Electronic Supplementary Information for

Ruthenium-catalyzed Olefin Metathesis Accelerated by Steric Effect of Backbone Substituent in Cyclic (Alkyl)(Amino)Carbenes

Jun Zhang,*[a] Shangfei Song,[a] Xiao Wang,[a] Jiajun Jiao,[a] and Min Shi*[a,b]

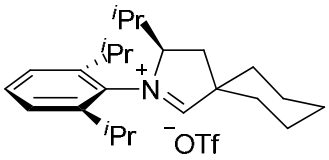
Experimental Section

General Information: Unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. Methyloleate (96% and 99%) was purchased from J&K Scientific LTD. and passed through activated alumina before use. 2,6-Diethyl-*N*-(2-methylpropylidene)aniline, 2,6-diisopropyl-*N*-(cyclohexylmethylene)aniline, 2,6-diisopropyl-*N*-(2-methylpropylidene)aniline were prepared as previously reported.[1,2] NMR spectra were recorded by using a Varian Mercury vx 300 MHz or Bruker 400 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on the HP-5989 instrument by EI/ESI methods. X-ray diffraction analysis was performed by using a Bruker Smart-1000 X-ray diffractometer. The GC analyses of reaction mixture were carried out on a flame ionization detector (FID). Column: HP-5 (30 m × 0.32 mm (i.d.) × 0.25μm). GC and column conditions: injector temperature 280°C; detector temperature 300°C; oven temperature, starting temperature 100°C, hold time 1 min, ramp rate 10 °C/min to 280 °C, hold time 4 min.

1. V. Lavallo, Y. Canac, C. Prasang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed*. **2005**, *44*, 5705.

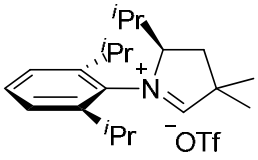
2. D. R. Anderson, V. Lavallo, D. J. O'Leary, G. Bertrand, R. H. Grubbs, *Angew. Chem., Int. Ed.* **2007**, *46*, 7262.

Preparation of pyrrolidinium salts 3a~3c by literature method[1,2]



3a

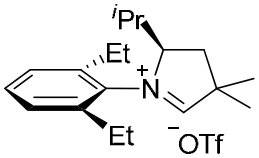
LDA (2.05 ml, 4.15 mmol, 2.0 M in THF) was added dropwise to a solution of 2,6-diisopropyl-N-(cyclohexylmethylene)aniline (0.94 g, 3.46 mmol) in Et_2O (15 mL) at 0 °C. After 20 mins, the mixture was warmed to room temperature and stirred for 4 h. Evacuated the solvent in vacuo and the residue was dissolved in Et_2O (20 mL), and 2-isopropyloxirane (0.36 g, 4.15 mmol) was added dropwise. After stirring overnight at room temperature, Tf_2O (1.16 g, 4.15 mmol) was added dropwise at –78 °C. The mixture was warmed to room temperature and stirred for 1 h. The resultant solid was filtered and then washed with Et_2O (30 ml) to give **3a** as a white solid (0.74 g, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.31 (s, 1H), 7.52 (t, J = 8.2 Hz, 1H), 7.31 (dd, J_1 = 8.2 Hz, J_2 = 8.2, 2H), 4.63 (q, J = 7.8 Hz,1H), 2.71-2.57 (m, 3H), 2.34-2.27 (m, 1H), 2.18, (t, J = 12.4 Hz,1H), 2.07 (dd, J_1 = 9.6 Hz, J_2 = 9.6, 2H), 1.31 (d, J = 6.4 Hz, 3H), 1.29 (d, J = 6.4 Hz, 3H), 1.25 (d, J = 6.4 Hz, 3H), 1.23 (d, J = 6.4 Hz, 3H), 1.00 (d, J = 6.8 Hz, 3H), 0.67 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =192.4, 143.2, 142.7, 131.9, 131.8, 125.4, 125.3, 120.5 (q, J = 318 Hz), 82.1, 53.2, 35.1, 33.2, 29.9, 29.8, 29.2, 25.4, 24.7, 24.3, 24.0 23.3, 23.0, 22.9, 21,5, 20.9, 20.8, 19.0; HRMS (EI): m/z [M – OTf^-] calcd. for $C_{24}H_{38}N^+$: 340.3004, found: 340.3002.



3b

LDA (2.05 mL, 4.10 mmol, 2.0 M in THF) was added dropwise to a solution of 2,6-diisopropyl-N-(2-methylpropylidene)aniline (0.8 g, 3.46 mmol) in Et_2O (15 mL) at 0 °C. After 20 mins, the mixture was warmed to room temperature and stirred for 4 h. Evacuated the solvent in vacuo and the residue was dissolved in Et_2O (20 mL), and 2-isopropyloxirane (0.36 g, 4.15 mmol) was added dropwise. After stirring overnight at room temperature, Tf_2O (1.16 g, 4.15 mmol) was added dropwise at –78 °C. The mixture was warmed to room temperature and stirred for 1 h. The resultant solid was filtered and then washed with Et_2O (30 ml) to give **3b** as a white solid (0.68 g, 47%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.38 (s, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.31 (dd, J_1 = 7.8 Hz, J_2 = 7.8, 2H), 4.63 (q, J = 7.5 Hz, 1H), 2.66-2.50 (m, 3H), 2.14 (dd, J_1 = 9.8 Hz, J_2 = 9.6 Hz, 1H), 1.93 (sept, J = 6.9 Hz, 1H),

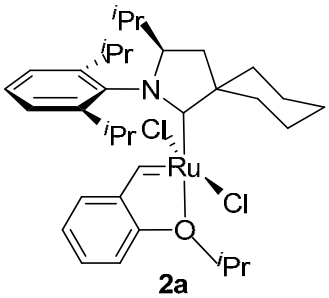
1.64 (s, 3H), 1.62 (s, 3H), 1.33 (d, J = 7.2 Hz, 3H), 1.32 (d, J = 7.2 Hz, 3H), 1.24 (d, J = 6.9 Hz, 3H), 1.23 (d, J = 6.6 Hz, 3H), 0.97 (d, J = 6.6 Hz, 3H), 0.63 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =193.5, 143.1, 142.6, 131.9, 131.8, 125.3, 125.2, 120.6 (q, J = 310 Hz), 82.2,48.1, 39.6, 29.8, 29.2, 29.1, 25.3, 24.8, 24.6, 23.1, 22.9, 22.7, 20.7 19.1; HRMS (EI): m/z [M – OTf $^-$] calcd. for $C_{21}H_{34}N^+$: 300.2691, found: 300.2689.



