

# Highly Efficient Catalysts for the Formation of Tetrasubstituted Olefins via Ring-Closing Metathesis

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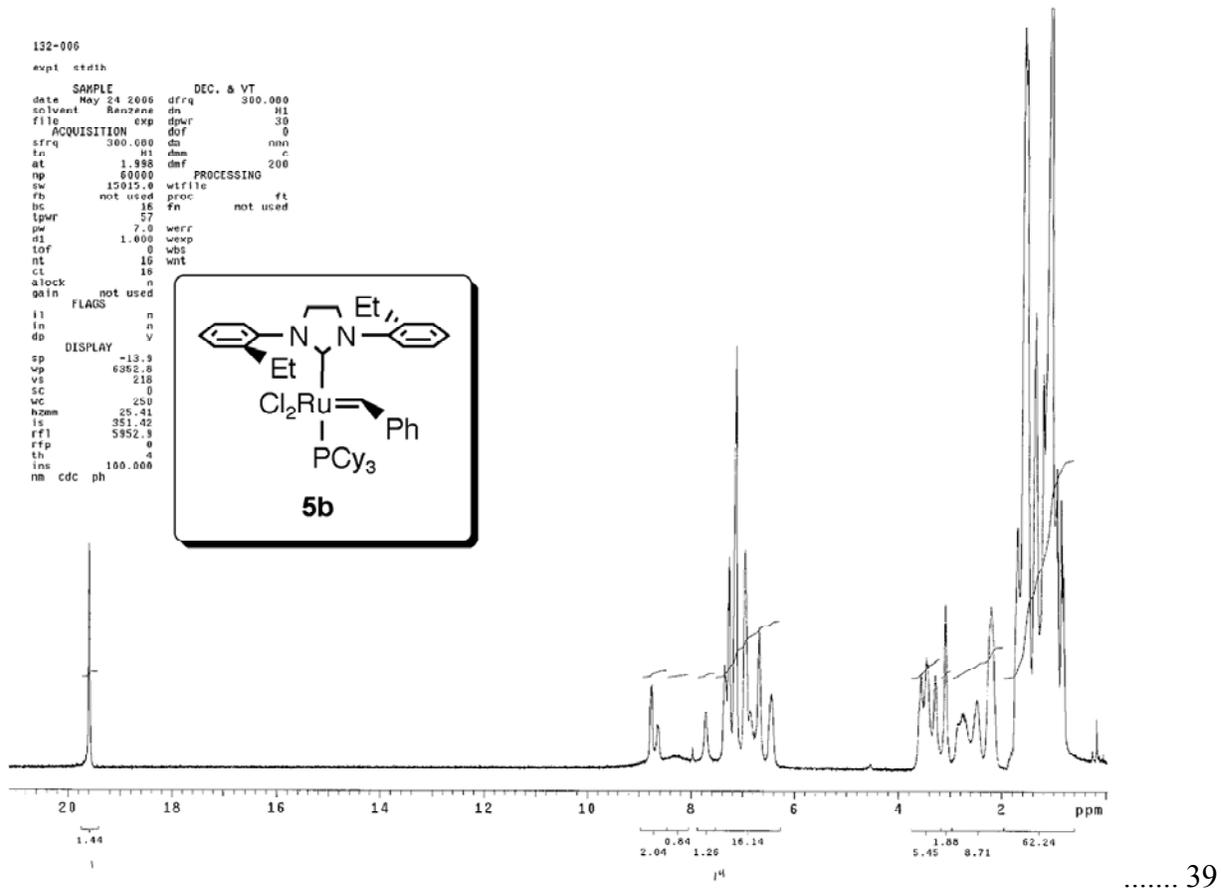
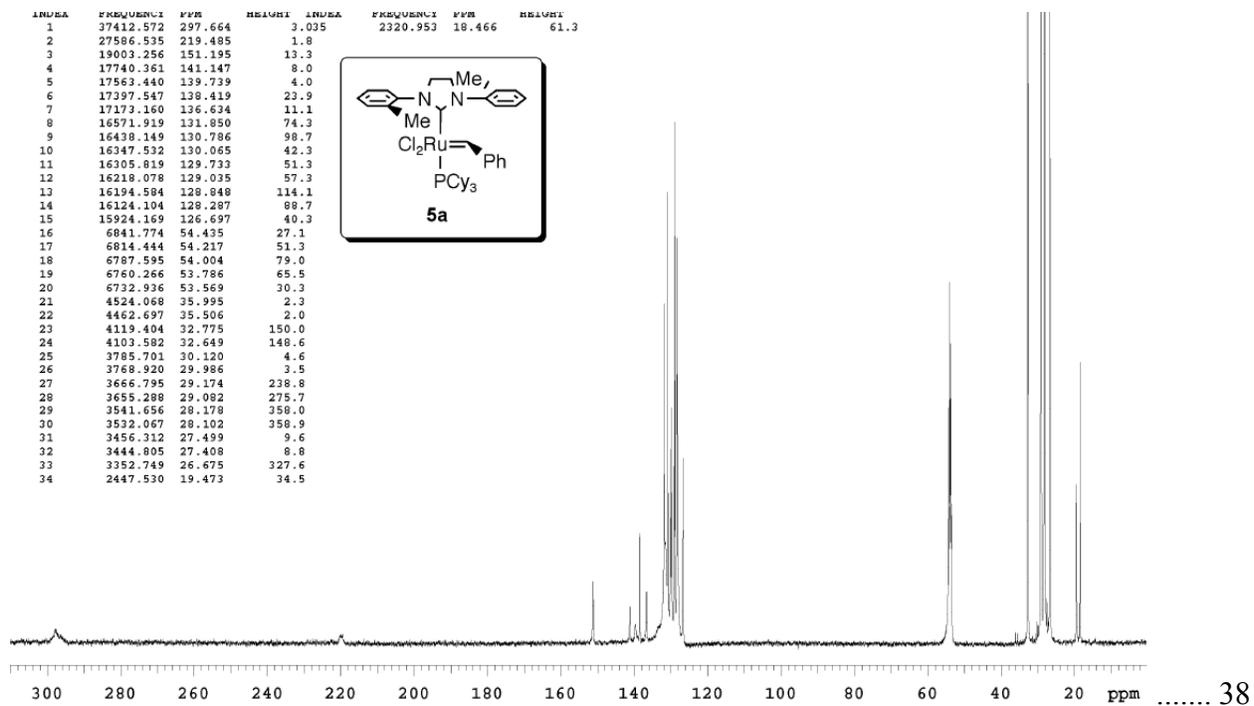
## Supporting Information

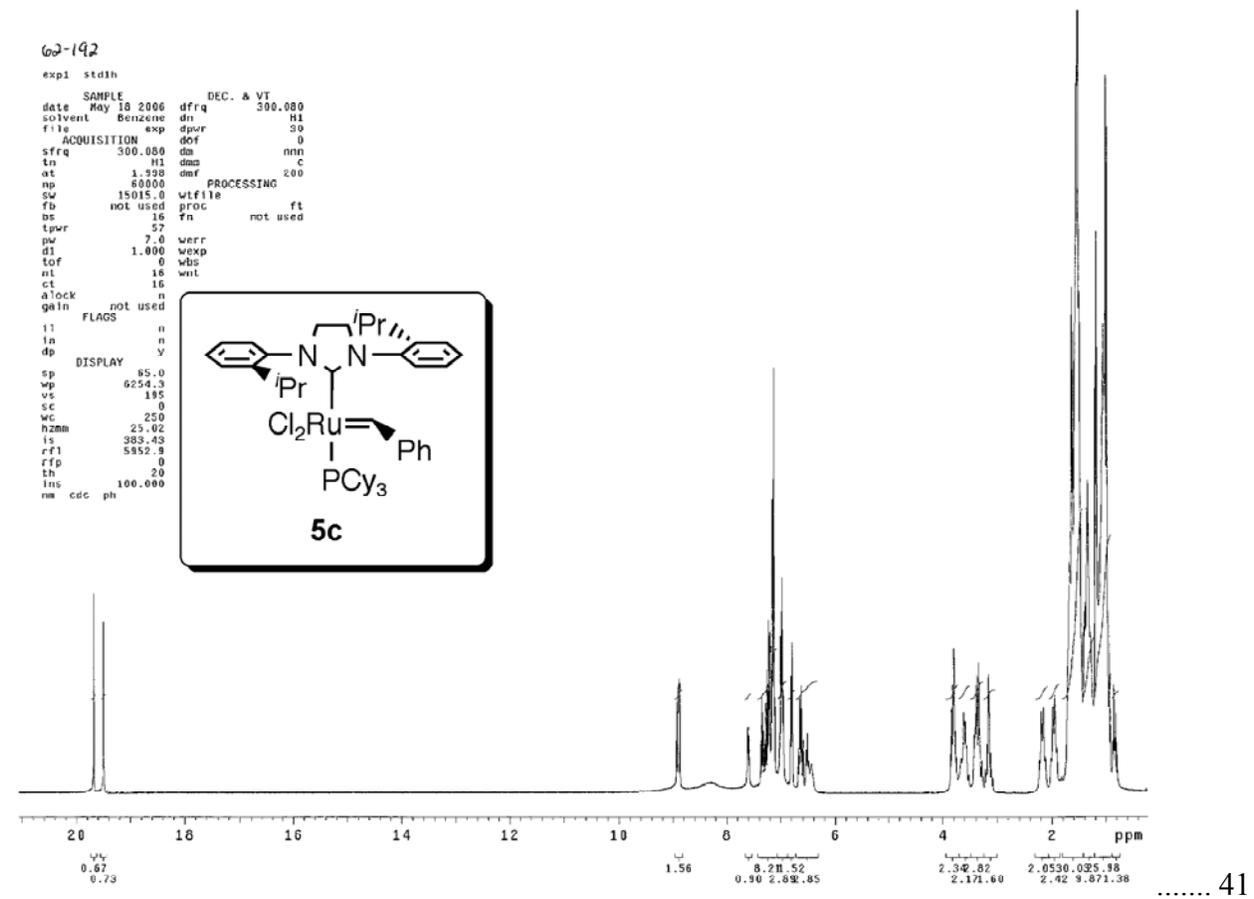
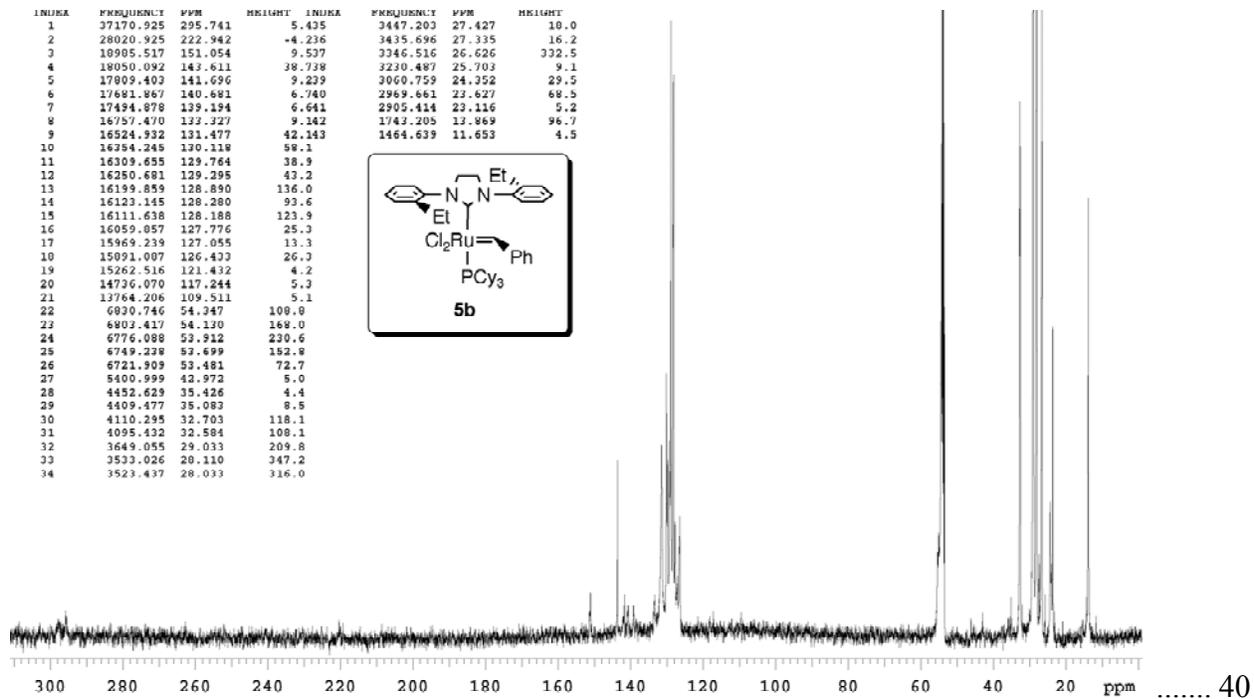
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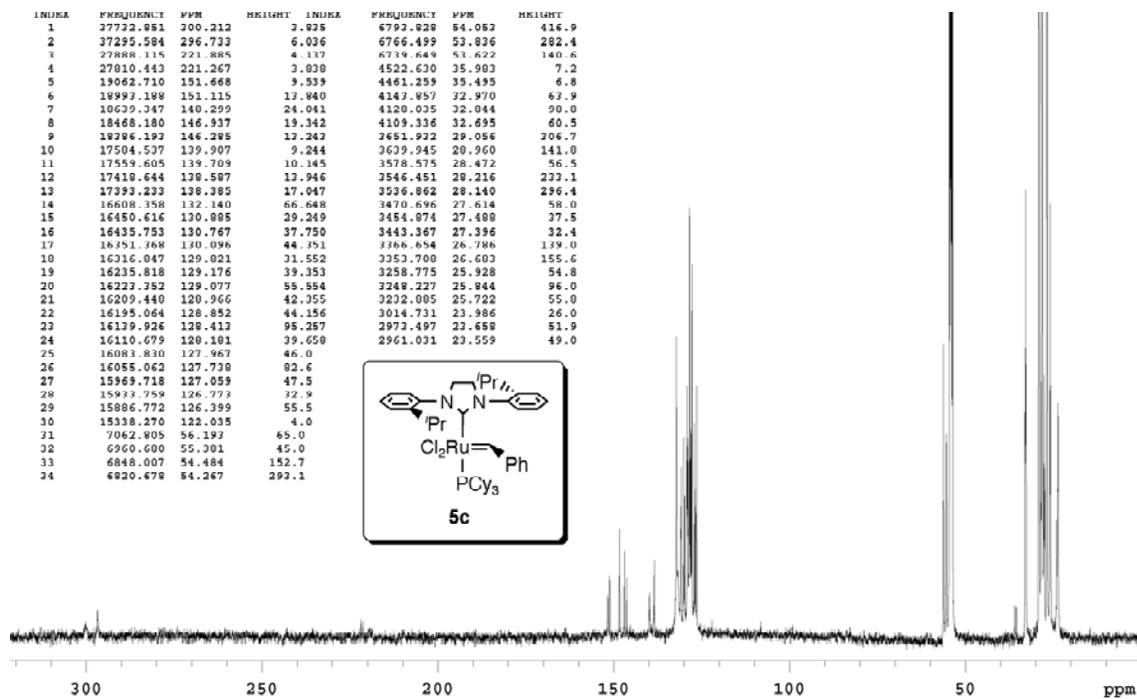
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<sup>1</sup> California Institute of Technology

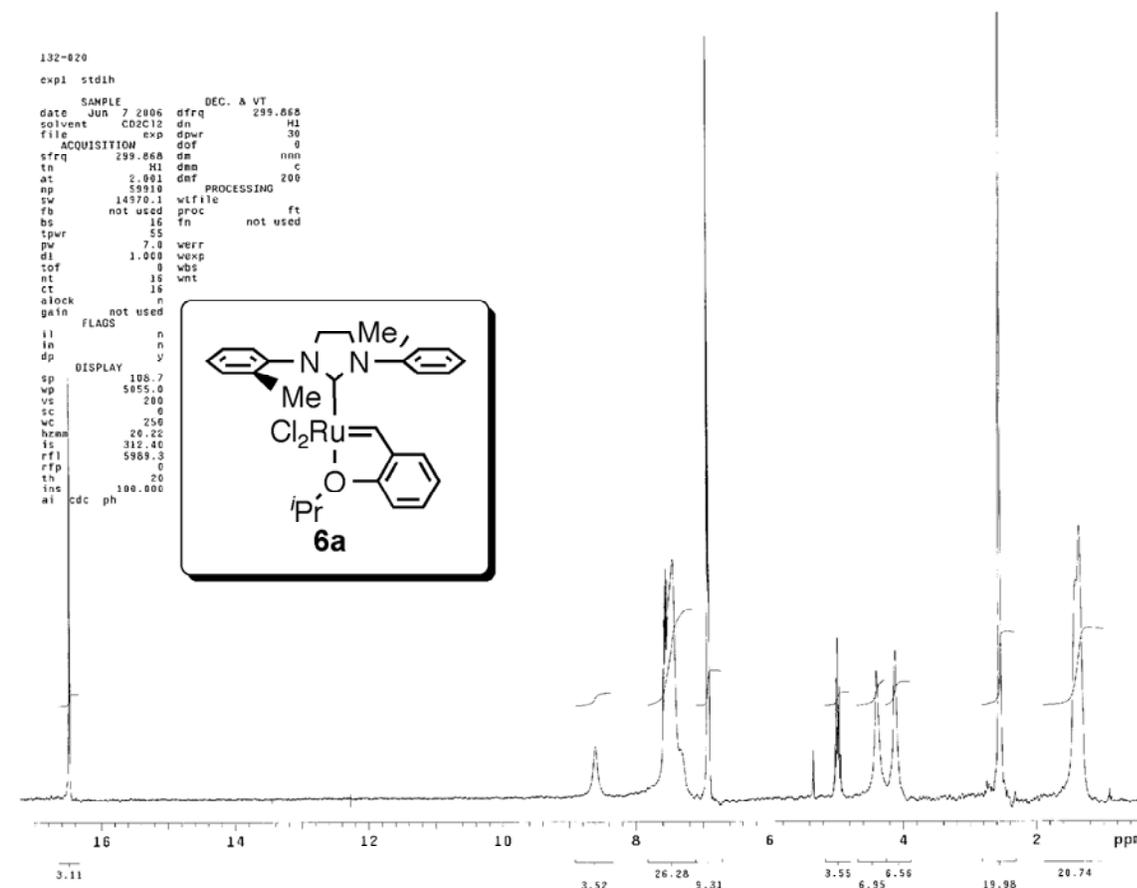
<sup>2</sup> Materia, Inc.





