Supplementary Information for

Oxidation-Promoted Activation of a Ferrocene C-H Bond by a Rhodium Complex

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General considerations

All manipulations were performed under an inert atmosphere of dry argon by using vacuum line and Schlenk tube techniques. Solvents for all syntheses were dried and degassed by standard methods before use, unless otherwise stated. 1,2-Ferrocenyl alcohol [1] and imidazolium salt [2] were prepared according to previously reported procedures.

Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer.

1D- and 2D-NMR spectra were recorded on a Bruker AV500 or a Bruker AV300 spectrometer. ^{1}H and ^{13}C chemical shifts (δ) are given in ppm (the residual peak of deuterated solvent was used as reference). ^{31}P chemical shifts are reported in ppm. Peaks are labeled as singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br). The proton and carbon assignments were confirmed with the help of selective $^{1}H\{^{31}P\}$, selective $^{13}C\{^{31}P\}$, COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{1}H-^{31}P HMBC and ROESY experiments.

Electrospray (ES) mass spectra were recorded at the Université Paul Sabatier by the Service Commun de Spectrométrie de Masse on a MS/MS API-365 (Perkin Elmer Sciex).

Cyclic voltammetry (CV) and square-wave voltammetry (SQW) experiments were carried out with an Autolab PGSTAT100 potentiostat (Metrohm). Experiments were performed at room temperature in a homemade airtight three–electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca 1cm² apparent surface. The working electrode was a Pt microdisk (0.5 mm diameter). The supporting electrolyte $[nBu_4N][BF_4]$ (Fluka, 99% electrochemical grade) was dried and degassed under argon. CH_2Cl_2 was freshly distilled over CaH_2 and acetonitrile over P_2O_5 prior to use. The solutions used during the electrochemical studies were typically 10^{-3} M in rhodium compound and 0,1 M in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling Ar and the working electrode was polished with a polishing machine (Presi P230).

For cyclic voltammetry, the step potential is 5mV. Controlled-potential electrolyses were undertaken in a three-electrode cell with Pt gauze working electrode (ca 7 cm²), reference and counter electrodes separated by two glass frits.

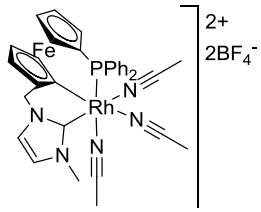
All electrochemical data are referenced versus ferrocene [3].

X-ray structural analyses. A single crystal of compound **4** was mounted under inert perfluoropolyether at the tip of a glass fiber and cooled in the cryostream of an Oxford-Diffraction XCALIBUR CCD diffractometer. The structure was solved by direct methods (SIR97 [4]) and refined by least-squares procedures on F^2 using SHELXL-97 [5]. All H atoms attached to carbon were introduced in calculation in idealized positions and treated as riding models. The drawing of the molecules was realized with the help of ORTEP32 [6]. Crystal data and refinement parameters are shown in Table 1.

Abbreviations:

Cp^P: cyclopentadienyl ring with the PPh_2 substituent.
Cp^C: cyclopentadienyl ring with the NHC substituent.
Fc: ferrocenyl.
Im: imidazol-2-ylidene.

$[Rh(L)(CH_3CN)_3]^{2+}.2BF_4^-$ complex 3:



A solution of thianthrenium tetrafluoroborate (30.5 mg, 0.10 mmol) in CH_3CN (3.5 mL) was added dropwise to a solution of **1** (50 mg, 0.07 mmol) in CH_3CN (7 mL). The mixture was stirred at room temperature for 48h and the solvent was evaporated in vacuo. The complex was precipitated with a CH_3CN/Et_2O (1/9) mixture several times until the ethereal solution was colorless. The complex was dried in vacuo to give an orange solid (35.8 mg, 74%).

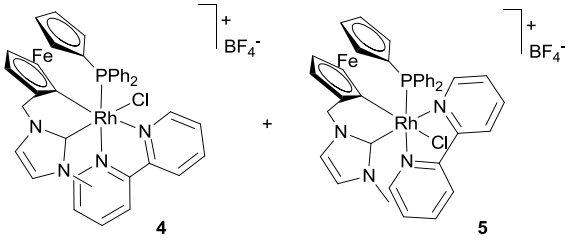
IR (ATR): ν_{max}/cm^{-1} 2940w (C-$H_{str.}$); 2322, 2293 and 2252 (w) (C≡$N_{str.}$); 1474, 1436 and 1405 (w/m) (C=$C_{str.}$); 1051-999vs (BF_4); 747, 696 and 684 (m/s) (C-$H_{bend.}$).

δ_H (500.33 MHz; CD_3CN; 228 K) 7.65-7.55 (3H, m; PPh_2), 7.53-7.46 (4H, m; *H*C=C Im + PPh_2), 7.43-7.40 (2H, m; PPh_2), 7.20 (1H, s; *H*C=C Im), 7.11 (2H, dd, ^3J(H,H)=11.5 Hz, J(P,H)=7.5 Hz; PPh_2), 5.63 (1H, br s; Cp^P), 4.89 (1H, d, ^2J(H,H)=16.1 Hz; CH_2 Im), 4.73-4.66 (4H, m; Cp^C + 2 x Cp^P + CH_2 Im), 4.58 (1H, s; Cp^C), 4.40 (1H, s; Cp^P), 4.18 (1H, s; Cp^C), 3.98 (3H, s; CH_3). δ_C (125.82 MHz; CD_3CN; 228 K) 147.19 (dd, ^1J(Rh,C)=47.2 Hz, ^2J(P,C)=11.4 Hz; quat C_{NHC}), 132.88 (d, J(P,C)=10.6 Hz; *o*-CH_{PPh2}), 132.87 (d, J(P,C)=47.7 Hz; quat C_{PPh2}), 132.75 (d, J(P,C)=2.1 Hz; *p*-CH_{PPh2}), 132.07 (d, J(P,C)=9.8 Hz; *o*-CH_{PPh2}), 131.30 (d, J(P,C)=2.6 Hz; *p*-CH_{PPh2}), 129.58 (d, J(P,C)=10.9 Hz; *m*-CH_{PPh2}), 128.57 (d, J(P,C)=10.7 Hz; *m*-CH_{PPh2}), 128.01 (d, J(P,C)=52.2 Hz; quat C_{PPh2}), 126.33 (*C*=C_{Im}), 124.10 (C=C_{Im}), 85.20 (br s; quat *C* Cp^C), 83.32 (d; J(P,C)=9.1 Hz; *C*H Cp^P), 76.11 (d, J(P,C)=12.6 Hz; *C*H Cp^P), 75.27 (*C*H Cp^C), 73.72 (d, J(P,C)=7.2 Hz; *C*H Cp^P), 73.26 (d, J(P,C)=6.9 Hz; *C*H Cp^P), 72.25 (*C*H Cp^C), 71.41 (d, J(P,C)=65.8 Hz; quat *C* Cp^P), 70.61 (*C*H Cp^C), 66.58 (app. dd, J(Rh,C)=30.2 Hz; quat *C* Cp^C), 50.45 (*C*$H_{2\ Im}$), 39.10 (*C*$H_{3\ Im}$). δ_P (202.54 MHz; CD_3CN; 228 K) 41.56 (d, ^1J(Rh,P)=138 Hz), 32.89 (d, ^1J(Rh,P)=118 Hz, <5%).

δ_H (500.33 MHz; CD_2Cl_2; 221 K) 7.58-7.39 (8H, m; PPh_2), 7.36 (1H, s; *H*C=C_{Im}), 7.16 (1H, s; *H*C=C $_{Im}$), 7.07-7.05 (2H, m; PPh_2), 5.42 (1H, br s; Cp^P), 4.81-4.76 (1H, m; C$H_{2\ Im}$), 4.71 (1H, s; Cp^P), 4.68 (2H, s; Cp^C+Cp^P), 4.56 (1H, s; Cp^C), 4.28 (1H, s; Cp^P), 4.20 (1H, s; Cp^C), 3.91 (3H, s; C$H_{3\ Im}$), 2.66 (3H, s; CH_3CN), 2.31 (3H, s; CH_3CN), 2.20 (3H, s; CH_3CN), 2.03 (CH_3CN, residual solvent) ; 2nd proton from C$H_{2\ Im}$ not found. δ_C (125.82 MHz; CD_2Cl_2; 221 K) 147.30 (dd, ^1J(Rh,C)=47.8 Hz, ^2J(P,C)=11.9 Hz; quat C_{NHC}), 132.89 (s; *p*-CH_{PPh2}), 132.54 (d, J(P,C)=10.1 Hz; *C*H_{PPh2}), 132.08 (d, J(P,C)=10.1 Hz; *C*H_{PPh2}), 131.71 (s; *p*-CH_{PPh2}), 129.77 (d, J(P,C)=11.3 Hz; *C*H_{PPh2}), 128.58 (d, J(P,C)=10.1 Hz; *C*H_{PPh2}), 127.91 (d, J(P,C)=52.8 Hz; quat C_{PPh2}), 126.13 (s; *C*=C_{Im}), 124.25 (s; C=C_{Im}), 123.92 (m; 2*CH$_3$*C*N), 122.05 (d, J(P,C)=18.9 Hz; CH_3*C*N), 117.71 (CH_3*C*N, residual solvent), 84.85 (br s; quat *C* Cp^C), 82.48 (d; J(P,C)=8.8 Hz; *C*H Cp^P), 76.04 (d, J(P,C)=11.7 Hz; *C*H Cp^P), 75.38 (*C*H Cp^C), 74.05+73.86 (m; 2**C*H Cp^P), 72.37 (*C*H Cp^C), 71.45 (m; *C*H Cp^C), 71.36 (d, J(P,C)=71.5 Hz; quat *C* Cp^P), 66.18 (app. dd, J(Rh,C)=27.8 Hz; quat *C* Cp^C), 51.01 (*C*$H_{2\ Im}$), 39.15 (*C*$H_{3\ Im}$), 4.18 (*C*H_3CN), 3.82 (*C*H_3CN), 3.67 (*C*H_3CN), 2.58 (*C*H_3CN, residual solvent). δ_P (202.54 MHz, CD_2Cl_2, 221 K) 50.93-50.60 (m, ca. 5%), 41.56 (d, ^1J(Rh,P)=138 Hz).

MS, ESI *m*/*z* 565 ([*M*-3xMeCN-H]$^+$, 100%) , 601 ([*M*-3xMeCN+Cl]$^+$, 36).

[Rh(L)(2,2'-bipyridyl)Cl]$^{+}$BF$_4^{-}$ complexes 4+5 from complex 1:



A solution of thianthrenium tetrafluoroborate (87.0 mg, 0.29 mmol) in CH_3CN (15 mL) was added dropwise to a solution of **1** (146 mg, 0.19 mmol) in CH_3CN (15 mL). The mixture was stirred at room temperature for 48h and the solvent was evaporated in vacuo. The complex was precipitated with a CH_3CN/Et_2O (1/9) mixture several times until the ethereal solution was colorless; 53 mg of unreacted complex **1** were recovered in the filtrate. Complex **3** (105 mg, 0.12 mmol) was dissolved in CH_2Cl_2 (10 mL) and 2,2'-bipyridine (19 mg, 0.12 mmol) was added. The mixture was stirred at room temperature for 1 hour and the solvent was concentrated in vacuo. The red solid was purified by column chromatography on neutral alumina (eluent: acetone → acetone/MeCN 1:1 → MeCN) to give a mixture of complexes **4** and **5** as a red-orange solid (75 mg, 46% from complex **1**) along with 30 mg of an unidentified pink-red solid. X-Ray quality crystals of **4** were obtained from slow evaporation of a $MeCN/C_6F_6$ solution.

IR (ATR): ν_{max}/cm^{-1} 3056w; 2960, 2924 and 2853 (m) (C-$H_{str.}$); 1602; 1468, 1445 and 1435 (m) (C=$C_{str.}$ or C=$N_{str.}$); 1260; 1100-1000vs (BF_4); 801, 765, 746, 732, 697 and 682 (s) (C-$H_{bend.}$).

Major isomer: α (**5**), minor isomer: β (**4**).

