Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for

Unusual Rearrangement of Modified PNP Ligand-based Ru Complexes Relevant to Alcohol Dehydrogenation Catalysis

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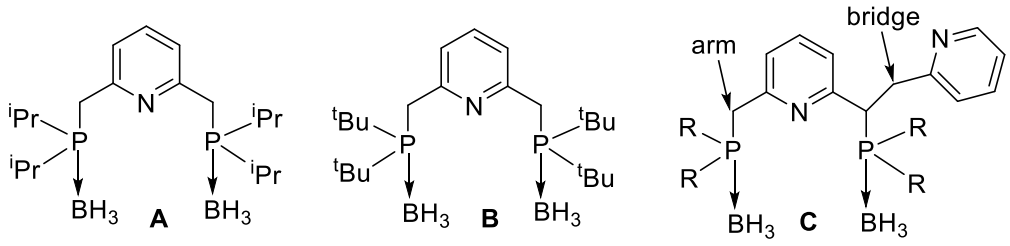
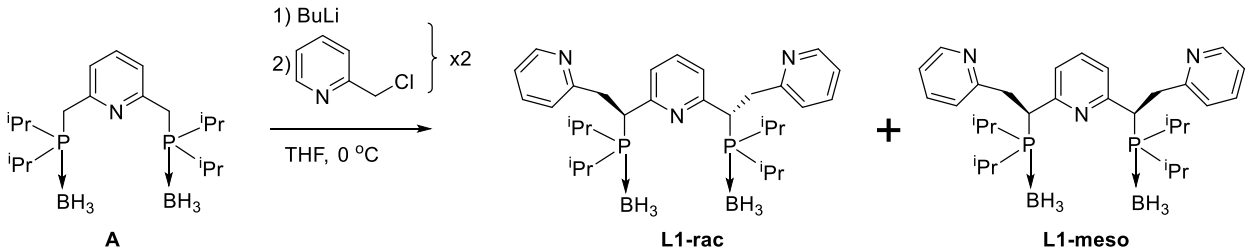
Experimental Procedures

General specification – All reactions were carried out under a nitrogen atmosphere using standard Schlenk and glove box techniques if not indicated otherwise. All reagents for which synthesis is not given were commercially available from Sigma-Aldrich, TCI and Nacalai Tesque and were used as received without further purification. NMR spectra were recorded on JEOL ECZ600R 600MHz, JEOL ECZ400S 400 MHz and Bruker Advance II 400 MHz spectrometers. Chemical shifts are reported in ppm and referenced to residual solvent resonance peaks. Abbreviations for the multiplicity of NMR signals are s (singlet), d (doublet), t (triplet), q (quartet), m (multiple), br (broad), v.t (virtual triplet), br.q (broad quartet), br.s (broad singlet), overlapping with major isomer (ov.maj), overlapping with minor isomer (ov.min), and tetramethyl silane (TMS). IR spectra were recorded using an Agilent Cary 630 spectrometer with a diamond ATR module. Elemental analyses were performed using an Exeter Analytical CE440 instrument. Electrospray Ionization Mass Spectrometry (ESI-MS) measurements were performed on a Thermo Scientific ETD apparatus. Ligands **A** and **B** were prepared according to the literature procedure.[1]Figure **C** correspond for the general nmr assignments.



Procedure for synthesis of borane complex of 2,6-bis(1-(diisopropylphosphaneyl)-2-(pyridin-2-yl)ethyl)pyridine.



Under an argon atmosphere in a flame dried flask, n-butyllithium (2.66 mmol) was added to a solution of **A** (2.72 mmol) in dry tetrahydrofuran (30 ml) at 0 °C and the mixture was stirred for two minutes, then 2-(chloromethyl)pyridine (2.66 mmol) was added to the reaction mixture, after

five minutes the same amount of n-butyllithium and 2-(chloromethyl)pyridine was sequentially added and the reaction mixture was allowed to reach room temperature and was stirred for 4 hours. Afterward the reaction mixture was quenched with water (30 ml) and extracted with diethyl ether (2×50 ml) and washed with a mixture of sodium bicarbonate (30 ml) and sodium chloride (30 ml). The extracted organic layers were combined and dried over magnesium sulfate and the desired product was isolated via flash column chromatography (diethyl ether: hexane, 1:1).

Ligand **L1** was obtained as a viscous liquid that solidifies to a white solid upon long periods of standing (**yield – 74%**). The ligand was obtained as a mixture of two diastereomers in a ratio of 1.63:1. It is possible to separate the diastereomers by careful flash column chromatography and increasing polarity very slowly from 2:3 ration onwards. However, the yields of pure diastereomer are very low, and it was not required for this project. The isomer mixture was used in subsequent reactions.

^{1}H NMR (600 MHz, $CDCl_3$): **major isomer** δ: 8.38 (m, 2H, py-*H*), 7.40-7.35 (m, 3H, ov.min, py-*H*), 7.10 (m, 2H, py-*H*), 6.99-6.96 (m, 2H, ov.min, py-*H*), 6.82 (d, 2H, *J* = 7.8 Hz, py-*H*), 4.14-4.08 (m, 2H, ov.min, arm-*H*), 3.62-3.47 (m, 4H, ov.min, bridge-*H*), 2.10-2.07 (m, 2H, ^{i}Pr-*H*), 1.92-1.85 (m, 2H, ov.min, ^{i}Pr-*H*), 1.22 (dd, 6H, *J* = 13.8, 7.2 Hz, ^{i}Pr-*Me*), 1.07 (dd, 6H, *J*=13.8, 7.2 Hz, ^{i}Pr-*Me*), 1.03-0.99 (m, 6H, ov.min, ^{i}Pr-*Me*), 0.92 (dd, 6H, *J*=13.8, 7.2 Hz, ^{i}Pr-*Me*), 0.6-0.1 (br.m, 6H, ov.min, BH_3). **minor isomer** δ: 8.40 (m, 2H, py-*H*), 7.40-7.35 (m, 3H, ov.maj, py-*H*), 7.09 (m, 2H, py-*H*), 6.99-6.96 (m, 2H, ov.maj, py-*H*), 6.85 (d, 2H, *J* = 7.8 Hz, py-*H*), 4.14-4.08 (m, 2H, ov.maj, arm-*H*), 3.62-3.47 (m, 4H, ov.maj, bridge-*H*), 2.30-2.23 (m, 2H, ^{i}Pr-*H*), 1.92-1.85 (m, 2H, ov.maj, ^{i}Pr-*H*), 1.29 (dd, 6H, *J* = 13.8, 7.2 Hz, ^{i}Pr-*Me*), 1.16 (dd, 6H, *J* =13.8, 7.2 Hz, ^{i}Pr-*Me*),1.03-0.99 (m, 6H, ov.maj, ^{i}Pr-*Me*), 0.89-0.85 (m, 6H, ^{i}Pr-*Me*), 0.6-0.1 (br.m, 6H, ov.maj, BH_3).

^{13}C NMR (151 MHz, $CDCl_3$): **major isomer** δ: 159.18-159.01 (py-*C*), 157.31(py-*C*), 149.35 (py-*C*), 136.26 (py-*C*), 136.03 (py-*C*), 123.56 (py-*C*), 123.32 (py-*C*), 121.36 (py-*C*), 41.28-40.96 (bridge-*C*), 38.05 (C_{arm}), 22.34-22.13 (^{i}Pr-*C*, d, $J_{P\text{-}C}$ = 21.14 Hz), 21.50-21.30 (^{i}Pr-*C*, d, $J_{P\text{-}C}$ = 7.55 Hz), 18.15-17.62 (m, ^{i}Pr-*Me*). **minor isomer** δ: 159.18-159.01 (py-*C*), 157.34 (py-*C*), 149.39 (py-*C*), 136.26 (py-*C*), 136.07 (py-*C*), 123.62 (py-*C*), 123.49 (py-*C*), 121.40 (py-*C*), 41.28-40.96 (bridge-*C*), 37.92 (C_{arm}), 22.19-22.00 (^{i}Pr-*C*, d, $J_{P\text{-}C}$ = 21.14 Hz), 21.45-21.25 (^{i}Pr-*C*, d, $J_{P\text{-}C}$ = 21.14 Hz), 18.15-17.62 (m, ^{i}Pr-*Me*).

^{31}P{1H} NMR (262 MHz, $CDCl_3$): δ 42.05-40.75 (br.q, 1P, both isomers overlap).

ESI-HRMS (m/z pos): Found (Calcd): $C_{31}H_{51}B_2N_3P_2$ $[M+H]^+$: 550.3813 (550.3817).

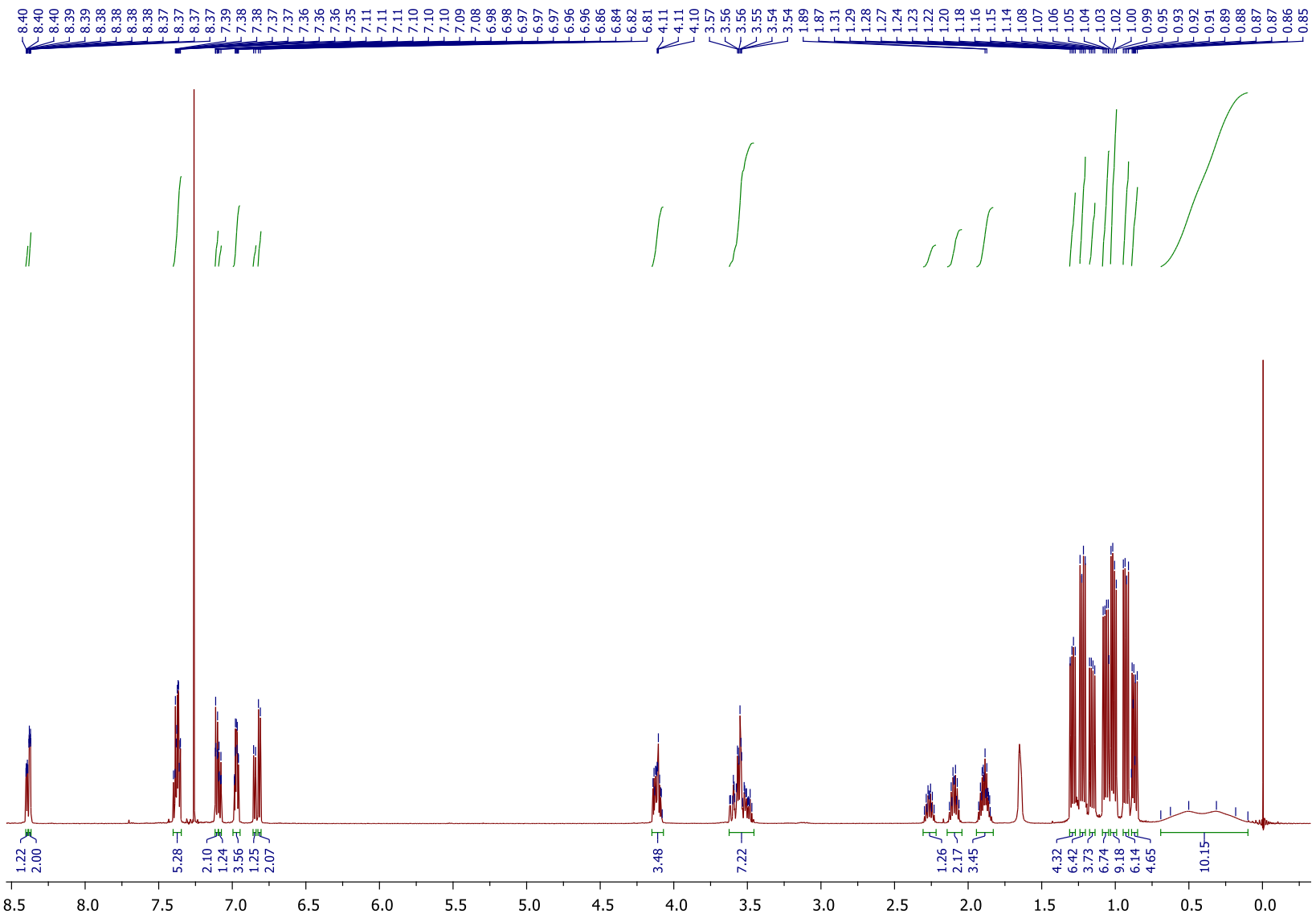


Figure S1. ^{1}H NMR spectrum of ligand **L1** in $CDCl_3$ at 23 °C.

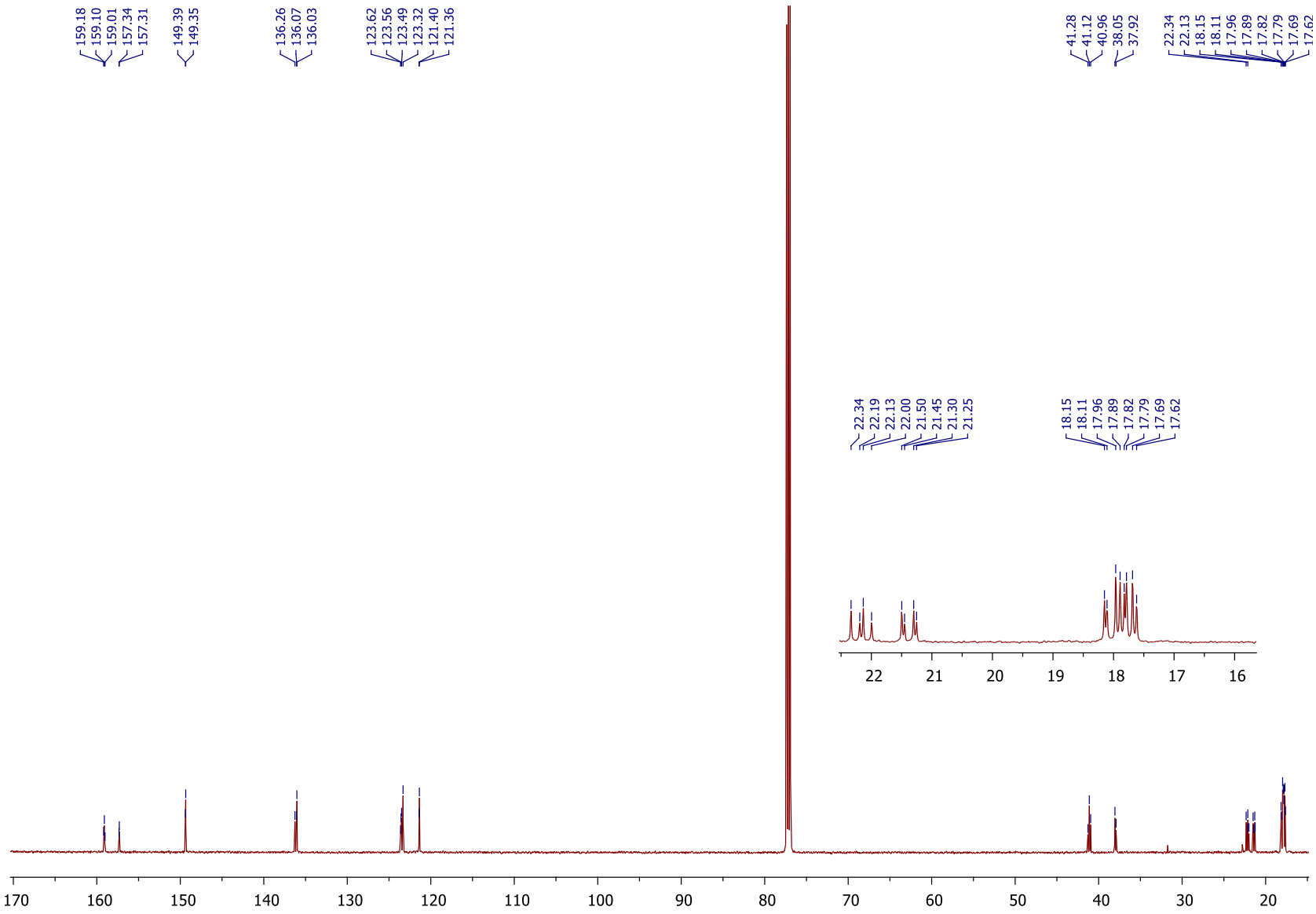


Figure S2. ^{13}C NMR spectrum of ligand **L1** in $CDCl_3$ at 23 °C.

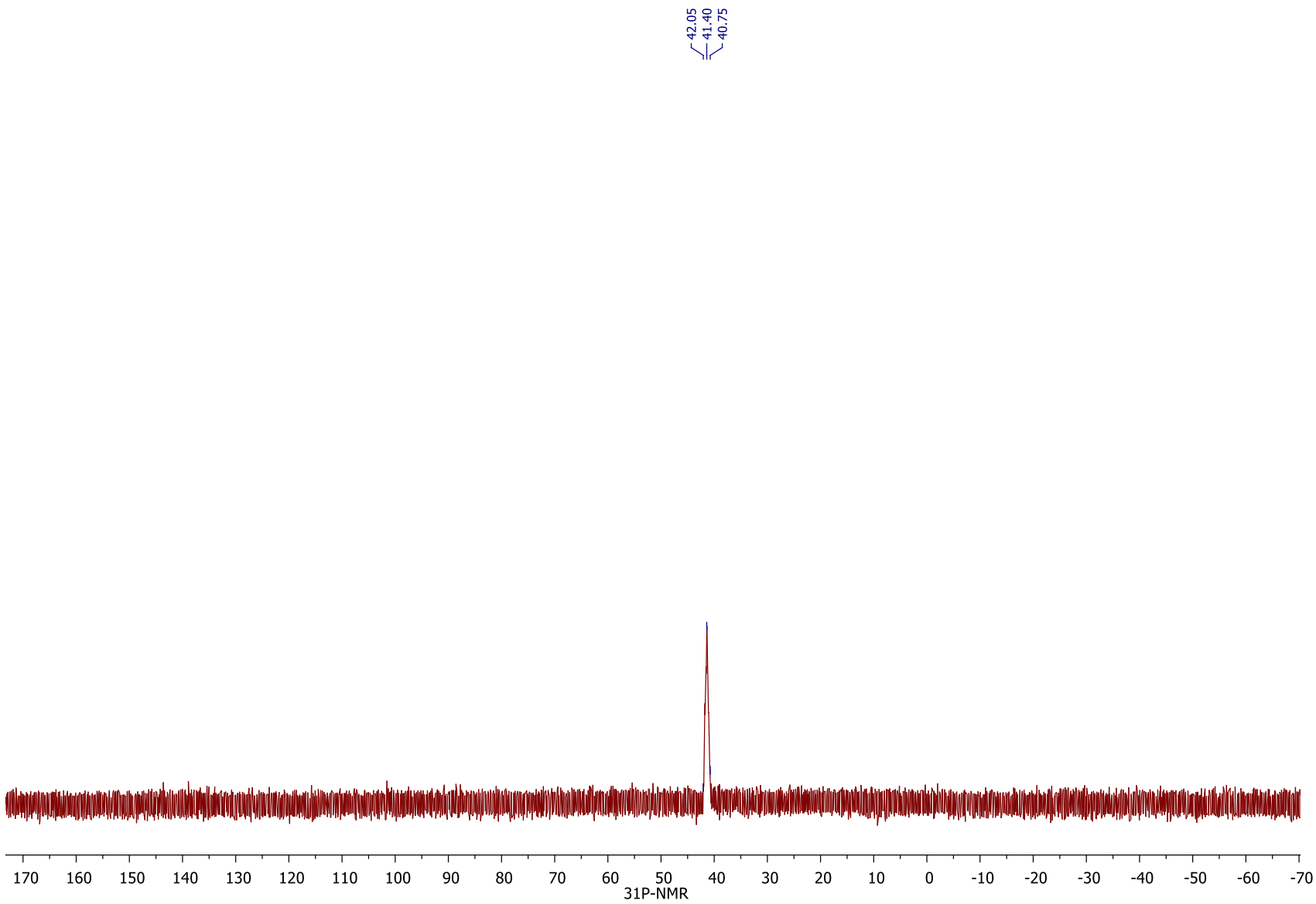


Figure S3. ^{31}P NMR spectrum of ligand **L1** in $CDCl_3$ at 23 ℃.

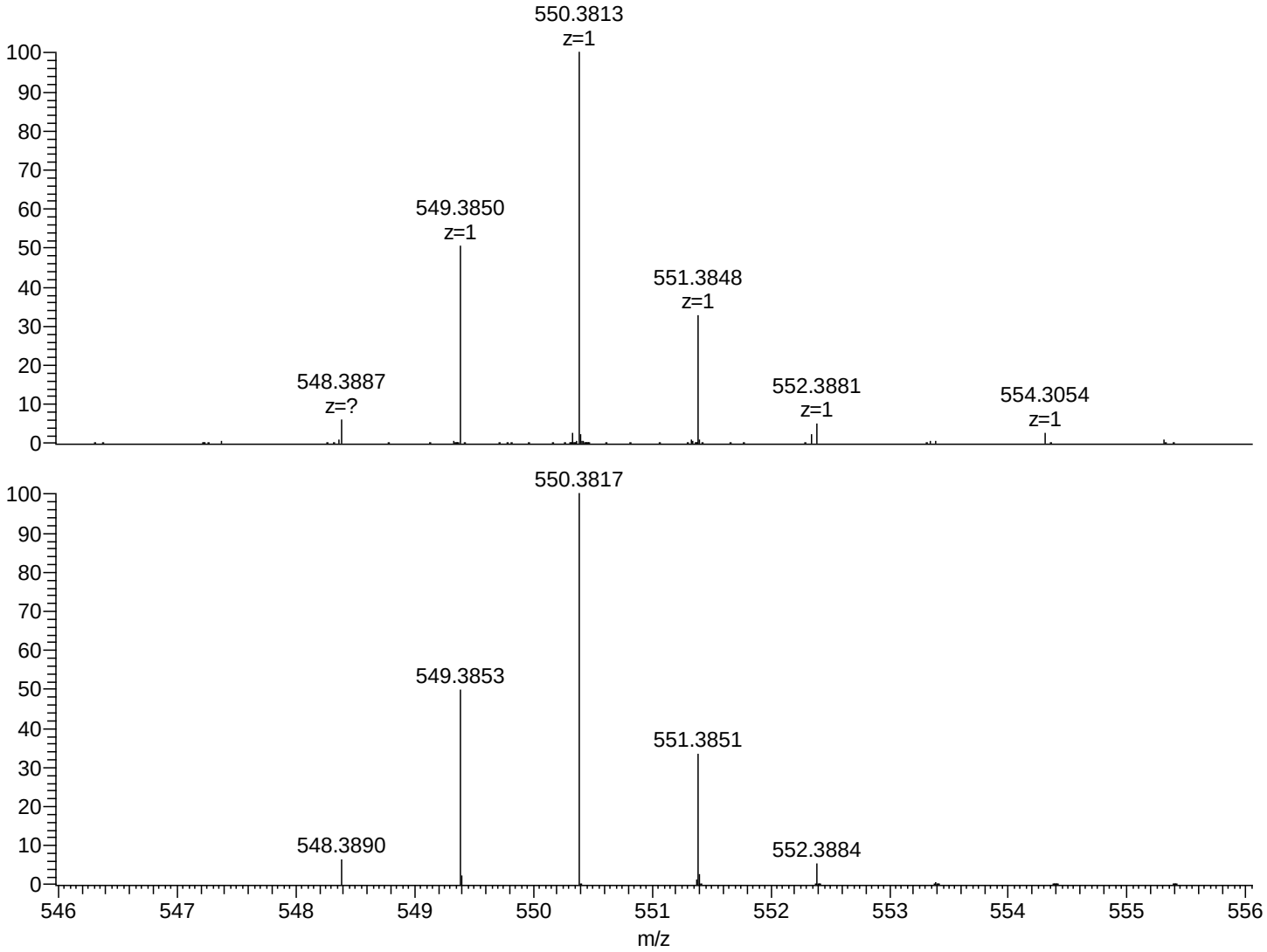
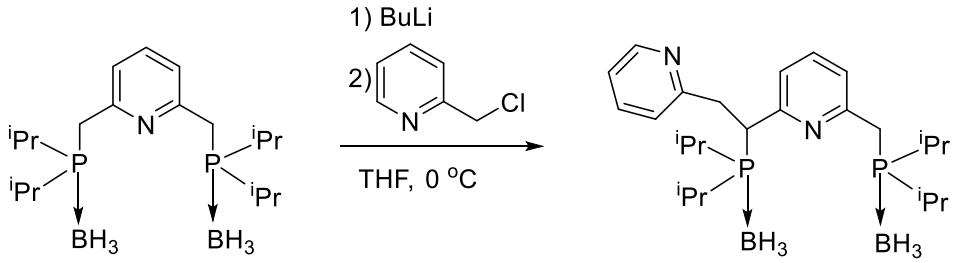


Figure S4. ESI - HRMS analysis in MeCN solution of **L1** (top) and simulated spectrum (below).

Procedure for synthesis of borane complex of 2-(1-(diisopropylphosphaneyl)-2-(pyridin-2-yl)ethyl)-6-((diisopropylphosphaneyl)methyl)pyridine.



Under an argon atmosphere in a flame dried flask n-butyllithium (2.66 mmol) was added to a solution of **A** (2.72 mmol) in dry tetrahydrofuran (30 ml) at 0 °C and the mixture was stirred for two minutes, then 2-(chloromethyl)pyridine (2.66 mmol) was added to the reaction mixture. The reaction was allowed to reach room temperature and was stirred for a further 4 hours. The reaction was quenched with water (20 ml), extracted with diethyl ether (2×50 ml) and washed with water, sodium bicarbonate (20 ml) and brine (20 ml). The collected organic layers were dried over magnesium sulfate and the desired product was isolated via flash column chromatography (diethyl ether: hexane, 7:13).

Ligand **L2** was obtained as a white solid. Yield 82%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.38 (d, 1H, *J* = 4.9 Hz, py-*H*), 7.46 (t, 1H, *J* = 7.7 Hz, py-*H*), 7.39 (t, 1H, *J* = 7.7 Hz, py-*H*), 7.17 (d, 1H, *J* = 7.7 Hz, py-*H*), 7.08 (d, 1H, *J* = 7.7 Hz, py-*H*), 6.98 (dd, 1H, *J* = 4.9, 7.7 Hz, py-*H*), 6.87 (d, 1H, *J* = 7.7Hz, py-*H*), 4.13 (td, 1H, *J* = 12.2, 2.7 Hz, arm-*H*), 3.64 (m, 1H, bridge-*H*), 3.53 (m, 1H, bridge-*H*), 3.11 (d, 2H, *J* = 11.1 Hz, arm-*H*), 2.28 (m, 1H, ^{i}Pr-*H*), 2.11 (dq, 1H, *J* = 14.3, 7.1 Hz, ^{i}Pr-*H*), 1.95 (m, 2H, ^{i}Pr-*H*), 1.31 (dd, 3H, *J* = 13.7, 7.1 Hz, ^{i}Pr-*Me*), 1.25 (dd, 3H, *J* = 13.7, 7.1 Hz, ^{i}Pr-*Me*), 1.14 (dd, 3H, *J* = 13.7, 7.1Hz, ^{i}Pr -*Me*), 1.09-1.00 (m, 15H, ^{i}Pr -*Me*), 0.6-0.03 (br.m, 6H, *BH*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$): δ 158.96 (py-*C*), 158.84 (py-*C*), 157.20 (py-*C*), 154.21 (py-*C*), 149.28 (py-*C*), 136.53 (py-*C*), 136.03 (py-*C*), 123.35 (py-*C*), 123.11 (py-*C*), 121.33 (py-*C*), 41.08 (*C*$_{arm}$, d, *J*$_{P-C}$ = 24.31 Hz), 37.80 (bridge-*C*), 30.39 (*C*$_{arm}$, d, *J*$_{P-C}$ = 26.31 Hz), 22.11-21.28 (m, ^{i}Pr-*C*), 17.96-16.92 (m, ^{i}Pr-*Me*).

^{31}P{1H} NMR (262 MHz, $CDCl_3$): δ 41.47-41.19 (br.q, 1P), 36.26-35.91 (br.q, 1P).

ESI - HRMS (m/z pos): Found (Calcd) : $C_{25}H_{46}B_2N_2P_2$ $[M+H]^+$: 459.3384 (459.3395).

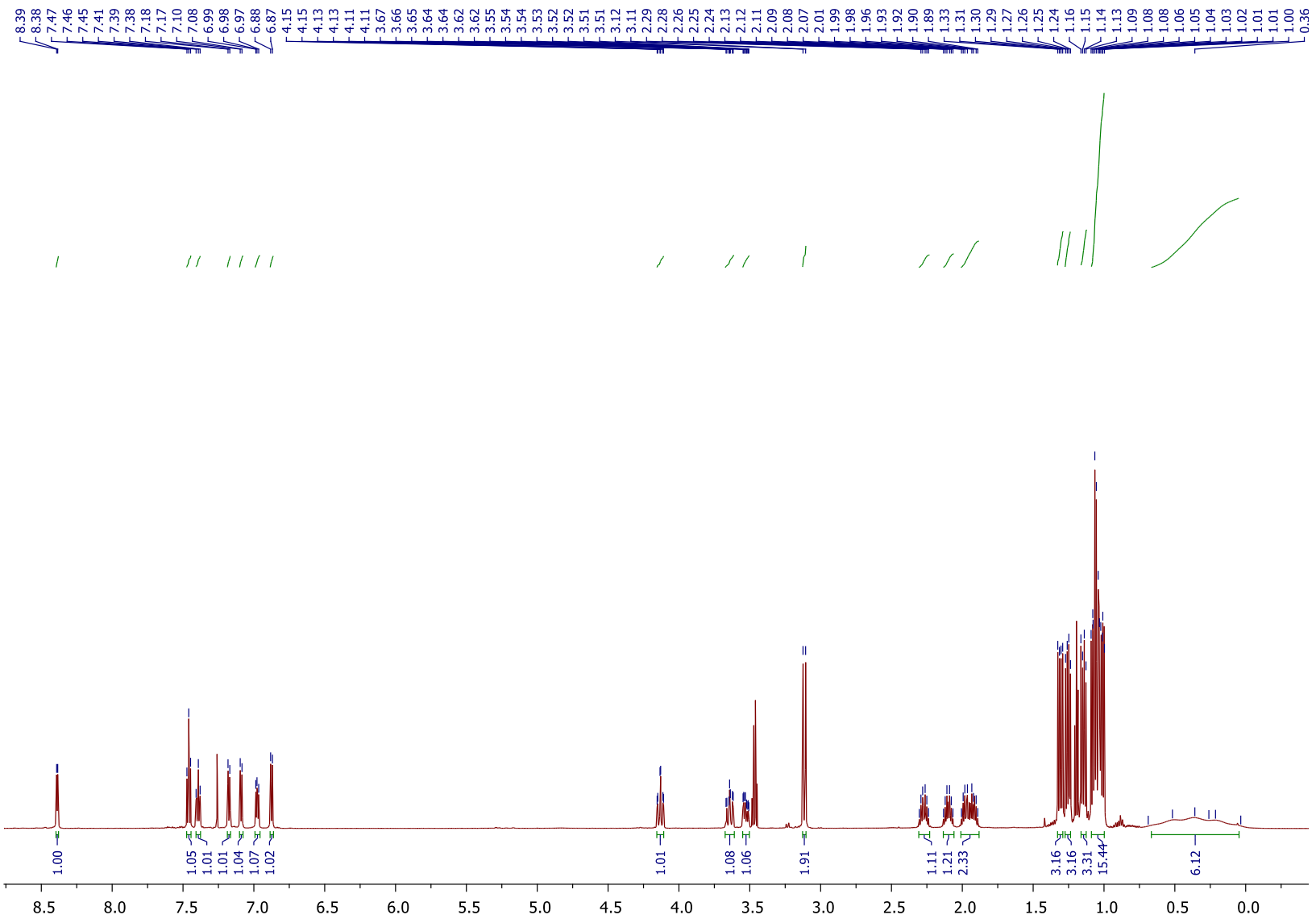


Figure S5. ^{1}H NMR spectrum of ligand **L2** in $CDCl_3$ at 23 ℃.

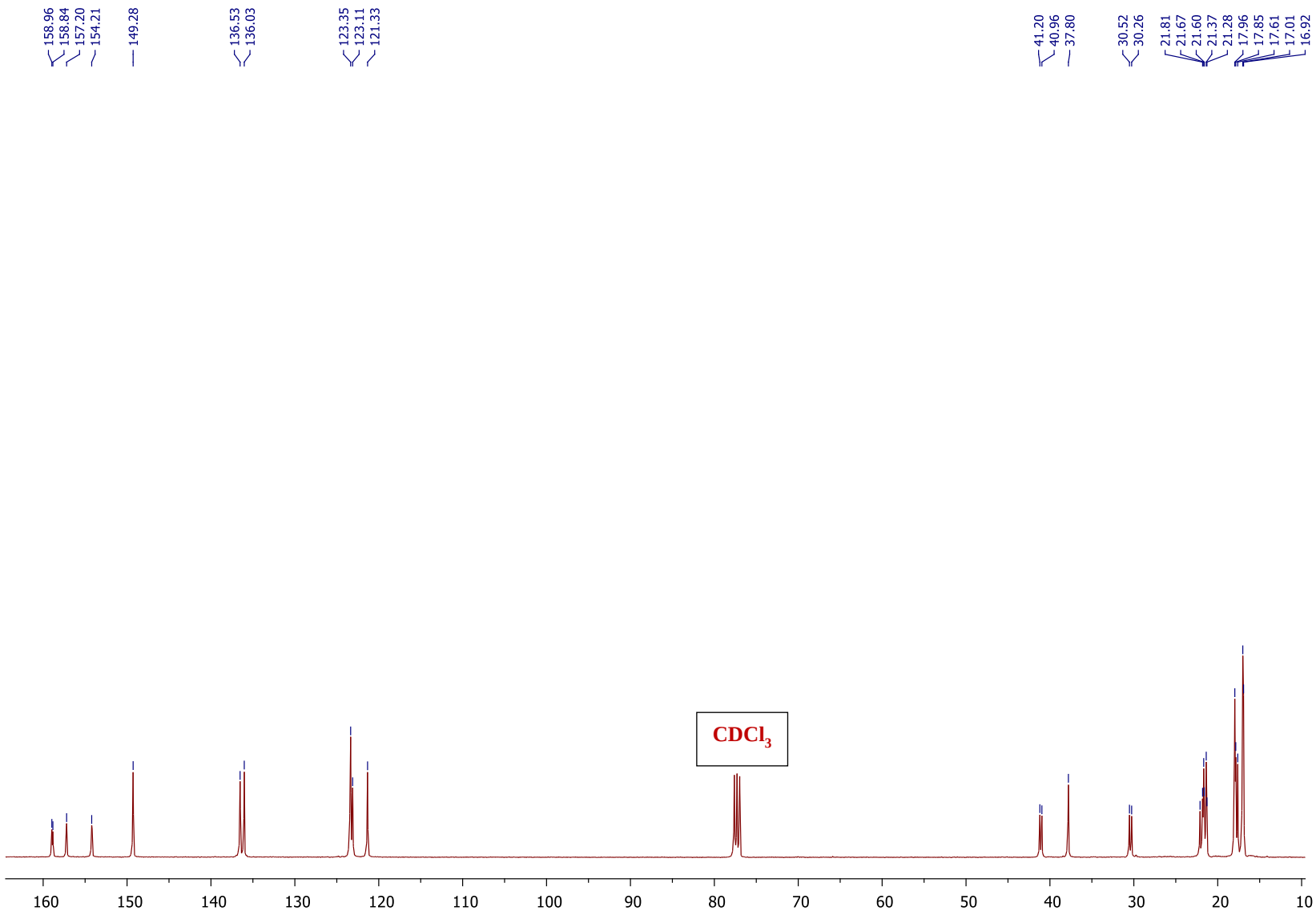


Figure S6. ^{13}C NMR spectrum of ligand **L2** in $CDCl_3$ at 23 °C.

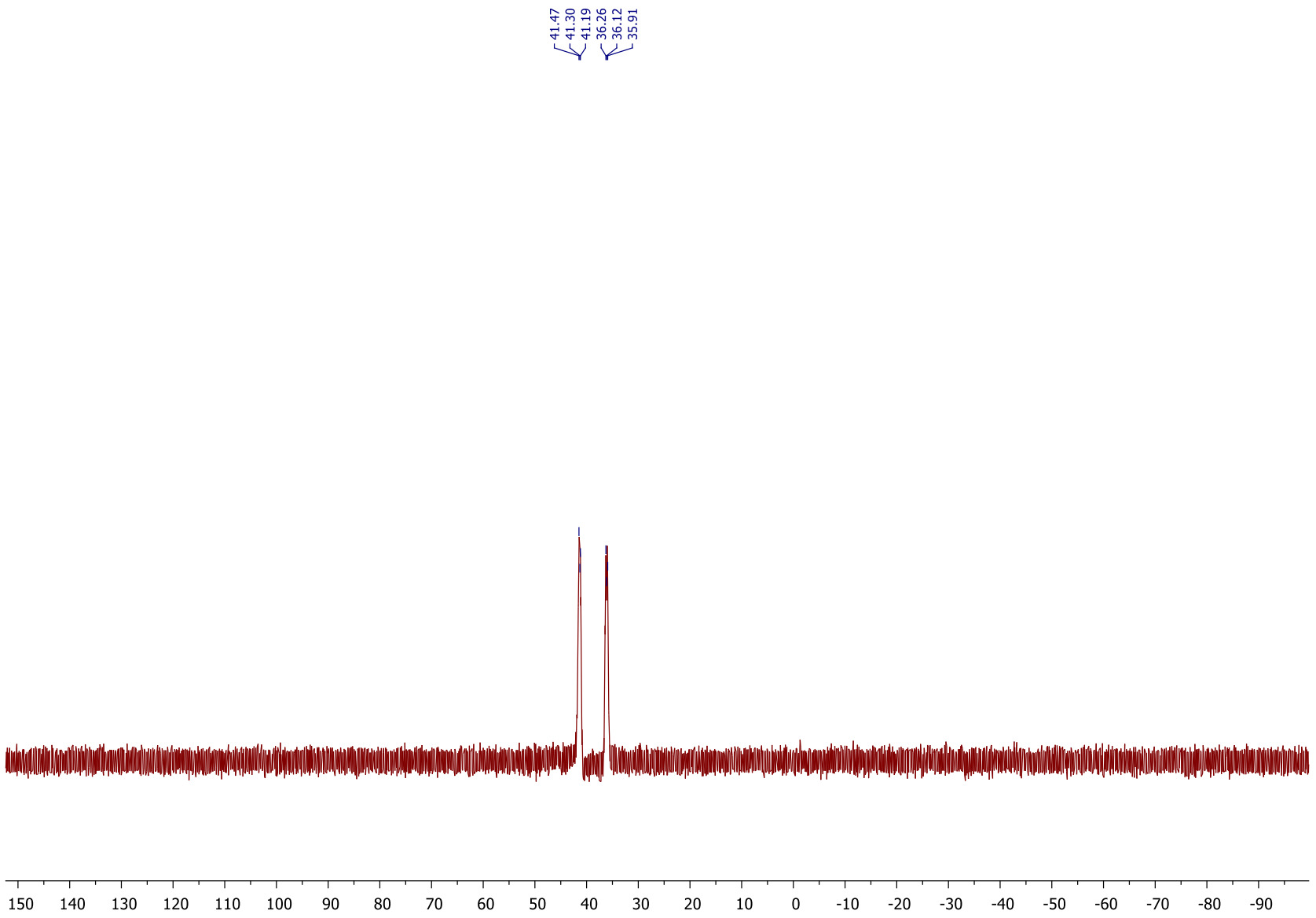


Figure S7. ^{31}P NMR spectrum of ligand **L2** in $CDCl_3$ at 23 °C.

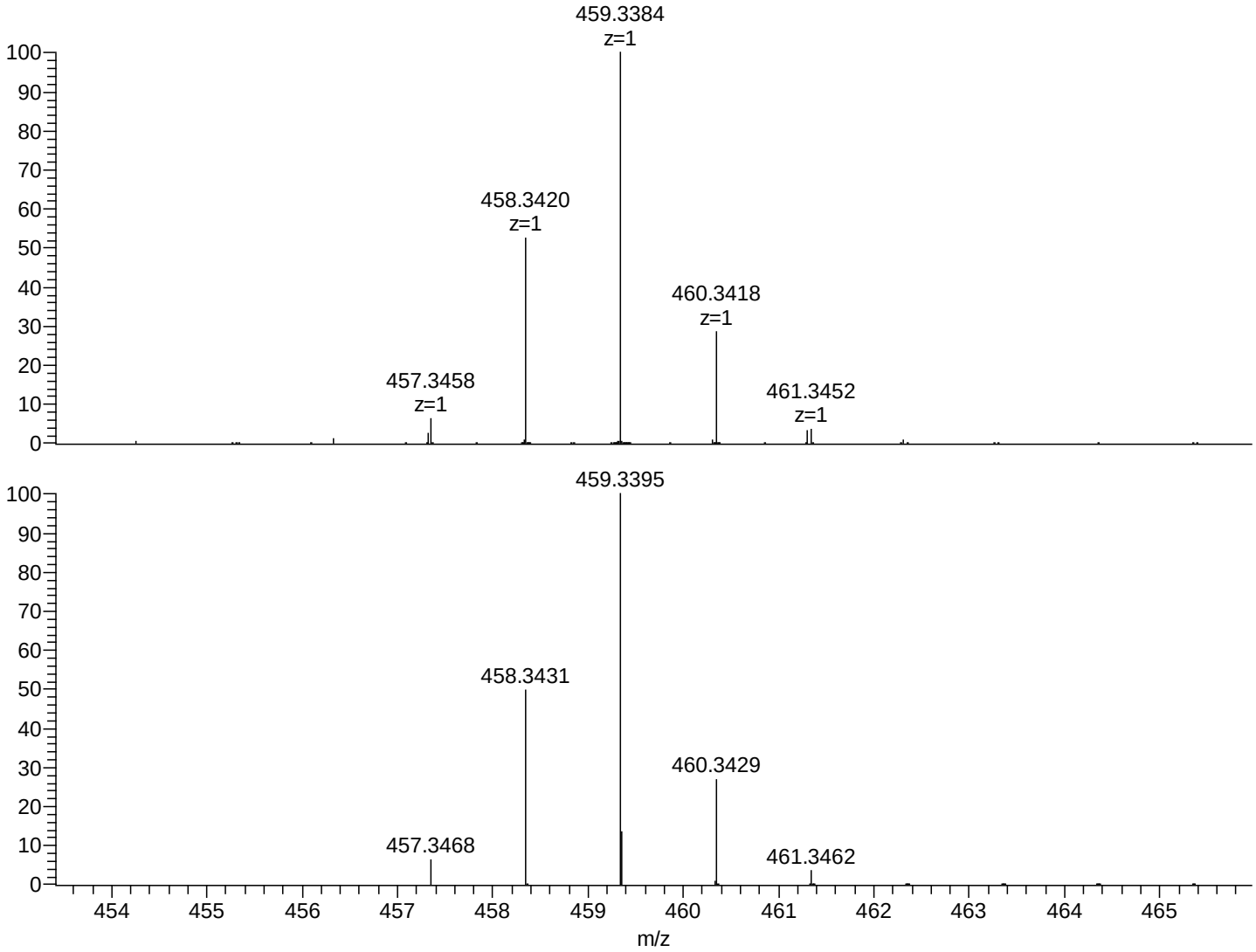
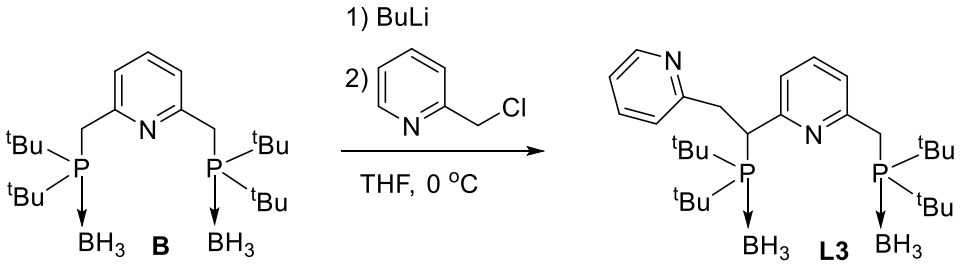


Figure S8. ESI - HRMS analysis in MeCN solution of **L2** (top) and simulated spectrum (below).

Procedure for synthesis of borane complex of 2-(1-(di-*tert*-butylphosphaneyl)-2-(pyridin-2-yl)ethyl)-6-((di-*tert*-butylphosphaneyl)methyl)pyridine.



Under an argon atmosphere in a flame dried flask n-butyllithium (2.66 mmol) was added to a solution of **B** (2.72mmol) in dry tetrahydrofuran (30 ml) at 0 ℃ and the mixture was stirred for two minutes, then 2-(chloromethyl)pyridine (2.66 mmol) was added to the reaction mixture. The reaction was allowed to reach room temperature and was stirred for a further 4 hours. The reaction was quenched with water (20 ml), extracted with diethyl ether (2×50 ml) and washed with water, sodium bicarbonate (20 ml) and brine (20 ml). The collected organic layers were dried over magnesium sulfate and the desired product was isolated via flash column chromatography (diethyl ether: hexane, 3:7).

Ligand **L3** was obtained as white solid. Yield 79%. ^{1}H NMR (600 MHz, C_6D_6): δ 8.37 (m, 1H, py-*H*), 7.32 (t, 1H, *J* = 4.4 Hz, py-*H*), 6.91 (td, 1H, *J* = 7.6, 1.8Hz, py-*H*), 6.87 (d, 2H, *J* = 4.4 Hz, py-*H*), 6.70 (d, 1H, *J* = 7.6 Hz, py-*H*), 6.51 (m, 1H, py-*H*), 4.62 (td, 1H, *J* = 11.5, 1.9 Hz, arm-*H*), 4.11 (dd, 1H, *J* = 13.2, 7.2 Hz, bridge-*H*), 3.82 (m, 1H, arm-*H*), 3.16 (t, 1H, *J* = 13.2 Hz, arm-*H*), 2.96 (dd, 1H, *J* = 14.1, 11.2 Hz, bridge-*H*), 1.46 (m, 9H, ^{t}Bu-*Me*)**,** 1.34 (m, 9H, ^{t}Bu-*Me*)**,** 1.10-1.04 (m, 18H, ^{t}Bu-*Me*)**,** 1.3-1.1 (br.m, 6H, *BH_3*).

^{13}C NMR (151 MHz, C_6D_6): δ 159.84 (py-*C*), 158.69 (py-*C*), 154.87 (py-*C*), 149.48 (py-*C*), 135.81 (py-*C*), 135.59 (py-*C*), 125.16 (py-*C*), 124.12 (py-*C*), 123.88 (py-*C*), 121.34 (py-*C*), 44.37 (*C_{arm}*, d, *J_{P-C}* = 18.71 Hz), 40.81 (bridge-*C*), 35.18 (^{t}Bu-*C*, d, *J_{P-C}* = 21.6 Hz), 34.81 (^{t}Bu-*C*, d, *J_{P-C}* = 21.9 Hz), 32.86 (^{t}Bu-*C*, d, *J_{P-C}* = 24.4 Hz), 32.52 (^{t}Bu-*C*, d, *J_{P-C}* = 24.9 Hz), 29.67 (^{t}Bu-*Me*), 29.53 (^{t}Bu-*Me*), 28.85 (*C_{arm}*, d, *J_{P-C}* = 22.6 Hz), 28.27 (^{t}Bu-*Me*), 28.08 (^{t}Bu-*Me*).

^{31}P{1H} NMR (262 MHz, C_6D_6): δ 57.21-57.00 (br.q, 1P), 48.38-48.14 (br.q, 1P).

ESI - HRMS (m/z pos): Found (Calcd) : $C_{29}H_{54}B_2N_2P_2$ $[M+H]^+$: 515.4032 (515.4021).

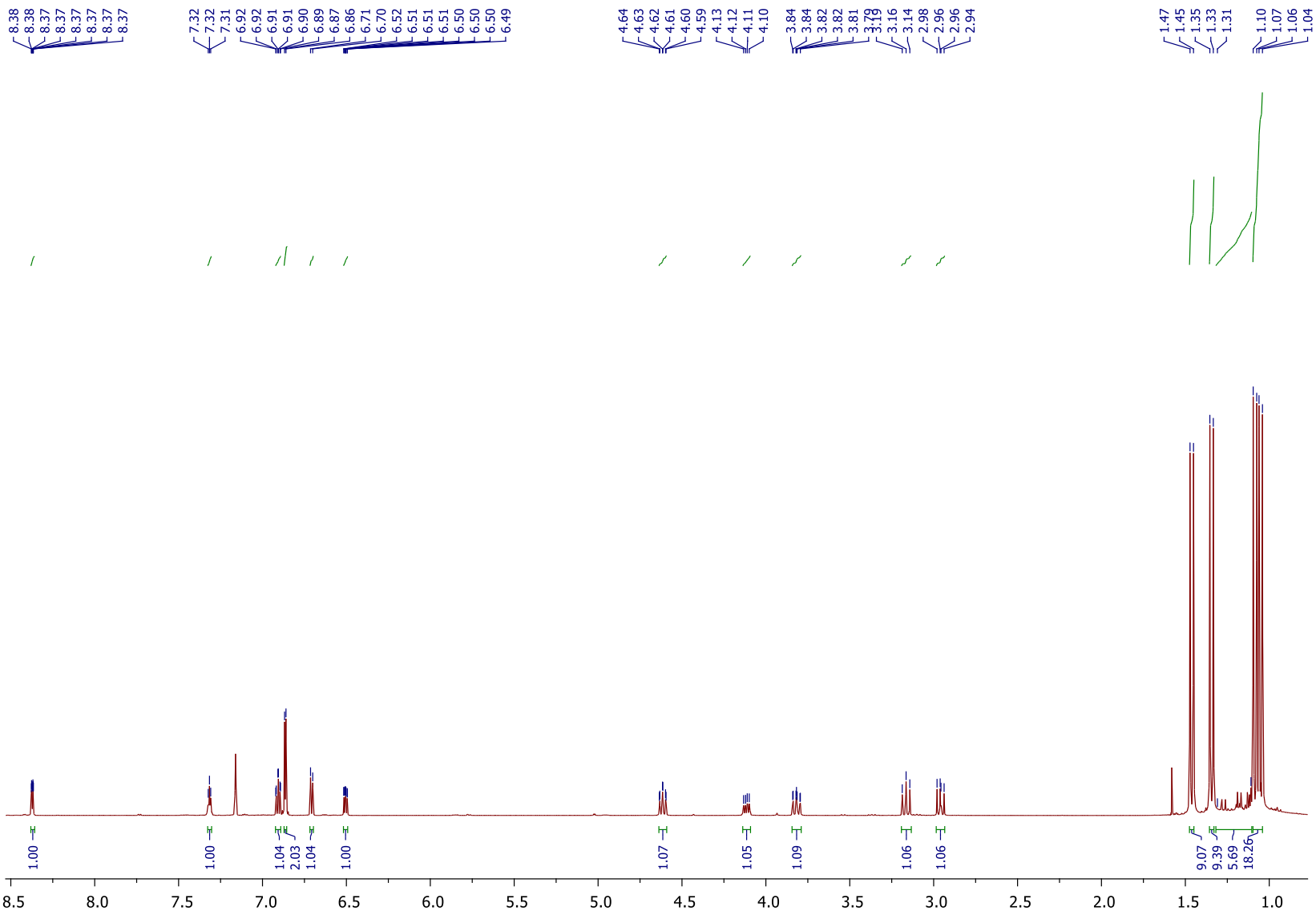


Figure S9. ^{1}H NMR spectrum of ligand **L3** in C_6D_6 at 23 °C.

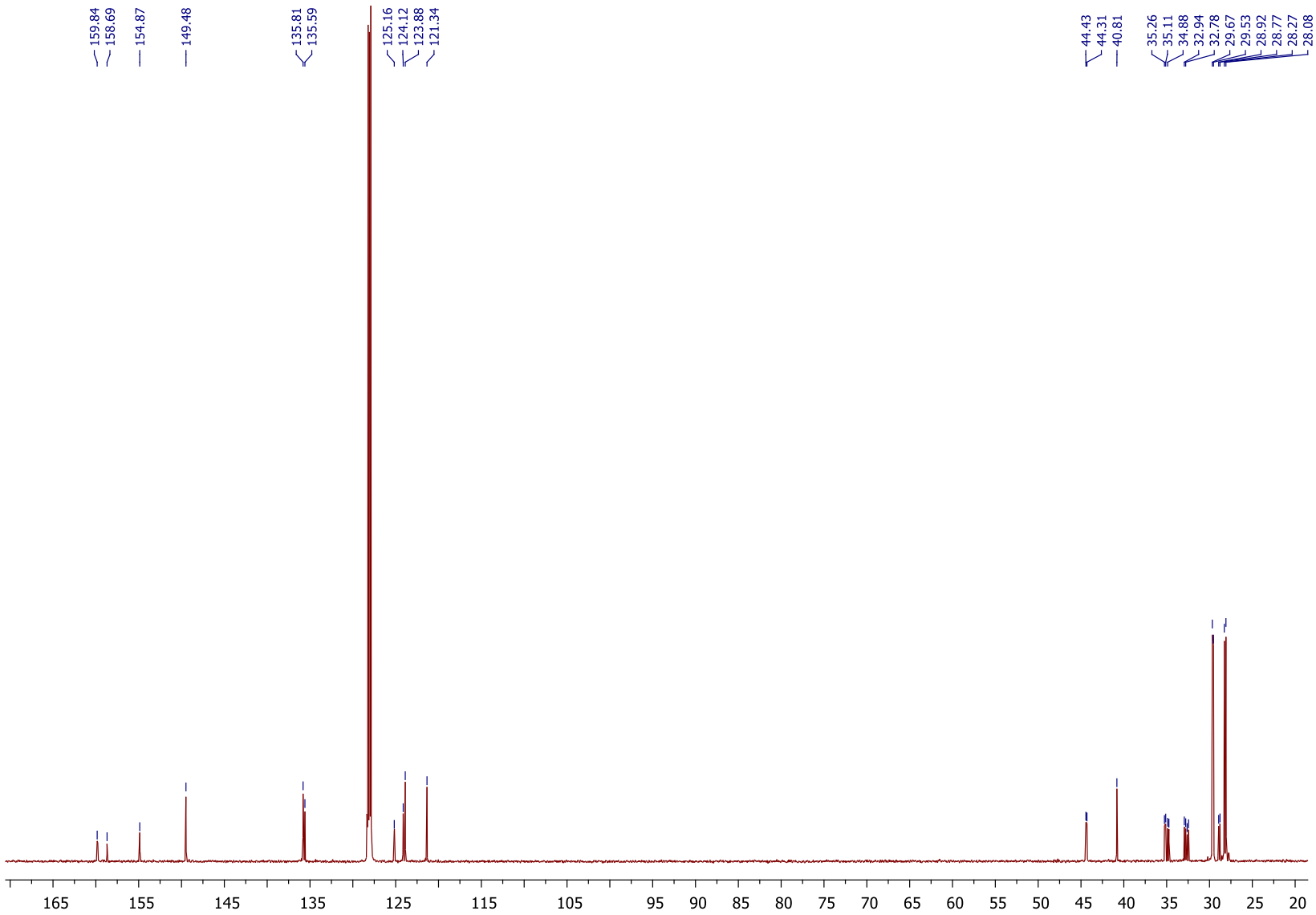


Figure S10. ^{13}C NMR spectrum of ligand **L3** in C_6D_6 at 23 °C.

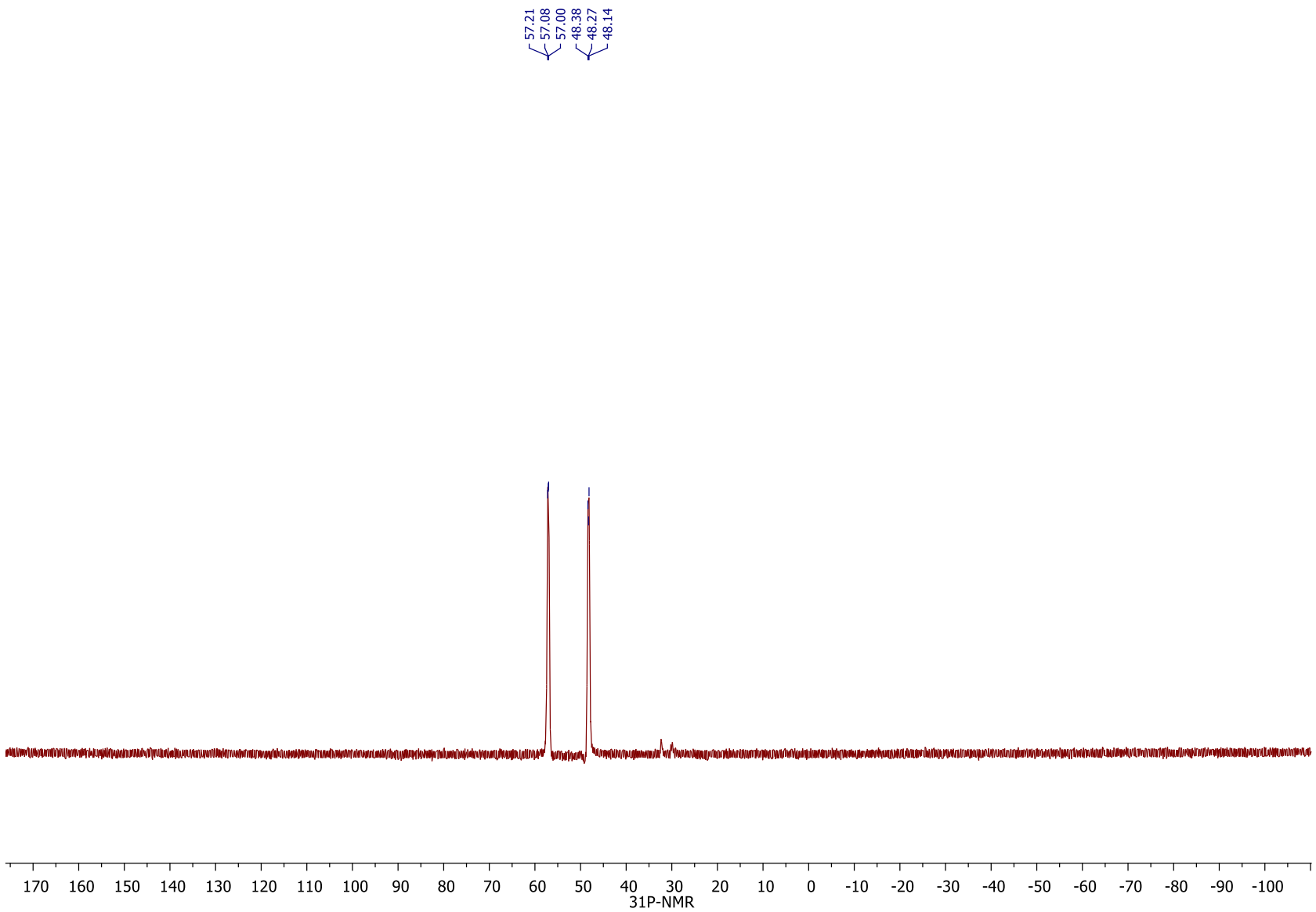


Figure S11. ^{31}P NMR spectrum of ligand **L3** in C_6D_6 at 23 °C.

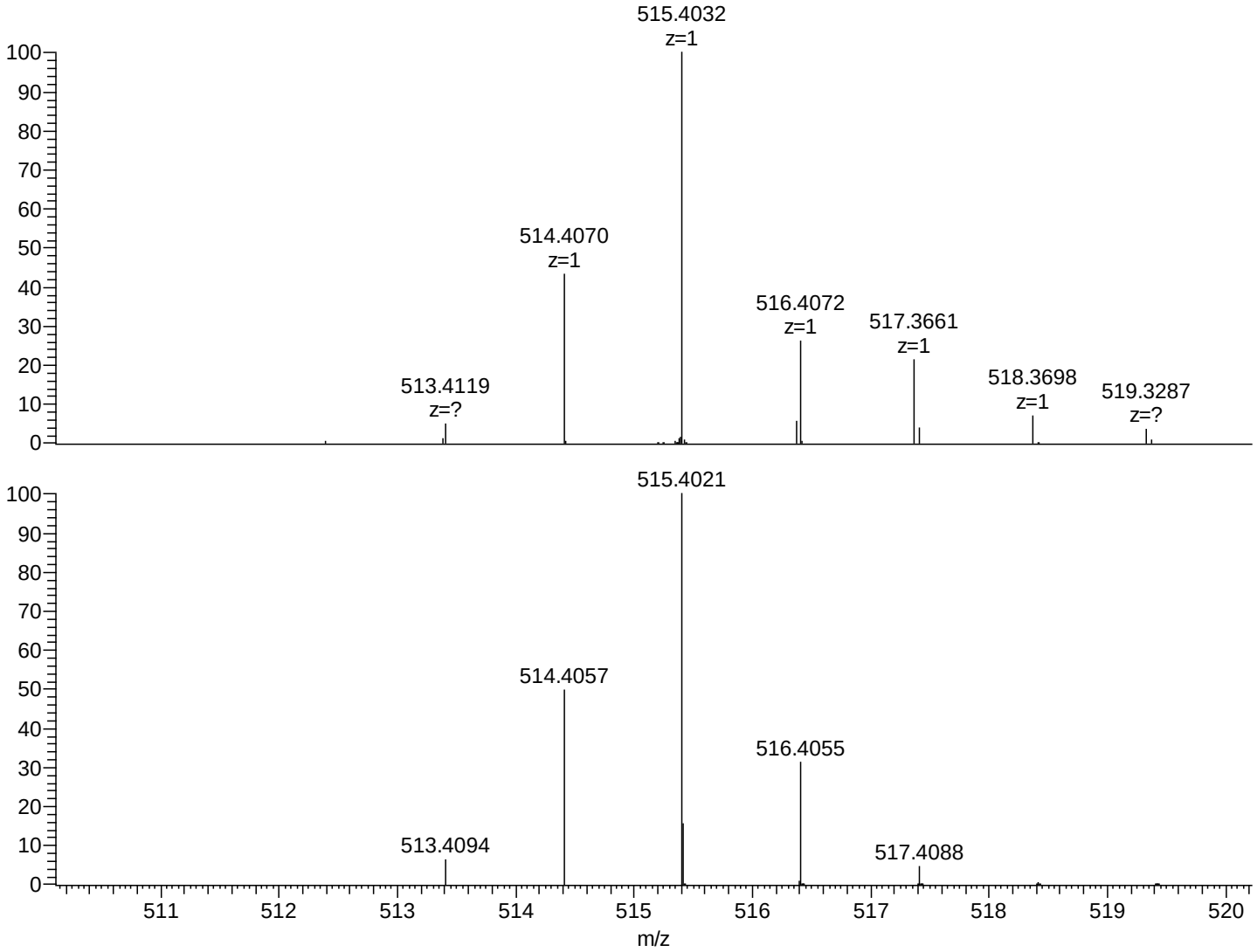
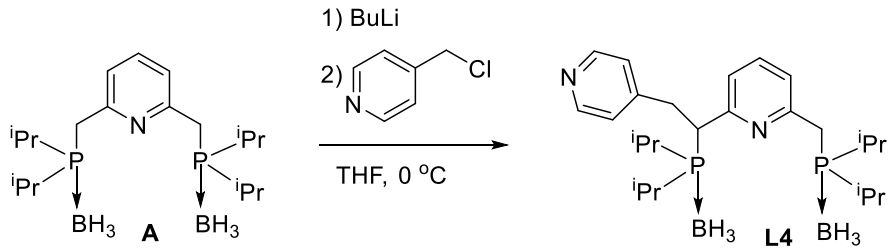


Figure S12. ESI - HRMS analysis in MeCN solution of **L3** (top) and simulated spectrum (below).

Procedure for synthesis of borane complex of 2-(1-(diisopropylphosphaneyl)-2-(pyridin-4-yl)ethyl)-6-((diisopropylphosphaneyl)methyl)pyridine.



Under an argon atmosphere in a flame dried flask n-butyllithium (2.66 mmol) was added to a solution of **B** (2.72mmol) in dry tetrahydrofuran (30 ml) at 0 ℃ and the mixture was stirred for two minutes, then 4-(chloromethyl)pyridine (2.66 mmol) was added to the reaction mixture. The reaction was allowed to reach room temperature and was stirred for a further 4 hours. The reaction was quenched with water (20 ml), extracted with diethyl ether (2×50 ml) and washed with water, sodium bicarbonate (20 ml) and brine (20 ml). The collected organic layers were dried over magnesium sulfate and the desired product was isolated via flash column chromatography (diethyl ether: hexane, 9:1). A common impurity that is always obtained in these reactions is the bis-pyridyl modified ligand. In the case of **L4**, we could not completely obtain pure product via traditional flash column chromatography that was free of the bis-pyridyl impurity that is present in ca. 5% amount. However, the associated metal complex **4** could be conveniently purified by crystallization. However, analytical samples of the pure ligand could be obtained by HPLC separation suggesting that pure ligand can be prepared conveniently by preparatory HPLC when required.

Ligand **L4** was isolated as a white solid. Yield 75%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.34 (d, 2H, *J* = 6.1Hz, py-*H*), 7.50 (t, 1H, *J* = 7.7 Hz, py-*H*), 7.19 (d, 1H, *J* = 7.7 Hz, py-*H*), 7.03 (d, 1H, *J* = 7.7 Hz, py-*H*), 6.86 (m, 2H, py-*H*), 3.52 (td, 1H, *J* = 11.6, 2.9 Hz, arm-*H*), 3.46-3.38 (m, 2H, arm-*H*), 3.16-3.13 (m, 2H, bridge-*H*), 2.21-2.14 (m, 2H, iPr-*H*), 2.02-1.89 (m, 2H, iPr-*H*), 1.25 (dd, 3H, *J* = 14, 7.2 Hz, ^{i}Pr-*Me*), 1.21 (dd, 3H, *J* = 14, 7.2 Hz, ^{i}Pr-*Me*), 1.13-1.03 (m, 18H, iPr-*Me*), 0.73-0.17 (br.m, 6H, BH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ 156.46 (py-*C*), 154.94 (py-*C*), 149.75 (py-*C*), 149.00 (py-*C*), 136.91 (py-*C*), 123.92 (py-*C*), 123.81 (py-*C*), 123.06 (py-*C*), 43.33 (C_{arm}, d, J_{P-C} = 22.6 Hz), 35.66 (bridge-*C*), 30.45 (C_{arm}, d, J_{P-C} = 25.9 Hz), 22.21 (^{i}Pr-*C*, d, J_{P-C} = 30.4 Hz), 21.99-21.76 (m, ^{i}Pr-

C), 21.45 (^{i}Pr-*C*, d, J_{P-C} = 30.4 Hz), 18.14 (^{i}Pr-*Me*), 17.79 (^{i}Pr-*Me*),17.60 (^{i}Pr-*Me*), 17.08-16.99 (m, ^{i}Pr-*Me*).

^{31}P{1H} NMR (262 MHz, $CDCl_3$): δ 42.78-42.53 (br.q, 1P), 36.61-36.30 (br.q, 1P).

ESI - HRMS (m/z pos): Found (Calcd) : $C_{25}H_{46}B_2N_2P_2$ $[M+H]^+$: 459.3386 (459.3395).

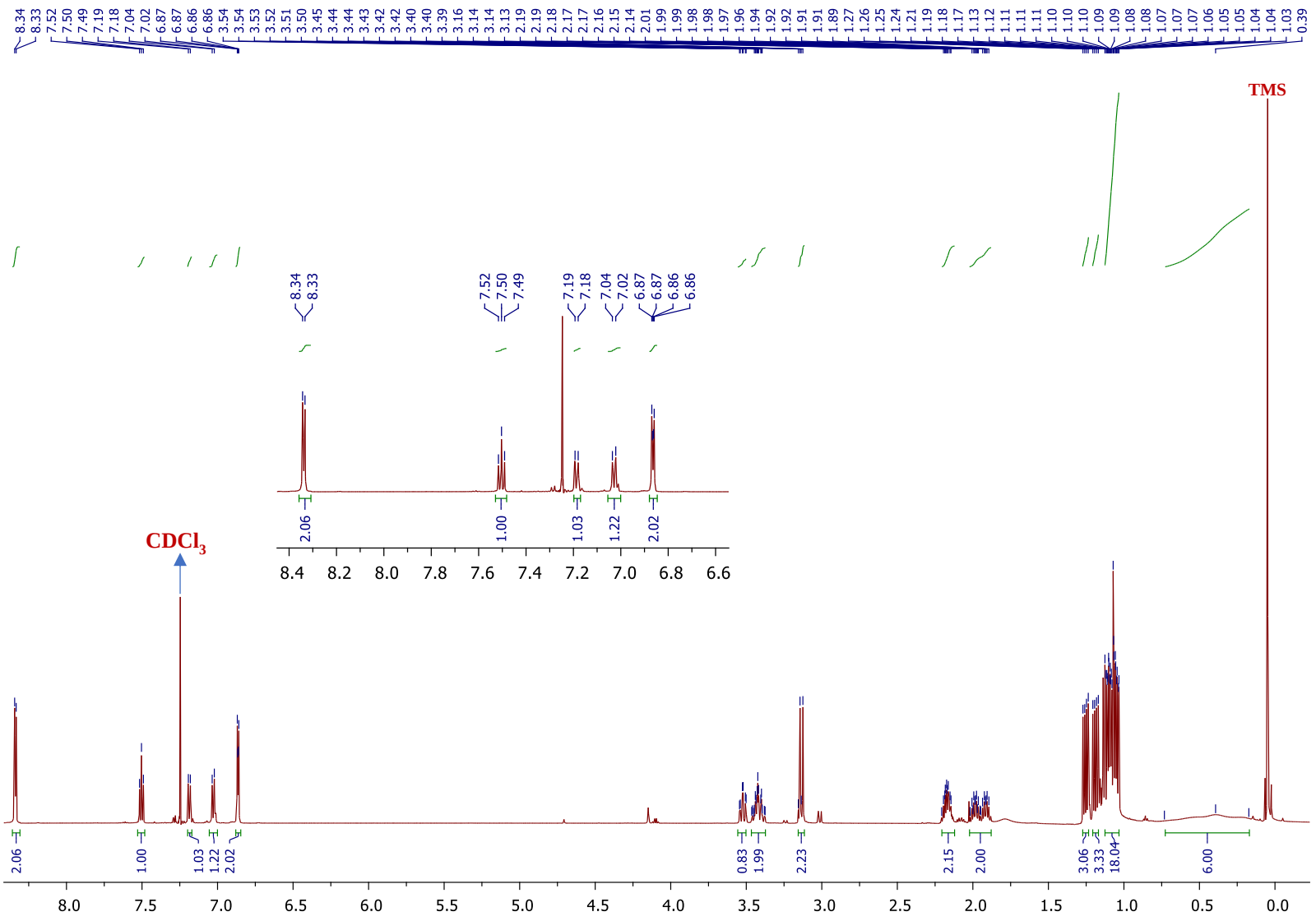


Figure S13. ^{1}H NMR spectrum of ligand **L4** in $CDCl_3$ at 23 °C.

