JOC The Journal of Organic Chemistry

Article

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α-Amidoalkylating Agents from *N*-Acyl-α-amino Acids: 1-(*N*-Acylamino)alkyltriphenylphosphonium Salts

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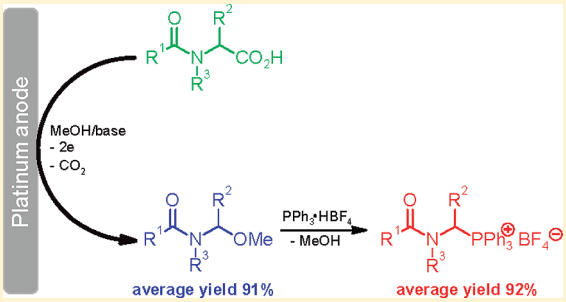
Supporting Information

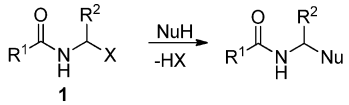
ABSTRACT: *N*-Acyl-α-amino acids were efficiently transformed in a two-step procedure into 1-*N*-(acylamino)alkyltriphenylphosphonium salts, new powerful α-amidoalkylating agents. The effect of the α-amino acid structure, the base used [MeONa or a silica gel-supported piperidine (SiO_2−Pip)], and the main electrolysis parameters (current density, charge consumption) on the yield and selectivity of the electrochemical decarboxylative α-methoxylation of *N*-acyl-α-amino acids (Hofer−Moest reaction) was investigated. For most proteinogenic and all studied unproteinogenic α-amino acids, very good results were obtained using a substoichiometric amount of SiO_2−Pip as the base. Only in the cases of *N*-acylated cysteine, methionine, and tryptophan, attempts to carry out the Hofer−Moest reaction in the applied conditions failed, probably because of the susceptibility of these α-amino acids to an electrochemical oxidation on the side chain. The methoxy group of *N*-(1-methoxyalkyl)amides was effectively displaced with the triphenylphosphonium group by dissolving an equimolar amount of *N*-(1-methoxyalkyl)amide and triphenylphosphonium tetrafluoroborate in CH_2Cl_2 at room temperature for 30 min, followed by the precipitation of 1-*N*-(acylamino)alkyltriphenylphosphonium salt with Et_2O.



INTRODUCTION

α-Amidoalkylation reactions play an important role in organic synthesis as a valuable extension of the Mannich reaction.[1−4] Numerous α-amidoalkylating reagents of a general structure **1** have been reported, where X represents some nucleofugal leaving group, usually OH, OR, OCOR, Cl, Br, I, NHCOR, SO_2Ar, or 1-benzotriazolyl (Scheme 1).[3,5−8]

Scheme 1. α-Amidoalkylating Agents and Their Reaction with Nucleophiles



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X = OH, OR, OCOR, Cl, Br, I, NHCOR, SO_2Ar, 1-benzotriazolyl

Limitations and disadvantages of most of the above-mentioned amidoalkylating agents have been reviewed by Katritzky et al.[3,9−11]

Recently, we described a simple and efficient synthesis of 1-(*N*-acylamino)alkyltriphenylphosphonium salts **4** by hydrolysis and decarboxylation of 4-phosphoranylidene-5(4*H*)-oxazolones **2** or their alkylation products **3** (Scheme 2).[12,13] We have also demonstrated that phosphonium salts **4** display strong amidoalkylating properties in the presence of organic bases such as DBU or $(i\text{-Pr})_2EtN$ (Hünig's base).[14] They react smoothly with nitrogen, sulfur, and oxygen nucleophiles in the presence of Hünig's base to afford the expected amidoalkylation products usually in good or very good yields.[14]

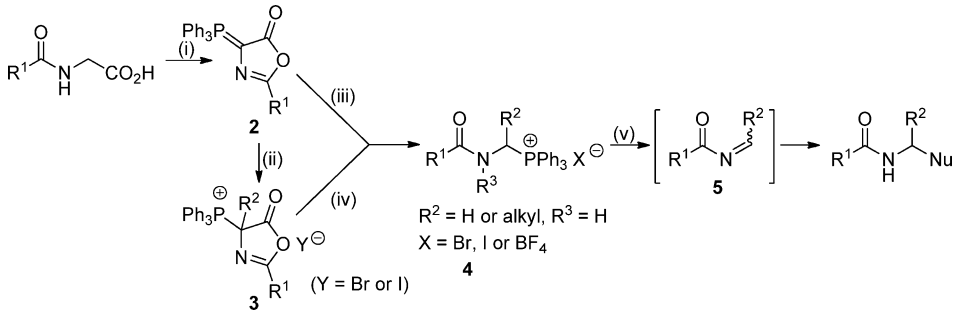
α-Amidoalkylation of dialkyl malonates or acetylacetates requires the use of a much stronger base (DBU) and provides the best results under the influence of microwave irradiation.[14] α-Amidoalkylation of enamines with 1-(*N*-acylamino)alkyltriphenylphosphonium salts in the presence of Hünig's base in a microwave reactor, followed by the hydrolysis of the corresponding iminium salt, produces the expected α-[1-(*N*-acylamino)alkyl]ketones in good yields.[14] α-Amidoalkylation of trialkylphosphites or dialkyl phosphonites with 1-(*N*-acylamino)alkyltriphenylphosphonium salts followed by a Michaelis−Arbuzov-like rearrangement offers a convenient and effective way to synthesize important α-(*N*-acylamino)alkanephosphonic or α-(*N*-acylamino)alkanephosphinic acid esters, respectively.[17]

As we have demonstrated, the deprotonation and elimination of triphenylphosphine from the phosphonium salts **4** leads to the corresponding highly reactive *N*-acylimines **5**, which are

Received: December 15, 2011
Published: January 16, 2012

   dx.doi.org/10.1021/jo202534u | *J. Org. Chem.* 2012, 77, 1952−1960

Scheme 2. Synthesis of 1-(*N*-Acylamino)alkyltriphenylphosphonium Salts 4 and Their Amidoalkylating Properties[a]



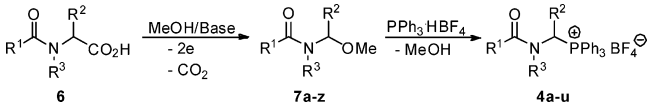
[a](i) (a) DCC, (b) Ph_3PBr_2, Et_3N;[15] (ii) R^2I or R^2Br;[16] (iii) H_2O, HBF_4;[12] (iv) H_2O;[12] (v) NuH, $(i\text{-Pr})_2EtN$, or DBU.[14]

responsible for the strong amidoalkylating properties of this reaction system.[14,18,19]

In contrast to many other known amidoalkylating reagents, α-(*N*-acylamino)alkyltriphenylphosphonium salts are stable, usually crystalline, easy-to-use compounds that can be stored for prolonged time under laboratory conditions and can be easily activated with organic bases, which is much more advantageous than the alternative usage of Lewis acids, usually recommended as catalysts for amidoalkylation reactions.

In this contribution, we report a new, convenient, very efficient, two-stage method for the synthesis of these powerful amidoalkylating agents from the *N*-acylated α-amino acids as starting materials (Scheme 3).

Scheme 3. Transformation of *N*-Acyl-α-amino Acids into 1-(*N*-Acylamino)alkyltriphenylphosphonium Salts



It is noteworthy that the possibility of employing in this synthesis a large variety of natural α-amino acids (both proteinogenic and unproteinogenic acids) as well as a nearly infinite array of unnatural α-amino acids provides potential access to a wide variety of structurally diverse amidoalkylating agents, which significantly broadens the scope of possible synthetic applications of 1-(*N*-acylamino)alkyltriphenylphosphonium salts as α-amidoalkylating agents.

RESULTS AND DISCUSSION

The first step of the transformation of *N*-acyl-α-amino acids into the corresponding 1-(*N*-acylamino)alkyltriphenylphosphonium salts involves the electrochemical decarboxylative α-methoxylation of *N*-acyl-α-amino acids **6** to *N*-(α-methoxyalkyl)amides **7** (the Hofer–Moest reaction). Since the pioneering works of Linstead et al.[20] on the electrolysis of *N*-acylamino acids, the Hofer–Moest decarboxylative α-methoxylation of *N*-acyl-α-amino acids has been studied by a number of authors.[21,22] Most of those investigations, however, were limited to relatively simple *N*-acylated α-amino acids such as glycine, sarcosine, hydrophobic α-amino acids with a simple aliphatic substituent at the α-position (alanine, valine, leucine, phenylalanine and their homologues), or proline and its cyclic homologues.[20,23] Matsumura et al.[24−26] and Onomura[27] also described the Hofer–Moest decarboxylative α-methoxylation of *N*,*O*-acetals derived from serine, whereas Steckhan applied this reaction to oxazolidin-2-one-4-carboxylic acids derived from threonine[28] and Kardasis et al.[29] to 2,5-piperazinediones derived from aminomalonic acid. The Hofer–Moest reactions were typically carried out in MeOH, in the presence of sodium methanolate,[20,23−27] organic bases (Et_3N, $(i\text{-Pr})_2EtN$, or pyridine),[28,30] or inorganic bases (NaOAc,[20,29] LiH, KOH, Cs_2CO_3).[24] Recently, Tajima et al. described the decarboxylative methoxylation of alanine and proline derivatives using 3-(1-piperidino)propyl functionalized silica gel (SiO_2–Pip) as the base, ionizing the *N*-acyl-α-amino acid into the corresponding carboxylate ion.[23]

In our studies, the Hofer–Moest decarboxylative α-methoxylation of *N*-acyl-α-amino acids was carried out in methanol, in an undivided cylindrical glass electrolyzer with a thermostatic jacket, a magnetic stirrer, and a cylindrical Pt mesh anode, at a constant current density (Figure 1).

