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Synthesis and antimicrobial activity of mono- and bisphosphonium salts based on tertiary phosphines and ethyl bromoacetate

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Experimental section

General details

NMR spectra were recorded on the Bruker Avance III instrument with an operating frequency of 122.4 MHz for $^{31}P\{^{1}H\}$ spectra (internal standard 85% H_3PO_4), an operating frequency of 100.6 MHz for $^{13}C\{^{1}H\}$ spectra (internal standard TMS) and an operating frequency of 400 MHz for $^{1}H\{^{31}P\}$ spectra (internal standard TMS) in a solution of D_2O or $CDCl_3$. IR spectra were recorded on the PerkinElmer UATR Two FT-IR Spectrometer (Spectrum Two). Thermal stability was studied using a STA 449C Jupiter synchronous microthermoanalyzer (Netzsch, Germany) at heating rate of 10 deg/min under argon atmosphere. 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.

New compounds

Samples of tertiary phosphines and ethyl bromacetate in a molar ratio of 1:1 were dissolved in acetonitrile and placed in a round-bottomed flask with a volume of 50 ml. A molar ratio of 1:2 was used for bisphosphines and ethyl bromacetate. The reactions were carried out at a

temperature of 60 ℃ for 5-8 hours. After the reaction completion, the volatiles were removed *in vacuo*. The products were extensively washed with diethyl ether and dried *in vacuo*.

*(2-Ethoxy-2-oxoethyl)triphenylphosphonium bromide (**1a**)*

Yield 82%, mp. 112-102°C. IR (ν/cm^{-1}): 747, 1017, 1109, 1159, 1187, 1317, 1435, 1708, 2987. $^{1}H\{^{31}P\}$ NMR spectrum (D_2O) δ_H, ppm (*J*/Hz): 0.76 (t, 3H, CH_2-$\underline{CH_3}$, J_{HH} 7.1), 3.82 (q, 2H, $\underline{CH_2}$-CH_3, J_{HH} 7.1 Hz), 4.62 (s, 2H, P-CH_2), 7.16-7.92 (m, 15H, Ph-P). $^{13}C\{^{1}H\}$ NMR spectrum (D_2O), δ_C, ppm, 100.6 MHz: 8.02 (d, P-$\underline{CH_2}$, $^{1}J_{PC}$ 58.3 Hz), 12.3 (s, CH_2-$\underline{CH_3}$), 63.7 (s, $\underline{CH_2}$-CH_3), 117.19 (d, C^{ipso}, $^{1}J_{PC}$ 89.3), 130.06 (d, C^{m}, $^{3}J_{PC}$ 13.4), 133.55 (d, C^{o}, $^{2}J_{PC}$ 10.8), 135.36 (d, C^{p}, $^{4}J_{PC}$ 3.2), 165.66 (d, P-CH_2-$\underline{C}$OO, $^{2}J_{PC}$ 4.2). $^{31}P\{^{1}H\}$ NMR spectrum (D_2O): δ_P 21.05 ppm. Elemental analysis: Found, %: C 61.63, H 5.14, Br 18.71, P 7.25. $C_{22}H_{22}BrO_2P$. Calculated, %: C 61.55, H 5.17, Br 18.61, P 7.22.

(2-Ethoxy-2-oxoethyl)(methyl)diphenylphosphonium bromide (**1b**)

Yield 78%. IR (ν/cm^{-1}): 687, 744, 997, 1021, 1113, 1187, 1250, 1437, 1720, 2978. $^{1}H\{^{31}P\}$ NMR spectrum (D_2O) δ_H, ppm (*J*/Hz): 0.81 (t, 3H, CH_2-$\underline{CH_3}$, J_{HH} 7.0), 2.44 (s, 3H, P-$\underline{CH_3}$), 3.85 (q, 2H, $\underline{CH_2}$-CH_3, J_{HH} 7.1 Hz), 4.62 (s, 2H, P-CH_2), 7.39-7.66 (m, 10H, Ph-P). $^{13}C\{^{1}H\}$ NMR spectrum (D_2O), δ_C, ppm, 100.6 MHz: 7.21 (d, P-$\underline{CH_3}$, $^{1}J_{PC}$ 56.8 Hz), 8.25 (d, P-$\underline{CH_2}$, $^{1}J_{PC}$ 57.8 Hz), 12.94 (s, CH_2-$\underline{CH_3}$), 65.8 (s, $\underline{CH_2}$-CH_3), 118.07 (d, C^{ipso}, $^{1}J_{PC}$ 88.8), 130.01 (d, C^{m}, $^{3}J_{PC}$ 12.9), 132.16 (d, C^{o}, $^{2}J_{PC}$ 10.6), 135.14 (d, C^{p}, $^{4}J_{PC}$ 3.1), 165.74 (d, P-CH_2-$\underline{C}$OO, $^{2}J_{PC}$ 4.4). $^{31}P\{^{1}H\}$ NMR spectrum (D_2O): δ_P 19.9 ppm. Elemental analysis: Found, %: C 55.69, H 5.51, Br 21.89, P 8.39. $C_{17}H_{20}BrO_2P$. Calculated, %: C 55.60, H 5.49, Br 21.76, P 8.43.

(2-Carboxyethyl)(2-ethoxy-2-oxoethyl)diphenylphosphonium bromide (**1c**)

Yield 89%, mp. 156-160°C. IR (ν/cm^{-1}): 688, 743, 804, 1022, 1112, 1185, 1248, 1369, 1437, 1721, 2900. $^{1}H\{^{31}P\}$ NMR spectrum (D_2O) δ_H, ppm (*J*/Hz): 0.83 (t, 3H, CH_2-$\underline{CH_3}$, J = 7.1), 2.53 (t, 2H, P-CH_2-$\underline{CH_2}$, J = 7.5), 3.18 (t, 2H, P-$\underline{CH_2}$-CH_2, J = 7.4), 3.86 (q, 2H, $\underline{CH_2}$-CH_3, J = 7.0), 4.62 (s, 2H, $\underline{CH_2}$), 7.42-7.76 (m, 10H, $\underline{Ph_2}$-P). $^{13}C\{^{1}H\}$ NMR spectrum (D_2O), δ_C, ppm,

100.6 MHz: 12.85 (s, CH_2-$\underline{C}H_3$), 17.26 (d, P-$\underline{C}H_2$, $^1J_{PC}$ = 54.6), 18.27 (d, $\underline{C}H_2$, $^1J_{PC}$ = 12.9), 26.25 (s, P-CH_2-$\underline{C}H_2$), 63.73 (s, $\underline{C}H_2$-CH_3), 115.96 (d, C^{ipso}, $^1J_{PC}$ = 86.9); 130.06 (d, C^m, $^3J_{PC}$ = 13.1), 132.88 (d, C^p, $^4J_{PC}$ = 10.4), 135.42 (d, C^o, $^2J_{PC}$ = 3.1), 165.59 (d, C(O)O, $^2J_{PC}$ = 3.5), 174.08 (d, COOH, $^3J_{PC}$ = 13.4). $^{31}P\{^1H\}$ NMR spectrum (D_2O): δ_P 24.5 ppm. Elemental analysis: Found, %: C 53.52, H 5.52, Br 18.93, P 7.39. $C_{19}H_{22}BrO_4P$. Calculated, %: C 53.66, H 5.21, Br 18.79, P 7.28.

Ethane-1,2-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide (**2a**)

Yield 69%, mp. 190-196°C. IR (ν/cm^{-1}): 721, 997, 1034, 1112, 1179, 1252, 1436, 1730, 2967. $^1H\{^{31}P\}$ NMR spectrum ($CDCl_3$) δ_H, ppm (*J*/Hz): 0.87 (t, 6H, CH_2-$\underline{CH_3}$, *J* = 7.0), 3.84 (s, 4H, P-($\underline{CH_2}$)$_2$), 3.38 (q, 4H, $\underline{CH_2}$-CH_3, *J* = 7.0), 5.22 (s, 4H, $\underline{CH_2}$), 7.46-7.81 (m, 20H, $\underline{Ph_2}$-P). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm, 100.6 MHz: 12.94 (s, CH_2-$\underline{C}H_3$), 22.11 (d, P-$\underline{C}H_2$, $^1J_{PC}$ = 52.1), 32.35 (s, P-($\underline{CH_2}$)$_2$), 65.8 (s, $\underline{C}H_2$-CH_3), 114.07 (d, C^{ipso}, $^1J_{PC}$ = 80.4); 130.01 (d, C^m, $^3J_{PC}$ = 16.5), 133.36 (d, C^p, $^4J_{PC}$ = 21.6), 135.29 (s, C^o), 166.73 (d, C(O)O, $^2J_{PC}$ = 4.3). $^{31}P\{^1H\}$ NMR spectrum (D_2O): δ_P 26.3 ppm. Elemental analysis: Found, %: C 55.83, H 5.31, Br 21.93, P 8.49. $C_{34}H_{38}Br_2O_4P_2$. Calculated, %: C 55.76, H 5.23, Br 21.82, P 8.46.

Propane-1,3-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide (**2b**)

Yield 72%. IR (ν/cm^{-1}): 721, 997, 1033, 1113, 1178, 1252, 1437, 1732, 2968. $^1H\{^{31}P\}$ NMR spectrum (D_2O) δ_H, ppm (*J*/Hz): 0.89 (t, 6H, CH_2-$\underline{CH_3}$, *J* = 7.0), 1.97 (m, 2H, CH_2-$\underline{CH_2}$), 3.69 (s, 4H, P-($\underline{CH_2}$)$_2$), 3.88 (q, 4H, $\underline{CH_2}$-CH_3, *J* = 7.1), 4.7 (s, 4H, $\underline{CH_2}$), 7.37-7.93 (m, 20H, $\underline{Ph_2}$-P). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm, 100.6 MHz: 12.94 (s, CH_2-$\underline{C}H_3$), 16.02 (s, P-CH_2-$\underline{C}H_2$-CH_2), 22.11 (d, P-$\underline{C}H_2$, $^1J_{PC}$ = 52.1), 31.35 (s, P-($\underline{CH_2}$)$_2$), 65.8 (s, $\underline{C}H_2$-CH_3), 114.33 (d, C^{ipso}, $^1J_{PC}$ = 80.4), 130.2 (d, C^m, $^3J_{PC}$ = 16.5), 133.30 (d, C^p, $^2J_{PC}$ = 21.6), 135.29 (s, C^o), 166.9 (d, C(O)O, $^2J_{PC}$ = 4.3). $^{31}P\{^1H\}$ NMR spectrum (D_2O): δ_P 24.23 ppm. Elemental analysis: Found, %: C 56.43, H 5.37, Br 21.53, P 8.39. $C_{35}H_{40}Br_2O_4P_2$. Calculated, %: C 56.32, H 5.4, Br 21.41, P 8.3.

Butane-1,4-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide (**2c**)

Yield 84%, mp. 166-167°C. IR (ν/cm^{-1}): 721, 997, 1033, 1111, 1173, 1252, 1450, 1730, 2966. $^{1}H\{^{31}P\}$ NMR spectrum (D_2O) δ_H, ppm (*J*/Hz): 0.84 (t, 6H, CH_2-$\underline{CH_3}$, *J* = 7.0), 2.91 (s, 8H, P-($\underline{CH_2}$)$_4$), 3.93 (q, 4H, $\underline{CH_2}$-CH_3, *J* = 7.0), 4.69 (s, 4H, $\underline{CH_2}$), 7.51-7.86 (m, 20H, $\underline{Ph_2}$-P). $^{13}C\{^{1}H\}$ NMR spectrum (D_2O), δ_C, ppm, 100.6 MHz: 13.7 (s, CH_2-$\underline{C}H_3$), 21.55 (d, P-CH_2, $^{1}J_{PC}$ = 50.6), 22.23 (d, ($\underline{C}H_2$)$_2$, $^{3}J_{PC}$ = 17.3), 30.59 (d, P-($\underline{CH_2}$)$_2$, $^{1}J_{PC}$ = 53.5), 62.74 (s, $\underline{C}H_2$-CH_3), 117.17 (d, C^{ipso}, $^{1}J_{PC}$ = 85.5); 130.18 (d, C^{m}, $^{3}J_{PC}$ = 12.9), 133.4 (d, C^{p}, $^{4}J_{PC}$ = 10.3), 134.9 (d, C^{o}, $^{2}J_{PC}$ = 3.1), 164.27 (d, C(O)O, $^{2}J_{PC}$ = 4.3). $^{31}P\{^{1}H\}$ NMR spectrum (D_2O): δ_P 24.3 ppm. Elemental analysis: Found, %: C 56.83, H 5.41, Br 21.13, P 8.49. $C_{36}H_{42}Br_2O_4P_2$. Calculated, %: C 56.86, H 5.57, Br 21.01, P 8.15.

