Supplementary Material (ESI) for Dalton Transactions

Cyclometallation of arylimines and nitrogen-containing heterocycles via room-temperature C-H bond activation with arene ruthenium(II) acetato complexes

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I. *General information.*

All reagents were obtained from commercial sources and used as received. THF and dichloromethane were over Braun MB-SPS-800 solvent purification system, and stored under an argon atmosphere. Methanol (anhydrous, HPLC grade, Aldrich) were used as received. Technical grade petroleum ether (40-60 °C b.p.) and ethyl acetate were used for chromatography column. Analytical TLC was performed on Merck 60F254 silica gel plates (0.25 mm thickness). Column chromatography was performed on Acros Organics Ultrapure silica gel (mesh size 40-60 μm, 60 A).

^{1}H NMR spectra were recorded in $CDCl_3$ at ambient temperature on Bruker AVANCE I 300, AVANCE III 400 spectrometers at and 300.1 and 400.1 MHz, using the solvent as internal standard (7.26 ppm). ^{13}C NMR spectra were obtained at 75 and 100 MHz and referenced to the internal solvent signals (central peak is 77.2 ppm). Chemical shift (δ) and coupling constants (*J*) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br. for broad.

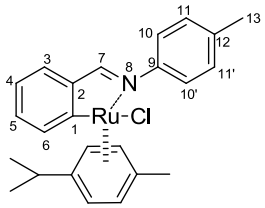
Infrared spectra were recorded on a Bruker IFS28 spectrometer using KBr pellets.

HRMS were measured on Waters Q-TOF 2.

II. General procedures for the reactions of imines with $[RuCl_2(p\text{-cymene})]_2$

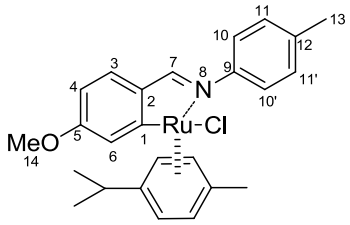
$[RuCl_2(p\text{-cymene})]_2$ (0.1 mmol, 61.2 mg), imines (0.2 mmol), KOAc (0.4 mmol, 40 mg) and methanol (5 mL) were introduced in a dried Schlenck tube under argon, equipped with magnetic stirring bar and the mixture was stirred at ambient temperature for 20 h. The solvent was then evaporated under vacuum and the desired product was purified by chromatography column on silica gel (0.5 mol% Et_3N) with a mixture of petrol ether/ethyl acetate as the eluent.

[RuCl{C_6H_4-1-C(H)=N(4-$CH_3C_6H_4$-$_k$*C*,*N*)}(*p*-cymene)] (3a)



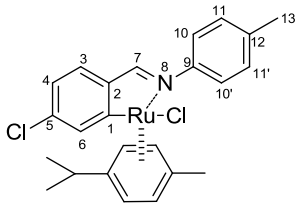
This compound was prepared from imine **2a**. The complex **3a** was purified by chromatography column on silica gel with a mixture of petroleum ether/ethyl acetate as the eluent (75:25), and was isolated as a orange solid (83 mg, 90%). R_f (petroleum ether/EtOAc 70:30) = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, 1H, *J* = 7.6 Hz, H_6), 8.10 (s, 1H, H_7), 7.66 (d, 2H, *J* = 8.4 Hz, H_{11}), 7.54 (d, 1H, *J* = 7.6 Hz, H_3), 7.23-7.17 (m, 3H, H_{10}, H_4 or H_5), 7.02 (t, 1H, *J* = 7.4 Hz, H_4 or H_5), 5.48 (d, 1H, *J* = 6.0 Hz, cymene), 5.22 (d, 1H, *J* = 6.0 Hz, cymene), 4.87 (d, 1H, *J* = 6 Hz, cymene), 4.83 (d, 1H, *J* = 6.0 Hz, cymene), 2.43-2.36 (m, 4H, H_{13}, C*H*MeMe'), 2.08 (s, 3H, Me cymene), 0.99 (d, 3H, *J* = 6.8 Hz, CH*Me*Me'), 0.85 (d, 3H, *J* = 6.8 Hz, CHMe*Me'*). The protons H_3, H_6, H_{10} have been assigned from a COSY experiment. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ =189.2 (C-Ru), 171.7, 152.8, 146.2, 139.3, 137.3, 130.3, 129.8, 129.4, 122.6, 122.3, 102.5, 100.7, 92.7, 89.6, 82.9, 82.4, 31.0, 23.1, 21.6, 21.3, 18.9. IR: *v* (C=N) 1579 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{24}H_{26}N^{35}ClNa^{102}Ru$ [M+ Na]$^+$ 488.0695, found 488.0708. *m/z* calcd for $C_{24}H_{26}N^{102}Ru$ [M- Cl]$^+$ 430.1109, found 430.1112.

[RuCl{(4-$OMeC_6H_4$)-1-C(H)=N(4-$CH_3C_6H_4$-$_k$*C*,*N*)}(*p*-cymene)] (3b)



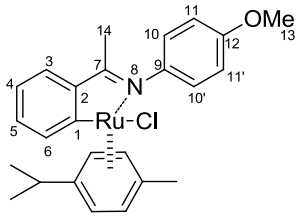
This compound was prepared from imine **2b** (45 mg, 0.2 mmol). The complex **3b** was purified by chromatography column on silica gel with a mixture of petroleum ether/ethyl acetate as the eluent (70:30), and was isolated as a red solid (77 mg, 77%). R_f (petroleum ether/EtOAc 70:30) = 0.30. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (s, 1H, H_7), 7.72 (d, 1H, *J* = 2.4 Hz, H_6), 7.63 (d, 2H, *J* = 8.4 Hz, H_{11}), 7.48 (d, 1H, *J* = 8.4 Hz, H_3), 7.19 (d, 2H, *J* = 8.4 Hz, H_{10}), 6.56 (dd, 1H, *J* = 2.4 Hz, *J* = 8.4 Hz, H_4), 5.44 (d, 1H, *J* = 6.0 Hz, cymene), 5.18 (d, 1H, *J* = 5.7 Hz, cymene), 4.83 (m, 2H, cymene), 3.92 (s, 3H, OMe), 2.41-2.35 (m, 4H, H_{13}, C*H*MeMe'), 2.08 (s, 3H, Me cymene), 0.99 (d, 3H, *J* = 6.9 Hz, CH*Me*Me'), 0.85 (d, 3H, *J* = 6.9 Hz, CHMe*Me'*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ =191.5 (C-Ru), 170.2, 160.3, 152.8, 139.7, 136.8, 131.1, 129.3, 123.6, 122.3, 109.0, 102.3, 100.1, 92.4, 89.2, 83.0, 82.2, 55.3, 30.9, 23.1, 21.6, 21.2, 18.9. IR: *v* (C=N) 1582 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{25}H_{28}NO^{35}ClNa^{102}Ru$ [M+ Na]$^+$ 518.0801, found 518.0817. *m/z* calcd for $C_{25}H_{28}NO^{102}Ru$ [M- Cl]$^+$ 460.1214, found 460.1212.

[RuCl{(4-ClC$_6$H$_4$)-1-C(H)=N(4-CH$_3$C$_6$H$_4$-$_k$*C,N*)}(*p*-cymene)] (3c)



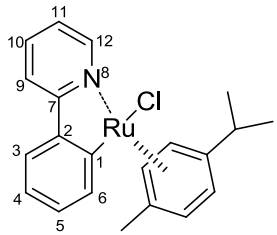
This compound was prepared from imine **2c** (45.8 mg, 0.2 mmol). The complex **3c** was purified by chromatography column on silica gel with a mixture of petroleum ether/ethyl acetate as the eluent (75:25) , and was isolated as a red solid (52 mg, 52%). R_f (petroleum ether/EtOAc 70:30) = 0.65. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, 1H, *J* = 1.8 Hz, H_6), 8.06 (s, 1H, H_7), 7.63 (d, 2H, *J* = 8.1 Hz, H_{11}), 7.45 (d, 1H, *J* = 7.8 Hz, H_3), 7.22 (d, 2H, *J* = 8.1 Hz, H_{10}), 7.01-6.97 (m, 1H, H_4), 5.47 (d, 1H, *J* = 6.0 Hz, cymene), 5.22 (d, 1H, *J* = 6.0 Hz, cymene), 4.90 (d, 1H, *J* = 6.0 Hz, cymene), 4.85 (d, 1H, *J* = 6.0 Hz, cymene), 2.42-2.33 (m, 4H, H_{13}, C*H*MeMe'), 2.10 (s, 3H, Me cymene), 0.98 (d, 3H, *J* = 6.9 Hz, CH*Me*Me'), 0.85 (d, 3H, *J* = 6.9 Hz, CHMe*Me'*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ =190.5 (C-Ru), 170.8, 152.5, 144.5, 138.5, 137.6, 136.0, 130.4, 129.5, 123.0, 122.2, 103.1, 100.9, 92.9, 89.4, 83.7, 82.6, 31.0, 23.0, 21.7, 21.3, 19.0. IR: *v* (C=N) 1578 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{24}H_{25}N^{35}Cl_2Na^{102}Ru$ $[M+ Na]^+$ 522.0305, found 522.0323. *m/z* calcd for $C_{24}H_{25}N^{35}Cl\,^{102}Ru$ $[M- Cl]^+$ 464.0719, found 464.0719.

[RuCl{C$_6$H$_4$-1-C(CH$_3$)=N(4-OCH$_3$C$_6$H$_4$-$_k$*C,N*)}(*p*-cymene)] (3d)



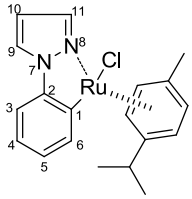
This compound was prepared from imine **2d** (45 mg, 0.2 mmol). The complex **3d** was purified by chromatography column on silica gel with a mixture of petroleum ether/ethyl acetate (70:30) as the eluent, and was isolated as a red solid (72 mg, 73%). R_f (petroleum ether/EtOAc 70:30) = 0.35 ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, 1H, *J* = 7.5 Hz, H_3 or H_6), 7.46 (d, 1H, *J* = 7.5 Hz, H_3 or H_6), 7.30-7.18 (m, 3H, H_{11}, H_4 or H_5), 7.05-6.96 (m, 3H, H_{10}, H_4 or H_5), 5.33 (d, 1H, *J* = 6.0 Hz, cymene), 4.95 (d, 1H, *J* = 6.0 Hz, cymene), 4.63 (d, 2H, *J* = 6.0 Hz, cymene), 3.91 (s, 3H, OMe), 2.57-2.48 (m, 1H, C*H*MeMe'), 2.27 (s, 3H, H_{14}), 2.02 (s, 3H, Me cymene), 1.01 (d, 3H, *J* = 6.9 Hz, CH*Me*Me'), 0.83 (d, 3H, *J* = 6.9 Hz, CHMe*Me'*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ =188.3 (C-Ru), 179.6, 157.8, 147.4, 146.4, 139.3, 130.1, 128.3, 121.9, 116.5, 114.8, 102.9, 102.6, 92.8, 90.4, 80.3, 80.2, 55.6, 30.8, 23.0, 21.3, 18.8, 16.9. IR: *v* (C=N) 1578 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{25}H_{28}NO^{35}ClNa^{102}Ru$ $[M+ Na]^+$ 518.0801, found 518.0811. *m/z* calcd for $C_{25}H_{28}NO\,^{102}Ru$ $[M- Cl]^+$ 460.1214, found 460.1211.

