**Electronic supplementary materials** *Mendeleev Commun.*, 2022, **32**, 792–794

# Synthesis of alkyl-*H*-phosphinic acid alkyl esters from red phosphorus and alkyl bromides

**Pavel A. Volkov, Kseniya O. Khrapova, Anton A. Telezhkin, Svetlana F. Malysheva, Lyudmila I. Larina and Boris A. Trofimov**

All reactions were carried out under an argon atmosphere. Alkyl bromides are commercial reagents (Aldrich). Alkyl-*H*-phosphinic acids **1a,b** were prepared from alkyl bromides and elemental phosphorus as previously described.[S1,S2] The reaction was monitored using $^{31}$P NMR spectra by the disappearance of peaks of the initial alkyl-*H*-phosphinic acids.

The $^{1}$H, $^{13}$C, and $^{31}$P NMR spectra were recorded on a Bruker DPX 400 and Bruker AV-400 spectrometers (400.13, 100.62, and 161.98 MHz, respectively) in $CDCl_3$ solutions and referenced to HMDS ($^{1}$H, $^{13}$C) and $H_3PO_4$ ($^{31}$P). The assignment of signals in $^{1}$H spectra was performed using 2D homonuclear correlation method COSY. Resonance signals of $^{13}$C were assigned with application of 2D heteronuclear correlation methods HSQC and HMBC. FT-IR spectra were obtained with a Varian 3100 FT-IR spectrometer. The C, H microanalyses were performed on a Flash EA 1112 Series elemental analyzer. The P content was determined by combustion method.

**Reaction of red phosphorus with butyl bromide (general procedure)**. A mixture of red phosphorus (3.1 g, 100 mmol), CTAB (1.1 g, 0.05 mmol), solution of $KOH{\cdot}0.5H_2O$ (20.0 g, 307 mmol) in water (722 mmol, 13 ml), and toluene (50 ml) was heated under an argon atmosphere to 65–70 °C. Then, solution of butyl bromide (4.11 g, 30 mmol) in toluene (10 ml) was added dropwise for 2 h, and the reaction mixture was additionally stirred at 65–70 °C for 4 h. The reaction mixture was cooled to room temperature, water (50 ml) was added, the aqueous layer was separated, acidified with HCl to pH 5 and extracted with methylene chloride (3 x 50 ml). Organic extract was dried over sodium sulfate, and the solvent was evaporated. The residue was dried under reduced pressure to give the target butyl-*H*-phosphinic acid **1c** (2.0 g, 55% yield).

**Butylphosphinic acid (1c).** Yield 2.0 g (55%), light yellow oil. $^{1}$H NMR (400.13 MHz, $CDCl_3$): δ 0.88 (t, 3H, $CH_3$, $^{3}J_{HH}$ = 6.9 Hz); 1.27–1.40 (m, 2H, $CH_2Me$); 1.54–1.63 (m, 2H, $CH_2Et$); 1.68–1.78 (m, 2H, $CH_2P$); 7.07 (d, 1H, PH, $^{1}J_{PH}$ = 541.7 Hz); 12.27 (s, 1H, OH). $^{13}$C NMR (100.62 MHz, $CDCl_3$): $\delta_C$ 13.9 ($CH_3$); 20.4 (d, $CH_2Et$, $^{3}J_{CP}$ = 2.8 Hz); 29.3 (d, $CH_2P$, $^{1}J_{CP}$ = 93.7 Hz); 32.6 (d, $CH_2Me$, $^{3}J_{CP}$ = 15.9 Hz). $^{31}$P NMR (161.98 MHz, $CDCl_3$): $\delta_P$ 38.2 ($^{1}J_{PH}$ =

543.9 Hz) [lit.:[S2] $\delta_P$ 37.5 ($^1J_{PH}$ = 540.2 Hz)]. IR (film): ν = 2959, 2934, 2871, 2656 br, 2361, 2171 sh, 1716, 1678, 1658, 1463, 1404, 1382, 1310, 1275, 1227, 1171, 1096, 1067, 983, 886, 787, 714, 517, 430 $cm^{-1}$. Anal. Calcd for $C_4H_{11}O_2P$: C, 39.35; H, 9.08; P, 25.37. Found: C, 39.51; H, 9.26; P, 25.17.

**Reaction of alkyl-*H*-phosphinic acids with alkyl bromides (general procedure)**. A mixture of alkyl-*H*-phosphinic acid **1** (3 mmol), alkyl bromide (9 mmol) and triethylamine (3.3 mmol, 303 mg) was stirred under an argon atmosphere at 60–65 °C for 9–10 h. Then, $Et_2O$ (4 ml) was added, the precipitated triethylammonium bromide was filtered off and additionally washed with $Et_2O$ (2 x 3 ml). The combined filtrate was evaporated under reduced pressure. The residue was purified by column chromatography on $SiO_2$ (eluent: ethyl acetate/MeCN, 3:1) to give the target alkyl alkyl-*H*-phosphinate **2**.

**Butyl octylphosphinate (2a).** Yield 485 mg (69%), waxy product. $^1$H NMR (400.13 MHz, $CDCl_3$): δ 0.69 (t, 3H, $CH_3$, OctylP, $^3J_{HH}$ = 7.0 Hz); 0.76 (t, 3H, $CH_3$, POBu, $^3J_{HH}$ = 7.2 Hz); 1.09 (m, 8H, $CH_2$Bu, $CH_2$Pr, $CH_2$Et, $CH_2$Me, OctylP); 1.21–1.28 (m, 4H, $CH_2$Pentyl, OctylP; $CH_2$Me, POBu); 1.35–1.44 (m, 2H, $CH_2$Hexyl, OctylP); 1.46–1.52 (m, 2H, $CH_2$Et, POBu); 1.54–1.62 (m, 2H, $CH_2$Heptyl, OctylP); 3.76–3.84, 3.89–3.96 (m, 2H, $CH_2$Pr, POBu); 6.88 (d, 1H, PH, $^1J_{PH}$ = 526.6 Hz). $^{13}$C NMR (100.62 MHz, $CDCl_3$): $\delta_C$ 13.3 ($CH_3$, POBu); 13.7 ($CH_3$, OctylP); 18.5 ($CH_2$Me, POBu); 20.5 (d, $CH_2$Hexyl, OctylP, $^2J_{CP}$ = 3.0 Hz); 22.3 ($CH_2$Me, OctylP); 28.5 (d, $CH_2$Heptyl, OctylP, $^1J_{CP}$ = 92.9 Hz); 28.7 ($CH_2$Et, OctylP); 28.8 ($CH_2$Pr, OctylP); 30.2 (d, $CH_2$Pentyl, OctylP, $^3J_{CP}$ = 15.1 Hz); 31.5 ($CH_2$Bu, OctylP); 32.2 (d, $CH_2$Et, POBu, $^3J_{CP}$ = 6.0 Hz); 65.7 (d, $CH_2$Pr, POBu, $^2J_{CP}$ = 7.3 Hz). $^{31}$P NMR (161.98 MHz, $CDCl_3$): $\delta_P$ 40.4. IR (film): ν = 3446, 3432, 2956, 2925, 2855, 2343, 1721, 1704, 1688, 1673, 1657, 1651, 1639, 1580, 1562, 1543, 1525, 1510, 1462, 1402, 1379, 1353, 1298, 1235, 1207, 1117, 1065, 1028, 973, 836, 792, 725, 517 $cm^{-1}$. Anal. Calcd for $C_{12}H_{27}O_2P$: C, 61.51; H, 11.61; P, 13.22. Found: C, 61.27; H, 11.49; P, 13.03.

**Ethyl hexylphosphinate (2b).** Yield 353 mg (66%), waxy product. $^1$H NMR (400.13 MHz, $CDCl_3$): δ 0.72 (t, 3H, $CH_3$, HexylP, $^3J_{HH}$ = 6.7 Hz); 1.09–1.15 (m, 4H, $CH_2$Et, $CH_2$Me, HexylP); 1.19 (t, 3H, $CH_3$, POEt, $^3J_{HH}$ = 7.0 Hz); 1.21–1.26 (m, 2H, $CH_2$Pr, HexylP); 1.39–1.46 (m, 2H, $CH_2$Bu, HexylP); 1.56–1.64 (m, 2H, $CH_2$Pentyl, HexylP); 3.90–3.94, 3.98–4.04 (m, 2H, $CH_2$Me, POEt); 6.91 (d, 1H, PH, $^1J_{PH}$ = 527.1 Hz). $^{13}$C NMR (100.62 MHz, $CDCl_3$): $\delta_C$ 13.7 ($CH_3$, HexylP); 16.0 (d, $CH_3$, POEt, $^3J_{CP}$ = 6.0 Hz); 20.4 (d, $CH_2$Bu, HexylP, $^2J_{CP}$ = 3.1 Hz); 22.1 ($CH_2$Me, HexylP); 28.5 (d, $CH_2$Pentyl, HexylP, $^1J_{CP}$ = 93.8 Hz); 29.8 (d, $CH_2$Pr, HexylP, $^3J_{CP}$ = 15.3 Hz); 31.1 ($CH_2$Et, HexylP); 62.1 (d, $CH_2$Me, POEt, $^2J_{CP}$ = 7.0 Hz). $^{31}$P NMR (161.98 MHz, $CDCl_3$): $\delta_P$ 40.9. IR (film): ν = 3419, 2956, 2929, 2860, 2345, 1735, 1682, 1651, 1639, 1573, 1558, 1542, 1520, 1509, 1487, 1461, 1397, 1378, 1315, 1294, 1216, 1192, 1100, 1044, 998, 960,

854, 787, 713, 529, 459 $cm^{-1}$. Anal. Calcd for $C_8H_{19}O_2P$: C, 53.92; H, 10.75; P, 17.38. Found: C, 54.06; H, 10.91; P, 17.15.

