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Symmetrical and unsymmetrical thiophosphoryl–thiocarbamate pincer ligands: cyclopalladation in solution and under solvent-free conditions

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Experimental section

General remarks

Unless otherwise noted, all manipulations were carried out in the normal atmosphere without taking precautions to exclude air and moisture. (3,5-Dimethoxyphenyl)diphenylphosphine was obtained from 1-bromo-3,5-dimethoxybenzene upon sequential treatment with Mg and Ph_2PCl according to the published procedure.[S1] (3-Hydroxyphenyl)diphenylphosphine sulfide was derived from the corresponding phosphine precursor by the addition of elemental sulfur.[S2] Diethyl- and dibutylthiocarbamoyl chlorides were synthesized by the reactions of commercially available thiuram disulfides with sulfuryl chloride.[S3] Tetrahydrofuran and toluene were distilled over sodium. Dichloromethane was distilled over P_2O_5. All other chemicals and solvents were used as purchased.

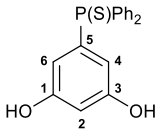
The NMR spectra were recorded on a Bruker Avance 400 spectrometer. The chemical shifts (δ) were referenced internally by the residual (^{1}H) or deuterated (^{13}C) solvent signals relative to tetramethylsilane. In most cases, the $^{13}C\{^1H\}$ NMR spectra were registered using the *J*MODECHO mode; the signals for the *C* nuclei bearing odd and even numbers of protons had opposite polarities. The NMR peak assignments for ligands **4b,c** and complexes **5b,c** were based on the results obtained earlier for the Me_2N-substituted analogs.[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. S4

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, Sunnyvale, CA, USA).

Syntheses

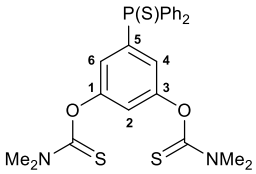
(3,5-Dihydroxyphenyl)diphenylphosphine sulfide 1



A stirred mixture of (3,5-dimethoxyphenyl)diphenylphosphine (4.00 g, 12.41 mmol) and 48% aq. HBr (25 mL) was refluxed for 8 h. After cooling to room temperature, the resulting precipitate was filtered off and dissolved in 3% aq. NaOH (100 mL). The solution obtained was treated with 30% aq. acetic acid (25 mL) and the target product was extracted with a mixture of toluene and EtOAc (1:1). The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness to give crude (3,5-dihydroxyphenyl)diphenylphosphine. The latter was dissolved in toluene (25 mL). Then elemental sulfur (0.40 g, 12.48 mmol) was added and the

reaction mixture was stirred at room temperature for 5 h. The solvent was removed under reduced pressure, and the residue obtained was purified by column chromatography on silica gel (eluent: CH_2Cl_2–EtOAc, 10:1) to give 3.15 g of compound **1** as an amorphous solid. Yield: 69%. $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 44.12 ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 6.39 (br. s, 1H, H(C2)), 6.68 (dd, 2H, H(C4) + H(C6), $^3J_{HP}$ = 14.4 Hz, $^4J_{HH}$ = 2.2 Hz), 7.39–7.44 (m, 4H, *m*-H in $P(S)Ph_2$), 7.47–7.51 (m, 2H, *o*-H in $P(S)Ph_2$), 7.67–7.72 (m, 4H, *o*-H in $P(S)Ph_2$) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 106.74 (s, C2), 111.83 (d, C4 and C6, $^2J_{CP}$ = 12.1 Hz), 128.65 (d, *m*-C in $P(S)Ph_2$, $^3J_{CP}$ = 12.5 Hz), 131.41 (d, *ipso*-C in $P(S)Ph_2$, $^1J_{CP}$ = 85.8 Hz), 131.96 (d, *p*-C in $P(S)Ph_2$, $^4J_{CP}$ = 1.9 Hz), 132.19 (d, *o*-C in $P(S)Ph_2$, $^2J_{CP}$ = 11.0 Hz), 134.00 (d, C5, $^1J_{CP}$ = 85.1 Hz), 157.01 (d, C1 and C3, $^3J_{CP}$ = 19.1 Hz) ppm. IR (KBr, ν/cm^{-1}): 461(w), 482(w), 508(m), 562(m), 614(m), 642(s) (νP=S), 682(m), 691(s), 714(s), 748(w), 849(br, w), 999(m), 1027(vw), 1042(vw), 1103(s), 1159(br, s), 1267(br, m), 1299(m), 1318(m), 1375(w), 1436(s), 1480(w), 1592(s), 1609(m), 3054(m), 3076(m), 3271(br, s) (νOH). Anal. Calcd for $C_{18}H_{15}O_2PS \cdot 0.5EtOAc$: C, 64.85; H, 5.17. Found: C, 64.63; H, 5.25%.

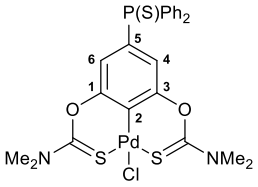
***O,O'*-[5-(Diphenylthiophosphoryl)-1,3-phenylene] bis(dimethylthiocarbamate) 2**



A solution of (3,5-dihydroxyphenyl)diphenylphosphine sulfide **1** (solvate with 0.5EtOAc) (1.30 g, 3.51 mmol) in THF (20 mL) was added dropwise to a stirred suspension of Bu^tOK (0.79 g, 7.04 mmol) in THF (20 mL) at 5–10 °C. The reaction mixture was stirred for 30 min at reduced temperature. Then a solution of $ClC(S)NMe_2$ (0.87 g, 7.04 mmol) in THF (25 mL) was added dropwise at 5–10 °C. The stirred reaction mixture was heated at 60 °C for 3 h. After cooling to room temperature, it was diluted with Et_2O and washed with water. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue obtained was crystallized from EtOAc to give 0.60 g of symmetrical ligand **2** as a white crystalline solid. Yield: 34%. Mp: 202–204 °C (EtOAc). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 42.95 ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 3.31 and 3.43 (both s, 6H + 6H, NMe_2), 7.05 (td, 1H, H(C2), $^4J_{HH}$ = 2.1 Hz, $^5J_{HP}$ = 0.7 Hz), 7.38 (dd, 2H, H(C4) + H(C6), $^3J_{HP}$ = 13.6 Hz, $^4J_{HH}$ = 2.1 Hz), 7.45–7.56 (m, 6H, *m*-H and *p*-H in $P(S)Ph_2$), 7.75–7.81 (m, 4H, *o*-H in $P(S)Ph_2$) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 38.90 and 43.35 (both s, NMe_2), 121.44 (d, C2, $^4J_{CP}$ = 1.3 Hz), 124.37 (d, C4 and C6, $^2J_{CP}$ = 11.3 Hz), 128.68 (d, *m*-C in $P(S)Ph_2$, $^3J_{CP}$ = 12.6 Hz), 131.73 (d, *p*-C in $P(S)Ph_2$, $^4J_{CP}$ = 2.8 Hz), 132.40 (d, *o*-C in $P(S)Ph_2$, $^2J_{CP}$ = 10.8 Hz), 132.43 (d, *ipso*-C in $P(S)Ph_2$, $^1J_{CP}$ = 86.3 Hz), 134.27 (d, C5, $^1J_{CP}$ = 84.3 Hz), 153.91 (d, C1 and C3, $^3J_{CP}$ = 18.9 Hz), 186.77

(s, C=S) ppm. IR (KBr, ν/cm^{-1}): 458(w), 479(vw), 513(m), 561(w), 614(vw), 646(m) (νP=S), 692(m), 719(s), 751(w), 877(w), 911(w), 998(w), 1009(w), 1029(w), 1105(s), 1138(s), 1173(s), 1250(s), 1280(m), 1296(m), 1393(s), 1408(m), 1419(m), 1436(m), 1482(w), 1538(br, s), 1586(w), 1598(w), 2938(w), 3074(vw). Anal. Calcd for $C_{24}H_{25}N_2O_2PS_3$: C, 57.58; H, 5.03; N, 5.60. Found: C, 57.54; H, 4.98; N, 5.47%.

Synthesis of symmetrical complex [κ^3-*S,C,S*-(L)Pd(II)Cl] 3 in solution



A solution of $PdCl_2(NCPh)_2$ (57 mg, 0.149 mmol) in CH_2Cl_2 (4 mL) was added slowly dropwise to a solution of ligand **2** (75 mg, 0.150 mmol) in CH_2Cl_2 (6 mL). In 15 min, the reaction mixture turned from dark red to light yellow. The solvent was removed under reduced pressure, and the resulting residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2–EtOH, 50:1) to give 79 mg of complex **3** as a light yellow crystalline solid. Yield: 83%. $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 42.42 ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 3.38 and 3.56 (both s, 6H + 6H, NMe_2), 7.19 (d, 2H, H(C4) + H(C6), $^3J_{CP}$ = 13.1 Hz), 7.47–7.52 (m, 4H, *m*-H in $P(S)Ph_2$), 7.54–7.59 (m, 2H, *p*-H in $P(S)Ph_2$), 7.73 (ddd, 4H, *o*-H in $P(S)Ph_2$, $^3J_{HP}$ = 13.6 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 39.98 and 43.86 (both s, NMe_2), 118.85 (d, C4 and C6, $^2J_{CP}$ = 11.6 Hz), 125.16 (d, C2, $^4J_{CP}$ = 1.7 Hz), 128.75 (d, *m*-C in $P(S)Ph_2$, $^3J_{CP}$ = 12.5 Hz), 131.40 (d, C5, $^1J_{CP}$ = 87.7 Hz), 131.97 (d, *p*-C in $P(S)Ph_2$, $^4J_{CP}$ = 2.7 Hz), 132.18 (d, *ipso*-C in $P(S)Ph_2$, $^1J_{CP}$ = 86.7 Hz), 132.22 (d, *o*-C in $P(S)Ph_2$, $^2J_{CP}$ = 11.0 Hz), 153.89 (d, C1 and C3, $^3J_{CP}$ = 18.9 Hz), 180.46 (s, C=S) ppm. IR (KBr, ν/cm^{-1}): 497(w), 519(m), 582(vw), 615(vw), 645(m) (νP=S), 691(m), 718(m), 757(w), 893(w), 1003(w), 1103(m), 1153(w), 1215(m), 1238(m), 1266(w), 1293(m), 1366(m), 1404(m), 1436(m), 1480(vw), 1559(s), 2928(vw), 3050(vw). Anal. Calcd for $C_{24}H_{24}ClN_2O_2PPdS_3$: C, 44.94; H, 3.77; N, 4.37. Found: C, 44.97; H, 3.94; N, 4.48%.

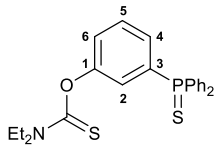
Solvent-free cyclopalladation of ligand 3 upon heating

Solid $PdCl_2(NCPh)_2$ (34 mg, 0.088 mmol) and ligand **2** (44 mg, 0.083 mmol) were manually ground in a mortar for 15 min, alternating periods of grinding with short breaks and scraping the reaction mixture with a spatula. The resulting mixture was heated at 65–70 °C for 15 min. The residue obtained was analyzed prior to any workup by IR spectroscopy (see Fig. S15) and after dissolution in $CDCl_3$ by ^{31}P NMR spectroscopy (Fig. S16 in the SI), which confirmed the formation of pincer complex **3** (in ~75% yield).

General procedure for the synthesis of unsymmetrical ligands 4b,c

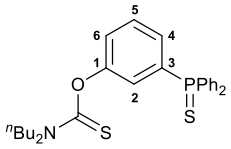
A mixture of (3-hydroxyphenyl)diphenylphosphine sulfide (0.652 g, 2.101 mmol) and NaH (used as a 60% dispersion in mineral oil; 0.084 g, 2.100 mmol) in THF (20 mL) was stirred at room temperature for 2 h until the evolution of H_2 stopped. Then a solution of the corresponding dialkylthiocarbamoyl chloride (2.100 mmol) in THF (15 mL) was added dropwise. The stirred reaction mixture was heated at 50 °C for 5 h. After cooling to room temperature, the resulting mixture was diluted with Et_2O 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 (eluent: CH_2Cl_2–hexane, 1:1) to give the target products as white crystalline solids.

***O*-[3-(Diphenylthiophosphoryl)phenyl] diethylthiocarbamate, 4b**



Yield: 0.700 g (78%). Mp: 120–122 °C. $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 42.96 ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 1.28–1.33 (m, 6H, Me), 3.68 and 3.88 (both q, 2H + 2H, CH_2N, $^3J_{HH}$ = 7.1 Hz), 7.24 (d, 1H, H(C6), $^3J_{HH}$ = 8.1 Hz), 7.45–7.58 (m, 9H, H_{Ar}), 7.75–7.81 (m, 4H, *o*-H in $P(S)Ph_2$) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 11.78 and 13.56 (both s, Me), 44.32 and 48.43 (both s, CH_2N), 126.16 (d, C6, $^4J_{CP}$ = 2.4 Hz), 127.03 (d, C5, $^3J_{CP}$ = 11.3 Hz), 128.62 (d, *m*-C in $P(S)Ph_2$, $^3J_{CP}$ = 13.2 Hz), 129.31 (d, C2 or C4, $^2J_{CP}$ = 14.1 Hz), 129.41 (d, C4 or C2, $^2J_{CP}$ = 10.1 Hz), 131.68 (d, *p*-C in $P(S)Ph_2$, $^4J_{CP}$ = 2.9 Hz), 132.39 (d, *o*-C in $P(S)Ph_2$, $^2J_{CP}$ = 10.3 Hz), 132.58 (d, *ipso*-C in $P(S)Ph_2$, $^1J_{CP}$ = 85.7 Hz), 134.17 (d, C3, $^1J_{CP}$ = 84.4 Hz), 153.87 (d, C1, $^3J_{CP}$ = 16.5 Hz), 186.36 (s, C=S) ppm. IR (KBr, ν/cm^{-1}): 509(m), 521(m), 613(w), 642(m) (νP=S), 692(m), 715(s), 744(w), 762(w), 801(w), 918(vw), 953(w), 998(w), 1070(w), 1097(s), 1116(m), 1157(w), 1205(s), 1245(w), 1300(m), 1322(m), 1364(w), 1383(w), 1408(m), 1430(m), 1437(s), 1458(w), 1473(m), 1519(s), 1580(w), 2873(vw), 2932(w), 2971(w), 3053(vw). Anal. Calcd for $C_{23}H_{24}NOPS_2$: C, 64.92; H, 5.68; N, 3.29. Found: C, 64.85; H, 5.57; N, 3.32%.

***O*-[3-(Diphenylthiophosphoryl)phenyl] dibutylthiocarbamate, 4c**



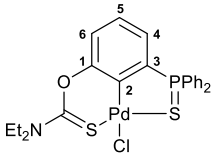
Yield: 0.850 g (84%). Mp: 97–99 °C. $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 42.97 ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 0.94 and 0.98 (both t, 3H + 3H, Me, $^3J_{HH}$ = 7.4 Hz), 1.31–1.43 and 1.63–1.77 (both m, 4H + 4H, CH_2), 3.59–3.62 and 3.76–3.80 (both m, 2H + 2H, CH_2N),

7.23 (d, 1H, H(C6), $^{3}J_{HH}$ = 8.0 Hz), 7.43–7.59 (m, 9H, H_{Ar}), 7.78 (dd, 4H, *o*-H in $P(S)Ph_2$, $^{3}J_{HP}$ = 13.4 Hz, $^{3}J_{HH}$ = 7.4 Hz) ppm. $^{13}C\{^{1}H\}$ NMR (100.61 MHz, $CDCl_3$): δ 13.82 and 13.89 (both s, Me), 20.13, 20.17, 20.59, and 30.34 (four s, CH_2), 49.70 and 53.69 (both s, CH_2N), 126.12 (d, C6, $^{4}J_{CP}$ = 2.5 Hz), 127.01 (d, C5, $^{3}J_{CP}$ = 11.3 Hz), 128.61 (d, *m*-C in $P(S)Ph_2$, $^{3}J_{CP}$ = 12.5 Hz), 129.35 (d, C2 or C4, $^{2}J_{CP}$ = 14.6 Hz), 129.37 (d, C4 or C2, $^{2}J_{CP}$ = 10.0 Hz), 131.67 (d, *p*-C in $P(S)Ph_2$, $^{4}J_{CP}$ = 2.9 Hz), 132.39 (d, *o*-C in $P(S)Ph_2$, $^{2}J_{CP}$ = 10.9 Hz), 132.58 (d, *ipso*-C in $P(S)Ph_2$, $^{1}J_{CP}$ = 85.5 Hz), 134.12 (d, C3, $^{1}J_{CP}$ = 84.8 Hz), 153.90 (d, C1, $^{3}J_{CP}$ = 16.5 Hz), 186.65 (s, C=S) ppm. IR (KBr, ν/cm^{-1}): 472(w), 507(m), 545(vw), 615(vw), 644(m) (νP=S), 694(m), 716(s), 726(m), 750(w), 803(w), 997(w), 1097(m), 1106(m), 1124(m), 1195(m), 1218(m), 1257(w), 1274(w), 1303(w), 1312(w), 1370(w), 1412(m), 1426(m), 1437(m), 1471(m), 1516(s), 1579(w), 2870(w), 2929(m), 2955(m), 3020(vw), 3051(vw). Anal. Calcd for $C_{27}H_{32}NOPS_2$: C, 67.33; H, 6.70; N, 2.91. Found: C, 67.30; H, 6.84; N, 3.05%.

General procedure for the synthesis of unsymmetrical complexes 5b,c in solution

A solution of $PdCl_2(NCPh)_2$ (64 mg, 0.167 mmol) in CH_2Cl_2 (5 mL) was added slowly dropwise to a solution of the corresponding ligand (0.167 mmol) in CH_2Cl_2 (6 mL). The reaction mixture was left under ambient conditions for 3 (in the case of ligand **4c**) or 12 h (in the case of **4b**). The solvent was removed under reduced pressure. The residue obtained was washed with Et_2O and purified by column chromatography on silica gel (eluent: CH_2Cl_2–EtOH, 100:1) to give the target complexes as light yellow crystalline solids.

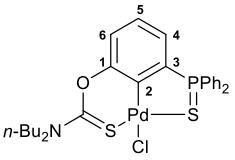
Complex [κ^3-*S,C,S′*-(L)Pd(II)Cl] 5b



Yield: 80 mg (85%). $^{31}P\{^{1}H\}$ NMR (161.98 MHz, $CDCl_3$): δ 48.45 ppm. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.32–1.38 (m, 6H, Me), 3.74 and 3.91 (both q, 2H + 2H, CH_2, $^{3}J_{HH}$ = 7.1 Hz), 6.85 (ddd, 1H, H(C4), $^{3}J_{HP}$ = 10.7 Hz, $^{3}J_{HH}$ = 7.3 Hz, $^{4}J_{HH}$ = 1.1 Hz), 7.03 (d, 1H, H(C6), $^{3}J_{HH}$ = 7.9 Hz), 7.08–7.13 (m, 1H, H(C5)), 7.52–7.56 (m, 4H, *m*-H in $P(S)Ph_2$), 7.62–7.65 (m, 2H, *p*-H in $P(S)Ph_2$), 7.81 (ddd, 4H, *o*-H in $P(S)Ph_2$, $^{3}J_{HP}$ = 13.5 Hz, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.2 Hz) ppm. $^{13}C\{^{1}H\}$ NMR (100.61 MHz, $CDCl_3$–$(CD_3)_2SO$): δ 11.28 and 12.96 (both s, Me), 45.35 and 48.48 (both s, CH_2N), 120.59 (d, C6, $^{4}J_{CP}$ = 3.0 Hz), 125.30 (d, C5, $^{3}J_{CP}$ = 15.3 Hz), 128.73 (d, *m*-C in $P(S)Ph_2$, $^{3}J_{CP}$ = 12.5 Hz), 128.75 (d, C4, $^{3}J_{CP}$ = 15.9 Hz), 129.14 (d, *ipso*-C in $P(S)Ph_2$, $^{1}J_{CP}$ = 80.7 Hz), 131.90 (d, *o*-C in $P(S)Ph_2$, $^{2}J_{CP}$ = 11.0 Hz), 132.65 (d, *p*-C in $P(S)Ph_2$, $^{4}J_{CP}$ = 2.7 Hz), 139.27 (d, C2, $^{2}J_{CP}$ = 24.6 Hz), 148.03 (d, C3, $^{1}J_{CP}$ = 106.7 Hz), 152.53 (d, C1, $^{3}J_{CP}$ = 21.7 Hz), 175.47 (s, C=S) ppm. IR (KBr, ν/cm^{-1}): 470(w), 518(m), 554(vw), 610(w) and 627(m) (both νP=S), 691(m), 708(m), 722(w), 731(m), 750(w), 785(w), 847(vw), 915(vw), 958(w),

998(w), 1081(w), 1103(m), 1108(m), 1144(m), 1183(w), 1216(m), 1250(m), 1293(m), 1314(m), 1358(w), 1380(w), 1394(w), 1437(s), 1456(m), 1481(w), 1538(s), 1571(w), 2870(vw), 2933(w), 2977(w), 3052(w). Anal. Calcd for $C_{23}H_{23}ClNOPPdS_2$: C, 48.77; H, 4.09; N, 2.47. Found: C, 48.18; H, 4.22; N, 2.49%.