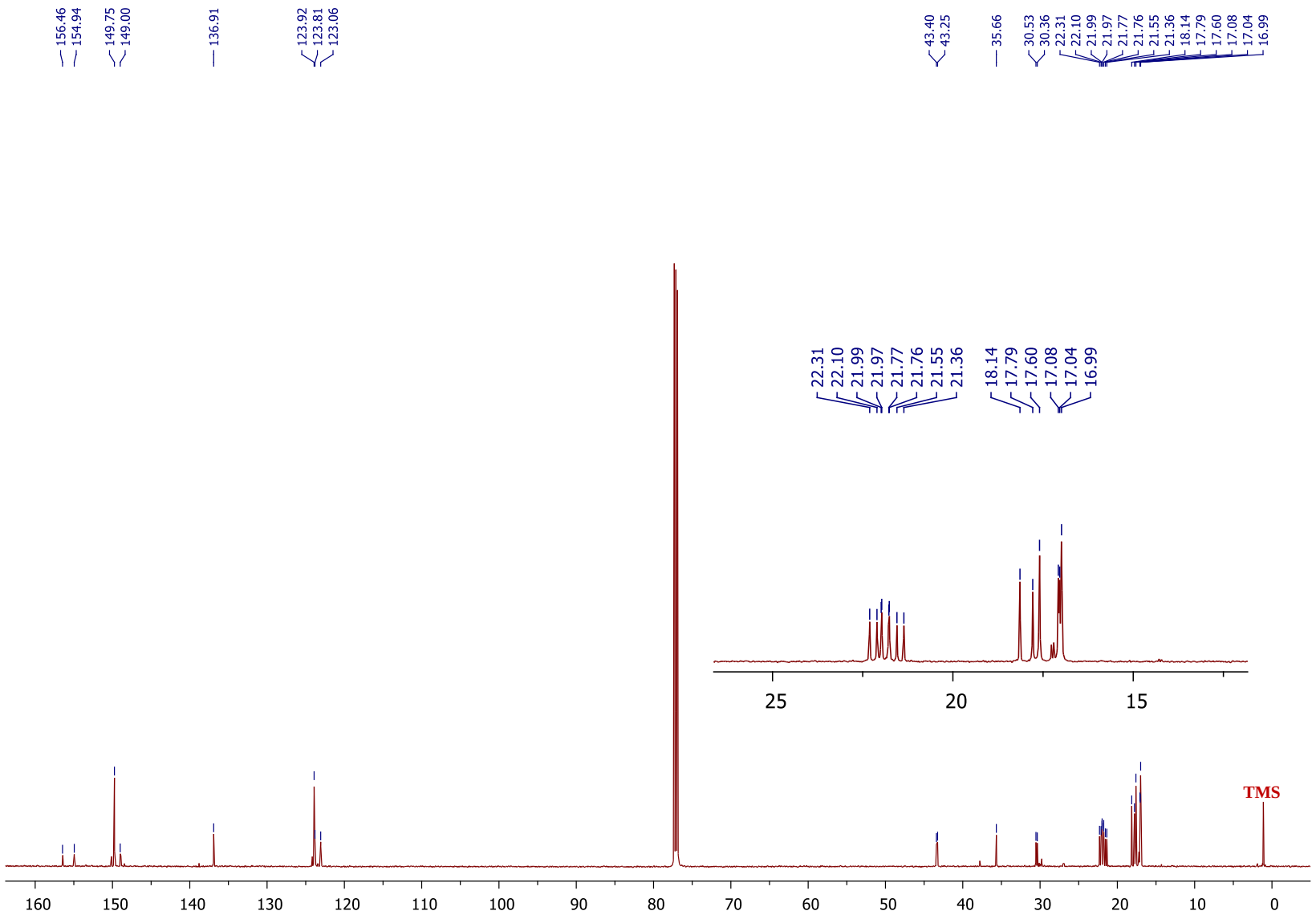


Figure S14. ^{13}C NMR spectrum of ligand **L4** in $CDCl_3$ at 23 °C.

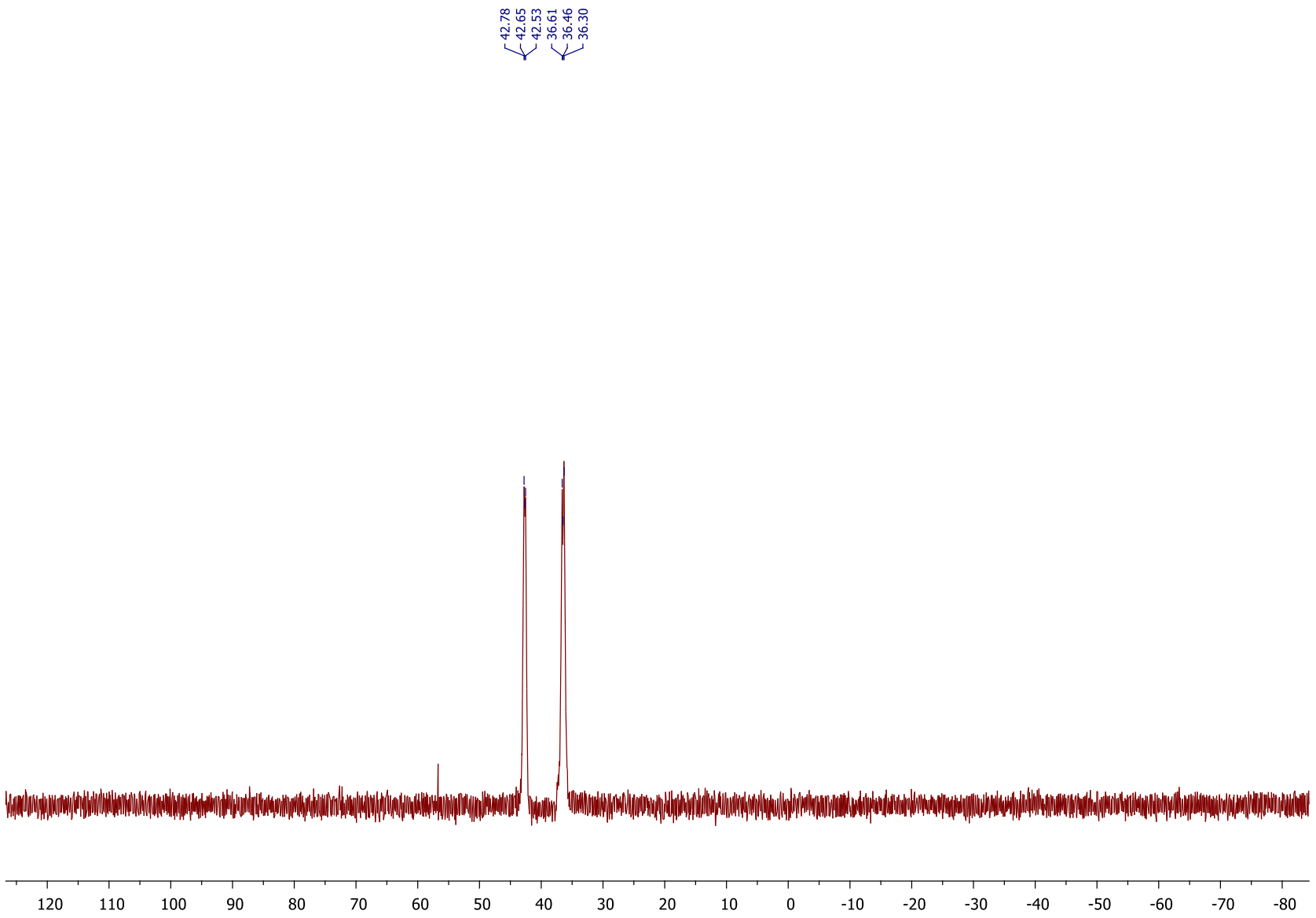


Figure S15. ^{31}P NMR spectrum of ligand **L4** in $CDCl_3$ at 23 °C.

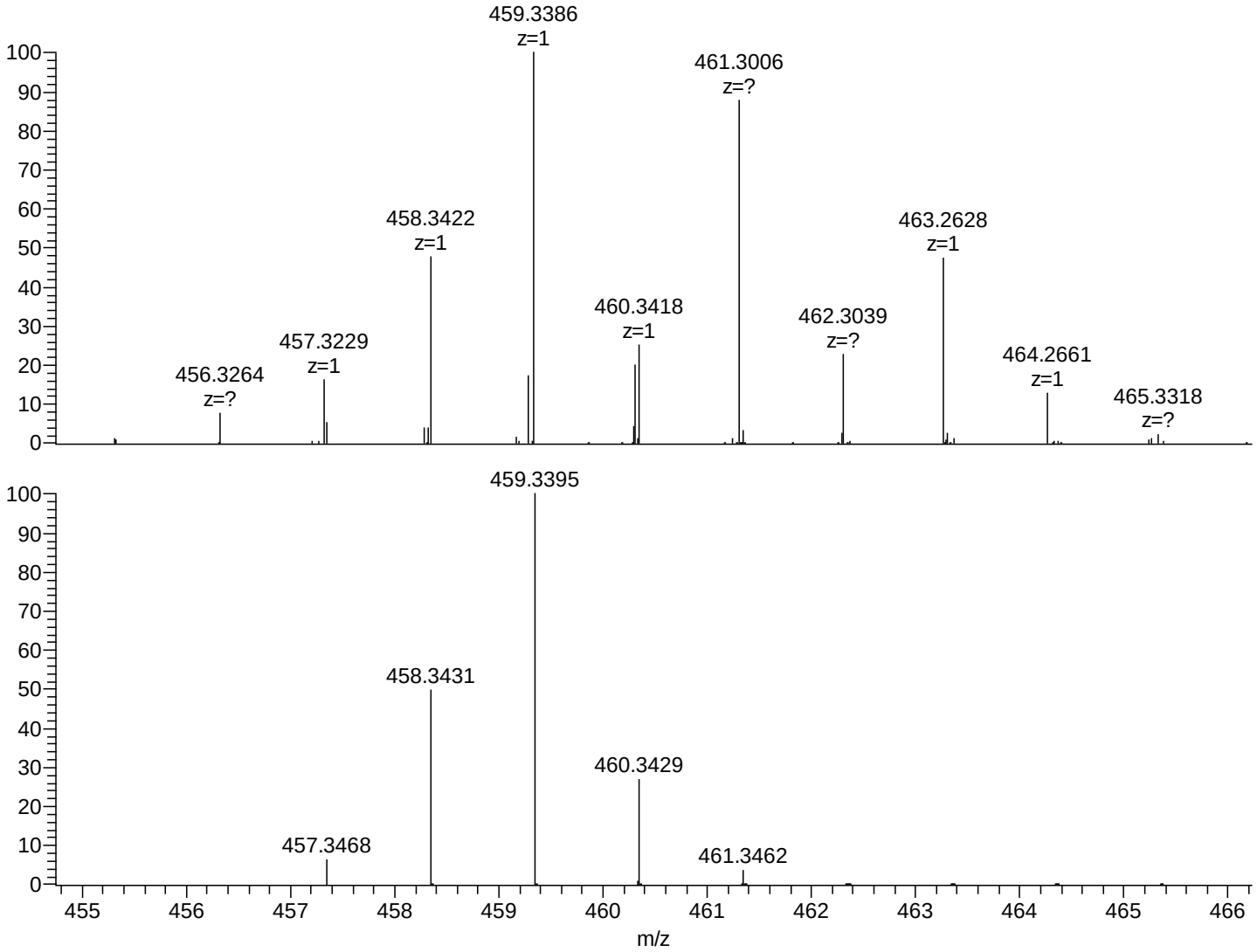
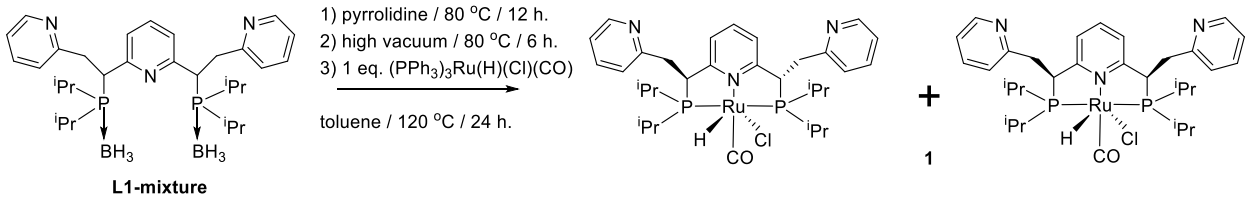


Figure S16. ESI - HRMS analysis in MeCN solution of **L4** (top) and simulated spectrum (below).

Procedure for synthesis of complex 1, [(*iPr*PNP(Bis)) Ru(CO)(H)(Cl)].



Under an inert atmosphere ligand **L1** (0.182 mmol, 100 mg) was deprotected by adding pyrrolidine (4 ml) at 80 ℃ for 12 hours in a closed 100 ml Schlenk flask. Afterward pyrrolidine was removed under high vacuum, and the system was left to heat at 80 ℃ for 6 hours under high vacuum to ensure the sublimation of pyrrolidine×BH_3.

The Schlenk flask was filled with argon and moved to the glovebox where the metal precursor carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) (0.182 mmol,173.3 mg) was added. 4 ml of toluene were added, and the mixture was stirred for 24 hours at 120 ℃. The resulting orange solution was filtered through celite, and the volatiles were removed in vacuum. The solids were completely dissolved in THF (2 ml) and then 7 ml of hexane was added. The yellow mixture was allowed to stand at -20 ℃ until yellow crystalline solids fell out of solution. The solution was then decanted, and the solids were washed twice with cold Et_2O and then hexane and dried under high vacuum for 4 hours to obtain complex **1** as a yellow, crystalline solid (82% yield). The crystals were very small, thus single crystals suitable for X-ray crystal structure analysis were formed by vapor diffusion of hexane into a DCM solution at room temperature.

Complex 1 formed as a mixture of two isomers in the ratio of 1.57:0.97 (i.e. the meso form of the ligand gave only one isomer where the chlorine was positioned *trans* to the pyridine groups). The isomer characterized by X-ray was of the meso ligand where Cl is *trans* to both arm pyridines.
^{1}H NMR (600 MHz, C_5D_5N): **major isomer** δ 8.69 (d, 2H, *J* = 4.5 Hz, py-*H*), 7.41 (t, 2H, *J* = 8.1 Hz, py-*H*), 7.08-7.04 (m, 2H, py-*H*), 6.85 (d, 2H, *J* = 8.1 Hz, py-*H*), 6.71-6.69 (m, 1H, py-*H*), 6.27 (d, 2H, *J* = 8.1 Hz, py-*H*), 4.38 (m, 4H, bridge-*H*), 3.54 (d, 2H, *J* = 15 Hz, arm-*H*), 2.38 (m, 4H, ^{i}Pr-*H*), 1.80 (dd, 6H, *J* = 17, 8.1Hz, ^{i}Pr-*Me*), 1.36-1.32 (m, 6H, ov.min, ^{i}Pr-*Me*), 1.24-1.18 (m, 6H, ov.min, ^{i}Pr-*Me*), 0.82 (dd, 6H, *J* = 17, 8.1Hz, ^{i}Pr-*Me*), -14.51 (v.t, 1H, $J_{P\text{-}H}$ = 16.8 Hz, Ru-*H*). **minor isomer**: δ 8.63 (d, 2H, *J* = 4.5 Hz, py-*H*), 7.50 (t, 2H, *J* = 8.1 Hz, py-*H*), 7.08-7.04 (m, 5H, py-*H*), 6.71-6.69 (m, 2H, py-*H*), 5.31 (m, 2H, bridge-*H*), 3.69 (d, 2H, *J* = 15 Hz, bridge-*H*), 3.43 (m, 2H, arm-*H*), 3.26 (m, 2H, ^{i}Pr-*H*), 2.79 (m, 2H, ^{i}Pr-*H*), 1.64-1.60 (m, 12H, ^{i}Pr-*Me*), 1.36-1.32

(m, 6H, ov.maj, ^{i}Pr-*Me*),1.24-1.18 (m, 6H, ov.maj, ^{i}Pr-*Me*), -14.35 (v.t, 1H, $J_{P\text{-}H}$ = 16.8 Hz, Ru-*H*).^{13}C NMR (151 MHz, C_5D_5N): **major isomer** δ 210.06 (*C*O), 168.23 (py-*C*), 159.92 (py-*C*), 137.13 (py-*C*), 137.69 (py-*C*, ov.min), 136.47 (py-*C*, ov.min), 125.33 (py-*C*, ov.min), 122.16 (py-*C*), 121.51 (py-*C*), 53.39 (C_{arm}), 41.47 (bridge-*C*), 28.20 (^{i}Pr-*C*), 23.31 (^{i}Pr-*C*), 21.80 (^{i}Pr-*Me*), 20.61 (^{i}Pr-*Me*), 19.66 (^{i}Pr-*Me*), 19.28 (^{i}Pr-*Me*). **minor isomer** δ 211.36 (*C*O), 166.87 (py-*C*), 159.80 (py-*C*), 137.24 (py-*C*), 137.69 (py-*C*, ov.maj), 136.47 (py-*C*, ov.maj), 125.33 (py-*C*, ov.maj), 122.44 (py-*C*), 120.68 (py-*C*), 50.01 (C_{arm}), 39.21 (bridge-*C*), 27.06 (^{i}Pr-*C*), 25.33 (^{i}Pr-*C*), 21.69 (^{i}Pr-*Me*), 21.03 (^{i}Pr-*Me*), 20.03 (^{i}Pr-*Me*), 17.49 (^{i}Pr-*Me*).

^{31}P{1H} NMR (262 MHz, C_5D_5N): **major isomer** δ (71.24); **minor isomer** δ **(**85.98).

IR (neat solid): ν (CO) 1906 cm^{-1} .

Anal. Calcd for $C_{32}H_{46}N_3P_2O_1Cl_1Ru_1$: C, 55.93; H, 6.75; N, 6.11. Found : C, 55.60; H, 6.71; N, 5.92.

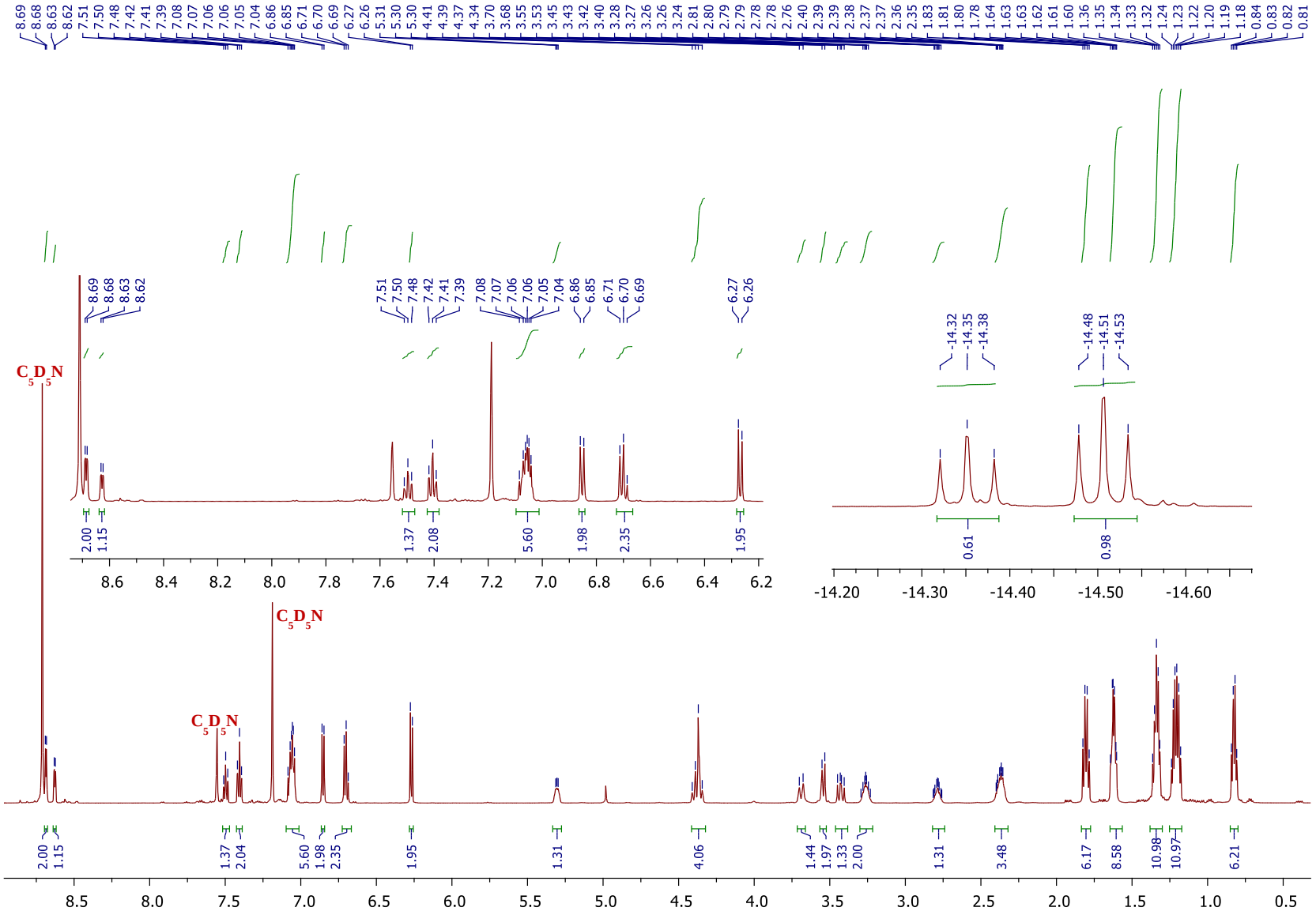


Figure S17. ^{1}H NMR spectrum of complex **1** in C_5D_5N at 23 ℃.

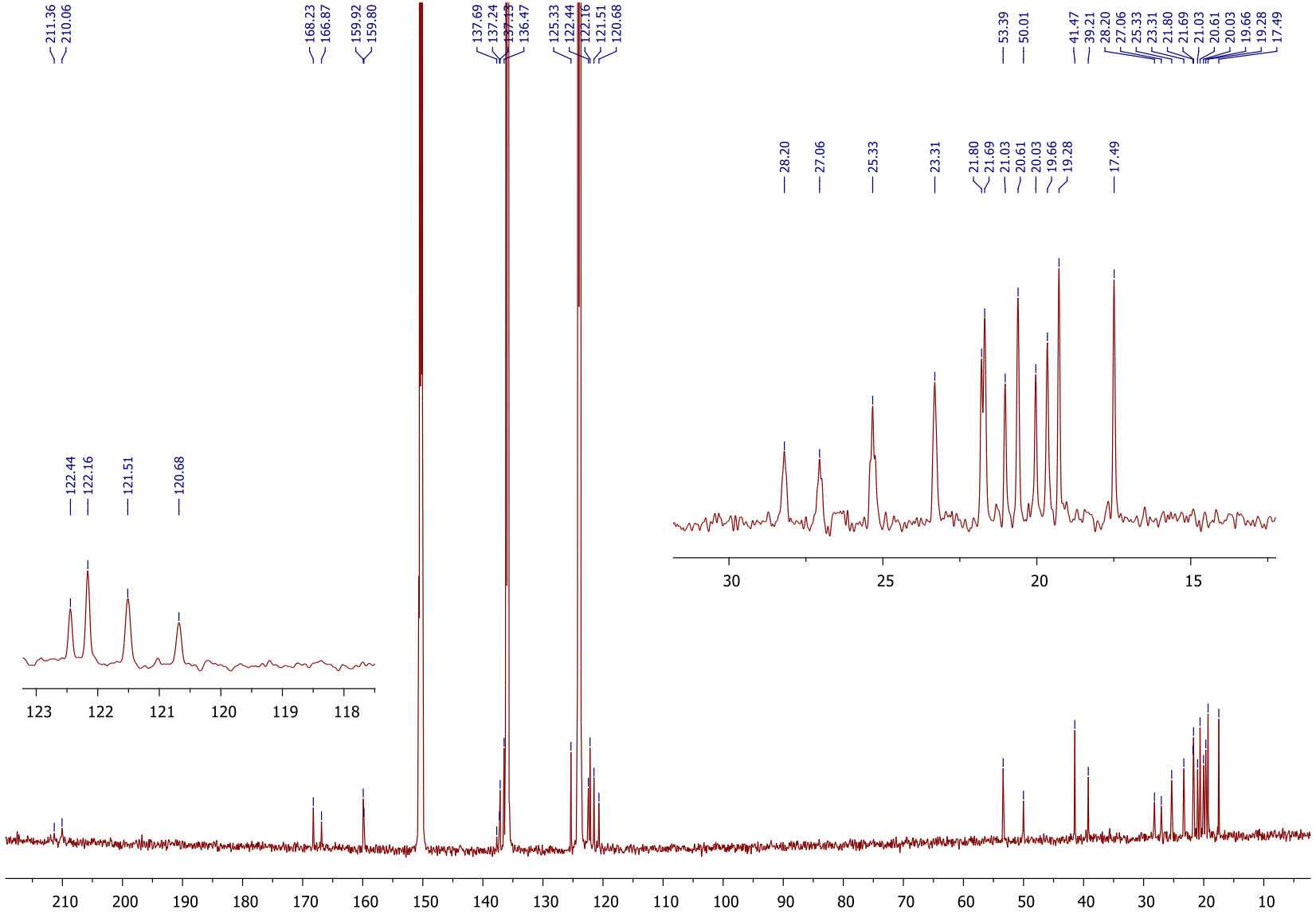


Figure S18. ^{13}C NMR spectrum of complex **1** in C_5D_5N at 23 °C.

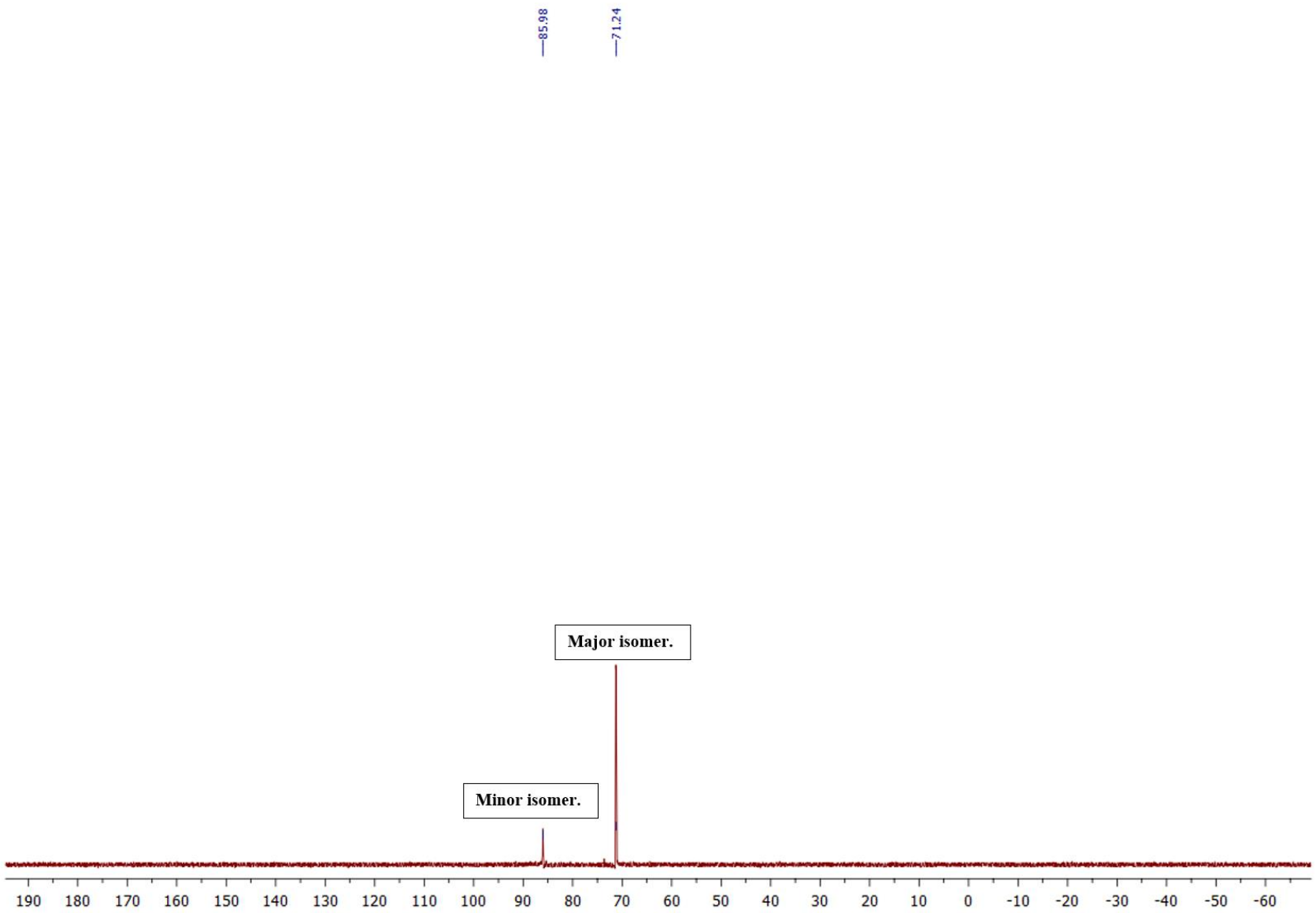


Figure S19. ^{31}P NMR spectrum of complex **1** in C_5D_5N at 23 °C.

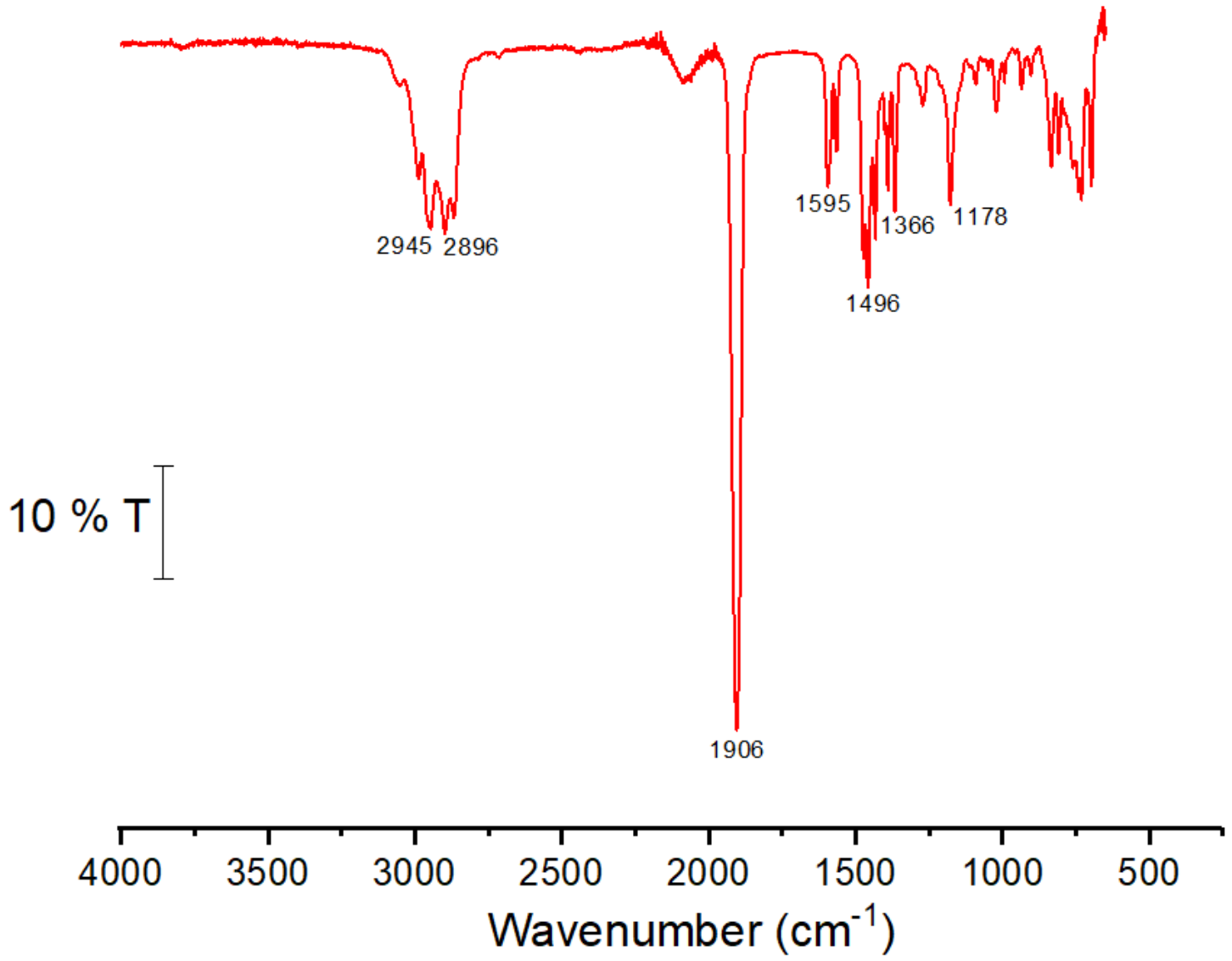
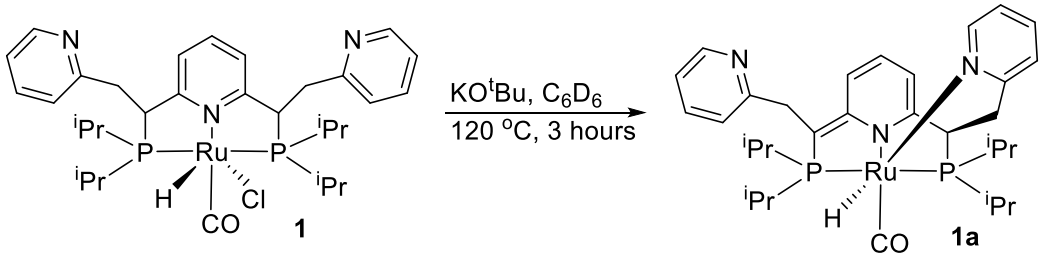


Figure S20. FT-IR (ATR) spectrum of complex **1**.

Complex 1a intermediate detected during the formation of complex 1b. Discussion of hydrogen transfer between intermediates as rate limiting step.



The complex **1a** is an intermediate in the synthesis of **1b** described below. Instead of heating, after adding ca. 1.1x molar excess of KO^{t}Bu to a solution of **1** in C_6D_6 in a Young tube, the solution was left at room temperature. A large number of intermediates were observed in the NMR after 10 minutes of reaction time. However, overnight all the intermediates disappeared to leave **1a** as a major complex, with **1b** (not present 10 minutes after deprotonation) also being present as a minor species. There was no further conversion to **1b** at room temperature, suggesting that at least one of the intermediates formed under kinetic control quickly at the beginning of the reaction competently converts to **1b**, whereas **1a** is a thermodynamic control intermediate and subsequently much higher temperature is required to transform the rest of the complex to **1b**. Likely, the more reactive intermediate(s) have one dearomatized arm pyridine; upon this arm binding to the metal, conversion to **1b** should be rapid (see computational section). After filtering through celite under an inert atmosphere, the solvent was allowed to slowly evaporate to give dark-red crystals which were found to be mixed crystals that contained both **1a** and **1b** in similar ratios to which they were seen in the NMR spectrum. Subsequently, the isolated crystals could be put into the NMR Young tube and heated further in C_6D_6 at 120 °C for three days to form the final complex **1b**. **1a** could be unambiguously assigned based on the combined NMR and X-ray data of these mixtures.

^{1}H NMR (600 MHz, C_6D_6): δ 8.97 (d, 1H, *J* = 4.8 Hz, py-*H*), 8.59 (d, 1H, *J* = 4.8 Hz, py-*H*), 7.45 (d, 1H, *J* = 4.8 Hz, py-*H*), 7.02 (m, 1H, py-*H*), 6.66 (m, 1H, py-*H*), 6.62 (m, 1H, py-*H*), 6.56 (m, 1H, py-*H*), 6.16 (m, 2H, py-*H*), 5.93 (d, 1H, *J* = 9.1 Hz, py-*H*), 5.45 (d, 1H, *J* = 6.1 Hz, py-*H*), 4.07 (m, 2H, bridge-*H*), 3.15 (t, 1H, arm-*H*), 3.02 (m, 1H, bridge-*H*), 2.87 (m, 1H, bridge-*H*), 2.51 (m,1H, ^{i}Pr-*H*), 2.30 (m,1H, ^{i}Pr-*H*), 1.86 (m,1H, ^{i}Pr-*H*), 1.67 (m,1H, ^{i}Pr-*H*), 1.52 (dd, 3H, *J* = 15.6, 6.9 Hz, ^{i}Pr-*Me*), 1.38 (dd, 3H, *J* = 15.6, 6.9 Hz, ^{i}Pr-*Me*), 1.11 (m, 12H, ^{i}Pr-*Me*), 0.77 (m, 6H, ^{i}Pr-*Me*), -14.62 (dd, 1H, $J_{P\text{-}H}$ = 25.9 , 12.2Hz, Ru-*H*). ^{31}P{1H} NMR (262 MHz, C_6D_6): δ 73.83 (d, 1P, $J_{P\text{-}P}$ = 236.5 Hz), 71.04 (d, 1P, $J_{P\text{-}P}$ = 236.5 Hz).

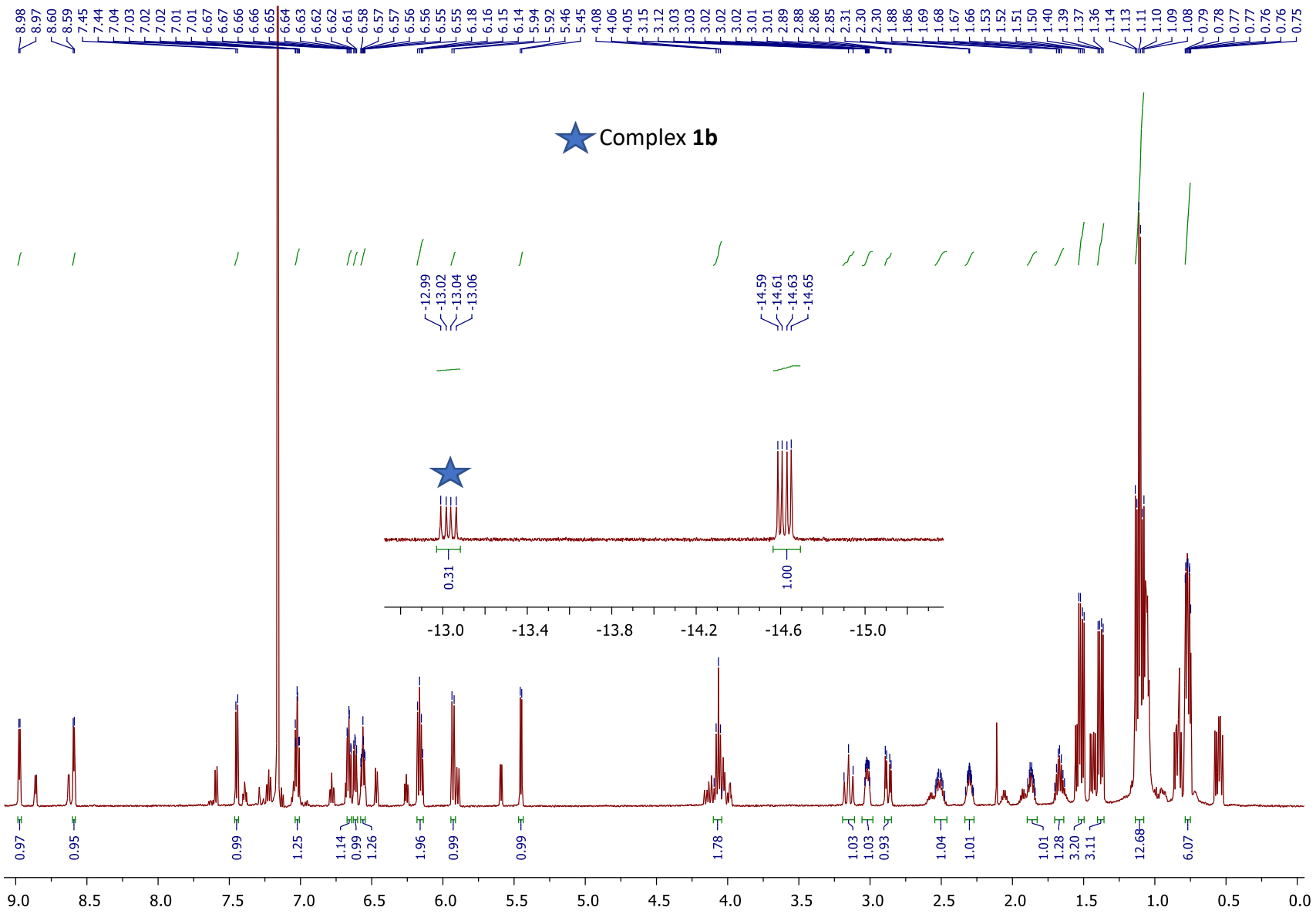


Figure S21. ^{1}H NMR spectrum of complex **1a** in C_6D_6 at 23 °C.

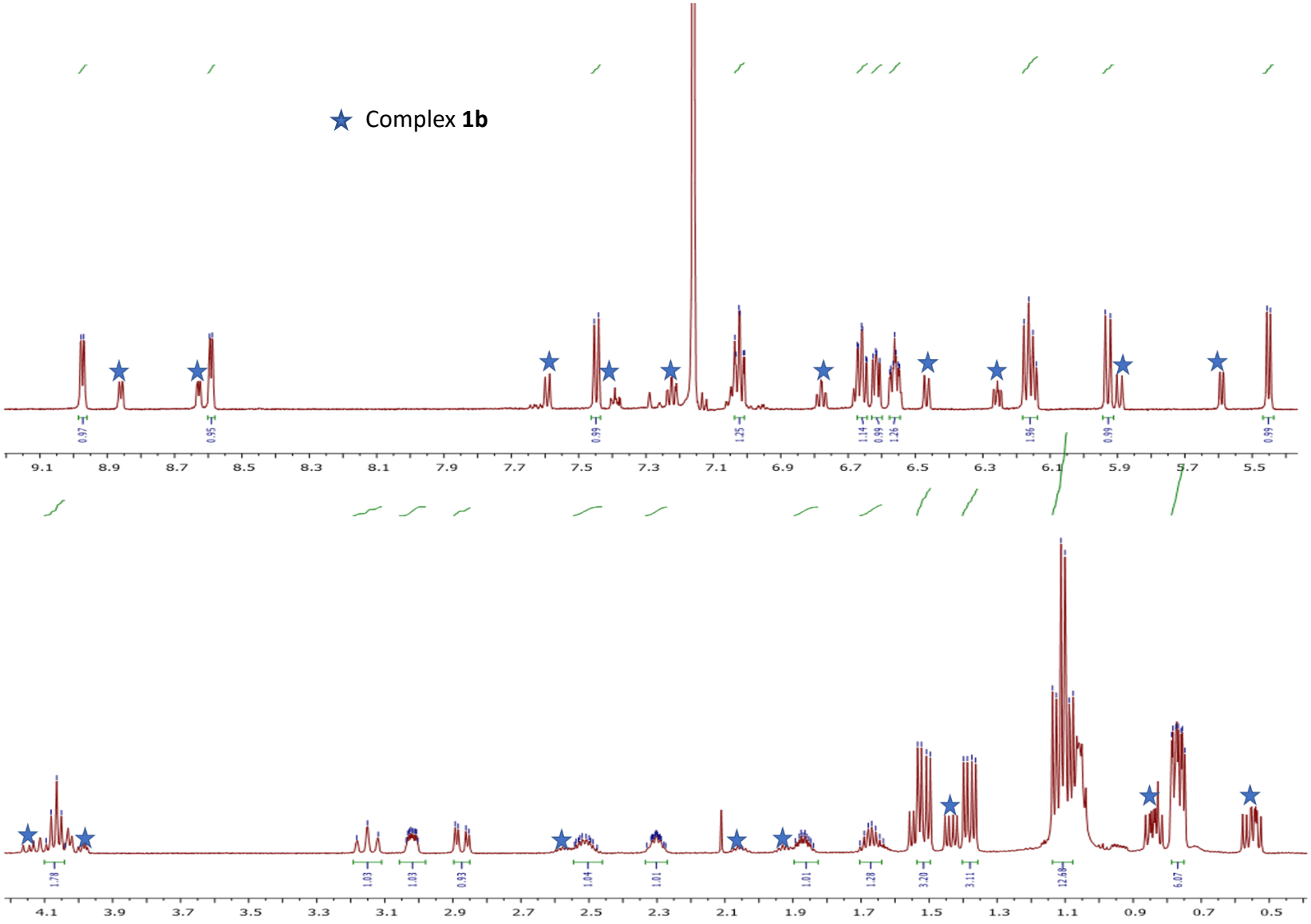


Figure S22. ^{1}H NMR spectrum zoom in view of aromatic (top) and aliphatic region (bottom) of complex **1a** in C_6D_6 at 23 °C.

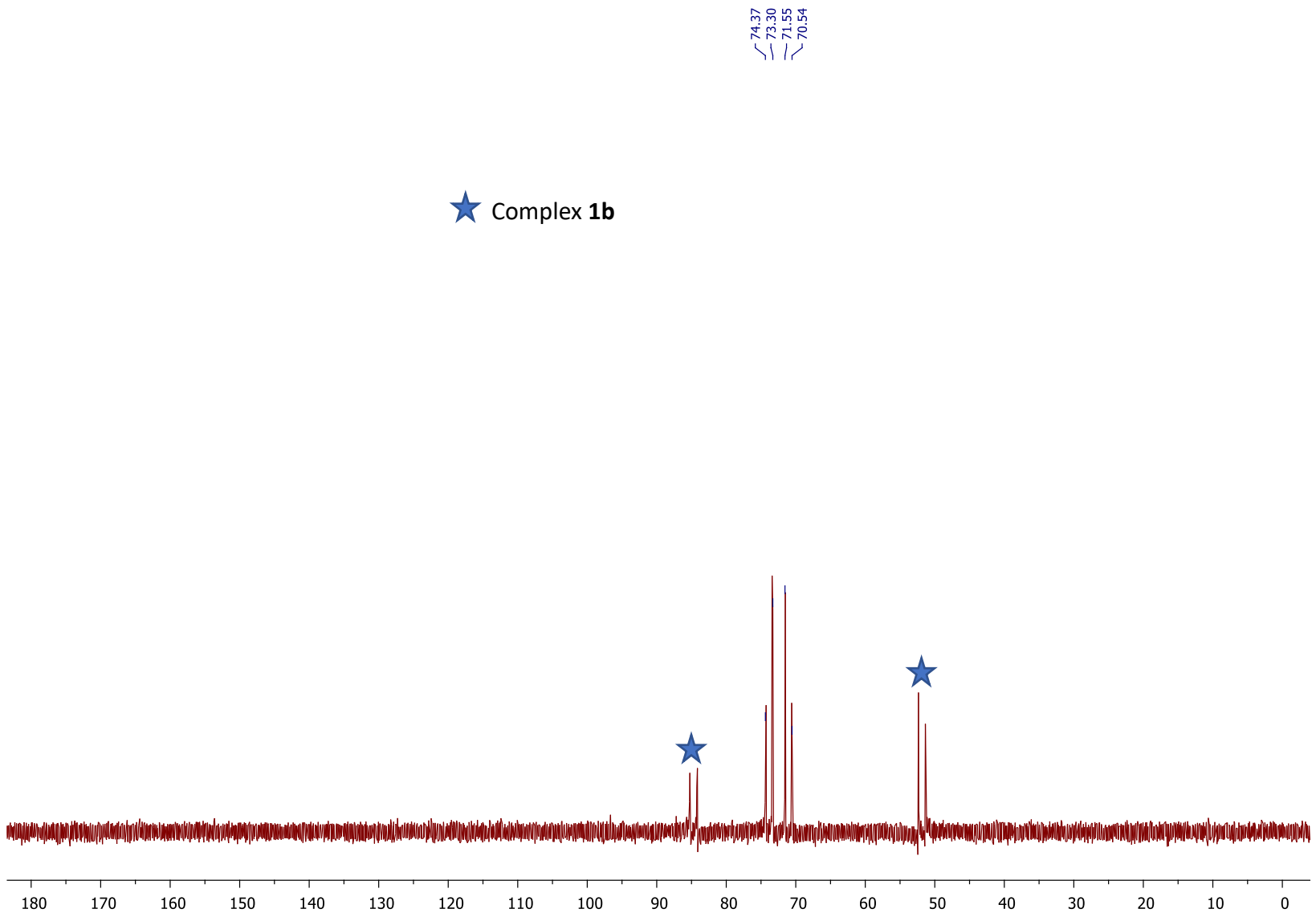
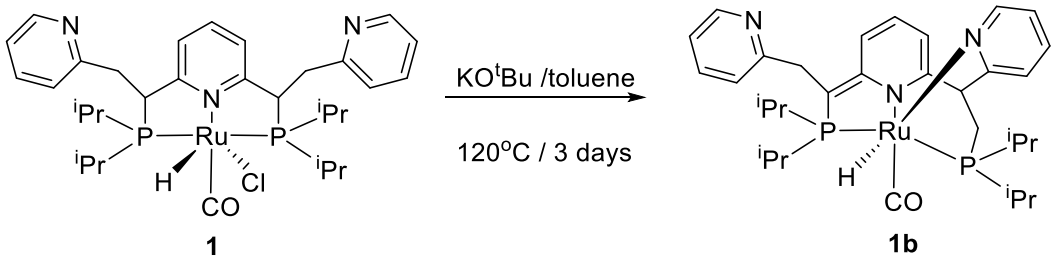


Figure S23. ^{31}P NMR spectrum of complex **1a** in C_6D_6 at 23 °C.

Procedure for synthesis of complex 1b.



In a glovebox under an inert atmosphere to a stirring solution of complex **1** (0.145 mmol, 100 mg) in toluene (5 ml), KOtBu (0.160 mmol, 17.9 mg) was added at room temperature. The resulting mixture was heated at 120 ℃ for three days. The red color solution was filtered through celite and all volatiles were removed under vacuum to give **1b** was as a bright, deep-red solid, yield 74%. Single crystals suitable for X-ray crystal structure analysis were formed via slow evaporation of a hexane solution at -30 ℃. Alternatively, the crystalline sample of **1a** analyzed above was used to form **1b** as well, in the absence of excess base.

^{1}H NMR (600 MHz, C_6D_6): δ 8.86 (d, 1H, *J* = 5.2 Hz, py-*H*), 8.63 (d, 1H, *J* = 5.2 Hz, py-*H*), 7.59 (d, 1H, *J* = 7.4 Hz, py-*H*), 7.22 (m, 1H, py-*H*), 6.78 (t, 1H, *J* = 7.4 Hz, py-*H*), 6.67 (m, 1H, py-*H*), 6.56 (m, 1H, py-*H*), 6.47 (d, 1H, *J* = 7.4 Hz, py-*H*), 6.26 (m, 1H, py-*H*), 5.89 (d, 1H, *J* = 9.4 Hz, py-*H*), 5.54 (d, 1H, *J* = 6.3 Hz, py-*H*), 4.14 (m,1H, bridge-*H*), 4.03 (m, 1H, bridge-*H*), 3.99 (m, 1H, arm-*H*), 2.58 (m, 1H, bridge-*H*), 2.06 (m, 1H, bridge-*H*), 1.93 (m, 1H, ^{i}Pr-*H*), 1.64 (m, 1H, ^{i}Pr-*H*), 1.54 (dd, 3H, *J* = 15.8, 6.9 Hz, ^{i}Pr-*Me*), 1.44 (dd, 3H, *J* = 15.8, 6.9 Hz, ^{i}Pr-*Me*), 1.06 (m, 5H, overlap of ^{i}Pr-*H* and ^{i}Pr-*Me*), 0.84 (m, 6H, ^{i}Pr-*Me*), 0.77 (dd, 3H, *J* = 15.8, 6.9 Hz, ^{i}Pr-*Me*), 0.55 (m, 6H, ^{i}Pr-*Me*), -13.03 (dd, 1H, $J_{P\text{-}H}$ = 28.2 Hz, 15.8 Hz, Ru-*H*).

^{13}C NMR (151 MHz, C_6D_6) δ 209.08 (*C*O), 168.59 (py-*C*), 164.30 (py-*C*),161.09 (py-*C*), 156.30 (py-*C*), 153.78 (py-*C*), 149.40 (py-*C*), 136.36 (py-*C*), 135.76 (py-*C*), 131.87 (py-*C*), 124.93 (py-*C*), 122.80 (py-*C*), 121.94 (py-*C*), 120.51 (py-*C*), 110.46 (py-*C*), 99.95 (py-*C*), 75.69 (C_{arm}, d, $J_{P\text{-}C}$ = 52.9 Hz), 56.31 (C_{arm}), 38.48 (bridge-*C*), 31.43 (bridge-*C*), 29.68 (^{i}Pr-*C*), 26.55 (^{i}Pr-*C*), 25.50 (^{i}Pr-*C*), 24.55 (^{i}Pr-*C*), 21.18 (^{i}Pr-*Me*), 20.02 (^{i}Pr-*Me*), 19.17 (^{i}Pr-*Me*), 18.73 (^{i}Pr-*Me*), 17.19 (^{i}Pr-*Me*), 17.04 (^{i}Pr-*Me*), 16.81 (^{i}Pr-*Me*), 15.07 (^{i}Pr-*Me*).

^{31}P{1H} NMR (262 MHz, C_6D_6): δ 84.71 (d, 1P, $J_{P\text{-}P}$ = 242.5 Hz), 51.89 (d, 1P, $J_{P\text{-}P}$ = 242.5 Hz).

IR (neat solid) : ν (CO) 1879 cm^{-1}.

Anal. Calcd for $C_{32}H_{45}N_3P_2O_1Ru_1$: C, 59.06; H, 6.97; N, 6.46. Found : C, 59.41; H, 6.84; N, 6.37.

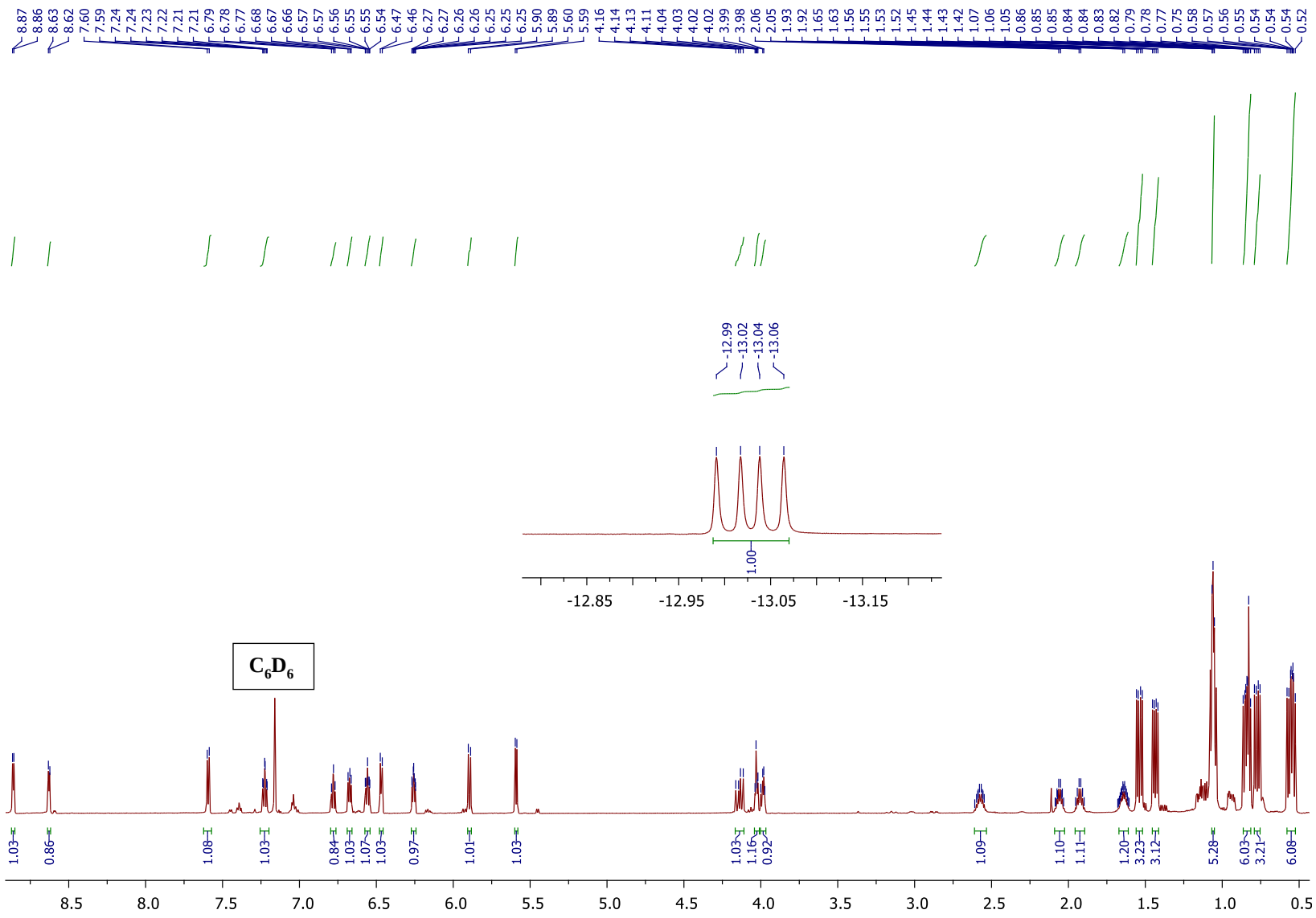


Figure S24. ^{1}H NMR spectrum of complex **1b** in C_6D_6 at 23 °C.

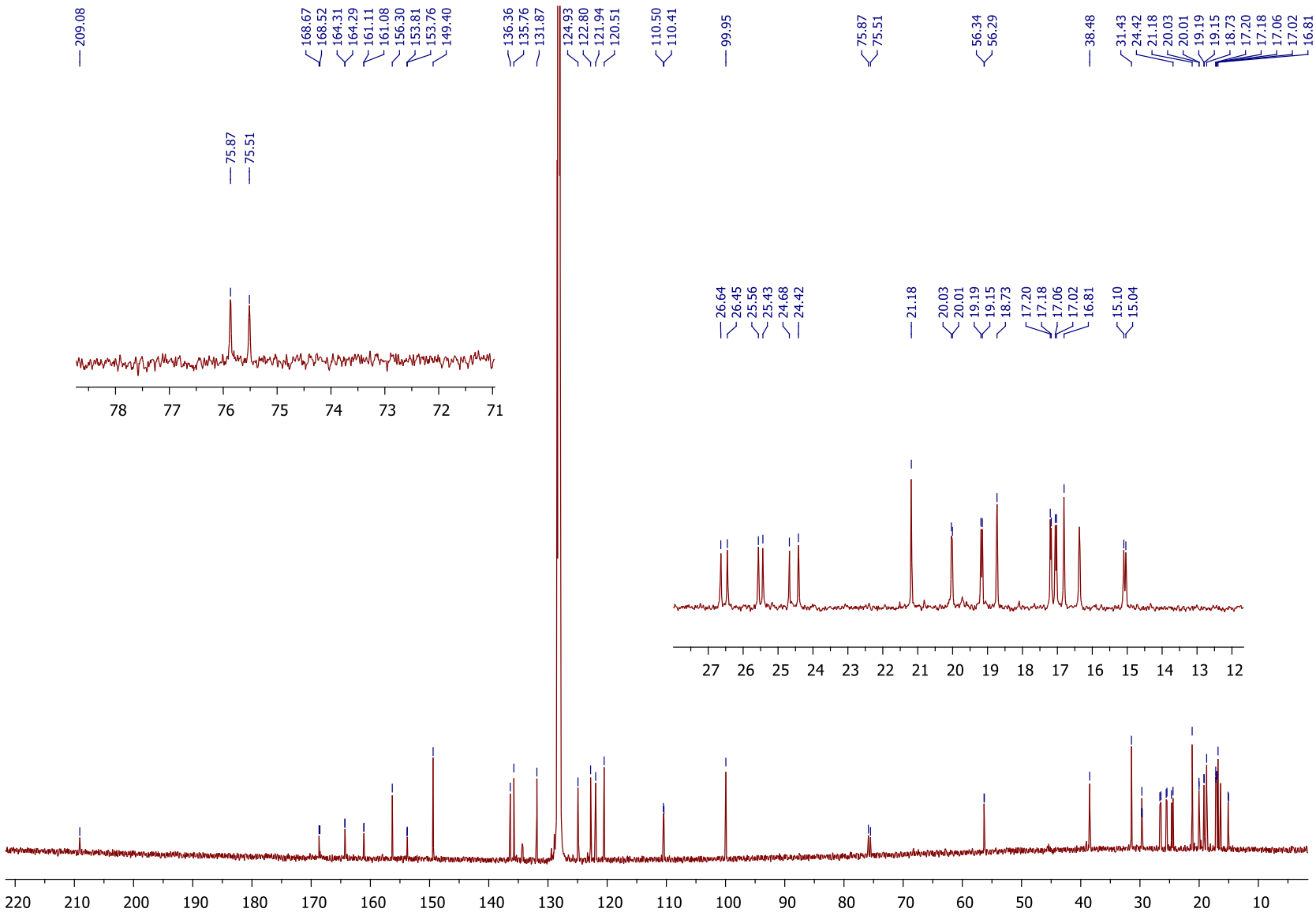


Figure S25. ^{13}C NMR spectrum of complex **1b** in C_6D_6 at 23 °C.

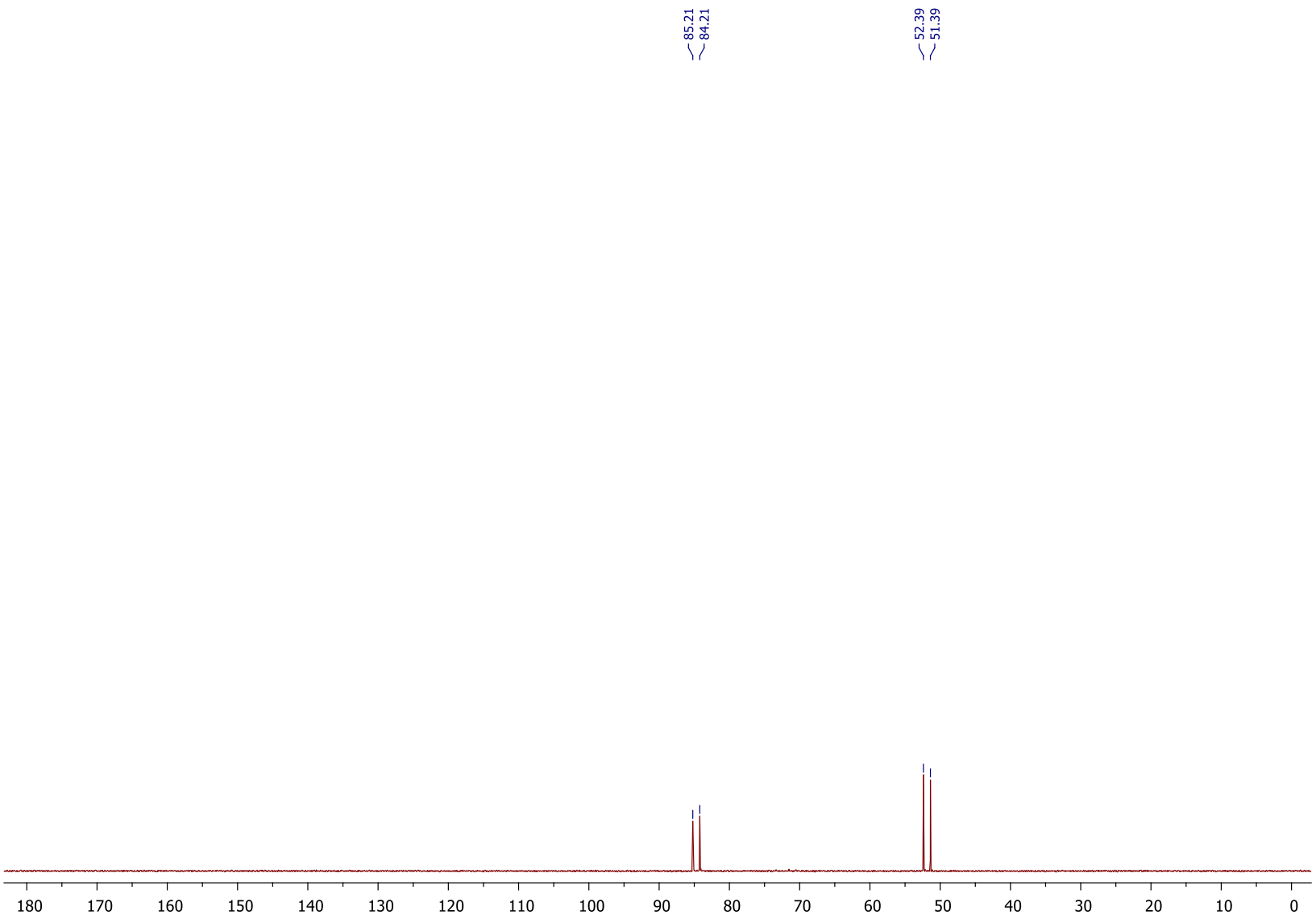


Figure S26. ^{31}P NMR spectrum of complex **1b** in C_6D_6 at 23 °C.

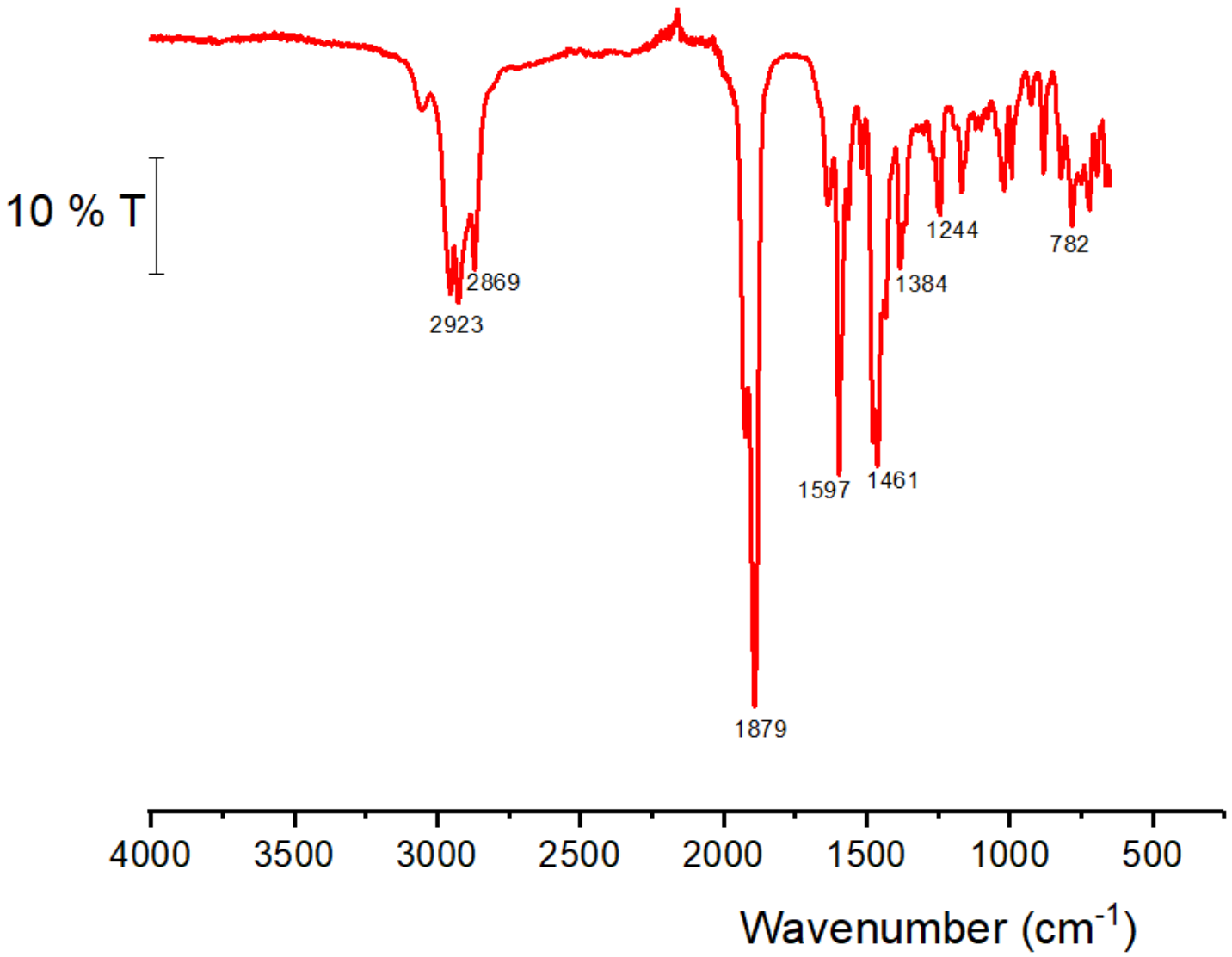
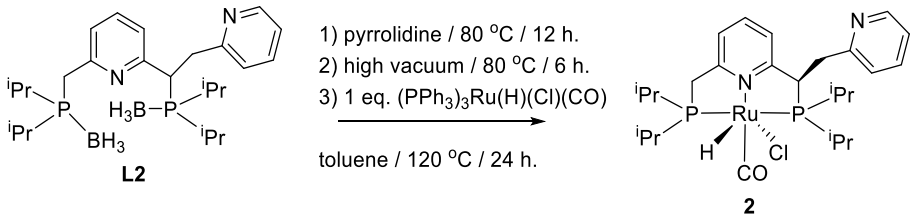


Figure S27. FT-IR (ATR) spectrum of complex **1b**.