**Butyl hexylphosphinate (2c).** Yield 402 mg (65%), waxy product. $^1H$ NMR (400.13 MHz, $CDCl_3$): δ 0.66–0.68 (m, 3H, $CH_3$, HexylP); 0.73 (t, 3H, $CH_3$, POBu, $^3J_{HH}$ = 7.3 Hz); 1.09 (m, 4H, $CH_2$Et, $CH_2$Me, HexylP); 1.18–1.23 (m, 4H, $CH_2$Pr, HexylP; $CH_2$Me, POBu); 1.33–1.41 (m, 2H, $CH_2$Bu, HexylP); 1.44–1.49 (m, 2H, $CH_2$Et, POBu); 1.52–1.59 (m, 2H, $CH_2$Pentyl, HexylP); 3.74–3.81, 3.86–3.94 (m, 2H, $CH_2$Pr, POBu); 6.86 (d, 1H, PH, $^1J_{PH}$ = 526.9 Hz). $^{13}C$ NMR (100.62 MHz, $CDCl_3$): $\delta_C$ 13.2 ($CH_3$, POBu); 13.6 ($CH_3$, HexylP); 18.5 ($CH_2$Me, POBu); 20.4 (d, $CH_2$Bu, HexylP, $^2J_{CP}$ = 2.9 Hz); 22.0 ($CH_2$Me, HexylP); 28.4 (d, $CH_2$Pentyl, HexylP, $^1J_{CP}$ = 93.4 Hz); 29.7 (d, $CH_2$Pr, HexylP, $^3J_{CP}$ = 15.1 Hz); 30.9 ($CH_2$Et, HexylP); 32.1 (d, $CH_2$Et, POBu, $^3J_{CP}$ = 5.9 Hz); 65.7 (d, $CH_2$Pr, POBu, $^2J_{CP}$ = 7.2 Hz). $^{31}P$ NMR (161.98 MHz, $CDCl_3$): $\delta_P$ 40.4. IR (film): ν = 3445, 3396, 2957, 2928, 2871, 2369, 1794, 1772, 1733, 1718, 1699, 1684, 1672, 1651, 1573, 1558, 1543, 1520, 1509, 1460, 1421, 1398, 1378, 1341, 1292, 1217, 1192, 1115, 1064, 1033, 978, 896, 789, 726, 520, 455 $cm^{-1}$. Anal. Calcd for $C_{10}H_{23}O_2P$: C, 58.23; H, 11.24; P, 15.02. Found: C, 58.46; H, 11.37; P, 14.87.

**Hexyl octylphosphinate (2d).** Yield 535 mg (68%), waxy product. $^1H$ NMR (400.13 MHz, $CDCl_3$): δ 0.83–0.85 (m, 3H, $CH_3$, OctylP); 0.86–0.88 (m, 3H, $CH_3$, POHexyl); 1.24–1.28 (m, 12H, $CH_2$Et, $CH_2$Me, POHexyl; $CH_2$Bu, $CH_2$Pr, $CH_2$Et, $CH_2$Me, OctylP); 1.31–1.38 (m, 4H, $CH_2$Pentyl, OctylP; $CH_2$Pr, POHexyl); 1.50–1.61 (m, 2H, $CH_2$Hexyl, OctylP); 1.63–1.70 (m, 2H, $CH_2$Bu, POHexyl); 1.72–1.77 (m, 2H, $CH_2$Heptyl, OctylP); 3.90–3.98, 4.04–4.11 (m, 2H, $CH_2$Pentyl, POHexyl); 7.04 (d, 1H, PH, $^1J_{PH}$ = 525.6 Hz). $^{13}C$ NMR (100.62 MHz, $CDCl_3$): $\delta_C$ 13.5 ($CH_3$, POHexyl); 13.6 ($CH_3$, OctylP); 20.4 (d, $CH_2$Hexyl, OctylP, $^2J_{CP}$ = 3.0 Hz); 22.1 ($CH_2$Me, POHexyl); 22.2 ($CH_2$Me, OctylP); 24.8 ($CH_2$Pr, POHexyl); 28.4 (d, $CH_2$Heptyl, OctylP, $^1J_{CP}$ = 93.7 Hz); 28.6 ($CH_2$Et, OctylP); 28.7 ($CH_2$Pr, OctylP); 29.9 (d, $CH_2$Bu, POHexyl, $^3J_{CP}$ = 9.9 Hz); 30.1 (d, $CH_2$Pentyl, OctylP, $^3J_{CP}$ = 11.4 Hz); 30.9 ($CH_2$Et, POHexyl); 31.4 ($CH_2$Bu, OctylP); 65.8 (d, $CH_2$Pentyl, POHexyl, $^2J_{CP}$ = 7.1 Hz). $^{31}P$ NMR (161.98 MHz, $CDCl_3$): $\delta_P$ 39.7. IR (film): ν = 3447, 3424, 2954, 2926, 2857, 2344, 1719, 1701, 1685, 1669, 1654, 1641, 1577, 1560, 1544, 1523, 1508, 1464, 1400, 1379, 1350, 1297, 1211, 1119, 1061, 990, 966, 851, 794, 726, 533, 455 $cm^{-1}$. Anal. Calcd for $C_{14}H_{31}O_2P$: C, 64.09; H, 11.91; P, 11.81. Found: C, 64.27; H, 12.07; P, 11.68.

**Butyl butylphosphinate (2e).** Yield 379 mg (71%), waxy product. $^1H$ NMR (400.13 MHz, $CDCl_3$): δ 0.90 (t, 3H, $CH_3$, BuP, $^3J_{HH}$ = 7.2 Hz); 0.91 (t, 3H, $CH_3$, POBu, $^3J_{HH}$ = 7.1 Hz); 1.34–1.44 (m, 4H, $CH_2$Me, BuP; $CH_2$Me, POBu); 1.49–1.58 (m, 2H, $CH_2$Et, BuP); 1.62–1.67 (m, 2H, $CH_2$Et, POBu); 1.69–1.78 (m, 2H, $CH_2$Pr, BuP); 3.91–3.99, 4.04–4.12 (m, 2H, $CH_2$Pr, POBu); 7.04 (d, 1H, PH, $^1J_{PH}$ = 525.4 Hz). $^{13}C$ NMR (100.62 MHz, $CDCl_3$): $\delta_C$ 12.9 ($CH_3$,

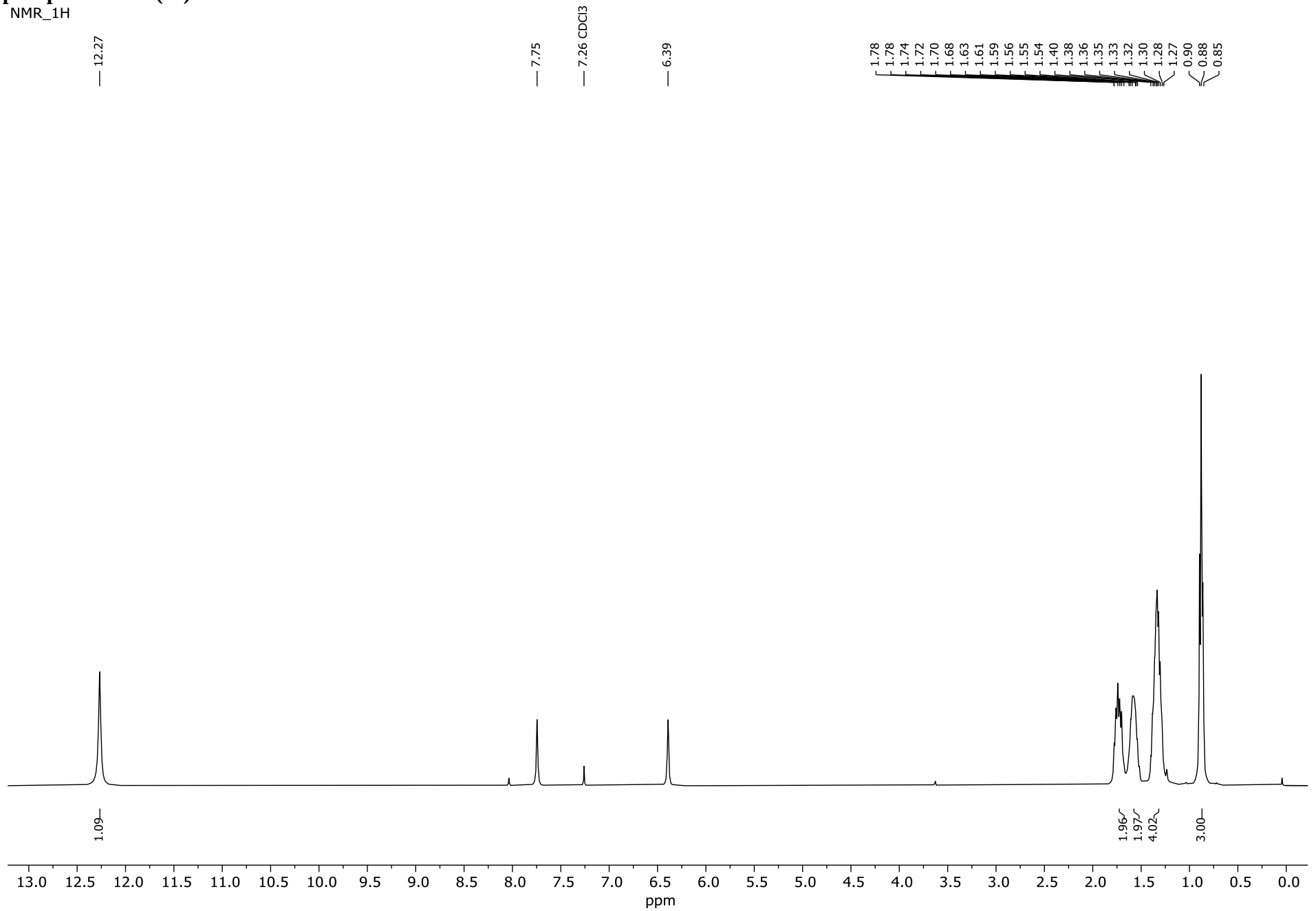
POBu); 13.0 ($CH_3$, BuP); 18.2 ($CH_2Me$, POBu); 22.2 (d, $CH_2Et$, BuP, $^3J_{CP}$ = 3.0 Hz); 22.9 (d, $CH_2Me$, BuP, $^3J_{CP}$ = 15.7 Hz); 27.9 (d, $CH_2Pr$, BuP, $^3J_{CP}$ = 93.7 Hz); 31.8 (d, $CH_2Et$, POBu, $^3J_{CP}$ = 6.0 Hz); 65.3 (d, $CH_2Pr$, POBu, $^3J_{CP}$ = 6.9 Hz). $^{31}$P NMR (161.98 MHz, $CDCl_3$): $\delta_P$ 39.3. IR (film): ν = 3446, 2959, 2933, 2873, 2361, 1719, 1700, 1684, 1669, 1657, 1642, 1562, 1543, 1523, 1510, 1462, 1402, 1381, 1348, 1310, 1235, 1197, 1120, 1065, 1031, 973, 885, 787, 730, 517, 441 $cm^{-1}$. Anal. Calcd for $C_8H_{19}O_2P$: C, 53.92; H, 10.75; P, 17.38. Found: C, 54.21; H, 10.58; P, 17.14.

