Supporting Information for XXXXXXX

The First Imidazolium-Substituted Metal Alkylidene

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Experimental details

General procedures

The organic reactions were carried out in oven-dried glassware. All manipulations of organometallic compounds were performed using standard Schlenk techniques, including flame-drying of Schlenkware under argon. Toluene, benzene, THF, CH_2Cl_2, hexane and pentane were purified in MBraun SPS purification columns.[1] All other chemicals were purchased commercially and used without further purification. F-254 TLC plates were used in order to follow the progress of the reactions, and to check the purity of synthesized products. The spots of substances on the thin-layer were visualized under UV light. Flash chromatography was carried out using SDS silica gel 60 (40-63 μm). ATR-IR spectra were recorded on a Nicolet-Impact 410 FTIR spectrometer and a Nicolet FT-7199 spectrometer. The spectra were reported as wavenumbers (ν) in cm^{-1}. MS, ESI-MS and HRMS mass spectra were recorded respectively on Finnigan MAT 8200 (70 eV), on Hewlett-Packard HP 5989 B MS-Engine and on Finnigan MAT 95 at Max-Planck-Institut für Kohlenforschung. Elemental analyses were performed using Elementar Vario EL III (University of Bergen) and by H. Kolbe (Mülheim/Ruhr). Thermodynamically corrected melting points were determined using a Büchi B-540 instrument. NMR spectra were recorded on Bruker DPX 300, AV 400, AV 500 and AV 600 spectrometers. The chemical shifts are reported downfield from tetramethylsilane (TMS) (δ scale) or calibrated to solvent residual peaks as an internal standard ($CDCl_3$: δ_C = 77.2 ppm, residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm; $(CD_3)_2SO$: δ_C = 39.5 ppm, residual $(CHD_2)CD_3SO$ in $(CD_3)_2SO$: δ_H = 2.50 ppm; CD_2Cl_2: δ_C = 53.8 ppm, residual $CHDCl_2$ in CD_2Cl_2: δ_H = 5.32 ppm.[2]

X-ray crystallography and crystal structure determination of complexes 3 and 4. Crystals suitable for diffraction experiments were mounted on a glass fiber (**3**) and in Paratone-N inside a nylon loop (Hampton research) (**4**). Data collection was done on a Bruker AXS SMART 2K CCD diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) performing ϖ scans in four φ positions, employing the SMART software package.[3] The collected images (2484 [**3**], 1888 [**4**]), were integrated using SAINT.[4] Numerical absorption correction was done using SHELXTL.[5] The structures were solved by direct methods and refined with standard difference Fourier techniques.[5] CCDC-645473 and 645474 contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre, via www.ccdc.cam.ac.uk/data_request/cif.

Synthetic protocols

1-(2,4,6-trimethylphenyl)-1H-imidazole. Glacial acetic acid (10 mL), aqueous formaldehyde (3 mL), and aqueous glyoxal (4.6 mL) were transferred to a round bottom flask (50 mL) and heated at 70ºC. A solution of glacial acetic acid (10 mL), ammonium acetate in water (3.08 g/2 mL), and mesitylamine (5.6 mL) was added drop-wise to the flask over a period of 30 min. The solution was continuously stirred and heated at 70 ºC for 18h. The reaction mixture was then cooled to room temperature and added drop-wise to a stirred solution of $NaHCO_3$ (29.4 g) in water (300 mL), resulting in precipitation of the product. The precipitate was isolated in a filter funnel and washed with water (3 × 20 mL) and air dried to achieve a brown-yellow solid (5.18 g). The raw product was re-crystallized using ethyl

acetate, to obtain the product 1-(2,4,6-trimethylphenyl)-1*H*-imidazole in a yield of 69.7 %. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.43 (m, 1H), 7.23 (m, 1H), 6.97 (m, 2H), 6.89 (m, 1H), 2.34 (s, 3H), 1.99 (s, 6H).

3-(2-hydroxy-5-nitrobenzyl)-1-(2,4,6-trimethylphenyl)imidazolium bromide (1). 1-(2,4,6-Trimethylphenyl)-1H-imidazole (0.61 g, 3.3 × 10^{-3} mol) and 2-hydroxy-5-nitrobenzyl bromide (0.76 g, 3.3 × 10^{-3} mol) were dissolved in toluene (8 mL) and refluxed for 18 h. During the course of the reaction, a pale yellow solid precipitated in the reaction mixture. After cooling to room temperature, the solid was isolated on a filter placed in a Büchner funnel, washed with methyl-tert-butyl ether (3 × 10 mL) and dried under vacuum to give a yield of 98.5% (1.35 g). M.p. = 276-278 ^{o}C (dec.). ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ = 11.83 (br, 1H), 9.59 (s, 1H), 8.39 (s, 1H), 8.21 (d, *J* = 8.6, 1H), 8.06 (s, 1H), 7.93 (s, 1H), 7.20-7.07 (m, 3H), 5.56 (s, 2H), 2.32 (s, 3H), 2.01 (s, 6H); ^{13}C NMR ($(CD_3)_2SO$, 101 MHz): δ = 162.4, 140.3, 139.4, 138.2, 134.3, 131.2, 129.2, 127.1, 126.9, 124.1, 123.3, 121.4, 115.9, 48.3, 20.6, 16.9. IR (film, cm^{-1}): 3161 (w), 3067 (w), 2943 (br), 1617 (w), 1593 (m), 1567 (w), 1549 (m), 1524 (m), 1495 (m), 1437 (m), 1388 (w), 1340 (s), 1281 (s), 1197 (m), 1154 (m), 1133 (w), 1118 (w), 1092 (m), 1068 (m), 935 (m), 925 (m), 897 (w), 856 (m), 843 (m), 831 (m), 820 (w), 790 (w), 770 (w), 753 (m), 747 (m), 732 (w), 700 (m), 664 (m); MS (ESI), m/z: 338 $[417 - Br]^+$. Elemental analysis, calculated for $C_{19}H_{20}N_3O_3Br$: C, 54.56; H, 4.82; N, 10.05; found: C, 54.84; H, 4.76; N, 9.88.

Synthesis of the silver complex (2). 3-(2-hydroxy-5-nitrobenzyl)-1-(2,4,6-trimethylphenyl) imidazolium bromide (**1**) (0.500 g, 1.20 × 10^{-3} mol) and silver(I) oxide (0.570 g, 2.46 × 10^{-3} mol) were added to a round bottom flask equipped with a cooler. Dried THF and benzene (8.5 mL + 8.5 mL), and molecular sieves (4Å, 1.12 g) were added to the flask. The reaction mixture was stirred at reflux for 3h, cooled to room temperature and diluted with CH_2Cl_2 (80 mL). The mixture was then filtered through a pad of celite (2/5 cm, w/l), that successively was washed with CH_2Cl_2 (3 × 20 mL). The solvent was removed under reduced pressure to provide a yellow solid, the silver complex, in a yield of ~65% (0.343 g). M.p. = 178-180 ^{o}C (dec.). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.14 (s, 1H), 7.76 (d, *J* = 7.9, 1H), 7.36 (s, 1H), 7.00 (s, 2H), 6.96 (s, 1H), 5.80 (d, *J* = 7.9, 1H), 5.23 (s, 2H), 2.39 (s, 3H), 1.93 (s, 6H). ^{13}C NMR ($CDCl_3$, 125.8 MHz):[6] δ = 174.6, 139.7, 136.4, 135.2, 134.6, 129.3, 127.5, 127.0, 124.4, 122.0, 121.7, 121.3, 50.7, 21.3, 18.0. IR (film, cm^{-1}): 3127(w), 2920 (w), 1589 (m), 1566 (w), 1469 (m), 1437 (w), 1408 (w), 1278 (s), 1253 (m), 1237 (m), 1188 (w), 1165 (w), 1151(m), 1085 (m), 1031 (w), 927 (m), 854 (w), 835 (m), 820 (w), 790 (w), 768 (w), 735 (w), 706 (w), 679 (w), 652 (m). Elemental analysis, calculated for $C_{19}H_{18}O_3N_3Ag$: C, 51.37; H, 4.08; N, 9.46; found: C, 50.49; H, 3.81; N, 8.92.

Synthesis of complex 3. Hoveyda first-generation catalyst (0.070 g, 1.2 × 10^{-4} mol) and **2** (0.058 g, 1.3 × 10^{-4} mol) were added to a 25 mL Schlenk flask. The flask was evacuated and back-filled with argon. Dry toluene (2.5 mL) and dry THF (2.5 mL) were added to the flask under argon. The mixture was stirred at 55 ºC for 2.5 h, followed by another addition of **2** (46 mg, 1.03 × 10^{-4} mol). The reaction was continued at the same temperature for another 2.5 h. Then, the mixture was cooled to room temperature and the solvent removed under reduced pressure. The residual, a dark-brown solid was passed through a silica gel column using diethyl ether/hexane (9:1) as eluent. The green fraction (**3**) and the orange fraction (**4**) were collected, concentrated and afforded 0.043 g (40 %) and 0.0032 g (2.8 %), respectively. Green fraction (**3**): ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 15.90 (s, 1H), 8.21 (d, *J* = 3.0 Hz, 1H), 8.03 (dd, *J* = 9.2, 3.0 Hz, 1H), 7.97 (d, *J* = 3.0 Hz, 1H), 7.71 (dd, *J* = 9.3, 3.0 Hz, 1H), 7.42-7.37 (m, 1H), 7.31 (d, *J* = 13.6 Hz, 1H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.21 (d, *J* = 1.9 Hz, 1H), 7.02 (s, 1H), 6.81-6.91 (m,4H), 6.67 (d, *J* = 9.2 Hz, 1H), 6.60 (d, *J* = 2.1 Hz, 1H), 6.37 (d, *J* = 1.9 Hz, 1H), 6.21 (s, 1H), 6.08 (s, 1H), 6.04 (d, *J* = 9.3 Hz, 1H), 6.01 (d, *J* = 13.8 Hz, 1H), 5.78

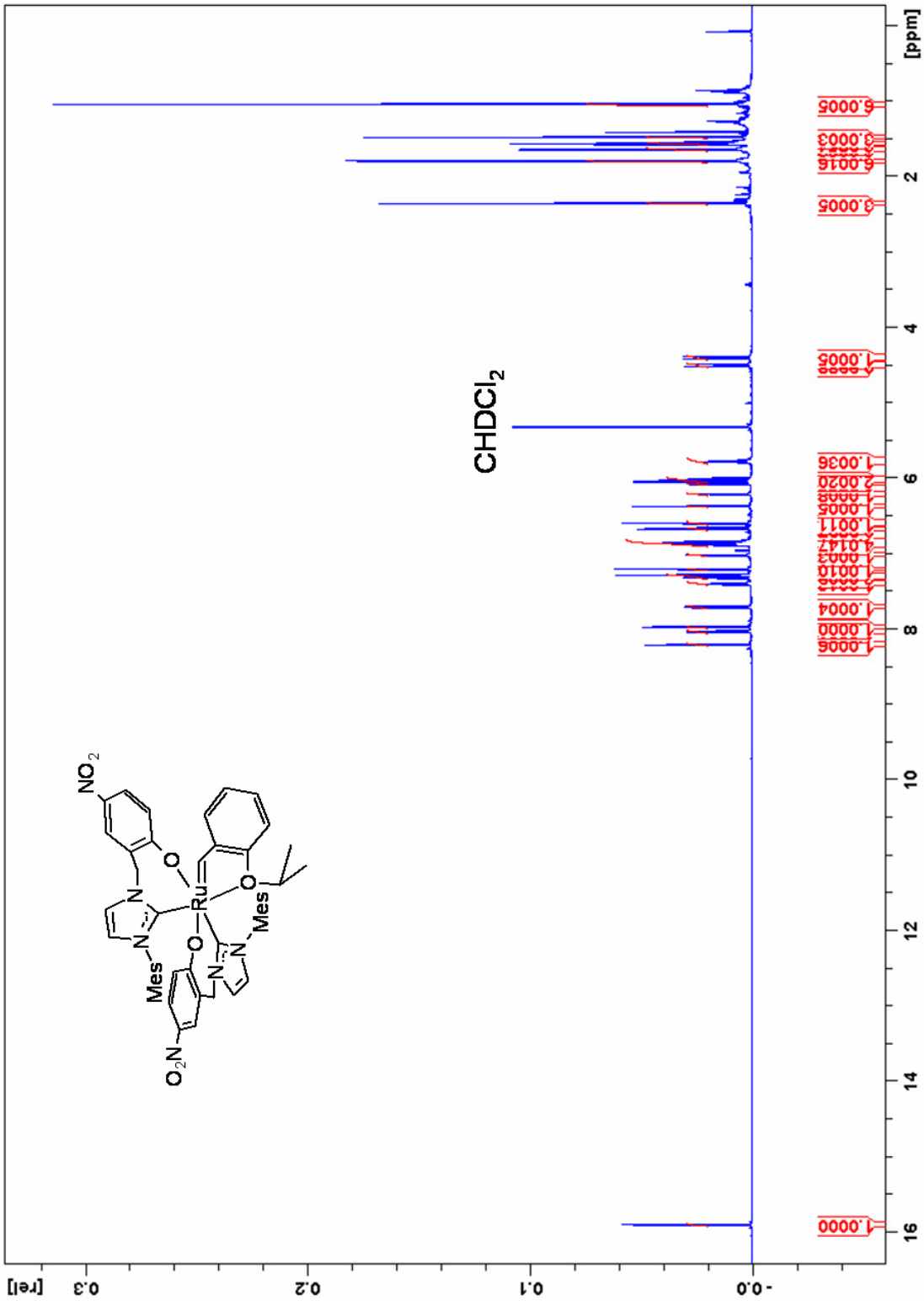
(septet, J = 6.7 Hz, 1H), 4.50 (d, J = 13.8 Hz, 1H), 4.40 (d, J = 13.6 Hz, 1H), 2.36 (s, 3H), 1.80 (s, 3H), 1.79 (s, 3H), 1.64 (d, J = 6.7 Hz, 3H), 1.56 (d, J = 6.7 Hz, 3H), 1.48 (s, 3H), 1.04 (s, 6H); ^{13}C NMR ((CD_2Cl_2, 125.8 MHz): δ = 297.9 (d, J = 9.8), 179.0, 177.7, 176.4, 173.1, 154.5, 146.0, 140.0, 138.6, 136.9, 136.3, 135.3, 135.2, 134.2, 133.6, 133.5, 130.1, 129.0, 128.9, 128.5, 127.7, 126.7, 126.5, 126.4, 125.9, 125.4, 125.2, 124.4, 123.6, 123.4, 121.9, 121,8, 120.4, 117.9, 77.8, 52.3, 51.2, 22.7, 21.9, 21.1, 20.9, 18.3, 17.5, 16.75, 16.66; IR (film, cm^{-1}): 3131 (w), 2922 (w), 2857 (w), 1935 (w), 1767 (w), 1591 (m), 1563 (m), 1476 (m), 1441 (m), 1404 (w), 1376 (m), 1348 (w), 1272 (s), 1246 (s), 1222 (m), 1183 (m), 1170 (m), 1149 (m), 1124 (m), 1110 (m), 1085 (s), 1034 (m), 1018 (m), 965 (w), 932 (m), 836 (m), 752 (m), 710 (m), 702 (m), 686 (m), 660 (m). MS (EI), m/z: 922 $[M]^+$. HRMS (ESIpos), m/z: 923.270932 $(M+H)^+$; calculated for $C_{48}H_{49}N_6O_7Ru$: 923.272688. Elemental analysis, calculated for $C_{48}H_{48}O_7N_6Ru$: C, 62.53; H, 5.25; N, 9.11; found: C, 62.21; H, 5.36; N, 8.76. An aliquot of complex **3** was crystallized by slow diffusion of pentane into a concentrated solution of **3** in CH_2Cl_2 at room temperature. A suitable crystal was selected and structurally characterized by X-ray diffraction.

Synthesis of complex 4. Hoveyda first-generation catalyst (0.135 g, 2.25×10^{-4} mol) and **2** (0.200 g, 4.45×10^{-4} mol) were added to a 25 mL Schlenk flask. The flask was evacuated and back-filled with argon. Dry THF (6 mL) was added to the flask under argon. The mixture was stirred at reflux for 7 h, and then cooled to room temperature, followed by removal of the solvent under reduced pressure. The residual, a dark-brown solid was passed through a silica gel column using diethyl ether/hexane (9:1) as eluent. The green fraction (**3**) and the orange fraction (**4**) were collected, concentrated and afforded 0.0132 g (6.30 %) and 0.0255 mg (11.9 %), respectively. Orange fraction (**4**): ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 8.05-8.00 (m, 2H), 7.83 (d, J = 2.9 Hz, 1H), 7.79 (dd, J = 9.1, 2.9 Hz, 1H), 7.25 (ddd, J = 8.5, 7.3, 1.8 Hz, 1H), 7.20 (d, J = 2.0 Hz, 1H), 6.99 (br s, 1H), 6.93 (d, J = 2.0 Hz, 1H), 6.88 (br s, 1H), 6.75-6.69 (m, 2H), 6.55-6.59 (m, 2H), 6.47 (dd, J = 7.6, 1.8 Hz, 1H), 6.38 (d, J = 2.0 Hz, 1H), 6.34 (d, J = 9.1 Hz, 1H), 6.27 (td, J = 7.3, 0.8 Hz, 1H) 6.11 (d, J = 14.1 Hz, 1H), 5.56 (d, J = 14.1 Hz, 1H), 4.55 (septet, J = 6.0 Hz, 1H), 4.48 (d, J = 14.1 Hz, 1H), 3.80 (d, J = 14.1 Hz, 1H), 2.35 (s, 3H), 2.16 (s, 6H), 1.85 (s, 3H), 1.59 (s, 3H), 1.47 (s, 3H), 1.37 (d, J = 6.0 Hz, 3H), 1.22 (d, J = 6.0 Hz, 3H); ^{13}C NMR ((CD_2Cl_2, 125.8 MHz): δ = 244.3, 179.9, 172.9, 171.6, 161.7, 149.2, 145.6, 140.3, 138.7, 138.3, 138.2, 137.7, 135.0, 134.5, 134.3, 133.9, 130.8, 130.5, 129.7, 129.2, 129.1, 128.9, 127,9, 127.0, 126.3, 126.1, 125.6, 125.0, 124.9, 123.1, 123.0, 121.9, 121.7, 120.8, 120.6, 120.5, 111.3, 70.0, 52.3, 49.4, 22.8, 22.14, 22.07, 21.1, 20.9, 19.0, 18.6, 18.3, 16.8. IR (film, cm^{-1}): 3165 (w), 3126 (w), 3098 (w), 3064 (w), 2963 (w), 2923 (w), 2845 (w), 1593 (m), 1564 (w), 1472 (m), 1439 (m), 1404 (w), 1382 (w), 1278 (s), 1258 (s), 1172 (m), 1153 (m), 1121 (m), 1087 (s), 1016 (s), 957 (m), 932 (m), 903 (m), 867 (m), 837 (m), 792 (s), 751 (m), 732 (m), 710 (m), 697 (m), 666 (m). MS (EI), m/z: 956 $[M]^+$. HRMS (ESIpos), m/z: 957.231375 $(M+H)^+$; calculated for $C_{48}H_{48}ClN_6O_7Ru$: 957.232952. Elemental analysis, calculated for $C_{48}H_{47}O_7N_6RuCl{\cdot}0.2CH_2Cl_2$: C, 59.47; H, 4.91; N, 8.64; found: C, 59.18; H, 5.26; N, 8.33. An aliquot of complex **4** was crystallized by slow diffusion of hexane into a concentrated solution of **4** in CH_2Cl_2 at room temperature. A suitable crystal was selected and structurally characterized by X-ray diffraction.

