydro-1-oxonaphthalen-2(1*H*)-ylidene)methylphosphonate (5b): Yield: 552 mg (75%); yellow oil, after flash column chromatography. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.12−1.45 (m, 6 H), 2.36−2.62 (m, 2 H), 2.88−3.19 (m, 2 H), 3.92−4.55 (m, 4 H), 6.78 (d, $^2J_{H,P}$ = 17.2 Hz, 1 H), 7.13−7.62 (m, 3 H), 7.90−8.05 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.8 (q, $^3J_{C,P}$ = 6 Hz), 29.1 (t), 29.2 (t), 62.4 (t, $^2J_{C,P}$ = 6 Hz), 121.6 (d, $^1J_{C,P}$ = 186 Hz), 127.7 (d), 128.9 (d), 132.7 (s), 134.5 (d), 144.6 (s), 153.7 (s, $^2J_{C,P}$ = 9 Hz), 186.4 (s, $^3J_{C,P}$ = 22 Hz) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 16.72 ppm. $C_{15}H_{19}O_4P$ (294.28): calcd.: C 61.22, H 6.51; found: C 61.29, H 6.65.

Diethyl (*E*)-2-Methyl-3-oxo-3-phenylprop-1-enylphosphonate (5c): Yield: 247 mg (35%); yellow oil, after flash column chromatography. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.22−1.36 (m, 6 H), 2.63 (s, 3 H), 4.06−4.17 (m, 4 H), 6.02 (d, $^2J_{H,P}$ = 20.3 Hz, 1 H), 7.41−7.58 (m, 3 H), 7.82−7.91 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.4 (q, $^3J_{C,P}$ = 6 Hz), 35.4 (q), 62.0 (t, $^2J_{C,P}$ = 6 Hz), 123.4 (d, $^1J_{C,P}$ = 183 Hz), 128.7 (d), 129.2 (d), 133.3 (d), 135.5 (s), 155.2 (s, $^2J_{C,P}$ = 5 Hz), 197.5 (s, $^3J_{C,P}$ = 23 Hz) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 16.51 ppm. $C_{14}H_{19}O_4P$ (282.27): calcd.: C 59.57, H 6.78; found: C 59.49, H 6.71.

General Procedure for the Aminoalkylation of Electron-Rich Aromatic Compounds: A solution of **2** (2.5 mmol) in abs. THF (5 mL) was added to a stirred solution of **9** (2.5 mmol) in abs. THF (25 mL). With the phenolic aromatic compounds, NEt_3 (2.5 mmol) was added to deprotonate the OH group before adding the iminium salt. The reaction mixture was then refluxed for 3 h and 2 M HCl (5 mL) was added after cooling. Extraction with diethyl ether (3 × 10 mL) was carried out to remove all nonbasic impurities. The aqueous phase was made basic by the addition of aqueous NH_3 (25 mL, conc. NH_3/H_2O 1:4) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. The crude products could be purified by flash column chromatography (SiO_2) using CH_2Cl_2/hexanes (1:1) as eluent.

Diethyl (Dimethylamino)(2-hydroxynaphthalen-1-yl)methylphosphonate (10a): Yield: 430 mg (51%); yellow oil, after flash column chromatography. IR (film): $\tilde{\nu}$ = 3609, 3290, 2988, 2451, 2187, 1717, 1551, 1465, 1369, 1227, 1037, 951, 699, 521 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.14−1.33 (m, 6 H), 2.43 (s, 6 H), 3.99−4.45 (m, 5 H), 7.16 (d, ^3J = 8.7 Hz, 1 H), 7.29−7.34 (m, 2 H), 7.43−7.59 (m, 1 H), 7.69−7.87 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.9 (q, $^3J_{C,P}$ = 11 Hz), 44.7 (q, $^3J_{C,P}$ = 12 Hz), 55.6 (d, $^1J_{C,P}$ = 187 Hz), 62.9 (t, $^2J_{C,P}$ = 15 Hz), 111.3 (s), 119.6 (d), 121.4 (d), 122.8 (d), 126.8 (d), 128.8 (s), 129.3 (d), 129.9 (d), 133.1 (s), 157.1 (s) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 19.72 (s) ppm. $C_{17}H_{24}NO_4P$ (337.35): calcd.: C 60.53, H 7.17, N 4.15; found: C 60.41, H 7.25, N 4.33.

