

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

Ian C. Stewart¹, Thay Ung², Alexandre A. Pletnev², Jacob M. Berlin¹, Robert H. Grubbs¹, Yann Schrodi^{*,2}

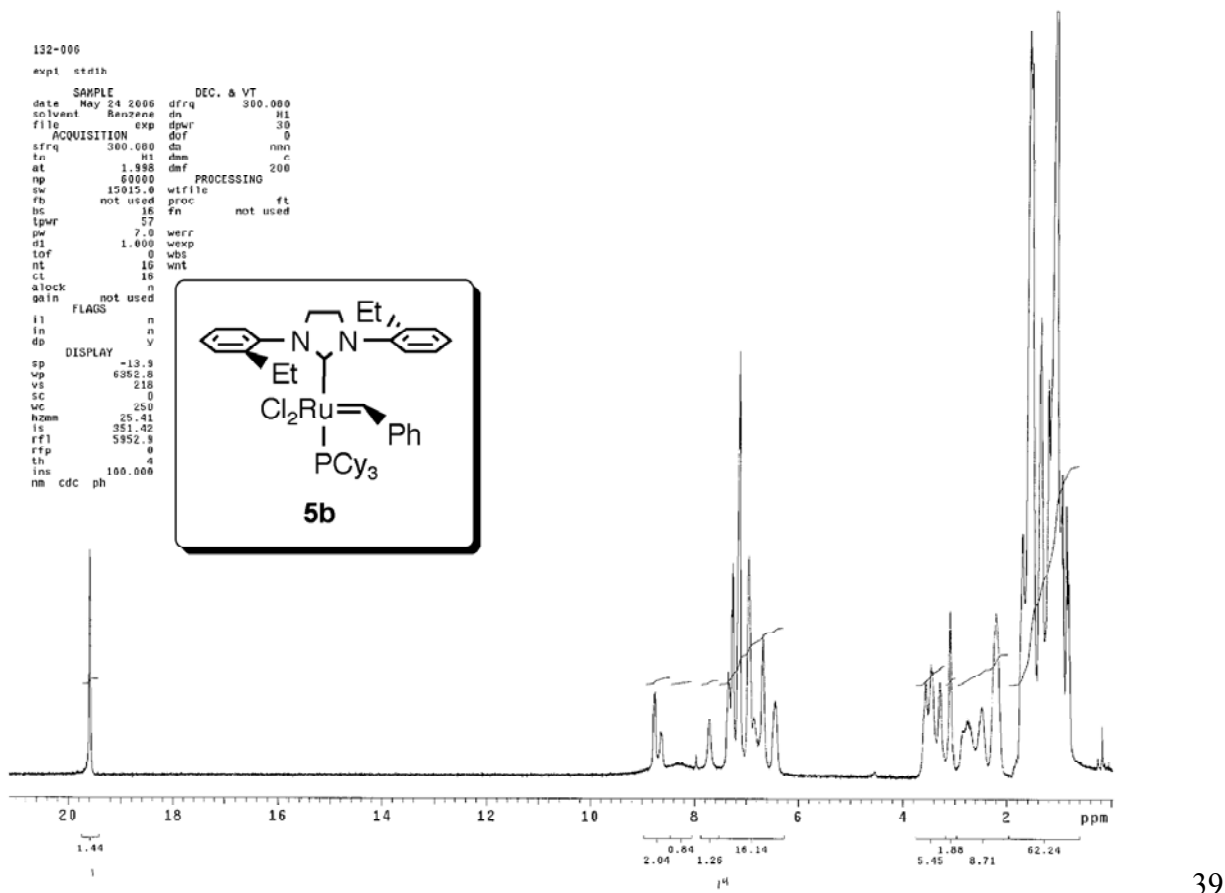
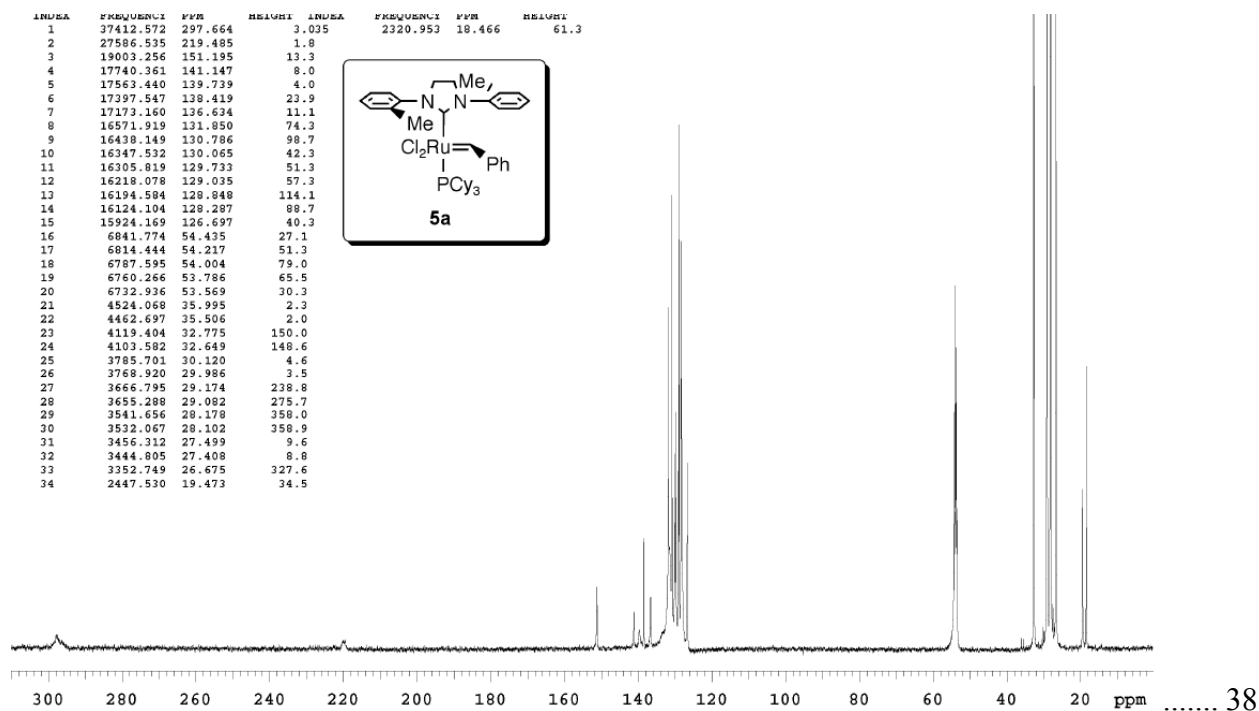
The Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, and Materia Inc., Pasadena, California 91107

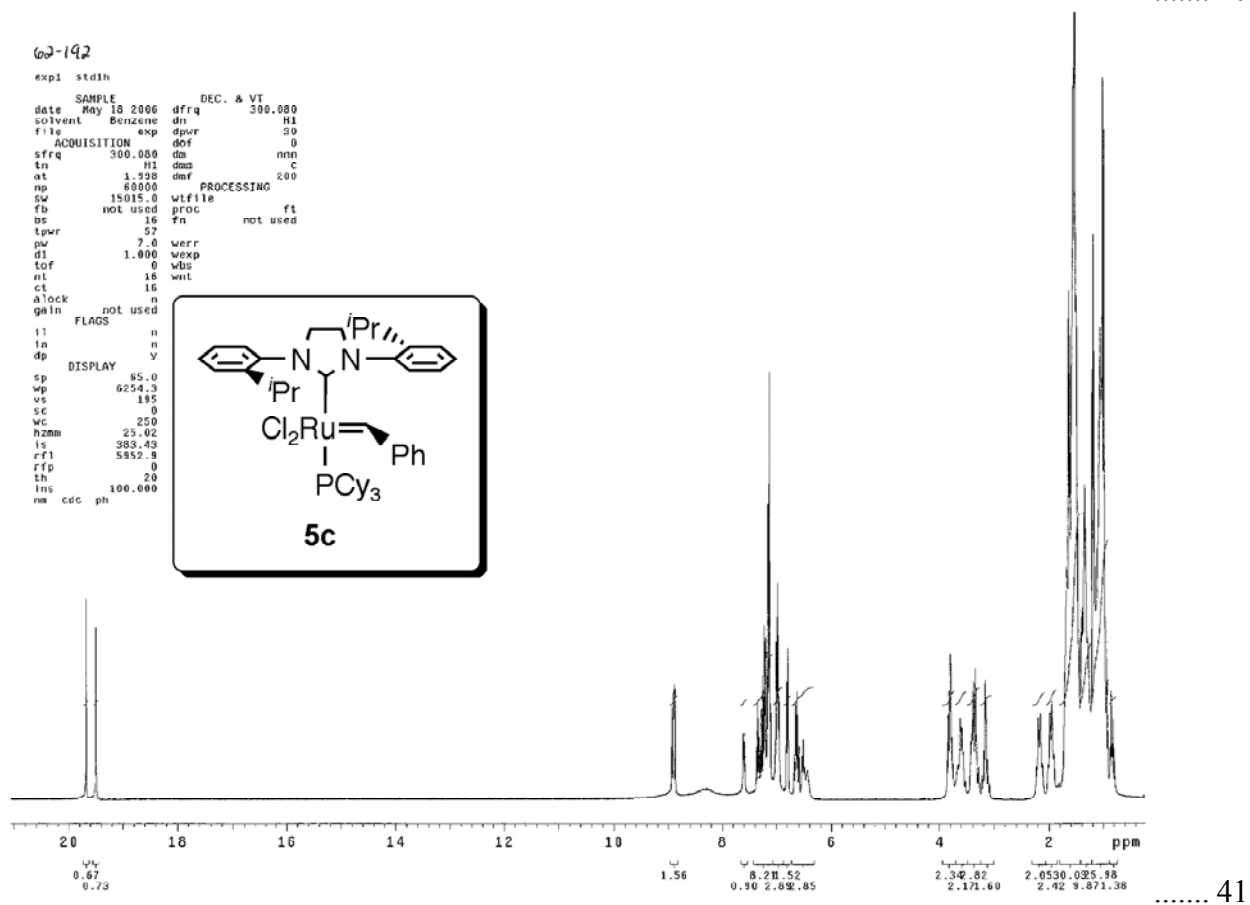
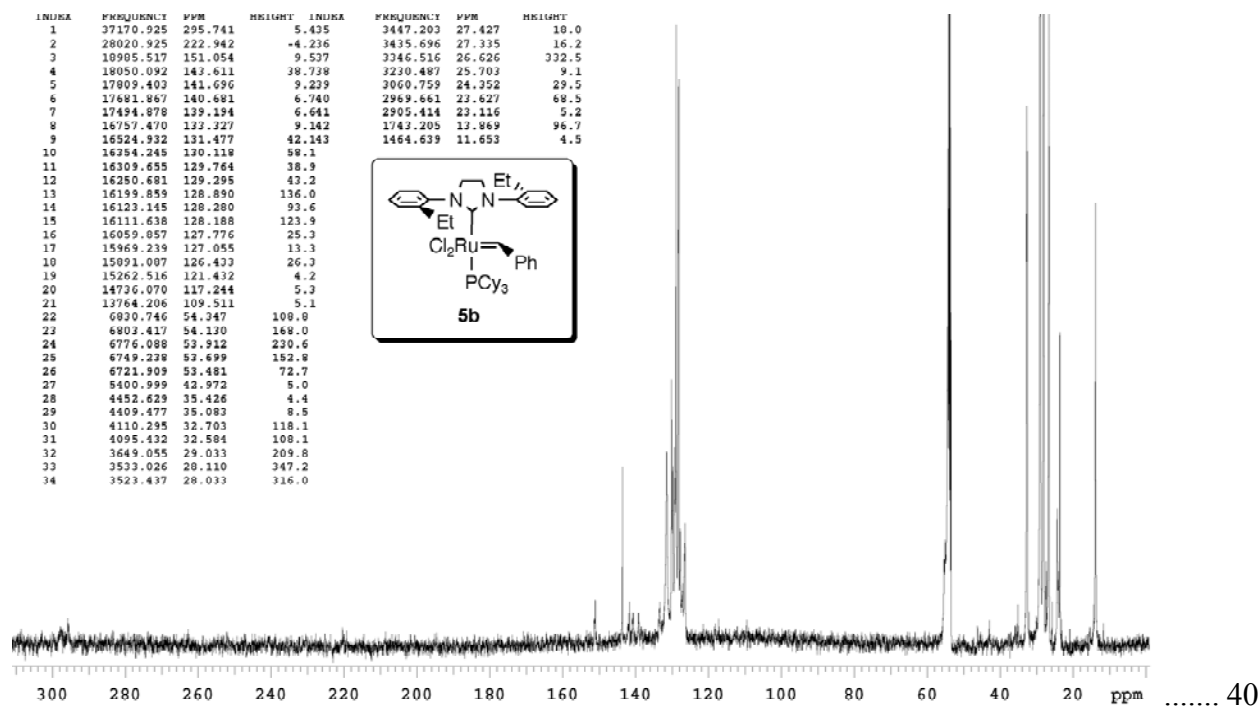
Supporting Information