III- Reaction of 2-Phenylpyridine with $[RuCl_2(p\text{-cymene})]_2$ (Complex 5) [1, 2, 3]



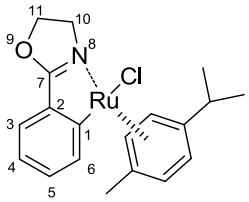
This compound was prepared from 2-phenylpyridine (0.2 mmol, 29 µL). The desired complex **5** was purified by chromatography column on silica gel with a mixture of petroleum ether/ethyl acetate (30/70) as the eluent, and isolated as a dark green solid (81 mg, 94%). R_f (petroleum ether/EtOAc 30:70) = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.16 (d, 1H, *J* = 5.2 Hz, H_{12}), 8.09 (d, 1H, *J* = 7.6 Hz, H_3), 7.65-7.53 (m, 3H, H_9, H_{10}, H_6), 7.11 (dd, 1H, *J* = 7.2 Hz, *J* = 7.2 Hz, H_4), 6.99-6.94 (m, 2H, H_5, H_{11}), 5.52-5.48 (m, 2H, cymene), 5.10 (d, 1H, *J* = 5.6 Hz, cymene), 4.91 (d, 1H, *J* = 5.6 Hz, cymene), 2.37 (sept, 1H, *J* = 6.8 Hz, C*H*MeMe'), 1.98 (s, 3H, Me cymene), 0.91 (d, 3H, *J* = 6.8 Hz, CH*Me*Me'), 0.81 (d, 3H, *J* = 6.8 Hz, CHMe*Me'*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 181.5 (C-Ru), 165.4, 154.7, 143.5, 139.7, 136.7, 129.5, 124.0, 122.6, 121.5, 118.9, 100.8, 100.6, 90.9, 89.7, 84.3, 82.3, 30.9, 22.6, 21.8, 18.9.

IV- Reaction of 1-phenyl-1*H*-pyrazole with $[RuCl_2(p\text{-cymene})]_2$ (Complex 7) [4]



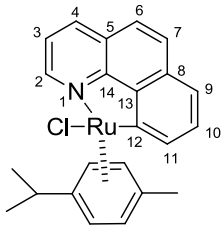
This compound was prepared from 1-phenyl-1*H*-pyrazole (0.2 mmol, 26.4 µL). The desired complex **7** was purified by chromatography column on silica gel with a mixture of petroleum ether/ethyl acetate (30:70) as the eluent, and was isolated as a greenish solid (65.0 mg, 79%) R_f (petroleum ether/EtOAc 30:70) = 0.40.^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, 1H, *J* = 7.2 Hz, H_6), 8.06 (d, 1H, *J* = 2.1 Hz, H_{11}), 7.91 (d, 1H, *J* = 2.7 Hz, H_9), 7.19-7.01 (m, 3H, H_3, H_4, H_5), 6.47 (t, 1H, *J* = 2.7 Hz, H_{10}), 5.57 (d, 2H, *J* = 6.0 Hz, cymene), 5.30 (d, 1H, *J* = 6.0 Hz, cymene), 5.09 (d, 1H, *J* = 6.0 Hz, cymene), 2.47-2.44 (sept, 1H, *J* = 6.9 Hz, C*H*MeMe'), 2.06 (s, 3H, Me cymene), 0.97 (d, 3H, *J* = 6.9 Hz, CH*Me*Me'), 0.93 (d, 3H, *J* = 6.9 Hz, CHMeMe'). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 161.9 (C-Ru), 142.2, 141.9, 140.2, 126.1, 125.0, 123.2, 111.5, 108.4, 100.09, 100.08, 88.7, 88.2, 84.2, 82.2, 30.7, 22.5, 22.0, 18.9.

V- Reaction of 2-phenyl-2-oxazoline with $[RuCl_2(p\text{-cymene})]_2$ (Complex 9)



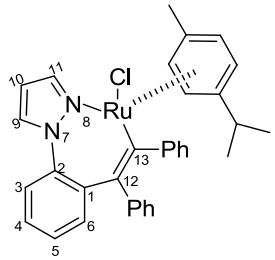
This compound was prepared from 2-phenyl-2-oxazoline (0.2 mmol, 26.3 µL). The desired complex **9** was purified by chromatography column on silica gel with a mixture of petroleum ether/ethyl acetate (30:70) as the eluent, and was isolated as a green solid (32.7 mg, 40%). R_f (petroleum ether/EtOAc 30:70) = 0.25 ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, 1H, *J* = 7.5 Hz, H_3 or H_6), 7.35 (d, 1H, *J* = 7.5 Hz, H_3 or H_6), 7.22 (t, 1H, *J* = 7.5 Hz, H_4 or H_5), 6.98 (t, 1H, *J* = 7.5 Hz, H_4 or H_5), 5.56 (d, 1H, *J* = 5.7 Hz, cymene), 5.46 (d, 1H, *J* = 5.7 Hz, cymene), 5.19 (d, 1H, *J* = 5.7 Hz, cymene), 4.99 (d, 1H, *J* = 5.7 Hz, cymene), 4.78-4.67 (m, 2H, H_{11}), 4.26-4.08 (m, 2H, H_{10}), 2.55 (sept, 1H, *J* = 6.9 Hz, C*H*MeMe'), 2.06 (s, 3H, Me cymene), 1.10 (d, 3H, *J* = 6.9 Hz, CH*Me*Me'), 1.00 (d, 3H, *J* = 6.9 Hz, CHMe*Me'*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 182.7 (C-Ru), 174.2, 139.3, 130.9, 130.7, 126.4, 122.3, 101.3, 99.3, 88.1, 87.5, 81.8, 81.0, 70.8, 54.4, 31.2, 22.8, 22.2, 19.1. IR: *v* (C=N) 1632 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{19}H_{22}NO^{35}ClNa^{102}Ru$ [M+ Na]$^+$ 440.0331, found 440.0336; *m/z* calcd for $C_{19}H_{22}NO$ ^{102}Ru [M- Cl]$^+$ 382.0745, found 482.0755.

VI- Reaction of benzo[*h*]quinoline with $[RuCl_2(p\text{-cymene})]_2$ (Complex 11)



This compound was prepared from benzo[*h*]quinoline (0.2 mmol, 35.8 mg). The desired complex **11** was purified by chromatography column on silica gel with a mixture of petroleum ether/ethyl acetate (50:50) as the eluent, and was isolated as a dark green solid (41.9 mg, 47%). R_f (petroleum ether/EtOAc 1:1) = 0.20. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.48 (d, 1H, *J* = 5.1 Hz, H_2), 8.41 (d, 1H, *J* = 6.9 Hz), 8.18 (d, 1H, *J* = 7.8 Hz), 7.78 (d, 1H, *J* = 8.7 Hz), 7.63-7.42 (m, 4H), 5.74 (d, 1H, *J* = 5.7 Hz, cymene), 5.66 (d, 1H, *J* = 6.0 Hz, cymene), 5.30 (d, 1H, *J* = 6.0 Hz, cymene), 5.13 (d, 1H, *J* = 6.0 Hz, cymene), 2.50 (m, 1H, C*H*MeMe'), 2.04 (s, 3H, Me cymene), 0.97 (d, 3H, *J* = 6.9 Hz, CH*Me*Me'), 0.84 (d, 3H, *J* = 6.9 Hz, CHMe*Me'*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ =178.4 (C-Ru), 155.3, 152.5, 140.5, 136.6, 135.4, 133.9, 129.7, 129.3, 126.9, 122.8, 121.1, 120.9, 101.5, 99.6, 89.7, 89.3, 83.6, 82.5, 30.9, 22.7, 21.8, 18.9. HRMS (ESI): *m/z* calcd for $C_{23}H_{22}N^{35}ClNa^{102}Ru$ [M+ Na]$^+$ 472.0382, found 472.0390. *m/z* calcd for $C_{23}H_{22}N^{102}Ru$ [M- Cl]$^+$ 414.0796, found 414.0797.

VII- Preparation of complex 12[5]



$[RuCl_2(p\text{-cymene})]_2$ (0.1 mmol, 61.2 mg), 1-phenyl-1*H*-pyrazole (0.2 mmol, 26.4 µL), diphenylacetylene (0.2 mmol, 35.6 mg), KOAc (0.4 mmol, 40 mg) and methanol (5 mL) were introduced in a dried Schlenck tube under Argon, equipped with magnetic stirring bar and was stirred at ambient temperature for 20 h. The solvent was then evaporated under vacuum and the desired product was purified by chromatography column on silica gel with a mixture of petrol ether/ethyl acetate (1:1) as the eluent. **12** was isolated as a dark green solid (79.3 mg, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.59 (d, 1H, *J* = 1.5 Hz, H_{11}), 7.88 (d, 1H, *J* = 1.5 Hz, H_9), 7.39-7.14 (m, 7H), 6.97-6.87 (m, 4H), 6.81-6.74 (m, 3H), 6.52 (t, 1H, *J* = 2.4 Hz, H_{10}), 5.57 (d, 1H, *J* = 5.1 Hz, cymene), 4.66 (d, 1H, *J* = 5.1 Hz, cymene), 4.52 (d, 1H, *J* = 5.1 Hz, cymene), 3.51 (d, 1H, *J* = 5.1 Hz, cymene), 2.83 (sept, *J* = 6.9 Hz,1H, C*H*MeMe'), 2.47 (s, 3H, Me cymene), 1.25 (d, 3H, *J* = 6.9 Hz, CH*Me*Me'), 1.10 (d, 3H, *J* = 6.9 Hz, CHMe*Me'*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ =183.3 (C-Ru), 152.5, 146.7, 146.0, 144.1, 137.7, 137.5, 133.7, 133.4, 131.6, 128.5, 128.2, 127.2, 126.3, 125.9, 125.5, 124.7, 123.1, 110.3, 107.8, 103.8, 96.4, 81.1, 78.9, 75.3, 31.4, 23.6, 23.2, 19.6.

References

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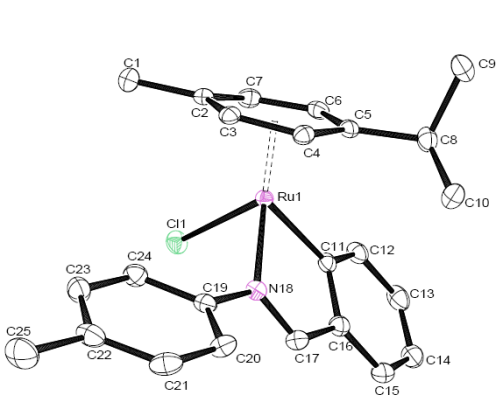
[3] E. Ferrer-Flegeau, C. Bruneau, P. H. Dixneuf and A. Jutand, *J. Am. Chem. Soc.*, 2011, **133,** 10161.