Complex [κ^3-*S,C,S′*-(L)Pd(II)Cl] 5c



Yield: 102 mg (98%). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 48.32 ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 0.94 and 1.00 (both t, 3H + 3H, Me, $^3J_{HH}$ = 7.3 Hz), 1.33–1.48 and 1.68–1.77 (both m, 4H + 4H, CH_2), 3.64–3.68 and 3.79–3.83 (both m, 2H + 2H, CH_2N), 6.85 (dd, 1H, H(C4), $^3J_{HP}$ = 10.8 Hz, $^3J_{HH}$ = 7.4 Hz), 6.99 (d, 1H, H(C6), $^3J_{HH}$ = 8.0 Hz), 7.08–7.13 (m, 1H, H(C5)), 7.51–7.56 (m, 4H, *m*-H in P(S)Ph_2), 7.61–7.65 (m, 2H, *p*-H in P(S)Ph_2), 7.81 (dd, 4H, *o*-H in P(S)Ph_2, $^3J_{HP}$ = 13.5 Hz, $^3J_{HH}$ = 7.5 Hz) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 13.79 and 13.82 (both s, Me), 20.05, 20.18, 28.76, and 30.23 (four s, CH_2), 51.13 and 54.48 (both s, CH_2N), 120.53 (d, C6, $^4J_{CP}$ = 2.8 Hz), 125.36 (d, C5, $^3J_{CP}$ = 15.2 Hz), 128.97 (d, C4, $^2J_{CP}$ = 15.7 Hz), 129.15 (d, *m*-C in P(S)Ph_2, $^3J_{CP}$ = 13.2 Hz), 129.97 (d, *ipso*-C in P(S)Ph_2, $^1J_{CP}$ = 80.4 Hz), 132.71 (d, *o*-C in P(S)Ph_2, $^2J_{CP}$ = 11.0 Hz), 132.94 (d, *p*-C in P(S)Ph_2, $^4J_{CP}$ = 2.8 Hz), 140.79 (d, C2, $^2J_{CP}$ = 24.6 Hz), 149.55 (d, C3, $^1J_{CP}$ = 106.8 Hz), 153.27 (d, C1, $^3J_{CP}$ = 21.7 Hz), 177.00 (s, C=S) ppm. IR (KBr, ν/cm^{-1}): 465(vw), 482(w), 514(m), 557(vw), 610(m) and 624(w) (both νP=S), 691(m), 707(m), 719(m), 746(m), 778(w), 877(vw), 998(w), 1105(m), 1145(m), 1206(m), 1222(m), 1242(m), 1264(m), 1278(m), 1312(m), 1376(w), 1396(w), 1437(s), 1456(m), 1482(w), 1532(s), 1572(w), 2871(w), 2931(m), 2957(m), 3053(vw). Anal. Calcd for $C_{27}H_{31}ClNOPPdS_2$: C, 52.09; H, 5.02; N, 2.25. Found: C, 51.94; H, 5.02; N, 2.39%.

Solvent-free synthesis of complexes 5b,c

Solid $PdCl_2(NCPh)_2$ (33 mg, 0.086 mmol) and the corresponding ligand (**4b** or **4c**, 0.086 mmol) were manually ground in a mortar for 15 min, alternating periods of grinding with short breaks and scraping the reaction mixture with a spatula. In the case of ligand **4b**, the IR spectrum of the resulting light beige powder replicated that of the authentic sample of pincer complex **5b** obtained by the solution-based method (compare Figs. S33 and S28 in the SI). The analytically pure sample was obtained by following heating at 65–70 °C for 5 min (for the IR spectrum of the resulting light yellow solid, see Fig. S34 in the SI). Anal. Calcd for $C_{23}H_{23}ClNOPPdS_2$: C, 48.77; H, 4.09; N, 2.47. Found: C, 48.45; H, 4.24; N, 2.84%. In the case of ligand **4c**, the resulting brown slightly oily residue was heated at 85–90 °C for 10 min and, after cooling to room temperature, rinsed with Et_2O and dried under vacuum. The light yellow solid obtained was

analyzed by IR spectroscopy (Fig. S36 in the SI) and elemental analysis which revealed the quantitative formation of pincer complex **5c**. Anal. Calcd for $C_{27}H_{31}ClNOPPdS_2$: C, 52.09; H, 5.02; N, 2.25. Found: C, 51.26; H, 5.24; N, 2.21%.

SEM and EDS analysis

The samples under consideration were placed onto electro-conductive carbon tape adhered to SEM sample holder and then installed in a vacuum chamber of a Prisma E (Thermo Fisher) scanning electron microscope. SEM imaging of the samples was performed at low voltage settings (~3 kV) in order to provide surface geometry at a number of magnifications. Energy-dispersive X-ray spectroscopy (EDS) was applied to the samples in color SEM imaging mode to resolve elemental anisotropy of the samples. EDS imaging voltage was set at 25kV to yield elemental composition through whole sample depth at 350× magnification.

References

S1. S. Lorraine, K. Abdur-Rashid, W. Jia, K. Abdur-Rashid, P. Maragh and T. Dasgupta, *Inorg. Chim. Acta*, 2020, **511**, 119850; https://doi.org/10.1016/j.ica.2020.119850.

S2. D. V. Aleksanyan, S. G. Churusova, Z. S. Klemenkova, R. R. Aysin, E. Yu. Rybalkina, Yu. V. Nelyubina, O. I. Artyushin, A. S. Peregudov and V. A. Kozlov, *Organometallics*, 2019, **38**, 1062; https://doi.org/10.1021/acs.organomet.8b00867.

S3. A. N. Pudovik, V. K. Khairullin, M. A. Vasyanina, R. M. Kamalov, O. N. Kataeva, I. A. Litvinov and V. A. Naumov, *Russ. Chem. Bull.*, 1989, **38**, 819; https://doi.org/10.1007/BF00953298.

S4. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1975.

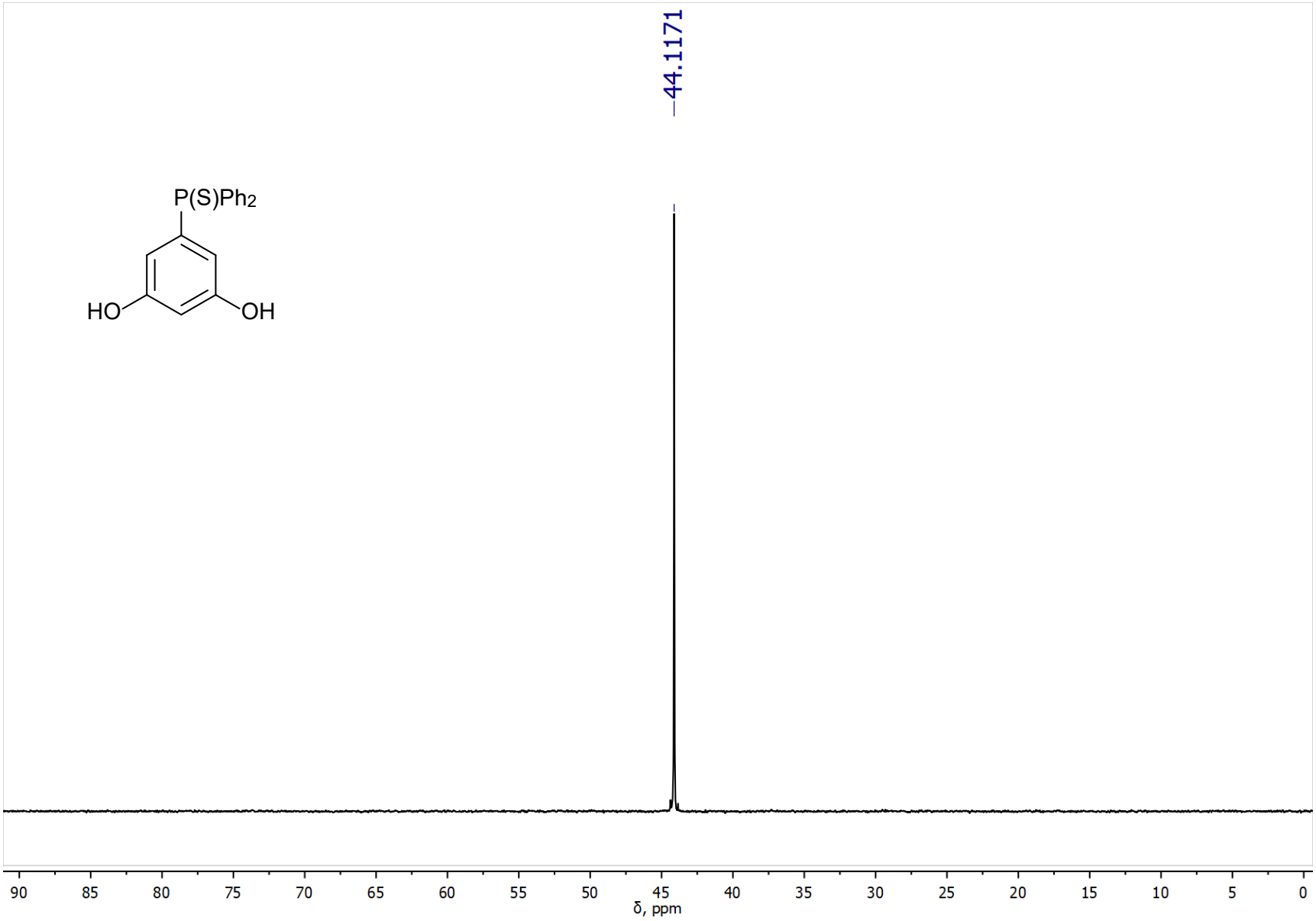


Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum of compound **1** (161.98 MHz, $CDCl_3$)

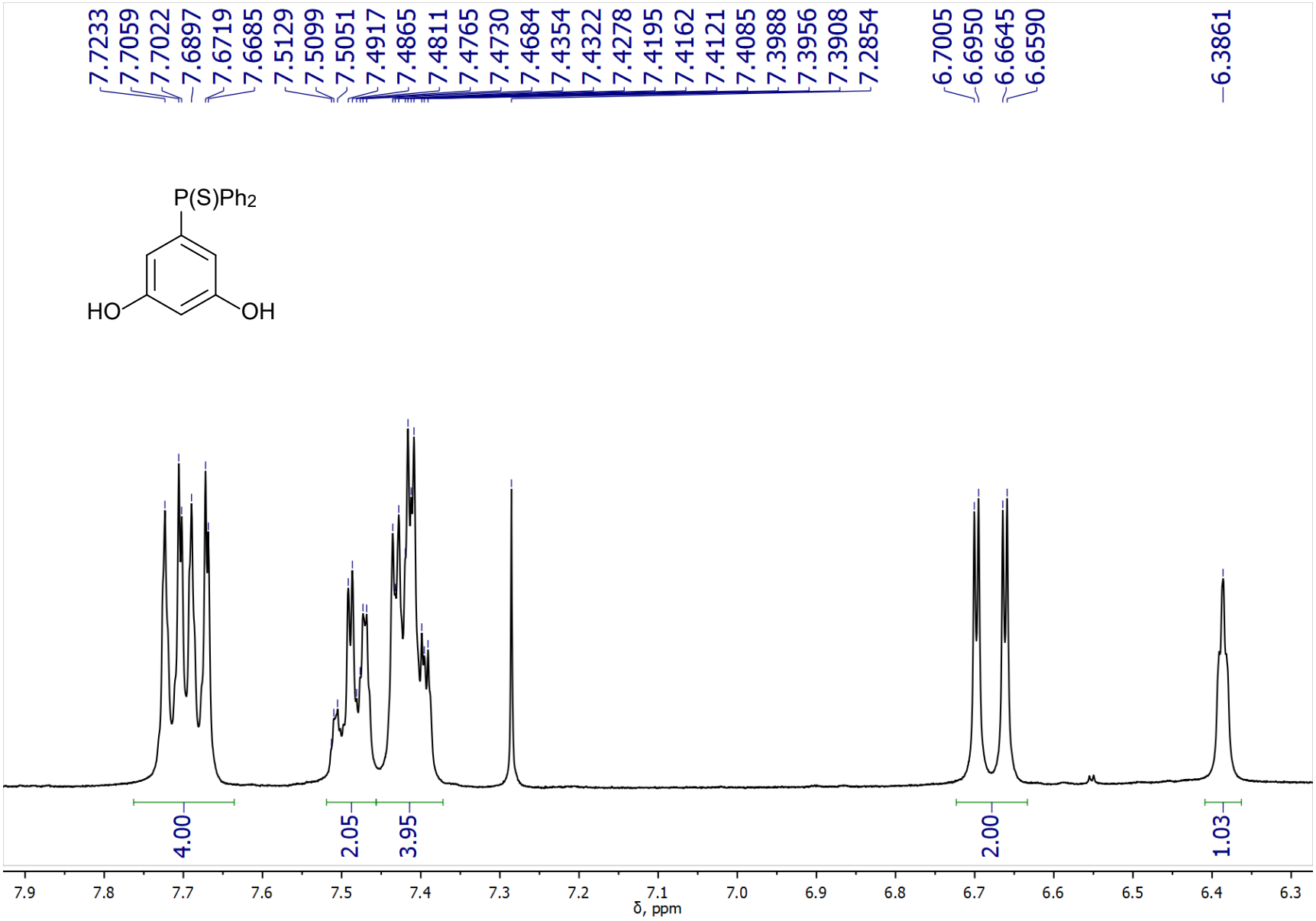


Figure S2. ^{1}H NMR spectrum of compound **1** (400.13 MHz, $CDCl_3$)

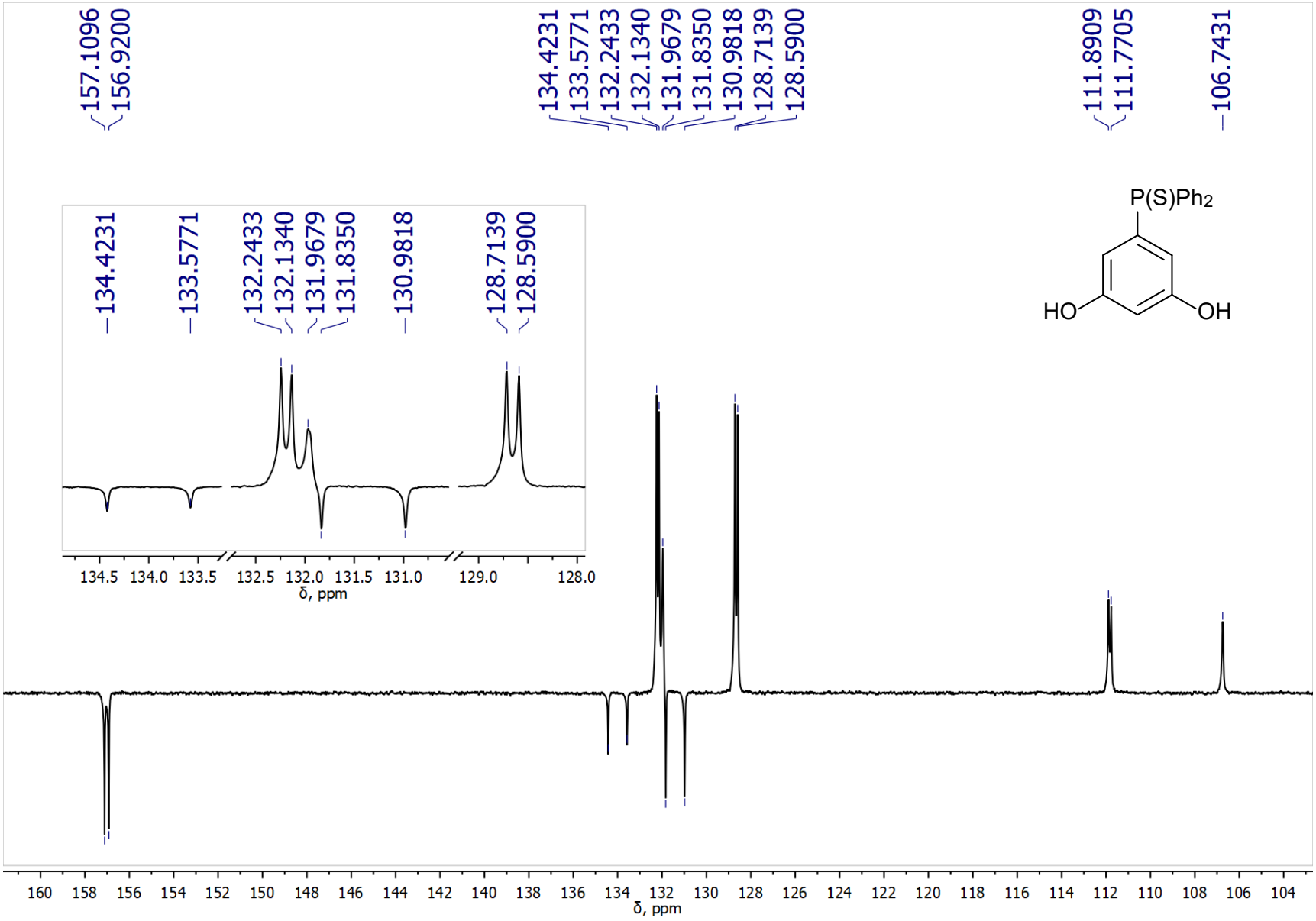


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1** (100.61 MHz, $CDCl_3$)

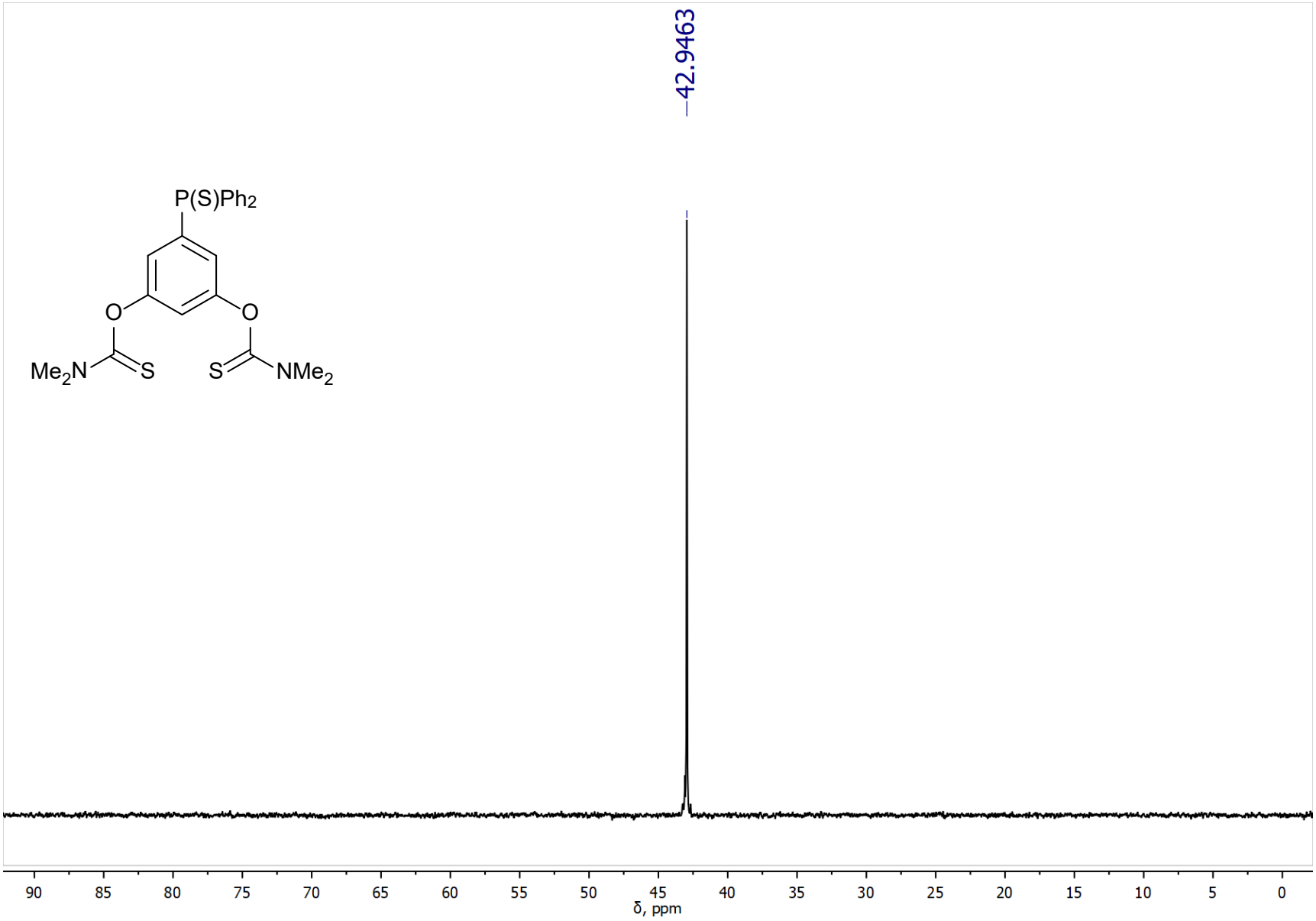


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of ligand **2** (161.98 MHz, $CDCl_3$)

