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Functionalized pyrazine-2-carboxamides in the synthesis of new palladium-based potential cytotoxic agents

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Experimental section

General remarks

All manipulations were carried out without taking precautions to exclude air and moisture. Dichloromethane and acetonitrile were distilled from P_2O_5. Triethylamine was distilled over sodium. The key thiophosphorylated amine derivatives were obtained according to the earlier developed methods by the sequential transformations of (hydroxymethyl)diphenylphosphine sulfide (**1a**) or the addition of $Ph_2P(S)H$ to hydrobenzamide followed by the acid hydrolysis (**1b**) [S1]. Pyrazine-2-carbonyl chloride hydrochloride was obtained by refluxing pyrazine-2-carboxylic acid with an excess of $SOCl_2$ in CH_2Cl_2 in the presence of DMF used as a catalyst [S2]. All other chemicals and solvents were used as purchased.

The NMR spectra were recorded on Bruker Avance 300 and Avance 500 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 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 the resulting complexes were based on the analysis of the ^1H–^1H-COSY, ^1H–^{13}C HSQC, and ^1H–^{13}C HMBC spectra.

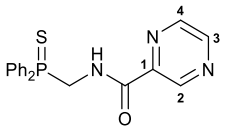
The IR spectra were recorded on a Nicolet Magna-IR750 FT spectrometer (resolution 2 cm^{-1}, 128 scans). The assignment of absorption bands in the IR spectra was made according to Ref. [S3].

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

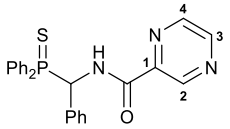
N-[(Diphenylthiophosphoryl)methyl]pyrazine-2-carboxamide 2a



A solution of Et_3N (0.405 g, 4.002 mmol) in dichloromethane (7 mL) was added dropwise to a stirred solution of amine hydrochloride **1a** (0.284 g, 1.000 mmol) in CH_2Cl_2 (15 mL) at –5 to 0 °C. The resulting solution was stirred upon cooling for 20 min. Then a solution of pyrazine-2-carbonyl chloride hydrochloride (0.179 g, 1.000 mmol) in CH_2Cl_2 (20 mL) was slowly added dropwise. The reaction mixture was stirred upon cooling for 30 min and left overnight. The resulting mixture was sequentially washed with water, aqueous solution of $NaHCO_3$, and again 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 CH_2Cl_2–MeOH from 100:1 to 50:1) to give 0.337 g of the target product as a light crystalline solid. Yield: 93%. $^{31}P\{^1H\}$ NMR (202.45 MHz, $CDCl_3$): δ 41.89 ppm. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 4.55 (vt, 2H, CH_2, $^2J_{HP} = {}^3J_{HH} = 6.1$ Hz), 7.47–7.56 (m, 6H, *m*-H and *p*-H in $P(S)Ph_2$), 7.88–7.93 (m, 4H, *o*-H in $P(S)Ph_2$), 8.57 (dd, 1H, H(C3), $^3J_{HH} = 2.5$ Hz, $^4J_{HH} = 1.6$ Hz), 8.60 (br. s, 1H, NH), 8.75 (d, 1H, H(C4), $^3J_{HH} = 2.5$ Hz), 9.32 (d, 1H, H(C2), $^4J_{HH} = 1.6$ Hz) ppm.

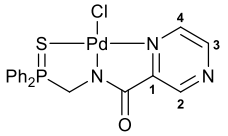
$^{13}C\{^{1}H\}$ NMR (125.76 MHz, $CDCl_3$): δ 41.20 (d, CH_2, $^{1}J_{CP}$ = 63.1 Hz), 128.93 (d, *m*-C in $P(S)Ph_2$, $^{3}J_{CP}$ = 12.3 Hz), 130.36 (d, *ipso*-C in $P(S)Ph_2$, $^{1}J_{CP}$ = 80.9 Hz), 131.35 (d, *o*-C in $P(S)Ph_2$, $^{2}J_{CP}$ = 10.5 Hz), 132.25 (d, *p*-C in $P(S)Ph_2$, $^{4}J_{CP}$ = 3.2 Hz), 142.93 (s, C3 or C4), 143.77 (s, C1), 144.32 (s, C4 or C3), 147.59 (s, C2), 162.87 (d, C=O, $^{3}J_{CP}$ = 4.9 Hz) ppm. IR (ν/cm^{-1}, KBr): 479(w), 502(m), 609(m) and 622(m) (both νP=S), 648(w), 689(w), 698(w), 707(m), 718(m), 740(m), 752(m), 770(w), 843(vw), 913(w), 1019(m), 1059(vw), 1110(m), 1186(vw), 1200(vw), 1299(vw), 1400(m), 1438(s), 1466(w), 1518(s) and 1525(s) (both C(O)NH), 1577(vw), 1677(s) (νC=O), 2843(vw), 2890(vw), 2925(vw), 2949(w), 3052(w), 3322(m) (νNH). Anal. Calcd for $C_{18}H_{16}N_3OPS \cdot 0.1CH_2Cl_2$: C, 60.08; H, 4.83; N, 11.61. Found: C, 60.01; H, 4.77; N, 11.65%.

***N*-[(Diphenylthiophosphoryl)(phenyl)methyl]pyrazine-2-carboxamide 2b**



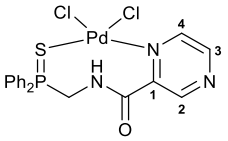
A solution of Et_3N (0.244 g, 2.411 mmol) in CH_2Cl_2 (8 mL) was added dropwise to a stirred solution of amine **1b** (0.259 g, 0.801 mmol) in CH_2Cl_2 (15 mL). The resulting solution was cooled to –5 °C. Then a solution of pyrazine-2-carbonyl chloride hydrochloride (0.144 g, 0.804 mmol) in CH_2Cl_2 (15 mL) was slowly added dropwise. The reaction mixture was stirred upon cooling for 30 min and left overnight. The resulting mixture was sequentially washed with water, aqueous solution of $NaHCO_3$, and again 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 CH_2Cl_2–MeOH from 100:1 to 70:1) to give 0.290 g of the target product as a white crystalline solid. Yield: 84%. $^{31}P\{^{1}H\}$ NMR (202.45 MHz, $CDCl_3$): δ 51.94 ppm. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 6.46 (dd, 1H, CH, $^{2}J_{HP}$ = 9.0 Hz, $^{3}J_{HH}$ = 10.0 Hz), 7.13–7.16 (m, 2H, H_{Ar}), 7.18–7.25 (m, 3H, H_{Ar}), 7.28–7.31 (m, 2H, H_{Ar}), 7.40–7.44 (m, 1H, H_{Ar}), 7.49–7.55 (m, 5H, H_{Ar}), 8.06–8.11 (m, 2H, *o*-H in P(S)Ph), 8.60–8.61 (m, 1H, H(C3)), 8.74 (d, 1H, H(C4), $^{3}J_{HH}$ = 2.5 Hz), 9.30 (d, 1H, H(C2), $^{4}J_{HH}$ = 1.4 Hz), 9.33 (dd, 1H, NH, $^{3}J_{HP}$ = 5.5 Hz, $^{3}J_{HH}$ = 10.0 Hz) ppm. $^{13}C\{^{1}H\}$ NMR (125.76 MHz, $CDCl_3$): δ 51.42 (d, CH, $^{1}J_{CP}$ = 59.9 Hz), 127.86 (d, *m*-C in Ph, $^{4}J_{CP}$ = 2.2 Hz), 128.22 (d, *m*-C in P(S)Ph, $^{3}J_{CP}$ = 12.3 Hz), 128.28 (d, *p*-C in Ph, $^{5}J_{CP}$ = 2.6 Hz), 128.59 (d, *o*-C in Ph, $^{3}J_{CP}$ = 4.5 Hz), 128.95 (d, *m*-C in P(S)Ph, $^{3}J_{CP}$ = 12.3 Hz), 129.69 (d, *ipso*-C in P(S)Ph, $^{1}J_{CP}$ = 81.5 Hz), 130.49 (d, *ipso*-C in P(S)Ph, $^{1}J_{CP}$ = 79.3 Hz), 131.58 (d, *o*-C in P(S)Ph, $^{2}J_{CP}$ = 9.5 Hz), 131.94 (d, *p*-C in P(S)Ph, $^{4}J_{CP}$ = 3.1 Hz), 132.01 (d, *o*-C in P(S)Ph, $^{2}J_{CP}$ = 10.0 Hz), 132.14 (d, *p*-C in P(S)Ph, $^{4}J_{CP}$ = 3.1 Hz), 133.98 (d, *ipso*-C in Ph, $^{2}J_{CP}$ = 0.7 Hz), 143.02 (s, C3 or C4), 143.83 (s, C1), 144.34 (s, C4 or C3), 147.61 (s, C2), 162.24 (d, C=O, $^{3}J_{CP}$ = 7.2 Hz) ppm. IR (ν/cm^{-1}, KBr): 480(w), 492(w), 527(m), 561(vw), 603(w) and 626(w) (both νP=S), 657(w), 698(m), 716(m), 745(w), 754(m), 791(w), 863(vw), 915(vw), 996(vw), 1021(m), 1056(vw), 1098(m), 1147(vw), 1172(w), 1310(w), 1353(w), 1400(m), 1437(m), 1466(w), 1497(m), 1515(br, s) (C(O)NH), 1579(w), 1675(s) (νC=O), 2953(w), 3049(w), 3325(br, w) (νNH). Anal. Calcd for $C_{24}H_{20}N_3OPS$: C, 67.12; H, 4.69; N, 9.78. Found: C, 67.04; H, 4.81; N, 9.81%.

Reaction of ligand 2a with $(PhCN)_2PdCl_2$ in the presence of Et_3N (synthesis of complex [κ^3-*S*,*N*,*N*-(L)$Pd^{II}Cl$] 3a)



A solution of $(PhCN)_2PdCl_2$ (38 mg, 0.099 mmol) in CH_2Cl_2 (4 mL) was slowly added dropwise to a solution of ligand **2a** (36 mg, 0.099 mmol) and Et_3N (12 mg, 0.119 mmol) in CH_2Cl_2 (6 mL). The reaction mixture was left under ambient conditions for 1 day. The resulting solution was purified by column chromatography on silica gel (eluent: CH_2Cl_2–MeOH (100:1)). The crude product was rinsed with CH_2Cl_2 and dried in air to give 19 mg of pincer complex **3a** as an orange crystalline solid. Yield: 39%. $^{31}P\{^1H\}$ NMR (121.49 MHz, $(CD_3)_2SO_3$): δ 62.56 ppm. ^1H NMR (500.13 MHz, $(CD_3)_2SO$): δ 5.11 (d, 2H, CH_2, $^2J_{HP}$ = 5.8 Hz), 7.67–7.71 (m, 4H, *m*-H in $P(S)Ph_2$), 7.75–7.79 (m, 2H, *p*-H in $P(S)Ph_2$), 7.99–8.03 (m, 4H, *o*-H in $P(S)Ph_2$), 8.74 (dd, 1H, H(C3), $^3J_{HH}$ = 3.0 Hz, $^4J_{HH}$ = 1.1 Hz), 8.92 (d, 1H, H(C2), $^4J_{HH}$ = 1.1 Hz), 9.03 (d, 1H, H(C4), $^3J_{HH}$ = 3.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (125.76 MHz, $(CD_3)_2SO$): δ 52.97 (d, CH_2, $^1J_{CP}$ = 74.9 Hz), 125.63 (d, *ipso*-C in $P(S)Ph_2$, $^1J_{CP}$ = 78.1 Hz), 130.13 (d, *m*-C in $P(S)Ph_2$, $^3J_{CP}$ = 12.3 Hz), 132.51 (d, *o*-C in $P(S)Ph_2$, $^2J_{CP}$ = 10.9 Hz), 134.45 (d, *p*-C in $P(S)Ph_2$, $^4J_{CP}$ = 3.1 Hz), 140.75 (s, C3), 146.31 (s, C1), 147.00 (s, C2), 150.95 (s, C4), 169.77 (d, C=O, $^3J_{CP}$ = 14.7 Hz) ppm. IR (ν/cm^{-1}, KBr): 476(m), 486(m), 501(m), 547(w), 578(m) (νP=S), 689(m), 702(m), 718(m), 745(m), 776(w), 851(vw), 861(w), 914(w), 999(vw), 1045(w), 1065(w), 1113(m), 1165(w), 1177(w), 1258(vw), 1281(w), 1366(m), 1426(w), 1438(m), 1586(m), 1632(s) (νC=O), 2820(vw), 2874(vw), 2923(w), 3025(vw), 3057(vw). Anal. Calcd for $C_{18}H_{15}ClN_3OPPdS$: C, 43.74; H, 3.06; N, 8.50. Found: C, 43.51; H, 3.17; N, 8.64%.

Reaction of ligand 2a with $(PCNh)_2PdCl_2$ in the absence of a base (synthesis of complex [κ^2-*S*,*N*-(LH)$Pd^{II}Cl_2$] 4)



A mixture of ligand **3a** (36 mg, 0.099 mmol) and $(PhCN)_2PdCl_2$ (38 mg, 0.099 mmol) in MeCN (10 mL) was stirred at room temperature for 1 h and left under ambient conditions for 1 day. The resulting precipitate was collected by filtration, rinsed with CH_2Cl_2 and Et_2O and dried in air to give 30 mg of complex **4** as a yellow crystalline solid. Yield: 57%. IR (ν/cm^{-1}, KBr): 503(m), 554(w), 581(m) (νP=S), 688(m), 704(m), 720(m), 748(m), 768(w), 850(br, w), 927(vw), 998(vw), 1073(vw), 1110(m), 1158(m), 1184(m), 1365(br, m), 1437(m), 1482(w), 1517(br, m) (C(O)NH), 1598(m), 1640(br, s) (νC=O), 1685(w), 2871(vw), 3056(w), 3090(w). Anal. Calcd for $C_{18}H_{16}Cl_2N_3OPPdS$: C, 40.74; H, 3.04; N, 7.92. Found: C, 39.92; H, 3.09; N, 7.77%.

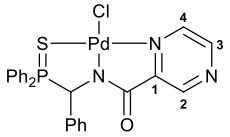
Reaction of ligand 2b with $(PhCN)_2PdCl_2$ in the presence of Et_3N

A solution of $(PhCN)_2PdCl_2$ (38 mg, 0.099 mmol) in CH_2Cl_2 (4 mL) was slowly added dropwise to a solution of ligand **2b** (43 mg, 0.100 mmol) and Et_3N (14 mg, 0.138 mmol) in CH_2Cl_2 (7 mL). The reaction mixture was left under ambient conditions for 1 day. The resulting solution was purified by column chromatography on silica gel (eluent: CH_2Cl_2–MeOH (100:1)). The crude product was recrystallized from a CH_2Cl_2–Et_2O mixture to give 35 mg of pincer complex **3b** as yellow crystals. Yield: 62%.

Reaction of ligand 3b with $(PhCN)_2PdCl_2$ in the absence of a base

A mixture of ligand **2b** (30 mg, 0.070 mmol) and $(PhCN)_2PdCl_2$ (27 mg, 0.070 mmol) in MeCN (10 mL) was stirred at room temperature for 4 h and left under ambient conditions for 1 day. The resulting solution was evaporated to dryness. The residue obtained was rinsed with Et_2O and dried in air to give 37 mg of pincer complex **3b** as a yellow crystalline solid. Yield: 93%.

