Supplementary Material

Microwave-assisted synthesis of dialkyl ω -azidoalkylphosphonates

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General information, general procedures and copies of NMR

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1. General information

NMR spectra were measured on Bruker Avance II Plus spectrometer (700 MHz for ^1H NMR, 176 MHz for ^{13}C NMR and 283 MHz for ^{31}P NMR) in CDCl_3 solution. ^1H and ^{13}C NMR spectra are referenced according to the residual peak of the solvent based on literature data. ^{31}P NMR chemical shifts are reported in ppm downfield from 85% H_3PO_4 as an external standard. Chemical shift (δ) are reported in ppm and coupling constants (J) in Hz. ^{31}P and ^{13}C NMR spectra were proton-decoupled. The assignment of the signals in ^1H NMR and ^{13}C NMR was supported by two-dimensional experiments (COSY, HMQC). IR spectra were measured on the FT-IR Alpha Bruker (ATR) instrument and were reported in cm^{-1} . Accurate mass measurements were performed by a peak matching technique in FAB positive ion detection mode on the Finnigan MAT 95 double focusing (BE geometry) mass spectrometer (Finnigan MAT, Bremen, Germany). A monomode microwave reactor (CEM Discover SP) equipped with an IntelliVent pressure control system was used. Dynamic method was applied and maximum pressure was set to 250 psi. Temperatures of the reactions mixtures were measured by external infrared sensor. Flash chromatography was performed with a glass column packed with Baker silica gel (30-60 μm). All reagents were purchased from commercial sources and used as obtained. The dialkyl ω -bromoalkylphosphonates **1a-e** - **4a-e** were prepared by the well established methods.

2. General procedure for the preparation of products **5a-e** – **7a-e**

Dialkyl ω -bromoalkylphosphonate (2.0 mmol) was added to the solution of NaN_3 (3.0 mmol, 1.5 eq) in H_2O (3 mL) placed in 10 mL pressure vial, equipped with magnetic stirrer. The reaction was carried under MW conditions. After that reaction mixture was extracted with Et_2O (4×10 mL). The combined organic layers were washed successively with water (5 mL) and brine (5 mL), dried over anhydrous MgSO_4 , and evaporated under reduced pressure. The

rest of the volatile material was removed at 35 °C/27 Pa to give pure product **5-7**. If necessary, product **5-7** was subjected to flash chromatography on silica gel.

Dimethyl 2-azidoethylphosphonate (5a). Colorless oil. Yield 43% (0.154 g). ³¹P NMR (283

MHz, CDCl₃): δ 29.63. ¹H NMR (700 MHz, CDCl₃): δ 3.76 (6 H, d, *J*_{HP}= 10.9 Hz, 2 x CH₃O), 3.56-3.52 (2 H, m, C(2)H₂N₃), 2.09-2.04 (2 H, m, PC(1)H₂). ¹³C NMR (176 MHz, CDCl₃): δ 52.5 (2 d, *J*_{CP}= 6.6 Hz, 2 x CH₃O), 45.2 (d, *J*_{CP}= 2.1 Hz, C(2)H₂N₃), 25.0 (d, *J*_{CP}= 141.1 Hz, PC(1)H₂). **FAB-HRMS:** *m/z* [M + H]⁺ calcd for C₄H₁₁N₃O₃P 180.0538, found 180.0535. **IR** (ATR) ν: 2097 (N₃), 1243 (P=O), 1015 (P-O-C), 818 cm⁻¹.

Dimethyl 3-azidopropylphosphonate [1] (5b). Colorless oil. Yield 68% (0.262 g). ³¹P NMR

(283 MHz, CDCl₃): δ 33.38. ¹H NMR (700 MHz, CDCl₃): δ 3.74 (6 H, d, *J*_{HP}= 10.8 Hz, 2 x CH₃O), 3.37 (2 H, d, *J*_{HH}= 6.6 Hz, C(3)H₂N₃), 1.89-1.79 (4 H, m, PC(1)H₂C(2)H₂). ¹³C NMR (176 MHz, CDCl₃): δ 52.4 (2 d, *J*_{CP}= 6.6 Hz, 2 x CH₃O), 51.4 (d, *J*_{CP}= 16.2 Hz, C(3)H₂N₃), 22.3 (d, *J*_{CP}= 4.7 Hz, C(2)H₂), 21.8 (d, *J*_{CP}= 143.0 Hz, PC(1)H₂). **FAB-HRMS:** *m/z* [M + H]⁺ calcd for C₅H₁₃N₃O₃P 194.0694, found 194.0693. **IR** (ATR) ν: 2093 (N₃), 1237 (P=O), 1020 (P-O-C), 805 cm⁻¹.

Dimethyl 4-azidobutylphosphonate [1] (5c). Colorless oil. Yield 73% (0.302 g). ³¹P NMR

(283 MHz, CDCl₃): δ 33.93. ¹H NMR (700 MHz, CDCl₃): δ 3.73 (6 H, d, *J*_{HP}= 10.8 Hz, 2 x CH₃O), 3.28 (2 H, t, *J*_{HH}= 6.3 Hz, C(4)H₂N₃), 1.78-1.73 (2 H, m, CH₂), 1.71-1.66 (4 H, m, 2 x CH₂). ¹³C NMR (176 MHz, CDCl₃): δ 52.3 (2 d, *J*_{CP}= 6.6 Hz, 2 x CH₃O), 50.9 (s, C(4)H₂N₃), 29.5 (d, *J*_{CP}= 15.7 Hz, C(3)H₂), 24.2 (d, *J*_{CP}= 141.6 Hz, PC(1)H₂), 19.8 (d, *J*_{CP}= 5.1 Hz, C(2)H₂). **FAB-HRMS:** *m/z* [M + H]⁺ calcd for C₆H₁₅N₃O₃P 208.0851, found 208.0856. **IR** (ATR) ν: 2092 (N₃), 1230 (P=O), 1021 (P-O-C), 810 cm⁻¹.