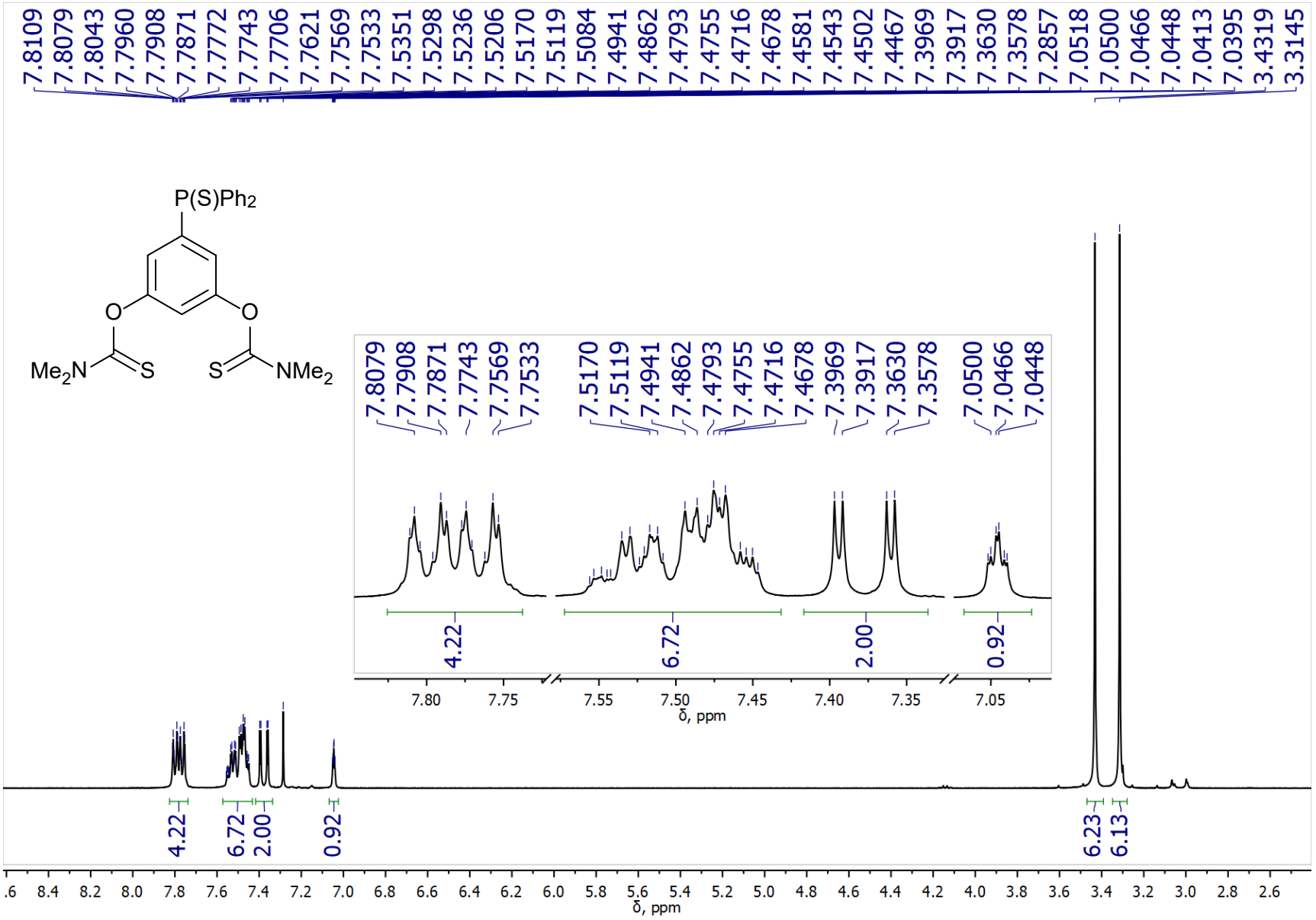


Figure S5. ^{1}H NMR spectrum of ligand **2** (400.13 MHz, $CDCl_3$)

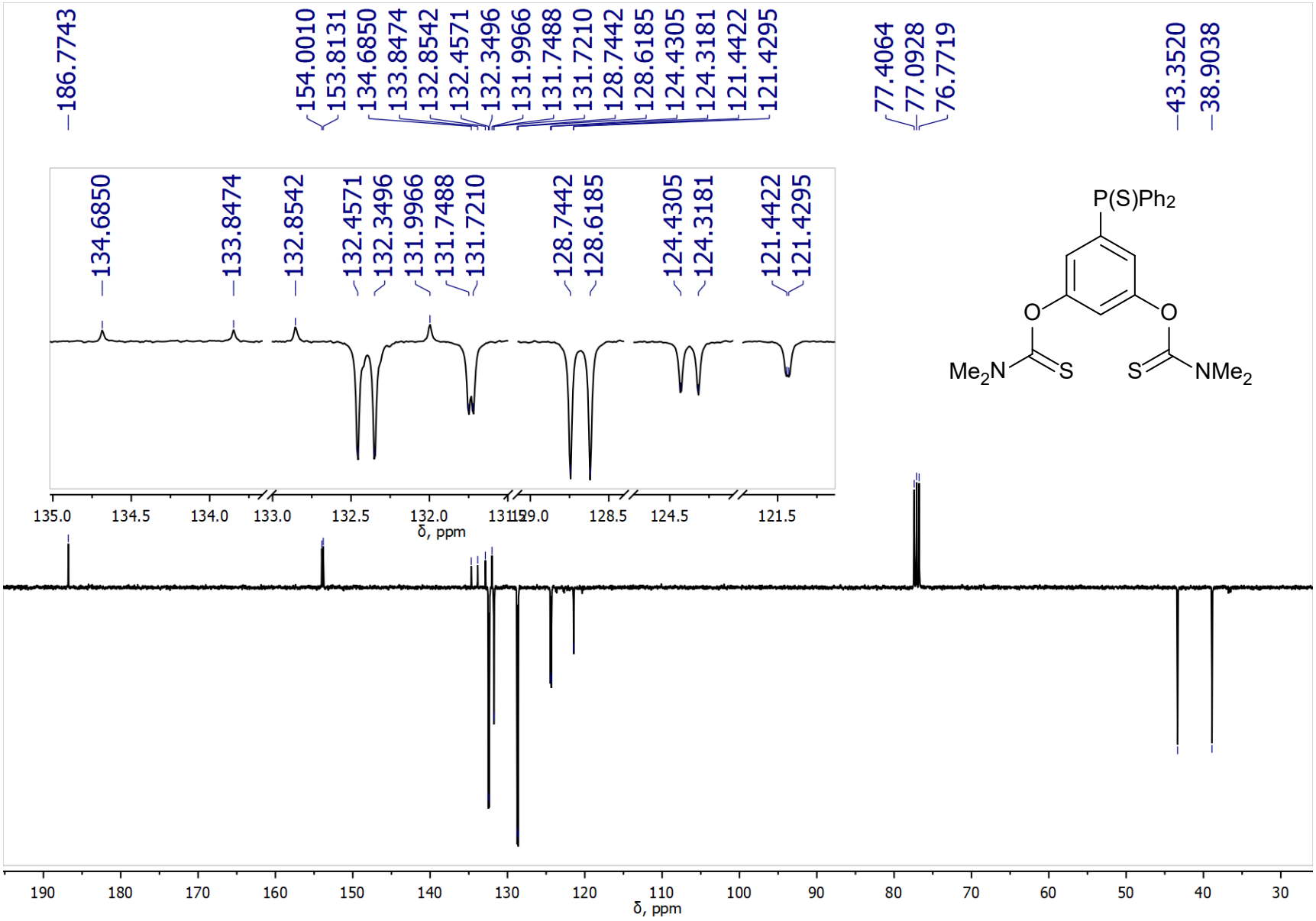


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of ligand **2** (100.61 MHz, $CDCl_3$)

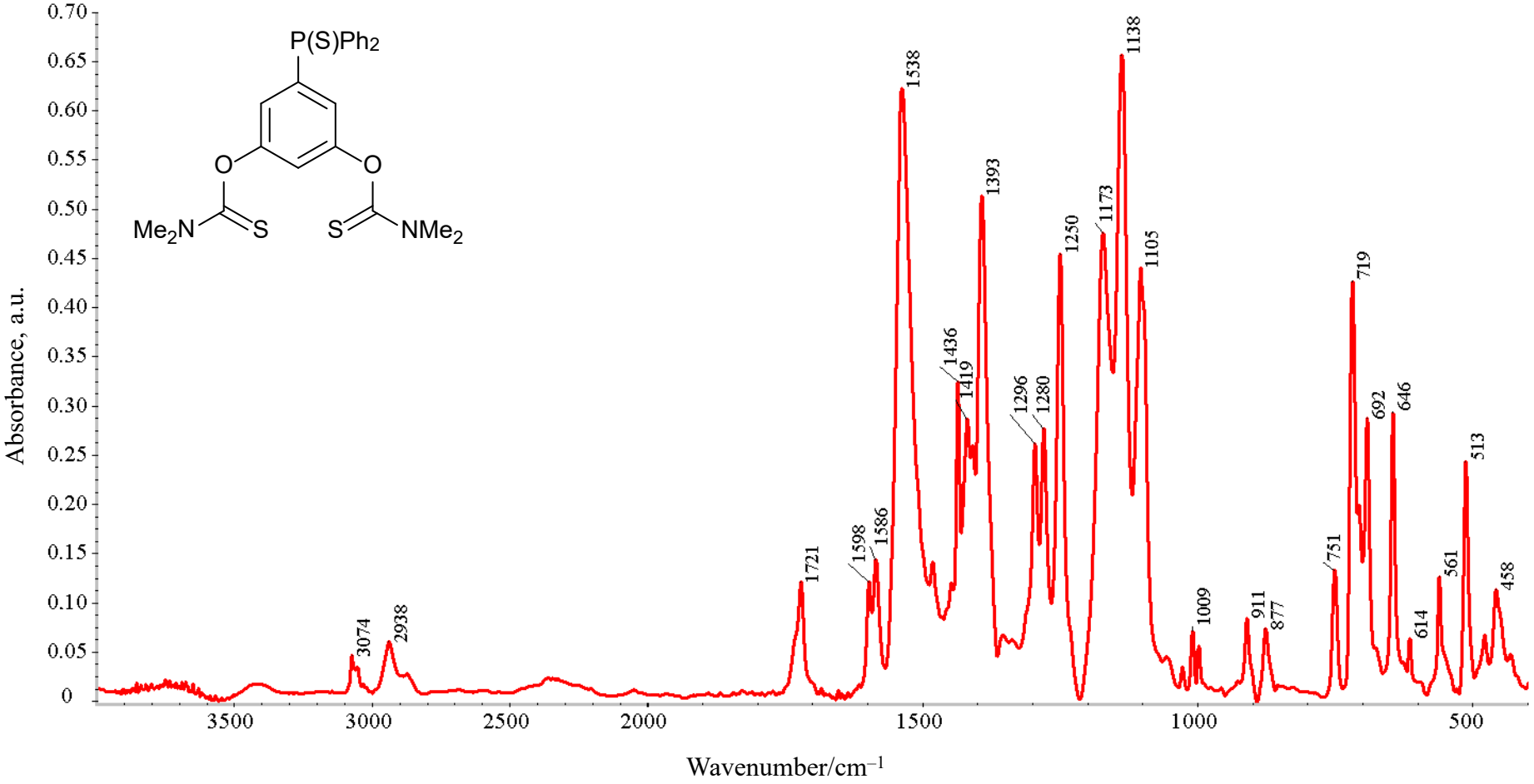


Figure S7. IR spectrum of ligand **2**

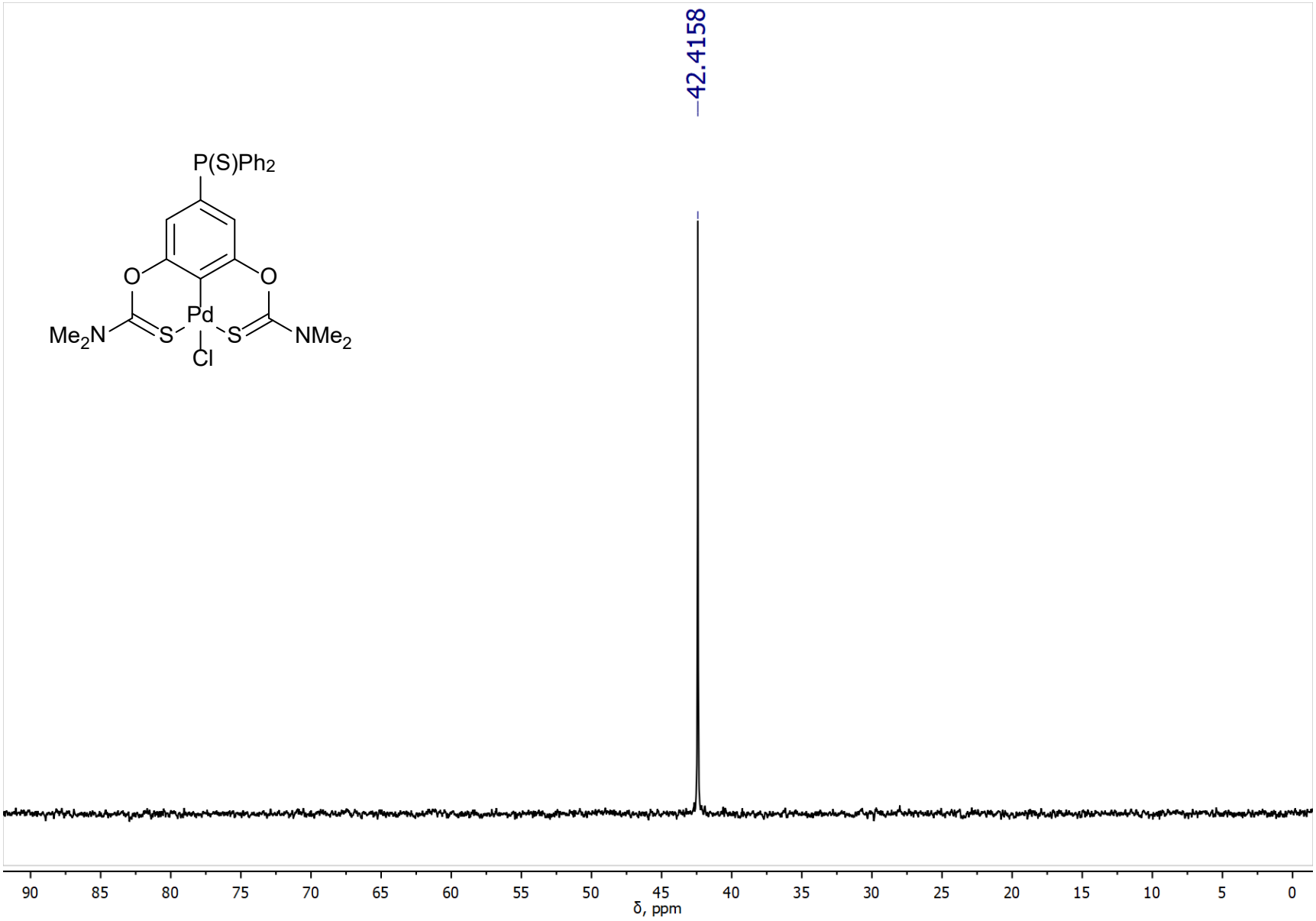


Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of complex **3** (161.98 MHz, $CDCl_3$)

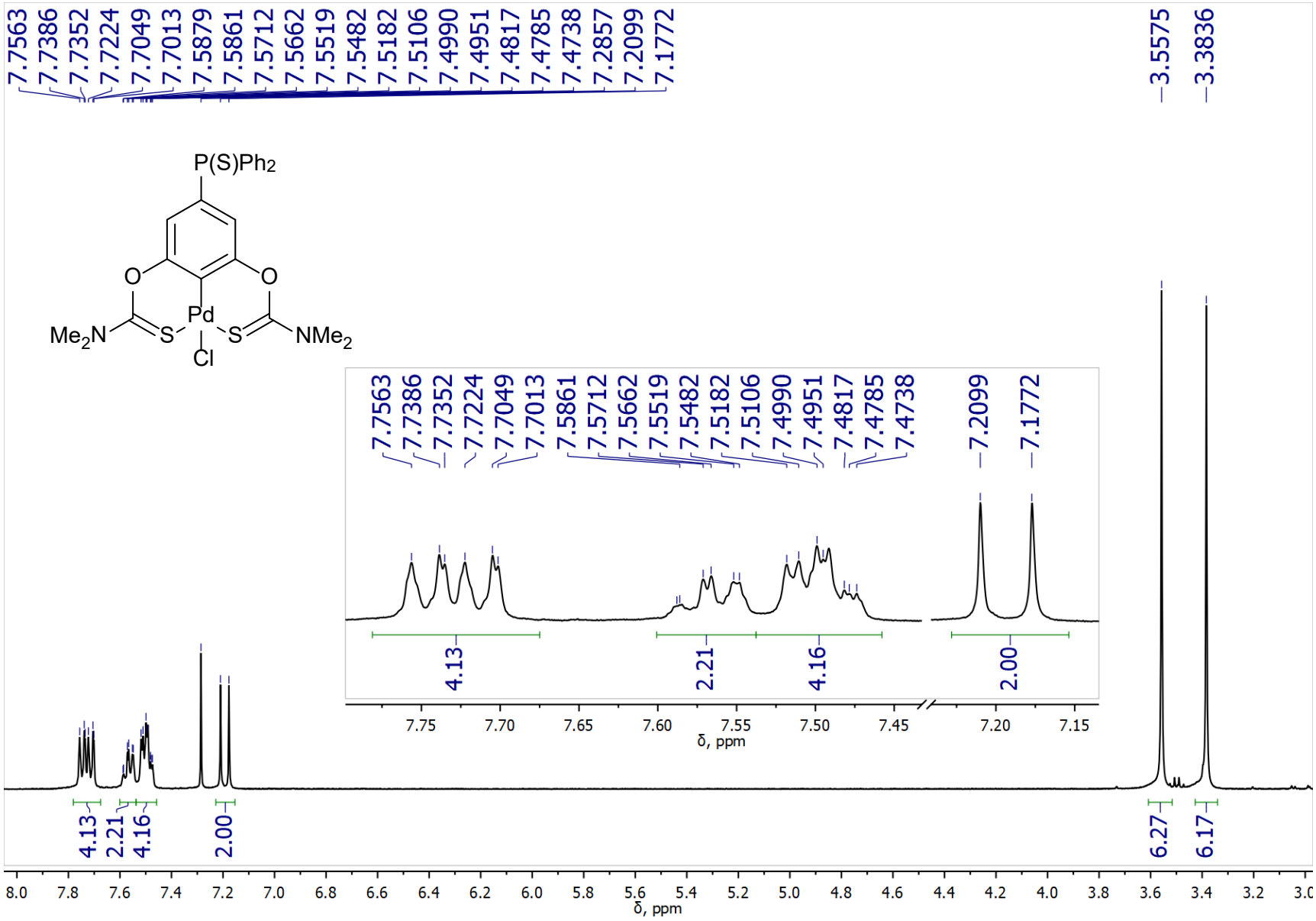


Figure S9. ^{1}H NMR spectrum of complex **3** (400.13 MHz, $CDCl_3$)

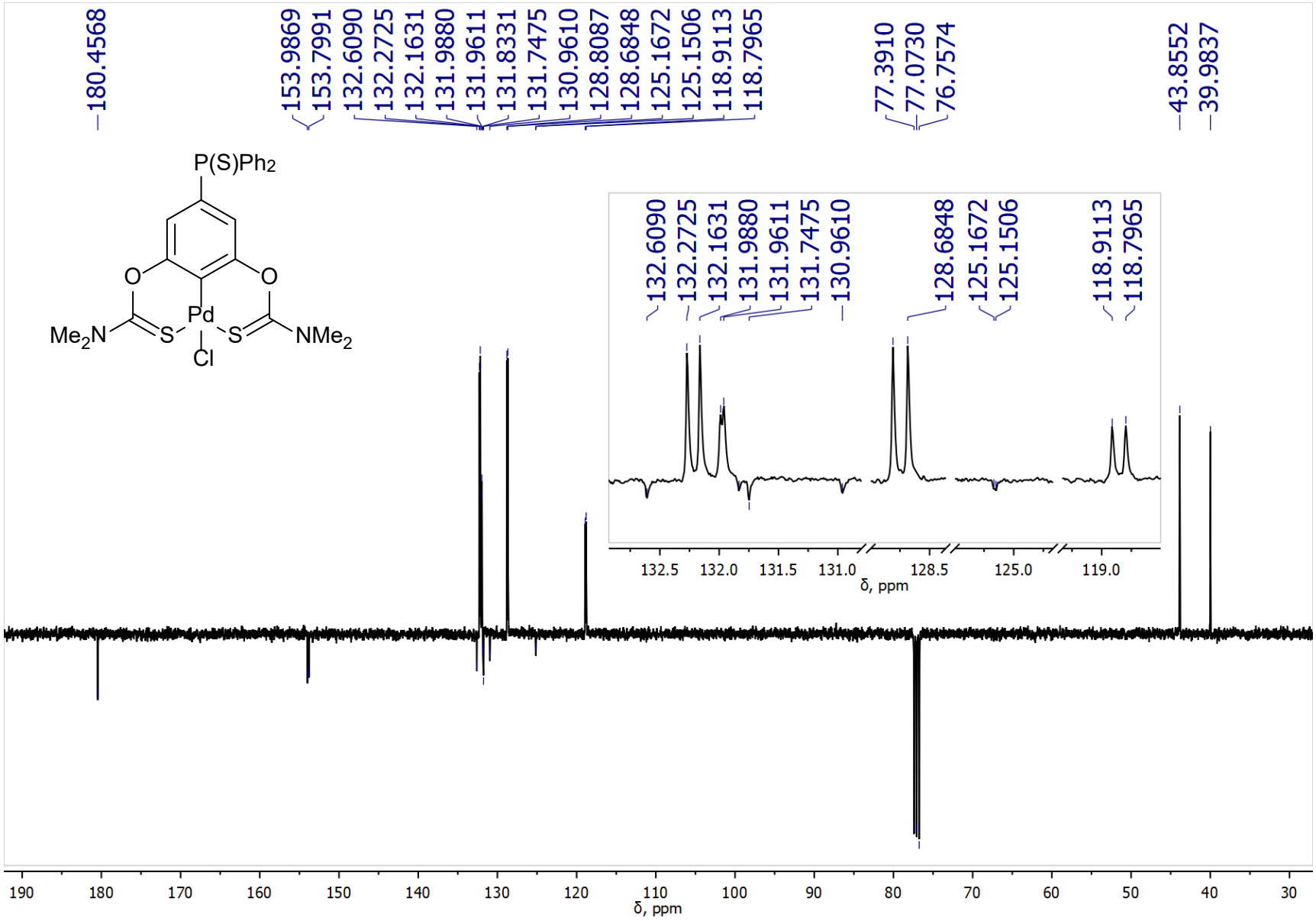


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of complex **3** (100.61 MHz, $CDCl_3$)

