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2,2,2-Trichloro-4-methoxybenzo-1,3,2-dioxaphosphole in the reactions with terminal acetylenes

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Experimental Section

General remarks. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using a Bruker Avance-400 NMR spectrometer. Elemental analysis was accomplished with an automated EuroVector EA3000 CHNS-O elemental analyzer (Euro-Vector, Milano, Italy). MALDI mass spectra were acquired using an Ultra flex III TOF/TOF spectrometer (Bruker Daltonics, Germany).

*1,2-Bis(trimethylsiloxy)-3-methoxybenzene **2**.* To a solution of 3-methoxycatechol **1** (1.68 g, 12 mmol) and NEt_3 (3.3 ml, 24 mmol) in dry benzene (20 ml), a solution of chlorotrimethylsilane (3.05 ml, 24 mmol) of in benzene (10 ml) was added dropwise. The mixture was stirred for 0.5 h at room temperature. Further, the reaction mixture was heated up to 90 °C and stirred for more 1.5 h. On the next day, the mixture was filtered and the filtrate was concentrated *in vacuo*. The residue

was the title product as a dark brown liquid which was used without additional purification. ^{1}H NMR (500 MHz, $CDCl_3$),δ: 0.28 (br. s, 9H, $C^{1}OSi\underline{Me}_3$), 0.31 (br. s, 9H, $C^{2}OSi\underline{Me}_3$), 3.82 (s, 3H, OCH_3), 6.54 (d. d, 1H, $C^{6}H$, ^{3}J8.2 Hz; ^{4}J 1.4 Hz), 6.57 (d. d, 1H, $C^{4}H$, ^{3}J8.3 Hz; ^{4}J 1.4 Hz), 6.8 (d. d, 1H, $C^{5}H$, ^{3}J 8.2 Hz).

*2-Chloro-4-methoxy-1,3,2-benzodioxaphosphole **3***. A solution of 1,2-bis(trimethylsiloxy)-3-methoxybenzene **2** (12 mmol) in dichloromethane (10 ml) was slowly added dropwise to a solution of phosphorus trichloride (1.6 ml, 18 mmol) in dichloromethane (5 ml). The mixture was stirred at room temperature under an argon atmosphere. The mixture was evaporated *in vacuo*. The residue contained 96% 2-chloro-4-methoxy-1,3,2-benzodioxaphosphole **3** as a light brown solid. ^{13}C NMR (100.6 MHz, $CDCl_3$), δ_C (hereinafter, an appearance of signal in ^{13}C-{^{1}H} NMR spectrum is given in parentheses): 56.43 q (s) (CH_3, $^{1}J_{HC}$ 145.1 Hz), 106.50 dd (s) (C^{7}, $^{1}J_{HC}$ 169.4 Hz, $^{3}J_{HC^{5}CC}$ 8.6 Hz), 108.84 dd (s) (C^{5}, $^{1}J_{HC}$ 161.3 Hz, $^{3}J_{HC^{7}CC}$ 8.1 Hz), 124.65 d (s) (C^{6}, $^{1}J_{HC}$ 163.7 Hz), 132.86 dd (d) (C^{3a}, $^{3}J_{HC^{5}CC}$ 15.6 Hz, $^{2}J_{POC}$ 7.5 Hz), 145.63 dddd (d) (C^{7a}, $^{3}J_{HC^{6}CC}$ 8.3 Hz, $^{3}J_{POCC}$ 7.5 Hz, $^{2}J_{HC^{7}C}$2.9 Hz,$^{4}J_{HC^{5}CCC}$ 1.4 Hz), 147.53 m (d) (C^{4}, $^{3}J_{POCC}$ 2.3 Hz).^{31}P-{^{1}H} NMR (162 MHz, CH_2Cl_2), δ_P: 175.5 (s).

*2,2,2-Trichloro-4-methoxy-1,3,2-benzodioxaphosphole **4***. To a solution of chlorophosphite **3** (12 mmol) in dichloromethane (10 ml), a suspension of phosphorus pentachloride (2.5 g, 12 mmol) in dichloromethane (10 ml) was added. The mixture was stirred for 3 h under argon atmosphere and concentrated *in vacuo*. The residue, a light brown glassy substance, contained 93% of the title product. ^{13}C NMR (100.6 MHz, $CDCl_3$), δ_C: 56.45 q (s) (CH_3, $^{1}J_{CH}$ 145.2 Hz), 103.63 ddd (d) (C^{7}, $^{1}J_{CH}$ 168.2 Hz, $^{3}J_{POCC}$ 17.8 Hz, $^{3}J_{HC^{5}CC}$ 8.3 Hz), 108.12 dd (s) (C^{5}, $^{1}J_{CH}$ 161.1 Hz, $^{3}J_{HC^{7}CC}$ 8.2 Hz), 123.5 d (s) (C^{6}, $^{1}J_{CH}$ 162.4 Hz), 131.48 br. s (s) (C^{3a}), 143.65 dd (s) (C^{7a}, $^{3}J_{HC^{6}CC}$ 13.2 Hz, $^{4}J_{HC^{5}CCC}$ 2.4 Hz), 144.45 m (d) (C^{4}, $^{3}J_{POCC}$ 19.4 Hz). ^{31}P-{^{1}H} NMR (162 MHz, CH_2Cl_2), δ_P: –25.4 (s).

*4-(4-Bromophenyl)-2,7-dichloro-5-methoxy-1,2-benzoxaphosphihine 2-oxide **5b*** was prepared from phosphorane **4** (7.5 mmol) and *p*-bromophenylacetylene (2.7 g, 15 mmol). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 3.40 (s, 3H, OCH_3), 6.19 (d, 1H, $C^{3}H$, $^{2}J_{PCH}$25.7 Hz), 6.72 (d, 1H, $C^{6}H$,^{4}J 1.6 Hz), 6.92 (d, 1H, $C^{8}H$,^{4}J 1.5 Hz), 7.29 (m, 2H, *AA'*-part of *AA'XX'*-spectrum, $C^{10,14}H$, ^{3}J 8.5 Hz), 7.40 (m, 2H, *XX'*-part of *AA'XX'*-spectrum, $C^{11,13}H$, ^{3}J 8.5 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ_C: 56.01 q (s) (OCH_3, $^{1}J_{HC}$ 145.8 Hz), 109.80 dd (s) (C^{6}, $^{1}J_{HC}$ 166.4 Hz, $^{3}J_{HC^{8}CC}$ 5.3 Hz), 110.31 m (d) (C^{4a}, $^{3}J_{POCC}$ 17.9), 112.89 ddd (d) (C^{8}, $^{1}J_{HC}$ 172.4 Hz, $^{3}J_{POCC}$ 7.7 Hz, $^{3}J_{HC^{6}CC}$ 5.5 Hz), 115.84 dd (d) (C^{3}, $^{1}J_{HC}$ 171.9 Hz, $^{1}J_{PC}$ 157.6 Hz), 121.11 m (s) (C^{12}, $^{3}J_{HC^{10,14}CC}$ 8.4 Hz, $^{2}J_{HCC}$ 4.2 Hz), 131.59 m (s) ($C^{10,14}$, $^{1}J_{HC}$ 167.9 Hz, $^{3}J_{HC^{14,10}CC}$ 5.4 Hz), 133.54 m (s) ($C^{11,13}$, $^{1}J_{HC}$ 165.1 Hz, $^{3}J_{HC^{13,11}CC}$ 6.5 Hz), 138.83 dd (s) (C^{7}, $^{2}J_{HC^{8}C}$ 4.7 Hz, $^{2}J_{HC^{6}C}$ 4.7 Hz), 139.29 ddd (d) (C^{9}, $^{3}J_{PCCC}$ 20.6 Hz,$^{3}J_{HCCC}$ 6.2 Hz, $^{3}J_{HCCC}$ 6.2 Hz), 151.82 dd (d) (C^{8a}, $^{2}J_{POC}$ 10.0 Hz, $^{2}J_{HC^{8}C}$ 4.5 Hz), 154.29 br. s (s) (C^{4}), 158.33 m (s) (C^{5}). ^{31}P / ^{31}P-{^{1}H} NMR (162 MHz, $CDCl_3$), δ_P:18.0 d (s) ($^{2}J_{PCH}$ 22.6 Hz).

*2,7-Dichloro-4-(4-chlorophenyl)-5-methoxy-1,2-benzoxaphosphihine 2-oxide **5c*** was prepared from phosphorane **4** (2.48 g, 9.0 mmol) and *p*-chlorophenylacetylene (2.5 g, 18 mmol). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 3.40 (s, 3H, OCH_3), 6.19 (d, 1H, $C^{3}H$, $^{2}J_{PCH}$25.7 Hz), 6.72 (d, 1H, $C^{6}H$, ^{4}J

1.7 Hz), 6.92 (d, 1H, C^8H, ^4J 1.7 Hz), 7.21 (m, 2H, *AA'*-part of *AA'XX'*-spectrum, $C^{10,14}H$, ^3J 8.7 Hz), 7.33 (m, 2H, *XX'*-part of *AA'XX'*-spectrum, $C^{11,13}H$, ^3J 8.7 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ_C: 55.95 q (s) (OCH_3, $^1J_{HC}$ 145.8 Hz), 109.82 dd (s) (C^6, $^1J_{HC}$166.5 Hz, $^3J_{HC^8CC}$ 5.2 Hz), 110.34 m (d) (C^{4a}, $^3J_{PCCC}$17.9 Hz), 112.82 ddd (d) (C^8, $^1J_{HC}$ 172.6 Hz,$^3J_{POCC}$ 7.8 Hz, $^3J_{HC^6CC}$ 5.3 Hz), 115.85 dd (d) (C^3, $^1J_{PC}$ 157.5 Hz, $^1J_{HC}$ 171.9 Hz), 128.64 m (s) ($C^{10,14}$, $^1J_{HC}$ 167.5 Hz, $^3J_{HC^{14,10}CC}$ 5.0 Hz), 133.33 m (s) ($C^{11,13}$, $^1J_{HC}$ 165.5 Hz, $^3J_{HC^{13,11}CC}$ 6.8 Hz), 134.79 m (s) (C^7), 138.77 ddd (d) (C^9, $^3J_{PCCC}$ 20.9 Hz, $^3J_{HCCC}$ 8.5 Hz, $^3J_{HCCC}$ 8.5 Hz), 138.78 m (s) (C^{12}, $^3J_{HCCC}$ 8.4 Hz), 151.80 dd (d) (C^{8a}, $^2J_{POC}$ 10.0 Hz, $^2J_{HC^8C}$ 4.4 Hz), 154.26 br. s (s) (C^4), 158.34 br. s (s) (C^5). ^{31}P / ^{31}P-{^1H} NMR (162 MHz, CH_2Cl_2), δ_P: 18.3 d (s) ($^2J_{PCH}$ 22.6 Hz).