Procedure for synthesis of complex 2, [(*iPr*PNP(Mono)) Ru(CO)(H)(Cl).



Under an inert atmosphere ligand **L2** (0.218 mmol, 100 mg) was deprotected by adding pyrrolidine (4 ml) at 80 ℃ for 12 hours in a 100 ml Schlenk flask. Afterwards pyrrolidine was removed under high vacuum, and the system was left to heat at 80 ℃ for 6 hours under high vacuum to ensure the sublimation of pyrrolidine×BH_3. The Schlenk flask was filled with argon and moved to the glovebox where the metal precursor carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) (0.218 mmol, 207.79 mg) was added. 4 ml of toluene were added, and the mixture was stirred for 24 hours at 120 ℃. The resulting solution was filtered through celite, and the volatiles were removed under high vacuum. The complex was dissolved in 2 ml of THF and then 8 ml of hexane were added, and the solution was cooled to -20 °C. After a few hours of standing a yellow solid fell out of solution. The solution was decanted, and the solids were washed two times with cold Et_2O (ca. 2 ml) and dried under high vacuum to afford complex **2** as a yellow solid in a yield of 84%. Crystals suitable for X-ray crystal structure analysis were formed by vapor diffusion of pentane into a THF solution at room temperature. Only one isomer formed preferentially, and this isomer was analyzed by X-ray and NMR spectroscopy.

^{1}H NMR (600 MHz, C_6D_6): δ 8.37 (d, 1H, *J* = 4.6 Hz, py-*H*), 6.80 (t, 1H, *J* = 7.1 Hz, py-*H*), 6.57 (d, 1H, *J* = 7.7 Hz, py-*H*), 6.49 (m, 1H, py-*H*), 6.46 (t, 1H, *J* = 7.7 Hz, py-*H*), 6.41 (d, 1H, *J* = 7.7 Hz, py-*H*), 6.26 (d, 1H, *J* = 7.7 Hz, py-*H*), 4.95 (t, 1H, *J* = 11.2 Hz, sub-arm-*H*), 3.56 (dd, 1H, *J* = 16.6, 8.8 Hz, bridge-*H*), 3.39 (m, 1H, arm-*H*), 3.24 (m, 1H, arm-*H*), 2.87 (m, 1H, ^{i}Pr-*H*), 2.72 (dd, 1H, *J* = 16.6, 9.6 Hz, bridge-*H*), 2.44 (m, 1H, ^{i}Pr-*H*), 1.98 (m, 1H, ^{i}Pr-*H*), 1.80 (m, 1H, ^{i}Pr-*H*), 1.52-1.43 (m, 9H, ^{i}Pr-*Me*), 1.17-1.08 (m, 9H, ^{i}Pr-*Me*), 1.03 (dd, 3H, *J* = 14.6, 7.6 Hz, ^{i}Pr-*Me*), 0.79 (dd, 3H, *J* = 14.6, 7.6 Hz), -14.36 (v.t , 1H, $J_{P\text{-}H}$ = 18.3 Hz, Ru-*H*).

^{13}C NMR (151 MHz, C_6D_6): δ 211.54 (*C*O), 166.08 (py-*C*), 163.36 (py-*C*), 159.78 (py-*C*), 149.88 (py-*C*), 136.24 (py-*C*), 135.85 (py-*C*), 123.02 (py-*C*), 121.54 (py-*C*), 119.64 - 119.52 (py-*C*), 50.37 (sub-C_{arm}, d, $J_{P\text{-}C}$ = 15.31 Hz), 40.78 (bridge-*C*), 39.08 (C_{arm}), 27.65 (^{i}Pr-*C*, d, $J_{P\text{-}C}$ = 16.1 Hz), 26.89 (^{i}Pr-*C*, d, $J_{P\text{-}C}$ = 20.6 Hz), 26.25 (^{i}Pr-*C*, d, $J_{P\text{-}C}$ =18.3 Hz), 24.69 (^{i}Pr -*C*, d, $J_{P\text{-}C}$ = 22.8 Hz),

21.24 (^{i}Pr-*Me*), 20.64 (^{i}Pr-*Me*), 20.43 (^{i}Pr-*Me*), 20.05 (^{i}Pr-*Me*), 19.57 (^{i}Pr-*Me*), 19.21 (^{i}Pr-*Me*), 18.92 (^{i}Pr-*Me*), 18.07 (^{i}Pr-*Me*).

^{31}P{1H} NMR (262 MHz, C_6D_6): δ 84.80 (d, 1P, $J_{P\text{-}P}$ = 261.3 Hz), 75.96 (d, 1P, $J_{P\text{-}P}$ = 261.3Hz).

IR (neat solid) : ν (CO) 1903 cm^{-1}.

Anal. Calcd for $C_{26}H_{41}N_2P_2O_1Cl_1Ru_1$: C, 52.39; H, 6.93; N, 4.70. Found : C, 52.56; H, 6.87; N, 4.58.

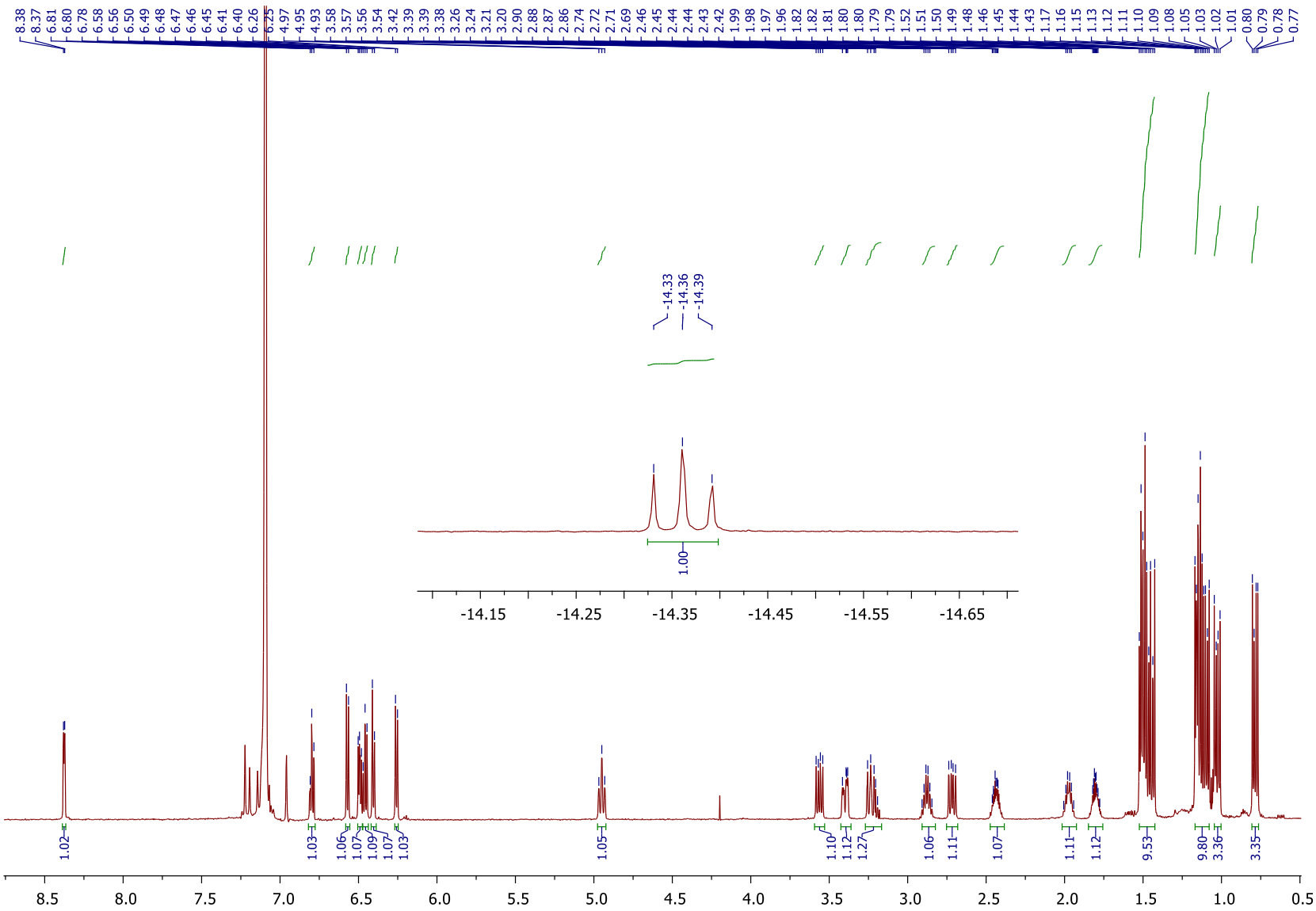


Figure S28. ^{1}H NMR spectrum of complex **2** in C_6D_6 at 23 °C.

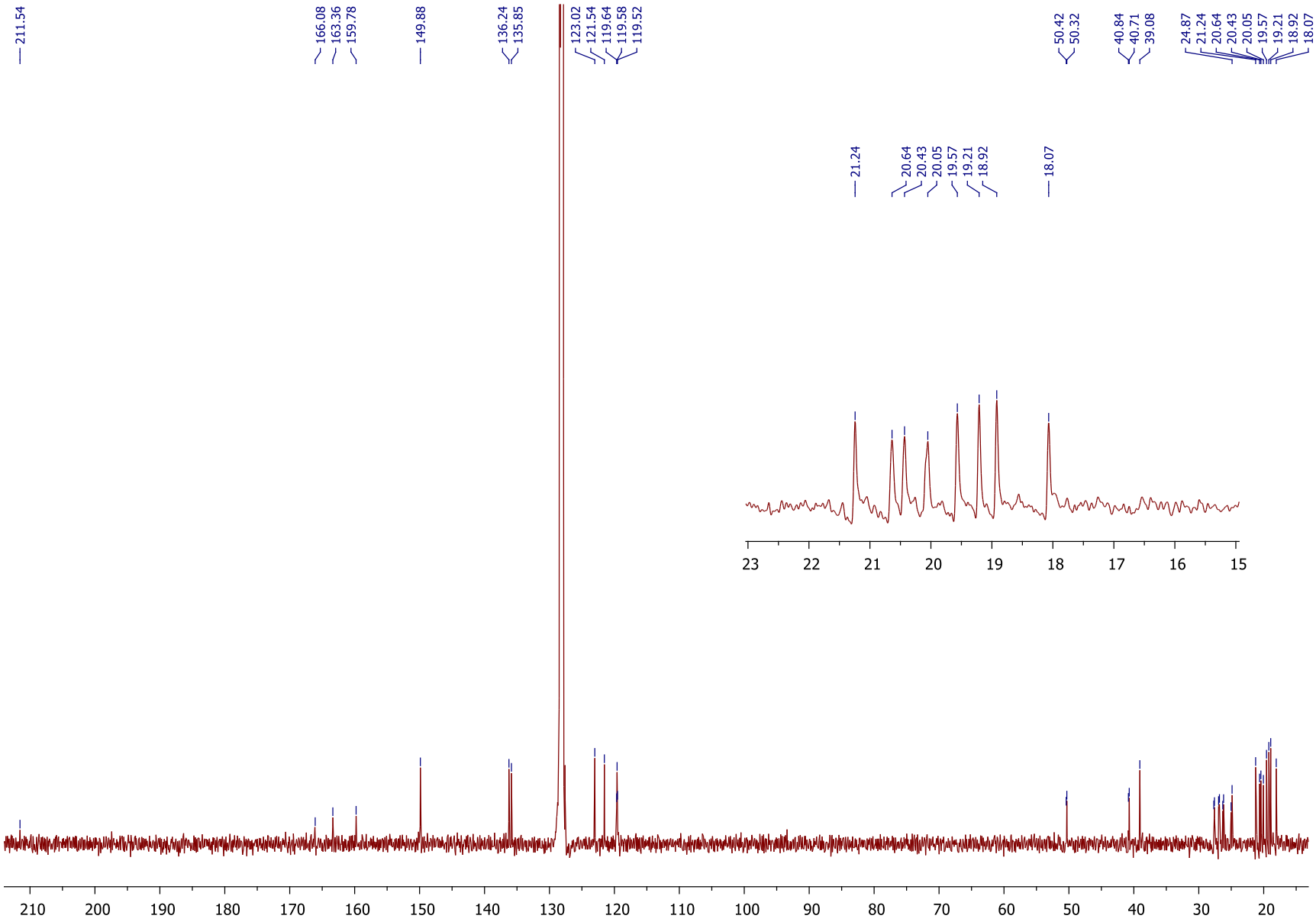


Figure S29. ^{13}C NMR spectrum of complex **2** in C_6D_6 at 23 ℃.

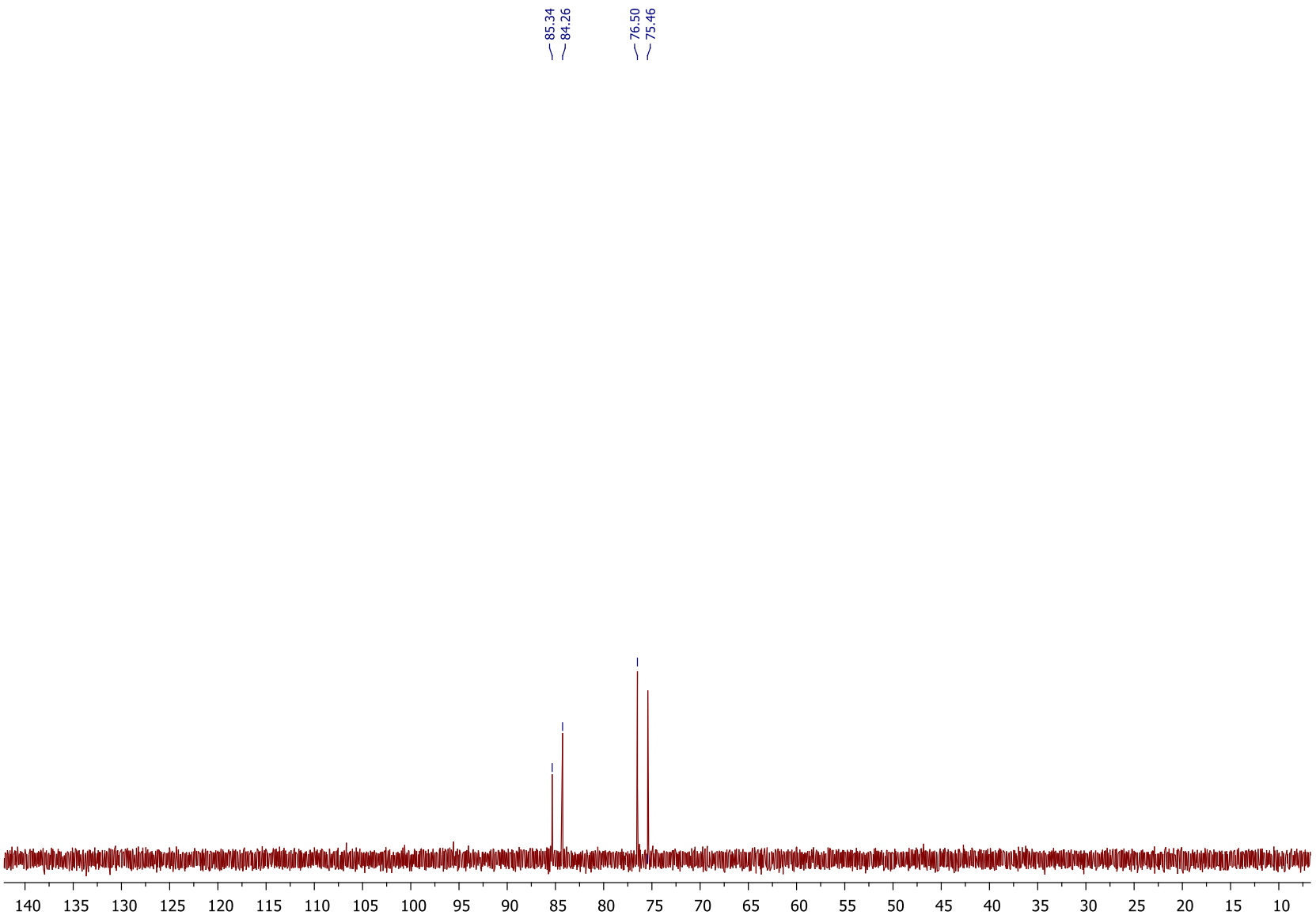


Figure S30. ^{31}P NMR spectrum of complex **2** in C_6D_6 at 23 °C.

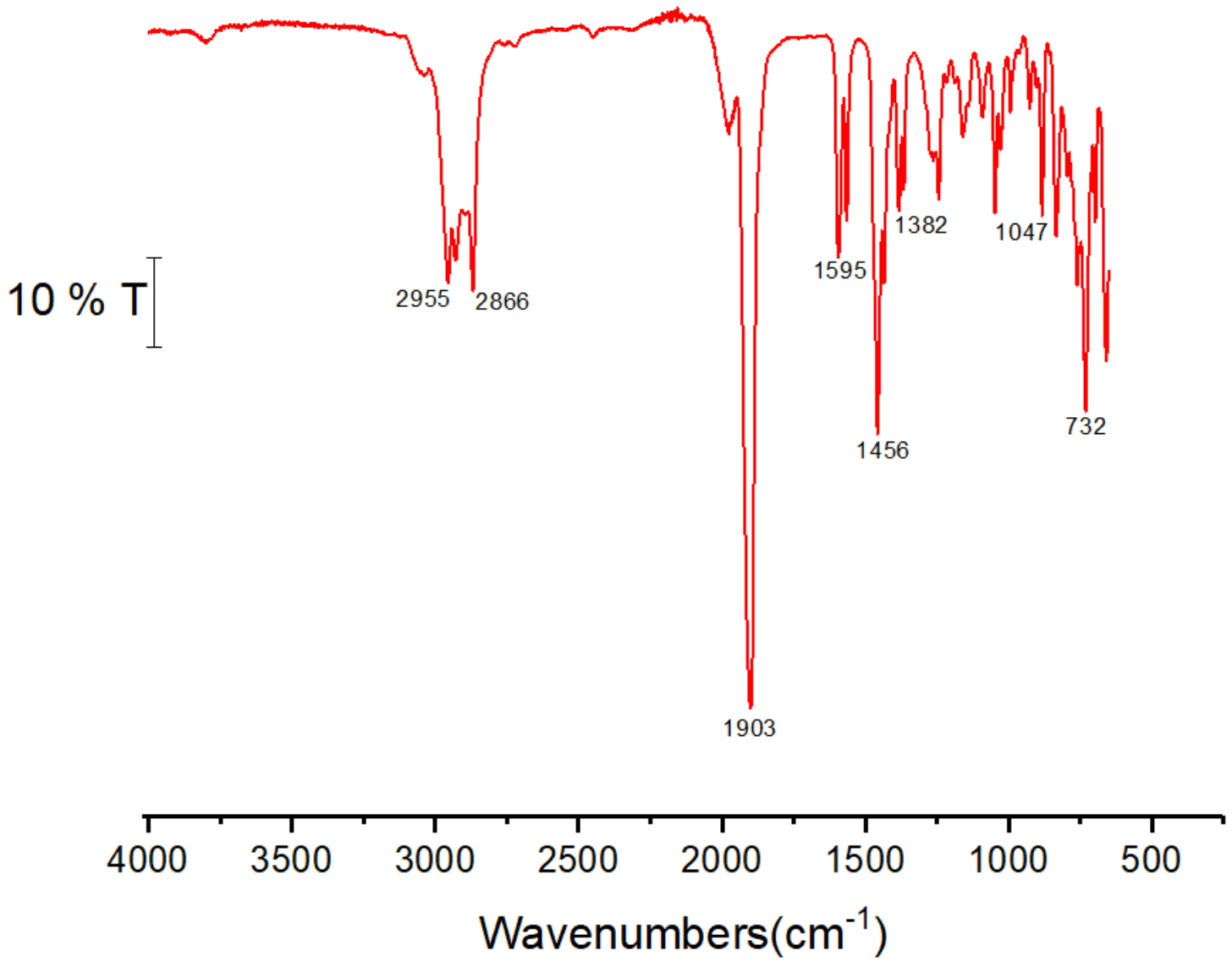
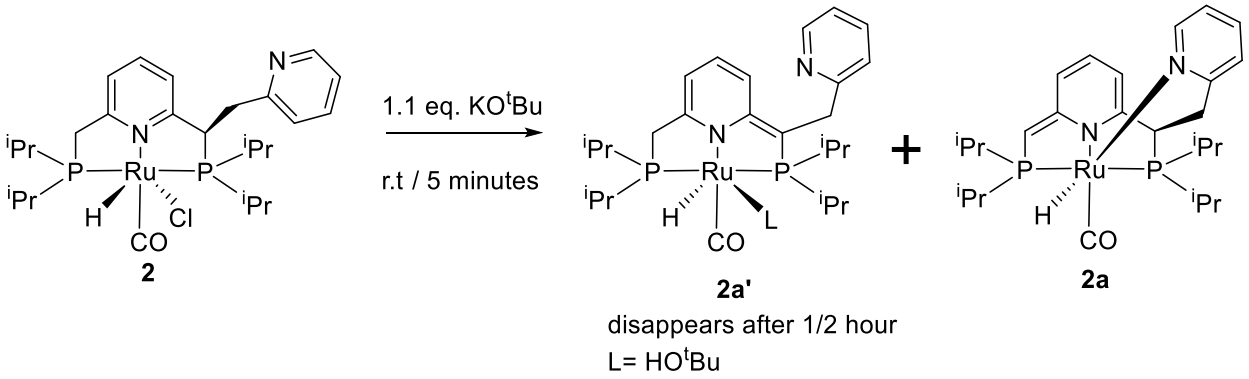


Figure S31. FT-IR (ATR) spectrum of complex **2**.

Characterization of complex 2a and discussion of the intermediacy of 2a' in C_6D_6.



Complex **2a** was detected as the major species after 1-hour *in-situ* reaction time during the formation of complex **2b** after deprotonation in C_6D_6 in an NMR Young tube. The three species present are **2a** (major), **2a'** and **2b**.

Short-lived complex **2a'** is characterized by a triplet at -15.49 ppm (Figure **S36**). The arm pyridine is still aromatized, as the *ortho*-H shift is at 8.76 ppm (Figure **S33**) however, this pyridine cannot coordinate to the metal due to geometric constraints, thus the *ortho* resonance is relatively upfield shifted when contrasted to **2a** and **2b**. Three out of the four bridge protons (Figure **S34**) for **2a'** are not overlapping with the signals of **2a**, with two doublets of doublets and 4.45 ppm and 2.69 ppm showing correlated constants consistent with a $J_{H\text{-}H}$ and $J_{H\text{-}P}$ pattern. The other bridging proton is a broad doublet at 4.19 ppm consistent with a position in a benzylic position next to the arm pyridine. This assignment of a trace species is speculative, but **2a'** is the major species when pyridine is used as a solvent after 5 hours of reaction time (see below experiment in C_5D_5N) where its definite assignment is confirmed by 2D spectroscopy. Despite the different chemical shifts in pyridine solvent, it's possible to contract the splitting patterns of **2a** and **2a'** and extend the conclusions to benzene solvent. In benzene, the coordinating ligand trans to the hydride is likely the tert-butanol generated during deprotonation, which limits the upfield shift of the hydride resonance to -15.5 ppm and also likely significantly stabilizes **2a'**, allowing for its observation.

The transformation of complex **2a** to **2b** was followed by kinetics (see kinetics section below) and the rate was measured starting at the point when **2a'** disappeared. At the beginning of the reaction where **2a'** was present, very trace amounts or no **2b** was observed. The amount of **2a'** disappearing was always greater than that of **2b** appearing when integrated against the solvent or base peak, suggesting that it is not directly converted to **2b** and must first be converted to **2a**. Transformation of all intermediate species to **2a** in a system with KO^{t}Bu in C_6D_6 suggests that hydrogen transfer

between the isomers is not rate limiting. In the kinetic runs, the transformation proceeds without regeneration of **2a'** and without any other isomers being detected on the NMR timescale. Thus, the rate-limiting step is C-C bond cleavage.

This is in contrast with complex **1** where after overnight at room temperature with KO^{t}Bu some **1b** was already present due to the presumed formation of an intermediate that could lead to **1b** more readily, however **1a** did not react further at room temperature to give **1b**, suggesting that hydrogen transfer between **1a** and another isomer is rate limiting.

In order to study the kinetics of only the C-C cleavage step, complex **1a** cannot be utilized, while **2a** is ideal.

Complex **2a**: ^{1}H NMR (600 MHz, C_6D_6): δ 9.02 (d, 1H, *J*=5.1 Hz, py-*H*), 6.63 (t, 1H, *J* = 7.3 Hz, py-*H*), 6.52 (t, 1H, *J* = 7.3 Hz, py-*H*), 6.34 (d, 1H, *J* = 8.8 Hz, py-*H*), 6.18 (t, 1H, *J* = 6.3 Hz, py-*H*), 6.16 (d, 1H, *J* = 8.8 Hz, py-*H*), 5.39 (d, 1H, *J* = 6.3 Hz, py-*H*), 3.72 (d, 1H, *J* = 3.8 Hz, dearom-arm-*H*), 3.13 (m, 1H, bridge-*H*), 2.99 (m, 1H, sub-arm-*H*), 2.89 (m, 1H, bridge-*H*), 2.30 (m, 1H, ^{i}Pr-*H*), 2.19 (m, 1H, ^{i}Pr-*H*), 1.86 (m, 1H, ^{i}Pr-*H*), 1.68 (m, 1H, ^{i}Pr-*H*), 1.55 (m, 6H, ^{i}Pr-*Me*), 1.22 (dd, 3H, *J* = 11.5, 7.1 Hz, ^{i}Pr-*Me*), 1.11 (m, 9H, ^{i}Pr-*Me*), 0.96 (dd, 3H, *J* = 11.5, 7.1 Hz, ^{i}Pr-*Me*), 0.78 (dd, 3H, *J*=11.5, 7.1 Hz, ^{i}Pr-*Me*), -14.71 (dd, 1H, J_{P-H} = 26.3, 12.2 Hz, Ru-*H*).

^{31}P{1H} NMR (262 MHz, C_6D_6): δ 70.87 (d, 1P, J_{P-P} = 234.1 Hz), 63.14 (d,1P, J_{P-P} =234.1 Hz).

Complex **2a'**: ^{1}H NMR (600 MHz, C_6D_6): δ 8.76 (d, 1H, *J* = 5.5 Hz, py-*H*), 7.89 (t, 1H, *J* = 8.1Hz, py-*H*), 7.71 (t, 1H, *J* = 8.1 Hz, py-*H*), 7.22 (t, 1H, *J* = 8.1 Hz, py-*H*), 7.03 (br.s, 1H, py-*H*), 6.84 (t, 1H, *J* = 8.1 Hz, py-*H*), 5.77 (m, 1H, *J* = 6.3 Hz, py-*H*), 4.46 (m, 1H, dearom-arm-*H*), 4.20 (m, 1H, bridge-*H*), 2.70 (m, 1H, sub-arm-*H*), 2.54 (br.s , 1H, bridge-*H*), 2.08 (br.s ,1H, arm-*H*), 1.44 (dd, 6H, *J* = 14.7, 6.8 Hz, ^{i}Pr-*Me*), 1.37 (dd, 6H, *J* = 14.7, 6.8 Hz, ^{i}Pr-*Me*), 0.93-0.98 (m, 4H, ^{i}Pr-*H*), 0.85-0.80 (m, 6H, ^{i}Pr-*Me*), 0.12 (dd, 6H, *J*=14.7, 6.8 Hz, ^{i}Pr-*Me*), -15.49 (v.t , 1H, J_{P-H} = 19.1 Hz, Ru-*H*).

^{31}P{1H} NMR (262 MHz, C_6D_6): δ 78.58 (d, 1P, J_{P-P} = 223.1 Hz), 64.59 (d,1P, J_{P-P} =223.1 Hz).

Note: NMR peak assignments for isolated complex **2b** is done in C_6D_6 (see below).

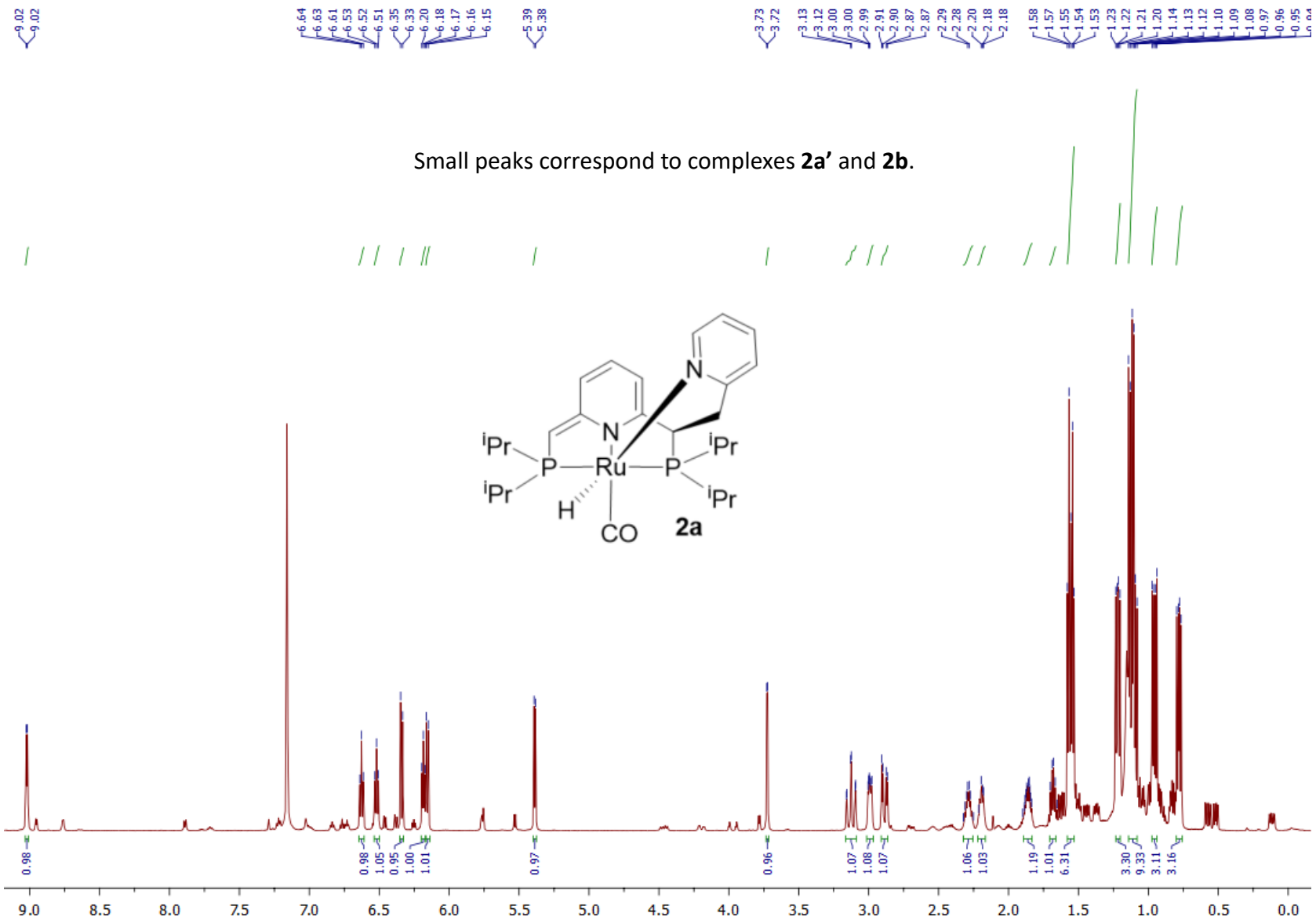


Figure S32. ^{1}H NMR spectrum of complex **2a** in C_6D_6 at 23 °C. Complexes **2a'** and **2b** are present in a small amount (see **S33-S36**).

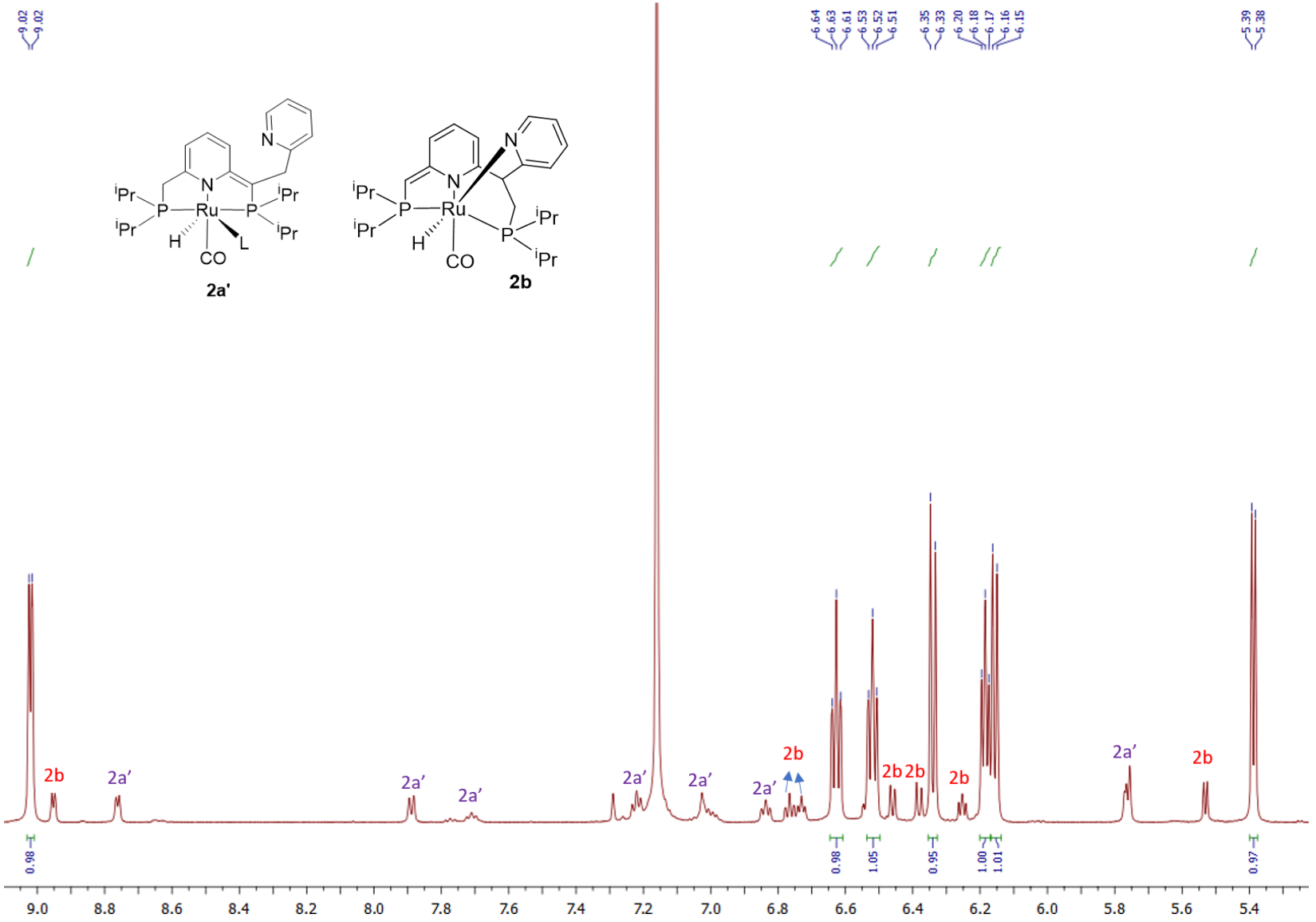


Figure S33. Expanded ^{1}H NMR spectrum for **2a'** and **2b** (9 ppm - 5.4 ppm) present in small amount along with major complex **2a** in C_6D_6 at 23 ℃.

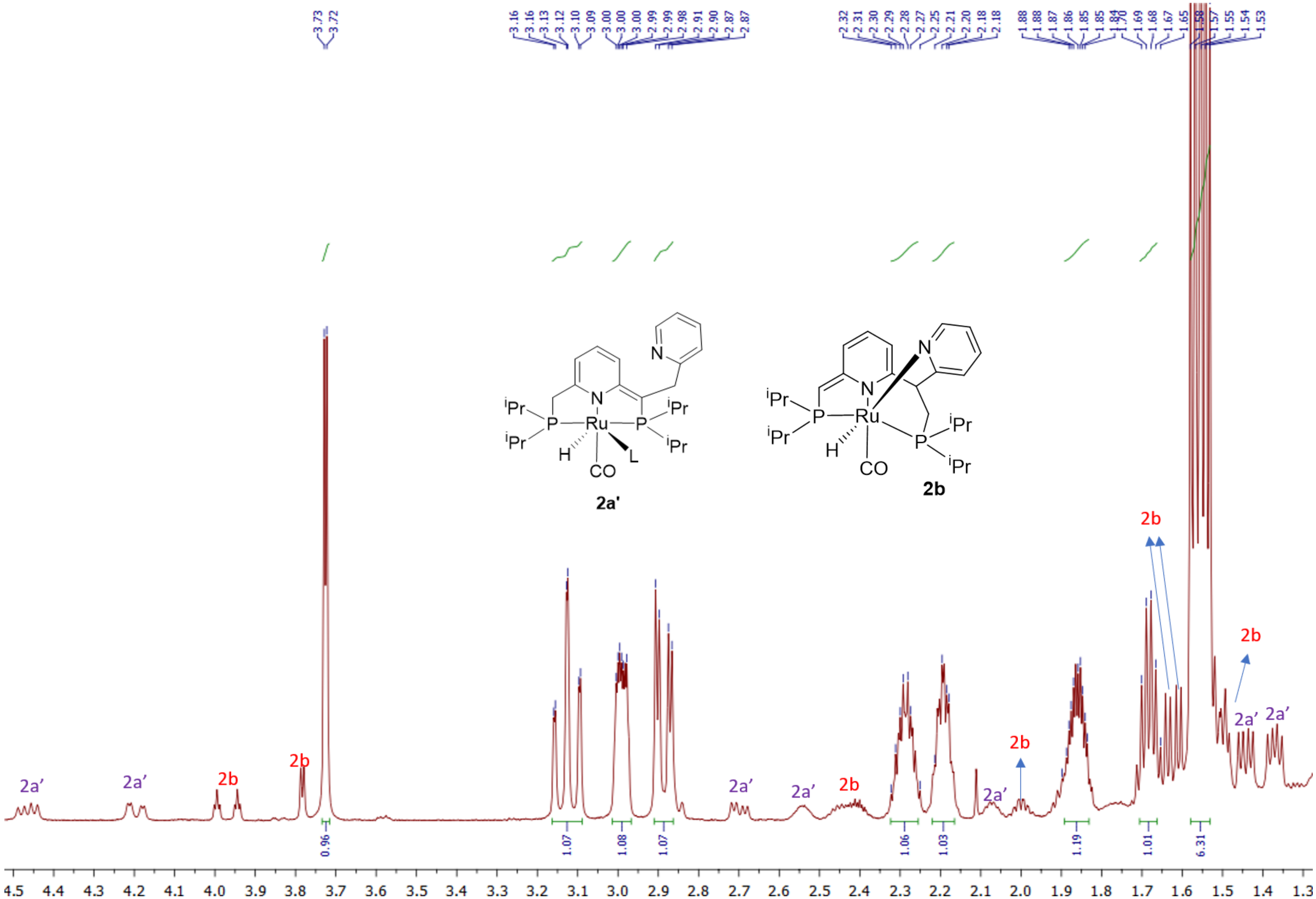


Figure S34. Expanded [1]H NMR spectrum for **2a’** and **2b** (4.5 ppm - 1.3 ppm) present in small amount along with major complex **2a** in C_6D_6 at 23 °C.

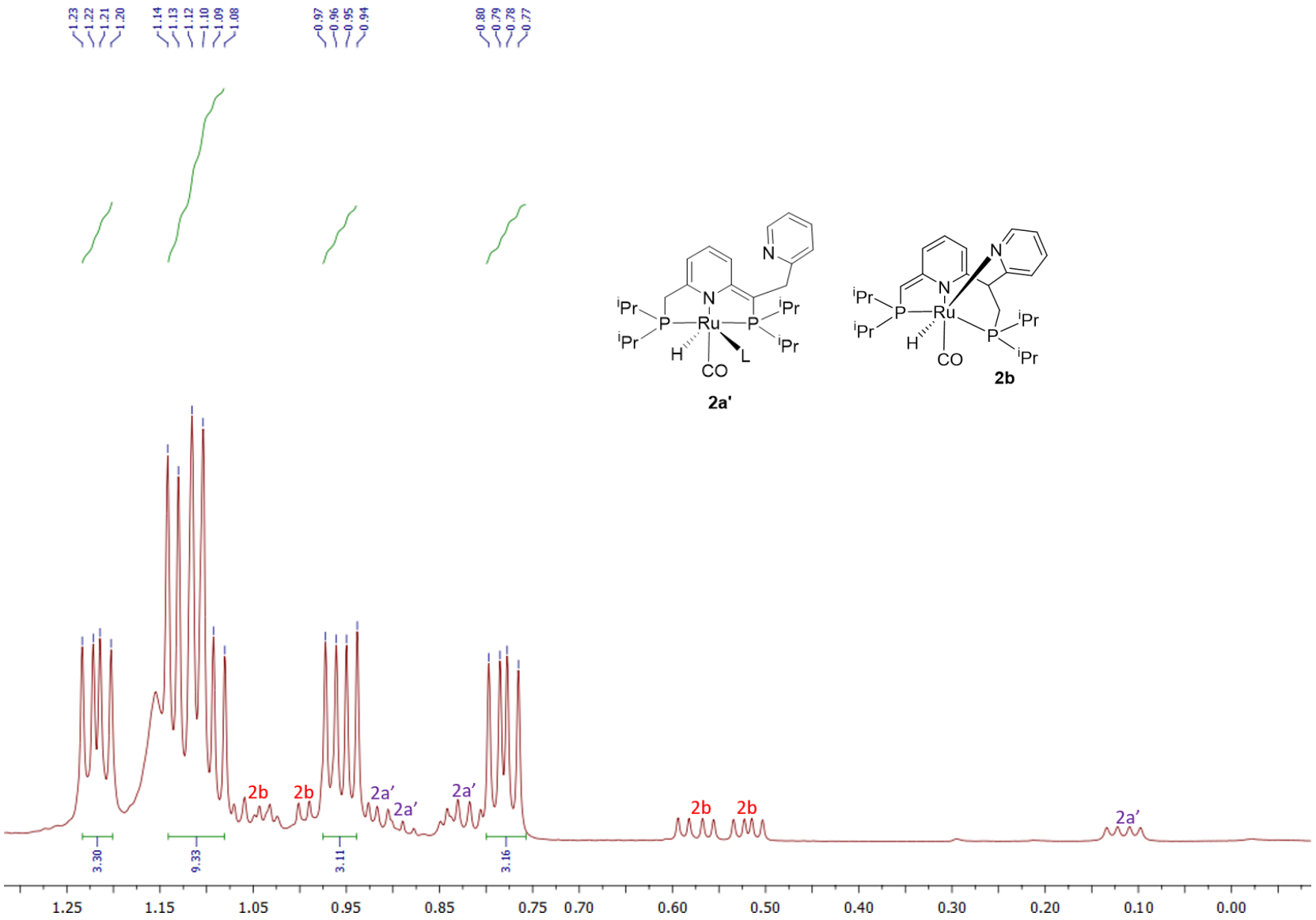


Figure S35. Expanded ^{1}H NMR spectrum for **2a'** and **2b** (1.2 ppm - 0.1 ppm) present in small amount along with major complex **2a** in C_6D_6 at 23 °C.

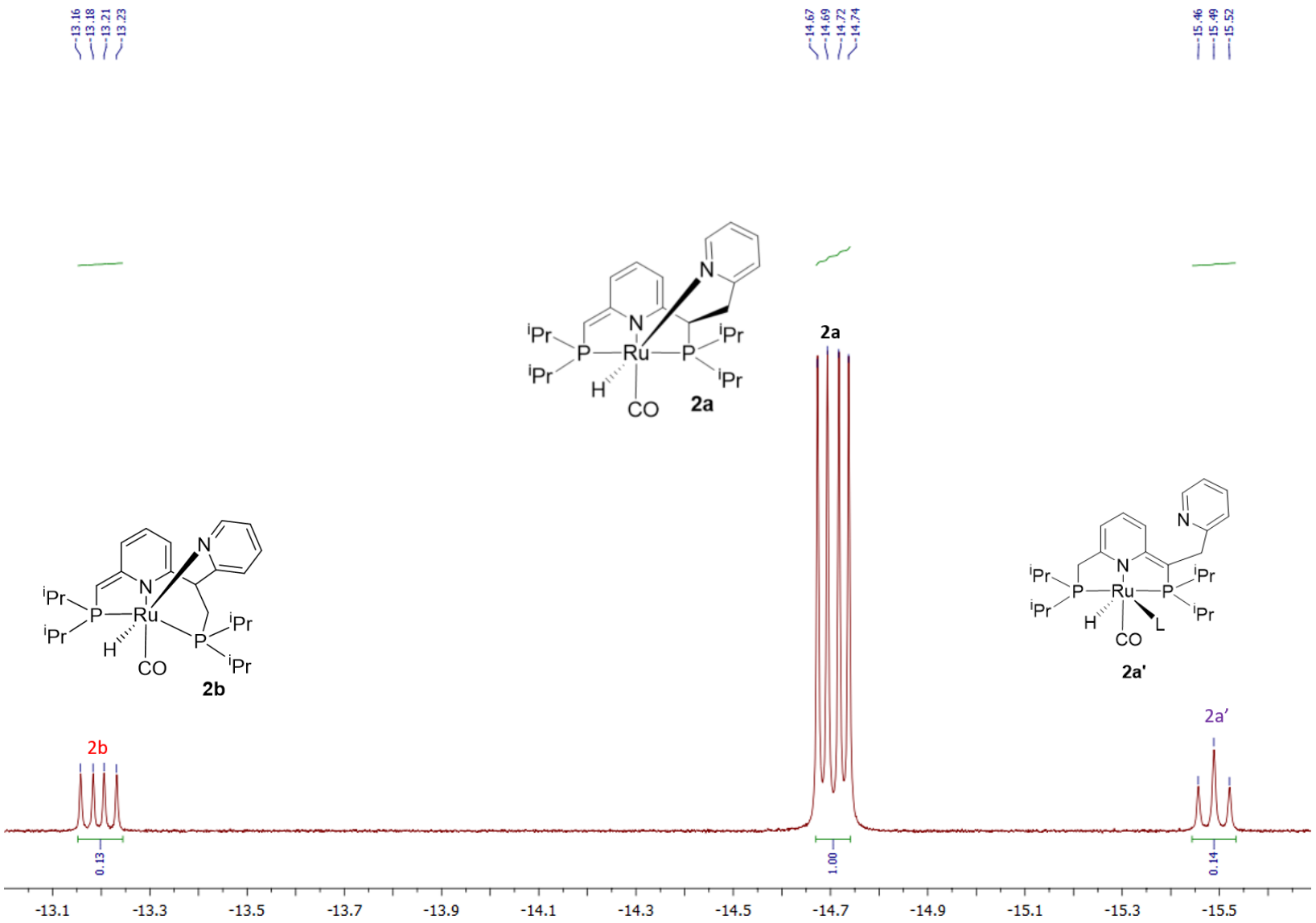


Figure S36. Expanded ^{1}H NMR spectrum for **2a'** and **2b** (1.2 ppm - 0.1 ppm) present in small amount along with major complex **2a** in C_6D_6 at 23 ℃.

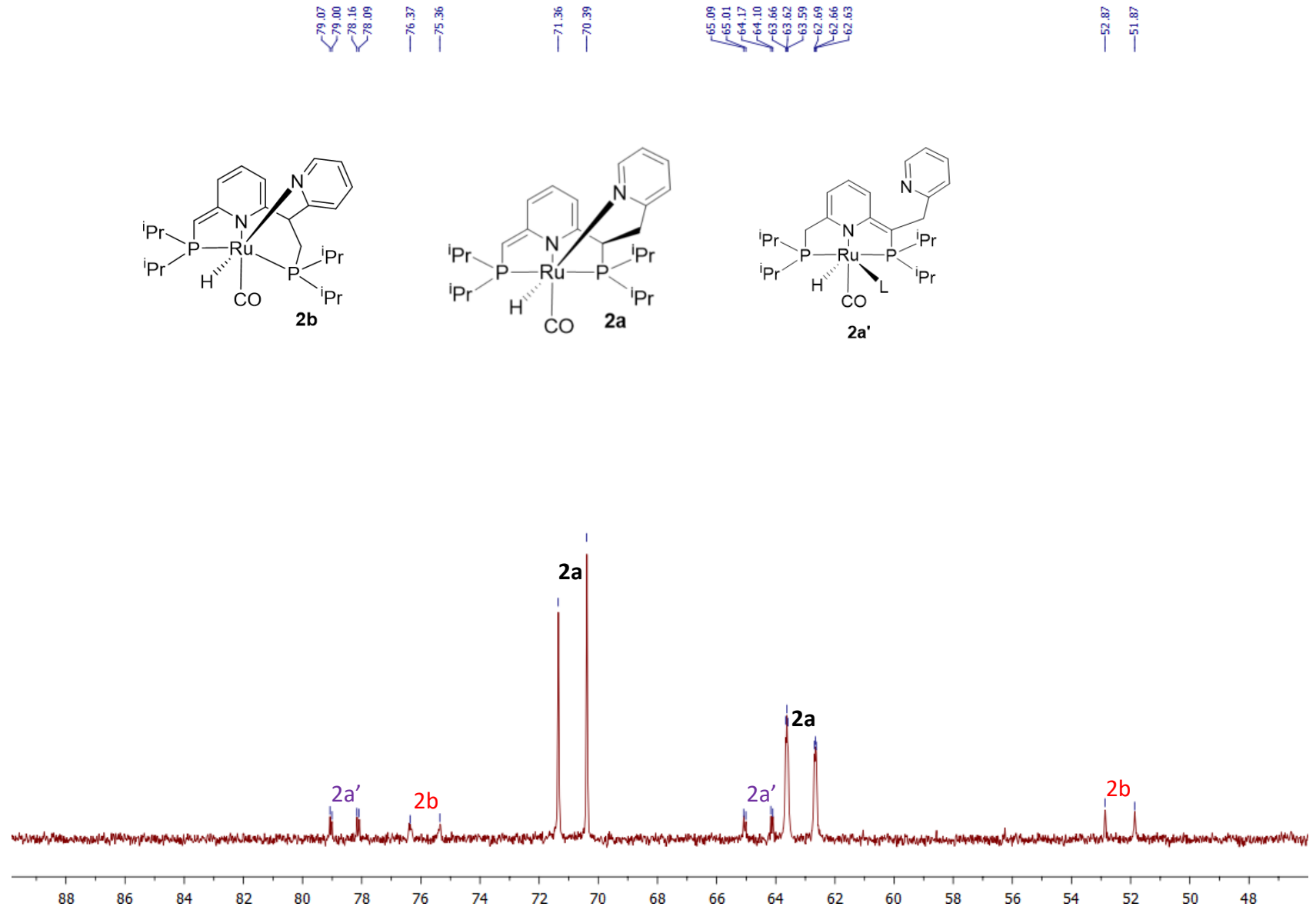
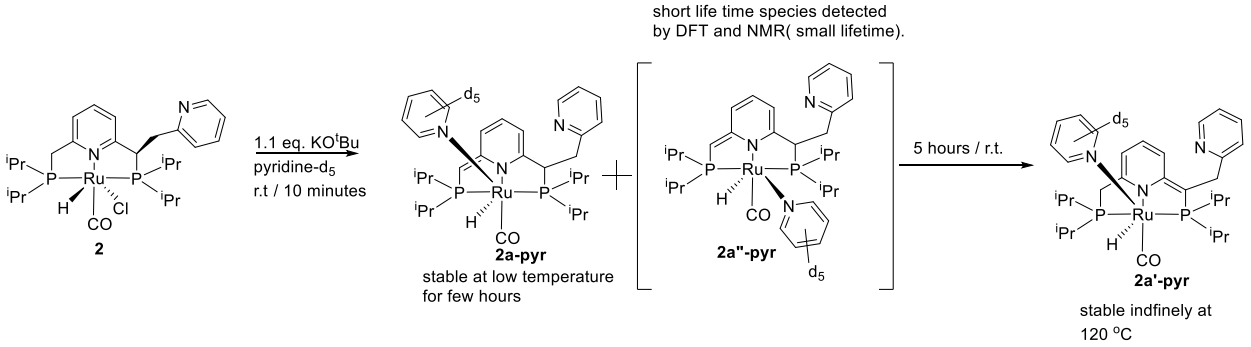


Figure S37. ^{31}P NMR spectrum of complex **2a** (major) and **2a'** and **2b** present in a minor amount in C_6D_6 at 23 °C.

Reactivity of complex 2 in C_5D_5N.



In pyridine-d_5 deprotonation of complex **2** leads to a different outcome than that of the non-coordinating solvent C_6D_6. **2a-pyr** is observed as the first major complex after deprotonation, but it is destabilized in relation to **2a'-pyr**, likely since coordination of the pyridine arm becomes less important in pyridine solvent and a tetra-substituted double bond is more stable than a tri-substituted one. **2b** is never formed in pyridine. For **2a-pyr**, the pyridine arm is likely decoordinated as the *ortho* pyridine-H resonance at 8.41 ppm the relatively upfield shifted, but it's impossible to tell if the arm is cis or trans-oriented to the hydride ligand.

There is another minor species present right after deprotonation with bridging peaks at 4.72 and 3.71 ppm, and two other overlapping proton peaks, and an associate hydride at -14.23 ppm. We tentatively assign this as the **2a''-pyr** complex where the pyridine arm is dearomatized in lieu of the central pyridine ring. **2a''-pyr** starts to rapidly disappear at room temperature. **2a-pyr** also starts to quickly disappear, but less rapidly; it is possible to obtain 2D spectral information at -5 °C and to make definite assignments for **2a-pyr**, which is characterized by two protons of the picolyl arm coupling with a single proton on the PNP backbone. HMQC shows the coupling of the proton signal on the dearomatized carbon to a downfield shifted, olefinic carbon and HMBC further confirms the connectivity between the three protons on the non-dearomatized side of the complex while the proton resonance at 3.6 ppm does not have a corresponding HMBC signal, ruling out the other two possible isomers.

During the 2D experiments, already a lot of **2a'-pyr** forms in-situ; aliphatic region of ^{1}H NMR difficult to interpret due to overlap with **2a''-pyr** and HO^{t}Bu/KO^{t}Bu Me peak (*see below*). Trace triphenyl phosphine is present in the reaction at 7.47 and 7.35 ppm in ^{1}H-NMR.

Complex **2a-pyr** - ^{1}H NMR (400 MHz, C_5D_5N) δ 8.55 (dd, *J* = 5.1, 1.7 Hz, 1H, py-*H*), 7.55-7.59 (td, *J*= 7.6, 1.9Hz, 1H,overlap with meta-H solvent peak, py-*H*) 7.39 – 7.35 (d, *J* = 7.7 Hz, 1H,

py-*H*), 7.02 (dd, *J* = 7.4, 4.9 Hz, 1H, py-*H*), 6.52 – 6.47 (m, 1H, py-*H*), 6.44 (d, *J* = 8.7 Hz, 1H, py-*H*) 5.40 (d, *J* = 6.5 Hz, 1H, py-*H*), 4.34 (t, *J* = 10.0 Hz, 1H, sub-arm-*H*), 3.67 (d, *J* = 4.2 Hz, 1H, dearom-arm-*H*), 3.43 – 3.31 (m, 2H, bridge-*H*), 2.32 – 2.08 (m, 3H, ^{i}Pr-*H*), 1.55-1.48 (m, 1H, ^{i}Pr-*H*), 1.36-1.45 (m, 6H, ^{i}Pr-*Me*) 1.38 – 1.28 (m, 6H, ^{i}Pr-*Me*), 1.23 (dd, *J* = 14.2, 6.8 Hz, 3H, ^{i}Pr-*Me*), 1.06 (dd, *J* = 13.0, 7.0 Hz, 3H, ^{i}Pr-*Me*), 0.94 (dd, *J* = 14.0, 7.3 Hz, 3H, ^{i}Pr-*Me*), 0.88 (dd, *J* = 13.0, 7.1 Hz, 3H, ^{i}Pr-*Me*), -14.45 (v.t, *J* = 18.8 Hz, 1H, Ru-*H*). ^{31}P NMR (162 MHz, C_5D_5N): δ 79.62 (d, 1P, $J_{P\text{-}P}$ = 225.1 Hz), 62.25 (d, 1P, $J_{P\text{-}P}$ = 225.1 Hz).

After half an hour at room temperature, complex **2a'-pyr** becomes major and it is eventually the only species left in solution after five hours at r.t. **2a'-pyr** does not convert further even after prolonged heating at 80 °C and overnight at 120 °C. Thus, it is possible to obtain clean spectral 2D data and to differentiate all signals from those of earlier present **2a-pyr**. The COSY data shows two sets of two protons each that do not couple to each other while the HSQC data place the proton signals on the non-dearomatized bridging carbons, affirming the identity of the final complex as **2a'-pyr**.

In complex **2a'-pyr** one CH_3 group is overlapping with the KO^{t}Bu and HO^{t}Bu resonances. Trace triphenyl phosphine is present in the reaction at 7.47 and 7.35 ppm in ^{1}H-NMR. The broad resonance in the aromatic region integrating to 1H at ~5.90 is likely HO^{t}Bu alcohol proton as it changes position depending on the concentration of complex in pyridine, during repeat experiments. This resonance is not affected by the transformation of **2a-pyr** to **2a'-pyr**.

Complex **2a'-pyr** - ^{1}H NMR (400 MHz, C_5D_5N) δ 8.78 (d, *J* = 4.8Hz, 1H, py-*H*), 7.49-7.54 (m, 2H, py-*H*), 7.07 (td, *J* = 5.2, 2.6 Hz, 1H, py-*H*), 6.72 (m, 1H, py-*H*), 6.06 (d, *J* = 9.0 Hz, 1H, py-*H*), 5.78 (d, *J* = 6.6 Hz, 1H, py-*H*), 4.02 (dd, *J* = 18.3, 8.6 Hz, 1H, arm-*H*), 3.95 (dd, *J* = 18.3, 8.6 Hz, 1H, arm-*H*), 3.10 (dd, *J* = 16.6, 11.4 Hz, 1H, bridge-*H*), 2.79 (dd, *J* = 16.4, 7.0 Hz, 1H, bridge-*H*), 2.23-2.31 (m, 1H, ^{i}Pr-*H*), 2.00-2.06 (m, 1H, ^{i}Pr-*H*), 1.91-1.99 (m, 1H, ^{i}Pr-*H*), 1.55-1.62 (m, 1H, ^{i}Pr-*H*), 1.37 (m, 3H, ^{i}Pr-*Me*), 1.13-1.22 (m, 9H, ^{i}Pr-*Me*), 1.13-109 (m, 6H, ^{i}Pr-*Me*), 1.03 (m, 3H, ^{i}Pr-*Me*), 0.94 (dd, *J* = 11.7, 7.0 Hz, 3H, ^{i}Pr-*Me*), -14.40 (v.t, 1H).

^{13}C NMR (151 MHz, C_5D_5N) δ 210.2 (*C*O), 168.3 (J_{PC} = 23.6 Hz, py-*C*), 164.4 (py-*C*), 160.0 (py-*C*), 136.6 (py-*C*), 134.6 (J_{PC} = 20.3 Hz, py-*C*), 133.4 (py-*C*), 123.3 (py-*C*), 121.4 (py-*C*), 110.4 (J_{PC} = 15.2 Hz, py-*C*)), 98.9 (J_{PC} = 11.2 Hz, py-*C*), 73.0 (C_{arm}), 40.1 (J_{PC} = 18.8 Hz, C_{arm}), 39.5 (bridge-*C*), 30.0 (J_{PC} = 21.0 Hz, ^{i}Pr-*C*), 28.1 (J_{PC} = 16.5 Hz, ^{i}Pr-*C*), 27.1 (J_{PC} = 32.4 Hz, ^{i}Pr-*C*),

25.2 (J_{PC} = 25.6 Hz, ^{i}Pr-*C*), 21.9 (^{i}Pr-*Me*), 21.4 (^{i}Pr-*Me*), 20.8 (^{i}Pr-*Me*), 20.6 (^{i}Pr-*Me*), 20.4 (^{i}Pr-*Me*), 20.3 (^{i}Pr-*Me*), 19.0 (^{i}Pr-*Me*), 18.3 (^{i}Pr-*Me*).

^{31}P NMR (162 MHz, C_5D_5N) δ 74.19 (d, 1P, J_{P-P} = 225.2 Hz), 67.26 (d, 1P, J_{P-P} = 225.2 Hz).

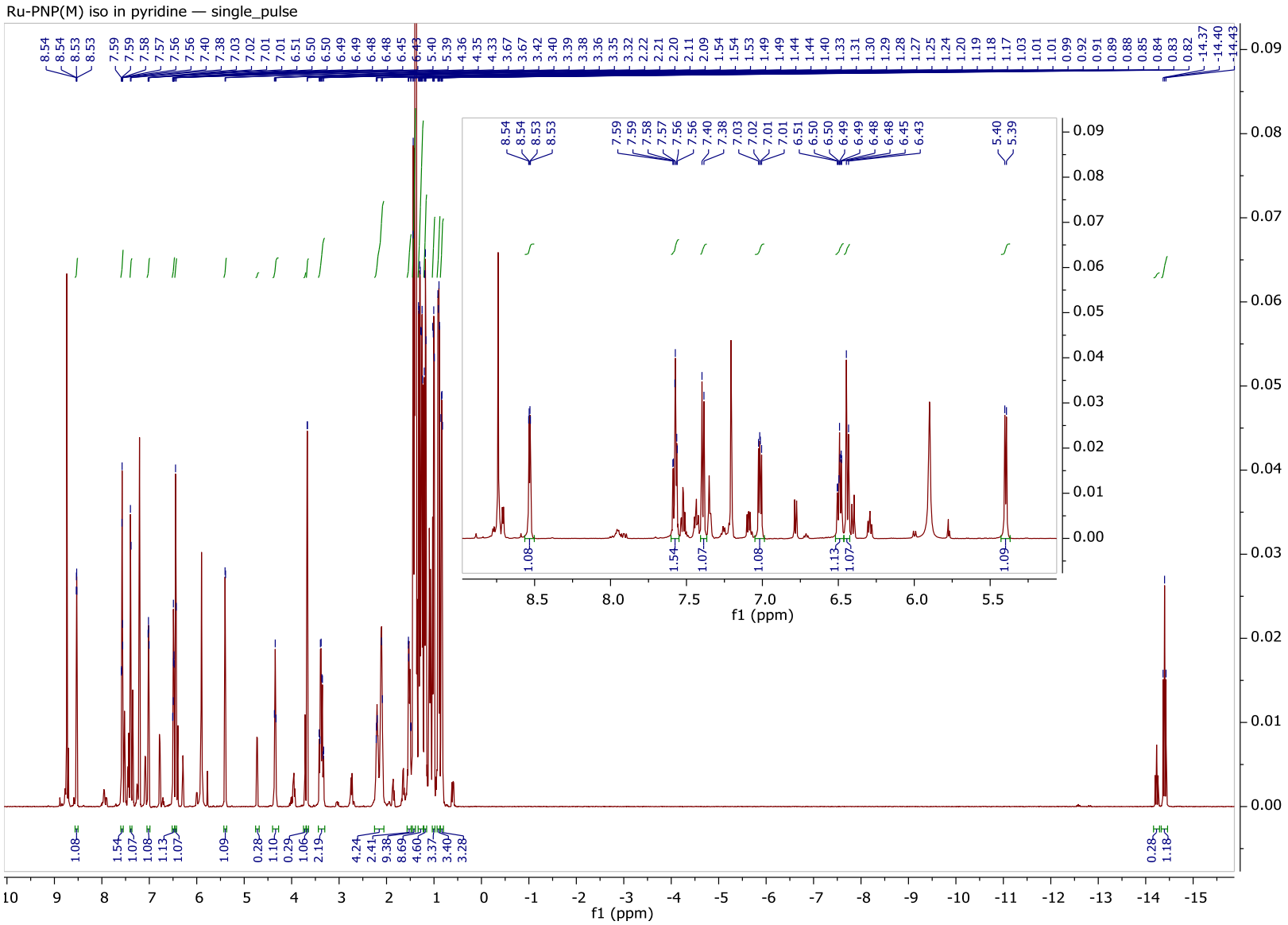


Figure S38. ^{1}H NMR of complex **2a-pyr** with aromatic region expansion in C_5D_5N at 23 °C.

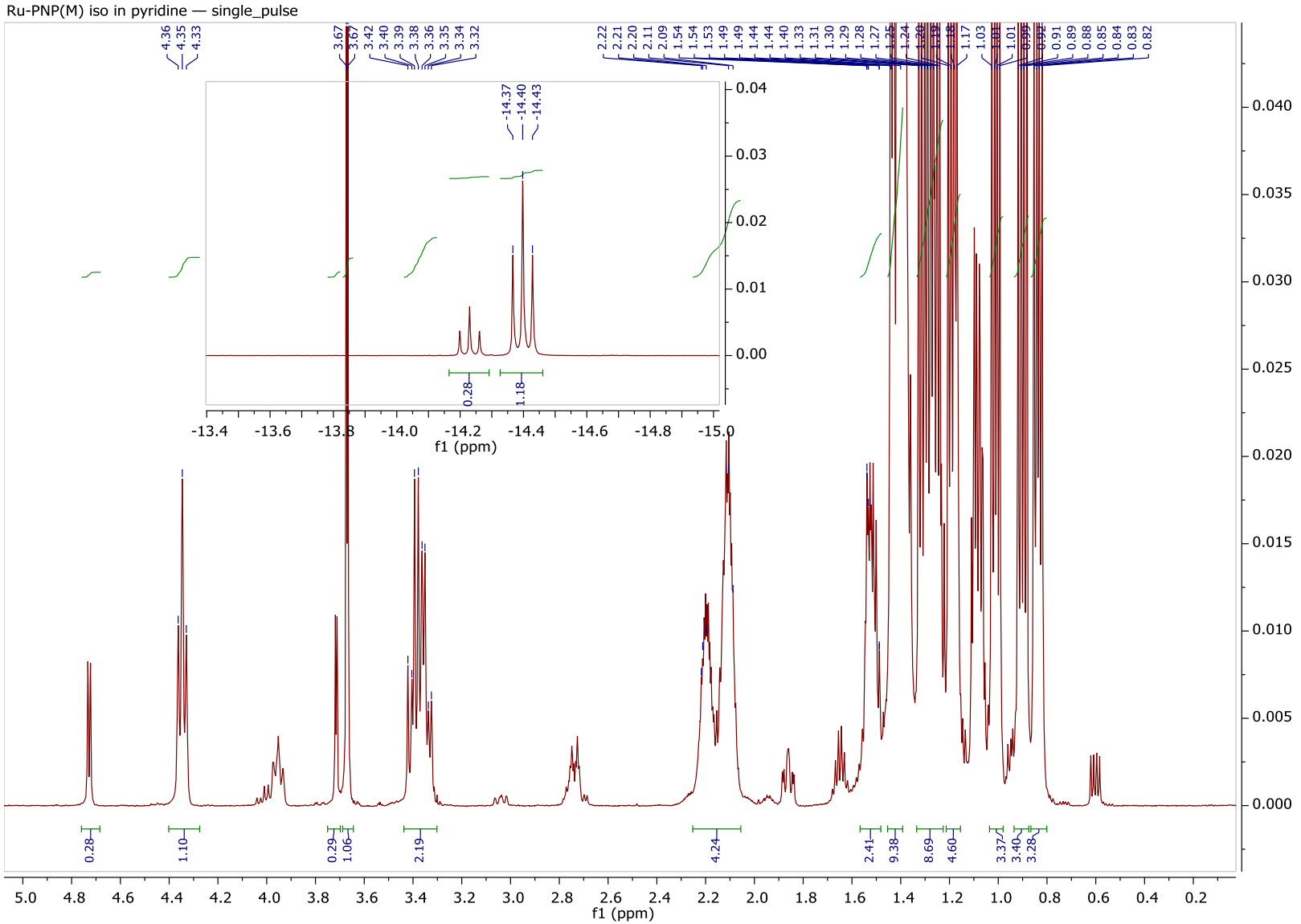


Figure S39. ^{1}H NMR spectrum of complex **2a-pyr** in C_5D_5N at 23 °C with aliphatic and hydride region expansion.

