Supplementary Information

Acid-promoted transformations of 1-(diphenylphosphoryl)allenes: synthesis of novel 1,4-dihydrophosphinoline 1-oxides

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General Remarks.

The NMR spectra of solutions of compounds in $CDCl_3$ were recorded on Bruker AVANCE III 400 spectrometers at 25 °C (at 400.13, 100.61 and 161.98 MHz for ^{1}H, ^{13}C and ^{31}P NMR spectra respectively). Chemical shifts are given in δ-values [ppm] referenced to the solvent: δ=7.26 (^{1}H) and 77.2 (^{13}C). Phosphorus chemical shifts were determined relative to external 85% phosphoric acid.

High-resolution mass spectra were recorded on a Bruker Micro-TOF mass spectrometer (ESI-MS) and Varian 902-MS Mass Spectrometer (MALDI-MS).

IR spectra of compounds in KBr were taken with a Bruker spectrometer.

Melting points were measured on a Kofler hot-stage (VEB Wägetechnik Rapido, PHMK 81/2969).

The reactions were monitored by thin-layer chromatography carried out on silica gel plates (Alugram SIL G/UV-254), using UV light for detection.

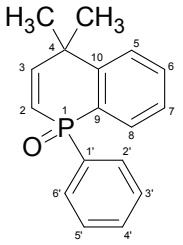
X-ray crystallography. Single crystal X-ray analysis was performed at single crystal diffractometer Agilent Technologies (Oxford Diffraction) «Supernova». A suitable crystal was selected and studied on the diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2,[1] the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.

CCDC 1026531 (**2a**), CCDC 1026529 (**2c**), CCDC 1026527 (**2d**), CCDC 1026526 (**2f**), CCDC 1029399 (**3a**), CCDC 1026528 (**3d**), CCDC 1029400 (**3e**), CCDC 1026532 (**3f**) contains the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst*., **2009**, *42*, 339-341.

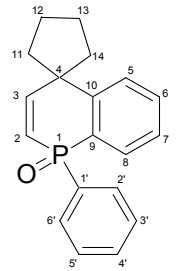
[2] SHELXS, G.M. Sheldrick, *Acta Cryst.,* **2008**, *A64*, 112-122.

***1-Phenyl-4,4-dimethyl-1,4-dihydrophosphinoline 1-oxide* (*2a*)**



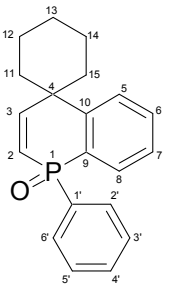
Colorless solid; mp 80–83°C (hydrate according to X-ray); **IR** (KBr), cm^{-1}: 655, 698, 720, 742, 776, 858, 915, 965, 1080, 1115, 1245, 1294, 1370, 1440, 1482, 1594, 1622, 2874, 2937, 2963, 2978, 3055; **^{1}H NMR** ($CDCl_3$, 400.13 MHz) δ, ppm: 1.52 s (3H, CH_3), 1.56 s (3H, CH_3), 6.20 dd (1H, C^2H, $^3J_{HH}$ 12.0 Hz, $^2J_{HP}$ 10.0 Hz), 6.76 dd (1H, C^3H, $^3J_{HH}$ 12.0 Hz, $^3J_{HP}$ 36.0 Hz), 7.26–7.30 m (1H, $H_{arom.}$), 7.39–7.54 m (5H, $H_{arom.}$), 7.61–7.70 m (3H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100.61 MHz) δ, ppm: 31.4 d (CH_3, $^4J_{CP}$ 2.0 Hz), 32.0 d (CH_3, $^4J_{CP}$ 2.0 Hz), 38.7 d (C^4, $^3J_{CP}$ 13.1 Hz), 117.5 d (C^2, $^1J_{CP}$ 99.6 Hz), 127.0 d (C^7, $^3J_{CP}$ 9.1 Hz), 127.1 d (C^5, $^3J_{CP}$ 11.1 Hz), 127.4 d (C^9, $^1J_{CP}$ 103.6 Hz), 128.6 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 12.1 Hz), 131.3 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 10.1 Hz), 131.6 d (C^6, $^4J_{CP}$ 2.0 Hz), 131.6 d (C^8, $^2J_{CP}$ 8.0 Hz), 131.9 d ($C^{4'}$, $^4J_{CP}$ 2.0 Hz), 134.6 d ($C^{1'}$, $^1J_{CP}$ 109.7 Hz), 149.1 d (C^{10}, $^2J_{CP}$ 8.0 Hz), 156.9 s (C^3); **^{31}P NMR** ($CDCl_3$, 161.98 MHz) δ, ppm: 5.4; **HRMS** (ESI): m/z calcd for $C_{17}H_{17}OPH$ $[M+H]^+$ 269.1090, found 269.1076; m/z calcd for $C_{17}H_{17}OPNa$ $[M+Na]^+$ 291.0904, found 291.0895.

1'-Phenyl-1'H-spiro[cyclopentane-1,4'-phosphinoline] 1'-oxide (2b)



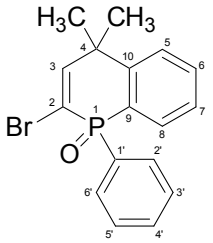
Colorless oil; **IR** (KBr), cm^{-1}: 654, 696, 720, 744, 774, 856, 915, 967, 1078, 1115, 1247, 1292, 1368, 1440, 1485, 1592, 1620, 2870, 2935, 2958, 2976, 3058; **^{1}H NMR** ($CDCl_3$, 400.13 MHz) δ, ppm: 1.96–2.25 m (8H, $C^{11}H_2$, $C^{12}H_2$, $C^{13}H_2$, $C^{14}H_2$), 6.14 dd (1H, C^2H, $^3J_{HH}$ 12.0 Hz, $^2J_{HP}$ 12.0 Hz), 6.85 dd (1H, C^3H, $^3J_{HH}$ 12.0 Hz, $^3J_{HP}$ 36.0 Hz), 7.23–7.26 m (1H, $H_{arom.}$), 7.37–7.49 m (5H, $H_{arom.}$), 7.61–7.68 m (3H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100.61 MHz) δ, ppm: 27.0 s (C^{12}), 27.1 s (C^{13}), 44.1 d (C^{11}, $^4J_{CP}$ 2.0 Hz), 44.9 d (C^{14}, $^4J_{CP}$ 2.0 Hz), 49.1 d (C^4, $^3J_{CP}$ 13.1 Hz), 115.6 d (C^2, $^1J_{CP}$ 99.6 Hz), 126.7 d (C^7, $^3J_{CP}$ 11.1 Hz), 127.2 d (C^5, $^3J_{CP}$ 8.0 Hz), 128.2 d (C^9, $^1J_{CP}$ 103.6 Hz), 128.6 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 13.1 Hz), 131.1 d (C^8, $^2J_{CP}$ 8.0 Hz), 131.3 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 10.1 Hz), 131.5 d (C^6, $^4J_{CP}$ 3.0 Hz), 132.0 d ($C^{4'}$, $^4J_{CP}$ 2.0 Hz), 134.7 d ($C^{1'}$, $^1J_{CP}$ 109.7 Hz), 150.2 d (C^{10}, $^2J_{CP}$ 7.0 Hz), 155.3 s (C^3); **^{31}P NMR** ($CDCl_3$, 161.98 MHz) δ, ppm: 4.8; **HRMS** (ESI): (ESI): m/z calcd for $C_{19}H_{19}OPH$ $[M+H]^+$ 295.1246, found 295.1238; m/z calcd for $C_{19}H_{19}OPNa$ $[M+Na]^+$ 317.1060, found 317.1055.

1'-Phenyl-1'H-spiro[cyclohexane-1,4'-phosphinoline] 1'-oxide (2c)



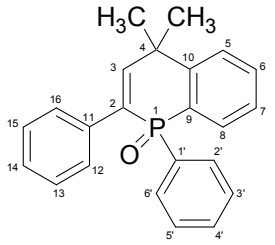
Colorless solid; mp 151–152°C; **IR** (KBr), cm^{-1}: 654, 694, 718, 745, 772, 854, 910, 965, 1076, 1115, 1245, 1290, 1366, 1438, 1485, 1590, 1618, 2872, 2932, 2958, 2974, 3060; **^{1}H NMR** ($CDCl_3$, 400.13 MHz) δ, ppm: 1.71–2.16 m (10H, $C^{11}H_2$, $C^{12}H_2$, $C^{13}H_2$, $C^{14}H_2$, $C^{15}H_2$), 6.34 dd (1H, $C^{2}H$, $^{3}J_{HH}$ 12.0 Hz, $^{2}J_{HP}$ 16.0 Hz), 7.26–7.30 m (1H, $H_{arom.}$), 7.40–7.70 m (9H, $8H_{arom.}$, $C^{3}H$), 7.53 dd (1H, $C^{3}H$, $^{3}J_{HH}$ 12.0 Hz, $^{3}J_{HP}$ 36.0 Hz); **^{13}C NMR** ($CDCl_3$, 100.61 MHz) δ, ppm: 22.2 s (C^{12}), 22.5 s (C^{14}), 25.8 s (C^{13}), 39.7 d (C^{11}, $^{4}J_{CP}$ 2.0 Hz), 40.0 d (C^{15}, $^{4}J_{CP}$ 2.0 Hz), 41.3 d (C^{4}, $^{3}J_{CP}$ 12.1 Hz), 118.7 d (C^{2}, $^{1}J_{CP}$ 98.6 Hz), 126.8 d (C^{7}, $^{3}J_{CP}$ 8.0 Hz), 126.9 d (C^{5}, $^{3}J_{CP}$ 11.1 Hz), 128.5 d (C^{9}, $^{1}J_{CP}$ 102.6 Hz), 128.6 d ($C^{3'}$, $C^{5'}$, $^{3}J_{CP}$ 13.1 Hz), 131.5 d ($C^{2'}$, $C^{6'}$, $^{2}J_{CP}$ 11.1 Hz), 131.6 d (C^{6}, $^{4}J_{CP}$ 3.0 Hz), 131.7 d (C^{8}, $^{2}J_{CP}$ 8.0 Hz), 131.8 d ($C^{4'}$, $^{4}J_{CP}$ 2.0 Hz), 134.7 d ($C^{1'}$, $^{1}J_{CP}$ 108.7 Hz), 150.6 d (C^{10}, $^{2}J_{CP}$ 7.0 Hz), 152.4 s (C^{3}); **^{31}P NMR** ($CDCl_3$, 161.98 MHz) δ, ppm: 4.3; **HRMS** (ESI): m/z calcd for $C_{20}H_{21}OPH$ $[M+H]^+$ 309.1403, found 309.1384; m/z calcd for $C_{20}H_{21}OPNa$ $[M+Na]^+$ 331.1217, found 331.1200.

***1-Phenyl-2-bromo-4,4-dimethyl-1,4-dihydrophosphinoline 1-oxide* (*2d*)**



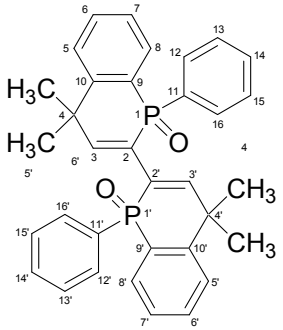
Colorless solid; mp 195–196°C; **IR** (KBr), cm^{-1}: 654, 692, 714, 743, 774, 852, 907, 962, 1072, 1113, 1247, 1293, 1364, 1436, 1482, 1592, 1616, 2872, 2929, 2956, 2976, 3058; **^{1}H NMR** ($CDCl_3$, 400.13 MHz) δ, ppm: 1.58 s (3H, CH_3), 1.61 s (3H, CH_3), 7.07 d (1H, $C^{3}H$, $^{3}J_{HP}$ 28.0 Hz), 7.30–7.35 m (1H, $H_{arom.}$), 7.42–7.46 m (2H, $H_{arom.}$), 7.49–7.55 m (3H, $H_{arom.}$), 7.62–7.72 m (3H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100.61 MHz) δ, ppm: 31.4 d (CH_3, $^{4}J_{CP}$ 2.0 Hz), 32.0 d (CH_3, $^{4}J_{CP}$ 2.0 Hz), 42.7 d (C^{4}, $^{3}J_{CP}$ 9.1 Hz), 113.6 d (C^{2}, $^{1}J_{CP}$ 97.6 Hz), 126.8 d (C^{9}, $^{1}J_{CP}$ 104.6 Hz), 127.0 d (C^{7}, $^{3}J_{CP}$ 9.1 Hz), 127.5 d (C^{5}, $^{3}J_{CP}$ 11.1 Hz), 128.7 d ($C^{3'}$, $C^{5'}$, $^{3}J_{CP}$ 13.1 Hz), 131.9 d ($C^{2'}$, $C^{6'}$, $^{2}J_{CP}$ 11.1 Hz), 132.1 d ($C^{1'}$, $^{1}J_{CP}$ 114.7 Hz), 132.2 d (C^{6}, $^{4}J_{CP}$ 3.0 Hz), 132.3 d ($C^{4'}$, $^{4}J_{CP}$ 3.0 Hz), 132.4 d (C^{8}, $^{2}J_{CP}$ 9.1 Hz), 148.4 d (C^{10}, $^{2}J_{CP}$ 8.0 Hz), 155.8 d (C^{3}, $^{2}J_{CP}$ 10.1 Hz); **^{31}P NMR** ($CDCl_3$, 161.98 MHz) δ, ppm: 6.9; **HRMS** (MALDI): m/z calcd for $C_{17}H_{16}BrOPH$ $[M+H]^+$ 347.0195, found 347.0197.

***1,2-Diphenyl-4,4-dimethyl-1,4-dihydrophosphinoline 1-oxide* (*2e*)**



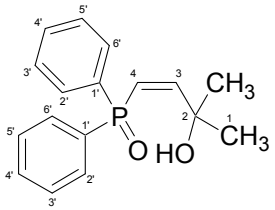
Colorless solid; mp 144–145°C; **IR** (KBr), cm^{-1}: 657, 694, 712, 748, 775, 850, 917, 969, 1070, 1108, 1242, 1290, 1367, 1430, 1484, 1597, 1613, 2870, 2934, 2952, 2980, 3060;**^{1}H NMR** ($CDCl_3$, 400.13 MHz) δ, ppm: 1.64 s (3H, CH_3), 1.66 s (3H, CH_3), 6.75 d (1H, C^3H, $^3J_{HP}$ 32.0 Hz), 7.21–7.38 m (7H, $H_{arom.}$), 7.49–7.60 m (6H, $H_{arom.}$), 7.71–7.76 m (1H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100.61 MHz) δ, ppm: 31.9 d (CH_3, $^4J_{CP}$ 2.0 Hz), 32.3 d (CH_3, $^4J_{CP}$ 2.0 Hz), 39.3 d (C^4, $^3J_{CP}$ 11.1 Hz), 126.7 d (C^7, $^3J_{CP}$ 9.1 Hz), 127.2 d (C^5, $^3J_{CP}$ 11.1 Hz), 128.0 s, 128.2 s, 128.2 d (C^2, $^1J_{CP}$ 100.6 Hz), 128.4 s, 128.6 s, 129.8 d (C^9, $^1J_{CP}$ 95.6 Hz), 131.35 s, 131.38 s, 131.41 s, 131.46 s, 131.81 s, 131.82 s, 131.85 s, 131.93 s, 134.3 d ($C^{1'}$, $^1J_{CP}$ 108.7 Hz), 137.4 d (C^{11}, $^2J_{CP}$ 8.0 Hz), 148.5 d (C^{10}, $^2J_{CP}$ 7.0 Hz), 153.6 d (C^3, $^2J_{CP}$ 7.0 Hz); **^{31}P NMR** ($CDCl_3$, 161.98 MHz) δ, ppm: 8.6; **HRMS** (ESI): m/z calcd for $C_{23}H_{23}O_2PH$ $[M+H]^+$ 363.1508, found 363.1502.

1,1'-Diphenyl-4,4,4',4'-tetramethyl-1,1',4,4'-tetrahydro -2,2'-biphosphinoline 1,1'-dioxide (2f)



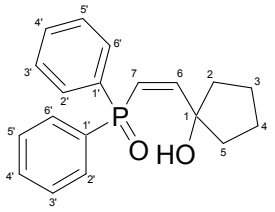
Colorless solid; mp 309–310°C; **IR** (KBr), cm^{-1}: 647, 695, 719, 743, 769, 926, 957, 1071, 1118, 1145, 1187, 1248, 1352, 1436, 1483, 1604, 1744, 1999, 2873, 2924, 2964, 3016, 3051, 3088, 3441; **^{1}H NMR** ($CDCl_3$, 400.13 MHz) δ, ppm: 1.41 s (6H, $2CH_3$), 1.63 s (6H, $2CH_3$), 7.12–7.22 m (10H, $H_{arom.}$), 7.28–7.32 m (2H, $H_{arom.}$), 7.42–7.46 m (6H, $H_{arom.}$), 7.89 d (2H, C^3H, $C^{3'}H$, $^3J_{HP}$ 48.0 Hz); **^{13}C NMR** ($CDCl_3$, 100.61 MHz) δ, ppm: 31.6 s ($2CH_3$), 32.2 s ($2CH_3$), 39.38 d (C^4, $^3J_{CP}$ 6.0 Hz), 39.43 d ($C^{4'}$, $^3J_{CP}$ 6.0 Hz), 123.5 d (C^2, $C^{2'}$, $^1J_{CP}$ 106.6 Hz), 126.50 s, 126.54 s, 126.58 s, 127.04 s, 128.08 s, 128.14 s, 128.20 s, 131.1 s, 131.56 s, 131.61 s, 131.65 s, 131.71 s, 131.76 s, 131.81 s, 133.16 d ($C^{11'}$, $^1J_{CP}$ 110.7 Hz), 133.21 d (C^{11}, $^1J_{CP}$ 111.7 Hz), 148.87 d (C^{10}, $^2J_{CP}$ 3.0 Hz), 148.90 d ($C^{10'}$, $^2J_{CP}$ 3.0 Hz), 155.99 d (C^3, $^2J_{CP}$ 5.0 Hz), 156.05 d ($C^{3'}$, $^2J_{CP}$ 6.0 Hz); **^{31}P NMR** ($CDCl_3$, 161.98 MHz) δ, ppm: 8.9; **HRMS** (MALDI): m/z calcd for $C_{34}H_{32}O_2P_2H$ $[M+H]^+$ 535.1950, found 535.1952.

(3Z)-2-Methyl-4-(diphenylphosphoryl)but-3-en-2-ol (3a)(lit.3)



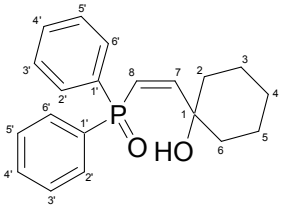
Colorless solid; mp 103–104°C; **IR** (KBr), cm^{-1}: 657, 695, 714, 756, 966, 1070, 1117, 1163, 1262, 1355, 1437, 1483, 1590, 1619, 2862, 2926, 2975, 3060, 3258; **^{1}H NMR** ($CDCl_3$, 400.13 MHz) δ, ppm: 1.44 s (6H, $2CH_3$), 5.93 dd (1H, C^4H, $^3J_{HH}$ 12.0 Hz, $^2J_{HP}$ 24.0 Hz), 6.50 s (1H, OH), 6.85 dd (1H, C^3H, $^3J_{HH}$ 12.0 Hz, $^3J_{HP}$ 40.0 Hz), 7.43–7.47 m (4H, $H_{arom.}$), 7.50–7.54 m (2H, $H_{arom.}$), 7.69–7.74 m (4H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100.61 MHz) δ, ppm: 30.5 s ($2CH_3$), 71.1 d (C^2, $^3J_{CP}$ 7.0 Hz), 117.9 d (C^4, $^1J_{CP}$ 98.6 Hz), 128.8 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 12.1 Hz), 131.4 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 10.1 Hz), 132.0 d ($C^{4'}$, $^4J_{CP}$ 3.0 Hz), 133.1 d ($C^{1'}$, $^1J_{CP}$ 106.6 Hz), 162.1 s (C^3); **^{31}P NMR** ($CDCl_3$, 161.98 MHz) δ, ppm: 26.7; **HRMS** (MALDI): m/z calcd for $C_{17}H_{19}O_2PH$ $[M+H]^+$ 287.1195, found 287.1193.

1-[(Z)-2-(Diphenylphosphoryl)ethenyl]cyclopentanol (3b)



Colorless solid; mp 121.5–123°C; **IR** (KBr), cm^{-1}: 659, 696, 712, 754, 966, 1072, 1119, 1160, 1265, 1357, 1430, 1490, 1592, 1611, 2865, 2925, 2978, 3064, 3260; **^{1}H NMR** ($CDCl_3$, 400.13 MHz) δ, ppm: 1.63–1.73 m (4H, C^2H_2, C^5H_2), 1.94–1.98 m (4H, C^3H_2, C^4H_2), 5.99 dd (1H, C^7H, $^3J_{HH}$ 12.0 Hz, $^2J_{HP}$ 24.0 Hz), 6.13 br s (1H, OH), 6.89 dd (1H, C^6H, $^3J_{HH}$ 12.0 Hz, $^3J_{HP}$ 40.0 Hz), 7.43–7.53 m (6H, $H_{arom.}$), 7.69–7.74 m (4H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100.61 MHz) δ, ppm: 24.2 s (C^3, C^4), 41.5 d (C^2, C^5, $^4J_{CP}$ 1.0 Hz), 81.7 d (C^1, $^3J_{CP}$ 7.0 Hz), 118.6 d (C^7, $^1J_{CP}$ 98.6 Hz), 128.8 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 12.1 Hz), 131.4 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 10.1 Hz), 132.0 d ($C^{4'}$, $^4J_{CP}$ 3.0 Hz), 133.3 d ($C^{1'}$, $^1J_{CP}$ 106.6 Hz), 161.1 s (C^6); **^{31}P NMR** ($CDCl_3$, 161.98 MHz) δ, ppm: 26.7; **HRMS** (ESI): m/z calcd for $C_{19}H_{21}O_2PH$ $[M+H]^+$ 313.1352, found 313.1348.

1-[(Z)-2-(Diphenylphosphoryl)ethenyl]cyclohexanol (3c)

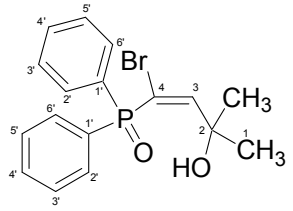


Colorless solid; mp 128–130°C (monohydrate); **IR** (KBr), cm^{-1}: 655, 698, 714, 754, 968, 1070, 1120, 1162, 1264, 1360, 1430, 1492, 1595, 1615, 2862, 2927, 2980, 3065, 3260; **^{1}H NMR** ($CDCl_3$, 400.13 MHz) δ, ppm: 1.43–1.85 m (10H, C^2H_2, C^3H_2, C^4H_2, C^5H_2, C^6H_2), 5.94 dd (1H, C^8H, $^3J_{HH}$ 12.0 Hz, $^2J_{HP}$ 24.0 Hz), 6.21 br s (1H, OH), 6.87 dd (1H, C^7H, $^3J_{HH}$ 12.0 Hz, $^3J_{HP}$ 40.0 Hz), 7.43–7.54 m (6H, $H_{arom.}$), 7.69–7.73 m (4H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100.61 MHz) δ, ppm: 21.9 s (C^3, C^5), 25.7 s (C^4), 38.2 s (C^2, C^6), 83.1 d (C^1, $^3J_{CP}$ 7.0 Hz), 120.1 d (C^8, $^1J_{CP}$ 98.6 Hz), 130.2 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 13.1 Hz), 132.8 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 10.1 Hz), 133.4 d ($C^{4'}$, $^4J_{CP}$ 3.0 Hz), 134.8 d ($C^{1'}$, $^1J_{CP}$ 106.6 Hz), 162.6 s (C^7); **^{31}P NMR**

[3] E. F. Nifant'ev, L. A. Solovetskaya, V. I. Maslennikova, N. M. Sergeev. *J. Gen. Chem. USSR (Engl. Transl.)*, **1987**, *57*, 449 - 453.