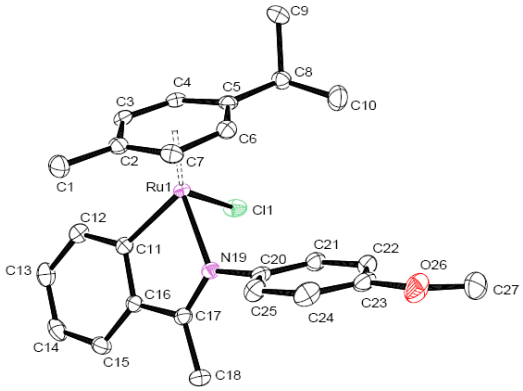
[4] Y. Boutadla, D. L. Davies, R. C. Jones and K. Singh, *Chem. Eur. J.* 2011, **17**, 3438.

[5] Y. Boutadla, D. L. Davies, O. Al-Duaij, J. Fawcett, R. C. Jones and K. Singh, *Dalton Trans.*, 2010, **39**, 10447

Table of crystallographic data for 3a** and **3d.



3a

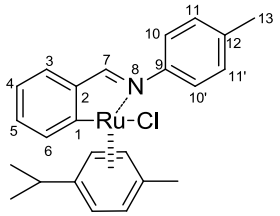


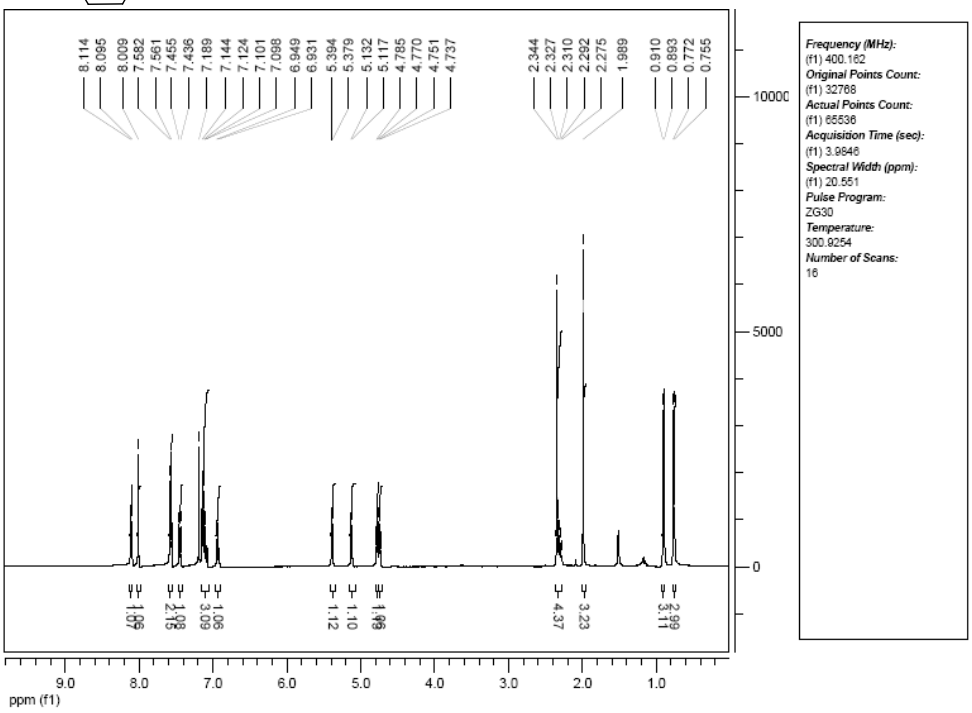
3d

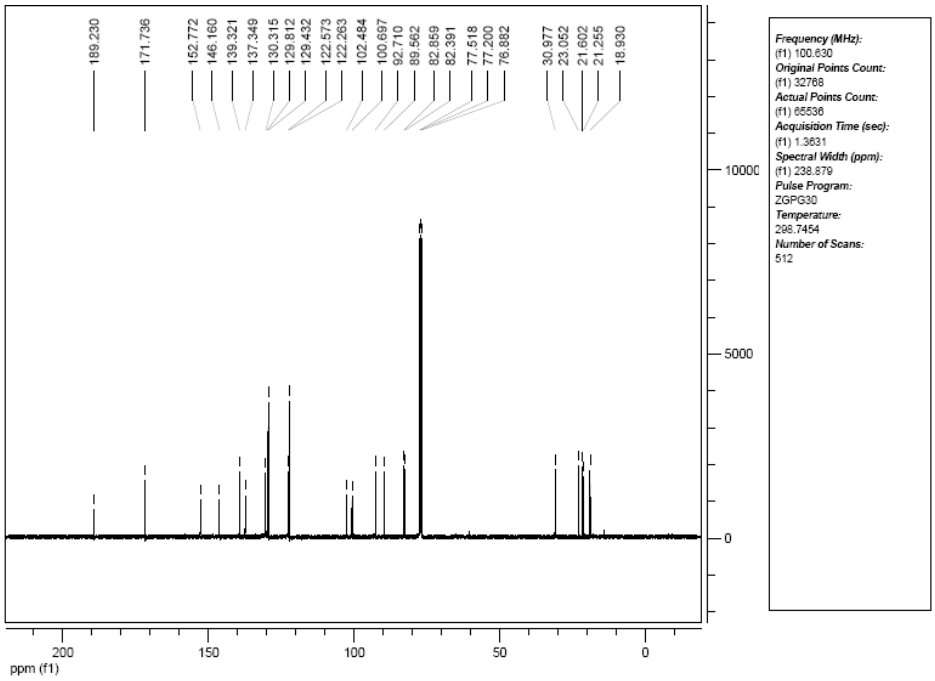
Complex	**3a**	**3d**
Empirical formula	C24H26ClNRu	C25H28ClNORu
Formula weight	464.98	495.00
T (K)	150(2)	150 (2)
λ(Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Color, habit	Orange, prism	Orange, prism
Crystal size (mm)	0.58×0.29 × 0.17	0.22 × 0.18 × 0.1
Space group	P 21/n	P -1
a (Å)	10.9423(3)	9.2982(2)
b (Å)	8.1961(2)	9.9096(2)
c (Å)	23.3753(7)	13.0735(2)
α (^{o})	90	100.5580(10)
β (^{o})	102.0690(10)	109.7180(10)
γ (^{o})	90	97.9670(10)
V (Å^3)	2050.06(10)	1088.32(4)
Z	4	2
Absorption coefficient (mm^{-1})	0.903	0.859
θ range (^{o})	3.13-27.47	3.12-27.48
Index range	-14≤h≤11, -10≤k≤9, -27≤l≤30	-12≤h≤11, -12≤k≤12, -16≤l≤15
Reflections collected	15025	13893
Independent reflections (R_{int})	4670 (0.0304)	4937 (0.0366)
Data/restraints/parameters	4670 / 0 / 248	4937/0/267
Goodness-of-fit on F^2	1.032	1.040
Final R indices [I>2σ(I)]	R_1=0.0230, wR_2=0.0538	R_1=0.0232, wR_2=0.0560
R indices (all data)	R_1=0.0262, wR_2=0.0553	R_1=0.0248, wR_2=0.0569
Largest diff. peak and hole (e. Å^3)	0.451 and -0.399	0.494 and -0.364

