Antitumor Activity of New Enantiopure Pybox-Ruthenium Complexes

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- **Experimental data for complexes 1c-7c.**
- **Selected NMR spectra:** ^{1}H, $^{31}P\{^{1}H\}$, $^{13}C\{^{1}H\}$, DEPT 135 and selected bidimensional NMR experiments COSY HH, HSQC and HMBC spectra for complexes **1a**, **2a**, **3a**, **5a**, **1b**, **2b**, and **6c**.
- **Antimicrobial Activity.**

  Experimental, Table 1 and Figure 1.
- **Crystal and refinement data for complexes 1b, 2a·CH_2Cl_2 and 3b (Table 2)**

Experimental data for complexes 1c-7c.

***trans*-[RuCl$_2${(*R*,*R*)-^{i}Pr-pybox}(PTA)] (1c):**

Yield: 0.397 g, 90%: $S_{293\ K}$ (H_2O): 31.40 mg/mL. ^{1}H NMR (300.13 MHz, CD_2Cl_2, 298 K) δ 7.81 (m, 3H, H ^{3,4,5} C_5H_3N), 4.85–4.69 (m, 10H, OCH_2 and NCH_2N), 4.56 (m, 6H, NCH_2P), 3.97 (m, 2H, C*H*^{i}Pr), 2.27 (m, 2H, C*H*Me$_2$), 1.07 (d, $^3J_{HH}$ = 7.6 Hz, 6H, CH*Me*$_2$), 0.72 (d, $^3J_{HH}$ = 6.4 Hz, 6H, CH*Me*$_2$) ppm. ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, 298 K) δ 164.9 (s, OCN), 147.6 (s, C^{2,6} C_5H_3N), 133.0 (s, C^4 C_5H_3N), 122.7 (s, C^{3,5} C_5H_3N), 73.6 (d, $^3J_{CP}$ = 6 Hz, NCH_2N), 72.4 (s, *C*H^{i}Pr), 71.1 (s, OCH_2), 53.3 (d, J_{CP} = 12 Hz, NCH_2P), 29.0 (s, *C*HMe$_2$), 19.1, 14.2 (2*s*, CH*Me*$_2$) ppm. ^{31}P{^{1}H} NMR (161.95 MHz, CD_2Cl_2, 298 K) δ – 41.0 (s) ppm.

***trans*-[RuCl$_2${(*R*,*R*)-^{i}Pr-pybox}(1-H-PTA)][Cl] (2c):**

Yield: 0.069 g, 80%. Conductivity (acetone, 293 K): Λ = 18 S cm^2 mol^{-1}. $S_{293\ K}$ (H_2O): 22.45 mg/mL. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K) δ 7.98 (m, 1H, H^4 C_5H_3N), 7.87 (m, 2H, H^{3,5} C_5H_3N), 4.99 (br, 5H, NCH_2N), 4.83 (m, 3H, OCH_2, NCH_2N), 4.70 (m, 2H, OCH_2), 4.60 (br, 6H, NCH_2P), 4.01 (m, 2H, C*H*^{i}Pr), 2.10 (m, 2H, C*H*Me$_2$), 1.08 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH*Me*$_2$), 0.72 (d, $^3J_{HH}$ = 6.0 Hz, 6H, CH*Me*$_2$) ppm. ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, 298 K) δ 164.8 (s, OCN), 147.5 (s, C^{2,6} C_5H_3N), 134.7 (s, C^4 C_5H_3N), 123.1 (s, C^{3,5} C_5H_3N), 72.2 (s, *C*H^{i}Pr), 72.1 (s, NCH_2N), 71.3 (s, OCH_2), 53.5 (s, NCH_2P), 29.2 (s, *C*HMe$_2$), 18.9, 14.1 (2*s*, CH*Me*$_2$) ppm. ^{31}P{^{1}H} NMR (161.95 MHz, CD_2Cl_2, 298 K) δ – 24.9 (s) ppm.

***trans*-[RuCl$_2${(*R*,*R*)-^{i}Pr-pybox}(1-CH$_3$-PTA)][I] (3c).**

Yield: 0.080 g, 80%. Conductivity (acetone, 293 K): Λ = 97 S cm^2 mol^{-1}. $S_{293\ K}$ (H_2O): 7.10 mg/mL. ^{1}H NMR (300.13 MHz, CD_2Cl_2, 298 K) δ 7.99 (m, 1H, H^4 C_5H_3N), 7.89 (m, 2H, H^{3,5} C_5H_3N), 5.69 (m, 2H, NCH_2N), 5.47 (m, 2H, NCH_2N), 4.96 (m, 2H,

NCH_2N), 4.85 (m, 2H, OCH_2), 4.74 (pt, 2H, $^3J_{HH}$ = 9.4 Hz, $^2J_{HH}$ = 9.4 Hz, OCH_2), 4.49 (m, 6H, NCH_2P), 4.21 (m, 2H, C*H*^{i}Pr), 3.29 (s, 3H, NCH_3), 2.06 (m, 2H, C*H*Me_2), 1.10 (d, $^3J_{HH}$ = 7.2 Hz, 6H, CH*Me*$_2$), 0.71 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH*Me*$_2$) ppm. $^{31}P\{^1H\}$ NMR (161.95 MHz, CD_2Cl_2, 298 K) δ – 16.0 (s) ppm.

***trans*-[RuCl$_2${(*R*,*R*)-^{i}Pr-pybox}(1-CH$_2$=CHCH$_2$-PTA)][I] (4c):**

Yield: 0.078 g, 75%. Conductivity (acetone, 293 K): Λ = 91 S cm^2 mol^{-1}. $S_{293\ K}$ (H_2O): 9.20 mg/mL. ^{1}H-NMR (400.13 MHz, CD_2Cl_2, 298 K) δ 7.99 (m, 1H, H^4 C_5H_3N), 7.90 (m, 2H, H^{3,5} C_5H_3N), 5.96 (m, 1H, CH_2=C*H*CH_2), 5.94– 5.85 (m, 3H, C*H*$_2$=CHCH$_2$ and R-NCH_2N), 5.47 (m, 1H, R-NCH_2N), 5.20 (m, 1H, R-NCH_2N), 5.03 (m, 1H, NCH_2N), 4.93 (m, 1H, R-NCH_2P), 4.80–4.71 (m, 6H, OCH_2, R-NCH_2P), 4.55–4.35 (m, 7H, NCH_2N, NCH_2P, CH_2=CHC*H*$_2$), 4.13 (m, 2H, C*H*^{i}Pr), 2.05 (m, 2H, C*H*Me_2), 1.10 (d, 6H, $^3J_{HH}$ = 6.4 Hz, CH*Me*$_2$), 0.72 (d, 6H, $^3J_{HH}$ = 5.2 Hz, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 298 K) δ 164.8 (s, OCN), 147.4 (s, C^{2,6} C_5H_3N), 135.3 (s, C^4 C_5H_3N), 130.5 (s, *C*H_2=CHCH$_2$), 123.3 (s, C^{3,5} C_5H_3N), 122.8 (CH_2=*C*HCH$_2$), 79.6, 79.2 (2*s*, R-NCH_2N), 73.3 (d, $^3J_{CP}$ = 5 Hz, NCH_2N), 72.0 (s, *C*H^{i}Pr), 71.5 (s, OCH_2), 70.4 (s, NCH_2N), 63.4 (s, CH_2=CH*C*H_2), 55.5 (d, J_{CP} = 16 Hz, R-NCH_2P), 50.6 (d, J_{CP} = 16 Hz, NCH_2P), 50.4 (d, J_{CP} = 14 Hz, NCH_2P), 29.4 (s, *C*HMe_2), 19.0, 14.3 (2*s*, CH*Me*$_2$) ppm. $^{31}P\{^1H\}$ NMR (161.95 MHz, CD_2Cl_2, 298 K) δ – 14.2 (s) ppm.

***trans*-[RuCl$_2${(*R*,*R*)-^{i}Pr-pybox}(1-CH≡CCH$_2$-PTA)][Br] (5c):**

Yield: 0.077 g, 79%. Conductivity (acetone, 293 K): Λ = 73 S cm^2 mol^{-1}. $S_{293\ K}$ (H_2O): 8.50 mg/mL. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K) δ 7.98 (m, 1H, H^4 C_5H_3N), 7.90 (m, 2H, H^{3,5} C_5H_3N), 5.96 (m, 2H, R-NCH_2N), 5.71 (m, 1H, R-NCH_2N), 5.50 (m, 1H, R-NCH_2N), 5.26 (m, 1H, CH≡CC*H*$_2$), 4.97–4.30 (m, 14H, CH≡CC*H*$_2$, NCH_2N, NCH_2P, OCH_2, C*H*≡CCH_2), 4.22 (m, 2H, C*H*^{i}Pr), 2.08 (m, 2H, C*H*Me_2), 1.10 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH*Me*$_2$), 0.72 (d, $^3J_{HH}$ = 6.4 Hz, 6H, CH*Me*$_2$) ppm.$^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 298 K) δ 164.7 (s, OCN), 147.4 (s, C^{2,6} C_5H_3N), 135.3 (s, C^4 C_5H_3N), 123.4 (s,

$C^{3,5}$ C_5H_3N), 81.9 (s, CH≡*C*CH_2), 79.7, 79.4 (2*s*, R-NCH_2N), 71.9 (s, *C*H^{i}Pr), 71.5 (s, OCH_2), 70.4 (s, NCH_2N), 70.1 (s, *C*H≡CCH_2), 55.7 (s, CH≡C*C*H_2), 51.2 (s, R-NCH_2P), 50.4 (d, J_{CP} = 16 Hz, NCH_2P), 50.2 (d, J_{CP} = 14 Hz, NCH_2P), 29.4 (s, *C*HMe_2), 19.0, 14.3 (s, CH*Me*$_2$) ppm.$^{31}P\{^1H\}$ NMR (161.95 MHz, CD_2Cl_2, 298 K) δ – 13.7 (s) ppm.

***trans*-[RuCl$_2${(*R*,*R*)-^{i}Pr-pybox}(1-PhCH$_2$-PTA)][Br] (6c):**

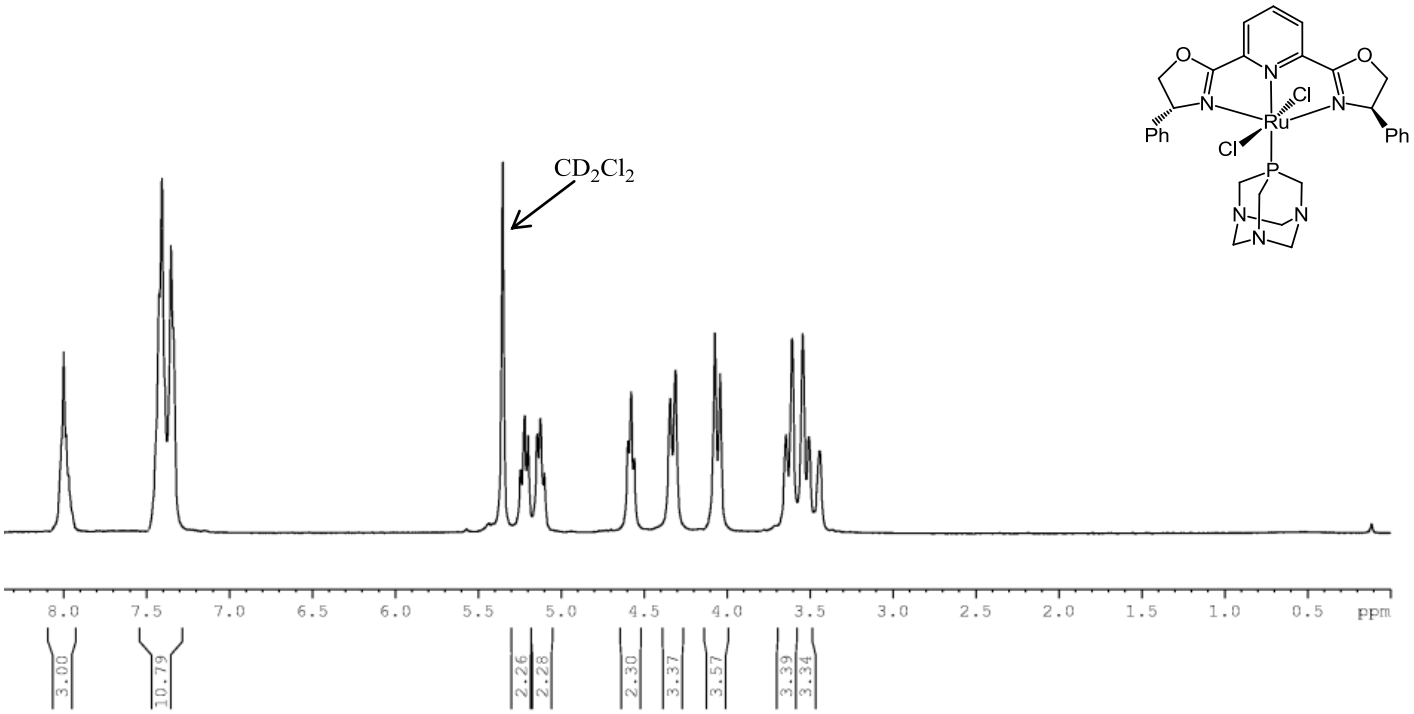
Yield: 0.094 g, 90%. Reaction time: 1.5 h. Conductivity (acetone, 293 K): Λ = 68 S cm^2 mol^{-1}. $S_{293\ K}$ (H_2O): 11.49 mg/mL. ^1H NMR (300.13, CD_2Cl_2, 298 K) δ 7.97 (m, 1H, H^4 C_5H_3N), 7.87 (m, 2H, $H^{3,5}$ C_5H_3N), 7.70–7.38 (m, 5H, Ph), 6.24 (m, 2H, NCH_2N), 5.23 (m, 1H, NCH_2N), 5.02 (m, 3H, NCH_2N), 4.81 (m, 4H, OCH_2, NCH_2P), 4.71 (m, 3H, OCH_2, NCH_2P), 4.54 (m, 3H, C*H*$_2$Ph, NCH_2P), 4.36 (m, 1H, NCH_2P), 4.12 (m, 1H, NCH_2P), 3.97 (m, 2H, C*H*^{i}Pr), 1.87 (m, 2H, C*H*Me_2), 0.89 (d, 6H, $^3J_{HH}$ = 7.2 Hz, CH*Me*$_2$), 0.64 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 298 K) δ 164.8, (d, $^4J_{CP}$ = 4.0 Hz, OCN), 147.4 (s, $C^{2,6}$ C_5H_3N), 135.3 (s, C^4 C_5H_3N), 133.2, 130.8, 129.5, 129.0, 128.7, 128.4 (6*s*, Ph), 125.4 (s, C^{ipso} Ph), 123.3 (s, $C^{3,5}$ C_5H_3N), 79.5, 79.2 (2*s*, R-NCH_2N), 72.1 (s, *C*H^{i}Pr), 71.3 (s, OCH_2), 70.2 (s, NCH_2N), 65.1 (s, Ph*C*H_2), 55.5 (d, J_{CP} = 5 Hz, R-NCH_2P), 50.8 (d, J_{CP} = 13 Hz, NCH_2P), 50.4 (d, J_{CP} = 14 Hz, NCH_2P), 29.3 (s, *C*HMe_2), 18.7, 14.3 (2*s*, CH*Me*$_2$) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 298 K) δ – 14.2 (s) ppm.

***trans*-[RuCl$_2${(*R*,*R*)-^{i}Pr-pybox}(1-PhCH$_2$-PTA)][Cl] (7c):**

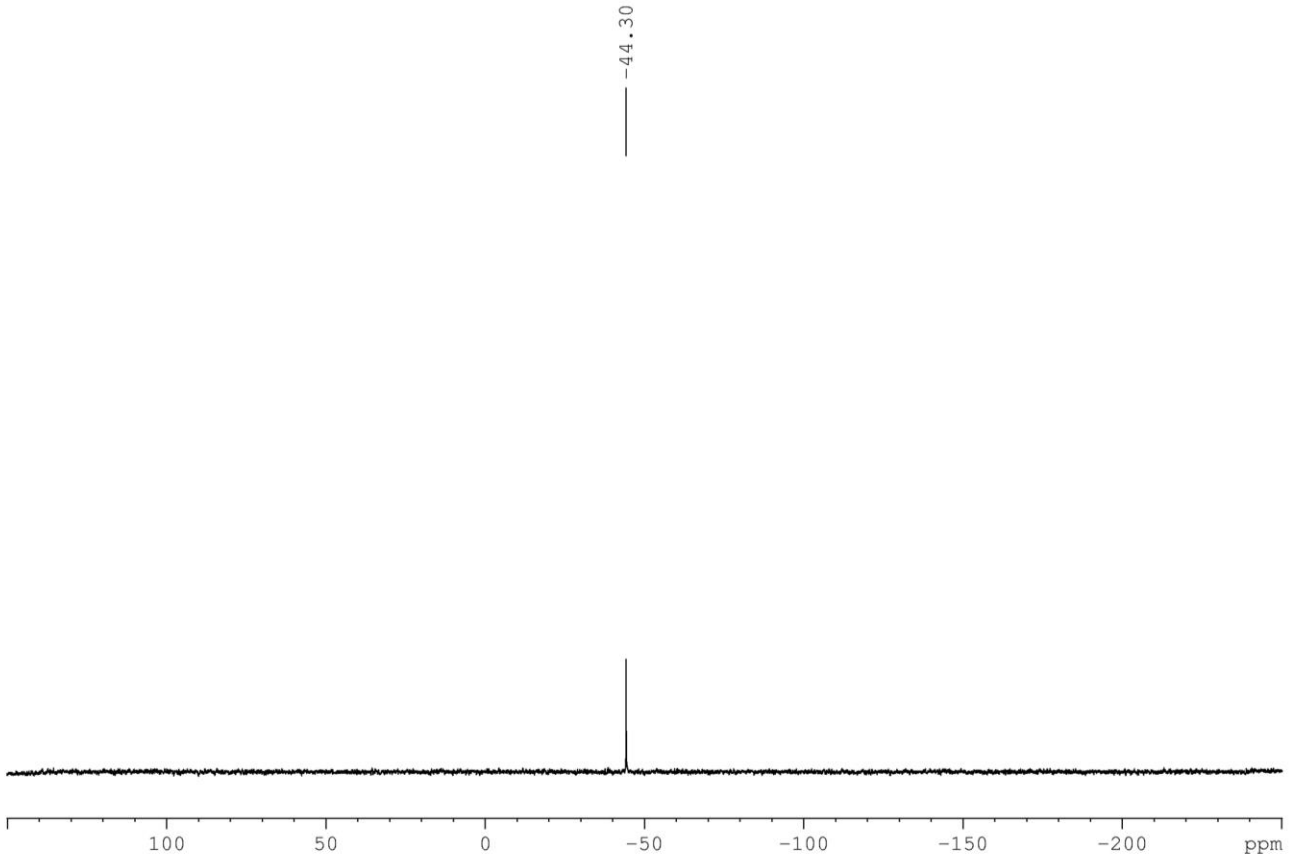
Yield: 0.088 g, 90%. Reaction time: 2 h. Conductivity (acetone, 293 K): Λ = 70 S cm^2 mol^{-1}. $S_{293\ K}$ (H_2O): 8.59 mg/mL. ^1H NMR (300.13 MHz, CD_2Cl_2, 298 K) δ 7.99 (m, 1H, H^4 C_5H_3N), 7.88 (m, 2H, $H^{3,5}$ C_5H_3N), 7.71–7.38 (3m, 5H, Ph), 6.26 (m, 2H, R-NCH_2N), 5.15 (m, 1H, R-NCH_2N), 5.01 (m, 3H, R-NCH_2N), 4.81 (m, 4H, OCH_2, NCH_2P), 4.71 (m, 3H, OCH_2, NCH_2P), 4.55 (m, 3H, C*H*$_2$Ph, NCH_2P), 4.36 (m, 1H, NCH_2P), 4.14 (m, 1H, NCH_2P), 3.98 (m, 2H, C*H*^{i}Pr), 1.87 (m, 2H, C*H*Me_2), 0.89 (d, $^3J_{HH}$ = 7.2 Hz, 6H, CH*Me*$_2$), 0.65 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR

(100.61 MHz, CD_2Cl_2, 298 K) δ 164.8 (d, $^4J_{CP}$ = 4.0 Hz, OCN), 147.4 (s, $C^{2,6}$ C_5H_3N), 135.3 (s, C^4 C_5H_3N), 133.2, 130.8, 129.5, 129.0, 128.7, 128.4 (6s, Ph), 125.4 (s, C^{ipso} Ph), 123.3 (br, $C^{3,5}$ C_5H_3N), 79.5, 79.2 (2*s*, R-NCH_2N), 72.1 (s, *C*H^{i}Pr), 71.3 (s, OCH_2), 70.2 (s, NCH_2N), 65.1 (s, Ph*C*H_2), 55.5 (d, J_{CP} = 5 Hz, R-NCH_2P), 50.8 (d, J_{CP} = 13 Hz, NCH_2P), 50.4 (d, J_{CP} = 14 Hz, NCH_2P), 29.3 (s, *C*HMe_2), 18.7, 14.3 (2*s*, CH*Me*$_2$) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 298 K) δ – 14.3 (s) ppm.