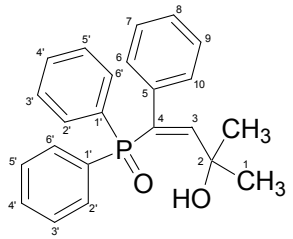
($CDCl_3$, 161.98 MHz) δ, ppm: 26.7; **HRMS** (ESI): m/z calcd for $C_{20}H_{23}O_2PH$ $[M+H]^+$ 327.1508, found 327.1496.

(3E)-2-Methyl-4-bromo-4-(diphenylphosphoryl)but-3-en-2-ol (3d)



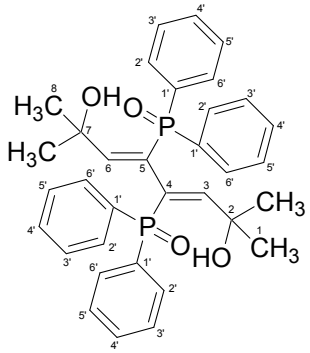
Colorless solid; mp 92.5–94°C; **IR** (KBr), cm^{-1}: 655, 698, 714, 754, 972, 1075, 1112, 1168, 1264, 1345, 1435, 1480, 1592, 1623, 2860, 2924, 2980, 3060, 3260; **^{1}H NMR** ($CDCl_3$, 400.13 MHz) δ, ppm: 1.51 s (6H, $2CH_3$), 6.97 s (1H, OH), 7.45 d (1H, C^3H, $^3J_{HP}$ 28.0 Hz), 7.48–7.53 m (4H, $H_{arom.}$), 7.59–7.62 m (2H, $H_{arom.}$), 7.83–7.88 m (4H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100.61 MHz) δ, ppm: 31.0 s ($2CH_3$), 71.9 d (C^2, $^3J_{CP}$ 3.0 Hz), 111.8 d (C^4, $^1J_{CP}$ 94.6 Hz), 128.7 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 13.1 Hz), 129.3 d ($C^{1'}$, $^1J_{CP}$ 110.7 Hz), 132.8 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 10.1 Hz), 132.9 d ($C^{4'}$, $^4J_{CP}$ 3.0 Hz), 165.3 d (C^3, $^2J_{CP}$ 8.0 Hz); **^{31}P NMR** ($CDCl_3$, 161.98 MHz) δ, ppm: 31.5; **HRMS** (ESI): m/z calcd for $C_{17}H_{18}BrO_2PNa$ $[M+Na]^+$ 387.0114, found 387.0106.

(3Z)-2-Methyl-4-phenyl-4-(diphenylphosphoryl)but-3-en-2-ol (3e)



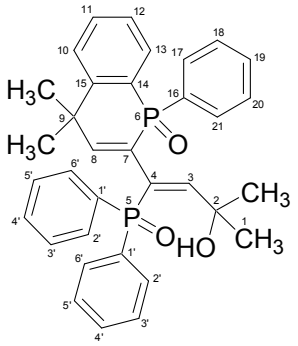
Colorless solid; mp 158–159°C; **IR** (KBr), cm^{-1}: 650, 698, 710, 754, 970, 1075, 1120, 1160, 1262, 1358, 1435, 1482, 1590, 1620, 2865, 2924, 2975, 3062, 3264; **^{1}H NMR** ($CDCl_3$, 400.13 MHz) δ, ppm: 1.56 s (6H, $2CH_3$), 6.70 s (1H, OH), 6.72 d (1H, C^3H, $^3J_{HP}$ 36.0 Hz), 6.99–7.12 m (4H, $H_{arom.}$), 7.34–7.38 m (4H, $H_{arom.}$), 7.46–7.50 m (2H, $H_{arom.}$), 7.55–7.60 m (4H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100.61 MHz) δ, ppm: 31.1 s ($2CH_3$), 70.6 d (C^2, $^3J_{CP}$ 5.0 Hz), 127.3 d ($C^{4'}$, $^4J_{CP}$ 1.0 Hz), 128.0 s (C^8), 128.3 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 13.1 Hz), 129.9 d (C^7, C^9, $^4J_{CP}$ 3.0 Hz), 131.4 d ($C^{1'}$, $^1J_{CP}$ 105.6 Hz), 132.0 d (C^4, $^1J_{CP}$ 91.6 Hz), 132.1 d (C^6, C^{10}, $^3J_{CP}$ 2.0 Hz), 132.7 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 10.1 Hz), 140.2 d (C^5, $^2J_{CP}$ 13.1 Hz), 162.2 d (C^3, $^2J_{CP}$ 6.0 Hz); **^{31}P NMR** ($CDCl_3$, 161.98 MHz) δ, ppm: 32.3; **HRMS** (ESI): m/z calcd for $C_{23}H_{23}O_2PH$ $[M+H]^+$ 363.1508, found 363.1499.

(3Z,5Z)-4,5-Bis(diphenylphosphoryl)-2,7-dimethylocta-3,5-diene-2,7-diol (3f)



Colorless solid; mp 177–179°C (hydrate according to X-ray); **IR** (KBr), cm^{-1}: 640, 694, 754, 847, 972, 1094, 1114, 1163, 1218, 1437, 1483, 1575, 1590, 1915, 1975, 2876, 2931, 2972, 3057, 3250; **^{1}H NMR** ($CDCl_3$, 400.13 MHz) δ, ppm: 1.27 s (12H, $4CH_3$), 6.39 dd (2H, C^3H, C^6H, $^3J_{HP}$ 40.0 Hz, $^4J_{HP}$ 4.0 Hz), 6.76 s (2H, 2OH), 7.33–7.38 m (8H, $H_{arom.}$), 7.47–7.52 m (12H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100.61 MHz) δ, ppm: 30.8 s ($4CH_3$), 70.47 d (C^2, $^3J_{CP}$ 1.0 Hz), 70.49 d (C^7, $^3J_{CP}$ 1.0 Hz), 127.4 d ($C^{1'}$, $^1J_{CP}$ 90.5 Hz), 127.5 d ($C^{1'}$, $^1J_{CP}$ 90.5 Hz), 128.37 s, 128.42 s, 128.48 s, 128.54 s, 128.59 s, 132.2 s ($C^{4'}$), 133.30 s, 133.35 s, 133.40 s, 133.45 s, 133.50 s, 162.81 d (C^3, $^2J_{CP}$ 5.0 Hz), 162.85 d (C^6, $^2J_{CP}$ 5.0 Hz); **^{31}P NMR** ($CDCl_3$, 161.98 MHz) δ, ppm: 31.3; **HRMS** (ESI): m/z calcd for $C_{34}H_{36}O_4P_2H$ $[M+H]^+$ 571.2162, found 571.2154.

(3Z)-2-Methyl-4-(diphenylphosphoryl)-4-(1-phenyl-1-oxido-4,4-dimethyl-1,4-dihydrophosphinolin-2-yl)but-3-en-2-ol (4a)



Colorless solid; mp 195–197°C; **IR** (KBr), cm^{-1}: 689, 708, 737, 771, 906, 961, 1092, 1119, 1150, 1199, 1233, 1333, 1361, 1397, 1436, 1482, 1592, 1623, 2864, 2928, 2969, 3058, 3224, 3424 ;**^{1}H NMR** ($CDCl_3$, 400.13 MHz) δ, ppm: 0.90 s (3H, CH_3), 0.96 s (3H, CH_3), 1.26 s (3H, CH_3), 1.32 s (3H, CH_3), 5.91 dd (1H, C^3H, $^3J_{HP}$ 36.0 Hz, $^4J_{HP}$ 4.0 Hz), 5.95 s (1H, OH), 6.30 dd (1H, C^8H, $^3J_{HP}$ 36.0 Hz, $^4J_{HP}$ 4.0 Hz), 7.24–7.59 m (15H, $H_{arom.}$), 7.70–7.74 m (2H, $H_{arom.}$), 7.98–8.02 m (2H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100.61 MHz) δ, ppm: 29.5 s (CH_3), 30.8 s ($2CH_3$), 32.0 s (CH_3), 39.0 d (C^9, $^3J_{CP}$ 10.1 Hz), 71.5 d (C^2, $^3J_{CP}$ 5.0 Hz), 125.20 s, 125.25 s, 126.10 s, 126.15 s, 126.56 s, 126.65 s, 127.14 s, 127.25 s, 127.65 s, 128.10 s, 128.23 s, 128.37 s, 128.58 s, 128.70 s, 131.43 s, 131. 45 s, 131.77 s, 131.84 s, 132.01 s, 132.03 s, 132.15 s, 132.26 s, 132.30 s, 132.40 s, 132.75 s, 133.09 s, 133.14 s, 133.23 s, 133.91 s, 134.17 s, 134.96 s, 148.64 s, 148.71 s, 149.13 s, 156.07 s, 156.12 s, 156.15 s, 156.20 s, 156.24 s, 163.32 d (C^3, $^2J_{CP}$ 5.0 Hz), 163.38 d (C^8, $^2J_{CP}$ 5.0 Hz); **^{31}P NMR** ($CDCl_3$, 161.98 MHz) δ, ppm: 8.9 d (P^6, $^3J_{PP}$ 8.1 Hz), 35.1 d (P^5, $^3J_{PP}$ 8.1 Hz); **HRMS** (MALDI): m/z calcd for $C_{34}H_{34}O_3P_2H$ $[M+H]^+$ 553.2056, found 553.2056.

^{1}H, ^{13}C, and ^{31}P NMR spectra of the compounds 2a-f, 3a-f, 4a

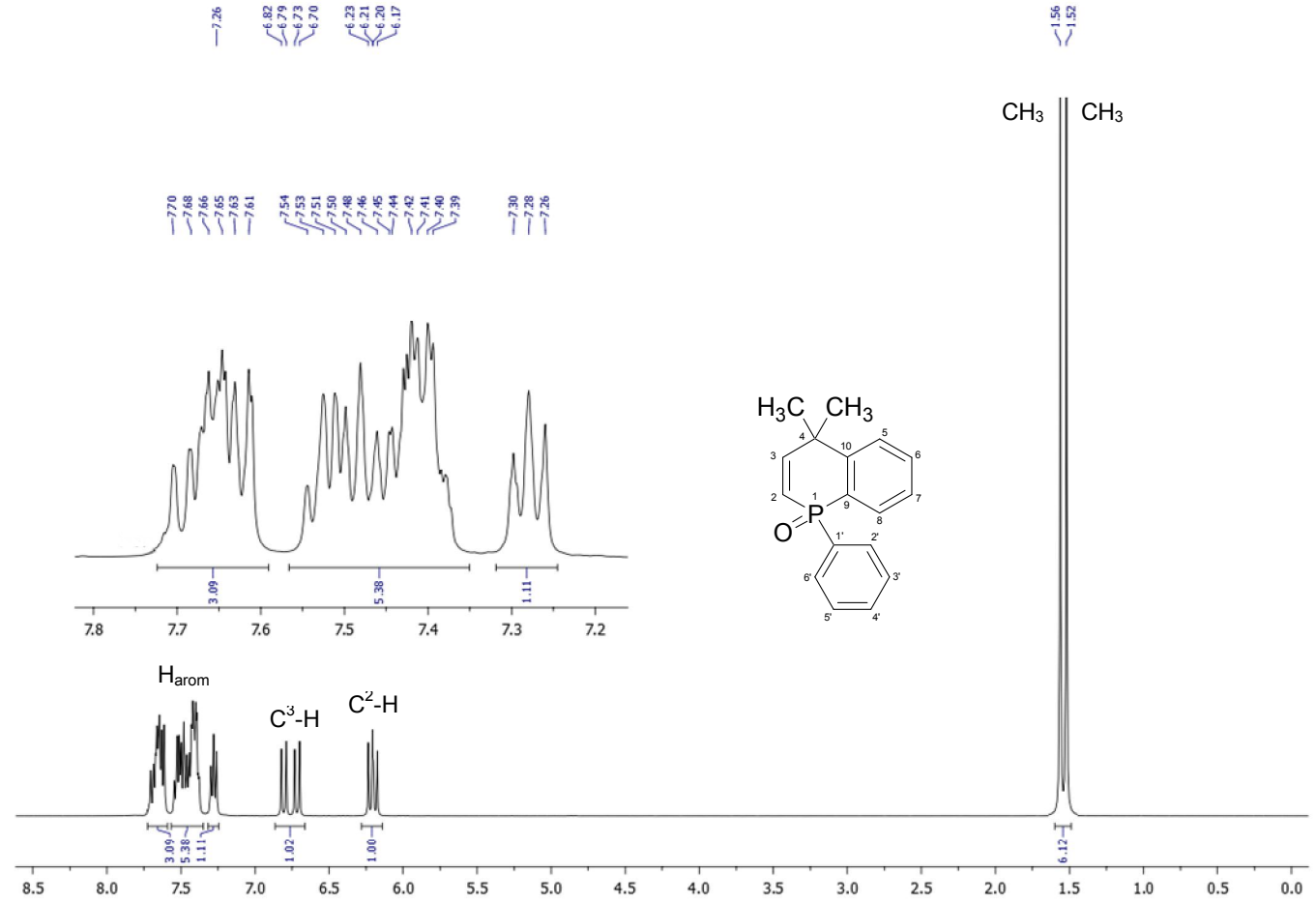


Fig. 1. ^{1}H NMR spectrum of the compound **2a** ($CDCl_3$, 400.13 MHz).

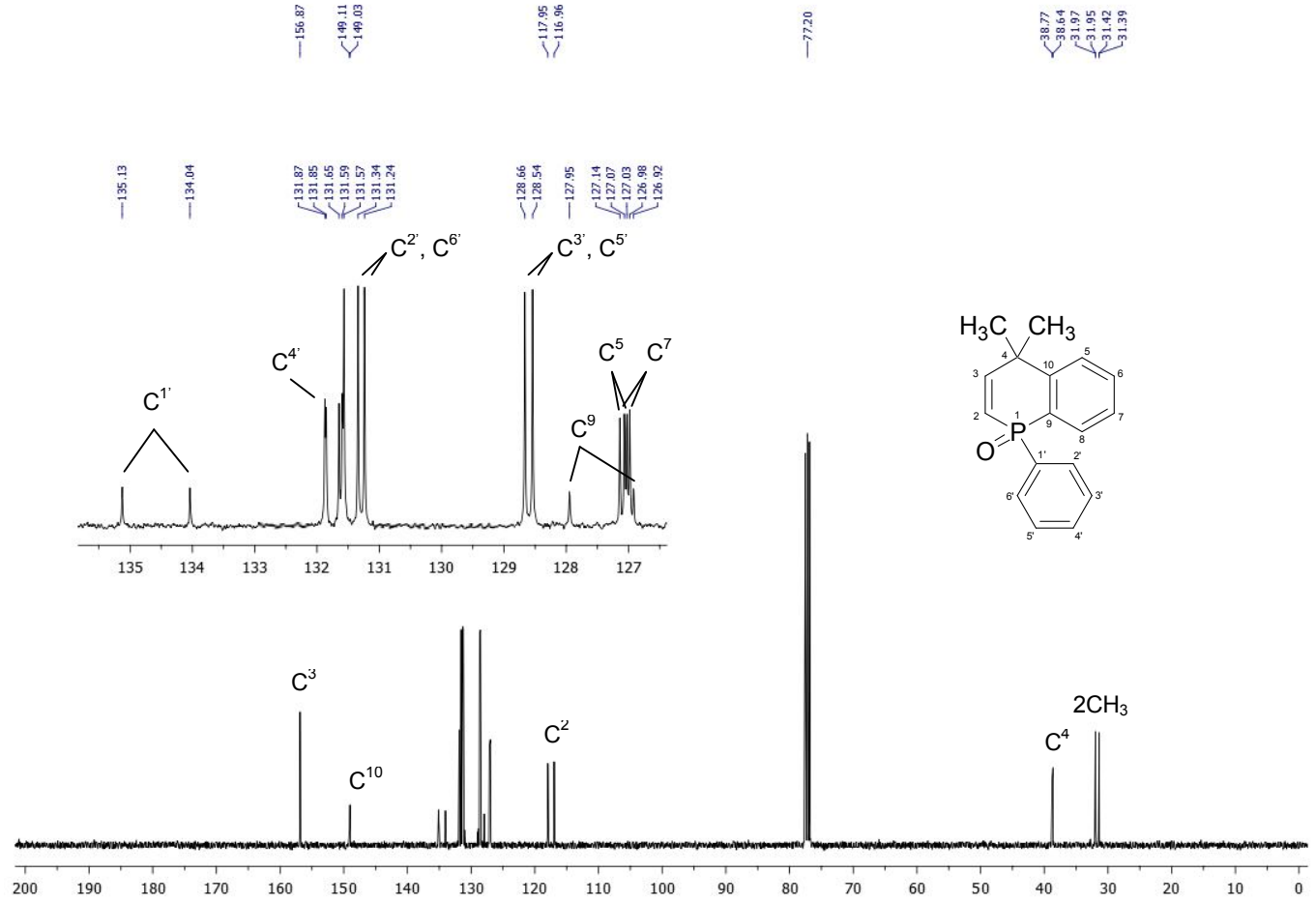


Fig. 2. ^{13}C NMR spectrum of the compound **2a** ($CDCl_3$, 100.61 MHz).

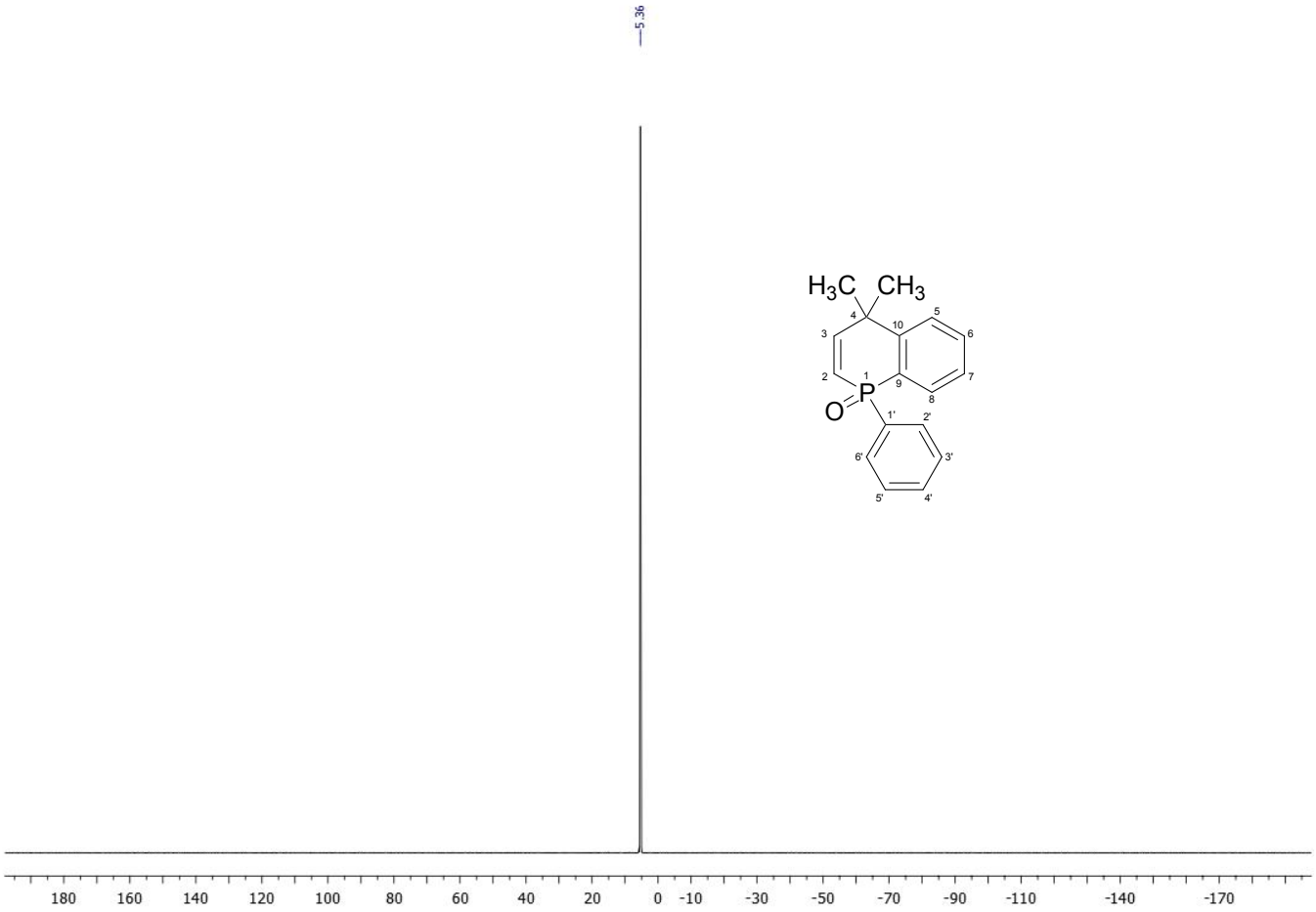


Fig. 3. ^{31}P NMR spectrum of the compound **2a** ($CDCl_3$, 161.98 MHz).