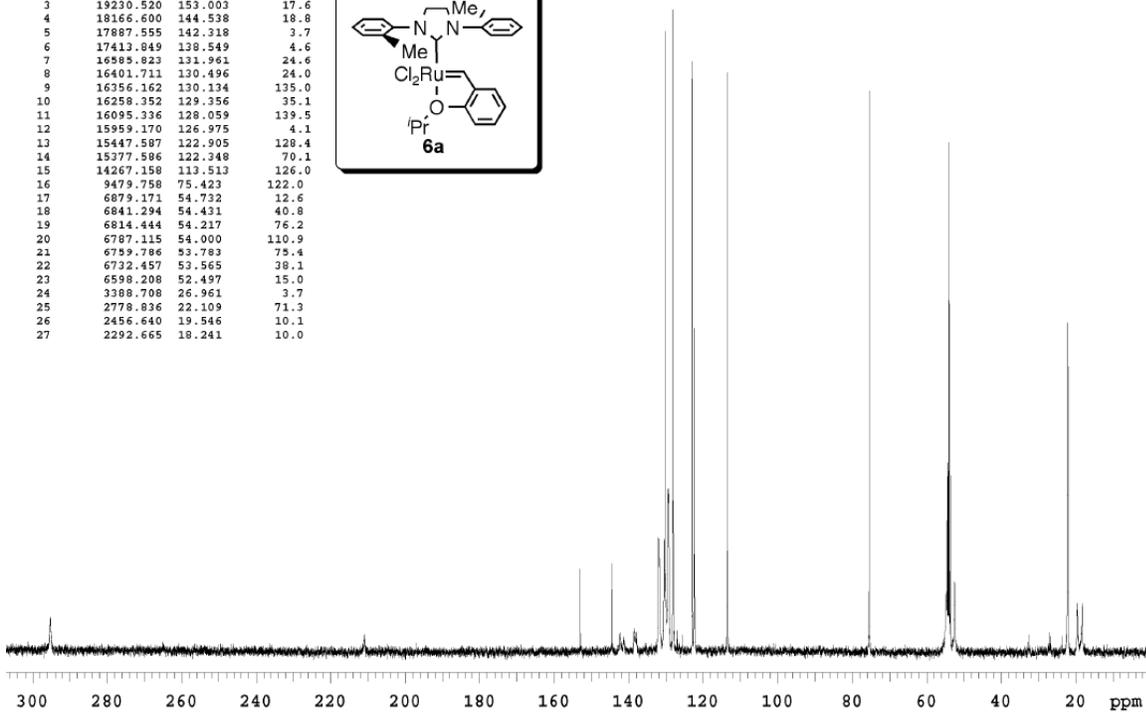
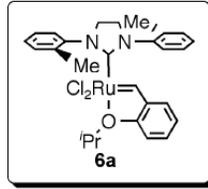


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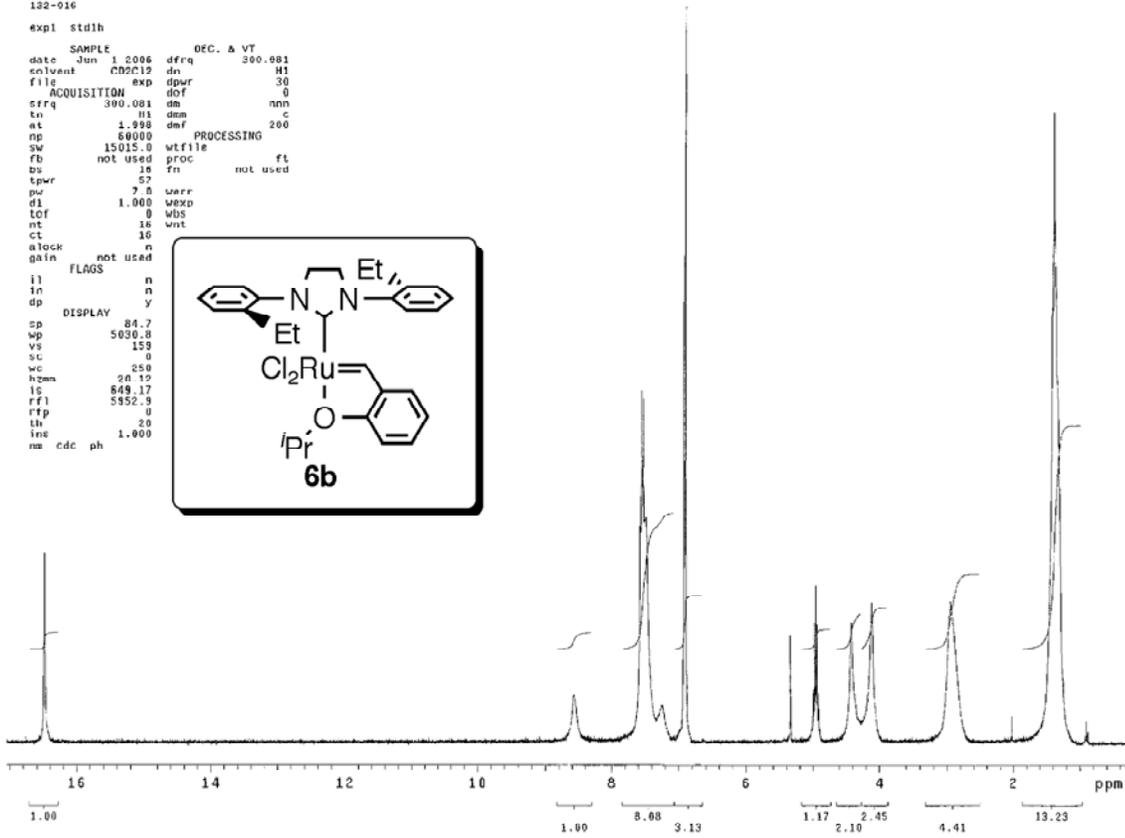
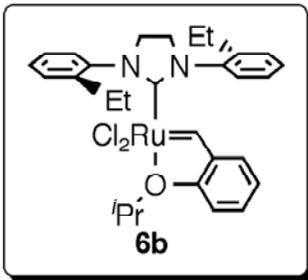
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12	15959.170	126.975	4.1
13	15447.587	122.905	128.4
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19	6814.444	54.217	76.2
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23	6598.208	52.497	15.0
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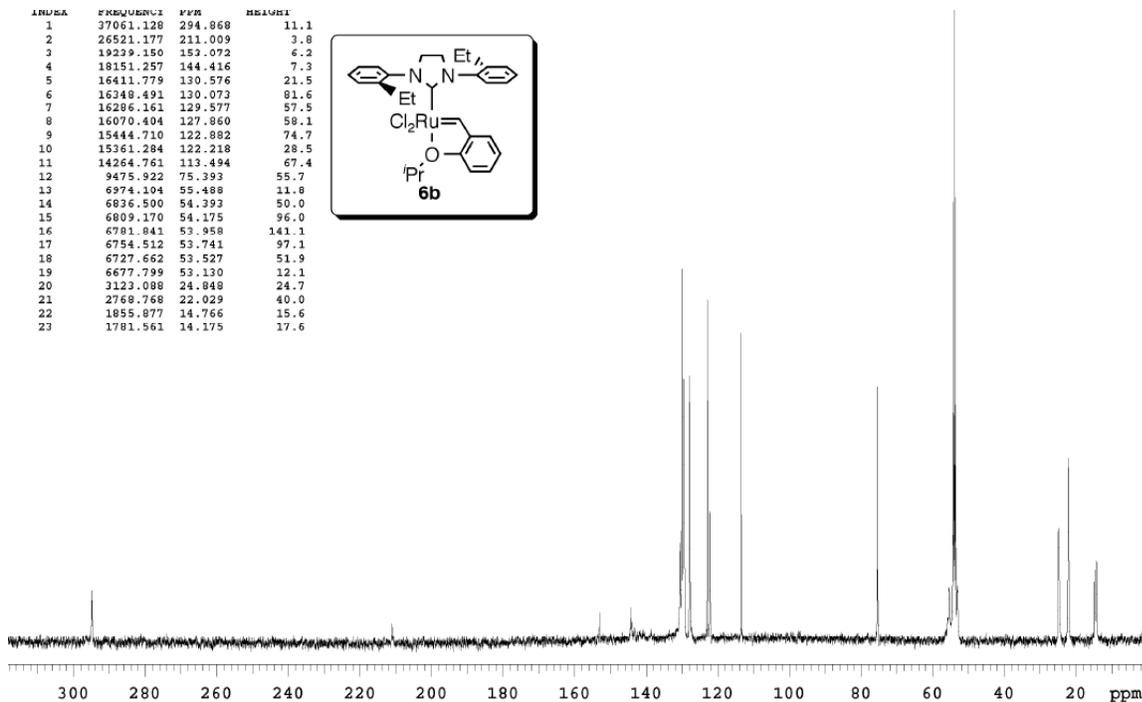
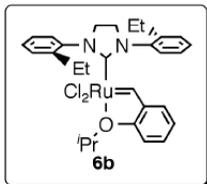
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18	6727.662	53.527	51.9
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20	3123.088	24.848	24.7
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23	1781.561	14.175	17.6



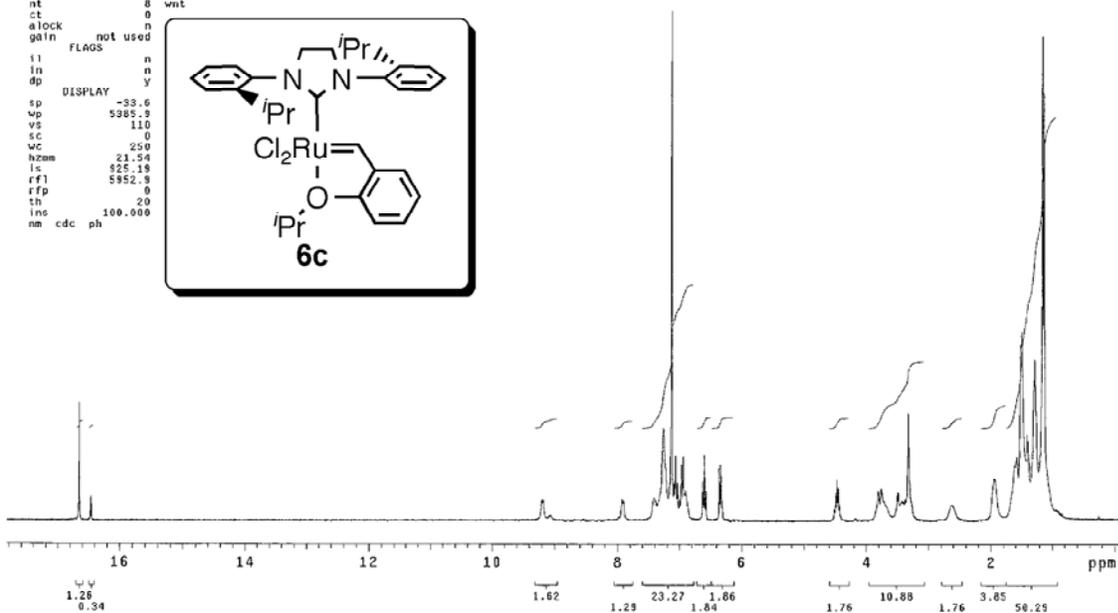
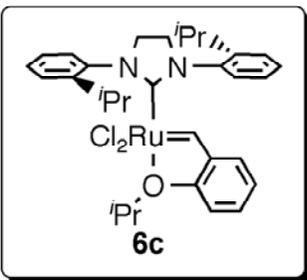
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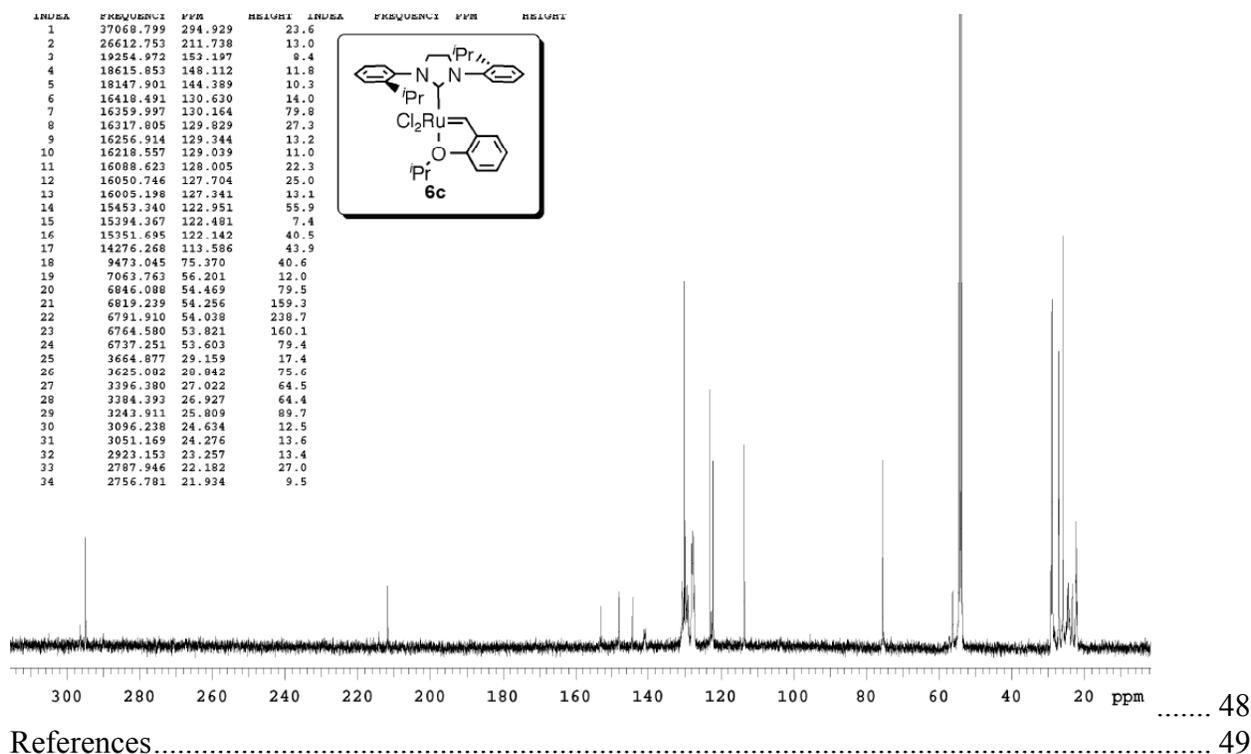
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ic 425.19
rfj 5952.9
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th 20
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nm cdc ph

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## GENERAL INFORMATION

NMR spectra were recorded on an Oxford 300 MHz NMR spectrometer running Varian VNMR software. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to internal solvent for  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra. Chemical shifts are reported in parts per million (ppm) downfield from  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$  NMR spectra. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), septet (sept), multiplet (m), and broad (br). Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization was performed with standard potassium permanganate stains or UV light. Flash column chromatography of organic compounds was performed using silica gel 60 (230-400 mesh), and flash column chromatography of ruthenium compounds was performed using silica gel 60 (230-400 mesh) from TSI Scientific (Cambridge, MA). All glassware was either oven dried or flame dried, and reactions were done under an atmosphere of argon unless otherwise noted. All organic solvents were dried by passage through solvent purification columns containing activated alumina. All commercial chemicals were used as obtained. Dichloro(phenylmethylene)bis(tricyclo-hexylphosphine) ruthenium complex was prepared according to a literature procedure.<sup>i</sup>

X-ray crystallographic structures were obtained by Mr. Larry M. Henling and Dr. Mike W. Day of the California Institute of Technology Beckman Institute X-Ray Crystallography Laboratory.

### GENERAL PROCEDURE FOR THE PREPARATION OF *N,N'*-DIARYL OXAMIDES

Oxalyl chloride (4.36 mL, 50 mmol) was added dropwise to a stirred solution of aniline (100 mmol, 2 equiv) and base (100 mmol, 2 equiv) in THF (200 mL) at 0 °C. Triethylamine or aqueous NaOH may be used as bases for this reaction. Upon addition, the reaction was allowed to warm up to room temperature and stirred for 1 h. The reaction mixture was then concentrated *in vacuo* and diluted with water (100 mL). The white precipitate was collected by filtration, washed with dilute HCl (100 mL), water (2 x 100 mL), and dried *in vacuo*.