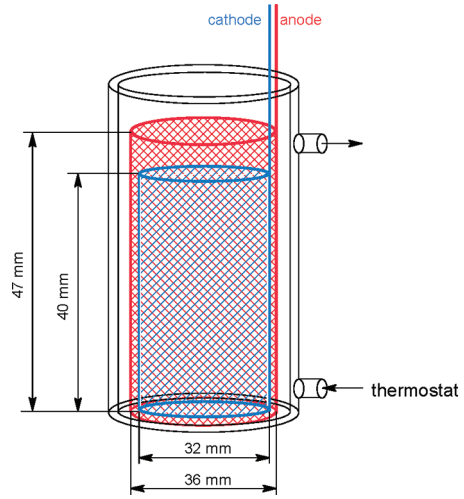


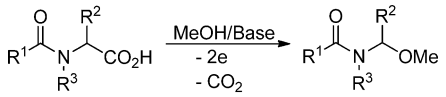
Figure 1. Electrolytic cell for the Hofer–Moest decarboxylative α-methoxylation of *N*-acyl-α-amino acids in the presence of SiO_2–Pip.

The effect of the α-amino acid structure, applied base [MeONa or a silica gel supported piperidine (SiO_2–Pip)], and the main electrolysis parameters (current density, charge consumption) on the reaction yield and selectivity was investigated. The results obtained are provided in Table 1.

The decarboxylative α-methoxylation of *N*-acyl-α-amino acids in the presence of MeONa was performed at a relatively low current density (1.1 A/dm^2) to avoid undesirable side reactions, e.g., the Kolbe reaction (Procedure A).[22] Alternatively, reactions were carried out in the presence of a substiochiometric amount of SiO_2–Pip (0.075 mol of piperidine per mol of substrate; Procedure B).

dx.doi.org/10.1021/jo202534u | *J. Org. Chem.* 2012, 77, 1952–1960

Table 1. Decarboxylative α-Methoxylation of *N*-Acyl-α-amino Acids 6 to *N*-(1-Methoxyalkyl)amides 7



6 7a-z

entry	substrate 6	base	charge [F/mol]	7	yield [%]
1	*N*-Ac-Gly-OH	MeONa	3.5	**7a**	59
2	*N*-Ac-Gly-OH	SiO_2–Pip	3.5	**7a**	96
3	*N*-Ac-D,L-Ala-OH	SiO_2–Pip	3.75	**7b**	93
4	*N*-Piv-D,L-Ala-OH	MeONa	3.0	**7c**	97
5	*N*-Piv-D,L-Ala-OH	SiO_2–Pip	3.75	**7c**	94
6	*N*-Cbz-L-Ala-OH	MeONa	3.0	**7d**	90
7	*N*-Cbz-L-Ala-OH	SiO_2–Pip	3.75	**7d**	94
8	*N*-Cbz-D,L-Ala-OH	SiO_2–Pip	3.75	**7d**	94
9	*N*-For-D,L-Ala-OH	SiO_2–Pip	3.75	**7e**	82
10	*N*-Cbz-Aib-OH	MeONa	3.3	**7f**	93
11	*N*-Cbz-L-Phe-OH	MeONa	3.0	**7g**	92
12	*N*-Ac-D,L-Phg-OH	MeONa	3.0	**7h**	88
13	*N*-Ac-D,L-Phg-OH	SiO_2–Pip	3.75	**7h**	93
14	*N*-Cbz-L-Phg-OH	SiO_2–Pip	3.75	**7i**	98
15	*N*-Cbz-D,L-Val-OH	MeONa	3.0	**7j**	94
16	*N*-Cbz-D,L-Val-OH	SiO_2–Pip	3.5	**7j**	97
17	*N*-Boc-L-Val-OH	MeONa	3.0	**7k**	81
18	*N*-Boc-L-Val-OH	SiO_2–Pip	3.75	**7k**	92
19	*N*-Cbz-L-Leu-OH	MeONa	3.0	**7l**	93
20	*N*-Cbz-L-Leu-OH	SiO_2–Pip	3.5	**7l**	86
21	*N*-Cbz-D,L-Leu-OH	SiO_2–Pip	3.75	**7l**	91
22	*N*-Cbz-L-Pro-OH	MeONa	3.0	**7m**	91
23	*N*-Cbz-L-Pro-OH	SiO_2–Pip	3.75	**7m**	93
24	*N*-Cbz-L-Asn-OH	MeONa	3.0	**7n**	63
25	*N*-Cbz-L-Asn-OH	SiO_2–Pip	3.75	**7n**	93
26	*N*-Cbz-L-Gln-OH	MeONa	3.0	**7o**	74
27	*N*-Cbz-L-Gln-OH	SiO_2–Pip	3.75	**7o**	95
28	*N*-Cbz-L-Ser(*O*-*t*-Bu)-OH	MeONa	3.0	**7p**	93
29	*N*-Cbz-L-Ser(*O*-*t*-Bu)-OH	SiO_2–Pip	3.75	**7p**	94
30	*N*-Cbz-L-Asp(*O*-*t*-Bu)-OH	MeONa	3.0	**7q**	96
31	*N*-Cbz-L-Asp(*O*-*t*-Bu)-OH	SiO_2–Pip	3.75	**7q**	79
32	*N*-Cbz-L-Glu(*O*-*t*-Bu)-OH	MeONa	3.0	**7r**	97
33	*N*-Cbz-L-Glu(*O*-*t*-Bu)-OH	SiO_2–Pip	3.75	**7r**	88
34	*N*-Cbz-L-Tyr(*O*-Bn)-OH	SiO_2–Pip	3.0	**7s**	80
35	*N*-Cbz-L-Lys(*N*-Cbz)-OH	SiO_2–Pip	3.75	**7t**	74
36	*N*-Boc-L-His(*N*-Bn)-OH	SiO_2–Pip	2.4	**7u**	91
37	*N*-Fmoc-L-Thr(*O*-*t*-Bu)-OH	SiO_2–Pip	3.75	**7v**	68[a]
38	*N*-Boc-D,L-Met-OH	MeONa	3.0	**7w**	–[b]
39	*N*-Boc-D,L-Met-OH	SiO_2–Pip	3.75	**7w**	–[b]
40	*N*-Cbz-L-Cys(*S*-Bn)-OH	SiO_2–Pip	3.75	**7x**	–[b]
41	*N*-Ac-D,L-Trp-OH	SiO_2–Pip	3.75	**7y**	–[b]
42	*N*-Boc-L-Trp(*N*-Bn)-OH	MeONa	3.0	**7z**	–[b]
43	*N*-Boc-L-Trp(*N*-Bn)-OH	SiO_2–Pip	3.75	**7z**	–[b]

[a]A mixture of diasteroisomers in a molar ratio of 3:2. [b]A multicomponent reaction mixture.

In the latter case, the relatively high resistance of the electrolyte required the placement of electrodes as close to one another as possible (see Figure 1) and the reduction of current density to 0.3 A/dm^2.

Upon the charge consumption of 3 F/mol, the substrate conversion was monitored using ^{1}H NMR spectroscopy. If necessary, the electrolysis was continued until all of the starting material was consumed (see Table 1).

The decarboxylative α-methoxylation of a variety of *N*-acyl-α-amino acids was investigated including α-amino acid derivatives with functionalized side chains at the α-position that were not yet explored in the Hofer–Moest reaction. It was demonstrated that, apart from the hydrophobic aliphatic and aromatic *N*-acyl-α-amino acids (alanine, valine, leucine, phenylalanine, and tyrosine), most extensively studied in this reaction, most other natural proteinogenic and unproteinogenic *N*-acyl-α-amino acids undergo a facile and efficient decarboxylative α-methoxylation, including those with a functionalized neutral-polar side chain (asparagine, glutamine, serine, threonine), a protected acidic side chain (aspartic acid, glutamic acid), or a basic side chain (histidine, lysine). However, in the case of *N*-acylated cysteine, methionine, and tryptophan, our attempts

dx.doi.org/10.1021/jo202534u | J. Org. Chem. 2012, 77, 1952–1960

to carry out the Hofer–Moest reaction failed; in all of these cases, multicomponent reaction mixtures were obtained, probably because of the susceptibility of these α-amino acids to electrochemical oxidation on the side chain. It appears that the nature of the *N*-acyl group does not markedly affect the course of the reaction.

Investigations on the effect of the base used in the reaction led to the conclusion that, in the most cases, better results were obtained using the silica gel supported piperidine. In a few cases of particularly hydrophilic amino acids (*N*-Ac-Gly-OH, *N*-Cbz-Asn-OH, *N*-Cbz-Gln-OH) the results were markedly improved. The obtained reaction yields using SiO_2–Pip were usually very good or even excellent. The main advantage obtained when SiO_2–Pip was used involved the simple workup procedure that eliminated the need to extract the product from an aqueous solution. Aqueous workups were especially difficult and ineffective in the case of products derived from polar, hydrophilic amino acids.

We also demonstrated that SiO_2–Pip could be used afresh many times after separation by filtration and washing with methanol. Five successive runs using *N*-Cbz-L-Ala-OH and the same portion of SiO_2–Pip afforded the expected product in yields 93.2%, 96.1%, 94.3%, 93.3%, and 93.9%, respectively.

The stereoselectivity of the Hofer–Moest reaction performed in the presence of SiO_2–Pip was studied, by comparing the reaction products obtained from *N*-Cbz-L-Ala-OH and *N*-Cbz-D,L-Ala-OH. Beforehand we stated that doublets at 1.30–1.31 ppm of methyl groups of both enantiomers of the expected *N*-(1-methoxyethyl)amide **7d** were well separated in the ^{1}H NMR spectra performed in the presence of quinine as a chiral solvating agent. As was expected, in both cases we obtained racemic mixtures of both enantiomers in a molar ratio of 1:1 (Figure 2).

