Electronic Supplementary Material (ESI) for RSC Advances.

Branched alkylphosphinic and disubstituted phosphinic and phosphonic acids: effective synthesis based on α-olefin dimers and applications in lanthanide extraction and separation

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Supplementary Information

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S1. General experimental remarks

Reagents and solvents.

Triisobutylaluminium solution (1M in hexane, Aldrich), MMAO-12 (1.05M in toluene, Aldrich), Et_2AlCl (1M in hexane, Aldrich), H_3PO_2 (50% aq., Aldrich), AIBN (Acros), 2?6-diisopropylphenol (Aldrich) and 2-ethylhexanol (Aldrich) were used as purchased. 1-Hexene, 4-methylpentene, 1-decene, 3-methyl-1-butene and vinylcyclohexane (95-98%, Aldrich) were stored over Na/K alloy and distilled before use under argon atmosphere. Isopropanol (Acros), isoamyl alcohol (Acros), methyl iodide (Fluka), triethylamine (ABCR), Me_3SiCl (Aldrich), PCl_3 (Fluka) and $PhPCl_2$ (98%, Aldrich) were refluxed under argon and distilled before use. CH_2Cl_2 was washed with aqueous Na_2CO_3, stirred with $CaCl_2$ powder, refluxed over CaH_2 for 8 h, and distilled. Methanol was distilled over magnesium methoxide. 2-(chloromethyl)pyridine was distilled under reduced pressure and stored at -20 °C.

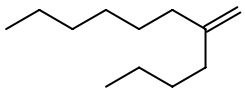
Zirconocene dichloride **2** was synthesized according to previously reported procedure.[1]

$CDCl_3$ was distilled over P_2O_5 and stored over 4 Å molecular sieves.

Chromatographic analysis was performed using a Kristall-2000M gas chromatograph.

[1] J. Graeper, G. Graeper and R. D. Graeper, *J. Organomet. Chem.*, 1995, **501**, 211–218

S2. Synthesis of α-olefin dimers.



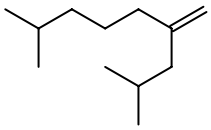
2-Butyl-1-octene (**3**).

Triisobutylaluminium solution (1 M in hexane, 5 mL, 5 mmol) and $[O(SiMe_2Cp)_2]ZrCl_2$ (**2**, 106 mg, 0.25 mmol) were added at 60 °C to 1-hexene (84.2 g, 1 mol). After 20 min of stirring, Et_2AlCl (1M in hexane, 0.5 mL, 0.25 mmol) and MMAO-12 (1.05 M in toluene, 2.4 mL, 2.5 mmol) were added. After 6 h of stirring, the mixture was cooled to room temperature, 5 mL of methanol and 2 mL of water were added. After 10 min of stirring, Na_2SO_4 (5 g) was added and the mixture was stirred for additional 10 min. After that, the mixture was filtered through the layer of silica, and distilled under reduced pressure. B.p. 103-105 °C/10 Torr. The yield 79.1 g (94%), colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.70 (s, 2H); 2.02 (t, 4h); 1.42 (m, 4H); 1.30 (br., 12H); 0.94 (t, ^3J = 7.38 Hz, 3H); 0.91 (t, ^3J = 7.38 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 150.48; 108.51; 36.29; 35.97; 32.02; 30.23; 29.35; 28.00; 22.93; 22.70; 14.25; 14.16.

Anal. calcd for $C_{12}H_{24}$ (%): C, 85.63; H, 14.37. Found: C, 85.55; H, 14.39. GC data: >98% of the main compound.



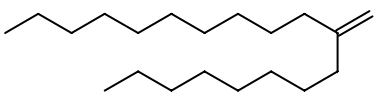
2-Isobutyl-6-methyl-1-heptene (**4**).

Prepared by the method used in the synthesis of **3** from 4-methylpentene (21.1 g, 0.25 mol). B.p. 100-102 °C/10 Torr. The yield 19.4 g (92%), colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.75 (s, 1H); 4.70 (s, 1H); 1.97 (t, ^3J = 7.9 Hz, 2H); 1.91 (d, ^3J = 7.7 Hz, 2H); 1.79 (sept, ^3J = 6.9 Hz, 1H); 1.57 (sept, ^3J = 6.8 Hz, 1H); 1.44 (m, 2H); 1.21 (m, 2H); 0.90 (d, ^3J = 6.9 Hz, 12H); 0.89 (d, ^3J = 6.8 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 149.08, 110.09, 46.21, 39.01, 36.19, 28.14, 26.23, 25.74, 22.82, 22.71.

Anal. calcd for $C_{12}H_{24}$ (%): C, 85.63; H, 14.37. Found: C, 85.51; H, 14.41. GC data: >98% of the main compound.



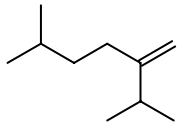
2-Octyl-1-dodecene (**5**).

Prepared by the method used in the synthesis of **3** from 1-decene (35.1 g, 0.25 mol). B.p. 122-125 °C/0.5 Torr. The yield 32.3 g (92%), colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.70 (s, 2H); 2.00 (t, (d, ^{3}J = 7.6 Hz, 4H); 1.42 (m, 4H); 1.28 (br., 28H); 6.37 (t, ^{3}J = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 150.54; 108.50; 36.28 (2C); 32.12 (2C); 29.85 (2C); 29.78; 29.74; 29.67 (2C); 29.56; 29.52; 28.04 (2C); 22.88 (2C); 14.27 (2C).

Anal. calcd for $C_{20}H_{40}$ (%): C, 85.63; H, 14.37. Found: C, 85.50; H, 14.42. GC data: >97% of the main compound.



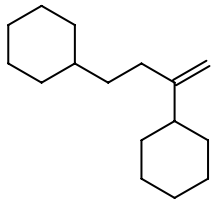
2-Isopropyl-5-methyl-1-hexene (**6**).

Prepared by the method used in the synthesis of **3** from 3-methyl-1-butene (35.1 g, 0.5 mol). Reaction temperature 50 °C. Reaction time 12 h. B.p. 42-44 °C/10 Torr. The yield 27.4 g (78%), colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.75 (s, 1H); 4.70 (s, 1H); 2.26 (sept, ^{3}J = 6.7 Hz, 1H); 2.04 (m, 2H); 1.57 (sept, ^{3}J = 6.7 Hz, 1H); 1.35 (m, 2H); 1.05 (d, ^{3}J = 6.7 Hz, 6H); 0.92 (d, ^{3}J = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 156.66; 106.12; 37.75; 33.97; 32.48; 28.17; 22.78 (2C); 22.08 (2C).

Anal. calcd for $C_{10}H_{20}$ (%): C, 85.63; H, 14.37. Found: C, 85.51; H, 14.48. GC data: >95% of the main compound. Contains ~ 3% of the reduction product.



[1-(2-Cyclohexylethyl)vinyl]cyclohexane (**7**).

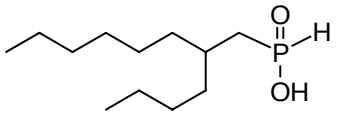
Prepared by the method used in the synthesis of **3** from vinylcyclohexane (33.0 g, 0.3 mol). Reaction time 8 h. B.p. 106-108 °C/1 Torr. The yield 27.7 g (84%), colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.69 (s, 1H); 4.67 (s, 1H); 2.02 (t, 3H); 1.87-1.61 (mm, 12H); 1.33-1.10 (mm, 12H); 0.91 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 156.22; 106.41; 44.43; 37.85; 36.28; 33.58 (2C); 32.72 (2C); 32.42; 27.03 (2C); 26.90; 26.61; 26.59 (2C).

Anal. calcd for $C_{16}H_{28}$ (%): C, 87.19; H, 12.81. Found: C, 87.05; H, 12.94. GC data: >95% of the main compound. Contains ~ 3% of the reduction product.

S3. Synthesis of phosphinic and phosphonic acids



2-Butyloctylphosphinic acid (**8**).

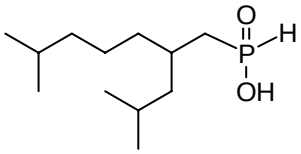
The mixture of 2-butyl-1-octene **3** (11.1 g, 66 mmol), 50% aq. H_3PO_2 (14.5 mL, 264 mmol) and *i*-PrOH (80 mL) was degassed under reduced pressure, filled with argon, and heated to 90 °C with stirring. AIBN was added in 7×100 mg portions within 3 h with 30 min intervals. The mixture was allowed to cool to room temperature, diluted by pentane (100 mL). Organic layer was washed by water (3×100 mL), dried over Na_2SO_4 and evaporated. The residue was purified by gradient column chromatography (silica 60-200, por. 40) using CH_2Cl_2–MeOH mixture (from 100:1 to 1:1 by volume). Oily product was dried *in vacuo*. The yield was 12.4 g (80%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 11.45 (s, 1H, P–OH); 7.83 & 6.48 (d, ^1J = 540 Hz, P–H); 1.83 (m, 1H, >CH–); 1.74-1.68 (mm, 2H, P–C<u>H</u>$_2$); 1.36 (m, 4H, >CH–C<u>H</u>$_2$); 1.25 (br, –CH_2–); 0.88 (t, ^3J = 6.4 Hz, 3H); 0.87 (t, ^3J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 34.65 (d, ^3J = 9.4 Hz); 34.29 (d, ^3J = 9.2 Hz); 35.43 & 34.44 (d, ^1J = 93.5 Hz); 32.04 (d, ^2J = 2.1 Hz); 31.91; 29.55; 28.46; 26.26; 22.91; 22.74; 14.17; 14.14.

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 22.43.

Anal. calcd for $C_{12}H_{27}O_2P$ (%): C, 61.51; H, 11.61; O, 13.66. Found: C, 61.64; H, 11.65; O, 13.70.



2-Isobutyl-6-methylheptylphosphinic acid (**9**).

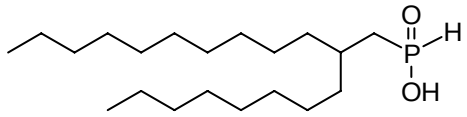
Prepared by the method used in the synthesis of **8** from 2-isobutyl-6-methyl-1-heptene **4** (11.1 g, 66 mmol). The yield was 13.2 g (85%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 12.37 (s, 1H, P–OH); 7.84 & 6.49 (d, ^1J = 539 Hz, P–H); 1.95-1.85 (m, 1H, >CH–); 1.73-1.68 (dd, $^2J_{H\text{-}P}$ = 16.7 Hz, ^3J = 7.7 Hz, 2H, P–C<u>H</u>$_2$); 1.62 (m, 1H); 1.51 (m, 1H); 1.38 – 1.10 (m, 8H); 0.88–0.84 (group d, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 44.65 (d, ^3J = 9.6 Hz); 39.21; 35.10 (d, ^3J = 9.2 Hz); 34.62 & 33.69 (d, ^1J = 93.5 Hz); 29.98 (d, ^2J = 2.3 Hz); 28.03; 25.27; 23.85; 22.85; 22.81; 22.76; 22.75.

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 37.53.

Anal. calcd for $C_{12}H_{27}O_2P$ (%): C, 61.51; H, 11.61; O, 13.66. Found: C, 61.46; H, 11.64; O, 13.73.



2-Octyldodecylphosphinic acid (**10**).

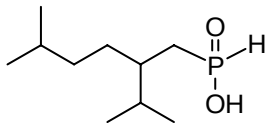
Prepared by the method used in the synthesis of **8** from 2-octyl-1-dodecene **5** (18.6 g, 66 mmol). The yield was 20.8 g (91%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 12.38 (s, 1H, P–OH); 7.79 & 6.45 (d, ^{1}J = 538 Hz, P–H); 1.83 (m, 1H, >CH–); 1.71-1.66 (dd, $^{2}J_{H\text{-}P}$ = 16.5 Hz, ^{3}J = 6.7 Hz, 2H, P–C<u>H</u>$_2$); 1.35 (m, 4H, >CH–C<u>H</u>$_2$); 1.25 (br, 28H, –CH_2–); 0.88 (t, ^{3}J = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 34.62 (d, ^{3}J = 9.5 Hz, 2C); 34.42 & 33.49 (d, ^{1}J = 93.8 Hz); 32.10 (d, ^{2}J = 2.6 Hz); 32.03; 32.01; 29.92 (2C); 29.77; 29.75; 29.74; 29.69; 29.47; 29.43; 26.30 (2C); 22.78 (2C); 14.18 (2C).

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 37.95.

Anal. calcd for $C_{20}H_{43}O_2P$ (%): C, 69.32; H, 12.51; O, 9.23. Found: C, 69.43; H, 12.47; O, 9.28.



2-Isopropyl-5-methylhexylphosphinic acid (**11**).

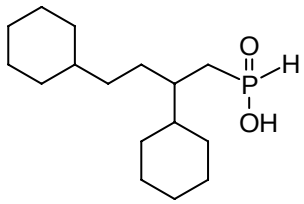
Prepared by the method used in the synthesis of **8** from 2-isopropyl-5-methyl-1-hexene **6** (9.26 g, 66 mmol). The yield was 10.4 g (76%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 10.68 (s, 1H, P–OH); 7.83 & 6.48 (d, ^{1}J = 540 Hz, P–H); 1.83 (m, 1H, >CH–); 1.78-1.10 (group m, 8H); 0.87-0.81 (group d, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 37.86 (d, J = 2.4 Hz); 36.26; 30.99 & 30.05 (d, ^{1}J = 94.0 Hz); 29.69 (d, ^{2}J = 10.4 Hz); 29.52 (d, ^{2}J = 6.8 Hz); 28.18; 22.67; 22.58; 19.28; 17.97.

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 39.37.

Anal. calcd for $C_{10}H_{23}O_2P$ (%): C, 58.23; H, 11.24; O, 15.51. Found: C, 58.15; H, 11.36; O, 15.46.



2,4-Dicyclohexylbutylphosphinic acid (**12**).

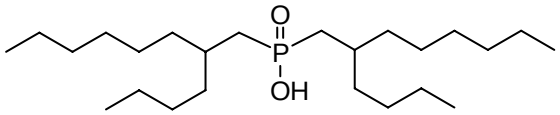
Prepared by the method used in the synthesis of **8** from [1-(2-cyclohexylethyl)vinyl]cyclo-hexane **7** (14.6 g, 66 mmol). The yield was 15.5 g (82%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 11.48 (s, 1H, P–OH); 7.80 & 6.45 (d, ^{1}J = 540 Hz, P–H); 1.82-0.80 (group m, 29H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 40.57 (d, J = 9.6 Hz); 38.01; 37.60 (d, J = 2.5 Hz); 34.88; 33.48 (2C); 31.58 & 30.65 (d, ^1J = 94.0 Hz); 29.84; 29.17 (d, J = 8.0 Hz); 28.88; 26.78; 26.74; 26.72; 26.67; 26.47 (2C).

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 38.89

Anal. calcd for $C_{16}H_{31}O_2P$ (%): C, 67.10; H, 10.91; O, 11.17. Found: C, 67.18; H, 10.88; O, 11.22.



Bis(2-butyloctyl)phosphinic acid (**13**).

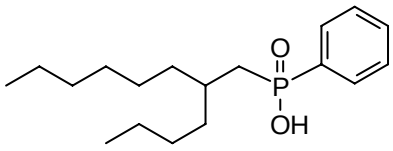
Mixture of phosphinic acid **8** (5.16 g, 22 mmol) and 1-hexene dimer **3** (3.70 g, 22 mmol) was degassed under reduced pressure, filled with argon, and heated to 145 °C with stirring. AIBN was added in 10×50 mg portions within 5 h with 30 min intervals. The mixture was allowed to cool to room temperature, and purified by gradient column chromatography (silica 60-200, por. 40) using $CHCl_3$–MeOH mixture (from 100:1 to 10:1 by volume). The yield was 6.52 g (73%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 10.45 (broad, 1H); 1.84 (m, 2H, –CH<); 1.60 (dd, ^2J = 13.7 Hz, ^3J = 7.1 Hz, 4H); 1.39 (br., 8H); 1.26 (br., 24H); 0.89 (t, ^3J = 6.7 Hz, 6H); 0.87 (t, ^3J = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 34.91 & 34.01 (d, ^1J = 91.2 Hz); 34.87 (d, ^3J = 8.1 Hz); 34.50 (d, ^3J = 8.1 Hz); 32.25 (d, ^2J = 3.9 Hz); 32.08; 29.79; 28.52; 26.32; 23.11; 22.84; 14.28; 14.25.

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 61.30

Anal. calcd for $C_{24}H_{51}O_2P$ (%): C, 71.59; H, 12.77; O, 7.95. Found: C, 71.71; H, 12.82; O, 7.99.



2-Butyloctyl(phenyl)phosphinic acid (**14**).

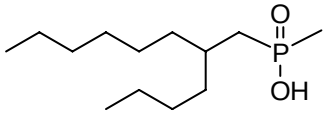
Dichlorophenylphosphine (9.23 g, 52 mmol) was cooled to 0 °C, and water (3 mL) was added with stirring. After 19 h, excess of water was removed under reduced pressure, 1-hexene dimer **3** (17.51 g, 105 mmol) and isoamyl alcohol (2 mL) were added. The mixture was heated to 145 °C with stirring. AIBN was added in 10×50 mg portions within 5 h with 30 min intervals. The mixture was allowed to cool to room temperature, water (5 mL) was added. After 2 h of reflux, water and isoamyl alcoohol were distilled off, the residue was purified by gradient column chromatography (silica 60-200, por. 40) using CH_2Cl_2–MeOH mixture (from 100:1 to 1:1 by volume). The yield was 6.78 g (42%). Viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 12.25 (broad, 1H); 7.70 (dd, $^{3}J_{H\text{-}H}$ = 8.1 Hz, $^{3}J_{H\text{-}P}$ = 10.8 Hz, 2H); 7.43 (t, ^{3}J = 8.1 Hz, 1H); 7.34 (m, 2H); 1.74 (dd, $^{3}J_{H\text{-}H}$ = 6.4 Hz, $^{2}J_{H\text{-}P}$ = 14.4 Hz, 2H); 1.65 (m, –CH<, 1H); 1.30-1.05 (m, 16H); 0.84 (t, ^{3}J = 7.1 Hz, 3H); 0.81 (t, ^{3}J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 134.12 & 132.82 (d, ^{1}J = 138.1 Hz); 131.5; 131.07 (d, J = 11.8 Hz); 128.25 (d, J = 11.8 Hz); 35.43 & 34.44 (d, ^{1}J = 99.5 Hz); 34.48 (d, ^{3}J = 8.6 Hz); 34.16 (d, ^{3}J = 8.6 Hz); 32.15; 31.90; 29.49; 28.25; 26.02; 22.85; 22.73; 14.18; 14.13.

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 46.06.

Anal. calcd for $C_{18}H_{31}O_2P$ (%): C, 69.65; H, 10.07; O, 10.31. Found: C, 69.60; H, 10.14; O, 10.39. Contains ~ 18% of the regioisomer.



2-Butyloctyl(methyl)phosphinic acid (**15**).

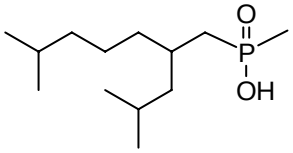
The mixture of alkylphosphinic acid **8** (2.34 g, 10 mmol), Me_3SiCl (3.17 mL, 25 mmol) and CH_2Cl_2 (10 mL) was cooled to 0 °C. Triethylamine (3.48 mL, 25 mmol) was added, the mixture was allowed to warm to room temperature and stirred for 2 h. After that, the mixture was cooled to 0 °C, and methyl iodide (1.25 g, 25 mmol) was added. After 16 h at room temperature, the mixture was diluted by pentane (30 mL). Organic layer was washed by water (3×100 mL), dried over Na_2SO_4 and evaporated. The residue was purified by gradient column chromatography (silica 60-200, por. 40) using CH_2Cl_2–MeOH mixture (from 100:1 to 1:1 by volume). The yield was 1.99 g (80%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 10.75 (broad, 1H); 1.79 (m, 1H, –CH<); 1.65 (dd, $^{3}J_{H\text{-}H}$ = 6.2 Hz, $^{2}J_{H\text{-}P}$ = 14.6 Hz, 2H); 1.44 (d, $^{2}J_{H\text{-}P}$ = 13.6 Hz, 3H, $–CH_3$); 1.37 (broad, 4H); 1.24 (broad, 12H); 0.87 (t, ^{3}J = 6.6 Hz, 3H); 0.86 (t, ^{3}J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 35.50 & 34.55 (d, ^{1}J = 95.1 Hz); 34.75 (d, ^{3}J = 8.3 Hz); 34.38 (d, ^{3}J = 8.3 Hz); 32.48 (d, J = 3.2 Hz); 31.99; 29.66; 28.48; 26.27; 23.01; 22.77; 16.52 & 15.60 (d, ^{1}J = 92.2 Hz); 14.20 (2C).

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 57.77.

Anal. calcd for $C_{13}H_{29}O_2P$, (%):C, 62.87; H, 11.77; O, 12.88. Found: C, 62.98; H, 11.83; O, 12.82%.



2-Isobutyl-6-methylheptyl(methyl)phosphinic acid (**16**).

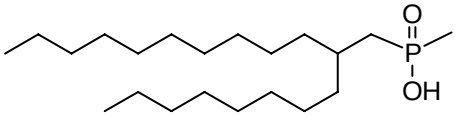
Prepared by the method used in the synthesis of **15** from 2-isobutyl-6-methylheptylphosphinic acid **9** (4.69 g, 20 mmol). The yield was 3.77 g (76%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 10.55 (broad, 1H); 1.86 (m, 1H, –CH<); 1.63 (m, 3H); 1.53 (m, 1H); 1.46 (d, $^{2}J_{H\text{-}P}$ = 14.0 Hz, 3H, $–CH_3$); 1.37 (m, 2H); 1.25 (m, 4H); 1.15 (m, 2H); 0.86 (group of d, 12H)

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 38.35 (d, J = 3.4 Hz); 36.41; 31.93 & 30.99 (d, ^{1}J = 95.6 Hz); 29.47 (d, ^{3}J = 6.7 Hz); 29.31 (d, ^{3}J = 9.1 Hz); 28.25; 22.75; 22.63; 19.19; 17.94; 16.30 & 15.38 (d, ^{1}J = 92.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 58.17.

Anal. calcd for $C_{13}H_{29}O_2P$ (%): C, 62.87; H, 11.77; O, 12.88. Found: C, 62.95; H, 11.84; O, 12.80.



Methyl(2-octyldodecyl)phosphinic acid (**17**).

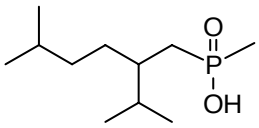
Prepared by the method used in the synthesis of **15** from 2-octyldodecylphosphinic acid **10** (4.15 g, 20 mmol). The yield was 3.17 g (72%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 11.77 (broad, 1H); 1.79 (m, 1H, –CH<); 1.64 (dd, $^{3}J_{H\text{-}H}$ = 6.6 Hz, $^{2}J_{H\text{-}P}$ = 15.4 Hz, 2H); 1.44 (d, $^{2}J_{H\text{-}P}$ = 13.6 Hz, 3H, $–CH_3$); 1.37 (broad, 4H); 1.24 (broad, 28H); 0.87 (t, ^{3}J = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 35.62 & 34.70 (d, ^{1}J = 93.2 Hz); 34.74 (d, ^{3}J = 8.5 Hz, 2C); 32.55 (d, J = 3.5 Hz); 32.06 (2C); 30.55 (2C); 29.83 (2C); 29.79 (2C); 29.50 (2C); 26.33 (2C); 22.82 (2C); 16.62 & 15.70 (d, ^{1}J = 92.2 Hz); 14.24 (2C).

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 56.75.

Anal. calcd for $C_{21}H_{45}O_2P$ (%): C, 69.96; H, 12.58; O, 8.87. Found: 70.02; H, 12.64; O, 8.88.



2-Isopropyl-5-methylhexyl(methyl)phosphinic acid (**18**).

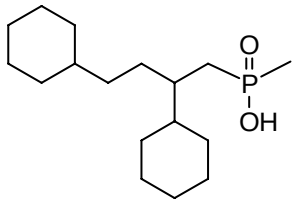
Prepared by the method used in the synthesis of **15** from 2-isopropyl-5-methylhexylphosphinic acid **11** (6.92 g, 20 mmol). The yield was 5.91 g (82%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 10.55 (broad, 1H); 1.86 (m, 1H); 1.63 (m, 2H); 1.45 (d, J = 13.7 Hz, 3H); 1.25 (m, 4H); 1.15 (m, 2H); 0.86 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 38.36 & 38.33 (d, J = 3.5 Hz); 36.41; 31.93 & 30.99 (d, ^{1}J = 95.0 Hz); 29.50 & 29.44 (d, J = 6.4 Hz); 29.36 & 29.27 (d, J = 8.8 Hz); 28.25, 22.75, 22.63, 19.19, 17.94, 16.30 & 15.38 (d, J = 93.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 58.2.

Anal. calcd for $C_{11}H_{25}O_2P$ (%): C, 59.98; H, 11.44; O, 14.53. Found: C, 59.83; H, 11.51; O, 14.59.



2,4-Dicyclohexylbutyl(methyl)phosphinic acid (**19**).

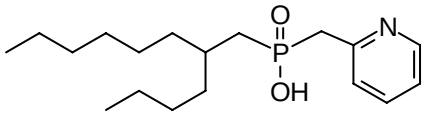
Prepared by the method used in the synthesis of **15** from 2,4-dicyclohexylbutylphosphinic acid **12** (5.73 g, 20 mmol). The yield was 4.09 g (68%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 10.86 (broad, 1H); 1.78-1.68 (m, 12H); 1.44 (d, J = 13.7 Hz, 3H); 1.38 (m, 2H); 1.25-1.05 (m, 13H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 40.29 & 40.21 (d, J = 8.8 Hz); 38.13 (2C); 35.06; 33.58; 33.53; 32.59 & 31.62 (d, ^{1}J = 95.2 Hz); 29.23 & 29.17 (d, J = 6.5 Hz); 29.80 & 28.78 (d, ^{1}J = 101.8 Hz); 26.83; 26.77; 26.52.

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 58.06.

Anal. calcd for $C_{17}H_{33}O_2P$ (%): C, 67.97; H, 11.07; O, 10.65. Found: C, 68.11; H, 11.11; O, 10.60.



2-Butyloctyl(2-pyridinylmethyl)phosphinic acid (**20**).

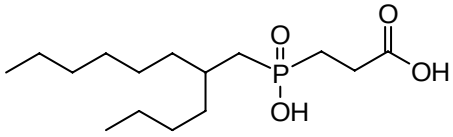
NEt_3 (4.18 mL, 30 mmol) was added to cooled (0 °C) solution of phosphinic acid **8** (2.34 g, 10 mmol), Me_3SiCl (3.8 mL, 30 mmol) and CH_2Cl_2 (10 mL). The mixture was allowed to warm to room temperature, stirred 2 h. Freshly distilled 2-chloromethylpyridine (2.55 g, 20 mmol) was added. After 16 h, the resulting mixture was washed by 1% HCl (20 mL), and evaporated under reduced pressure. The residue was purified by gradient column chromatography (silica 60-200, por. 40) using $CHCl_3$–MeOH mixture (from 100:1 to 1:1 by volume). The yield was 2.02 g (62%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 11.62 (broad, 1H); 8.44 (m, 2H); 7.67 (m,1H); 7.43 (m, 1H); 7.15 (m, 1H); 2.02 (d, $^{3}J_{H\text{-}P}$ = 3.3 Hz, 2H); 1.82 (m, 1H); 1.56 (m, 2H); 1.32 (m, 4H); 1.18 (br, 12H); 0.83 (t, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 154.12; 147.37; 138.35; 125.88; 121.78; 40.82 & 40.07 (d, ^{1}J = 76.8 Hz); 34.72 (d, J = 8.4 Hz); 34.54 & 33.60 (d, ^{1}J = 95.8 Hz); 34.33 (d, J = 8.4 Hz); 32.42 (d, J = 4.0 Hz); 32.02; 29.77; 28.43; 26.25; 23.07; 22.76; 14.24; 14.19.

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 43.24.

Anal. calcd for $C_{18}H_{32}NO_2P$ (%): C, 66.43; H, 9.91; N, 4.30; O, 9.83. Found: C, 66.28; H, 9.97; N, 4.22; O, 9.88.



3-[(2-Butyloctyl)(hydroxy)phosphoryl]propanoic acid (**21**).

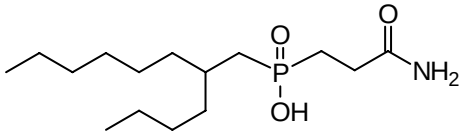
NEt_3 (4.18 mL, 30 mmol) was added to cooled (0 °C) solution of phosphinic acid **8** (2.34 g, 10 mmol), Me_3SiCl (3.8 mL, 30 mmol) and CH_2Cl_2 (10 mL). The mixture was allowed to warm to room temperature, stirred 2 h. Acrylic acid (0.86 g, 12 mmol) was added. After 16 h, the resulting mixture was washed by 5% HCl (10 mL), and evaporated under reduced pressure. The residue was purified by gradient column chromatography (silica 60-200, por. 40) using $CHCl_3$–MeOH mixture (from 100:1 to 1:1 by volume). The yield was 2.45 g (80%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 10.94 (broad, 2H); 2.62 (m, 2H); 2.01 (m, 2H); 1.81 (m, –CH<, 1H); 1.66 (dd, $^3J_{H\text{-}H}$ = 6.0 Hz, $^2J_{H\text{-}P}$ = 13.5 Hz, 2H); 1.35 (m, 4H); 1.23 (broad, 12H); 1.30-1.05 (m, 16H); 0.86 (t, ^3J = 6.8 Hz, 3H); 0.85 (t, ^3J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 176.91; 176.75; 34.60 (d, ^3J = 8.5 Hz); 34.21 (d, ^3J = 8.5 Hz); 33.66 & 32.06 (d, ^1J = 160.9 Hz); 32.73 & 32.02 (d, ^1J = 72.9 Hz); 31.83; 29.51; 28.26; 26.43; 26.06; 25.18; 24.27; 22.85; 22.63; 14.05 (*2*).

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 59.14.

Anal. calcd for $C_{15}H_{31}O_4P$ (%): C, 58.80; H, 10.20; O, 20.89. Found: C, 58.68; H, 10.28; O, 20.76.



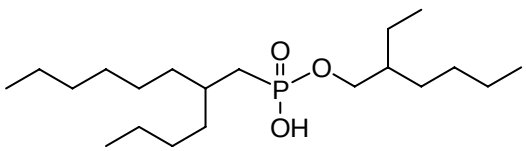
3-Amino-3-oxopropyl(2-butyloctyl)phosphinic acid (**22**).

Prepared by the method used in the synthesis of **21**. Acrylamide (0.85 g, 12 mmol) was added instead of acrylic acid. The yield was 2.75 g (80%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.04 (broad, 3H); 2.64 (m, 2H); 2.04 (m, 2H); 1.81 (m, 1H, –CH<); 1.66 (dd, $^3J_{H\text{-}H}$ = 6.0 Hz, $^2J_{H\text{-}P}$ = 13.4 Hz, 2H); 1.37 (m, 4H); 1.25 (broad, 12H); 0.88 (t, ^3J = 6.8 Hz, 3H); 0.87 (t, ^3J = 6.9 Hz, 3H).

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 56.96.

Anal. calcd for $C_{15}H_{32}NO_3P$ (%): C, 58.99; H, 10.56; N, 4.59; O, 15.72. Found: C, 59.12; H, 10.61; N, 4.55; O, 15.79.



2-Ethylhexyl hydrogen 2-butyloctylphosphonate (**23**).

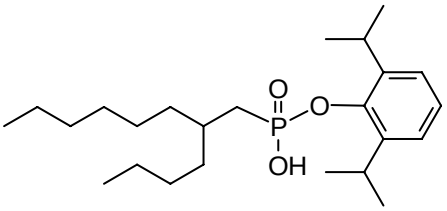
Triisobutylaluminium (1 M in hexane, 80 mL, 80 mmol) was added to **3** (33.6 g, 200 mmol). The mixture was heated to 140 °C (hexane was distilled off).After 20 h of stirring, the mixture was cooled to room temperature, transferred into dropping funnel, and added dropwise to cooled (0 °C) PCl_3 (68.7 g, 500 mmol). The mixture was heated to 90 °C. After 16 h of stirring at this temperature, the mixture was evaporated under reduced pressure, and the residue was distilled *in vacuo*. The fraction having B. p. 115–125 °C, containing c.a. 85% of the desired compound $C_{12}H_{25}PCl_2$, was used for the synthesis of phosphonates without purification. $C_{12}H_{25}PCl_2$ (3.08 g, 11.4 mmol) was dissolved in CCl_4, SO_2Cl_2 (1.0 mL, 12.45 mmol) was added. After 16 h of stirring, the mixture was evaporated under reduced pressure, the residue was dissolved in CH_2Cl_2 (20 mL). After cooling to 0 °C, pyridine (1.0 mL, 12 mmol) and 2-ethylhexanol (1.50 g, 11.5 mmol) were added. After 16 h at room tepmerature, pentane (10 mL) was added. The organic layer was washed by water and evaporated. The residue was purified by column chromatography (silica 60-200, por. 40) using CH_2Cl_2–MeOH mixture (from 100:1 to 1:1 by volume). The yield was 2.57 g (55 %).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 11.25 (broad, 1H); 3.90 (m, 2H); 1.84-1.75 (m, 1H, –CH<); 1.69 (dd, ^2J = 19.1 Hz, ^3J = 6.4 Hz, 2H); 1.51 (m, 1H); 1.42-1.32 (broad, 6H); 1.32-1.20 (broad, 18H); 0.88 (group t, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 66.46 & 66.38 (d, ^2J = 7.4 Hz); 34.53 (d, ^3J = 9.8 Hz); 34.16 (d, ^3J = 9.8 Hz); 32.83 (d, ^2J = 4.1 Hz); 32.04; 31.05 & 39.64 (d, ^1J = 140.8 Hz); 30.13; 29.71; 29.04; 28.52; 26.32; 23.44; 23.12; 23.04; 22.82; 14.28 (2C); 14.18; 11.06.

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 35.90

Anal. calcd for $C_{20}H_{43}O_3P$ (%): C, 66.26; H, 11.96; O, 13.24. Found: C, 66.38; H, 12.02; O, 13.26.



2,6-Diisopropylphenyl hydrogen 2-butyloctylphosphonate (**24**).

Prepared by the method used in the synthesis of **23**. 2,6-Diisopropylphenol (2.05 g, 11.5 mmol) and Et_3N (1.67 mL, 12 mmol) were utilized. The yield was 2.57 g (55%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 12.25 (broad, 1H); 7.09 (m, 3H); 3.44 (sept, ^3J = 6.9 Hz, 2H, –CH<); 1.90-1.83 (m, 1H, –CH<); 1.78 (dd, ^2J = 18.7 Hz, ^3J = 6.4 Hz, 2H); 1.39 (m, 4H); 1.28 (m,12H); 1.16 (d, ^3J = 6.9 Hz, 12H); 0.91 (t, ^3J = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 144.65 (d, ^2J = 11.9 Hz); 144.14; 125.44; 124.13; 34.54 & 34.44 (d, ^3J = 10.4 Hz); 34.17 & 34.07(d, ^3J = 9.8 Hz); 32.83 (d, ^2J = 4.5 Hz); 32.04; 31.56 & 30.13 (d, ^1J = 143.8 Hz); 29.67; 28.43; 27.13; 26.22; 23.67; 23.01; 22.81; 14.25 (2C).

^{31}P NMR (162 MHz, $CDCl_3$, δ, ppm): 31.36.

Anal. calcd for $C_{24}H_{43}O_3P$ (%): C, 70.21; H, 10.56; O, 11.69. Found: C, 70.15; H, 10.60; O, 11.66.