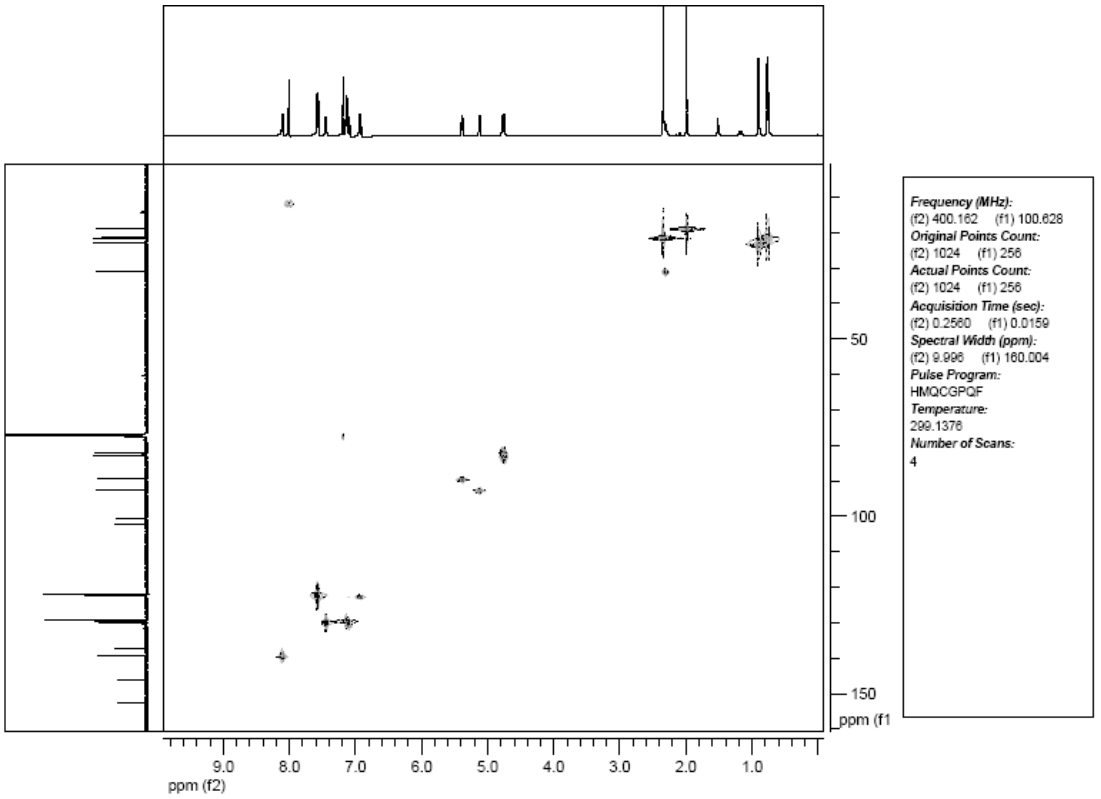
^{1}H NMR and ^{13}C NMR spectrum

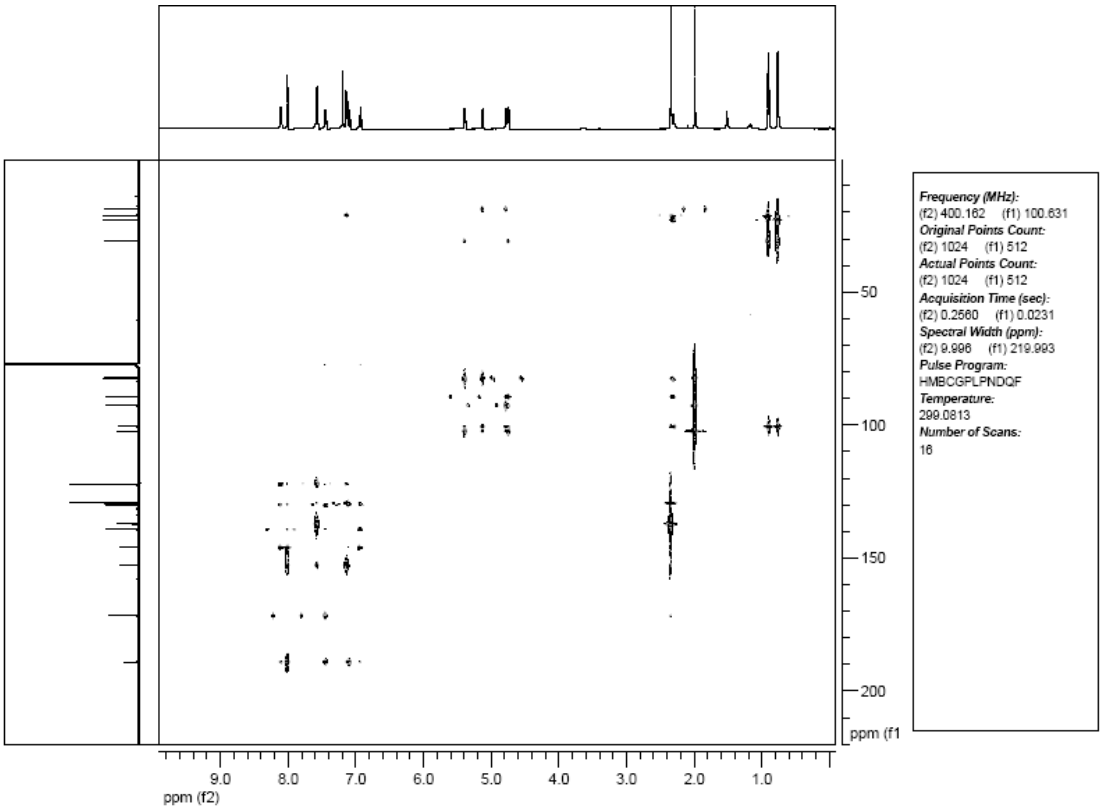
Complex **3a**



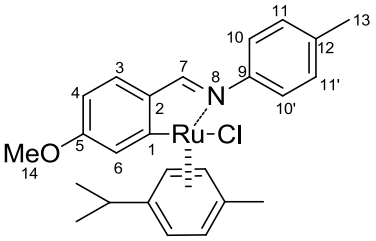


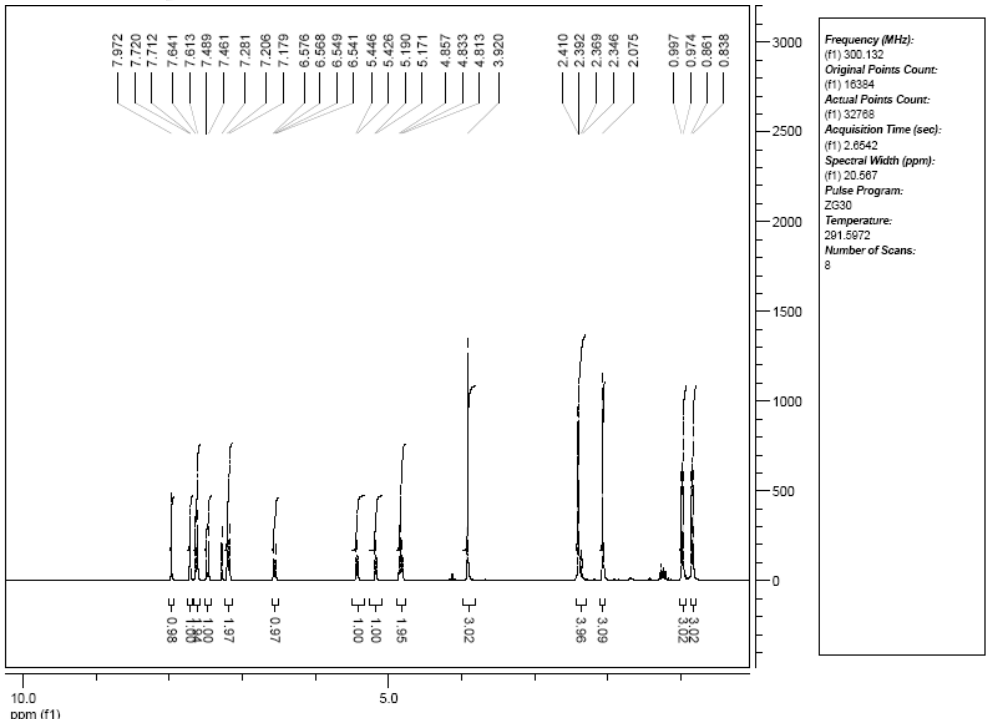


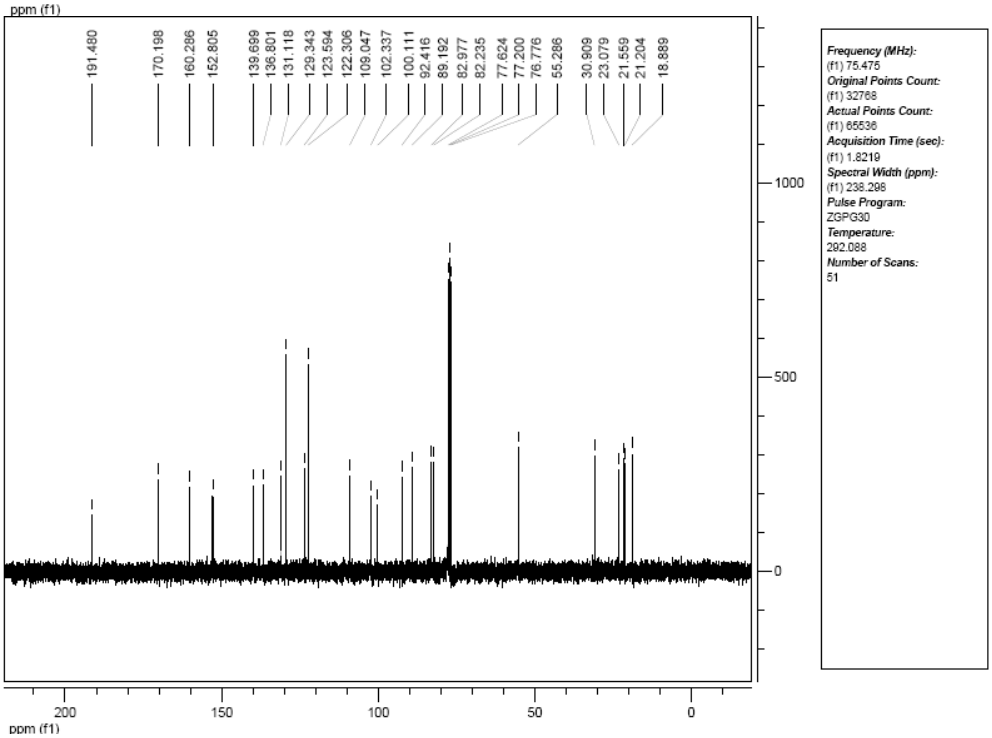

Frequency (MHz):
(f2) 400.162 (f1) 100.628
Original Points Count:
(f2) 1024 (f1) 256
Actual Points Count:
(f2) 1024 (f1) 256
Acquisition Time (sec):
(f2) 0.2560 (f1) 0.0159
Spectral Width (ppm):
(f2) 9.996 (f1) 160.004
Pulse Program:
HMQCGPQF
Temperature:
299.1376
Number of Scans:
4
50
100
150
ppm (f1
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
ppm (f2)


Frequency (MHz):
(f2) 400.162 (f1) 100.631
Original Points Count:
(f2) 1024 (f1) 512
Actual Points Count:
(f2) 1024 (f1) 512
Acquisition Time (sec):
(f2) 0.2560 (f1) 0.0231
Spectral Width (ppm):
(f2) 9.996 (f1) 219.993
Pulse Program:
HMBCGPLPNDQF
Temperature:
299.0813
Number of Scans:
16
50
100
150
200
ppm (f1
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
ppm (f2)