δ_H (500.33 MHz; d_6-acetone; 297 K) 9.51 (α, 1H, d, J(H,H)=5.5 Hz; bipy), 8.86 (α, d; bipy), 8.76 (α, 1H, d, J(H,H)=8.0 Hz; bipy), 8.72-8.65 (α+β, 6H, m; bipy), 8.43 (α, 1H, t, J(H,H)=7.8 Hz; bipy), 8.27-8.16 (α+β, 4H, m; bipy+PPh_2), 8.06 (β, 2H, app. dd, J(H,H)=7.5 Hz; PPh_2), 7.86 (α, 1H, d, ^3J(H,H)=1.5 Hz; *H*C=CH Im), 7.77 (α, 1H, t, J(H,H)=6.6 Hz; bipy), 7.73-7.67 (α, 3H, m; bipy+PPh_2), 7.65-7.62 (β, 1H, m; PPh_2), 7.59-7.56 (β, 1H, m; bipy), 7.56-7.53 (α, 2H, m; PPh_2), 7.51-7.48 (β, 4H, m; PPh_2), 7.43-7.35 (α+β, 5H, m; bipy+PPh_2), 7.41 (α+β, 2H, s; *H*C=CH Im), 7.31 (β, 1H, d, ^3J(H,H)=1.5 Hz; *H*C=CH Im), 7.28 (α, 2H, app. td; PPh_2), 7.15 (α, 2H, app. dd; PPh_2), 5.93 (α, 1H, d, ^2J(H,H)=16.5 Hz; FcC*H*$_2$Im), 5.60 (β, 1H, s; Fc^P), 5.43 (α, 1H, d, ^2J(H,H)=16.5 Hz; FcC*H*$_2$Im), 5.31 (α, 1H, s; Fc^P), 5.28 (α, 1H, s; Fc^P), 5.21 (β, 1H, s; Fc^C), 5.20-5.13 (β, 2H, m; FcC*H*$_2$Im), 4.66 (β, 1H, s; Fc^C), 4.61 (α+β, 2H, s; Fc^P), 4.57 (β, 1H, s; Fc^P), 4.43 (β, 1H, s; Fc^P), 4.42 (α, 1H, s; Fc^C), 4.30 (α, 1H, s; Fc^P), 4.23 (β, 1H, s; Fc^C), 3.97 (α, 1H, t, J(H,H)=2.2 Hz; Fc^C), 3.59 (α, 1H, s; Fc^C), 3.50 (α, 3H, s; C*H*$_3$Im), 2.72 (β, 3H, s; C*H*$_3$Im).

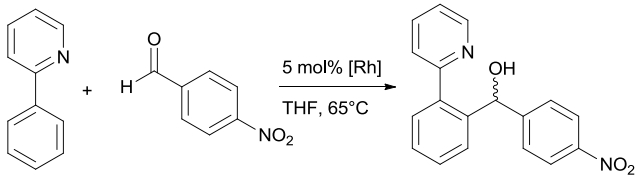
δ_C (125.82 MHz; d_6-acetone; 297 K) 159.41 (α; C_{bipy}), 156.44 (β, d, J(P,C)=1.9 Hz; quat C_{bipy}), 156.34 (α, d, J(P,C)=1.5 Hz; quat C_{bipy}), 155.97 (β, d, J(P,C)=2.2 Hz; quat C_{bipy}), 155.33 (α, d, J(P,C)=2.1 Hz; quat C_{bipy}), 154.44 (β, app. dd, J(Rh,C)=48.9 Hz; quat C_{NHC}), 154.34 (α, app. dd, J(Rh,C)=47.4 Hz; quat C_{NHC}), 154.29 (α; C_{bipy}), 154.13-154.11 (α; CH_{bipy}), 152.64 (β; CH_{bipy}), 150.72 (α; $CH_{arom.}$), 149.76 (β; $CH_{arom.}$), 140.34 (α; $CH_{arom.}$), 140.07 ($CH_{arom.}$), 139.79+139.70 (α; $CH_{arom.}$), 138.95 ($CH_{arom.}$), 136.30 (α, app. d; quat C_{PPh2}), 136.30-136.08 (α, $CH_{arom.}$), 135.31 (β, d, J(P,C)=9.0 Hz; CH_{PPh2}), 134.79 (β, d, J(P,C)=39.9 Hz; quat C_{PPh2}), 133.58 (β, d, J(P,C)=10.2 Hz; CH_{PPh2}), 132.03 (β, dd, J(P,C)=42.7 Hz, J(P,C)=1.5 Hz; quat C_{PPh2}), 131.95 (α, d, J(P,C)=2.3 Hz; CH_{PPh2}), 131.66 (α, d,

J(P,C)=9.4 Hz; *C*H$_{PPh2}$), 131.64 (*β*, d, *J*(P,C)=2.2 Hz; *C*H$_{PPh2}$), 131.15 (*α*, d, *J*(P,C)=38.6 Hz; quat *C*$_{PPh2}$), 130.68 (*β*, d, *J*(P,C)=2.6 Hz; *C*H$_{PPh2}$), 130.02 (*β*, d, *J*(P,C)=2.5 Hz; *C*H$_{PPh2}$), 129.13 (*α*, d, *J*(P,C)=9.5 Hz; *C*H$_{PPh2}$), 128.45 (*α*, d, *J*(P,C)=9.8 Hz; *C*H$_{PPh2}$), 128.23 (*α*, d, *J*(P,C)=9.7 Hz; *C*H$_{PPh2}$), 128.07 (*α*; H*C*=CH$_{Im}$), 127.67 (*β*, d, *J*(P,C)=9.8 Hz; *C*H$_{PPh2}$), 127.58 (*α*, d, *J*(P,C)=3.5 Hz; *C*H$_{PPh2}$), 126.75 (*α*; *C*H$_{arom.}$), 126.55 (*β*, d, *J*(P,C)=3.2 Hz; *C*H$_{PPh2}$), 126.42 (*β*; H*C*=CH$_{Im}$), 126.39 (*β*; H*C*=CH$_{Im}$), 125.54 (*α*; H*C*=CH$_{Im}$), 124.39 (*C*H$_{arom.}$), 124.15 (*C*H$_{arom.}$), 124.01 (*β*, d, *J*(P,C)=3.2 Hz; *C*H$_{PPh2}$), 123.83 (*C*H$_{arom.}$), 84.97 (*α*, d, *J*(P,C)=59.8 Hz; quat *C* Fc^{P}), 84.03 (*β*, d, *J*(P,C)=2.3 Hz; quat *C* Fc$^{C}_{Im}$), 82.99 (*α*; quat *C* Fc$^{C}_{Im}$), 80.95 (*α*, d, *J*(P,C)=62.8 Hz; quat *C* Fc^{P}), 79.82 (*β*, d, *J*(P,C)=7.5 Hz; *C*H Fc^{P}), 77.30 (*α*, d, *J*(P,C)=9.1 Hz; *C*H Fc^{P}), 77.23 (*β*; *C*H Fc^{C}), 76.94 (*β*, d, *J*(P,C)=12.5 Hz; *C*H Fc^{P}), 76.61 (*β*, app. dd, *J*(Rh,C)=31.1 Hz; quat *C* Fc$^{C}_{Rh}$), 74.76 (*α*, d, *J*(P,C)=10.8 Hz; *C*H Fc^{P}), 72.30 (*α*; *C*H Fc^{C}), 71.85 (*α*+*β*, d, *J*(P,C)=6.4 Hz; *C*H Fc^{P}), 71.71 (*β*, d, *J*(P,C)=6.4 Hz; *C*H Fc^{P}), 71.32 (*α*; *C*H Fc^{C}), 70.59 (*β*; *C*H Fc^{C}), 70.48 (*β*; *C*H Fc^{C}), 69.70 (*α*, d, *J*(P,C)=7.5 Hz; *C*H Fc^{P}), 69.35 (*α*; *C*H Fc^{C}), 62.94 (*α*, dd, *J*(Rh,C)=33.7 Hz, *J*(P,C)=5.0 Hz; quat *C* Fc$^{C}_{Rh}$), 51.47 (*α*; *C*H$_{2Im}$), 51.43 (*β*; *C*H$_{2Im}$), 40.00 (*α*; *C*H$_{3Im}$), 36.98 (*β*; *C*H$_{3Im}$).

δ_P (202.54 MHz; d_6-acetone; 297 K) 35.85 (*α*, d, *J*(Rh,P)=127.8 Hz), 31.50 (*β*, d, *J*(Rh,P)=127.4 Hz).

MS, ESI *m*/*z* 757 (M^+, 100%) . HRMS, ESI : calcd for C37H32N4PClFeRh 755.0504; found 755.0522.

Arylation of 4-nitrobenzaldehyde with 2-phenylpyridine [7]:



4-Nitrobenzaldehyde (56.0 mg, 0.37 mmole) and complex **3** (8.0 mg, 0.09 mmole) were placed in a dry Schlenk and THF (0.5 mL) was added. 2-Phenylpyridine (26.5 μL, 0.19 mmole) was added and the Schlenk was sealed and placed in a preheated bath. The mixture was stirred at 65°C for 24h, and the solvent was removed in vacuo. The residue was analyzed by ^{1}H NMR and the conversion into the desired alcohol (33%) was determined by integration of characteristic signals: 2-phenylpyridine: 8.68 ppm, 1H, C(6)*H*; alcohol: 8.55 ppm, 1H, C(6)*H* or 5.58 ppm, 1H, C*H*(OH).

Cyclic voltammogram of complex 3 in MeCN, 20h after interruption of electrolysis :