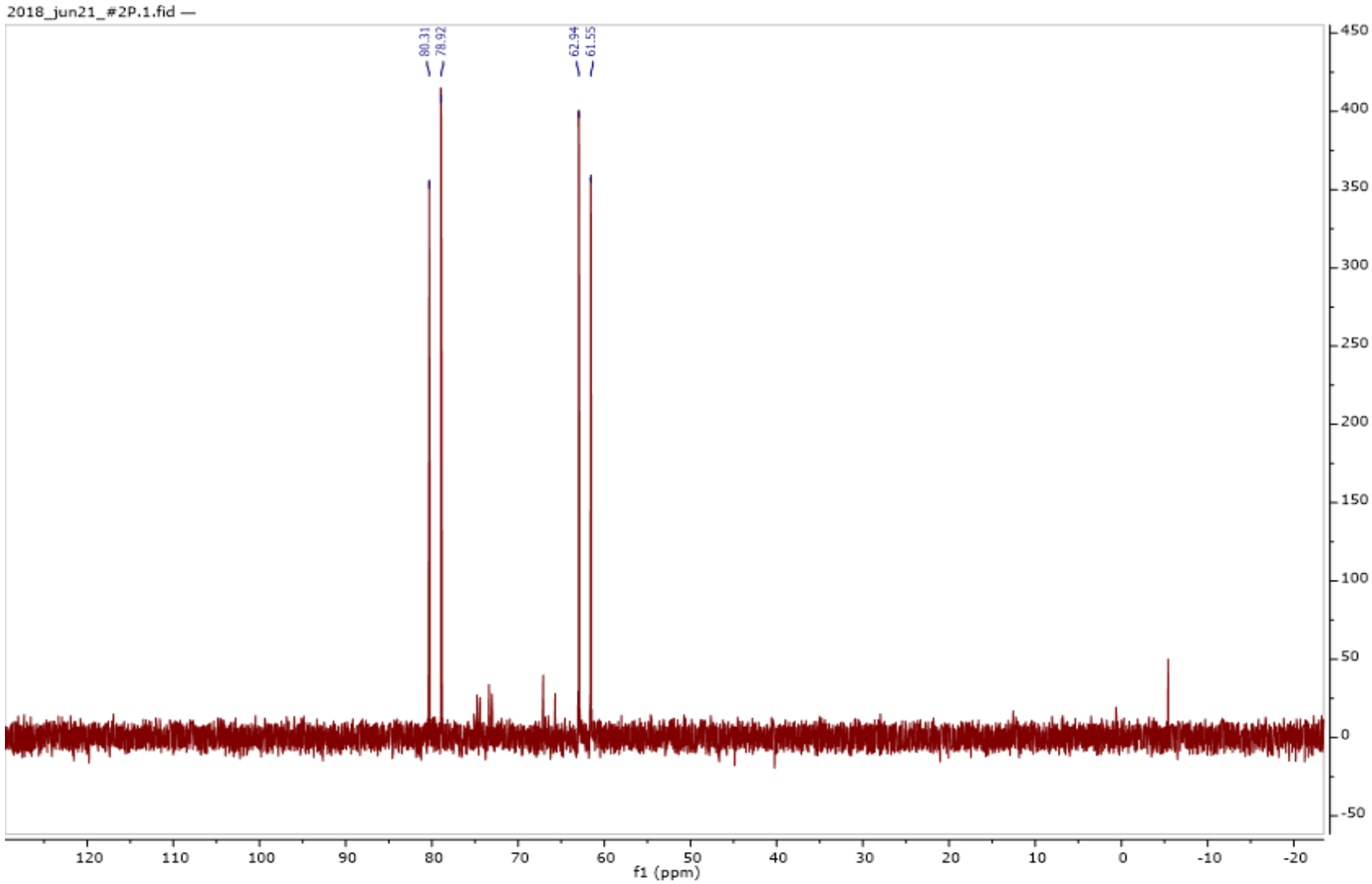


Figure S40. ^{31}P NMR spectrum of complex **2a-pyr** in C_5D_5N at 23 °C (**2a''-pyr** disappears and **2a'-pyr** begins appearing).

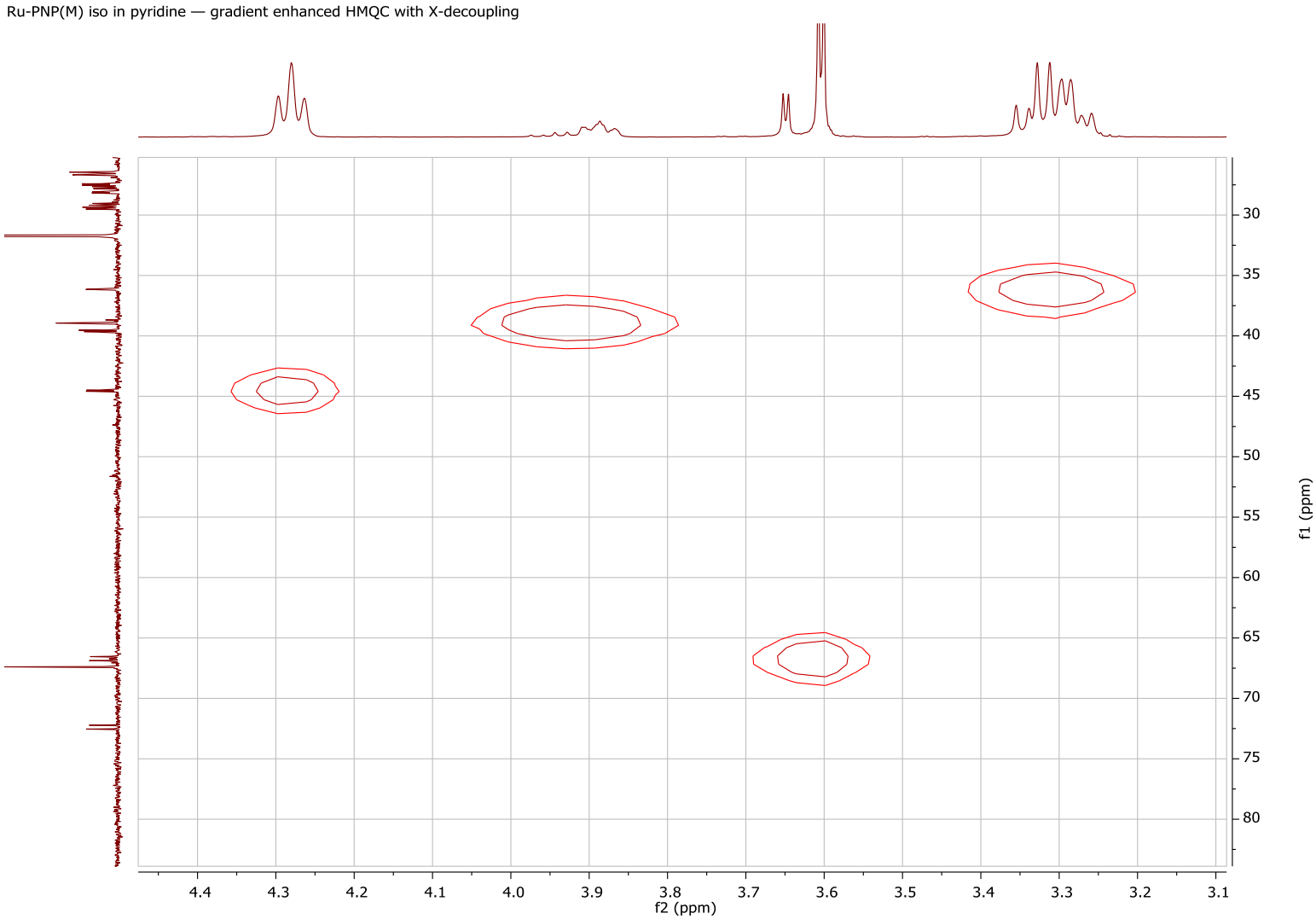


Figure S41. HMQC spectrum of complex **2a-pyr** C_5D_5N at -5 °C bridging proton region expanded. The 3.9 ppm signal from complex **2a'** that forms during acquisition.

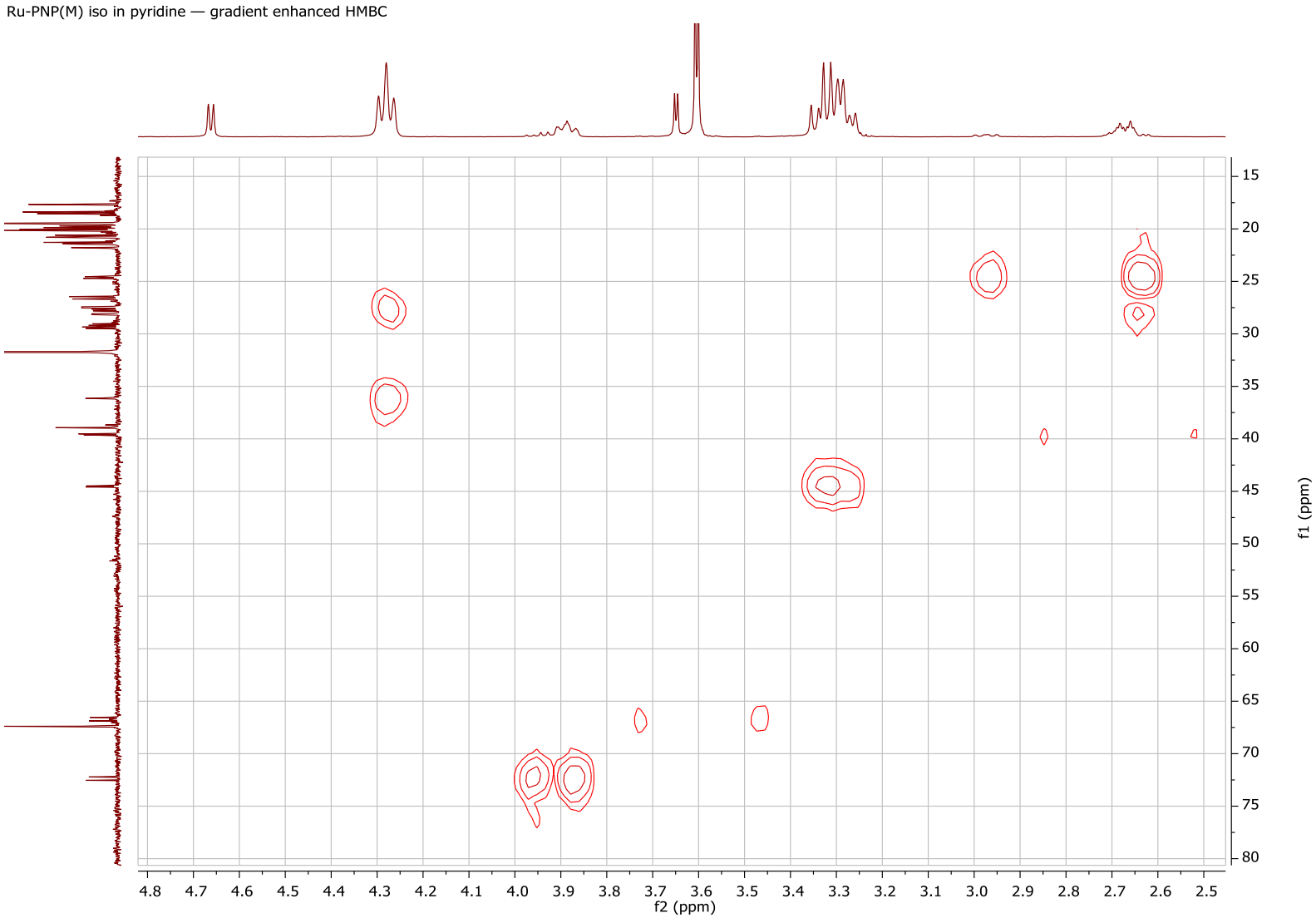


Figure S42. HMBC spectrum of complex **2a-pyr** C_5D_5N at -5 °C bridging proton region expanded. 3.9, 2.9, and 2.6 ppm signals from complex **2a'-pyr** that forms during acquisition.

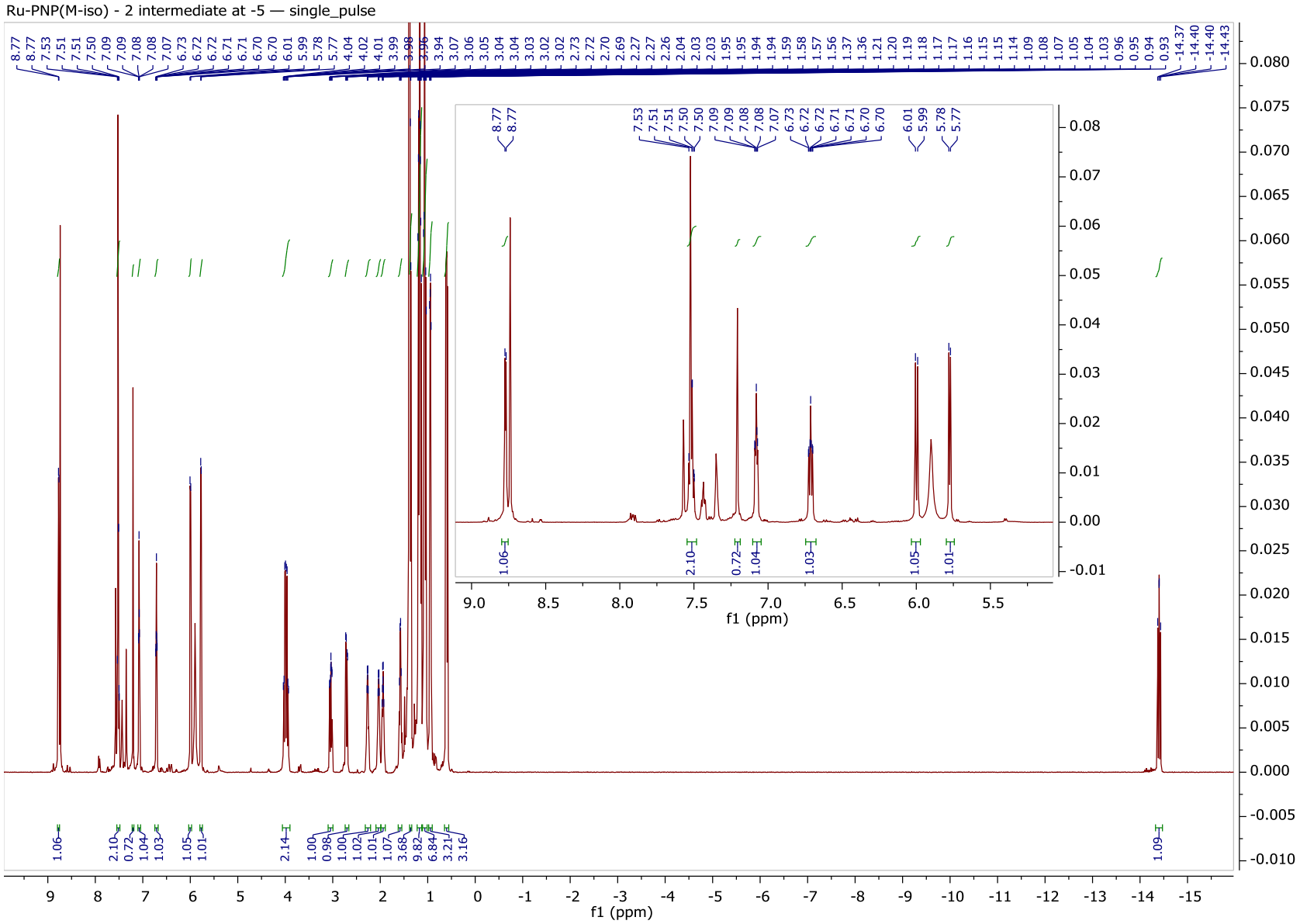


Figure S43. ^{1}H NMR of complex **2a'-pyr** with aromatic region expansion in C_5D_5N at 23 °C.

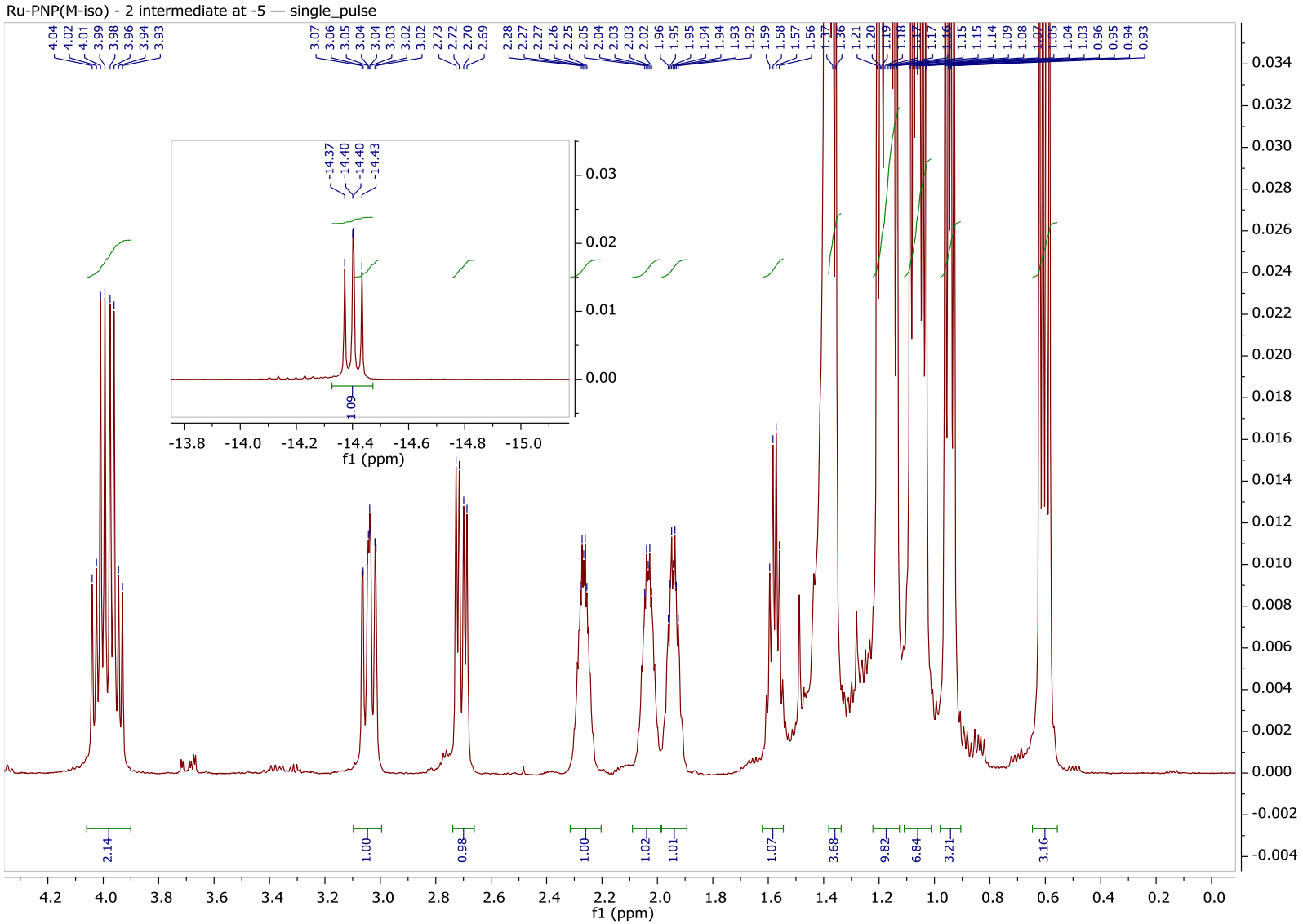


Figure S44. ^{1}H NMR spectrum zoom in view of an aliphatic region of complex **2a'-pyr** along with hydride region expansion C_5D_5N at 23 °C.

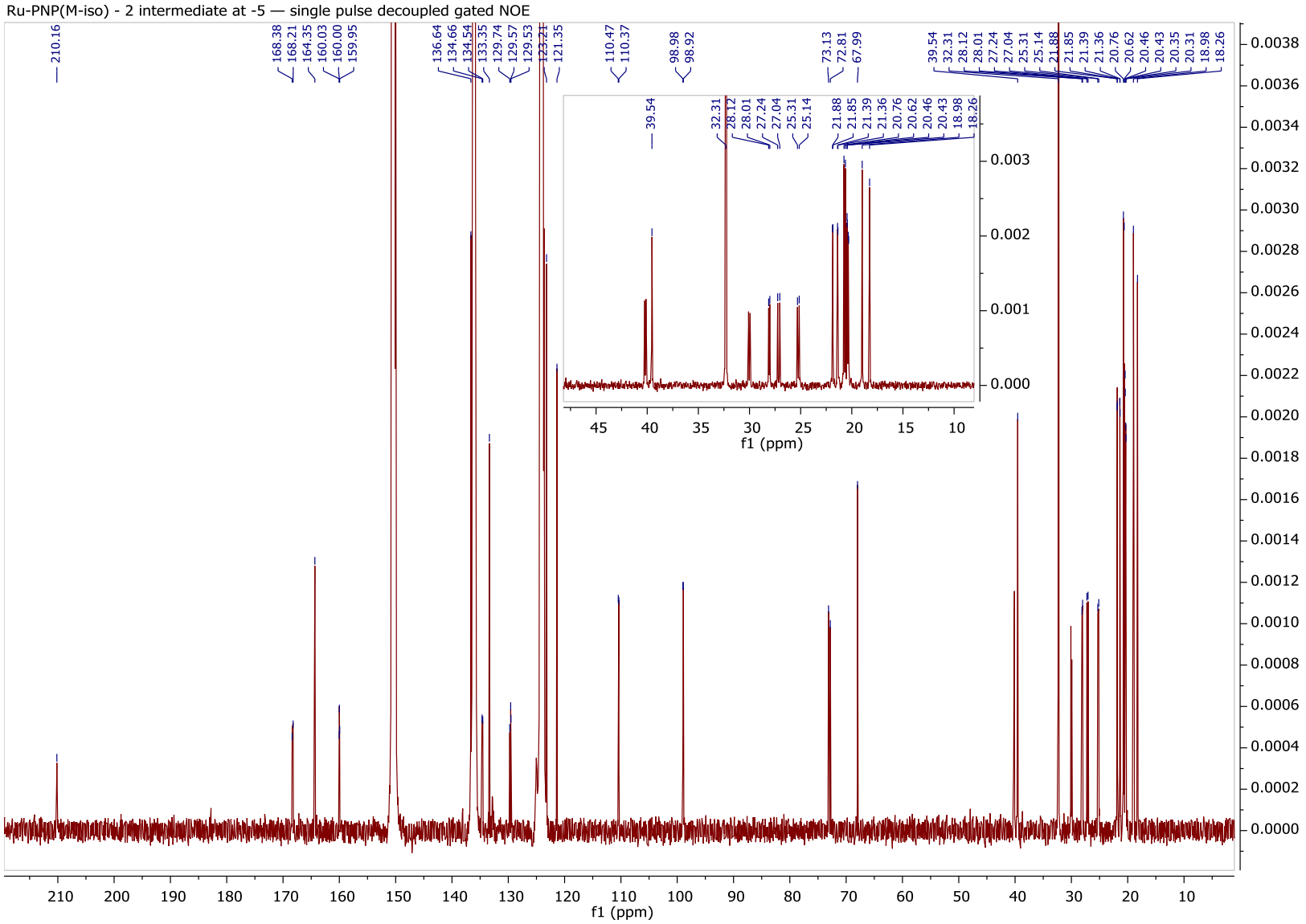


Figure S45. ^{13}C NMR spectrum of complex **2a'-pyr** in C_5D_5N at -5 °C. PPh_3 impurity at 129.5 and 130ppm. KO^{t}Bu at 68.0 and 32.3ppm.

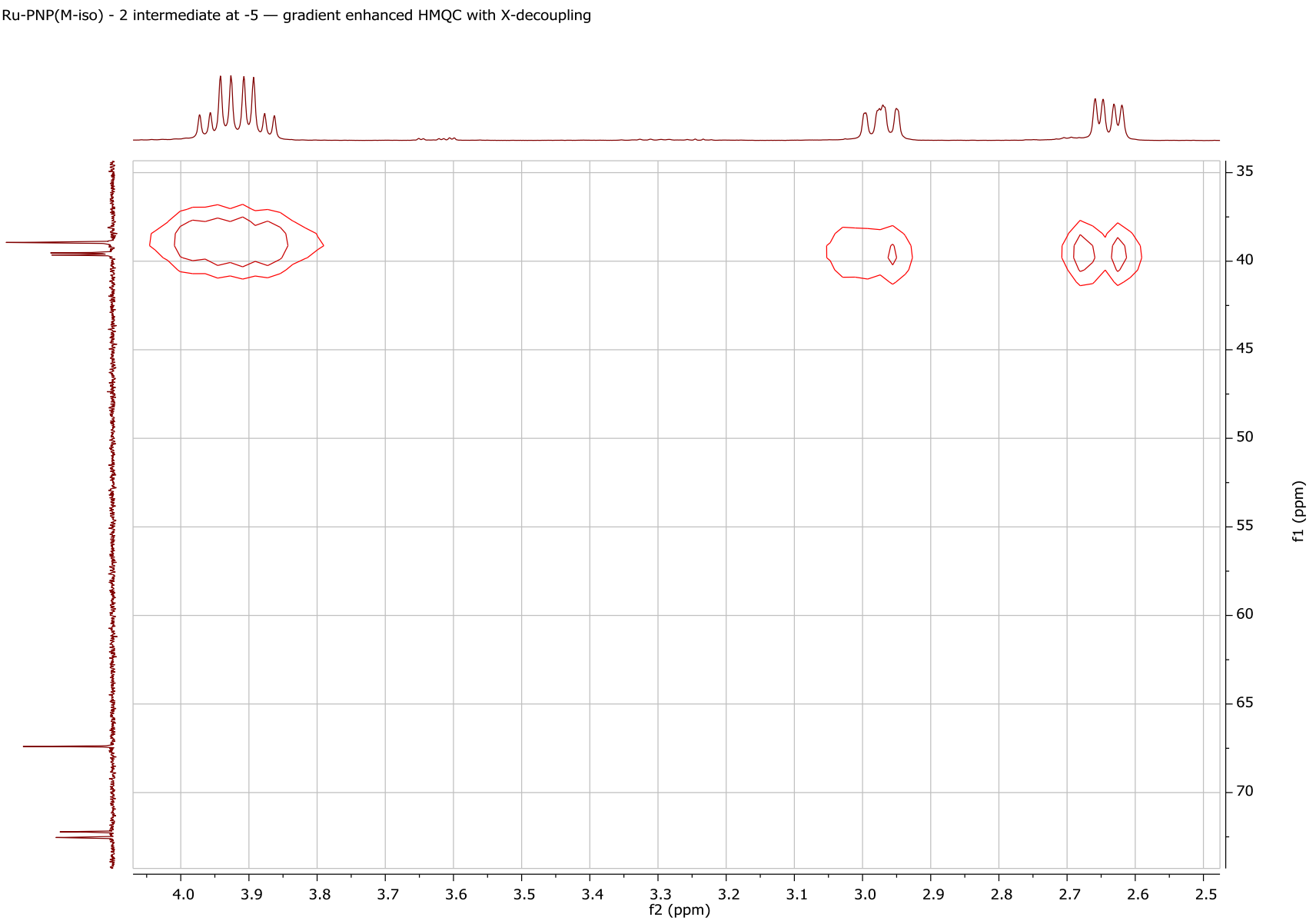


Figure S46. HSQC spectrum of complex **2a'-pyr** C_5D_5N at -5 ℃ bridging proton region expanded.

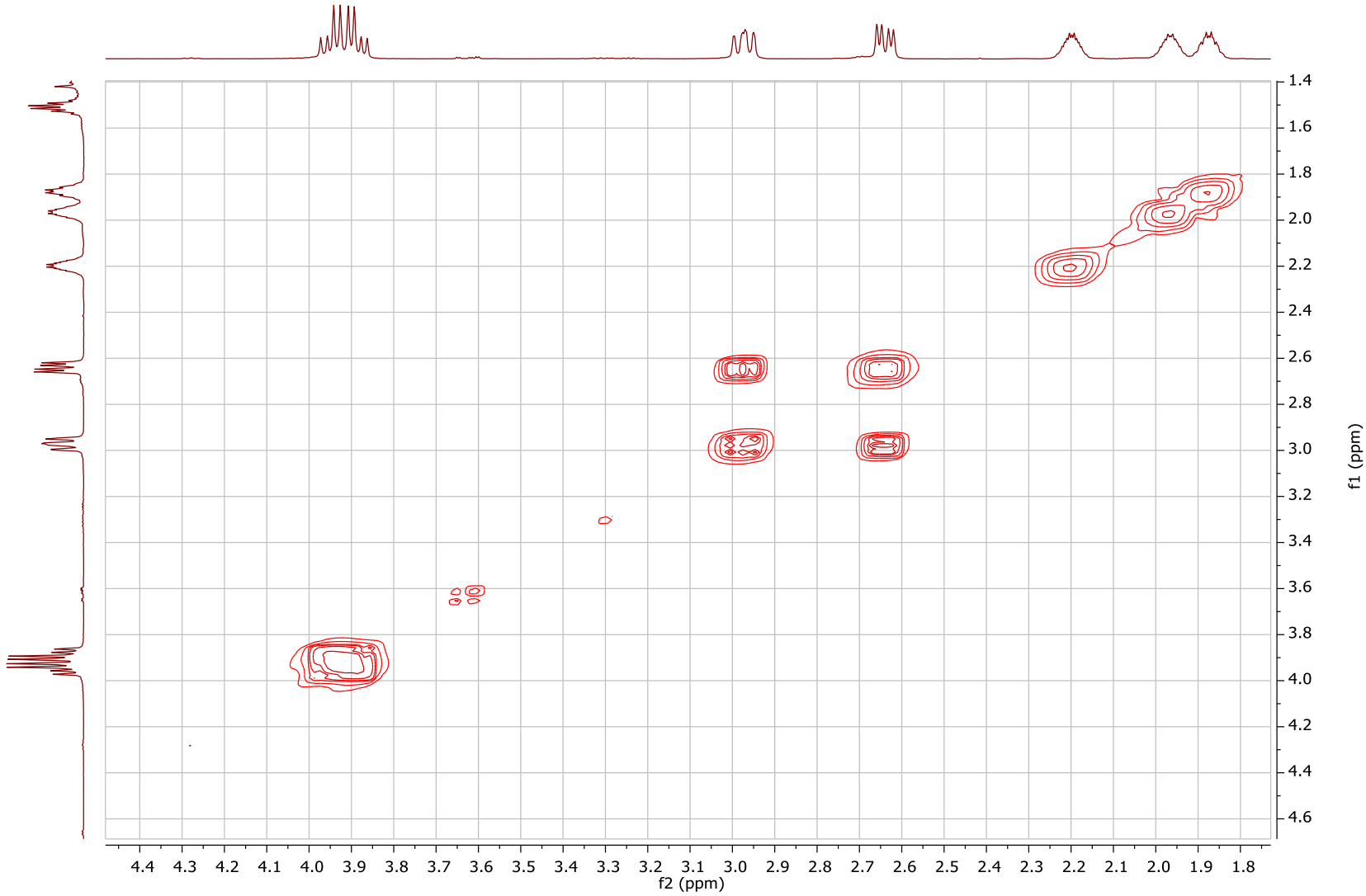


Figure S47. COSY spectrum of complex **2a'-pyr** C_5D_5N at -5 °C bridging region expanded.

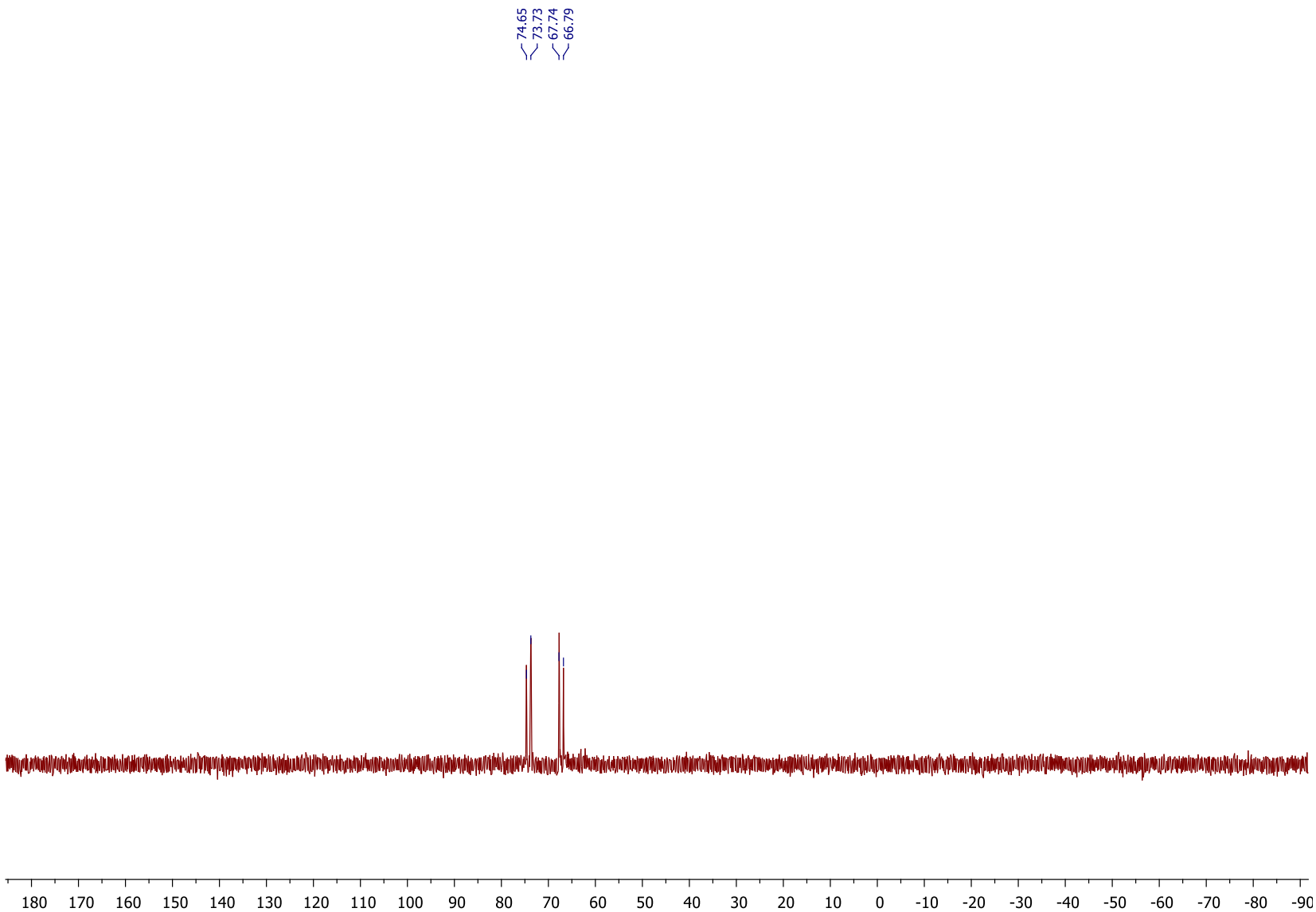
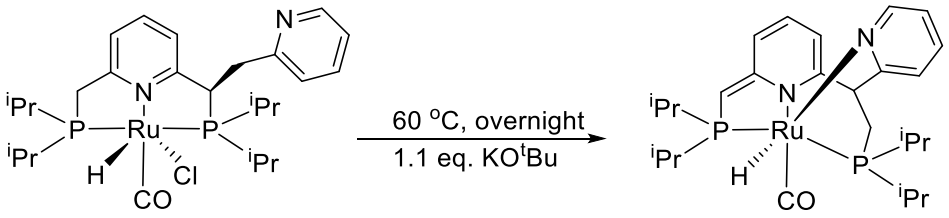


Figure S48. ^{31}P NMR spectrum of complex **2a'-pyr** C_5D_5N at 23 °C.

Procedure for synthesis of complex 2b.



2 **2b**

In a glovebox under an inert atmosphere to a solution of complex **2** (0.167 mmol, 100 mg) in toluene (5 ml), KOtBu (0.184 mmol, 20.6 mg) was slowly added at room temperature. The resulting mixture was heated at 60 ℃ for overnight in a Schleck flask. Subsequently the red color solution was filtered through celite and all volatiles were removed under vacuum to afford **2b** as a red powder. Single crystals suitable for X-ray crystal structure analysis were formed by slow evaporation of a pentane solution at -30 ℃. Coordinated *ortho* pyridine peak is characteristically downfield shifted to 8.95 ppm, similar to **2a**. The red color complex was isolated in 80% yield.

^{1}H NMR (600 MHz, C_6D_6): δ 8.95 (d, 1H, *J* = 5.1 Hz, py-*H*), 6.71 (t, 1H, *J* = 7.6 Hz, py-*H*), 6.54 (m, 1H, py-*H*), 6.46 (d, 1H, *J* = 7.6 Hz, py-*H*), 6.38 (d, 1H, *J* = 7.6 Hz, py-*H*), 6.25 (t, 1H, *J* = 6.2 Hz, py-*H*), 5.53 (d, 1H, *J* = 6.2 Hz, py-*H*), 3.97 (dt, 1H, *J* =30.4, 3.9 Hz, arm-H), 3.78 (d, 1H, *J* = 4.5 Hz, arm-*H*), 2.42 (m, 1H, ^{i}Pr-*H*), 2.01 (m, 1H,bridge -*H*), 1.90 (m, 1H, bridge -*H*), 1.60-1.64 (m, 4H, overlap of ^{i}Pr-*Me* and ^{i}Pr-*H*), 1.56 (dd, 3H, *J* = 12.6, 6.8 Hz, ^{i}Pr-*Me*), 1.13-1.16 (m, 2H, ^{i}Pr-*Me*), 1.05 (dd, 3H, *J* = 16.3, 6.8 Hz, ^{i}Pr-*Me*), 0.98 (dd, 3H, *J* =16.3, 6.8 Hz, ^{i}Pr-*Me*), 0.92 (dd, 3H, *J* = 12.6, 6.8 Hz, ^{i}Pr-*Me*), 0.82 (dd, 3H, *J*=12.6, 6.8 Hz, ^{i}Pr-*Me*), 0.58 (dd, 3H, *J* = 12.6, 6.8 Hz, ^{i}Pr-*Me*), 0.52 (dd, 3H, *J* = 12.6, 6.8 Hz, ^{i}Pr-*Me*), -13.19 (dd, 1H, $J_{P\text{-}H}$ = 29.1, 15.5 Hz, Ru-H).

^{13}C NMR (151 MHz, C_6D_6): δ 208.99 (*C*O), 171.56 (py-*C*), 161.19 (py-*C*), 156.48 (py-*C*), 153.25 (py-*C*), 136.21 (py-*C*), 130.72 (py-*C*), 124.88 (py-*C*), 121.66 (py-*C*), 113.49 (py-*C*), 99.22 (py-*C*), 68.27 (d, dearom-C_{arm}, $J_{P\text{-}C}$ = 55.2 Hz), 56.06 (bridge-*C*), 29.84 (s), 26.71-25.55 (m), 20.76 (s), 20.46 (s, ^{i}Pr-*Me*), 19.25(s, ^{i}Pr-*Me*), 17.87(s, ^{i}Pr-*Me*), 17.15 (s, ^{i}Pr-*Me*), 17.02 (s, ^{i}Pr-*Me*), 16.75 (s, ^{i}Pr-*Me*), 16.31 (s, ^{i}Pr-*Me*), 15.33 (s, ^{i}Pr-*Me*).

^{31}P{1H} NMR (262 MHz, C_6D_6): δ 75.86 (d, 1P, $J_{P\text{-}P}$ = 241.9 Hz), 52.33 (d, 1P, $J_{P\text{-}P}$ = 241.9 Hz).

IR (neat solid) : ν (CO) 1897 cm^{-1}.

Anal. Calcd for $C_{26}H_{40}N_2P_2O_1Ru_1$: C, 55.80; H, 7.20; N, 5.01. Found: C, 55.91; H, 7.57; N, 4.33.

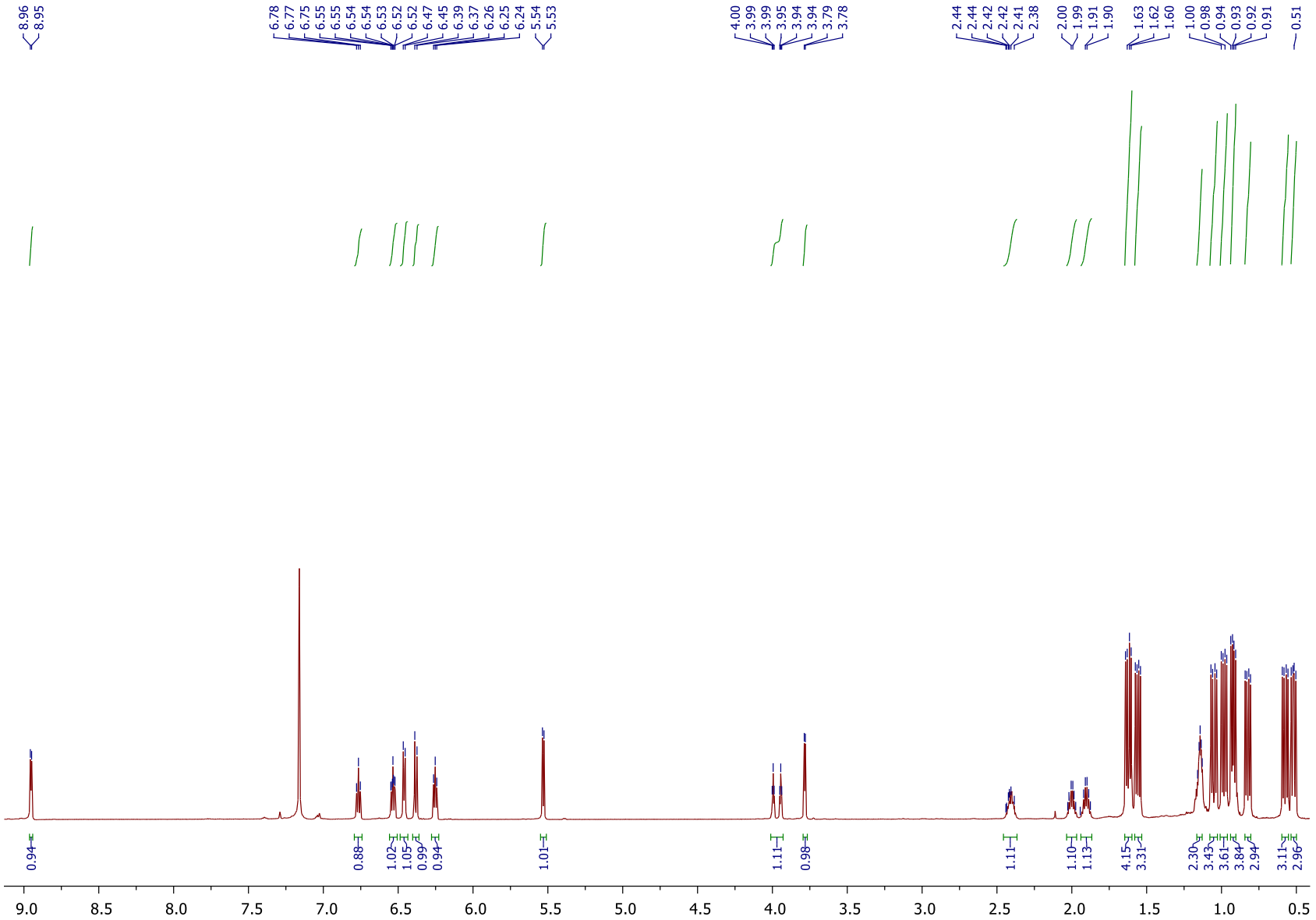


Figure S49. ^{1}H NMR spectrum of complex **2b** in C_6D_6 at 23 °C.

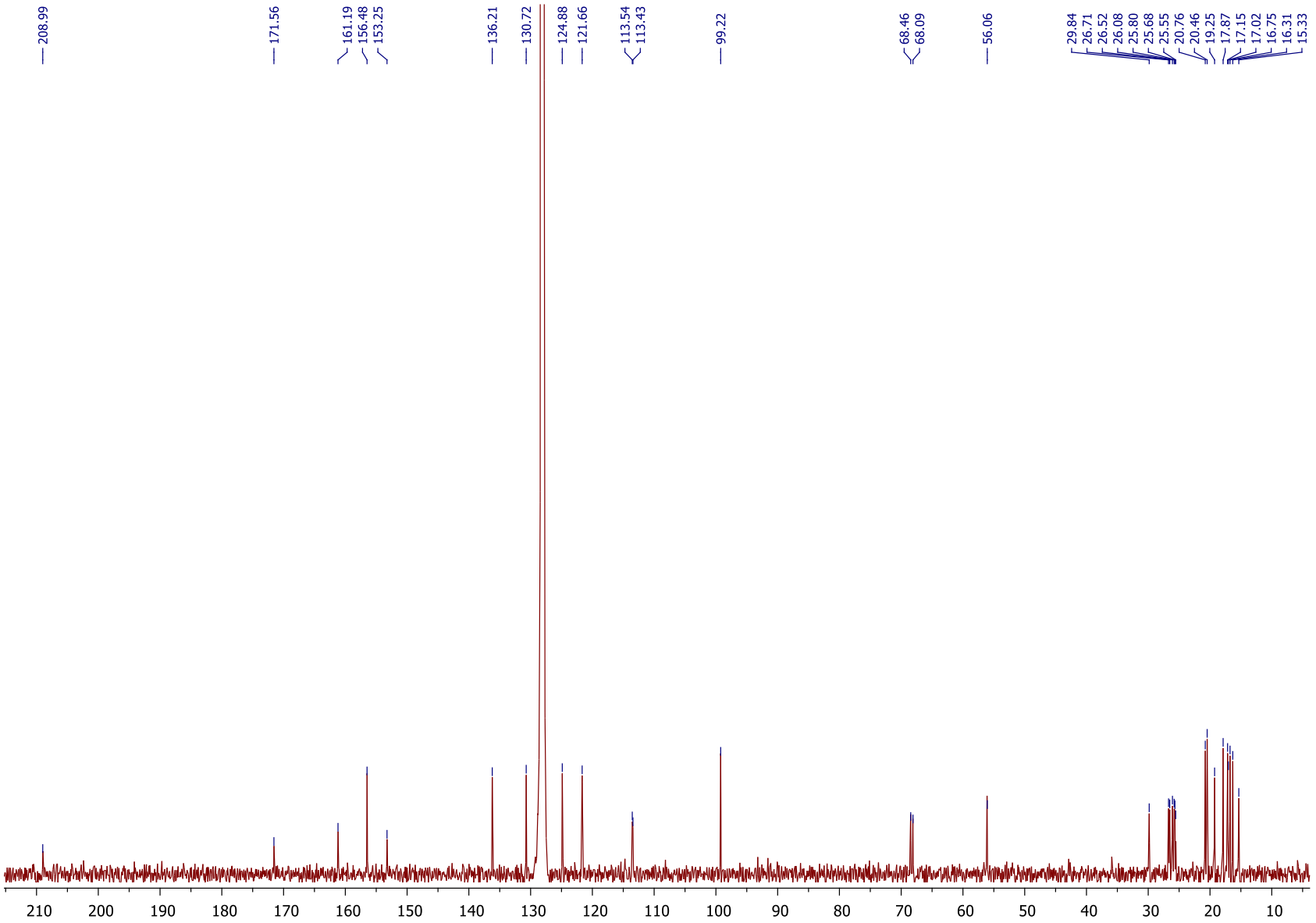


Figure S50. ^{13}C NMR spectrum of complex **2b** in C_6D_6 at 23 °C.

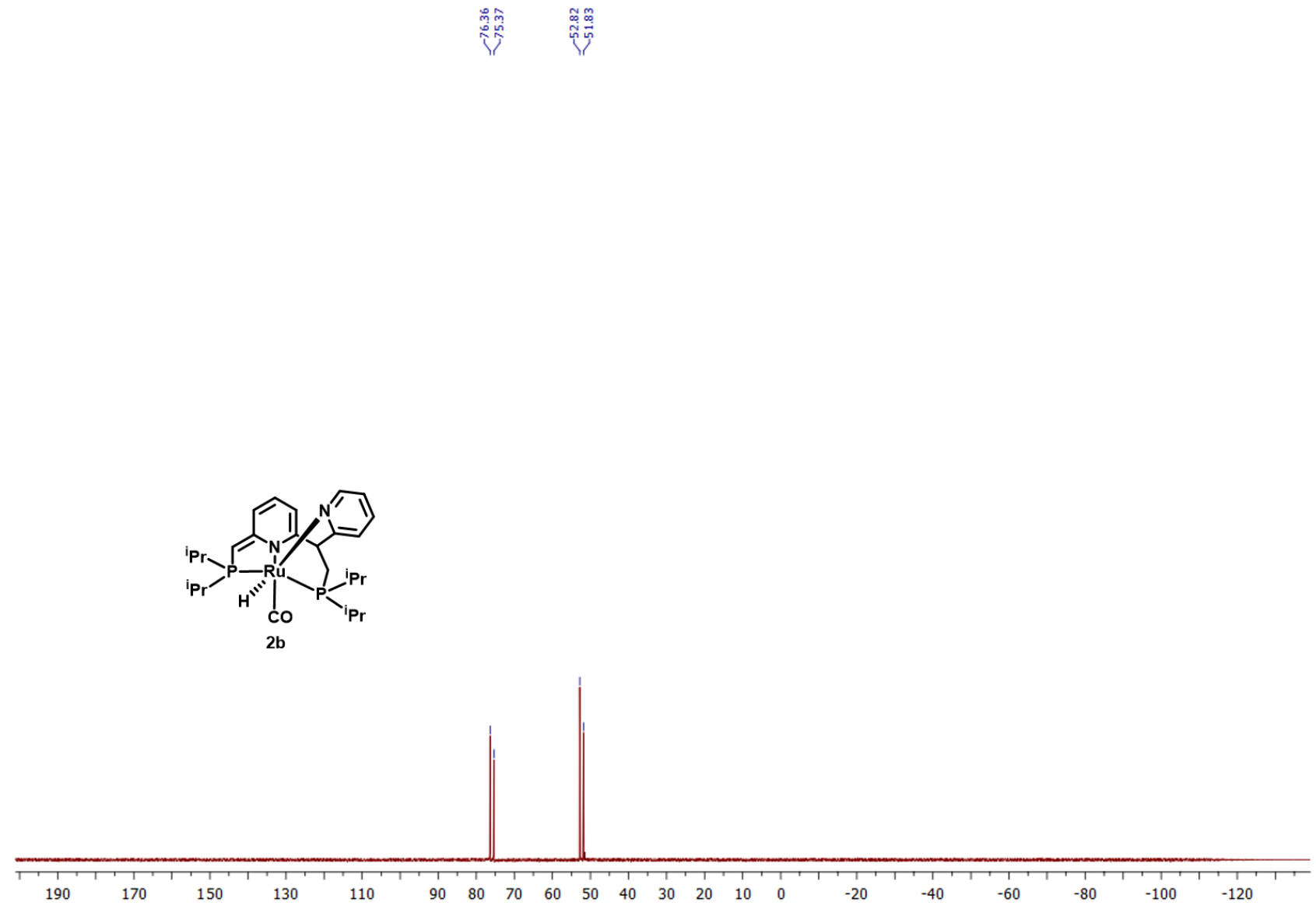


Figure S51. ^{31}P NMR spectrum of complex **2b** in C_6D_6 at 23 ℃.

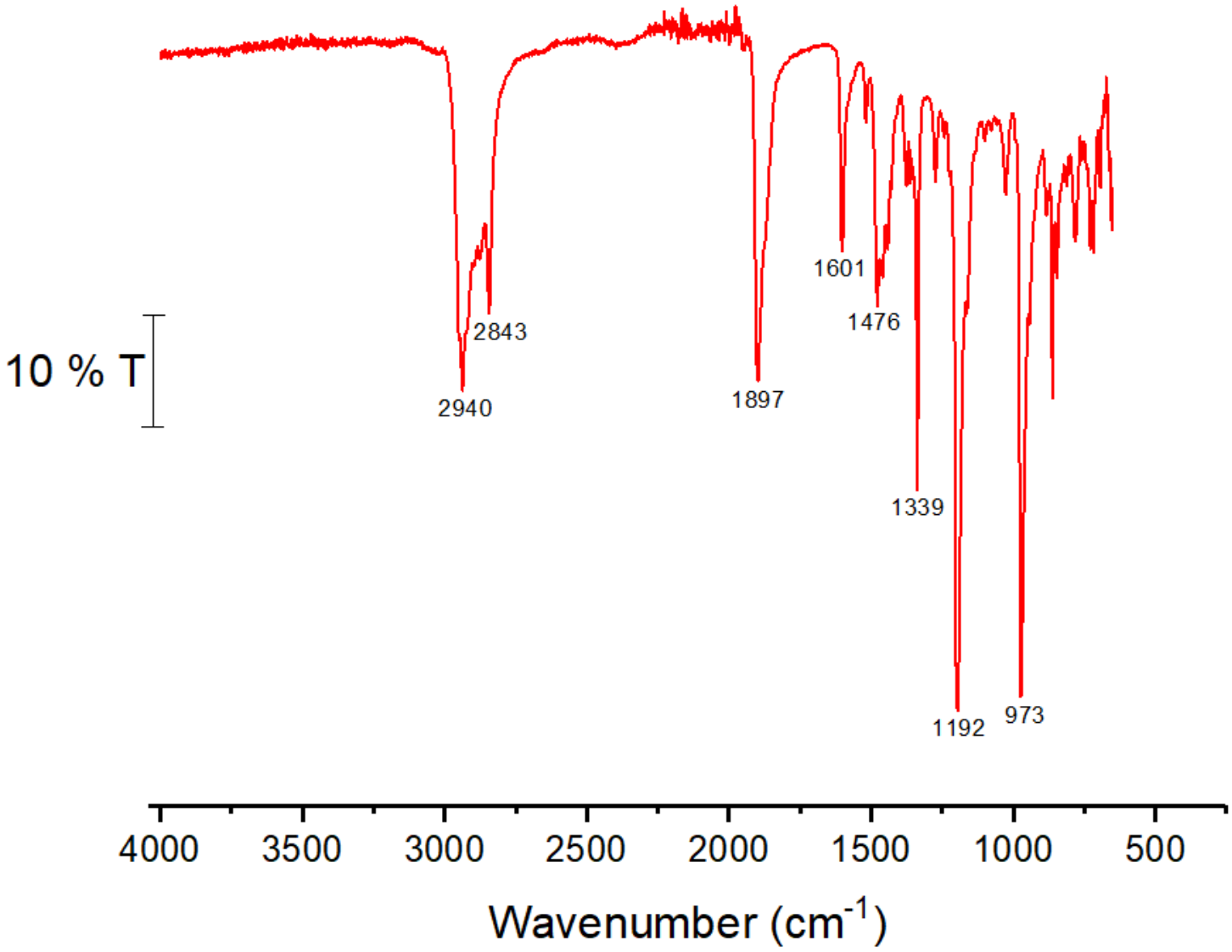
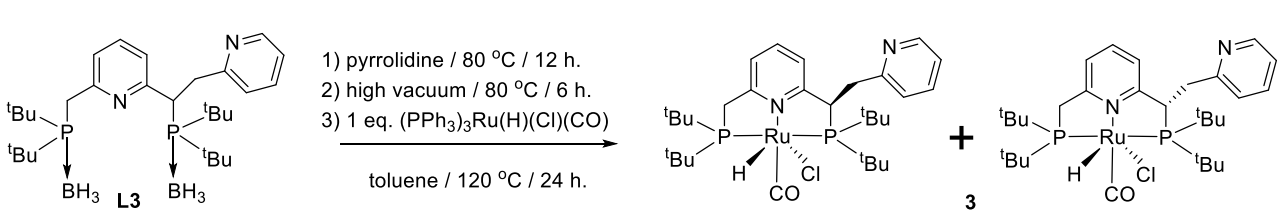


Figure S52. FT-IR (ATR) spectrum of complex **2b**.

Procedure for synthesis of complex 3, [(*tBu*PNP(M)) Ru(CO)(H)(Cl).



Under an inert atmosphere ligand **L3** (0.194 mmol, 100 mg) was deprotected by adding pyrrolidine (4 ml) at 80 ℃ for 12 hours in a 100 ml Schlenk flask. Afterwards pyrrolidine was removed under high vacuum, and the system was left to heat at 80 ℃ for 6 hours under high vacuum to ensure the sublimation of pyrrolidine×BH_3. The Schlenk flask was filled with argon and moved to the glovebox where the metal precursor carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) (0.194 mmol, 185.17 mg) was added in 4 ml of toluene, and the mixture was stirred for 24 hours at 120 ℃. The resulting solution was filtered through celite, and the volatiles were removed under high vacuum. The complex was dissolved in 2 ml of THF and then 8 ml of hexane was added, and the solution was cooled to -20 °C. After a few hours of standing a yellow solid fell out of solution. The solution was decanted, and the solids were washed two times with cold Et_2O (*ca*. 2 ml) and dried under high vacuum to afford complex **3** as a yellow solid in 81% yield. The complex was present as a mixture of two isomers in a ratio of 1.00:0.60. However, the complex is only sparingly soluble in C_6D_6, with the isomers having different solubility profiles, so the true ratio likely reflects the one observed in pyridine-d_5 (see below). Crystals suitable for X-ray crystal structure analysis were formed by cooling a concentrated diethyl ether solution down to -30 ℃. The isomer analyzed by X-ray had the pyridine arm *cis* to the chlorine ligand. We could not determine whether this was the major isomer, as steric hinderance from the Cl ligand is not an issue when observing the X-ray structure (see X-Ray section below).

Complex 3 NMR in Benzene. ^{1}H NMR (600 MHz, C_6D_6): **major isomer** δ 8.42 (m, 1H, py-*H*), 7.12 (m, 1H, py-*H*), 6.82 (m, 1H, py-*H*), 6.68 (d, 1H, *J* = 7.90 Hz, py-*H*), 6.55 (m, 1H, py-*H*), 6.44 (m, 1H, py-*H*), 6.28 (d, 1H, *J* = 7.98 Hz, py-*H*), 5.97(t, 1H, *J* = 13.2 Hz, sub-arm-*H*), 4.23 (m, 1H, arm-*H*), 3.93 (m, 1H, bridge-*H*), 3.51(m, 1H, arm-*H*), 2.69 (m, 1H, bridge-*H*), 1.66 (m, 9H, ^{t}Bu-*Me*, ov.min), 1.40 (m, 9H, ^{t}Bu-*Me*), 1.16 (dd, 18H, *J* = 29.7, 12.4 Hz, ^{t}Bu-*Me*), -14.64 (v.t , 1H, $J_{P\text{-}H}$ = 19.34 Hz, Ru-*H*). **minor isomer** δ 8.27 (m, 1H, py-*H*), 6.97 (m, 1H, py-*H*), 6.86 (m, 1H, py-*H*), 6.64 (d, 1H, *J*=7.93 Hz, py-*H*), 6.50 (m, 1H, py-*H*), 6.41(m, 1H, py-*H*), 6.38 (d, 1H, *J* =

7.88 Hz, py-*H*), 4.98 (t, 1H, *J* = 12.8 Hz, sub-arm-*H*), 4.02 (m, 1H, arm-*H*), 3.93 (m, 1H, bridge-*H*), 3.29 (m, 1H, arm-*H*), 2.93 (m, 1H, bridge-*H*), 1.66 (m, 9H, ^{t}Bu-*Me*, ov.maj), 1.51 (m, 9H, ^{t}Bu-*Me*), 1.40 (m, 9H, ^{t}Bu-*Me*), 0.93 (m, 9H, ^{t}Bu-*Me*),-14.51(v.t , 1H, J_{P-H} =19.34 Hz, Ru-*H*).

^{13}C NMR (151 MHz,C_6D_6): **major isomer** δ 210.57 (*C*O), 166.99 (py-*C*), 163.15 (py-*C*), 159.60 (py-*C*), 149.83 (py-*C*, ov.min), 136.87 (py-*C*), 135.11 (py-*C*, ov.min), 122.24 (py-*C*), 121.70 (py-*C*), 119.84 (py-*C*, ov.min), 119.11 (py-*C*), 49.44 (d), 40.59 (s), 40.19 (s), 38.15-37.55 (^{t}Bu-*C*, ov.min), 35.96 (^{t}Bu-*C*, d, J_{P-C} = 19.1 Hz), 32.90 (^{t}Bu-*Me*), 31.19-31.03 (^{t}Bu-*Me*). **minor isomer** δ 210.24 (*C*O), 166.47 (py-*C*), 164.13 (py-*C*), 159.98 (py-*C*), 149.83 (py-*C*,ov.maj), 136.42 (py-*C*), 136.11 (py-*C*, ov.maj), 124.05 (py-*C*), 121.48 (py-*C*), 119.84 (py-*C*, ov.maj), 118.82 (py-*C*), 49.24 (d), 39.64 (d), 39.30 (s), 38.15-37.55 (^{t}Bu-*C*, ov.maj), 35.01 (^{t}Bu-*C*, d, J_{P-C} = 19.1 Hz), 32.17 (^{t}Bu-*Me*), 30.38-30.31 (^{t}Bu-*Me*), 29.30 (^{t}Bu-*Me*).

^{31}P{1H} NMR (262 MHz, C_6D_6): δ **major isomer** 108.12 (d, 1P, J_{P-P} = 256.7 Hz), 93.07 (d, 1P, J_{P-P} = 256.7 Hz). **minor isomer** δ 102.48 (d, 1P, J_{P-P} = 256.7 Hz), 88.41(d, 1P, J_{P-P} = 256.7 Hz).

Complex 3 NMR in Pyridine. Complex was present in mixture of two isomer in the ratio of 1.00:0.78. ^{1}H NMR (600 MHz, C_5D_5N) **major isomer** δ 8.68 (d, 1H, *J* = 4.3 Hz, py-*H*), 7.51 (m, 1H, py-*H*), 7.39 (m, 1H, ov.min, py-*H*), 7.25 (d, 2H, *J* = 7.6 Hz, py-*H*), 6.99 (m, 2H, py-*H*), 6.02 (t, 1H, *J* = 10.9 Hz, sub-arm-*H*), 4.10 (dd, 1H, *J* = 15.9, 6.1 Hz, bridge-*H*), 3.92 (dd, 1H, *J* = 16.5, 8.8 Hz, bridge-*H*), 3.65 (dd, 2H, *J* = 15.8, 11.4 Hz, arm-*H*), 1.82 (d, 9H, *J* = 12.8 Hz, ^{t}Bu-*Me*), 1.56 (d, 9H, *J* = 12.8 Hz, ^{t}Bu-*Me*), 1.41 (d, 9H, *J* = 12.8 Hz, ^{t}Bu-*Me*), 1.35 (d, 9H, *J* = 12.8 Hz, ^{t}Bu-*Me*), -14.51(m, 1H, ov.min, Ru-*H*). **minor isomer** δ 8.62 (d, 1H, *J* = 4.3 Hz, py-*H*), 7.62 (d, 1H, *J* = 7.6 Hz, py-*H*), 7.44 (m, 1H, py-*H*), 7.39 (m, 1H, ov.maj, py-*H*), 7.32 (d, 1H, *J* = 7.6 Hz, py-*H*), 7.10 (m, 2H, py-*H*), 5.18(m, 1H, sub-arm-*H*), 4.55 (dd, 1H, *J* = 15.9, 6.1 Hz, bridge-*H*), 4.20 (br.m, 2H, arm-*H*), 3.37 (dd, 1H, *J* = 16.5, 8.8 Hz, bridge-*H*), 1.76 (d, 9H, *J* = 12.8 Hz, ^{t}Bu-*Me*), 1.64 (m, 18H, ^{t}Bu-*Me*), 1.11 (d, 9H, *J* = 12.8 Hz, ^{t}Bu-*Me*), -14.51 (m, 1H, ov.maj, Ru-*H*).

^{31}P{1H} NMR (262 MHz, C_5D_5N): δ **major isomer** 106.55 (d, 1P, J_{P-P} = 252.5 Hz), 91.87 (d, 1P, J_{P-P} = 252.5 Hz). **minor isomer** δ 104 (d, 1P, J_{P-P} = 252.5 Hz), 90.11 (d, 1P, J_{P-P} = 252.5 Hz).

IR (neat solid) : ν (CO) 1905 cm^{-1}.

Anal. Calcd for $C_{30}H_{49}N_2P_2O_1Cl_1Ru_1$: C, 55.25; H, 7.57; N, 4.30. Found : C, 55.71; H, 7.52; N, 4.30.

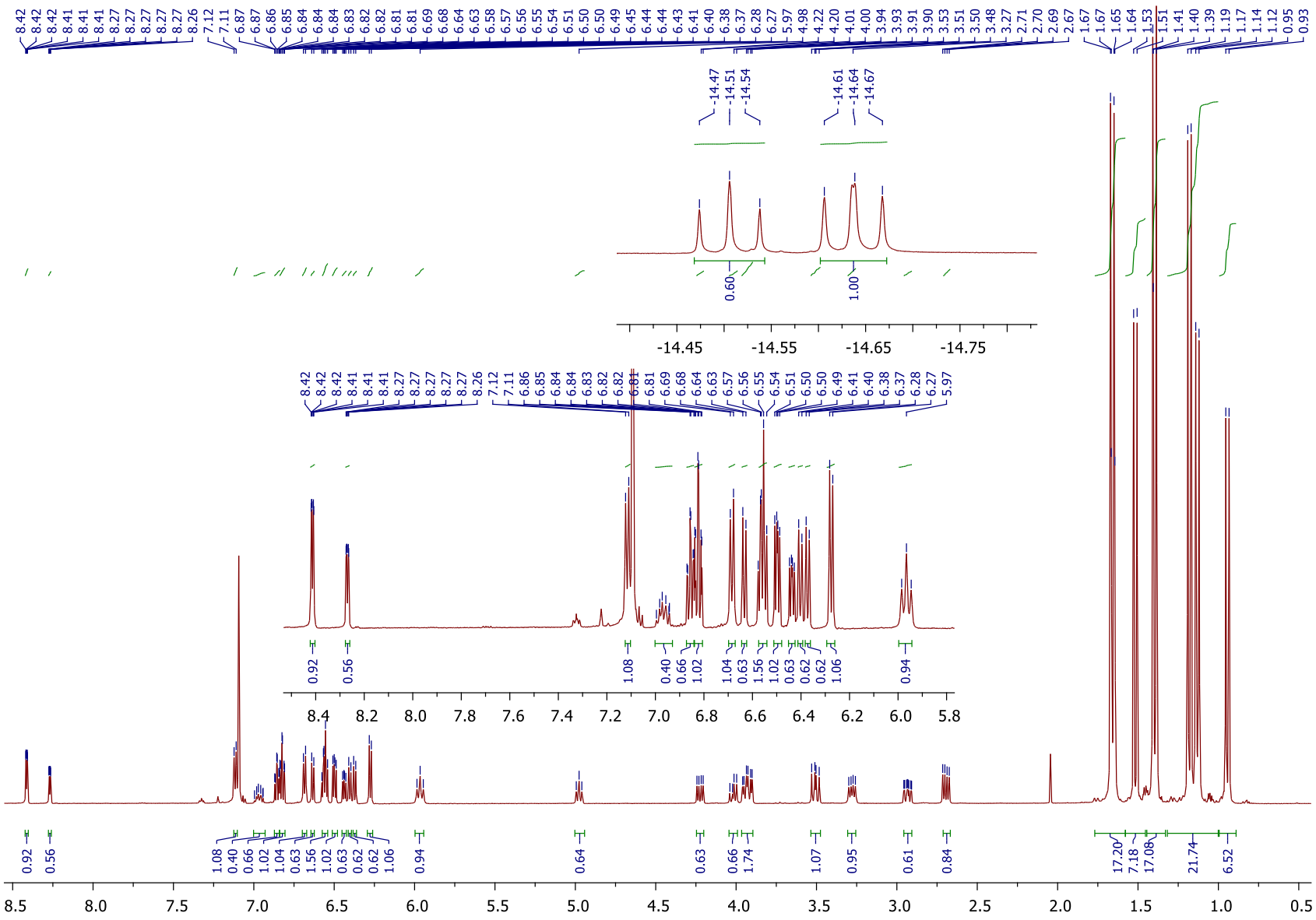


Figure S53. ^{1}H NMR spectrum of complex **3** in C_6D_6 at 23 °C.