Hexane-1,6-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide (**2d**)

Yield 71%, mp. 195-200°C. IR (ν/cm^{-1}): 688; 746; 817; 1011; 1111; 1189; 1209; 1310;1436; 1713; 2780. $^{1}H\{^{31}P\}$ NMR spectrum (D_2O) δ_H, ppm (*J*/Hz): 0.95 (t, 6H, CH_2-$\underline{CH_3}$, *J* = 7.0), 1.51 (s, 8H, ($\underline{CH_2}$)$_4$), 3.38 (m, 4H P-CH_2), 3.92 (q, 4H, $\underline{CH_2}$-CH_3, *J* = 7.1), 4.89 (s, 4H, $\underline{CH_2}$), 7.51-7.86 (m, 20H, $\underline{Ph_2}$-P). $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm, 100.6 MHz: 13.73 (s, CH_2-$\underline{C}H_3$), 21.09 (d, P-CH_2, $^{1}J_{PC}$ = 50.6), 22.38 (d, ($\underline{C}H_2$)$_2$, $^{3}J_{PC}$ = 17.3), 28.28 (d, P-CH_2-CH_2, $^{2}J_{PC}$ = 17.4), 30.76 (d, P-($\underline{CH_2}$)$_2$, $^{1}J_{PC}$ = 53.5), 65.2 (s, $\underline{C}H_2$-CH_3), 117.28 (d, C^{ipso}, $^{1}J_{PC}$ = 85.5); 129.55 (d, C^{m}, $^{3}J_{PC}$ = 12.9), 133.47 (d, C^{p}, $^{4}J_{PC}$ = 10.3), 134.78 (d, C^{o}, $^{2}J_{PC}$ = 3.1), 164.56 (d, C(O)O, $^{2}J_{PC}$ = 4.1). $^{31}P\{^{1}H\}$ NMR spectrum (D_2O): δ_P 24.8 ppm. Elemental analysis: Found, %: C 57.77, H 5.82, Br 20.23, P 7.79. $C_{38}H_{46}Br_2O_4P_2$. Calculated, %: C 57.87, H 5.88, Br 20.27, P 7.86.

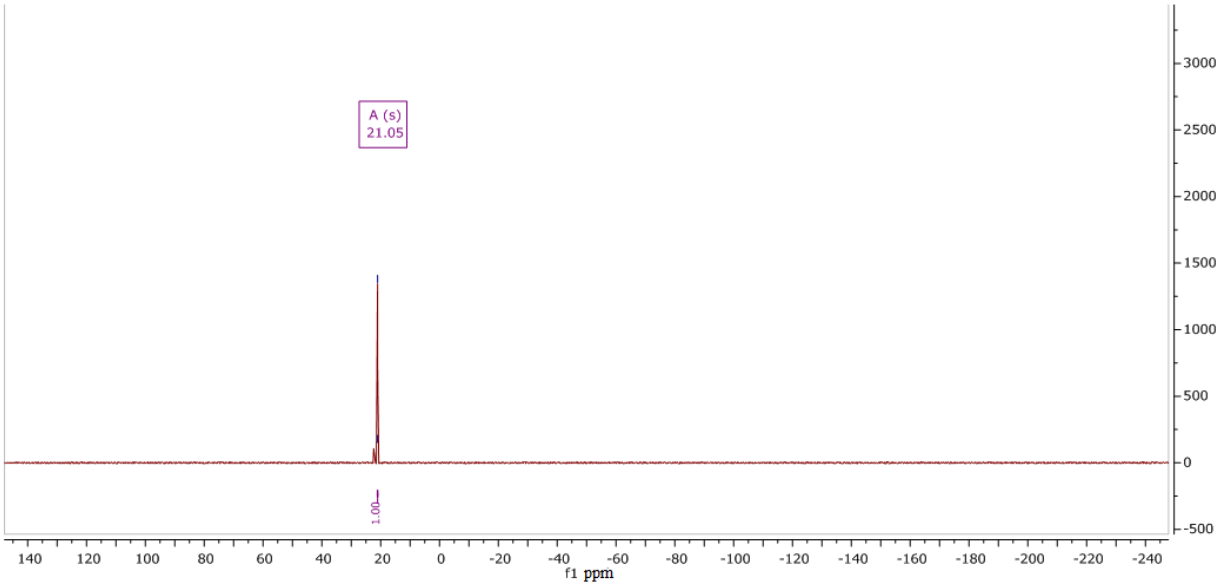

Figure S1 $^{31}P\{^{1}H\}$ NMR spectrum of (2-ethoxy-2-oxoethyl)triphenylphosphonium bromide **1a** (D_2O, 162 MHz)

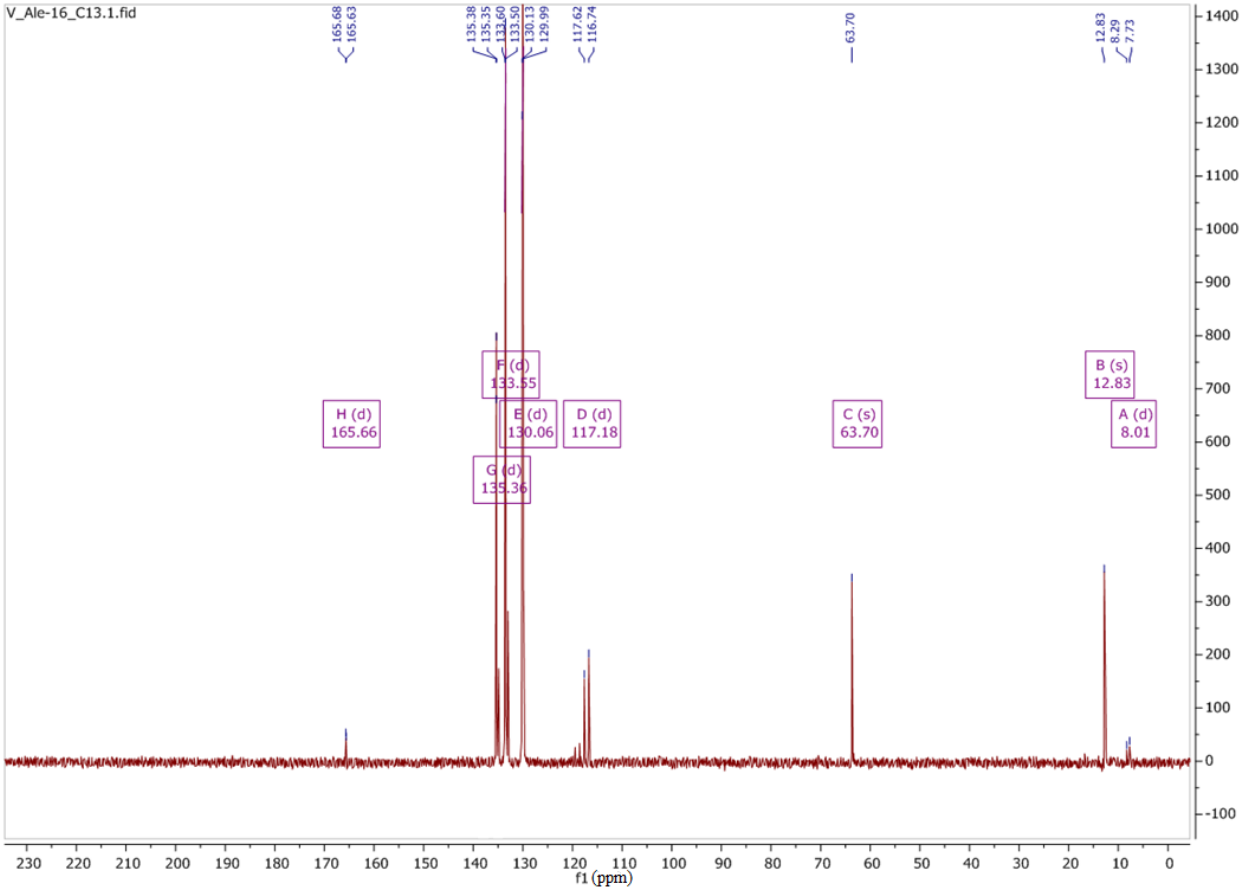

Figure S2 $^{13}C\{^{1}H\}$ NMR spectrum of (2-ethoxy-2-oxoethyl)triphenylphosphonium bromide **1a** (D_2O, 100.6 MHz)

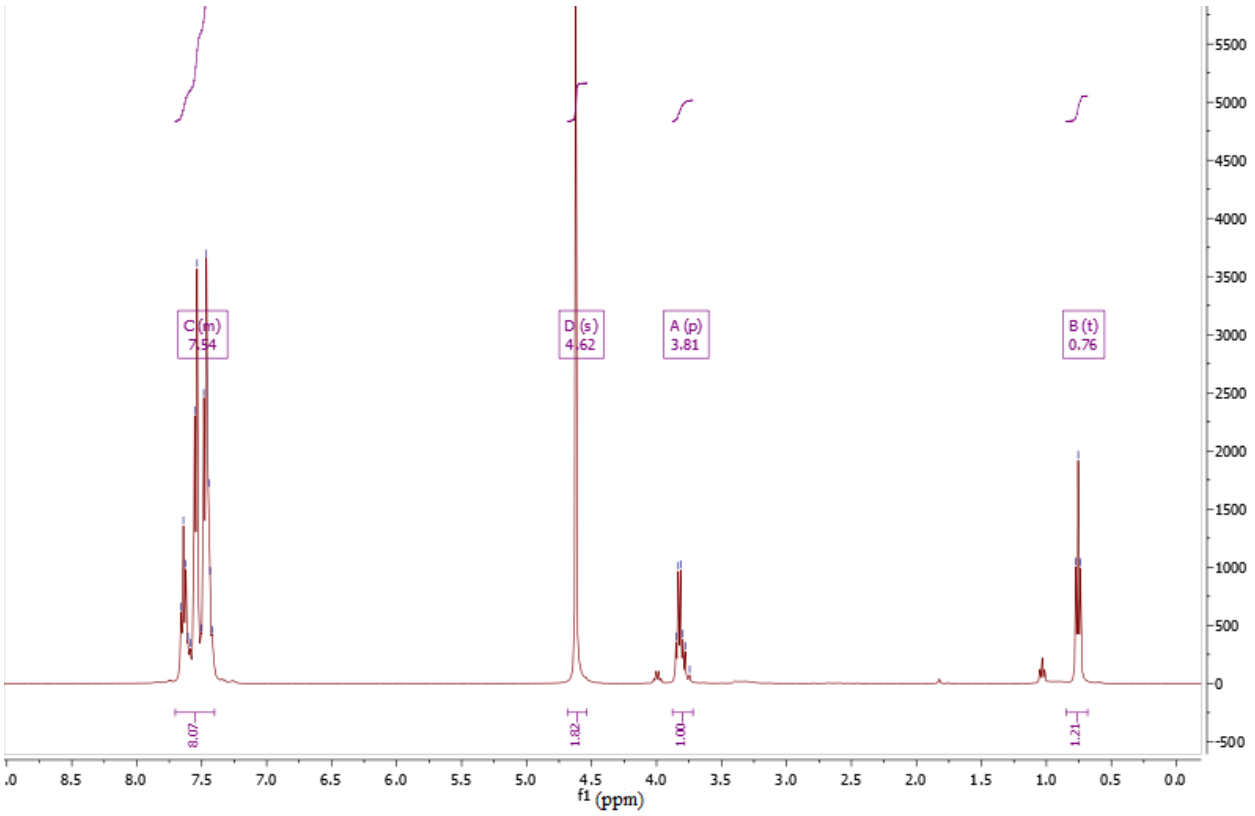

Figure S3 $^{1}H\{^{31}P\}$ NMR spectrum of (2-ethoxy-2-oxoethyl)triphenylphosphonium bromide **1a** (D_2O, 400 MHz)