3c

LDA (2.05 ml, 4.15 mmol, 1.0 M in THF) was added dropwise to a solution of 2,6-diethyl-N-(2-methylpropylidene)aniline (0.78 g, 3.46 mmol) in Et_2O (15 mL) at 0 °C. After 20 mins, the mixture was warmed to room temperature and stirred for 4 h. Evacuated the solvent in vacuo and the residue was dissolved in Et_2O (20 mL), and 2-isopropyloxirane (0.36 g, 4.15 mmol) was added dropwise. After stirring overnight at room temperature, Tf_2O (1.16 g, 4.15 mmol) was added dropwise at –78 °C. The mixture was warmed to room temperature and stirred for 1 h. The resultant solid was filtered and then washed with Et_2O (30 ml) to give **3c** as a white solid (0.57 g, 42 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.37 (s, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.30 (dd, J_1 = 7.8 Hz, J_2 = 7.8 Hz, 2H), 4.78-4.72 (m, 1H), 2.61-2.43 (m, 5H), 2.13 (dd, J_1 = 10.0 Hz, J_2 = 10.0 Hz, 1H), 2.00-1.91 (m, 1H), 1.64 (d, J = 14.0 Hz, 6H), 1.31 (t, J = 7.5 Hz, 6H), 0.91 (d, J = 6.8 Hz, 6H), 0.71 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =193.1, 138.0, 137.4, 133.4, 131.3, 127.4, 127.3, 120.4 (q, J = 322 Hz), 80.6, 47.9, 38.6, 29.3, 24.9, 24.0, 23.9, 23.0, 20.2, , 18.2, 14.4, 14.0; HRMS (EI): m/z [M – OTf $^-$] calcd. for $C_{19}H_{30}N^+$: 272.2378, found: 272.2375.

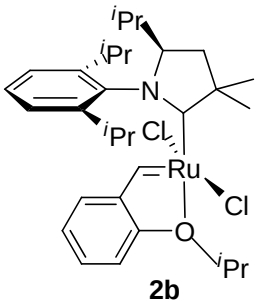
Preparation of CDDC-Ru complexes 2a~2c by literature method[2]



2a

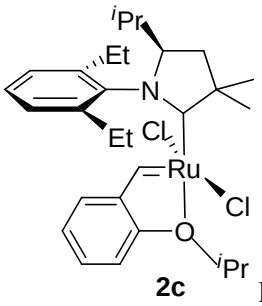
KHMDS (0.6 mL, 1.0 M in hexane) was added dropwise to a suspension of **3a** (244 mg, 0.5 mmol) and $RuCl_2(PCy_3)(=CH–o\text{-}O^iPrC_6H_4)$ (300 mg, 0.5 mmol) in toluene (5 mL)

at -40°C. After 10 mins, the mixture was warmed to 60°C and stirred for 4 h. Evacuated the solvent in vacuo and the residue was purified by column chromatography on silica gel (PE/EA = 15/1 → 8/1) to give the product **2a** as green powder (119 mg, 37%). ^{1}H NMR (400 MHz, CDCl3) δ = 16.4 (s, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.42 (dd, J_1 = 7.6 Hz, J_2 = 7.6, 2H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.85-6.78 (m, 2H), 5.20-5.13 (m, *J* = 6.6 Hz, 1H), 4.13-4.07 (m, 1H), 3.23-3.15 (m, 2H), 3.03-2.94 (m, Hz, 2H), 2.67 (d, *J* = 13.2 Hz, 1H), 2.50-2.45 (m, 1H), 1.99-1.74 (m, 12H), 1.53-1.47 (m, 2H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.17 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.64 (d, *J* = 6.8 Hz, 3H), 0.44 (d, *J* = 6.8 Hz,3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* = 296.4, 268.6, 152.6, 147.3, 146.7, 143.3, 139.6, 130.7, 129.5, 125.5, 125.3, 123.6, 121.8, 113.2, 79.8, 74.9, 61.6, 36.5, 35.8, 29.5, 27.9, 27.6, 26.8, 25.9, 24.9, 24.7, 24.4, 23.4, 22.5, 22.0, 21.9, 20.9; HRMS (EI): m/z $[M]^+$ calcd. for $C_{34}H_{49}Cl_2NORu$: 659.2235, found: 659.2234.



2b

KHMDS (0.6 mL, 1.0 M in hexane) was added dropwise to a suspension of **3b** (224 mg, 0.5 mmol) and $RuCl_2(PCy_3)(=CH–o\text{-}O^iPrC_6H_4)$ (300 mg, 0.5 mmol) in toluene (5 mL) at -40°C. After 10 mins, the mixture was warmed to 60°C and stirred for 4 h. Evacuated the solvent in vacuo and the residue was purified by column chromatography on silica gel (PE/EA = 15/1 → 8/1) to give the product **2b** as green powder (120 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* = 16.31 (s, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 6.9 Hz,1H), 7.42 (dd, J_1 = 7.9 Hz, J_2 = 7.9, 2H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.86-6.79 (m, 2H), 5.20-5.14 (m, 1H), 4.19-4.13 (m, 1H), 3.03-2.95 (m, 2H), 2.12-2.06(m, 2H), 2.00-1.90 (m, 1H), 1.83, (d, *J* = 6.4 Hz), 1.74 (d, *J* = 6.0 Hz), 1.27 (t, *J* = 6.8 Hz), 1.19 (d, *J* = 6.4 Hz), 0.90 (d, *J* = 6.4 Hz, 6H), 0.64 (d, *J* = 6.4 Hz, 3H), 0.43 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ =295.6, 268.8, 152.6, 147.3, 146.8, 143.1, 139.6, 130.6, 129.6, 125.5, 125.3, 123.4, 121.8, 113.1, 79.8, 75.0, 55.9, 43.3, 29.4, 28.3, 28.1, 27.9, 27.6, 26.5, 25.9, 24.9, 24.8, 24.7, 24.4, 24.3, 22.5, 22.3, 22.1, 21.8, 20.8; HRMS (EI): m/z $[M]^+$ calcd. for $C_{31}H_{45}Cl_2NORu$: 619.1922, found: 619.1930.