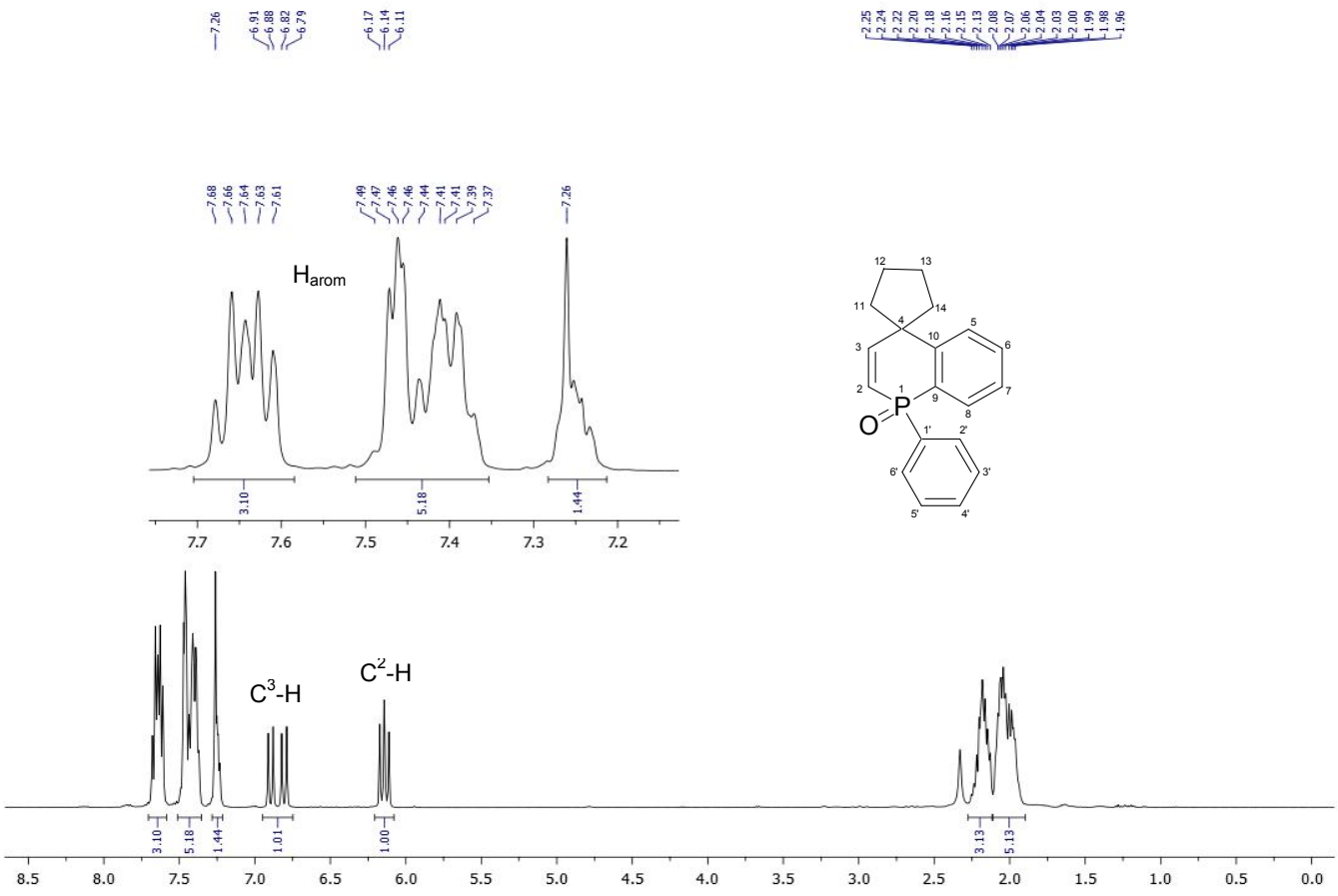


Fig. 4. ^{1}H NMR spectrum of the compound **2b** ($CDCl_3$, 400.13 MHz).

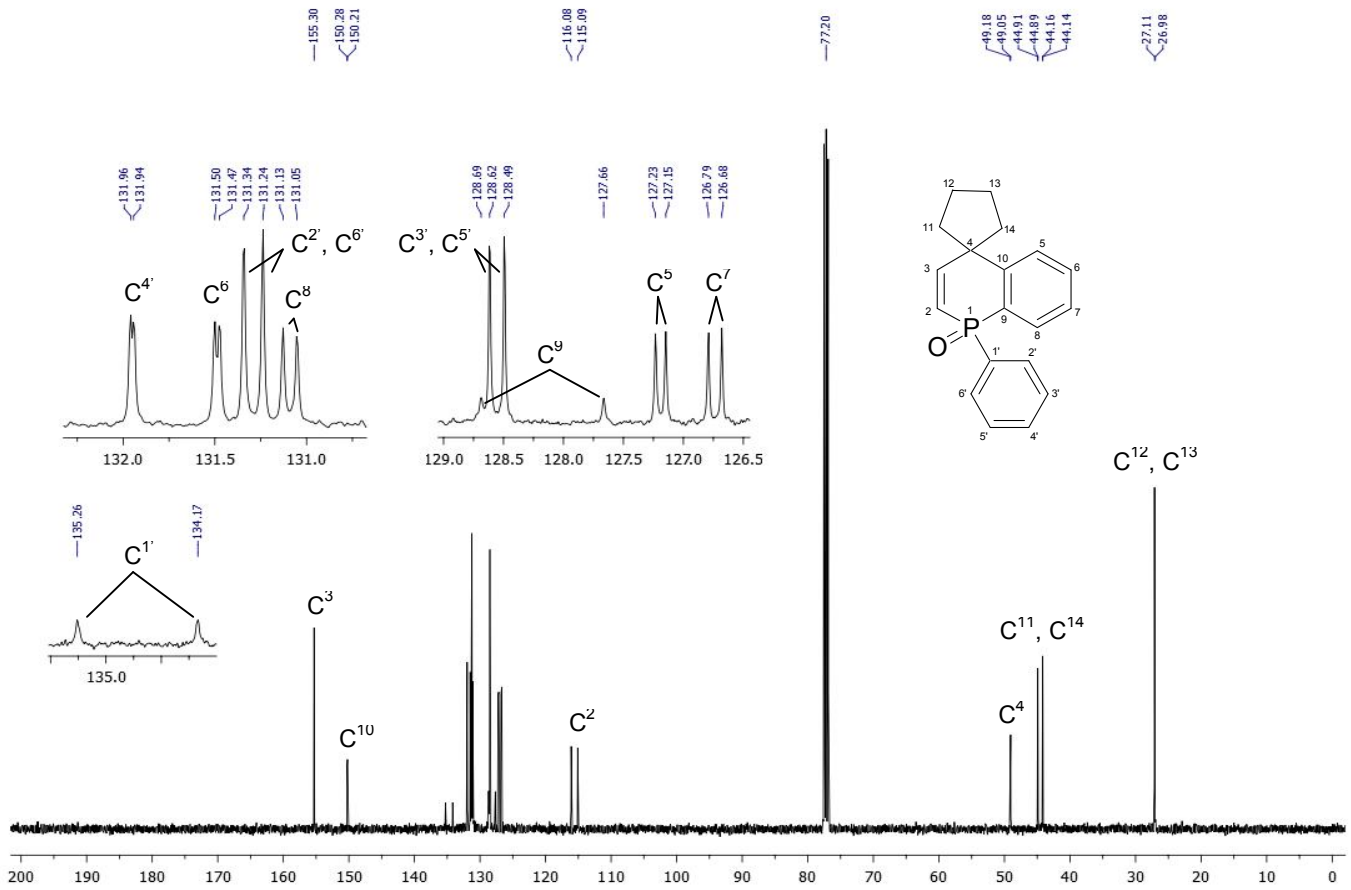


Fig. 5. ^{13}C NMR spectrum of the compound **2b** ($CDCl_3$, 100.61 MHz).

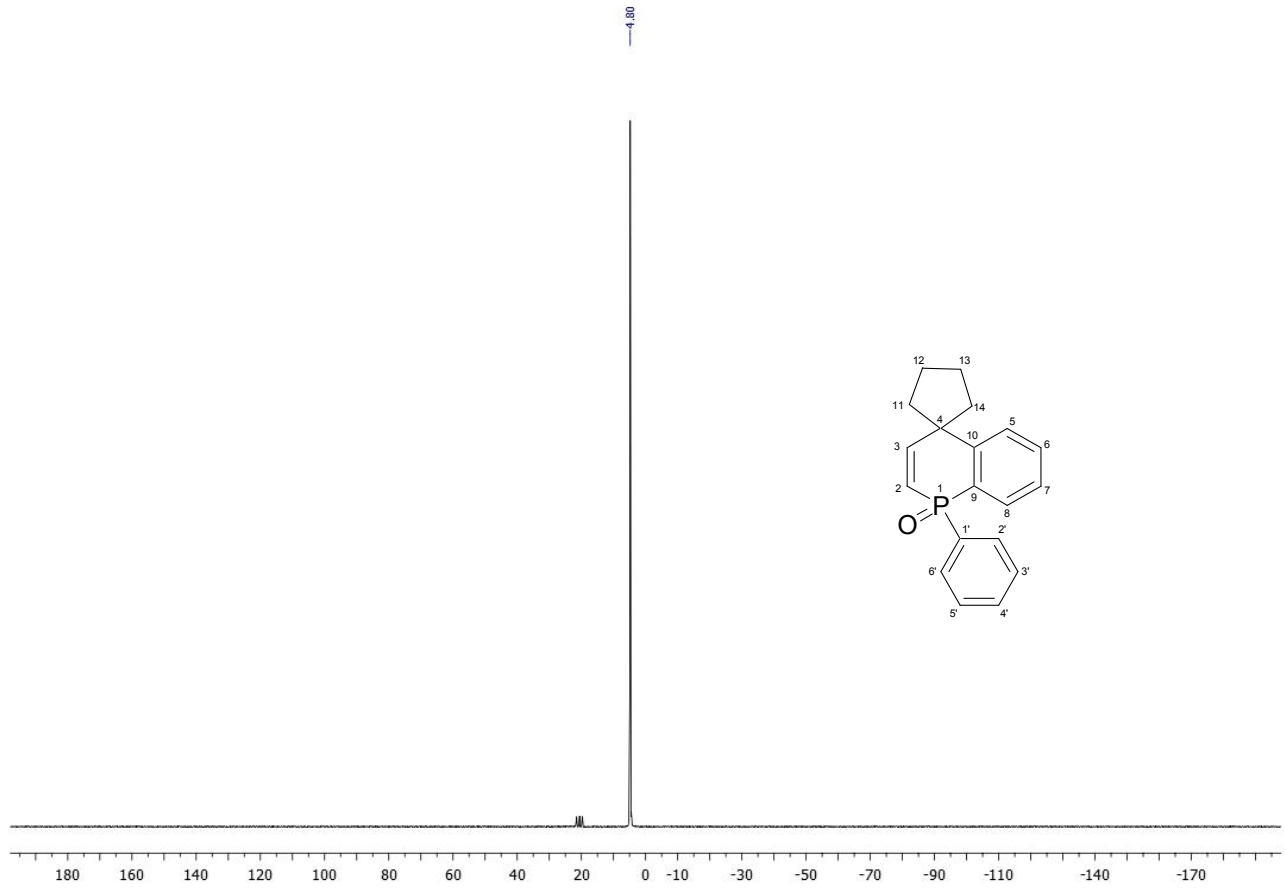


Fig. 6. ^{31}P NMR spectrum of the compound **2b** ($CDCl_3$, 161.98 MHz).

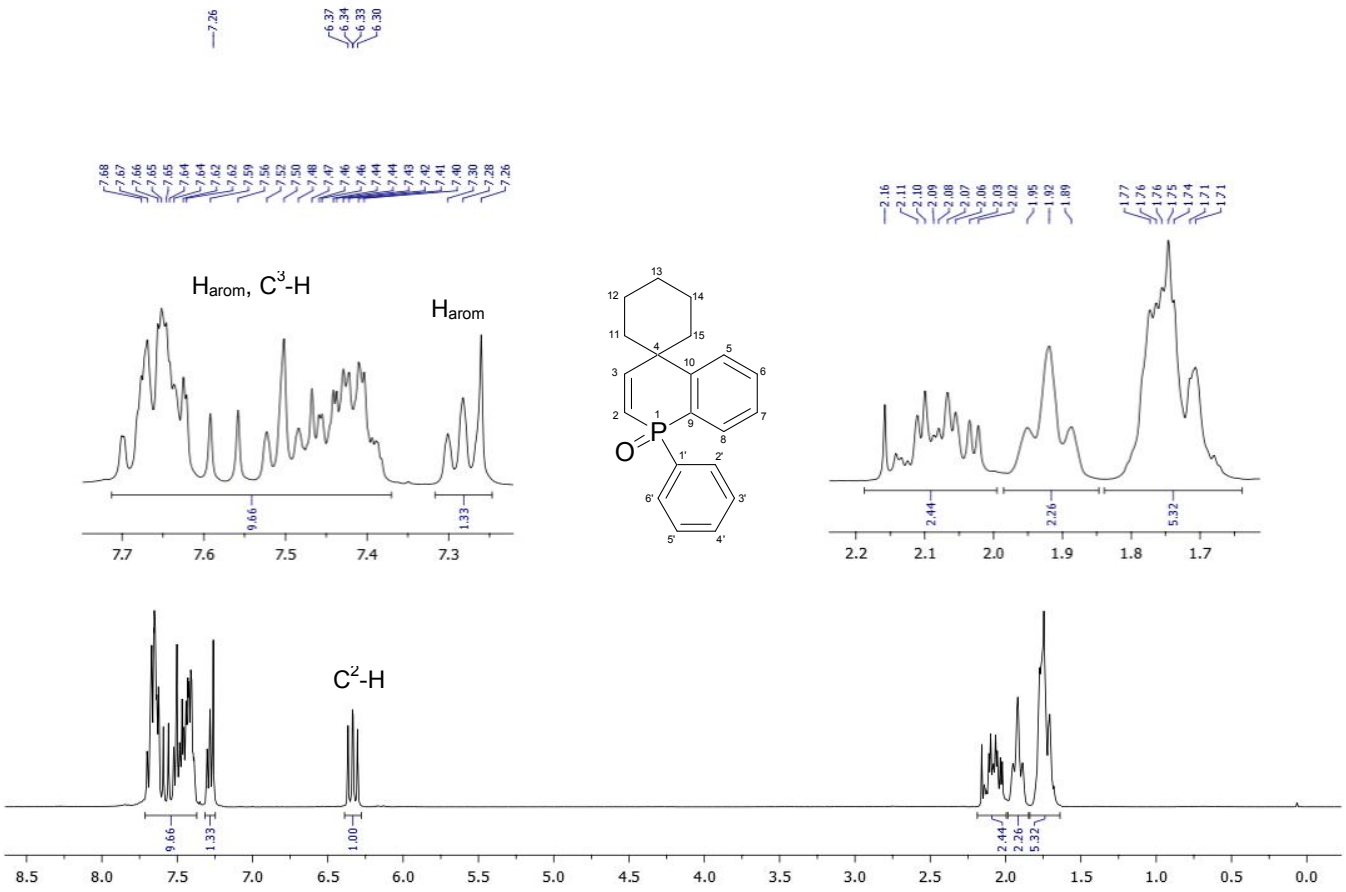


Fig. 7. ^{1}H NMR spectrum of the compound **2c** ($CDCl_3$, 400.13 MHz).

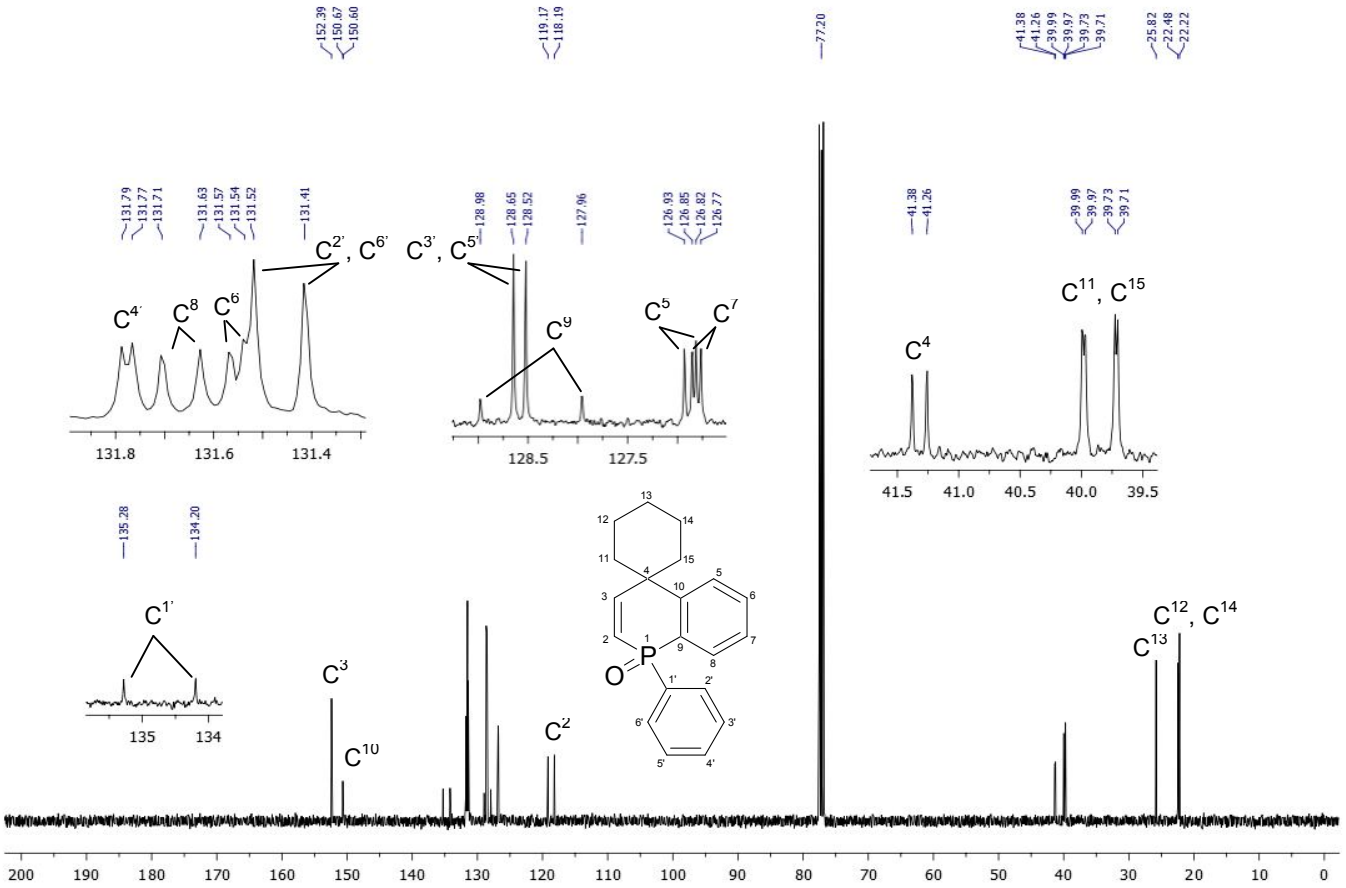


Fig. 8. ^{13}C NMR spectrum of the compound **2c** ($CDCl_3$, 100.61 MHz).

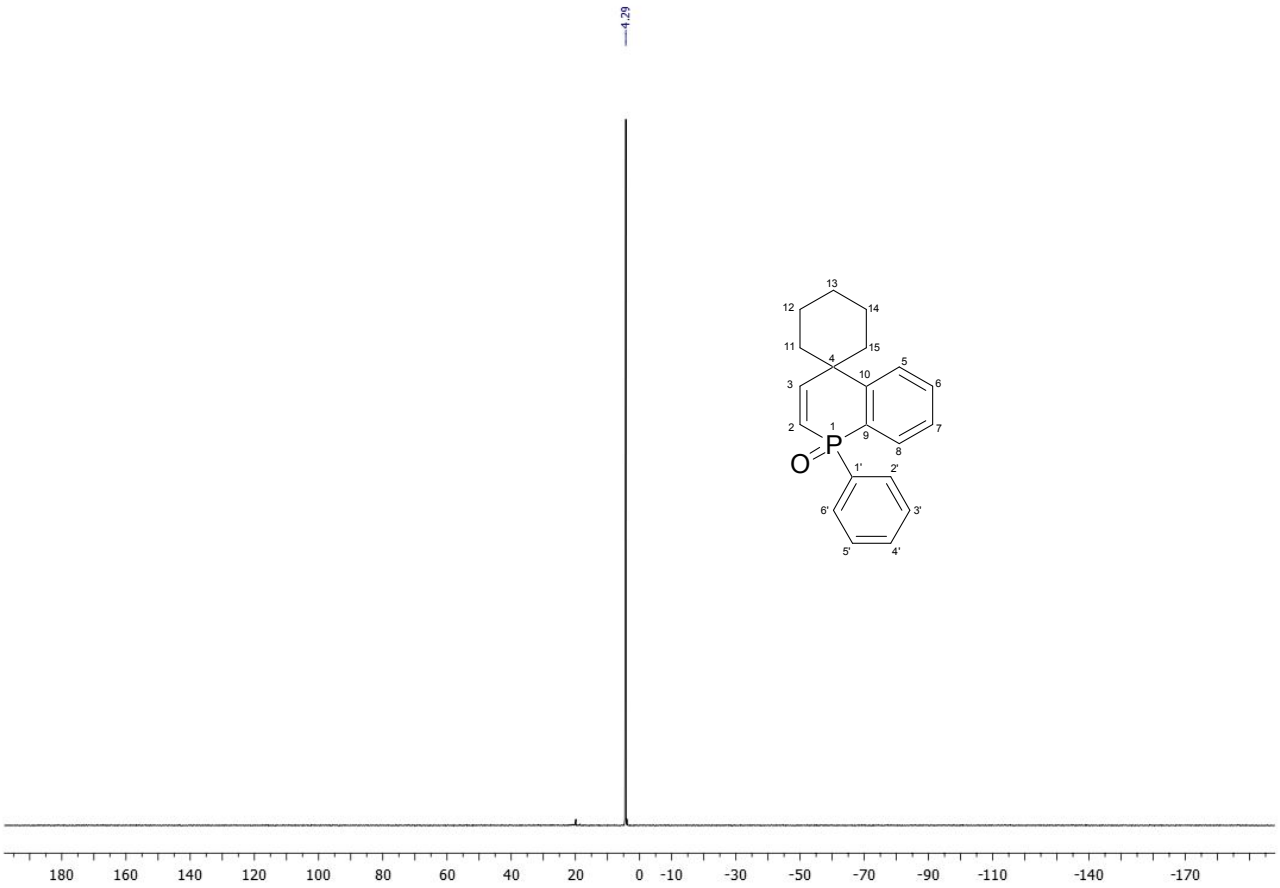


Fig. 9. ^{31}P NMR spectrum of the compound **2c** ($CDCl_3$, 161.98 MHz).