Dimethyl 5-azidopentylphosphonate (5d). Colorless oil. Yield 74% (0.327 g). ^{31}P NMR

(283 MHz, CDCl_3): δ 34.43. ^1H NMR (700 MHz, CDCl_3): δ 3.72 (6 H, d, $J_{\text{HP}} = 10.8$ Hz, 2 x CH_3O), 3.26 (2 H, d, $J_{\text{HH}} = 6.8$ Hz, $\text{C}(5)\text{H}_2\text{N}_3$),

1.76-1.71 (2 H, m, CH_2), 1.65-1.57 (4 H, m, 2 x CH_2), 1.48-1.43 (2 H, m, CH_2). ^{13}C NMR (176 MHz, CDCl_3): δ 52.2 (2 d, $J_{\text{CP}} = 6.6$ Hz, 2 x CH_3O), 51.1 (s, $\text{C}(5)\text{H}_2\text{N}_3$), 28.4 (s, $\text{C}(4)\text{H}_2$), 27.6 (d, $J_{\text{CP}} = 16.5$ Hz, $\text{C}(3)\text{H}_2$), 24.5 (d, $J_{\text{CP}} = 141.0$ Hz, $\text{PC}(1)\text{H}_2$), 22.0 (d, $J_{\text{CP}} = 5.1$ Hz, $\text{C}(2)\text{H}_2$). **FAB-HRMS:** m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_7\text{H}_{17}\text{N}_3\text{O}_3\text{P}$ 222.1007, found 222.1012. **IR** (ATR) ν : 2091 (N_3), 1235 ($\text{P}=\text{O}$), 1023 ($\text{P}-\text{O}-\text{C}$), 808 cm^{-1} .

Dimethyl 6-azidohexylphosphonate (5e). Colorless oil. Yield 72% (0.339 g). ^{31}P NMR (283

MHz, CDCl_3): δ 34.75. ^1H NMR (700 MHz, CDCl_3): δ 3.72 (6 H, d, $J_{\text{HP}} = 10.7$ Hz, 2 x CH_3O), 3.25 (2 H, t, $J_{\text{HH}} = 6.9$ Hz, $\text{C}(6)\text{H}_2\text{N}_3$),

1.75-1.70 (2 H, m, CH_2), 1.63-1.57 (4 H, m, 2 x CH_2), 1.42-1.35 (4 H, m, 2 x CH_2). ^{13}C NMR (176 MHz, CDCl_3): δ 52.2 (d, $J_{\text{CP}} = 6.3$ Hz, 2 x CH_3O), 51.3 (s, $\text{C}(6)\text{H}_2\text{N}_3$), 29.9 (d, $J_{\text{CP}} = 16.3$ Hz, $\text{C}(3)\text{H}_2$), 28.5 (s, CH_2), 26.2 (s, CH_2), 24.5 (d, $J_{\text{CP}} = 140.8$ Hz, $\text{PC}(1)\text{H}_2$), 22.2 (d, $J_{\text{CP}} = 5.2$ Hz, $\text{C}(2)\text{H}_2$). **FAB-HRMS:** m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_8\text{H}_{19}\text{N}_3\text{O}_3\text{P}$ 236.1164, found 236.1168. **IR** (ATR) ν : 2091 (N_3), 1244 ($\text{P}=\text{O}$), 1025 ($\text{P}-\text{O}-\text{C}$), 810 cm^{-1} .

Diethyl 2-azidoethylphosphonate [2] (6a). Colorless oil. Yield 60% (0.248 g) after flash

chromatography (hexane/acetone 2 : 1). ^{31}P NMR (283 MHz, CDCl_3): δ 26.85. ^1H NMR (700 MHz, CDCl_3): δ 4.16-4.07 (4 H, m, 2 x CH_3CH_2),

3.53 (2 H, dt, $J_{\text{HP}} = 12.1$ Hz, $J_{\text{HH}} = 7.7$ Hz, $\text{C}(2)\text{H}_2\text{N}_3$), 2.05 (2 H, dt, $J_{\text{HP}} = 18.6$ Hz, $J_{\text{HH}} = 7.7$ Hz, $\text{PC}(1)\text{H}_2$), 1.33 (6 H, t, $J_{\text{HH}} = 7.1$ Hz, 2 x CH_3CH_2). ^{13}C NMR (176 MHz, CDCl_3): δ 61.8 (d, $J_{\text{CP}} = 6.4$ Hz, 2 x CH_3CH_2), 45.3 (d, $J_{\text{CP}} = 2.2$ Hz, $\text{C}(2)\text{H}_2\text{N}_3$), 25.9 (d, $J_{\text{CP}} = 140.9$ Hz, $\text{PC}(1)\text{H}_2$), 16.3 (d, $J_{\text{CP}} = 6.0$ Hz, 2 x CH_3CH_2). **FAB-HRMS:** m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_6\text{H}_{15}\text{N}_3\text{O}_3\text{P}$ 208.0851, found 208.0858. **IR** (ATR) ν : 2096 (N_3), 1240 ($\text{P}=\text{O}$), 1018 ($\text{P}-\text{O}-\text{C}$), 960 cm^{-1} .