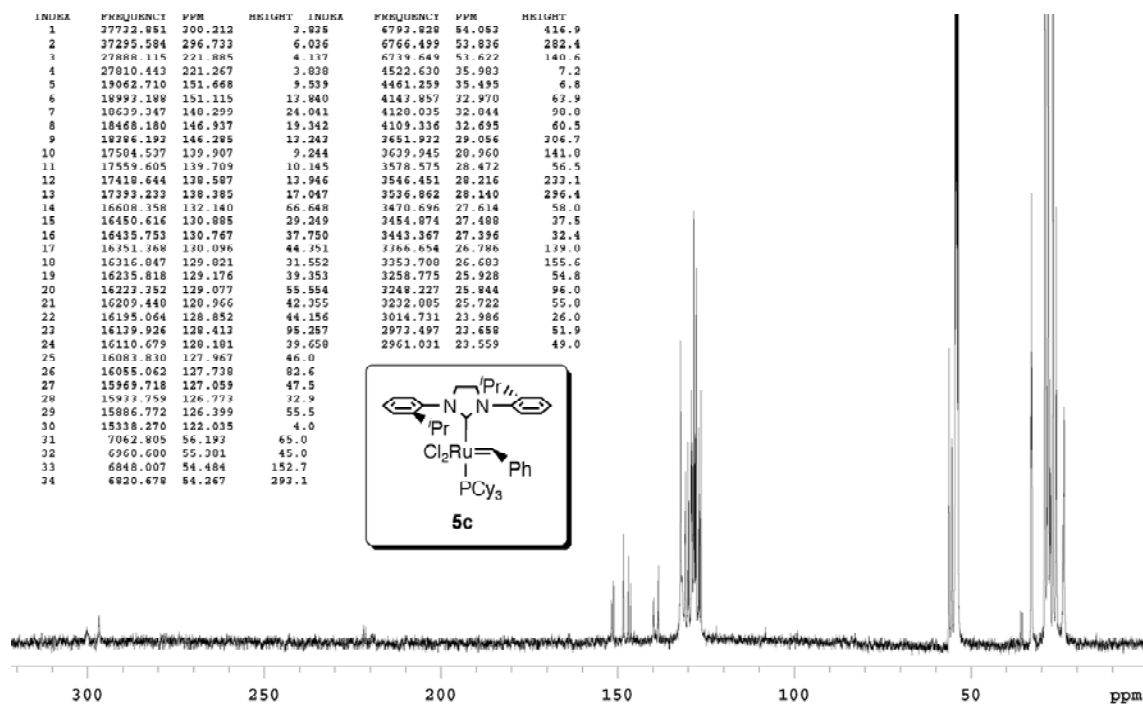
| | |
|--|----|
| General information | 9 |
| General procedure for the preparation of <i>N,N'</i> -Diaryl oxamides | 10 |
| General procedure for the preparation of <i>N,N'</i> -Diarylethylenediamine hydrochloride..... | 10 |
| General procedure for the preparation of imidazolinium chloride | 10 |
| General procedure for the preparation of catalysts 5a-c | 11 |
| General procedure for the preparation of catalysts 6a-c | 12 |
| General procedure for the RCM of 7 (monitored by GC) | 14 |
| General procedure for activity plots of ring-closing metathesis..... | 18 |
| RCM of Diethyl diallylmalonate (S1)..... | 18 |
| RCM of Diethyl allylmethylmalonate (S3)..... | 21 |
| RCM of Diethyl dimethylmalonate (9)..... | 23 |
| General RCM procedure for Table 2. | 26 |
| Isolated yield for 10. | 26 |
| Isolated yield for S5. | 27 |
| X-ray diffraction data for 6a | 29 |
| ¹ H and ¹³ C NMR Spectra of 5a-c and 6a-c | 37 |

¹ California Institute of Technology

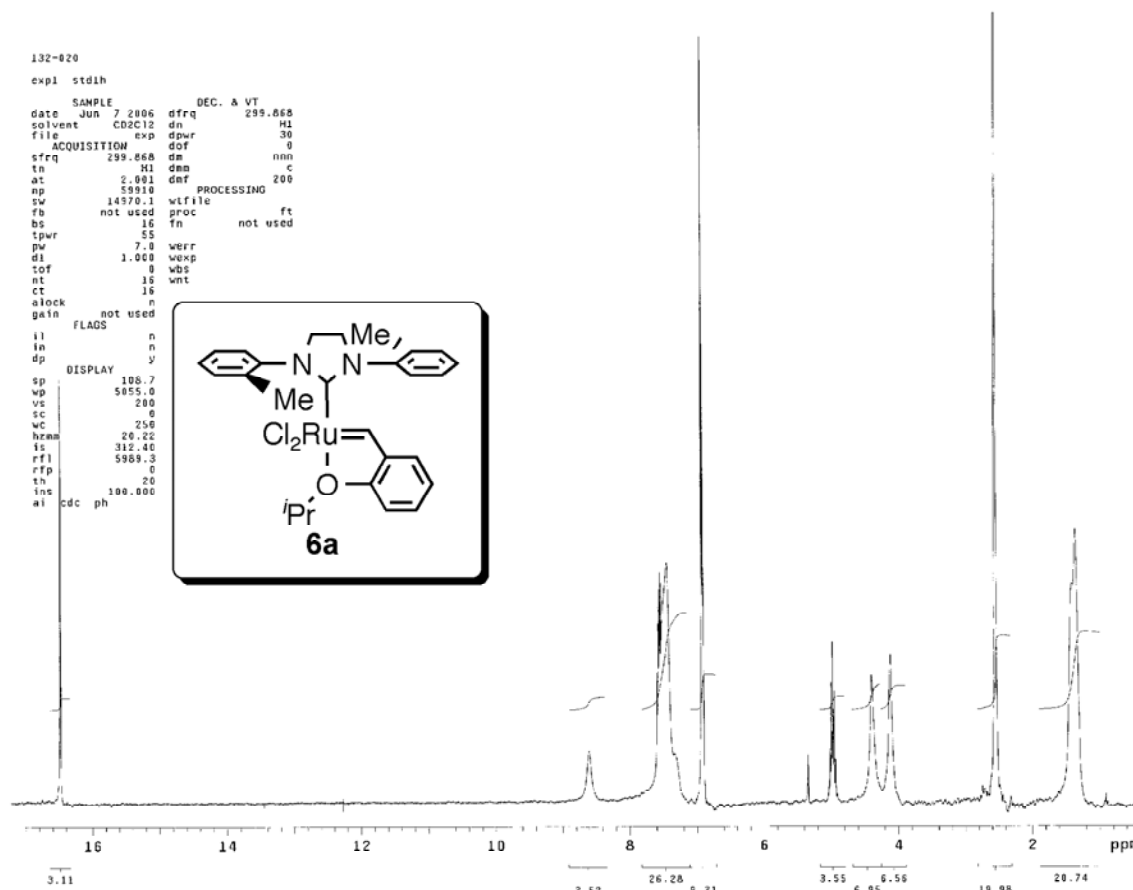
² Materia, Inc.



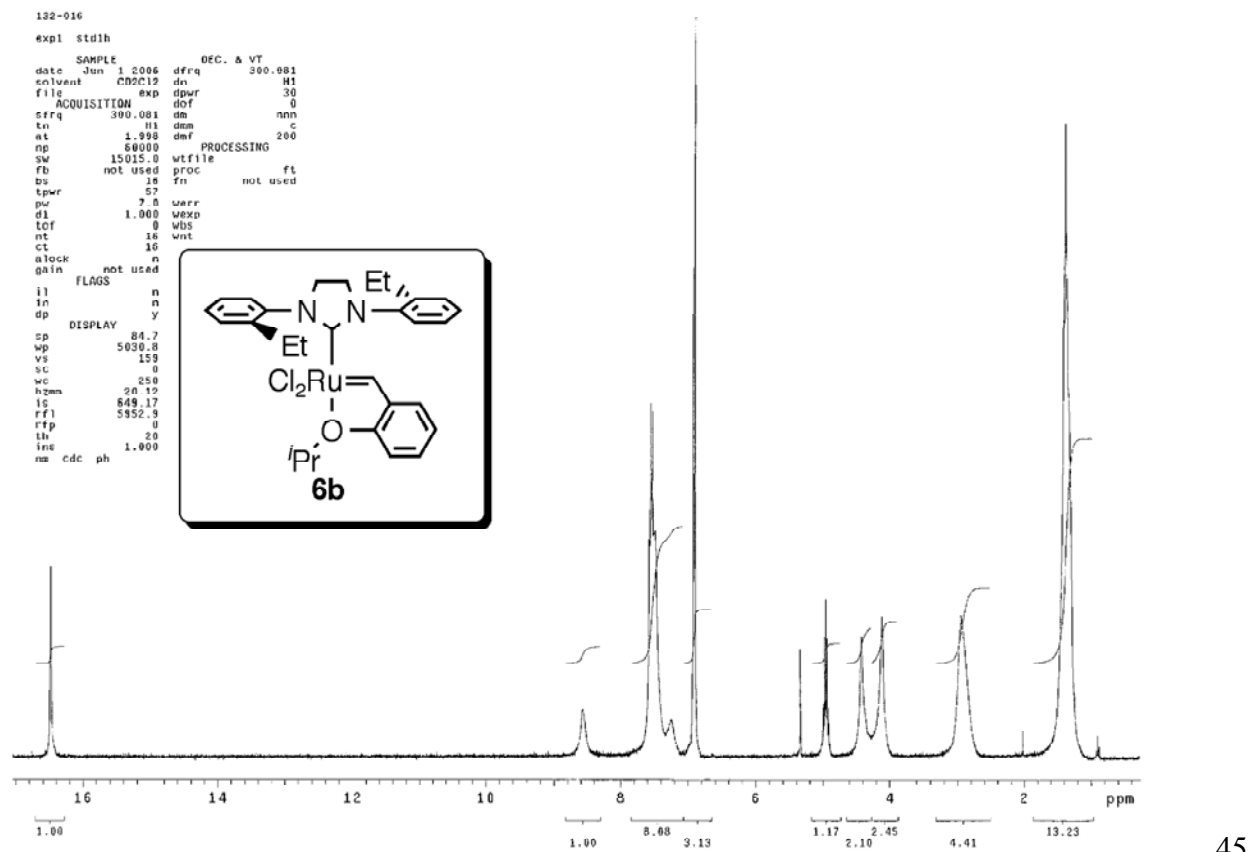
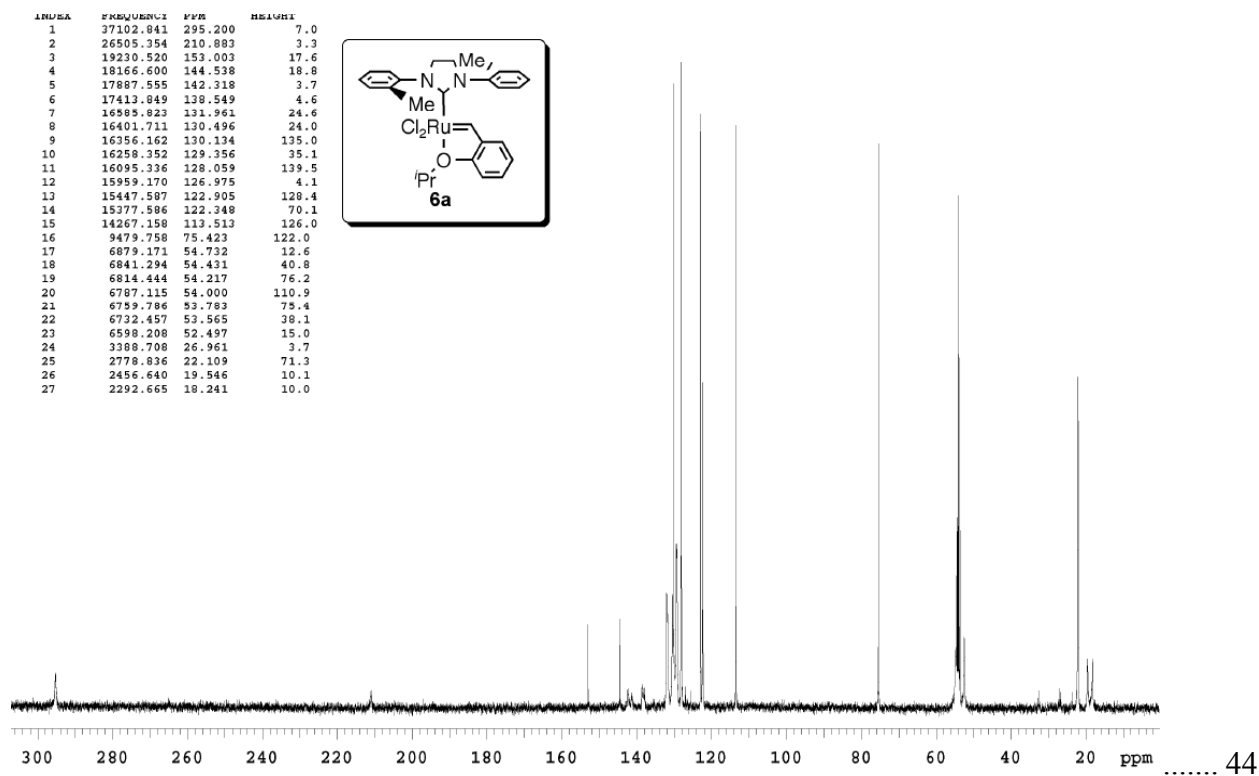