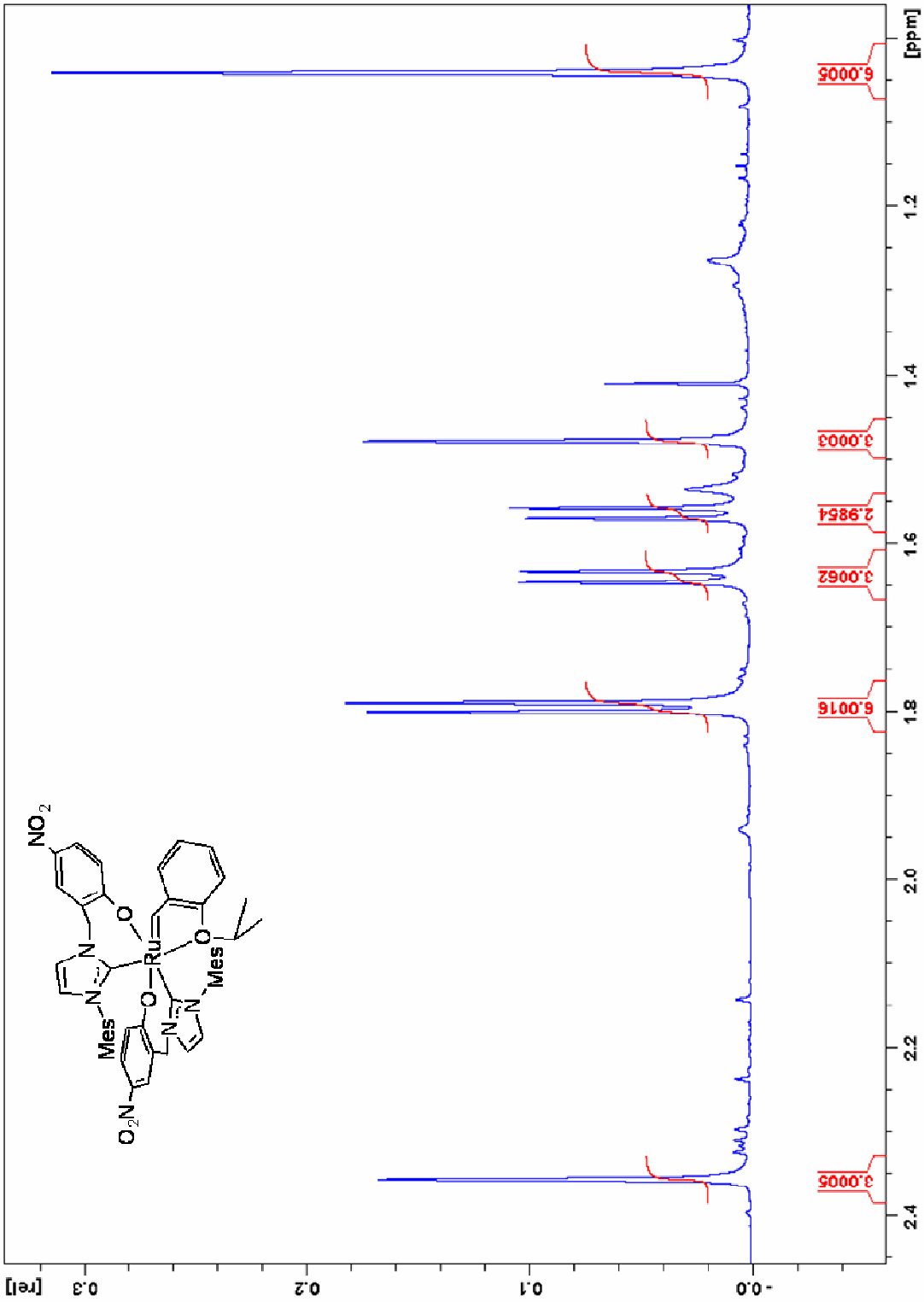
Analytical results for complex 3

NMR, MS and IR spectra of complex 3

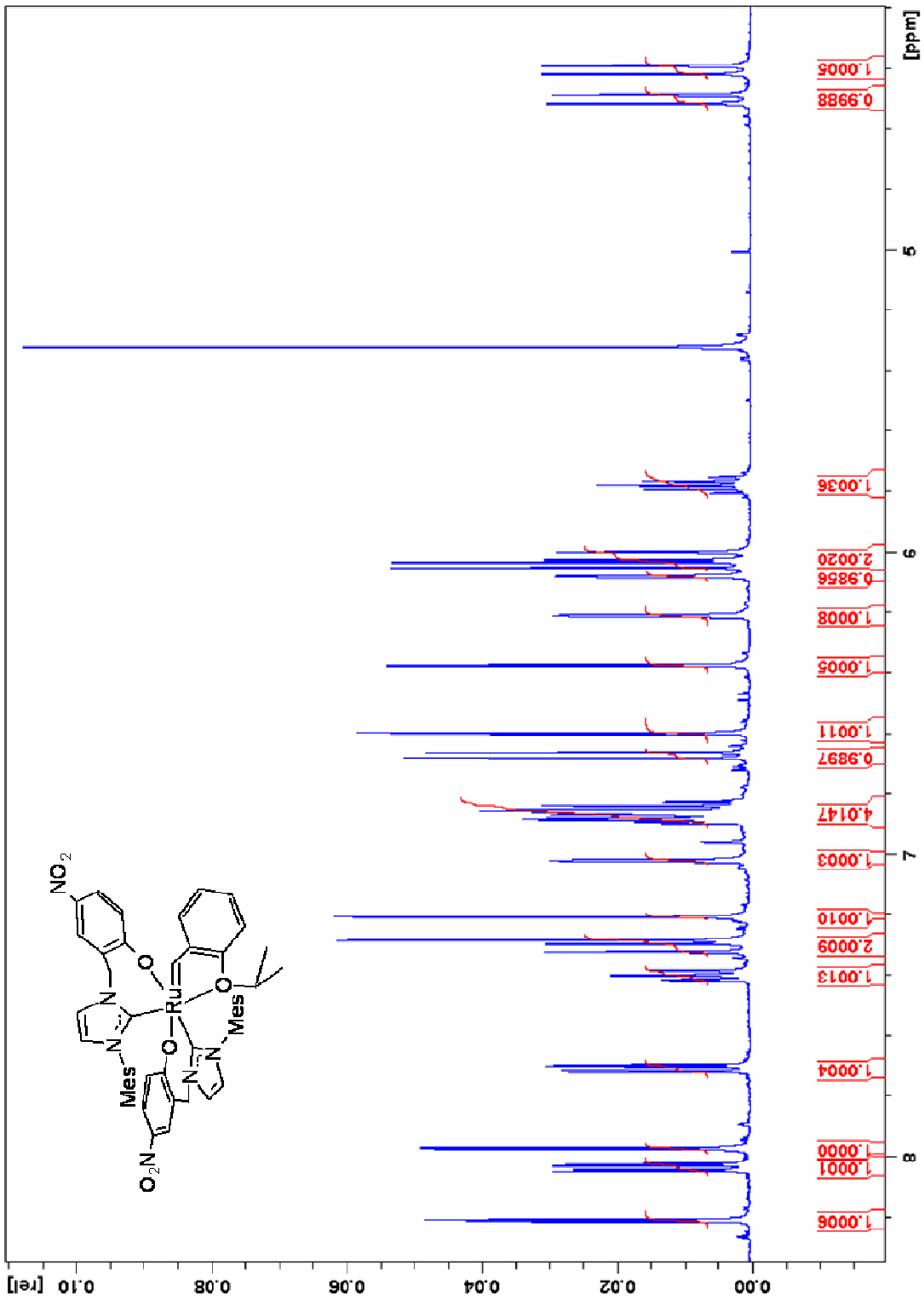
^{1}H NMR spectrum of complex 3



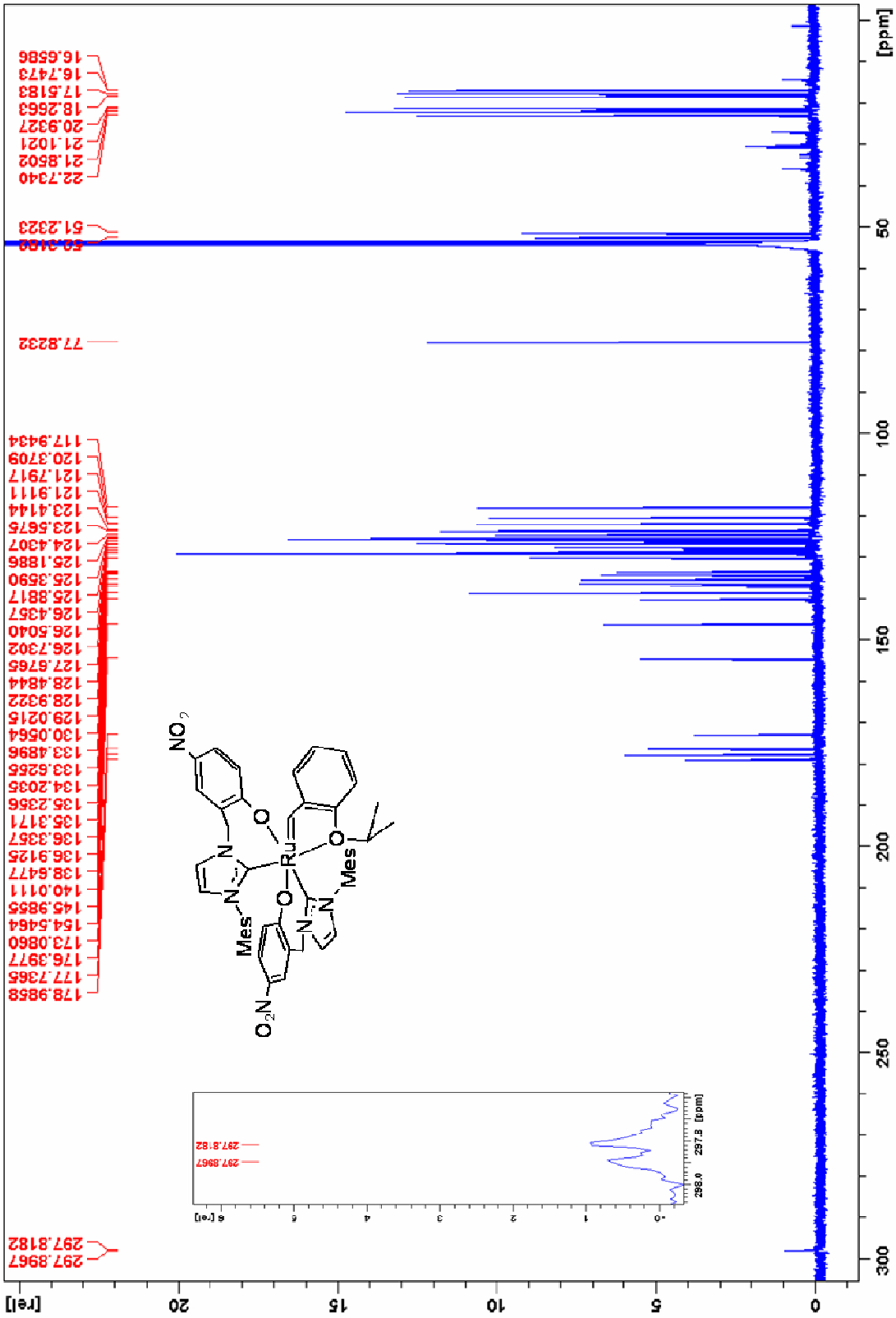
^{1}H NMR spectrum of complex 3 (2.10–2.45 ppm)



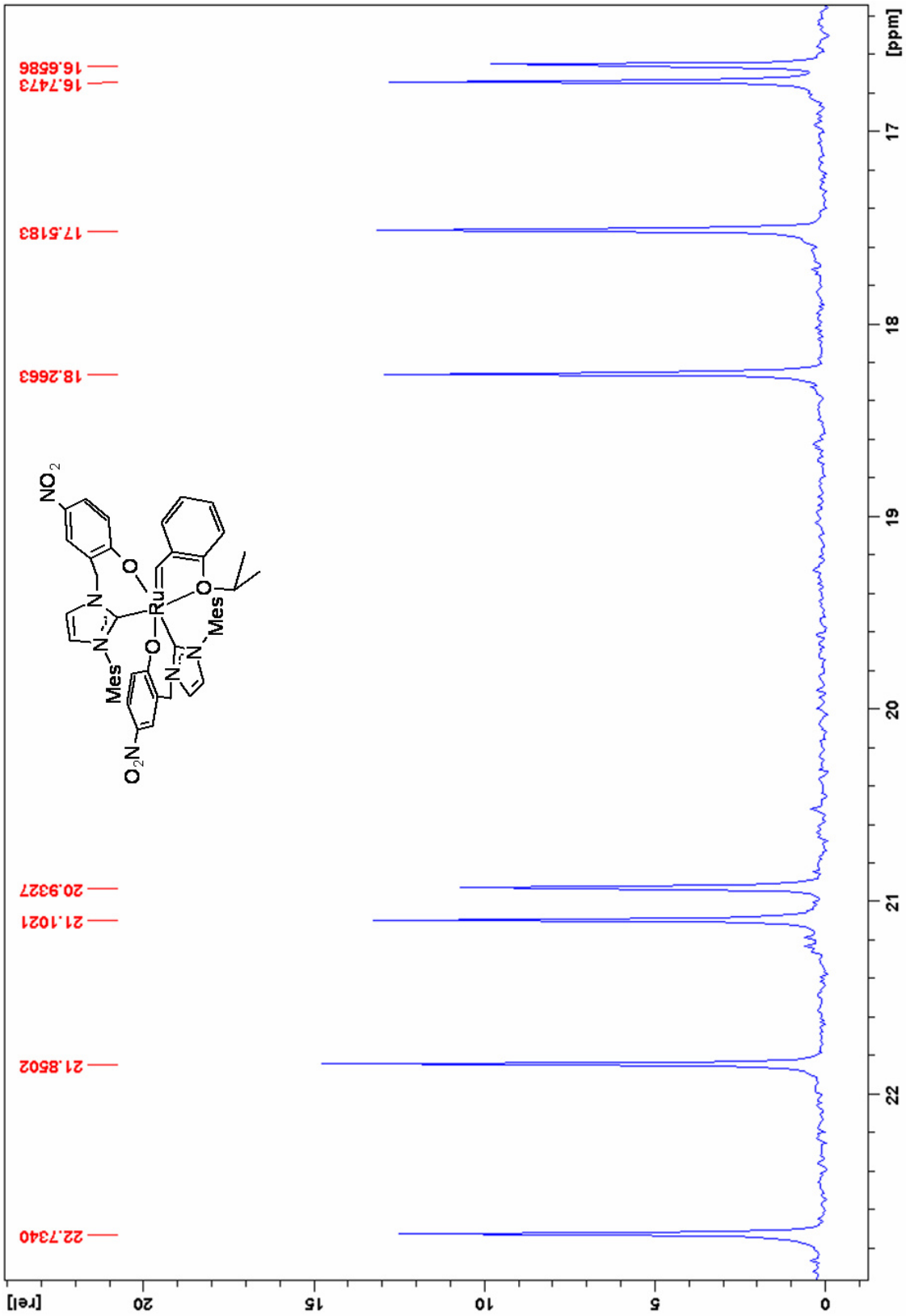
^{1}H NMR spectrum of complex 3 (4.20–8.40 ppm)



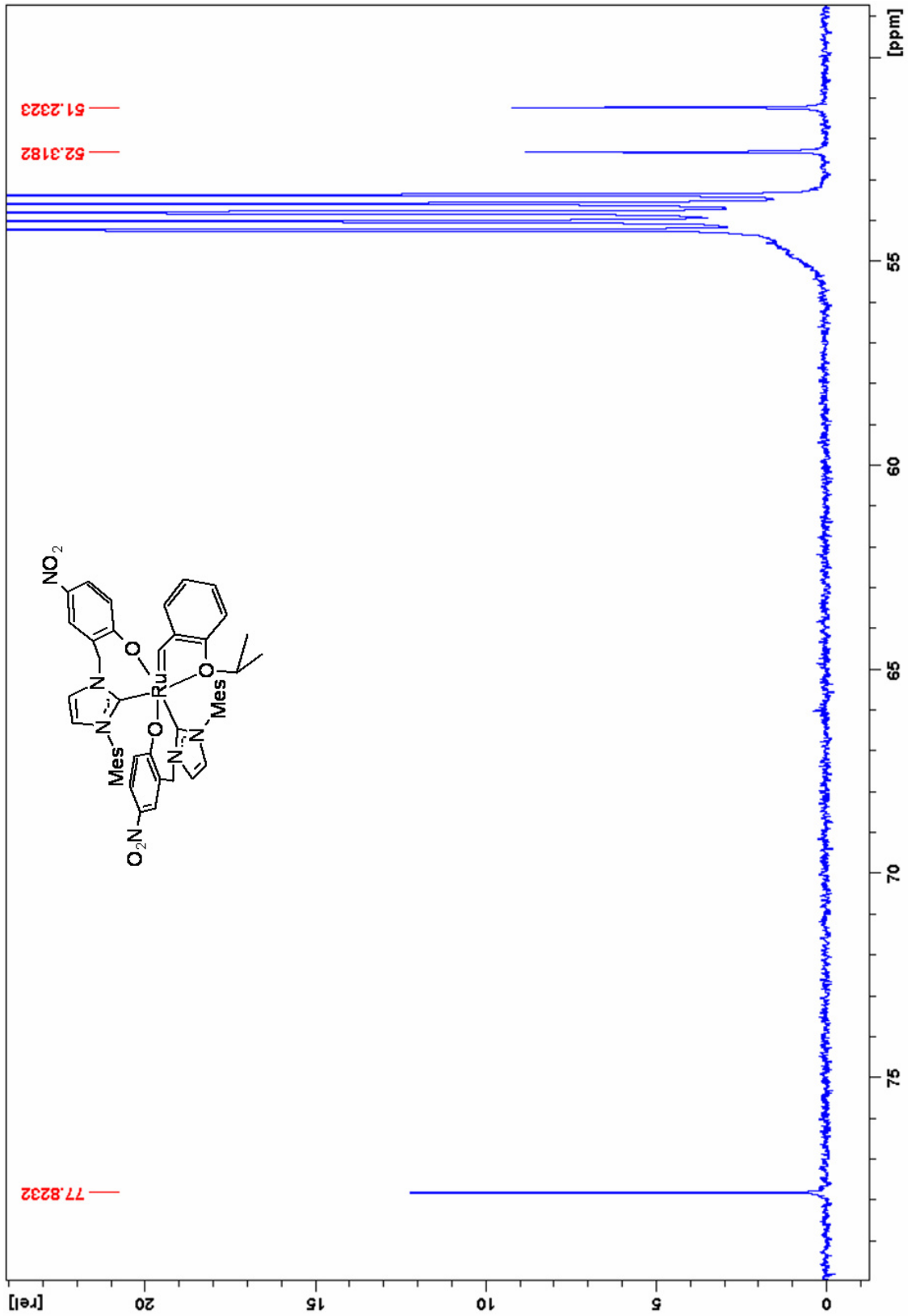
^{13}C NMR spectrum of complex 3



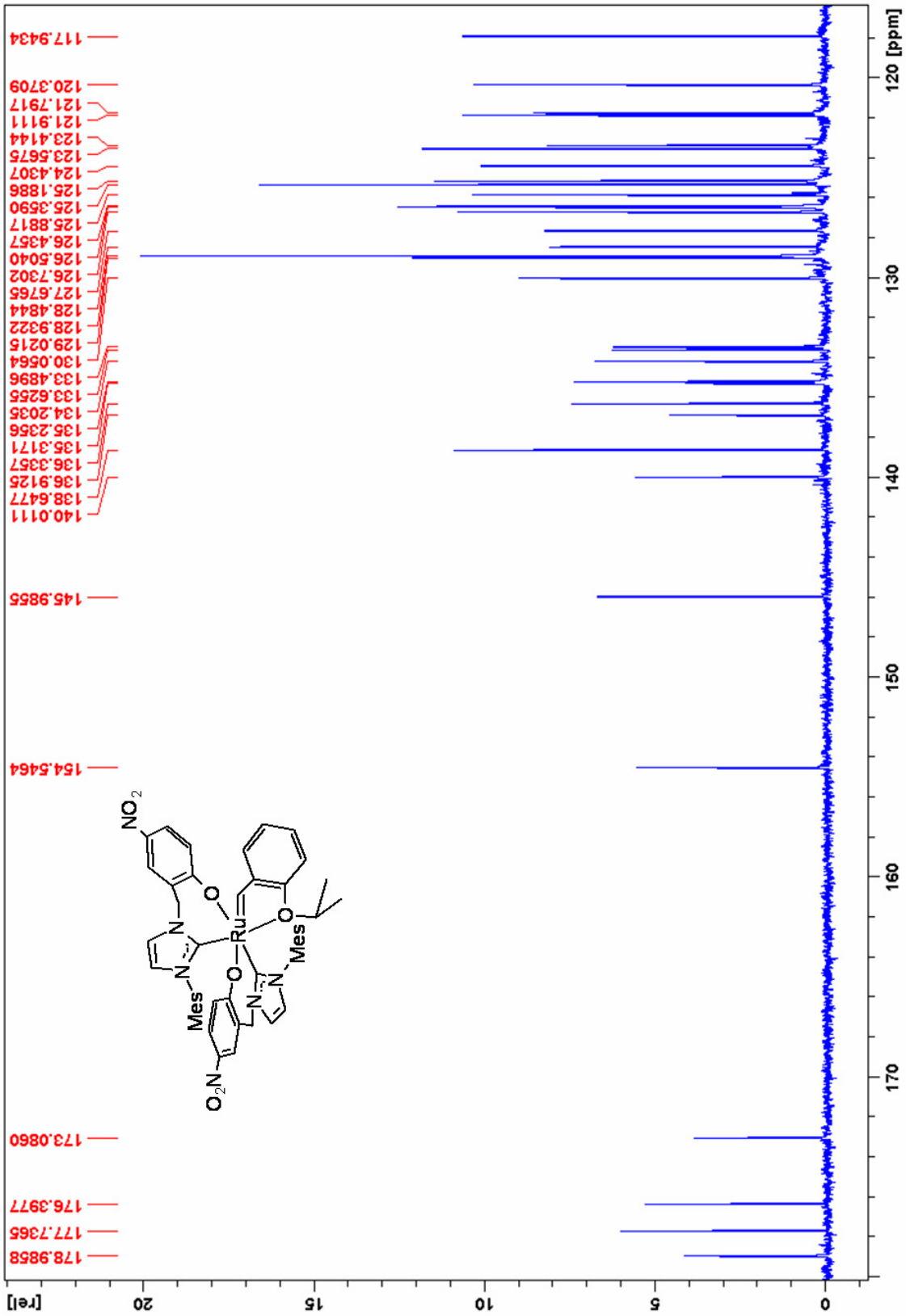
^{13}C NMR spectrum of complex 3 (16.4–23)



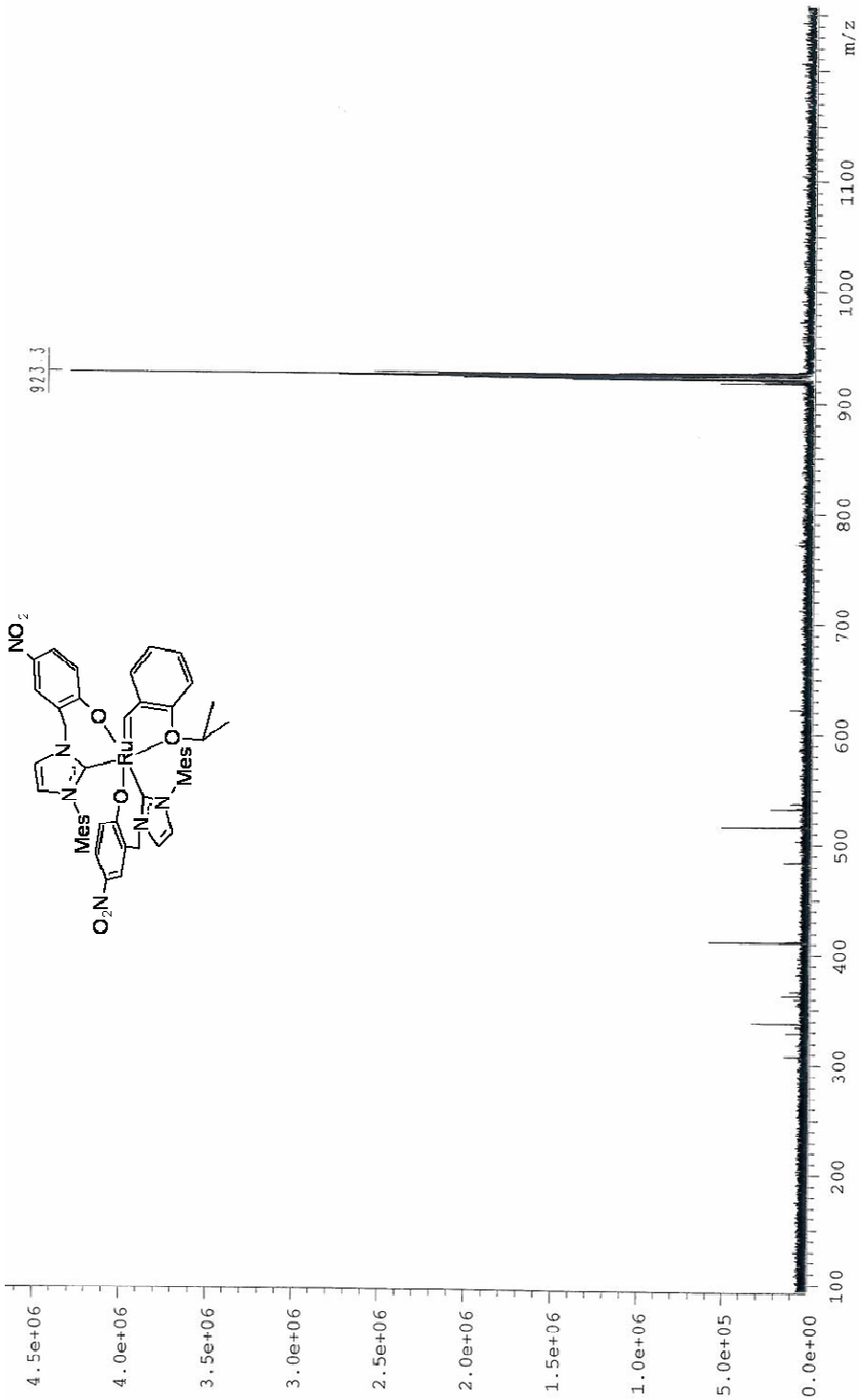
^{13}C NMR spectrum of complex 3 (49–80 ppm)