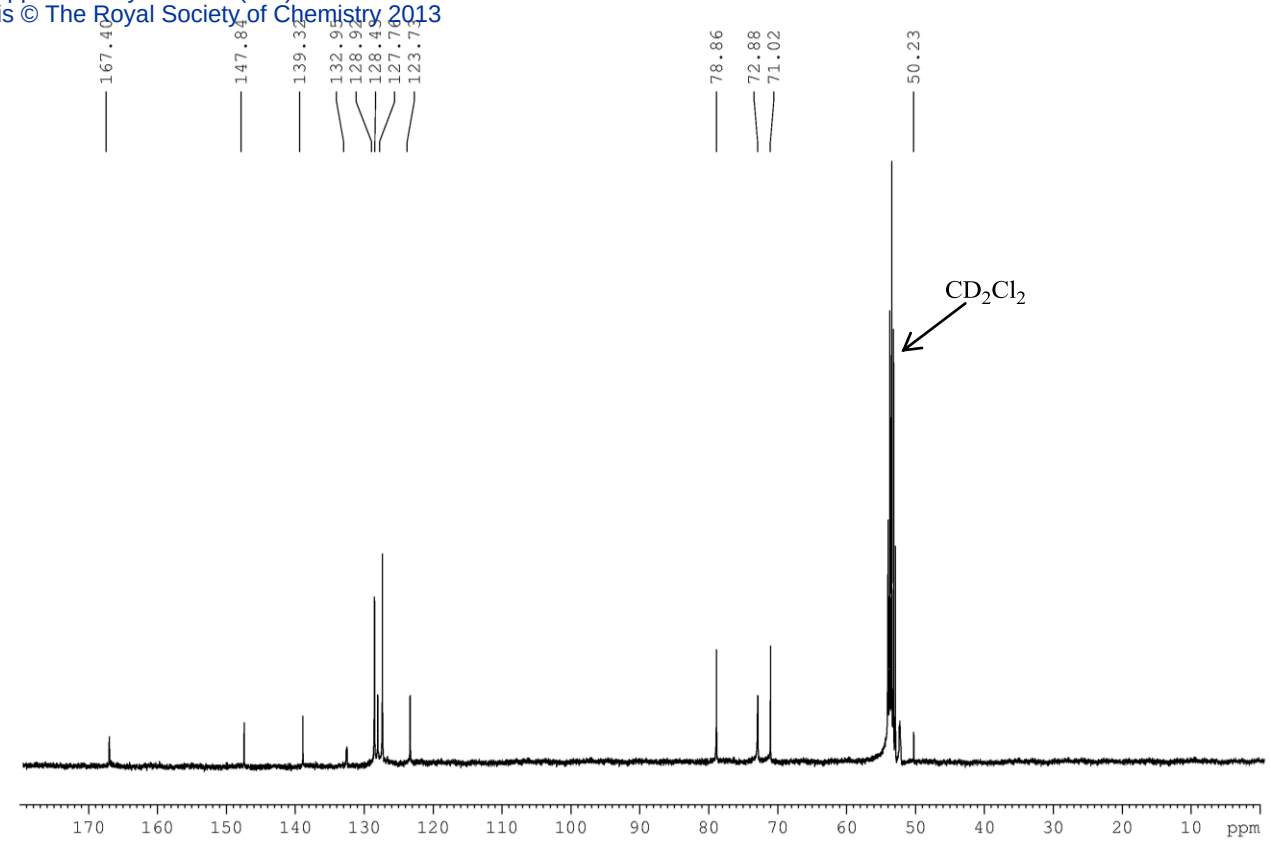
Selected NMR spectra:



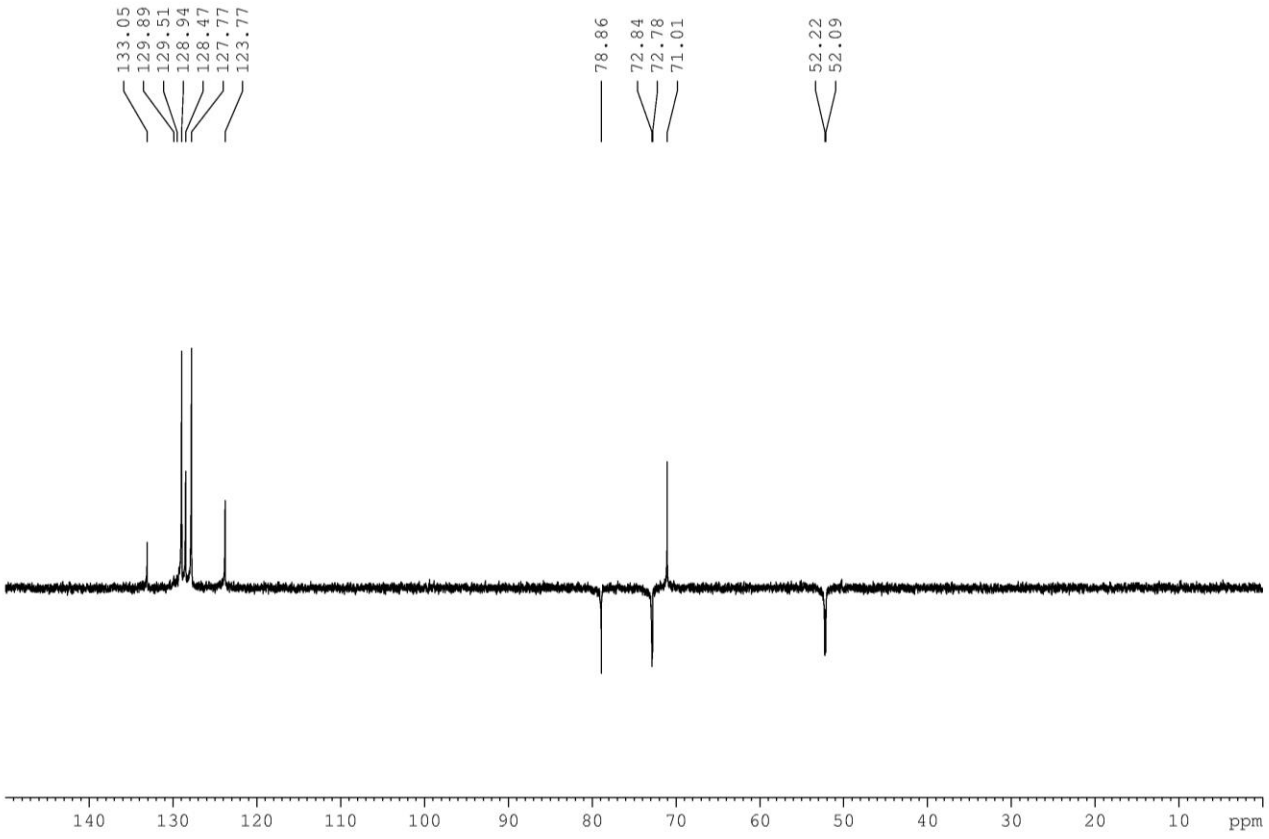
^{1}H NMR spectrum (CD_2Cl_2, 298 K, NAV400) of complex **1a**



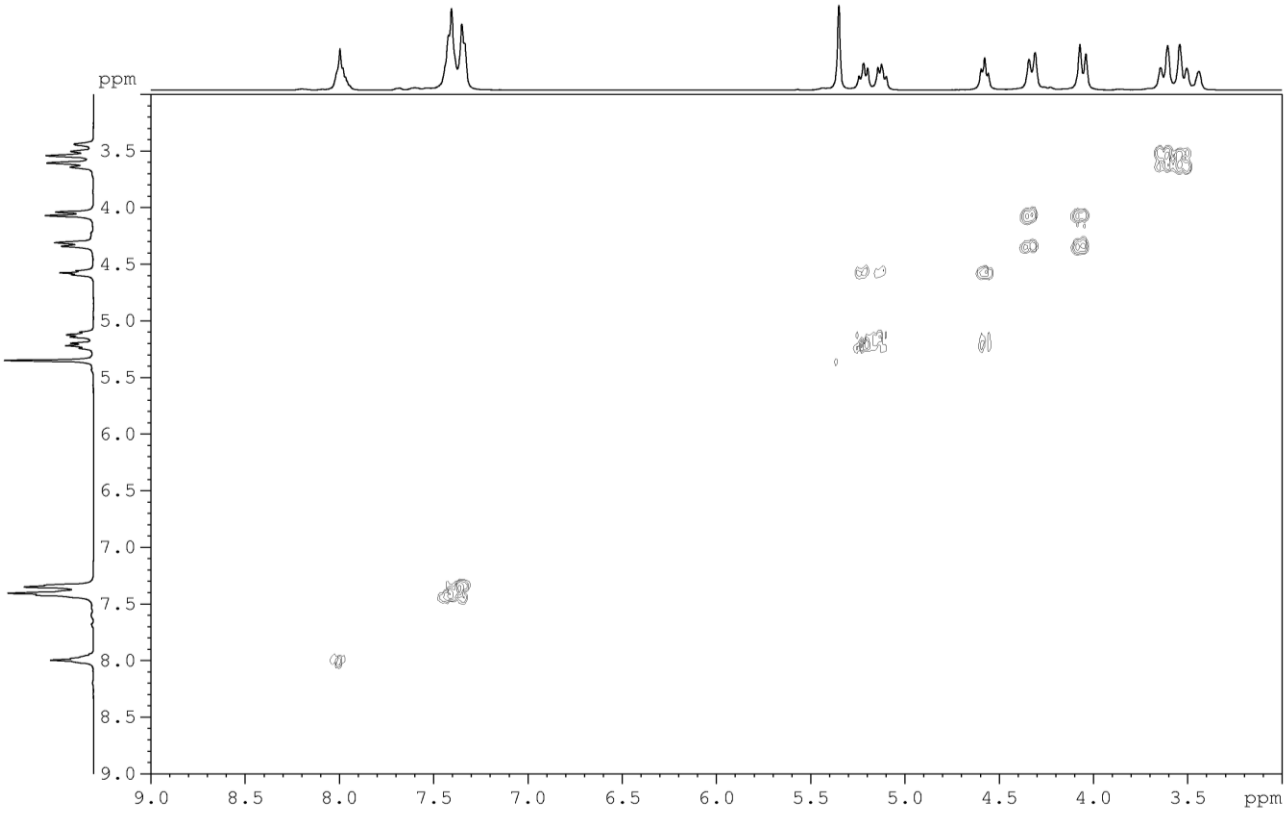
^{31}P NMR spectrum (CD_2Cl_2, 298 K, NAV400) of complex **1a**



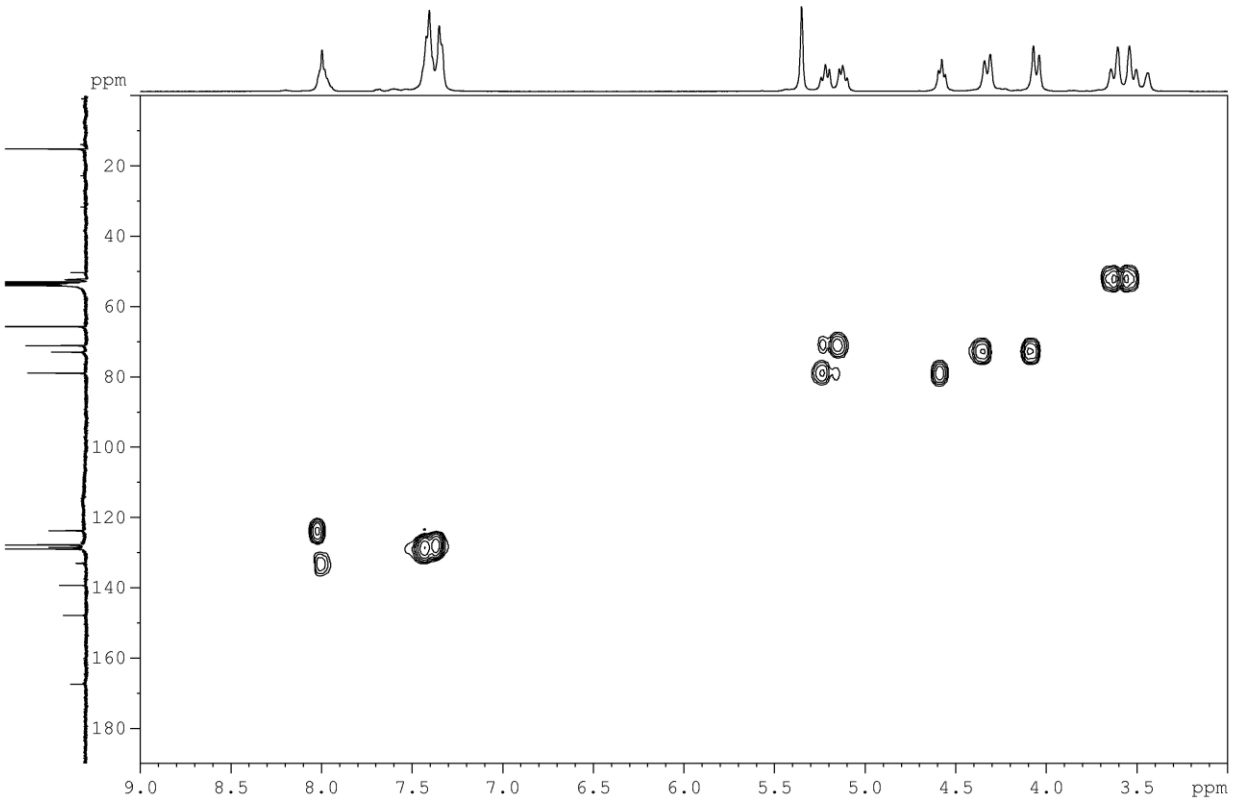
^{13}C NMR spectrum (CD_2Cl_2, 298 K, NAV400) of complex **1a**



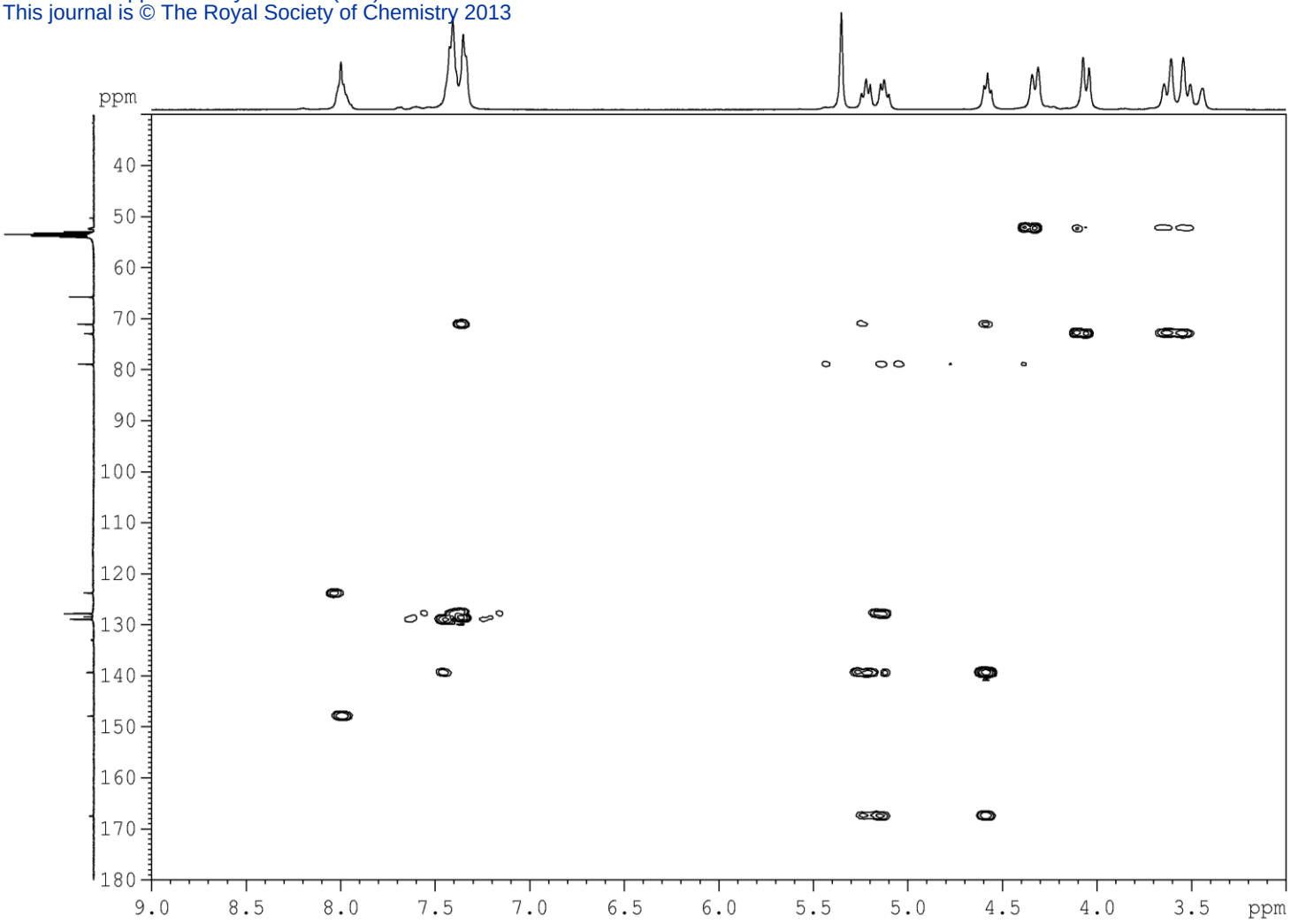
DEPT-135 NMR spectrum (CD_2Cl_2, 298 K, NAV400) of complex **1a**



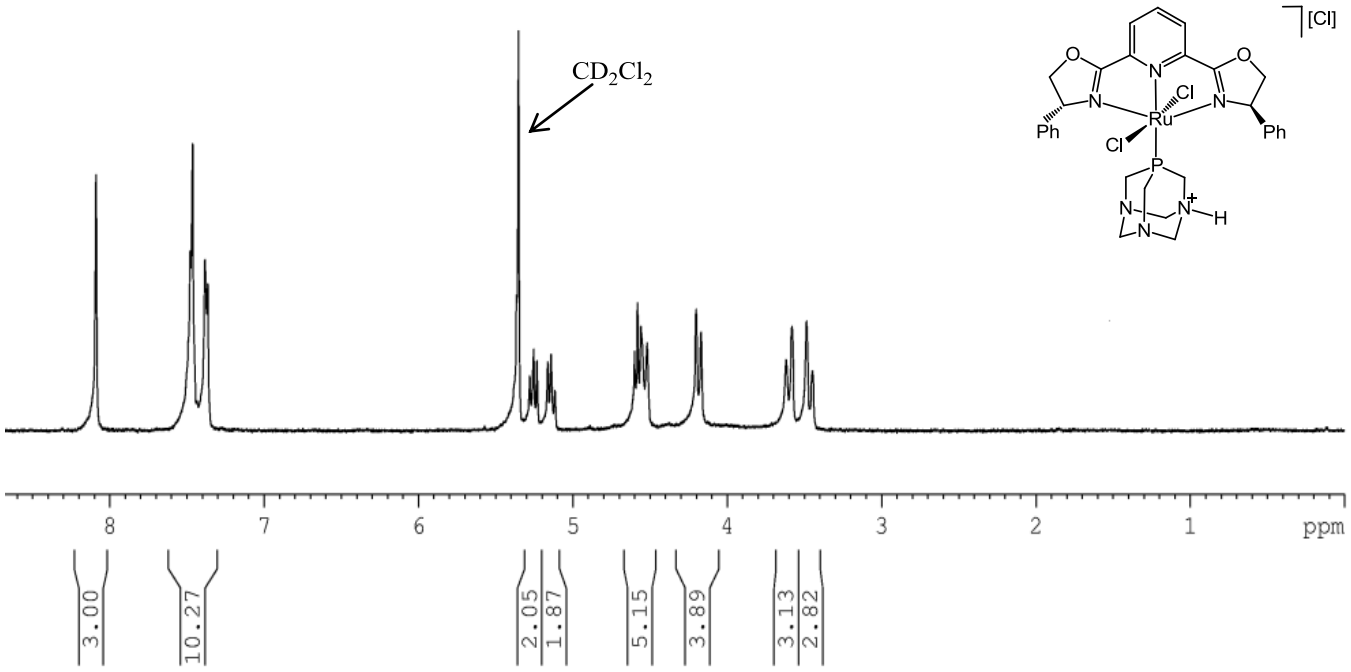
COSY HH NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **1a**



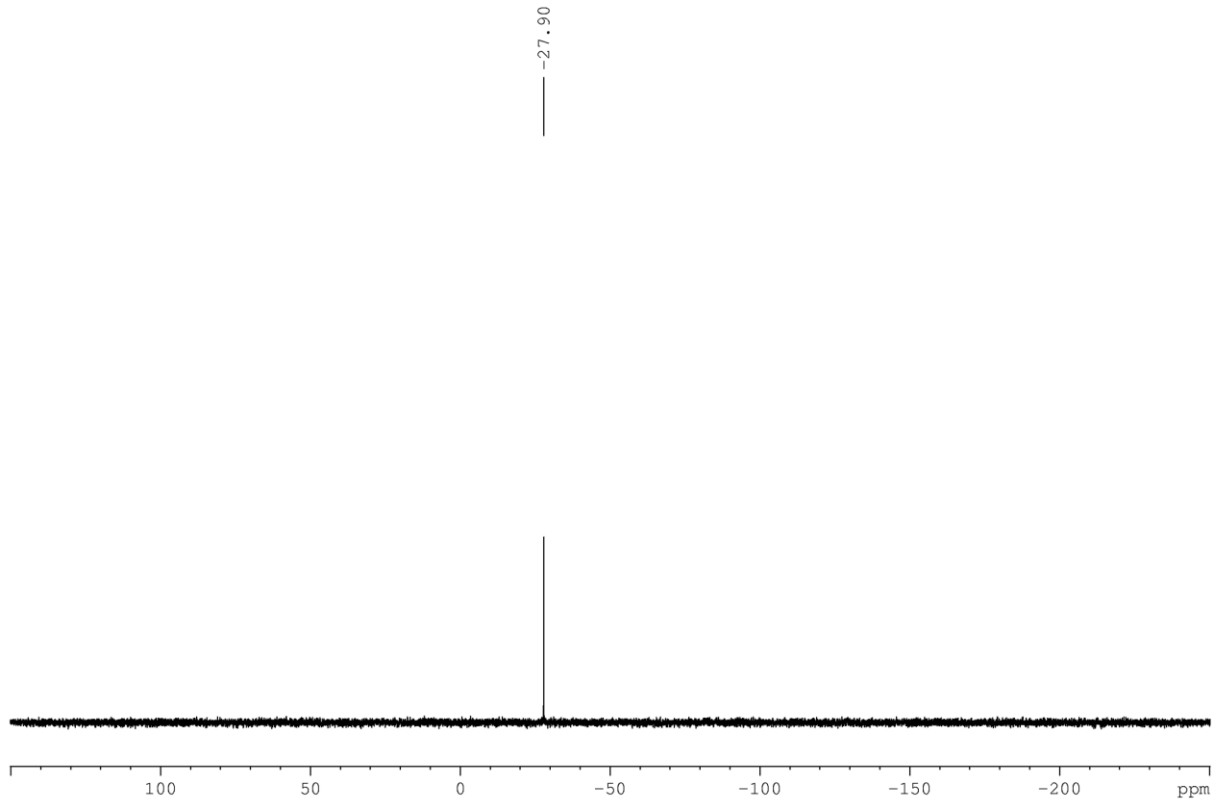
HSQC NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **1a**



