Electronic supplementary materials. *Mendeleev Commun.*, 2019, **29**, 506–508

The reaction of 4-(1,3,2-benzodioxaphosphol-2-yloxy)-3-*tert*-butylpent-4-en-2-one with hexafluoroacetone

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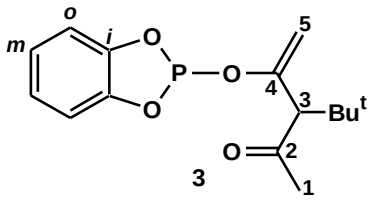
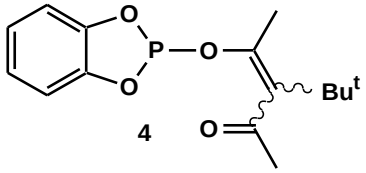
Table of contents

General remarks. NMR spectra were recorded using a 400 MHz spectrometer (400 MHz, ^{1}H; 162.0 MHz, ^{31}P; 376.3 MHz, ^{19}F; 100.6 MHz, ^{13}C) at 25 °C in $CDCl_3$, chemical shifts were measured relative to the signals of the solvent. High-resolution mass spectra (HRMS) were measured in EI mode with magnetic mass analyzers. Elemental analysis was performed on EuroVector-3000 instrument (C, H, N) or manually by pyrolysis in an oxygen stream (P).

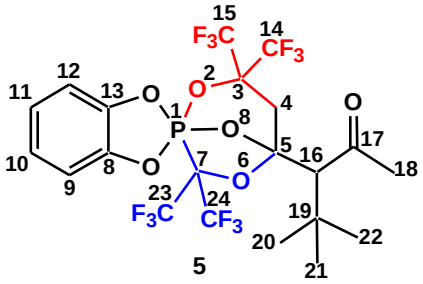




4-(1,3,2-Benzodioxaphosphol-2-yloxy)-3-*tert*-butylpent-4-en-2-one 3. ***Method A.*** In a three-necked 100 ml flask equipped with a stirrer, a reflux condenser, and an inlet for argon, there were placed benzene (100 ml), 3-*tert*-butylacetylacetone **1** (12.4 g, 79 mmol), triethylamine (12.2 ml, 87 mmol), chlorotrimethylsilane (3.5 ml, 28 mmol) and 2-chlorobenzo-1,3,2-dioxaphosphole **2** (13.9 g, 79 mmol). The mixture was heated (80 °C) for 64 hours, then cooled, the precipitate was filtered off, the filtrate was concentrated on a rotary evaporator, the residue was diluted with pentane (50 ml) and kept at 4 °C in a refrigerator for 12 hours. The precipitate formed was filtered off, the filtrate was concentrated on a rotary evaporator, and the residue was distilled in vacuum. Yield of the mixture of compounds **3** and **4** (4 : 1) was 13.3 g (57%), bp 116−121 °C (0.2 Torr). ^{31}P-{^{1}H} spectrum, $CDCl_3$: δ_P 129.8 ppm (s) (**3**) (80%), δ_P 130.0 ppm (s) (**4**) (20%).

Method B. In a 100 ml three-necked flask equipped with a stirrer, a reflux condenser, and an inlet for argon, were placed toluene (100 ml), 3-*tert*-butylacetylacetone **1** (11.2 g, 72 mmol), triethylamine (12.2 ml, 87 mmol), catalytic quantity of zinc chloride (250 mg) and 2-chloro-1,3,2-benzodioxaphosphole **2** (12.5 g, 72 mmol). The mixture was heated at 110 °C for 22 h and cooled. The precipitate was filtered off, the filtrate was concentrated on a rotary evaporator, the residue was diluted with pentane (50 ml) and kept at 4 °C in a refrigerator for 12 hours. The resulting precipitate was filtered off, the filtrate was concentrated on a rotary evaporator, and the residue was distilled in vacuum. Yield of compound **3** was 18.5 g (88%), bp 117−120 °C (0.1 Torr). IR (film), cm^{-1}: 3069, 2958, 2909, 2870, 1718, 1637, 1591, 1477, 1420, 1397, 1366, 1355, 1333, 1304, 1229, 1151, 1094, 1035, 1010, 978, 922, 845, 795, 744, 714, 666. ^{1}H NMR spectrum, δ ppm, *J* Hz: 7.11 and 6.99 two m (C_6H_4, 4H), 4.84 ddd (H-5, 1H, $^{2}J_{HH}$ 2.3 Hz, $^{4}J_{PH}$ 1.1-1.2 Hz, $^{4}J_{HH}$ 1.1 Hz), 4.56 d (H-5, 1H, $^{2}J_{HH}$ 2.3 Hz), 3.01 d (H-3, 1H, $^{4}J_{HH}$ 1.1 Hz), 2.11 s (H-1, 3H), 0.99 s [(CH_3)$_3$C, 9H]. ^{13}C NMR spectrum, δ_C ppm, *J* Hz (hereinafter a view of signal in ^{13}C-{^{1}H} NMR spectrum is in parentheses): 205.64 dq (s) (C^{2}, $^{2}J_{HC^1C}$ 5.8 Hz, $^{2}J_{HC^3C}$ 5.8 Hz), 151.62 dtd (d) (C^{4}, $^{2}J_{HC^3C}$ 7.1 Hz, $^{2}J_{HC^5C}$ 5.1 Hz, $^{2}J_{POC}$ 3.0 Hz), 144.70 dddd (d) (C^{i}, $^{3}J_{HC^mCC}$ 7.8-7.9 Hz, $^{3}J_{HC^oCC}$ 7.8-7.9 Hz, $^{3}J_{POCC}$ 7.9 Hz, $^{2}J_{HC^oC}$ 2.4 Hz), 122.96 ddd (d) (C^{m}, $^{1}J_{HC}$ 162.9 Hz, $^{3}J_{HC^oCC}$ 8.1 Hz, $^{4}J_{POCCC}$ 4.5 Hz), 112.8 br. ddd (br. d) (C^{o}, $^{1}J_{HC}$ 163.3 Hz, $^{3}J_{HC^mCC}$ 8.2 Hz, $^{3}J_{POCC}$ 4.1 Hz), 100.96 tdd (d) (C^{5}, $^{1}J_{HC}$ 159.0 Hz, $^{3}J_{POCC}$ 15.1 Hz, $^{3}J_{HC^3CC}$ 3.3 Hz), 66.71 br. d (s) (C^{3}, $^{1}J_{HC}$ 126.1 Hz), 34.08 ddecet (s) (Me$_3$*C*, $^{2}J_{HC^3C}$ 3.9 Hz, $^{2}J_{HCC}$ 3.9 Hz), 31.95 q (s) (C^{1}, $^{1}J_{HC}$ 127.5 Hz), 28.23 qseptd (s) [(*C*H$_3$)$_3$C, $^{1}J_{HC}$ 125.6 Hz, $^{3}J_{HCCC}$ 4.5 Hz, $^{3}J_{HCCC}$ 4.2-4.4 Hz]. ^{31}P-

{^{1}H} NMR spectrum, 162.0 MHz, $CDCl_3$: δ_P 129.8 ppm (s). Mass-spectrum (ESI HRMS), *m*/*z*: 294.1022 $[M]^{+\bullet}$ (Calculated 294.1021). Found, %: C, 61.11; H, 6.77; P, 10.44. Calculated for $C_{15}H_{19}O_4P$, %: C, 61.22; H, 6.51; P, 10.53.



3,3,7,7-Tetrakis(trifluoromethyl)-1,1-*o*-phenylenedioxa-5-(1-*tert*-butyl-2-oxopropyl)-2,6,8-trioxa-1-phosphabicyclo[4.3.2^{1,5}]octane 5. Hexafluoroacetone (4.65 g, 28 mmol) was condensed into a solution of compound **3** (4.0 g, 14 mmol) in CCl_4 (20 ml) cooled under argon to −40 °C. The mixture was kept until reaching 20 °C for 8 hours. The next day, a crystalline precipitate of compound **5** was formed, which was filtered and dried under vacuum (0.1 Torr). Yield was 5.7 g (67%), mp 107−109 °C. IR spectrum (Nujol), cm^{-1}: 1713, 1629, 1600, 1489, 1422, 1402, 1356, 1340, 1326, 1296, 1281, 1242, 1200, 1154, 1123, 1054, 1042, 1019, 974, 946, 925, 898, 878, 853, 839, 810, 775, 751, 723, 709, 700, 668, 636, 559, 547, 523, 504, 426. ^{1}H NMR spectrum, δ ppm, *J* Hz: 1.18 s [$C(CH_3)_3$, 9H], 2.24 s (H-18, 3H), 2.73 (C^4H_X, 1H, $^2J_{AX}$ 17.1 Hz, $^4J_{FH}$ 1.0, $^4J_{PH}$ 1.0), 3.49 s (H-16, 1H), 3.51 br. d (C^4H_A, 1H, $^2J_{AX}$ 17.1 Hz), 7.02 dddd (H-11, 1H, $^3J_{H^{12}H}$ 7.9 Hz, $^4J_{H^{10}H}$ 6.7 Hz, $^5J_{PH}$ 2.4 Hz, $^4J_{H^9H}$ 1.3 Hz), 7.08-7.11 m, (H-9, H-10, 2H), 7.20 ddd (H-12, 1H, $^3J_{H^{11}H}$ 7.9 Hz, $^4J_{PH}$ 1.5-1.6 Hz, $^3J_{H^{10}H}$ 1.3-1.4 Hz). ^{13}C NMR spectrum, δ_C ppm, *J* Hz: 209.44 m (s) (C^{17}, $^2J_{HC^{18}C}$ 5.0-5.1, $^2J_{HC^{16}C}$ 2.9-3.1 Hz), 144.71 m (s) (C^{13}, $^3J_{HC^{11}CC}$ 8.2 Hz, $^3J_{HC^9CC}$ 6.8 Hz, $^2J_{HC^{12}C}$ 1.4-1.5 Hz), 140.53 dddd (d) (C^8, $^3J_{HC^{10}CC}$ 12.0-12.5 Hz, $^3J_{HC^{12}CC}$ 8.2-8.5 Hz, $^2J_{HC^{19}C}$ 4.7-5.1 Hz, $^2J_{POC}$ 3.3 Hz), 124.60 dd (s) (C^{11}, $^1J_{HC}$ 163.0 Hz, $^3J_{HC^9CC}$ 7.1 Hz), 122.39 ddd (s) (C^{10}, $^1J_{HC}$ 165.7 Hz, $^3J_{HC^{12}CC}$ 7.3 Hz, $^2J_{HC^9C}$ 1.8 Hz), 122.04 qdq (qdq) ($C^{23}F_3$, $^1J_{FC}$ 290.1 Hz, $^2J_{PC^7C}$ 6.4 Hz, $^3J_{FC^{24}C^7C}$ 2.2 Hz), 121.74 qdd (q) ($C^{15}F_3$, $^1J_{FC}$ 288.1 Hz, $^3J_{HC^4C^3C}$ 7.0 Hz, $^3J_{HC^4C^3C}$ 4.7 Hz), 121.20 br. qd (br. qd) ($C^{22}F_3$, $^1J_{FC}$ 286.0 Hz, $^2J_{PC^7C}$ 2.0 Hz), 121.13 br. qd (br. qdd) ($C^{14}F_3$, $^1J_{FC}$ 285.6 Hz, $^3J_{POC^3C}$ 15.3-16.0 Hz, $^3J_{HC^4C^3C}$ 5.6 Hz), 111.85 ddd (d) (C^{12}, $^1J_{HC}$ 167.1 Hz, $^3J_{POC^{13}C}$ 18.5 Hz, $^3J_{HC^{10}CC}$ 7.1 Hz), 111.46 ddddd (d) (C^9, $^1J_{HC}$ 166.6 Hz, $^3J_{POC^8C}$ 12.6 Hz, $^3J_{HC^{11}CC}$ 8.6 Hz, $^2J_{HC^{10}C}$ 1.2-1.3 Hz, $^4J_{HC^{12}CC^{10}C}$ 1.2-1.3 Hz), 80.27 sept.d (sept.ddd) (C^3, $^2J_{FC^{14,15}C}$ 31.7 Hz, $^2J_{POC}$ 7.8 Hz, $^2J_{HC^4C}$ 4.1 Hz, $^2J_{HC^4C}$ 1.7-1.8 Hz), 75.31 d.sept (d.sept) (C^7, $^1J_{PC}$ 165.8 Hz, $^2J_{FC^{23,24}C}$ 31.5 Hz), 103.87 br. dm (br. d) (C^{16}, $^1J_{HC}$ 130.0 Hz, $^3J_{POC^5C}$ 1.8 Hz), 36.06 qd (s) (C^{18}, $^1J_{HC}$ 127.9 Hz, $^3J_{HC^{16}CC}$ 1.0 Hz), 34.61 m (s) (C^{19}, $^2J_{HC^{20\text{-}22}C}$ 3.9 Hz, $^2J_{HC^{16}C}$ 3.9 Hz), 33.96 br. td (br. s) (C^4, $^1J_{HC}$ 135.6 Hz, $^3J_{HC^{16}CC}$ 4.4 Hz), 29.14 q.sept.d (s) ($C^{20\text{-}22}$, $^1J_{HC}$ 126.1 Hz, $^3J_{HC^{20\text{-}22}CC}$ 4.4 Hz, $^3J_{HC^{16}CC}$ 4.4 Hz). ^{19}F NMR spectrum, δ_F ppm, *J* Hz: −67.94 m ($C^{23}F_3$, $^4J_{FC^{24}CC^{23}F}$ 11.5-12.0 Hz, $^7J_{FC^{15}C^{23}F}$ 11.5-12.0 Hz), −68.01 m ($C^{24}F_3$, $^4J_{FC^{23}CC^{24}F}$ 11.5 Hz, $^3J_{PC^7C^{24}F}$ 6.3 Hz), −73.63 q ($C^{14}F_3$, $^4J_{FC^{15}CC^{14}F}$ 11.5 Hz), −77.13 qq ($C^{15}F_3$, $^4J_{FC^{14}CC^{15}F}$ 11.5 Hz, $^7J_{FC^{23}C^{15}F}$ 11.5 Hz). ^{31}P / ^{31}P-{^{1}H} NMR spectra, δ_P ppm, *J* Hz: –28.5

br. q (br. q) ($^3J_{FCCP}$ 5.0 Hz). Mass-spectrum (ESI HRMS), *m*/*z*: 626.0727 $[M]^{+\bullet}$ (Calculated 626.0728). Found, %: 40.11; H, 3.18; P, 5.03. Calculated for $C_{21}H_{19}F_{12}O_6P$, %: C, 40.27; H, 3.06; P, 4.95.

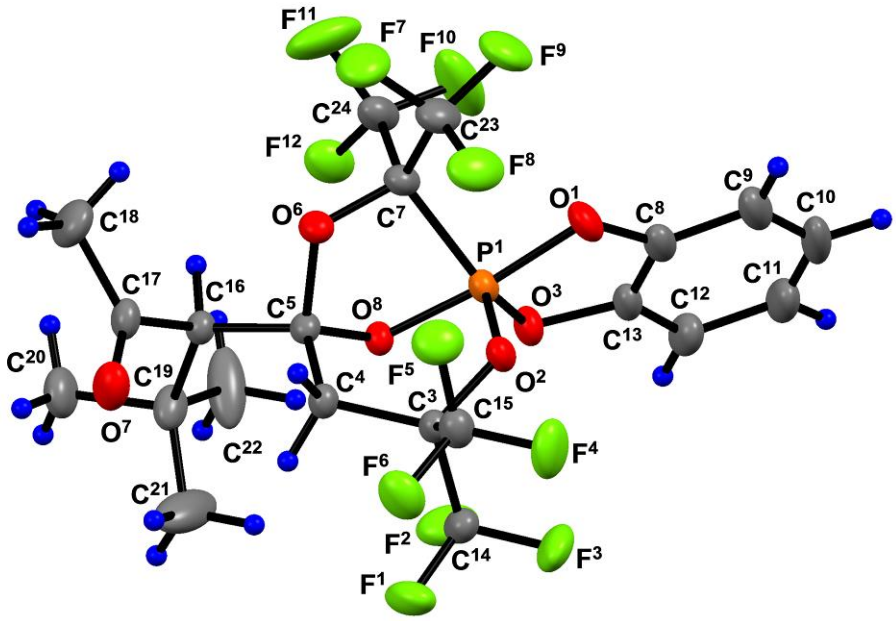


Figure S1. Geometry of molecule **5** in the crystal ($P^1_SC^5_SC^{16}_R$ / $P^1_RC^5_RC^{16}_S$-diastereoisomer, $P^1_RC^5_RC^{16}_S$-enantiomer is shown). Non-hydrogen atoms are shown as thermal ellipsoids with a probability of 30%.

Table S1. Bond lengths in the molecule of compound (**5**).

bond	*d*, Å	bond	*d*, Å	bond	*d*, Å	bond	*d*, Å	bond	*d*, Å
P^1–O^1	1.676(3)	F^4–C^{15}	1.321(4)	O^1–C^8	1.381(4)	C^7–C^{24}	1.551(5)	C^{17}–C^{18}	1.492(6)
P^1–O^2	1.603(3)	F^5–C^{15}	1.316(4)	O^3–C^{13}	1.394(4)	C^8–C^9	1.381(5)	C^{19}–C^{20}	1.534(7)
P^1–O^3	1.618(3)	F^6–C^{15}	1.329(4)	O^6–C^7	1.409(4)	C^8–C^{13}	1.361(5)	C^{19}–C^{21}	1.501(8)
P^1–O^8	1.668(2)	F^7–C^{23}	1.330(5)	O^8–C^5	1.397(4)	C^9–C^{10}	1.411(8)	C^{19}–C^{22}	1.540(5)
P^1–C^7	1.899(4)	F^8–C^{23}	1.313(5)	C^3–C^{14}	1.549(5)	C^{10}–C^{11}	1.370(9)	O^2–C^3	1.430(4)
F^1–C^{14}	1.311(4)	F^9–C^{23}	1.323(5)	C^4–C^5	1.536(4)	C^{11}–C^{12}	1.395(6)	O^6–C^5	1.488(4)
F^2–C^{14}	1.308(5)	F^{10}–C^{24}	1.316(5)	C^5–C^{16}	1.553(4)	C^3–C^4	1.551(4)	O^7–C^{17}	1.202(5)
F^3–C^{14}	1.327(4)	F^{11}–C^{24}	1.312(6)	C^7–C^{23}	1.550(6)	C^{16}–C^{19}	1.558(5)	C^3–C^{15}	1.548(5)

Table S2. Bond angles in the molecule of compound (**5**).

