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

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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

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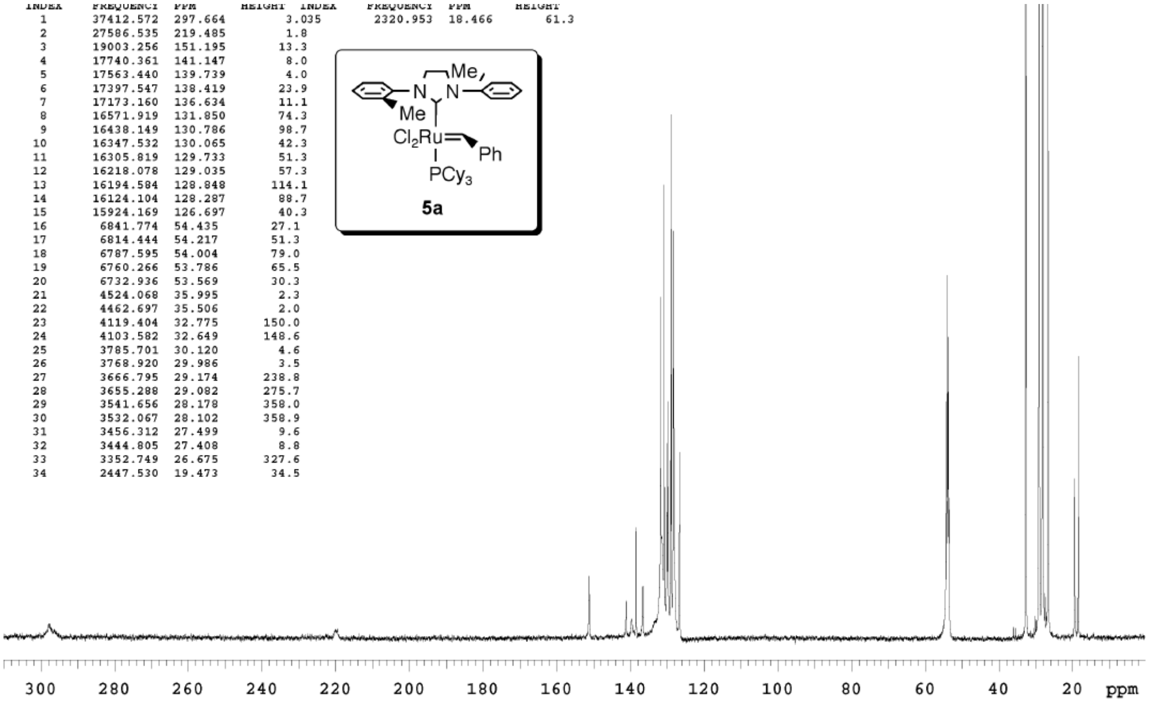
[1] California Institute of Technology
[2] Materia, Inc.



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  7       17173.160  136.634      11.1
  8       16571.919  131.850      74.3
  9       16438.149  130.786      98.7
 10       16347.532  130.065      42.3
 11       16305.819  129.733      51.3
 12       16218.078  129.035      57.3
 13       16194.584  128.848     114.1
 14       16124.104  128.287      88.7
 15       15924.169  126.697      40.3
 16        6841.774  54.435       27.1
 17        6814.444  54.217       51.3
 18        6787.595  54.004       79.0
 19        6760.266  53.786       65.5
 20        6732.936  53.569       30.3
 21        4524.068  35.995        2.3
 22        4462.697  35.506        2.0
 23        4119.404  32.775      150.0
 24        4103.582  32.649      148.6
 25        3785.701  30.120        4.6
 26        3768.920  29.986        3.5
 27        3666.795  29.174      238.8
 28        3655.288  29.082      275.7
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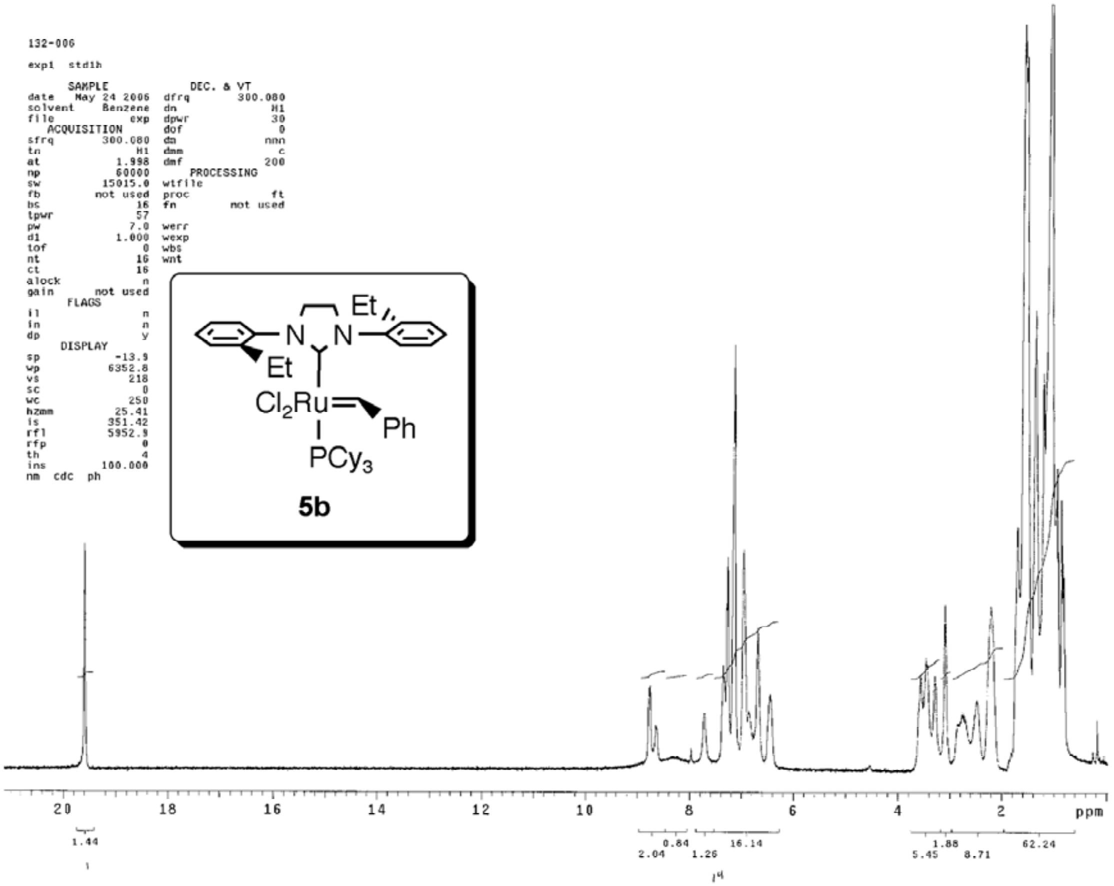

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132-006

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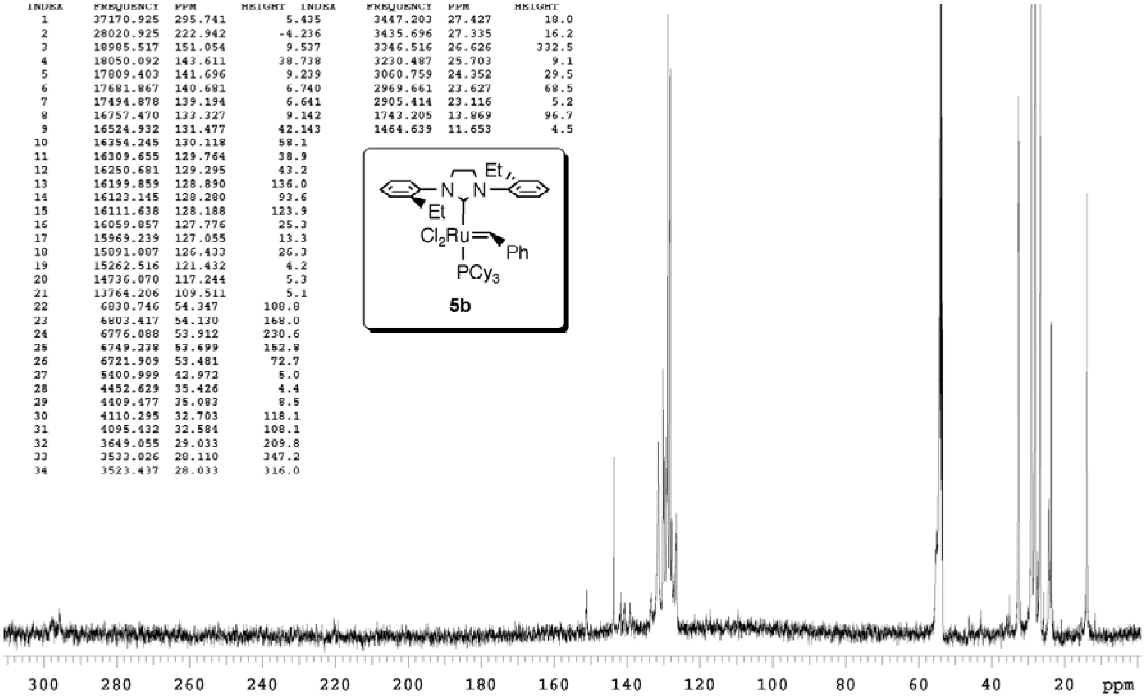