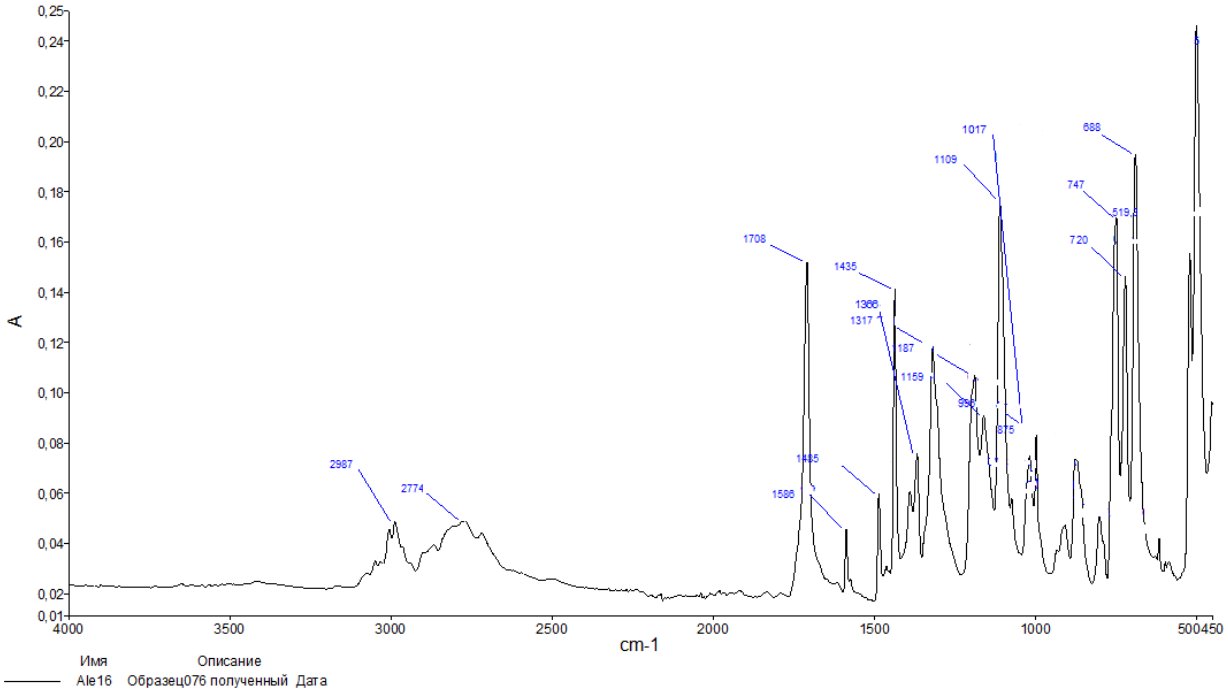

Figure S4 IR-spectrum of (2-ethoxy-2-oxoethyl)triphenylphosphonium bromide **1a**

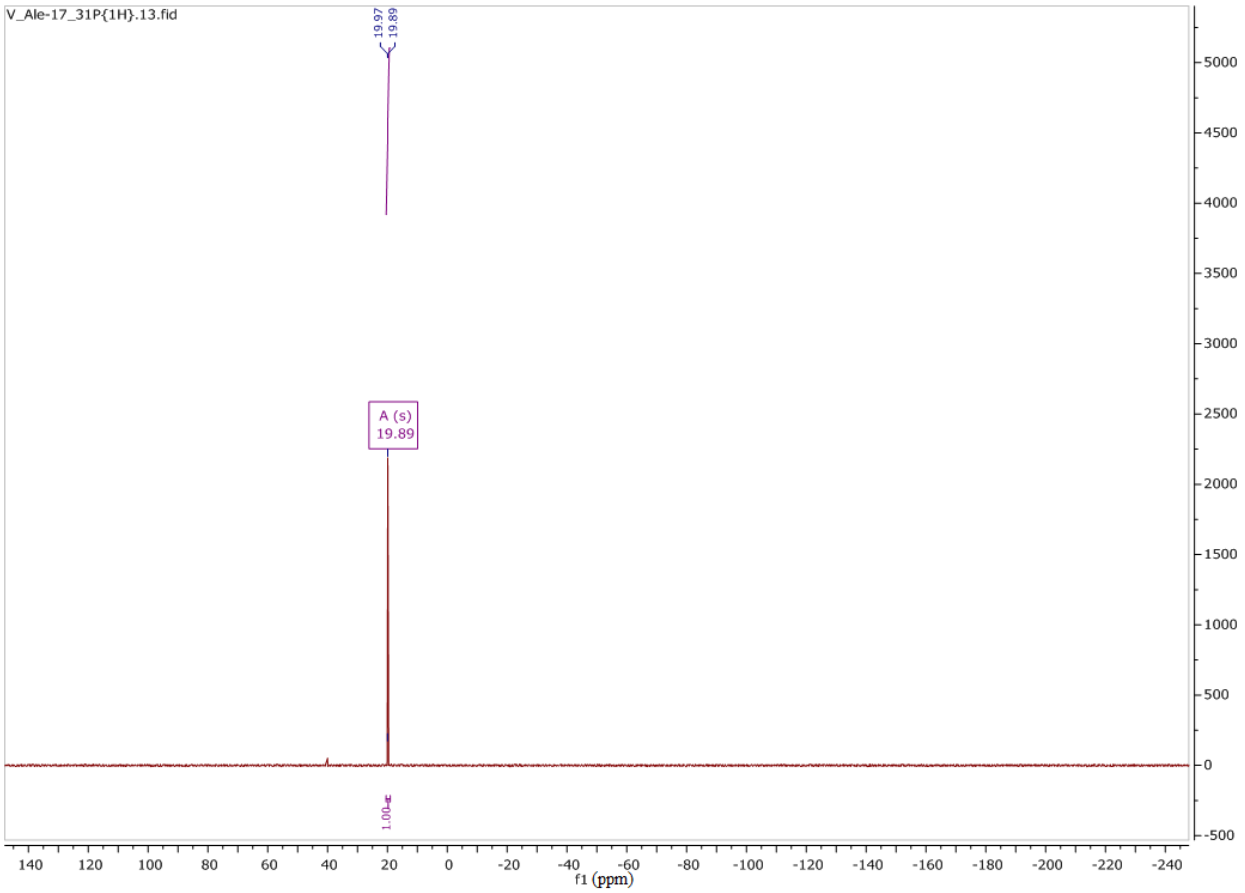

Figure S5 $^{31}P\{^{1}H\}$ NMR spectrum of (2-ethoxy-2-oxoethyl)(methyl)diphenylphosphonium bromide **1b** (D_2O, 162 MHz)

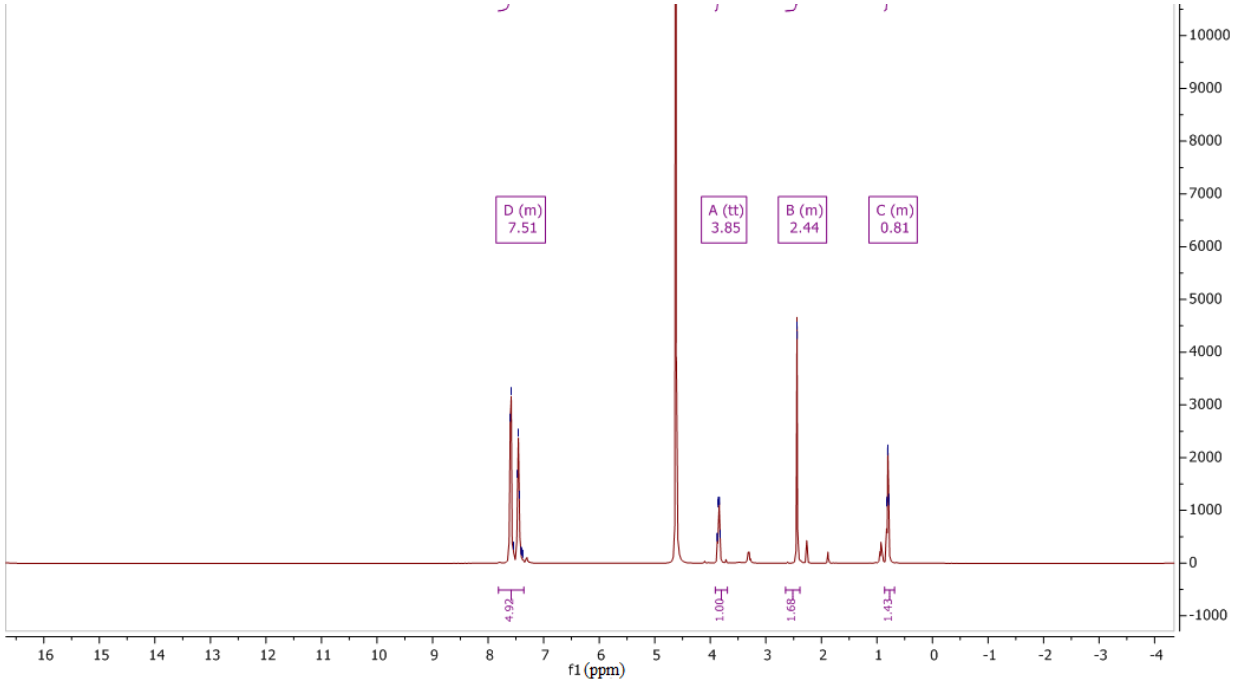

Figure S6 $^{1}H\{^{31}P\}$ NMR spectrum of (2-ethoxy-2-oxoethyl)(methyl)diphenylphosphonium bromide **1b** (D_2O, 400 MHz)

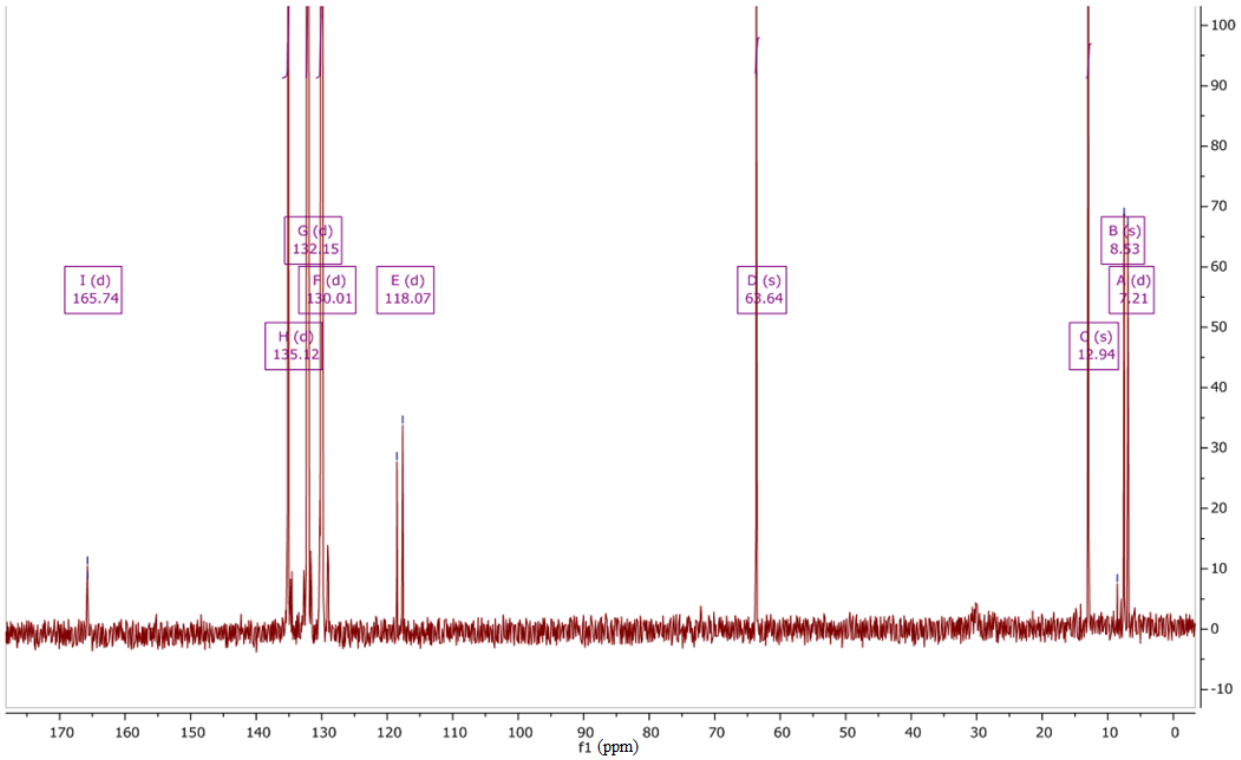

Figure S7 $^{13}C\{^{1}H\}$ NMR spectrum of (2-ethoxy-2-oxoethyl)(methyl)diphenylphosphonium bromide **1b** (D_2O, 106 MHz)

