

## Branched alkylphosphinic acids demonstrate explicit anti-wear effect

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#### S1. General experimental remarks

Triisobutylaluminium solution (1 M in hexane, Sigma-Aldrich), MMAO-12 (1.25 M in toluene, Sigma-Aldrich), Et<sub>2</sub>AlCl (1 M in hexane, Sigma-Aldrich), H<sub>3</sub>PO<sub>2</sub> (50% aq., Sigma-Aldrich), AIBN (Acros) were used as purchased. Hex-1-ene, oct-1-ene, dec-1-ene, 4-methylpent-1-ene and 3-methylbut-1-ene (95-98%, Sigma-Aldrich) were stored over Na/K alloy and distilled before use under argon atmosphere. 2-Propanol (Sigma-Aldrich) was distilled over CaH<sub>2</sub> under argon atmosphere. All of the synthesis experiments were conducted under an argon atmosphere. Zirconium precatalyst (Scheme 2) was synthesized according to previously reported procedure [J. Gräper, G. Paolucci, R. D. Fischer, *J. Organomet. Chem.*, 1995, **501**, 211].

CDCl<sub>3</sub> was distilled over P<sub>2</sub>O<sub>5</sub> and stored over 4 Å molecular sieves. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400 MHz) at 20 °C. The chemical shifts are reported in ppm relative to the solvent residual peaks.

The control of the purity of  $\alpha$ -olefin dimers was performed using gas chromatography (GC) method. GC analysis was carried out with a KRISTALL-2000M gas chromatograph equipped with a SolGel-1ms (60 m × 0.25 mm × 0.25 μm) column and a flame ionization detector. Helium was used as a carrier gas at a rate of 1.364 ml min<sup>-1</sup> and with a split ratio of 73.3:1. The injector temperature was 320 °C, and the column temperature was 200 °C within 5 min and then was raised from 200 to 300 °C at a rate of 10 deg min<sup>-1</sup>.

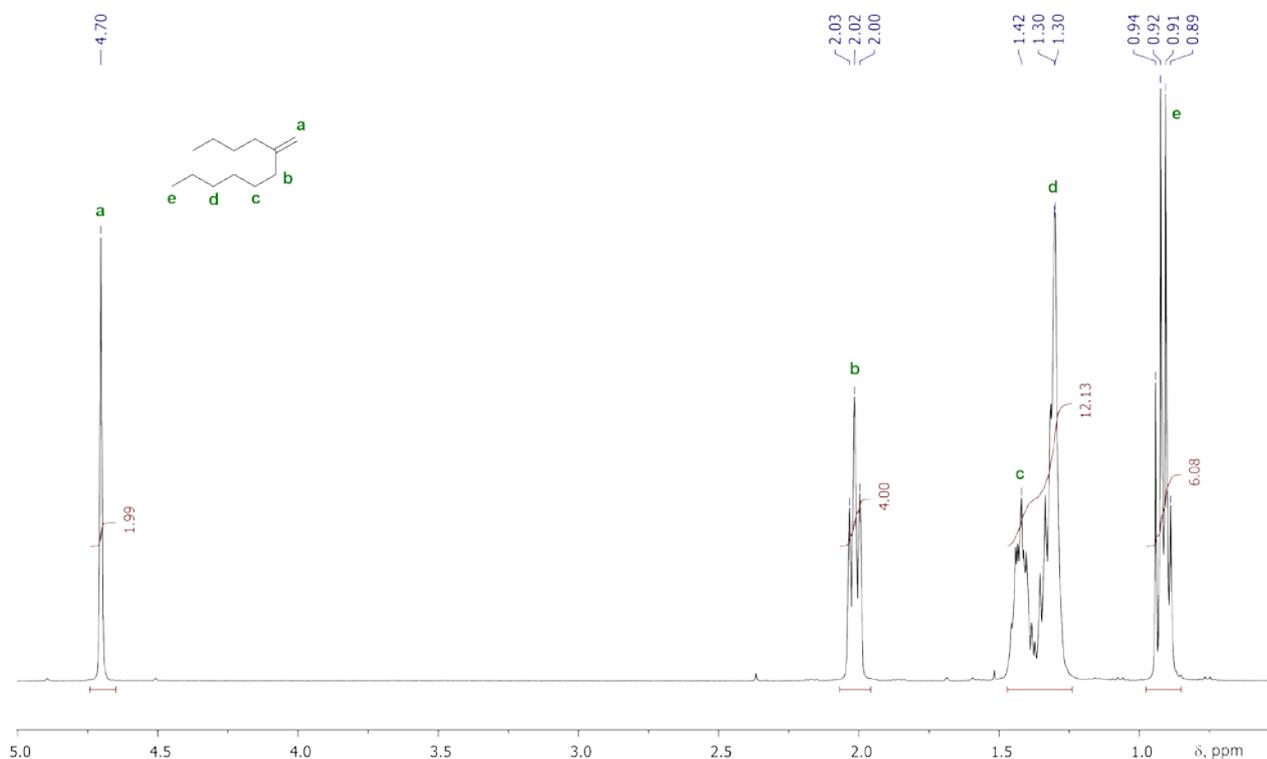
Elemental analysis (C, H) was performed on a Perkin Elmer Series II CHNS/O Analyzer 2400.

## S2. Synthesis and NMR spectra of $\alpha$ -olefin dimers 1a–e

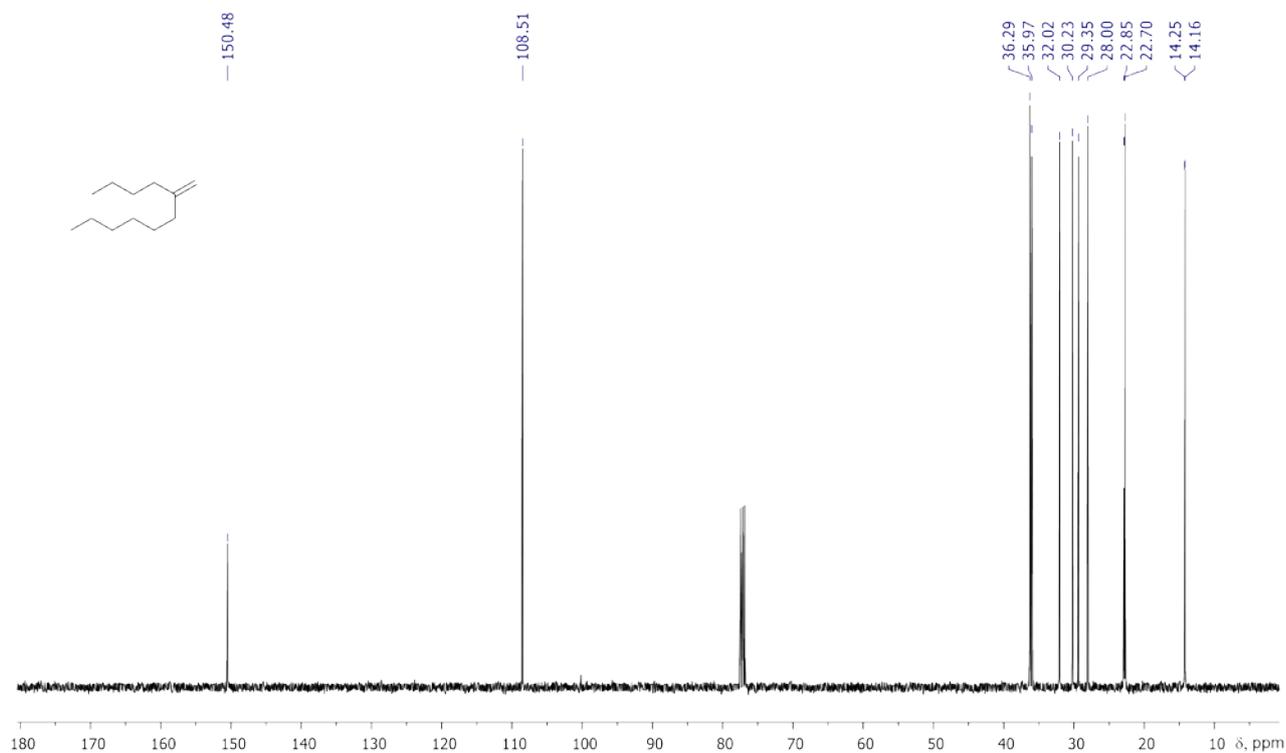
### 5-Methylideneundecane (**1a**).

Triisobutylaluminium solution (1 M in hexane, 5 ml, 5 mmol) and  $[\text{O}(\text{SiMe}_2\text{Cp})_2]\text{ZrCl}_2$  (106 mg, 0.25 mmol) were added at 60 °C to hex-1-ene (84.2 g, 1 mol). After 20 min of stirring,  $\text{Et}_2\text{AlCl}$  (1 M in hexane, 0.5 ml, 0.25 mmol) and MMAO-12 (1.25 M in toluene, 2.0 ml, 2.5 mmol) were added. After 6 h of stirring, the mixture was cooled to room temperature, methanol (5 ml) and water (2 ml) were added. After 10 min of stirring,  $\text{Na}_2\text{SO}_4$  (5 g) was added, and the mixture was stirred for additional 10 min. After that, the mixture was filtered through a layer of silica, and distilled under reduced pressure. B.p. 103-105 °C/10 Torr. The yield was 79.1 g (94%), colourless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , 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).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ,  $\delta$ , 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. GC data: >98% of the main compound.