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  3     18985.517   151.054     9.537          3346.516   26.626     332.5
  4     18050.092   143.611    38.738          3230.487   25.703       9.1
  5     17809.403   141.696     9.239          3060.759   24.352      29.5
  6     17681.867   140.681     6.740          2969.661   23.627      68.5
  7     17494.878   139.194     6.641          2905.414   23.116       5.2
  8     16757.470   133.327     9.142          1743.205   13.869      96.7
  9     16524.932   131.477    42.143          1464.639   11.653       4.5
 10     16354.245   130.118    58.1
 11     16309.655   129.764    38.9
 12     16250.681   129.295    43.2
 13     16199.859   128.890   136.0
 14     16123.145   128.280    93.6
 15     16111.638   128.188   123.9
 16     16059.857   127.776    25.3
 17     15969.239   127.055    13.3
 18     15891.087   126.433    26.3
 19     15262.516   121.432     4.2
 20     14736.070   117.244     5.3
 21     13764.206   109.511     5.1
 22      6830.746   54.347    108.8
 23      6803.417   54.130    168.0
 24      6776.088   53.912    230.6
 25      6749.238   53.699    152.8
 26      6721.909   53.481     72.7
 27      5400.999   42.972      5.0
 28      4452.629   35.426      4.4
 29      4409.477   35.083      8.5
 30      4110.295   32.703    118.1
 31      4095.432   32.584    108.1
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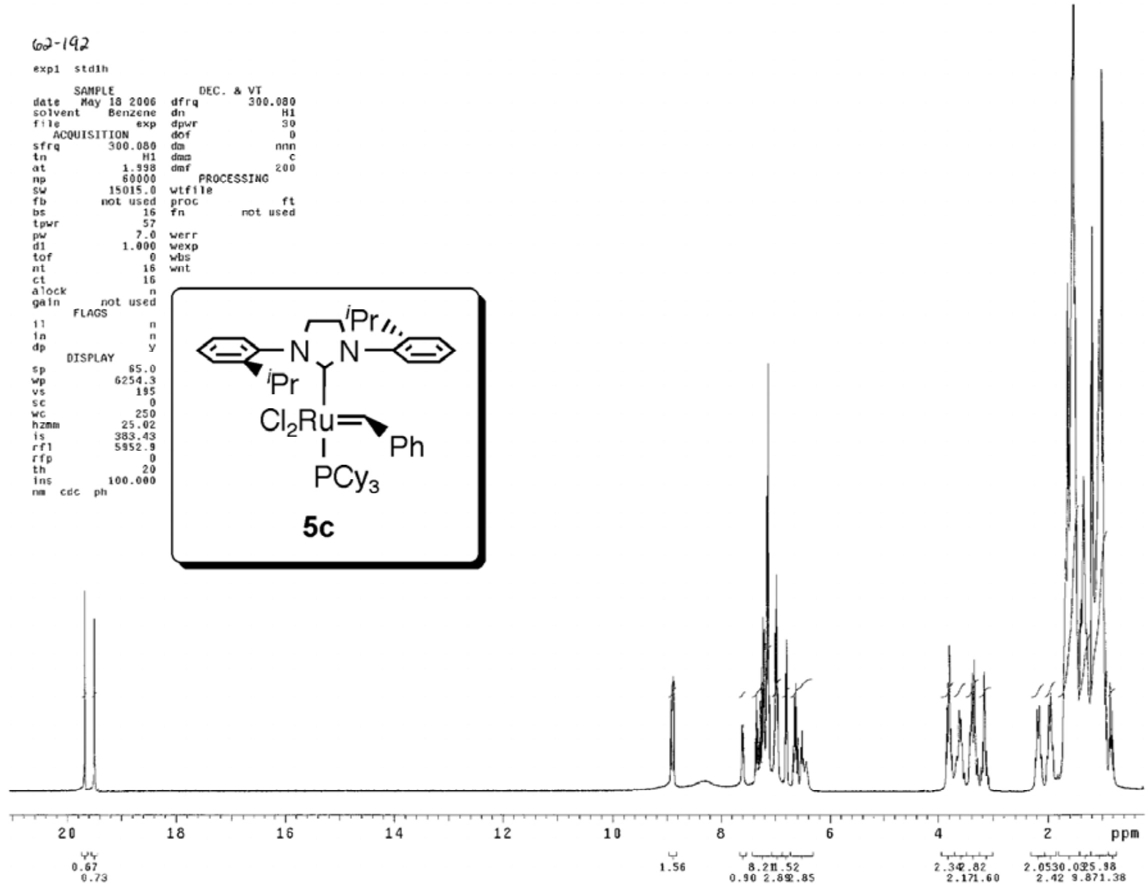
5b

.... 40



62-192

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dp                y
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nm   cdc   ph
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5c

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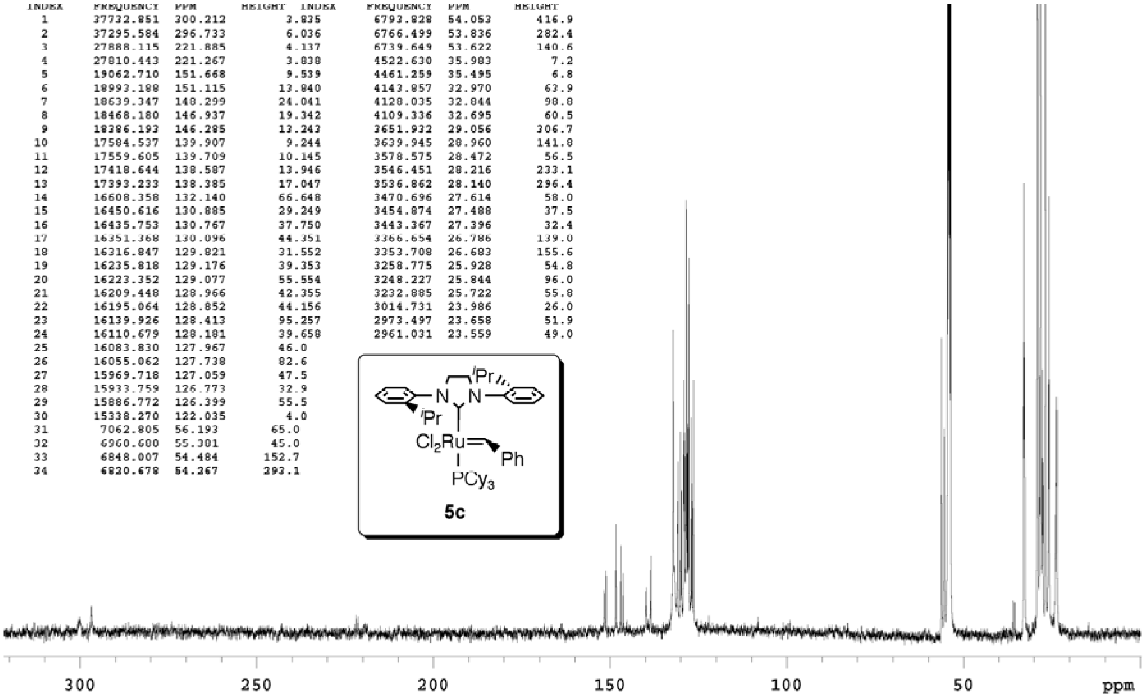

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  2     37295.584  296.733       6.036       6766.499  53.836     282.4
  3     27888.115  221.885       4.137       6739.649  53.622     140.6
  4     27810.443  221.267       3.838       4522.630  35.983       7.2
  5     19062.710  151.668       9.539       4461.259  35.495       6.8
  6     18993.188  151.115      13.840       4143.857  32.970      63.9
  7     18639.347  148.299      24.041       4128.035  32.844      98.8
  8     18468.180  146.937      19.342       4109.336  32.695      60.5
  9     18386.193  146.285      13.243       3651.932  29.056     306.7
 10     17504.537  139.907       9.244       3639.945  28.960     141.8
 11     17559.605  139.709      10.145       3578.575  28.472      56.5
 12     17418.644  138.587      13.946       3546.451  28.216     233.1
 13     17393.233  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       3454.874  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     16316.847  129.821      31.552       3353.708  26.683     155.6
 19     16235.818  129.176      39.353       3258.775  25.928      54.8
 20     16223.352  129.077      55.554       3248.227  25.844      96.0
 21     16209.448  128.966      42.355       3232.885  25.722      55.8
 22     16195.064  128.852      44.156       3014.731  23.986      26.0
 23     16139.926  128.413      95.257       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     15933.759  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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 34      6820.678  54.267    293.1
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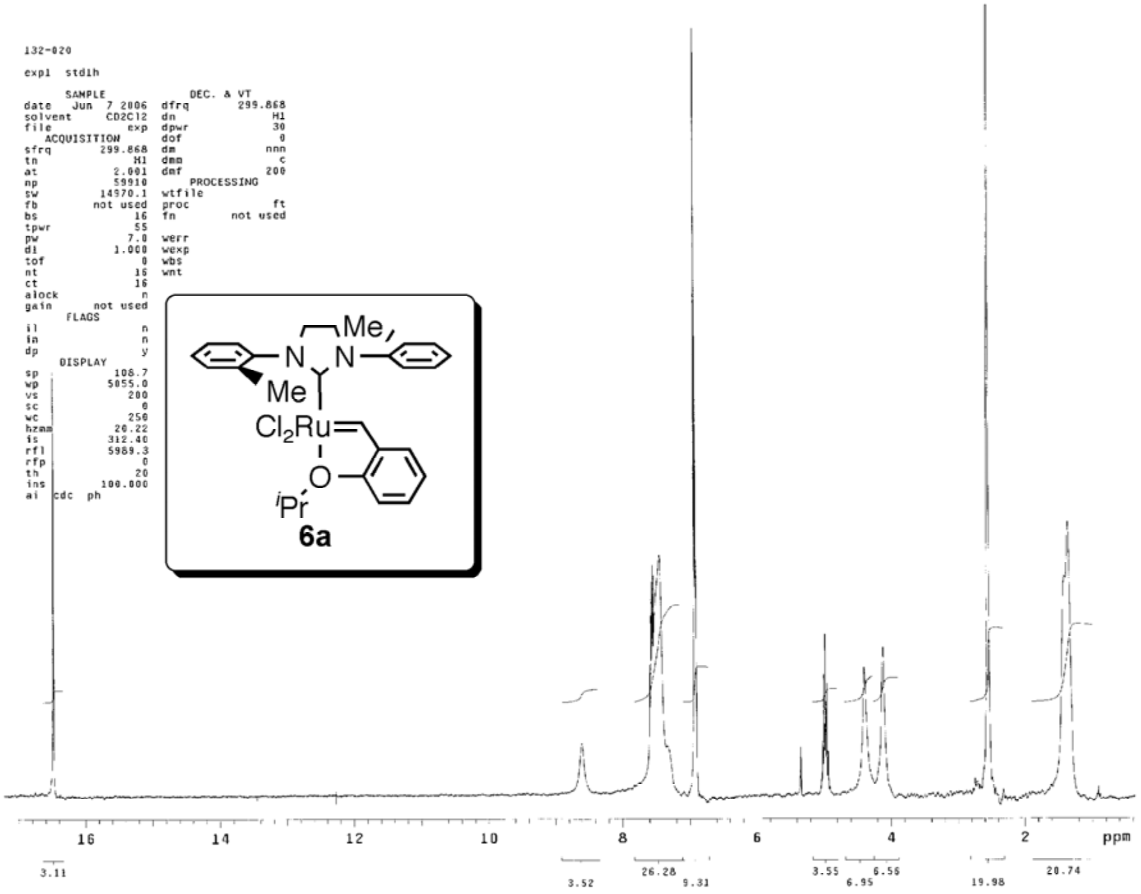