Diethyl 3-azidopropylphosphonate [3] (**6b**). Colorless oil. Yield 73% (0.323 g) after flash

chromatography (hexane/acetone 2 : 1). ^{31}P NMR (283 MHz, CDCl_3): δ

30.74. ^1H NMR (700 MHz, CDCl_3): δ 4.13-4.04 (4 H, m, 2 x CH_3CH_2),

3.36 (2 H, t, $J_{\text{HH}} = 6.6$ Hz, $\text{C}(3)\text{H}_2\text{N}_3$), 1.89-1.84 (2 H, m, CH_2), 1.81-1.76 (2 H, m, CH_2), 1.31

(6 H, t, $J_{\text{HH}} = 7.1$ Hz, 2 x CH_3CH_2). ^{13}C NMR (176 MHz, CDCl_3): δ 61.3 (d, $J_{\text{CP}} = 6.5$ Hz, 2 x

CH_3CH_2), 51.4 (d, $J_{\text{CP}} = 16.4$ Hz, $\text{C}(3)\text{H}_2\text{N}_3$), 22.8 (d, $J_{\text{CP}} = 143.0$ Hz, $\text{PC}(1)\text{H}_2$), 22.4 (d, $J_{\text{CP}} =$

4.8 Hz, $\text{C}(2)\text{H}_2$), 16.4 (d, $J_{\text{CP}} = 6.0$ Hz, 2 x CH_3CH_2). **FAB-HRMS**: m/z $[\text{M} + \text{H}]^+$ calcd for

$\text{C}_7\text{H}_{17}\text{N}_3\text{O}_3\text{P}$ 222.1007, found 222.1008. **IR** (ATR) ν : 2093 (N_3), 1236 ($\text{P}=\text{O}$), 1019 ($\text{P}-\text{O}-\text{C}$),

953 cm^{-1} .

Diethyl 4-azidobutylphosphonate [4, 5] (**6c**). Colorless oil. Yield 78% (0.367 g) after flash

chromatography (hexane/acetone 2 : 1). ^{31}P NMR (283 MHz, CDCl_3): δ

31.33. ^1H NMR (700 MHz, CDCl_3): δ 4.13-4.04 (4 H, m, 2 x CH_3CH_2),

3.29 (2 H, t, $J_{\text{HH}} = 6.4$ Hz, $\text{C}(4)\text{H}_2\text{N}_3$), 1.76-1.71 (2 H, m, CH_2), 1.70-1.67 (4 H, m, 2 x CH_2),

1.31 (6 H, t, $J_{\text{HH}} = 7.1$ Hz, 2 x CH_3CH_2). ^{13}C NMR (176 MHz, CDCl_3): δ 61.5 (d, $J_{\text{CP}} = 6.2$ Hz,

2 x CH_3CH_2), 50.9 (s, $\text{C}(4)\text{H}_2\text{N}_3$), 29.5 (d, $J_{\text{CP}} = 15.8$ Hz, $\text{C}(3)\text{H}_2$), 25.2 (d, $J_{\text{CP}} = 141.7$ Hz,

$\text{PC}(1)\text{H}_2$), 19.9 (d, $J_{\text{CP}} = 5.1$ Hz, $\text{C}(2)\text{H}_2$), 16.4 (d, $J_{\text{CP}} = 5.9$ Hz, 2 x CH_3CH_2). **FAB-HRMS**:

m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_8\text{H}_{19}\text{N}_3\text{O}_3\text{P}$ 236.1164, found 236.1169. **IR** (ATR) ν : 2092 (N_3), 1230

($\text{P}=\text{O}$), 1021 ($\text{P}-\text{O}-\text{C}$), 953 cm^{-1} .

Diethyl 5-azidopentylphosphonate [4, 5] (**6d**). Colorless oil. Yield 84% (0.418 g) after flash

chromatography (hexane/acetone 2 : 1). ^{31}P NMR (283 MHz,

CDCl_3): δ 31.86. ^1H NMR (700 MHz, CDCl_3): δ 4.13-4.04 (4 H, m, 2

x CH_3CH_2), 3.27 (2 H, t, $J_{\text{HH}} = 6.9$ Hz, $\text{C}(5)\text{H}_2\text{N}_3$), 1.75-1.70 (2 H, m, CH_2), 1.66-1.59 (4 H,

m, 2 x CH_2), 1.49-1.45 (2 H, m, CH_2), 1.32 (6 H, t, $J_{\text{HH}} = 7.1$ Hz, 2 x CH_3CH_2). ^{13}C NMR

(176 MHz, CDCl_3): δ 61.5 (d, $J_{\text{CP}} = 6.6$ Hz, 2 x CH_3CH_2), 51.2 (s, $\text{C}(5)\text{H}_2\text{N}_3$), 28.4 (s,

$\text{C}(4)\text{H}_2$), 27.6 (d, $J_{\text{CP}} = 16.7$ Hz, $\text{C}(3)\text{H}_2$), 25.6 (d, $J_{\text{CP}} = 141.1$ Hz, $\text{PC}(1)\text{H}_2$), 22.1 (d, $J_{\text{CP}} = 5.2$

Hz, C(2)H₂), 16.5 (d, J_{CP} = 6.0 Hz, 2 x CH₃CH₂). **FAB-HRMS**: m/z [M + H]⁺ calcd for C₉H₂₁N₃O₃P 250.1320, found 250.1323. **IR** (ATR) ν : 2092 (N₃), 1236 (P=O), 1022 (P-O-C), 955 cm⁻¹.