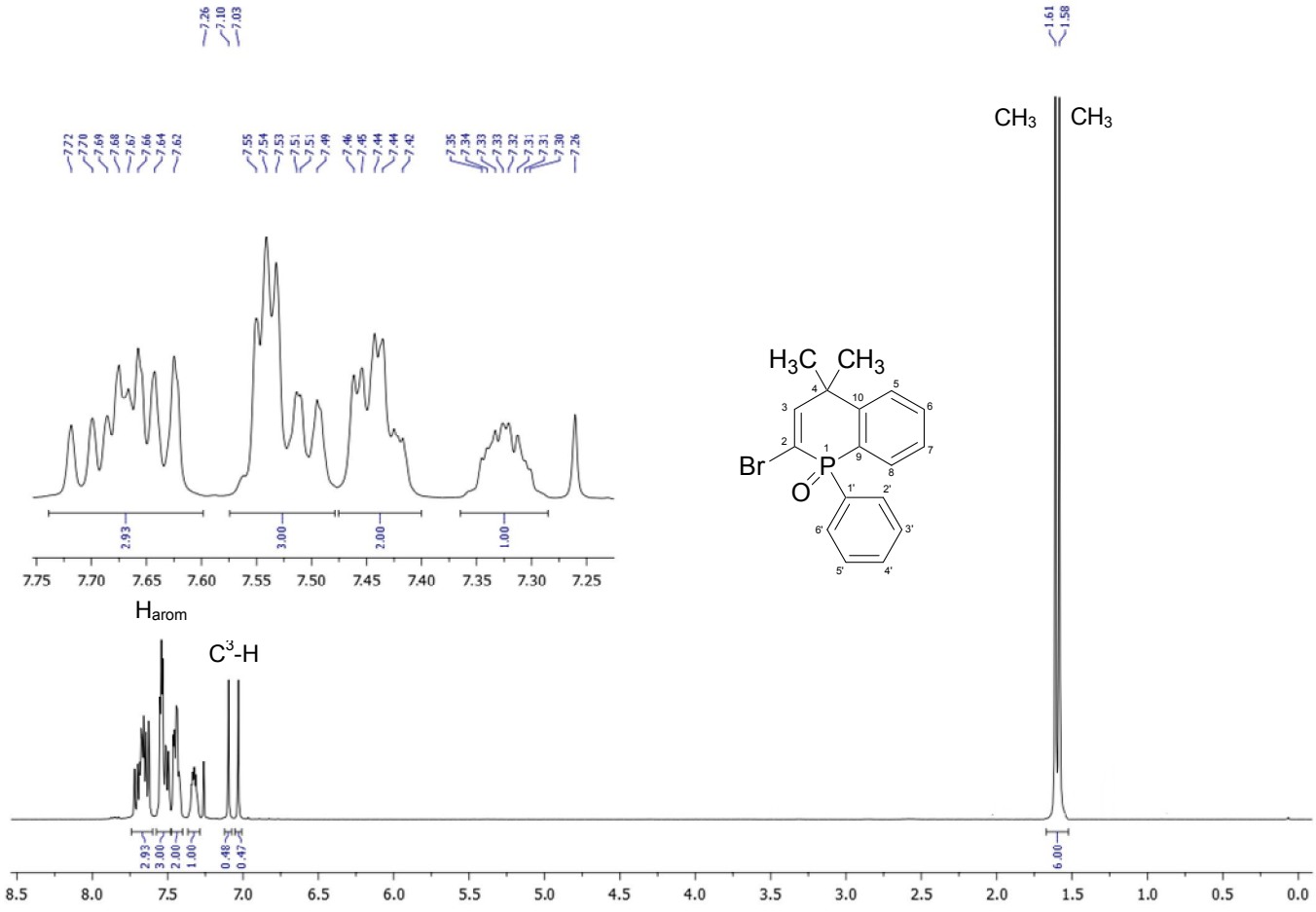


Fig. 10. ^{1}H NMR spectrum of the compound **2d** ($CDCl_3$, 400.13 MHz).

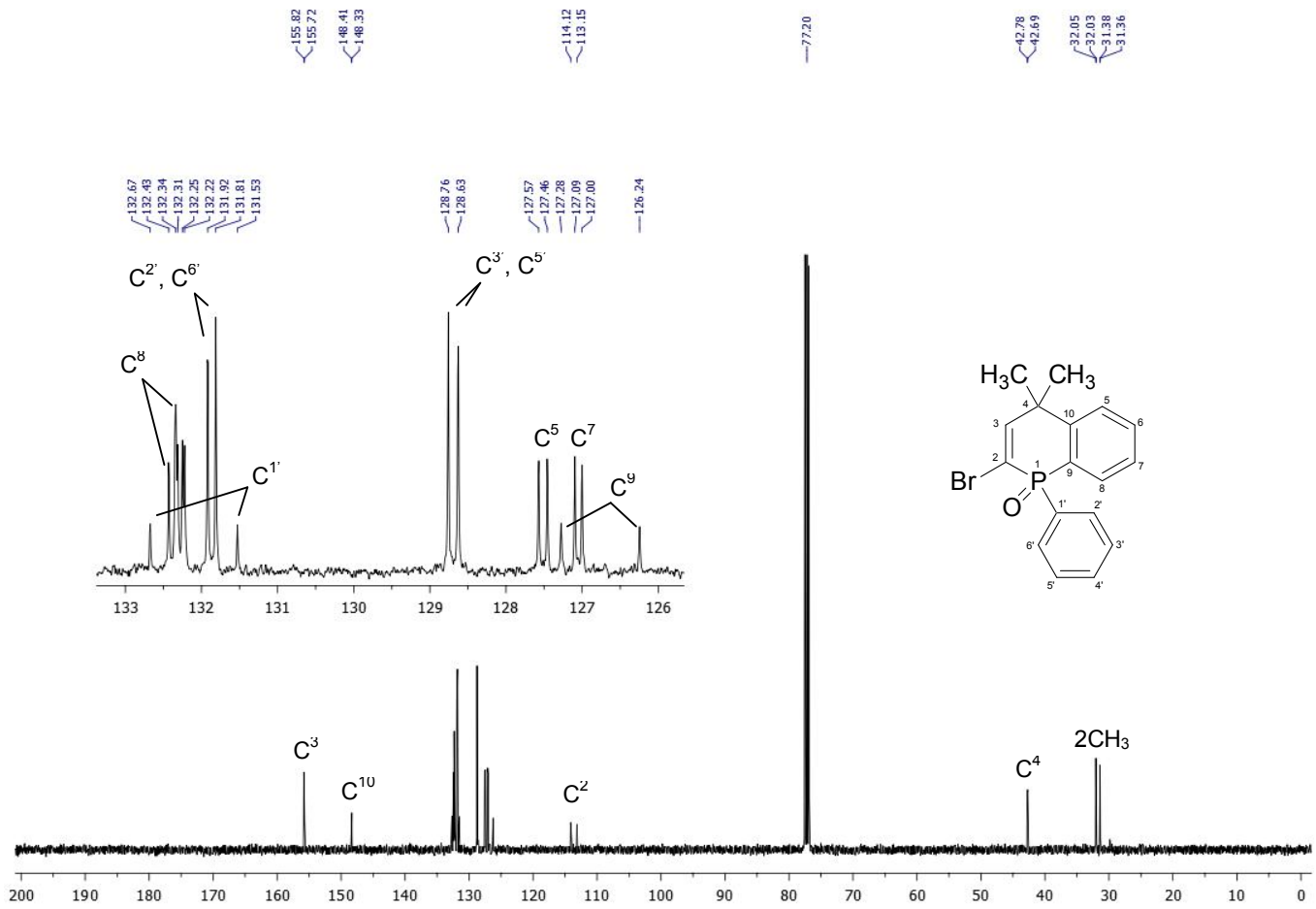


Fig. 11. ^{13}C NMR spectrum of the compound **2d** ($CDCl_3$, 100.61 MHz).

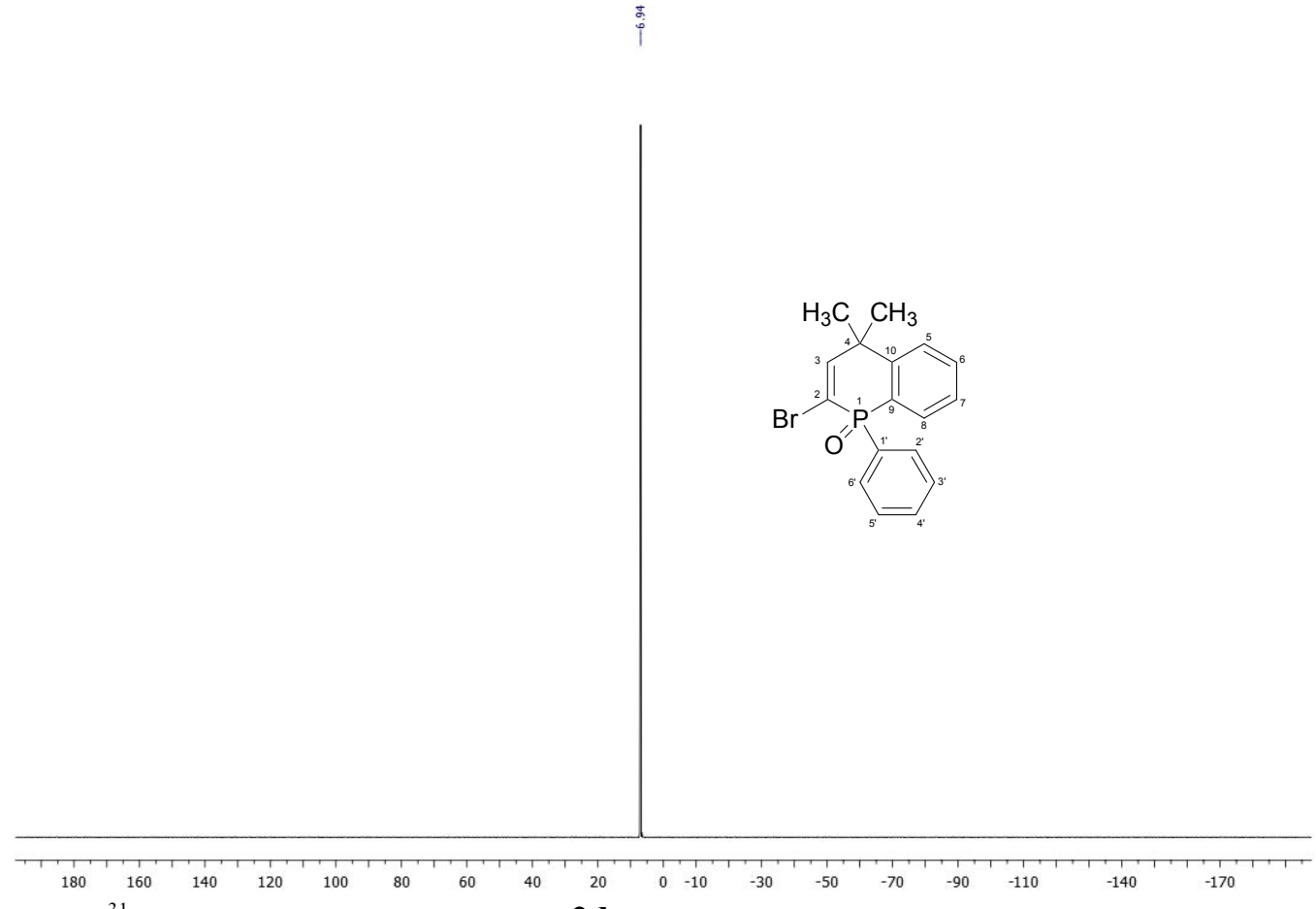


Fig. 12. ^{31}P NMR spectrum of the compound **2d** ($CDCl_3$, 161.98 MHz).

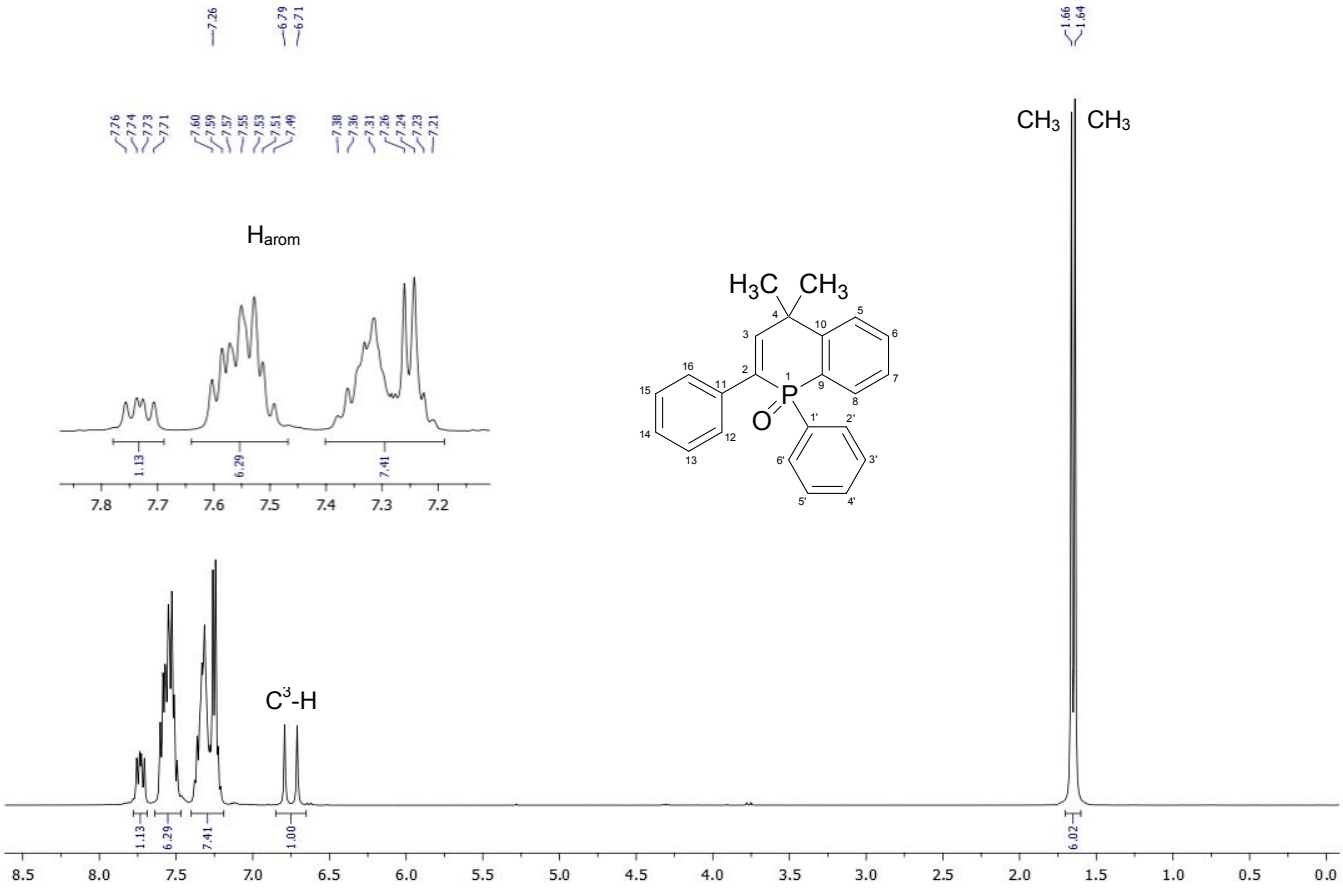


Fig. 13. ^{1}H NMR spectrum of the compound **2e** ($CDCl_3$, 400.13 MHz).

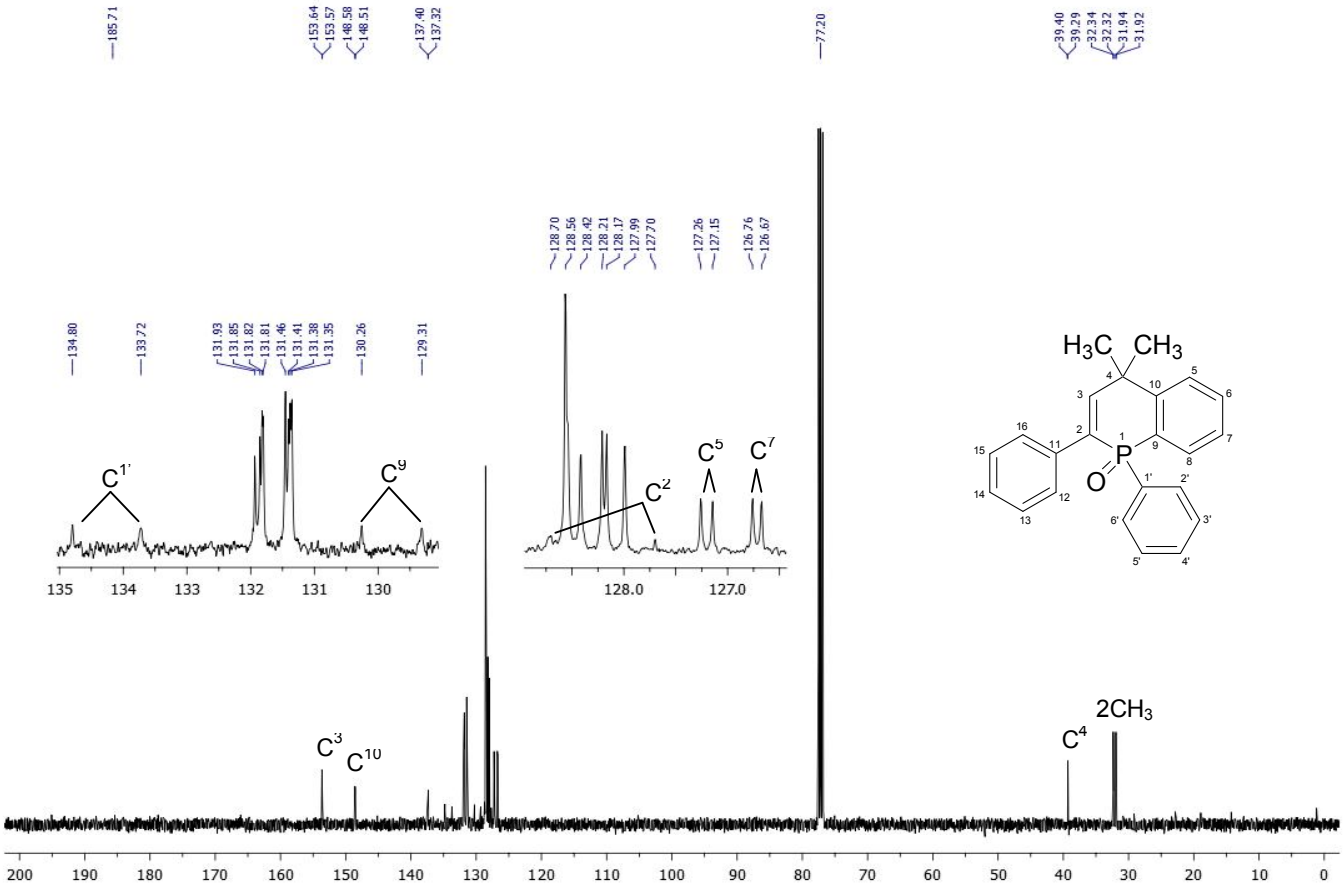


Fig. 14. ^{13}C NMR spectrum of the compound **2e** ($CDCl_3$, 100.61 MHz).

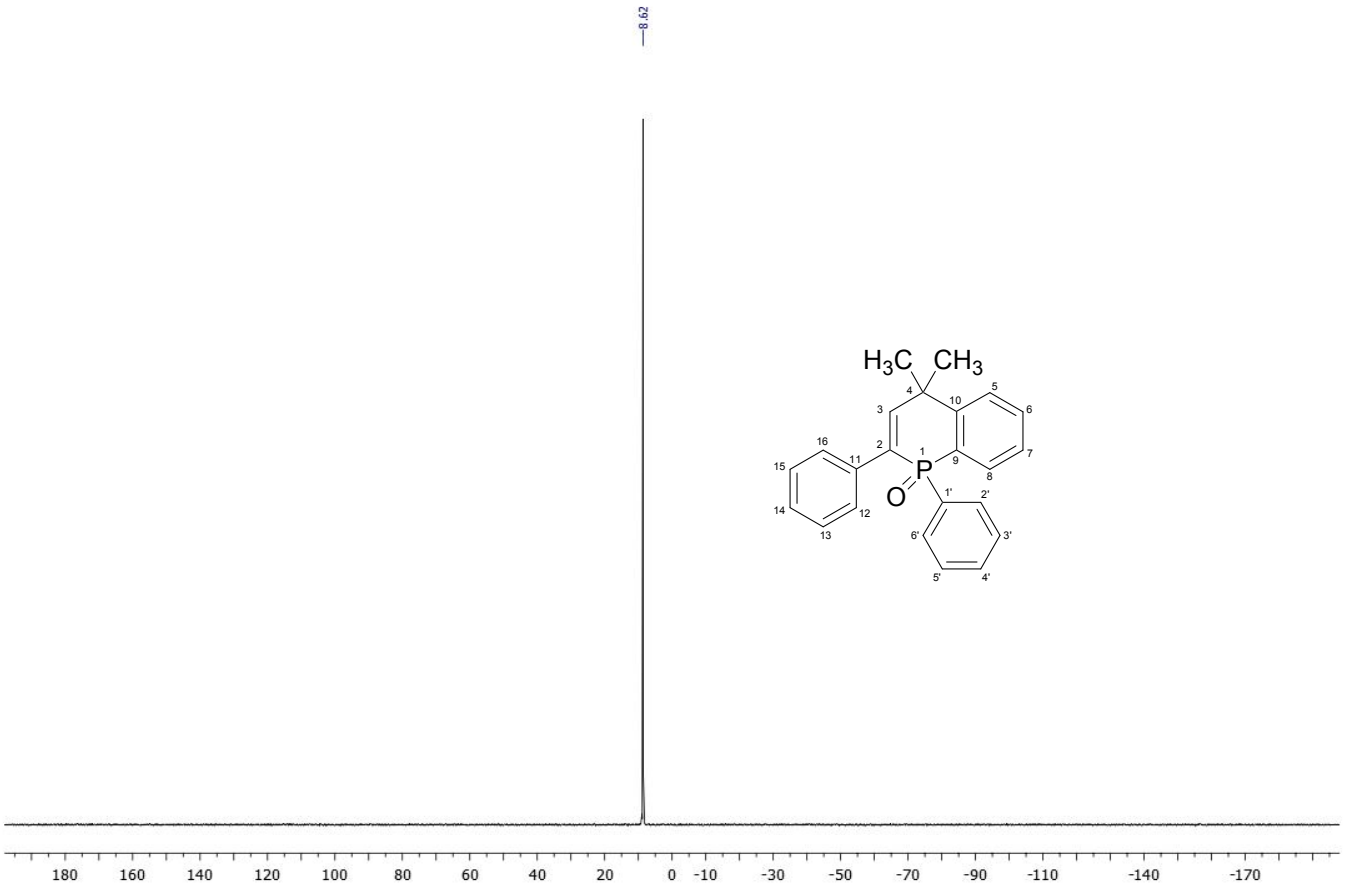


Fig. 15. ^{31}P NMR spectrum of the compound **2e** ($CDCl_3$, 161.98 MHz).