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.... 43

INDEX	FREQUENCY	PPM	HEIGHT
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3	19230.520	153.003	17.6
4	18166.600	144.538	18.8
5	17887.555	142.318	3.7
6	17413.849	138.549	4.6
7	16585.823	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
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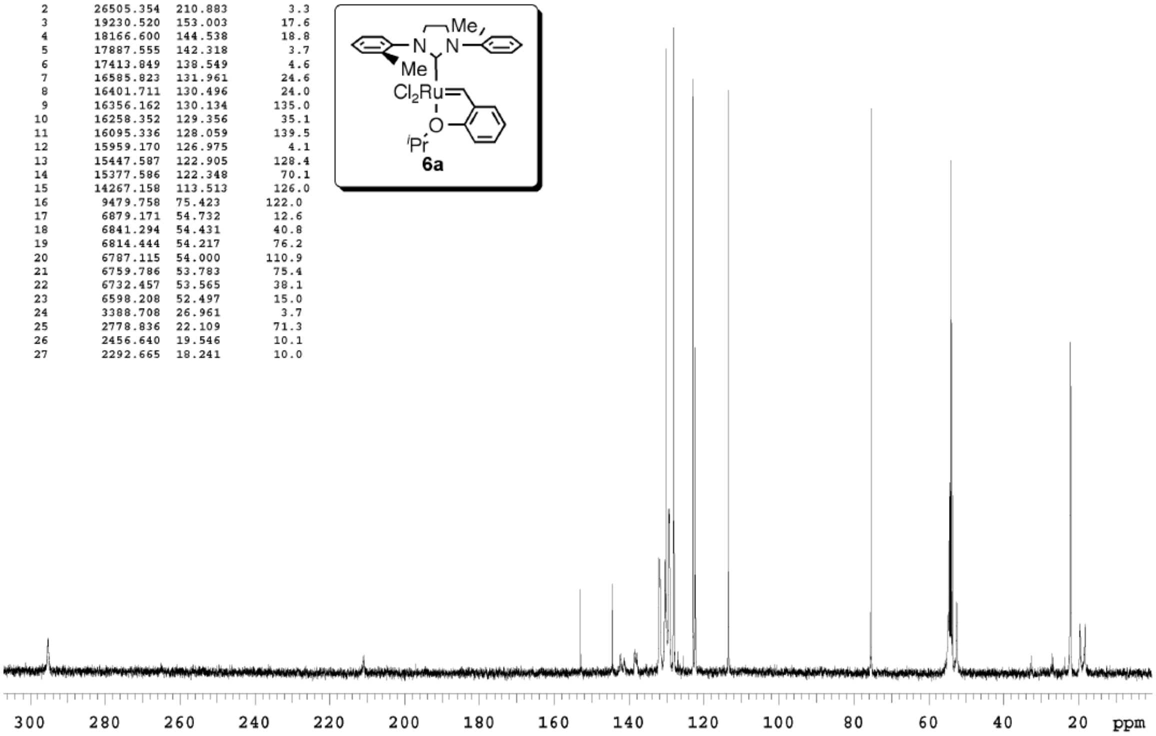

6a

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132-016

expl  stdlh

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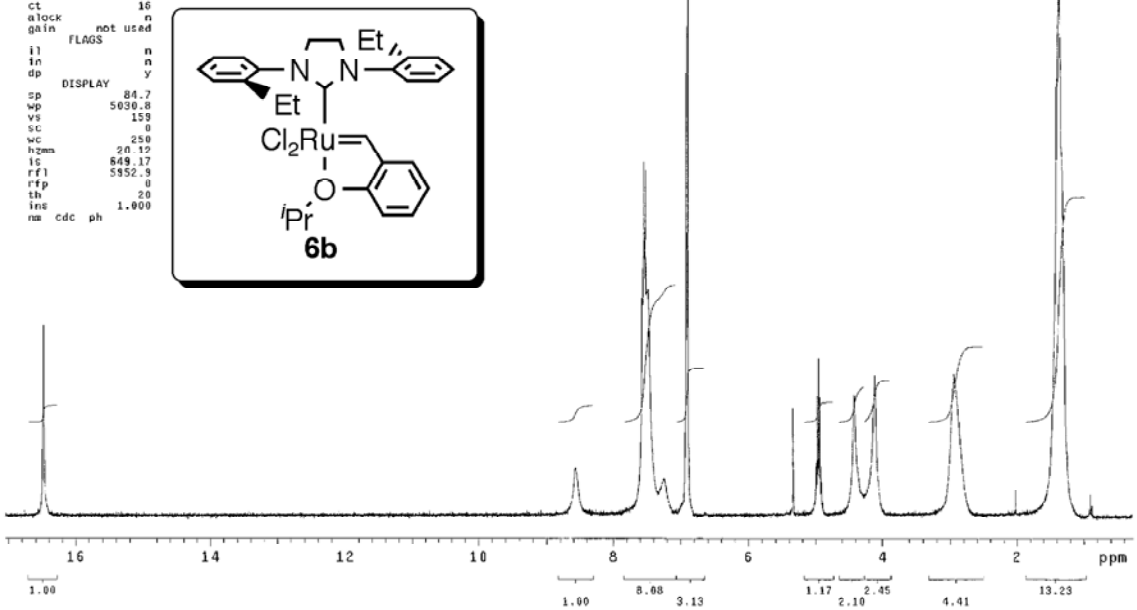
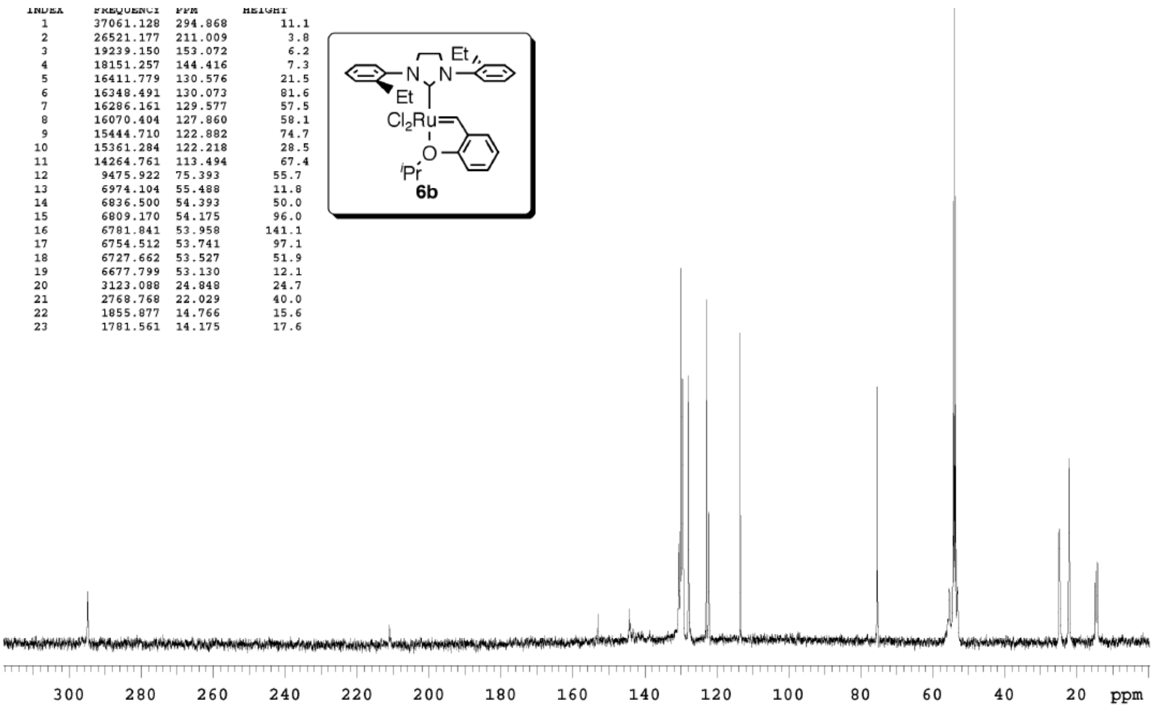