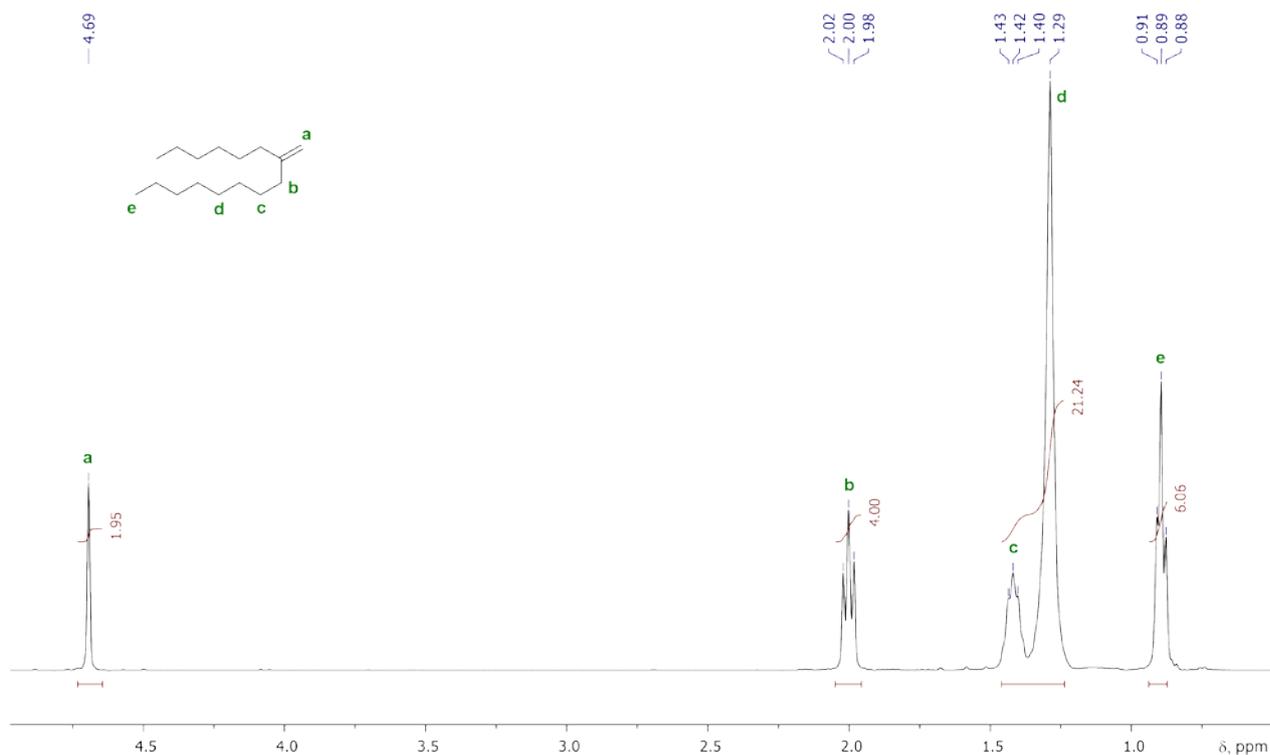


**Figure S1.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 20 °C, 400 MHz) of 5-methylideneundecane (**1a**)

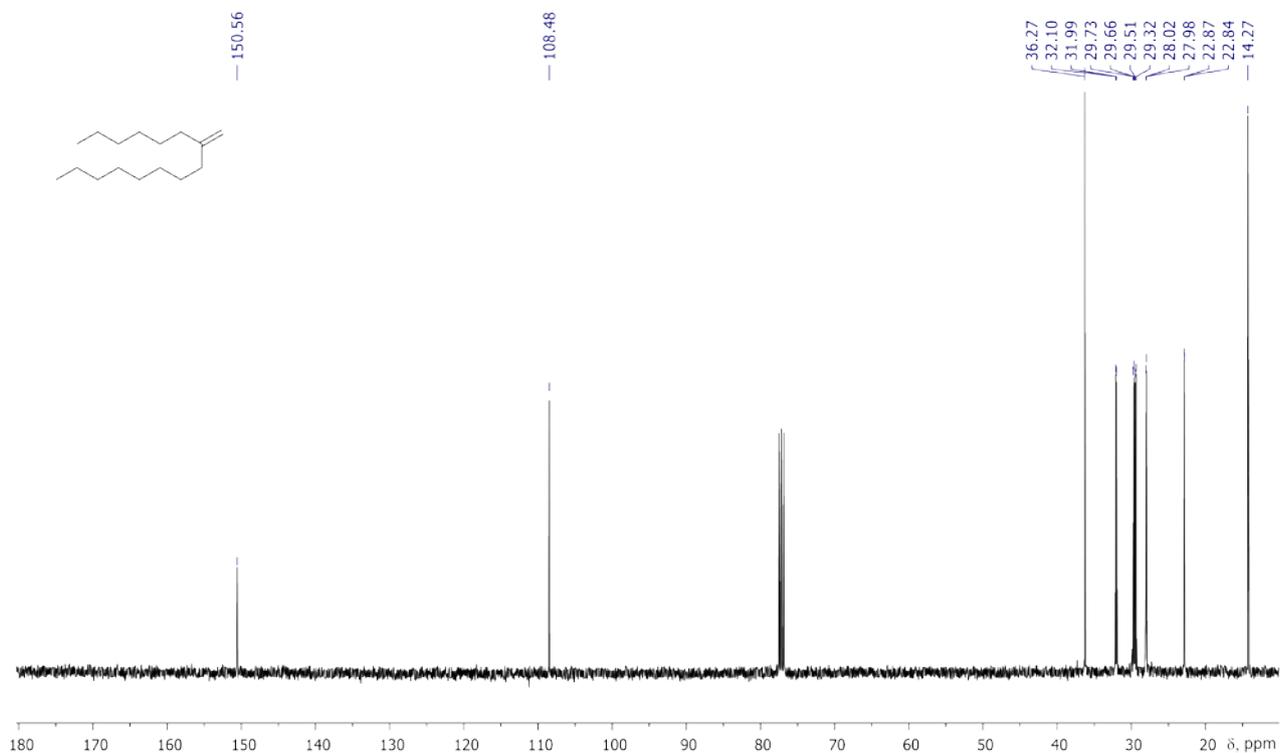


**Figure S2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (CDCl<sub>3</sub>, 20 °C, 101 MHz) of 5-methylideneundecane (**1a**)

7-Methylidenepentadecane (**1b**) was prepared from oct-1-ene (28.1 g, 0.25 mol) similarly to **1a**. B.p. 112 °C (7 Torr). The yield was 26.4 g (94%), colourless liquid.  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.69 (s, 2H), 2.00 (t, 4H), 1.42 (m, 4H), 1.29 (br, 16H), 0.89 (t,  $^3J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  150.56; 108.48; 36.27; 32.10; 31.99; 29.73; 29.66; 29.51; 29.32; 28.02; 27.98; 22.87; 22.84; 14.27. GC data: >98% of the main compound.

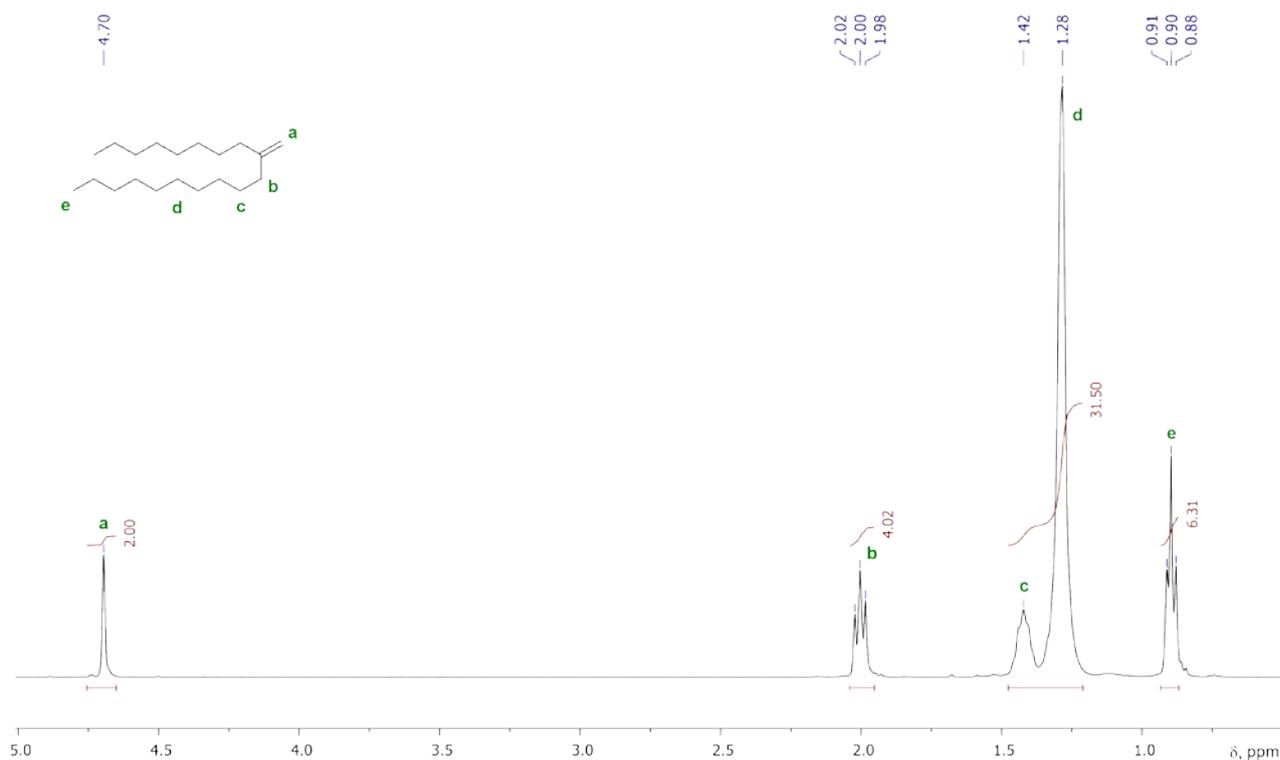


**Figure S3.**  $^1\text{H}$  NMR spectrum (CDCl<sub>3</sub>, 20 °C, 400 MHz) of 7-methylidenepentadecane (**1b**)

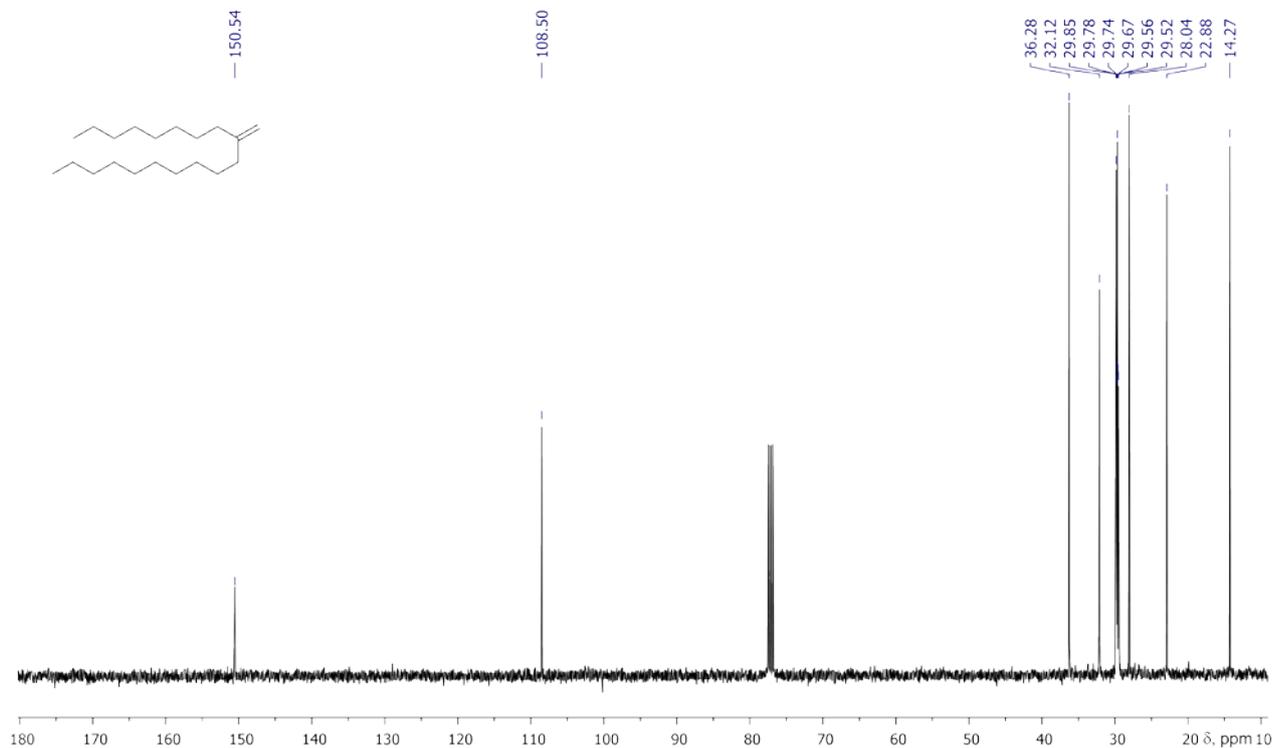


**Figure S4.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ , 20 °C, 101 MHz) of 7-methylidenepentadecane (**1b**)

9-Methylidenenonadecane (**1c**) was prepared from dec-1-ene (35.1 g, 0.25 mol) similarly to **1a**. B.p. 122-125 °C/0.5 Torr. The yield was 32.3 g (92%), colourless liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 4.70 (s, 2H); 2.00 (t, (d,  $^3J = 7.6$  Hz, 4H); 1.42 (m, 4H); 1.28 (br., 28H); 6.37 (t,  $^3J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ,  $\delta$ , 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). GC data: >97%.