2,7-Dichloro-4-(4-chloromethyl)-5-methoxy-1,2-benzoxaphosphihine 2-oxide ***5d*** was prepared from phosphorane **4** (3 g, 11 mmol) and 3-chloropropyne (1.57 ml, 22 mmol). ^1H NMR (400 MHz, $CDCl_3$), δ: 3.94 (s, 3H, OCH_3), 4.78 (d, 1H, *A*-part of *AB*-spectrum, C^9H, $^2J_{AB}$ 13.0-14.0 Hz), 4.84 (d, 1H, *B*-part of *AB*-spectrum, C^9H, $^2J_{AB}$ 13.0-14.0 Hz), 6.68 (d, 1H, C^3H, $^2J_{PCH}$22.5 Hz), 6.84 (d, 1H, C^6H, ^4J1.5 Hz), 6.91 (d, 1H, C^8H, ^4J 1.8 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$)δ_C: 47.30 tdd (d) (C^9, $^1J_{HC}$ 156.2 Hz, $^3J_{PCCC}$ 22.1 Hz, $^3J_{HC^3CC}$ 7.9 Hz), 56.86 q (s) (OCH_3, $^1J_{HC}$ 146.3 Hz), 109.29 m (s) (C^{4a}, $^3J_{POCC}$18.1 Hz), 109.55 dd (s) (C^6, $^1J_{HC}$166.7 Hz, $^3J_{HC^8CC}$ 5.3 Hz), 113.21 ddd (d) (C^8, $^1J_{HC}$ 173.0 Hz, $^3J_{POCC}$ 8.3 Hz, $^3J_{HC^6CC}$ 5.1 Hz), 114.70 dd (d) (C^3, $^1J_{HC}$ 171.6 Hz, $^1J_{PC}$ 159.5 Hz), 138.55 dt (s) (C^7, $^2J_{HC^8C}$ 4.8 Hz, $^2J_{HC^6C}$ 4.8 Hz), 151.71 dd (d) (C^{8a}, $^2J_{POC}$ 10.1 Hz, $^2J_{HC^8C}$ 4.5 Hz), 154.29 m (d) (C^4, $^2J_{PCC}$ 3.0 Hz), 158.46 br. s (d) (C^5, $^4J_{PCCCC}$ 1.9 Hz). ^{31}P / ^{31}P-{^1H} NMR (162 MHz, $CDCl_3$), δ_P: 19.5 d (s) ($^2J_{PCH}$ 22.2 Hz).

Hydrolysis of4-(4-bromophenyl)-2,7-dichloro-5-methoxy-1,2-benzoxaphosphihine 2-oxide ***5b***. To a solution of dioxaphosphinine **5b** in 1,4-dioxane (8 ml). water (3 ml) was added. On the next day, the resulting solution was evaporated dry *in vacuo* (15 Torr), and benzene (10 ml) was added. The formation of mixture of 4-(4-bromophenyl)-7-chloro-2-hydroxy-5-methoxy-1,2-benzoxaphosphinine 2-oxide **7b** and *E*-2-(4-bromophenyl)-2-(4-chloro-6-hydroxy-2-methoxyphenyl)ethenylphosphonic acid **6b** as a light precipitate was observed. The mixture of compounds **6b** and **7b** was filtered and dried *in vacuo* at 60 °C.

4-(4-Bromophenyl)-7-chloro-2-hydroxy-5-methoxy-1,2-benzoxaphosphinine 2-oxide ***7b***. ^1H NMR (400 MHz, DMSO-d_6), δ: 3.41 (s, 3H, OCH_3), 6.25 (d, 1H, C^3H, $^2J_{PCH}$19.4 Hz), 6.95 (d, 1H, C^8H, ^4J 1.9 Hz), 7.04 (d, 1H, C^6H, ^4J 1.8 Hz), 7.16 (m, 2H, *AA'*-part of *AA'XX'*-spectrum, $C^{10,14}H$, ^3J8.5 Hz), 7.54 (m, 2H, *XX'*-part of *AA'XX'*-spectrum, $C^{11,13}H$, ^3J8.5 Hz). ^{13}C NMR (100.6 MHz, DMSO-d_6), δ_C: 56.57 q (s) (OCH_3, $^1J_{HC}$ 145.9 Hz), 108.93 dd (s) (C^6, $^1J_{HC}$ 167.9 Hz, $^3J_{HC^8CC}$ 5.1 Hz), 111.64 m (d) (C^{4a}, $^3J_{POCC}$ 16.1 Hz), 112.58 ddd (d) (C^8, $^1J_{HC}$ 171.7 Hz, $^3J_{POCC}$ 6.4 Hz,$^3J_{HC^6CC}$ 5.1 Hz), 119.35 dd (d) (C^3, $^1J_{PC}$ 171.8 Hz, $^1J_{HC}$ 164.3 Hz), 121.33 m (s) (C^{12}, $^3J_{HC^{10,14}CC}$ 8.4 Hz, $^2J_{HCC}$ 4.2 Hz), 128.88 m (s) ($C^{10,14}$, $^1J_{HC}$ 162.4 Hz, $^3J_{HC^{14,10}CC}$ 7.0 Hz), 131.19 m (s) ($C^{11,13}$, $^1J_{HC}$ 167.0 Hz, $^3J_{HC^{13,11}CC}$ 5.5 Hz), 136.05 dd (s) (C^7, $^2J_{HC^8C}$ 5.2 Hz, $^2J_{HC^6C}$ 4.3 Hz), 140.96 m (d) (C^9, $^3J_{PCCC}$ 18.4 Hz,$^3J_{HC^3CC}$ 14.6 Hz, $^3J_{HCCC}$ 7.7 Hz), 153.17 dd (d) (C^{8a}, $^2J_{POC}$ 7.2 Hz, $^2J_{HC^8C}$ 4.2 Hz),

156.45 br. s (s) (C^4), 158.35 m (s) (C^5). ^{31}P / ^{31}P-{^1H} NMR (162 MHz, DMSO-d_6), δ_P: 4.7 d (s) ($^2J_{PCH}$ 19.1 Hz). MS (MALDI-TOF), *m/z*: 402.95 (calc. for $C_{15}H_{11}BrClO_4P$, *m/z*: 401.58).

E-2-(4-Bromophenyl)-2-(4-chloro-6-hydroxy-2-methoxyphenyl)ethenylphosphonic acid ***6b***. ^1H NMR (400 MHz, DMSO-d_6), δ: 3.60 (s, 3H, OCH_3), 6.37 (d, 1H, C^2H, $^2J_{PCH}$ 13.4 Hz), 6.51 (d, 1H, $C^{5'}H$, ^4J 1.8 Hz), 6.53 (d, 1H, $C^{3'}H$, ^4J 1.8), 7.21 (m, 2H, *AA'*-part of *AA'XX'*-spectrum, $C^{2'',6''}H$, ^3J 8.6 Hz), 7.50 (m, 2H, *XX'*-part of *AA'XX'*-spectrum, $C^{3'',5''}H$, ^3J 8.6 Hz). ^{13}C NMR (100.6 MHz, DMSO-d_6), δ_C: 56.38 q (s) (OCH_3, $^1J_{HC}$ 144.6 Hz), 103.44 dd (s) ($C^{5'}$, $^1J_{HC}$ 166.1 Hz, $^3J_{HC^{3'}CC}$ 4.9 Hz), 109.1 dd (s) ($C^{3'}$,$^1J_{HC}$ 165.7 Hz, $^3J_{HC^{5'}CC}$ 4.9 Hz), 114.33 m (d) ($C^{1'}$, $^3J_{PCCC}$7.2 Hz), 122.05 m (s) ($C^{4''}$, $^3J_{HC^{2'',6''}CC}$ 11.2 Hz, $^2J_{HCC}$ 3.0 Hz), 122.78 dd (d) (C^1, $^1J_{PC}$ 186.3 Hz,$^1J_{HC}$ 149.3 Hz), 128.63 dd (s) ($C^{2'',6''}$, $^1J_{HC}$ 161.1 Hz, $^3J_{HC^{6''},2''CC}$ 7.0 Hz), 131.70 dd (s) ($C^{3'',5''}$, $^1J_{HC}$ 167.0 Hz, $^3J_{HC^{5''},3''CC}$ 5.2 Hz), 133.34 dd (s) ($C^{4'}$, $^2J_{HC^{5'}C}$ 5.0 Hz, $^2J_{HC^{3'}C}$ 4.3 Hz), 139.86 m (d) ($C^{1''}$, $^3J_{PCCC}$ 22.0 Hz, $^3J_{HC^2CC}$ 14.6 Hz, $^3J_{HC^{3''},5''CC}$ 7.7 Hz), 149.03 m (s)($C^{6'}$), 156.45 br. s (s) (C^2), 158.95 br. s (s) ($C^{2'}$). ^{31}P / ^{31}P-{^1H} NMR (162 MHz, DMSO-d_6), δ_P: 10.4 d (s)($^2J_{PCH}$ 13.5 Hz). MALDI-TOF: 420.95 *m/z* (calc. for $C_{15}H_{13}BrClO_5P$ 419.59).