**References**

S1. N. K. Gusarova, A. O. Sutyrina, V. A. Kuimov, S. F. Malysheva, N. A. Belogorlova, P. A. Volkov and B. A. Trofimov, *Mendeleev Commun.* 2019, **29**, 328.

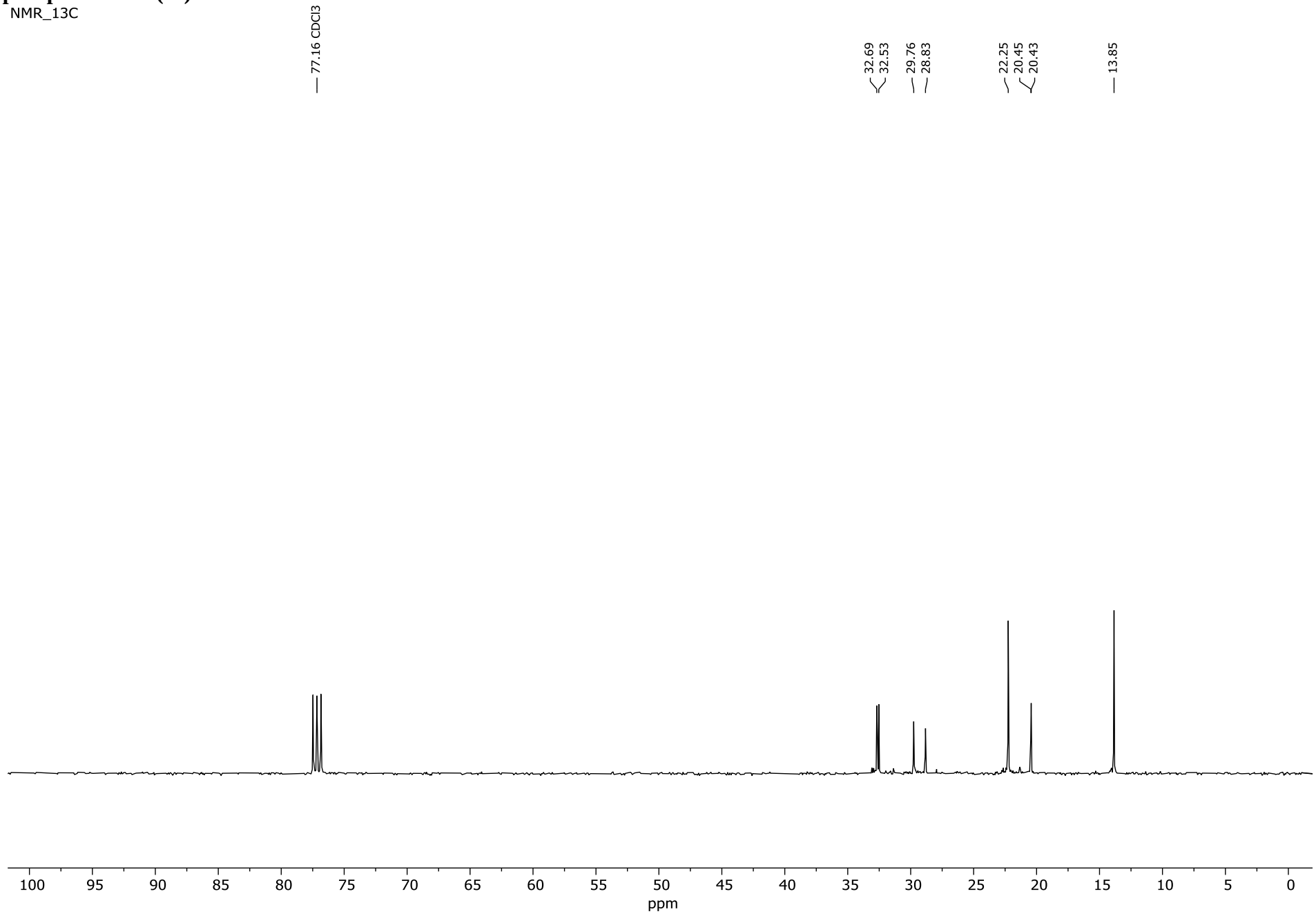
S2. V. A. Kuimov, S. F. Malysheva, N. A. Belogorlova, N. K. Gusarova and B. A. Trofimov, *Org. Biomol. Chem.* 2021, **19**, 10587.