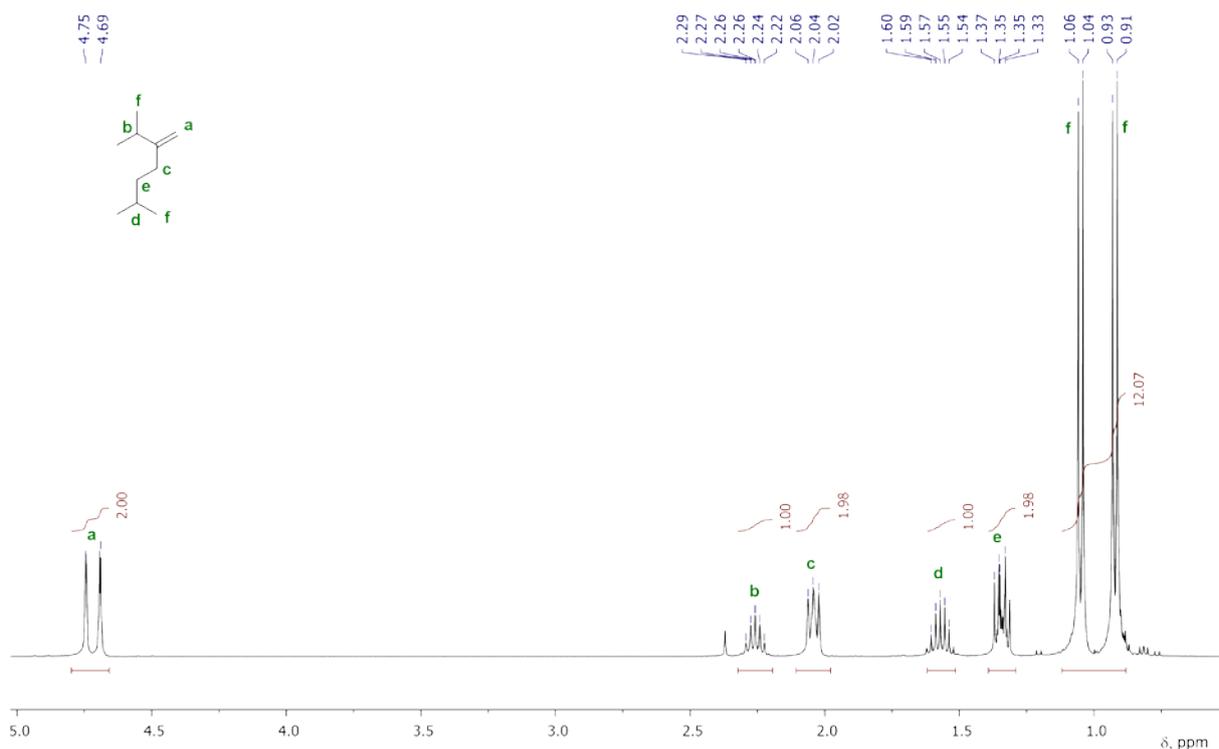


**Figure S5.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 20 °C, 400 MHz) of 9-methylidenenonadecane (**1c**)

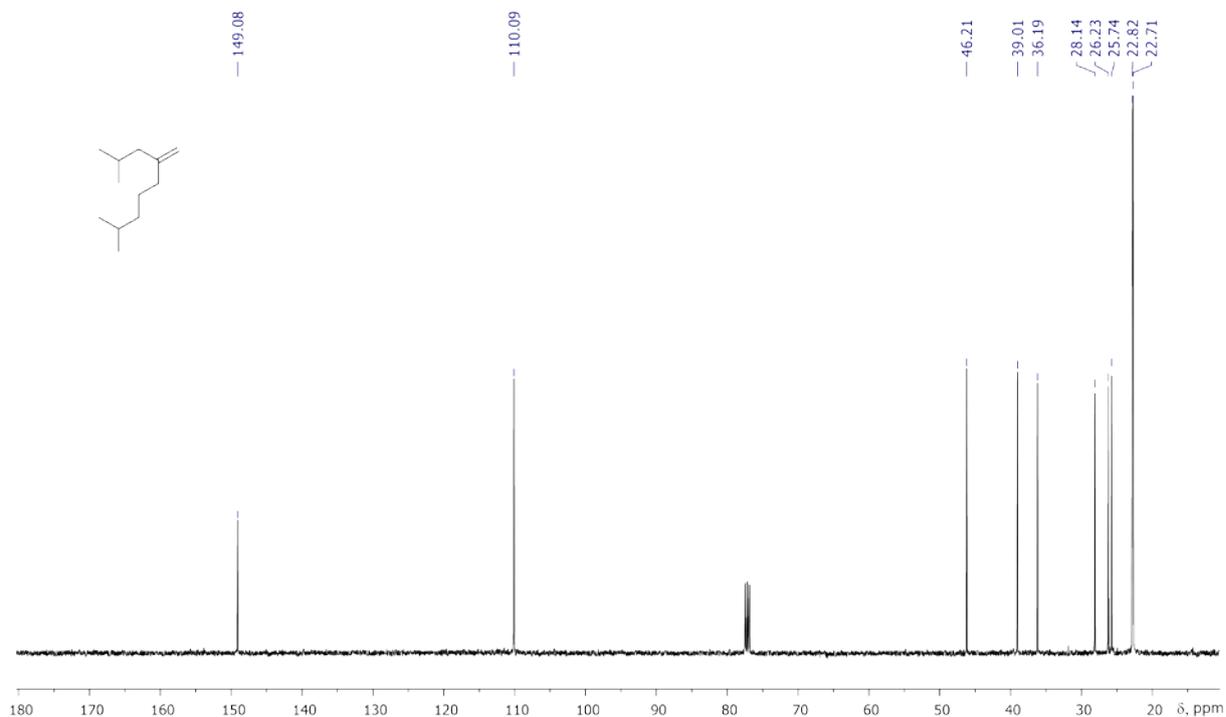


**Figure S6.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (CDCl<sub>3</sub>, 20 °C, 101 MHz) of 9-methylenenonadecane (1c)

2,6-Dimethyl-3-methylideneheptane (1d) was prepared from 3-methylbut-1-ene (35.1 g, 0.5 mol) similarly to 1a at 50 °C (12 h). B.p. 42-44 °C/10 Torr. The yield was 27.4 g (78%), colourless liquid.  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 4.75 (s, 1H); 4.70 (s, 1H); 2.26 (sept,  $^3J = 6.7$  Hz, 1H); 2.04 (m, 2H); 1.57 (sept,  $^3J = 6.7$  Hz, 1H); 1.35 (m, 2H); 1.05 (d,  $^3J = 6.7$  Hz, 6H); 0.92 (d,  $^3J = 6.7$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 156.66; 106.12; 37.75; 33.97; 32.48; 28.17; 22.78 (2C); 22.08 (2C). GC data: >95% of the main compound. Contains ~ 3% of the reduction product.

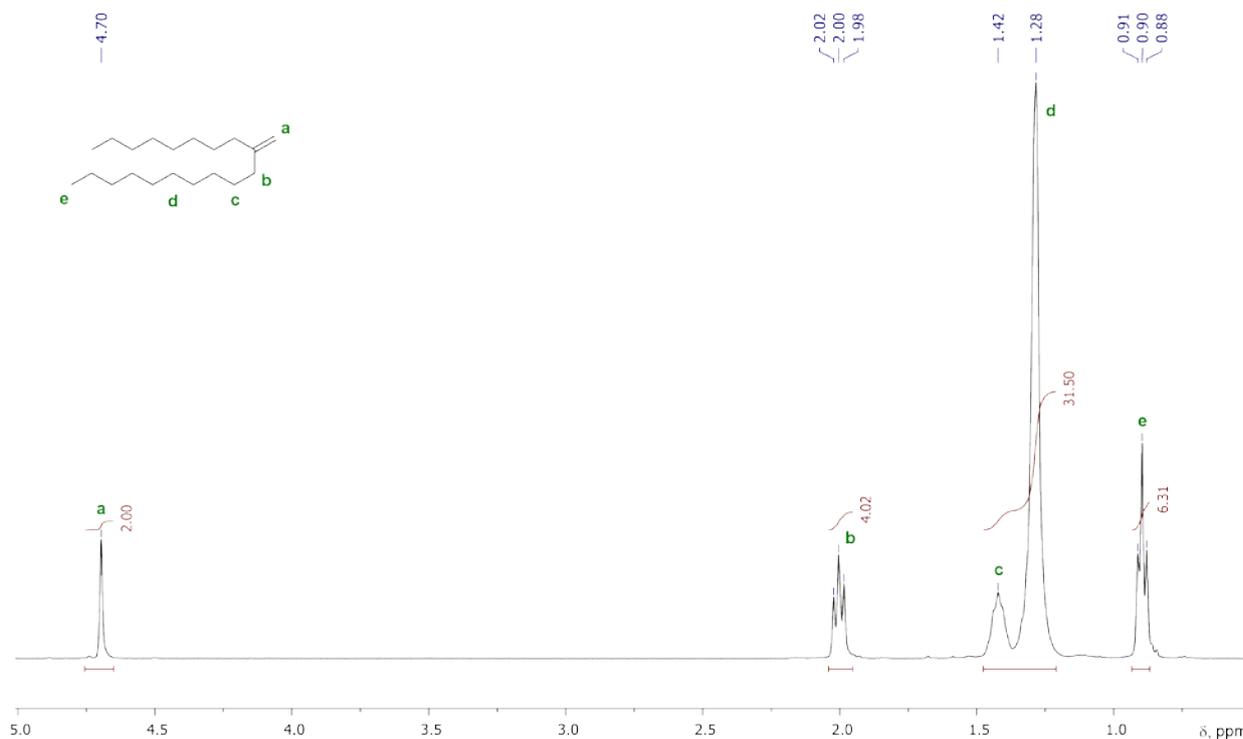


**Figure S7.**  $^1\text{H}$  NMR spectrum (CDCl<sub>3</sub>, 20 °C, 400 MHz) of 2,6-dimethyl-3-methylideneheptane (1d)

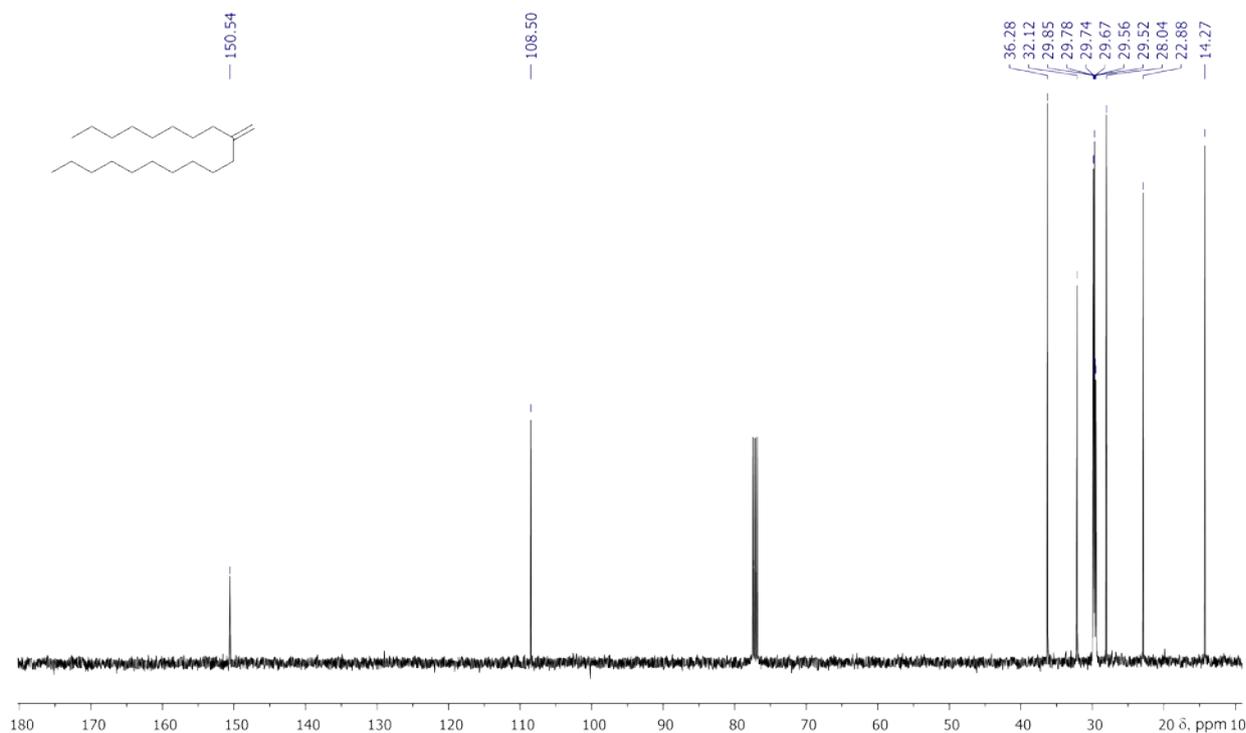


**Figure S8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ , 20 °C, 101 MHz) of 2,6-dimethyl-3-methylideneheptane (**1d**)

2,8-Dimethyl-4-methylidenenonane (**1e**) was prepared from 4-methylpent-1-ene (21.1 g, 0.25 mol) similarly to **1a**. B.p. 100-102 °C/10 Torr. The yield was 19.4 g (92%), colourless liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , 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).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 149.08, 110.09, 46.21, 39.01, 36.19, 28.14, 26.23, 25.74, 22.82, 22.71. GC data: >98%.

