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Simultaneous formation of P–C/P–O-cage phosphoranes in the reaction of 2-[(2-methylcarbonyl)phenyloxy]-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane with hexafluoroacetone

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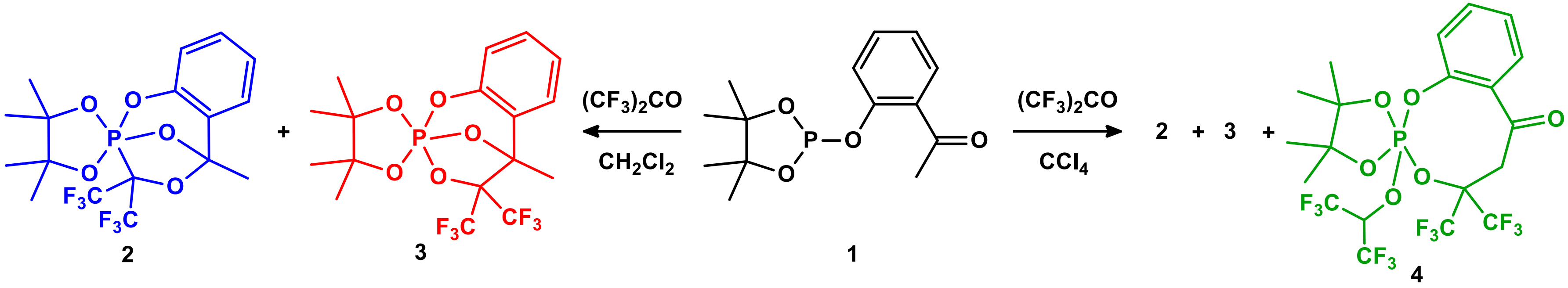
Numbers of investigated compounds

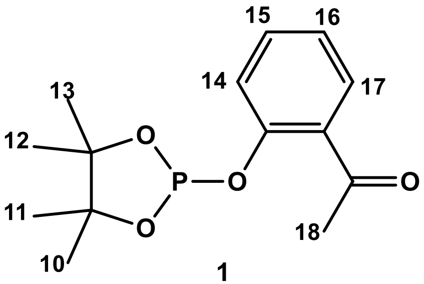


General remarks, experimental procedures and detail interpretation of the NMR spectra

Commercially available solvents were purified according to the standard procedures. All reactions were run under an argon atmosphere. Mass spectra were recorded on AmaZon X (ESI) Bruker mass spectrometers. IR spectra were recorded on a Vector 22 instrument. NMR experiments were carried out on 400 MHz [400 MHz (^{1}H), 376.5 MHz (^{19}F), 161.9 MHz (^{31}P) and 100.6 MHz (^{13}C)] or 600 MHz [600 MHz (^{1}H), 242.9 MHz (^{31}P), 150.9 MHz (^{13}C)] spectrometers. Chemical shifts (δ) are given in parts per million relative to the residual ^{1}H and ^{13}C signal of $CDCl_3$, CD_2Cl_2 or acetone-d_6 and the signals are designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants (*J*) are in hertz (Hz). Mass spectra (EI) were taken on a DFS Thermo Electron Corporation instrument (Germany). The energy of ionizing electrons was 70 eV, the temperature of the ion source was 280°C, a system of direct input of the sample into the ion source was used, and temperature of the evaporator was 250°C. Elemental analysis was performed on a CHNS-O analyzer; the phosphorus content was determined by the pyrolysis under oxygen flow.

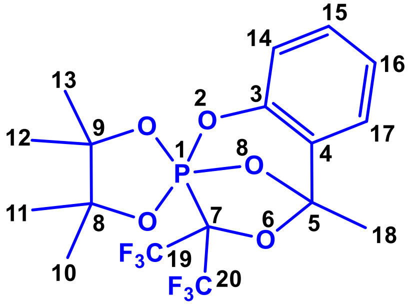
Reaction of 2-(2-methylcarbonylphenyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane ***1*** *with hexafluoroacetone in tetrachloromethane*. To a solution of phospholane **1** (3.1 g, 0.011 mol) in tetrachloromethane (30 ml) in an argon atmosphere, hexafluoroacetone (3.65 g, 0.022 mol, weight gain) was condensed at –40°C. The reaction mass was tightly closed, kept for 3 hours until reaching 20°C and then for 12 hours at 20°C. After 3 days, a crystalline precipitate was formed, which was filtered off, washed with a small amount of carbon tetrachloride and dried in a vacuum of 12 Torr to afford 1.23 g (25%) 4,4,5,5,5'-pentamethyl-3',3'-bis(trifluoromethyl)-3'H,5'H-2λ^5-spiro[[1,3,2]dioxaphospholane-2,2'-[2,5]epoxybenzo[*f*][1,4,2]dioxaphosphepine] **2**, mp 140-141 °C (from CCl_4). Found, %: C 45.33, H 4.47, P 7.02. $C_{17}H_{19}F_6O_5P$. Calculated, %: C 45.55, H 4.27, P 6.91. Mass-spectrum EI: *m*/*z* calcd for C $C_{17}H_{19}F_6O_5P$ $[M]^+$ 448, found 448.

Reaction of dioxaphospholane ***1*** *with hexafluoroacetone in dichloromethane*. To a solution of phospholane **1** (5.63 g, 0.02 mol) in dichloromethane (50 ml) in an argon atmosphere, hexafluoroacetone (6.63 g, by weight gain) was condensed at –40 °C. The reaction mass was tightly closed, kept for 3 hours until reaching 20 °C and then for 3 days at 20 °C. The solvent was removed in vacuum 12 Torr, pentane (30 ml) was added to the residue, and the obtained solution was kept at 5°C for 8 days. This resulted in the formation of a crystalline precipitate, which was filtered off, washed with cold pentane, and dried in vacuo of 12 Torr to afford 2.95 g (33%) 4,4,5,5,5'-pentamethyl-4',4'-bis(trifluoromethyl)-4',5'-dihydro-2λ^5-spiro[[1,3,2]dioxaphospholane-2,2'-[2,5]epoxybenzo[*d*][1,3,2]dioxaphosphepine] **3**, mp 159-161 °C (from pentane). Found, %: C 45.33, H 4.47, P 7.02. $C_{17}H_{19}F_6O_5P$. Calculated, %: C 45.55, H 4.27, P 6.91. Mass-spectrum EI: *m*/*z* calcd for C $C_{17}H_{19}F_6O_5P$ $[M]^+$ 448, found 448.



1

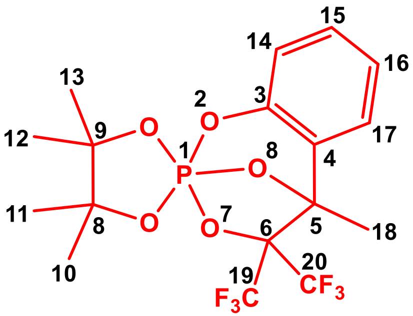
4,4,5,5-tetramethyl-2-[(2-methylcarbonyl)phenyloxy]-1,3,2-dioxaphospholane (**1**). Colorless oil, yield is 97%. Mass-spectrum ESI: 282. ^{1}H NMR spectrum (400 MHz, CCl_4/C_6D_6 = 7/1, δ ppm, *J* Hz): 7.77 ddd (H^{17}, 1H, $^{3}J_{HH}$ 7.9-8.0, $^{4}J_{HH}$ 1.0), 7.26 dddd (H^{15}, 1H, $^{3}J_{HH}$ 8.1, $^{3}J_{HH}$ 7.5, $^{5}J_{PH}$ 1.8, $^{4}J_{HH}$ 1.7), 7.07 br. d (H^{14}, 1H, $^{3}J_{HH}$ 8.1), 7.0 dddd (H^{16}, 1H, $^{3}J_{HH}$ 7.8, $^{3}J_{HH}$ 7.5, $^{4}J_{HH}$ 1.7, $^{6}J_{PH}$ 1.4), 2.57 br. s (H^{18}, 3H), 1.22, 1.23, 1.36 and 1.37, four s (H^{10-13}, 12H). ^{31}P-{^{1}H} NMR spectrum (162.0 MHz, CCl_4/C_6D_6 = 7/1, δ_P ppm): 138.2 (s).



2

4,4,5,5,5'-Pentamethyl-3',3'-bis(trifluoromethyl)-3'H,5'H-2λ^{5}-spiro[[1,3,2]dioxaphospholane-2,2'-[2,5]epoxybenzo[f][1,4,2]dioxaphosphepine] (**2**). Mp 140-141 °C (from CCl_4). Found, %: C 45.33, H 4.47, P 7.02. $C_{17}H_{19}F_6O_5P$. Calculated, %: C 45.55, H 4.27, P 6.91. Mass-spectrum EI: *m/z* calcd for C $C_{17}H_{19}F_6O_5P$ $[M]^+$ 448, found 448. IRS, cm^{-1} (pellet KBr): 3015, 2996, 2941, 1617, 1591, 1490, 1466, 1396, 1387, 1377, 1296, 1275, 1256, 1225, 1205, 1157, 1149, 1136, 1115, 1089, 1066, 1037, 1008, 994, 956, 938, 911, 866, 855, 838, 806, 788, 755, 729, 713, 685, 669, 639, 580, 549, 516, 485, 466, 452, 424, 406. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 7.92 br. dd (H^{17}, 1H, $^{3}J_{HH}$ 7.9-8.0, $^{4}J_{HH}$ 1.0), 7.27 br. d (H^{14}, 1H, $^{3}J_{HH}$ 7.6), 7.26 ddd (H^{15}, 1H, $^{3}J_{HH}$ 8.0, $^{3}J_{HH}$ 7.4, $^{4}J_{HH}$ 1.6, $^{5}J_{POCCCH}$ 1.4), 7.03 br ddd (H^{16}, 1H, $^{3}J_{HH}$ 7.6, $^{3}J_{HH}$ 7.4, $^{4}J_{HH}$ 1.0), 1.95 d (H^{18}, 3H, $^{4}J_{POCCH}$ 2.0), 1.53 and 1.34 two s (H^{10}, H^{12}, 6H), 1.42 br. s (H^{11}, H^{13}, 6H). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$, δ_C ppm, *J* Hz) (hereinafter a view of signal in ^{13}C-{^{1}H} NMR spectrum is in parentheses): 151.35 m (d) (C^3, $^{3}J_{HC^{15}CC}$ 10.9, $^{3}J_{HC^{17}CC}$ 9.6, $^{2}J_{POC}$ 6.7, $^{2}J_{HC^{14}C}$ 5.1), 127.49 m (d) (C^4, $^{3}J_{POCC}$ 4.0), 99.05 m (d) (C^5, $^{2}J_{HC^{18}C}$ 4.0, $^{3}J_{HC^{17}CC}$ 4.0-4.5, $^{2}J_{POC}$ 2.8,), 78.81 dqq (dqq) (C^7, $^{1}J_{PC}$ 152.3, $^{2}J_{FCC}$ 31.0, $^{2}J_{FCC}$ 30.3), 81.01 m (d) (C^8, $^{2}J_{HCC}$ 3.6, $^{3}J_{HCCC}$ 3.6-3.7, $^{2}J_{POC}$ 3.6), 81.55 m (d) (C^9, $^{2}J_{HCC}$ 3.6, $^{3}J_{HCCC}$ 3.6, $^{2}J_{POC}$ 3.1), 23.16 qdq (d) (C^{10}, $^{1}J_{HC}$ 127.5, $^{3}J_{POCC}$ 12.6, $^{3}J_{HCCC}$ 4.0), 25.11 qq (s) (C^{11}, $^{1}J_{HC}$ 127.4, $^{3}J_{HCCC}$ 4.0), 23.62 qdq (d) (C^{12}, $^{1}J_{HC}$ 127.5, $^{3}J_{POCC}$ 13.0, $^{3}J_{HCCC}$ 4.1), 25.06 qqm (m) (C^{13}, $^{1}J_{HC}$ 127.4, $^{3}J_{HCCC}$ 4.0, $^{6}J_{FCCPOCC}$ 1.5), 118.04 ddddd (d) (C^{14}, $^{1}J_{HC}$ 162.7, $^{3}J_{POCC}$ 12.1, $^{3}J_{HC^{16}CC}$ 8.0, $^{2}J_{HC^{15}C}$ 1.4, $^{4}J_{HC^{17}CCC}$ 1.5), 124.67 ddd (s) (C^{15}, $^{1}J_{HC}$ 158.7, $^{3}J_{HC^{17}CC}$ 8.7, $^{2}J_{HC^{14}C}$ 2.6), 123.31 ddd (s) (C^{16}, $^{1}J_{HC}$ 160.2, $^{3}J_{HC^{14}CC}$ 8.4, $^{2}J_{HC^{17}C}$ 1.6), 130.63 dddd (d) (C^{17}, $^{1}J_{HC}$ 160.3, $^{3}J_{HC^{15}CC}$ 8.7, $^{2}J_{HC^{16}C}$ 1.7-1.8, $^{4}J_{POCCC}$ 1.8), 23.77 qd (d) (C^{18}, $^{1}J_{HC}$ 129.1, $^{3}J_{POCC}$ 5.9), 122.34 qdq (qdq) (C^{19}, $^{1}J_{FC}$ 286.9, $^{3}J_{FCCC}$ 2.8-2.9, $^{2}J_{PCC}$ 2.0), 122.25 qdq (qdq) (C^{20}, $^{1}J_{FC}$ 285.8, $^{3}J_{FCCC}$ 2.8-2.9, $^{2}J_{PCC}$ 2.7-2.8). ^{19}F-{^{1}H} NMR spectrum (376.5 MHz, $CDCl_3$, δ_F ppm, *J* Hz): –68.21 qd (CF_3, 3F, $^{4}J_{FF}$ 10.0, $^{3}J_{PCCF}$ 3.1), –69.16 qd (CF_3, 3F, $^{4}J_{FF}$ 10.0, $^{3}J_{PCCF}$ 4.3). ^{31}P-{^{1}H} NMR spectrum (242.9 MHz, toluene, δ_P ppm): –29.5 (m). ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, δ_P ppm): –30.0 (br. s). ^{31}P-{^{1}H} NMR spectrum (242.9 MHz, $CDCl_3$, δ_P ppm, *J* Hz): –29.9 (qq) ($^{3}J_{FCCP}$ 4.4, $^{3}J_{FCCP}$ 3.1).

^{1}H NMR spectrum (400 MHz, DMCO-d_6, δ ppm, J Hz): 7.47 dd (H^{17}, 1H, $^{3}J_{HH}$ 7.6, $^{4}J_{HH}$ 1.6), 7.37 ddddd (H^{15}, 1H, $^{3}J_{HH}$ 8.1, $^{3}J_{HH}$ 7.6, $^{5}J_{POCCCH}$ 1.7, $^{4}J_{HH}$ 1.6), 7.12 ddd (H^{16}, 1H, $^{3}J_{HH}$ 7.6, $^{3}J_{HH}$ 7.6, $^{5}J_{POCCCH}$ 1.2), 7.01 dd (H^{14}, 1H, $^{3}J_{HH}$ 8.1, $^{4}J_{POCCH}$ 1.0), 1.87 d (H^{18}, 3H, $^{4}J_{POCCH}$ 2.0), 1.46, 1.37, 1.32, 1.29 four s (H^{10}, H^{11}, H^{12}, H^{13}, 12H). ^{13}C NMR spectrum (100.6 MHz, DMCO-d_6, δ_C ppm, J Hz): 150.35 m (d) (C^{3}, $^{2}J_{POC}$ 6.9), 126.21 m (d) (C^{4}, $^{3}J_{POCC}$ 4.6), 98.73 m (d) (C^{5}, $^{2}J_{POC}$ 4.3, $^{2}J_{HCC}$ 4.5), 78.55 dqq (dqq) (C^{7}, $^{1}J_{PC}$ 152.0, $^{2}J_{FCC}$ 31.9, $^{2}J_{FCC}$ 30.2), 81.02 m (d) (C^{8}, $^{2}J_{HCC}$ 3.9-4.2, $^{3}J_{HCCC}$ 3.0-3.5, $^{2}J_{POC}$ 3.3), 81.25 m (d) (C^{9}, $^{2}J_{HCC}$ 3.9-4.2, $^{3}J_{HCCC}$ 3.0-3.5, $^{2}J_{POC}$ 2.8), 22.54 qdq (d) (C^{10}, $^{1}J_{HC}$ 128.0, $^{3}J_{POCC}$ 12.1, $^{3}J_{HCCC}$ 4.3), 24.63 qq (s) (C^{11}, $^{1}J_{HC}$ 127.2, $^{3}J_{HCCC}$ 4.3), 23.14 qdq (d) (C^{12}, $^{1}J_{HC}$ 127.2, $^{3}J_{POCC}$ 12.6, $^{3}J_{HCCC}$ 4.0), 24.49 qm (br. s) (C^{13}, $^{1}J_{HC}$ 129.3, $^{3}J_{HCCC}$ 4.3, $^{6}J_{FCCPOCC}$ 1.0-1.1), 117.57 ddddd (d) (C^{14}, $^{1}J_{HC}$ 163.6, $^{3}J_{POCC}$ 12.8, $^{3}J_{HCCC}$ 8.0, $^{2}J_{HC^{15}C}$ 1.5, $^{4}J_{HC^{17}CCC}$ 1.5), 125.02 ddd (s) (C^{15}, $^{1}J_{HC}$ 161.1, $^{3}J_{HCCC}$ 8.8, $^{2}J_{HCC}$ 1.7), 123.48 ddd (s) (C^{16}, $^{1}J_{HC}$ 162.4, $^{3}J_{HCCC}$ 7.7, $^{2}J_{HC^{17}C}$ 1.6), 131.03 dddd (d) (C^{17}, $^{1}J_{HC}$ 161.6, $^{3}J_{HCCC}$ 8.4, $^{2}J_{HC^{16}C}$ 1.8, $^{4}J_{POCCC}$ 1.7), 23.25 qd (d) (C^{18}, $^{1}J_{HC}$ 129.2, $^{3}J_{POCC}$ 5.9), 121.98 qm (qm) (C^{19,20}, $^{1}J_{FC}$ 286.9, $^{2}J_{PCC}$ 2.8, $^{3}J_{FCCC}$ 2.4). ^{19}F-{^{1}H} NMR spectrum (376.5 MHz, DMCO-d_6, δ_F ppm, J Hz): –67.31 qd (CF_3, 3F, $^{4}J_{FF}$ 10.0, $^{3}J_{PCCF}$ 3.0), –68.65 qd (CF_3, 3F, $^{4}J_{FF}$ 10.0, $^{3}J_{PCCF}$ 4.3). ^{31}P-{^{1}H} NMR spectrum (162.0 MHz, DMCO-d_6, δ_P ppm): –30.0 (br. s).



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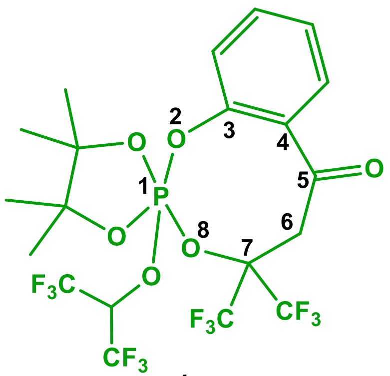
4,4,5,5,5'-Pentamethyl-4',4'-bis(trifluoromethyl)-4',5'-dihydro-2λ^{5}-spiro[[1,3,2]dioxaphospholane-2,2'-[2,5]epoxybenzo[d][1,3,2]dioxaphosphepine] (**3**). Mp 159-161 °C (from pentane). Found, %: C 45.43, H 4.55, P 6.77. $C_{17}H_{19}F_6O_5P$. Calculated, %: C 45.55, H 4.27, P 6.91. Mass-spectrum EI: m/z calcd for C $C_{17}H_{19}F_6O_5P$ [M]$^{+}$ 448, found 448. IRS, cm^{-1} (pellet KBr): 3045, 3008, 2990, 2979, 1610, 1585, 1488, 1454, 1391, 1378, 1306, 1294, 1246 sh, 1239 sh, 1231, 1216, 1180, 1161, 1141, 1114, 1080, 1043, 1020, 1010, 993, 977, 946, 918, 878, 849, 832, 815, 797, 777, 763, 744, 717, 707, 682, 661, 637, 586, 563, 537, 498, 481, 451, 429. ^{1}H NMR spectrum (600 MHz, acetone-d_6, δ ppm, J Hz): 7.39 br. d (H^{17}, 1H, $^{3}J_{HH}$ 8.1), 7.37 br. ddd (H^{15}, 1H, $^{3}J_{HH}$ 8.1, $^{3}J_{HH}$ 7.2, $^{4}J_{HH}$ 1.4), 7.14 ddd (H^{16}, 1H, $^{3}J_{HH}$ 8.1, $^{3}J_{HH}$ 7.2, $^{4}J_{HH}$ 1.1), 6.99 br. d (H^{16}, 1H, $^{3}J_{HH}$ 8.1), 1.96 br. s (H^{18}, 3H), 1.34 and 1.41 two s (H^{10}, H^{13}, 6H), 1.42 br. s (H^{11}, H^{12}, 6H). ^{13}C NMR spectrum (150.9 MHz, $CDCl_3$, δ_C ppm, J Hz): 153.28 m (d) (C^{3}, $^{3}J_{HC^{15}CC}$ 11.0, $^{3}J_{HC^{17}CC}$ 9.0, $^{2}J_{POC}$ 6.6, $^{2}J_{HC^{14}C}$ 5.7), 128.62 m (d) (C^{4}, $^{3}J_{POCC}$ 4.4, $^{4}J_{FCCCC}$ 1.0), 76.65 br. dq (br. s) (C^{5}, $^{2}J_{HC^{18}C}$ 4.7, $^{3}J_{HC^{17}CC}$ 4.0), 83.04 septdq (septd) (C^{6}, $^{2}J_{FCC}$ 28.7, $^{2}J_{POC}$ 6.6, $^{3}J_{HC^{18}CC}$ 30.3), 79.62 m (d) (C^{8}, $^{2}J_{HCC}$ 3.6-3.7, $^{3}J_{HCCC}$ 3.6-3.7, $^{2}J_{POC}$ 3.5), 83.16 m (d) (C^{9}, $^{2}J_{HCC}$ 3.6-3.7, $^{3}J_{HCCC}$ 3.6-3.7, $^{2}J_{POC}$ 2.8), 23.44 qdq (d) (C^{10}, $^{1}J_{HC}$ 128.3, $^{3}J_{POCC}$ 8.4, $^{3}J_{HCCC}$ 4.4), 23.49 qdq (d) (C^{11}, $^{1}J_{HC}$ 127.2, $^{3}J_{POCC}$ 5.5, $^{3}J_{HCCC}$ 4.1), 23.83 qdq (d) (C^{12}, $^{1}J_{HC}$ 127.0, $^{3}J_{POCC}$ 8.4, $^{3}J_{HCCC}$ 4.0), 24.20 qdq (d) (C^{13}, $^{1}J_{HC}$ 126.8, $^{3}J_{POCC}$ 6.1, $^{3}J_{HCCC}$ 4.3), 118.82 ddddd (d) (C^{14}, $^{1}J_{HC}$ 162.8, $^{3}J_{POCC}$ 14.1, $^{3}J_{HC^{16}CC}$ 8.1, $^{2}J_{HC^{15}C}$ 1.5, $^{4}J_{HC^{17}CCC}$ 1.5), 128.61 dd (s) (C^{15}, $^{1}J_{HC}$ 160.2, $^{3}J_{HC^{17}CC}$ 8.3), 124.13 ddd (s) (C^{16}, $^{1}J_{HC}$ 162.5, $^{3}J_{HC^{14}CC}$ 8.0, $^{2}J_{HC^{17}C}$ 0.8), 131.54 dddd (d) (C^{17}, $^{1}J_{HC}$ 161.7, $^{3}J_{HC^{15}CC}$ 8.7, $^{4}J_{POCCC}$ 2.2, $^{2}J_{HC^{16}C}$ 1.9), 21.52 qdm (dm) (C^{18}, $^{1}J_{HC}$ 130.1, $^{3}J_{POCC}$ 14.4, $^{4}J_{FCCCC}$ 1.6), 122.88 qd (qd) (C^{19}, $^{1}J_{FC}$ 286.0, $^{3}J_{POCC}$ 12.2), 123.15 qd (qd) (C^{20}, $^{1}J_{FC}$ 289.0, $^{3}J_{POCC}$ 2.6). ^{19}F-{^{1}H} NMR spectrum (376.5 MHz, acetone-d_6, δ_F ppm, *J* Hz): –70.61 q (CF$_3$, 3F, $^{4}J_{FF}$ 10.4), –73.24 br. q (CF$_3$, 3F, $^{4}J_{FF}$ 10.4). ^{31}P-{^{1}H} NMR spectrum (242.9 MHz, acetone-d_6, δ_P ppm): –35.3 (m).

^{1}H NMR spectrum (600 MHz, CDCl$_3$, δ ppm, *J* Hz): 7.29 m (H^{15}, 1H, $^{3}J_{HH}$ 8.2, $^{3}J_{HH}$ 7.4, $^{4}J_{HH}$ 1.6, $^{4}J_{PH}$ 1.4), 7.19 br. d (H^{17}, 1H, $^{3}J_{HH}$ 7.8), 7.06 ddd (H^{16}, 1H, $^{3}J_{HH}$ 7.8, $^{3}J_{HH}$ 7.4, $^{4}J_{HH}$ 1.5), 6.97 dd (H^{14}, 1H, $^{3}J_{HH}$ 8.2, $^{4}J_{HH}$ 1.5), 1.98 br. s (H^{18}, 3H), 1.38 and 1.44 two s (H^{10}, H^{12}, 6H), 1.43 br. s (H^{11}, H^{13}, 6H). ^{13}C NMR spectrum (100.6 MHz, CDCl$_3$, δ_C ppm, *J* Hz): 152.36 m (dq) (C^{3}, $^{3}J_{HC^{15}CC}$ 10.8, $^{3}J_{HC^{17}CC}$ 9.5, $^{2}J_{POC}$ 6.8, $^{2}J_{HC^{14}C}$ 5.4, $^{4}J_{HC^{16}CCC}$ 1.4, $^{4}J_{FCCCCC}$ 0.7), 127.71 br. m (dm) (C^{4}, $^{3}J_{POCC}$ 4.4, $^{4}J_{FCCCC}$ 1.0), 75.96 br. dq (br. s) (C^{5}, $^{2}J_{HC^{18}C}$ 4.6-4.7, $^{3}J_{HC^{17}CC}$ 4.6-4.7), 82.37 septdq (septd) (C^{6}, $^{2}J_{FCC}$ 30.3, $^{2}J_{POC}$ 6.2, $^{3}J_{HC^{18}CC}$ 3.4), 78.99 m (d) (C^{8}, $^{3}J_{HC^{12,13}CC}$ 3.5-3.6, $^{2}J_{HC^{10,11}C}$ 3.5-3.6, $^{2}J_{POC}$ 3.4), 82.70 m (d) (C^{9}, $^{3}J_{HC^{10,11}CC}$ 3.5-3.6, $^{2}J_{HC^{12,13}C}$ 3.5-3.6, $^{2}J_{POC}$ 2.5), 23.11 qdq (d) (C^{10}, $^{1}J_{HC}$ 127.2, $^{3}J_{POCC}$ 9.4, $^{3}J_{HCCC}$ 4.1), 23.28 qdq (d) (C^{11}, $^{1}J_{HC}$ 127.4, $^{3}J_{POCC}$ 5.6, $^{3}J_{HCCC}$ 4.1), 23.42 qdq (d) (C^{12}, $^{1}J_{HC}$ 127.3, $^{3}J_{POCC}$ 8.9, $^{3}J_{HCCC}$ 4.1), 23.86 qdq (d) (C^{13}, $^{1}J_{HC}$ 127.3, $^{3}J_{POCC}$ 5.4, $^{3}J_{HCCC}$ 4.1), 118.43 ddddd (d) (C^{14}, $^{1}J_{HC}$ 162.8, $^{3}J_{POCC}$ 14.4, $^{3}J_{HC^{16}CC}$ 8.0, $^{2}J_{HC^{15}C}$ 1.5, $^{4}J_{HC^{17}CCC}$ 1.5), 130.37 dddd (s) (C^{15}, $^{1}J_{HC}$ 160.1, $^{3}J_{HC^{17}CC}$ 8.8, $^{4}J_{POCCC}$ 2.3, $^{2}J_{HC^{14}C}$ 2.3-2.4), 123.16 ddm (s) (C^{16}, $^{1}J_{HC}$ 162.4, $^{3}J_{HC^{14}CC}$ 8.2, $^{2}J_{HC^{17}C}$ 2.4-3.4, $^{2}J_{HC^{15}C}$ 1.0), 126.74 br. dd (q) (C^{17}, $^{1}J_{HC}$ 160.1, $^{3}J_{HC^{15}CC}$ 8.7, $^{5}J_{FCCCCC}$ 1.6), 21.25 qdm (dm) (C^{18}, $^{1}J_{HC}$ 129.3, $^{3}J_{POCC}$ 13.5, $^{4}J_{FCCCC}$ 1.6), 121.73 br. qd (qdq) (C^{19}, $^{1}J_{FC}$ 286.2, $^{3}J_{POCC}$ 12.2, $^{3}J_{FCCC}$ 1.0), 122.10 qd (qd) (C^{20}, $^{1}J_{FC}$ 289.6, $^{3}J_{POCC}$ 2.6). ^{19}F-{^{1}H} NMR spectrum (376.5 MHz, CDCl$_3$, δ_F ppm, *J* Hz): –70.04 q (CF$_3$, 3F, $^{4}J_{FF}$ 10.3), –72.71 br. q (CF$_3$, 3F, $^{4}J_{FF}$ 10.3). ^{31}P-{^{1}H} NMR (242.94 MHz, CDCl$_3$, δ_P ppm): –35.8 (br. s).

Mass-spectrum EI: *m/z* calcd for $C_{20}H_{19}F_{12}O_6P$ [M]$^{+}$ 614, found 614. ^{31}P-{^{1}H} и ^{31}P NMR spectra (162.0 MHz, CCl$_4$/CDCl$_3$ = 1/1, δ_P ppm): –64.5 s(d) ($^{3}J_{HCOP}$ 14.6 Hz). ^{19}F-{^{1}H} NMR spectrum (376.5 MHz, CCl$_4$/CDCl$_3$ = 1/1, δ_F ppm, *J* Hz): –74.03 and –74.14 two m (OCH(CF$_3$)$_2$, 6F, $^{4}J_{FF}$ 8.3), –77.69 br. q (CF$_3$, 3F, $^{4}J_{FF}$ 10.0), –78.50 q (CF$_3$, 3F, $^{4}J_{FF}$ 10.0). ^{1}H NMR spectrum (400 MHz, CCl$_4$/CDCl$_3$ = 1/1, δ ppm, *J* Hz): 1.39, 1.31, 1.30, 1.25 four s (4Me), 5.94 br. s (H^{5B}), 5.40 br. s (H^{5A}), 5.42 dsept (OCH, $^{3}J_{POCH}$ 14.4, $^{3}J_{FCCH}$ 5.8).



4

Table S1. Crystal Data and Refinement Details for compounds (**2**) and (**3**).

Parameter	M37 (**2**), 100 K	M37 (**2**), 296 K	M39 (**3**), 296 K
Color, habitus		Colorless, formless	Colorless, formlessc
Crystal dimensions, мм	0.30 × 0.30 × 0.20	0.50 × 0.30 × 0.15	0.30 × 0.20 × 0.10
Moiety Formula Sum Formula	$C_{17}H_{19}F_6O_5P$ $C_{17}H_{19}F_6O_5P$	$C_{17}H_{19}F_6O_5P$ $C_{17}H_{19}F_6O_5P$	$C_{17}H_{19}F_6O_5P$ $C_{17}H_{19}F_6O_5P$
Molecular mass	448.29	448.29	448.29
Temperature	100(2) K	296(2) K	296(2) K
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Cell parameters, Å, angles, degrees	*a* = 12.8493(7), *b* = 9.8769(5), *c* = 15.0305(9), β = 99.350(2)°	*a* = 12.972(6), *b* = 9.919(4), *c* = 15.183(7), β = 99.482(6)°	*a* = 14.320(4), *b* = 10.422(3), *c* = 12.856(4), β = 94.930(4)°
Cell volume, $Å^3$	1882.20(18)	1926.9(15)	1911.6(10)
Z	4	4	4
D(calc), g/$см^3$	1.582	1.545	1.558
μMo, $мм^{-1}$	0.231	0.226	0.228
Absorption correction	multi-scan	multi-scan	multi-scan
Radiation (λ, Å)	MoK_α, 0.71073	MoK_α, 0.71073	MoK_α, 0.71073
F(000)	920	920	920
Total reflections, independent reflections	38896, 5968	16448, 3783	14497, 3744
R(int)	0.038	0.048	0.032
Observed reflections, I > 2σ(I)	4971	2797	2763
R-factors, I > 2σ(I)	R^1 = 0.0349, wR^2 = 0.0869	R^1 = 0.0427, wR^2 = 0.1011	R^1 = 0.0355, wR^2 = 0.0889
R-factors, (all)	R^1 = 0.0459, wR^2 = 0.0932	R^1 = 0.0618, wR^2 = 0.1116	R^1 = 0.0543, wR^2 = 0.0991
goodness of fit	1.03	1.024	1.03

Refined number parameters, N par	267	267	267
Data set	$-18 \le h \le 18$, $-14 \le k \le 14$, $-21 \le l \le 21$	$-16 \le h \le 16$, $-12 \le k \le 12$, $-18 \le l \le 18$	$-17 \le h \le 17$, $-12 \le k \le 12$, $-15 \le l \le 15$
Theta Min-Max [Deg]	3.4, 31.0	2.5, 26.0	2.4, 26.0
Completeness to theta	0.995	0.999	0.998
Min. and Max. Resd. Dens., e·Å^{-3}	–-0.43, 0.43	–0.32, 0.24	–0.28, 0.21

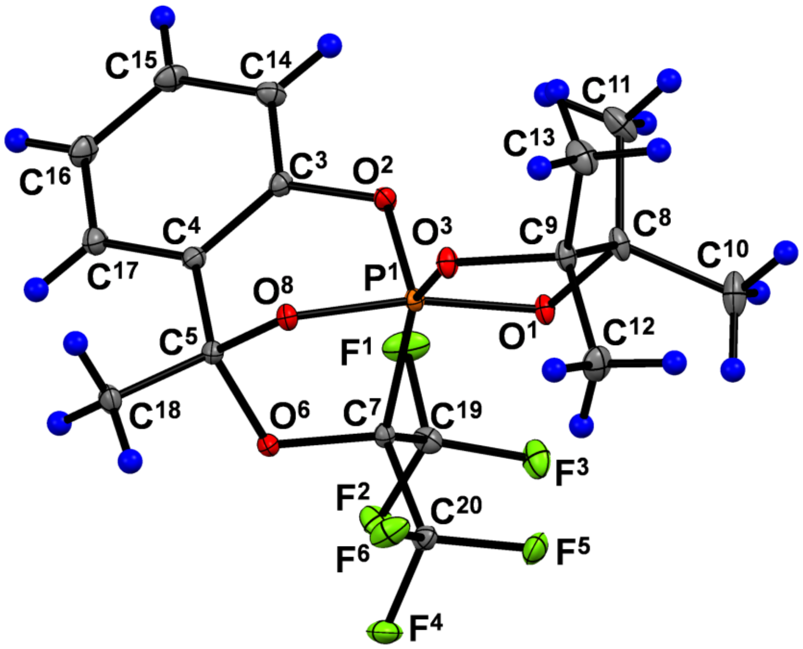


Figure S1. Molecular structure of (**2**) (100 K) and atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

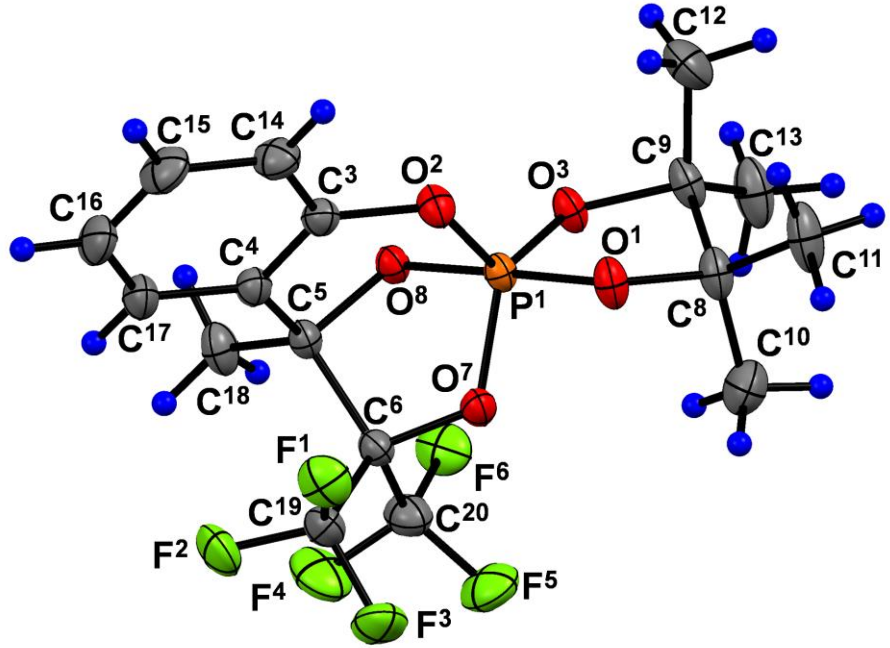


Figure S2. Molecular structure of (**3**) and atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

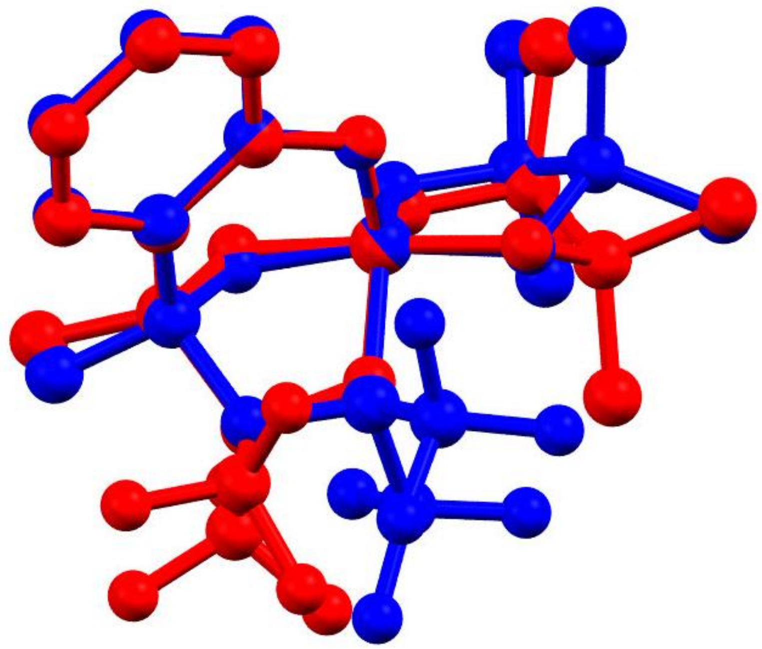


Figure S3. Overlap of the molecules **2** (blue) and **3** (red). An almost complete coincidence of the bicyclic systems conformations and a slight difference in the conformation of the spiro-linked dioxaphospholane cycle are shown.