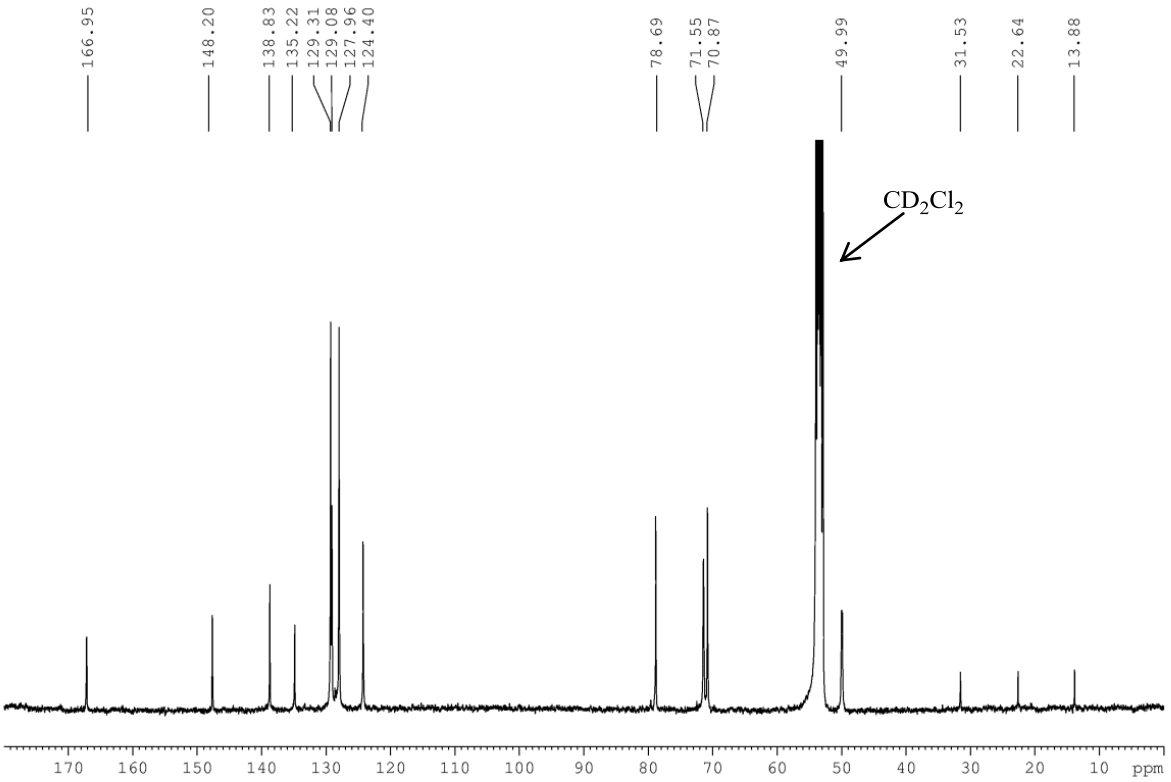
HMBC NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **1a**



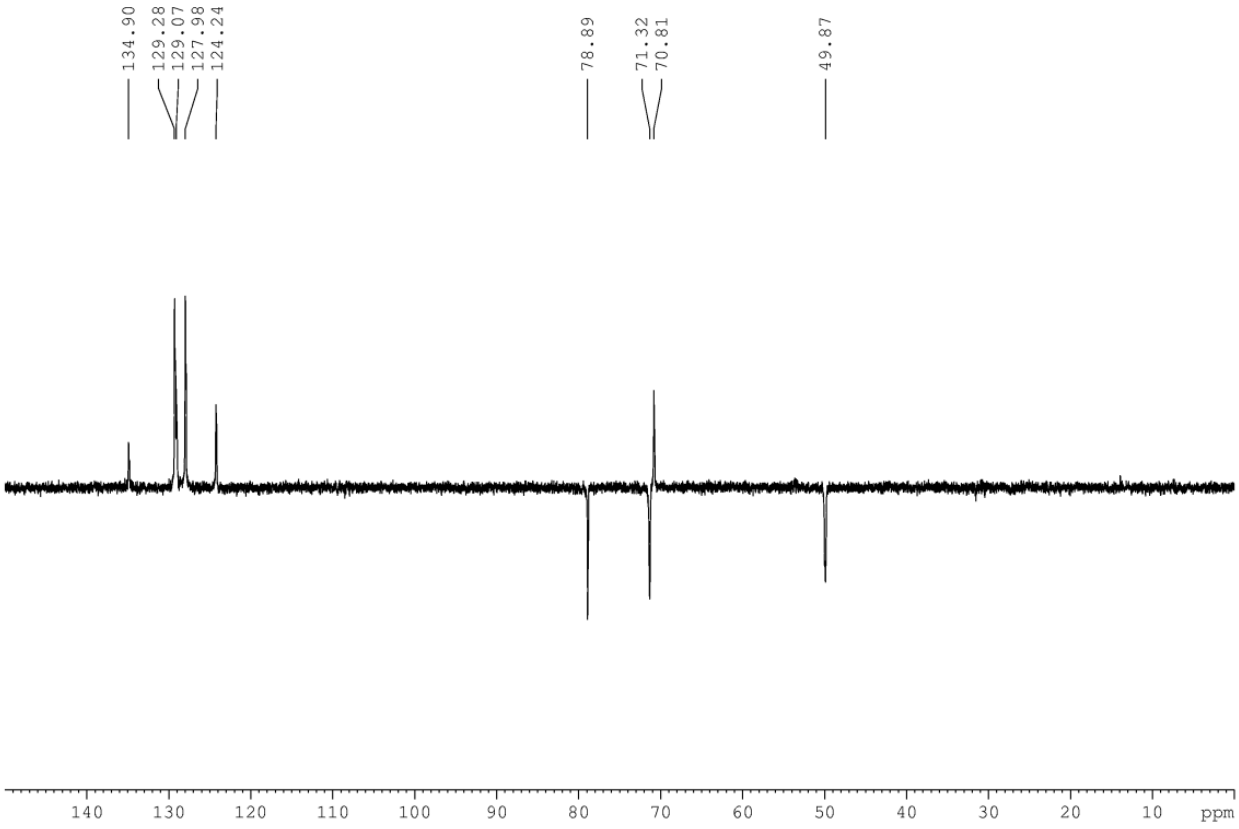
^{1}H NMR spectrum (CD_2Cl_2, 298 K, NAV400) of complex **2a**



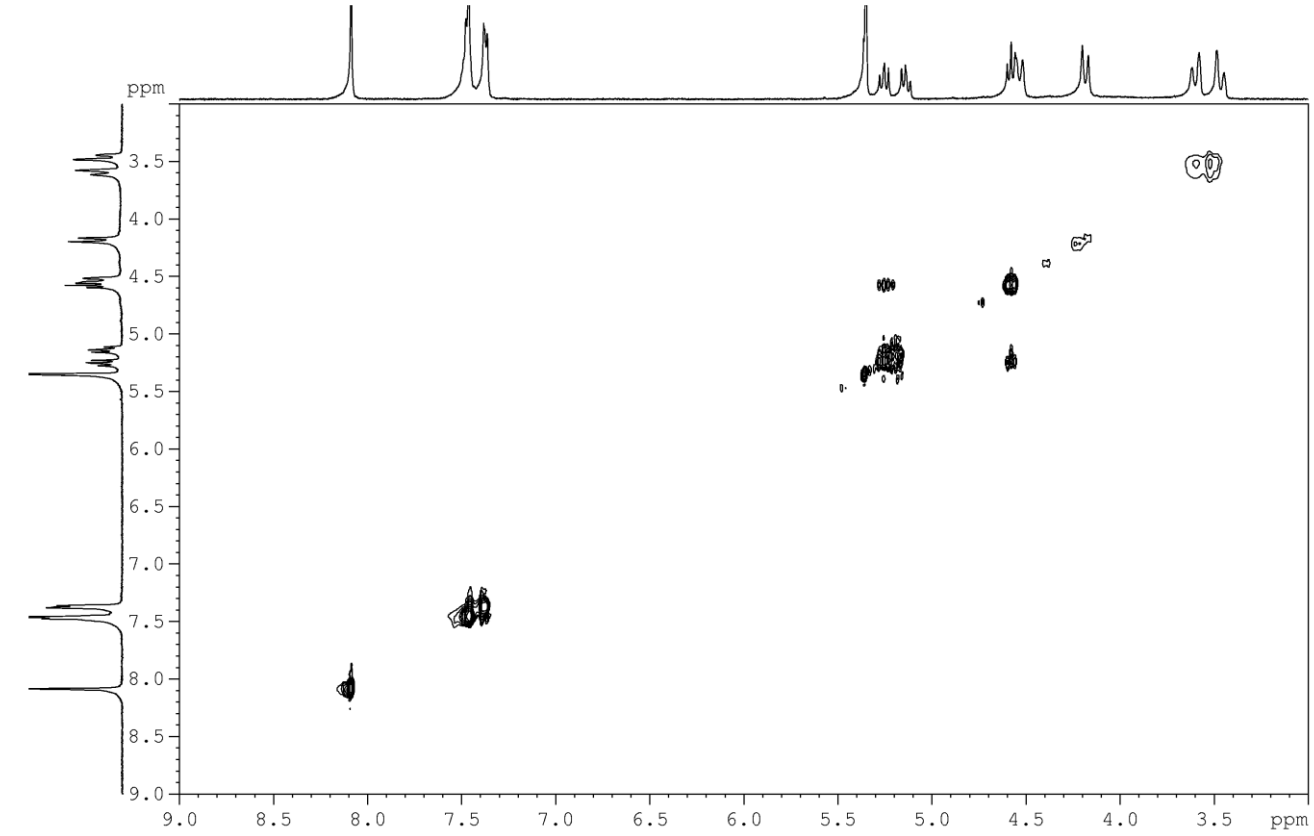
^{31}P NMR spectrum (CD_2Cl_2, 298 K, NAV400) of complex **2a**



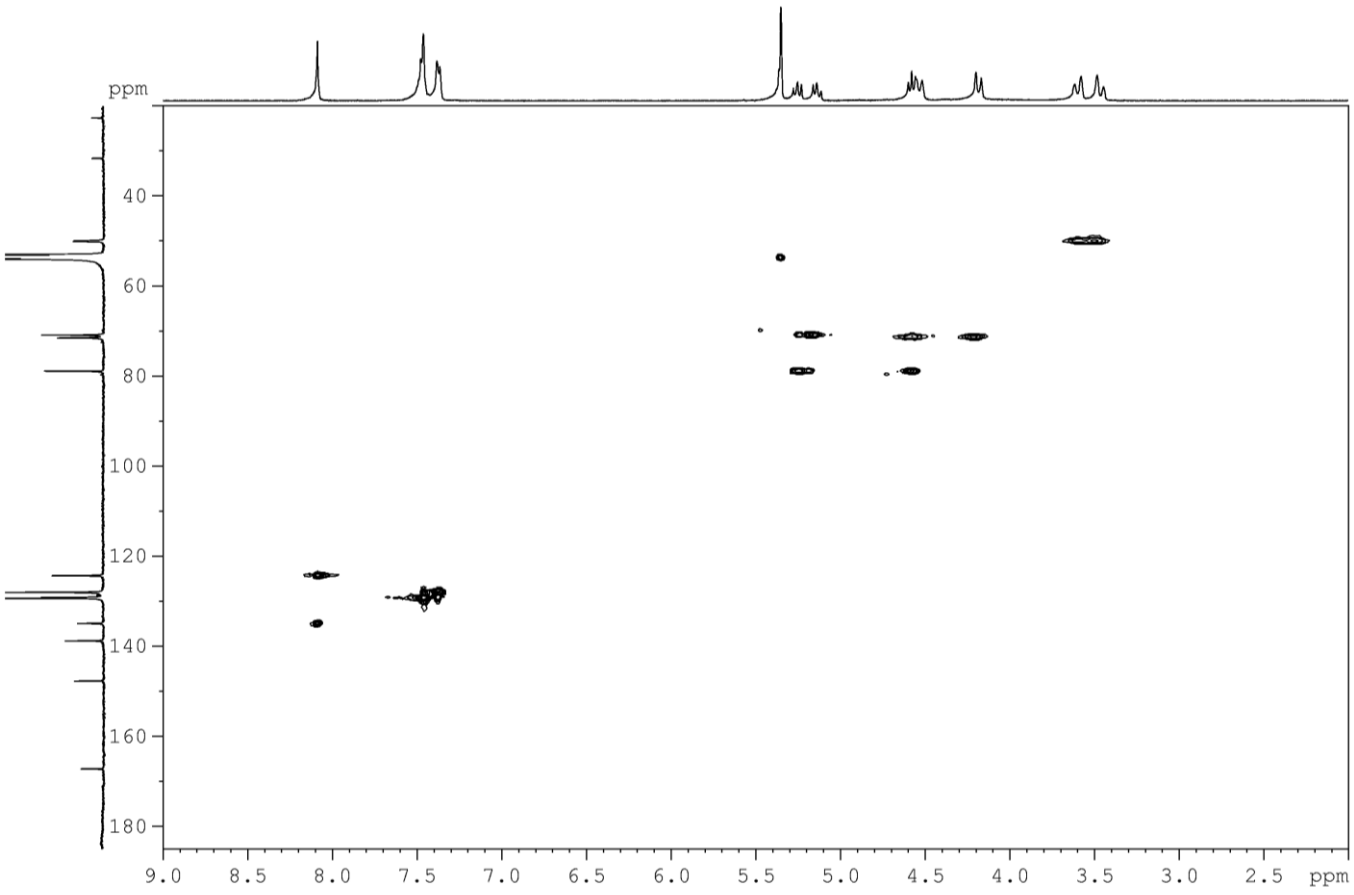
^{13}C NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **2a**



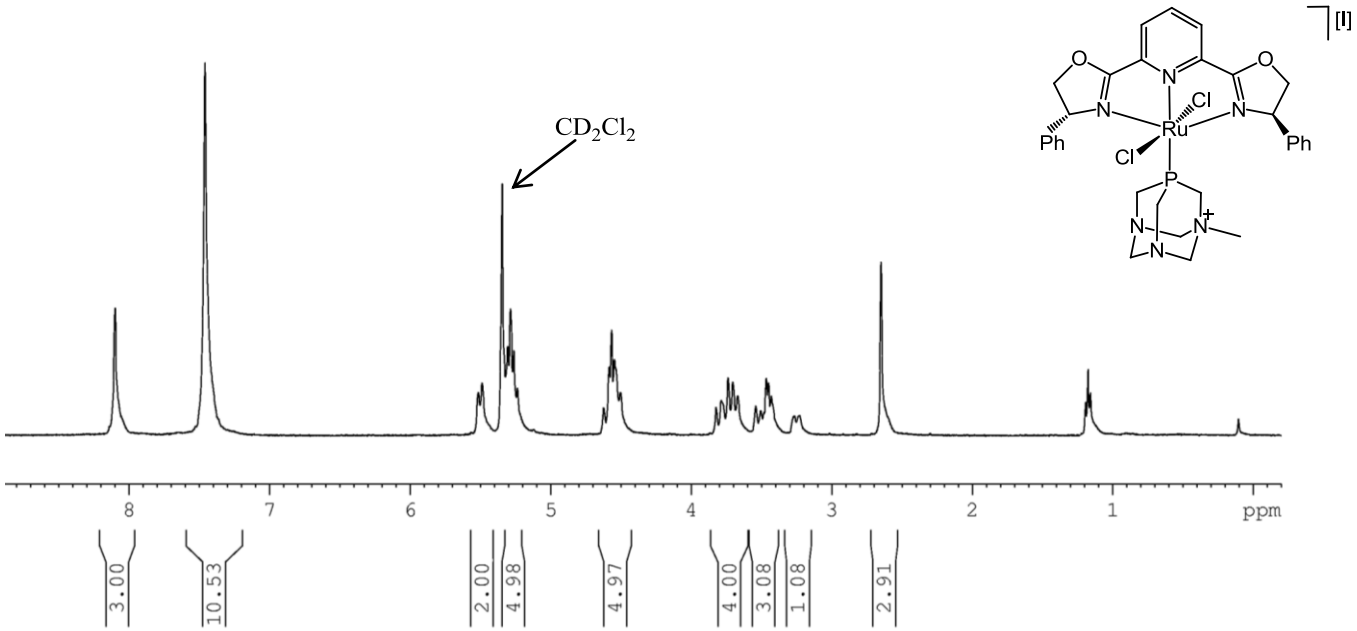
DEPT135- NMR spectrum (CD_2Cl_2, 298 K, NAV400) of complex **2a**



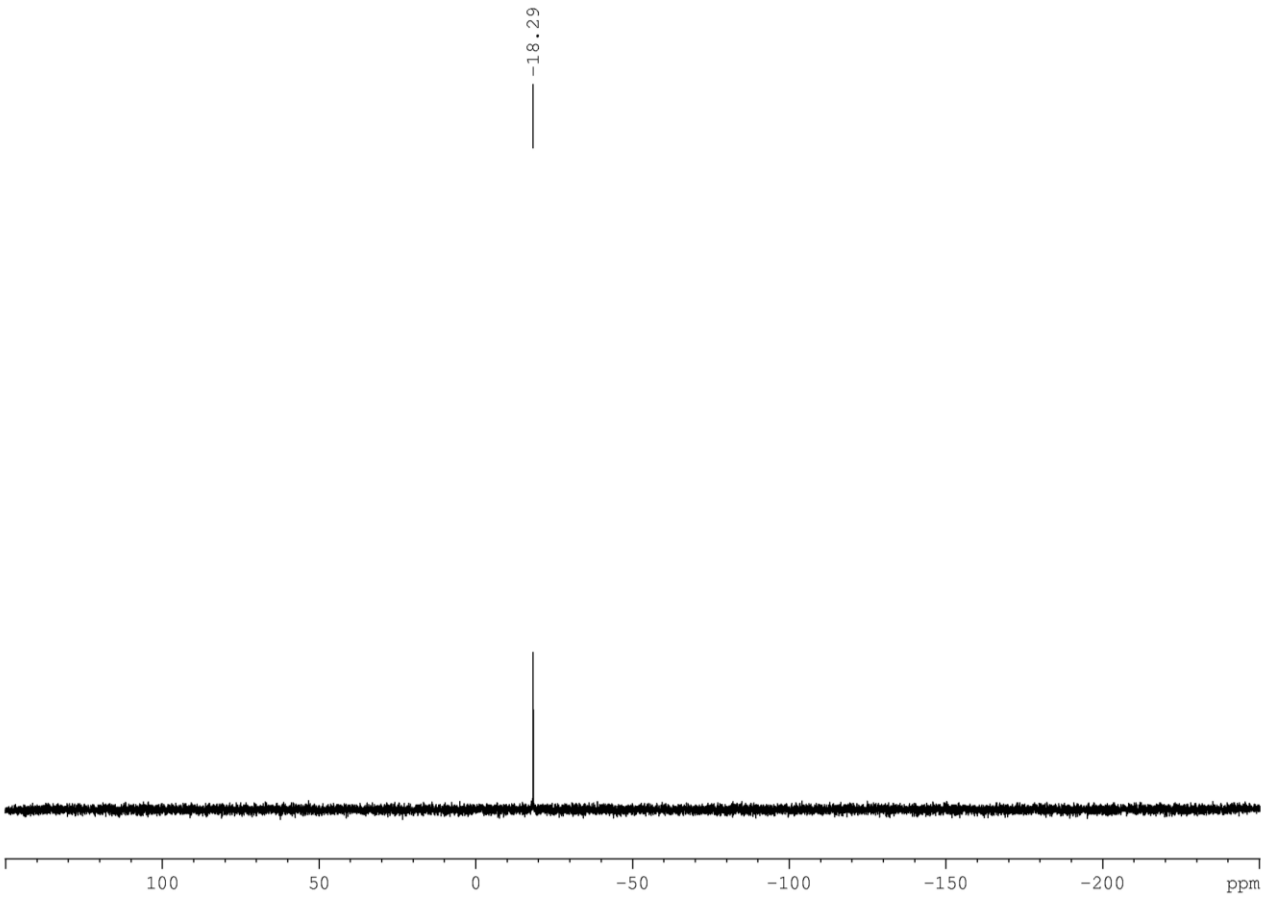
COSY HH NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **2a**