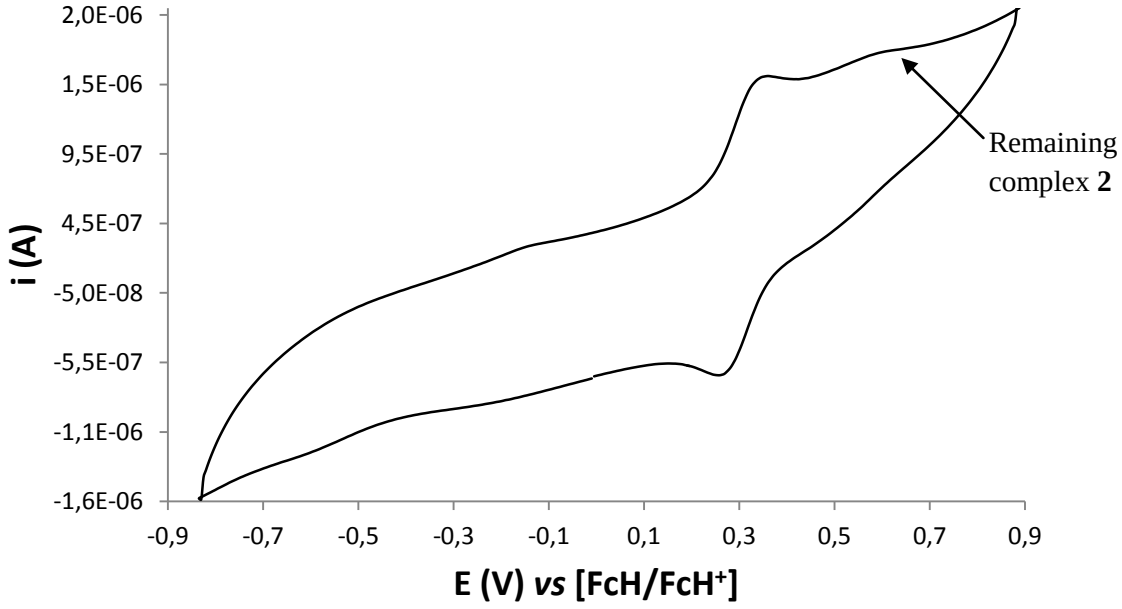
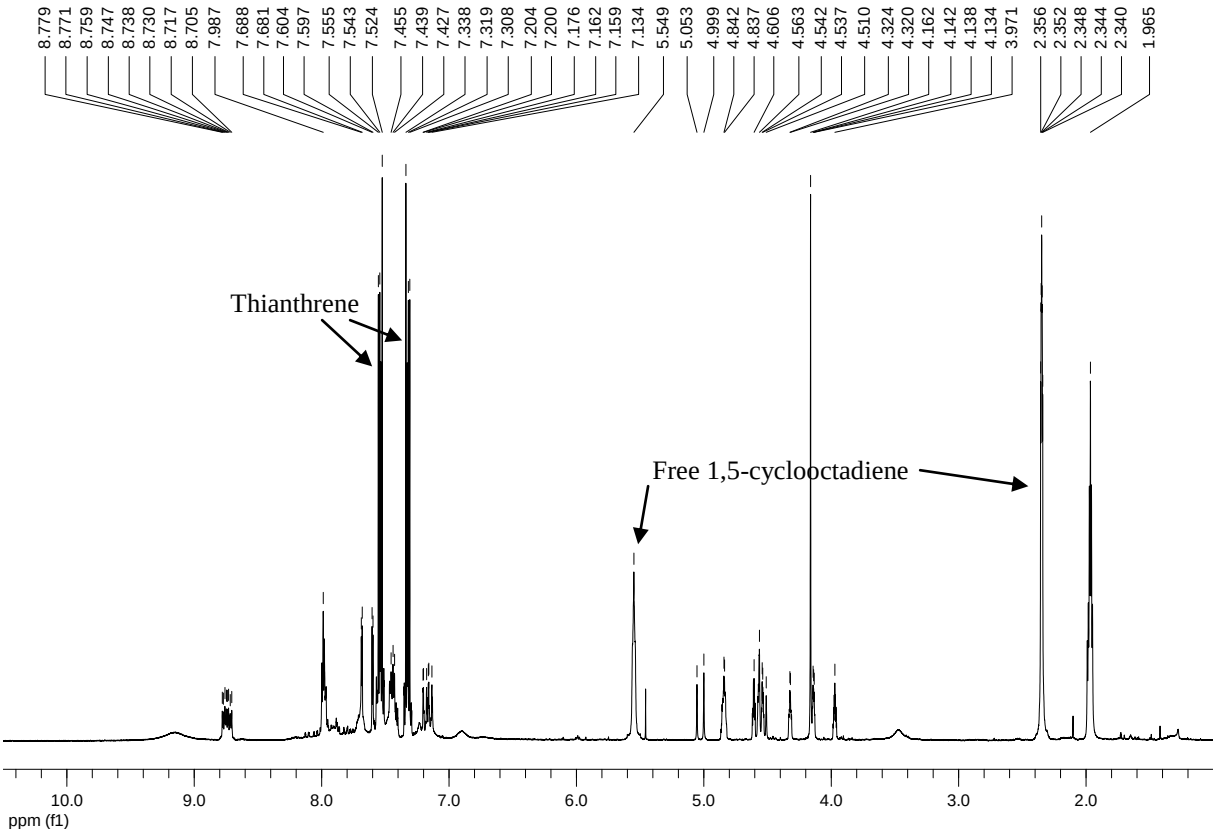
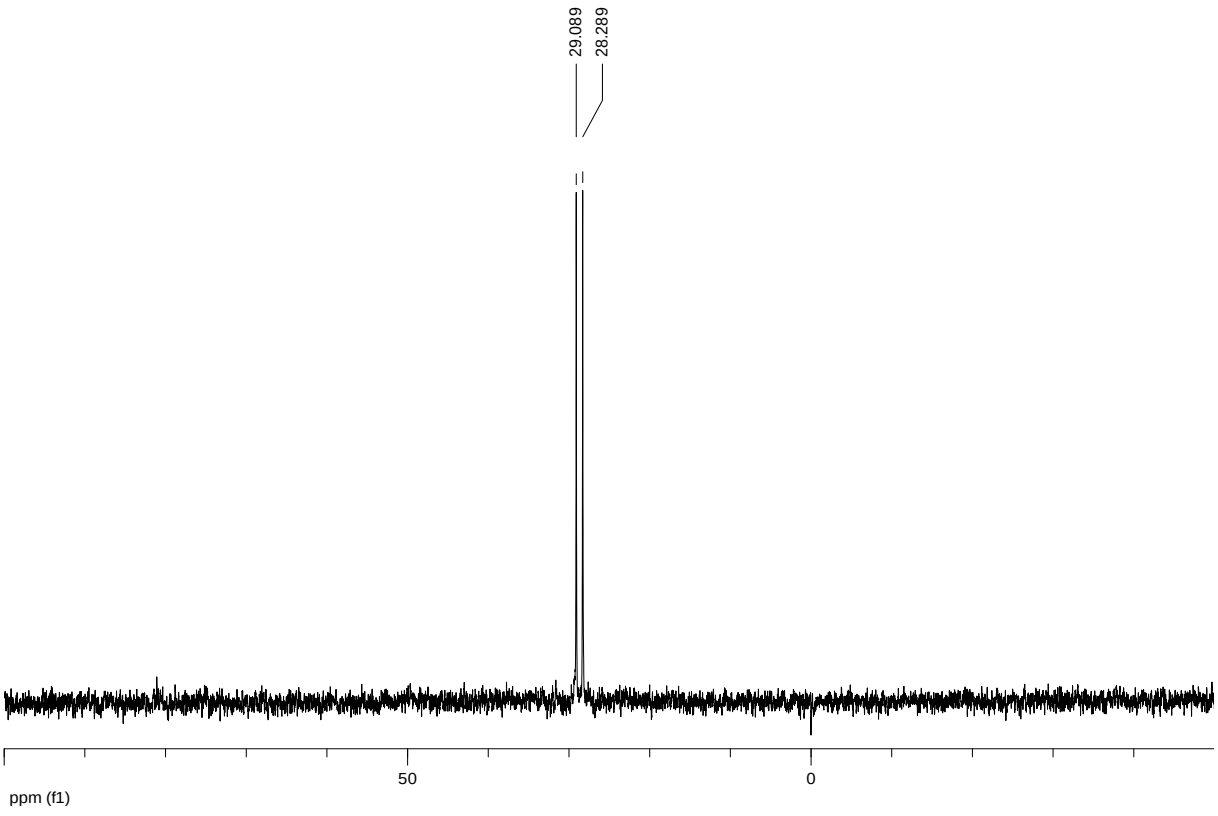


Figure 2. Cyclic voltammogram on a Pt microelectrode, 1 mM in MeCN with nBu$_4$NBF$_4$ (0.1M) at a scan rate of 0.2 V s^{-1}.

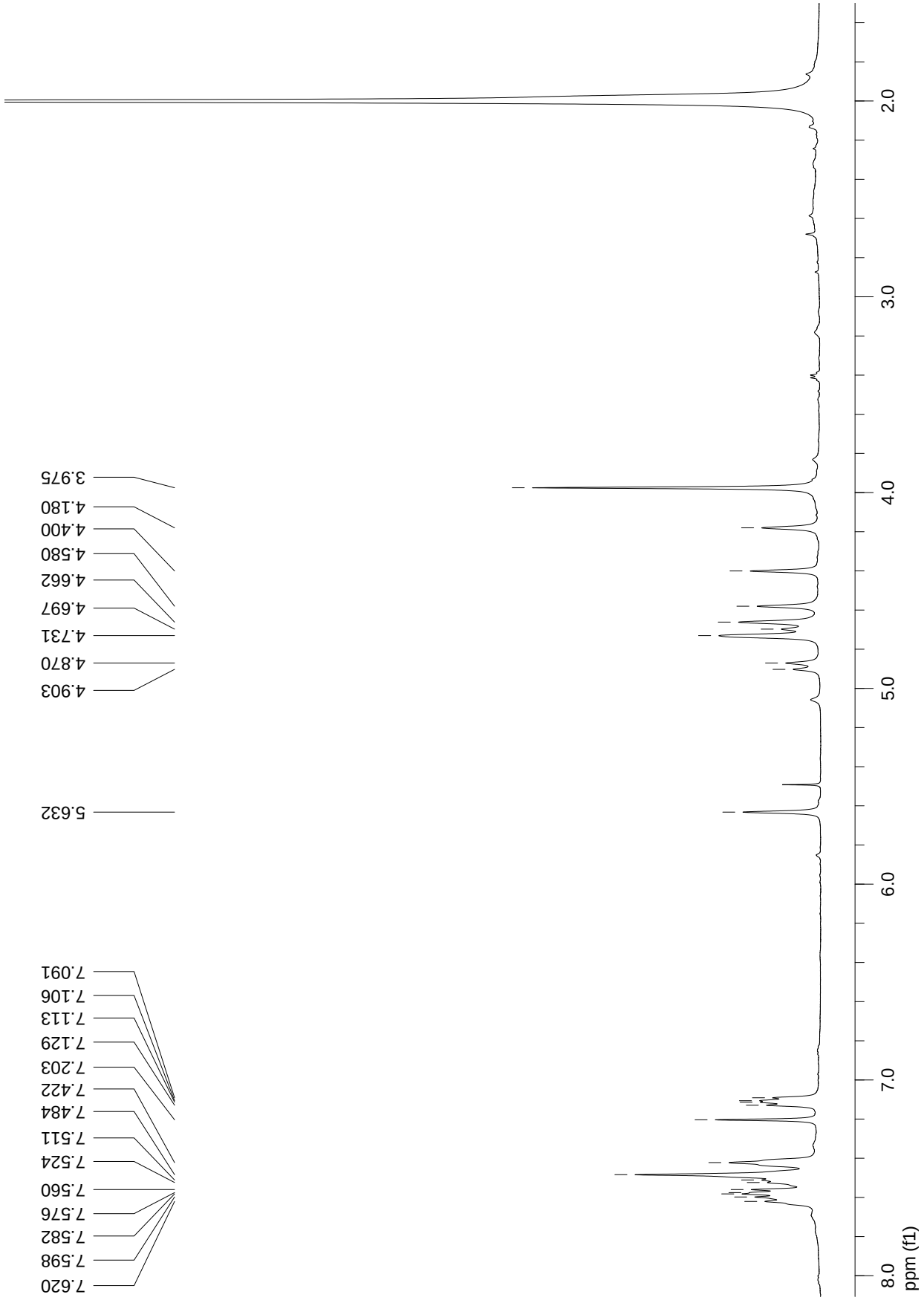
^{1}H NMR spectrum of complex **2** (300 MHz, CD_3CN, 298 K) (t=4h15 after addition of [Th][BF_4]):



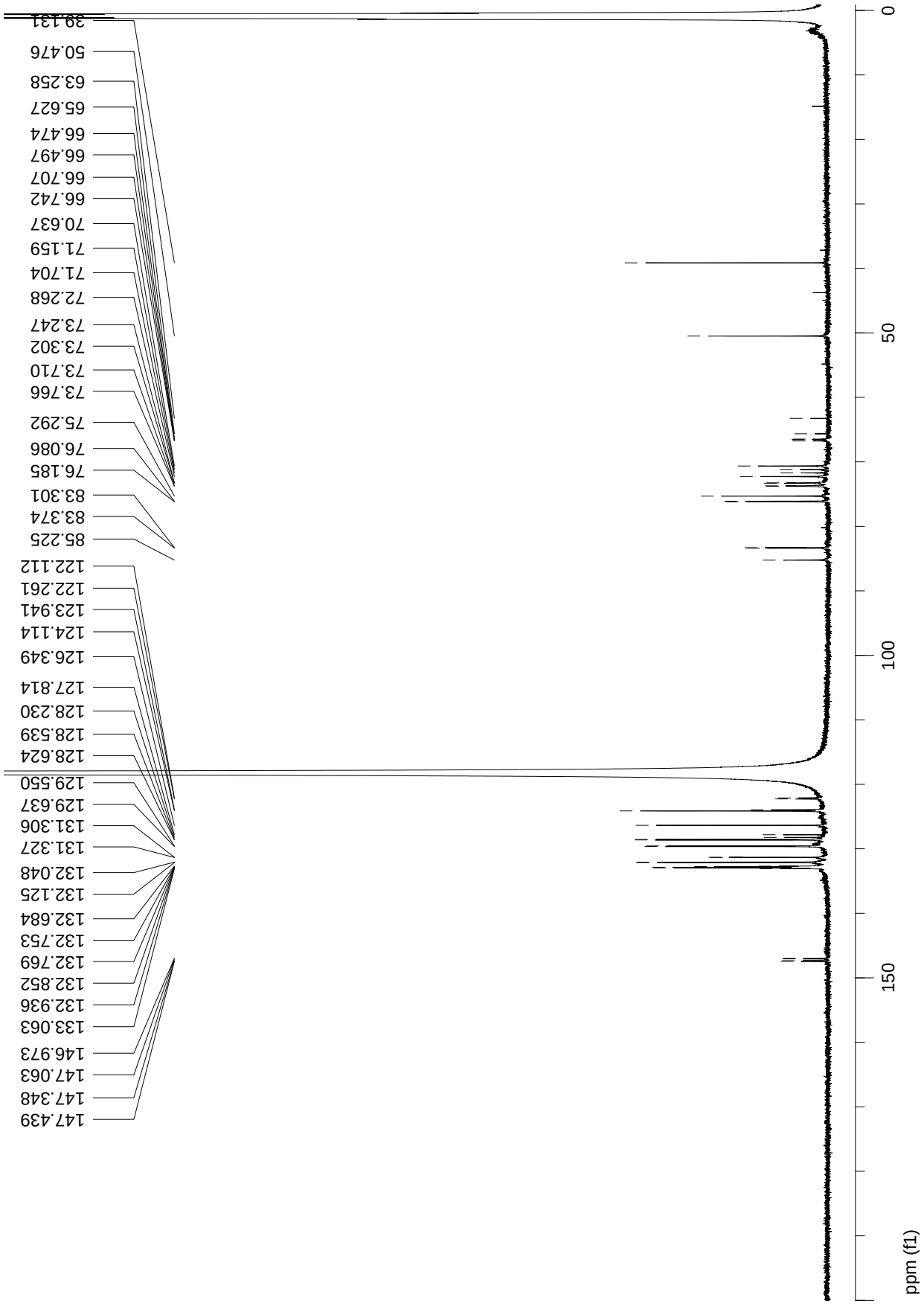
^{31}P NMR spectrum of complex **2** (121.5 MHz, CD_3CN, 298 K) (t=4h15 after addition of [Th][BF_4]):



