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Palladium(II) pincer complexes of *N*-(thiophosphorylalkyl)picolinamides: effect of the length of the P^V-pendant arm on the cytotoxic activity

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Experimental section

General remarks

Unless otherwise mentioned, all manipulations were carried out in the normal atmosphere without taking precautions to exclude air and moisture. Tetrahydrofuran was distilled over sodium benzophenone ketyl. Dichloromethane was distilled from P_2O_5. Triethylamine was distilled over sodium. The key thiophosphorylated amines were obtained by the addition of elemental sulfur to the corresponding P^{III}-predecessors, *in situ* generated by the slightly modified literature procedure [S1]. All other chemicals and solvents were used as purchased.

The NMR spectra were recorded on Bruker Avance 300 and Avance 400 spectrometers, and the chemical shifts (δ) were referenced internally by the residual (^{1}H) or deuterated (^{13}C) solvent signals relative to tetramethylsilane or externally to H_3PO_4 (^{31}P). In all cases, the $^{13}C\{^1H\}$ NMR spectra were registered using the *J*MODECHO mode; the signals for the *C* nuclei bearing odd and even numbers of protons had opposite polarities. The NMR peak assignments were based on the previously reported data [S2].

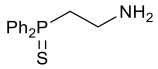
The IR spectra were recorded on a Nicolet Magna-IR750 FT spectrometer (resolution 2 cm^{-1}, 128 scans). The assignment of absorption bands in the IR spectra was made according to Ref. [S3].

Column chromatography was carried out using Macherey-Nagel silica gel 60 (MN Kieselgel 60, 70–230 mesh).

Melting points were determined with an MPA 120 EZ-Melt automated melting point apparatus (Stanford Research Systems).

Syntheses

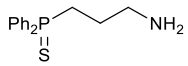
(2-Aminoethyl)diphenylphosphine sulfide 1



Potassium *tert*-butoxide (2.420 g, 21.566 mmol) was added portionwise to a stirred solution of Ph_2PH (1.605 g, 8.620 mmol) in THF (30 mL) under an argon atmosphere. The reaction mixture was stirred at room temperature for 1 h. Then 2-bromoethylamine hydrobromide (1.768 g, 8.629 mmol) was added to the solution of *in situ* generated potassium diphenylphosphide. The resulting mixture was stirred at room temperature for 5 h and left overnight. Then elemental sulfur (0.277 g, 8.640 mmol) was added, and the reaction mixture was stirred at room temperature for another 5 h and left overnight. The precipitate was filtered off and washed with Et_2O. The filtrate was diluted with dichloromethane and washed with water. The organic phase was separated and treated with dilute HCl until pH ~2–3. The aqueous phase was separated and treated with Na_2CO_3 until pH ~8–9. The target product was extracted with dichloromethane. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness to give 0.959 g of the target amine as a light-yellow amorphous solid.

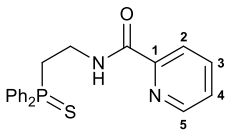
Yield: 43%. The product can be stored unchanged at least for several months under an inert atmosphere. $^{31}P\{^{1}H\}$ NMR (121.49 MHz, $CDCl_3$): δ 39.15 ppm. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.88 (br. s, 2H, NH_2), 2.63–2.72 (m, 2H, $CH_2P(S)$), 3.04–3.13 (m, 2H, CH_2N), 7.41–7.52 (m, 6H, *m*-H and *p*-H in $P(S)Ph_2$), 7.80–7.87 (m, 4H, *o*-H in $P(S)Ph_2$) ppm. $^{13}C\{^{1}H\}$ NMR (100.61 MHz, $CDCl_3$): δ 35.74 (d, $CH_2P(S)$, $^{1}J_{CP}$ = 55.3 Hz), 36.36 (s, CH_2N), 128.56 (d, *m*-C in $P(S)Ph_2$, $^{3}J_{CP}$ = 12.5 Hz), 130.80 (d, *o*-C in $P(S)Ph_2$, $^{2}J_{CP}$ = 10.3 Hz), 131.41 (d, *p*-C in $P(S)Ph_2$, $^{4}J_{CP}$ = 2.6 Hz), 132.64 (d, *ipso*-C in $P(S)Ph_2$, $^{1}J_{CP}$ = 80.4 Hz) ppm. IR (ν/cm^{-1}, thin film): 490(m), 516(m), 611(m) and 623(m) (both νP=S), 692(s), 709(s), 741(s), 784(m), 875(w), 922(w), 998(m), 1027(w), 1070(w), 1103(s), 1160(w), 1182(w), 1311(w), 1388(w), 1436(s), 1481(m), 1574(w), 1588(w), 1609(m), 1660(w), 2875(w), 2943(w), 3053(m), 3074(w), 3283(br, w) and 3353(br, w) (both νNH). Anal. Calcd for $C_{14}H_{16}NPS$: C, 64.35; H, 6.17; N, 5.36. Found: C, 64.14; H, 6.07; N, 5.30%.

(3-Aminopropyl)diphenylphosphine sulfide 2



Potassium *tert*-butoxide (3.151 g, 28.081 mmol) was added portionwise to a stirred solution of Ph_2PH (2.614 g, 14.039 mmol) in THF (30 mL) under an argon atmosphere. The reaction mixture was stirred at room temperature for 1 h. Then 3-bromopropylamine hydrobromide (3.073 g, 14.037 mmol) was added to the solution of *in situ* generated potassium diphenylphosphide. The resulting mixture was diluted with THF (5 mL) and stirred at room temperature for 0.5 h. Then elemental sulfur (0.451 g, 14.067 mmol) was added, and the reaction mixture was stirred at room temperature for 1 h and left overnight. The precipitate was filtered off and washed with Et_2O. The filtrate was diluted with dichloromethane and washed with water. The organic phase was separated and treated with dilute HCl until pH ~2–3. The aqueous phase was separated and treated with Na_2CO_3 until pH ~8–9. The target product was extracted with dichloromethane. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness to give 2.017 g of the target amine as a light-yellow highly viscous oil which slowly solidifies. Yield: 50%. The product gradually decomposes even upon storage under an inert atmosphere. $^{31}P\{^{1}H\}$ NMR (121.49 MHz, $CDCl_3$): δ 43.09 ppm. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.34 (br. s, 2H, NH_2), 1.67–1.80 (m, 2H, CH_2), 2.46–2.56 (m, 2H, $CH_2P(S)$), 2.73–2.78 (m, 2H, CH_2N), 7.40–7.50 (m, 6H, *m*-H and *p*-H in $P(S)Ph_2$), 7.79–7.87 (m, 4H, *o*-H in $P(S)Ph_2$) ppm. $^{13}C\{^{1}H\}$ NMR (100.61 MHz, $CDCl_3$): δ 26.22 (d, CH_2, $^{2}J_{CP}$ = 2.2 Hz), 30.05 (d, $CH_2P(S)$, $^{1}J_{CP}$ = 58.0 Hz), 42.65 (d, CH_2N, $^{3}J_{CP}$ = 17.6 Hz), 128.67 (d, *m*-C in $P(S)Ph_2$, $^{3}J_{CP}$ = 11.7 Hz), 131.10 (d, *o*-C in $P(S)Ph_2$, $^{2}J_{CP}$ = 10.3 Hz), 131.50 (d, *p*-C in $P(S)Ph_2$, $^{4}J_{CP}$ = 2.9 Hz), 132.79 (d, *ipso*-C in $P(S)Ph_2$, $^{1}J_{CP}$ = 80.1 Hz) ppm. Anal. Calcd for $C_{15}H_{18}NPS\cdot0.67H_2O$: C, 62.70; H, 6.78; N, 4.87. Found: C, 62.65; H, 6.60; N, 4.56%.

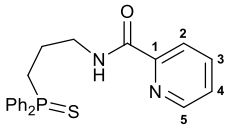
***N*-[2-(Diphenylthiophosphoryl)ethyl]picolinamide 3**



A stirred solution of picolinic acid (0.122 g, 0.991 mmol) in CH_2Cl_2 (10 mL) was cooled to –5 °C (ice/NaCl) under an argon atmosphere. Then Et_3N (0.17 mL, 1.220 mmol) was added. The resulting mixture was stirred upon cooling for 30 min. Then a solution of isobutyl chloroformate

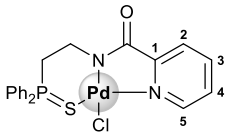
(0.151 g, 1.106 mmol) in CH_2Cl_2 (7 mL) was added dropwise. The reaction mixture was stirred for 30 min, keeping the temperature at *ca.* –5 °C. Then a solution of amine **1** (0.259 g, 0.991 mmol) in CH_2Cl_2 (10 mL) was added dropwise. The reaction mixture was stirred upon cooling for 1 h and, after removal of a cooling bath, for another 1 h, and left overnight. The resulting mixture was diluted with CH_2Cl_2 (30 mL) and washed with water. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue obtained was purified by column chromatography on silica gel (gradient elution with a petroleum ether–acetone mixture, from 5:1 to 3:1) to give 0.272 g of the target amide as a white solid. Yield: 75%. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 39.48 ppm. ^1H NMR (300.13 MHz, $CDCl_3$): δ 2.89–2.97 (m, 2H, $CH_2P(S)$), 3.86–3.98 (m, 2H, CH_2N), 7.37–7.43 (m, 7H, *m*-H and *p*-H in $P(S)Ph_2$ + H(C4)), 7.77–7.83 (m, 1H, H(C3)), 7.84–7.92 (m, 4H, *o*-H in $P(S)Ph_2$), 8.06 (d, 1H, H(C2), $^3J_{HH}$ = 7.8 Hz), 8.30–8.34 (br. m, 1H, NH), 8.46 (dd, 1H, H(C5), $^3J_{HH}$ = 4.7 Hz, $^4J_{HH}$ = 1.7 Hz) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 31.77 (d, $CH_2P(S)$, $^1J_{CP}$ = 56.4 Hz), 34.27 (s, CH_2N), 121.82 and 126.16 (both s, C2 and C4), 128.69 (d, *m*-C in $P(S)Ph_2$, $^3J_{CP}$ = 12.5 Hz), 130.96 (d, *o*-C in $P(S)Ph_2$, $^2J_{CP}$ = 10.3 Hz), 131.48 (d, *p*-C in $P(S)Ph_2$, $^4J_{CP}$ = 2.2 Hz), 132.53 (d, *ipso*-C in $P(S)Ph_2$, $^1J_{CP}$ = 79.8 Hz), 137.14 (s, C3), 148.07 (s, C5), 149.34 (s, C1), 164.74 (s, C(O)NH) ppm. IR (ν/cm^{-1}, KBr): 469(w), 488(w), 496(w), 537(w), 601(s) (νP=S), 621(w), 690(m), 701(m), 712(m), 730(m), 743(m), 748(w), 796(vw), 820(vw), 840(w), 984(vw), 999(w), 1041(vw), 1106(m), 1142(vw), 1162(vw), 1244(vw), 1313(w), 1362(w), 1403(w), 1426(m), 1437(m), 1465(w), 1483(w), 1521(br, s) (C(O)NH), 1570(w), 1592(w), 1675(s) (νC=O), 2909(vw), 2936(w), 2958(w), 3021(vw), 3053(w), 3395(br, m) (νNH). Anal. Calcd for $C_{20}H_{19}N_2OPS$: C, 65.56; H, 5.23; N, 7.65. Found: C, 65.45; H, 5.39; N, 7.54%.