### GENERAL PROCEDURE FOR THE PREPARATION OF *N,N'*-DIARYLETHYLENEDIAMINE

#### HYDROCHLORIDE

Borane-tetrahydrofuran complex (1.0 M solution in THF, 125 mL, 6.25 equiv) was added dropwise with stirring to solid oxamide (20 mmol) at room temperature. The reaction mixture was refluxed overnight, allowed to cool to r.t. and excess borane was quenched by careful, dropwise addition of water until no more gas evolution was observed. The reaction mixture was concentrated *in vacuo*, extracted with ether and the organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>. 2M HCl in ether (30 mL, 3 equiv) was then added to the dry organic extracts and the resulting white precipitate was collected by filtration, washed with a small amount of ethanol and dried *in vacuo*.

### GENERAL PROCEDURE FOR THE PREPARATION OF IMIDAZOLINIUM CHLORIDE

Triethyl orthoformate (150 mL) was added to the diamine hydrochloride 3 in a 250 mL r.b. flask. The flask was equipped with a distillation head and heated for about 1 h, during which ethanol distilled over at 78-80 °C, followed by about 70 mL of triethyl orthoformate at 135-140 °C. The reaction mixture was then allowed to cool to r.t., diluted with hexanes and the white precipitate was collected by filtration, washed with hexanes and ether and dried *in vacuo*. The following dihydroimidazolium salts were prepared by this procedure:

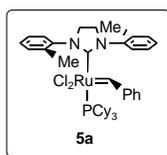
**1,3-Bis(*o*-tolyl)-imidazolinium chloride.** Obtained in 93% yield as a white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.83 (s, 1H), 7.78-7.21 (d, 8H), 4.64 (s, 4H), 2.43 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (75.41 MHz, CDCl<sub>3</sub>): δ 157.48, 134.37, 133.44, 131.57, 129.82, 127.64, 126.68, 52.89, 18.12. HR-MS (FAB<sup>+</sup>) Calculated for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>, 251.1548; found, 251.1557.

**1,3-Bis(2-ethylphenyl)-imidazolinium chloride.** Obtained in 74% yield as a white solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  9.04 (1H, s), 7.92 (2H, d,  $J = 7.5$  Hz), 7.47-7.30 (6H, m), 4.64 (4H, s), 2.78 (4H, q,  $J = 7.8$  Hz), 1.31 (6H, t,  $J = 7.8$  Hz).

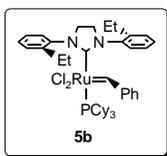
**1,3-Bis(2-isopropylphenyl)-imidazolinium chloride.** Obtained in 84% yield as a white solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.22 (d,  $^3J_{\text{HH}} = 7.2$  Hz, 2H), 8.04 (s, 1H), 7.34 (m, 6H), 4.73 (s, 4H), 3.06 (m, 2H), 1.29 (d,  $^3J_{\text{HH}} = 6.0$  Hz, 12H).

#### GENERAL PROCEDURE FOR THE PREPARATION OF CATALYSTS 5A-C

Potassium bis(trimethylsilyl)amide (1.4 g, 7.0 mmol, 1.23 equiv) was added to a suspension of the appropriate imidazolinium chloride (6.7 mmol, 1.15 equiv) in toluene (60 mL) under argon. The reaction mixture was stirred at room temperature for 30 min, then dichloro(phenylmethylene)bis(tricyclohexylphosphine) ruthenium complex (4.7 g, 5.7 mmol) was added and stirring was continued for 1.5 h at room temperature. The reaction mixture was then concentrated and catalysts **5a-c** were purified by column chromatography on silica gel: unreacted dichloro(phenylmethylene)bis(tricyclohexylphosphine) ruthenium complex was first eluted with 1:9 EtOAc-hexanes, then **5a-c** were eluted with 1:3 EtOAc-hexanes. The catalysts were obtained as brown solids upon drying *in vacuo*.

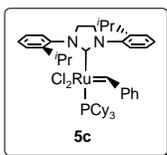


**Catalyst 5a.** **5a** was prepared according to the above general procedure and was obtained in 66% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  19.61 (s), 8.70 (br), 7.64 (br), 7.31-6.76 (m), 6.59 (m), 6.34 (br), 3.53-3.01 (m), 2.62 (s), 2.20-2.04 (br), 1.67-1.06 (m).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  27.87 (s), 25.15 (s).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  18.47, 19.47, 26.67, 27.50 (d,  $J = 12$  Hz), 28.14 (d,  $J = 10$  Hz), 29.13 (d,  $J = 12$  Hz), 32.71 (d,  $J = 16$  Hz), 53.78 (br), 126.69, 128.28 (br), 128.84, 129.03, 129.73, 130.06, 131.85, 136.63, 138.42, 139.69, 141.13, 151.19, 219.49 (m), 297.66 (m). HR-MS ( $\text{FAB}^+$ ) Calculated for  $\text{C}_{42}\text{H}_{57}\text{N}_2\text{Cl}_2\text{PRu}$ , 792.2680; found, 792.2678.



**Catalyst 5b.** **5b** was prepared according to the above general procedure and

was obtained in 60% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  19.59 (s), 8.74-8.62 (m), 8.25 (br), 7.71 (br), 7.34-6.85 (m), 6.67 (br), 6.44 (br), 3.55-3.07 (m), 2.79-2.19 (m), 1.69-0.91 (m), 1.67-1.06 (m).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  25.75 (s), 25.04 (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  13.96, 23.71, 24.44, 26.72, 27.47 (d,  $J = 12$  Hz) 28.15 (d,  $J = 10$  Hz), 29.12 (br), 32.73 (d,  $J = 16$  Hz), 54.50 (br), 126.50, 127.86, 128.28, 128.37, 128.98, 129.38, 129.86, 130.21, 131.56 (br), 143.70, 151.13, 220.26 (m), 295.55 (m). HR-MS (FAB $^+$ ) Calculated for  $\text{C}_{44}\text{H}_{61}\text{N}_2\text{Cl}_2\text{PRu}$ , 820.2993; found, 920.2951.



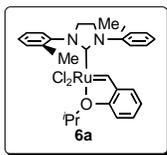
**Catalyst 5c.** **5c** was prepared according to the above general procedure and

was obtained in 68% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  19.68 (s), 19.49 (s), 8.93-8.87 (m), 8.30 (b), 7.60 (d), 7.34-7.12 (m), 6.97 (t), 6.80 (d), 6.70-6.44 (m), 3.85-3.08 (m), 2.22-2.12 (q), 2.02-1.91 (q), 1.66-0.97 (m).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  26.33 (s), 23.92 (s).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  23.51, 23.60, 25.67, 25.79, 25.87, 26.68 (d,  $J = 13$  Hz), 27.34, 27.43, 28.12 (d,  $J = 10$  Hz), 28.42, 28.95 (d,  $J = 13$  Hz), 32.72 (d,  $J = 19$  Hz), 32.85 (d,  $J = 16$  Hz), 55.33, 56.14, 126.35, 126.72, 127.01, 127.68, 127.91, 128.13, 128.36, 128.80, 128.91, 129.02, 129.12, 129.77, 130.04, 130.71, 130.83, 132.08, 138.33, 138.53, 139.65, 139.85, 146.23, 146.23, 146.88, 148.24, 148.30, 151.06, 151.61, 221.51 (d,  $J = 76$  Hz), 296.66 (m). HR-MS (FAB $^+$ ) Calculated for  $\text{C}_{46}\text{H}_{65}\text{N}_2\text{Cl}_2\text{PRu}$ , 848.3306; found, 848.3326.

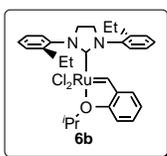
#### GENERAL PROCEDURE FOR THE PREPARATION OF CATALYSTS 6A-C.

2-Isopropoxy- $\beta$ -methylstyrene (0.89 g, 5.1 mmol, 2 equiv) was added to a solution of catalyst **5** (2.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (25 mL). The reaction mixture was refluxed for 1 h, then a 2.0 N solution of HCl in methanol (1.8 mL, 3.6 mmol, 1.5 equiv) was added and the mixture was refluxed for another hour, followed by evaporation to dryness *in vacuo*. The residue was dissolved in a minimal amount of  $\text{CH}_2\text{Cl}_2$  and catalyst **6** was precipitated by addition of pentane. The solids were collected by filtration and the catalysts purified by column chromatography on silica gel

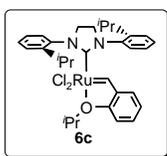
(eluted with 1:5 EtOAc-hexanes). The catalysts were obtained as green crystalline solids upon drying *in vacuo*.



**Catalyst 6a.** **6a** was prepared according to the above general procedure and was obtained in 71% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  16.47 (s, 1H), 8.59 (s, 1H), 7.43 (br, 8H), 6.91 (d,  $^3J_{\text{HH}} = 5.1$  Hz, 3H), 4.97 (m, 1H), 4.38 (s, 2H), 4.10 (s, 2H), 2.53 (s, 6H), 1.34 (br, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  18.24, 19.55, 22.11, 52.50, 54.73, 75.42, 113.51, 122.35, 122.91, 128.06, 129.36, 130.13, 130.50, 131.97, 138.56 (m), 142.32, 144.54, 153.00, 210.89, 295.21. HR-MS (FAB $^+$ ) Calculated for  $\text{C}_{27}\text{H}_{30}\text{N}_2\text{Cl}_2\text{OPRu}$ , 570.0779; found, 570.0788.



**Catalyst 6b.** **6b** was prepared according to the above general procedure and was obtained in 68%.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  16.48 (s, 1H), 8.56 (br, 1H), 7.53 (m, 8H), 6.89 (d,  $^3J_{\text{HH}} = 6.6$  Hz, 3H), 4.95 (m, 1H), 4.42 (s, 2H), 4.10 (s, 2H), 2.93 (br, 4H), 1.37 (br, 12H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  14.22, 14.80, 24.86, 53.17, 55.41, 75.44, 113.54, 122.26, 122.92, 127.91, 129.91, 130.12, 130.62, 144.47, 153.11, 211.06, 294.93. HR-MS (FAB $^+$ ) Calculated for  $\text{C}_{29}\text{H}_{34}\text{N}_2\text{Cl}_2\text{ORu}$ , 598.1092; found, 598.1109.



**Catalyst 6c.** **6c** was prepared according to the above general procedure and was obtained in 77% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  16.65 (s), 16.46 (s), 9.18 (m), 7.90 (d), 7.40-6.93 (m), 6.59 (t), 6.34 (d,  $^3J_{\text{HH}} = 7.5$  Hz), 4.47 (m), 3.80-3.32 (m), 2.66 (br), 1.95-1.12 (m).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  22.14 (m), 23.22, 24.24, 24.60, 25.77, 26.89, 26.98, 28.80, 29.12, 56.16, 75.33, 113.55, 122.10, 122.44, 122.91, 127.30, 127.67, 127.97, 129.00, 129.31, 129.79, 130.13, 130.59, 140.79 (m), 144.35, 148.07, 153.16, 211.70, 294.89. HR-MS (FAB $^+$ ) Calculated for  $\text{C}_{31}\text{H}_{38}\text{N}_2\text{Cl}_2\text{ORu}$ , 626.1405; found, 626.1365.

### GENERAL PROCEDURE FOR THE RCM OF 7 (MONITORED BY GC)

A round bottom flask filled with an atmosphere of argon was charged with a degassed solution of dimethyl 2,2-di(2-methylallyl)malonate (**7**) in CH<sub>2</sub>Cl<sub>2</sub> (0.1 M). The catalyst was added as a solid (5 mol %) and the flask was equipped with a reflux condenser and a bubbler outlet. The reaction vessel was immersed in an oil bath heated at the desired temperature. The progress of conversion to product was monitored by GC analysis after removing the catalyst by treating the aliquot with a solution of tris(hydroxymethyl)phosphine in isopropanol (1.0 M), heating the quenched mixture at 60 °C for 1 h, diluting it with water and extracting with ethyl acetate.

The reaction mixtures were analyzed by gas chromatography (GC) using a flame ionization detector (FID). The following conditions and equipment were used:

Column: Rtx-5, 30m x 0.25mm (ID) x 0.25µm film thickness.  
Manufacturer: Restek

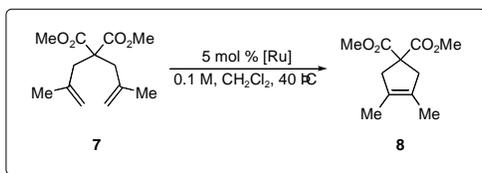
GC and column conditions: Injector temperature: 250°C  
Detector temperature: 280°C

Oven temperature: Starting temperature: 100°C, hold time: 1 minute.  
Ramp rate 10°C/min to 250°C, hold time: 12 minutes.  
Carrier gas: Helium

Mean gas velocity: 31.3 ± 3.5% cm/sec (calculated)

Split ratio: ~50:1

The product percentages given in Table 1 and Tables S1-S10 were determined by dividing the GC area of the product by the sum of the GC areas of product and substrate. The accuracy of this method was assessed by analyzing mixtures of substrate and product of known ratios. It was established that this method gives product percentages with 95 % accuracy (above 80 % conversion) and with 90 % accuracy (below 80 % conversion).



**Table S1:** RCM of **7** with 5 mol % of **1** at 40 °C

Time (h)	Product (GC%)
0.5	3.0
1	4.2
3	15.7
18	44.7
24	49.8
42	54.5

**Table S2:** RCM of **7** with 5 mol % of **2** at 40 °C

Time (h)	Product (GC%)
0.5	4.7
1	9.1
3	22.0
24	40.4
72	40.9

**Table S3:** RCM of **7** with 5 mol % of **3** at 40 °C

Time (h)	Product (GC%)
0.5	0.0
1	0.0
2	0.0
3	0.0
20	0.0
24	0.0

**Table S4:** RCM of **7** with 5 mol % of **4** at 40 °C

<b>Time (h)</b>	<b>Product (GC%)</b>
0.5	0.0
1	0.0
2	2.6
3	7.0
20	24.2

**Table S5:** RCM of **7** with 5 mol % of **5a** at 40 °C

<b>Time (h)</b>	<b>Product (GC%)</b>
0.25	80.9
0.5	83.7
0.75	85.4
1	86.4
1.5	87.5
2	86.7
4	86.8

**Table S6:** RCM of **7** with 5 mol % of **5b** at 40 °C

<b>Time (h)</b>	<b>Product (GC%)</b>
0.25	61.5
0.5	69.9
0.75	70.7
1	70.9
2	70.6
4	72.3
20	72.8

**Table S7:** RCM of **7** with 5 mol % of **5c** at 40 °C

<b>Time (h)</b>	<b>Product (GC%)</b>
0.25	71.5
0.5	73.0
0.75	73.1
1	74.3
1.5	75.0
2	75.5
4	75.1

**Table S8:** RCM of **7** with 5 mol % of **6a** at 40 °C

<b>Time (h)</b>	<b>Product (GC%)</b>
0.5	30.6
1	44.7
3	65.1
18	69.9
24	70.0
42	68.8

**Table S9:** RCM of **7** with 5 mol % of **6b** at 40 °C

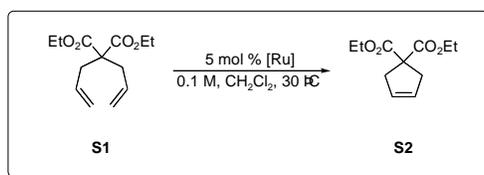
<b>Time (h)</b>	<b>Product (GC%)</b>
-----------------	----------------------

Time (h)	Product (GC%)
0.25	0.7
0.50	3.3
0.75	11.8
1	21.5
2	34.7
4	42.9
8	55.9
24	58.6

**Table S10:** RCM of **7** with 5 mol % of **6c** at 40 °C

Time (h)	Product (GC%)
0.25	0.7
0.50	2.9
0.75	9.3
1	15.6
1.5	24.2
2	27.5
6	32.0
24	32.5