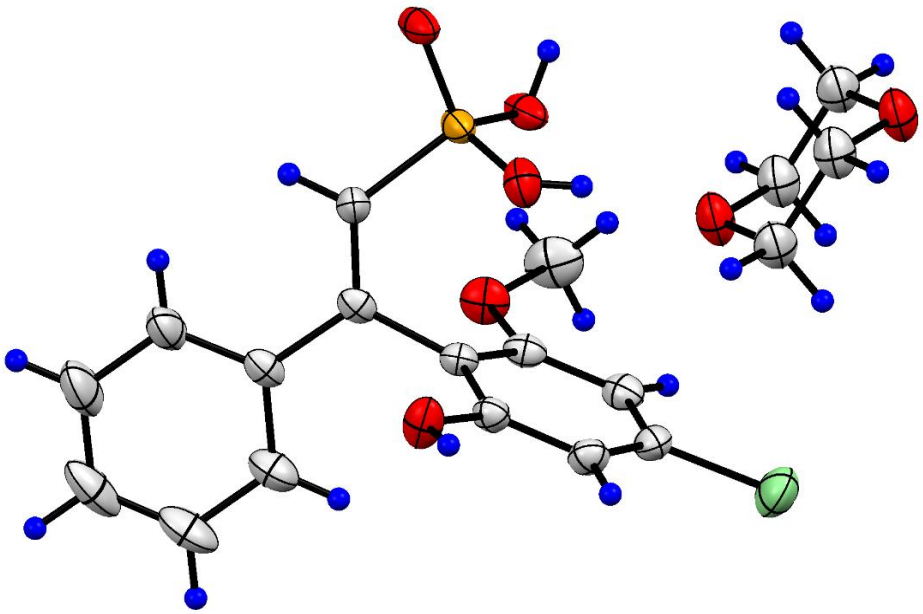

Figure S1. Geometry of molecule **6a** in the crystal (solvate with dioxane). Non-hydrogen atoms are shown in view of thermal ellipsoids with a probability of 30%.

Table S1. Bond lengths in the molecule of compound **6a**.

bond	*d*, Å	bond	*d*, Å	bond	*d*, Å	bond	*d*, Å	bond	*d*, Å
Cl^1–C^6	1.740(2)	C^9–C^{14}	1.383(3)	O^5–C^4	1.360(3)	O^{1S}–C^{3S}	1.427(3)	C^4–C^5	1.385(3)
P^1–O^2	1.489(2)	C^9–C^{10}	1.382(3)	O^5–C^{15}	1.430(3)	C^1–C^2	1.332(3)	C^5–C^6	1.371(3)
P^1–O^3	1.545(2)	C^{10}–C^{11}	1.374(4)	O^1–H^1	0.77(3)	C^2–C^9	1.482(3)	C^6–C^7	1.366(3)
P^1–O^4	1.536(2)	C^{11}–C^{12}	1.361(5)	O^3–H^3	0.81(3)	C^2–C^3	1.501(3)	C^7–C^8	1.382(3)
P^1–C^1	1.760(2)	C^{12}–C^{13}	1.363(5)	O^4–H^4	0.84(3)	C^3–C^8	1.386(3)	–	–
O^1–C^8	1.348(3))	C^{13}–C^{14}	1.378(4	O^{1S}–C^{2S}	1.426(3)	C^3–C^4	1.390(3)	–	–

Table S2. Bond angles in the molecule of compound (**6a**).

Angle	φ (grad)	Angle	φ (grad)	Angle	φ (grad)	Angle	φ (grad)
O^2–P^1–O^3	110.2(1)	C^2–C^9–C^{14}	120.3(2)	P^1–C^1–C^2	126.4(2)	O^5–C^4–C^5	124.3(2)
O^2–P^1–O^4	112.7(1)	C^2–C^9–C^{10}	122.0(2)	C^1–C^2–C^3	119.1(2)	C^4–C^5–C^6	118.3(2)
O^2–P^1–C^1	108.9(1)	C^9–C^{10}–C^{11}	121.0(2)	C^1–C^2–C^9	123.1(2)	Cl^1–C^6–C^7	118.3(2)
O^3–P^1–O^4	107.9(1)	C^{10}–C^{11}–C^{12}	120.2(3)	C^3–C^2–C^9	117.8(2)	Cl^1–C^6–C^5	118.9(2)
O^3–P^1–C^1	108.3(1)	C^{11}–C^{12}–C^{13}	120.0(3)	C^4–C^3–C^8	118.6(2)	C^5–C^6–C^7	122.8(2)
O^4–P^1–C^1	108.7(1)	C^{12}–C^{13}–C^{14}	120.1(3)	C^2–C^3–C^4	121.9(2)	C^6–C^7–C^8	118.2(2)
C^4–O^5–C^{15}	118.5(2)	C^9–C^{14}–C^{13}	120.9(3)	C^2–C^3–C^8	119.4(2)	O^1–C^8–C^7	122.7(2)
O^1–C^8–C^3	116.0(2)	P^1–O^4–H^4	113(2)	O^5–C^4–C^3	114.9(2)	C^3–C^8–C^7	121.2(2)
C^{10}–C^9–C^{14}	117.8(2)	C^{2S}–O^{1S}–C^{3S}	111.1(2)	C^3–C^4–C^5	120.8(2)	–	–

Table S3. Torsion angles in the molecule of compound (**6a**).

Angle	τ (grad)	Angle	τ (grad)	Angle	τ (grad)
O^2–P^1–C^1–C^2	–169.2(2)	P^1–C^1–C^2–C^3	–0.9(3)	C^3–C^2–C^9–C^{14}	–5.7(3)
O^3–P^1–C^1–C^2	–49.4(2)	P^1–C^1–C^2–C^9	177.4(2)	C^9–C^2–C^3–C^4	101.3(2)
O^4–P^1–C^1–C^2	67.6(2)	C^1–C^2–C^3–C^4	–80.3(3)	C^1–C^2–C^3–C^8	96.1(2)
C^{15}–O^5–C^4–C^3	162.7(2)	C^9–C^2–C^3–C^8	–82.3(3)	C^2–C^3–C^4–C^5	173.2(2)
C^{15}–O^5–C^4–C^5	–18.1(3)	C^1–C^2–C^9–C^{10}	–5.5(3)	C^2–C^3–C^4–O^5	–7.6(3)
C^{3S}–O^{1S}–C^{2S}–C^{3S_a}	57.9(3)	C^1–C^2–C^9–C^{14}	175.9(2)	C^2–C^3–C^8–O^1	5.0(3)
C^2S–O^1S–C^{3S}–C^{2S_a}	–57.7(3)	C^3–C^2–C^9–C^{10}	172.8(2)	C^2–C^3–C^8–C^7	–173.7(2)
C^4–C^3–C^8–O^1	–178.5(2)	C^8–C^3–C^4–O^5	176.0(2)	O^5–C^4–C^5–C^6	–178.2(2)
C^4–C^3–C^8–C^7	2.8(3)	C^8–C^3–C^4–C^5	–3.2(3)	C^3–C^4–C^5–C^6	0.9(3)

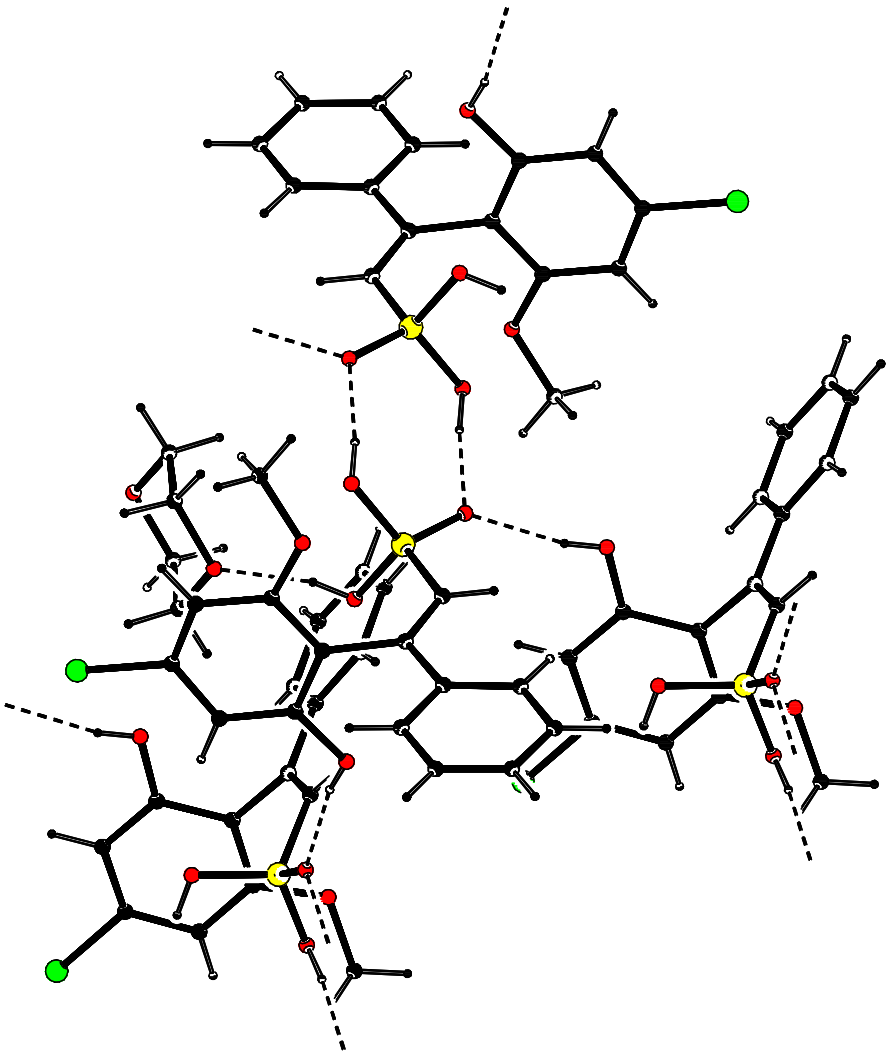

Figure S2. Hydrogen bonds system for the molecule **6a** in the crystal (solvate with dioxane).

