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New phosphonium salts based on 3-(diphenylphosphino)propanoic and ω-haloalkanoic acids

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Experimental Section

General remarks. NMR spectra were recorded on the Bruker Avance III instrument with an operating frequency of 122.4 MHz for ^{31}P NMR spectra (external standard 85% H_3PO_4), and an operating frequency of 400.0 MHz for ^{1}H NMR spectra (internal standard TMS) in a solution of D_2O. IR spectra were recorded on the PerklinElmer UATR Two FT-IR Spectrometer (Spectrum Two). The elemental analysis was carried out on a CHNS analyzer EuroEA3028-HT-OM (Eurovector SpA, Italy). The samples were weighed on Sartorius CP2P (Germany) microbalances in tin capsules. Callidus 4.1 software was used to perform quantitative measurements and evaluate the data received. All chemicals purchased from Sigma-Aldrich were reagent grade and used without purification.

Samples of 3-(diphenylphosphino)propanoic acid **1** and ω-haloalkamoic acids in the molar ratio 1:1 were dissolved in acetonitrile. A stirred reaction mixture was heated on a water bath at 80 °C for 10 h. In case of 3-chloropropanoic acid, the mixture was heated for 20 hours. After the reaction completion, the volatiles were removed *in vacuo*. The products were extensively washed with diethyl ether and dried *in vacuo*.

The phosphonium salts **2a-f** were dissolved in acetonitrile and treated with 1 M alkali solution to obtain the corresponding carboxylate phosphabetaines **3a-f**. After the reaction completion, the volatiles were removed *in vacuo*. The products were extensively washed with diethyl ether and dried *in vacuo*. All betaines were crystalline substances.

(2-Carboxyethyl)(carboxymethyl)diphenylphosphonium bromide **2a** Colourless crystals, mp 210-212 °C, yield: 80%. IR (ν/cm^{-1}): 1048, 1215, 1240, 1380, 1438, 1720, 3000. ^{1}H NMR spectrum (D_2O) δ_H, ppm (J/Hz): 1.79 (s, 2H, P-CH_2), 2.46 (t, 2H, P-CH_2-$\underline{CH_2}$, J_{HH} 7.3), 3.12 (t, 2H, P-CH_2, J_{HH} 7.3 Hz), 7.33-7.79 (m, 10H, Ph-P). ^{13}C NMR spectrum (D_2O), δ_C, ppm, 100.6 MHz: 17.85 (d, P-$\underline{CH_2}$-CH_2, $^{1}J_{PC}$ 55.1 Hz), 24.18 (d, P-$\underline{CH_2}$-COOH, $^{1}J_{PC}$ 73.0 Hz), 27.01 (s, P-CH_2-$\underline{CH_2}$), 117.16 (d, C^{ipso}, $^{1}J_{PC}$ 87.2), 130.83 (d, C^{o}, $^{2}J_{PC}$ 13.0), 133.58 (d, C^{m}, $^{3}J_{PC}$ 10.1), 136.07 (d, C^{p}, $^{4}J_{PC}$ 2.3), 168.21 (d, P-CH_2-$\underline{C}$OOH, $^{2}J_{PC}$ 3.8), 174.7 (d, CH_2-CH_2-$\underline{C}$OOH, $^{3}J_{PC}$ 13.9). ^{31}P NMR spectrum (D_2O): δ_P 25.27 ppm. Elemental analysis: Found, %: C 50.91, H 4.52, Br 19.72, P 7.87. $C_{17}H_{18}BrO_4P$. Calculated, %: C 51.41, H 4.57, Br 20.12, P 7.80.

Bis(2-carboxyethyl)diphenylphosphonium bromide **2b** Colourless crystals, mp 180-182 °C, yield: 81%. IR (ν/cm^{-1}): 1047, 1213, 1240, 1381, 1437, 1720, 2998. ^{1}H NMR spectrum (D_2O) δ_H, ppm (J/Hz): 2.57 (t, 4H, P(CH_2-$\underline{CH_2}$)$_2$, J_{HH} 7.4), 3.17 (t, 4H, P($\underline{CH_2}$-CH_2)$_2$, J_{HH} 7.5 Hz), 7.55-7.86 (m, 10H, Ph-P). ^{13}C NMR spectrum (D_2O), δ_C, ppm, 100.6 MHz: 16.79 (d, P($\underline{CH_2}$-CH_2)$_2$, $^{1}J_{PC}$ 54.1 Hz), 26.45 (s, P(CH_2-$\underline{CH_2}$)$_2$), 116.37 (d, C^{ipso}, $^{1}J_{PC}$ 84.9), 130.52 (d, C^{o}, $^{2}J_{PC}$ 12.5), 133.39 (d, C^{m}, $^{3}J_{PC}$ 9.9), 135.70 (d, C^{p}, $^{4}J_{PC}$ 2.1), 174.58 (d, $\underline{C}$OOH, $^{3}J_{PC}$ 13.8). ^{31}P NMR spectrum (D_2O): δ_P 27.42 ppm. Elemental analysis: Found, %: C 53.05, H 4.72, Br 18.43, P 7.60. $C_{18}H_{20}BrO_4P$. Calculated, %: C 52.57, H 4.90, Br 19.43, P 7.53.

(2-Carboxyethyl)(3-carboxypropyl)diphenylphosphonium bromide **2c** Colourless crystals, mp 119-120 °C, yield: 77%. IR (ν/cm^{-1}): 1049, 1210, 1240, 1260, 1380, 1437, 1720, 3000. ^{1}H NMR spectrum (D_2O) δ_H, ppm (J/Hz): 1.48-1.33 (m, 2H, P-CH_2-$\underline{CH_2}$-CH_2-COOH), 2.18 (t, 2H, $\underline{CH_2}$-COOH, J_{HH} 7.1), 2.49 (t, 2H, P-CH_2-$\underline{CH_2}$, J_{HH} 7.4), 2.78 (t, 2H, P-$\underline{CH_2}$-CH_2-CH_2, J_{HH} 7.3), 3.06 (t, 2H, P-$\underline{CH_2}$-CH_2, J_{HH} 7.4 Hz), 7.46-7.84 (m, 10H, Ph-P). ^{13}C NMR spectrum (D_2O), δ_C, ppm, 100.6 MHz: 15.89 (d, P-$\underline{CH_2}$-CH_2-COOH, $^{1}J_{PC}$ 54.1 Hz), 19.86 (d, P-$\underline{CH_2}$-$(CH_2)_2$, $^{1}J_{PC}$ 50.7 Hz), 20.37 (d, CH_2-$\underline{CH_2}$-CH_2, $^{2}J_{PC}$ 54.0 Hz), 24.98 (d, P-CH_2-$\underline{CH_2}$-COOH, $^{2}J_{PC}$ 16.7 Hz), 31.55 (s, CH_2-CH_2-$\underline{CH_2}$), 116.75 (d, C^{ipso}, $^{1}J_{PC}$ 84.6), 130.15 (d, C^{o}, $^{2}J_{PC}$ 12.3), 132.76 (d, C^{m}, $^{3}J_{PC}$ 9.6), 135.16 (d, C^{p}, $^{4}J_{PC}$ 2.5), 175.14 (d, $\underline{C}$OOH, $^{3}J_{PC}$ 14.2), 177.79 (s, $(CH_2)_3$-$\underline{C}$OOH). ^{31}P NMR spectrum (D_2O): δ_P 27.20 ppm. Elemental analysis: Found, %: C 54.10, H 5.25, Br 18.64, P 7.24. $C_{19}H_{22}BrO_4P$. Calculated, %: C 53.66, H 5.21, Br 18.79, P 7.28.