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



$^{31}P\{^1H\}$ NMR (202.45 MHz, $CDCl_3$): δ 68.25 ppm. ^1H NMR (500.13 MHz, $CDCl_3$): δ 6.49 (d, 1H, CH, $^2J_{HP}$ = 2.6 Hz), 7.10–7.15 (m, 2H, *o*-H in P(S)Ph), 7.19–7.22 (m, 2H, *m*-H in Ph), 7.25–7.30 (m, 3H, *m*-H in P(S)Ph + *p*-H in Ph), 7.49–7.53 (m, 1H, *p*-H in P(S)Ph), 7.59 (dd, 2H, *o*-H in Ph, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 2.0 Hz), 7.68–7.72 (m, 2H, *m*-H in P(S)Ph), 7.74–7.78 (m, 1H, *p*-H in P(S)Ph), 8.13–8.17 (m, 2H, *o*-H in P(S)Ph), 8.89 (d, 1H, H(C4), $^3J_{HH}$ = 3.1 Hz), 9.01 (dd, 1H, H(C3), $^3J_{HH}$ = 3.1 Hz, $^4J_{HH}$ = 1.1 Hz), 9.06 (d, 1H, H(C2), $^4J_{HH}$ = 1.1 Hz) ppm. $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): δ 64.70 (d, CH, $^1J_{CP}$ = 71.7 Hz), 124.64 (d, *ipso*-C in P(S)Ph, $^1J_{CP}$ = 75.4 Hz), 125.94 (d, *ipso*-C in P(S)Ph, $^1J_{CP}$ = 78.1 Hz), 128.09 (d, *o*-C in Ph, $^3J_{CP}$ = 4.8 Hz), 128.24 (d, *m*-C in Ph, $^4J_{CP}$ = 2.8 Hz), 128.71 (d, *m*-C in P(S)Ph, $^3J_{CP}$ = 12.1 Hz), 128.98 (d, *p*-C in Ph, $^5J_{CP}$ = 3.6 Hz), 129.92 (d, *m*-C in P(S)Ph, $^3J_{CP}$ = 12.6 Hz), 132.51 (d, *o*-C in P(S)Ph, $^2J_{CP}$ = 9.7 Hz), 132.75 (d, *o*-C in P(S)Ph, $^2J_{CP}$ = 9.9 Hz), 133.45 (s, *ipso*-C in Ph), 133.76 (d, *p*-C in $P(S)Ph_2$, $^4J_{CP}$ = 2.8 Hz), 140.17 (s, C3), 146.75 (s, C1), 147.42 (s, C2), 149.44 (s, C4), 169.75 (d, C=O, $^3J_{CP}$ = 15.0 Hz) ppm. IR (ν/cm^{-1}, KBr): 475(m), 501(m), 528(m), 571(m) and 579(w) (both νP=S), 687(m), 707(m), 748(m), 778(w), 861(vw), 998(vw), 1060(vw), 1107(br, m), 1162(w), 1178(w), 1283(w), 1362(br, m), 1420(w), 1437(m), 1453(w), 1492(w), 1584(m), 1628(s) (νC=O), 2902(vw), 2910(vw), 3058(w). Anal. Calcd for $C_{24}H_{19}ClN_3OPPdS$: C, 50.54; H, 3.36; N, 7.37. Found: C, 50.29; H, 3.51; N, 7.47%.

Cytotoxicity studies

The cytotoxicity of the compounds obtained was investigated on human colorectal carcinoma (HCT116), breast cancer (MCF7), prostate adenocarcinoma (PC3), chronic myelogenous leukemia (K562 and K562/iS9), multiple plasmacytoma (AMO1), and acute lymphoblastic leukemia (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].

References

S1. A. V. Konovalov, S. G. Churusova, D. V. Aleksanyan, E. Yu. Rybalkina, S. A. Aksenova, A. S. Peregudov, Z. S. Klemenkova and V. A. Kozlov, *Org. Biomol. Chem*., 2023, **21**, 8379; https://doi.org/10.1039/d3ob01309j.

S2. R. Juza, I. Vojtechova, K. Stefkova-Mazochova, W. Dehaen, T. Petrasek, L. Prchal, T. Kobrlova, J. Janousek, P. Vlcek, E. Mezeiova, D. Svozil, J. Zdarova Krasova, J. Pejchal, H. Stark, G. Satala, A. J. Bojarski, M. Kubacka, S. Mogilski, A. Randakova, K. Musilek, J. Korabecny, *Eur. J. Med. Chem*., 2022, **232**, 114193; https://doi.org/10.1016/j.ejmech.2022.114193.

S3. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1975; https://doi.org/10.1007/978-94-011-6017-9.

S4. D. V. Aleksanyan, A. V. Konovalov, S. G. Churusova, E. Yu. Rybalkina, A. S. Peregudov, S. A. Aksenova, E. I. Gutsul, Z. S. Klemenkova and V. A. Kozlov, *Pharmaceutics*, 2023, **15**, 1088; https://doi.org/10.3390/pharmaceutics15041088.

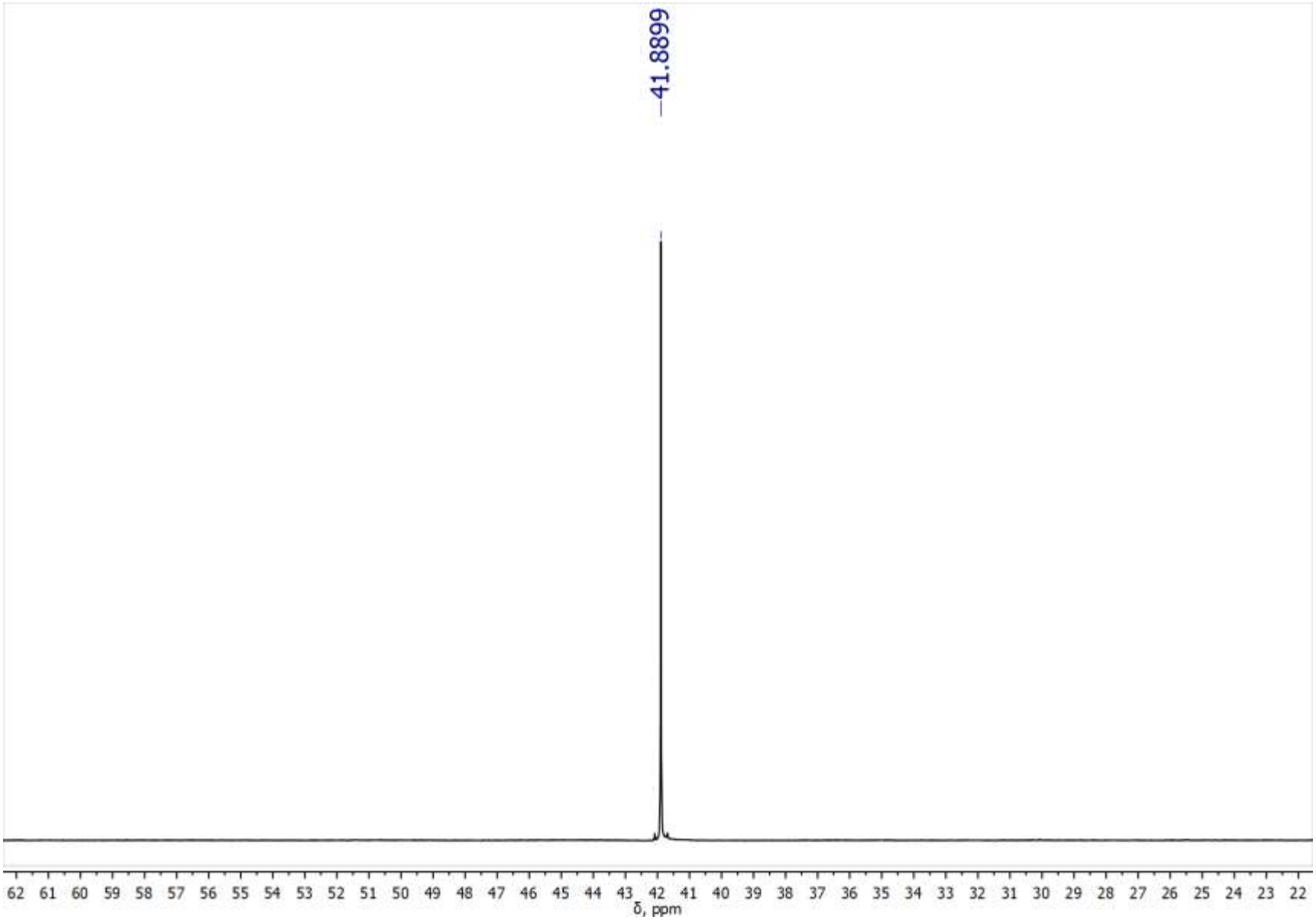


Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum of ligand **2a** (202.45 MHz, $CDCl_3$)

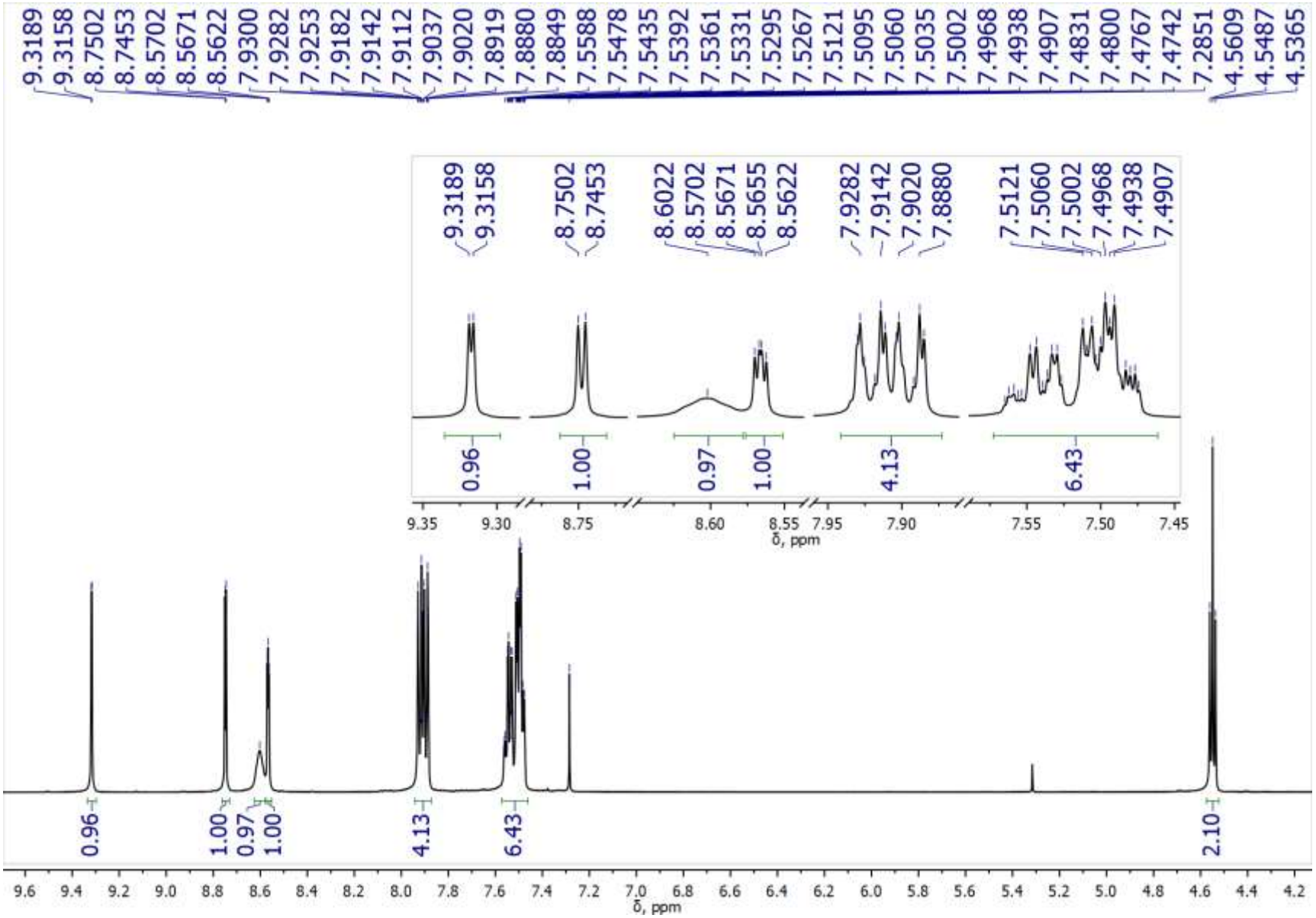


Figure S2. ^{1}H NMR spectrum of ligand **2a** (500.13 MHz, $CDCl_3$)

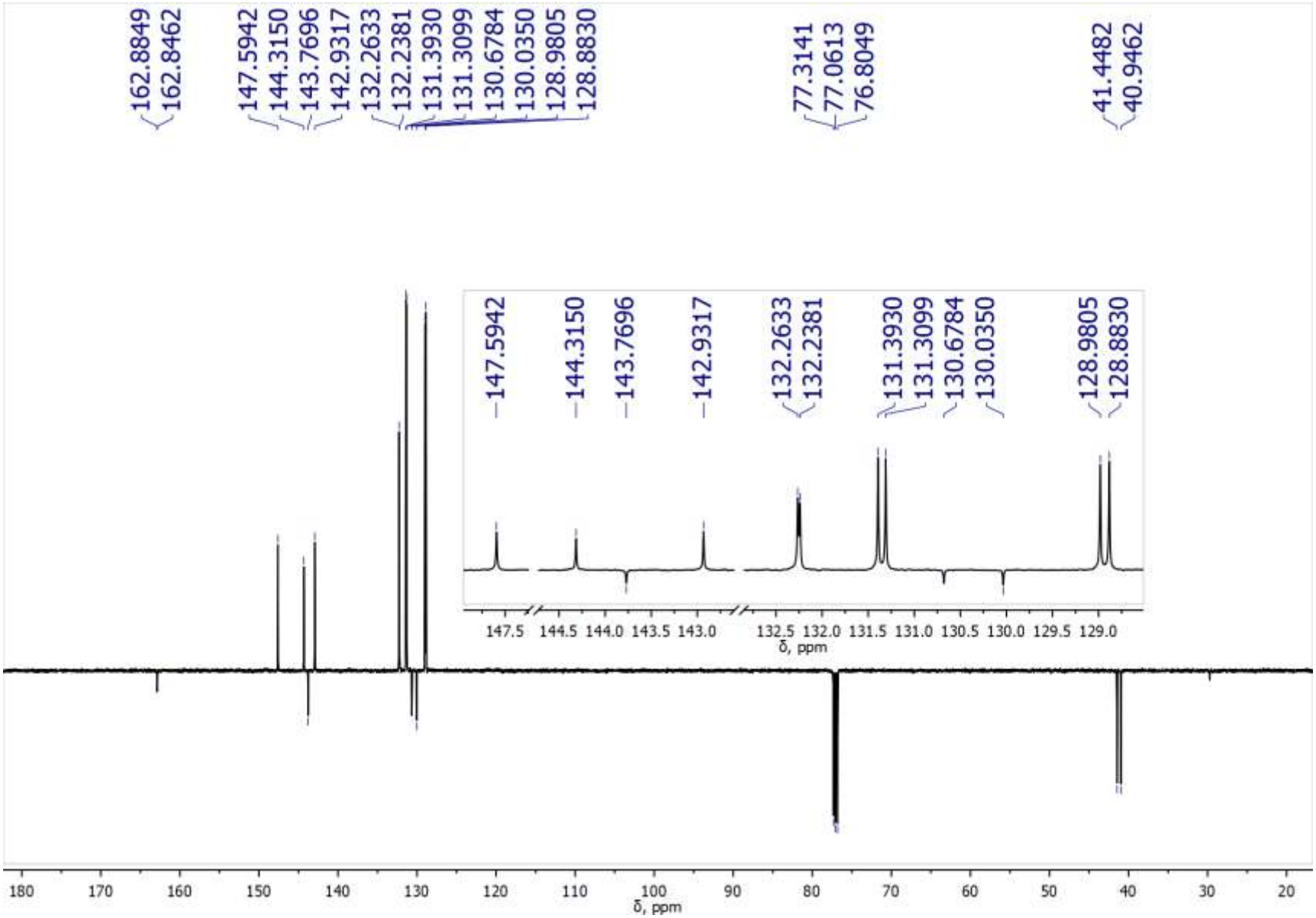


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of ligand **2a** (125.76 MHz, $CDCl_3$)