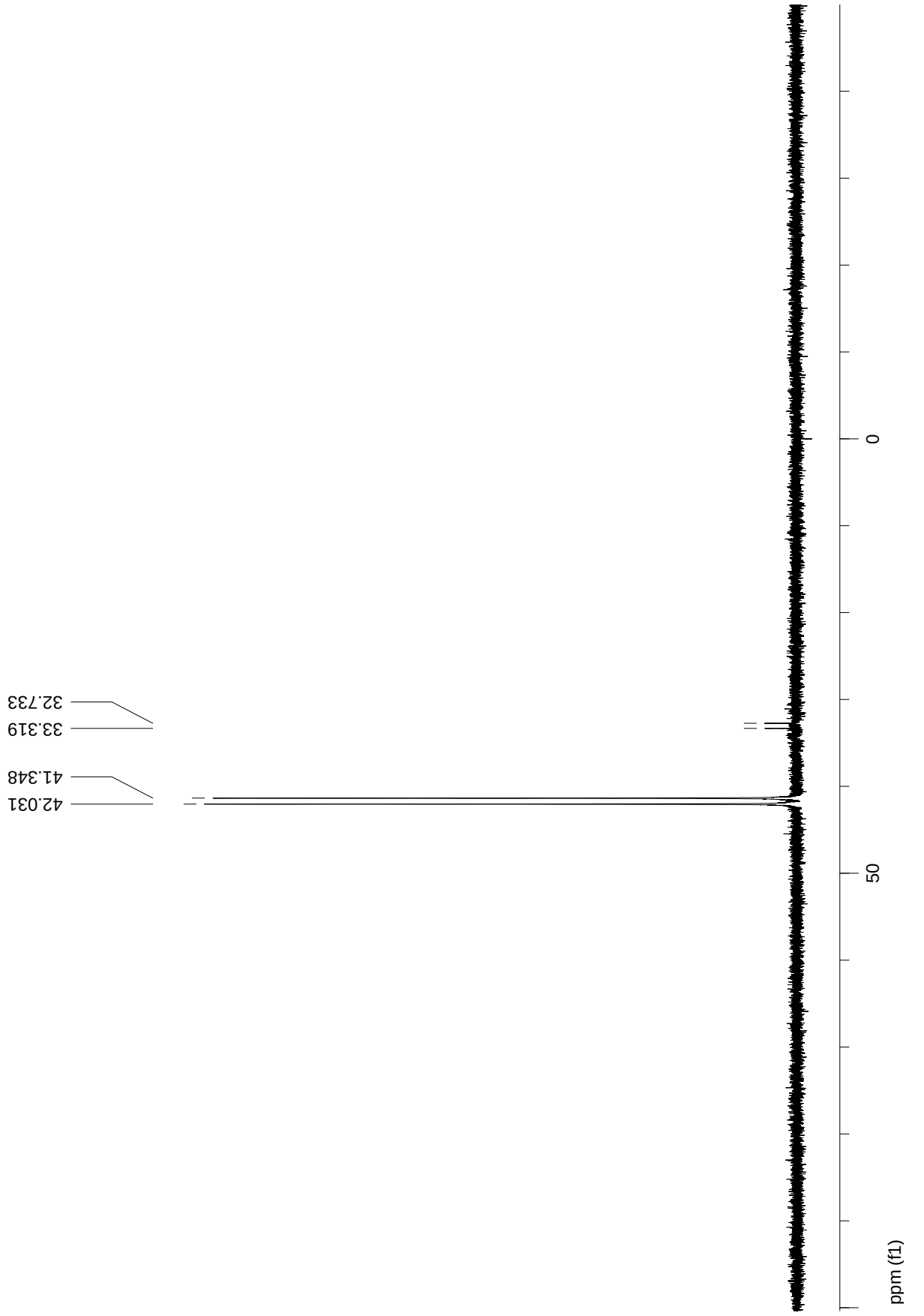
^{1}H NMR spectrum of complex **3** (500.33 MHz, CD_3CN, 228 K):



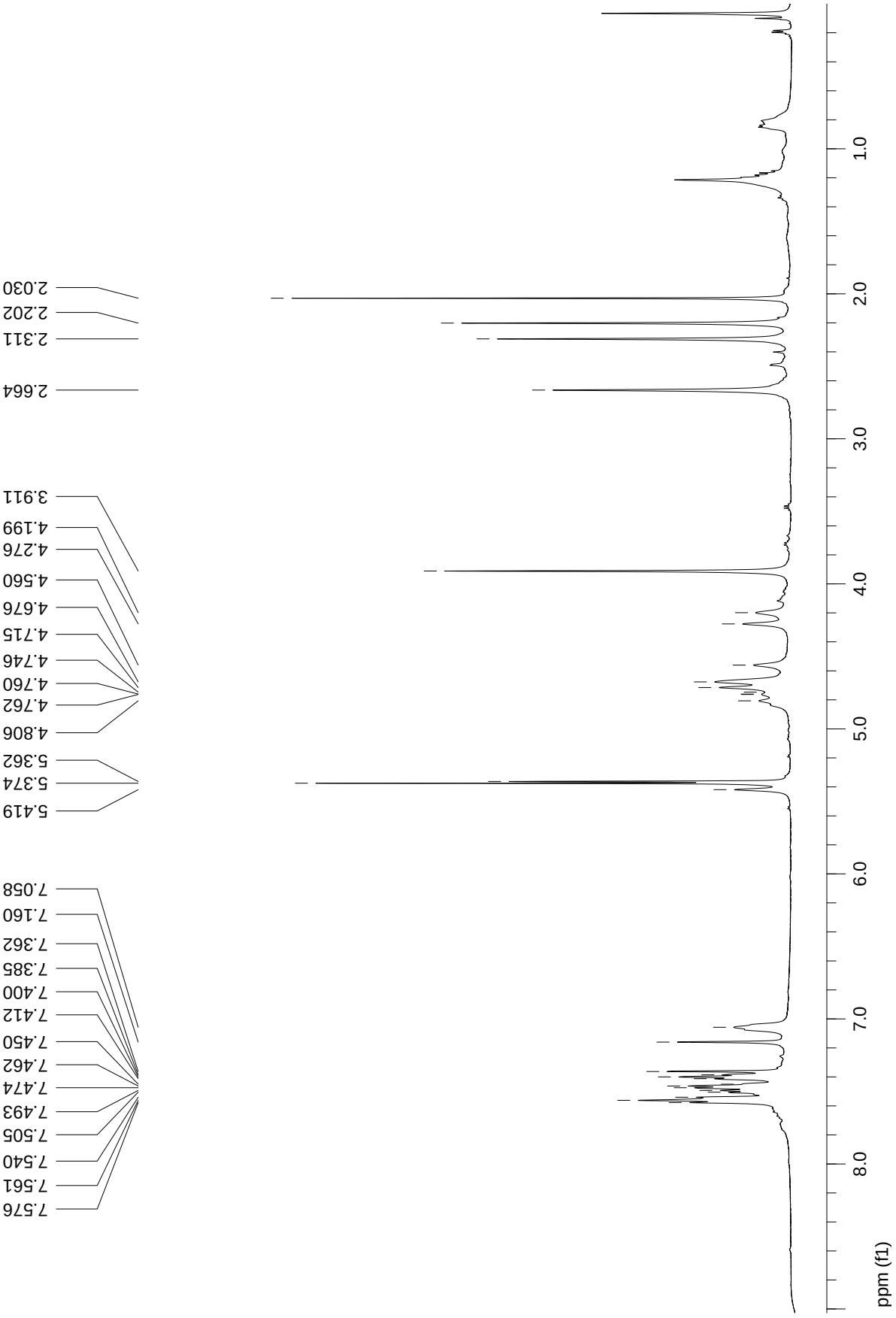
^{13}C NMR spectrum of complex **3** (125.82 MHz, CD_3CN, 228 K):



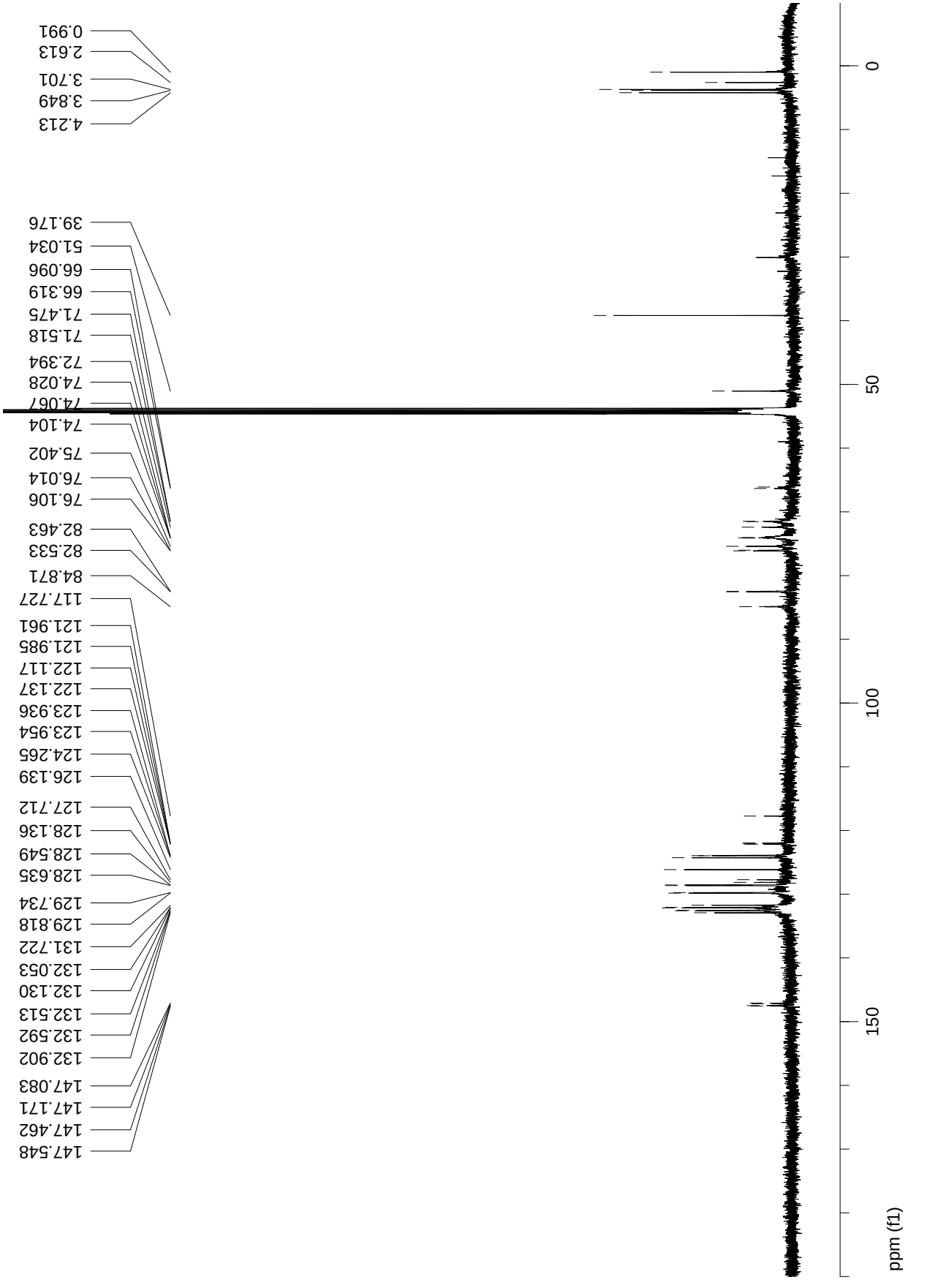
^{31}P NMR spectrum of complex **3** (125.82 MHz, CD_3CN, 228 K):