S4. Copies of NMR spectra

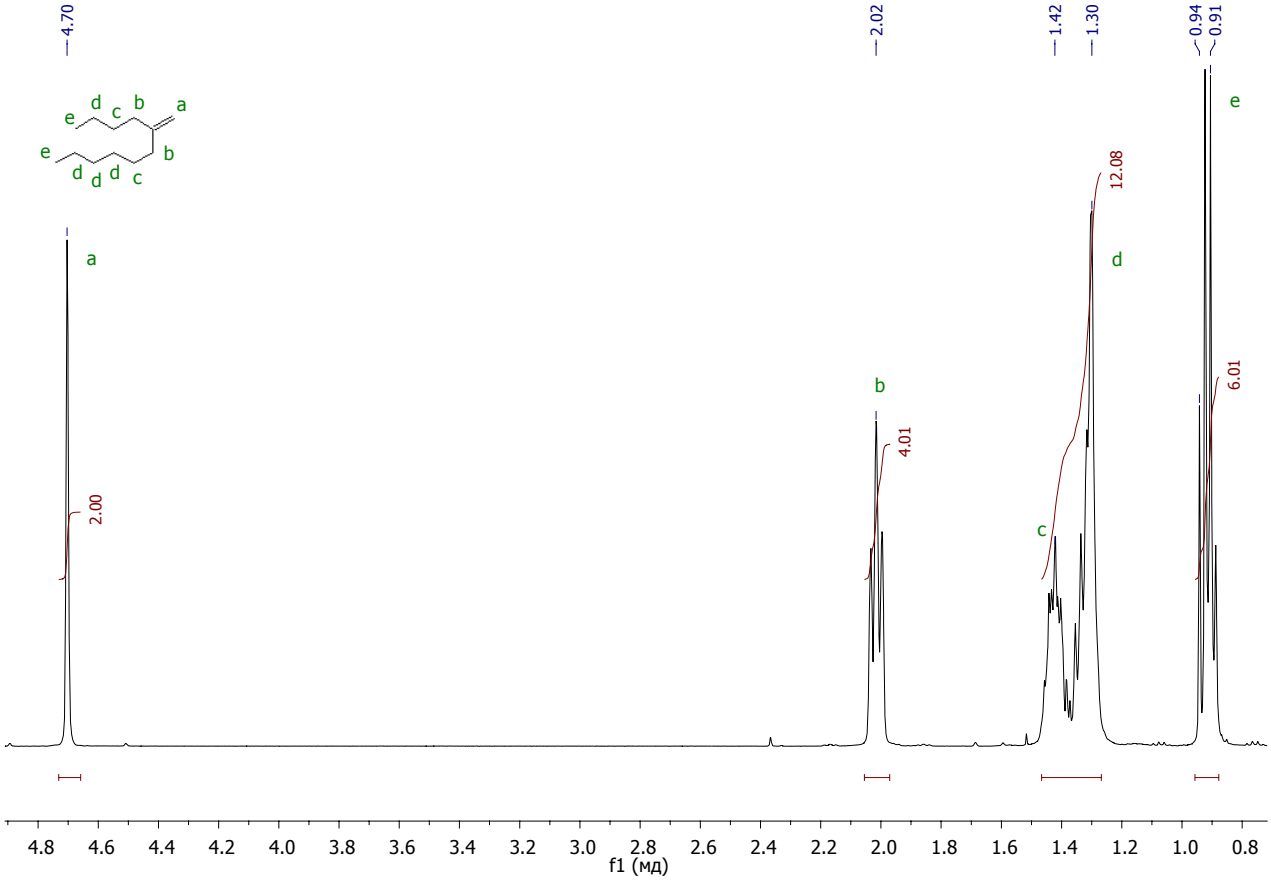


Fig. S1. [1]H NMR spectra of 2-butyl-1-octene **3**.

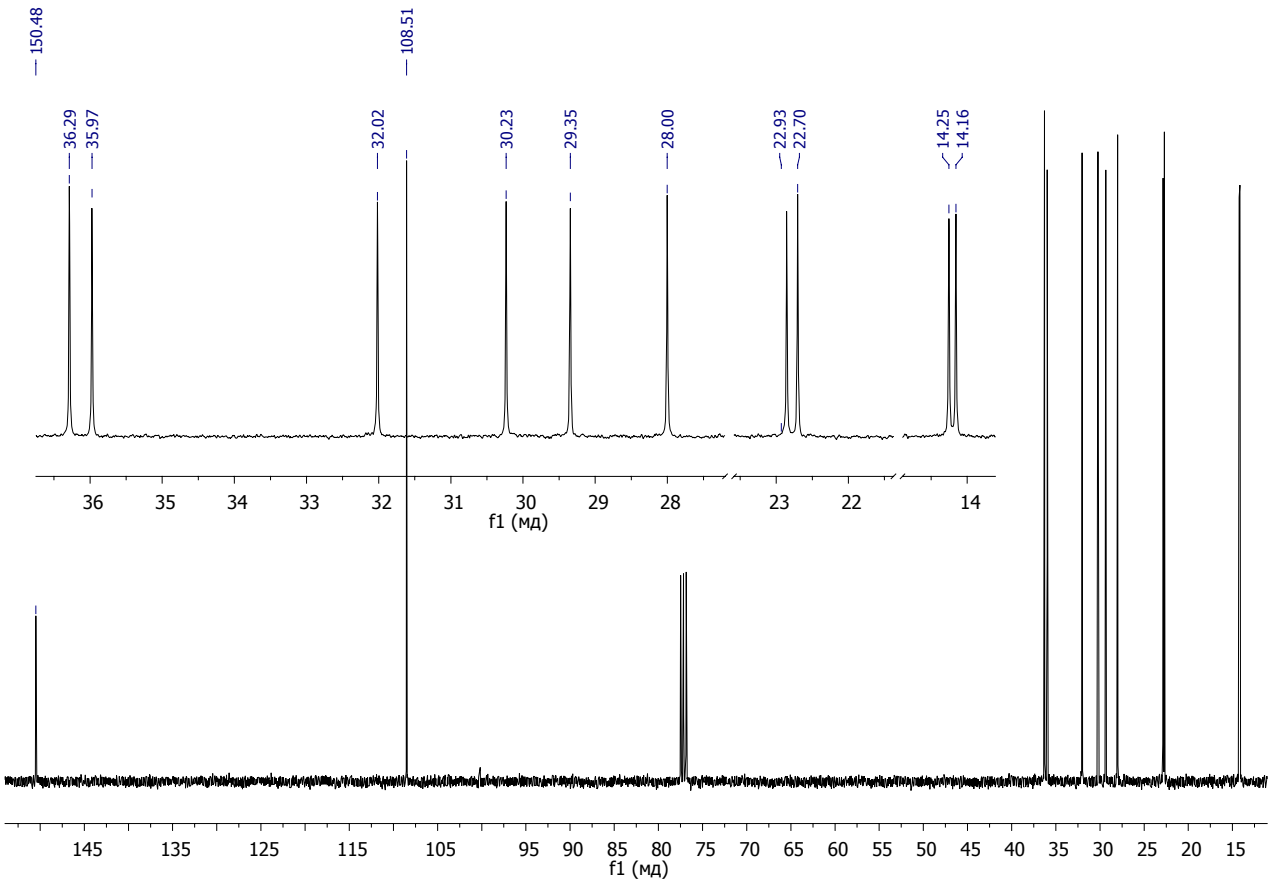


Fig. S2. [13]C NMR spectra of 2-butyl-1-octene **3**.

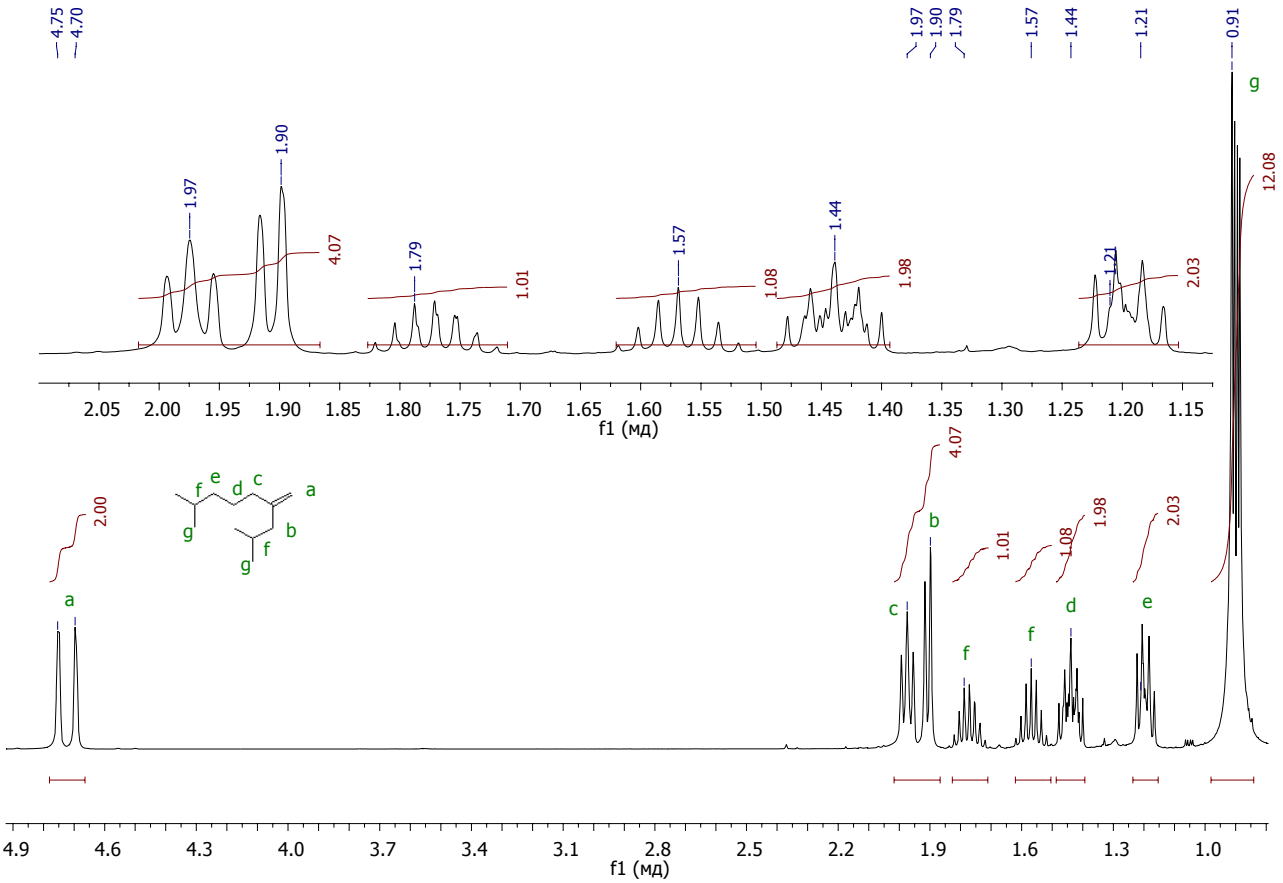


Fig. S3. [1]H NMR spectra of 2-(2-methylpropyl)-6-methyl-1-heptene **4**.

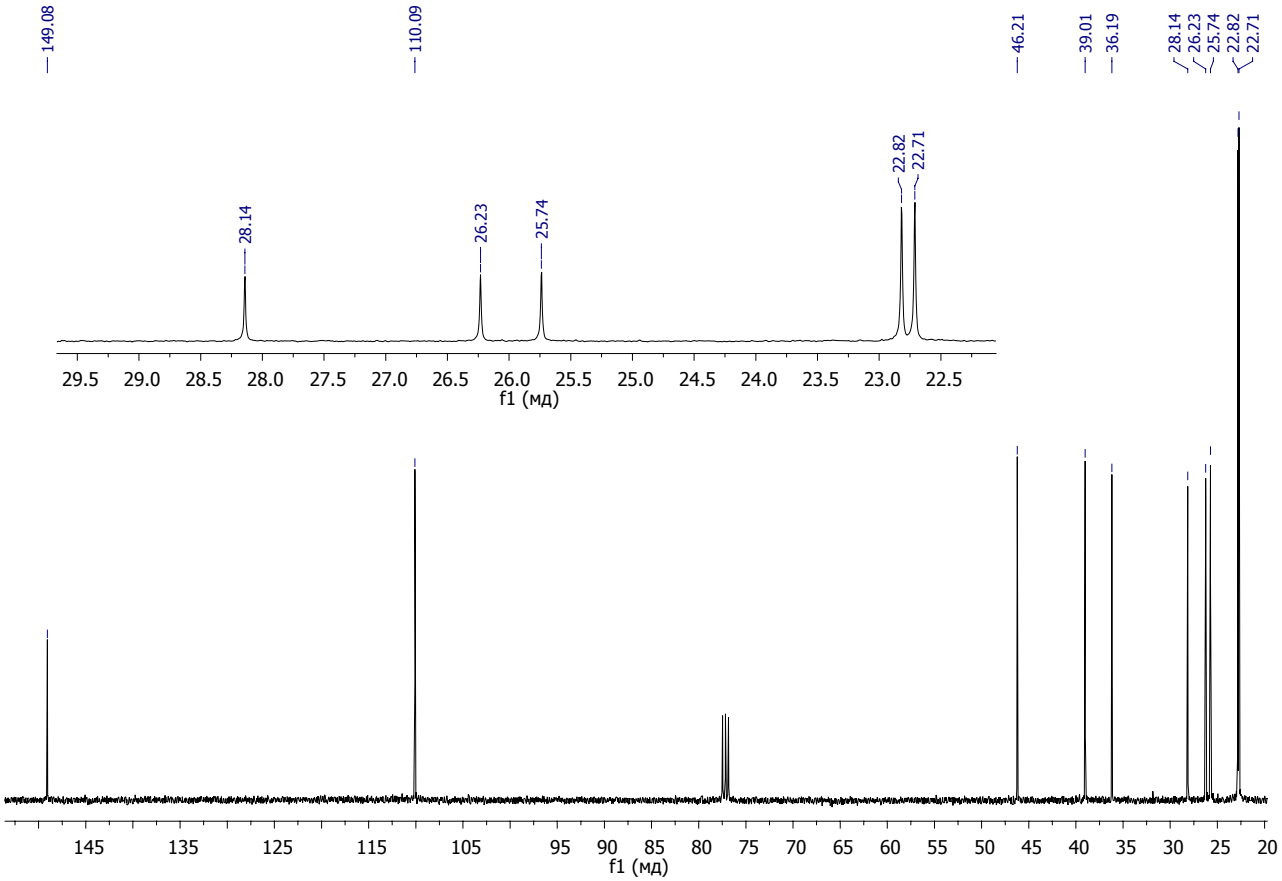


Fig. S4. [13]C NMR spectra of 2-(2-methylpropyl)-6-methyl-1-heptene **4**.

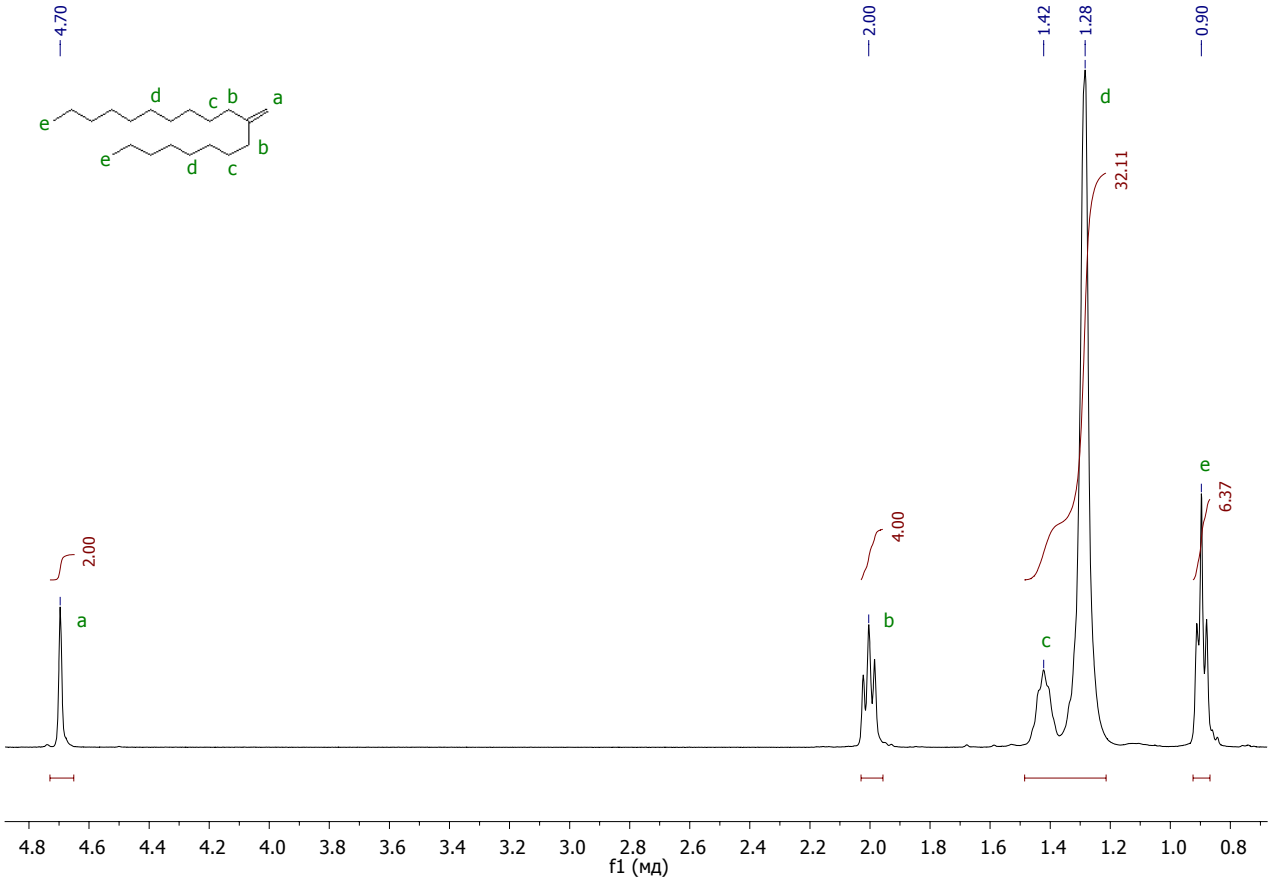


Fig. S5. ^{1}H NMR spectra of 2-octyl-1-dodecene **5**.

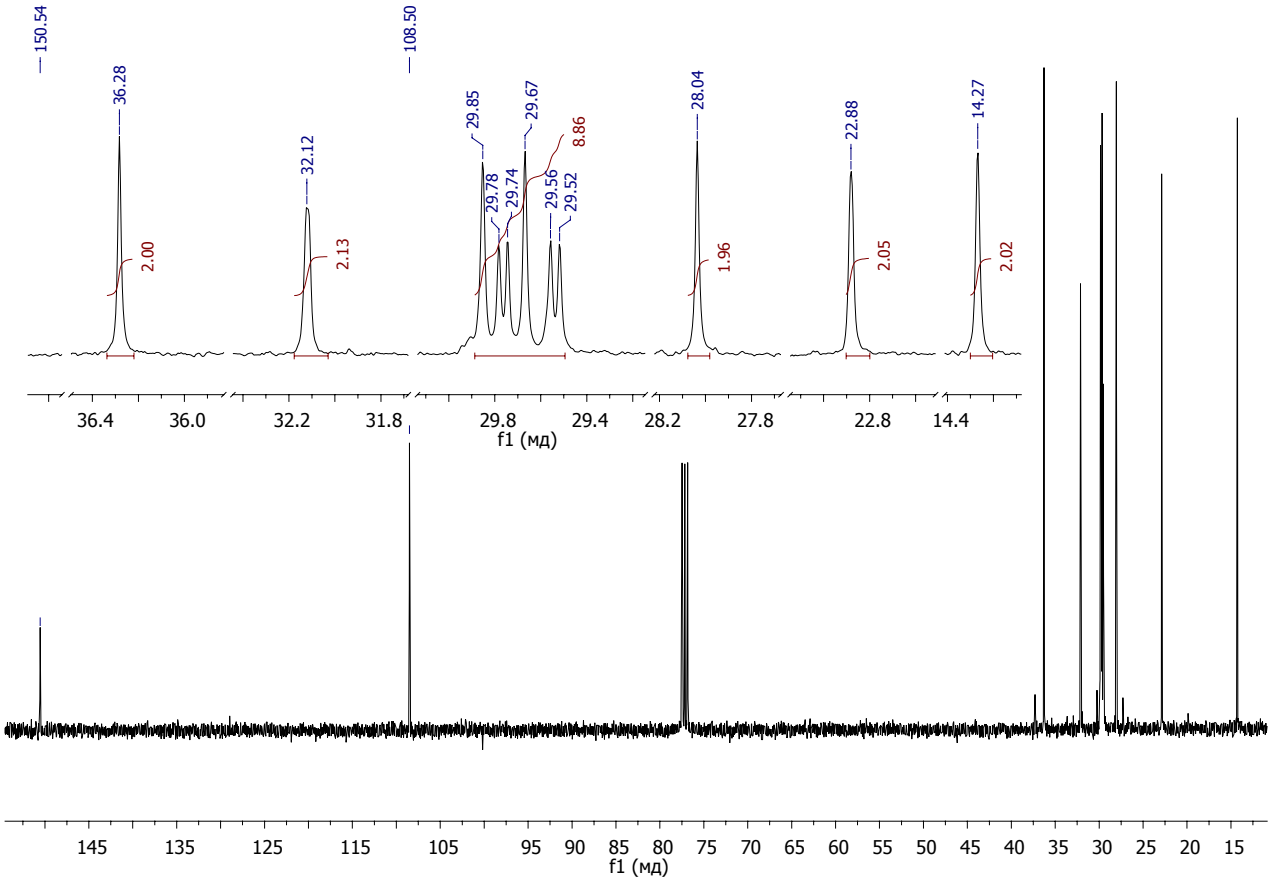


Fig. S6. ^{13}C NMR spectra of 2-octyl-1-dodecene **5**.

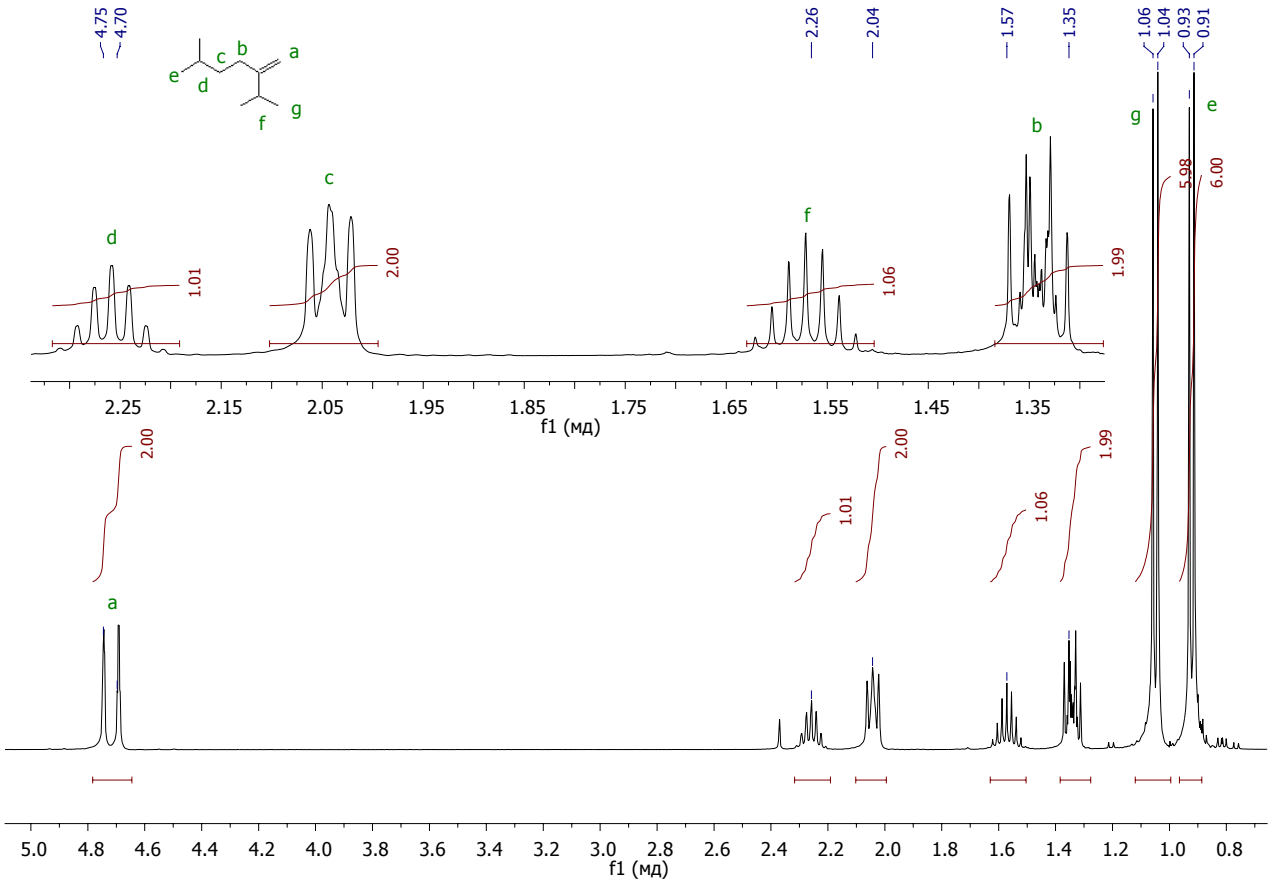


Fig. S7. [1]H NMR spectra of 2-(2-methylethyl)-5-methyl-1-hexene **6**.

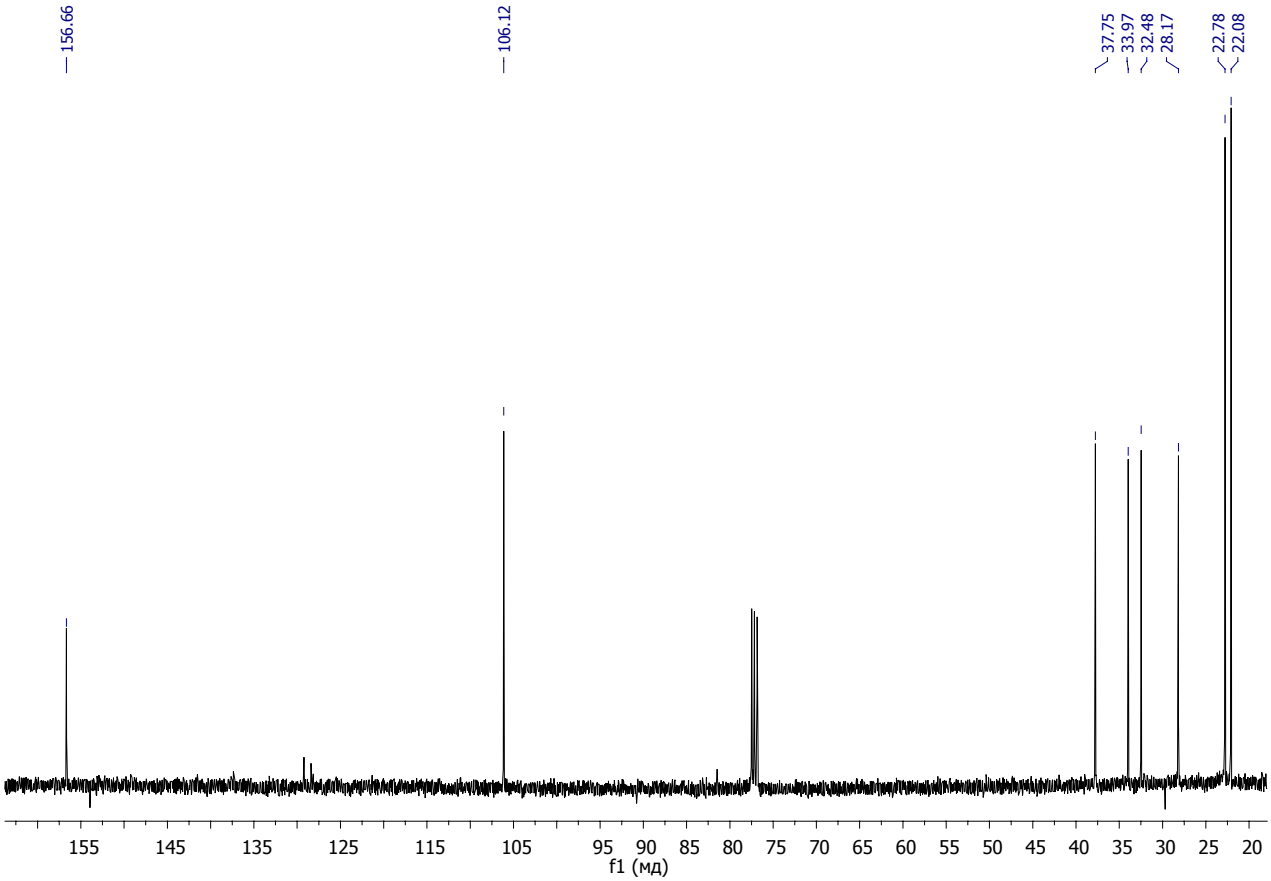


Fig. S8. [13]C NMR spectra of 2-(2-methylethyl)-5-methyl-1-hexene **6**.

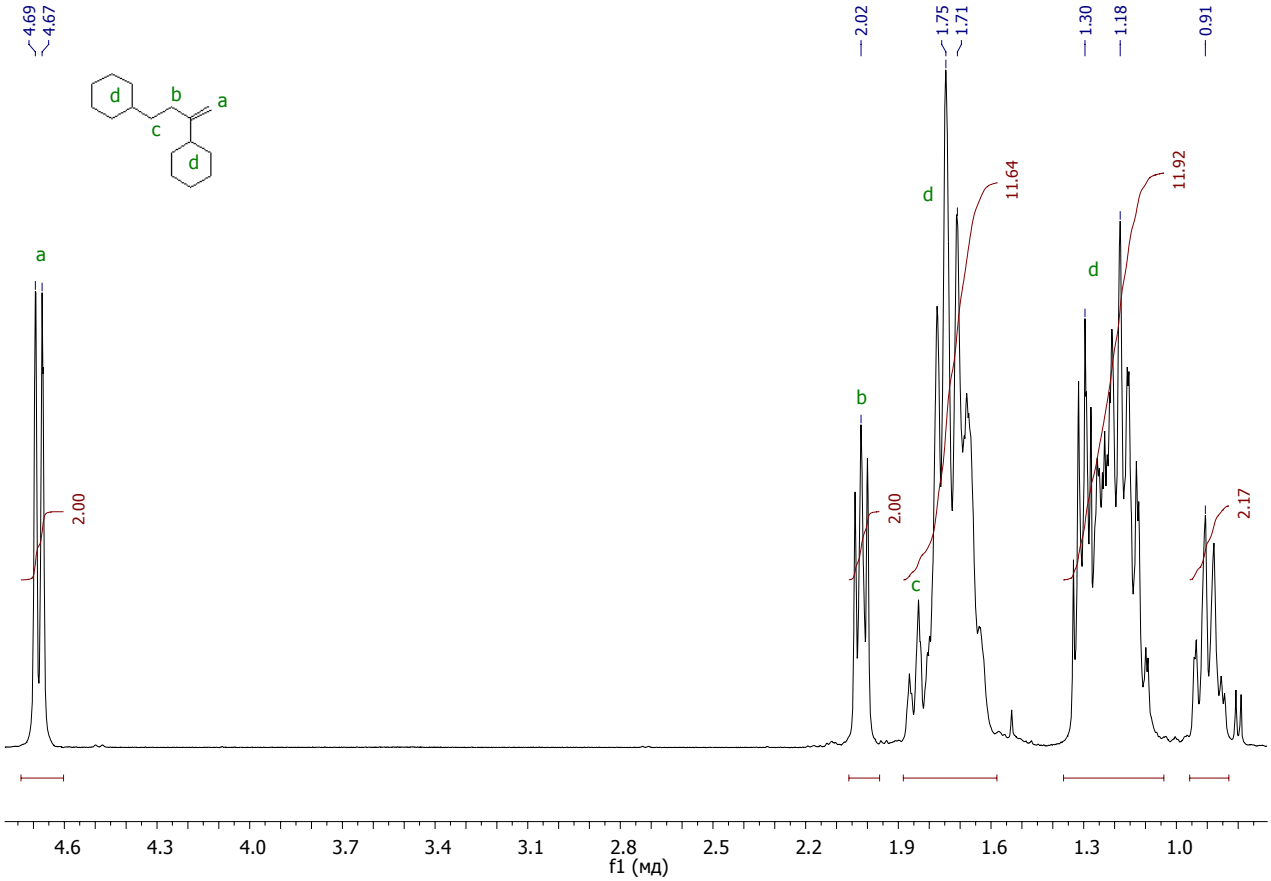


Fig. S9. ^{1}H NMR spectra of (3-cyclohexyl-3-butenyl)cyclohexane **7**.

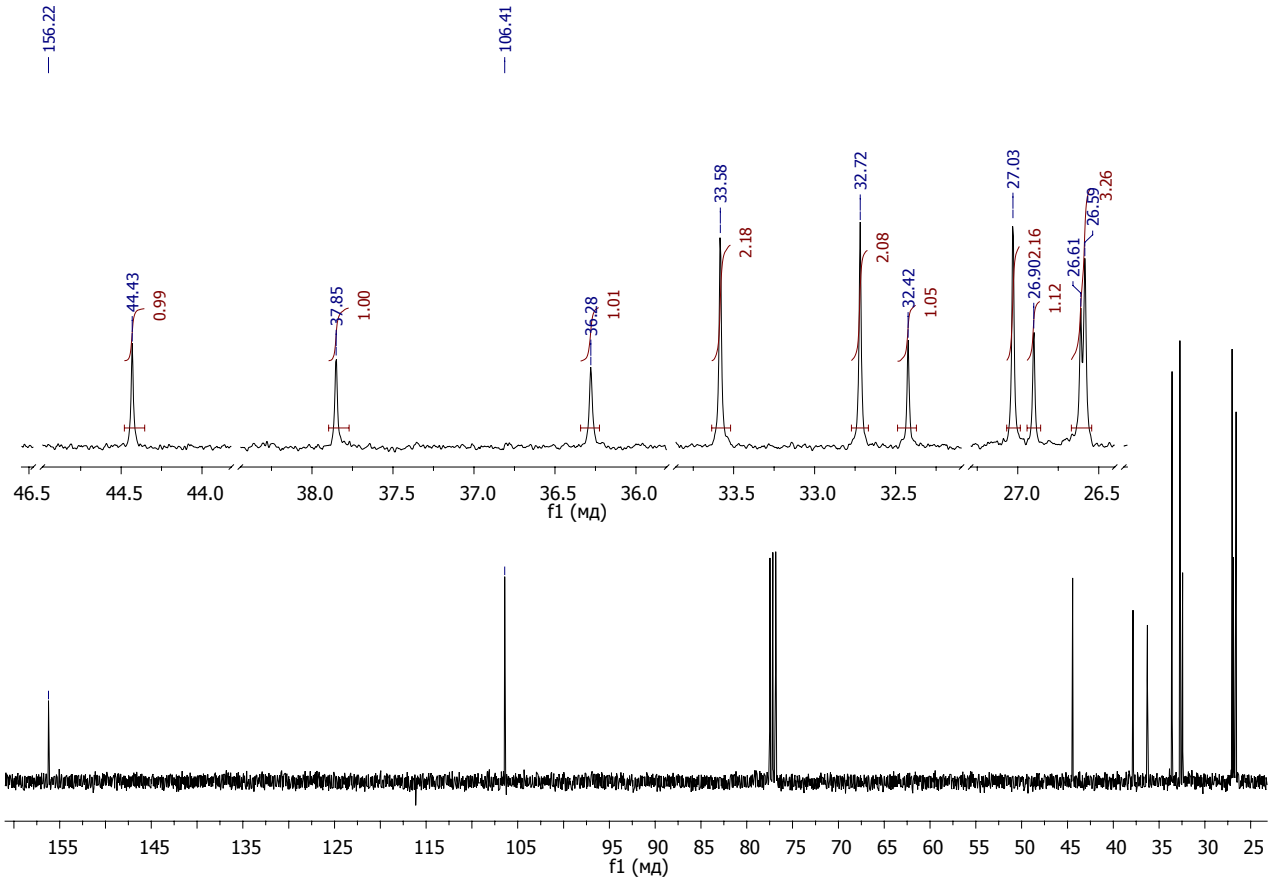


Fig. S10. ^{13}C NMR spectra of (3-cyclohexyl-3-butenyl)cyclohexane **7**.