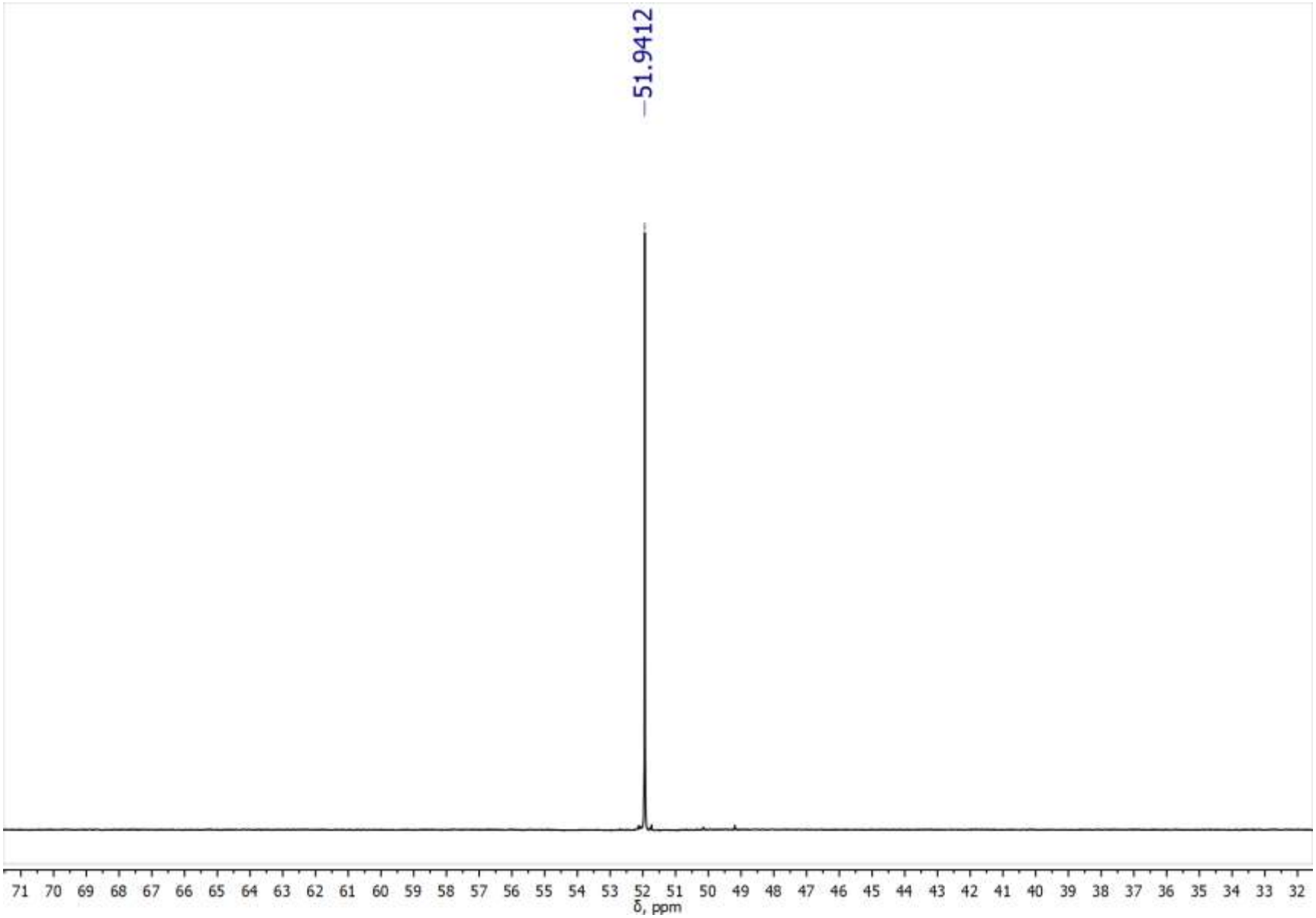


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of ligand **2b** (202.45 MHz, $CDCl_3$)

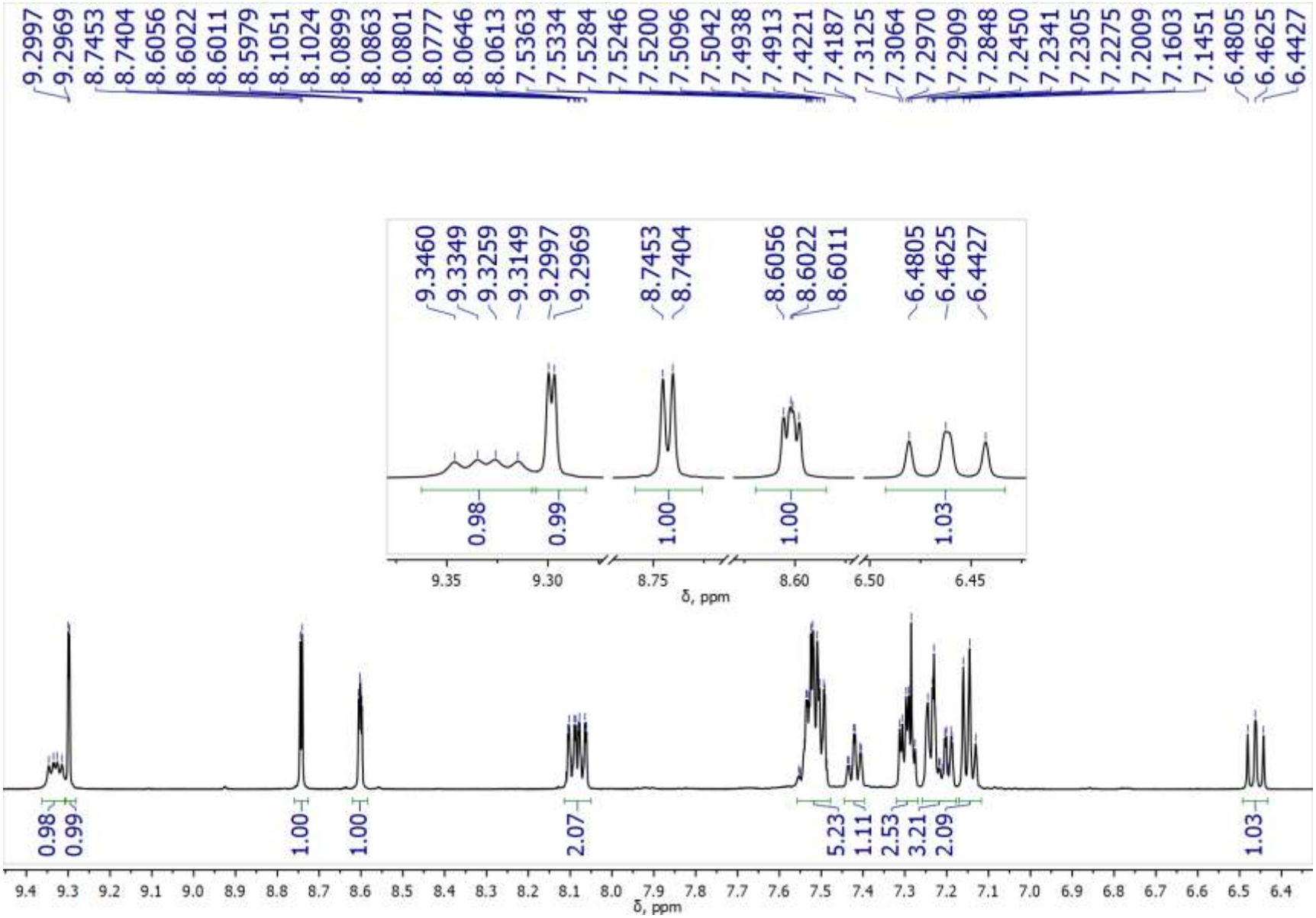


Figure S5. ^{1}H NMR spectrum of ligand **2b** (500.13 MHz, $CDCl_3$)

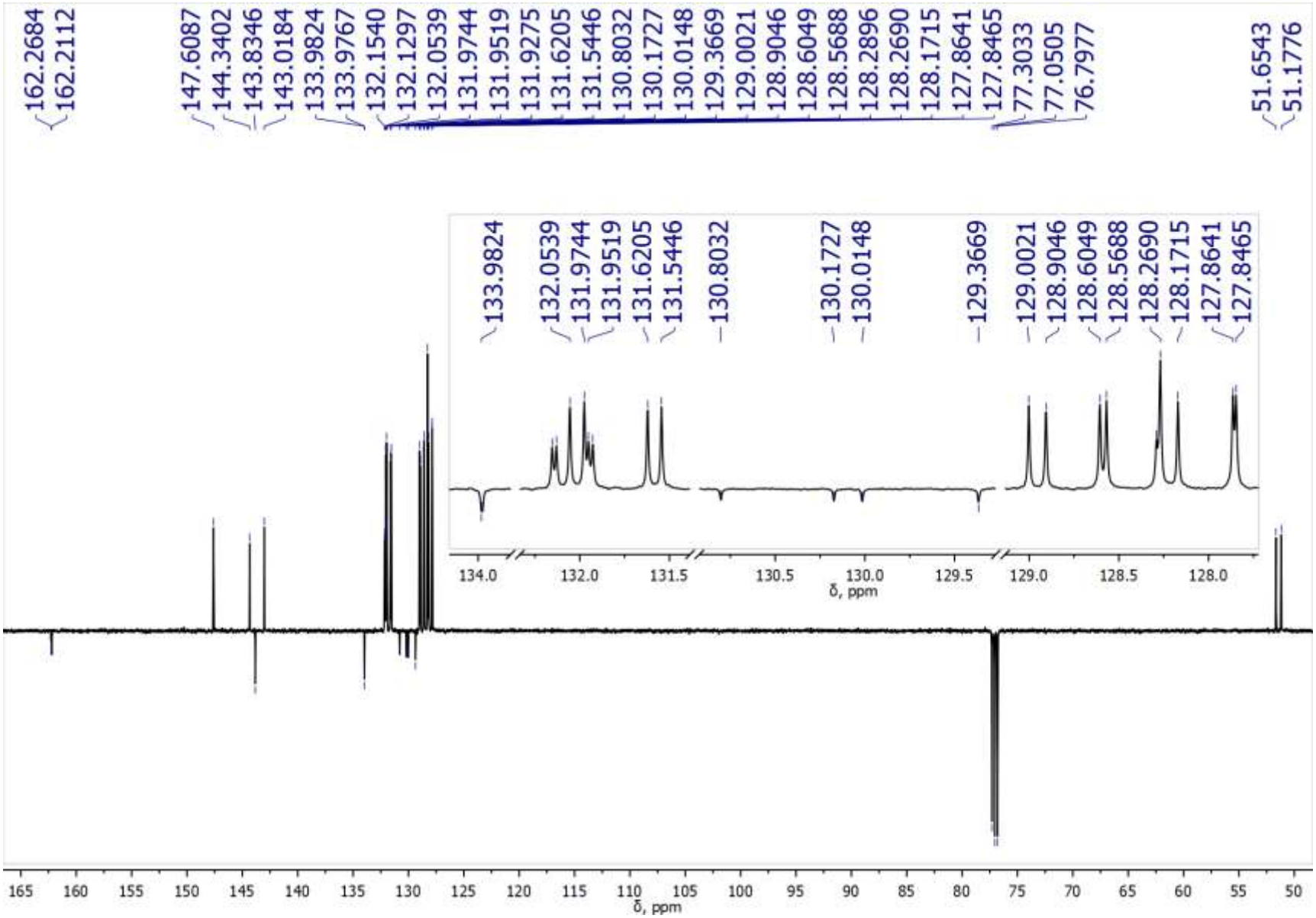


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of ligand **2b** (125.76 MHz, $CDCl_3$)

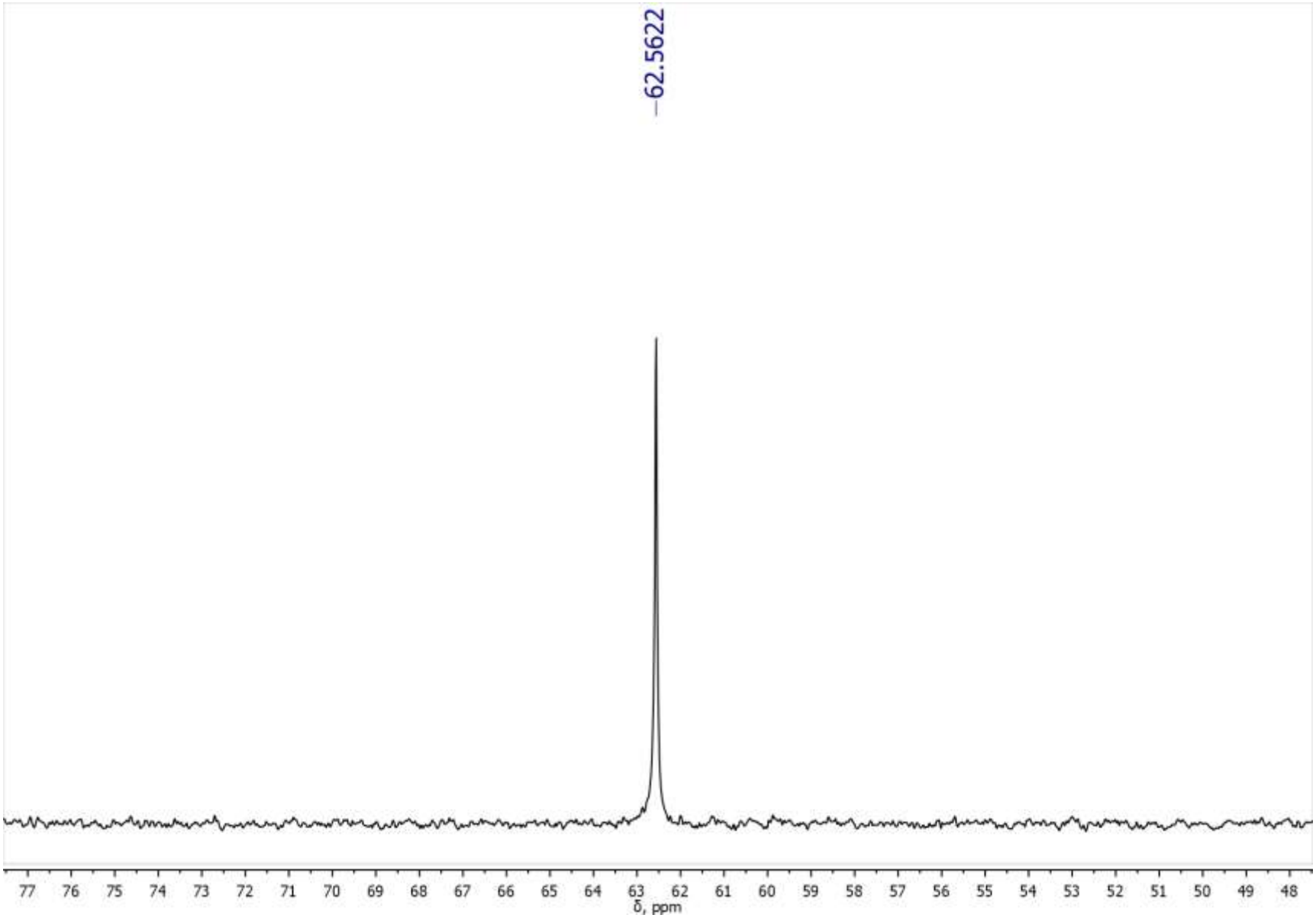


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of complex **3a** (121.49 MHz, $(CD_3)_2SO$)