Table S2. Bond lengths and bond angles for molecule (**2**).

bond length	***d*, Å**	**bond length**	***d*, Å**	**bond length**	***d*, Å**	**bond length**	***d*, Å**
$P^1–O^1$	1.636(1)	$F^4–C^{20}$	1.335(1)	$O^8–C^5$	1.403(1)	$C^8–C^9$	1.555(2)
$P^1–O^2$	1.6039(8)	$F^5–C^{20}$	1.338(1)	$C^3–C^4$	1.394(2)	$C^8–C^{10}$	1.528(2)
$P^1–O^3$	1.6072(9)	$F^6–C^{20}$	1.341(1)	$C^3–C^{14}$	1.383(2)	$C^8–C^{11}$	1.519(2)
$P^1–O^8$	1.6679(9)	$O^1–C^8$	1.459(2)	$C^4–C^5$	1.517(2)	$C^9–C^{12}$	1.516(2)
$P^1–C^7$	1.936(1)	$O^2–C^3$	1.400(2)	$C^4–C^{17}$	1.393(2)	$C^9–C^{13}$	1.529(2)
$F^1–C^{19}$	1.336(1)	$O^3–C^9$	1.463(2)	$C^5–C^{18}$	1.505(2)	$C^{14}–C^{15}$	1.3926(2)
$F^2–C^{19}$	1.345(1)	$O^6–C^5$	1.476(2)	$C^7–C^{19}$	1.545(2)	$C^{15}–C^{16}$	1.390(2)
$F^3–C^{19}$	1.333(2)	$O^6–C^7$	1.408(2)	$C^7–C^{20}$	1.547(2)	$C^{16}–C^{17}$	1.393(2)
bond angle	**φ, deg.**	**bond angle**	**φ, deg.**	**bond angle**	**φ, deg.**	**bond angle**	**φ, deg.**
$O^1–P^1–O^2$	95.73(5)	$P^1–O^8–C^5$	111.58(7)	$O^1–C^8–C^9$	101.72(9)	$C^8–C^9–C^{13}$	113.9(1)
$O^1–P^1–O^3$	91.75(4)	$P^1–C^7–O^6$	106.64(7)	$O^6–C^7–C^{19}$	106.03(9)	$C^{12}–C^9–C^{13}$	110.6(1)
$O^1–P^1–O^8$	167.12(5)	$P^1–C^7–C^{19}$	116.24(7)	$O^6–C^7–C^{20}$	106.15(9)	$F^1–C^{19}–F^2$	106.6(1)
$O^1–P^1–C^7$	89.10(5)	$P^1–C^7–C^{20}$	111.18(7)	$C^{19}–C^7–C^{20}$	109.93(9)	$F^1–C^{19}–F^3$	107.7(1)
$O^2–P^1–O^3$	114.43(5)	$O^2–C^3–C^{14}$	115.9(1)	$O^1–C^8–C^{10}$	109.0(1)	$F^1–C^{19}–C^7$	111.5(1)
$O^2–P^1–O^8$	96.89(4)	$C^4–C^3–C^{14}$	122.2(1)	$O^1–C^8–C^{11}$	107.6(1)	$F^2–C^{19}–F^3$	106.3(1)
$O^2–P^1–C^7$	106.75(5)	$O^6–C^5–O^8$	105.39(9)	$C^9–C^8–C^{10}$	113.0(1)	$F^2–C^{19}–C^7$	110.5(1)
$O^3–P^1–O^8$	85.39(4)	$O^6–C^5–C^4$	109.37(9)	$C^9–C^8–C^{11}$	114.4(1)	$F^3–C^{19}–C^7$	114.0(1)
$O^3–P^1–C^7$	138.49(5)	$O^6–C^5–C^{18}$	106.91(9)	$C^{10}–C^8–C^{11}$	110.5(1)	$F^4–C^{20}–F^5$	107.0(1)
$O^8–P^1–C^7$	84.80(5)	$O^8–C^5–C^4$	108.83(9)	$O^3–C^9–C^8$	103.00(9)	$F^4–C^{20}–F^6$	107.16(9)
$P^1–O^1–C^8$	113.81(7)	$O^8–C^5–C^{18}$	109.8(1)	$O^3–C^9–C^{12}$	106.8(1)	$F^4–C^{20}–C^7$	111.79(9)
$P^1–O^2–C^3$	123.54(7)	$C^4–C^5–C^{18}$	116.0(1)	$O^3–C^9–C^{13}$	106.8(1)	$F^5–C^{20}–F^6$	106.6(1)
$P^1–O^3–C^9$	116.70(8)	$C^5–O^6–C^7$	111.28(9)	$C^8–C^9–C^{12}$	114.9(1)	$F^5–C^{20}–C^7$	114.0(1)

Table S3. Torsion bond angles for molecule (**2**).

torsion angle	τ, deg.	torsion angle	τ, deg.	torsion angle	τ, deg.	torsion angle	τ, deg.
$O^2–P^1–O^1–C^8$	92.10(8)	$O^2–P^1–C^7–C^{19}$	45.5(1)	$C^7–O^6–C^5–O^8$	–26.6(1)	$O^6–C^7–C^{20}–F^4$	51.3(1)
$O^3–P^1–O^1–C^8$	–22.67(8)	$O^3–P^1–C^7–C^{19}$	–141.85(8)	$C^5–O^6–C^7–C^{19}$	–125.76(9)	$O^6–C^7–C^{20}–F^5$	172.82(9)
$C^7–P^1–O^1–C^8$	–161.16(8)	$O^1–P^1–C^7–O^6$	–168.17(7)	$P^1–O^8–C^5–C^{18}$	163.07(8)	$O^6–C^7–C^{20}–F^6$	–67.6(1)
$O^1–P^1–O^2–C^3$	148.71(9)	$O^2–P^1–C^7–O^6$	–72.46(8)	$P^1–O^8–C^5–O^6$	48.3(1)	$C^{20}–C^7–C^{19}–F^3$	–50.3(1)
$O^3–P^1–O^2–C^3$	–116.74(9)	$O^3–P^1–C^7–O^6$	100.20(9)	$P^1–O^8–C^5–C^4$	–69.0(1)	$C^{19}–C^7–C^{20}–F^5$	58.6(1)
$O^8–P^1–O^2–C^3$	–28.7(1)	$O^8–P^1–C^7–C^{19}$	141.13(9)	$O^2–C^3–C^4–C^5$	5.0(2)	$C^{19}–C^7–C^{20}–F^6$	178.18(9)
$C^7–P^1–O^2–C^3$	57.9(1)	$O^1–P^1–C^7–C^{20}$	76.54(8)	$O^2–C^3–C^4–C^{17}$	–175.7(1)	$O^6–C^7–C^{19}–F^1$	73.3(1)
$O^1–P^1–O^3–C^9$	–1.06(8)	$P^1–O^1–C^8–C^{11}$	157.29(9)	$C^{17}–C^4–C^5–C^{18}$	–24.3(2)	$O^6–C^7–C^{19}–F^2$	–45.0(1)
$O^2–P^1–O^3–C^9$	–98.16(8)	$P^1–O^1–C^8–C^9$	36.7(1)	$C^3–C^4–C^5–O^8$	30.5(2)	$O^6–C^7–C^{19}–F^3$	–164.59(9)
$O^8–P^1–O^3–C^9$	166.37(8)	$P^1–O^1–C^8–C^{10}$	–82.9(1)	$C^{17}–C^4–C^5–O^8$	–148.7(1)	$P^1–C^7–C^{19}–F^1$	–45.0(1)
$C^7–P^1–O^3–C^9$	89.6(1)	$P^1–O^2–C^3–C^{14}$	–178.51(9)	$C^3–C^4–C^5–C^{18}$	154.9(1)	$P^1–C^7–C^{19}–F^2$	–163.30(8)
$O^2–P^1–O^8–C^5$	65.06(8)	$P^1–O^2–C^3–C^4$	–1.9(2)	$C^{17}–C^4–C^5–O^6$	96.6(1)	$C^{19}–C^7–C^{20}–F^4$	–62.9(1)
$O^3–P^1–O^8–C^5$	179.15(8)	$P^1–O^3–C^9–C^{13}$	–98.8(1)	$C^3–C^4–C^5–O^6$	–84.2(1)	$O^1–C^8–C^9–O^3$	–33.3(1)
$C^7–P^1–O^8–C^5$	–41.23(8)	$P^1–O^3–C^9–C^8$	21.5(1)	$C^{20}–C^7–C^{19}–F^1$	–172.38(9)	$O^1–C^8–C^9–C^{12}$	–149.1(1)
$O^2–P^1–C^7–C^{20}$	172.25(8)	$P^1–O^3–C^9–C^{12}$	142.91(9)	$C^{20}–C^7–C^{19}–F^2$	69.3(1)	$C^{10}–C^8–C^9–C^{13}$	–161.4(1)
$O^3–P^1–C^7–C^{20}$	–15.1(1)	$C^5–O^6–C^7–P^1$	–1.3(1)	$P^1–C^7–C^{19}–F^3$	77.1(1)	$C^{11}–C^8–C^9–O^3$	–149.0(1)
$O^8–P^1–C^7–C^{20}$	–92.10(8)	$C^5–O^6–C^7–C^{20}$	117.3(1)	$P^1–C^7–C^{20}–F^4$	166.91(8)	$C^{11}–C^8–C^9–C^{12}$	95.2(1)
$O^8–P^1–C^7–O^6$	23.18(7)	$C^7–O^6–C^5–C^{18}$	–143.42(9)	$P^1–C^7–C^{20}–F^5$	–71.6(1)	$C^{11}–C^8–C^9–C^{13}$	–33.8(2)
$O^1–P^1–C^7–C^{19}$	–50.22(9)	$C^7–O^6–C^5–C^4$	90.3(1)	$P^1–C^7–C^{20}–F^6$	48.0(1)	$O^1–C^8–C^9–C^{13}$	81.9(1)

Table S4. Bond lengths and bond angles for molecule (**3**).

bond length	***d*, Å**	**bond length**	***d*, Å**	**bond length**	***d*, Å**	**bond length**	***d*, Å**
$P^1–O^1$	1.632(2)	$O^7–C^6$	1.410(3)	$C^3–C^4$	1.390(3)	$C^8–C^9$	1.540(3)
$P^1–O^2$	1.611(2)	$O^8–C^5$	1.425(2)	$C^3–C^{14}$	1.375(3)	$C^8–C^{10}$	1.520(3)
$P^1–O^3$	1.590(2)	$F^1–C^{19}$	1.320(3)	$C^4–C^5$	1.521(3)	$C^8–C^{11}$	1.513(4)
$P^1–O^7$	1.634(2)	$F^2–C^{19}$	1.326(3)	$C^4–C^{17}$	1.395(3)	$C^9–C^{12}$	1.503(4)
$P^1–O^8$	1.669(2)	$F^3–C^{19}$	1.326(3)	$C^5–C^6$	1.569(3)	$C^9–C^{13}$	1.512(4)
$O^1–C^8$	1.446(3)	$F^4–C^{20}$	1.337(3)	$C^5–C^{18}$	1.516(3)	$C^{14}–C^{15}$	1.379(4)
$O^2–C^3$	1.393(3)	$F^5–C^{20}$	1.320(3)	$C^6–C^{19}$	1.537(3)	$C^{15}–C^{16}$	1.372(4)
$O^3–C^9$	1.464(3)	$F^6–C^{20}$	1.323(3)	$C^6–C^{20}$	1.540(3)	$C^{16}–C^{17}$	1.376(4)
bond angle	**φ, deg.**	**bond angle**	**φ, deg.**	**bond angle**	**φ, deg.**	**bond angle**	**φ, deg.**
$O^1–P^1–O^2$	89.57(8)	$O^2–C^3–C^{14}$	115.9(2)	$P^1–O^8–C^5$	110.1(1)	$C^{10}–C^8–C^{11}$	110.0(3)
$O^1–P^1–O^3$	92.06(8)	$O^3–C^9–C^{12}$	106.7(2)	$C^3–C^4–C^5$	118.3(2)	$C^{12}–C^9–C^{13}$	111.0(2)
$O^1–P^1–O^7$	89.64(8)	$O^3–C^9–C^8$	102.4(2)	$C^3–C^4–C^{17}$	117.6(2)	$C^{19}–C^6–C^{20}$	109.9(2)
$O^1–P^1–O^8$	176.30(8)	$O^3–C^9–C^{13}$	107.3(2)	$C^4–C^5–C^6$	113.6(2)	$F^1–C^{19}–F^2$	107.6(2)
$O^2–P^1–O^3$	122.98(9)	$O^7–C^6–C^{19}$	107.0(2)	$C^4–C^5–C^{18}$	111.6(2)	$F^1–C^{19}–F^3$	106.6(2)
$O^2–P^1–O^7$	108.90(8)	$O^7–C^6–C^{20}$	105.9(2)	$C^4–C^3–C^{14}$	121.4(2)	$F^1–C^{19}–C^6$	111.9(2)
$O^2–P^1–O^8$	94.07(8)	$O^7–C^6–C^5$	104.8(2)	$C^5–C^4–C^{17}$	123.9(2)	$F^2–C^{19}–F^3$	107.4(2)
$O^3–P^1–O^7$	128.10(8)	$O^8–C^5–C^4$	106.0(2)	$C^5–C^6–C^{19}$	114.4(2)	$F^2–C^{19}–C^6$	110.6(2)
$O^3–P^1–O^8$	85.39(7)	$O^8–C^5–C^6$	99.8(2)	$C^5–C^6–C^{20}$	114.1(2)	$F^3–C^{19}–C^6$	112.5(2)
$O^7–P^1–O^8$	89.82(7)	$O^8–C^5–C^{18}$	108.8(2)	$C^6–C^5–C^{18}$	115.8(2)	$F^4–C^{20}–F^5$	107.0(2)
$O^1–C^8–C^9$	101.6(2)	$P^1–O^1–C^8$	113.5(1)	$C^8–C^9–C^{13}$	114.3(2)	$F^4–C^{20}–F^6$	107.8(2)
$O^1–C^8–C^{10}$	107.6(2)	$P^1–O^2–C^3$	122.0(1)	$C^8–C^9–C^{12}$	114.3(2)	$F^4–C^{20}–C^6$	111.3(2)
$O^1–C^8–C^{11}$	108.5(2)	$P^1–O^3–C^9$	116.0(1)	$C^9–C^8–C^{10}$	114.1(2)	$F^5–C^{20}–F^6$	106.6(2)
$O^2–C^3–C^4$	122.6(2)	$P^1–O^7–C^6$	115.6(1)	$C^9–C^8–C^{11}$	114.4(2)	$F^5–C^{20}–C^6$	111.8(2)

Table S5. Torsion angles for molecule (**3**).

torsion angle	τ, deg.	torsion angle	τ, deg.	torsion angle	τ, deg.	torsion angle	τ, deg.
$O^1–P^1–O^2–C^3$	–146.5(2)	$P^1–O^1–C^8–C^{11}$	–83.6(2)	$O^7–C^6–C^{19}–F^3$	–72.4(2)	$C^5–C^6–C^{20}–F^5$	164.0(2)
$O^1–P^1–O^3–C^9$	–4.7(2)	$P^1–O^2–C^3–C^4$	1.2(3)	$O^7–C^6–C^{20}–F^4$	168.8(2)	$C^5–C^6–C^{20}–F^6$	44.4(3)
$O^1–P^1–O^7–C^6$	172.1(1)	$P^1–O^2–C^3–C^{14}$	178.1(2)	$O^7–C^6–C^{20}–F^5$	49.2(3)	$C^{10}–C^8–C^9–O^3$	–151.7(2)
$O^2–P^1–O^1–C^8$	–143.9(2)	$P^1–O^3–C^9–C^{12}$	–94.4(2)	$O^7–C^6–C^{20}–F^6$	–70.4(2)	$C^{10}–C^8–C^9–C^{12}$	–36.8(3)
$O^2–P^1–O^3–C^9$	86.1(2)	$P^1–O^3–C^9–C^{13}$	146.5(2)	$O^8–C^5–C^6–C^{20}$	–79.7(2)	$C^{10}–C^8–C^9–C^{13}$	92.7(3)
$O^2–P^1–O^7–C^6$	82.7(2)	$P^1–O^3–C^9–C^8$	25.9(2)	$O^8–C^5–C^6–C^{19}$	152.6(2)	$C^{11}–C^8–C^9–O^3$	80.4(2)
$O^2–P^1–O^8–C^5$	–72.6(1)	$P^1–O^7–C^6–C^5$	–13.1(2)	$O^8–C^5–C^6–O^7$	35.7(2)	$C^{11}–C^8–C^9–C^{12}$	–164.7(2)
$O^3–P^1–O^1–C^8$	–20.9(2)	$P^1–O^7–C^6–C^{19}$	–134.9(2)	$C^3–C^4–C^5–O^8$	–26.6(3)	$C^{11}–C^8–C^9–C^{13}$	–35.2(3)
$O^3–P^1–O^2–C^3$	121.3(2)	$P^1–O^7–C^6–C^{20}$	107.9(2)	$C^3–C^4–C^5–C^6$	81.9(2)	$C^{17}–C^4–C^5–C^6$	–103.7(2)
$O^3–P^1–O^7–C^6$	–95.6(2)	$P^1–O^8–C^5–C^4$	71.7(2)	$C^4–C^5–C^6–O^7$	–76.7(2)	$C^{17}–C^4–C^5–C^{18}$	29.5(3)
$O^3–P^1–O^8–C^5$	164.6(1)	$P^1–O^8–C^5–C^6$	–46.5(2)	$C^3–C^4–C^5–C^{18}$	–145.0(2)	$C^{17}–C^4–C^5–O^8$	147.8(2)
$O^7–P^1–O^1–C^8$	107.2(2)	$P^1–O^8–C^5–C^{18}$	–168.2(2)	$C^3–C^{14}–C^{15}–C^{16}$	0.1(4)	$C^{18}–C^5–C^6–C^{19}$	–90.9(2)
$O^7–P^1–O^3–C^9$	–95.9(2)	$O^1–C^8–C^9–O^3$	–36.3(2)	$C^4–C^3–C^{14}–C^{15}$	1.1(4)	$C^{18}–C^5–C^6–C^{20}$	36.8(3)
$O^7–P^1–O^2–C^3$	–57.0(2)	$O^1–C^8–C^9–C^{12}$	78.7(2)	$C^4–C^5–C^6–C^{19}$	40.2(2)	$C^{18}–C^5–C^6–O^7$	152.2(2)
$O^7–P^1–O^8–C^5$	36.3(1)	$O^1–C^8–C^9–C^{13}$	–151.9(2)	$C^4–C^5–C^6–C^{20}$	167.9(2)	$C^{19}–C^6–C^{20}–F^4$	53.5(3)
$O^8–P^1–O^2–C^3$	34.2(2)	$O^2–C^3–C^4–C^5$	–9.5(3)	$C^5–C^4–C^{17}–C^{16}$	–174.7(2)	$C^{19}–C^6–C^{20}–F^5$	–66.1(3)
$O^8–P^1–O^3–C^9$	178.0(2)	$O^2–C^3–C^4–C^{17}$	175.7(2)	$C^5–C^6–C^{19}–F^1$	–68.1(2)	$C^{19}–C^6–C^{20}–F^6$	174.3(2)
$O^8–P^1–O^7–C^6$	–11.6(1)	$O^2–C^3–C^{14}–C^{15}$	–175.9(2)	$C^5–C^6–C^{19}–F^2$	51.9(3)	$C^{20}–C^6–C^{19}–F^1$	162.1(2)
$P^1–O^1–C^8–C^9$	37.3(2)	$O^7–C^6–C^{19}–F^1$	47.6(2)	$C^5–C^6–C^{19}–F^3$	172.0(2)	$C^{20}–C^6–C^{19}–F^2$	–77.9(2)
$P^1–O^1–C^8–C^{10}$	157.4(2)	$O^7–C^6–C^{19}–F^2$	167.5(2)	$C^5–C^6–C^{20}–F^4$	–76.5(3)	$C^{20}–C^6–C^{19}–F^3$	42.2(3)

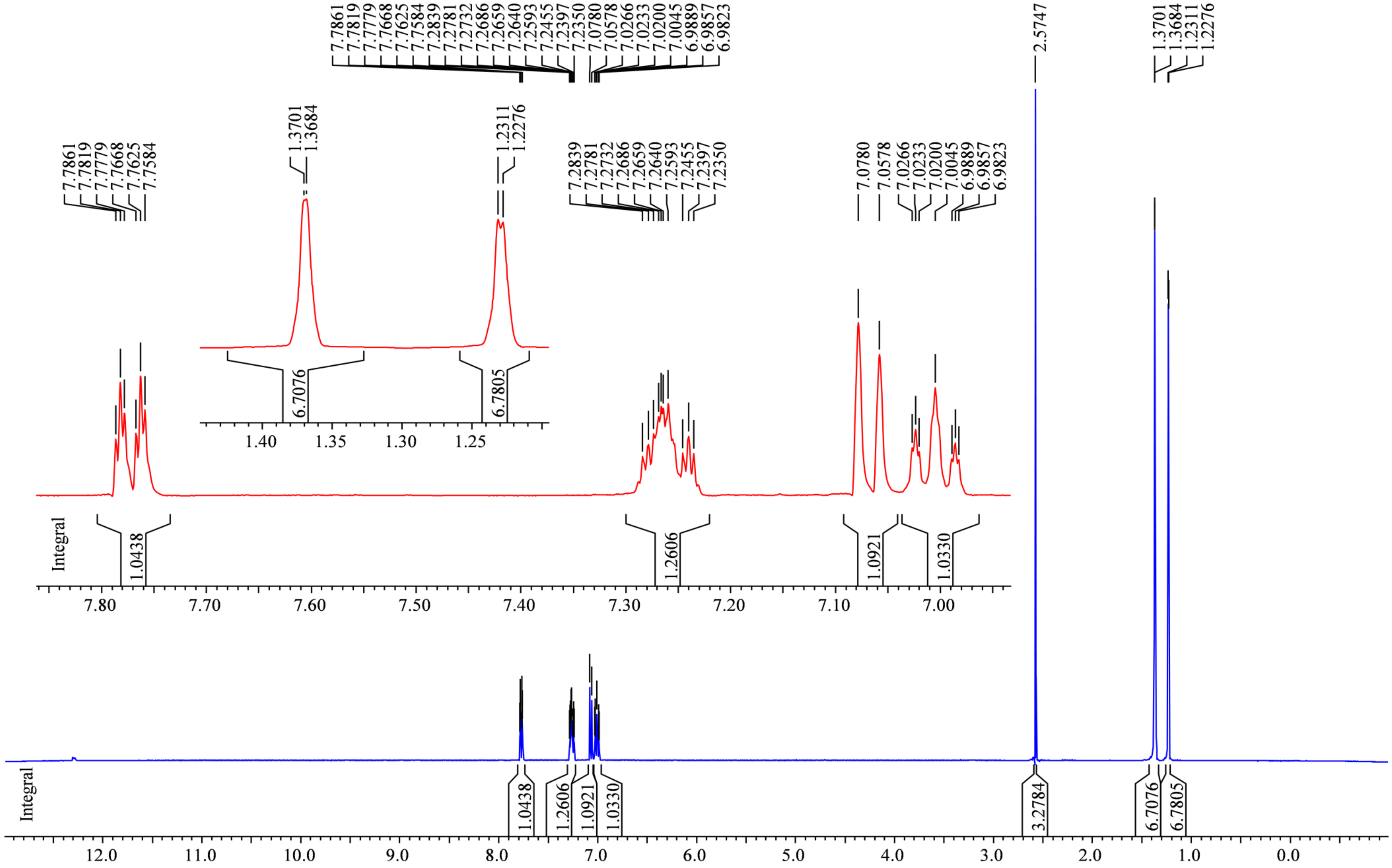


Figure S4. ^{1}H NMR spectrum (400.0 MHz, CCl_4/C_6D_6 = 7/1) of the dioxaphospholane (**1**).

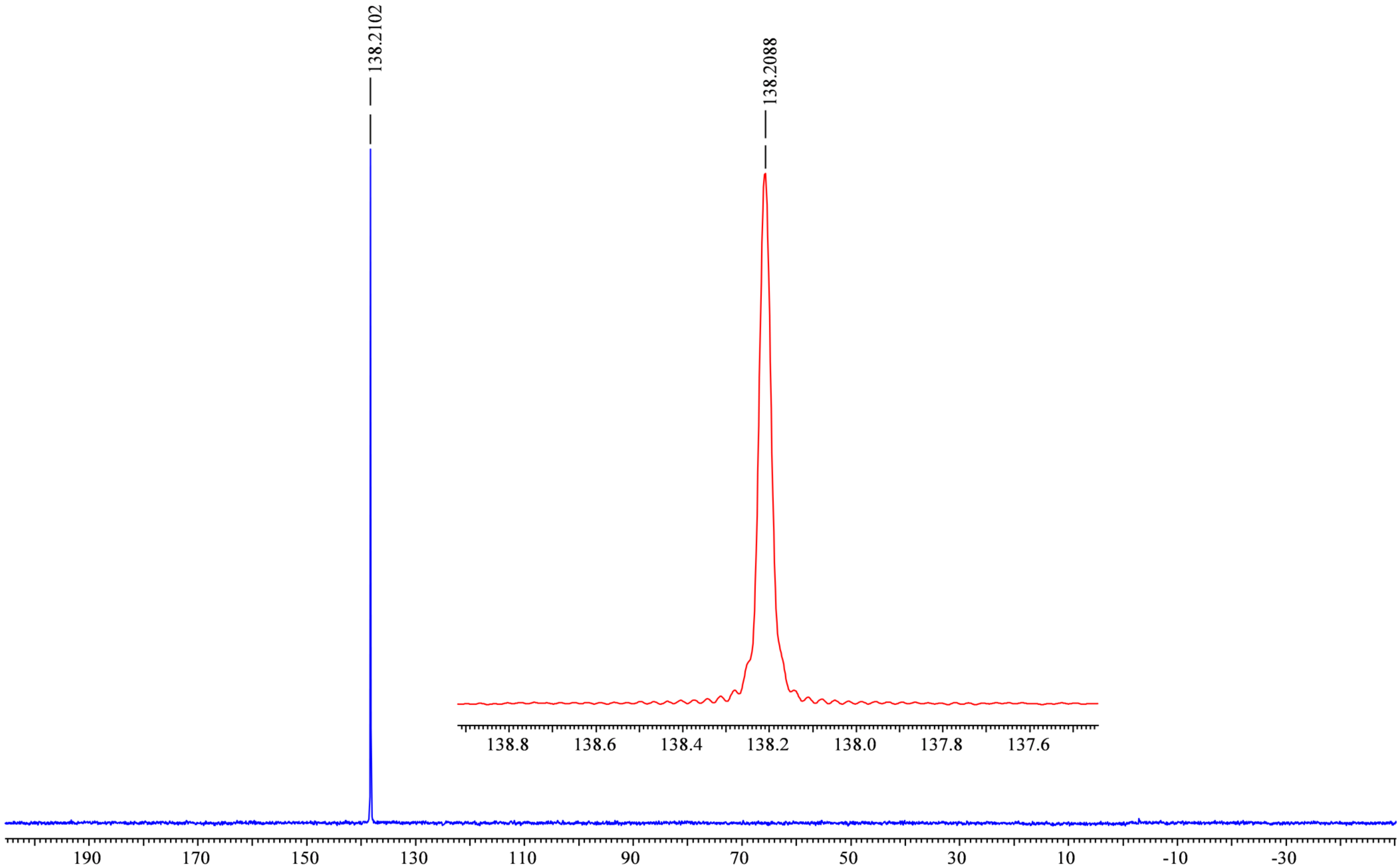


Figure S5. ^{31}P-{^{1}H} NMR (blue) and ^{31}P NMR (red) spectra (162.0 MHz, CCl_4/C_6D_6 = 7/1) of the dioxaphospholane (**1**).

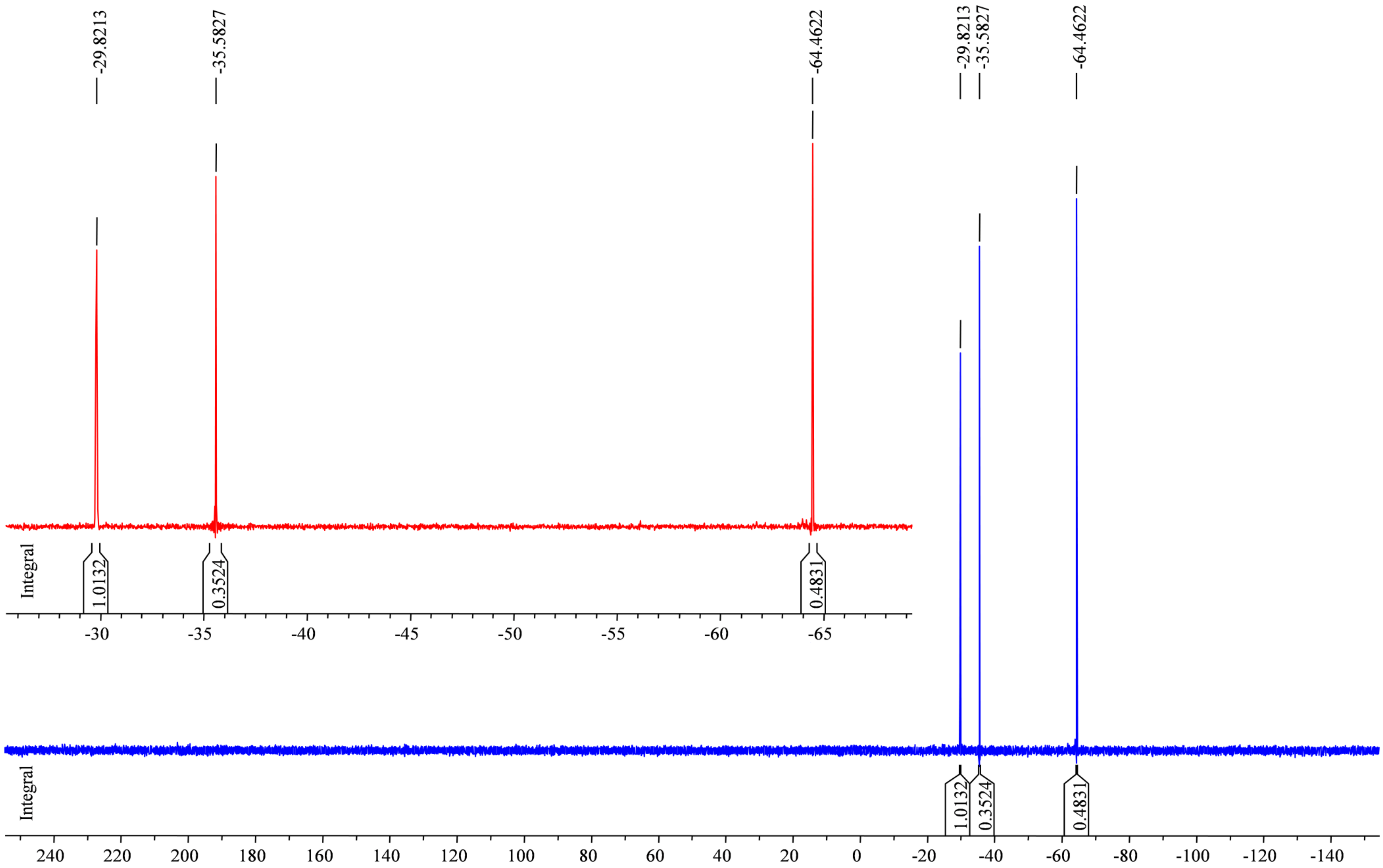


Figure S6. $^{31}P-\{^{1}H\}$ NMR spectrum (162.0 MHz, $CCl_4/CDCl_3$ = 1/1) of the dioxaphospholane (**1**) and hexafluoroacetone reaction mixture in CCl_4.

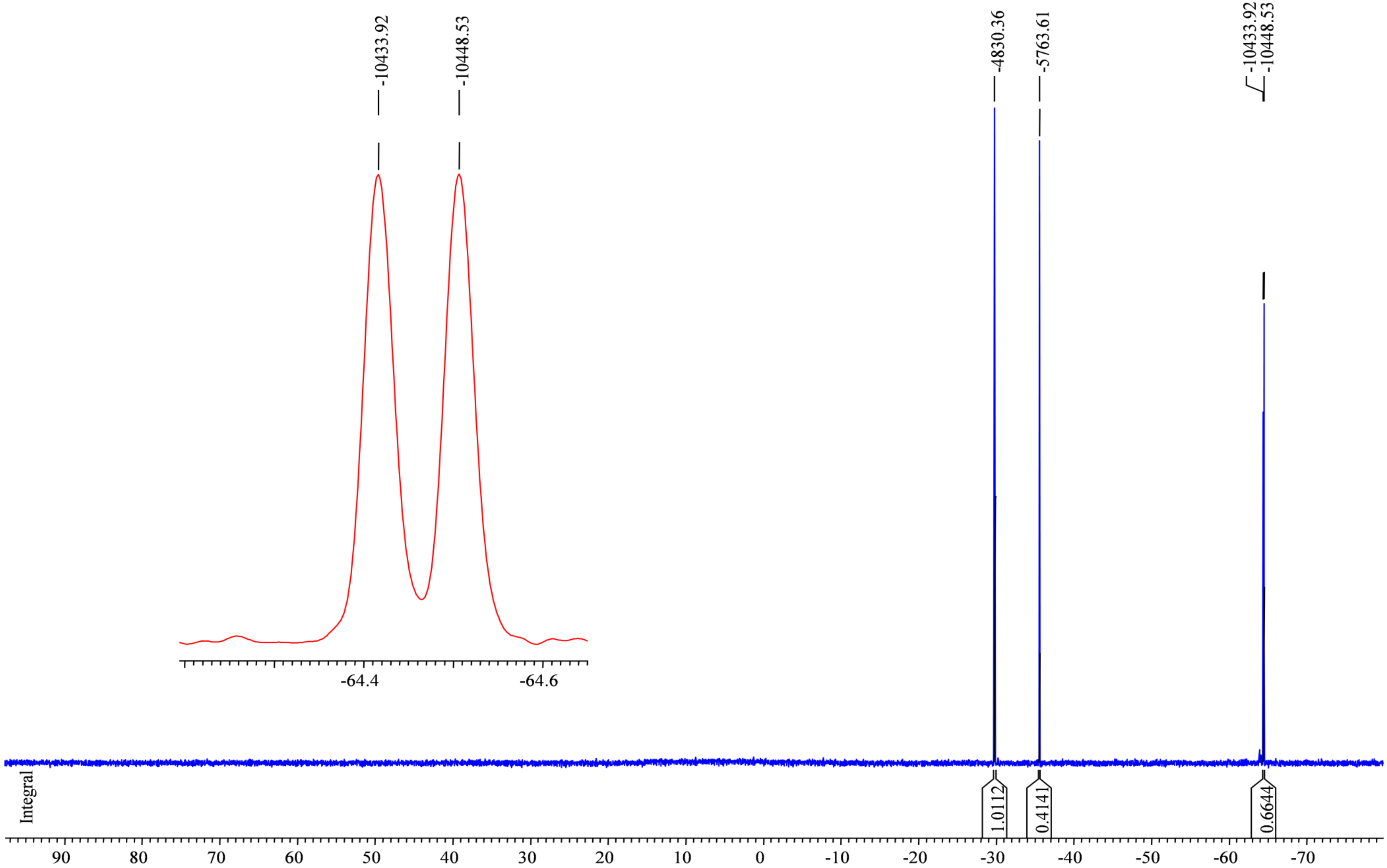


Figure S7. ^{31}P NMR spectrum (162.0 MHz, $CCl_4/CDCl_3$ = 1/1) of the dioxaphospholane (**1**) and hexafluoroacetone reaction mixture in CCl_4.

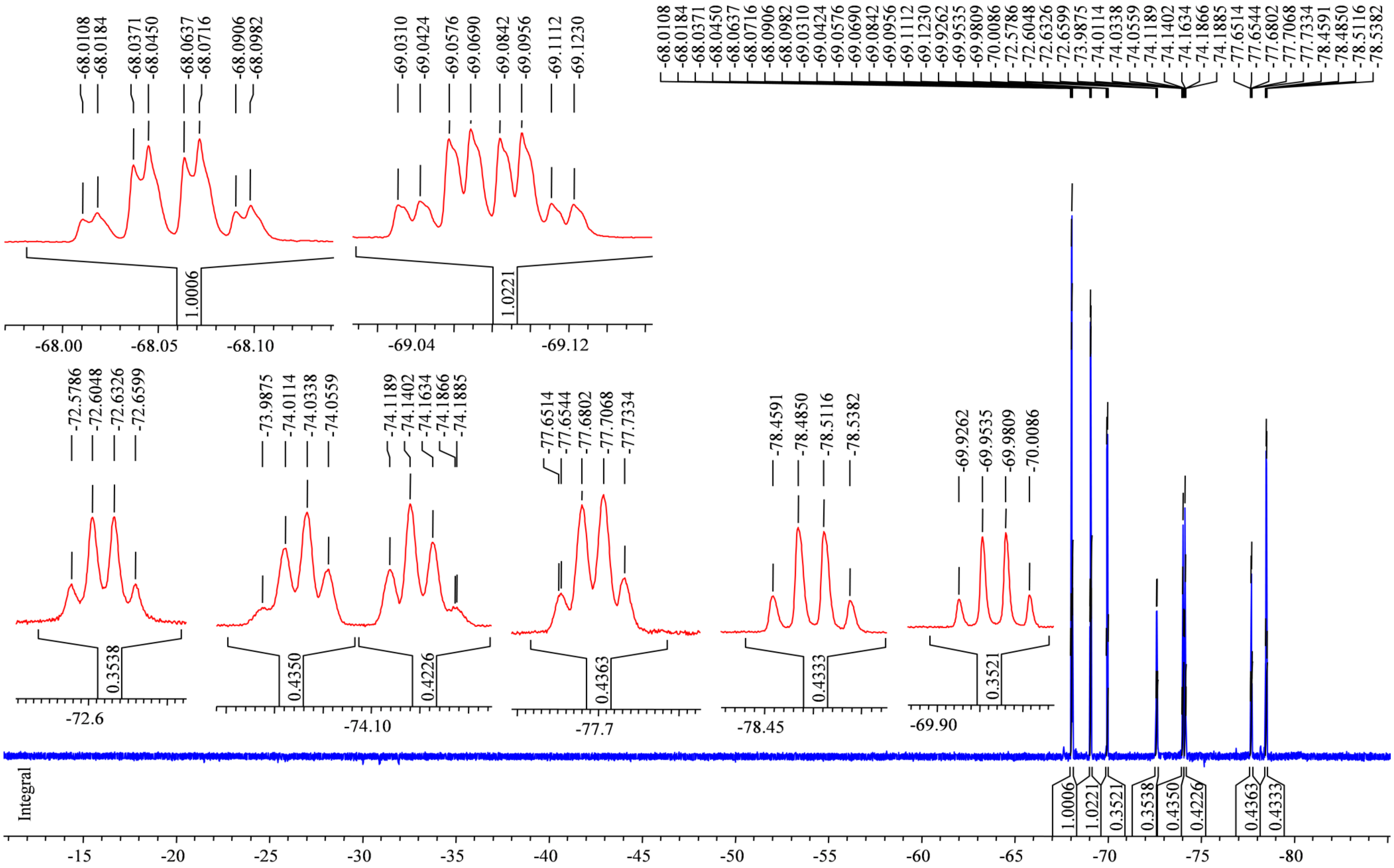


Figure S8. ^{19}F-{^{1}H} NMR spectrum (376.5 MHz, CCl_4/$CDCl_3$ = 1/1) of the dioxaphospholane (**1**) and hexafluoroacetone reaction mixture in CCl_4.