(4-Carboxybutyl)(2-carboxyethyl)diphenylphosphonium bromide **2d** Yellow oil, yield: 79%. IR (ν/cm^{-1}): 689, 741, 799, 1113, 1186, 1223, 1395, 1437, 1715, 2919, 3385. ^{1}H NMR spectrum (D_2O) δ_H, ppm (J/Hz): 1.46-1.31 (m, 2H, $\underline{CH_2}$-CH_2-CH_2-COOH), 1.55 (dt, 2H, $\underline{CH_2}$-CH_2-COOH, J_{HH} 14.2, 7.0 Hz), 2.18 (t, 2H, $\underline{CH_2}$-COOH, J_{HH} 7.0), 2.49 (t, 2H, P-CH_2-$\underline{CH_2}$, J_{HH} 7.4), 2.78 (t, 2H, P-$\underline{CH_2}$-CH_2-CH_2, J_{HH} 7.2), 3.06 (t, 2H, P-$\underline{CH_2}$-CH_2, J_{HH} 7.4 Hz), 7.48-7.86 (m, 10H, Ph-P). ^{13}C NMR spectrum (D_2O), δ_C, ppm, 100.6 MHz: 15.96 (d, P-$\underline{CH_2}$-CH_2-COOH, $^{1}J_{PC}$ 54.0 Hz), 19.76 (d, P-$\underline{CH_2}$-$(CH_2)_3$, $^{1}J_{PC}$ 50.8 Hz), 20.28 (d, CH_2-$\underline{CH_2}$-$(CH_2)_2$, $^{2}J_{PC}$ 54.0 Hz), 24.78 (d, P-CH_2-$\underline{CH_2}$-COOH, $^{2}J_{PC}$ 16.9 Hz), 26.01 (s, $(CH_2)_2$-$\underline{CH_2}$-CH_2), 32.65 (s, $(CH_2)_2$-CH_2-$\underline{CH_2}$), 116.65 (d, C^{ipso}, $^{1}J_{PC}$ 84.6), 130.05 (d, C^{o}, $^{2}J_{PC}$ 12.3), 132.79 (d, C^{m}, $^{3}J_{PC}$ 9.6), 135.06 (d, C^{p}, $^{4}J_{PC}$ 2.5), 174.14 (d, $\underline{C}$OOH, $^{3}J_{PC}$ 14.0), 177.67 (s, $(CH_2)_4$-$\underline{C}$OOH). ^{31}P NMR spectrum (D_2O): δ_P 26.77 ppm. Elemental analysis: Found, %: C 55.19, H 5.48, Br 18.35, P 7.11. $C_{20}H_{24}BrO_4P$. Calculated, %: C 54.68, H 5.51, Br 18.19, P 7.05.

(2-Carboxyethyl)(7-carboxyheptyl)diphenylphosphonium bromide **2e** Yellow oil, yield: 74%. IR (ν/cm^{-1}): 689, 743, 804, 900, 996, 1113, 1186, 1232, 1392, 1437, 1715, 2858, 2927, 3386. ^{1}H NMR spectrum (D_2O) δ_H, ppm (J/Hz): 1.15-1.21 (m, 10H, $(\underline{CH_2})_5$-CH_2-COOH), 2.13 (t, 2H, $\underline{CH_2}$-COOH, J_{HH} 7.3), 2.48 (t, H, P-CH_2-$\underline{CH_2}$, J_{HH} 7.4), 2.75 (t, 2H, P-$\underline{CH_2}$-$(CH_2)_5$, J_{HH} 7.2), 3.04 (t, 2H, P-$\underline{CH_2}$-CH_2, J_{HH} 7.4 Hz), 7.48-7.78 (m, 10H, Ph-P). ^{31}P NMR spectrum (D_2O): δ_P 26.83 ppm. Elemental analysis: Found, %: C 57.12, H 6.25, Br 16.68, P 6.39. $C_{21}H_{26}BrO_4P$. Calculated, %: C 57.39, H 6.28, Br 16.60, P 6.43.

(2-Carboxyethyl)(9-carboxynonyl)diphenylphosphonium bromide **2f** Yellow oil, yield: 78%. IR (ν/cm^{-1}): 690, 743, 801, 899, 996, 1112, 1160, 1384, 1437, 1722, 2855, 2926. ^{1}H NMR spectrum (D_2O) δ_H, ppm (J/Hz): 0.86-1.42 (m, 14H, $(\underline{CH_2})_7$-CH_2-COOH), 2.12 (t, 2H, $\underline{CH_2}$-COOH, J_{HH} 7.3), 2.48 (t, H, P-CH_2-$\underline{CH_2}$, J_{HH} 7.4), 2.73 (t, 2H, P-$\underline{CH_2}$-$(CH_2)_5$, J_{HH} 7.2), 3.03 (t, 2H, P-$\underline{CH_2}$-CH_2, J_{HH} 7.4 Hz), 7.47-7.75 (m, 10H, Ph-P). ^{31}P NMR spectrum (D_2O): δ_P 26.92 ppm. Elemental analysis: Found, %: C 58.75, H 6.69, Br 15.61, P 6.05. $C_{22}H_{28}BrO_4P$. Calculated, %: C 58.94, H 6.73, Br 15.69, P 6.08.

Bis(2-carboxyethyl)diphenylphosphonium chloride **2g** Colourless crystals, mp 186-189 °C, yield: 65%. IR (ν/cm^{-1}): 940, 1046, 1112, 1141, 1160, 1179, 1220, 1391, 1437, 1736, 2829. ^{1}H NMR spectrum (D_2O) δ_H, ppm (J/Hz): 2.55 (t, 4H, $P(CH_2$-$\underline{CH_2})_2$, J_{HH} 7.3), 3.16 (t, 4H, $P(\underline{CH_2}$-$CH_2)_2$, J_{HH} 7.4 Hz), 7.45-7.75 (m, 10H, Ph-P). ^{13}C NMR spectrum (D_2O), δ_C, ppm, 100.6 MHz: 16.81 (d, $P(\underline{CH_2}$-$CH_2)_2$, $^{1}J_{PC}$ 54.3 Hz), 26.39 (s, $P(CH_2$-$\underline{CH_2})_2$), 116.35 (d, C^{ipso}, $^{1}J_{PC}$ 84.7), 130.51 (d, C^{o}, $^{2}J_{PC}$ 12.4), 133.39 (d, C^{m}, $^{3}J_{PC}$ 9.9), 135.70 (d, C^{p}, $^{4}J_{PC}$ 2.1), 174.45 (d, $\underline{C}$OOH, $^{3}J_{PC}$ 13.6). ^{31}P NMR spectrum (D_2O): δ_P 27.24 ppm. Elemental analysis: Found, %: C 58.39, H 5.47, Cl 9.77, P 8.48. $C_{18}H_{20}ClO_4P$. Calculated, %: C 58.97, H 5.50, Cl 9.73, P 8.53.

6-Hydroxy-6-oxo-4,4-diphenyl-4-phosphoniahexanoate 3**a** Colourless crystals, mp 221-223 °C, yield: 95%. IR (ν/cm^{-1}): 1047, 1218, 1238, 1340, 1438, 1553, 3000. ^{1}H NMR spectrum (D_2O) δ_H, ppm (J/Hz): 1.70 (s, 2H, P-CH_2), 2.22 (t, 2H, P-CH_2-$\underline{CH_2}$, J_{HH} 7.3), 3.00 (t, 2H, P-CH_2, J_{HH} 7.3 Hz), 7.20-7.77 (m, 10H, Ph-P). ^{13}C NMR spectrum (D_2O), δ_C, ppm, 100.6 MHz: 17.80 (d, P-$\underline{CH_2}$-CH_2, $^{1}J_{PC}$ 55.2 Hz), 24.22 (d, P-$\underline{CH_2}$-COOH, $^{1}J_{PC}$ 73.1 Hz), 27.12 (s, P-CH_2-$\underline{CH_2}$), 117.15 (d, C^{ipso}, $^{1}J_{PC}$ 87.2), 130.93 (d, C^{o}, $^{2}J_{PC}$ 13.0), 133.78 (d, C^{m}, $^{3}J_{PC}$ 10.1), 136.27 (d, C^{p}, $^{4}J_{PC}$ 2.3), 168.31 (d, P-CH_2-$\underline{C}$OOH, $^{2}J_{PC}$ 3.7), 174.8 (d, CH_2-CH_2-$\underline{C}$OOH, $^{3}J_{PC}$ 13.9). ^{31}P NMR spectrum (D_2O): δ_P 22.13 ppm. Elemental analysis: Found, %: C 64.89, H 5.46, P 9.82. $C_{17}H_{17}O_4P$. Calculated, %: C 64.56, H 5.42, P 9.79.

X-Ray Crystallography. Data set for single crystal of compound $(C_{17}H_{18}O_4P)^+$, Br^- was collected on a Bruker AXS Kappa APEX II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods using APEX3 [S1] for data collection, SAINT [S2] for data reduction, SHELXT [S3] for structure solution, SHELXL [S3] for structure refinement by full-matrix least-squares against F^2, and SADABS [S4] for multi-scan absorption correction. Hydrogen atoms at carbon atoms were placed into calculated positions and refined as "riding" atoms. Hydrogen atoms of the carboxyl groups were revealed from difference Fourier map and refined isotropically. CCDC 2035123 contains the supplementary crystallographic data for this paper.