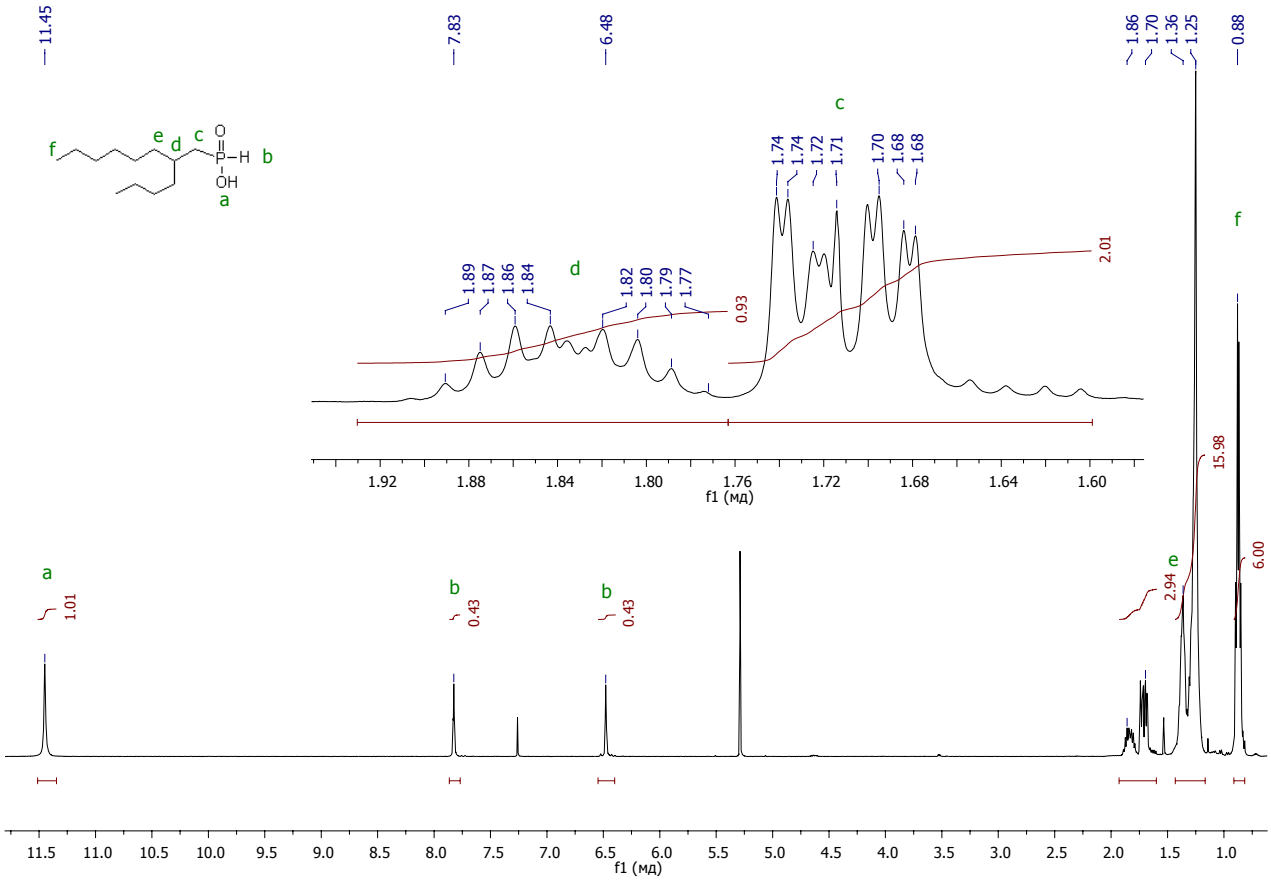


Fig. S11. ^{1}H NMR spectra of 2-butyloctylphosphinic acid **8**.

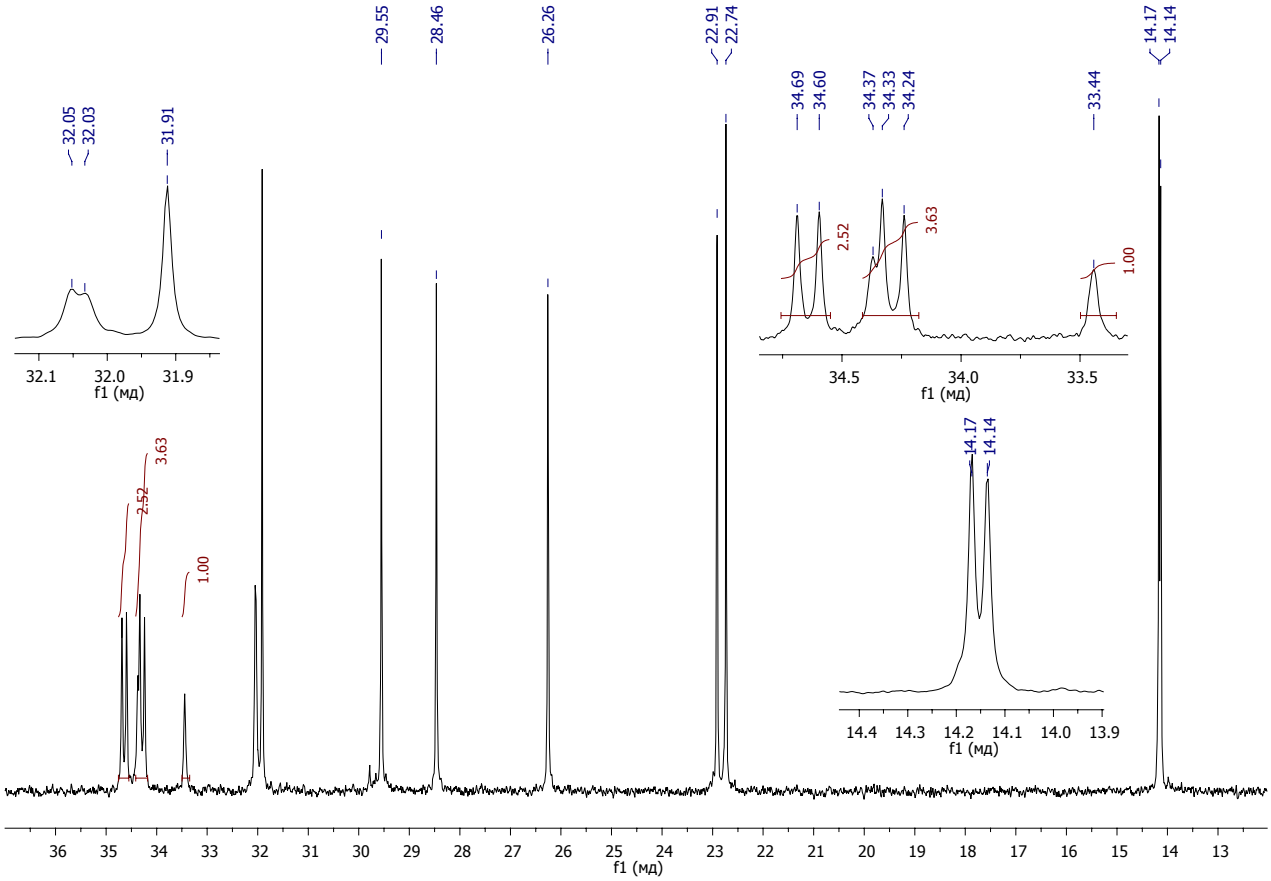


Fig. S12. ^{13}C NMR spectra of 2-butyloctylphosphinic acid **8**.

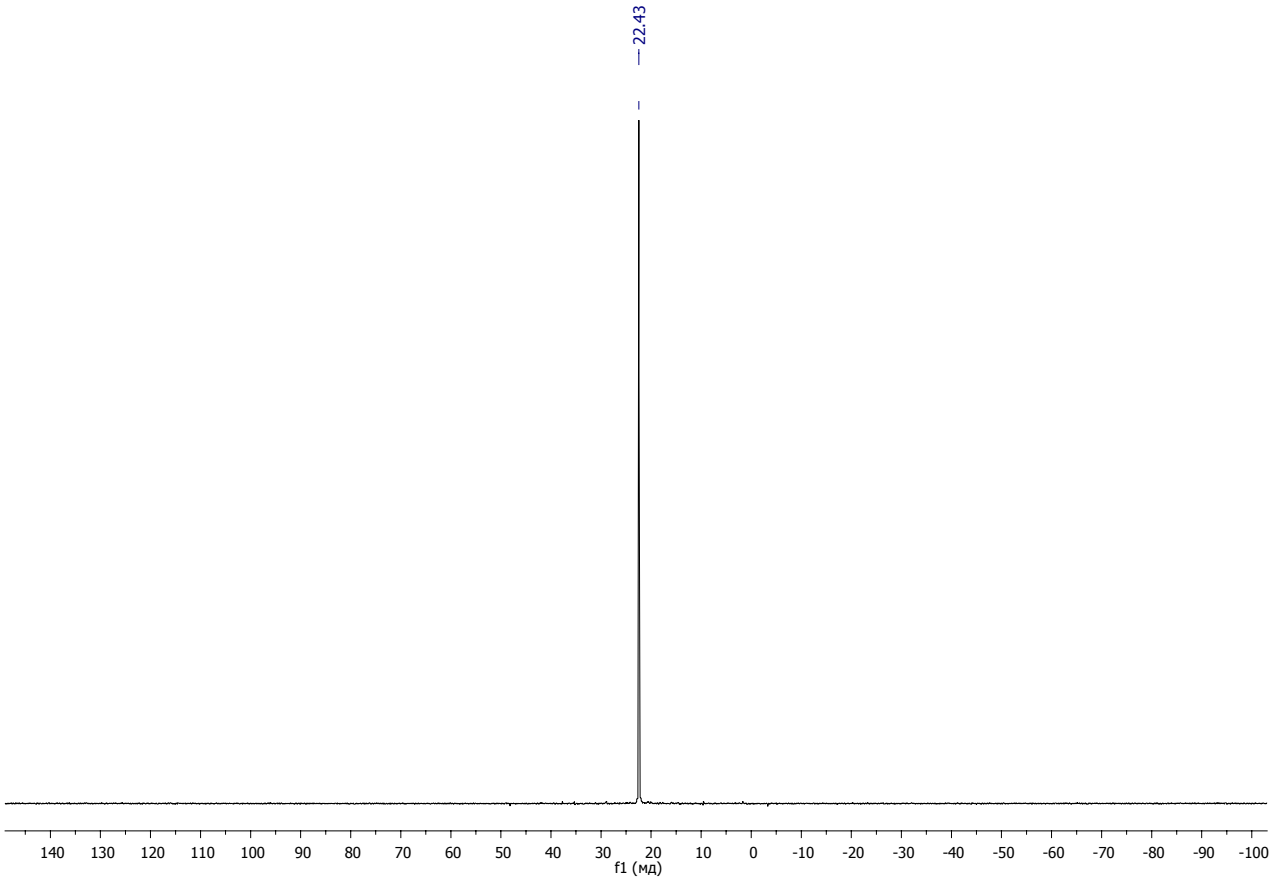


Fig. S13. ^{31}P NMR spectra of 2-butyloctylphosphinic acid **8**.

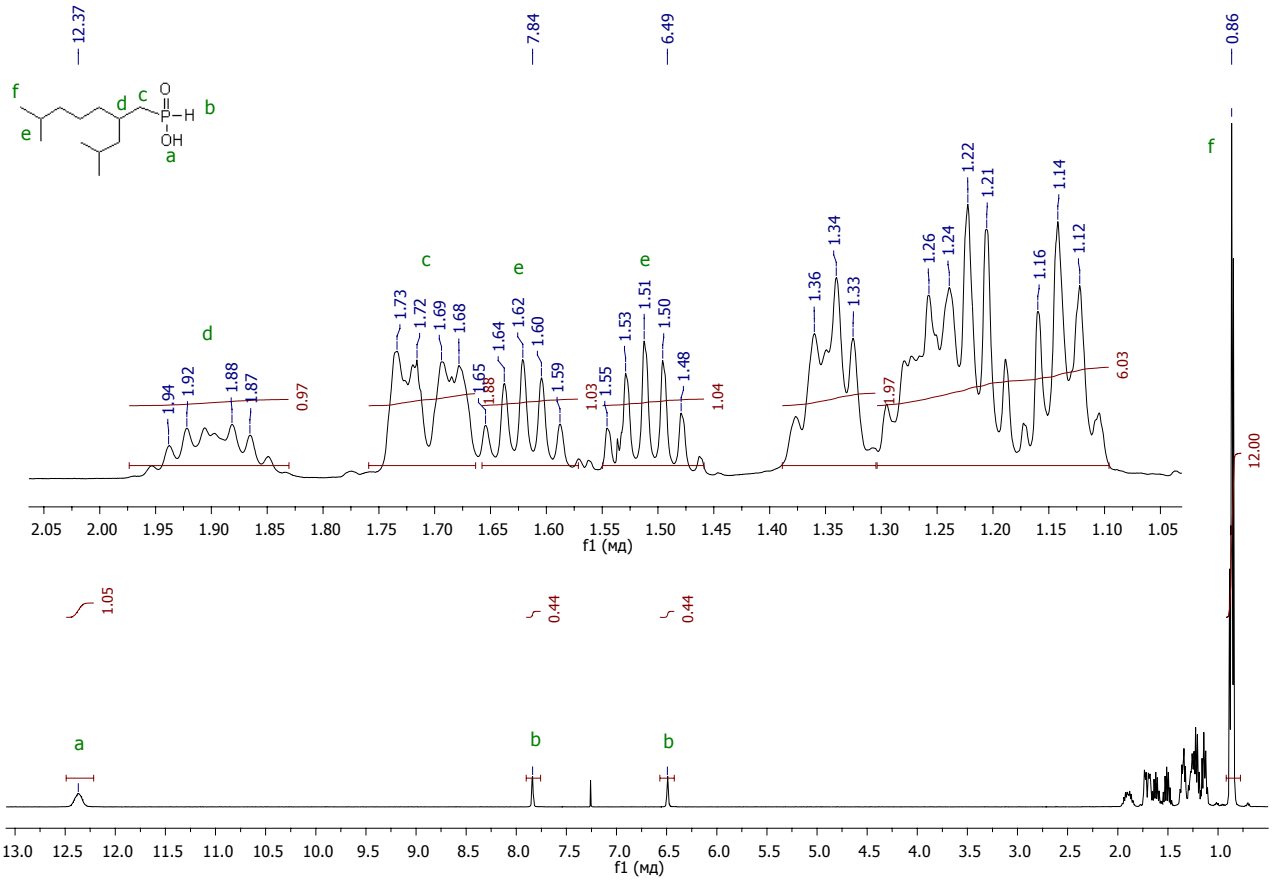


Fig. S14. ^{1}H NMR spectra of 2-isobutyl-6-methylheptylphosphinic acid **9**.

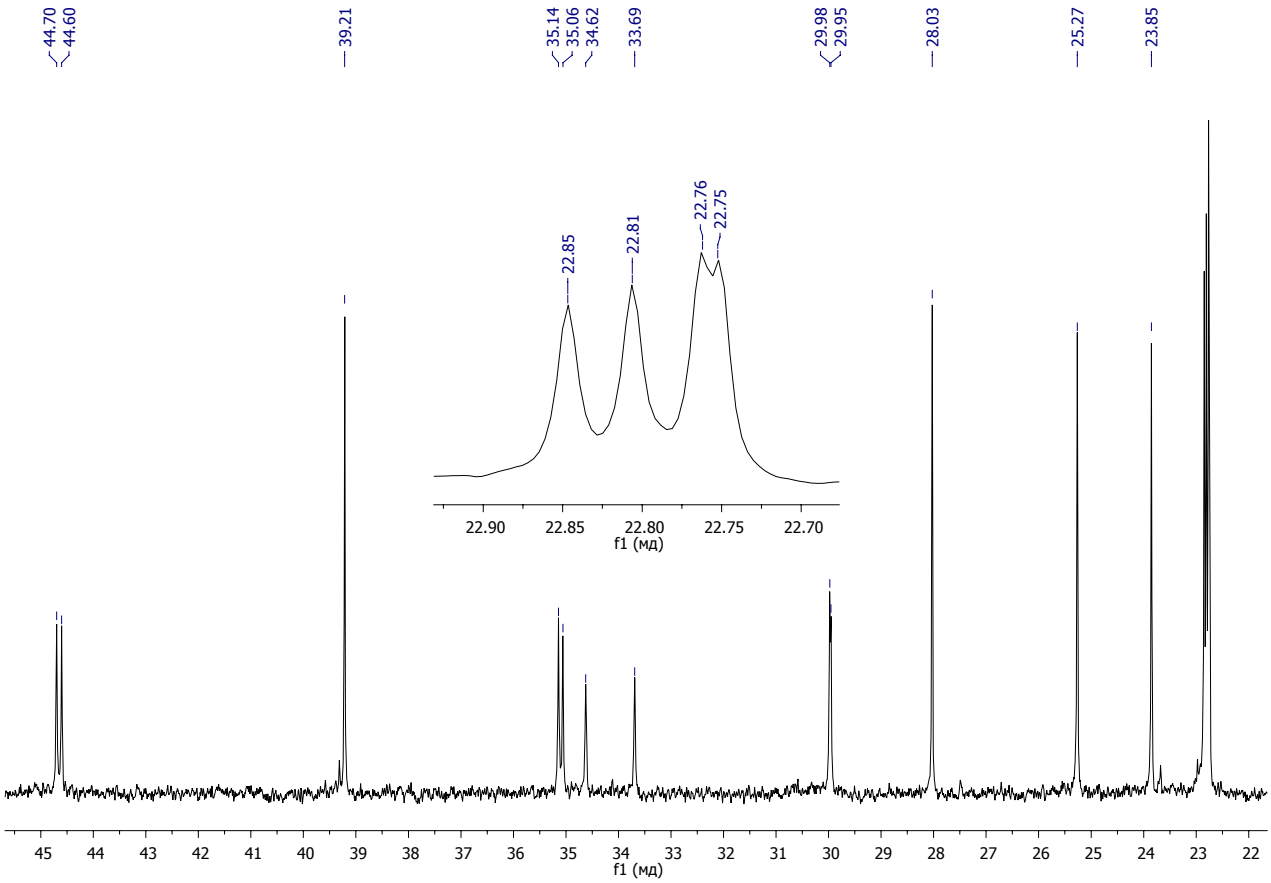


Fig. S15. ^{13}C NMR spectra of 2-isobutyl-6-methylheptylphosphinic acid **9**.

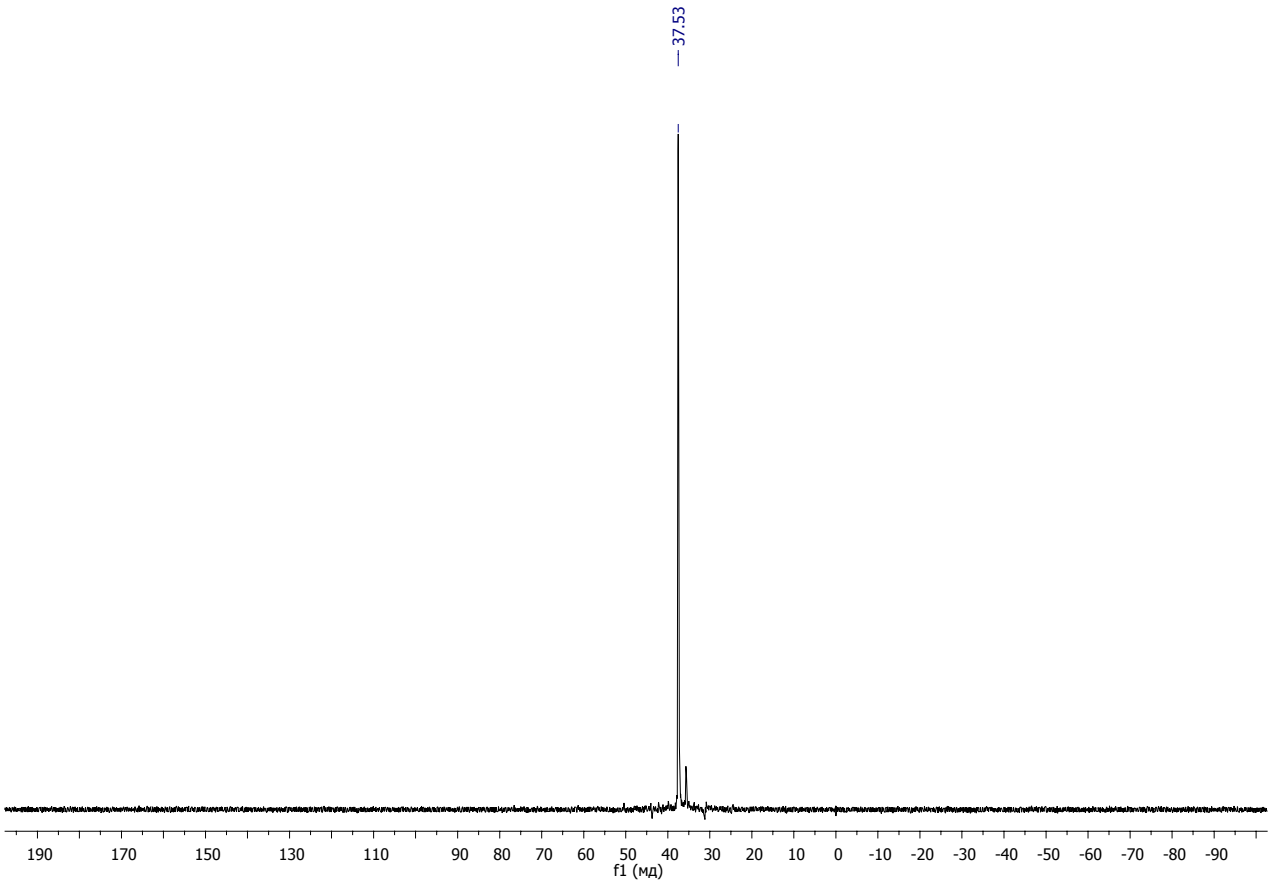


Fig. S16. ^{31}P NMR spectra of 2-isobutyl-6-methylheptylphosphinic acid **9**.

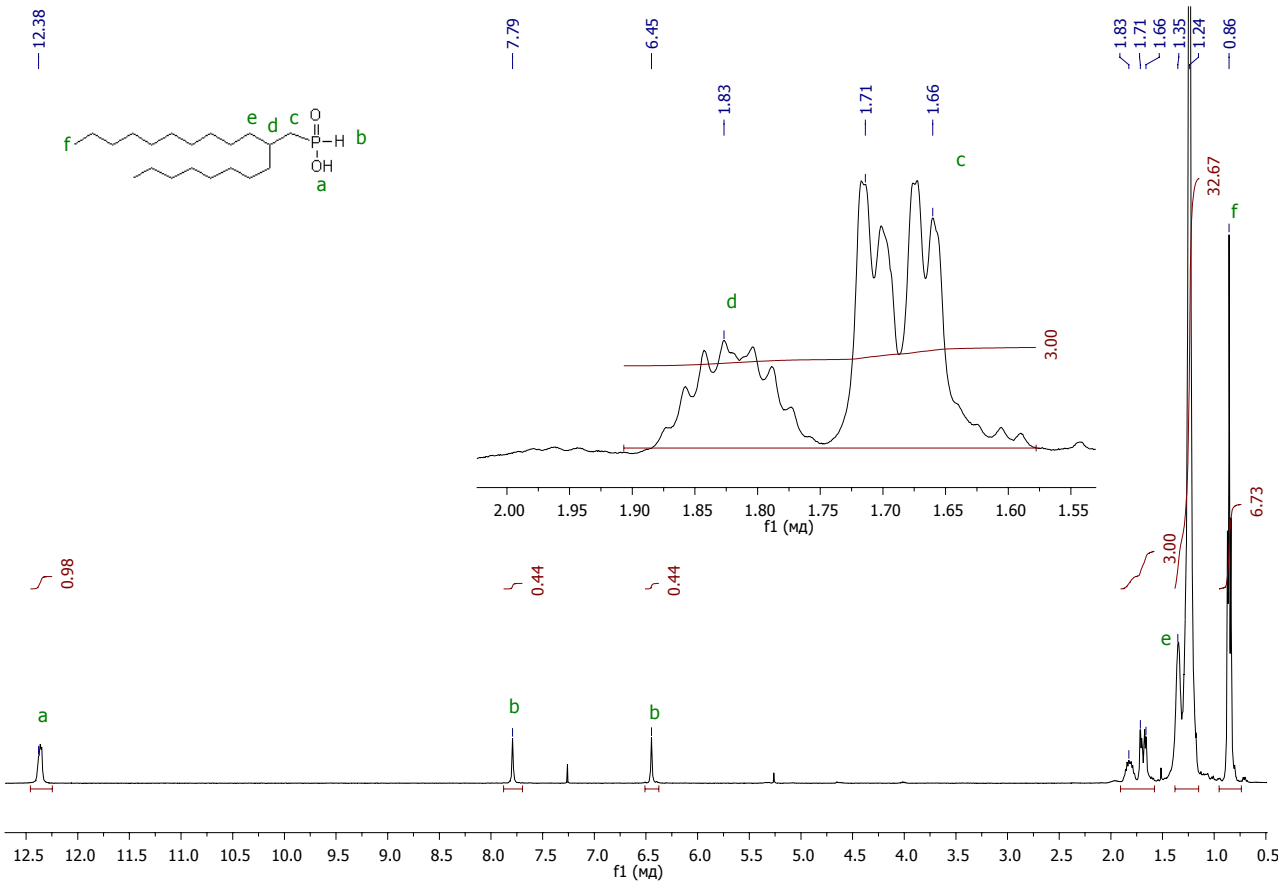


Fig. S17. [1]H NMR spectra of 2-octyldodecylphosphinic acid **10**.

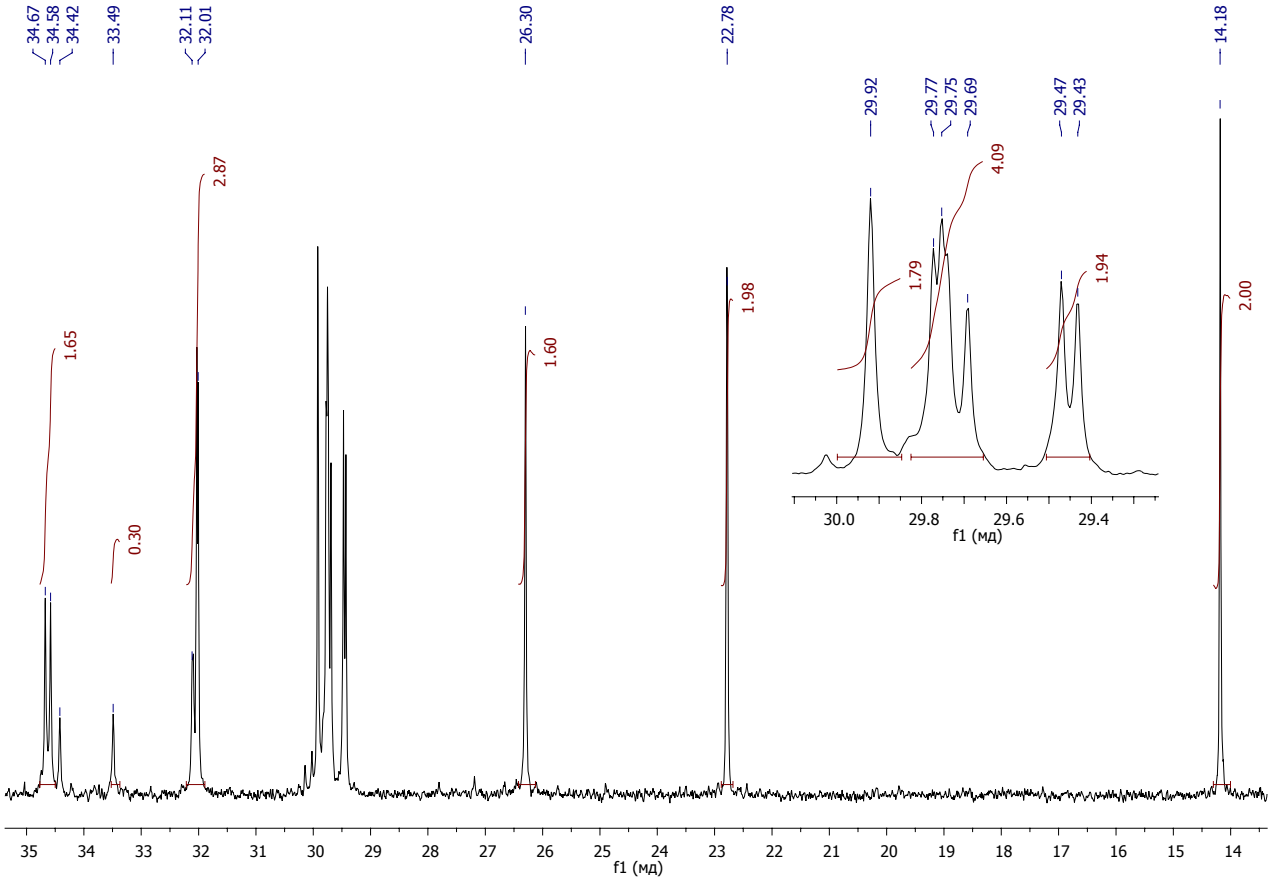


Fig. S18. [13]C NMR spectra of 2-octyldodecylphosphinic acid **10**.

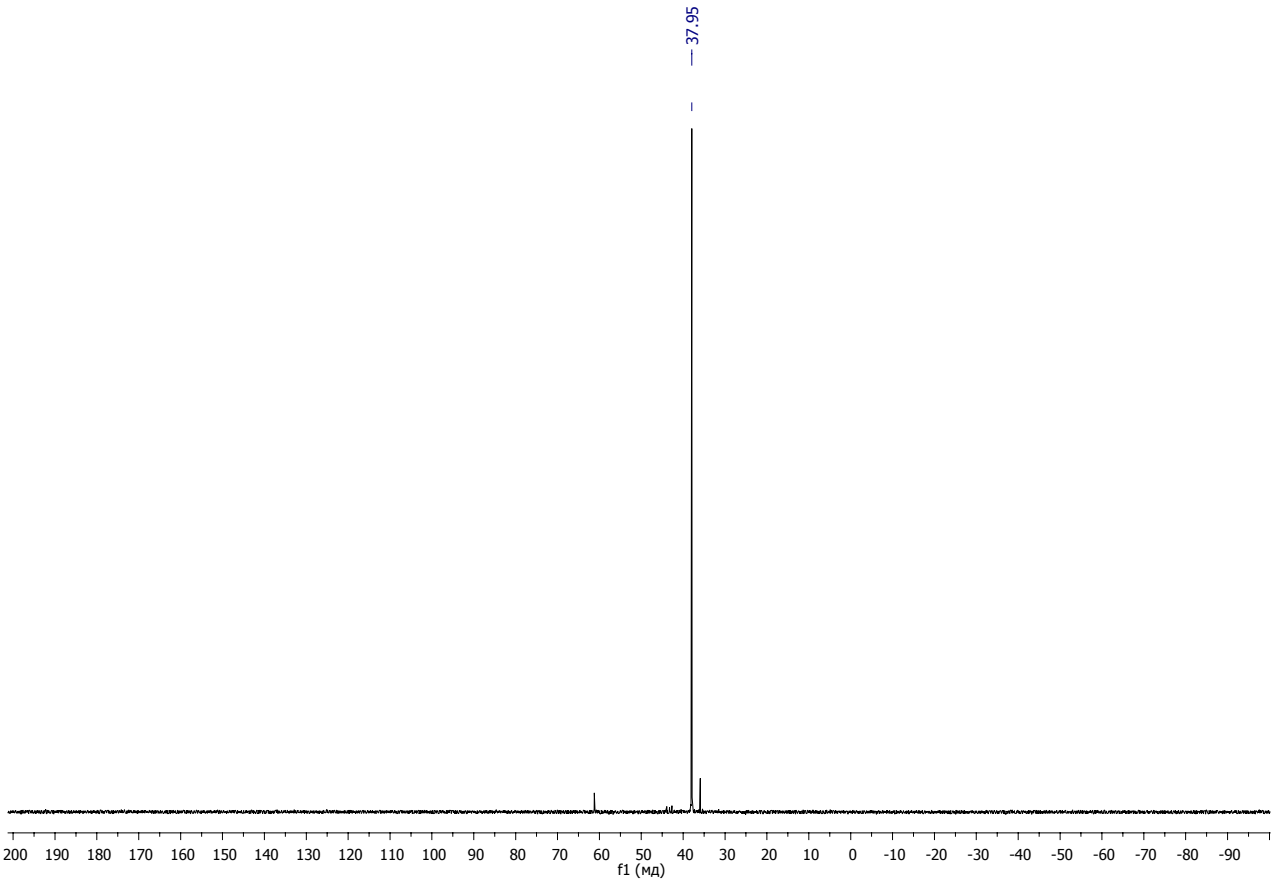


Fig. S19. ^{31}P NMR spectra of 2-octyldodecylphosphinic acid **10**.

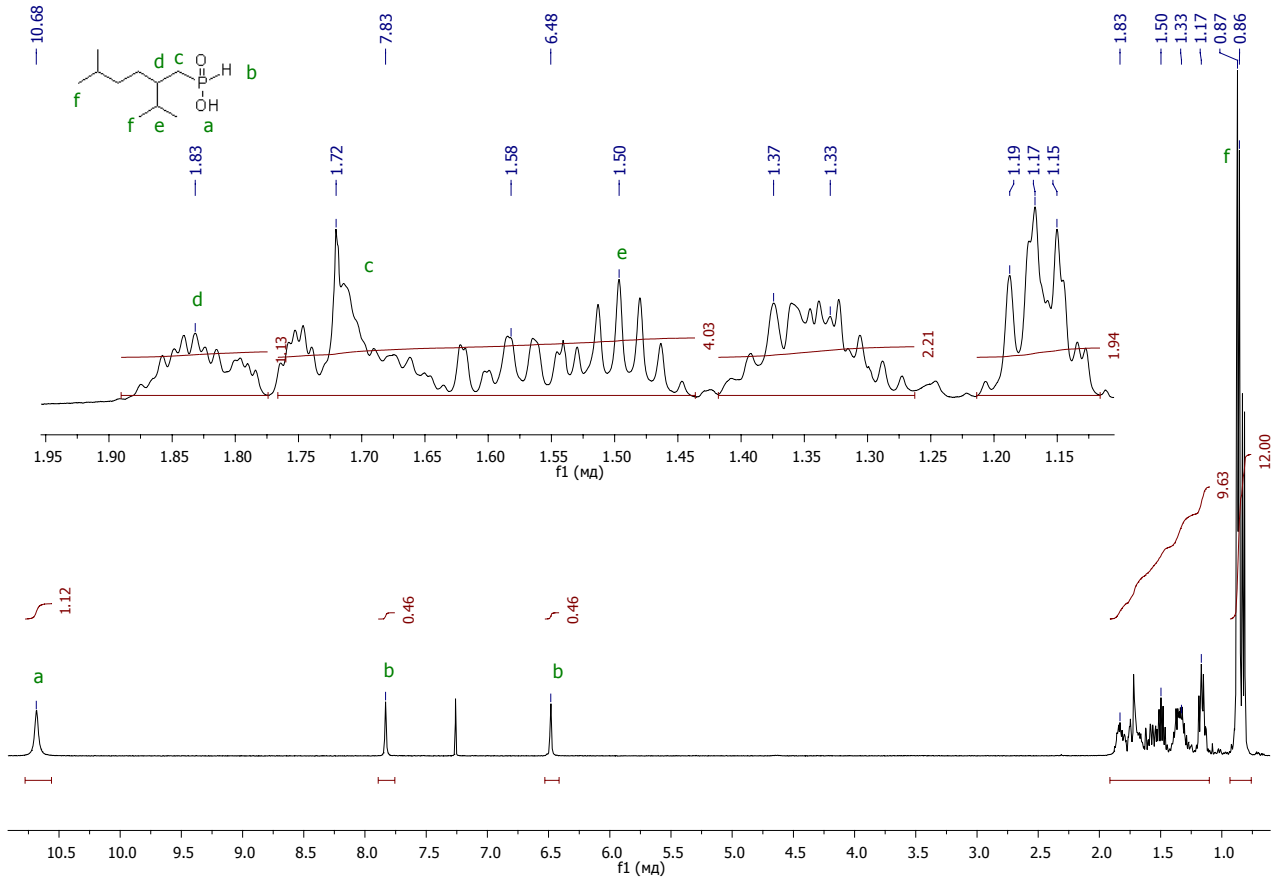


Fig. S20. ^{1}H NMR spectra of 2-isopropyl-5-methylhexylphosphinic acid **11**.