Angle	φ (grad)	Angle	φ (grad)	Angle	φ (grad)	Angle	φ (grad)
O^1–P^1–O^2	91.5(1)	C^4–C^3–C^{15}	108.9(2)	F^{10}–C^{24}–C^7	110.9(3)	F^1–C^{14}–C^3	111.6(3)
O^1–P^1–O^3	91.7(1)	C^{14}–C^3–C^{15}	110.1(3)	F^{11}–C^{24}–C^7	112.5(4)	F^2–C^{14}–F^3	106.9(3)
O^1–P^1–O^8	171.2(1)	C^3–C^4–C^5	113.3(2)	P^1–C^7–O^6	103.4(2)	F^2–C^{14}–C^3	111.8(3)
O^1–P^1–C^7	91.7(1)	O^6–C^5–O^8	106.0(2)	P^1–C^7–C^{23}	117.1(2)	F^3–C^{14}–C^3	111.9(3)
O^2–P^1–O^3	116.6(1)	O^6–C^5–C^4	107.7(2)	P^1–C^7–C^{24}	110.2(3)	F^4–C^{15}–F^5	107.1(3)
O^2–P^1–O^8	97.3(1)	O^6–C^5–C^{16}	103.9(2)	O^6–C^7–C^{23}	105.2(3)	F^4–C^{15}–F^6	107.7(3)
O^2–P^1–C^7	107.5(1)	O^8–C^5–C^4	109.1(2)	O^6–C^7–C^{24}	111.0(3)	F^4–C^{15}–C^3	112.8(3)
O^3–P^1–O^8	85.2(1)	O^8–C^5–C^{16}	112.6(2)	C^{23}–C^7–C^{24}	109.5(3)	F^5–C^{15}–F^6	107.6(3)
O^3–P^1–C^7	135.6(1)	C^4–C^5–C^{16}	116.7(3)	O^1–C^8–C^9	126.8(4)	F^5–C^{15}–C^3	110.7(3)
O^8–P^1–C^7	84.8(1)	C^5–C^{16}–C^{17}	107.7(2)	O^1–C^8–C^{13}	111.3(3)	F^6–C^{15}–C^3	110.8(3)
P^1–O^1–C^8	111.7(2)	C^{17}–C^{16}–C^{19}	112.2(3)	C^9–C^8–C^{13}	121.8(4)	C^5–C^{16}–C^{19}	120.4(2)
P^1–O^2–C^3	125.7(2)	O^7–C^{17}–C^{18}	121.5(4)	C^8–C^9–C^{10}	115.2(4)	O^7–C^{17}–C^{16}	121.2(3)
P^1–O^3–C^{13}	113.3(2)	C^{16}–C^{19}–C^{20}	108.2(4)	C^9–C^{10}–C^{11}	122.4(4)	C^{16}–C^{17}–C^{18}	117.3(3)
C^5–O^6–C^7	112.2(2)	C^{16}–C^{19}–C^{22}	108.0(3)	C^{10}–C^{11}–C^{12}	121.7(5)	C^{16}–C^{19}–C^{21}	114.8(4)
P^1–O^8–C^5	111.1(2)	C^{20}–C^{19}–C^{22}	105.8(3)	C^{11}–C^{12}–C^{13}	115.2(4)	C^{20}–C^{19}–C^{21}	111.1(4)
O^2–C^3–C^4	114.9(2)	F^7–C^{23}–F^8	107.5(4)	O^3–C^{13}–C^8	111.1(3)	C^{21}–C^{19}–C^{22}	108.5(4)
O^2–C^3–C^{14}	107.4(2)	F^7–C^{23}–C^7	109.9(3)	O^3–C^{13}–C^{12}	125.2(3)	F^7–C^{23}–F^9	107.4(3)
O^2–C^3–C^{15}	103.2(2)	F^8–C^{23}–C^7	111.5(3)	C^8–C^{13}–C^{12}	123.7(3)	F^8–C^{23}–F^9	108.0(3)
C^4–C^3–C^{14}	112.0(2)	F^{10}–C^{24}–F^{11}	109.1(3)	F^1–C^{14}–F^2	108.2(3)	F^9–C^{23}–C^7	112.4(3)

Table S3. Torsion angles in the molecule of compound (**5**).

Angle	τ (grad)	Angle	τ (grad)	Angle	τ (grad)	Angle	τ (grad)
O^2–P^1–O^1–C^8	107.7(2)	O^3–P^1–C^7–O^6	114.9(2)	C^4–C^3–C^{15}–F^6	59.5(3)	C^{24}–C^7–C^{23}–F^7	72.4(4)
O^3–P^1–O^1–C^8	–9.0(2)	O^8–P^1–C^7–O^6	37.2(2)	C^{14}–C^3–C^{15}–F^4	57.2(4)	C^{24}–C^7–C^{23}–F^8	–168.6(3)
C^7–P^1–O^1–C^8	–144.7(2)	P^1–O^1–C^8–C^{13}	7.3(3)	C^{14}–C^3–C^{15}–F^6	–63.6(3)	C^{24}–C^7–C^{23}–F^9	–47.1(4)
O^1–P^1–O^2–C^3	173.0(2)	P^1–O^2–C^3–C^{14}	92.2(3)	O^2–C^3–C^{14}–F^3	54.4(4)	P^1–C^7–C^{24}–F^{10}	–56.2(4)
O^3–P^1–O^2–C^3	–94.3(2)	P^1–O^2–C^3–C^{15}	–151.5(2)	O^2–C^3–C^{15}–F^5	62.8(3)	P^1–C^7–C^{24}–F^{11}	–178.7(3)
O^8–P^1–O^2–C^3	–6.1(2)	P^1–O^2–C^3–C^4	–33.1(3)	C^{15}–C^3–C^{14}–F^2	–177.2(3)	P^1–C^7–C^{24}–F^{12}	62.3(4)
C^7–P^1–O^2–C^3	80.7(2)	P^1–O^3–C^{13}–C^{12}	173.6(3)	C^4–C^3–C^{14}–F^3	–178.7(3)	O^6–C^7–C^{24}–F^{10}	–170.1(3)
O^1–P^1–O^3–C^{13}	8.3(2)	C^5–O^6–C^7–C^{23}	–145.8(2)	C^{15}–C^3–C^{14}–F^1	61.5(3)	O^6–C^7–C^{24}–F^{11}	67.4(4)
O^2–P^1–O^3–C^{13}	–84.2(2)	C^5–O^6–C^7–P^1	–22.4(3)	C^{14}–C^3–C^{15}–F^5	177.1(3)	O^6–C^7–C^{24}–F^{12}	–51.7(4)
O^8–P^1–O^3–C^{13}	–179.9(2)	C^7–O^6–C^5–C^4	109.6(3)	C^{15}–C^3–C^{14}–F^3	–57.3(4)	C^{23}–C^7–C^{24}–F^{10}	74.1(4)
C^7–P^1–O^3–C^{13}	102.6(2)	C^7–O^6–C^5–C^{16}	–126.0(2)	O^2–C^3–C^{15}–F^4	–57.2(3)	C^{23}–C^7–C^{24}–F^{11}	–48.4(4)
O^2–P^1–O^8–C^5	62.1(2)	C^7–O^6–C^5–O^8	–7.1(3)	C^4–C^3–C^{14}–F^1	–59.9(4)	C^{23}–C^7–C^{24}–F^{12}	–167.4(3)
O^3–P^1–O^8–C^5	178.4(2)	C^5–O^6–C^7–C^{24}	95.8(3)	C^4–C^3–C^{14}–F^2	61.5(3)	O^6–C^7–C^{23}–F^7	–47.0(3)
C^7–P^1–O^8–C^5	–44.9(2)	P^1–O^8–C^5–C^{16}	152.4(2)	C^3–C^4–C^5–C^{16}	157.9(3)	O^6–C^7–C^{23}–F^8	72.0(4)
O^8–P^1–C^7–C^{23}	152.4(3)	P^1–O^8–C^5–O^6	39.4(2)	C^3–C^4–C^5–O^6	–85.8(3)	P^1–C^7–C^{23}–F^7	–161.2(2)
O^1–P^1–C^7–C^{24}	90.4(2)	P^1–O^8–C^5–C^4	–76.3(2)	C^3–C^4–C^5–O^8	28.9(3)	P^1–C^7–C^{23}–F^8	–42.2(4)
O^2–P^1–C^7–C^{24}	–177.5(2)	C^{14}–C^3–C^4–C^5	–100.0(3)	O^6–C^5–C^{16}–C^{19}	162.2(3)	C^5–C^{16}–C^{17}–O^7	–71.1(4)
O^3–P^1–C^7–C^{24}	–-3.8(3)	O^2–C^3–C^{14}–F^2	–65.5(3)	C^4–C^5–C^{16}–C^{17}	51.0(3)	C^5–C^{16}–C^{17}–C^{18}	108.4(3)
O^8–P^1–C^7–C^{24}	–81.5(2)	C^{15}–C^3–C^4–C^5	138.0(3)	C^4–C^5–C^{16}–C^{19}	–79.4(4)	C^{19}–C^{16}–C^{17}–O^7	63.7(4)
O^1–P^1–C^7–C^{23}	–35.7(3)	O^2–C^3–C^{14}–F^1	173.1(3)	O^6–C^5–C^{16}–C^{17}	–67.4(3)	C^{19}–C^{16}–C^{17}–C^{18}	–116.8(4)
O^2–P^1–C^7–C^{23}	56.4(3)	O^2–C^3–C^4–C^5	22.8(4)	O^8–C^5–C^{16}–C^{17}	178.3(2)	C^5–C^{16}–C^{19}–C^{20}	–70.6(4)
O^3–P^1–C^7–C^{23}	–129.9(3)	O^2–C^3–C^{15}–F^6	–178.0(2)	O^8–C^5–C^{16}–C^{19}	47.9(4)	C^5–C^{16}–C^{19}–C^{21}	54.1(5)
O^1–P^1–C^7–O^6	–150.9(2)	C^4–C^3–C^{15}–F^4	–179.7(3)	P^1–C^7–C^{23}–F^9	79.3(3)	C^5–C^{16}–C^{19}–C^{22}	175.3(3)
O^2–P^1–C^7–O^6	–58.8(2)	C^4–C^3–C^{15}–F^5	–59.7(3)	O^6–C^7–C^{23}–F^9	–166.5(3)	C^{17}–C^{16}–C^{19}–C^{21}	–74.3(4)

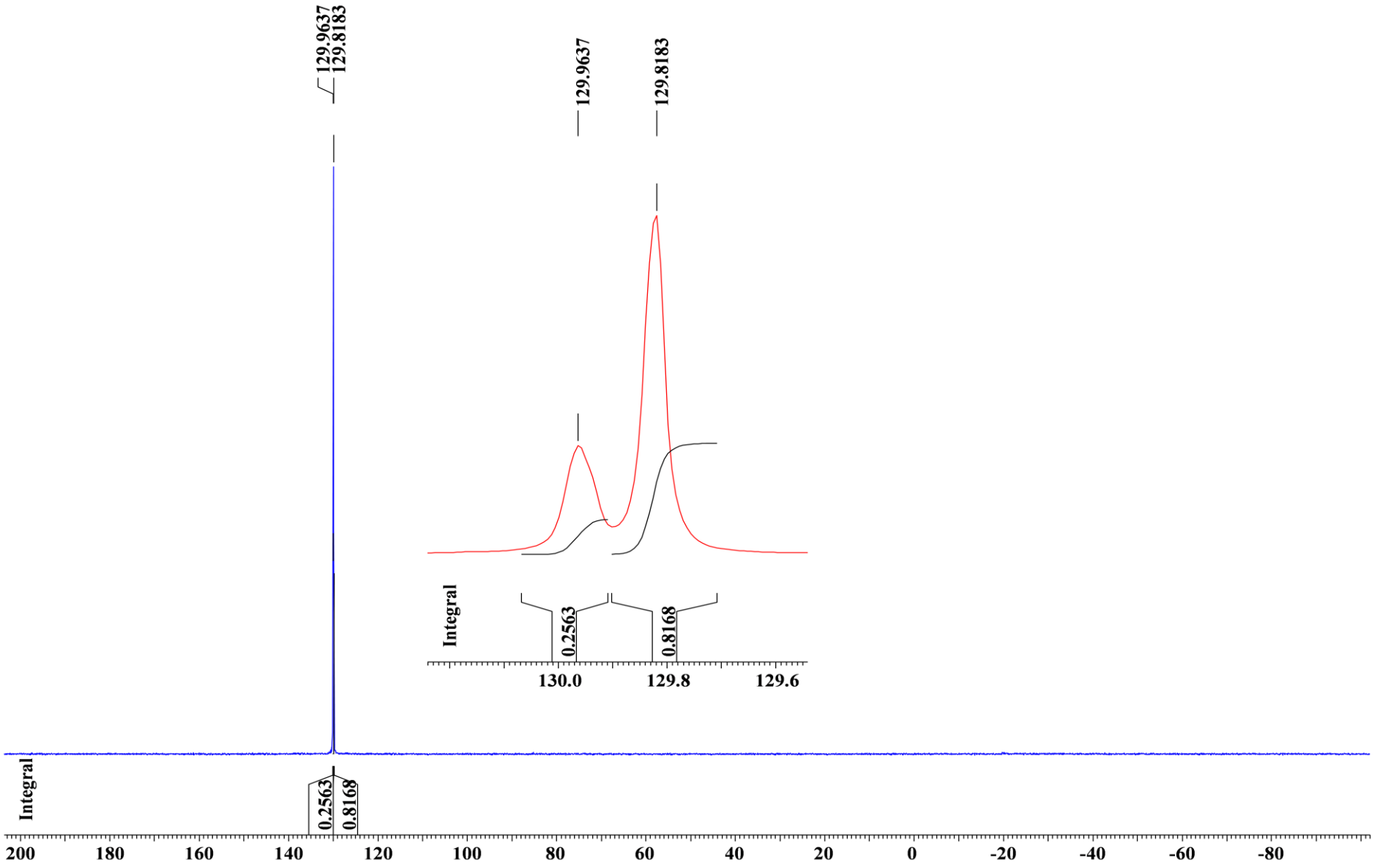


Figure S2. ^{31}P-{^{1}H} NMR spectrum (162.0 MHz, $CDCl_3$, 25°C) of phospholes (**3**, **4**) mixture (procedure *a*).

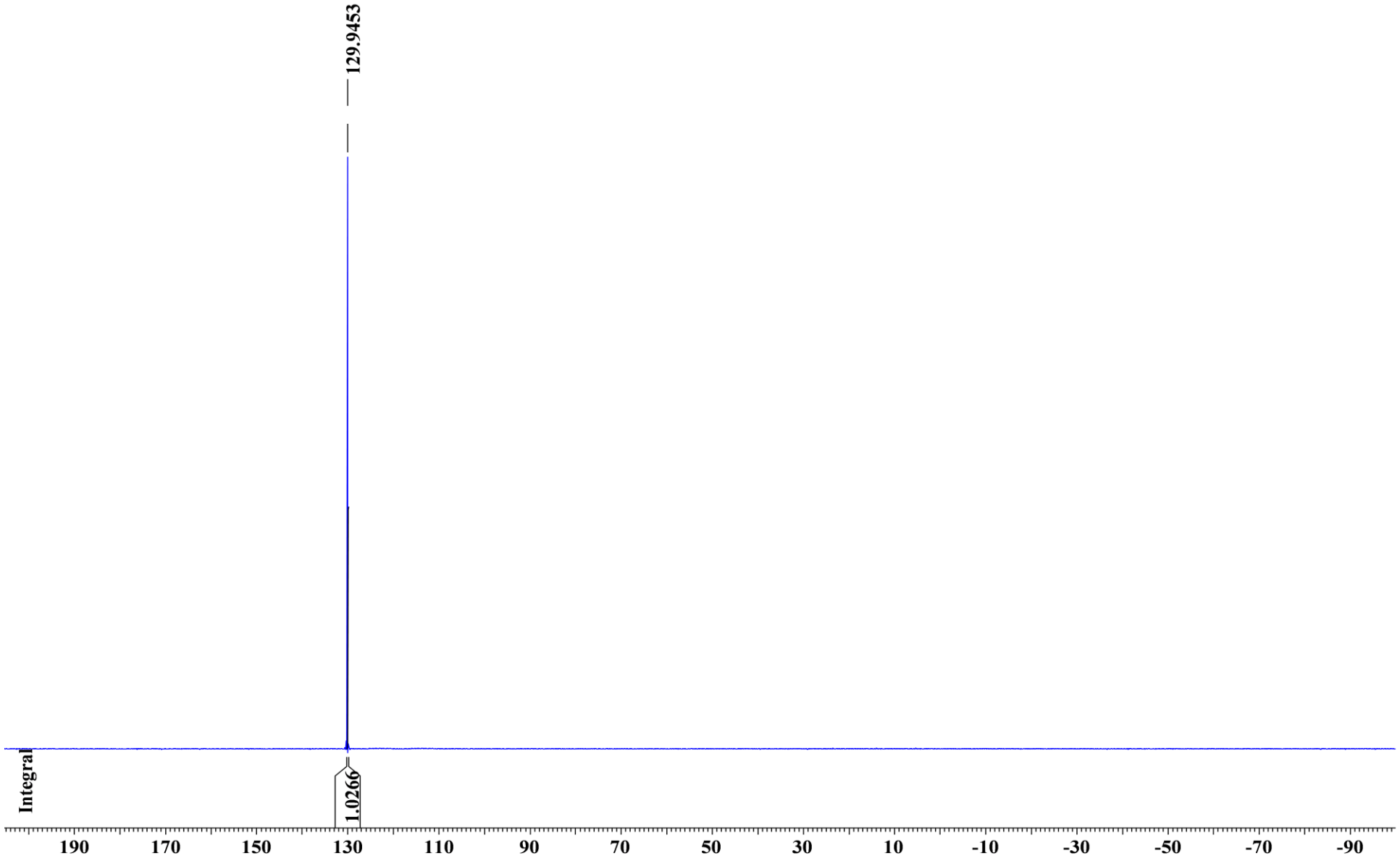


Figure S3. ^{31}P-{^{1}H} NMR spectrum (162.0 MHz, $CDCl_3$, 25°C) of phosphole (**3**) (procedure *b*).

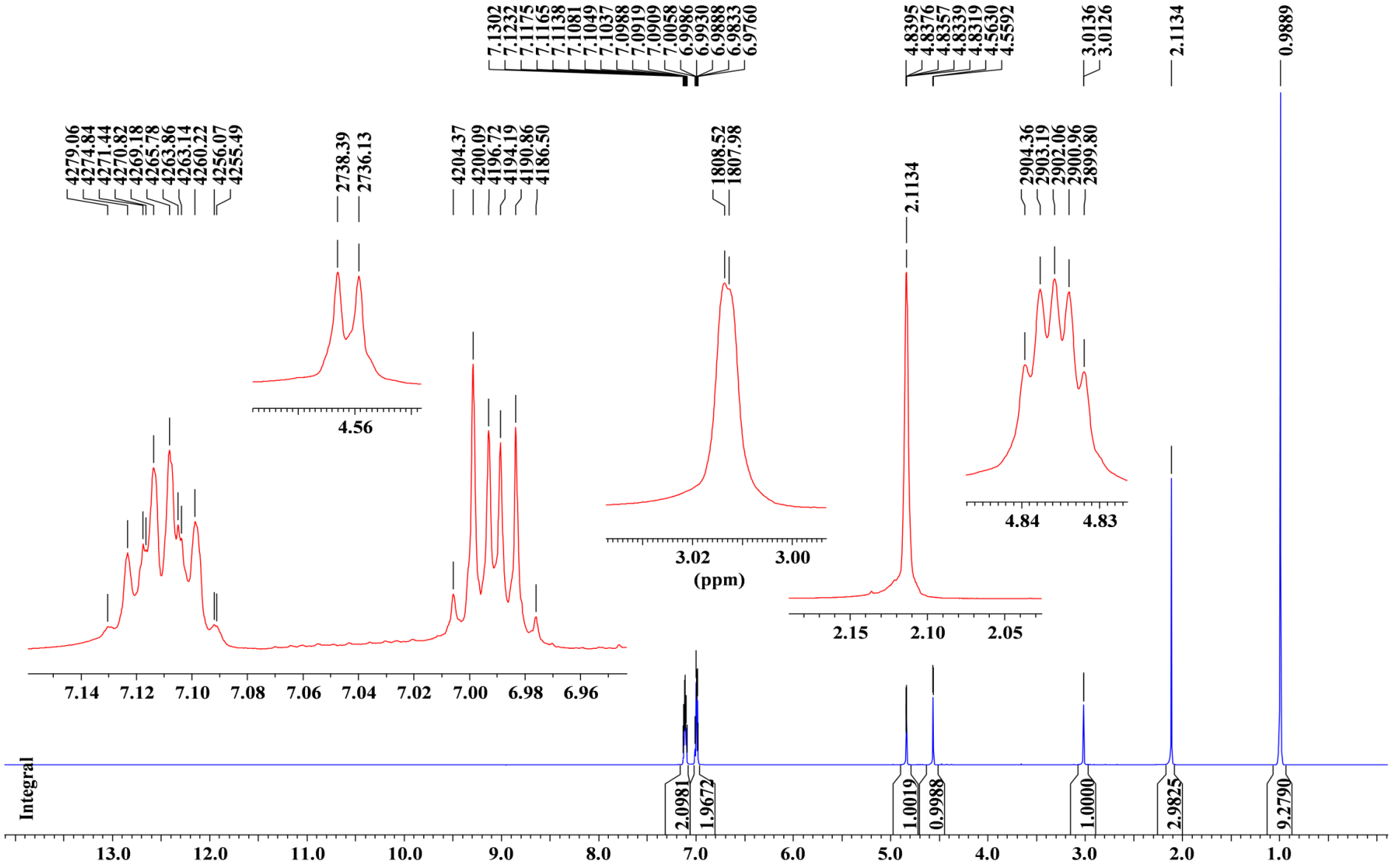


Figure S4. ^{1}H NMR spectrum (400.0 MHz, $CDCl_3$, 25°C) of phosphole (**3**).