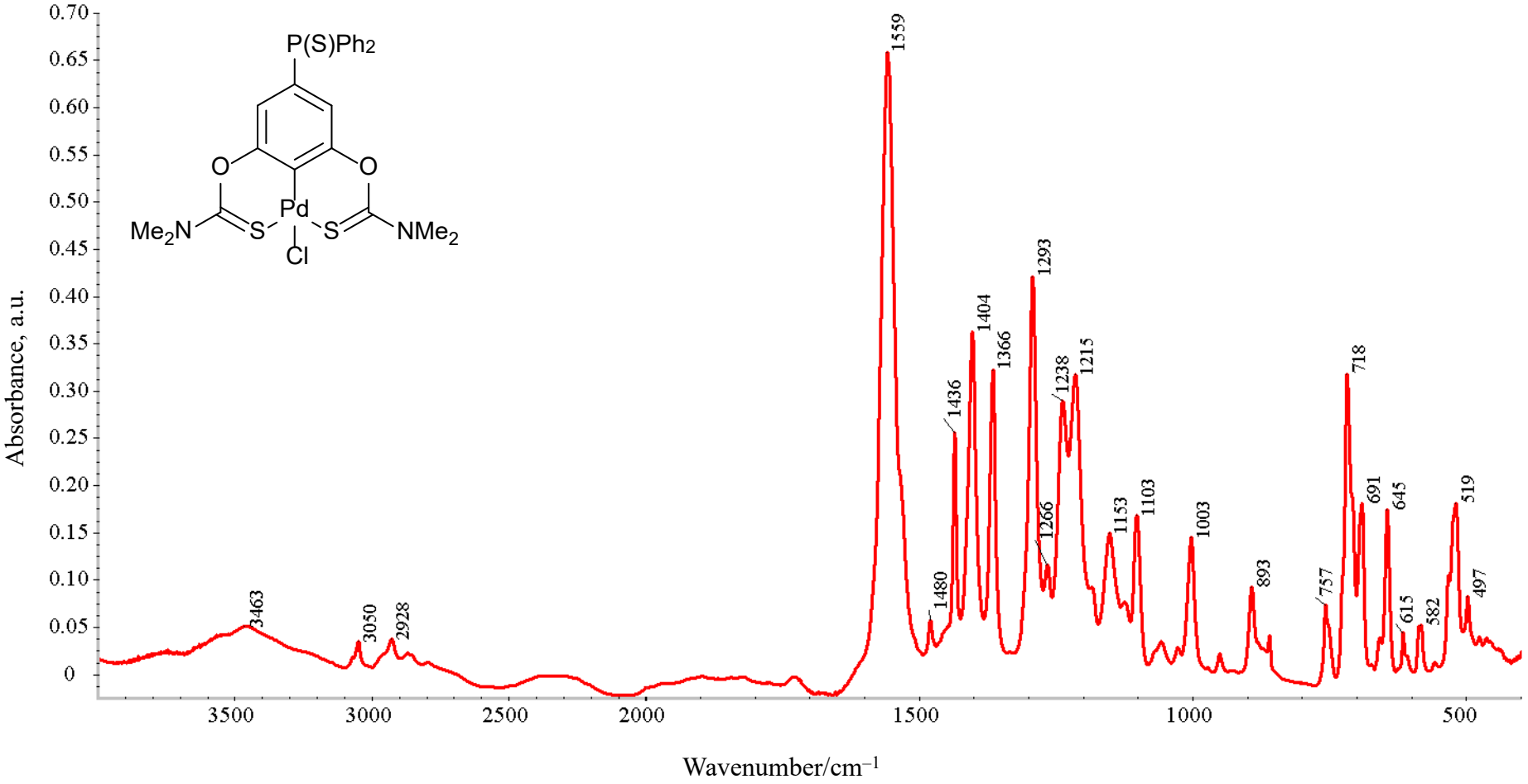


Figure S11. IR spectrum of complex **3**

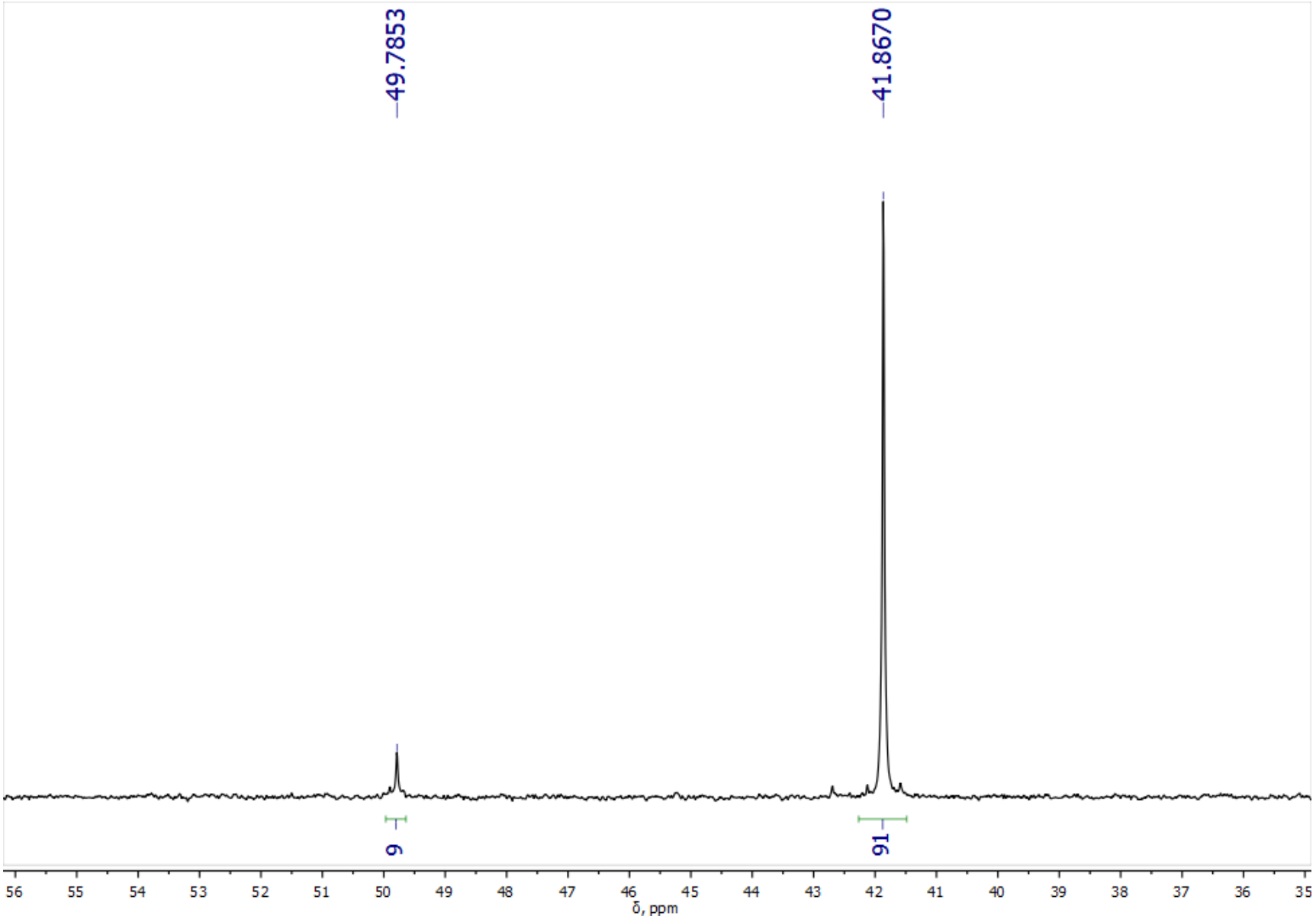


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of the crude product of the reaction between ligand **2** and $PdCl_2(NCPh)_2$ in CH_2Cl_2 (161.98 MHz, D_2O)

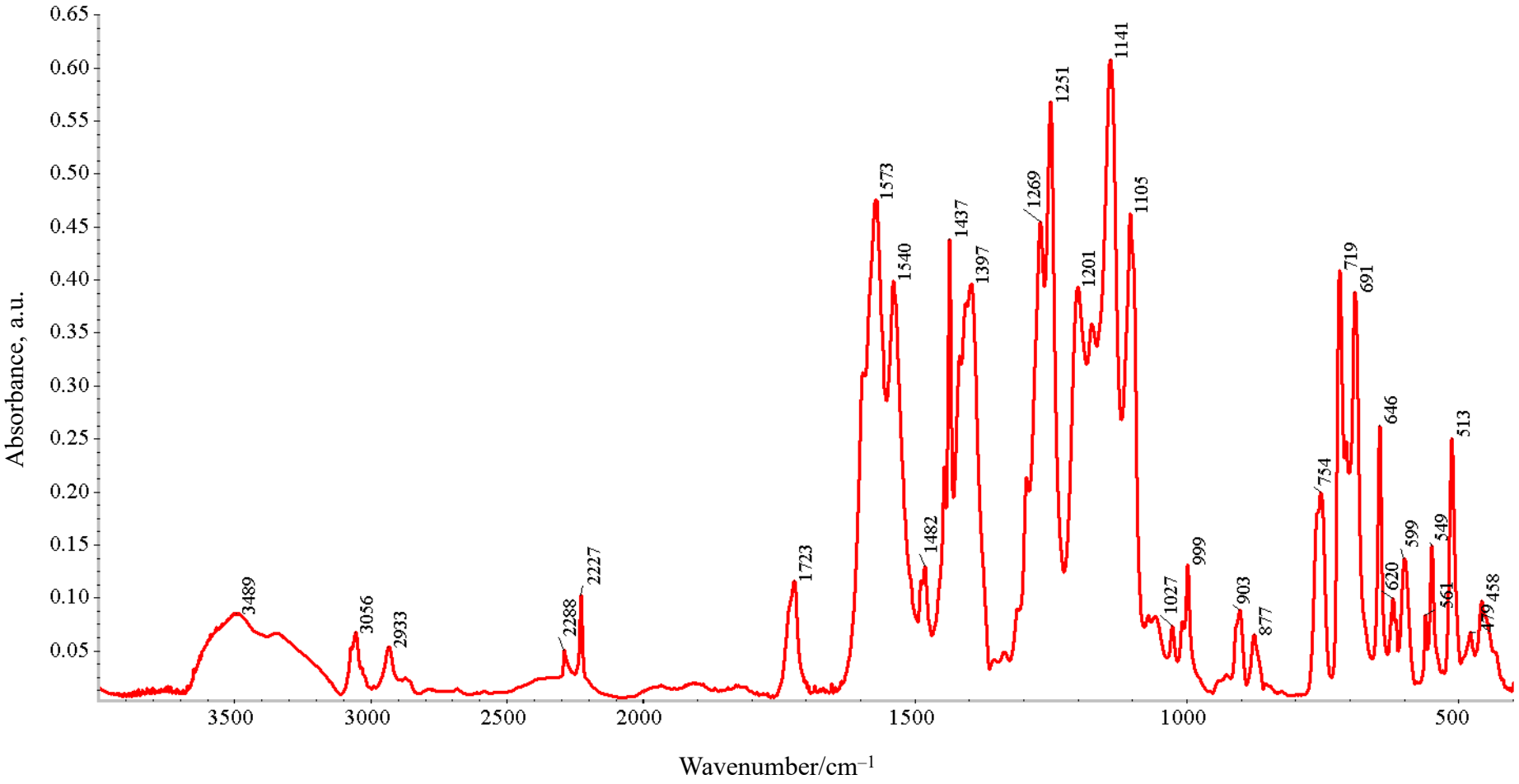


Figure S13. IR spectrum of a solid residue obtained by grinding ligand **2** with $PdCl_2(NCPh)_2$ in a mortar

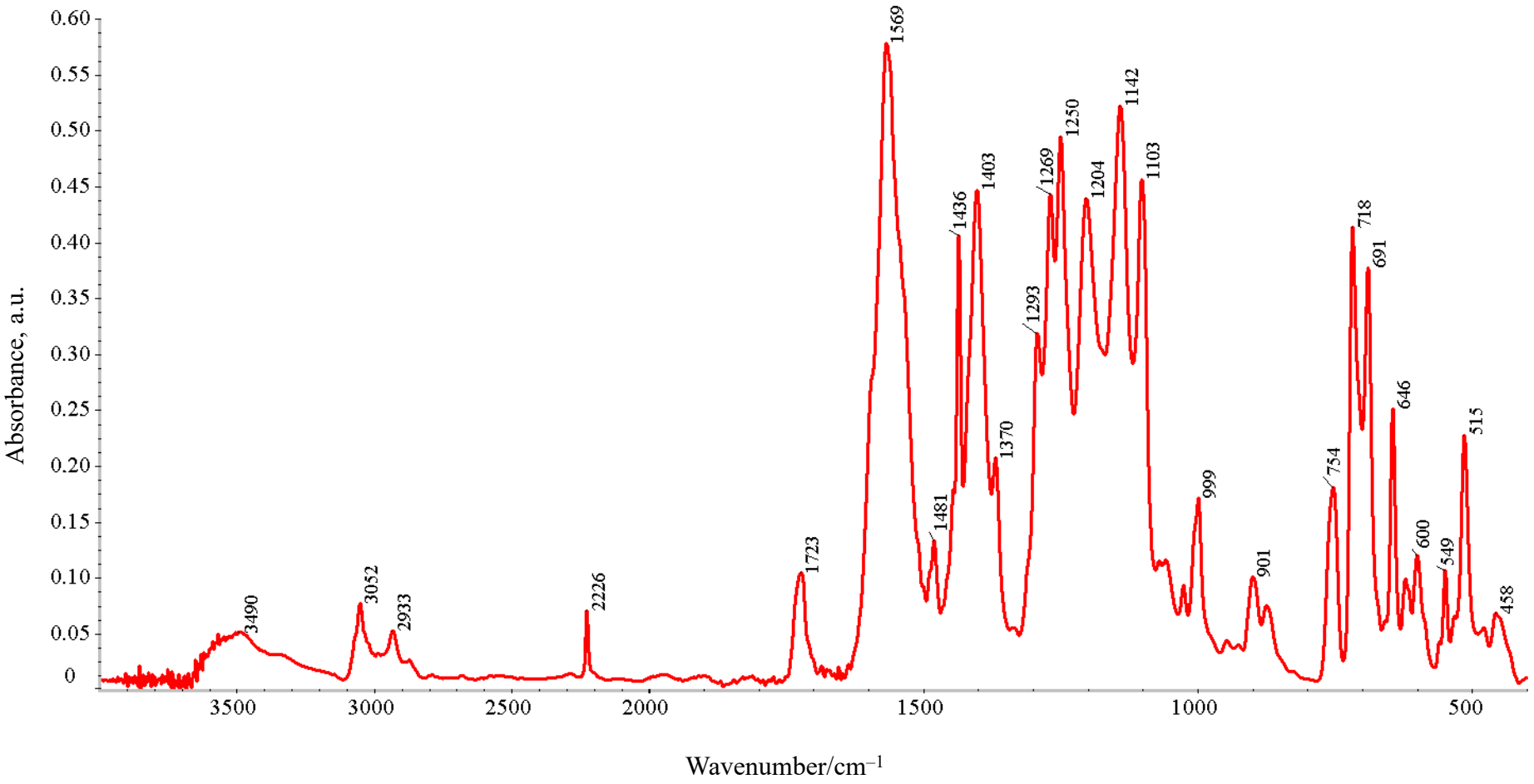


Figure S14. IR spectrum of a solid residue obtained by grinding ligand **2** with $PdCl_2(NCPh)_2$ in a Narva DDR GM 9458 vibration ball mill for 30 min

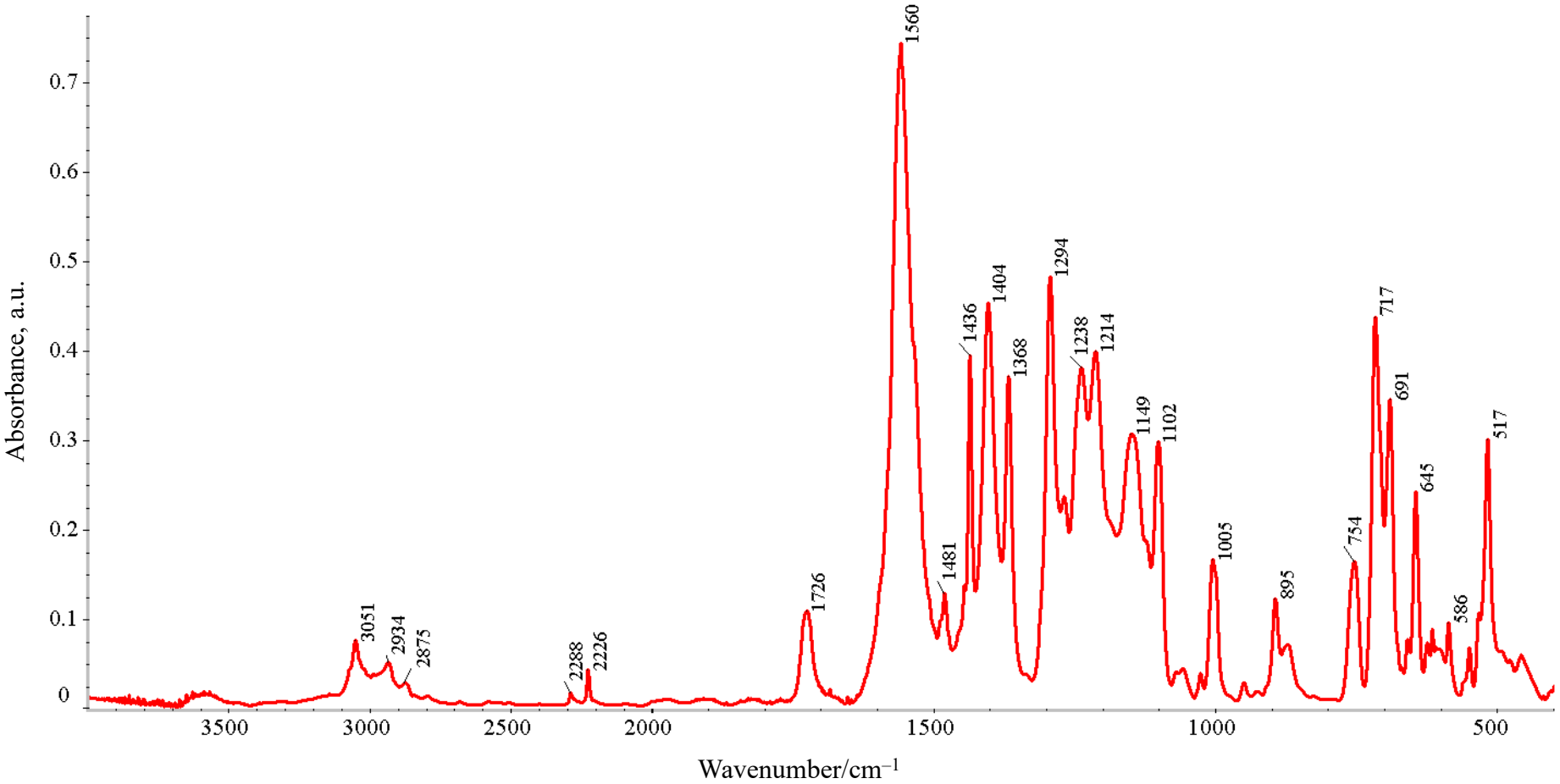


Figure S15. IR spectrum of a solid residue obtained after heating the ground mixture of ligand **2** with $PdCl_2(NCPh)_2$ at 65–70 °C for 15 min

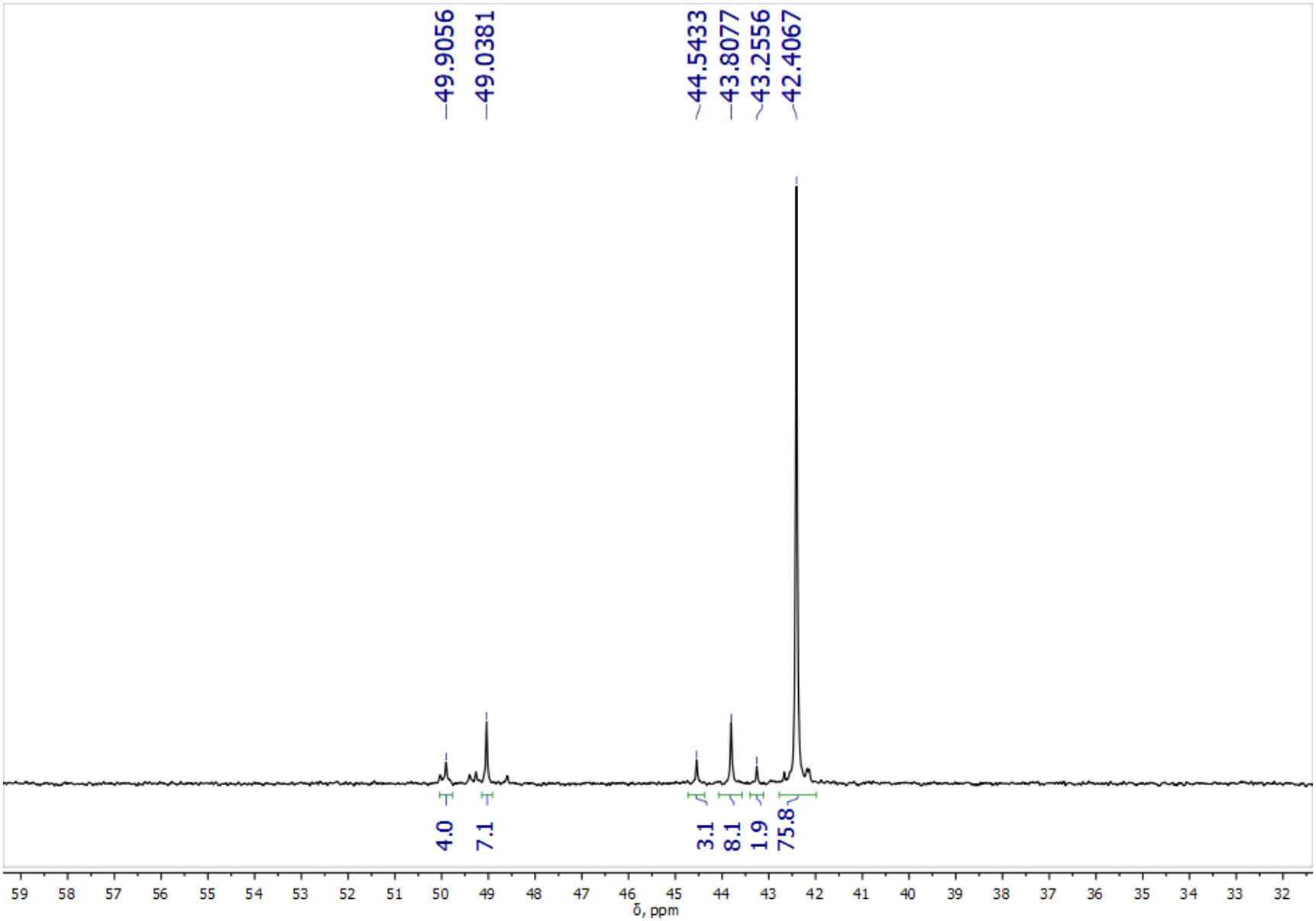


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of a solid residue obtained after heating the ground mixture of ligand **2** with $PdCl_2(NCPh)_2$ at 65–70 °C for 15 min (161.98 MHz, $CDCl_3$)