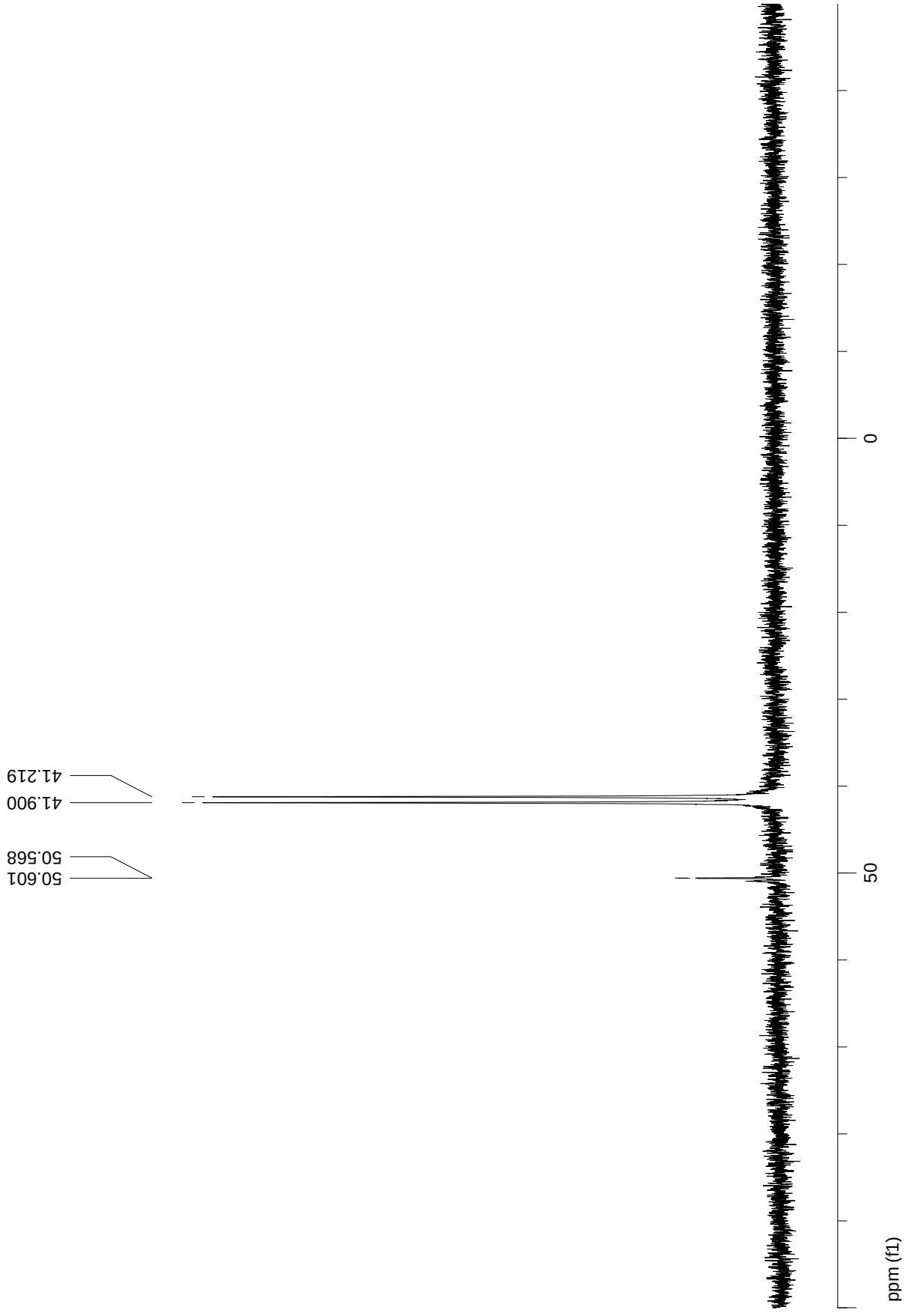
^{1}H NMR spectrum of complex **3** (500.33 MHz, CD_2Cl_2, 221 K):



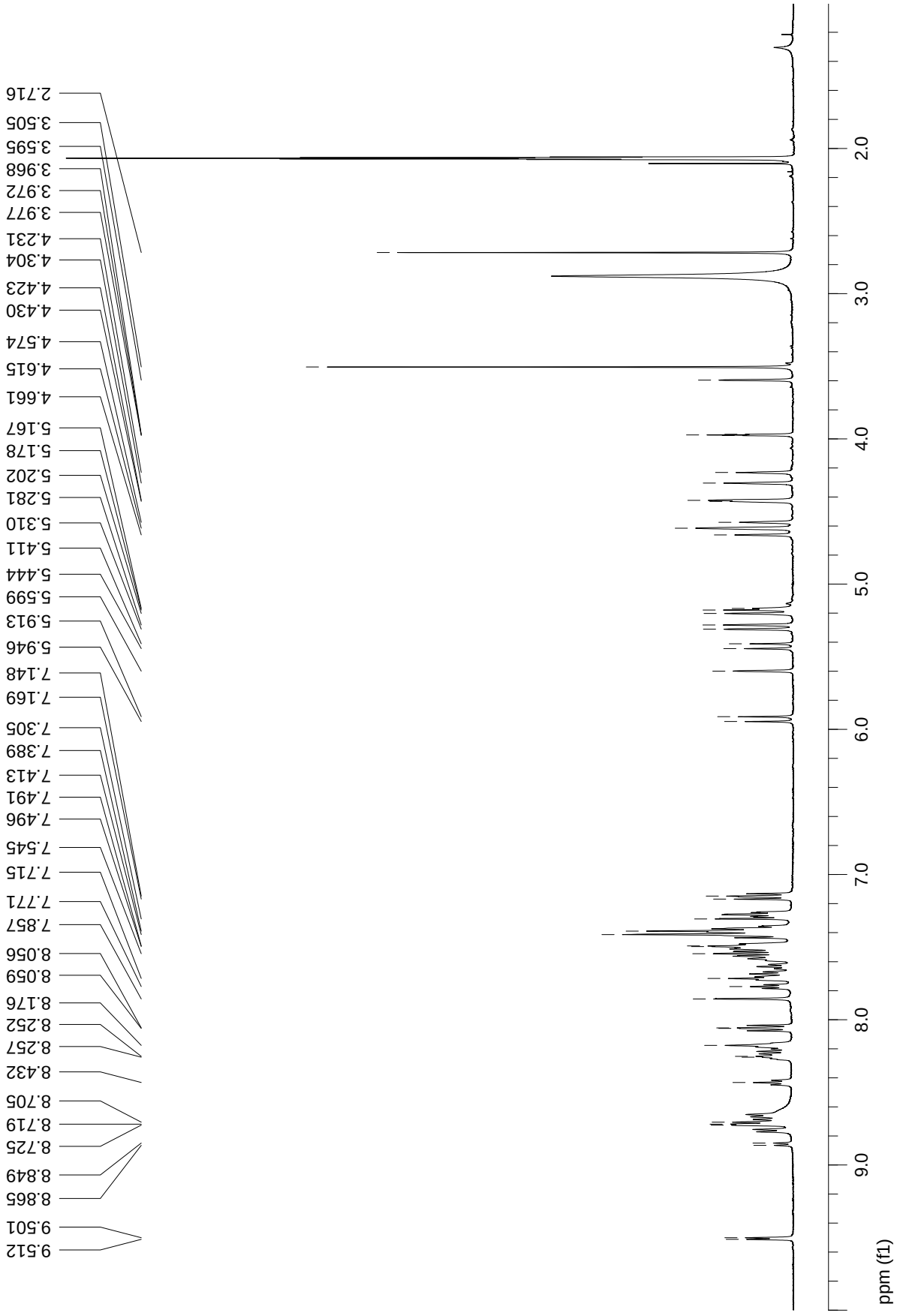
^{13}C NMR spectrum of complex **3** (500.33 MHz, CD_2Cl_2, 221 K):



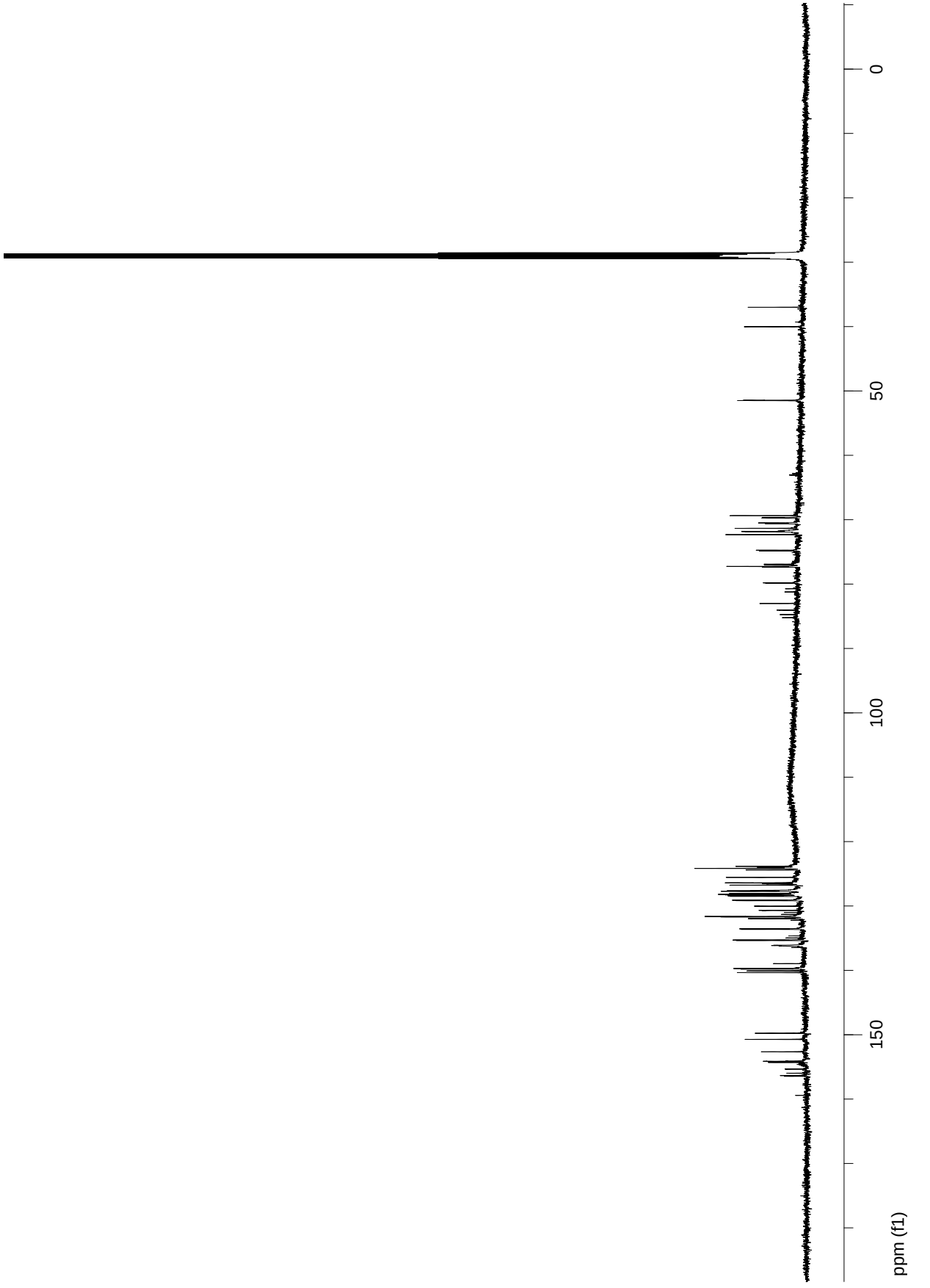
^{31}P NMR spectrum of complex **3** (500.33 MHz, CD_2Cl_2, 221 K):