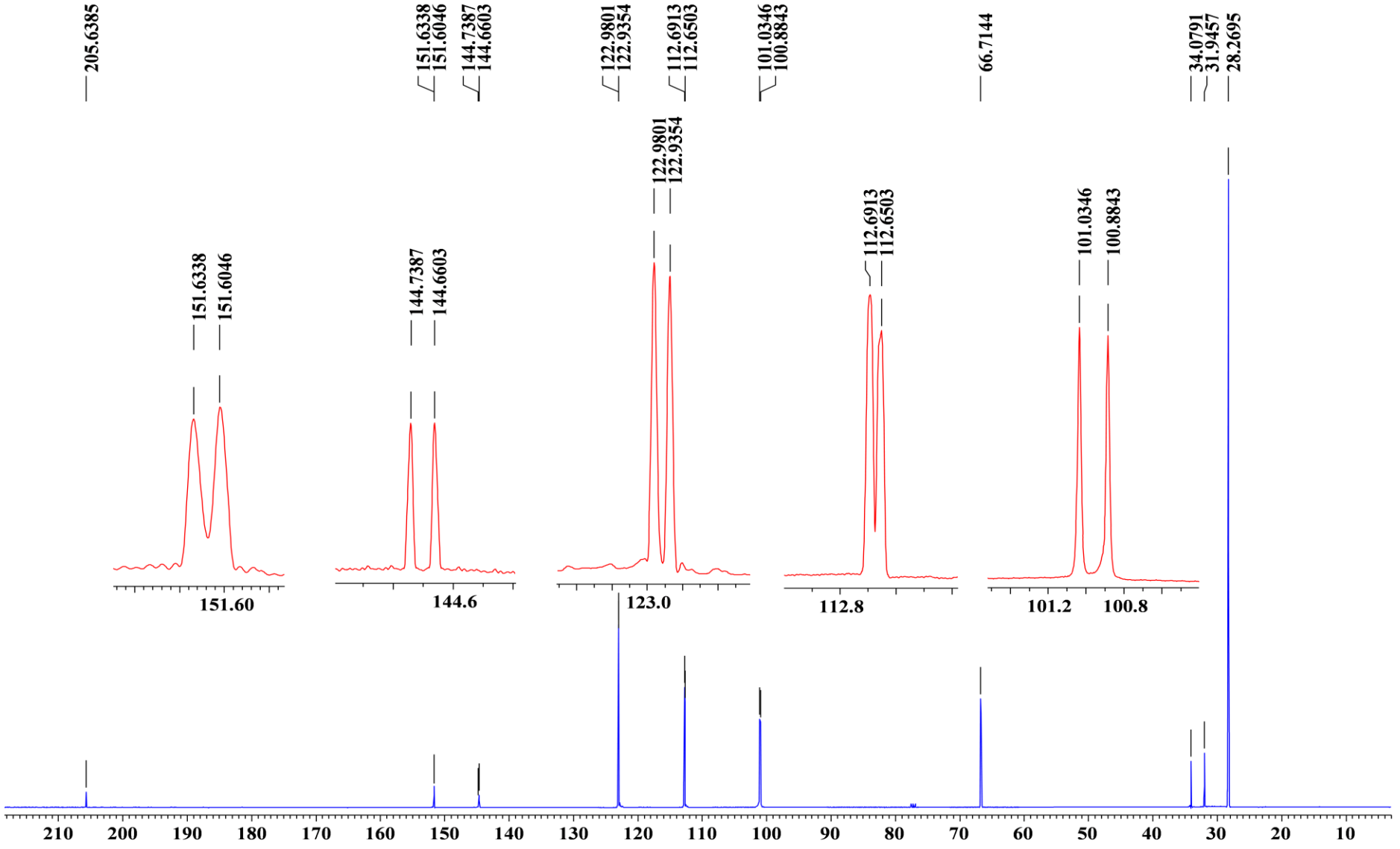


Figure S5. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$, 25°C) of phosphole (**3**).

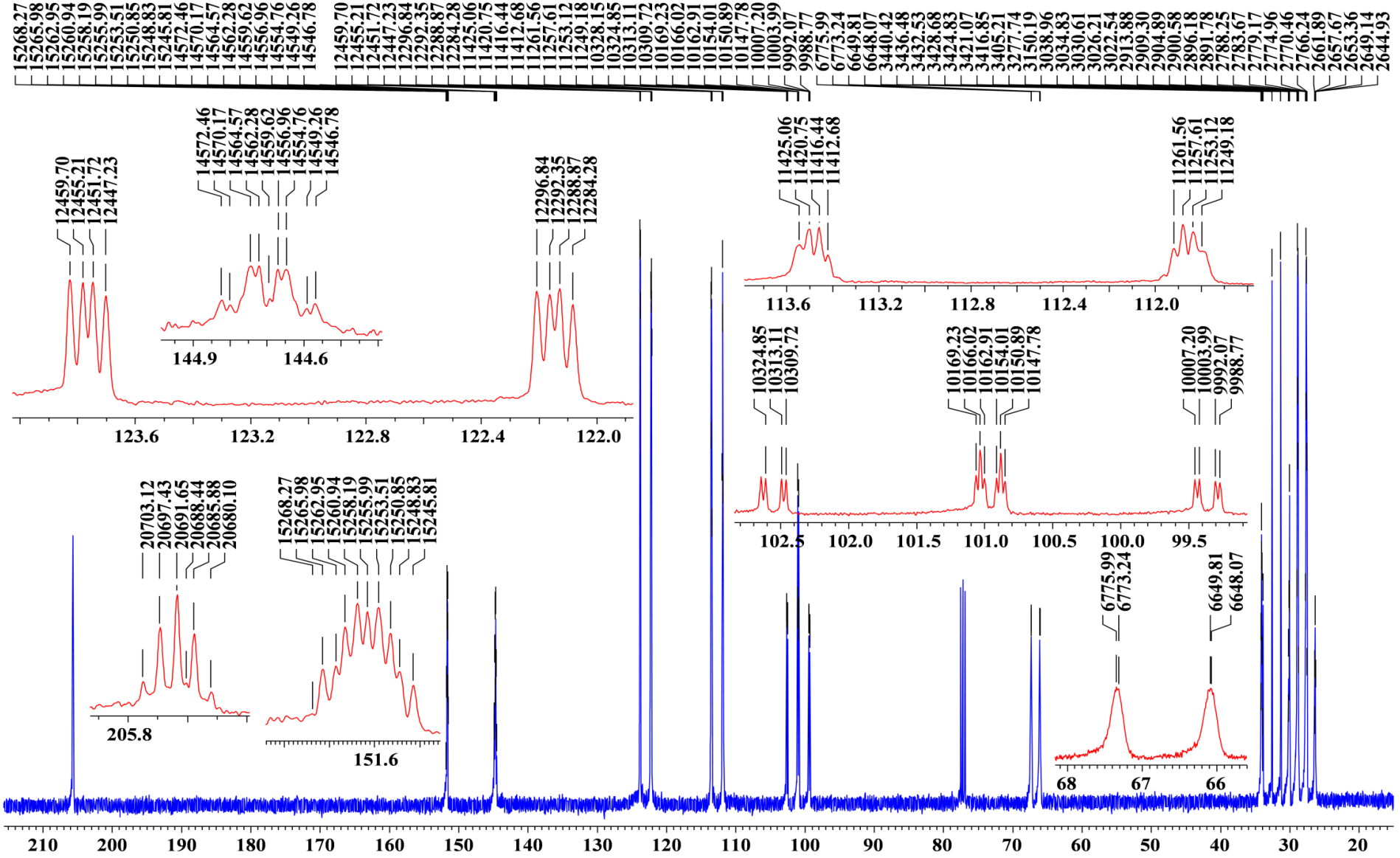


Figure S6. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$, 25°C) of phosphole (**3**).

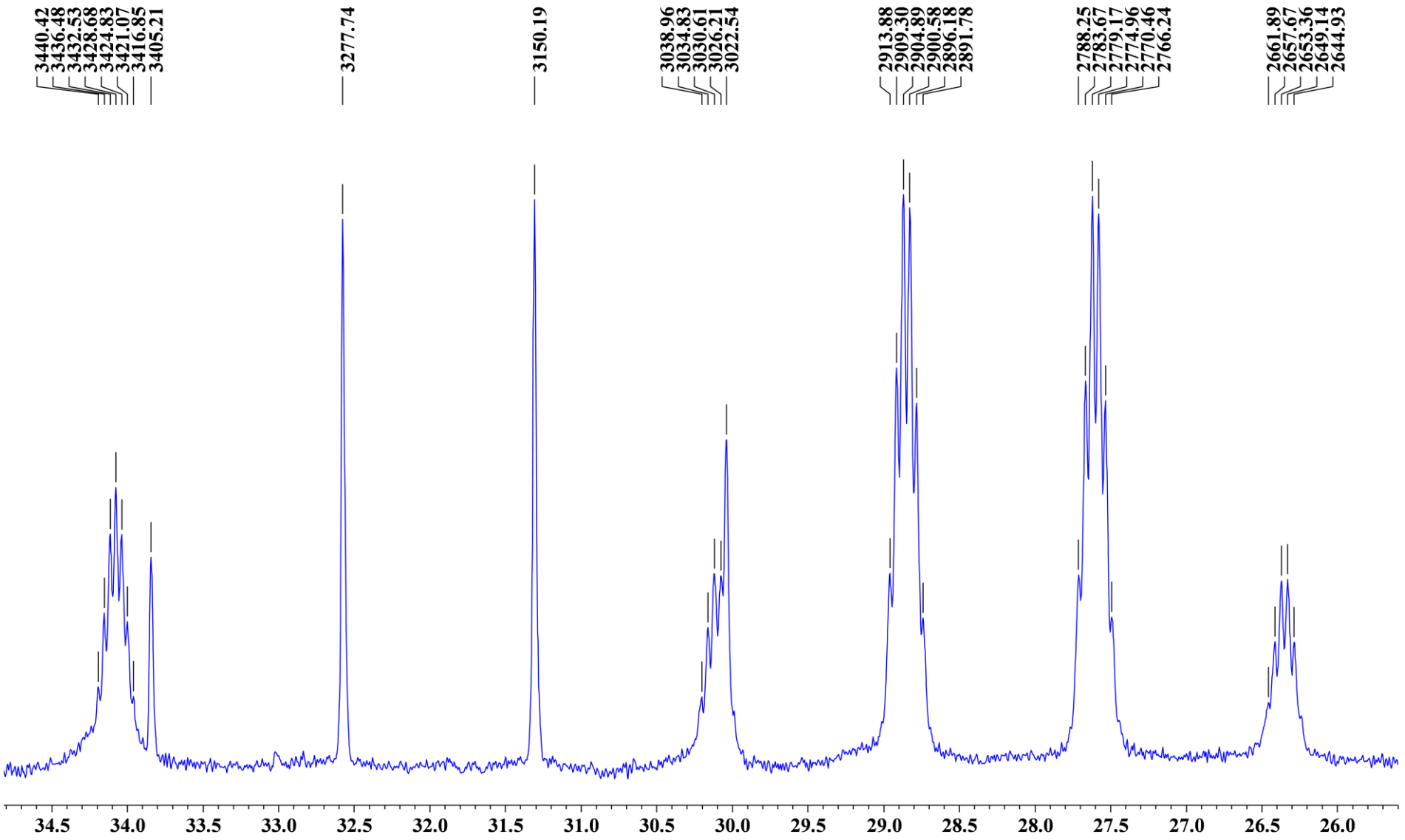


Figure S7. High-field region of ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$, 25°C) of phosphole (**3**).

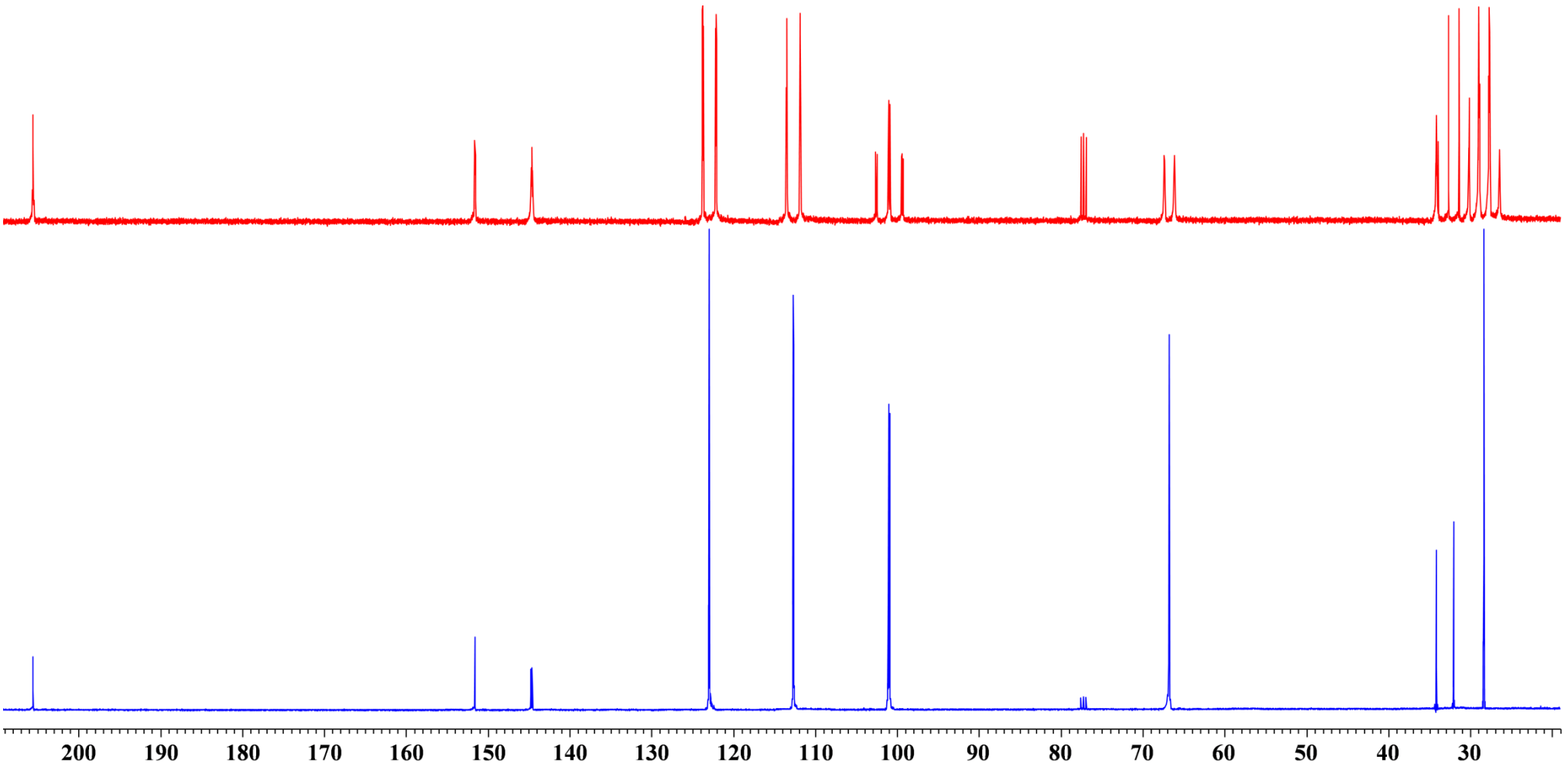


Figure S8. ^{13}C and ^{13}C-{^{1}H} NMR spectra (100.6 MHz, $CDCl_3$, 25°C) of phosphole (**3**).

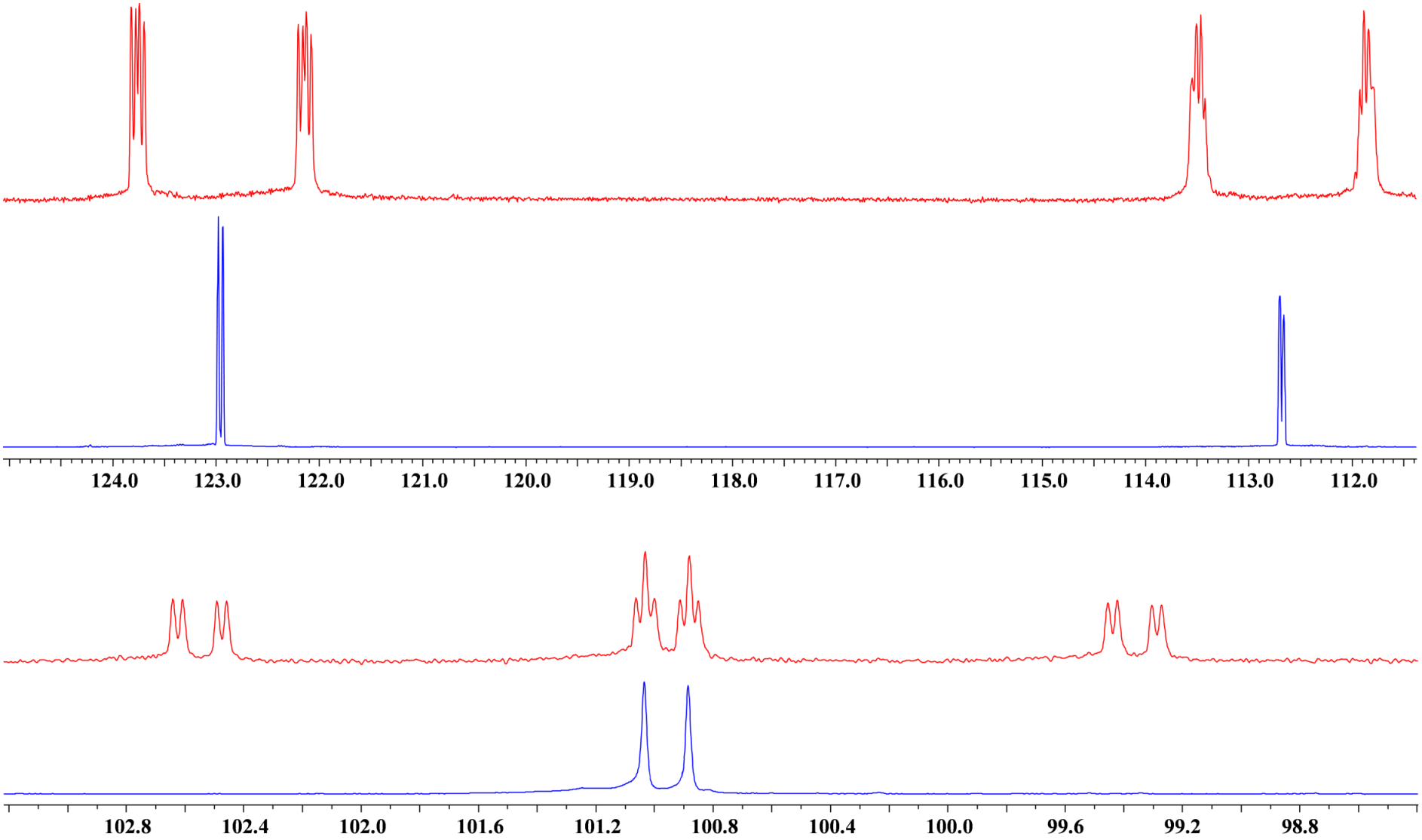


Figure S9. The fragments of ^{13}C and ^{13}C-{^{1}H} NMR spectra (100.6 MHz, $CDCl_3$, 25°C) of phosphole (**3**).