***N*-[3-(Diphenylthiophosphoryl)propyl]picolinamide 4**



A stirred solution of picolinic acid (0.133 g, 1.080 mmol) in CH_2Cl_2 (10 mL) was cooled to –5 °C (ice/NaCl) under an argon atmosphere. Then Et_3N (0.19 mL, 1.363 mmol) was added. The resulting mixture was stirred upon cooling for 30 min. Then a solution of isobutyl chloroformate (0.169 g, 1.237 mmol) in CH_2Cl_2 (7 mL) was added dropwise. The reaction mixture was stirred for 30 min, keeping the temperature at *ca.* –5 °C. Then a solution of amine **2** (0.310 g, 1.079 mmol) in CH_2Cl_2 (10 mL) was added dropwise. The reaction mixture was stirred upon cooling for 30 min and, after removal of a cooling bath, for another 30 min, and left overnight. The resulting mixture was diluted with CH_2Cl_2 (30 mL) and washed with water. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue obtained was purified by column chromatography on silica gel (gradient elution with a petroleum ether–acetone mixture, from 5:1 to 3:1) to give 0.284 g of the target amide as a white solid. Yield: 69%. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 42.73 ppm. ^1H NMR (300.13 MHz, $CDCl_3$): δ 1.92–2.05 (m, 2H, CH_2), 2.52–2.61 (m, 2H, $CH_2P(S)$), 3.56–3.62 (m, 2H, CH_2N), 7.42–7.54 (m, 7H, *m*-H and *p*-H in $P(S)Ph_2$ + H(C4)), 7.80–7.88 (m, 5H, *o*-H in $P(S)Ph_2$ + H(C3)), 8.12–8.15 (m, 1H, NH), 8.18 (d, 1H, H(C2), $^3J_{HH}$ = 7.8 Hz), 8.55 (dd, 1H, H(C5), $^3J_{HH}$ = 4.7 Hz, $^4J_{HH}$ = 1.5 Hz) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 22.87 (d, CH_2, $^2J_{CP}$ = 1.4 Hz), 29.84 (d, $CH_2P(S)$, $^1J_{CP}$ = 57.6 Hz), 39.35 (d, CH_2N, $^3J_{CP}$ = 18.1 Hz), 122.03 and 126.08 (both s, C2 and C4), 128.54 (d, *m*-C in $P(S)Ph_2$, $^3J_{CP}$ = 12.5 Hz), 130.91 (d, *o*-C in $P(S)Ph_2$, $^2J_{CP}$ = 10.3 Hz), 131.40 (d, *p*-C in $P(S)Ph_2$, $^4J_{CP}$ = 2.9 Hz), 132.36 (d, *ipso*-C in $P(S)Ph_2$, $^1J_{CP}$ = 80.7 Hz), 137.20 (s, C3), 147.93 (s, C5), 149.49 (s, C1), 164.33 (s, C(O)NH) ppm. IR (ν/cm^{-1}, KBr): 492(w), 516(m), 613(m) and 624(m) (both νP=S), 669(w), 691(m), 704(w), 715(m), 739(m), 754(m), 763(w), 782(w), 815(w), 872(vw), 995(w), 1026(vw), 1099(w), 1108(m), 1169(vw), 1243(w), 1286(w), 1374(vw), 1436(m), 1463(w), 1483(w), 1536(br, s) (C(O)NH), 1567(w), 1588(w), 1666(s) (νC=O), 2874(vw), 2935(w), 3055(w), 3327(br, m) ((νNH). Anal. Calcd for $C_{21}H_{21}N_2OPS$: C, 66.30; H, 5.56; N, 7.36. Found: C, 66.39; H, 5.61; N, 7.27%.

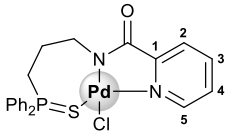
Complex [κ^3-*S*,*N*,*N*-(L)Pd^{II}Cl] 5



A solution of $PdCl_2(PhCN)_2$ (42 mg, 0.109 mmol) in CH_2Cl_2 (5 mL) was slowly added dropwise to a solution of ligand **3** (40 mg, 0.109 mmol) and Et_3N (20 mg, 0.198 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was left under ambient conditions for 1 day and then purified by column chromatography on silica gel (eluent: CH_2Cl_2–EtOH, 30:1) to give 49 mg of complex **5** as a yellow crystalline solid. Yield: 88%. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 41.76 ppm. ^1H NMR (300.13 MHz, $CDCl_3$): δ 2.88–2.95 (m, 2H, $CH_2P(S)$), 3.80–3.93 (m, 2H, CH_2N), 7.42–7.46 (m, 1H, H(C4) or H(C3)), 7.54–7.67 (m, 6H, *m*-H and *p*-H in $P(S)Ph_2$), 7.84–7.98 (m, 6H, *o*-H in $P(S)Ph_2$ + H(C3) or H(C4) + H(C2)), 9.13 (d, 1H, H(C5), $^3J_{HH}$ = 5.5 Hz) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 33.78 (d, $CH_2P(S)$, $^1J_{CP}$ = 52.8 Hz), 37.94 (d, CH_2N, $^2J_{CP}$ = 6.8 Hz), 125.18 and 126.34 (both s, C2 and C4), 128.55 (d, *ipso*-C in $P(S)Ph_2$, $^1J_{CP}$ = 82.0 Hz), 129.49 (d, *m*-C in $P(S)Ph_2$, $^3J_{CP}$ = 12.5 Hz), 131.74 (d, *o*-C in $P(S)Ph_2$, $^2J_{CP}$ = 10.3

Hz), 133.23 (d, *p*-C in $P(S)Ph_2$, $^4J_{CP}$ = 3.2 Hz), 139.65 (s, C3), 147.75 (s, C5), 154.39 (s, C1), 171.73 (s, C(O)N) ppm. IR (ν/cm^{-1}, KBr): 459(vw), 485(w), 500(w), 585(m) (νP=S), 615(vw), 658(vw), 678(m), 690(m), 703(m), 717(m), 744(m), 763(w), 815(w), 848(vw), 980(w), 997(vw), 1035(vw), 1048(vw), 1082(w), 1111(m), 1150(w), 1195(vw), 1262(w), 1286(m), 1342(w), 1388(m), 1436(m), 1478(w), 1571(m), 1600(s), 1628(s) (νC=O), 3014(vw), 3049(vw), 3075(vw). Anal. Calcd for $C_{20}H_{18}ClN_2OPPdS$: C, 47.35; H, 3.58; N, 5.52. Found: C, 47.44; H, 3.76; N, 5.57%.

Complex [κ^3-*S*,*N*,*N*-(L)Pd^{II}Cl] 6



A solution of $PdCl_2(PhCN)_2$ (38 mg, 0.099 mmol) in CH_2Cl_2 (4 mL) was slowly added dropwise to a solution of ligand **4** (38 mg, 0.100 mmol) and Et_3N (11 mg, 0.109 mmol) in CH_2Cl_2 (4 mL). The reaction mixture was left under ambient conditions for 1 day and then purified by column chromatography on silica gel (eluent: CH_2Cl_2–EtOH, 30:1) to give 46 mg of complex **6** as an organe crystalline solid. Yield: 89%. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 42.91 ppm. ^1H NMR (300.13 MHz, $CDCl_3$): δ 2.12–2.30 (m, 2H, CH_2), 3.25–3.33 (m, 2H, $CH_2P(S)Ph_2$), 3.91 (t, 2H, CH_2N, $^3J_{HH}$ = 6.5 Hz), 7.46–7.51 (m, 1H, H(C4) or H(C3)), 7.59–7.71 (m, 6H, *m*-H and *p*-H in $P(S)Ph_2$), 7.94–8.07 (m, 6H, *o*-H in $P(S)Ph_2$ + H(C3) or H(C4) + H(C2)), 9.21 (d, 1H, H(C5), $^3J_{HH}$ = 5.4 Hz) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 23.12 (d, CH_2, $^2J_{CP}$ = 5.3 Hz), 28.55 (d, $CH_2P(S)$, $^1J_{CP}$ = 50.5 Hz), 41.05 (d, CH_2N, $^3J_{CP}$ = 1.9 Hz), 124.91 and 126.19 (both s, C2 and C4), 127.48 (d, *ipso*-C in $P(S)Ph_2$, $^1J_{CP}$ = 80.5 Hz), 129.35 (d, *m*-C in $P(S)Ph_2$, $^3J_{CP}$ = 12.5 Hz), 131.62 (d, *o*-C in $P(S)Ph_2$, $^2J_{CP}$ = 10.3 Hz), 133.05 (d, *p*-C in $P(S)Ph_2$, $^4J_{CP}$ = 2.9 Hz), 139.74 (s, C3), 147.56 (s, C5), 154.54 (s, C1), 171.90 (s, C(O)N) ppm. IR (ν/cm^{-1}, KBr): 456(w), 495(m), 562(m) and 576(m) (both νP=S), 684(m), 697(w), 708(m), 728(m), 734(m), 762(m), 807(w), 838(vw), 895(w), 998(w), 1043(w), 1094(w), 1112(m), 1146(w), 1179(w), 1220(w), 1261(w), 1282(m), 1289(w), 1319(w), 1341(w), 1353(m), 1378(w), 1394(m), 1436(m), 1485(w), 1569(m), 1596(s), 1621(s) (νC=O), 2856(vw), 2920(w), 2957(vw), 3057(vw), 3080(vw). Anal. Calcd for $C_{21}H_{20}ClN_2OPPdS$: C, 48.38; H, 3.87; N, 5.37. Found: C, 48.11; H, 3.99; N, 5.31%.

Interaction of the thiophosphoryl-functionalized Pd^{II} pincer complexes with adesonine 5'-monophosphate disodium salt

A solution of complex **5**, **A** or **B** (R = Ph) (0.026 mmol) in $(CD_3)_2SO$ (0.5 mL) was added to a solution of adesonine 5'-monophosphate disodium salt (12 mg, 0.031 mmol) in D_2O (0.1 mL). In the case of complex **5**, the resulting solution was left under ambient conditions for 15 days, and the reaction course was monitored by ^{31}P NMR spectroscopy (Fig. S19). In the case of complexes **A** and **B**, mixing of the reagents led to gradual (for compound **A**) or immediate (for compound **B**) precipitation of a light solid, which was separated and dissolved in $(CD_3)_2SO$. The ^{31}P NMR spectroscopic studies revealed that the precipitates obtained were the starting pincer complexes (Figs. S20,S21).

Cytotoxicity studies

The cytotoxicity of the compounds obtained was investigated on human colorectal carcinoma (HCT116), breast cancer (MCF7), prostate adenocarcinoma (PC3), glioblastoma (U251), ovarian adenocarcinoma (Scov3), chronic myelogenous leukemia (K562 and K562/iS9), multiple plasmacytoma (AMO1), and acute lymphoblastic leukemia (H9 and MOLT4) cell lines, as well as human embryonic kidney (HEK293) and mammary epithelial (HBL100 and HBL100/Dox) cells used as non-cancerous cell lineages. All the cell lines were obtained from American Type Culture Collection (ATCC). The tested compounds were initially dissolved in DMSO. Cisplatin was obtained from a commercial source (as an infusion concentrate in natural saline solution). The experiments were performed using the conventional MTT assay (ICN Biomedicals, Germany) according to the previously published procedure [S4].

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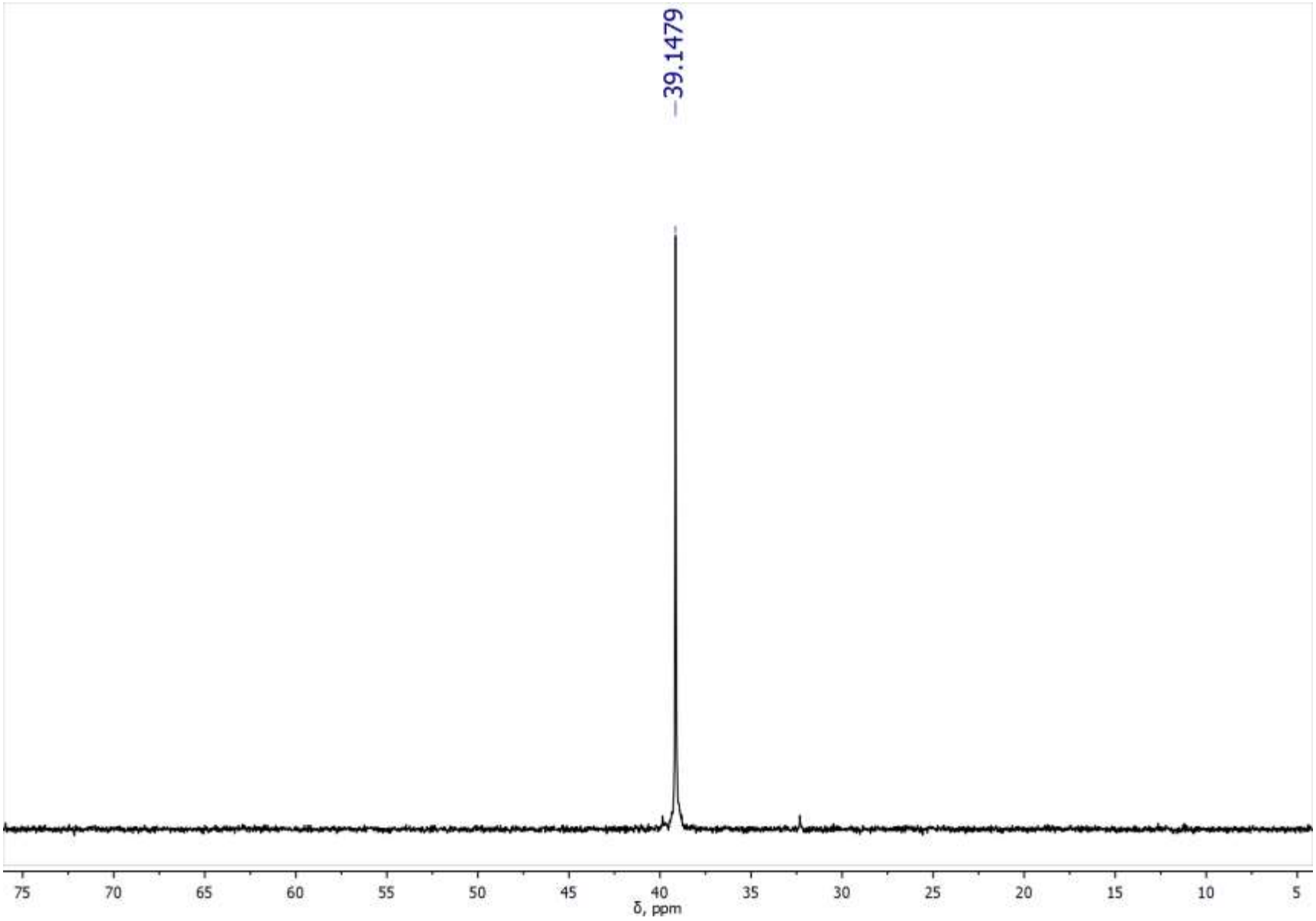

Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum of amine **1** (121.49 MHz, $CDCl_3$)

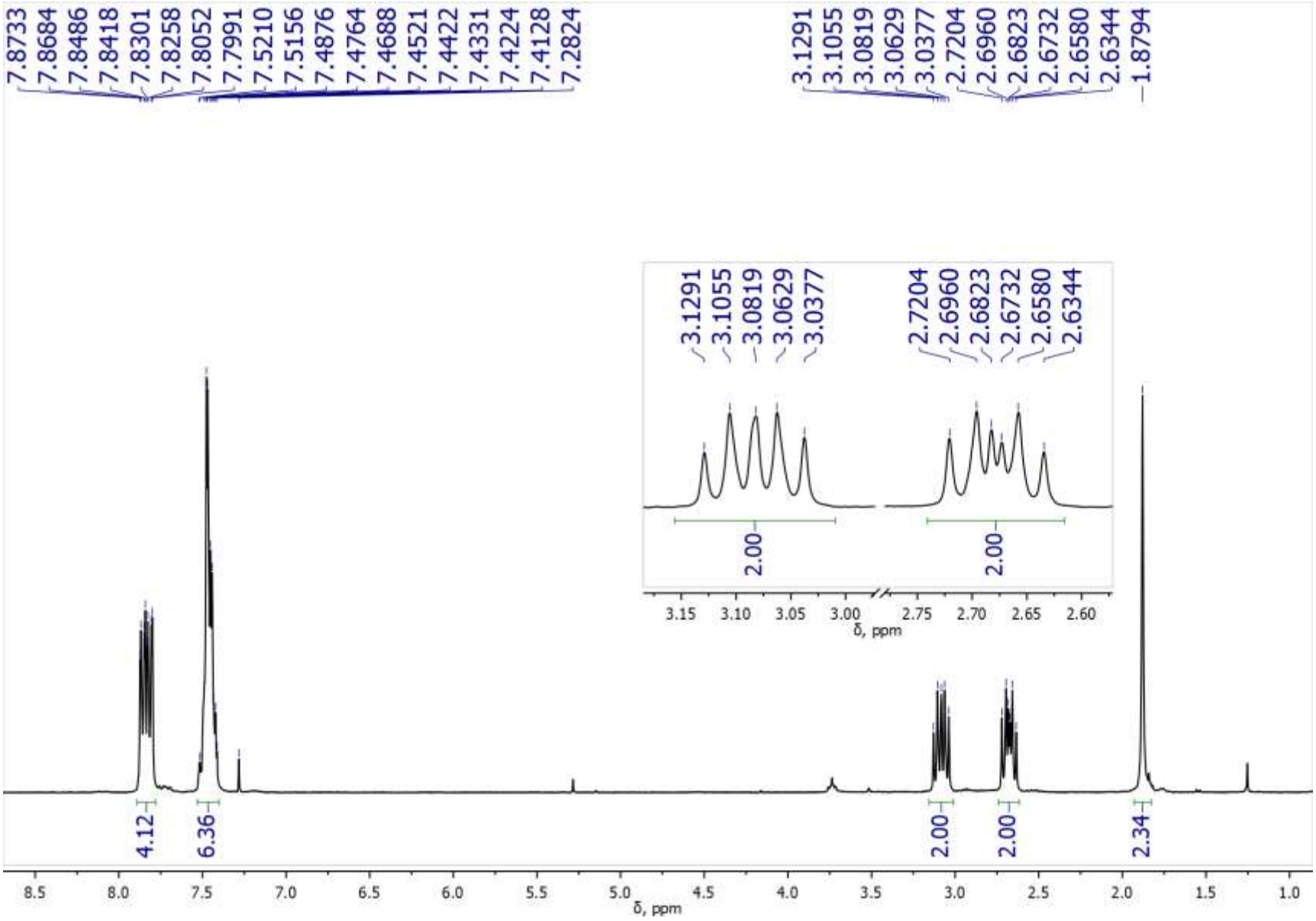

Figure S2. ^{1}H NMR spectrum of amine **1** (300.13 MHz, $CDCl_3$)

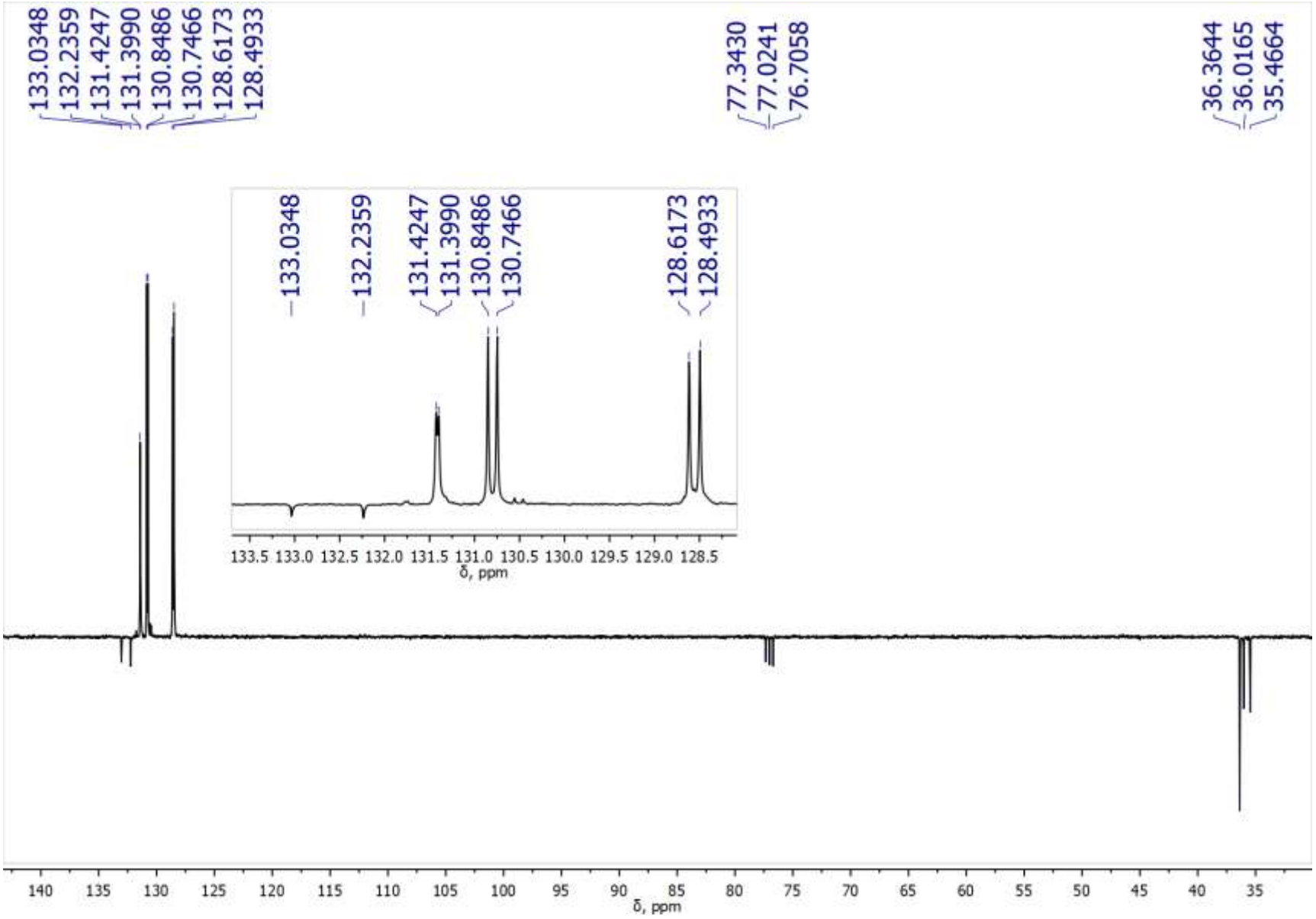

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of amine **1** (100.61 MHz, $CDCl_3$)

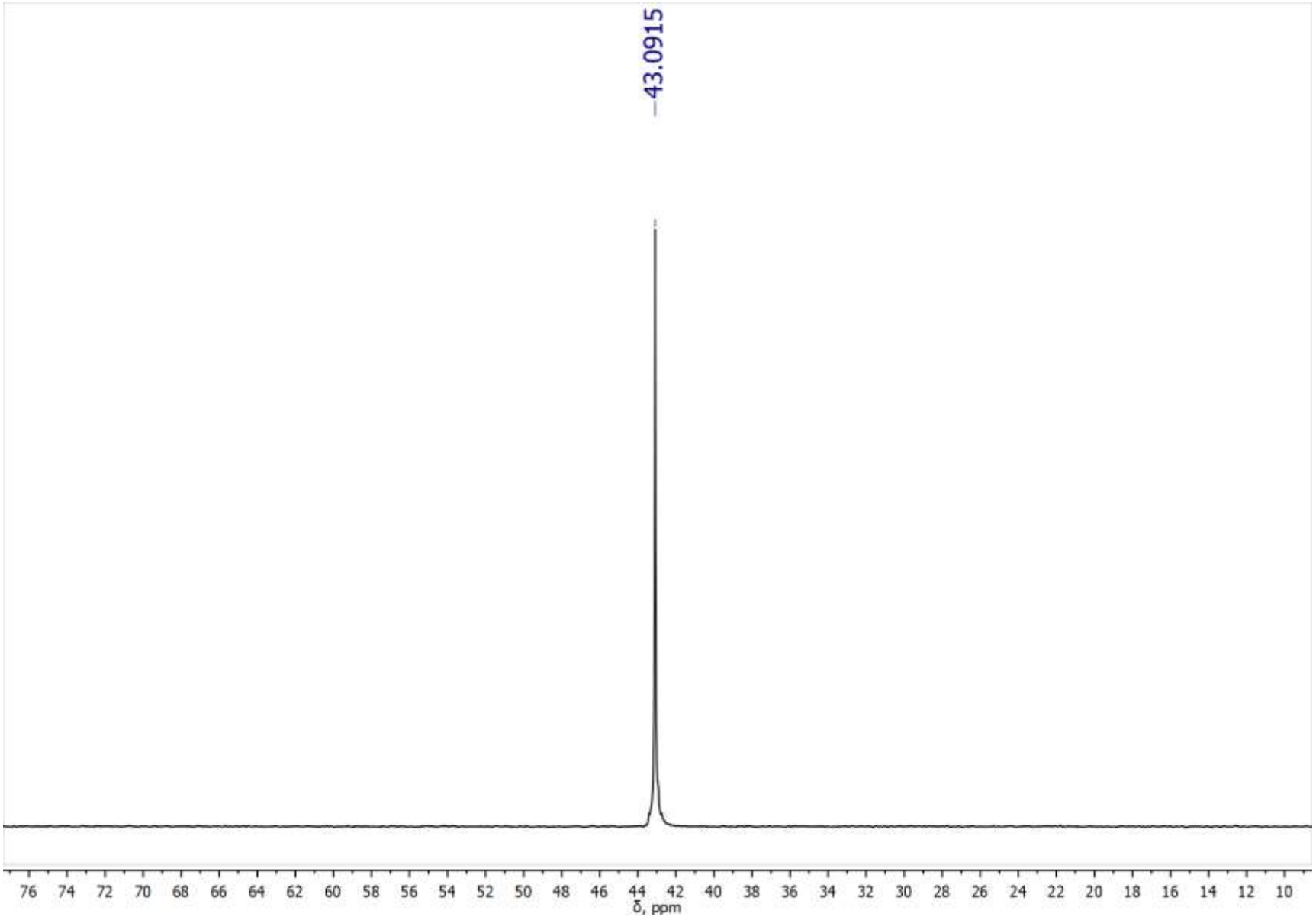

Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of amine **2** (121.49 MHz, $CDCl_3$)