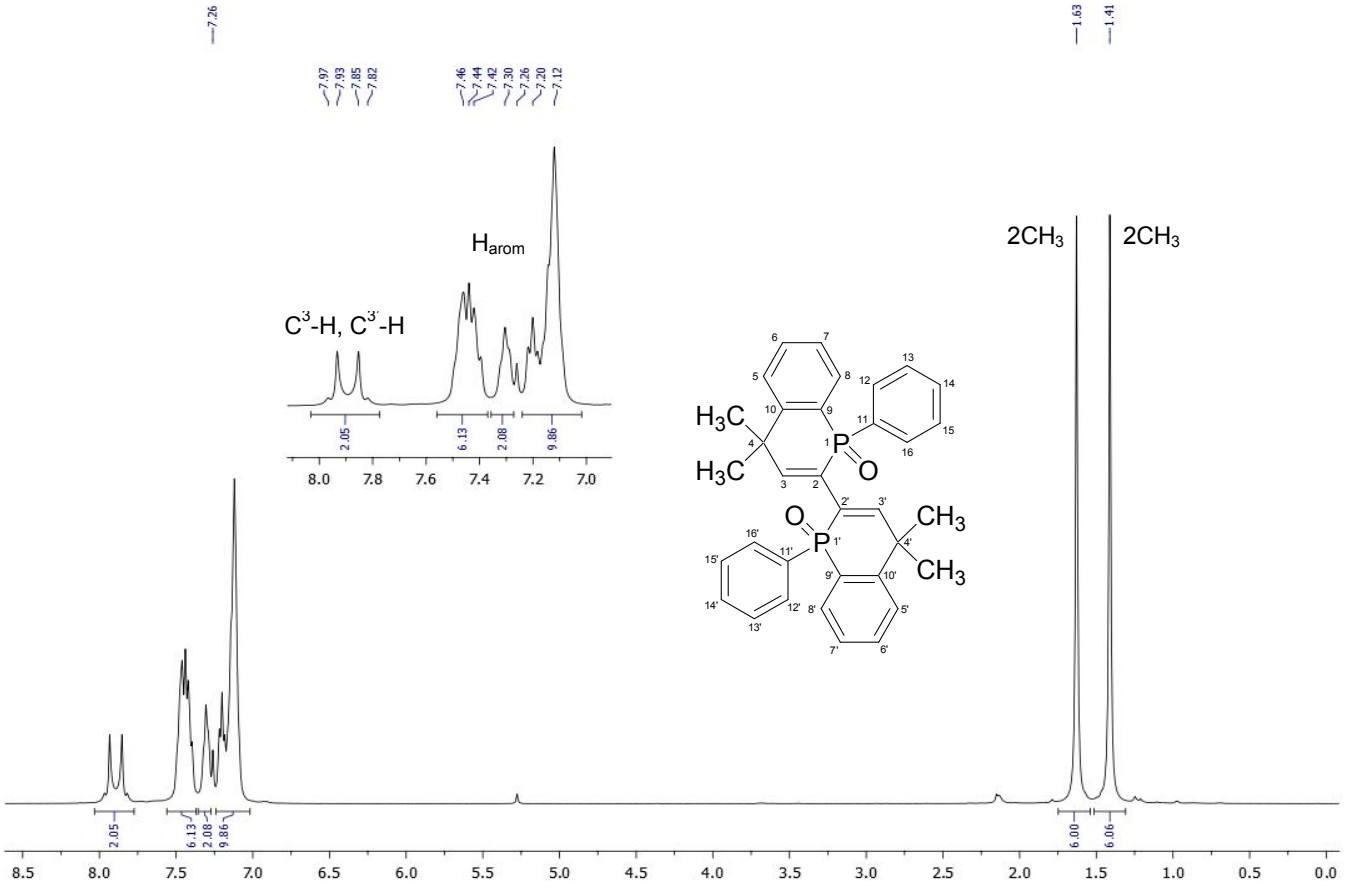


Fig. 16. ^{1}H NMR spectrum of the compound **2f** ($CDCl_3$, 400.13 MHz).

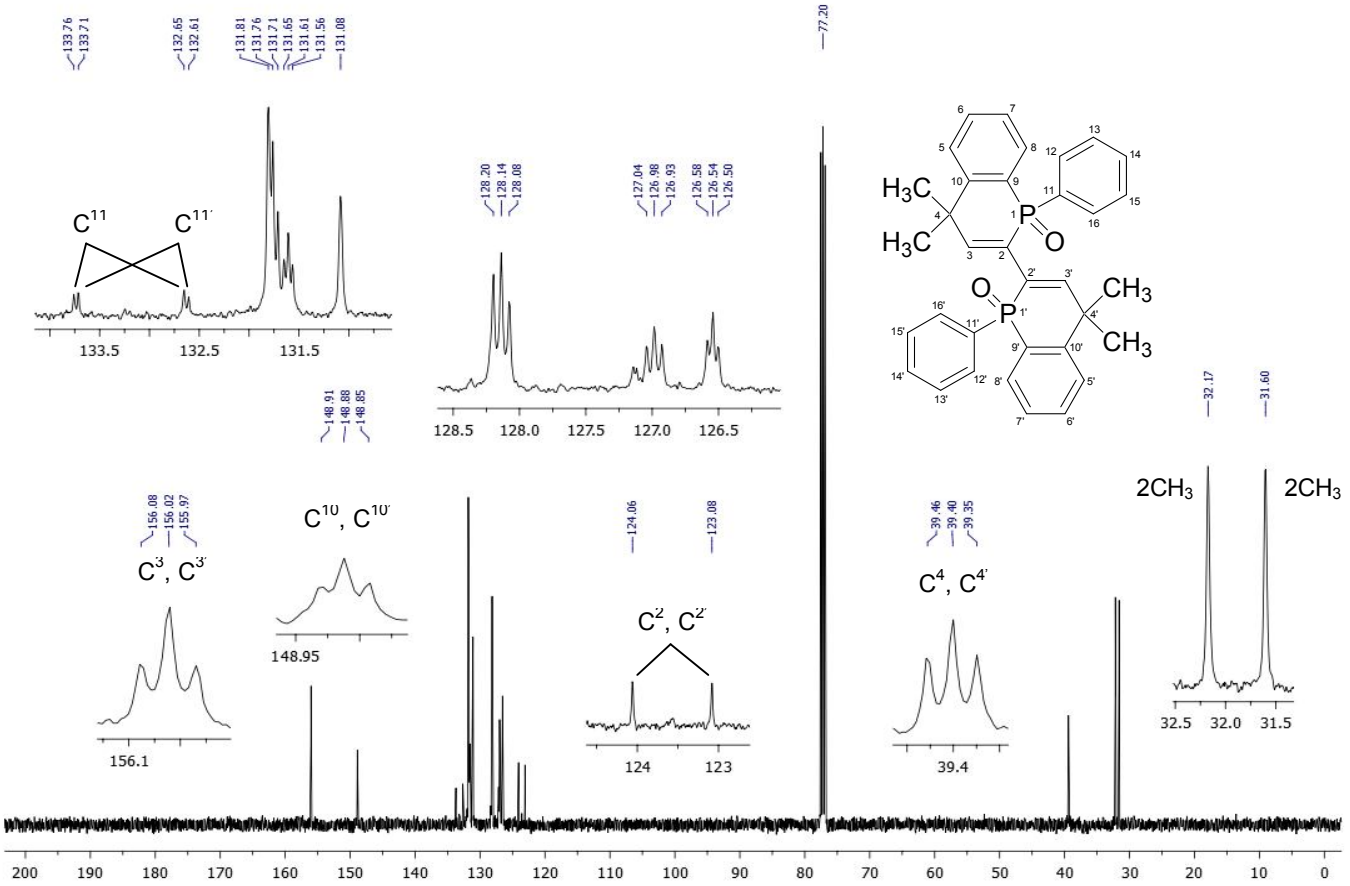


Fig. 17. ^{13}C NMR spectrum of the compound **2f** ($CDCl_3$, 100.61 MHz).

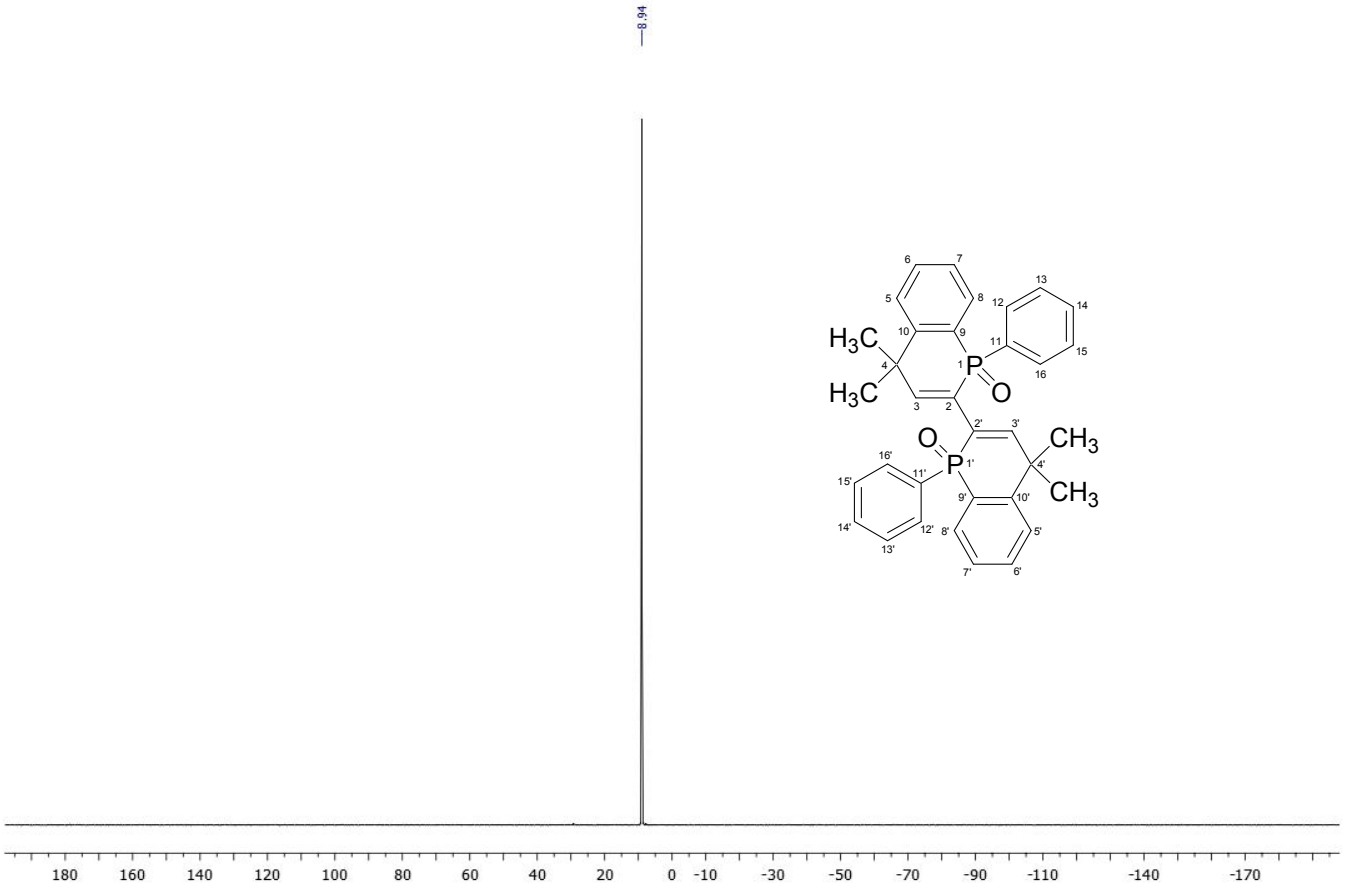


Fig. 18. ^{31}P NMR spectrum of the compound **2f** ($CDCl_3$, 161.98 MHz).

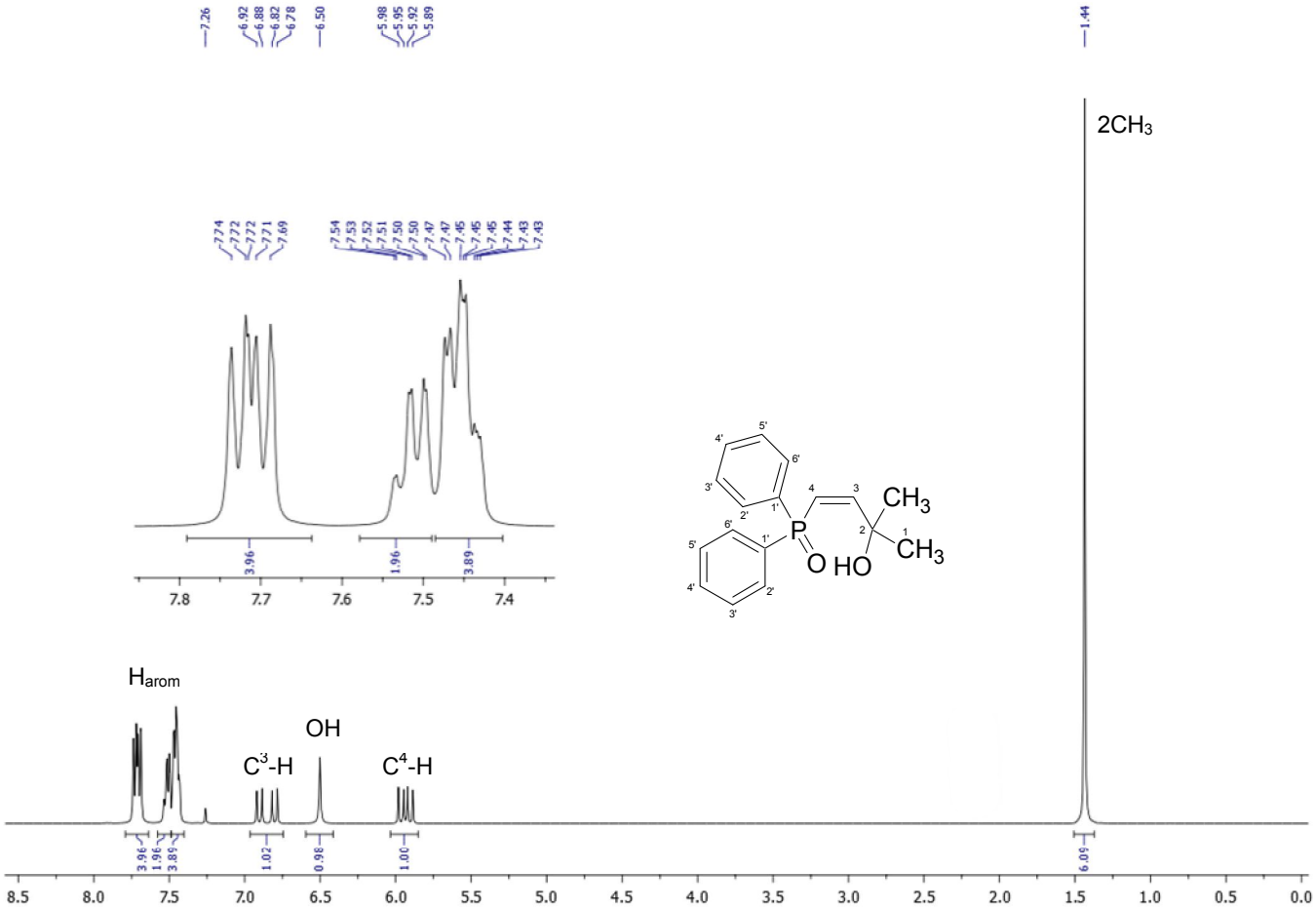


Fig. 19. ^{1}H NMR spectrum of the compound **3a** ($CDCl_3$, 400.13 MHz).

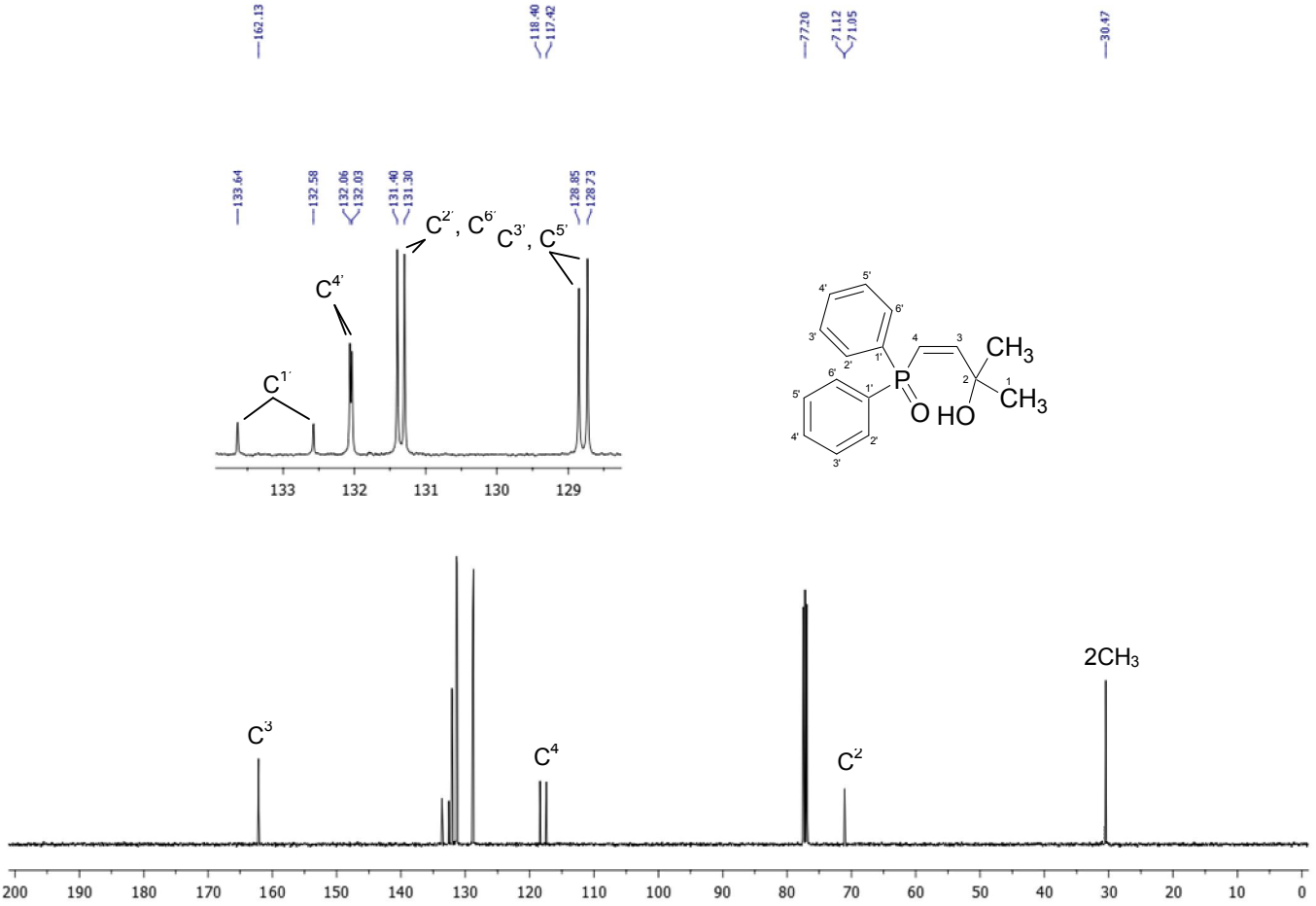


Fig. 20. ^{13}C NMR spectrum of the compound **3a** ($CDCl_3$, 100.61 MHz).

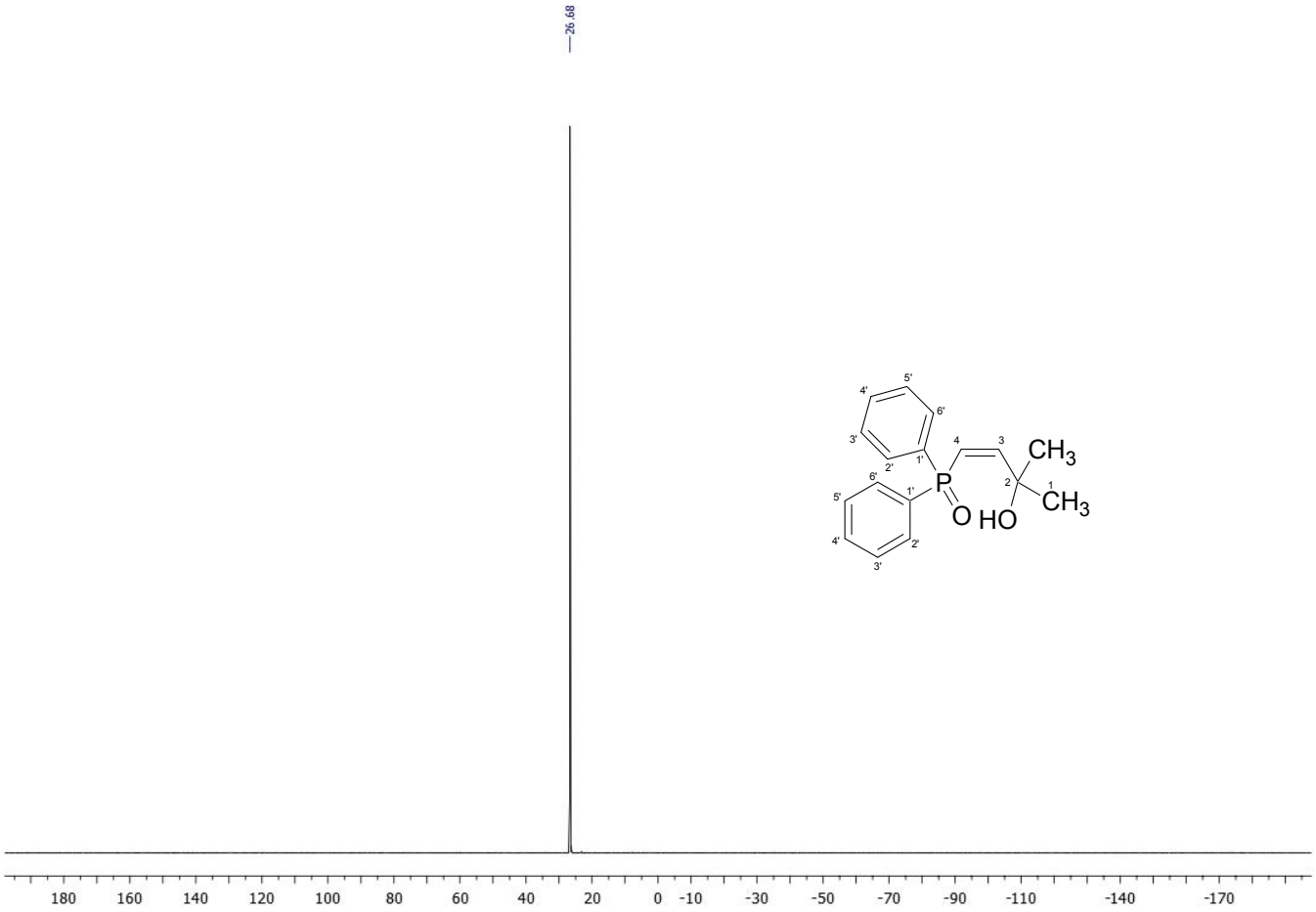


Fig. 21. ^{31}P NMR spectrum of the compound **3a** ($CDCl_3$, 161.98 MHz).