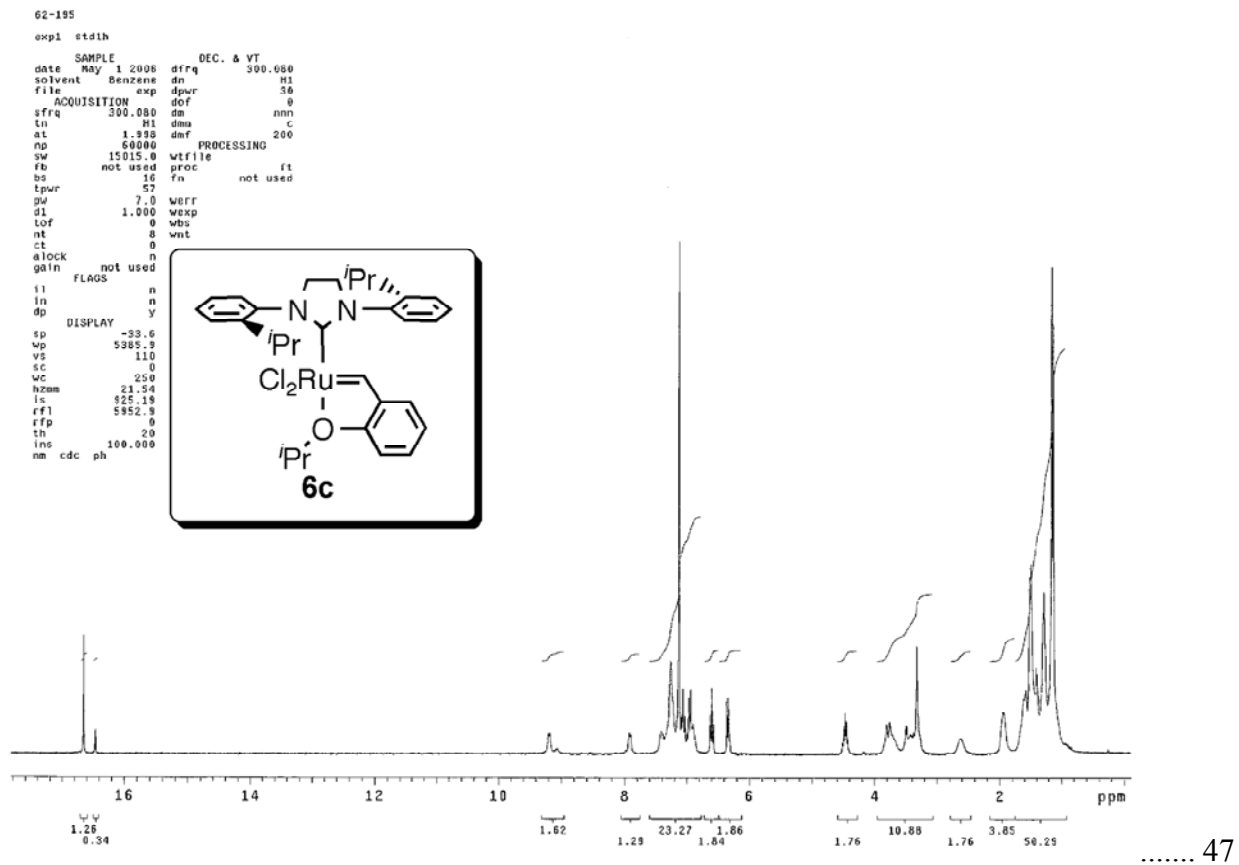
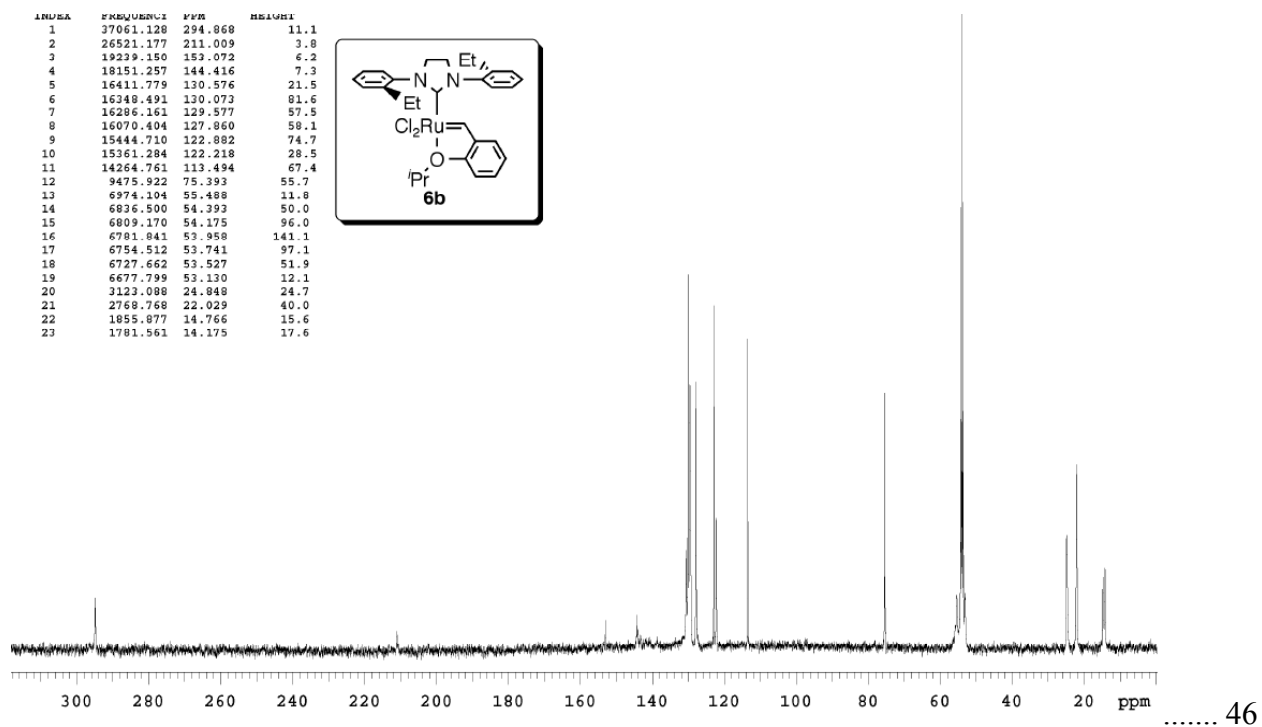


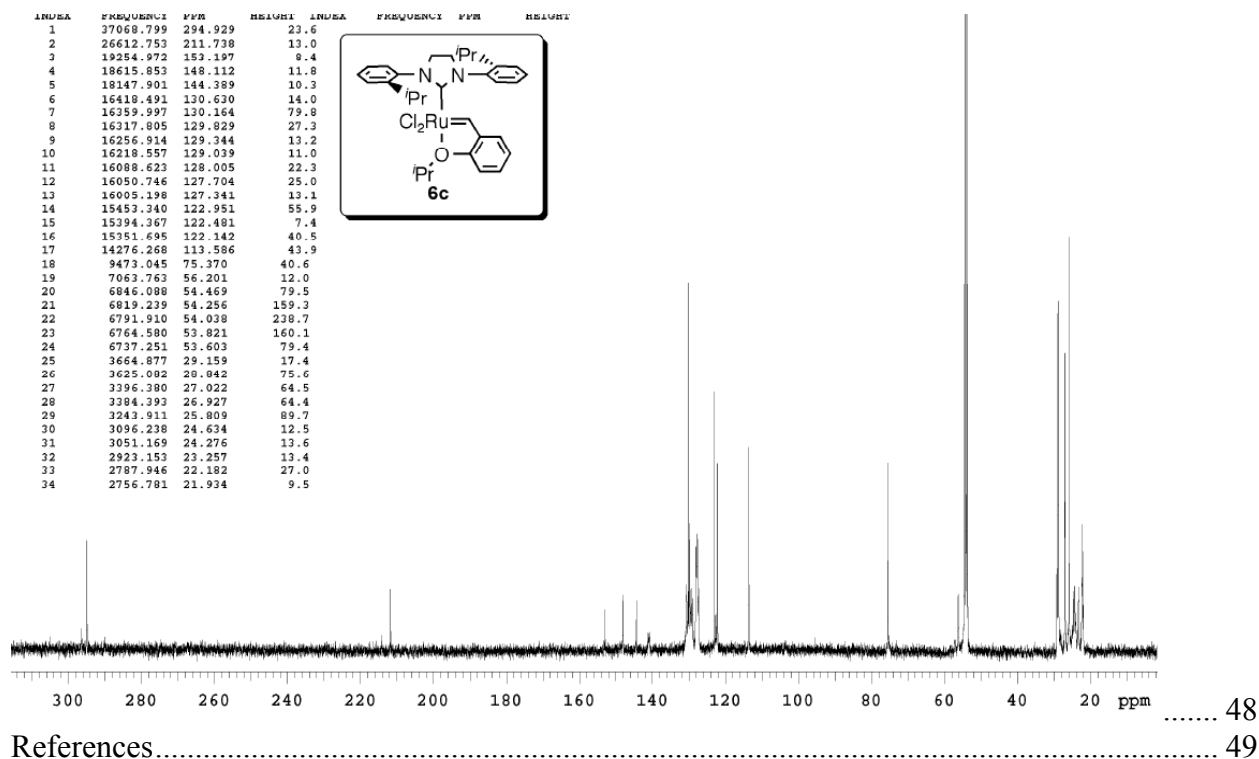
..... 42



..... 43







List of Tables

| | |
|--|----|
| Table S1: RCM of 7 with 5 mol % of 1 at 40 °C..... | 15 |
| Table S2: RCM of 7 with 5 mol % of 2 at 40 °C..... | 15 |
| Table S3: RCM of 7 with 5 mol % of 3 at 40 °C..... | 15 |
| Table S4: RCM of 7 with 5 mol % of 4 at 40 °C..... | 16 |
| Table S5: RCM of 7 with 5 mol % of 5a at 40 °C..... | 16 |
| Table S6: RCM of 7 with 5 mol % of 5b at 40 °C..... | 16 |
| Table S7: RCM of 7 with 5 mol % of 5c at 40 °C..... | 17 |
| Table S8: RCM of 7 with 5 mol % of 6a at 40 °C..... | 17 |
| Table S9: RCM of 7 with 5 mol % of 6b at 40 °C..... | 17 |
| Table S10: RCM of 7 with 5 mol % of 6c at 40 °C..... | 18 |
| Table S11. Crystal Data for 6a..... | 29 |
| Table S12. Structure solution and refinement for 6a..... | 29 |
| Table S13. Atomic Coordinates for 6a..... | 31 |
| Table S14. Selected bond lengths [Å] and angles [°] for 6a..... | 32 |
| Table S15. Bond lengths [Å] and angles [°] for 6a..... | 32 |
| Table S16. Anisotropic displacement parameters (Å ² x 10 ⁴) for 6a..... | 34 |

List of Figures

| | |
|--|----|
| Figure S1. RCM of S1 using catalysts 1 and 5a (1 mol%, 30 °C, CD ₂ Cl ₂). | 19 |
| Figure S2. RCM of S1 using catalysts 3 and 6a (1 mol%, 30 °C, CD ₂ Cl ₂). | 20 |
| Figure S3. RCM of S3 using catalysts 1 and 5a (1 mol%, 30 °C, CD ₂ Cl ₂). | 21 |
| Figure S4. RCM of S3 using catalysts 3 and 6a (1 mol%, 30 °C, CD ₂ Cl ₂). | 22 |
| Figure S5. RCM of 9 using catalysts 1 and 5a (5 mol%, 30 °C, CD ₂ Cl ₂). | 23 |
| Figure S6. RCM of 9 using catalysts 4 and 6a (5 mol%, 30 °C, CD ₂ Cl ₂). | 24 |

| | |
|---|----|
| Figure S7. RCM of 9 using catalysts 6a (2.5 mol%, 60 °C, C ₆ D ₆)..... | 25 |
| Figure S8. ORTEP drawing of <i>syn</i> -6a | 35 |
| Figure S9. ORTEP drawing of <i>anti</i> -6a | 35 |
| Figure S10. ORTEP drawing of superimposed <i>syn</i> - and <i>anti</i> -6a..... | 36 |

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 ^1H NMR and ^{13}C NMR spectra. Chemical shifts are reported in parts per million (ppm) downfield from H_3PO_4 for ^{31}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.ⁱ

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 Na₂SO₄. 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:

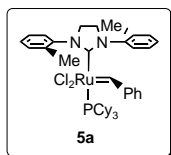
1,3-Bis(*o*-tolyl)-imidazolinium chloride. Obtained in 93% yield as a white solid. ¹H NMR (300 MHz, CDCl₃): δ 8.83 (s, 1H), 7.78-7.21 (d, 8H), 4.64 (s, 4H), 2.43 (s, 6H). ¹³C{¹H} NMR (75.41 MHz, CDCl₃): δ 157.48, 134.37, 133.44, 131.57, 129.82, 127.64, 126.68, 52.89, 18.12. HR-MS (FAB⁺) Calculated for C₁₇H₁₉N₂, 251.1548; found, 251.1557.

1,3-Bis(2-ethylphenyl)-imidazolinium chloride. Obtained in 74% yield as a white solid. ^1H NMR (300 MHz, CD_2Cl_2) δ 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).

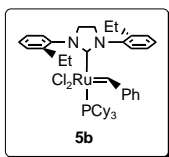
1,3-Bis(2-isopropylphenyl)-imidazolinium chloride. Obtained in 84% yield as a white solid. ^1H NMR (300 MHz, CDCl_3): δ 8.22 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2H), 8.04 (s, 1H), 7.34 (m, 6H), 4.73 (s, 4H), 3.06 (m, 2H), 1.29 (d, $^3J_{\text{HH}} = 6.0$ Hz, 12H).

GENERAL PROCEDURE FOR THE PREPARATION OF CATALYSTS **5a-c**

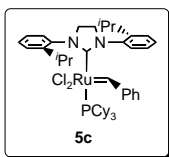
Potassium bis(trimethylsilyl)amide (1.4 g, 7.0 mmol, 1.23 equiv) was added to a suspension of the appropriate imidazolinium chloride (6.7 mmol, 1.15 equiv) in toluene (60 mL) under argon. The reaction mixture was stirred at room temperature for 30 min, then dichloro(phenylmethylene)bis(tricyclohexylphosphine) 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. ^1H NMR (300 MHz, C_6D_6): δ 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, C_6D_6): δ 27.87 (s), 25.15 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2): δ 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 (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. ^1H NMR (300 MHz, C_6D_6): δ 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, C_6D_6): δ 25.75 (s), 25.04 (s). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 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.

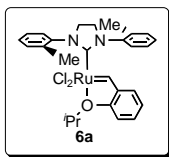


Catalyst 5c. **5c** was prepared according to the above general procedure and was obtained in 68% yield. ^1H NMR (300 MHz, C_6D_6): δ 19.68 (s), 19.49 (s), 8.93-8.87 (m), 8.30 (b), 7.60 (d), 7.34-7.12 (m), 6.97 (t), 6.80 (d), 6.70-6.44 (m), 3.85-3.08 (m), 2.22-2.12 (q), 2.02-1.91 (q), 1.66-0.97 (m). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6): δ 26.33 (s), 23.92 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2): δ 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.

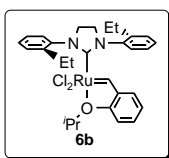
GENERAL PROCEDURE FOR THE PREPARATION OF CATALYSTS 6A-C.

2-Isopropoxy- β -methylstyrene (0.89 g, 5.1 mmol, 2 equiv) was added to a solution of catalyst **5** (2.5 mmol) in CH_2Cl_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 CH_2Cl_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

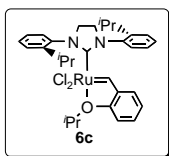
(eluted with 1:5 EtOAc-hexanes). The catalysts were obtained as green crystalline solids upon drying *in vacuo*.



Catalyst 6a. **6a** was prepared according to the above general procedure and was obtained in 71% yield. ^1H NMR (300 MHz, CD_2Cl_2): δ 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, CD_2Cl_2): δ 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%. ^1H NMR (300 MHz, CD_2Cl_2): δ 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, CD_2Cl_2): δ 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. ^1H NMR (300 MHz, C_6D_6): δ 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, CD_2Cl_2): δ 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 CH₂Cl₂ (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).