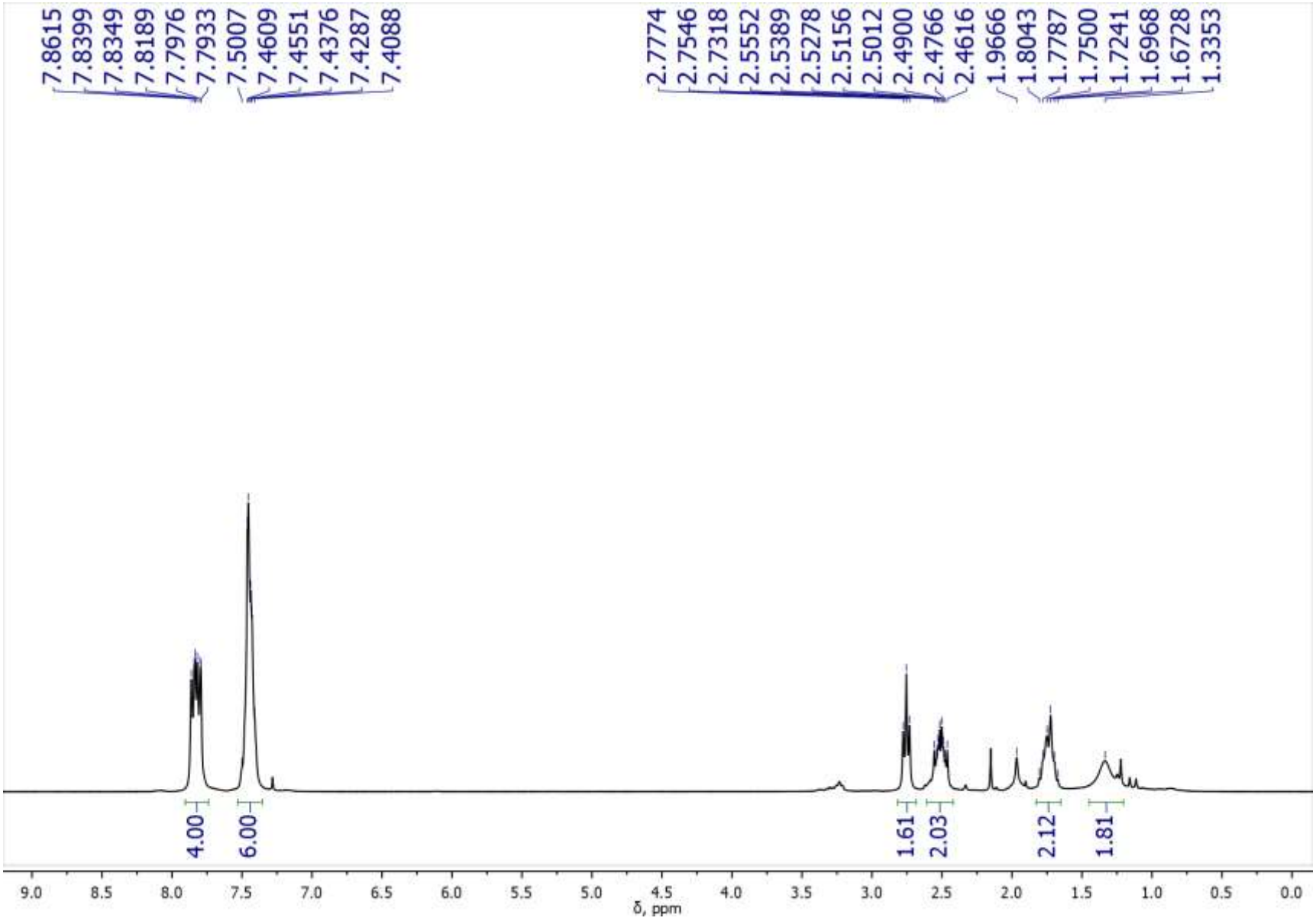

Figure S5. ^{1}H NMR spectrum of amine **2** (300.13 MHz, $CDCl_3$)

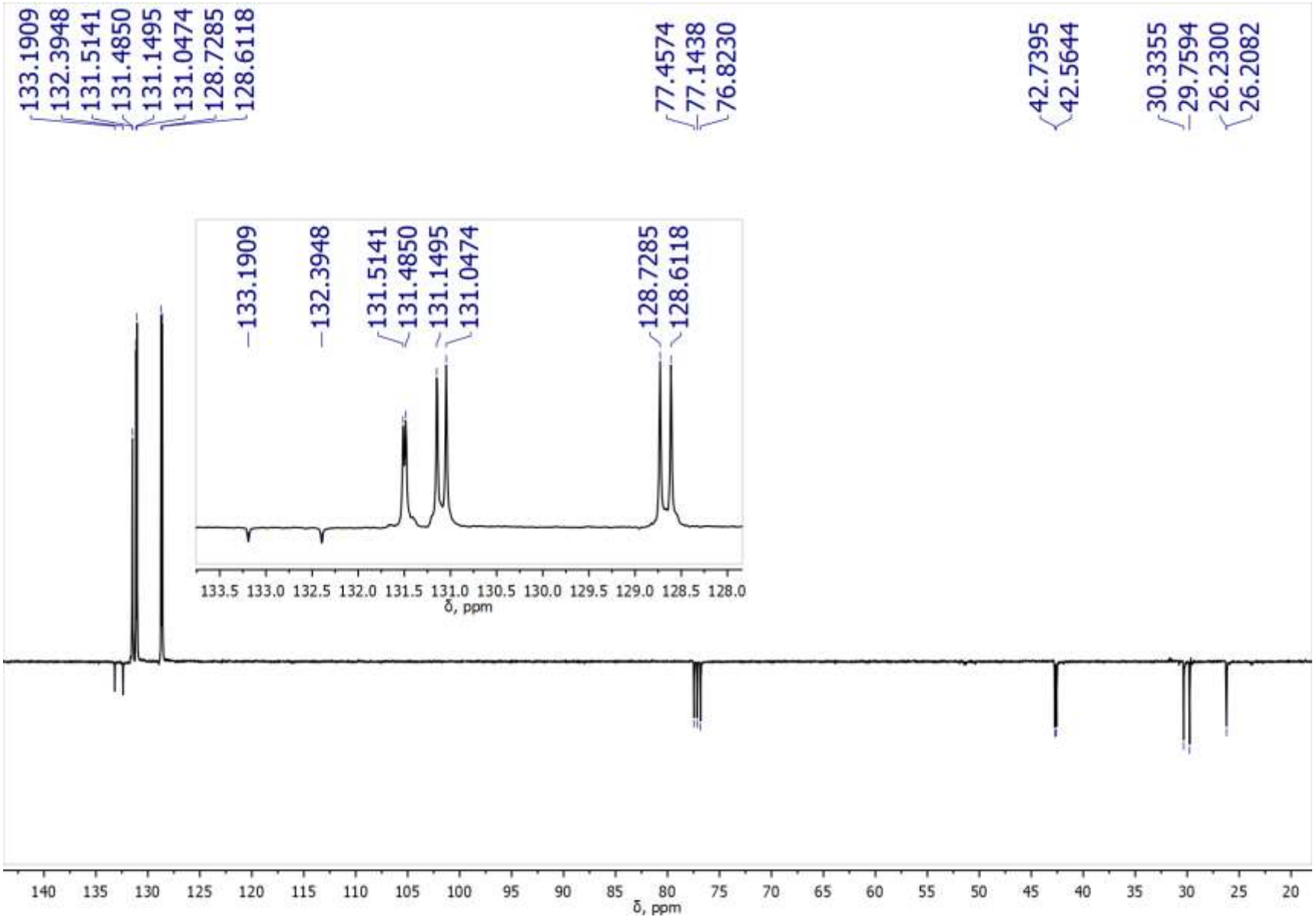

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of amine **2** (100.61 MHz, $CDCl_3$)

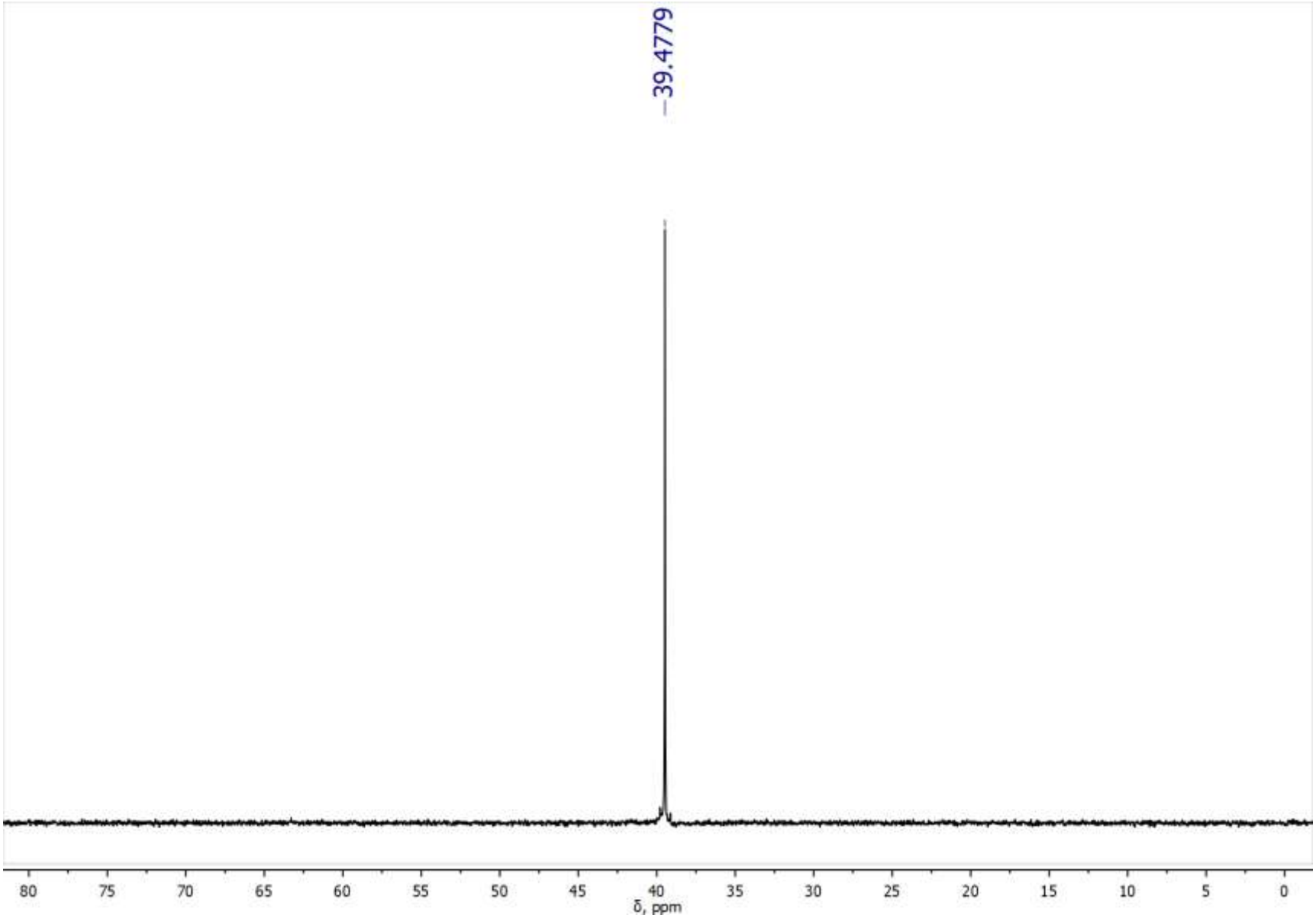

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of ligand **3** (121.49 MHz, $CDCl_3$)

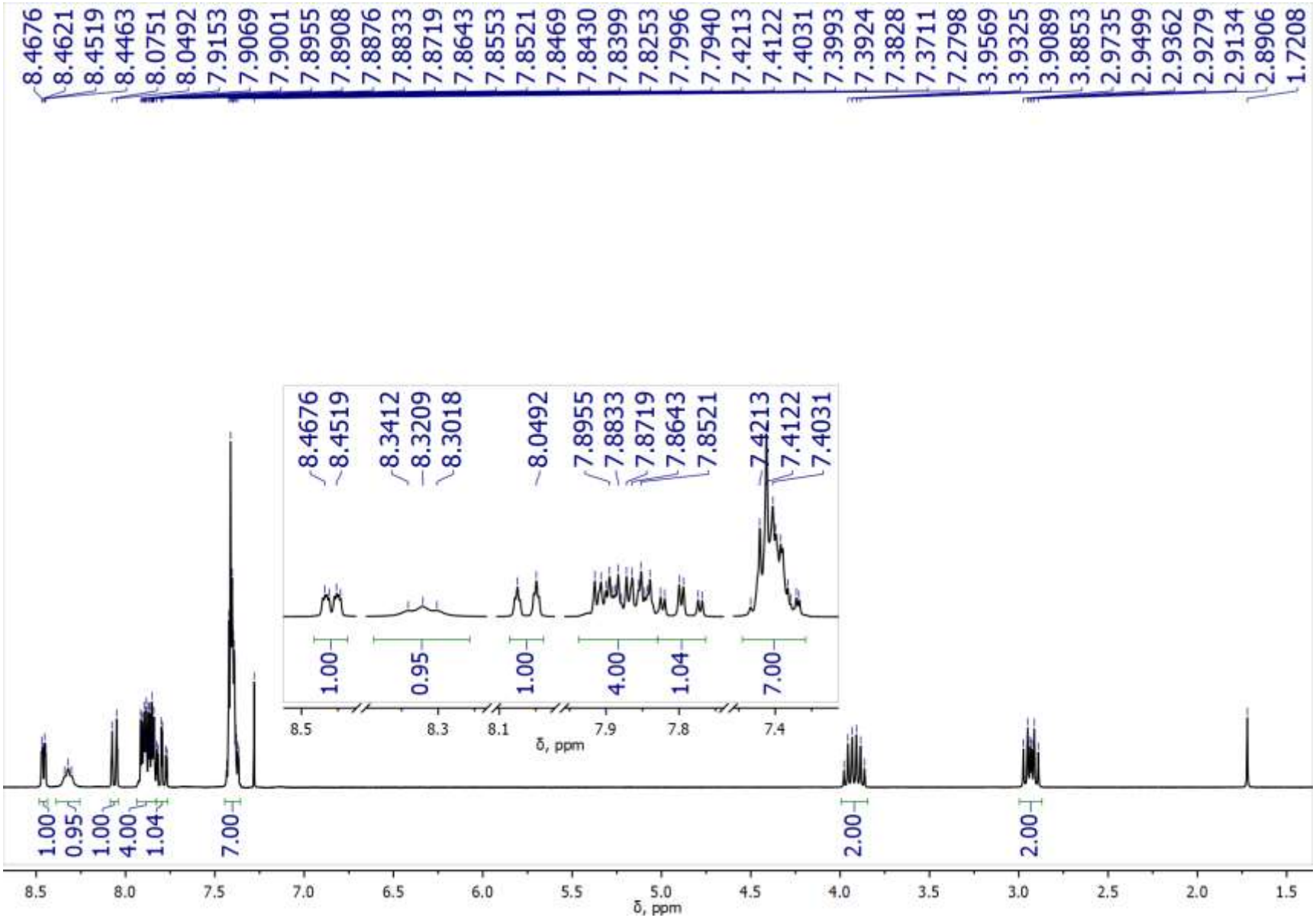

Figure S8. ^{1}H NMR spectrum of ligand **3** (300.13 MHz, $CDCl_3$)