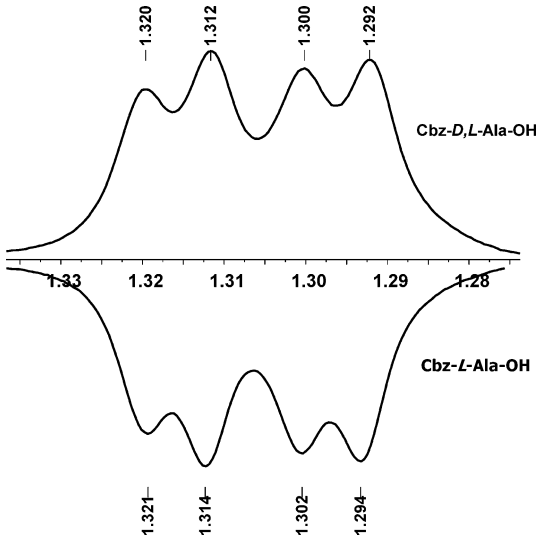


Figure 2. Doublets of methyl groups of both enantiomers of *N*-(1-methoxyethyl)amide **7d** obtained from *N*-Cbz-L-Ala-OH and *N*-Cbz-D,L-Ala-OH at 1.30 ppm (J = 6.0 Hz) and 1.31 ppm (J = 6.0 Hz); $CDCl_3$, **7d**:quinine molar ratio of 1:5.

A similar racemization in a Hofer–Moest decarboxylative α-methoxylation of *N*-acyl-α-amino acids carried out in the presence of sodium methoxide was reported by Matsumura et al.[31] In the case of the threonine derivative **7v** with the additional stereogenic center in the side chain, a mixture of both diasteromers was obtained.

The methoxy group of *N*-(1-methoxyalkyl)amides **7** was effectively displaced by the triphenylphosphonium group by heating a homogeneous mixture of the amide with triphenylphosphonium tetrafluoroborate at 45–70 °C under reduced pressure (0.1–0.2 mmHg) for 2 h (Table 2, Procedure C). In many cases, however, a higher reaction yield could be achieved by simply dissolving equimolar amounts of *N*-(1-methoxyalkyl)amide and triphenylphosphonium tetrafluoroborate in CH_2Cl_2 at room temperature for 30 min, followed by the precipitation of the product with Et_2O (Table 2, Procedure D).

The *N*-(1-methoxyalkyl)amide derived from histidine (**7u**) was an exception; its reaction with an equimolar amount of triphenylphosphonium tetrafluoroborate resulted in the protonation of the imidazole moiety, without the displacement of the methoxy group. However, this transformation was achieved using two equivalents of triphenylphosphonium tetrafluoroborate per one equivalent of the corresponding *N*-(1-methoxyalkyl)amide affording a reaction mixture, which contained about 80% the expected phosphonium salt with the protonated imidazole moiety (see Experimental). Attempts to isolate the pure protonated phosphonium salt **4u** by crystallization failed.

CONCLUSIONS

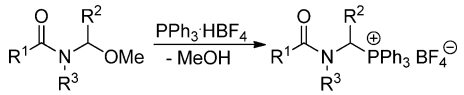
A new, convenient, efficient, two-stage transformation of *N*-acylated α-amino acids into 1-(*N*-acylamino)alkyltriphenylphosphonium salts has been developed. The first step of the transformation consists in the electrochemical decarboxylative α-methoxylation of *N*-acylated α-amino acids to the corresponding *N*-(1-methoxyalkyl)amides (Hofer–Moest reaction) in the presence of a base (MeONa or SiO_2–Pip). For most proteinogenic and all unproteinogenic α-amino acids studied, very good results were obtained using a substoichiometric amount of the SiO_2–Pip as a base. A significant advantage of the application of SiO_2–Pip is the facile workup procedure of reaction mixtures, which eliminates a difficult extraction of the hydrophilic product from an aqueous solution. The Hofer–Moest decarboxylative α-methoxylation of *N*-Cbz-L-Ala-OH in the presence of SiO_2–Pip gave a racemic mixture of the expected benzyl *N*-(1-methoxyethyl)carbamate. The methoxy group of *N*-(1-methoxyalkyl)amides was effectively displaced by the triphenylphosphonium group by dissolving equimolar amounts of *N*-(1-methoxyalkyl)amide and triphenylphosphonium tetrafluoroborate in CH_2Cl_2 at room temperature for 30 min, followed by the precipitation of the product with Et_2O or by heating a homogeneous mixture of the amide with triphenylphosphonium tetrafluoroborate at 45–70 °C under reduced pressure. The possibility of employing in this synthesis a large range of natural α-amino acids (both proteinogenic and unproteinogenic), as well as an unlimited number of unnatural α-amino acids, potentially provided access to a wide variety of structurally diverse amidoalkylating agents that significantly widen the scope of possible synthetic applications of 1-(*N*-acylamino)-alkyltriphenylphosphonium salts as α-amidoalkylating agents.

EXPERIMENTAL SECTION

General Methods. Melting points were determined in capillaries and are uncorrected. IR spectra were measured on a FT-IR spectrophotometer (ATR method). ^{1}H and ^{13}C NMR spectra were recorded at operating frequencies of 300 and 75.5 MHz, respectively, using TMS as the resonance shift standard. ^{31}P NMR spectra were recorded at operating frequencies of 121.5 or 242.8 MHz, with 80% orthophosphoric acid as an external resonance shift standard. All chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hz.

dx.doi.org/10.1021/jo202534u | J. Org. Chem. 2012, 77, 1952–1960

Table 2. Transformation of *N*-(1-Methoxyalkyl)amides 7 to 1-(*N*-acylamino)alkyltriphenylphosphonium Salts 4



7a-u **4a-u**

entry	7	R^1	R^2	R^3	procedure[a]	temp [°C]	4	yield [%]
1	**7a**	Me	H	H	C	60	**4a**	67
2	**7a**	Me	H	H	D	60	**4a**	98
3	**7b**	Me	Me	H	C	45	**4b**	74
4	**7b**	Me	Me	H	D	25	**4b**	96
5	**7c**	*t*-Bu	Me	H	C	70	**4c**	93
6	**7c**	*t*-Bu	Me	H	D	25	**4c**	85
7	**7d**	BnO	Me	H	C	45	**4d**	99
8	**7d**	BnO	Me	H	D	25	**4d**	97
9	**7e**	H	Me	H	D	25	**4e**	92
10	**7g**	BnO	Bn	H	C	45	**4g**	97
11	**7h**	Me	Ph	H	C	70	**4h**	95
12	**7h**	Me	Ph	H	D	25	**4h**	92
13	**7i**	BnO	Ph	H	D	25	**4i**	99
14	**7j**	BnO	*i*-Pr	H	C	45	**4j**	89
15	**7j**	BnO	*i*-Pr	H	D	25	**4j**	83
16	**7k**	*t*-BuO	*i*-Pr	H	C	45	**4k**	90
17	**7k**	*t*-BuO	*i*-Pr	H	D	25	**4k**	96
18	**7l**	BnO	*i*-Bu	H	C	45	**4l**	82
19	**7m**	BnO	$(CH_2)_3$		C	45	**4m**	99
20[b]	**7n**	BnO	CH_2CONH_2	H	C	45	**4n**	100
21[b]	**7n**	BnO	CH_2CONH_2	H	D	25	**4n**	84
22[b]	**7o**	BnO	$(CH_2)_2CONH_2$	H	C	45	**4o**	100
23[b]	**7o**	BnO	$(CH_2)_2CONH_2$	H	D	25	**4o**	90
24	**7p**	BnO	CH_2O-*t*-Bu	H	C	70	**4p**	91
25	**7p**	BnO	CH_2O-*t*-Bu	H	D	25	**4p**	95
26	**7q**	BnO	CH_2CO_2-*t*-Bu	H	D	25	**4q**	79
27	**7r**	BnO	$(CH_2)_2CO_2$-*t*-Bu	H	C	45	**4r**	92
28	**7r**	BnO	$(CH_2)_2CO_2$-*t*-Bu	H	D	25	**4r**	90
29	**7s**	BnO	*p*-$CH_2C_6H_4OBn$	H	D	25	**4s**	94
30	**7t**	BnO	$(CH_2)_4NHCbz$	H	D	25	**4t**	-[c]
31	**7u**	*t*-BuO	(1-benzylimidazol-5yl)methyl	H	D	25	**4u**	-[d]

[a]Procedure C, reactions in a homogeneous melt; procedure D, reactions in a solution. [b]Reactions carried out in acetonitrile. [c]A multicomponent reaction mixture. [d]The reaction mixture contained about 80% of the expected phosphonium salt with the protonated imidazole moiety (see Experimental Section). Attempts to isolate the pure phosphonium salt failed.

Electrochemical Decarboxylative α-Methoxylation of *N*-Acyl-α-amino Acids 6; General Procedures. *Procedure A.* To an undivided cylindrical glass electrolyzer (85 cm^3) with a thermostatic jacket, equipped with a cylindrical Pt mesh anode (47 cm^2), a cathode made of platinized titanium (plate, 8 cm^2), and a magnetic stirrer, methanol (30 cm^3), *N*-acyl-α-amino acid **6** (3.0 mmol), and MeONa (1.8 mmol, methanolic solution) were added. The electrolysis was carried out while stirring at a current density of 1.1 A/dm^2 at 0 °C until 3−3.5 F/mol charge (Table 1) had passed. After evaporation of methanol in vacuo, methylene chloride (20 cm^3) was added to the residue, and the mixture was washed with 5% hydrochloric acid solution (5 cm^3) and water (10 cm^3). The organic layer was dried with $MgSO_4$, the drying agent was filtered out, and methylene chloride was evaporated under reduced pressure to obtain *N*-(1-methoxyalkyl)-amide **7** (Table 1).

Procedure B. To an undivided cylindrical glass electrolyzer (85 cm^3) with a thermostatic jacket, equipped with a magnetic stirrer, a cylindrical Pt mesh anode (47 cm^2), and a similar cathode (44 cm^2), arranged concentrically to one another at a distance of 2.5 ± 0.5 mm (Figure 1), methanol (30 cm^3), *N*-acyl-α-amino acid **7** (3.0 mmol), and SiO_2−Pip (200 mg, 0.22 mmol) were added. The electrolysis was carried out while stirring at a current density of 0.3 A/dm^2 at 10 °C until 2.4−3.75 F/mol charge had passed (Table 1). SiO_2−Pip was filtered out, and methanol was evaporated under reduced pressure to obtain *N*-(1-methoxyalkyl)amide **7** (Table 1).