**GENERAL PROCEDURE FOR ACTIVITY PLOTS OF RING-CLOSING METATHESIS.**<sup>ii</sup>

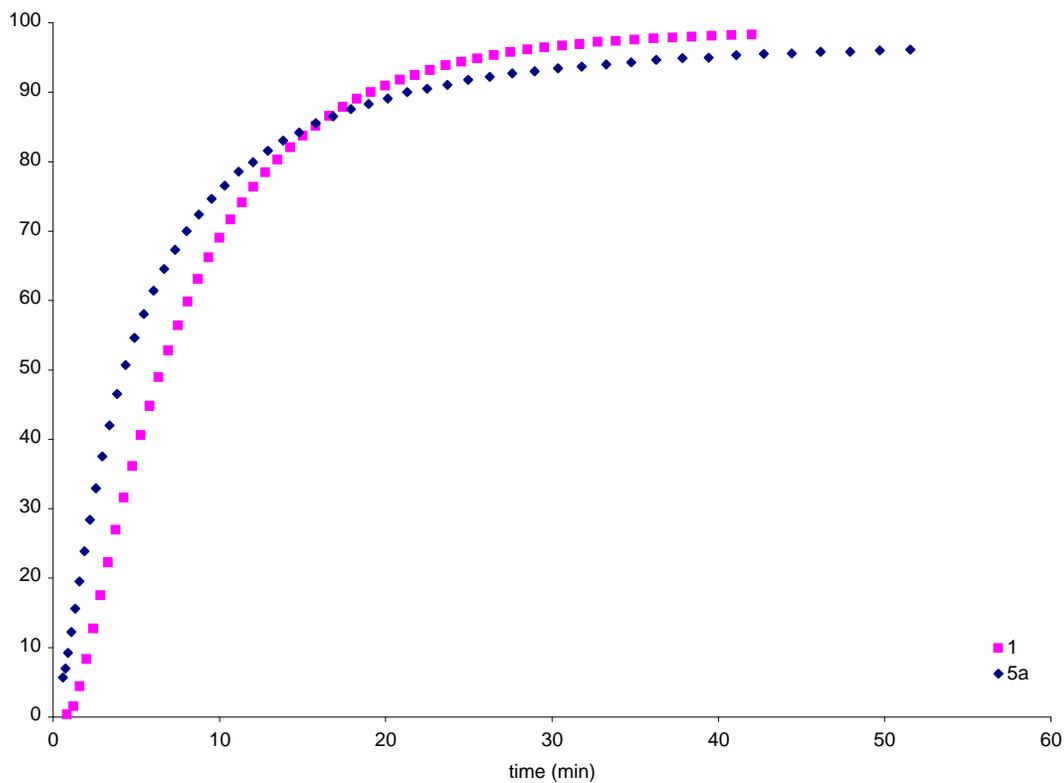


**RCM OF DIETHYL DIALLYLMALONATE (S1)**

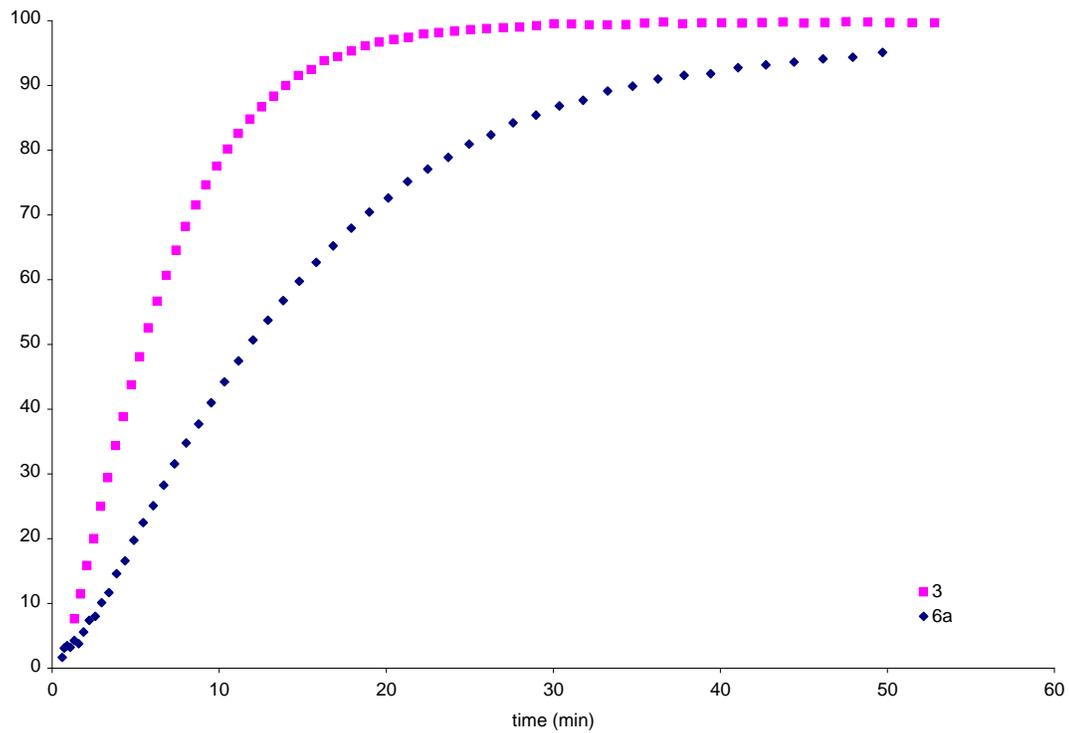
An NMR tube with a screw-cap septum top was charged inside a glovebox with catalyst stock solution (0.002 M, 0.4 mL, 0.80  $\mu$ mol, 1.0 mol%) and CD<sub>2</sub>Cl<sub>2</sub> (0.4 mL). The sample was equilibrated at 30 °C in the NMR probe before **S1** (19.3  $\mu$ L, 19.2 mg, 0.080 mmol, 0.1 M) was added via syringe. Data points were collected over an appropriate period of time using the

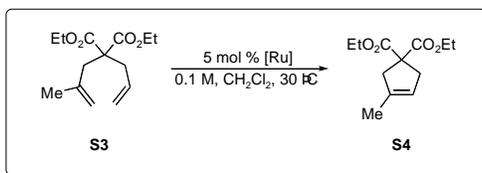
Varian array function. The conversion to **S2** was determined by comparing the ratio of the integrals of the methylene protons in the starting material,  $\delta$  2.61 (dt), with those in the product,  $\delta$  2.98 (s).

**Figure S1.** RCM of **S1** using catalysts **1** and **5a** (1 mol%, 30 °C, CD<sub>2</sub>Cl<sub>2</sub>).



**Figure S2.** RCM of **S1** using catalysts **3** and **6a** (1 mol%, 30 °C, CD<sub>2</sub>Cl<sub>2</sub>).

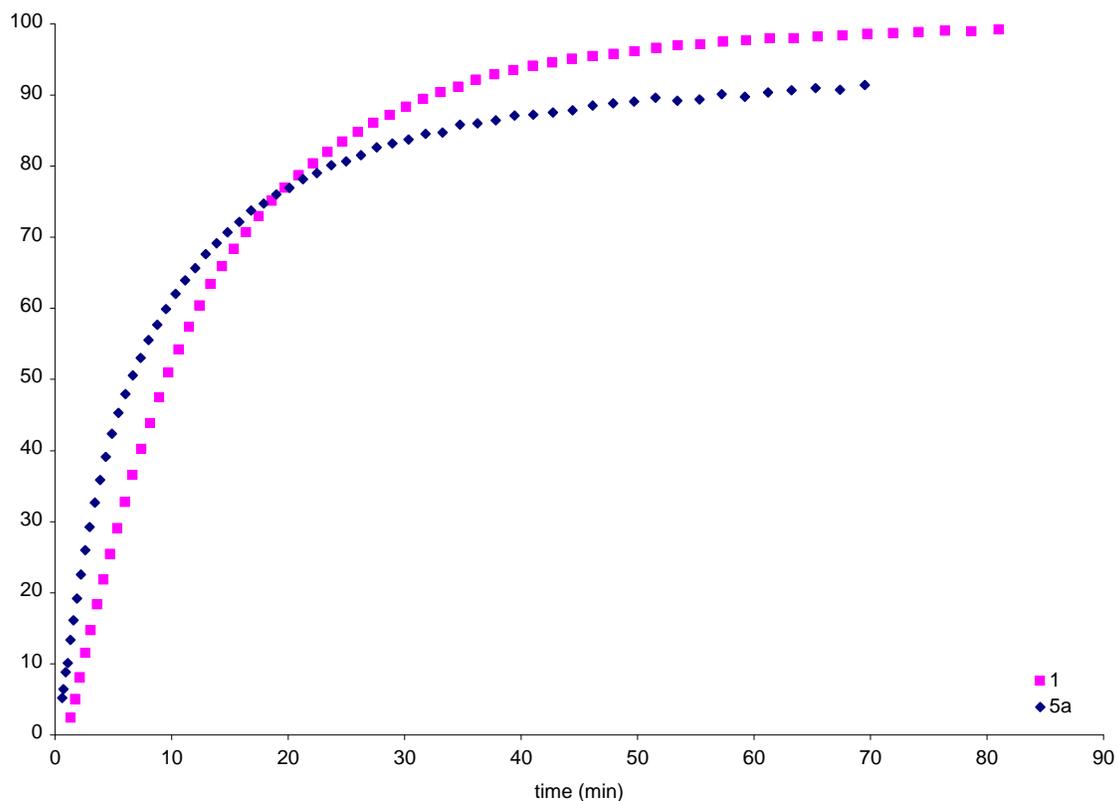




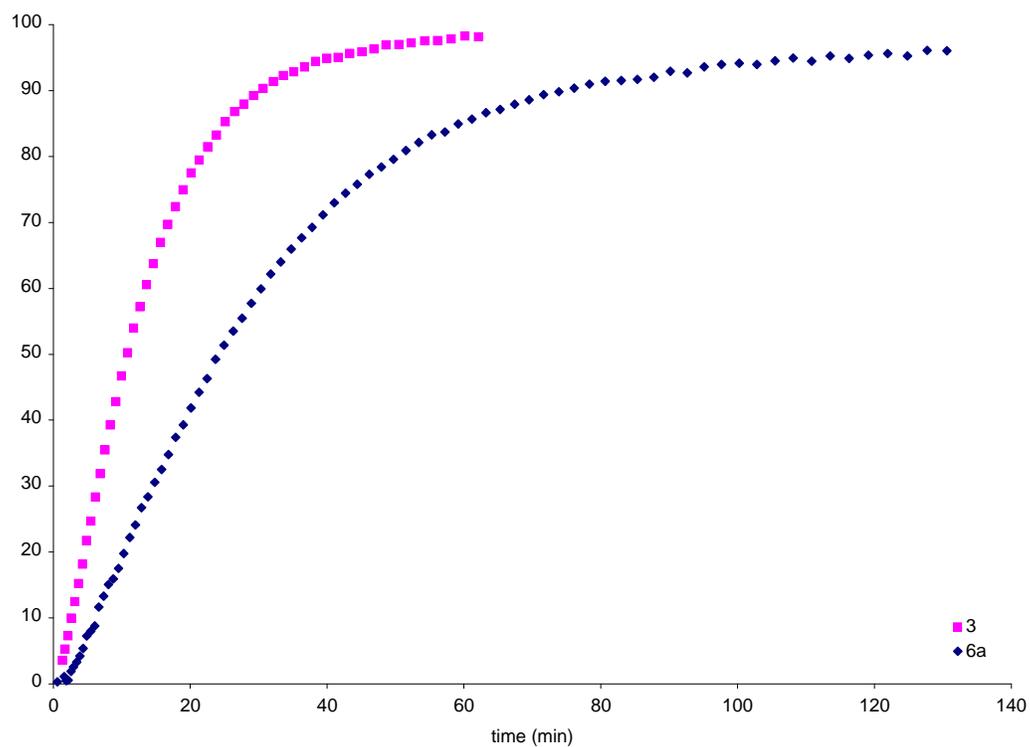
### RCM OF DIETHYL ALLYLMETHALLYLMALONATE (S3)

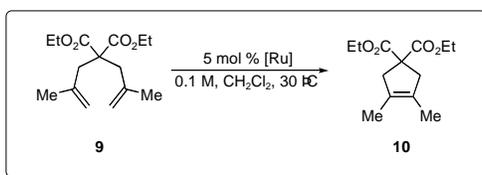
An NMR tube with a screw-cap septum top was charged inside a glovebox with catalyst stock solution (0.002 M, 0.4 mL, 0.80  $\mu\text{mol}$ , 1.0 mol%) and  $\text{CD}_2\text{Cl}_2$  (0.4 mL). The sample was equilibrated at 30 °C in the NMR probe before **S3** (20.5  $\mu\text{L}$ , 20.4 mg, 0.080 mmol, 0.1 M) was added via syringe. Data points were collected over an appropriate period of time using the Varian array function. The conversion to **S4** was determined by comparing the ratio of the integrals of the methylene protons in the starting material,  $\delta$  2.67 (s), 2.64 (dt), with those in the product,  $\delta$  2.93 (s), 2.88 (m).

**Figure S3.** RCM of **S3** using catalysts **1** and **5a** (1 mol%, 30 °C,  $\text{CD}_2\text{Cl}_2$ ).



**Figure S4.** RCM of **S3** using catalysts **3** and **6a** (1 mol%, 30 °C, CD<sub>2</sub>Cl<sub>2</sub>).

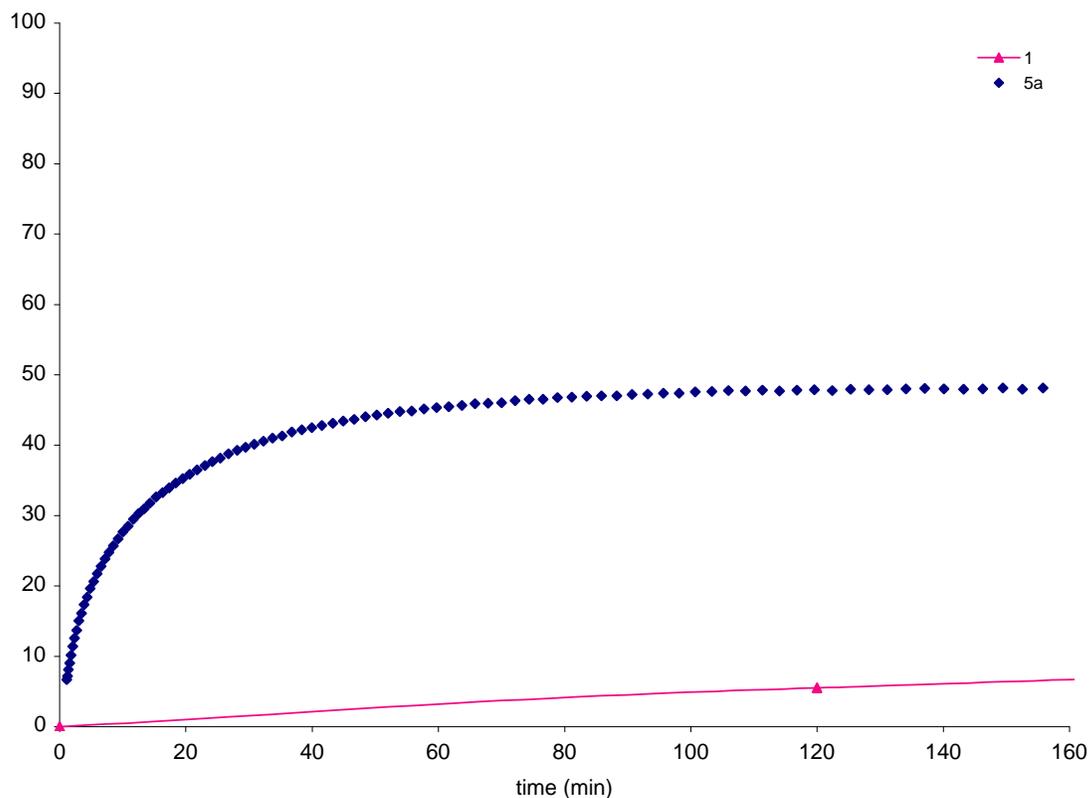




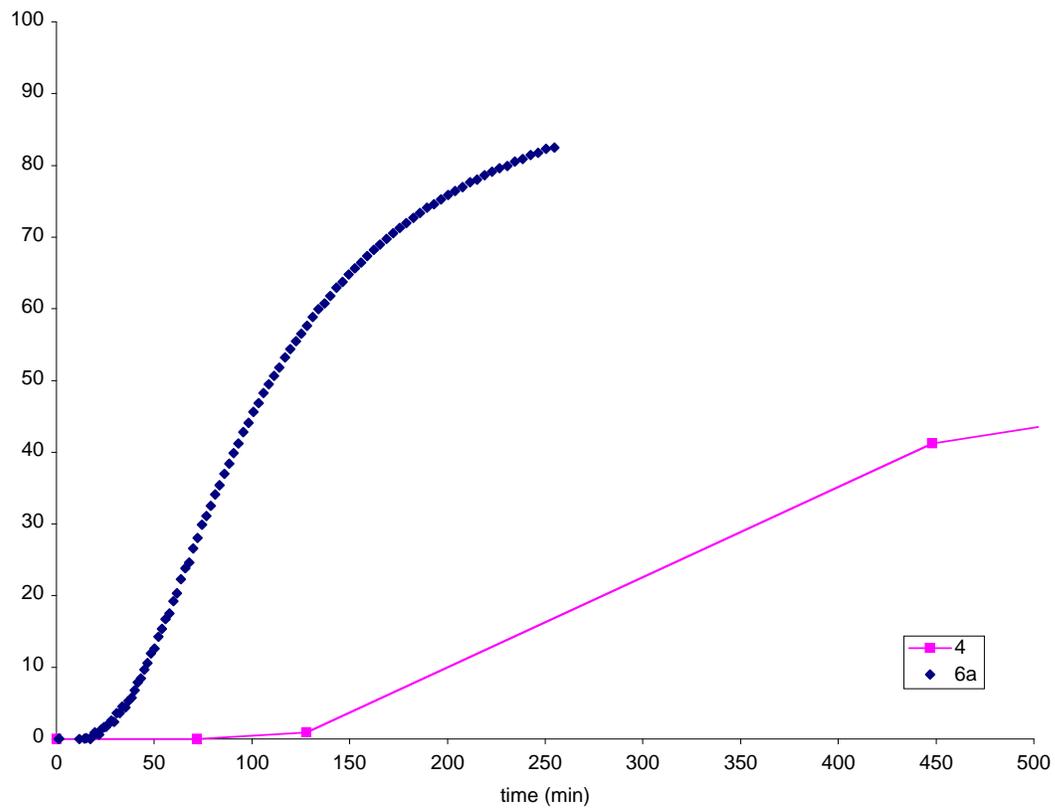
### RCM OF DIETHYL DIMETHALLYLMALONATE (**9**)

An NMR tube with a screw-cap septum top was charged inside a glovebox with catalyst stock solution (0.005 M in C<sub>6</sub>D<sub>6</sub> or CD<sub>2</sub>Cl<sub>2</sub>, 0.8 mL, 4.0 μmol, 5.0 mol%). The sample was equilibrated at 30 °C or 60 °C in the NMR probe before **9** (21.6 μL, 21.5 mg, 0.080 mmol, 0.1 M) was added via syringe. Data points were collected over an appropriate period of time using the Varian array function. The conversion to **10** was determined by comparing the ratio of the integrals of the methylene protons in the starting material, δ 2.71 (s), with those in the product, δ 2.89 (s).