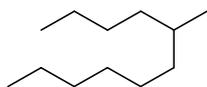


**Figure S9.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 20 °C, 400 MHz) of 2,8-dimethyl-4-methylidenenonane (**1e**)



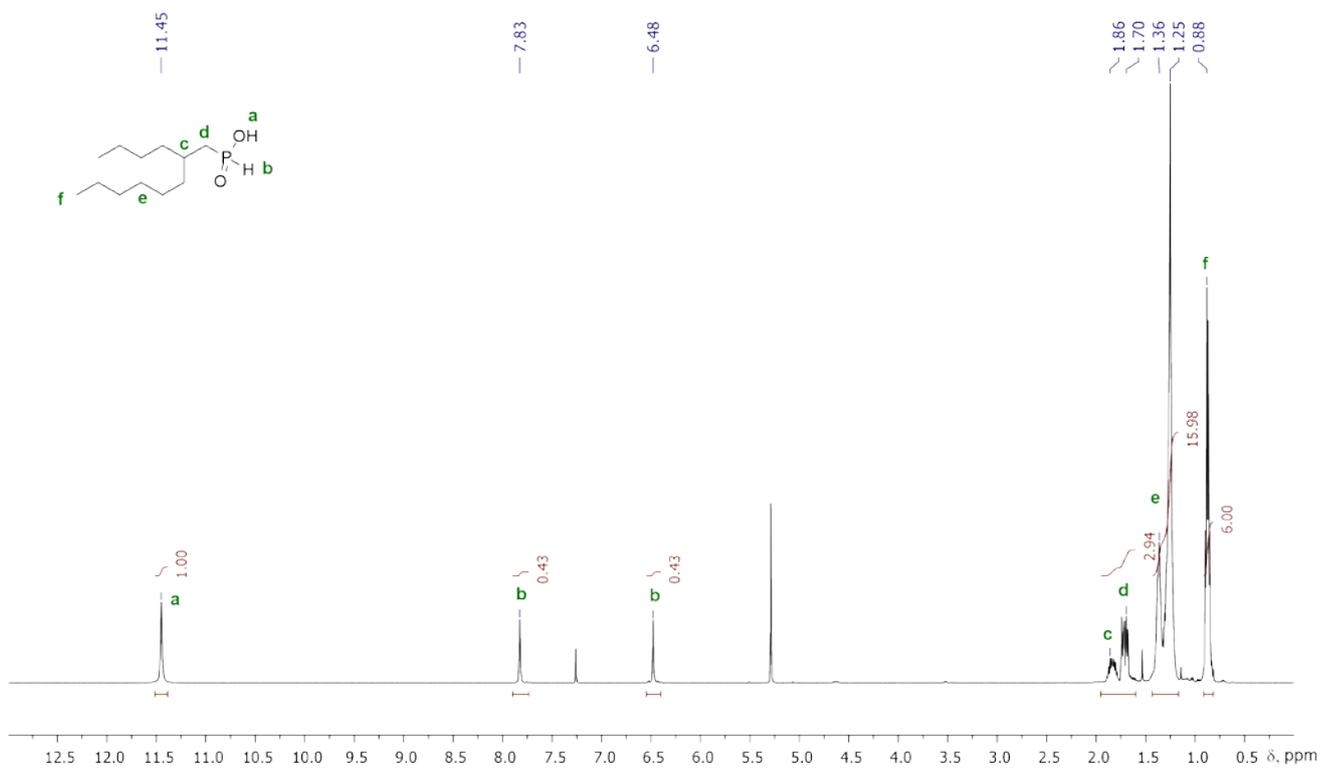
**Figure S10.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 20 °C, 101 MHz) of 2,8-dimethyl-4-methylidenenonane (**1e**)

### S3. Synthesis and NMR spectra of phosphinic acids 2a–e

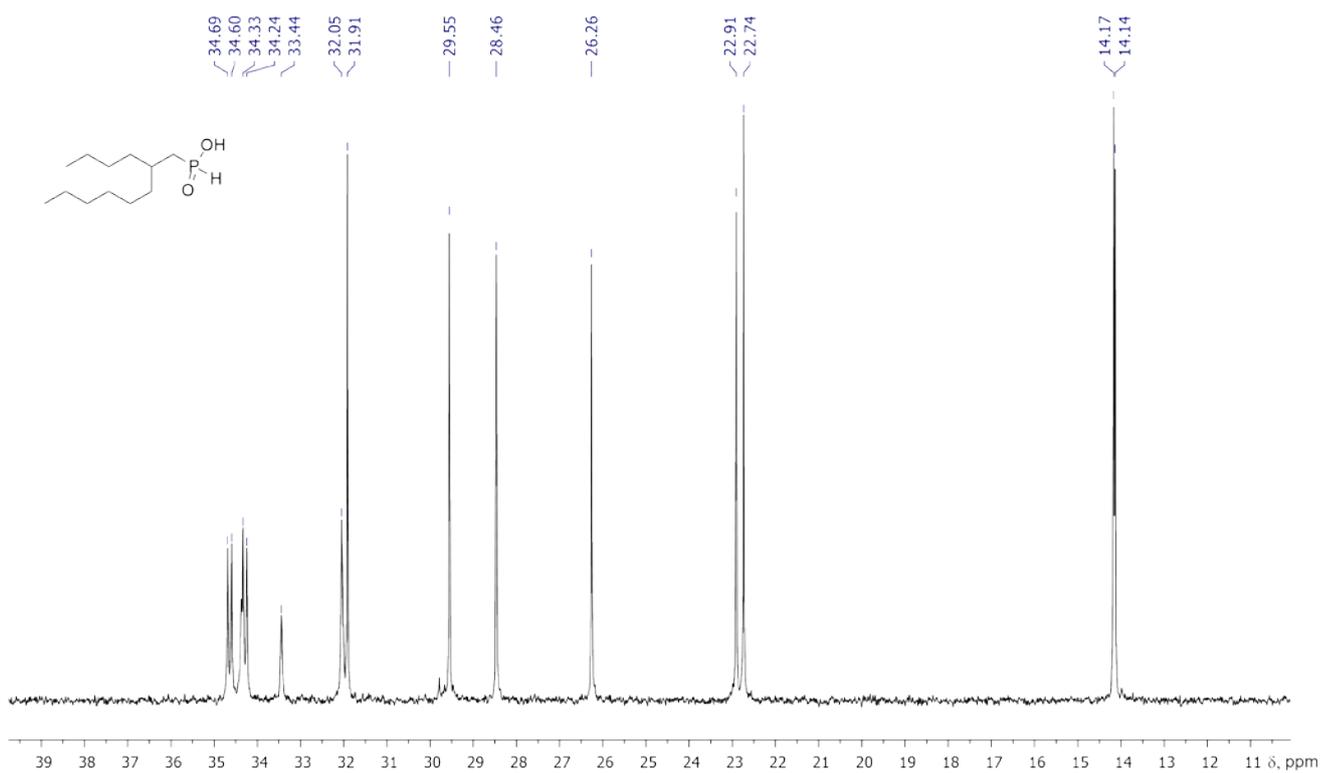


(*2-Butyloctyl*)phosphinic acid (**2a**). A mixture of 5-methylideneundecane **1a** (11.1 g, 66 mmol), 50% aq.  $\text{H}_3\text{PO}_2$  (14.5 ml, 264 mmol) and *i*-PrOH (80 ml) was degassed under reduced pressure, filled with argon, and heated to 90 °C with stirring. AIBN was added in 7×100 mg portions within 3 h with 30 min intervals. The mixture was allowed to cool to room temperature and diluted with pentane (100 ml). The organic layer was washed with water (3×100 ml), dried over  $\text{Na}_2\text{SO}_4$  and evaporated. The residue was purified by gradient column chromatography (silica 60-200, por. 40) using  $\text{CH}_2\text{Cl}_2$ –MeOH mixture (from 100:1 to 1:1 by volume). Oily product was dried *in vacuo*. The yield was 12.4 g (80%).

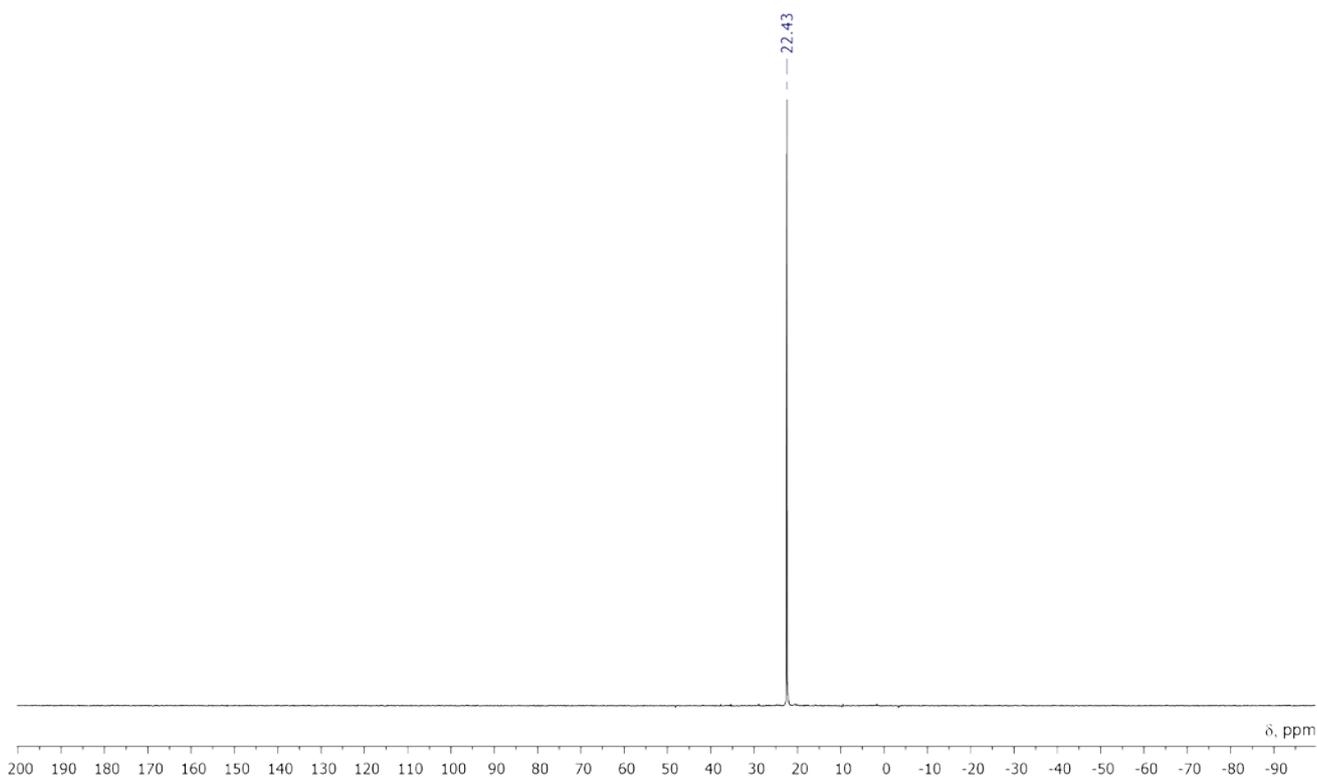
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 11.45 (s, 1H, P–OH); 7.83 & 6.48 (d,  $^1J = 540$  Hz, P–H); 1.83 (m, 1H, >CH–); 1.74–1.68 (mm, 2H, P– $\underline{\text{CH}_2}$ ); 1.36 (m, 4H, >CH– $\underline{\text{CH}_2}$ ); 1.25 (br, – $\text{CH}_2$ –); 0.88 (t,  $^3J = 6.4$  Hz, 3H); 0.87 (t,  $^3J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ,  $\delta$ , 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.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 22.43.