Diethyl 6-azidohexylphosphonate [4] (**6e**). Colorless oil. Yield 80% (0.421 g) after flash

chromatography (hexane/acetone 2 : 1). **³¹P NMR** (283 MHz, CDCl₃): δ 32.11. **¹H NMR** (700 MHz, CDCl₃): δ 4.07-3.98 (4 H,

m, 2 x CH₃CH₂), 3.21 (2 H, t, J_{HH} = 6.9 Hz, C(6)H₂N₃), 1.69-1.64 (2 H, m, PC(1)H₂), 1.59-1.52 (4 H, m, C(2)H₂, C(5)H₂), 1.38-1.31 (4 H, m, C(3)H₂, C(4)H₂), 1.27 (6 H, t, J_{HH} = 7.1 Hz, 2 x CH₃CH₂), **¹³C NMR** (176 MHz, CDCl₃): δ 61.4 (d, J_{CP} = 6.5 Hz, 2 x CH₃CH₂), 51.3 (s, C(6)H₂N₃), 30.0 (d, J_{CP} = 16.6 Hz, C(3)H₂), 28.6 (s, C(5)H₂), 26.2 (s, C(4)H₂), 25.6 (d, J_{CP} = 140.9 Hz, PC(1)H₂), 22.3 (d, J_{CP} = 5.1 Hz, C(2)H₂), 16.4 (d, J_{CP} = 6.0 Hz, 2 x CH₃CH₂). **FAB-HRMS**: m/z [M + H]⁺ calcd for C₁₀H₂₃N₃O₃P 264.1477, found 264.1476. **IR** (ATR) ν : 2092 (N₃), 1243 (P=O), 1024 (P-O-C), 953 cm⁻¹.

Diisopropyl 2-azidoethylphosphonate (**7a**). Colorless oil. Yield 39% (0.183 g) after flash

chromatography (hexane/acetone 1 : 1). **³¹P NMR** (283 MHz, CDCl₃): δ 24.53. **¹H NMR** (700 MHz, CDCl₃): δ 4.71 (2 H, d, J_{HP} = 7.9 Hz, J_{HH} =

6.2 Hz, 2 x (CH₃)₂CH), 3.52-3.49 (2 H, m, C(2)H₂N₃), 2.04-1.99 (2 H, m, PC(1)H₂), 1.32 (12 H, d, J_{HH} = 6.2 Hz, 2 x (CH₃)₂CH). **¹³C NMR** (176 MHz, CDCl₃): δ 70.6 (d, J_{CP} = 6.6 Hz, 2 x (CH₃)₂CH), 45.7 (s, C(2)H₂N₃), 27.2 (d, J_{CP} = 141.5 Hz, PC(1)H₂), 24.0 (2 d, J_{CP} = 4.6 Hz, J_{CP} = 4.0 Hz, 2 x (CH₃)₂CH). **FAB-HRMS**: m/z [M + H]⁺ calcd for C₈H₁₉N₃O₃P 236.1164, found 236.1155. **IR** (ATR) ν : 2096 (N₃), 1242 (P=O), 976 (P-O-C), 887 cm⁻¹.

Diisopropyl 3-azidopropylphosphonate (**7b**). Colorless oil. Yield 77% (0.383 g). **³¹P NMR**

(283 MHz, CDCl₃): δ 28.62. **¹H NMR** (700 MHz, CDCl₃): δ 4.69 (2 H, d, J_{HP} = 8.0 Hz, J_{HH} = 6.2 Hz, 2 x (CH₃)₂CH), 3.36 (2 H, d, J_{HH} = 6.6

Hz, C(3)H₂N₃), 1.89-1.83 (2 H, m, CH₂), 1.77-1.72 (2 H, m, CH₂), 1.31 (12 H, d, J_{HH} = 6.2

Hz, 2 x (CH₃)₂CH). **¹³C NMR** (176 MHz, CDCl₃): δ 70.1 (d, *J*_{CP}= 6.6 Hz, 2 x (CH₃)₂CH), 51.6 (d, *J*_{CP}= 16.8 Hz, C(3)H₂N₃), 24.2 (d, *J*_{CP}= 144.2 Hz, PC(1)H₂), 24.1 (2 d, *J*_{CP}= 4.6 Hz, *J*_{CP}= 4.0 Hz, 2 x (CH₃)₂CH), 22.6 (d, *J*_{CP}= 4.9 Hz, C(2)H₂). **FAB-HRMS**: *m/z* [M + H]⁺ calcd for C₉H₂₁N₃O₃P 250.1320, found 250.1318. **IR** (ATR) ν: 2095 (N₃), 1232 (P=O), 974 (P-O-C), 894 cm⁻¹.

Diisopropyl 4-azidobutylphosphonate (7c). Colorless oil. Yield 80% (0.421 g) after flash

chromatography (hexane/acetone 2 : 1). **³¹P NMR** (283 MHz, CDCl₃): δ 29.24. **¹H NMR** (700 MHz, CDCl₃): δ 4.68 (2 H, d, *J*_{HP}= 8.0 Hz, *J*_{HH}= 6.2 Hz, 2 x (CH₃)₂CH), 3.28 (2 H, t, *J*_{HH}= 6.2 Hz, C(4)H₂N₃), 1.71-1.65 (6 H, m, 3 x CH₂), 1.30 (12 H, dd, *J*_{HH}= 6.2 Hz, *H*_{HP}= 1.8 Hz, 2 x (CH₃)₂CH). **¹³C NMR** (176 MHz, CDCl₃): δ 69.9 (d, *J*_{CP}= 6.7 Hz, 2 x (CH₃)CH), 50.9 (s, C(4)H₂N₃), 29.6 (d, *J*_{CP}= 16.1 Hz, C(3)H₂), 26.5 (d, *J*_{CP}= 142.9 Hz, PC(1)H₂), 24.1 (2 d, *J*_{CP}= 5.0 Hz, *J*_{CP}= 4.3 Hz, 2 x (CH₃)₂CH), 20.1 (d, *J*_{CP}= 5.2 Hz, C(2)H₂). **FAB-HRMS**: *m/z* [M + H]⁺ calcd for C₁₀H₂₃N₃O₃P 264.1477, found 264.1473. **IR** (ATR) ν: 2093 (N₃), 1229 (P=O), 973 (P-O-C), 887 cm⁻¹.