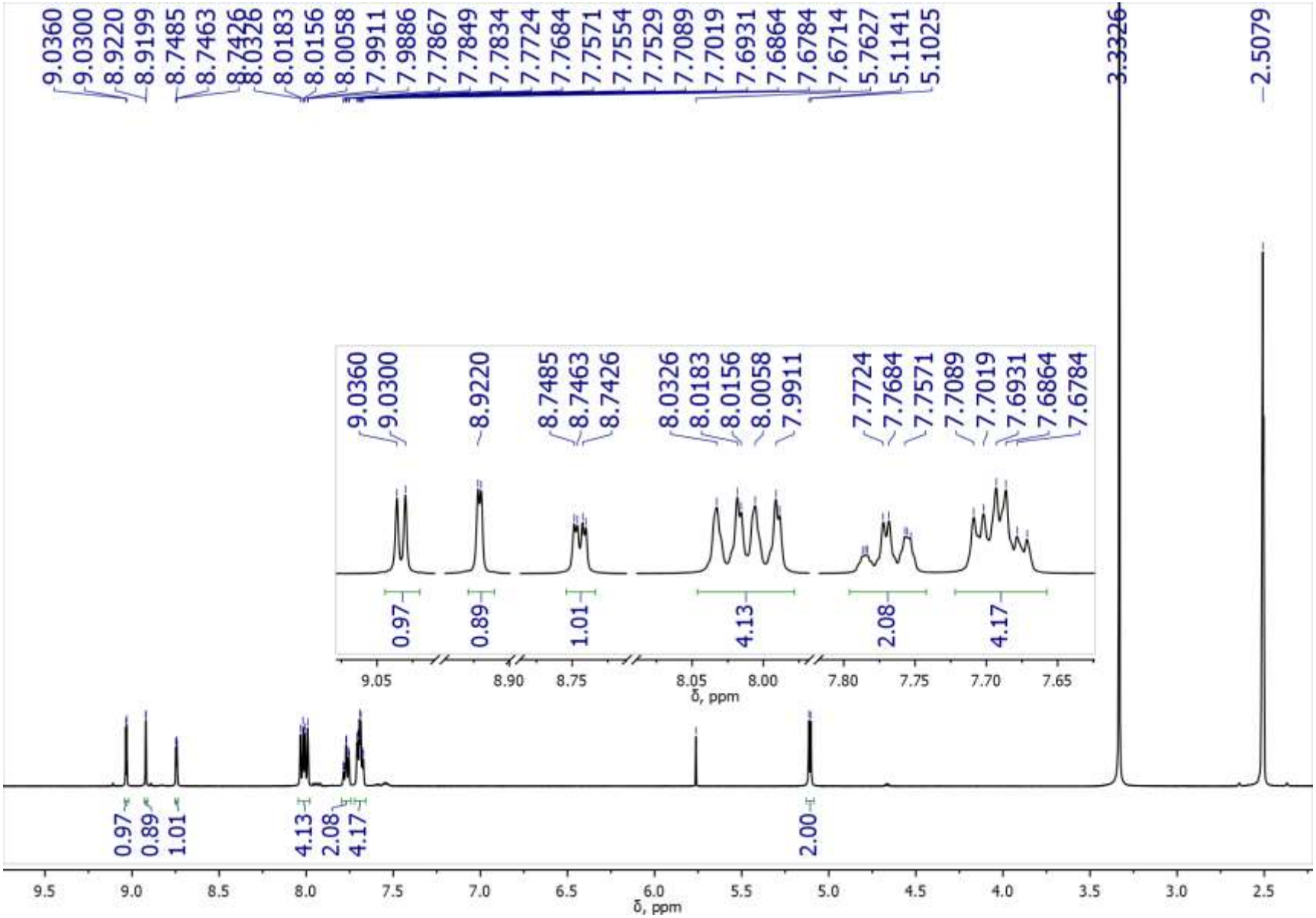


Figure S8. ^{1}H NMR spectrum of complex **3a** (500.13 MHz, $(CD_3)_2SO$)

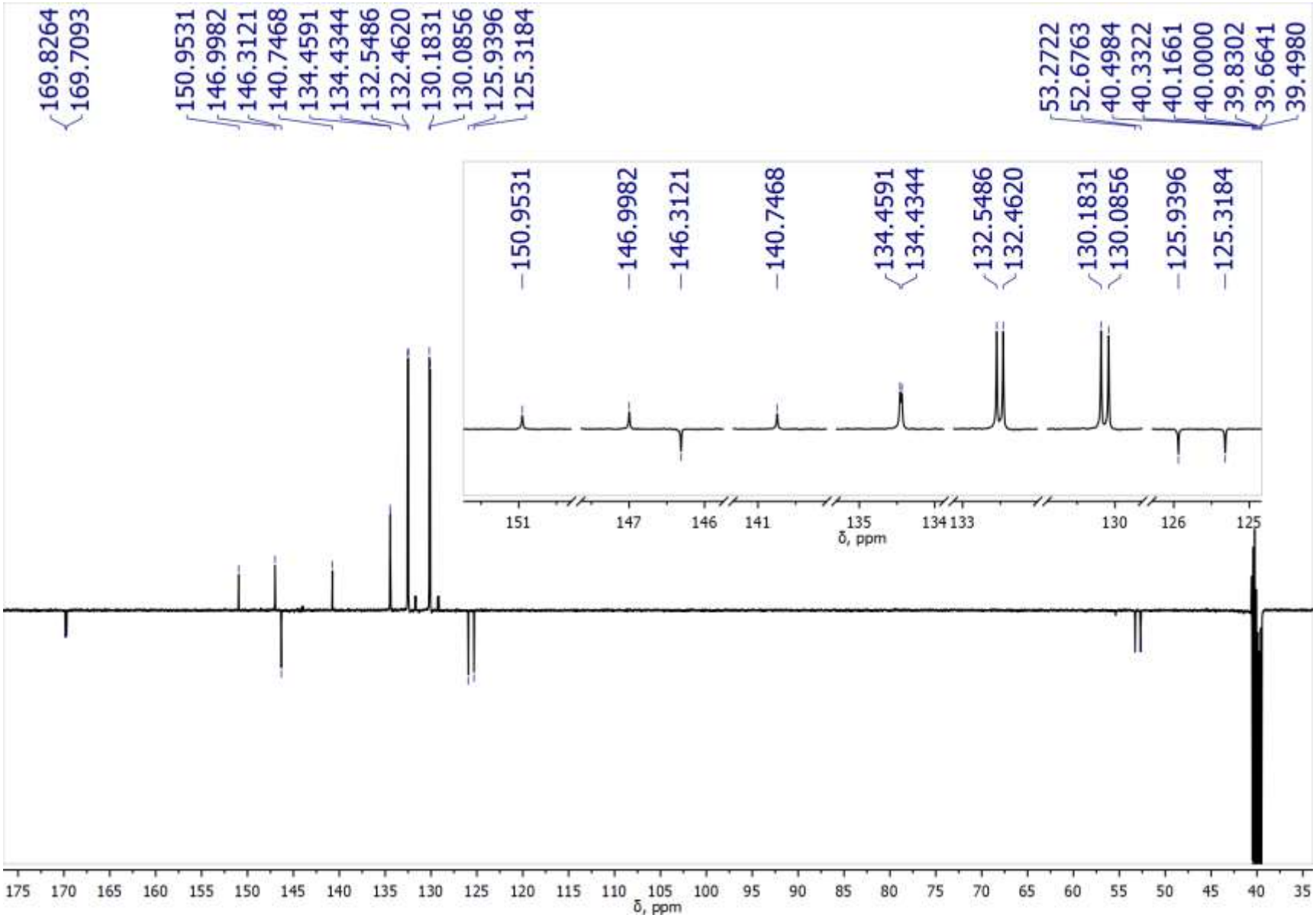


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of complex **3a** (125.76 MHz, $(CD_3)_2SO$)

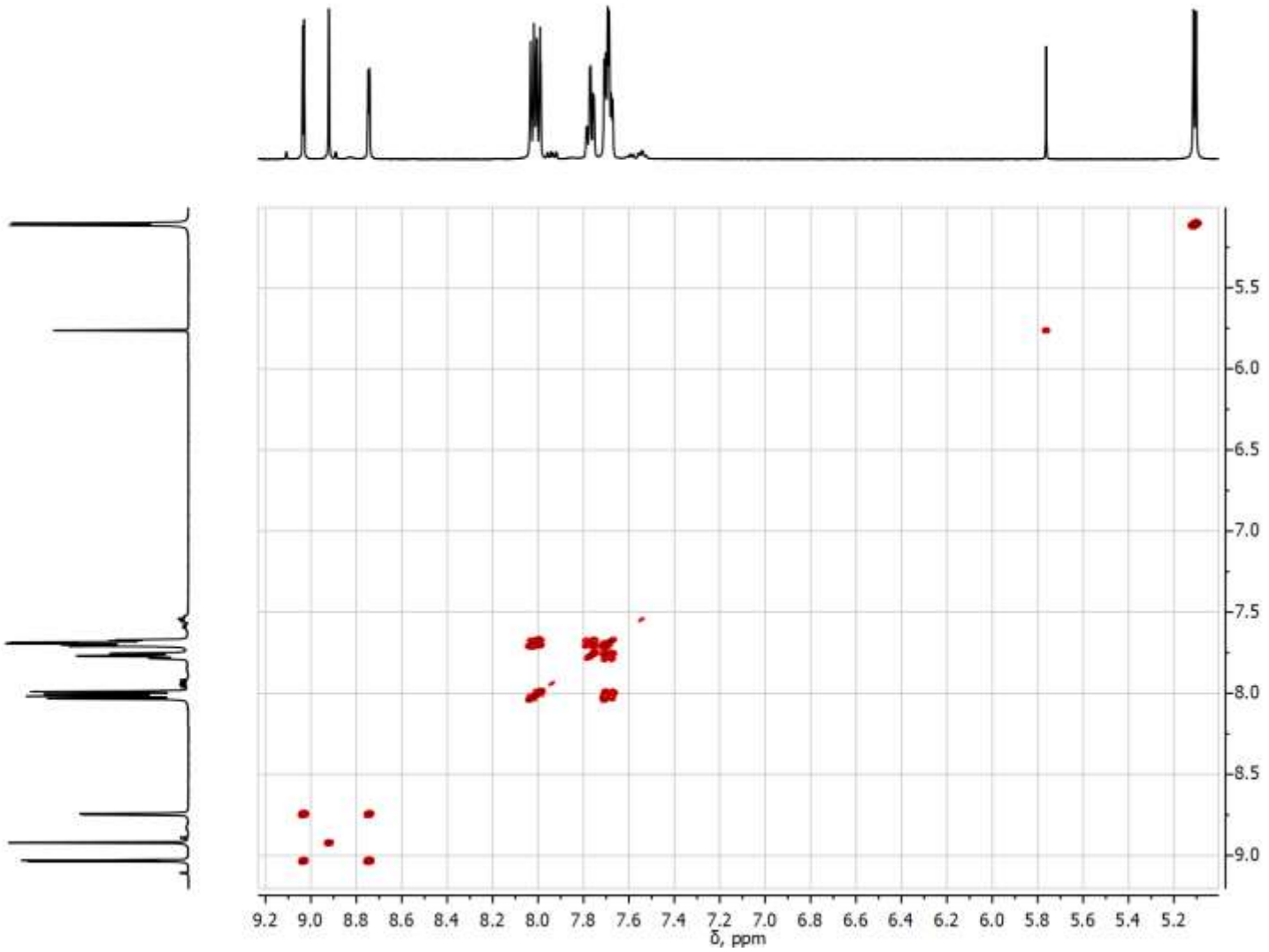


Figure S10. $^{1}H–^{1}H$ COSY spectrum of complex **3a** (500.13 MHz, $(CD_3)_2SO$)

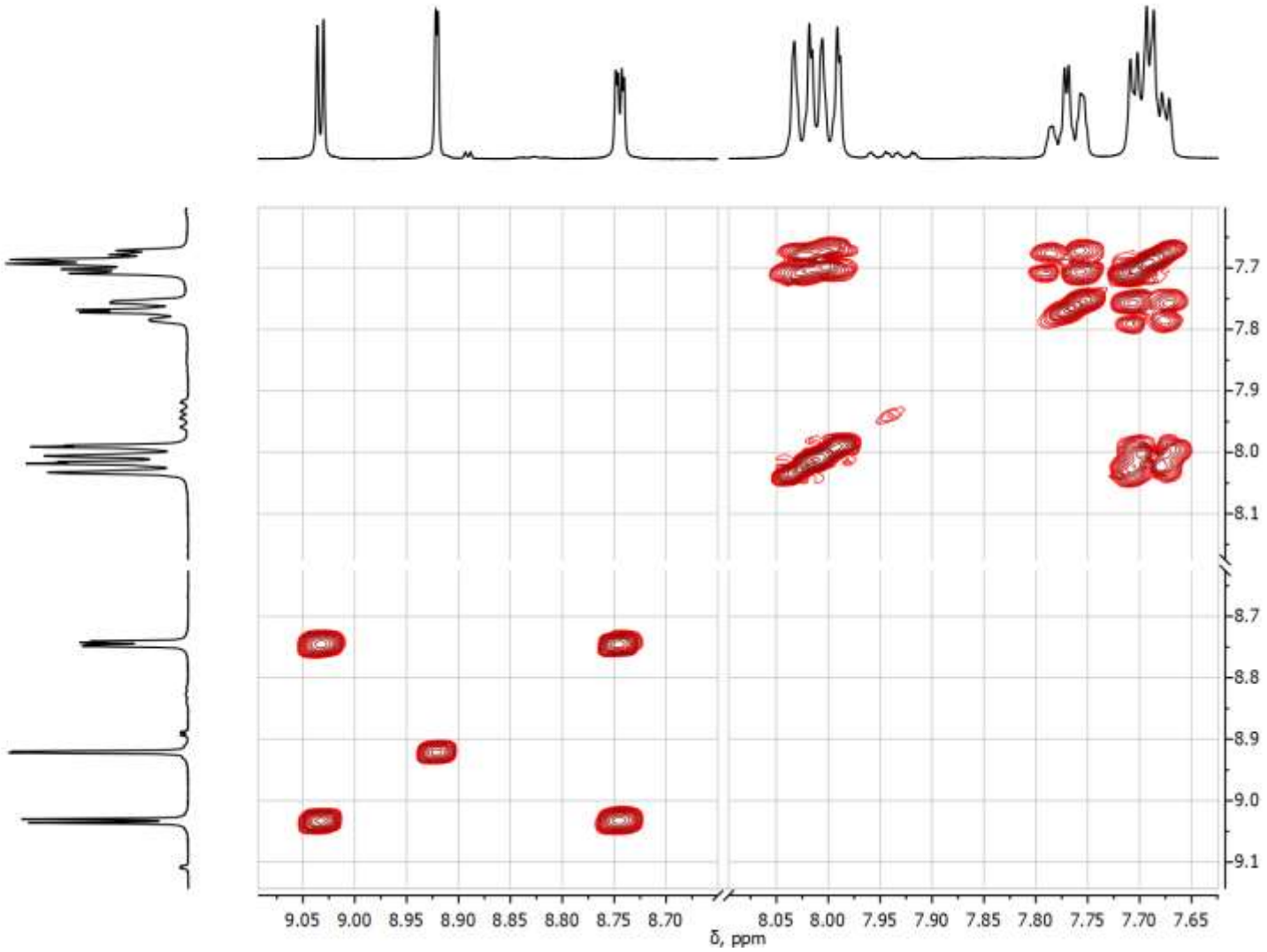


Figure S11. Fragments of the $^{1}H–^{1}H$ COSY spectrum of complex **3a** (500.13 MHz, $(CD_3)_2SO$)