**Butylphosphinic acid (1c)**



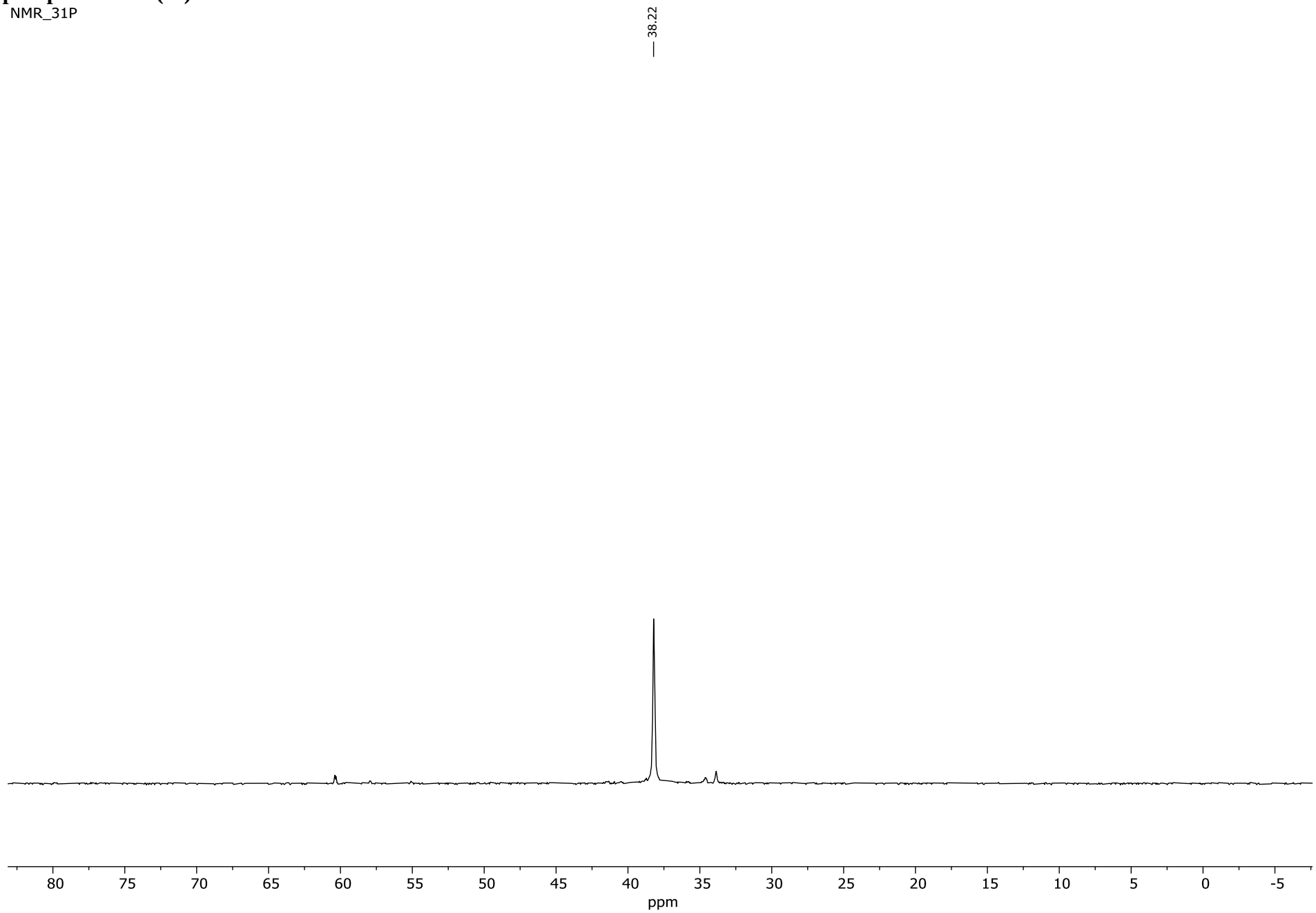
**Butylphosphinic acid (1c)**

NMR_13C

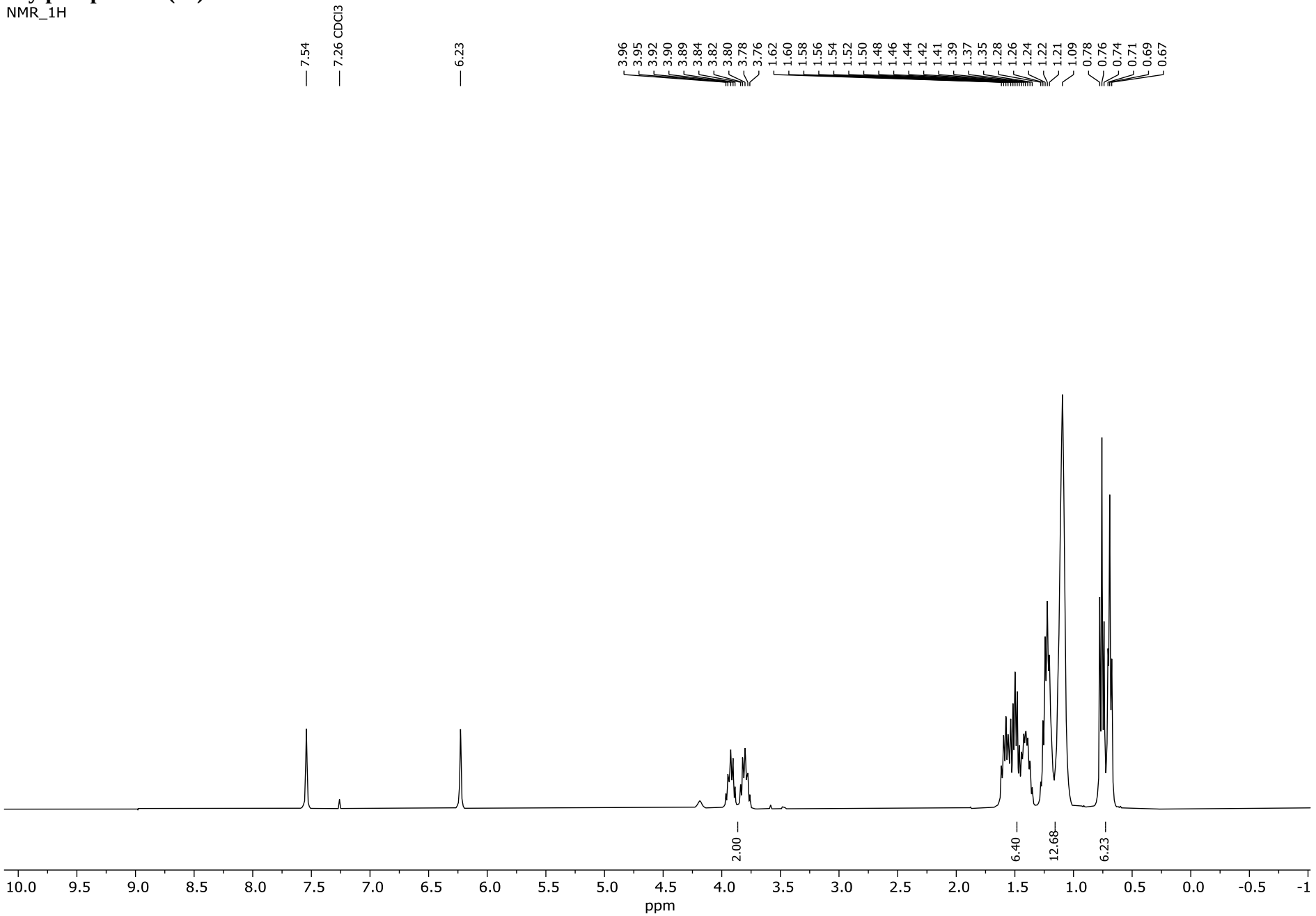


**Butylphosphinic acid (1c)**

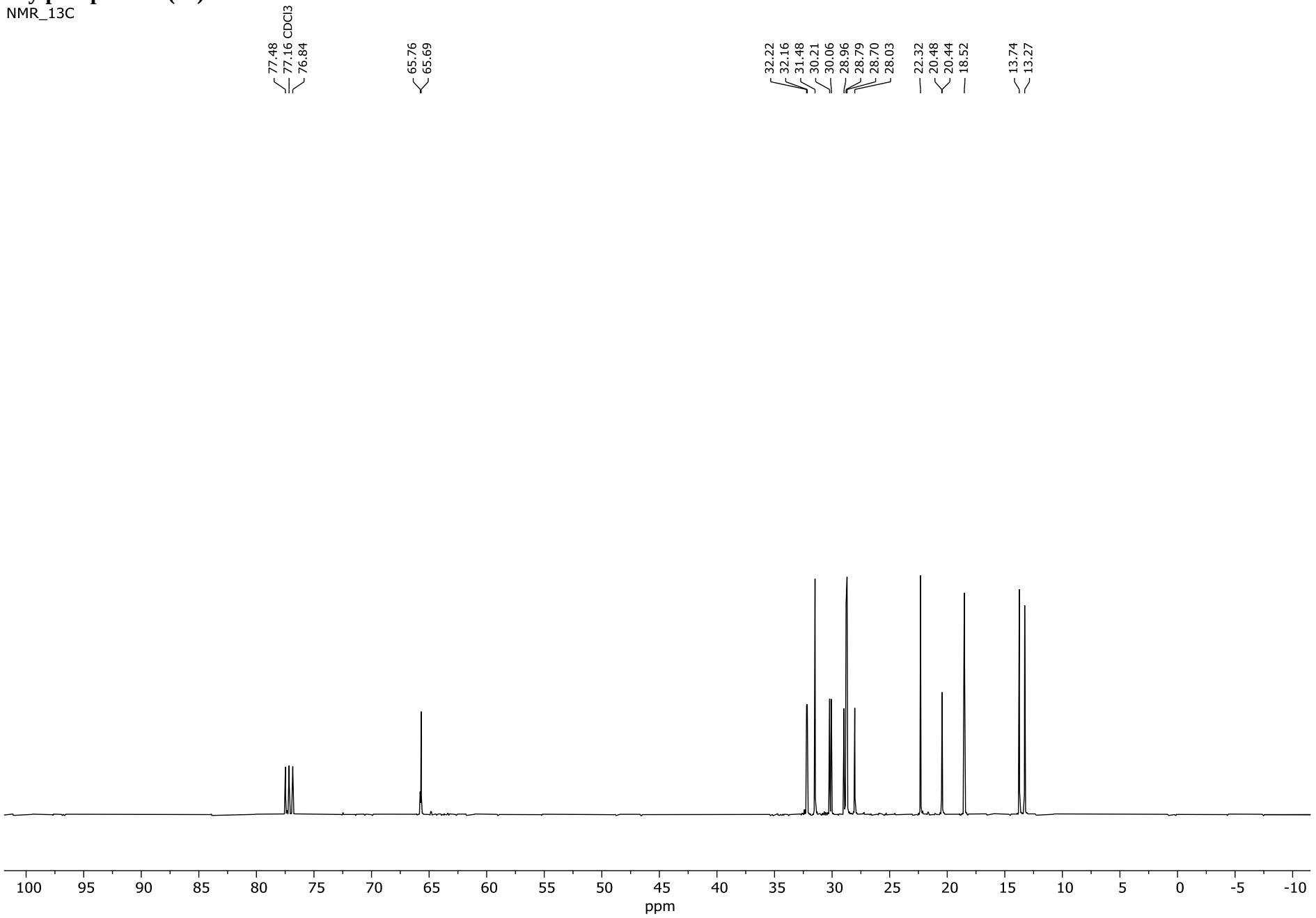
NMR_31P



**Butyl octylphosphinate (2a)**

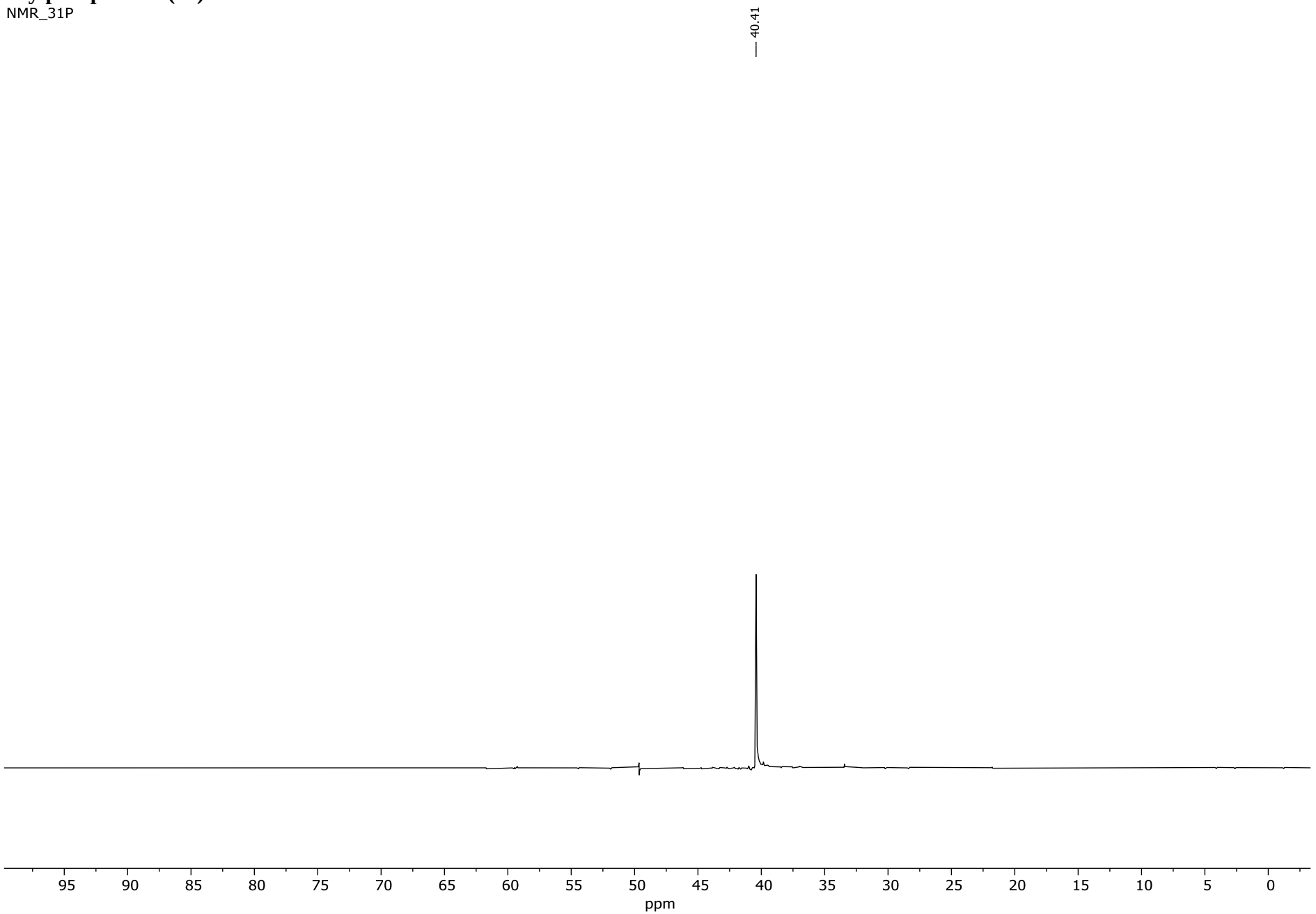