Transformation of *N*-(1-Methoxyalkyl)amides 7 to 1-(*N*-Acylamino)alkyltriphenylphosphonium Salts 4; General Procedures. *Procedure C.* To a solution of *N*-(1-methoxyalkyl)amide **7** (1.25 mmol) in dichloromethane (2 cm^3) was added triphenylphosphine tetrafluoroborate (438 mg, 1.25 mmol). After obtaining a homogeneous solution, the solvent was evaporated to dryness, and the residue was heated at 45−70 °C (Table 2) under reduced pressure (1−2 mmHg) for 1.5 h. Recrystallization of the residue using CH_2Cl_2/Et_2O (1:2, v/v), CH_3CN/Et_2O (1:2, v/v), or ethyl acetate yielded, in most cases, 1-(*N*-acylamino)alkyltriphenylphosphonium salts **4** as colorless crystals.

Procedure D. To a stirred solution of *N*-(1-methoxyalkyl)amide **7** (1.27 mmol) in dichloromethane (0.7 cm^3) was added triphenylphosphine tetrafluoroborate (445 mg, 1.27 mmol). The homogeneous mixture was allowed to react at 25 °C for 30 min, and 1-(*N*-acylamino)alkyltriphenylphosphonium salt **4** was precipitated with Et_2O, separated by filtration, and dried under reduced pressure.

Reaction of *tert*-Butyl *N*-[2-(1-benzylimidazol-5-yl)-1-methoxyethyl]carbamate 7u with Triphenylphosphonium Tetrafluoroborate. To a solution of *tert*-butyl *N*-[2-(1-benzylimidazol-5-yl)-1-methoxyethyl]carbamate (24.3 mg, 0.07 mmol) in deuterated chloroformm (0.7 cm^3) was added triphenylphosphine tetrafluoroborate

dx.doi.org/10.1021/jo202534u | J. Org. Chem. 2012, 77, 1952−1960

(25.7 mg, 0.07 mmol). The composition of the obtained mixture was monitored using ^{1}H NMR. After 10 min another portion of triphenylphosphine tetrafluoroborate (25.7 mg, 0.07 mmol) was added. After 40 min the reaction mixture contained about 80% of the expected phosphonium salt **4u** with the protonated imidazole moiety. Attempts to isolate the pure phosphonium salt by precipitation with Et_2O failed.

***N*-(Methoxymethyl)acetamide[20] (7a).** Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.63 (br s, 1H), 4.66 (d, J = 9.0 Hz, 2H), 3.34 (s, 3H), 2.05 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.0, 71.3, 55.8, 23.2 ppm; IR (ATR) 3300, 1664, 1538, 1369, 1280, 1127, 1060 cm^{-1}.

***N*-(1-Methoxyethyl)acetamide[20] (7b).** Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.10 (br s, 1H), 5.27 (dq, J = 9.0, 5.9 Hz, 1H), 3.33 (s, 3H), 2.03 (s, 3H), 1.33 (d, J = 5.7 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 170.2, 77.6, 55.5, 23.3, 21.4 ppm; IR (ATR) 3278, 1656, 1537, 1374, 1129, 1090, 1051 cm^{-1}.

***N*-(1-Methoxyethyl)pivaloylamide (7c).** Colorless crystals, mp 65−66 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (br s, 1H), 5.34 (dq, J = 9.6, 6.0 Hz, 1H), 3.31 (s, 3H), 1.34 (d, J = 6.0 Hz, 3H), 1.22 (s, 9H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 178.5, 77.7, 55.5, 38.8, 27.5, 21.6 ppm; IR (ATR) 3327, 2969, 2936, 1645, 1526, 1194, 1126, 1091 cm^{-1}. Anal. Calcd for $C_8H_{17}NO_2$: C, 60.35; H, 10.76; N, 8.80. Found: C, 60.05; H, 11.03; N, 8.68.

Benzyl *N*-(1-Methoxyethyl)carbamate[32] (7d). Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.30 (m, 5H), 5.20 (d, J = 10.2 Hz, 1H), 5.11 (s, 2H), 5.04 (dq, J = 10.2, 5.6 Hz, 1H), 3.33 (s, 3H), 1.32 (d, J = 6.0 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 155.8, 136.2, 128.5, 128.2, 128.0, 80.1, 66.7, 55.2, 21.6 ppm; IR (ATR) 3316, 1700, 1526, 1239, 1070 cm^{-1}.

***N*-(1-Methoxyethyl)formamide[33,34] (7e).** Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$)[a] Major rotamer: δ 8.27 (d, J = 0.8 Hz, 1H), 6.27 (br s, 1H), 5.35 (ddq, J = 9.6, 0.7, 6.1 Hz, 1H), 3.35 (s, 3H), 1.36 (d, J = 6.0 Hz, 3H); minor rotamer: δ 8.21 (d, J = 11.7 Hz, 1H), 6.55 (br s, 1H), 4.64 (dq, J = 10.1, 5.8 Hz, 1H), 3.30 (s, 3H), 1.45 (d, J = 6.0 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$)[a] Major rotamer: δ 161.1, 76.2, 55.7, 21.4 ppm; minor rotamer: δ 163.8, 81.5, 54.3, 21.8 ppm; IR (ATR) 3274, 2987, 1667, 1525, 1385, 1088, 1045 cm^{-1}. [a]Two rotamers in a molar ratio of 63:37.

Benzyl *N*-(1-Methoxy-1-methylethyl)carbamate[35] (7f). Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.30 (m, 5H), 5.14 (br s, 1H), 5.08 (s, 2H), 3.22 (s, 3H), 1.54 (s, 6H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 154.2, 136.4, 128.5, 128.1, 128.0, 84.5, 66.3, 49.3, 26.0 ppm; IR (ATR) 3331, 1713, 1530, 1264, 1072 cm^{-1}.

Benzyl *N*-(1-Methoxy-2-phenylethyl)carbamate[36] (7g). Colorless crystals, mp 85−86 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39−7.18 (m, 10H), 5.14 (ddd, J = 10.8, 5.6, 5.6 Hz, 1H), 5.12 (d, J = 12.3 Hz, 1H), 5.08 (s, 2H), 3.33 (s, 3H), 2.93 (d, J = 5.4 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 155.9, 136.2, 135.8, 129.6, 128.5, 128.4, 128.1, 128.0, 126.7, 84.5, 66.3, 49.3, 26.0 ppm; IR (ATR) 3329, 1689, 1523, 1247, 1088, 1028 cm^{-1}.

***N*-(1-Methoxy-1-phenylmethyl)acetamide[37] (7h).** Colorless crystals, mp 89−91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.29 (m, 5H), 6.18 (d, J = 9.3 Hz, 1H), 6.10 (d, J = 9.3 Hz, 1H), 3.44 (s, 3H), 2.03 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 170.2, 139.2, 128.6, 128.5, 125.8, 81.3, 55.9, 23.3 ppm; IR (ATR) 3289, 1655, 1538, 1089, 1066 cm^{-1}.

Benzyl *N*-(1-Methoxy-1-phenylmethyl)carbamate[38] (7i). Colorless crystals, mp 77−79 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.31 (m, 10H), 5.89 (d, J = 9.6 Hz, 1H), 5.33 (d, J = 8.4 Hz, 1H), 5.16 (s, 2H), 3.47 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 155.9, 139.0, 136.1, 128.6, 128.6, 128.5, 128.2, 128.1, 125.8, 84.0, 67.1, 55.7 ppm; IR (ATR) 3288, 1693, 1537, 1250, 1086, 1048 cm^{-1}.

Benzyl *N*-(1-Methoxy-2-methylpropyl)carbamate[39] (7j). Colorless crystals, mp 97−99 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.29 (m, 5H), 5.13 (s, 2H), 5.03 (d, J = 9.6 Hz, 1H), 4.64 (dd, J = 10.4, 5.9 Hz, 1H), 3.35 (s, 3H), 1.90−1.74 (m, 1H), 0.94 (d, J = 6.6 Hz, 3H), 0.91 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.4, 136.3, 128.5, 128.2, 128.0, 87.8, 66.9, 55.7, 33.0, 17.7, 17.1 ppm; IR (ATR) 3292, 1688, 1535, 1245, 1099, 1025 cm^{-1}.

***tert*-Butyl *N*-(1-Methoxy-2-methylpropyl)carbamate[40] (7k).** Colorless crystals, mp 29−30 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.79 (d, J = 10.2 Hz, 1H), 4.57 (dd, J = 10.4, 5.6 Hz, 1H), 3.34 (s, 3H), 1.90−1.70 (m, 1H), 1.46 (s, 9H), 0.94 (d, J = 6.9 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 155.8, 87.1, 79.5, 55.6, 33.0, 28.3, 17.8, 17.2 ppm; IR (ATR) 3268, 1682, 1530, 1364, 1248, 1172, 1154, 1084, 1012 cm^{-1}.

Benzyl *N*-(1-Methoxy-3-methylbutyl)carbamate[39] (7l). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.26 (m, 5H), 5.12 (s, 2H), 5.06 (d, J = 10.5 Hz, 1H), 4.94 (ddd, J = 9.9, 6.5, 6.5 Hz, 1H), 3.35 (s, 3H), 1.80−1.63 (m, 1H), 1.60−1.51 (m, 1H), 1.42−1.33 (m, 1H), 0.92 (d, J = 6.6 Hz, 6H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.0, 136.2, 128.5, 128.2, 128.0, 82.3, 66.8, 55.4, 44.5, 24.5, 22.6, 22.4 ppm; IR (ATR) 3320, 2955, 1700, 1523, 1224, 1088, 1046, 1026 cm^{-1}.