6b

.... 45



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4	18151.257	144.416	7.3
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6	16348.491	130.073	81.6
7	16286.161	129.577	57.5
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
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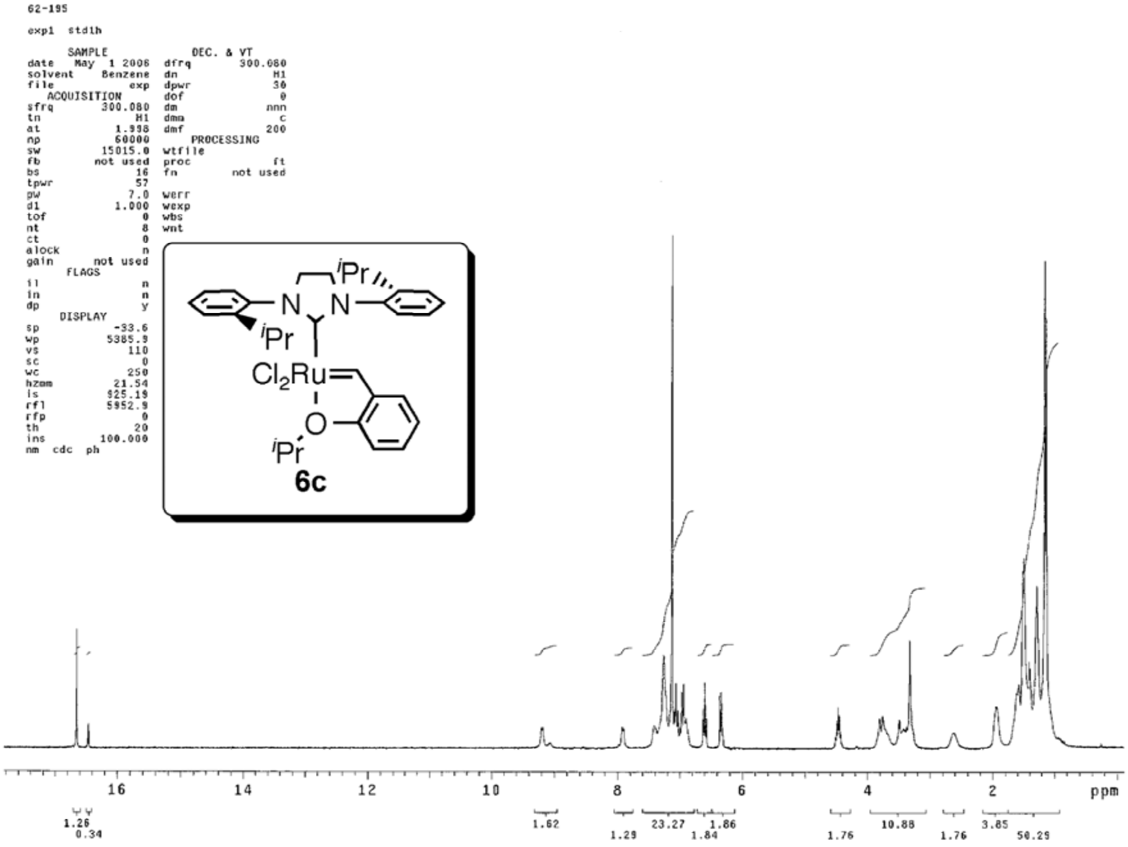

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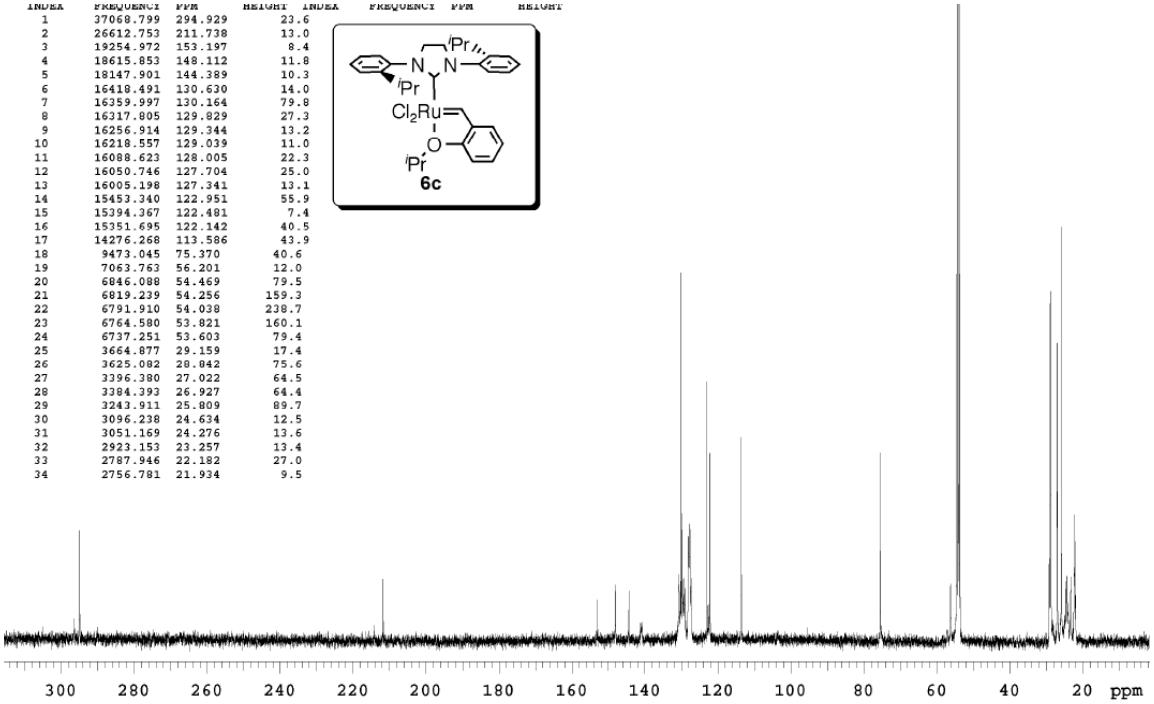