Diisopropyl 5-azidopentylphosphonate (7d). Colorless oil. Yield 71% (0.394 g) after flash

chromatography (hexane/acetone 1 : 1). **³¹P NMR** (283 MHz, CDCl₃): δ 29.77. **¹H NMR** (700 MHz, CDCl₃): δ 4.67 (2 H, d, *J*_{HP}= 7.9 Hz, *J*_{HH}= 6.2 Hz, 2 x (CH₃)₂CH), 3.26 (2 H, t, *J*_{HH}= 6.9 Hz, C(5)H₂N₃), 1.69-1.64 (2 H, m, CH₂), 1.63-1.57 (4 H, m, 2 x CH₂), 1.47-1.42 (2 H, m, CH₂), 1.30 (12 H, 2 d, *J*_{HH}= 6.2 Hz, 2 x (CH₃)₂CH). **¹³C NMR** (176 MHz, CDCl₃): δ 69.8 (d, *J*_{CP}= 6.7 Hz, 2 x (CH₃)₂CH), 51.2 (s, C(5)H₂N₃), 28.4 (s, C(4)H₂), 27.7 (d, *J*_{CP}= 17.1 Hz, C(3)H₂), 26.9 (d, *J*_{CP}= 142.4 Hz, PC(1)H₂), 24.1 (2 d, *J*_{CP}= 5.1 Hz, *J*_{CP}= 4.3 Hz, 2 x (CH₃)₂CH), 22.3 (d, *J*_{CP}= 5.2 Hz, C(2)H₂). **FAB-HRMS**: *m/z* [M + H]⁺ calcd for C₁₁H₂₅N₃O₃P 278.1633, found 278.1629. **IR** (ATR) ν: 2092 (N₃), 1222 (P=O), 975 (P-O-C), 888 cm⁻¹.

Diisopropyl 6-azidohexylphosphonate (7e). Colorless oil. Yield 66% (0.384 g) after flash

chromatography (hexane/acetone 1 : 1). ^{31}P NMR (283 MHz, CDCl_3): δ 30.10. ^1H NMR (700 MHz, CDCl_3): δ 4.67 (2 H, d, $J_{\text{HP}} = 7.9$ Hz, $J_{\text{HH}} = 6.2$ Hz, 2 x $(\text{CH}_3)\text{CH}$), 3.25 (2 H, t, $J_{\text{HH}} = 6.9$ Hz, $\text{C}(6)\text{H}_2\text{N}_3$), 1.69-1.64 (2 H, m, CH_2), 1.62-1.56 (4 H, m, 2 x CH_2), 1.42-1.36 (4 H, m, 2 x CH_2), 1.30 (12 H, 2d, $J_{\text{HH}} = 6.2$ Hz, 2 x $(\text{CH}_3)_2\text{CH}$).

^{13}C NMR (176 MHz, CDCl_3): δ 69.7 (d, $J_{\text{CP}} = 6.6$ Hz, 2 x $(\text{CH}_3)_2\text{CH}$), 51.3 (s, $\text{C}(6)\text{H}_2\text{N}_3$), 30.1 (d, $J_{\text{CP}} = 16.9$ Hz, $\text{C}(3)\text{H}_2$), 28.6 (s, CH_2), 26.9 (d, $J_{\text{CP}} = 142.1$ Hz, $\text{PC}(1)\text{H}_2$), 26.2 (s, CH_2), 24.1 (2 d, $J_{\text{CP}} = 4.6$ Hz, $J_{\text{CP}} = 4.1$ Hz, 2 x $(\text{CH}_3)_2\text{CH}$), 22.5 (d, $J_{\text{CP}} = 5.3$ Hz, $\text{C}(2)\text{H}_2$). **FAB-HRMS:** m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{27}\text{N}_3\text{O}_3\text{P}$ 292.1790, found 292.1784. **IR** (ATR) ν : 2091 (N_3), 1241 ($\text{P}=\text{O}$), 975 ($\text{P}-\text{O}-\text{C}$), 887 cm^{-1} .

3. General procedure for the preparation of products 8b-e

Sodium azide (3.0 mmol, 1.5 eq) was added to the solution of dialkyl ω -bromoalkylphosphonate (2.0 mmol) in DMF (3 mL) placed in a 10 mL pressure vial, equipped with magnetic stirrer. Then azidation was carried under MW irradiation. After that, reaction mixture was evaporated under reduced pressure. Semi-solid product was dissolved in Et_2O (30 mL), washed with H_2O (2×3 mL), brine (5 mL) and dried over MgSO_4 . The solvent was evaporated under reduced pressure and the rest of the volatile material was removed at 35 $^\circ\text{C}/27$ Pa to give pure product 8.