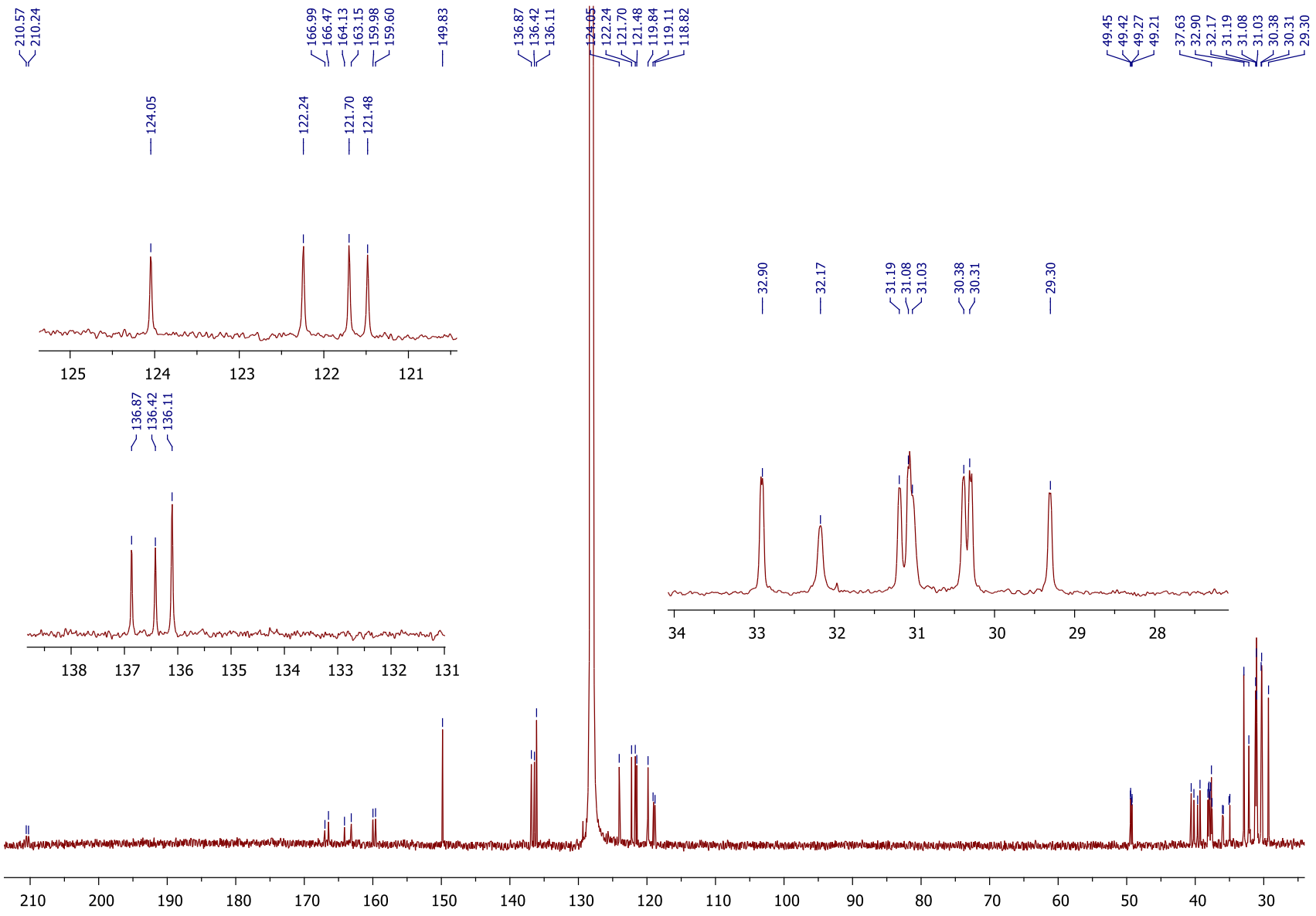


Figure S54. ^{13}C NMR spectrum of complex **3** in C_6D_6 at 23 ℃.

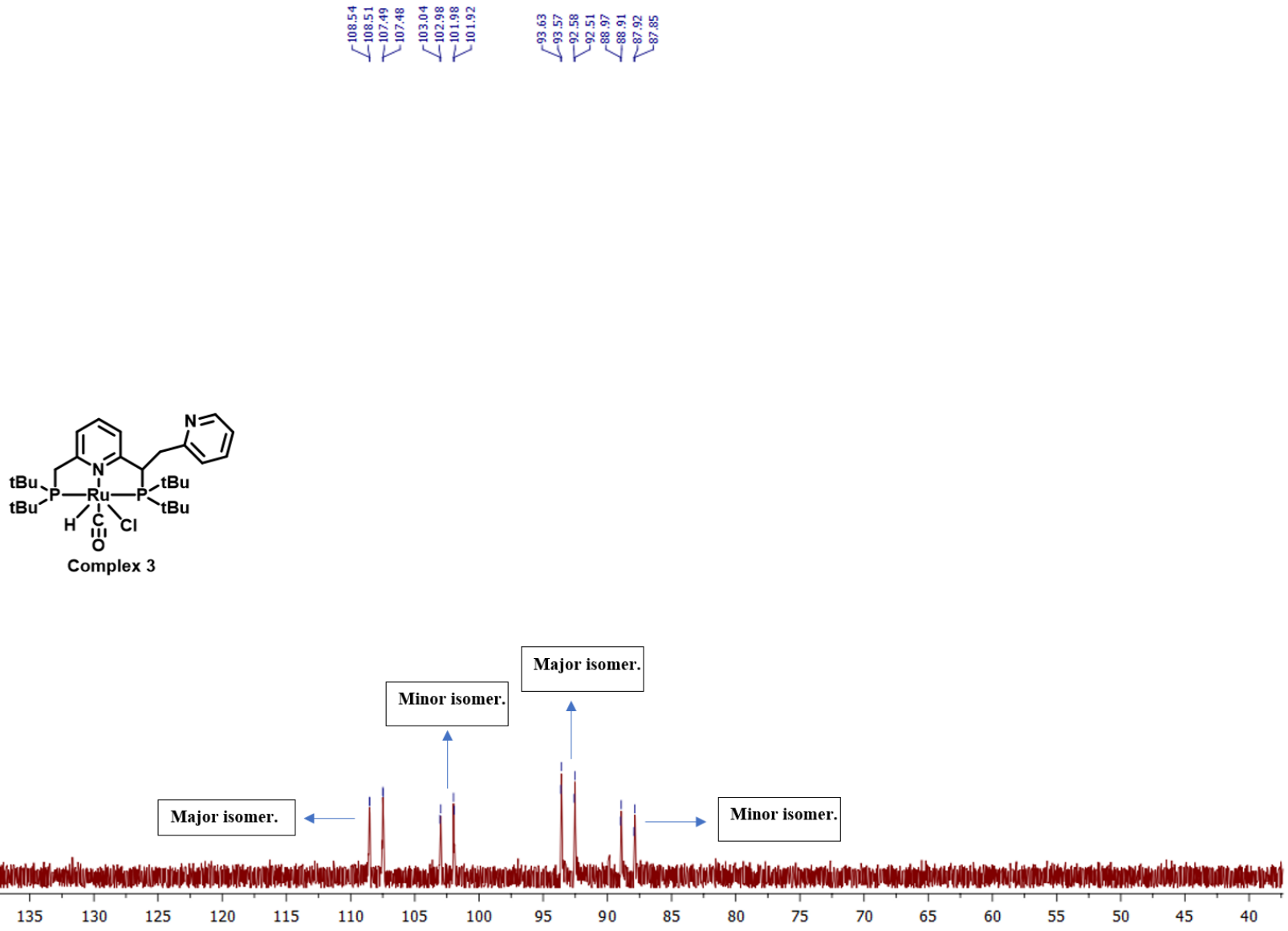


Figure S55. ^{31}P NMR spectrum of complex **3** in C_6D_6 at 23 ℃.

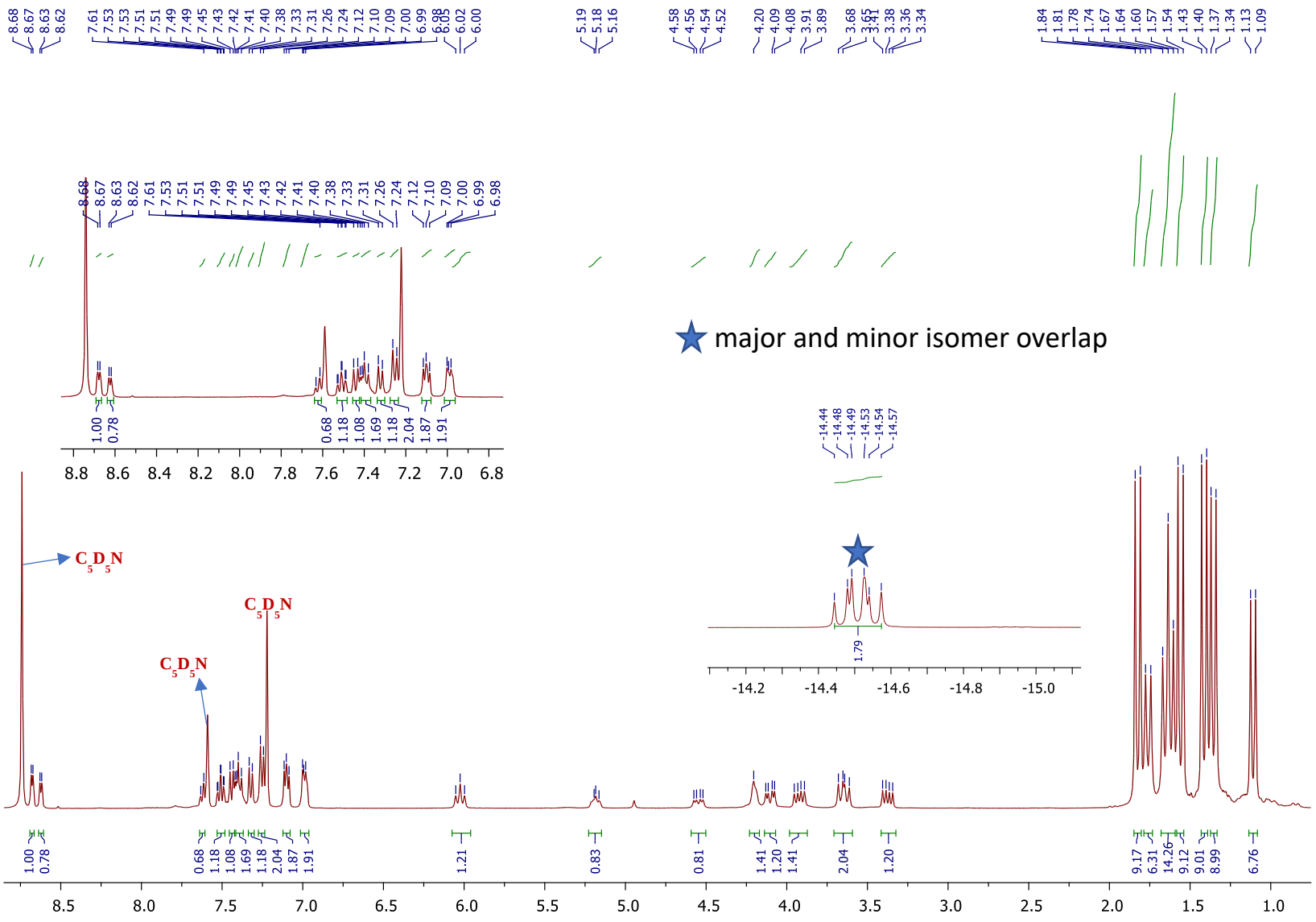


Figure S56. ^{1}H NMR spectrum of complex **3** in C_5D_5N at 23 °C.

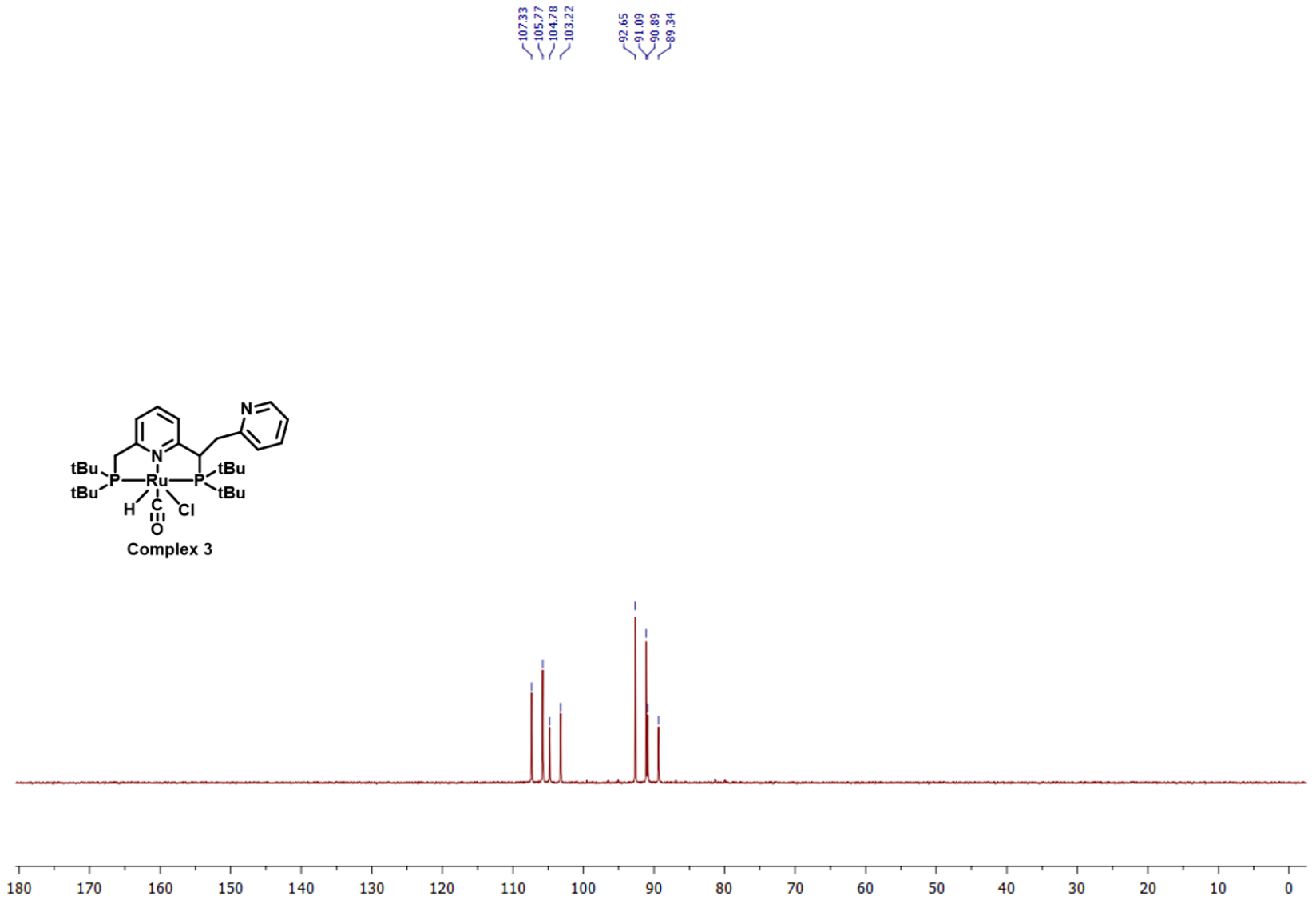


Figure S57. ^{31}P NMR spectrum of complex **3** in C_5D_5N at 23 °C.

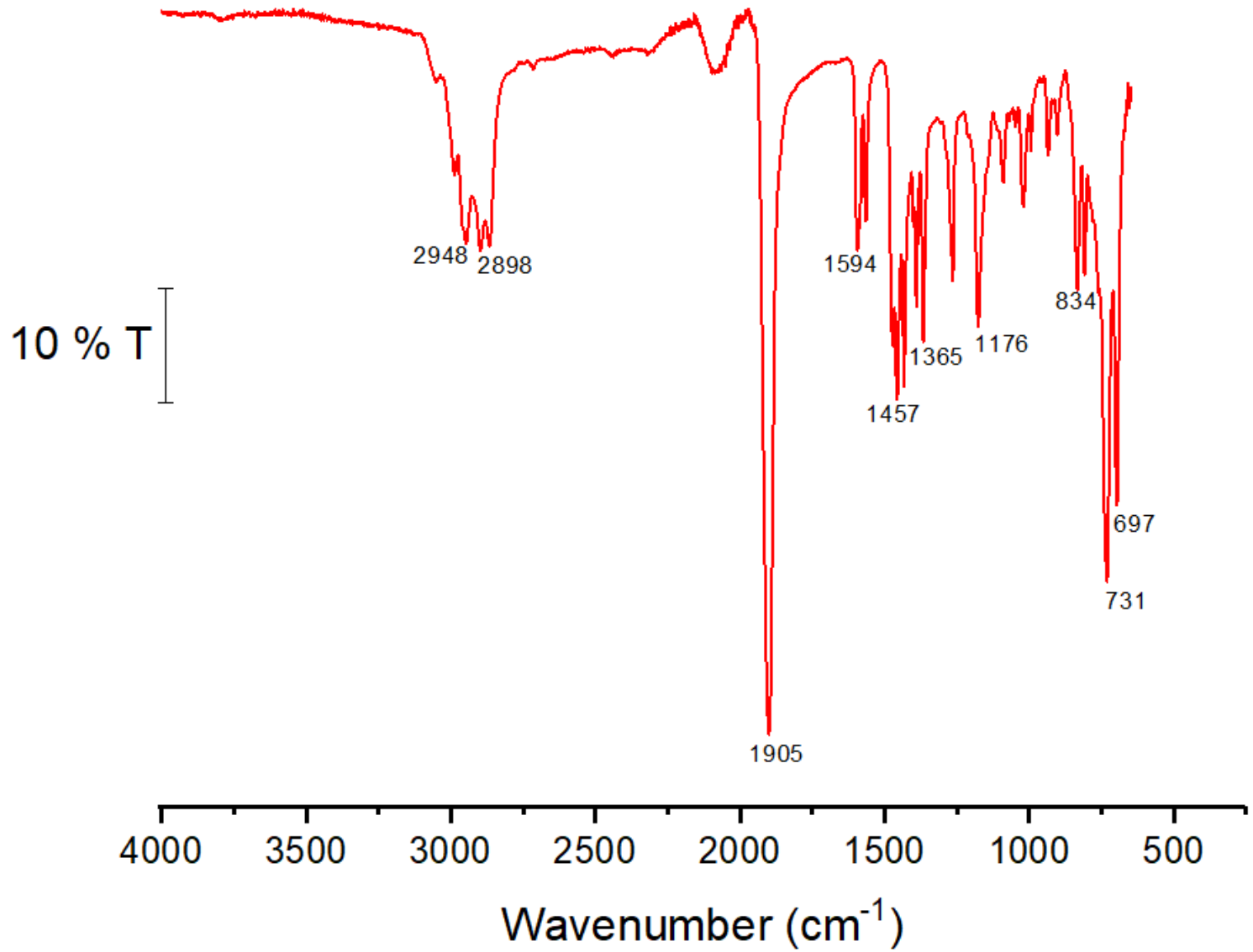
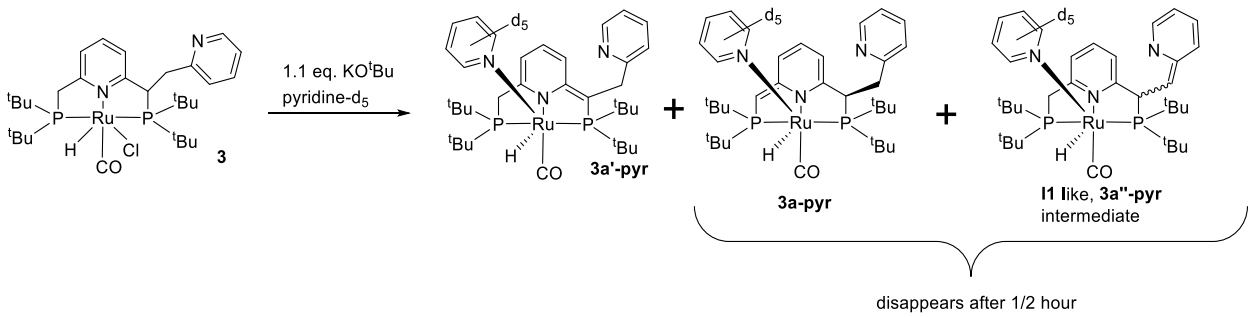


Figure S58. FT-IR (ATR) spectrum of complex **3**.

Complex 3 deprotonation NMR in C_5D_5N and discussion of 3a'-pyr .



Complex **3a'-pyr** was detected after ten minutes *in situ* during the formation of complex **3b** after deprotonation in pyridine-d_5 along with two other species, one of which can be assigned to either **3a-pyr** or an intermediate **3a'-pyr** with the outer pyridine dearomatized, but a pyridine solvent molecule coordinating to the metal. The assignments of these two shorts - lived complexes are ambiguous, although a parallel can be made from the experiment above where **2a''** was detected in pyridine. The assignments of the short-lived complexes are discussed after **3a'-pyr** below.

3'-pyr becomes a major species in pyridine solution after overnight equilibration at room temperature. By this time the only organometallic complexes are **3a'-pyr** and **3b**. After heating at 80 °C for eight hours, full conversion to **3b** is observed. The assignment of **3a'-pyr** was arrived at by comparison with the crystal structure of **1a** and NMR shifts of complexes **1a** and **2a**, as well as the experiment where the analogous **2a'** complex was formed above in pyridine-d_5 and its 2D spectra, were obtained, showing that **3a'-pyr** has an identical splitting pattern in the bridging proton region. Finally, a HMBC and HMQC was also obtained for **3a'-pyr** while cooling the solution to -10 °C. This led us to assign the 4.22 ppm signal of two protons on the same carbon to the benzylic outer pyridine and the signals at 3.27 and 2.96 ppm as two protons on the arm of one carbon the PNP backbone. The presence of three protons on only two carbons rules out the possibility that this complex is **3a'-pyr** or **3a-pyr**. The pyridine arm is not coordinated and the peak of the *ortho* proton is overlapping with the solvent. In contrast **3a'-pyr** has an upfield shifted *ortho* CH peak dearomatized arm pyridine and **3a-pyr** has fluxional coordination behavior, thus the broad CH *ortho* resonance is shifted downfield only by 0.1ppm relative to the solvent peak.

Only complex **3b** has a clear coordinated pyridine arm in the pyridine solvent, with a shift of 9.19 ppm.

Complex **3a'-pyr**: ^{1}H NMR (600 MHz, C_5D_5N): δ 8.76 (d, 1H, *J* = 4.9 Hz, py-*H*), 7.51 (d, 2H, *J* = 4.9 Hz, py-*H*), 7.05 (m, 1H, py-*H*), 6.71 (t, 1H, *J* = 7.3 Hz, py-*H*), 5.92 (d, 1H, *J* = 6.5, py-*H*), 5.83 (d, 1H, *J* = 9.1 Hz, py-*H*),), 4.13-4.34 (m, 2H, bridge-*H*), 3.27 (ddd, *J* = 16.7, 11.3, 2.7 Hz, 1H, arm-*H*), 2.96 (dd, *J* = 16.7, 5.7 Hz, 1H, arm-*H*), 1.57 (d, 9H, *J* = 12.4 Hz, ^{t}Bu-*Me*), 1.36 (d, 9H, *J* =12.4 Hz, ^{t}Bu-*Me*), 1.12 (d, 9H, *J*=12.4 Hz, ^{t}Bu-*Me*), 1.04 (d, 9H, *J*=12.4 Hz, ^{t}Bu-*Me*), -14.62 (v.t , 1H, J_{P-H} =20.1 Hz, Ru-*H*).

^{13}C NMR (151 MHz, C_5D_5N): δ 210.5 (*C*O), 168.6 (d, J_{P-C}=23.8Hz, py-*C*), 163.8 (py-*C*), 160.1 (py-*C*), 156.8 (py-*C*), 133.3 (py-*C*), 121.2 (py-*C*), 111.4 (d, J_{P-C} = 14.6 Hz, py-*C*), 99.9 (d, J_{P-C} = 11.4 Hz, py-*C*), 71.7 (d, J_{P-C} = 40.7 Hz, dearomatized arm-*C*), 42.3 (bridge-*C*), 39.9 (d, J_{P-C} = 23.8 Hz, ^{t}Bu-*C*), 37.7 (d, J_{P-C} = 8.2 Hz, ^{t}Bu-*C*), 37.4 (d, J_{P-C} = 20.5 Hz, ^{t}Bu-*C*), 36.2 (d, J_{P-C} = 13.2 Hz, C_{arm}), 32.8 (^{t}Bu-*C*), 32.5 (^{t}Bu-*Me*), 32.3 (^{t}Bu-*Me*), 29.9 (^{t}Bu-*Me*), 29.3 (^{t}Bu-*Me*).

^{31}P{1H} NMR (262 MHz, C_5D_5N): δ 88.50 (d, 1P, J_{P-P} = 226.7 Hz), 80.75 (d, 1P, J_{P-P} = 226.7 Hz).

Note: Two aromatic carbons are not assigned, with HMBC and HMQC suggesting that they overlap with pyridine solvent peaks. Small impurities are peaks of complex **3b** which starts appearing during the experiment. Peaks of ^{t}BuOH are at 35.0 and 67.5 ppm. Proton spectrum was also obtained at -10 °C for the 2D spectra, but the presented 1D slices were obtained at room temperature. Eventually, all the species converted to **3b**, whose spectrum matches that of the complex synthesized in benzene as an isolated complex **3b** (*see below*).

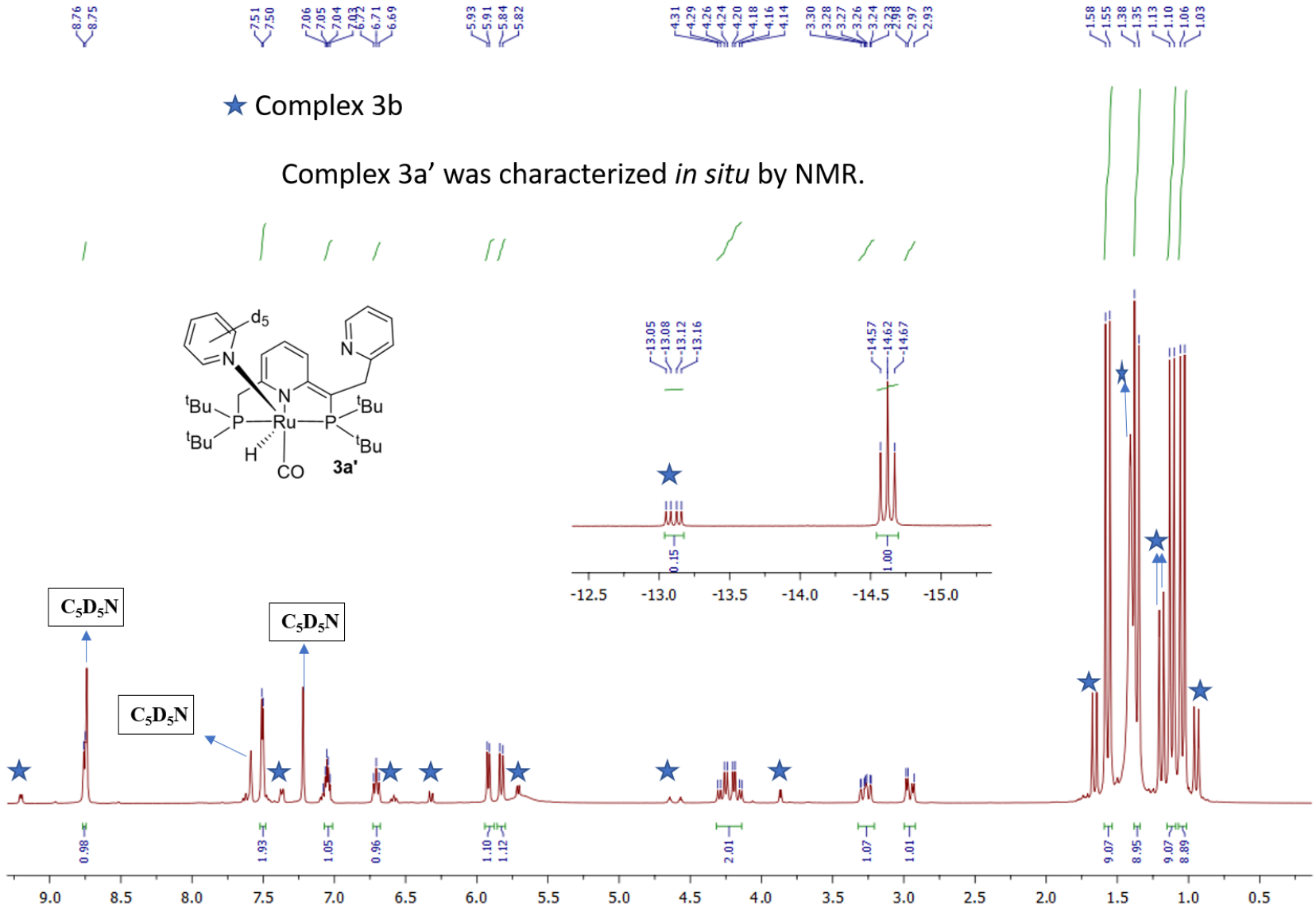


Figure S59. ^{1}H NMR spectrum of complex **3a’-pyr** in C_5D_5N at 23 °C.

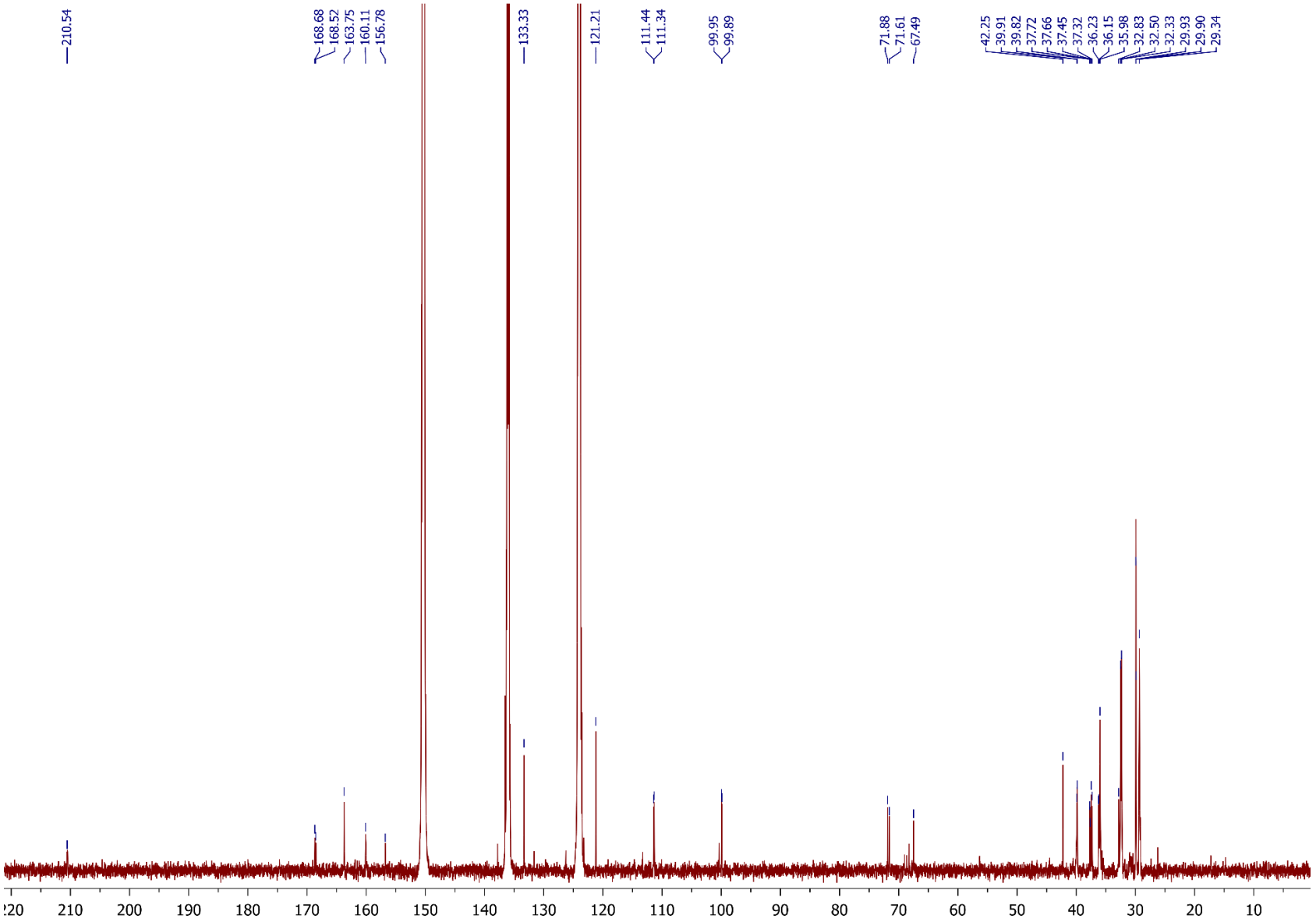


Figure S60. ^{13}C NMR of complex **3a'-pyr** in C_5D_5N at 23 °C.

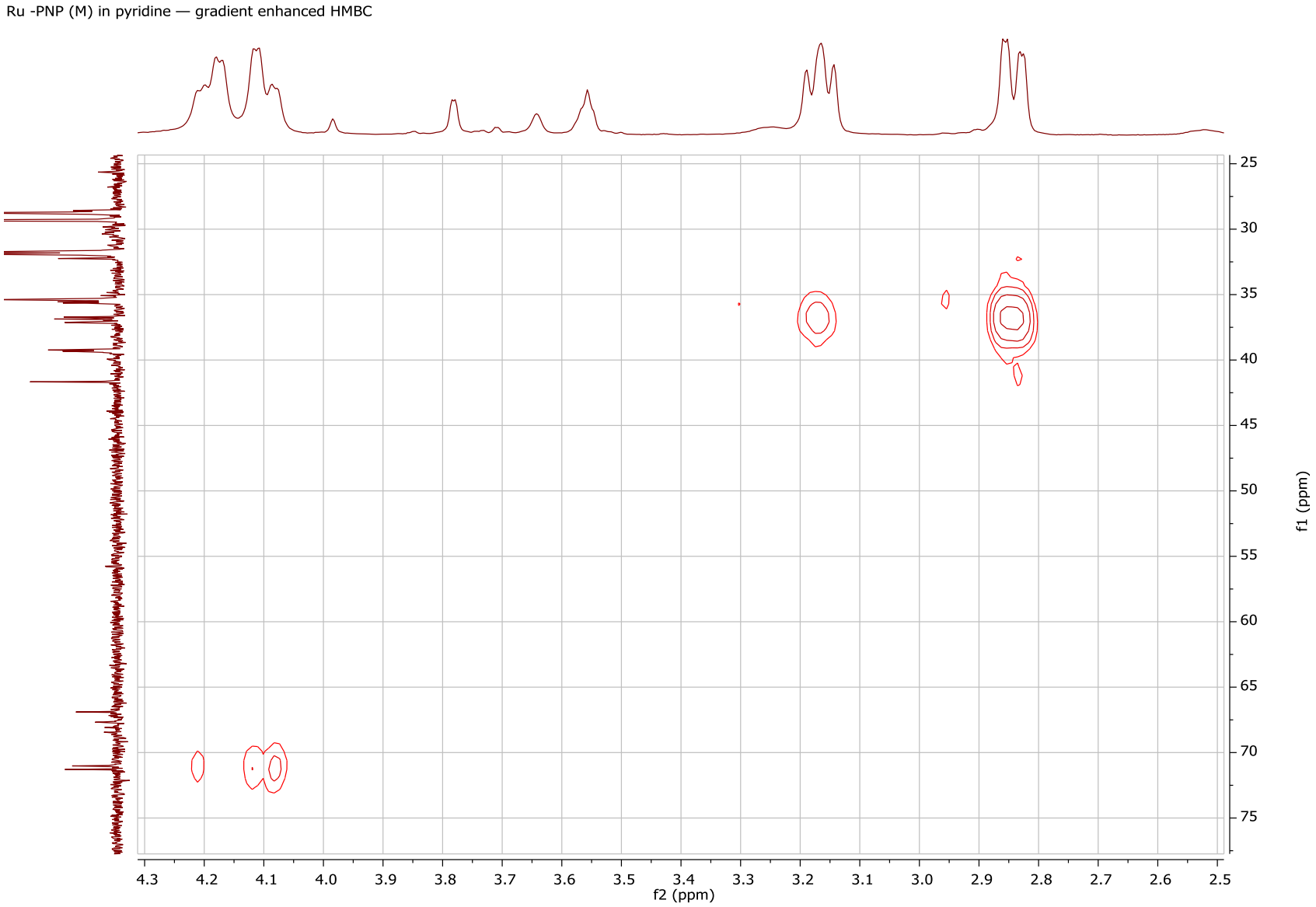


Figure S61. Complex **3a'-pyr** HMBC expansion of bridging proton region in C_5D_5N at -10 °C.

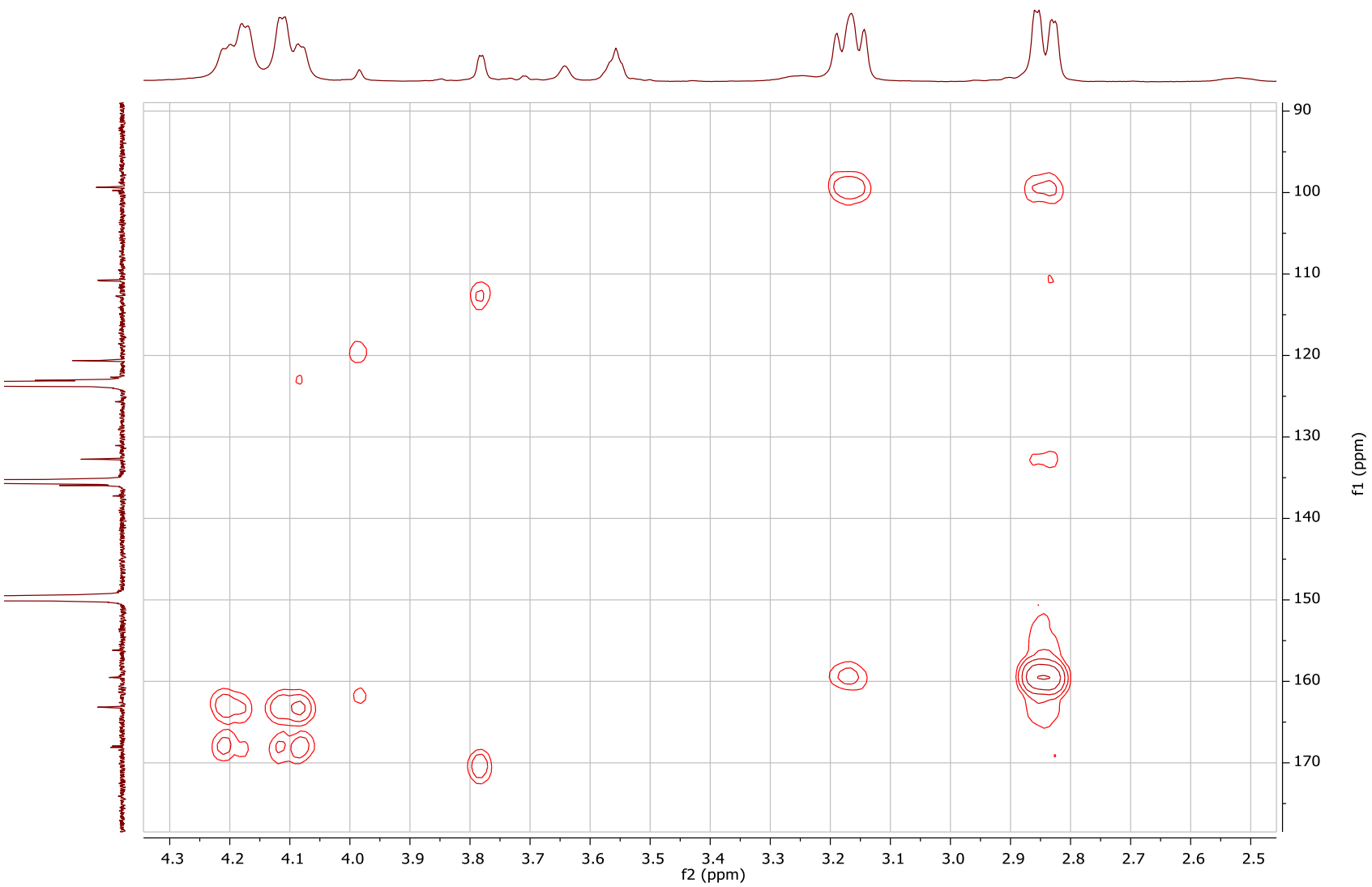


Figure S62. Complex **3a'-pyr** HMBC expansion of bridging proton region in C_5D_5N at -10 °C.

BC expansion of the bridging proton region in pyridine-d_5

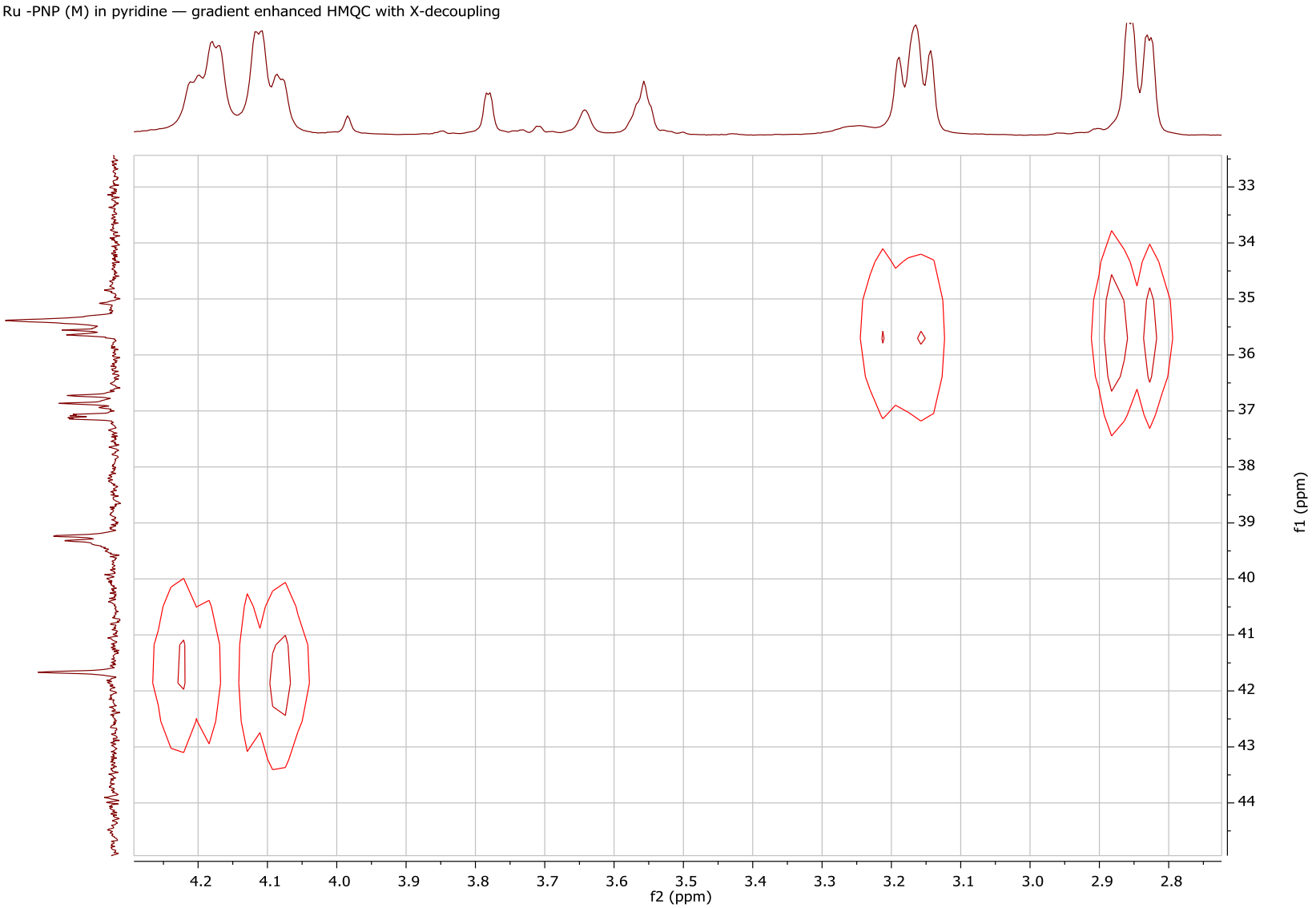


Figure S63. Complex **3a'-pyr** HMQC expansion of bridging proton region in C_5D_5N at -10 °C.

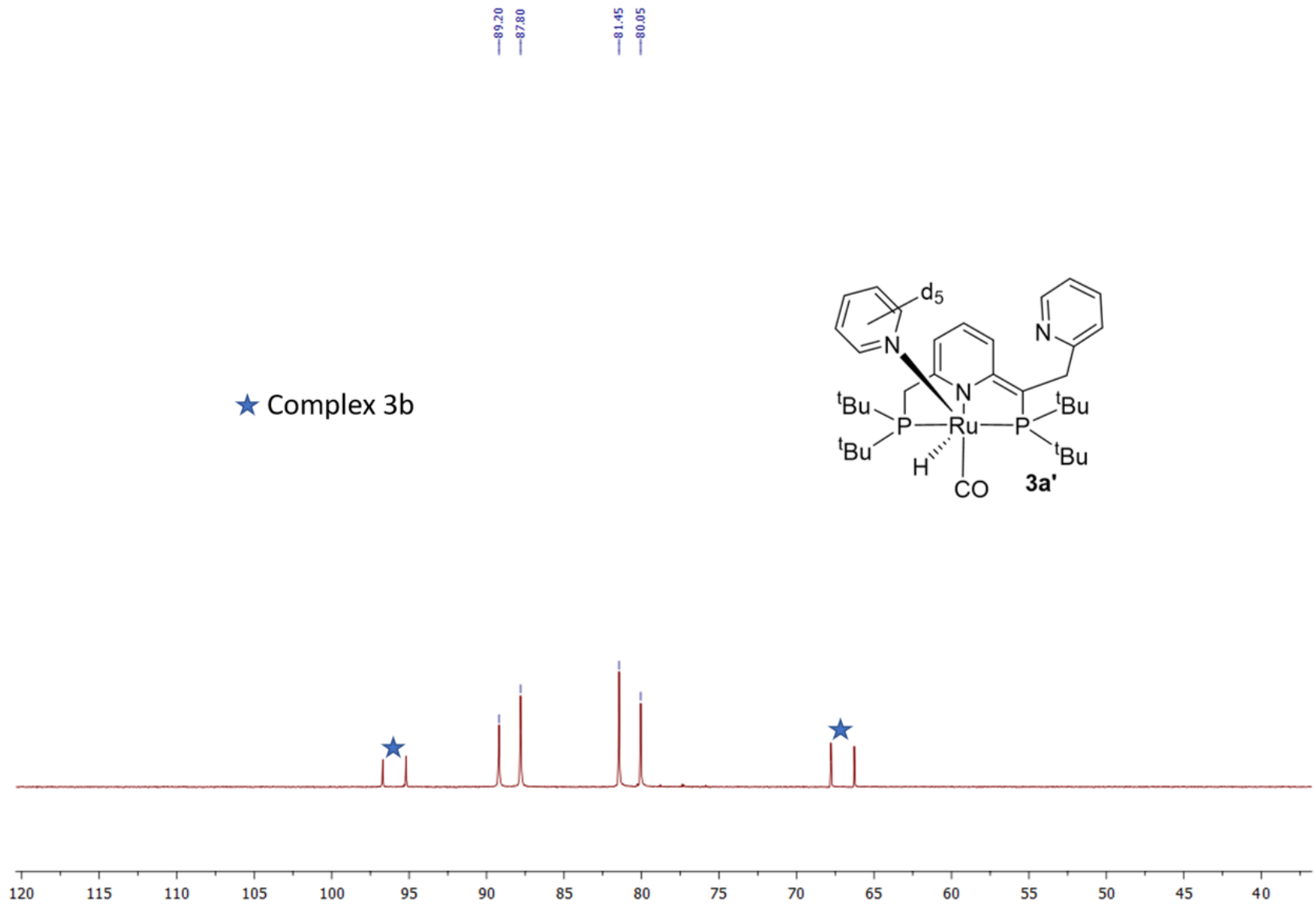
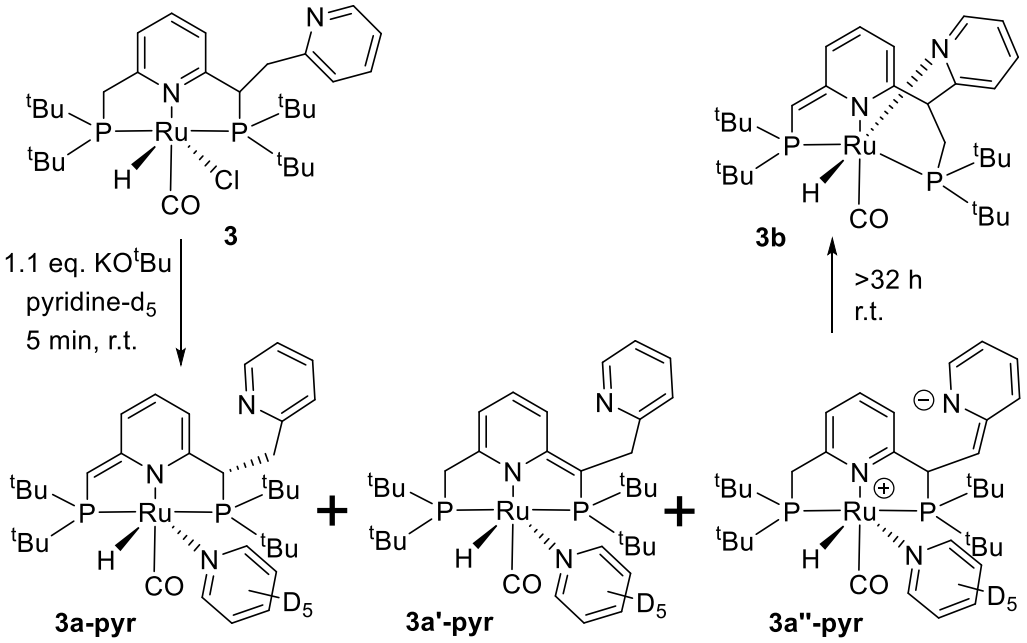


Figure S64. ^{31}P NMR spectrum of complex **3a'-pyr** in C_5D_5N at 23 °C.

Spectrum in pyridine-d_5 five minutes after addition of base.



All the signals for the four complexes (**3a-pyr**, **3a'-pyr** , **3a" -pyr** and **3b**) can be observed in the phosphorus NMR (see Figure **S68)** five minutes after addition of base.

^{31}P NMR (162 MHz, C_5D_5N): δ 96.03 (d, J_{PP} = 227.3 Hz, **3a-pyr**), 92.05 (d, J_{PP} = 229.1 Hz, **3a'-pyr**), 88.51 (d, J_{PP} = 226.8 Hz, **3a'-pyr**), 80.76 (d, J_{PP} = 226.8 Hz, **3a'-pyr**), 78.09 (d, J_{PP} = 227.3 Hz, **3a-pyr**), 75-79 (broad, 1P, **3a'-pyr**) 67.02 (d, J_{PP} = 243.5 Hz, **3b**).

One of the phosphorus signals of the final product **3b** is overlapping with the most downfield shifted phosphine of **3a-pyr**. This complex has a splitting pattern very similar to that of **2a** seen in C_5D_5N and the assignment is mostly based on that species, even though there can be significant differences in proton shifts due to the steric differences between ^{i}Pr and ^{t}Bu groups. Thus, the triplet at 4.65 ppm is the proton on the aromatized PNP arm and is coupled to the two protons on the picolyl benzylic position. In **3a-pyr** these protons are well separated and found at 3.62 and 3.87 ppm as doublets of doublets where a roofing effect can be observed. The last proton on the dearomatized PNP arm is a doublet at 3.81ppm with a small J_{PH} coupling as in **2a**.

3a'-pyr has a fluxional phosphine resonance at 67 ppm probably due to competition for binding from the pyridine arm and the pyridine solvent and it cannot be assigned as a *cis* or *trans* complex.

The fluxional behavior of one phosphine in **3a'-pyr** is translated into the ^{1}H-NMR where some of the peaks of this species are broadened relative to others.

Below are the assignments of most of the aromatic peaks and bridging protons of species **3a'-pyr** and **3a** in pyridine. Since at this point **3a'-pyr** was also present in significant amounts and even **3b** was visible in non-trivial amounts, the definite assignment could not be made for all peaks due to overlap, although all four bridging protons of **3a-pyr** have been identified. The CH_3 protons could not reliably be assigned.

Complex 3a-pyr: ^{1}H NMR (400 MHz, C_5D_5N) δ 8.55 (d, *J* = 4.8 Hz, 1H), 7.63 (m, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 6.50 (t, *J* = 7.9 Hz, 1H), 6.43 (d, *J* = 8.7 Hz, 1H), 5.48 (d, *J* = 6.6 Hz, 1H), 4.64 (t, *J* = 9.9 Hz, 1H), 3.86 (dd, *J* = 16.2, 7.3 Hz, 1H), 3.81 (d, *J* = 4.0 Hz, 1H), 3.62 (dd, *J* = 16.2, 9.9 Hz, 1H), -14.57 (dd, *J* = 21.0, 18.5 Hz, 1H).

Complex 3a'-pyr : ^{1}H NMR (400 MHz, C_5D_5N) δ 8.84 (br.s, 1H), 7.57 – 7.47 (m, 1H), 7.18 – 6.98 (m, 2H), 6.53 (br.s, 1H), 6.38 (s, 1H), 4.95 (s, 1H), 4.56 (s, 1H), 4.37 (bs, 1H), 3.75 (d, *J* = 3.3 Hz, 1H), 3.45 (s, 1H), 2.84 (s, 1H), -14.70 (broad v.t, *J* = 21.2 Hz, 1H).

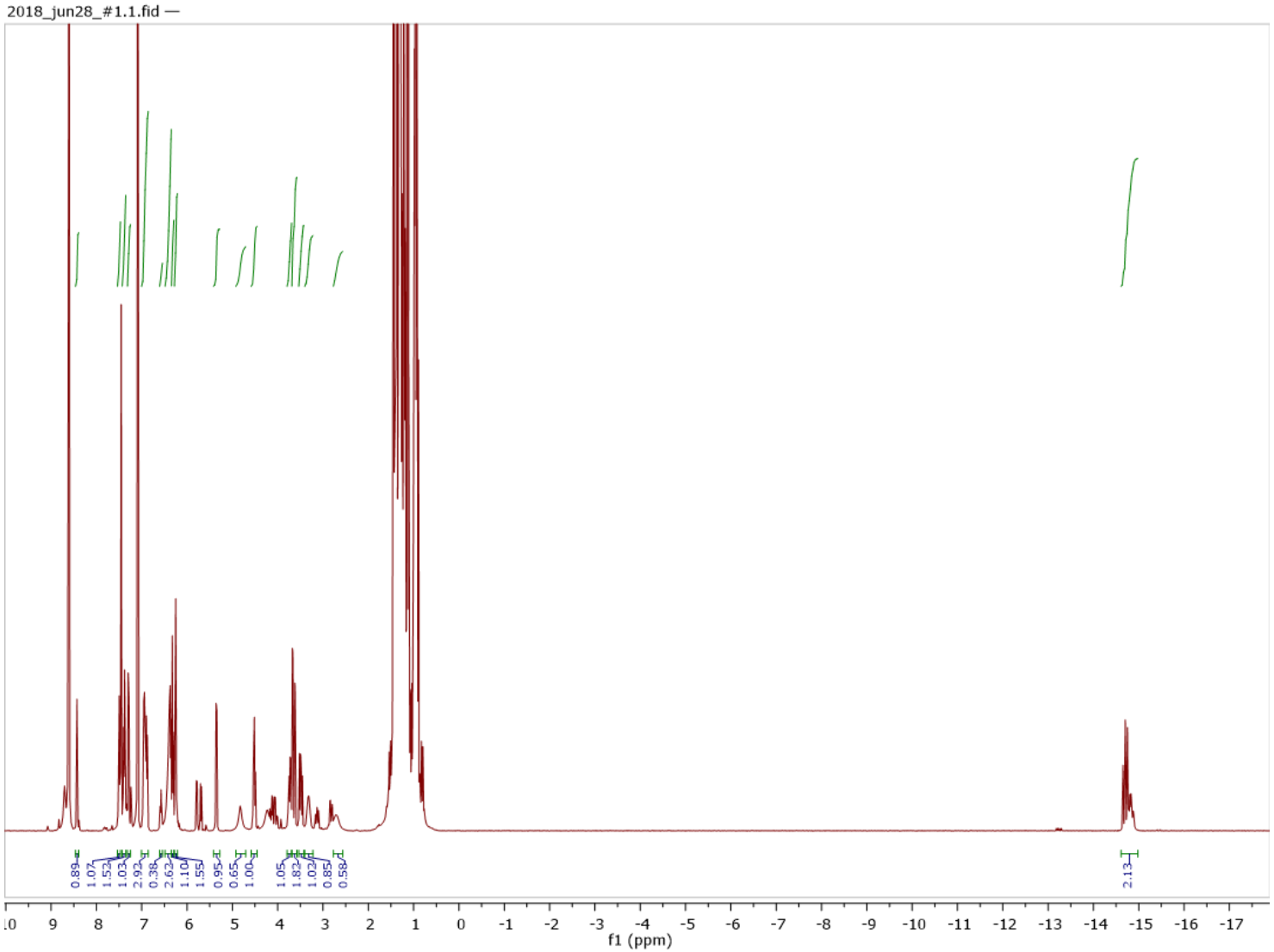


Figure S65. ^{1}H NMR spectrum of complexes **3a-pyr** and **3a”-pyr** in C_5D_5N at 23 °C. This spectrum was observed after 5 minutes. The two minor complexes are identified as **3a’-pyr** and **3b**.

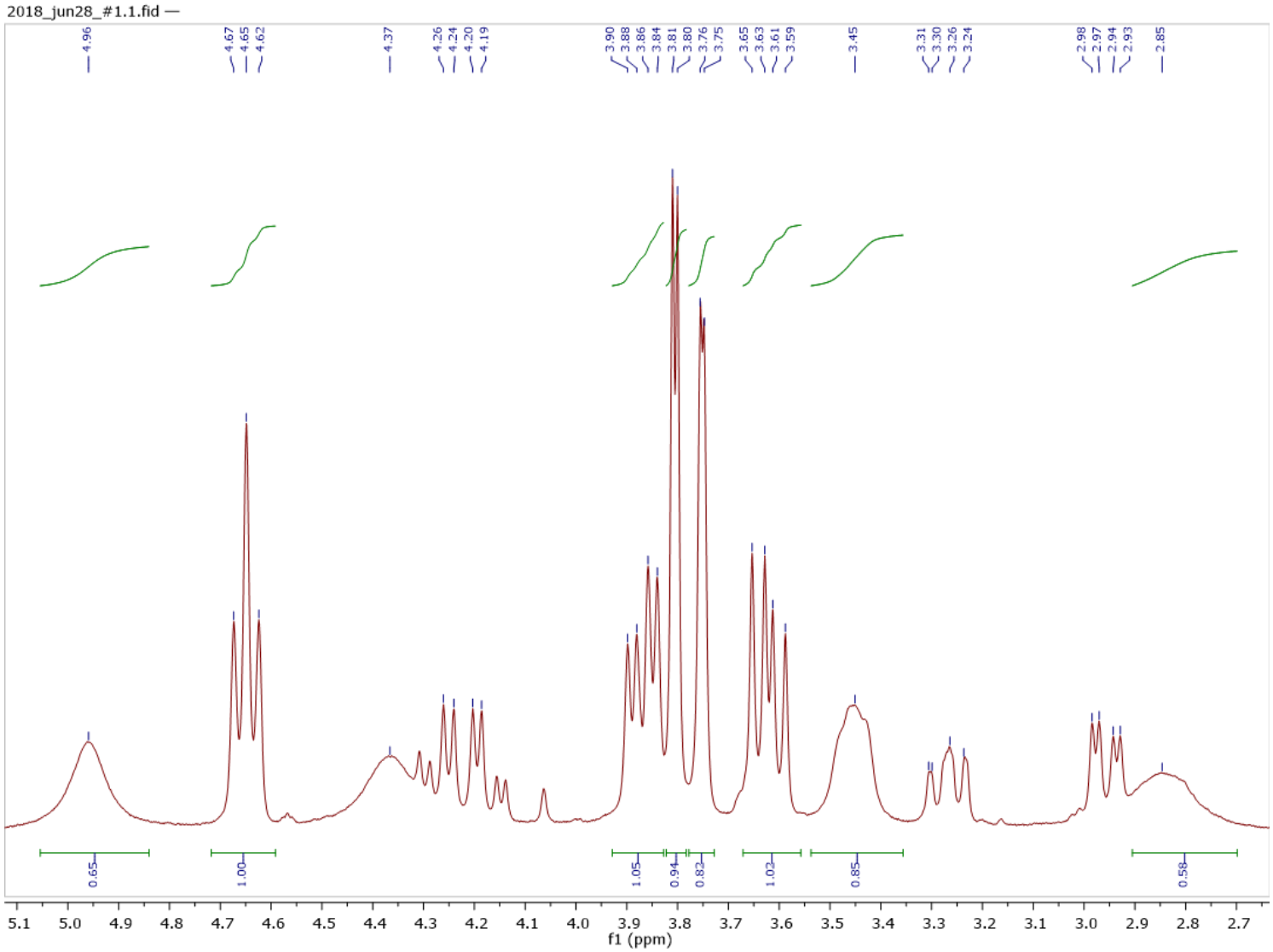


Figure S66. ^{1}H NMR spectrum of bridging proton expansion of complex **3a" -pyr** in C_5D_5N at 23 °C. Broad resonances that integrate close to 1H are tentatively assigned to **3a'-pyr** .

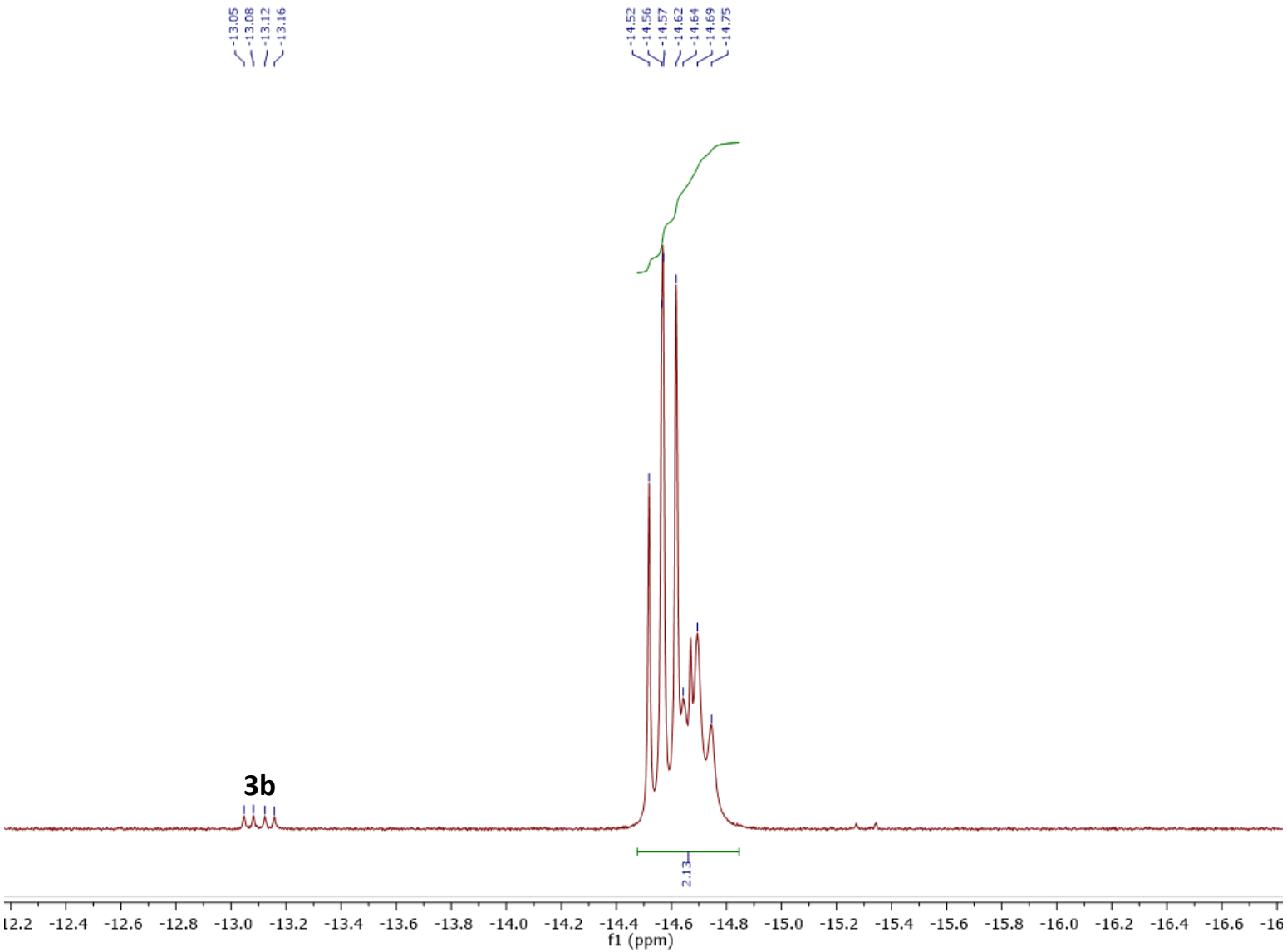


Figure S67. ^{1}H NMR spectrum of hydride region expansion for complex **3a-pyr, 3a" -pyr** as major species and **3b** as minor species in C_5D_5N at 23 °C.

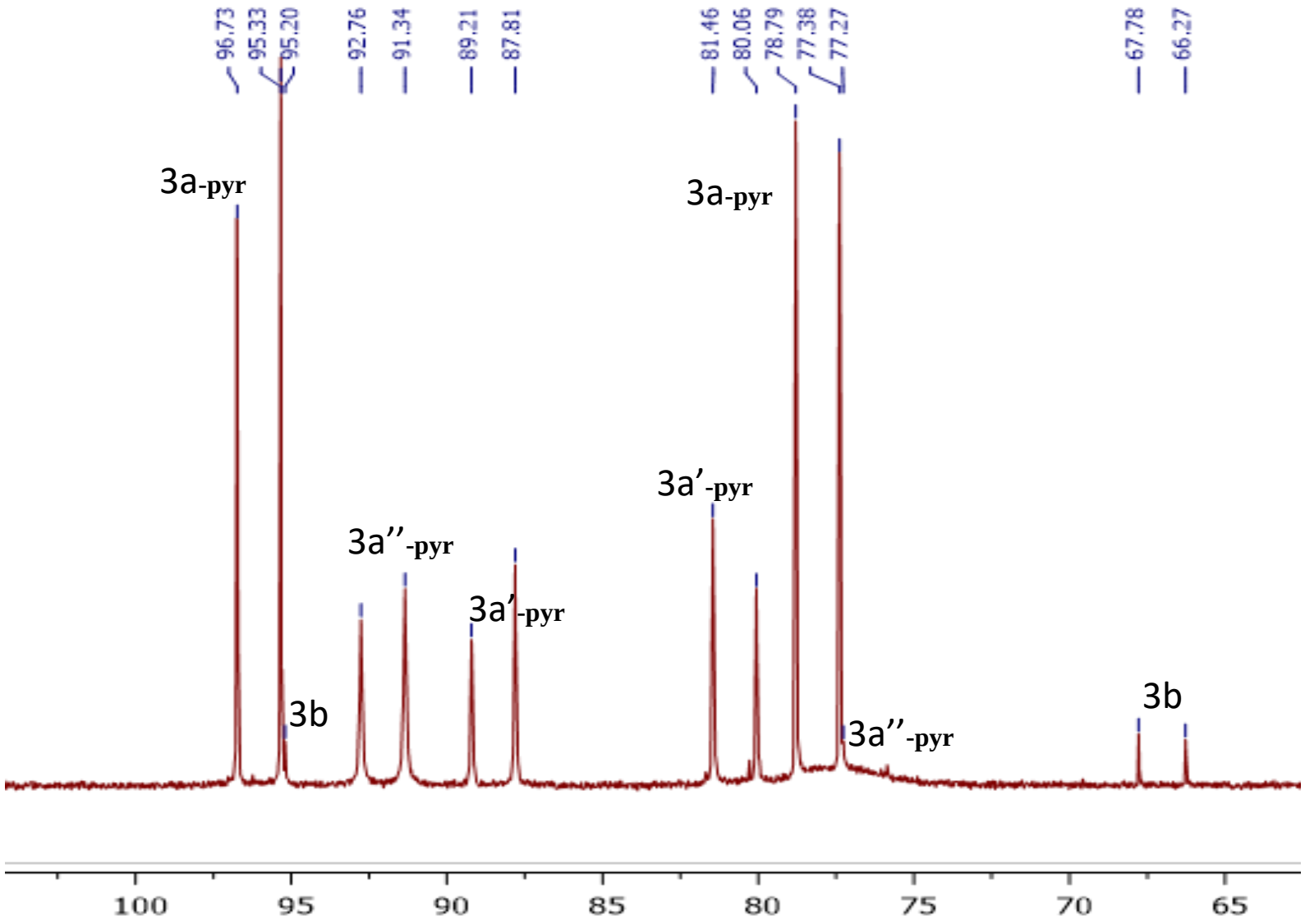
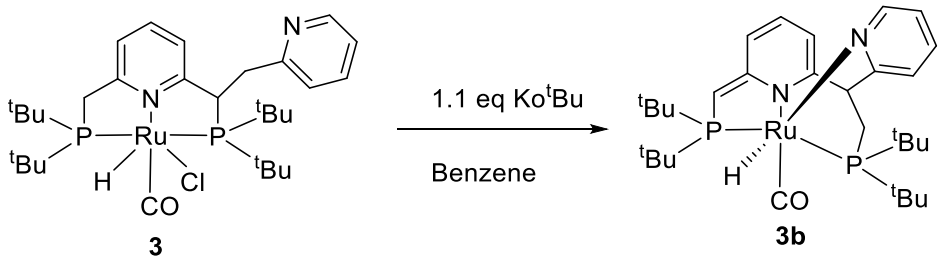


Figure S68. ^{31}P NMR spectrum at 23 °Cfor the complexes (**3a -pyr**, **3a'-pyr**, **3a" -pyr** and **3b)** observed 10 minutes after addition of base in C_5D_5N.