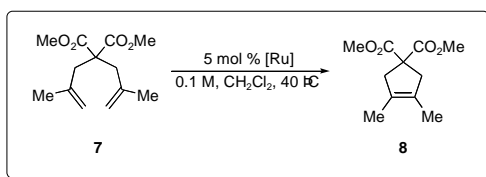


Table S1: RCM of **7** with 5 mol % of **1** at 40 °C

| 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

| Time (h) | Product (GC%) |
|-----------------|----------------------|
| 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

| Time (h) | Product (GC%) |
|-----------------|----------------------|
| 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

| Time (h) | Product (GC%) |
|-----------------|----------------------|
| 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

| Time (h) | Product (GC%) |
|-----------------|----------------------|
| 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

| Time (h) | Product (GC%) |
|-----------------|----------------------|
| 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

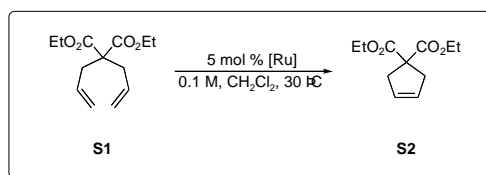
| Time (h) | Product (GC%) |
|-----------------|----------------------|
|-----------------|----------------------|

| 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.ⁱⁱ



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 μ mol, 1.0 mol%) and CD₂Cl₂ (0.4 mL). The sample was equilibrated at 30 °C in the NMR probe before **S1** (19.3 μ 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, δ 2.61 (dt), with those in the product, δ 2.98 (s).

Figure S1. RCM of **S1** using catalysts **1** and **5a** (1 mol%, 30 °C, CD₂Cl₂).

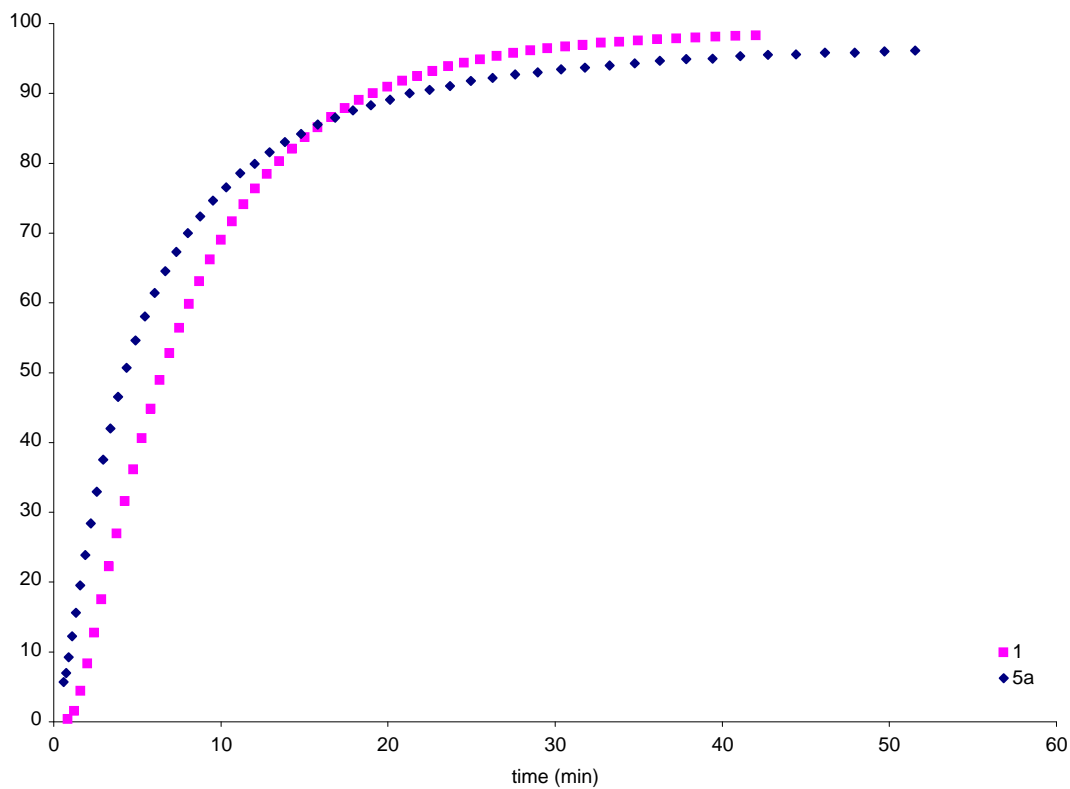
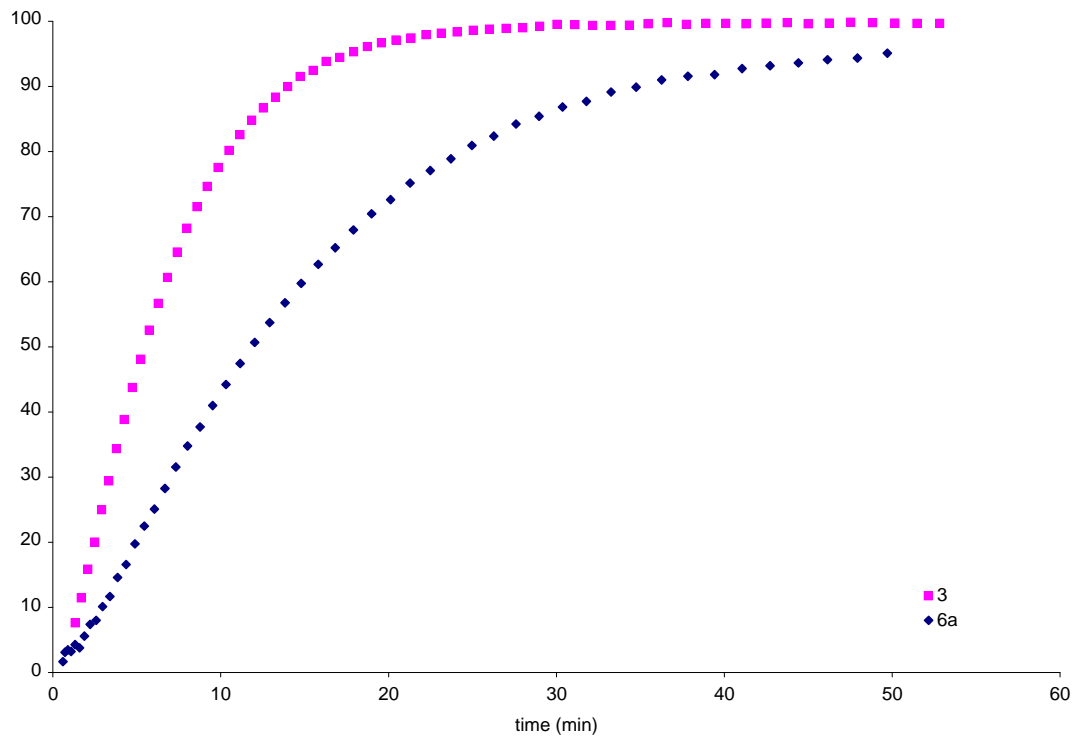
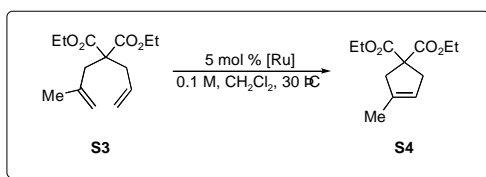


Figure S2. RCM of **S1** using catalysts **3** and **6a** (1 mol%, 30 °C, CD₂Cl₂).





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 μmol , 1.0 mol%) and CD_2Cl_2 (0.4 mL). The sample was equilibrated at 30 °C in the NMR probe before **S3** (20.5 μL , 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, δ 2.67 (s), 2.64 (dt), with those in the product, δ 2.93 (s), 2.88 (m).

Figure S3. RCM of **S3** using catalysts **1** and **5a** (1 mol%, 30 °C, CD_2Cl_2).

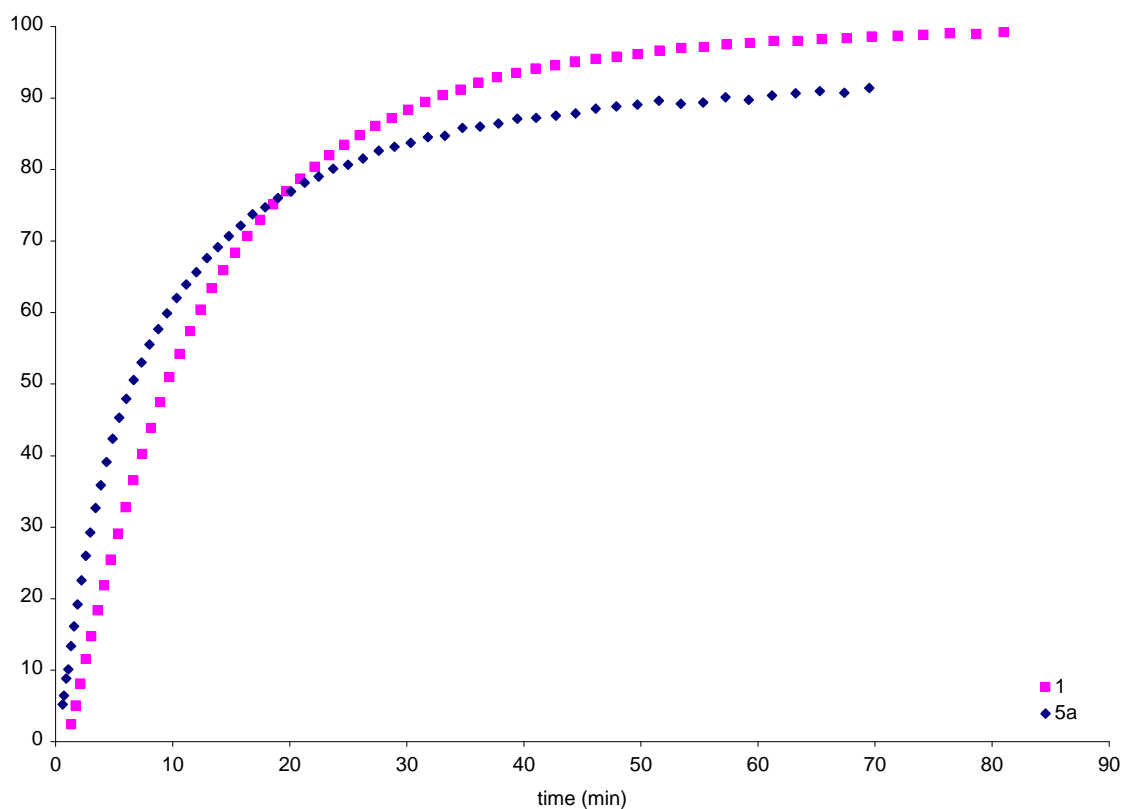
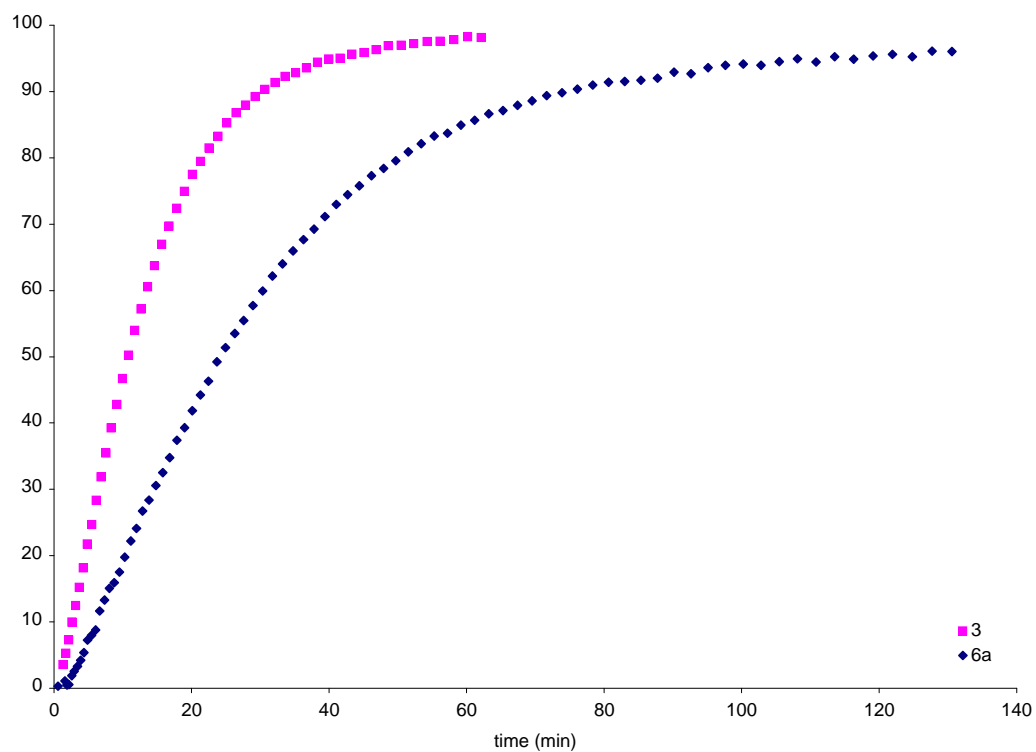
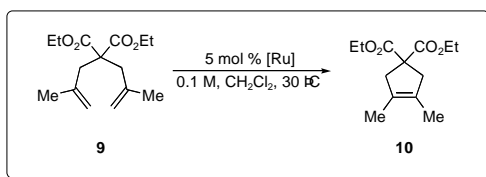


Figure S4. RCM of **S3** using catalysts **3** and **6a** (1 mol%, 30 °C, CD₂Cl₂).





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 C₆D₆ or CD₂Cl₂, 0.8 mL, 4.0 μ mol, 5.0 mol%). The sample was equilibrated at 30 °C or 60 °C in the NMR probe before **9** (21.6 μ L, 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, CD₂Cl₂).