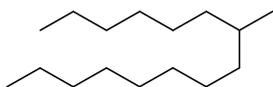
**Figure S11.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 20 °C, 400 MHz) of (2-butyloctyl)phosphinic acid (2a)



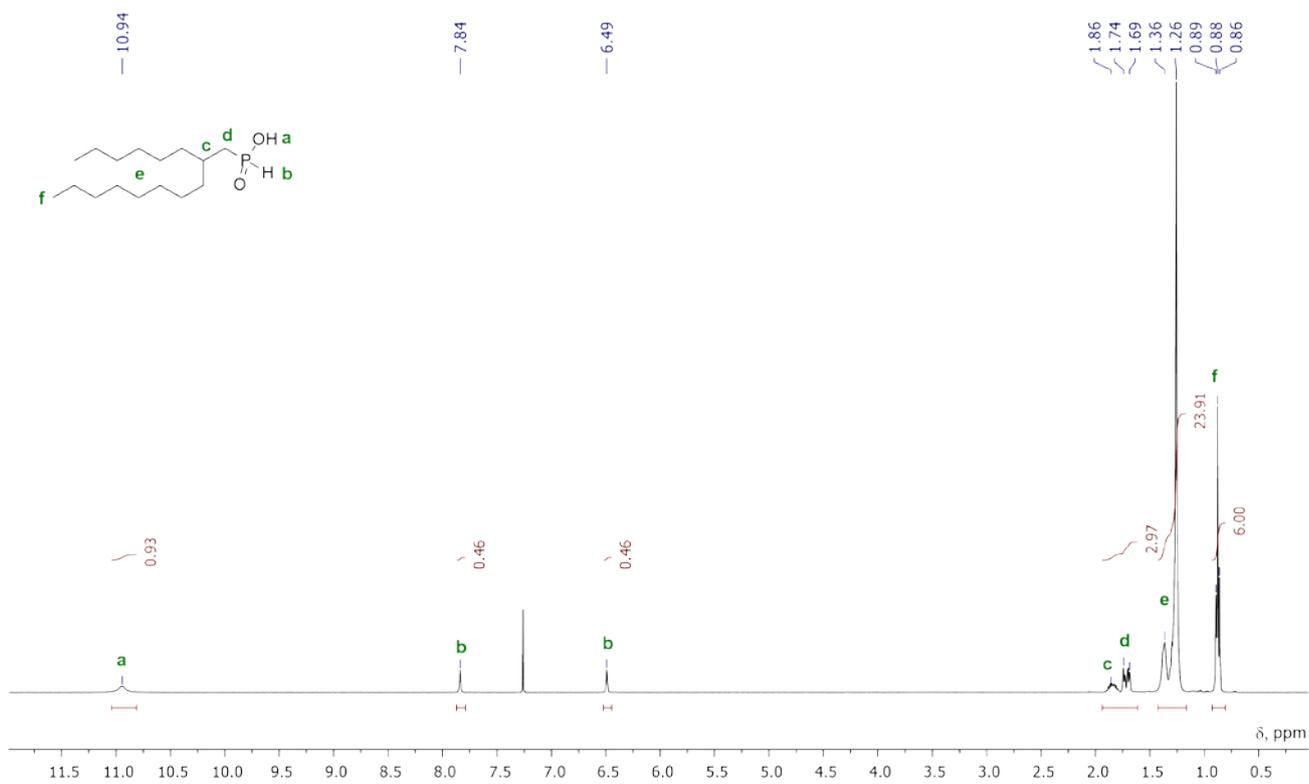
**Figure S12.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CDCl<sub>3</sub>, 20 °C, 101 MHz) of (2-butyloctyl)phosphinic acid (2a)



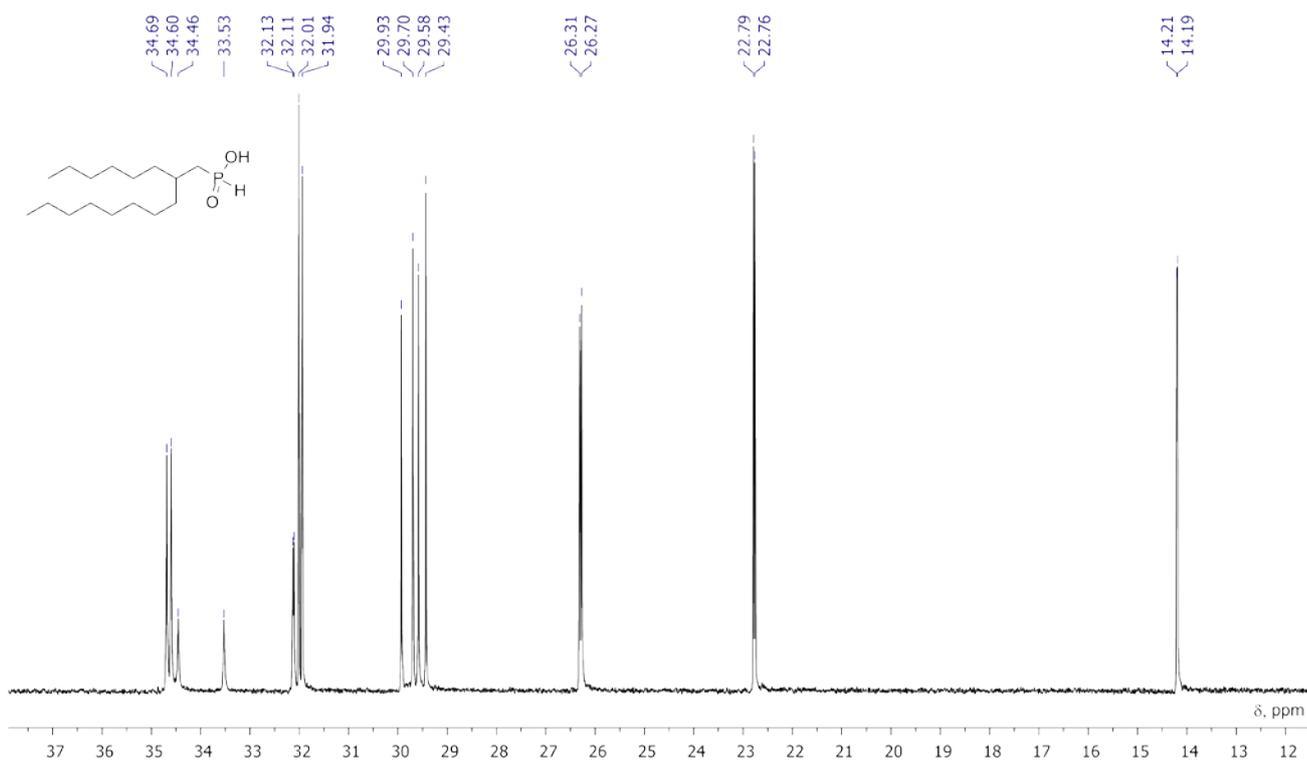
**Figure S13.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ , 20 °C, 162 MHz) of (2-butyloctyl)phosphinic acid (**2a**)



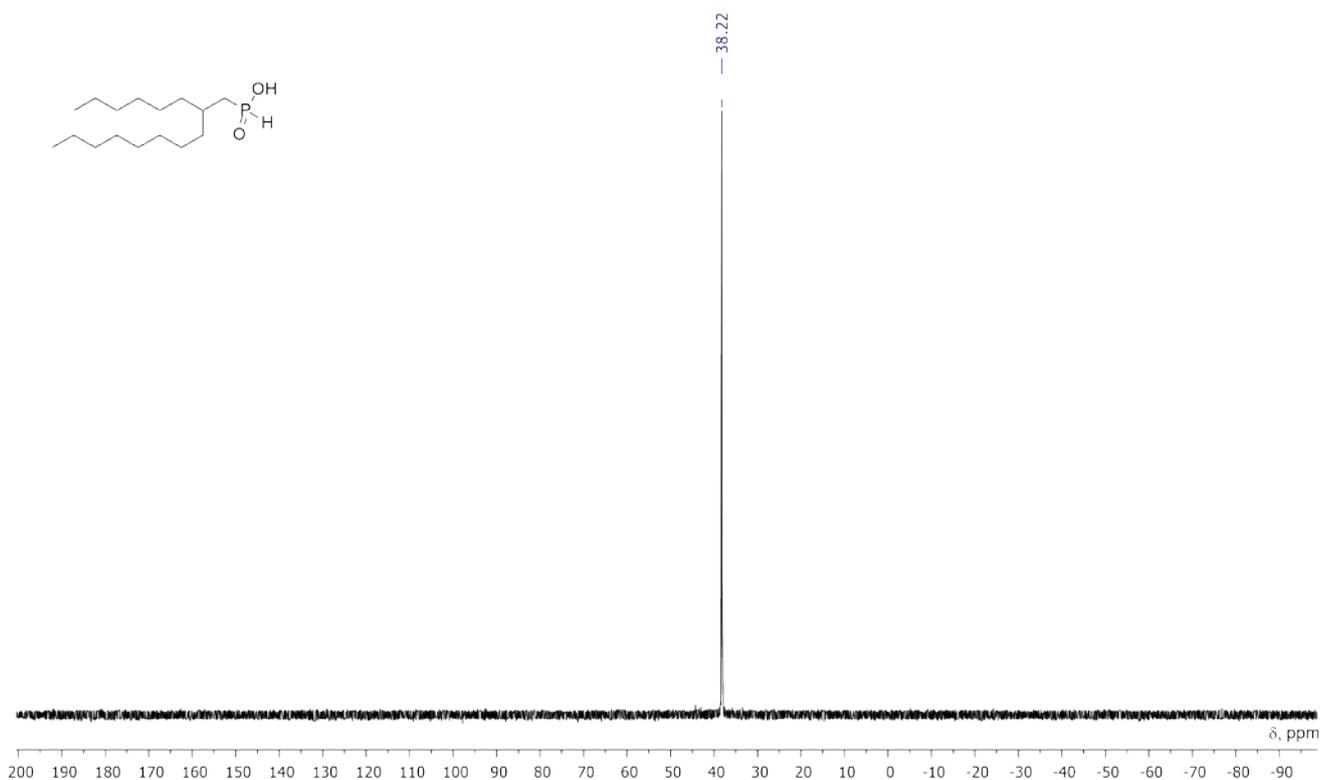
(2-Hexyldecyl)phosphinic acid (**2b**) was prepared similarly to **2a** from 7-methylidenepentadecane **1b** (11.21 g, 50 mmol). The yield was 12.9 g (89%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 10.94 (s, 1H, P-OH); 7.84 & 6.49 (d,  $^1J = 540$  Hz, P-H); 1.86 (m, 1H, >CH-); 1.74-1.69 (dd,  $^2J_{\text{H-P}} = 16.5$  Hz,  $^3J = 6.6$  Hz, 2H, P- $\text{CH}_2$ ); 1.36 (m, 4H, >CH- $\text{CH}_2$ ); 1.26 (br, 24H, - $\text{CH}_2$ -); 0.88 (t,  $^3J = 6.6$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 34.64 (d,  $^3J = 9.5$  Hz, 2C); 34.46 & 33.53 (d,  $^1J = 93.9$  Hz); 32.12 (d,  $^2J = 2.5$  Hz); 32.01; 31.94; 29.93; 29.70; 29.58; 29.43; 26.31; 26.27; 22.79; 22.76; 14.21; 14.19.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 38.22. Anal. calcd for  $\text{C}_{16}\text{H}_{35}\text{O}_2\text{P}$  (%): C, 66.17; H, 12.15; O, 11.02. Found: C, 66.26; H, 12.20; O, 10.92.