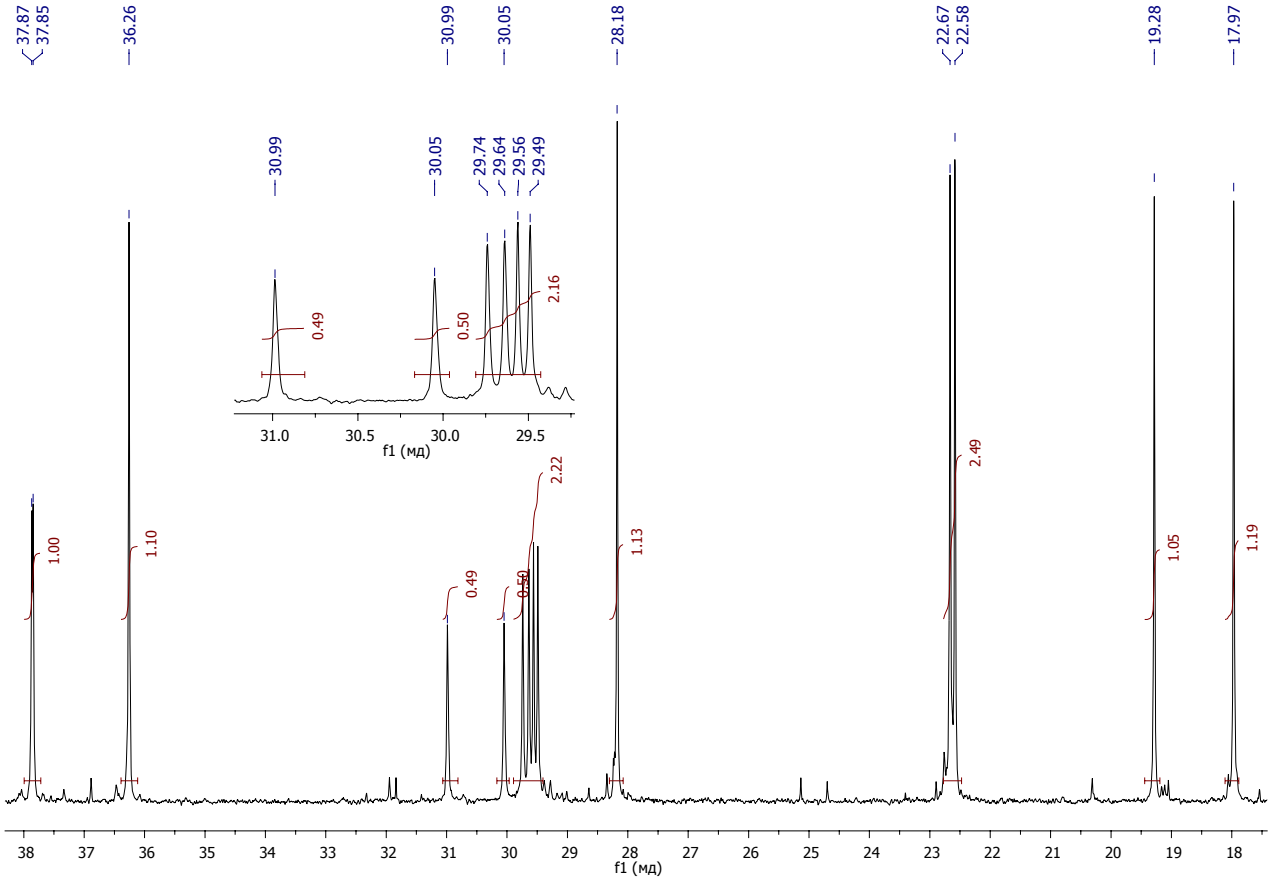


Fig. S21. ^{13}C NMR spectra of 2-isopropyl-5-methylhexylphosphinic acid **11**.

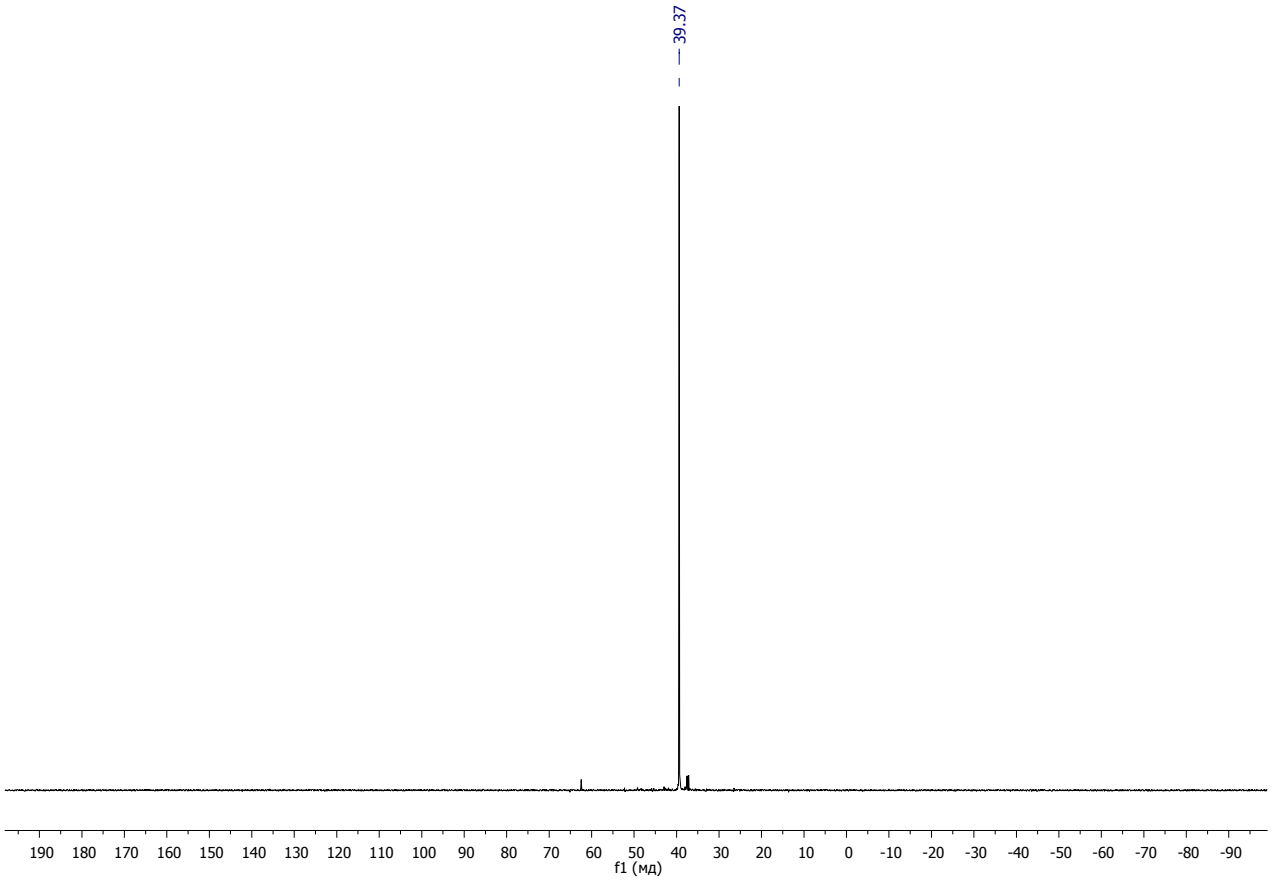


Fig. S22. ^{31}P NMR spectra of 2-isopropyl-5-methylhexylphosphinic acid **11**.

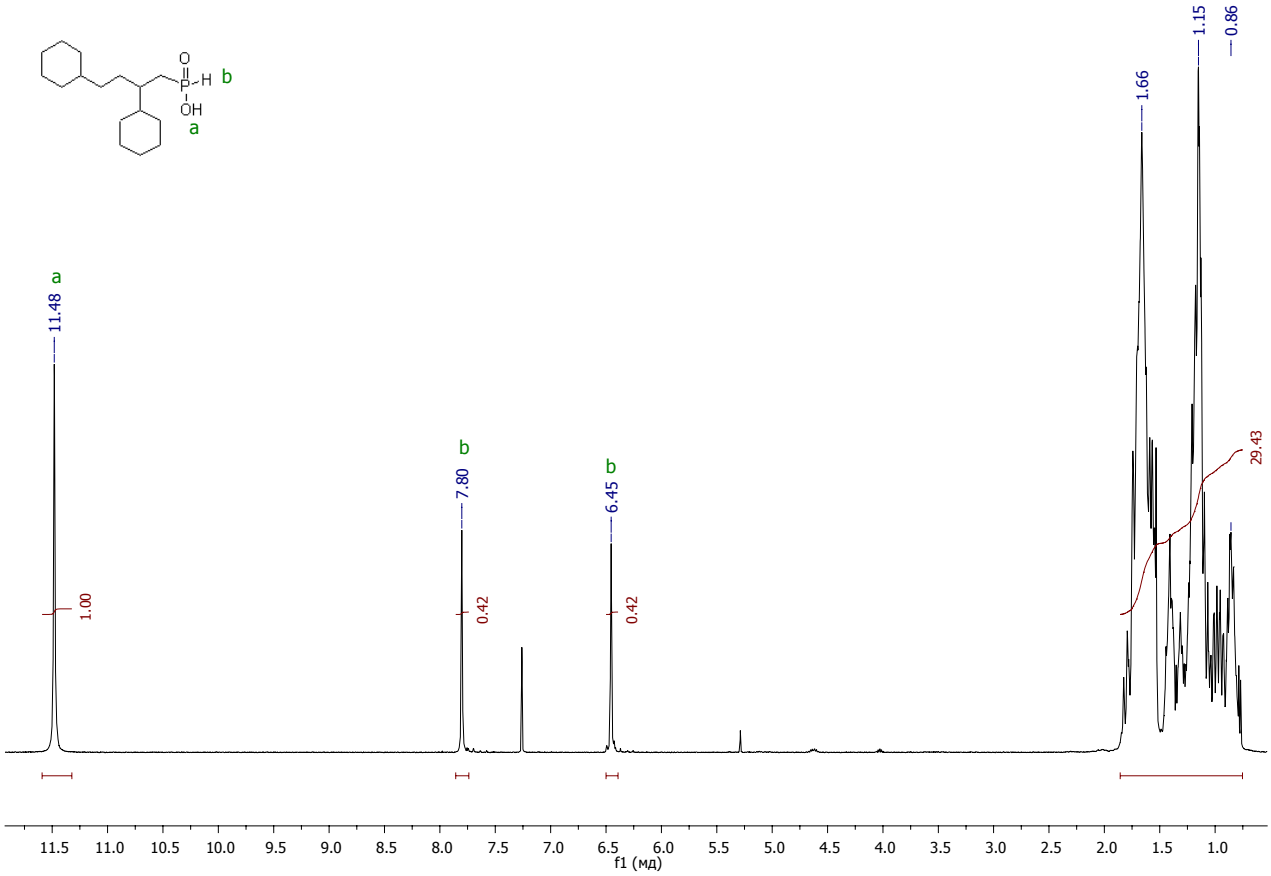


Fig. S23. [1]H NMR spectra of 2,4-dicyclohexylbutylphosphinic acid **12**.

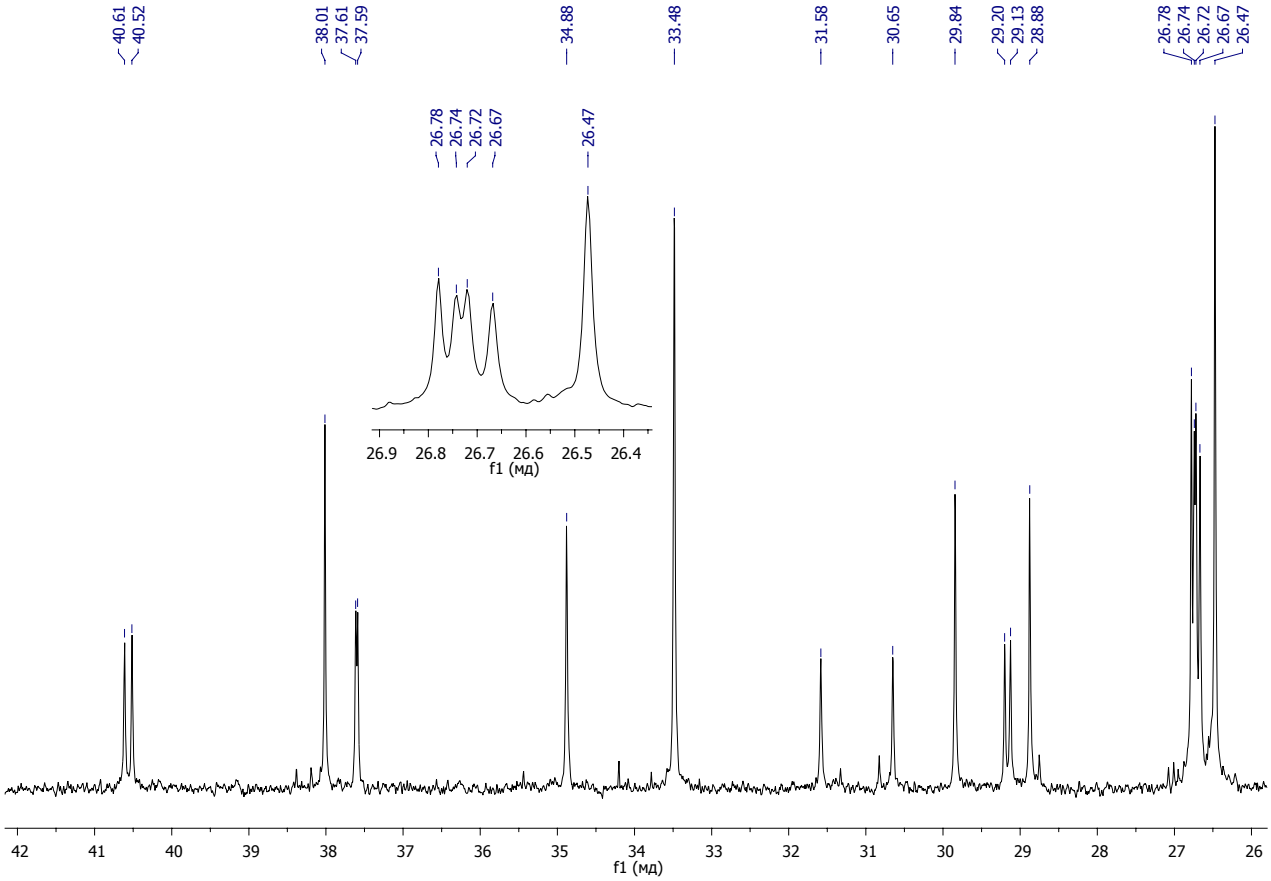


Fig. S24. [13]C NMR spectra of 2,4-dicyclohexylbutylphosphinic acid **12**.

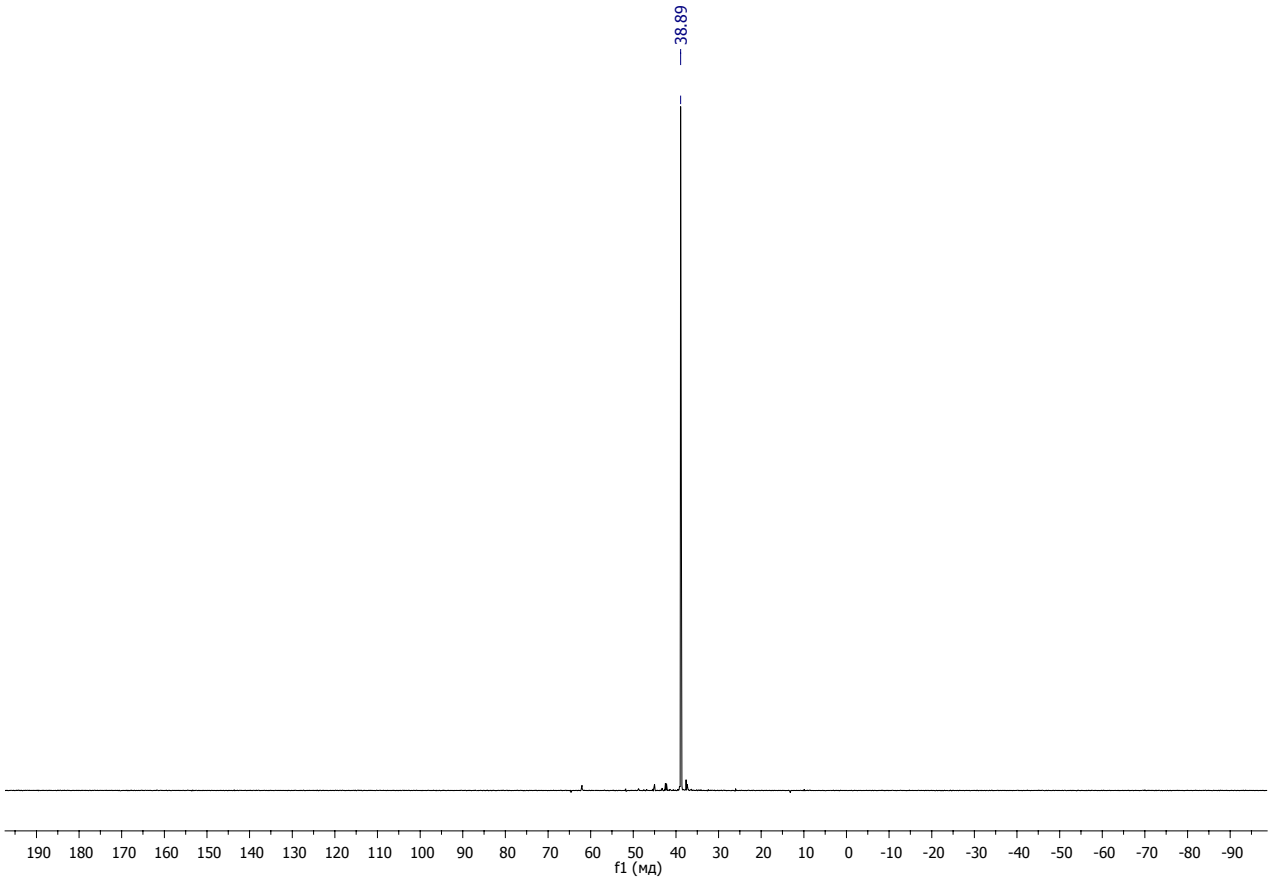


Fig. S25. ^{31}P NMR spectra of 2,4-dicyclohexylbutylphosphinic acid **12**.

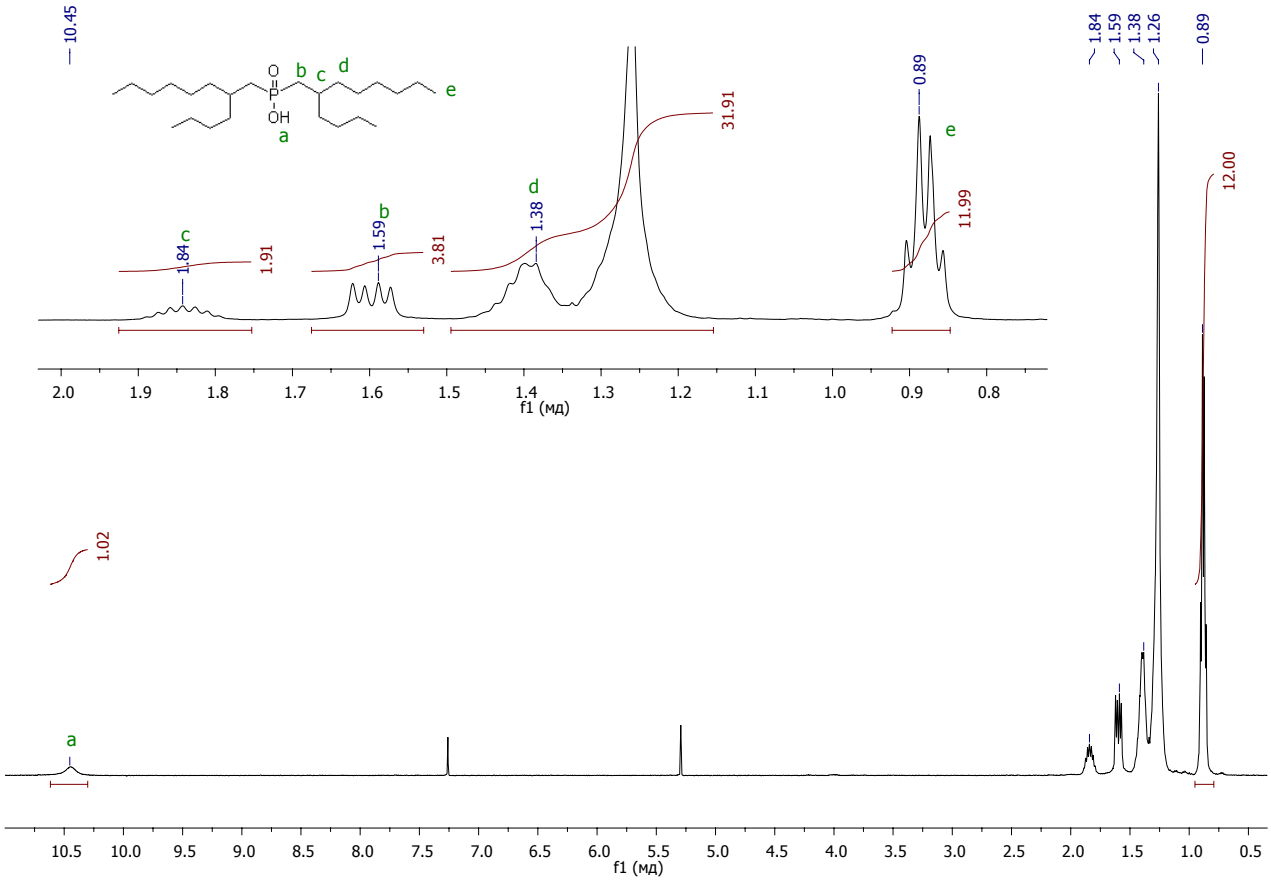


Fig. S26. ^{1}H NMR spectra of bis(2-butyloctyl)phosphinic acid **13**.

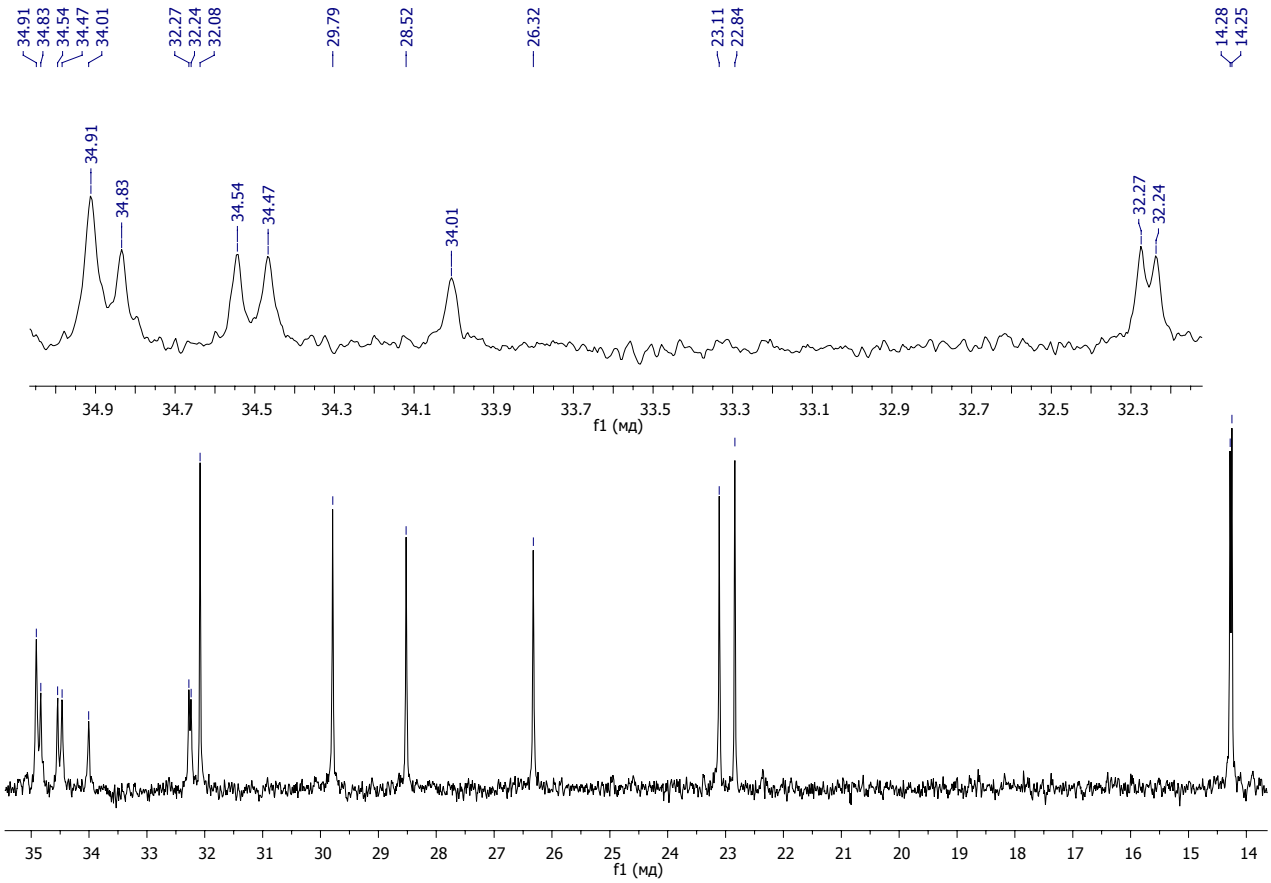


Fig. S27. ^{13}C NMR spectra of bis(2-butyloctyl)phosphinic acid **13**.

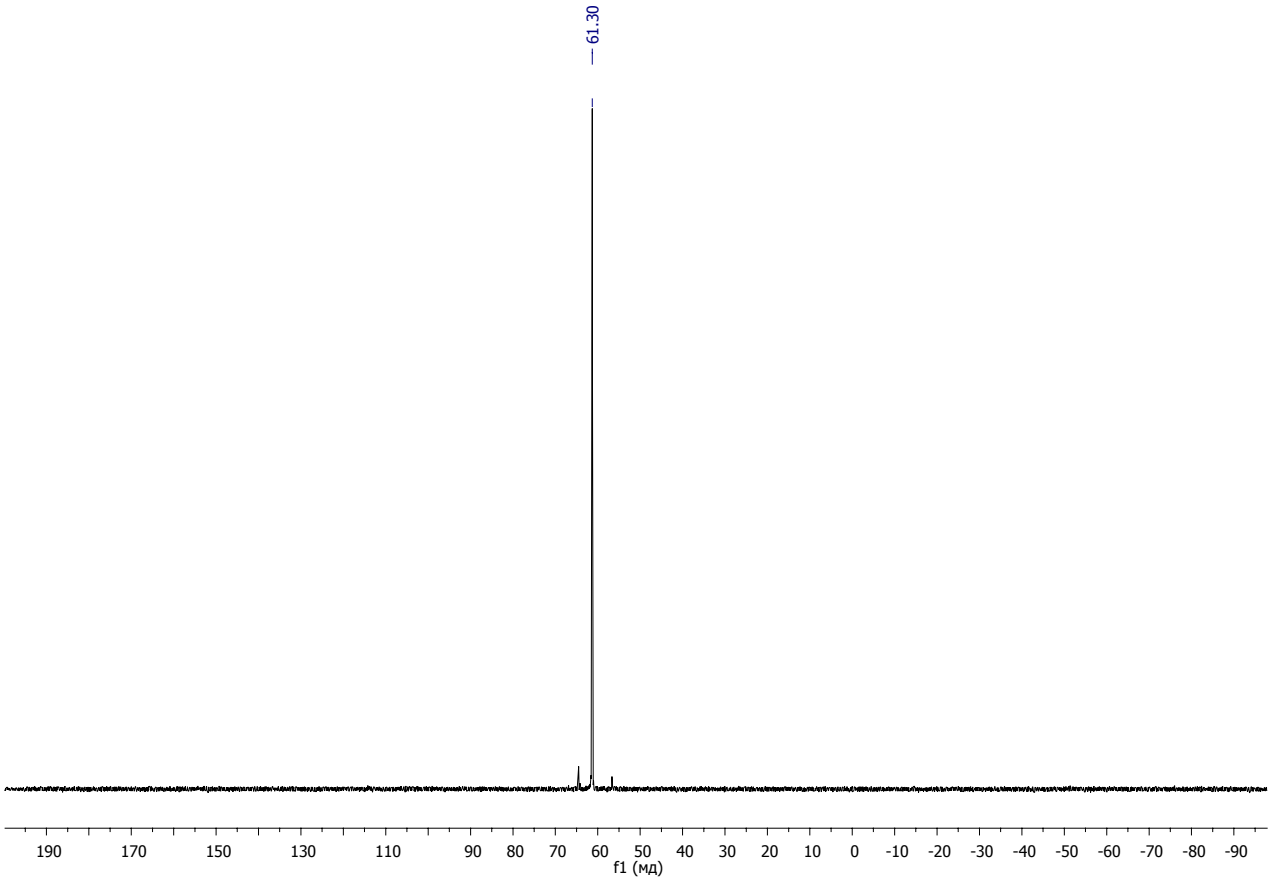


Fig. S28. ^{31}P NMR spectra of bis(2-butyloctyl)phosphinic acid **13**.

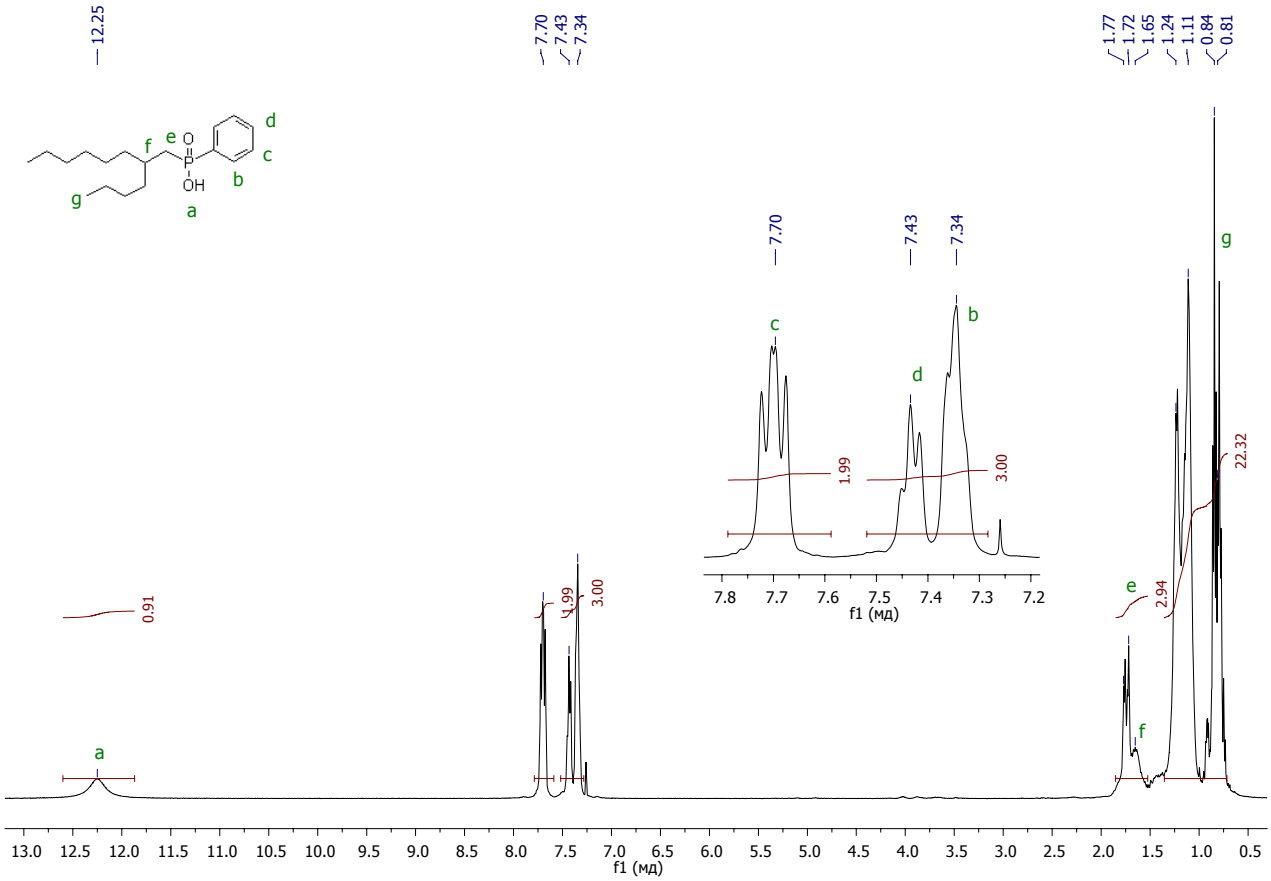


Fig. S29. [1]H NMR spectra of 2-butyloctyl(phenyl)phosphinic acid **14**.

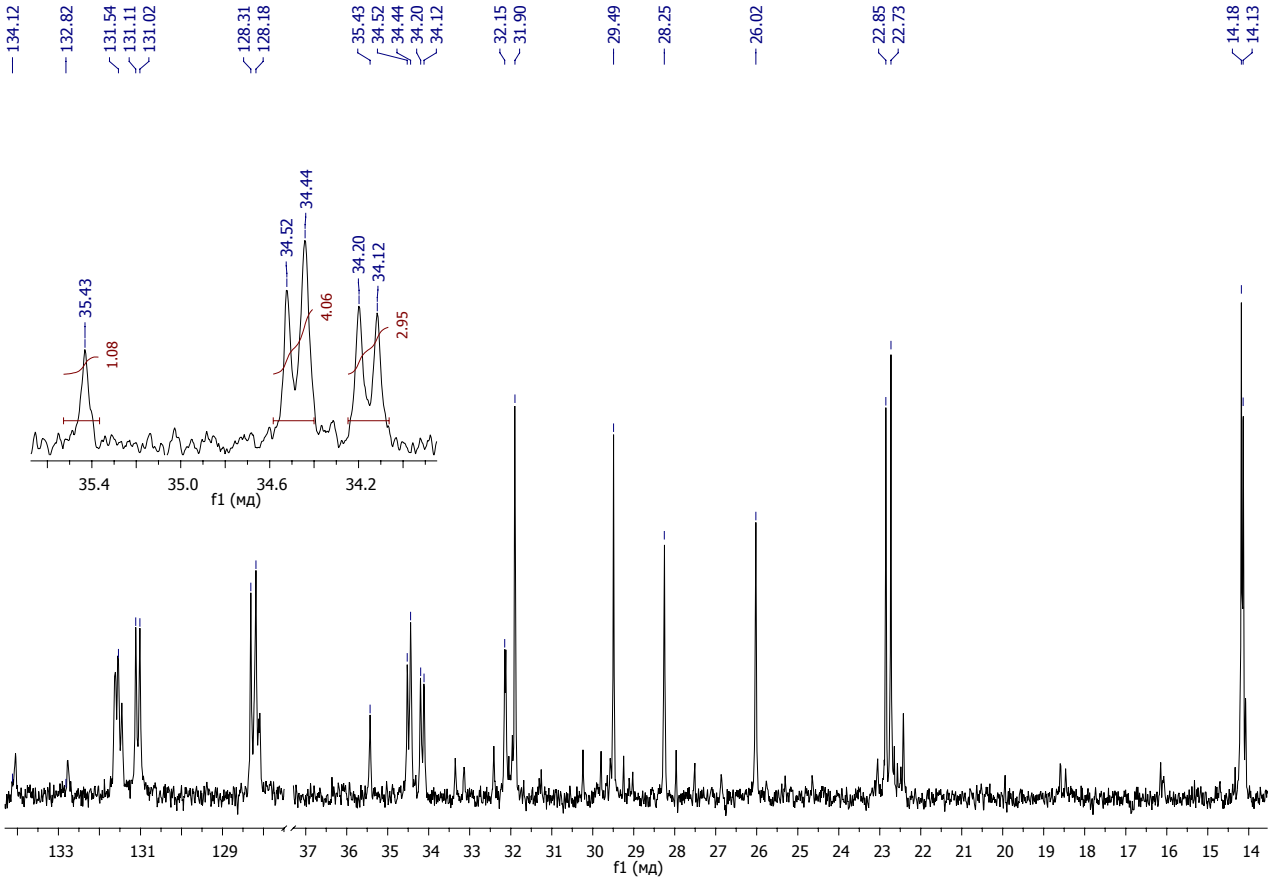


Fig. S30. [13]C NMR spectra of 2-butyloctyl(phenyl)phosphinic acid **14**.