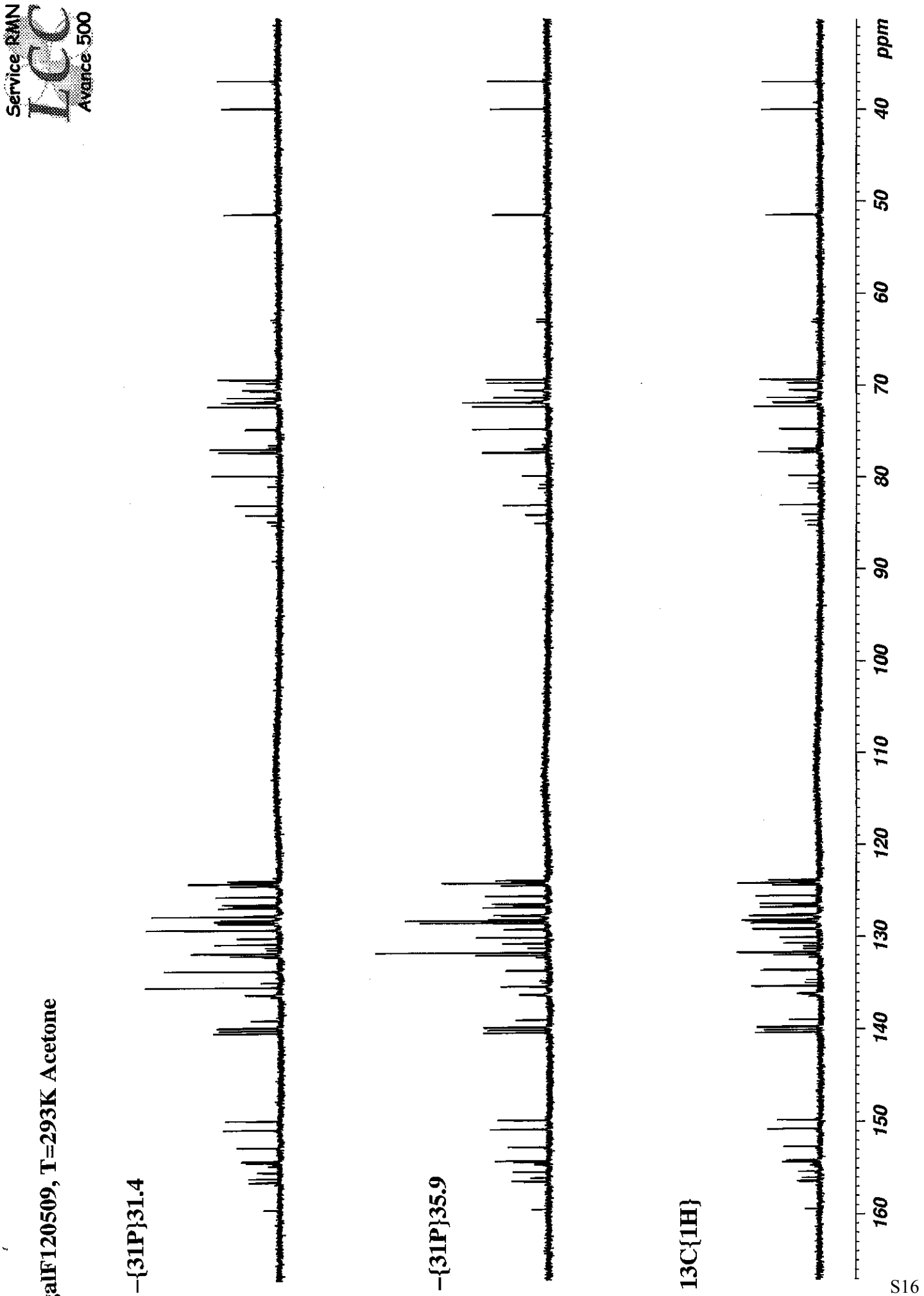
^{1}H NMR spectrum of complex **4** (500.33 MHz, $(CD_3)_2CO$, 297 K):



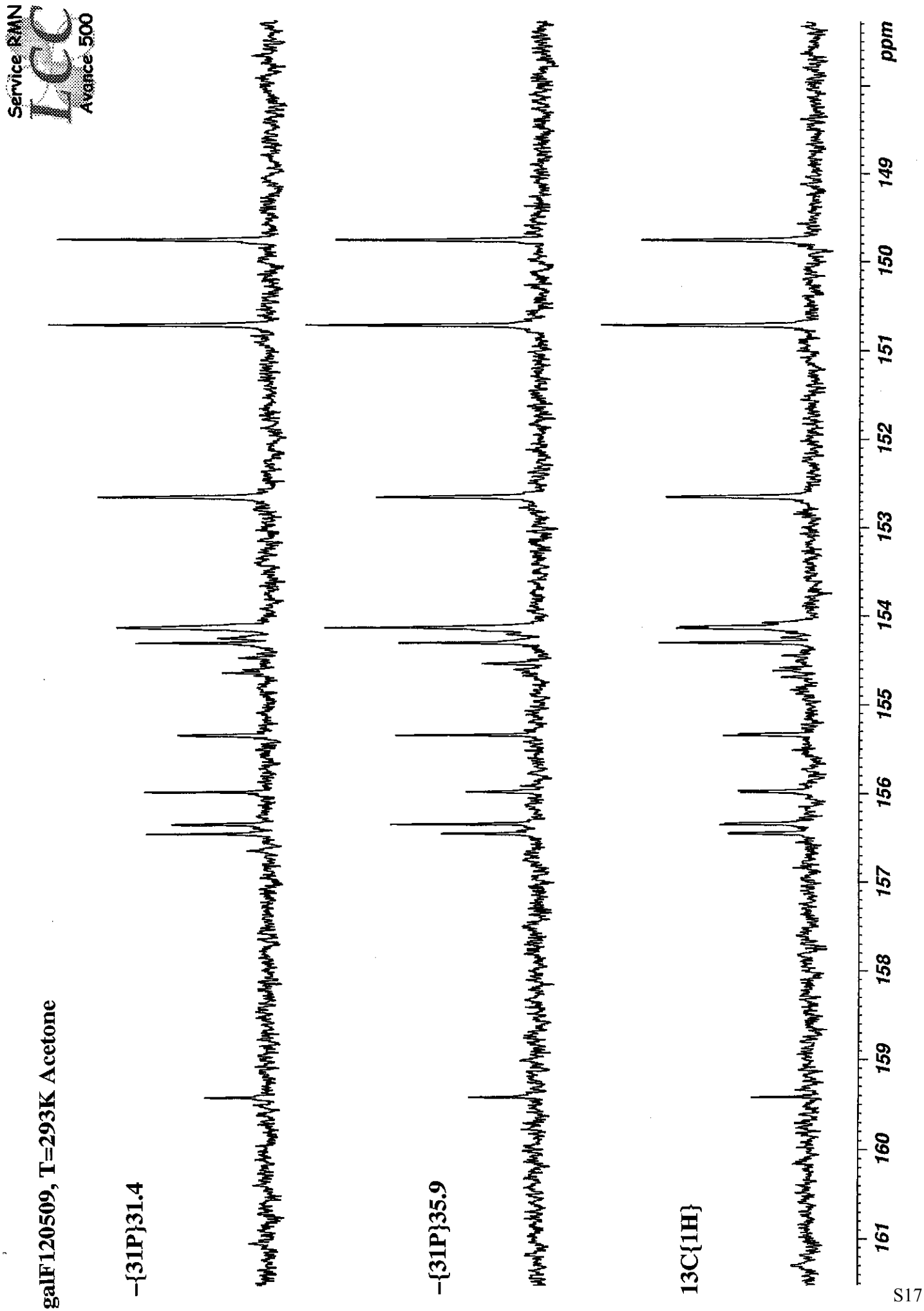
^{13}C NMR spectrum of complex **4** (125.82 MHz, $(CD_3)_2CO$, 297 K):



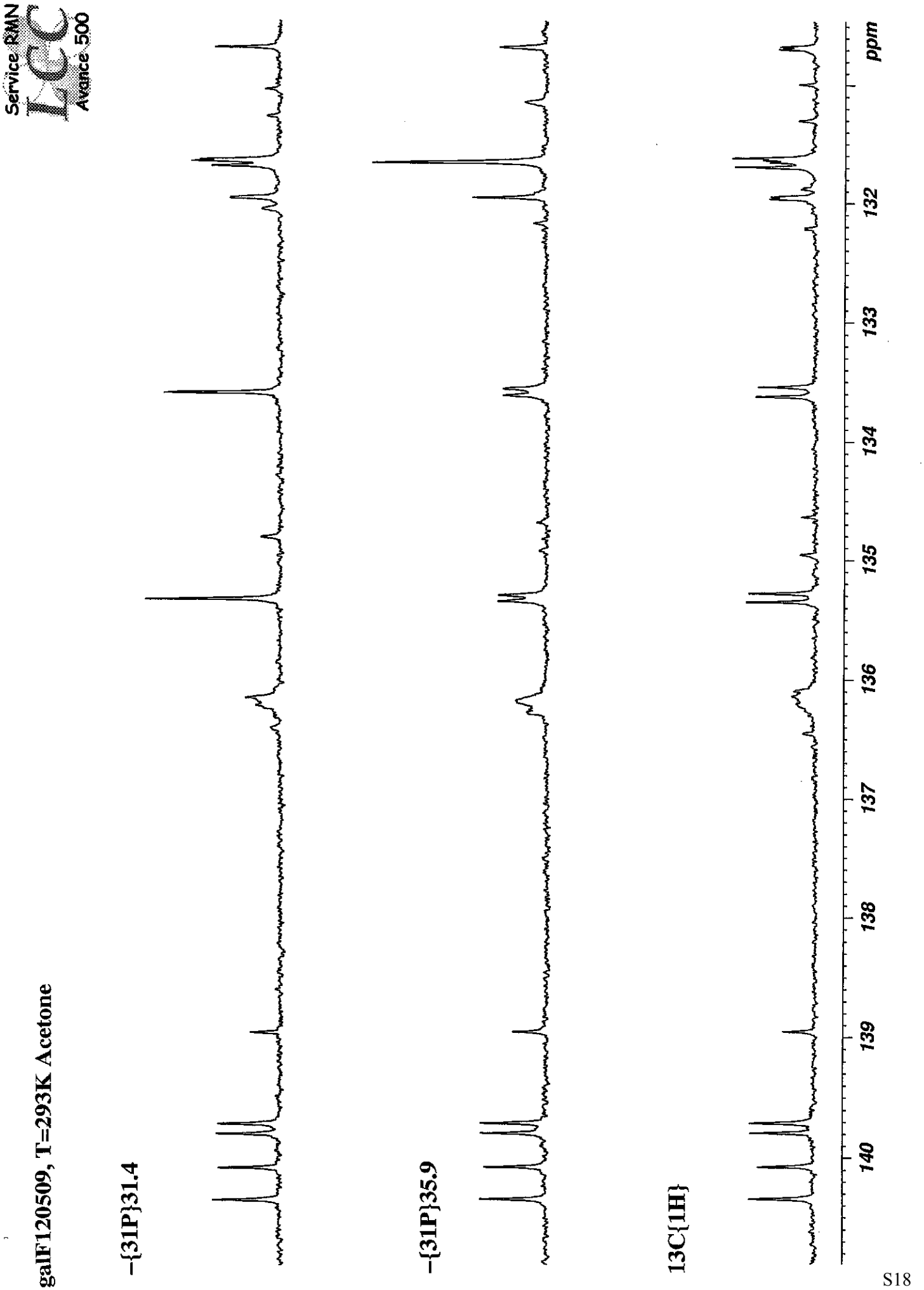
$^{13}C\{^1H\}$ spectrum of (**4**)$_2$[**5**]$_3$(CD_3COCD_3, 293K) (bottom)
$^{13}C\{^1H\}\{^{31}P\}$ spectra with selective decoupling at 35.9 ppm (middle) and 31.4 ppm (top)