Procedure for Synthesis of Complex 3b.



In a glovebox to a solution of complex **3** (0.153 mmol, 100 mg) in benzene (5 ml), KOtBu (0.168 mmol, 18.9 mg) was slowly added at room temperature. The resulting mixture was stirred at room temperature for half an hour. Subsequently the red color solution was filtered through celite and all volatiles were removed under vacuum to afford complex **3b** as a red solid in 77% yield.

^{1}H NMR (600 MHz, C_6D_6): δ 8.97 (d, 1H, *J* = 5.4 Hz, py-*H*), 6.71 (m, 1H, py-*H*), 6.46 (m, 1H, py-*H*), 6.42 (d, 1H, *J* = 7.6 Hz, py-*H*), 6.29 (d, 1H, *J* = 8.7, py-*H*), 6.22 (m, 1H, py-*H*), 5.47 (m, 1H, py-*H*), 3.94 (dt, 1H, *J*=30.2, 4.1 Hz, arm -*H*), 3.89 (d, 1H, *J* = 4.1 Hz, dearom-arm -*H*), 1.66 (d, 9H, *J* = 12.5 Hz, ^{t}Bu-*Me*), 1.38 (m, 1H, bridge-*H*), 1.15 (d, 9H, *J* = 12.5 Hz, ^{t}Bu-*Me*), 1.06 (d, 9H, *J* = 12.5 Hz, ^{t}Bu-*Me*), 0.99 (m, 1H, bridge-*H*), 0.74 (d, 9H, *J* = 12.5 Hz, ^{t}Bu-*Me*), -13.10 (dd, 1H, $J_{P\text{-}H}$ = 30.6, 13.7 Hz, Ru-*H*).

^{13}C NMR (151 MHz, C_6D_6): δ 211.16 (*C*O), 170.67 (py-*C*), 161.06 (py-*C*), 156.40 (py-*C*), 153.14 (py-*C*), 136.35 (py-*C*), 130.97 (py-*C*), 1e25.08 (py-*C*), 122.16 (py-*C*), 113.78 (py-*C*), 99.60 (py-*C*), 69.43 (d, $J_{P\text{-}C}$ = 52.2 Hz), 56.67 , 40.43 , 37.11 (^{t}Bu-*C*), 35.90 (^{t}Bu-*C*), 35.57 (^{t}Bu-*C*), 32.68 (^{t}Bu-*Me*), 29.89 (^{t}Bu-*Me*), 29.34 (^{t}Bu-*Me*), 29.07 (^{t}Bu-*Me*), 17.30 (^{t}Bu-*C*).

^{31}P{1H} NMR (262 MHz, C_6D_6): δ 96.33 (d, 1P, $J_{P\text{-}P}$ = 244 Hz), 67.33 (d, 1P, $J_{P\text{-}P}$ = 244 Hz).

IR (neat solid) : ν (CO) 1895 cm^{-1}.

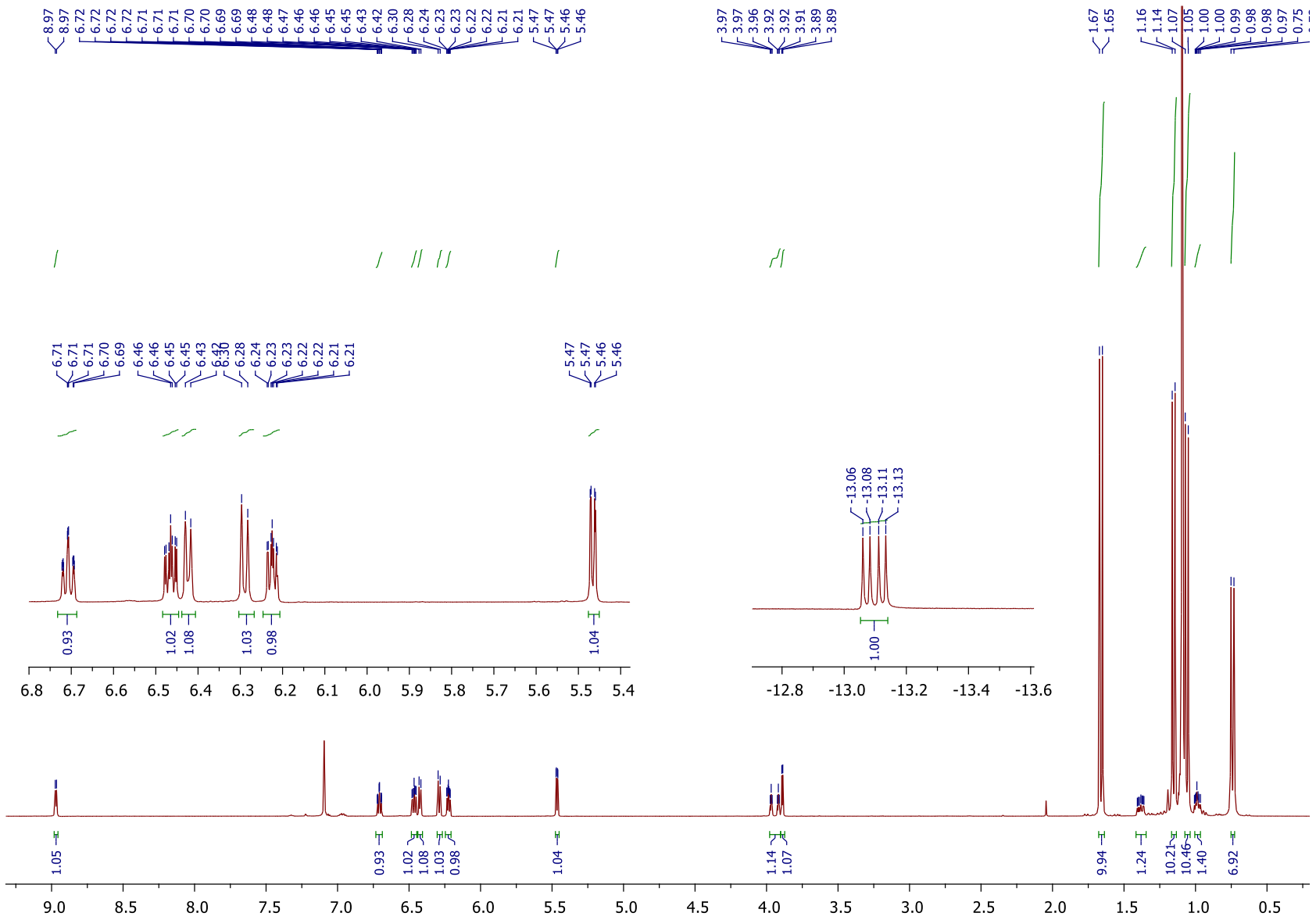


Figure S69. ^{1}H NMR spectrum of complex **3b** in C_6D_6 at 23 °C.

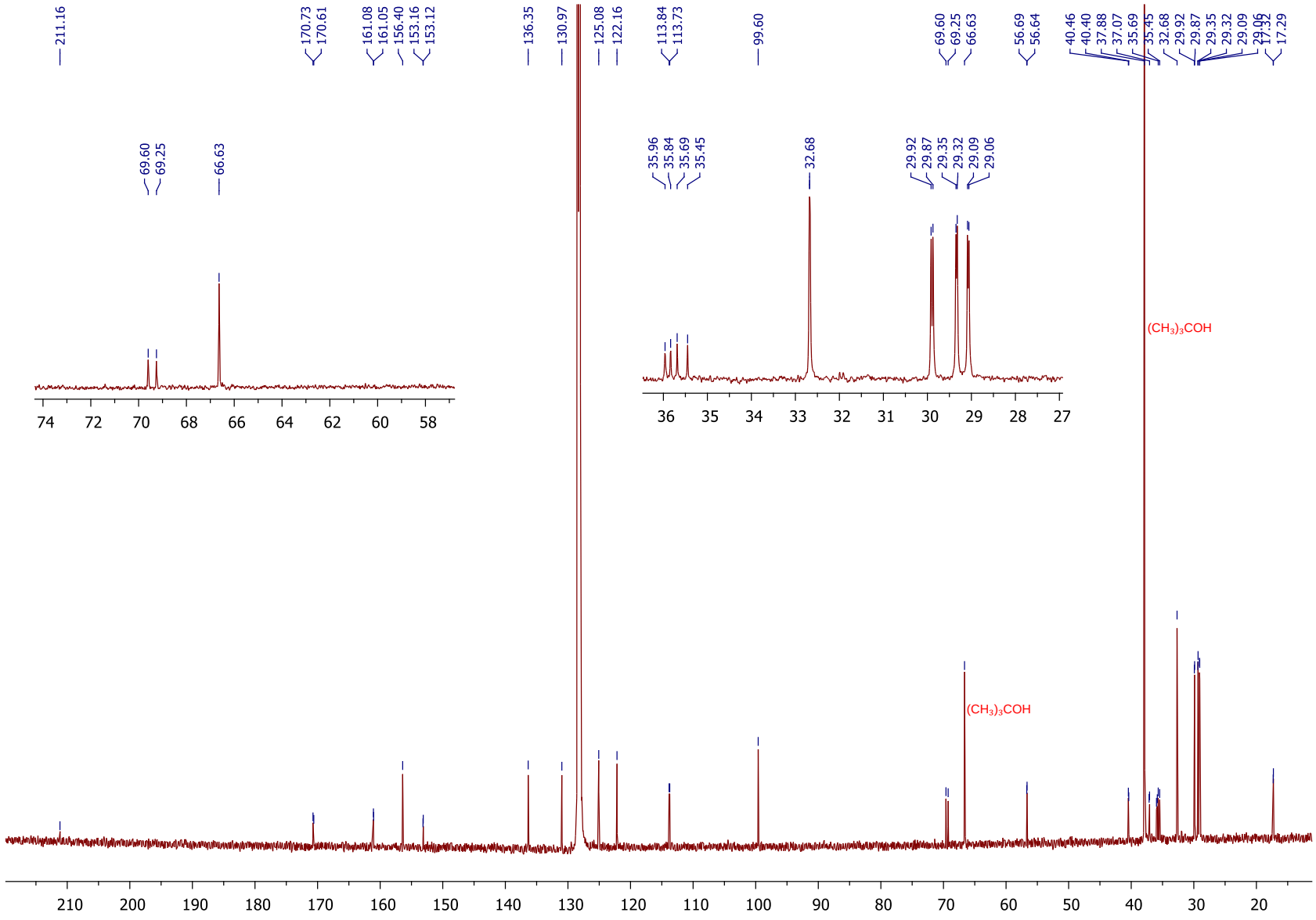


Figure S70. ^{13}C NMR spectrum of complex **3b** in C_6D_6 at 23 °C.

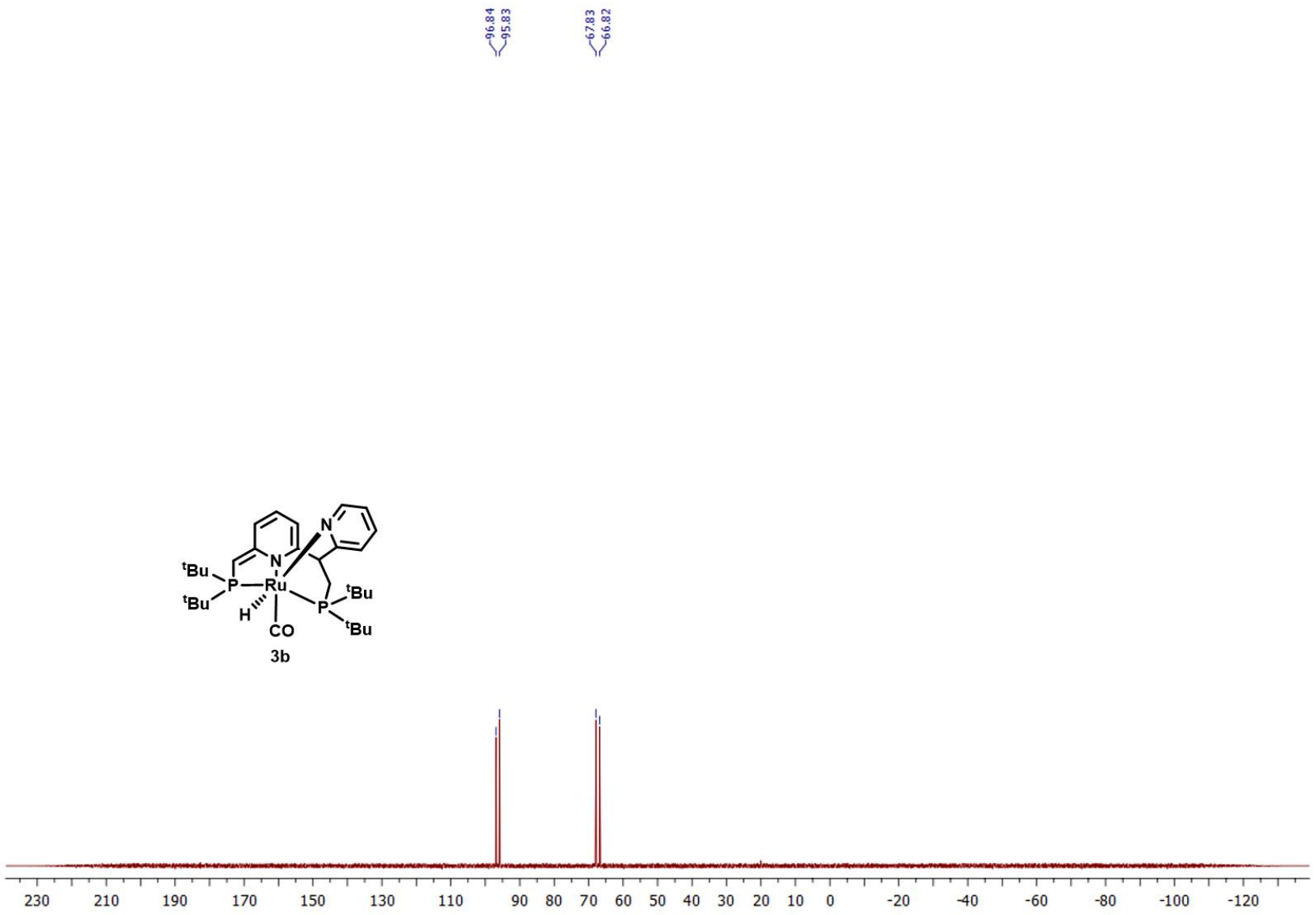


Figure S71. ^{31}P NMR spectrum of complex **3b** in C_6D_6 at 23 °C.

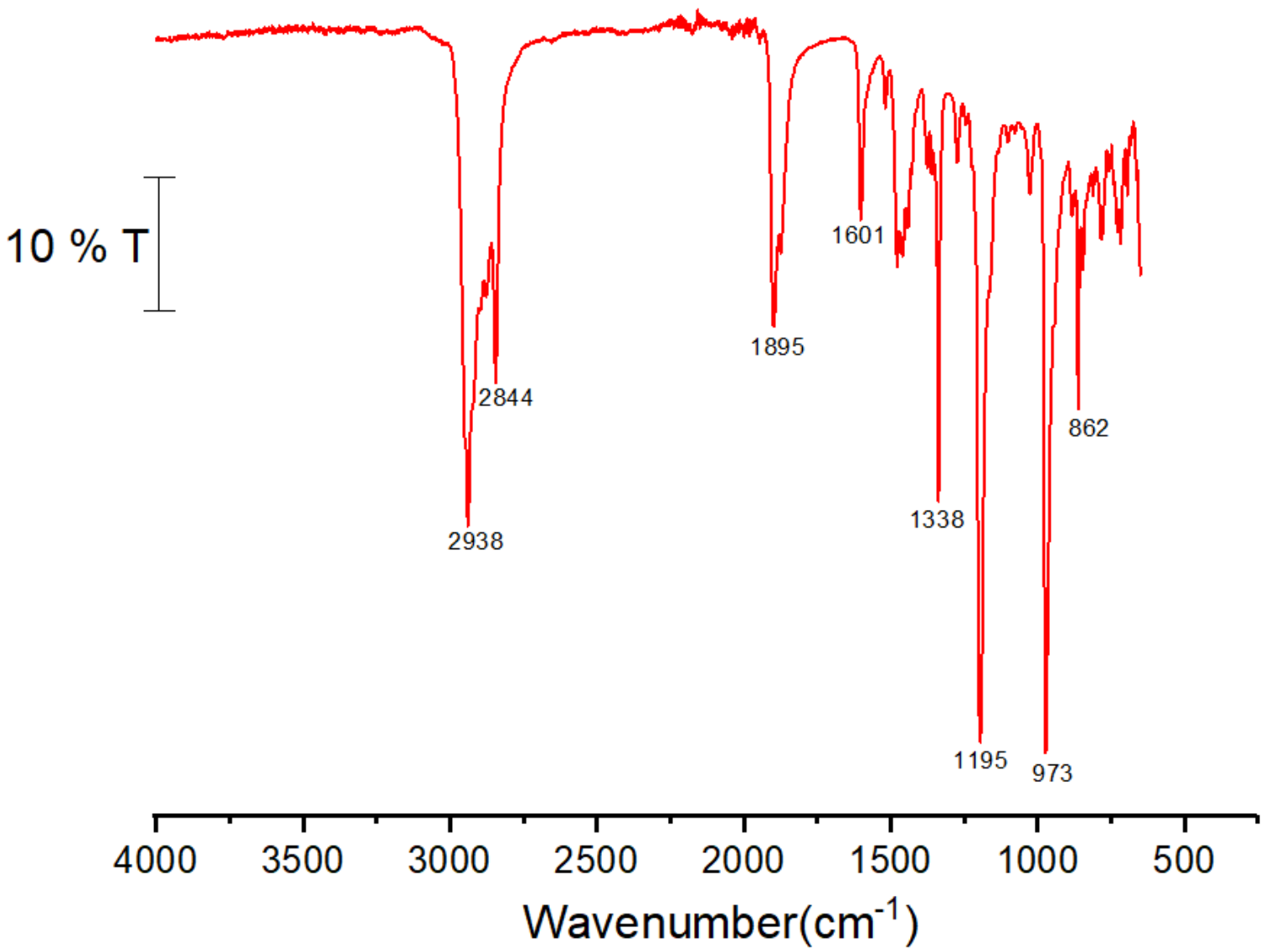
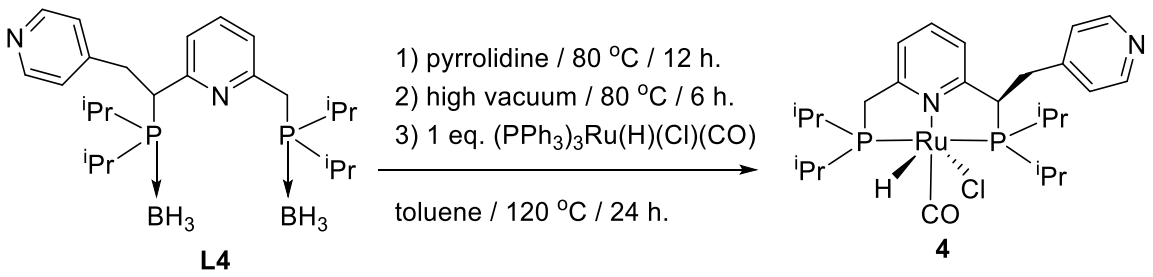


Figure S72. FT-IR (ATR) spectrum of complex **3b**.

Procedure for Synthesis of Complex 4, [(*iPr*PNP(M-*para*)) Ru(CO)(H)(Cl).



Under an inert atmosphere ligand **L4** (0.218 mmol, 100 mg) was deprotected by adding pyrrolidine (4 ml) at 80 ℃ for 12 hours in a 100 ml Schlenk flask. Afterward pyrrolidine was removed under high vacuum, and the system was left to heat at 80 ℃ for 6 hours under high vacuum to ensure the sublimation of pyrrolidine×BH_3. The Schlenk flask was filled with argon and moved to the glovebox where the metal precursor carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) (0.218 mmol, 207.79 mg) was added. 4 ml of toluene were added, and the mixture was stirred for 24 hours at 120 ℃. The resulting solution was filtered through celite, and the volatiles were removed under high vacuum. The complex was dissolved in 2 ml of THF and then 8 ml of hexane was added, and the solution was cooled to -20 ℃. After a few hours of standing a yellow, crystalline solid fell out of solution. The solution was decanted, and the solids were washed three times with cold Et_2O (*ca*. 2 ml) and dried under high vacuum to afford complex **4** as a yellow solid in 77% yield. We were able to separate the complex from the bis-pyridyl ligand impurity and its associated complexes at this stage (i.e. after crystallization). Since the crystals were too small for analysis, single crystals suitable for X-ray crystal structure analysis were formed by vapor diffusion of ether into an acetone solution at room temperature. The complex was present in a mixture of two isomers in a ratio of 0.9:0.1 in solution while in the solid-state crystal analyzed the ratio was closer to 8:2. The major isomer in the solid state had the pyridine *trans* to the Cl ligand and this was assumed to be the major isomer in solution, but reliable identification was not possible. For the minor isomer, the integration could not be reliably assigned due to significant overlap with the major isomer that is present in much larger amounts; peaks that are not overlapping are starred in the spectrum.

^{1}H NMR (600 MHz, THF-d_8): δ 8.38 (d, 2H, *J* = 5.5 Hz, py-*H*), 7.30 (t, 1H, *J* = 7.7 Hz, py-*H*), 7.22 (d, 1H, *J* = 7.7 Hz, py-*H*), 6.95 (d, 2H, *J* = 5.5 Hz, py-*H*), 6.47 (d, 1H, *J* = 7.7 Hz, py-*H*),

4.53 (t, 1H, *J* = 11.4 Hz, sub-arm-*H*), 3.96 (m, 1H, bridge-*H*), 3.51 (m, 1H, bridge-*H*), 3.46 (m, 1H, arm-*H*), 3.25 (m, 1H, arm-*H*), 2.87 (m, 1H, ^{i}Pr-*H*), 2.61 (m, 1H, ^{i}Pr-*H*), 2.39 (m, 1H, ^{i}Pr-*H*), 2.28 (m, 1H, ^{i}Pr-*H*), 1.49 (dd, 3H, *J* = 15.9, 6.6 Hz, ^{i}Pr-*Me*), 1.43-1.19 (m,18H, ^{i}Pr-*Me*), 1.04 (dd, 3H, *J* = 15.9, 6.6 Hz, ^{i}Pr-*Me*), -14.52 (v.t , 1H, J_{P-H} = 18.42 Hz, Ru-*H*).^{13}C NMR (151 MHz, THF-d_8) : δ 209.90 (*C*O), 164.91 (py-*C*), 164.26 (py-*C*), 150.61 (py-*C*), 148.64 (py-*C*), 137.01 (py-*C*), 124.53 (py-*C*), 120.92 (py-*C*), 120.78 (py-*C*), 51.07 (C_{arm}, d, J_{P-C} = 15.65), 40.99 (d, C_{arm}, J_{P-C} = 20.93 Hz), 36.00 (bridge-*C*), 27.88 (^{i}Pr-*C*), 27.59 (^{i}Pr-*C*), 26.54 (^{i}Pr-*C*), 25.25 (^{i}Pr-*C*, overlap with THF-d_8 peak), 20.86 (^{i}Pr-*Me*), 20.66 (^{i}Pr-*Me*), 20.37 (^{i}Pr-*Me*), 20.06 (^{i}Pr-*Me*), 19.66 (^{i}Pr-*Me*), 19.32 (^{i}Pr-*Me*), 19.10 (^{i}Pr-*Me*), 18.09 (^{i}Pr-*Me*).

^{31}P{1H} NMR (262 MHz, THF-d_8): δ 85.60 (d, 1P, J_{P-P} = 262.9 Hz), 76.68 (d, 1P, J_{P-P} = 262.9 Hz).

IR (neat solid) : ν (CO) 1907 cm^{-1}.

Anal. Calcd for $C_{26}H_{41}N_2P_2O_1Cl_1Ru_1$: C, 52.39; H, 6.93; N, 4.70. Found : C, 52.74; H, 6.92; N, 4.62.

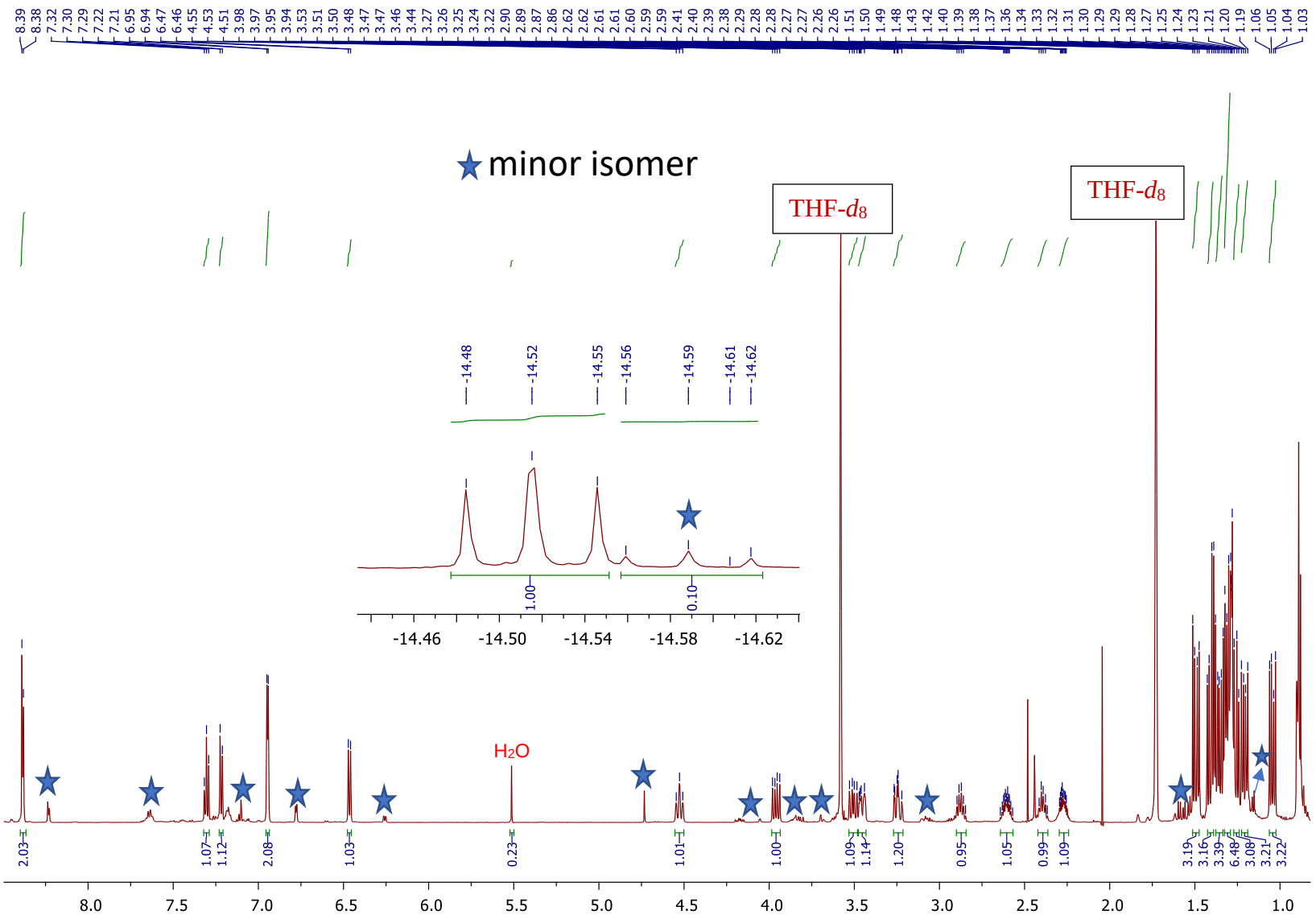


Figure S73. ^{1}H NMR spectrum of complex **4** in THF-d_8 at 23 °C. Minor isomer is present in small amount, could not be integrated.

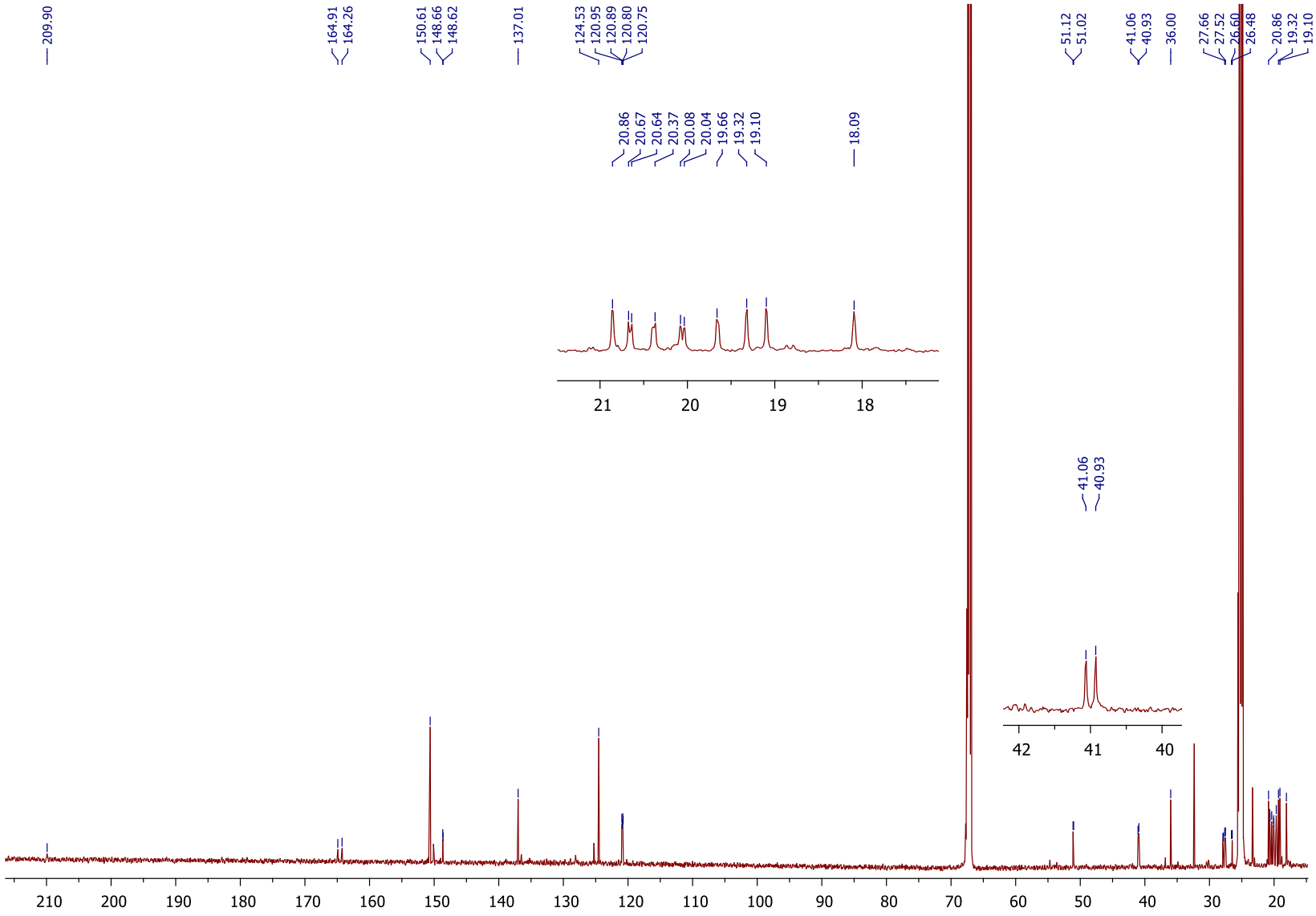


Figure S74. ^{13}C NMR spectrum of complex **4** in THF-d_8 at 23 °C.

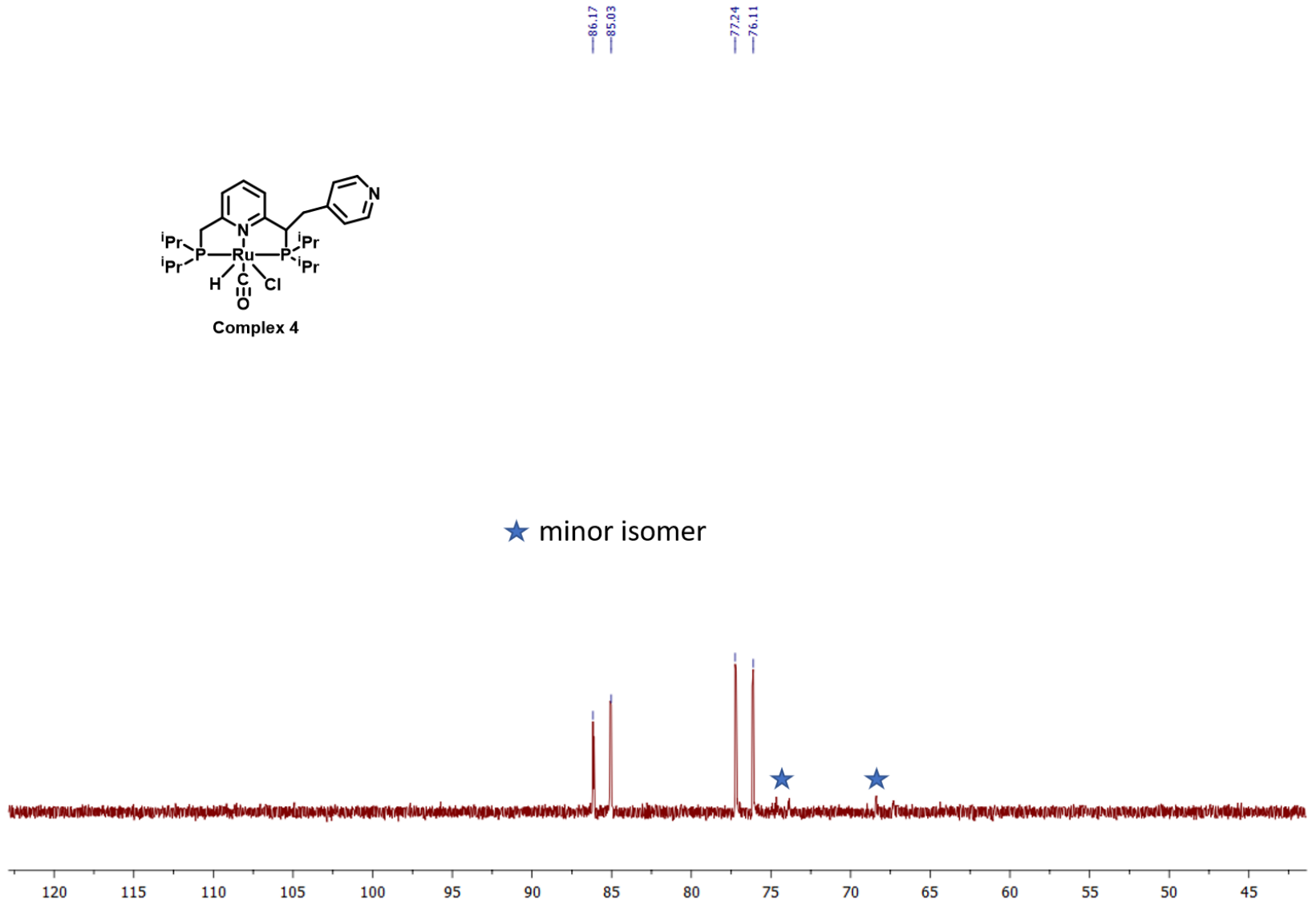


Figure S75. ^{31}P NMR spectrum of complex **4** in THF-d_8 at 23 °C.

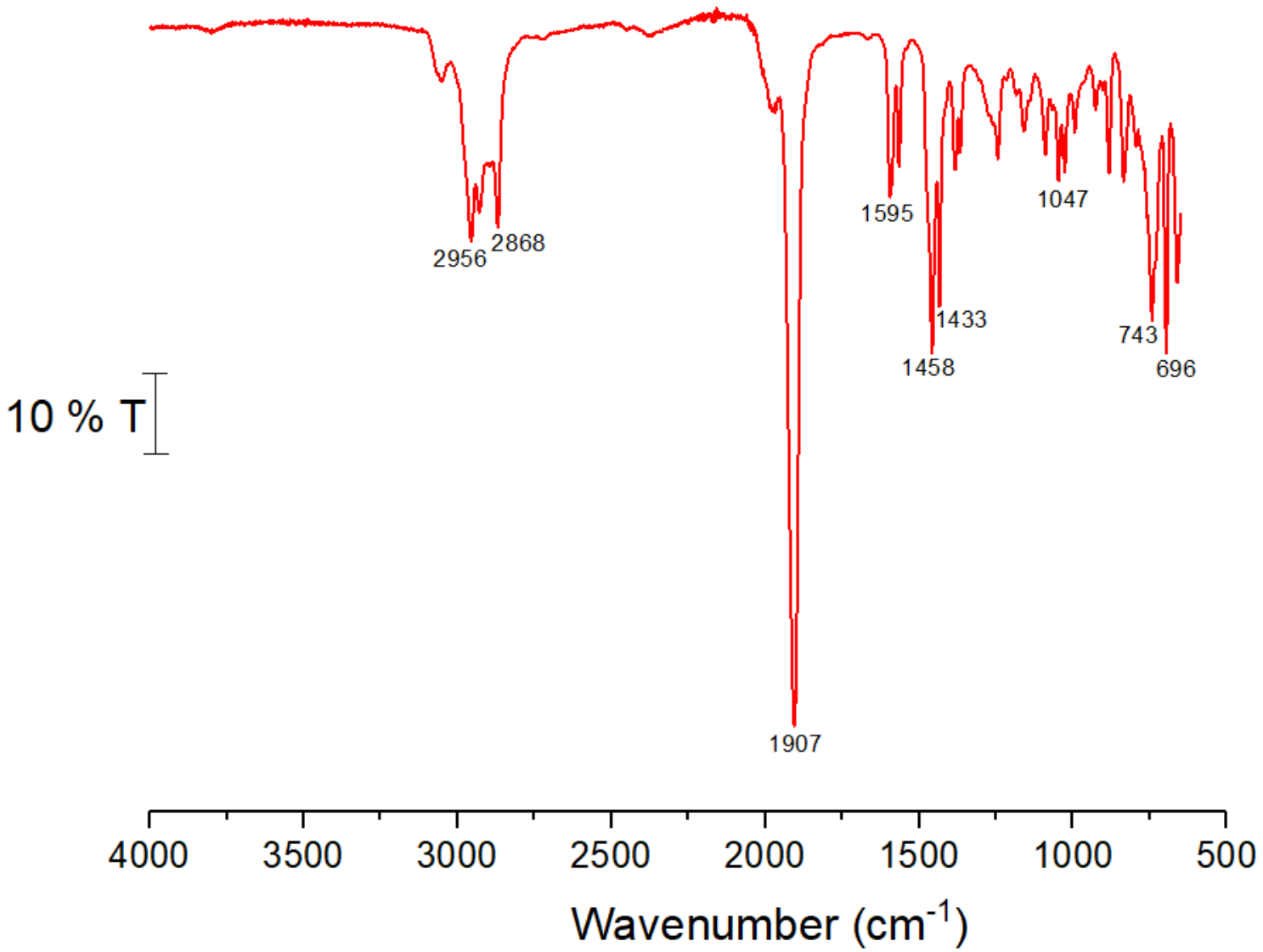
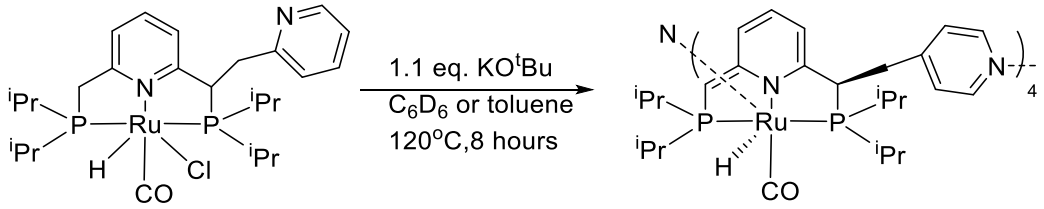


Figure S76. FT-IR (ATR) spectrum of complex **4**.

Procedure for Synthesis of Complex 4a'.



4 **4a'**

In a glovebox to a solution of complex **4** (0.167 mmol, 100 mg) in toluene (5 ml), KOtBu (0.184 mmol, 20.70 mg) was added at room temperature. The resulting mixture was heated at 120 ℃ for 8 hours. During this time, an orange, crystalline solid fell out of solution. After cooling, the toluene was decanted, and the orange solid was washed with THF and acetone (2x). The complex proved to be insoluble in every solvent (including DMSO) except pyridine. Some of the orange crystals proved to be amenable to X-ray crystallography, which unambiguously identified the orange crystals as complex **4a'** (72% yield). A better crystal was obtained by performing the reaction on a 5 mg scale in a Young tube in C_6D_6, and subsequently heating the tube at 120 °C for 1 day. The NMR in pyridine-d_5 showed one species that corresponded to the tetramer **4a'**. However, it is very likely that in pyridine, the tetramer is broken up into monomer species with coordinated pyridine solvent.

^{1}H NMR (600 MHz, C_5D_5N): δ 8.67 (d, 2H, *J* = 5.7 Hz, py-*H*), 7.41 (d, 2H, *J* = 5.7 Hz, py-*H*), 6.72 (m, 1H, py-*H*), 5.82(d, 1H, *J* = 9 Hz, py-*H*), 5.78 (d, 1H, *J* = 6.5 Hz, py-*H*), 3.59 (m, 2H, bridge-*H*), 3.08 (m, 1H, arm-*H*), 2.77 (m, 1H, arm-*H*), 2.25(m, 1H, ^{i}Pr-*H*), 2.06 (m, 1H, ^{i}Pr-*H*), 1.87 (m, 1H, ^{i}Pr-*H*), 1.65 (m, 1H, ^{i}Pr-*H*), 1.39 (dd, 3H, *J* = 15.4, 6.9 Hz, ^{i}Pr-*Me*), 1.23-1.14 (m, 9H, ^{i}Pr-*Me*), 1.09-1.04 (m, 6H, ^{i}Pr-*Me*), 0.98 (dd, 3H, *J* = 12.5, 7.1 Hz, ^{i}Pr-*Me*), 0.64 (dd, 3H, *J* = 14.5, 7.2 Hz, ^{i}Pr-*Me*), -14.48 (v.t *J*= 18.66 Hz, Ru-*H*).

^{13}C NMR (151 MHz, C_5D_5N) : δ 210.18 (*C*O), 174.67 (py-*C*), 168.38 (py-*C*), 159.99 (py-*C*), 133.45 (py-*C*), 125.19 (py-*C*, overlapping with C_5D_5N), 110.32 (py-*C*), 99.27 (py-*C*), 40.15 (C_{arm}, d, $J_{P\text{-}C}$ =18.31 Hz), 35.51 (bridge-*C*), 30.06 (d, C_{arm}, $J_{P\text{-}C}$ = 22 Hz), 28.12 (^{i}Pr-*C*, d, $J_{P\text{-}C}$ = 15.3 Hz), 27.08 (^{i}Pr-*C*, d, $J_{P\text{-}C}$ = 31.4 Hz), 25.71 (^{i}Pr-*C*, d, 1C, $J_{P\text{-}C}$ = 24 Hz), 21.99, 21.33 (^{i}Pr-*Me*), 20.77 (^{i}Pr-*Me*), 20.58 (^{i}Pr-*Me*), 20.35 (^{i}Pr-*Me*), 19.03 (^{i}Pr-*Me*), 18.47 (^{i}Pr-*Me*).

$^{31}P\{1H\}$ NMR (262 MHz, C_5D_5N): δ 73.48 (d, 1P, J_{P-P} = 225.4 Hz), 66.32 (d, 1P, J_{P-P} = 225.4 Hz).

Anal. Calcd for $C_{26}H_{40}N_2P_2O_1Ru_1$: C, 55.80; H, 7.20; N, 5.01. Found : C, 55.76; H, 7.60; N, 4.44.

IR (neat solid) : ν (CO) 1892 cm^{-1}.

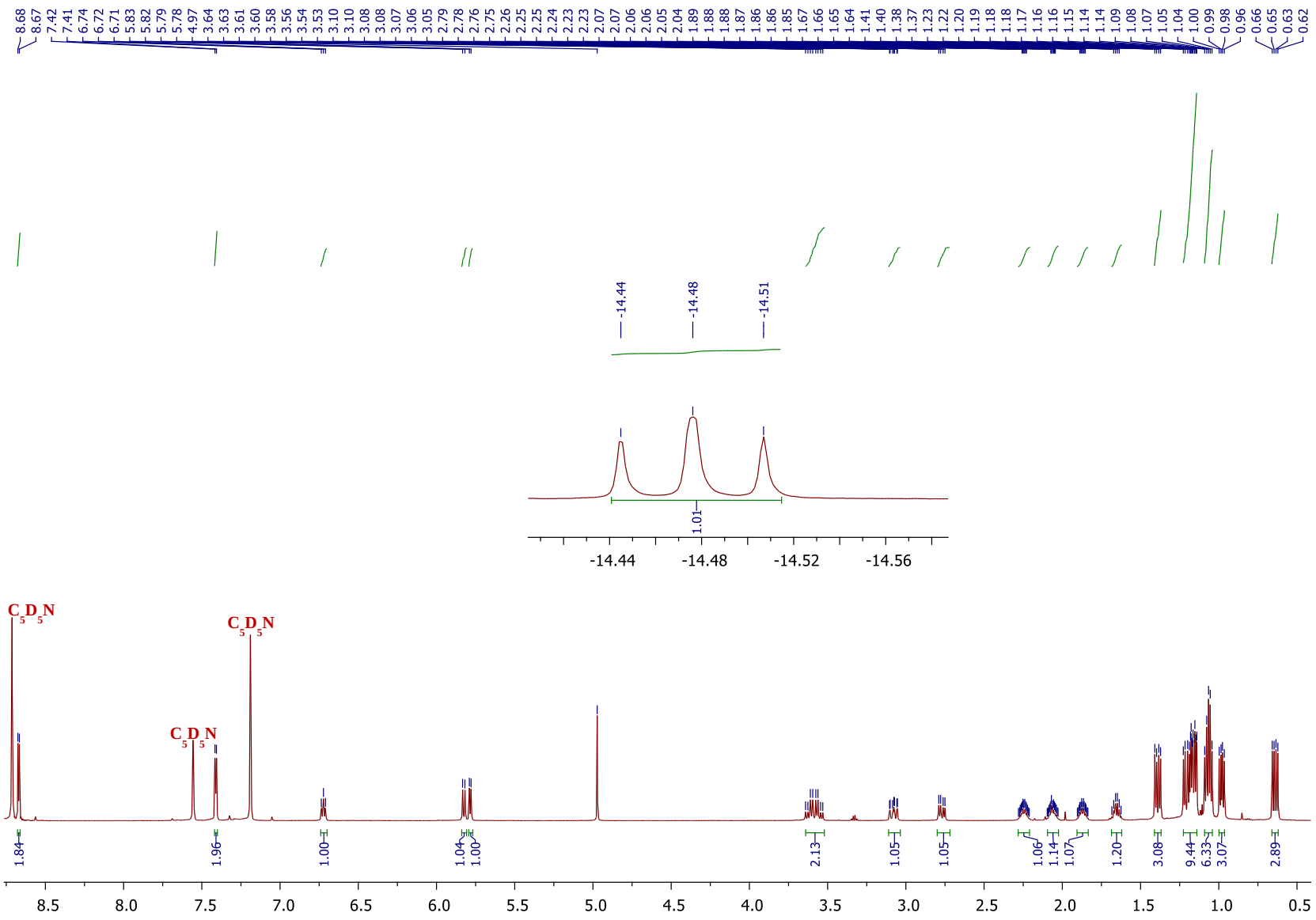


Figure S77. ^{1}H NMR spectrum of complex **4a'** in C_5D_5N at 23 °C.

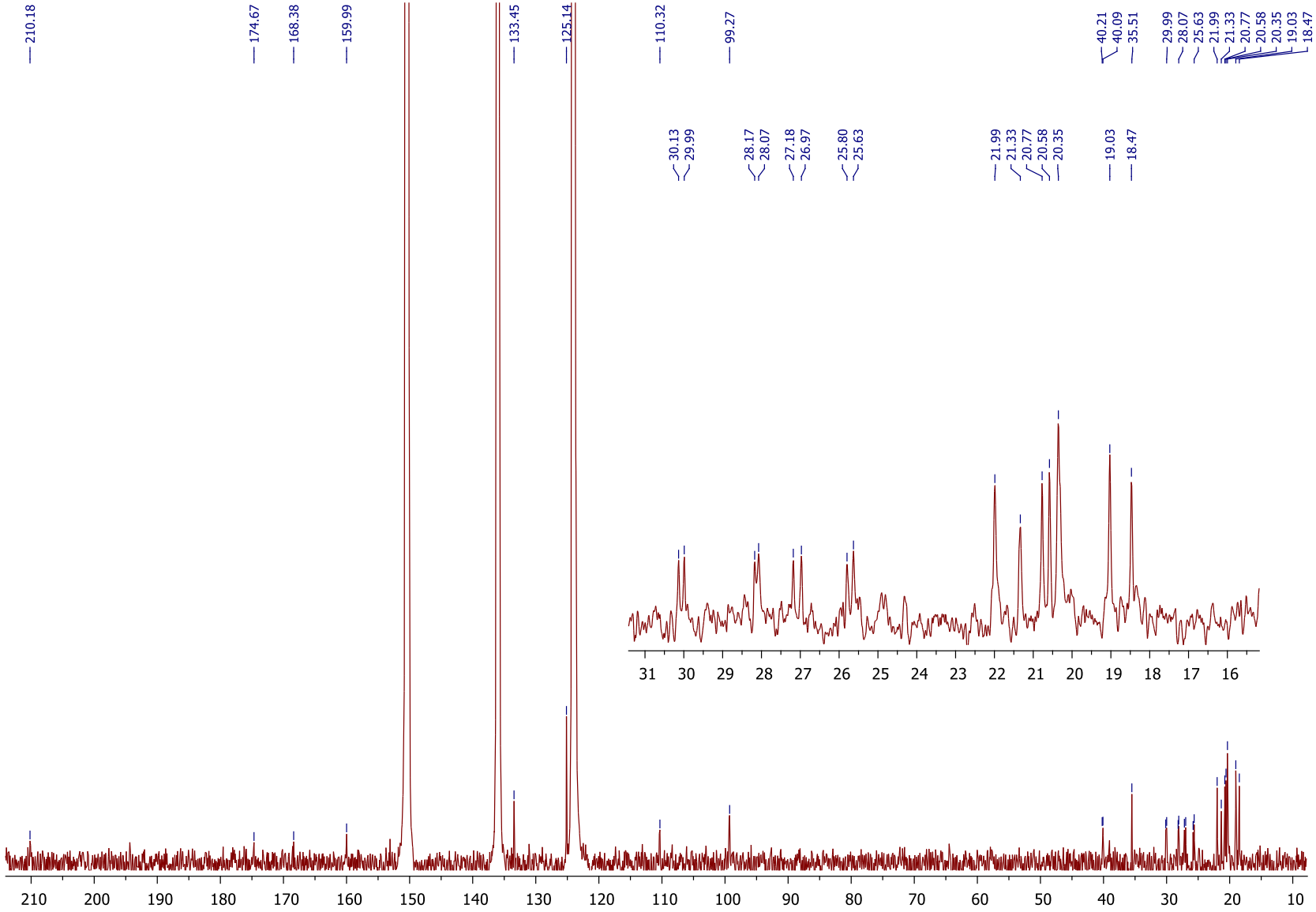


Figure S78. ^{13}C NMR spectrum of complex **4a'** in C_5D_5N at 23 °C.

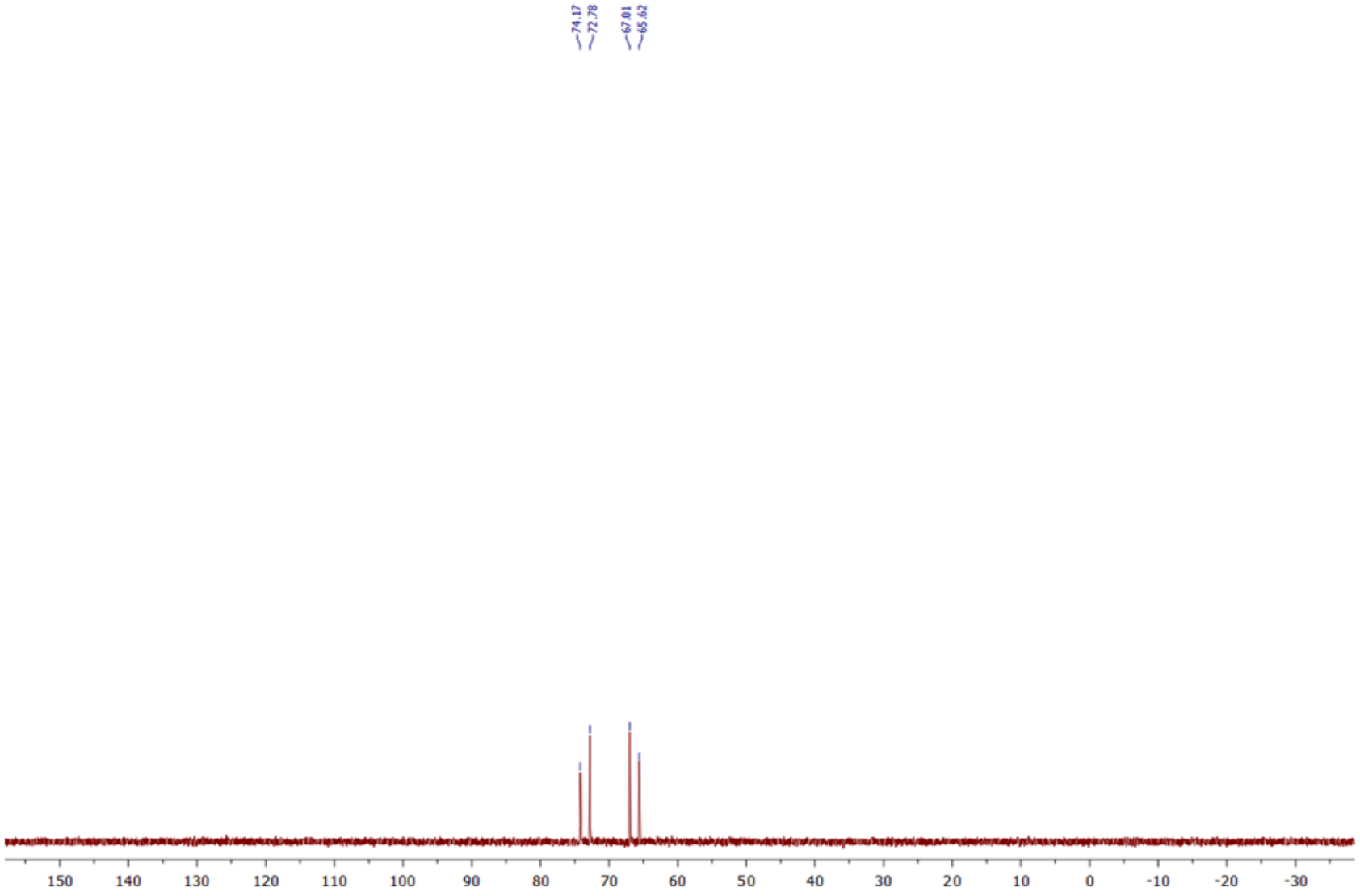


Figure S79. ^{31}P NMR spectrum of complex **4a'** in C_5D_5N at 23 °C.

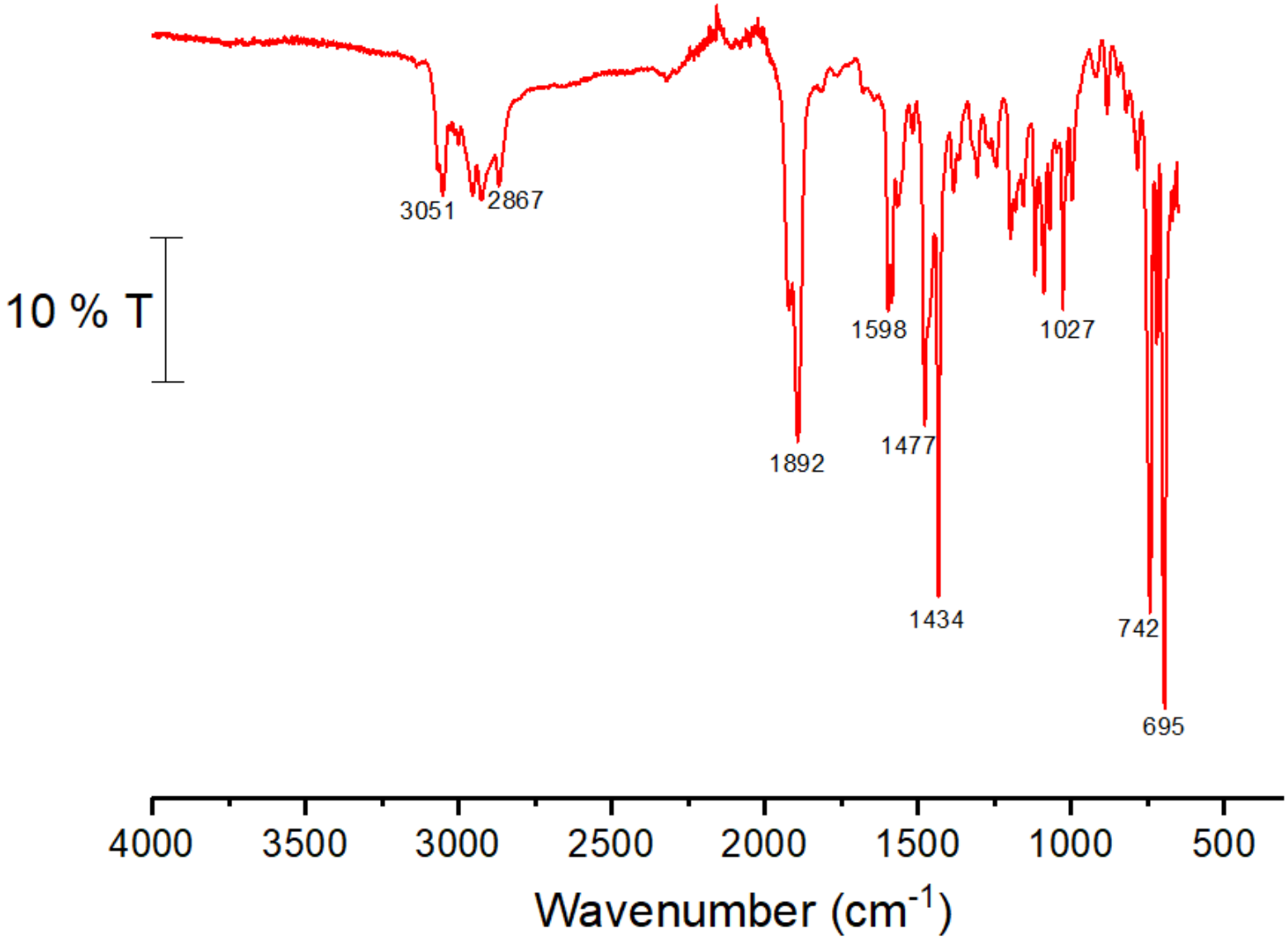
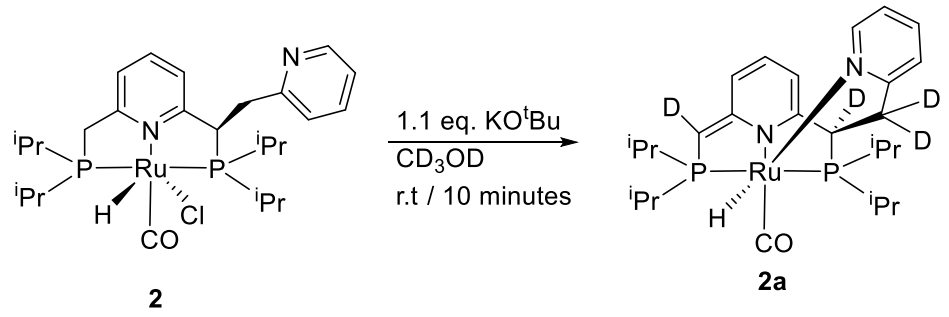


Figure S80. FT-IR (ATR) spectrum of complex **4a**'.

Deuteration Experiment.



2 **2a**

The deuteration experiment was carried out to check if selective deuteration could be obtained on one of the benzylic positions in order to learn the fate of the associated carbon atom experimentally. After dissolving **2** in methanol and adding an excess of base, complex **2a** could be observed. The spectrum did not show greater deuteration at one of the positions with respect to other ones. After 20 more minutes, the methanol solvent was evaporated, the sample re-dissolved in C_6D_6 and filtered through celite. The NMR obtained afterward showed **2a** as a major species where all positions were deuterated to the statistical maximum equally. This sample could be easily converted to deuterated **2b** after mild heating at 60 °C overnight.

The experiment suggests that hydride transfer between isomers **2a**, **2a'**, and **2a''** is rapid at least in methanol solvent as compared to the transformation to **2b**. The rate of transfer may depend on the alcohol (HO^{t}Bu produced during the reaction). Although after filtering through celite and evaporating under high vacuum would get rid of most alcohol, trace water or alcohol that catalyze hydride transfer cannot be discounted. Rate measurements show quick equilibration of all isomers to **2a** in benzene, after which the measured $\Delta G^{\neq}$ for **2a→2b** corresponded to the DFT identified isomerization transition state energy.

Catalytic Experiments.

The complexes **1-3**, as well as C-C rearrangement complexes **1-3b**, and complexes **4**, **4a'**, and **5** were tested in catalytic experiments where 5 mg of each species was put into an NMR Young tube, filled with 0.4 ml of C_6D_6 and 2 eq. of KO^tBu were added. Afterward, 20 equivalents of ethanol were added with a micro syringe. An initial NMR was obtained at room temperature and then the solutions were heated at 80 °C for eight hours. An NMR was obtained afterward, and the amounts of ethyl acetate and ethanol could be directly determined. The NMR tube headspace allows full conversion to ethyl acetate in the case of complex **5**. We found that all C-C rearrangement species **1b**,**2b**,**3b** (as well as insoluble **4a'**) were completely inactive in catalyzing the transformation of ethanol to ethyl acetate. However, **1-3** activated with base gave the activity of a few turnovers for the formation of ethyl acetate in a Young NMR tube, presumably via their active **1-3a'-pyrD5** arm unbound intermediate species before rearrangement occurred. The tube with complex **5** also contained the dihydride complex as the only organometallic species, that was implicated in earlier work as the catalytic intermediate. This reaction mixture was heated for one week at 80 °C and exhibited no changes in the spectrum. The temperature was raised to 150 °C, much more than the time and temperature required for typical alcohol dehydrogenation experiments, and the dihydride complex was found to persist as the major species (>90%).

Catalytic experiments were subsequently carried out on a larger scale with the same amount of base and complex in 100 mL Schlenk tubes equipped with a stir bar with complex **5** in 4 mL of toluene solvent. In these cases, 100, 200, and larger equivalents of hexanol were added and the solution was heated for one day at 120 °C. The mixtures were subsequently analyzed by GC/FID. Full conversion to hexyl hexanoate was observed with 100 and 200 equivalents, while hexanol was found when larger amounts of starting alcohol were used, and its amount did not change with reaction time. Since the reaction is reversible, H_2 present in the headspace of the Schlenk tube could have created an equilibrium. We found the closed system reaction consistently reproducible in terms of yields and conversion amounts when compared to open systems that allow H_2 to be driven off and can give larger yields. Full conversion with 200 equivalents and persistence of the dihydride intermediate under harsh reaction conditions suggests a robust catalyst when the atmosphere is strictly controlled.

X-ray Structure Determination Details

The X-ray diffraction data for the single crystals were collected on a Rigaku XtaLab PRO instrument (κ-goniometer) with a PILATUS3 R 200K hybrid pixel array detector using Mo*Kα* (0.71073 Å) or Cu*Kα* (1.54184 Å) radiation monochromated by means of multilayer optics. The performance mode of MicroMax^{TM}-003 microfocus sealed X-ray tubes was 50 kV, 0.60 mA. The diffractometer was equipped with a Rigaku GN2 system for low-temperature experiments. Suitable crystals of appropriate dimensions were mounted on loops in random orientations. Preliminary unit cell parameters were determined with three sets of a total of 10 narrow frame scans in the case of a Mo-source and six sets of a total of 10 narrow frame scans at two different 2θ positions in the case of a Cu-source. The data were collected according to recommended strategies in a ω-scan mode. Final cell constants were determined by the global refinement of reflections from the complete data sets using the Lattice wizard module. Images were indexed and integrated with "smart" background evaluation using the *CrysAlis*^{Pro} data reduction package (1.171.39.20a or 1.171.39.46, Rigaku Oxford Diffraction). Analysis of the integrated data did not show any decay. Data were corrected for systematic errors and absorption using the *ABSPACK* module: Numerical absorption correction based on Gaussian integration over a multifaceted crystal model and empirical absorption correction based on spherical harmonics (according to the point group symmetry using equivalent reflections). The *GRAL* module and the *ASSIGN SPACEGROUP* routine of the *WinGX* suite were used for the analysis of systematic absences and space group determination.

The structures were solved by the direct methods using *SHELXT*-2018/2 [2] and refined by the full-matrix least-squares on F^2 using *SHELXL*-2018/3,[3] which uses a model of atomic scattering based on spherical atoms. Calculations were mainly performed using the *WinGX*-2018.3 suite of programs.[4] Non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms H1, H1A, and H1B bound to ruthenium center were determined by difference Fourier maps, and these atoms were refined isotropically. The positions of the hydrogen atoms of methyl groups were found using rotating group refinement with idealized tetrahedral angles. The other hydrogen atoms were inserted at the calculated positions and refined as riding atoms.

Remarkably, the red crystals obtained at the stage of formation of **1a** turned out to be a *mixed crystal* (in other words, a *solid solution*)[5] of constitutional isomers **1a** (the main component with a volume fraction of 0.771(4) and **1b**, which takes the form of substitutional disordering at the same

symmetrically independent site of the crystal structure. Comparing with the geometry of **1b** measured from the orangish red crystals of the individual complex, the dearomatized pincer backbone of **1b** in the solid solution phase (for simplicity **1b***) appeared to be somewhat distorted (**Fig. S82**). Interestingly, the studied crystals of **4** belong to a *solid solution* of diastereomers, namely the same site of the crystal structure can be occupied by the molecules with *R* (the main component with a volume fraction of 0.782(6) or *S* configuration of the carbon atom C17 (**Fig. S87**). A positional disordering of the C11-pivot picolyl and P1-pivot isopropyl substituents in the case of complex **1** and the picolyl arm at C17 in the case of complex **3** was observed. The disorder was resolved using free variables and reasonable restraints on geometry and anisotropic displacement parameters.

Complexes **3** and **4a'** crystallize as solvates with diethyl ether (1:0.5) and benzene (1:2), respectively. The tetrameric complex **4a'** localized on the crystallographic inversion center (the $P\bar{1}$ space group), hence the asymmetric cell contains half of the molecule ($Z' = 0.5$).

All the compounds studied have no unusual bond lengths and angles, but the geometry of molecule **1b*** is somewhat distorted. Molecular structures of the investigated complexes in the crystalline phase, as well as accepted partial numbering, are presented as ORTEP diagrams in Figures **S81-S88**. Selected bond lengths and angles are appended to the captions.

Crystallographic data for 1. $C_{32}H_{46}ClN_3OP_2Ru$, yellow plank (0.426 × 0.127 × 0.087 mm^3), formula weight 687.18, monoclinic, $P2_1/n$ (No. 14), a = 9.61551(16) Å, b = 22.9604(3) Å, c = 15.1753(3) Å, β = 105.4479(19)°, V = 3229.31(10) Å^3, Z = 4, Z' = 1, T = 95(2) K, d_{calc} = 1.413 g cm^{-3}, μ(CuK_α) = 5.850 mm^{-1}, F(000) = 1432; $T_{max/min}$ = 1.000/0.190; 57657 reflections were collected (3.583° ≤ θ ≤ 68.999°, index ranges: –11 ≤ h ≤ 11, –27 ≤ k ≤ 27, –18 ≤ l ≤ 18), 6003 of which were unique, R_{int} = 0.0975, R_σ = 0.0359; completeness to θ of 67.684° 99.8 %. The refinement of 458 parameters with 298 restraints converged to R_1 = 0.0486 and wR_2 = 0.1315 for 5704 reflections with $I > 2\sigma(I)$ and R_1 = 0.0499 and wR_2 = 0.1325 for all data with S = 1.069 and residual electron density, $\rho_{max/min}$ = 1.592 and –0.950 e Å^{-3}. The crystals were grown by vapor diffusion of hexane into a DCM solution at room temperature.