2c

KHMDS (0.6 mL, 1.0 M in hexane) was added dropwise to a suspension of **3c** (216 mg, 0.5 mmol) and $RuCl_2(PCy_3)(=CH–o\text{-}O^iPrC_6H_4)$ (300 mg, 0.5 mmol) in toluene (5 mL) at -40°C. After 10 mins, the mixture was warmed to 60°C and stirred for 4 h. Evacuated the solvent in vacuo and the residue was purified by column chromatography on silica gel (PE/EA = 15/1 → 8/1) to give the product **2c** as green powder (46 mg, 17%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 16.20 (s, 1H), 7.59-7.52 (m, 2H), 7.33 (dd, J_1 = 7.2 Hz, J_1 = 7.2 Hz 2H), 6.93 (d, J = 8.0 Hz, 1H), 6.85(s, 2H), 5.19-5.16 (m, 1H), 4.28 (m, 1H), 2.61 (m, 4H), 2.29 (s, 3H), 1.76 (d, J = 7.2 Hz, 6H), 1.20 (m, J = 4.8 Hz, 12H), 0.91 (d, J = 6.8 Hz, 3H), 0.44 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ =298.2, 268.1, 152.3, 143.8, 142.6, 141.6, 141.4, 130.7, 129.0, 126.6, 123.6, 121.9, 113.0, 78.5, 74.9, 55.8, 43.8, 30.9, 29.6, 29.5, 27.8, 24.1, 23.3, 22.5, 22.0, 21.9, 21.8, 20.7; HRMS (EI): m/z $[M]^+$ calcd. for $C_{29}H_{41}Cl_2NORu$: 591.1609, found: 591.1604.

General ring-closing metathesis procedure:

An NMR tube with a rubber septum was charged with 0.80 mL of a CD_2Cl_2 (at 30 °C) or C_6D_6 (at 60 °C) solution of catalyst (0.80μmol). After the sample was equilibrated at the appropriate temperature, diolefin (0.080 mmol) was injected into the tube. The reaction was monitored after an appropriate period of time. The conversion was determined by comparing the ratio of the integrals of the methylene protons in the starting material with those in the product.

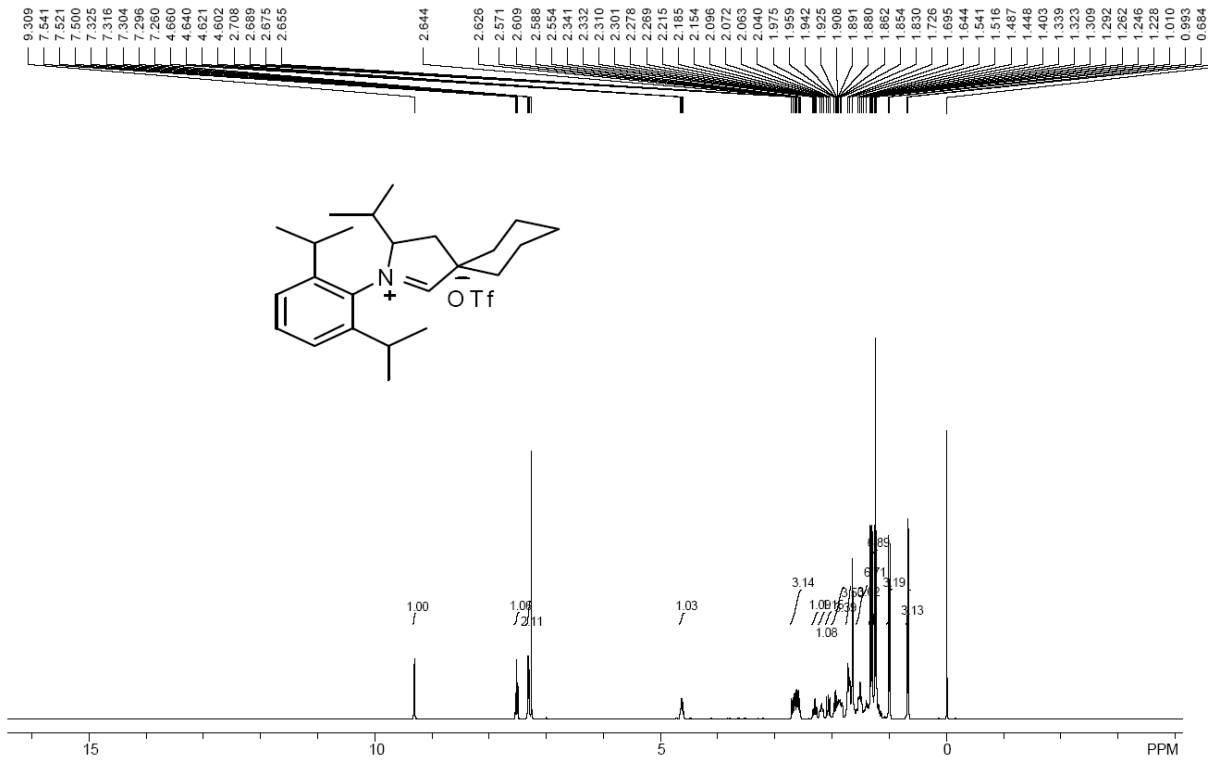
General ethenolysis procedure:

