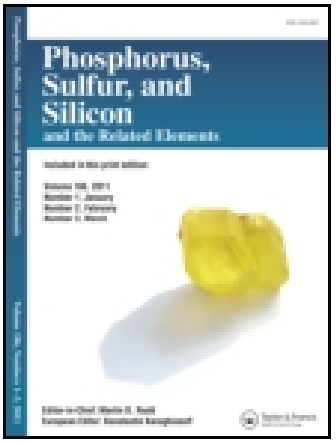

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

A Simple and Catalyst-Free One-Pot Synthesis of α-Aminophosphonates in Polyethylene Glycol

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Accepted author version posted online: 04 Jan 2012.Published online: 07 Jun 2012.

To cite this article: M. Anil Kumar & Kap Duk Lee (2012) A Simple and Catalyst-Free One-Pot Synthesis of α-Aminophosphonates in Polyethylene Glycol, Phosphorus, Sulfur, and Silicon and the Related Elements, 187:8, 899-905, DOI: 10.1080/10426507.2011.645174

To link to this article: http://dx.doi.org/10.1080/10426507.2011.645174

Phosphorus, Sulfur, and Silicon, 187:899–905, 2012

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2011.645174

A SIMPLE AND CATALYST-FREE ONE-POT SYNTHESIS OF α-AMINOPHOSPHONATES IN POLYETHYLENE GLYCOL

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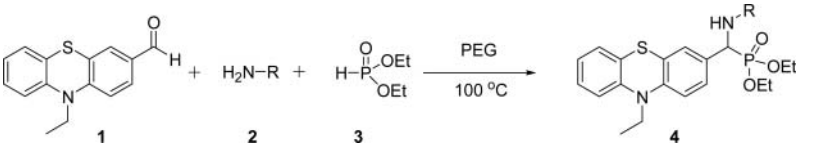
Department of Nanomaterial Chemistry, Dongguk University, Gyeongju, South Korea

GRAPHICAL ABSTRACT



Abstract *A simple and efficient method has been developed for the one-pot synthesis of α-aminophosphonates using polyethylene glycol (PEG) as a green reaction media.*

Keywords α-Aminophosphonates; PEG; three-component reaction

INTRODUCTION

Conventional synthetic procedures invariably use organic solvents as a reaction media to provide a homogeneous phase, which allows uniform molecular interactions to facilitate the reaction efficiently. Generally, organic solvents are harmful to the environment and human being. Development of a synthetic protocol that is nature-friendly, simple, efficient and cost effective remains an ever-challenging objective.[1]

α-Aminophosphonates, being structural analogs to α-amino acids, have received considerable interest as pharmacological agents,[2] peptide mimetics,[3] enzyme inhibitors,[4] and also play an important role in hapten design for antibody generation.[5] They also have a wide range of antiviral[6] and antifungal properties and are extensively used as insecticides and herbicides.[7] Therefore, greater attention has been paid to these compounds due to their promising biological activity. Among the various synthetic methods reported for the synthesis of α-aminophosphonates, a one-pot reaction starting from aldehyde, amine, and dialkyl phosphite is the most direct and efficient one that avoids isolating an imine as an intermediate.[8] A variety of Lewis and Brønsted acid catalysts have been reported for the synthesis of α-aminophosphonates.[9] Ionic liquids have also been used as a reaction media for three component synthesis of α-aminophosphonates.[10] Recently, $CoCl_2.6H_2O$,[11] $[Yb(PFO)_3]$,[12] $NanoFe_3O_4$,[13] $KHSO_4$,[14] and $ZrOCl_2.8H_2O$[15] have also been reported for the synthesis of α-aminophosphonates.

Received 26 September 2011; accepted 23 November 2011.
This work was supported by the Dongguk University Research Fund of 2011.
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Table 1 The effect of various solvents in one-pot synthesis of **4a**

Solvent	Time (h)	Yield (%)[a]
PEG	6	91
Toluene	12	55
Ethanol	12	40
THF	12	25

[a]Isolated yields.