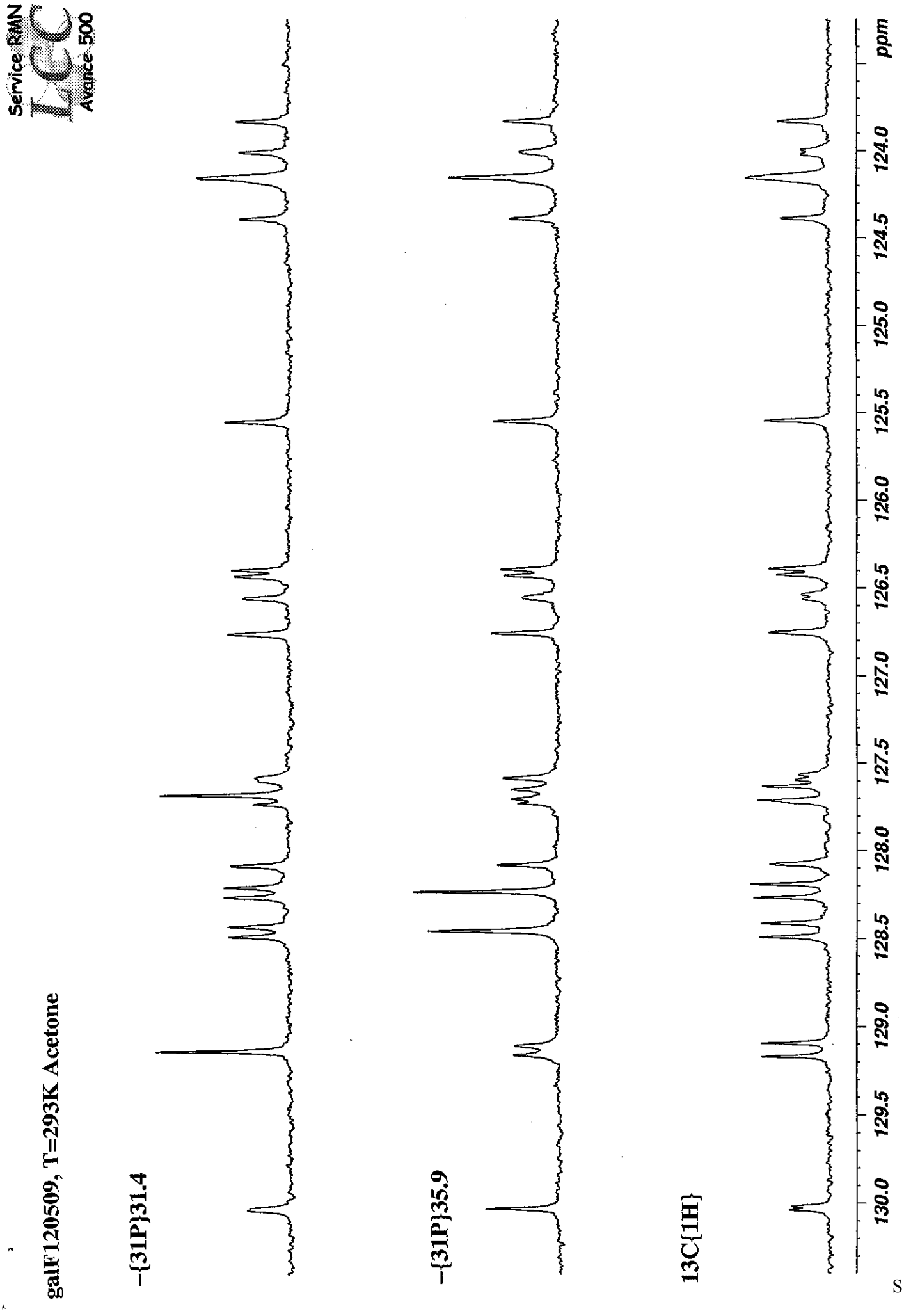
$^{13}C\{^{1}H\}$ spectrum of (4)+(5) (CD_3COCD_3, 293K) (bottom)
$^{13}C\{^{1}H\}\{^{31}P\}$ spectra with selective decoupling at 35.9 ppm (middle) and 31.4 ppm (top)



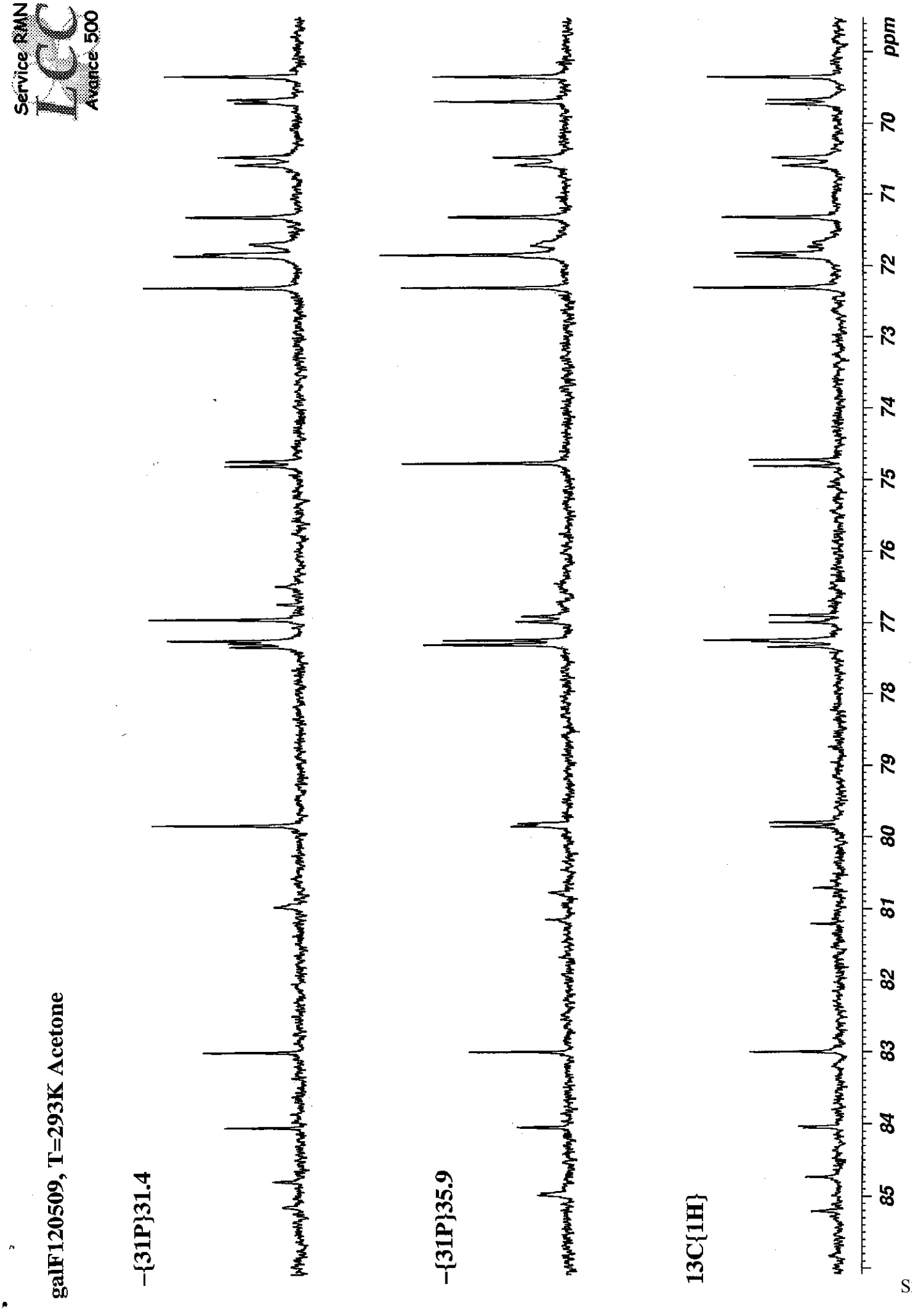
$^{13}C\{^1H\}$ spectrum of **(4)**+**(5)** (CD_3COCD_3, 293K) (bottom)
$^{13}C\{^1H\}\{^{31}P\}$ spectra with selective decoupling at 35.9 ppm (middle) and 31.4 ppm (top)



$^{13}C\{^{1}H\}$ spectrum of (4)+(5) (CD_3COCD_3, 293K) (bottom)
$^{13}C\{^{1}H\}\{^{31}P\}$ spectra with selective decoupling at 35.9 ppm (middle) and 31.4 ppm (top)



$^{13}C\{^1H\}$ spectrum of **(4)**+**(5)** (CD_3COCD_3, 293K) (bottom)
$^{13}C\{^1H\}\{^{31}P\}$ spectra with selective decoupling at 35.9 ppm (middle) and 31.4 ppm (top)



^{31}P NMR spectrum of complex **4** (202.54 MHz, $(CD_3)_2CO$, 297 K):

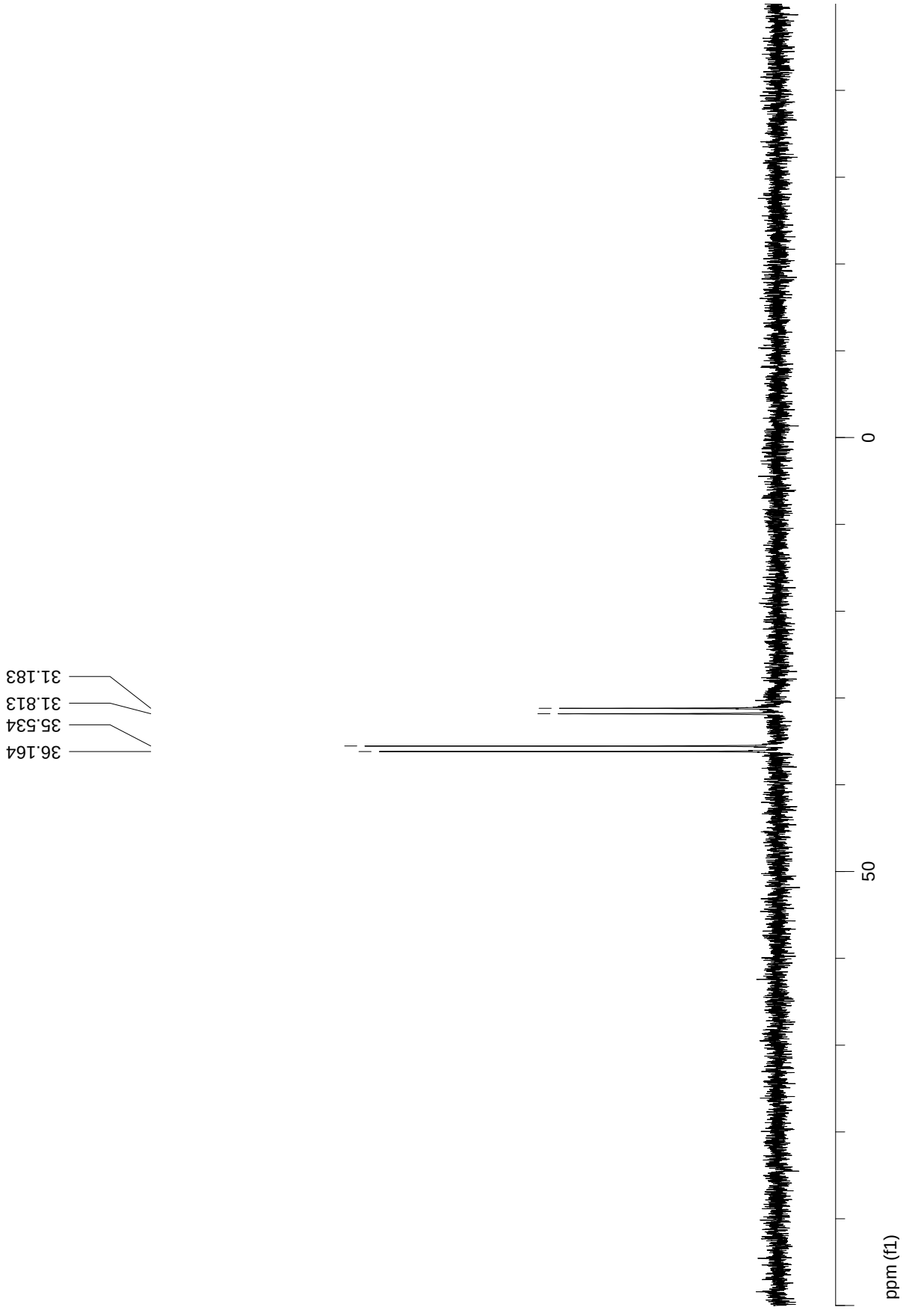


Table 1 Crystal data and structure refinement

Identification code	**4**
Empirical formula	$[C_{37}H_{32}ClFeN_4PRh]$ (BF_4), $(CH_3CN)_2$
Formula weight	926.76
Temperature,K	180(2)
Wavelength , Å	0.71073
Crystal system	Triclinic
Space group	P -1
a, Å	10.9788(3)
b, Å	13.0213(4)
c, Å	15.2286(4)
α,°	109.575(2)
β,°	90.802(2)
γ,°	110.176(2)
V, $Å^3$	1904.59(9)
Z	2
Dcalc, Mg/m^3	1.616
μ, mm^{-1}	0.986
F(000)	940
Crystal size, mm^3	0.56 x 0.25 x 0.15
θ°, range	2.63 to 26.37
Reflections collected	32054
Independent reflections [Rint]	7775 (0.0315)
Completness	99.8
Absorption correction	Multi-scan
Max. and min. transmission	1.0 and 0.804
Refinement method	F^2
Data / restraints / parameters	7775 / 0 / 508
GOF on F^2	1.053
R1, wR2 [I>2σ(I)]	0.0287, 0.0715
R1, wR2 (all data)	0.0345, 0.0757
Largest diff. peak and hole	1.026 and -0.729

Table 2 Bond lengths [Å] and angles [°] for **4**.