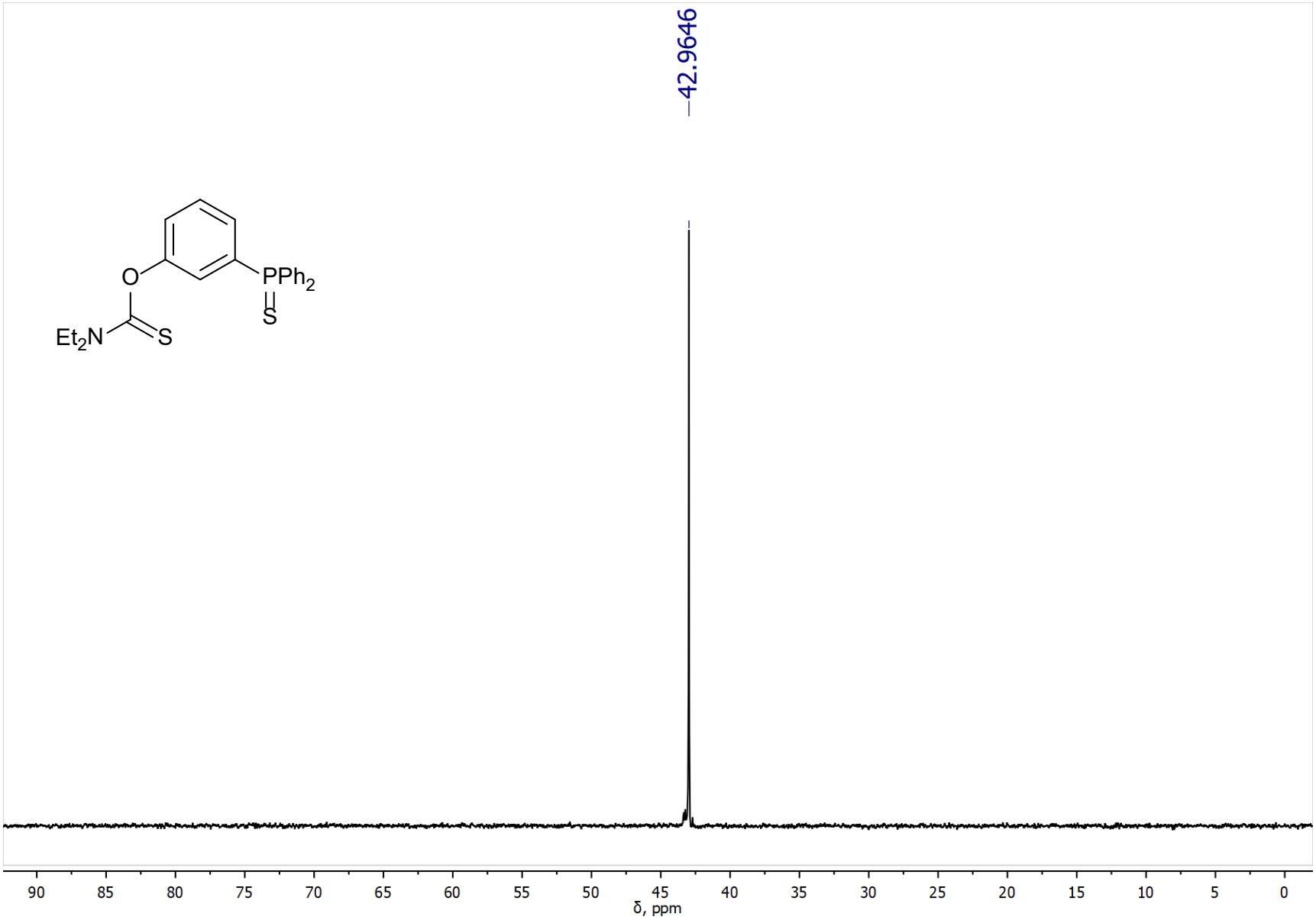


Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of ligand **4b** (161.98 MHz, $CDCl_3$)

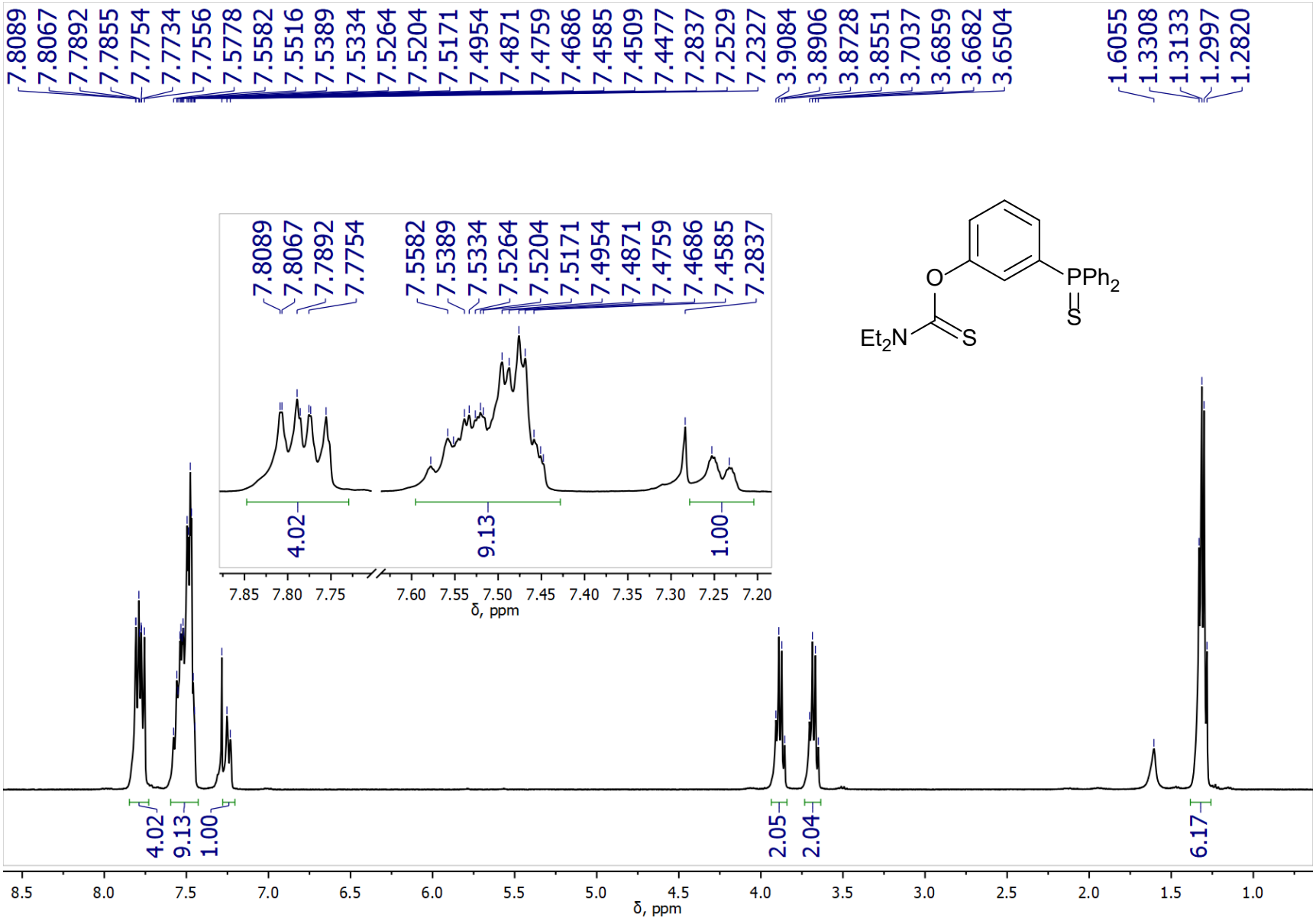


Figure S18. ^{1}H NMR spectrum of ligand **4b** (400.13 MHz, $CDCl_3$)

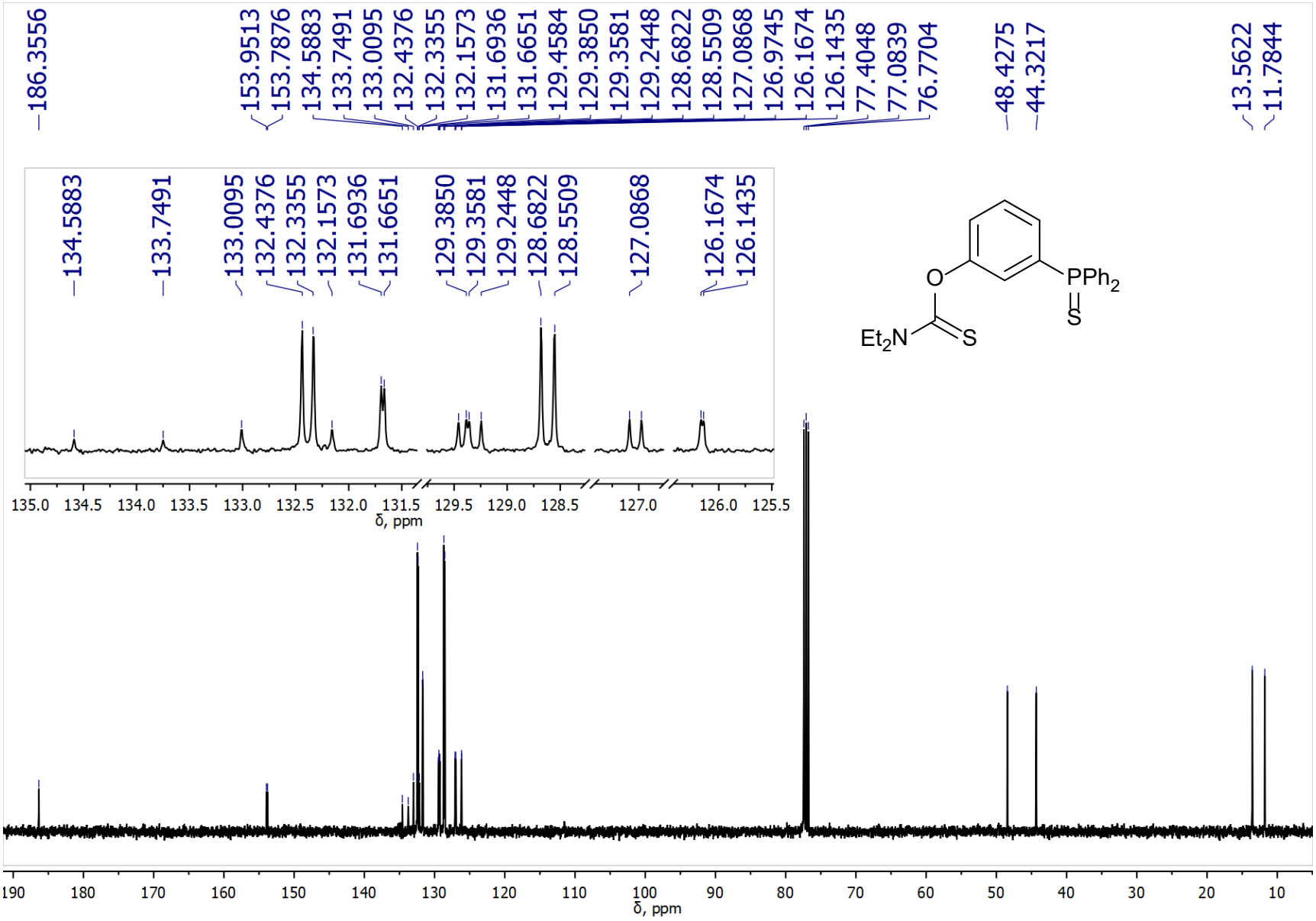


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of ligand **4b** (100.61 MHz, $CDCl_3$)

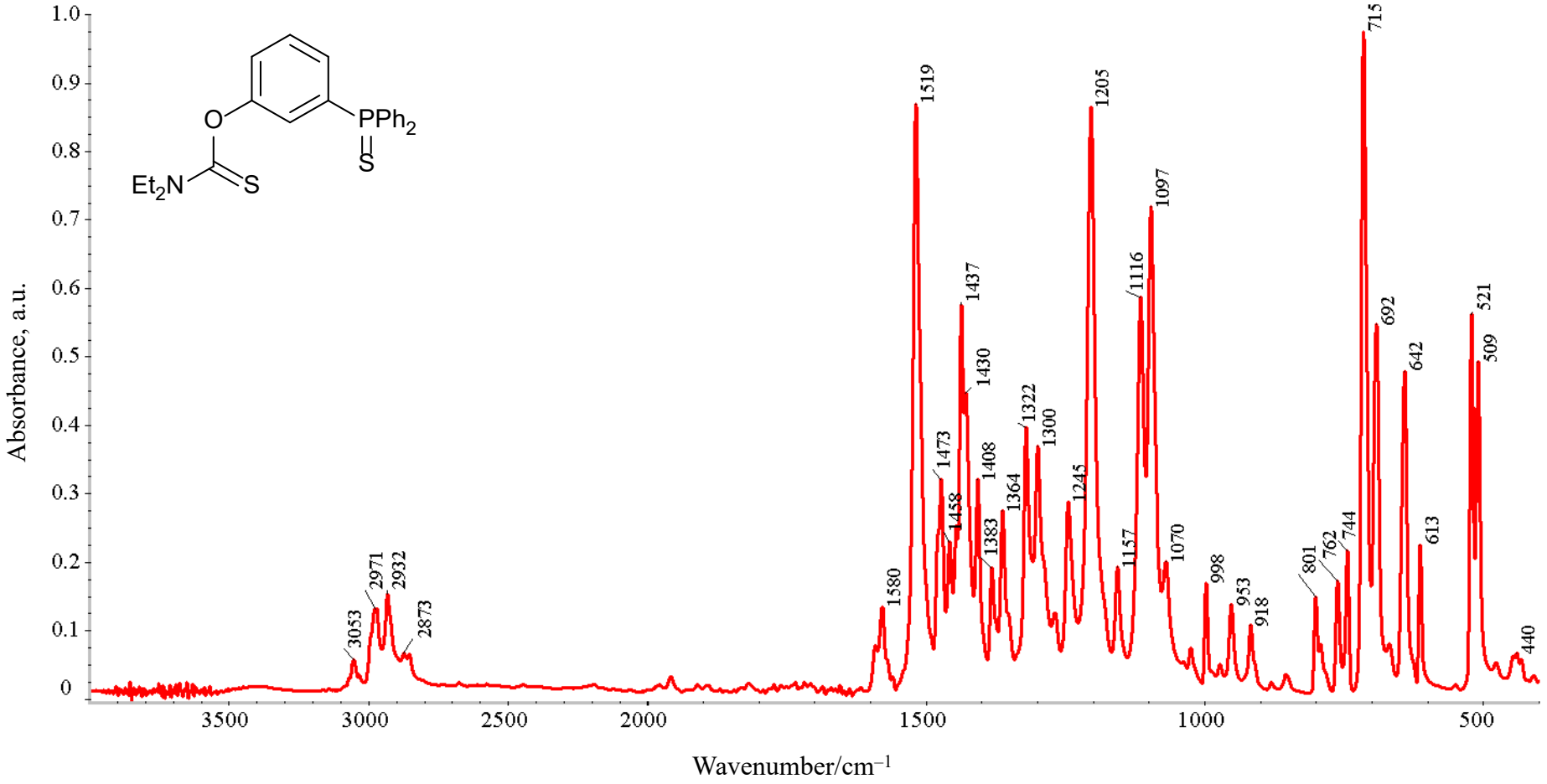


Figure S20. IR spectrum of ligand **4b**

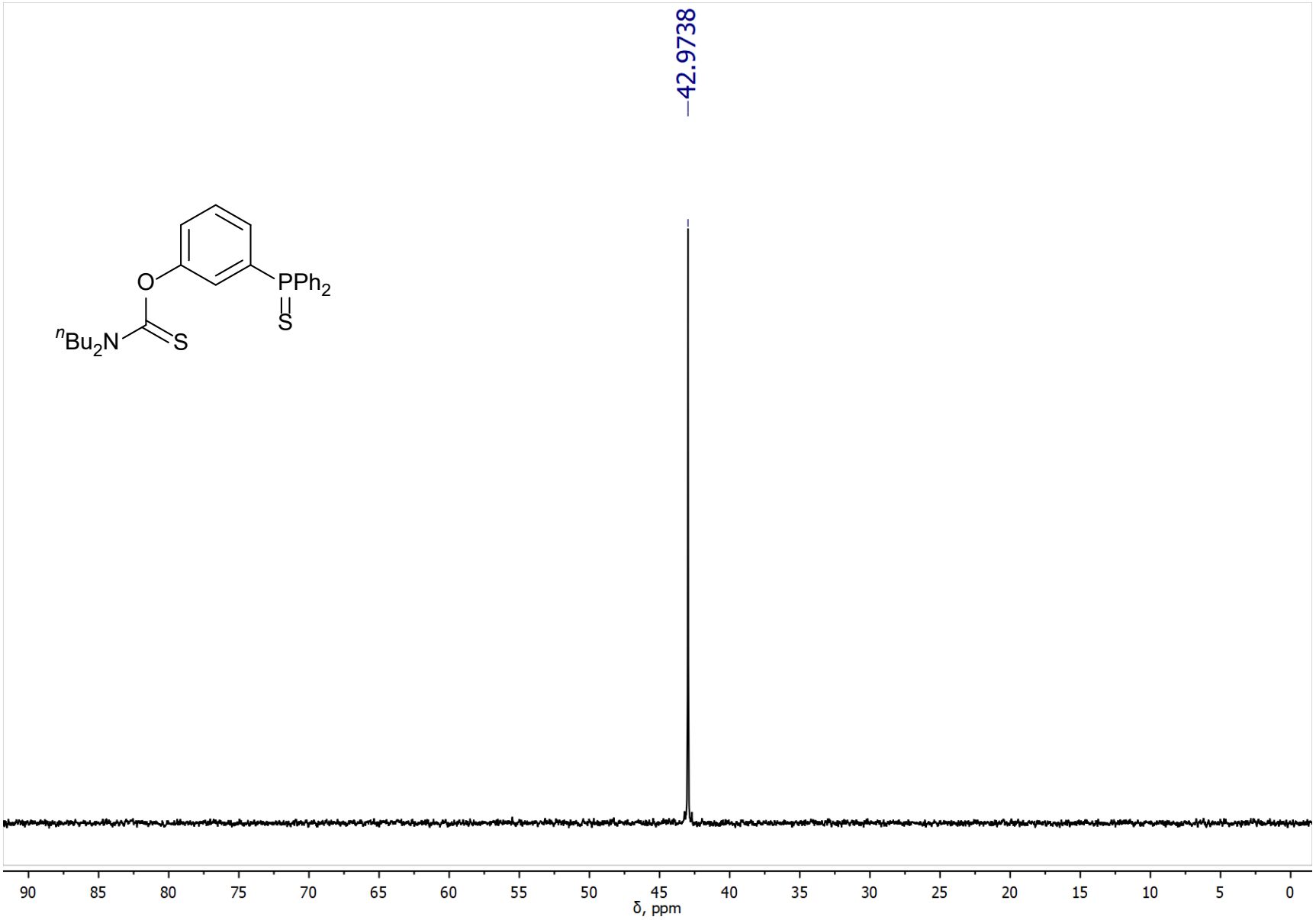


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of ligand **4c** (161.98 MHz, $CDCl_3$)