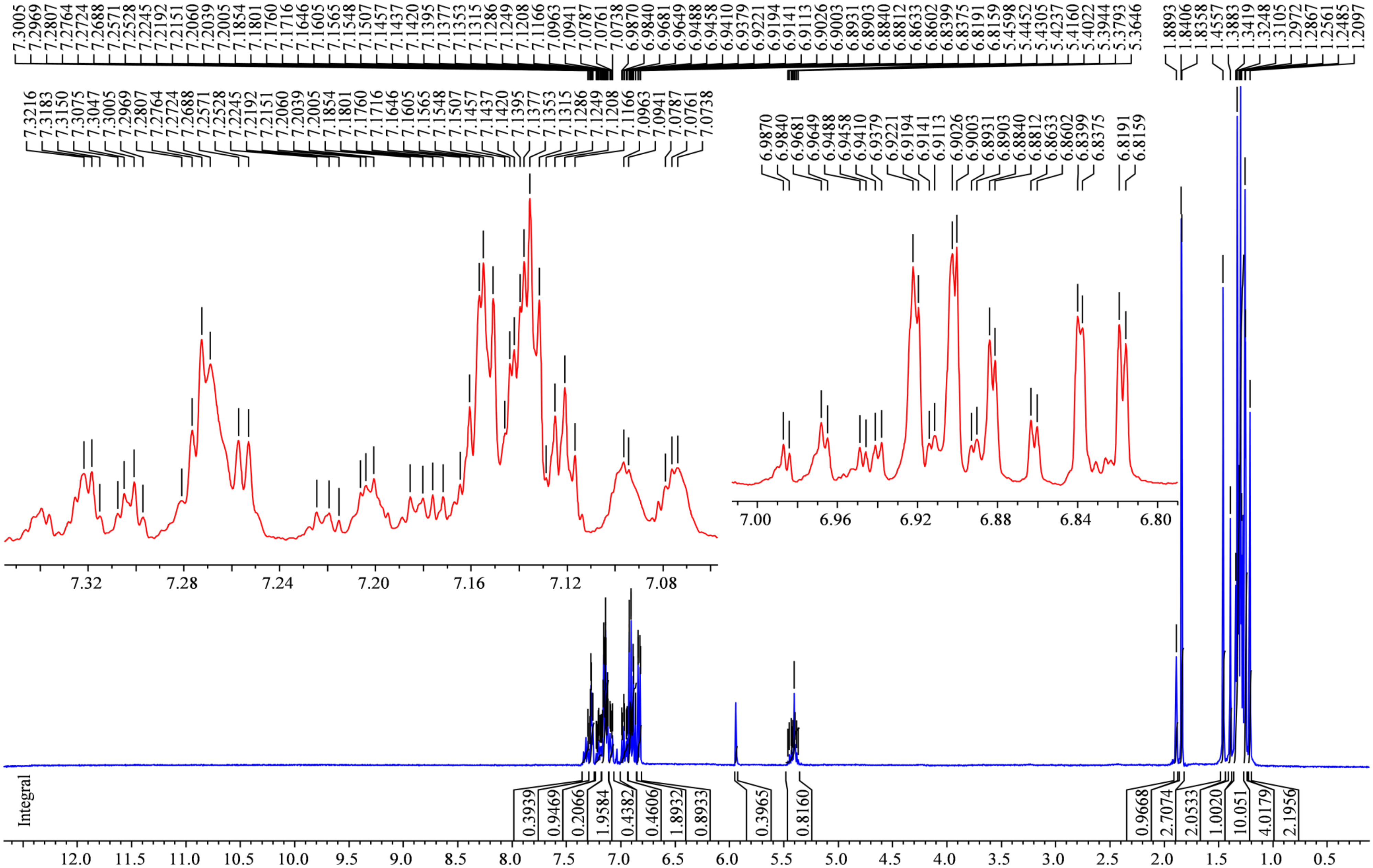


Figure S9. ^{1}H NMR spectrum (400 MHz, $CCl_4/CDCl_3$ = 1/1) of the dioxaphospholane (**1**) and hexafluoroacetone reaction mixture in CCl_4.

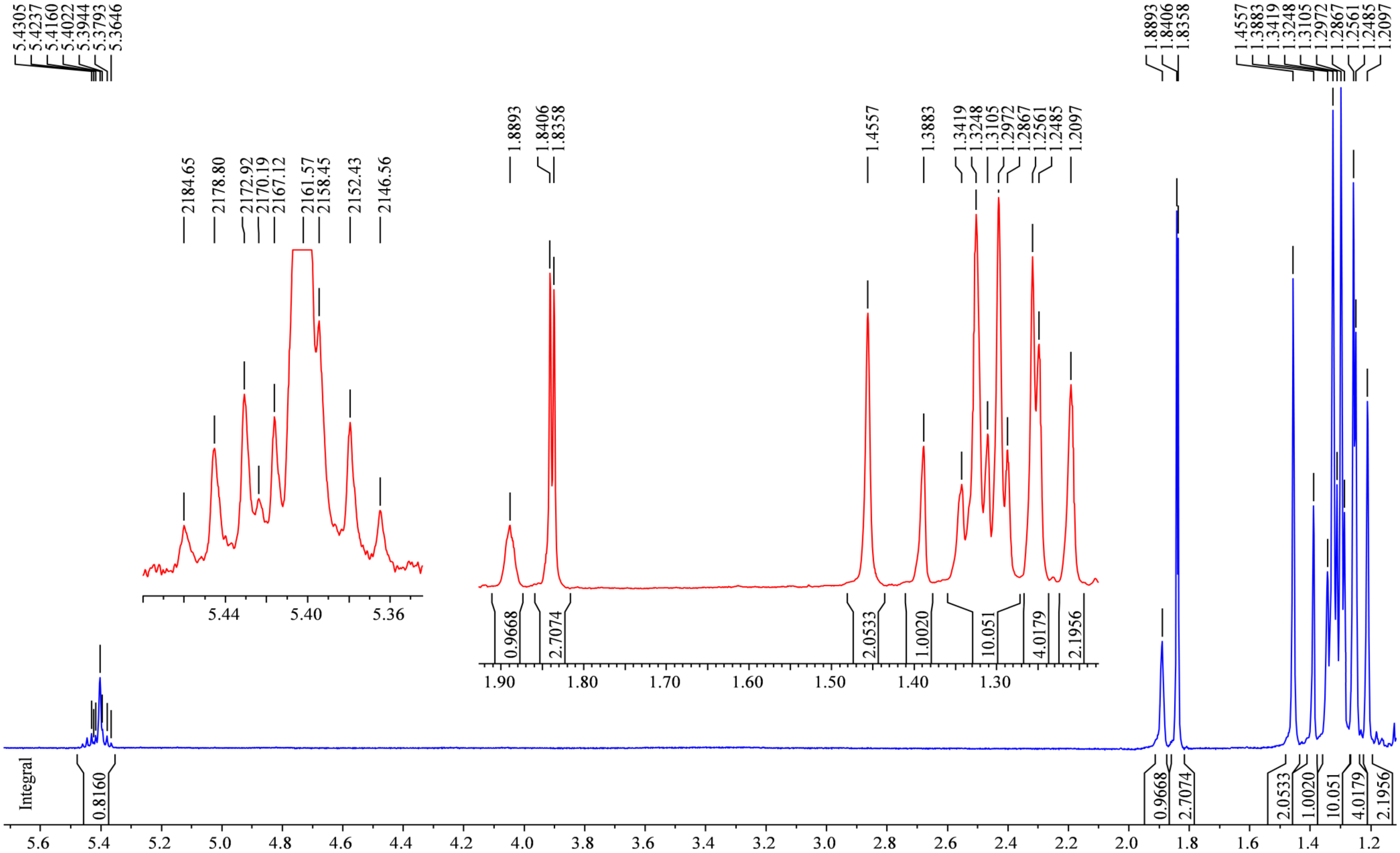


Figure S10. High-field fragment of [1]H NMR spectrum (400 MHz, $CCl_4/CDCl_3$ = 1/1) of the dioxaphospholane (**1**) and hexafluoroacetone reaction mixture in CCl_4.

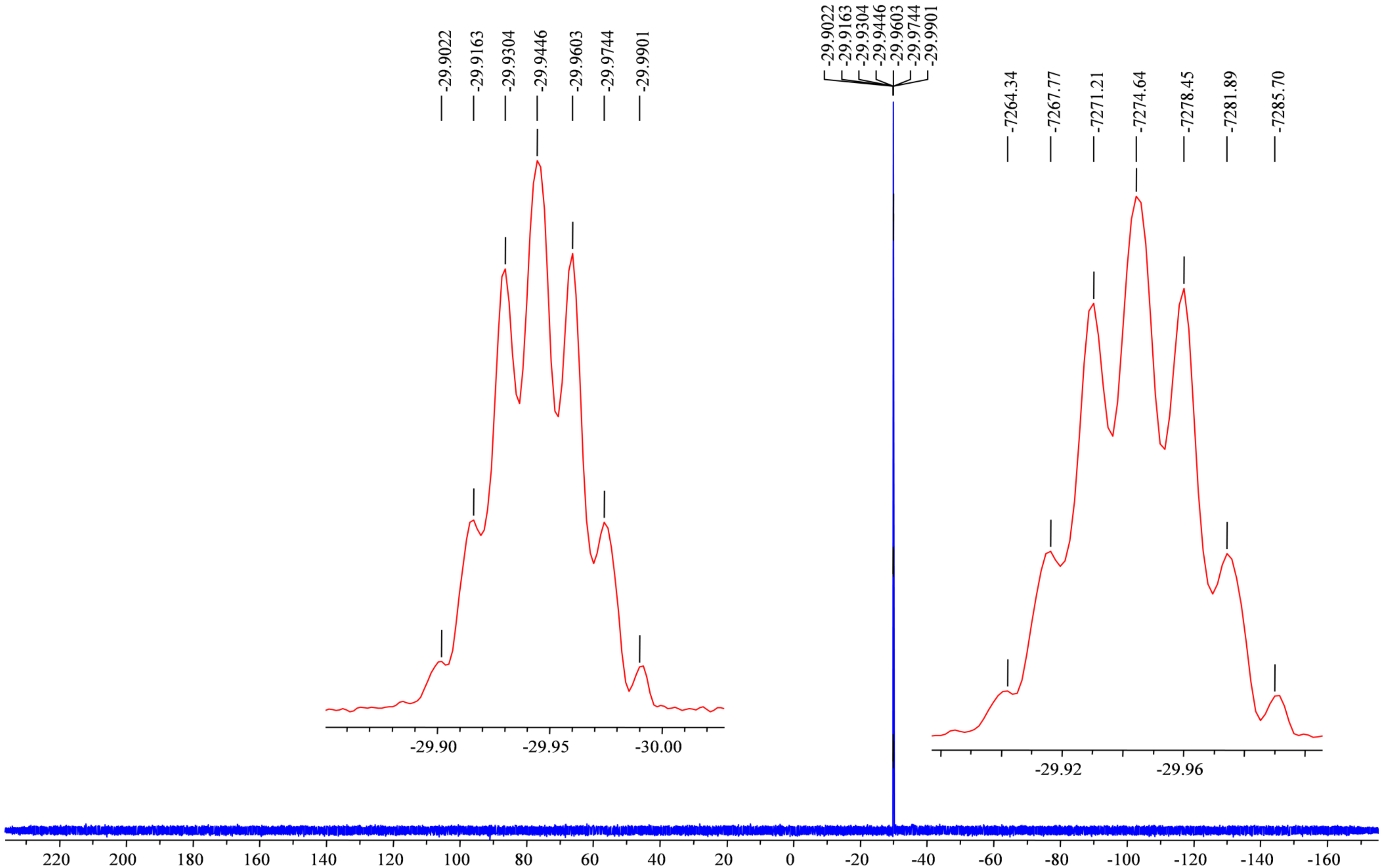


Figure S11. $^{31}P-\{^{1}H\}$ NMR spectrum (242.94 MHz, $CDCl_3$) of phosphorane (**2**).

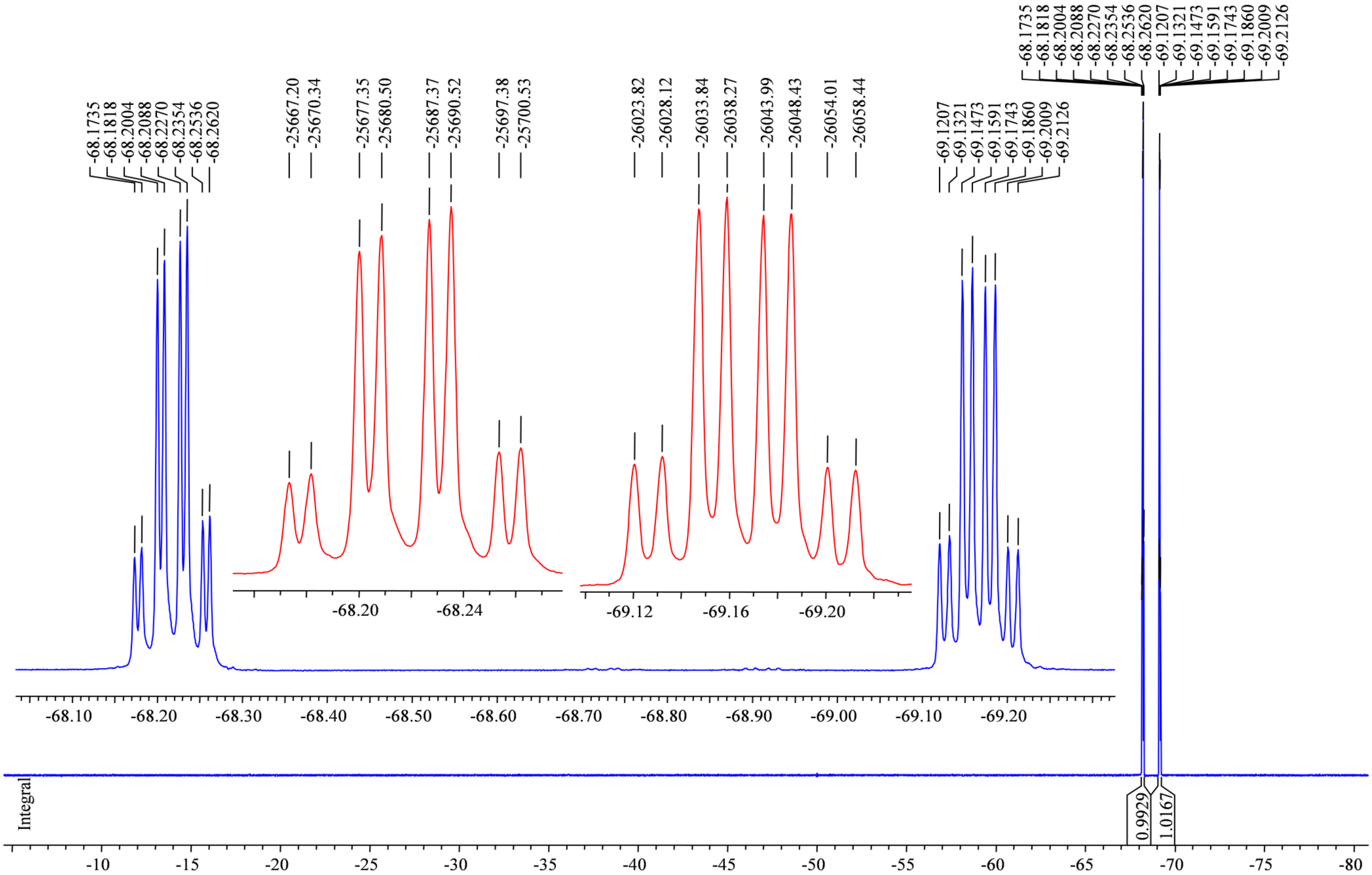


Figure S12. ^{19}F-{^{1}H} NMR spectrum (376.5 MHz, $CDCl_3$) of phosphorane (**2**).

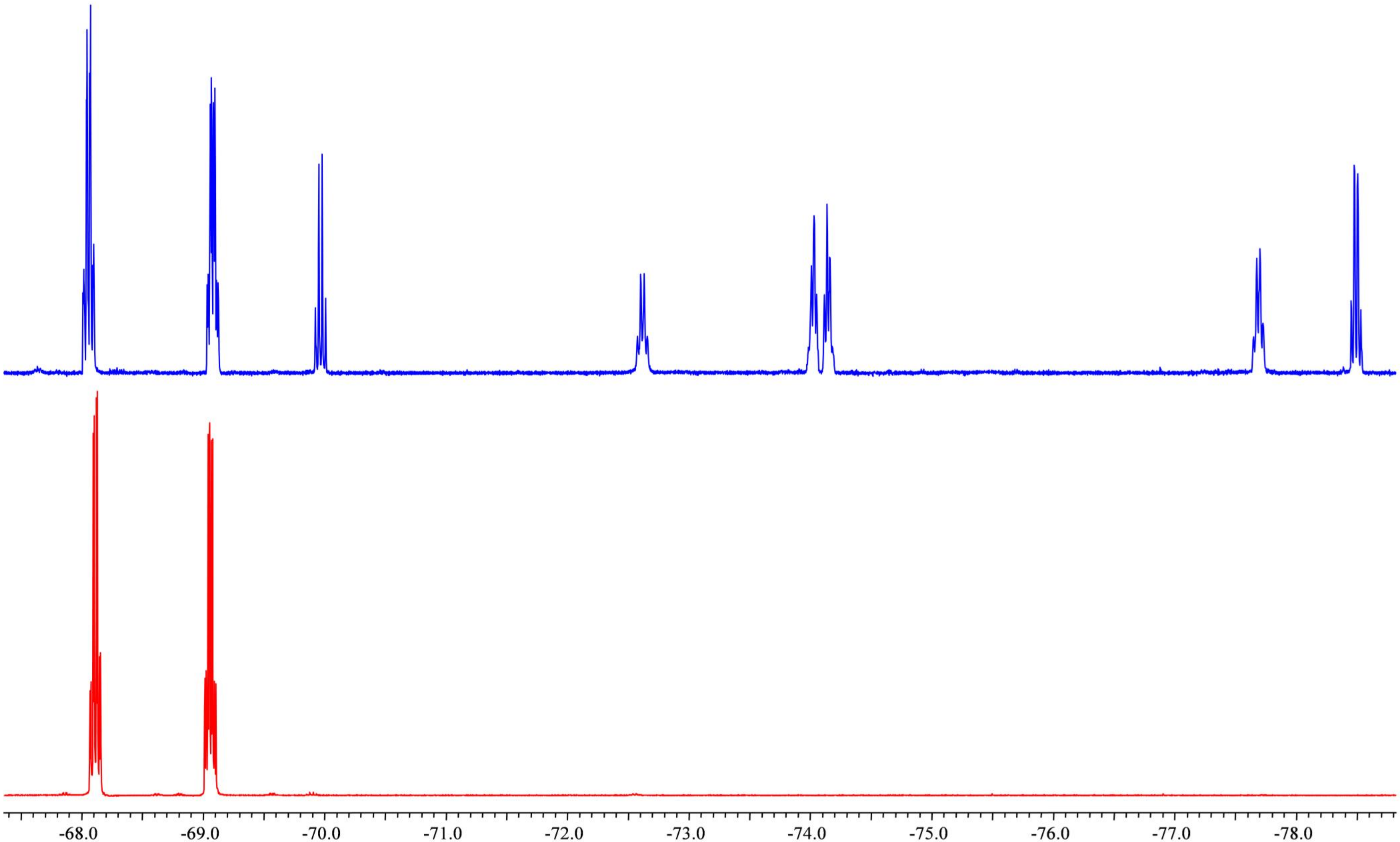


Figure S13. $^{19}F-\{^{1}H\}$ NMR spectra (376.5 MHz, $CDCl_3$) of phosphorane (**3**) (red) and the dioxaphospholane (**1**) and hexafluoroacetone reaction mixture in CCl_4 (blue) (376.5 MHz, $CCl_4/CDCl_3$ = 1/1).

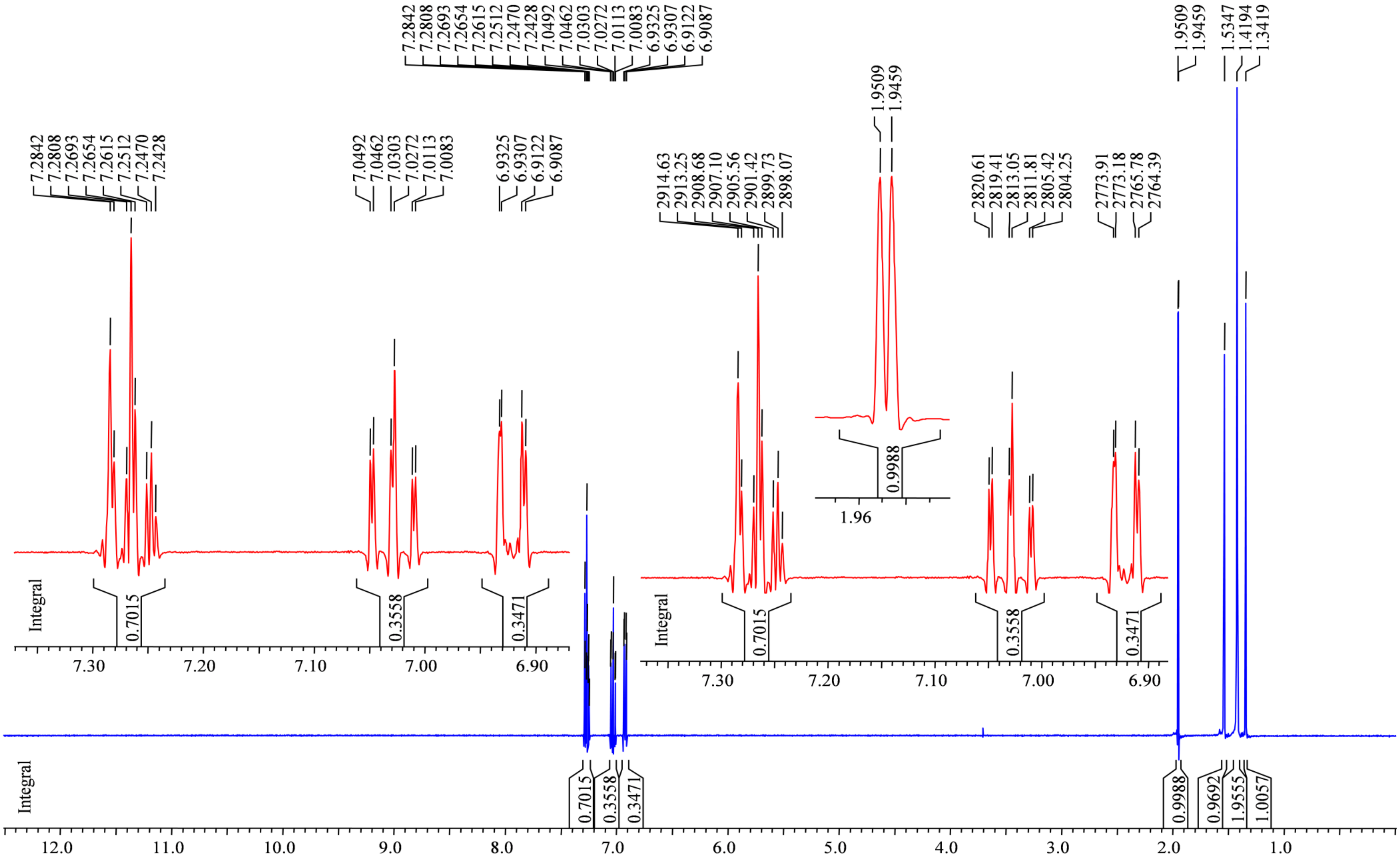


Figure S14. [1]H NMR spectrum (400 MHz, $CDCl_3$) of phosphorane (**2**).

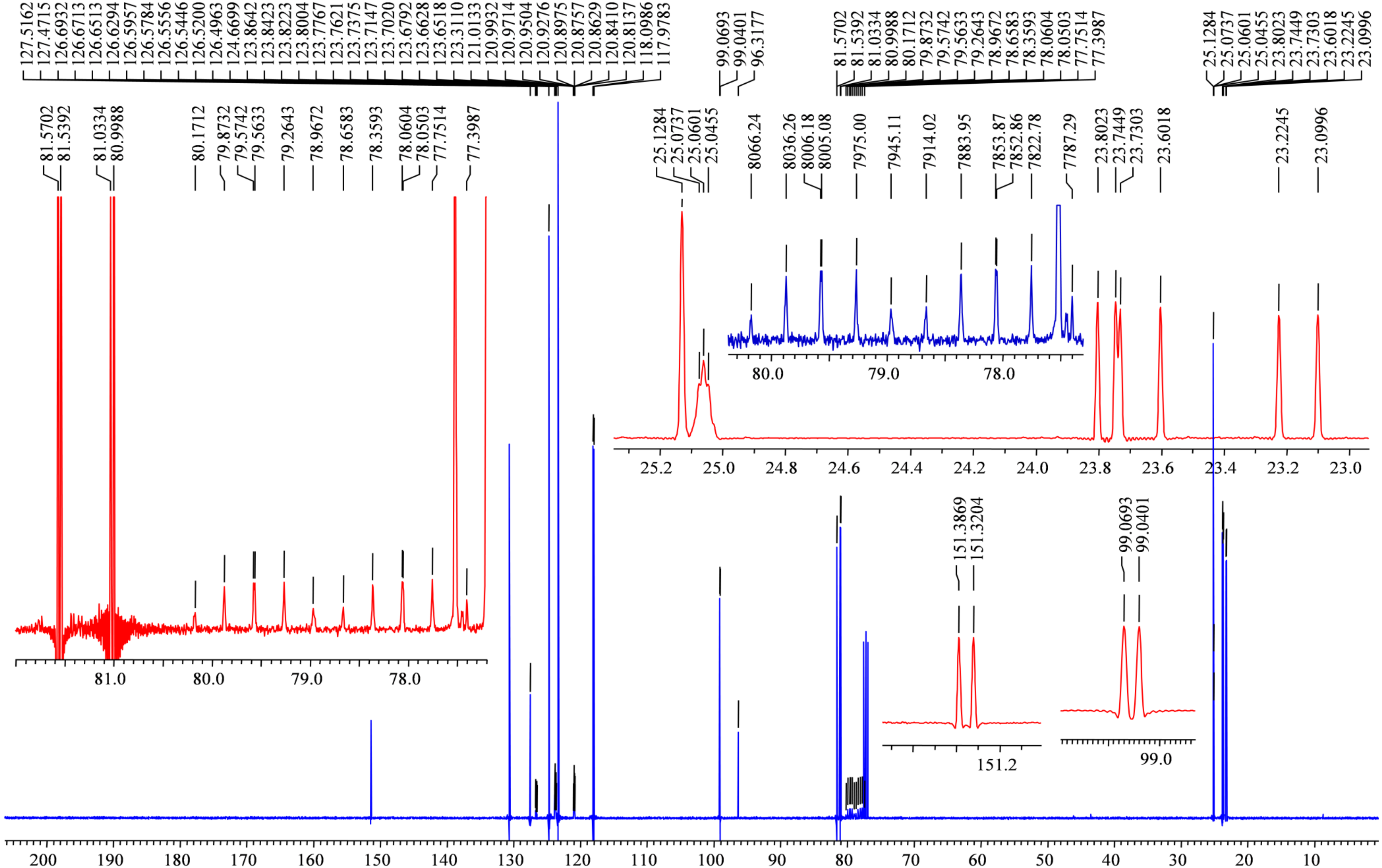


Figure S15. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of phosphorane (**2**).

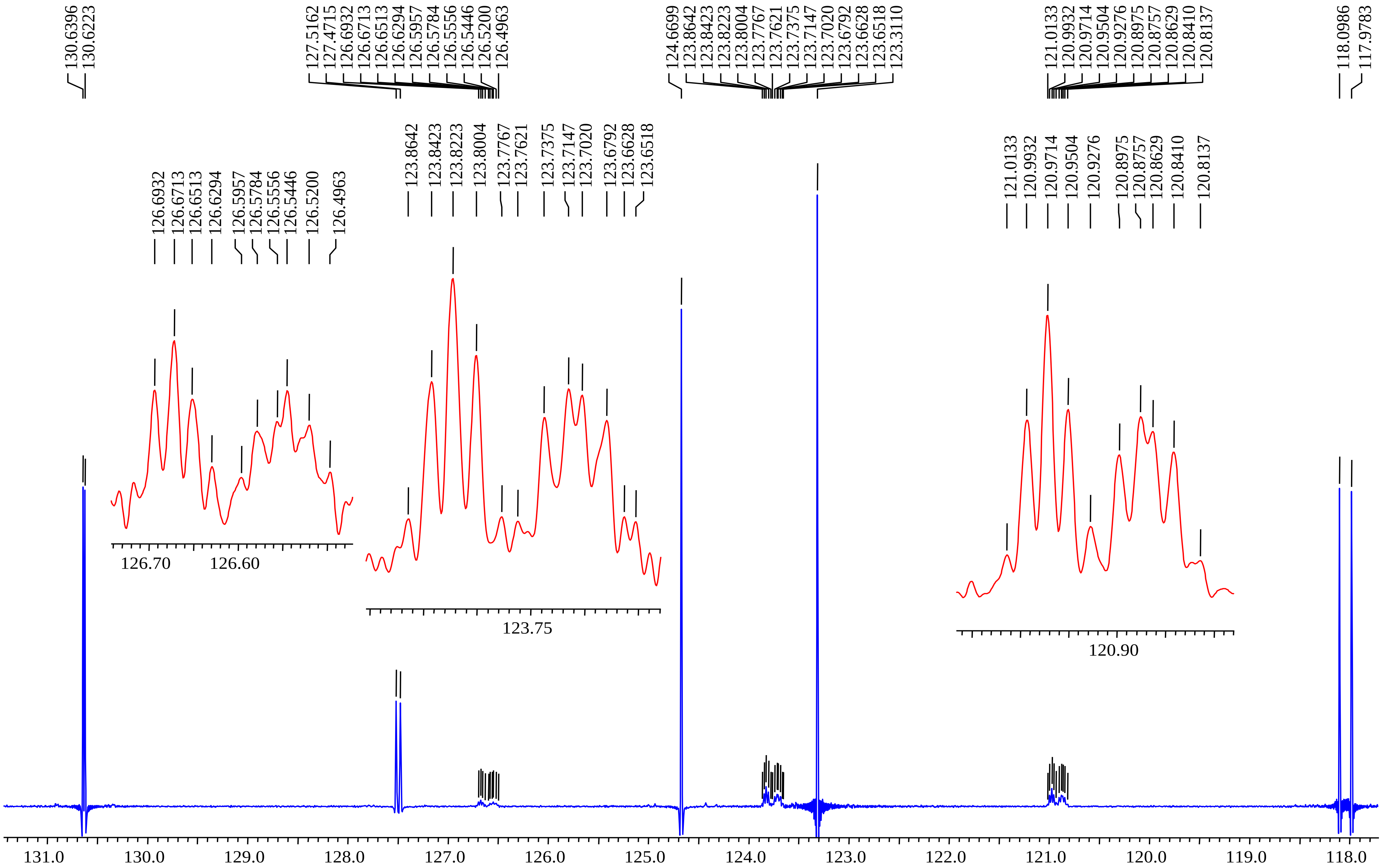


Figure S16. The 118-131 ppm region of ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of phosphorane (**2**).

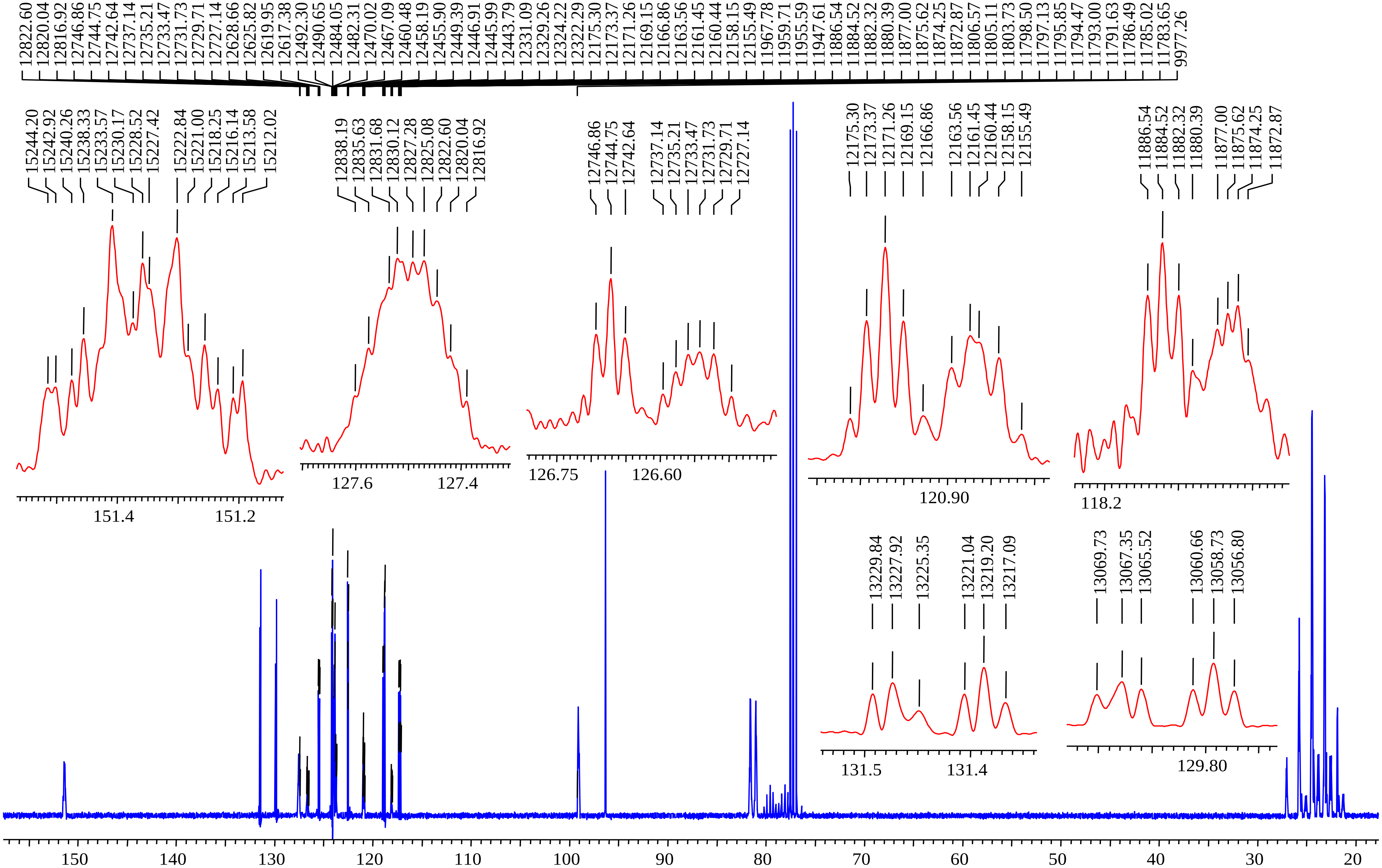


Figure S17. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of phosphorane (**2**).

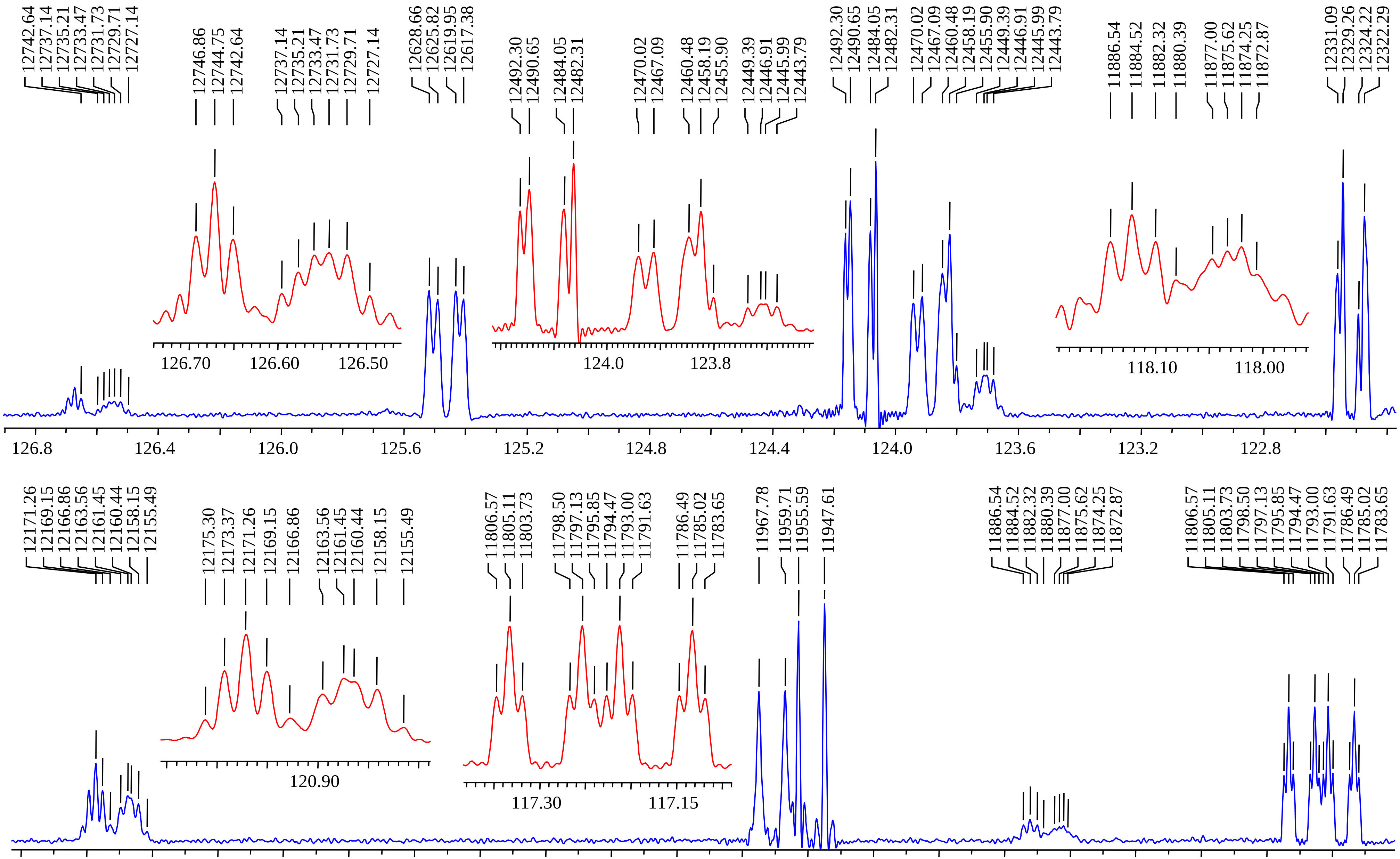


Figure S18. The 117-121 and 122-127 ppm regions of ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of phosphorane (**2**).