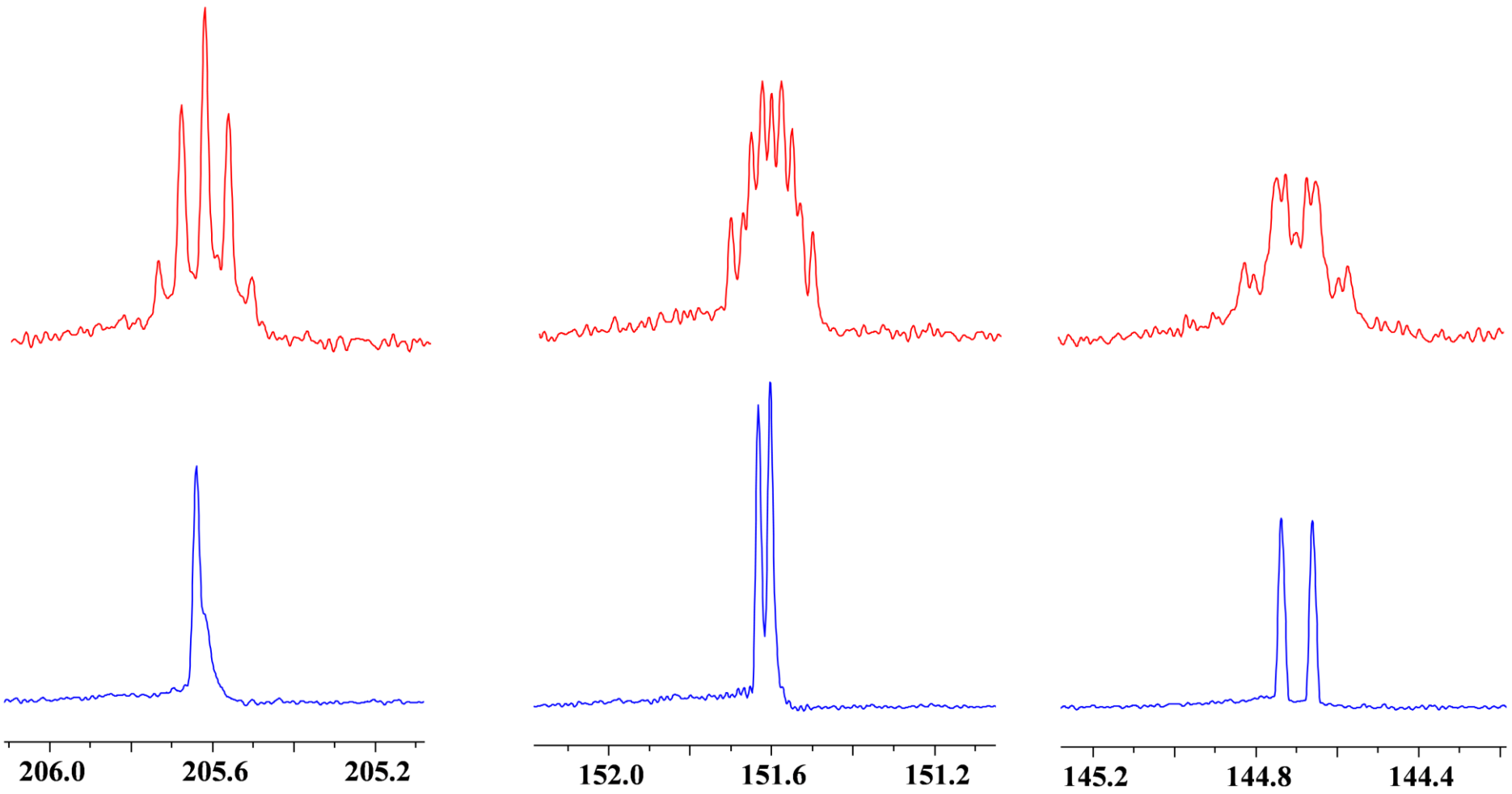


Figure S10. The low-field fragments of ^{13}C and ^{13}C-{^{1}H} NMR spectra (100.6 MHz, $CDCl_3$, 25°C) of phosphole (**3**).

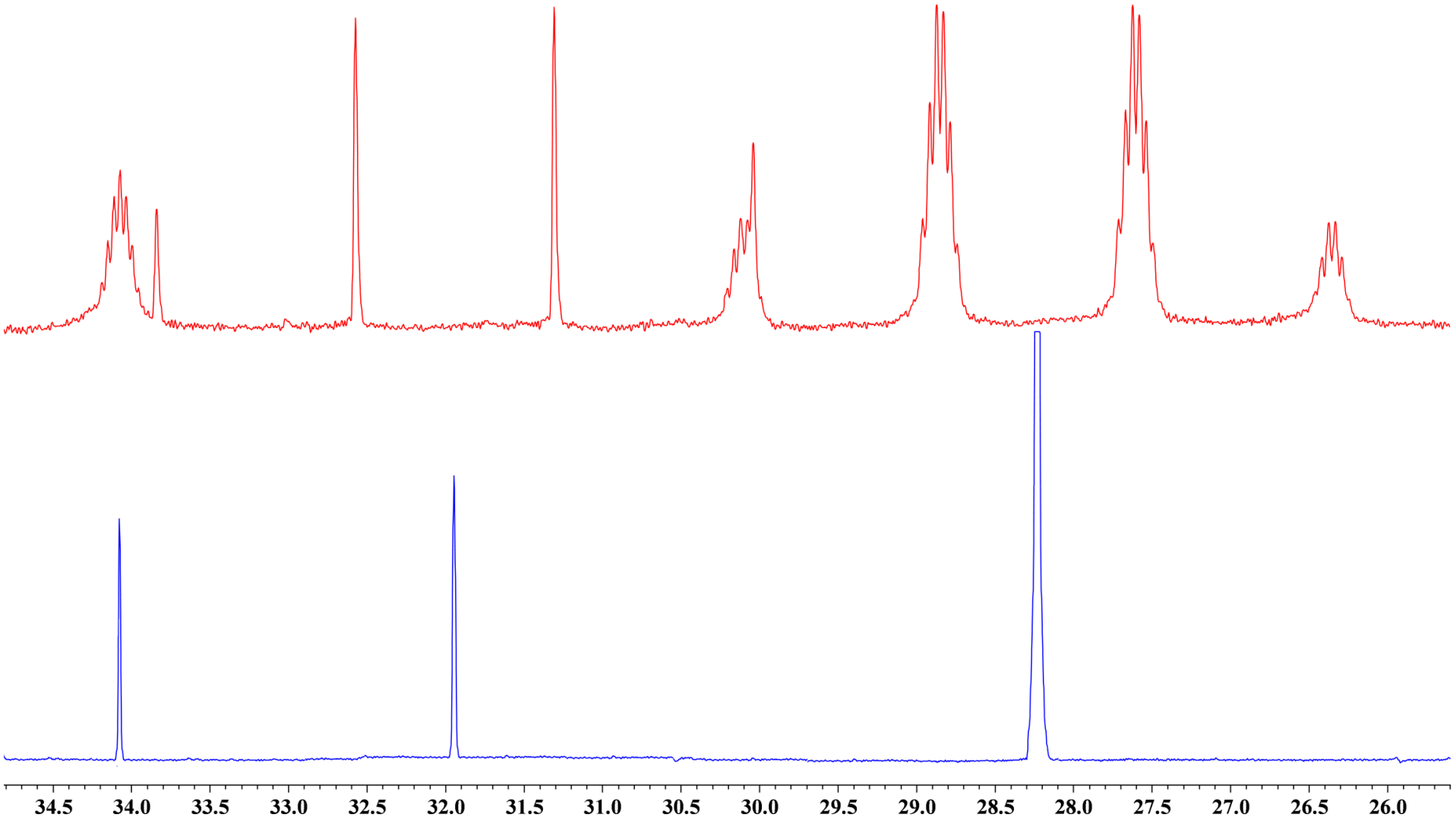


Figure S11. The high-field fragments of ^{13}C and ^{13}C-{^{1}H} NMR spectra (100.6 MHz, $CDCl_3$, 25°C) of phosphole (**3**).

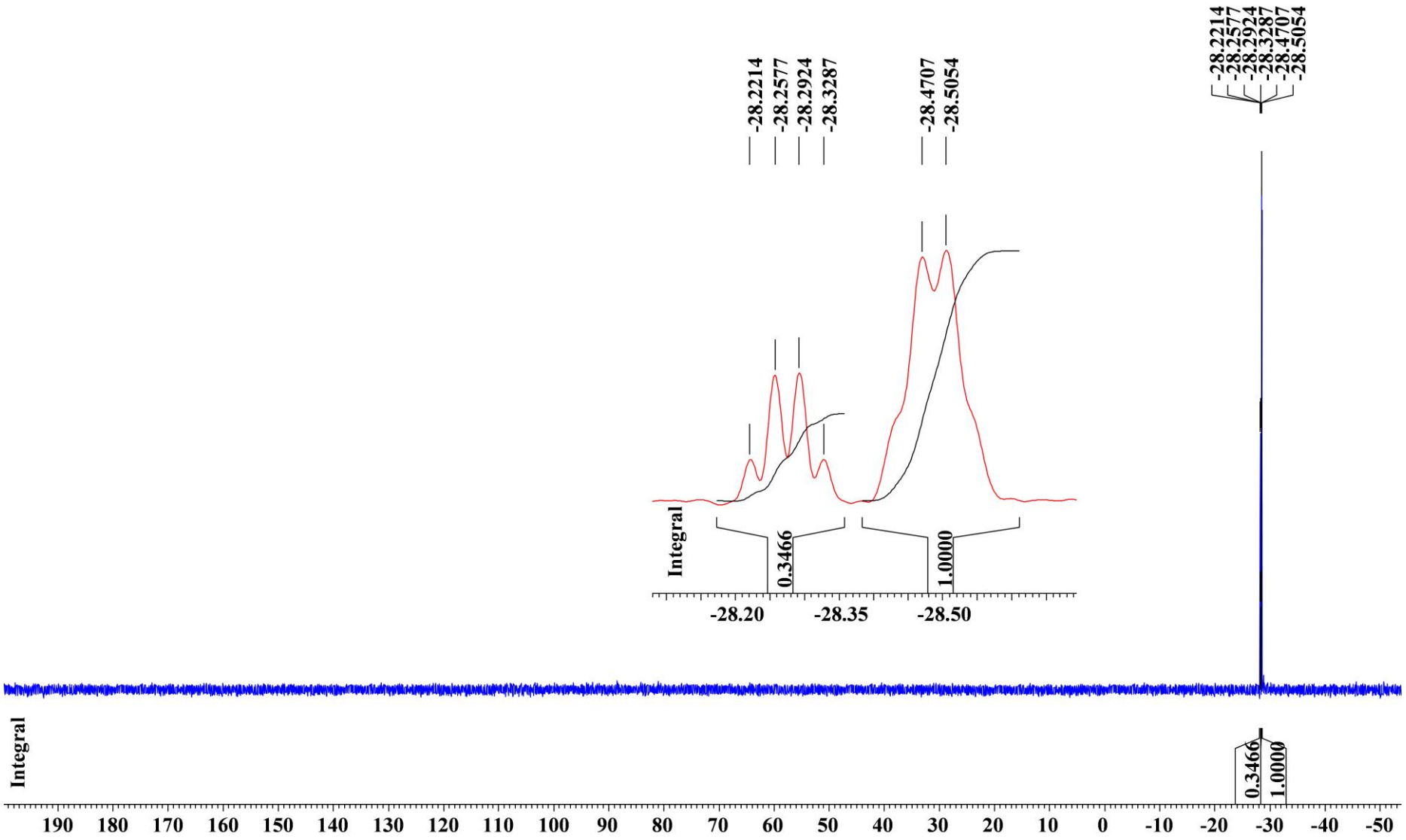


Figure S12. ^{31}P-{^{1}H} NMR spectrum (162.0 MHz, $CDCl_3$, 25°C) of phosphoranes (**5**, **6**) mixture.

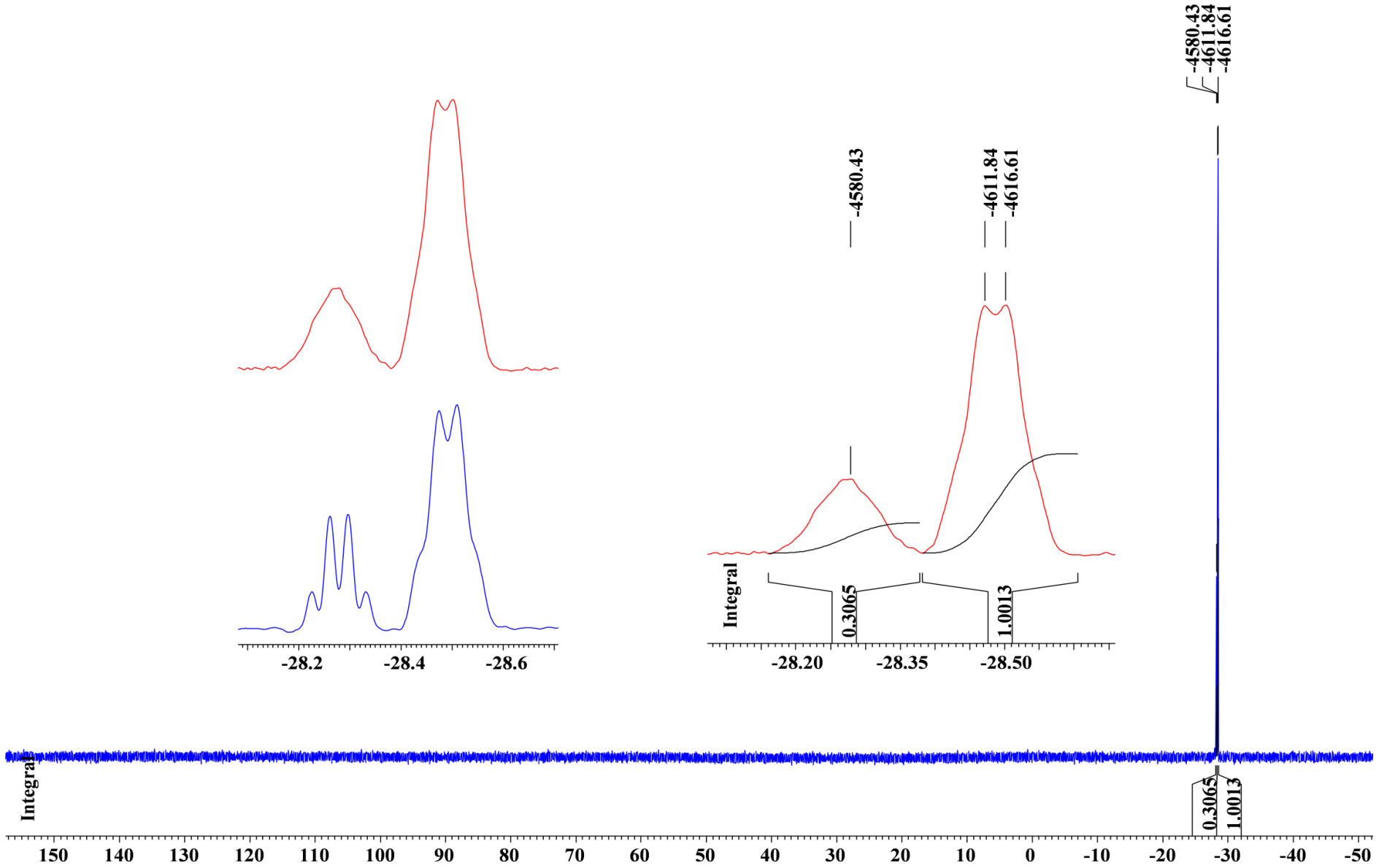


Figure S13. ^{31}P and ^{31}P-{^{1}H} NMR spectra (162.0 MHz, $CDCl_3$, 25°C) of phosphoranes (**5**, **6**) mixture.

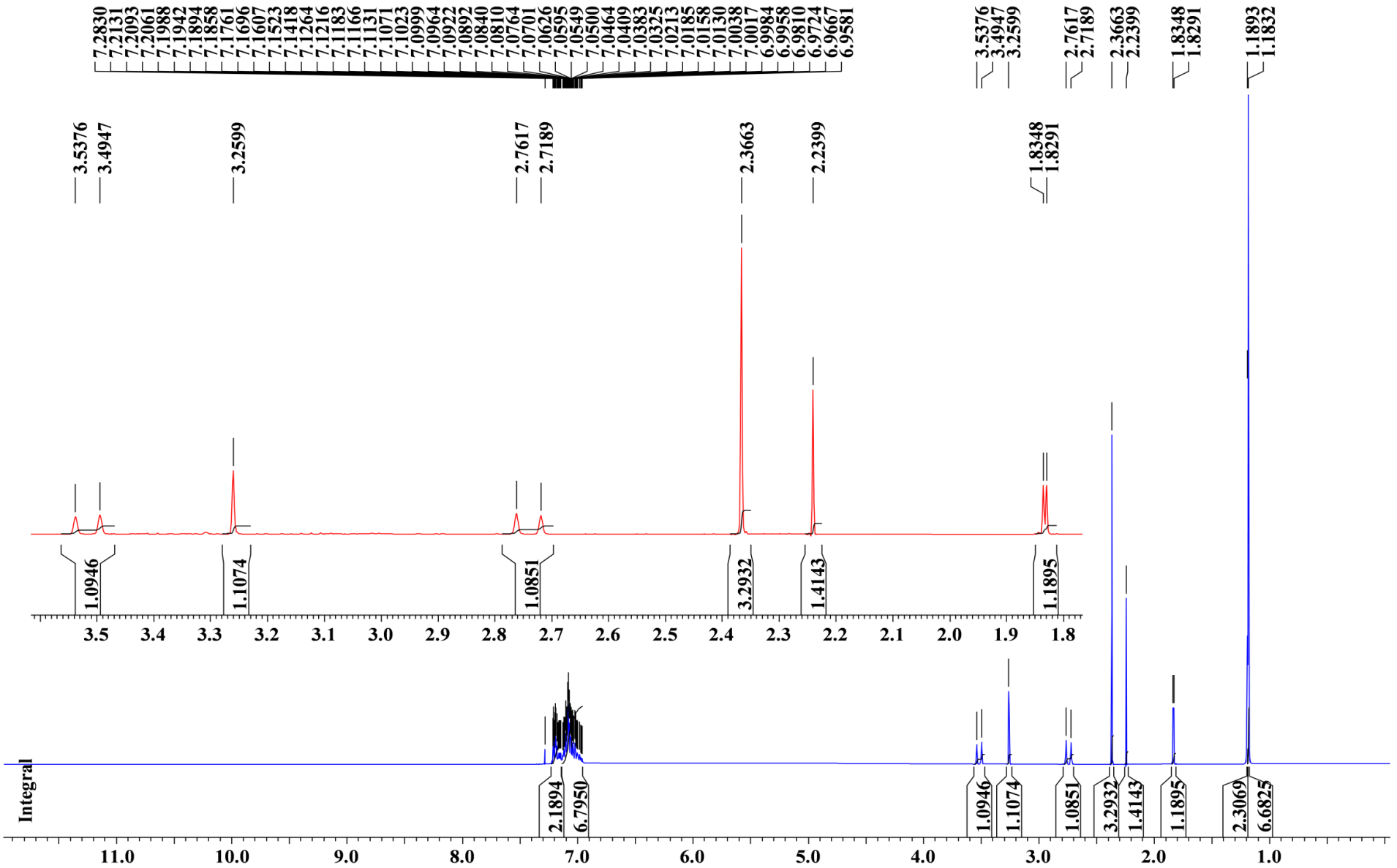


Figure S14. ^{1}H NMR spectrum (400.0 MHz, $CDCl_3$, 25°C) of phosphoranes (**5**, **6**) mixture.