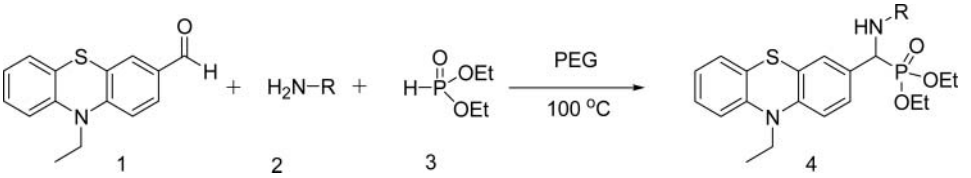
Keeping in view the disadvantages associated in few of the earlier protocols, as well as an increasing importance of α-aminophosphonates in pharmaceutical/industrial chemistry, still there is a scope for the development of an efficient and environmentally benign protocol for the synthesis of α-aminophosphonates.

Recently, polyethylene glycol (PEG) has received considerable attention in organic synthesis as an alternative green reaction media with unique properties such as thermal stability, nonvolatility, commercial availability, and recyclability.[16] On the other hand, PEG is nontoxic, inexpensive, nonhalogenated, and water soluble, which facilitates its removal from the reaction product. Consequently, PEG has been utilized as a green reaction media for various transformations such as carbon–carbon and carbon–heteroatom coupling,[17] substitution,[18] oxidation,[19] addition,[20] and reduction reactions.[21]

Owing to the numerous advantages associated with this cheap and green media, herein we wish to report a green and efficient protocol for the synthesis of α-aminophosphonates using PEG-400 as a reaction medium without adding any catalyst. To the best of our knowledge, there are no reports for the synthesis of α-aminophosphonates using PEG-400 as a reaction medium under catalyst-free conditions.

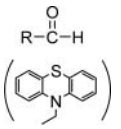
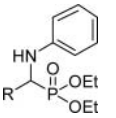
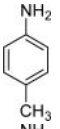
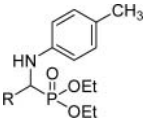
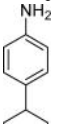
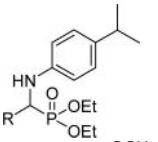
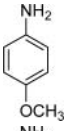
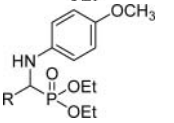
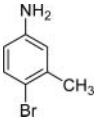
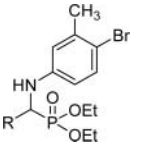
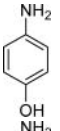
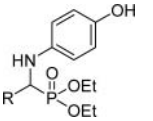
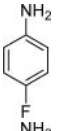
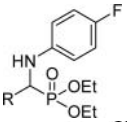
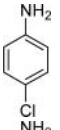
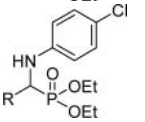
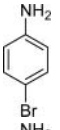
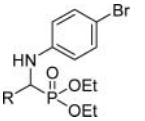
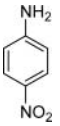
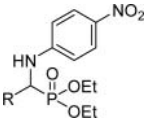
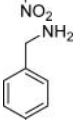
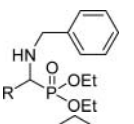
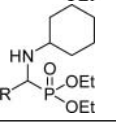
RESULTS AND DISCUSSION

We first attempted the coupling of 10-ethyl-10*H*-phenothiazine-3-carbaldehyde, aniline, and diethyl phosphite in PEG-400 (1 g). Though the reaction was complete in 24 h at room temperature, the corresponding product was obtained in low yield (30%). However, the yield was dramatically increased by increasing the temperature to 100 °C. Under optimized conditions, the reaction proceeds well at 100 °C and the desired α-aminophosphonate **4a** was obtained in 91% yield (Scheme 1). Next, we carried out the above reaction in different solvents such as toluene, ethanol, THF, and PEG-400 (Table 1) to know the efficiency of PEG-400. Interestingly, PEG-400 was found to be more effective in the synthesis of **4a** in terms of reaction time (6 h) and yields (91%). PEG-400 not only acts as the solvent but also accelerates the imine formation as well as phosphite nucleophilic addition to the imine



Scheme 1

Table 2 Synthesis of α-aminophosphonates using PEG as a reaction medium

Entry	Aldehyde	Amine	Product	Yield (%)[a]
a				91
b				88
c				90
d				89
e				87
f				86
g				92
h				93
i				90
j				88
k				82
l				80

[a]Isolated Yields.

carbon by increasing its electrophilicity through hydrogen bonding by its hydroxyl group with the imine nitrogen.