Diisobutyl 3-azidopropylphosphonate (8b). Colorless oil. Yield 87% (0.482 g). ^{31}P NMR

(283 MHz, CDCl_3): δ 30.49. ^1H NMR (700 MHz, CDCl_3): δ 3.82-3.74 (4 H, m, 2 x CH_2O), 3.38 (2 H, t, $J_{\text{HH}} = 6.7$ Hz, $\text{C}(3)\text{H}_2\text{N}_3$), 1.92 (2 H, sep, $J_{\text{HH}} = 6.7$ Hz, 2 x $(\text{CH}_3)_2\text{CH}$), 1.91-1.85 (2 H, m, CH_2), 1.84-1.79 (2 H, m, CH_2), 0.94 (12 H, d, $J_{\text{HH}} = 6.7$ Hz, 2 x $(\text{CH}_3)_2\text{CH}$).

^{13}C NMR (176 MHz, CDCl_3): δ 71.6 (d, $J_{\text{CP}} = 6.9$ Hz, 2 x CH_2O), 51.5 (d, $J_{\text{CP}} = 16.5$ Hz, $\text{C}(3)\text{H}_2\text{N}_3$), 29.2 (d, $J_{\text{CP}} = 6.4$ Hz, 2 x

(CH₃)₂CH), 22.6 (d, J_{CP} = 143.4 Hz, PC(1)H₂), 22.5 (d, J_{CP} = 4.8 Hz, C(2)H₂), 18.7 (s, 2 x (CH₃)₂CH). **FAB-HRMS**: m/z [M + H]⁺ calcd for C₁₁H₂₅N₃O₃P 278.1633, found 278.1637. **IR** (ATR) ν : 2094 (N₃), 1237 (P=O), 1043, 1003 (P-O-C), 864 cm⁻¹.

Diisobutyl 4-azidobutylphosphonate (8c). Colorless oil. Yield 87% (0.506 g). **³¹P NMR**

(283 MHz, CDCl₃): δ 31.07. **¹H NMR** (700 MHz, CDCl₃): δ 3.82-3.74 (4 H, m, 2 x CH₂O), 3.29 (2 H, t, J_{HH} = 6.3 Hz, C(4)H₂N₃), 1.92 (2 H, sep, J_{HH} = 6.7 Hz, 2 x (CH₃)₂CH), 1.79-1.68 (6 H, m, 3 x CH₂),

0.93 (12 H, d, J_{HH} = 6.7 Hz, 2 x (CH₃)₂CH). **¹³C NMR** (176 MHz, CDCl₃): δ 71.5 (d, J_{CP} = 6.9 Hz, 2 x CH₂O), 50.9 (s, C(4)H₂N₃), 29.6 (d, J_{CP} = 15.6 Hz, C(3)H₂), 29.3 (d, J_{CP} = 6.4 Hz, 2 x (CH₃)₂CH), 25.0 (d, J_{CP} = 142.1 Hz, PC(1)H₂), 20.0 (d, J_{CP} = 5.1 Hz, C(2)H₂), 18.7 (s, 2 x (CH₃)₂CH). **FAB-HRMS**: m/z [M + H]⁺ calcd for C₁₂H₂₇N₃O₃P 292.1790, found 292.1785. **IR** (ATR) ν : 2093 (N₃), 1233 (P=O), 1043, 1003 (P-O-C), 851 cm⁻¹.

Diisobutyl 5-azidopentylphosphonate (8d). Colorless oil. Yield 78% (0.476 g). **³¹P NMR**

(283 MHz, CDCl₃): δ 31.57. **¹H NMR** (700 MHz, CDCl₃): δ 3.81-3.73 (4 H, m, 2 x CH₂O), 3.27 (2 H, t, J_{HH} = 6.9 Hz, C(5)H₂N₃), 1.92 (2 H, sep, J_{HH} = 6.7 Hz, 2 x (CH₃)₂CH), 1.76-1.71 (2 H, m,

CH₂), 1.67-1.58 (4 H, m, 2 x CH₂), 1.49-1.44 (2 H, m, CH₂), 0.93 (12 H, d, J_{HH} = 6.7 Hz, 2 x (CH₃)₂CH). **¹³C NMR** (176 MHz, CDCl₃): δ 71.5 (d, J_{CP} = 6.9 Hz, 2 x CH₂O), 51.2 (s, C(5)H₂N₃), 29.3 (d, J_{CP} = 6.3 Hz, 2 x (CH₃)₂CH), 28.4 (s, C(4)H₂), 27.7 (d, J_{CP} = 16.5 Hz, C(3)H₂), 25.3 (d, J_{CP} = 141.6 Hz, PC(1)H₂), 22.2 (d, J_{CP} = 5.2 Hz, C(2)H₂), 18.7 (s, 2 x (CH₃)₂CH). **FAB-HRMS**: m/z [M + H]⁺ calcd for C₁₃H₂₉N₃O₃P 306.1946, found 306.1939. **IR** (ATR) ν : 2092 (N₃), 1239 (P=O), 1044, 1004 (P-O-C), 858 cm⁻¹.