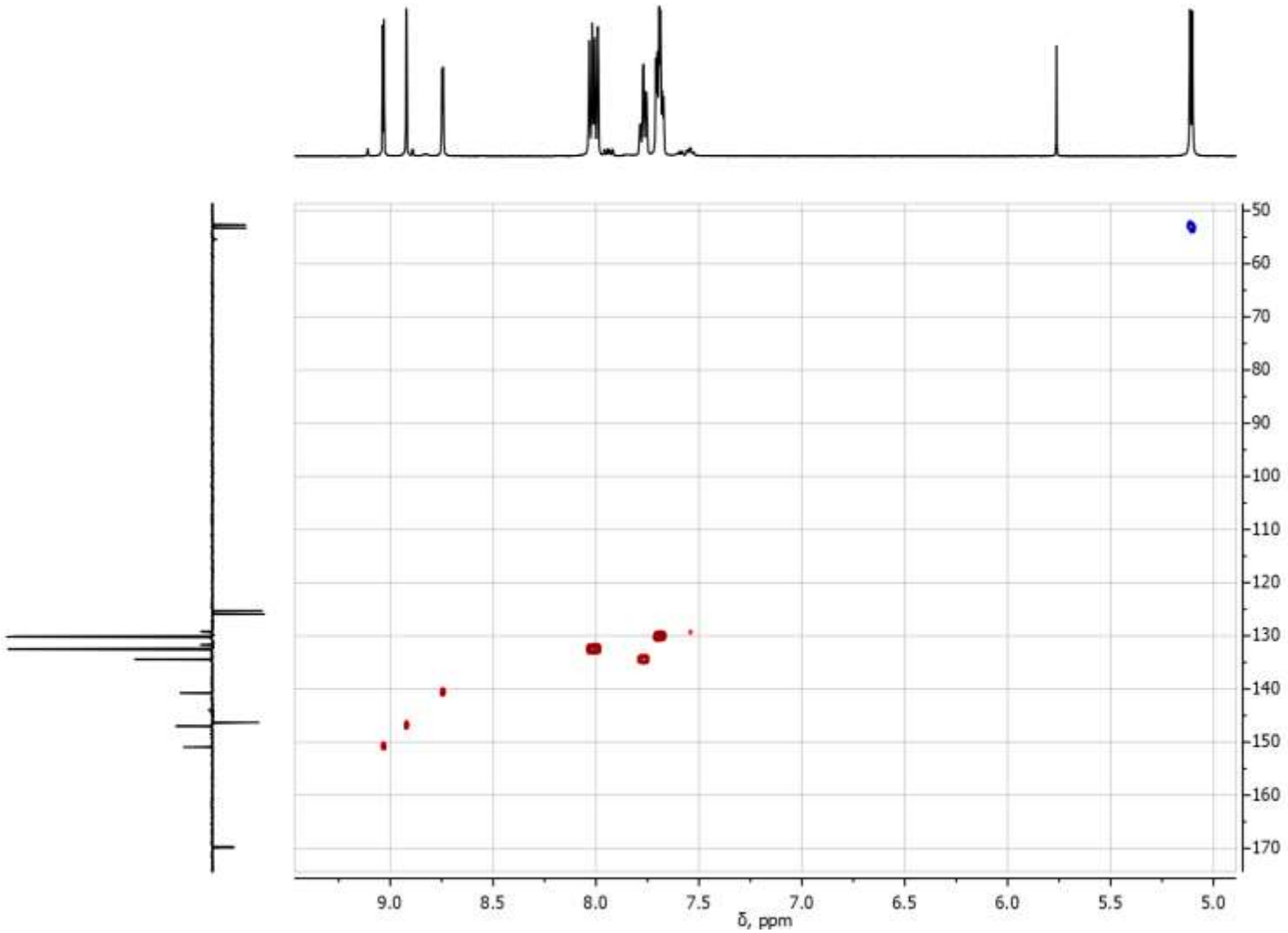


Figure S12. ^{1}H–^{13}C HSQC spectrum of complex **3a** ($(CD_3)_2SO$)

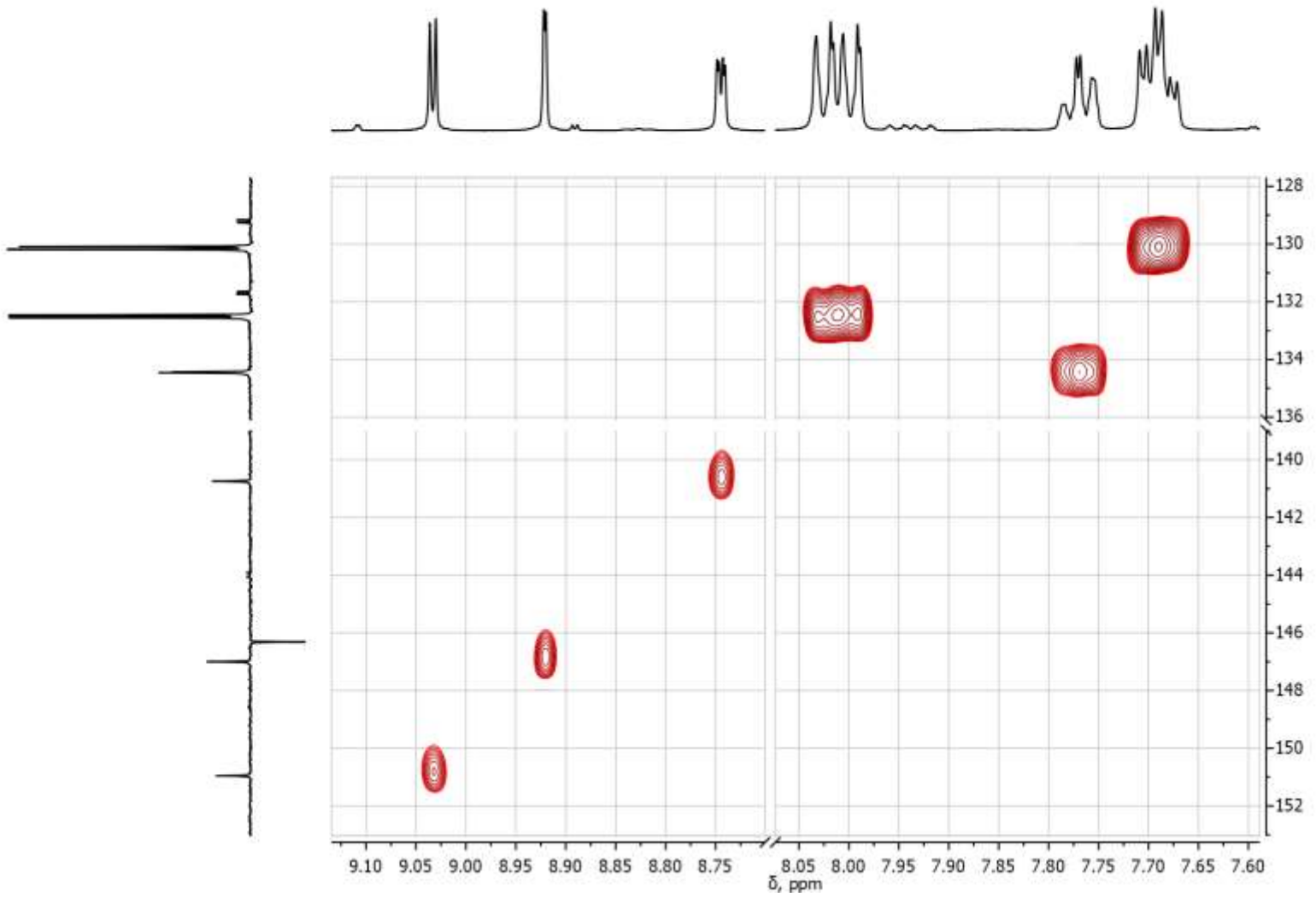


Figure S13. Fragments of the $^{1}H–^{13}C$ HSQC spectrum of complex **3a** ($(CD_3)_2SO$)

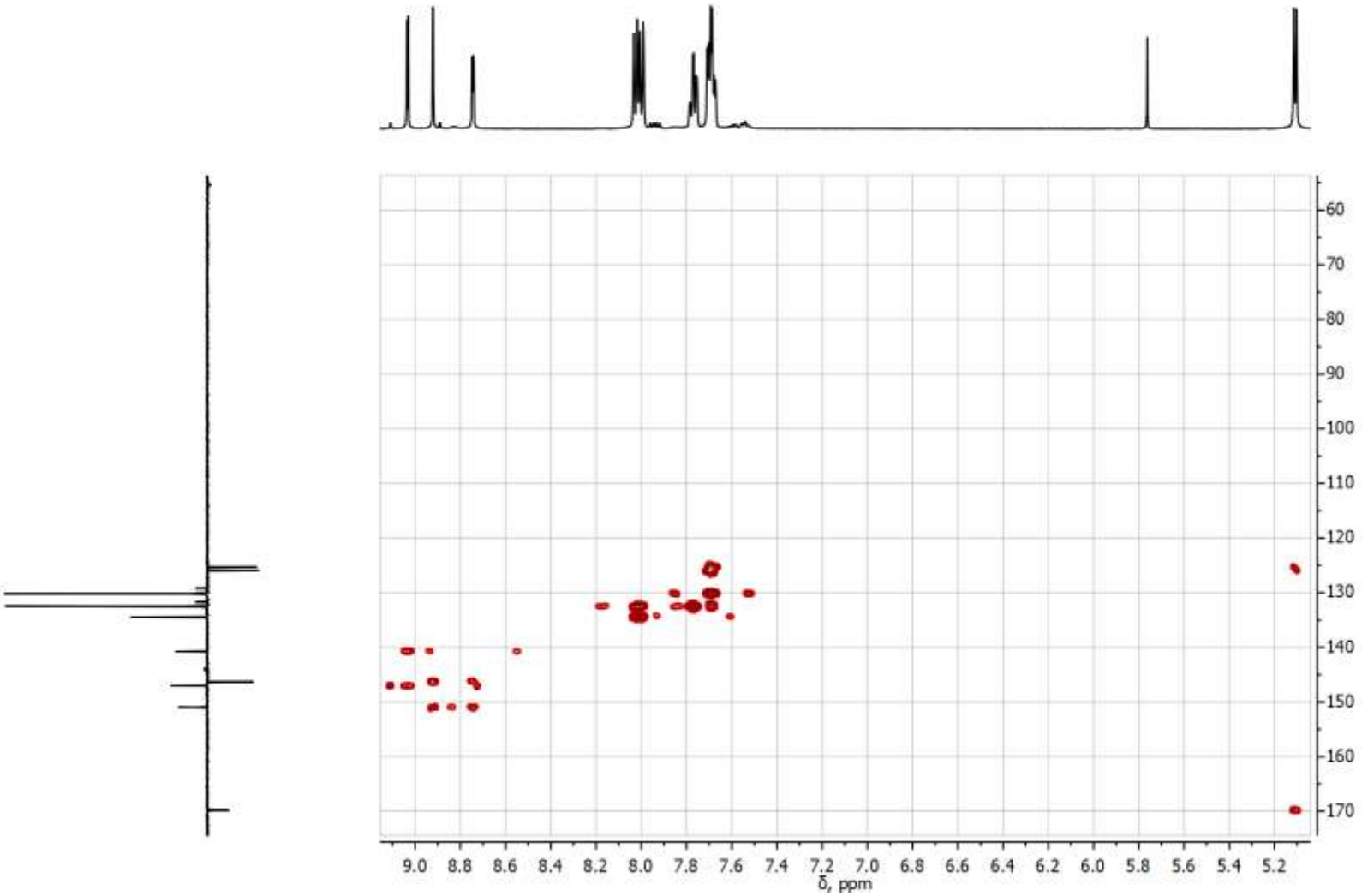


Figure S14. $^{1}H–^{13}C$ HMBC spectrum of complex **3a** ($(CD_3)_2SO$)

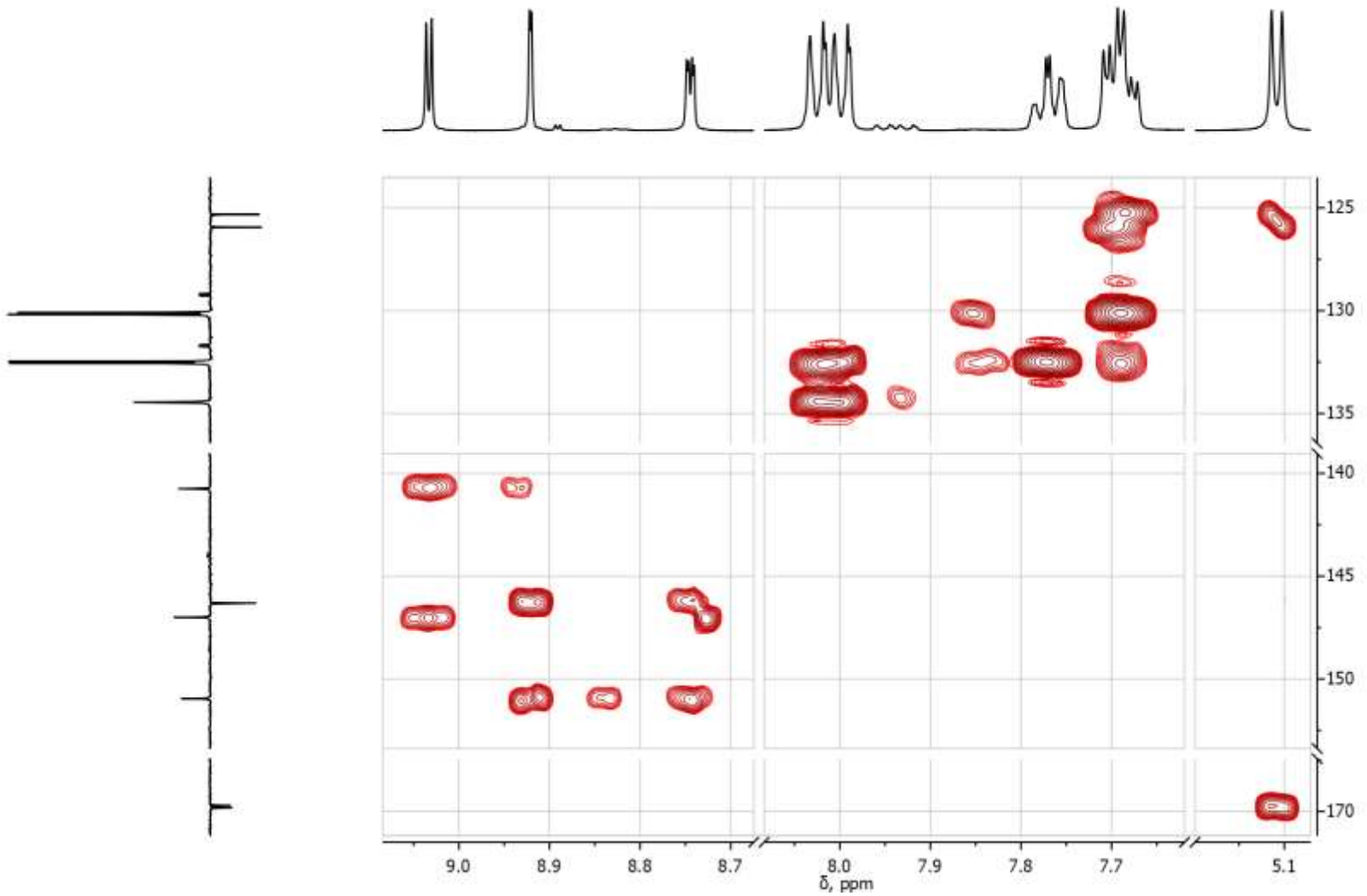


Figure S15. Fragments of the $^{1}H–^{13}C$ HMBC spectrum of complex **3a** ($(CD_3)_2SO$)