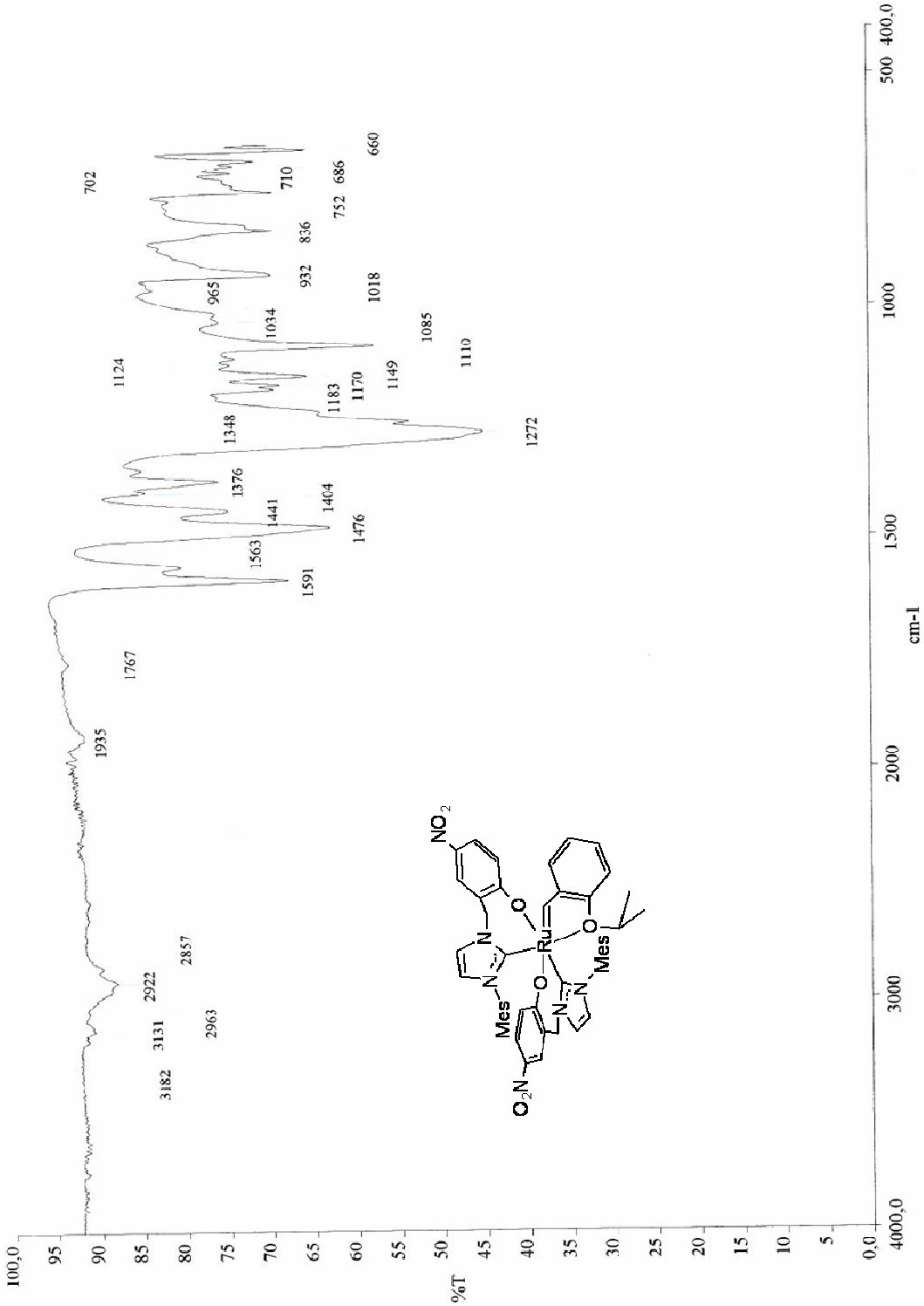
^{13}C NMR spectrum of complex 3 (116–180 ppm)



MS (ESIpos) spectrum of complex 3



IR spectrum of complex 3



X-ray crystallographic data for complex 3

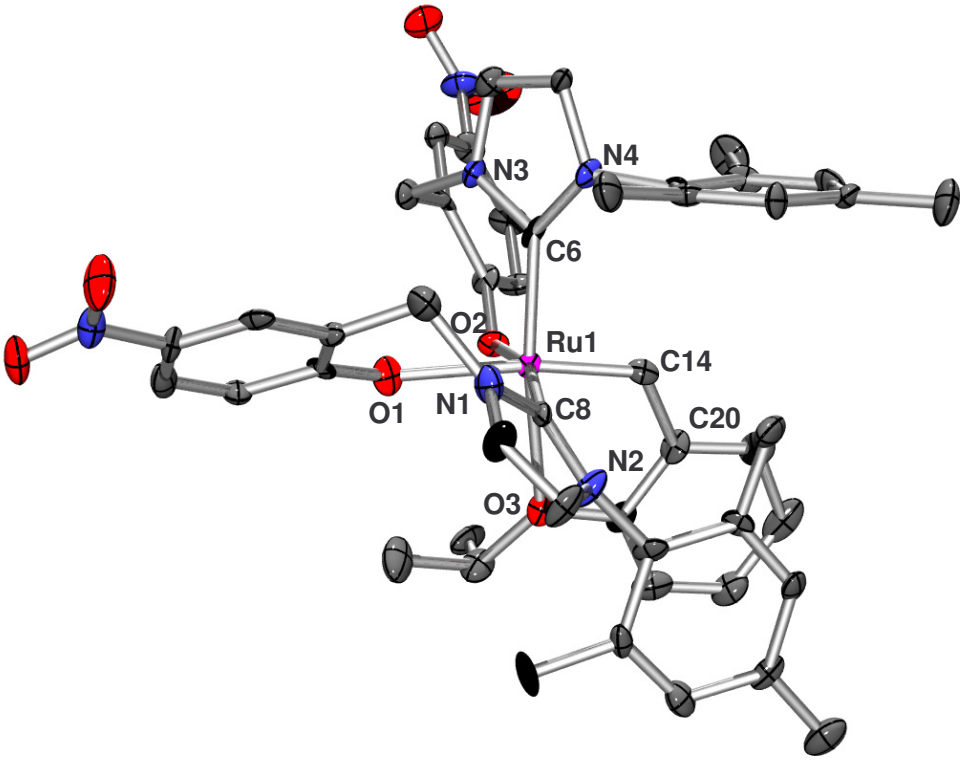


Figure S1. General diagram of complex 3 with the anisotropic displacement parameters drawn at the 50% probability level.

Table S1. Selected bond distances (pm) and bond angles (deg) for complex 3.

bond distances		bond angles	
Ru1-C6	200	N1-C8-N2	103
Ru1-C8	207	N3-C6-N4	103
Ru1-C14	184	O1-Ru1-C8	85
Ru1-O1	209	O1-Ru1-C14	172
Ru1-O2	224	O2-Ru1-C6	95
Ru1-O3	238	O2-Ru1-C8	165
C6-N3	139	O3-Ru1-C6	167
C6-N4	136	O3-Ru1-C14	78
C8-N1	136	O2-Ru1-O1	84
C8-N2	138	C6-Ru1-C14	94
C4-C14	147	C8-Ru1-C14	95

Table S2. Crystal data and structure refinement for complex 3.

Identification code	Complex 3	
Empirical formula	C48 H48 N6 O7 Ru	
Formula weight	921.99	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 14.4807(10) Å	α= 90°.
	b = 15.9232(11) Å	β= 110.2520(10)°.
	c = 20.1442(13) Å	γ = 90°.
Volume	4357.7(5) $Å^3$	
Z	4	
Density (calculated)	1.405 Mg/m^3	
Absorption coefficient	0.419 mm^{-1}	
F(000)	1912	
Crystal size	0.150 x 0.084 x 0.016 mm^3	
Theta range for data collection	1.51 to 25.05°.	
Index ranges	-17<=h<=17, -18<=k<=18, -23<=l<=23	
Reflections collected	46204	
Independent reflections	7709 [R(int) = 0.1722]	
Completeness to theta = 25.05°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.99330 and 0.95352	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7709 / 0 / 554	
Goodness-of-fit on F^2	1.099	
Final R indices [I>2sigma(I)]	R1 = 0.0819 (5203 reflections), wR2 = 0.1535	
R indices (all data)	R1 = 0.1326, wR2 = 0.1689	
Largest diff. peak and hole	1.130 and -1.227 e.$Å^{-3}$	

Experimental details

The crystal was very small and produced only very limited scattering albeit of good Bragg profile quality. R(int) is 17%. The data were integrated to 0.84 Å. Hence the data quality is somewhat limited and e.g. anistropic refinement not entirely satisfactory. Cf. cif item _refine_special_details or the below paragraph.

Refinment details

Refinement of F^2^ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2^, conventional R-factors R are based on F, with F set to zero for negative F^2^. The threshold expression of F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2^ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. All H-atoms were geometrically fixed (AFIX 13, 23 and 33) and the H-atoms given a $U_{(iso)}$ 1.20 (AFIX 13, 23) and 1.5 (AFIX 33) times that of the respective pivot atoms.

Due to the poor observations to parameter ratio, the methyl groups were NOT subjected to fitting using Fourier minimization. AFIX 33 was used instead. This produces alerts in

checkCIF report (380) on short H---H distances within the structure, due to not optimally rotated (positioned) CH~3~ group H-atoms. Atom C30 would not respond to anisotropic refinement and was thus kept isotropic.

The largest positive residual density (1.13 e/Å^3) is located 1.09 Å from atom Ru1. The largest negative residual density (-1.23 e/Å^3) is located 1.06 Å from atom C40.

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for complex 3. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	9433(1)	7970(1)	2283(1)	14(1)
O(1)	8227(3)	9051(3)	1928(2)	21(1)
C(1)	10127(5)	8899(5)	2742(4)	21(2)
N(1)	9863(4)	8773(4)	982(3)	23(1)
N(2)	9970(4)	7428(4)	1011(3)	23(2)
O(2)	8409(3)	6961(3)	1665(2)	23(1)
C(2)	9630(5)	9692(4)	2738(3)	17(2)
O(3)	8672(3)	7817(3)	2985(2)	22(1)
C(3)	10109(6)	10392(5)	3137(4)	28(2)
N(3)	7870(5)	4313(4)	-212(3)	24(2)
N(4)	11513(4)	7141(3)	2976(3)	19(1)
C(4)	9602(7)	11149(5)	3104(4)	33(2)
O(4)	8598(4)	4055(3)	-334(3)	37(1)
N(5)	10309(4)	6430(3)	3081(3)	18(1)
O(5)	7032(4)	4003(3)	-479(3)	34(1)
C(5)	8646(6)	11195(5)	2664(4)	31(2)
N(6)	9203(5)	6267(5)	5550(3)	34(2)
C(6)	8165(6)	10524(5)	2276(4)	26(2)
O(6)	9461(4)	5531(4)	5633(3)	35(1)
O(7)	9075(6)	6680(4)	6021(3)	64(2)
C(7)	8644(5)	9766(4)	2315(4)	21(2)
C(8)	7138(5)	9005(5)	1649(4)	27(2)
C(9)	6730(6)	8953(5)	2242(4)	36(2)
C(10)	6852(6)	8262(5)	1159(5)	40(2)
C(11)	9823(5)	8093(4)	1390(4)	19(2)
C(12)	10007(6)	8512(5)	364(4)	30(2)
C(13)	10062(5)	7677(5)	381(4)	25(2)
C(14)	10003(5)	6533(4)	1215(4)	18(2)
C(15)	9033(5)	6115(4)	946(3)	16(2)
C(16)	8892(5)	5439(4)	494(4)	21(2)
C(17)	7989(5)	5020(4)	266(4)	20(2)
C(18)	7231(5)	5256(4)	501(4)	23(2)
C(19)	7359(5)	5918(5)	951(4)	25(2)
C(20)	8267(5)	6362(4)	1207(3)	19(2)
C(21)	9706(5)	9657(4)	1073(4)	21(2)
C(22)	10482(5)	10134(4)	1509(4)	20(2)
C(23)	10317(5)	10983(4)	1560(4)	23(2)
C(24)	9424(6)	11371(4)	1200(4)	22(2)
C(25)	8669(5)	10870(5)	756(4)	24(2)
C(26)	8795(5)	10010(5)	676(4)	23(2)
C(27)	11465(5)	9757(5)	1879(4)	30(2)
C(28)	9233(6)	12294(4)	1282(4)	33(2)
C(29)	7984(6)	9510(5)	149(4)	36(2)
C(30)	10503(5)	7166(4)	2793(3)	15(2)

C(31)	11897(5)	6416(4)	3369(4)	22(2)
C(32)	11155(5)	5982(5)	3436(4)	24(2)
C(33)	9356(5)	6162(4)	3121(4)	19(2)
C(34)	9153(5)	6616(4)	3718(4)	18(2)
C(35)	9286(5)	6222(4)	4363(4)	21(2)
C(36)	9074(5)	6669(5)	4880(4)	23(2)
C(37)	8733(6)	7496(5)	4776(4)	30(2)
C(38)	8612(5)	7874(5)	4135(4)	27(2)
C(39)	8813(5)	7452(5)	3594(4)	21(2)
C(40)	12197(5)	7765(4)	2939(3)	14(2)
C(41)	12560(5)	8319(5)	3508(4)	21(2)
C(42)	13301(5)	8879(5)	3515(4)	24(2)
C(43)	13705(5)	8879(4)	2989(4)	21(2)
C(44)	13363(5)	8295(4)	2448(4)	20(2)
C(45)	12630(5)	7717(4)	2412(4)	20(2)
C(46)	12209(6)	8254(5)	4136(4)	34(2)
C(47)	14505(6)	9486(5)	2991(5)	34(2)
C(48)	12368(5)	7054(5)	1842(4)	28(2)

Table S4. Bond lengths [Å] and angles [°] for complex 3.

Ru(1)-C(1)	1.848(7)
Ru(1)-C(30)	1.999(6)
Ru(1)-C(11)	2.072(7)
Ru(1)-O(3)	2.087(5)
Ru(1)-O(2)	2.246(5)
Ru(1)-O(1)	2.379(5)
O(1)-C(7)	1.394(8)
O(1)-C(8)	1.481(8)
C(1)-C(2)	1.450(9)
C(1)-H(1A)	0.9500
N(1)-C(11)	1.373(9)
N(1)-C(12)	1.394(9)
N(1)-C(21)	1.447(9)
N(2)-C(11)	1.365(9)
N(2)-C(13)	1.380(9)
N(2)-C(14)	1.479(9)
O(2)-C(20)	1.294(8)
C(2)-C(7)	1.392(10)
C(2)-C(3)	1.409(10)
O(3)-C(39)	1.308(8)
C(3)-C(4)	1.401(11)
C(3)-H(3A)	0.9500
N(3)-O(4)	1.234(8)
N(3)-O(5)	1.246(7)
N(3)-C(17)	1.452(9)
N(4)-C(30)	1.380(8)
N(4)-C(31)	1.401(8)
N(4)-C(40)	1.422(8)
C(4)-C(5)	1.363(11)
C(4)-H(4A)	0.9500
N(5)-C(30)	1.378(8)
N(5)-C(32)	1.384(9)
N(5)-C(33)	1.473(8)
C(5)-C(6)	1.365(11)
C(5)-H(5A)	0.9500
N(6)-O(7)	1.219(8)
N(6)-O(6)	1.225(8)
N(6)-C(36)	1.446(9)
C(6)-C(7)	1.381(10)
C(6)-H(6A)	0.9500
C(8)-C(10)	1.504(11)
C(8)-C(9)	1.508(10)
C(8)-H(8A)	1.0000
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800

C(10)-H(10C)	0.9800
C(12)-C(13)	1.331(10)
C(12)-H(12A)	0.9500
C(13)-H(13A)	0.9500
C(14)-C(15)	1.478(9)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.378(9)
C(15)-C(20)	1.437(9)
C(16)-C(17)	1.397(10)
C(16)-H(16A)	0.9500
C(17)-C(18)	1.389(10)
C(18)-C(19)	1.362(10)
C(18)-H(18A)	0.9500
C(19)-C(20)	1.422(10)
C(19)-H(19A)	0.9500
C(21)-C(22)	1.388(10)
C(21)-C(26)	1.402(10)
C(22)-C(23)	1.384(10)
C(22)-C(27)	1.486(10)
C(23)-C(24)	1.389(10)
C(23)-H(23A)	0.9500
C(24)-C(25)	1.397(10)
C(24)-C(28)	1.516(10)
C(25)-C(26)	1.398(10)
C(25)-H(25A)	0.9500
C(26)-C(29)	1.509(10)
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(31)-C(32)	1.324(10)
C(31)-H(31A)	0.9500
C(32)-H(32A)	0.9500
C(33)-C(34)	1.517(9)
C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900
C(34)-C(35)	1.394(9)
C(34)-C(39)	1.412(10)
C(35)-C(36)	1.379(10)
C(35)-H(35A)	0.9500
C(36)-C(37)	1.396(10)
C(37)-C(38)	1.381(10)
C(37)-H(37A)	0.9500
C(38)-C(39)	1.393(10)
C(38)-H(38A)	0.9500

C(40)-C(41)	1.397(9)
C(40)-C(45)	1.409(9)
C(41)-C(42)	1.391(10)
C(41)-C(46)	1.522(10)
C(42)-C(43)	1.377(10)
C(42)-H(42A)	0.9500
C(43)-C(44)	1.387(10)
C(43)-C(47)	1.508(10)
C(44)-C(45)	1.387(10)
C(44)-H(44A)	0.9500
C(45)-C(48)	1.508(10)
C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(46)-H(46D)	0.9800
C(47)-H(47A)	0.9800
C(47)-H(47D)	0.9800
C(47)-H(47B)	0.9800
C(48)-H(48D)	0.9800
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800

C(1)-Ru(1)-C(30)	93.7(3)
C(1)-Ru(1)-C(11)	95.4(3)
C(30)-Ru(1)-C(11)	96.4(3)
C(1)-Ru(1)-O(3)	94.4(2)
C(30)-Ru(1)-O(3)	94.2(2)
C(11)-Ru(1)-O(3)	165.0(2)
C(1)-Ru(1)-O(2)	172.0(3)
C(30)-Ru(1)-O(2)	94.2(2)
C(11)-Ru(1)-O(2)	85.0(2)
O(3)-Ru(1)-O(2)	83.74(17)
C(1)-Ru(1)-O(1)	77.6(2)
C(30)-Ru(1)-O(1)	167.4(2)
C(11)-Ru(1)-O(1)	93.6(2)
O(3)-Ru(1)-O(1)	77.48(17)
O(2)-Ru(1)-O(1)	94.38(17)
C(7)-O(1)-C(8)	116.8(5)
C(7)-O(1)-Ru(1)	107.0(4)
C(8)-O(1)-Ru(1)	130.7(4)
C(2)-C(1)-Ru(1)	120.7(5)
C(2)-C(1)-H(1A)	119.6
Ru(1)-C(1)-H(1A)	119.6
C(11)-N(1)-C(12)	110.4(6)
C(11)-N(1)-C(21)	130.6(6)
C(12)-N(1)-C(21)	118.8(6)
C(11)-N(2)-C(13)	112.0(6)
C(11)-N(2)-C(14)	126.1(6)
C(13)-N(2)-C(14)	121.9(6)
C(20)-O(2)-Ru(1)	146.5(4)
C(7)-C(2)-C(3)	118.6(6)
C(7)-C(2)-C(1)	118.7(6)

C(3)-C(2)-C(1)	122.7(6)
C(39)-O(3)-Ru(1)	137.8(4)
C(4)-C(3)-C(2)	120.6(7)
C(4)-C(3)-H(3A)	119.7
C(2)-C(3)-H(3A)	119.7
O(4)-N(3)-O(5)	123.6(6)
O(4)-N(3)-C(17)	118.4(6)
O(5)-N(3)-C(17)	118.0(6)
C(30)-N(4)-C(31)	110.5(6)
C(30)-N(4)-C(40)	131.2(5)
C(31)-N(4)-C(40)	117.2(5)
C(5)-C(4)-C(3)	118.3(7)
C(5)-C(4)-H(4A)	120.8
C(3)-C(4)-H(4A)	120.8
C(30)-N(5)-C(32)	112.5(6)
C(30)-N(5)-C(33)	126.9(6)
C(32)-N(5)-C(33)	120.0(6)
C(4)-C(5)-C(6)	122.2(7)
C(4)-C(5)-H(5A)	118.9
C(6)-C(5)-H(5A)	118.9
O(7)-N(6)-O(6)	122.1(7)
O(7)-N(6)-C(36)	118.8(7)
O(6)-N(6)-C(36)	119.0(7)
C(5)-C(6)-C(7)	120.3(7)
C(5)-C(6)-H(6A)	119.8
C(7)-C(6)-H(6A)	119.8
C(6)-C(7)-C(2)	119.9(7)
C(6)-C(7)-O(1)	124.8(7)
C(2)-C(7)-O(1)	115.2(6)
O(1)-C(8)-C(10)	107.7(6)
O(1)-C(8)-C(9)	111.1(6)
C(10)-C(8)-C(9)	112.5(7)
O(1)-C(8)-H(8A)	108.5
C(10)-C(8)-H(8A)	108.5
C(9)-C(8)-H(8A)	108.5
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
N(2)-C(11)-N(1)	103.3(6)
N(2)-C(11)-Ru(1)	123.6(5)
N(1)-C(11)-Ru(1)	132.4(5)
C(13)-C(12)-N(1)	107.6(7)

C(13)-C(12)-H(12A)	126.2
N(1)-C(12)-H(12A)	126.2
C(12)-C(13)-N(2)	106.6(7)
C(12)-C(13)-H(13A)	126.7
N(2)-C(13)-H(13A)	126.7
C(15)-C(14)-N(2)	113.4(6)
C(15)-C(14)-H(14A)	108.9
N(2)-C(14)-H(14A)	108.9
C(15)-C(14)-H(14B)	108.9
N(2)-C(14)-H(14B)	108.9
H(14A)-C(14)-H(14B)	107.7
C(16)-C(15)-C(20)	119.9(6)
C(16)-C(15)-C(14)	119.9(6)
C(20)-C(15)-C(14)	119.9(6)
C(15)-C(16)-C(17)	119.9(7)
C(15)-C(16)-H(16A)	120.1
C(17)-C(16)-H(16A)	120.1
C(18)-C(17)-C(16)	121.3(6)
C(18)-C(17)-N(3)	120.5(6)
C(16)-C(17)-N(3)	118.2(6)
C(19)-C(18)-C(17)	119.6(7)
C(19)-C(18)-H(18A)	120.2
C(17)-C(18)-H(18A)	120.2
C(18)-C(19)-C(20)	121.5(7)
C(18)-C(19)-H(19A)	119.3
C(20)-C(19)-H(19A)	119.3
O(2)-C(20)-C(19)	121.6(6)
O(2)-C(20)-C(15)	120.7(6)
C(19)-C(20)-C(15)	117.7(6)
C(22)-C(21)-C(26)	122.5(7)
C(22)-C(21)-N(1)	118.9(6)
C(26)-C(21)-N(1)	118.4(6)
C(23)-C(22)-C(21)	117.4(7)
C(23)-C(22)-C(27)	121.1(6)
C(21)-C(22)-C(27)	121.5(7)
C(22)-C(23)-C(24)	123.3(7)
C(22)-C(23)-H(23A)	118.4
C(24)-C(23)-H(23A)	118.4
C(23)-C(24)-C(25)	117.5(7)
C(23)-C(24)-C(28)	123.1(7)
C(25)-C(24)-C(28)	119.5(7)
C(24)-C(25)-C(26)	121.9(7)
C(24)-C(25)-H(25A)	119.0
C(26)-C(25)-H(25A)	119.0
C(25)-C(26)-C(21)	117.5(7)
C(25)-C(26)-C(29)	119.8(7)
C(21)-C(26)-C(29)	122.6(7)
C(22)-C(27)-H(27A)	109.5
C(22)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(22)-C(27)-H(27C)	109.5