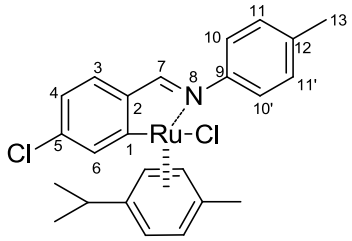
Complex **3b**

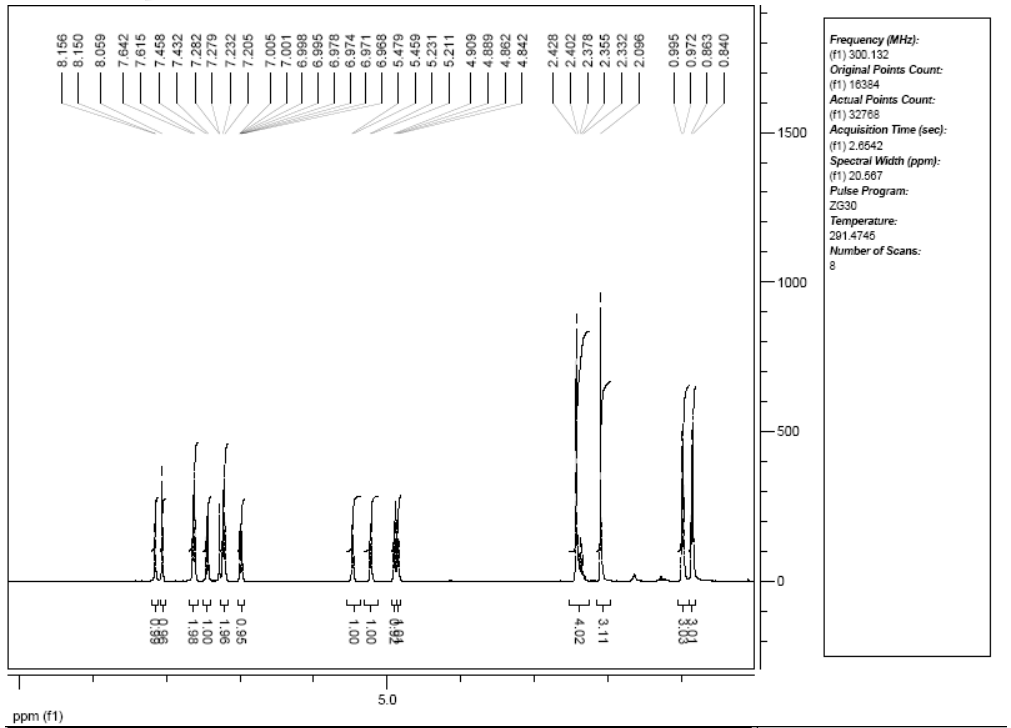

11
13
10
12
3
7
8
9
11'
4
N
2
10'
Ru-Cl
MeO
5
1
6
14

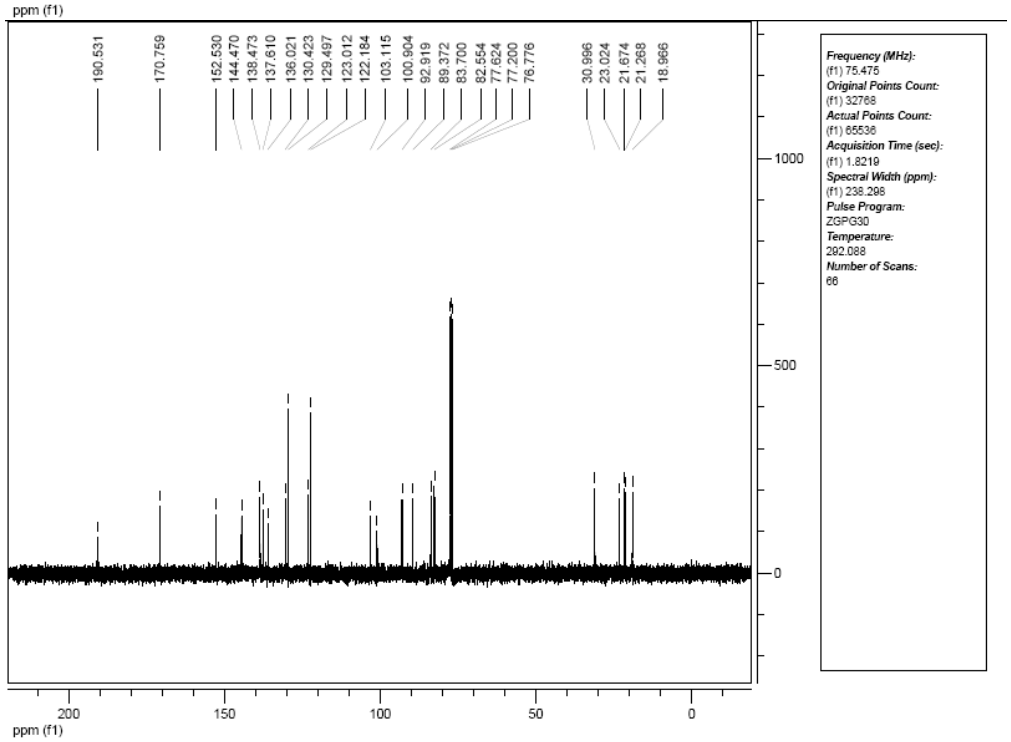

7.972
7.720
7.712
7.641
7.613
7.489
7.461
7.281
7.206
7.179
6.576
6.568
6.549
6.541
5.446
5.426
5.190
5.171
4.857
4.833
4.813
3.920
2.410
2.392
2.369
2.346
2.075
0.997
0.974
0.861
0.838
0.98
1.80
1.00
1.97
0.97
1.00
1.00
1.95
3.02
3.96
3.09
3.02
3.20
3000
2500
2000
1500
1000
500
0
10.0
5.0
ppm (f1)
Frequency (MHz):
(f1) 300.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 2.6542
Spectral Width (ppm):
(f1) 20.567
Pulse Program:
ZG30
Temperature:
291.5972
Number of Scans:
8


191.480
170.198
160.286
152.805
139.699
136.801
131.118
129.343
123.594
122.306
109.047
102.337
100.111
92.416
89.192
82.977
82.235
77.624
77.200
76.776
55.286
30.909
23.079
21.559
21.204
18.889
1000
500
0
200
150
100
50
0
ppm (f1)
Frequency (MHz):
(f1) 75.475
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 65536
Acquisition Time (sec):
(f1) 1.8219
Spectral Width (ppm):
(f1) 238.298
Pulse Program:
ZGPG30
Temperature:
292.088
Number of Scans:
51

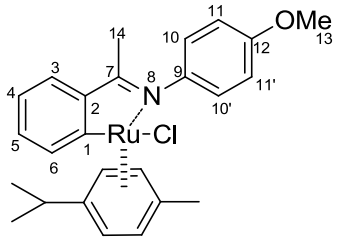
Complex **3c**

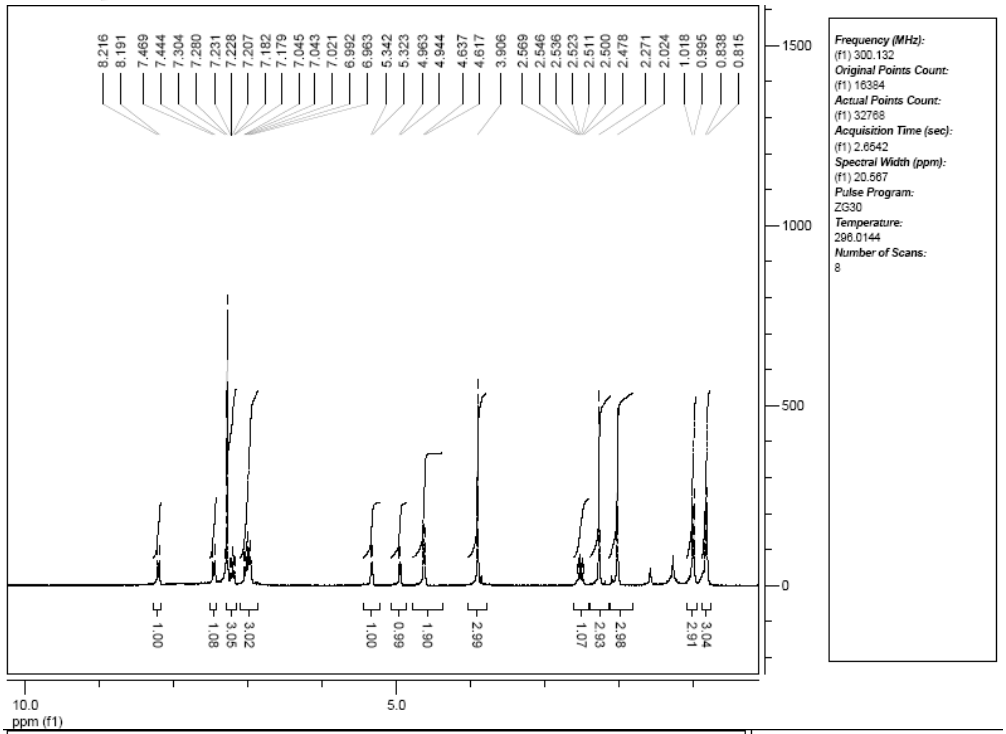

11
13
10
12
3
7
8
9
11'
4
N
2
10'
Ru-Cl
Cl
5
1
6

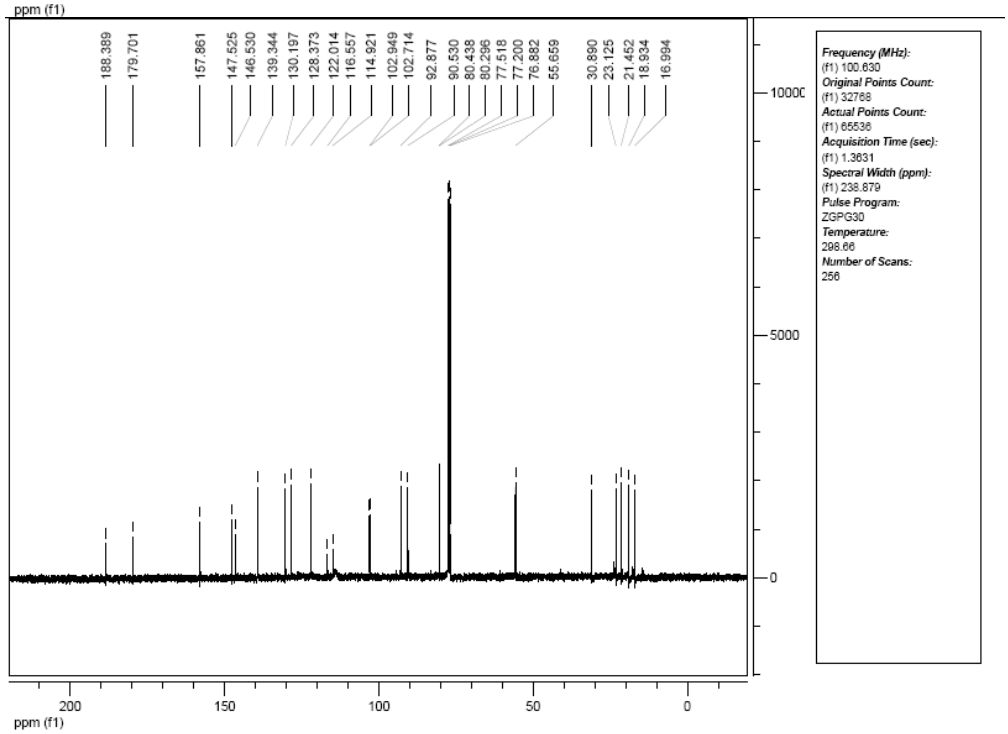

8.156
8.150
8.059
7.642
7.615
7.458
7.432
7.282
7.279
7.232
7.205
7.005
7.001
6.998
6.995
6.978
6.974
6.971
6.968
5.479
5.459
5.231
5.211
4.909
4.889
4.862
4.842
2.428
2.402
2.378
2.355
2.332
2.096
0.995
0.972
0.863
0.840
1500
1000
500
0
0.98
1.98
1.00
1.98
0.96
1.00
1.00
4.02
3.11
3.03
3.01
5.0
ppm (f1)
Frequency (MHz):
(f1) 300.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 2.6542
Spectral Width (ppm):
(f1) 20.667
Pulse Program:
ZG30
Temperature:
291.4745
Number of Scans:
8


190.531
170.759
152.530
144.470
138.473
137.610
136.021
130.423
129.497
123.012
122.184
103.115
100.904
92.919
89.372
83.700
82.554
77.624
77.200
76.776
30.996
23.024
21.674
21.268
18.966
1000
500
0
200
150
100
50
0
ppm (f1)
Frequency (MHz):
(f1) 75.475
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 65536
Acquisition Time (sec):
(f1) 1.8219
Spectral Width (ppm):
(f1) 238.298
Pulse Program:
ZGPG30
Temperature:
292.088
Number of Scans:
66