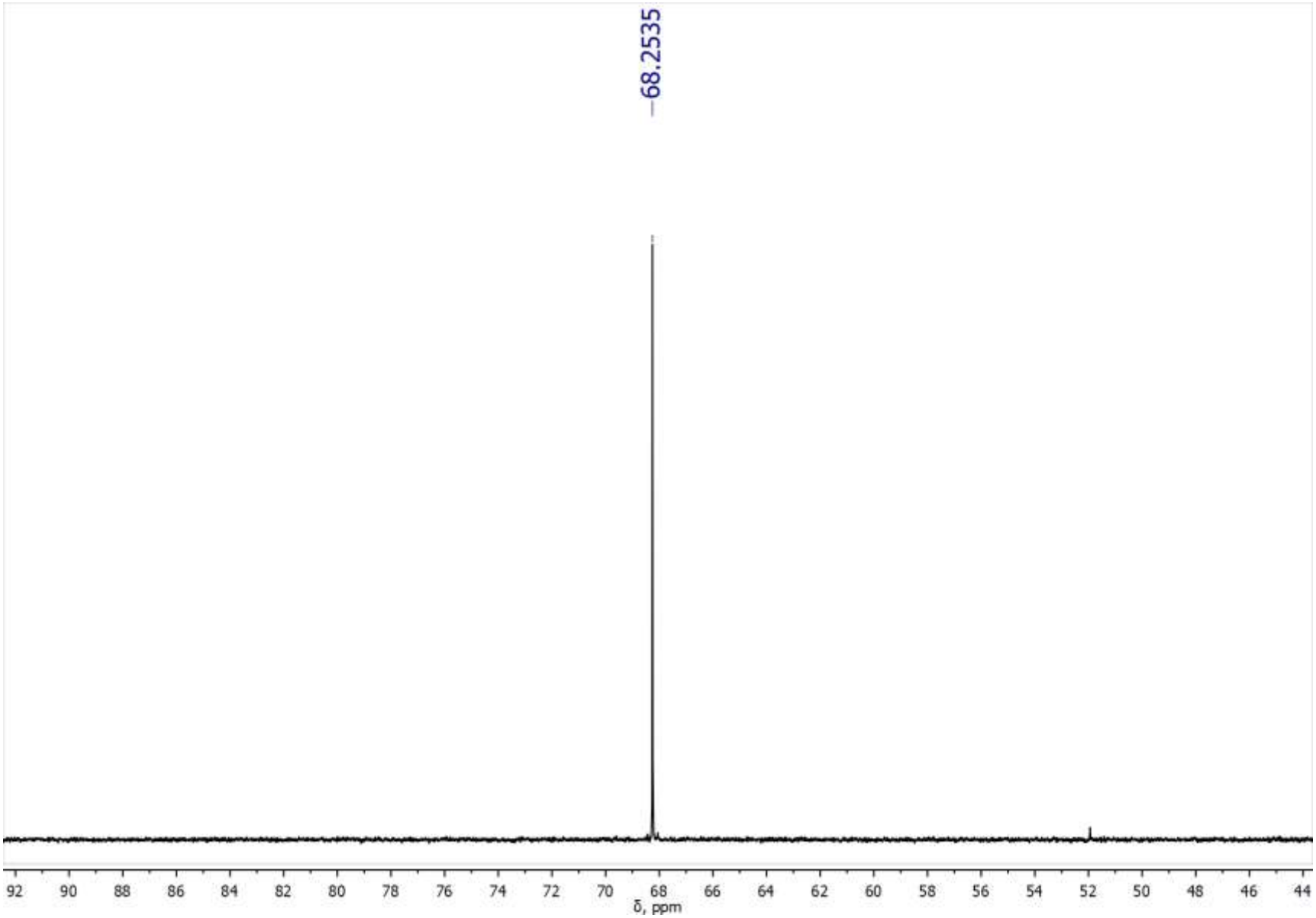


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of complex **3b** (202.45 MHz, $CDCl_3$)

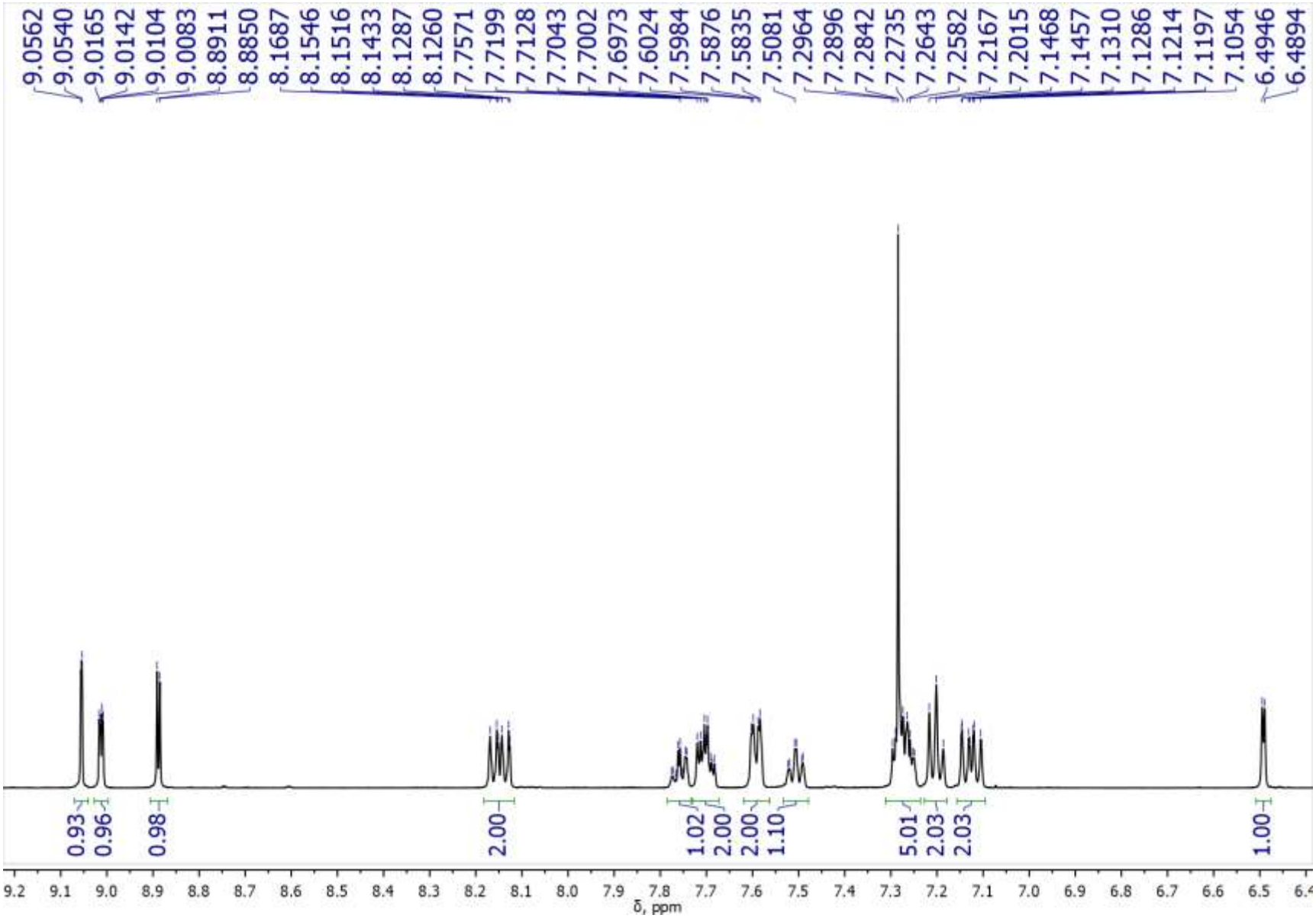


Figure S17. ^{1}H NMR spectrum of complex **3b** (500.13 MHz, $CDCl_3$)

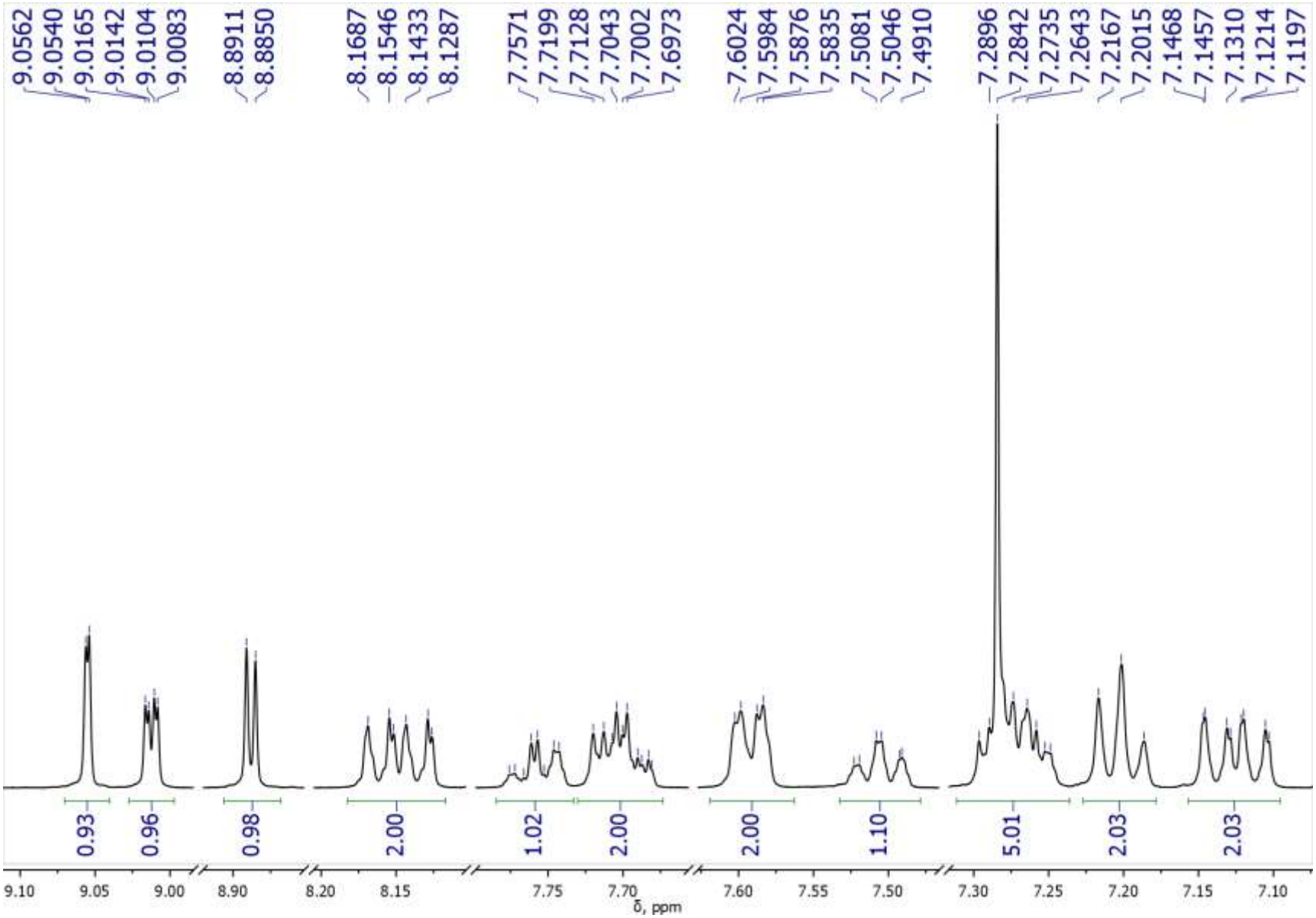


Figure S18. Fragments of the ^{1}H NMR spectrum of complex **3b** (500.13 MHz, $CDCl_3$)

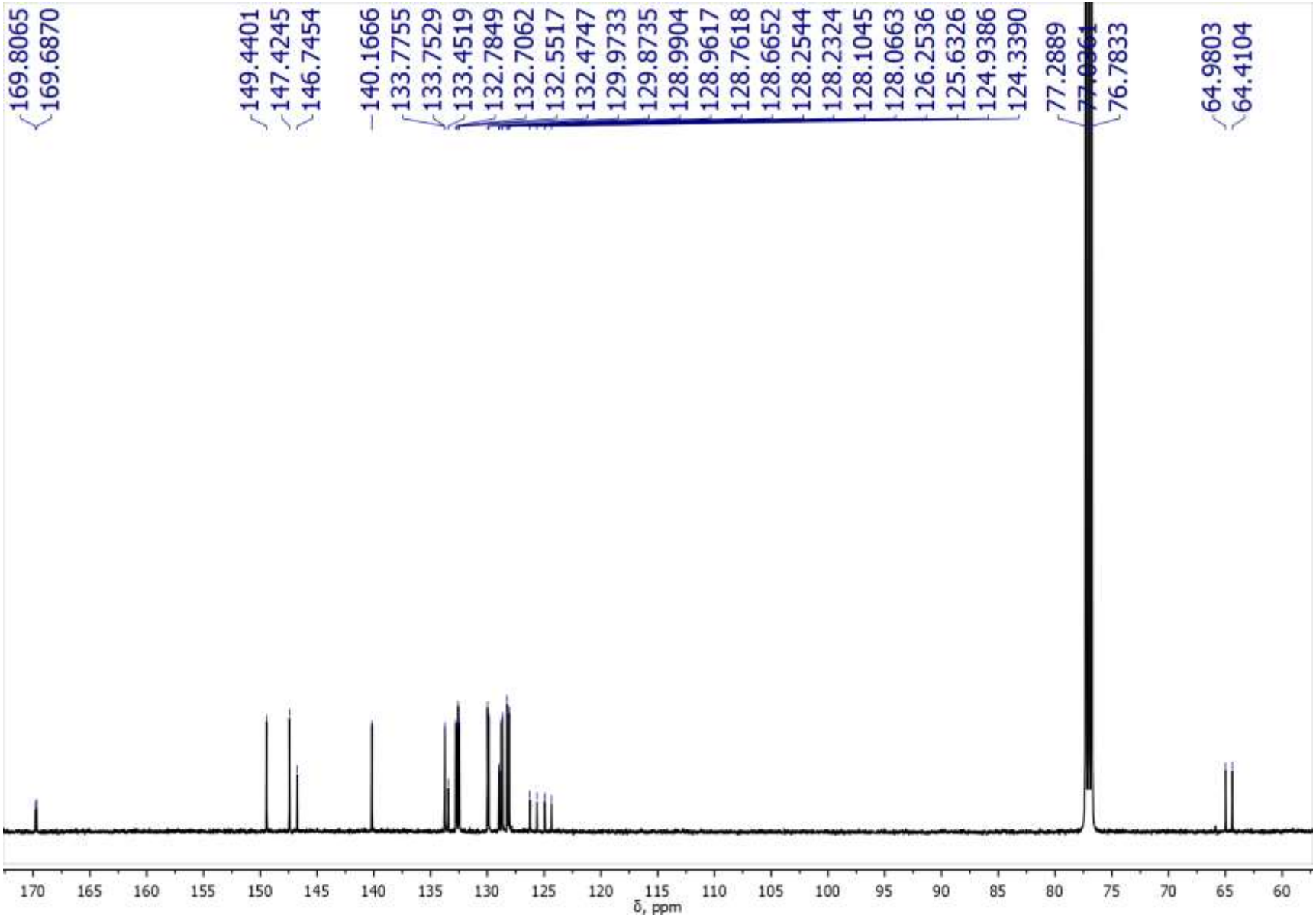


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of complex **3b** (125.76 MHz, $CDCl_3$)