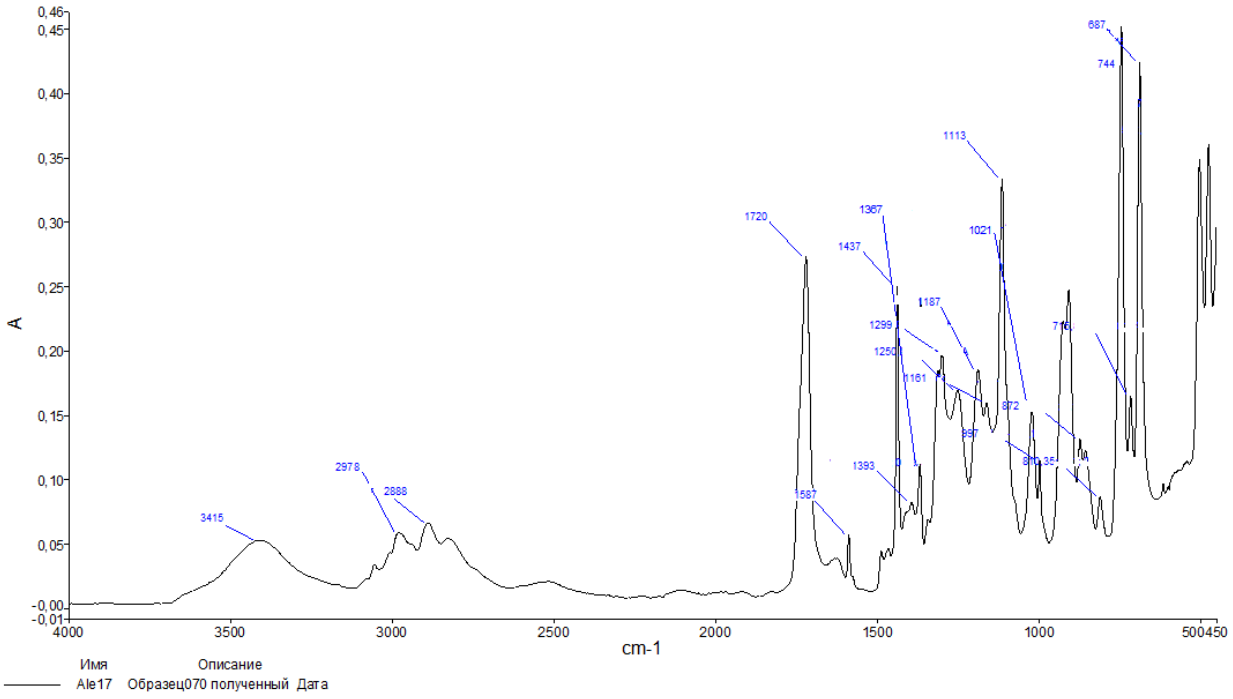

Figure S8 IR-spectrum of (2-ethoxy-2-oxoethyl)(methyl)diphenylphosphonium bromide **1b**

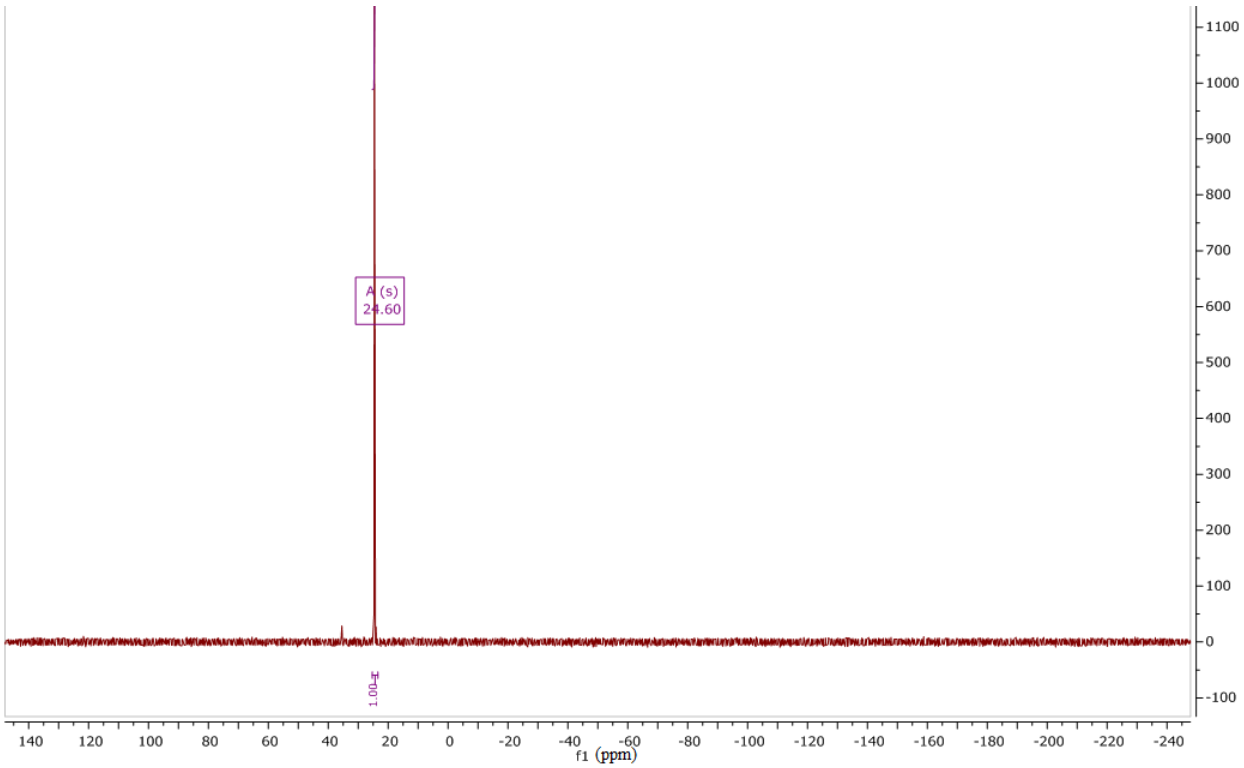

Figure S9 $^{31}P\{^{1}H\}$ NMR spectrum of (2-carboxyethyl)(2-ethoxy-2-oxoethyl)diphenylphosphonium bromide **1c** (D_2O, 162 MHz)

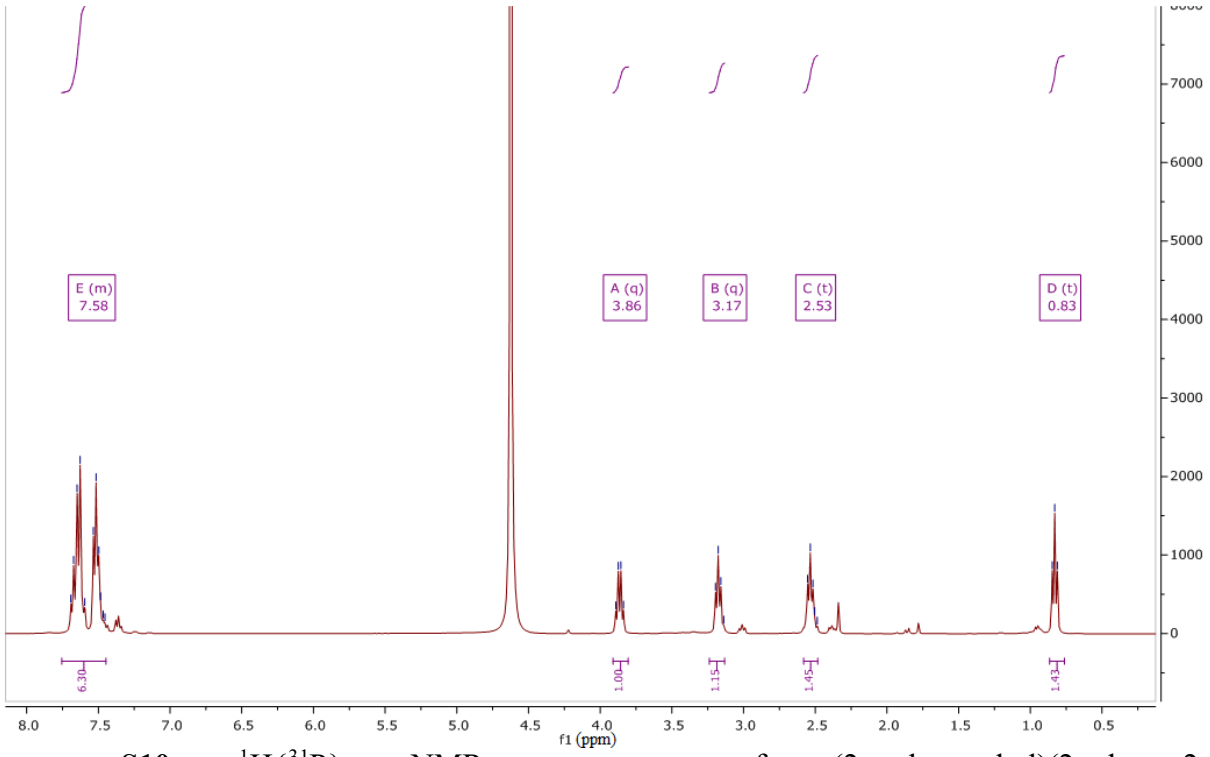

Figure S10 $^{1}H\{^{31}P\}$ NMR spectrum of (2-carboxyethyl)(2-ethoxy-2-oxoethyl)diphenylphosphonium bromide **1c** (D_2O, 400 MHz)

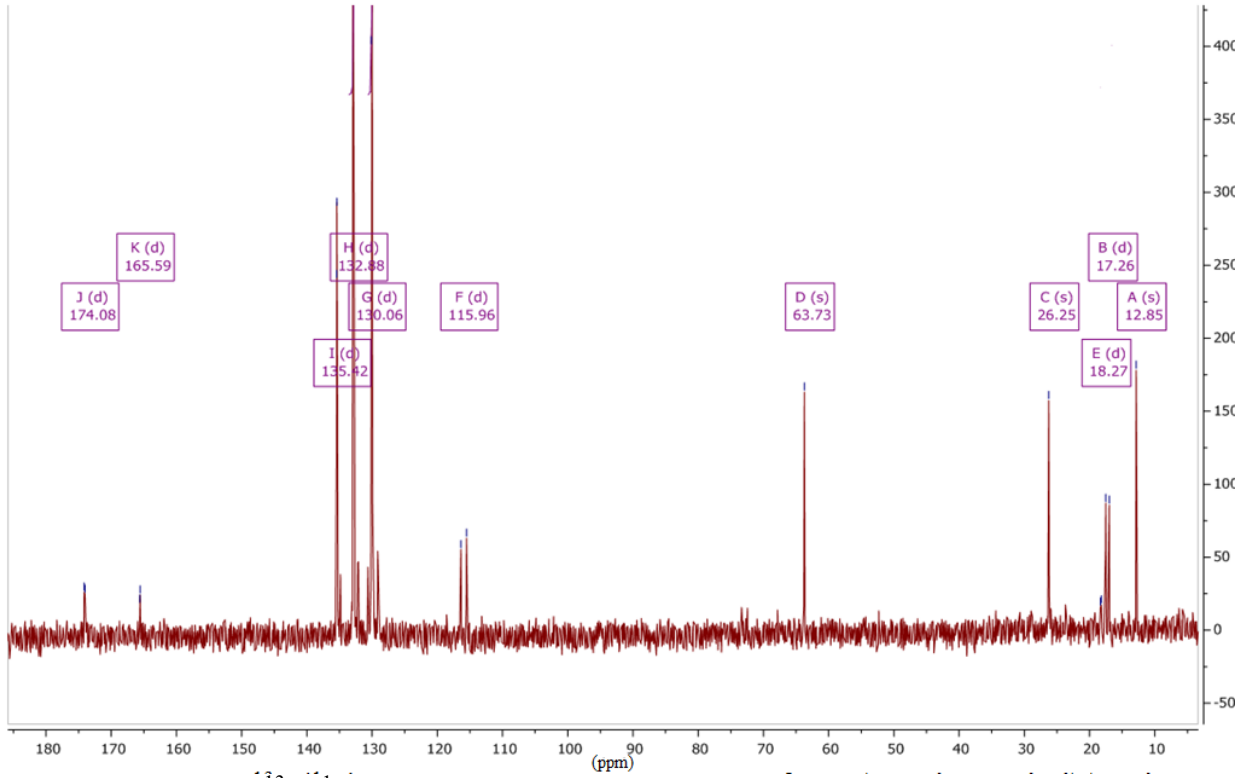

Figure S11 $^{13}C\{^{1}H\}$ NMR spectrum of (2-carboxyethyl)(2-ethoxy-2-oxoethyl)diphenylphosphonium bromide **1c** (D_2O, 100.6 MHz)