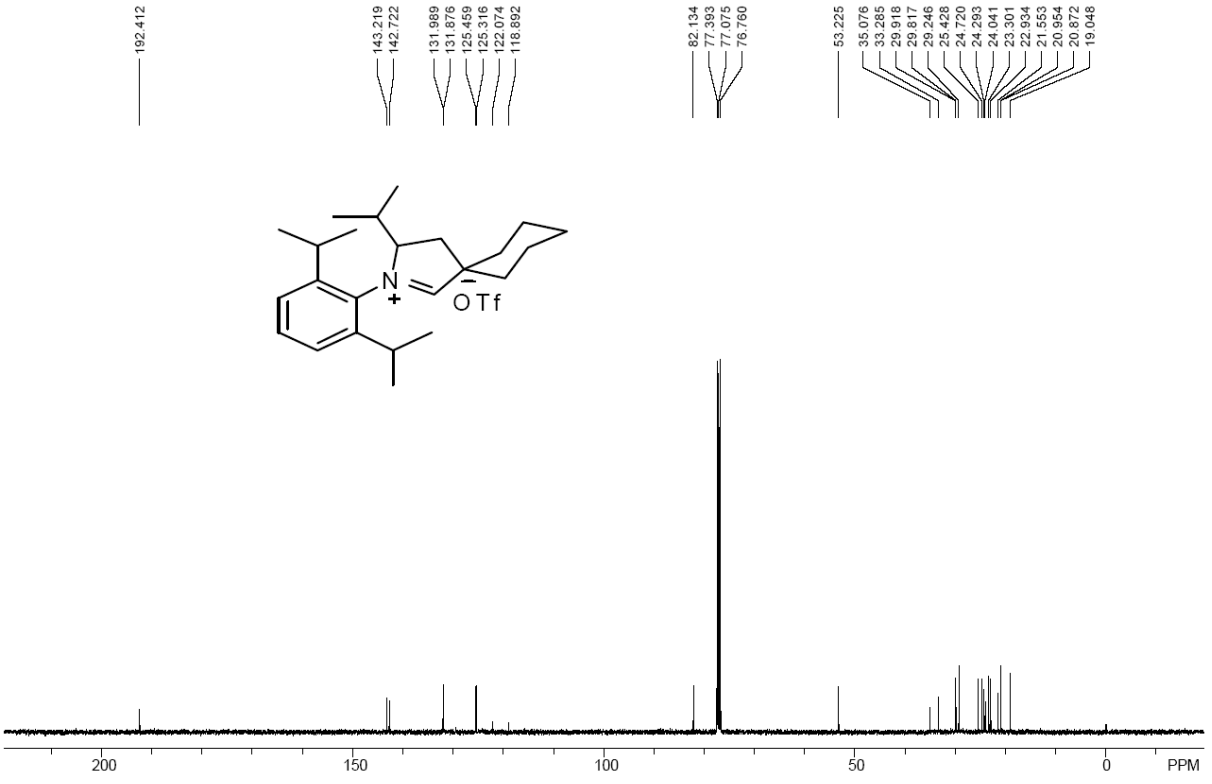
A solution of olefin metathesis catalyst of an appropriate concentration was prepared in dried CH_2Cl_2, and the desired volume of this solution was added to the methyl oleate (3g). The mixture was transferred into a vacuum-dried reaction vessel under ethylene flow. Then the reactor was closed, placed in an oil bath at 40°C, and pressurized to 150 psi. At the end of each experiment, the reactor

was cooled to 0 °C and depressurized. A small sample was passed over a short silica plug and analyzed by GC.

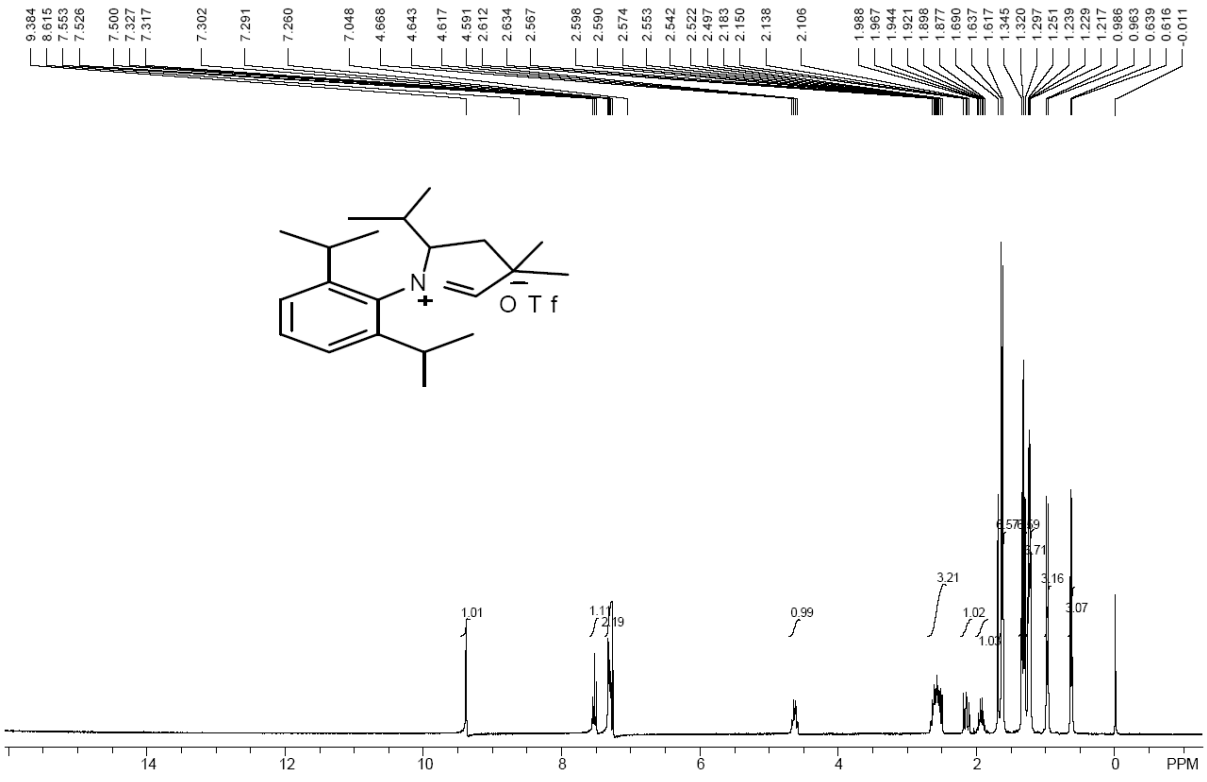
NMR Spectra:

3a





3b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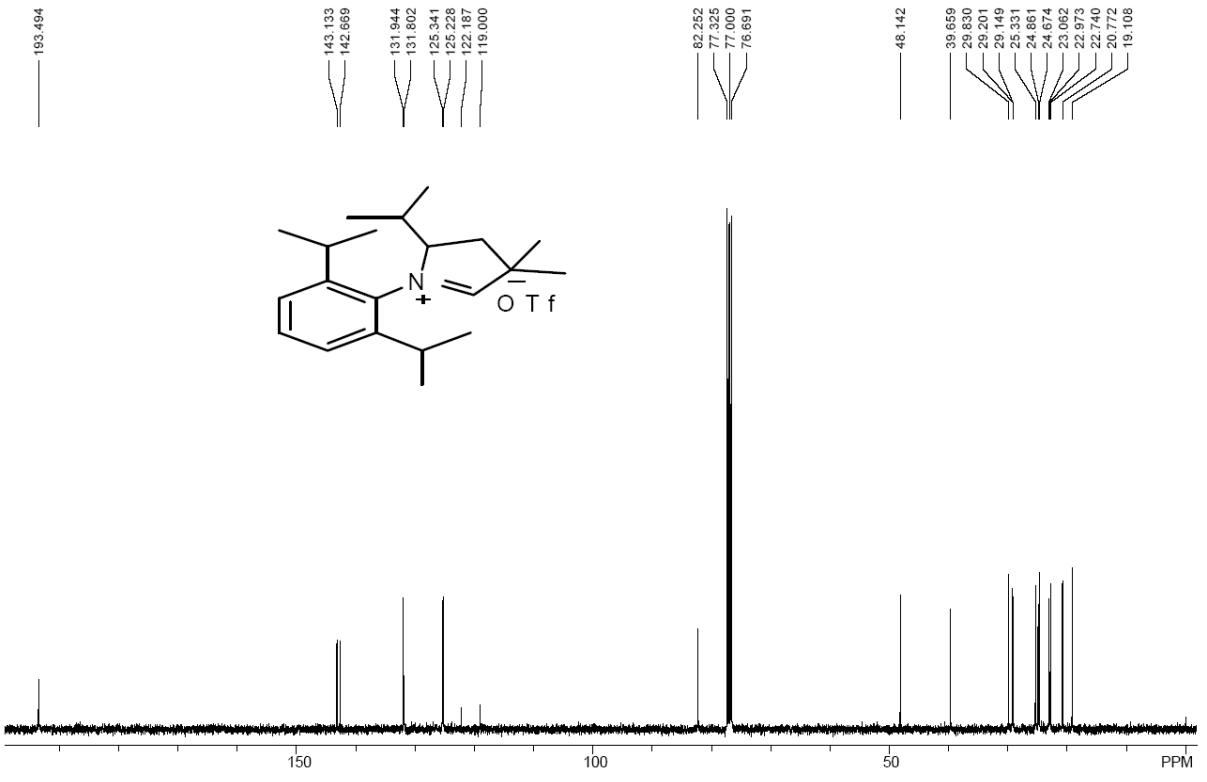
PPM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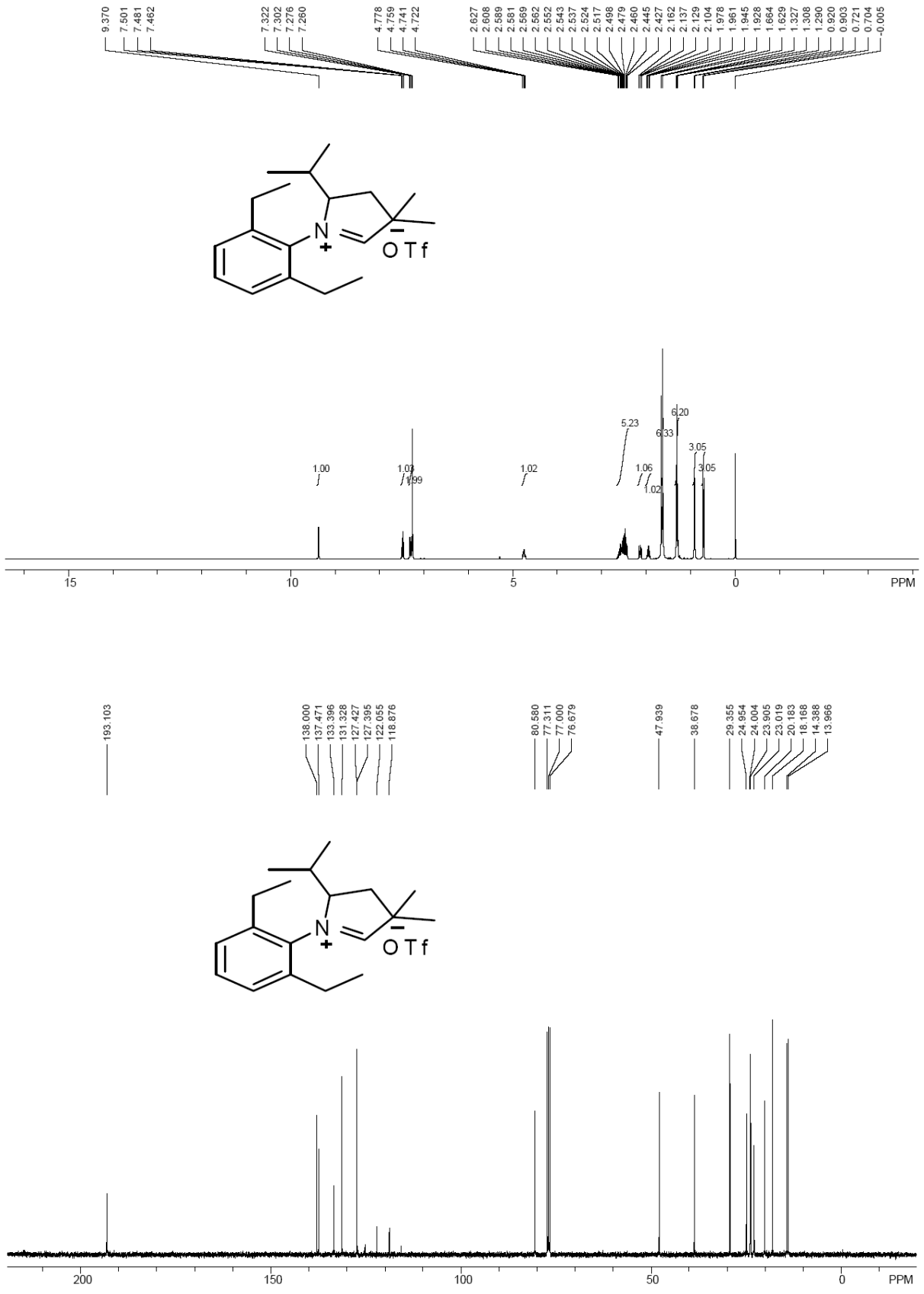
3c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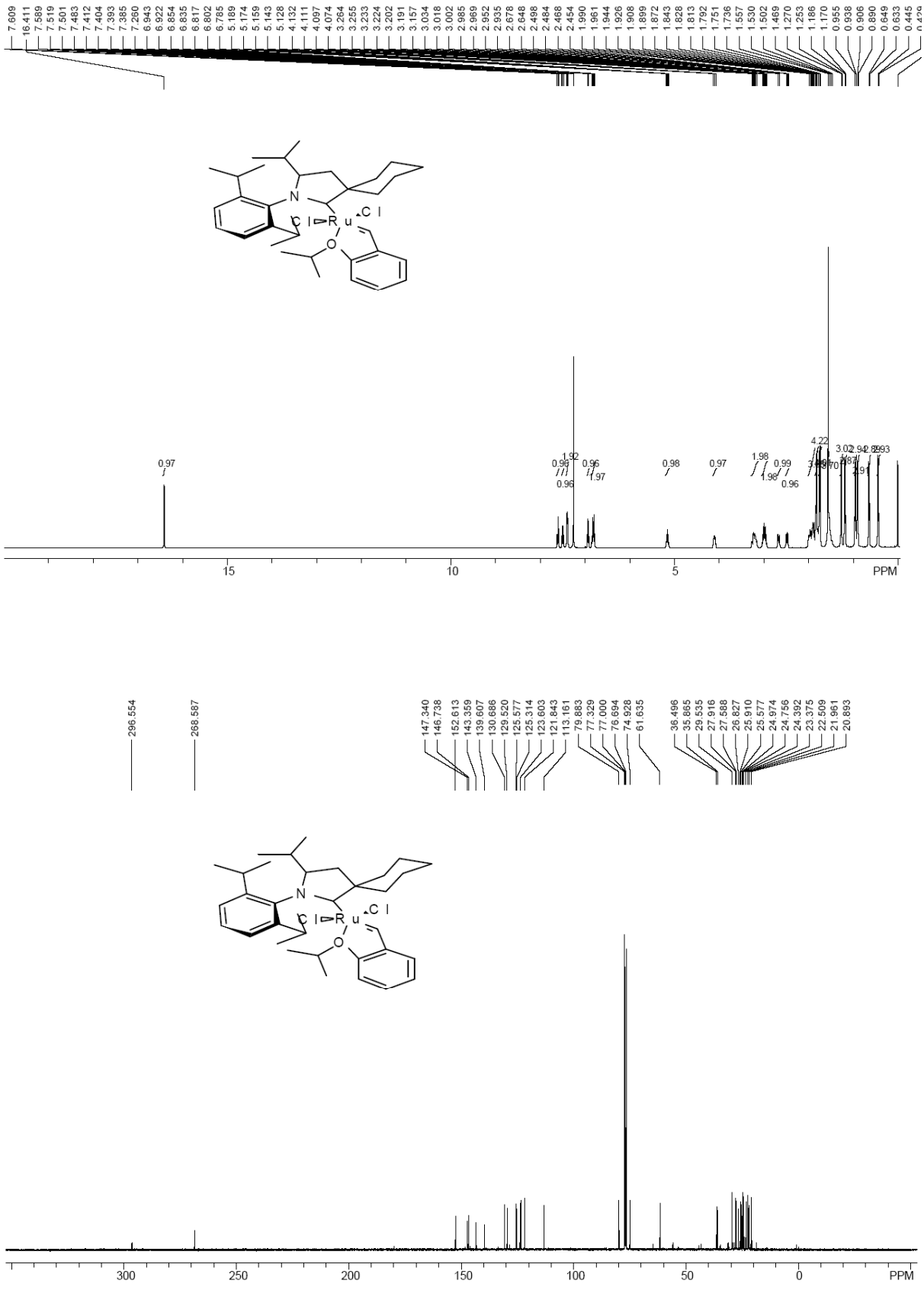
PPM