Diethyl (Dimethylamino)(2-hydroxy-5-methylphenyl)methylphosphonate (10b): Yield: 429 mg (57%); yellow oil, after flash column chromatography. IR (film): $\tilde{\nu}$ = 3615, 3277, 2976, 2458, 2178, 1709, 1546, 1471, 1322, 1251, 1066, 934, 705 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.12−1.29 (m, 6 H), 2.24 (s, 3 H), 2.47 (s, 6 H), 3.94−4.37 (m, 5 H), 6.68 (d, ^3J = 8 Hz, 1 H), 6.91 (s, 1 H), 6.98−7.08 (m, 1 H), 9.69 (br. s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.8 (q, $^3J_{C,P}$ = 11 Hz), 20.9 (q), 44.1 (q, $^3J_{C,P}$ = 13 Hz), 55.9 (d, $^1J_{C,P}$ = 191 Hz), 63.2 (t, $^2J_{C,P}$ = 16 Hz), 117.4 (d), 118.5 (s), 129.1 (s), 130.3 (d), 131.1 (d), 155.0 (s) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 19.72 (s) ppm. $C_{17}H_{24}NO_4P$ (337.35): calcd.: C 60.53, H 7.17, N 4.15; found: C 60.41, H 7.25, N 4.33.

Diethyl (Dimethylamino)(1-methyl-1*H*-indol-3-yl)methylphosphonate (10c): Yield: 348 mg (43%); yellow oil, after flash column chromatography. IR (film): $\tilde{\nu}$ = 3488, 2979, 2933, 2462, 2225, 1660, 1536, 1471, 1369, 1241, 1025, 966, 746, 539 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.14−1.33 (m, 6 H), 2.43 (s, 6 H), 3.99−4.45 (m, 5 H), 7.16 (d, ^3J = 8.6 Hz, 1 H), 7.29−7.34 (m, 2 H), 7.43−7.59 (m, 1 H), 7.69−7.87 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.7 (q, $^3J_{C,P}$ = 17 Hz), 33.2 (q, $^5J_{C,P}$ = 8 Hz), 44.4 (q, $^3J_{C,P}$ = 10 Hz), 58.2 (d, $^1J_{C,P}$ = 164 Hz), 62.7 (t, $^2J_{C,P}$ = 16 Hz), 103.6 (s), 109.5 (d, $^5J_{C,P}$ = 7 Hz), 119.3 (d, $^4J_{C,P}$ = 11 Hz), 119.8 (d), 122.0 (d), 129.9 (s), 130.8 (d, $^3J_{C,P}$ = 4 Hz), 136.8 (s), 111.3 (s), 119.6 (d), 121.4 (d), 122.8 (d), 126.8 (d), 128.8 (s), 129.3 (d), 129.9 (d), 133.1 (s), 157.1 (s) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 23.03 (s) ppm. $C_{14}H_{24}NO_4P$ (301.32): calcd.: C 55.80, H 8.03, N 4.65; found: C 55.71, H 8.11, N 4.55.

Diethyl (Dimethylamino)(1-methyl-1*H*-pyrrol-2-yl)methylphosphonate (10d): Yield: 405 mg (59%); yellow oil, after flash column chromatography. IR (film): $\tilde{\nu}$ = 3477, 2985, 2945, 2453, 2219, 1666, 1527, 1484, 1355, 1235, 1025, 756, 557 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.14−1.18 (m, 3 H), 1.25−1.29 (m, 3 H), 2.35 (s, 6 H), 3.61 (s, 3 H), 3.95−4.16 (m, 5 H), 6.03 (s, 1 H), 6.42 (s, 1 H), 6.63 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.7 (q, $^3J_{C,P}$ = 20 Hz), 34.5 (q), 43.6 (q, $^3J_{C,P}$ = 12 Hz), 59.2 (d, $^1J_{C,P}$ = 240 Hz), 63.0 (t, $^2J_{C,P}$ = 29 Hz), 107.2 (d), 112.3 (d), 123.5 (d), 127.4 (s) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 23.01 (s) ppm. $C_{12}H_{23}N_2O_3P$ (274.30): calcd.: C 52.54, H 8.45, N 10.21; found: C 52.81, H 8.52, N 10.04.