**Butyl octylphosphinate (2a)**



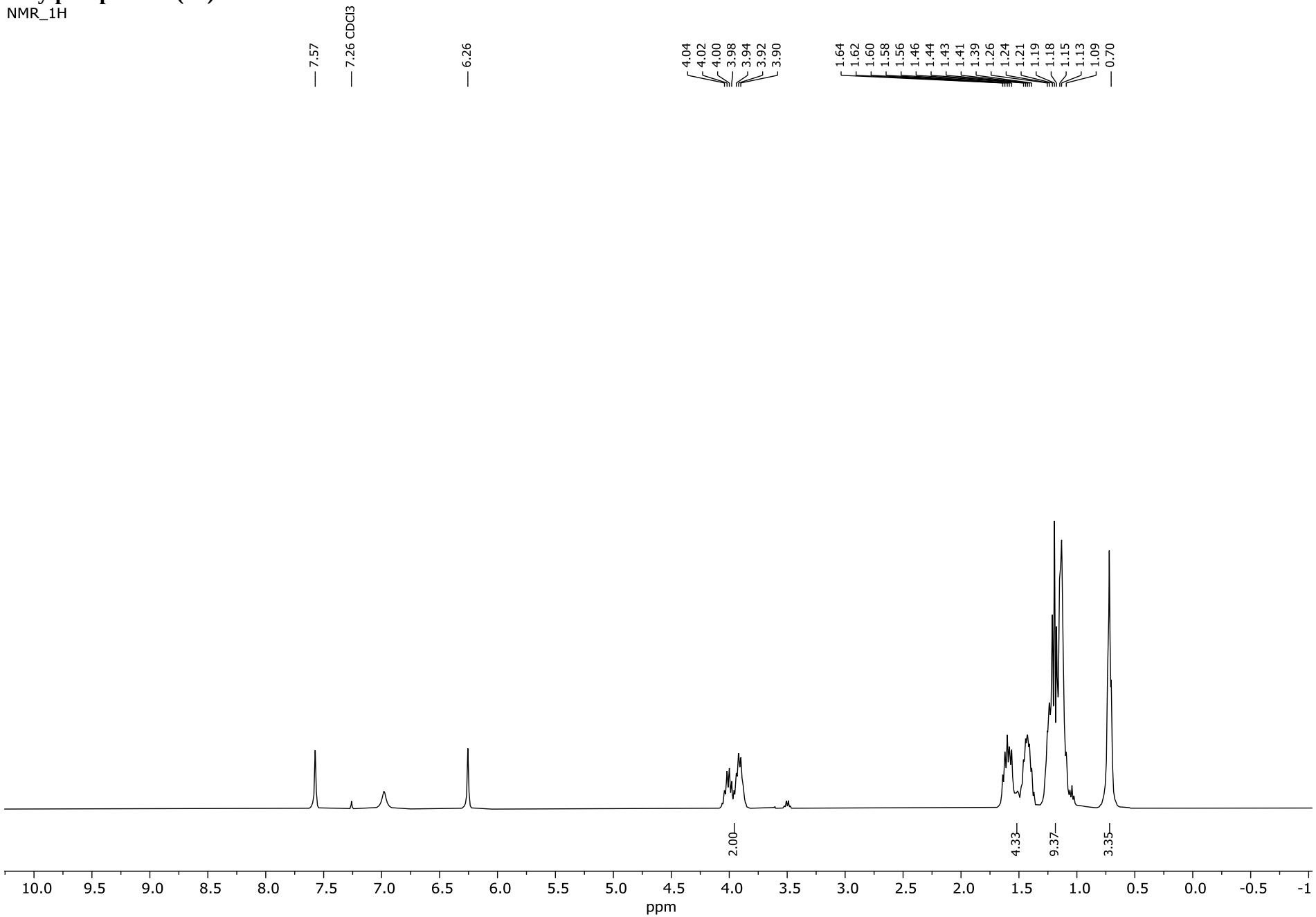
**Butyl octylphosphinate (2a)**

NMR_31P

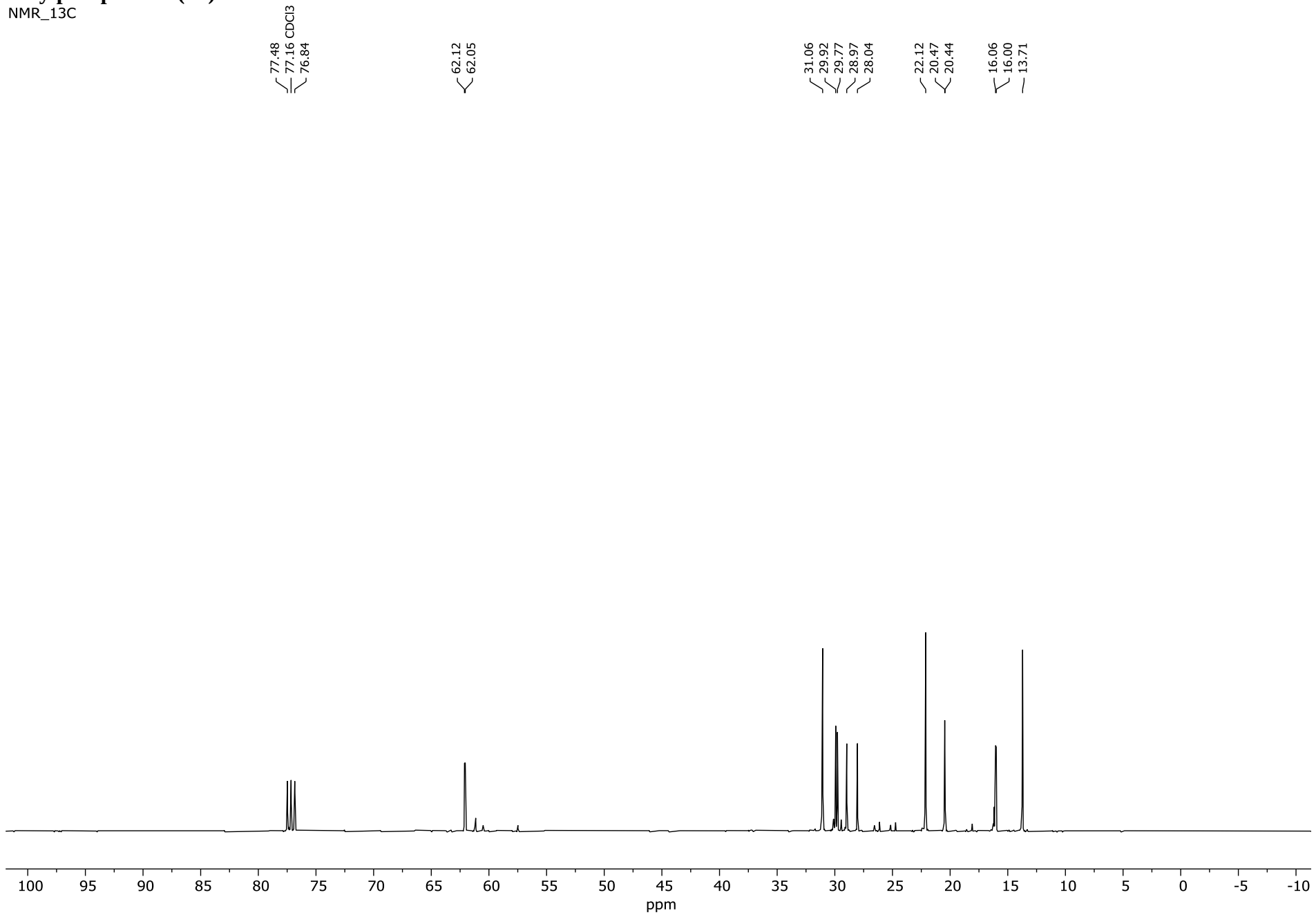


**Ethyl hexylphosphinate (2b)**

NMR_1H

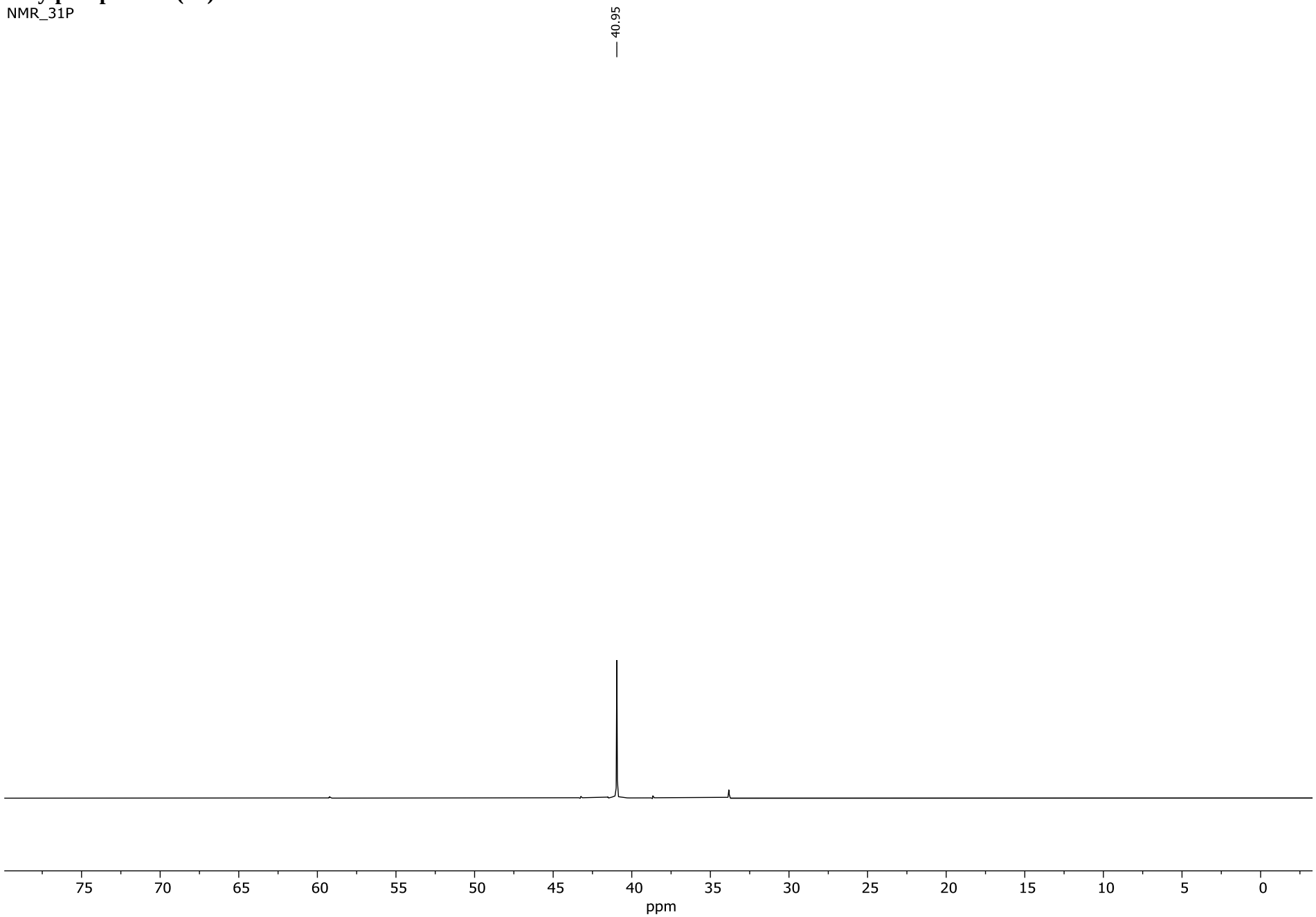