The scope and generality of the PEG-400 promoted three-component reaction, was examined with various structurally diverse amines and diethyl phosphite. The results are summarized in Table 2. This method works well not only with aromatic amines but also with aliphatic amines such as benzyl amine and cyclohexylamine. All compounds were characterized by ^{1}H, ^{13}C, ^{31}P NMR, IR, and mass spectroscopy. ^{1}H NMR spectra of compounds **4a–j** showed doublet in the region of 4.55–4.67 ppm (J = 21.4–24.2 Hz) that is a characteristic peak for the methine proton.

CONCLUSION

In summary, we have developed a simple and efficient methodology for the one-pot synthesis of a novel series of α-aminophosphonates under catalyst-free conditions using PEG-400 as an environmentally benign medium. In this reaction, PEG-400 acts as an efficient "green" promoter. The advantages of this method are simple and mild experimental conditions, avoiding hazardous solvents and toxic organic reagents.

EXPERIMENTAL SECTION

The 10-Ethyl-10*H*-phenothiazine-3-carbaldehyde was prepared by the ethylation[22] followed by formylation of phenothiazine.[23] Melting points were determined in open capillaries using Electrothermal (IA 9100) digital melting point apparatus and are uncorrected. IR spectra were recorded on Bruker (Tensor 37) FT-IR spectrometer using KBr pellets. ***^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a VARIAN 200 MHz instrument with an internal standard of tetramethylsilane. Mass spectra (EI) were recorded on JEOL JMS-700 mass spectrometer.

Experimental Procedure

A mixture of 10-ethyl-10*H*-phenothiazine-3-carbaldehyde (0.255g, 1 mmol), amine (0.093g, 1 mmol), and diethyl phosphite (0.179g, 1.3 mmol) was added to PEG (1 g) and the mixture was heated to 100 °C and stirred for 6–7 h. After completion of the reaction as monitored by TLC, the mixture was then diluted with cold water and the resulting precipitate was filtered and washed with water. The residue was dried and purified by column chromatography over silica gel (ethyl acetate/hexane, 70–230 mesh) to give pure α-aminophosphonate. In the case of oily products (**4k** and **4l**), the products were extracted with ethyl acetate, washed with water, and dried over sodium sulfate. Removal of the solvent followed by purification on column chromatography over silica gel afforded pure α-aminophosphonate.

Entry 4a: pale yellow solid; Mp: 164–165 °C; IR (KBr): 3308, 2982, 1600, 1266, 1024, 963 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.17 (t, J = 7.4 Hz, 3H), 1.29 (t, J = 6.8 Hz, 3H), 1.38 (t, J = 6.8 Hz, 3H), 3.68–4.20 (m, 6H), 4.63 (d, J = 24.4 Hz, 1H), 6.55–6.60 (m, 2H), 6.65–6.91 (m, 4H), 7.06–7.24 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 12.8, 16.3, 41.7, 55.1 (d, $J_{P\text{-}C}$ = 150.2 Hz), 63.2 (d, $J_{P\text{-}C}$ = 7.6 Hz), 113.8, 114.9, 118.4, 122.3, 123.8, 124.5, 126.5, 127.2, 129.1, 129.6, 144.5, 146.0, 146.3; ^{31}P NMR ($CDCl_3$): δ 23.6; MS (EI) *m/z*: 468 (M^+); Anal. calcd for $C_{25}H_{29}N_2O_3PS$: C, 64.08; H, 6.24; N, 5.98; Found: C, 64.12; H, 6.18; N, 5.95.

Entry 4b: pale yellow solid; Mp: 159–161 °C; IR (KBr): 3316, 2982, 1525, 1273, 1022, 989 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.17 (t, $J = 7.8$ Hz, 3H), 1.25–1.42 (m, 6H), 2.18 (s, 3H), 3.72–4.18 (m, 6H), 4.61 (d, $J = 21.4$ Hz, 2H), 6.49 (d, $J = 8.0$ Hz, 2H), 6.77–6.93 (m, 5H), 7.07–7.24 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 12.8, 16.3, 20.3, 41.7, 55.4 (d, $J_{P\text{-}C} = 151.7$ Hz), 63.2, 113.9, 114.9, 122.3, 123.9, 124.4, 126.5, 127.2, 127.6, 129.6, 143.7, 144.0, 144.6; ^{31}P NMR ($CDCl_3$): δ 23.7; MS (EI) *m/z*: 482 (M^+); Anal. calcd for $C_{26}H_{31}N_2O_3PS$: C, 64.71; H, 6.47; N, 5.80; Found: C, 64.79; H, 6.40; N, 5.75.