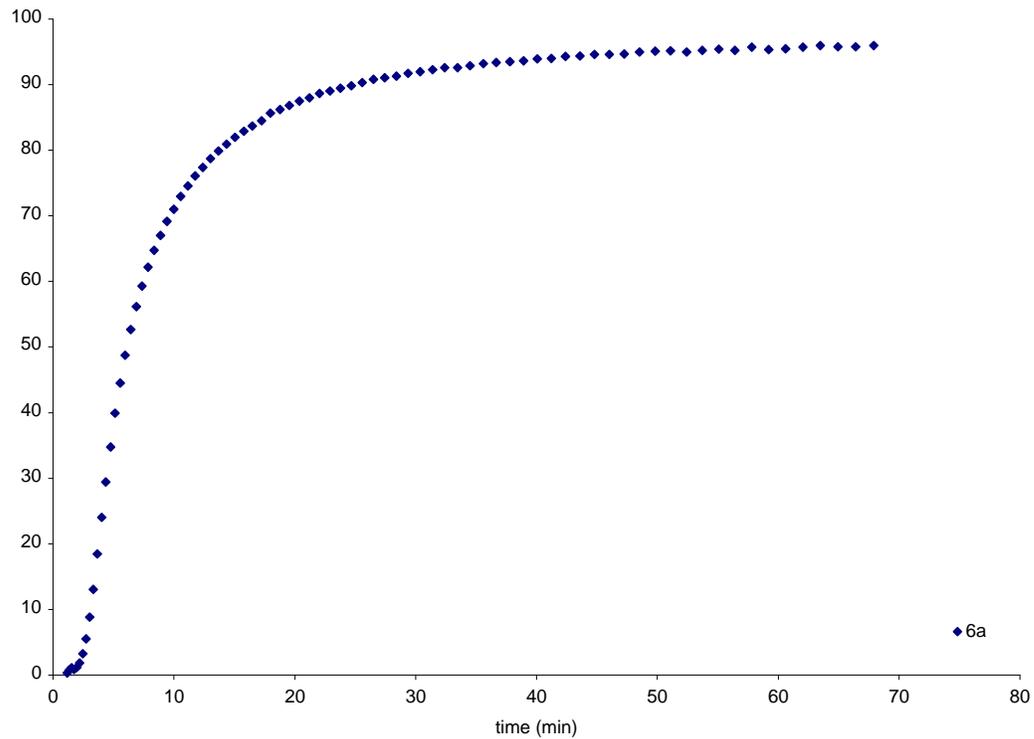
**Figure S5.** RCM of **9** using catalysts **1** and **5a** (5 mol%, 30 °C, CD<sub>2</sub>Cl<sub>2</sub>).



**Figure S6.** RCM of **9** using catalysts **4** and **6a** (5 mol%, 30 °C, CD<sub>2</sub>Cl<sub>2</sub>).

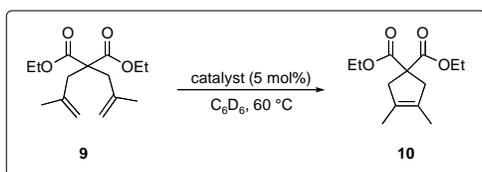


**Figure S7.** RCM of **9** using catalysts **6a** (2.5 mol%, 60 °C, C<sub>6</sub>D<sub>6</sub>).



### GENERAL RCM PROCEDURE FOR TABLE 2.<sup>iii</sup>

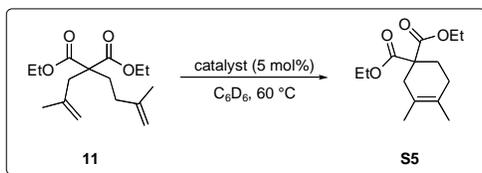
An NMR tube with a screw-cap septum top was charged inside a glovebox with catalyst stock solution (0.005 M in C<sub>6</sub>D<sub>6</sub>, 0.8 mL, 4.0 μmol, 5.0 mol%). The appropriate substrate (**11-18**, 0.080 mmol, 0.1 M) was added via syringe and the sample placed in an oil bath regulated at 60 °C. <sup>1</sup>H NMR spectra were taken at regular intervals. Conversion was determined by comparing the ratio of the integrals of the signals described below:



The SM methylene signal at 2.99 ppm was compared to the product signal at 3.14 ppm.

### ISOLATED YIELD FOR **10**.

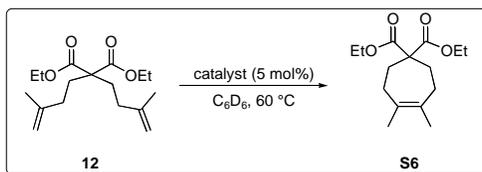
In an argon-filled glove box, a 20 mL vial equipped with a stir bar was charged with **9** (472 mg, 1.76 mmol), toluene (17.6 mL), and catalyst **6a** (50 mg, 0.088 mmol, 5 mol %). The vial was then capped with a septum screw-cap, taken out of the glove box and heated to 60 °C for 1 hour while stirring and flushing the headspace with argon. The reaction mixture was treated to remove the catalyst: it was poured into a 2.0 M solution of tris(hydroxymethyl)phosphine in isopropanol (10 mL) and this mixture heated to 60 °C for 1 hour. The colorless solution was diluted with water (10 mL) and the organic phase was extracted with diethyl ether (2 x 10 mL), dried with magnesium sulfate, filtered and concentrated by rotary evaporation. The residue was purified by flash chromatography using hexanes as eluant before flushing the product with ethyl acetate. The fractions containing the product were combined and the volatiles were removed under vacuum to give **10** (422 mg, 1.75 mmol, 100% yield).



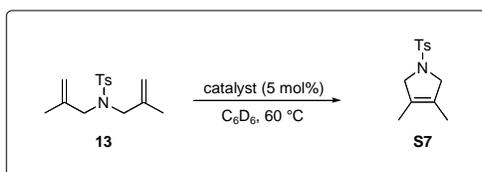
The SM methylene signal at 2.72 ppm was compared to the product signal at 2.63 ppm.

#### ISOLATED YIELD FOR S5.

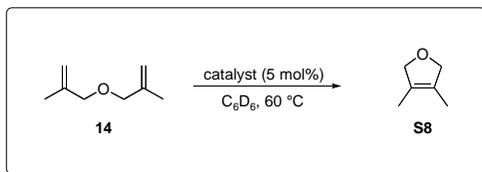
A 10 mL 2-neck round-bottom flask was outfitted with a reflux condenser and a septum, and flame-dried under vacuum. After cooling to r.t., **6a** (5.1 mg, 0.009 mmol, 5 mol%) was added as a solid. Dry degassed benzene (1.8 mL) was added via syringe, followed by **11** (52  $\mu$ L, 0.185 mmol) via syringe. The septum was replaced with a ground-glass stopper, and the solution was stirred at 60 °C for 1 h. The solution was cooled to r.t., and concentrated via rotary evaporation. Column chromatography (SiO<sub>2</sub>, 5% EtOAc:hexanes) afforded **S5** as a colorless oil (47 mg, 0.185, 100%).



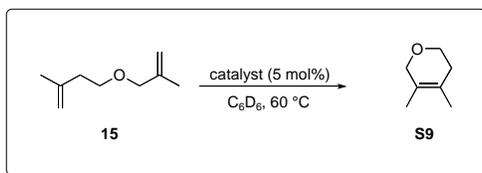
The SM methyl group signal at 1.59 ppm was compared to the product signal at 1.50 ppm.



The SM methyl group signal at 3.62 ppm was compared to the product signal at 3.84 ppm.



The SM methylene signal at 3.68 ppm was compared to the product signal at 4.45 ppm.



The SM methylene signal at 3.51 ppm was compared to the product signal at 3.76 ppm.

## X-RAY DIFFRACTION DATA FOR 6A

**Table S11.** Crystal Data for **6a**<sup>iv</sup>

Empirical formula	C <sub>27</sub> H <sub>30</sub> N <sub>2</sub> OCl <sub>2</sub> Ru	
Formula weight	570.50	
Crystallization Solvent	Benzene/pentane	
Crystal Habit	Block	
Crystal size	0.34 x 0.28 x 0.14 mm <sup>3</sup>	
Crystal color	Dark green	
Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoK $\alpha$	
Data Collection Temperature	100(2) K	
$\theta$ range for 33816 reflections used in lattice determination	2.34 to 41.57°	
Unit cell dimensions	a = 11.5794(3) Å b = 13.9350(4) Å c = 16.6418(5) Å	$\beta$ = 105.5780(10)°
Volume	2586.66(13) Å <sup>3</sup>	
Z	4	
Crystal system	Monoclinic	
Space group	P2 <sub>1</sub> /c	
Density (calculated)	1.465 Mg/m <sup>3</sup>	
F(000)	1168	
$\theta$ range for data collection	1.83 to 41.89°	
Completeness to $\theta = 41.89^\circ$	83.1 %	
Index ranges	-20 $\leq$ h $\leq$ 20, -25 $\leq$ k $\leq$ 25, -28 $\leq$ l $\leq$ 30	
Data collection scan type	$\omega$ scans at 7 $\phi$ settings	
Reflections collected	79070	
Independent reflections	14920 [R <sub>int</sub> = 0.0822]	
Absorption coefficient	0.835 mm <sup>-1</sup>	
Absorption correction	None	
Max. and min. transmission	0.8921 and 0.7645	

**Table S12.** Structure solution and refinement for **6a**

Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods

Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	14920 / 15 / 332
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F <sup>2</sup>	1.350
Final R indices [I>2σ(I), 10742 reflections]	R1 = 0.0348, wR2 = 0.0652
R indices (all data)	R1 = 0.0575, wR2 = 0.0688
Type of weighting scheme used	Sigma
Weighting scheme used	w=1/σ <sup>2</sup> (Fo <sup>2</sup> )
Max shift/error	0.002
Average shift/error	0.000
Largest diff. peak and hole	1.532 and -1.125 e.Å <sup>-3</sup>

**Table S13.** Atomic Coordinates for **6a**

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **6a**.  
 $U(\text{eq})$  is defined as the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	$U_{\text{eq}}$	Occ
Ru(1)	2308(1)	7881(1)	4144(1)	13(1)	1
Cl(1)	4001(1)	7354(1)	5170(1)	20(1)	1
Cl(2)	510(1)	7840(1)	3070(1)	21(1)	1
O(1)	1253(1)	7777(1)	5129(1)	19(1)	1
N(1)	3747(1)	7208(1)	3081(1)	21(1)	1
N(2)	3374(1)	8725(1)	2819(1)	18(1)	1
C(1)	3211(1)	7990(1)	3305(1)	15(1)	1
C(2)	4111(2)	7365(1)	2308(1)	30(1)	1
C(3)	4132(1)	8459(1)	2266(1)	26(1)	1
C(4)	3626(1)	6248(1)	3360(1)	24(1)	1
C(5)	4658(2)	5721(1)	3737(1)	31(1)	1
C(6)	4494(2)	4784(1)	3986(1)	40(1)	1
C(7)	3367(2)	4386(1)	3866(1)	42(1)	1
C(8)	2360(2)	4917(1)	3492(1)	38(1)	1
C(9)	2494(2)	5858(1)	3236(1)	28(1)	1
C(10)	5894(2)	6144(1)	3902(1)	40(1)	1
C(11)	3010(2)	9703(1)	2852(1)	16(1)	0.914(2)
C(12)	3802(1)	10388(1)	3313(1)	18(1)	0.914(2)
C(13)	3374(1)	11330(1)	3324(1)	21(1)	0.914(2)
C(14)	2222(2)	11579(1)	2878(1)	23(1)	0.914(2)
C(15)	1456(1)	10893(1)	2413(1)	22(1)	0.914(2)
C(16)	1851(1)	9952(1)	2406(1)	20(1)	0.914(2)
C(17)	5050(2)	10127(1)	3804(1)	27(1)	0.914(2)
C(11B)	3366(10)	9686(5)	3060(9)	15(4)	0.086(2)
C(12B)	2437(7)	10334(6)	2723(6)	14(2)	0.086(2)
C(13B)	2553(8)	11270(5)	3047(7)	12(2)	0.086(2)
C(14B)	3558(9)	11550(5)	3665(7)	14(3)	0.086(2)
C(15B)	4470(8)	10897(6)	3991(6)	15(3)	0.086(2)
C(16B)	4394(7)	9976(5)	3659(6)	8(2)	0.086(2)
C(17B)	1349(10)	10045(9)	2048(9)	31(4)	0.086(2)
C(18)	2351(1)	9129(1)	4498(1)	15(1)	1
C(19)	1810(1)	9379(1)	5154(1)	14(1)	1
C(20)	1840(1)	10317(1)	5467(1)	19(1)	1
C(21)	1284(1)	10539(1)	6085(1)	22(1)	1
C(22)	697(1)	9816(1)	6398(1)	23(1)	1
C(23)	670(1)	8871(1)	6116(1)	21(1)	1
C(24)	1220(1)	8662(1)	5490(1)	16(1)	1
C(25)	679(1)	6957(1)	5418(1)	23(1)	1
C(26)	1224(2)	6064(1)	5147(1)	30(1)	1
C(27)	-670(1)	7000(1)	5046(1)	33(1)	1

**Table S14.** Selected bond lengths [Å] and angles [°] for **6a**

Ru(1)-C(18)	1.8329(11)	C(18)-Ru(1)-C(1)	100.45(5)
Ru(1)-C(1)	1.9611(11)	C(18)-Ru(1)-O(1)	78.71(4)
Ru(1)-O(1)	2.2979(8)	C(1)-Ru(1)-O(1)	179.15(4)
Ru(1)-Cl(1)	2.3445(3)	C(18)-Ru(1)-Cl(1)	96.76(4)
Ru(1)-Cl(2)	2.3523(3)	C(1)-Ru(1)-Cl(1)	92.38(4)
		O(1)-Ru(1)-Cl(1)	87.76(3)
		C(18)-Ru(1)-Cl(2)	102.05(4)
		C(1)-Ru(1)-Cl(2)	89.65(4)
		O(1)-Ru(1)-Cl(2)	90.49(3)
		Cl(1)-Ru(1)-Cl(2)	160.382(12)

**Table S15.** Bond lengths [Å] and angles [°] for **6a**

Ru(1)-C(18)	1.8329(11)	C(12B)-C(17B)	1.501(2)
Ru(1)-C(1)	1.9611(11)	C(13B)-C(14B)	1.386(2)
Ru(1)-O(1)	2.2979(8)	C(14B)-C(15B)	1.389(2)
Ru(1)-Cl(1)	2.3445(3)	C(15B)-C(16B)	1.390(2)
Ru(1)-Cl(2)	2.3523(3)	C(18)-C(19)	1.4404(15)
O(1)-C(24)	1.3766(14)	C(19)-C(20)	1.4042(16)
O(1)-C(25)	1.4664(14)	C(19)-C(24)	1.4074(16)
N(1)-C(1)	1.3550(14)	C(20)-C(21)	1.3869(17)
N(1)-C(4)	1.4352(16)	C(21)-C(22)	1.392(2)
N(1)-C(2)	1.4742(16)	C(22)-C(23)	1.3952(18)
N(2)-C(1)	1.3503(15)	C(23)-C(24)	1.3912(16)
N(2)-C(11B)	1.399(6)	C(25)-C(26)	1.5167(19)
N(2)-C(11)	1.4316(16)	C(25)-C(27)	1.519(2)
N(2)-C(3)	1.4794(15)		
C(2)-C(3)	1.526(2)	C(18)-Ru(1)-C(1)	100.45(5)
C(4)-C(9)	1.383(2)	C(18)-Ru(1)-O(1)	78.71(4)
C(4)-C(5)	1.400(2)	C(1)-Ru(1)-O(1)	179.15(4)
C(5)-C(6)	1.397(2)	C(18)-Ru(1)-Cl(1)	96.76(4)
C(5)-C(10)	1.503(3)	C(1)-Ru(1)-Cl(1)	92.38(4)
C(6)-C(7)	1.382(3)	O(1)-Ru(1)-Cl(1)	87.76(3)
C(7)-C(8)	1.381(3)	C(18)-Ru(1)-Cl(2)	102.05(4)
C(8)-C(9)	1.400(2)	C(1)-Ru(1)-Cl(2)	89.65(4)
C(11)-C(16)	1.392(2)	O(1)-Ru(1)-Cl(2)	90.49(3)
C(11)-C(12)	1.402(2)	Cl(1)-Ru(1)-Cl(2)	160.382(12)
C(12)-C(13)	1.4038(19)	C(24)-O(1)-C(25)	119.21(9)
C(12)-C(17)	1.501(2)	C(24)-O(1)-Ru(1)	109.69(7)
C(13)-C(14)	1.386(2)	C(25)-O(1)-Ru(1)	131.09(7)
C(14)-C(15)	1.389(2)	C(1)-N(1)-C(4)	124.61(10)
C(15)-C(16)	1.3902(19)	C(1)-N(1)-C(2)	112.39(10)
C(11B)-C(16B)	1.392(3)	C(4)-N(1)-C(2)	119.80(10)
C(11B)-C(12B)	1.402(2)	C(1)-N(2)-C(11B)	122.8(7)
C(12B)-C(13B)	1.404(2)	C(1)-N(2)-C(11)	127.49(10)