H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(24)-C(28)-H(28A)	109.5
C(24)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(24)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(26)-C(29)-H(29A)	109.5
C(26)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(26)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
N(5)-C(30)-N(4)	102.4(5)
N(5)-C(30)-Ru(1)	121.7(5)
N(4)-C(30)-Ru(1)	135.8(5)
C(32)-C(31)-N(4)	108.1(6)
C(32)-C(31)-H(31A)	125.9
N(4)-C(31)-H(31A)	125.9
C(31)-C(32)-N(5)	106.4(6)
C(31)-C(32)-H(32A)	126.8
N(5)-C(32)-H(32A)	126.8
N(5)-C(33)-C(34)	110.4(5)
N(5)-C(33)-H(33A)	109.6
C(34)-C(33)-H(33A)	109.6
N(5)-C(33)-H(33B)	109.6
C(34)-C(33)-H(33B)	109.6
H(33A)-C(33)-H(33B)	108.1
C(35)-C(34)-C(39)	121.1(7)
C(35)-C(34)-C(33)	121.6(6)
C(39)-C(34)-C(33)	117.4(6)
C(36)-C(35)-C(34)	118.4(7)
C(36)-C(35)-H(35A)	120.8
C(34)-C(35)-H(35A)	120.8
C(35)-C(36)-C(37)	122.2(7)
C(35)-C(36)-N(6)	119.1(7)
C(37)-C(36)-N(6)	118.7(7)
C(38)-C(37)-C(36)	118.4(7)
C(38)-C(37)-H(37A)	120.8
C(36)-C(37)-H(37A)	120.8
C(37)-C(38)-C(39)	121.8(7)
C(37)-C(38)-H(38A)	119.1
C(39)-C(38)-H(38A)	119.1
O(3)-C(39)-C(38)	120.7(6)
O(3)-C(39)-C(34)	121.1(7)
C(38)-C(39)-C(34)	118.1(7)
C(41)-C(40)-C(45)	120.8(6)
C(41)-C(40)-N(4)	118.0(6)
C(45)-C(40)-N(4)	120.1(6)
C(42)-C(41)-C(40)	118.9(6)

C(42)-C(41)-C(46)	120.9(7)
C(40)-C(41)-C(46)	120.0(6)
C(43)-C(42)-C(41)	121.6(7)
C(43)-C(42)-H(42A)	119.2
C(41)-C(42)-H(42A)	119.2
C(42)-C(43)-C(44)	118.2(6)
C(42)-C(43)-C(47)	122.0(7)
C(44)-C(43)-C(47)	119.8(7)
C(43)-C(44)-C(45)	123.0(7)
C(43)-C(44)-H(44A)	118.5
C(45)-C(44)-H(44A)	118.5
C(44)-C(45)-C(40)	117.2(6)
C(44)-C(45)-C(48)	119.3(6)
C(40)-C(45)-C(48)	123.4(6)
C(41)-C(46)-H(46A)	109.5
C(41)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
C(41)-C(46)-H(46D)	109.5
H(46A)-C(46)-H(46D)	109.5
H(46B)-C(46)-H(46D)	109.5
C(43)-C(47)-H(47A)	109.5
C(43)-C(47)-H(47D)	109.5
H(47A)-C(47)-H(47D)	109.5
C(43)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
H(47D)-C(47)-H(47B)	109.5
C(45)-C(48)-H(48D)	109.5
C(45)-C(48)-H(48A)	109.5
H(48D)-C(48)-H(48A)	109.5
C(45)-C(48)-H(48B)	109.5
H(48D)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5

Table S5. Torsion angles [°] for complex 3.

C(1)-Ru(1)-O(1)-C(7)	-7.0(4)
C(30)-Ru(1)-O(1)-C(7)	40.5(11)
C(11)-Ru(1)-O(1)-C(7)	-101.8(4)
O(3)-Ru(1)-O(1)-C(7)	90.4(4)
O(2)-Ru(1)-O(1)-C(7)	173.0(4)
C(1)-Ru(1)-O(1)-C(8)	-159.3(6)
C(30)-Ru(1)-O(1)-C(8)	-111.7(10)
C(11)-Ru(1)-O(1)-C(8)	106.0(5)
O(3)-Ru(1)-O(1)-C(8)	-61.9(5)
O(2)-Ru(1)-O(1)-C(8)	20.7(5)
C(30)-Ru(1)-C(1)-C(2)	-163.3(6)
C(11)-Ru(1)-C(1)-C(2)	99.9(6)
O(3)-Ru(1)-C(1)-C(2)	-68.8(5)
O(2)-Ru(1)-C(1)-C(2)	7(2)
O(1)-Ru(1)-C(1)-C(2)	7.4(5)
C(1)-Ru(1)-O(2)-C(20)	128.0(17)
C(30)-Ru(1)-O(2)-C(20)	-61.5(8)
C(11)-Ru(1)-O(2)-C(20)	34.6(8)
O(3)-Ru(1)-O(2)-C(20)	-155.3(8)
O(1)-Ru(1)-O(2)-C(20)	127.8(8)
Ru(1)-C(1)-C(2)-C(7)	-7.1(9)
Ru(1)-C(1)-C(2)-C(3)	173.6(5)
C(1)-Ru(1)-O(3)-C(39)	-85.6(7)
C(30)-Ru(1)-O(3)-C(39)	8.4(7)
C(11)-Ru(1)-O(3)-C(39)	143.6(9)
O(2)-Ru(1)-O(3)-C(39)	102.2(7)
O(1)-Ru(1)-O(3)-C(39)	-161.9(7)
C(7)-C(2)-C(3)-C(4)	-0.5(11)
C(1)-C(2)-C(3)-C(4)	178.7(7)
C(2)-C(3)-C(4)-C(5)	-1.5(11)
C(3)-C(4)-C(5)-C(6)	2.0(12)
C(4)-C(5)-C(6)-C(7)	-0.3(12)
C(5)-C(6)-C(7)-C(2)	-1.8(11)
C(5)-C(6)-C(7)-O(1)	-178.3(6)
C(3)-C(2)-C(7)-C(6)	2.2(10)
C(1)-C(2)-C(7)-C(6)	-177.1(6)
C(3)-C(2)-C(7)-O(1)	179.0(6)
C(1)-C(2)-C(7)-O(1)	-0.3(9)
C(8)-O(1)-C(7)-C(6)	-21.4(9)
Ru(1)-O(1)-C(7)-C(6)	-178.0(6)
C(8)-O(1)-C(7)-C(2)	162.1(6)
Ru(1)-O(1)-C(7)-C(2)	5.4(7)
C(7)-O(1)-C(8)-C(10)	171.2(6)
Ru(1)-O(1)-C(8)-C(10)	-38.8(8)
C(7)-O(1)-C(8)-C(9)	-65.2(8)
Ru(1)-O(1)-C(8)-C(9)	84.9(7)
C(13)-N(2)-C(11)-N(1)	-2.0(8)
C(14)-N(2)-C(11)-N(1)	179.6(6)

C(13)-N(2)-C(11)-Ru(1)	170.0(5)
C(14)-N(2)-C(11)-Ru(1)	-8.3(10)
C(12)-N(1)-C(11)-N(2)	1.4(8)
C(21)-N(1)-C(11)-N(2)	176.0(7)
C(12)-N(1)-C(11)-Ru(1)	-169.7(5)
C(21)-N(1)-C(11)-Ru(1)	5.0(11)
C(1)-Ru(1)-C(11)-N(2)	146.0(6)
C(30)-Ru(1)-C(11)-N(2)	51.6(6)
O(3)-Ru(1)-C(11)-N(2)	-83.3(11)
O(2)-Ru(1)-C(11)-N(2)	-42.0(5)
O(1)-Ru(1)-C(11)-N(2)	-136.1(5)
C(1)-Ru(1)-C(11)-N(1)	-44.5(7)
C(30)-Ru(1)-C(11)-N(1)	-138.9(7)
O(3)-Ru(1)-C(11)-N(1)	86.2(11)
O(2)-Ru(1)-C(11)-N(1)	127.5(7)
O(1)-Ru(1)-C(11)-N(1)	33.4(7)
C(11)-N(1)-C(12)-C(13)	-0.3(9)
C(21)-N(1)-C(12)-C(13)	-175.6(7)
N(1)-C(12)-C(13)-N(2)	-1.0(9)
C(11)-N(2)-C(13)-C(12)	2.0(9)
C(14)-N(2)-C(13)-C(12)	-179.6(7)
C(11)-N(2)-C(14)-C(15)	90.7(8)
C(13)-N(2)-C(14)-C(15)	-87.5(8)
N(2)-C(14)-C(15)-C(16)	119.1(7)
N(2)-C(14)-C(15)-C(20)	-66.7(8)
C(20)-C(15)-C(16)-C(17)	2.8(10)
C(14)-C(15)-C(16)-C(17)	177.0(6)
C(15)-C(16)-C(17)-C(18)	-1.7(10)
C(15)-C(16)-C(17)-N(3)	179.8(6)
O(4)-N(3)-C(17)-C(18)	-170.6(7)
O(5)-N(3)-C(17)-C(18)	9.8(10)
O(4)-N(3)-C(17)-C(16)	7.9(10)
O(5)-N(3)-C(17)-C(16)	-171.7(6)
C(16)-C(17)-C(18)-C(19)	1.2(11)
N(3)-C(17)-C(18)-C(19)	179.7(6)
C(17)-C(18)-C(19)-C(20)	-2.0(11)
Ru(1)-O(2)-C(20)-C(19)	-175.6(5)
Ru(1)-O(2)-C(20)-C(15)	5.2(12)
C(18)-C(19)-C(20)-O(2)	-176.1(7)
C(18)-C(19)-C(20)-C(15)	3.1(10)
C(16)-C(15)-C(20)-O(2)	175.7(6)
C(14)-C(15)-C(20)-O(2)	1.5(10)
C(16)-C(15)-C(20)-C(19)	-3.5(10)
C(14)-C(15)-C(20)-C(19)	-177.7(6)
C(11)-N(1)-C(21)-C(22)	84.0(9)
C(12)-N(1)-C(21)-C(22)	-101.8(8)
C(11)-N(1)-C(21)-C(26)	-100.6(9)
C(12)-N(1)-C(21)-C(26)	73.6(9)
C(26)-C(21)-C(22)-C(23)	2.1(10)
N(1)-C(21)-C(22)-C(23)	177.3(6)
C(26)-C(21)-C(22)-C(27)	-174.9(7)

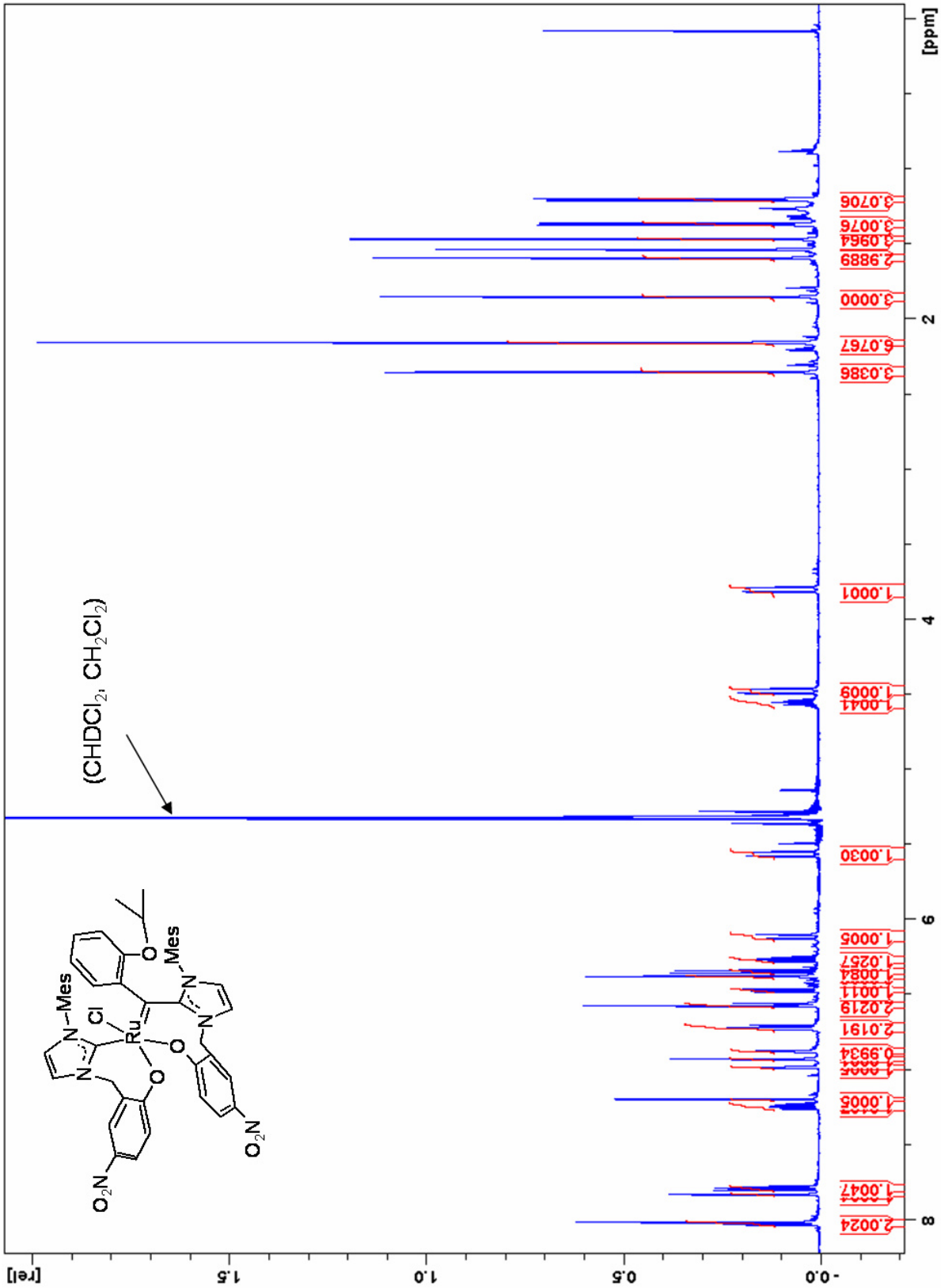
N(1)-C(21)-C(22)-C(27)	0.3(10)
C(21)-C(22)-C(23)-C(24)	0.1(11)
C(27)-C(22)-C(23)-C(24)	177.1(7)
C(22)-C(23)-C(24)-C(25)	-1.3(11)
C(22)-C(23)-C(24)-C(28)	177.3(7)
C(23)-C(24)-C(25)-C(26)	0.4(10)
C(28)-C(24)-C(25)-C(26)	-178.3(7)
C(24)-C(25)-C(26)-C(21)	1.6(10)
C(24)-C(25)-C(26)-C(29)	-175.5(7)
C(22)-C(21)-C(26)-C(25)	-3.0(10)
N(1)-C(21)-C(26)-C(25)	-178.2(6)
C(22)-C(21)-C(26)-C(29)	174.0(7)
N(1)-C(21)-C(26)-C(29)	-1.2(10)
C(32)-N(5)-C(30)-N(4)	1.3(7)
C(33)-N(5)-C(30)-N(4)	172.7(6)
C(32)-N(5)-C(30)-Ru(1)	-177.5(5)
C(33)-N(5)-C(30)-Ru(1)	-6.0(9)
C(31)-N(4)-C(30)-N(5)	-0.9(7)
C(40)-N(4)-C(30)-N(5)	-168.8(6)
C(31)-N(4)-C(30)-Ru(1)	177.5(5)
C(40)-N(4)-C(30)-Ru(1)	9.6(11)
C(1)-Ru(1)-C(30)-N(5)	134.1(5)
C(11)-Ru(1)-C(30)-N(5)	-130.0(5)
O(3)-Ru(1)-C(30)-N(5)	39.5(5)
O(2)-Ru(1)-C(30)-N(5)	-44.5(5)
O(1)-Ru(1)-C(30)-N(5)	87.9(11)
C(1)-Ru(1)-C(30)-N(4)	-44.1(7)
C(11)-Ru(1)-C(30)-N(4)	51.8(7)
O(3)-Ru(1)-C(30)-N(4)	-138.7(7)
O(2)-Ru(1)-C(30)-N(4)	137.2(7)
O(1)-Ru(1)-C(30)-N(4)	-90.3(12)
C(30)-N(4)-C(31)-C(32)	0.3(8)
C(40)-N(4)-C(31)-C(32)	170.1(6)
N(4)-C(31)-C(32)-N(5)	0.5(8)
C(30)-N(5)-C(32)-C(31)	-1.2(8)
C(33)-N(5)-C(32)-C(31)	-173.2(6)
C(30)-N(5)-C(33)-C(34)	-78.0(8)
C(32)-N(5)-C(33)-C(34)	92.9(7)
N(5)-C(33)-C(34)-C(35)	-102.2(7)
N(5)-C(33)-C(34)-C(39)	78.5(8)
C(39)-C(34)-C(35)-C(36)	0.1(10)
C(33)-C(34)-C(35)-C(36)	-179.2(6)
C(34)-C(35)-C(36)-C(37)	0.1(11)
C(34)-C(35)-C(36)-N(6)	179.6(6)
O(7)-N(6)-C(36)-C(35)	175.4(7)
O(6)-N(6)-C(36)-C(35)	-2.7(11)
O(7)-N(6)-C(36)-C(37)	-5.0(11)
O(6)-N(6)-C(36)-C(37)	176.9(7)
C(35)-C(36)-C(37)-C(38)	-0.4(11)
N(6)-C(36)-C(37)-C(38)	-180.0(7)
C(36)-C(37)-C(38)-C(39)	0.5(12)

Ru(1)-O(3)-C(39)-C(38)	133.4(6)
Ru(1)-O(3)-C(39)-C(34)	-47.7(10)
C(37)-C(38)-C(39)-O(3)	178.5(7)
C(37)-C(38)-C(39)-C(34)	-0.3(11)
C(35)-C(34)-C(39)-O(3)	-178.9(6)
C(33)-C(34)-C(39)-O(3)	0.4(10)
C(35)-C(34)-C(39)-C(38)	0.0(10)
C(33)-C(34)-C(39)-C(38)	179.3(6)
C(30)-N(4)-C(40)-C(41)	86.2(9)
C(31)-N(4)-C(40)-C(41)	-81.1(8)
C(30)-N(4)-C(40)-C(45)	-105.9(8)
C(31)-N(4)-C(40)-C(45)	86.9(8)
C(45)-C(40)-C(41)-C(42)	5.8(10)
N(4)-C(40)-C(41)-C(42)	173.7(6)
C(45)-C(40)-C(41)-C(46)	-169.0(6)
N(4)-C(40)-C(41)-C(46)	-1.1(9)
C(40)-C(41)-C(42)-C(43)	-2.3(10)
C(46)-C(41)-C(42)-C(43)	172.5(7)
C(41)-C(42)-C(43)-C(44)	-0.8(10)
C(41)-C(42)-C(43)-C(47)	179.8(7)
C(42)-C(43)-C(44)-C(45)	0.5(11)
C(47)-C(43)-C(44)-C(45)	179.9(7)
C(43)-C(44)-C(45)-C(40)	2.8(10)
C(43)-C(44)-C(45)-C(48)	-174.5(7)
C(41)-C(40)-C(45)-C(44)	-6.0(10)
N(4)-C(40)-C(45)-C(44)	-173.6(6)
C(41)-C(40)-C(45)-C(48)	171.2(7)
N(4)-C(40)-C(45)-C(48)	3.6(10)