Entry 4c: light brown solid; Mp: 60–62 °C; IR (KBr): 3301, 2956, 1522, 1235, 1022, 967 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.13–1.20 (m, 9H), 1.28 (t, $J = 7.6$ Hz, 3H), 1.38 (t, $J = 6.2$ Hz, 3H), 2.64–2.85 (m, 1H), 3.68–4.20 (m, 7H), 4.60 (d, $J = 23.6$ Hz, 1H), 6.51 (d, $J = 8.0$ Hz, 2H), 6.78–6.92 (m, 3H), 6.97 (d, $J = 8.0$ Hz, 2H), 7.08–7.23 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 12.8, 16.3, 24.1, 33.1, 41.8, 55.4 (d, $J_{P\text{-}C} = 151.7$ Hz), 63.2 (d, $J_{P\text{-}C} = 6.0$ Hz), 113.8, 114.9, 122.3, 123.9, 124.4, 126.5, 127.0, 127.2, 127.3, 129.9, 138.9, 144.0, 144.3, 144.6; ^{31}P NMR ($CDCl_3$): δ 23.7; MS (EI) *m/z*: 510 (M^+); Anal. calcd for $C_{28}H_{35}N_2O_3PS$: C, 65.86; H, 6.91; N, 5.49; Found: C, 65.81; H, 6.90; N, 5.45.

Entry 4d: light brown solid; Mp: 132–134 °C; IR (KBr): 3302, 2977, 1512, 1464, 1208, 1020, 975 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.17 (t, $J = 6.6$ Hz, 3H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.38 (t, $J = 7.0$ Hz, 3H), 3.68 (s, 3H), 3.78–4.16 (m, 6H), 4.56 (d, $J = 23.8$ Hz, 1H), 6.50–6.56 (m, 2H), 6.65–6.92 (m, 5H), 7.07–7.24 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 12.8, 16.3, 41.8, 55.6, 56.1 (d, $J_{P\text{-}C} = 150.2$ Hz), 63.2, 114.7, 114.9, 115.2, 122.3, 123.9, 124.5, 126.6, 127.2, 129.8, 140.1, 140.4, 144.6, 152.6; ^{31}P NMR ($CDCl_3$): δ 23.8; MS (EI) *m/z*: 498 (M^+); Anal. calcd for $C_{26}H_{31}N_2O_4PS$: C, 62.63; H, 6.27; N, 5.62; Found: C, 62.69; H, 6.22; N, 5.68.

Entry 4e: yellow solid; Mp: 180–182 °C; IR (KBr): 3311, 2981, 1601, 1212, 1023, 968 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.17 (t, $J = 7.0$ Hz, 3H), 1.29 (t, $J = 6.6$ Hz, 3H), 1.38 (t, $J = 6.8$ Hz, 3H), 2.24 (s, 3H), 3.70–4.19 (m, 7H), 4.56 (d, $J = 24.0$ Hz, 1H), 6.25 (dd, $J = 8.9$, 2.2 Hz, 1H), 6.48 (d, $J = 2.2$ Hz, 1H), 6.77–6.92 (m, 3H), 7.07–7.21 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 12.8, 16.3, 23.0, 41.8, 55.0 (d, $J_{P\text{-}C} = 151.7$ Hz), 63.3, 112.7, 112.9, 114.9, 116.3, 122.3, 123.8, 124.6, 126.4, 126.6, 127.2, 129.2, 132.6, 138.2, 144.5, 144.7, 145.3, 145.6; ^{31}P NMR ($CDCl_3$): δ 23.3; MS (EI) *m/z*: 560 (M^+), 562 (M+2); Anal. calcd for $C_{26}H_{30}BrN_2O_3PS$: C, 55.62; H, 5.39; N, 4.99; Found: C, 55.58; H, 5.33; N, 4.95.