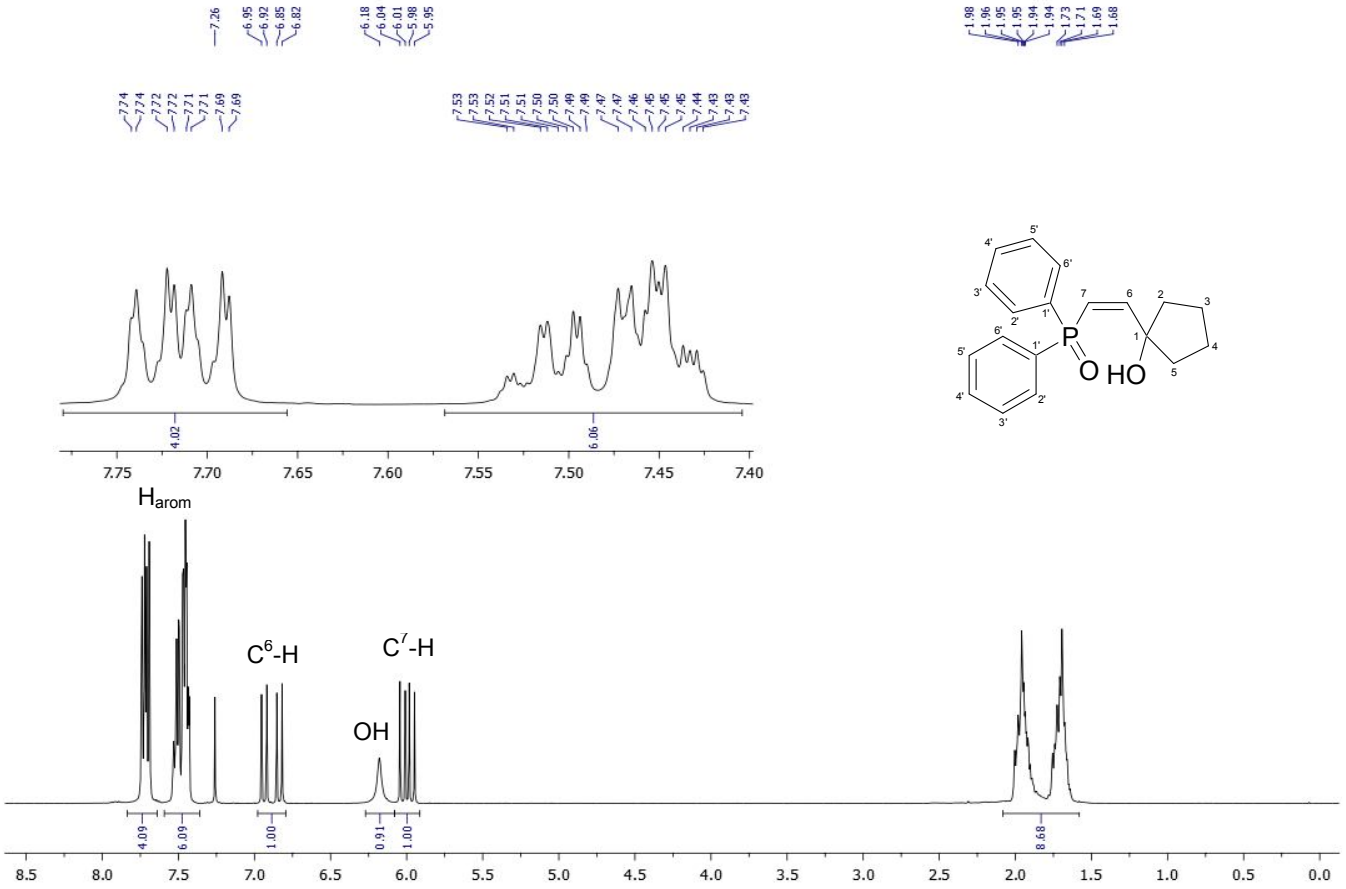


Fig. 22. ^{1}H NMR spectrum of the compound **3b** ($CDCl_3$, 400.13 MHz).

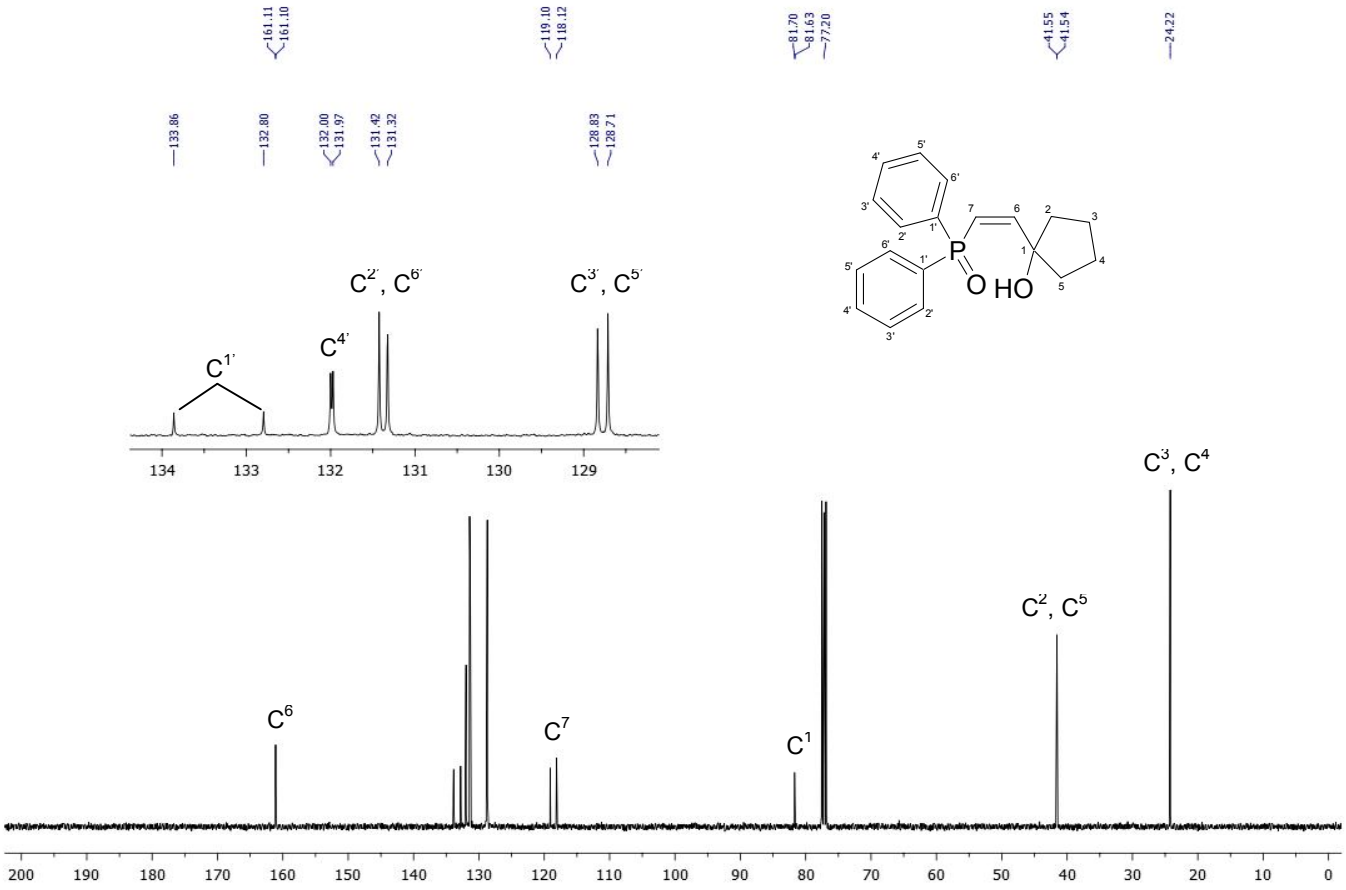


Fig. 23. ^{13}C NMR spectrum of the compound **3b** ($CDCl_3$, 100.61 MHz).

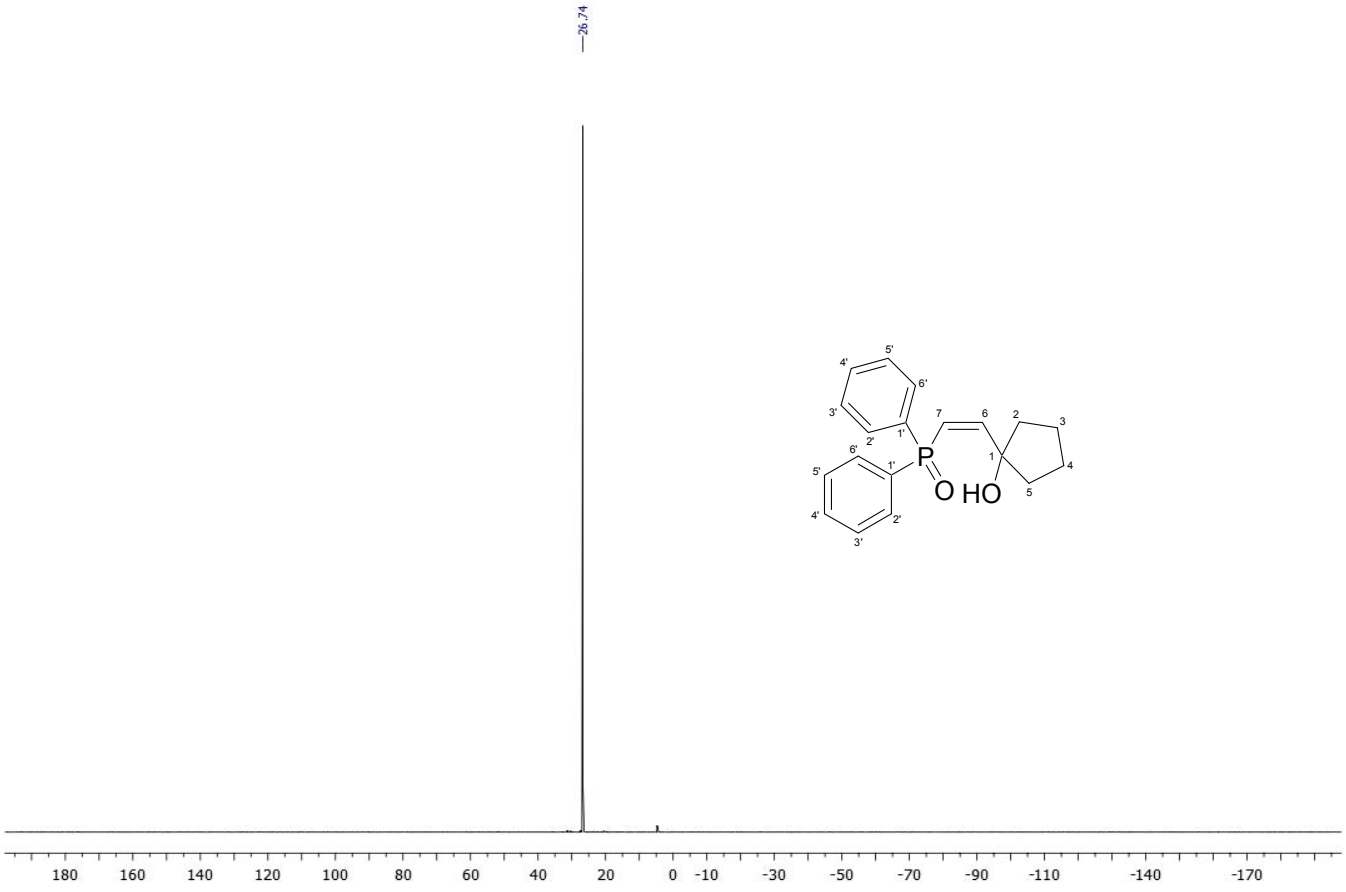


Fig. 24. ^{31}P NMR spectrum of the compound **3b** ($CDCl_3$, 161.98 MHz).

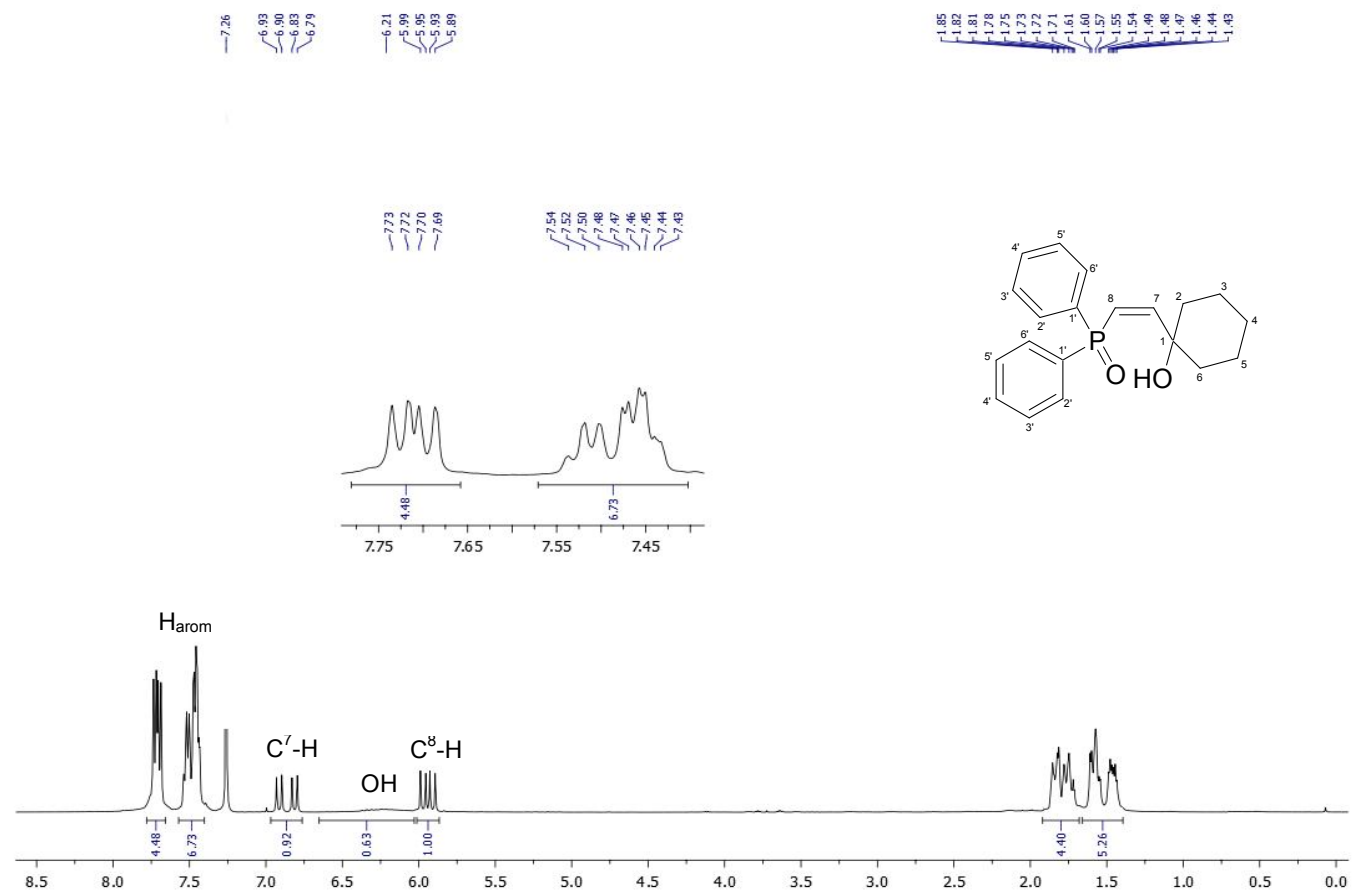


Fig. 25. ^{1}H NMR spectrum of the compound **3c** ($CDCl_3$, 400.13 MHz).

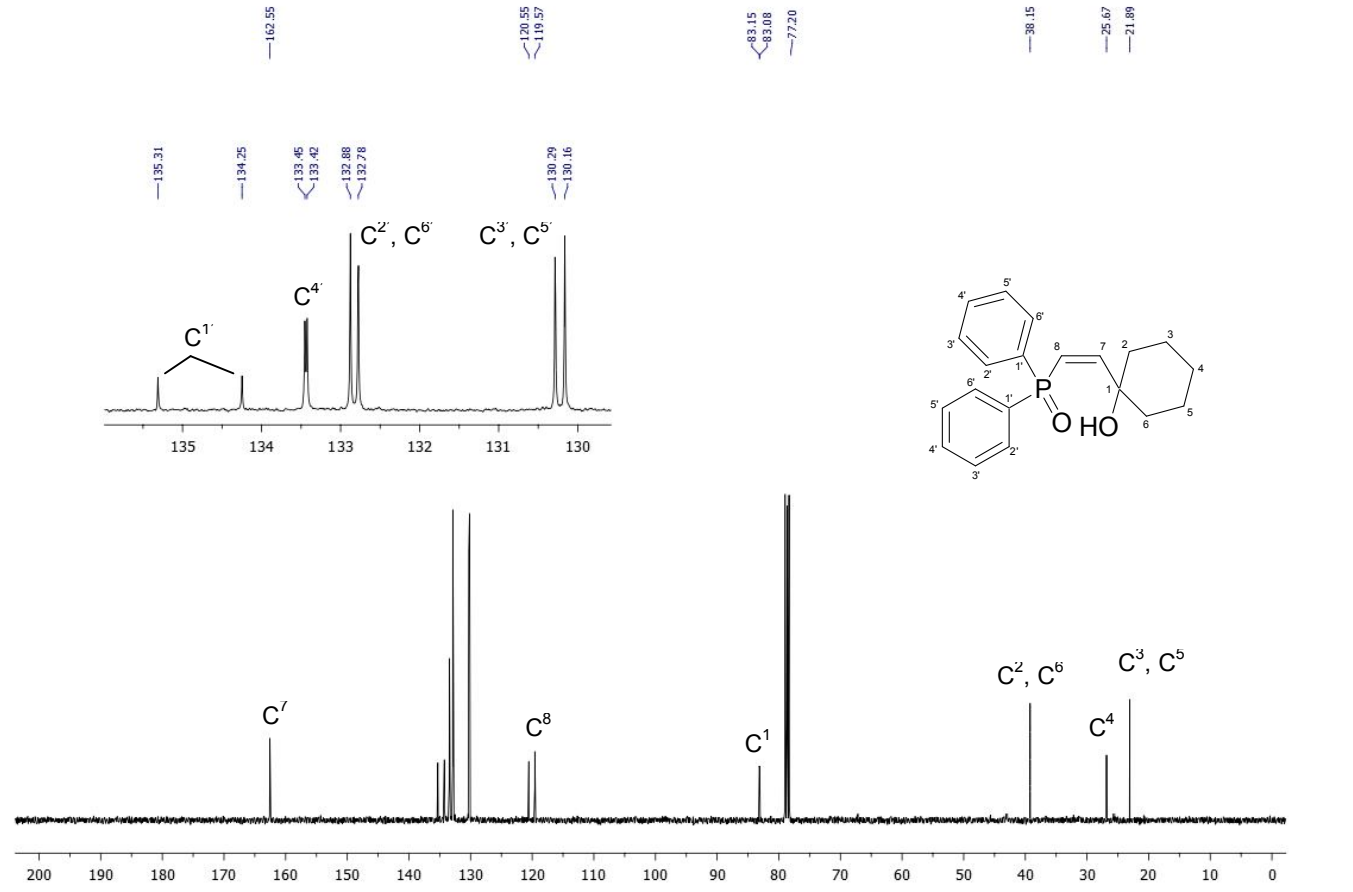


Fig. 26. ^{13}C NMR spectrum of the compound **3c** ($CDCl_3$, 100.61 MHz).

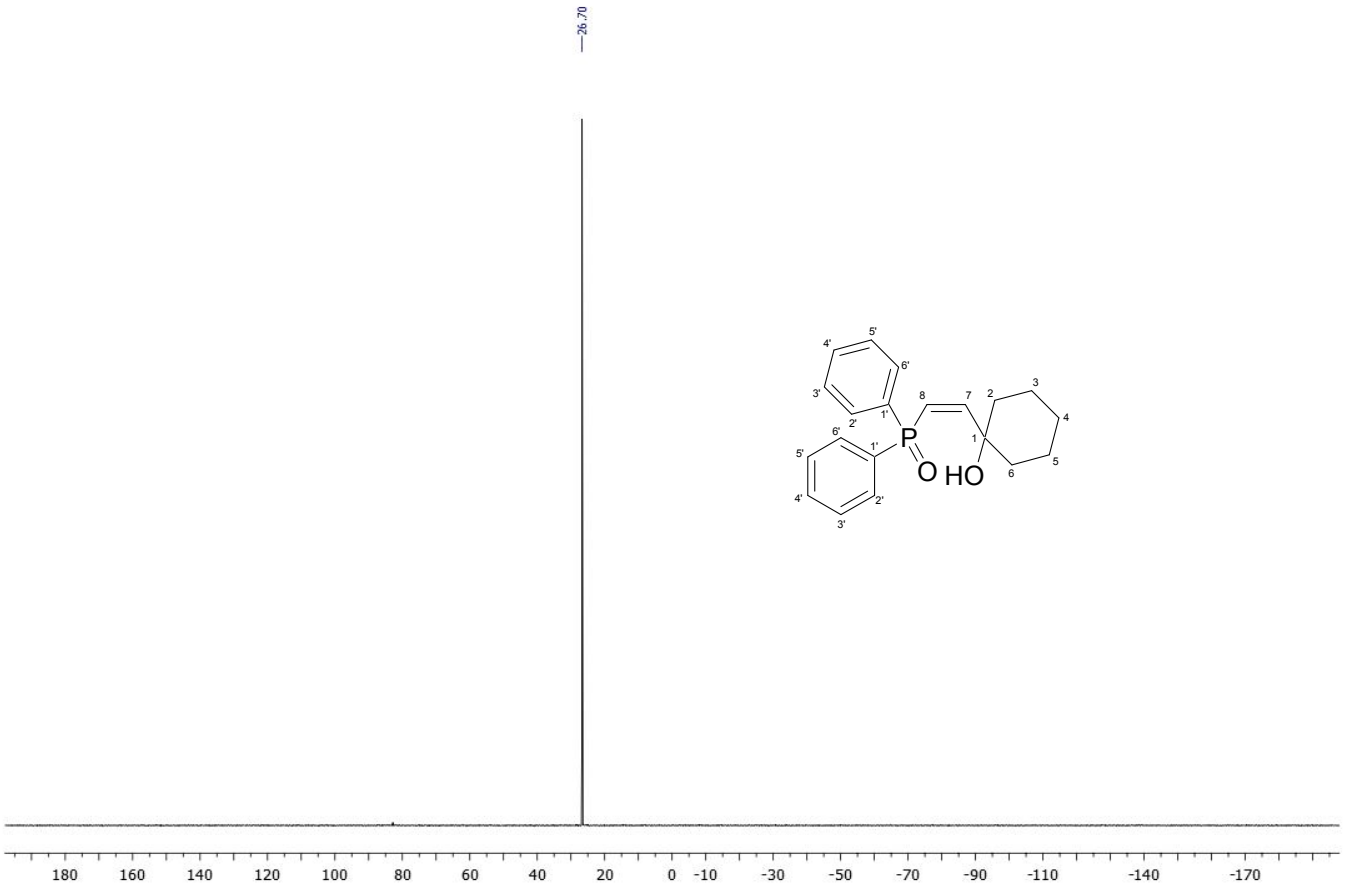


Fig. 27. ^{31}P NMR spectrum of the compound **3c** ($CDCl_3$, 161.98 MHz).