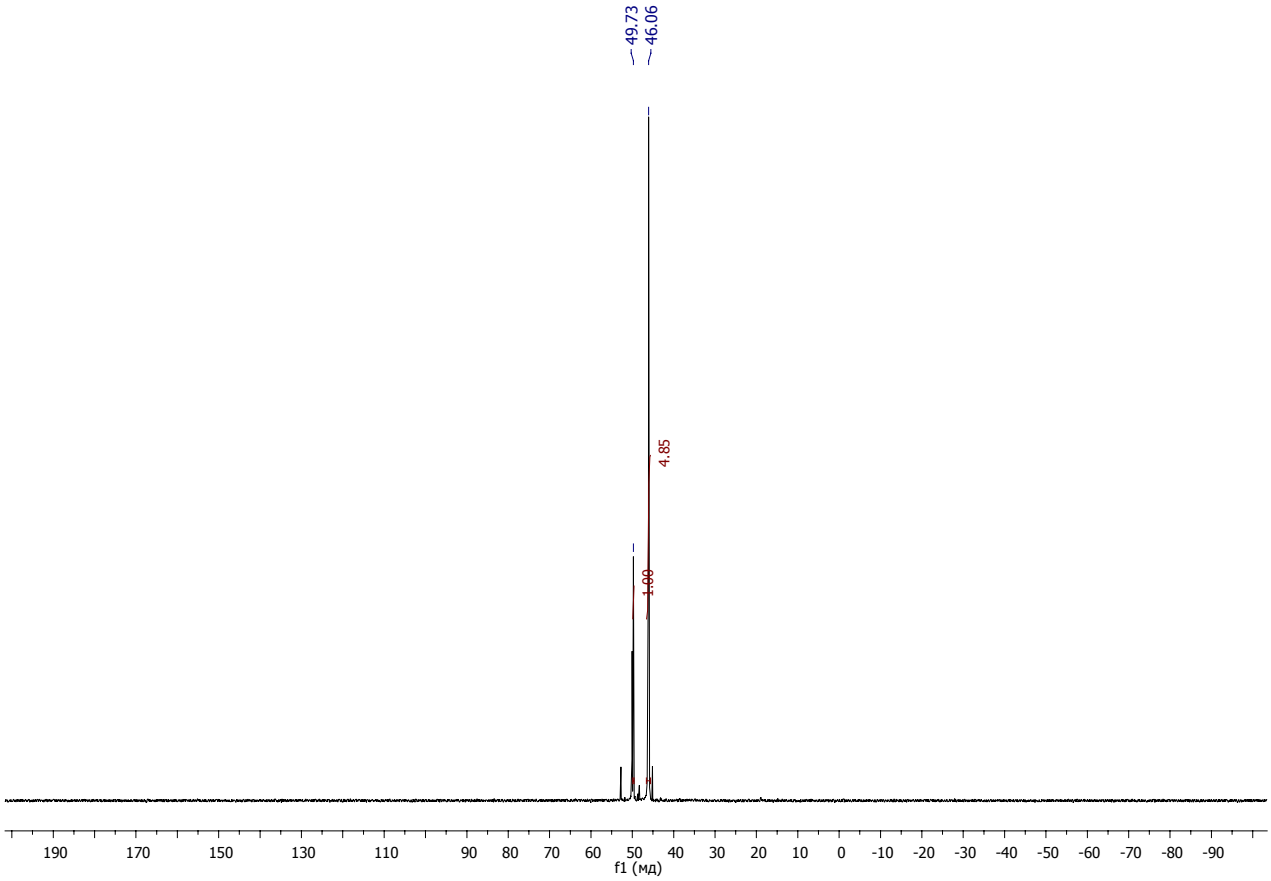


Fig. S31. ^{31}P NMR spectra of 2-butyloctyl(phenyl)phosphinic acid **14**.

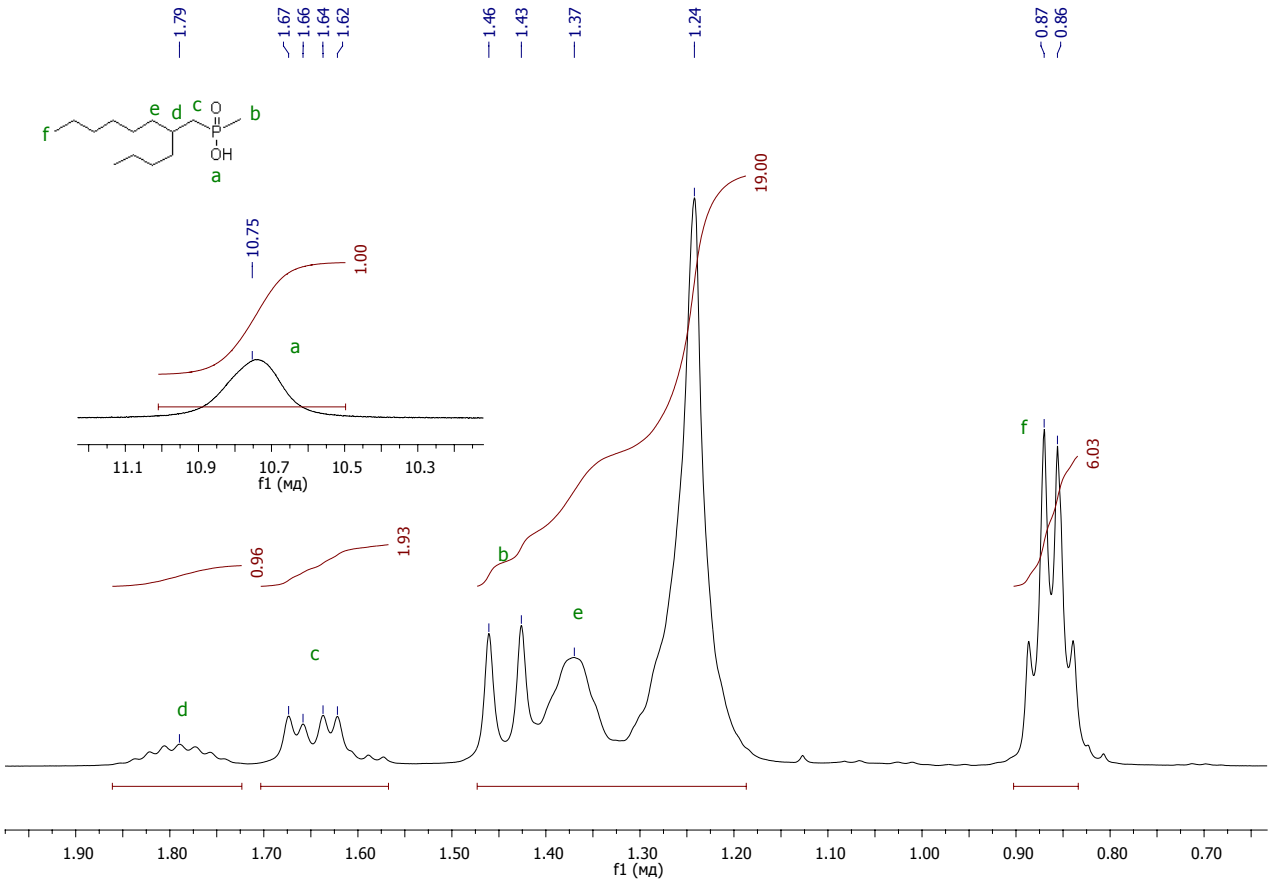


Fig. S32. ^{1}H NMR spectra of 2-butyloctyl(methyl)phosphinic acid **15**.

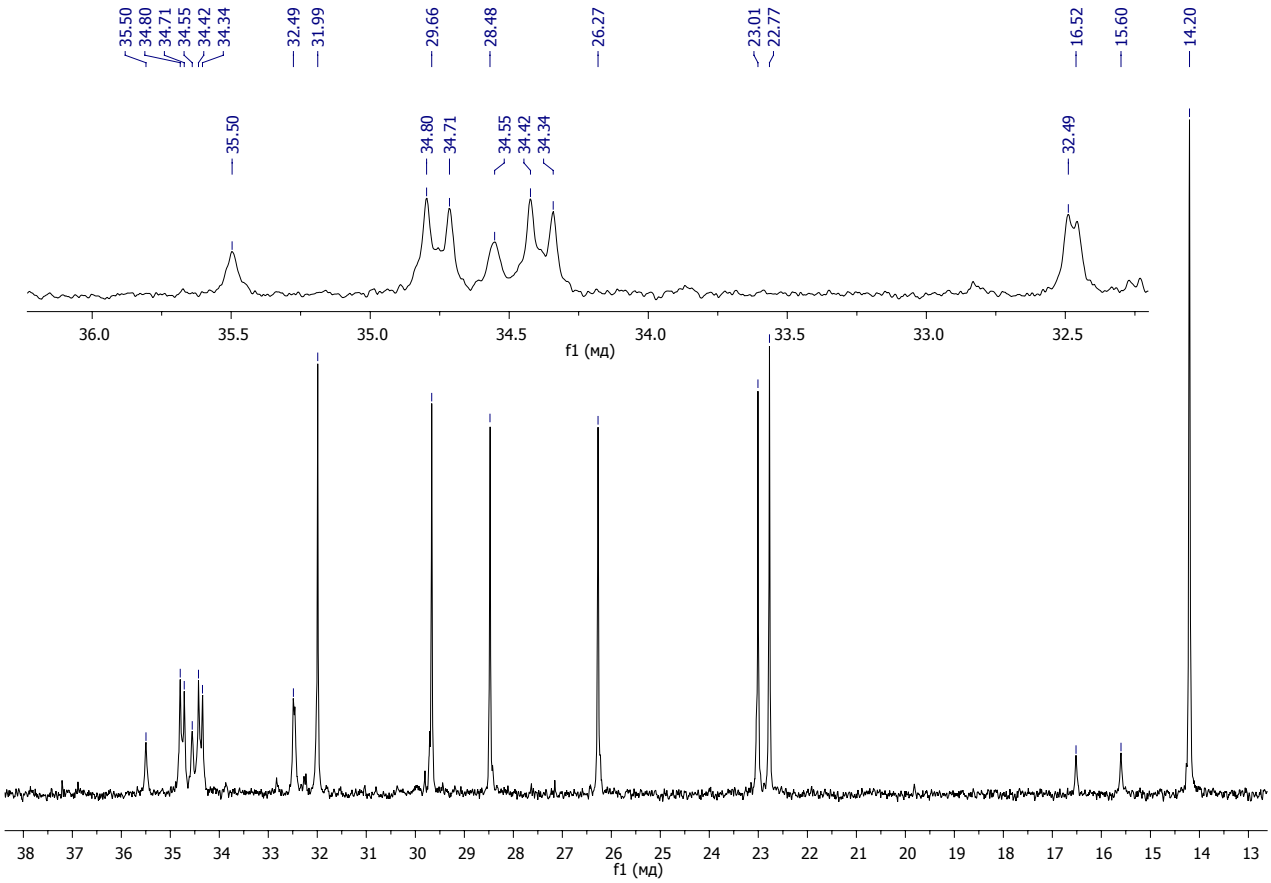


Fig. S33. ^{13}C NMR spectra of 2-butyloctyl(methyl)phosphinic acid **15**.

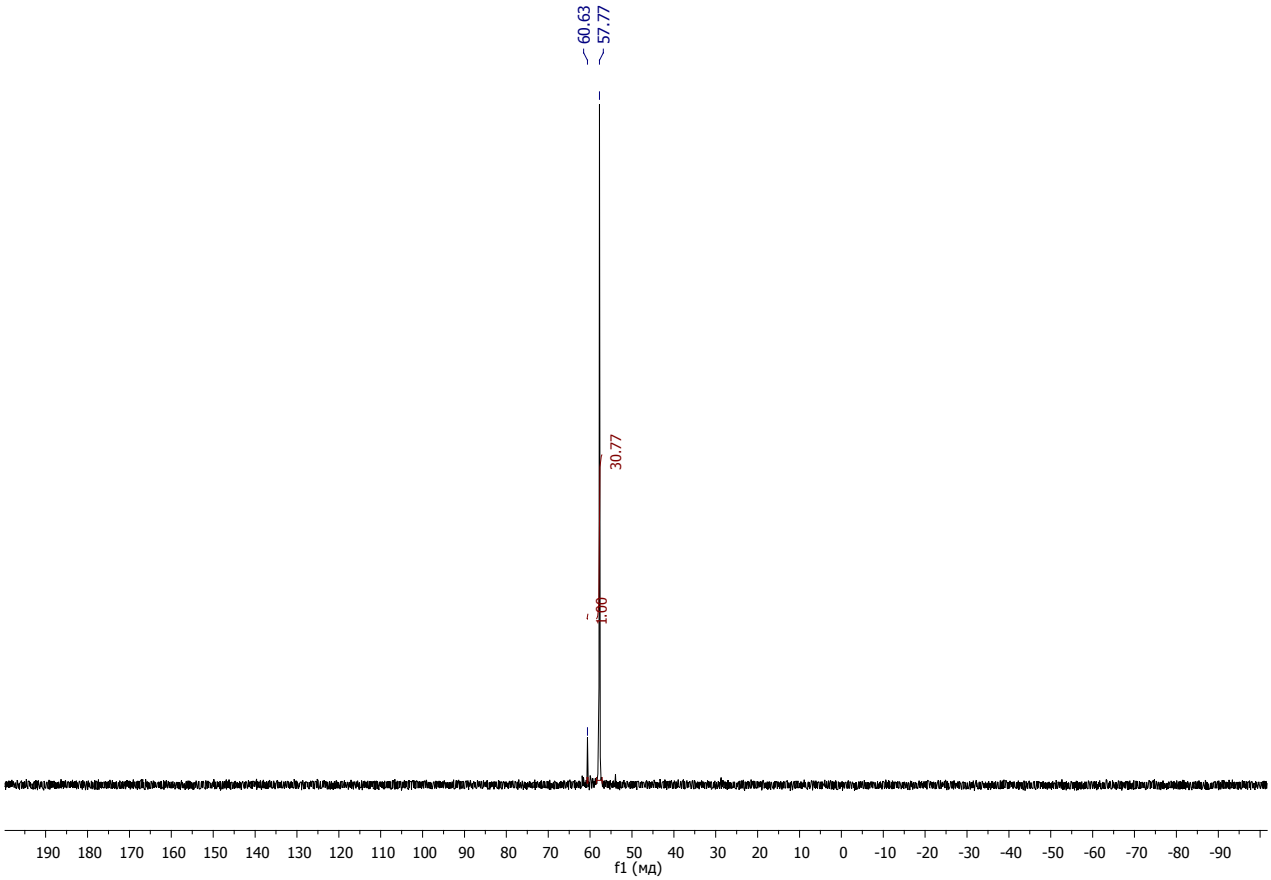


Fig. S34. ^{31}P NMR spectra of 2-butyloctyl(methyl)phosphinic acid **15**.

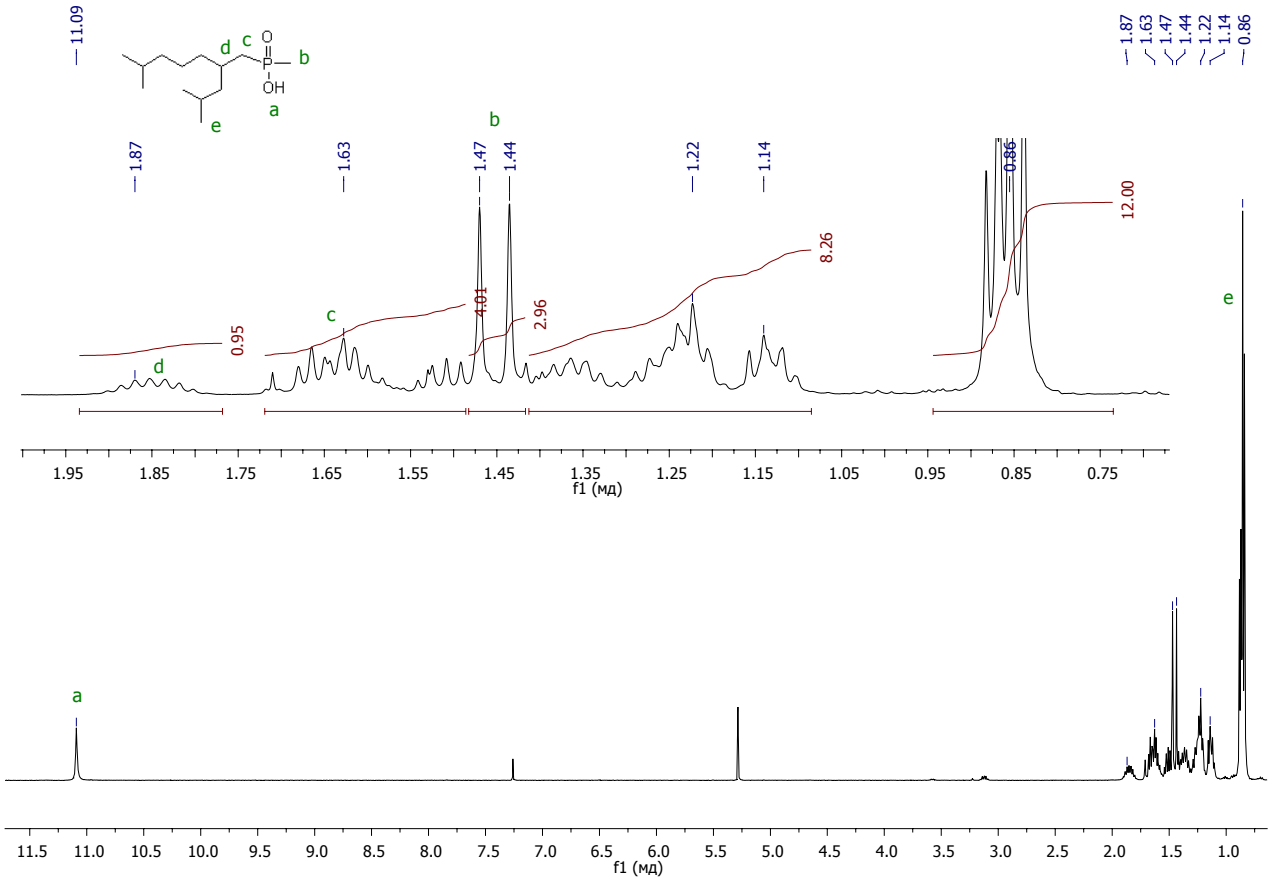


Fig. S35. [1]H NMR spectra of 2-isobutyl-6-methylheptyl(methyl)phosphinic acid **16**.

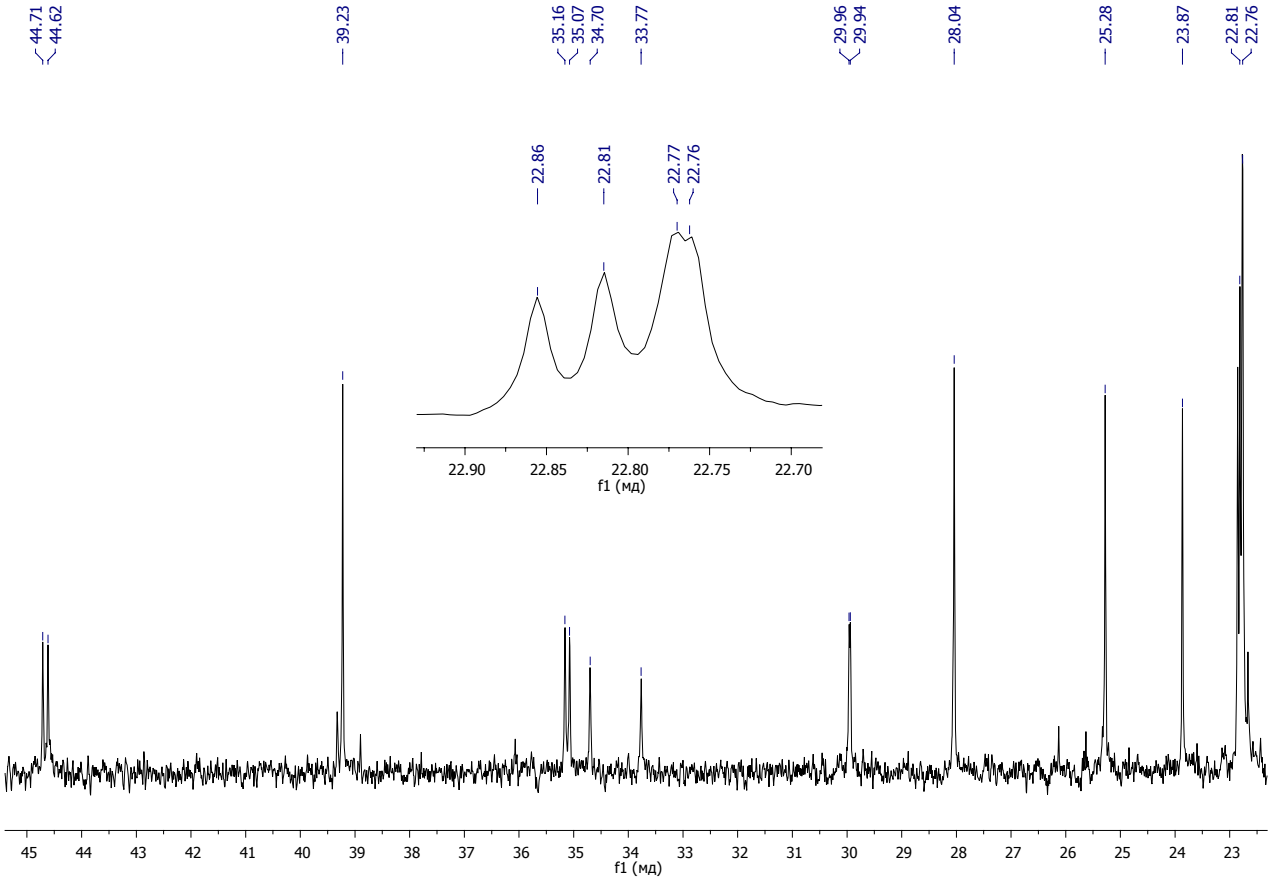


Fig. S36. [13]C NMR spectra of 2-isobutyl-6-methylheptyl(methyl)phosphinic acid **16**.

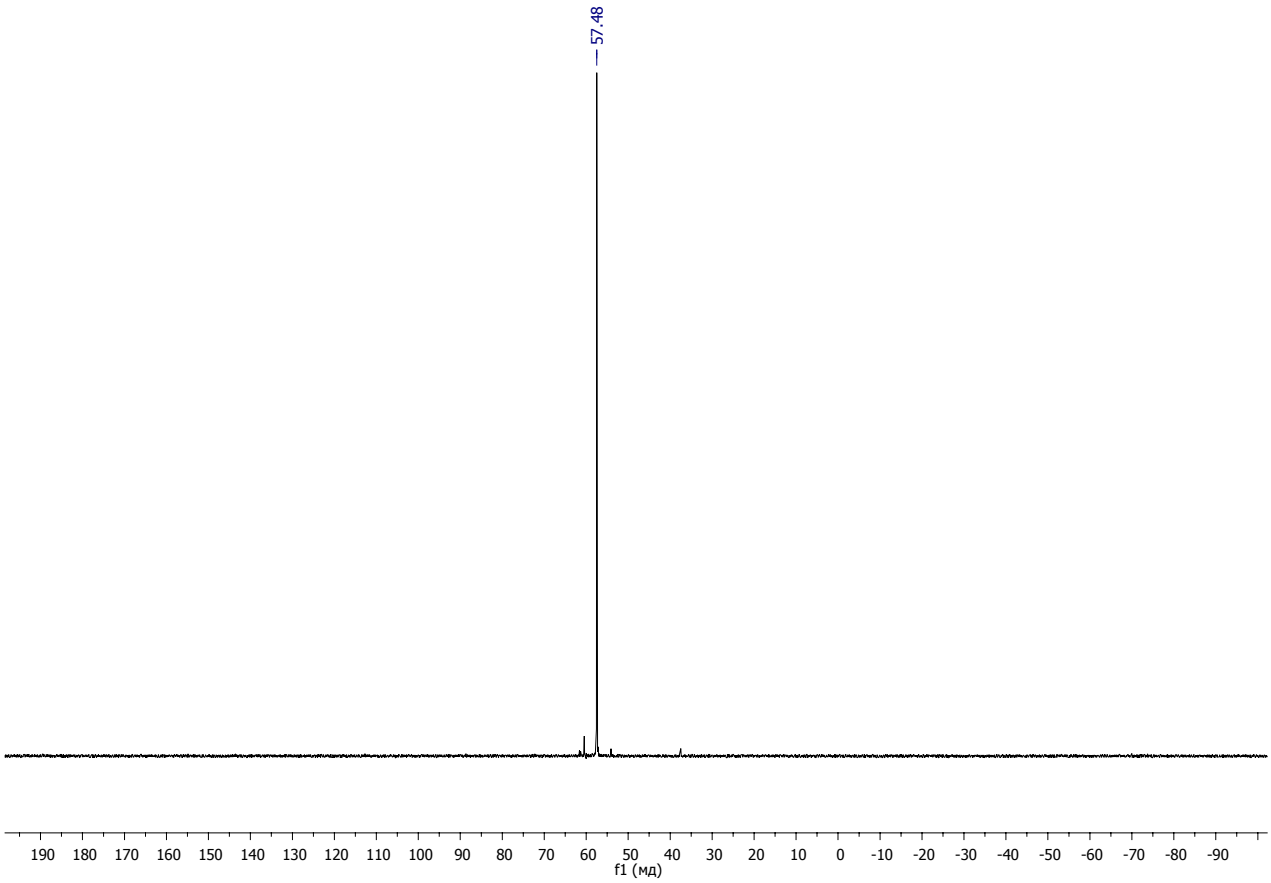


Fig. S37. ^{31}P NMR spectra of 2-isobutyl-6-methylheptyl(methyl)phosphinic acid **16**.

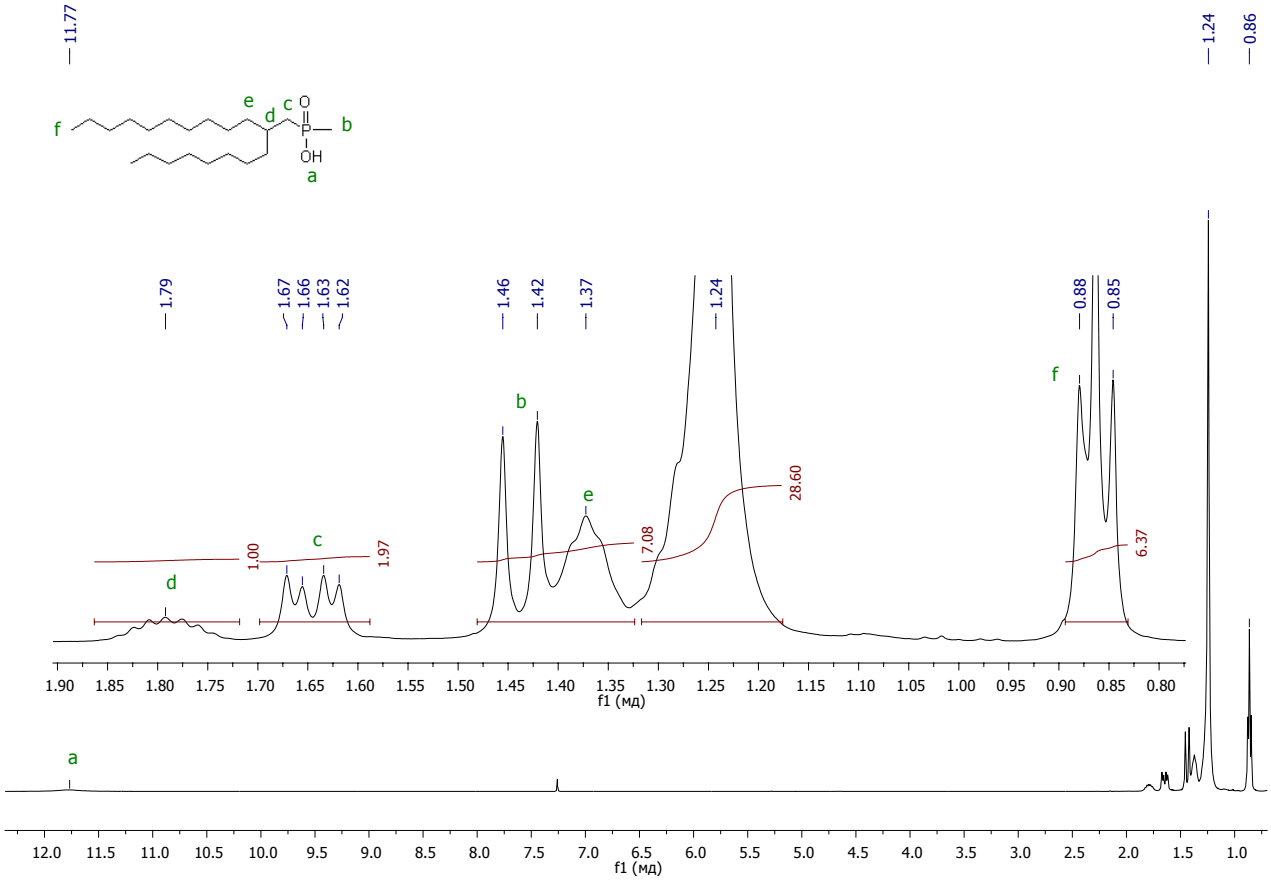


Fig. S38. ^{1}H NMR spectra of methyl(2-octyldodecyl)phosphinic acid **17**.

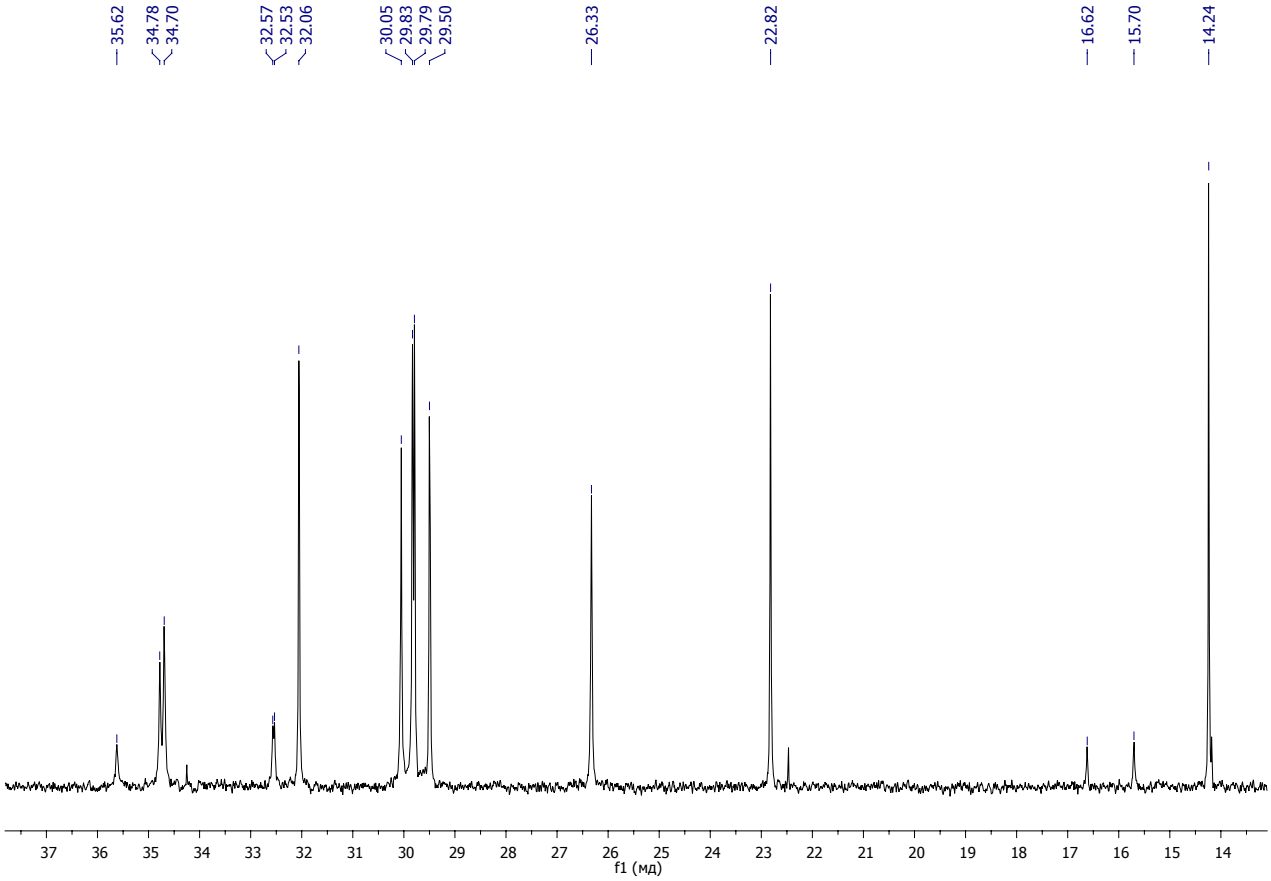


Fig. S39. ^{13}C NMR spectra of methyl(2-octyldodecyl)phosphinic acid **17**.

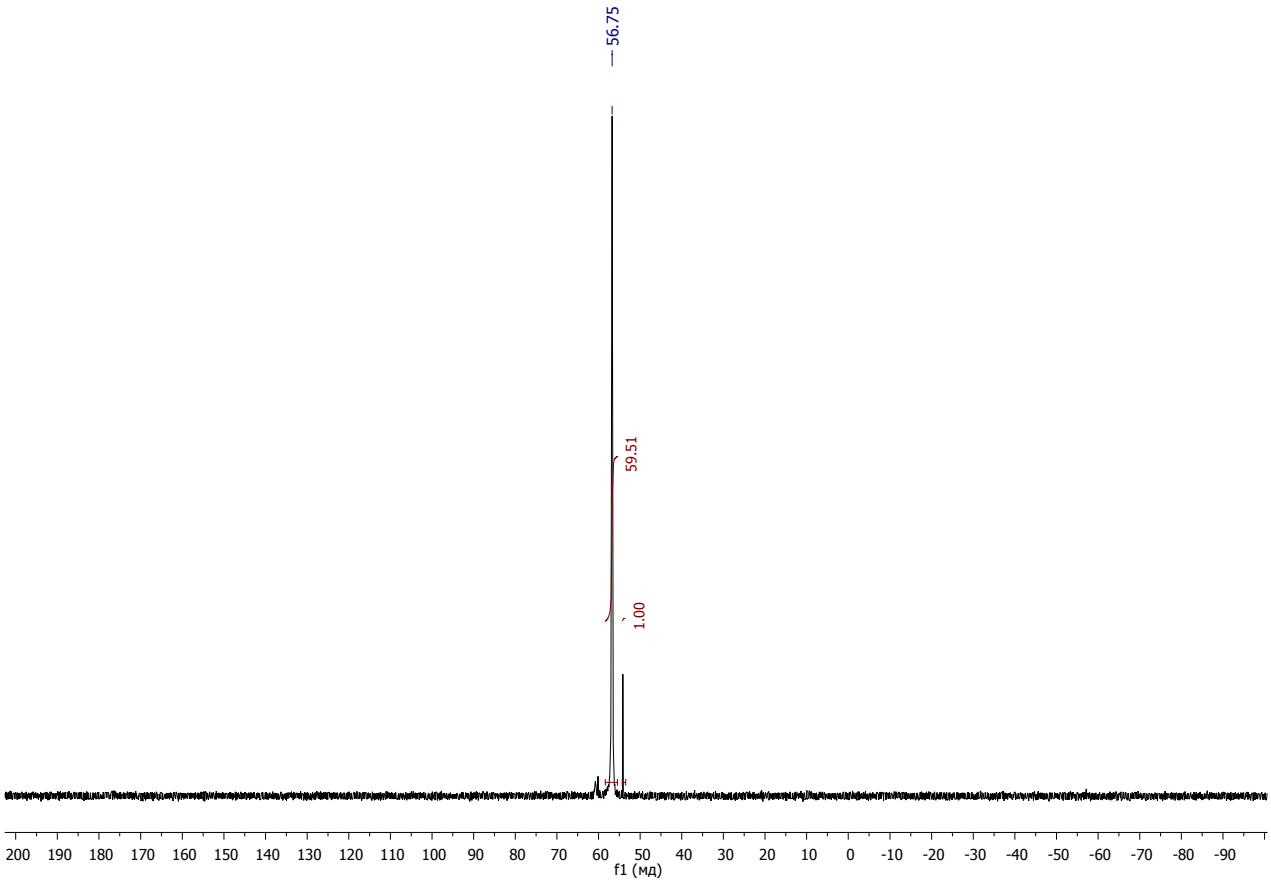


Fig. S40. ^{31}P NMR spectra of methyl(2-octyldodecyl)phosphinic acid **17**.