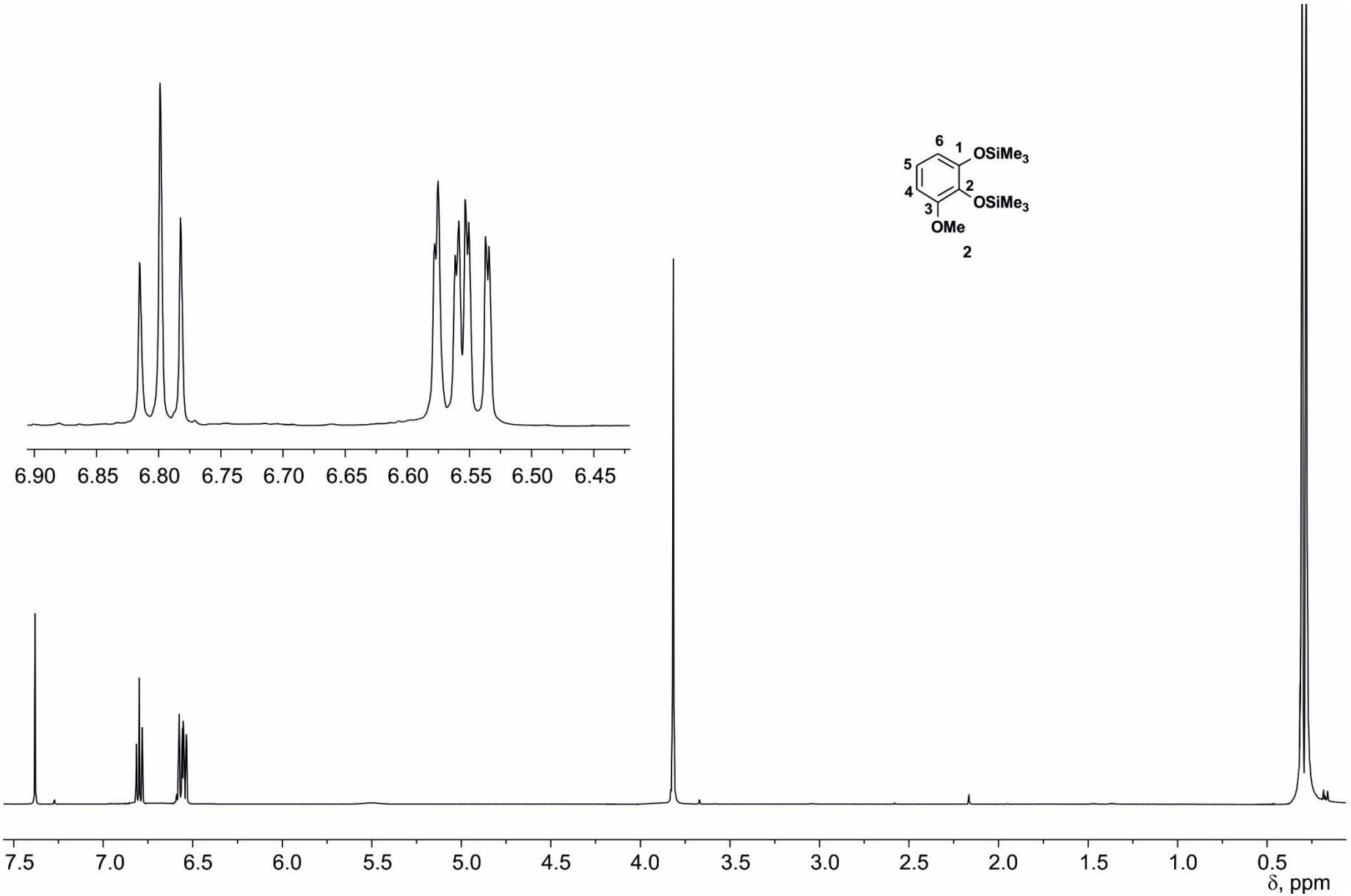

Figure S3. ^{1}H NMR spectrum (400.0 MHz, $CDCl_3$, 25°C) of ether **2**.

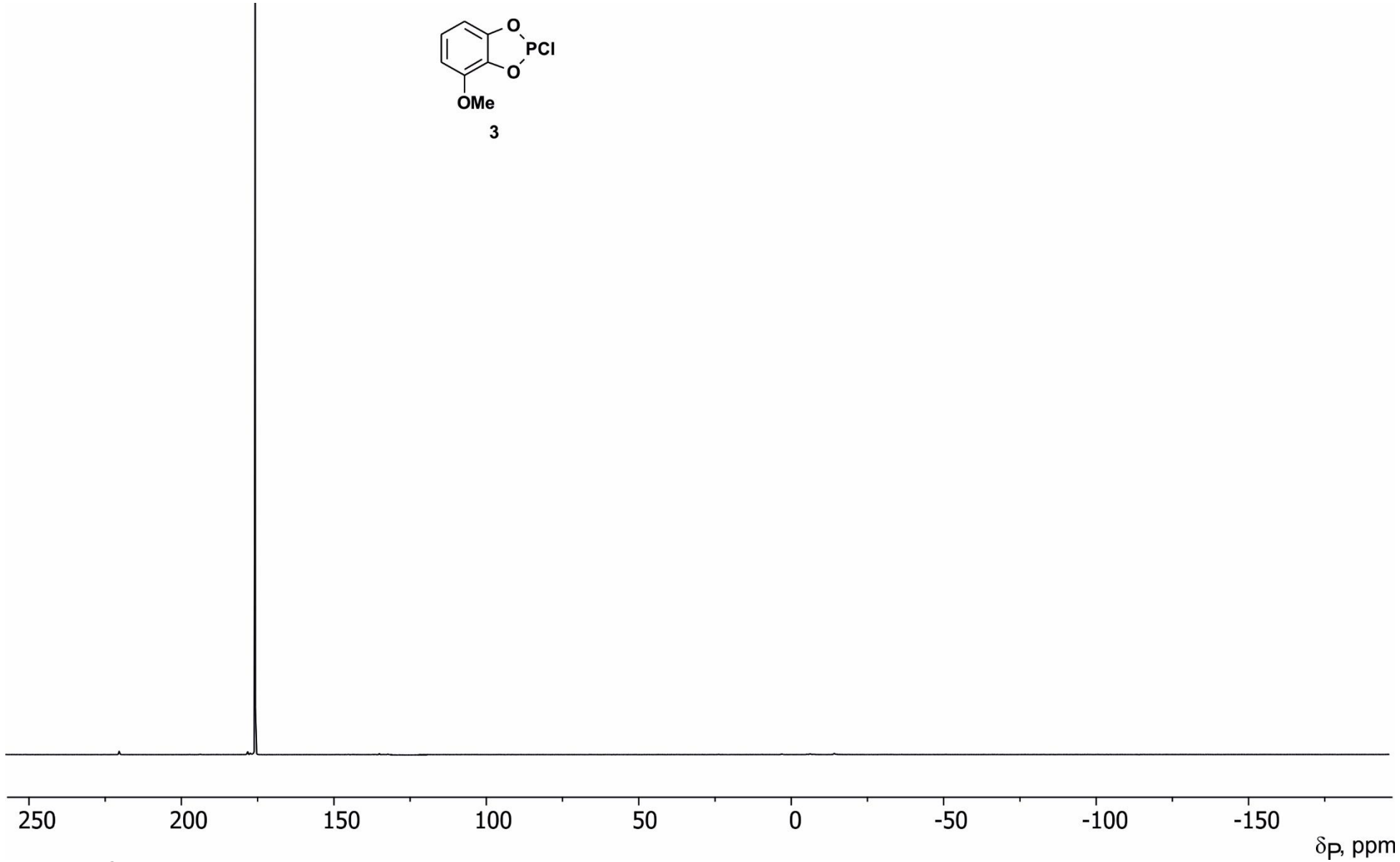

Figure S4. ^{31}P-{^{1}H} NMR spectrum (162.0 MHz, $CDCl_3$, 25°C) of phosphole **3**.

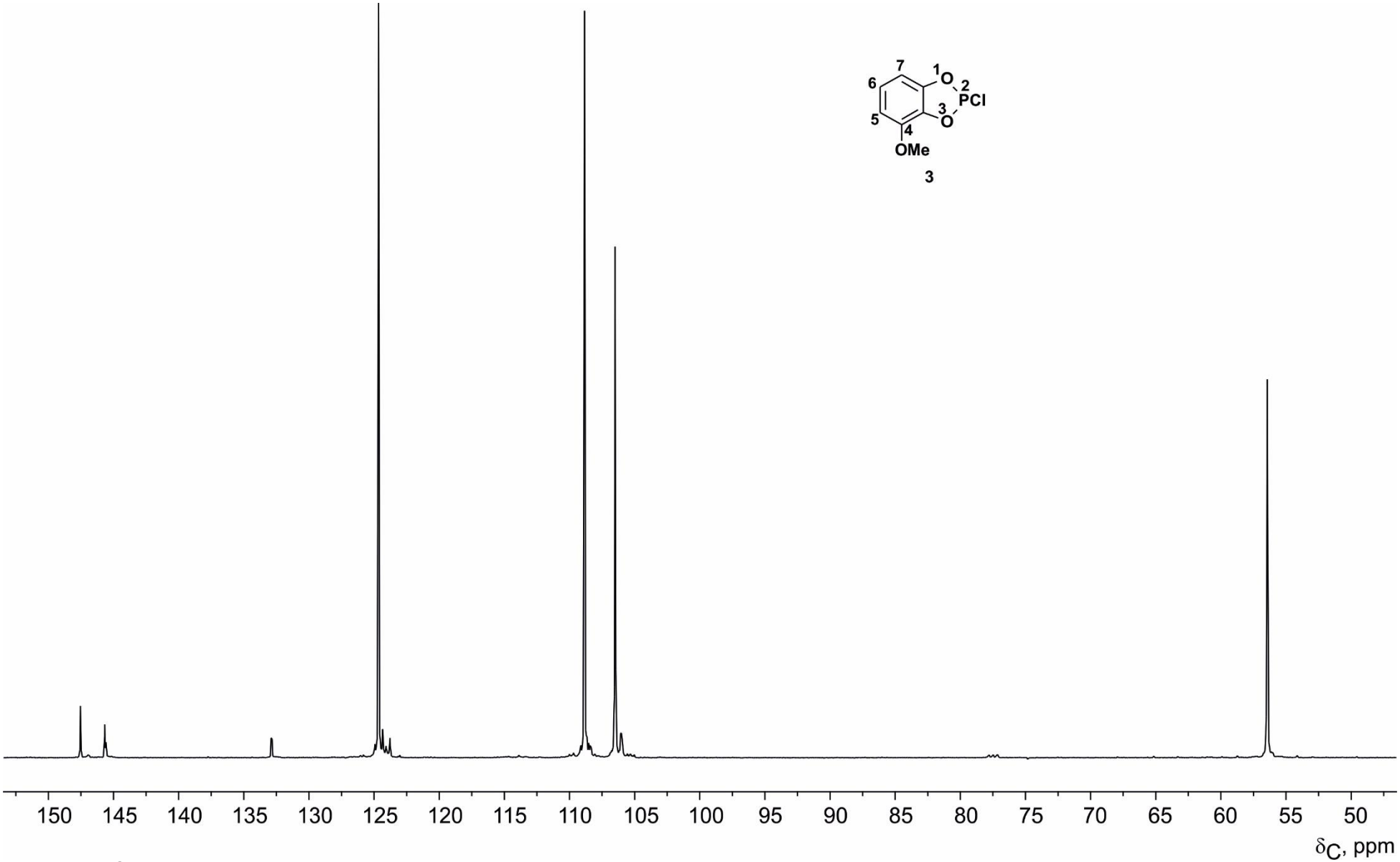

Figure S5. ^{13}C-{^{1}H} NMR spectrum (100.9 MHz, $CDCl_3$, 25°C) of phosphole **3**.