***N*-(Benzyloxycarbonyl)-2-methoxypyrolidine[41] (7m).** Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$)[a] δ 7.40−7.26[b] (m, 5H), 5.17[c] and 5.16[c] (s, 2H), 5.26−5.20[c] and 5.17−5.16[c] (m, 1H), 3.57−3.48[c] and 3.45−3.32[c] (m, 2H), 3.39[c] and 3.26[c] (s, 3H), 2.20−1.65[b] (m, 4H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$)[a] δ 155.7[c] and 154.8[c], 136.6[b], 128.4[b], 127.9[b], 127.7[b], 89.1[c] and 88.5[c], 67.0[c] and 66.8[c], 55.9[c] and 55.3[c], 45.8[c] and 45.7[c], 32.5[c] and 31.9[c], 22.6[c] and 21.6[c] ppm; IR (ATR) 2943, 1701, 1402, 1356, 1079 cm^{-1}. [a]Two diastereomers with stereogenic centers at C_α and N. [b]Overlapping signals of both diastereomers. [c]Separate signals from both diasteromers.

Benzyl *N*-(2-Carbamoyl-1-methoxyethyl)carbamate (7n). Colorless crystals, mp 154−155 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.89 (d, J = 9.6 Hz, 1H), 7.40−7.26 (m, 5H), 7.36 (d, J = 9.6 Hz, 1H), 6.86 (br s, 1H), 5.09 (ddd, J = 9.4, 7.4, 5.3 Hz, 1H), 5.06 (s, 2H), 3.16 (s, 3H), 2.46 (dd, J = 14.4, 7.2 Hz, 1H), 2.29 (dd, J = 14.4, 5.1 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 170.6, 155.8, 136.9, 128.4, 127.9, 127.8, 80.7, 65.4, 54.4, 40.8 ppm; IR (ATR) 3382, 3324, 3189, 1687, 1653, 1527, 1277, 1218, 1102, 1041, 1016 cm^{-1}. Anal. Calcd for $C_{12}H_{16}N_2O_4$: C, 57.13; H, 6.39; N, 11.10. Found: C, 56.93; H, 6.11; N, 11.05.

Benzyl *N*-(3-Carbamoyl-1-methoxypropyl)carbamate (7o). Colorless crystals, mp 132−133 °C; ^{1}H NMR (300 MHz, CD_3CN) δ 7.42−7.28 (m, 5H), 6.25 (d, J = 7.5 Hz, 1H), 6.15 (br s, 1H), 5.69 (br s, 1H), 5.08 (s, 2H), 4.79 (ddd, J = 9.6, 6.3, 6.3 Hz, 1H), 3.24 (s, 3H), 2.21 (ddd, J = 7.4, 7.4, 3.3 Hz, 2H), 1.91−1.70 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, CD_3CN) δ 175.4, 157.2, 138.2, 129.5, 128.9, 128.6, 83.8, 67.0, 55.4, 31.2, 31.0 ppm; IR (ATR) 3406, 3308, 1683, 1661, 1533, 1270, 1054 cm^{-1}. Anal. Calcd for $C_{13}H_{18}N_2O_4$: C, 58.63; H, 6.81; N, 10.52. Found: C, 58.32; H, 6.53; N, 10.43.

Benzyl *N*-(2-*tert*-Butoxy-1-methoxyethyl)carbamate (7p). Colorless crystals, mp 36−38 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.26 (m, 5H), 5.64 (d, J = 9.3 Hz, 1H), 5.14 (s, 2H), 5.00 (ddd, J = 9.9, 3.0, 3.0 Hz, 1H), 3.54 (dd, J = 9.6, 2.4 Hz, 1H), 3.43 (dd, J = 9.8, 3.8 Hz, 1H), 3.39 (s, 3H), 1.19 (s, 9H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.2, 136.3, 128.5, 128.2, 128.0, 82.0, 73.5, 66.9, 63.4, 55.8, 27.3 ppm; IR (ATR) 3344, 1696, 1526, 1268, 1195, 1098, 1055 cm^{-1}. Anal. Calcd for $C_{15}H_{23}NO_4$: C, 64.03; H, 8.24; N, 4.98. Found: C, 63.80; H, 8.47; N, 4.92.

Benzyl *N*-(2-*tert*-Butoxycarbonyl-1-methoxyethyl)-carbamate (7q). Colorless crystals, mp 48−50 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.28 (m, 5H), 5.97 (d, J = 9.9 Hz, 1H), 5.20 (ddd, J = 9.9, 5.0, 5.0 Hz, 1H), 5.13 (s, 2H), 3.36 (s, 3H), 2.61 (dd, J = 15.3, 4.8 Hz, 1H), 2.55 (dd, J = 15.3, 4.8 Hz, 1H), 1.43 (s, 9H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.2, 155.9, 136.2, 128.5, 128.2, 128.1, 81.4, 80.1, 66.8, 55.7, 41.1, 28.0 ppm; IR (ATR) 3347, 1716, 1539, 1317, 1208, 1162, 1009 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{23}NO_5Na$ $[M + Na]^+$ 332.1468, found 332.1471.

Benzyl *N*-(3-*tert*-Butoxycarbonyl-1-methoxypropyl)-carbamate (7r). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.28 (m, 5H), 5.27 (d, J = 9.9 Hz, 1H), 5.12 (s, 2H), 5.20 (ddd, J = 9.9, 6.2, 6.2 Hz, 1H), 3.34 (s, 3H), 2.41−2.22 (m, 2H), 1.99−1.81 (m, 2H), 1.43 (s, 9H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.3, 156.0, 136.2, 128.5, 128.2, 128.0, 82.9, 80.5, 66.8, 55.6, 30.9, 30.4, 28.0 ppm; IR (ATR) 3324, 2978, 1705, 1523, 1248, 1151, 1047 cm^{-1}. Anal. Calcd for $C_{17}H_{25}NO_5$: C, 62.99; H, 8.05; N, 4.44. Found: C, 63.14; H, 8.05; N, 4.33.

Benzyl *N*-[1-Methoxy-2-(4-benzyloxyphenyl)ethyl]-carbamate (7s). Cream-colored crystals, mp 105−107 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−6.86 (m, 14H), 5.17−5.05 (m, 1H), 5.08 (s, 2H), 5.03 (s, 2H), 5.00 (d, J = 10.5 Hz, 1H), 3.34 (s, 3H), 2.87 (d, J = 5.1 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 155.9, 137.7, 137.0, 136.2, 130.7, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.4, 114.8, 83.5, 70.0, 66.8, 55.7, 40.7 ppm; IR (ATR) 3307, 1698, 1534, 1511, 1260, 1237, 1048, 1025 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{25}NO_4Na$ [M + Na]$^+$ 414.1676, found 414.1679.

Benzyl *N*-[5-(Benzyloxycarbonylamino)-1-methoxypentyl]-carbamate (7t). Colorless crystals, mp 108−109 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.75 (d, J = 9.3 Hz, 1H) 7.41−7.30 (m, 10H), 7.25 (d, J = 5.6 Hz, 1H), 5.06 (s, 2H), 5.01 (s, 2H), 4.69 (ddd, J = 9.3, 6.3, 6.3 Hz, 1H), 3.17 (s, 3H), 2.97 (ddd, J = 6.3, 6.3, 6.3 Hz, 2H) 1.61−1.25 (m, 6H) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 156.2, 156.1, 137.3, 137.0, 128.4, 128.3, 127.8, 127.8, 127.7, 127.7, 83.1, 65.3, 65.1, 54.1, 40.1, 33.8, 29.0, 22.0 ppm; IR (ATR) 3291, 1689, 1541, 1258, 1227, 1042 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{28}N_2O_5Na$ [M + Na]$^+$ 423.1890, found 423.1901.

***tert*-Butyl *N*-[2-(1-Benzylimidazol-5-yl)-1-methoxyethyl]-carbamate (7u).** Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (br s, 1H), 7.40−7.10 (m, 5H), 6.74 (br s, 1H), 6.13 (d, J = 9.9 Hz, 1H), 5.14−5.05 (m, 1H), 5.05 (s, 2H), 3.34 (s, 3H), 2.89 (d, J = 4.2 Hz, 2H), 1.44 (s, 9H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 155.7, 137.6, 136.7, 136.0, 128.9, 128.2, 127.3, 117.3, 81.6, 79.3, 55.4, 50.8, 33.4, 28.3 ppm; IR (ATR) 3341, 2981, 2925, 1683, 1519, 1365, 1159, 1091, 1047, 741 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{26}N_3O_3$ [M$^+$] 332.1969, found 332.1981.

Fluorenylmethyl *N*-(2-*tert*-Butoxy-1-methoxypropyl)-carbamate (7v). Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$)[a] δ 7.80−7.28[b] (m, 8H), 5.57[c] (d, J = 9.6 Hz, 1H) and 5.45[c] (d, J = 10.5 Hz, 1H), 4.77[c] (dd, J = 10.2, 2.7 Hz, 1H) and 4.65[c] (dd, J = 9.8, 1.7 Hz, 1H), 4.60−4.38[b] (m, 3H), 4.27−4.20[b] (m, 1H), 3.34[c] and 3.32[c] (s, 3H), 1.21[c] and 1.19[c] (s, 9H), 1.09[b] (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.6[c] and 156.1[c], 143.9[c], 143.8[c], 142.9[c], 141.3[c], 127.6[c], 127.2[c], 127.0[c], 127.0[c], 125.0[c], 124.7[c], 120.1[c], 120.0[c], 86.0[c] and 85.0[c], 74.1[c] and 74.0[c], 69.0[c] and 68.1[c], 66.7[b], 56.0[c] and 55.4[c], 47.2[c] and 47.1[c], 28.5[c] and 28.4[c], 19.5[c] and 18.1[c] ppm; IR (ATR) 2974, 2977, 1712, 1495, 1194, 1076, 738 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{29}NO_4Na$ [M + Na]$^+$ 406.1989, found 406.1995. [a]Two diastereomers in a molar ratio of 3:2. [b]Overlapping signals of both diastereomers. [c]Separate signals from both diasteromers.