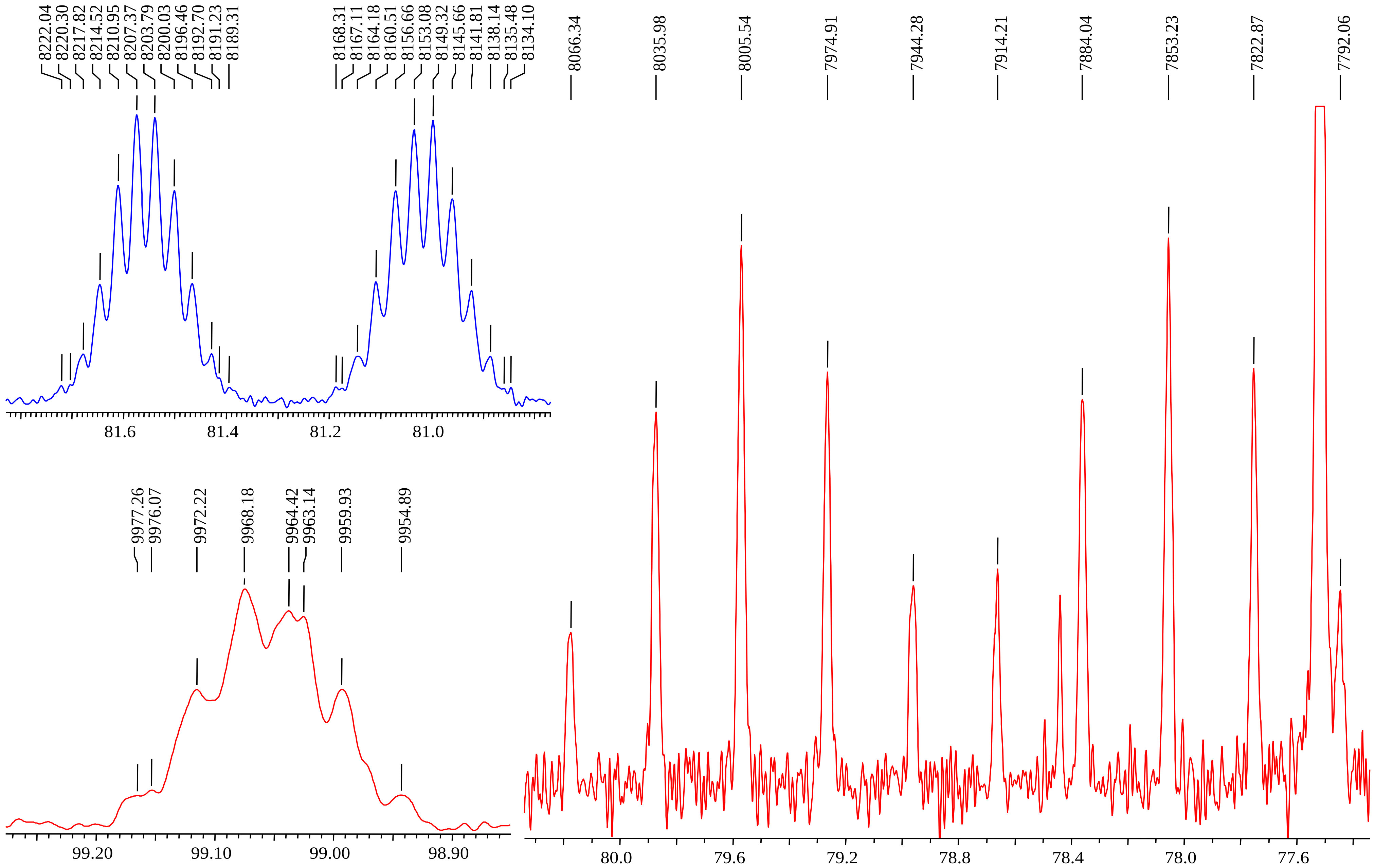


Figure S19. The fragments of ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of phosphorane (**2**).

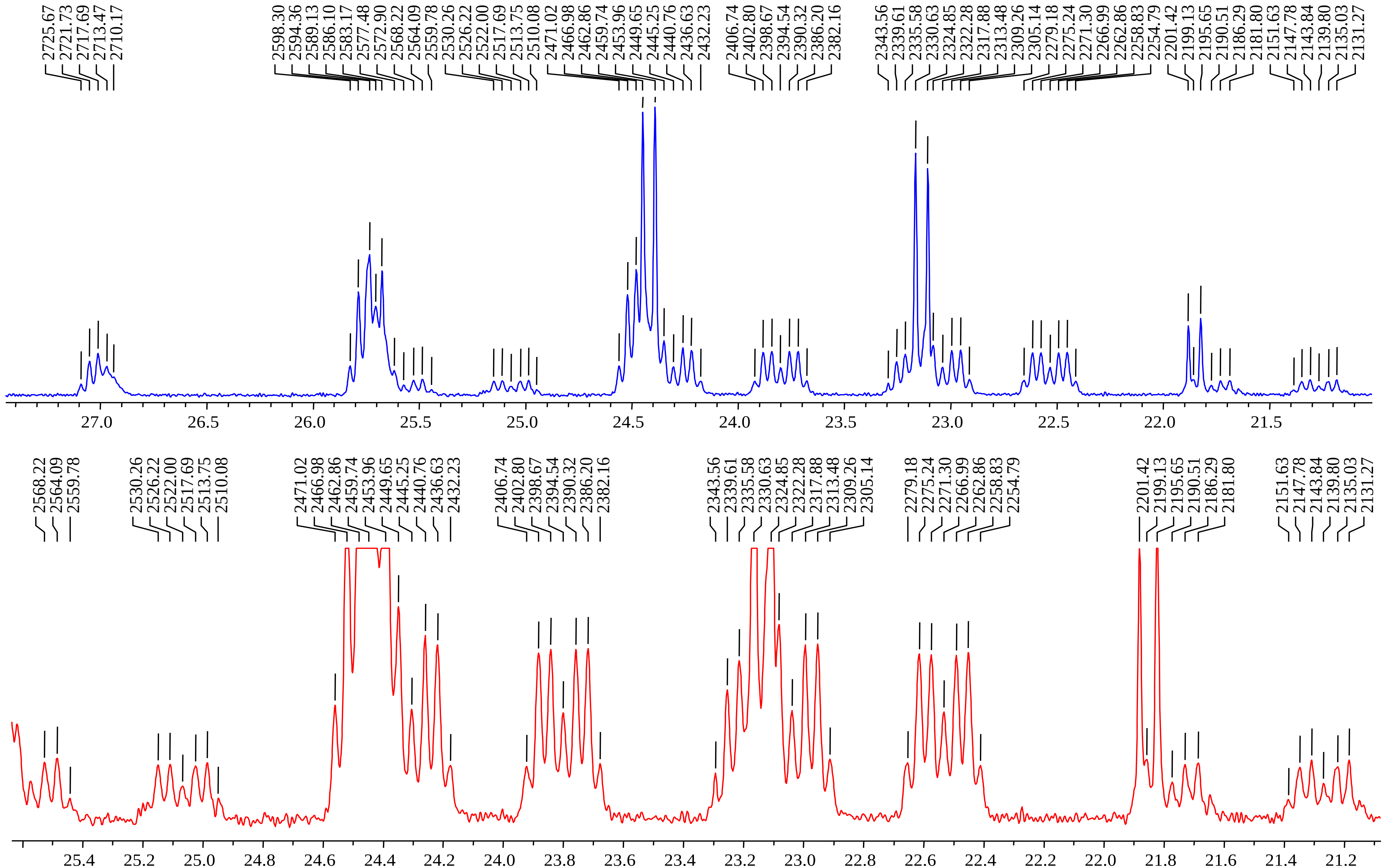


Figure S20. High-field fragments of ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of phosphorane (**2**).

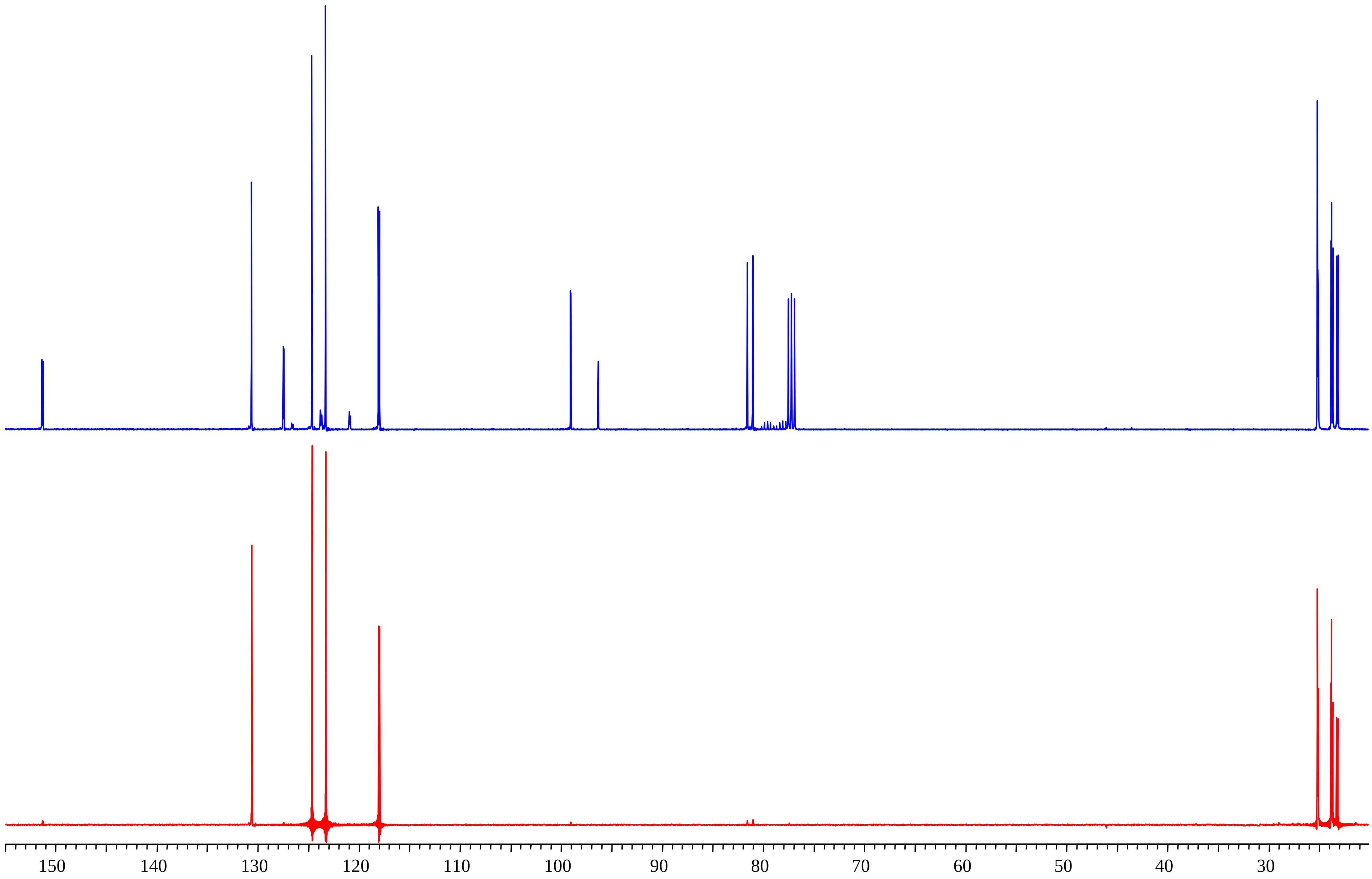


Figure S21. ^{13}C-{^{1}H} and ^{13}C-{^{1}H}-dept NMR spectra (100.6 MHz, $CDCl_3$) of phosphorane (**2**).

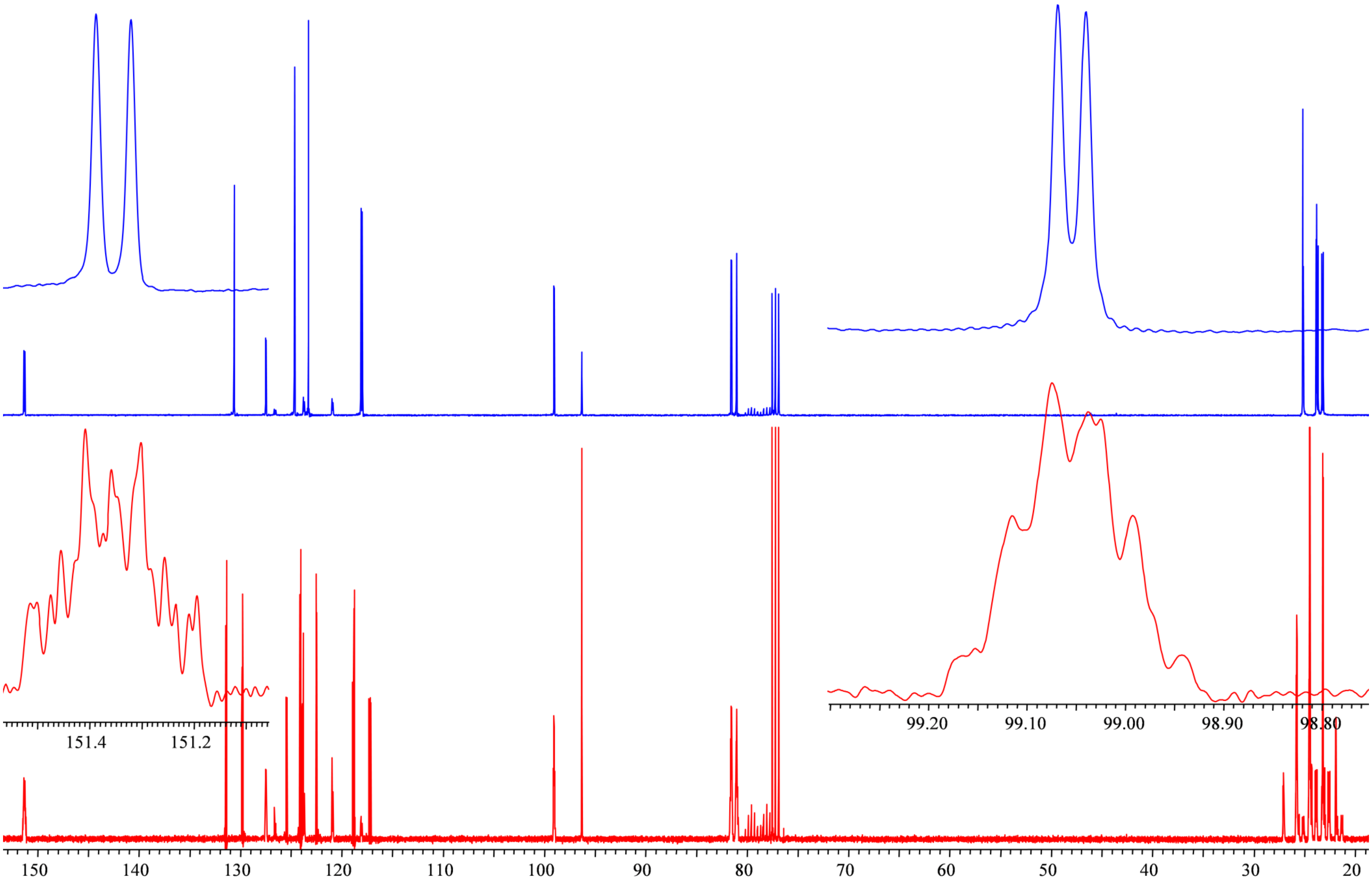


Figure S22. ^{13}C-{^{1}H} and ^{13}C NMR spectra (100.6 MHz, $CDCl_3$) of phosphorane (**2**).

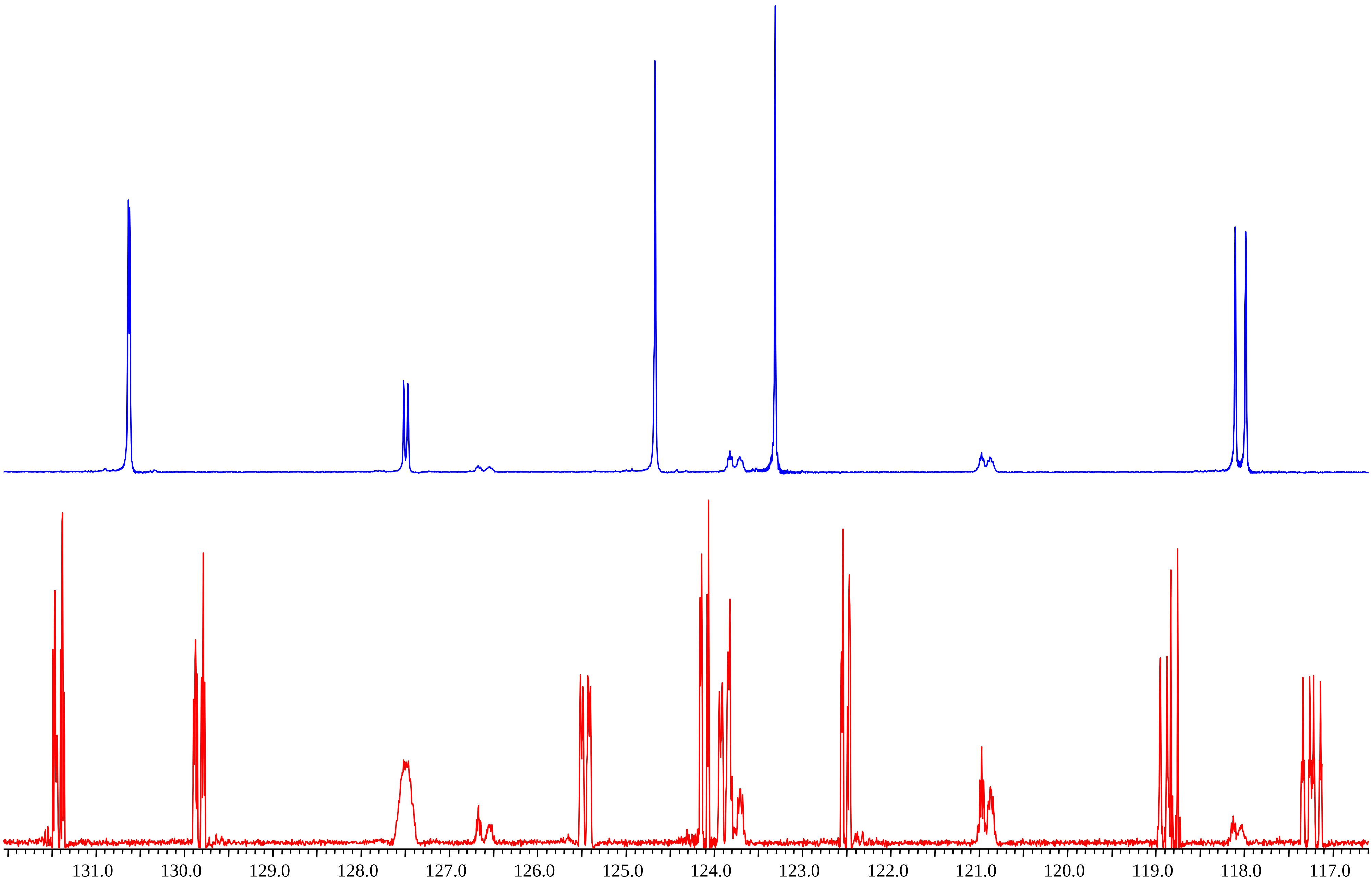


Figure S23. The 116-132 ppm region of $^{13}C-\{^{1}H\}$ and ^{13}C NMR spectra (100.6 MHz, $CDCl_3$) of phosphorane (**2**).

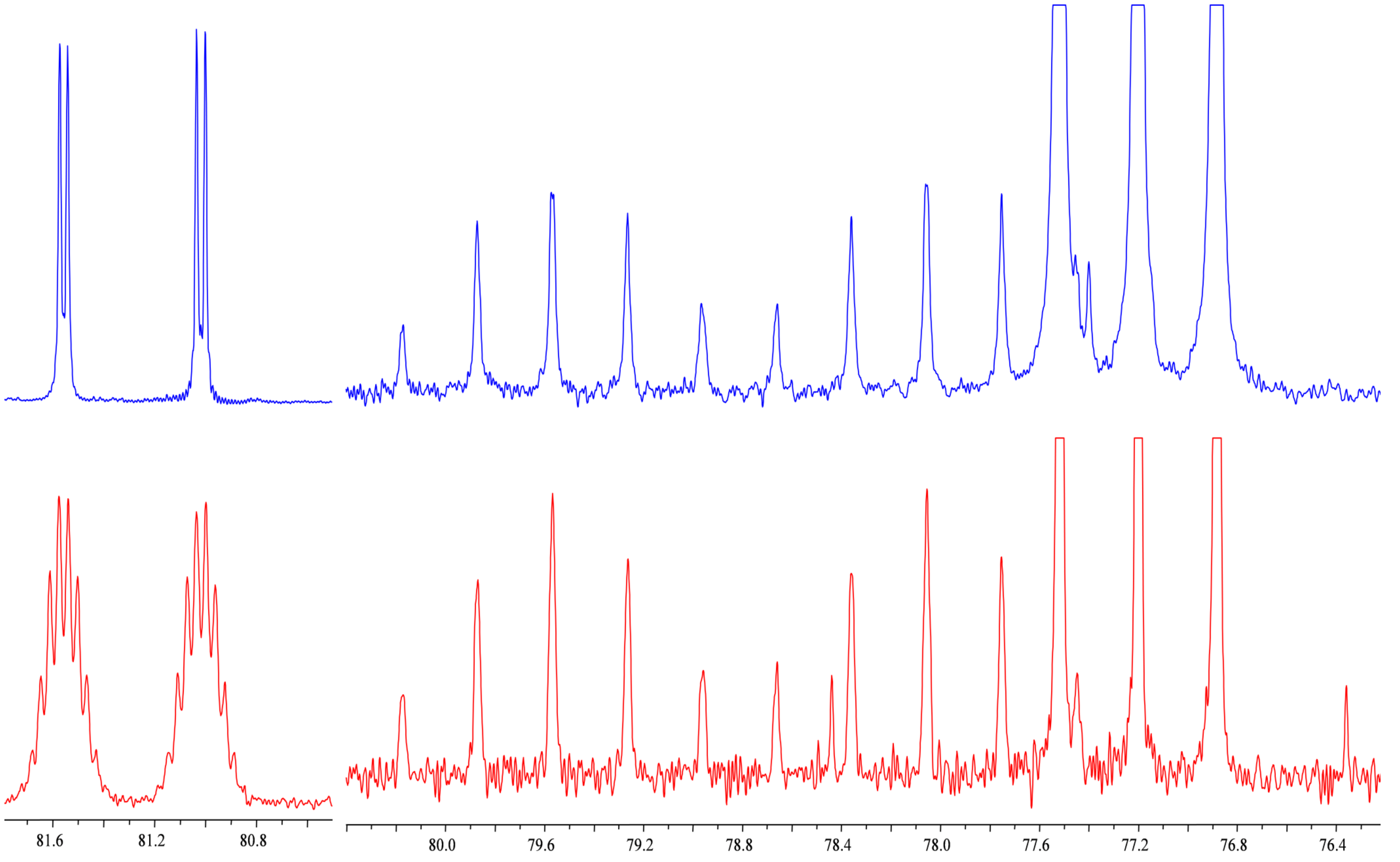


Figure S24. The 76-82 ppm region of ^{13}C-{^{1}H} and ^{13}C NMR spectra (100.6 MHz, $CDCl_3$) of phosphorane (**2**).

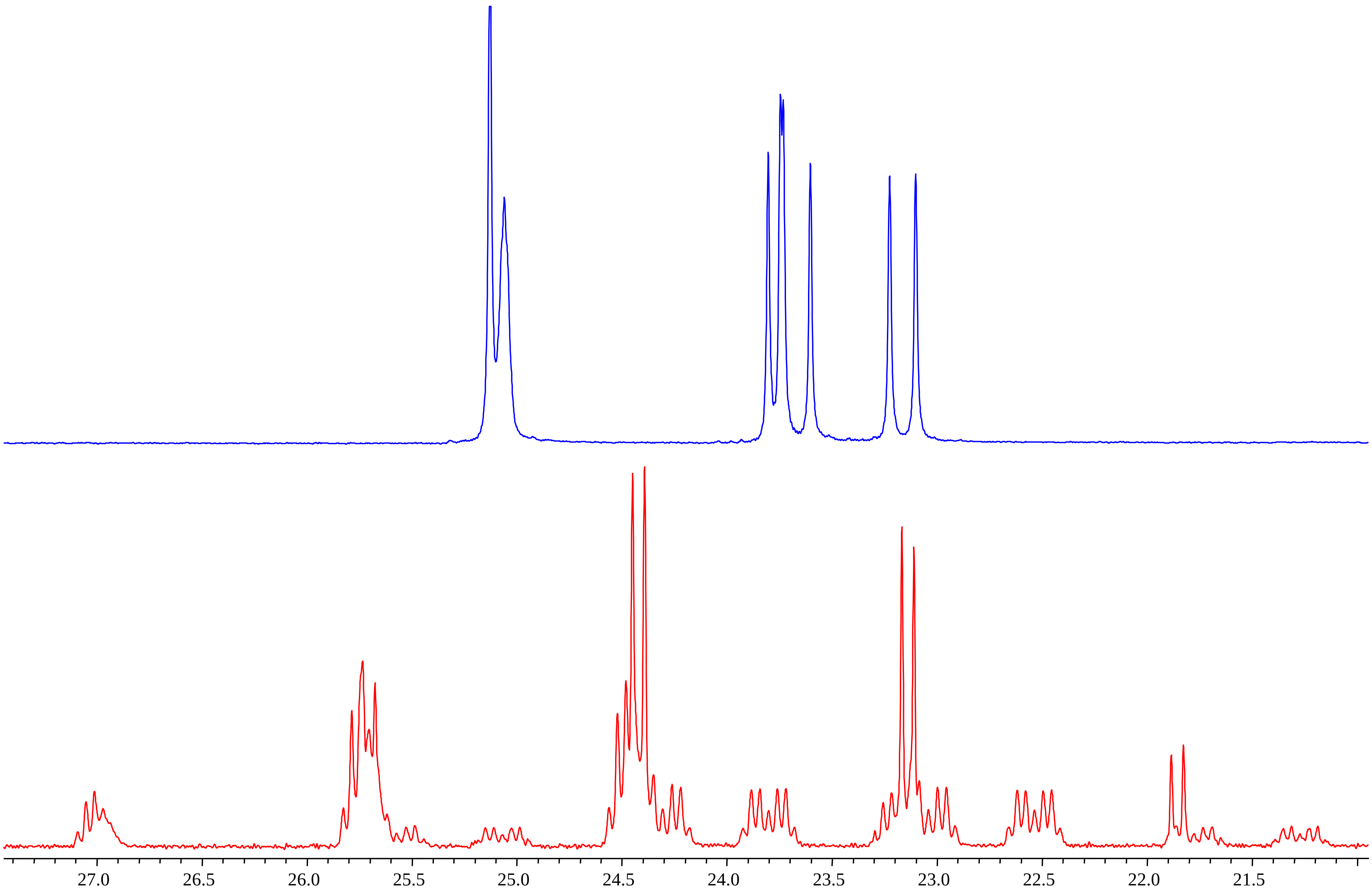


Figure S25. High-field fragment of ^{13}C-{^{1}H} and ^{13}C NMR spectra (100.6 MHz, $CDCl_3$) of phosphorane (**2**).

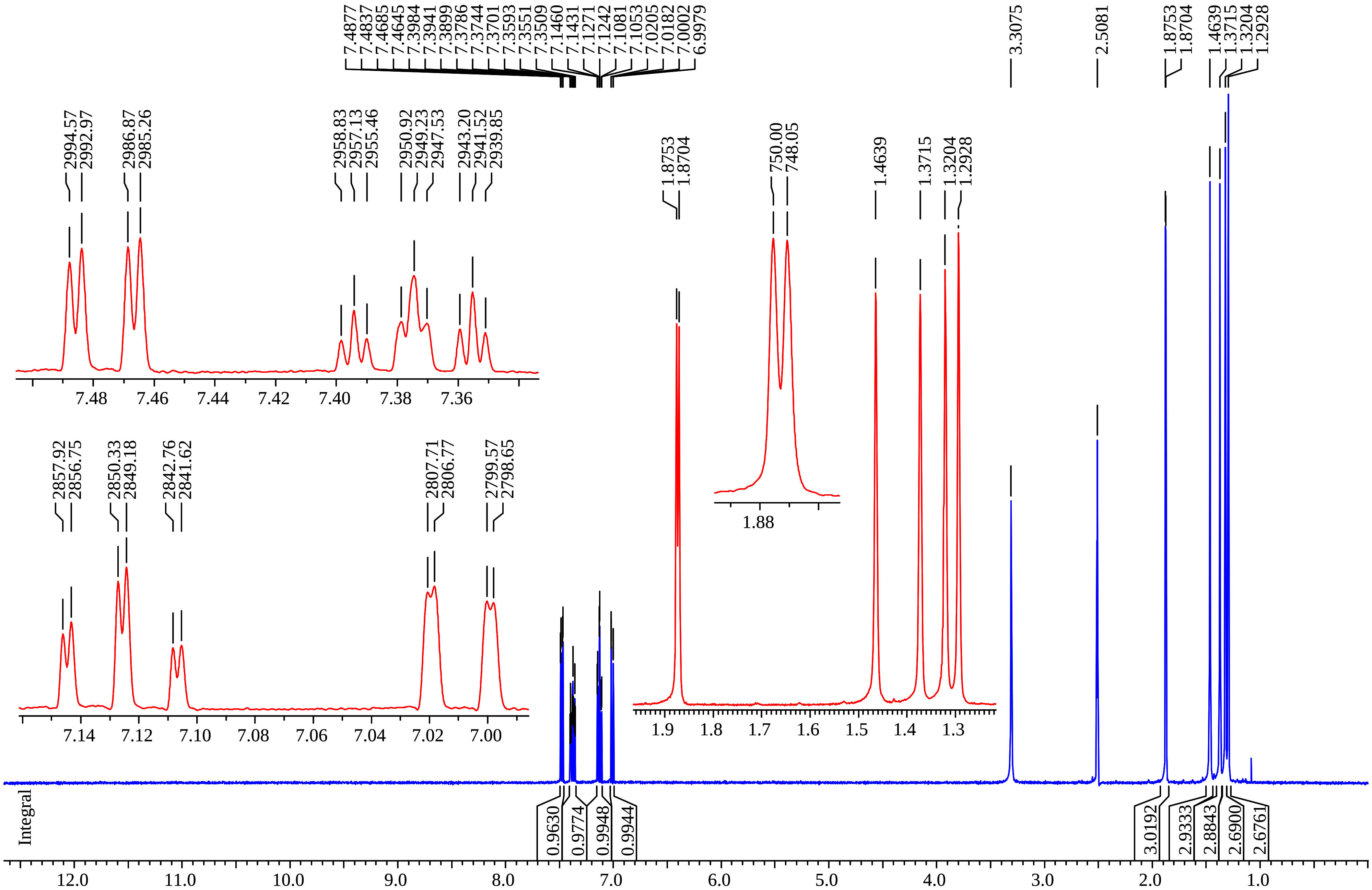


Figure S26. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of phosphorane (**2**); peak with δ 3.31 refers to water impurity in DMSO.

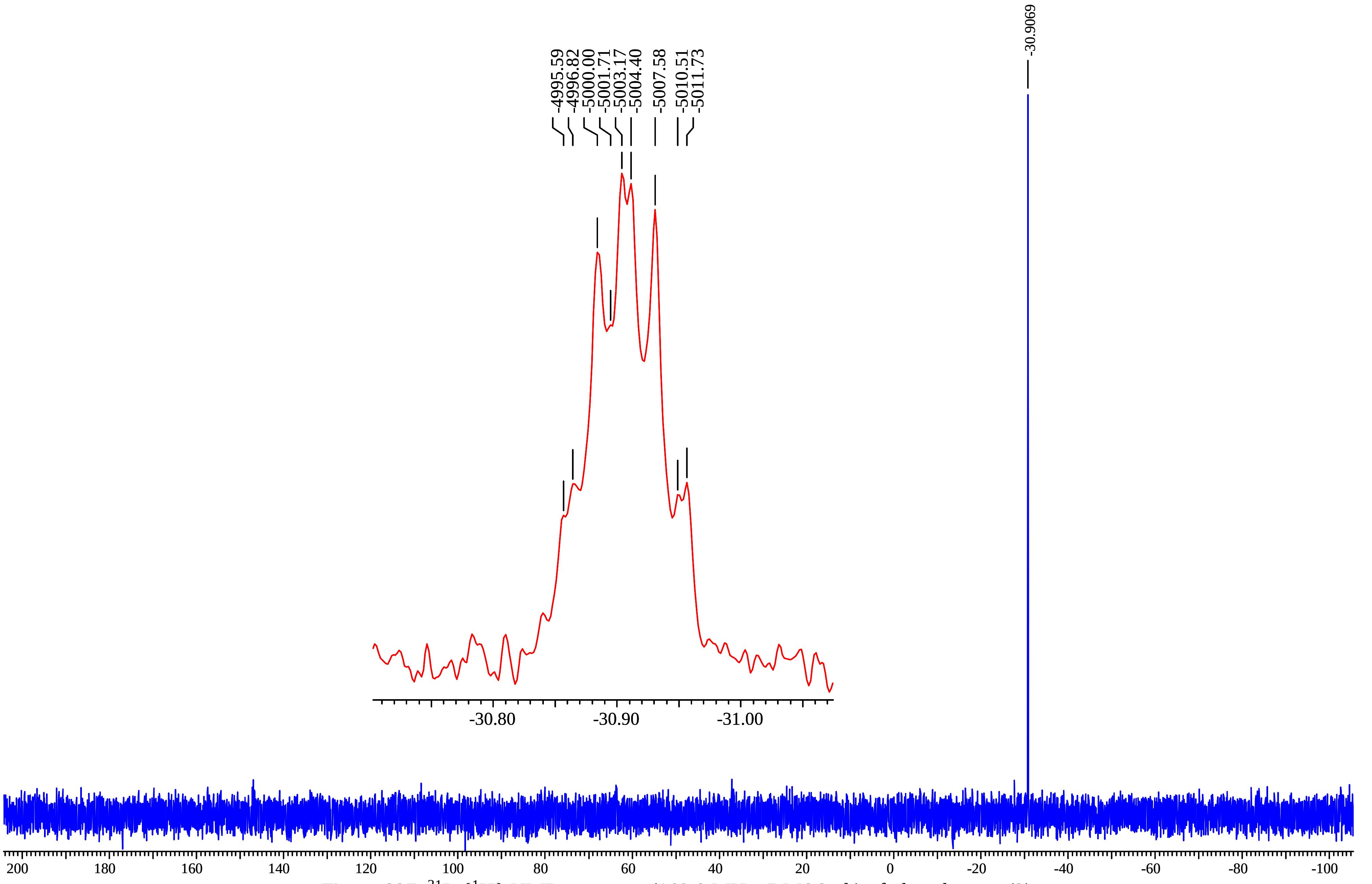


Figure S27. ^{31}P-{^{1}H} NMR spectrum (162.0 MHz, DMSO-d_6) of phosphorane (**2**).

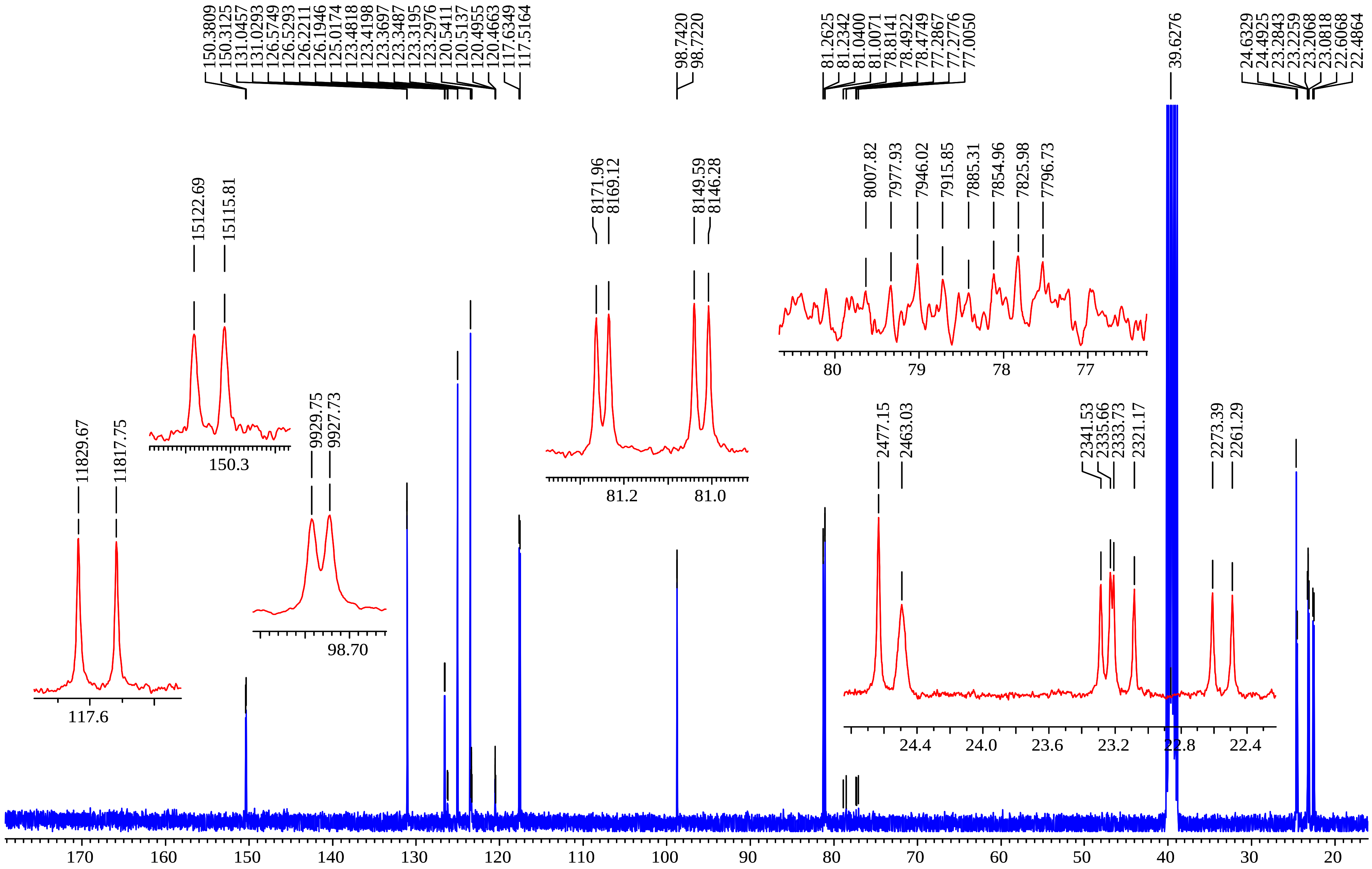


Figure S28. $^{13}C-\{^{1}H\}$ NMR spectrum (100.6 MHz, DMSO-d_6) of phosphorane (**2**).