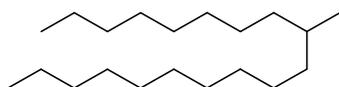
**Figure S14.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 20 °C, 400 MHz) of (2-hexyldecyl)phosphinic acid (**2b**)



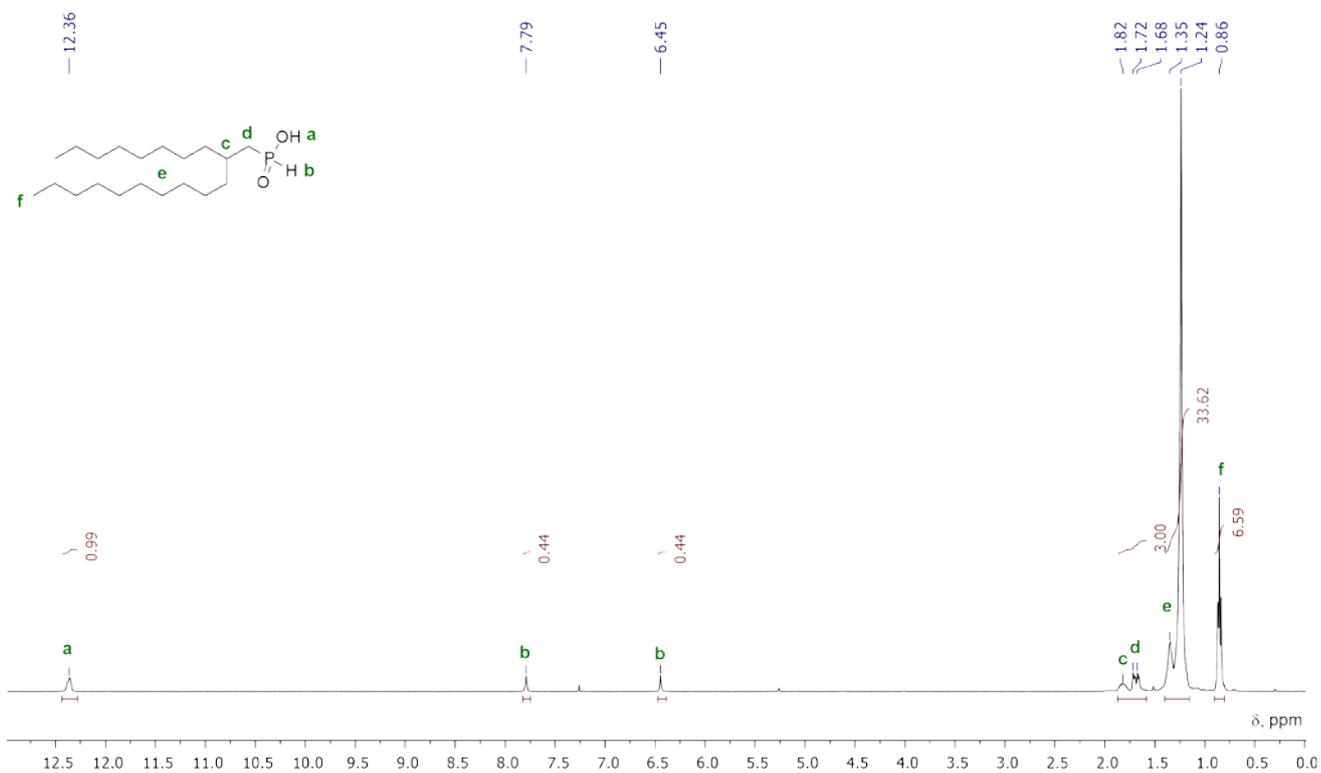
**Figure S15.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 20 °C, 101 MHz) of (2-hexyldecyl)phosphinic acid (**2b**)



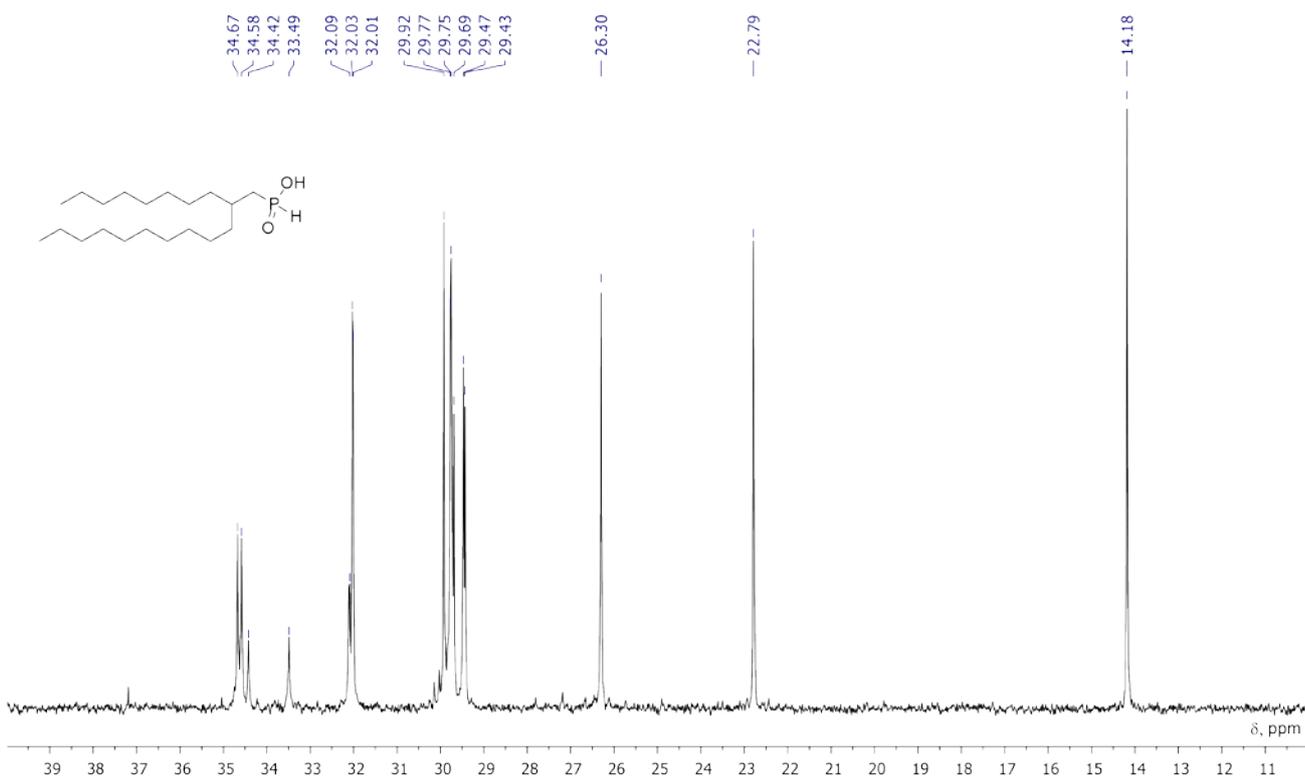
**Figure S16.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ , 20 °C, 162 MHz) of (2-hexyldecyl)phosphinic acid (**2b**)



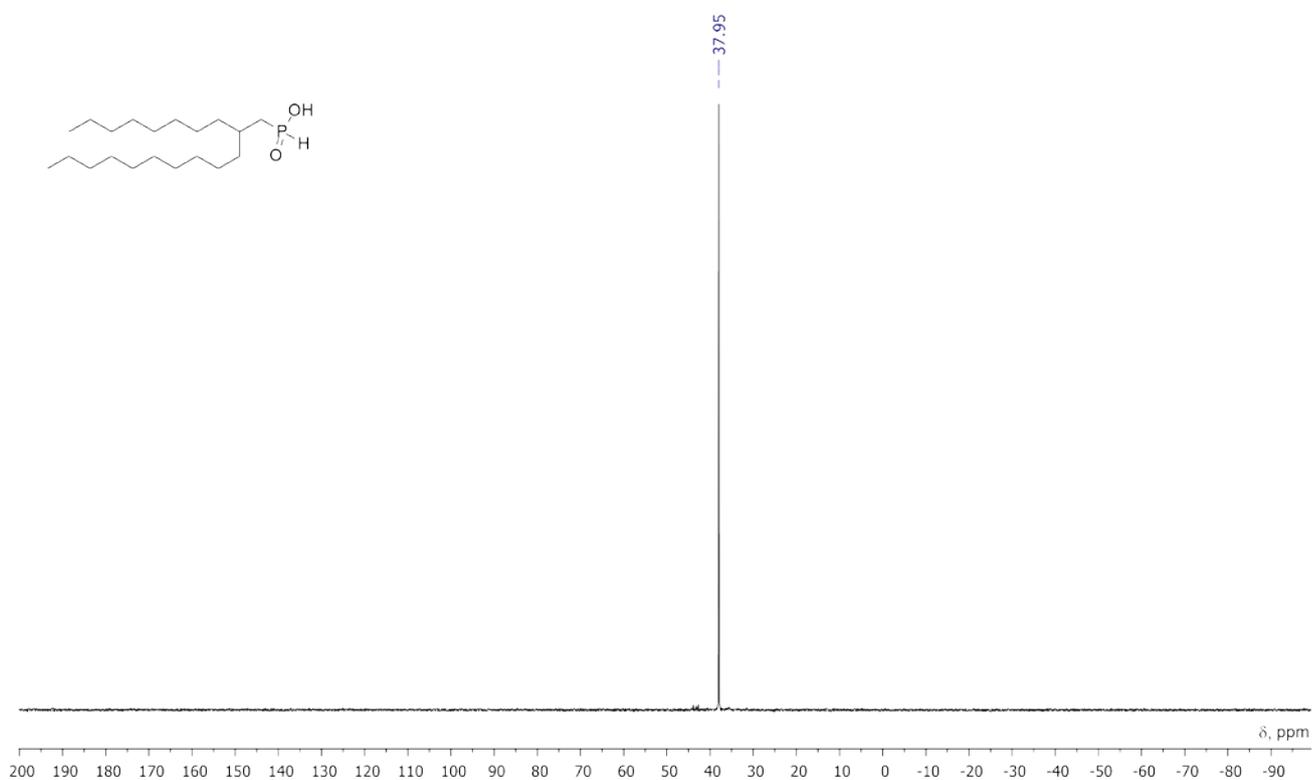
(2-Octyldodecyl)phosphinic acid (**2c**) was prepared similarly to **2a** from 9-methylidenenonadecane **1c** (18.6 g, 66 mmol). The yield was 20.8 g (91%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 12.38 (s, 1H, P–OH); 7.79 & 6.45 (d,  $^1J = 538$  Hz, P–H); 1.83 (m, 1H, >CH–); 1.71–1.66 (dd,  $^2J_{\text{H-P}} = 16.5$  Hz,  $^3J = 6.7$  Hz, 2H, P–CH<sub>2</sub>); 1.35 (m, 4H, >CH–CH<sub>2</sub>); 1.25 (br, 28H, –CH<sub>2</sub>–); 0.88 (t,  $^3J = 6.7$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 34.62 (d,  $^3J = 9.5$  Hz, 2C); 34.42 & 33.49 (d,  $^1J = 93.8$  Hz); 32.10 (d,  $^2J = 2.6$  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).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 37.95.