1-(*N*-Acetylamino)methyltriphenylphosphonium Tetrafluoroborate (4a). Colorless crystals, mp 169−170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88−7.66 (m, 16H), 5.06 (dd, J = 6.3, 3.3 Hz, 2H), 1.80 (d, J = 1.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.7, 135.2 (d, J = 2.9 Hz), 133.9 (d, J = 9.8 Hz), 130.2 (d, J = 12.6 Hz), 116.9 (d, J = 84.3 Hz), 36.9 (d, J = 58.3 Hz), 21.9 ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 21.0 ppm; IR (ATR) 3383, 1685, 1519, 1438, 1260, 1056, 1017 cm^{-1}. Anal. Calcd for $C_{21}H_{21}BF_4NOP$: C, 59.89; H, 5.03; P, 7.35. Found: C, 59.86; H, 4.76; P, 7.46.

***N*-(1-Acetylamino)ethyltriphenylphosphonium Tetrafluoroborate (4b).** Colorless crystals, mp 154−155 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87−7.62 (m, 16H), 5.92 (ddq, J = 9.0, 6.9, 7.2 Hz, 1H), 1.86 (d, J = 0.9 Hz, 3H), 1.66 (dd, J = 17.4, 7.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.6, 135.3 (d, J = 3.0 Hz), 134.1 (d, J = 9.4 Hz), 130.4 (d, J = 12.3 Hz), 116.7 (d, J = 82.0 Hz), 43.7 (d, J = 55.1 Hz), 22.2, 17.3 (d, J = 4.6 Hz) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 28.1 ppm; IR (ATR) 3257, 3044, 1669, 1536, 1441, 1372, 1304, 1108, 1045 cm^{-1}. Anal. Calcd for $C_{22}H_{23}BF_4NOP$: C, 60.72; H, 5.33; P, 7.12. Found: C, 60.46; H, 5.18; P, 7.32.

1-(*N*-Pivaloylamino)ethyltriphenylphosphonium Tetrafluoroborate (4c). Colorless crystals, mp 163−164 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85−7.68 (m, 16H), 5.80 (ddq, J = 7.5, 7.5, 7.5 Hz, 1H), 1.72 (dd, J = 17.6, 7.4 Hz, 3H), 0.91 (s, 9H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 179.3 (d, J = 2.2 Hz), 134.8 (d, J = 2.9 Hz), 134.3 (d, J = 9.3 Hz), 130.0 (d, J = 12.4 Hz), 117.8 (d, J = 82.0 Hz), 45.1 (d, J = 53.5 Hz), 38.4, 26.6, 17.3 (d, J = 4.5 Hz) ppm; ^{31}P NMR (242.8 MHz, $CDCl_3$) δ 29.8 ppm; IR (ATR) 3373, 1660, 1511, 1438, 1184, 1053 cm^{-1}. Anal. Calcd for $C_{25}H_{29}BF_4NOP$: C, 62.91; H, 6.12; P, 6.49. Found: C, 62.88; H, 6.37; P, 6.22.

1-(*N*-Benzyloxycarbonylamino)ethyltriphenylphosphonium Tetrafluoroborate (4d). Colorless crystals, mp 140−142 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80−7.19 (m, 20H), 6.86 (d, J = 9.0 Hz, 1H), 5.65 (ddq, J = 9.0, 6.6, 7.4 Hz, 1H), 4.97 (d, J = 12.3 Hz, 1H), 4.88 (d, J = 12.3 Hz, 1H), 1.72 (dd, J = 17.3, 7.4 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.1, 135.8, 135.2 (d, J = 2.9 Hz), 134.2 (d, J = 9.2 Hz), 130.3 (d, J = 12.2 Hz), 128.4, 128.0, 127.9, 116.6 (d, J = 81.2 Hz), 67.3, 46.7 (d, J = 55.0 Hz), 17.4 (d, J = 5.3 Hz) ppm; ^{31}P NMR (242.8 MHz, $CDCl_3$) δ 27.2 ppm; IR (ATR) 3470, 1703, 1409, 1107 cm^{-1}. Anal. Calcd for $C_{28}H_{27}BF_4NO_2P$: C, 63.78; H, 5.16; P, 5.87. Found: C, 63.35; H, 5.23; P, 5.91.

1-(*N*-Formylamino)ethyltriphenylphosphonium Tetrafluoroborate (4e). Colorless crystals, mp 121−122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.91−7.67 (m, 16H), 6.05 (ddq, J = 9.3, 7.5, 7.2 Hz, 1H), 1.65 (dd, J = 17.1, 7.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 162.2, 135.5 (d, J = 2.8 Hz), 134.1 (d, J = 9.4 Hz), 130.6 (d, J = 12.4 Hz), 116.2 (d, J = 82.4 Hz), 41.2 (d, J = 57.7 Hz), 17.2 (d, J = 4.3 Hz) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 27.6 ppm; IR (ATR) 3174, 3009, 1661, 1525, 1438, 1105, 1047 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{21}NOP$ [M$^+$] 334.1355, found 334.1365.

1-(*N*-Benzyloxycarbonylamino)-2-phenylethyltriphenylphosphonium Tetrafluoroborate (4g). Colorless crystals, mp 152−154 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82−7.09 (m, 25H), 7.03 (d, J = 9.3 Hz, 1H), 5.75−5.63 (m, 1H), 4.86 (d, J = 12.6 Hz, 1H), 4.78 (d, J = 12.6 Hz, 1H), 3.40 (ddd, J = 14.4, 11.1, 8.3 Hz, 1H), 3.14 (ddd, J = 14.0, 4.8, 4.0 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.3 (d, J = 3.1 Hz), 135.9, 135.3 (d, J = 3.1 Hz), 134.2 (d, J = 9.4 Hz), 130.5 (d, J = 12.2 Hz), 129.1, 128.8, 128.3, 127.8, 127.7, 127.7, 127.5, 116.6 (d, J = 81.3 Hz), 67.1, 52.7 (d, J = 51.5 Hz), 37.0 (d, J = 7.2 Hz) ppm; ^{31}P NMR (242.8 MHz, $CDCl_3$) δ 26.5 ppm; IR (ATR) 3329, 1720, 1522, 1439, 1236, 1109, 1061 cm^{-1}. Anal. Calcd for $C_{34}H_{31}BF_4NO_2P$: C, 67.68; H, 5.18; P, 5.13. Found: C, 67.49; H, 5.61; P, 4.71.

1-(*N*-Acetylamino)phenylmethyltriphenylphosphonium Tetrafluoroborate (4h). Colorless crystals, mp 221−222 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (d, J = 9.3 Hz, 1H), 7.90−7.09 (m, 20H), 6.96 (dd, J = 9.8, 9.7 Hz, 1H), 1.99 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.5, 135.3 (d, J = 2.9 Hz), 134.5 (d, J = 9.1 Hz), 130.1 (d, J = 12.3 Hz), 130.1, 130.0, 129.4, 129.3, 115.8 (d, J = 80.6 Hz), 53.9 (d, J = 52.6 Hz), 22.2 ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 24.7 ppm; IR (ATR) 3341, 3291, 1690, 1520, 1438, 1097, 1054 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{25}NOP$ [M$^+$] 410.1668, found 410.1682.

1-(*N*-Benzyloxycarbonylamino)phenylmethyltriphenylphosphonium Tetrafluoroborate (4i). Colorless crystals, mp 177−179 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82−7.04 (m, 26H), 6.64 (dd, J = 9.9, 9.9 Hz, 1H), 4.99 (d, J = 12.3 Hz, 1H), 4.90 (d, J = 12.6 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.2, 135.7, 135.3 (d, J = 2.9 Hz), 134.6 (d, J = 9.1 Hz), 130.2 (d, J = 12.3 Hz), 129.4, 129.4, 129.2, 129.1, 128.3, 127.9, 127.8, 115.8 (d, J = 80.8 Hz), 67.6, 56.5 (d, J = 54.0 Hz) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.9 ppm; IR (ATR) 3314, 1703, 1526, 1438, 1055, 1011 cm^{-1}; HRMS (ESI) calcd for $C_{33}H_{29}NO_2P$ [M$^+$] 502.1930, found 502.1935.

1-(*N*-Benzyloxycarbonylamino)-2-methylpropyltriphenylphosphonium Tetrafluoroborate (4j). Colorless resin. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80−7.15 (m, 20H), 7.01 (d, J = 8.7 Hz, 1H), 5.38−5.29 (m, 1H), 4.88 (d, J = 12.6 Hz, 1H), 4.78 (d, J = 12.6 Hz, 1H), 2.73−2.59 (m, 1H), 1.00 (d, J = 6.3 Hz, 3H), 0.89 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.3, 135.7, 134.8 (d, J = 2.9 Hz), 134.4 (d, J = 9.4 Hz), 130.1 (d, J = 12.3 Hz), 128.3, 127.9, 127.7, 117.9 (d, J = 80.3 Hz), 67.1, 55.7 (d, J = 48.1 Hz), 29.6 (d, J = 6.2 Hz), 21.2 (d, J = 4.7 Hz), 19.2 (d, J = 7.7 Hz) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 27.5 ppm; IR (ATR) 3332, 2970, 1713, 1518, 1438, 1233, 1054 cm^{-1}. Anal. Calcd for $C_{30}H_{31}BF_4NO_2P{\cdot}H_2O$: C, 62.84; H, 5.80; P, 5.40. Found: C, 62.63; H, 5.82; P, 5.24.