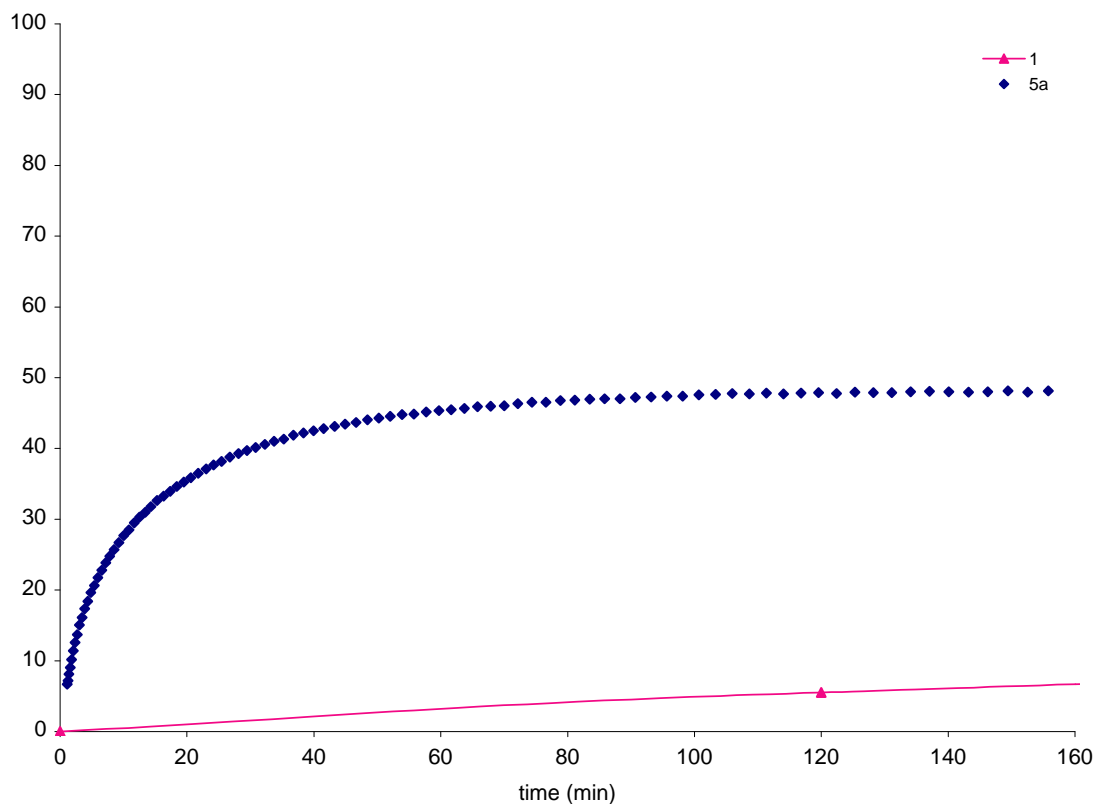


Figure S6. RCM of **9** using catalysts **4** and **6a** (5 mol%, 30 °C, CD₂Cl₂).

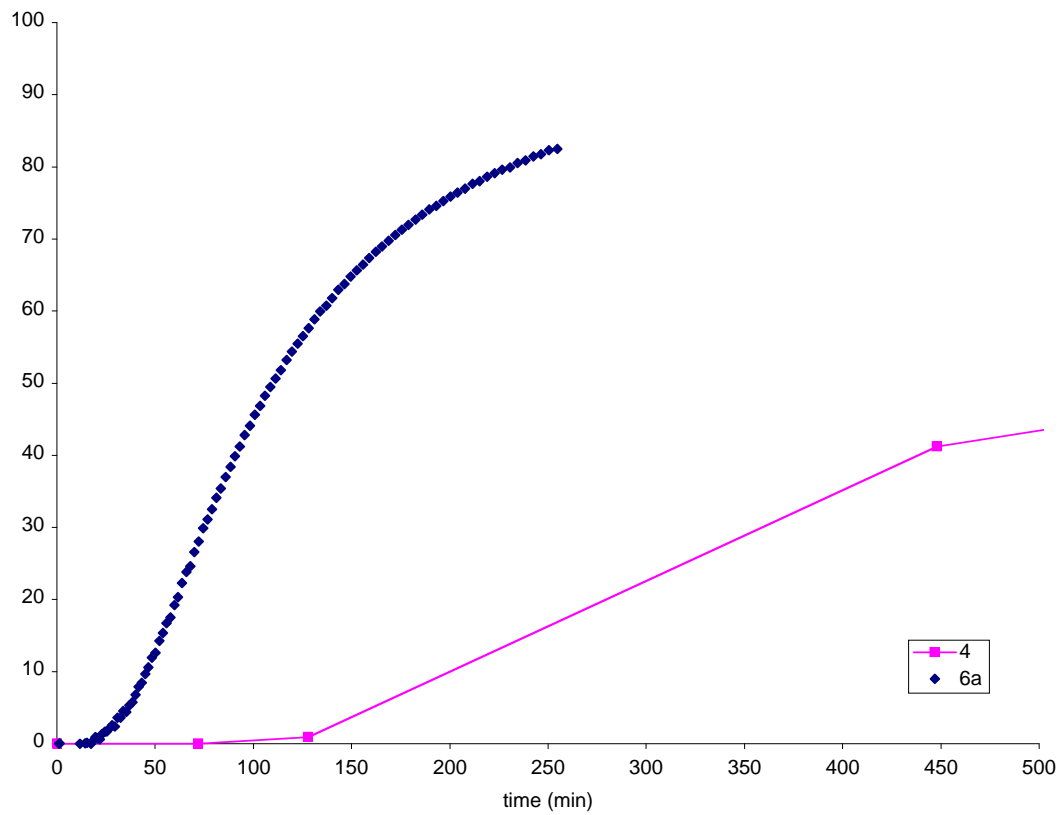
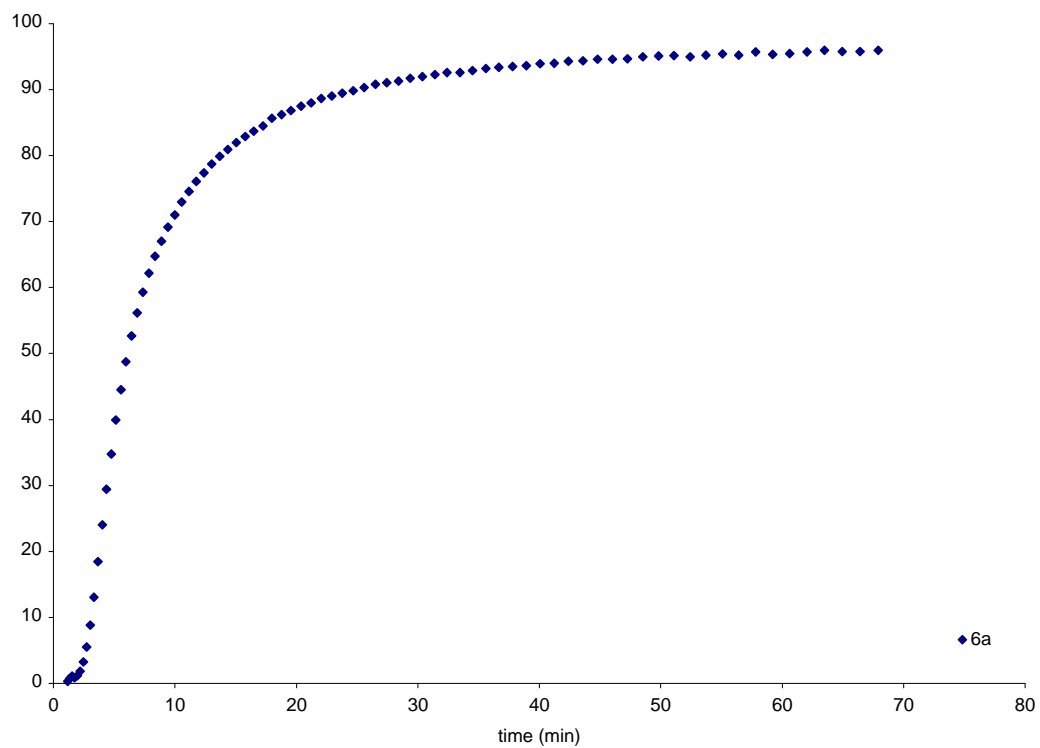
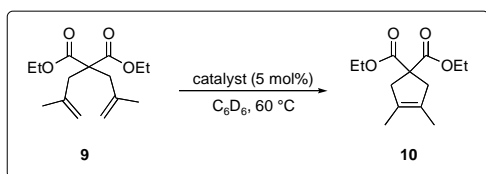


Figure S7. RCM of **9** using catalysts **6a** (2.5 mol%, 60 °C, C₆D₆).



GENERAL RCM PROCEDURE FOR TABLE 2.ⁱⁱⁱ

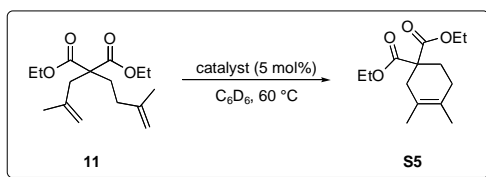
An NMR tube with a screw-cap septum top was charged inside a glovebox with catalyst stock solution (0.005 M in C₆D₆, 0.8 mL, 4.0 μ mol, 5.0 mol%). The appropriate substrate (**11-18**, 0.080 mmol, 0.1 M) was added via syringe and the sample placed in an oil bath regulated at 60 °C. ¹H NMR spectra were 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**.

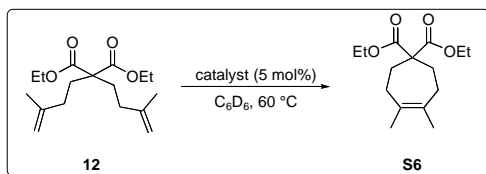
In an argon-filled glove box, a 20 mL vial equipped with a stir bar was charged with **9** (472 mg, 1.76 mmol), toluene (17.6 mL), and catalyst **6a** (50 mg, 0.088 mmol, 5 mol %). The vial was then capped with a septum screw-cap, taken out of the glove box and heated to 60 °C for 1 hour while stirring 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).



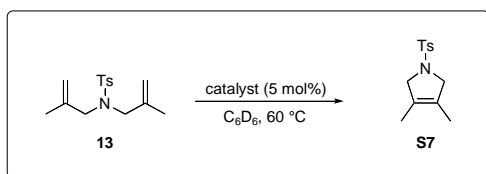
The SM methylene signal at 2.72 ppm was compared to the product signal at 2.63 ppm.

ISOLATED YIELD FOR S5.

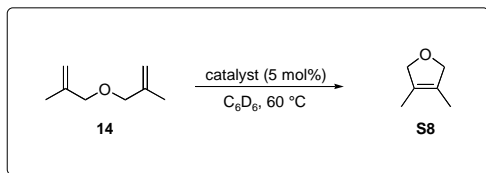
A 10 mL 2-neck round-bottom flask was outfitted with a reflux condensor and a septum, and flame-dried under vacuum. After cooling to r.t., **6a** (5.1 mg, 0.009 mmol, 5 mol%) was added as a solid. Dry degassed benzene (1.8 mL) was added via syringe, followed by **11** (52 μ L, 0.185 mmol) via syringe. The septum was replaced with a ground-glass stopper, and the solution was stirred at 60 $^\circ$ C for 1 h. The solution was cooled to r.t., and concentrated via rotary evaporation. Column chromatography (SiO₂, 5% EtOAc:hexanes) afforded **S5** as a colorless oil (47 mg, 0.185, 100%).



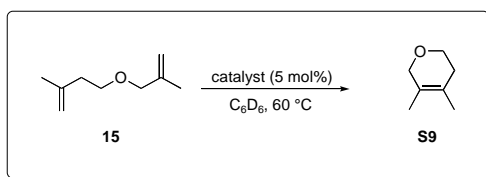
The SM methyl group signal at 1.59 ppm was compared to the product signal at 1.50 ppm.



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**^{iv}

| | | |
|--|--|-------------------------|
| Empirical formula | C ₂₇ H ₃₀ N ₂ OCl ₂ Ru | |
| Formula weight | 570.50 | |
| Crystallization Solvent | Benzene/pentane | |
| Crystal Habit | Block | |
| Crystal size | 0.34 x 0.28 x 0.14 mm ³ | |
| Crystal color | Dark green | |
| Type of diffractometer | Bruker SMART 1000 | |
| Wavelength | 0.71073 Å MoK α | |
| Data Collection Temperature | 100(2) K | |
| θ 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 | β = 105.5780(10)° |
| Volume | 2586.66(13) Å ³ | |
| Z | 4 | |
| Crystal system | Monoclinic | |
| Space group | P2 ₁ /c | |
| Density (calculated) | 1.465 Mg/m ³ | |
| F(000) | 1168 | |
| θ range for data collection | 1.83 to 41.89° | |
| Completeness to θ = 41.89° | 83.1 % | |
| Index ranges | -20 \leq h \leq 20, -25 \leq k \leq 25, -28 \leq l \leq 30 | |
| Data collection scan type | ω scans at 7 ϕ settings | |
| Reflections collected | 79070 | |
| Independent reflections | 14920 [R _{int} = 0.0822] | |
| Absorption coefficient | 0.835 mm ⁻¹ | |
| 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 ² |
| Data / restraints / parameters | 14920 / 15 / 332 |
| Treatment of hydrogen atoms | Riding |
| Goodness-of-fit on F ² | 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 | $w=1/\sigma^2(F_o^2)$ |
| Max shift/error | 0.002 |
| Average shift/error | 0.000 |
| Largest diff. peak and hole | 1.532 and -1.125 e.Å ⁻³ |

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_{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) | | |

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^{11} | U^{22} | U^{33} | U^{23} | U^{13} | U^{12} |
|-------|----------|----------|----------|----------|----------|----------|
| 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**