Fe(1)-Ct(1)	1.6207(12)	Fe(1)-Ct2(1)	1.6205(14)
Rh(1)-C(1)	2.028(2)	Rh(1)-C(11)	2.022(2)
Rh(1)-N(3)	2.104(2)	Rh(1)-N(4)	2.156(2)
Rh(1)-P(1)	2.3210(6)	Rh(1)-Cl(1)	2.4313(6)
P(1)-C(6)	1.804(2)	C(2)-C(221)	1.481(3)
P(1)-C(111)	1.825(2)	P(1)-C(121)	1.840(2)
N(2)-C(11)	1.358(3)	N(1)-C(11)	1.359(3)
N(2)-C(12)	1.380(3)	N(1)-C(13)	1.373(3)
N(2)-C(211)	1.458(3)	N(1)-C(221)	1.465(3)
N(3)-C(311)	1.333(3)	N(4)-C(415)	1.336(3)
N(3)-C(315)	1.350(3)	N(4)-C(411)	1.350(3)
C(1)-C(2)	1.422(3)	C(6)-C(10)	1.429(3)
C(1)-C(5)	1.439(3)	C(6)-C(7)	1.442(3)
C(2)-C(3)	1.428(3)	C(7)-C(8)	1.415(4)
C(3)-C(4)	1.411(4)	C(8)-C(9)	1.403(4)
C(4)-C(5)	1.426(4)	C(9)-C(10)	1.415(4)
C(12)-C(13)	1.330(4)	C(124)-C(125)	1.377(5)
C(111)-C(112)	1.387(3)	C(125)-C(126)	1.388(4)
C(111)-C(116)	1.395(3)	C(311)-C(312)	1.374(4)
C(112)-C(113)	1.384(4)	C(312)-C(313)	1.381(4)
C(113)-C(114)	1.378(4)	C(313)-C(314)	1.375(4)
C(114)-C(115)	1.376(4)	C(314)-C(315)	1.384(4)
C(115)-C(116)	1.381(3)	C(315)-C(411)	1.478(3)
C(121)-C(122)	1.391(4)	C(411)-C(412)	1.386(4)
C(121)-C(126)	1.391(3)	C(412)-C(413)	1.381(4)
C(122)-C(123)	1.388(4)	C(413)-C(414)	1.371(4)
C(123)-C(124)	1.365(5)	C(414)-C(415)	1.376(4)
N(5)-C(511)	1.126(5)	N(6)-C(611)	1.129(4)
C(511)-C(512)	1.454(6)	C(611)-C(612)	1.442(6)
B(1)-F(11)	1.392(5)	B(1)-F(12)	1.378(5)
B(1)-F(13)	1.378(5)	B(1)-F(14)	1.348(5)

Ct(1)-Fe(1)-Ct(2)	172.13(7)		
C(11)-Rh(1)-C(1)	89.97(9)	N(3)-Rh(1)-P(1)	175.08(5)
C(11)-Rh(1)-N(3)	86.40(8)	N(4)-Rh(1)-P(1)	101.58(6)
C(1)-Rh(1)-N(3)	94.51(8)	C(11)-Rh(1)-Cl(1)	168.68(7)
C(11)-Rh(1)-N(4)	97.38(8)	C(1)-Rh(1)-Cl(1)	87.57(7)
C(1)-Rh(1)-N(4)	168.75(8)	N(3)-Rh(1)-Cl(1)	82.78(5)
N(3)-Rh(1)-N(4)	77.56(8)	N(4)-Rh(1)-Cl(1)	83.56(5)
C(11)-Rh(1)-P(1)	88.92(7)	P(1)-Rh(1)-Cl(1)	101.98(2)
C(1)-Rh(1)-P(1)	87.00(7)		
C(6)-P(1)-C(111)	103.18(11)	N(2)-C(11)-Rh(1)	129.29(17)
C(6)-P(1)-C(121)	103.25(11)	N(1)-C(11)-Rh(1)	126.39(17)
C(111)-P(1)-C(121)	100.36(11)	C(13)-C(12)-N(2)	107.2(2)
C(6)-P(1)-Rh(1)	113.85(8)	C(12)-C(13)-N(1)	107.1(2)
C(111)-P(1)-Rh(1)	118.15(8)	C(112)-C(111)-C(116)	119.0(2)
C(121)-P(1)-Rh(1)	115.92(8)	C(112)-C(111)-P(1)	121.12(18)
C(11)-N(1)-C(13)	111.1(2)	C(116)-C(111)-P(1)	119.64(18)
C(11)-N(1)-C(221)	130.2(2)	C(113)-C(112)-C(111)	120.3(2)
C(13)-N(1)-C(221)	118.4(2)	C(114)-C(113)-C(112)	120.3(2)
C(11)-N(2)-C(12)	110.6(2)	C(115)-C(114)-C(113)	119.7(2)
C(11)-N(2)-C(211)	129.3(2)	C(114)-C(115)-C(116)	120.7(2)
C(12)-N(2)-C(211)	120.1(2)	C(115)-C(116)-C(111)	120.0(2)
C(311)-N(3)-C(315)	119.4(2)	C(122)-C(121)-C(126)	118.6(2)
C(311)-N(3)-Rh(1)	124.84(17)	C(122)-C(121)-P(1)	120.85(19)
C(315)-N(3)-Rh(1)	115.70(16)	C(126)-C(121)-P(1)	120.56(19)
C(415)-N(4)-C(411)	118.4(2)	C(123)-C(122)-C(121)	120.6(3)
C(415)-N(4)-Rh(1)	127.11(16)	C(124)-C(123)-C(122)	120.1(3)
C(411)-N(4)-Rh(1)	114.31(16)	C(123)-C(124)-C(125)	120.3(3)
C(2)-C(1)-C(5)	105.8(2)	C(124)-C(125)-C(126)	120.1(3)
C(2)-C(1)-Rh(1)	126.33(17)	C(125)-C(126)-C(121)	120.3(3)
C(5)-C(1)-Rh(1)	127.80(18)	N(1)-C(221)-C(2)	114.8(2)
C(1)-C(2)-C(3)	109.7(2)	N(3)-C(311)-C(312)	122.6(2)
C(1)-C(2)-C(221)	126.8(2)	C(311)-C(312)-C(313)	118.1(3)
C(3)-C(2)-C(221)	123.4(2)	C(314)-C(313)-C(312)	119.9(2)
C(4)-C(3)-C(2)	107.5(2)	C(313)-C(314)-C(315)	119.1(3)

C(3)-C(4)-C(5)	108.0(2)	N(3)-C(315)-C(314)	120.8(2)
C(4)-C(5)-C(1)	109.0(2)	N(3)-C(315)-C(411)	116.4(2)
C(10)-C(6)-C(7)	106.4(2)	C(314)-C(315)-C(411)	122.7(2)
C(10)-C(6)-P(1)	124.19(18)	N(4)-C(411)-C(412)	121.4(2)
C(7)-C(6)-P(1)	127.80(19)	N(4)-C(411)-C(315)	115.9(2)
C(8)-C(7)-C(6)	107.9(2)	C(412)-C(411)-C(315)	122.8(2)
C(9)-C(8)-C(7)	108.8(2)	C(413)-C(412)-C(411)	119.1(3)
C(8)-C(9)-C(10)	108.1(2)	C(414)-C(413)-C(412)	119.5(3)
C(9)-C(10)-C(6)	108.8(2)	C(413)-C(414)-C(415)	118.5(3)
N(2)-C(11)-N(1)	104.0(2)	N(4)-C(415)-C(414)	123.1(2)
N(5)-C(511)-C(512)	179.3(5)	N(6)-C(611)-C(612)	179.0(4)
F(14)-B(1)-F(13)	109.1(3)	F(14)-B(1)-F(11)	110.8(4)
F(14)-B(1)-F(12)	112.6(4)	F(13)-B(1)-F(11)	104.0(4)
F(13)-B(1)-F(12)	109.3(3)	F(12)-B(1)-F(11)	110.7(3)

Table 3 Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12···N5^{i}	0.95	2.54	3.420 (5)	154
C211—H21*C*···F11^{i}	0.98	2.47	3.291 (4)	141
C221—H22*B*···F11^{ii}	0.99	2.48	3.123 (4)	122
C221—H22*B*···F12^{ii}	0.99	2.49	3.319 (4)	141
C512—H51*C*···F12	0.98	2.49	3.361 (5)	149
C612—H61*B*···F13	0.98	2.49	3.088 (6)	119
C112—H112···Cl1	0.95	2.47	3.248 (3)	139
C123—H123···F13^{iii}	0.95	2.39	3.297 (5)	159
C414—H414···F14^{iii}	0.95	2.46	3.230 (5)	138

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*, −*y*, −*z*+1.

Table 4 Least-squares planes (x,y,z in crystal coordinates) and deviations from them (Å)
(* indicates atom used to define plane)

Plane 1: 8.6640 (0.0086) x - 4.3941 (0.0159) y + 8.8768 (0.0156) z = 9.9550 (0.0057)
* 0.0065 (0.0015) C1 * -0.0044 (0.0016) C2 * 0.0006 (0.0016) C3 * 0.0035 (0.0016) C4 * -0.0061 (0.0016) C5 -0.0545 (0.0041) Rh1 0.9420 (0.0050) Cl1 -0.5123 (0.0054) C11 -0.4190 (0.0051) N1 0.0529 (0.0046) C221 Rms deviation of fitted atoms = 0.0047
Plane 2: 9.5713 (0.0073) x - 3.3156 (0.0169) y + 6.4617 (0.0184) z = 5.9059 (0.0077)
* -0.0044 (0.0016) C10 * -0.0055 (0.0017) C8 * 0.0028 (0.0016) C7 * 0.0010 (0.0015) C6 * 0.0062 (0.0017) C9 0.3567 (0.0040) P1 Rms deviation of fitted atoms = 0.0044
Plane 3 : - 7.0694 (0.0030) x + 11.0248 (0.0041) y + 1.8280 (0.0111) z = 0.0441 (0.0108)
* -0.0445 (0.0022) C414 * 0.0598 (0.0023) C314 * -0.0551 (0.0022) C312

* 0.0310 (0.0022) C411 * -0.0509 (0.0019) C311 * -0.0220 (0.0023) C412 * 0.0368 (0.0022) C315 * 0.0159 (0.0022) C313 * 0.0140 (0.0019) C415 * -0.0462 (0.0023) C413 * -0.0046 (0.0017) N3 * 0.0657 (0.0018) N4 0.0484 (0.0020) Rh1 Rms deviation of fitted atoms = 0.0417
Plane 4 : 6.6608 (0.0116) x - 3.6021 (0.0172) y + 11.5034 (0.0130) z = 11.1929 (0.0081)
* -0.0042 (0.0014) C11 * 0.0024 (0.0017) C13 * -0.0050 (0.0017) C12 * 0.0011 (0.0016) N1 * 0.0057 (0.0015) N2 Rms deviation of fitted atoms = 0.0041
Angle between planes 1 and 2 = 10.88 (0.17)
Angle between planes 1 and 3 = 71.10 (0.07)
Angle between planes 1 and 4 = 14.78 (0.17)
Angle between planes 2 and 3 = 69.84 (0.07)

Computational details

The calculations were carried out with the Gaussian09 suite of programs.[8] The geometry optimizations were performed without any symmetry constraint using the B3LYP functional.[9,10] The standard 6-31G basis functions were used for all light atoms (H, C, N) and also for Cl, whereas the P, Fe, and Rh atoms were described with the LANL2DZ basis functions which included an effective core potential. A d polarization function (α = 0.387) [11] was added to the P atom and an f polarization function (α = 1.35) [12] to the Rh atom.

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