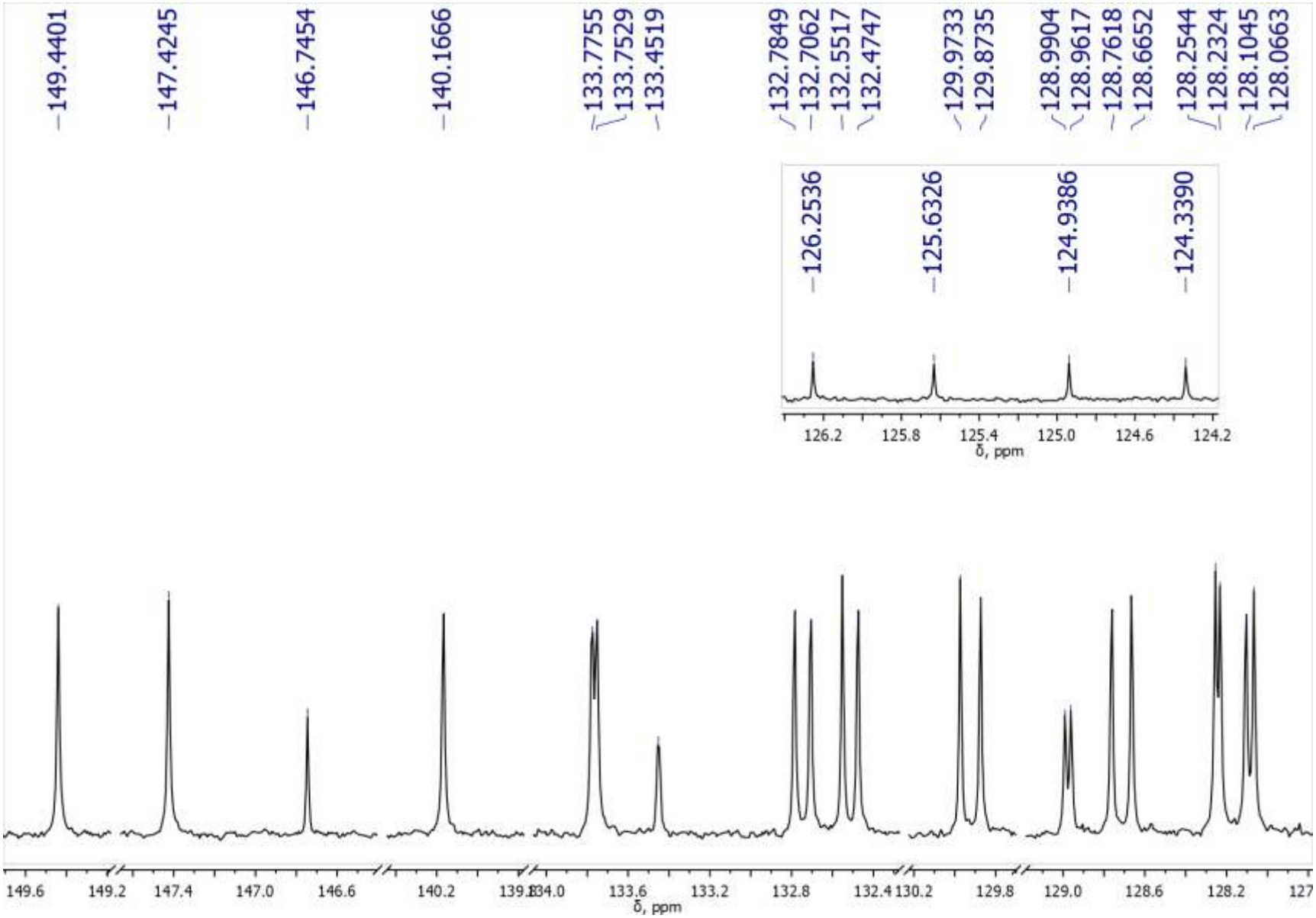


Figure S20. Fragments of the $^{13}C\{^{1}H\}$ NMR spectrum of complex **3b** (125.76 MHz, $CDCl_3$)

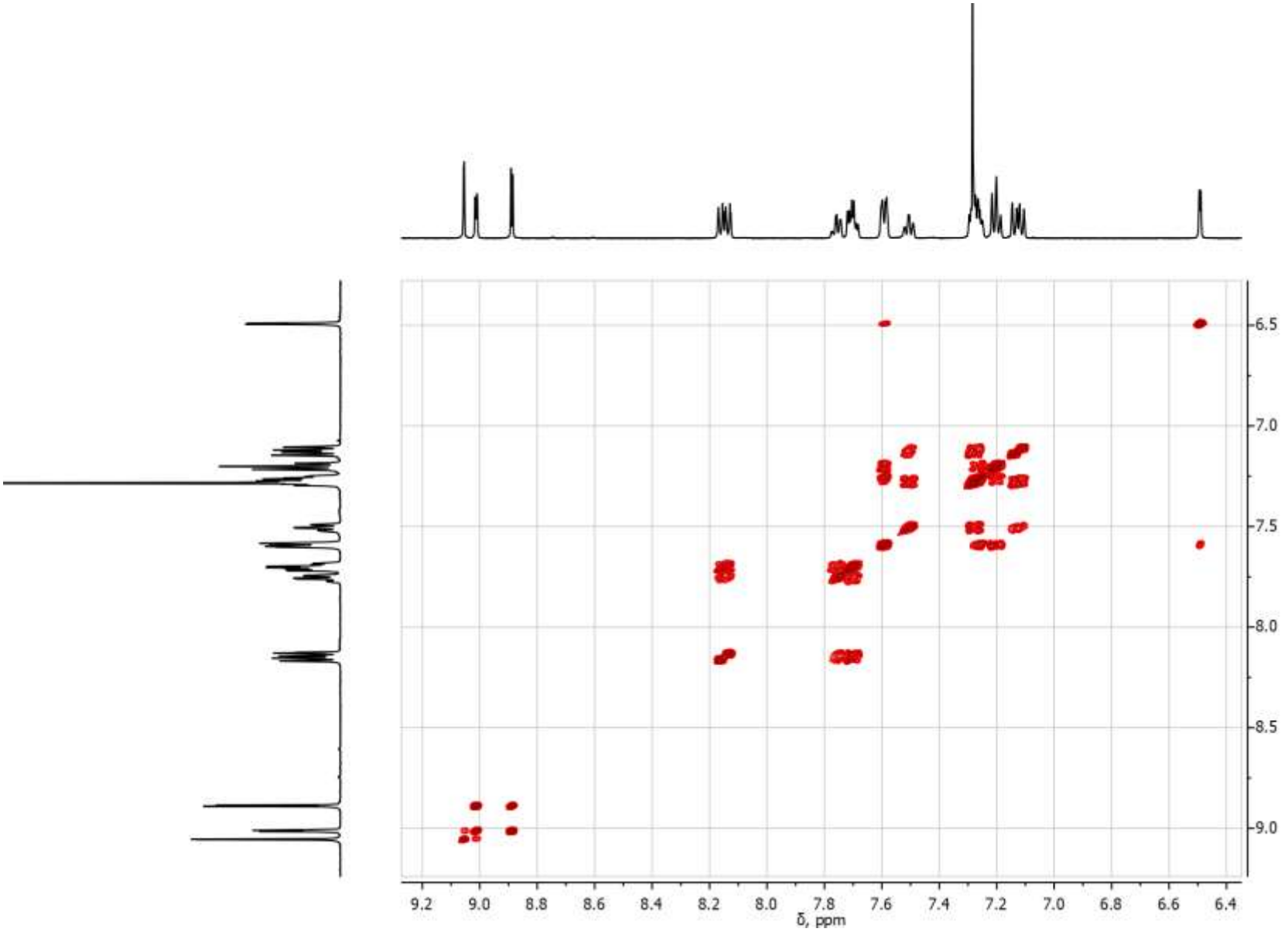


Figure S21. ^{1}H–^{1}H COSY spectrum of complex **3b** (500.13 MHz, $CDCl_3$)

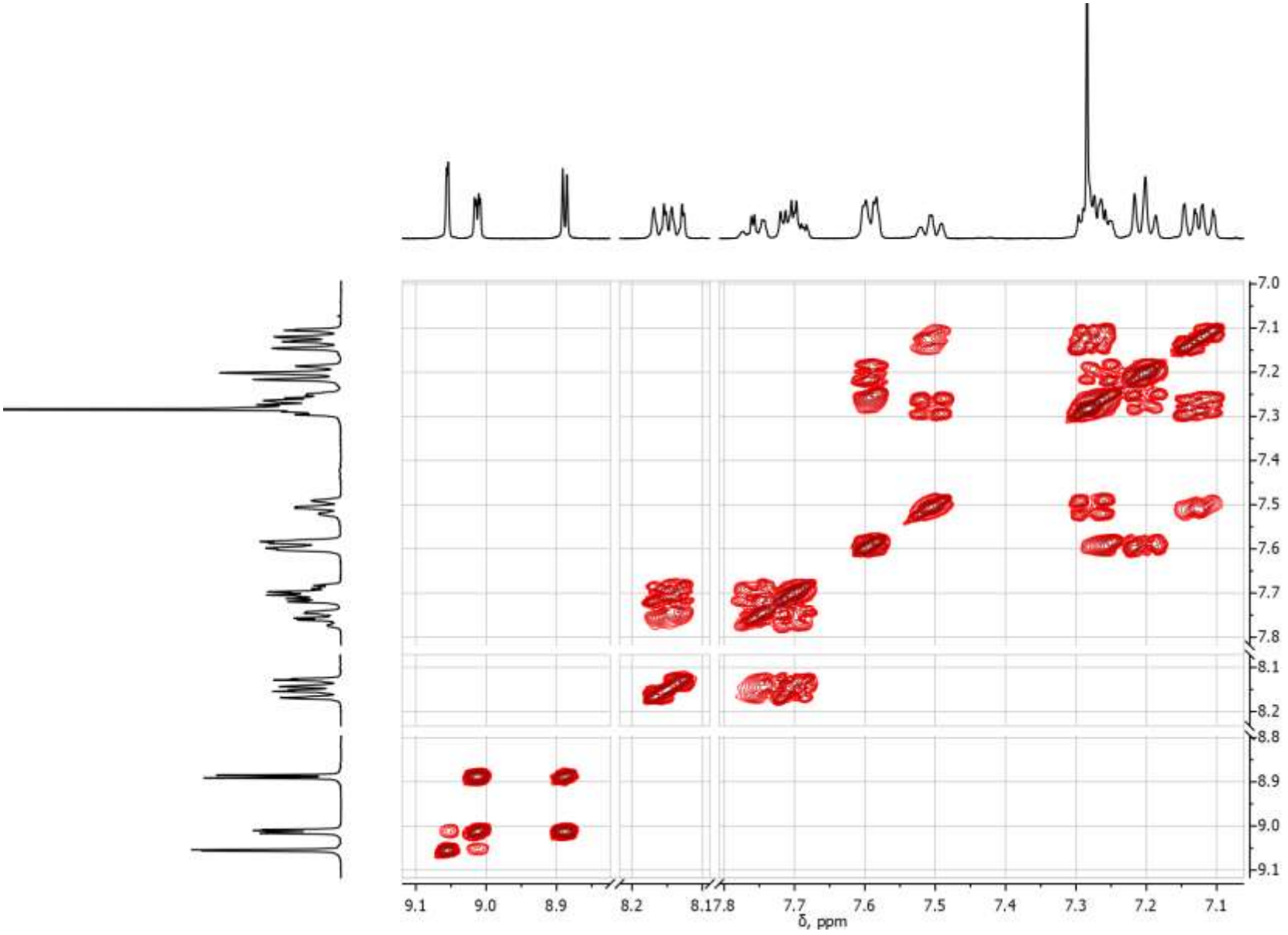


Figure S22. Fragments of the ^{1}H–^{1}H COSY spectrum of complex **3b** (500.13 MHz, $CDCl_3$)

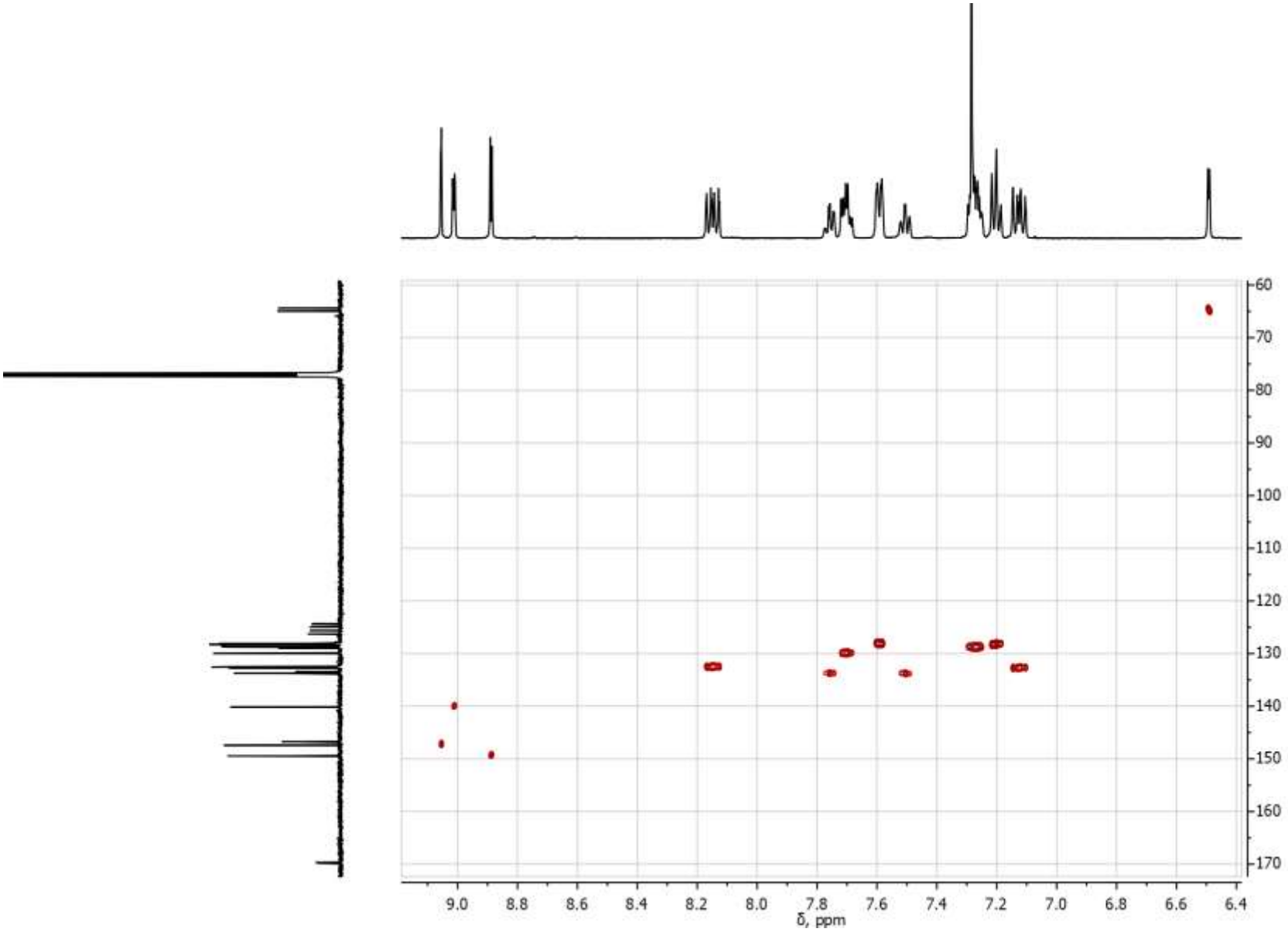


Figure S23. $^{1}H–^{13}C$ HSQC spectrum of complex **3b** ($CDCl_3$)