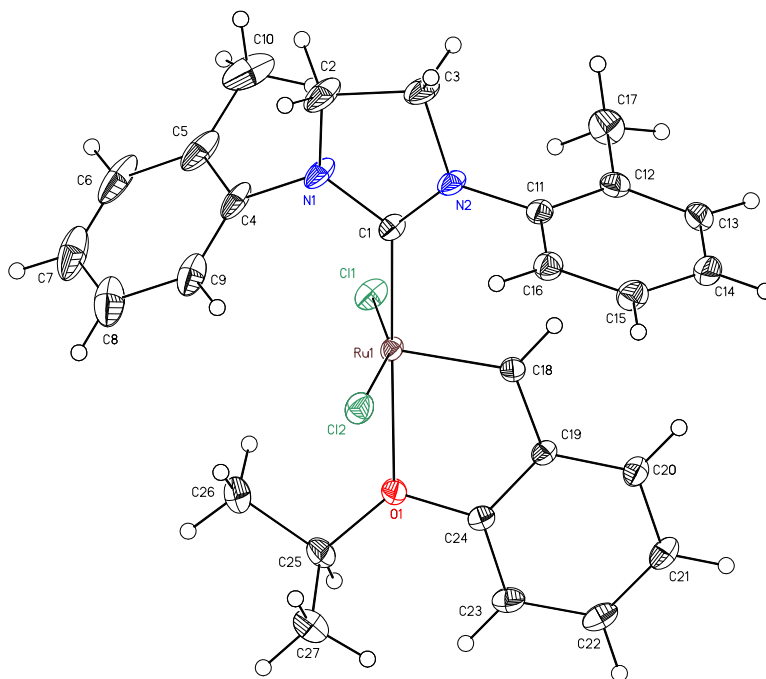


Figure S9. ORTEP drawing of *anti*-**6a**

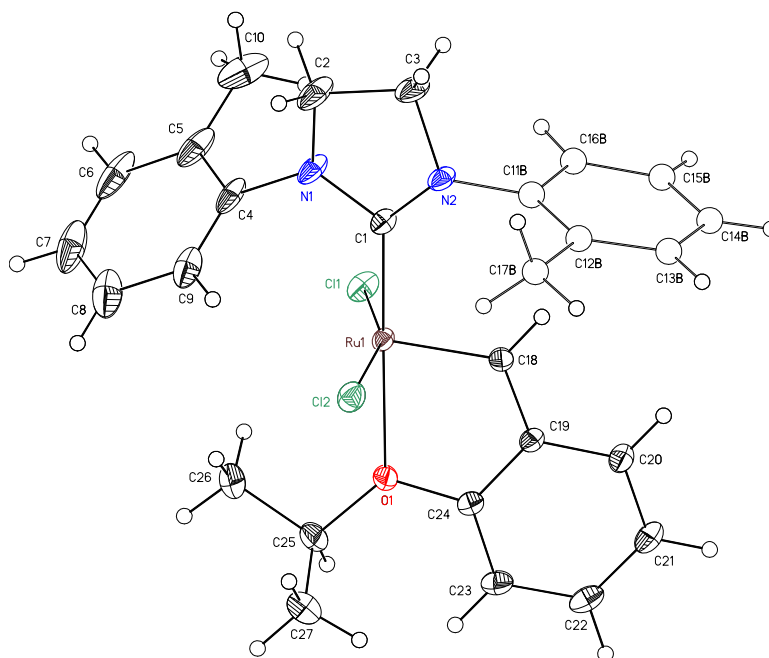
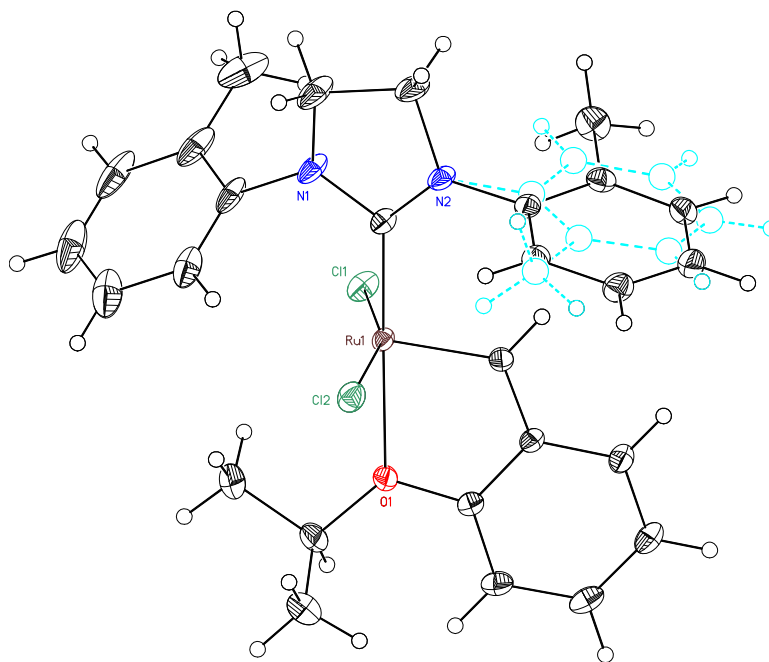
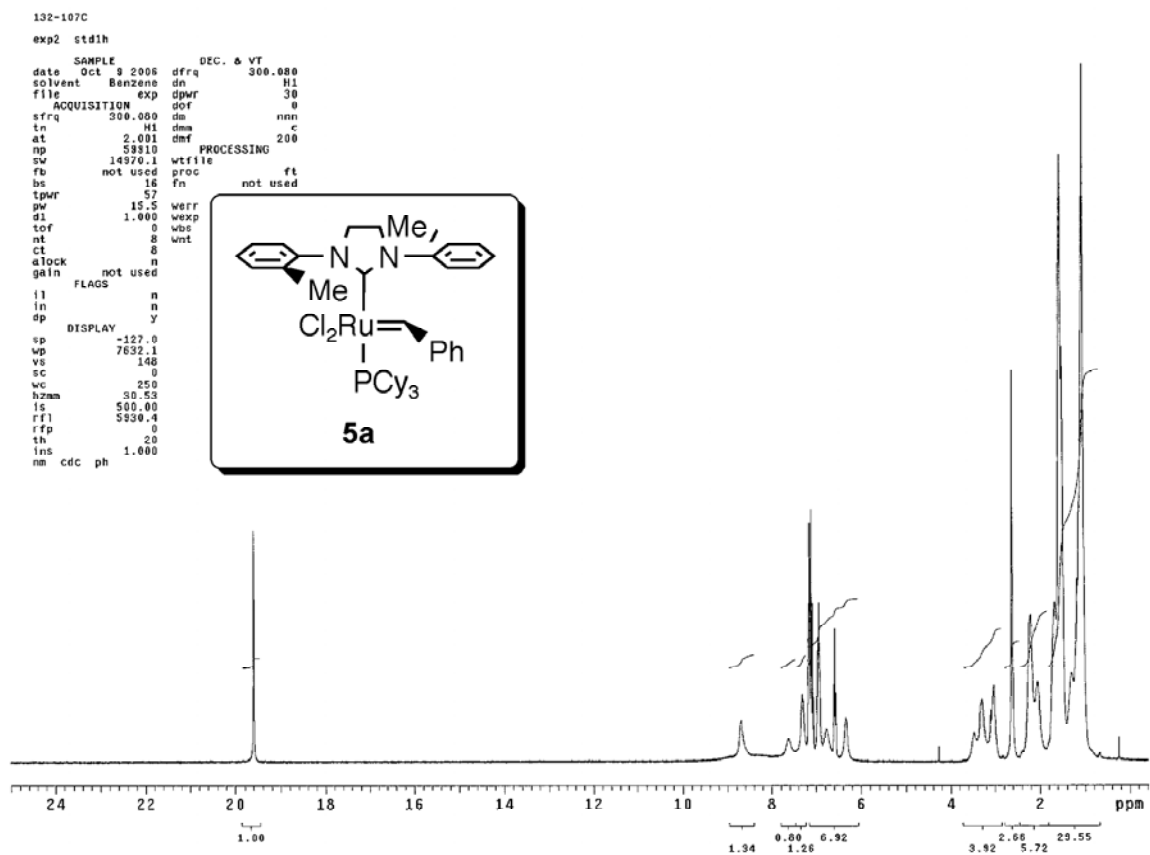
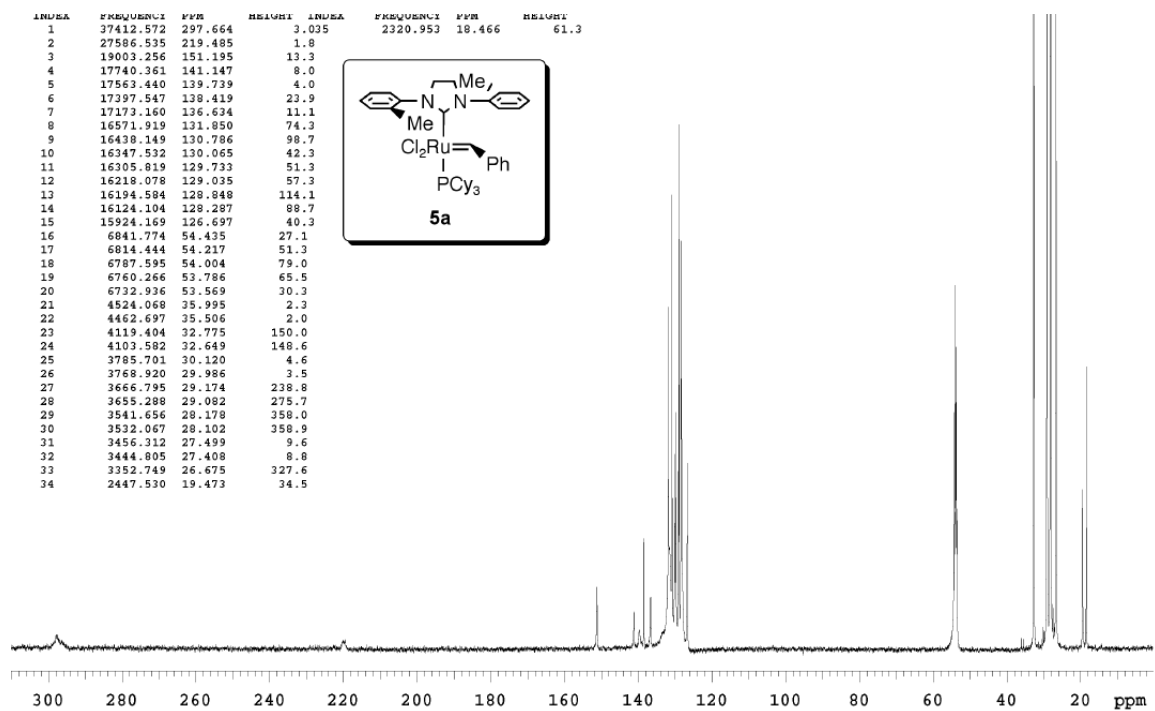


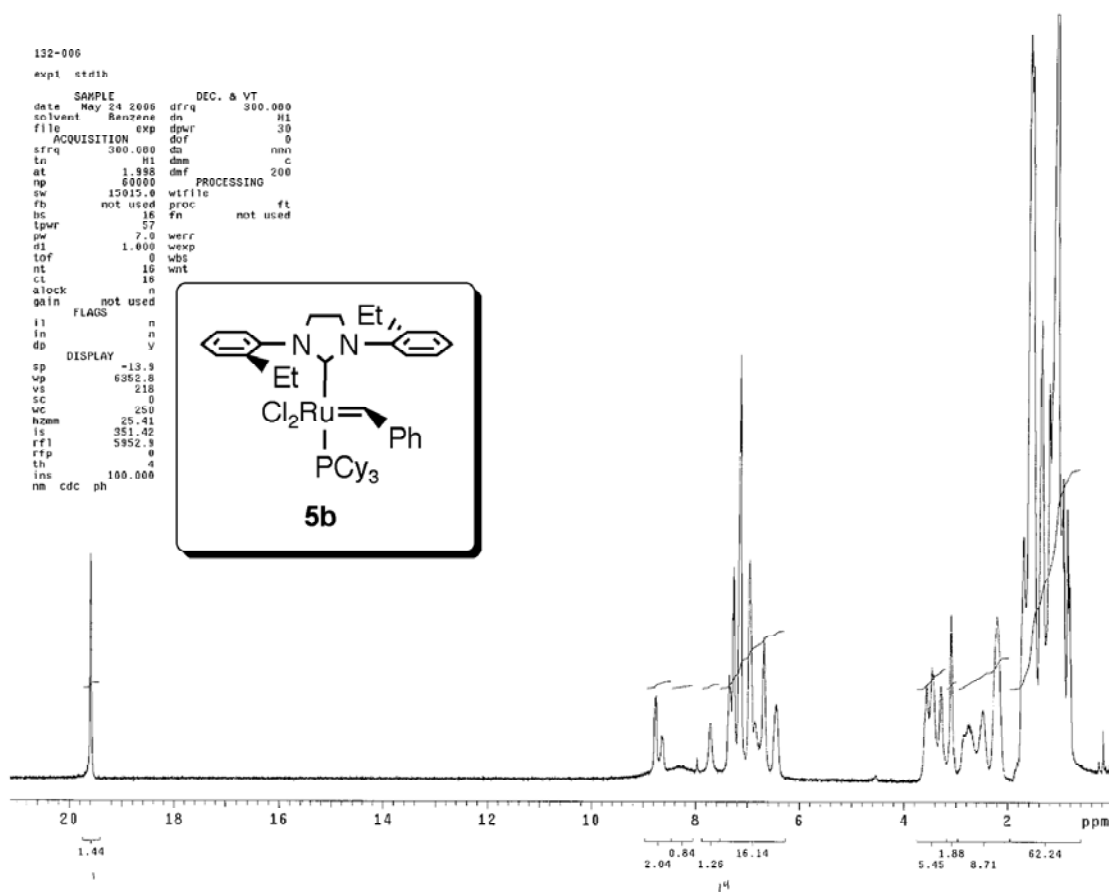
Figure S10. ORTEP drawing of superimposed *syn*- and *anti*-**6a**