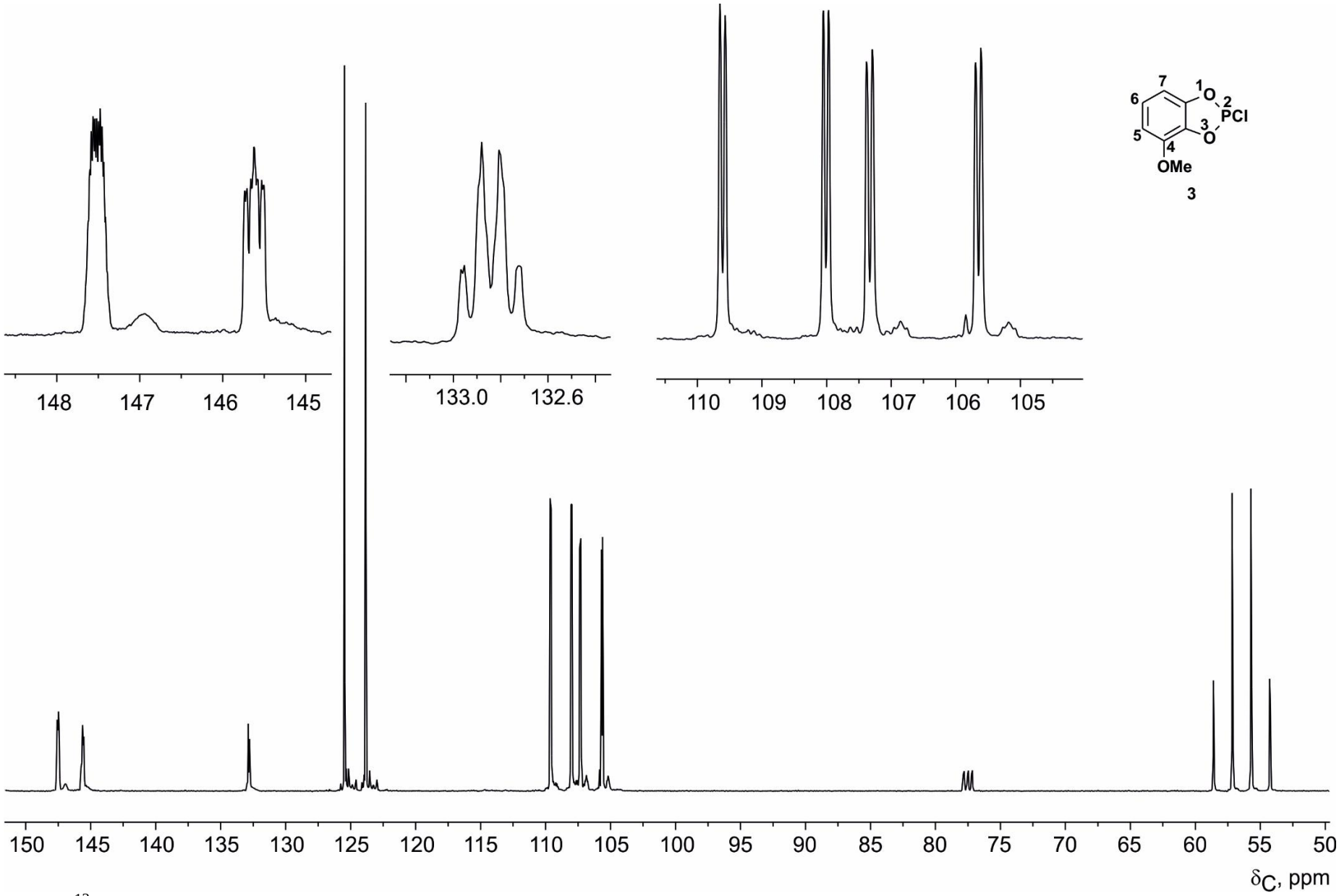

Figure S6. ^{13}C NMR spectrum (100.9 MHz, $CDCl_3$, 25°C) of phosphole **3**.

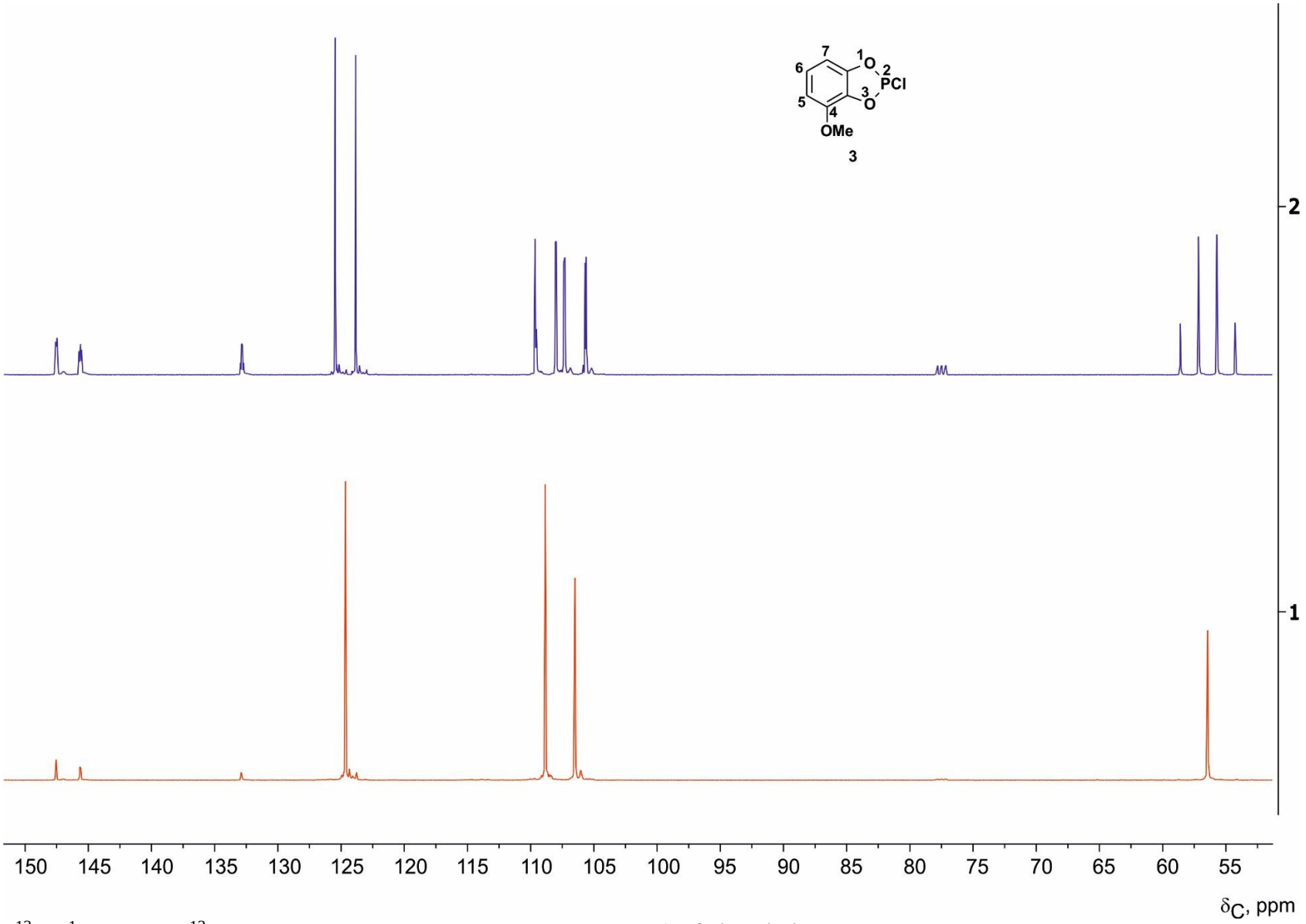

Figure S7. ^{13}C-{^{1}H} (1) and ^{13}C (2) NMR spectra (100.9 MHz, $CDCl_3$, 25°C) of phosphole **3**.