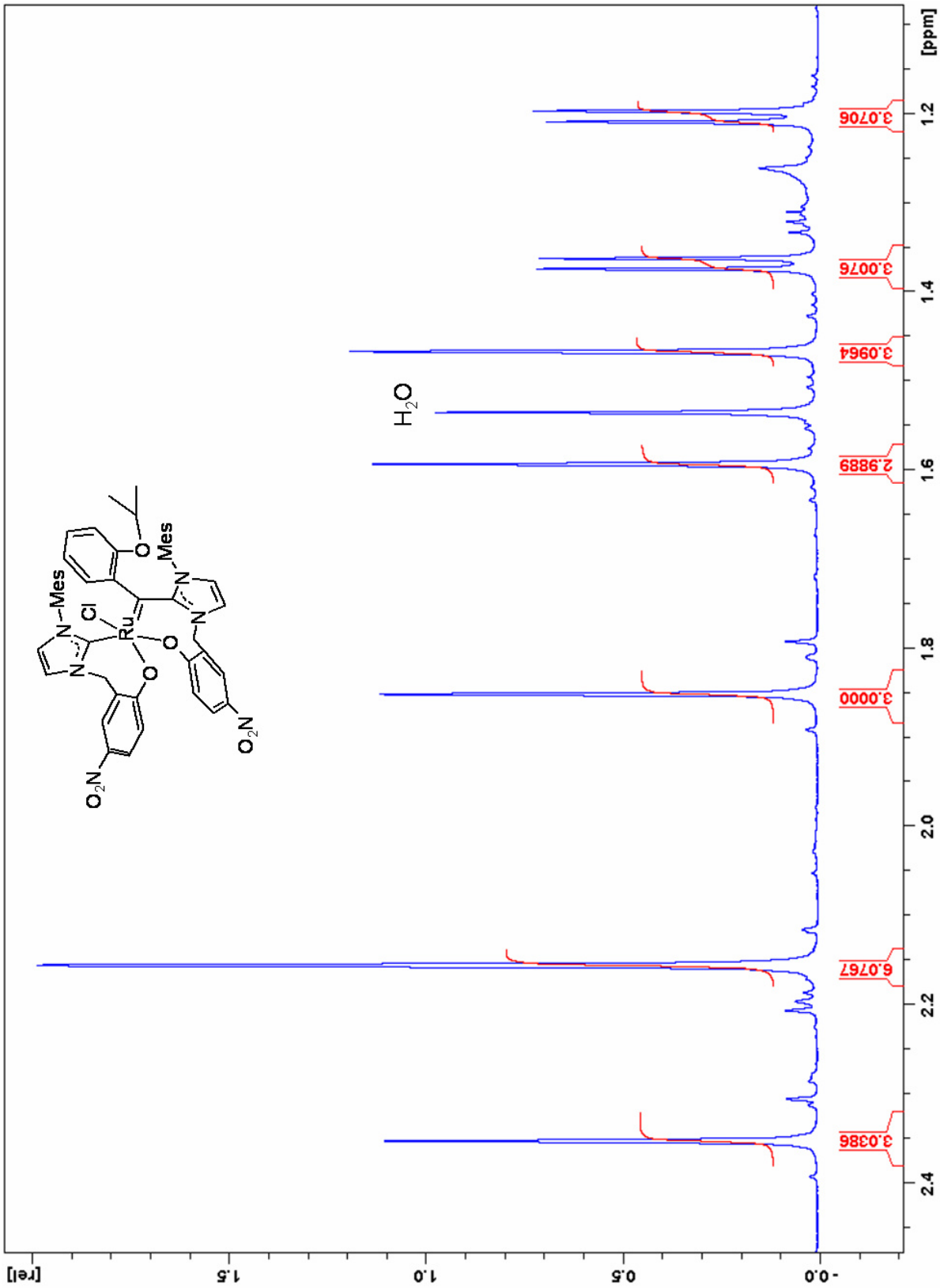
Analytical results for complex 4

NMR, MS and IR spectra of complex 4

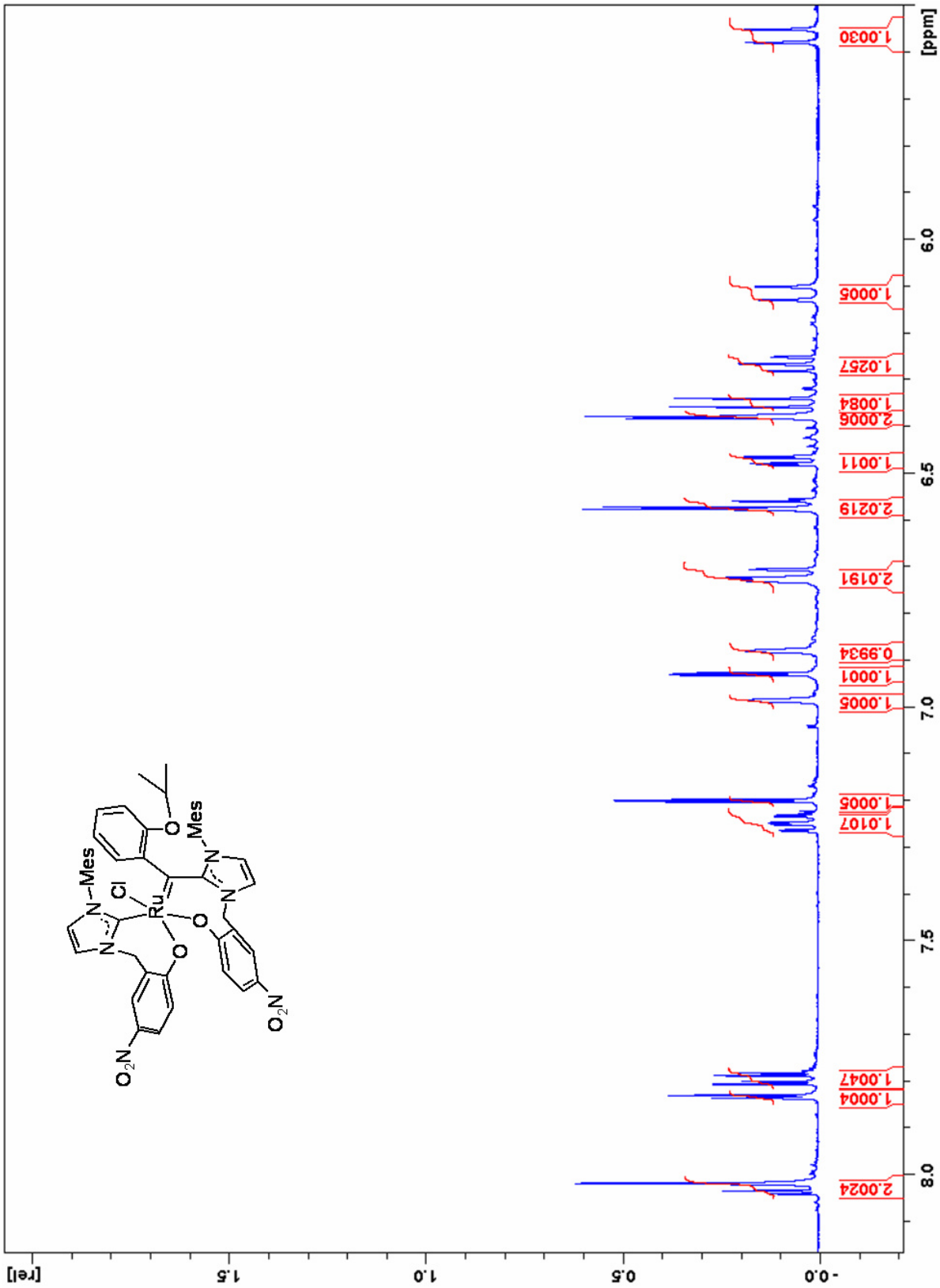
^{1}H NMR spectrum of complex 4



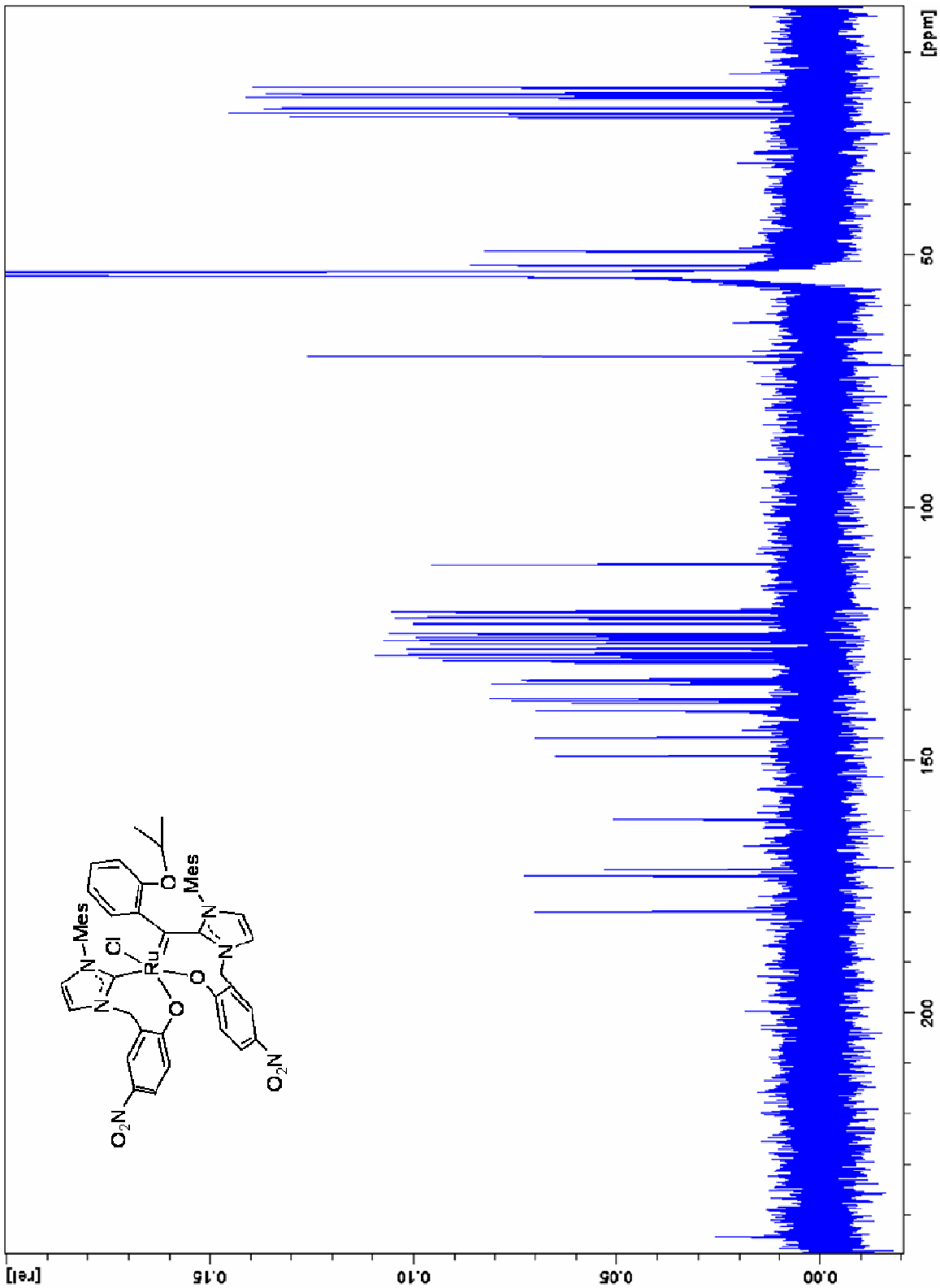
^{1}H NMR spectrum of complex 4 (1.1–2.5 ppm)



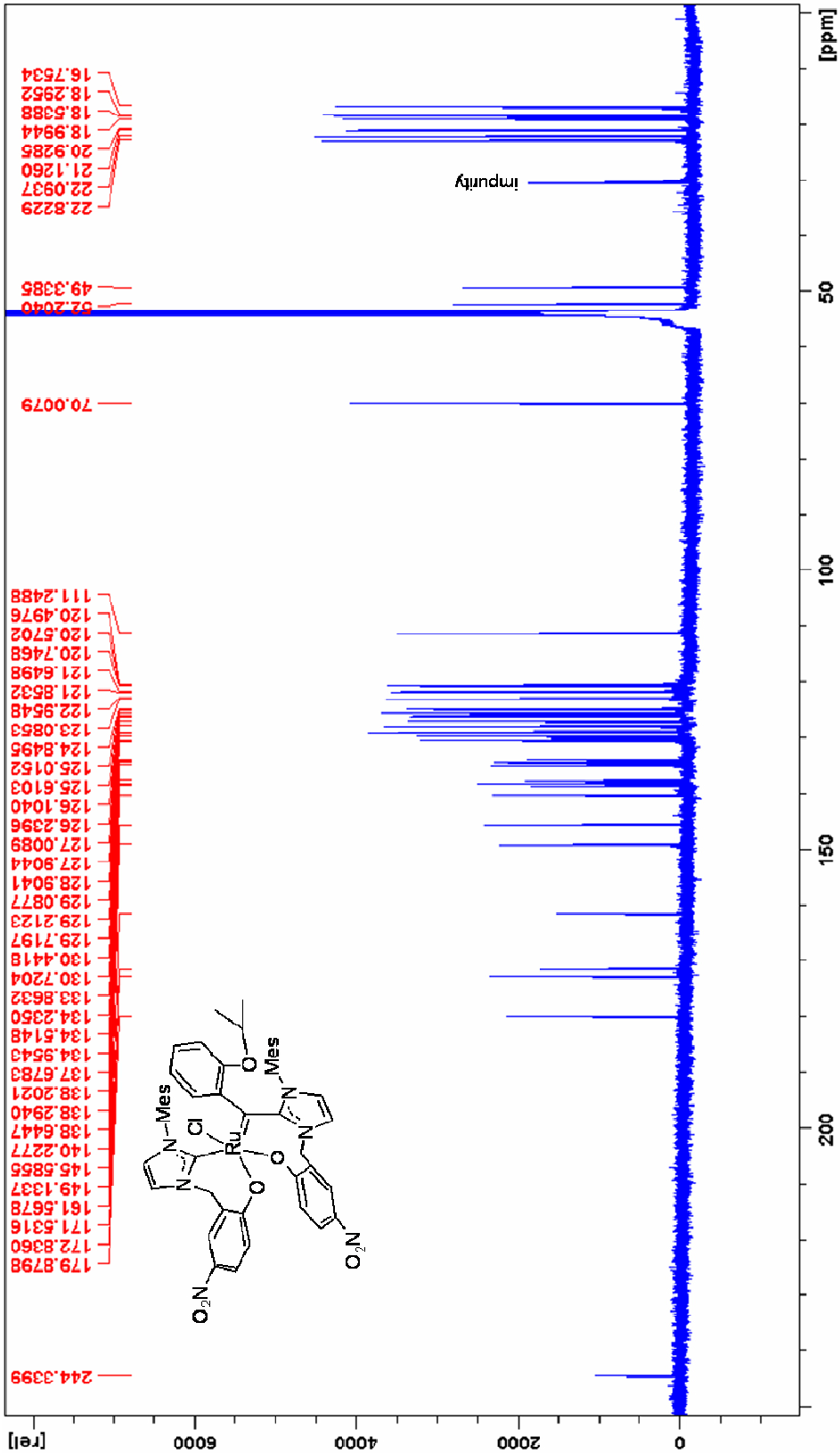
^{1}H NMR spectrum of complex 4 (5.5–8.2 ppm)



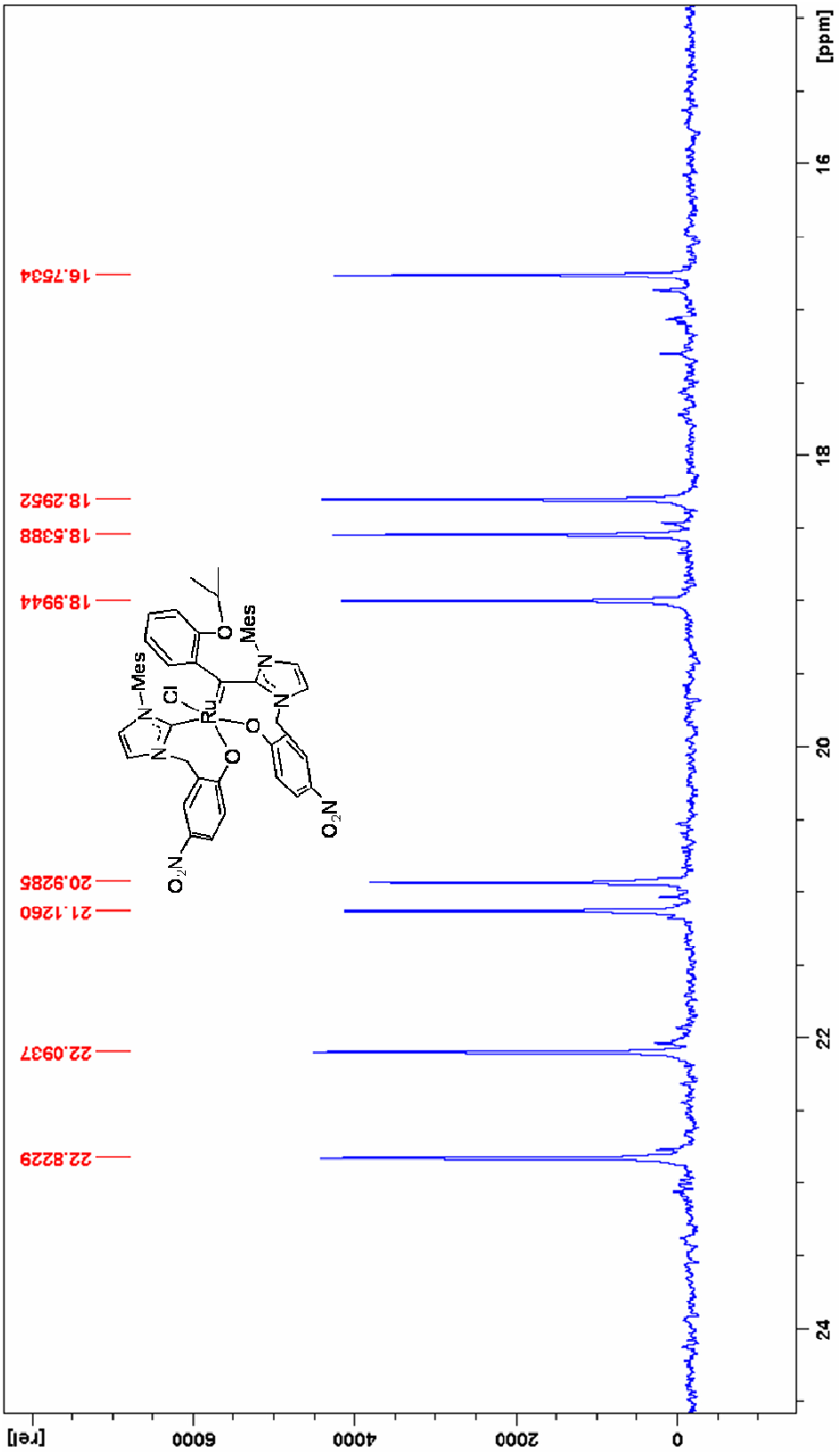
^{13}C NMR spectrum of complex 4 (4 mg of crystallized compound)



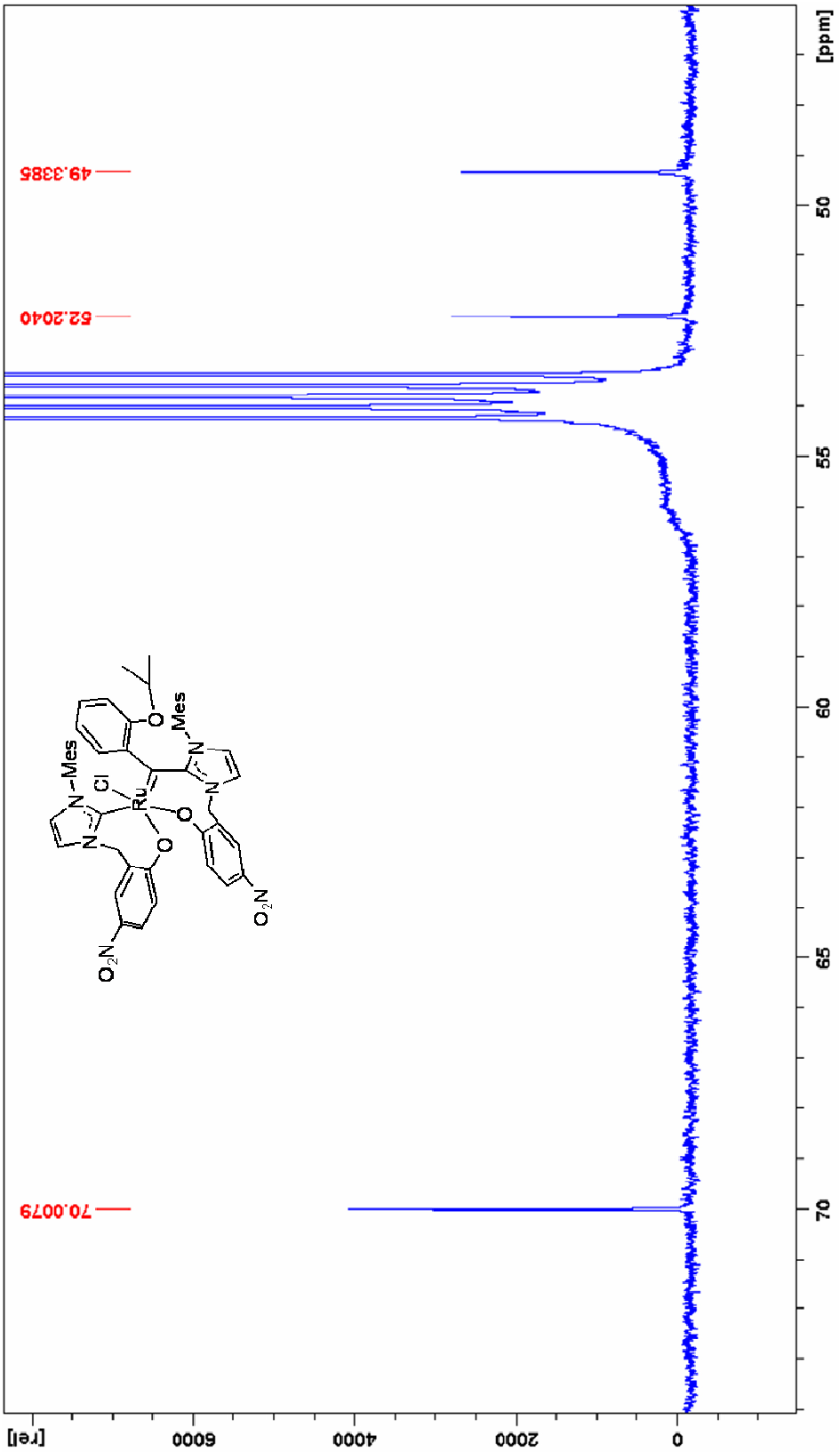
^{13}C NMR spectrum of complex 4



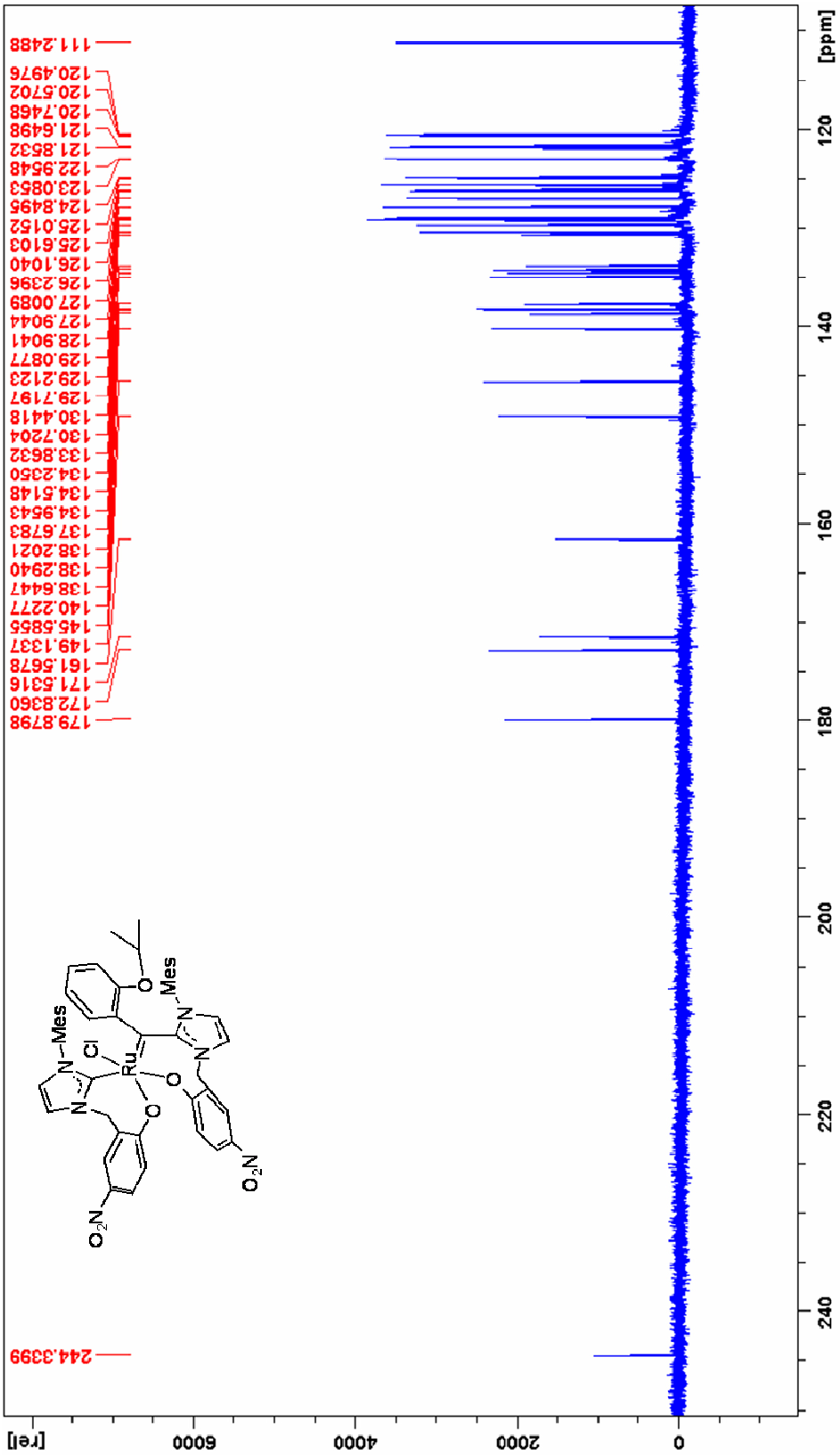
^{13}C NMR spectrum of complex 4 (15–24.5 ppm)