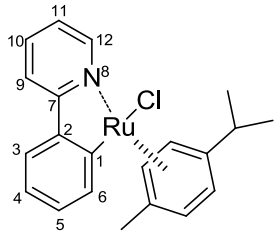
Complex **3d**

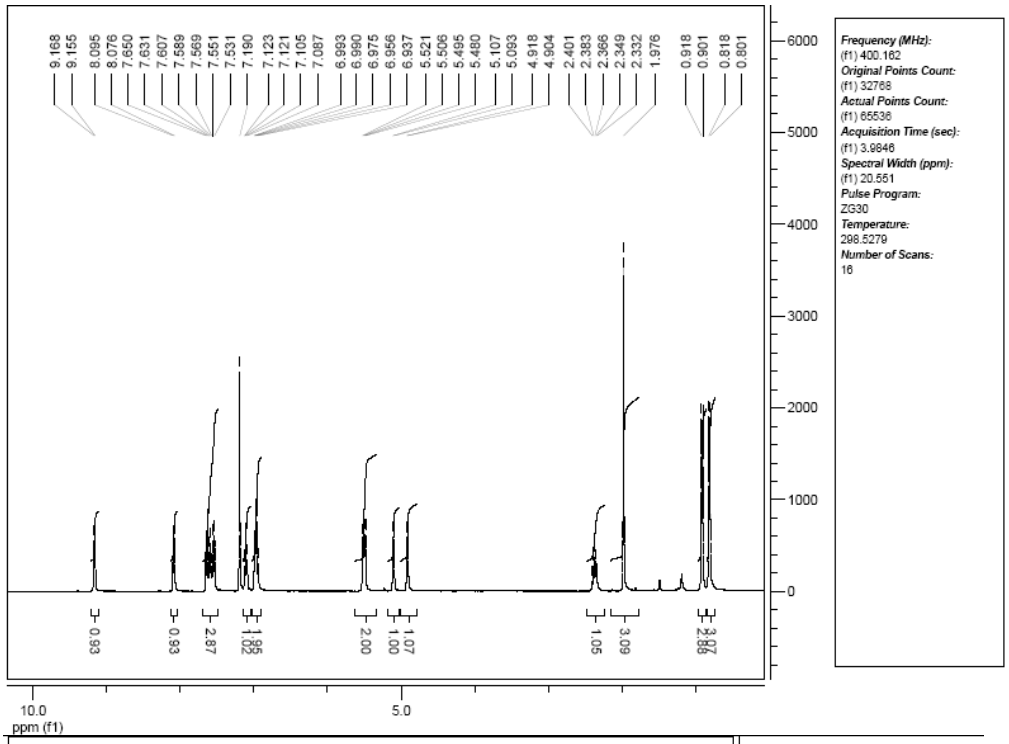

OMe
Ru-Cl
N

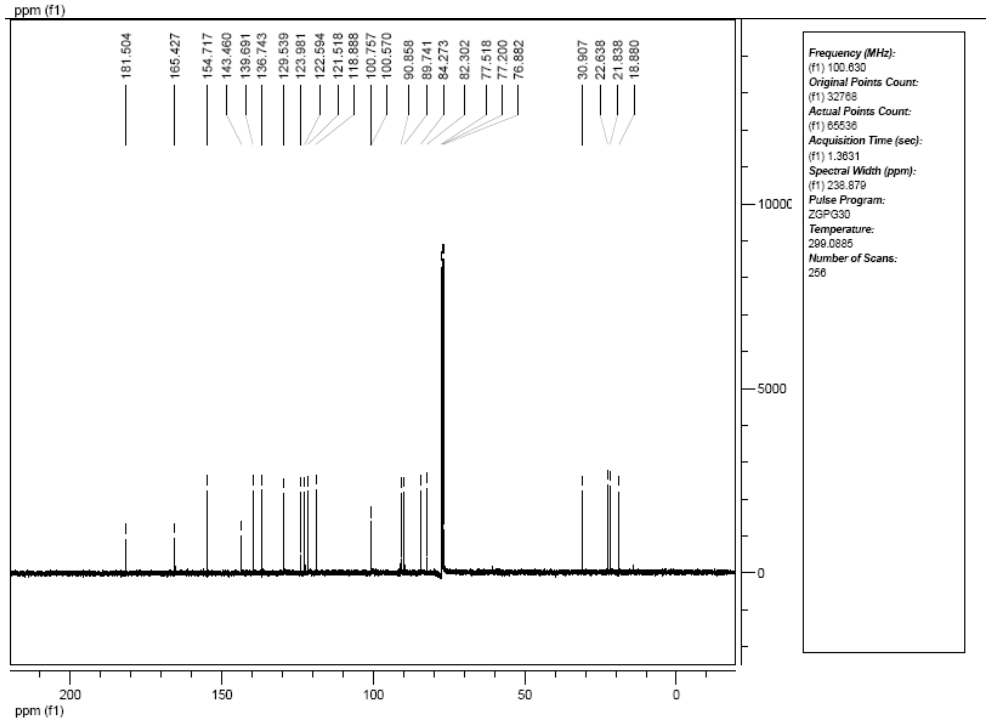

8.216 8.191 7.469 7.444 7.304 7.280 7.231 7.228 7.207 7.182 7.179 7.045 7.043 7.021 6.992 6.963 5.342 5.323 4.963 4.944 4.637 4.617 3.906 2.569 2.546 2.536 2.523 2.511 2.500 2.478 2.271 2.024 1.018 0.995 0.838 0.815
1.00 1.08 3.06 3.02 1.00 0.99 1.90 2.99 1.07 2.33 2.98 3.91 3.04
1500
1000
500
0
10.0
5.0
ppm (f1)
Frequency (MHz):
(f1) 300.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 2.6542
Spectral Width (ppm):
(f1) 20.567
Pulse Program:
ZG30
Temperature:
296.0144
Number of Scans:
8


188.389 179.701 157.861 147.525 146.530 139.344 130.197 128.373 122.014 116.557 114.921 102.949 102.714 92.877 90.530 80.438 80.296 77.518 77.200 76.882 55.659 30.890 23.125 21.452 18.934 16.994
10000
5000
0
200
150
100
50
0
ppm (f1)
Frequency (MHz):
(f1) 100.630
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 65536
Acquisition Time (sec):
(f1) 1.3631
Spectral Width (ppm):
(f1) 238.879
Pulse Program:
ZGPG30
Temperature:
298.66
Number of Scans:
256

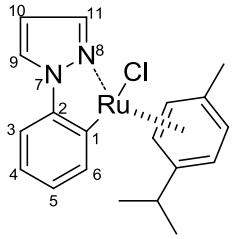
Complex **5**

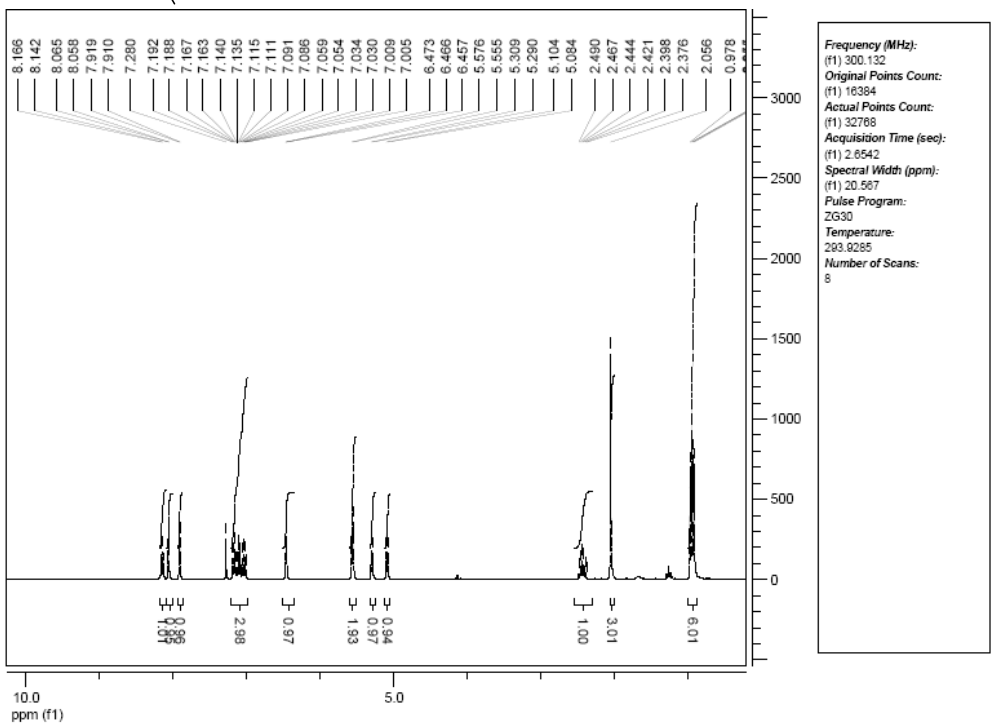

11
10
12
N
8
9
7
Cl
Ru
2
3
1
4
6
5

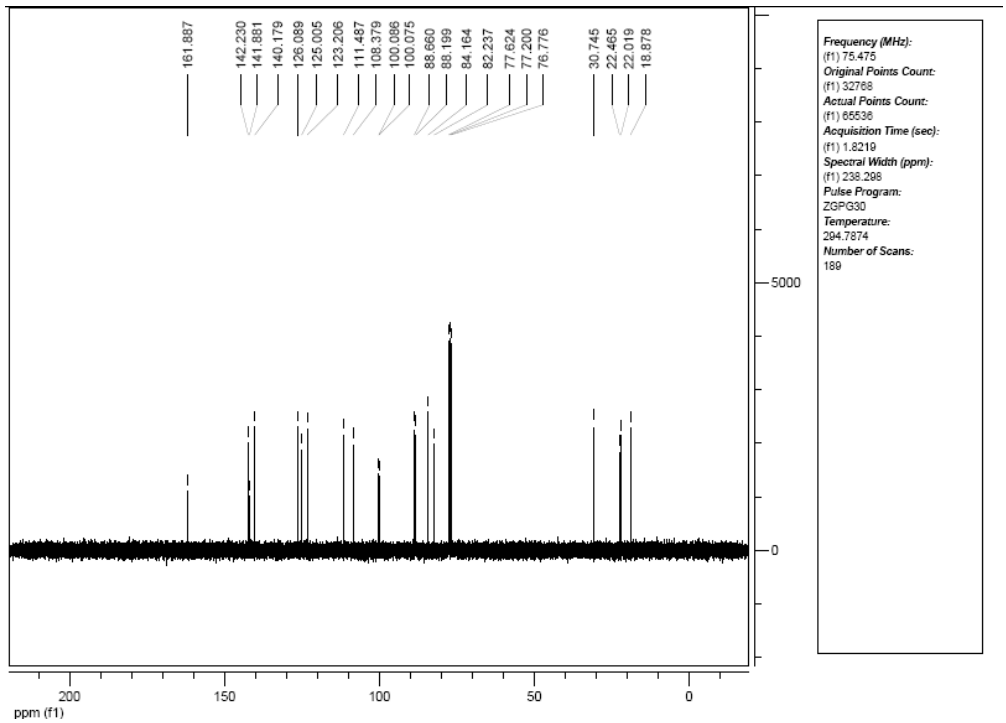

9.168
9.155
8.095
8.076
7.650
7.631
7.607
7.589
7.569
7.551
7.531
7.190
7.123
7.121
7.105
7.087
6.993
6.990
6.975
6.956
6.937
5.521
5.506
5.495
5.480
5.107
5.093
4.918
4.904
2.401
2.383
2.366
2.349
2.332
1.976
0.918
0.901
0.818
0.801
0.93
0.93
2.87
1.02
1.05
2.00
1.00
1.07
1.05
3.09
3.07
2.98
6000
5000
4000
3000
2000
1000
0
10.0
5.0
ppm (f1)
Frequency (MHz):
(f1) 400.162
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 65536
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.551
Pulse Program:
ZG30
Temperature:
298.5279
Number of Scans:
16