Crystallographic data for 1a × 1b*. $C_{32}H_{45}N_3OP_2Ru$, red plate (0.298 × 0.150 × 0.047 mm^3), formula weight 650.72, monoclinic, $P2_1/c$ (No. 14), a = 15.5325(3) Å, b = 11.26257(18) Å, c = 18.0248(3) Å, β = 93.8953(15)°, V = 3145.91(9) Å^3, Z = 4, Z' = 1, T = 94(2) K, d_{calc} =

1.374 g cm^{-3}, μ(MoK_α) = 0.629 mm^{-1}, F(000) = 1360; $T_{max/min}$ = 1.000/0.789; 54940 reflections were collected (2.235° ≤ θ ≤ 30.181°, index ranges: –21 ≤ h ≤ 21, –15 ≤ k ≤ 15, –25 ≤ l ≤ 23), 8387 of which were unique, R_{int} = 0.0336, R_σ = 0.0230; completeness to θ of 25.242° 99.9 %. The refinement of 481 parameters with 492 restraints converged to R_1 = 0.0249 and wR_2 = 0.0584 for 7583 reflections with $I > 2\sigma(I)$ and R_1 = 0.0296 and wR_2 = 0.0599 for all data with S = 1.037 and residual electron density, $\rho_{max/min}$ = 0.696 and –0.445 e Å^{-3}. The crystals were grown by evaporation of a benzene solution at room temperature.

Crystallographic data for 1b. $C_{32}H_{45}N_3OP_2Ru$, bright, deep red plank (0.240 × 0.043 × 0.037 mm^3), formula weight 650.72, monoclinic, $P2_1/c$ (No. 14), a = 15.8290(2) Å, b = 11.21034(13) Å, c = 17.8393(2) Å, β = 94.5817(12)°, V = 3155.45(7) Å^3, Z = 4, Z' = 1, T = 95(2) K, d_{calc} = 1.370 g cm^{-3}, μ(MoK_α) = 0.627 mm^{-1}, F(000) = 1360; $T_{max/min}$ = 1.000/0.491; 96335 reflections were collected (2.229° ≤ θ ≤ 31.497°, index ranges: –22 ≤ h ≤ 23, –16 ≤ k ≤ 16, –26 ≤ l ≤ 26), 10344 of which were unique, R_{int} = 0.0680, R_σ = 0.0360; completeness to θ of 25.242° 99.9 %. The refinement of 364 parameters with no restraints converged to R_1 = 0.0248 and wR_2 = 0.0595 for 9302 reflections with $I > 2\sigma(I)$ and R_1 = 0.0298 and wR_2 = 0.0613 for all data with S = 1.033 and residual electron density, $\rho_{max/min}$ = 0.488 and –0.820 e Å^{-3}. The crystals were grown by slow evaporation of a hexane solution at –30 °C.

Crystallographic data for 2. $C_{26}H_{41}ClN_2OP_2Ru$, pale yellow prism (0.294 × 0.248 × 0.110 mm^3), formula weight 596.07, monoclinic, $P2_1/n$ (No. 14), a = 8.86132(11) Å, b = 28.0653(3) Å, c = 11.24724(14) Å, β = 98.8474(12)°, V = 2763.85(6) Å^3, Z = 4, Z' = 1, T = 95(2) K, d_{calc} = 1.432 g cm^{-3}, μ(MoK_α) = 0.801 mm^{-1}, F(000) = 1240; $T_{max/min}$ = 1.000/0.383; 167376 reflections were collected (1.971° ≤ θ ≤ 32.282°, index ranges: –13 ≤ h ≤ 13, –41 ≤ k ≤ 42, –16 ≤ l ≤ 16), 9493 of which were unique, R_{int} = 0.0546, R_σ = 0.0200; completeness to θ of 25.242° 99.9 %. The refinement of 310 parameters with no restraints converged to R_1 = 0.0265 and wR_2 = 0.0552 for 9062 reflections with $I > 2\sigma(I)$ and R_1 = 0.0289 and wR_2 = 0.0557 for all data with S = 1.175 and residual electron density, $\rho_{max/min}$ = 0.713 and –0.625 e Å^{-3}. The crystals were grown by vapor diffusion of pentane into a THF solution at room temperature.

Crystallographic data for 2b. $C_{26}H_{40}N_2OP_2Ru$, red prism (0.294 × 0.197 × 0.143 mm^3), formula weight 559.61, monoclinic, $P2_1/c$ (No. 14), a = 10.66363(14) Å, b = 11.49601(18) Å, c = 21.7803(3) Å, β = 94.7191(12)°, V = 2660.98(7) Å^3, Z = 4, Z' = 1, T = 95(2) K, d_{calc} = 1.397 g cm^{-3}, μ(MoK_α) = 0.730 mm^{-1}, F(000) = 1168; $T_{max/min}$ = 1.000/0.515; 82249 reflections

were collected (2.570° ≤ θ ≤ 32.310°, index ranges: –15 ≤ *h* ≤ 15, –17 ≤ *k* ≤ 16, –32 ≤ *l* ≤ 32), 8885 of which were unique, R_{int} = 0.0351, R_σ = 0.0195; completeness to θ of 25.242° 99.9 %. The refinement of 301 parameters with no restraints converged to R_1 = 0.0201 and wR_2 = 0.0477 for 8343 reflections with $I > 2\sigma(I)$ and R_1 = 0.0223 and wR_2 = 0.0483 for all data with S = 1.052 and residual electron density, $\rho_{max/min}$ = 0.553 and –0.599 *e* Å^{-3}. The crystals were grown by slow evaporation of a pentane solution at –30 ℃.

Crystallographic data for 3. $C_{30}H_{49}ClN_2OP_2Ru \times 0.5(C_4H_{10}O)$, yellow prism (0.077 × 0.056 × 0.043 mm^3), formula weight 689.23, triclinic, $P\bar{1}$ (No. 2), a = 12.0950(2) Å, b = 12.3732(2) Å, c = 14.4676(2) Å, α = 65.1332(15)°, β = 67.9561(15)°, γ = 62.8294(17)°, V = 1701.99(6) Å^3, Z = 2, Z' = 1, T = 95(2) K, d_{calc} = 1.345 g cm^{-3}, μ(MoK_α) = 0.661 mm^{-1}, F(000) = 726; $T_{max/min}$ = 1.000/0.864; 83651 reflections were collected (2.106° ≤ θ ≤ 30.998°, index ranges: –17 ≤ *h* ≤ 17, –17 ≤ *k* ≤ 17, –20 ≤ *l* ≤ 20), 10774 of which were unique, R_{int} = 0.0641, R_σ = 0.0351; completeness to θ of 25.242° 99.9 %. The refinement of 446 parameters with 250 restraints converged to R_1 = 0.0277 and wR_2 = 0.0679 for 9834 reflections with $I > 2\sigma(I)$ and R_1 = 0.0320 and wR_2 = 0.0695 for all data with S = 1.032 and residual electron density, $\rho_{max/min}$ = 1.152 and –0.925 *e* Å^{-3}. The crystals were grown from a concentrated diethyl ether solution by cooling to –30 ℃.

Crystallographic data for 4. $C_{26}H_{41}ClN_2OP_2Ru$, yellow plate (0.133 × 0.032 × 0.022 mm^3), formula weight 596.07, monoclinic, $P2_1/c$ (No. 14), a = 16.45910(11) Å, b = 8.04650(5) Å, c = 22.02981(18) Å, β = 108.8904(8)°, V = 2760.44(4) Å^3, Z = 4, Z' = 1, T = 93(2) K, d_{calc} = 1.434 g cm^{-3}, μ(CuK_α) = 6.740 mm^{-1}, F(000) = 1240; $T_{max/min}$ = 1.000/0.516; 65544 reflections were collected (2.838° ≤ θ ≤ 72.119°, index ranges: –20 ≤ *h* ≤ 20, –9 ≤ *k* ≤ 9, –27 ≤ *l* ≤ 27), 5430 of which were unique, R_{int} = 0.0978, R_σ = 0.0315; completeness to θ of 67.684° 100 %. The refinement of 404 parameters with 372 restraints converged to R_1 = 0.0610 and wR_2 = 0.1400 for 5277 reflections with $I > 2\sigma(I)$ and R_1 = 0.0614 and wR_2 = 0.1409 for all data with S = 1.117 and residual electron density, $\rho_{max/min}$ = 1.892 and –0.824 *e* Å^{-3}. The crystals were grown by vapor diffusion of pentane into an acetone solution at room temperature.

Crystallographic data for 4a'. $C_{104}H_{160}N_8O_4P_8Ru_4 \times 2(C_6H_6)$, orange plank (0.130 × 0.099 × 0.046 mm^3), formula weight 2394.65, triclinic, $P\bar{1}$ (No. 2), a = 10.94363(16) Å, b = 14.5049(2) Å, c = 19.0279(3) Å, α = 93.9991(12)°, β = 94.2369(12)°, γ = 98.3955(12)°, V = 2969.94(8) Å^3, Z = 1, Z' = 0.5, T = 93(2) K, d_{calc} = 1.339 g cm^{-3}, μ(MoK_α) = 0.659 mm^{-1}, F(000) = 1252; $T_{max/min}$ = 1.000/0.721; 200131 reflections were collected (1.888° ≤ θ ≤ 32.997°, index ranges: –16 ≤ *h* ≤ 16,

$-22 \leq k \leq 22, -29 \leq l \leq 28$), 22235 of which were unique, R_{int} = 0.0604, R_σ = 0.0294; completeness to θ of 25.242° 99.9 %. The refinement of 704 parameters with 253 restraints converged to R_1 = 0.0263 and wR_2 = 0.0661 for 19676 reflections with $I > 2\sigma(I)$ and R_1 = 0.0317 and wR_2 = 0.0680 for all data with S = 1.047 and residual electron density, $\rho_{max/min}$ = 1.408 and –0.701 e Å^{-3}. The sample was obtained during the reaction from a benzene solution.

The crystallographic data for the investigated compounds have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1890854 (**1**), 1890855 (**1a × 1b* –** a mixed crystal of **1a** and **1b***), 1890856 (**1b**), 1890857 (**2**), 1890858 (**2b**), 1890859 (**3**), 1890860 (**4**), and 1890861 (**4a'**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

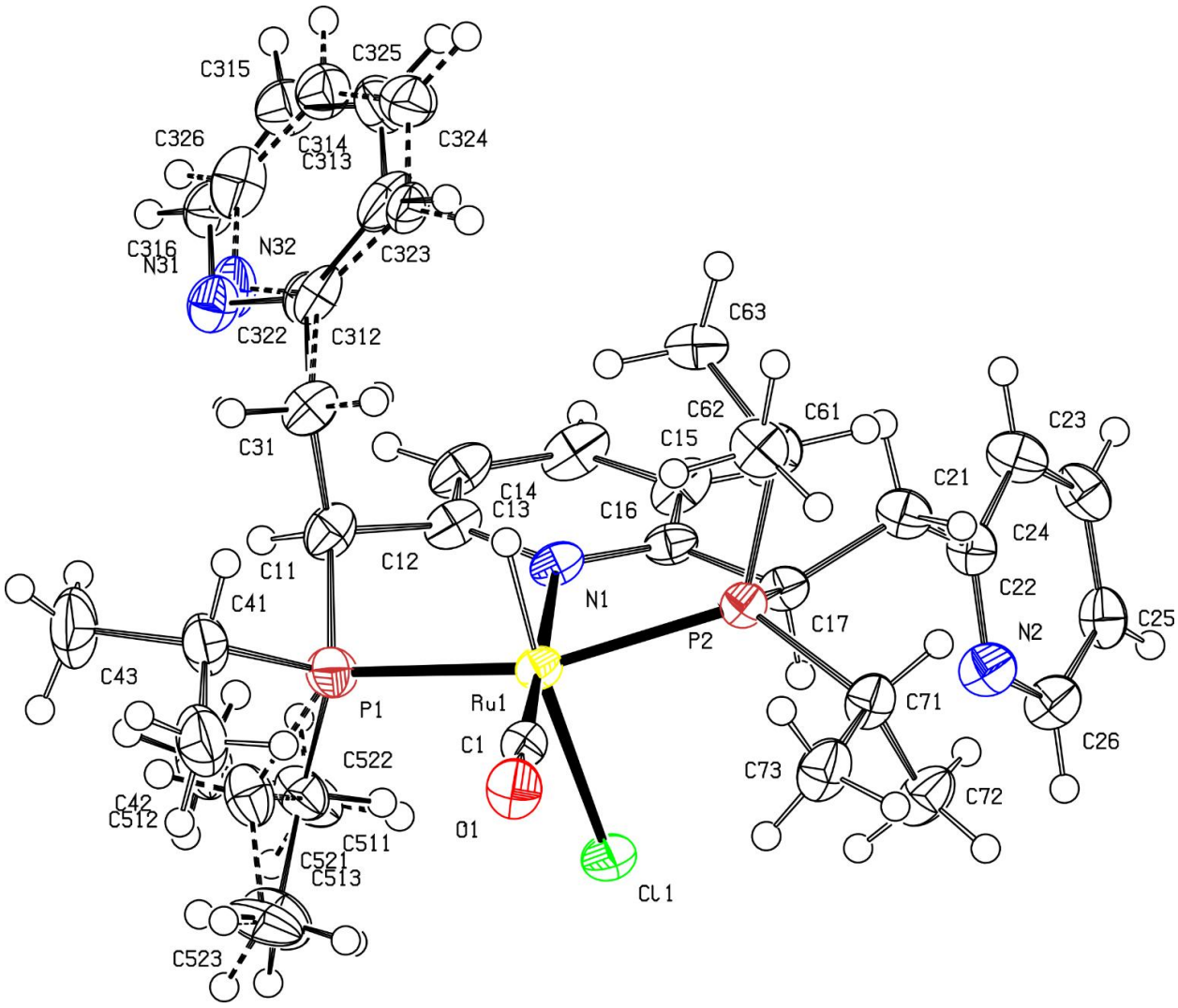
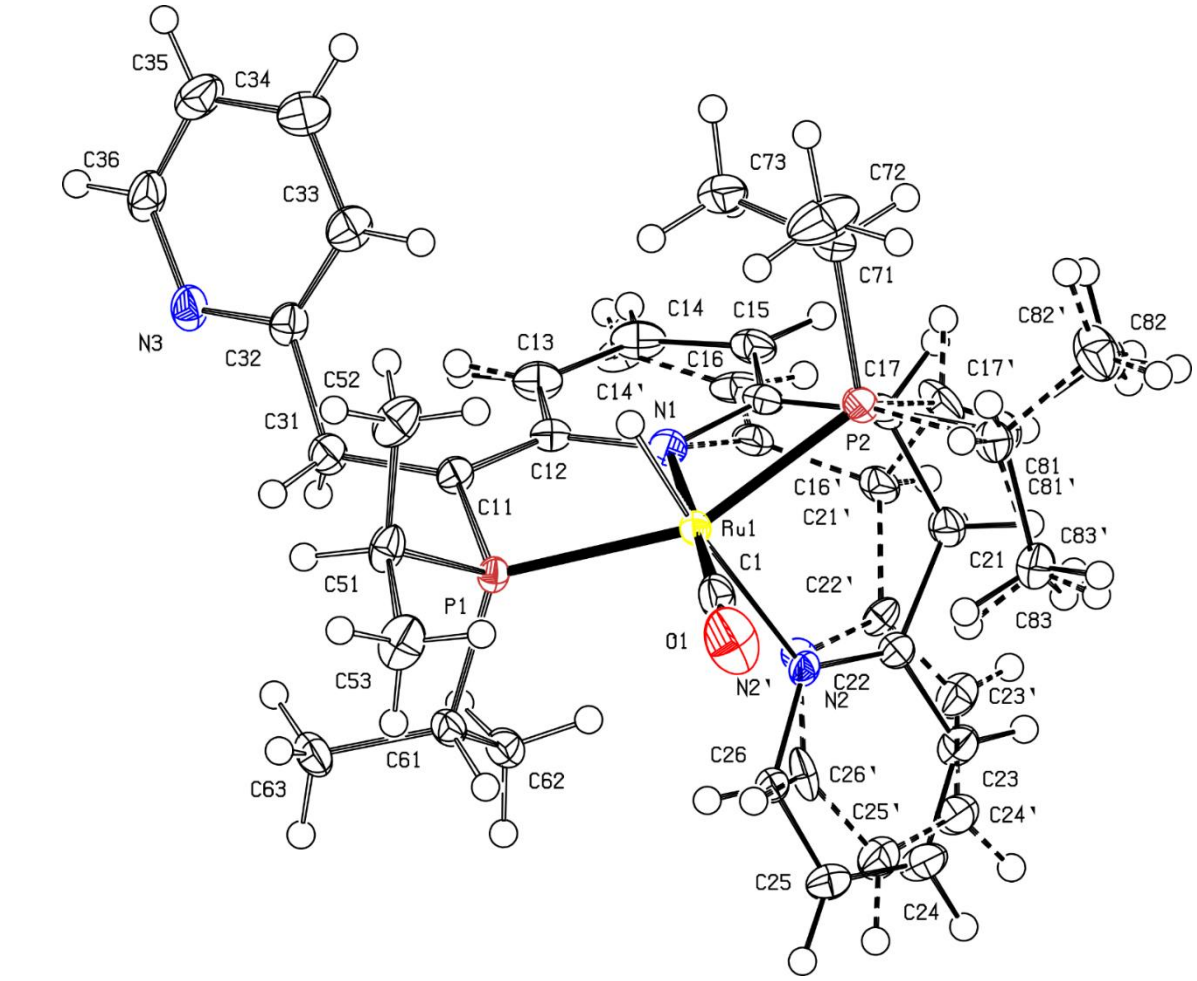
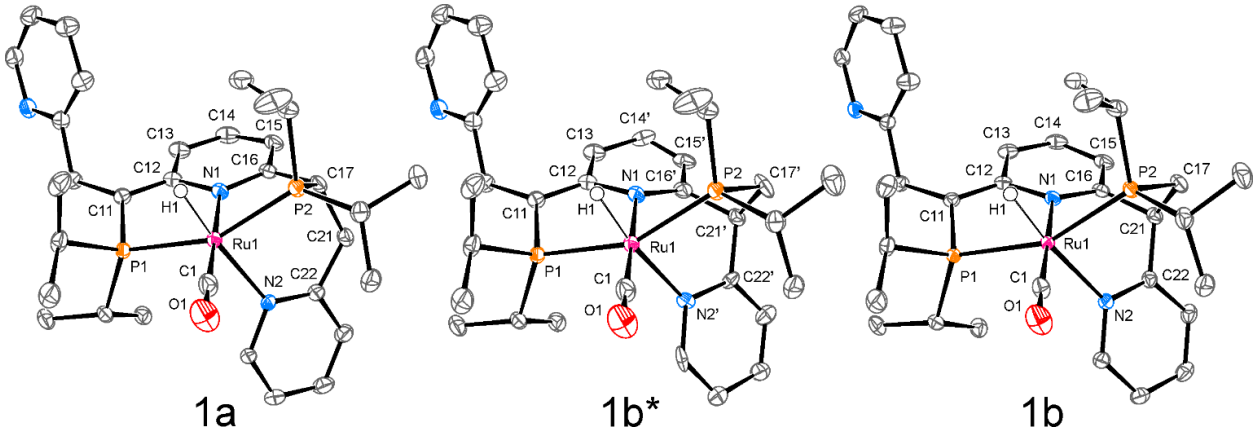


Figure S81. ORTEP diagram showing 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound **1** according to single crystal X-ray diffraction data. Selected interatomic distances [Å]: Ru1–C1 1.830(4), Ru1–N1 2.167(3), Ru1–P1 2.3271(9), Ru1–P2 2.3075(9), Ru1–Cl1 2.5406(9), Ru1–H1 1.523(19), C11–C12 1.512(5), N1–C12 1.356(4), C12–C13 1.395(5), C13–C14 1.375(6), C14–C15 1.381(6), C15–C16 1.392(5), C16–C17 1.511(5), N1–C16 1.357(5).



(a)



(b)

Figure S82. ORTEP diagram showing 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound **1a × 1b*** according to SCXRD (a) and comparison of molecules **1a, 1b*** and **1b** (b). Selected interatomic distances for **1a × 1b*** [Å]: Ru1–C1

1.8404(16), Ru1–N1 2.1319(12), Ru1–N2 2.273(5), Ru1–N2' 2.265(18), Ru1–P2 2.2956(4), Ru1–P1 2.3286(3), Ru1–H1 1.549(18), C11–C12 1.3845(19), N1–C12 1.3997(18), C12–C13 1.4417(19), C13–C14' 1.344(10), C13–C14 1.377(4), C14–C15 1.402(4), C15–C16 1.382(3), C16–C17 1.518(3), C17–C21 1.533(3), N1–C16 1.343(2), N1–C16' 1.430(6), C14'–C15' 1.383(11), C15'–C16' 1.378(8), C16'–C21' 1.535(10), C17'–C21' 1.530(9).

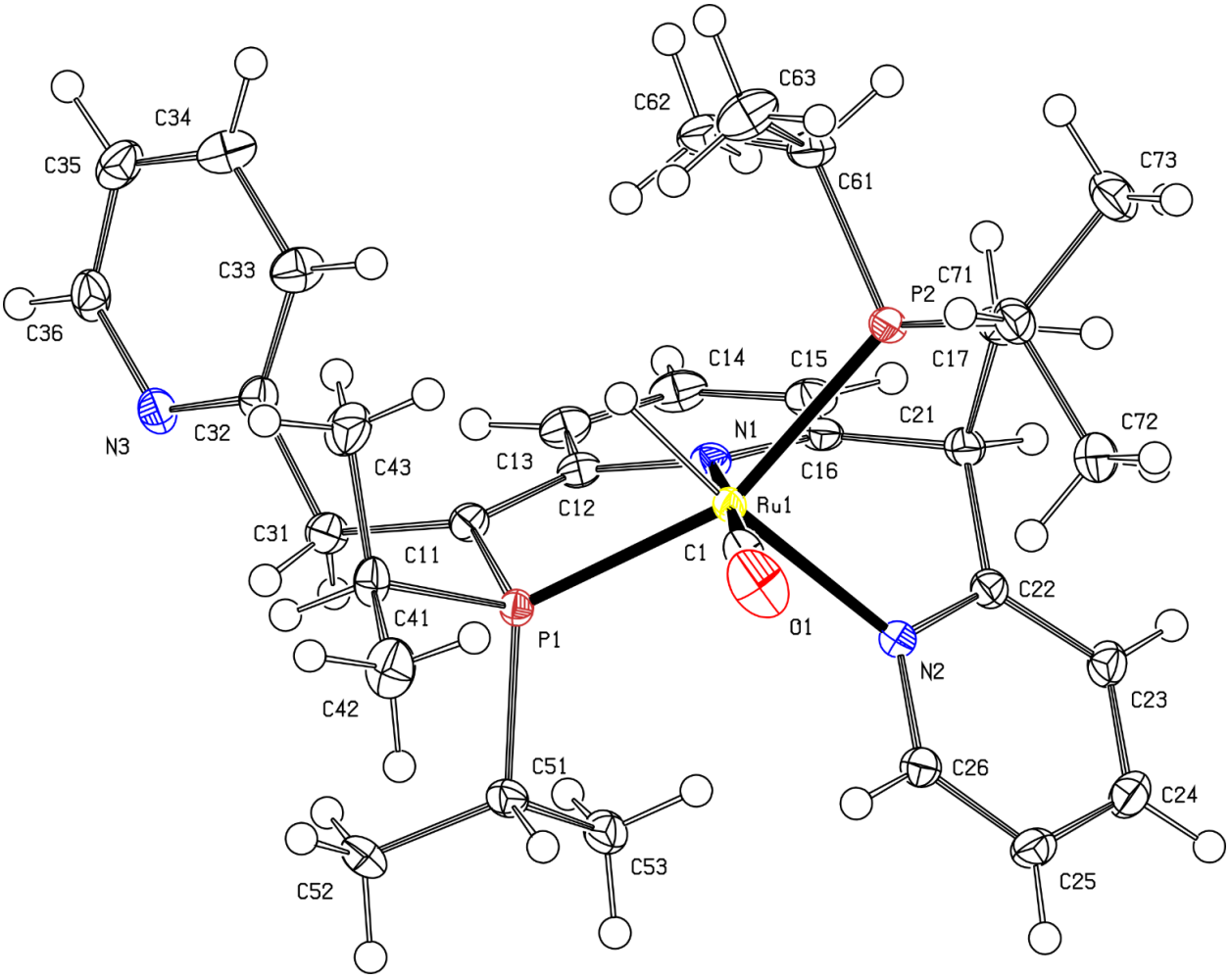


Figure S83. ORTEP diagram showing 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound **1b** according to single crystal X-ray diffraction data. Selected interatomic distances [Å]: Ru1–C1 1.8367(12), Ru1–N1 2.1582(10), Ru1–N2 2.2088(10), Ru1–P1 2.3247(3), Ru1–P2 2.3189(3), Ru1–H1 1.523(19), C11–C12 1.3906(16), C12–C13 1.4436(16), N1–C12 1.3999(15), C13–C14 1.3656(18), C14–C15 1.4070(19), C15–C16 1.3852(17), C16–C21 1.5189(17), C17–C21 1.5478(17), N1–C16 1.3535(15).

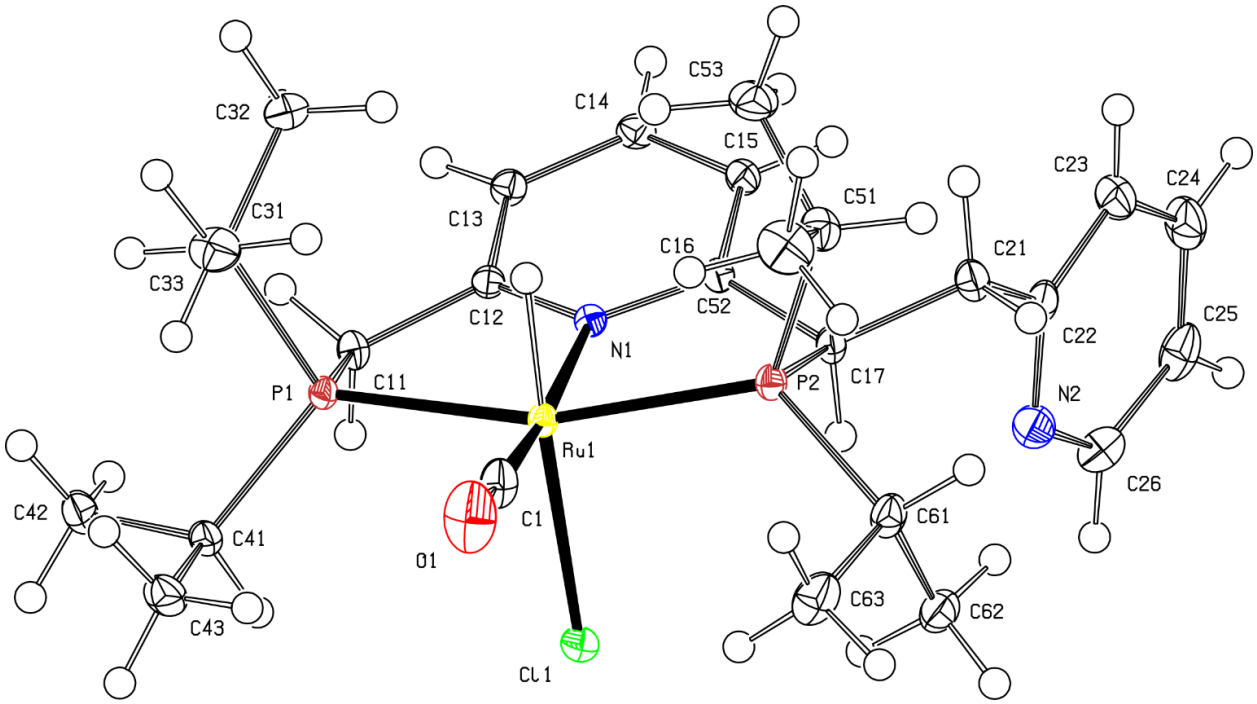


Figure S84. ORTEP diagram showing 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound **2** according to single crystal X-ray diffraction data. Selected interatomic distances [Å]: Ru1–C1 1.8393(14), Ru1–N1 2.1759(11), Ru1–P1 2.3049(3), Ru1–P2 2.3072(3), Ru1–Cl1 2.5498(3), Ru1–H1 1.52(2), C11–C12 1.5031(17), N1–C12 1.3559(16), C12–C13 1.3935(18), C13–C14 1.3837(18), C14–C15 1.3888(18), C15–C16 1.3911(18), C16–C17 1.5138(18), C17–C21 1.5344(18), N1–C16 1.3623(16).

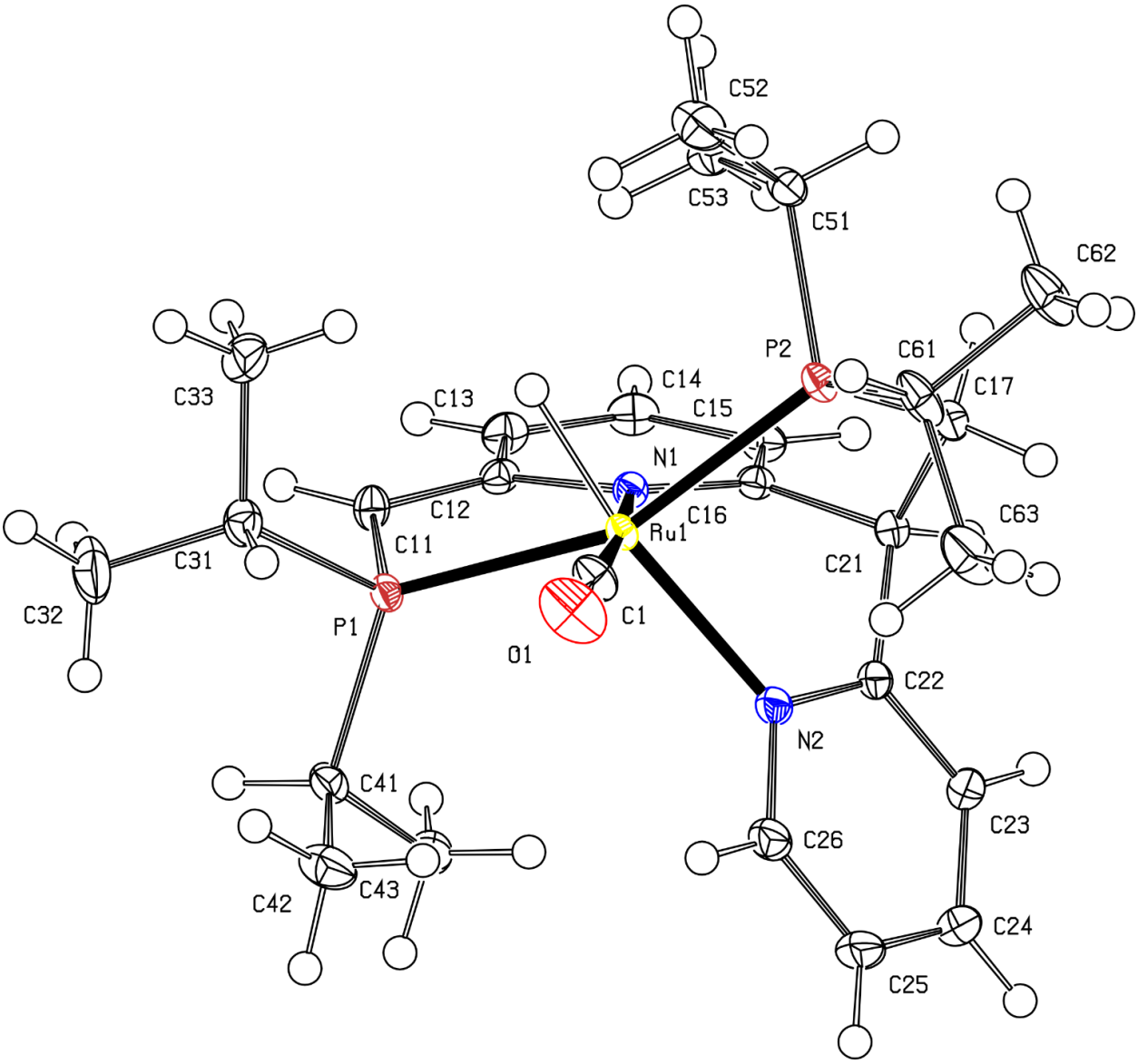


Figure S85. ORTEP diagram showing 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound **2b** according to single crystal X-ray diffraction data. Selected interatomic distances [Å]: Ru1–C1 1.8367(11), Ru1–N1 2.1391(8), Ru1–N2 2.2209(9), Ru1–P2 2.3162(3), Ru1–P1 2.3235(3), Ru1–H1 1.575(17), C11–C12 1.3853(15), N1–C12 1.3982(13), C12–C13 1.4406(14), C13–C14 1.3615(16), C14–C15 1.4123(15), C15–C16 1.3814(14), C16–C21 1.5151(14), C17–C21 1.5546(14), N1–C16 1.3541(13).

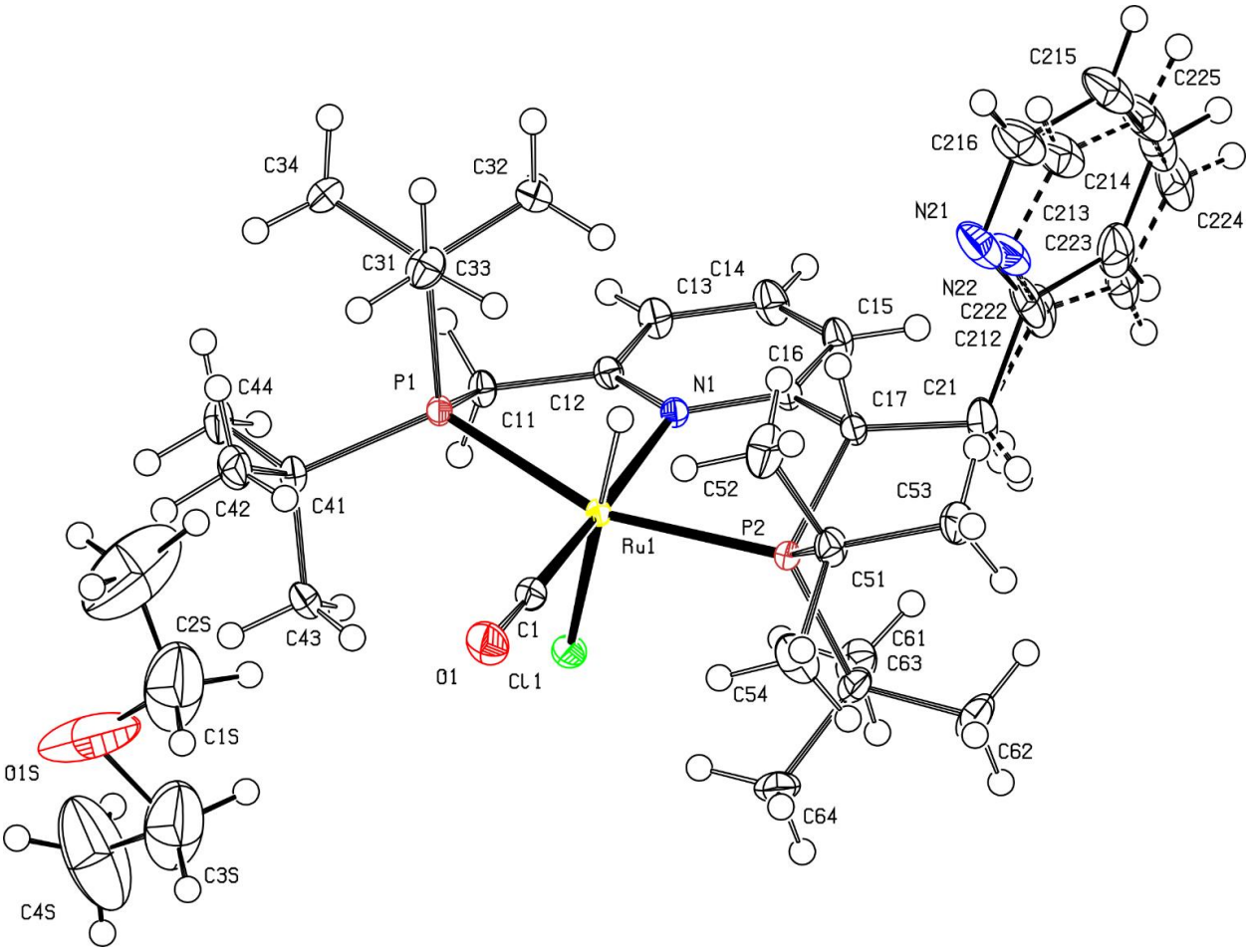
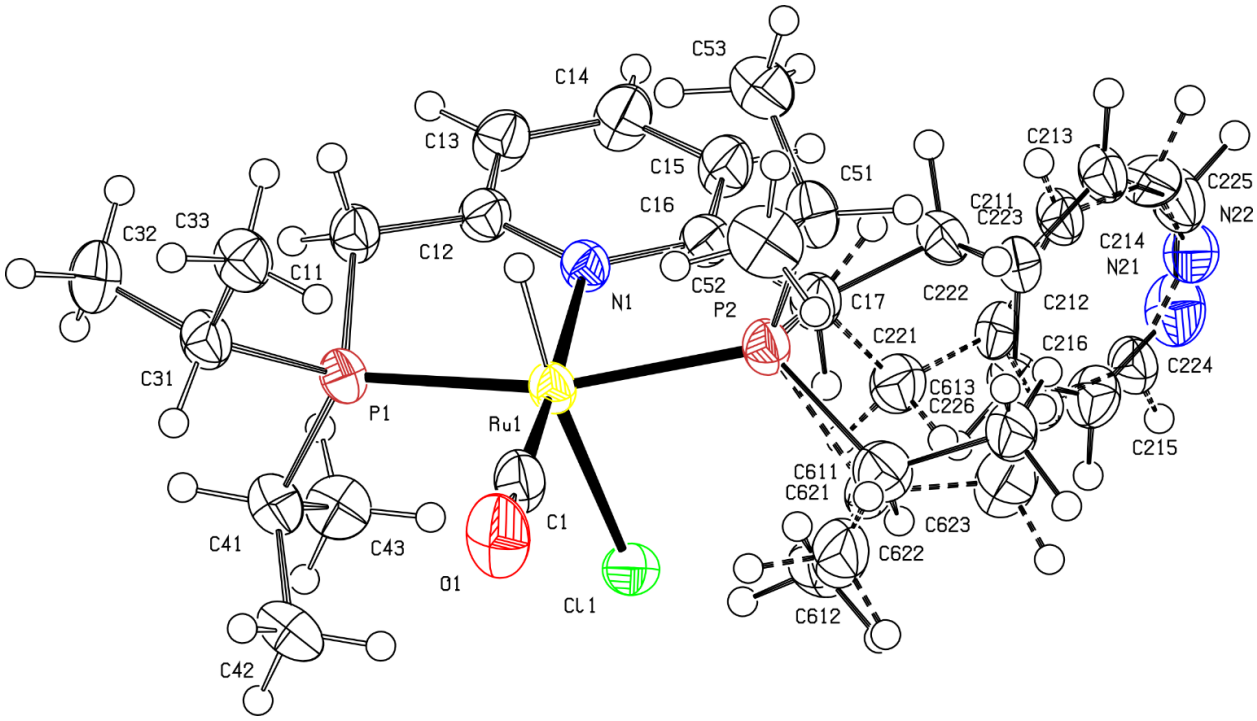
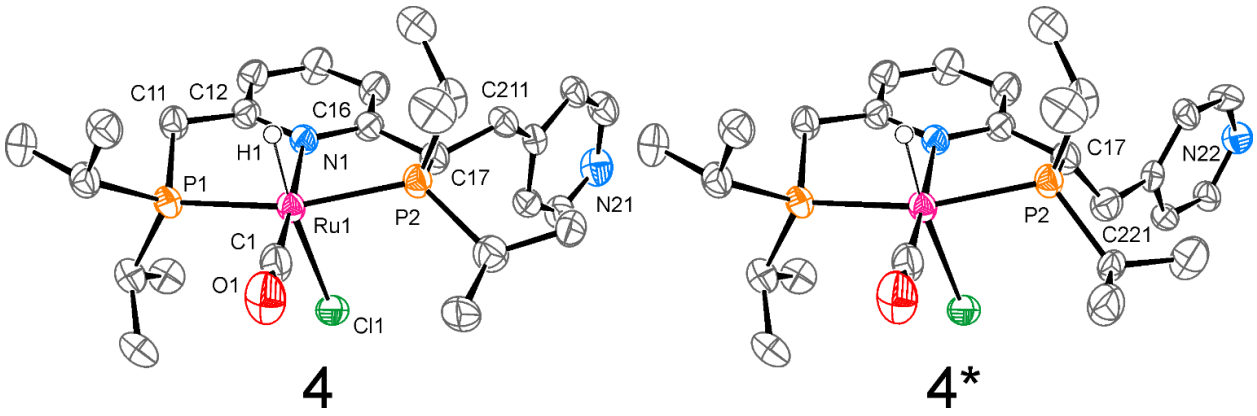


Figure S86. ORTEP diagram showing 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound **3** according to single crystal X-ray diffraction data. Selected interatomic distances [Å]: Ru1–C1 1.8433(15), Ru1–N1 2.1375(11), Ru1–P1 2.3409(3), Ru1–P2 2.3452(3), Ru1–Cl1 2.5421(3), Ru1–H1 1.53(2), C12–C13 1.3920(19), N1–C12 1.3601(17), C13–C14 1.384(2), C14–C15 1.390(2), C15–C16 1.391(2), C16–C17 1.5202(19), C17–C21 1.5381(19), N1–C16 1.3590(16).

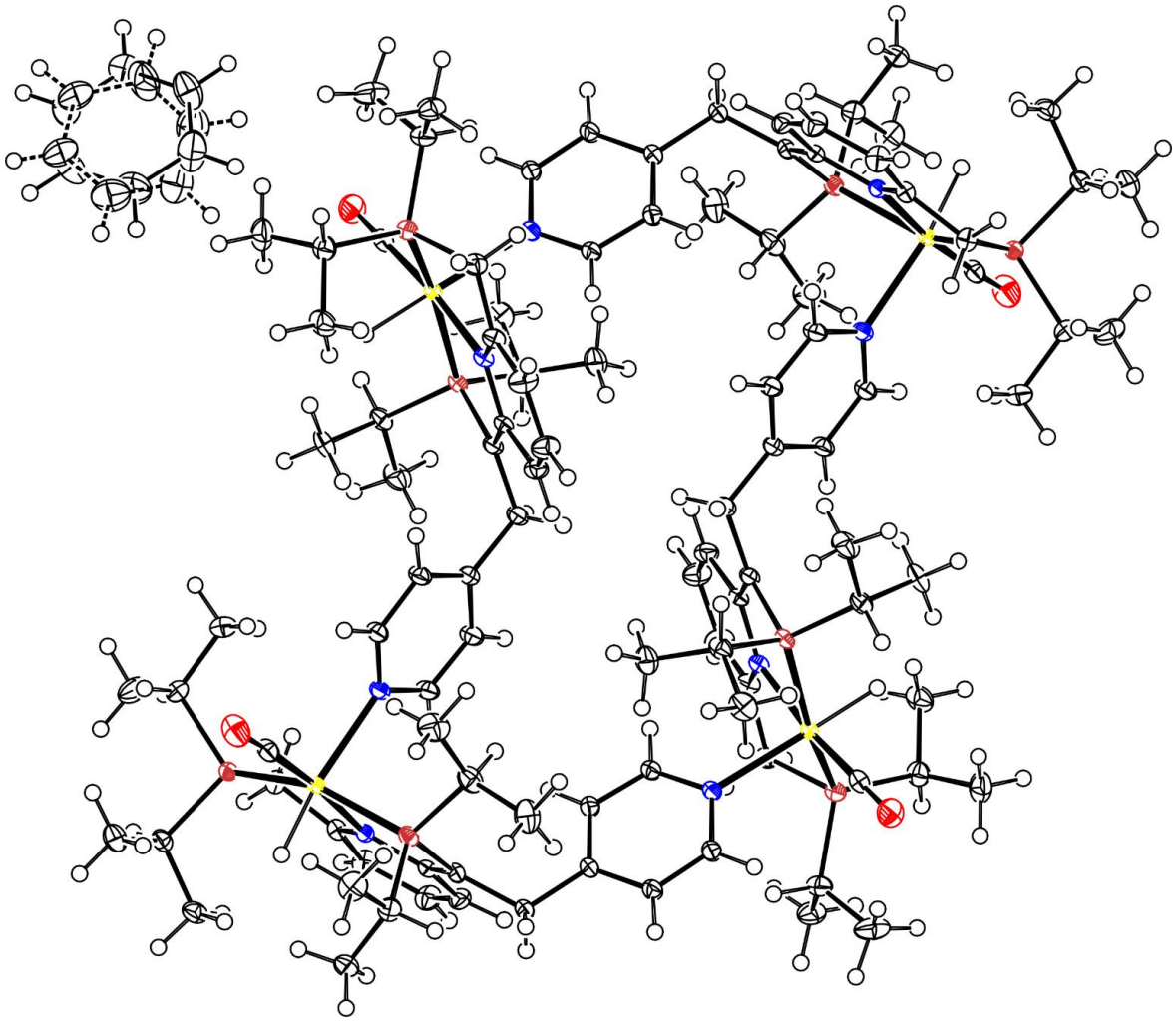


(a)

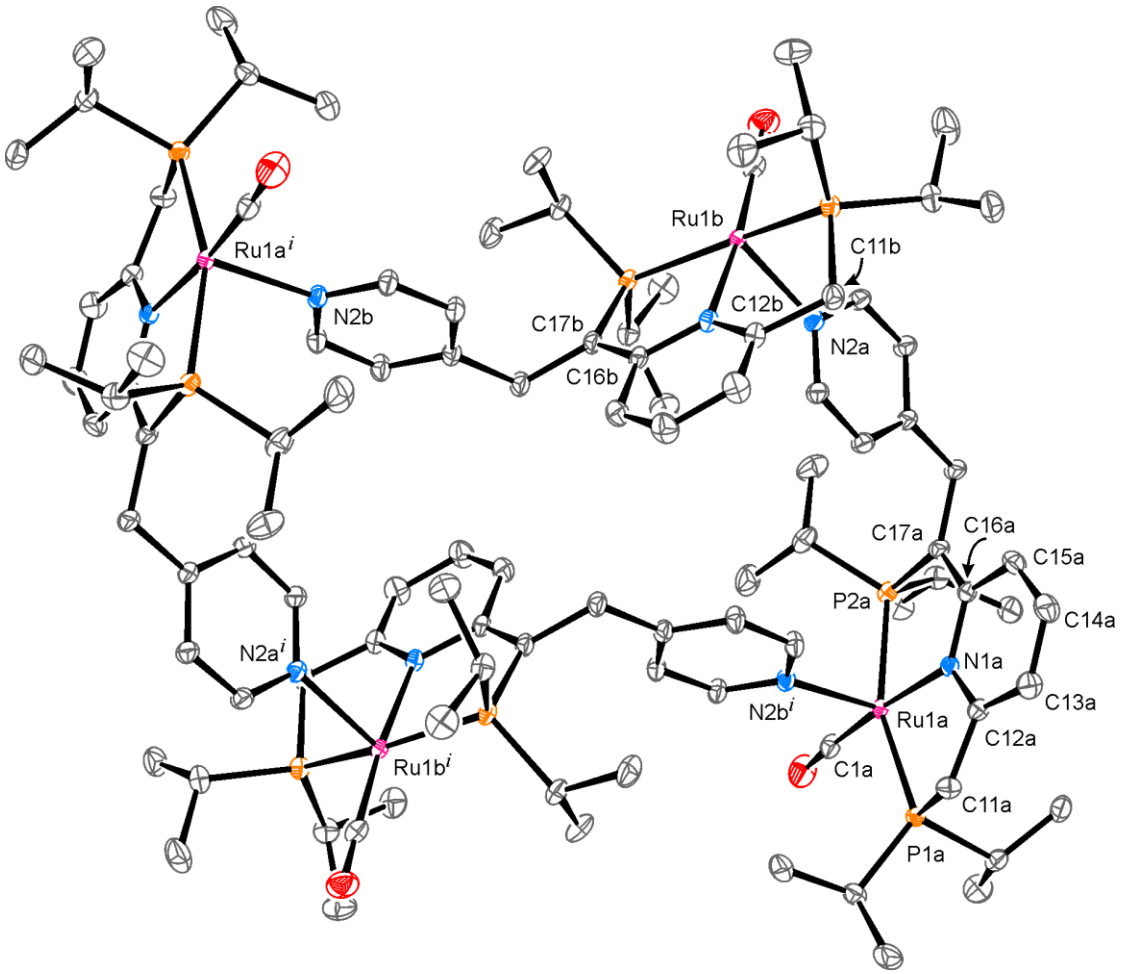


(b)

Figure S87. ORTEP diagram showing 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound **4** according to single crystal X-ray diffraction data (a) and comparison of diastereomeric molecules **4** and **4*** (b). Selected interatomic distances [Å]: Ru1–C1 1.837(3), Ru1–N1 2.152(2), Ru1–P2 2.3115(7), Ru1–P1 2.3136(6), Ru1–Cl1 2.5596(7), Ru1–H1 1.525(18), C11–C12 1.493(4), C12–C13 1.391(4), N1–C12 1.358(3), C13–C14 1.375(4), C14–C15 1.385(4), C15–C16 1.386(4), C16–C17 1.516(4), C17–C221 1.453(12), C17–C211 1.504(4), N1–C16 1.360(3).



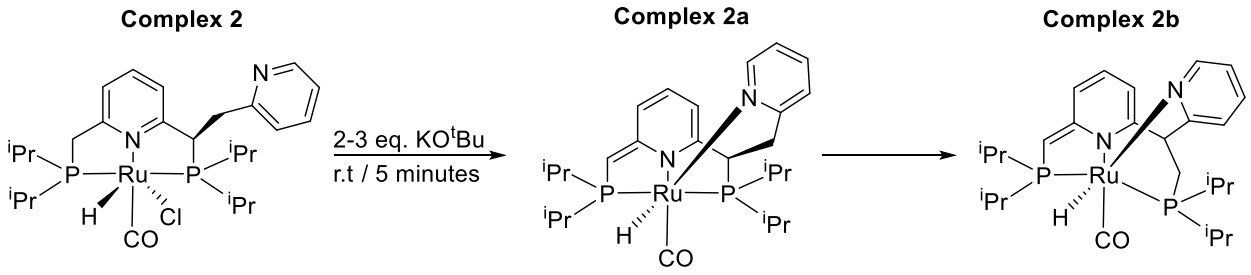
(a)



(b)

Figure S88. ORTEP diagram showing 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound **4a'** with (a) and without solvent molecule (b) according to single crystal X-ray diffraction data. Selected interatomic distances [Å]: Ru1A–C1A 1.8416(12), Ru1A–N2B^{i} 2.2525(10), N2A–Ru1B 2.2234(10), Ru1A–N1A 2.1535(9), Ru1A–P1A 2.3048(3), Ru1A–P2A 2.3317(3), Ru1A–H1A 1.541(14), N1A–C12A 1.3609(14), C11A–C12A 1.5094(16), C12A–C13A 1.3788(16), C13A–C14A 1.4073(18), C14A–C15A 1.3596(18), C15A–C16A 1.4455(16), C16A–C17A 1.3939(16), C17A–C21A 1.5090(15), C21A–C22A 1.5112(16), N1A–C16A 1.3993(14), Ru1B–C1B 1.8379(12), Ru1B–N1B 2.1414(9), Ru1B–P1B 2.3136(3), Ru1B–P2B 2.3278(3), Ru1B–H1B 1.561(14), N1B–C12B 1.3595(15), C11B–C12B 1.5100(16), C12B–C13B 1.3780(17), C13B–C14B 1.4126(18), C14B–C15B 1.3602(18), C15B–C16B 1.4437(16), C16B–C17B 1.3894(16), C17B–C21B 1.5169(16), C21B–C22B 1.5186(16), N1B–C16B 1.4018(14). Equivalent atoms are labelled by the sign *i* (1–x, 1–y, 1–z).

Reaction Kinetic –



Complex **2** was selected as a model for the kinetics experiment.

Abbreviation for kinetics experiment –

Complex 2 – **2[Ru]**

Complex 2a – **2a[Ru]**

Complex 2b – **2b[Ru]**

(4 mg) of **2[Ru]** was dissolved in (700 **µl)** toluene-d_8 via micro syringe in Teflon© sealed Pyrex© J. Young NMR tubes and inserted into a 600 MHz spectrometer which had been pre-calibrated to the desired temperature (40 ℃, 45 ℃, 50 ℃, 55 ℃ and 60 ℃).^{1}H NMR spectra were collected every 900 seconds for a period of 12 or 18 hours. The variation in the signature signal of **2[Ru],** intermediate **2a[Ru]** and product **2b[Ru]** was tracked for kinetic analysis by the integration of hydride signals.

The reaction proceeds via 2**[Ru]** → **2a[Ru]** → **2b[Ru]** and the rate constant was determined using reaction simulation and linear data-fitting program in origin from initial reaction rates. The rate constant for **2a[Ru]** → **2b[Ru]** was measured after full consumption of **2[Ru]** and disappearance of minor isomer **2a'.** The consumption of **2a[Ru]** follows first-order decay. The first order rate was also confirmed by measuring the rate at different concentrations of **2** at the same temperature (50 ℃).

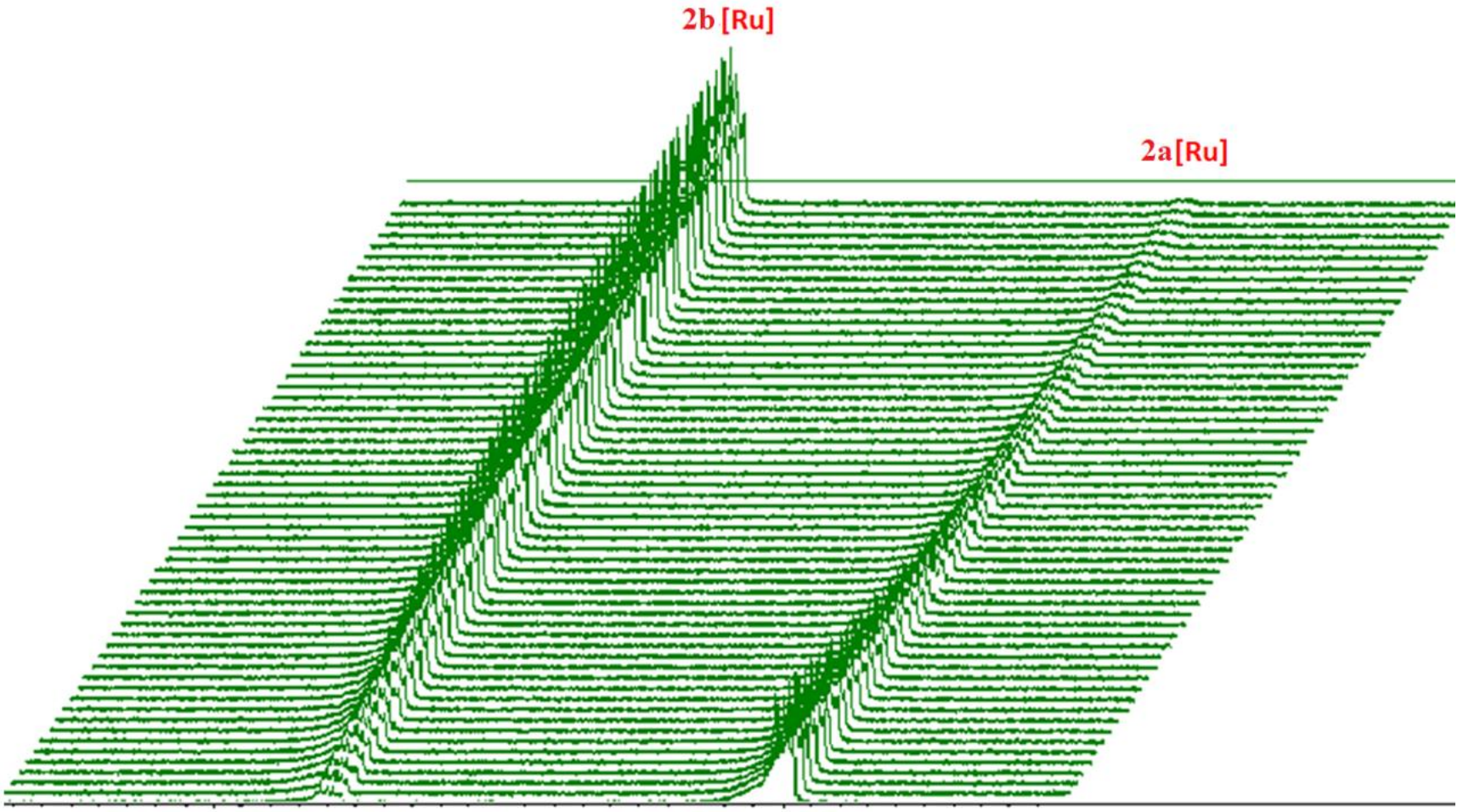


Figure S89. Partial ^{1}H NMR (600 MHz, toluene-d_8) demonstrating the conversion of **2a[Ru]** to **2b[Ru]** in hydride region upon thermolysis at 60 °C.

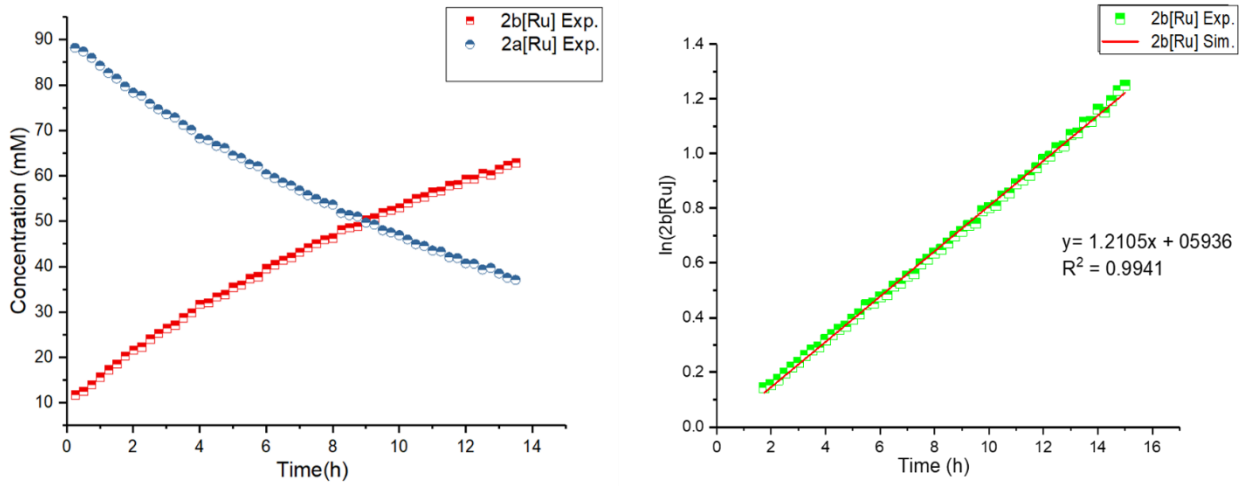


Figure S90. Left: Experimentally measured concentrations and fitted data for **2a[Ru]** → **2b[Ru]** in at 40 °C; Right: Time dependent ln[**2b[Ru]**].

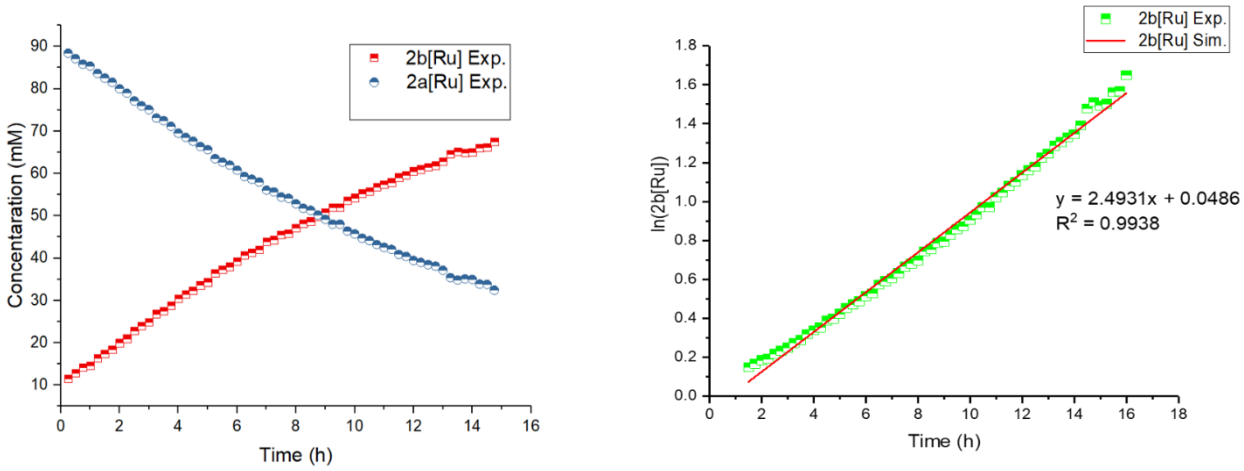


Figure S91. Left: Experimentally measured concentrations and fitted data for **2a[Ru]** → **2b[Ru]** in at 45 °C; Right: Time dependent ln[**2b[Ru]**].

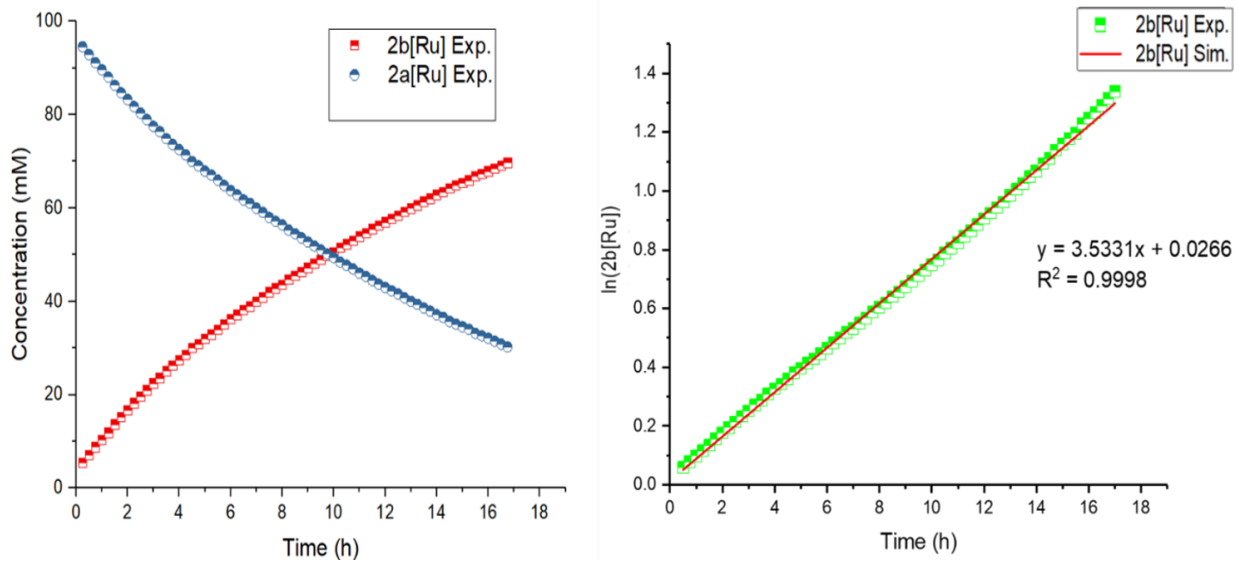


Figure S92. Left: Experimentally measured concentrations and fitted data for **2a[Ru]** → **2b[Ru]** in at 50 °C; Right: Time dependent ln[**2b[Ru]**].

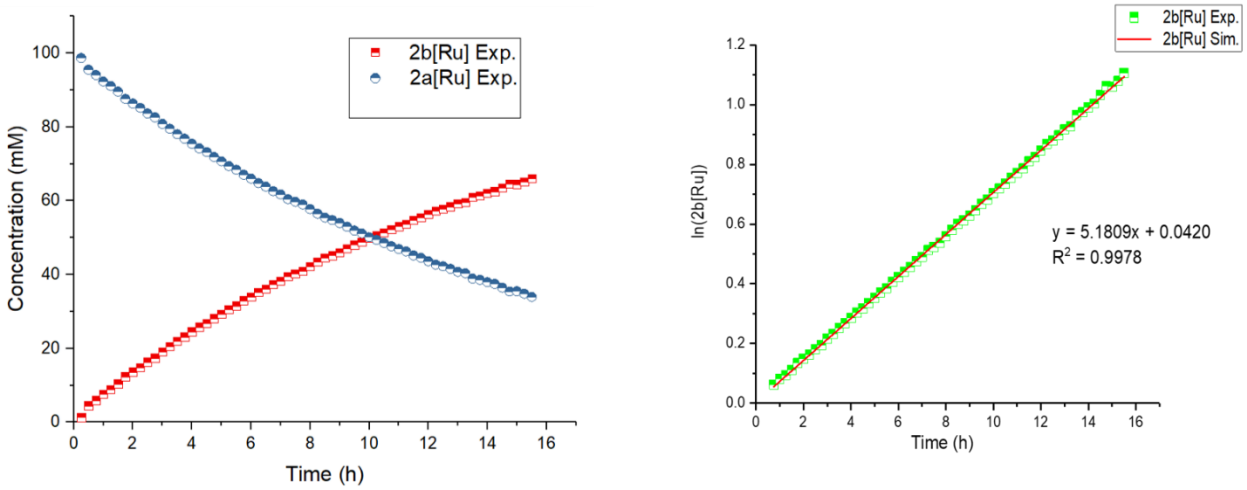


Figure S93. Left: Experimentally measured concentrations and fitted data for **2a[Ru]** → **2b[Ru]** in at 55 °C; Right: Time dependent ln[**2b[Ru]**].

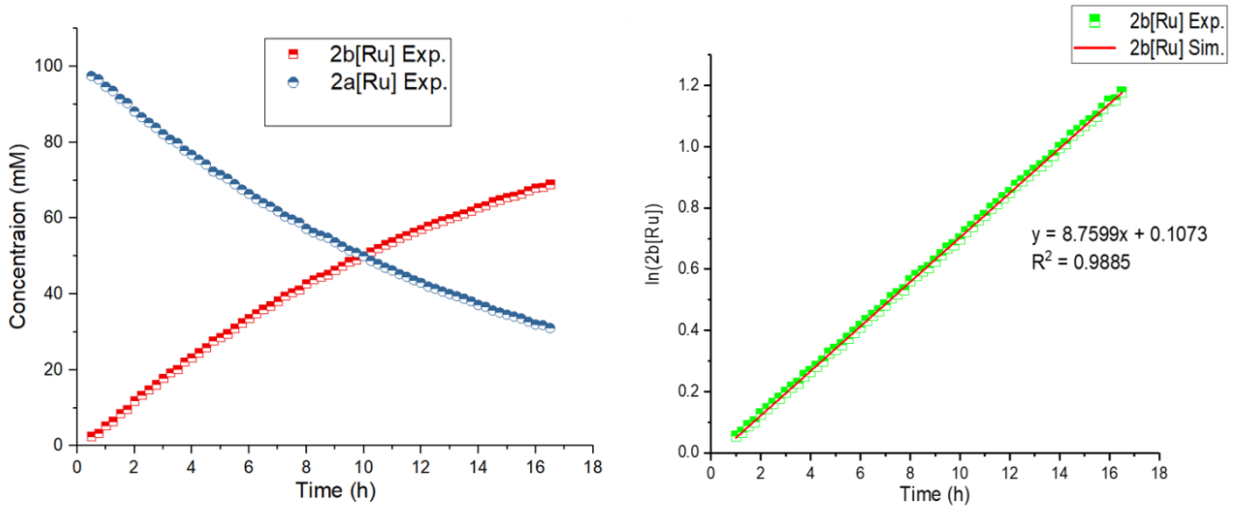


Figure S94. Left: Experimentally measured concentrations and fitted data for **2a[Ru]** → **2b[Ru]** in at 60 °C; Right: Time dependent ln[**2b[Ru]**].

Note: For (**Figure S90- S94**) 2b[Ru] Sim. corresponds to the linear fit regression.

Rate constants obtained for **2b[Ru]** complex at constant concentration –

Temperature	**Rate constant**
40 °C	1.2105
45 °C	2.4931
50 °C	3.5331
55 °C	5.1809
60 °C	8.7559

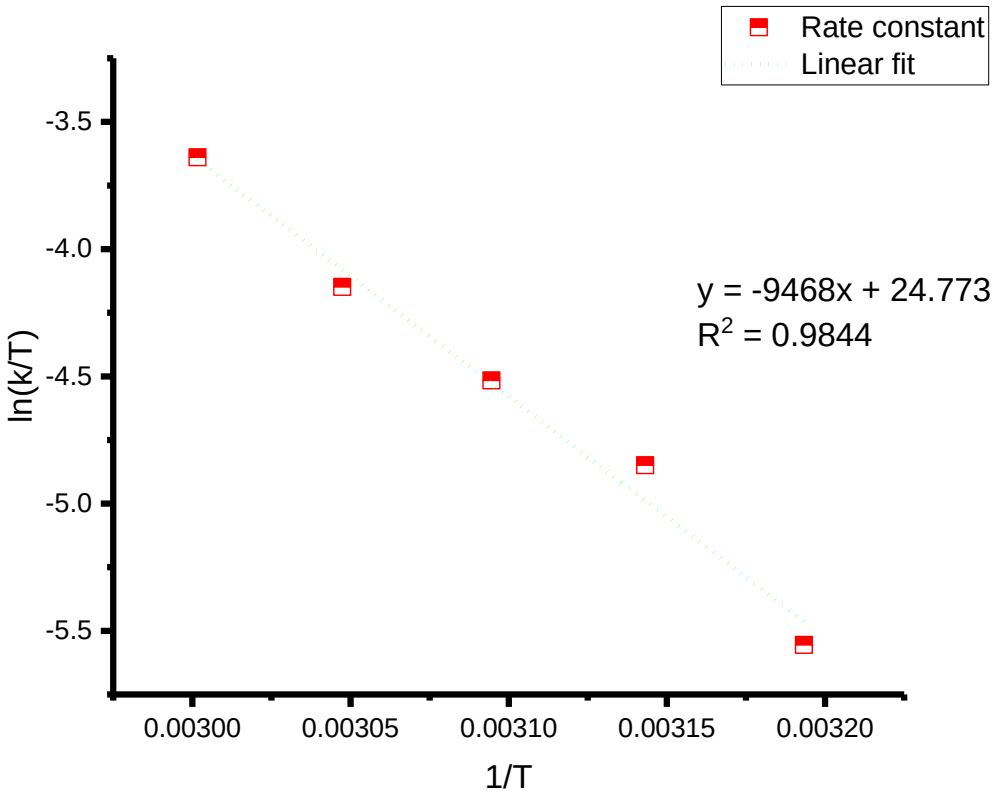


Figure S95. Eyring plot for **2b[Ru]**. Experimentally determined rate constants (square) and linear regression (dotted lines).