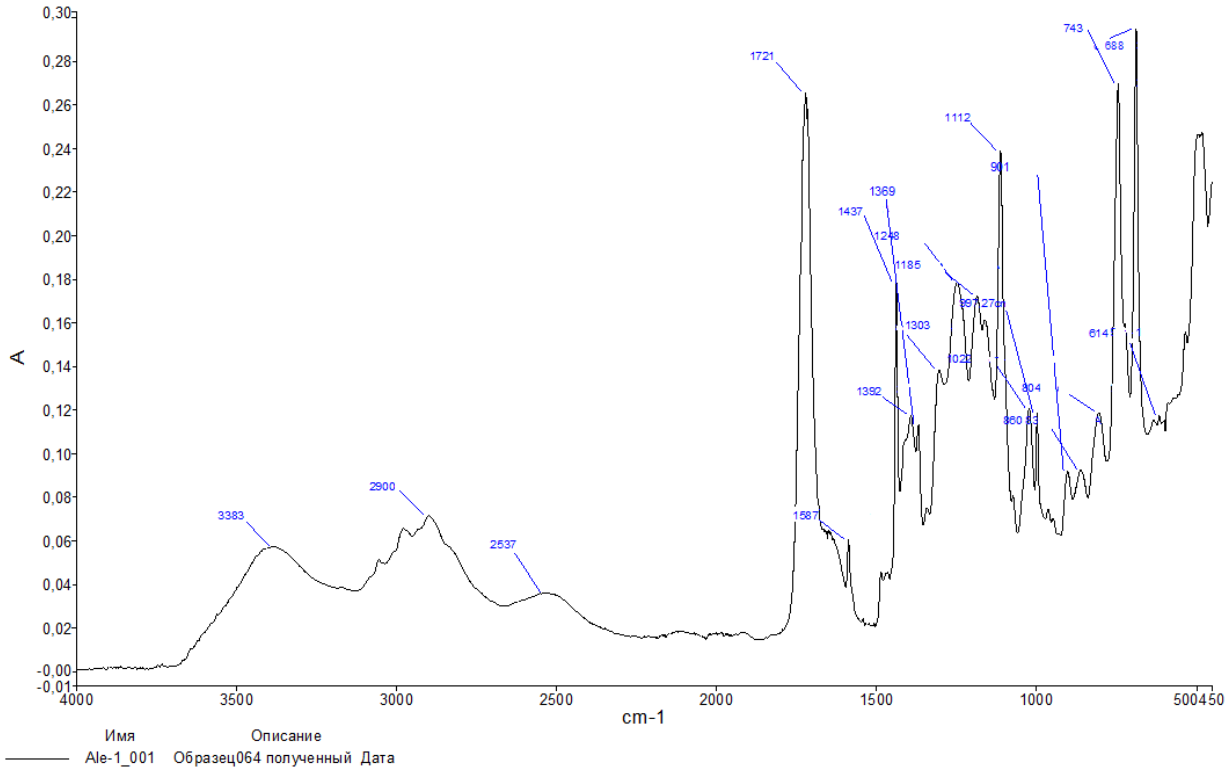

Figure S12 IR-spectrum of (2-carboxyethyl)(2-ethoxy-2-oxoethyl)diphenylphosphonium bromide **1c**

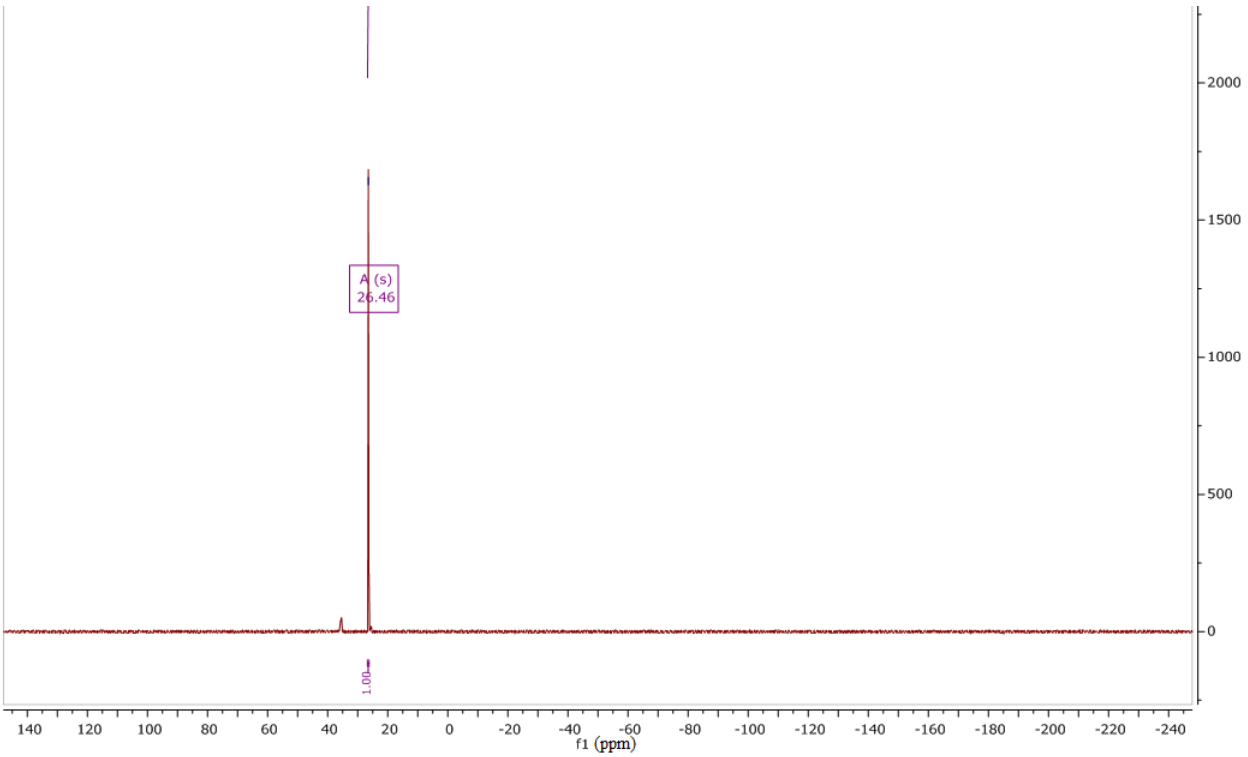

Figure S13 $^{31}P\{^{1}H\}$ NMR spectrum of ethane-1,2-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2a** (D_2O, 162 MHz)

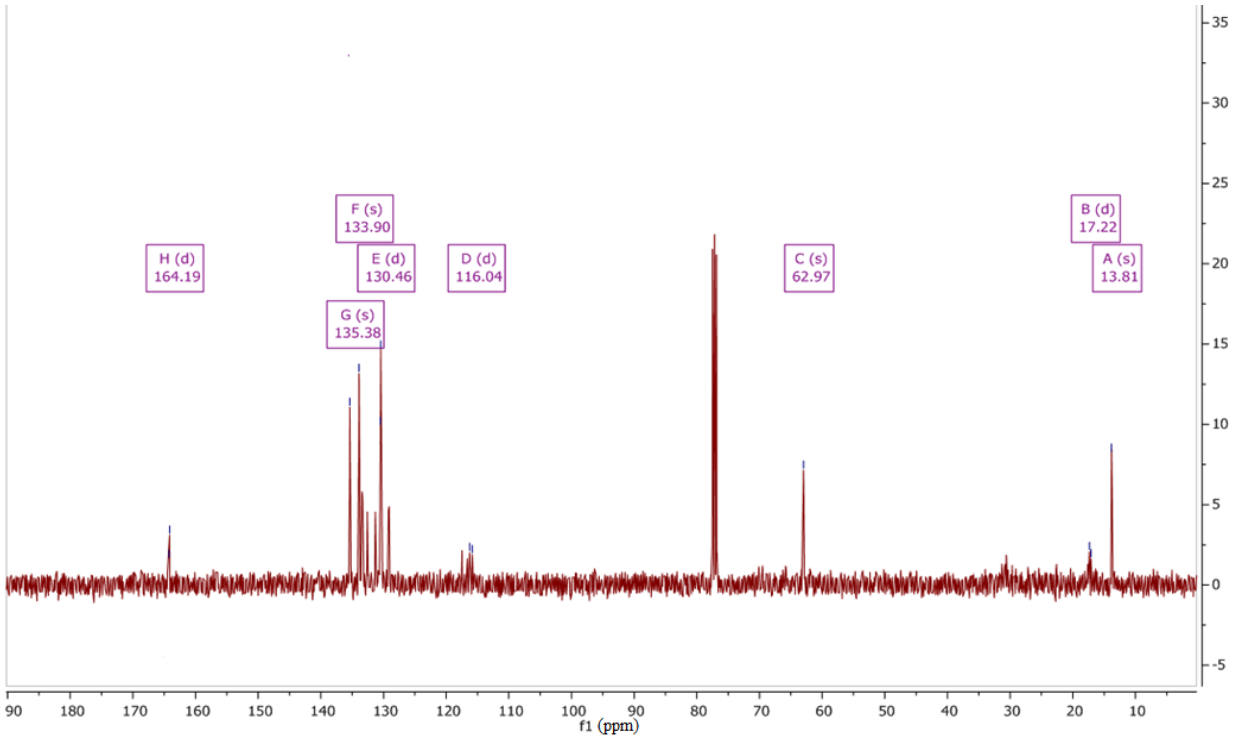

Figure S14 $^{13}C\{^{1}H\}$ NMR spectrum of ethane-1,2-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2a** ($CDCl_3$, 100.6 MHz)

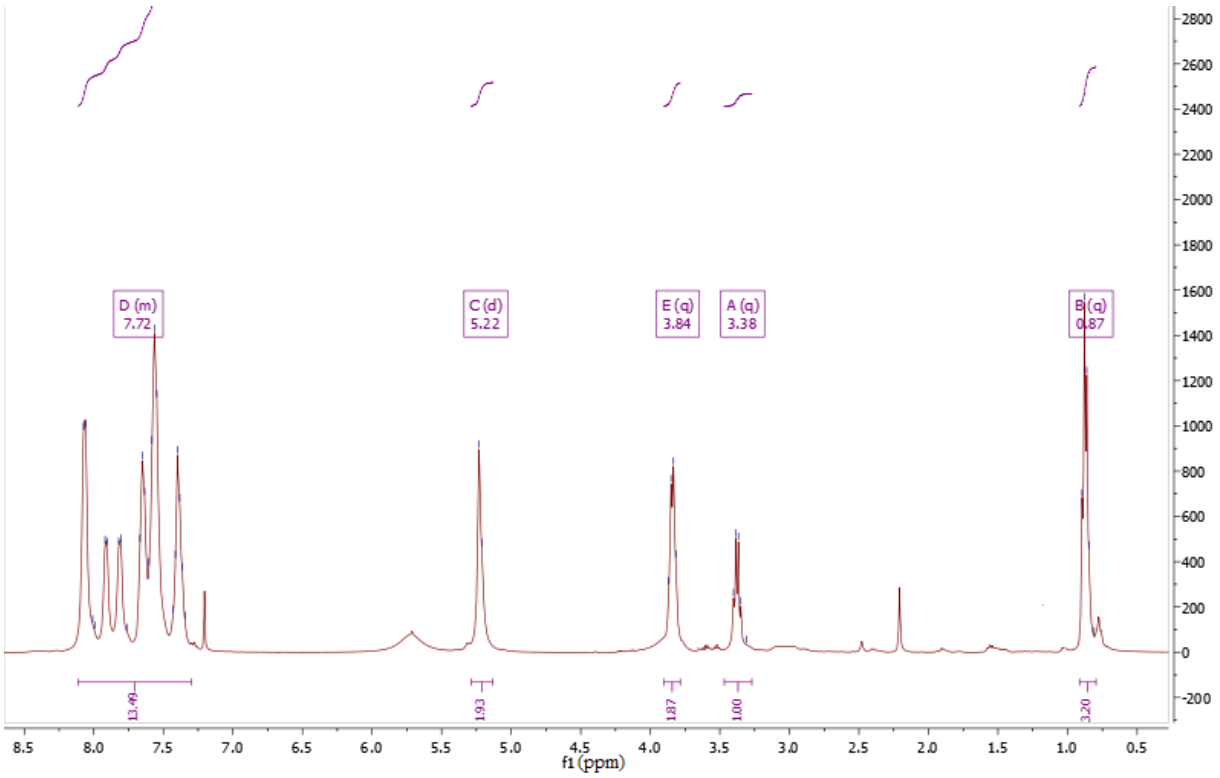

Figure S15 $^{1}H\{^{31}P\}$ NMR spectrum of ethane-1,2-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2a** ($CDCl_3$, 400 MHz)