181.504
165.427
154.717
143.460
139.691
136.743
129.539
123.981
122.594
121.518
118.888
100.757
100.570
90.858
89.741
84.273
82.302
77.518
77.200
76.882
30.907
22.638
21.838
18.880
10000
5000
0
200
150
100
50
0
ppm (f1)
Frequency (MHz):
(f1) 100.630
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 65536
Acquisition Time (sec):
(f1) 1.3631
Spectral Width (ppm):
(f1) 238.879
Pulse Program:
ZGPG30
Temperature:
299.0885
Number of Scans:
256

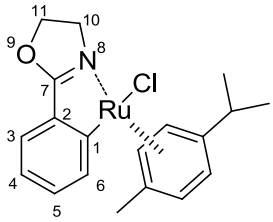
Complex **7**

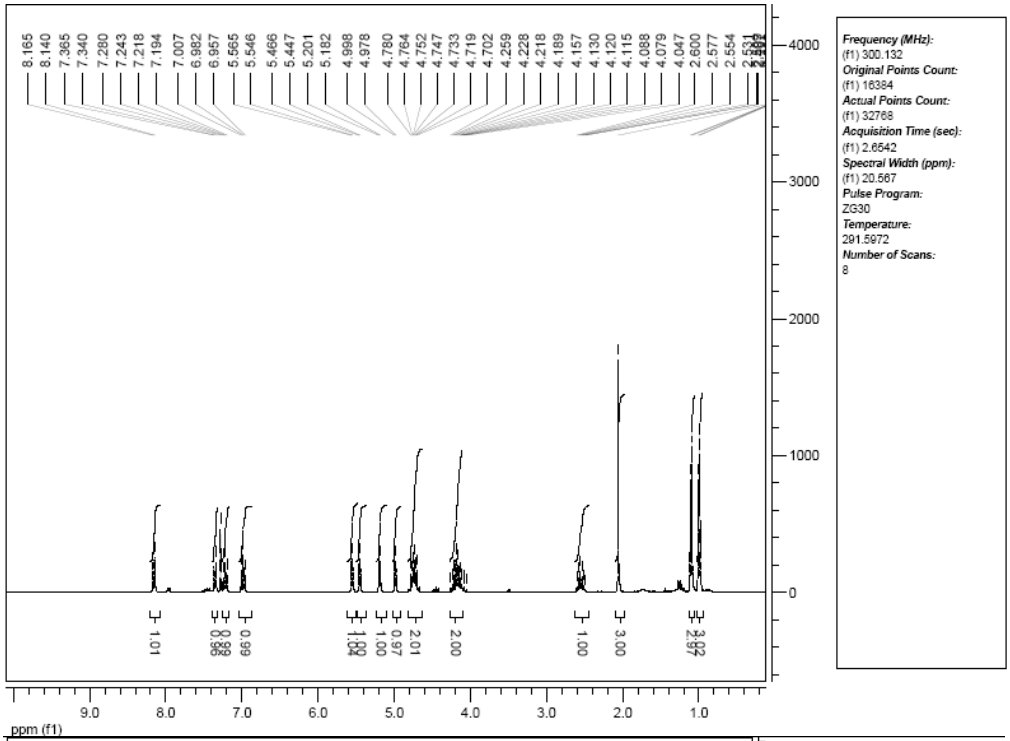

10
11
9
N
8
N
7
Cl
Ru
2
3
1
4
6
5

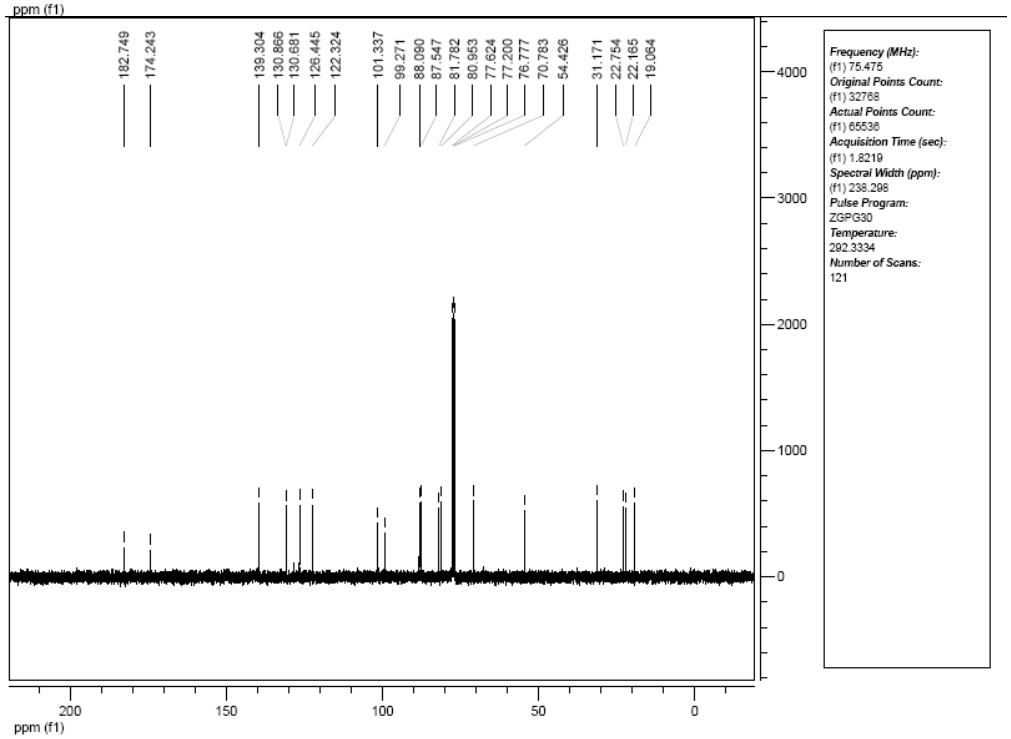

8.166
8.142
8.065
8.058
7.919
7.910
7.280
7.192
7.188
7.167
7.163
7.140
7.135
7.115
7.111
7.091
7.086
7.059
7.054
7.034
7.030
7.009
7.005
6.473
6.466
6.457
5.576
5.555
5.309
5.290
5.104
5.084
2.490
2.467
2.444
2.421
2.398
2.376
2.056
0.978
3000
2500
2000
1500
1000
500
0
2.98
0.97
1.93
0.97
0.94
1.00
3.01
6.01
10.0
5.0
ppm (f1)
Frequency (MHz):
(f1) 300.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 2.6542
Spectral Width (ppm):
(f1) 20.567
Pulse Program:
ZG30
Temperature:
293.9285
Number of Scans:
8


161.887
142.230
141.881
140.179
126.089
125.005
123.206
111.487
108.379
100.086
100.075
88.660
88.199
84.164
82.237
77.624
77.200
76.776
30.745
22.465
22.019
18.878
5000
0
200
150
100
50
0
ppm (f1)
Frequency (MHz):
(f1) 75.475
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 65536
Acquisition Time (sec):
(f1) 1.8219
Spectral Width (ppm):
(f1) 238.298
Pulse Program:
ZGPG30
Temperature:
294.7874
Number of Scans:
189