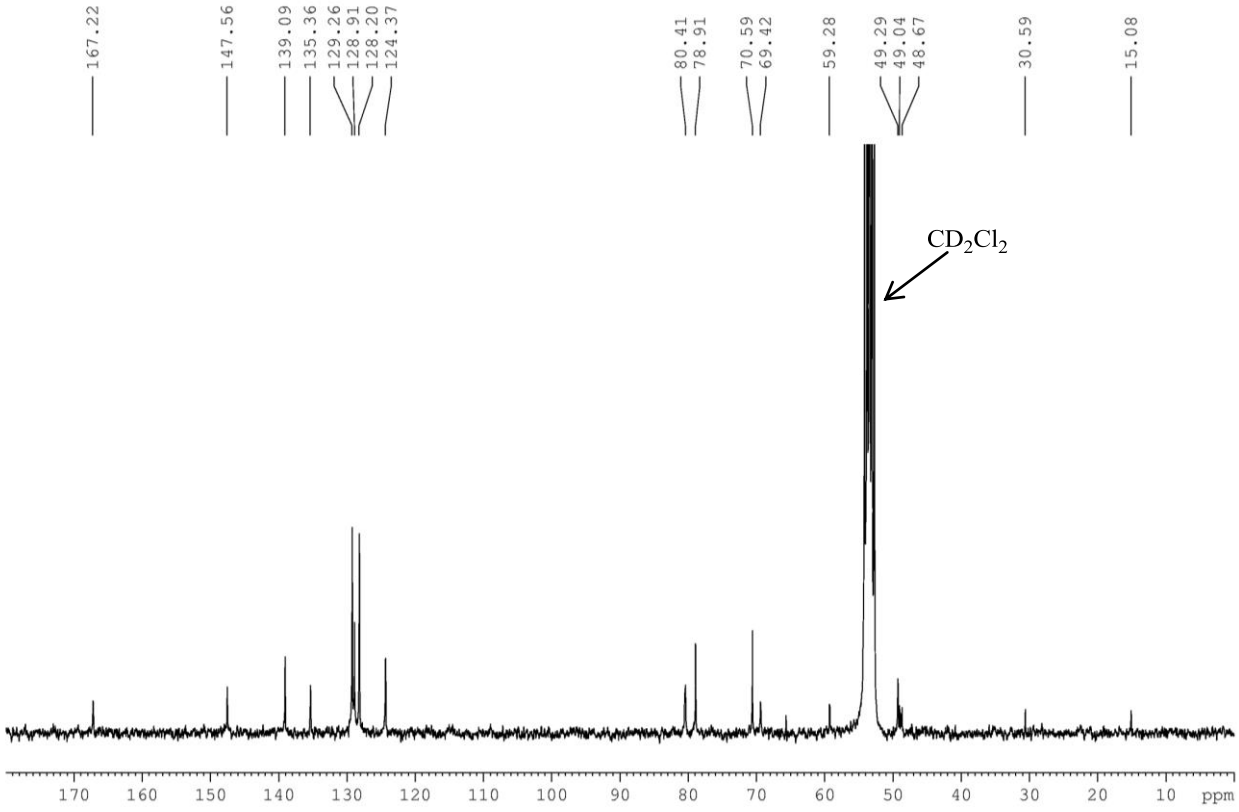
HSQC NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **2a**



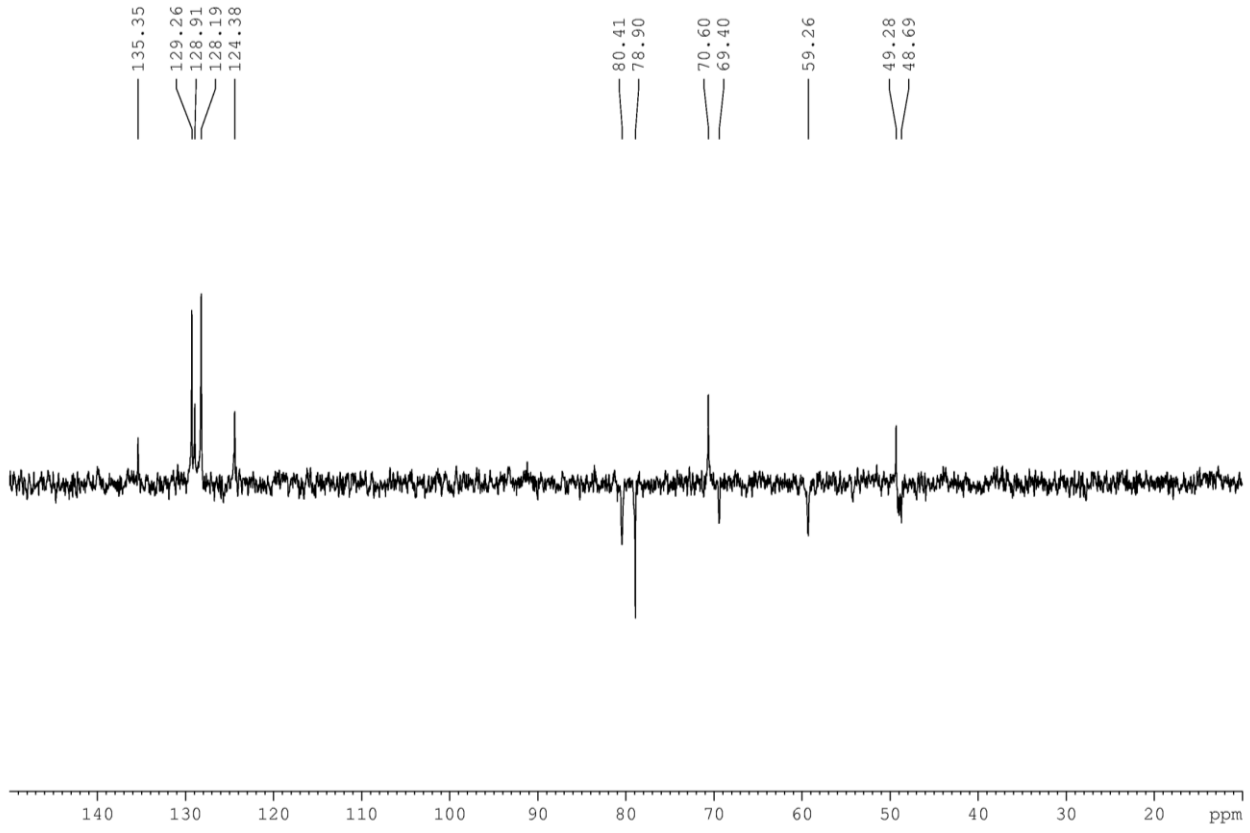
^{1}H NMR spectrum (CD_2Cl_2, 298 K, NAV400) of complex **3a**



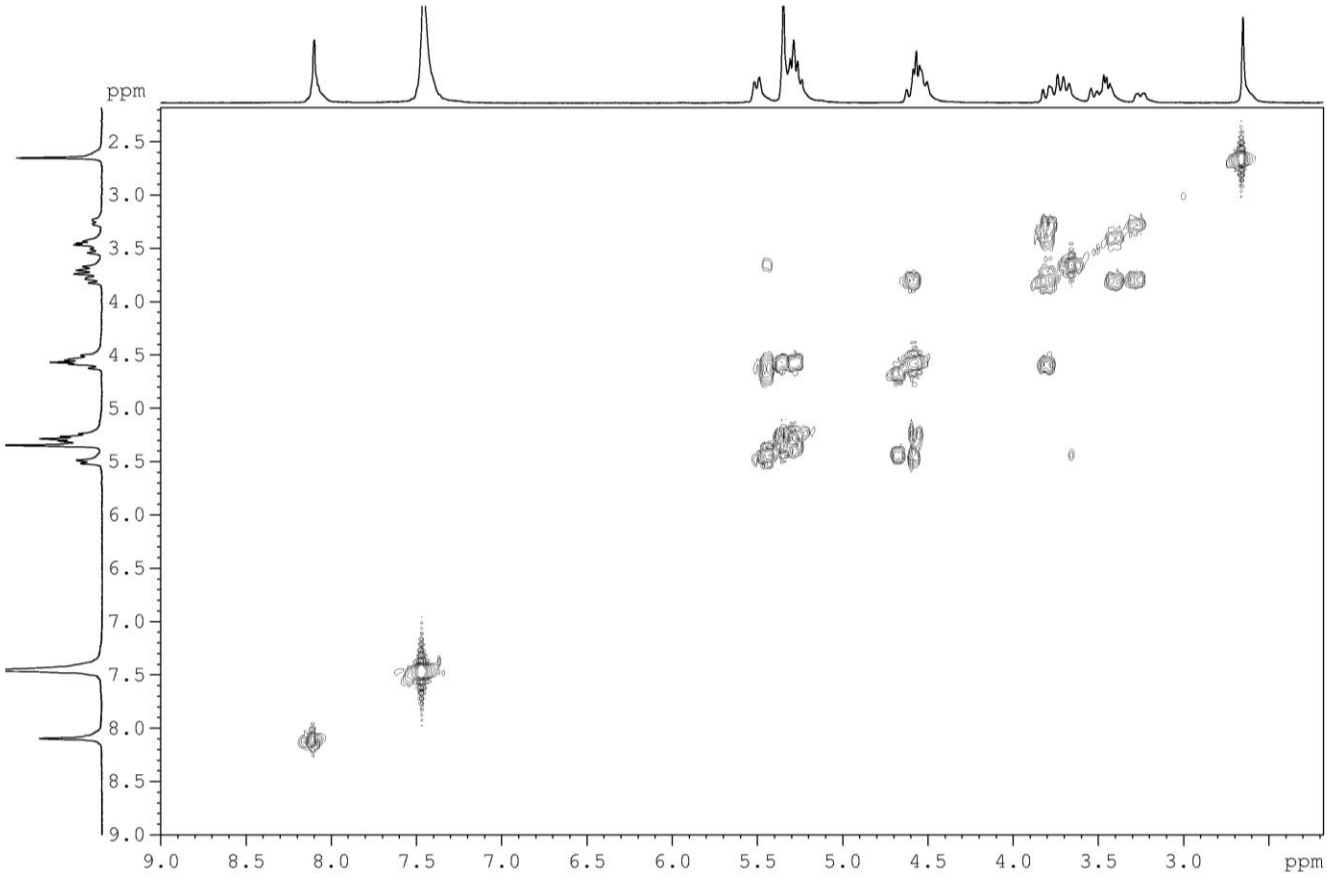
^{31}P NMR spectrum (CD_2Cl_2, 298 K, NAV400) of complex **3a**



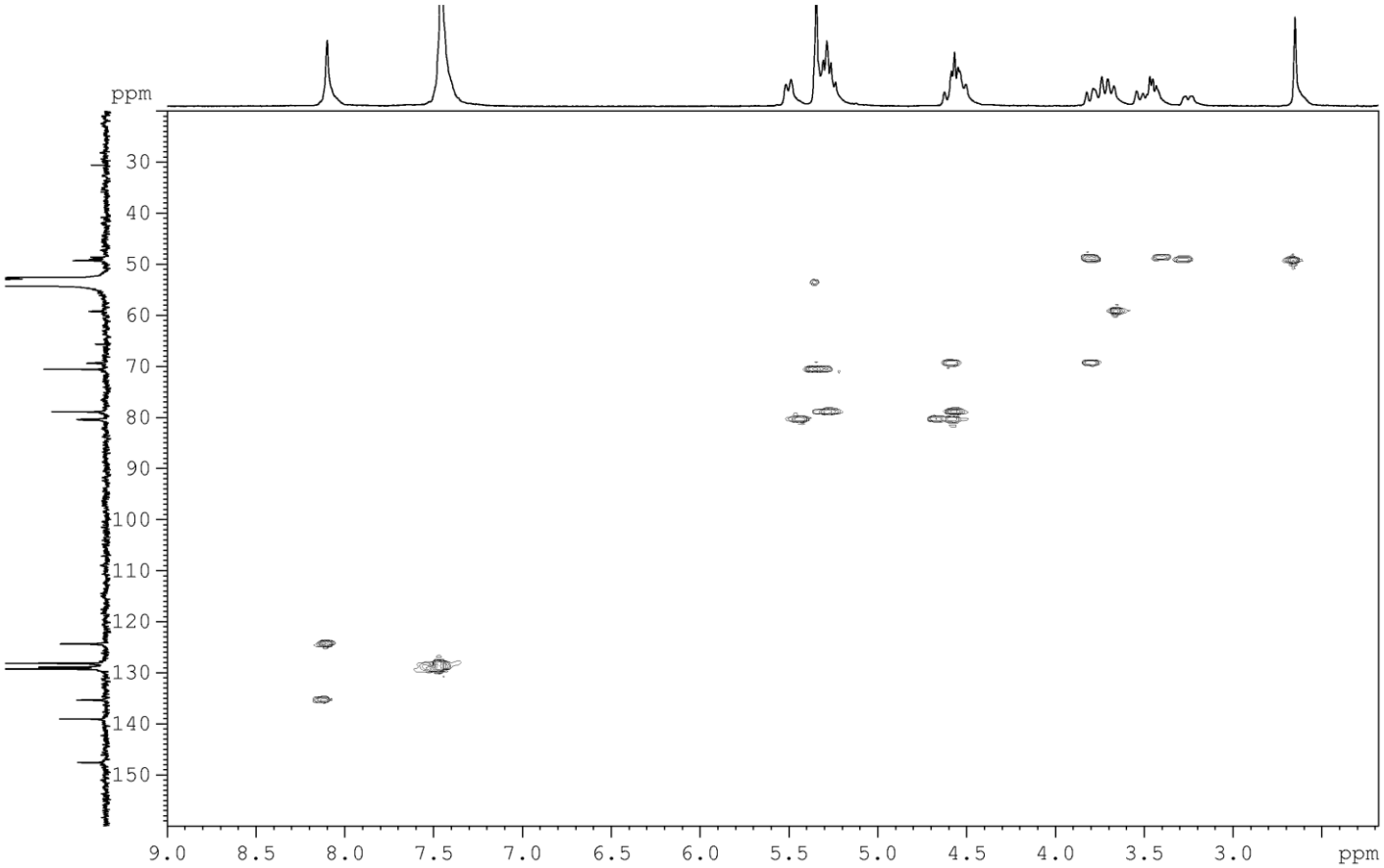
^{13}C NMR spectrum (CD_2Cl_2, 298 K, AV300) of complex **3a**



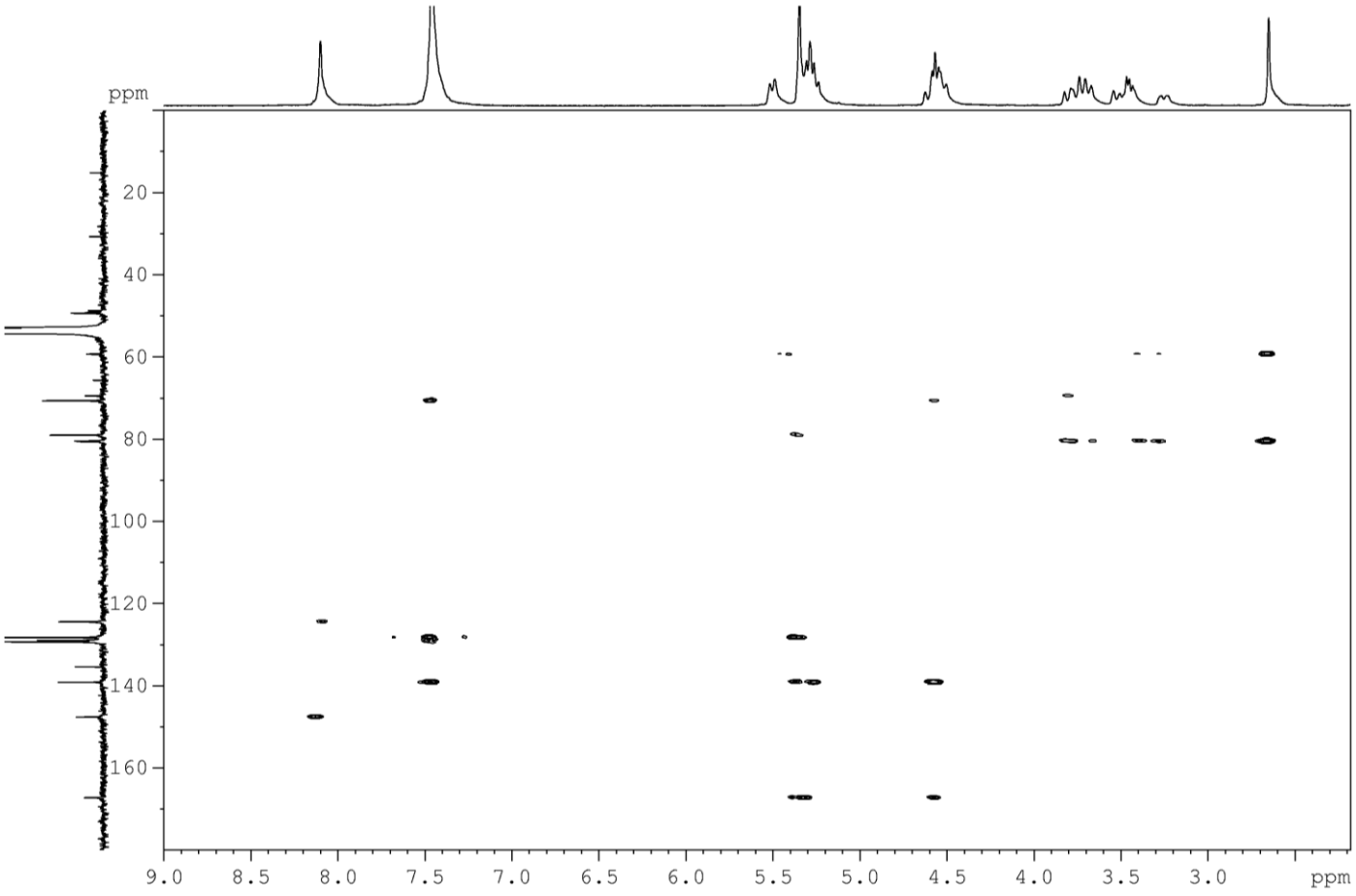
DEPT-135 NMR spectrum (CD_2Cl_2, 298 K, AV300) of complex **3a**



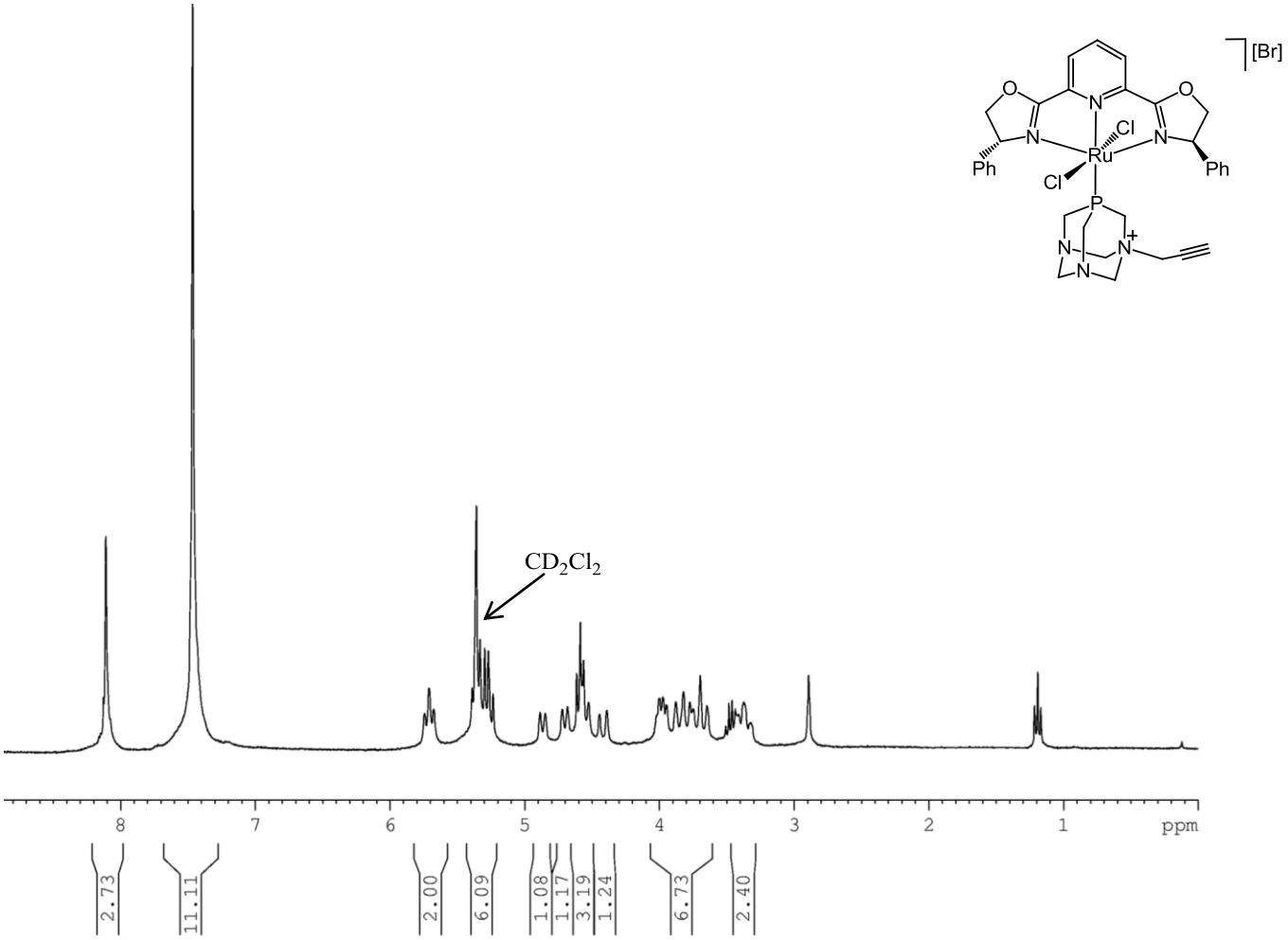
COSY HH NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **3a**