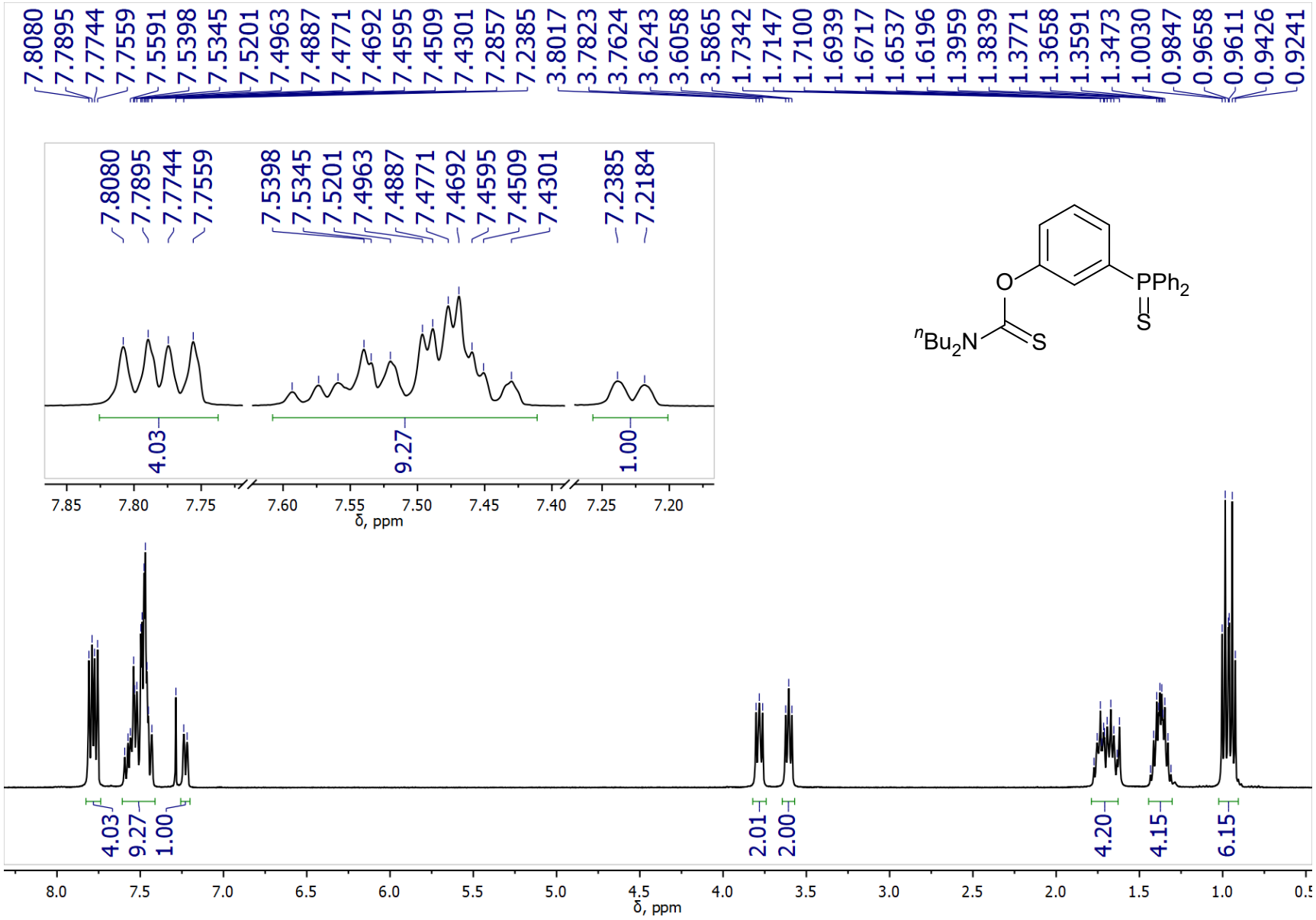


Figure S22. ^{1}H NMR spectrum of ligand **4c** (400.13 MHz, $CDCl_3$)

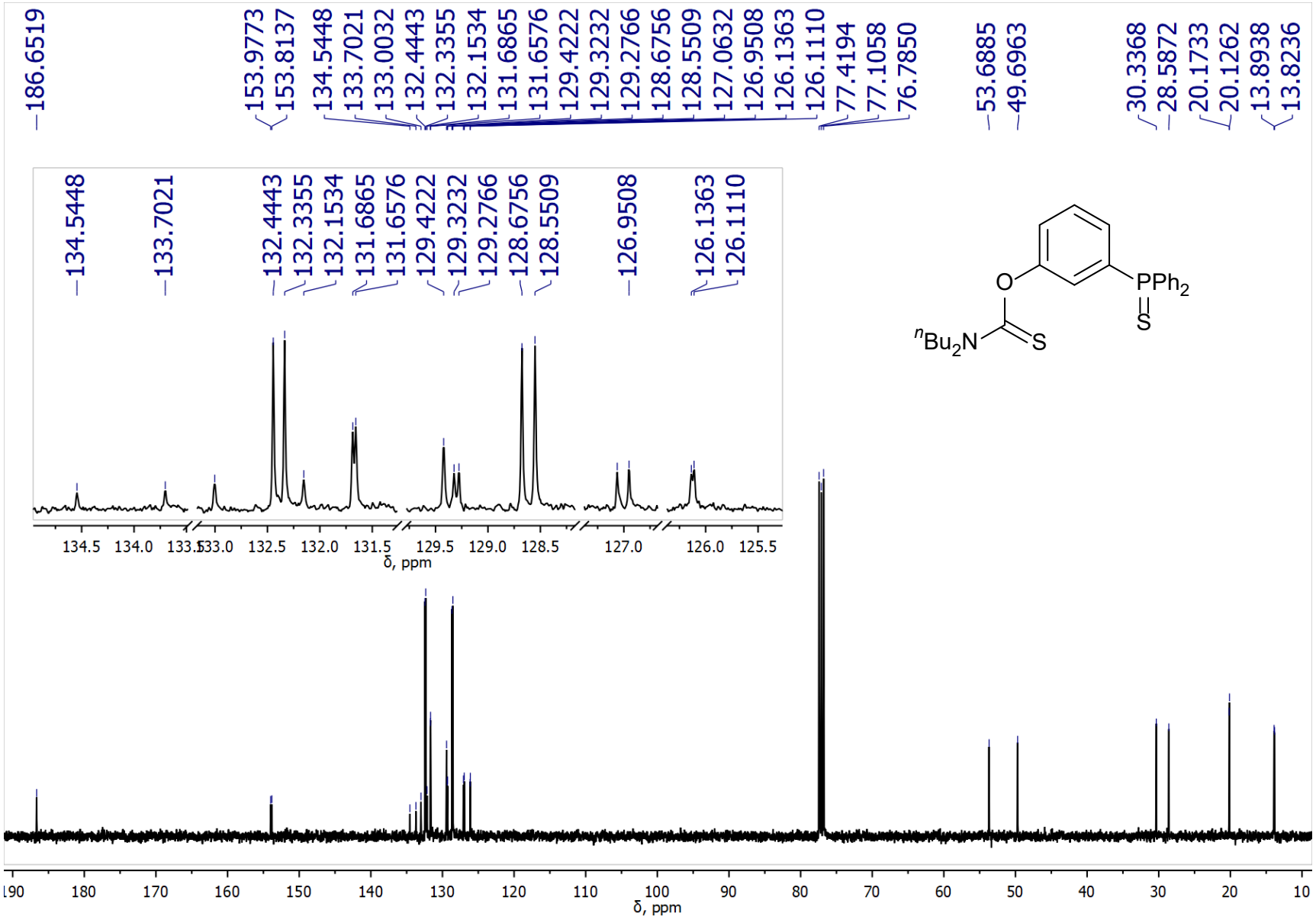


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of ligand **4c** (100.61 MHz, $CDCl_3$)

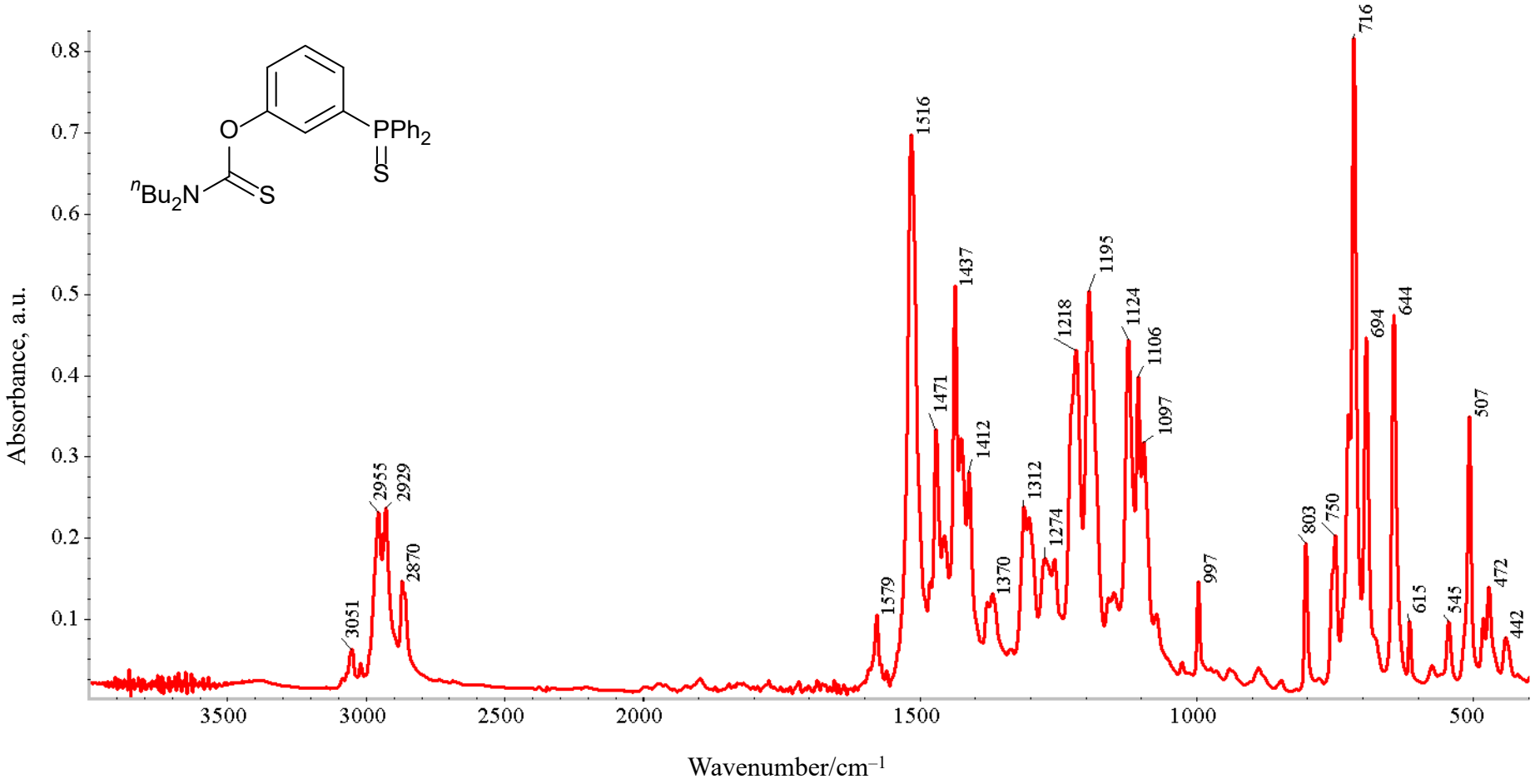


Figure S24. IR spectrum of ligand **4c**

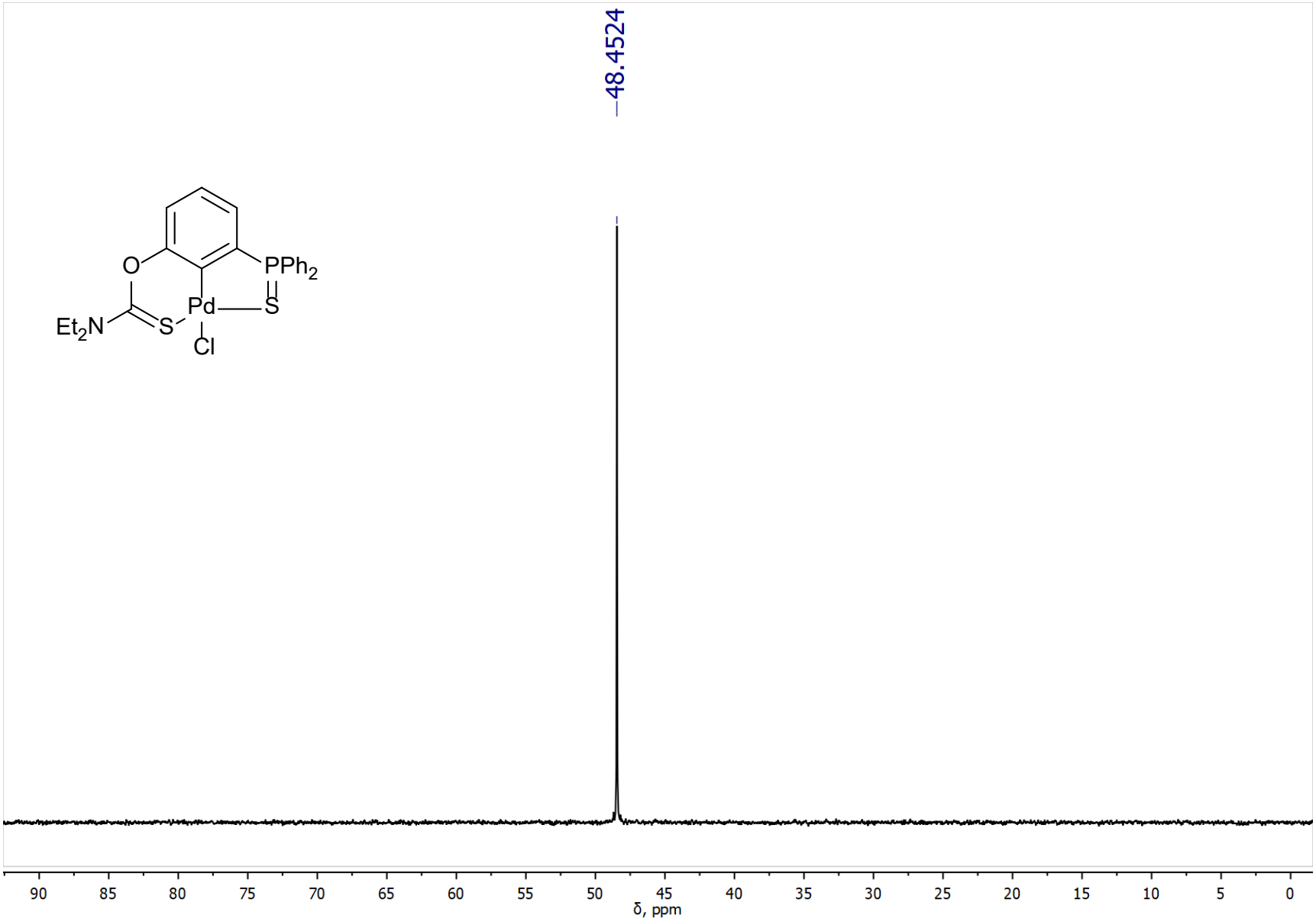


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum of complex **5b** (161.98 MHz, $CDCl_3$)

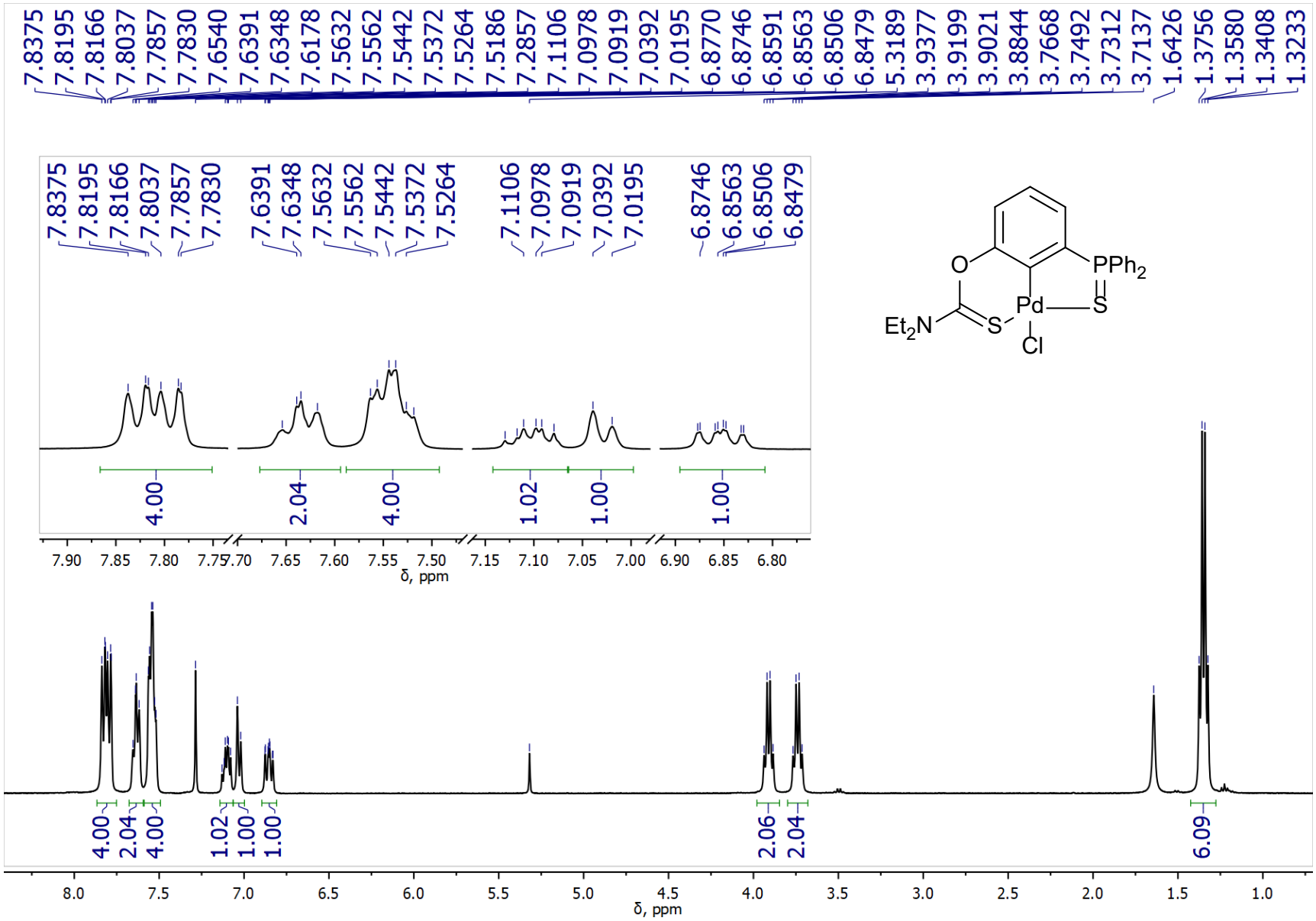


Figure S26. ^{1}H NMR spectrum of complex **5b** (400.13 MHz, $CDCl_3$)

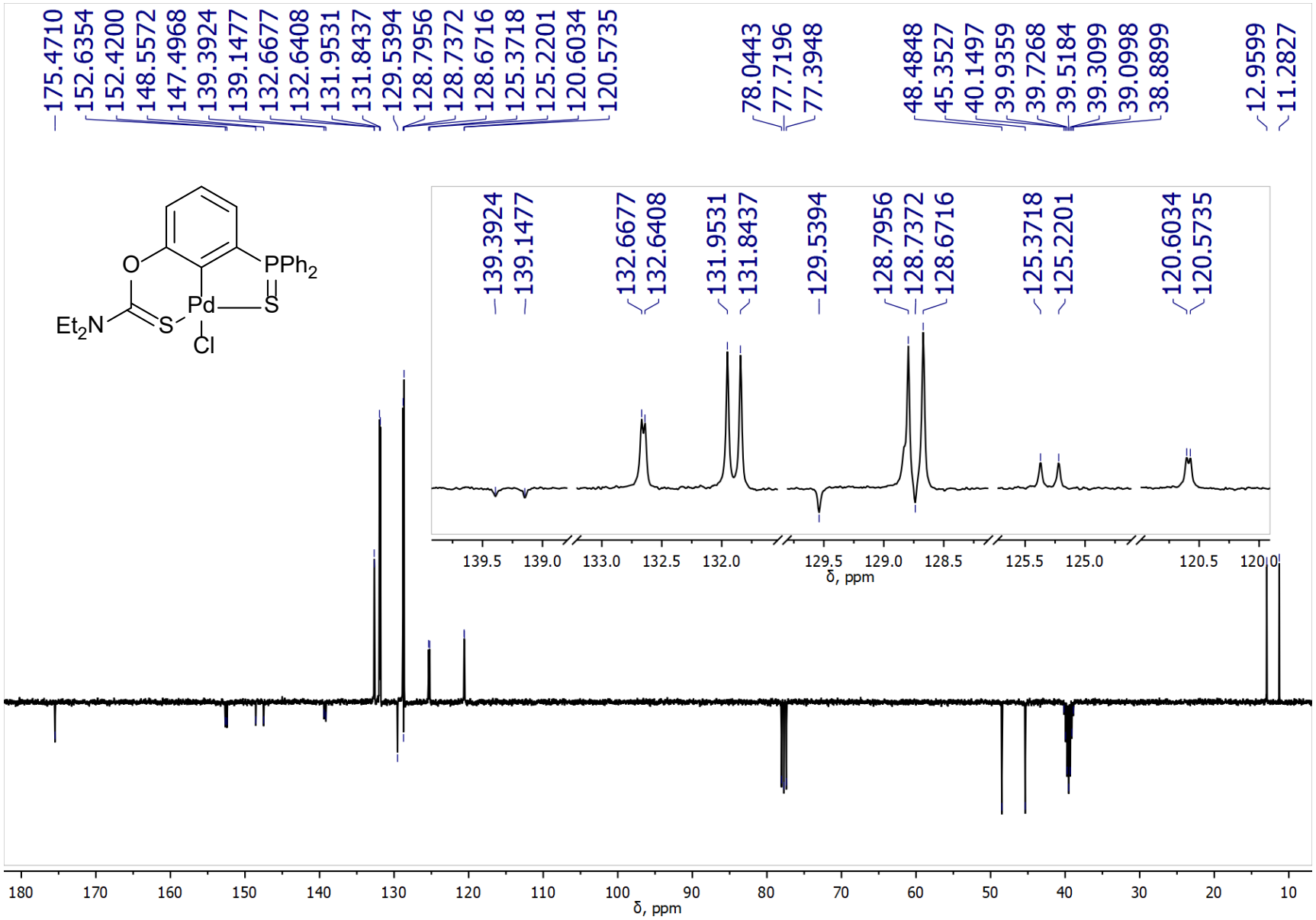


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of complex **5b** (100.61 MHz, $CDCl_3$–$(CD_3)_2SO$)