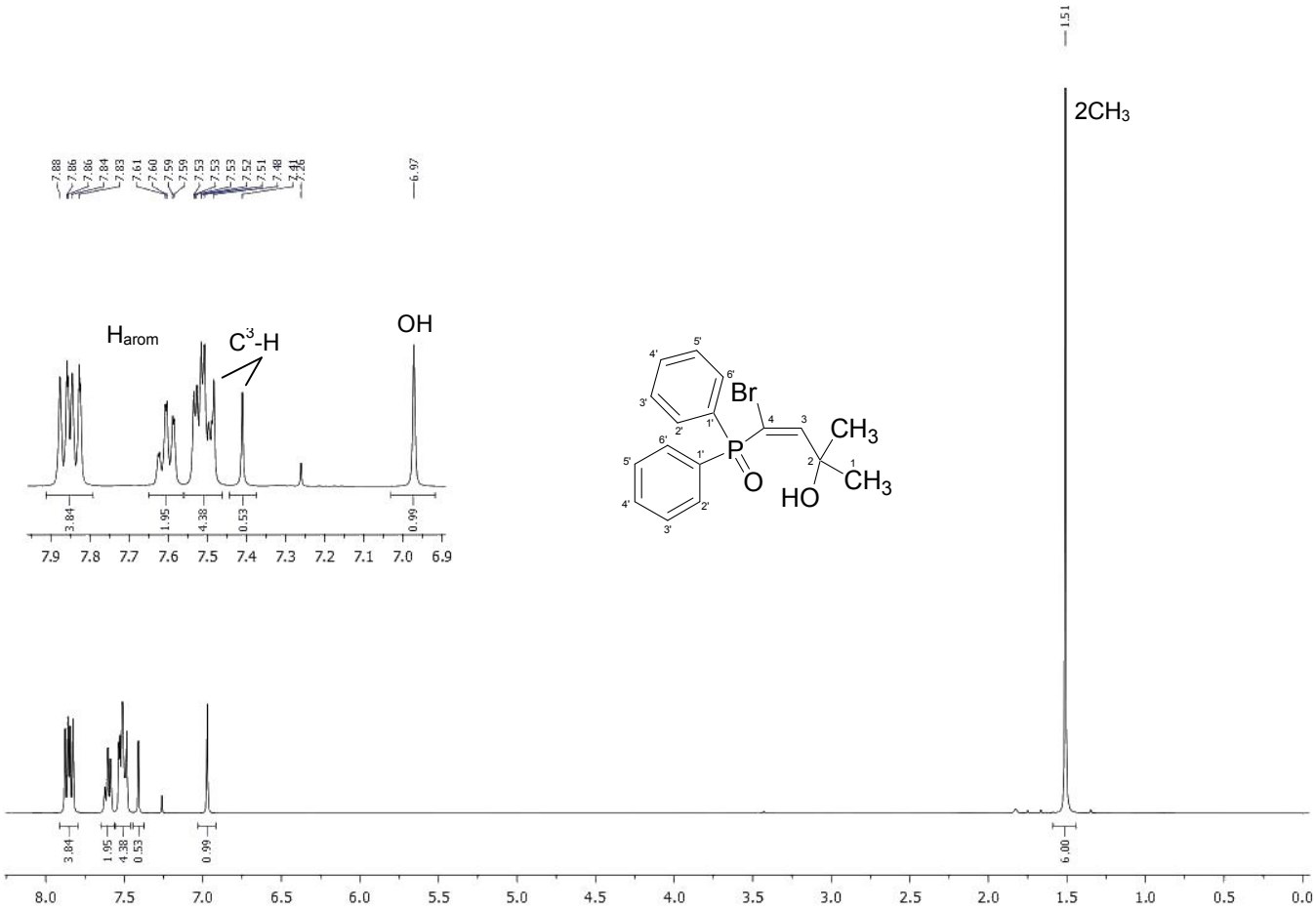


Fig. 28. ^{1}H NMR spectrum of the compound **3d** ($CDCl_3$, 400.13 MHz).

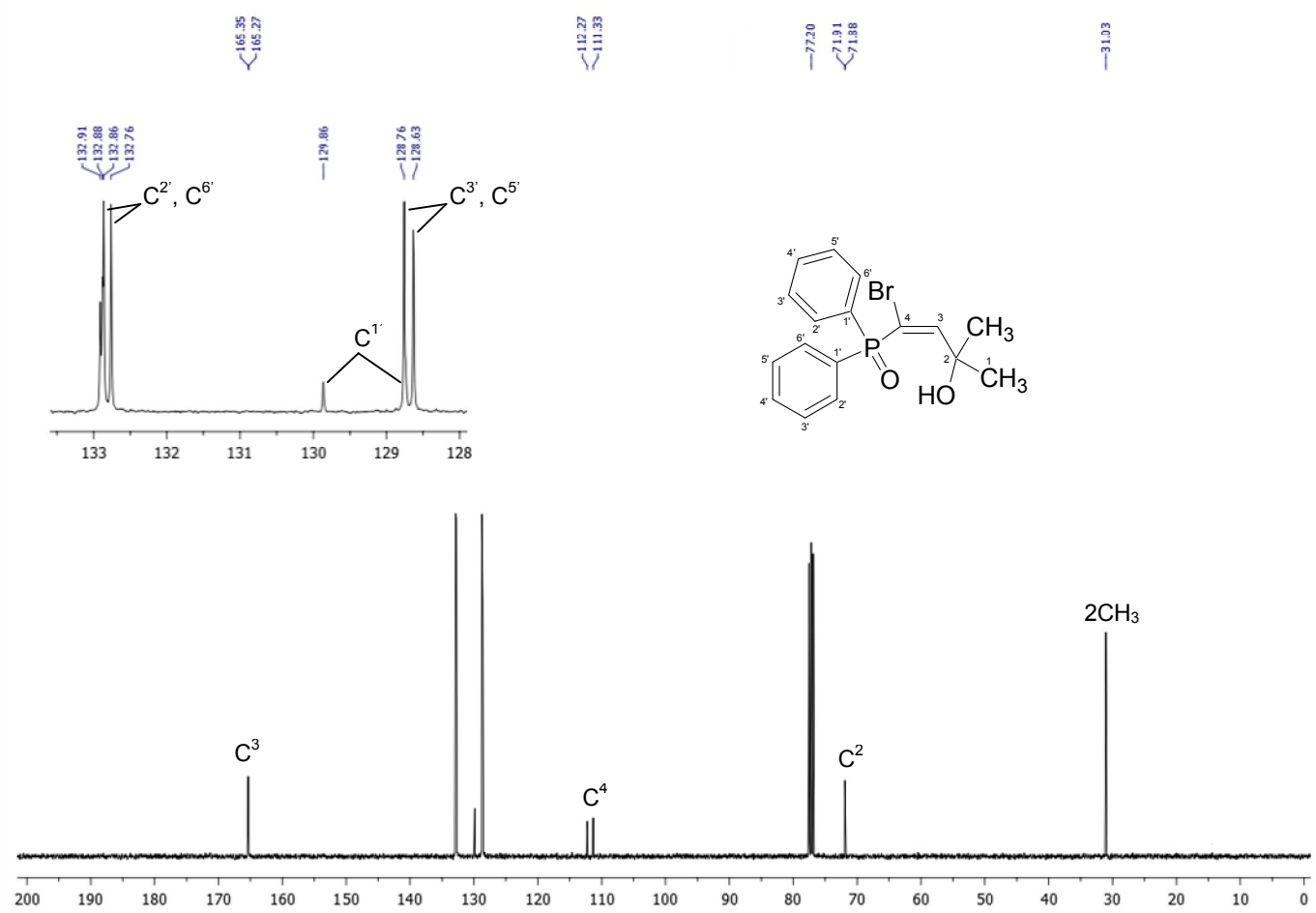


Fig. 29. ^{13}C NMR spectrum of the compound **3d** ($CDCl_3$, 100.61 MHz).

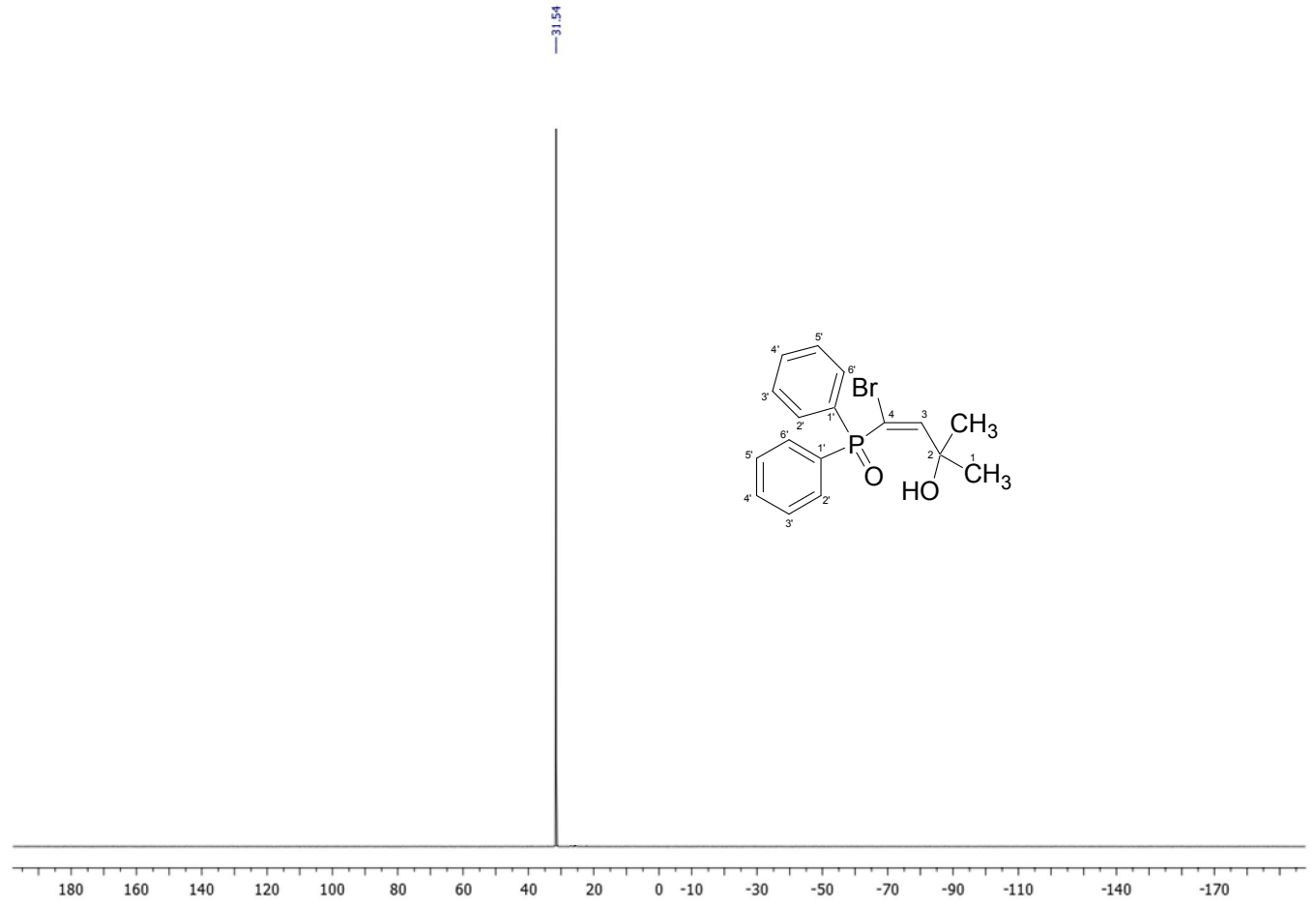


Fig. 30. ^{31}P NMR spectrum of the compound **3d** ($CDCl_3$, 161.98 MHz).

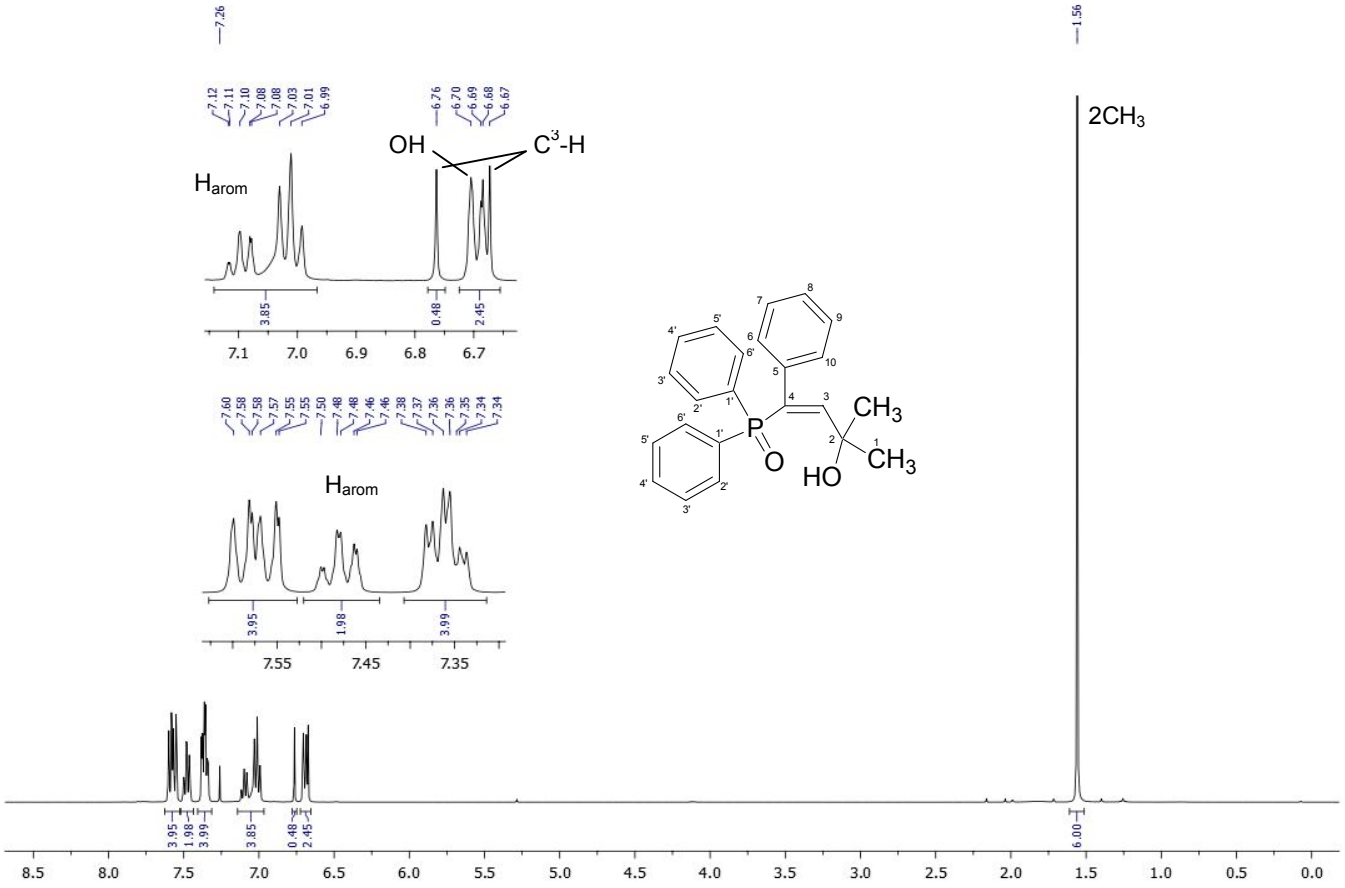


Fig. 31. ^{1}H NMR spectrum of the compound **3e** ($CDCl_3$, 400.13 MHz).

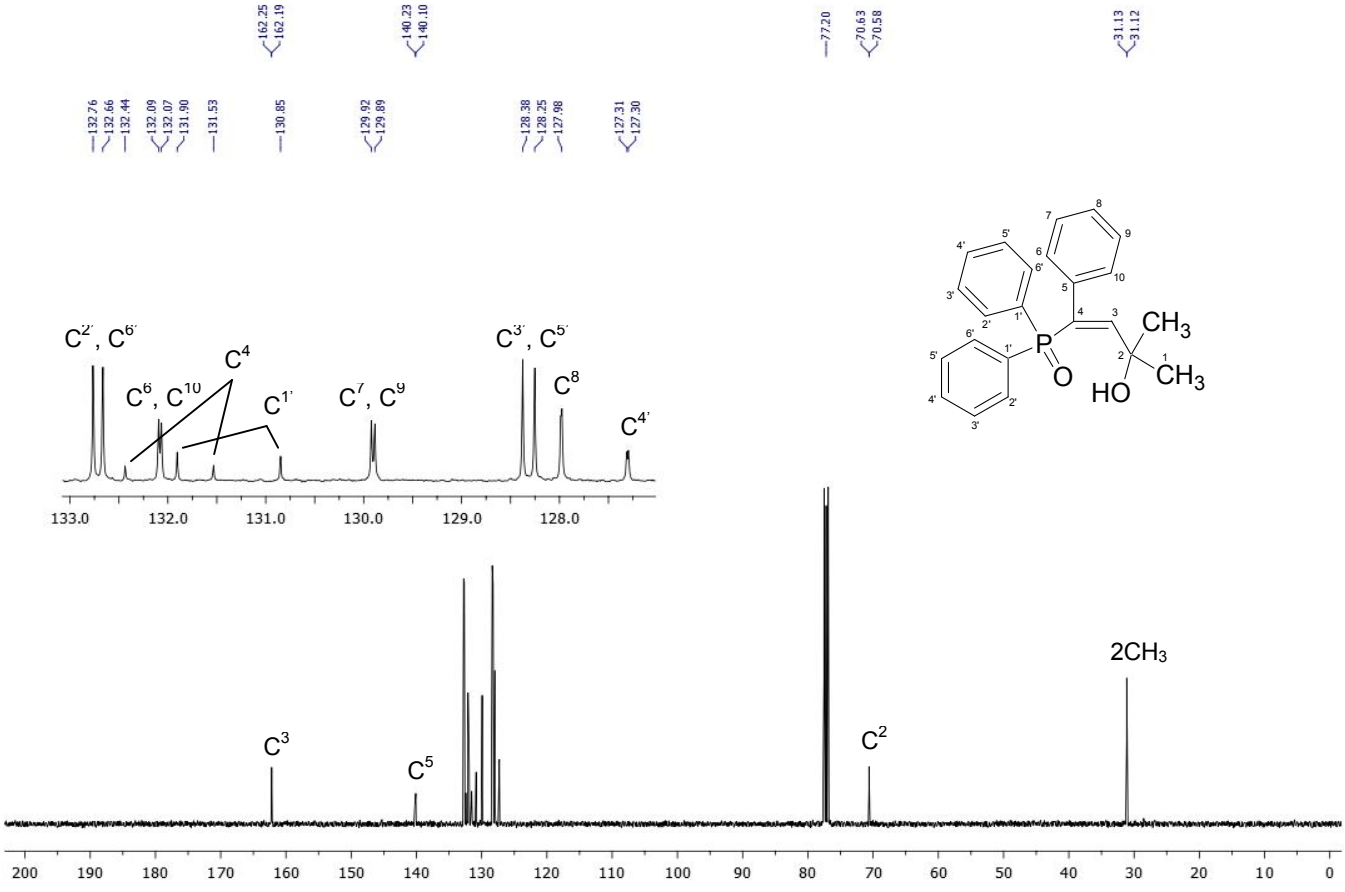


Fig. 32. ^{13}C NMR spectrum of the compound **3e** ($CDCl_3$, 100.61 MHz).

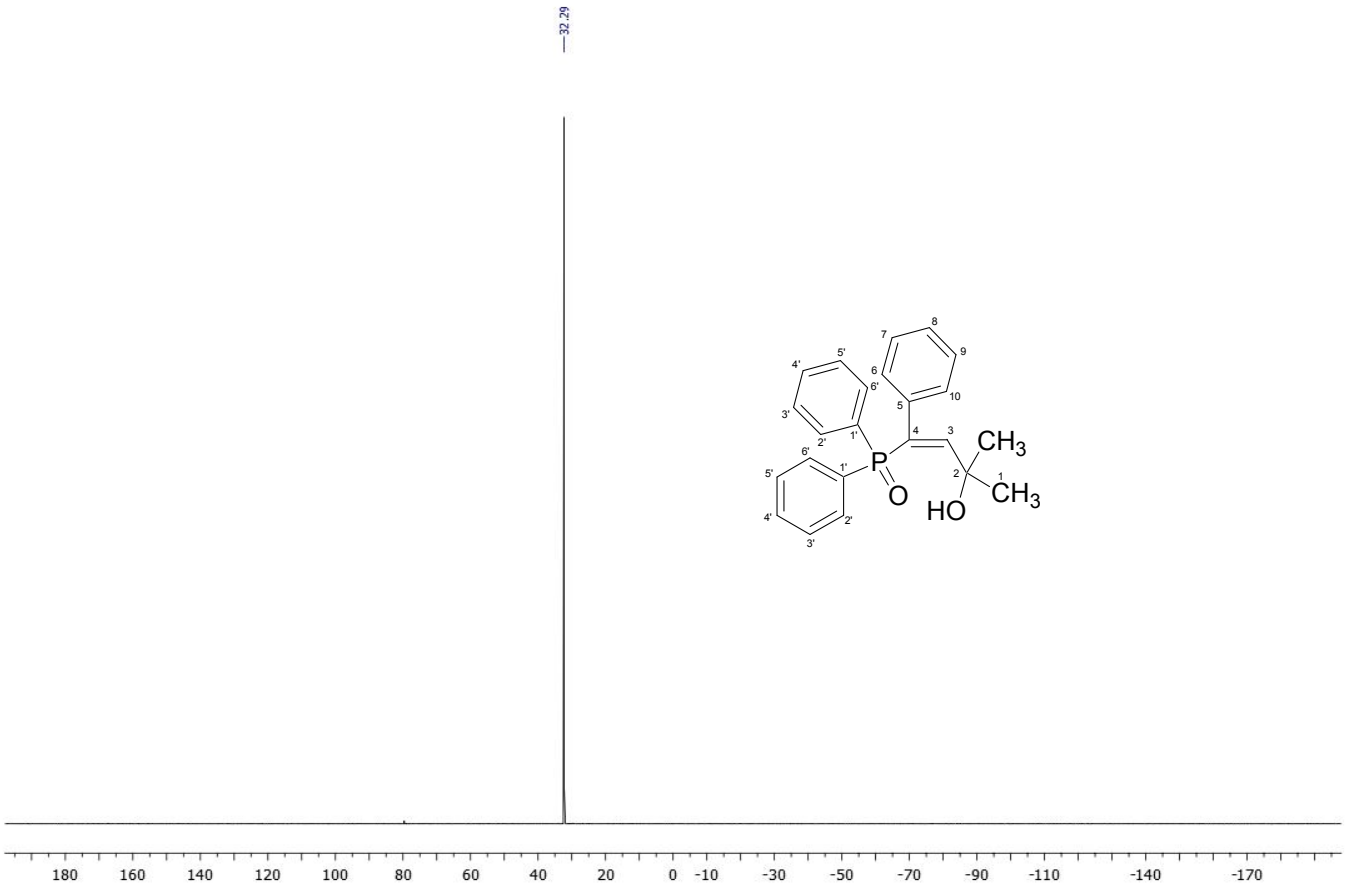


Fig. 33. ^{31}P NMR spectrum of the compound **3e** ($CDCl_3$, 161.98 MHz).