2a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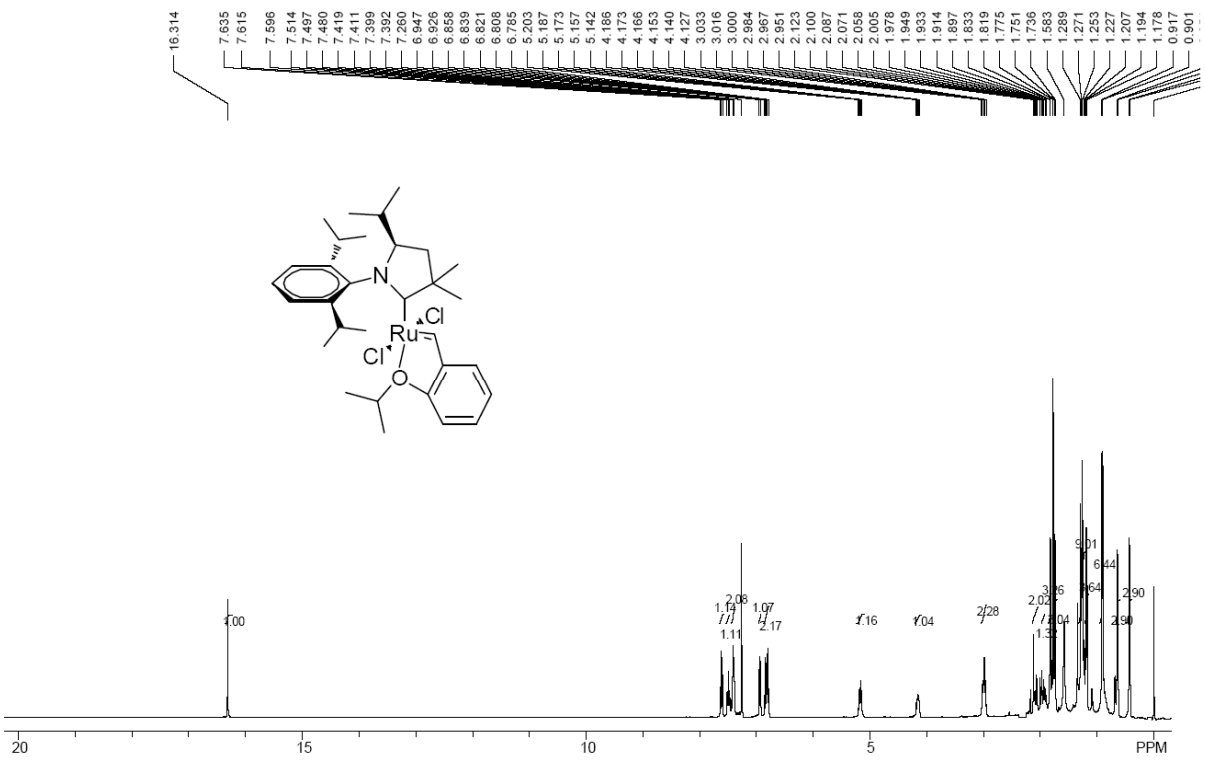
2b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Ru
Cl
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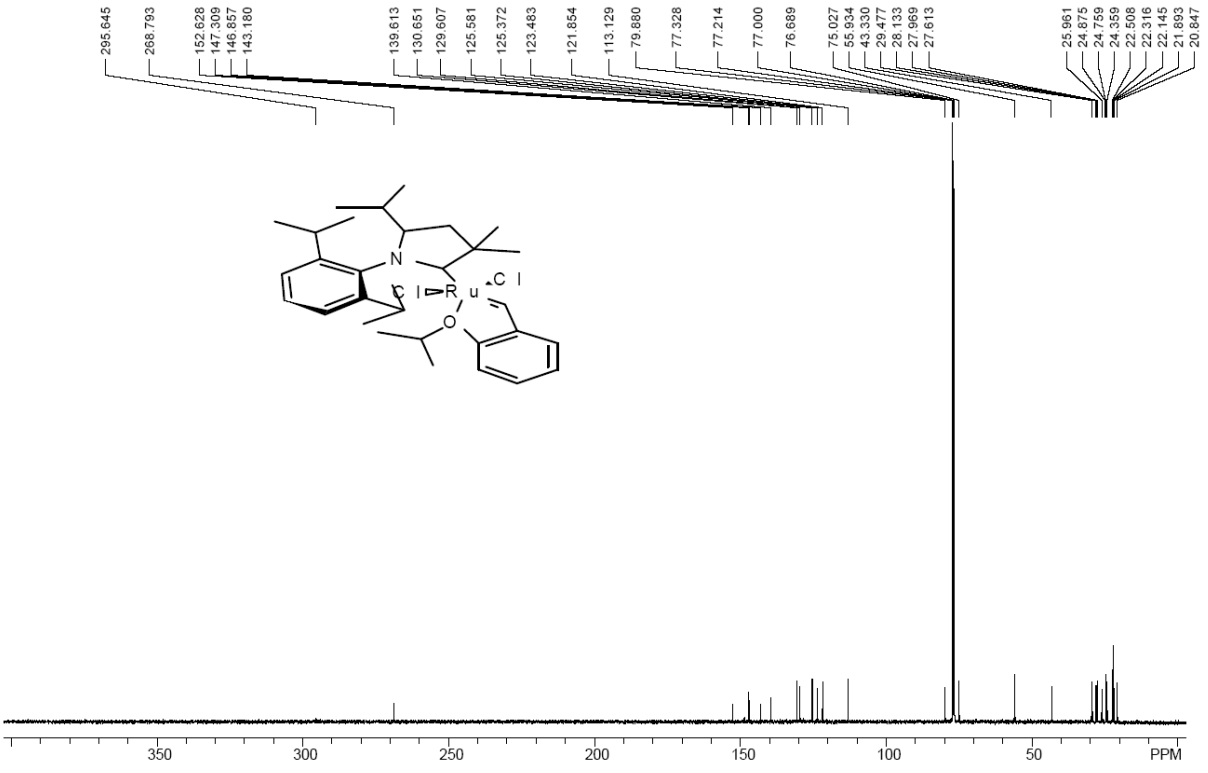
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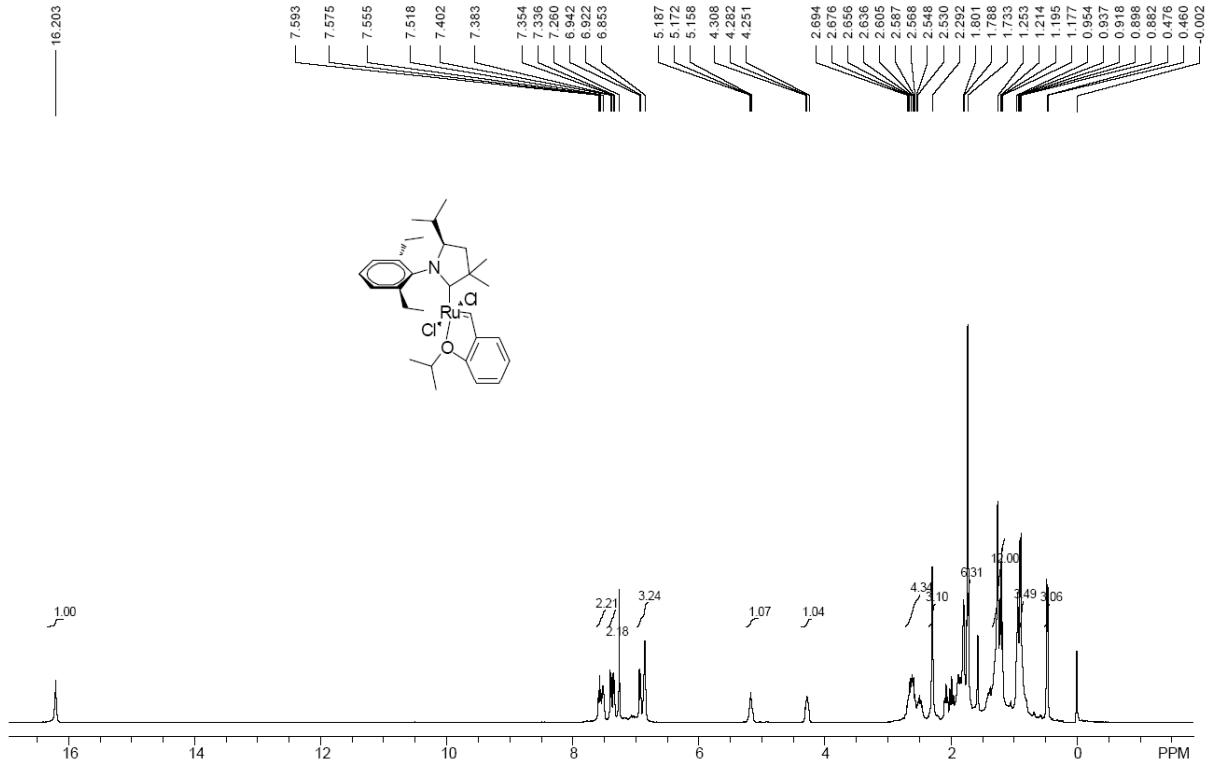