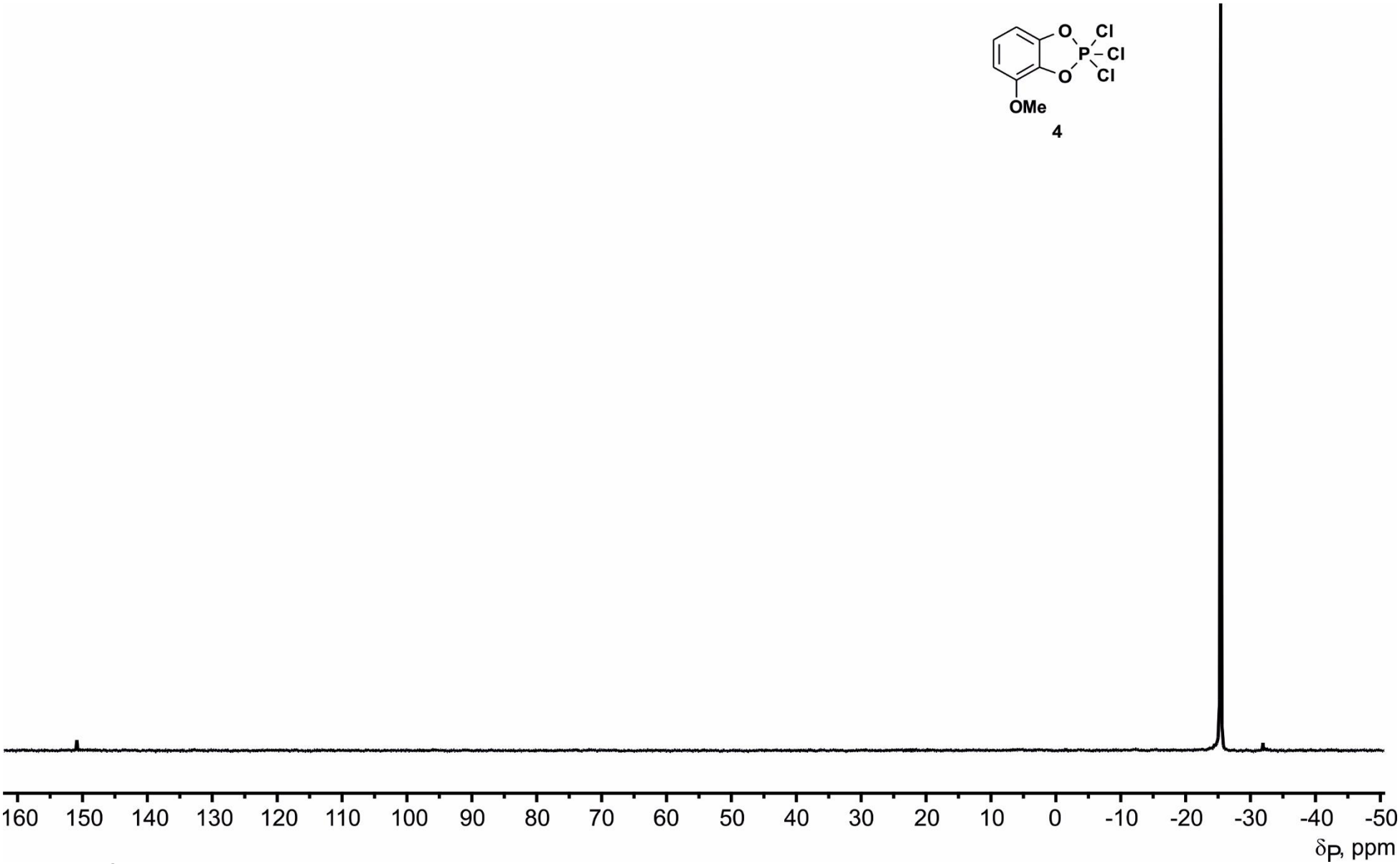

Figure S8. ^{31}P-{^{1}H} NMR spectrum (162 MHz, $CDCl_3$, 25°C) of phosphole **4**.

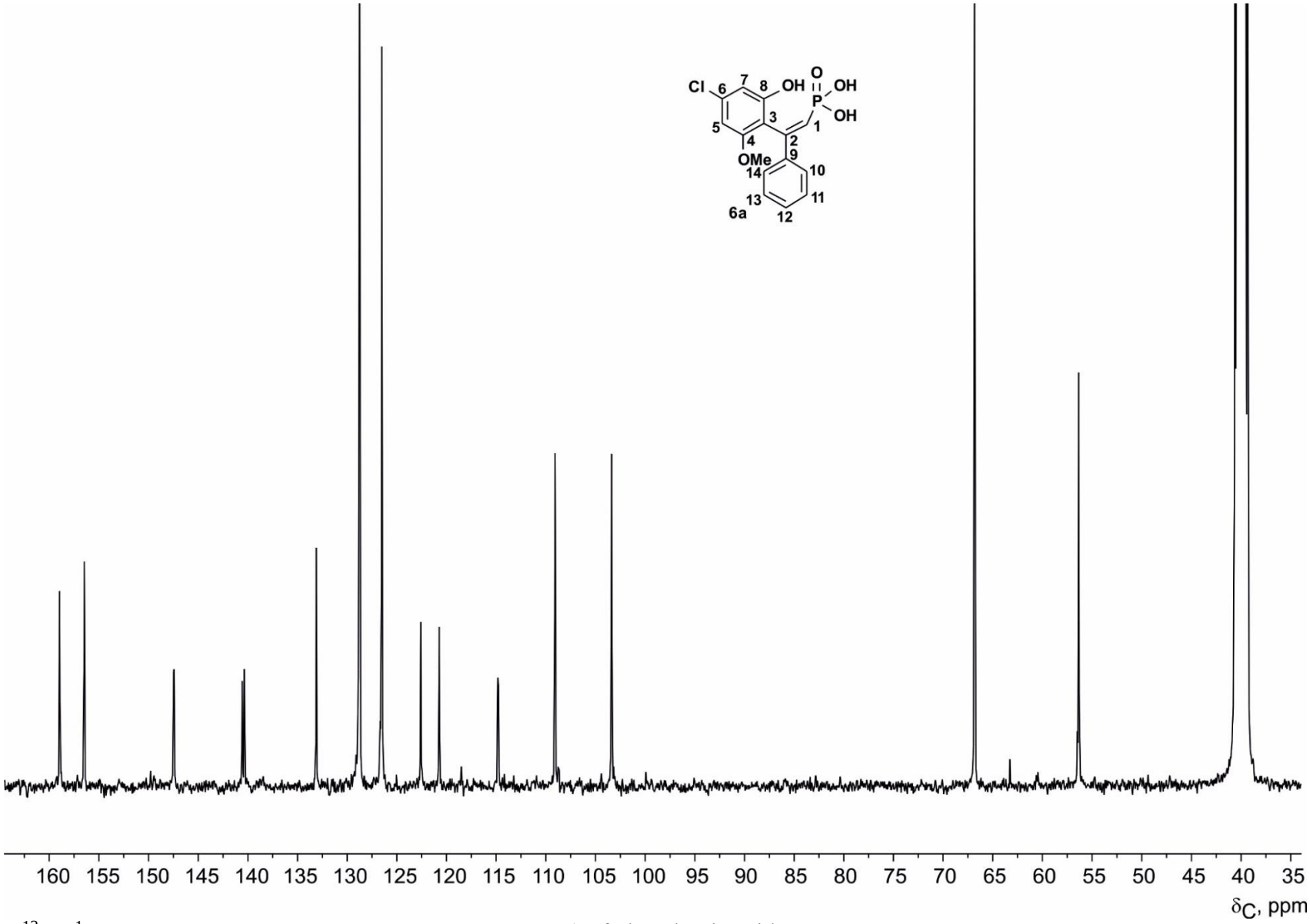

Figure S9. ^{13}C-{^{1}H} NMR spectrum (100.9 MHz, DMSO-d_6, 25°C) of phosphonic acid **6a**.

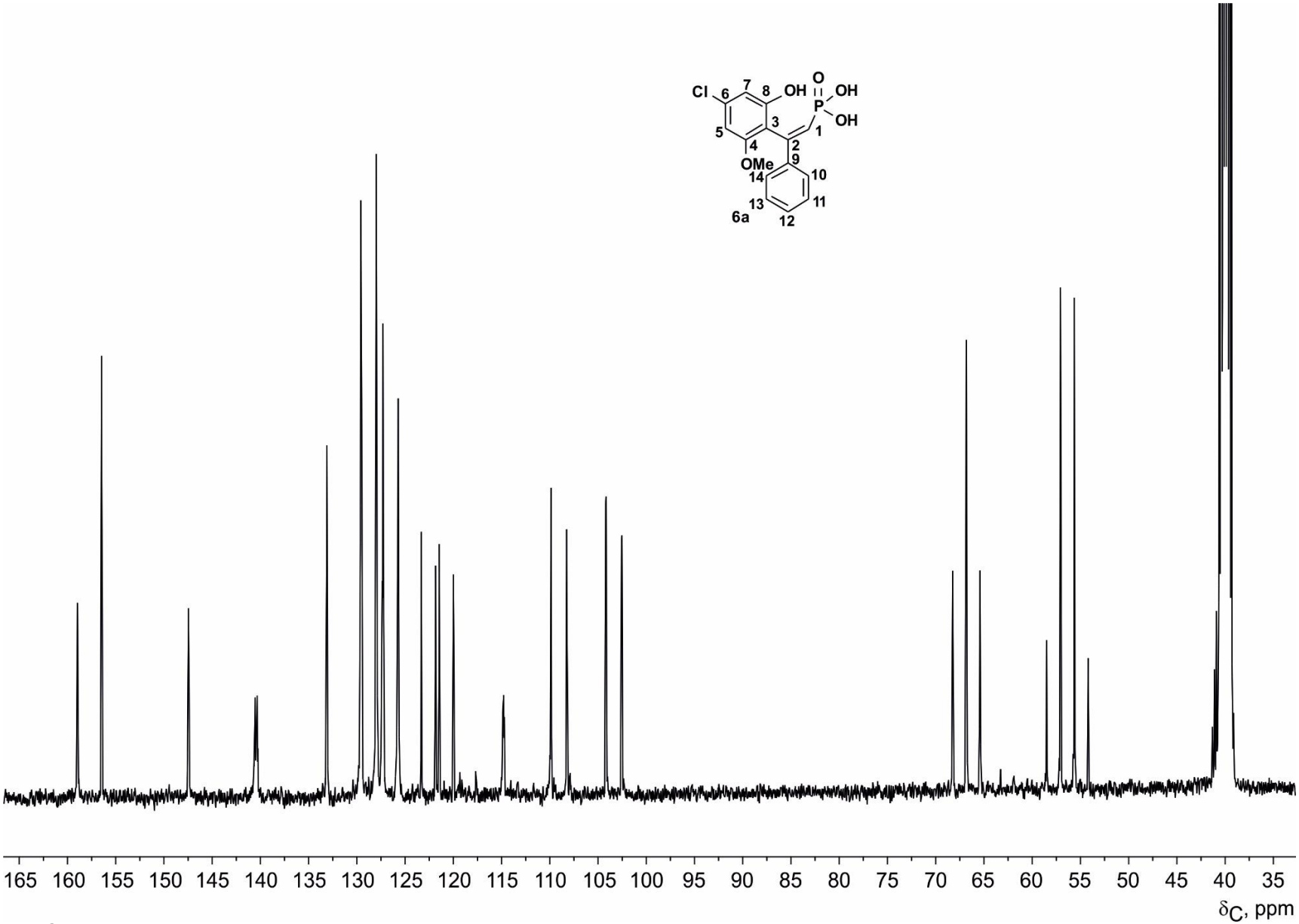

Figure S10. ^{13}C NMR spectrum (100.9 MHz, DMSO-d_6, 25°C) of phosphonic acid **6a**.