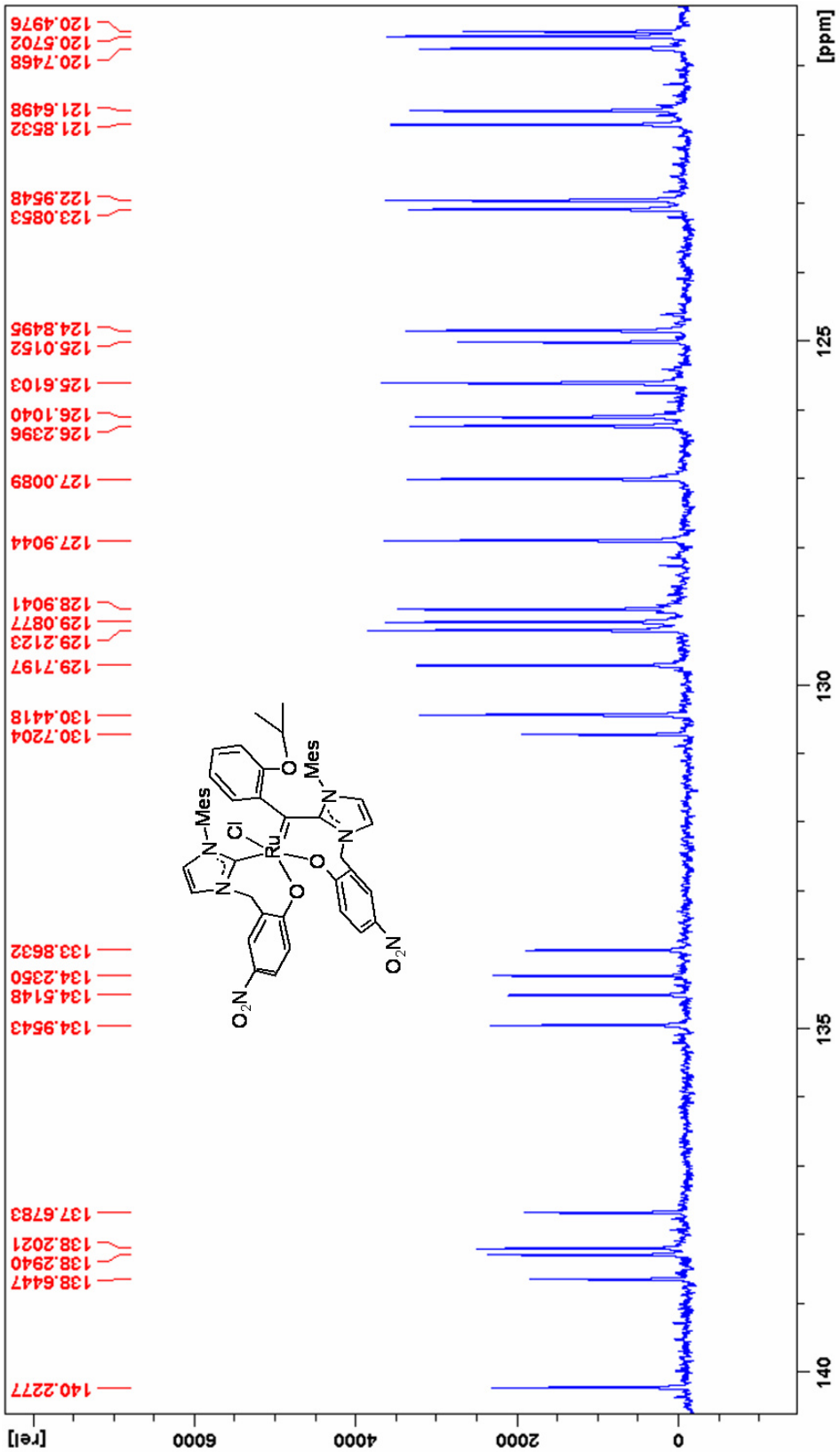
^{13}C NMR spectrum of complex 4 (46–74 ppm)



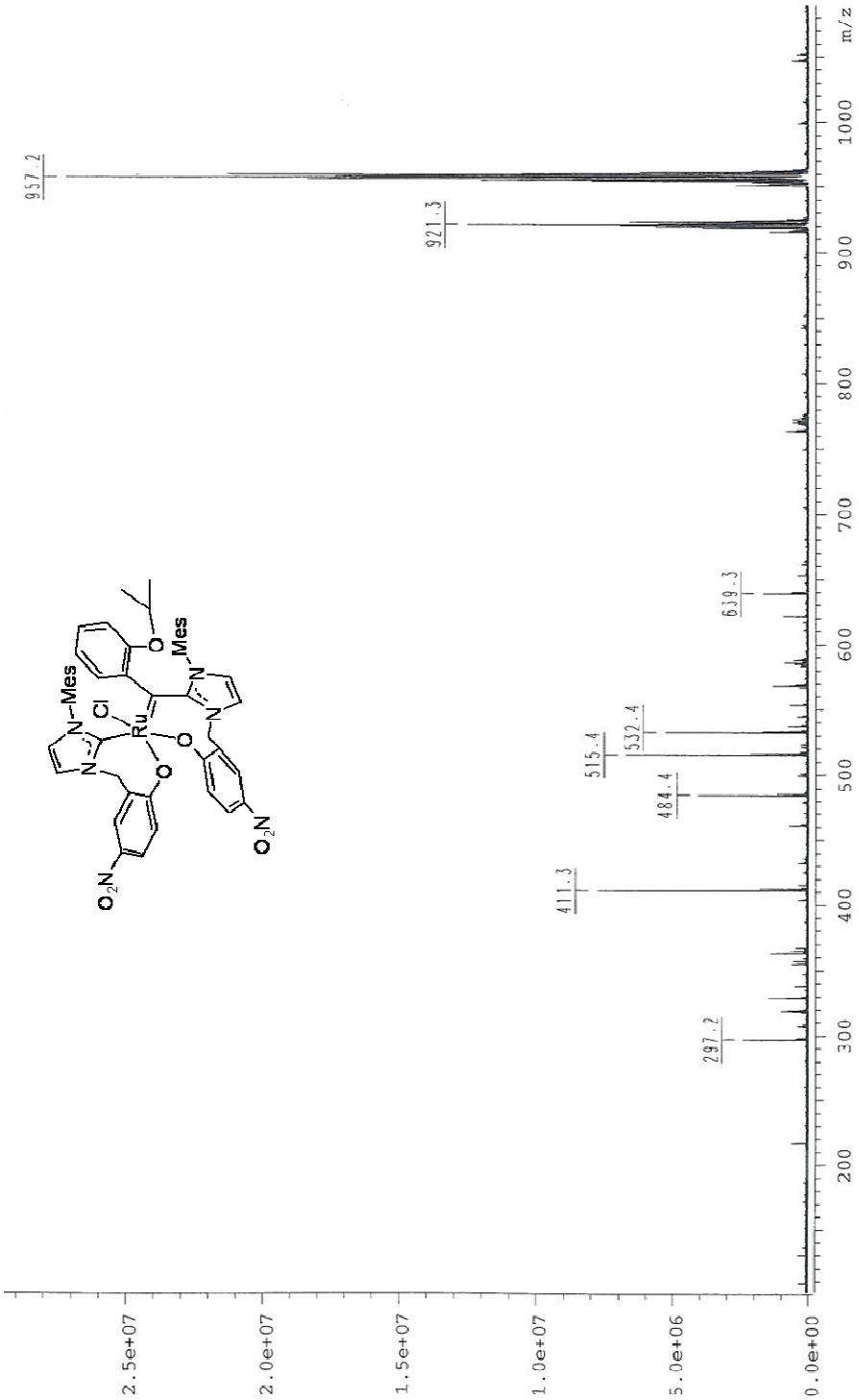
^{13}C NMR spectrum of complex 4 (105–250 ppm)



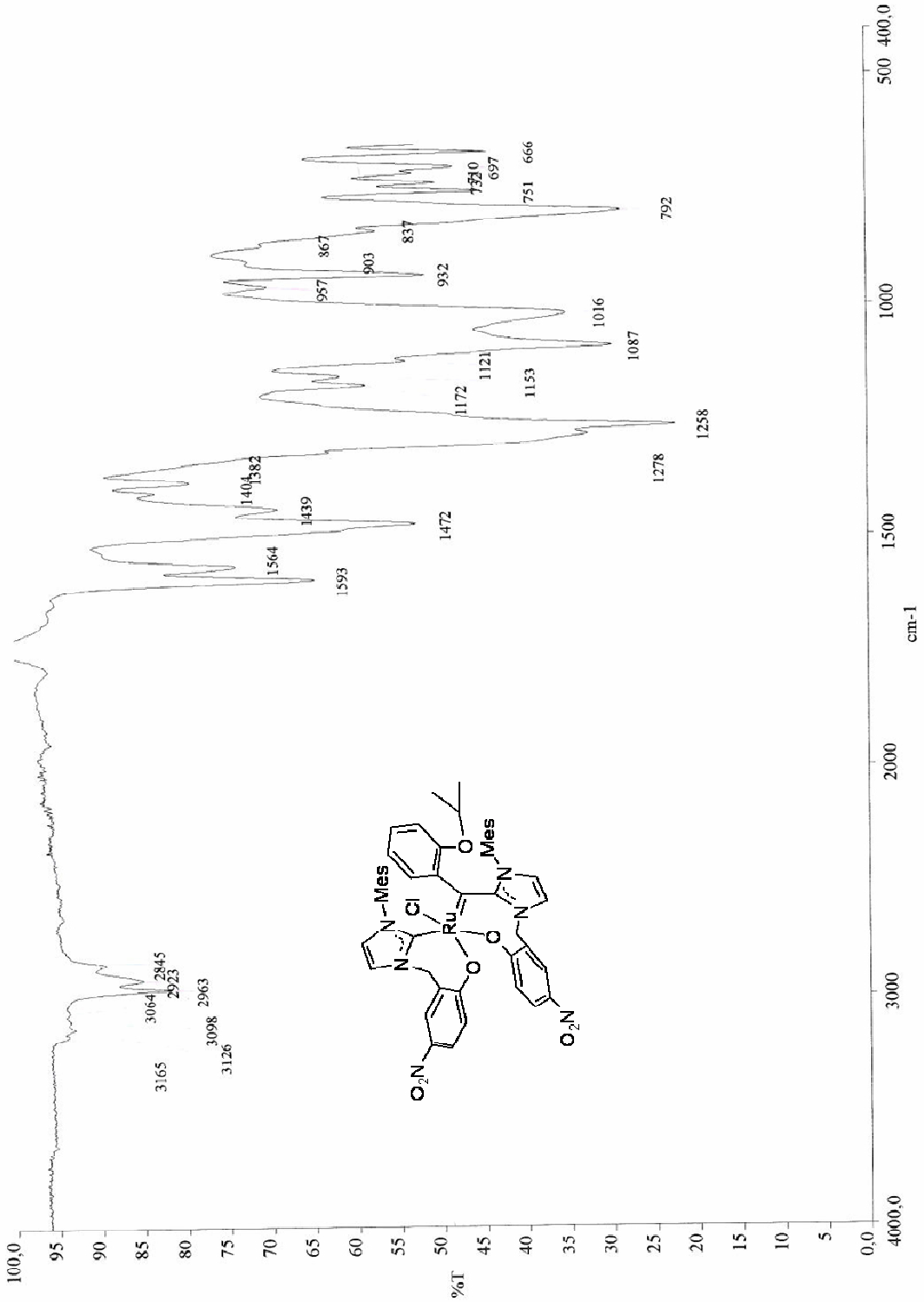
^{13}C NMR spectrum of complex 4 (120−141 ppm)



MS (ESIpos) spectrum of complex 4



IR spectrum of complex 4



X-ray crystallographic data for Complex 4

Table S6. Crystal data and structure refinement for complex 4.

Identification code	Complex 4	
Empirical formula	C49 H49 Cl3 N6 O7 Ru	
Formula weight	1041.36	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.9968(5) Å	α= 90°.
	b = 15.9651(8) Å	β= 90°.
	c = 26.2519(12) Å	γ = 90°.
Volume	4608.9(4) $Å^3$	
Z	4	
Density (calculated)	1.501 Mg/m^3	
Absorption coefficient	0.574 mm^{-1}	
F(000)	2144	
Crystal size	0.21 x 0.11 x 0.10 mm^3	
Theta range for data collection	2.25 to 23.28°.	
Index ranges	-12<=h<=12, -17<=k<=17, -29<=l<=29	
Reflections collected	45393	
Independent reflections	6641 [R(int) = 0.0801]	
Completeness to theta = 23.29°	99.8 %	
Absorption correction	Numerical	
Max. and min. transmission	0.95363 and 0.88786	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6641 / 0 / 604	
Goodness-of-fit on F^2	1.082	
Final R indices [I>2sigma(I)]	R1 = 0.0415 (5751 reflections), wR2 = 0.0953	
R indices (all data)	R1 = 0.0558, wR2 = 0.1036	
Absolute structure parameter	0.12(4)	
Largest diff. peak and hole	1.221 and -0.664 e.$Å^{-3}$	

Experimental details

The crystal diffraction quality was very limited. Integration of raw data was therefore terminated at 0.90 Å resolution. The outermost shell 0.93-0.90 Å has an internal intensity R-value of 26% and a mean I/sigma of 5. The crystal structure was also refined as a racemic twin with a final refined Flack parameter of 0.12(4).

Refinement details

Refinement of F^2^ against ALL reflections, except for 1 0 1, 0 1 2, 0 0 2, 0 1 1 and 2 2 0 which were evidently in error due to shadowing or removed during integration due to too large Lorentz functions (peak width). The weighted R-factor wR and goodness of fit S are based on F^2^, conventional R-factors R are based on F, with F set to zero for negative F^2^. The threshold expression of F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2^

are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. All H atoms in the structure were geometrically positioned (AFIX 43, 23, 137) and their U_{iso} constrained to be 1.2 (AFIX 43 and 23) and 1.5 (AFIX 137) times that of the parent atom. The largest positive residual density (1.22 e/Å^3) is located 1.22 Å from atom H1SB. The largest negative residual density (-0.66 e/ e/Å^3) is located 0.74 Å from atom Cl2S.

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for complex 4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	5493(1)	5769(1)	1662(1)	22(1)
Cl(1)	5211(1)	7196(1)	1770(1)	36(1)
O(1)	6083(4)	5815(3)	2427(1)	30(1)
N(1)	2627(4)	5297(3)	2606(2)	29(1)
C(1)	3946(5)	5383(3)	1824(2)	21(1)
N(2)	4232(4)	4523(3)	2631(2)	25(1)
O(2)	6671(3)	4819(2)	1560(1)	27(1)
C(2)	3642(5)	5089(4)	2342(2)	24(1)
O(3)	8577(4)	3133(3)	3797(2)	43(1)
N(3)	5419(5)	6460(3)	557(2)	29(1)
C(3)	5232(5)	5835(4)	908(2)	26(1)
O(4)	9791(4)	4189(3)	3893(2)	43(1)
N(4)	4967(4)	5159(3)	609(2)	26(1)
C(4)	2894(5)	5384(4)	1465(2)	21(1)
N(5)	8851(5)	3863(4)	3705(2)	34(1)
O(5)	7254(5)	2020(3)	-92(2)	60(2)
C(5)	2599(6)	4856(5)	3058(2)	40(2)
O(6)	8866(5)	1818(3)	363(2)	63(2)
N(6)	7925(6)	2199(4)	269(2)	47(2)
C(6)	3604(6)	4374(5)	3072(2)	37(2)
O(7)	2770(3)	3945(2)	1615(2)	26(1)
C(7)	5387(5)	4093(3)	2511(2)	28(1)
C(8)	6434(5)	4471(4)	2794(2)	24(1)
C(9)	7117(5)	3997(4)	3130(2)	31(2)
C(10)	8104(5)	4352(4)	3377(2)	27(1)
C(11)	8395(5)	5194(3)	3303(2)	25(1)
C(12)	7717(5)	5667(4)	2984(2)	28(1)
C(13)	6717(5)	5324(4)	2722(2)	26(1)
C(14)	1715(5)	5917(4)	2468(2)	26(1)
C(15)	1968(6)	6737(4)	2551(2)	36(2)
C(16)	1078(6)	7325(4)	2400(2)	40(2)
C(17)	-5(6)	7076(4)	2179(2)	34(2)
C(18)	-237(6)	6227(4)	2123(2)	35(2)
C(19)	602(6)	5627(4)	2275(2)	33(2)
C(20)	3123(6)	7020(4)	2820(3)	42(2)
C(21)	-927(7)	7711(5)	1995(3)	51(2)
C(22)	292(6)	4723(4)	2242(3)	45(2)
C(23)	5275(6)	6160(4)	62(2)	34(2)
C(24)	5000(6)	5359(4)	98(2)	34(2)
C(25)	4874(5)	4302(4)	803(2)	27(1)
C(26)	6106(5)	3914(4)	852(2)	25(1)
C(27)	6914(5)	4212(4)	1237(2)	28(1)
C(28)	8056(6)	3815(5)	1274(3)	52(2)
C(29)	8359(6)	3155(5)	973(3)	49(2)

C(30)	7571(6)	2877(4)	607(3)	39(2)
C(31)	6448(5)	3251(4)	551(2)	28(1)
C(32)	5881(5)	7298(4)	625(2)	30(2)
C(33)	5099(5)	7965(4)	545(2)	31(2)
C(34)	5607(6)	8757(4)	559(2)	31(1)
C(35)	6812(6)	8902(4)	641(2)	30(2)
C(36)	7551(6)	8225(4)	731(2)	32(2)
C(37)	7117(6)	7413(4)	725(2)	33(2)
C(38)	3748(6)	7842(4)	473(3)	39(2)
C(39)	7324(6)	9793(4)	632(2)	37(2)
C(40)	7943(6)	6668(4)	818(3)	41(2)
C(41)	2338(5)	4616(4)	1343(2)	24(1)
C(42)	1468(5)	4585(4)	967(2)	30(2)
C(43)	1077(5)	5311(4)	737(2)	29(1)
C(44)	1589(6)	6076(4)	859(2)	31(2)
C(45)	2505(5)	6101(4)	1215(2)	27(1)
C(46)	2623(6)	3107(4)	1414(2)	31(2)
C(47)	3689(5)	2617(4)	1630(3)	38(2)
C(48)	1415(6)	2764(4)	1580(3)	41(2)
C(1S)	3446(10)	10890(8)	663(4)	106(4)
Cl(2S)	2720(2)	10195(2)	306(1)	83(1)
Cl(3S)	4733(2)	11314(2)	364(1)	85(1)

Table S8. Bond lengths [Å] and angles [°] for complex 4.