2c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Cl
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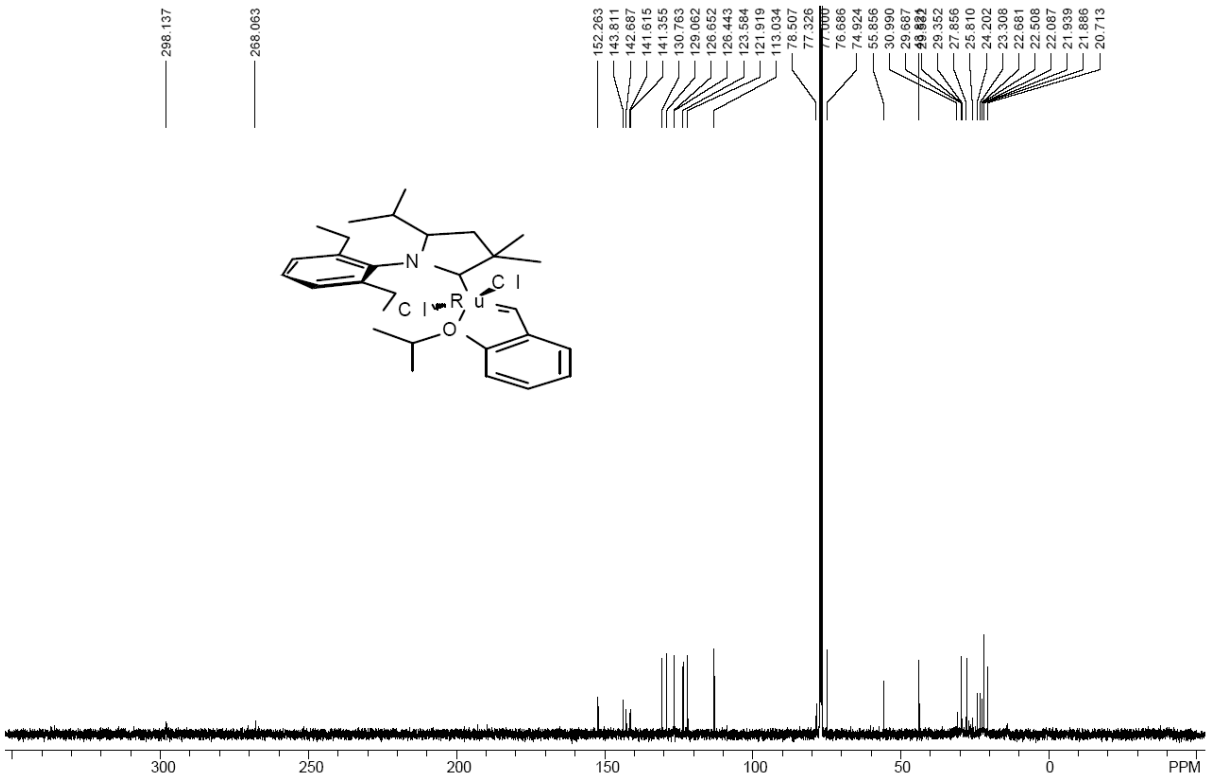
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20.713
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Cl
Ru
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300
250
200
150
100
50
0
PPM