Crystal data: formula $(C_{17}H_{18}O_4P)^+$, Br^-, M = 397.19 g mol^{-1}, triclinic, space group P–1 (No. 2), Z = 2, a = 8.0672(5) Å, b = 9.4323(6) Å, c = 12.7937(8) Å, α = 88.123(3)°, β = 82.330(3)°, γ = 65.723(3)°, V = 879.21(10) Å^3, ρ_{calc} = 1.500 g cm^{-3}, μ = 2.445 mm^{-1}, 42122 reflections collected (*–10≤ h ≤ 10, –12 ≤ k ≤ 12, –17 ≤ l ≤ 17*), θ range = 1.607° to 28.872°, 4578 independent (R_{int} = 0.0249) and 4437 observed reflections [$I \geq 2\ \sigma(I)$], 216 refined parameters, R_1 = 0.0182, wR^2 = 0.0472, goodness of fit S = 1.049, max(min). Residual electron density 0.362 (–0.482) eÅ^{-3}.

References

[S1] Bruker. APEX3 Crystallography Software Suite, Bruker AXS, Inc., Madison, WI, USA. 2016.

[S2] Bruker. SAINT. Crystallography Software Suite, Bruker AXS, Inc., Madison, WI, USA. 2016.

[S3] Sheldrick, G. M. A Short History of SHELX. Acta Crystallogr. Sect. A Found. Crystallogr. 2008, 64 (1), 112–122. https://doi.org/10.1107/S0108767307043930.

[S4] Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. Comparison of Silver and Molybdenum Microfocus X-Ray Sources for Single-Crystal Structure Determination. J. Appl. Crystallogr. 2015, 48 (1), 3–10. https://doi.org/10.1107/S1600576714022985.

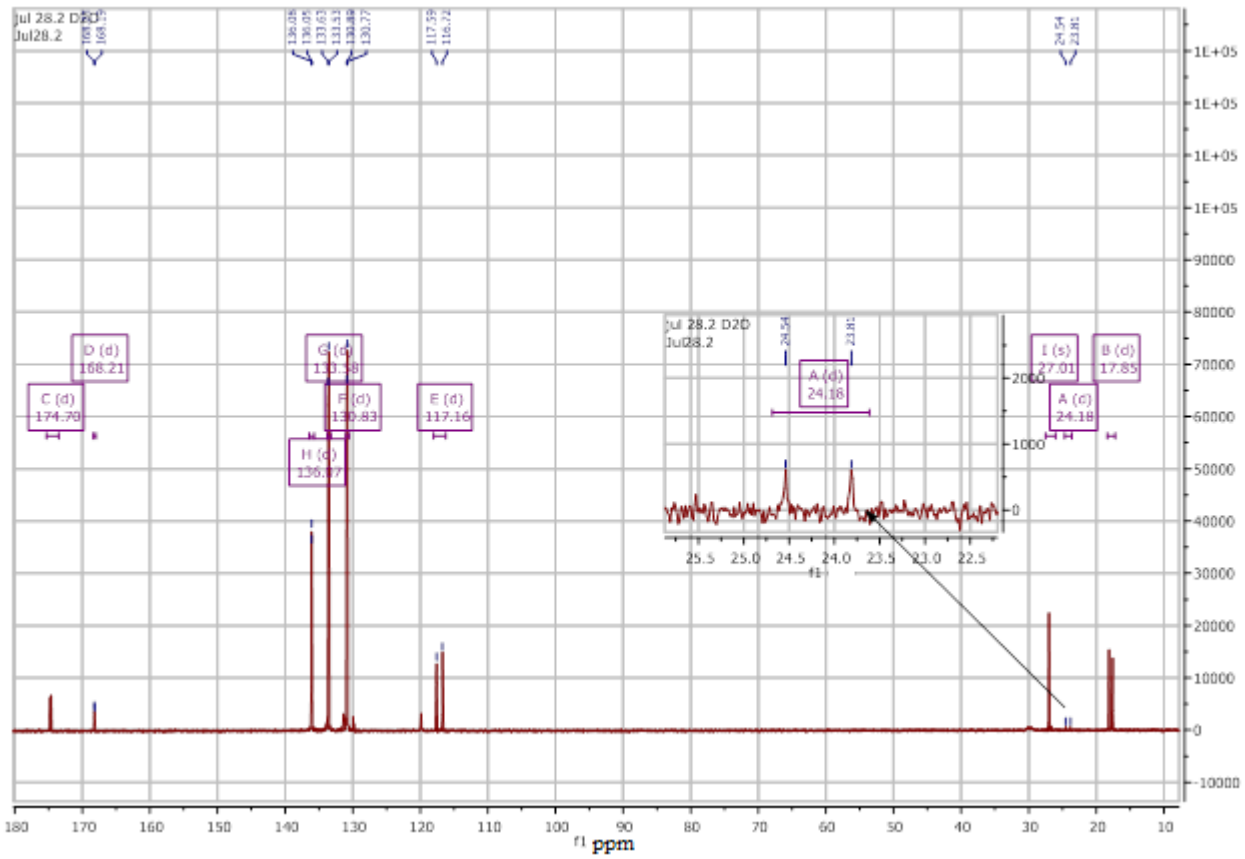

Figure S1 $^{13}C\{^{1}H\}$ NMR spectrum of phosphonium salt **2a** (100.6 MHz, D_2O).

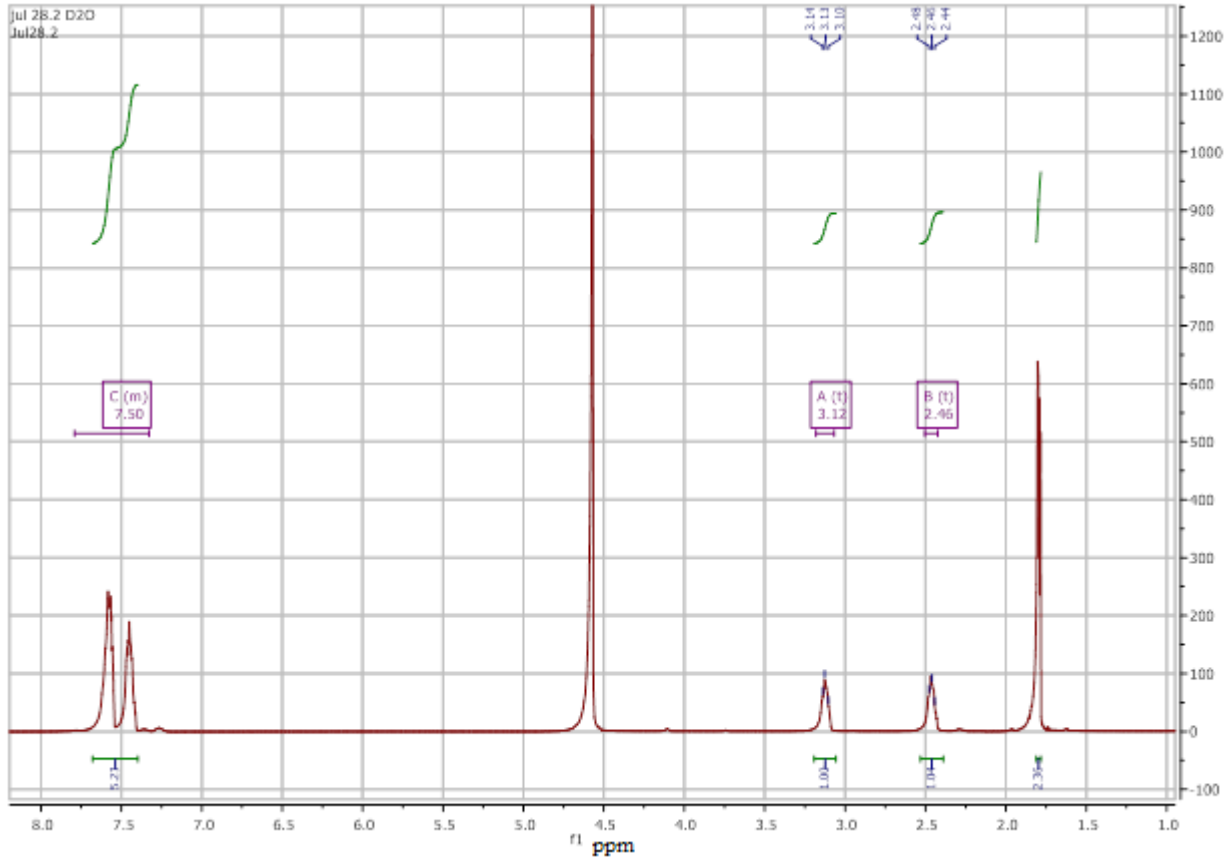

Figure S2 $^{1}H\{^{31}P\}$ NMR spectrum of phosphonium salt **2a** (400 MHz, D_2O).