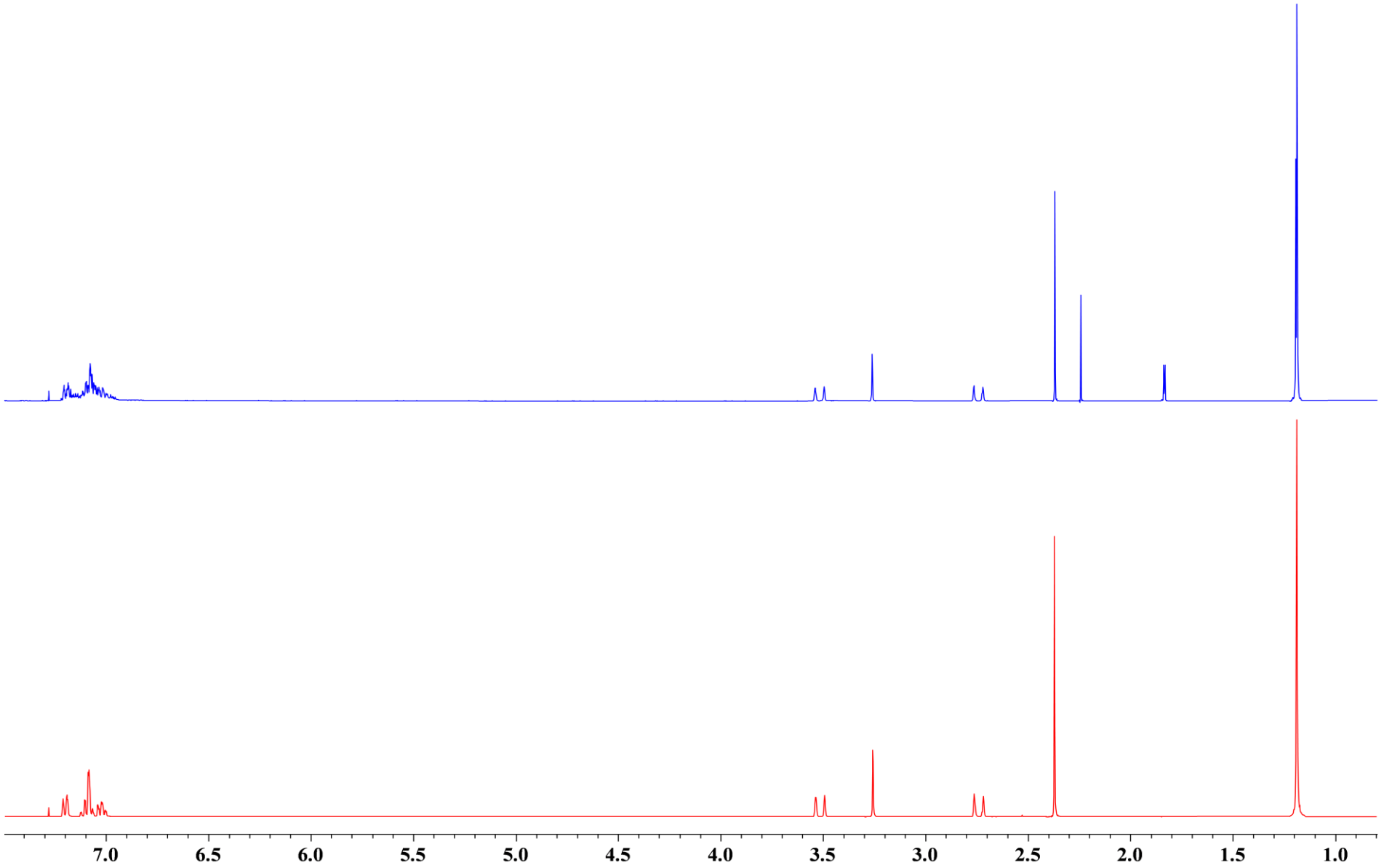


Figure S15. ^{1}H NMR spectra (400.0 MHz, $CDCl_3$, 25°C) of phosphoranes (**5**, **6**) mixture (blue) and phosphorane (**6**).

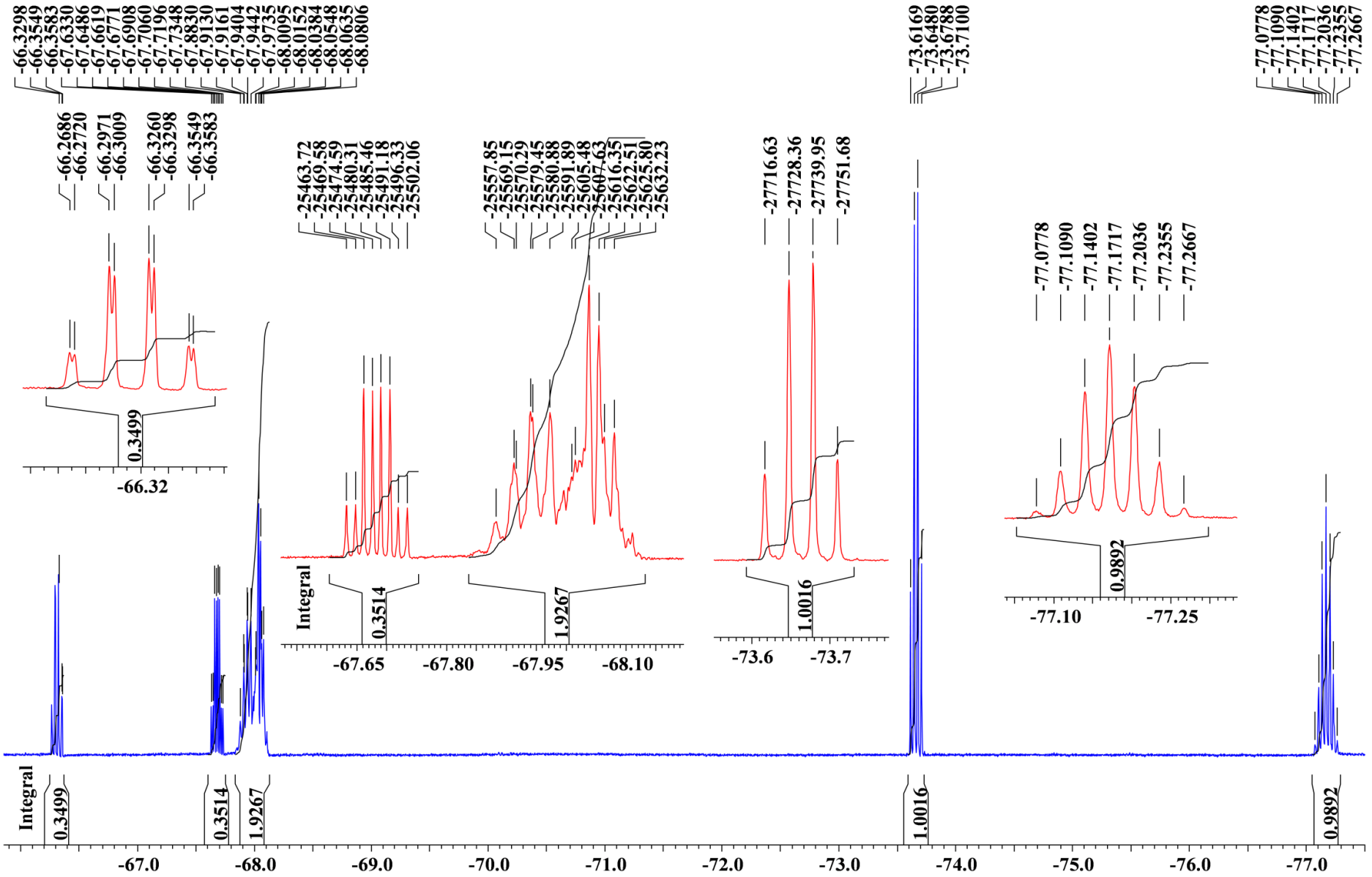


Figure S16. ^{19}F NMR spectrum (386.5 MHz, $CDCl_3$, 25°C) of phosphoranes (**5**, **6**) mixture.

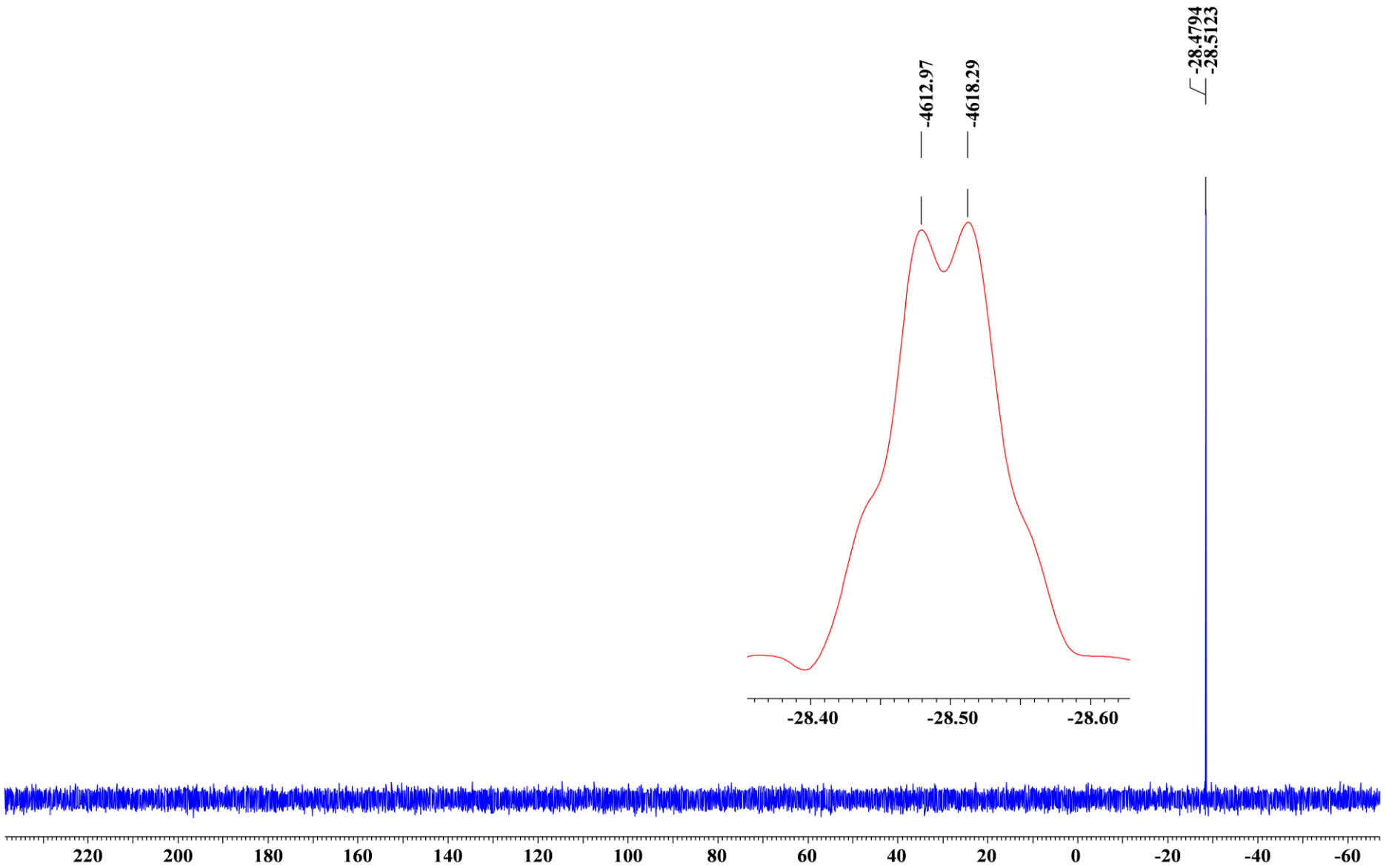


Figure S17. ^{31}P-{^{1}H} NMR spectrum (162.0 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

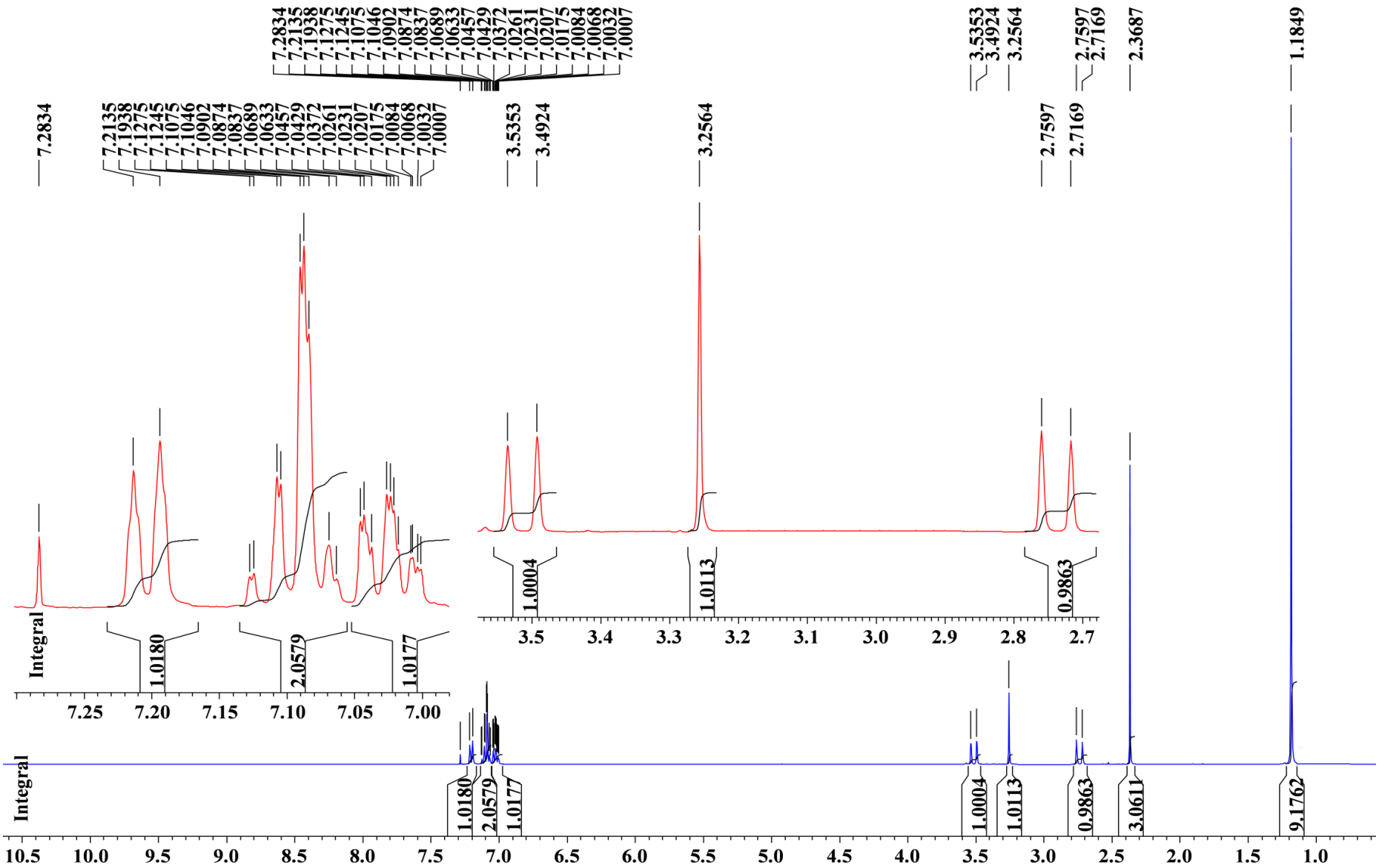


Figure S18. ^{1}H NMR spectrum (400.0 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

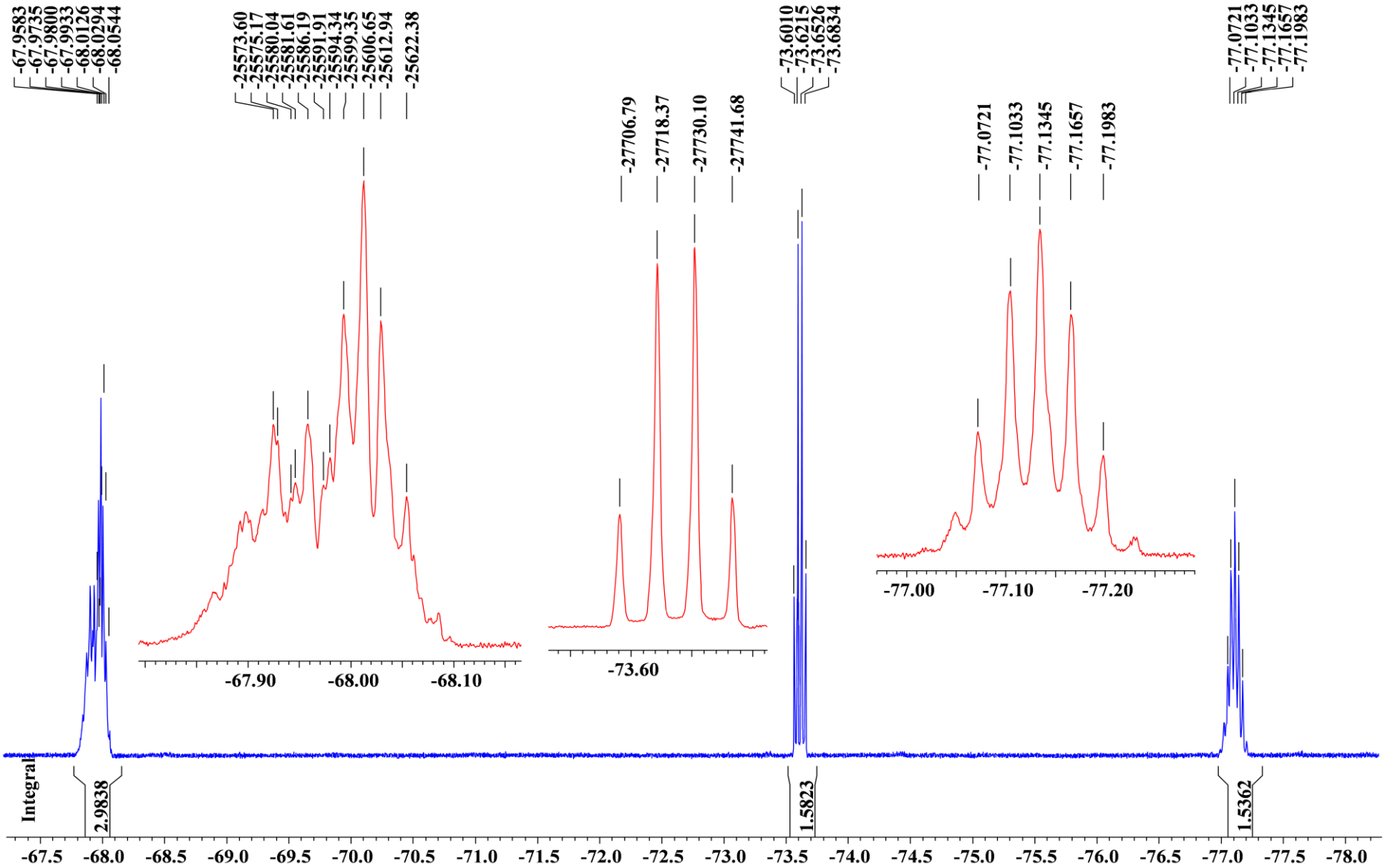


Figure S19. ^{19}F NMR spectrum (386.5 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