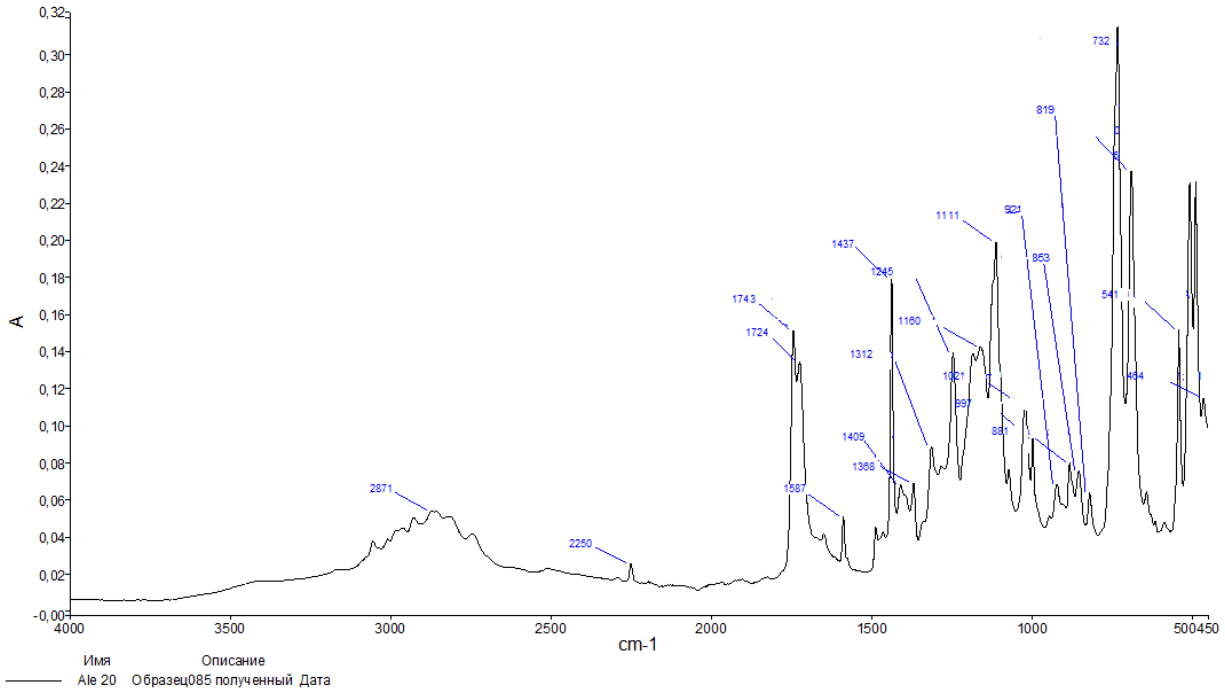

Figure S16 IR-spectrum of ethane-1,2-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2a**

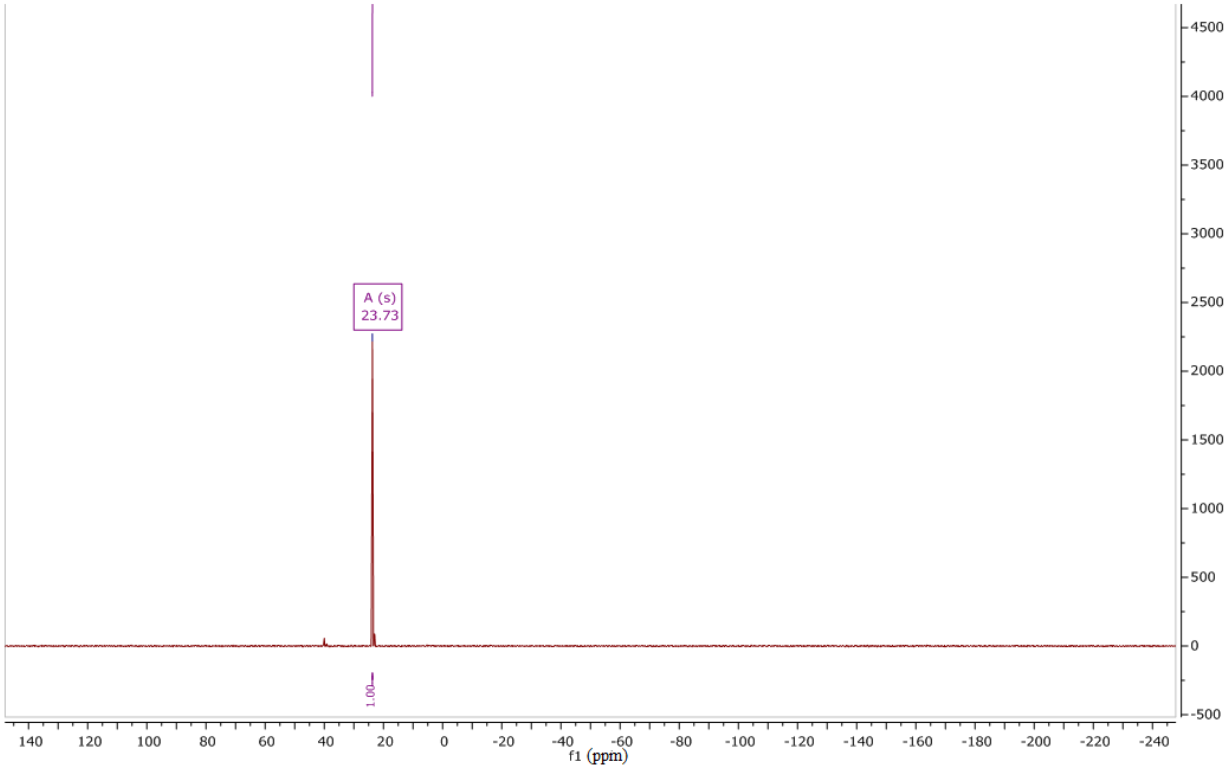

Figure S17 $^{31}P\{^{1}H\}$ NMR spectrum of propane-1,3-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2b** (D_2O, 162 MHz)

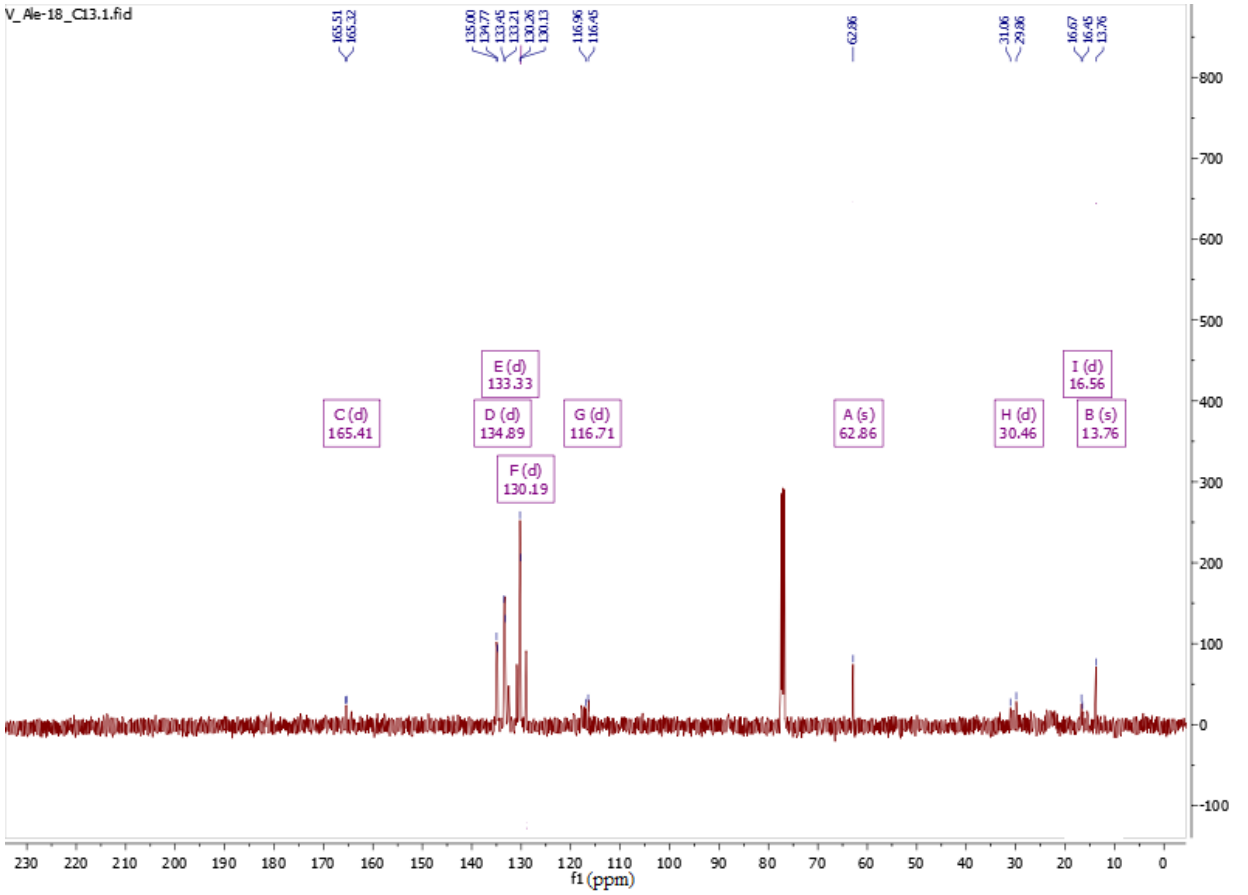

Figure S18 $^{13}C\{^{1}H\}$ NMR spectrum of propane-1,3-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2b** ($CDCl_3$, 100.6 MHz)

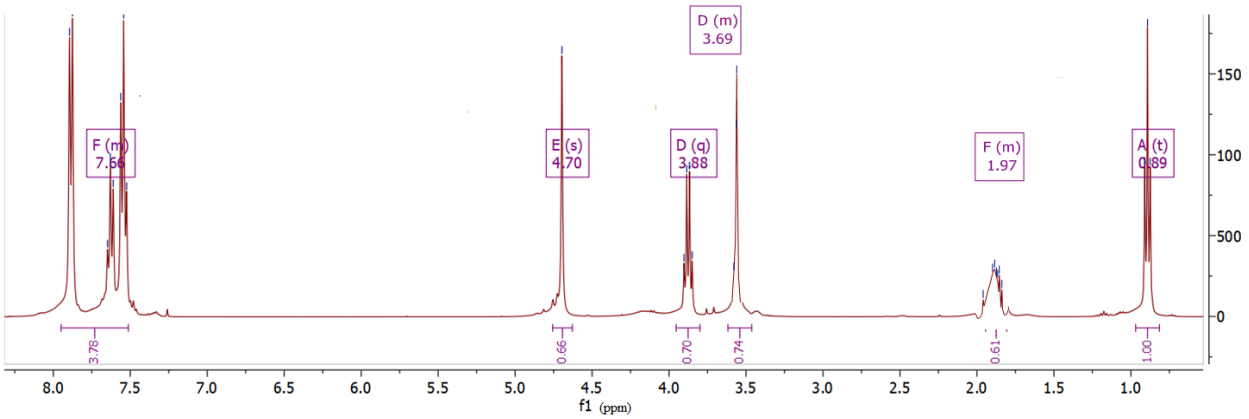

Figure S19 $^{1}H\{^{31}P\}$ NMR spectrum of propane-1,3-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2b** (D_2O, 400 MHz)

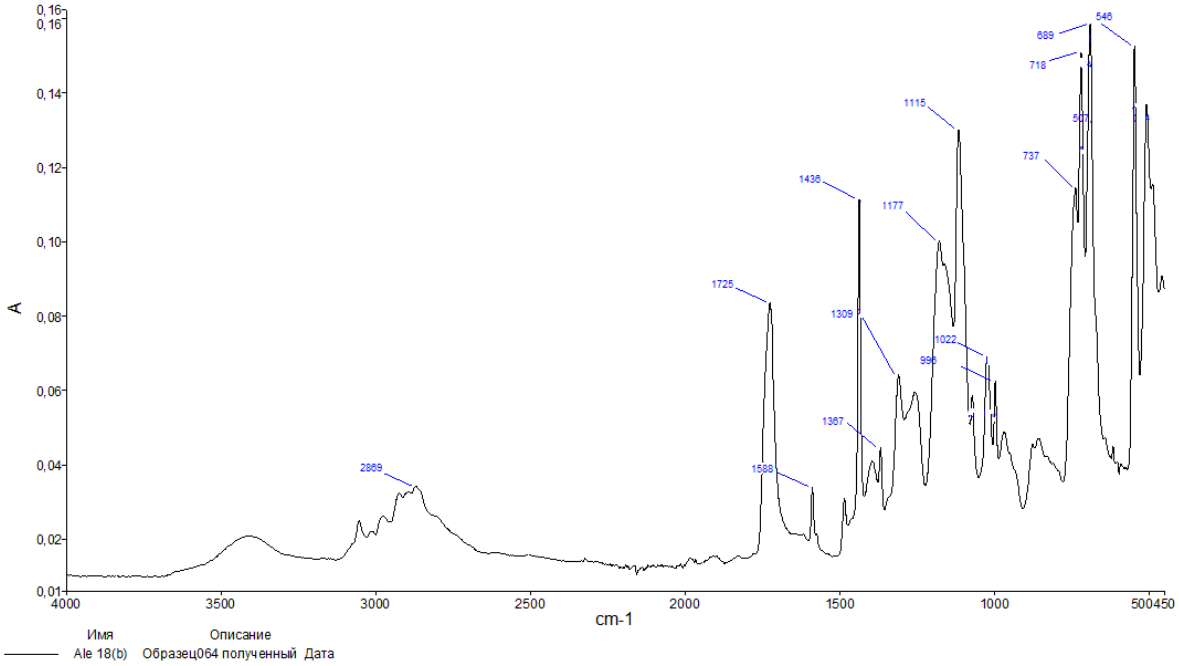

Figure S20 IR-spectrum of propane-1,3-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2b**