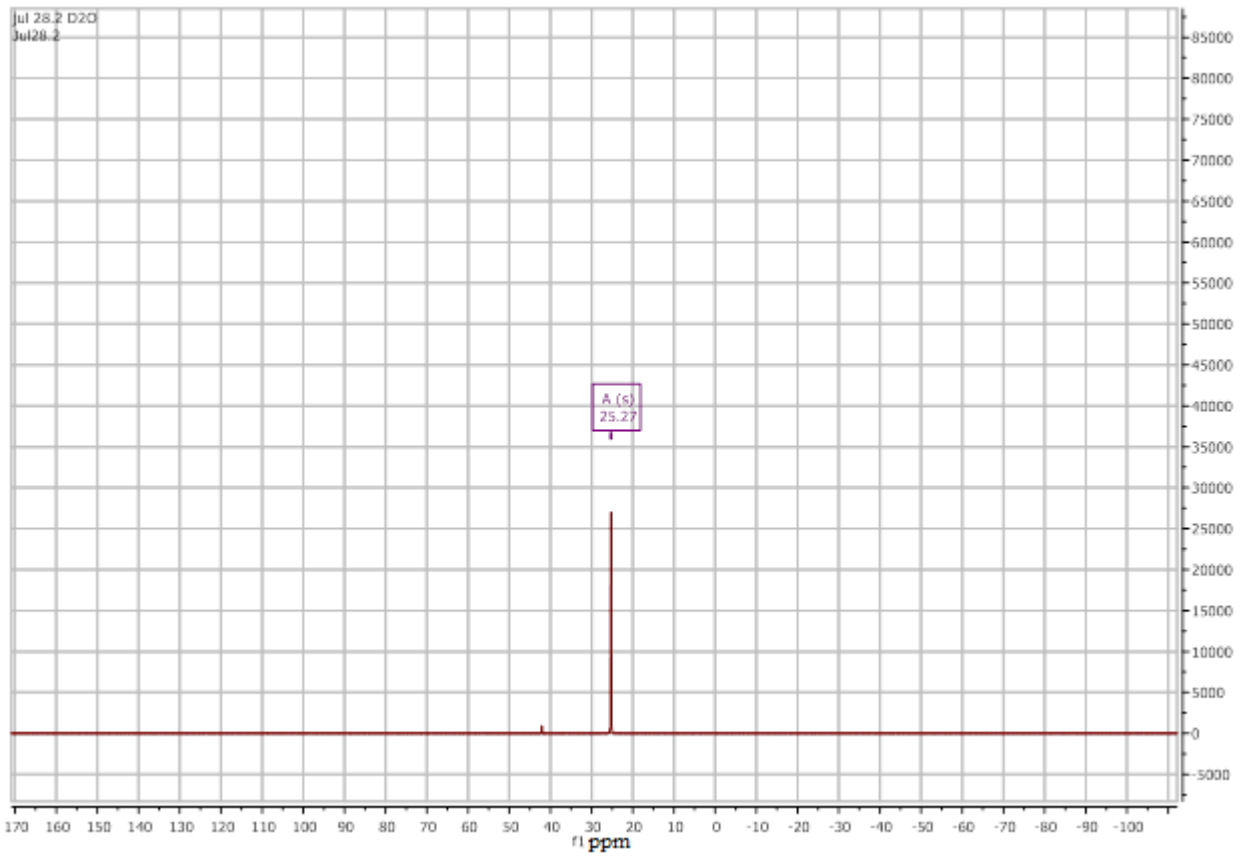

Figure S3 $^{31}P\{^{1}H\}$ NMR spectrum of phosphonium salt **2a** (122.4 MHz, D_2O).

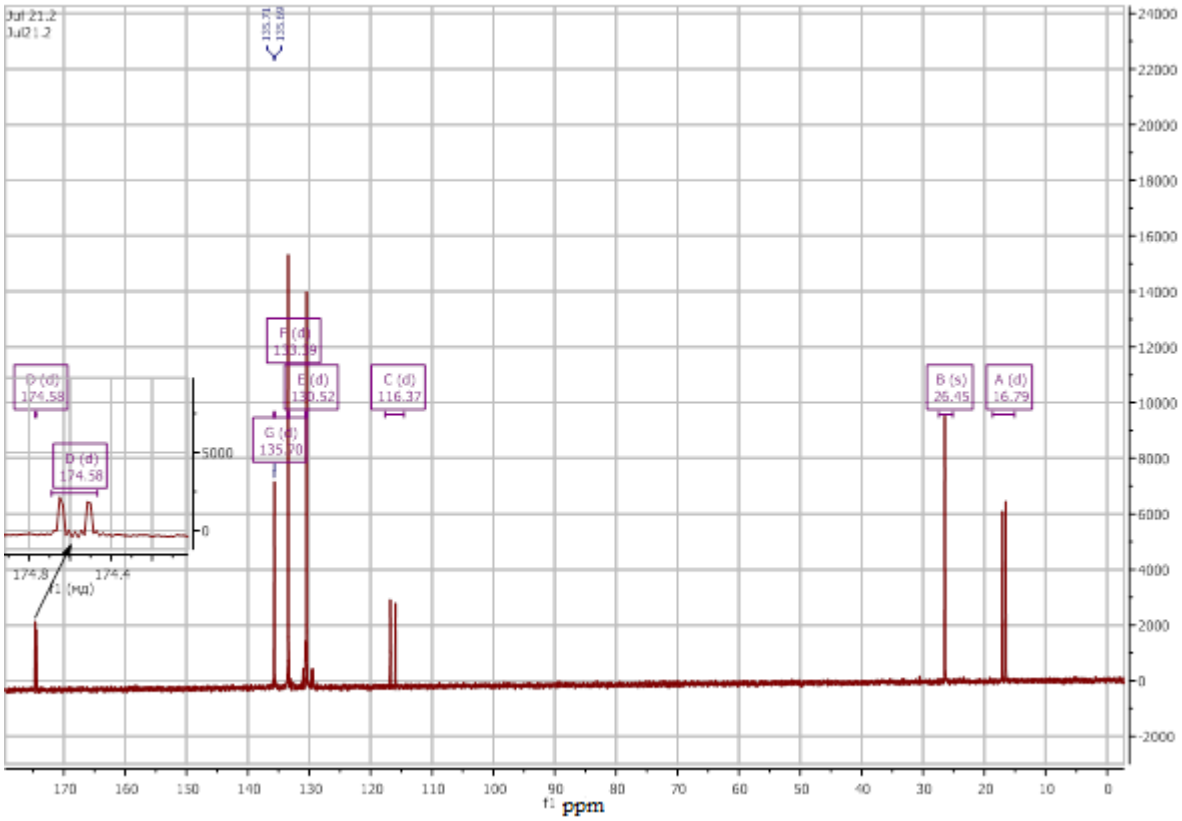

Figure S4 $^{13}C\{^{1}H\}$ NMR spectrum of phosphonium salt **2b** (100.6 MHz, D_2O).