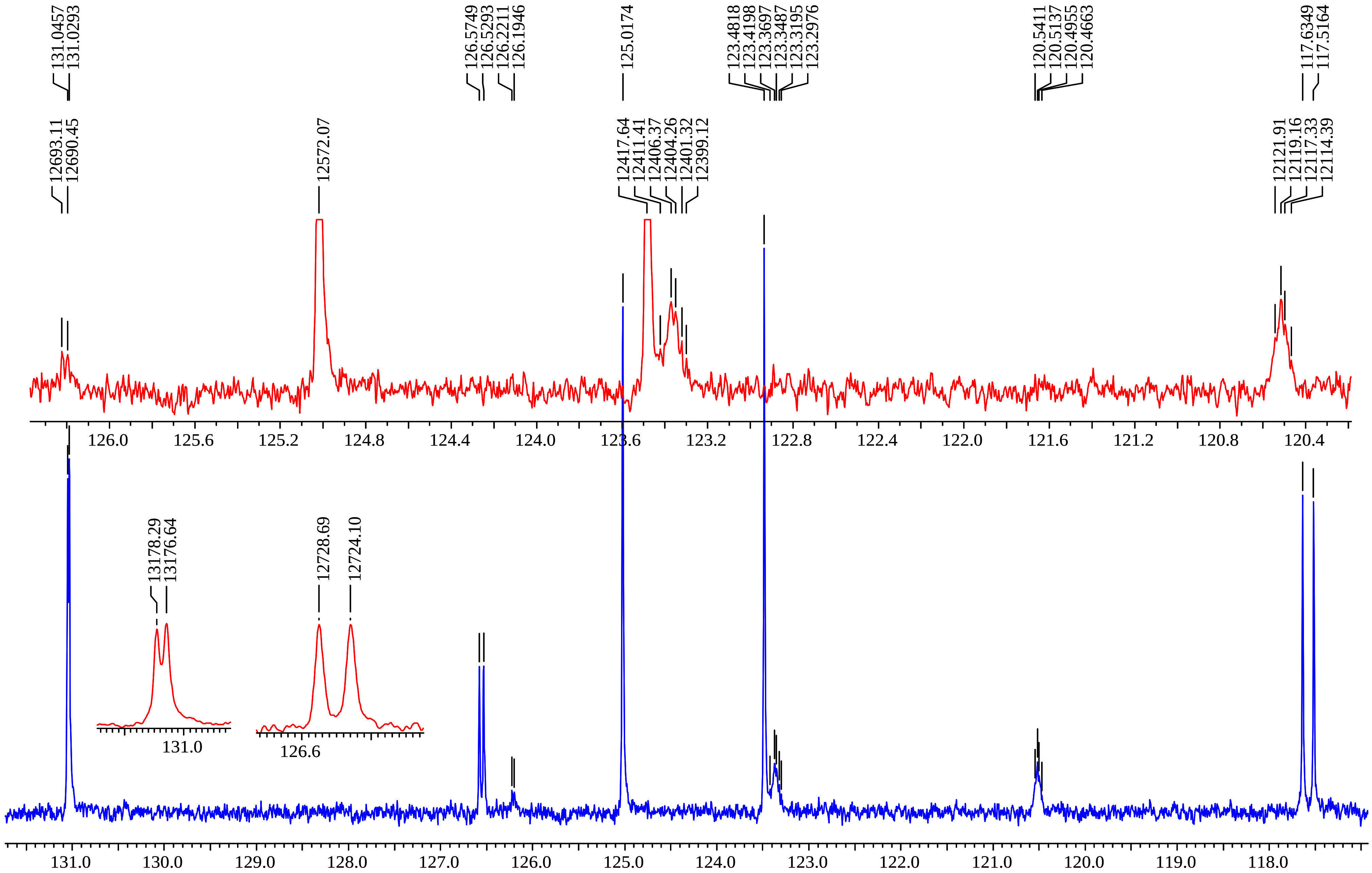


Figure S29. The 117-132 ppm region of ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, DMSO-d_6) of phosphorane (**2**).

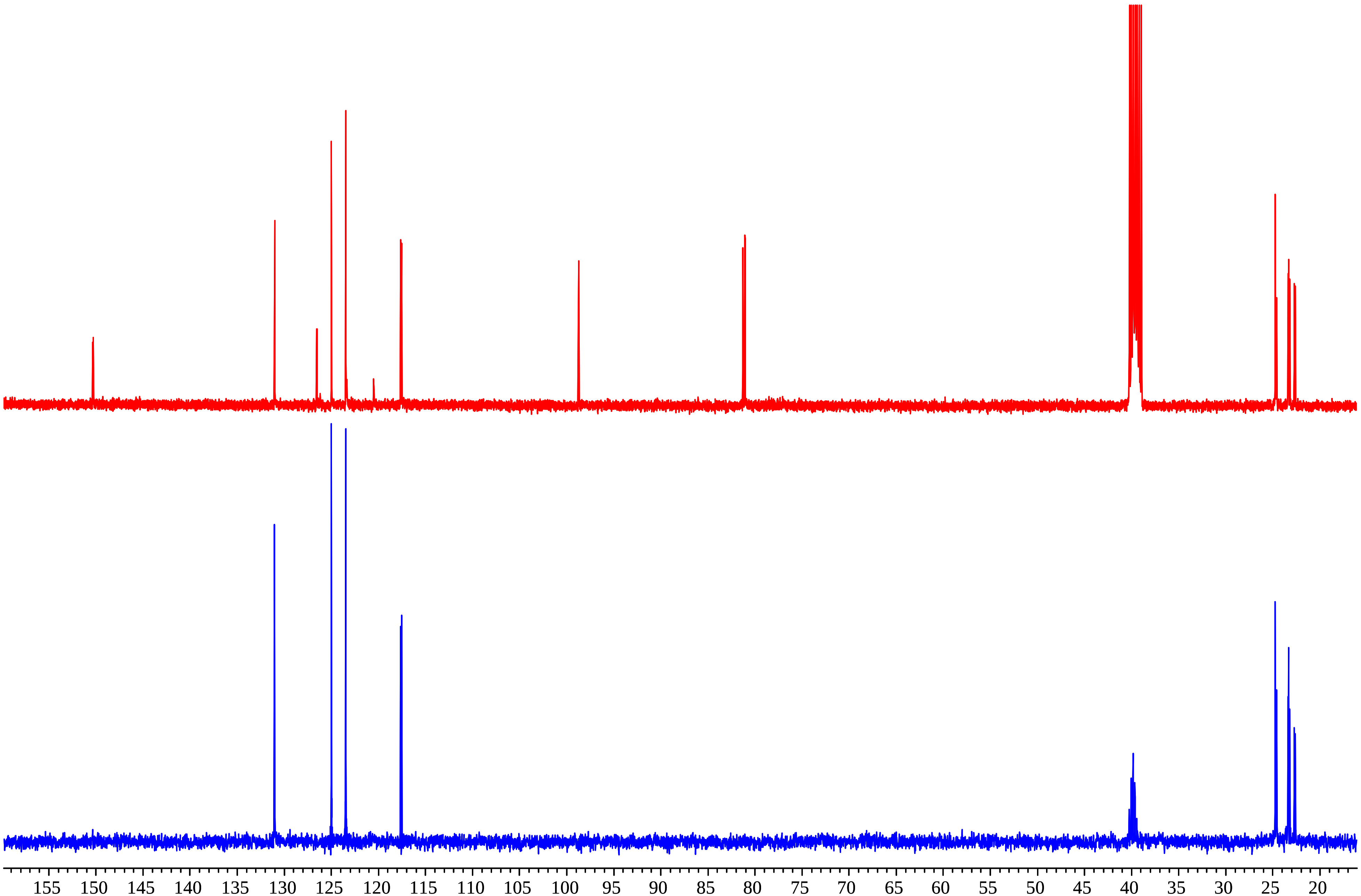


Figure S30. ^{13}C-{^{1}H} and ^{13}C-{^{1}H}-dept NMR spectra (100.6 MHz, DMSO-d_6) of phosphorane (**2**).

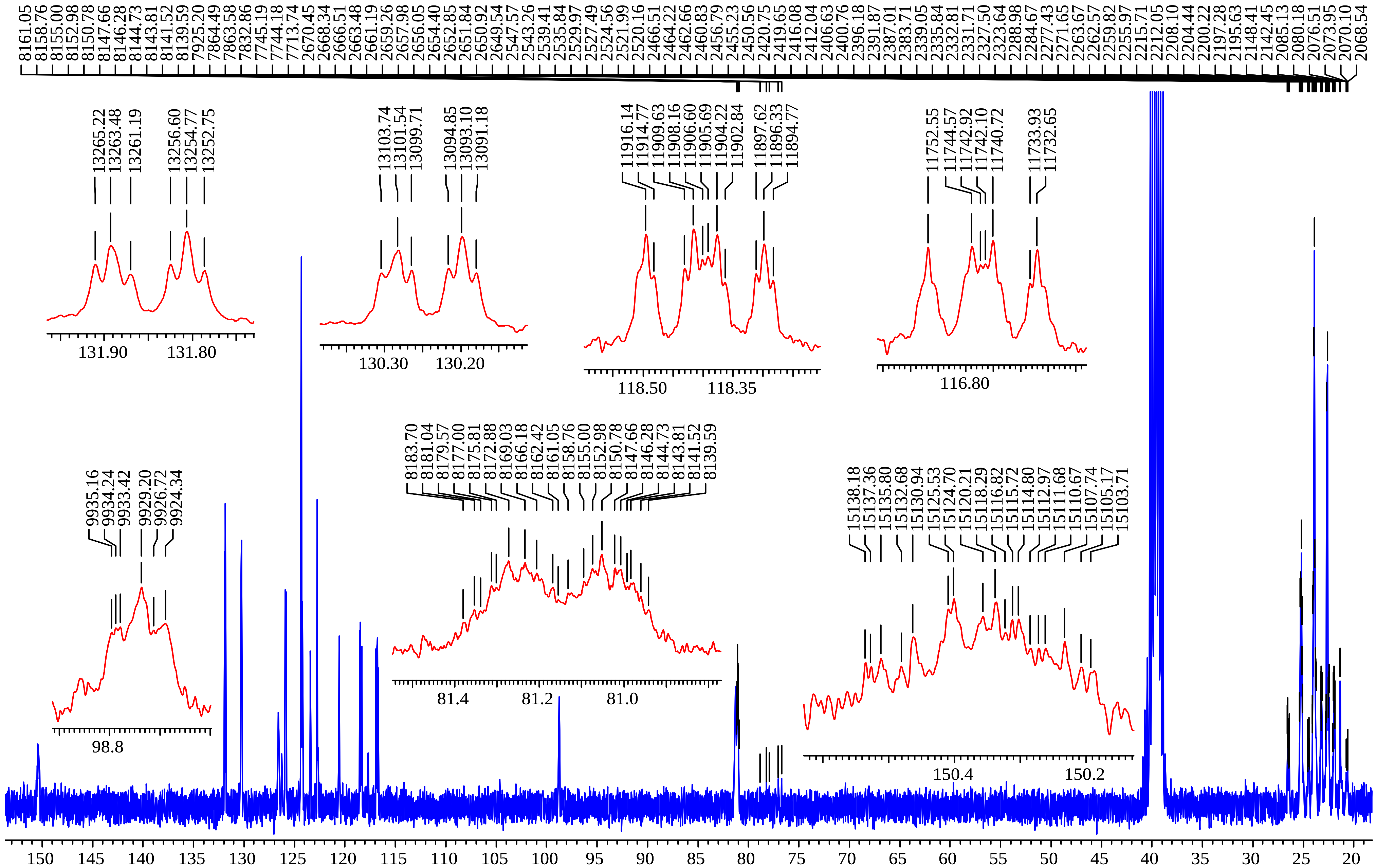


Figure S31. ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6) of phosphorane (**2**).

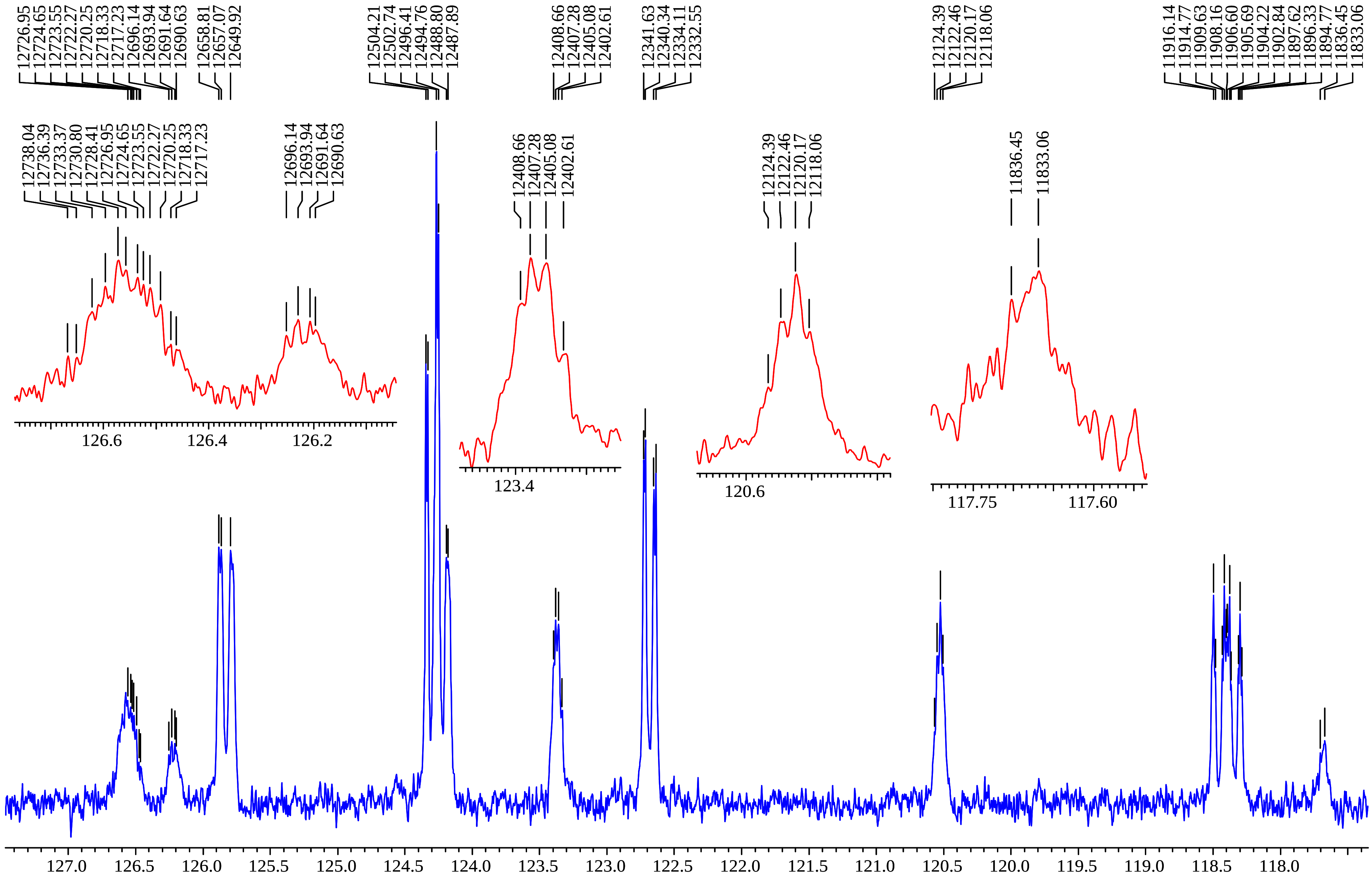


Figure S32. The 117-128 ppm region of ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6) of phosphorane (**2**).

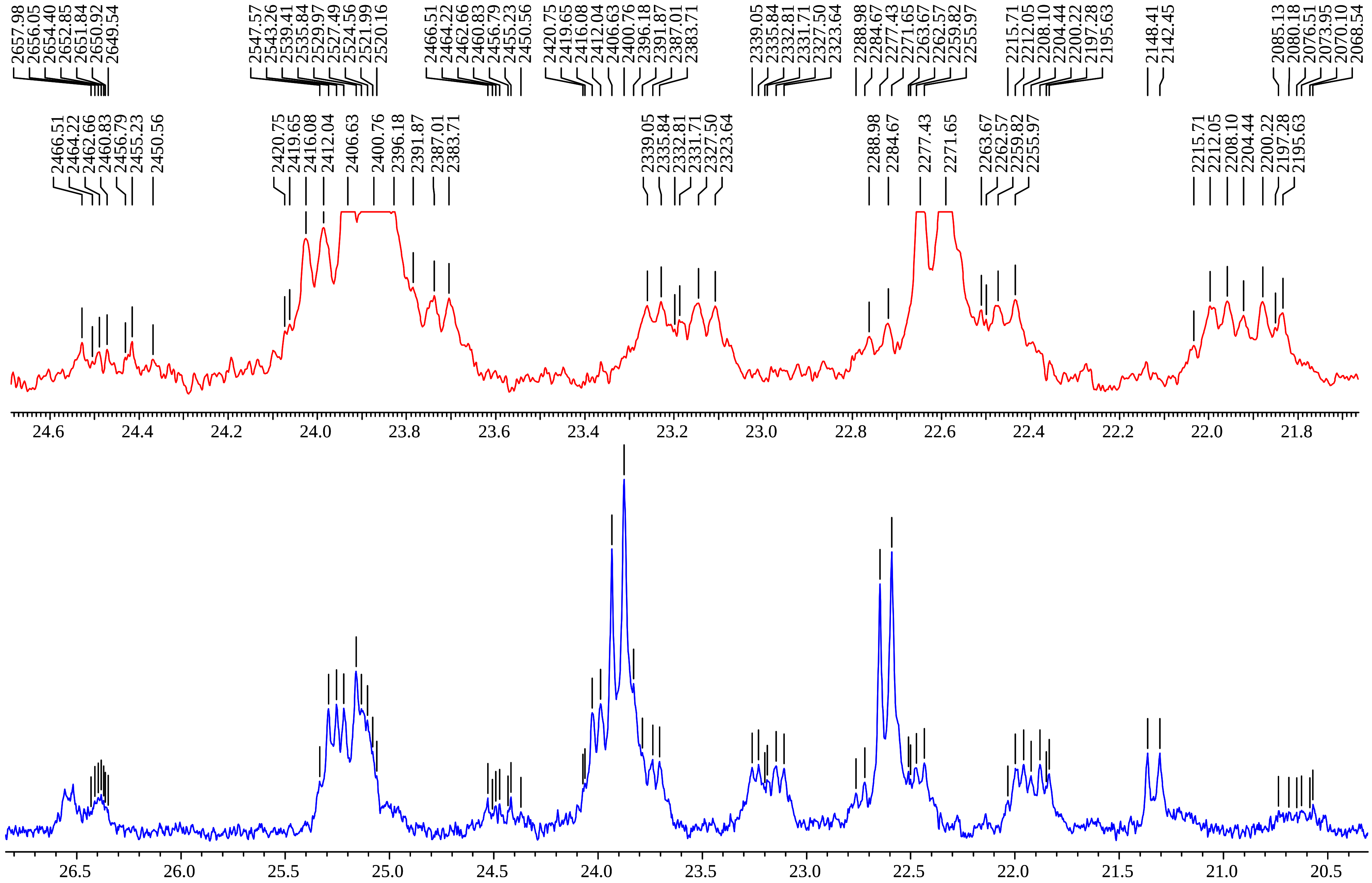


Figure S33. The 20-27 ppm region of ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6) of phosphorane (**2**).

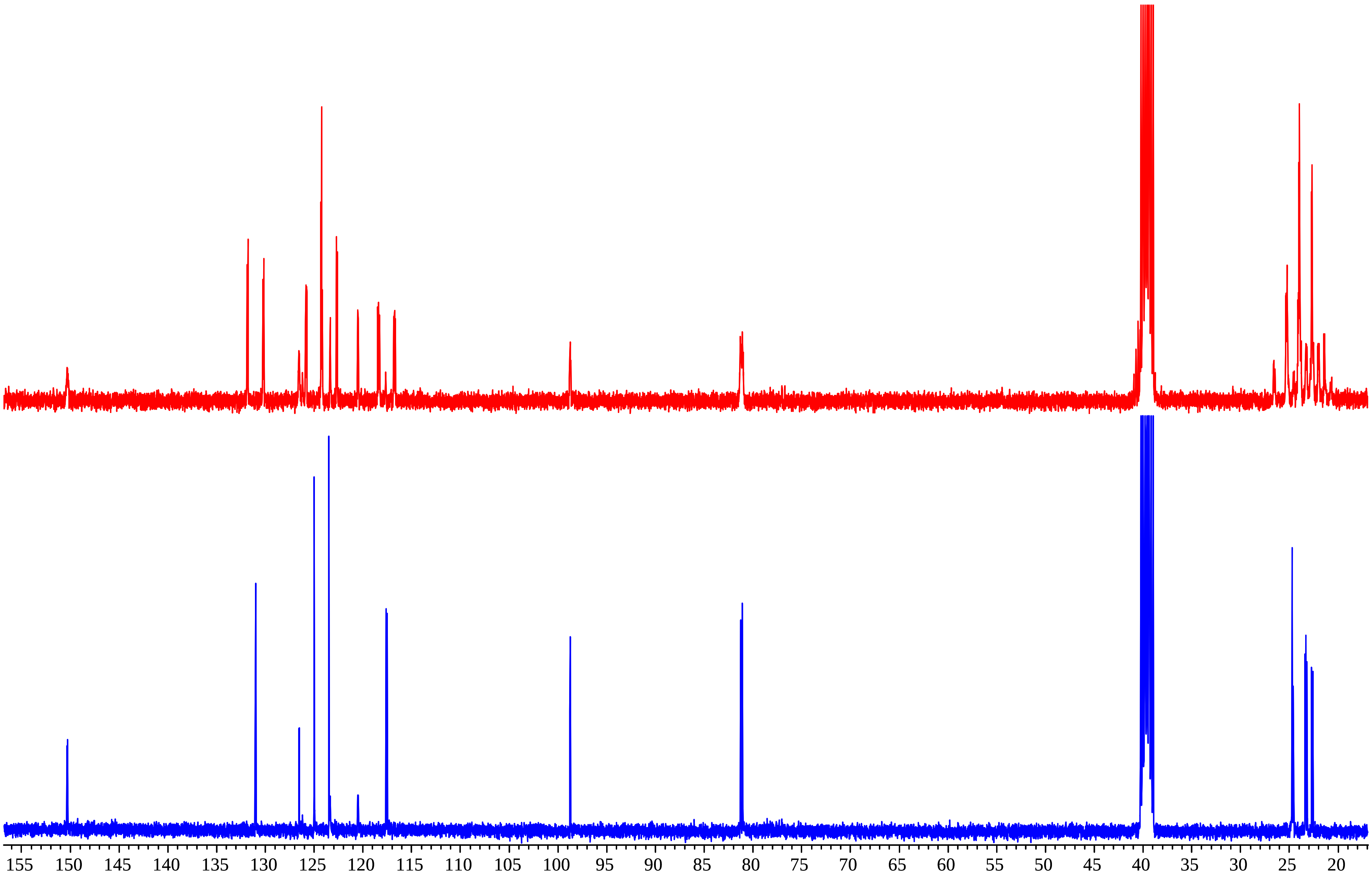


Figure S34. $^{13}C-\{^{1}H\}$ and ^{13}C NMR spectra (100.6 MHz, DMSO-d_6) of phosphorane (**2**).

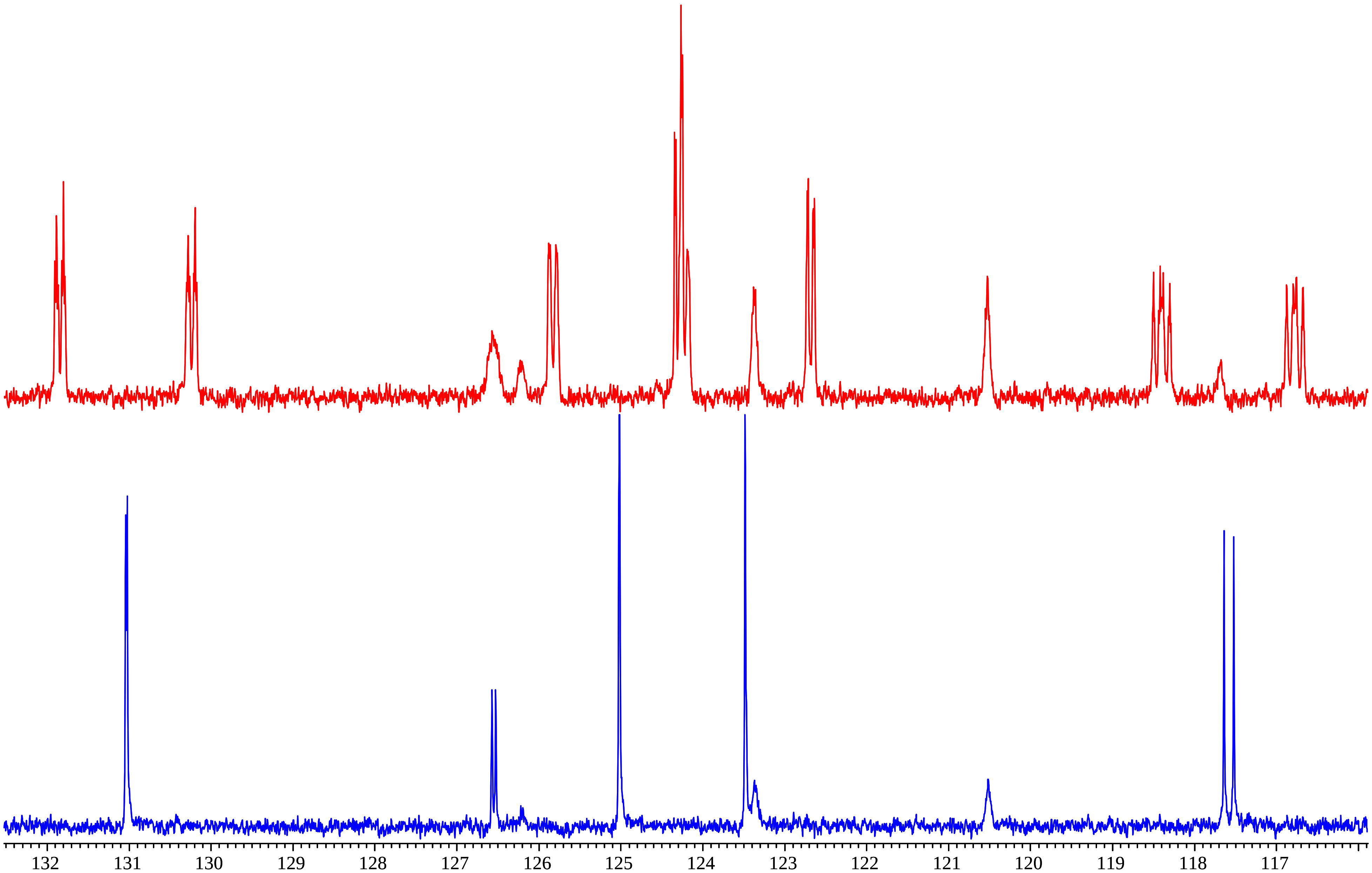


Figure S35. The 116-132 ppm region of ^{13}C-{^{1}H} and ^{13}C-{^{1}H}-dept NMR spectra (100.6 MHz, DMSO-d_6) of phosphorane (**2**).

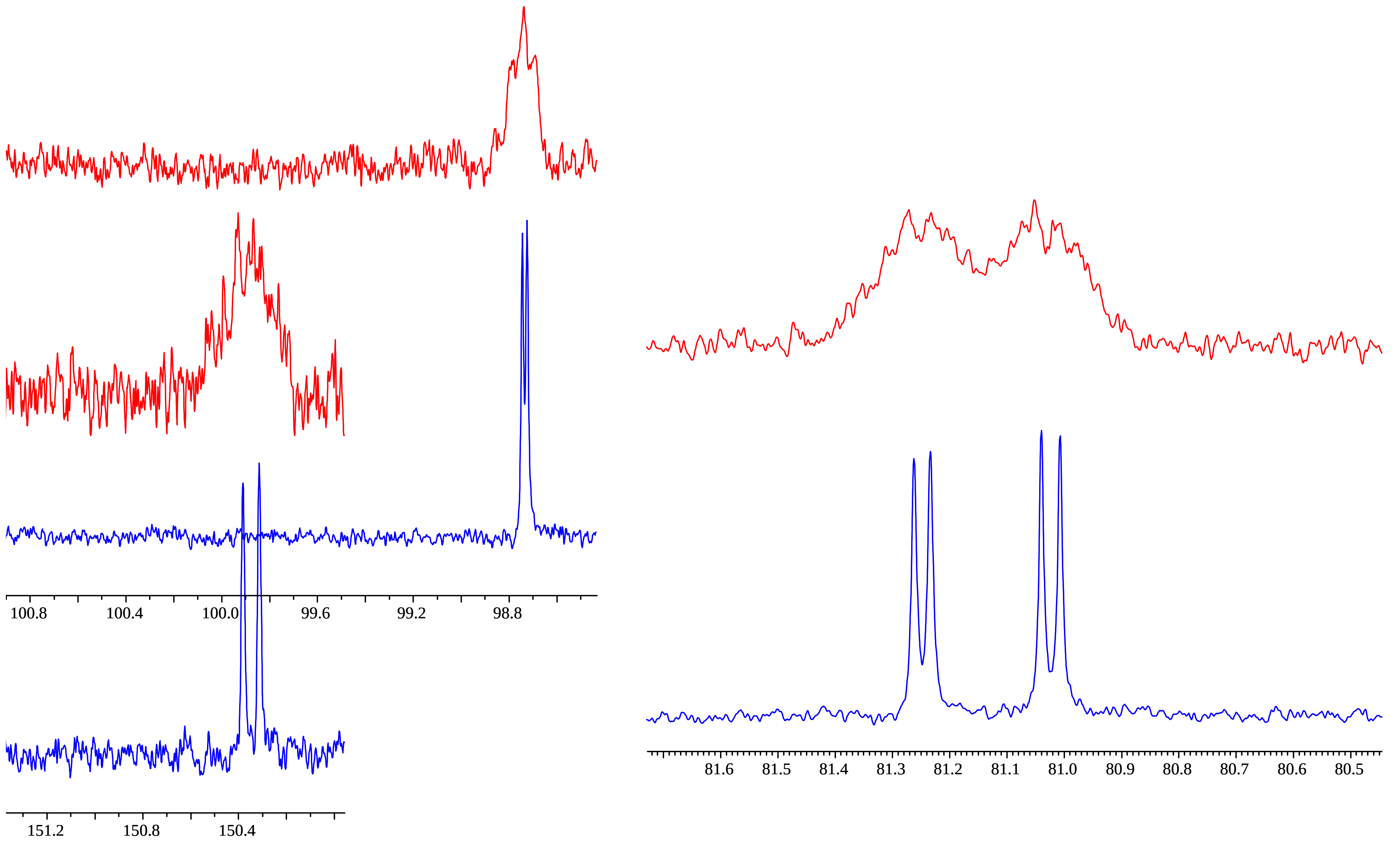


Figure S36. Fragments of ^{13}C-{^{1}H} and ^{13}C NMR spectra (100.6 MHz, DMSO-d_6) of phosphorane (**2**).

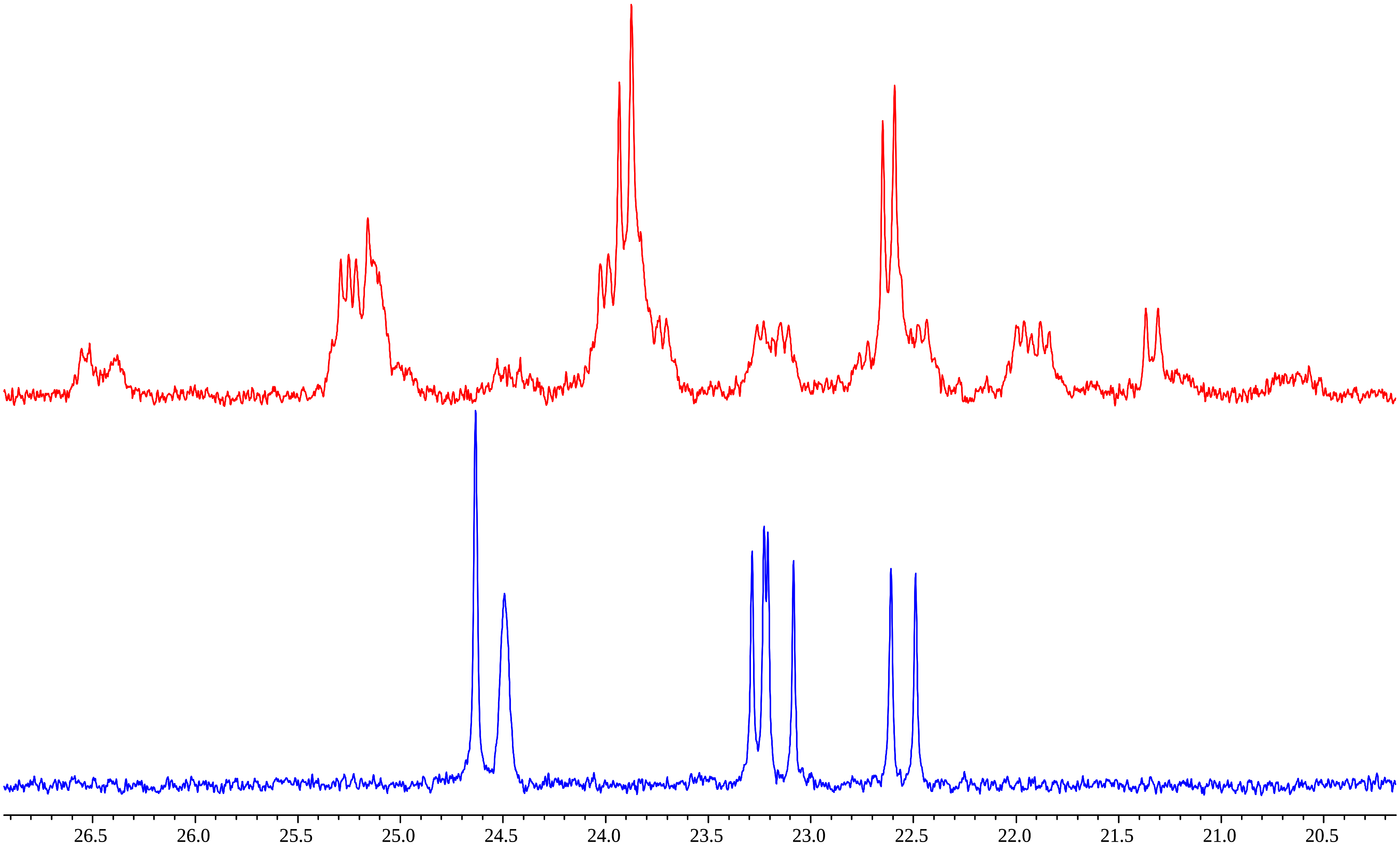
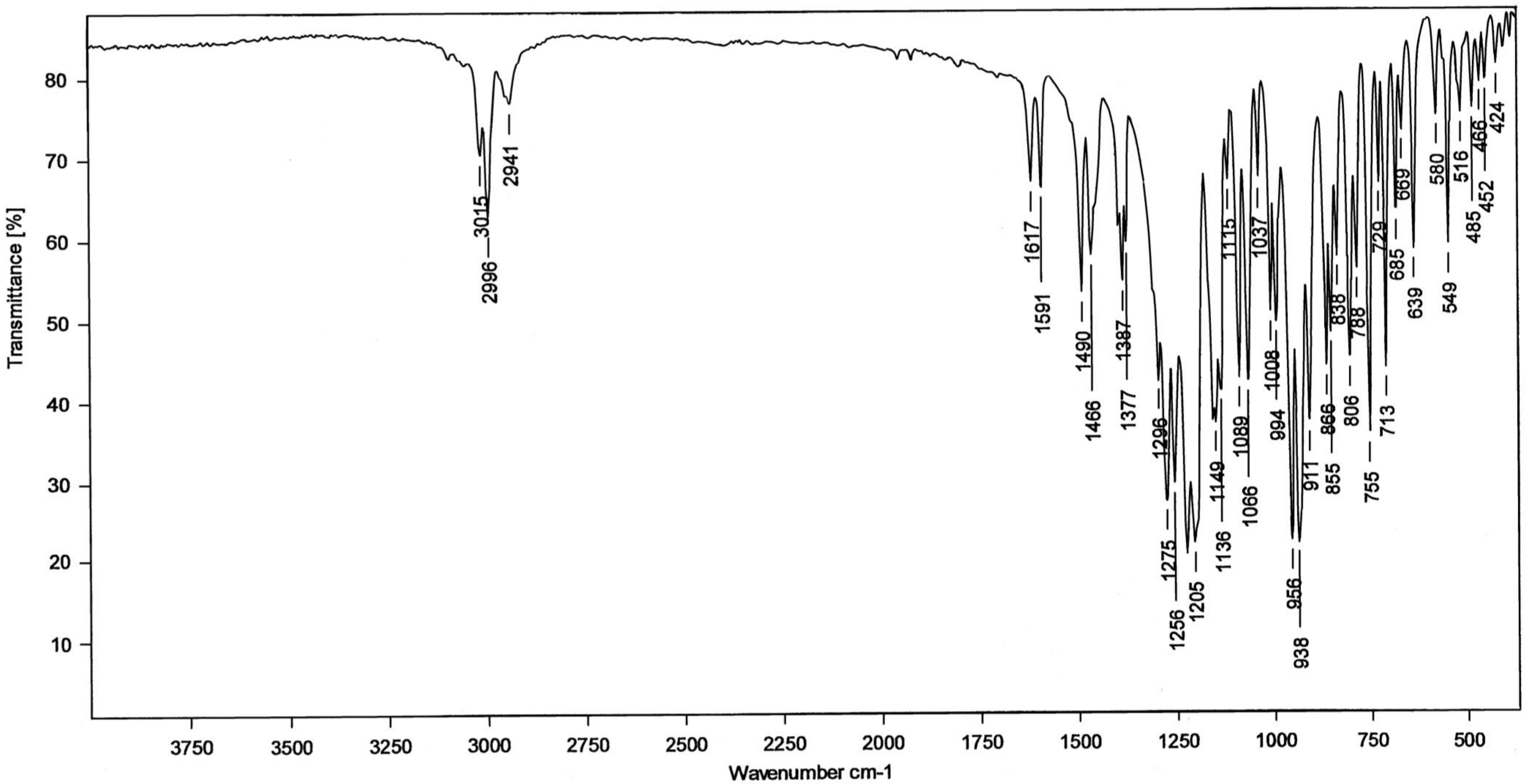


Figure S37. High-field fragment of $^{13}C-\{^{1}H\}$ and ^{13}C NMR spectra (100.6 MHz, DMSO-d_6) of phosphorane (**2**).