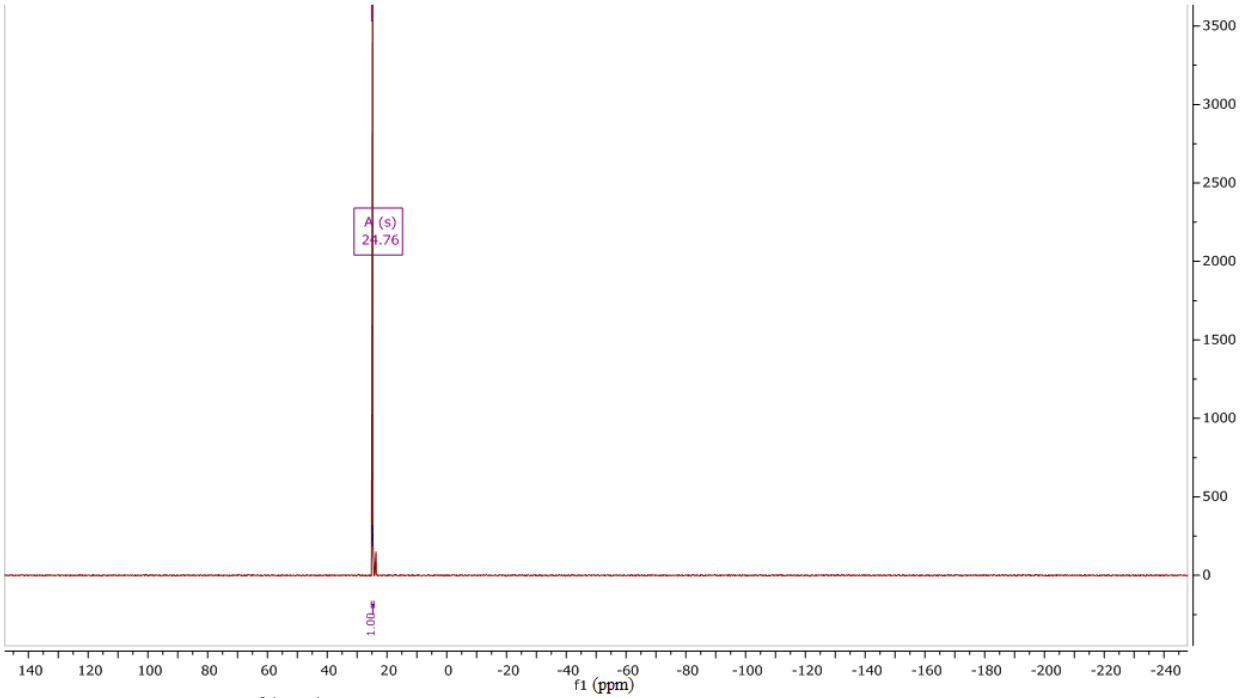

Figure S21 $^{31}P\{^{1}H\}$ NMR spectrum of butane-1,4-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2c** (D_2O, 162 MHz)

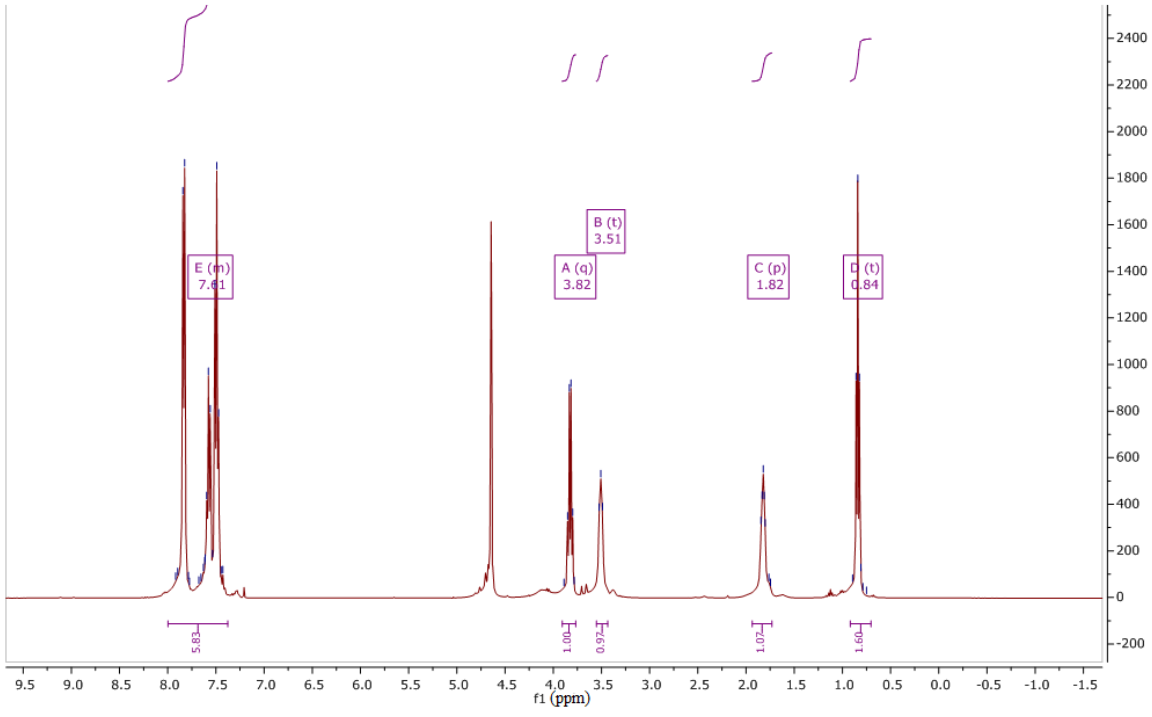

Figure S22 $^{1}H\{^{31}P\}$ NMR spectrum of butane-1,4-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2c** (D_2O, 400 MHz)

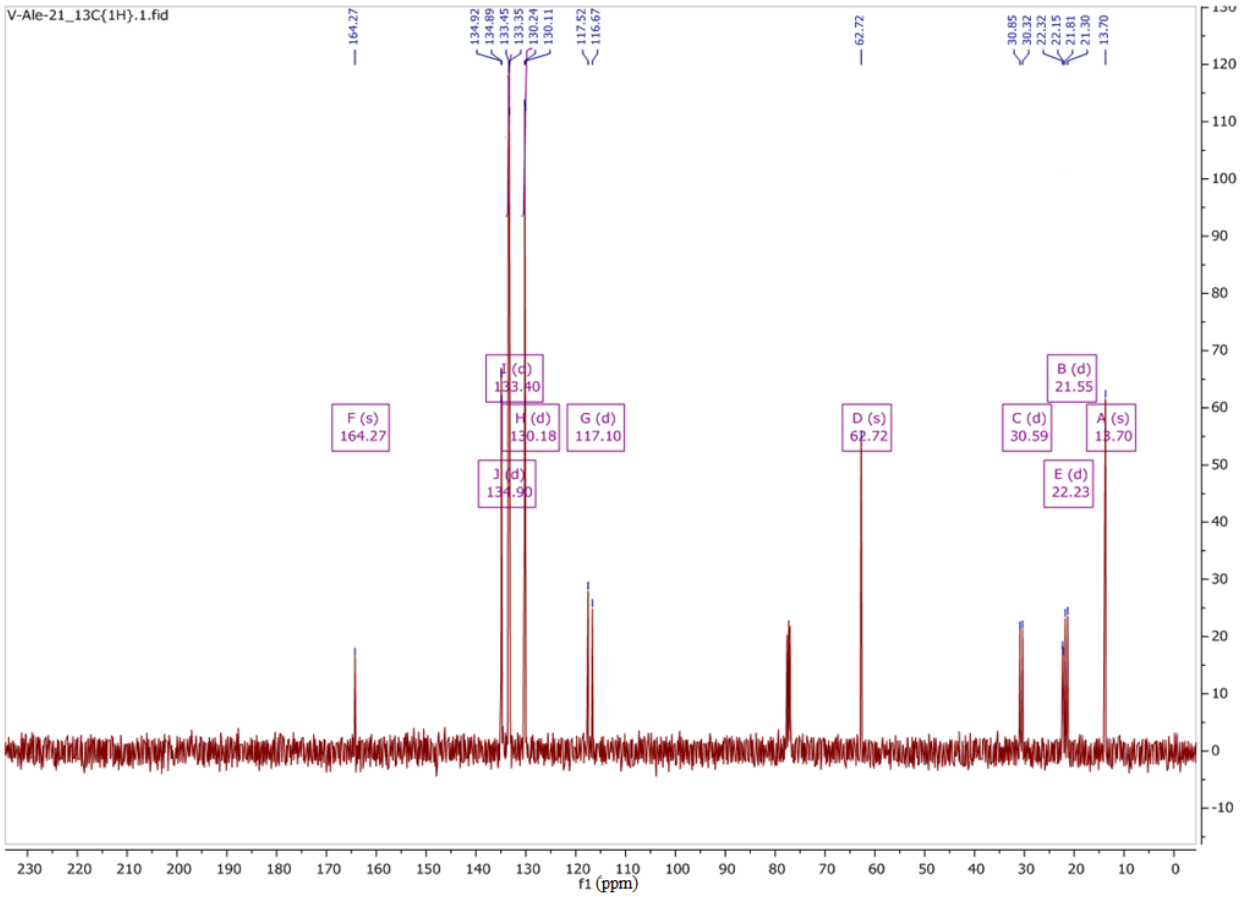

Figure S23 $^{13}C\{^{1}H\}$ NMR spectrum of butane-1,4-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2c** (D_2O, 100.6 MHz)

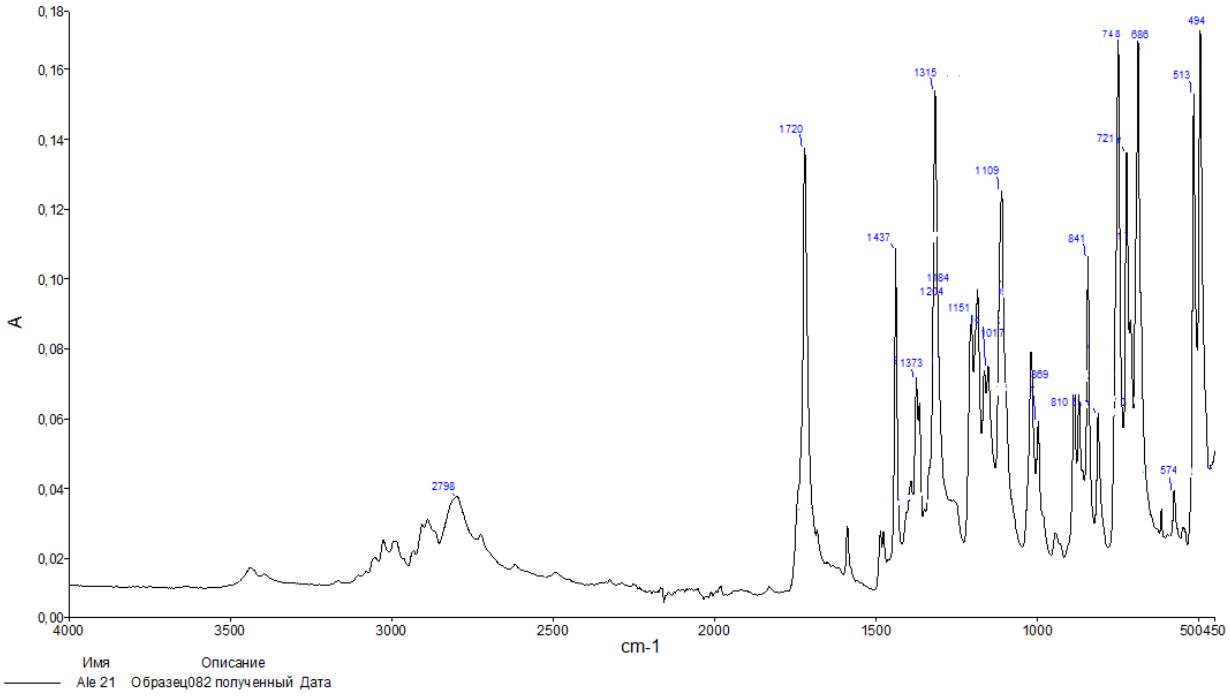

Figure S24 IR-spectrum of butane-1,4-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2c**