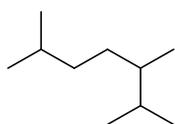
**Figure S17.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 20 °C, 400 MHz) of (2-octyldodecyl)phosphinic acid (**2c**)



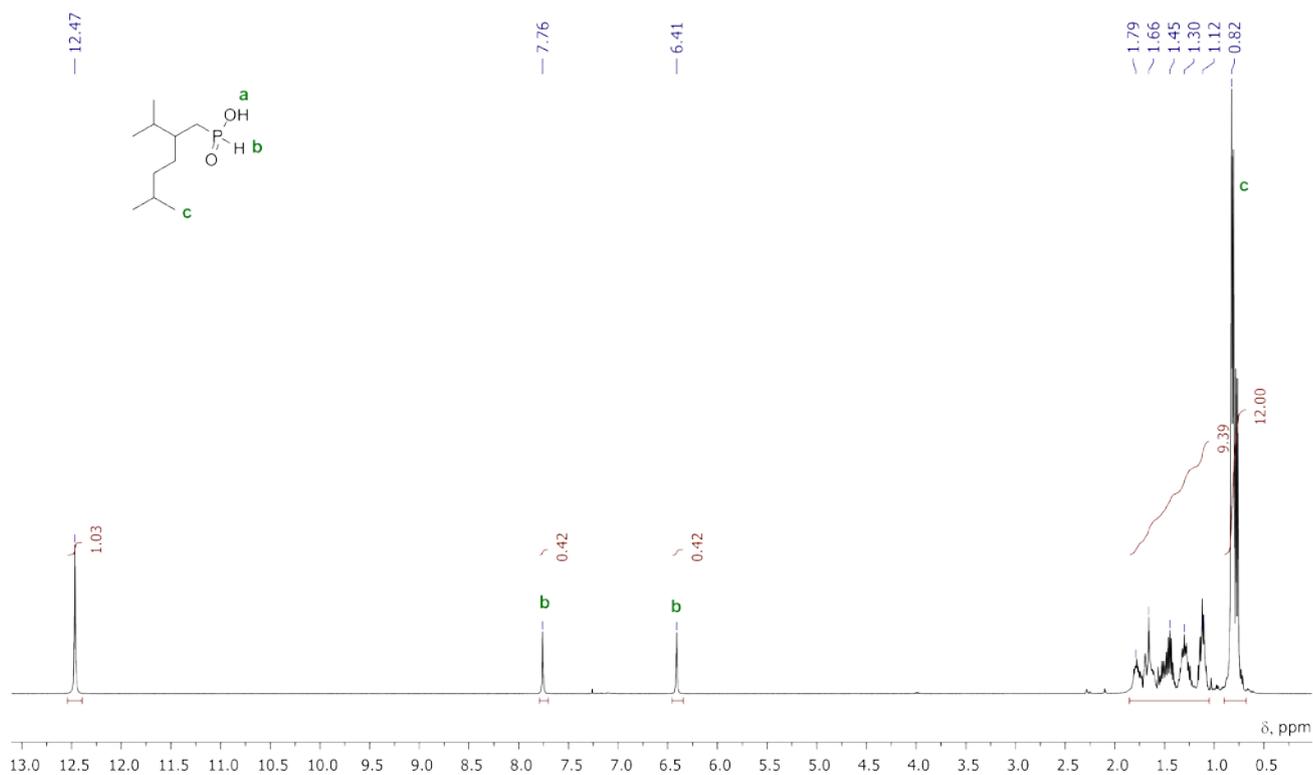
**Figure S18.** <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 20 °C, 101 MHz) of (2-octyldodecyl)phosphinic acid (**2c**)



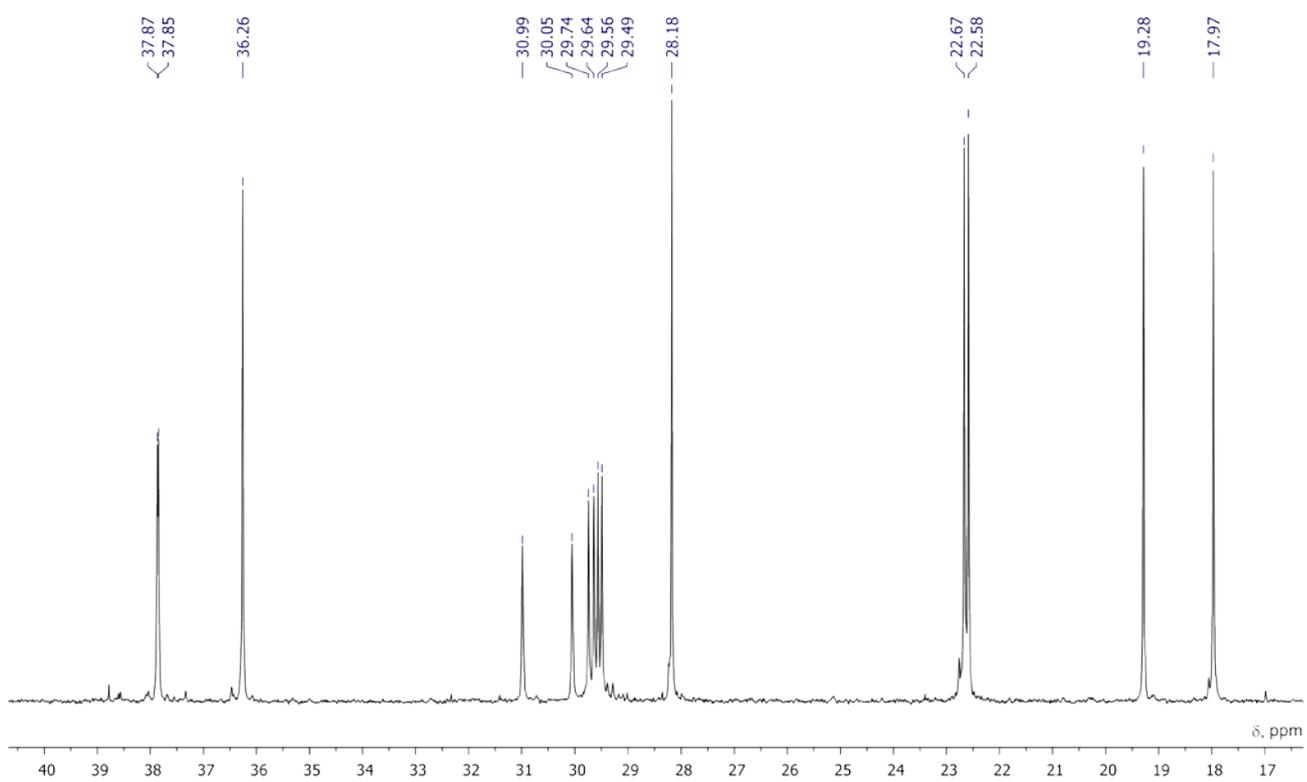
**Figure S19.**  $^{31}\text{P}$  NMR spectrum ( $\text{CDCl}_3$ , 20 °C, 162 MHz) of (2-octyldodecyl)phosphinic acid (**2c**)



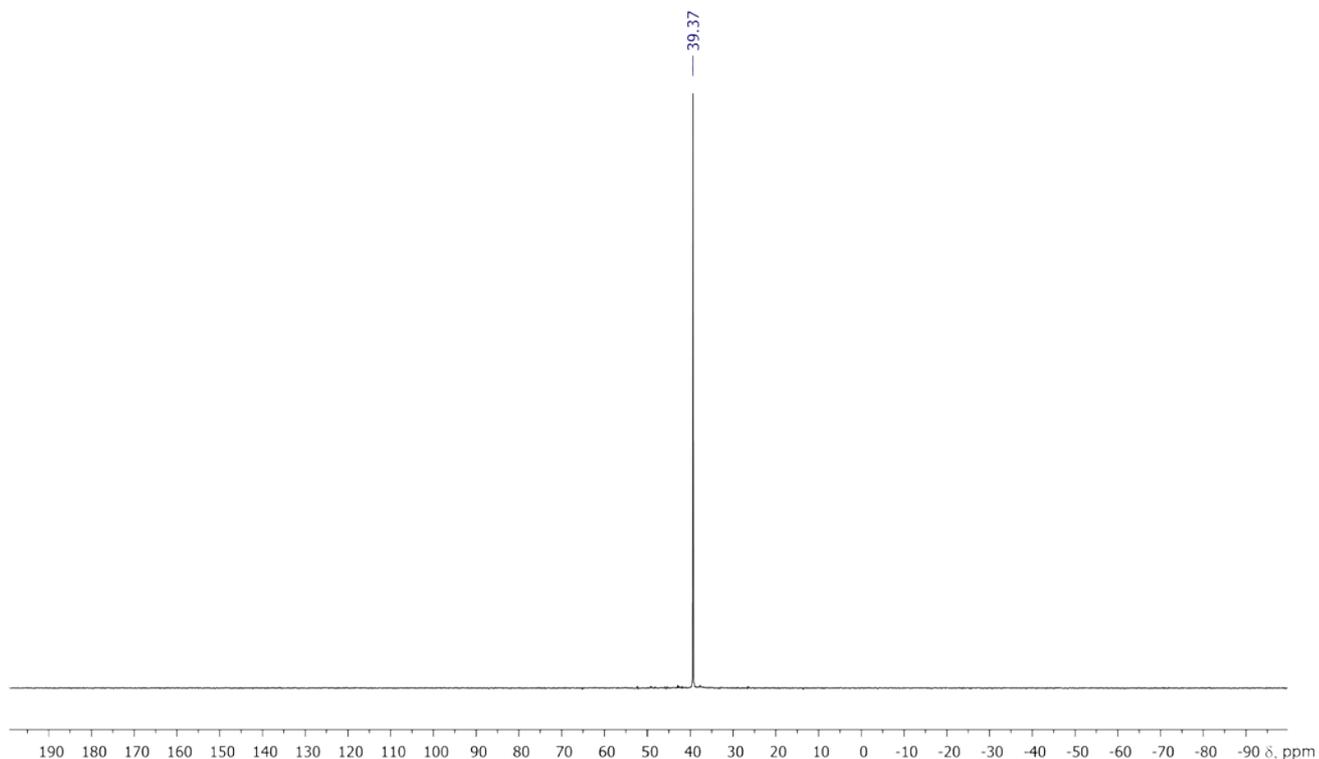
(2-Isopropyl-5-methylhexyl)phosphinic acid (**2d**) was prepared similarly to **2a** from 2,6-dimethyl-3-methylideneheptane **1d** (9.26 g, 66 mmol). The yield was 10.4 g (76%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 10.68 (s, 1H, P–OH); 7.83 & 6.48 (d,  $^1J = 540$  Hz, P–H); 1.83 (m, 1H, >CH–); 1.78-1.10 (group m, 8H); 0.87-0.81 (group d, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 37.86 (d,  $J = 2.4$  Hz); 36.26; 30.99 & 30.05 (d,  $^1J = 94.0$  Hz); 29.69 (d,  $^2J = 10.4$  Hz); 29.52 (d,  $^2J = 6.8$  Hz); 28.18; 22.67; 22.58; 19.28; 17.97.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 39.37.



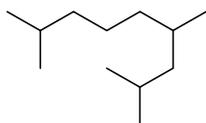
**Figure S20.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of (2-isopropyl-5-methylhexyl)phosphinic acid (**2d**)



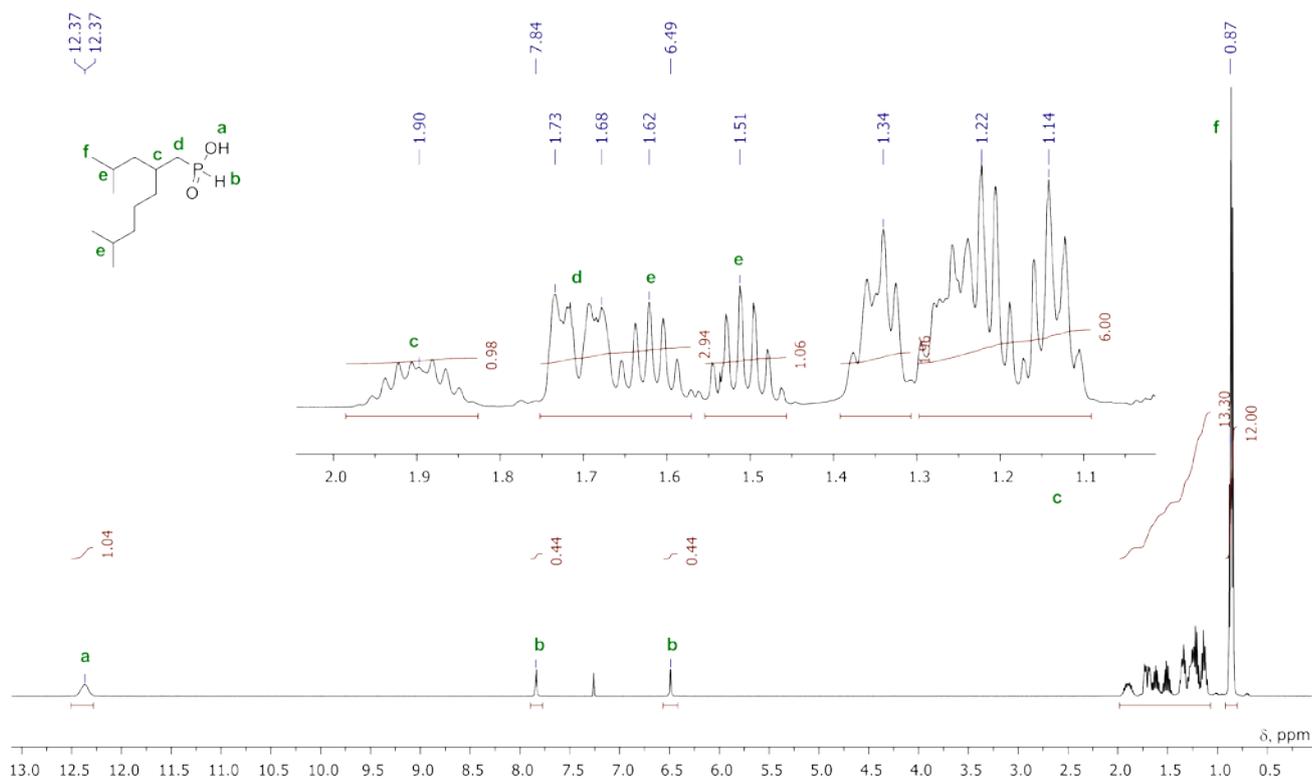
**Figure S21.** <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of (2-isopropyl-5-methylhexyl)phosphinic acid (**2d**)