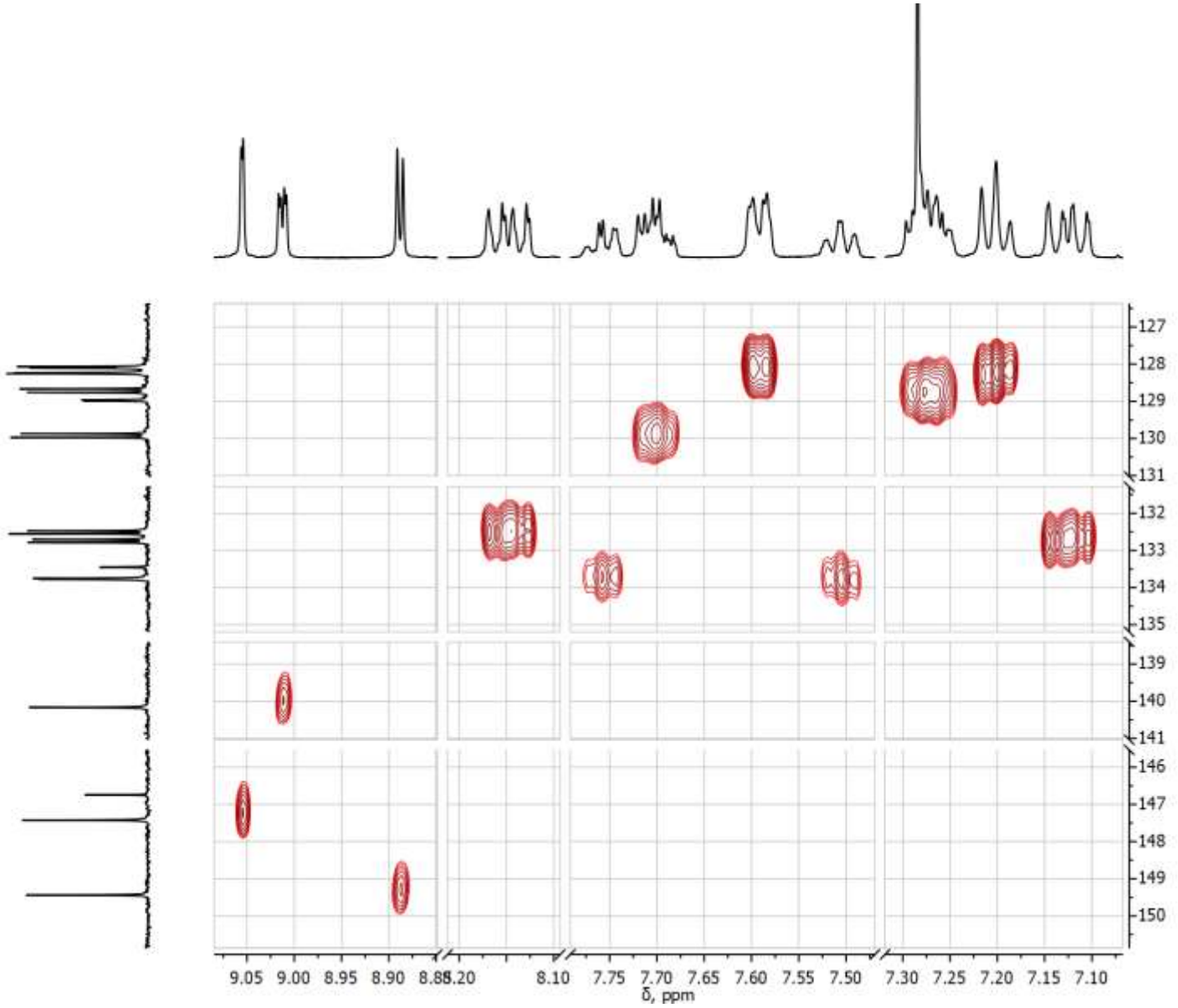


Figure S24. Fragments of the ^{1}H–^{13}C HSQC spectrum of complex **3b** ($CDCl_3$)

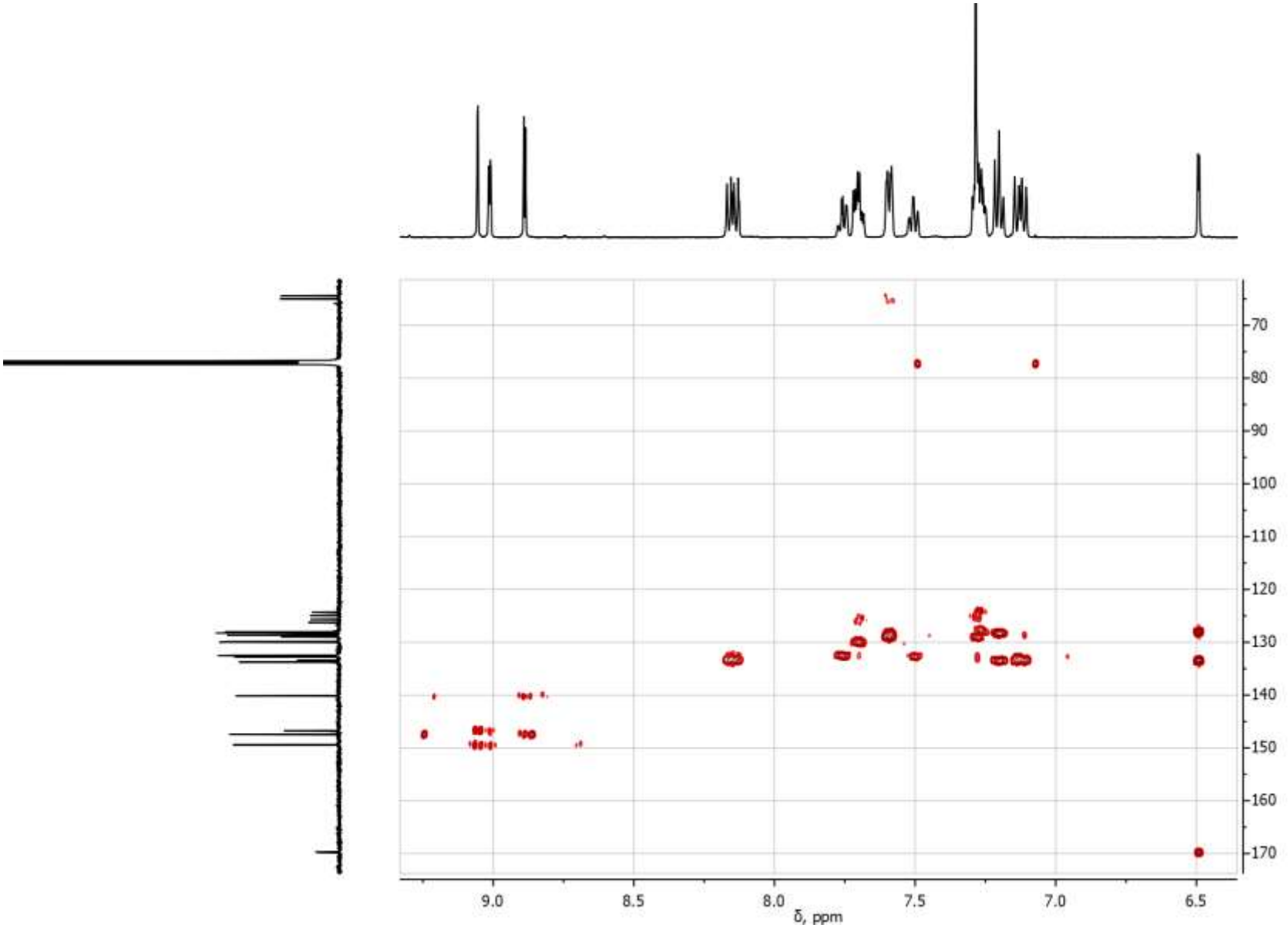


Figure S25. $^{1}H–^{13}C$ HMBC spectrum of complex **3b** ($CDCl_3$)

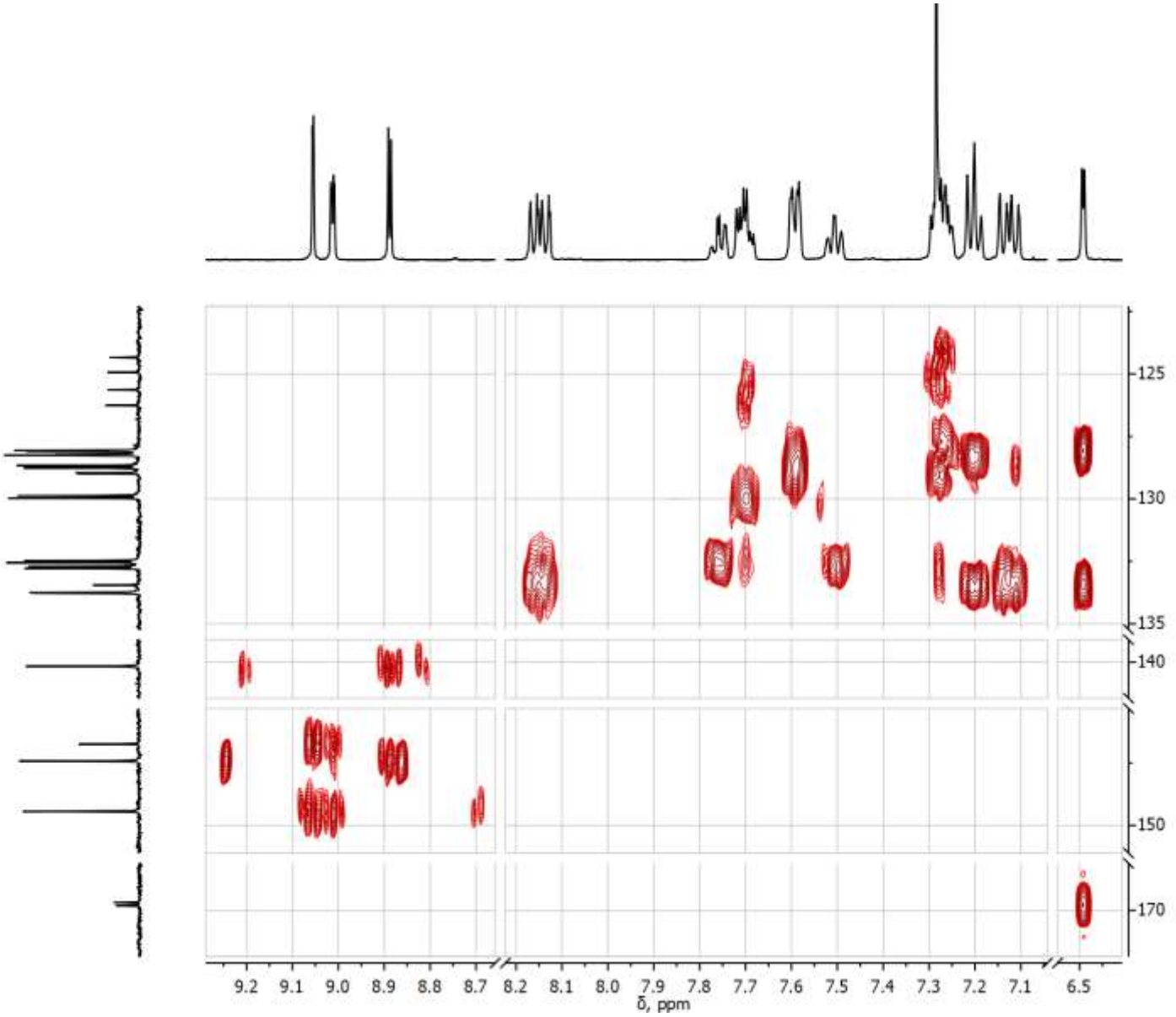


Figure S26. Fragments of the $^{1}H–^{13}C$ HMBC spectrum of complex **3b** ($CDCl_3$)

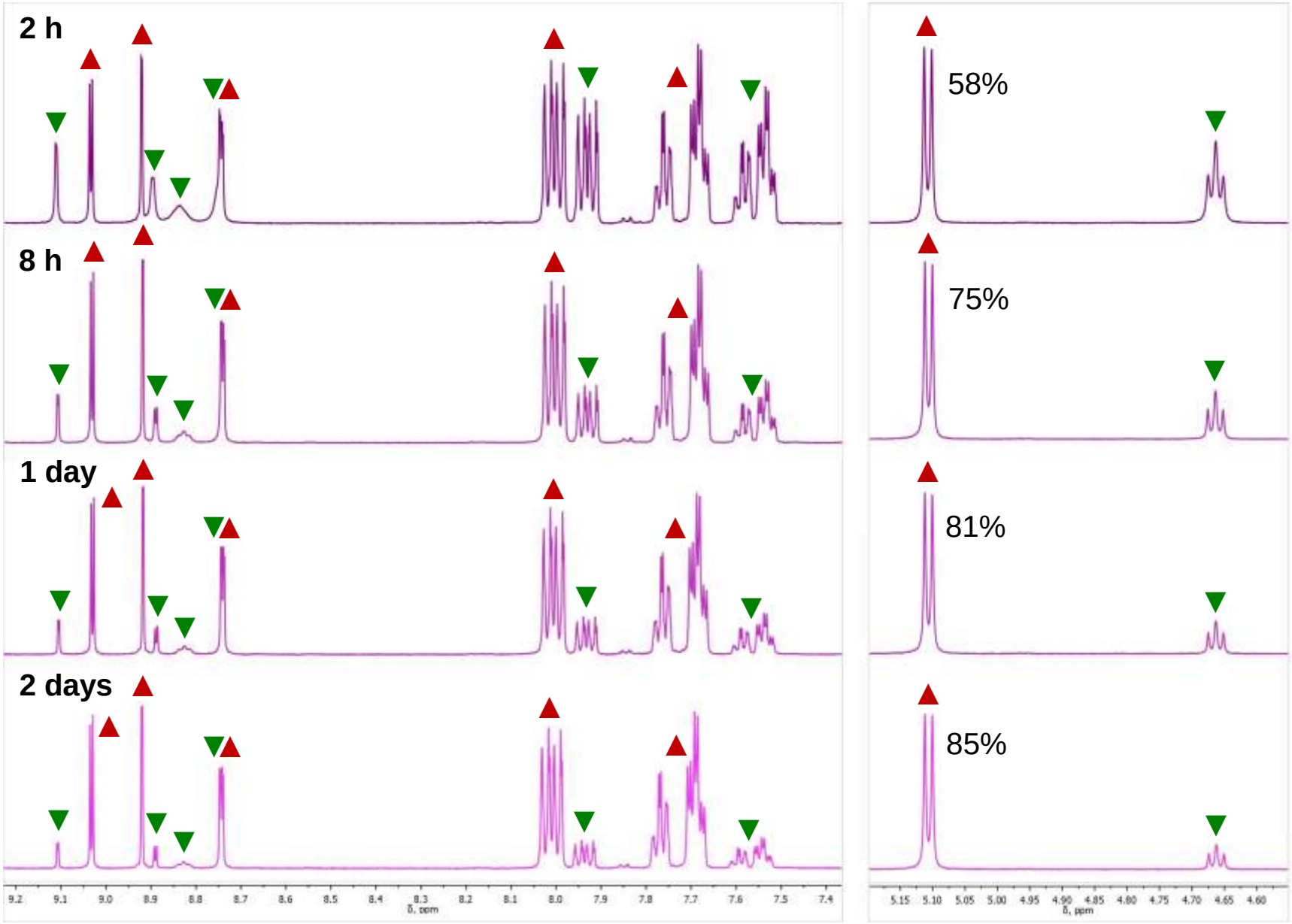


Figure S27. Fragments of the ^{1}H NMR spectra of complex **4** in $(CD_3)_2SO$ in 2 h, 8 h, 1 day and 2 days after dissolution

▼ signals of the bidentately bound complex; ▲ signals of the pincer complex