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  3      19254.972  153.197      8.4
  4      18615.853  148.112     11.8
  5      18147.901  144.389     10.3
  6      16418.491  130.630     14.0
  7      16359.997  130.164     79.8
  8      16317.805  129.829     27.3
  9      16256.914  129.344     13.2
 10      16218.557  129.039     11.0
 11      16088.623  128.005     22.3
 12      16050.746  127.704     25.0
 13      16005.198  127.341     13.1
 14      15453.340  122.951     55.9
 15      15394.367  122.481      7.4
 16      15351.695  122.142     40.5
 17      14276.268  113.586     43.9
 18       9473.045  75.370     40.6
 19       7063.763  56.201     12.0
 20       6846.088  54.469     79.5
 21       6819.239  54.256    159.3
 22       6791.910  54.038    238.7
 23       6764.580  53.821    160.1
 24       6737.251  53.603     79.4
 25       3664.877  29.159     17.4
 26       3625.082  28.842     75.6
 27       3396.380  27.022     64.5
 28       3384.393  26.927     64.4
 29       3243.911  25.809     89.7
 30       3096.238  24.634     12.5
 31       3051.169  24.276     13.6
 32       2923.153  23.257     13.4
 33       2787.946  22.182     27.0
 34       2756.781  21.934      9.5
```

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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}H 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 Na_2SO_4. 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:

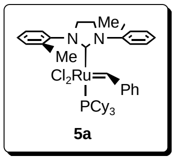
1,3-Bis(*o*-tolyl)-imidazolinium chloride. Obtained in 93% yield as a white solid. ^1H NMR (300 MHz, $CDCl_3$): δ 8.83 (s, 1H), 7.78-7.21 (d, 8H), 4.64 (s, 4H), 2.43 (s, 6H). $^{13}C\{^1H\}$ NMR (75.41 MHz, $CDCl_3$): δ 157.48, 134.37, 133.44, 131.57, 129.82, 127.64, 126.68, 52.89, 18.12. HR-MS (FAB$^+$) Calculated for $C_{17}H_{19}N_2$, 251.1548; found, 251.1557.

1,3-Bis(2-ethylphenyl)-imidazolinium chloride. Obtained in 74% yield as a white solid. ^{1}H 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. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (d, $^3J_{HH}$ = 7.2 Hz, 2H), 8.04 (s, 1H), 7.34 (m, 6H), 4.73 (s, 4H), 3.06 (m, 2H), 1.29 (d, $^3J_{HH}$ = 6.0 Hz, 12H).

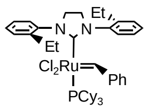
GENERAL PROCEDURE FOR THE PREPARATION OF CATALYSTS 5A-C

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(tricyclo-hexylphosphine) 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*.



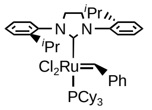
5a

Catalyst 5a. 5a was prepared according to the above general procedure and was obtained in 66% yield. ^{1}H 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). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 27.87 (s), 25.15 (s). $^{13}C\{^1H\}$ 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 $C_{42}H_{57}N_2Cl_2PRu$, 792.2680; found, 792.2678.



5b

Catalyst 5b. **5b** was prepared according to the above general procedure and was obtained in 60% yield. ^{1}H 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). $^{31}P\{^1H\}$ 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 $C_{44}H_{61}N_2Cl_2PRu$, 820.2993; found, 920.2951.