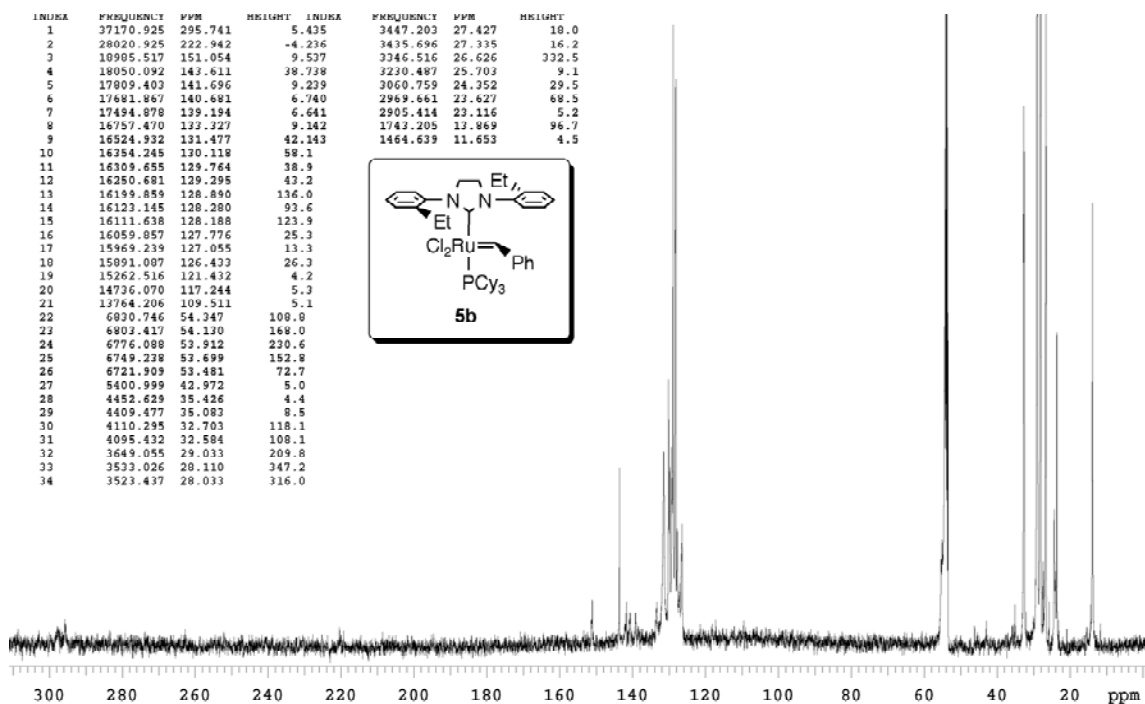


^1H AND ^{13}C NMR SPECTRA OF 5A-C AND 6A-C









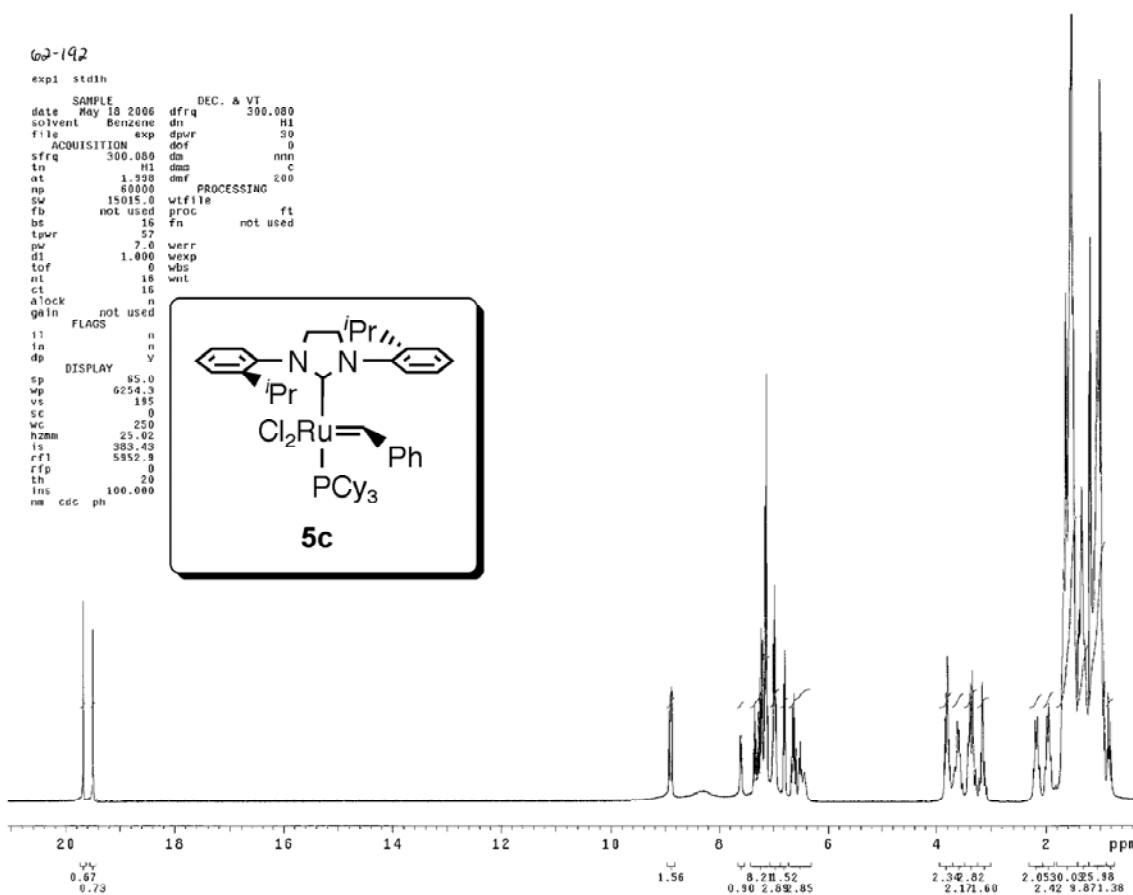
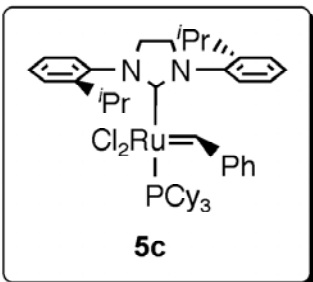
60-192

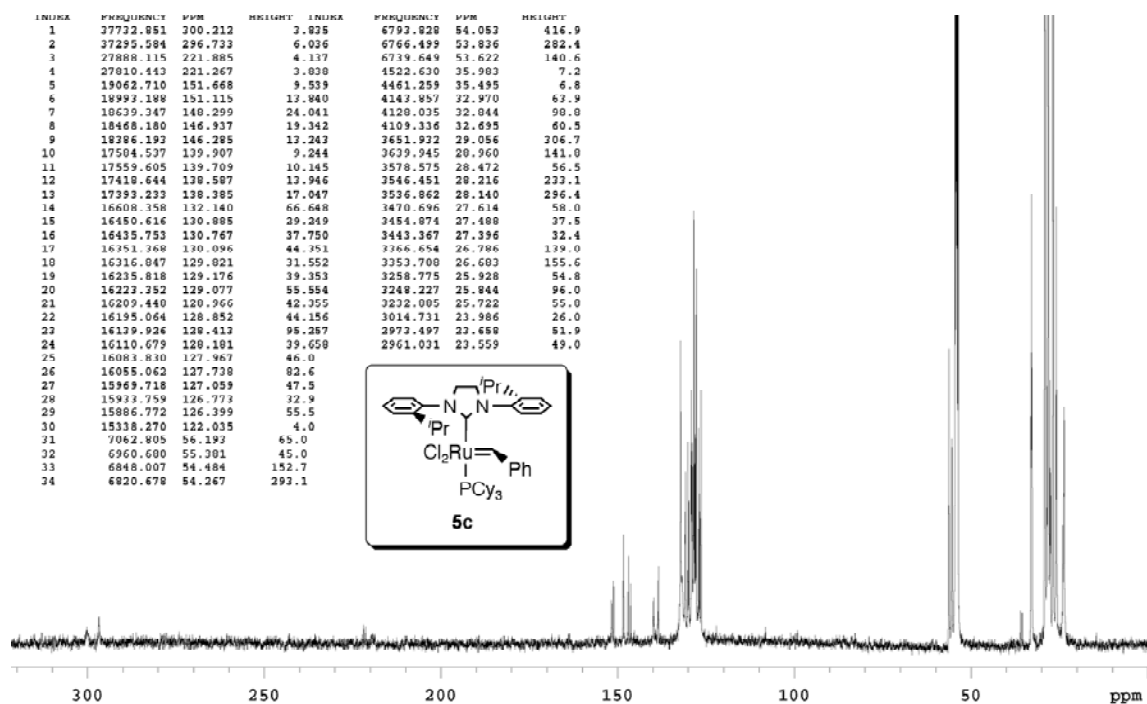
exp1 std1h

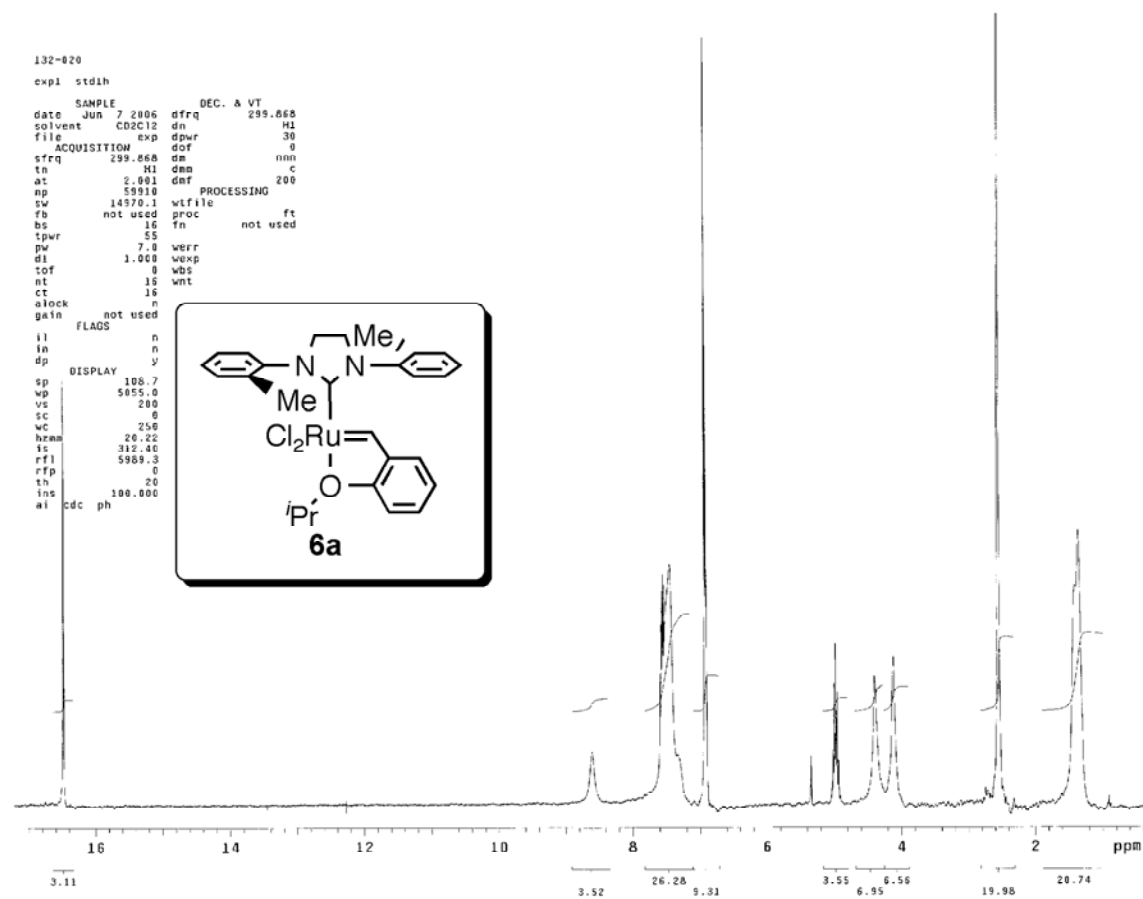
```

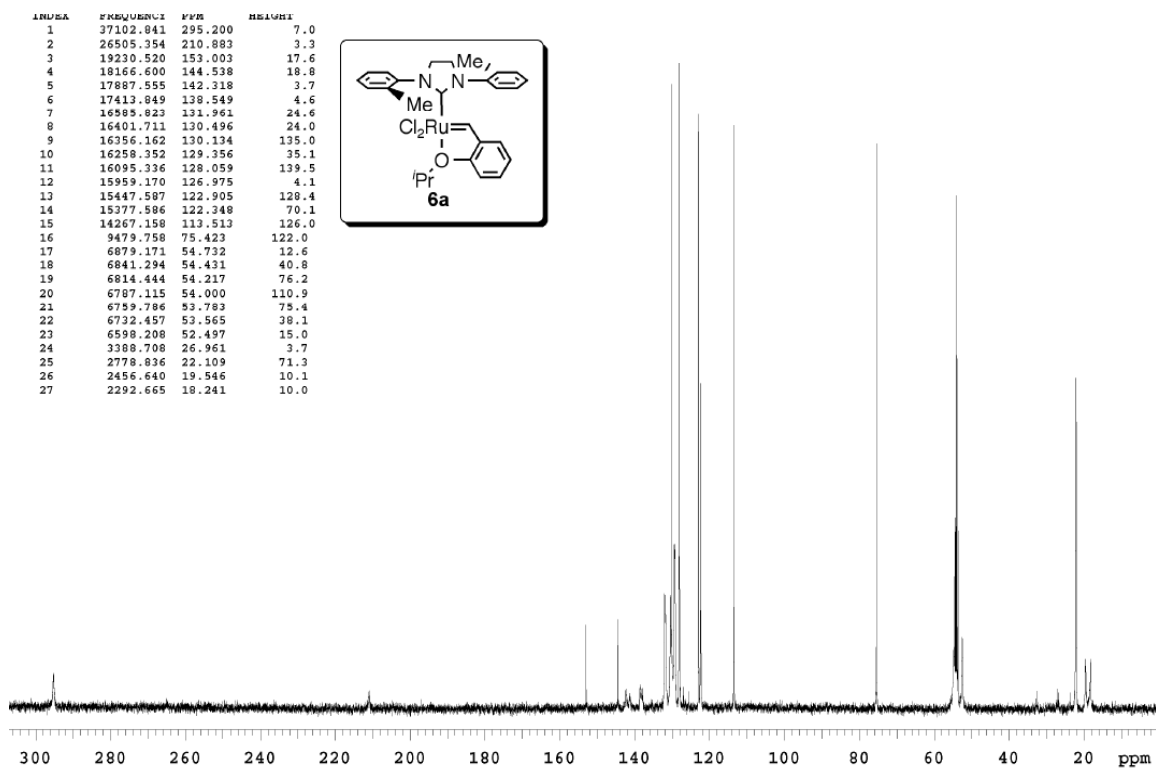
SAMPLE          DEC. & VT
date May 18 2006 dfrq 300.080
solvent Benzene dn H1
file exp dpr 30
ACQUISITION    dof 0
sfrq 300.080 da nnn
in H1 dmz C
at 1.998 dmf 200
np 60000
su 15015.0 wifile PROCESSING
fb not used proc ft
bs 16 fn not used
tpwr 57
pu 7.0 werr
d1 1.000 wexp
tof 0 wbs
nt 16 wnt
ct 16
alock not used
gain not used
FLAGS
i1 n
in n
dp v
DISPLAY
sp 85.0
vp 6254.3
vs 185
sc 0
wg 25.0
hzmm 23.02
is 383.43
rf1 5852.9
rfp 0
th 20
ins 100.000
nm cdc ph