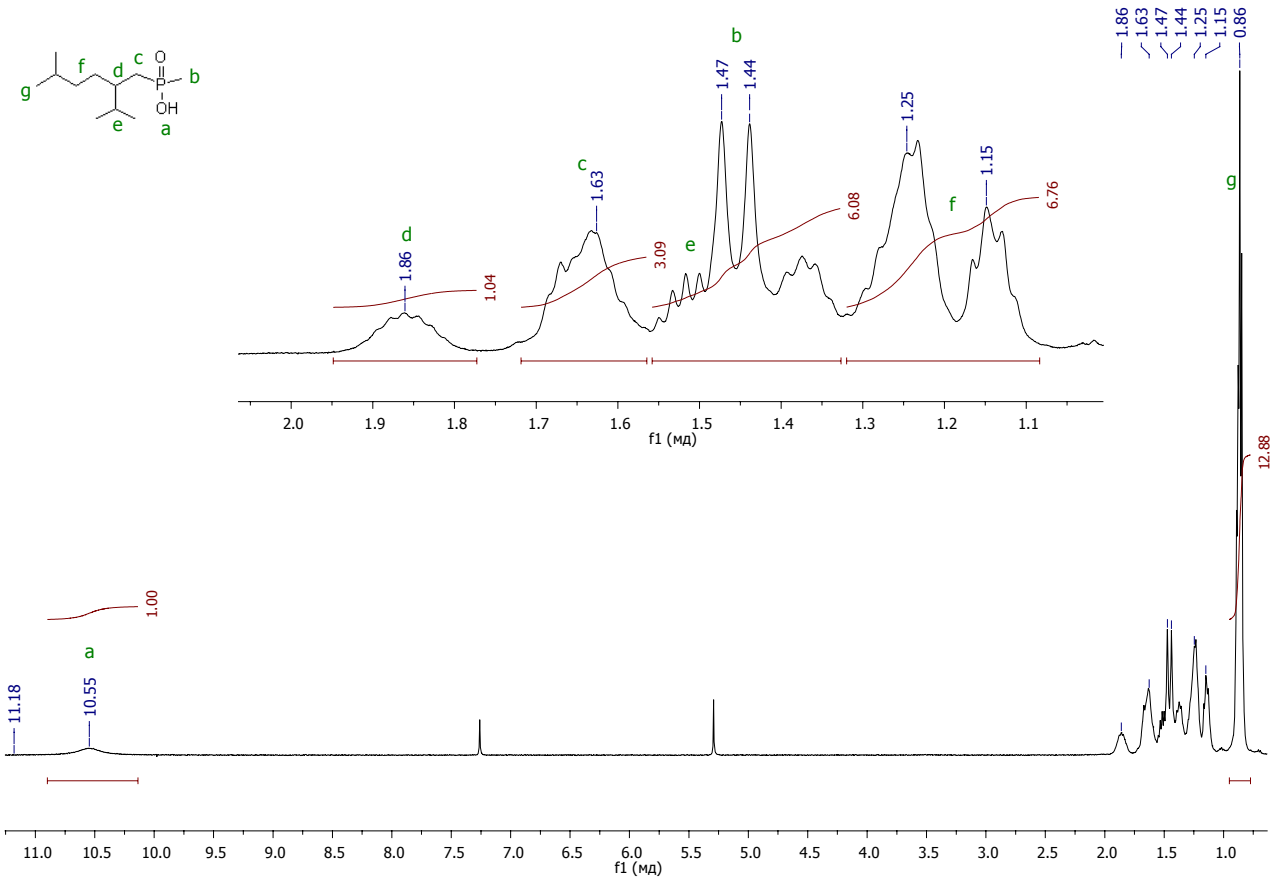


Fig. S41. ^{1}H NMR spectra of 2-isopropyl-5-methylhexyl(methyl)phosphinic acid **18**.

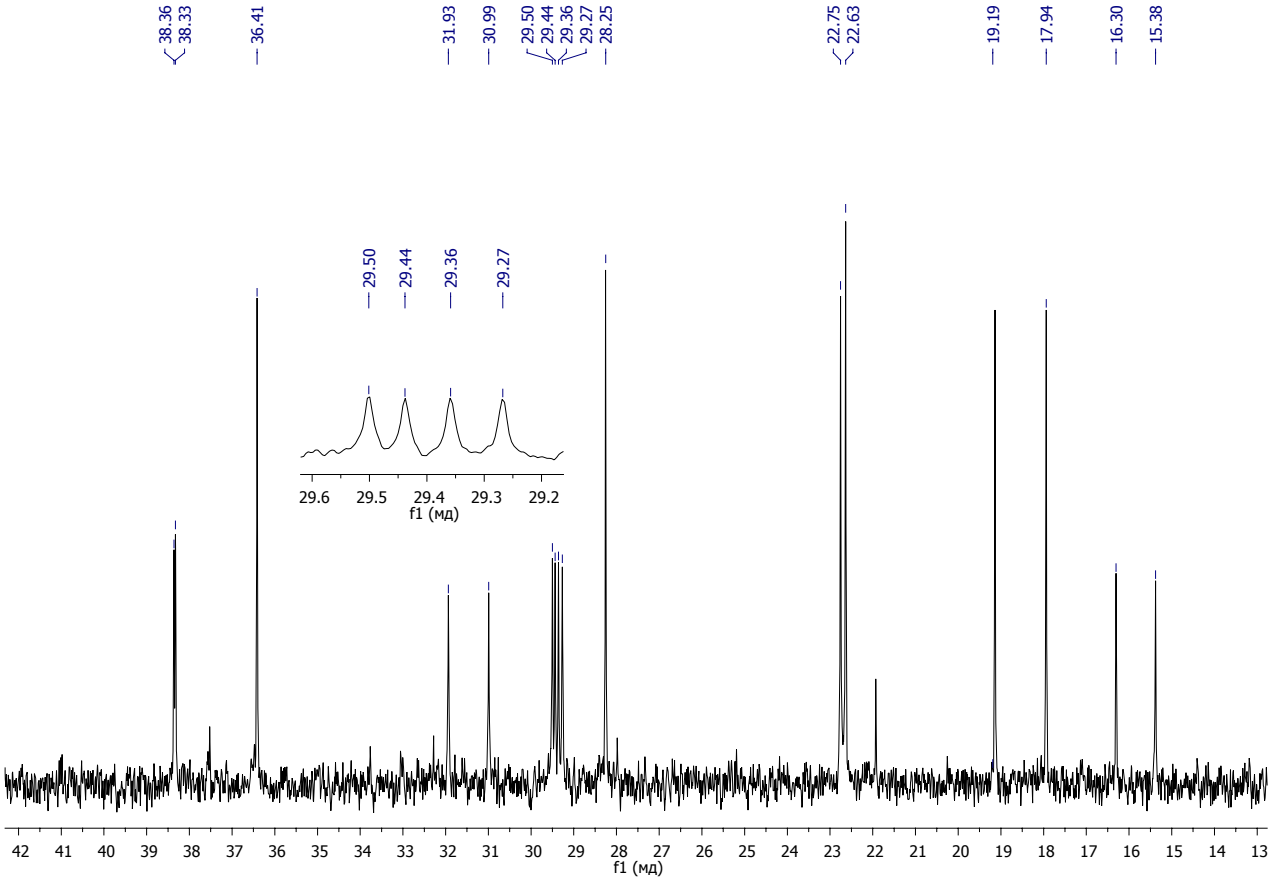


Fig. S42. ^{13}C NMR spectra of 2-isopropyl-5-methylhexyl(methyl)phosphinic acid **18**.

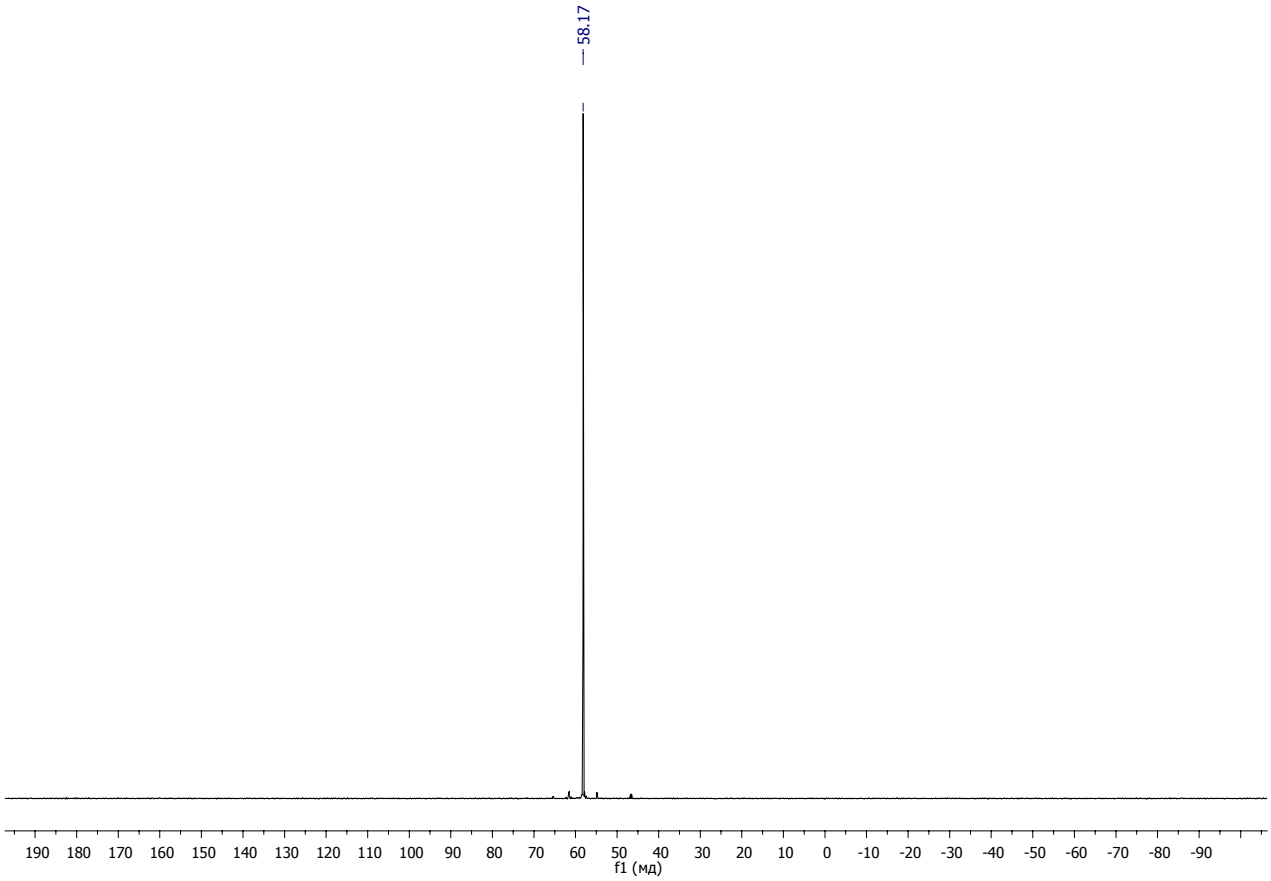


Fig. S43. ^{31}P NMR spectra of 2-isopropyl-5-methylhexyl(methyl)phosphinic acid **18**.

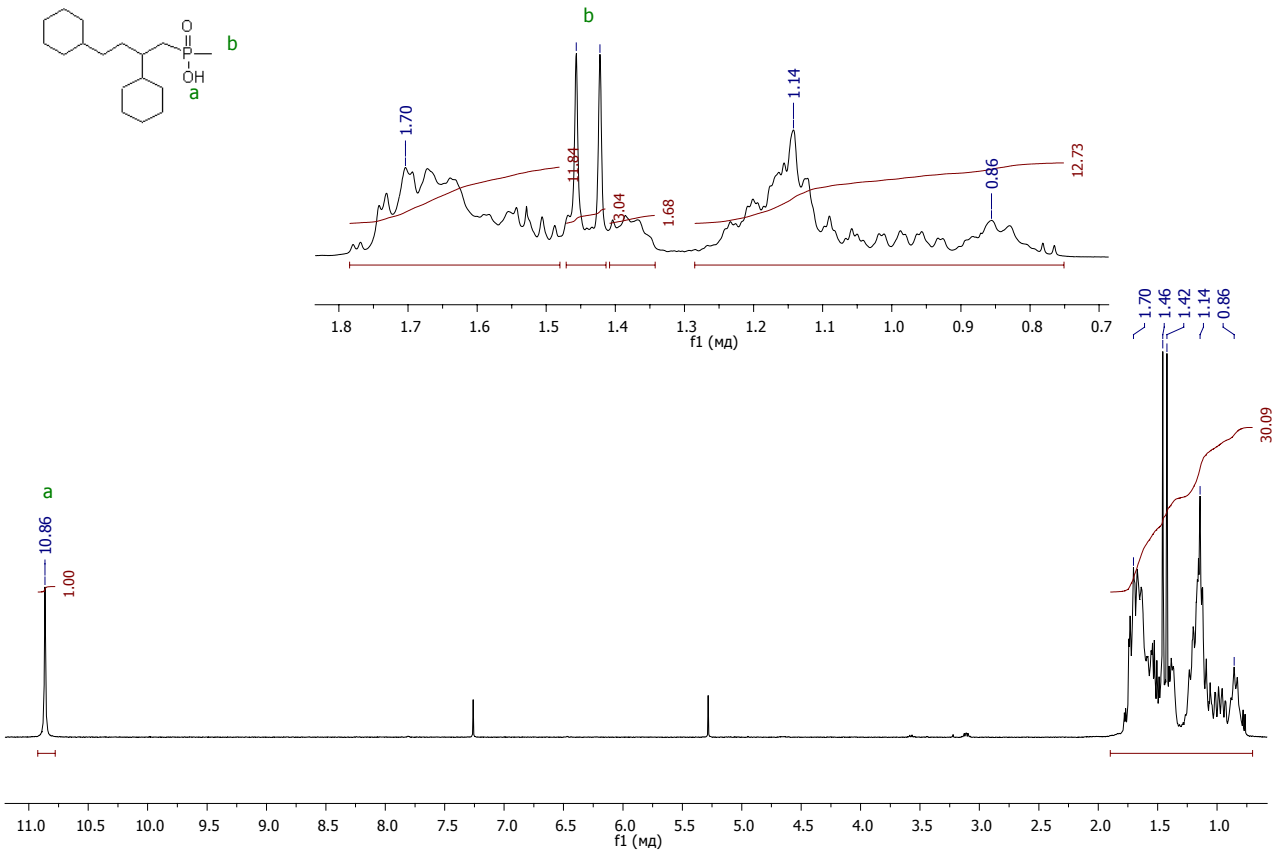


Fig. S44. ^{1}H NMR spectra of 2,4-dicyclohexylbutyl(methyl)phosphinic acid **19**.

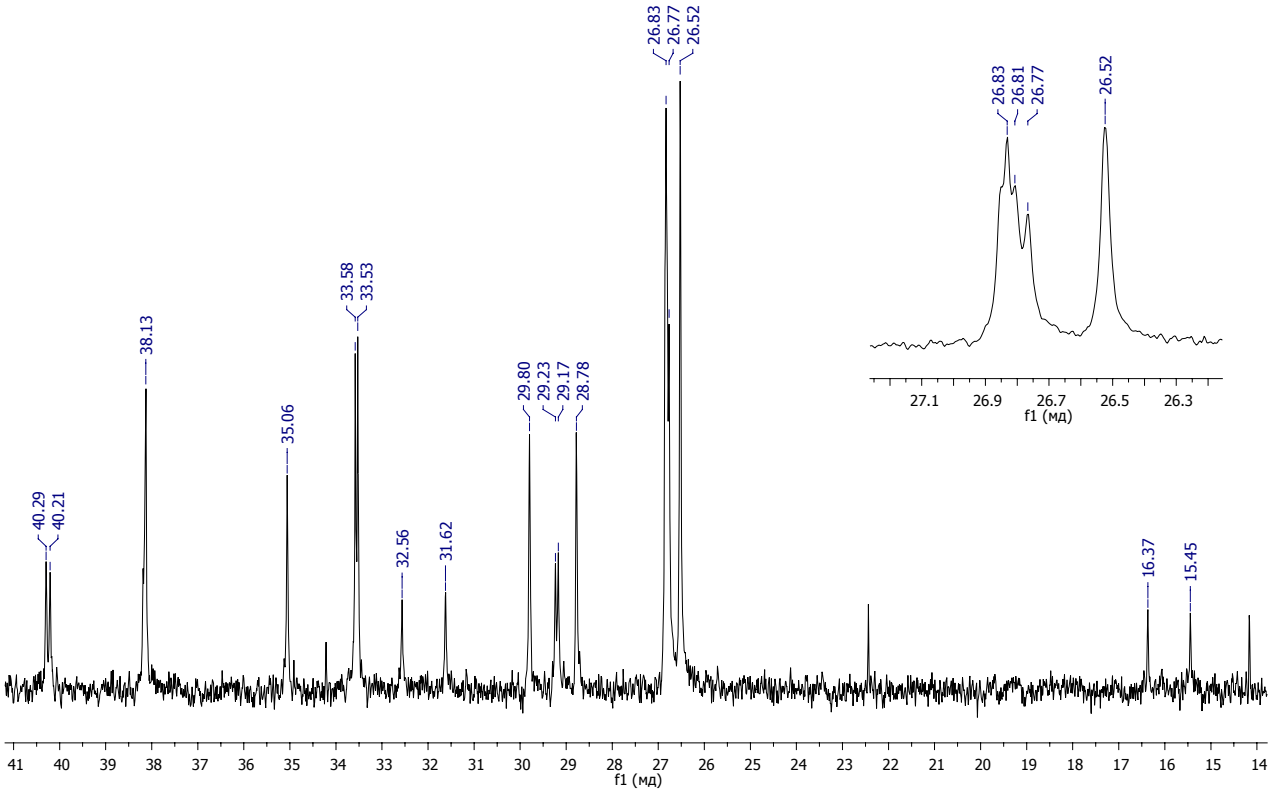


Fig. S45. ^{13}C NMR spectra of 2,4-dicyclohexylbutyl(methyl)phosphinic acid **19**.

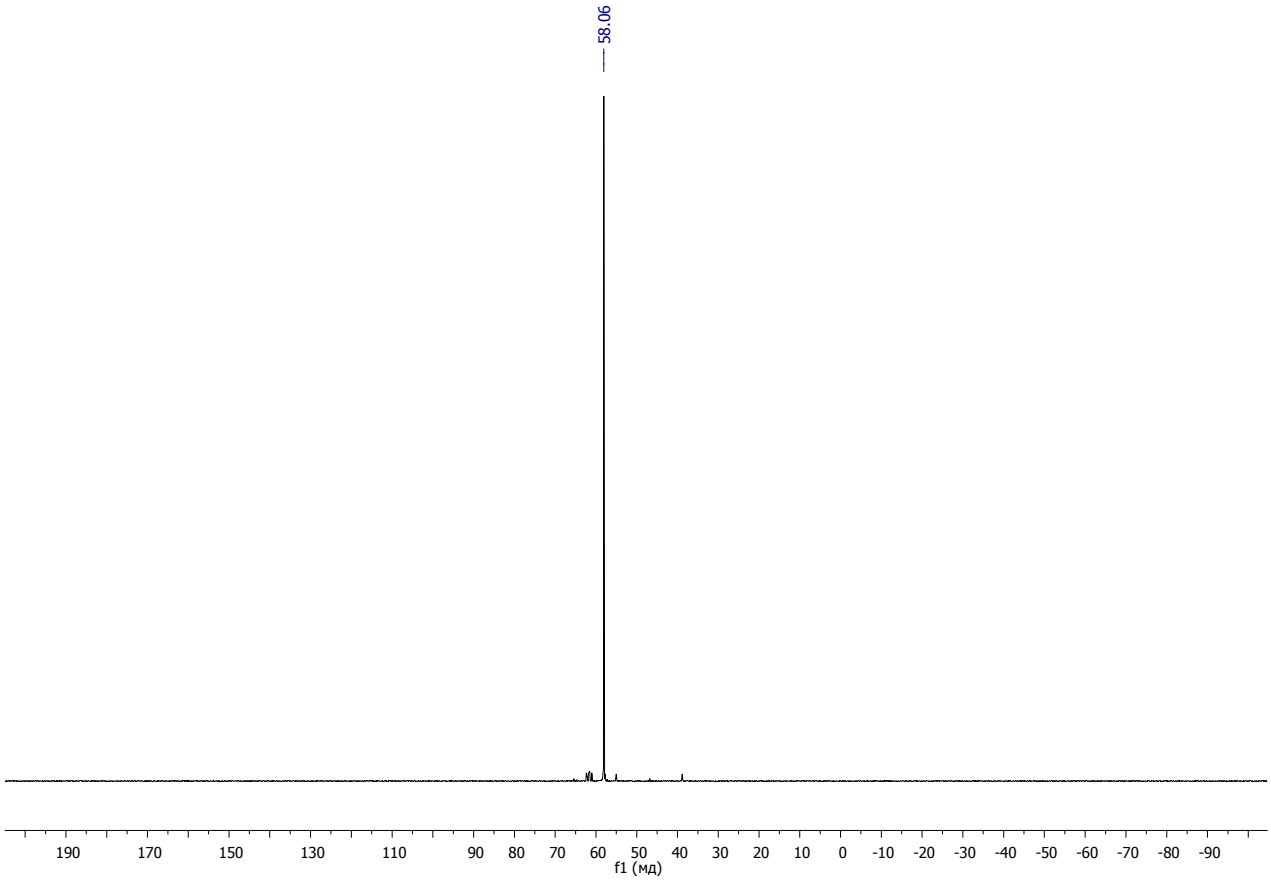


Fig. S46. ^{31}P NMR spectra of 2,4-dicyclohexylbutyl(methyl)phosphinic acid **19**.

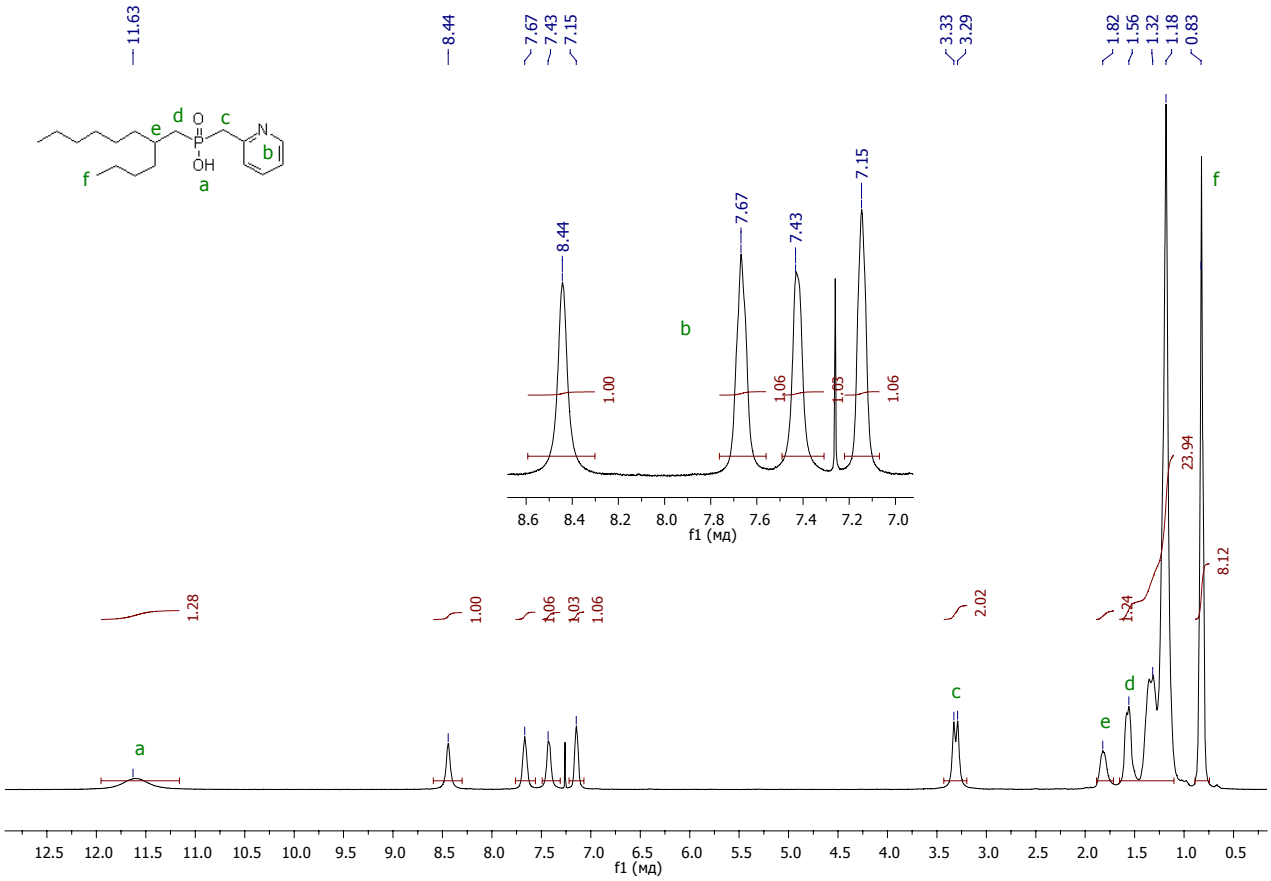


Fig. S47. ^{1}H NMR spectra of 2-butyloctyl(2-pyridinylmethyl)phosphinic acid **20**.

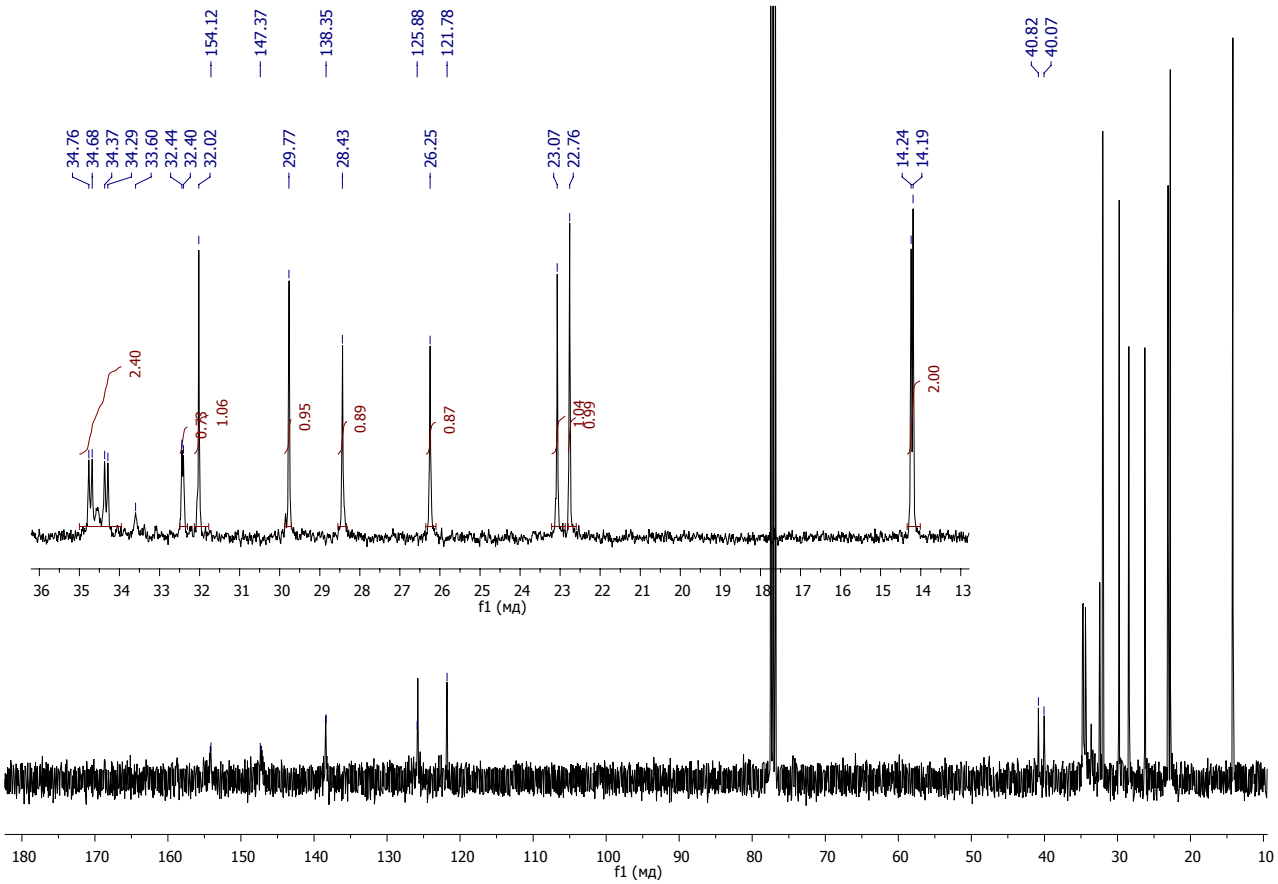


Fig. S48. ^{13}C NMR spectra of 2-butyloctyl(2-pyridinylmethyl)phosphinic acid **20**.

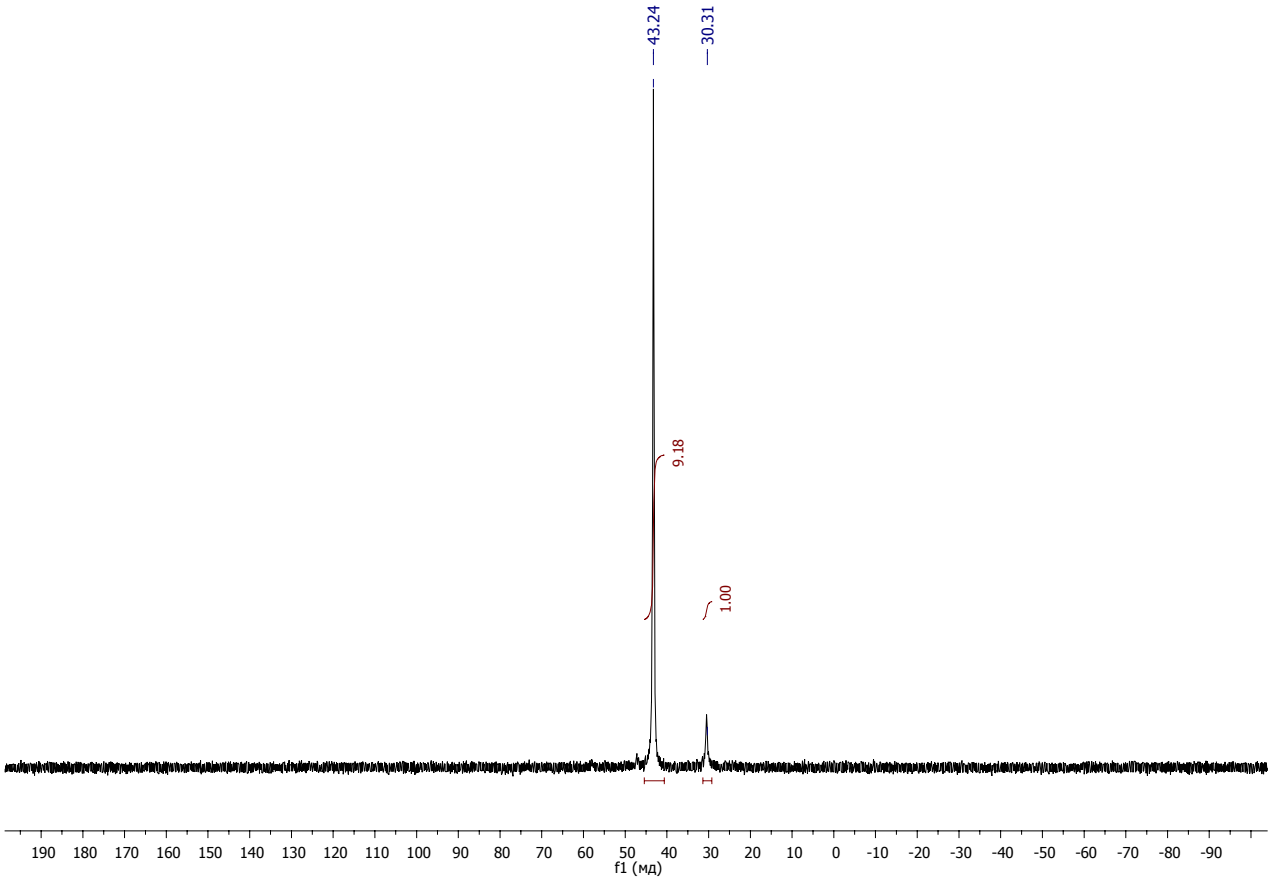


Fig. S49. ^{31}P NMR spectra of 2-butyloctyl(2-pyridinylmethyl)phosphinic acid **20**.

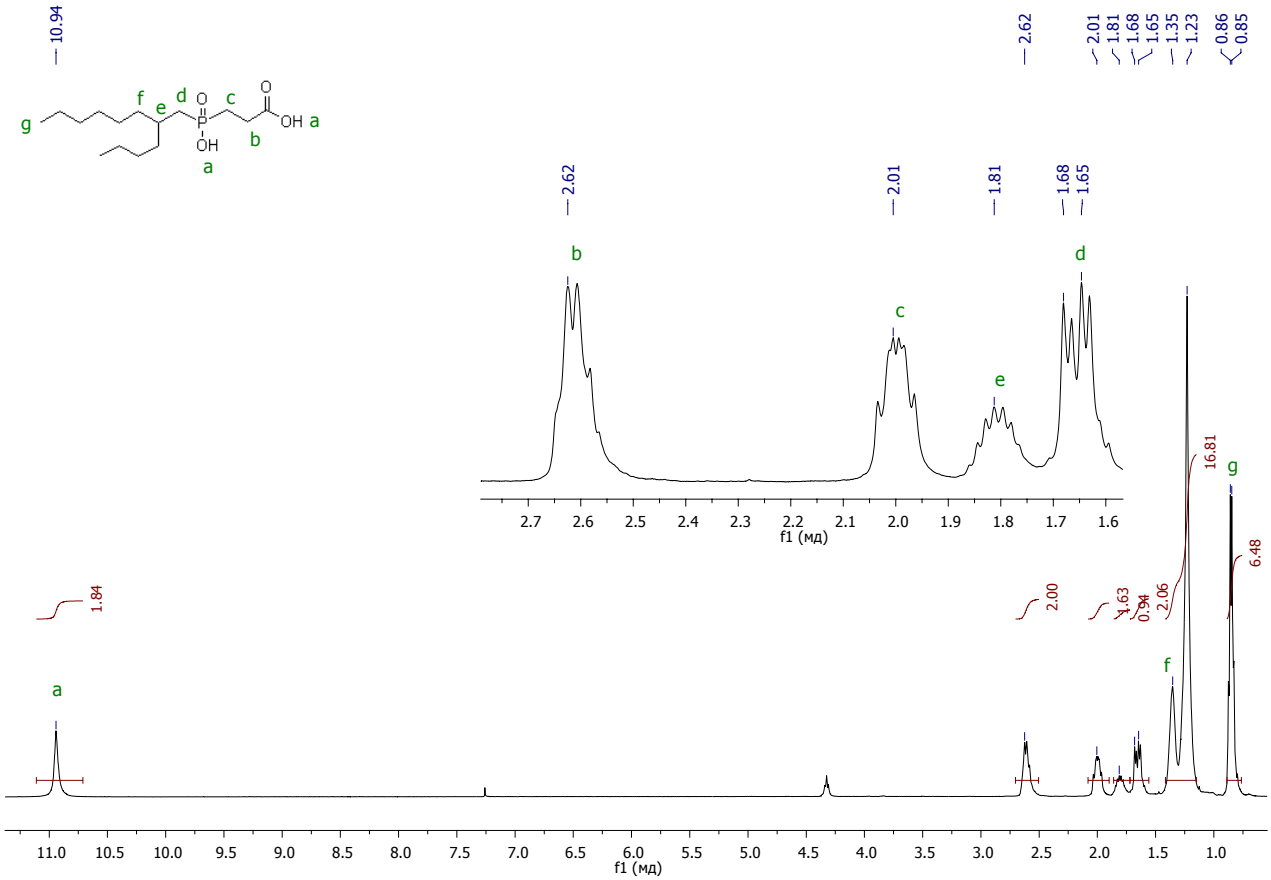


Fig. S50. ^{1}H NMR spectra of 3-[(2-butyloctyl)(hydroxy)phosphoryl]propanoic acid **21**.