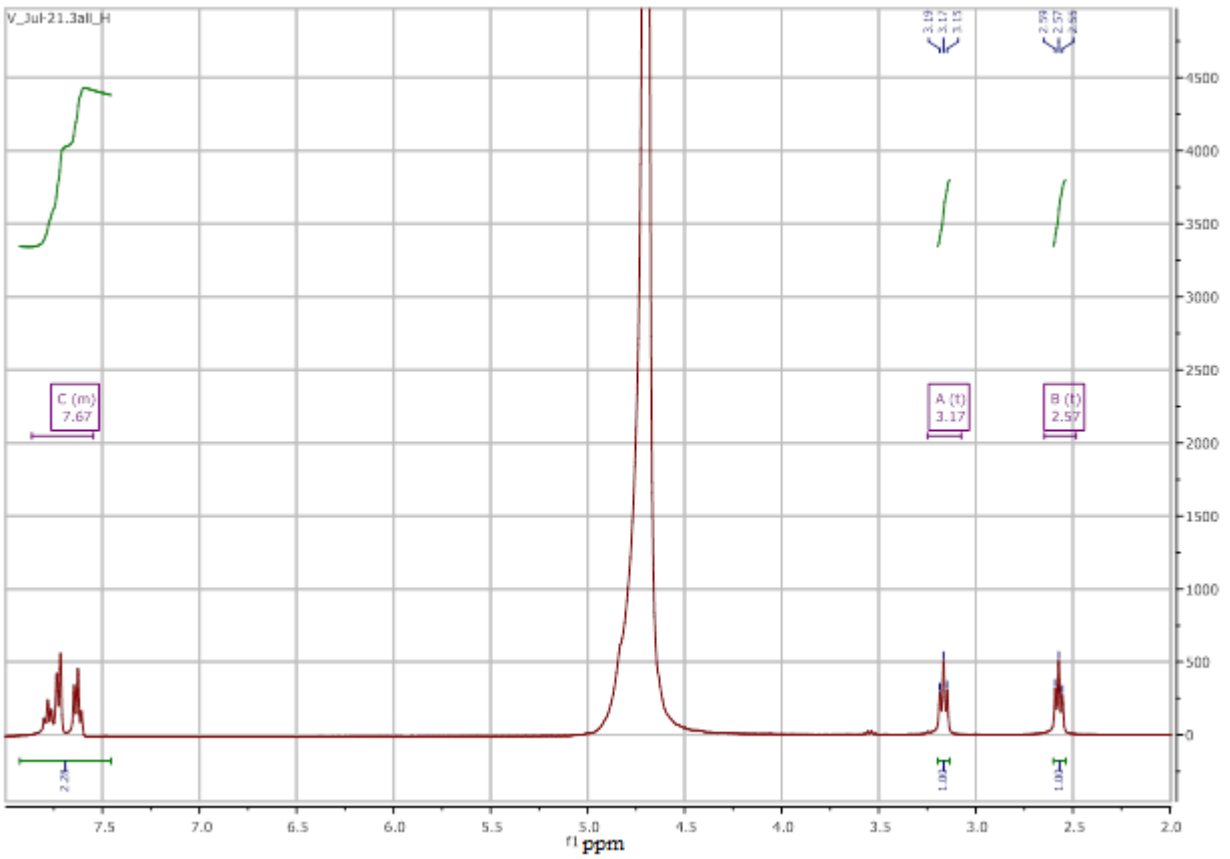

Figure S5 $^{1}H\{^{31}P\}$ NMR spectrum of phosphonium salt **2b** (400 MHz, D_2O).

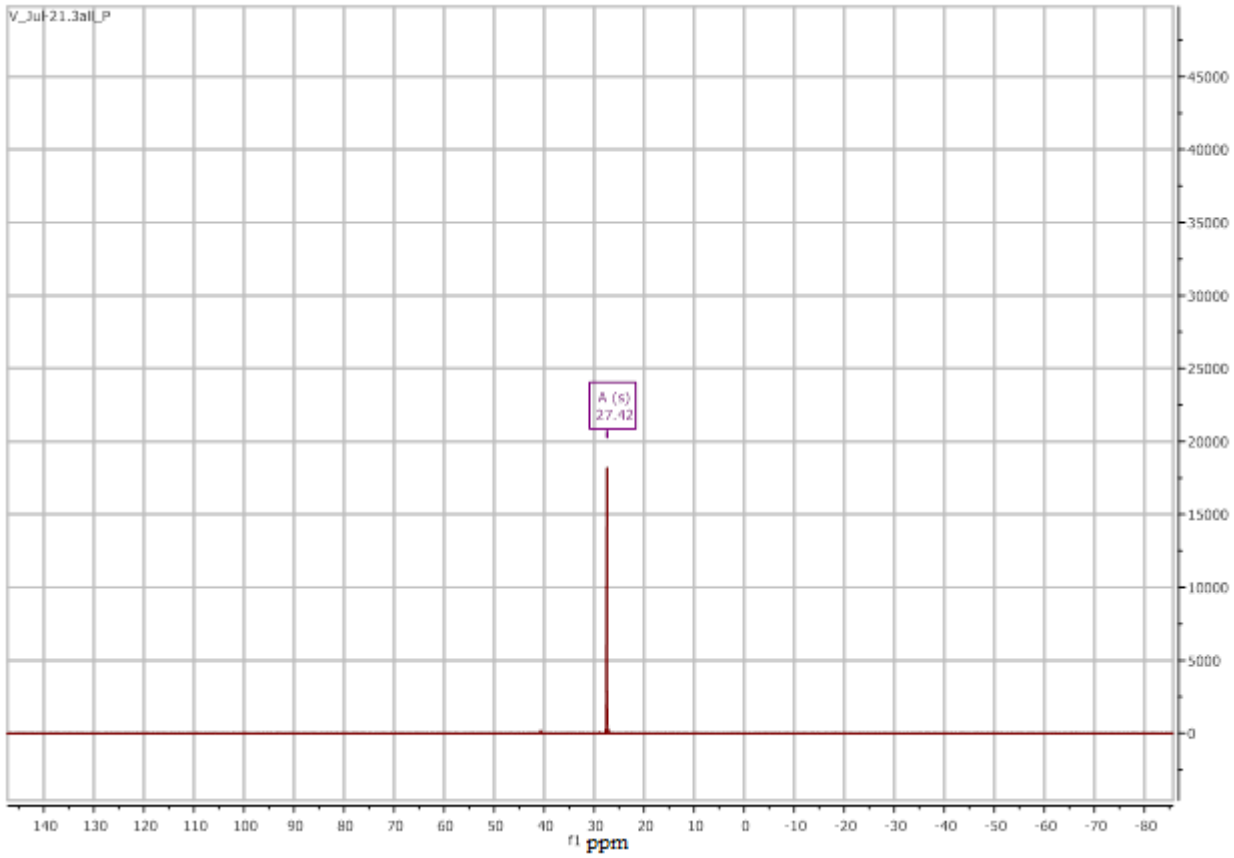

Figure S6 $^{31}P\{^{1}H\}$ NMR spectrum of phosphonium salt **2b** (122.4 MHz, D_2O).

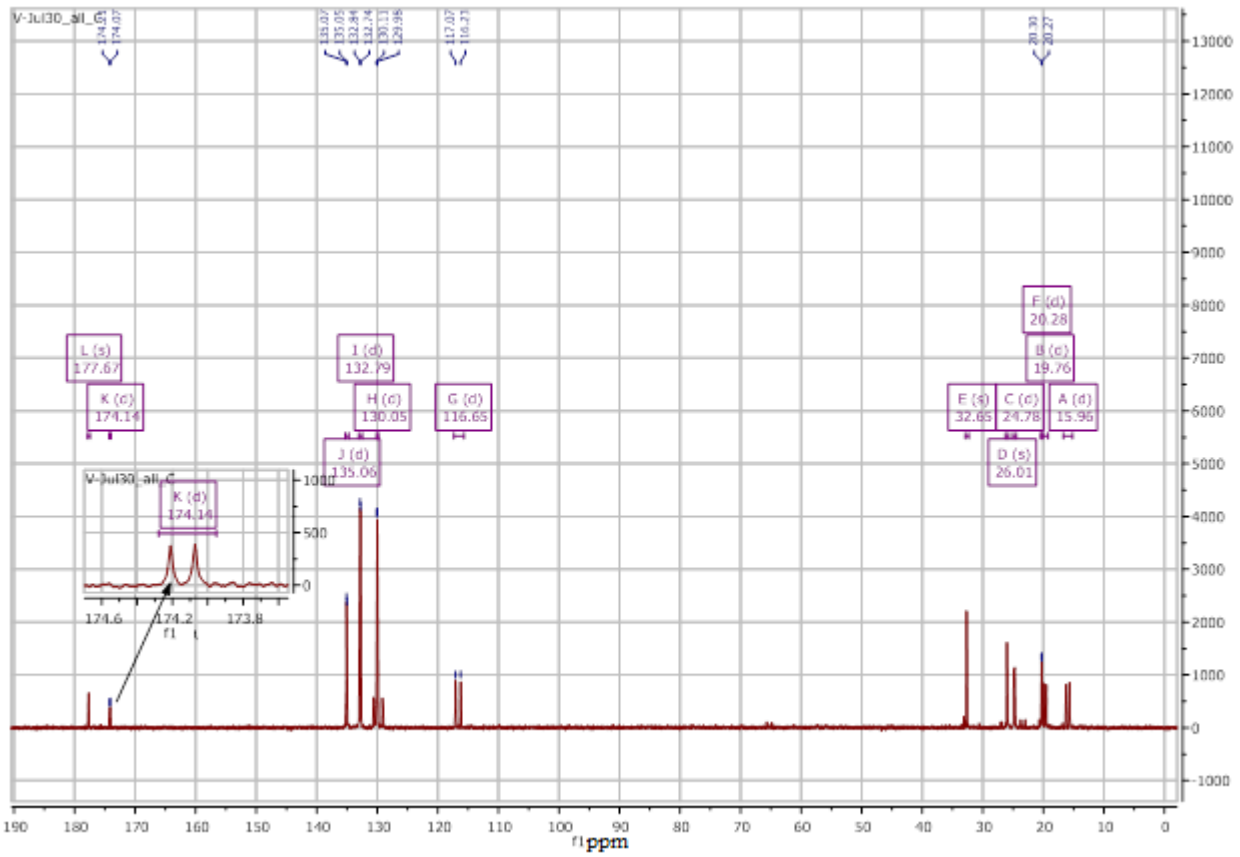

Figure S7 $^{13}C\{^{1}H\}$ NMR spectrum of phosphonium salt **2d** (100.6 MHz, D_2O).