Diisobutyl 6-azidohexylphosphonate (8e). Colorless oil. Yield 80% (0.511 g). **³¹P NMR**

(283 MHz, CDCl₃): δ 31.89. **¹H NMR** (700 MHz, CDCl₃): δ 3.80-3.72 (4 H, m, 2 x CH₂O), 3.25 (2 H, t, J_{HH} = 6.9 Hz,

C(6)H₂N₃), 1.91 (2 H, sep, $J_{\text{HH}} = 6.7$ Hz, 2 x (CH₃)₂CH), 1.75-1.71 (2 H, m, CH₂), 1.64-1.57 (4 H, m, 2 x CH₂), 1.43-1.35 (4 H, m, 2 x CH₂), 0.93 (12 H, d, $J_{\text{HH}} = 6.7$ Hz, 2 x (CH₃)₂CH). **¹³C NMR** (176 MHz, CDCl₃): δ 71.5 (d, $J_{\text{CP}} = 6.9$ Hz, 2 x CH₂O), 51.4 (s, C(6)H₂N₃), 30.1 (d, $J_{\text{CP}} = 16.4$ Hz, C(3)H₂), 29.3 (d, $J_{\text{CP}} = 6.4$ Hz, 2 x (CH₃)₂CH), 28.6 (s, CH₂), 26.3 (s, CH₂), 25.3 (d, $J_{\text{CP}} = 141.3$ Hz, PC(1)H₂), 22.4 (d, $J_{\text{CP}} = 5.3$ Hz, C(2)H₂), 18.7 (s, 2 x (CH₃)₂CH). **FAB-HRMS**: m/z [M + H]⁺ calcd for C₁₄H₃₁N₃O₃P 320.2103, found 320.2097. **IR** (ATR) ν : 2092 (N₃), 1243 (P=O), 1044, 1004 (P-O-C), 859 cm⁻¹.

4. Copies of ¹H, ¹³C and ³¹P NMR and IR spectra of target compounds 5a-e - 8b-e

Figure S1. ³¹ P NMR of compound 5a (283 MHz).	S13
Figure S2. ¹ H NMR of compound 5a (700 MHz).	S13
Figure S4. ³¹ P NMR of compound 5b (283 MHz).	S14
Figure S5. ¹ H NMR of compound 5b (700 MHz).	S15
Figure S6. ¹³ C NMR of compound 5b (176 MHz).	S15
Figure S7. ³¹ P NMR of compound 5c (283 MHz).	S16
Figure S8. ¹ H NMR of compound 5c (700 MHz).	S16
Figure S9. ¹³ C NMR of compound 5c (176 MHz).	S17
Figure S10. ³¹ P NMR of compound 5d (283 MHz).	S17
Figure S11. ¹ H NMR of compound 5d (700 MHz).	S18
Figure S12. ¹³ C NMR of compound 5d (176 MHz).	S18
Figure S13. ³¹ P NMR of compound 5e (283 MHz).	S19
Figure S14. ¹ H NMR of compound 5e (700 MHz).	S19
Figure S15. ¹³ C NMR of compound 5e (176 MHz).	S20
Figure S16. ³¹ P NMR of compound 6a (283 MHz).	S20
Figure S18. ¹³ C NMR of compound 6a (176 MHz).	S21
Figure S19. ³¹ P NMR of compound 6b (283 MHz).	S22
Figure S20. ¹ H NMR of compound 6b (700 MHz).	S22

Figure S21. ^{13}C NMR of compound 6b (176 MHz).....	S23
Figure S22. ^{31}P NMR of compound 6c (283 MHz).	S23
Figure S23. ^1H NMR of compound 6c (700 MHz).	S24
Figure S24. ^{13}C NMR of compound 6c (176 MHz).	S24
Figure S25. ^{31}P NMR of compound 6d (283 MHz).	S25
Figure S26. ^1H NMR of compound 6d (700 MHz).....	S25
Figure S27. ^{13}C NMR of compound 6d (176 MHz).....	S26
Figure S28. ^{31}P NMR of compound 6e (283 MHz).	S26
Figure S29. ^1H NMR of compound 6e (700 MHz).	S27
Figure S30. ^{13}C NMR of compound 6e (176 MHz).	S27
Figure S31. H-C HMQC of compound 6e (700 MHz).....	S28
Figure S32. HH COSY of compound 6e (700 MHz).	S28
Figure S33. ^{31}P NMR of compound 7a (283 MHz).	S29
Figure S34. ^1H NMR of compound 7a (700 MHz).	S29
Figure S35. ^{13}C NMR of compound 7a (176 MHz).....	S30
Figure S36. ^{31}P NMR of compound 7b (283 MHz).	S30
Figure S37. ^1H NMR of compound 7b (700 MHz).....	S31
Figure S38. ^{13}C NMR of compound 7b (176 MHz).....	S31
Figure S39. ^{31}P NMR of compound 7c (283 MHz).	S32
Figure S40. ^1H NMR of compound 7c (700 MHz).	S32
Figure S41. ^{13}C NMR of compound 7c (176 MHz).	S33
Figure S42. ^{31}P NMR of compound 7d (283 MHz).	S33
Figure S43. ^1H NMR of compound 7d (700 MHz).....	S34
Figure S44. ^{13}C NMR of compound 7d (176 MHz).....	S34
Figure S45. ^{31}P NMR of compound 7e (283 MHz).	S35
Figure S46. ^1H NMR of compound 7e (700 MHz).	S35
Figure S47. ^{13}C NMR of compound 7e (176 MHz).	S36

Figure S48. ^{31}P NMR of compound 8b (283 MHz).....	S36
Figure S49. ^1H NMR of compound 8b (700 MHz).....	S37
Figure S50. ^{13}C NMR of compound 8b (176 MHz).....	S37
Figure S51. ^{31}P NMR of compound 8c (283 MHz).	S38
Figure S52. ^1H NMR of compound 8c (700 MHz).	S38
Figure S53. ^{13}C NMR of compound 8c (176 MHz).	S39
Figure S54. ^{31}P NMR of compound 8d (283 MHz).	S39
Figure S55. ^1H NMR of compound 8d (700 MHz).....	S40
Figure S56. ^{13}C NMR of compound 8d (176 MHz).....	S40
Figure S57. ^{31}P NMR of compound 8e (283 MHz).	S41
Figure S58. ^1H NMR of compound 8e (700 MHz).	S41
Figure S59. ^{13}C NMR of compound 8e (176 MHz).	S42

Figure S1. ³¹P NMR of compound **5a** (283 MHz, CDCl₃).