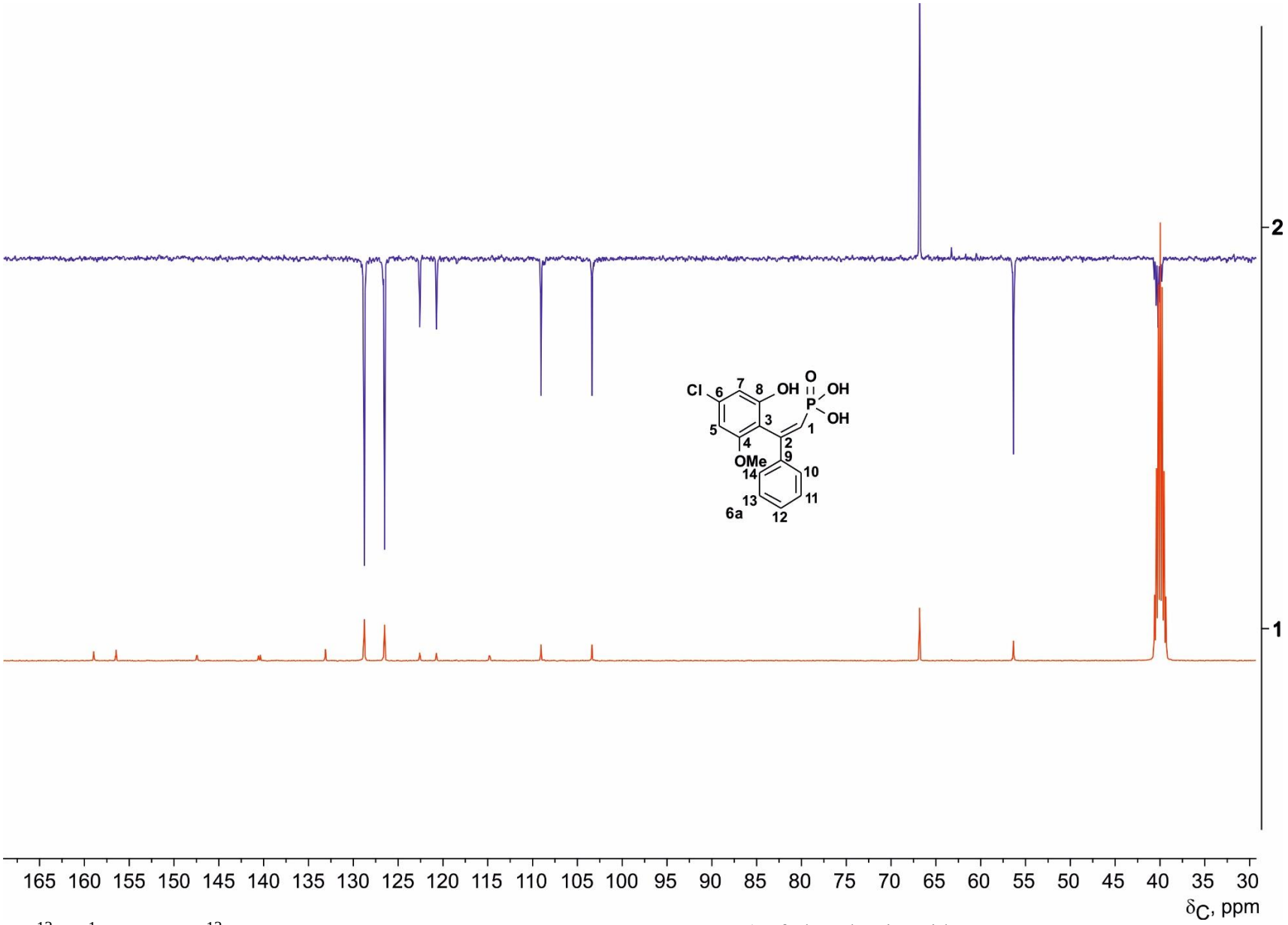

Figure S11. ^{13}C-{^{1}H} (1) and ^{13}C-dept (2) NMR spectra (100.9 MHz, DMSO-d_6, 25°C) of phosphonic acid **6a**.

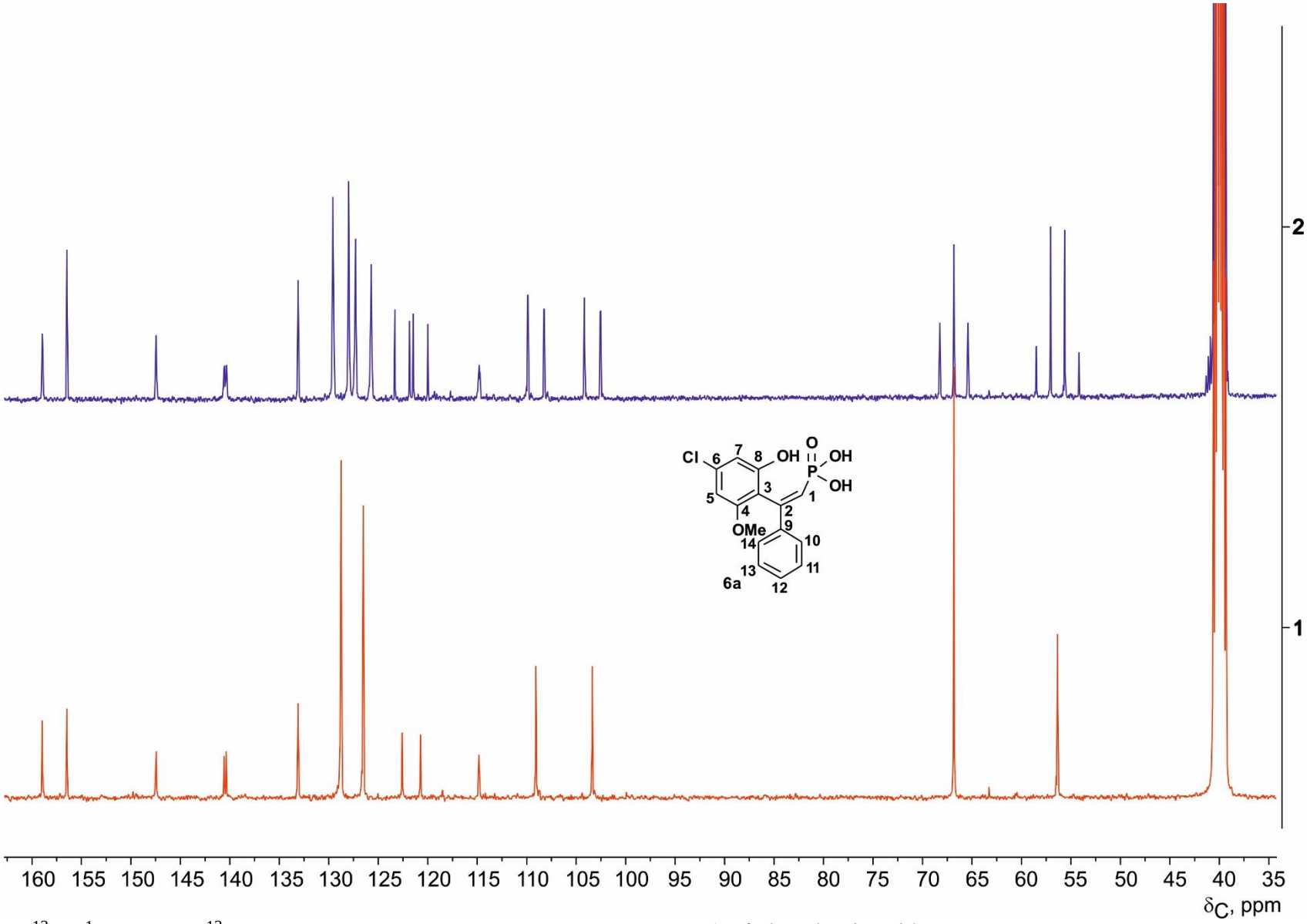

Figure S12. ^{13}C-{^{1}H} (1) and ^{13}C (2) NMR spectra (100.9 MHz, DMSO-d_6, 25°C) of phosphonic acid **6a**