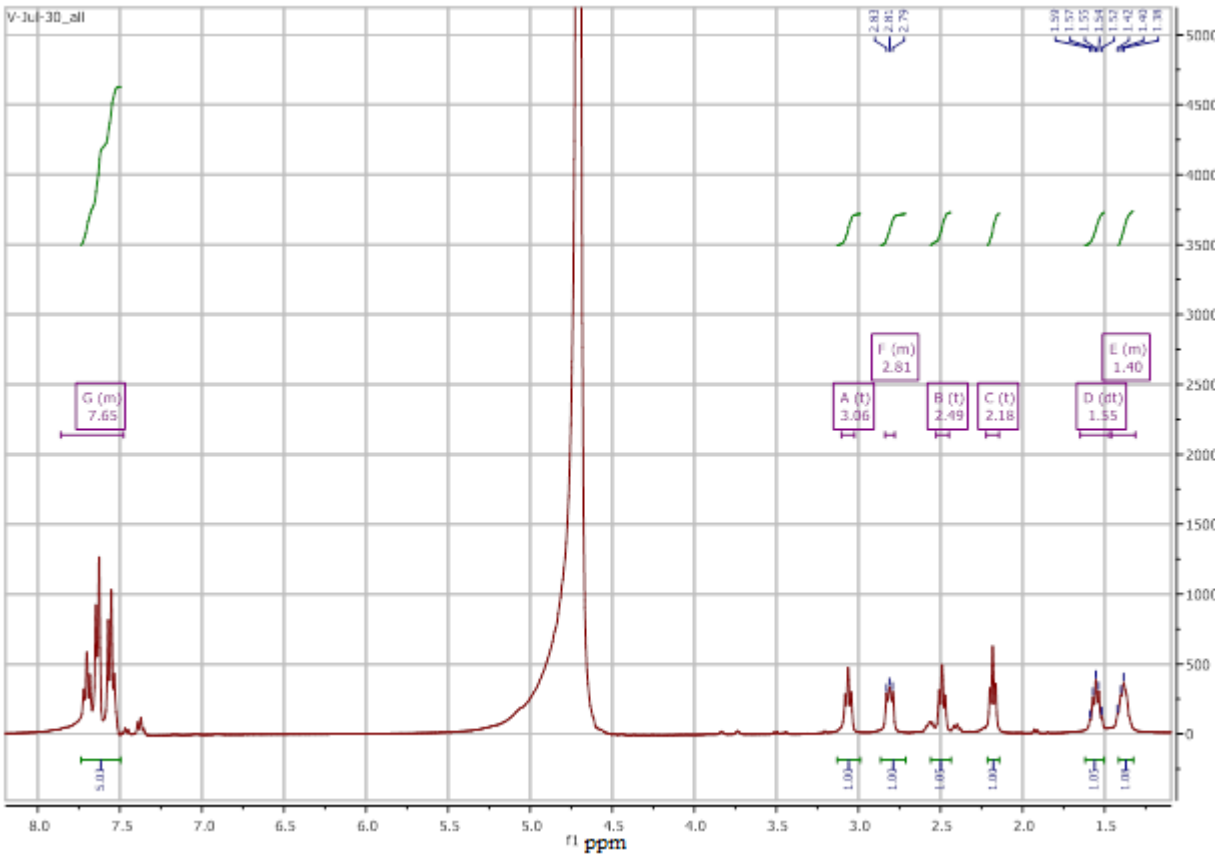

Figure S8 $^{1}H\{^{31}P\}$ NMR spectrum of phosphonium salt **2d** (400 MHz, D_2O).

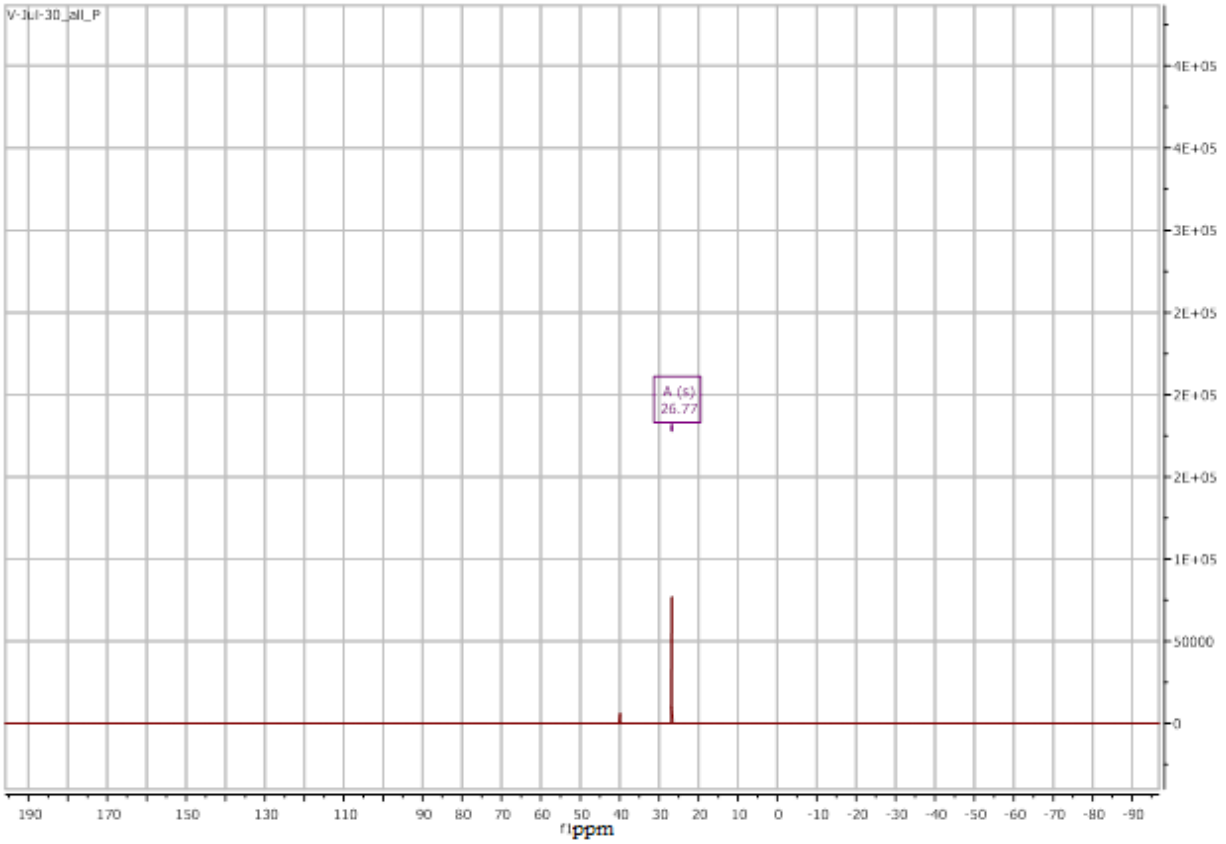

Figure S9 $^{31}P\{^{1}H\}$ NMR spectrum of phosphonium salt **2d** (122.4 MHz, D_2O).