Sample Name DIM 293

Operator Name Sasha

Instrument Type Tensor 27

Resolution 4

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Date of Measurement 06/02/2020

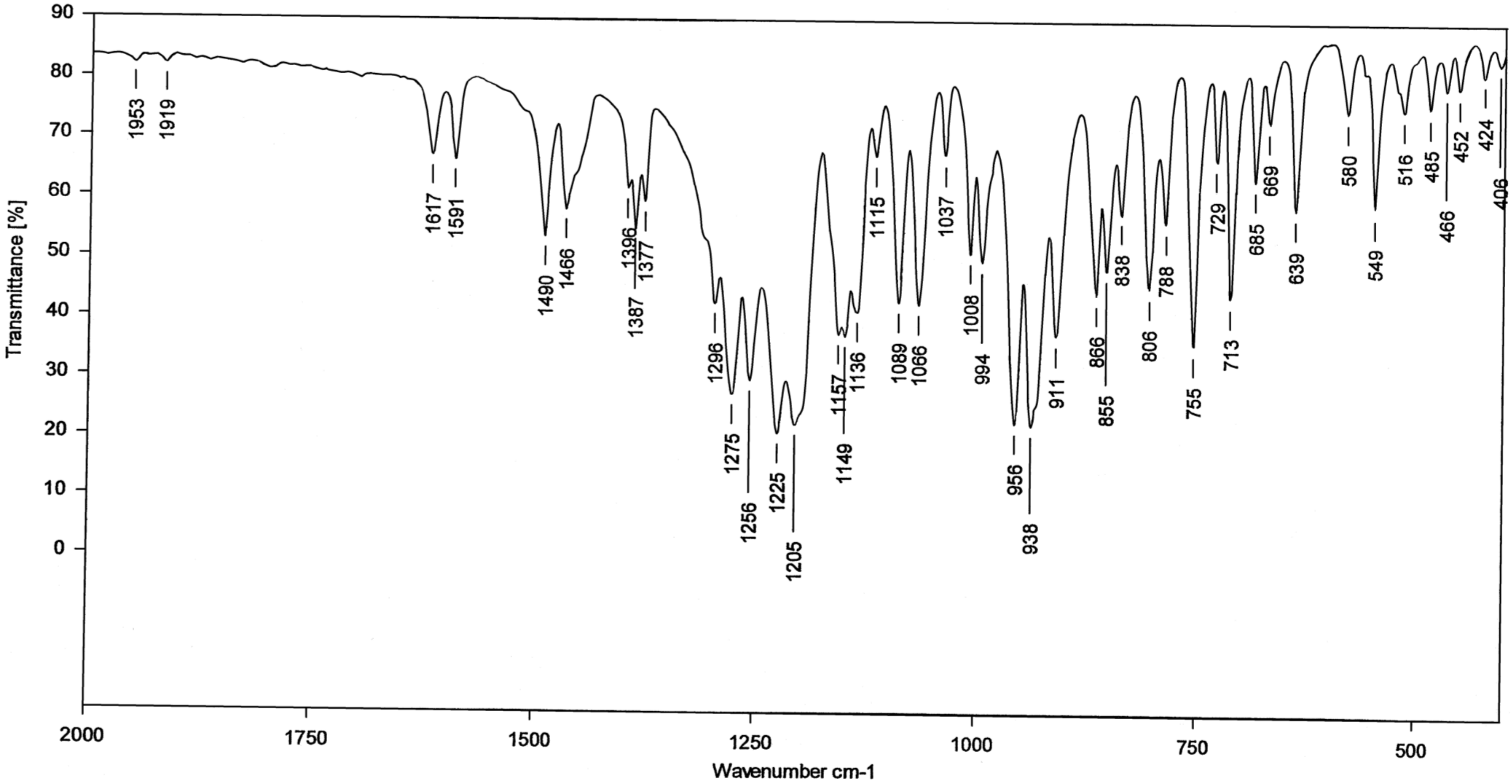
Sample Form KBr

Time of Measurement 2:54:34 PM

Filename DIM 293.0

PCO

Figure S38. IR spectrum (400-4000 cm^{-1}, KBr pellet) of phosphorane (**2**).



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Instrument Type Tensor 27

Resolution 4

Path of File E:\work\2020

Date of Measurement 06/02/2020

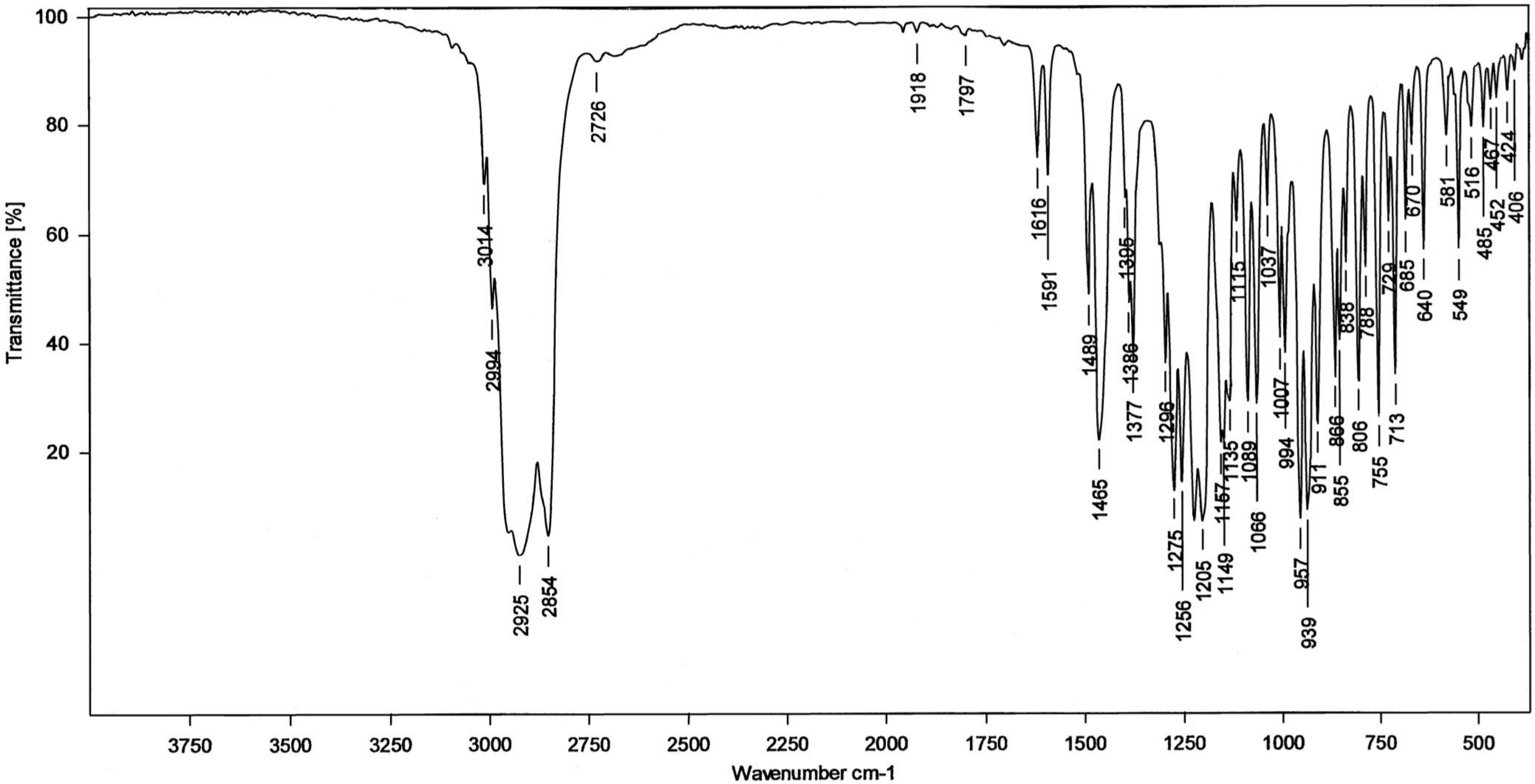
Sample Form KBr

Time of Measurement 2:54:34 PM

Filename DIM 293.0

PCO

Figure S39. Fragment of IR spectrum (400-2000 cm^{-1}, KBr pellet) of phosphorane (**2**).



Sample Name DIM 293 vaz

Operator Name Sasha

Instrument Type Tensor 27

Resolution 4

Path of File E:\work\2020

Date of Measurement 06/02/2020

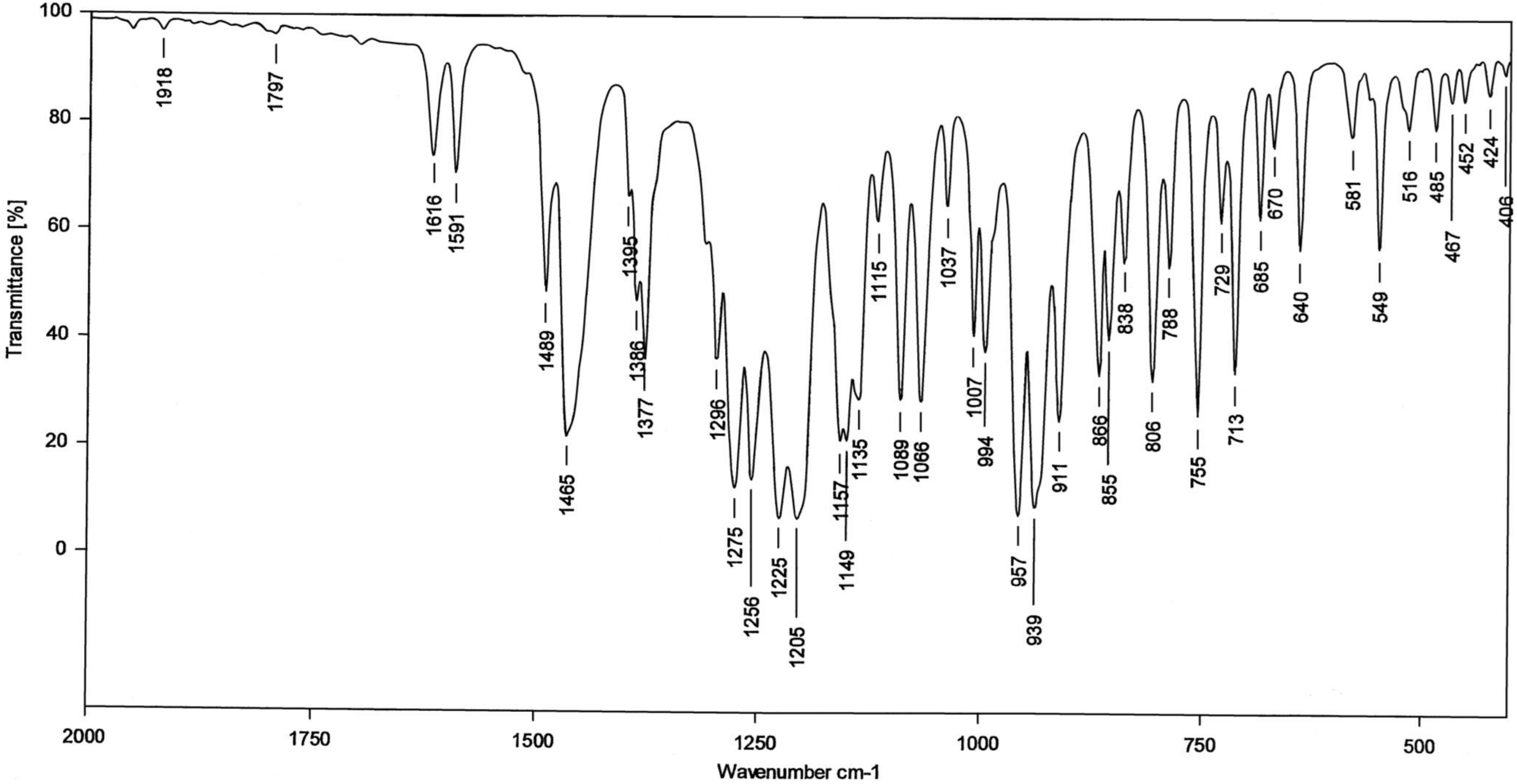
Sample Form vazelin

Time of Measurement 3:03:07 PM

Filename DIM 293 vaz.1

PCO

Figure S40. IR spectrum (400-4000 cm^{-1}, Vaseline oil) of phosphorane (**2**).



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Operator Name Sasha

Instrument Type Tensor 27

Resolution 4

Path of File E:\work\2020

Date of Measurement 06/02/2020

Sample Form vazelin

Time of Measurement 3:03:07 PM

Filename DIM 293 vaz.1

PCO

Figure S41. Fragment of IR spectrum (400-2000 cm^{-1}, Vaseline oil) of phosphorane (**2**).

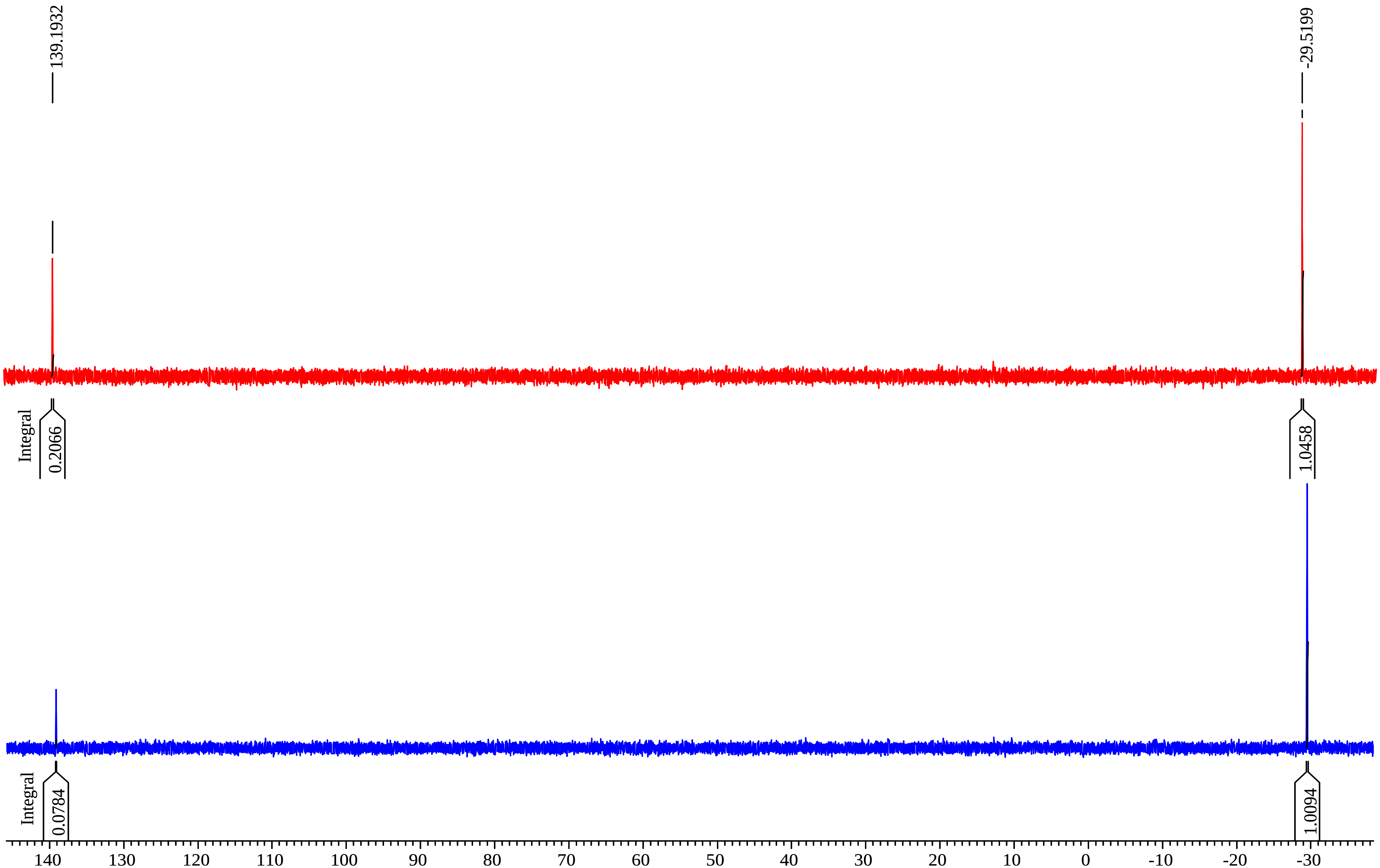


Figure S42. ^{31}P-{^{1}H} spectra (162.0 MHz, toluene) of phosphorane (**2**) under toluene reflux (1 h, blue; 2 h, red).

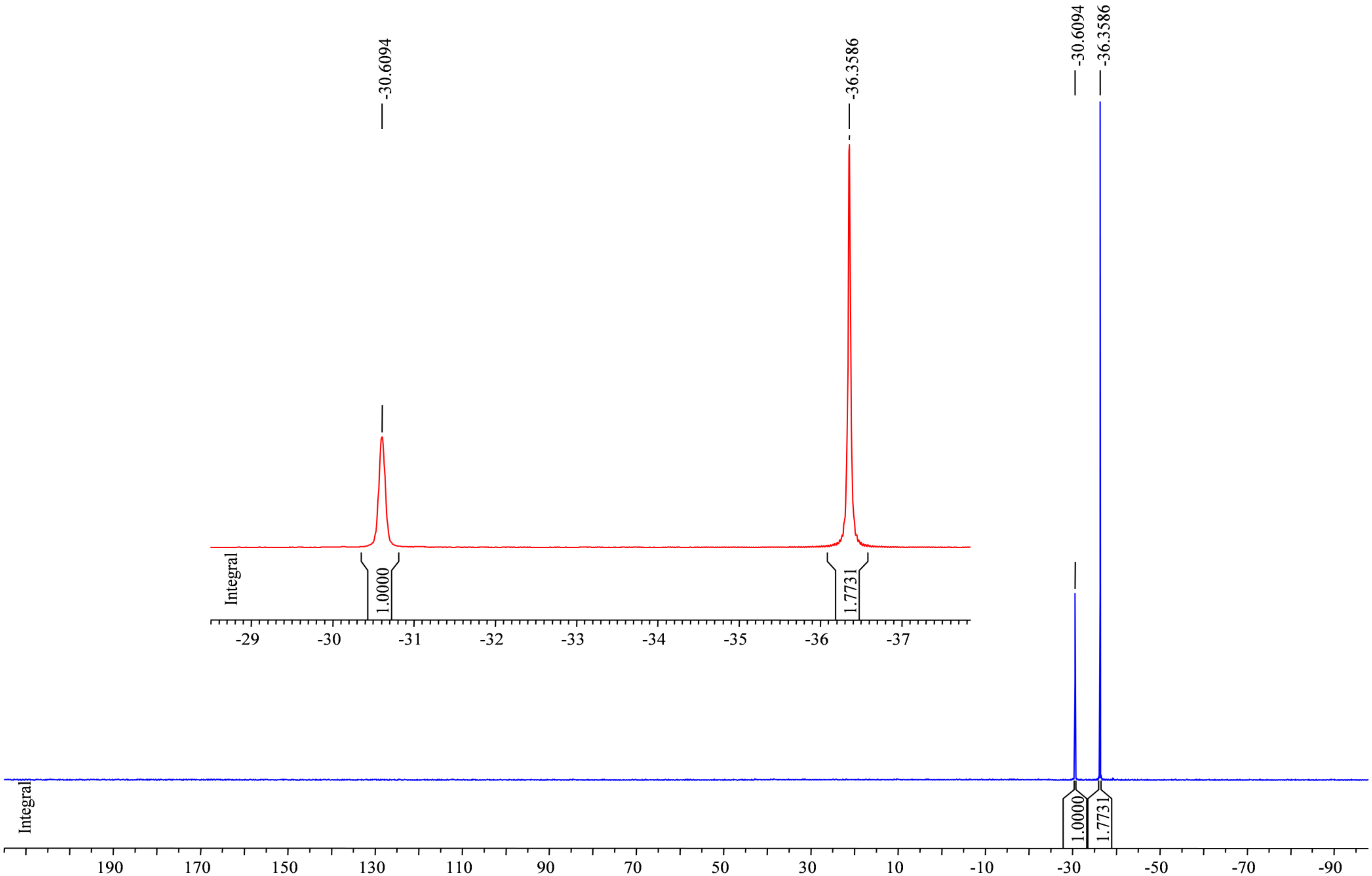


Figure S43. ^{31}P-{^{1}H} spectrum (162.0 MHz, $CDCl_3$) of the dioxaphospholane (**1**) and hexafluoroacetone reaction mixture (CH_2Cl_2).

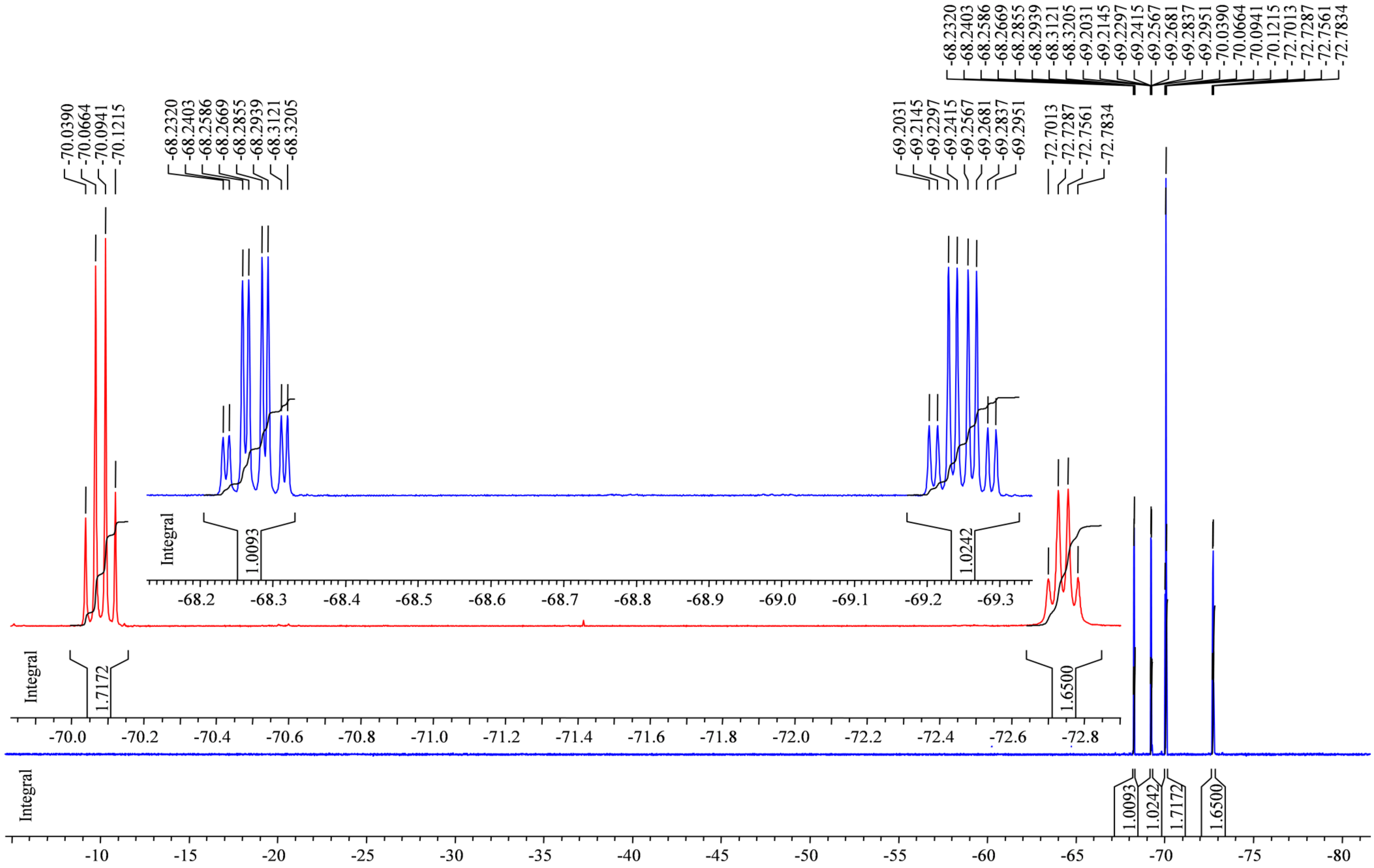


Figure S44. ^{19}F-{^{1}H} spectrum (376.5.0 MHz, $CDCl_3$) of the dioxaphospholane (**1**) and hexafluoroacetone reaction mixture (CH_2Cl_2).

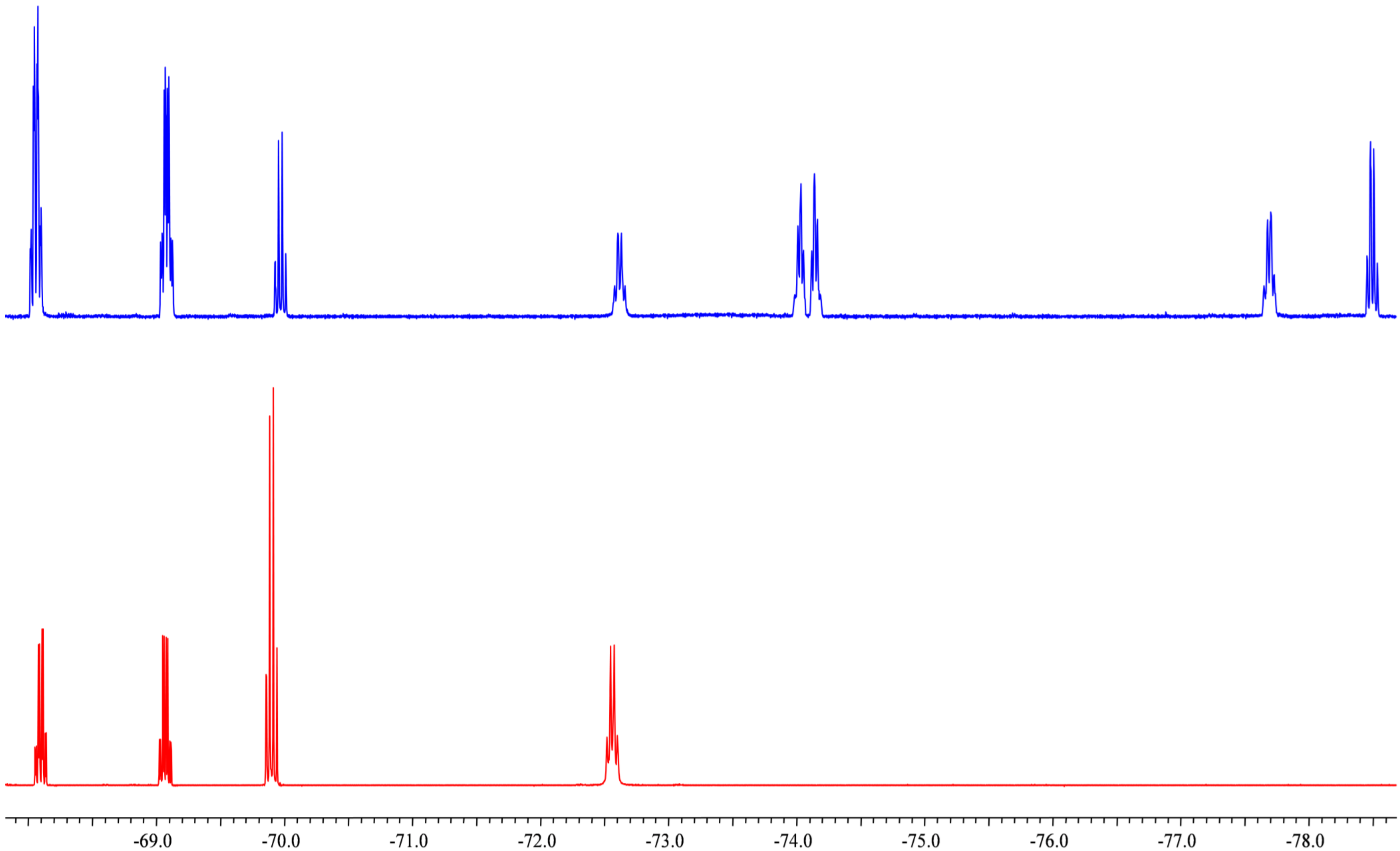


Figure S45. $^{19}F-\{^{1}H\}$ spectra (376.5 MHz, $CDCl_3$) of the dioxaphospholane (**1**) and hexafluoroacetone reaction mixtures (CH_2Cl_2, red; CCl_4, blue).

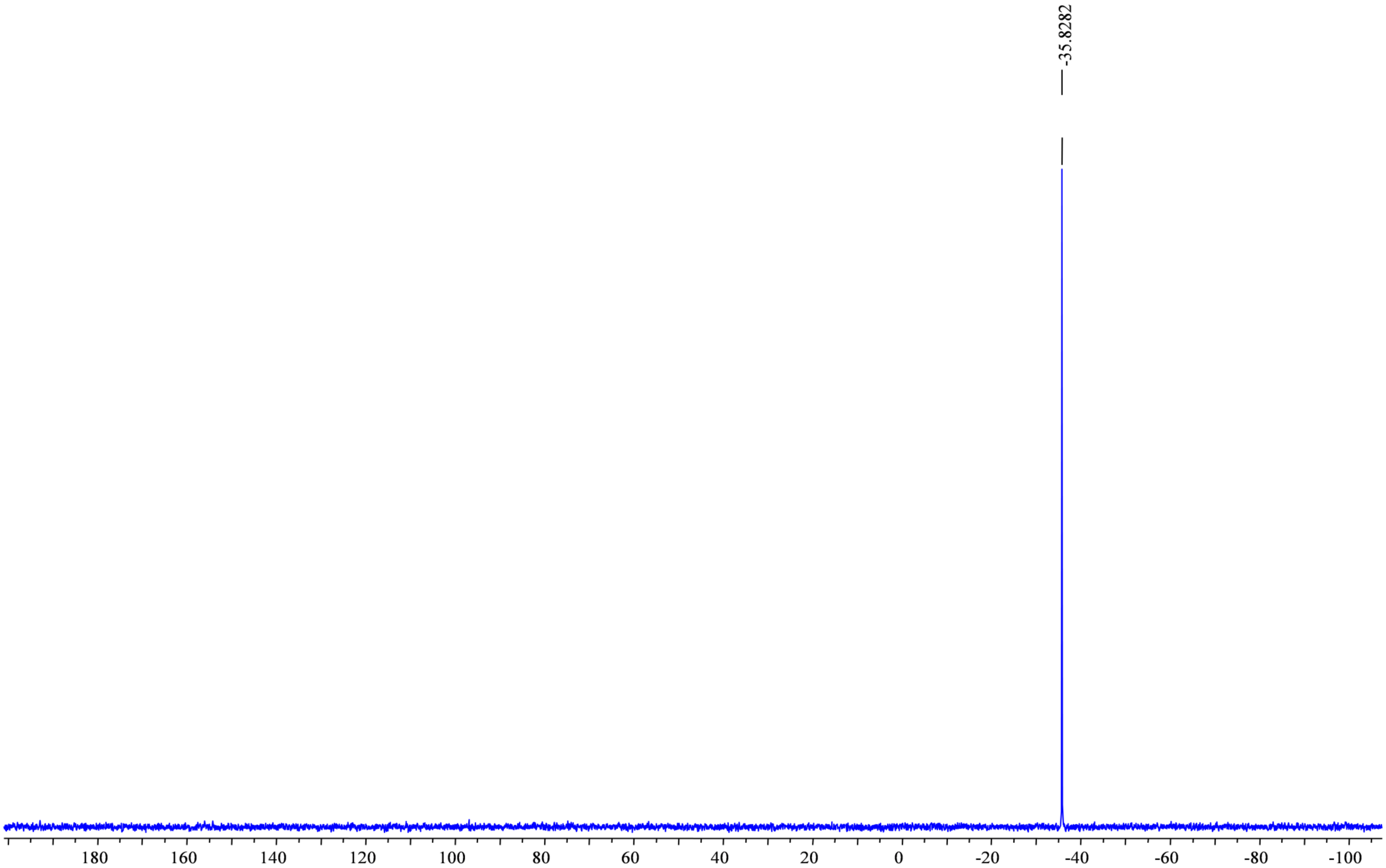


Figure S46. ^{31}P-{^{1}H} NMR spectrum (242.94 MHz, $CDCl_3$) of phosphorane (**3**).

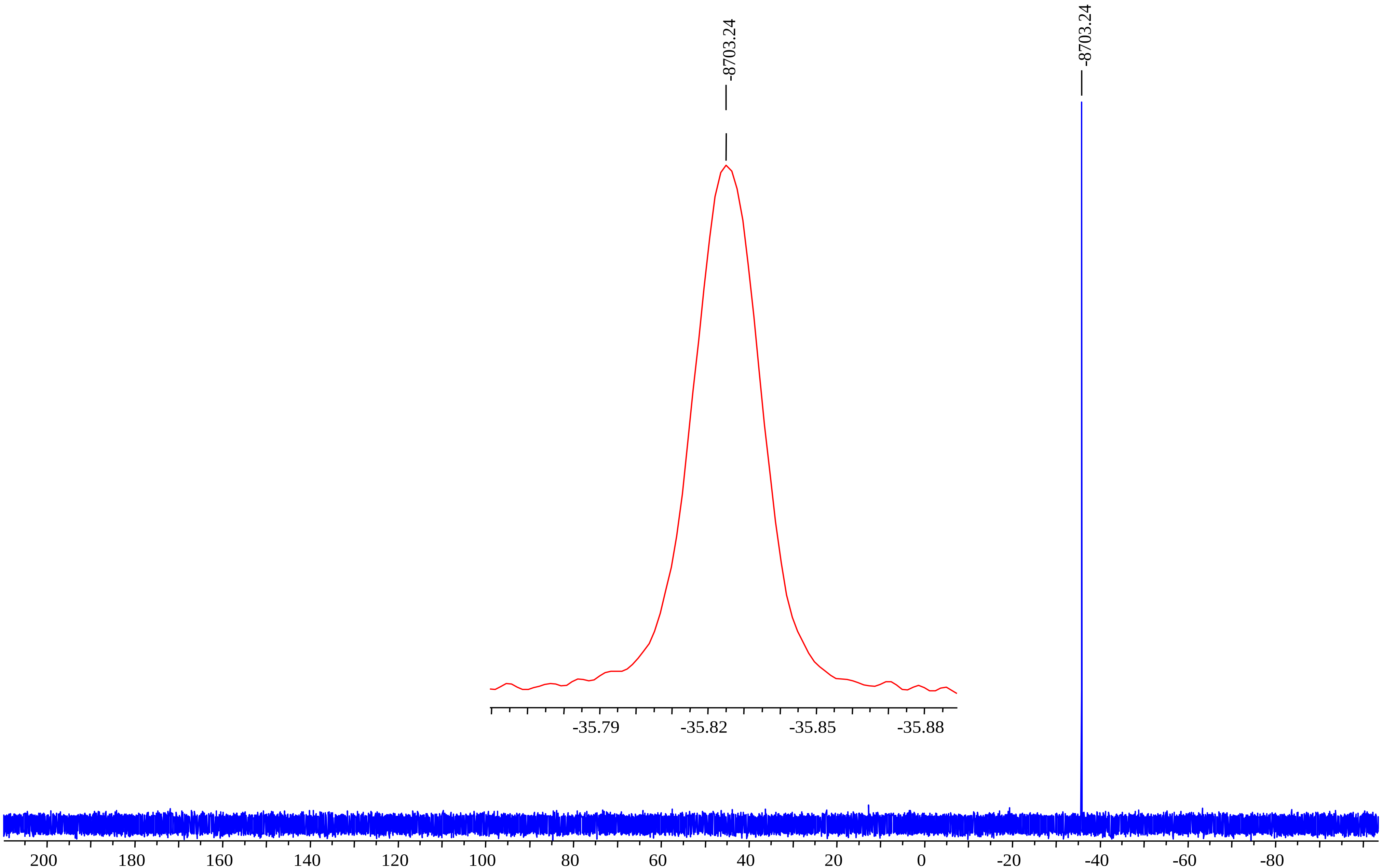


Figure S47. $^{31}P-\{^{1}H\}$ NMR spectrum (242.94 MHz, acetone-d_6) of phosphorane (**3**).

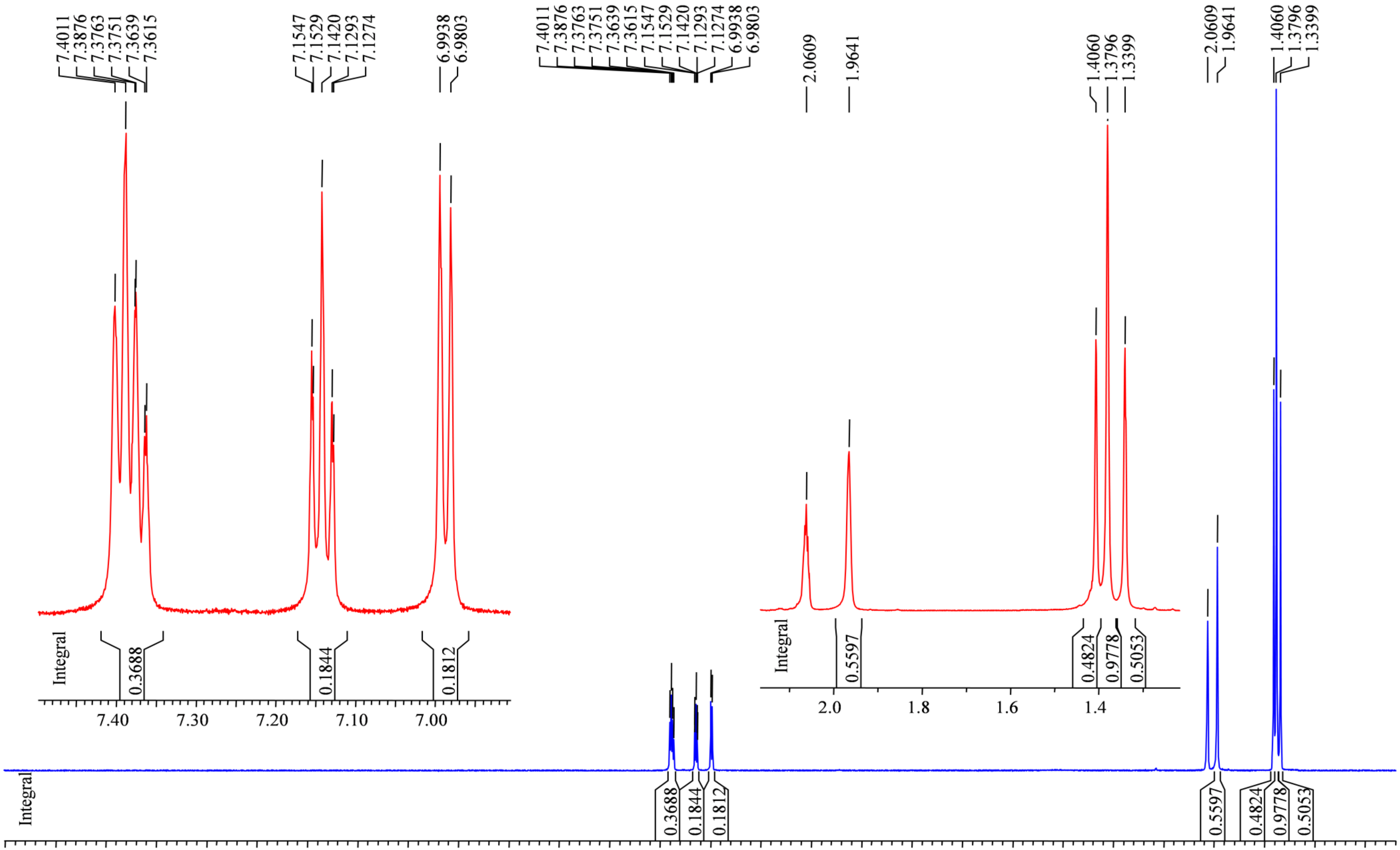


Figure S48. [1]H NMR spectrum (400 MHz, $CDCl_3$) of phosphorane (**3**).