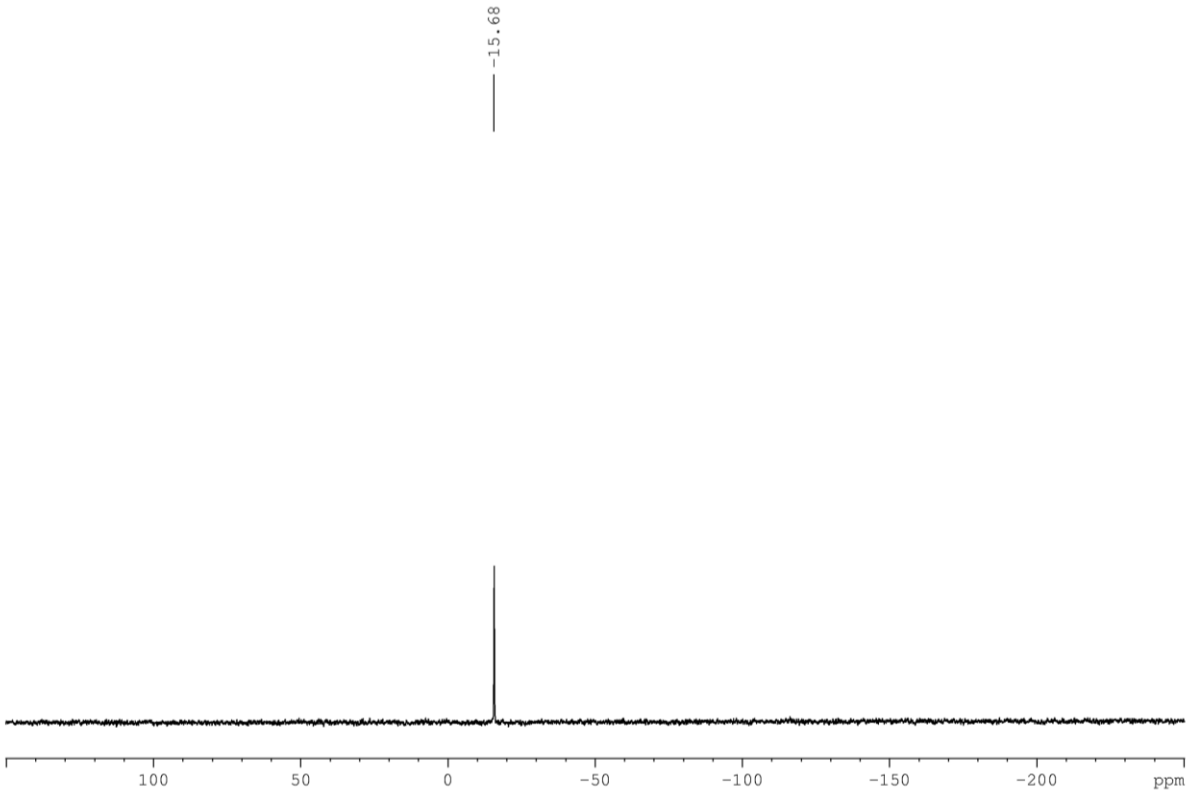
HSQC NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **3a**



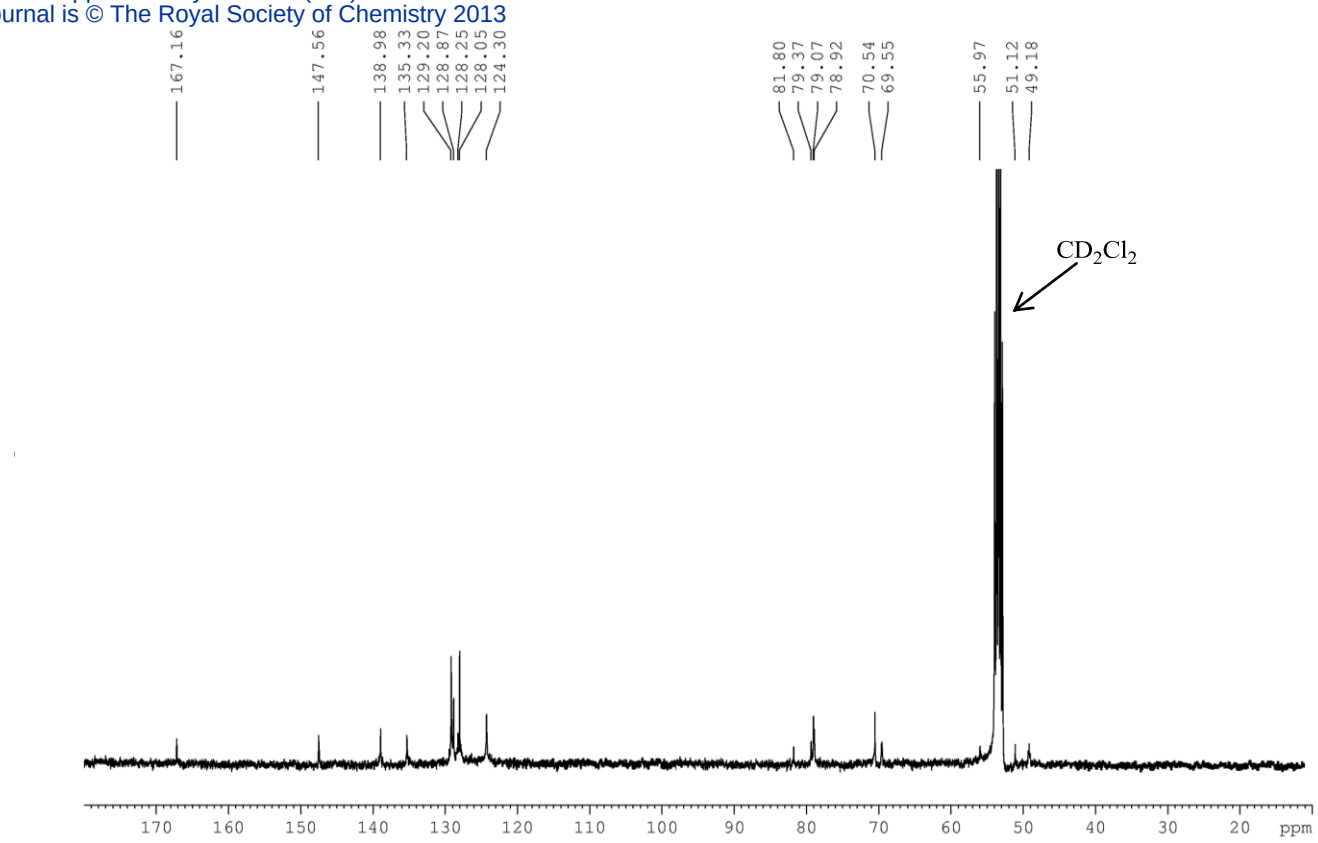
HMBC NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **3a**



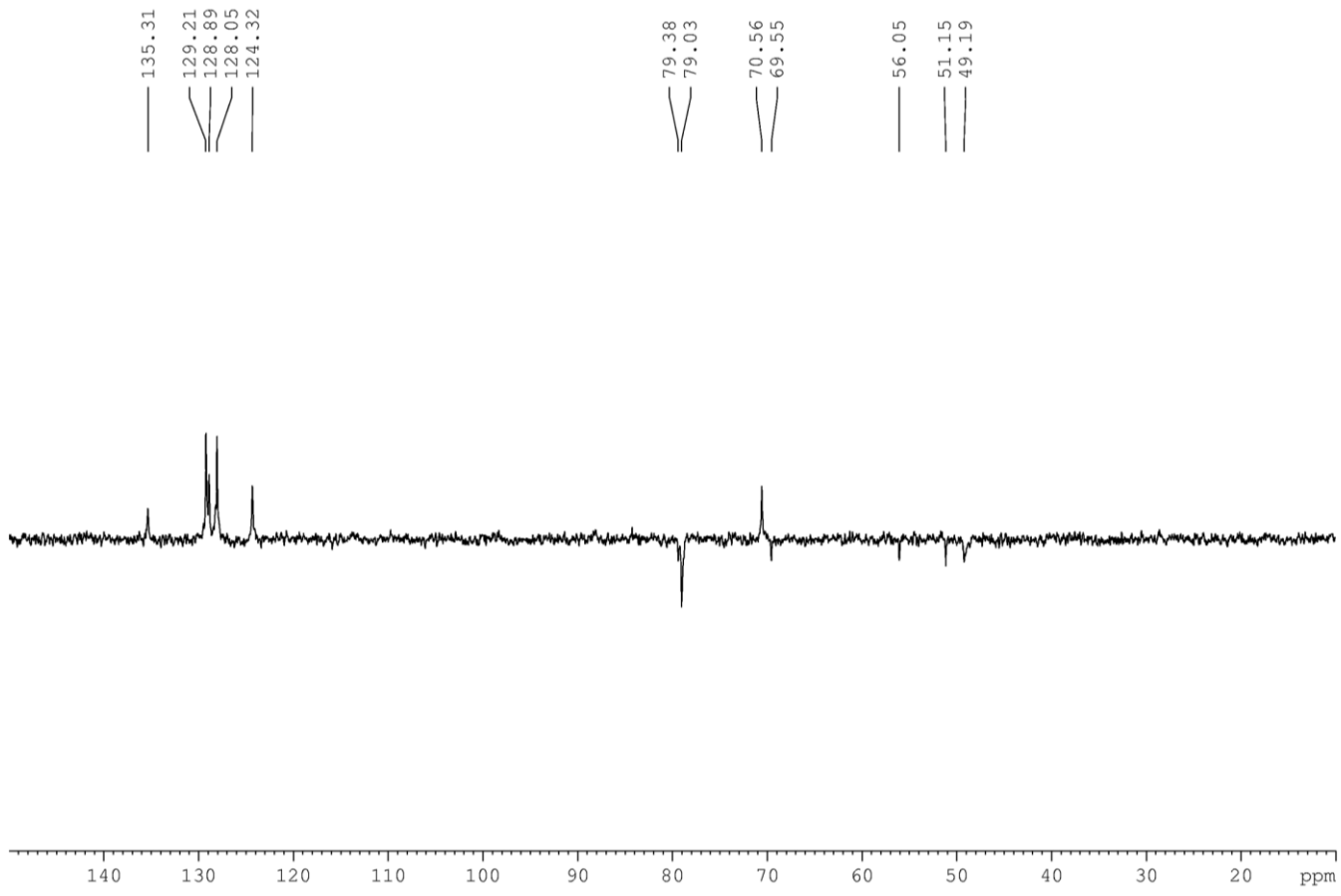
^{1}H NMR spectrum (CD_2Cl_2, 298 K, AV300) of complex **5a**



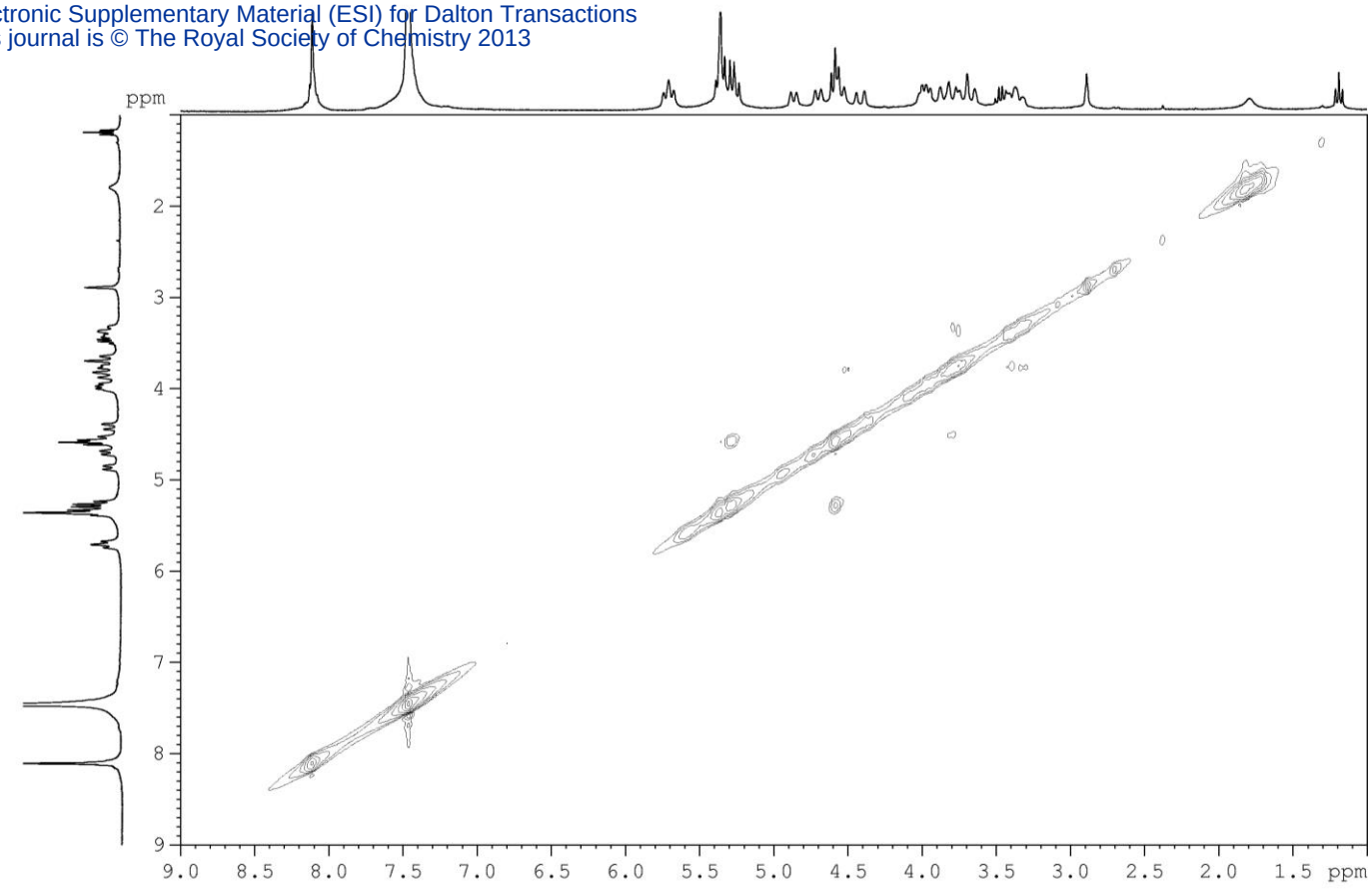
^{31}P NMR spectrum (CD_2Cl_2, 298 K, AV300) of complex **5a**



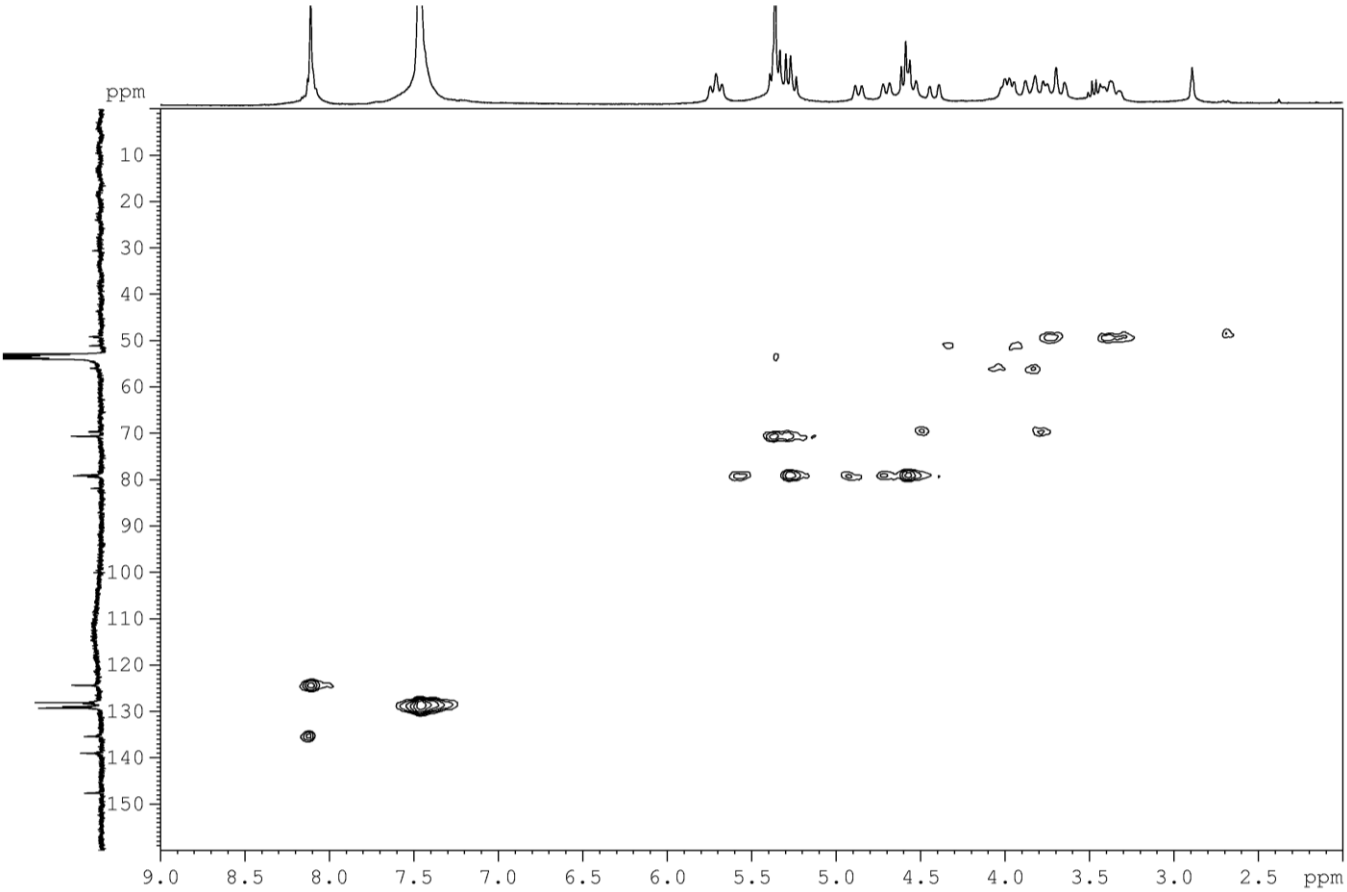
^{13}C NMR spectrum (CD_2Cl_2, 298 K, NAV400) of complex **5a**



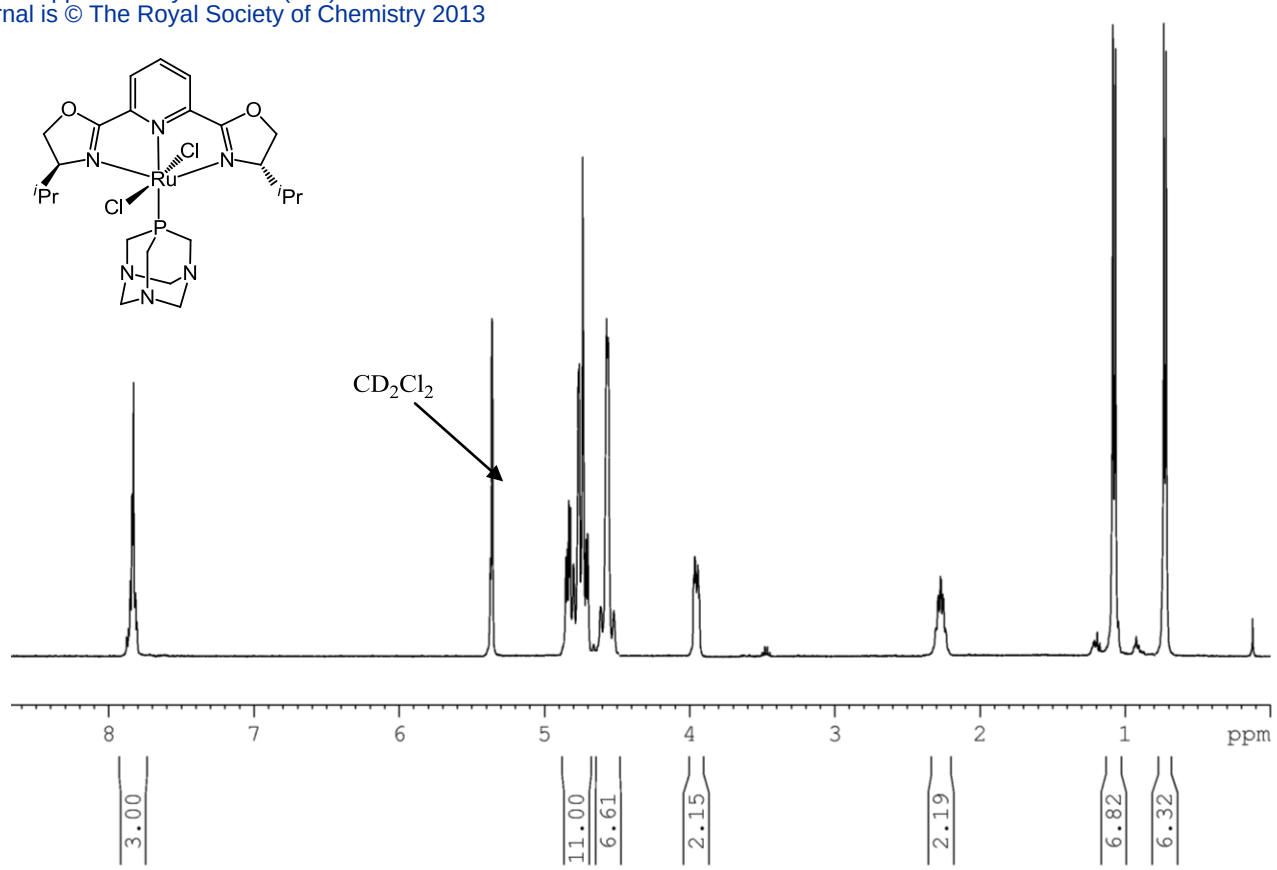
DEPT-135 NMR spectrum (CD_2Cl_2, 298 K, NAV400) of complex **5a**