C(11B)-N(2)-C(11)	18.8(3)	C(14)-C(15)-C(16)	119.42(14)
C(1)-N(2)-C(3)	112.63(10)	C(15)-C(16)-C(11)	120.24(14)
C(11B)-N(2)-C(3)	118.0(8)	C(16B)-C(11B)-N(2)	114.4(5)
C(11)-N(2)-C(3)	119.52(10)	C(16B)-C(11B)-C(12B)	121.08(18)
N(2)-C(1)-N(1)	107.24(10)	N(2)-C(11B)-C(12B)	124.4(5)
N(2)-C(1)-Ru(1)	132.26(8)	C(11B)-C(12B)-C(13B)	117.48(18)
N(1)-C(1)-Ru(1)	120.34(8)	C(11B)-C(12B)-C(17B)	121.73(19)
N(1)-C(2)-C(3)	101.52(10)	C(13B)-C(12B)-C(17B)	120.79(19)
N(2)-C(3)-C(2)	101.69(10)	C(14B)-C(13B)-C(12B)	121.37(18)
C(9)-C(4)-C(5)	121.43(13)	C(13B)-C(14B)-C(15B)	120.29(18)
C(9)-C(4)-N(1)	119.31(12)	C(14B)-C(15B)-C(16B)	119.32(19)
C(5)-C(4)-N(1)	119.25(14)	C(15B)-C(16B)-C(11B)	120.2(2)
C(6)-C(5)-C(4)	117.10(17)	C(19)-C(18)-Ru(1)	119.54(8)
C(6)-C(5)-C(10)	120.72(15)	C(20)-C(19)-C(24)	118.62(10)
C(4)-C(5)-C(10)	122.14(14)	C(20)-C(19)-C(18)	122.29(11)
C(7)-C(6)-C(5)	122.04(16)	C(24)-C(19)-C(18)	119.08(10)
C(8)-C(7)-C(6)	120.02(15)	C(21)-C(20)-C(19)	120.87(12)
C(7)-C(8)-C(9)	119.32(18)	C(20)-C(21)-C(22)	119.09(12)
C(4)-C(9)-C(8)	120.10(15)	C(21)-C(22)-C(23)	121.77(11)
C(16)-C(11)-C(12)	121.15(12)	C(24)-C(23)-C(22)	118.40(12)
C(16)-C(11)-N(2)	117.96(13)	O(1)-C(24)-C(23)	125.86(11)
C(12)-C(11)-N(2)	120.89(15)	O(1)-C(24)-C(19)	112.93(9)
C(11)-C(12)-C(13)	117.54(14)	C(23)-C(24)-C(19)	121.21(11)
C(11)-C(12)-C(17)	121.70(13)	O(1)-C(25)-C(26)	106.31(10)
C(13)-C(12)-C(17)	120.73(14)	O(1)-C(25)-C(27)	110.04(11)
C(14)-C(13)-C(12)	121.32(14)	C(26)-C(25)-C(27)	112.08(13)
C(13)-C(14)-C(15)	120.31(13)		

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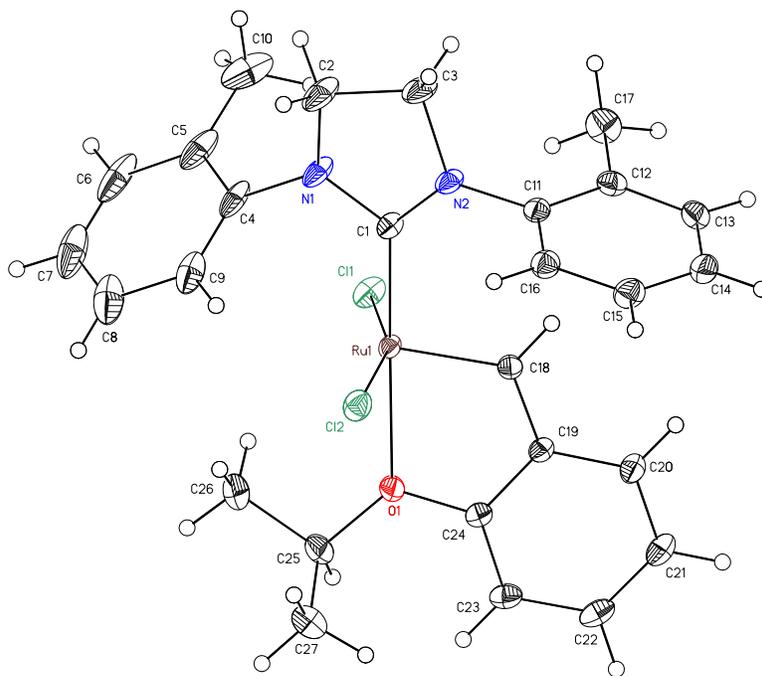
**Table S16.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^4$ ) for **6a**

The anisotropic displacement factor exponent takes the form:

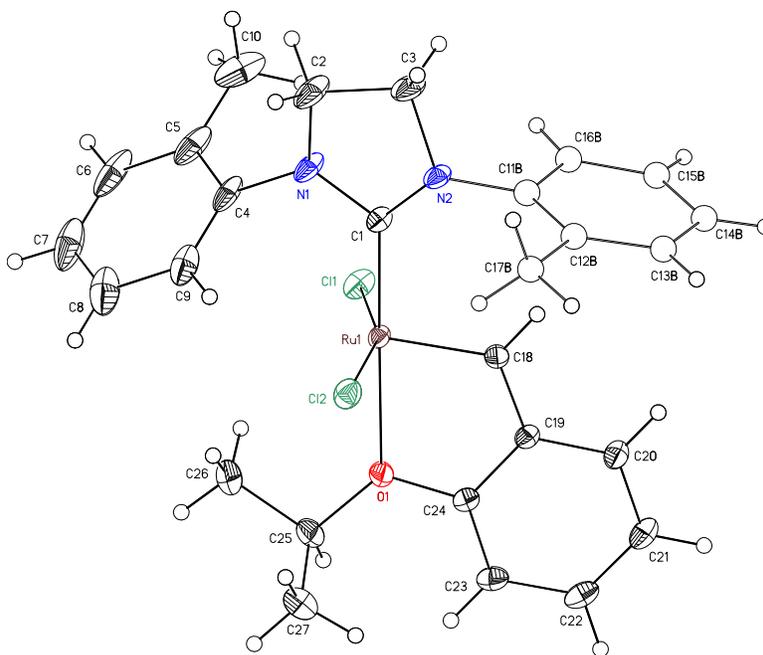
$$-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$$

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
Ru(1)	167(1)	116(1)	121(1)	0(1)	60(1)	17(1)
Cl(1)	254(2)	225(1)	131(1)	30(1)	55(1)	80(1)
Cl(2)	185(1)	205(1)	218(1)	-50(1)	26(1)	5(1)
O(1)	250(5)	147(4)	205(4)	-14(3)	129(4)	-27(3)
N(1)	341(6)	188(4)	149(5)	31(4)	136(4)	115(4)
N(2)	239(6)	168(4)	164(5)	26(4)	123(4)	52(4)
C(1)	165(5)	155(5)	116(5)	11(4)	32(4)	42(4)
C(2)	483(10)	270(6)	216(7)	51(5)	220(7)	162(6)
C(3)	347(8)	272(6)	226(6)	33(5)	201(6)	75(6)
C(4)	426(8)	186(5)	123(5)	21(4)	113(5)	146(6)
C(5)	498(10)	301(7)	146(6)	44(5)	128(6)	232(7)
C(6)	749(13)	286(7)	191(7)	75(6)	184(8)	319(8)
C(7)	882(15)	184(6)	225(7)	42(5)	191(9)	129(8)
C(8)	682(13)	206(6)	263(8)	-1(6)	131(8)	1(7)
C(9)	473(9)	181(5)	191(6)	8(5)	86(6)	80(6)
C(10)	416(10)	569(11)	260(8)	102(7)	149(7)	271(9)
C(11)	210(9)	159(6)	142(7)	19(4)	96(6)	8(5)
C(12)	179(7)	209(6)	181(6)	27(5)	77(5)	-6(5)
C(13)	238(8)	188(6)	228(7)	4(5)	103(6)	-35(5)
C(14)	261(8)	174(6)	288(8)	16(5)	128(6)	26(6)
C(15)	192(7)	219(6)	254(7)	28(5)	53(6)	47(5)
C(16)	210(7)	196(6)	186(6)	6(5)	68(5)	8(5)
C(17)	216(8)	295(7)	268(8)	27(6)	14(6)	6(6)
C(18)	186(6)	149(4)	146(5)	-7(4)	76(4)	-12(4)
C(19)	158(6)	150(4)	132(5)	-4(4)	49(4)	18(4)
C(20)	222(6)	156(5)	184(6)	-18(4)	62(5)	16(5)
C(21)	275(7)	212(5)	193(6)	-49(5)	78(5)	47(5)
C(22)	237(7)	295(6)	176(6)	-30(5)	91(5)	63(5)
C(23)	214(6)	255(6)	188(6)	-7(5)	108(5)	5(5)
C(24)	155(6)	171(5)	147(5)	-6(4)	52(4)	10(4)
C(25)	278(7)	187(5)	261(6)	22(5)	128(5)	-48(5)
C(26)	381(9)	162(5)	406(9)	-3(6)	171(7)	-41(6)
C(27)	286(8)	301(7)	419(9)	-15(6)	148(7)	-82(6)

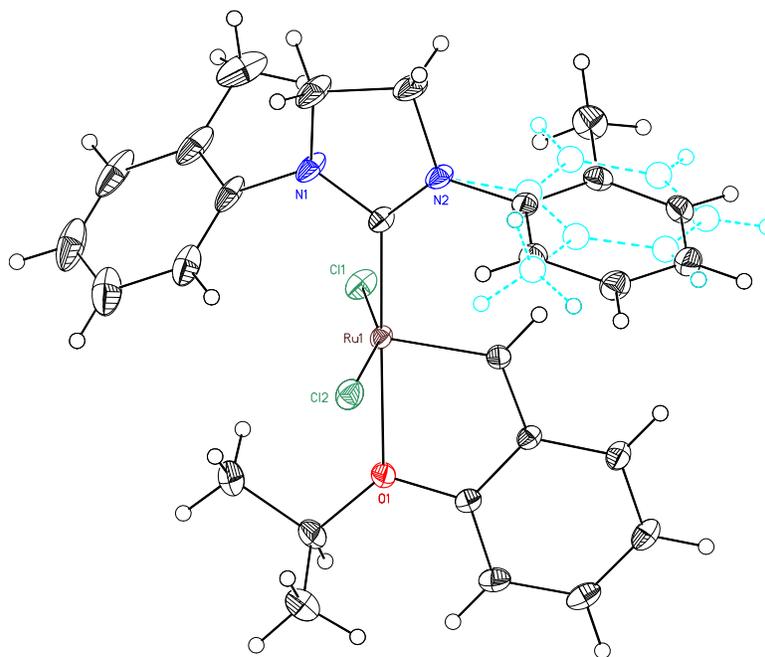
**Figure S8.** ORTEP drawing of *syn-6a*



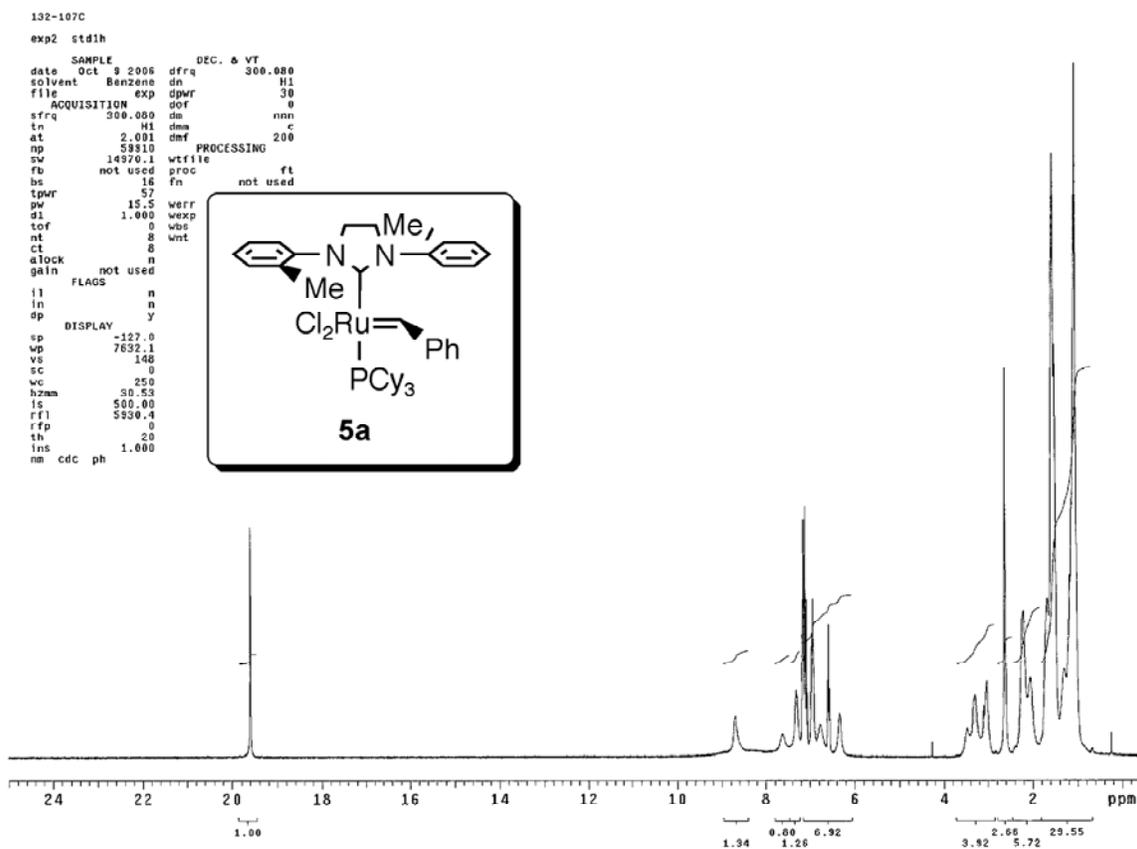
**Figure S9.** ORTEP drawing of *anti-6a*