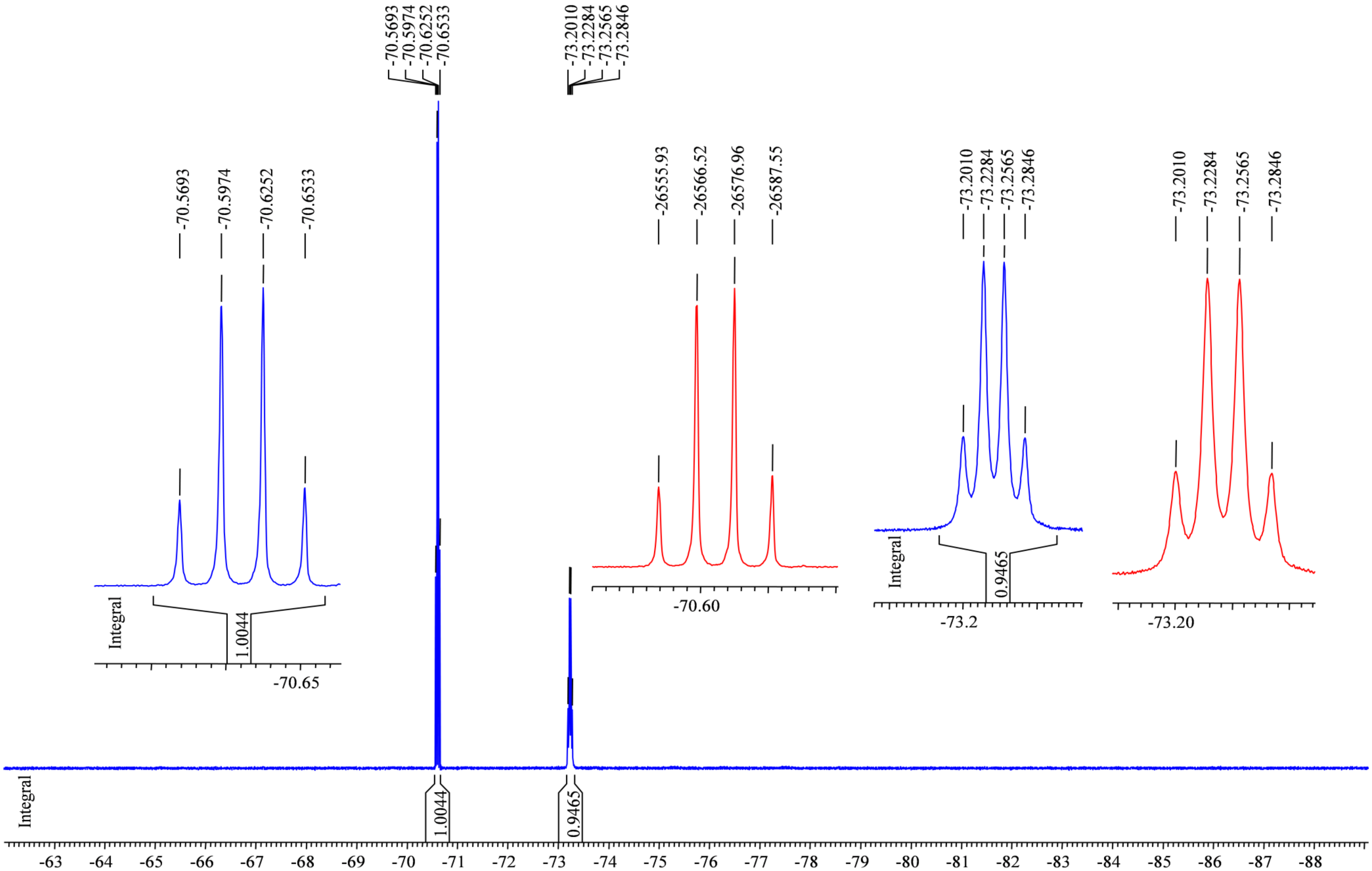


Figure S49. ^{19}F-{^{1}H} NMR spectrum (386.5 MHz, $CDCl_3$) of phosphorane (**3**).

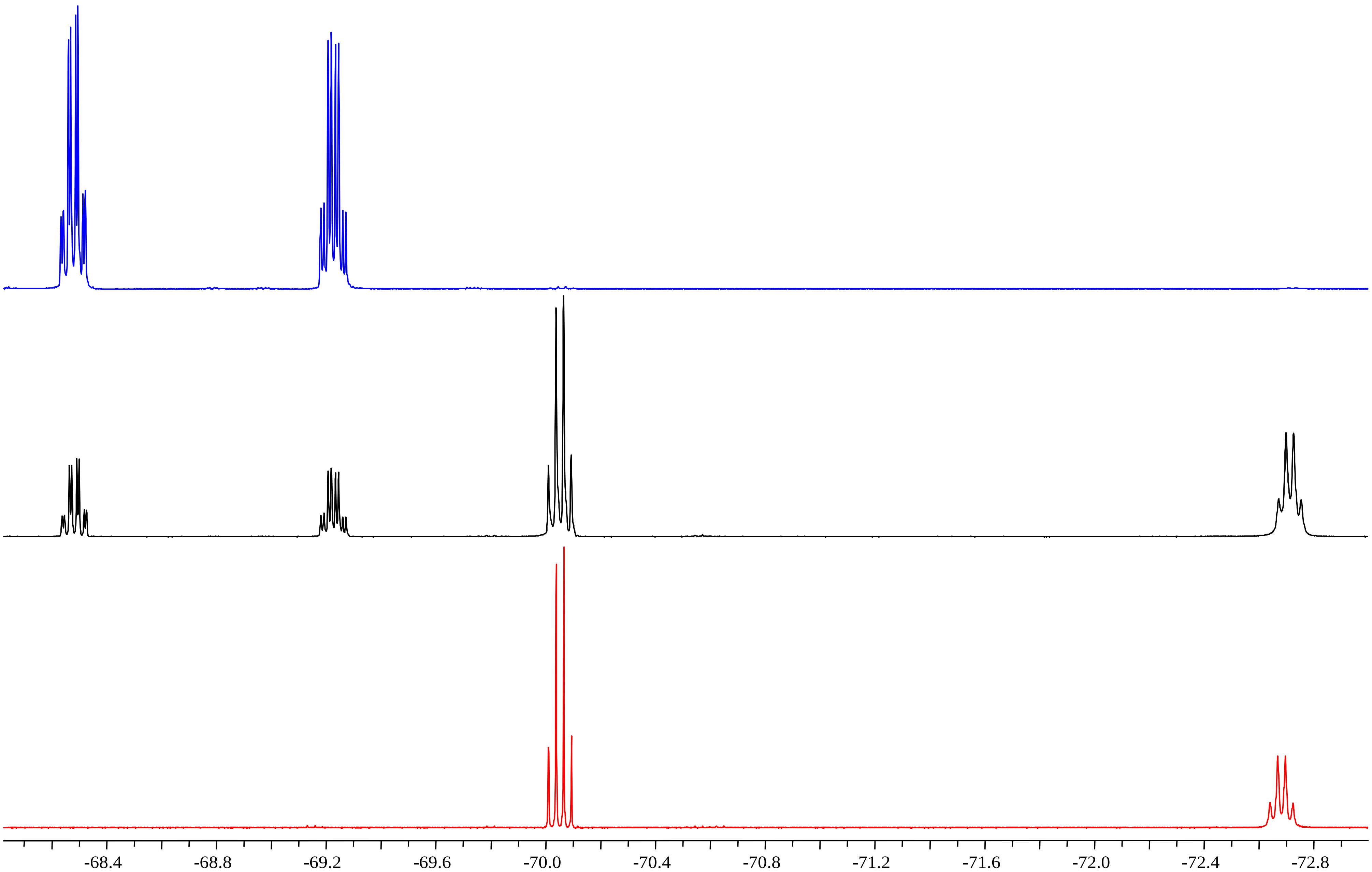


Figure S50. $^{19}F-\{^{1}H\}$ NMR spectra (386.5 MHz, $CDCl_3$) of phosphorane (**2**) (blue), (**3**) (red) and the phosphoranes (**2**, **3**) mixture (black).

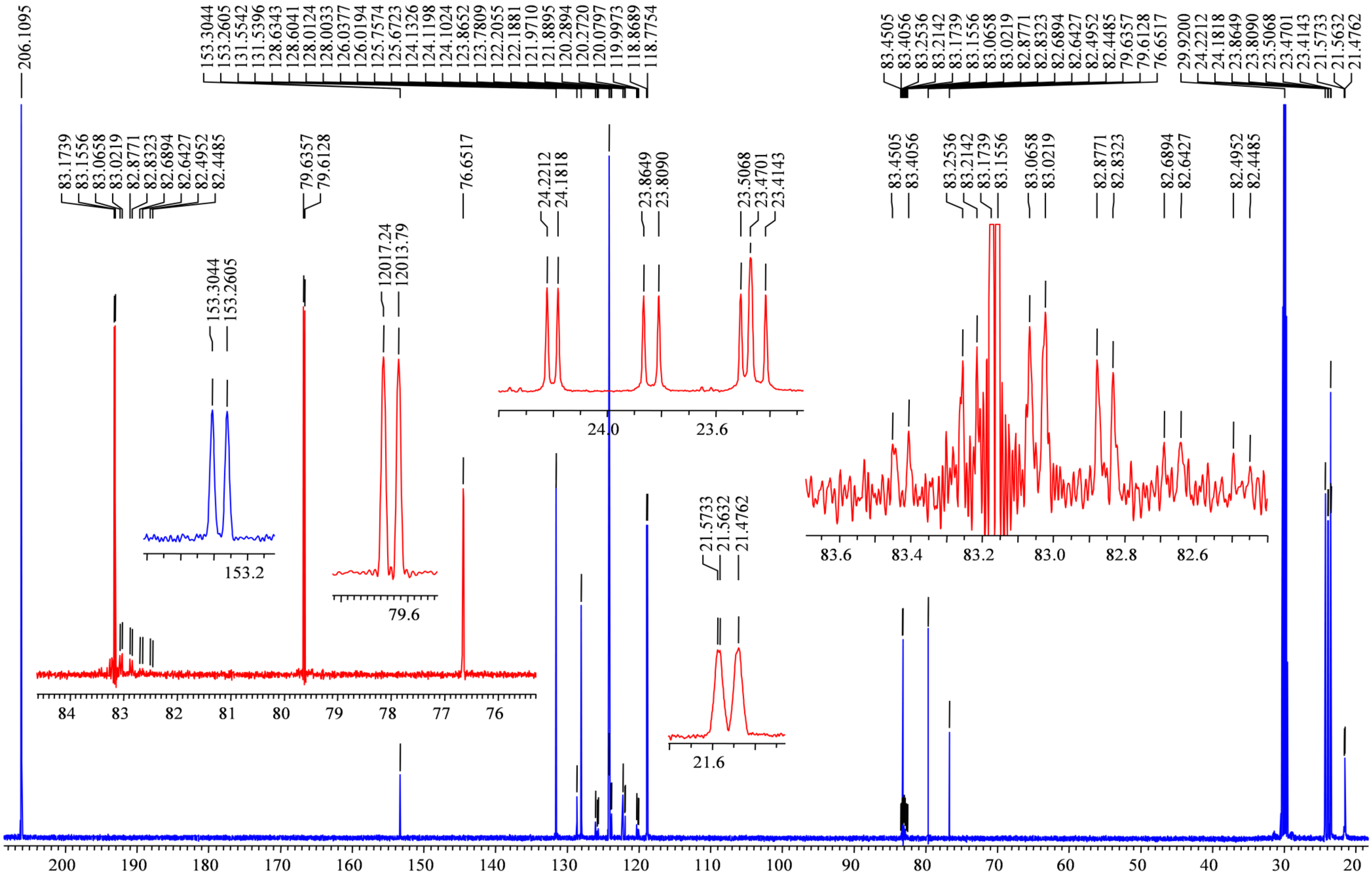


Figure S51. $^{13}C-\{^{1}H\}$ NMR spectrum (150.9 MHz, acetone-d_6) of compound (**3**).

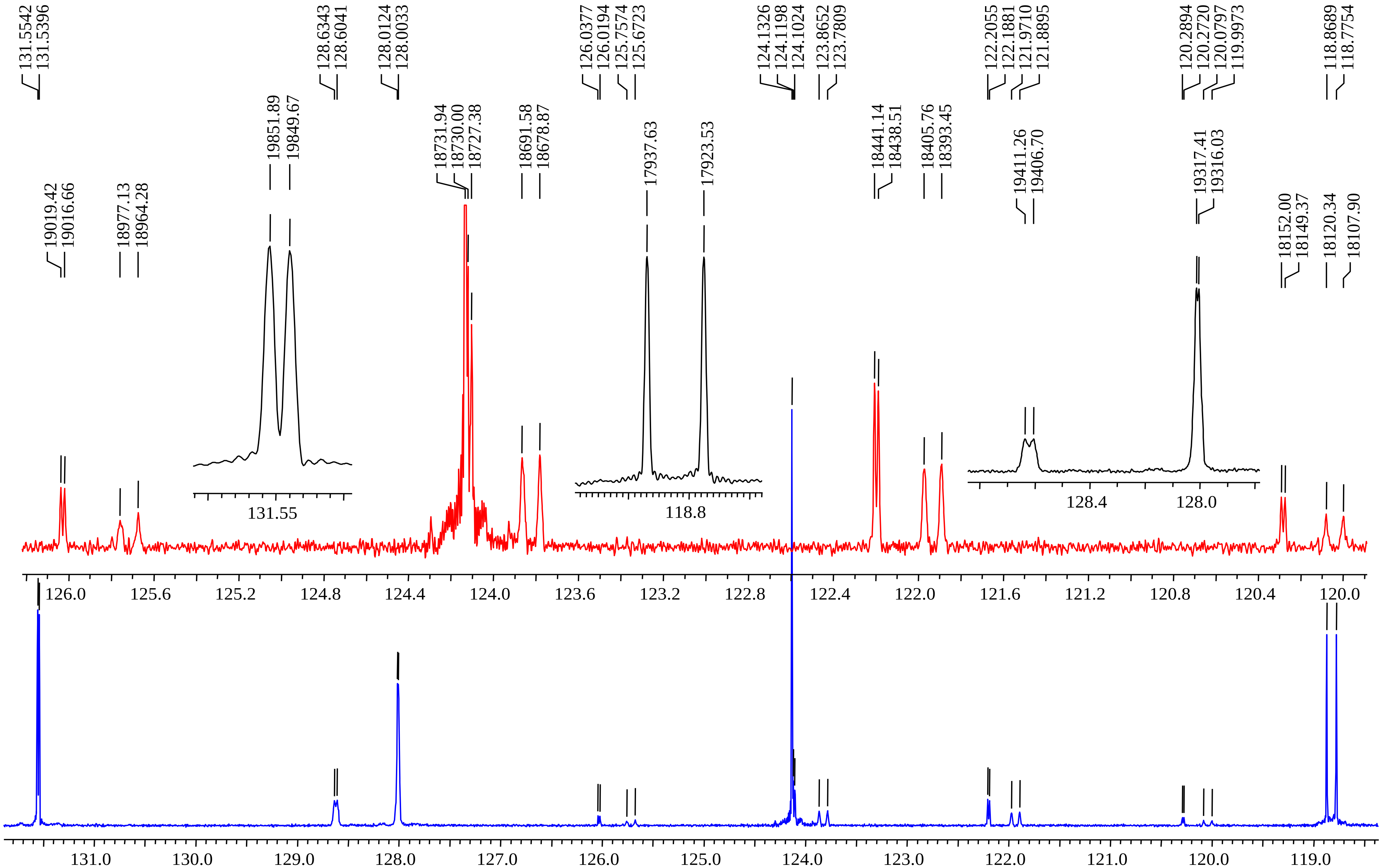


Figure S52. The 118-132 ppm region of ^{13}C-{^{1}H} NMR spectrum (150.9 MHz, acetone-d_6) of phosphorane (**3**).

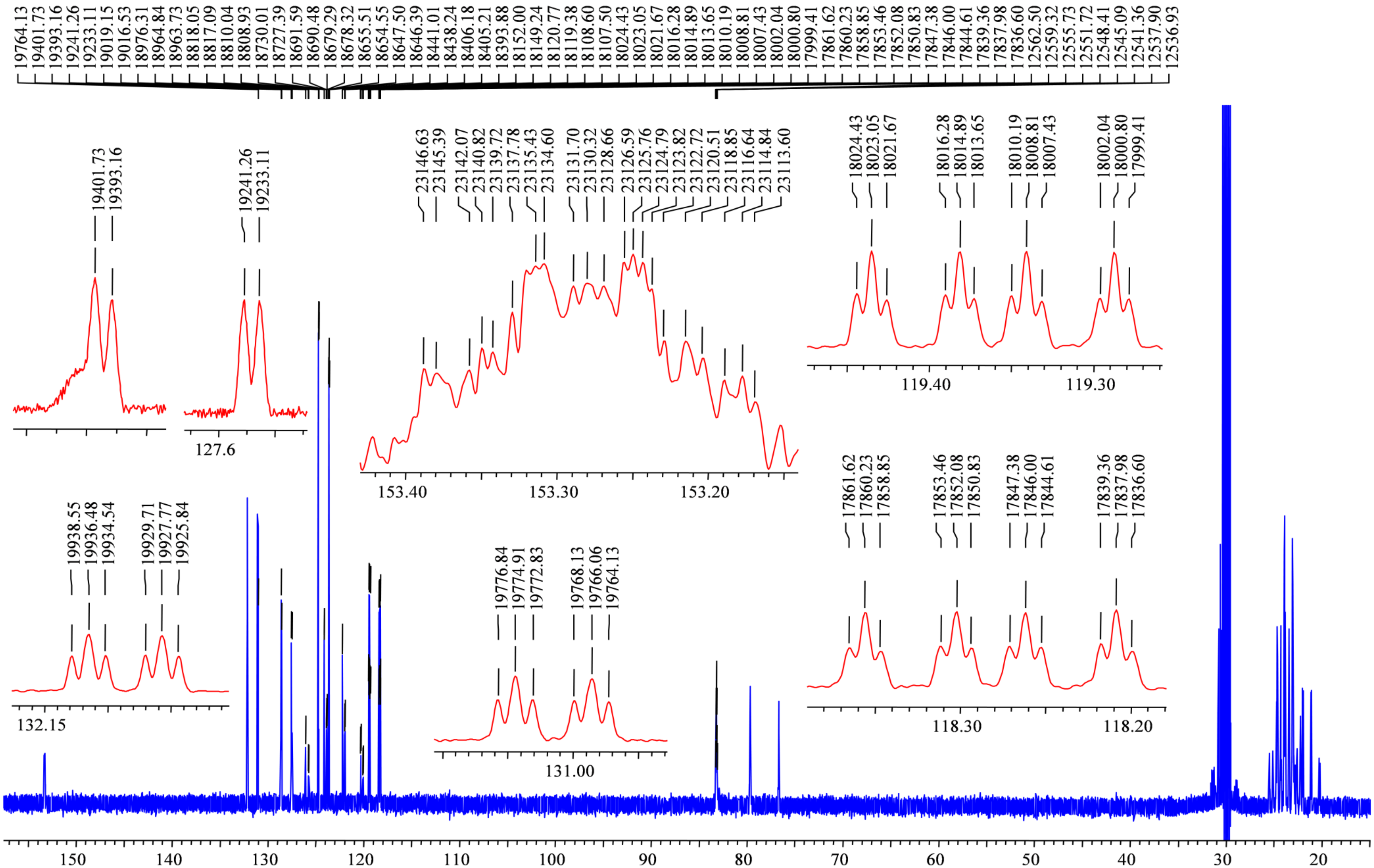


Figure S53. ^{13}C NMR spectrum (150.9 MHz, acetone-d_6) of phosphorane (**3**).

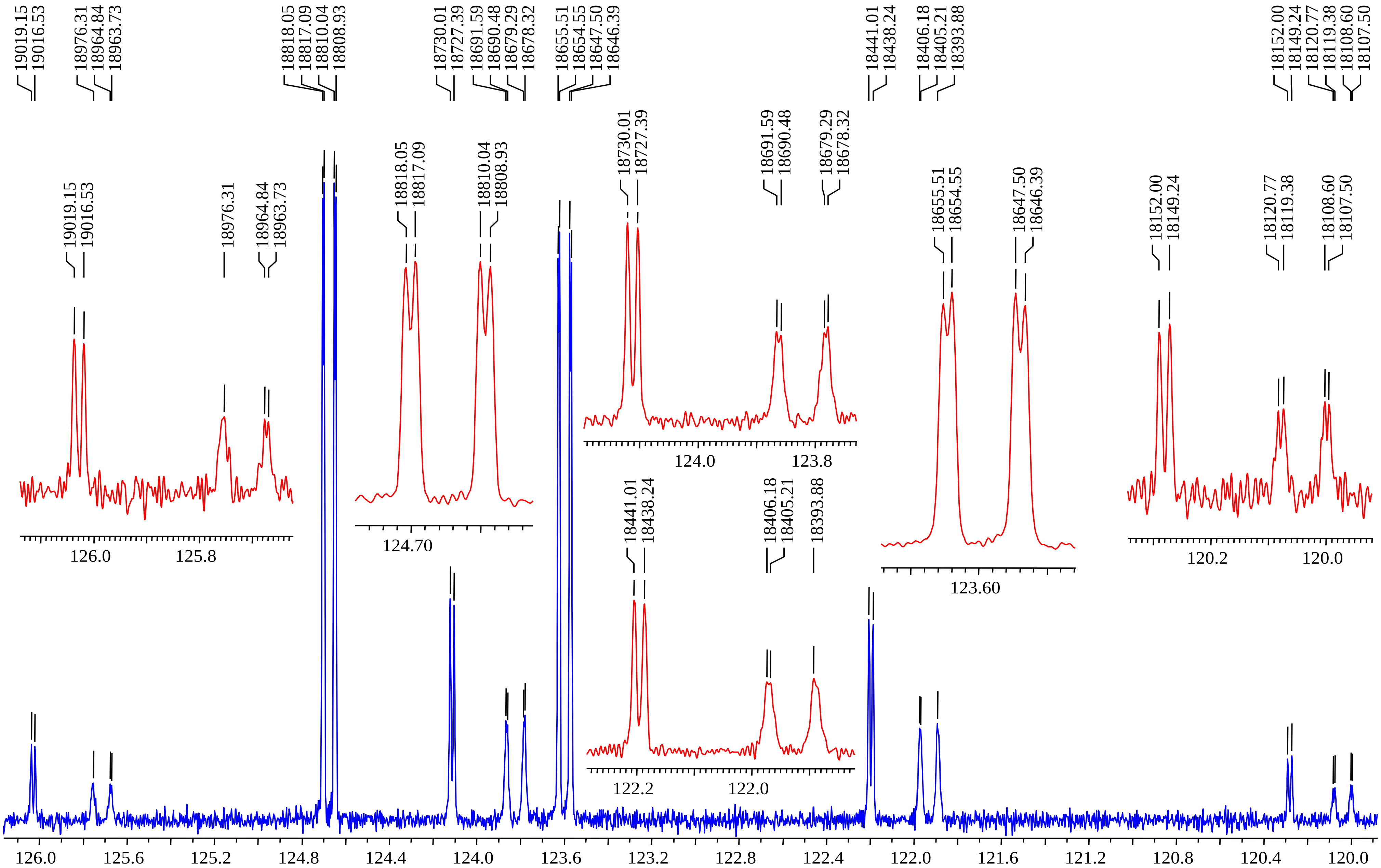


Figure S54. The 119-127 ppm region of ^{13}C NMR spectrum (150.9 MHz, acetone-d_6) of phosphorane (**3**).

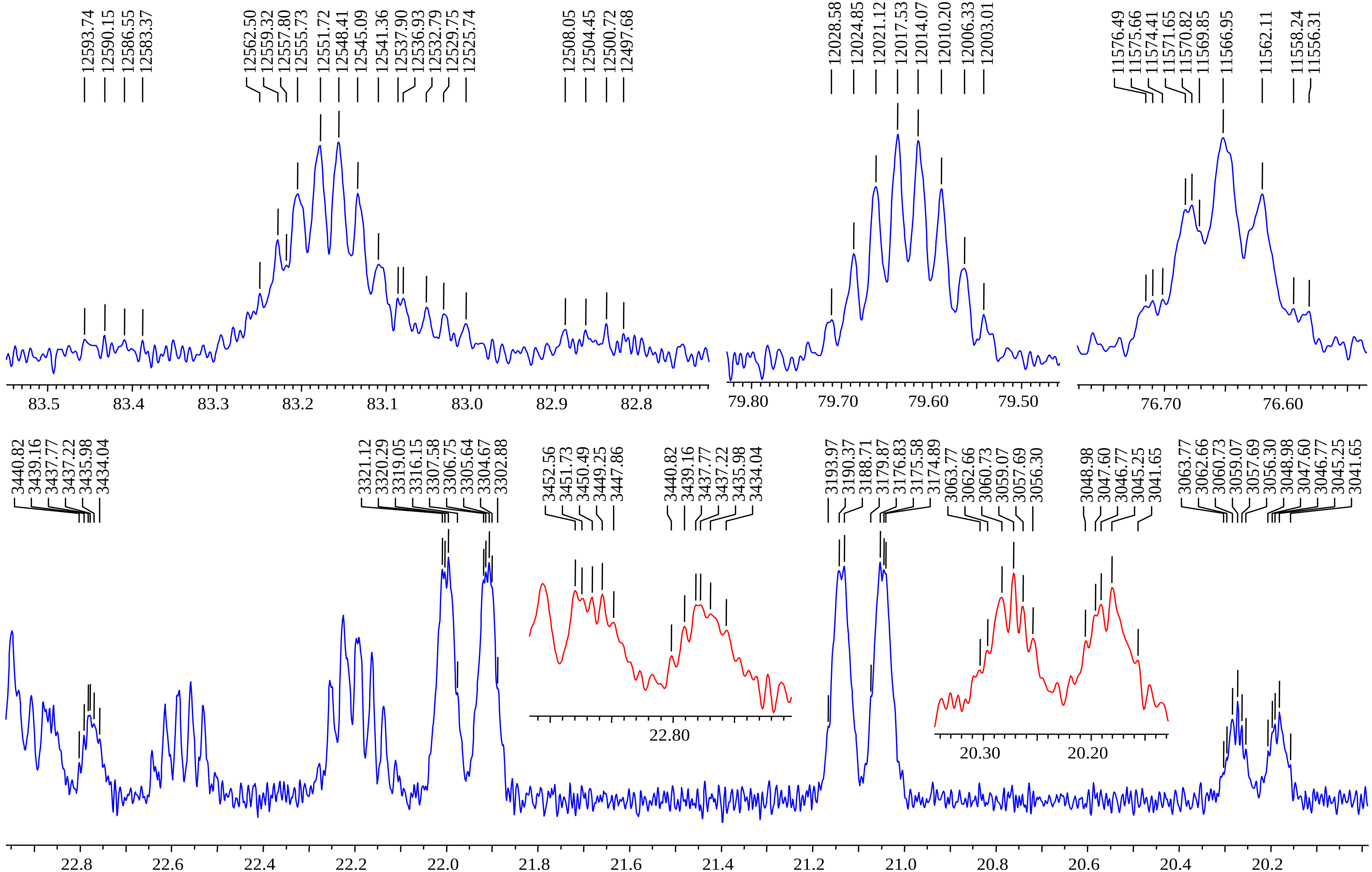


Figure S55. The 19-23, 76-80 and 82-84 ppm regions of ^{13}C NMR spectrum (150.9 MHz, acetone-d_6) of phosphorane (**3**).

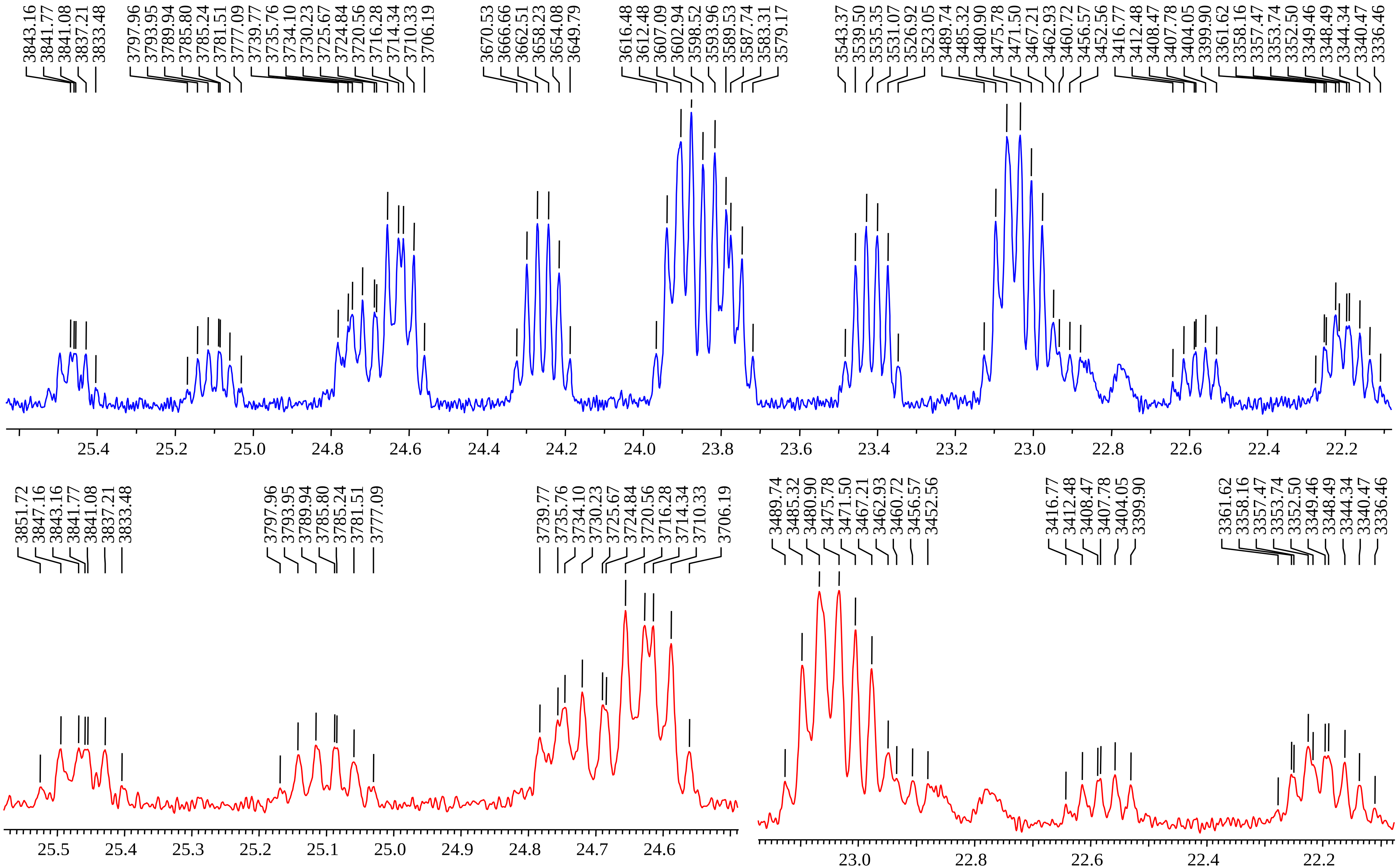


Figure S56. High-field fragment of ^{13}C NMR spectrum (150.9 MHz, acetone-d_6) of phosphorane (**3**).

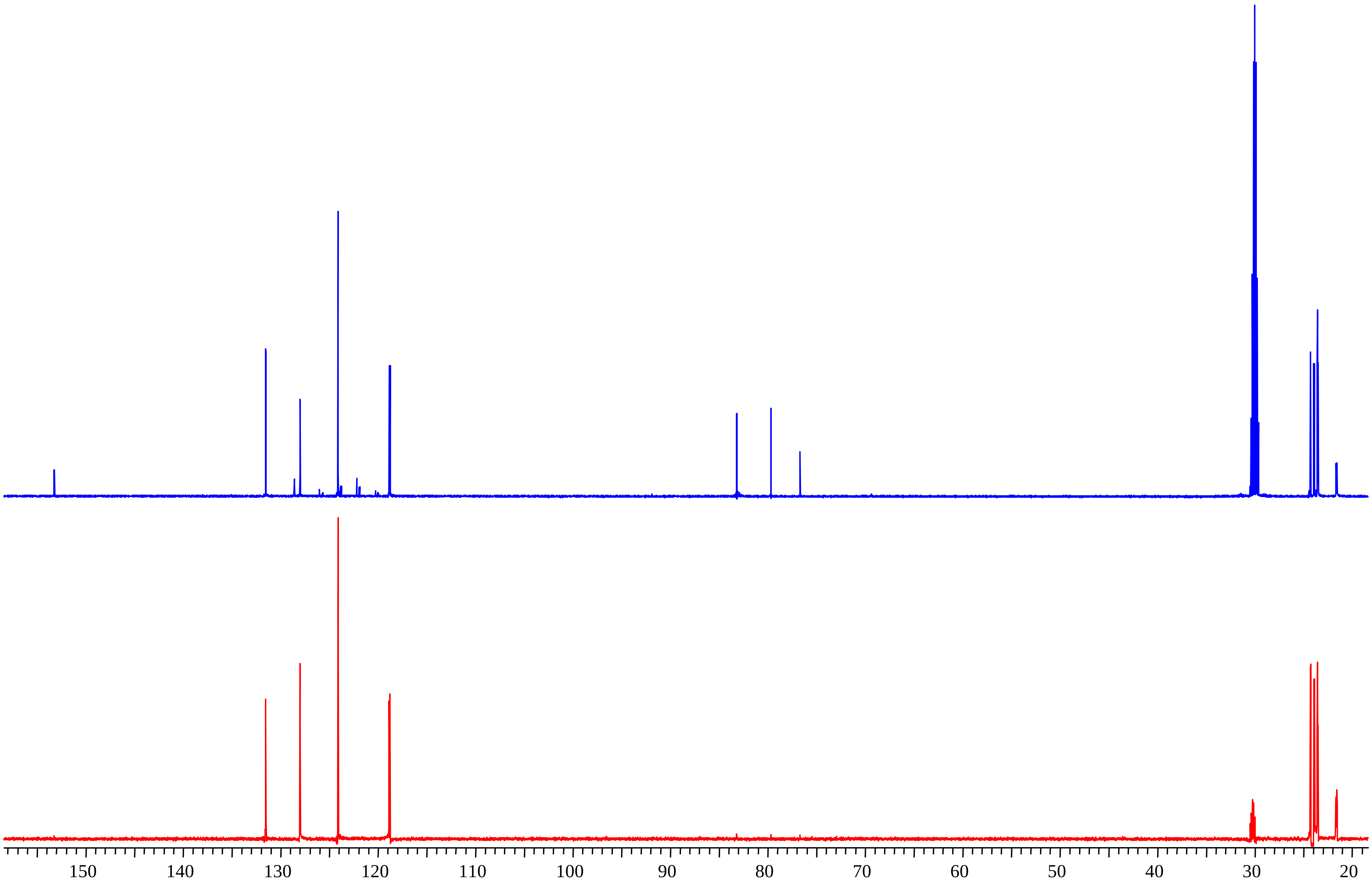


Figure S57. ^{13}C-{^{1}H} and ^{13}C-{^{1}H}-dept NMR spectra (150.9 MHz, acetone-d_6) of phosphorane (**3**).

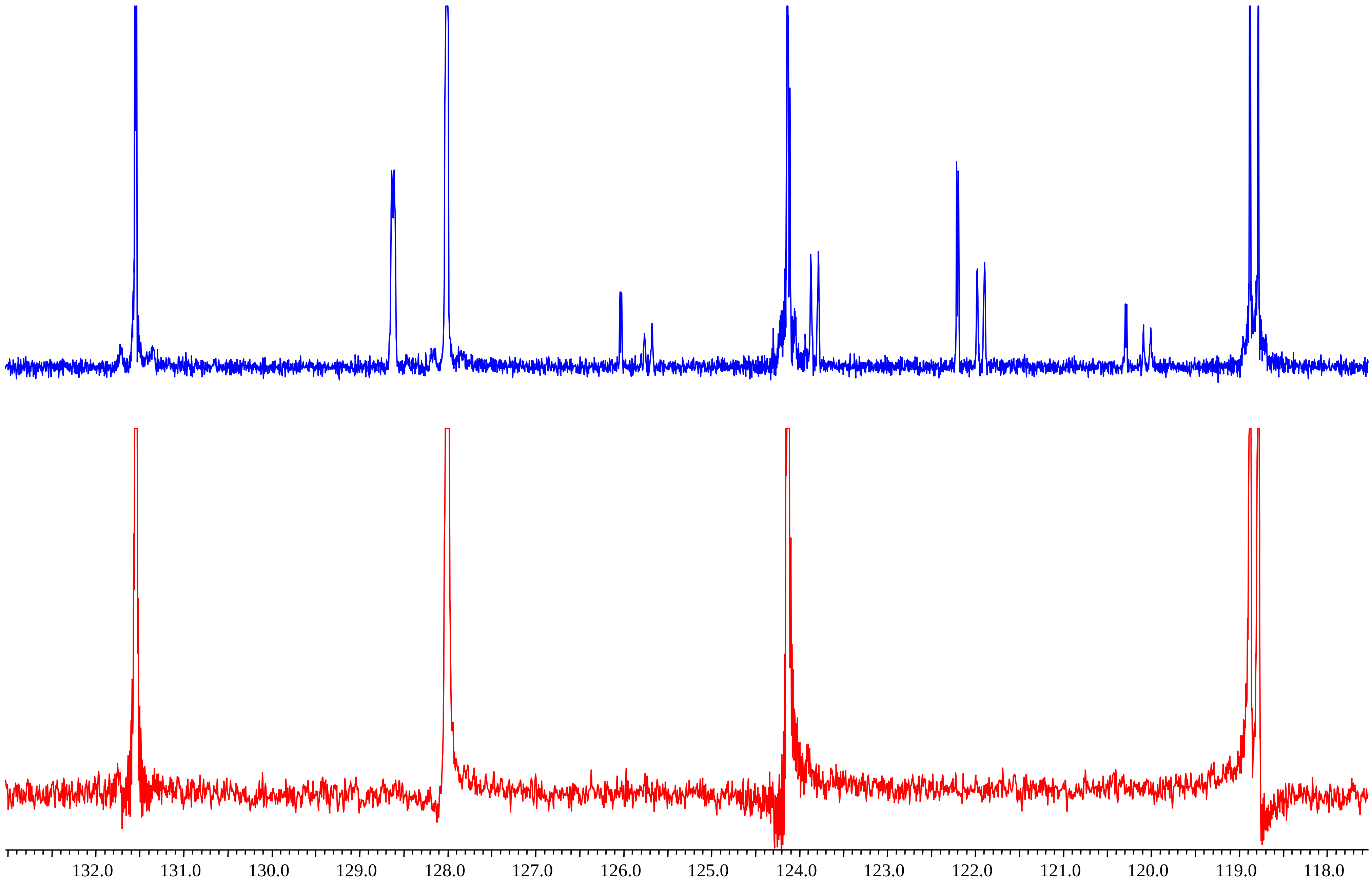


Figure S58. Low-field fragment of ^{13}C-{^{1}H} and ^{13}C-{^{1}H}-dept NMR spectra (150.9 MHz, acetone-d_6) of phosphorane (**3**).