X-Ray Crystallography.

Crystallographic measurements were made on a Bruker Smart Apex 100 CCD area detector using graphite monochromated Mo-Kαradiation ($\lambda_{\text{Mo-K}\alpha}$ = 0.71073 Å). The structures were solved by directed methods (SHELXS-97) and refined on F^2 by full-matrix least squares (SHELX-97) using all unique data. All the calculations were carried out with the SHELXTL18 program.[3]

Key details of the crystal and structure refinement data are summarized in Table S1–S2. Further crystallographic details may be found in the respective CIF files, which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The CCDC reference numbers for **2a** was assigned as 938870.

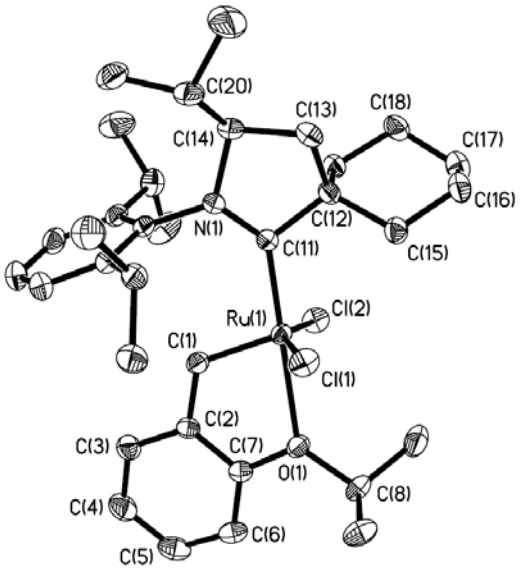

Figure S1 Views of the single-crystal structure of Ru complex **2a**. H atoms have been omitted for clarity.

3. G. M. Sheldrick, SHELL-97, Program for crystal structure refinement, University of Göttingen: Göttingen, Germany, 1997.

Table S1. Crystal Data, Data Collection, and Structure Refinement for **2a**

	2a
Identification code	a11202b
Formula	$C_{34}H_{49}Cl_2NORu$
Formula weight	659.71
T, K	293(2)
crystal system	Orthorhombic
space group	P2(1)2(1)2(1)
a, Å	10.914(4)
b, Å	11.526(4)
c, Å	26.138(9)
α, deg	90
β, deg	90
γ, deg	90
Volume, Å ^{3}	3288(2)
Z	4
D_{calc}, Mg / m^3	1.333
absorption coefficient, mm^{-1}	0.665
F(000)	1384
crystal size, mm	0.20 x 0.15 x 0.12
2θ range, deg	1.56 to 27.01
reflections collected /unique	15624 / 6903 [R(int) = 0.0272]
data / restraints / parameters	6903 / 0 / 360
goodness of fit on F^2	1.005
final R indices [$I > 2\sigma(I)$]^a	R1 = 0.0238, wR2 = 0.0525
R indices (all data)	R1 = 0.0260, wR2 = 0.0532
lgst diff peak and hole, e/Å^3	0.316 and -0.258