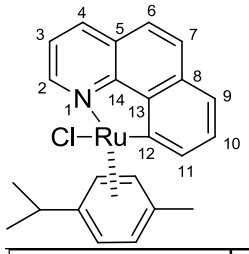
Complex **9**

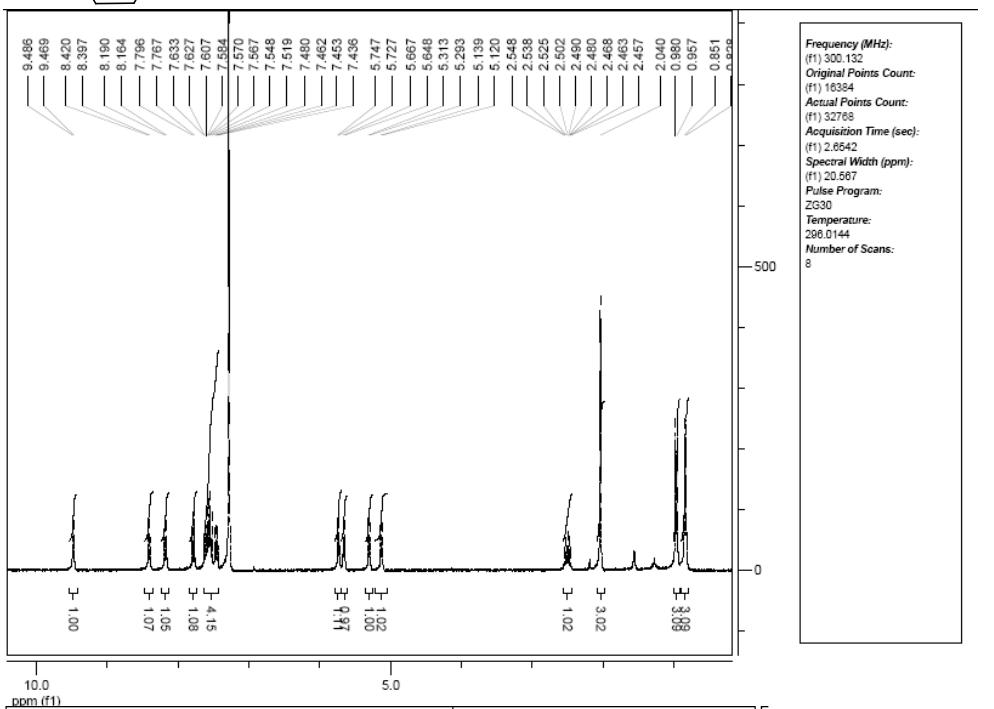

11
10
9
O
N
8
7
Cl
Ru
2
3
1
4
6
5

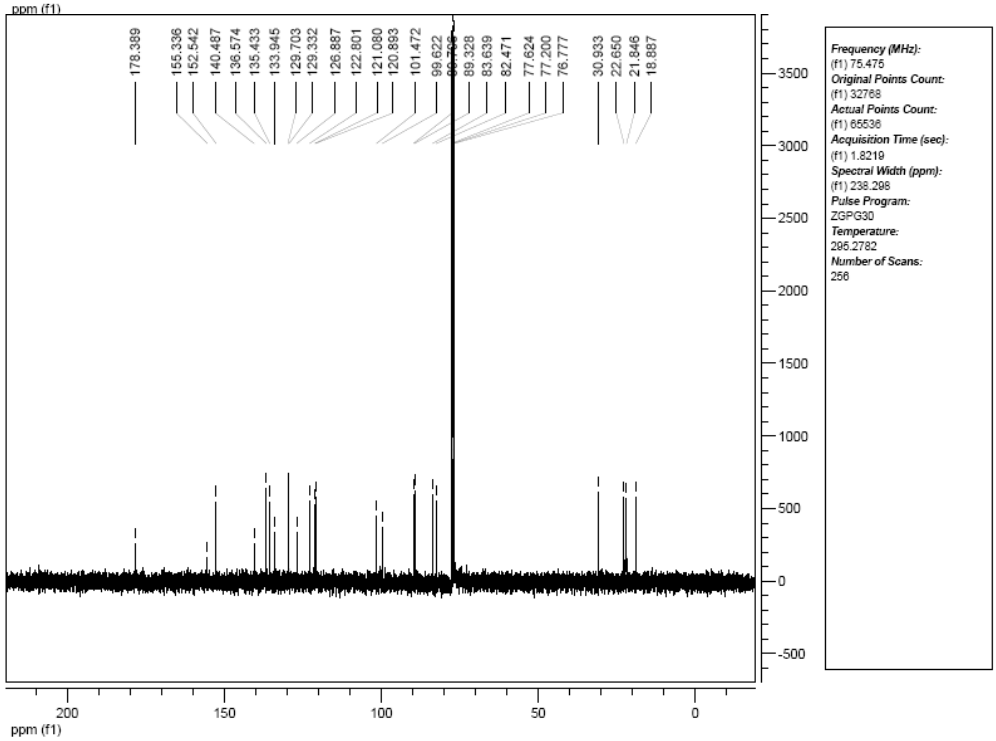

8.165
8.140
7.365
7.340
7.280
7.243
7.218
7.194
7.007
6.982
6.957
5.565
5.546
5.466
5.447
5.201
5.182
4.998
4.978
4.780
4.764
4.752
4.747
4.733
4.719
4.702
4.259
4.228
4.218
4.189
4.157
4.130
4.120
4.115
4.088
4.079
4.047
2.600
2.577
2.554
1.01
0.99
2.00
1.00
3.00
2.97
4000
3000
2000
1000
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
Frequency (MHz):
(f1) 300.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 2.6542
Spectral Width (ppm):
(f1) 20.567
Pulse Program:
ZG30
Temperature:
291.5972
Number of Scans:
8


182.749
174.243
139.304
130.866
130.681
126.445
122.324
101.337
99.271
88.090
87.547
81.782
80.953
77.624
77.200
76.777
70.783
54.426
31.171
22.754
22.165
19.064
4000
3000
2000
1000
0
200
150
100
50
0
ppm (f1)
Frequency (MHz):
(f1) 75.475
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 65536
Acquisition Time (sec):
(f1) 1.8219
Spectral Width (ppm):
(f1) 238.298
Pulse Program:
ZGPG30
Temperature:
292.3334
Number of Scans:
121

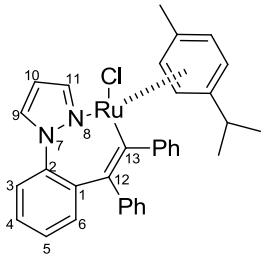
Complex **11**

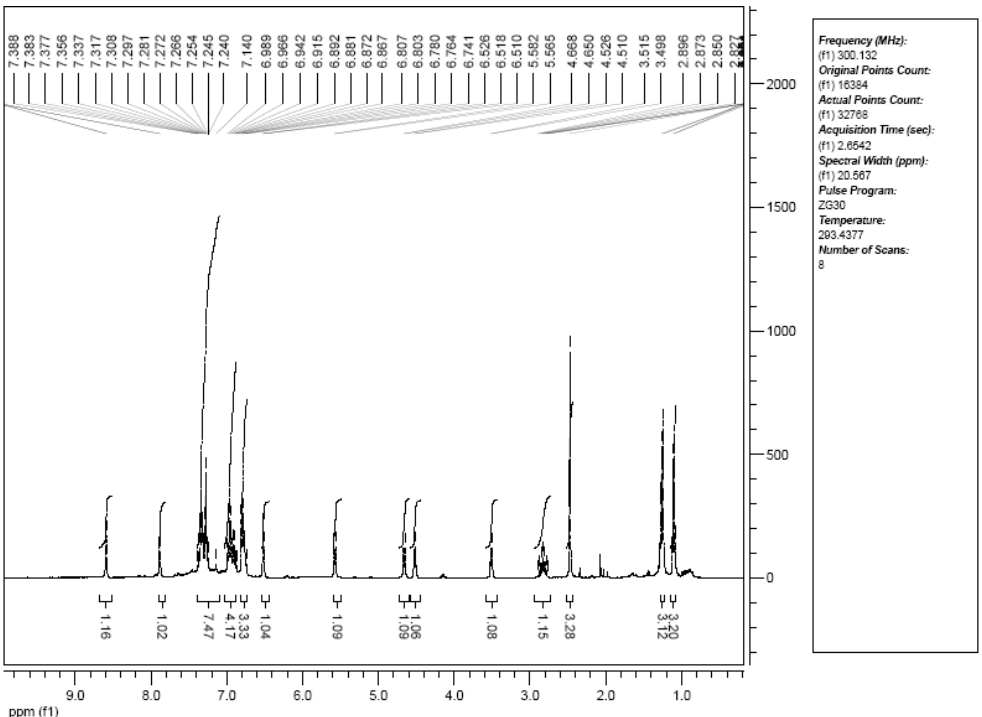

1
2
3
4
5
6
7
8
9
10
11
12
13
14
N
Cl–Ru

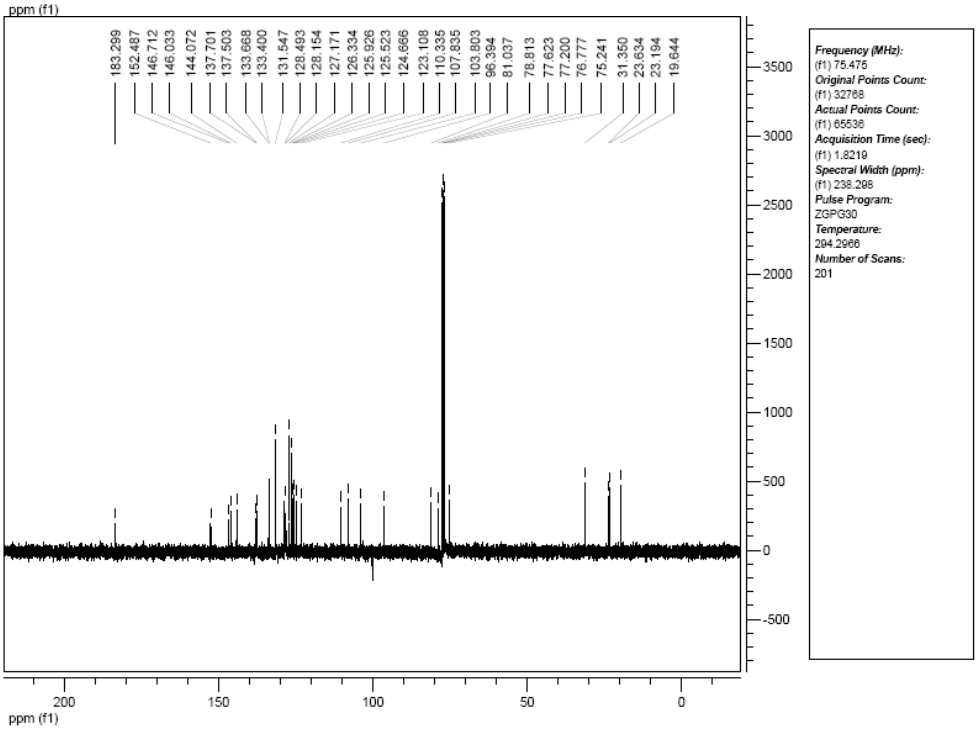

9.486
9.469
8.420
8.397
8.190
8.164
7.796
7.767
7.633
7.627
7.607
7.584
7.570
7.567
7.548
7.519
7.480
7.462
7.453
7.436
5.747
5.727
5.667
5.648
5.313
5.293
5.139
5.120
2.548
2.538
2.525
2.502
2.490
2.480
2.468
2.463
2.457
2.040
0.980
0.957
0.851
1.00
1.07
1.05
1.08
4.15
9.43
1.00
1.02
1.02
3.02
8.88
500
0
10.0
5.0
ppm (f1)
Frequency (MHz):
(f1) 300.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 2.6542
Spectral Width (ppm):
(f1) 20.567
Pulse Program:
ZG30
Temperature:
296.0144
Number of Scans:
8


178.389
155.336
152.542
140.487
136.574
135.433
133.945
129.703
129.332
126.887
122.801
121.080
120.893
101.472
99.622
89.328
83.639
82.471
77.624
77.200
76.777
30.933
22.650
21.846
18.887
3500
3000
2500
2000
1500
1000
500
0
-500
200
150
100
50
0
ppm (f1)
Frequency (MHz):
(f1) 75.475
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 65536
Acquisition Time (sec):
(f1) 1.8219
Spectral Width (ppm):
(f1) 238.298
Pulse Program:
ZGPG30
Temperature:
296.2782
Number of Scans:
256

Complex **12**


Cl
Ru
N
N
Ph
Ph
1
2
3
4
5
6
7
8
9
10
11
12
13


7.388
7.383
7.377
7.356
7.337
7.317
7.308
7.297
7.281
7.272
7.266
7.254
7.245
7.240
7.140
6.989
6.966
6.942
6.915
6.892
6.881
6.872
6.867
6.807
6.803
6.780
6.764
6.741
6.526
6.518
6.510
6.582
5.565
4.668
4.650
4.526
4.510
3.515
3.498
2.896
2.873
2.850
2.827
1.16
1.02
7.47
4.17
3.33
1.04
1.00
1.00
1.00
1.08
1.15
3.28
3.12
3.20
Frequency (MHz):
(f1) 300.132
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 2.6542
Spectral Width (ppm):
(f1) 20.567
Pulse Program:
ZG30
Temperature:
293.4377
Number of Scans:
8
ppm (f1)


183.299
152.487
146.712
146.033
144.072
137.701
137.503
133.668
133.400
131.547
128.493
128.154
127.171
126.334
125.926
125.523
124.666
123.108
110.335
107.835
103.803
96.394
81.037
78.813
77.623
77.200
76.777
75.241
31.350
23.634
23.194
19.644
Frequency (MHz):
(f1) 75.475
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 65536
Acquisition Time (sec):
(f1) 1.8219
Spectral Width (ppm):
(f1) 238.298
Pulse Program:
ZGPG30
Temperature:
294.2966
Number of Scans:
201
ppm (f1)