Activation parameters for **2a[Ru] → 2b[Ru]**

Slope	**-9468.48**
Intercept	**24.773**
$\Delta H^{\neq}$ (kcal·mol^{-1})	**18.8**
$\Delta S^{\neq}$(cal·mol^{-1}·K^{-1})	**-20.9**
$\Delta G^{\neq}$ (323.15K) (kcal·mol^{-1})	**25.5**

Computational Studies-

All computations were carried out using Gaussian 16 program suite. [6] Geometry optimization and frequency calculations were performed using B97D3/def2SV level of theory in the gas phase.[7] All the reactants, intermediates and products were confirmed to have no imaginary frequency and the transition states with single imaginary frequency. Finally, single point energies in benzene with PCM solvent model[8] were found using MN15/def2TZVP level of theory.[9]

Cartesian coordinates and absolute electronic energies at the B97D3/def2SV level

2a

E(RB97D3) = -1975.70477563 A.U.

Ru	0.161053	-0.169636	-0.618449
C	0.355749	0.223895	-2.403486
O	0.497173	0.443655	-3.549198
N	0.025355	-0.838893	1.442997
C	1.181222	-1.311178	2.079364
C	-1.184150	-0.914981	2.047308
C	-1.368034	-1.445598	3.321646
C	-0.219774	-1.942946	3.999179
C	1.018873	-1.884213	3.396856
P	2.471468	-0.248846	-0.068312
P	-2.059973	-0.742364	-0.558658
N	-0.514841	1.916915	0.074173
C	0.158767	2.951188	-0.484330
C	-1.459406	2.197564	1.001710
C	-0.011475	4.284145	-0.115641
C	-0.924243	4.578054	0.908083
C	-1.652476	3.522079	1.455822
H	0.881284	2.677875	-1.258348
H	0.578945	5.065343	-0.610365
H	-1.073801	5.607551	1.260436
H	-2.405336	3.708668	2.232913
C	-2.466685	1.179119	1.528260
C	-2.345128	-0.336944	1.258974
H	-3.454996	1.527441	1.161882
H	-2.508527	1.300201	2.629998
H	-3.289760	-0.791122	1.614452
C	2.413878	-1.194455	1.435202
H	3.327595	-1.484550	1.969930
H	-0.322667	-2.378722	5.003866
H	1.911716	-2.269389	3.906078
H	-2.366880	-1.484595	3.772401
H	0.504255	-1.681468	-0.964865
C	-2.494264	-2.561942	-0.768459
C	-1.826990	-3.454484	0.287039
H	-0.727482	-3.337452	0.259343
H	-2.163388	-3.218497	1.312947
H	-2.071481	-4.517098	0.079839
C	-2.106667	-3.016079	-2.187363
H	-1.009511	-2.960932	-2.322426
H	-2.427298	-4.066637	-2.342601
H	-2.576478	-2.401795	-2.980876
C	-3.117690	1.521330	-1.964542
H	-3.150975	2.221641	-1.107884
H	-2.113879	1.585594	-2.422577
H	-3.863266	1.873245	-2.707887
C	3.605922	-1.127560	-1.297023
C	2.991198	-2.447020	-1.784666
H	2.756592	-3.106519	-0.924287
H	2.055997	-2.281246	-2.347454
H	3.709241	-2.976570	-2.445753
C	3.503231	1.279763	0.391119
C	3.839301	2.174455	-0.80998
H	4.396661	3.076564	-0.478626
H	4.467430	1.650117	-1.555682
H	2.927088	2.519428	-1.333868
C	2.818509	2.037992	1.535733
H	2.666732	1.376895	2.410229
H	3.439772	2.903480	1.849412
H	1.827051	2.418870	1.234941
C	-3.446385	0.080560	-1.544913
H	-3.595956	-2.640407	-0.656907
H	4.452735	0.869862	0.792446

2a'

E(RB97D3) = -1975.69322617 A.U.

Ru	-1.158527	-0.679926	0.028284
C	-1.856612	-2.353123	0.335040
O	-2.306415	-3.418374	0.544056
N	-0.287852	1.279200	-0.228639
C	-1.027193	2.408697	-0.003693
C	1.034246	1.374850	-0.709051
C	1.527406	2.696574	-1.021037
C	0.739004	3.812146	-0.850327
C	-0.572767	3.683290	-0.318519
P	-3.107616	0.572748	0.273625
P	1.050685	-1.314203	-0.372152
N	3.877907	1.402772	0.767419
C	4.783810	1.789955	1.675498
C	4.292505	0.725638	-0.315883
C	6.155728	1.517579	1.570755
C	6.597720	0.811705	0.441275
C	5.656191	0.417867	-0.516310
H	4.391675	2.344767	2.544735
H	6.854462	1.844819	2.352601
H	7.661731	0.566028	0.313213
H	5.966392	-0.139346	-1.411632
C	3.246136	0.284792	-1.341903
C	1.817299	0.219180	-0.865983
H	3.569122	-0.698613	-1.738162
H	3.33407	0.971049	-2.216026
H	-1.490828	-0.934098	-1.473111
C	-2.362489	2.230543	0.690249
H	-2.18865	2.217928	1.786043
H	1.134102	4.807152	-1.101548
H	-1.199381	4.560379	-0.119024
H	2.552062	2.806542	-1.387637
H	-3.041588	3.080039	0.484963
C	1.458853	-2.609561	-1.663215
C	0.897884	-2.171619	-3.023061
H	-0.209114	-2.161751	-2.995042
H	1.235396	-1.151536	-3.291438
H	1.219878	-2.874394	-3.819808
C	0.953578	-4.00004	-1.257051
H	-0.14781	-4.003098	-1.148908
H	1.221212	-4.746039	-2.034620
H	1.388898	-4.344889	-0.298992
C	1.565710	-0.868448	2.302922
H	2.044663	0.087375	2.012042
H	0.476297	-0.685085	2.430799
H	1.973786	-1.189935	3.284288
C	-4.174604	0.912823	-1.237627
C	-3.291482	1.463754	-2.370347
H	-2.897898	2.469012	-2.121248
H	-2.422922	0.807679	-2.565116
H	-3.885284	1.550848	-3.303579
C	-4.290425	0.207538	1.681268
C	-5.168217	-1.008872	1.340778
H	-5.865833	-1.215151	2.178442
H	-5.777957	-0.849300	0.430961
H	-4.550209	-1.914531	1.184032
C	-3.490017	-0.040781	2.970992
H	-2.903596	0.845285	3.283400
H	-4.177054	-0.296639	3.803784
H	-2.784027	-0.884377	2.834105
C	1.816788	-1.944057	1.232916
H	2.567276	-2.636772	-1.729045
H	-4.936284	1.099261	1.821393

2a"

E(RB97D3) = -1975.70266914 A.U.

Ru	0.115475	-0.322076	-0.649950
C	0.205682	-0.086717	-2.462435
O	0.282413	0.020874	-3.628818
N	0.042565	-0.821151	1.483302
C	1.159684	-1.210524	2.153656
C	-1.154062	-0.729298	2.129221
C	-1.257079	-1.050299	3.497685
C	-0.117274	-1.440275	4.198833
C	1.115243	-1.511125	3.520602
P	2.410492	-0.276585	-0.170938
P	-2.159252	-0.706622	-0.465703
N	-0.457199	1.816694	-0.134550
C	0.143107	2.784639	-0.863689
C	-1.299625	2.188228	0.915115
C	0.108562	4.141315	-0.569492
C	-0.585535	4.530261	0.609230
C	-1.261930	3.576523	1.337248
H	0.699111	2.429195	-1.740430
H	0.620780	4.864211	-1.215278
H	-0.588419	5.580688	0.935857
H	-1.824183	3.853838	2.239117
C	-2.209340	1.317002	1.523471
C	-2.314119	-0.176436	1.337537
H	-2.787842	1.720602	2.365034
H	-3.266583	-0.535950	1.770514
H	0.403832	-1.893221	-0.901798
C	2.423657	-1.378084	1.347056
H	3.320967	-1.232521	1.978288
H	-0.179268	-1.698619	5.264913
H	2.029943	-1.823884	4.038546
H	-2.233826	-0.977696	3.992456
H	2.457048	-2.419903	0.966551
C	-2.756536	-2.482557	-0.590788
C	-2.151900	-3.362315	0.511179
H	-1.046323	-3.306175	0.484295
H	-2.487186	-3.059103	1.521622
H	-2.449317	-4.420591	0.357369
C	-2.414090	-3.029862	-1.986463
H	-1.316957	-3.039013	-2.132580
H	-2.796993	-4.065967	-2.095962
H	-2.854918	-2.421089	-2.800723
C	-3.033767	1.538776	-2.020984
H	-2.846091	2.300234	-1.243817
H	-2.104540	1.407568	-2.603844
H	-3.821430	1.925748	-2.701384
C	3.625914	-1.100843	-1.353576
C	3.064835	-2.402351	-1.944861
H	2.903438	-3.170420	-1.161661
H	2.100465	-2.236153	-2.453256
H	3.788452	-2.816838	-2.676999
C	3.364680	1.221920	0.462308
C	3.720068	2.187963	-0.677306
H	4.282710	3.055184	-0.273951
H	4.352493	1.713448	-1.454021
H	2.809505	2.580829	-1.163695
C	2.580515	1.917142	1.588191
H	2.459254	1.264120	2.474888
H	3.121828	2.828961	1.913625
H	1.574698	2.214178	1.246785
C	-3.504558	0.216942	-1.401434
H	-3.860049	-2.454078	-0.470424
H	4.306798	0.820474	0.890988

C	-4.835105	-0.034487	-0.895579	C	3.293930	-2.340050	1.131351	C	-4.777472	0.398859	-0.558795
H	-5.617456	0.302866	-1.607196	H	3.669908	-2.674742	2.121601	H	-5.597211	0.792727	-1.195022
H	-5.079881	-1.073146	-0.600167	H	3.452985	-3.171879	0.416864	H	-5.126469	-0.553919	-0.112879
H	-4.918761	0.603552	0.005903	H	3.917850	-1.486122	0.810352	H	-4.597211	1.125496	0.257164
H	-3.451191	-0.530375	-2.470011	H	1.219474	-2.843502	1.491546	H	-3.732294	-0.482860	-2.231311
C	5.013915	-1.370889	-0.730554	C	-5.372875	1.831446	-0.959236	C	5.024790	-1.318465	-0.755673
H	5.640669	-1.898811	-1.479635	H	-5.923494	2.030863	-1.902247	H	5.684556	-1.804015	-1.504438
H	5.539522	-0.434647	-0.462904	H	-6.092622	1.392357	-0.241476	H	5.512258	-0.373755	-0.450987
H	4.966682	-2.010361	0.174127	H	-5.044430	2.811524	-0.558589	H	4.985609	-1.985753	0.129359
H	3.676677	-0.432308	-2.159681	H	-4.542807	-0.090320	-1.537209	H	3.700290	-0.364861	-2.181240

TS

E(RB97D3) = -1975.66655910 A.U.

Ru	0.085279	-0.255441	-0.627394
C	0.009754	-0.249631	-2.459954
O	-0.031663	-0.244457	-3.634857
N	0.192729	-0.345589	1.538608
C	1.187805	-1.039867	2.145240
C	-0.894018	0.143131	2.274448
C	-0.937898	-0.157807	3.696578
C	0.063423	-0.900324	4.2756
C	1.179499	-1.342536	3.504633
P	2.382981	-0.350394	-0.264885
P	-2.174131	-0.764422	-0.243896
N	-0.411432	1.879428	-0.301952
C	0.036888	2.810632	-1.173595
C	-1.123214	2.282614	0.784304
C	-0.156665	4.180715	-1.001924
C	-0.843054	4.618073	0.142229
C	-1.324826	3.656409	1.0339
H	0.575778	2.418142	-2.043648
H	0.230191	4.885383	-1.748811
H	-1.010013	5.687640	0.328338
H	-1.880814	3.958391	1.93053
C	-1.703612	1.274339	1.724247
C	-2.504189	0.047212	1.288798
H	-2.228354	1.806773	2.532506
H	-3.386942	-0.194293	1.895543
H	0.348317	-1.839687	-0.687175
C	2.351918	-1.440971	1.25799
H	3.304700	-1.419326	1.822919
H	0.023817	-1.120042	5.352836
H	2.008325	-1.896279	3.959132
H	-1.776703	0.230212	4.289376
H	2.204857	-2.476324	0.889967
C	-2.574643	-2.573152	0.076255
C	-1.674406	-3.135096	1.185808
H	-0.617946	-3.144927	0.858243
H	-1.730291	-2.530539	2.110086
H	-1.977301	-4.175944	1.425832
C	-2.478040	-3.410676	-1.206108
H	-1.456980	-3.350117	-1.633471
H	-2.690719	-4.476991	-0.981672
H	-3.195751	-3.085482	-1.984426
C	-3.255913	1.239804	-1.888529
H	-3.403793	1.876733	-0.993430
H	-2.241757	1.429280	-2.282396
H	-3.993105	1.552311	-2.657287
C	3.521769	-1.229322	-1.477100
C	2.877282	-2.507112	-2.037909
H	2.705331	-3.256526	-1.239643
H	1.905547	-2.299213	-2.517911
H	3.554129	-2.964684	-2.788735
C	3.416739	1.122586	0.310464
C	3.729346	2.054707	-0.869910
H	4.280443	2.950794	-0.516111
H	4.351100	1.564430	-1.644803
H	2.795569	2.401384	-1.352844
C	2.730155	1.875779	1.460784
H	2.552733	1.228607	2.340327
H	3.373465	2.721785	1.781724
H	1.754743	2.286741	1.146949
C	-3.449445	-0.240959	-1.539381
H	-3.623444	-2.581052	0.440481
H	4.367328	0.702113	0.699436
C	-4.890522	-0.529924	-1.097884
H	-5.609150	-0.154210	-1.856855
H	-5.085713	-1.611424	-0.963312
H	-5.113599	-0.018704	-0.138630
H	-3.208642	-0.844205	-2.439372

I1

E(RB97D3) = -1975.68415002 A.U.

Ru	0.088025	-0.363663	-0.432745
C	-0.043616	-0.940515	-2.163743
O	-0.078062	-1.317925	-3.275413
N	0.422135	0.272440	1.638254
C	1.571079	-0.093110	2.265921
C	-0.502426	1.034397	2.280028
C	-0.310675	1.391833	3.632184
C	0.831264	0.967689	4.309383
C	1.800067	0.225670	3.611376
P	2.411843	-0.264338	-0.360641
P	-2.127406	-0.961234	0.174035
N	-0.691620	1.691233	-0.706948
C	-0.547387	2.337828	-1.886875
C	-1.479578	2.243028	0.254686
C	-1.151841	3.561331	-2.170603
C	-1.950625	4.155990	-1.176867
C	-2.107039	3.488031	0.037712
H	0.079270	1.833147	-2.632144
H	-0.998056	4.034287	-3.148554
H	-2.437567	5.125575	-1.350666
H	-2.730101	3.913840	0.834700
C	-1.751281	1.459798	1.529656
C	-2.664780	0.282117	1.254431
H	-2.292308	2.147465	2.202928
H	-3.512008	0.139749	1.939610
H	0.461976	-1.871767	-0.025889
C	2.616728	-0.795690	1.432065
H	3.630124	-0.614869	1.841509
H	0.990614	1.239199	5.362365
H	2.732210	-0.091692	4.094112
H	-1.065157	2.012170	4.132693
H	2.433296	-1.889734	1.442439
C	-2.266916	-2.633581	1.056451
C	-1.378162	-2.638707	2.305205
H	-0.306340	-2.610697	2.027903
H	-1.587935	-1.755720	2.939872
H	-1.556650	-3.555489	2.907063
C	-1.977650	-3.823991	0.134191
H	-0.973030	-3.725839	-0.324486
H	-2.000674	-4.775993	0.706608
H	-2.718919	-3.909664	-0.683274
C	-3.395387	0.155369	-2.065089
H	-3.686824	0.998972	-1.407128
H	-2.409059	0.391018	-2.501310
H	-4.130675	0.085337	-2.894539
C	3.450858	-1.493180	-1.340417
C	2.833870	-2.900292	-1.334789
H	2.786445	-3.323328	-0.311149
H	1.811071	-2.900663	-1.746895
H	3.460914	-3.579539	-1.948919
C	3.396271	1.344544	-0.458995
C	3.485984	1.798783	-1.923976
H	3.982337	2.788985	-1.992505
H	4.063546	1.091841	-2.550233
H	2.473206	1.896561	-2.364374
C	2.743651	2.422684	0.419797
H	2.751324	2.147178	1.491131
H	3.294162	3.380539	0.312663
H	1.692103	2.590555	0.122053
C	-3.359724	-1.150268	-1.264803
H	-3.323482	-2.682056	1.395583
H	4.418163	1.146148	-0.073943
C	-4.760477	-1.524794	-0.762160
H	-5.496667	-1.489070	-1.593691
H	-4.799313	-2.542955	-0.329199
H	-5.094651	-0.804209	0.013566
H	-2.960803	-1.957627	-1.911844

2b

E(RB97D3) = -1975.71756098 A.U.

Ru	0.152559	-0.227245	-0.476052
C	0.275334	-0.336185	-2.302361
O	0.393312	-0.400097	-3.470426
N	0.241929	-0.091615	1.694913
C	1.450510	-0.466125	2.306782
C	-0.775455	0.395963	2.436867
C	-0.773957	0.37047	3.831944
C	0.351977	-0.201007	4.485027
C	1.442313	-0.605541	3.743813
P	2.483045	-0.150028	-0.177122
P	-2.027606	-1.027532	-0.278265
N	-0.690429	1.81273	-0.287798
C	-0.430284	2.764348	-1.214775
C	-1.567318	2.096493	0.711030
C	-1.012935	4.031502	-1.198119
C	-1.899858	4.346794	-0.158052
C	-2.169976	3.364849	0.801250
H	0.279272	2.476093	-1.998229
H	-0.764375	4.756744	-1.983162
H	-2.373033	5.336034	-0.096544
H	-2.864383	3.56971	1.626074
C	-1.961214	1.008898	1.702658
C	-2.895866	-0.045447	1.048253
H	-2.573007	1.508838	2.474468
H	-3.770772	0.471874	0.612192
H	-3.273007	-0.722227	1.838039
C	2.595068	-0.640945	1.523283
H	3.556188	-0.844257	2.012919
H	0.365635	-0.289346	5.581174
H	2.344552	-0.997444	4.231000
H	-1.619410	0.777919	4.398709
H	0.566614	-1.766420	-0.391463
C	-2.192698	-2.801251	0.316946
C	-1.392196	-3.019065	1.611105
H	-0.317010	-2.825996	1.439949
H	-1.720381	-2.355829	2.434623
H	-1.517034	-4.067691	1.951644
C	-1.747390	-3.780549	-0.780207
H	-0.696015	-3.583555	-1.068634
H	-1.813305	-4.823070	-0.406100
H	-2.371859	-3.713017	-1.692590
C	-3.223007	0.548654	-2.273009
H	-3.688395	1.228522	-1.530874
H	-2.211910	0.934283	-2.496878
H	-3.830457	0.601812	-3.199759
C	3.510674	-1.343927	-1.219415
C	2.937171	-2.767238	-1.179619
H	2.842161	-3.120882	-0.132946
H	1.937323	-2.818388	-1.645203
H	3.612017	-3.460857	-1.724234
C	3.427148	1.485852	-0.372253
C	3.476990	1.932253	-1.839172
H	3.937272	2.939303	-1.929158
H	4.067536	1.239479	-2.468963
H	2.457232	1.987709	-2.272592
C	2.795279	2.545925	0.537610
H	2.745409	2.189841	1.584408
H	3.391049	3.482807	0.512067
H	1.765718	2.784680	0.214682
C	-3.174742	-0.900842	-1.761436
H	-3.270610	-2.955347	0.531519
H	4.459391	1.299859	-0.009900
C	-4.578641	-1.475451	-1.524539
H	-5.195187	-1.366679	-2.441045
H	-4.552611	-2.550583	-1.264857
H	-5.103464	-0.940833	-0.706461
H	-2.659037	-1.509575	-2.532159

C	4.923566	-1.512546	-0.914693	C	4.926942	-1.52967	-0.915293	C	4.990517	-1.344699	-0.802394
H	5.545788	-2.019466	-1.681300	H	5.485036	-2.246578	-1.552772	H	5.561982	-2.062623	-1.427384
H	5.456788	-0.590751	-0.613618	H	5.426266	-0.547229	-1.011130	H	5.469696	-0.354392	-0.917505
H	4.874552	-2.182144	-0.032286	H	5.037255	-1.870426	0.134315	H	5.102137	-1.661568	0.254406
H	3.610504	-0.504455	-2.312925	H	3.387247	-1.10676	-2.379271	H	3.428241	-0.962164	-2.257831

3a

E(RB97D3) = -2132.71153574 A.U.

Ru	0.098360	-0.145960	-0.495177
C	0.224556	-0.037096	-2.322472
O	0.310568	0.008212	-3.495329
N	0.003604	-0.433775	1.654671
C	1.138645	-0.888682	2.336303
C	-1.179030	-0.293198	2.296772
C	-1.346713	-0.541657	3.657412
C	-0.214422	-0.998575	4.386823
C	0.993112	-1.174653	3.745313
P	2.442167	-0.449016	-0.026374
P	-2.178368	-0.535897	-0.281168
N	-0.377047	2.083723	-0.093480
C	0.348317	2.961985	-0.826351
C	-1.239885	2.582023	0.823189
C	0.318933	4.343618	-0.646626
C	-0.492323	4.861453	0.373241
C	-1.277740	3.967089	1.100804
H	0.996538	2.515860	-1.583319
H	0.940490	4.989122	-1.279448
H	-0.523860	5.938861	0.585101
H	-1.961085	4.332252	1.879018
C	-2.326142	1.754233	1.498238
C	-2.336058	0.211224	1.450345
H	-3.286872	2.140818	1.100409
H	-2.328499	2.028956	2.572481
H	-3.289065	-0.099170	1.919479
C	2.341167	-1.039005	1.646562
H	3.233640	-1.345115	2.205244
H	-0.304627	-1.218554	5.460614
H	1.874294	-1.535414	4.291238
H	-2.326908	-0.410834	4.131169
H	0.285106	-1.706103	-0.617051
C	-2.651670	-2.401205	-0.062053
C	-4.151481	-2.631367	0.196673
H	-4.778183	-2.393156	-0.681028
H	-4.313598	-3.704548	0.430808
H	-4.519696	-2.048766	1.064430
C	-1.867309	-2.983229	1.134891
H	-0.784283	-2.791538	1.050392
H	-2.214481	-2.582387	2.103701
H	-2.027005	-4.081454	1.148800
C	-2.201065	-3.176307	-1.320240
H	-1.122957	-3.023786	-1.508170
H	-2.375891	-4.259679	-1.151550
H	-2.753191	-2.890390	-2.229950
C	-3.511865	0.314929	-1.394941
C	-2.974598	1.684635	-1.865770
H	-2.852150	2.412743	-1.047312
H	-2.003316	1.581419	-2.379093
H	-3.702344	2.118240	-2.582970
C	-3.711303	-0.529963	-2.670964
H	-4.219039	-1.489181	-2.472280
H	-4.344984	0.038584	-3.382739
H	-2.746959	-0.739153	-3.172744
C	-4.864792	0.527576	-0.688502
H	-4.774732	1.155305	0.218092
H	-5.554070	1.056586	-1.381017
H	-5.352672	-0.416194	-0.396229
C	3.351369	-1.833470	-1.027082
C	3.911998	-1.279873	-2.348526
H	3.138728	-0.736407	-2.926116
H	4.769286	-0.603128	-2.184265
H	4.271189	-2.122056	-2.977650
C	2.342120	-2.952247	-1.350919
H	1.830481	-3.308432	-0.435897
H	1.574974	-2.615265	-2.069889
H	2.891779	-3.809059	-1.797056
C	4.472668	-2.467889	-0.181115
H	4.053169	-2.969178	0.711411
H	4.998137	-3.237357	-0.786883
H	5.225803	-1.739089	0.159799
C	3.615207	1.097200	0.062201

3a'

E(RB97D3) = -2132.71421239 A.U.

Ru	1.006388	0.605725	0.051606
C	1.904720	2.183152	0.341065
O	2.513581	3.171495	0.526298
N	-0.018124	-1.256599	-0.294041
C	0.652583	-2.445287	-0.249243
C	-1.361790	-1.212273	-0.714375
C	-1.935153	-2.443956	-1.210654
C	-1.218607	-3.620413	-1.207545
C	0.104196	-3.643979	-0.693496
P	2.870297	-0.789426	0.159696
P	-1.169519	1.454273	-0.213938
N	-4.187124	-1.051350	1.171839
C	-4.931282	-1.875132	1.918953
C	-4.437430	-0.960772	-0.146333
C	-5.970054	-2.666746	1.405328
C	-6.245537	-2.571469	0.033763
C	-5.471118	-1.707347	-0.749825
H	-4.686576	-1.908443	2.994065
H	-6.542936	-3.335645	2.061398
H	-7.048629	-3.168564	-0.421188
H	-5.652569	-1.615152	-1.829658
C	-3.573470	-0.010172	-0.972650
C	-2.094339	-0.015778	-0.647276
H	-3.980286	1.005717	-0.811111
H	-3.768852	-0.230209	-2.047544
H	1.247532	0.823081	-1.470981
C	2.023522	-2.436349	0.390586
H	1.892563	-2.555266	1.485146
H	-1.673791	-4.541134	-1.600205
H	0.680026	-4.574392	-0.629709
H	-2.952176	-2.431393	-1.611440
H	2.637365	-3.291080	0.050655
C	-1.424064	2.762086	-1.600952
C	-2.748355	3.541237	-1.499178
H	-2.782979	4.185154	-0.601153
H	-2.848356	4.204491	-2.385105
H	-3.631308	2.876404	-1.485363
C	-1.387888	1.977558	-2.928490
H	-0.494557	1.325697	-2.983965
H	-2.280671	1.339073	-3.056016
H	-1.348147	2.694426	-3.776427
C	-0.250051	3.761482	-1.589907
H	0.705484	3.254875	-1.811261
H	-0.421505	4.534349	-2.369558
H	-0.139480	4.279474	-0.620982
C	-1.754548	2.090207	1.500369
C	-1.232901	0.995241	2.460026
H	-1.648694	0.005488	2.191230
H	-0.120885	0.941136	2.444776
H	-1.535946	1.231409	3.502649
C	-1.094356	3.435821	1.846355
H	-1.491954	4.265205	1.231122
H	-1.308821	3.683964	2.908091
H	0.003586	3.405033	1.721083
C	-3.280869	2.189762	1.661323
H	-3.753033	1.199422	1.536762
H	-3.511775	2.543023	2.690216
H	-3.736580	2.910102	0.958475
C	3.875185	-0.983873	-1.453420
C	4.336626	0.413230	-1.916637
H	3.475414	1.096900	-2.030568
H	5.048163	0.878604	-1.211290
H	4.845511	0.322974	-2.899293
C	2.897104	-1.556664	-2.504067
H	2.599627	-2.597610	-2.277797
H	1.975437	-0.950624	-2.577661
H	3.396087	-1.555423	-3.495676
C	5.081938	-1.928777	-1.325544
H	4.792529	-2.926070	-0.940148
H	5.533312	-2.081345	-2.328780
H	5.870910	-1.514766	-0.670924
C	3.988582	-0.647984	1.707020

3a"

E(RB97D3) = -2132.70976007 A.U.

Ru	0.003382	-0.298103	-0.580465
C	-0.112043	-0.243219	-2.404201
O	-0.225602	-0.275141	-3.573873
N	0.039179	-0.646321	1.570144
C	1.100621	-1.256639	2.162822
C	-1.039518	-0.261459	2.304395
C	-1.049063	-0.433690	3.703900
C	0.045603	-1.029218	4.328806
C	1.138502	-1.455571	3.547283
P	2.360333	-0.548213	-0.203106
P	-2.287179	-0.370787	-0.185915
N	-0.148130	1.926562	-0.233644
C	0.568801	2.704943	-1.074526
C	-0.844801	2.521868	0.818695
C	0.772525	4.069415	-0.915192
C	0.203685	4.678360	0.237643
C	-0.575009	3.921796	1.085794
H	1.025020	2.173636	-1.919763
H	1.364987	4.633617	-1.644674
H	0.380283	5.742647	0.451586
H	-1.037849	4.373380	1.973440
C	-1.826186	1.862653	1.567849
C	-2.171466	0.393630	1.552242
H	-2.285136	2.435107	2.384437
H	-3.118870	0.236989	2.100254
H	0.071569	-1.903188	-0.721510
C	2.180367	-1.748380	1.235776
H	3.119273	-1.959718	1.775669
H	0.050016	-1.182190	5.416598
H	2.004277	-1.949864	4.003737
H	-1.922388	-0.101836	4.278787
H	1.829786	-2.693490	0.778917
C	-3.022051	-2.143732	0.064058
C	-4.497526	-2.142206	0.504376
H	-5.178997	-1.747936	-0.269299
H	-4.812261	-3.186001	0.717021
H	-4.649041	-1.557922	1.433373
C	-2.208241	-2.862638	1.162315
H	-1.128907	-2.864425	0.931783
H	-2.356189	-2.410948	2.160159
H	-2.553125	-3.916208	1.220054
C	-2.838637	-2.947444	-1.241567
H	-1.783717	-2.915697	-1.572705
H	-3.114342	-4.007220	-1.056279
H	-3.470756	-2.580892	-2.066955
C	-3.550416	0.717412	-1.153341
C	-2.832616	1.954830	-1.733609
H	-2.478900	2.633515	-0.943768
H	-1.974074	1.676628	-2.367938
H	-3.561536	2.508833	-2.361919
C	-4.116422	-0.070987	-2.351874
H	-4.761291	-0.915498	-2.053977
H	-4.739299	0.616495	-2.960995
H	-3.306996	-0.451840	-3.004352
C	-4.683170	1.207884	-0.229592
H	-4.274105	1.841450	0.580712
H	-5.384357	1.832738	-0.822535
H	-5.267722	0.385277	0.217430
C	3.355215	-1.516866	-1.535401
C	3.348799	-0.680360	-2.833705
H	2.322081	-0.496549	-3.193930
H	3.851948	0.294579	-2.713126
H	3.889923	-1.239980	-3.625381
C	2.622628	-2.846209	-1.819435
H	2.696937	-3.552839	-0.969852
H	1.554230	-2.687107	-2.046955
H	3.101553	-3.333282	-2.694265
C	4.804638	-1.843611	-1.134100
H	4.859102	-2.387138	-0.170577
H	5.253398	-2.499463	-1.909873
H	5.436979	-0.940265	-1.067389
C	3.480649	0.818972	0.611002

C	3.677358	1.823407	-1.302886	C	5.019563	0.479593	1.509073	C	4.043608	1.751608	-0.478206
H	3.810573	2.916194	-1.156235	H	5.529054	0.681994	2.474647	H	4.507418	2.636187	0.006379
H	4.524499	1.470898	-1.918403	H	5.800563	0.204052	0.776228	H	4.826345	1.260889	-1.086426
H	2.763323	1.667396	-1.904632	H	4.541031	1.420305	1.177950	H	3.249082	2.125500	-1.149141
C	2.973215	2.015166	1.126407	C	3.033395	-0.241596	2.853118	C	2.583769	1.645422	1.558569
H	2.914030	1.506705	2.107129	H	2.218442	-0.977042	3.005225	H	2.165337	1.031309	2.376367
H	3.591092	2.931827	1.240217	H	3.604293	-0.175665	3.803140	H	3.203889	2.439982	2.023785
H	1.953484	2.328163	0.854209	H	2.571265	0.744888	2.659673	H	1.749739	2.125505	1.031343
C	5.041624	0.779447	0.542130	C	4.702096	-1.959191	2.088772	C	4.639956	0.262651	1.464721
H	5.617057	0.200012	-0.202347	H	5.407043	-2.301210	1.311609	H	5.332826	-0.390419	0.910676
H	5.591158	1.730752	0.713728	H	5.286708	-1.797065	3.019257	H	5.230849	1.121230	1.848396
H	5.032985	0.221912	1.498880	H	3.987709	-2.779742	2.291480	H	4.271168	-0.287861	2.350956

TS

E(RB97D3) = -2132.67567784 A.U.

Ru	0.019534	-0.277654	-0.511535
C	-0.127879	-0.642496	-2.299083
O	-0.220768	-0.898346	-3.444855
N	0.210272	0.005545	1.628943
C	1.143831	-0.681738	2.332908
C	-0.767570	0.759741	2.281846
C	-0.756273	0.771138	3.735143
C	0.188093	0.047808	4.424287
C	1.189448	-0.690150	3.724604
P	2.348359	-0.545714	-0.147764
P	-2.296042	-0.470144	-0.006575
N	-0.230251	1.910119	-0.593338
C	0.273436	2.608449	-1.635299
C	-0.870891	2.577597	0.401524
C	0.192177	3.996450	-1.738617
C	-0.428335	4.707166	-0.698617
C	-0.955675	3.985158	0.375119
H	0.768057	2.007820	-2.407705
H	0.614698	4.505652	-2.613665
H	-0.506234	5.802230	-0.729377
H	-1.458150	4.503801	1.201176
C	-1.497866	1.827166	1.534097
C	-2.437412	0.629035	1.373859
H	-1.933937	2.556552	2.233714
H	-3.313329	0.630719	2.034980
H	0.103582	-1.857247	-0.270193
C	2.158205	-1.432322	1.499376
H	3.105005	-1.579906	2.047663
H	0.193957	0.069092	5.523946
H	1.968547	-1.248871	4.254237
H	-1.502611	1.381585	4.260119
H	1.754684	-2.431231	1.249822
C	-2.796523	-2.202947	0.676343
C	-4.281369	-2.282999	1.076056
H	-4.955177	-2.255946	0.200293
H	-4.464818	-3.245800	1.599215
H	-4.570604	-1.469704	1.769739
C	-1.939254	-2.442117	1.937327
H	-0.862171	-2.421192	1.700677
H	-2.128181	-1.683742	2.718140
H	-2.185255	-3.442553	2.351684
C	-2.469141	-3.308515	-0.347231
H	-1.417636	-3.238162	-0.681722
H	-2.616862	-4.299980	0.131331
H	-3.117893	-3.272191	-1.239061
C	-3.586459	0.108837	-1.339335
C	-2.993082	1.345533	-2.042807
H	-2.800159	2.167930	-1.330026
H	-2.052709	1.112298	-2.569658
H	-3.724422	1.716612	-2.791736
C	-3.834797	-0.982523	-2.394317
H	-4.417993	-1.829242	-1.988532
H	-4.421840	-0.554223	-3.234973
H	-2.888369	-1.373022	-2.813454
C	-4.911485	0.543194	-0.684345
H	-4.738387	1.337489	0.067631
H	-5.588204	0.952757	-1.465054
H	-5.442004	-0.287641	-0.189531
C	3.283241	-1.797481	-1.273110
C	3.333034	-1.242002	-2.713129
H	2.324490	-0.997870	-3.089985
H	3.964926	-0.342170	-2.801442
H	3.764371	-2.015658	-3.382616
C	2.472811	-3.112614	-1.306610
H	2.451122	-3.618184	-0.322487

I1

E(RB97D3) = -2132.69328306 A.U.

Ru	0.012897	-0.366848	-0.321725
C	-0.194932	-1.282655	-1.883999
O	-0.293168	-1.895947	-2.883200
N	0.395668	0.620886	1.601981
C	1.445035	0.209677	2.362083
C	-0.386428	1.651824	2.009115
C	-0.163642	2.259760	3.263443
C	0.869354	1.806759	4.082519
C	1.703387	0.774753	3.617551
P	2.369006	-0.550941	-0.114321
P	-2.325042	-0.459098	0.263138
N	-0.381334	1.674975	-1.068380
C	-0.101322	2.014453	-2.346556
C	-1.079666	2.542481	-0.287905
C	-0.479355	3.229050	-2.915908
C	-1.184836	4.147918	-2.116317
C	-1.478269	3.796650	-0.798565
H	0.454846	1.264843	-2.922891
H	-0.224285	3.448693	-3.959872
H	-1.492798	5.123244	-2.517586
H	-2.033417	4.483509	-0.146797
C	-1.513710	2.107727	1.106478
C	-2.613673	1.070474	1.030539
H	-1.942585	3.005543	1.583930
H	-3.549216	1.303051	1.554670
H	0.116700	-1.791493	0.401725
C	2.348939	-0.826941	1.750740
H	3.344866	-0.822631	2.228440
H	1.053441	2.272398	5.060588
H	2.553803	0.418091	4.210726
H	-0.805037	3.094294	3.573608
H	1.905817	-1.830362	1.890711
C	-2.676568	-1.892973	1.538482
C	-4.146143	-1.894599	1.995186
H	-4.829579	-2.249478	1.202236
H	-4.265732	-2.581870	2.860850
H	-4.474546	-0.887676	2.320853
C	-1.793880	-1.581682	2.763340
H	-0.721120	-1.649199	2.509753
H	-1.992937	-0.563991	3.150148
H	-2.006674	-2.318100	3.567548
C	-2.291005	-3.281633	0.998597
H	-1.263791	-3.278077	0.587622
H	-2.327831	-4.023447	1.826170
H	-2.975672	-3.636788	0.209859
C	-3.612457	-0.607112	-1.194672
C	-3.118496	0.347854	-2.299322
H	-2.985039	1.371872	-1.903909
H	-2.166129	0.017059	-2.746083
H	-3.876439	0.390329	-3.110509
C	-3.728148	-2.029220	-1.764625
H	-4.273298	-2.704933	-1.079735
H	-4.299976	-2.001973	-2.717646
H	-2.739527	-2.473493	-1.983739
C	-4.995352	-0.095209	-0.747232
H	-4.914822	0.928901	-0.334440
H	-5.674093	-0.058499	-1.626776
H	-5.471574	-0.740803	0.010303
C	3.227970	-2.132435	-0.802117
C	3.177287	-2.115392	-2.345417
H	2.145372	-2.015285	-2.722008
H	3.788419	-1.307966	-2.782501
H	3.581176	-3.077147	-2.725610
C	2.425977	-3.361819	-0.319196
H	2.483434	-3.498670	0.777587

3b

E(RB97D3) = -2132.72730581 A.U.

Ru	0.080190	-0.237737	-0.364908
C	0.185939	-0.745366	-2.117160
O	0.311293	-1.041872	-3.250305
N	0.213804	0.387764	1.727197
C	1.338192	-0.042713	2.448440
C	-0.705993	1.180668	2.315859
C	-0.695052	1.477630	3.678930
C	0.327968	0.898035	4.476826
C	1.324730	0.157106	3.878136
P	2.429275	-0.451751	-0.005856
P	-2.228688	-0.659127	-0.034519
N	-0.455431	1.902921	-0.665390
C	-0.081204	2.576533	-1.777001
C	-1.250382	2.535432	0.237794
C	-0.444879	3.897235	-2.038516
C	-1.234430	4.572930	-1.096345
C	-1.635793	3.875408	0.048042
H	0.539271	2.012074	-2.479458
H	-0.105341	4.382634	-2.962152
H	-1.535660	5.617584	-1.251518
H	-2.264190	4.362276	0.804945
C	-2.880548	0.735831	1.022076
C	-1.793578	1.767611	1.433804
H	-3.670571	1.272316	0.468745
H	-3.345745	0.344904	1.945294
H	-2.325263	2.510602	2.054362
C	2.421653	-0.597019	1.766082
H	3.325961	-0.854863	2.330077
H	0.339808	1.065466	5.563735
H	2.153472	-0.257595	4.466513
H	-1.460337	2.131648	4.113176
H	0.276662	-1.748929	0.075574
C	3.527111	1.100715	-0.412374
C	3.296928	-2.030364	-0.671442
H	3.455607	1.458419	-1.907611
H	4.058786	0.781001	-2.534964
H	2.417004	1.419252	-2.278637
H	3.838838	2.489519	-2.065173
C	2.863406	2.228625	0.407276
H	3.028511	2.089350	1.491975
H	3.291946	3.208591	0.108350
H	1.772347	2.249921	0.239059
C	4.988533	0.961628	0.036319
H	5.564628	0.271232	-0.608324
H	5.493135	1.951822	-0.013058
H	5.055151	0.607257	1.083970
C	3.771779	-1.834584	-2.123324
H	2.972500	-1.423066	-2.768149
H	4.652671	-1.169090	-2.184962
H	4.073785	-2.816524	-2.545768
C	4.490196	-2.419737	0.228648
H	4.143834	-2.713288	1.237236
H	5.008628	-3.294263	-0.218937
H	5.231779	-1.611695	0.341841
C	2.299262	-3.205477	-0.630696
H	1.474227	-3.074239	-1.352182
H	2.841156	-4.140604	-0.888676
H	1.862644	-3.324311	0.379238
C	-3.405875	-0.583114	-1.562358
C	-4.911272	-0.513281	-1.229108
H	-5.467755	-0.263610	-2.157099
H	-5.310699	-1.472338	-0.858710
H	-5.151699	0.268154	-0.483504
C	-3.018855	0.702698	-2.326419
H	-1.952516	0.700809	-2.605137

H	1.431961	-2.946625	-1.632531	H	1.362140	-3.299005	-0.604134	H	-3.622841	0.764448	-3.255496
H	2.958789	-3.806701	-2.023657	H	2.861040	-4.269568	-0.786585	C	-3.151039	-1.792485	-2.482914
C	4.707860	-2.123360	-0.788074	C	4.687054	-2.290908	-0.336288	H	-3.551033	-2.727780	-2.052386
H	4.717785	-2.491374	0.256489	H	4.786303	-2.236561	0.765399	H	-3.671470	-1.626756	-3.449813
H	5.132766	-2.926850	-1.426354	H	5.061458	-3.286877	-0.654044	H	-2.077847	-1.935805	-2.701367
H	5.388345	-1.256032	-0.862209	H	5.354695	-1.535252	-0.788257	C	-2.574012	-2.234544	1.011945
C	3.525138	0.929443	0.324917	C	3.549274	0.986555	-0.283888	C	-1.780655	-2.078690	2.327689
C	4.151839	1.528920	-0.947716	C	3.969076	1.132197	-1.758853	H	-1.949159	-2.984293	2.947196
H	4.641495	2.493199	-0.695052	H	4.434693	2.128209	-1.913602	H	-0.699573	-1.982942	2.135079
H	4.925254	0.873817	-1.388684	H	4.712883	0.371889	-2.059788	H	-2.097295	-1.202159	2.923507
H	3.384704	1.735631	-1.719832	H	3.096977	1.059378	-2.438649	C	-4.065561	-2.428440	1.336165
C	2.674130	2.029555	0.997267	C	2.733508	2.238784	0.107754	H	-4.636474	-2.768650	0.453847
H	2.136122	1.661727	1.887052	H	2.465045	2.243490	1.178922	H	-4.171956	-3.210585	2.116796
H	3.353912	2.846645	1.319867	H	3.355566	3.138640	-0.082699	H	-4.541664	-1.506566	1.721688
H	1.936517	2.458161	0.302974	H	1.805001	2.326476	-0.476784	C	-2.034652	-3.480885	0.280599
C	4.627205	0.534543	1.329773	C	4.793913	0.948364	0.623628	H	-0.993038	-3.325742	-0.056759
H	5.249071	-0.312885	0.997186	H	5.448075	0.080348	0.440755	H	-2.047401	-4.343663	0.979164
H	5.302475	1.404307	1.477864	H	5.397758	1.862781	0.439571	H	-2.648547	-3.756156	-0.594846
H	4.197420	0.287958	2.318999	H	4.517348	0.958338	1.695151	H	-3.219946	1.619572	-1.739077

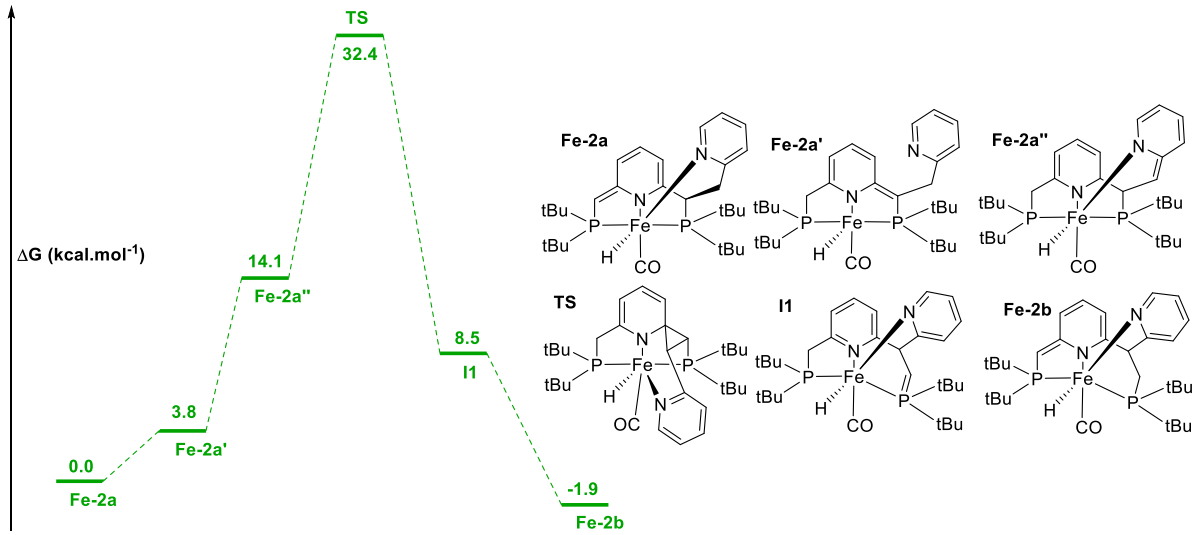


Figure S96. Energy profile for iron substituted complex CC rearrangement.

Cartesian coordinates and absolute electronic energies for Fe substituted complexes at the B97D3/def2SV level

Fe-2a
E(RB97D3) = -3301.58532763 A.U.

C	0.180612	-0.064728	-2.099978
O	0.253225	-0.126834	-3.274871
N	-0.025585	-0.401796	1.637274
C	1.082591	-0.939063	2.301683
C	-1.205824	-0.272021	2.283539
C	-1.389605	-0.566761	3.632581
C	-0.271588	-1.073169	4.349838
C	0.930691	-1.263280	3.700955
P	2.318696	-0.472703	-0.057982
P	-2.083631	-0.468416	-0.297167
N	-0.276827	1.975951	-0.104671
C	0.453791	2.815628	-0.884799
C	-1.107985	2.550742	0.807593
C	0.493821	4.198593	-0.735344
C	-0.254432	4.781701	0.298161
C	-1.069815	3.939015	1.054705
H	1.044364	2.335377	-1.665727
H	1.124491	4.795739	-1.405608
H	-0.225016	5.862557	0.490107
H	-1.728305	4.350935	1.830960
C	-2.254440	1.804248	1.477179

Fe-2a'
E(RB97D3) = -3301.58430709 A.U

C	1.814979	1.941695	0.529616
O	2.405313	2.929351	0.786565
N	0.062176	-1.258177	-0.198691
C	0.721540	-2.458141	-0.166003
C	-1.283935	-1.215951	-0.626238
C	-1.881329	-2.450787	-1.085953
C	-1.176544	-3.632608	-1.076528
C	0.158952	-3.654631	-0.591647
P	2.842325	-0.742907	0.193197
P	-0.983458	1.419238	-0.203901
N	-4.191057	-0.882743	1.161593
C	-5.015752	-1.627080	1.907805
C	-4.390596	-0.821701	-0.166997
C	-6.089896	-2.362563	1.383301
C	-6.308675	-2.301113	-0.000462
C	-5.449583	-1.520705	-0.783641
H	-4.810666	-1.638653	2.991718
H	-6.731913	-2.964585	2.040356
H	-7.134330	-2.859263	-0.464758
H	-5.586246	-1.455976	-1.872196
C	-3.447907	0.050694	-0.990893

Fe-2a''
E(RB97D3) = -3301.58421911 A.U.

C	-0.081641	-0.469113	-2.248693
O	-0.189336	-0.593840	-3.414989
N	0.052321	-0.502988	1.614532
C	1.122917	-1.033377	2.260118
C	-1.031090	-0.059884	2.298711
C	-1.035420	-0.077229	3.709663
C	0.070508	-0.585317	4.390382
C	1.169721	-1.081835	3.656588
P	2.291804	-0.567216	-0.197083
P	-2.167190	-0.452024	-0.198608
N	-0.248063	1.966094	-0.379094
C	0.459718	2.678181	-1.276851
C	-0.970352	2.616752	0.612067
C	0.621806	4.058706	-1.233879
C	0.013970	4.744555	-0.144668
C	-0.755650	4.043341	0.759772
H	0.933297	2.087175	-2.073369
H	1.208195	4.579981	-1.999722
H	0.152902	5.829286	-0.024669
H	0.152902	5.829286	-0.024669
H	-1.245624	4.556759	1.598279

C	-2.331721	0.266687	1.427342	C	-1.986113	-0.005456	-0.603775	C	-1.928878	1.963695	1.394689
H	-3.185102	2.238264	1.055690	H	-3.811060	1.089753	-0.886725	C	-2.172611	0.479367	1.472614
H	-2.261727	2.085910	2.549464	H	-3.605357	-0.205424	-2.063934	H	-2.435196	2.560732	2.164982
H	-3.308192	-0.020806	1.861905	H	1.299140	0.764054	-1.256175	H	-3.130819	0.289738	1.992572
C	2.260941	-1.135963	1.584977	C	2.115141	-2.440899	0.416465	H	0.105726	-1.884176	-0.578126
H	3.150842	-1.513825	2.102319	H	2.044923	-2.605522	1.510540	C	2.184087	-1.616118	1.365224
H	-0.369279	-1.326756	5.415532	H	-1.645578	-4.557222	-1.443162	H	3.143609	-1.756220	1.890825
H	1.800173	-1.672753	4.231192	H	0.734431	-4.586050	-0.534903	H	0.079678	-0.618700	5.488434
H	-2.372386	-0.436495	4.100902	H	-2.907092	-2.432540	-1.464255	H	2.042096	-1.514028	4.161644
H	0.219594	-1.535714	-0.454987	H	2.741445	-3.258628	0.012687	H	-1.912021	0.303718	4.248688
C	-2.584690	-2.332694	-0.124065	C	-1.080028	2.634975	-1.692251	H	1.833555	-2.612009	1.030883
C	-4.095801	-2.543980	0.072334	C	-2.387228	3.446487	-1.744313	C	-2.853390	-2.219765	0.202745
H	-4.682448	-2.288238	-0.827472	H	-2.476219	4.150965	-0.897276	C	-4.338861	-2.211863	0.604433
H	-4.282429	-3.616652	0.290265	H	-2.401681	4.050300	-2.677172	H	-5.006506	-1.932412	-0.228635
H	-4.487576	-1.961711	0.929872	H	-3.283109	2.799945	-1.758917	H	-4.632745	-3.230077	0.936897
C	-1.855641	-2.942264	1.092815	C	-0.979135	1.759715	-2.959083	H	-4.528681	-1.518741	1.447561
H	-0.770757	-2.748120	1.057910	H	-0.078560	1.115981	-2.934692	C	-2.054674	-2.817609	1.383558
H	-2.244389	-2.563439	2.054208	H	-1.860306	1.103598	-3.078192	H	-0.970635	-2.834157	1.175997
H	-2.014117	-4.040592	1.073708	H	-0.908789	2.417161	-3.852037	H	-2.222528	-2.273626	2.331660
C	-2.090977	-3.099657	-1.371272	C	0.113784	3.609579	-1.668633	H	-2.392093	-3.864478	1.535733
H	-0.997866	-2.993443	-1.489840	H	1.073351	3.069831	-1.742045	C	-2.609081	-3.137156	-1.013377
H	-2.317803	-4.178051	-1.235005	H	0.037861	4.298685	-2.536827	H	-1.533406	-3.158181	-1.269759
H	-2.572884	-2.778129	-2.308361	H	0.144322	4.224359	-0.751533	H	-2.927064	-4.171333	-0.761794
C	-3.354758	0.401885	-1.469389	C	-1.638780	2.205296	1.416023	H	-3.166379	-2.826466	-1.911220
C	-2.786233	1.766949	-1.919755	C	-1.201225	1.185569	2.493134	C	-3.450906	0.474505	-1.300677
H	-2.666036	2.487225	-1.094029	H	-1.635997	0.188764	2.283944	H	-2.480867	2.455887	-1.266477
H	-1.809003	1.657213	-2.420894	H	-0.095108	1.100466	2.543788	H	-1.903758	1.392903	-2.585703
H	-3.495936	2.216621	-2.645231	H	-1.558516	1.515708	3.492196	H	-3.531705	2.132853	-2.678222
C	-3.525901	-0.435412	-2.754468	C	-0.985960	3.571303	1.686913	C	-3.957851	-0.445630	-2.428535
H	-4.050338	-1.389269	-2.575340	H	-1.341952	4.345342	0.980494	H	-4.568785	-1.287645	-2.061518
H	-4.132047	0.143956	-3.481552	H	-1.265586	3.909449	2.708030	H	-4.601149	0.154480	-3.105588
H	-2.550181	-0.651435	-3.228751	H	0.116162	3.538650	1.636292	H	-3.121122	-0.845613	-3.032477
C	-4.726124	0.635049	-0.806693	C	-3.170598	2.342549	1.480853	C	-4.627475	1.005215	-0.455222
H	-4.656238	1.284385	0.086468	H	-3.661608	1.353967	1.445334	H	-4.271676	1.741227	0.290669
H	-5.393990	1.149366	-1.530654	H	-3.443560	2.817956	2.448292	H	-5.339726	1.526973	-1.129403
H	-5.223500	-0.300510	-0.504740	H	-3.572720	2.984785	0.677343	H	-5.18607	0.210701	0.067235
C	3.110886	-1.845636	-1.162620	C	3.785172	-0.837614	-1.469791	C	3.268945	-1.655087	-1.445405
C	3.691453	-1.252268	-2.458985	C	4.163225	0.588482	-1.919800	C	3.302815	-0.926742	-2.806207
H	2.959604	-0.603720	-2.974850	H	3.264153	1.224339	-2.019798	H	2.287312	-0.721856	-3.184505
H	4.608867	-0.665705	-2.272389	H	4.855973	1.084899	-1.217069	H	3.856899	0.025153	-2.759436
H	3.959916	-2.076412	-3.153540	H	4.664002	0.533732	-2.909181	H	3.813575	-1.575883	-3.548243
C	2.030818	-2.883214	-1.530589	C	2.789166	-1.430260	-2.493508	C	2.499761	-2.980879	-1.636572
H	1.507863	-3.253161	-0.628502	H	2.541472	-2.485262	-2.273580	H	2.533650	-3.616053	-0.730472
H	1.280462	-2.479233	-2.231865	H	1.842180	-0.859527	-2.513872	H	1.443143	-2.805331	-1.901034
H	2.523816	-3.749417	-2.022895	H	3.245709	-1.389549	-3.504471	H	2.979915	-3.552112	-2.458256
C	4.206351	-2.611801	-0.390191	C	5.039020	-1.726379	-1.420043	C	4.703707	-1.989335	-1.001010
H	3.774421	-3.149239	0.475311	H	4.815397	-2.748081	-1.055500	H	4.729906	-2.448759	0.006085
H	4.664170	-3.365414	-1.065888	H	5.454393	-1.825176	-2.445574	H	5.142623	-2.720272	-1.712744
H	5.014387	-1.960864	-0.019316	H	5.833238	-1.294003	-0.784648	H	5.358067	-1.099342	-1.005059
C	3.594328	0.998246	0.065166	C	4.025719	-0.574682	1.683442	C	3.417981	0.890343	0.435240
C	3.717193	1.763623	-1.275004	C	5.008155	0.588649	1.454835	C	3.970662	1.687177	-0.761590
H	3.846771	2.851561	-1.094526	H	5.560071	0.792265	2.396984	H	4.400002	2.642239	-0.392833
H	4.588570	1.421424	-1.862272	H	5.758509	0.346595	0.680277	H	4.778252	1.145310	-1.290190
H	2.831357	1.630117	-1.920931	H	4.486463	1.518156	1.162689	H	3.177474	1.938376	-1.488607
C	3.010889	1.915282	1.164512	C	3.111663	-0.225879	2.880917	C	2.549761	1.835931	1.294676
H	2.941341	1.379532	2.130112	H	2.340111	-1.001339	3.057349	H	2.083173	1.319803	2.153002
H	3.674140	2.796918	1.297972	H	3.724645	-0.152817	3.803874	H	3.210002	2.629341	1.703410
H	2.002888	2.285582	0.918693	H	2.598405	0.741008	2.728793	H	1.756483	2.320733	0.711534
C	4.988878	0.555733	0.540292	C	4.803648	-1.864766	2.008606	C	4.587193	0.423587	1.330010
H	5.536187	-0.021323	-0.227536	H	5.444989	-2.195848	1.173803	H	5.218703	-0.350277	0.867443
H	5.603602	1.452804	0.774946	H	5.462395	-1.677735	2.883237	H	5.234487	1.300414	1.545737
H	4.925324	-0.052165	1.463184	H	4.131641	-2.700831	2.278265	H	4.227100	0.046865	2.306009
Fe	0.065125	-0.065743	-0.395122	Fe	1.012152	0.483743	0.147532	Fe	0.024869	-0.378964	-0.555355

TS

E(RB97D3) = -3301.54720374 A.U.

C	-0.058053	-0.721499	-2.175579
O	-0.138552	-1.031398	-3.311671
N	0.222373	0.161732	1.628411
C	1.139819	-0.509036	2.357305
C	-0.799504	0.889837	2.231054
C	-0.799754	0.961759	3.683399
C	0.152767	0.281031	4.407065
C	1.168397	-0.477355	3.750254
P	2.262616	-0.525097	-0.169626
P	-2.153516	-0.554586	-0.032458

I1

E(RB97D3) = -3301.56880857 A.U.

C	-0.026963	-0.718100	-1.917272
O	-0.008339	-1.120087	-3.024698
N	0.337538	0.410229	1.660553
C	1.360581	-0.126863	2.375391
C	-0.510800	1.283530	2.263662
C	-0.374599	1.599802	3.631700
C	0.634515	1.003962	4.384780
C	1.531421	0.134523	3.740022
P	2.253927	-0.479243	-0.199821
P	-2.185439	-0.546476	0.121997

Fe-2b

E(RB97D3) = -3301.60183537 A.U.

C	0.215129	-0.721338	-2.015581
O	0.329025	-1.010097	-3.155015
N	0.192571	0.507995	1.693303
C	1.326175	0.124979	2.413245
C	-0.732909	1.312670	2.243518
C	-0.696070	1.708449	3.582760
C	0.364641	1.214248	4.387965
C	1.355578	0.438195	3.821179
P	2.335265	-0.400699	-0.044544
P	-2.044266	-0.778911	-0.010479

N	-0.352396	1.987393	-0.703416	N	-0.404962	1.798721	-0.735145	N	-0.616053	1.941890	-0.770994
C	0.119409	2.661029	-1.767433	C	-0.146262	2.342614	-1.949547	C	-0.307886	2.588644	-1.911331
C	-1.003117	2.642969	0.283640	C	-1.146951	2.528472	0.148888	C	-1.430384	2.539620	0.128901
C	-0.019262	4.042888	-1.911012	C	-0.550951	3.619500	-2.330491	C	-0.764573	3.874528	-2.209472
C	-0.659754	4.752905	-0.881177	C	-1.270328	4.399774	-1.407428	C	-1.579918	4.524374	-1.270253
C	-1.146537	4.045965	0.222881	C	-1.565019	3.838078	-0.164458	C	-1.913747	3.843277	-0.093265
H	0.628367	2.050017	-2.525034	H	0.396802	1.703793	-2.653834	H	0.327726	2.038546	-2.614640
H	0.369003	4.548684	-2.804021	H	-0.304641	3.990418	-3.333264	H	-0.479520	4.351820	-3.155512
H	-0.785757	5.842572	-0.943493	H	-1.596110	5.418788	-1.657068	H	-1.955594	5.540048	-1.453823
H	-1.659691	4.571194	1.038580	H	-2.144592	4.399552	0.580159	H	-2.560574	4.312959	0.659099
C	-1.589359	1.878126	1.427929	C	-1.621153	1.859038	1.427282	C	-1.878550	1.762736	1.356435
C	-2.426094	0.606954	1.283401	C	-2.646271	0.786782	1.124830	C	-2.832249	0.592571	0.995178
H	-2.097419	2.587355	2.099643	H	-2.111681	2.641237	2.032233	H	-2.483302	2.463709	1.958494
H	-3.330562	0.567953	1.905195	H	-3.623516	0.871243	1.615815	H	-3.686298	0.996525	0.425924
H	0.150001	-1.753415	-0.231540	H	0.132124	-1.560030	0.156760	H	-3.234856	0.185496	1.940609
C	2.129043	-1.309169	1.541227	C	2.331957	-0.973789	1.607493	C	2.374914	-0.497832	1.732428
H	3.094110	-1.429686	2.064480	H	3.344418	-0.927799	2.048802	H	3.294982	-0.741522	2.276150
H	0.148133	0.347246	5.505252	H	0.749934	1.234132	5.453015	H	0.406669	1.468886	5.457163
H	1.937406	-1.020373	4.310544	H	2.365832	-0.328232	4.280843	H	2.207294	0.083065	4.415752
H	-1.560325	1.578756	4.180403	H	-1.070441	2.317794	4.084027	H	-1.472716	2.365993	3.991494
H	1.717109	-2.323318	1.375064	H	2.009633	-2.033362	1.633526	H	0.325164	-1.633956	0.064045
C	-2.555957	-2.280421	0.738632	C	-2.442179	-2.232048	1.077681	C	-2.253489	-2.334227	1.109122
C	-4.038354	-2.418516	1.124704	C	-3.912324	-2.448659	1.470772	C	-3.711533	-2.599096	1.523532
H	-4.696745	-2.474196	0.239779	H	-4.552985	-2.675705	0.599132	H	-4.305092	-3.027954	0.696897
H	-4.180335	-3.357540	1.701669	H	-3.986746	-3.313944	2.165196	H	-3.728247	-3.338368	2.351669
H	-4.375677	-1.580404	1.764511	H	-4.324682	-1.563797	1.995399	H	-4.225715	-1.688013	1.884747
C	-1.710715	-2.416165	2.023376	C	-1.618462	-2.103553	2.372791	C	-1.404118	-2.097302	2.379272
H	-0.630853	-2.378086	1.801719	H	-0.540106	-2.034346	2.148607	H	-0.334201	-1.978850	2.135417
H	-1.933792	-1.620415	2.757040	H	-1.909522	-1.204344	2.948949	H	-1.720960	-1.204665	2.950266
H	-1.931536	-3.399457	2.489580	H	-1.782493	-3.002085	3.005583	H	-1.517216	-2.980319	3.042091
C	-2.150677	-3.413145	-0.224022	C	-1.915901	-3.447400	0.292516	C	-1.690983	-3.578527	0.392291
H	-1.081741	-3.333194	-0.497602	H	-0.901726	-3.253071	-0.104550	H	-0.672307	-3.392848	0.007013
H	-2.307471	-4.392567	0.276288	H	-1.855355	-4.328996	0.967667	H	-1.638122	-4.419579	1.115067
H	-2.741027	-3.414798	-1.154804	H	-2.565152	-3.730819	-0.553141	H	-2.326084	-3.903322	-0.449031
C	-3.482398	-0.149059	-1.391747	C	-3.430524	-0.542138	-1.382124	C	-3.251906	-0.871719	-1.513759
C	-2.961922	1.058223	-2.197023	C	-3.017968	0.620774	-2.306916	C	-2.986863	0.393091	-2.363725
H	-2.755985	1.926717	-1.546595	H	-2.950951	1.570529	-1.743211	H	-3.149999	1.330957	-1.798267
H	-2.045442	0.817399	-2.761203	H	-2.055979	0.436230	-2.812879	H	-1.962226	0.408038	-2.768881
H	-3.741278	1.363423	-2.927832	H	-3.791108	0.745867	-3.094872	H	-3.691550	0.396198	-3.221442
C	-3.702102	-1.321259	-2.363985	C	-3.432012	-1.851656	-2.184820	C	-2.932119	-2.111493	-2.376083
H	-4.244545	-2.159634	-1.890407	H	-3.943688	-2.665804	-1.639630	H	-3.329868	-3.036526	-1.921207
H	-4.321099	-0.972496	-3.218275	H	-3.984001	-1.703247	-3.138746	H	-3.415428	-1.999501	-3.369144
H	-2.749195	-1.701354	-2.776563	H	-2.410718	-2.187411	-2.441394	H	-1.848130	-2.239876	-2.545380
C	-4.821043	0.275758	-0.754834	C	-4.854064	-0.221742	-0.885611	C	-4.753721	-0.892198	-1.159287
H	-4.688246	1.171747	-0.118516	H	-4.871637	0.752081	-0.361603	H	-5.057442	-1.804355	-0.619697
H	-5.539412	0.529869	-1.563960	H	-5.538576	-0.152394	-1.758973	H	-5.070272	-0.016321	-0.560380
H	-5.281440	-0.514887	-0.139143	H	-5.260130	-0.988506	-0.205456	H	-5.336056	-0.863395	-2.104353
C	3.189467	-1.846982	-1.218056	C	3.053487	-2.021156	-1.030926	C	3.224900	-1.988105	-0.666776
C	3.298581	-1.371361	-2.683140	C	3.486036	-1.677768	-2.469115	C	3.709177	-1.839298	-2.120795
H	2.316143	-1.082305	-3.094784	H	2.677334	-1.183510	-3.038929	H	2.902514	-1.482102	-2.786834
H	3.992706	-0.524222	-2.802670	H	4.380728	-1.028648	-2.483751	H	4.570146	-1.150922	-2.206572
H	3.687573	-2.206620	-3.302957	H	3.749780	-2.613950	-3.004239	H	4.044294	-2.829326	-2.497278
C	2.352504	-3.147061	-1.214530	C	2.015897	-3.163557	-1.084408	C	2.237203	-3.170663	-0.600453
H	2.236481	-3.572778	-0.199975	H	1.608594	-3.410500	-0.086127	H	1.796768	-3.268031	0.410074
H	1.348098	-2.996105	-1.645313	H	1.170082	-2.932906	-1.750515	H	1.418041	-3.073172	-1.334927
H	2.880258	-3.904331	-1.831412	H	2.521334	-4.073308	-1.472753	H	2.788867	-4.108326	-0.827445
C	4.590687	-2.177784	-0.672700	C	4.267851	-2.532857	-0.228075	C	4.414238	-2.351045	0.250250
H	4.556223	-2.526694	0.377687	H	3.965047	-2.961272	0.745911	H	4.061593	-2.632768	1.259850
H	5.033670	-2.995864	-1.279305	H	4.766221	-3.343871	-0.800468	H	4.944203	-3.227087	-0.179975
H	5.278534	-1.316088	-0.735992	H	5.016786	-1.748118	-0.040874	H	5.146486	-1.533991	0.357867
C	3.462927	0.971949	0.188387	C	3.458059	1.035741	-0.303723	C	3.410058	1.155858	-0.504393
C	4.160042	1.432695	-1.103289	C	3.422410	1.620409	-1.730683	C	3.313078	1.490214	-2.001681
H	4.656720	2.408707	-0.916779	H	3.952760	2.595941	-1.736351	H	3.815061	2.462568	-2.197863
H	4.940566	0.728180	-1.445295	H	3.918040	0.970801	-2.472105	H	3.792235	0.731843	-2.642715
H	3.433276	1.580428	-1.926938	H	2.388280	1.802484	-2.067000	H	2.261796	1.587446	-2.323190
C	2.614839	2.151742	0.710339	C	2.866059	2.093458	0.654840	C	2.765119	2.304179	0.302449
H	1.969242	1.860742	1.556894	H	2.956152	1.790926	1.714791	H	2.952579	2.193337	1.386547
H	3.301631	2.954810	1.054563	H	3.422462	3.046134	0.529400	H	3.191896	3.274619	-0.029417
H	1.975668	2.576757	-0.080725	H	1.800696	2.280045	0.437303	H	1.670547	2.330222	0.155758
C	4.506753	0.643207	1.275261	C	4.919613	0.776185	0.100139	C	4.880220	1.024572	-0.081364
H	5.063835	-0.288744	1.082577	H	5.451803	0.135687	-0.627050	H	4.968758	0.697256	0.973387
H	5.245555	1.471924	1.325761	H	5.458683	1.747668	0.130679	H	5.444403	0.318607	-0.719505
H	4.035989	0.567665	2.273770	H	5.010502	0.322580	1.106728	H	5.383538	2.013235	-0.164113
Fe	0.050059	-0.301514	-0.535083	Fe	0.045498	-0.147241	-0.315300	Fe	0.101420	-0.245644	-0.392167

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