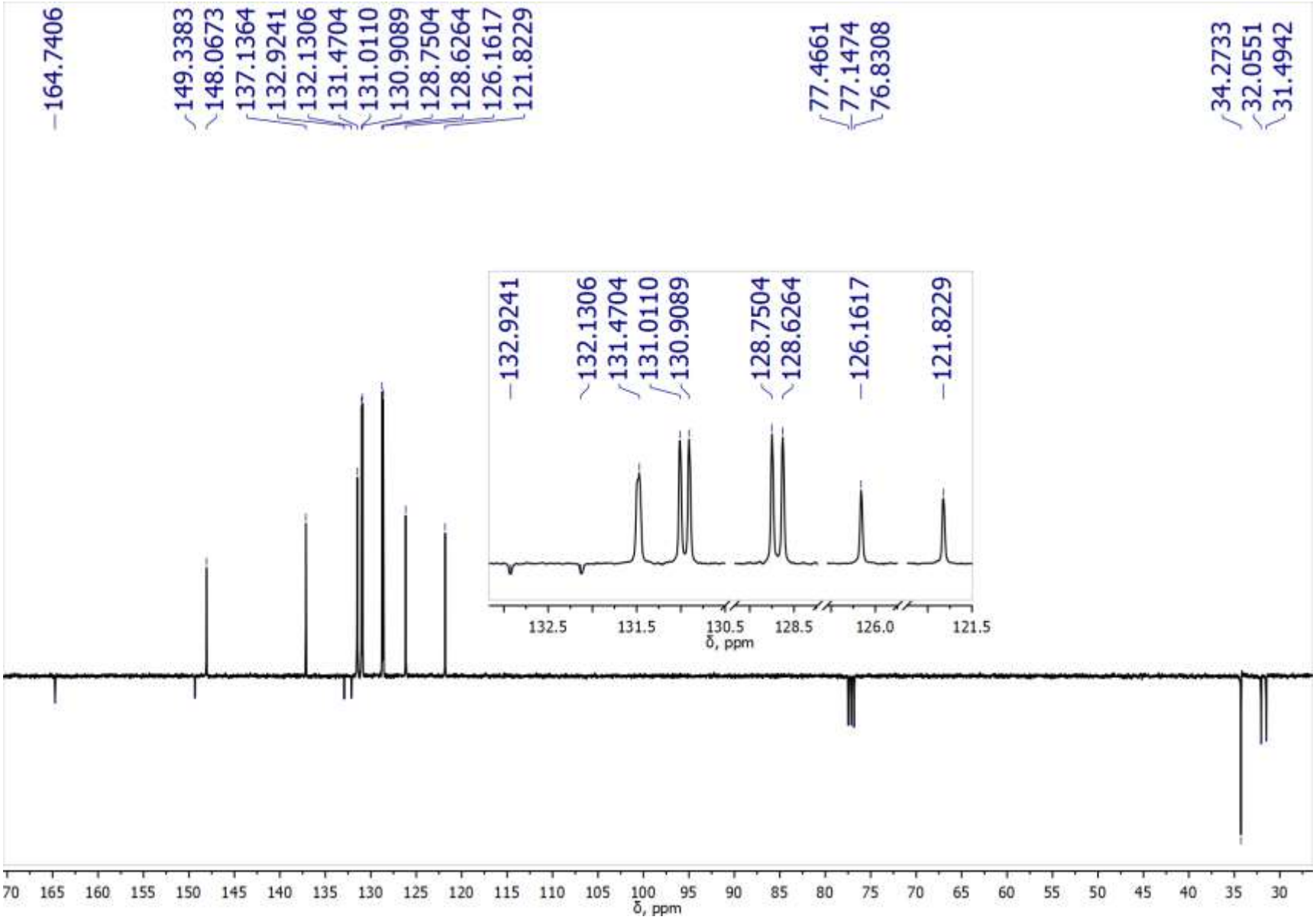

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of ligand **3** (100.61 MHz, $CDCl_3$)

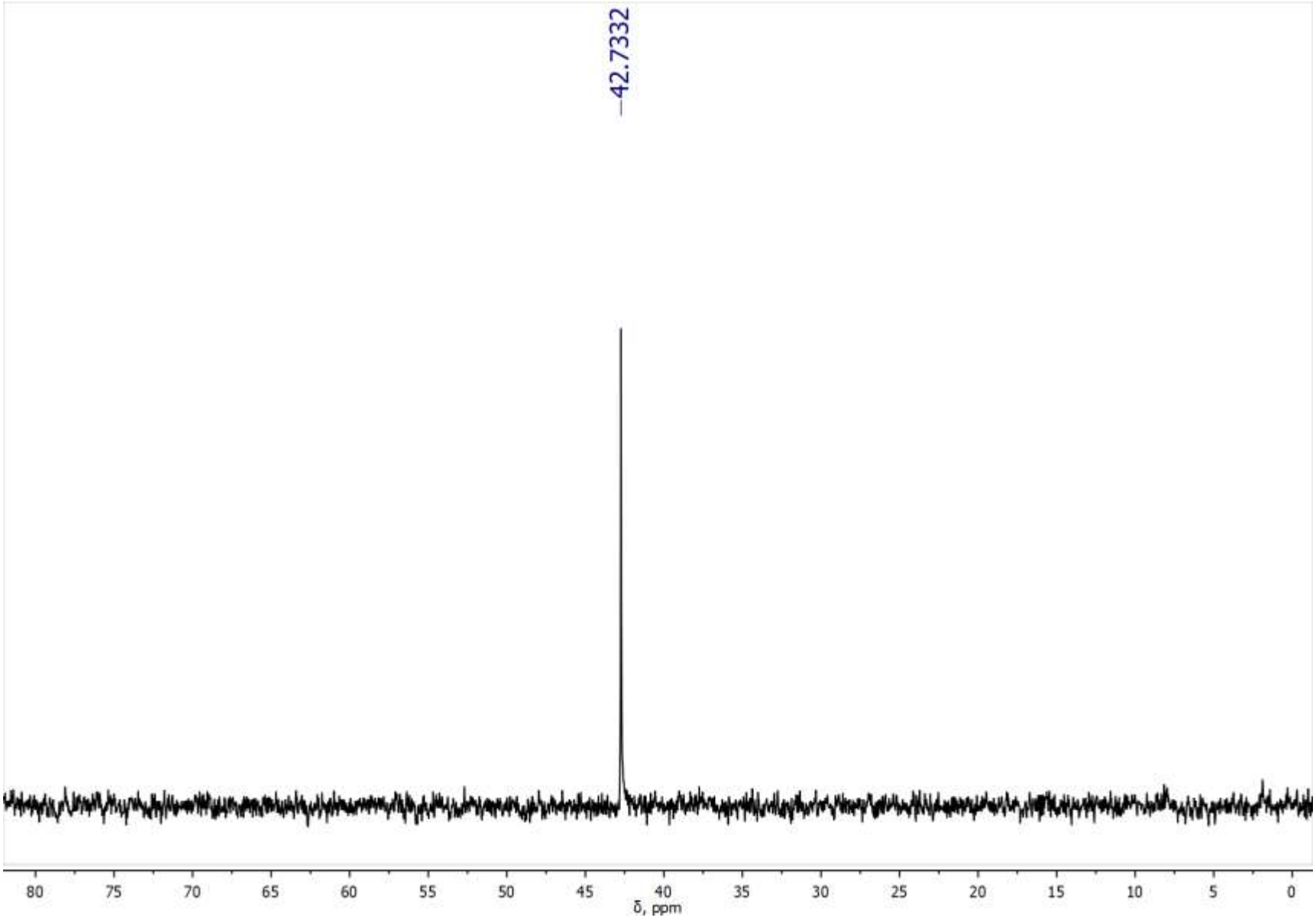

Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of ligand **4** (121.49 MHz, $CDCl_3$)

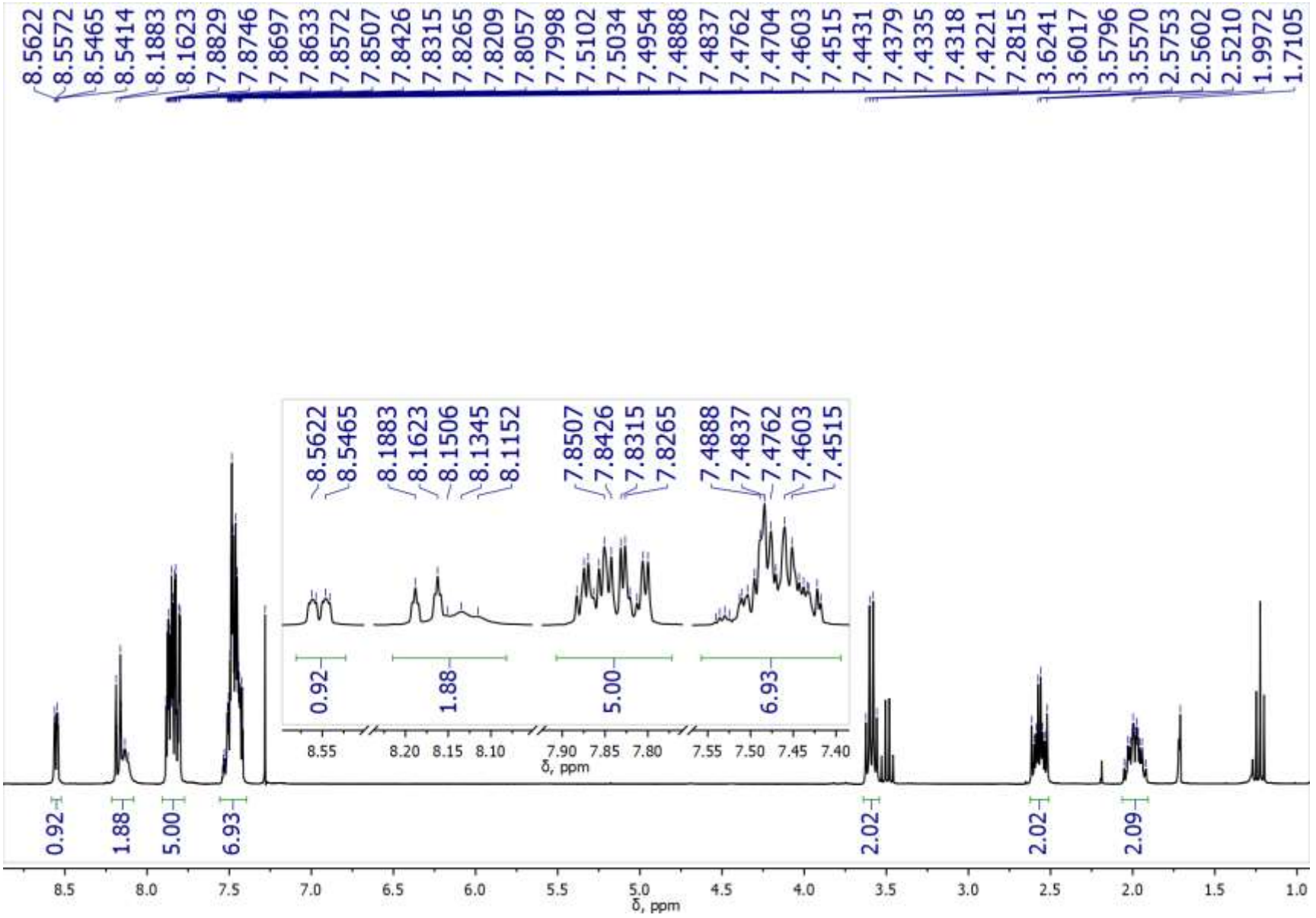

Figure S11. ^{1}H NMR spectrum of ligand **4** (300.13 MHz, $CDCl_3$)