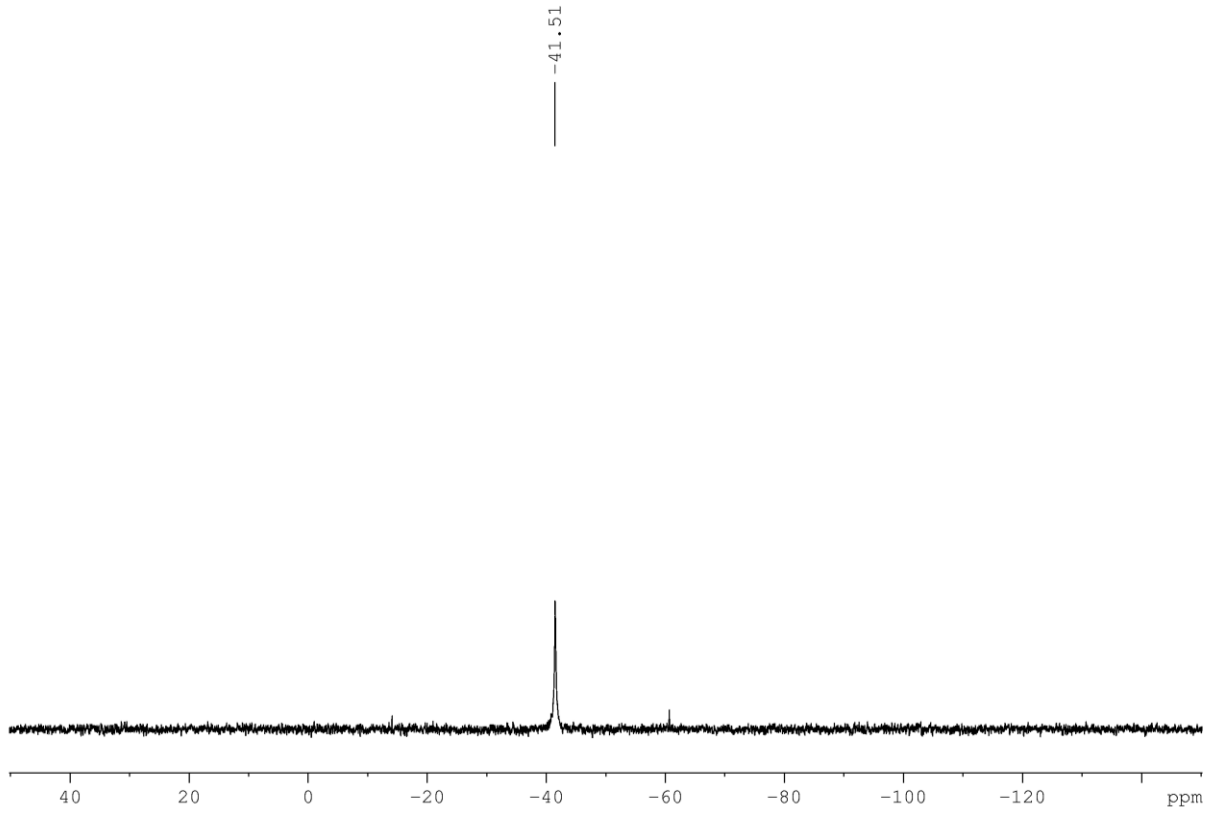
COSY HH NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **5a**



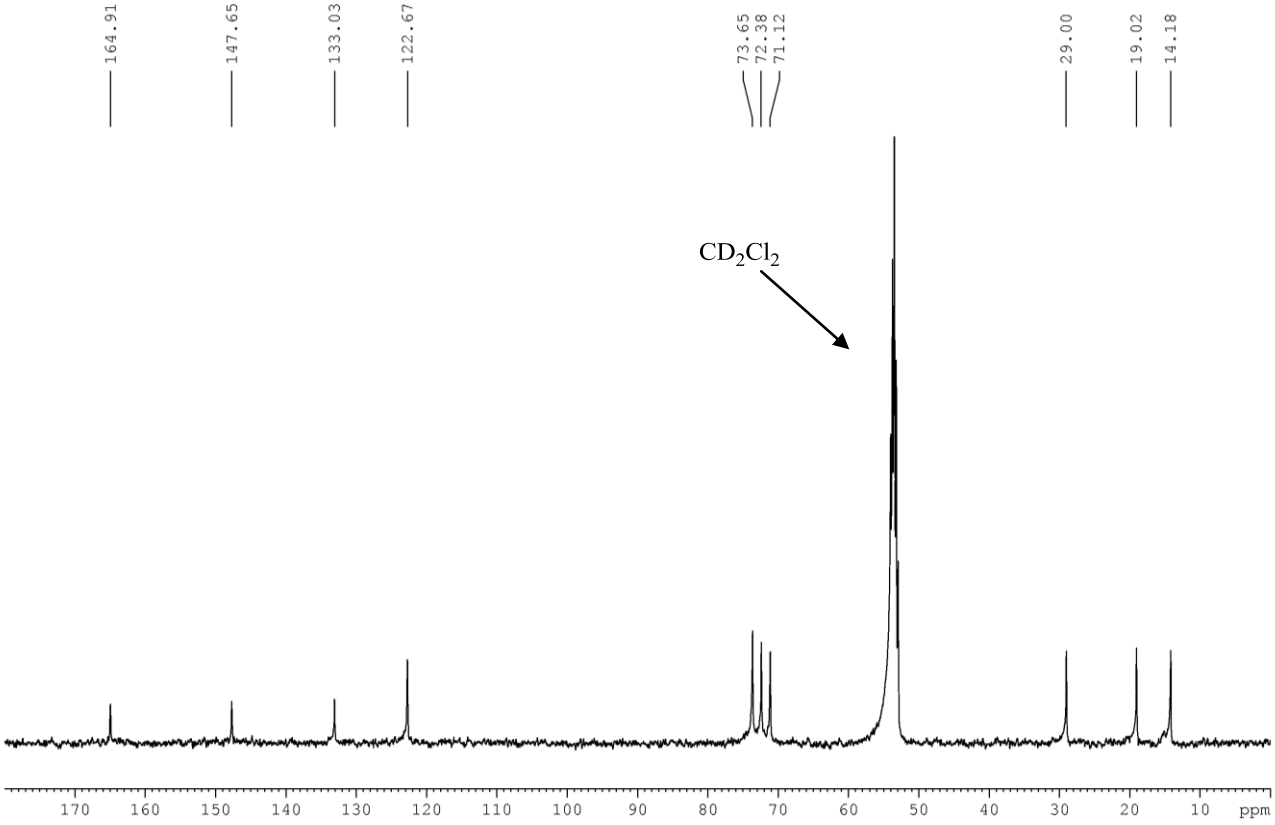
HSQC NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **5a**



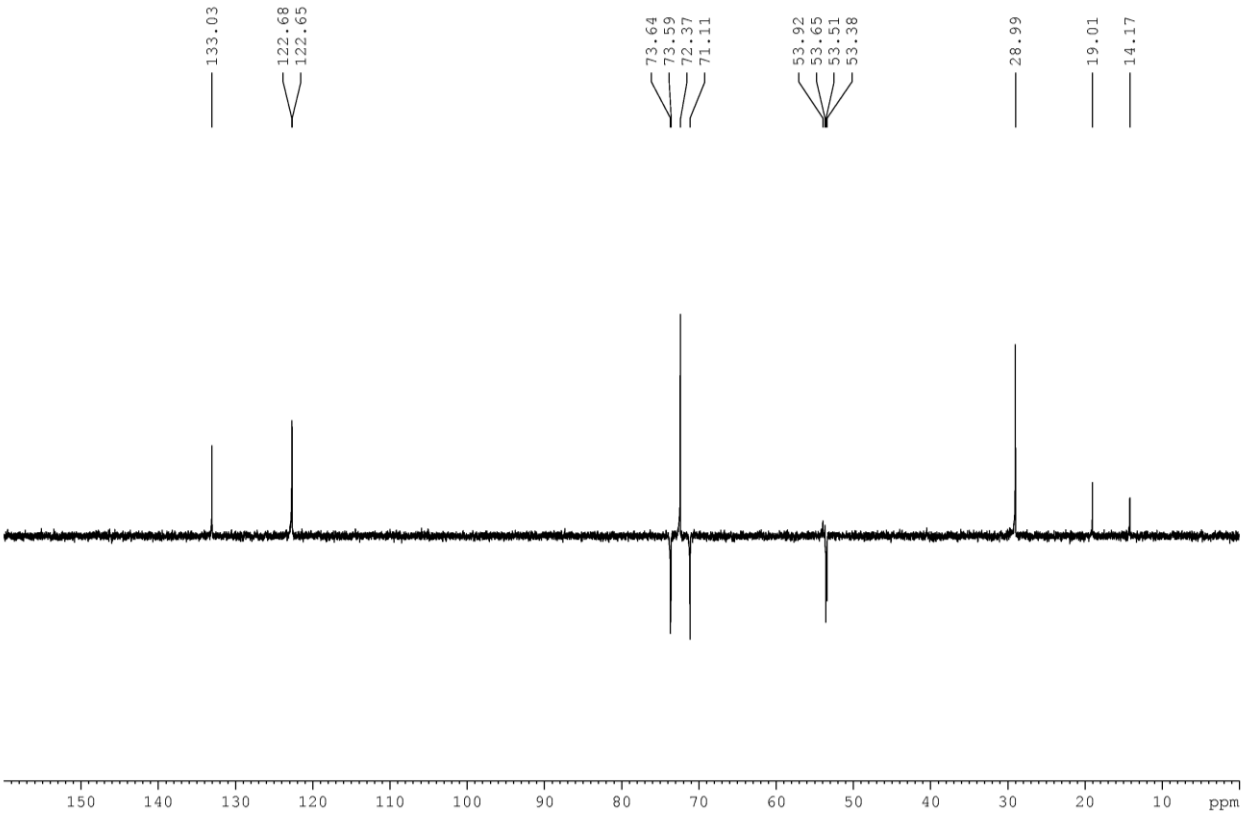
^{1}H NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **1b**



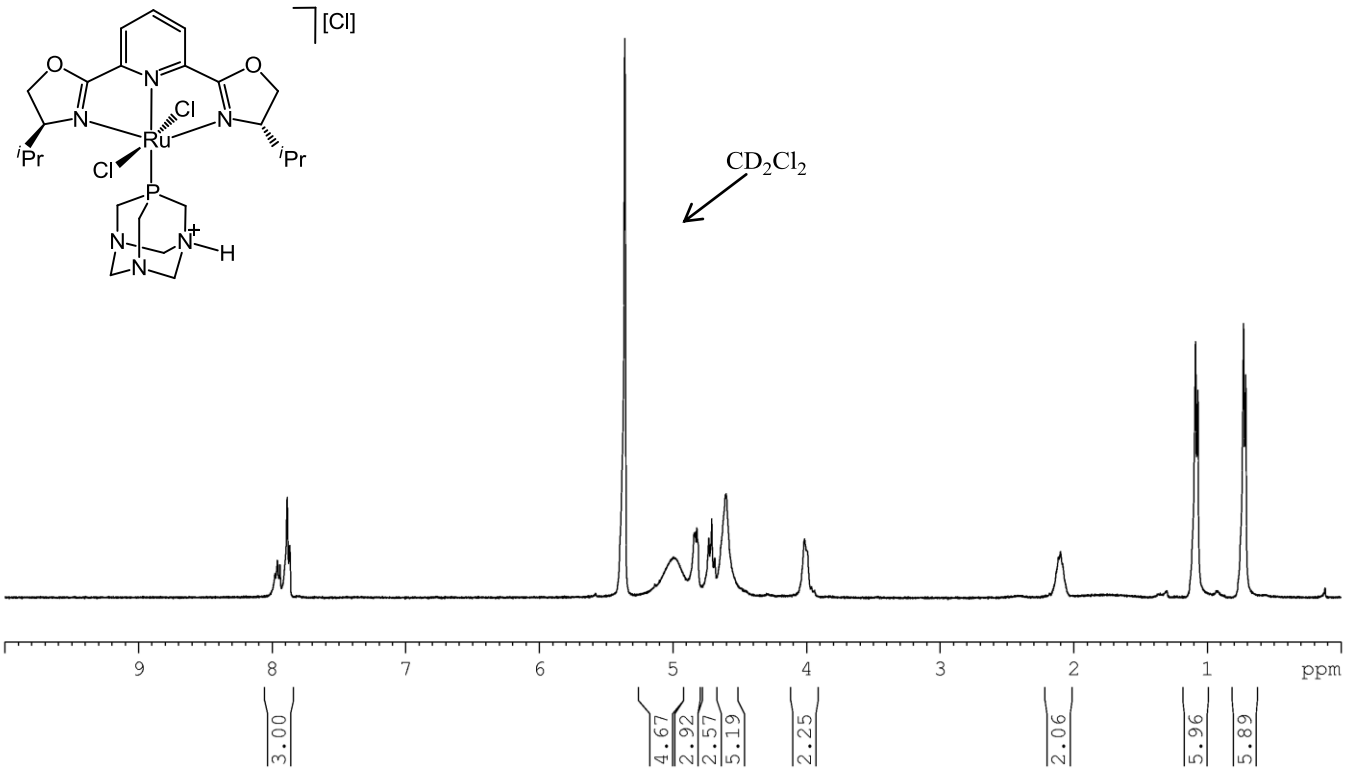
^{31}P NMR spectrum (CD_2Cl_2, 298K, AV400) of complex **1b**



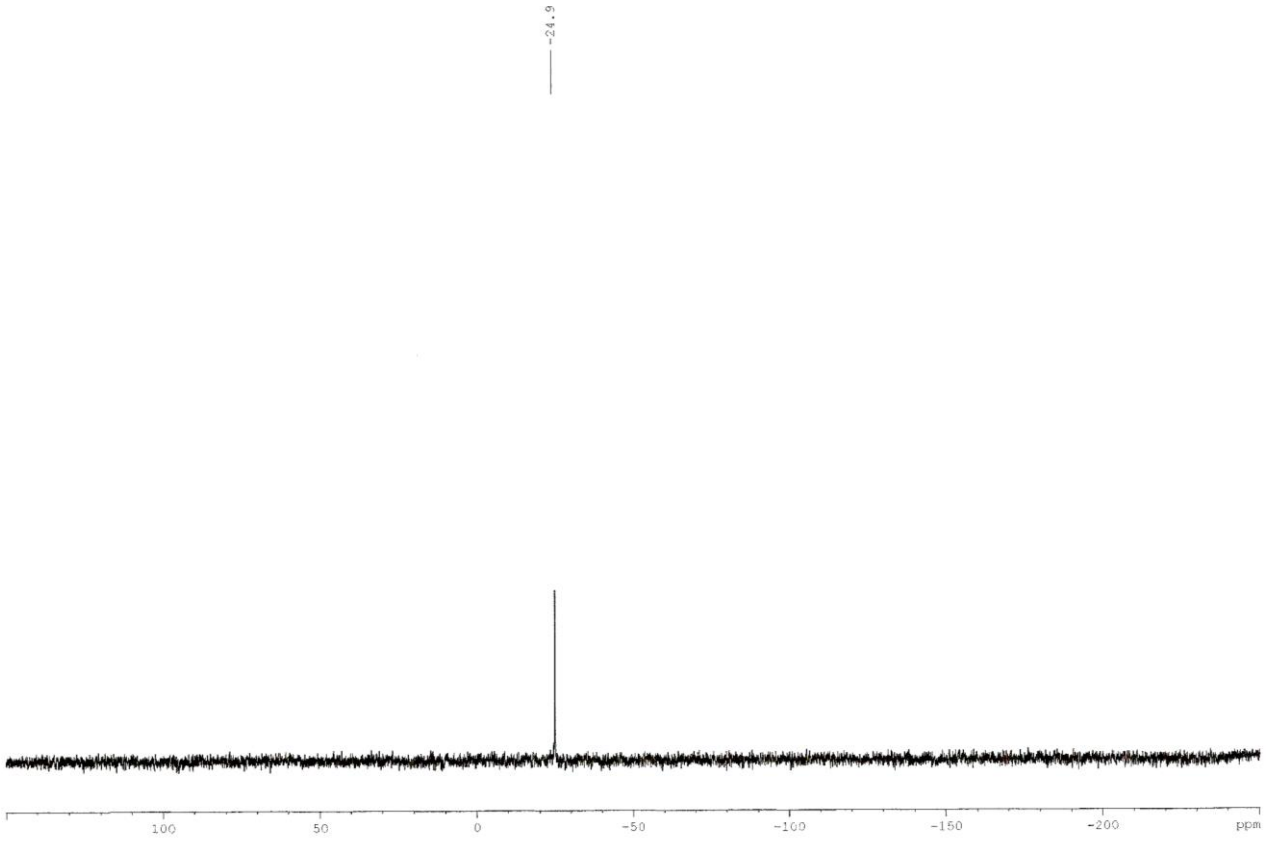
^{13}C NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **1b**



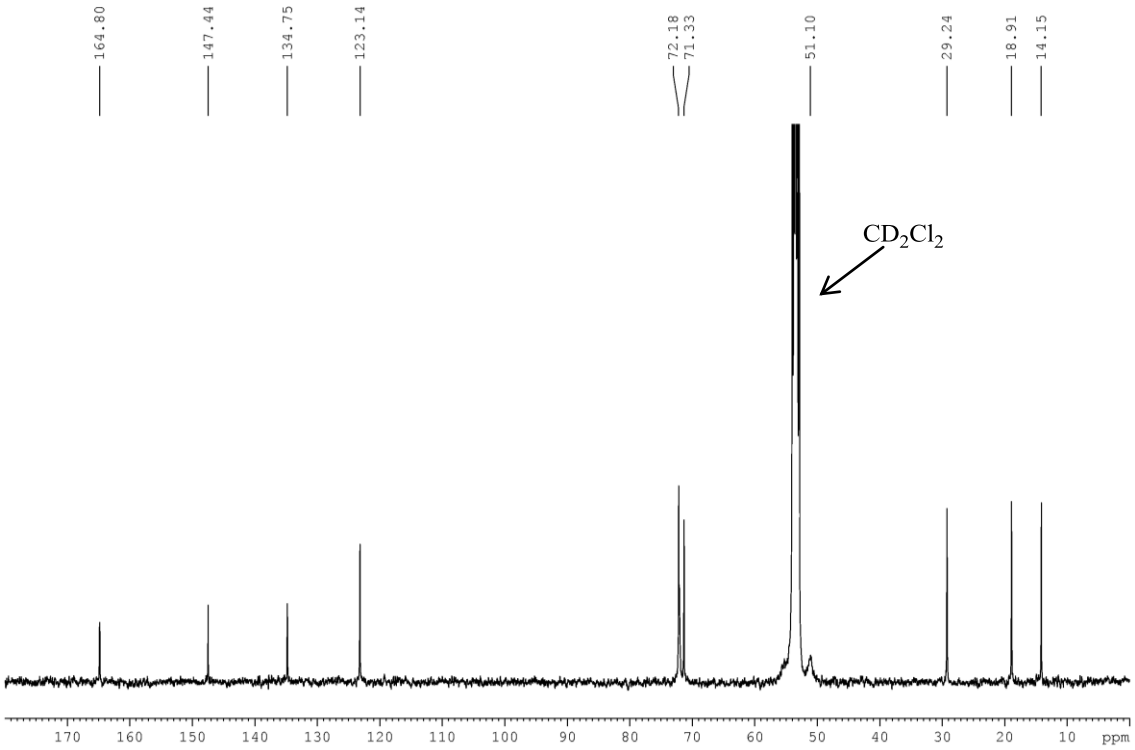
DEPT-135 NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **1b**