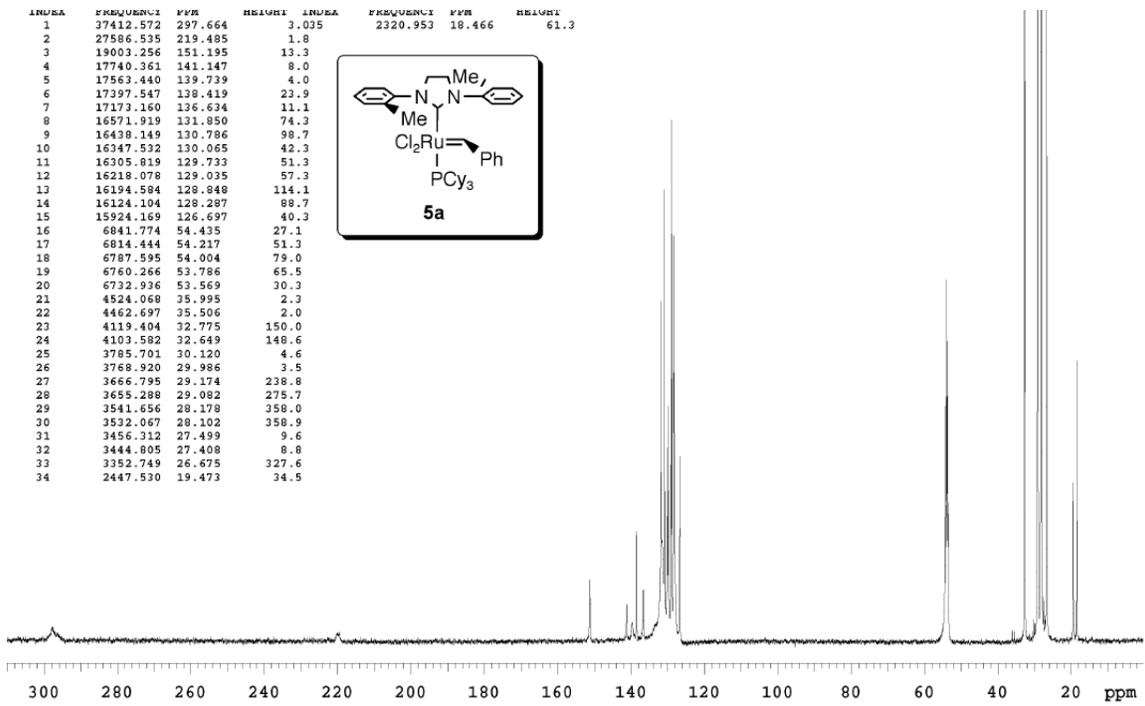


**Figure S10.** ORTEP drawing of superimposed *syn*- and *anti*-**6a**



# $^1\text{H}$ AND $^{13}\text{C}$ NMR SPECTRA OF 5A-C AND 6A-C

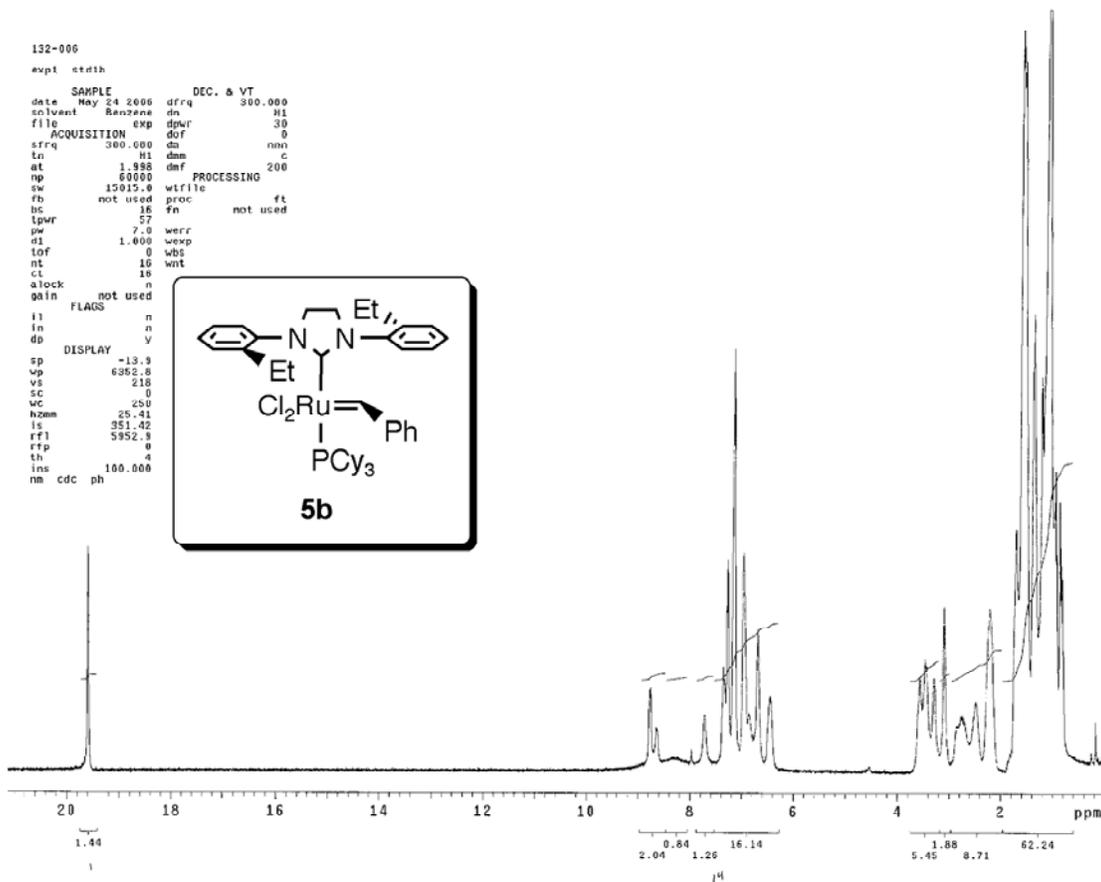
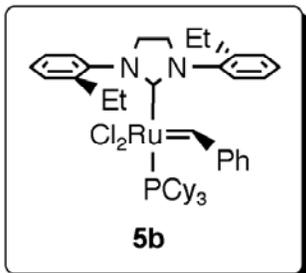


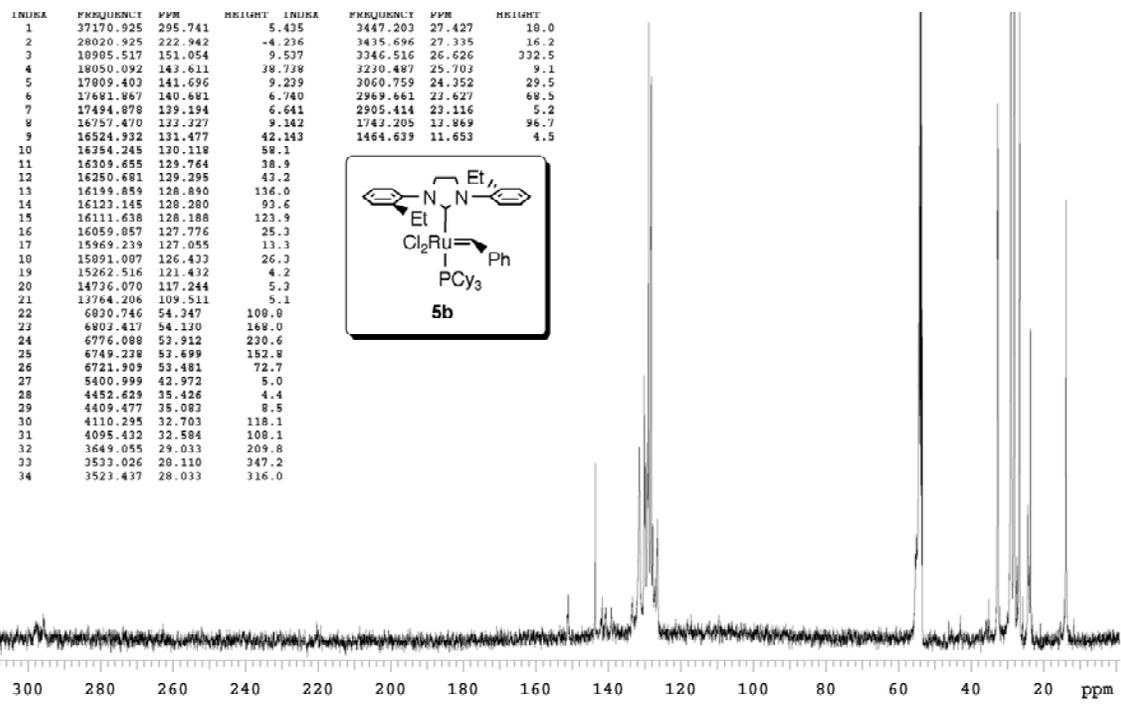


132-006

expt etdth

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tn      H1        dam     c
at      1.998     dmf     200
np      60000
sw      15015.0   wfile
fb      not used  proc   ft
hc      16       fn     not used
lpwr    57
pw      7.0      werr
d1      1.000    wexp
tof     0        wbs
nt      16      wnt
cl      16
alock   not used
gain    not used
FLACS   n
i1      n
in      n
dp      y
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nm cdc ph
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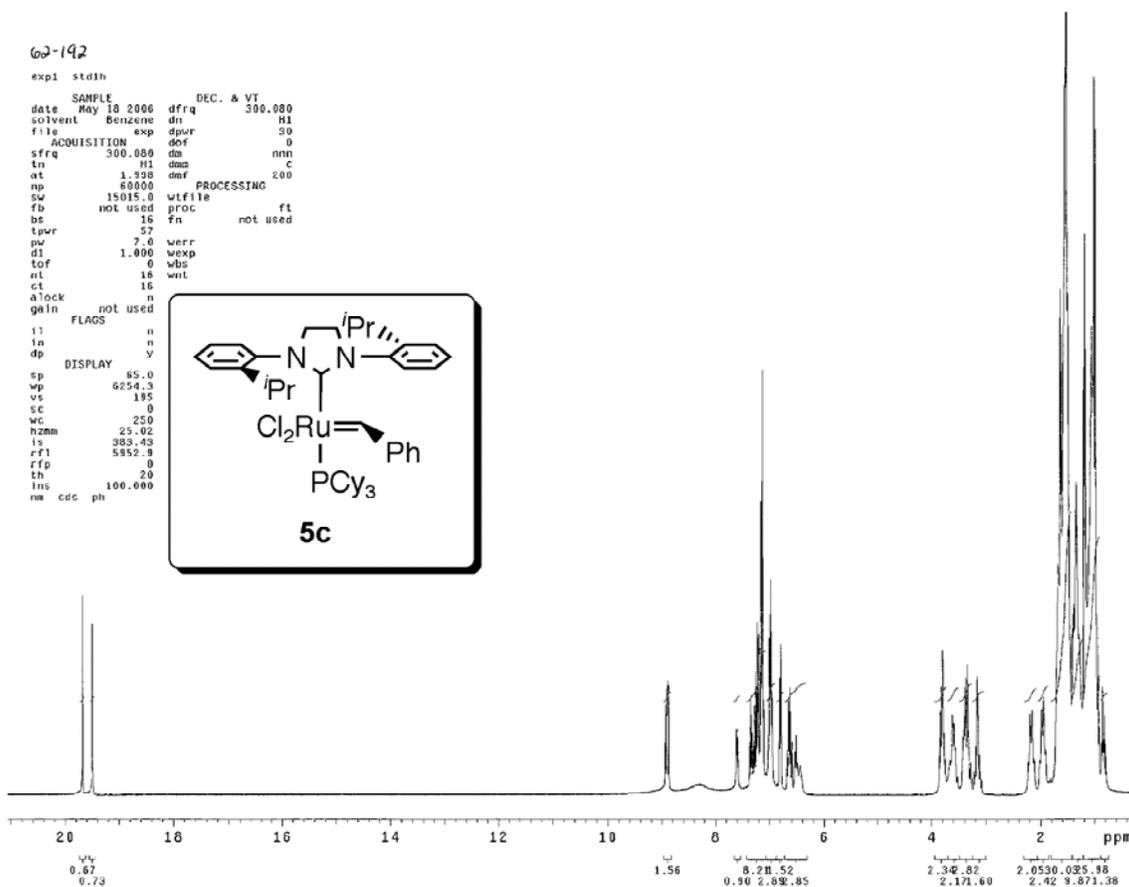
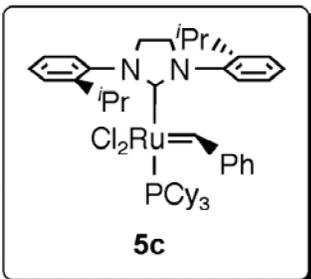




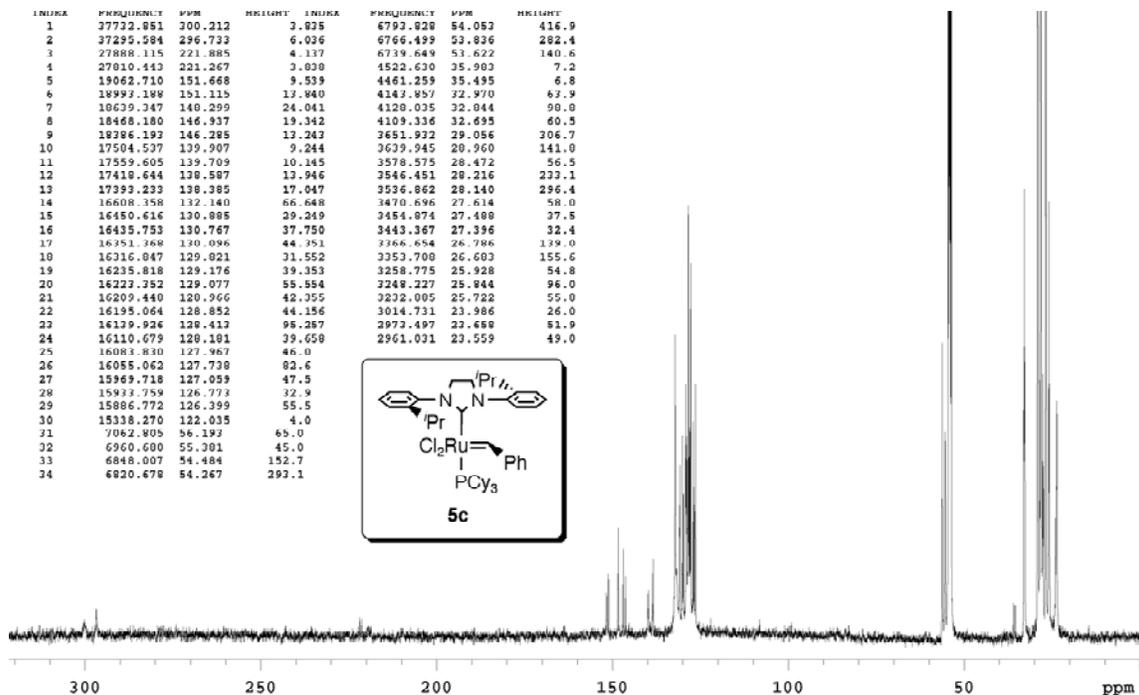
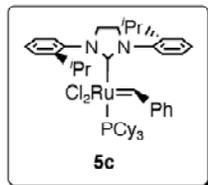
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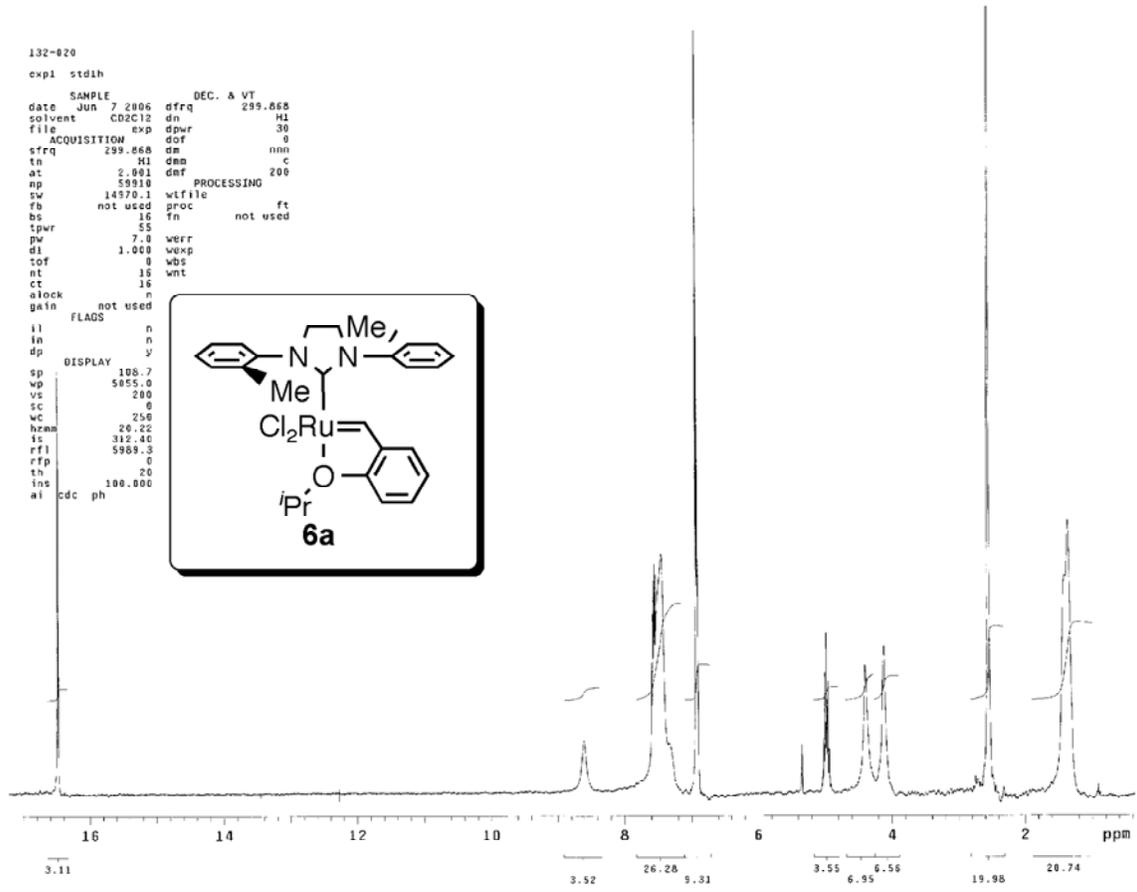
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at 1.998 dmf 200
np 60000
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fb not used proc ft
bs 16 fn not used
tpwr 57
pw 7.0 wevr
d1 1.000 wexp
tof 0 wbs
nt 18 wnt
ct 16
alock not used n
gain n
FLAGS
i1 n
fn n
dp y
DISPLAY
sp 85.0
wp 6254.3
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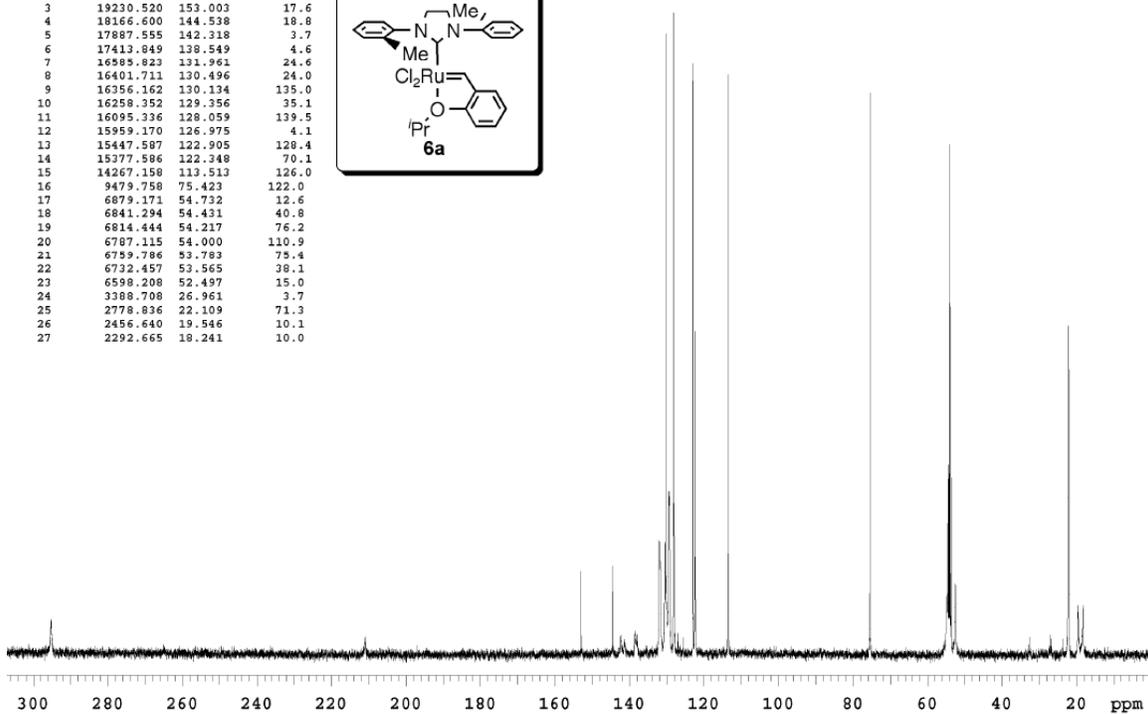
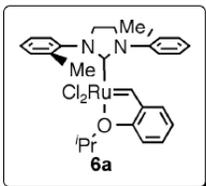