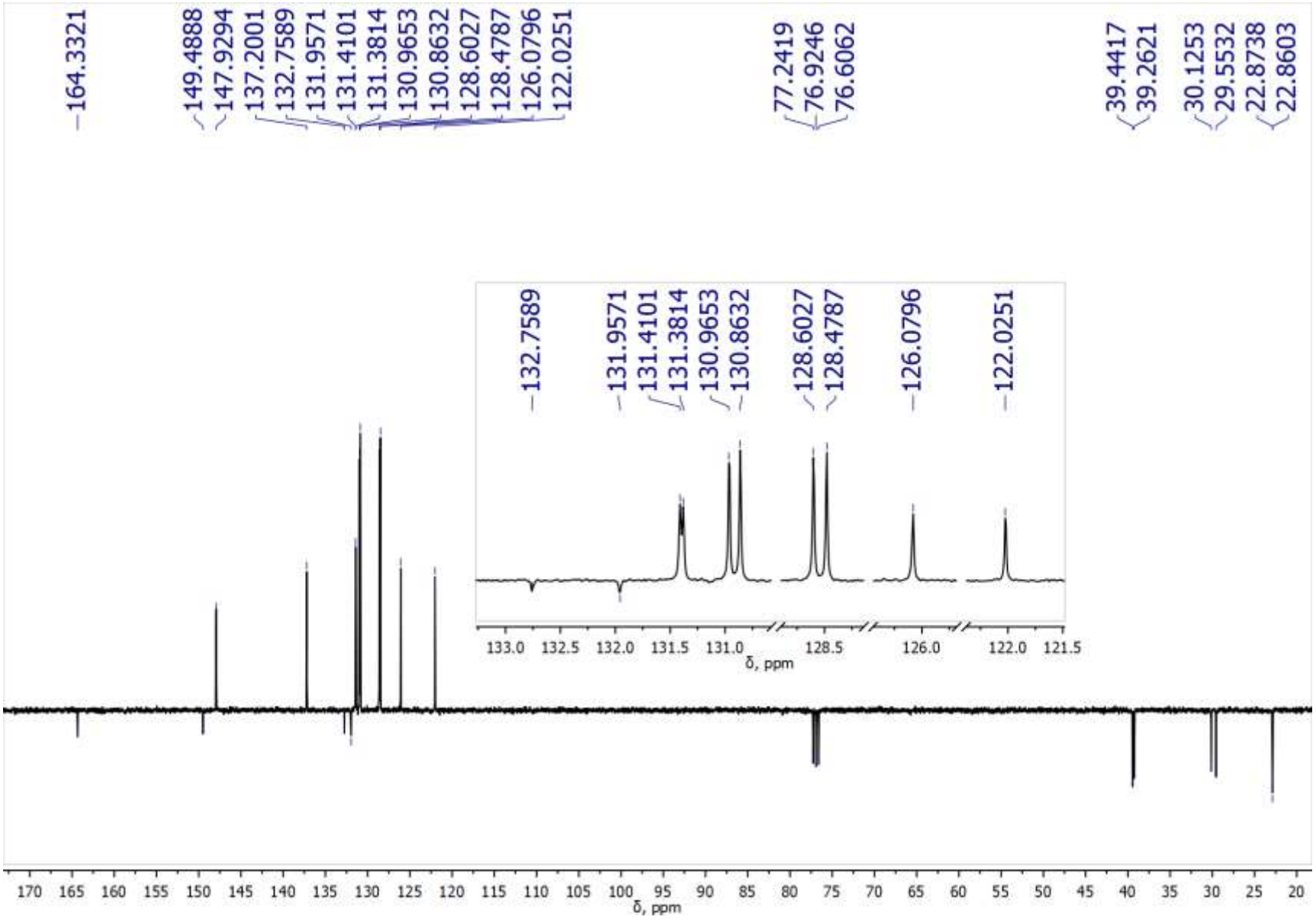

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of ligand **4** (100.61 MHz, $CDCl_3$)

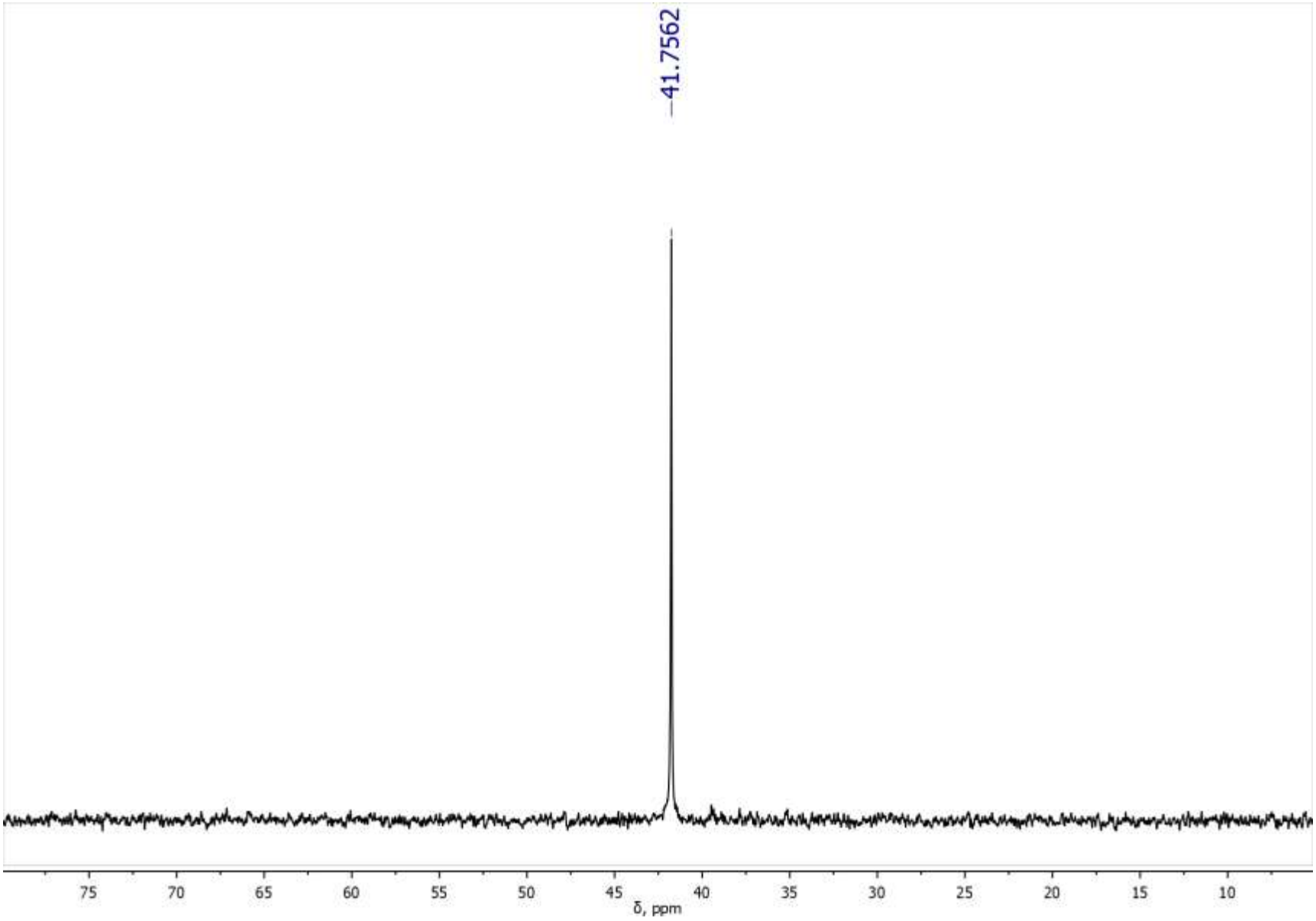

Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of complex **5** (121.49 MHz, $CDCl_3$)

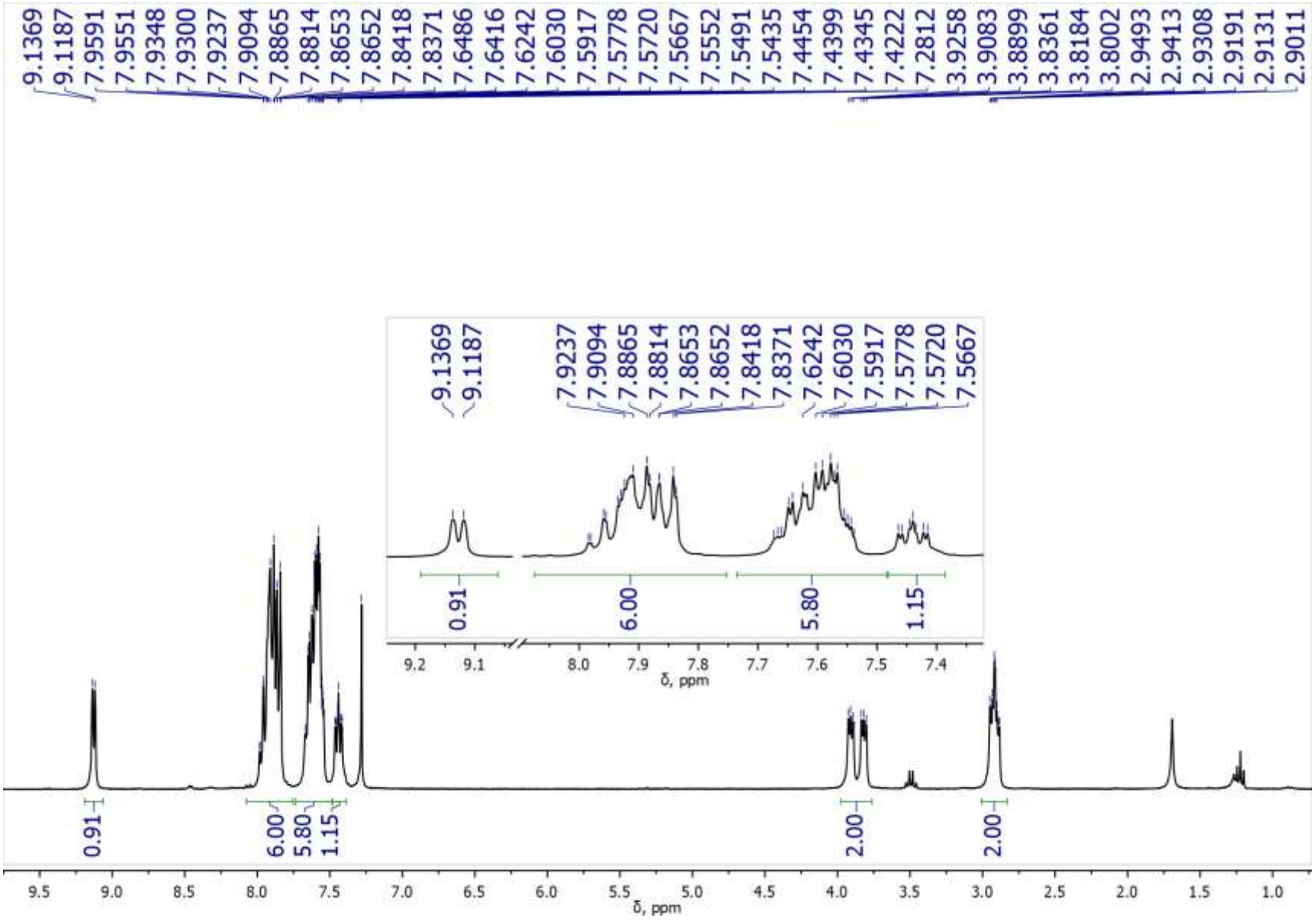

Figure S14. ^{1}H NMR spectrum of complex **5** (300.13 MHz, $CDCl_3$)