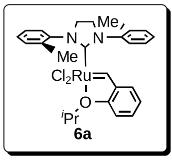


5c

Catalyst 5c. **5c** was prepared according to the above general procedure and was obtained in 68% yield. ^{1}H 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). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 26.33 (s), 23.92 (s). $^{13}C\{^1H\}$ 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 $C_{46}H_{65}N_2Cl_2PRu$, 848.3306; found, 848.3326.

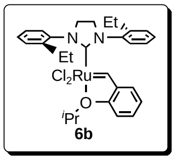
GENERAL PROCEDURE FOR THE PREPARATION OF CATALYSTS **6**A-C.

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*.



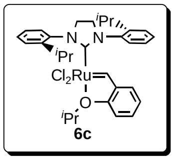
6a

Catalyst 6a. **6a** was prepared according to the above general procedure and was obtained in 71% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 16.47 (s, 1H), 8.59 (s, 1H), 7.43 (br, 8H), 6.91 (d, $^3J_{HH}$ = 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}C{^{1}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 $C_{27}H_{30}N_2Cl_2OPRu$, 570.0779; found, 570.0788.



6b

Catalyst 6b. **6b** was prepared according to the above general procedure and was obtained in 68%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 16.48 (s, 1H), 8.56 (br, 1H), 7.53 (m, 8H), 6.89 (d, $^3J_{HH}$ = 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}C{^{1}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 $C_{29}H_{34}N_2Cl_2ORu$, 598.1092; found, 598.1109.



6c

Catalyst 6c. **6c** was prepared according to the above general procedure and was obtained in 77% yield. ^{1}H 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, $^3J_{HH}$ = 7.5 Hz), 4.47 (m), 3.80-3.32 (m), 2.66 (br), 1.95-1.12 (m). ^{13}C{^{1}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 $C_{31}H_{38}N_2Cl_2ORu$, 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_2Cl_2 (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 immerged 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 ^{o}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).

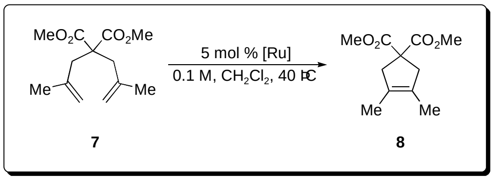


Table S1: RCM of **7** with 5 mol % of **1** at 40 ˚C

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

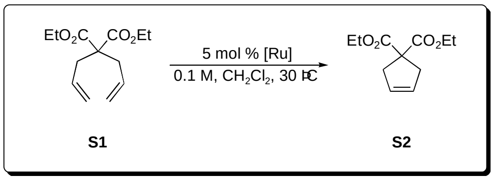
Time (h)	Product (GC%)

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 μmol, 1.0 mol%) and CD_2Cl_2 (0.4 mL). The sample was equilibrated at 30 º C in the NMR probe before **S1** (19.3 μL, 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, CD_2Cl_2).

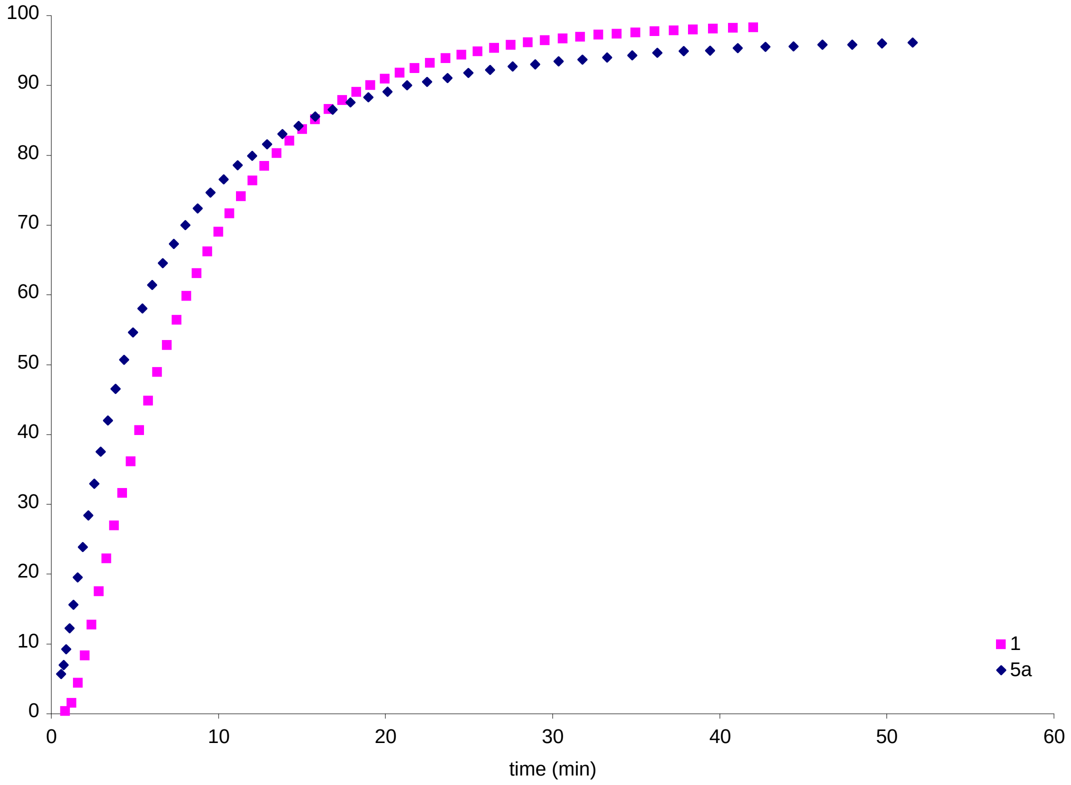
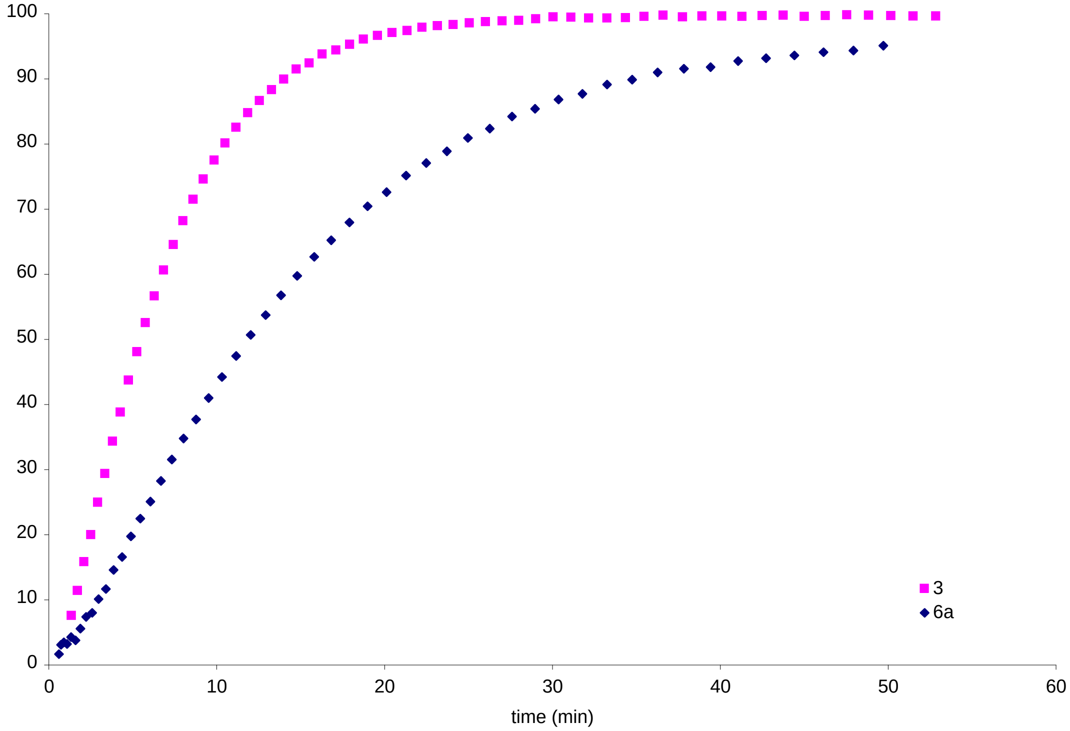
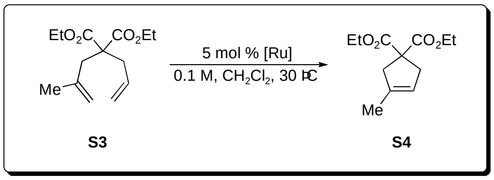


Figure S2. RCM of **S1** using catalysts **3** and **6a** (1 mol%, 30 ˚C, CD_2Cl_2).





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$_2$Cl$_2$ (0.4 mL). The sample was equilibrated at 30 º 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$_2$Cl$_2$).

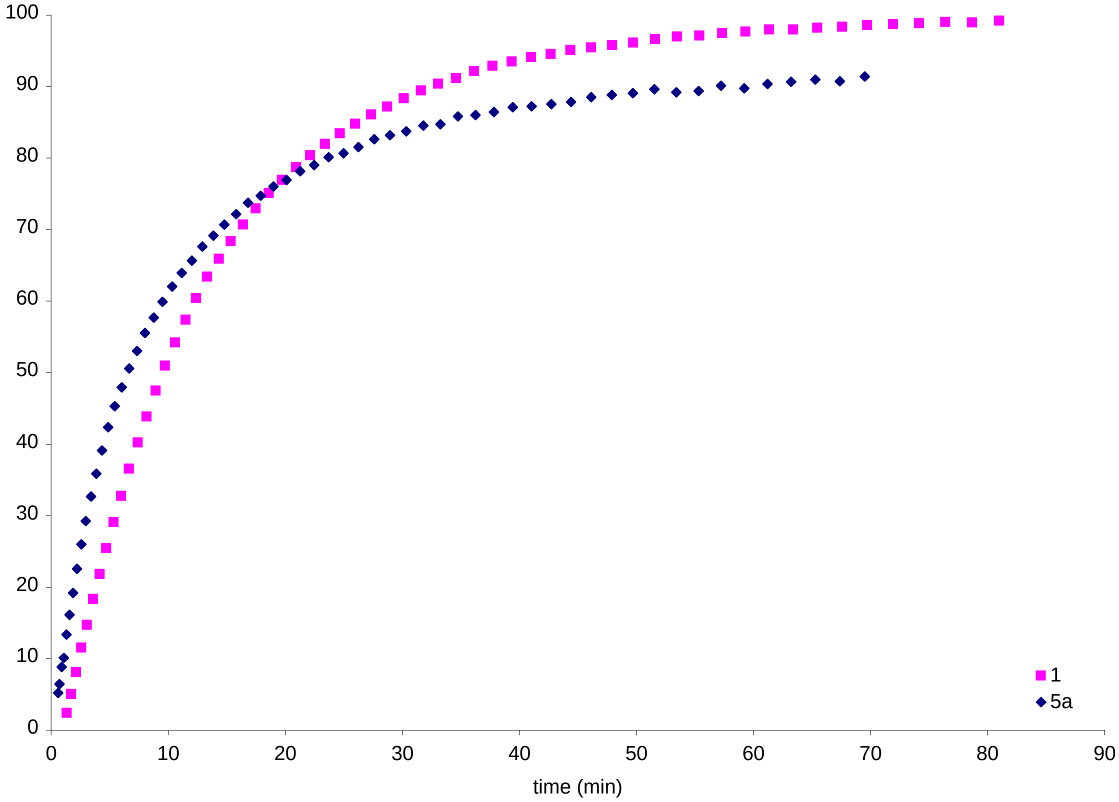
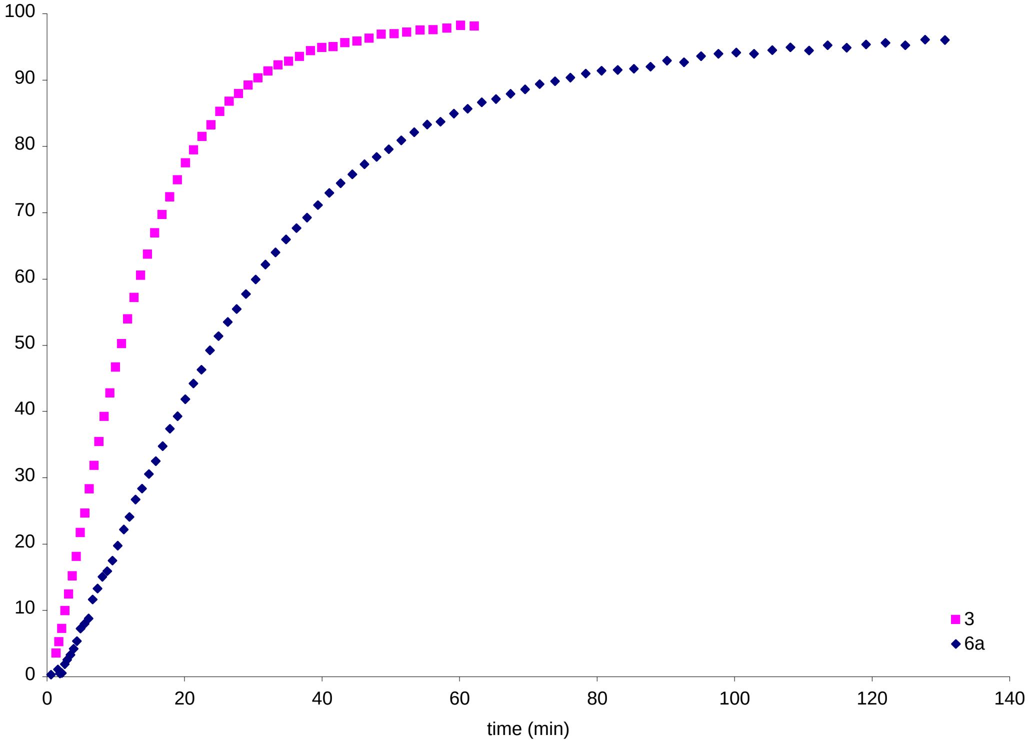