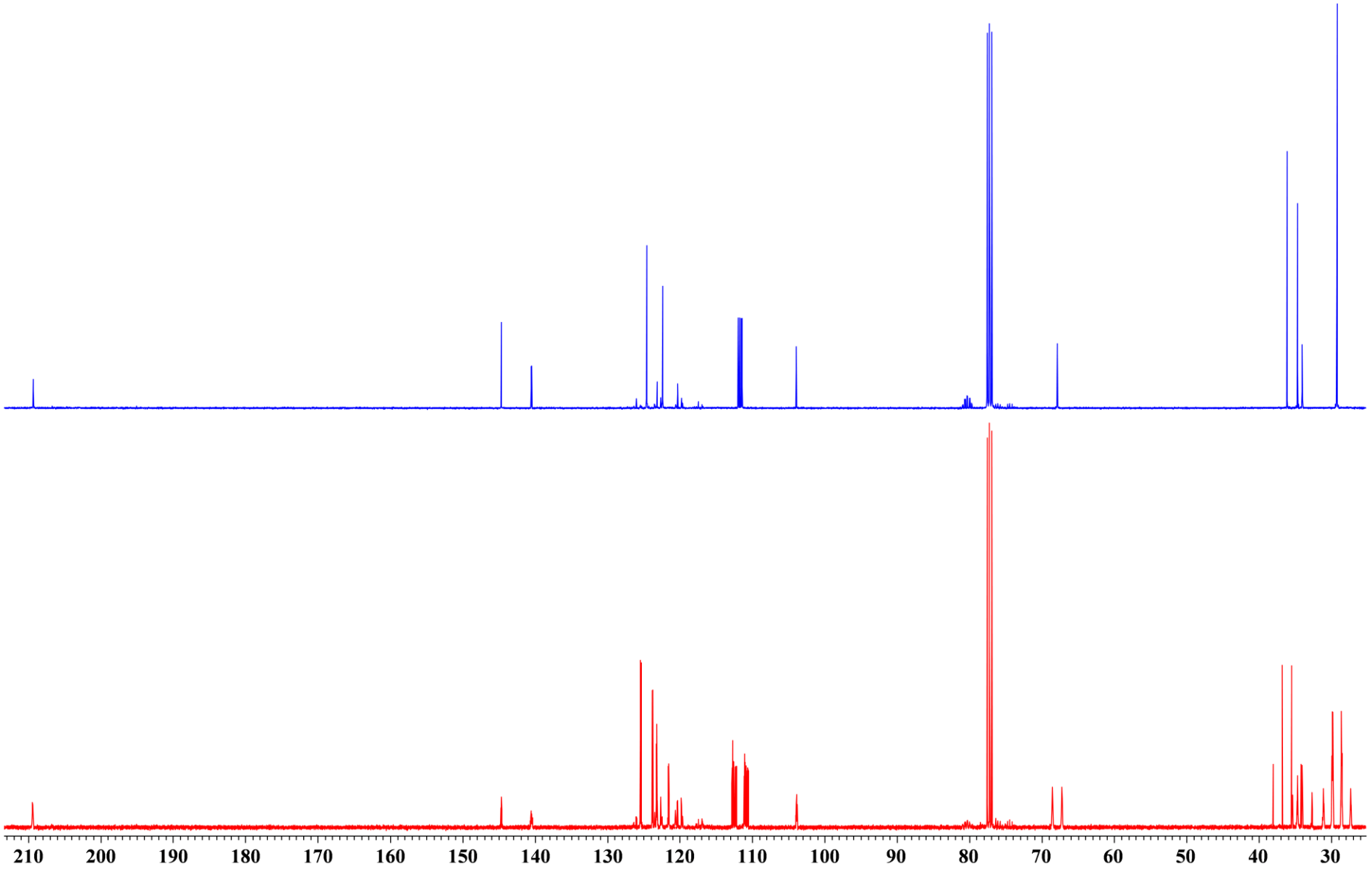


Figure S20. ^{13}C and ^{13}C-{^{1}H} NMR spectra (100.6 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

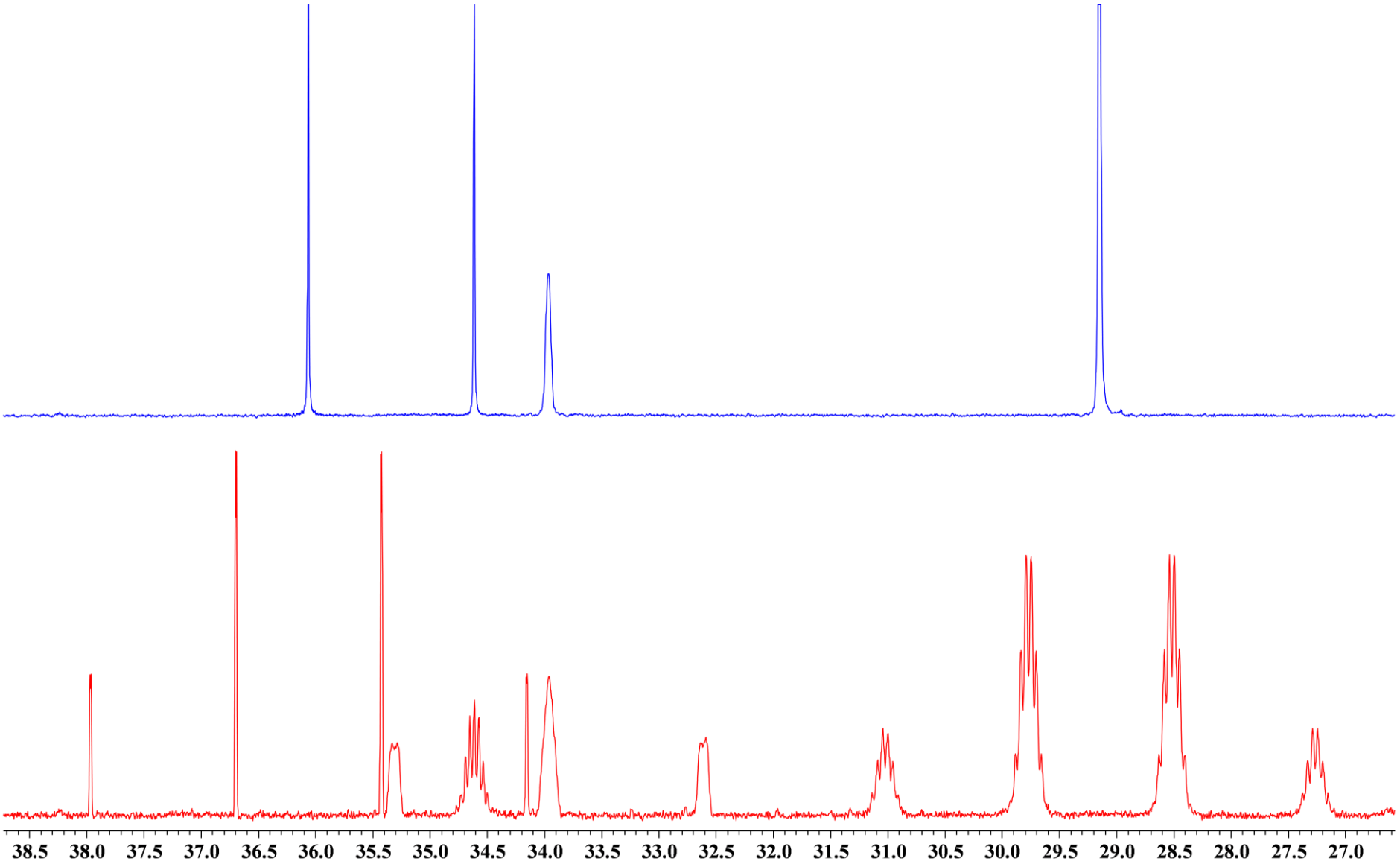


Figure S21. High-field regions of ^{13}C and ^{13}C-{^{1}H} NMR spectra (100.6 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

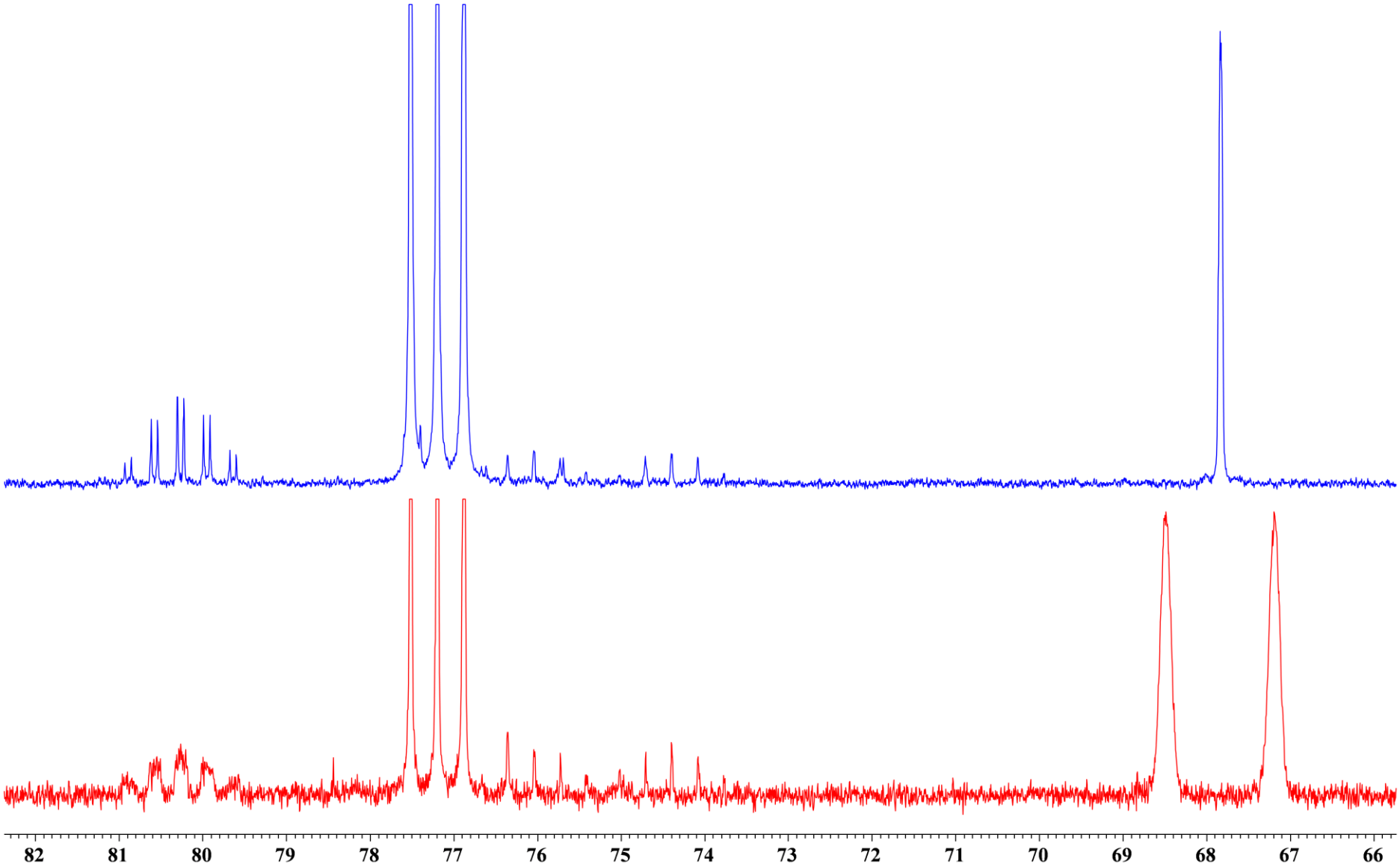


Figure S22. C^3, C^4 and C^7 region of ^{13}C and ^{13}C-{^1H} NMR spectra (100.6 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

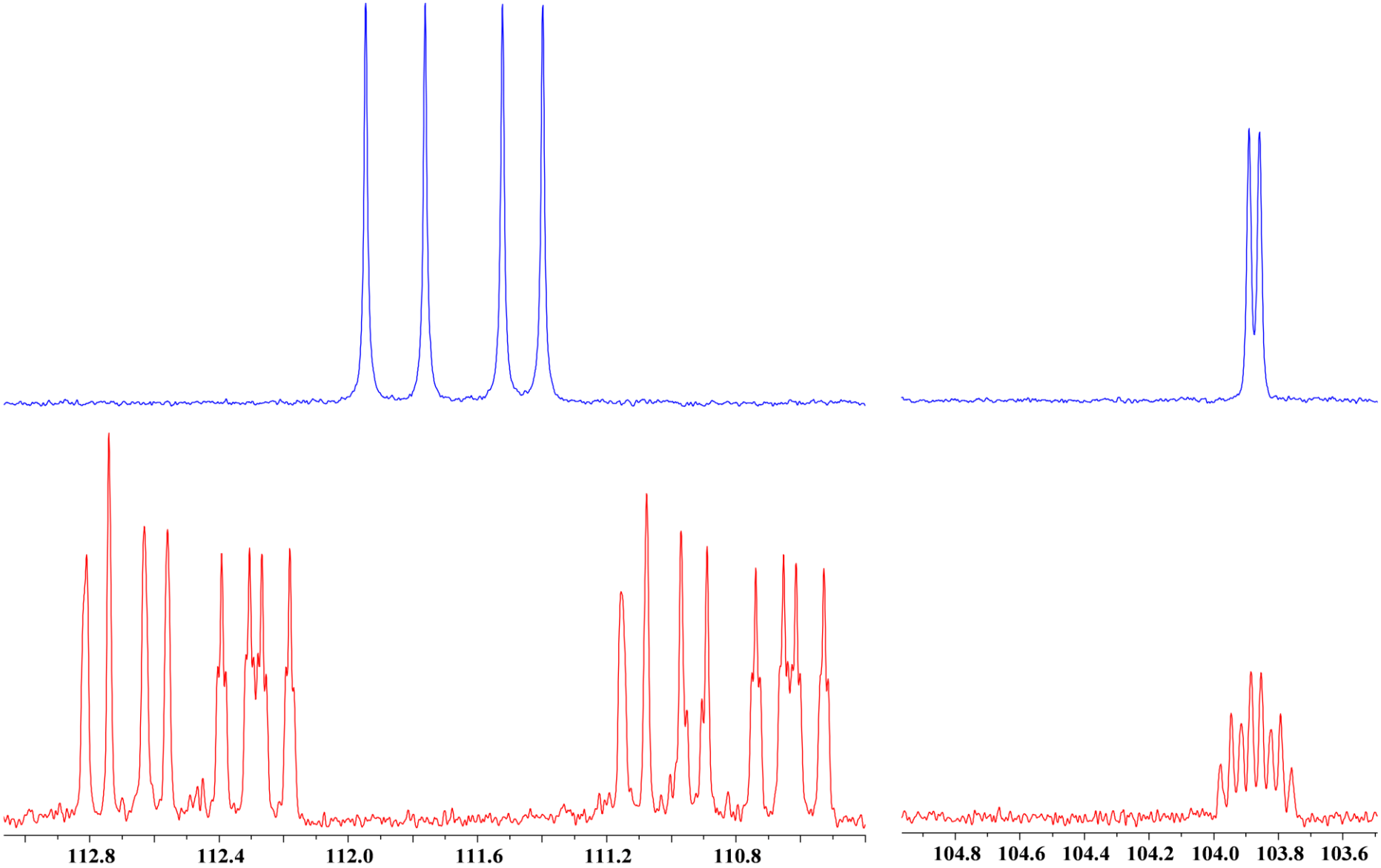


Figure S23. C^{9}, C^{12} and C^{5} regions of ^{13}C and ^{13}C-{^{1}H} NMR spectra (100.6 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

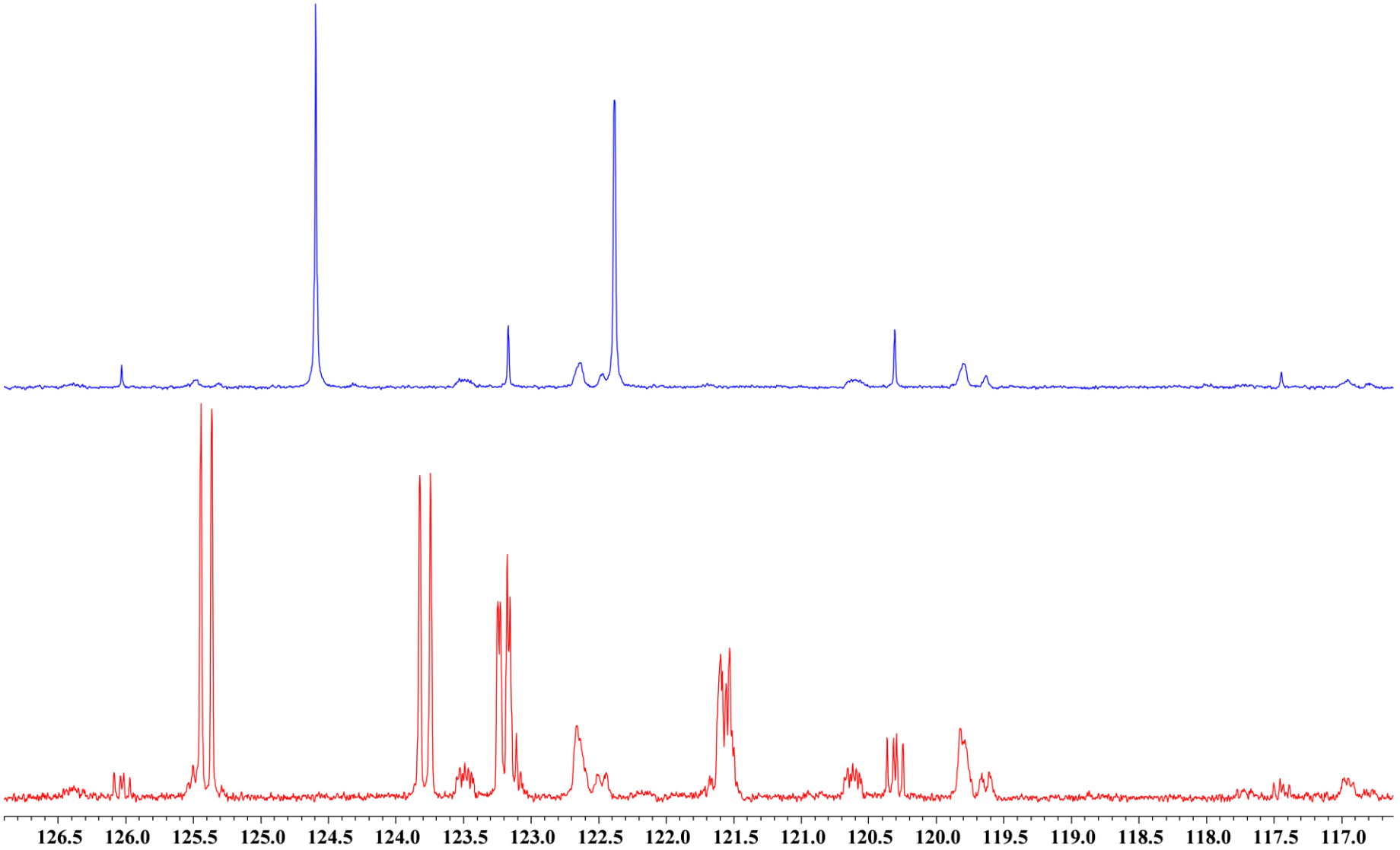


Figure S24. Aromatic carbons and CF_3-groups region of ^{13}C and ^{13}C-{^1H} NMR spectra (100.6 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

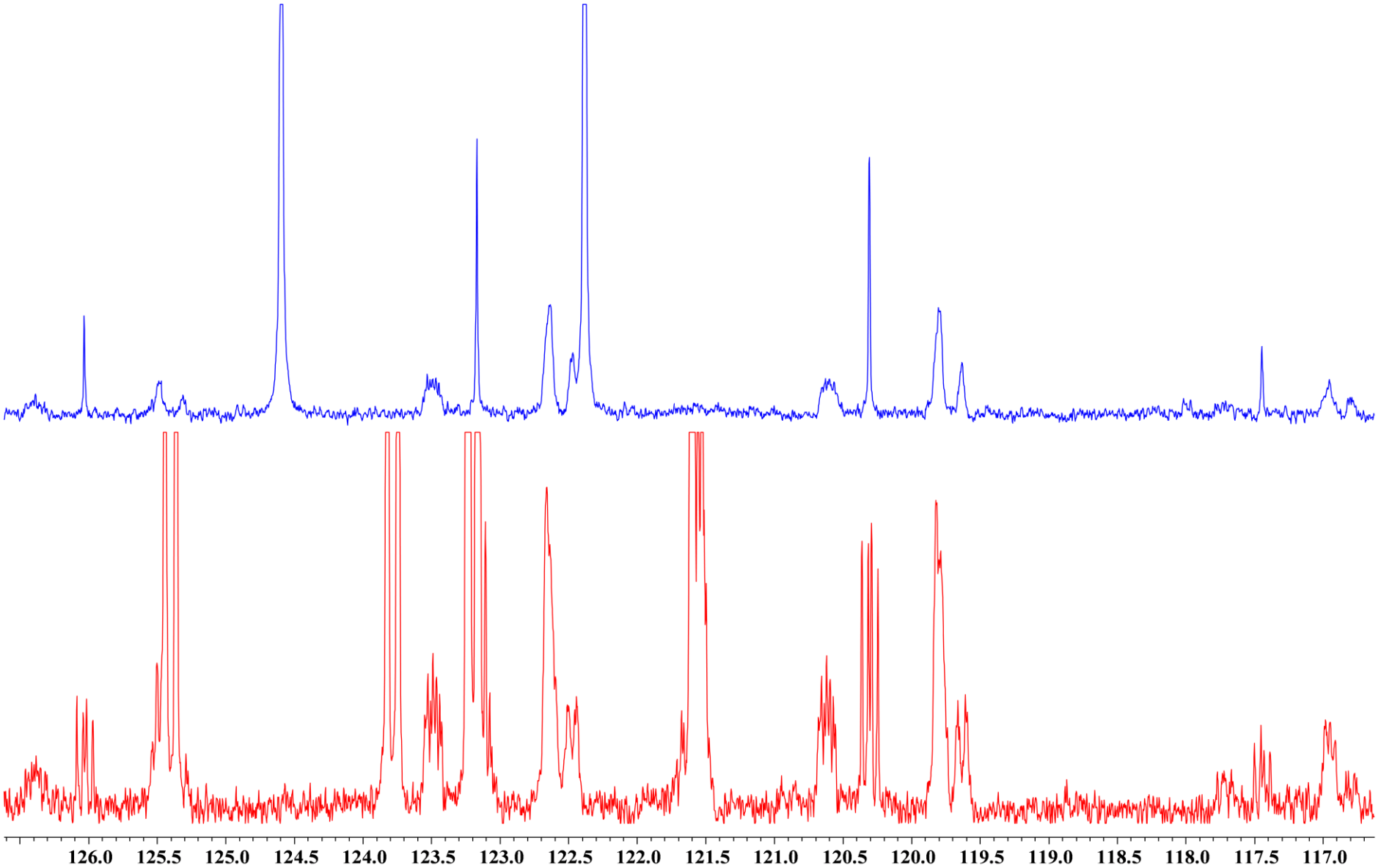


Figure S25. CF_3-groups region of ^{13}C and ^{13}C-{^{1}H} NMR spectra (100.6 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