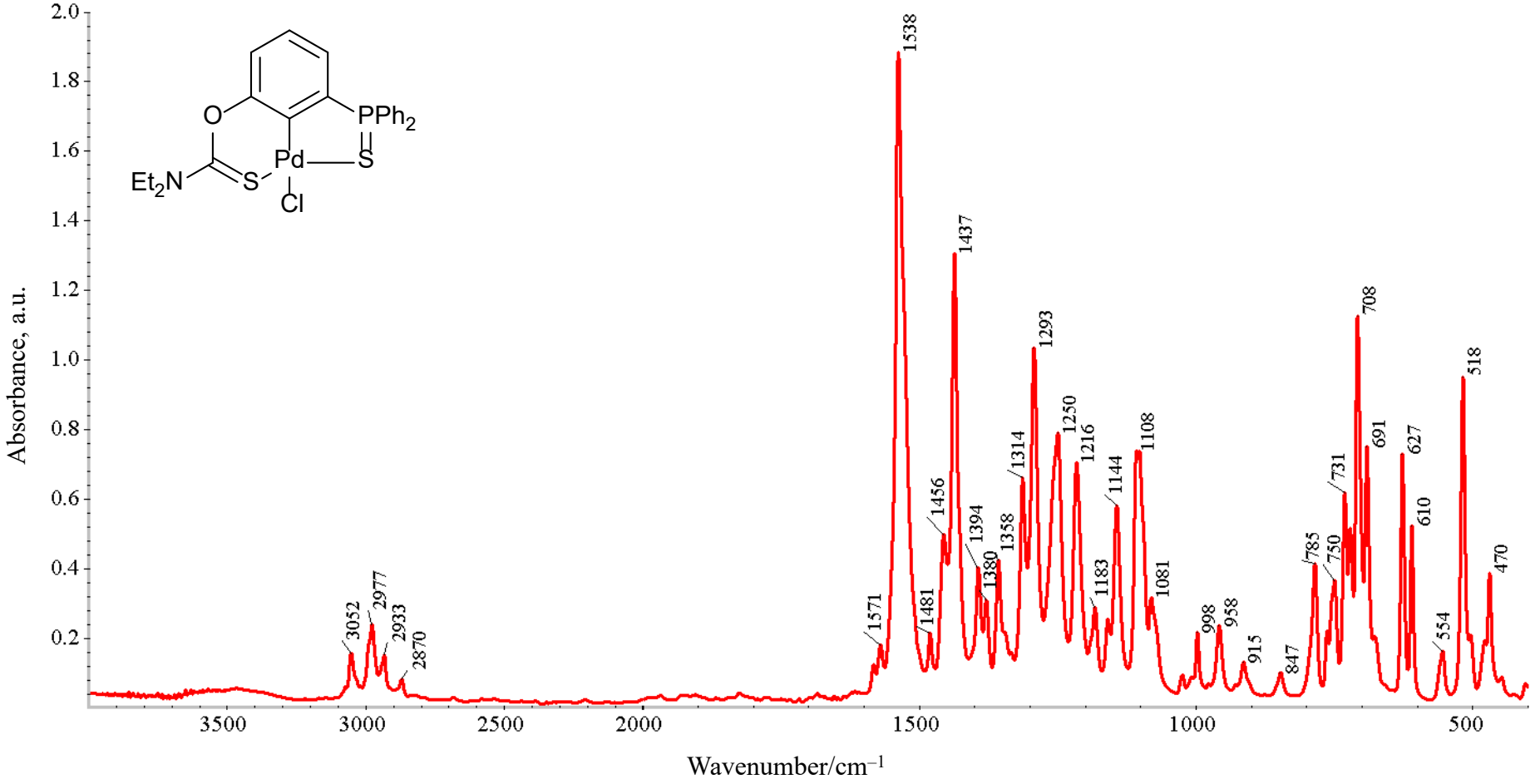


Figure S28. IR spectrum of complex **5b**

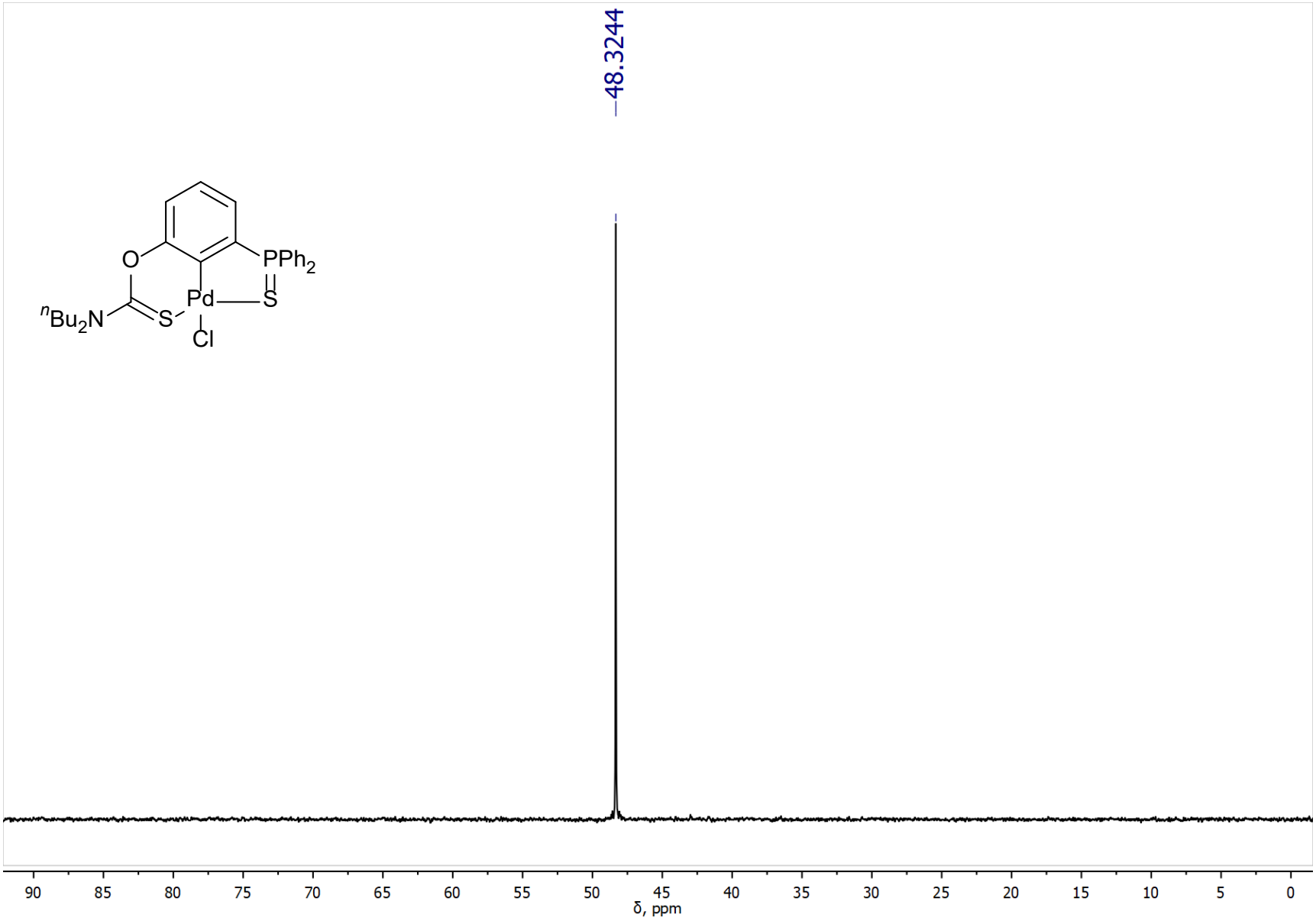


Figure S29. $^{31}P\{^{1}H\}$ NMR spectrum of complex **5c** (161.98 MHz, $CDCl_3$)

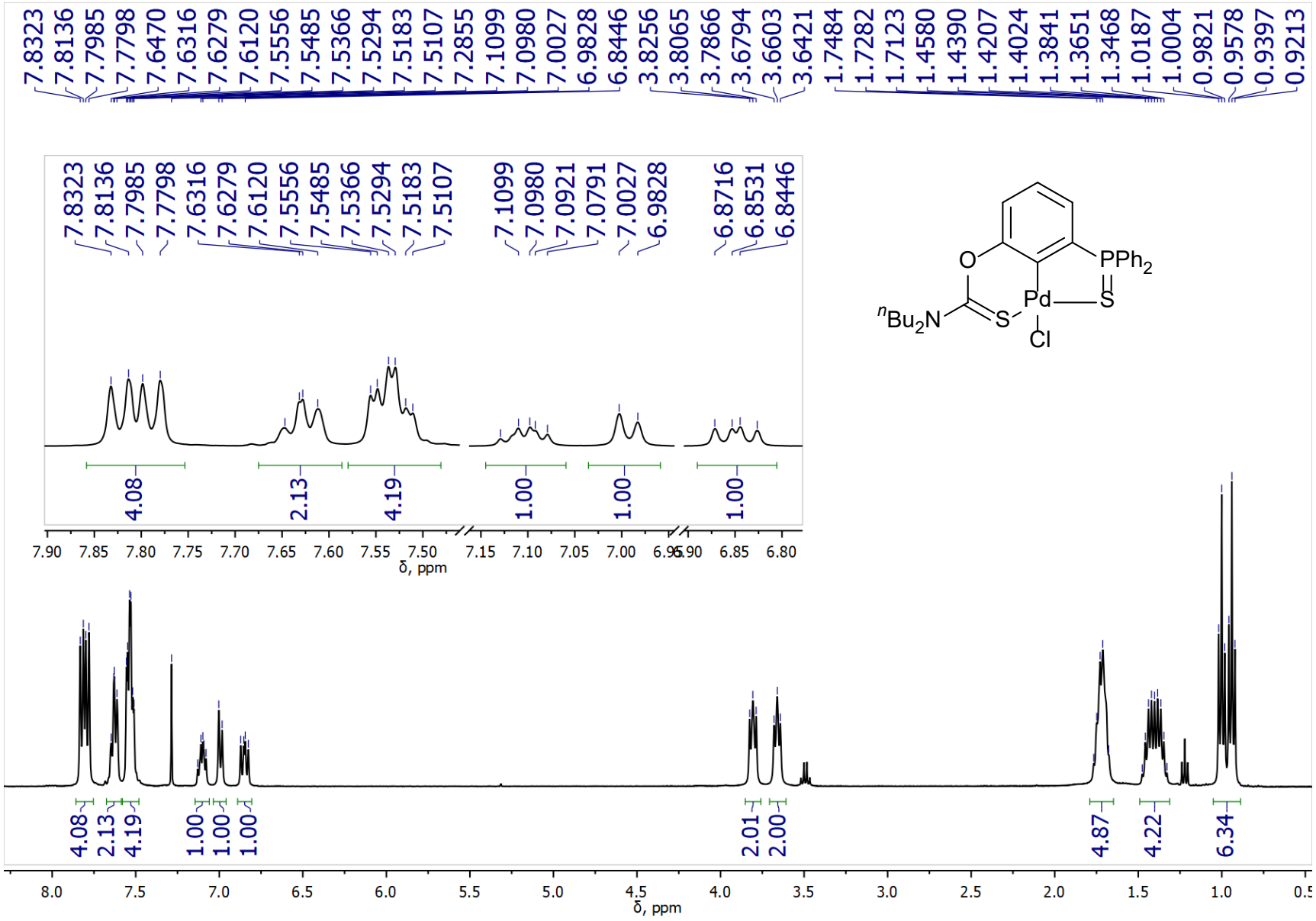


Figure S30. ^{1}H NMR spectrum of complex **5c** (400.13 MHz, $CDCl_3$)

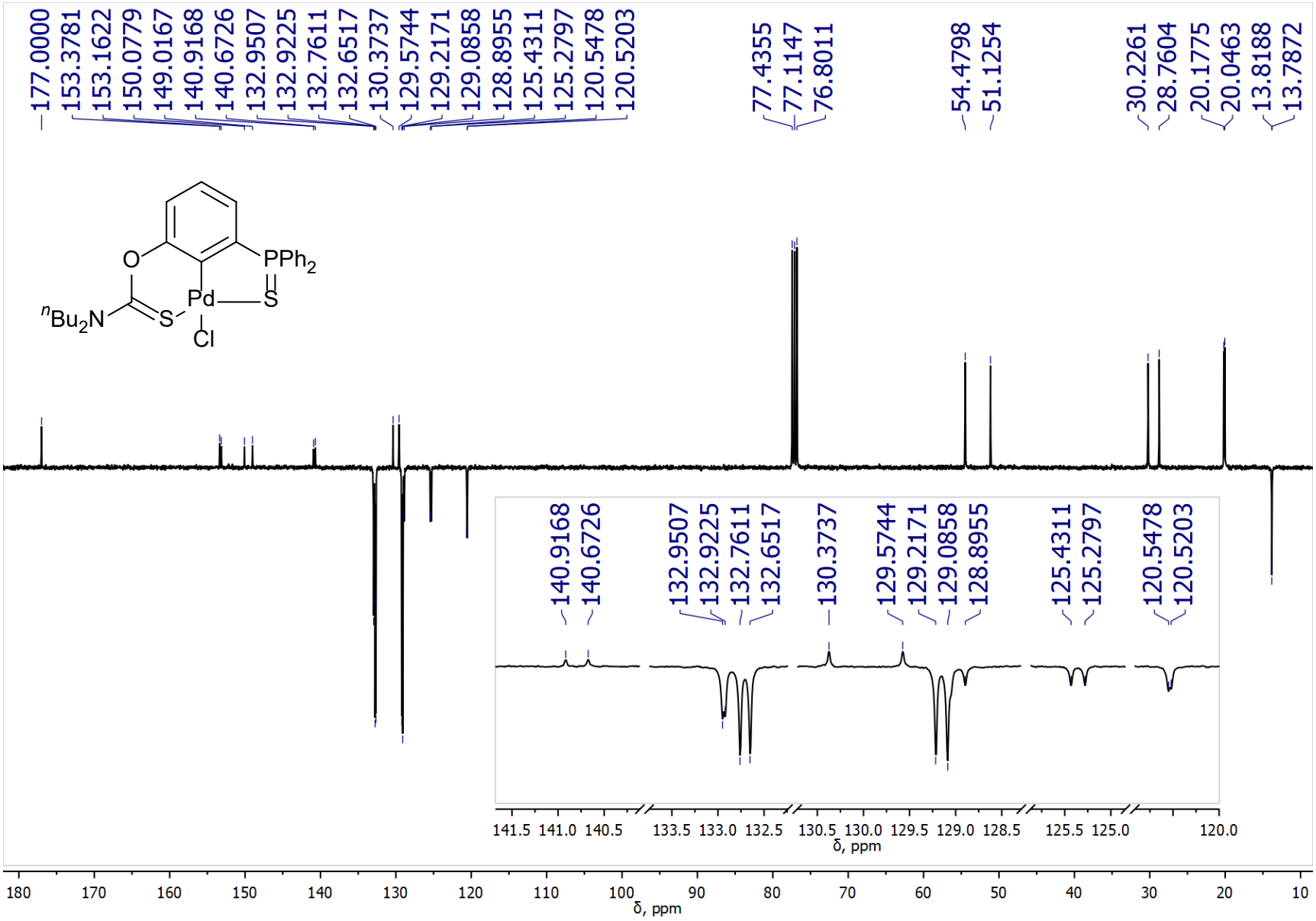


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of complex **5c** (100.61 MHz, $CDCl_3$)

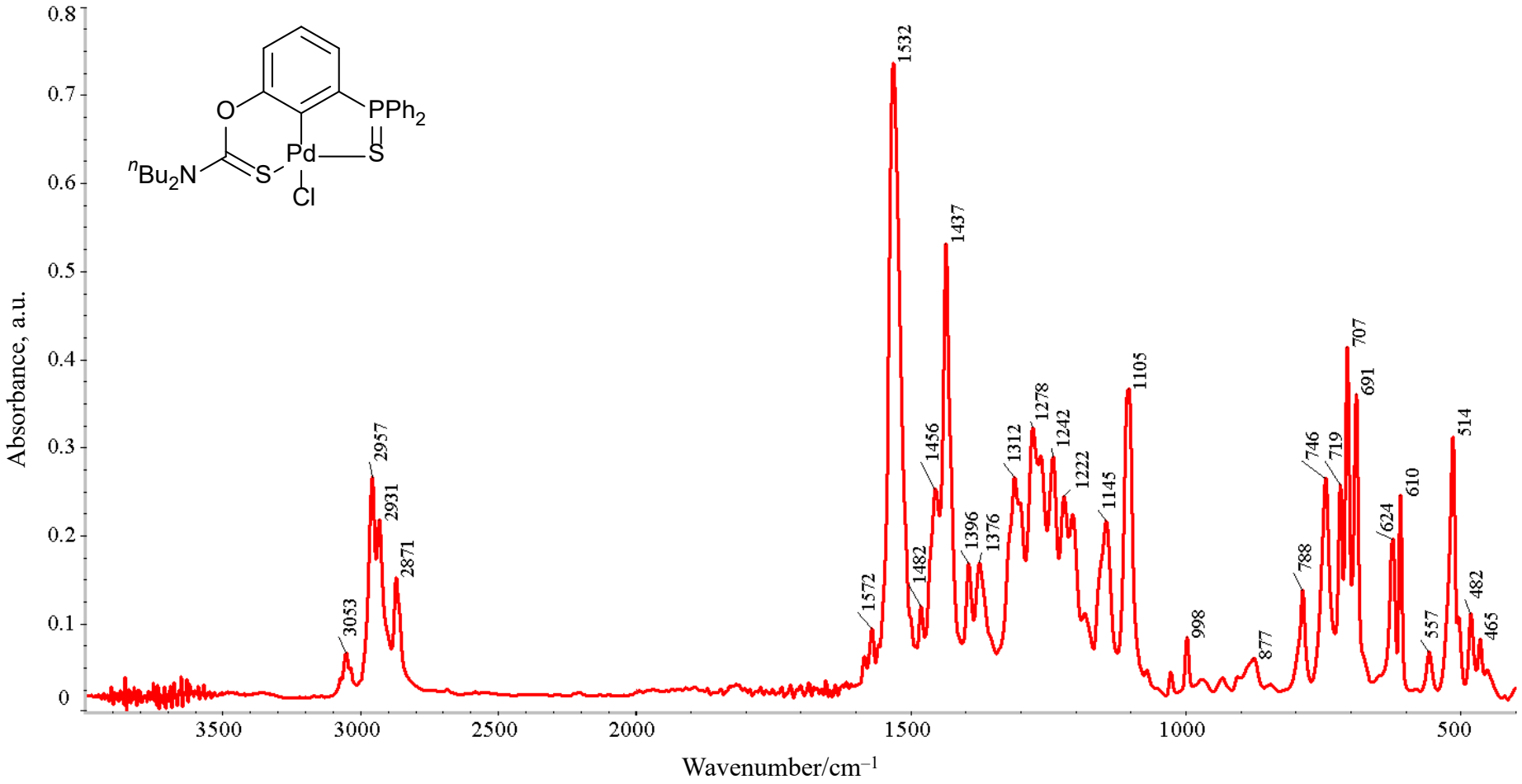


Figure S32. IR spectrum of complex **5c**

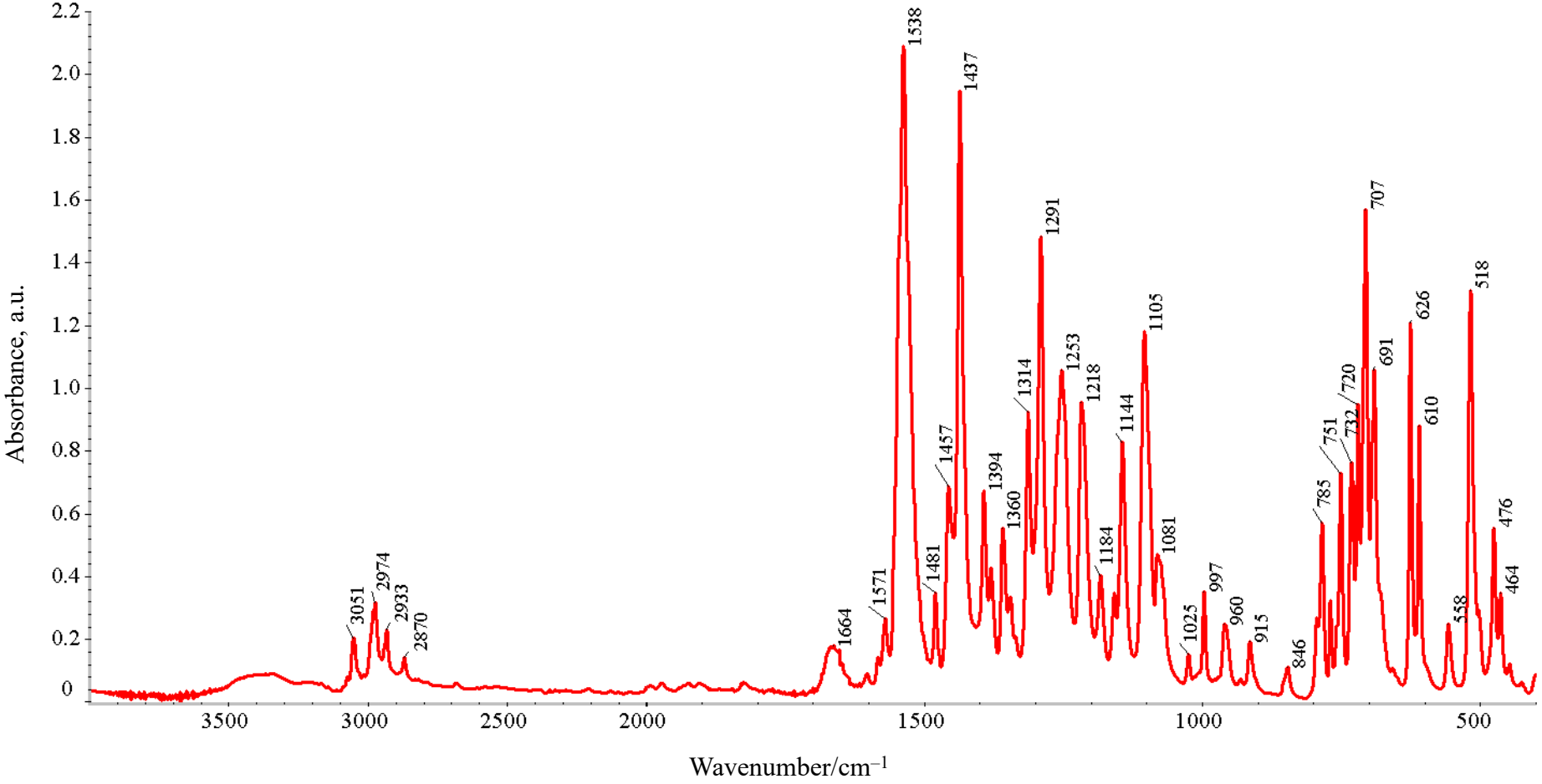


Figure S33. IR spectrum of a solid residue obtained by grinding ligand **4b** with $PdCl_2(NCPh)_2$ in a mortar