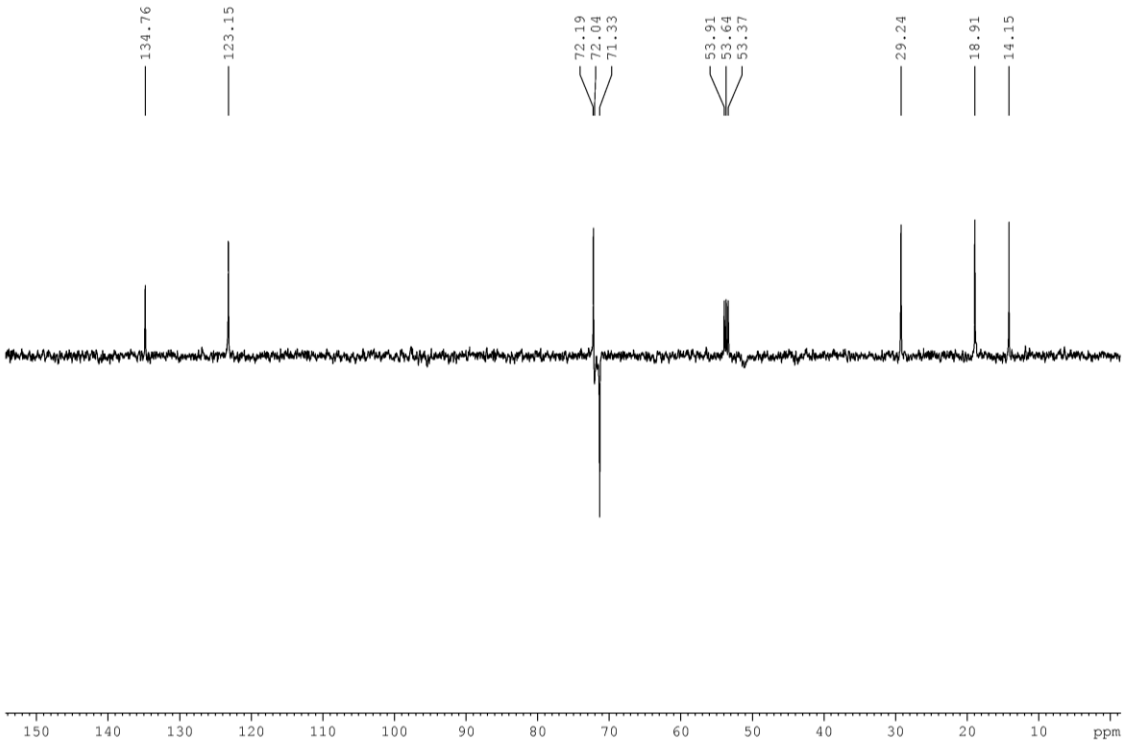
^{1}H NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **2b**



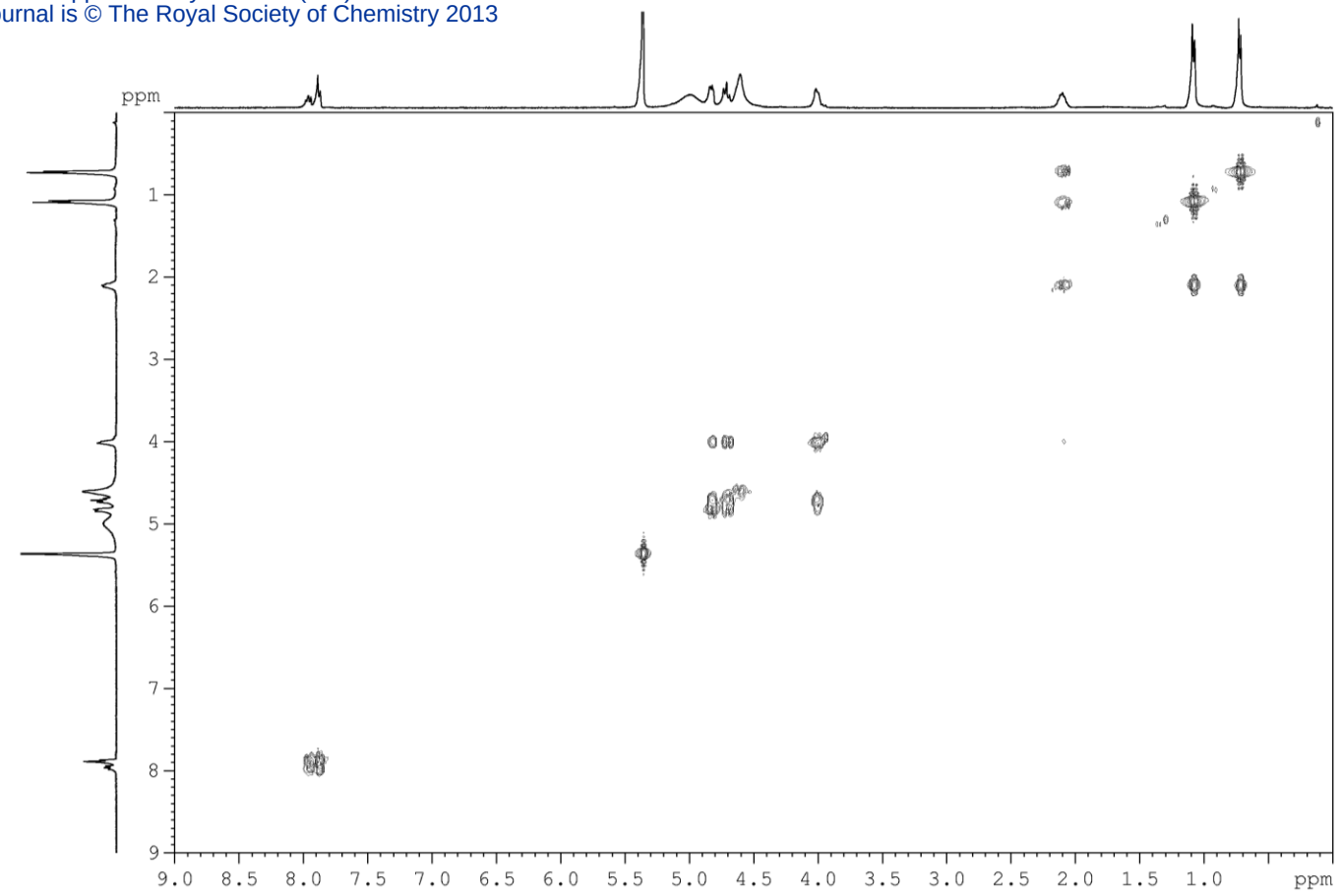
^{31}P NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **2b**



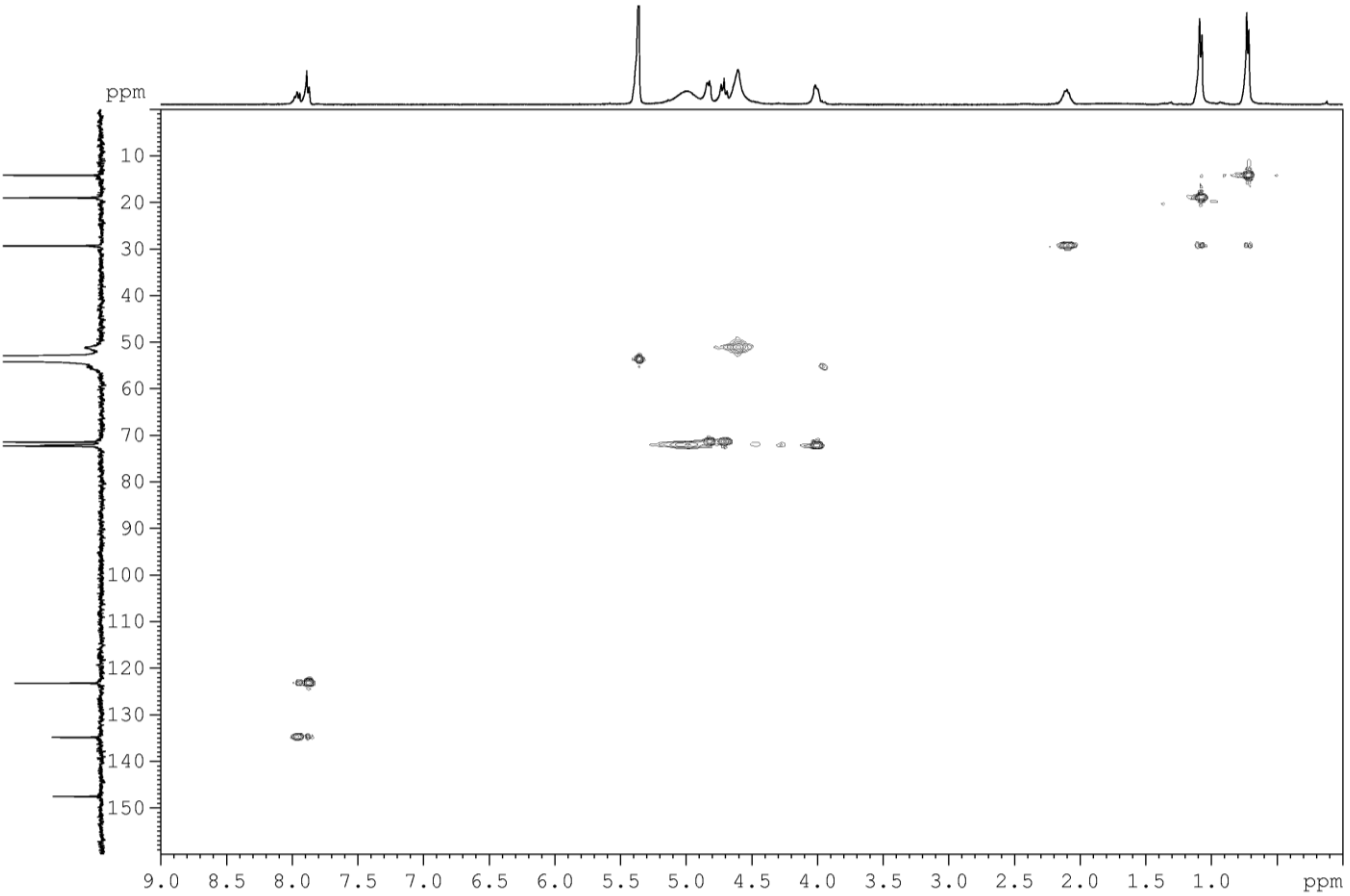
^{13}C NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **2b**



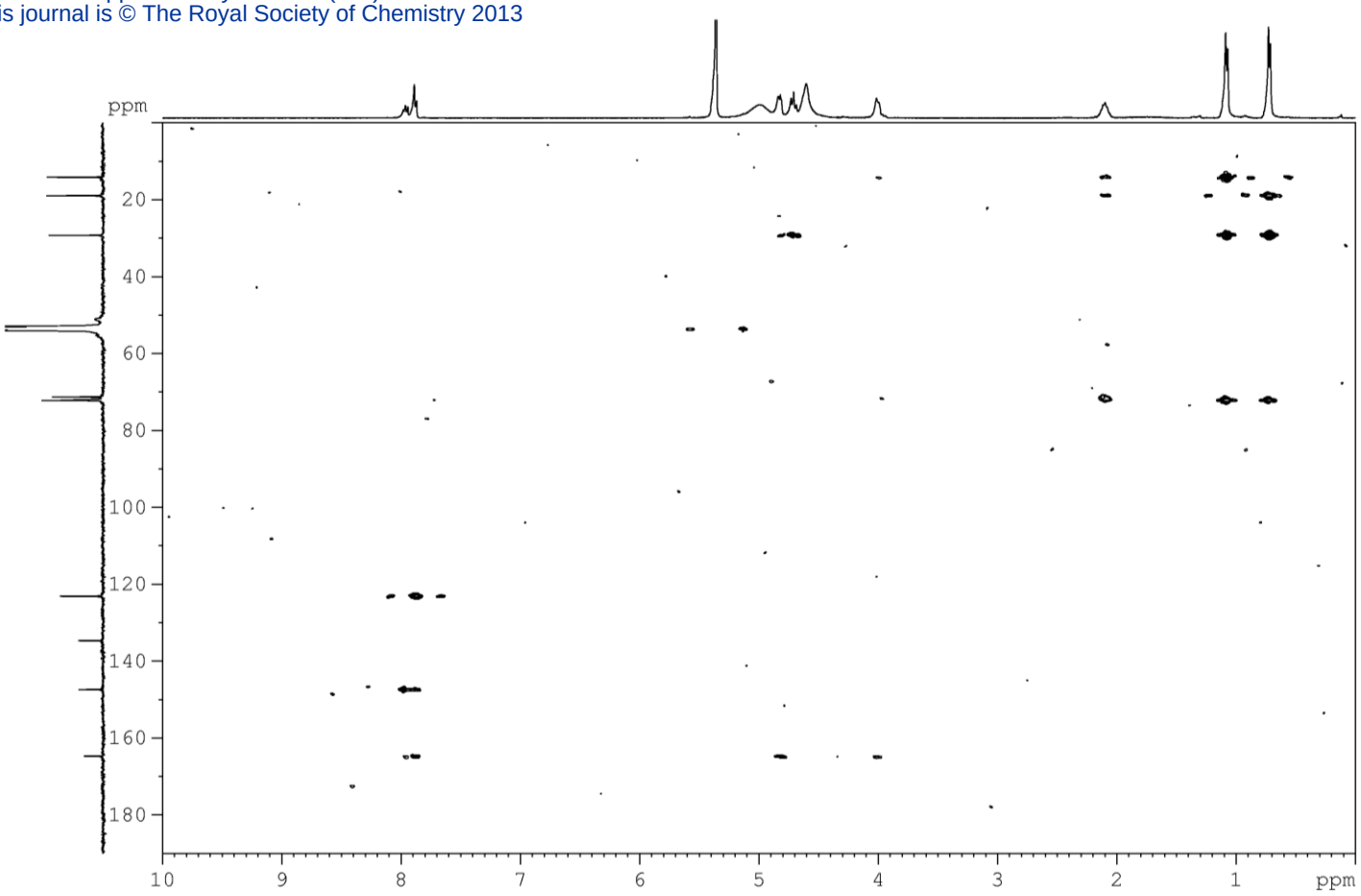
DEPT 135 NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **2b**



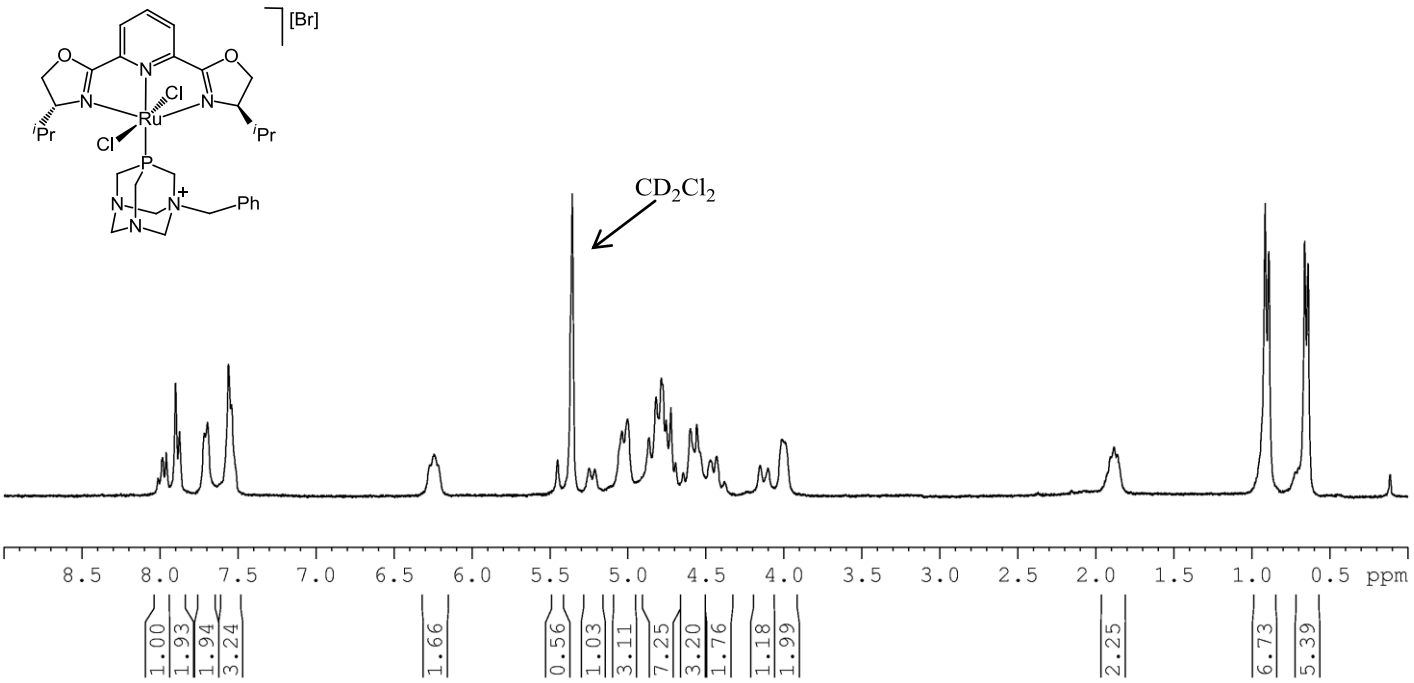
COSY HH NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **2b**



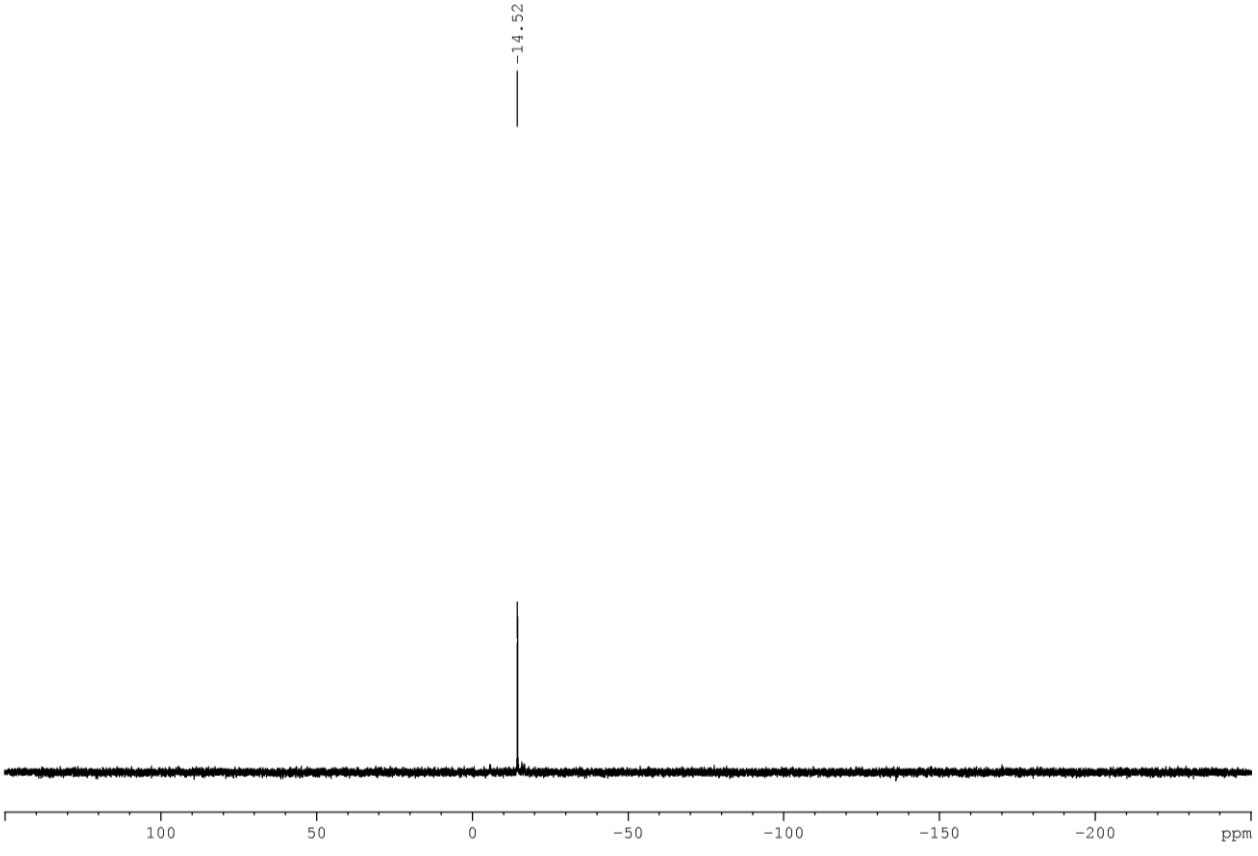
HSQC NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **2b**



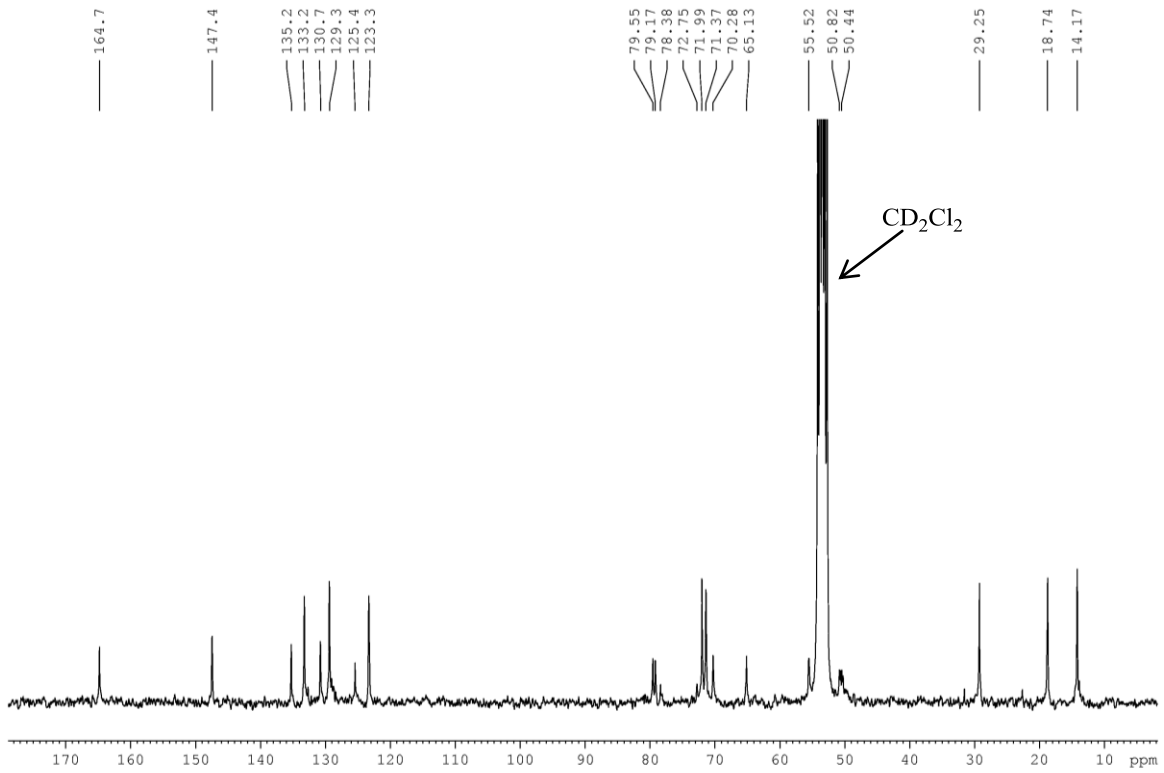
HMBC NMR spectrum (CD_2Cl_2, 298 K, AV400) of complex **2b**