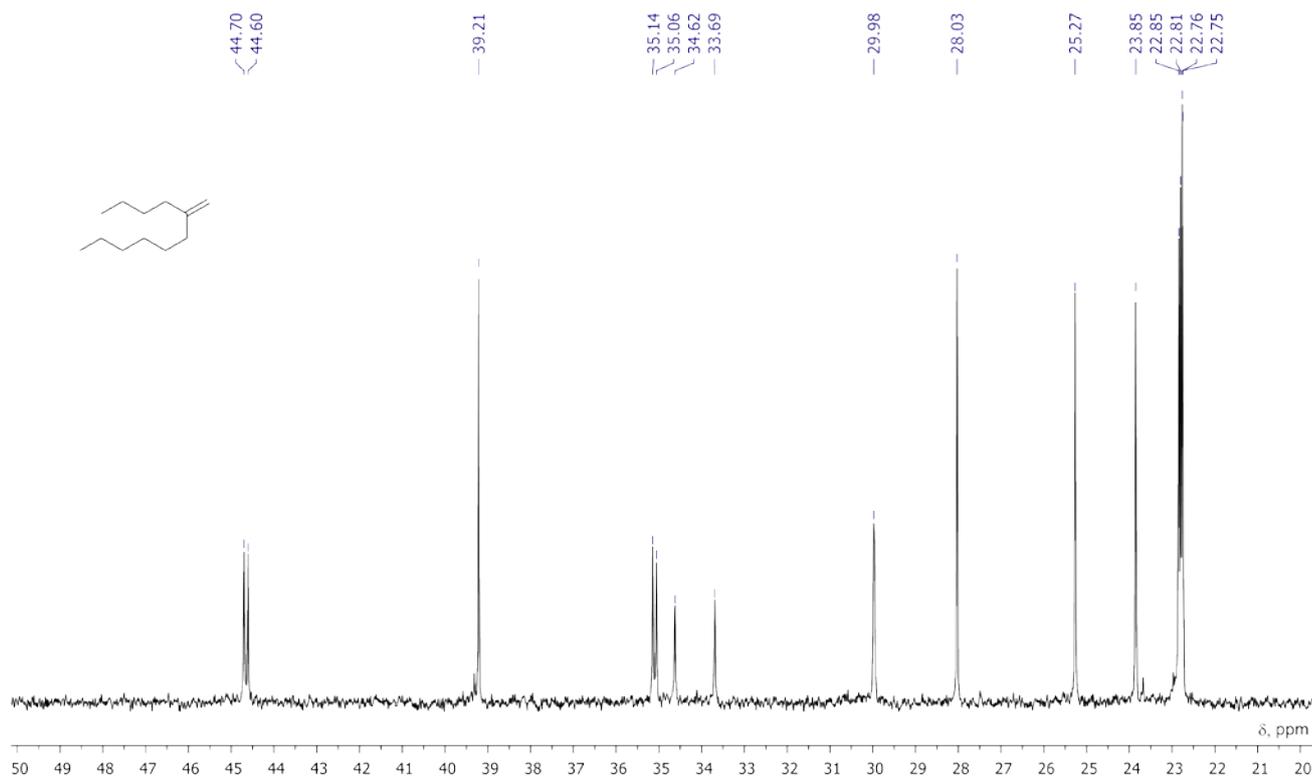
**Figure S22.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ) of (2-isopropyl-5-methylhexyl)phosphinic acid (**2d**)



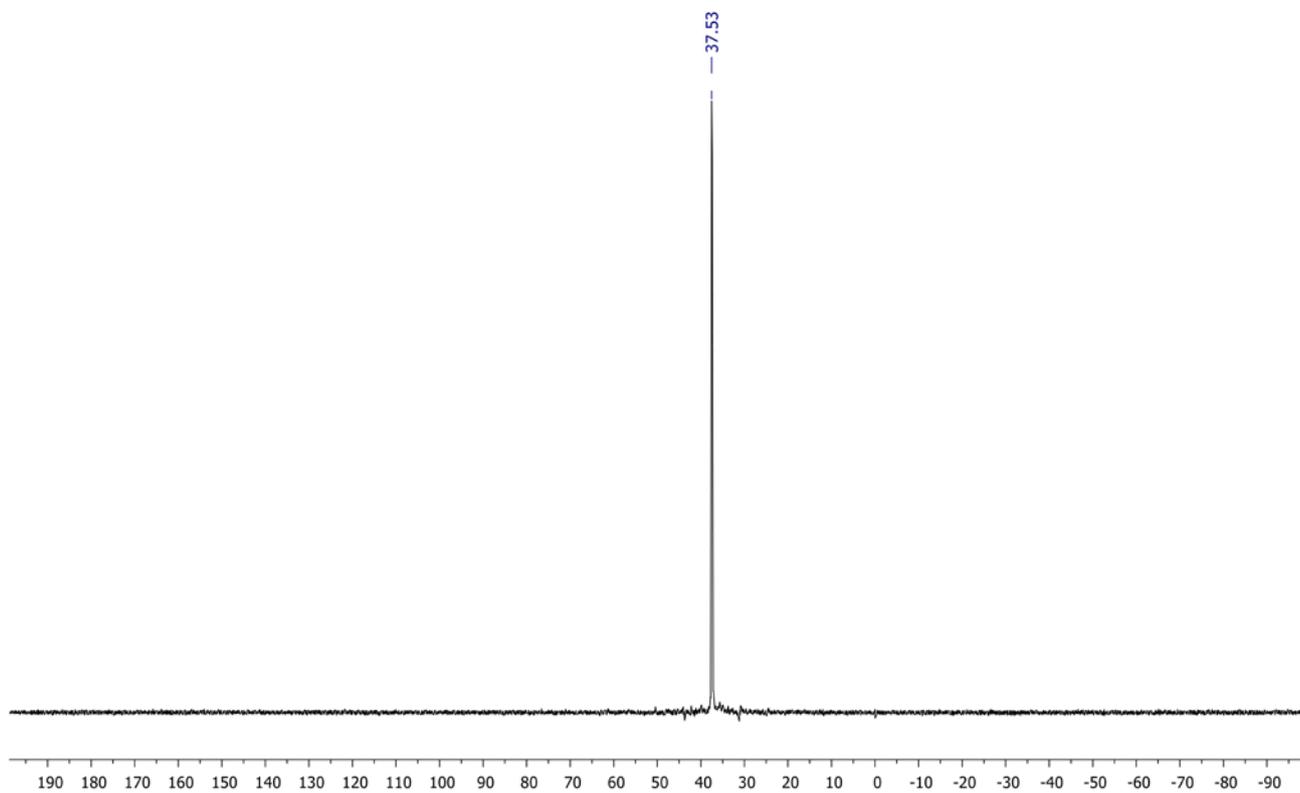
(2-Isobutyl-6-methylheptyl)phosphinic acid (**2e**) was prepared similarly to **2a** from 2,8-dimethyl-4-methylidenenonane **1e** (11.1 g, 66 mmol). The yield was 13.2 g (85%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 12.37 (s, 1H, P–OH); 7.84 & 6.49 (d,  $^1J = 539$  Hz, P–H); 1.95–1.85 (m, 1H, >CH–); 1.73–1.68 (dd,  $^2J_{\text{H-P}} = 16.7$  Hz,  $^3J = 7.7$  Hz, 2H, P–CH<sub>2</sub>); 1.62 (m, 1H); 1.51 (m, 1H); 1.38 – 1.10 (m, 8H); 0.88–0.84 (group d, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ,  $\delta$ , 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.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 37.53.



**Figure S23.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 20  $^\circ\text{C}$ , 400 MHz) of (2-isobutyl-6-methylheptyl)phosphinic acid (**2e**)



**Figure S24.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ , 20  $^\circ\text{C}$ , 101 MHz) of (2-isobutyl-6-methylheptyl)phosphinic acid (**2e**)



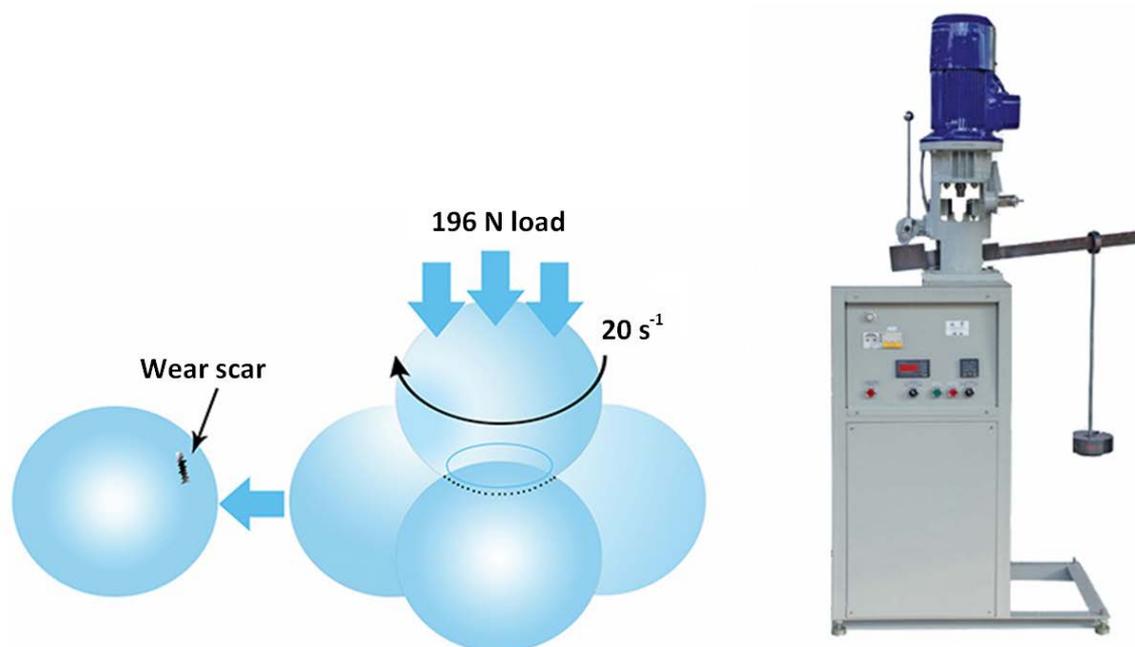
**Figure S25.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ , 20 °C, 162 MHz) of (2-isobutyl-6-methylheptyl)phosphinic acid (**2e**)

## S4. Anti-wear properties of compounds 2a–e

The solutions of **2a–e** were prepared by stirring of specified amounts of additives in base oils tested (Table S1) at 20 °C for 1 h. Four-ball tester ChMT-1 with 196 N load (Figure S26) was used for the determination of wear scar diameters. All experiments were conducted at 20 °C within 1 hour.

**Table S1** Viscosity of base oils used

Entry	Oil	Kinematic viscosity at 40 °C, cSt
1	DOS	11.4
2	PAO-4	18.5
3	PAB	23.5
5	PO	43.0
6	PMS-300	207.6



**Figure S26.** The common scheme of four-ball tester (left) and ChMT-1 equipment (right) used in our study