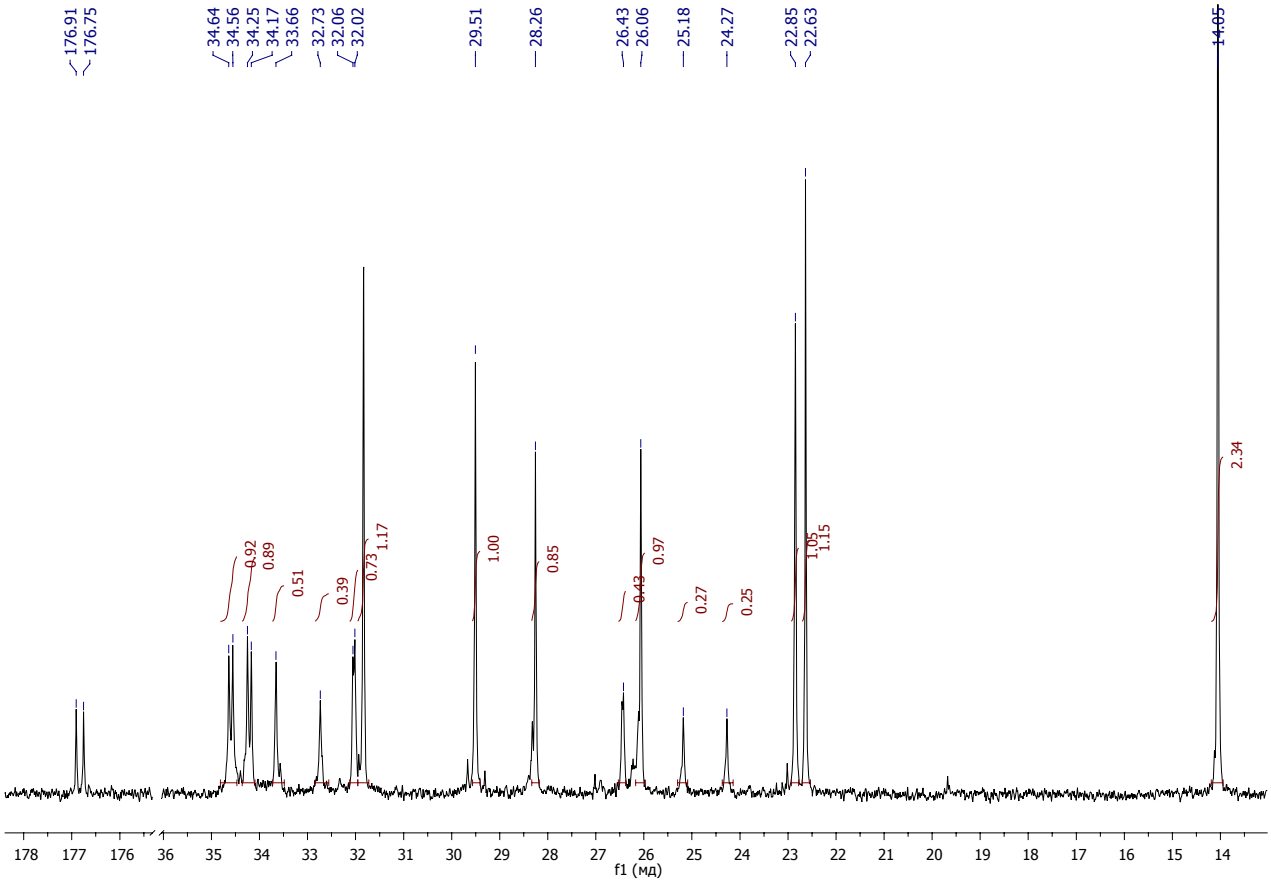


Fig. S51. ^{13}C NMR spectra of 3-[(2-butyloctyl)(hydroxy)phosphoryl]propanoic acid **21**.

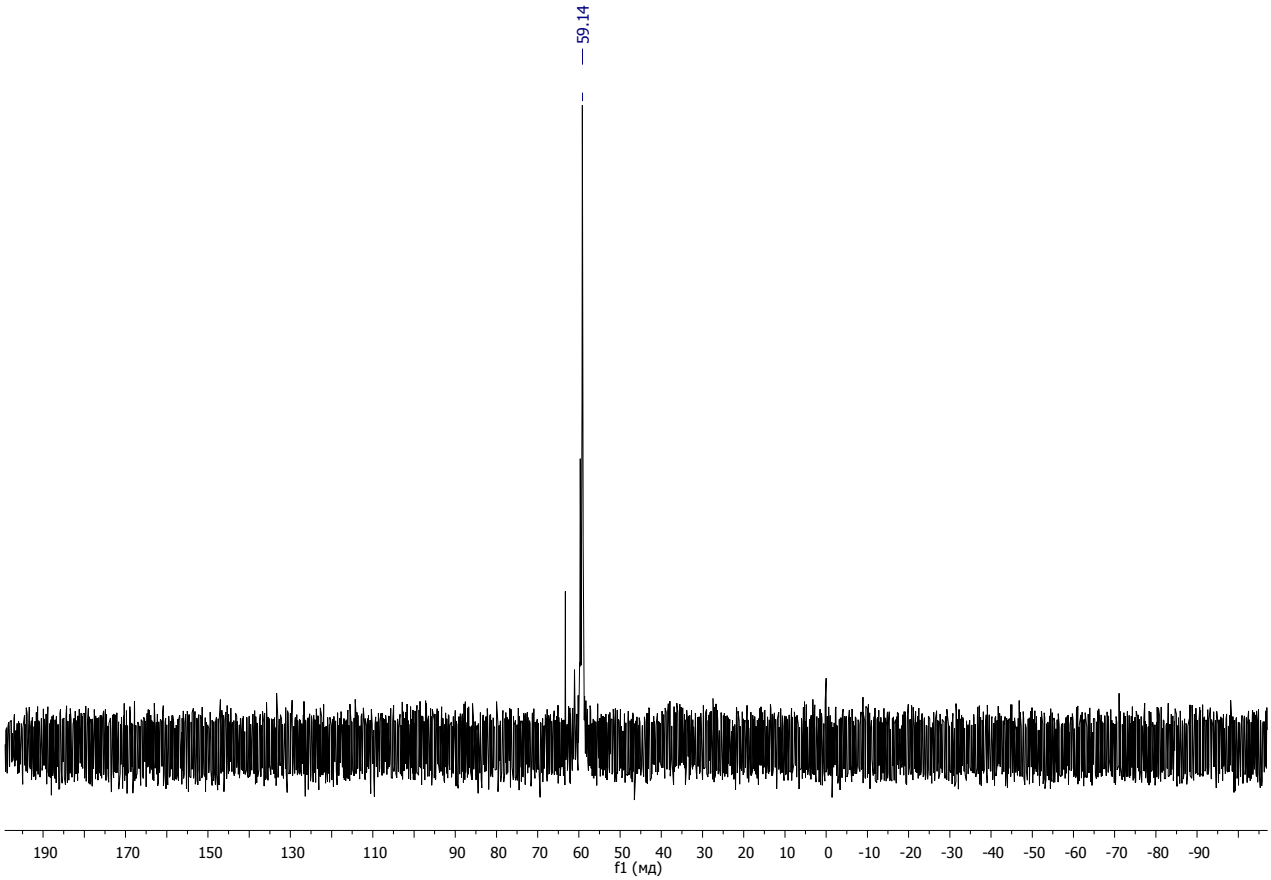


Fig. S52. ^{31}P NMR spectra of 3-[(2-butyloctyl)(hydroxy)phosphoryl]propanoic acid **21**.

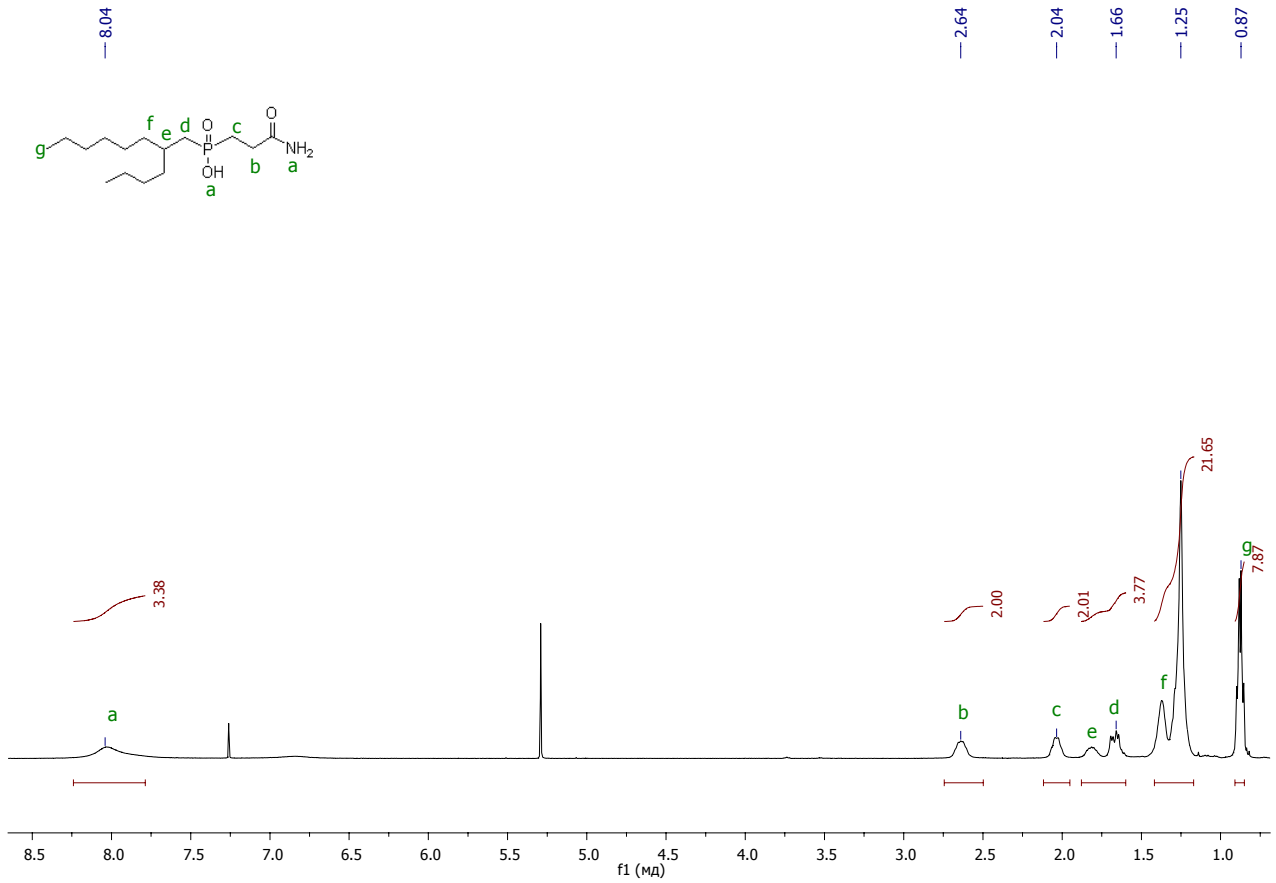


Fig. S53. [1]H NMR spectra of 3-amino-3-oxopropyl(2-butyloctyl)phosphinic acid **22**.

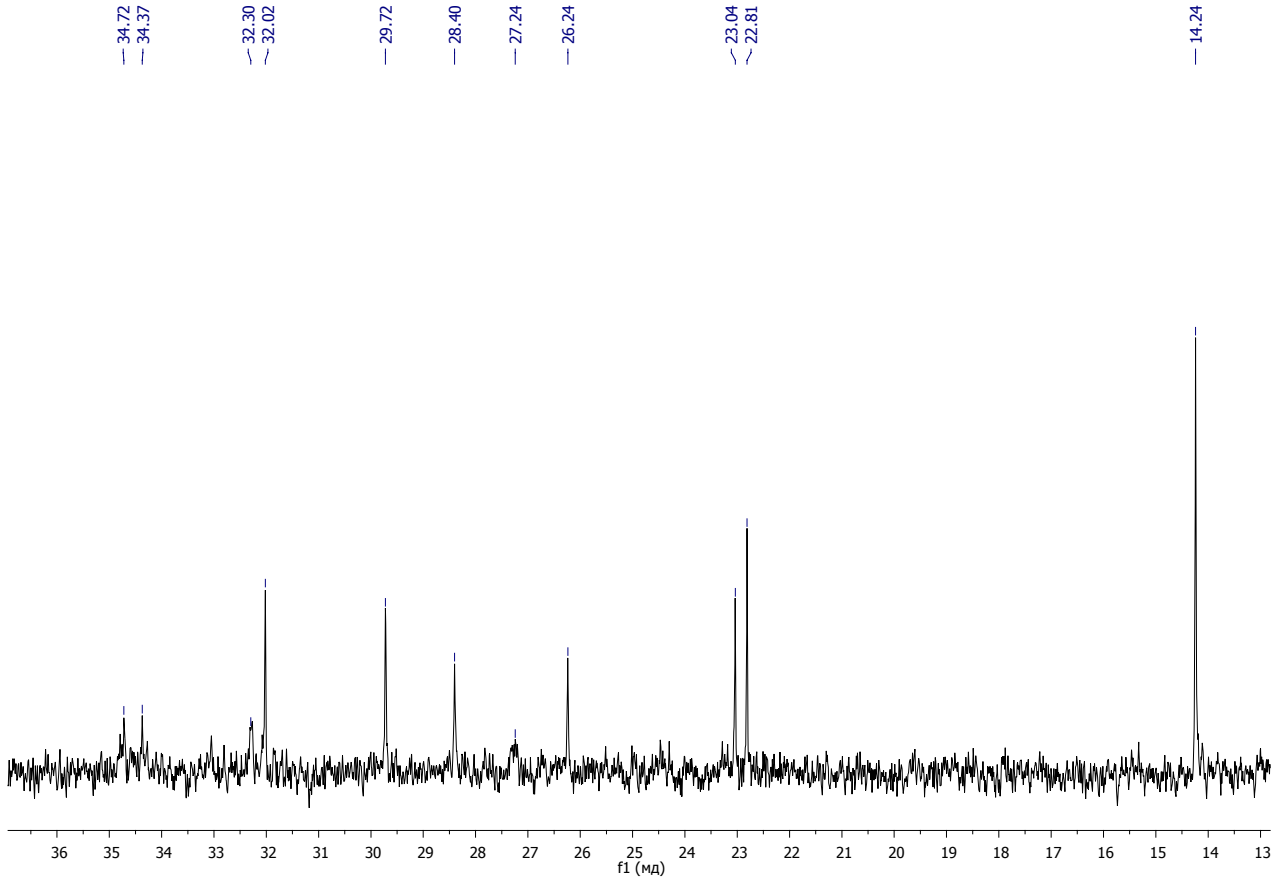


Fig. S54. [13]C NMR spectra of 3-amino-3-oxopropyl(2-butyloctyl)phosphinic acid **22**.

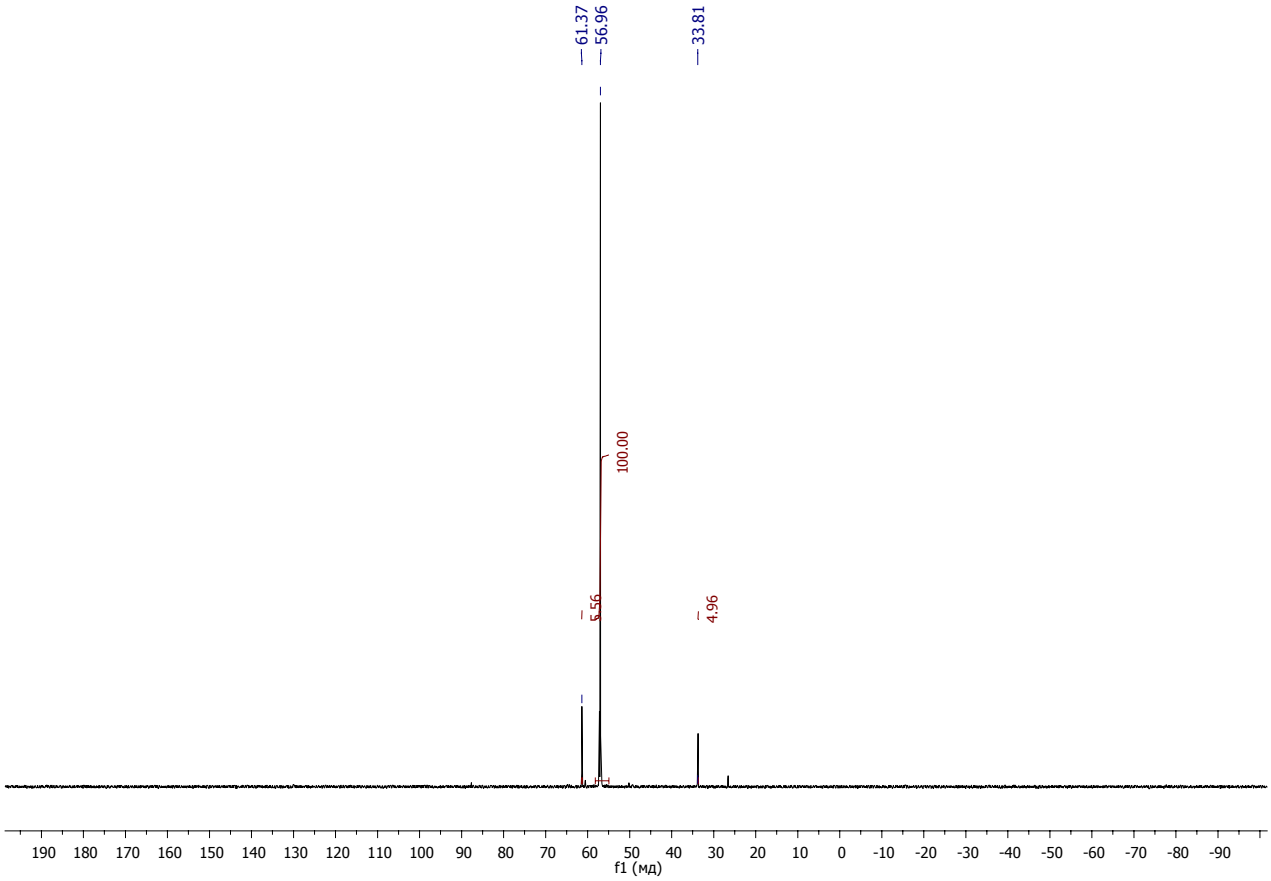


Fig. S55. ^{31}P NMR spectra of 3-amino-3-oxopropyl(2-butyloctyl)phosphinic acid **22**.

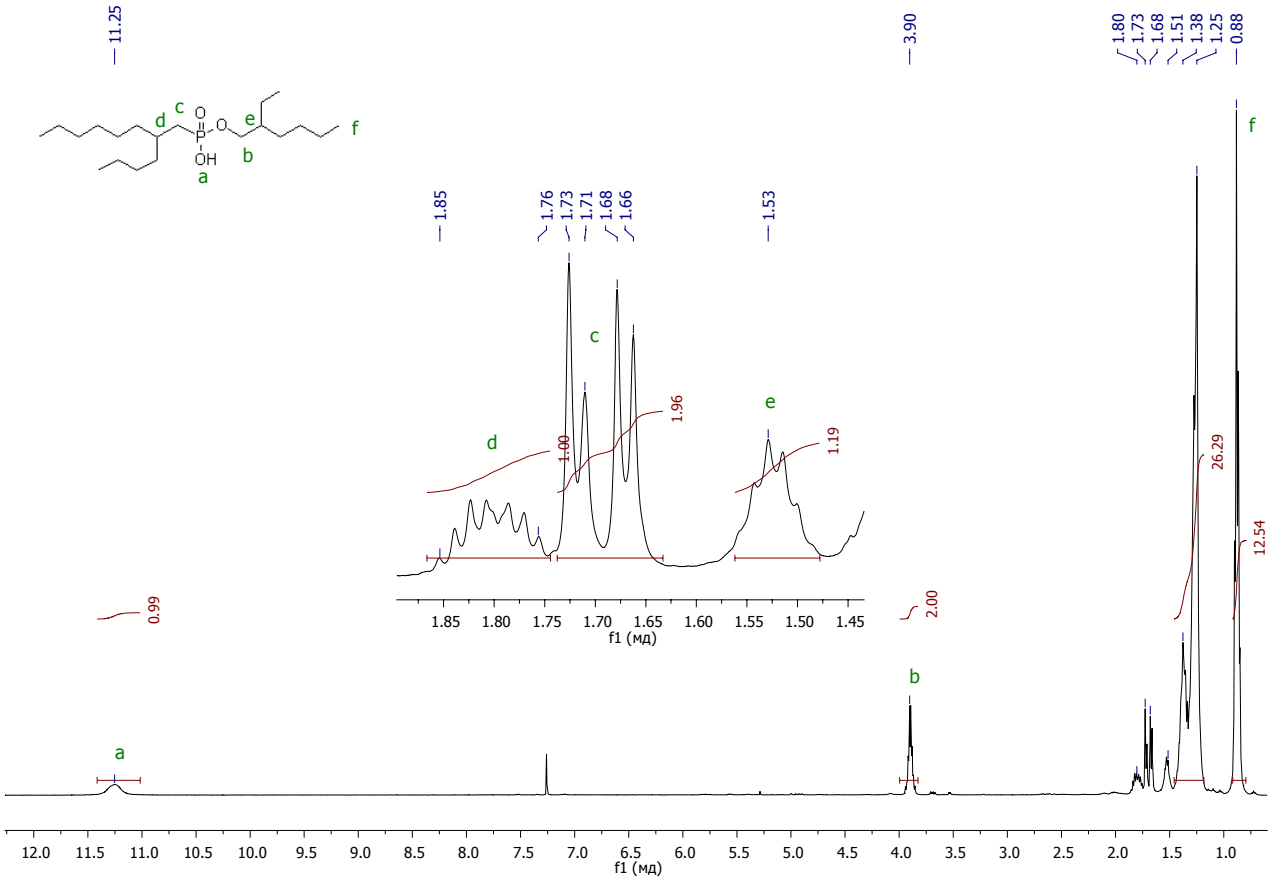


Fig. S56. ^{1}H NMR spectra of 2-ethylhexyl hydrogen 2-butyloctylphosphonate **23**.

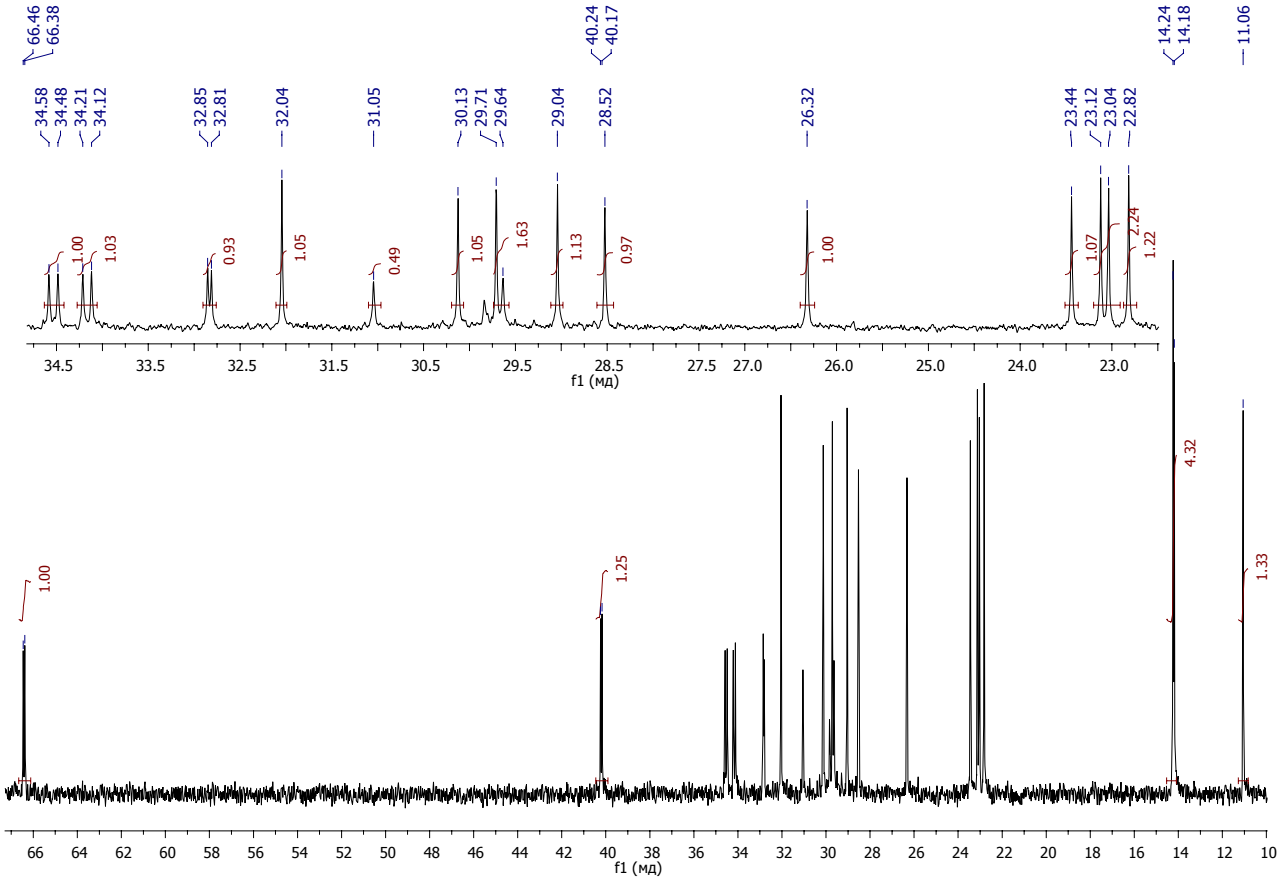


Fig. S57. ^{13}C NMR spectra of 2-ethylhexyl hydrogen 2-butyloctylphosphonate **23**.

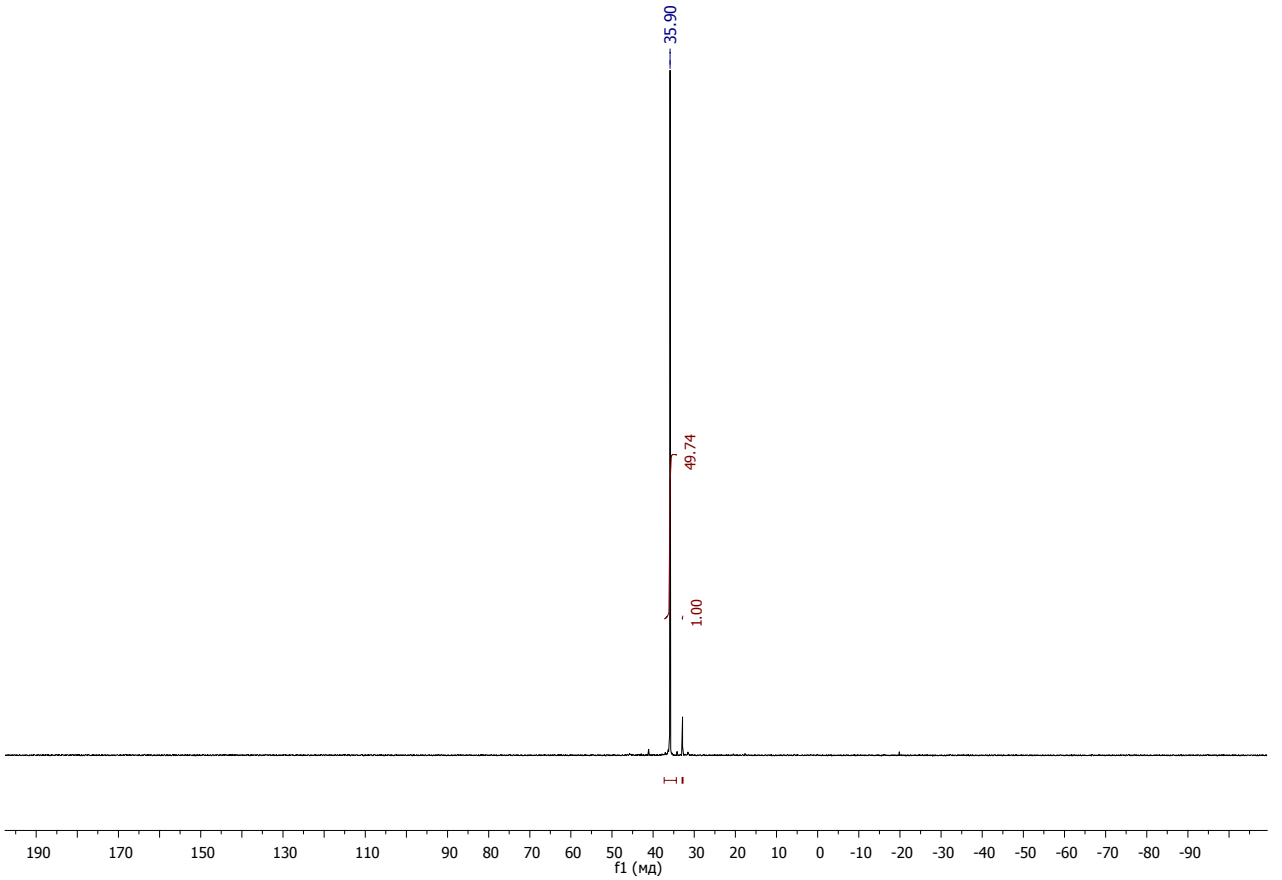


Fig. S58. ^{31}P NMR spectra of 2-ethylhexyl hydrogen 2-butyloctylphosphonate **23**.

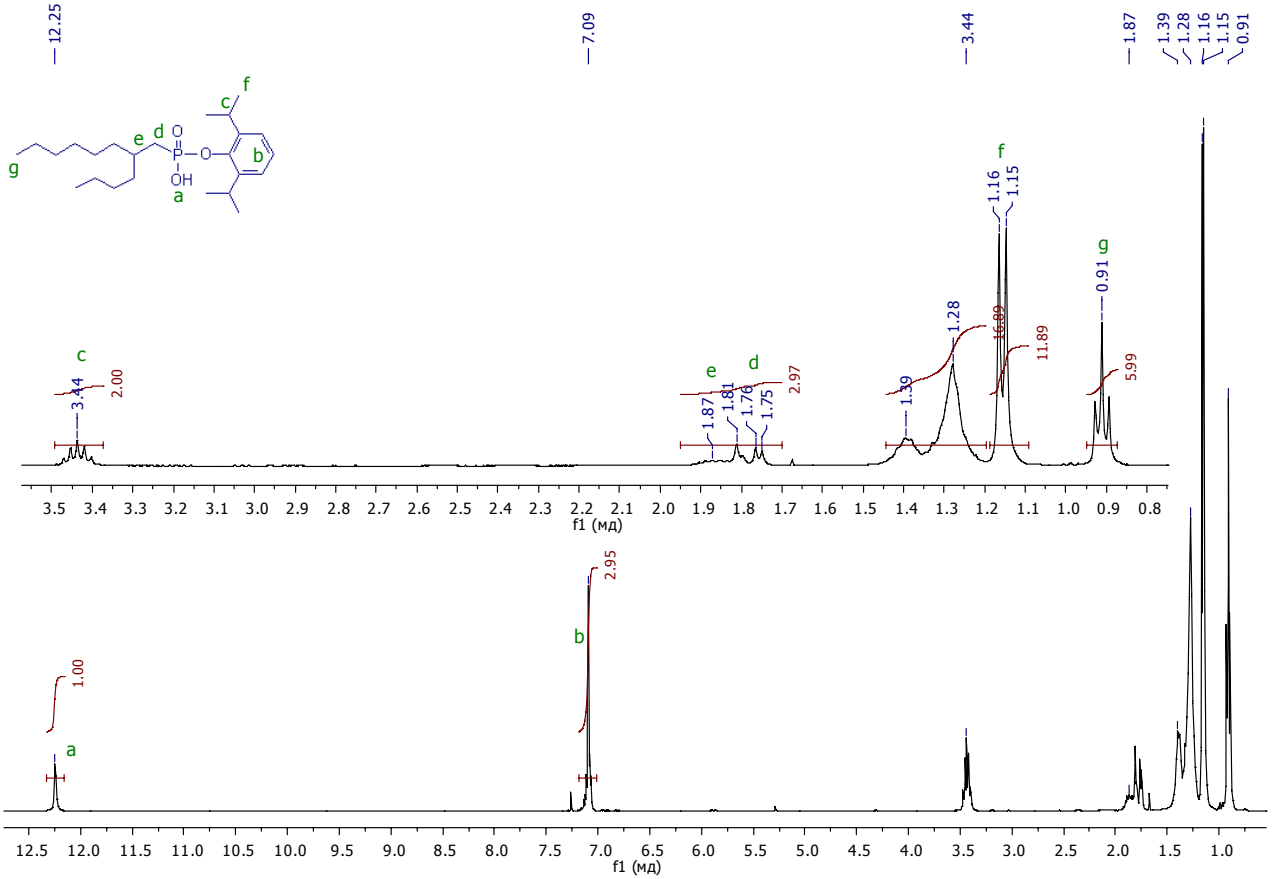


Fig. S59. [1]H NMR spectra of 2,6-diisopropylphenyl hydrogen 2-butyloctylphosphonate **23**.

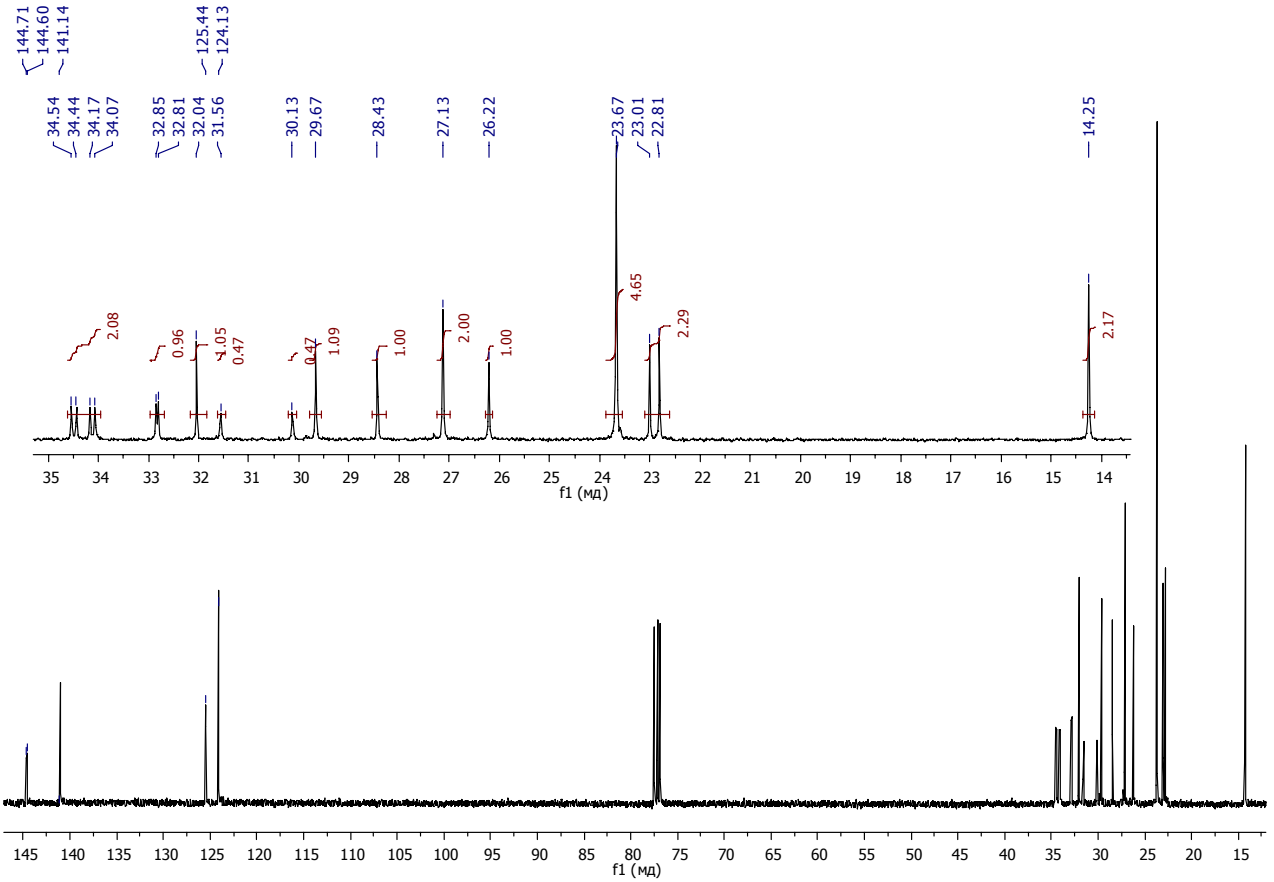


Fig. S60. [13]C NMR spectra of 2,6-diisopropylphenyl hydrogen 2-butyloctylphosphonate **23**.