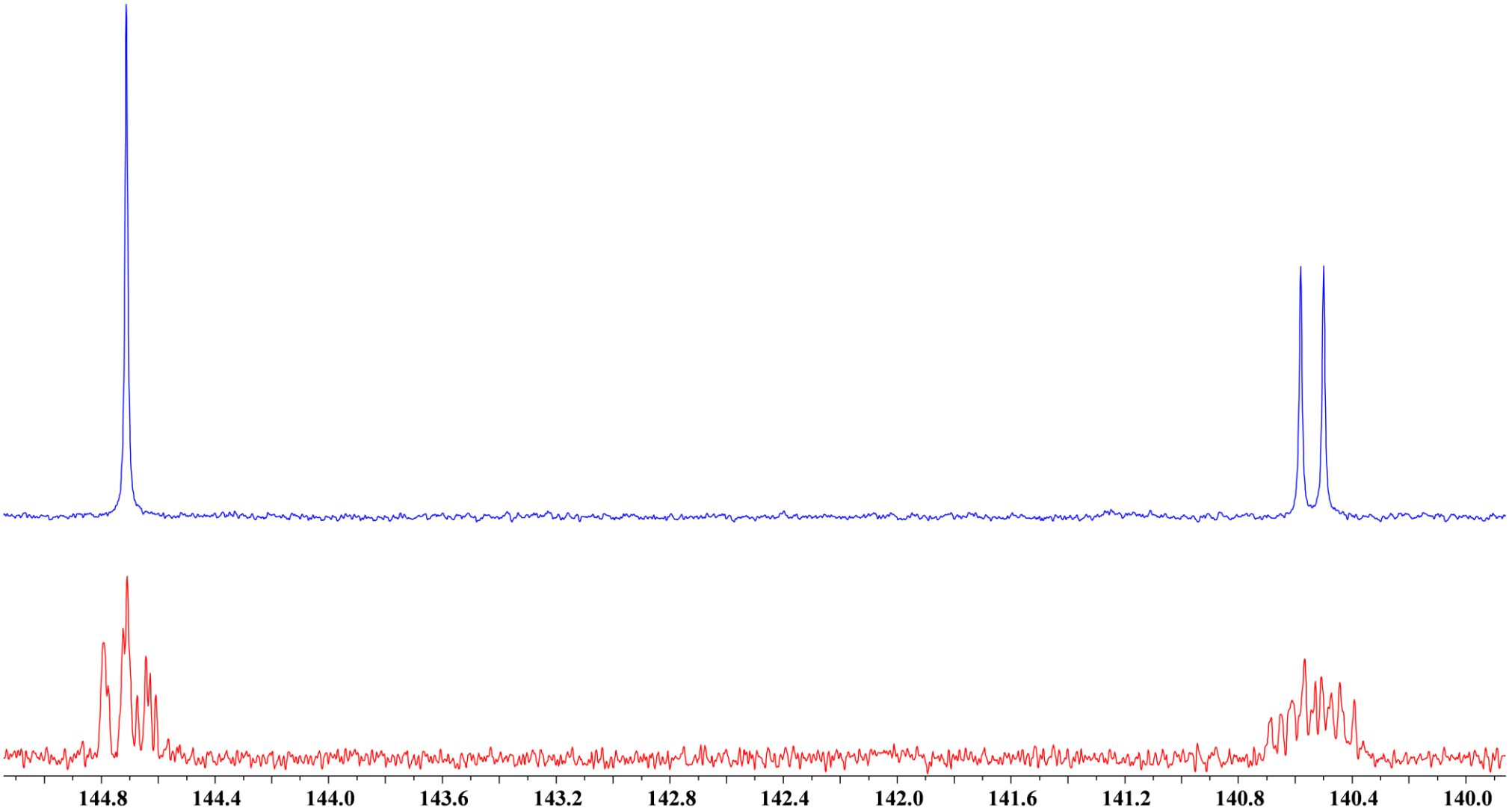


Figure S26. Low-field region of ^{13}C and ^{13}C-{^{1}H} NMR spectra (100.6 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

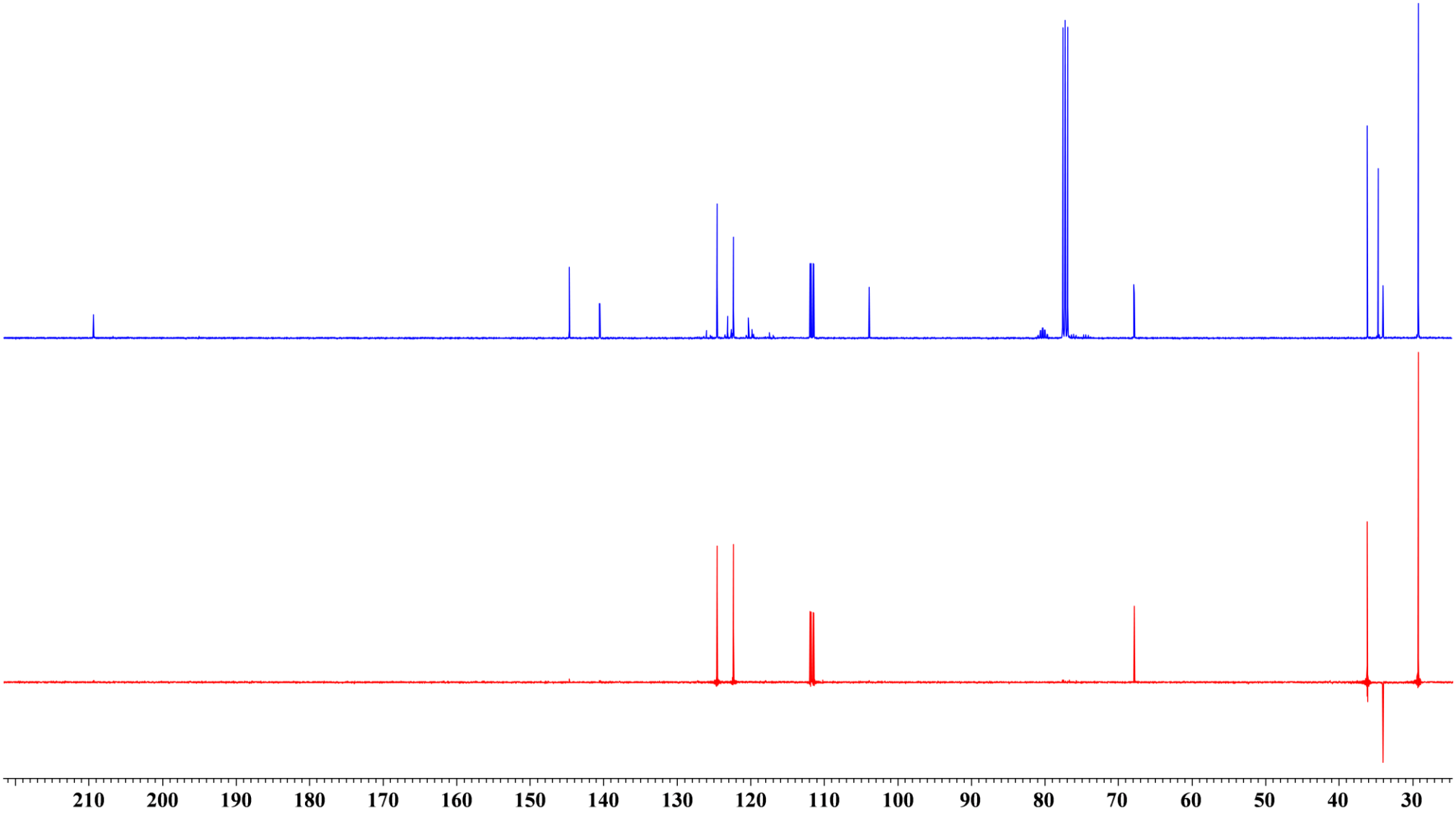


Figure S27. ^{13}C-{^{1}H} and ^{13}C-dept NMR spectra (100.6 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

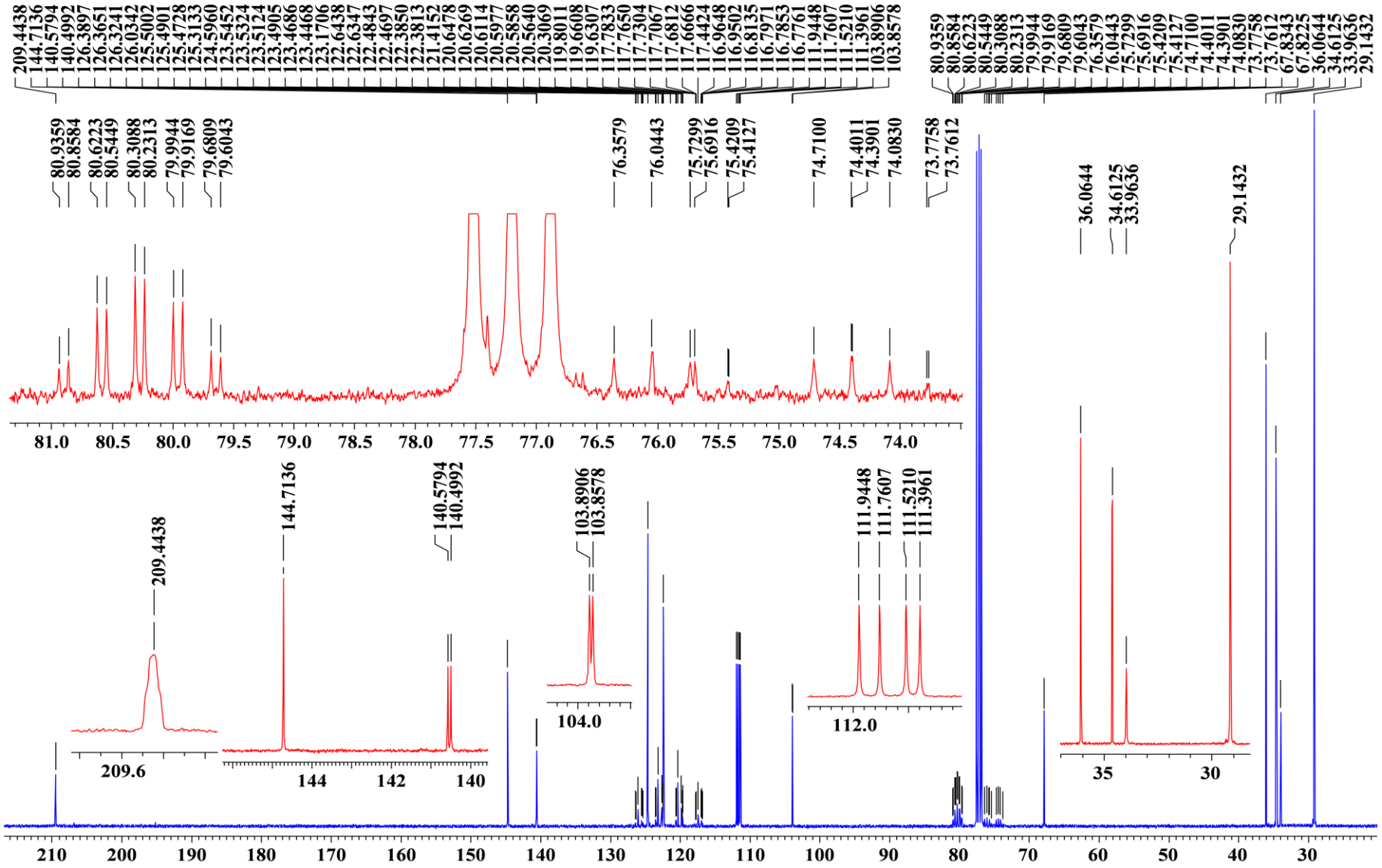


Figure S28. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

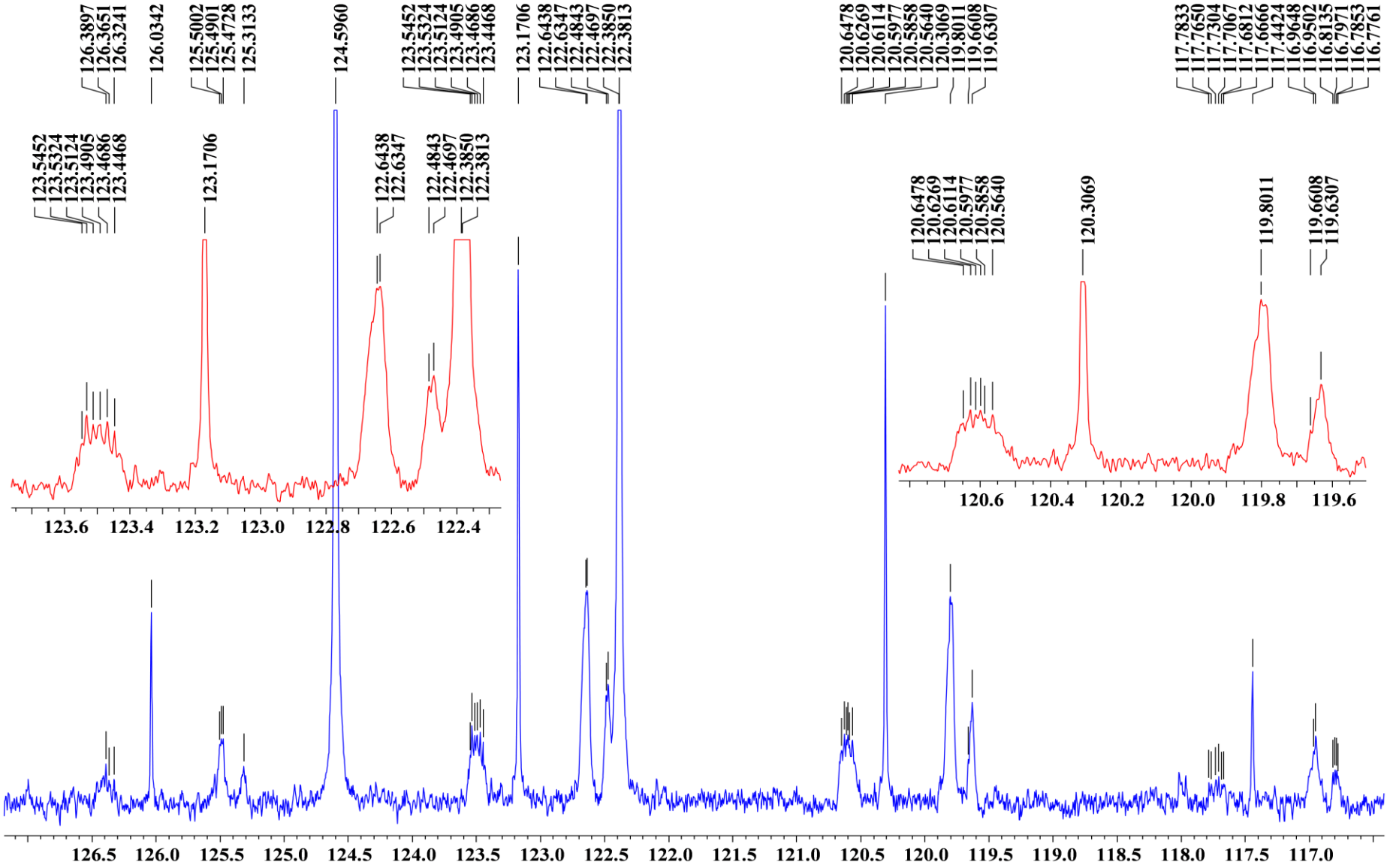


Figure S29. Aromatic carbons and CF_3-groups region of ^{13}C-{^1H} NMR spectrum (100.6 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