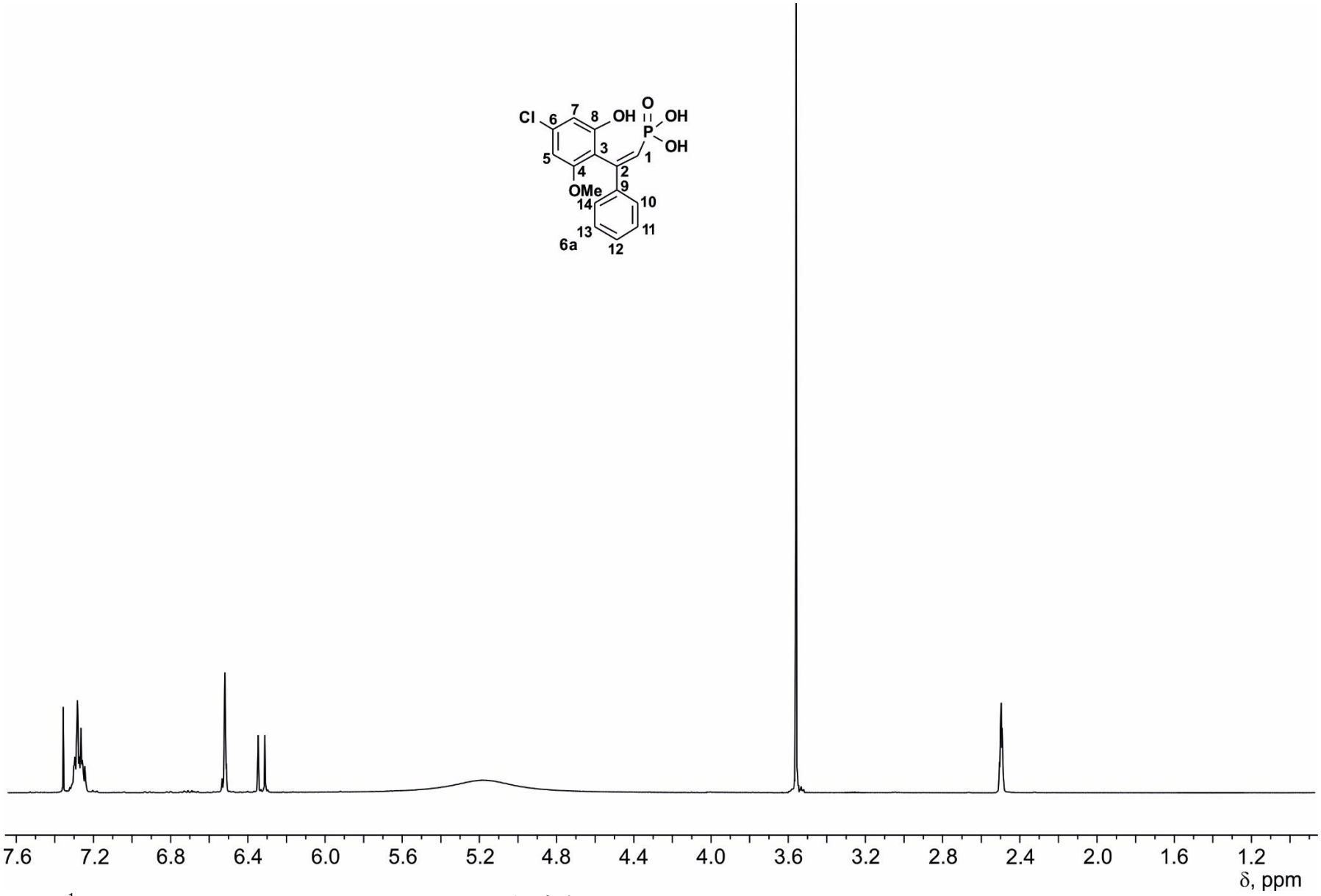

Figure S13. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 25°C) of phosphonic acid **6a**

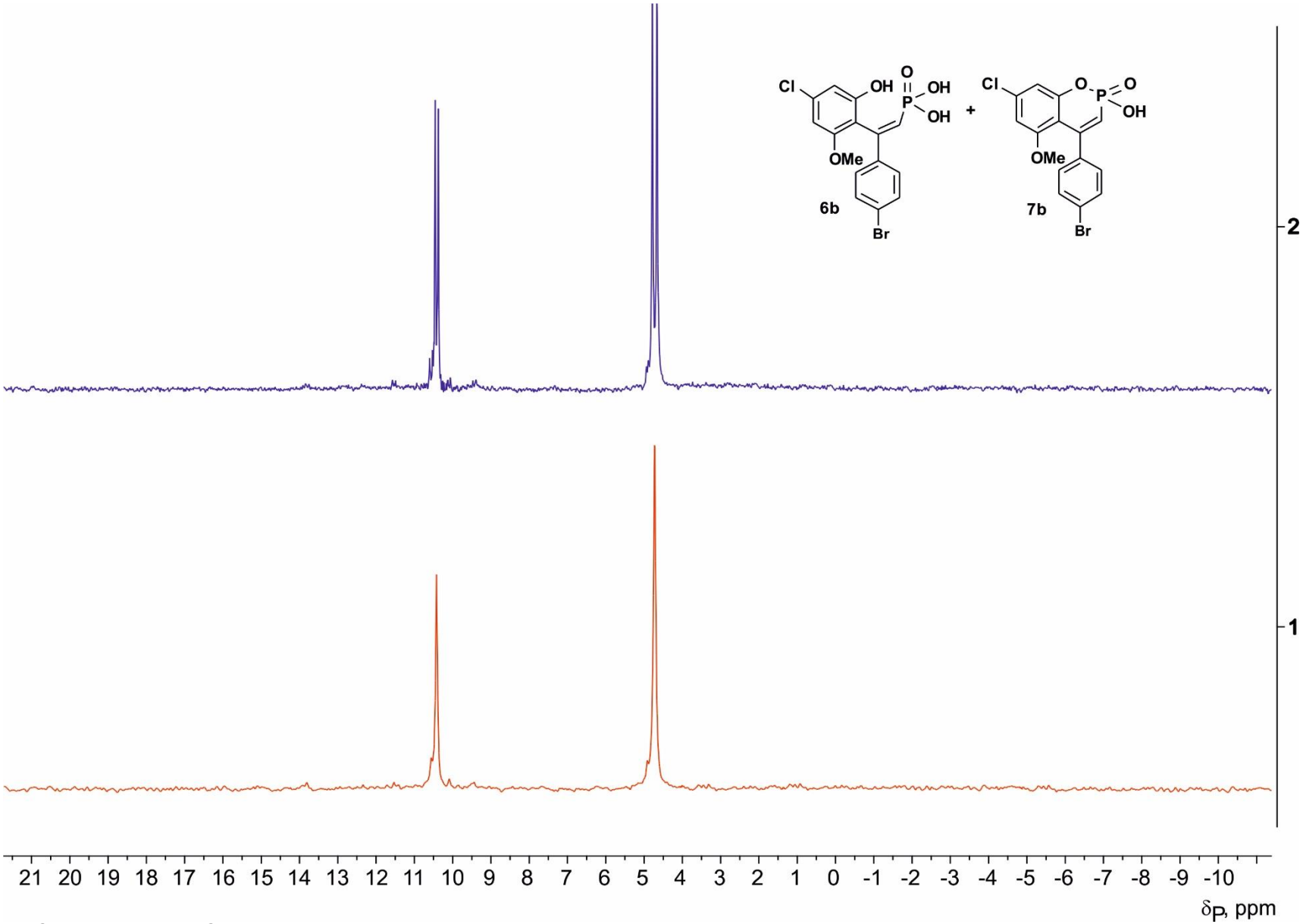

Figure S14. ^{31}P-{^{1}H} (1) and ^{31}P (2) NMR spectra (162 MHz, DMSO-d_6, 25°C) of phosphonic acid **6b**,**7b** mixture.

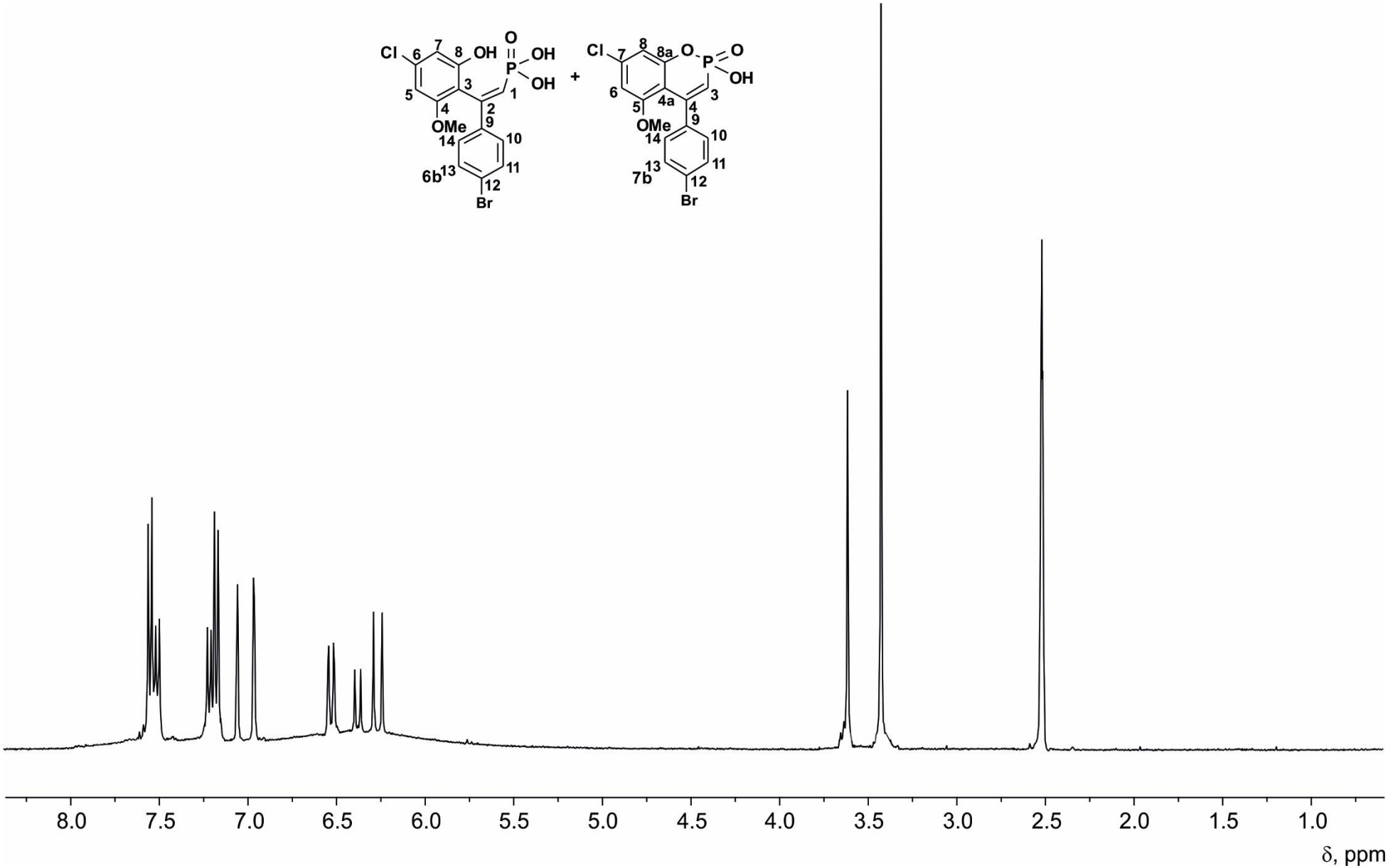

Figure S15. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 25°C) of phosphonic acid **6b**,**7b** mixture.