Entry 4f: white solid; Mp: 160-161 °C; IR (KBr): 3268, 2978, 1515, 1240, 1095, 967 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.17 (t, $J = 7.6$ Hz, 3H), 1.28 (t, $J = 7.4$ Hz, 3H), 1.38 (t, $J = 7.4$ Hz, 3H), 3.73–4.18 (m, 6H), 4.55 (d, $J = 24.0$ Hz, 1H), 6.46 (d, $J = 8.4$ Hz, 2H), 6.62 (d, $J = 8.6$ Hz, 2H), 6.76–6.93 (m, 3H), 7.07–7.21 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 12.8, 16.2, 41.7, 56.1 (d, $J_{P\text{-}C} = 154.4$ Hz), 63.4, 114.9, 115.4, 116.1, 122.3, 123.8, 124.3, 126.5, 127.2, 129.6, 139.4, 139.7, 144.5, 149.2; ^{31}P NMR ($CDCl_3$): δ 23.8; MS (EI) *m/z*: 484 (M^+); Anal. calcd for $C_{25}H_{29}N_2O_4PS$: C, 61.97; H, 6.03; N, 5.78; Found: C, 61.94; H, 5.95; N, 5.75.

Entry 4g: pale yellow solid; Mp: 184–186 °C; IR (KBr): 3311, 2985, 1508, 1237, 1024, 970 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.17 (t, $J = 7.6$ Hz, 3H), 1.30 (t, $J = 7.4$ Hz, 3H), 1.39 (t, $J = 6.8$ Hz, 3H), 3.68–4.19 (m, 6H), 4.56 (d, $J = 24.0$ Hz, 1H), 6.46–6.53 (m, 2H), 6.76–6.93 (m, 5H), 7.08–7.22 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 12.8, 16.3, 41.8, 55.8 (d, $J_{P\text{-}C} = 151.7$ Hz), 63.3 (d, $J_{P\text{-}C} = 4.5$ Hz), 114.7, 114.9, 115.4, 115.8, 122.3, 123.8, 124.6, 126.5, 127.2, 129.4, 142.3, 142.6, 144.5, 144.7, 153.9, 158.6; ^{31}P NMR ($CDCl_3$): δ 23.5; MS (EI) *m/z*: 486 (M^+); Anal. calcd for $C_{25}H_{28}FN_2O_3PS$: C, 61.72; H, 5.80; N, 5.76; Found: C, 61.76; H, 5.86; N, 5.70.

Entry 4h: pale yellow solid; Mp:185–186 °C; IR (KBr): 3330, 2981, 1598, 1274, 1054, 986 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.17 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.0 Hz, 3H), 1.39 (t, J = 7.2 Hz, 3H), 3.71–4.19 (m, 6H), 4.57 (d, J = 23.2 Hz, 1H), 6.47–6.53 (m, 2H), 6.78–6.93 (m, 3H), 7.02–7.21 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 12.8, 16.3, 41.8, 55.3 (d, $J_{P\text{-}C}$ = 151.7 Hz), 63.3, 114.9, 122.4, 123.1, 123.8, 124.6, 126.5, 127.3, 129.0, 144.5, 144.6, 144.9; ^{31}P NMR ($CDCl_3$): δ 23.3; MS (EI) *m/z*: 502 (M^+); Anal. calcd for $C_{25}H_{28}ClN_2O_3PS$: C, 59.70; H, 5.61; N, 5.57; Found: C, 59.76; H, 5.55; N, 5.50.

Entry 4i: yellow solid; Mp: 172–174 °C; IR (KBr): 3308, 2981, 1593, 1463, 1235, 1023, 970 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.17 (t, J = 6.8 Hz, 3H), 1.30 (t, J = 7.0 Hz, 3H), 1.39 (t, J = 6.8 Hz, 3H), 3.71–4.19 (m, 6H), 4.56 (d, J = 23.6 Hz, 1H), 6.45 (d, J = 8.4 Hz, 2H), 6.78–6.93 (m, 3H), 7.08–7.21 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 12.8, 16.3, 41.8, 55.1 (d, $J_{P\text{-}C}$ = 151.7 Hz), 63.3, 110.1, 115.0, 115.5, 122.4, 123.8, 124.7, 126.5, 127.3, 129.1, 132.9, 144.5, 144.8, 145.1, 145.4; ^{31}P NMR ($CDCl_3$): δ 23.2; MS (EI) *m/z*: 546 (M^+), 548 (M+2); Anal. calcd for $C_{25}H_{28}BrN_2O_3PS$: C, 54.85; H, 5.16; N, 5.12; Found: C, 54.89; H, 5.10; N, 5.06.