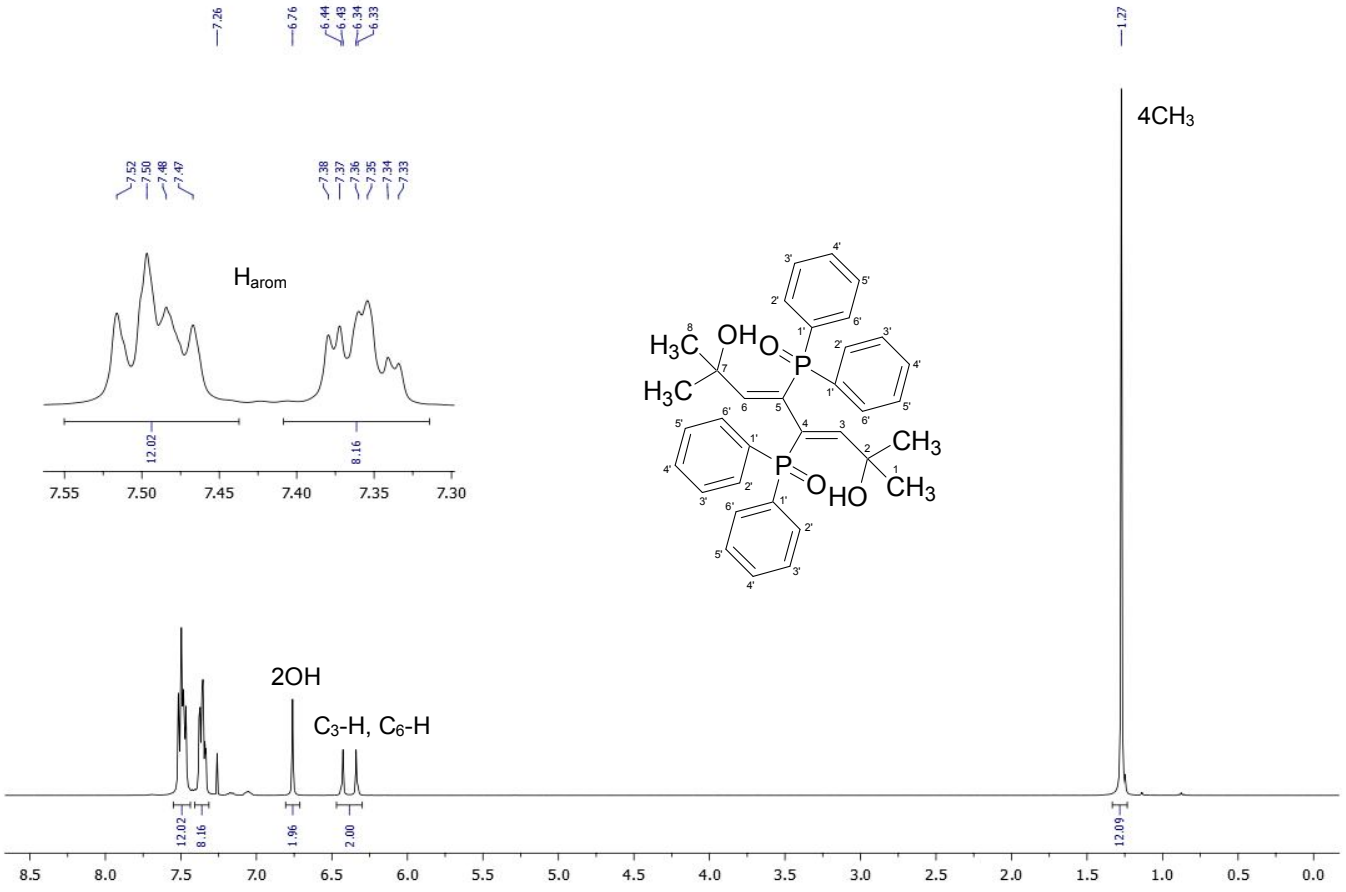


Fig. 34. ^{1}H NMR spectrum of the compound **3f** ($CDCl_3$, 400.13 MHz).

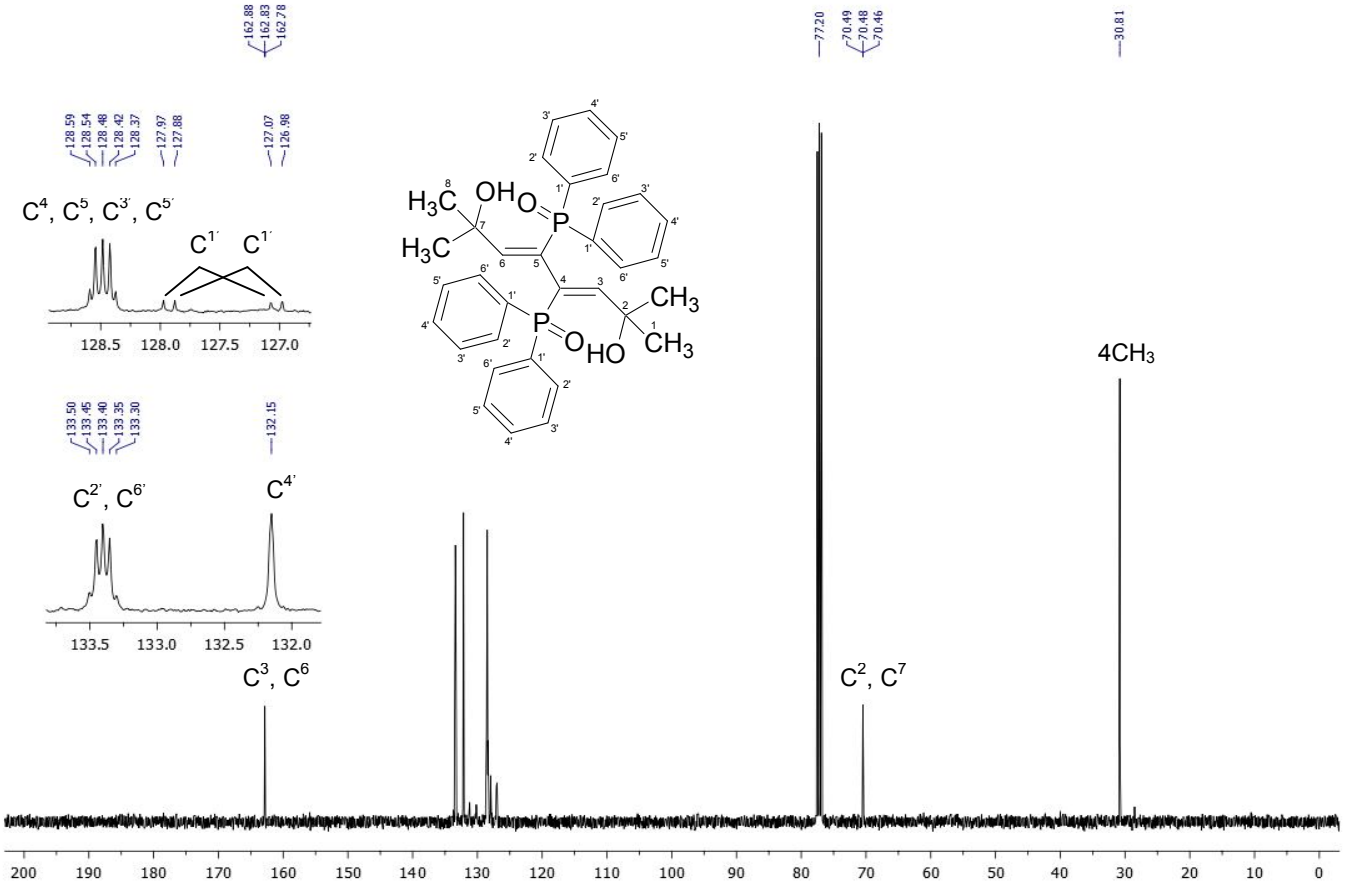


Fig. 35. ^{13}C NMR spectrum of the compound **3f** ($CDCl_3$, 100.61 MHz).

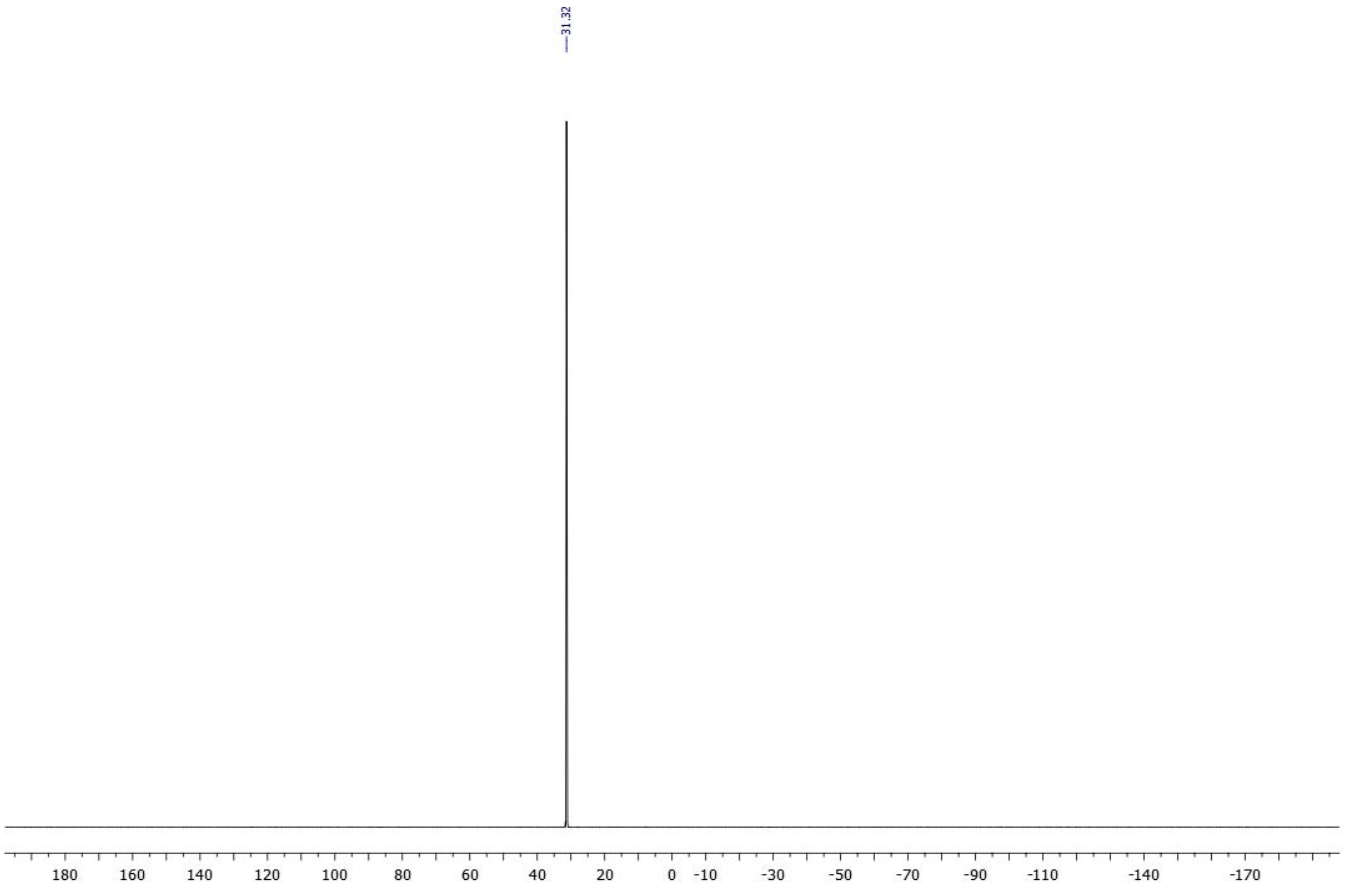


Fig. 36. ^{31}P NMR spectrum of the compound **3f** ($CDCl_3$, 161.98 MHz).

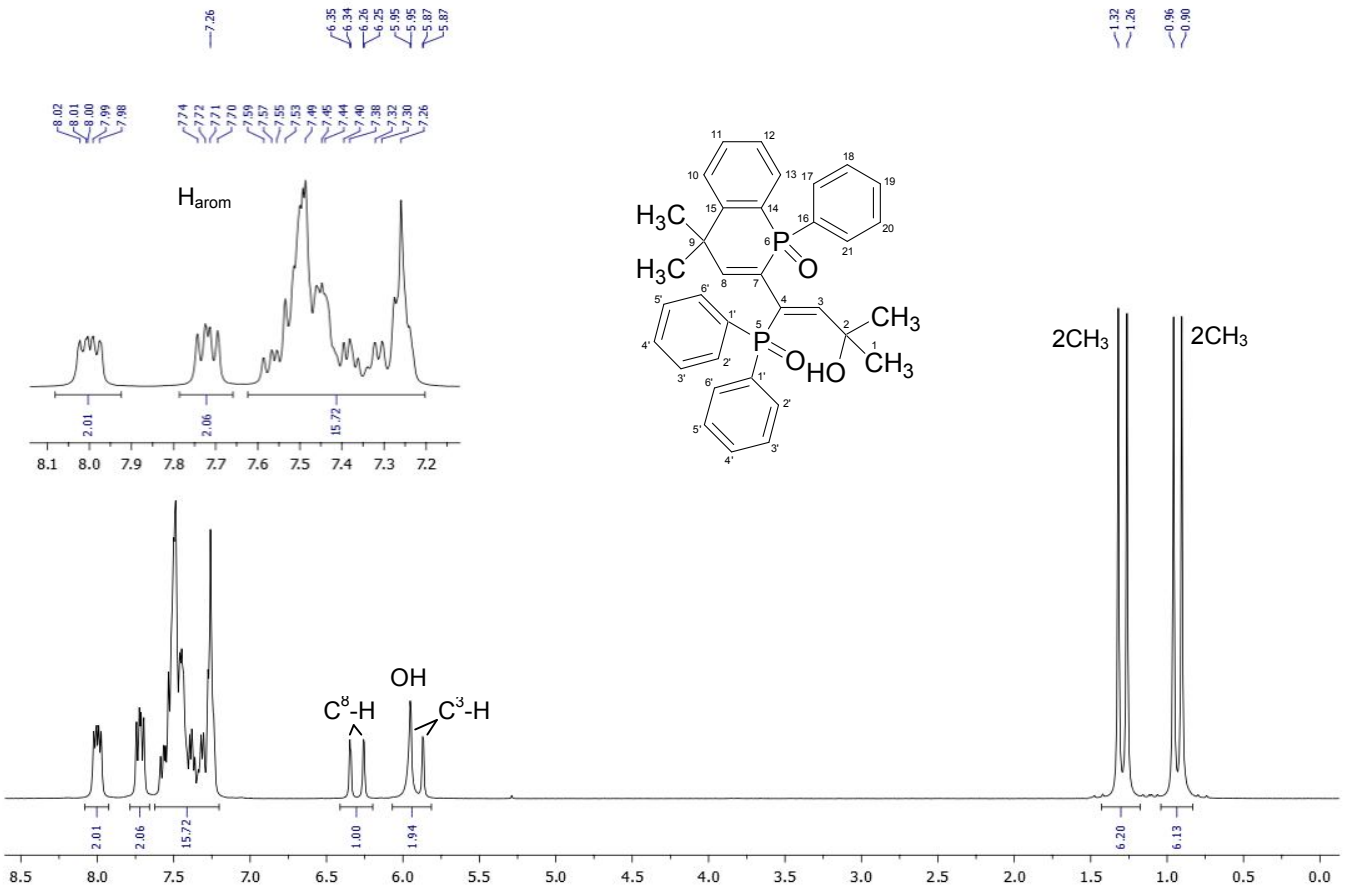


Fig. 37. ^{1}H NMR spectrum of the compound **4a** ($CDCl_3$, 400.13 MHz).

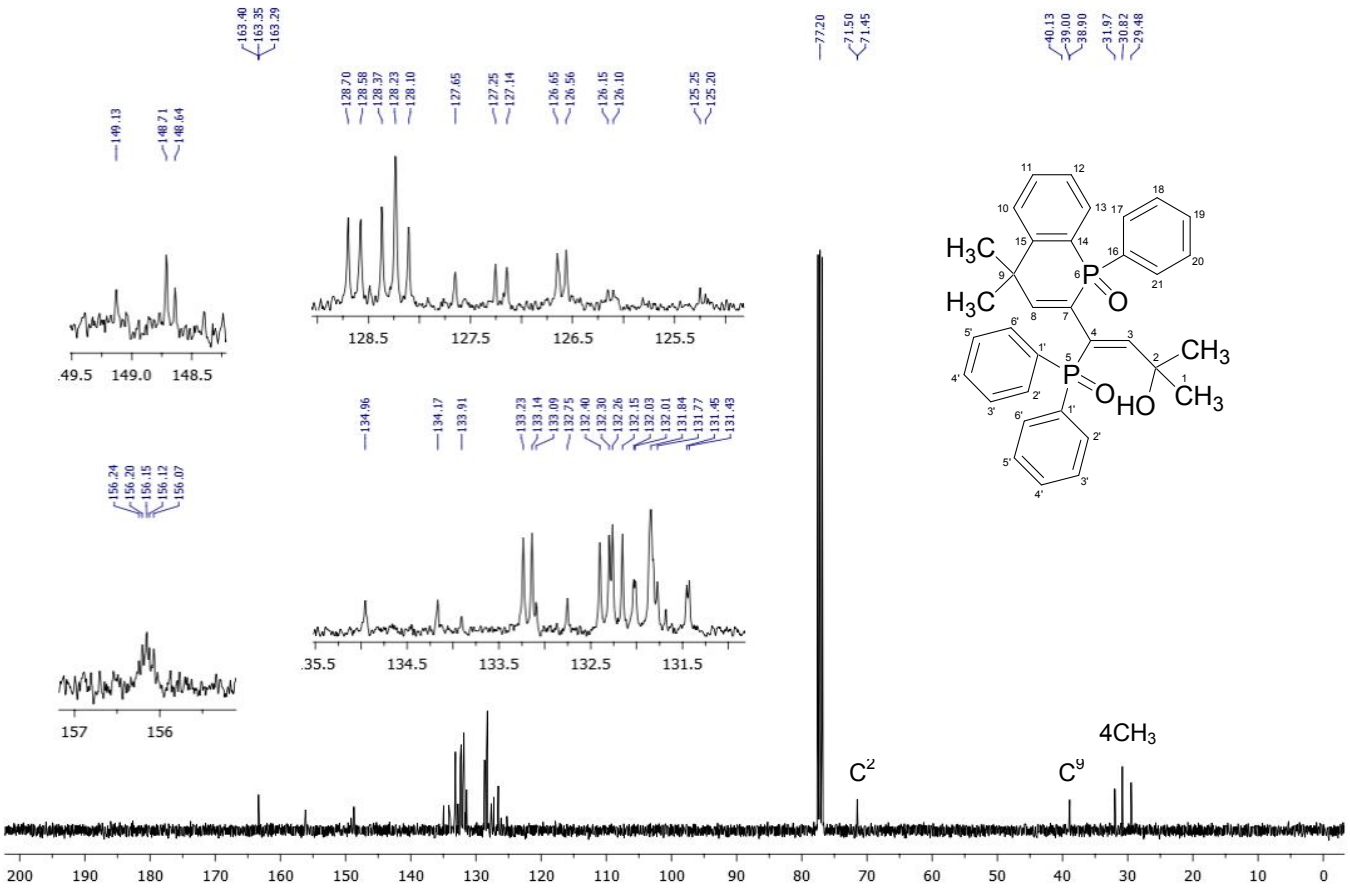


Fig. 38. ^{13}C NMR spectrum of the compound **4a** ($CDCl_3$, 100.61 MHz).

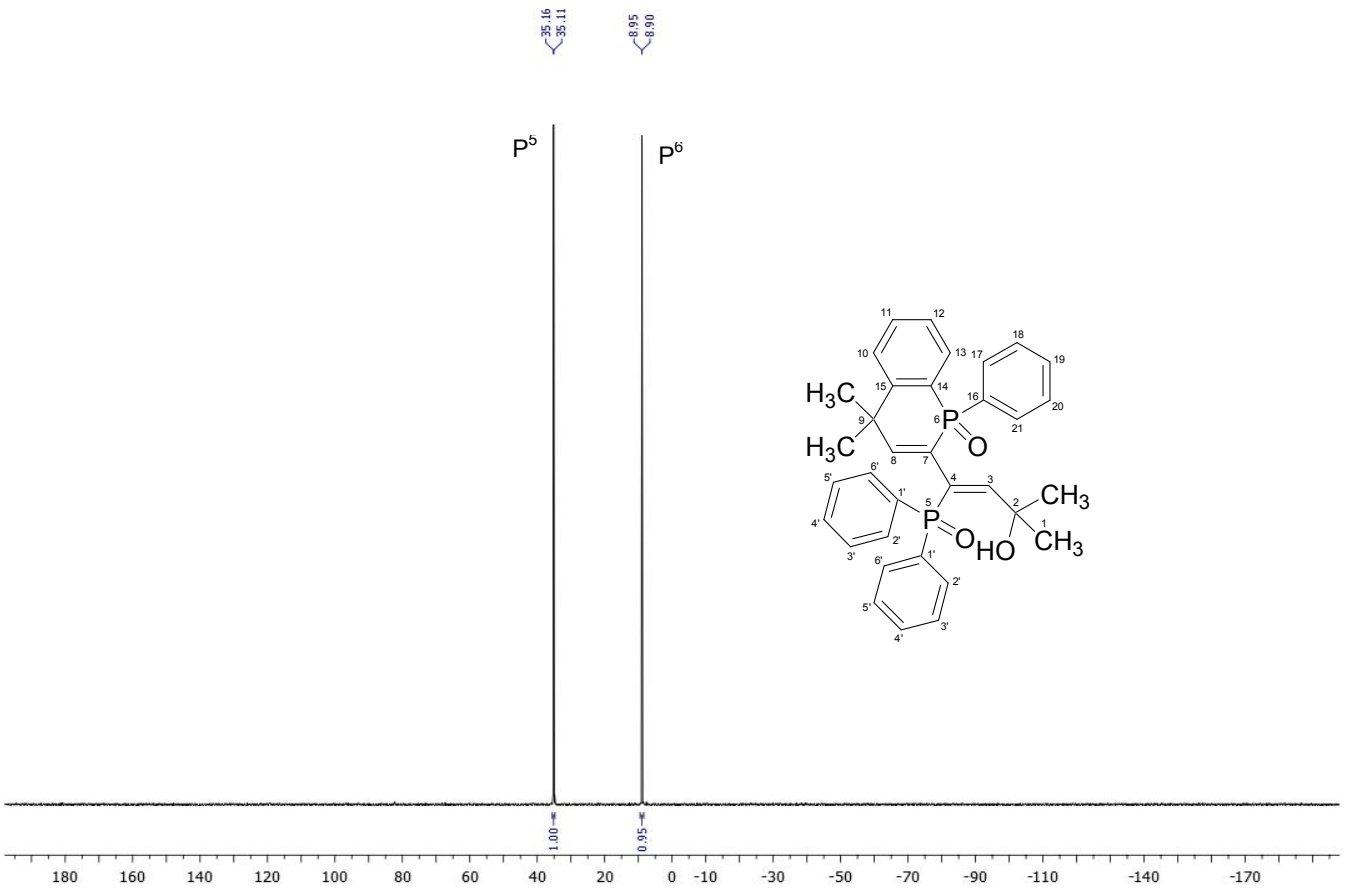


Fig. 39. ^{31}P NMR spectrum of the compound **4a** ($CDCl_3$, 161.98 MHz).