Ru(1)-C(1)	1.859(5)
Ru(1)-C(3)	2.003(5)
Ru(1)-O(2)	2.012(4)
Ru(1)-O(1)	2.111(4)
Ru(1)-Cl(1)	2.3177(15)
O(1)-C(13)	1.305(7)
N(1)-C(2)	1.355(7)
N(1)-C(5)	1.380(8)
N(1)-C(14)	1.455(8)
C(1)-C(2)	1.479(8)
C(1)-C(4)	1.492(8)
N(2)-C(2)	1.346(7)
N(2)-C(6)	1.369(7)
N(2)-C(7)	1.477(7)
O(2)-C(27)	1.314(7)
O(3)-N(5)	1.229(7)
N(3)-C(3)	1.373(7)
N(3)-C(23)	1.393(7)
N(3)-C(32)	1.442(8)
C(3)-N(4)	1.365(7)
O(4)-N(5)	1.258(7)
N(4)-C(24)	1.380(7)
N(4)-C(25)	1.464(8)
C(4)-C(45)	1.386(8)
C(4)-C(41)	1.407(8)
N(5)-C(10)	1.424(7)
O(5)-N(6)	1.233(7)
C(5)-C(6)	1.346(9)
C(5)-H(5)	0.9500
O(6)-N(6)	1.225(7)
N(6)-C(30)	1.454(8)
C(6)-H(6)	0.9500
O(7)-C(41)	1.372(6)
O(7)-C(46)	1.447(7)
C(7)-C(8)	1.497(8)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.385(8)
C(8)-C(13)	1.409(8)
C(9)-C(10)	1.386(8)
C(9)-H(9)	0.9500
C(10)-C(11)	1.394(8)
C(11)-C(12)	1.353(8)
C(11)-H(11)	0.9500
C(12)-C(13)	1.407(8)
C(12)-H(12)	0.9500
C(14)-C(15)	1.356(9)
C(14)-C(19)	1.403(9)

C(15)-C(16)	1.413(9)
C(15)-C(20)	1.521(9)
C(16)-C(17)	1.383(9)
C(16)-H(16)	0.9500
C(17)-C(18)	1.388(9)
C(17)-C(21)	1.512(9)
C(18)-C(19)	1.389(9)
C(18)-H(18)	0.9500
C(19)-C(22)	1.486(9)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-C(24)	1.317(8)
C(23)-H(23)	0.9500
C(24)-H(24)	0.9500
C(25)-C(26)	1.495(8)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-C(31)	1.372(8)
C(26)-C(27)	1.429(8)
C(27)-C(28)	1.410(9)
C(28)-C(29)	1.359(10)
C(28)-H(28)	0.9500
C(29)-C(30)	1.367(9)
C(29)-H(29)	0.9500
C(30)-C(31)	1.379(9)
C(31)-H(31)	0.9500
C(32)-C(33)	1.385(9)
C(32)-C(37)	1.396(8)
C(33)-C(34)	1.383(9)
C(33)-C(38)	1.510(8)
C(34)-C(35)	1.362(9)
C(34)-H(34)	0.9500
C(35)-C(36)	1.373(9)
C(35)-C(39)	1.530(9)
C(36)-C(37)	1.381(9)
C(36)-H(36)	0.9500
C(37)-C(40)	1.517(9)
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-H(40A)	0.9800

C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
C(41)-C(42)	1.377(8)
C(42)-C(43)	1.376(9)
C(42)-H(42)	0.9500
C(43)-C(44)	1.381(9)
C(43)-H(43)	0.9500
C(44)-C(45)	1.376(8)
C(44)-H(44)	0.9500
C(45)-H(45)	0.9500
C(46)-C(48)	1.502(9)
C(46)-C(47)	1.520(8)
C(46)-H(46)	1.0000
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
C(1S)-Cl(2S)	1.657(11)
C(1S)-Cl(3S)	1.754(11)
C(1S)-H(1SA)	0.9900
C(1S)-H(1SB)	0.9900

C(1)-Ru(1)-C(3)	96.4(2)
C(1)-Ru(1)-O(2)	111.7(2)
C(3)-Ru(1)-O(2)	90.04(19)
C(1)-Ru(1)-O(1)	94.3(2)
C(3)-Ru(1)-O(1)	169.1(2)
O(2)-Ru(1)-O(1)	87.43(16)
C(1)-Ru(1)-Cl(1)	100.09(17)
C(3)-Ru(1)-Cl(1)	92.88(18)
O(2)-Ru(1)-Cl(1)	147.51(12)
O(1)-Ru(1)-Cl(1)	83.67(12)
C(13)-O(1)-Ru(1)	135.1(4)
C(2)-N(1)-C(5)	109.3(5)
C(2)-N(1)-C(14)	127.4(5)
C(5)-N(1)-C(14)	123.1(5)
C(2)-C(1)-C(4)	114.0(5)
C(2)-C(1)-Ru(1)	121.5(4)
C(4)-C(1)-Ru(1)	124.4(4)
C(2)-N(2)-C(6)	110.4(5)
C(2)-N(2)-C(7)	127.3(5)
C(6)-N(2)-C(7)	122.2(5)
C(27)-O(2)-Ru(1)	140.6(3)
N(2)-C(2)-N(1)	106.0(5)
N(2)-C(2)-C(1)	128.5(5)
N(1)-C(2)-C(1)	125.3(5)
C(3)-N(3)-C(23)	110.9(5)
C(3)-N(3)-C(32)	130.1(5)
C(23)-N(3)-C(32)	118.3(5)

N(4)-C(3)-N(3)	102.8(4)
N(4)-C(3)-Ru(1)	123.8(4)
N(3)-C(3)-Ru(1)	132.8(4)
C(3)-N(4)-C(24)	111.7(5)
C(3)-N(4)-C(25)	123.7(5)
C(24)-N(4)-C(25)	123.8(5)
C(45)-C(4)-C(41)	118.6(5)
C(45)-C(4)-C(1)	122.6(5)
C(41)-C(4)-C(1)	118.6(5)
O(3)-N(5)-O(4)	121.2(5)
O(3)-N(5)-C(10)	119.8(5)
O(4)-N(5)-C(10)	118.9(5)
C(6)-C(5)-N(1)	107.3(6)
C(6)-C(5)-H(5)	126.3
N(1)-C(5)-H(5)	126.3
O(6)-N(6)-O(5)	123.1(6)
O(6)-N(6)-C(30)	118.1(6)
O(5)-N(6)-C(30)	118.8(6)
C(5)-C(6)-N(2)	106.9(6)
C(5)-C(6)-H(6)	126.5
N(2)-C(6)-H(6)	126.5
C(41)-O(7)-C(46)	119.5(4)
N(2)-C(7)-C(8)	111.6(4)
N(2)-C(7)-H(7A)	109.3
C(8)-C(7)-H(7A)	109.3
N(2)-C(7)-H(7B)	109.3
C(8)-C(7)-H(7B)	109.3
H(7A)-C(7)-H(7B)	108.0
C(9)-C(8)-C(13)	119.6(5)
C(9)-C(8)-C(7)	120.8(5)
C(13)-C(8)-C(7)	119.6(5)
C(8)-C(9)-C(10)	119.9(6)
C(8)-C(9)-H(9)	120.1
C(10)-C(9)-H(9)	120.1
C(9)-C(10)-C(11)	120.6(5)
C(9)-C(10)-N(5)	120.7(5)
C(11)-C(10)-N(5)	118.7(5)
C(12)-C(11)-C(10)	119.9(5)
C(12)-C(11)-H(11)	120.1
C(10)-C(11)-H(11)	120.1
C(11)-C(12)-C(13)	121.0(6)
C(11)-C(12)-H(12)	119.5
C(13)-C(12)-H(12)	119.5
O(1)-C(13)-C(12)	118.3(5)
O(1)-C(13)-C(8)	122.8(5)
C(12)-C(13)-C(8)	118.9(6)
C(15)-C(14)-C(19)	123.8(6)
C(15)-C(14)-N(1)	118.4(5)
C(19)-C(14)-N(1)	117.8(5)
C(14)-C(15)-C(16)	117.0(6)
C(14)-C(15)-C(20)	122.2(6)

C(16)-C(15)-C(20)	120.8(6)
C(17)-C(16)-C(15)	121.6(6)
C(17)-C(16)-H(16)	119.2
C(15)-C(16)-H(16)	119.2
C(16)-C(17)-C(18)	118.9(6)
C(16)-C(17)-C(21)	121.2(6)
C(18)-C(17)-C(21)	119.9(6)
C(17)-C(18)-C(19)	121.4(6)
C(17)-C(18)-H(18)	119.3
C(19)-C(18)-H(18)	119.3
C(18)-C(19)-C(14)	117.1(6)
C(18)-C(19)-C(22)	120.1(6)
C(14)-C(19)-C(22)	122.9(6)
C(15)-C(20)-H(20A)	109.5
C(15)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(15)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(17)-C(21)-H(21A)	109.5
C(17)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(17)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(19)-C(22)-H(22A)	109.5
C(19)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(19)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(24)-C(23)-N(3)	107.1(6)
C(24)-C(23)-H(23)	126.5
N(3)-C(23)-H(23)	126.5
C(23)-C(24)-N(4)	107.4(6)
C(23)-C(24)-H(24)	126.3
N(4)-C(24)-H(24)	126.3
N(4)-C(25)-C(26)	110.7(5)
N(4)-C(25)-H(25A)	109.5
C(26)-C(25)-H(25A)	109.5
N(4)-C(25)-H(25B)	109.5
C(26)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	108.1
C(31)-C(26)-C(27)	119.6(6)
C(31)-C(26)-C(25)	121.2(5)
C(27)-C(26)-C(25)	119.1(5)
O(2)-C(27)-C(28)	118.0(5)
O(2)-C(27)-C(26)	125.2(5)
C(28)-C(27)-C(26)	116.8(6)
C(29)-C(28)-C(27)	121.9(7)
C(29)-C(28)-H(28)	119.1

C(27)-C(28)-H(28)	119.1
C(28)-C(29)-C(30)	120.3(6)
C(28)-C(29)-H(29)	119.9
C(30)-C(29)-H(29)	119.9
C(29)-C(30)-C(31)	120.1(6)
C(29)-C(30)-N(6)	120.1(6)
C(31)-C(30)-N(6)	119.8(6)
C(26)-C(31)-C(30)	121.2(6)
C(26)-C(31)-H(31)	119.4
C(30)-C(31)-H(31)	119.4
C(33)-C(32)-C(37)	122.1(6)
C(33)-C(32)-N(3)	118.4(5)
C(37)-C(32)-N(3)	119.2(6)
C(34)-C(33)-C(32)	116.6(6)
C(34)-C(33)-C(38)	121.3(6)
C(32)-C(33)-C(38)	122.0(6)
C(35)-C(34)-C(33)	123.5(6)
C(35)-C(34)-H(34)	118.2
C(33)-C(34)-H(34)	118.2
C(34)-C(35)-C(36)	118.0(6)
C(34)-C(35)-C(39)	120.8(6)
C(36)-C(35)-C(39)	121.1(6)
C(35)-C(36)-C(37)	122.1(6)
C(35)-C(36)-H(36)	118.9
C(37)-C(36)-H(36)	118.9
C(36)-C(37)-C(32)	117.5(6)
C(36)-C(37)-C(40)	121.8(6)
C(32)-C(37)-C(40)	120.7(6)
C(33)-C(38)-H(38A)	109.5
C(33)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(33)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(35)-C(39)-H(39A)	109.5
C(35)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(35)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(37)-C(40)-H(40A)	109.5
C(37)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(37)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
O(7)-C(41)-C(42)	125.9(5)
O(7)-C(41)-C(4)	114.4(5)
C(42)-C(41)-C(4)	119.7(6)
C(43)-C(42)-C(41)	120.1(6)
C(43)-C(42)-H(42)	120.0

C(41)-C(42)-H(42)	120.0
C(42)-C(43)-C(44)	121.1(5)
C(42)-C(43)-H(43)	119.5
C(44)-C(43)-H(43)	119.5
C(45)-C(44)-C(43)	118.8(6)
C(45)-C(44)-H(44)	120.6
C(43)-C(44)-H(44)	120.6
C(44)-C(45)-C(4)	121.5(6)
C(44)-C(45)-H(45)	119.2
C(4)-C(45)-H(45)	119.2
O(7)-C(46)-C(48)	109.2(5)
O(7)-C(46)-C(47)	104.6(5)
C(48)-C(46)-C(47)	112.7(5)
O(7)-C(46)-H(46)	110.0
C(48)-C(46)-H(46)	110.0
C(47)-C(46)-H(46)	110.0
C(46)-C(47)-H(47A)	109.5
C(46)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
C(46)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(46)-C(48)-H(48A)	109.5
C(46)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(46)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5
Cl(2S)-C(1S)-Cl(3S)	113.2(6)
Cl(2S)-C(1S)-H(1SA)	108.9
Cl(3S)-C(1S)-H(1SA)	108.9
Cl(2S)-C(1S)-H(1SB)	108.9
Cl(3S)-C(1S)-H(1SB)	108.9
H(1SA)-C(1S)-H(1SB)	107.7

Table S9. Anisotropic displacement parameters ($Å^2 \times 10^3$) for complex 4. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U22	U33	U23	U13	U^{12}
Ru(1)	21(1)	23(1)	21(1)	-1(1)	-2(1)	0(1)
Cl(1)	48(1)	29(1)	31(1)	1(1)	0(1)	2(1)
O(1)	37(2)	25(2)	29(2)	-2(2)	-4(2)	5(2)
N(1)	28(3)	36(3)	22(3)	-1(2)	-2(2)	0(3)
C(1)	20(3)	17(3)	25(3)	-4(2)	-3(2)	6(2)
N(2)	23(3)	30(3)	21(2)	-3(2)	-4(2)	2(2)
O(2)	20(2)	35(2)	26(2)	-8(2)	1(2)	-2(2)
C(2)	24(3)	24(3)	24(3)	0(3)	-3(3)	0(3)
O(3)	40(3)	40(3)	49(3)	19(2)	-10(2)	0(2)
N(3)	27(3)	32(3)	26(3)	4(2)	-2(2)	4(3)
C(3)	24(3)	30(3)	24(3)	2(3)	0(2)	6(3)
O(4)	39(3)	48(3)	41(2)	0(2)	-17(2)	1(3)
N(4)	29(3)	26(3)	25(3)	-3(2)	-4(2)	5(2)
C(4)	21(3)	25(3)	18(3)	-3(2)	3(2)	1(3)
N(5)	25(3)	42(4)	33(3)	4(3)	-1(3)	5(3)
O(5)	52(3)	63(4)	66(4)	-39(3)	3(3)	6(3)
C(5)	36(4)	57(5)	28(4)	6(3)	2(3)	-3(4)
O(6)	49(3)	55(3)	84(4)	-31(3)	4(3)	21(3)
N(6)	39(4)	45(4)	57(4)	-20(3)	4(3)	5(3)
C(6)	32(4)	51(5)	29(3)	13(3)	1(3)	1(3)
O(7)	28(2)	20(2)	30(2)	4(2)	-4(2)	0(2)
C(7)	29(3)	26(3)	29(3)	4(3)	-2(3)	7(3)
C(8)	21(3)	29(4)	23(3)	0(3)	-1(3)	2(3)
C(9)	28(3)	29(4)	36(3)	2(3)	1(3)	1(3)
C(10)	25(3)	31(3)	26(3)	-6(3)	-5(3)	7(3)
C(11)	25(3)	28(3)	23(3)	-3(3)	2(3)	0(3)
C(12)	29(3)	27(3)	29(3)	-2(3)	-2(3)	3(3)
C(13)	31(3)	26(3)	22(3)	-1(3)	1(3)	1(3)
C(14)	30(3)	31(4)	18(3)	2(3)	3(2)	5(3)
C(15)	37(4)	44(4)	28(4)	-3(3)	6(3)	1(3)
C(16)	48(4)	35(4)	37(4)	-3(3)	14(3)	4(3)
C(17)	36(4)	37(4)	30(4)	-1(3)	1(3)	9(3)
C(18)	24(4)	51(4)	29(3)	-1(3)	1(3)	5(3)
C(19)	33(3)	40(4)	27(3)	-2(3)	8(3)	-2(3)
C(20)	45(4)	41(4)	40(4)	-7(3)	8(3)	-9(3)
C(21)	53(5)	53(5)	47(4)	1(4)	5(3)	25(4)
C(22)	30(4)	50(4)	56(5)	-4(4)	4(3)	-1(4)
C(23)	34(4)	50(4)	18(3)	5(3)	-4(3)	-3(3)
C(24)	37(4)	45(4)	21(3)	-4(3)	-6(3)	-2(3)
C(25)	21(3)	29(3)	32(3)	-9(3)	-1(2)	1(3)
C(26)	26(3)	29(3)	22(3)	-4(3)	4(3)	-7(3)
C(27)	24(3)	29(3)	32(3)	-1(3)	-2(3)	5(3)
C(28)	29(4)	63(5)	64(5)	-20(4)	-21(4)	18(4)
C(29)	30(4)	58(5)	59(5)	-27(4)	-8(4)	19(4)
C(30)	30(4)	39(4)	47(4)	-19(3)	5(3)	3(3)

C(31)	23(3)	32(4)	28(3)	-7(3)	2(3)	1(3)
C(32)	30(4)	39(4)	21(3)	3(3)	3(3)	-7(3)
C(33)	26(3)	37(4)	30(3)	6(3)	5(3)	2(3)
C(34)	33(4)	35(4)	26(3)	6(3)	-1(3)	3(3)
C(35)	28(4)	35(4)	26(3)	12(3)	-1(3)	-2(3)
C(36)	30(4)	36(4)	31(4)	0(3)	-1(3)	-8(3)
C(37)	32(4)	45(4)	22(3)	14(3)	-1(3)	0(3)
C(38)	25(4)	42(4)	52(4)	10(4)	-4(3)	-1(3)
C(39)	34(4)	40(4)	39(4)	11(3)	-8(3)	-5(3)
C(40)	32(4)	53(5)	39(4)	16(3)	-4(3)	2(3)
C(41)	19(3)	28(3)	25(3)	6(3)	1(3)	3(3)
C(42)	26(3)	32(4)	31(4)	-6(3)	-2(3)	2(3)
C(43)	26(3)	35(4)	26(3)	3(3)	-9(3)	1(3)
C(44)	30(4)	34(4)	29(4)	4(3)	-4(3)	9(3)
C(45)	23(3)	28(3)	29(3)	6(3)	3(3)	1(3)
C(46)	33(4)	29(4)	31(3)	0(3)	-3(3)	-1(3)
C(47)	27(3)	38(4)	48(4)	-1(4)	-2(3)	1(3)
C(48)	38(4)	29(3)	54(5)	6(4)	-7(3)	2(3)
C(1S)	106(9)	115(10)	97(8)	-37(8)	29(7)	-6(8)
Cl(2S)	81(2)	70(2)	98(2)	4(1)	-30(2)	-2(1)
Cl(3S)	60(2)	72(2)	121(2)	10(1)	-2(1)	1(1)

Table S10. Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3) for complex 4.

	x	y	z	U(eq)
H(5)	1986	4886	3312	48
H(6)	3833	4002	3338	45
H(7A)	5543	4130	2141	34
H(7B)	5317	3493	2603	34
H(9)	6910	3428	3191	37
H(11)	9068	5434	3477	30
H(12)	7918	6240	2936	34
H(16)	1226	7905	2452	48
H(18)	-987	6052	1978	42
H(20A)	3195	6730	3147	63
H(20B)	3089	7626	2878	63
H(20C)	3829	6887	2607	63
H(21A)	-854	8224	2198	76
H(21B)	-1747	7480	2033	76
H(21C)	-776	7839	1636	76
H(22A)	1038	4389	2261	68
H(22B)	-121	4611	1918	68
H(22C)	-247	4572	2525	68
H(23)	5360	6474	-243	41
H(24)	4851	4987	-178	41
H(25A)	4371	3963	568	33
H(25B)	4470	4307	1140	33
H(28)	8629	4015	1515	62
H(29)	9122	2885	1017	59
H(31)	5903	3047	300	33
H(34)	5088	9226	508	37
H(36)	8389	8317	799	39
H(38A)	3374	8374	373	59
H(38B)	3385	7649	793	59
H(38C)	3607	7424	206	59
H(39A)	8137	9795	785	56
H(39B)	6787	10164	826	56
H(39C)	7375	9989	279	56
H(40A)	8794	6846	792	62
H(40B)	7778	6234	563	62
H(40C)	7791	6443	1159	62
H(42)	1137	4061	865	36
H(43)	446	5287	490	35
H(44)	1312	6575	699	37
H(45)	2881	6622	1291	32
H(46)	2670	3118	1033	37
H(47A)	4452	2886	1528	56
H(47B)	3668	2042	1500	56
H(47C)	3633	2607	2003	56
H(48A)	767	3150	1477	61

H(48B)	1408	2702	1951	61
H(48C)	1281	2217	1421	61
H(1SA)	3699	10619	985	127
H(1SB)	2879	11350	750	127

Table S11. Torsion angles [°] for complex 4.

C(1)-Ru(1)-O(1)-C(13)	98.2(5)
C(3)-Ru(1)-O(1)-C(13)	-90.1(12)
O(2)-Ru(1)-O(1)-C(13)	-13.4(5)
Cl(1)-Ru(1)-O(1)-C(13)	-162.1(5)
C(3)-Ru(1)-C(1)-C(2)	170.6(4)
O(2)-Ru(1)-C(1)-C(2)	78.0(5)
O(1)-Ru(1)-C(1)-C(2)	-11.0(5)
Cl(1)-Ru(1)-C(1)-C(2)	-95.3(4)
C(3)-Ru(1)-C(1)-C(4)	-13.1(5)
O(2)-Ru(1)-C(1)-C(4)	-105.7(4)
O(1)-Ru(1)-C(1)-C(4)	165.3(4)
Cl(1)-Ru(1)-C(1)-C(4)	81.0(5)
C(1)-Ru(1)-O(2)-C(27)	70.6(6)
C(3)-Ru(1)-O(2)-C(27)	-26.4(6)
O(1)-Ru(1)-O(2)-C(27)	164.2(6)
Cl(1)-Ru(1)-O(2)-C(27)	-121.8(5)
C(6)-N(2)-C(2)-N(1)	-0.1(6)
C(7)-N(2)-C(2)-N(1)	179.4(5)
C(6)-N(2)-C(2)-C(1)	-175.1(6)
C(7)-N(2)-C(2)-C(1)	4.5(9)
C(5)-N(1)-C(2)-N(2)	0.1(6)
C(14)-N(1)-C(2)-N(2)	176.7(5)
C(5)-N(1)-C(2)-C(1)	175.2(5)
C(14)-N(1)-C(2)-C(1)	-8.1(9)
C(4)-C(1)-C(2)-N(2)	131.8(6)
Ru(1)-C(1)-C(2)-N(2)	-51.5(8)
C(4)-C(1)-C(2)-N(1)	-42.2(8)
Ru(1)-C(1)-C(2)-N(1)	134.5(5)
C(23)-N(3)-C(3)-N(4)	-0.4(6)
C(32)-N(3)-C(3)-N(4)	-171.0(6)
C(23)-N(3)-C(3)-Ru(1)	170.7(4)
C(32)-N(3)-C(3)-Ru(1)	0.1(10)
C(1)-Ru(1)-C(3)-N(4)	-61.9(5)
O(2)-Ru(1)-C(3)-N(4)	50.0(4)
O(1)-Ru(1)-C(3)-N(4)	126.5(10)
Cl(1)-Ru(1)-C(3)-N(4)	-162.4(4)
C(1)-Ru(1)-C(3)-N(3)	128.6(6)
O(2)-Ru(1)-C(3)-N(3)	-119.5(5)
O(1)-Ru(1)-C(3)-N(3)	-43.1(14)
Cl(1)-Ru(1)-C(3)-N(3)	28.1(5)
N(3)-C(3)-N(4)-C(24)	0.5(6)
Ru(1)-C(3)-N(4)-C(24)	-171.6(4)
N(3)-C(3)-N(4)-C(25)	170.4(5)
Ru(1)-C(3)-N(4)-C(25)	-1.7(7)
C(2)-C(1)-C(4)-C(45)	122.1(6)
Ru(1)-C(1)-C(4)-C(45)	-54.5(7)
C(2)-C(1)-C(4)-C(41)	-63.2(7)
Ru(1)-C(1)-C(4)-C(41)	120.2(5)