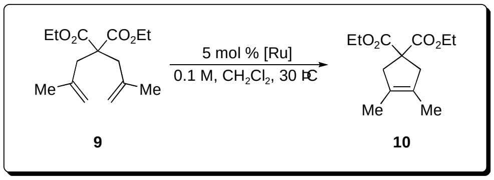


Figure S4. RCM of **S3** using catalysts **3** and **6a** (1 mol%, 30 ˚C, CD_2Cl_2).





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_6D_6 or CD_2Cl_2, 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_2Cl_2).

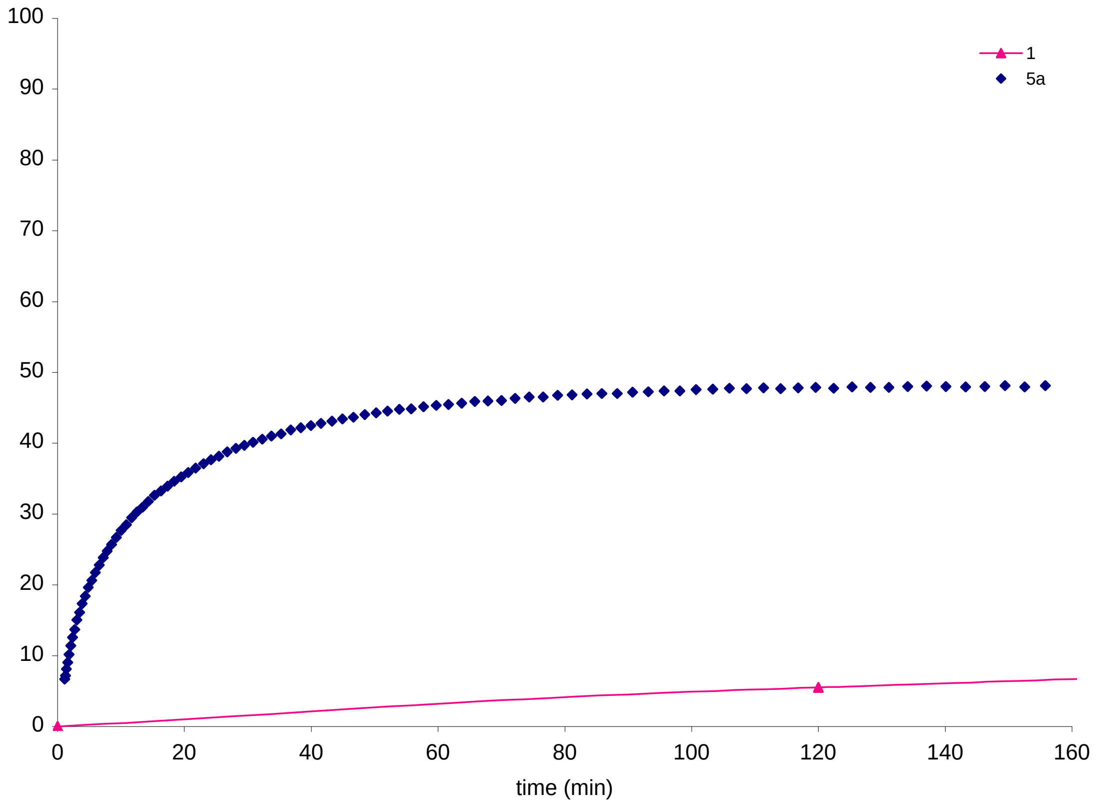


Figure S6. RCM of **9** using catalysts **4** and **6a** (5 mol%, 30 ˚C, CD_2Cl_2).

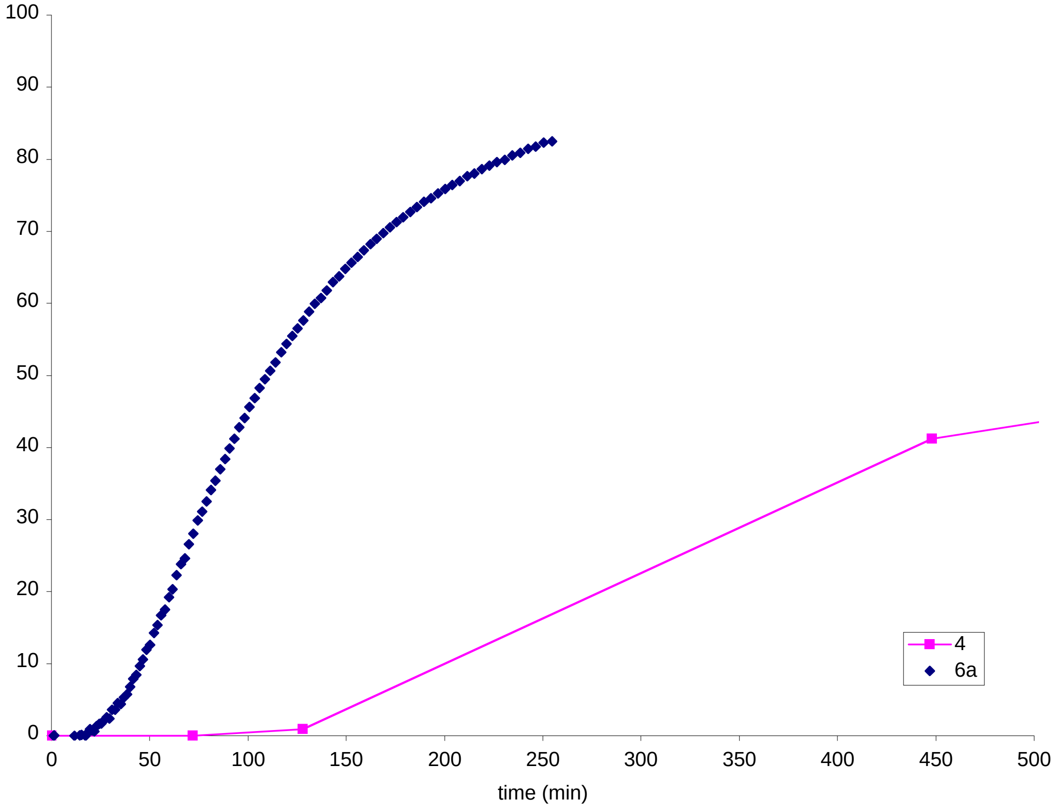
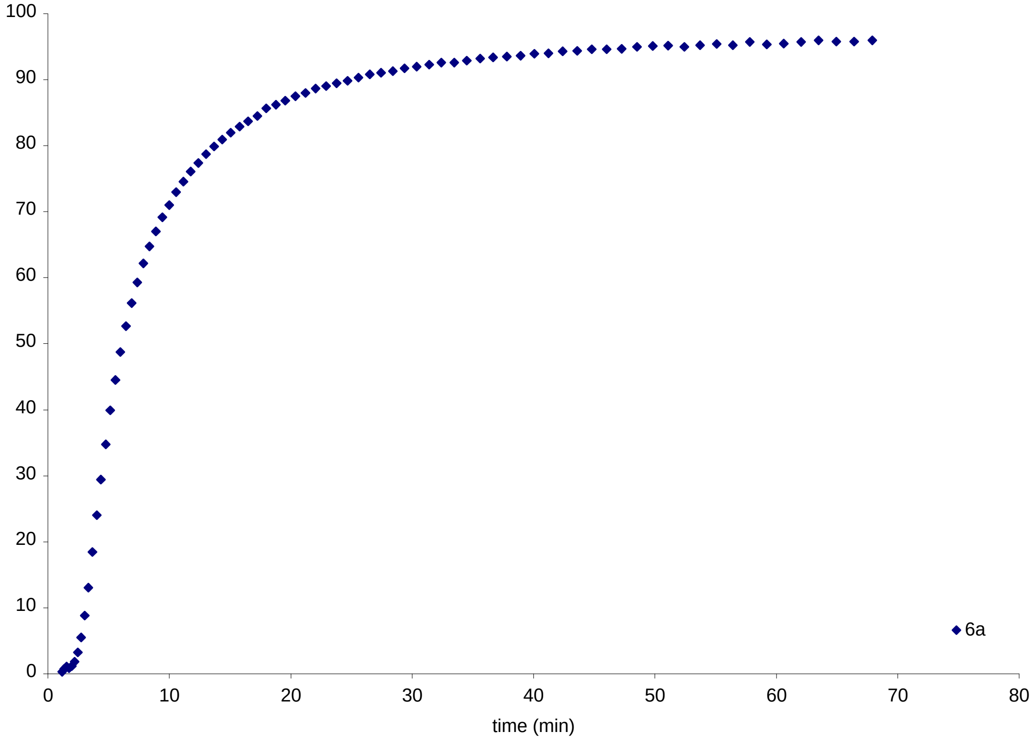
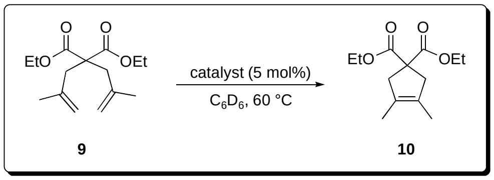


Figure S7. RCM of **9** using catalysts **6a** (2.5 mol%, 60 ˚C, C_6D_6).



GENERAL RCM PROCEDURE FOR TABLE 2.[iii]

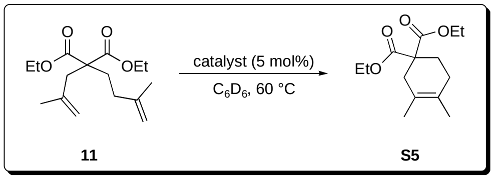
An NMR tube with a screw-cap septum top was charged inside a glovebox with catalyst stock solution (0.005 M in C_6D_6, 0.8 mL, 4.0 µmol, 5.0 mol%). The appropriate substrate (**11-18**, 0.080 mmol, 0.1 M) was added via syringe and the sample placed in an oil bath regulated at 60 ºC. ^{1}H NMR spectra 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.

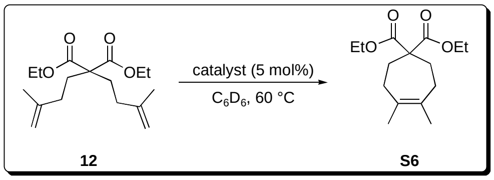
In an argon-filled glove box, a 20 mL vial equipped with a stir bar was charged with **9** (472 mg, 1.76 mmol), toluene (17.6 mL), and catalyst **6a** (50 mg, 0.088 mmol, 5 mol %). The vial was then capped with a septum screw-cap, taken out of the glove box and heated to 60 °C for 1 hour while stirring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



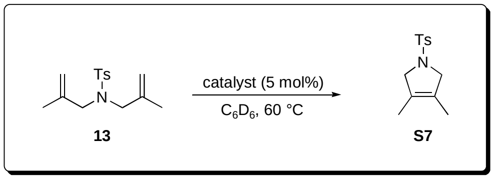
The SM methylene signal at 2.72 ppm was compared to the product signal at 2.63 ppm.

ISOLATED YIELD FOR S5.

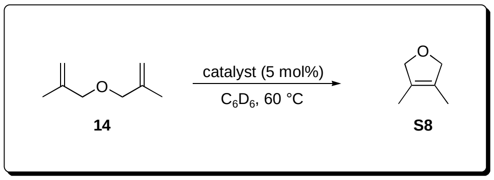
A 10 mL 2-neck round-bottom flask was outfitted with a reflux condensor and a septum, and flame-dried under vacuum. After cooling to r.t., **6a** (5.1 mg, 0.009 mmol, 5 mol%) was added as a solid. Dry degassed benzene (1.8 mL) was added via syringe, followed by **11** (52 µL, 0.185 mmol) via syringe. 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_2, 5% EtOAc:hexanes) afforded **S5** as a colorless oil (47 mg, 0.185, 100%).



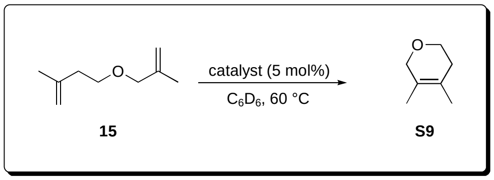
The SM methyl group signal at 1.59 ppm was compared to the product signal at 1.50 ppm.



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	$C_{27}H_{30}N_2OCl_2Ru$	
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 MoKα	
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	β= 105.5780(10)°
	c = 16.6418(5) Å	
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	$-20 \le h \le 20$, $-25 \le k \le 25$, $-28 \le l \le 30$	
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 [$I>2\sigma(I)$, 10742 reflections]	R1 = 0.0348, *w*R2 = 0.0652
R indices (all data)	R1 = 0.0575, *w*R2 = 0.0688
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
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 (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **6a**. U(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(1)-N(2)-C(3)	112.63(10)
C(11B)-N(2)-C(3)	118.0(8)
C(11)-N(2)-C(3)	119.52(10)
N(2)-C(1)-N(1)	107.24(10)