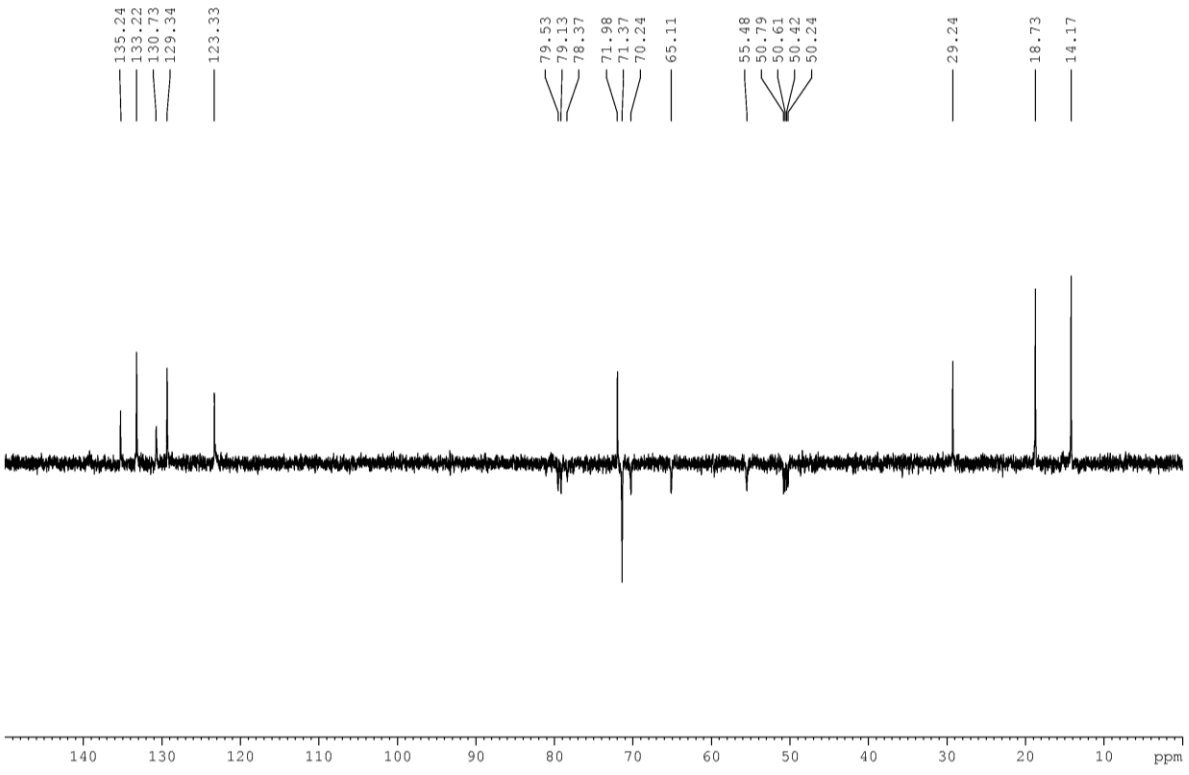
^{1}H NMR spectrum (CD_2Cl_2, 298 K, DPX300) of complex **6c**



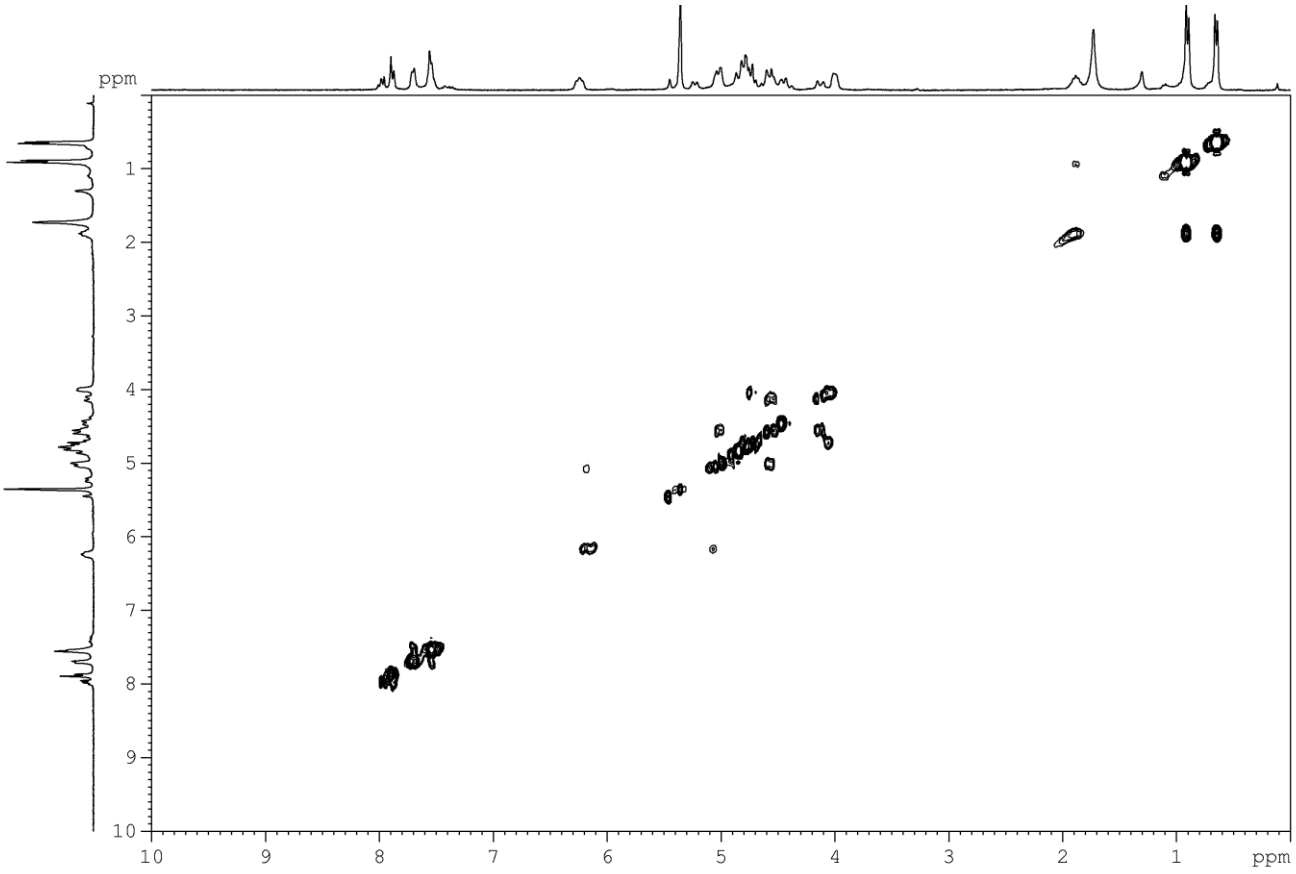
^{31}P NMR spectrum (CD_2Cl_2, 298 K, DPX300) of complex **6c**



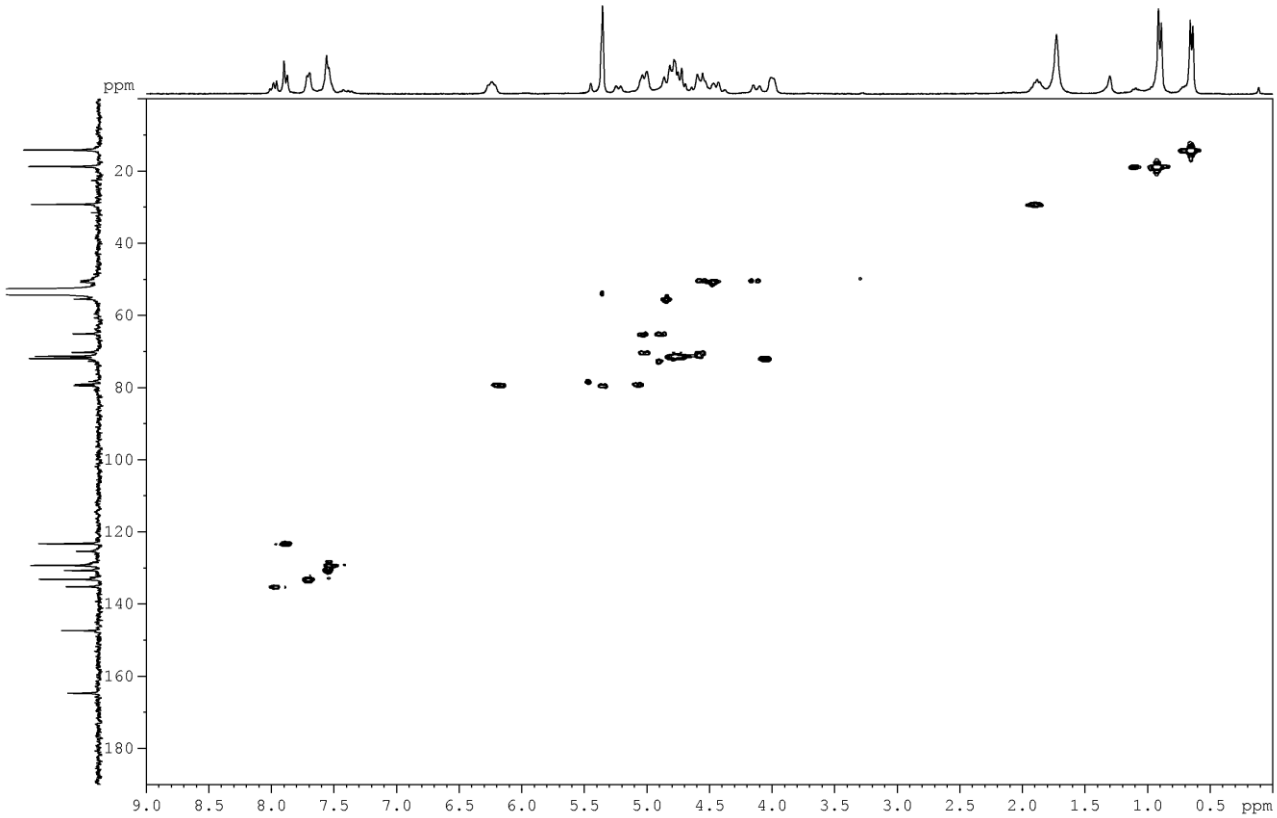
^{13}C NMR spectrum (CD_2Cl_2, 298 K, AV300) of complex **6c**



DEPT-135 NMR spectrum (CD_2Cl_2, 298 K, AV300) of complex **6c**



COSY HH NMR spectrum (CD_2Cl_2, 298 K, AV300) of complex **6c**



HSQC NMR spectrum (CD_2Cl_2, 298 K, AV300) of complex **6c**

Antimicrobial Activity.

Experimental

Microbial cytotoxicity of ruthenium compounds was measured against two yeasts (*Candida albicans* ATCC 14053 and *Candida parapsilosis*), and different bacteria: *Micrococcus luteus* ATCC 9341, *Bacillus subtilis* ATCC 19659, *Escherichia coli* C600 ATCC 23724, *Streptomyces coelicolor* A3(2), *Streptomyces antibioticus* ATCC 11891, *Streptomyces glaucescens* DSM 40716 and *Pseudomonas aeruginosa* PAO1 ATCC 15692. The antimicrobial activity was tested according to the Kirby Bauer disc diffusion method [20]. The microorganisms were mixed at known concentrations with Mueller Hinton and poured into petri dishes (9 cm in diameter; 10 mL of culture medium per plate). The ruthenium complex was pipetted onto sterile filter paper disks (0.5 cm in diameter) and the solvent evaporated before placing them on the cultures. Plates were maintained at 4ºC during 1 hour, and then incubated at 30ºC for the yeasts and *Streptomyces*, and 37 ºC for the rest of bacteria. Different amounts per disc were used depending of the compound solubility [355 µg (**1a**), 310 µg (**2a**), 255 µg (**3a**), 160 µg (**4a**), 360 µg (**5a**), 255 µg (**6a**), 595 µg (**1b**), 430 µg (**2b**), 395 µg (**3b**), 530 µg (**4b**), 400 µg (**5b**), 530 µg (**6b**), 530 µg (**1c**), 1090 µg (**2c**), 355 µg (**3c**), 475 µg (**4c**), 430 µg (**5c**), 545 µg (**6c**)]. For the compounds that were effective against microbes the size of the growth inhibition halos was measured in mm.

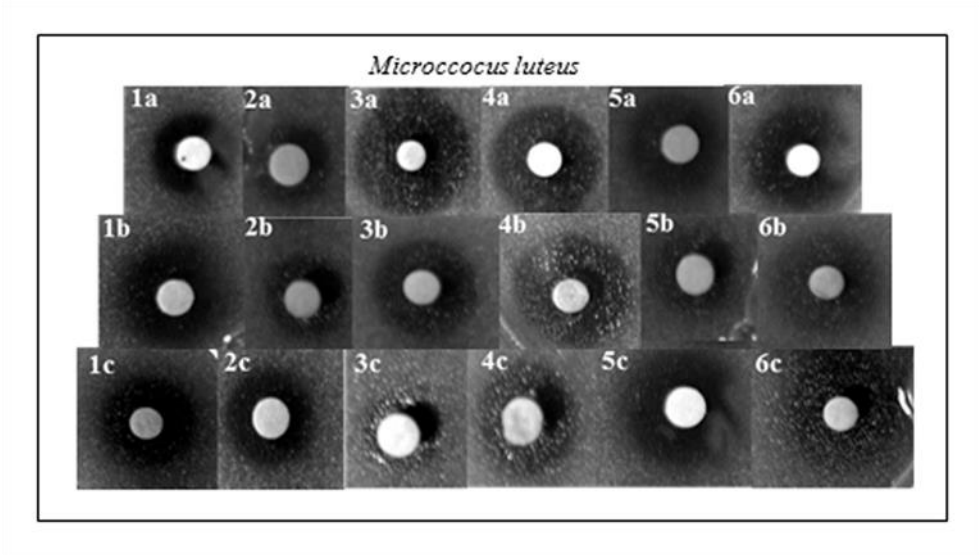


Figure 1. DNA antimicrobial activity of the ruthenium complexes against *Micrococcus luteus*. Ruthenium complex used per disc: 355 µg (**1a**), 310 µg (**2a**), 255 µg (**3a**), 160 µg (**4a**), 360 µg (**5a**), 255 µg (**6a**), 595 µg (**1b**), 430 µg (**2b**), 395 µg (**3b**), 530 µg (**4b**), 400 µg (**5b**), 530 µg (**6b**), 530 µg (**1c**), 1090 µg (**2c**), 355 µg (**3c**), 475 µg (**4c**), 430 µg (**5c**), 545 µg (**6c**).

Table 1: Inhibition halos (mm) of the ruthenium complexes against different microorganisms.

Compound[a]		*Micrococcus luteus*	*Bacillus subtillis*	*E. coli* c600	*Streptomyces coelicolor*	*Streptomyces antibioticus*
trans-[$RuCl_2$\{(*R*,*R*)-Ph-pybox\}(PTA)]	**1a**	12	7	-	-	7
trans-[$RuCl_2$\{(*S*,*S*)-^{i}Pr-pybox\}(PTA)]	**1b**	17	15	-	13	11
trans-[$RuCl_2$\{(*R*,*R*)-^{i}Pr-pybox\}(PTA)]	**1c**	17	14	-	9	10
trans-[$RuCl_2$\{(*R*,*R*)-Ph-pybox\}(1-H-PTA)][Cl]	**2a**	14	6	5	-	6
trans-[$RuCl_2$\{(*S*,*S*)-^{i}Pr-pybox\}(1-H-PTA)][Cl]	**2b**	15	6	-	-	8
trans-[$RuCl_2$\{(*R*,*R*)-^{i}Pr-pybox\}(1-H-PTA)][Cl]	**2c**	15	10	-	-	10
trans-[$RuCl_2$\{(*R*,*R*)-Ph-pybox\}(1-CH_3-PTA)][I]	**3a**	27	7	5	27	22
trans-[$RuCl_2$\{(*S*,*S*)-^{i}Pr-pybox\}(1-CH_3-PTA)][I]	**3b**	19	9	-	12	20
trans-[$RuCl_2$\{(*R*,*R*)-^{i}Pr-pybox\}(1-CH_3-PTA)][I]	**3c**	13	8	-	-	10
trans-[$RuCl_2$\{(*R*,*R*)-Ph-pybox\}(1-CH_2=$CHCH_2$-PTA)][I]	**4a**	21	6	5	9	13
trans-[$RuCl_2$\{(*S*,*S*)-^{i}Pr-pybox\}(1-CH_2=$CHCH_2$-PTA)][I]	**4b**	21	8	-	17	20
trans-[$RuCl_2$\{(*R*,*R*)-^{i}Pr-pybox\}(1-CH_2=$CHCH_2$-PTA)][I]	**4c**	17	10	-	10	14
trans-[$RuCl_2$\{(*R*,*R*)-Ph-pybox\}(1-HC≡CCH_2-PTA)][Br]	**5a**	17	6	-	6	12
trans-[$RuCl_2$\{(*S*,*S*)-^{i}Pr-pybox\}(1-HC≡CCH_2-PTA)][Br]	**5b**	13	7	-	-	8
trans-[$RuCl_2$\{(*R*,*R*)-^{i}Pr-pybox\}(1-HC≡CCH_2-PTA)][Br]	**5c**	19	10	-	-	13
trans-[$RuCl_2$\{(*R*,*R*)-Ph-pybox\}(1-$PhCH_2$-PTA)][Br]	**6a**	20	7	-	17	13
trans-[$RuCl_2$\{(*S*,*S*)-^{i}Pr-pybox\}(1-$PhCH_2$-PTA)][Br]	**6b**	18	8	-	11	13
trans-[$RuCl_2$\{(*R*,*R*)-^{i}Pr-pybox\}(1-$PhCH_2$-PTA)][Br]	**6c**	18	14	-	6	11

[a]Ruthenium complex used per disc: 355 µg (**1a**), 310 µg (**2a**), 255 µg (**3a**), 160 µg (**4a**), 360 µg (**5a**), 255 µg (**6a**), 595 µg (**1b**), 430 µg (**2b**), 395 µg (**3b**), 530 µg (**4b**), 400 µg (**5b**), 530 µg (**6b**), 530 µg (**1c**), 1090 µg (**2c**), 355 µg (**3c**), 475 µg (**4c**), 430 µg (**5c**), 545 µg (**6c**).

Crystal and refinement data for complexes 1b, 2a·CH_2Cl_2 and 3b

Table 2. Crystal Data and Structure Refinement for Complexes **1b**, **2a**·CH_2Cl_2 and **3b**

	1b	**2a**·CH_2Cl_2	**3b**
Empirical formula	$C_{23}H_{35}Cl_2N_6O_2PRu$	$C_{30}H_{34}Cl_5N_6O_2PRu$	$C_{24}H_{38}Cl_2IN_6O_2PRu$
Formula weight	630.51	819.92	772.45
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	1.5418	1.5418	1.5418
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1$	$C222_1$
a (Å)	11.7278(1)	10.5635(1)	13.5047(2)
b (Å)	12.5536(1)	14.7654(1)	23.2490(5)
c (Å)	18.5962(2)	11.8752(1)	24.3739(4)
A (deg)	90	90	90
β (deg)	90	107.283(1)	90
γ (deg)	90	90	90
Volume (Å^3)	2737.85(4)	1768.60(3)	7652.7(2)
Z	4	2	8
$\rho_{calculated}$ (Mg m^{-3})	1.530	1.540	1.341
μ (mm^{-1})	7.246	7.797	11.540
F (000)	1296	832	3088
Crystal size (mm^3)	0.046 x 0.04 x 0.02	0.145 x 0.06 x 0.008	0.13 x 0.081 x 0.039
θ range (deg)	4.25 to 73.85	3.90 to 73.97	3.63 to 74.01
Index ranges	$-14 \le h \le 13$	$-12 \le h \le 7$	$-15 \le h \le 15$
	$-14 \le k \le 15$	$-17 \le k \le 10$	$-26 \le k \le 28$
	$-23 \le l \le 19$	$-14 \le l \le 14$	$-29 \le l \le 26$
No. of reflns. collected	15044	6937	10478
No. of independent reflns.	5210 [R(int) = 0.0429]	4524 [R(int) = 0.0399]	6104 [R(int) = 0.0260]
Completeness to θ_{max} (%)	99.7	99.4	91.7
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
No. of parameters/restraints	320/0	419/3	325/0
Goodness-of-fit on F^2	1.093	1.103	1.108
R_1 [$I > 2\sigma(I)$][a]	R_1 = 0.0364, wR_2 = 0.0998	R_1 = 0.0376, wR_2 = 0.0974	R_1 = 0.0502, wR_2 = 0.1395
R (all data)	R_1 = 0.0443, wR_2 = 0.1168	R_1 = 0.0441, wR_2 = 0.1160	R_1 = 0.0555, wR_2 = 0.1446
Absolute structure parameter	0.020(11)	0.022(15)	0.015(15)
Largest diff. peak and hole (e Å^{-3})	0.592 and - 0.678	1.031 and - 0.841	1.287 and - 0.683

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$.