Diethyl (Dimethylamino)(5-methylfuran-2-yl)methylphosphonate (10e): Yield: 433 mg (63%); yellow oil. IR (film): $\tilde{\nu}$ = 3469, 2940, 2856, 2446, 2378, 2318, 1651, 1532, 1479, 1361, 1221, 1201, 1043, 978, 776, 543 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.15−1.27 (m, 6 H), 2.33 (s, 3 H), 2.45 (s, 6 H), 4.17−4.32 (m, 5 H), 5.99 (s, 1 H), 6.46 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9 (q), 16.8 (q, $^3J_{C,P}$ = 18 Hz), 43.8 (q, $^3J_{C,P}$ = 9 Hz), 59.2 (d, $^1J_{C,P}$ = 162 Hz), 62.9 (t, $^2J_{C,P}$ = 14 Hz), 106.7 (d), 112.5 (d, $^3J_{C,P}$ = 4 Hz), 145.2 (s, $^2J_{C,P}$ = 11 Hz), 152.5 (s, $^5J_{C,P}$ = 2 Hz) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 19.65 (s) ppm. MS (70 eV, EI): *m/z* (%) = 275 (3) [M$^+$], 194 (34), 138 (100), 95 (19), 42 (32). $C_{12}H_{22}NO_4P$ (275.28): calcd.: C 52.36, H 8.06, N 5.09; found: C 52.55, H 8.27, N 4.89.

Diethyl (Dimethylamino)(4-dimethylaminophenyl)methylphosphonate Hydrochloride (10f): Yield: 482 mg (55%); pale yellow solid. IR

(KBr): $\tilde{\nu}$ = 3414, 2932, 2850, 2801, 2252, 1741, 1624, 1511, 1491, 1322, 1223, 1030, 946, 529 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 6.8 Hz, 3 H), 1.41 (t, ^3J = 6.8 Hz, 3 H), 3.03 (s, 6 H), 3.26 (s, 6 H), 4.03−4.46 (m, 4 H), 5.06 (d, $^2J_{H,P}$ = 17.3 Hz, 1 H), 7.91 (d, ^3J = 7.7 Hz, 2 H), 8.07 (d, ^3J = 7.7 Hz, 2 H), 9.74 (br, 1 H) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 16.8 (q, $^3J_{C,P}$ = 10 Hz), 34.9 (q), 42.2 (q), 64.4 (t, $^2J_{C,P}$ = 26 Hz), 64.7 (d, $^2J_{C,P}$ = 150 Hz), 115.5 (d), 119.5 (s), 132.8 (d, $^2J_{C,P}$ = 7 Hz), 150.1 (s) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 14.14 (s) ppm. MS (70 eV, EI): *m/z* (%) = 350 (2) [M^+], 331 (11), 279 (13), 194 (72), 148 (48), 138 (100). $C_{15}H_{28}ClN_2O_3P$ (350.82): calcd.: C 51.35, H 8.04, N 7.99; found: C 51.49, H 7.99, N 8.11.

General Procedure for the Aminoalkylation of Organoallylic Compounds 11: The organoallylic derivatives **11** (2.5 mmol) were added to a solution of **2** (0.57 g, 2.5 mmol) in abs. CH_2Cl_2 (10 mL) at ambient temperature. After a reaction time of 15 h the mixture was quenched with 6 M HCl (5 mL) and the aqueous layer was washed with Et_2O several times. The aqueous layer was basified by the addition of aqueous saturated $NaHCO_3$ solution and 2 M NaOH to pH 8−9. The product was extracted with CH_2Cl_2, the combined organic layers were dried (Na_2SO_4) and the solvent was removed in vacuo.

Diethyl 1-(Dimethylamino)but-3-enylphosphonate (12): Yield: 523 mg (89%); yellow oil. IR (film): $\tilde{\nu}$ = 2985, 2938, 2873, 2798, 1643, 1444, 1392, 1228, 1162, 1043, 1024, 966, 791, 582 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.24 (dt, ^3J = 7.1, $^4J_{H,P}$ = 4.8 Hz, 6 H), 2.27−2.50 (m, 2 H), 2.39 (d, $^4J_{H,P}$ = 2.0 Hz, 6 H), 2.76−2.93 (m, 1 H), 3.94−4.19 (m, 4 H), 4.90−5.08 (m, 2 H), 5.67−5.88 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.8 (q, $^3J_{C,P}$ = 2.5 Hz), 31.4 (t, $^2J_{C,P}$ = 6.4 Hz), 42.5 (q, $^3J_{C,P}$ = 4.4 Hz), 61.4 (t, $^2J_{C,P}$ = 7.4 Hz), 62.5 (d, $^1J_{C,P}$ = 140.8 Hz), 116.7 (t), 136.6 (d, $^3J_{C,P}$ = 13.8 Hz) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 27.2 (s) ppm. MS (EI, 80 eV): *m/z* (%) = 279 (8) [M^+]. $C_{10}H_{22}NO_3P$ (235.26): calcd.: C 51.05, H 9.43, N 5.95; found: C 50.96, H 9.38, N 6.01.

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