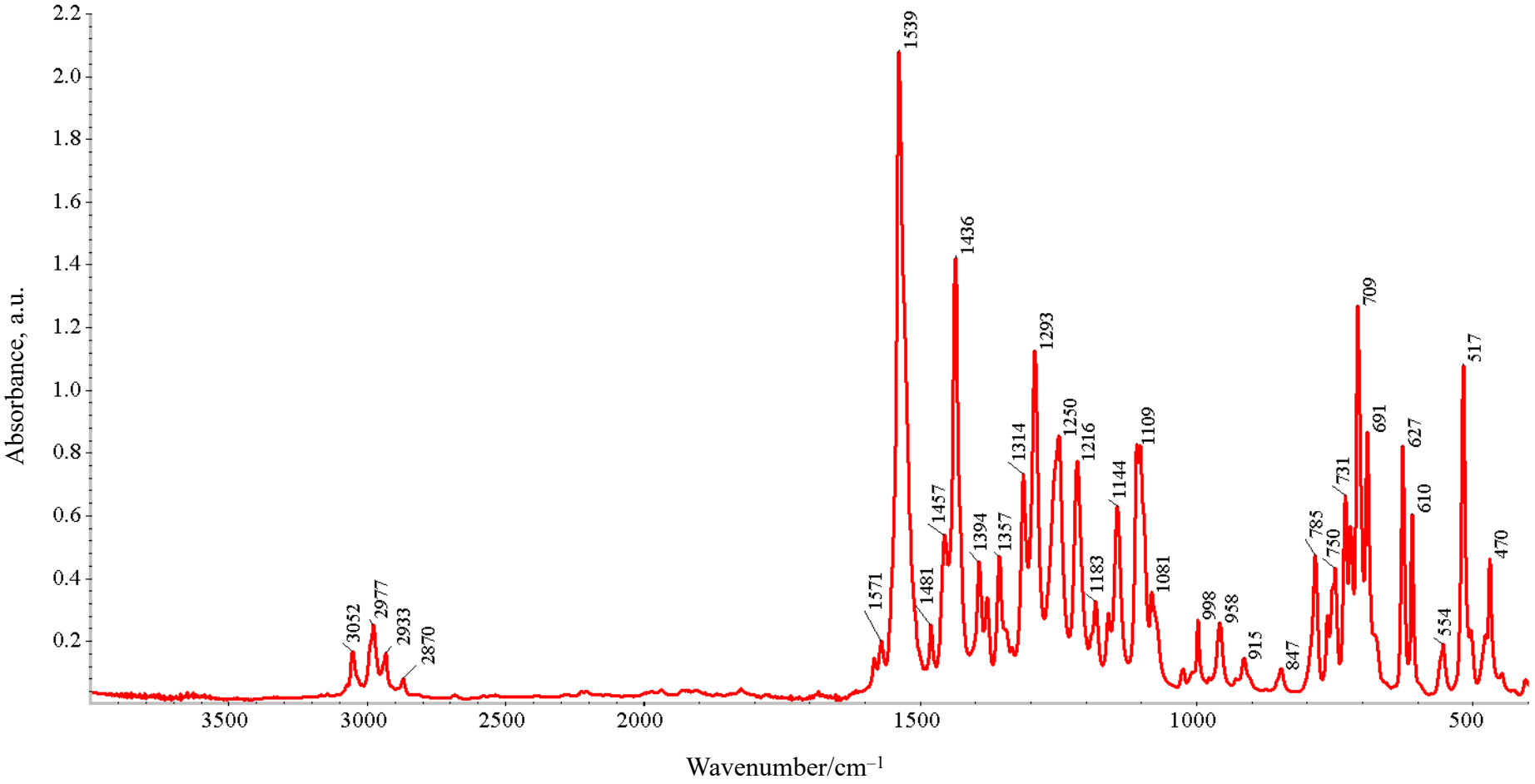


Figure S34. IR spectrum of a solid residue obtained after heating the ground mixture of ligand **4b** with $PdCl_2(NCPh)_2$ at 65–70 °C for 5 min

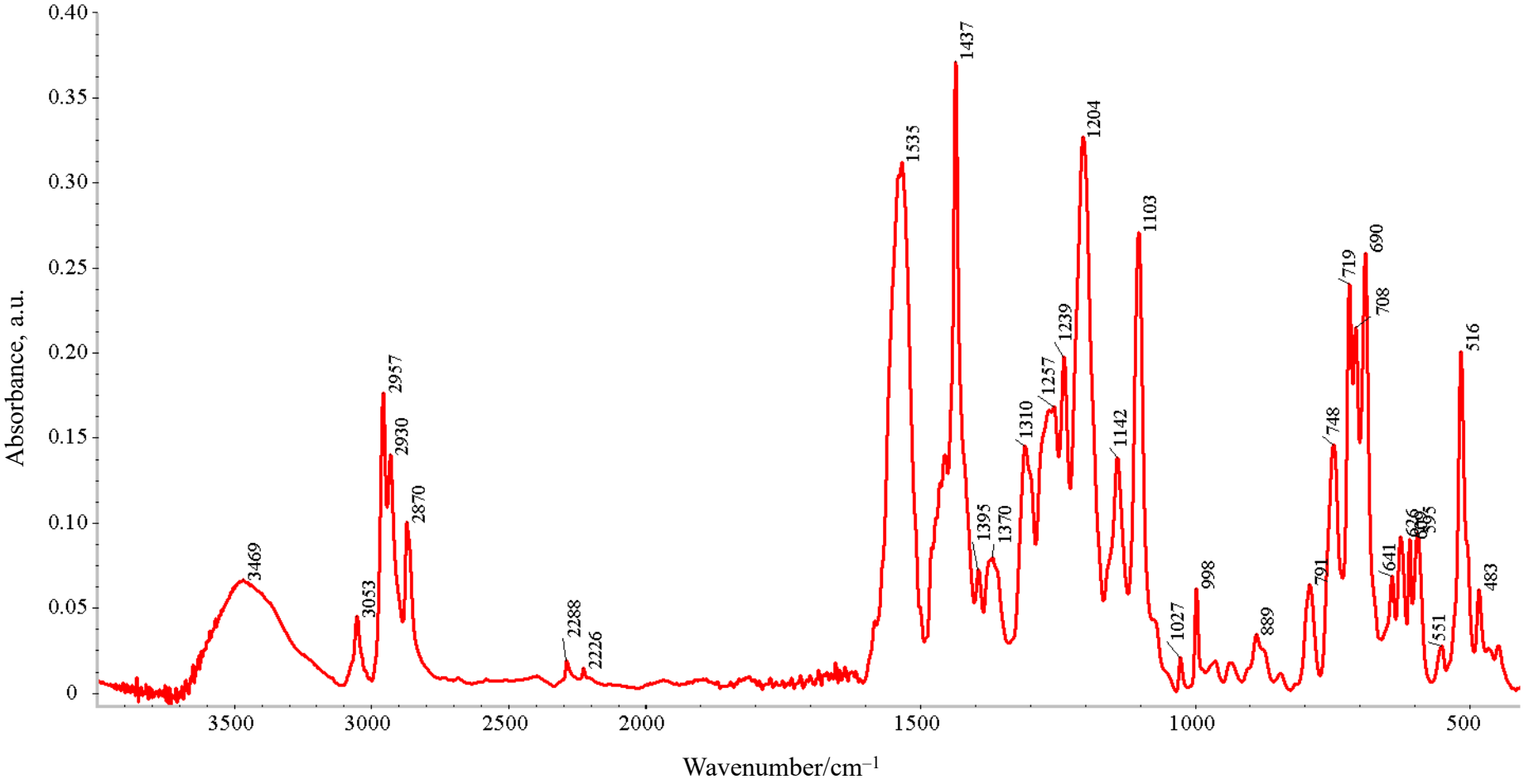


Figure S35. IR spectrum of a solid residue obtained by grinding ligand **4c** with $PdCl_2(NCPh)_2$ in a mortar

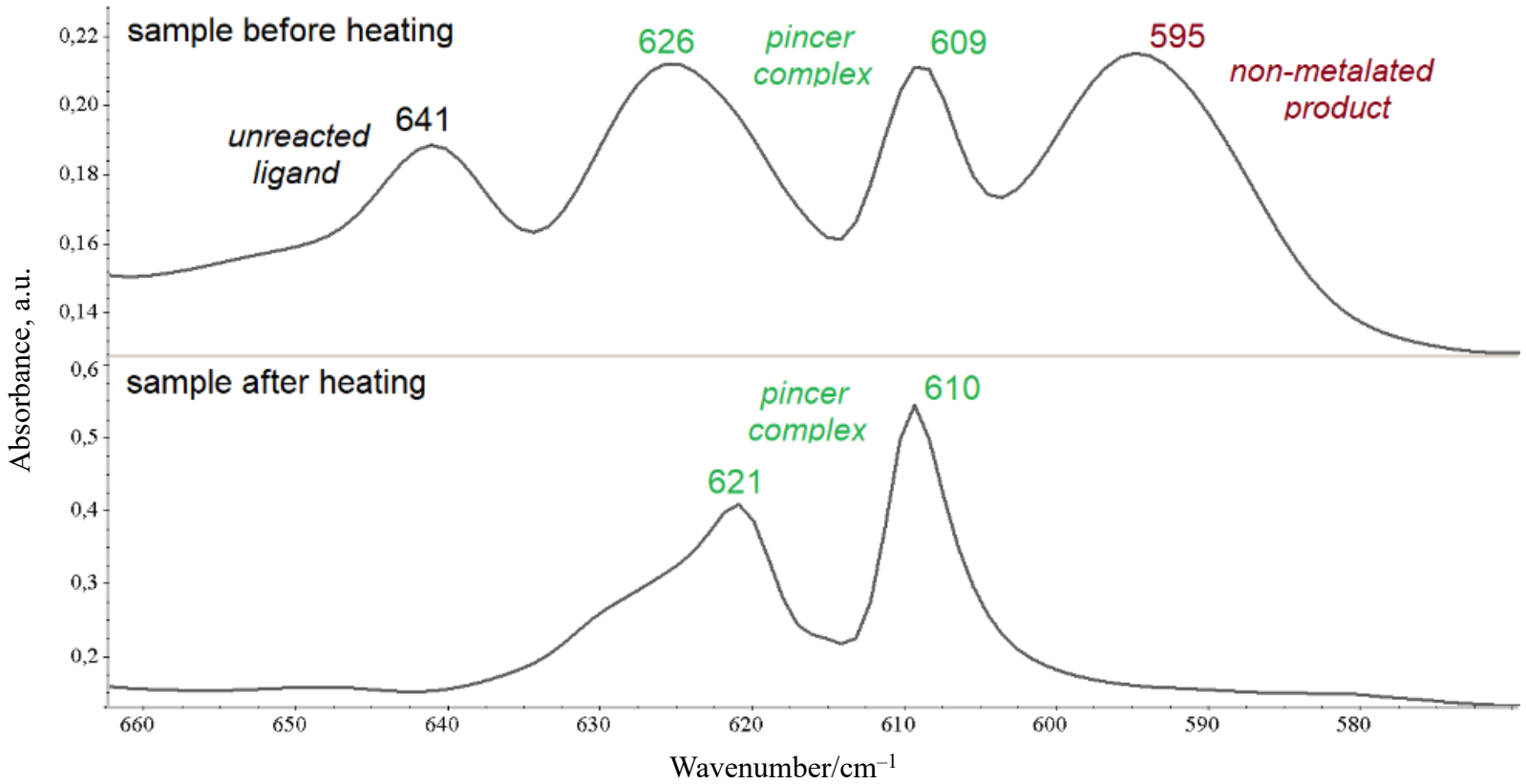


Figure S36. Fragments of the IR spectra of the samples obtained by grinding ligand **4c** with $PdCl_2(NCPh)_2$ in a mortar (top) and after subsequent heating (bottom) (the region of P=S bond stretches)

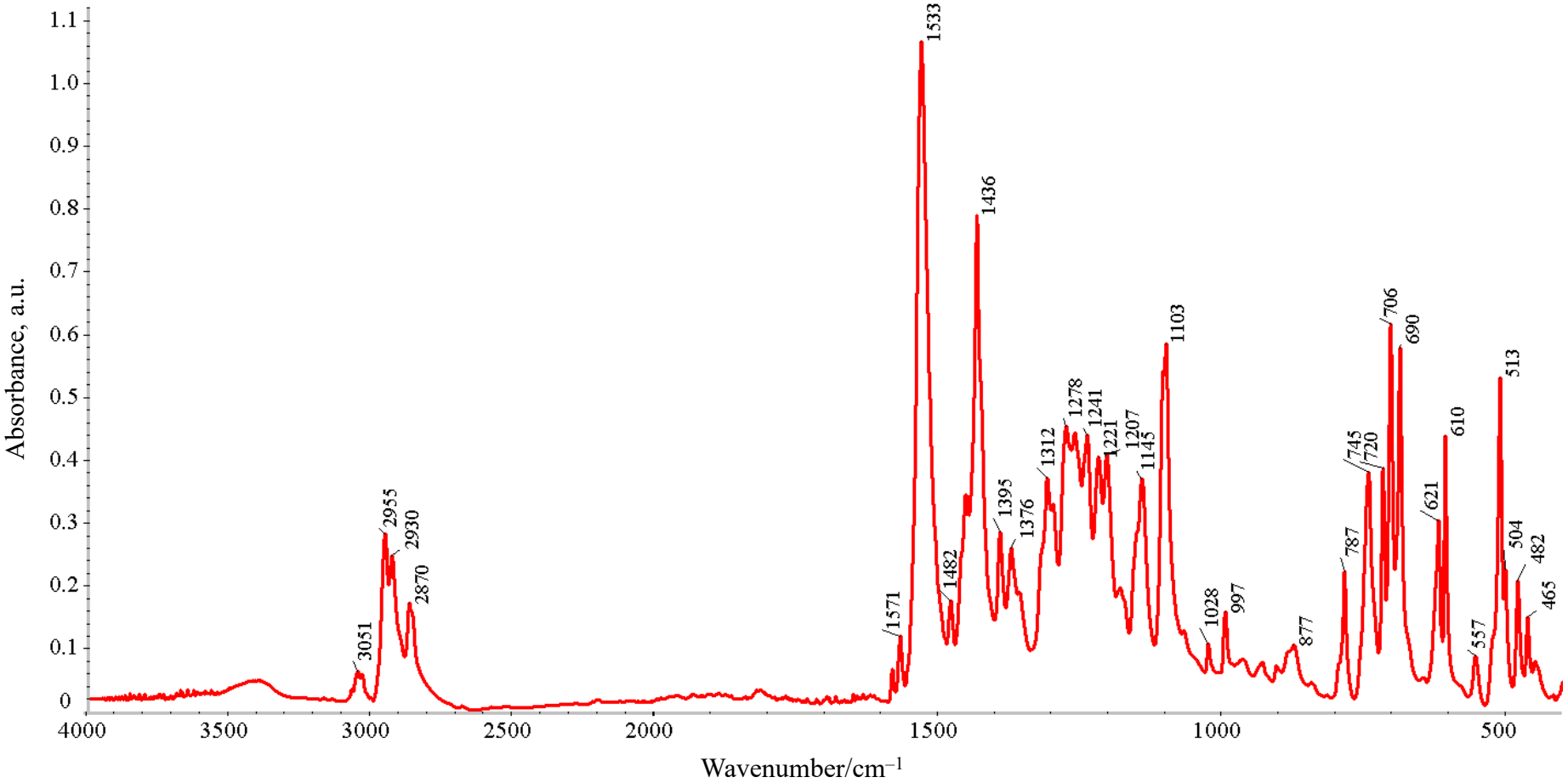


Figure S37. IR spectrum of a solid residue obtained after heating the ground mixture of ligand **4c** with $PdCl_2(NCPh)_2$ at 85–90 °C for 15 min

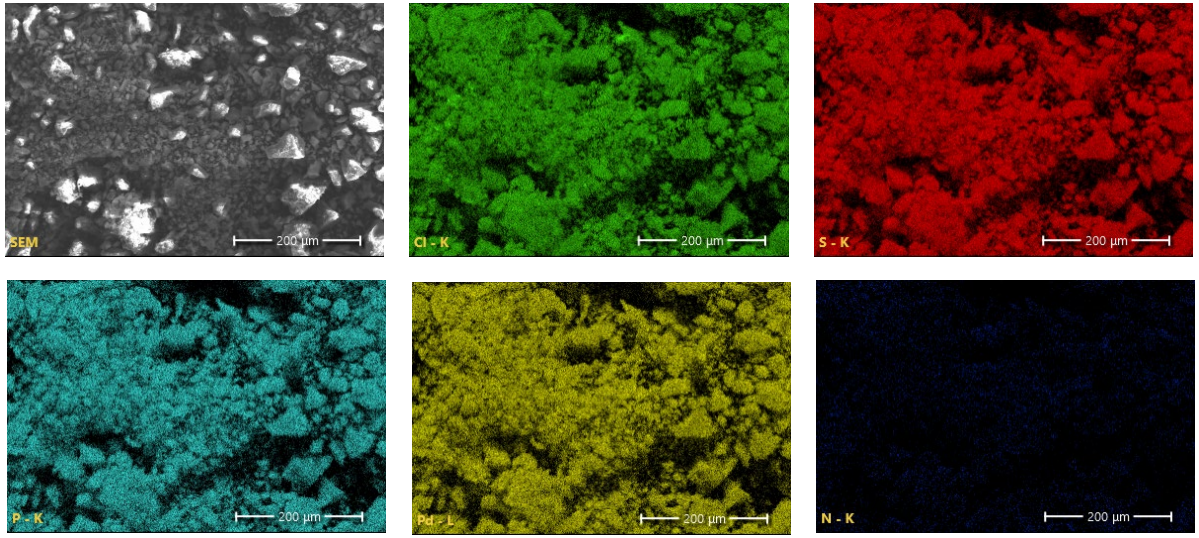


Figure S38. EDS elemental distribution maps for a solid residue obtained by grinding ligand **4c** with $PdCl_2(NCPh)_2$ (350× magnification, 25 kV)

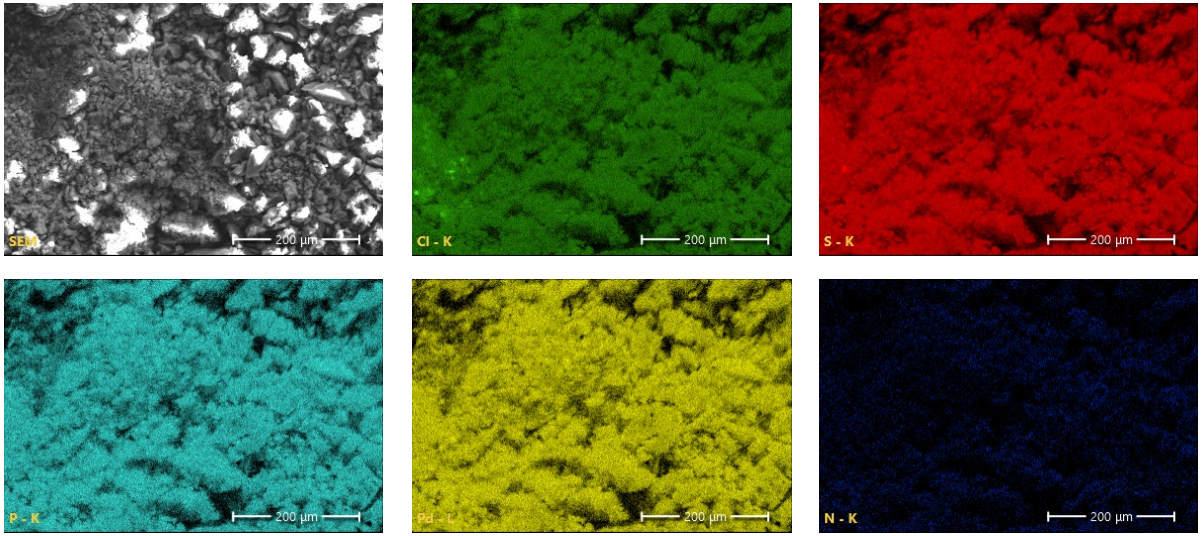


Figure S39. EDS elemental distribution maps for a solid residue obtained after heating the ground mixture at 85–90 °C for 15 min (right) (350× magnification, 25 kV)