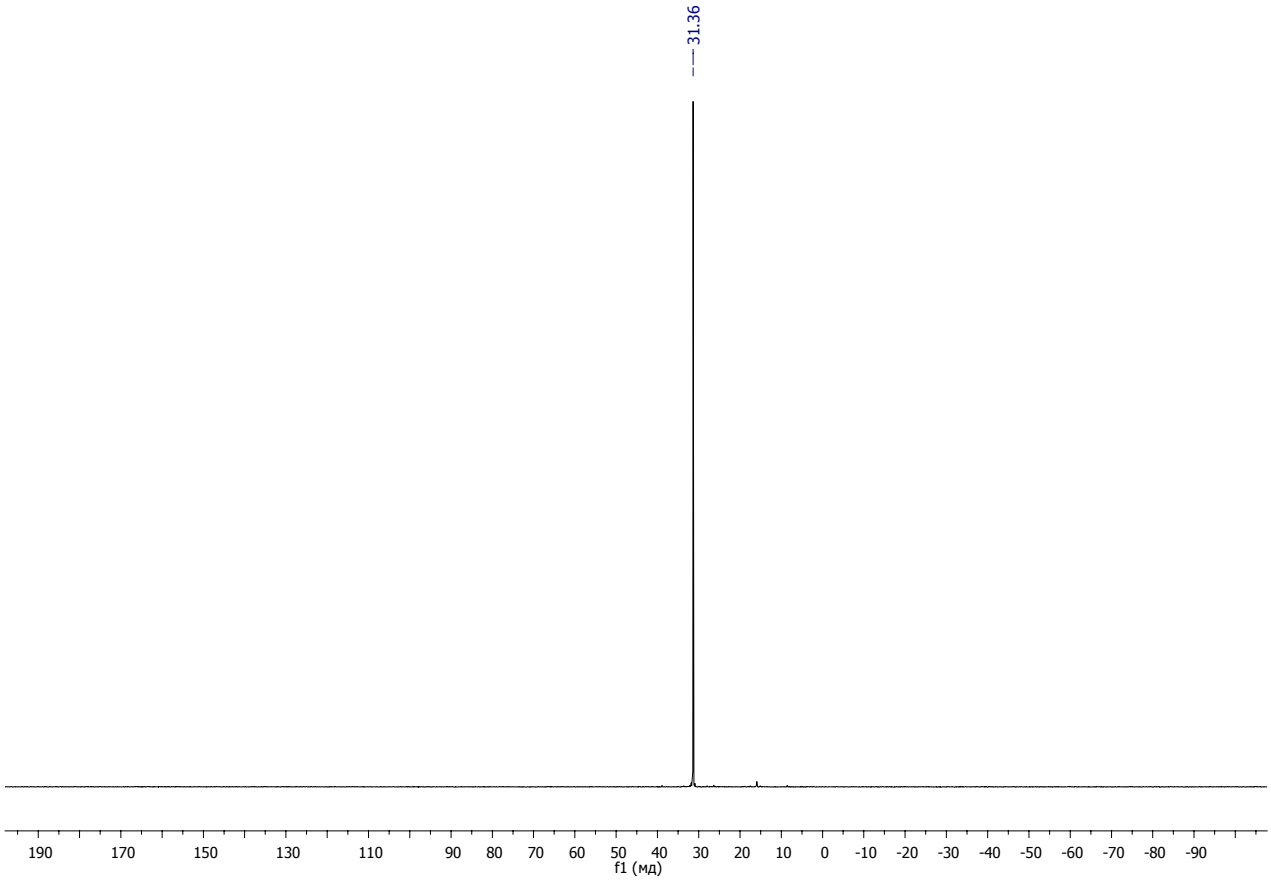


Fig. S61. ^{31}P NMR spectra of 2,6-diisopropylphenyl hydrogen 2-butyloctylphosphonate **23**.

S5. Extraction experimental details.

Digital pH meter calibrated daily with pH = 4.01 and pH = 7.00 standard buffer solutions was employed to measure pH values of the aqueous phase. The concentration of rare earth ions in the aqueous phase after proper dilution was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with the Agilent 7500c G 3155B instrument. If determined concentrations of heavy lanthanides (Dy, Lu) were rather low, the ICP-AES analyses were repeated without dilution. Two solutions with exact concentrations of $2.00 \cdot 10^{-3}$M and of $2.00 \cdot 10^{-5}$M for each lanthanide were used to control the accuracy of the ICP-AES measurements.

The lanthanide mixture solutions were prepared from $LnCl_3$ solutions of determined concentrations, NaCl and HCl. The solutions contained $2.00 \cdot 10^{-3}$M of each lanthanide (Ln=La, Pr, Nd, Dy, Lu; with the total lanthanide concentration $[Ln]_0=1.00 \cdot 10^{-2}$M), 1.00 M NaCl (to keep ionic strength of the water phase at 1 M) and possessed pH = 2.00 or 3.00. Extractants (HL) were dissolved in decane to reach the required concentration (0.200 M, 0.142 M or 0.0667 M). All extraction experiments were carried out at room temperature with an aqueous to organic phase volume ratio of 1:1. Two phases were vigorously stirred for 12 hours. The equilibrium pH and the lanthanide concentration in the aqueous phase were measured after phase separation by gravity settling.

Distribution ratio (D), extraction efficiency (E), separation factor for a pair of rare-earth elements Ln_1 and Ln_2 ($\beta_{Ln1/Ln2}$), and extraction equilibrium constant (K_{ex}) were calculated in the usual manner, according to the formulae below.

$[Ln]_{org}$ is a concentration of a rare-earth element in an organic phase after extraction. $[Ln]_0$ and $[Ln]_{aq}$ are rare-earth concentrations in a water phase before and after extraction. V_{org} and V_{aq} are volumes of organic and water phases, correspondingly.

$$D = \frac{[Ln]_{org}}{[Ln]_{aq}};$$

Herein $V_{org} = V_{aq}$;

$$D = \frac{[Ln]_0 - [Ln]_{aq}}{[Ln]_{aq}}$$

By definition

$$E(\%) = \frac{[Ln]_{org} \cdot V_{org}}{[Ln]_{org} \cdot V_{org} + [Ln]_{aq} \cdot V_{aq}} \times 100\%$$

Herein

$$E(\%) = \frac{[Ln]_{org}}{[Ln]_{org} + [Ln]_{aq}} \times 100\% = \frac{D}{D+1} \times 100\%$$

$$\beta_{Ln1/Ln2} = \frac{[Ln_1]_{org} \cdot [Ln_2]_{aq}}{[Ln_1]_{aq} \cdot [Ln_2]_{org}} = \frac{D_{Ln1}}{D_{Ln2}}$$

By definition, $\beta \geq 1$ and $D_{Ln1} \geq D_{Ln2}$.

It is commonly accepted that dialkylphosporic, dialkylphosphonic and dialkylphosphinic acids HL exist in non-polar media mainly as dimers $(HL)_2$. The extraction equilibrium for each lanthanide and its constant can be represented by the following equations.

$$Ln^{3+}_{(aq)} + 3(HL)_{2(org)} \rightleftharpoons [Ln(HL_2)_3]_{(org)} + 3H^+_{(aq)}$$

$$K_{ex} = \frac{[Ln(HL_2)_3]_{org}[H^+]^3_{aq}}{[Ln^{3+}]_{aq}[(HL)_2]^3_{org}} = D\frac{[H^+]^3_{aq}}{[(HL)_2]^3_{org}}$$

$$\lg K_{ex} = \lg D - 3\,pH - 3\lg[(HL)_2]_{org}$$

The equilibrium concentration of the HL acid dimer in organic phase, $[(HL)_2]_{org}$, was calculated according to

$$[(HL)_2]_{org} = \frac{[HL]_0 - 6 \cdot \sum_{Ln}[Ln(HL_2)_3]_{org}}{2},$$

where $[HL]_0$ is the initial concentration in organic solvent before extraction, not taking into account its existence as a dimer.

Table 1. Lanthanide concentration in organic and aqueous phases

Entry	Extractant HL	Extractant $[HL]_0$	Initial pH	Lanthanide concentration in organic phase (mmol/L) [La]	[Pr]	[Nd]	[Dy]	[Lu]	Lanthanide concentration in aqueous phase (mmol/L) [La]	[Pr]	[Nd]	[Dy]	[Lu]
1	P204	0.200M	2.00	1.545	1.876	1.902	2.000	2.000	$4.552\cdot10^{-1}$	$1.235\cdot10^{-1}$	$9.831\cdot10^{-2}$	$4.590\cdot10^{-4}$	$5.970\cdot10^{-5}$
2	**8**	0.200M	2.00	1.988	1.995	1.995	1.999	2.000	$1.184\cdot10^{-2}$	$4.560\cdot10^{-3}$	$4.769\cdot10^{-3}$	$5.246\cdot10^{-4}$	$1.194\cdot10^{-5}$
3	**10**	0.200M	2.00	1.975	1.991	1.991	1.999	2.000	$2.520\cdot10^{-2}$	$9.120\cdot10^{-3}$	$9.154\cdot10^{-3}$	$5.902\cdot10^{-4}$	$1.194\cdot10^{-5}$
4	P204	0.200M	3.00	1.753	1.941	1.953	2.000	2.000	$2.472\cdot10^{-1}$	$5.920\cdot10^{-2}$	$4.692\cdot10^{-2}$	$1.836\cdot10^{-4}$	$4.179\cdot10^{-6}$
5	**8**	0.200M	3.00	1.997	1.999	1.999	2.000	2.000	$2.960\cdot10^{-3}$	$1.200\cdot10^{-3}$	$1.231\cdot10^{-3}$	$2.295\cdot10^{-4}$	$3.881\cdot10^{-6}$
6	**10**	0.200M	3.00	1.989	1.996	1.996	2.000	2.000	$1.152\cdot10^{-2}$	$4.080\cdot10^{-3}$	$4.077\cdot10^{-3}$	$3.279\cdot10^{-4}$	$2.388\cdot10^{-5}$
7	**10**	0.142M	3.00	1.902	1.968	1.969	1.999	2.000	$9.840\cdot10^{-2}$	$3.200\cdot10^{-2}$	$3.077\cdot10^{-2}$	$9.836\cdot10^{-4}$	$5.552\cdot10^{-6}$
8	P204	0.067M	3.00	$2.880\cdot10^{-1}$	1.000	1.154	1.995	1.999	1.712	1.000	$8.462\cdot10^{-1}$	$5.246\cdot10^{-3}$	$1.194\cdot10^{-3}$
9	**8**	0.067M	3.00	1.124	1.619	1.623	1.996	2.000	$8.760\cdot10^{-1}$	$3.810\cdot10^{-1}$	$3.770\cdot10^{-1}$	$3.738\cdot10^{-3}$	$1.791\cdot10^{-5}$
10	**10**	0.067M	3.00	$9.440\cdot10^{-1}$	1.496	1.508	1.984	2.000	1.056	$5.040\cdot10^{-1}$	$4.923\cdot10^{-1}$	$1.639\cdot10^{-2}$	$2.388\cdot10^{-4}$
11	**13**	0.067M	3.00	$8.800\cdot10^{-2}$	$9.600\cdot10^{-2}$	$8.462\cdot10^{-2}$	$2.492\cdot10^{-1}$	1.648	1.912	1.904	1.915	1.751	$3.522\cdot10^{-1}$
12	**14**	0.067M	3.00	$1.429\cdot10^{-1}$	$8.571\cdot10^{-1}$	1.103	1.997	2.000	1.857	1.143	$8.966\cdot10^{-1}$	$2.875\cdot10^{-3}$	$5.714\cdot10^{-5}$
13	**15**	0.067M	3.00	$1.360\cdot10^{-1}$	$2.320\cdot10^{-1}$	$2.538\cdot10^{-1}$	1.948	1.999	1.864	1.768	1.746	$5.246\cdot10^{-2}$	$5.970\cdot10^{-4}$
14	**16**	0.067M	3.00	$1.336\cdot10^{-1}$	$2.048\cdot10^{-1}$	$3.226\cdot10^{-1}$	1.943	1.999	1.866	1.795	1.677	$5.675\cdot10^{-2}$	$8.862\cdot10^{-4}$
15	**17**	0.067M	3.00	$7.143\cdot10^{-2}$	$1.429\cdot10^{-1}$	$2.069\cdot10^{-1}$	1.968	2.000	1.929	1.857	1.793	$3.250\cdot10^{-2}$	$4.000\cdot10^{-4}$
16	**18**	0.067M	3.00	$1.336\cdot10^{-1}$	$2.048\cdot10^{-1}$	$3.226\cdot10^{-1}$	1.968	2.000	1.866	1.795	1.677	$3.250\cdot10^{-2}$	$2.708\cdot10^{-4}$
17	**19**	0.067M	3.00	$1.336\cdot10^{-1}$	$2.048\cdot10^{-1}$	$2.647\cdot10^{-1}$	1.933	1.999	1.866	1.795	1.735	$6.706\cdot10^{-2}$	$9.231\cdot10^{-4}$
18	**20**	0.067M	3.00	$2.880\cdot10^{-1}$	$8.320\cdot10^{-1}$	$8.846\cdot10^{-1}$	1.908	1.999	1.712	1.168	1.115	$9.180\cdot10^{-2}$	$1.194\cdot10^{-3}$
19	**21**	0.067M	3.00	$5.200\cdot10^{-1}$	$9.200\cdot10^{-1}$	$9.077\cdot10^{-1}$	1.967	2.000	1.480	1.080	1.092	$3.279\cdot10^{-2}$	$3.582\cdot10^{-4}$
20	**22**	0.067M	3.00	$6.000\cdot10^{-1}$	1.1360	1.154	1.993	2.000	1.400	$8.640\cdot10^{-1}$	$8.462\cdot10^{-1}$	$6.557\cdot10^{-3}$	$1.194\cdot10^{-4}$
21	**23**	0.067M	3.00	$4.286\cdot10^{-1}$	$8.571\cdot10^{-1}$	$9.655\cdot10^{-1}$	1.977	1.998	1.571	1.143	1.034	$2.313\cdot10^{-2}$	$2.114\cdot10^{-3}$
22	**24**	0.067M	3.00	$1.429\cdot10^{-1}$	$3.571\cdot10^{-1}$	$4.138\cdot10^{-1}$	1.850	1.998	1.857	1.643	1.586	$1.500\cdot10^{-1}$	$2.286\cdot10^{-3}$

Table 2. Lanthanide extraction efficiency (%) and distribution ratio (*D*).

Entry	Extractant		Initial	Extraction efficiency, %					Distribution ratio				
	HL	$[HL]_0$	pH	La	Pr	Nd	Dy	Lu	La	Pr	Nd	Dy	Lu
1	P204	0.200M	2.00	77.24	93.82	95.08	99.98	100.00	3.39	$1.52\cdot10^{1}$	$1.93\cdot10^{1}$	$4.36\cdot10^{3}$	$3.35\cdot10^{4}$
2	**8**	0.200M	2.00	99.41	99.77	99.76	99.97	100.00	$1.68\cdot10^{2}$	$4.38\cdot10^{2}$	$4.18\cdot10^{2}$	$3.81\cdot10^{3}$	$1.67\cdot10^{5}$
3	**10**	0.200M	2.00	98.74	99.54	99.54	99.97	100.00	$7.84\cdot10^{1}$	$2.18\cdot10^{2}$	$2.17\cdot10^{2}$	$3.39\cdot10^{3}$	$1.67\cdot10^{5}$
4	P204	0.200M	3.00	87.64	97.04	97.65	99.99	100.00	7.09	$3.28\cdot10^{1}$	$4.16\cdot10^{1}$	$1.09\cdot10^{4}$	$4.79\cdot10^{5}$
5	**8**	0.200M	3.00	99.85	99.94	99.94	99.99	100.00	$6.75\cdot10^{2}$	$1.67\cdot10^{3}$	$1.62\cdot10^{3}$	$8.71\cdot10^{3}$	$5.15\cdot10^{5}$
6	**10**	0.200M	3.00	99.42	99.80	99.80	99.98	100.00	$1.73\cdot10^{2}$	$4.89\cdot10^{2}$	$4.90\cdot10^{2}$	$6.10\cdot10^{3}$	$8.37\cdot10^{4}$
7	**10**	0.142M	3.00	95.08	98.40	98.46	99.95	100.00	$1.93\cdot10^{1}$	$6.15\cdot10^{1}$	$6.40\cdot10^{1}$	$2.03\cdot10^{3}$	$3.60\cdot10^{5}$
8	P204	0.0667M	3.00	14.40	50.00	57.69	99.74	99.94	$1.68\cdot10^{-1}$	1.00	1.36	$3.80\cdot10^{2}$	$1.67\cdot10^{3}$
9	**8**	0.0667M	3.00	56.20	80.95	81.15	99.81	100.00	1.28	4.25	4.31	$5.34\cdot10^{2}$	$1.12\cdot10^{5}$
10	**10**	0.0667M	3.00	47.20	74.80	75.38	99.18	99.99	$8.94\cdot10^{-1}$	2.97	3.06	$1.21\cdot10^{2}$	$8.37\cdot10^{3}$
11	**13**	0.0667M	3.00	4.40	4.80	4.23	12.46	82.39	$4.60\cdot10^{-2}$	$5.04\cdot10^{-2}$	$4.42\cdot10^{-2}$	$1.42\cdot10^{-1}$	4.68
12	**14**	0.0667M	3.00	7.14	42.86	55.17	99.86	100.00	$7.69\cdot10^{-2}$	$7.50\cdot10^{-1}$	1.23	$6.95\cdot10^{2}$	$3.50\cdot10^{4}$
13	**15**	0.0667M	3.00	6.80	11.60	12.69	97.38	99.97	$7.30\cdot10^{-2}$	$1.31\cdot10^{-1}$	$1.45\cdot10^{-1}$	$3.71\cdot10^{1}$	$3.35\cdot10^{3}$
14	**16**	0.0667M	3.00	6.68	10.24	16.13	97.16	99.96	$7.16\cdot10^{-2}$	$1.14\cdot10^{-1}$	$1.92\cdot10^{-1}$	$3.42\cdot10^{1}$	$2.26\cdot10^{3}$
15	**17**	0.0667M	3.00	3.57	7.14	10.34	98.38	99.98	$3.70\cdot10^{-2}$	$7.69\cdot10^{-2}$	$1.15\cdot10^{-1}$	$6.05\cdot10^{1}$	$5.00\cdot10^{3}$
16	**18**	0.0667M	3.00	6.68	10.24	16.13	98.38	99.99	$7.16\cdot10^{-2}$	$1.14\cdot10^{-1}$	$1.92\cdot10^{-1}$	$6.05\cdot10^{1}$	$7.39\cdot10^{3}$
17	**19**	0.0667M	3.00	6.68	10.24	13.24	96.65	99.95	$7.16\cdot10^{-2}$	$1.14\cdot10^{-1}$	$1.53\cdot10^{-1}$	$2.88\cdot10^{1}$	$2.17\cdot10^{3}$
18	**20**	0.0667M	3.00	14.40	41.60	44.23	95.41	99.94	$1.68\cdot10^{-1}$	$7.12\cdot10^{-1}$	$7.93\cdot10^{-1}$	$2.08\cdot10^{1}$	$1.67\cdot10^{3}$
19	**21**	0.0667M	3.00	26.00	46.00	45.38	98.36	99.98	$3.51\cdot10^{-1}$	$8.52\cdot10^{-1}$	$8.31\cdot10^{-1}$	$6.00\cdot10^{1}$	$5.58\cdot10^{3}$
20	**22**	0.0667M	3.00	30.00	56.80	57.69	99.67	99.99	$4.29\cdot10^{-1}$	1.31	1.36	$3.04\cdot10^{2}$	$1.67\cdot10^{4}$
21	**23**	0.0667M	3.00	21.43	42.86	48.28	98.84	99.89	$2.73\cdot10^{-1}$	$7.50\cdot10^{-1}$	$9.33\cdot10^{-1}$	$8.55\cdot10^{1}$	$9.45\cdot10^{2}$
22	**24**	0.0667M	3.00	7.14	17.86	20.69	92.50	99.89	$7.69\cdot10^{-2}$	$2.17\cdot10^{-1}$	$2.61\cdot10^{-1}$	$1.23\cdot10^{1}$	$8.74\cdot10^{2}$

Table 3. Separation factor (β) for some lanthanide pairs and estimated lg K_{ex}.

Entry	Extractant		Initial	Final	Separation factor β						lg K_{ex}				
	HL	$[HL]_0$	pH	pH	$\beta_{Pr/La}$	$\beta_{Nd/La}$	$\beta_{Nd/Pr}$	$\beta_{Dy/Nd}$	$\beta_{Lu/Nd}$	$\beta_{Lu/Dy}$	La	Pr	Nd	Dy	Lu
1	P204	0.200M	2.00	1.39	4.48	5.70	1.27	225	1730	7.69	-0.21	0.44	0.54	2.90	3.78
2	**8**	0.200M	2.00	1.40	2.61	2.49	1.05	9.11	400	43.9	1.49	1.90	1.89	2.84	4.49
3	**10**	0.200M	2.00	1.46	2.79	2.78	1.00	15.6	770	49.4	0.98	1.42	1.42	2.61	4.31
4	P204	0.200M	3.00	1.48	4.62	5.87	1.27	262	11500	43.9	-0.14	0.52	0.62	3.04	4.69
5	**8**	0.200M	3.00	1.51	2.47	2.41	1.03	5.37	317	59.2	1.76	2.16	2.14	2.87	4.65
6	**10**	0.200M	3.00	1.54	2.83	2.84	1.00	12.5	171	13.7	1.08	1.53	1.53	2.63	3.77
7	**10**	0.142M	3.00	1.52	3.18	3.31	1.04	31.8	5630	177	0.87	1.38	1.39	2.89	5.14
8	P204	0.0667M	3.00	1.54	5.94	8.11	1.36	279	1230	4.40	0.16	0.94	1.07	3.52	4.16
9	**8**	0.0667M	3.00	1.50	3.31	3.36	1.01	124	25900	209	1.86	2.38	2.38	4.48	6.80
10	**10**	0.0667M	3.00	1.53	3.32	3.43	1.03	39.5	2730	69.2	1.42	1.94	1.96	3.55	5.39
11	**13**	0.0667M	3.00	2.01	1.10	1.04	1.14	3.22	106	32.9	-2.65	-2.61	-2.67	-2.16	-0.65
12	**14**	0.0667M	3.00	1.52	9.75	16.0	1.64	564	28400	50.4	-0.21	0.78	1.00	3.75	5.45
13	**15**	0.0667M	3.00	1.80	1.80	1.99	1.11	255	23000	90.2	-1.42	-1.16	-1.12	1.29	3.25
14	**16**	0.0667M	3.00	1.54	1.59	2.69	1.69	178	11700	65.9	-0.64	-0.44	-0.21	2.04	3.86
15	**17**	0.0667M	3.00	1.58	2.08	3.12	1.50	525	43300	82.6	-1.09	-0.77	-0.59	2.13	4.04
16	**18**	0.0667M	3.00	1.51	1.59	2.69	1.69	315	38400	122	-0.54	-0.34	-0.11	2.38	4.47
17	**19**	0.0667M	3.00	1.53	1.59	2.13	1.34	189	14200	75.1	-0.62	-0.42	-0.29	1.98	3.86
18	**20**	0.0667M	3.00	2.66	4.23	4.71	1.11	26.2	2110	80.5	-3.33	-2.71	-2.66	-1.24	0.66
19	**21**	0.0667M	3.00	1.61	2.42	2.37	1.03	72.2	6720	93.0	0.24	0.62	0.61	2.47	4.44
20	**22**	0.0667M	3.00	1.61	3.07	3.18	1.04	223	12300	55.1	0.49	0.98	0.99	3.34	5.08
21	**23**	0.0667M	3.00	1.73	2.75	3.42	1.24	91.6	1010	11.1	-0.25	0.19	0.28	2.24	3.29
22	**24**	0.0667M	3.00	2.56	2.83	3.39	1.20	47.3	3350	70.9	-3.63	-3.18	-3.10	-1.43	0.42

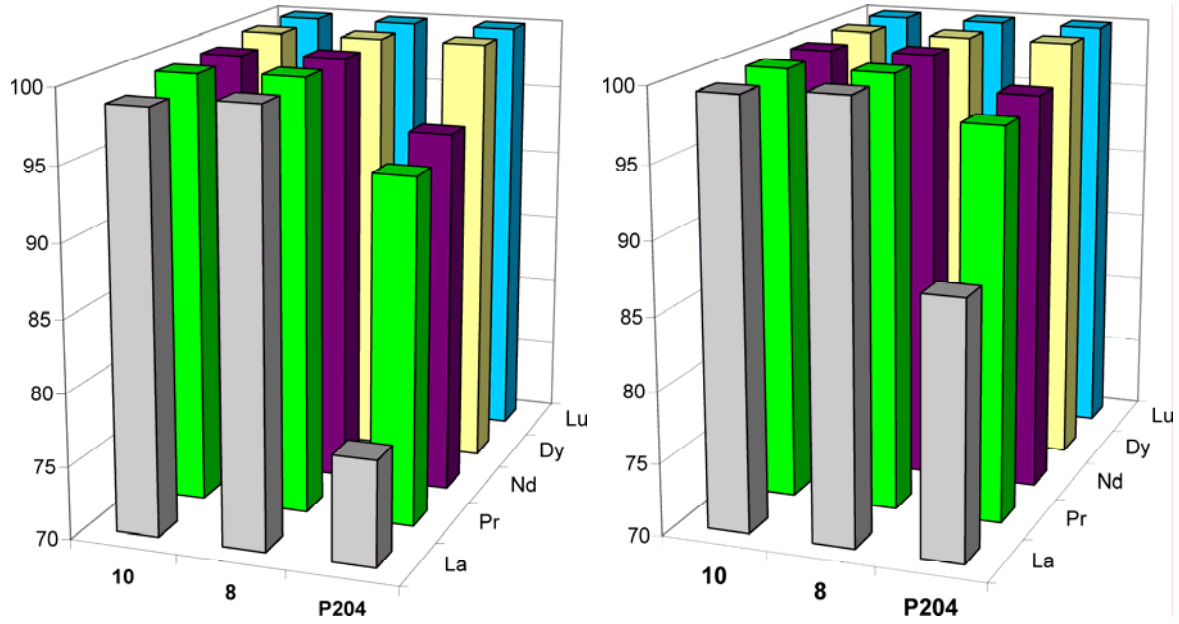


Figure S62. Lanthanide extraction efficiency (%) for extractants P204, **8**, and **10** at initial water phase pH being 2.0 (left) and 3.0 (right) and at $[HL]_0$=0.200M.

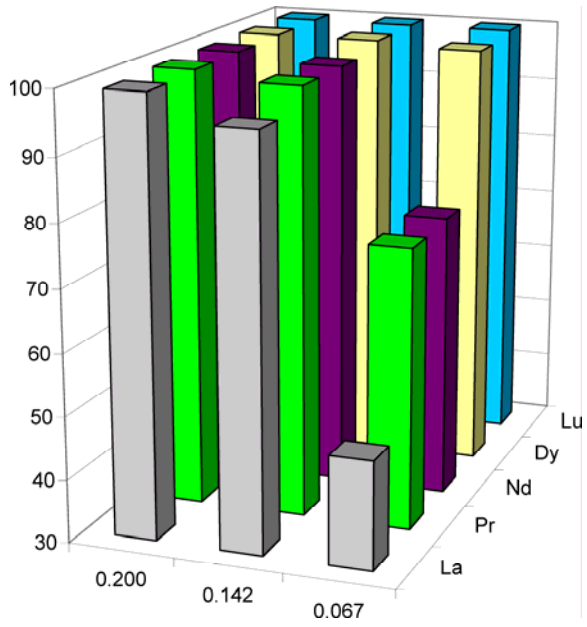


Figure S63. Lanthanide extraction efficiency (%) at different initial concentration of **10** (0.200M, 0.142M, and 0.067M) at initial water phase pH=3.0.

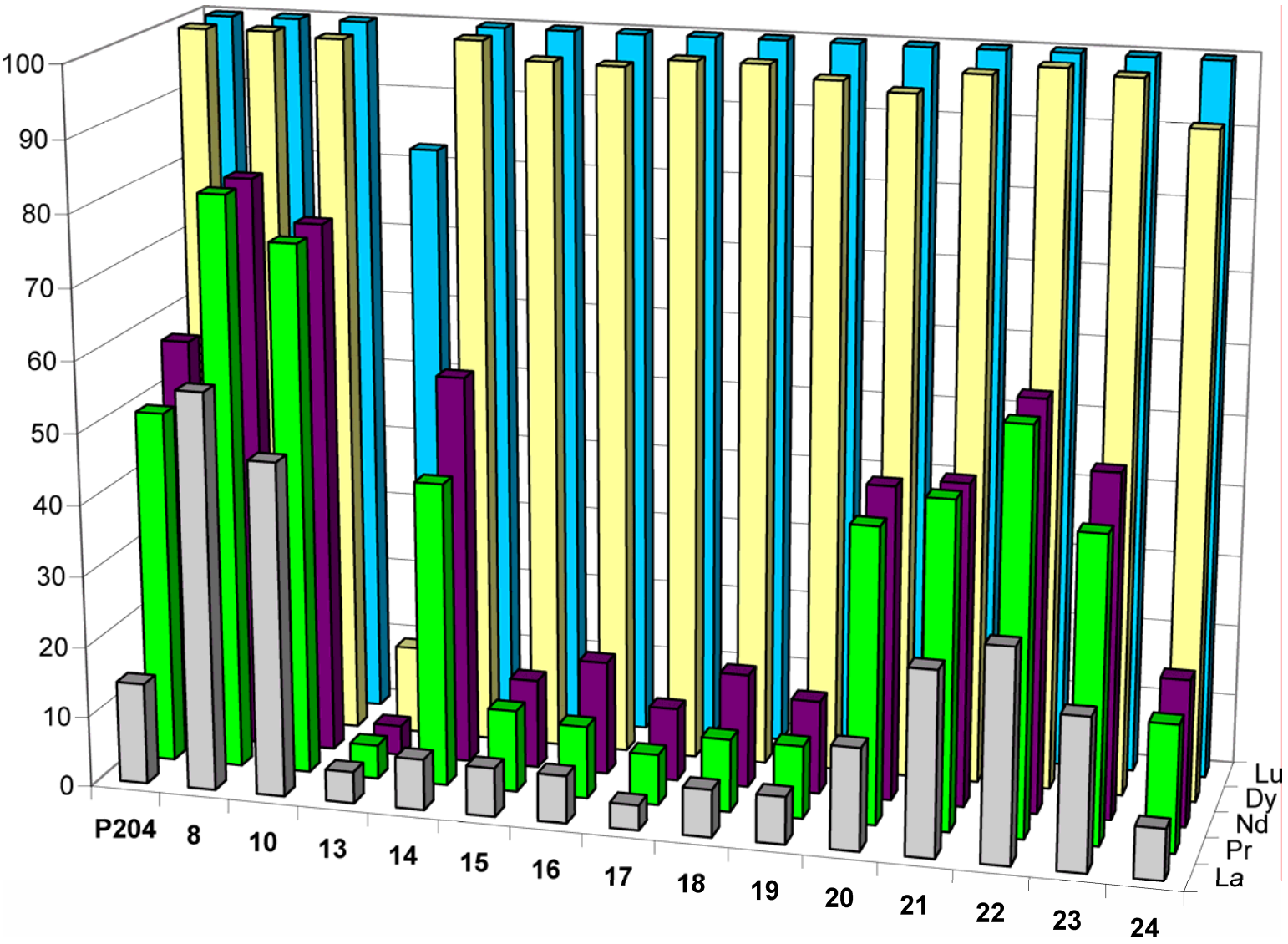


Figure S64. Lanthanide extraction efficiency (%) for various HL acids at initial concentration $[HL]_0$=0.067M and initial water phase pH=3.0.

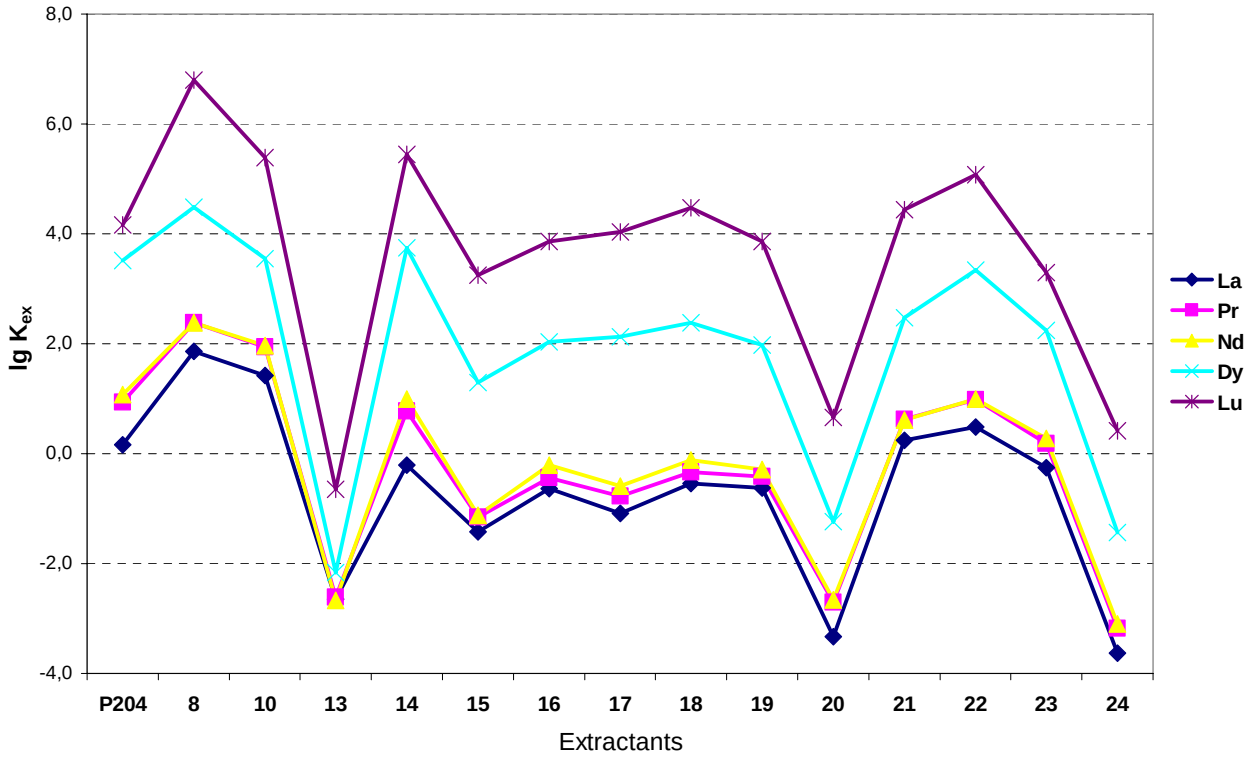


Figure S65. Lg K_{ex} values for different lanthanides and extractants. Extraction conditions: $[HL]_0$=0.0667M, initial pH = 3.00, $[Ln]_0$=1.00·10^{-2}M (2.00·10^{-3}M of each Ln)

With the exceptions of **20** and **24**, there is a positive correlation between the lg K_{ex} values and the general extraction ability of the studied acids HL.