**Ethyl hexylphosphinate (2b)**



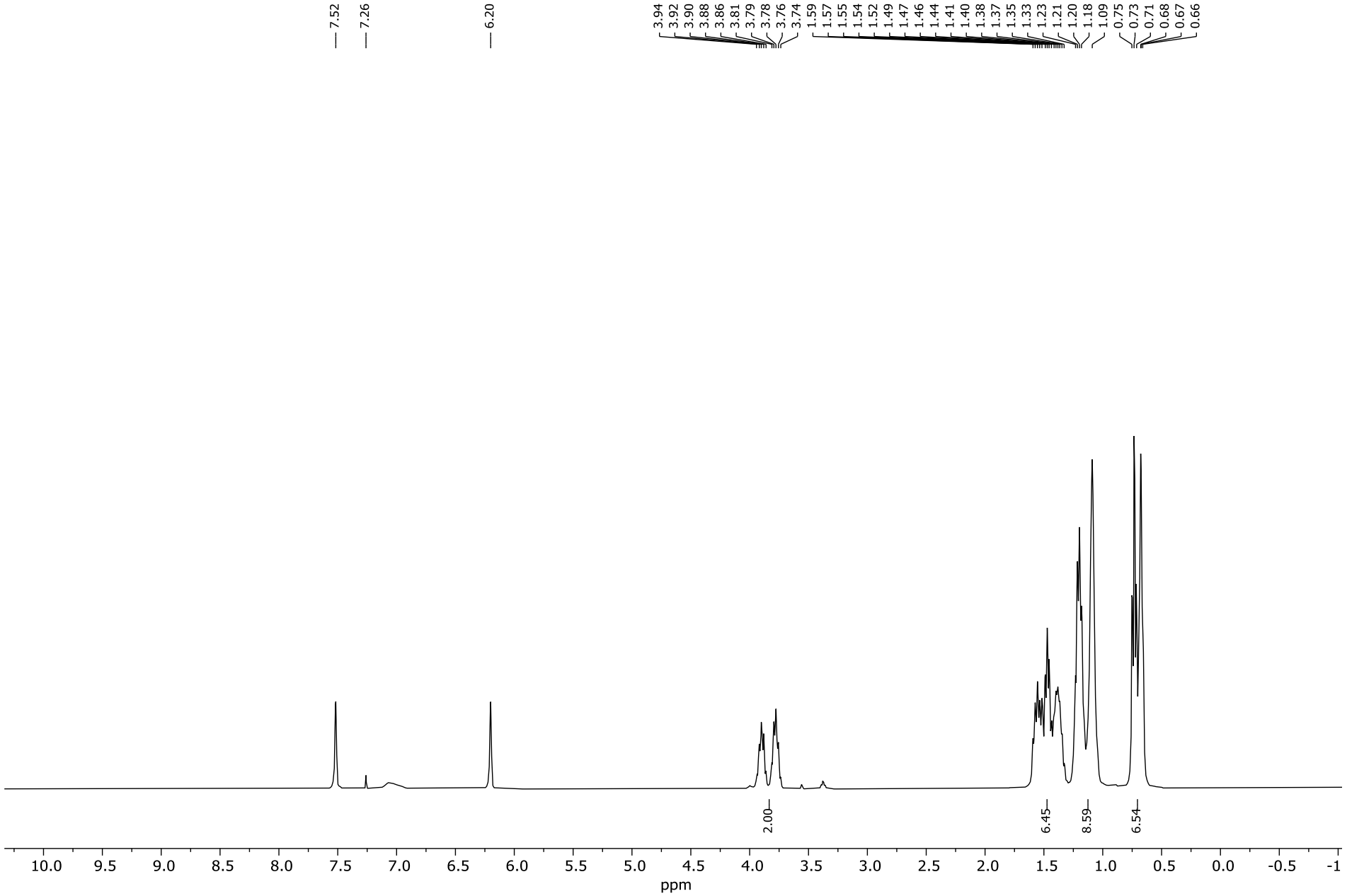
**Ethyl hexylphosphinate (2b)**

NMR_31P



**Butyl hexylphosphinate (2c)**

NMR_1H



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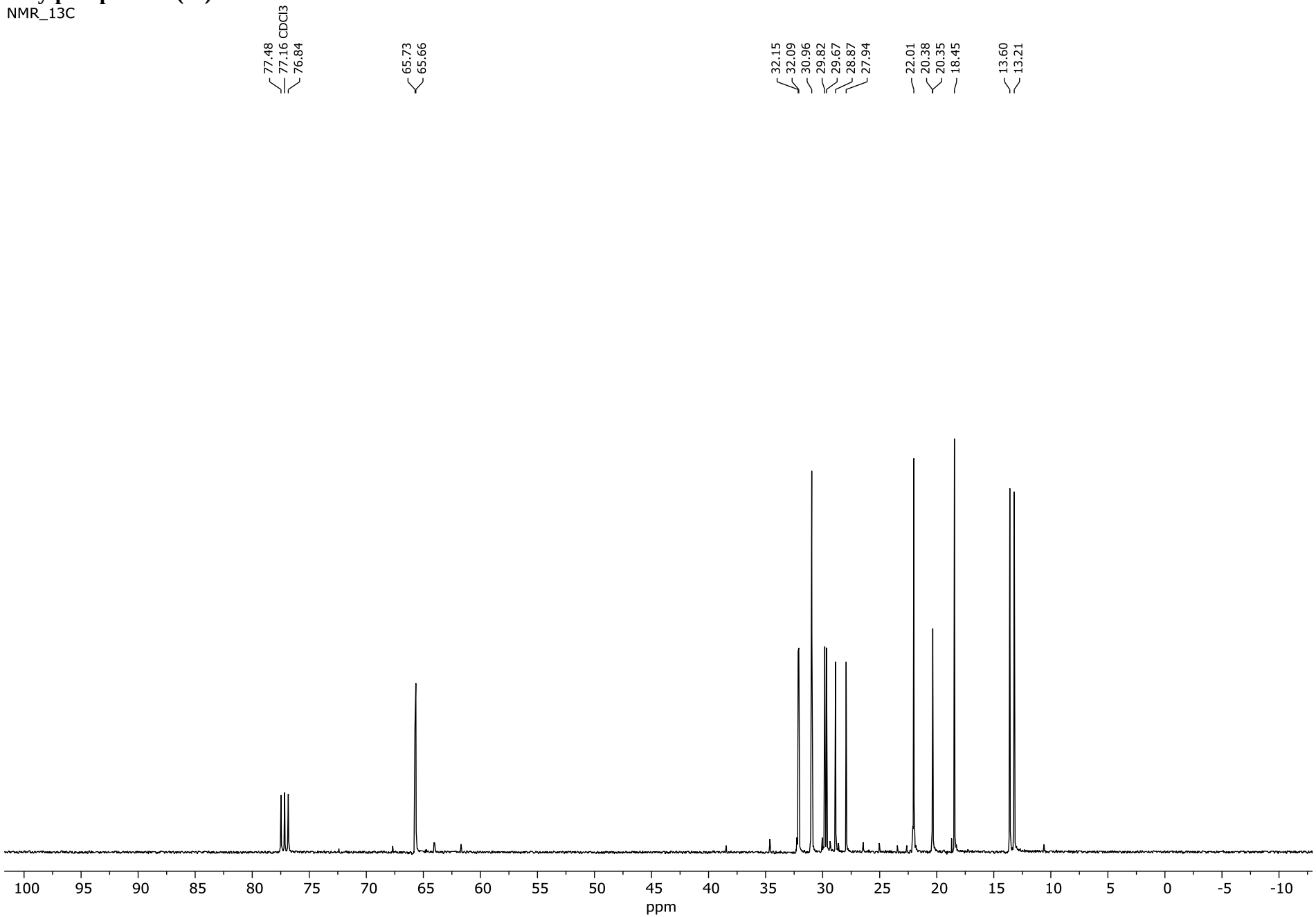
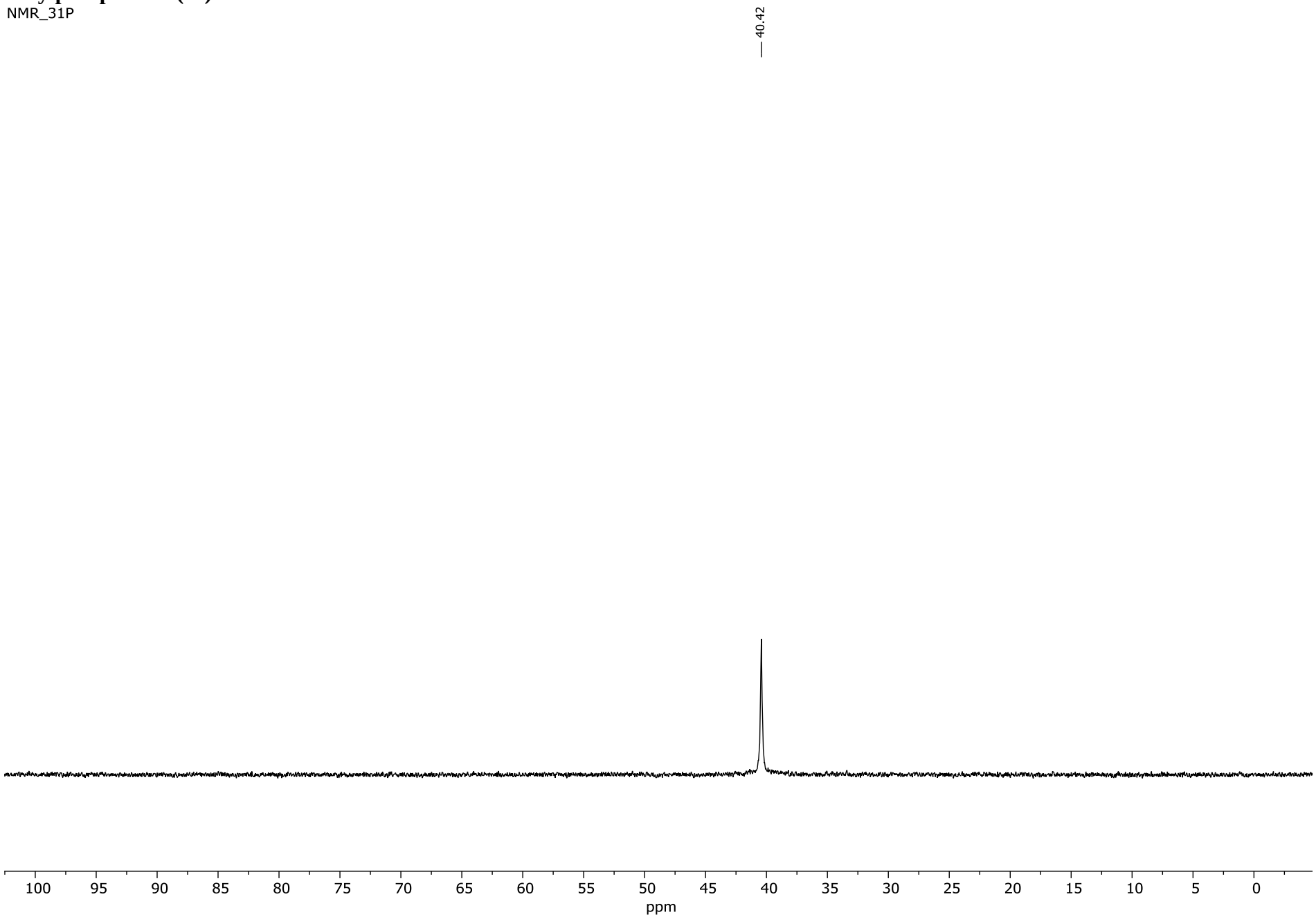
NMR_13C