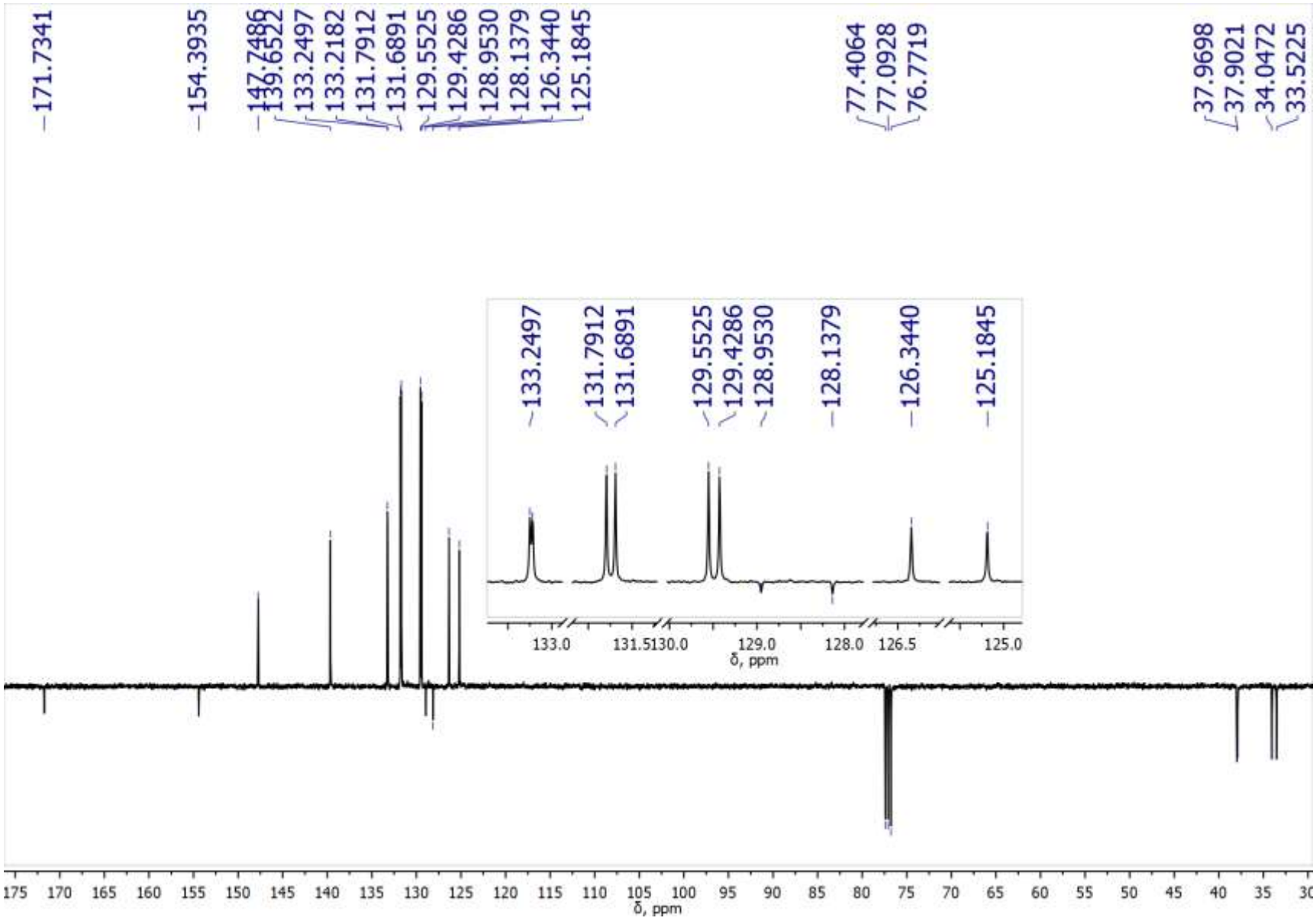

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of complex **5** (100.61 MHz, $CDCl_3$)

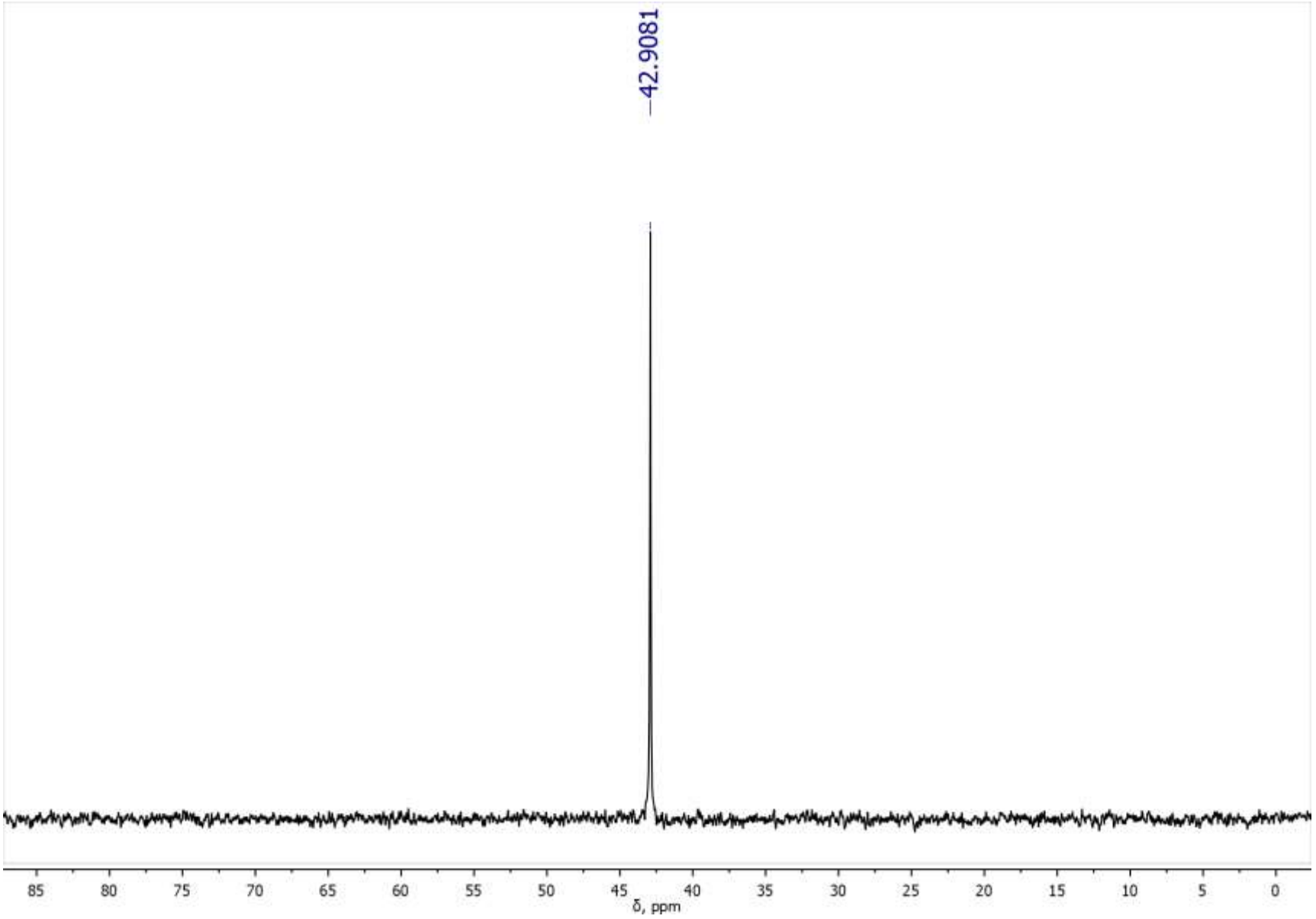

Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of complex **6** (121.49 MHz, $CDCl_3$)

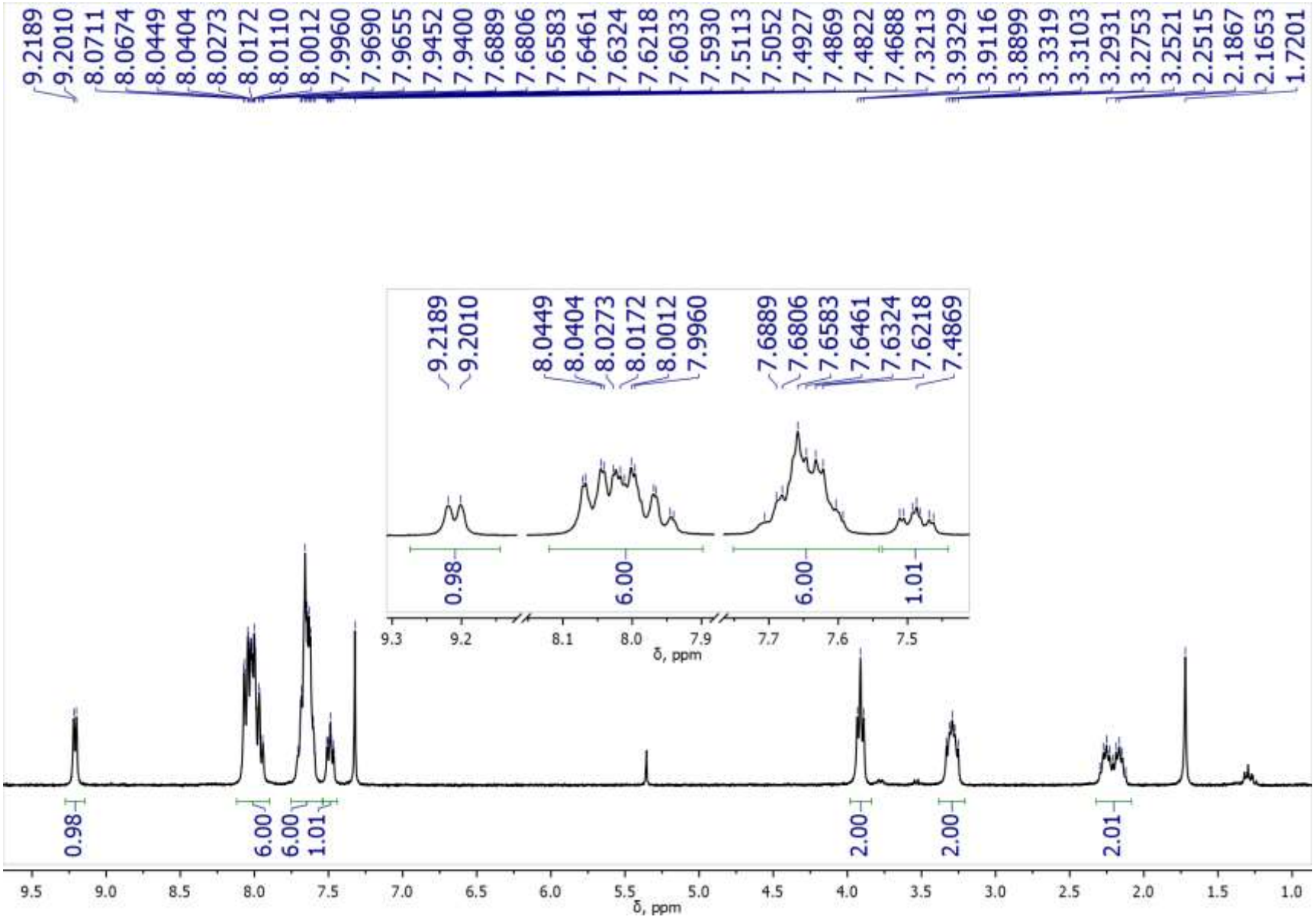

Figure S17. ^{1}H NMR spectrum of complex **6** (300.13 MHz, $CDCl_3$)

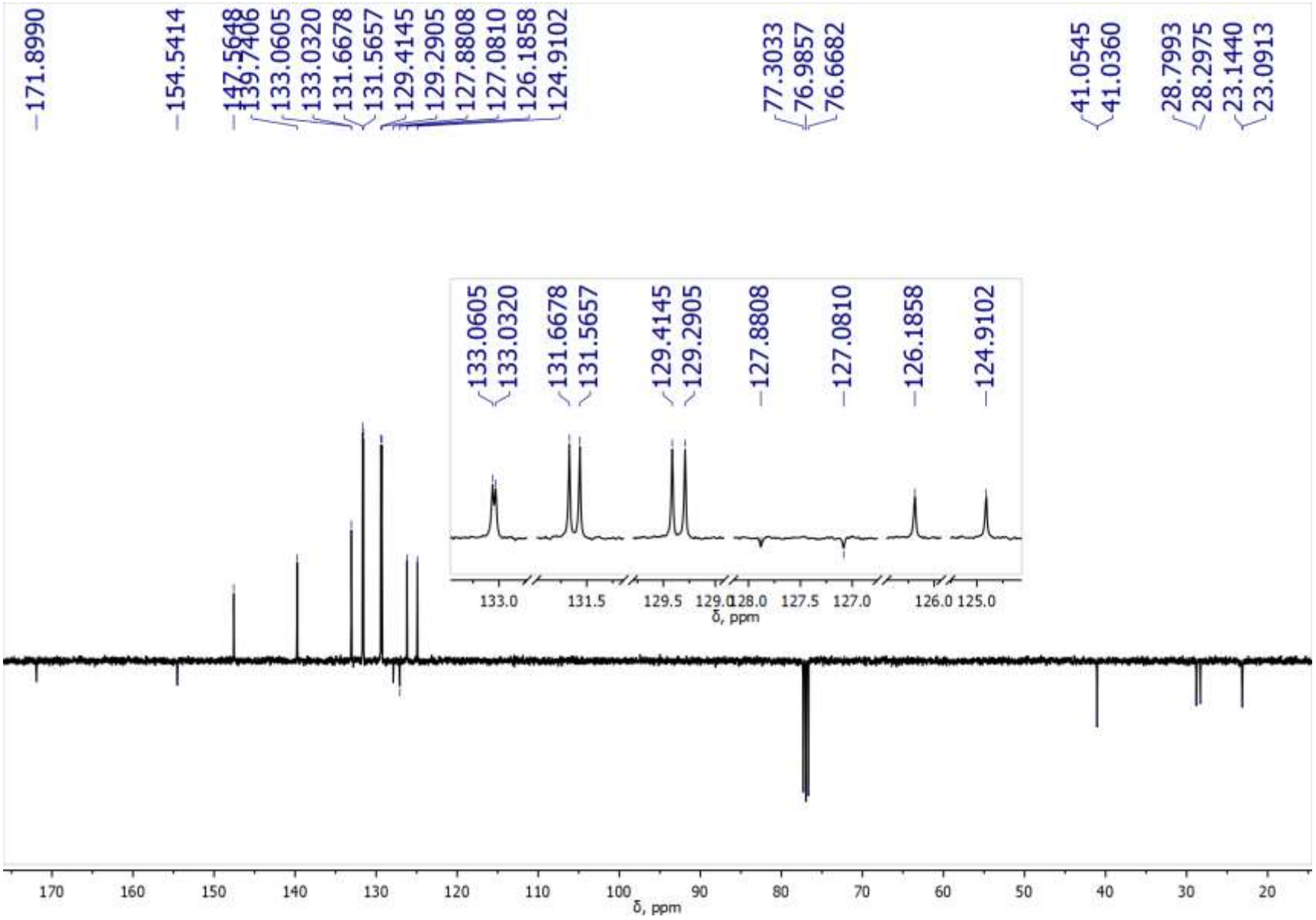

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of complex **6** (100.61 MHz, $CDCl_3$)