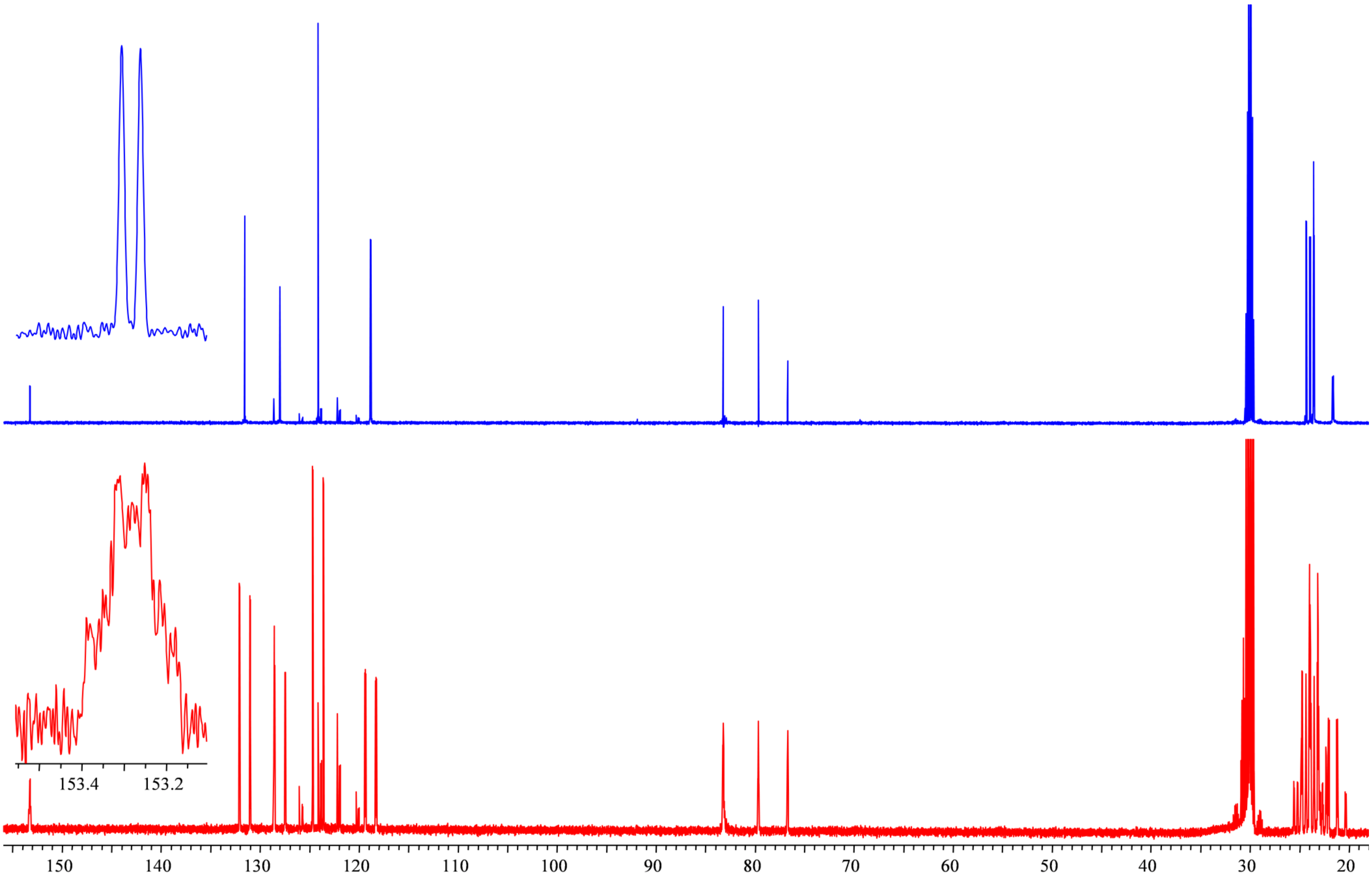


Figure S59. $^{13}C-\{^{1}H\}$ and ^{13}C NMR spectra (150.9 MHz, acetone-d_6) of compound (**3**).

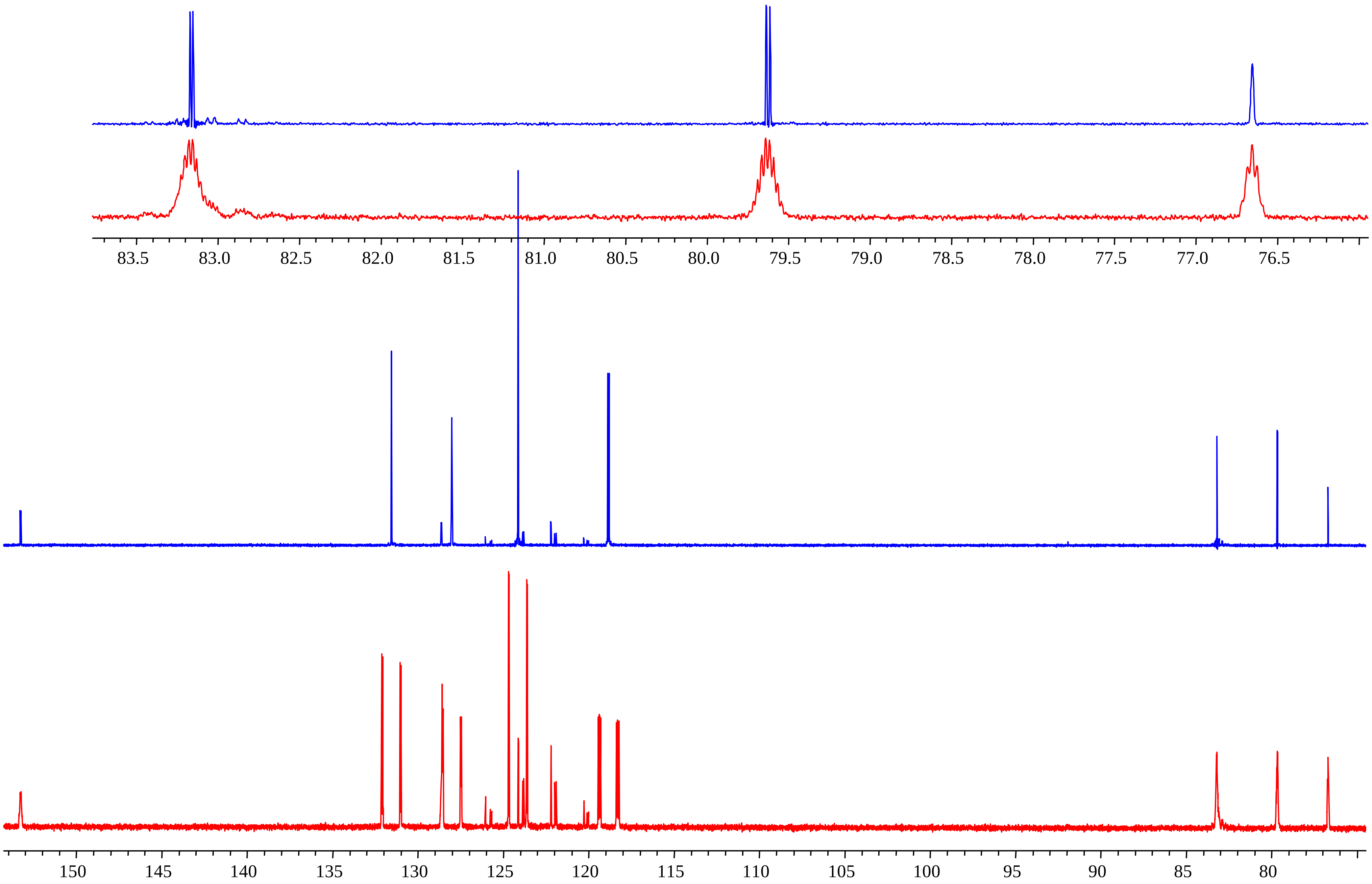


Figure S60. The 75-155 ppm region of $^{13}C-\{^{1}H\}$ and ^{13}C NMR spectra (150.9 MHz, acetone-d_6) of compound (**3**).

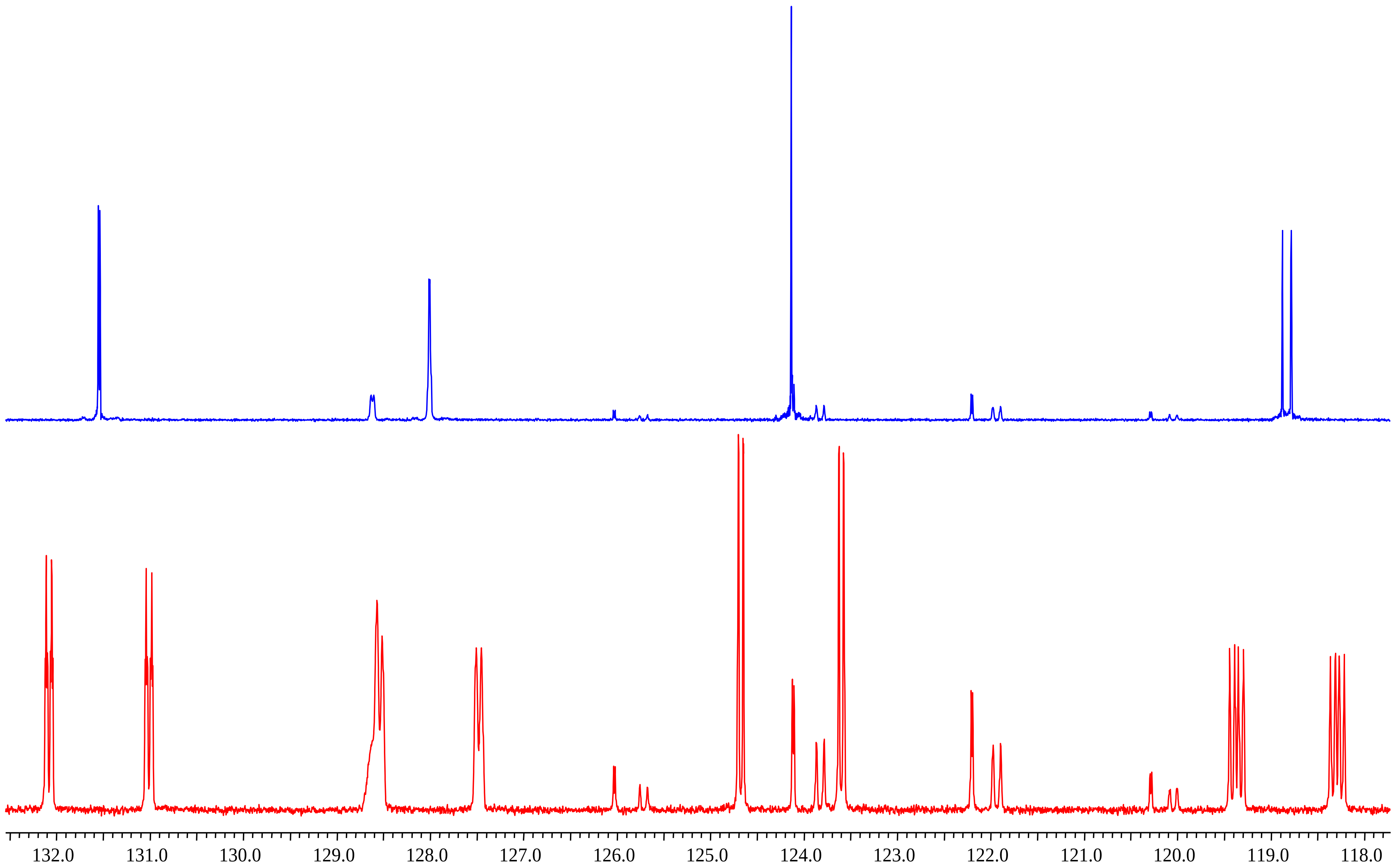


Figure S61. The 118-133 ppm region of ^{13}C-{^{1}H} and ^{13}C NMR spectra (150.9 MHz, acetone-d_6) of compound (**3**).

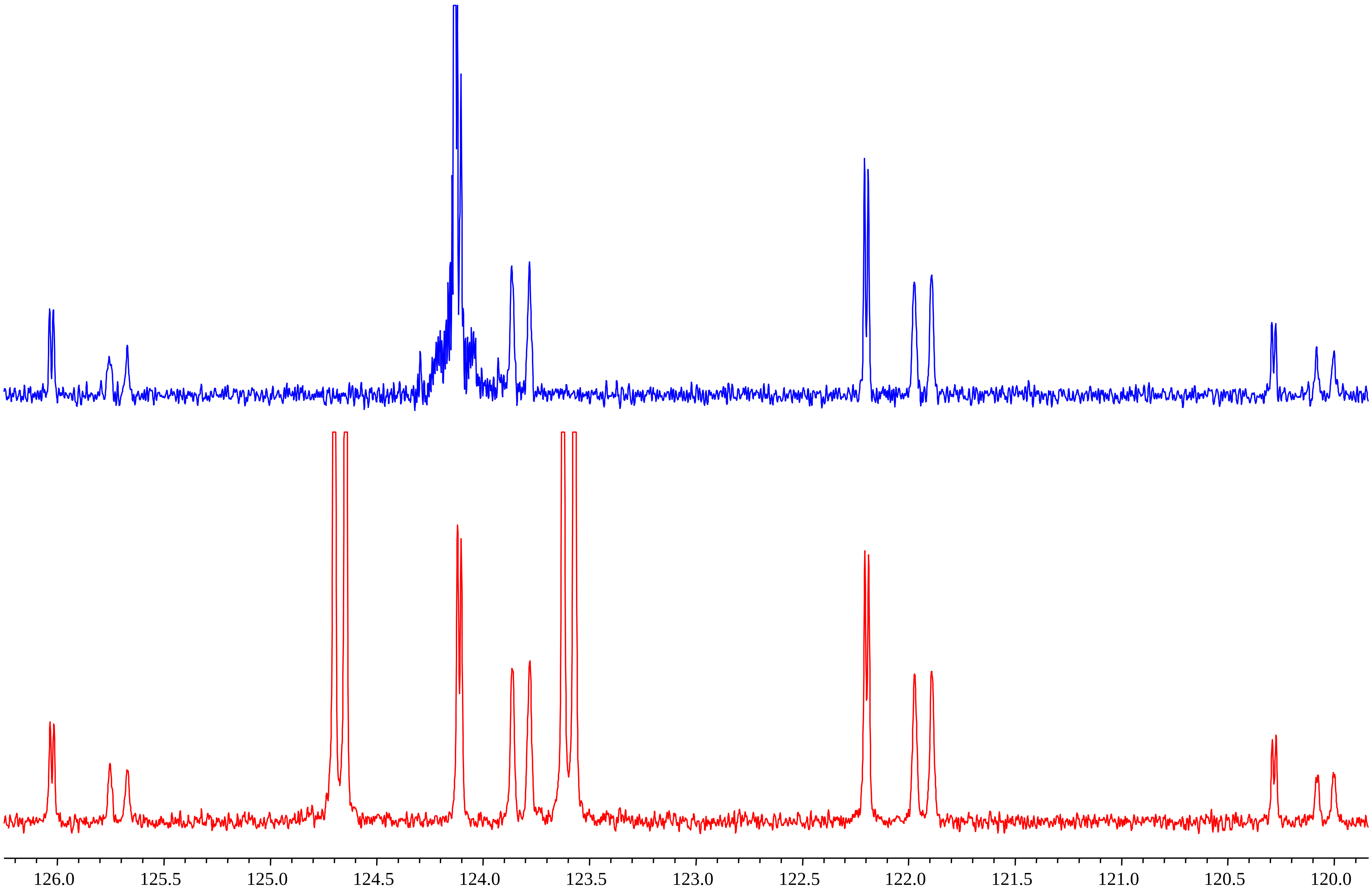


Figure S62. The 120-127 ppm region of ^{13}C-{^{1}H} and ^{13}C NMR spectra (150.9 MHz, acetone-d_6) of compound (**3**).

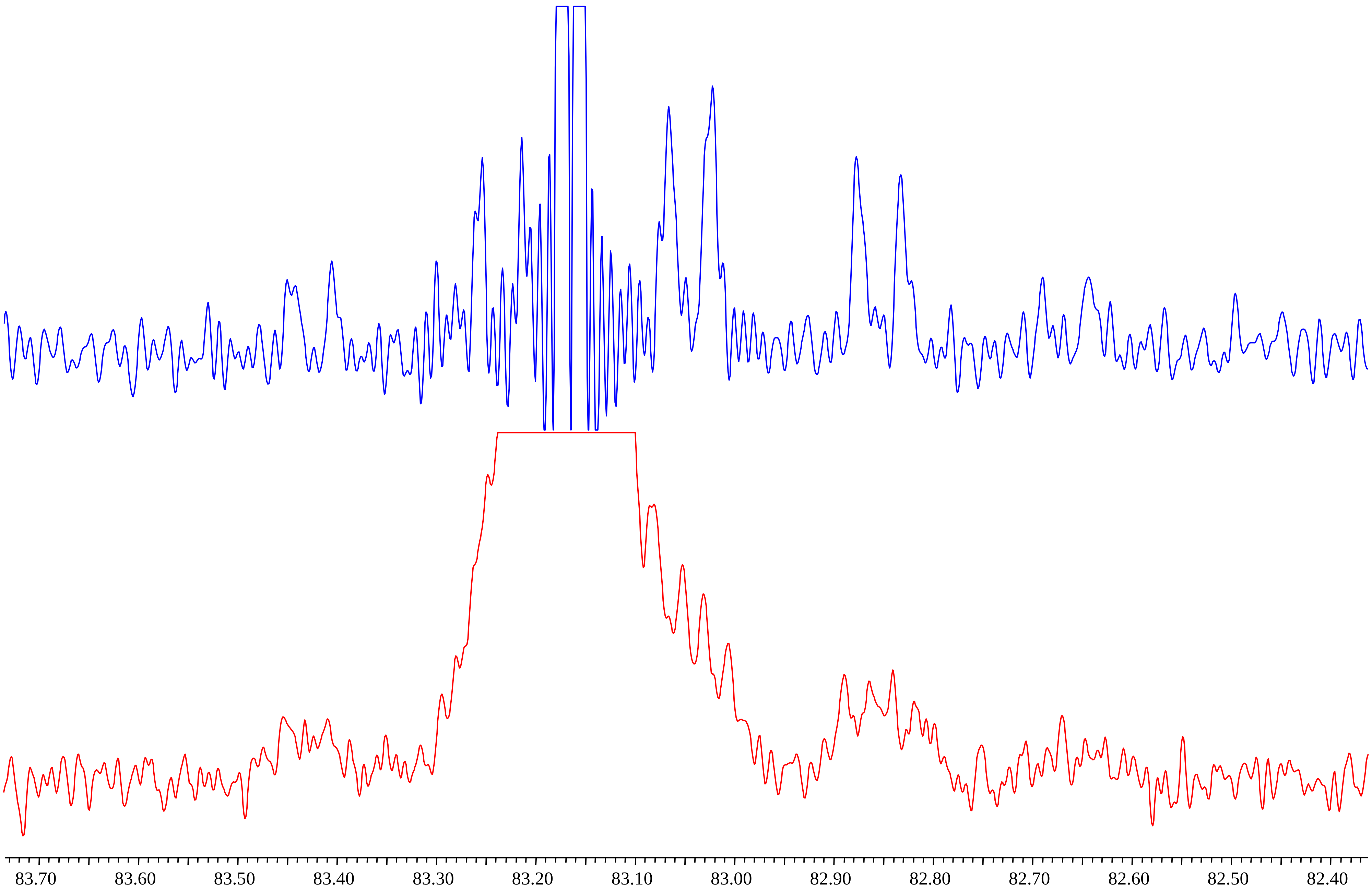


Figure S63. The 82-84 ppm region of $^{13}C-\{^1H\}$ and ^{13}C NMR spectra (150.9 MHz, acetone-d_6) of compound (**3**).

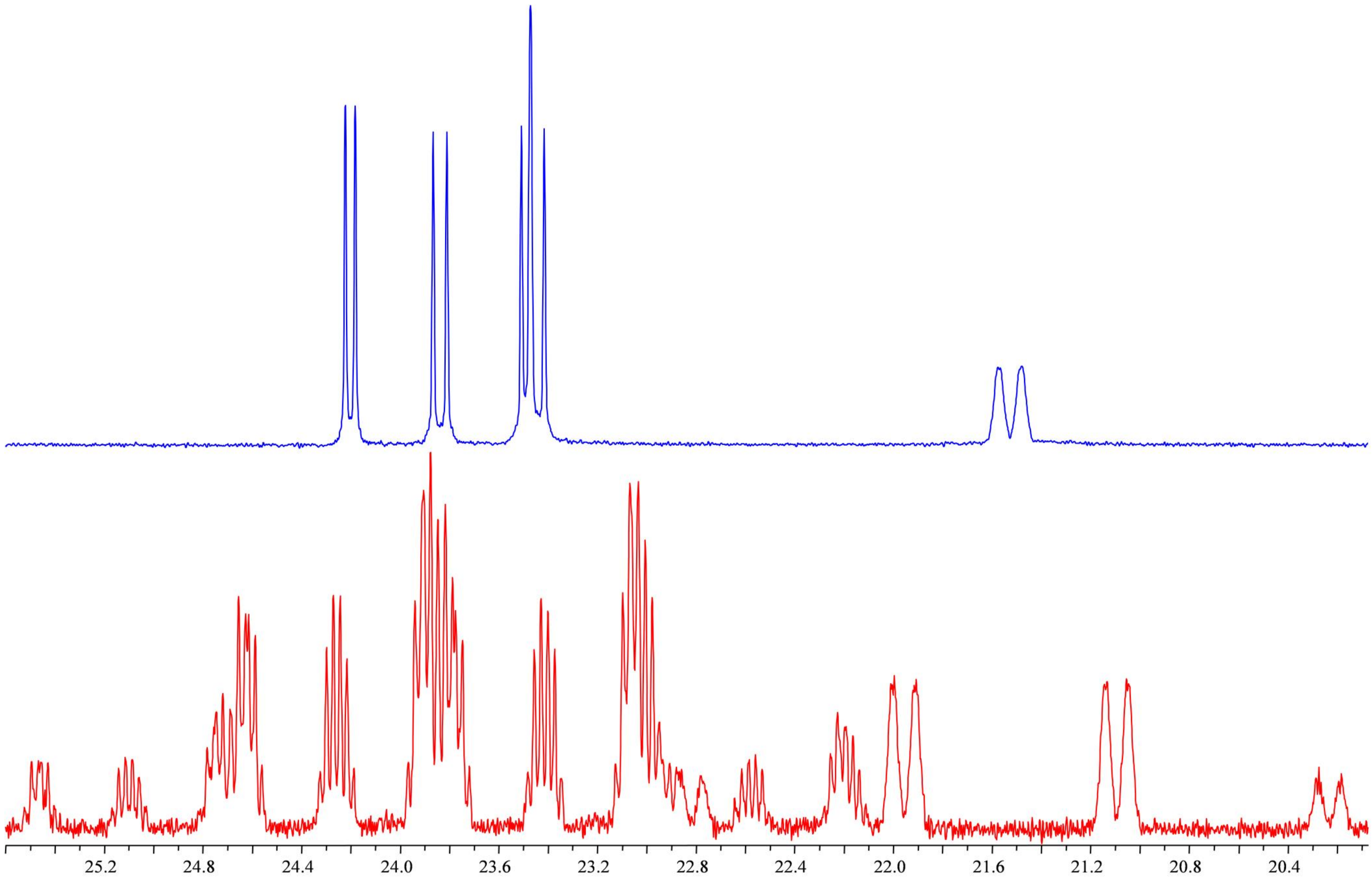


Figure S64. High-field fragment of ^{13}C-{^{1}H} and ^{13}C NMR spectra (150.9 MHz, acetone-d_6) of compound (**3**).

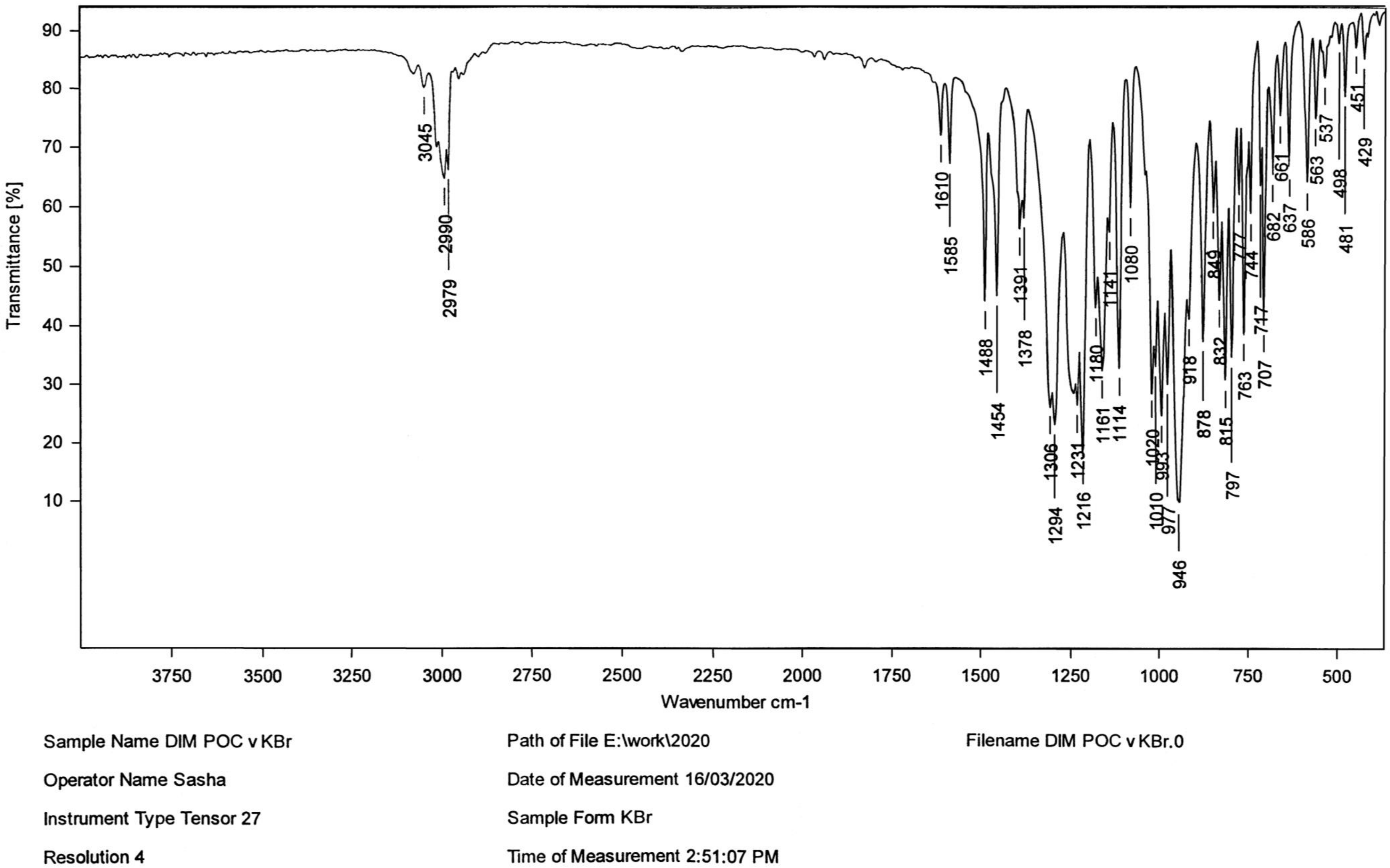
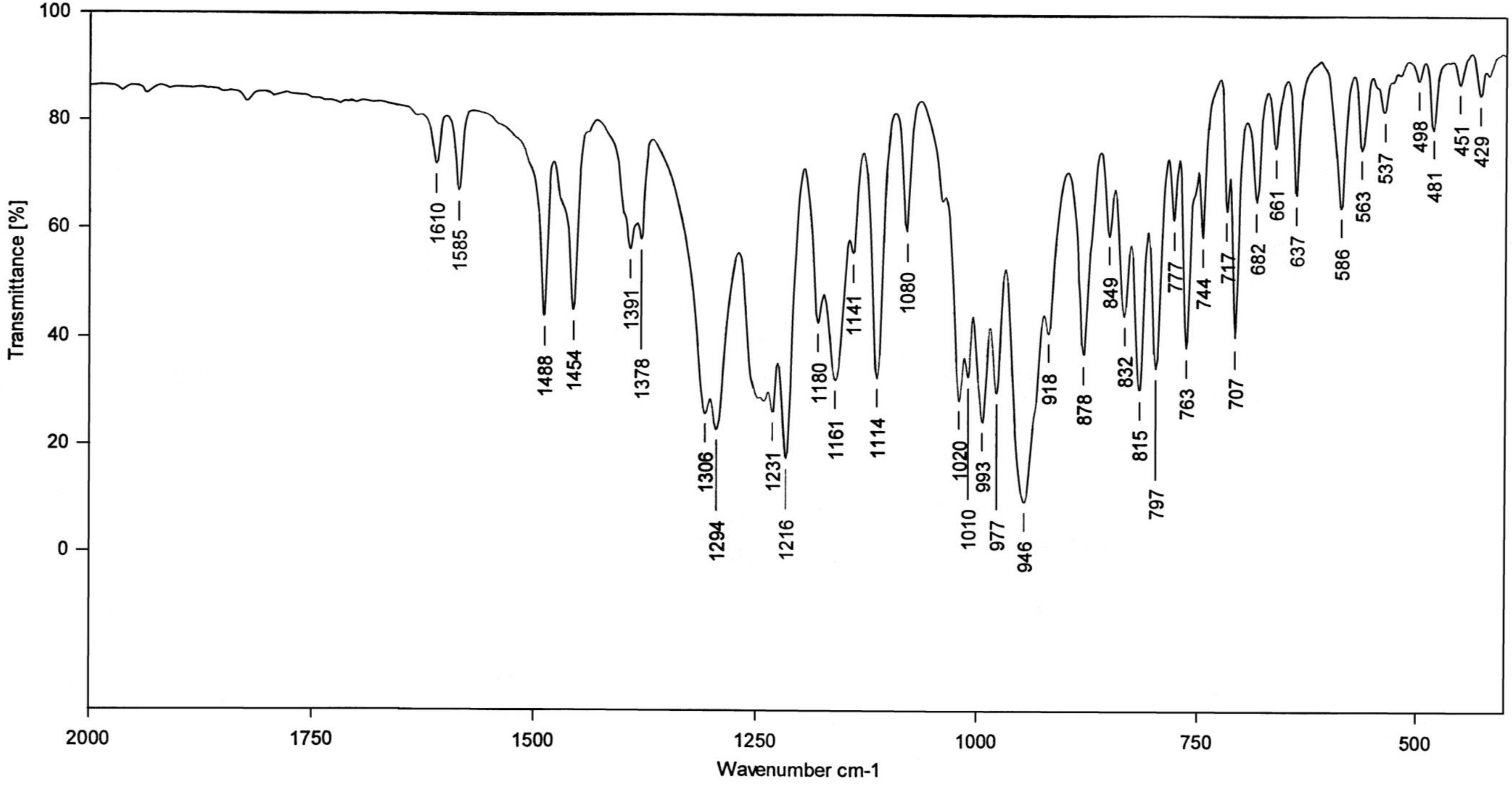


Figure S65. IR spectrum (400-4000 cm^{-1}, KBr pellet) of phosphorane (**3**).



Sample Name DIM POC v KBr

Operator Name Sasha

Instrument Type Tensor 27

Resolution 4

Path of File E:\work\2020

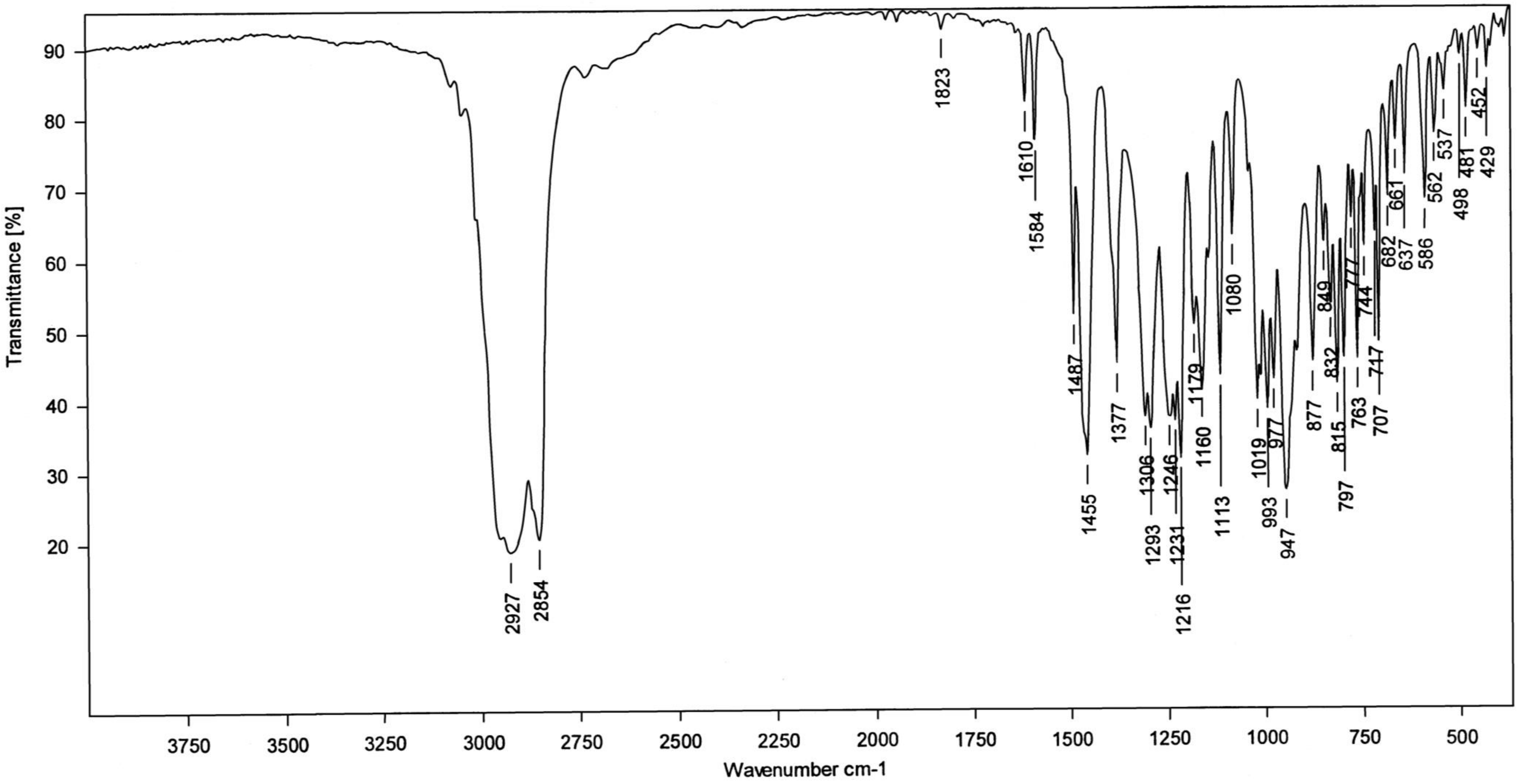
Date of Measurement 16/03/2020

Sample Form KBr

Time of Measurement 2:51:07 PM

Filename DIM POC v KBr.0

Figure S66. Fragment of IR spectrum (400-2000 cm^{-1}, KBr pellet) of phosphorane (**3**).



Sample Name DIM POC v vas

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Filename DIM POC v vas.0

Operator Name Sasha

Date of Measurement 16/03/2020

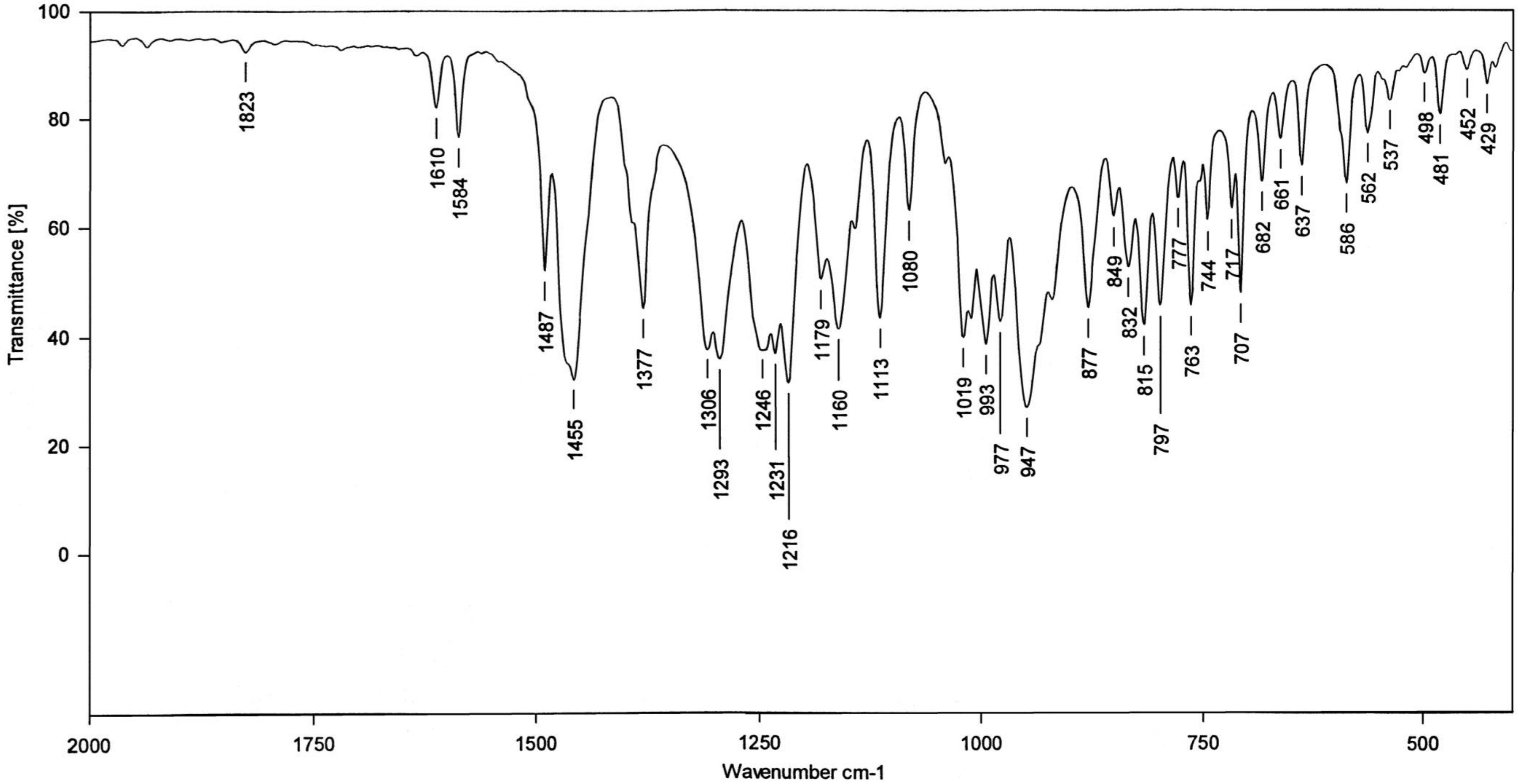
Instrument Type Tensor 27

Sample Form vazelin

Resolution 4

Time of Measurement 2:58:55 PM

Figure S67. IR spectrum (400-4000 cm^{-1}, Vaseline oil) of phosphorane (**3**).



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Operator Name Sasha	Date of Measurement 16/03/2020	
Instrument Type Tensor 27	Sample Form vazelin	
Resolution 4	Time of Measurement 2:58:55 PM	

Figure S68. Fragment of IR spectrum (400-2000 cm^{-1}, Vaseline oil) of phosphorane (**3**).