Entry 4j: yellow solid; Mp: 225–226 °C; IR (KBr): 3294, 2928, 1601, 1467, 1231, 1021, 989 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.17 (t, J = 6.8 Hz, 3H), 1.27–1.42 (m, 6H), 3.67–4.17 (m, 6H), 4.67 (dd, J = 23.3, 7.2 Hz, 1H), 5.46–5.55 (m, 1H), 6.55 (d, J = 9.0 Hz, 2H), 6.79–6.94 (m, 3H), 7.07–7.22 (m, 4H), 8.02 (d, J = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 12.8, 16.3, 41.8, 54.6 (d, $J_{P\text{-}C}$ = 153.2 Hz), 63.6 (d, $J_{P\text{-}C}$ = 24.2 Hz), 112.4, 115.1, 122.5, 123.6, 125.1, 126.0, 126.3, 126.5, 126.6, 127.3, 128.2, 139.0, 144.3, 145.1, 151.6, 151.9; ^{31}P NMR ($CDCl_3$): δ 22.3; MS (EI) *m/z*: 513 (M^+); Anal. calcd for $C_{25}H_{28}N_3O_5PS$: C, 58.47; H, 5.50; N, 8.18; Found: C, 58.43; H, 5.43; N, 8.12.

Entry 4k: Viscous liquid; IR (KBr): 3435, 2979, 1495, 1239, 1052, 986 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.18 (t, J = 7.6 Hz, 3H), 1.28 (t, J = 7.4 Hz, 3H), 1.42 (t, J = 7.2 Hz, 3H), 3.52 (d, J = 13.0 Hz, 1H), 3.77–4.16 (m, 8H), 6.82–6.94 (m, 3H), 7.11-7.20 (m, 4H) 7.23-7.34 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 12.8, 16.3, 41.8, 50.8 (d, $J_{P\text{-}C}$ = 16.6 Hz), 58.3 (d, $J_{P\text{-}C}$ = 154.7 Hz), 62.9, 114.8, 114.9, 122.3, 124.0, 124.4, 127.2, 127.5, 127.7, 128.4, 128.7, 138.5, 144.6, 144.7; ^{31}P NMR ($CDCl_3$): δ 25.5; MS (EI) *m/z*: 482 (M^+); Anal. calcd for $C_{26}H_{31}N_2O_3PS$: C, 64.71; H, 6.47; N, 5.80; Found: C, 64.65; H, 6.41; N, 5.74.

Entry 4l: Viscous liquid; IR (KBr): 3456, 2979, 2927, 1494, 1238, 1025, 964 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.01–1.21 (m, 7H), 1.30 (t, J = 7.2 Hz, 3H), 1.41 (t, J = 7.4 Hz, 3H), 1.45–1.89 (m, 8H), 2.26–2.39 (m, 1H), 3.76–4.20 (m, 7H), 6.80–6.94 (m, 3H), 7.10–7.24 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 12.8, 16.3, 24.3, 24.8, 30.0, 31.8, 34.3, 41.7, 53.2 (d, $J_{P\text{-}C}$ = 15.2 Hz), 56.5 (d, $J_{P\text{-}C}$ = 154.7 Hz), 62.6 (d, $J_{P\text{-}C}$ = 7.5 Hz), 63.1 (d, $J_{P\text{-}C}$ = 6.1 Hz), 114.7, 114.9, 122.2, 124.1, 127.1, 127.2, 130.5, 144.4, 144.6; ^{31}P NMR ($CDCl_3$): δ 25.2; MS (EI) *m/z*: 474 (M^+); Anal. calcd for $C_{25}H_{35}N_2O_3PS$: C, 63.27; H, 7.43; N, 5.90; Found: C, 63.21; H, 7.39; N, 5.84.

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