1-(*N*-*tert*-Butoxycarbonylamino)-2-methylpropyltriphenylphosphonium Tetrafluoroborate (4k). Colorless crystals, mp 116−117 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85−7.62 (m, 15H), 6.59 (d, J = 9.0 Hz, 1H), 5.31 (ddd, J = 8.8, 8.8, 8.8 Hz, 1H), 2.70−2.54 (m, 1H), 1.19 (s, 9H), 0.98 (d, J = 6.6 Hz, 3H), 0.90 (d, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 155.5, 134.7, 134.6 (d, J = 9.1 Hz),

130.0 (d, J = 12.2 Hz), 118.7 (d, J = 80.1 Hz), 80.8, 55.1 (d, J = 46.7 Hz), 29.5 (d, J = 6.7 Hz), 27.8, 21.2 (d, J = 4.3 Hz), 19.2 (d, J = 8.0 Hz) ppm; ^{31}P NMR (242.8 MHz, $CDCl_3$) δ 27.7 ppm; IR (ATR) 3346, 2976, 1702, 1508, 1438, 1250, 1154, 1054 cm^{-1}. Anal. Calcd for $2C_{27}H_{33}BF_4NO_2P{\cdot}H_2O$: C, 61.15; H, 6.46; P, 5.84. Found: C, 61.09; H, 6.30; P, 5.43.

1-(*N*-Benzyloxycarbonylamino)-3-methylbutyltriphenylphosphonium Tetrafluoroborate (4l). Colorless crystals, mp 93−94 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80−7.19 (m, 20H), 6.90 (d, J = 9.3 Hz, 1H), 5.64−5.51 (m, 1H), 5.02 (d, J = 12.6 Hz, 1H), 4.87 (d, J = 12.6 Hz, 1H), 2.34−2.20 (m, 1H), 1.98−1.83 (m, 1H), 1.45−1.32 (m, 1H), 0.95 (d, J = 6.9 Hz, 3H), 0.93 (d, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.5 (d, J = 3.2 Hz), 135.9, 135.2 (d, J = 2.9 Hz), 134.0 (d, J = 9.2 Hz), 130.3 (d, J = 12.2 Hz), 128.3, 127.9, 127.8, 116.6 (d, J = 81.4 Hz), 67.3, 49.5 (d, J = 53.8 Hz), 39.5 (d, J = 4.3 Hz), 25.3 (d, J = 12.2 Hz), 22.2, 20.8 ppm; ^{31}P NMR (242.8 MHz, $CDCl_3$) δ 26.2 ppm; IR (ATR) 3315, 2957, 1698, 1525, 1344, 1223, 1045 cm^{-1}. Anal. Calcd for $2C_{31}H_{33}BF_4NO_2P{\cdot}H_2O$: C, 64.37; H, 5.93. Found: C, 64.09; H, 5.96.

***N*-Benzyloxycarbonyl-2-pyrolidinyltriphenylphosphonium Tetrafluoroborate (4m).** Colorless crystals, mp 88−90 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77−7.07 (m, 20H), 6.15−5.79 (m, 1H), 4.81 (d, J = 12.7 Hz, 1H), 4.73 (d, J = 12.6 Hz, 1H); 3.71−3.56 (m, 1H), 3.31−3.02 (m, 1H), 2.89−2.60 (m, 1H), 2.31−2.07 (m, 1H), 2.07−1.84 (m, 1H), 1.71−1.40 (m, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 154.7 (d, J = 1.4 Hz), 135.2, 134.7 (d, J = 2.9 Hz), 134.1 (d, J = 9.2 Hz), 129.9 (d, J = 12.2 Hz), 128.4, 128.1, 128.0, 117.5 (d, J = 82.5 Hz), 67.7, 55.6 (d, J = 55.3 Hz), 47.9, 30.3, 24.2 ppm; ^{31}P NMR (242.8 MHz, $CDCl_3$) δ 27.2 ppm; IR (ATR) 3064, 1698, 1485, 1439, 1357, 1191, 1109, 1058 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{29}NO_2P$ [M$^+$] 466.1930, found 466.1940.

1-(*N*-Benzyloxycarbonylamino)-2-carbamoylethyltriphenylphosphonium Tetrafluoroborate (4n). Colorless crystals, mp 151−152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84−7.10 (m, 20H), 6.86 (d, J = 9.9 Hz, 1H), 6.85 (s, 1H), 6.11−5.98 (m, 1H), 5.49 (s, 1H), 4.92 (d, J = 12.3 Hz, 1H), 4.80 (d, J = 12.3 Hz, 1H), 3.21 (ddd, J = 15.3, 8.8, 5.8 Hz, 1H), 2.91−2.75 (m, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 170.2, 155.7 (d, J = 4.2 Hz), 135.6, 135.3 (d, J = 2.9 Hz), 134.4 (d, J = 9.4 Hz), 130.4 (d, J = 12.4 Hz), 128.4, 128.2, 128.1, 116.4 (d, J = 81.7 Hz), 67.6, 48.8 (d, J = 56.9 Hz), 36.4 ppm; ^{31}P NMR (242.8 MHz, $CDCl_3$) δ 27.1 ppm; IR (ATR) 3361, 1722, 1682, 1525, 1439, 1255, 1108, 1058 cm^{-1}. HRMS (FD) calcd for $C_{29}H_{28}N_2O_3P$ [M$^+$] 483.1838, found 483.1814.

1-(*N*-Benzyloxycarbonylamino)-3-carbamoylpropyltriphenylphosphonium Tetrafluoroborate (4o). Colorless crystals, mp 122−124 °C; ^{1}H NMR (300 MHz, CD_3CN) δ 7.91−7.19 (m, 20H), 6.30 (d, J = 9.9 Hz, 1H), 6.23 (s, 1H), 5.98−5.80 (m, 1H), 5.86 (s, 1H), 5.09 (d, J = 12.6 Hz, 1H), 4.97 (d, J = 12.3 Hz, 1H), 2.44−2.35 (m, 2H), 2.35−2.25 (m, 1H), 1.82−1.67 (m, 1H) ppm; ^{13}C NMR (75.5 MHz, CD_3CN) δ 174.3, 157.4 (d, J = 5.1 Hz), 137.4, 136.4 (d, J = 3.0 Hz), 135.4 (d, J = 9.5 Hz), 131.1 (d, J = 12.3 Hz), 129.6, 129.2, 128.8, 117.6 (d, J = 82.7 Hz), 68.3, 49.0 (d, J = 60.6 Hz), 30.2, 27.0 ppm; ^{31}P NMR (242.8 MHz, $CDCl_3$) δ 26.3 ppm; IR (ATR) 3367, 1716, 1673, 1525, 1439, 1241, 1109, 1058 cm^{-1}. Anal. Calcd for $C_{30}H_{30}BF_4N_2O_3P$: C, 61.66; H, 5.17. Found: C, 61.79; H, 5.49.

1-(*N*-Benzyloxycarbonylamino)-2-*tert*-butoxyethyltriphenylphosphonium Tetrafluoroborate (4p). Colorless crystals, mp 146−147 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80−7.11 (m, 20H), 7.02 (d, J = 9.3 Hz, 1H), 5.83−5.63 (m, 1H), 4.89 (d, J = 12.3 Hz, 1H), 4.76 (d, J = 12.6 Hz, 1H), 4.05 (ddd, J = 10.4, 10.4, 10.4 Hz, 1H), 3.89 (ddd, J = 29.1, 9.0, 5.4 Hz, 1H), 0.78 (s, 9H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.0, 135.6, 134.7 (d, J = 9.5 Hz), 134.6, 129.7 (d, J = 12.5 Hz), 128.3, 128.0, 127.8, 117.9 (d, J = 82.4 Hz), 75.1, 67.2, 59.2, 51.9 (d, J = 51.8 Hz), 26.6 ppm; ^{31}P NMR (242.8 MHz, $CDCl_3$) δ 32.0 ppm; IR (ATR) 3304, 2981, 1716, 1519, 1438, 1230, 1074 cm^{-1}. Anal. Calcd for $C_{32}H_{35}BF_4NO_3P$: C, 64.12; H, 5.89; P, 5.17. Found: C, 63.83; H, 5.87; P, 4.79.

1-(*N*-Benzyloxycarbonylamino)-2-*tert*-butoxycarbonylethyltriphenylphosphonium Tetrafluoroborate (4q). Colorless resin. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83−7.13 (m, 20H), 7.07 (d, J = 8.7 Hz, 1H), 6.06 (m, 1H), 4.85 (d, J = 12.6 Hz, 1H), 4.76 (d, J = 12.3 Hz, 1H), 3.29−3.06 (m, 2H), 1.23 (s, 9H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.8 (d, J = 8.7 Hz), 156.0, 135.6, 134.8 (d, J = 2.8 Hz), 134.7 (d, J = 9.4 Hz), 130.0 (d, J = 12.4 Hz), 128.4, 128.0, 127.9, 117.3 (d, J = 82.1 Hz), 82.4, 67.2, 47.3 (d, J = 54.7 Hz), 37.1 (d, J = 6.7 Hz), 27.7 ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 29.1 ppm; IR (ATR) 3329, 2981, 1721, 1523, 1439, 1232, 1051 cm^{-1}; HRMS (FD) calcd for $C_{33}H_{35}NO_4P$ [M$^+$] 540.2304, found 540.2308.

1-(*N*-Benzyloxycarbonylamino)-3-*tert*-butoxycarbonylpropyltriphenylphosphonium Tetrafluoroborate (4r). Colorless crystals, mp 84−86 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83−7.19 (m, 20H), 6.79 (d, J = 9.6 Hz, 1H), 5.89−5.75 (m, 1H), 5.01 (d, J = 12.6 Hz, 1H), 4.90 (d, J = 12.3 Hz, 1H), 2.67−2.42 (m, 2H), 2.25−2.02 (m, 2H), 1.42 (s, 9H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.9, 156.5 (d, J = 3.0 Hz), 136.0, 135.1 (d, J = 2.7 Hz), 134.1 (d, J = 9.4 Hz), 130.3 (d, J = 12.4 Hz), 128.3, 127.8, 127.7, 116.5 (d, J = 81.5 Hz), 81.2, 67.2, 48.8 (d, J = 56.8 Hz), 30.1 (d, J = 13.7 Hz), 27.9, 26.1 (d, J = 8.1 Hz) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 26.9 ppm; IR (ATR) 3304, 1717, 1520, 1439, 1230, 1074 cm^{-1}. Anal. Calcd for $C_{34}H_{37}BF_4NO_4P$: C, 63.66; H, 5.81; P, 4.83. Found: C, 63.30; H, 6.14; P, 5.11.