```





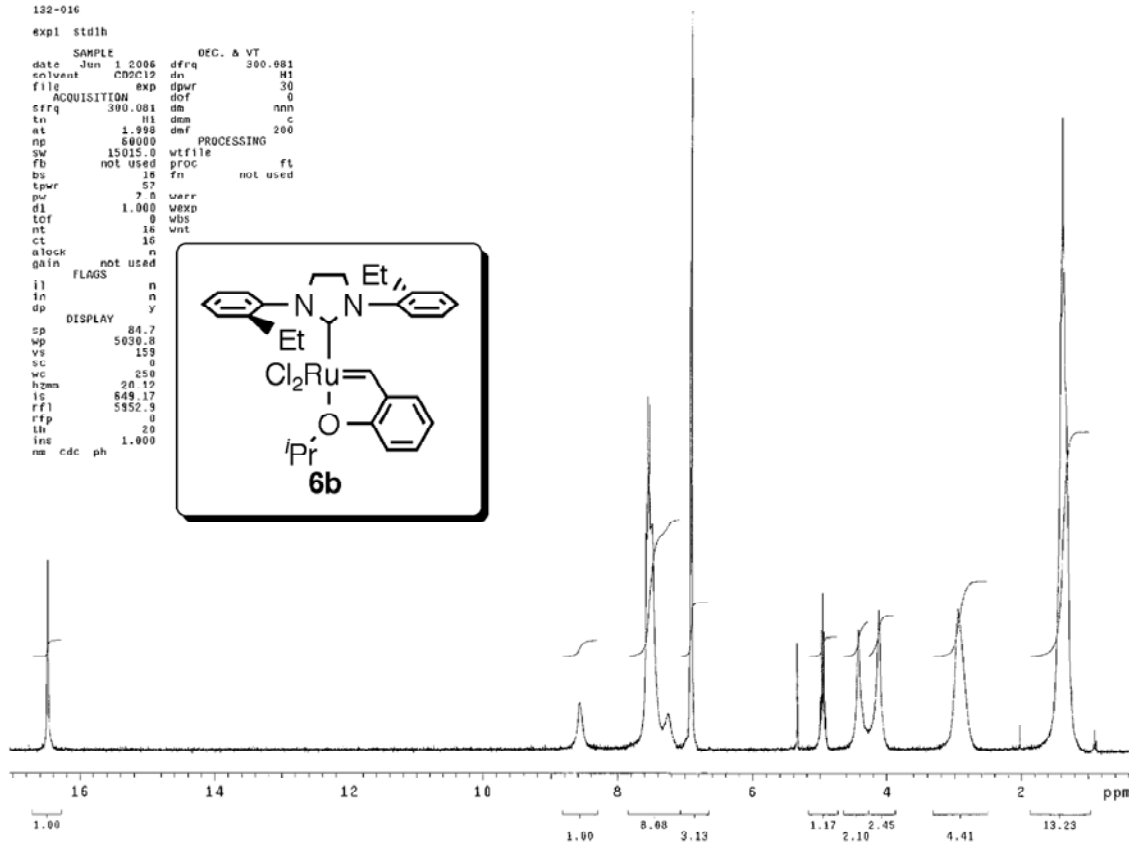
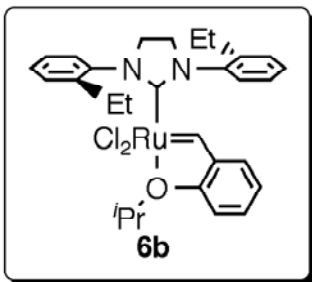


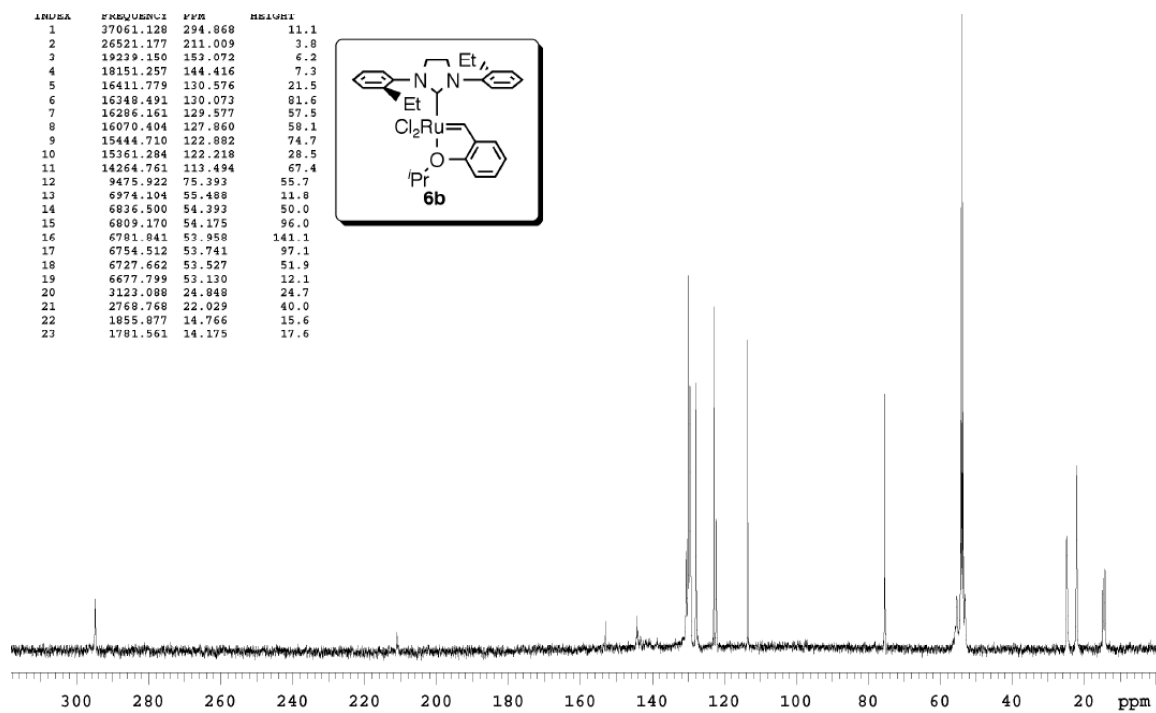


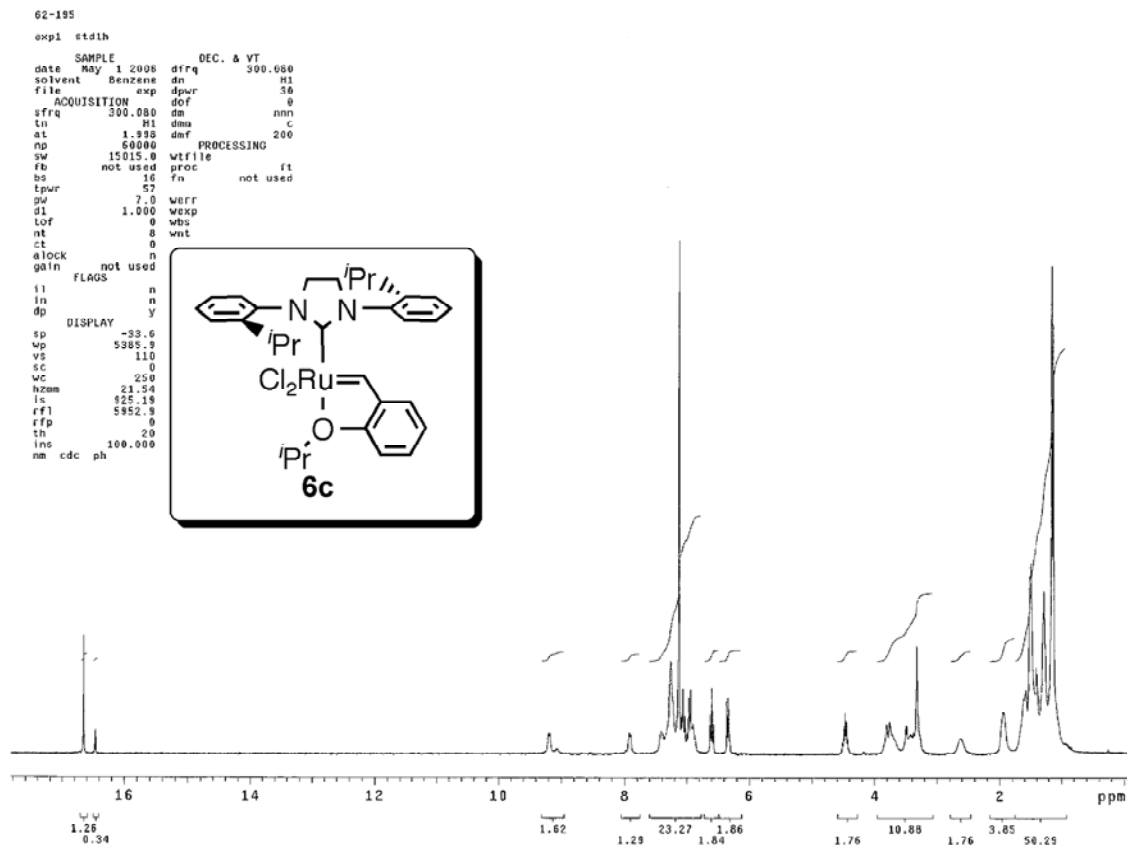
132-016

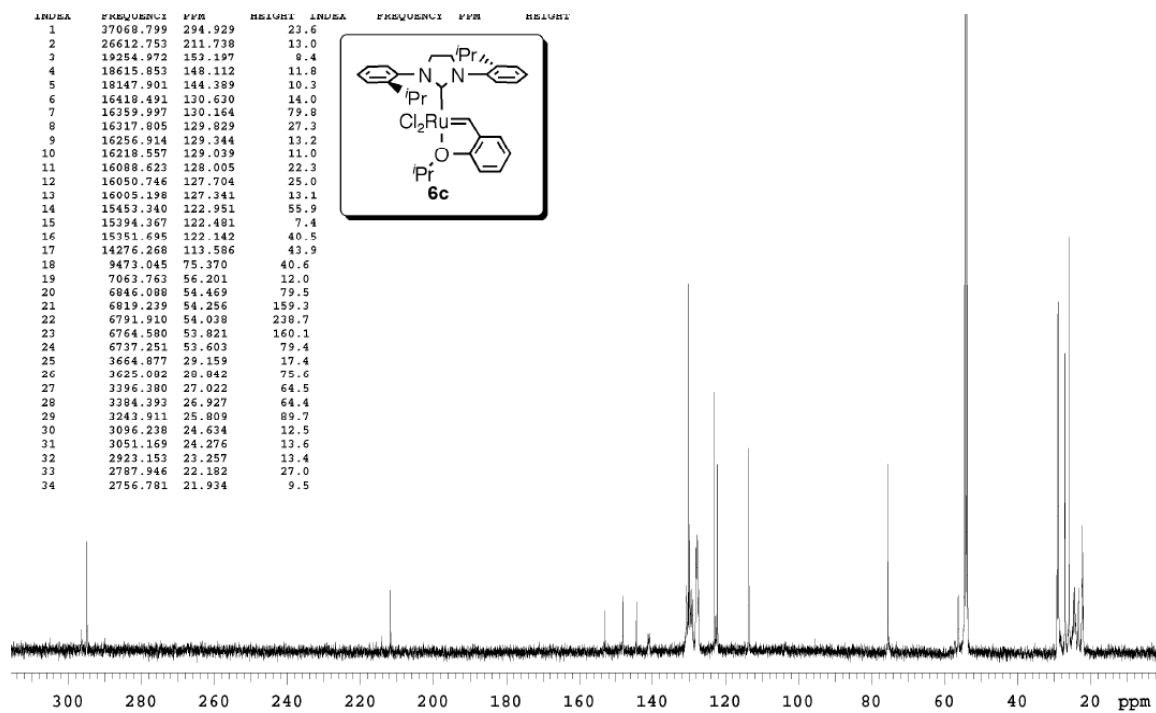
expl std1h

| SAMPLE | | DEC. & VT | |
|-------------|------------|------------|----------|
| date | Jun 1 2006 | dfrq | 300.081 |
| solvent | CDCl3 | ds | M1 |
| file | exp | dpwr | 30 |
| ACQUISITION | | | |
| sfreq | 300.081 | dsf | 0 |
| tn | 11 | dm | nm |
| at | 1.998 | dmf | 200 |
| ng | 6000 | PROCESSING | |
| sw | 15015.0 | wtfile | |
| fb | not used | proc | ft |
| bs | 16 | fn | not used |
| tpwr | 57 | | |
| pr | 7.0 | uarr | |
| dl | 1.000 | WEXP | |
| tcf | 0 | WBS | |
| nt | 16 | WST | |
| ct | 16 | | |
| alock | n | | |
| gain | not used | | |
| il | FLAGS | n | |
| tn | | n | |
| dp | | y | |
| DISPLAY | | | |
| zp | 84.7 | | |
| wp | 5030.8 | | |
| vs | 159 | | |
| sc | 0 | | |
| vc | 250 | | |
| hzm | 20.12 | | |
| ls | 849.17 | | |
| rfl | 5852.9 | | |
| rtp | 0 | | |
| ln | 2.0 | | |
| ins | 1.000 | | |
| na | cdc | ph | |









REFERENCES

- ⁱ Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100-110.
- ⁱⁱ For complete details, see: Ritter, T.; Hejl, A.; Wenzel, A. G.; Funk, T. W.; Grubbs, R. H. *Organometallics* **2006**, *25*, 5740-5745.
- ⁱⁱⁱ 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.
- ^{iv} 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.