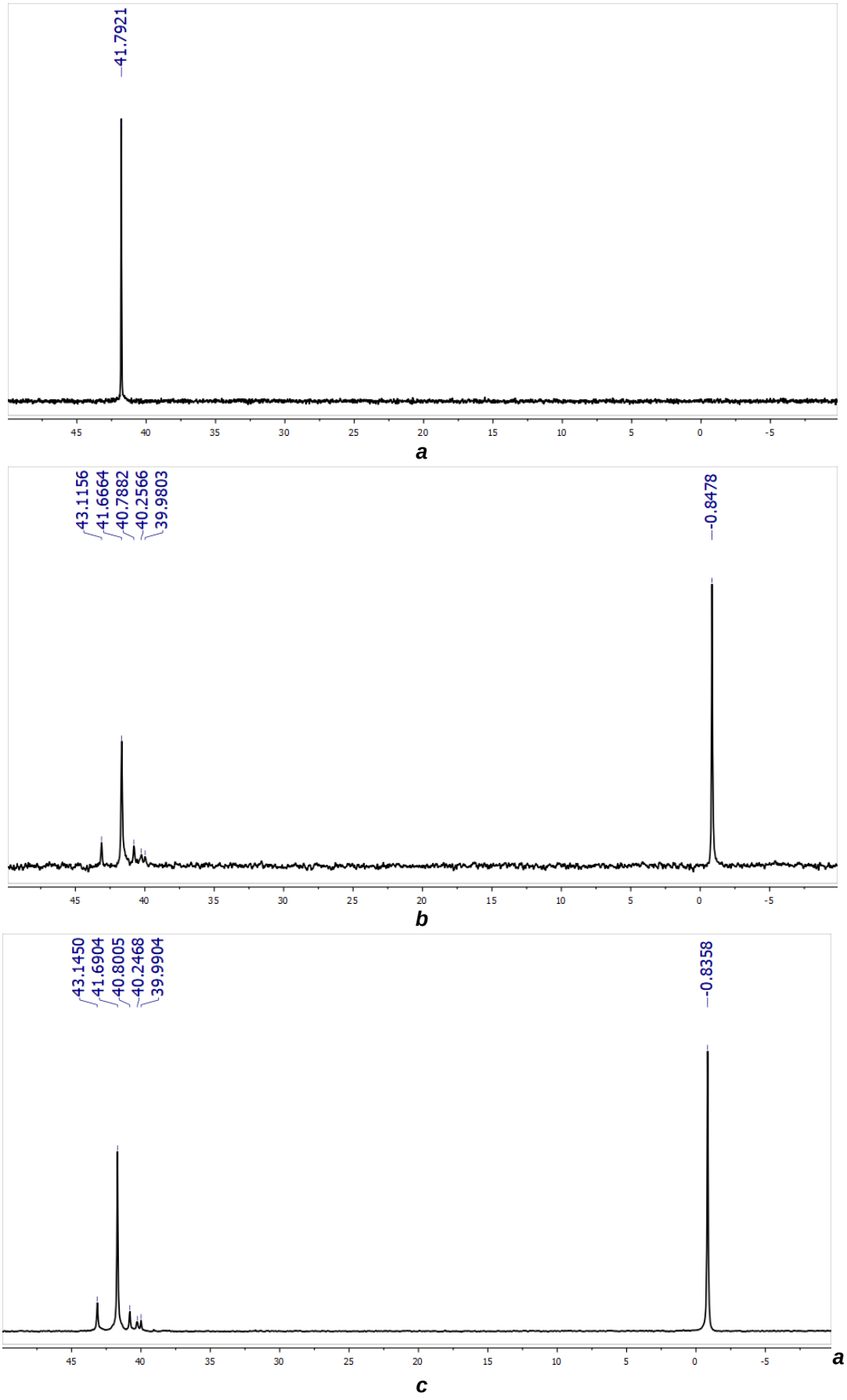

Figure S19. $^{31}P\{^{1}H\}$ NMR spectra of complex **5** in $(CD_3)_2SO$ (***a***) and its mixture with adenosine 5'-monophosphate disodium salt in $(CD_3)_2SO–D_2O$ (5:1) in 1 (***b***) and 15 (***c***) days after mixing the reagents

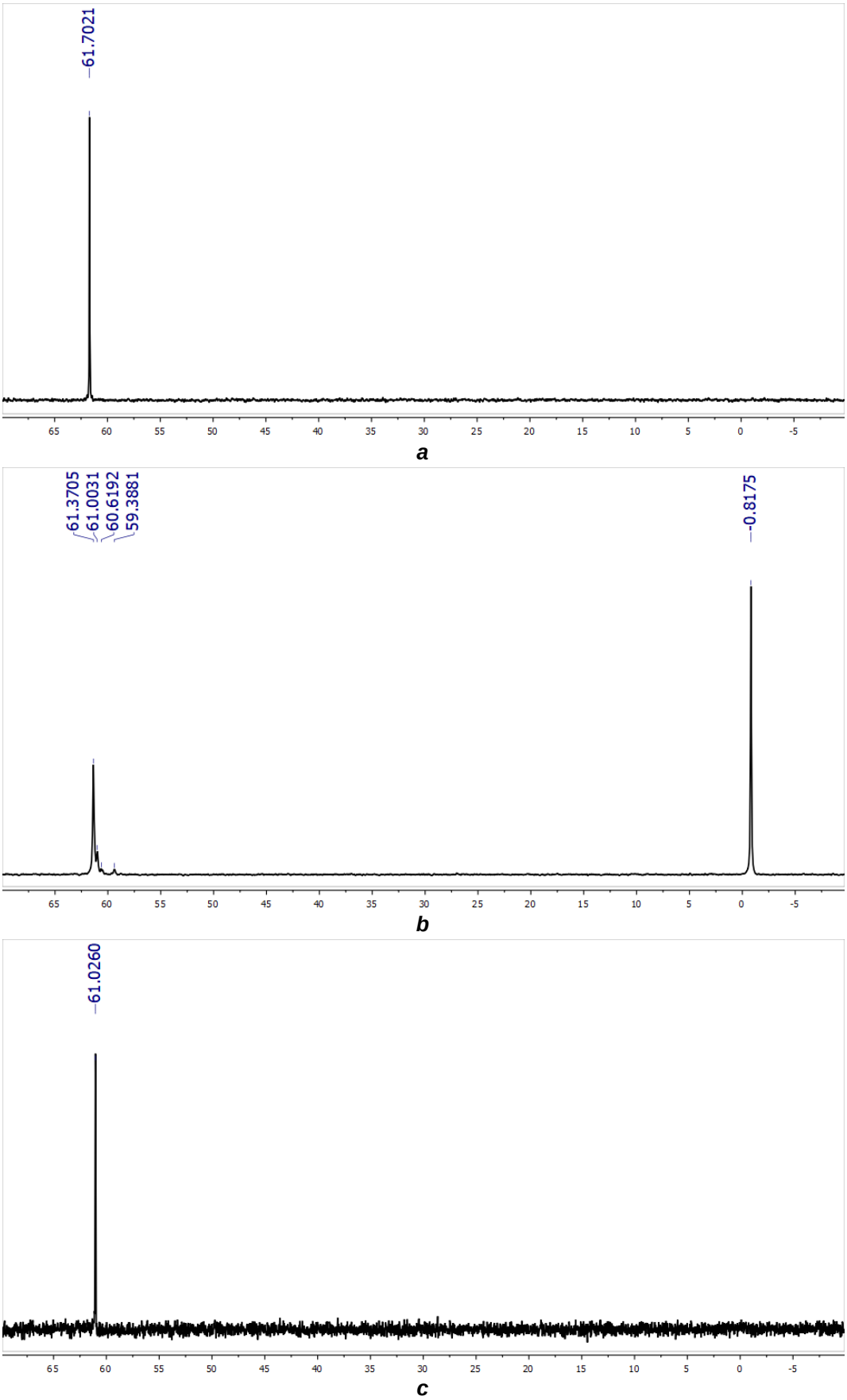

Figure S20. $^{31}P\{^{1}H\}$ NMR spectra of complex **A** in $(CD_3)_2SO$ (***a***), its mixture with adenosine 5'-monophosphate disodium salt in $(CD_3)_2SO–D_2O$ (5:1) in 1 h after mixing the reagents (***b***), and a solution of the resulting precipitate in $(CD_3)_2SO$ (***c***)

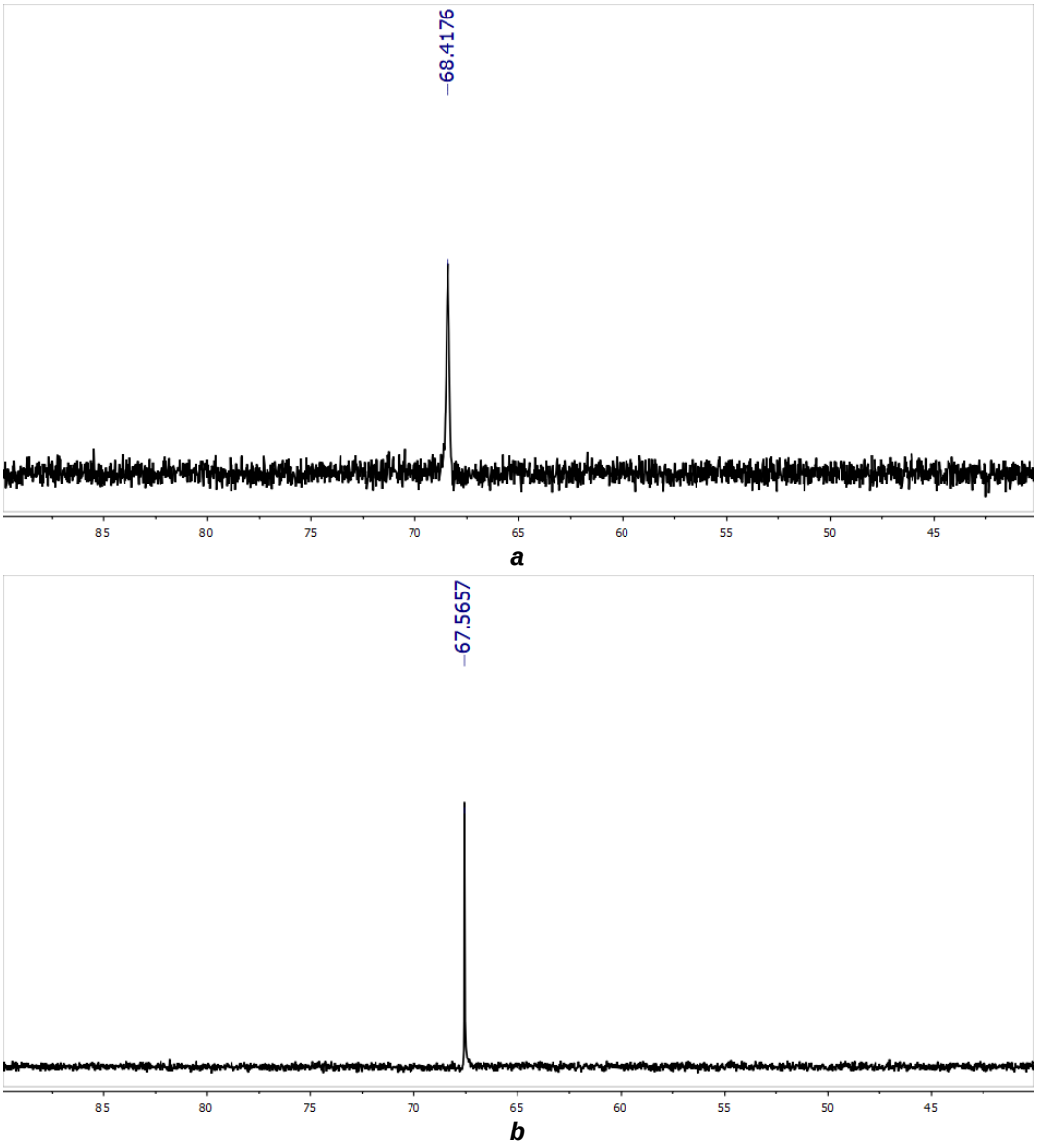

Figure S21. $^{31}P\{^{1}H\}$ NMR spectra of complex **B** in $(CD_3)_2SO$ (***a***) and a precipitate formed upon mixing it with a solution of adenosine 5'-monophosphate disodium salt in D_2O in $(CD_3)_2SO$ (***b***)