C(2)-N(1)-C(5)-C(6)	0.0(7)
C(14)-N(1)-C(5)-C(6)	-176.8(6)
N(1)-C(5)-C(6)-N(2)	-0.1(8)
C(2)-N(2)-C(6)-C(5)	0.2(7)
C(7)-N(2)-C(6)-C(5)	-179.4(5)
C(2)-N(2)-C(7)-C(8)	102.1(6)
C(6)-N(2)-C(7)-C(8)	-78.4(6)
N(2)-C(7)-C(8)-C(9)	119.8(6)
N(2)-C(7)-C(8)-C(13)	-59.4(7)
C(13)-C(8)-C(9)-C(10)	-2.7(9)
C(7)-C(8)-C(9)-C(10)	178.2(5)
C(8)-C(9)-C(10)-C(11)	2.1(9)
C(8)-C(9)-C(10)-N(5)	-177.0(5)
O(3)-N(5)-C(10)-C(9)	-4.6(8)
O(4)-N(5)-C(10)-C(9)	174.7(5)
O(3)-N(5)-C(10)-C(11)	176.2(5)
O(4)-N(5)-C(10)-C(11)	-4.4(8)
C(9)-C(10)-C(11)-C(12)	-0.6(9)
N(5)-C(10)-C(11)-C(12)	178.5(5)
C(10)-C(11)-C(12)-C(13)	-0.1(9)
Ru(1)-O(1)-C(13)-C(12)	128.0(5)
Ru(1)-O(1)-C(13)-C(8)	-52.7(8)
C(11)-C(12)-C(13)-O(1)	178.8(5)
C(11)-C(12)-C(13)-C(8)	-0.5(9)
C(9)-C(8)-C(13)-O(1)	-177.3(5)
C(7)-C(8)-C(13)-O(1)	1.8(9)
C(9)-C(8)-C(13)-C(12)	2.0(8)
C(7)-C(8)-C(13)-C(12)	-178.9(5)
C(2)-N(1)-C(14)-C(15)	-78.6(8)
C(5)-N(1)-C(14)-C(15)	97.7(7)
C(2)-N(1)-C(14)-C(19)	104.1(7)
C(5)-N(1)-C(14)-C(19)	-79.6(7)
C(19)-C(14)-C(15)-C(16)	-4.5(9)
N(1)-C(14)-C(15)-C(16)	178.3(5)
C(19)-C(14)-C(15)-C(20)	172.3(6)
N(1)-C(14)-C(15)-C(20)	-4.8(9)
C(14)-C(15)-C(16)-C(17)	0.2(9)
C(20)-C(15)-C(16)-C(17)	-176.8(6)
C(15)-C(16)-C(17)-C(18)	2.7(9)
C(15)-C(16)-C(17)-C(21)	-177.0(6)
C(16)-C(17)-C(18)-C(19)	-1.4(9)
C(21)-C(17)-C(18)-C(19)	178.3(6)
C(17)-C(18)-C(19)-C(14)	-2.6(9)
C(17)-C(18)-C(19)-C(22)	176.0(6)
C(15)-C(14)-C(19)-C(18)	5.8(9)
N(1)-C(14)-C(19)-C(18)	-177.1(5)
C(15)-C(14)-C(19)-C(22)	-172.7(6)
N(1)-C(14)-C(19)-C(22)	4.4(8)
C(3)-N(3)-C(23)-C(24)	0.1(7)
C(32)-N(3)-C(23)-C(24)	172.0(5)
N(3)-C(23)-C(24)-N(4)	0.2(7)

C(3)-N(4)-C(24)-C(23)	-0.5(7)
C(25)-N(4)-C(24)-C(23)	-170.3(5)
C(3)-N(4)-C(25)-C(26)	-81.7(6)
C(24)-N(4)-C(25)-C(26)	86.9(7)
N(4)-C(25)-C(26)-C(31)	-113.5(6)
N(4)-C(25)-C(26)-C(27)	69.9(7)
Ru(1)-O(2)-C(27)-C(28)	164.6(5)
Ru(1)-O(2)-C(27)-C(26)	-15.9(10)
C(31)-C(26)-C(27)-O(2)	-177.3(5)
C(25)-C(26)-C(27)-O(2)	-0.6(9)
C(31)-C(26)-C(27)-C(28)	2.1(9)
C(25)-C(26)-C(27)-C(28)	178.8(6)
O(2)-C(27)-C(28)-C(29)	176.6(7)
C(26)-C(27)-C(28)-C(29)	-2.8(11)
C(27)-C(28)-C(29)-C(30)	2.7(13)
C(28)-C(29)-C(30)-C(31)	-1.7(12)
C(28)-C(29)-C(30)-N(6)	176.7(7)
O(6)-N(6)-C(30)-C(29)	9.5(10)
O(5)-N(6)-C(30)-C(29)	-172.3(7)
O(6)-N(6)-C(30)-C(31)	-172.1(6)
O(5)-N(6)-C(30)-C(31)	6.2(10)
C(27)-C(26)-C(31)-C(30)	-1.3(9)
C(25)-C(26)-C(31)-C(30)	-177.9(6)
C(29)-C(30)-C(31)-C(26)	1.1(10)
N(6)-C(30)-C(31)-C(26)	-177.4(6)
C(3)-N(3)-C(32)-C(33)	-112.8(7)
C(23)-N(3)-C(32)-C(33)	77.2(7)
C(3)-N(3)-C(32)-C(37)	72.6(8)
C(23)-N(3)-C(32)-C(37)	-97.4(7)
C(37)-C(32)-C(33)-C(34)	1.3(9)
N(3)-C(32)-C(33)-C(34)	-173.1(5)
C(37)-C(32)-C(33)-C(38)	-175.8(6)
N(3)-C(32)-C(33)-C(38)	9.9(9)
C(32)-C(33)-C(34)-C(35)	0.5(9)
C(38)-C(33)-C(34)-C(35)	177.6(6)
C(33)-C(34)-C(35)-C(36)	-2.1(9)
C(33)-C(34)-C(35)-C(39)	177.7(6)
C(34)-C(35)-C(36)-C(37)	2.0(9)
C(39)-C(35)-C(36)-C(37)	-177.9(6)
C(35)-C(36)-C(37)-C(32)	-0.3(9)
C(35)-C(36)-C(37)-C(40)	179.2(6)
C(33)-C(32)-C(37)-C(36)	-1.4(9)
N(3)-C(32)-C(37)-C(36)	172.9(5)
C(33)-C(32)-C(37)-C(40)	179.1(6)
N(3)-C(32)-C(37)-C(40)	-6.6(8)
C(46)-O(7)-C(41)-C(42)	20.1(8)
C(46)-O(7)-C(41)-C(4)	-157.8(5)
C(45)-C(4)-C(41)-O(7)	-179.1(5)
C(1)-C(4)-C(41)-O(7)	6.0(7)
C(45)-C(4)-C(41)-C(42)	2.9(8)
C(1)-C(4)-C(41)-C(42)	-172.0(5)

O(7)-C(41)-C(42)-C(43)	177.3(6)
C(4)-C(41)-C(42)-C(43)	-4.9(9)
C(41)-C(42)-C(43)-C(44)	3.4(9)
C(42)-C(43)-C(44)-C(45)	0.2(9)
C(43)-C(44)-C(45)-C(4)	-2.2(9)
C(41)-C(4)-C(45)-C(44)	0.7(9)
C(1)-C(4)-C(45)-C(44)	175.3(5)
C(41)-O(7)-C(46)-C(48)	-87.7(6)
C(41)-O(7)-C(46)-C(47)	151.4(5)

Computational details

Geometry optimization.

Geometry optimizations were performed using the OLYP density functional as implemented in the Gaussian 03 suite of programs.[7] The OLYP functional consists of Handy's OPTX[8] modification of Becke's exchange functional and the correlation functional due to Lee, Yang, and Parr.[9] This functional has been reported to be superior to the related BLYP functional and other pure density functionals.[10] Numerical integrations were performed using the default pruned "fine" grid of Gaussian 03, consisting of 75 radial shells and 302 angular points per shell. Geometries were converged to a maximum force and displacement of 0.00045 hartree/bohr and 0.0018 bohr, respectively, whereas the corresponding self-consistent-field (SCF) procedure was converged to a RMS change of the density matrix below 1.0×10^{-8}. The stationary geometries were characterized by the eigenvalues of the analytically calculated Hessian matrix.

Hay and Wadt effective core potentials (ECPs) were applied for chlorine and ruthenium.[11, 12] For ruthenium, the ECP replaced the 1s, 2s, 2p, 3s, 3p and 3d electrons whereas the 4s, 4p, 4d, 5s and 5p orbitals were represented by the Hay and Wadt (5s,6p) primitive basis set [12] contracted to [3s,3p,2d]. The 3s and 3p orbitals of Cl were described by the Hay and Wadt (3s,3p) primitive basis set[11] augmented with a single polarization d primitive[13] and contracted to [2s,2p,1d].
Carbon, nitrogen, oxygen, and hydrogen atoms were described by standard Dunning and Hay valence double-ζ basis sets.[14] Single d polarization functions[13] were added to the basis sets of the two oxygen atoms bound to ruthenium (O1 and O2), the alkylidene carbon atom (C1), the aryl carbon atom bound to the alkylidene (C4), and the nitrogen atoms (N1—N4) and the carbene carbon atoms (C2 and C3) of the two NHC rings.

Single-point (SP) energy evaluations

Total energies and properties were obtained in single point (SP) energy evaluations using the three-parameter hybrid density functional method of Becke (termed "B3LYP"),[15] as implemented in the Gaussian 03 set of programs.[7] Atomic partial charges were calculated using natural population analysis (NPA)[16] as implemented in the Natural Bond Orbital (NBO) program.[17] In a broad comparative study involving experimentally determined charges and those of several different schemes for population analysis, NPA was found to offer the most accurate and consistent description of charge transfer processes of donor–acceptor complexes of transition metals.[18] Natural resonance theory (NRT)[19] calculations were performed using the Natural Bond Orbital (NBO) program.[17]

The SP calculations involved basis sets that were improved compared to those used in the geometry optimizations: For ruthenium, the Hay and Wadt primitive basis set,[12] (5s,6p), was contracted to [4s,4p,3d]. A diffuse s function was added to the basis sets of all elements except ruthenium, whereas a diffuse p function was added to all elements except ruthenium and hydrogen. The diffuse s function for hydrogen and the diffuse p functions were taken from ref [13]. For the other elements, the diffuse s functions were added in an even-tempered manner. For hydrogen, a p polarization function was added, whereas a d polarization function was added to the basis sets of all carbon, nitrogen, and oxygen atoms for which a polarization

function was not included in the geometry optimization basis set.[13] These diffuse and polarization functions were added to the geometry optimization basis sets described above and contracted to [4s,1p] for hydrogen and [4s,4p,1d] for first-row elements as well as for the valence of chlorine.

Computational results

Natural population analysis

Table S12. Natural charge analysis of complex 4.

Atom	Natural charge	Group	Natural charge
Ru1	0.69	2-OiPr-Phenyl	–0.02
C1	–0.01	Ligand I[b]	0.00
C2	0.43	Ligand I [$NO_2(C_6H_3)O$]	–0.73
C3	0.34	Ligand I [1-Mes-2CH_2-imidazol-2ylidene]	0.73
C4	–0.18	Ligand II[c]	–0.25
Cl1	–0.43	Ligand II [$NO_2(C_6H_3)O$]	–0.60
O1	–0.74	Ligand II [1-Mes-2CH_2-imidazol-2ylidene]	0.36
O2	–0.69		

[a] The natural charges have been obtained using natural population analysis[16] and are given in multiples of the elementary charge. [b] NHC bound to the alkylidene carbon atom. [c] NHC bound to ruthenium.

Natural resonance theory (NRT) calculations

The NRT calculation involved 18 reference structures that produced a total of 2416 different resonance structures. Whereas most of these structures (2229) have a very low weight (< 0.10%), the 187 most important resonance structures have individual weights in the range 0.10%–3.77%, resulting in a combined weight of 93.73 %. The analysis presented in Table S2 below is based on the latter most important resonance structures.

Table S13. Combined weights (%) of dissociated, singly bonded or doubly bonded resonance structures for key bonds of the model of complex 4.[a]

Bond	% Dissociated	% Single bond	% Double bond
Ru1–C1	0.12	23.15	70.46
C1–C2		82.62	11.11
Ru1–Cl1	50.42	43.31	
Ru1–O2	50.61	42.84	0.28
Ru1–O1	66.84	26.89	
Ru1–C3	29.33	61.58	2.82

a] The analysis is based on the 187 most important resonance structures as explained in the accompanying text.

[

Cartesian coordinates of optimized geometries

Complex 4 (singlet)

Ru	0.036407	0.514873	-0.578954
Cl	1.904242	1.112089	-1.880914
O	-0.408375	-0.893964	-2.234426
N	1.952629	-3.013923	-0.080990
N	-0.241651	-2.979131	-0.123964
O	-5.399968	-4.780565	-2.867460
O	-5.238868	-3.957564	-4.986567
N	-4.835016	-4.017354	-3.755363
C	2.916562	6.234790	-4.187096
H	2.194297	6.940138	-4.623132
H	3.195665	5.522598	-4.982066
H	3.822425	6.797486	-3.919919
N	0.675318	3.439259	0.392477
O	-2.000629	0.610929	-0.448981
C	3.035182	-2.213893	-2.692851
H	2.137201	-1.599411	-2.580896
H	2.711622	-3.226865	-2.983341
H	3.611011	-1.800541	-3.529879
C	0.352406	4.281564	1.465739
H	0.645669	5.321985	1.485457
N	-0.444753	2.252617	1.836235
O	-6.028371	2.741810	3.994906
C	3.605278	3.946033	0.288740
H	4.457604	4.635860	0.360466
H	4.006380	2.949228	0.046728
H	3.135467	3.879592	1.276971
O	-7.398357	2.659334	2.178690

N	-6.244612	2.500427	2.739779
C	7.600807	-1.715127	-0.517101
H	8.024703	-2.031508	-1.481671
H	8.201491	-2.168871	0.283239
H	7.732835	-0.622165	-0.450049
O	0.086553	-1.977628	3.019116
C	0.185585	2.146925	0.607212
C	3.749556	-3.535089	2.241942
H	2.661446	-3.597014	2.314591
H	4.115213	-2.965909	3.107217
H	4.149956	-4.558516	2.332717
C	-1.965124	-2.868377	3.944439
H	-2.494830	-1.954239	3.644875
H	-2.466258	-3.277615	4.834300
H	-2.052431	-3.605613	3.134577
C	-3.698221	-3.200929	-3.352864
C	1.188727	-1.103512	3.073492
C	-3.245338	-3.246484	-2.012780
H	-3.769738	-3.895467	-1.311846
C	4.223750	-2.906361	0.942302
C	3.352671	0.724780	3.019247
H	4.191839	1.420244	2.989524
C	1.569708	-0.500219	1.824717
C	-2.944919	1.101907	0.350190
C	-1.393736	1.246780	2.371152
H	-1.440837	1.377135	3.460176
H	-0.985620	0.258280	2.165239
C	3.374275	-2.673057	-0.170460
C	-1.668227	-2.535595	-0.173181
H	-1.710660	-1.563184	0.318527

H	-2.255815	-3.253474	0.414085
C	3.151485	5.107754	-1.907276
H	4.214828	5.354388	-1.924307
C	-2.156295	-2.469340	-1.603400
C	-0.493053	-2.575217	4.266485
H	-0.448277	-1.814045	5.063036
C	-1.947179	-1.604288	-3.903411
H	-1.427480	-0.961990	-4.615193
C	0.144467	-4.268474	-0.446766
H	-0.568406	-5.042829	-0.694226
C	-0.357119	3.536061	2.370374
H	-0.798883	3.815024	3.317677
C	-1.095484	4.182100	-1.843421
H	-1.610397	4.798576	-2.591783
H	-1.563277	4.377547	-0.868637
H	-1.295948	3.129886	-2.095465
C	2.644137	4.387662	-0.801846
C	1.875204	-0.771536	4.265577
H	1.588613	-1.210466	5.218127
C	6.132680	-2.089855	-0.403054
C	-2.767415	1.404930	1.749039
C	-1.457624	-1.607987	-2.544583
C	0.959349	5.184189	-2.928916
H	0.303932	5.495444	-3.744166
C	3.886477	-2.258070	-1.436782
C	1.260934	4.064013	-0.791924
C	5.263395	-1.955248	-1.511761
H	5.666994	-1.618221	-2.467569
C	2.334589	5.503149	-2.988975
C	0.838112	-0.762929	0.544899

C	1.519679	-4.293700	-0.421090
H	2.213509	-5.094751	-0.633437
C	0.290364	-3.835018	4.682693
H	1.348070	-3.619395	4.880040
H	0.233665	-4.600196	3.895416
H	-0.146084	-4.257894	5.600465
C	-5.126869	2.025900	1.918084
C	-3.854323	1.859860	2.508600
H	-3.736445	2.095156	3.565254
C	5.596278	-2.590820	0.801601
H	6.255851	-2.751286	1.656416
C	0.850219	-2.191917	0.102678
C	-3.039034	-2.372228	-4.301413
H	-3.400651	-2.351196	-5.327667
C	2.953030	0.136648	4.236390
H	3.472223	0.378782	5.165533
C	-5.325617	1.738780	0.544488
H	-6.312184	1.870825	0.105411
C	0.394804	4.477142	-1.843939
C	-4.249295	1.286112	-0.220457
H	-4.376907	1.045251	-1.275380
C	2.655411	0.412381	1.838882
H	2.943804	0.862100	0.892958

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Complex 4 (triplet)

Ru	-0.027524	0.693673	0.587156
Cl	-2.013229	1.447129	1.583412
O	0.480615	-0.322768	2.368341
N	-2.181966	-2.879038	0.384934

N	0.002570	-2.859682	0.667844
O	4.970976	-4.620444	3.684188
O	4.994659	-3.384194	5.596588
N	4.541301	-3.636634	4.410869
C	-2.071950	6.702289	3.849488
H	-1.264955	7.311581	4.281511
H	-2.442646	6.039207	4.649300
H	-2.896470	7.375118	3.574935
N	-0.232574	3.548648	-0.669715
O	2.048344	0.516334	0.227280
C	-3.335169	-1.681838	2.805411
H	-2.406108	-1.130264	2.635971
H	-3.071317	-2.650131	3.260884
H	-3.918992	-1.118917	3.544080
C	0.142926	4.241461	-1.821962
H	0.009922	5.309438	-1.922633
N	0.604409	2.089806	-2.056304
O	5.938280	1.276278	-4.745438
C	-3.013113	4.521564	-0.646863
H	-4.025252	4.843609	-0.370961
H	-3.050035	3.451594	-0.881977
H	-2.740042	5.050129	-1.573770
O	7.447830	1.138495	-3.044929
N	6.231862	1.142671	-3.488438
C	-7.801043	-1.387330	0.399661
H	-8.283999	-1.599633	1.365481
H	-8.374338	-1.898693	-0.385535
H	-7.894406	-0.302581	0.223929
O	-0.388560	-2.284556	-2.738514
C	0.039435	2.188158	-0.803375

C	-3.905102	-3.678475	-1.909976
H	-2.817969	-3.777602	-1.919593
H	-4.214750	-3.227143	-2.862146
H	-4.335888	-4.693096	-1.874940
C	1.620915	-3.346358	-3.561282
H	2.202450	-2.445173	-3.327615
H	2.108434	-3.860329	-4.403158
H	1.647530	-4.015485	-2.689878
C	3.490172	-2.774001	3.867181
C	-1.408851	-1.320128	-2.869057
C	2.989786	-3.023173	2.567140
H	3.409887	-3.853432	2.001235
C	-4.409200	-2.858669	-0.735031
C	-3.402559	0.683648	-2.996552
H	-4.180209	1.447830	-3.033476
C	-1.712957	-0.562737	-1.676122
C	2.992081	0.684380	-0.682553
C	1.299732	0.880365	-2.565451
H	1.236103	0.893595	-3.660807
H	0.752556	0.015817	-2.192818
C	-3.591043	-2.492694	0.364928
C	1.441205	-2.506902	0.636907
H	1.540865	-1.638895	-0.015772
H	1.980525	-3.348679	0.181481
C	-2.448908	5.594884	1.579440
H	-3.470617	5.977408	1.592887
C	1.981635	-2.218525	2.022960
C	0.173263	-2.991658	-3.932566
H	0.183609	-2.285505	-4.779897
C	1.971216	-0.899155	4.112792

H	1.555632	-0.070824	4.686807
C	-0.454641	-4.082851	1.133465
H	0.205091	-4.828093	1.555958
C	0.679755	3.321703	-2.691822
H	1.105516	3.454348	-3.677254
C	1.645277	4.122023	1.539493
H	2.236707	4.692742	2.267105
H	2.126664	4.231068	0.557756
H	1.723814	3.061050	1.819908
C	-2.037588	4.806542	0.482568
C	-2.083921	-1.058951	-4.084102
H	-1.852302	-1.623135	-4.984642
C	-6.341771	-1.811469	0.399697
C	2.737322	0.852894	-2.094726
C	1.439634	-1.115458	2.791172
C	-0.266068	5.393823	2.609010
H	0.423036	5.627664	3.422252
C	-4.141051	-1.885157	1.534422
C	-0.709444	4.299015	0.488002
C	-5.509124	-1.539733	1.511795
H	-5.937018	-1.057839	2.392349
C	-1.587379	5.890683	2.660008
C	-0.946881	-0.774569	-0.416763
C	-1.815908	-4.101332	0.949072
H	-2.545514	-4.861823	1.189209
C	-0.667863	-4.234392	-4.284233
H	-1.709644	-3.979140	-4.514022
H	-0.662727	-4.949311	-3.449259
H	-0.238152	-4.735888	-5.164855
C	5.137950	0.991907	-2.529343

C	3.801932	1.003987	-2.991540
H	3.622358	1.129698	-4.058229
C	-5.776419	-2.493162	-0.697252
H	-6.407827	-2.756572	-1.547670
C	-1.039321	-2.085840	0.194065
C	2.975208	-1.706466	4.646328
H	3.371546	-1.533216	5.644462
C	-3.077675	-0.060123	-4.149065
H	-3.589896	0.126147	-5.094743
C	5.417843	0.837225	-1.146922
H	6.451762	0.833114	-0.808295
C	0.203066	4.602239	1.535988
C	4.363320	0.690166	-0.245549
H	4.555690	0.564299	0.819597
C	-2.722727	0.431475	-1.791240
H	-2.975028	0.993845	-0.896371

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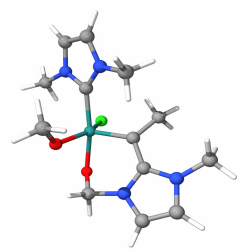

Model of complex 4

Ru	-0.333054	-0.720676	0.006532
C	0.951142	0.487238	-0.642536
C	0.665156	1.435583	-1.808622
N	3.402782	1.252111	-0.341787
C	2.346221	0.340426	-0.198979
C	4.542266	0.738683	0.270328
N	2.868560	-0.712777	0.504599
C	4.195661	-0.496416	0.784291

O	-0.287817	-0.917318	1.973515
C	3.402845	2.602995	-0.930017
C	2.090621	-2.129568	0.809700
O	1.105068	-2.295632	-0.053949
Cl	-0.964978	-1.549005	-2.210835
C	-0.774570	-0.019068	2.961119
N	-2.162439	1.858638	0.287641
C	-1.970072	0.497802	0.048720
C	-3.516400	2.205412	0.295801
N	-3.275614	0.027801	-0.072599
C	-4.217271	1.044296	0.075849
C	-1.133981	2.839781	0.643687
C	-3.671132	-1.388377	-0.165623
H	1.293142	1.153758	-2.672790
H	0.828254	2.504809	-1.602423
H	-0.373286	1.303809	-2.121087
H	5.483471	1.271821	0.294490
H	4.802134	-1.216988	1.317982
H	3.160182	2.575346	-1.997526
H	4.406277	3.028631	-0.812485
H	2.688451	3.257012	-0.413139
H	1.822212	-1.995422	1.877189
H	2.921298	-2.862212	0.700566
H	-0.128114	0.877776	3.070498
H	-0.771483	-0.547982	3.934161
H	-1.809106	0.328807	2.775844
H	-3.867276	3.218545	0.444186
H	-5.283801	0.874562	0.005985
H	-1.412118	3.346231	1.580097
H	-1.021841	3.596789	-0.147193

H	-0.184276	2.323096	0.789716
H	-3.763978	-1.829573	0.839424
H	-2.926639	-1.937327	-0.749646
H	-4.638466	-1.458204	-0.680888

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[6] The carbene peaks are invisible even if a large number of scans (20 000) are performed. A reason for this could be the low solubility of the complex in $CDCl_3$ or other suitable deuterated solvents.

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