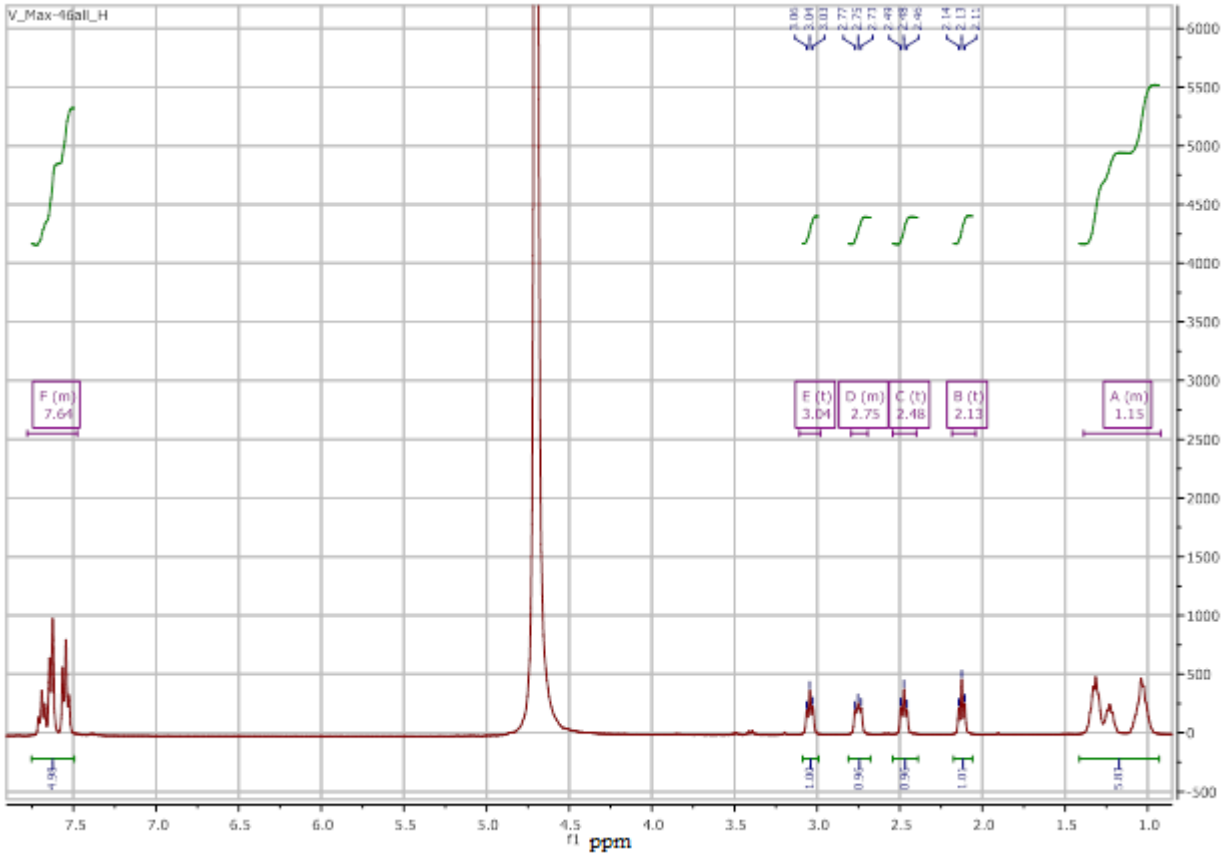

Figure S10 $^{1}H\{^{31}P\}$ NMR spectrum of phosphonium salt **2e** (400 MHz, D_2O).

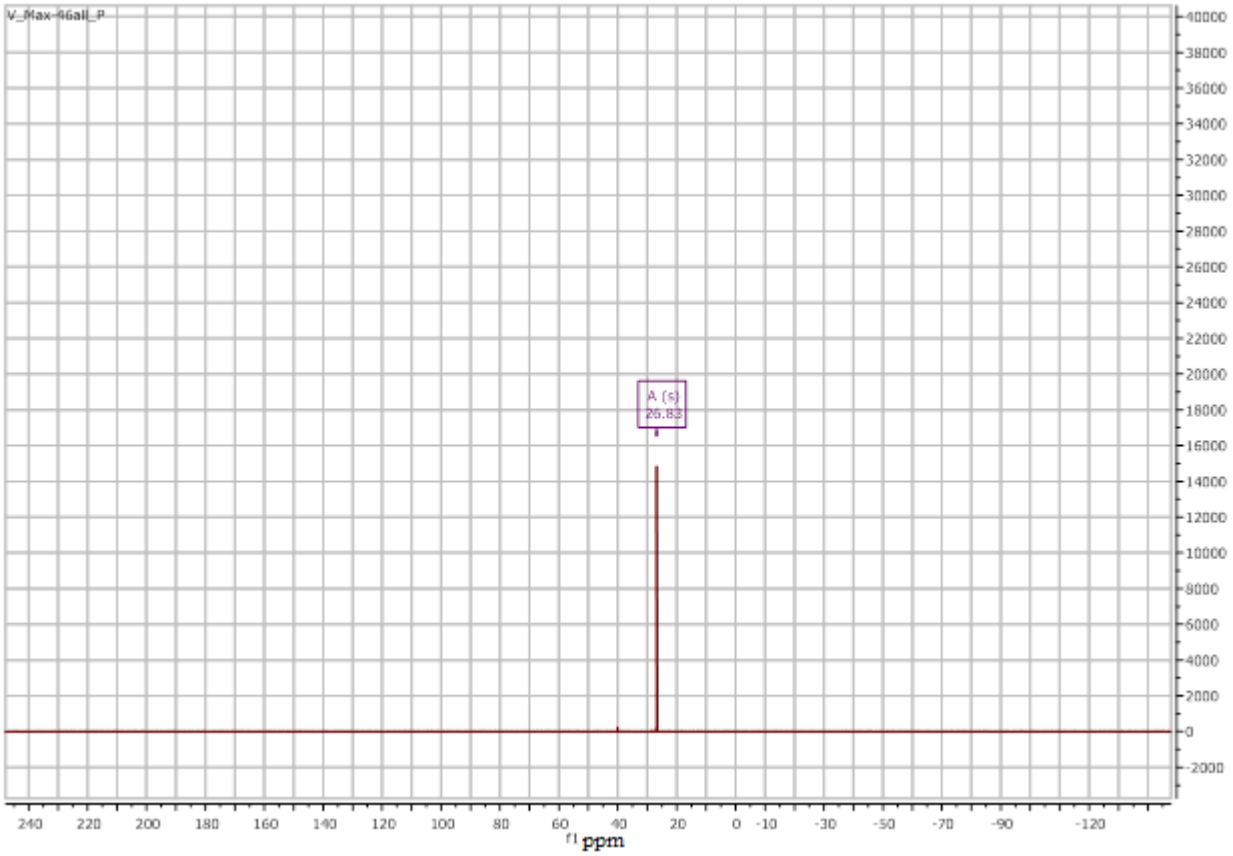

Figure S11 $^{31}P\{^{1}H\}$ NMR spectrum of phosphonium salt **2e** (122.4 MHz, D_2O).