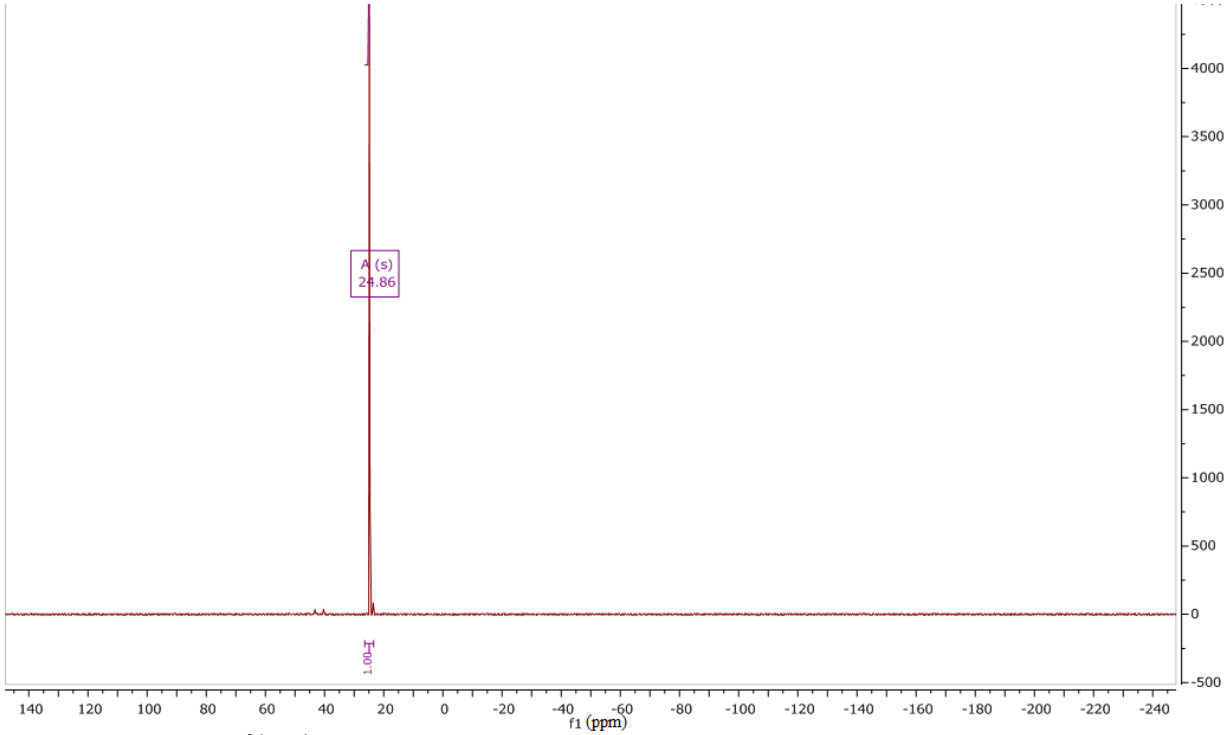

Figure S25 $^{31}P\{^{1}H\}$ NMR spectrum of hexane-1,6-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2d** (D_2O, 162 MHz)

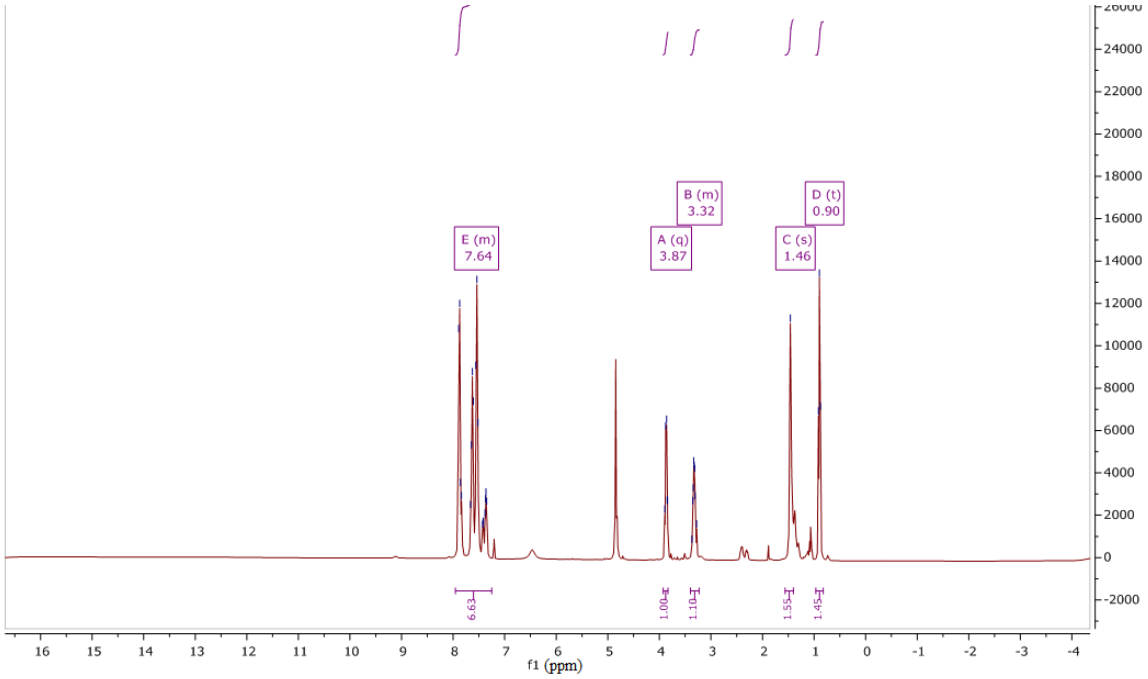

Figure S26 $^{1}H\{^{31}P\}$ NMR spectrum of hexane-1,6-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2d** (D_2O, 400 MHz)

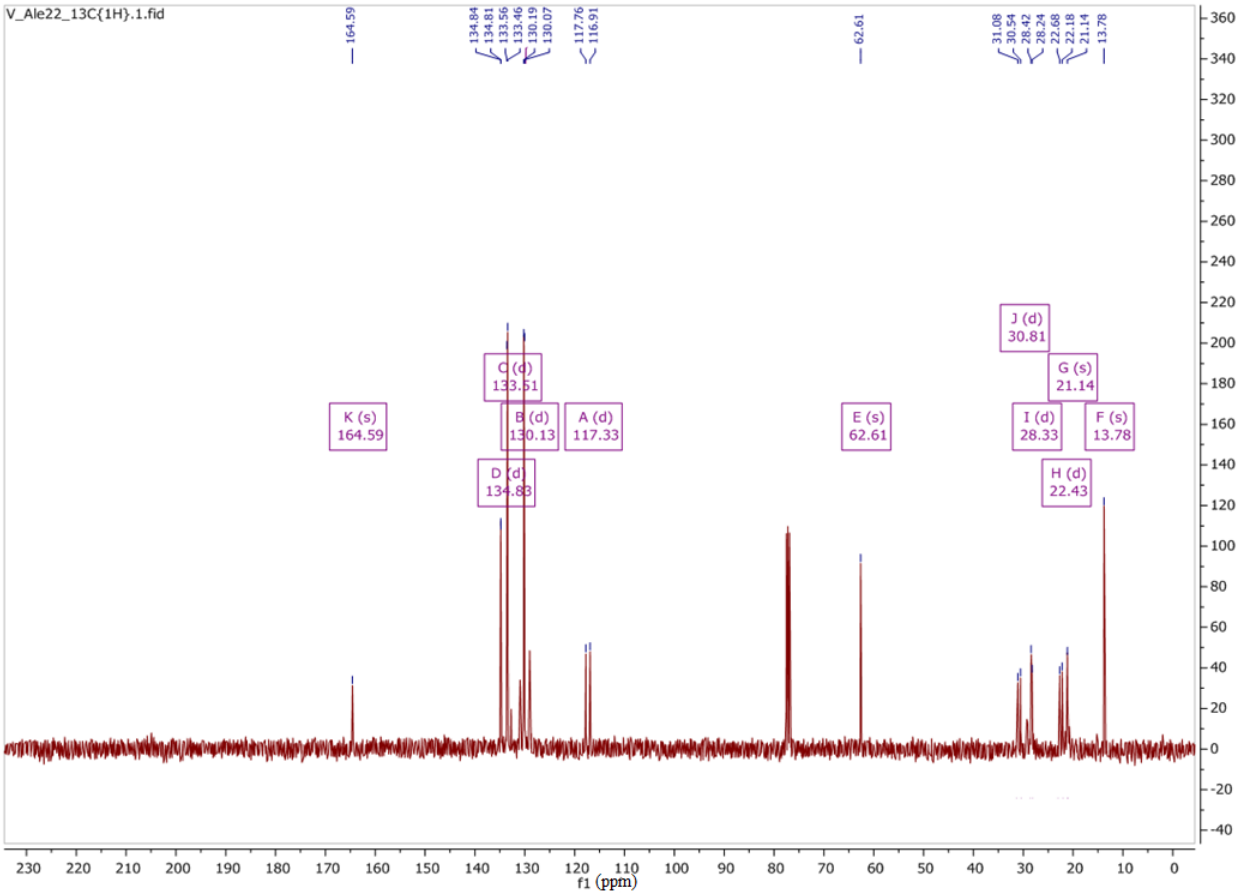

Figure S27 $^{13}C\{^{1}H\}$ NMR spectrum of hexane-1,6-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2d** (D_2O, 100.6 MHz)

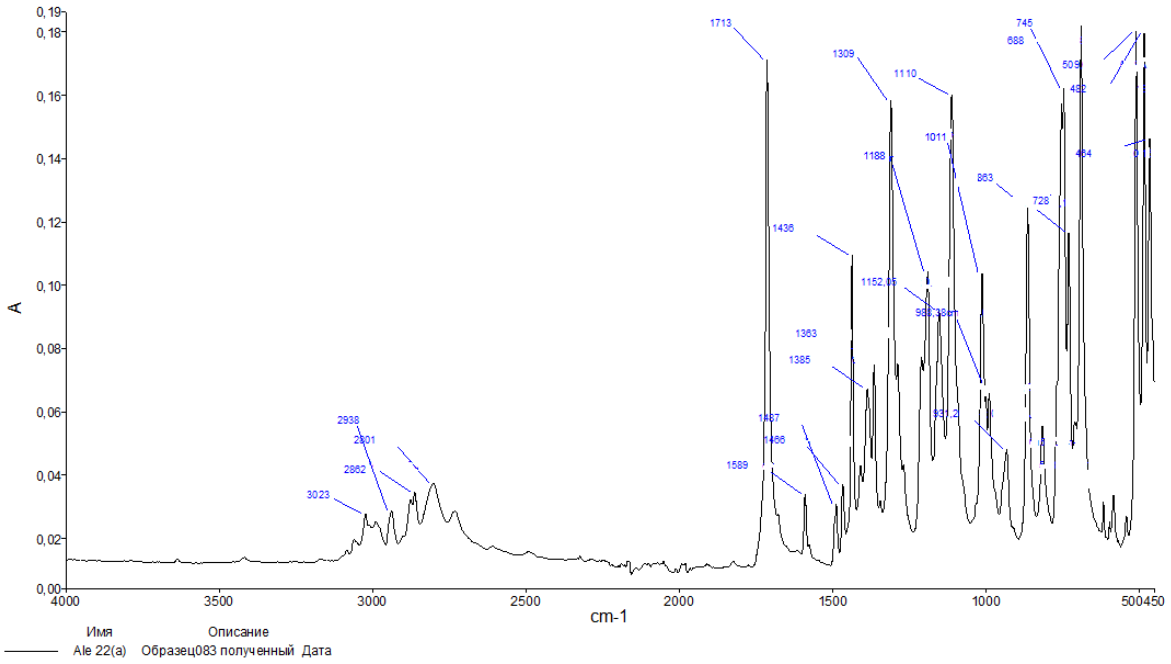

Figure S28 IR-spectrum of hexane-1,6-diylbis[(2-ethoxy-2-oxoethyl)diphenylphosphonium] dibromide **2d**

Table S1. Some characteristics of phosphonium salts **1a-c** and **2a-d**.

Compound	mp, °C	NMR ^{31}P, δ_P ppm	ν, cm^{-1}		Yield, %
			ν(C=O)	ν(C-O)	
1a	112-120	21.1	1708	1109	82
1b	hygroscopic powder	19.9	1720	1113	78
1c	156-160	24.5	1721	1112	89
2a	190-196	26.3	1743	1111	69
2b	hygroscopic powder	24.2	1725	1115	72
2c	166-167	24.3	1720	1109	84
2d	195-200	24.8	1713	1111	71