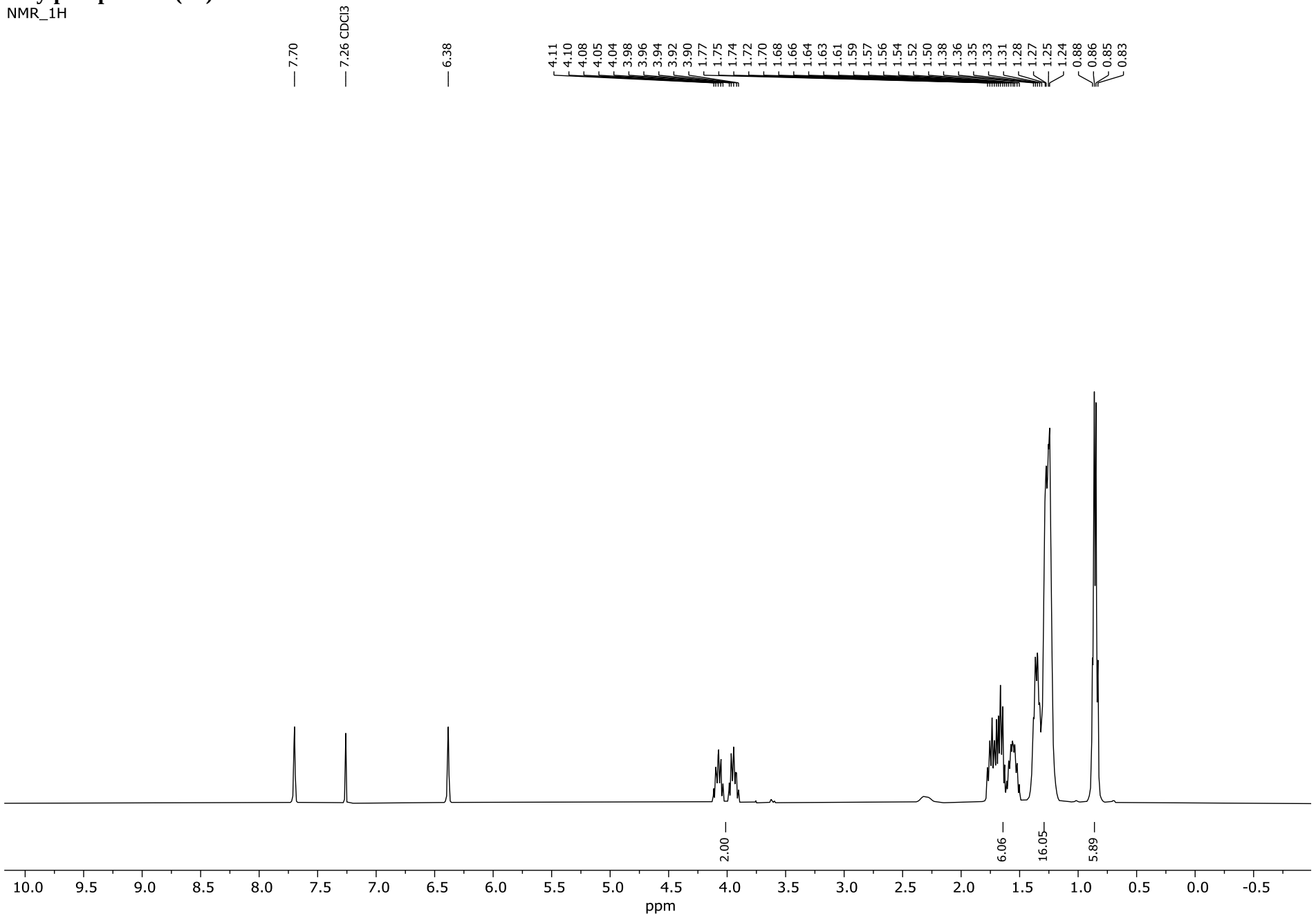
**Butyl hexylphosphinate (2c)**

NMR_31P



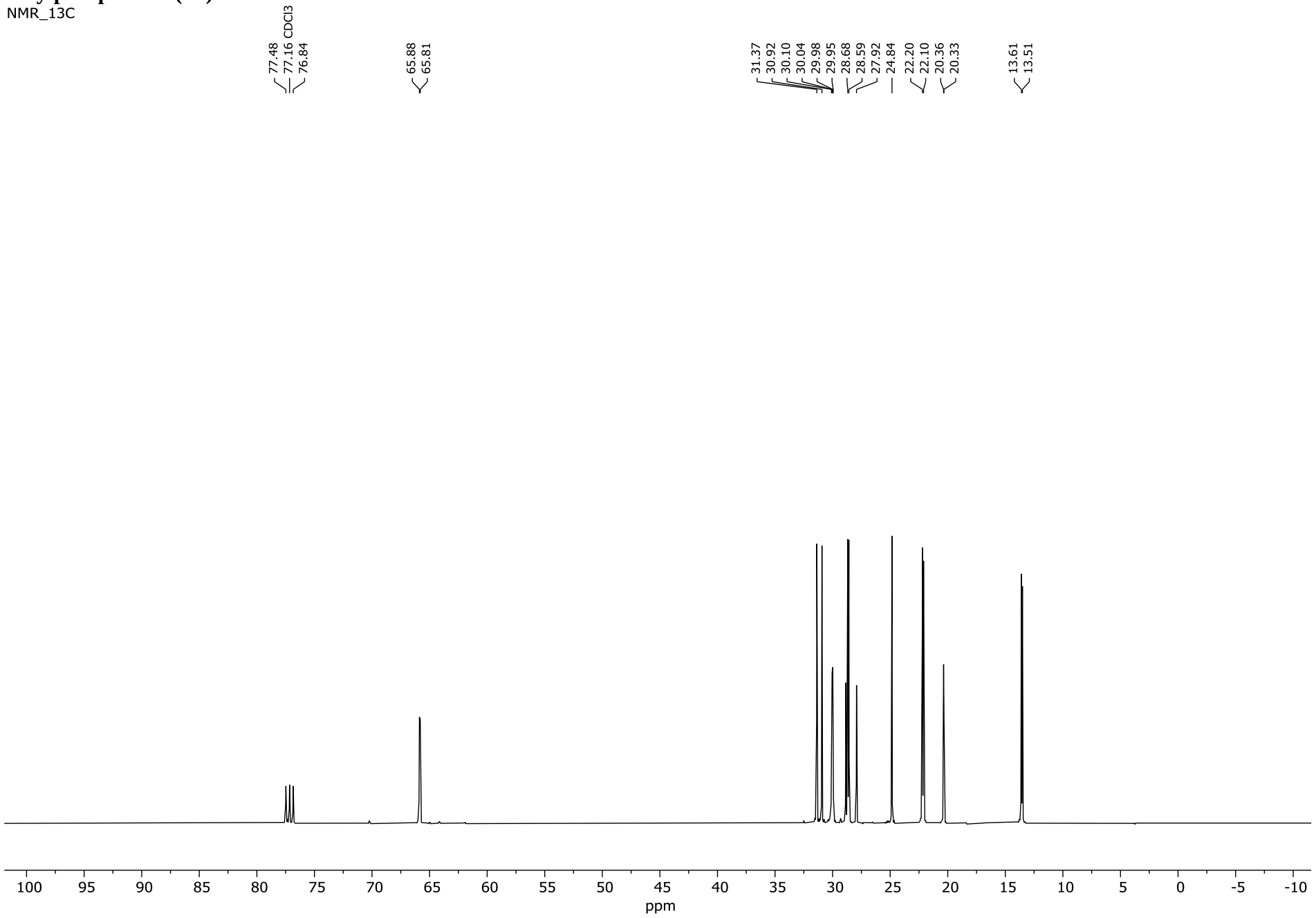
**Hexyl octylphosphinate (2d)**

NMR_1H



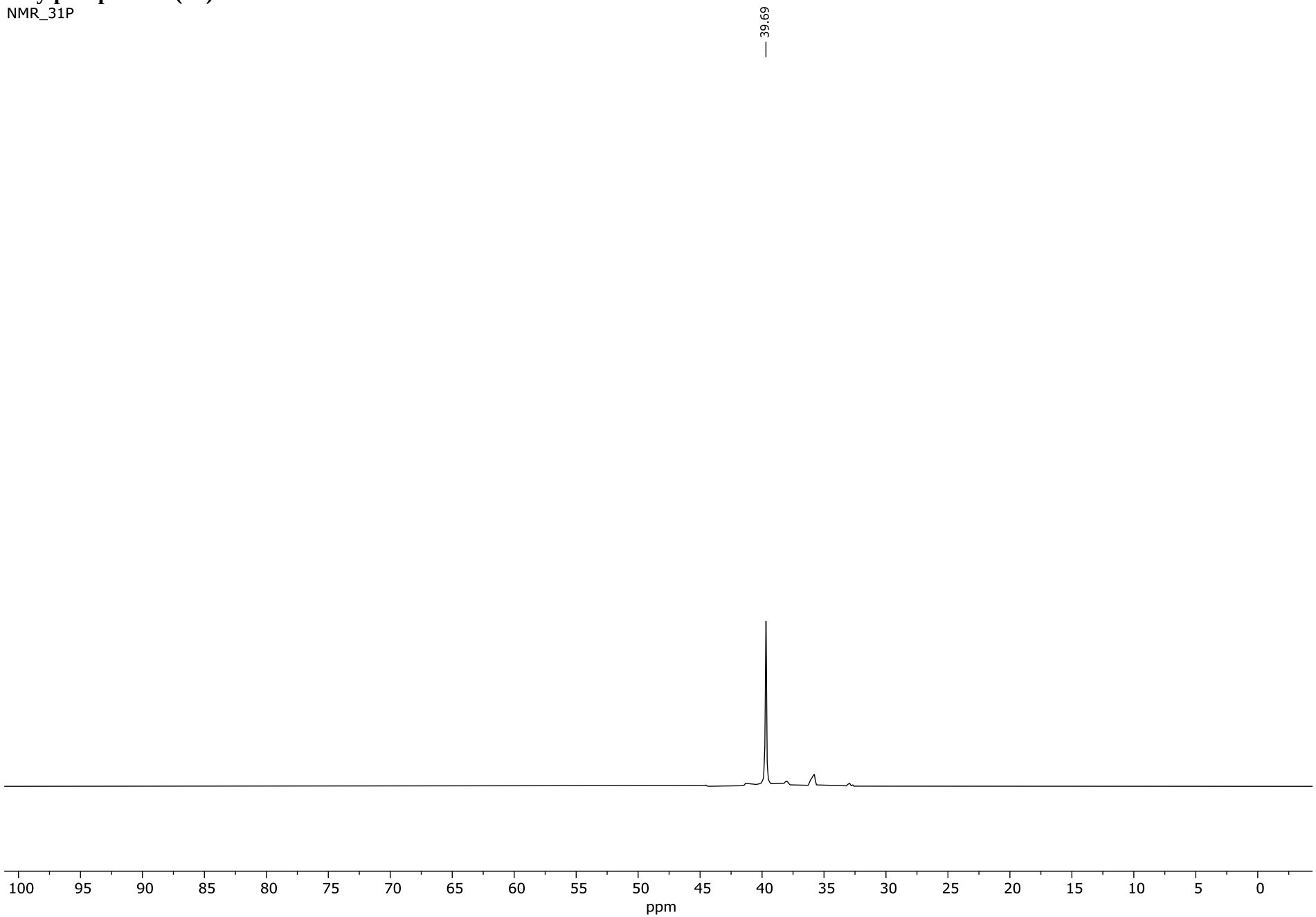
**Hexyl octylphosphinate (2d)**

NMR_13C