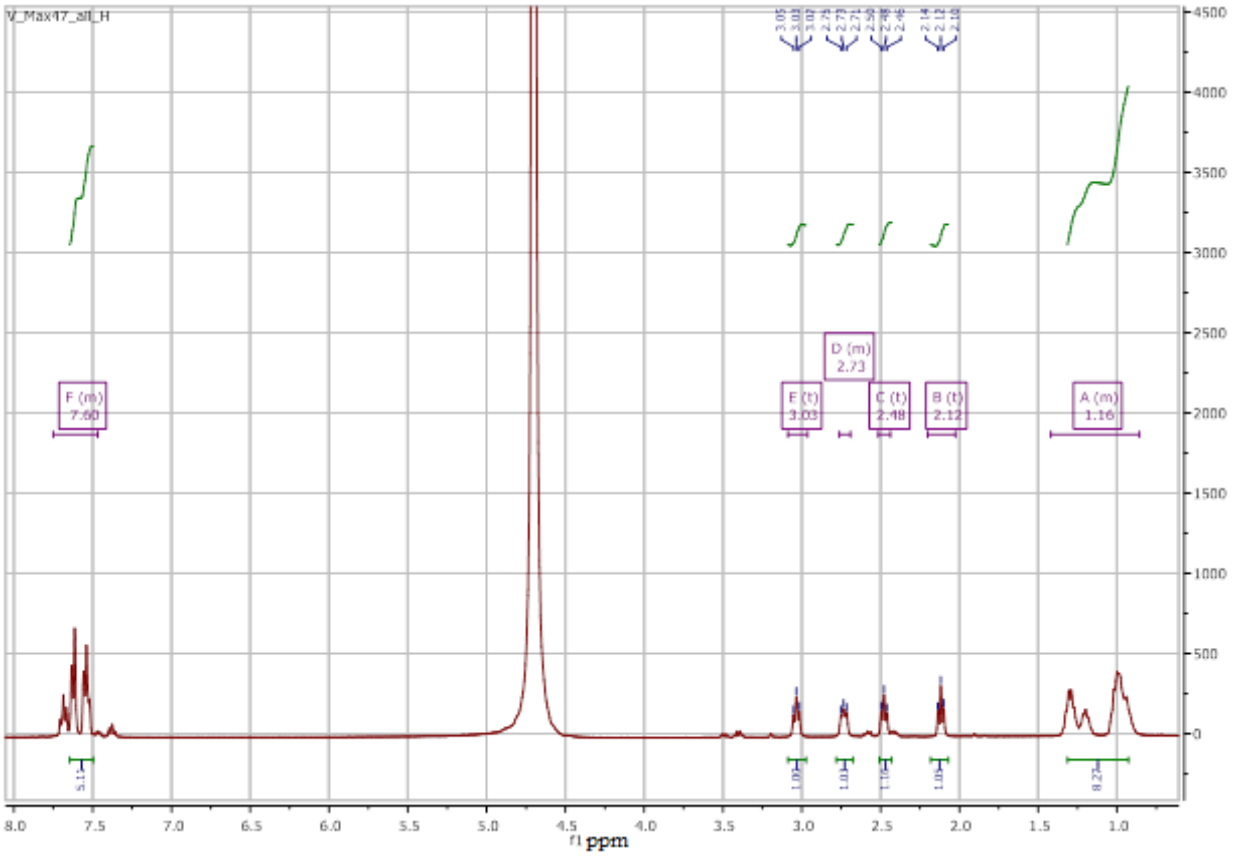

Figure S12 $^{1}H\{^{31}P\}$ NMR spectrum of phosphonium salt **2f** (400 MHz, D_2O).

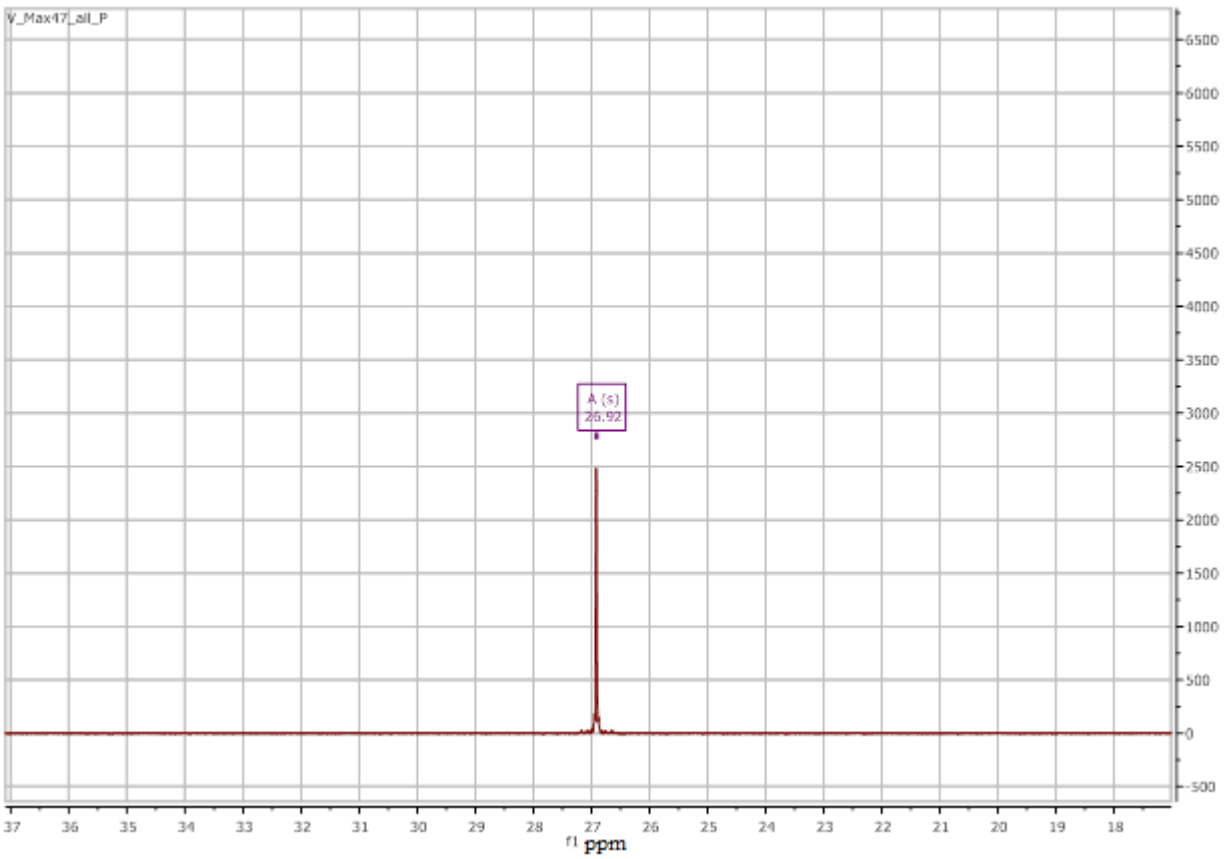

Figure S13 $^{31}P\{^{1}H\}$ NMR spectrum of phosphonium salt **2f** (122.4 MHz, D_2O).

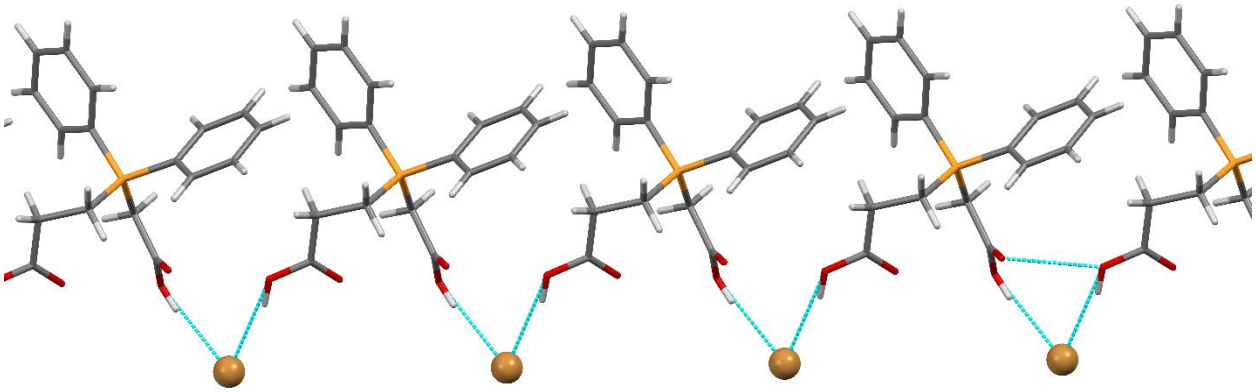

Figure S14 A fragment of crystal packing of (2-carboxyethyl)(carboxymethyl)-diphenylphosphonium bromide **2a** showing hydrogen bonds of carboxylic groups with bromine anions.

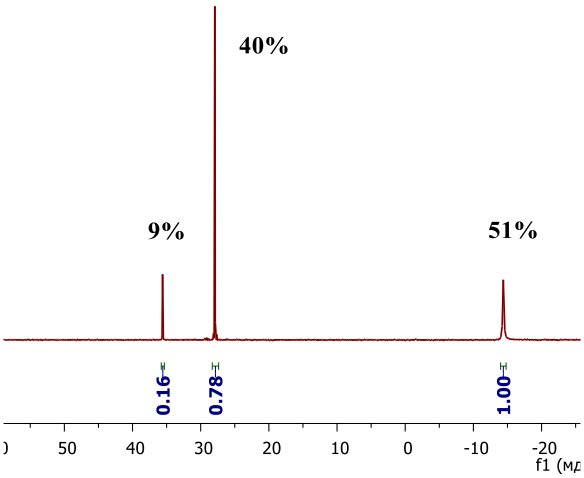

Figure S15 NMR ^{31}P spectrum of the reaction mixture of the reaction with 4-chlorobutyric acid

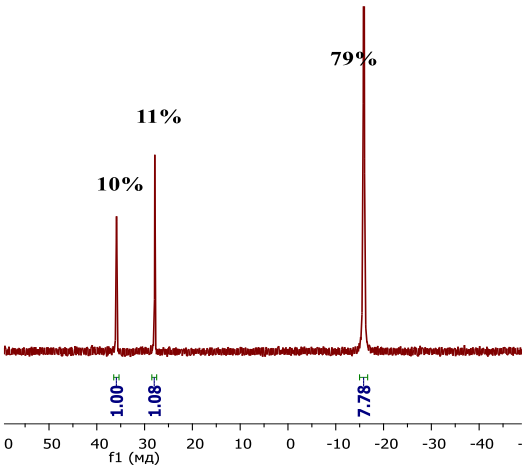

Figure S16 NMR ^{31}P spectrum of the reaction mixture of the reaction with 5-chlorovaleric acid