Figure S2. ¹H NMR of compound **5a** (700 MHz, CDCl₃).

Figure S3. ^{13}C NMR of compound **5a** (176 MHz, CDCl_3).

Figure S4. ^{31}P NMR of compound **5b** (283 MHz, CDCl_3).

Figure S5. ¹H NMR of compound **5b** (700 MHz, CDCl₃).

Figure S6. ¹³C NMR of compound **5b** (176 MHz, CDCl₃).

Figure S7. ³¹P NMR of compound **5c** (283 MHz, CDCl₃).

Figure S8. ¹H NMR of compound **5c** (700 MHz, CDCl₃).

Figure S9. ^{13}C NMR of compound **5c** (176 MHz, CDCl_3).

Figure S10. ^{31}P NMR of compound **5d** (283 MHz, CDCl_3).

Figure S11. ¹H NMR of compound **5d** (700 MHz, CDCl₃).

Figure S12. ¹³C NMR of compound **5d** (176 MHz, CDCl₃).

Figure S13. ^{31}P NMR of compound **5e** (283 MHz, CDCl_3).

Figure S14. ^1H NMR of compound **5e** (700 MHz, CDCl_3).

Figure S15. ¹³C NMR of compound **5e** (176 MHz, CDCl₃).

Figure S16. ³¹P NMR of compound **6a** (283 MHz, CDCl₃).

Figure S17. ^1H NMR of compound **6a** (700 MHz, CDCl_3).

Figure S18. ^{13}C NMR of compound **6a** (176 MHz, CDCl_3)

Figure S19. ³¹P NMR of compound **6b** (283 MHz, CDCl₃).

Figure S20. ¹H NMR of compound **6b** (700 MHz, CDCl₃).

Figure S21. ^{13}C NMR of compound **6b** (176 MHz, CDCl_3).

Figure S22. ^{31}P NMR of compound **6c** (283 MHz, CDCl_3).

Figure S23. ^1H NMR of compound **6c** (700 MHz, CDCl_3).

Figure S24. ^{13}C NMR of compound **6c** (176 MHz, CDCl_3).

Figure S25. ^{31}P NMR of compound **6d** (283 MHz, CDCl_3).

Figure S26. ^1H NMR of compound **6d** (700 MHz, CDCl_3).

Figure S27. ^{13}C NMR of compound **6d** (176 MHz, CDCl_3).

Figure S28. ^{31}P NMR of compound **6e** (283 MHz, CDCl_3).

Figure S29. ¹H NMR of compound **6e** (700 MHz, CDCl₃).

Figure S30. ¹³C NMR of compound **6e** (176 MHz, CDCl₃).

Figure S31. H-C HMQC of compound **6e** (700 MHz, CDCl_3).

Figure S32. HH COSY of compound **6e** (700 MHz, CDCl_3).

Figure S33. ^{31}P NMR of compound **7a** (283 MHz, CDCl_3).

Figure S34. ^1H NMR of compound **7a** (700 MHz, CDCl_3).

Figure S35. ^{13}C NMR of compound **7a** (176 MHz, CDCl_3).

Figure S36. ^{31}P NMR of compound **7b** (283 MHz, CDCl_3).

Figure S37. ¹H NMR of compound **7b** (700 MHz, CDCl₃).

Figure S38. ¹³C NMR of compound **7b** (176 MHz, CDCl₃).

Figure S39. ^{31}P NMR of compound **7c** (283 MHz, CDCl_3).

Figure S40. ^1H NMR of compound **7c** (700 MHz, CDCl_3).

Figure S41. ¹³C NMR of compound **7c** (176 MHz, CDCl₃).

Figure S42. ³¹P NMR of compound **7d** (283 MHz, CDCl₃).

Figure S43. ¹H NMR of compound **7d** (700 MHz, CDCl₃).

Figure S44. ¹³C NMR of compound **7d** (176 MHz, CDCl₃).

Figure S45. ^{31}P NMR of compound **7e** (283 MHz, CDCl_3).

Figure S46. ^1H NMR of compound **7e** (700 MHz, CDCl_3).

Figure S49. ¹H NMR of compound **8b** (700 MHz, CDCl₃).

Figure S50. ¹³C NMR of compound **8b** (176 MHz, CDCl₃).

Figure S51. ^{31}P NMR of compound **8c** (283 MHz, CDCl_3).

Figure S52. ^1H NMR of compound **8c** (700 MHz, CDCl_3).

Figure S53. ¹³C NMR of compound **8c** (176 MHz, CDCl₃).

Figure S54. ³¹P NMR of compound **8d** (283 MHz, CDCl₃).

Figure S55. ¹H NMR of compound **8d** (700 MHz, CDCl₃).

Figure S56. ¹³C NMR of compound **8d** (176 MHz, CDCl₃).

Figure S57. ^{31}P NMR of compound **8e** (283 MHz, CDCl_3).

Figure S58. ^1H NMR of compound **8e** (700 MHz, CDCl_3).

Figure S59. ¹³C NMR of compound **8e** (176 MHz, CDCl₃).

5. References

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