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2	37295.584	296.733	6.036	6766.499	53.826	282.4	
3	27888.115	221.885	4.137	6739.649	51.622	140.6	
4	27010.443	221.267	3.030	4522.620	35.903	7.2	
5	19062.710	151.668	9.539	4461.259	35.495	6.8	
6	18993.198	151.115	12.840	4143.857	32.970	63.9	
7	18629.347	140.299	24.041	4120.035	32.044	90.0	
8	18468.180	146.937	19.362	4109.336	32.695	60.5	
9	18286.193	146.285	12.242	3651.922	29.056	306.7	
10	17504.537	139.907	9.244	3639.945	29.960	141.0	
11	17559.605	139.709	10.145	3578.575	28.472	56.5	
12	17419.644	139.587	13.946	3546.451	28.216	233.1	
13	17393.293	138.385	17.047	3536.862	28.140	296.4	
14	16608.358	132.140	66.648	3470.696	27.614	58.0	
15	16450.616	130.885	29.249	3464.874	27.488	37.5	
16	16435.753	130.767	37.750	3443.367	27.396	32.4	
17	16351.368	130.096	44.351	3366.654	26.786	139.0	
18	16316.047	129.021	31.552	3353.700	26.603	155.6	
19	16235.818	129.176	39.353	3258.775	25.928	54.8	
20	16223.352	129.077	55.594	3248.227	25.844	96.0	
21	16209.440	120.906	42.355	3232.005	25.722	55.0	
22	16195.064	128.852	44.156	3014.731	23.986	26.0	
23	16129.926	128.412	95.287	2973.497	23.658	51.9	
24	16110.679	128.181	39.658	2961.031	23.559	49.0	
25	16083.830	127.967	46.0				
26	16055.062	127.738	82.6				
27	15969.718	127.059	47.5				
28	15833.759	126.773	32.9				
29	15886.772	126.399	55.5				
30	15338.270	122.035	4.0				
31	7062.805	56.193	65.0				
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33	6848.007	54.484	152.7				
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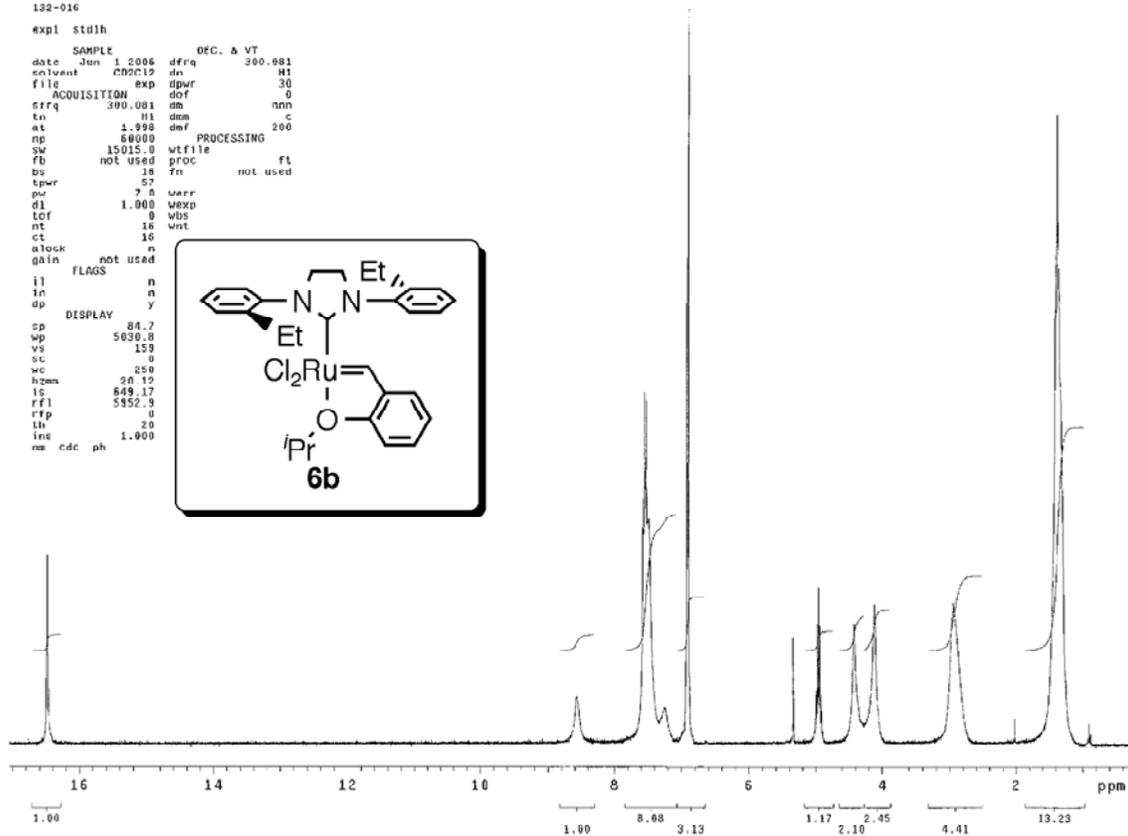
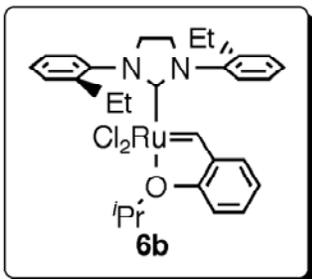
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4	18166.600	144.538	18.8
5	17887.555	142.318	3.7
6	17413.849	138.549	4.6
7	16988.823	131.961	24.6
8	16401.711	130.496	24.0
9	16356.162	130.134	135.0
10	16258.352	129.356	35.1
11	16095.336	128.059	139.5
12	15959.170	126.975	4.1
13	15447.587	122.905	128.4
14	15377.586	122.348	70.1
15	14267.158	113.513	126.0
16	9479.758	75.423	122.0
17	6879.171	54.732	12.6
18	6841.294	54.431	40.8
19	6814.444	54.217	76.2
20	6787.115	54.000	110.9
21	6759.786	53.783	75.4
22	6732.457	53.565	38.1
23	6598.208	52.497	15.0
24	3388.708	26.961	3.7
25	2778.836	22.109	71.3
26	2456.640	19.546	10.1
27	2292.665	18.241	10.0



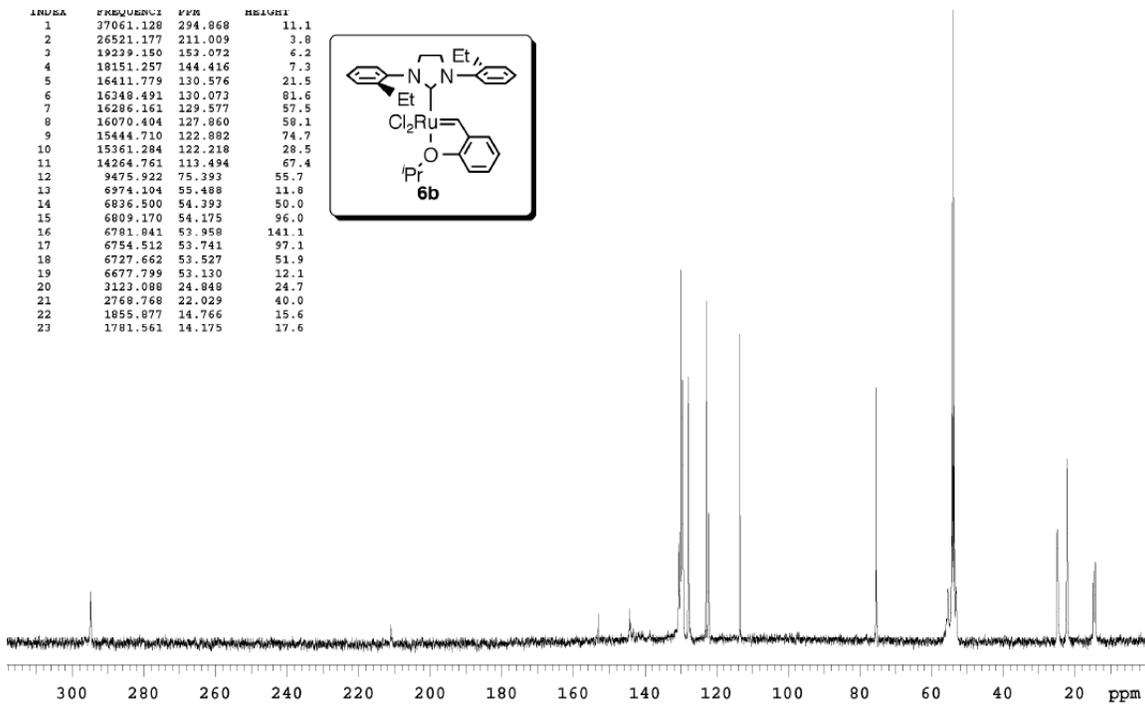
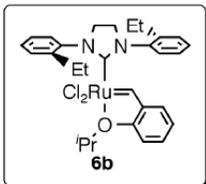
132-016

expl std1h

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ng          60000
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ct         16
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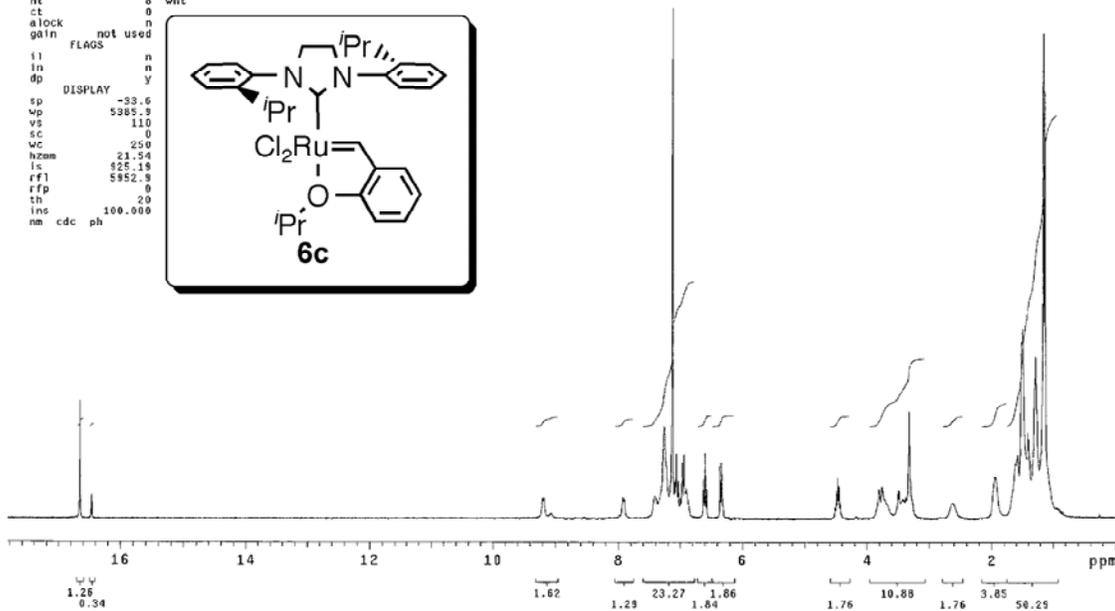
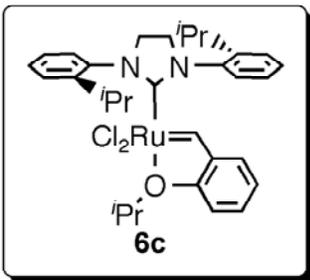
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4	18151.257	144.416	7.3
5	16411.779	130.576	21.5
6	16348.491	130.073	81.6
7	16286.161	129.577	97.5
8	16070.404	127.860	58.1
9	15444.710	122.882	74.7
10	15361.284	122.218	28.5
11	14264.761	113.494	67.4
12	9475.922	75.393	55.7
13	6974.104	55.488	11.8
14	6836.500	54.393	50.0
15	6809.170	54.175	96.0
16	6781.841	53.958	141.1
17	6754.512	53.741	97.1
18	6727.662	53.527	51.9
19	6677.799	53.130	12.1
20	3123.088	24.848	24.7
21	2768.768	22.029	40.0
22	1855.877	14.766	15.6
23	1781.561	14.175	17.6

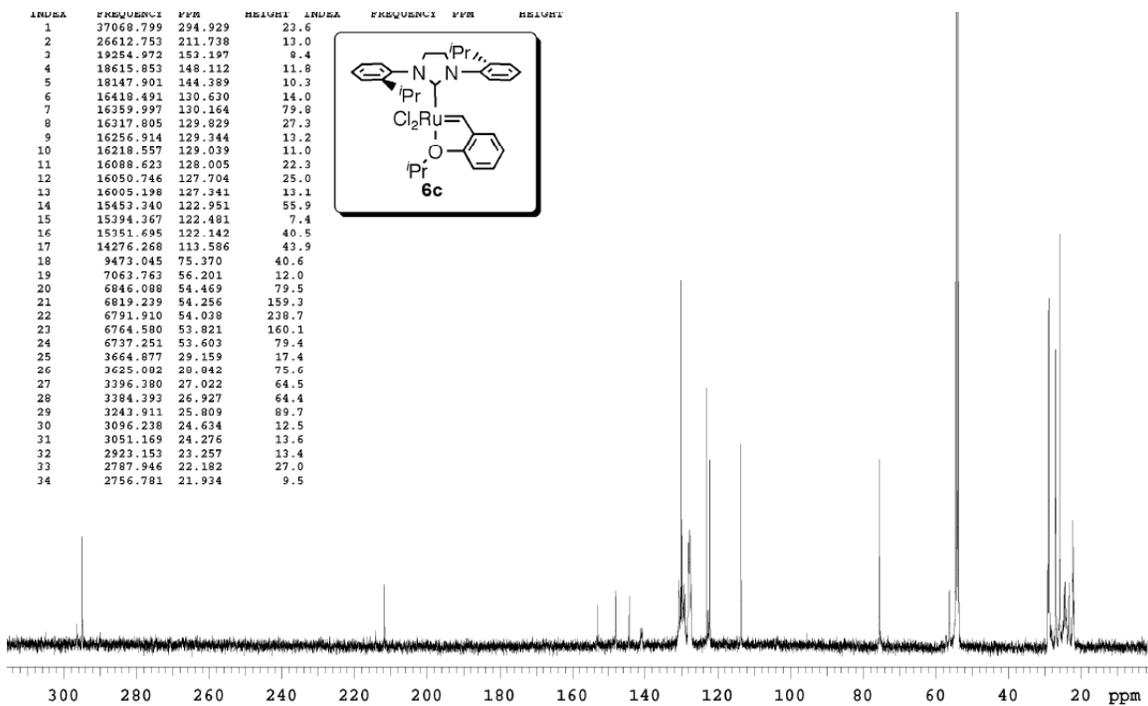


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expl stdlh

```
SAMPLE DEC. & VT
date May 1 2006 dfrq 300.080
solvent Benzene dn H1
file exp dpar 18
ACQUISITION dof 0
sfrq 300.080 dm nnn
tn H1 dma c
at 1.908 dmf 200
np 60000 PROCESSING
sw 15015.0 wtfi18
fb not used proc rt
bs 16 fn not used
lpar 57
gw 7.0 werr
d1 1.000 wexp
Lof 0 wbs
nt 8 wst
ct 0
a lock not used
gain not used
FLAGS
ll n
ln n
dp y
DISPLAY
sp -33.6
wp 5385.9
vs 110
vc 0
hzam 21.54
ls 825.18
rf1 5952.9
rfp 0
th 20
ins
nm cdc ph
```





## REFERENCES

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- <sup>i</sup> Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100-110.
- <sup>ii</sup> For complete details, see: Ritter, T.; Hejl, A.; Wenzel, A. G.; Funk, T. W.; Grubbs, R. H. *Organometallics* **2006**, *25*, 5740-5745.
- <sup>iii</sup> For syntheses of the substrates and isolation procedures for **S6-S9**, see: Berlin, J. M.; Campbell, K.; Ritter, T.; Funk, T. W.; Chlenov, A.; Grubbs, R. H. *Org. Lett.* In Press.
- <sup>iv</sup> Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 635259.