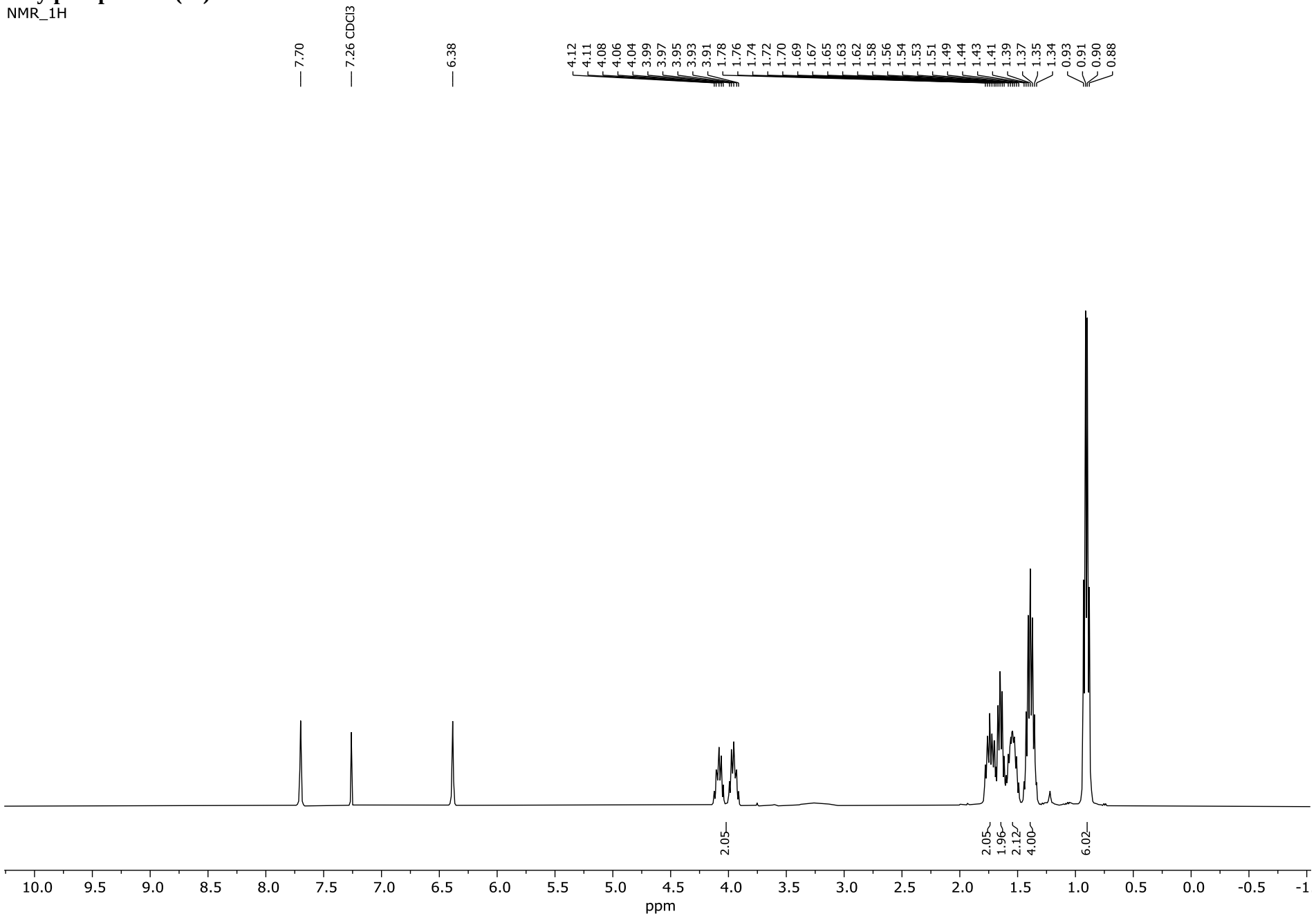
**Hexyl octylphosphinate (2d)**

NMR_31P



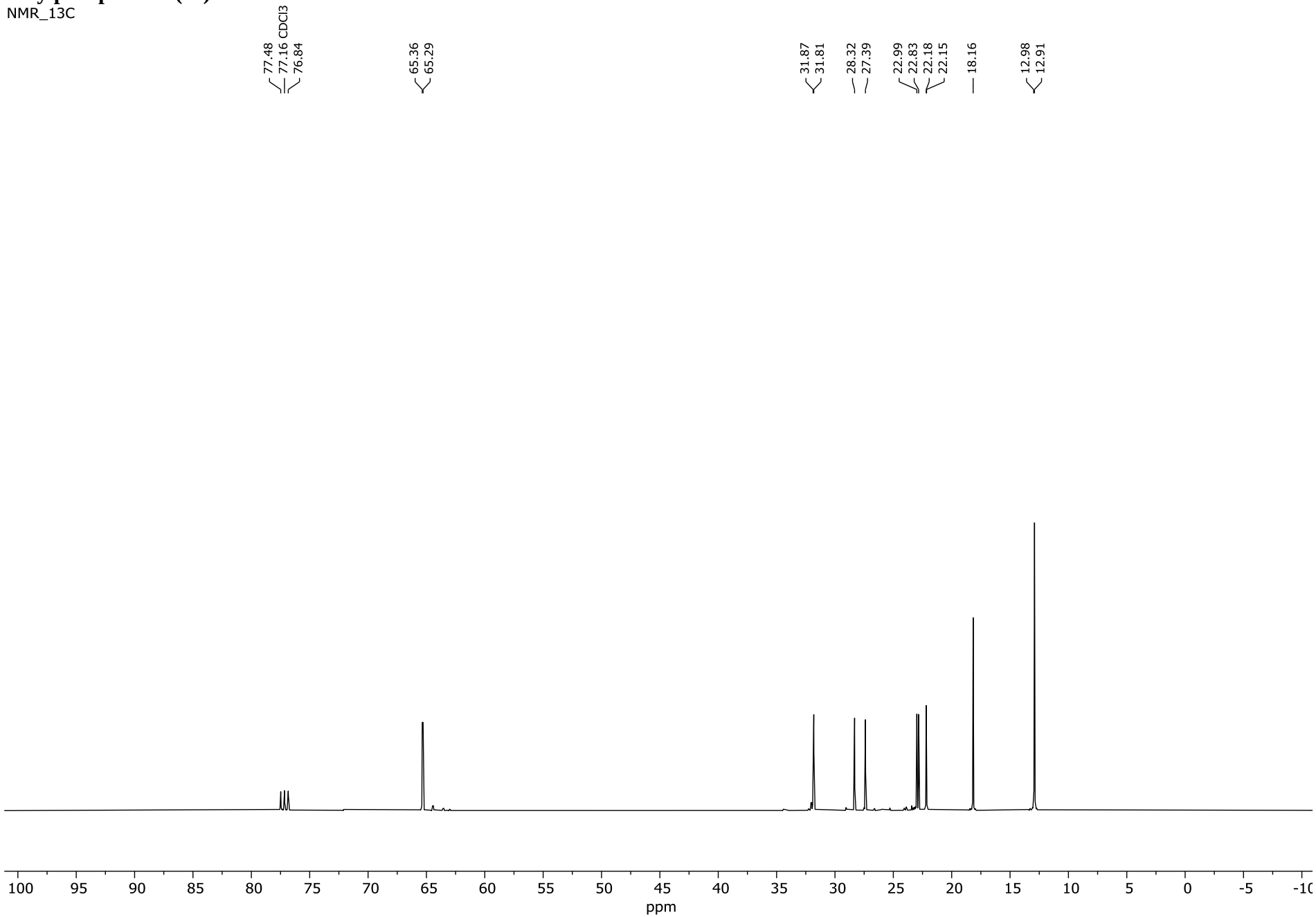
**Butyl butylphosphinate (2e)**

NMR_1H



**Butyl butylphosphinate (2e)**

NMR_13C



**Butyl butylphosphinate (2e)**

NMR_31P