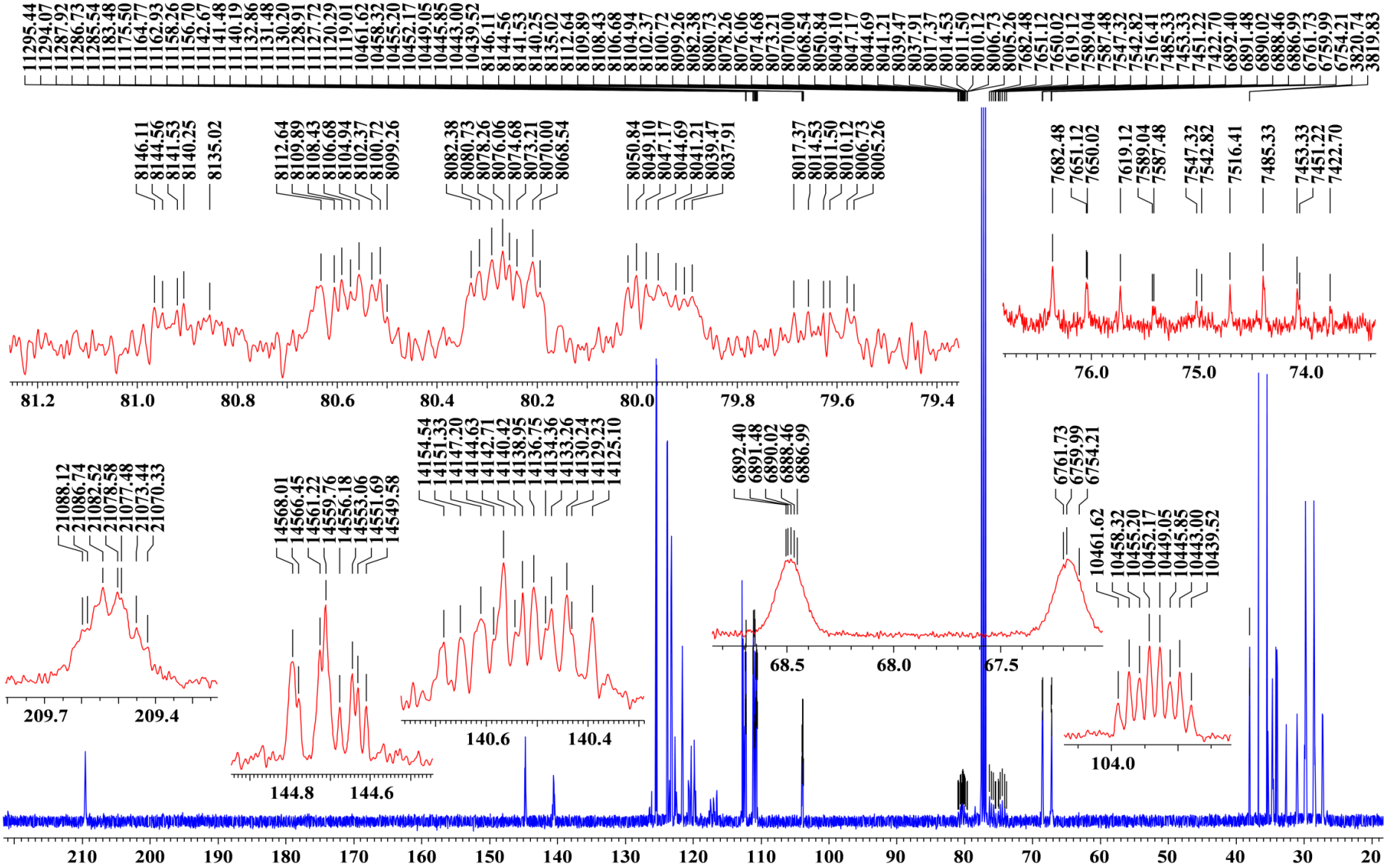


Figure S30. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

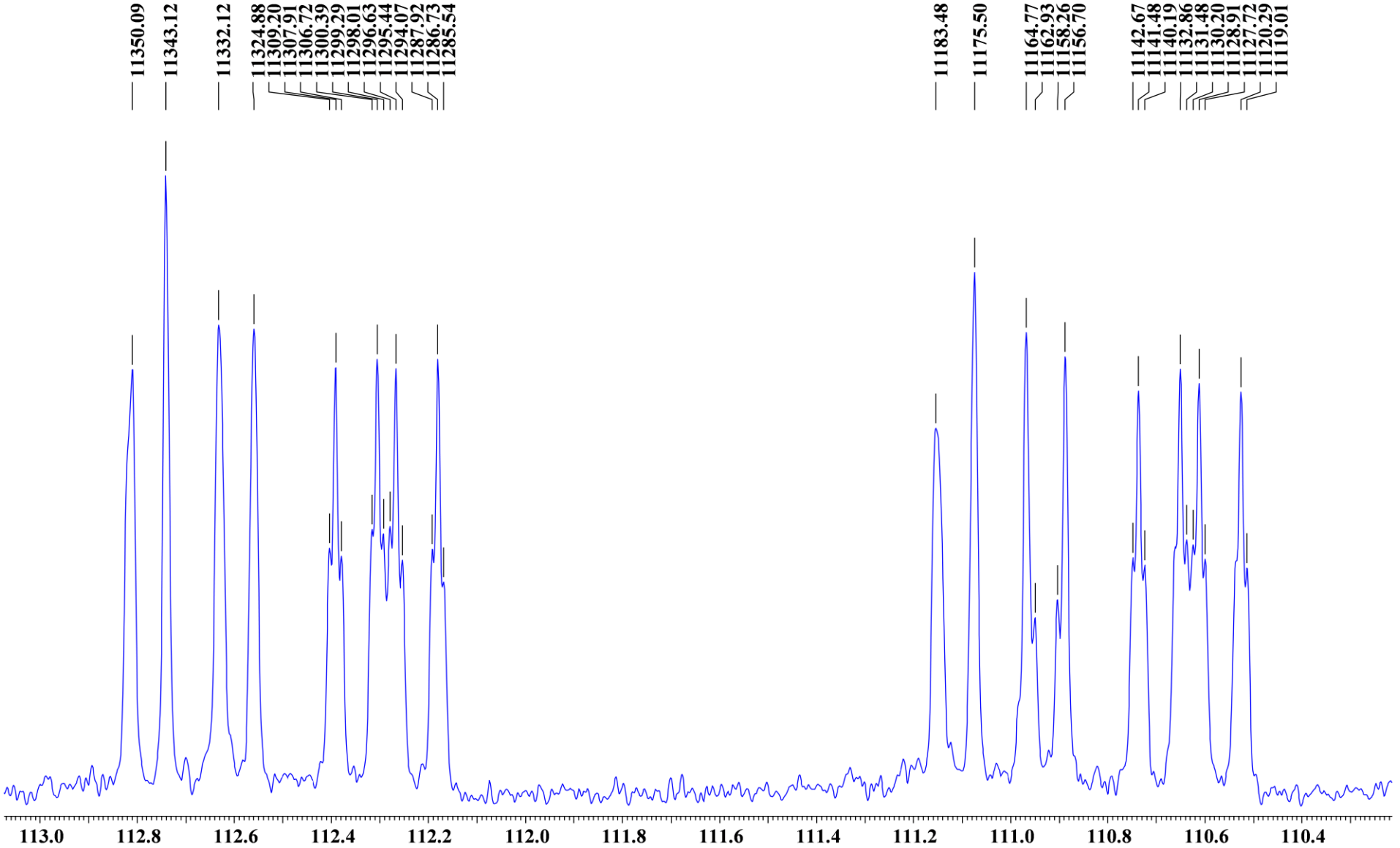


Figure S31. C^{9} and C^{12}-atoms region of ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

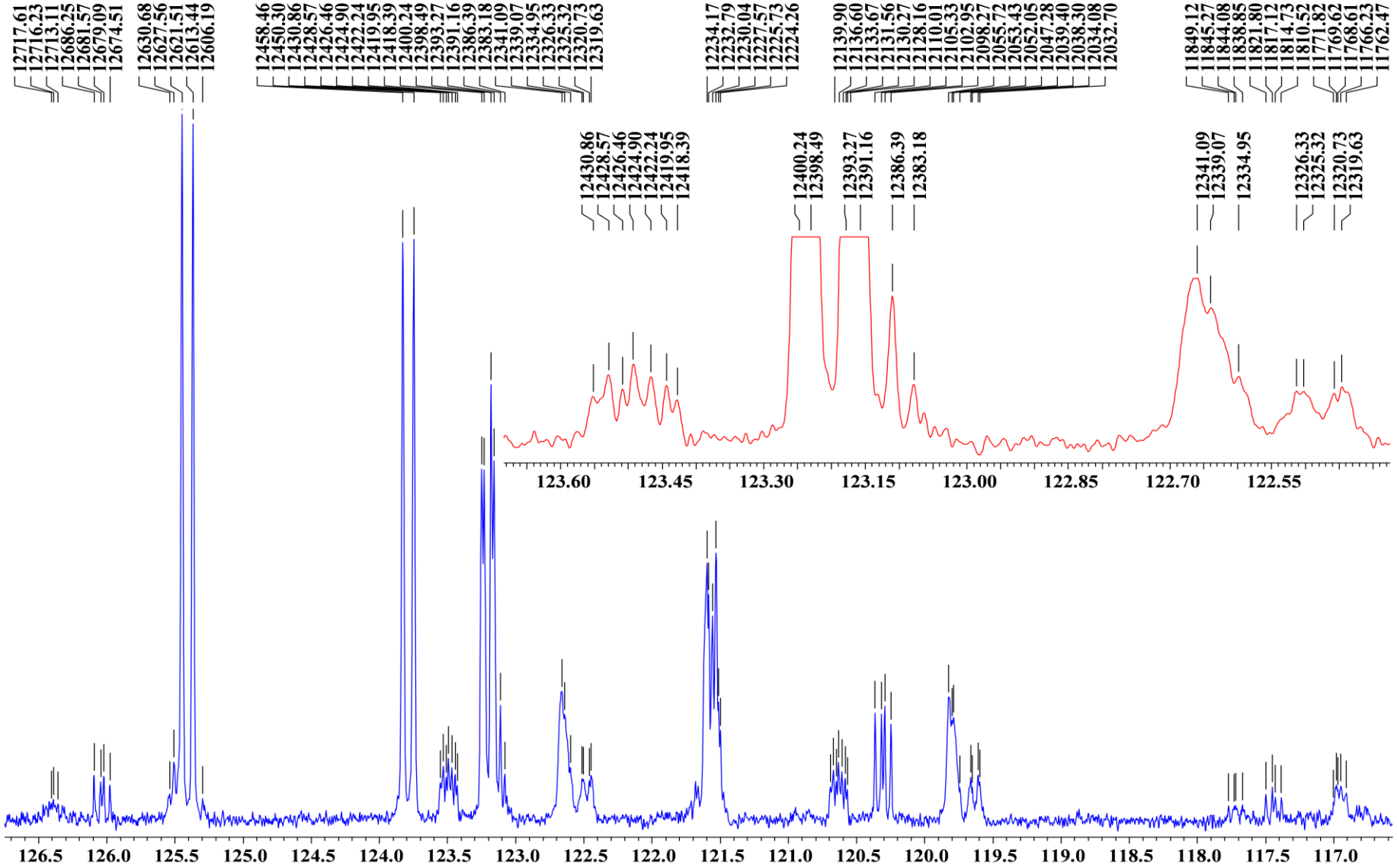


Figure S32. Aromatic carbons and CF_3-groups region of ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

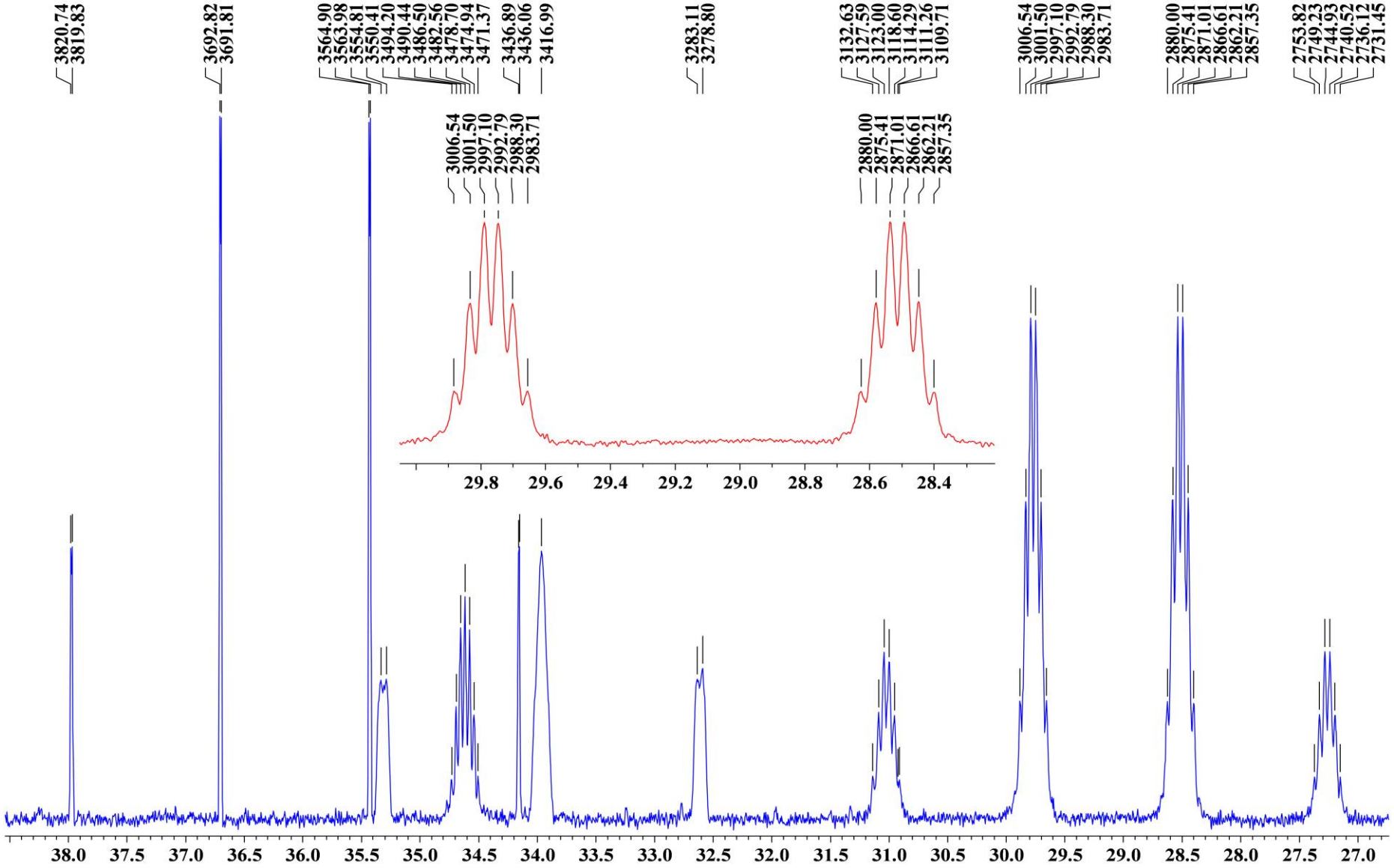


Figure S33. High-field region of ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$, 25°C) of phosphorane (**6**).

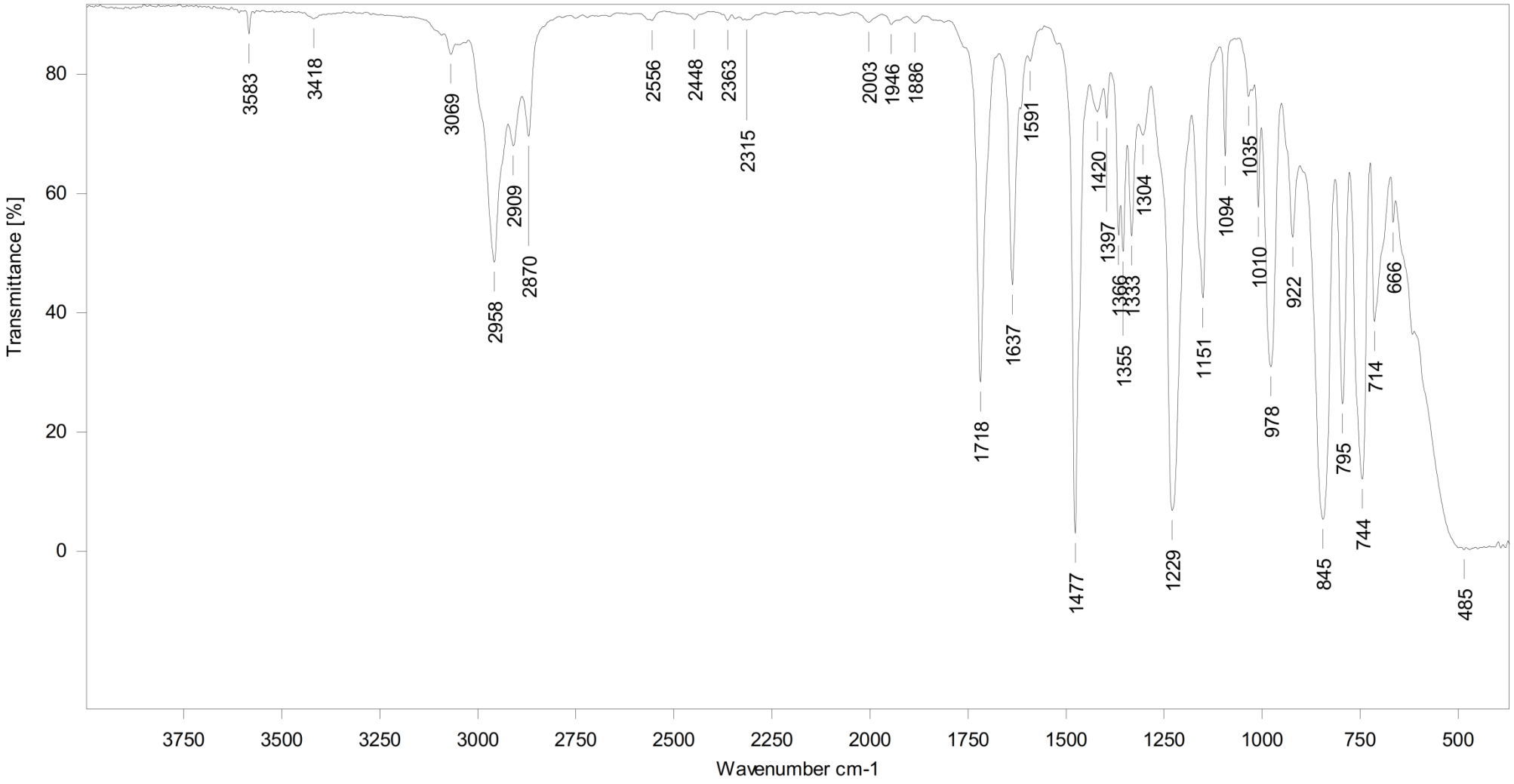


Figure S34. IR Spectrum (Nujol) of phosphole (**3**).

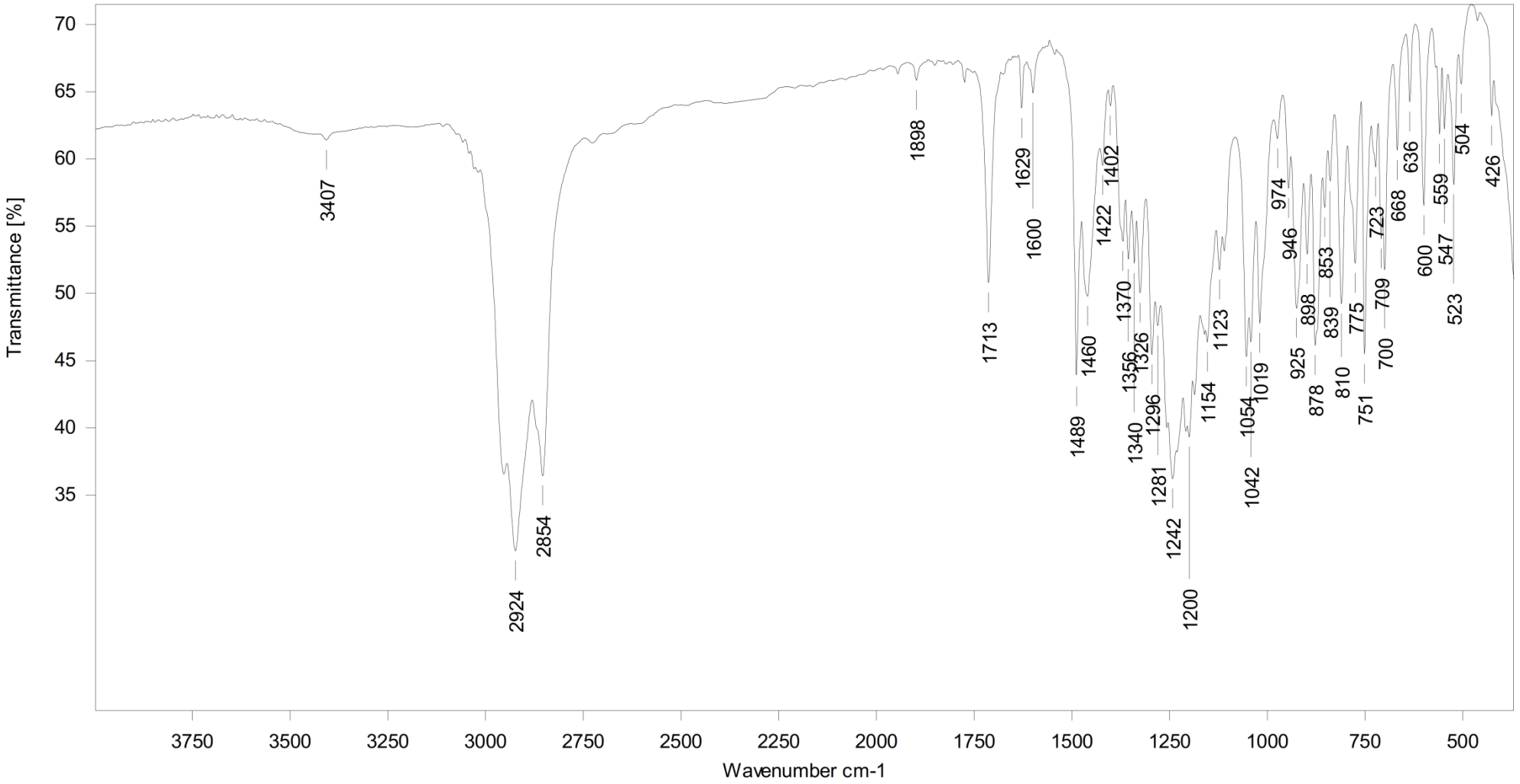


Figure S35. IR Spectrum (Nujol) of phosphorane (**6**).