1-(*N*-Benzyloxycarbonylamino)-2-(4-benzyloxyphenyl)-ethyltriphenylphosphonium Tetrafluoroborate (4s). Colorless crystals, mp 139−140 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81−6.78 (m, 29H), 7.00 (d, J = 9.3 Hz, 1H), 5.64 (ddd, J = 19.0, 9.3, 3.2 Hz, 1H), 4.96 (s, 2H), 4.86 (d, J = 12.6 Hz, 1H), 4.78 (d, J = 12.6 Hz, 1H), 3.33 (ddd, J = 14.3, 10.7, 8.9 Hz, 1H), 3.10 (ddd, J = 14.4, 4.2, 4.2 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 158.1, 156.3 (d, J = 3.4 Hz), 136.8, 135.9, 135.2 (d, J = 2.7 Hz), 134.2 (d, J = 9.4 Hz), 130.4 (d, J = 12.0 Hz), 128.5, 128.3, 127.9, 127.8, 127.6, 127.4, 127.1, 127.0, 116.7 (d, J = 80.5 Hz), 115.2, 69.8, 67.0, 52.8 (d, J = 50.0 Hz), 36.2 (d, J = 7.8 Hz) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 26.2 ppm; IR (ATR) 3139, 1709, 1511, 1439, 1331, 1246, 1057, 1036 cm^{-1}. Anal. Calcd for $C_{41}H_{37}BF_4NO_3P$: C, 69.40; H, 5.26; P, 4.37. Found: C, 69.00; H, 5.48; P, 4.21.

1-Benzyl-5-[2-(*N*-*tert*-butoxycarbonylamino)-2-triphenylphosphonioethyl]imidazolium Ditetrafluoroborate (4u). (Prepared *in situ*) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (br s, 1H), 7.84−7.26 (m, 21H), 6.38 (d, J = 9.0 Hz, 1H), 5.93−5.78 (m, 1H), 5.24 (s, 2H), 3.35−3.21 (m, 2H), 1.08 (s, 9H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 154.9 (d, J = 3.2 Hz), 135.4, 134.3 (d, J = 9.6 Hz), 132.8, 130.5 (d, J = 12.4 Hz), 129.3, 129.2, 128.9, 128.7, 128.6, 122.1, 117.8 (d, J = 85.9 Hz), 81.5, 53.4, 48.3 (d, J = 55.1 Hz), 27.6, 26.2 (d, J = 11.2 Hz) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 26.2 ppm.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra of *N*-(1-methoxyalkyl)amides **7c**, **7n**−**7v** and 1-(*N*-acylamino)alkyltriphenylphosphonium salts **4**; IR spectra and ^{31}P NMR of selected 1-(*N*-acylamino)alkyltriphenylphosphonium salts. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The financial help of the Ministry of Science and Higher Education of Poland (Grant No. N N204 165636) is gratefully acknowledged.

■ REFERENCES

(1) (a) Zaug, H. E. *Synthesis* **1970**, 49−73. (b) Zaug, H. E. *Synthesis* **1984**, 85−110. Zaug, H. E. *Synthesis* **1984**, 181−212.

(2) Katrizky, A. R.; Manju, K.; Singh, S. K.; Meher, N. K. *Tetrahedron* **2005**, *61*, 2555−2581.
(3) Katrizky, A. R.; Lan, X.; Yang, J. Z.; Denisko, O. V. *Chem. Rev.* **1998**, *98*, 409−548.
(4) Petrini, M. *Chem. Rev.* **2005**, *105*, 3949−3977.
(5) Zoller, U.; Ben-Ishai, D. *Tetrahedron* **1975**, *31*, 863−866.
(6) (a) Caputo, R.; Cassano, E.; Longobardo, L.; Palumbo, G. *Tetrahedron* **1995**, *51*, 12337−12350. (b) Caputo, R.; Cassano, E.; Longobardo, L.; Palumbo, G. *Tetrahedron Lett.* **1995**, *36*, 167−168.
(7) Marianacci, O.; Micheletti, G.; Bernardi, L.; Fini, F.; Fochi, M.; Pettersen, D.; Sgarzani, V.; Ricci, A. *Chem.—Eur. J.* **2007**, *13*, 8338−8351.
(8) Das, B.; Damodar, K.; Bhunia, N. *J. Org. Chem.* **2009**, *74*, 5607−5609.
(9) Katrizky, A. R.; Pernak, J.; Fan, W.-Q.; Saczewski, F. *J. Org. Chem.* **1991**, *56*, 4439−4443.
(10) Katrizky, A. R.; Fan, W.-Q.; Black, M.; Pernak, J. *J. Org. Chem.* **1992**, *57*, 547−549.
(11) Katrizky, A. R.; Lan, X.; Yang, J. Z.; Fan, W.-Q. *Synthesis* **1994**, 445−456.
(12) Mazurkiewicz, R.; Październiok-Holewa, A.; Grymel, M. *Tetrahedron Lett.* **2008**, *49*, 1801−1803.
(13) Mazurkiewicz, R.; Październiok-Holewa, A.; Grymel, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **2009**, *184*, 1017−1027.
(14) Mazurkiewicz, R.; Październiok-Holewa, A.; Orlińska, B.; Stecko, S. *Tetrahedron Lett.* **2009**, *50*, 4606−4609.
(15) Mazurkiewicz, R.; Pierwocha, A. *Monatsh. Chem.* **1996**, *127*, 219−225.
(16) Mazurkiewicz, R.; Pierwocha, A. *Monatsh. Chem.* **1997**, *128*, 893−900.
(17) Mazurkiewicz, R.; Październiok-Holewa, A.; Kononienko, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2010**, *185*, 1986−1992.
(18) Mazurkiewicz, R.; Adamek, J.; Mrowiec-Białoń, J.; Październiok-Holewa, A. *Thermochim. Acta* **2011**, *512*, 22−27.
(19) Mazurkiewicz, R.; Październiok-Holewa, A.; Adamek, J.; Zielińska, K.; Piernikarczyk, K. *Arkivoc*, in press.
(20) Linstead, R. P.; Shephard, B. R.; Weedon, B. C. L. *J. Chem. Soc.* **1951**, 2854−2858.
(21) (a) Horikawa, H.; Iwasaki, T.; Matsumoto, K.; Miyoshi, M. *Tetrahedron Lett.* **1976**, *17*, 191−194. (b) Iwasaki, T.; Horikawa, H.; Matsumoto, K.; Miyoshi, M. *J. Org. Chem.* **1977**, *42*, 2419−2423. (c) Iwasaki, T.; Horikawa, H.; Matsumoto, K.; Miyoshi, M. *J. Org. Chem.* **1979**, *44*, 1552−1554. (d) Iwasaki, T.; Horikawa, H.; Matsumoto, K. *Bull. Soc. Chem. Jpn* **1979**, *52*, 826−830.
(22) Lund, H.; Hammerlich, O. *Organic Electrochemistry*; Marcel Dekker: New York, 2001.
(23) Tajima, T.; Kurihara, H.; Fuchigami, T. *J. Am. Chem. Soc.* **2007**, *129*, 6680−6681.
(24) Matsumura, Y.; Tanaka, T.; Wanyoike, G. N.; Maki, T.; Onomura, O. *J. Electroanal. Chem.* **2001**, *507*, 71−74.
(25) Matsumura, Y.; Wanyoike, G. N.; Onomura, O.; Maki, T. *Electrochim. Acta* **2003**, *48*, 2957−2966.
(26) Wanyoike, G. N.; Onomura, O.; Maki, T.; Matsumura, Y. *Org. Lett.* **2002**, *11*, 1875−1877.
(27) Onomura, O. *Yakugaku Zasshi* **2002**, *122*, 983−987.
(28) Zietlow, A.; Steckhan, E. *J. Org. Chem.* **1994**, *59*, 5658−5661.
(29) Kardasis, G.; Brungs, P.; Steckhan, E. *Tetrahedron* **1998**, *54*, 3471−3478.
(30) Seebach, D.; Charczuk, R.; Gerber, Ch.; Renaud, P. *Helv. Chim. Acta* **1989**, *72*, 401−425.
(31) Matsumura, Y.; Shirakawa, Y.; Satoh, Y.; Umino, M.; Tanaka, T.; Maki, T.; Onomura, O. *Org. Lett.* **2000**, *2*, 1689−1691.
(32) Wieber, G. M.; Hegedus, L. S.; Akermark, B.; Michalson, E. T. *J. Org. Chem.* **1989**, *54*, 4649−4653.
(33) Oftring, A.; Hahn, E.; Fikentscher, R. German Patent 3,520, 829, 1986.
(34) WSS: Spectral data were obtained from Wiley Subscription Services, Inc. (U.S.).
(35) Matsuo, J.; Tanaki, Y.; Kido, A.; Ishibashi, H. *Chem. Commun.* **2006**, 2896−2898.
(36) Chorev, M.; MacDonald, S. A.; Goodman, M. *J. Org. Chem.* **1984**, *49*, 821−827.
(37) Phan, X. T.; Shannon, P. J. *J. Org. Chem.* **1983**, *48*, 5164−5170.
(38) Krebs, A.; Bolm, C. *Tetrahedron* **2011**, *67*, 4055−4060.
(39) Harding, E. K.; Liu, L. T.; Farrar, D. G.; Coleman, M. T.; Tansey, S. K. *Synth. Commun.* **1991**, *21*, 1409−1417.
(40) Kise, N.; Ueda, N. *J. Org. Chem.* **1999**, *64*, 7511−7514.
(41) Shono, T.; Matsumura, Y.; Uchida, K.; Tsubata, K.; Makino, A. *J. Org. Chem.* **1984**, *49*, 300−304.