N(2)-C(1)-Ru(1)	132.26(8)
N(1)-C(1)-Ru(1)	120.34(8)
N(1)-C(2)-C(3)	101.52(10)
N(2)-C(3)-C(2)	101.69(10)
C(9)-C(4)-C(5)	121.43(13)
C(9)-C(4)-N(1)	119.31(12)
C(5)-C(4)-N(1)	119.25(14)
C(6)-C(5)-C(4)	117.10(17)
C(6)-C(5)-C(10)	120.72(15)
C(4)-C(5)-C(10)	122.14(14)
C(7)-C(6)-C(5)	122.04(16)
C(8)-C(7)-C(6)	120.02(15)
C(7)-C(8)-C(9)	119.32(18)
C(4)-C(9)-C(8)	120.10(15)
C(16)-C(11)-C(12)	121.15(12)
C(16)-C(11)-N(2)	117.96(13)
C(12)-C(11)-N(2)	120.89(15)
C(11)-C(12)-C(13)	117.54(14)
C(11)-C(12)-C(17)	121.70(13)
C(13)-C(12)-C(17)	120.73(14)
C(14)-C(13)-C(12)	121.32(14)
C(13)-C(14)-C(15)	120.31(13)
C(14)-C(15)-C(16)	119.42(14)
C(15)-C(16)-C(11)	120.24(14)
C(16B)-C(11B)-N(2)	114.4(5)
C(16B)-C(11B)-C(12B)	121.08(18)
N(2)-C(11B)-C(12B)	124.4(5)
C(11B)-C(12B)-C(13B)	117.48(18)
C(11B)-C(12B)-C(17B)	121.73(19)
C(13B)-C(12B)-C(17B)	120.79(19)
C(14B)-C(13B)-C(12B)	121.37(18)
C(13B)-C(14B)-C(15B)	120.29(18)
C(14B)-C(15B)-C(16B)	119.32(19)
C(15B)-C(16B)-C(11B)	120.2(2)
C(19)-C(18)-Ru(1)	119.54(8)
C(20)-C(19)-C(24)	118.62(10)
C(20)-C(19)-C(18)	122.29(11)
C(24)-C(19)-C(18)	119.08(10)
C(21)-C(20)-C(19)	120.87(12)
C(20)-C(21)-C(22)	119.09(12)
C(21)-C(22)-C(23)	121.77(11)
C(24)-C(23)-C(22)	118.40(12)
O(1)-C(24)-C(23)	125.86(11)
O(1)-C(24)-C(19)	112.93(9)
C(23)-C(24)-C(19)	121.21(11)
O(1)-C(25)-C(26)	106.31(10)
O(1)-C(25)-C(27)	110.04(11)
C(26)-C(25)-C(27)	112.08(13)

Table S16. Anisotropic displacement parameters (Å^{2}x 10^4) for **6a**

The anisotropic displacement factor exponent takes the form:

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

	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**

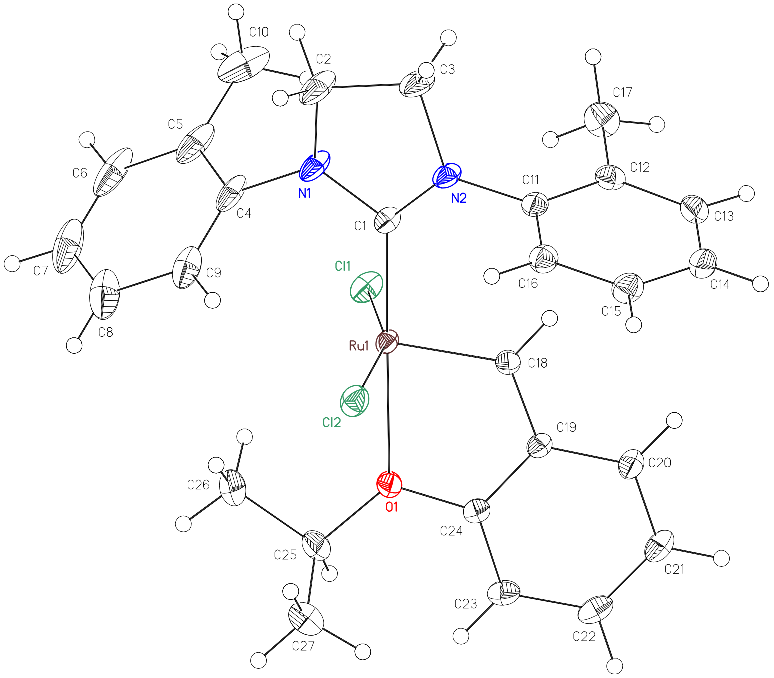


Figure S9. ORTEP drawing of *anti*-**6a**

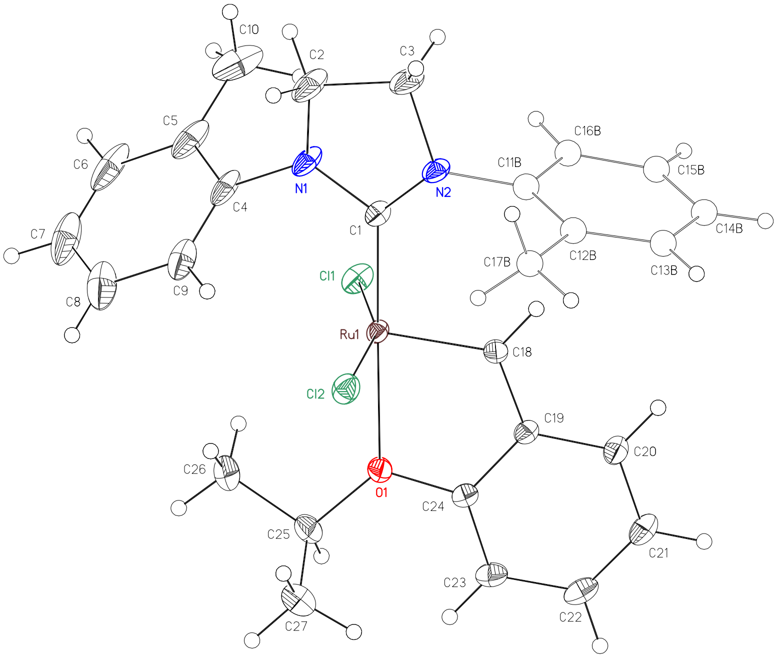
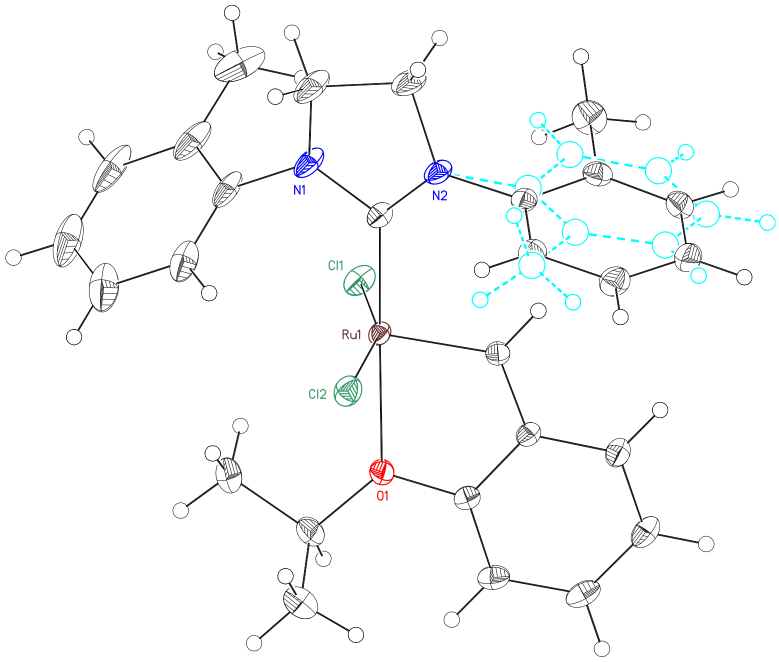
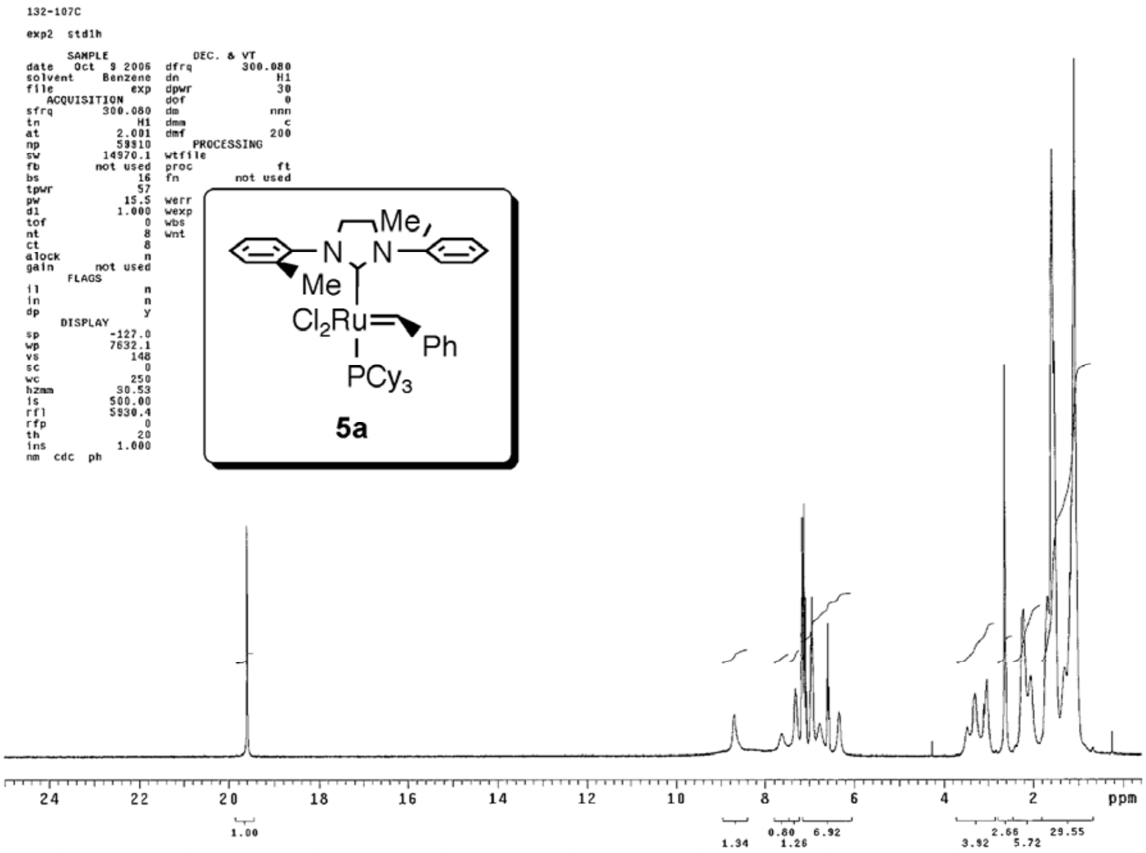


Figure S10. ORTEP drawing of superimposed *syn*- and *anti*-**6a**



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



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132-107C

exp2  std1h

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solvent    Benzene   dn                H1
file           exp   dpwr              30
   ACQUISITION       dof                0
sfrq       300.080   dm               nnn
tn              H1   dmm                c
at           2.001   dmf              200
np           59910        PROCESSING
sw         14970.1   wtfile
fb        not used   proc              ft
bs              16   fn          not used
tpwr            57
pw            15.5   werr
d1           1.000   wexp
tof              0   wbs
nt               8   wnt
ct               8
alock            n
gain      not used
       FLAGS
il               n
in               n
dp               y
      DISPLAY
sp          -127.0
wp          7632.1
vs             148
sc               0
wc             250
hzmm         30.53
is          500.00
rfl         5930.4
rfp              0
th              20
ins          1.000
nm  cdc  ph
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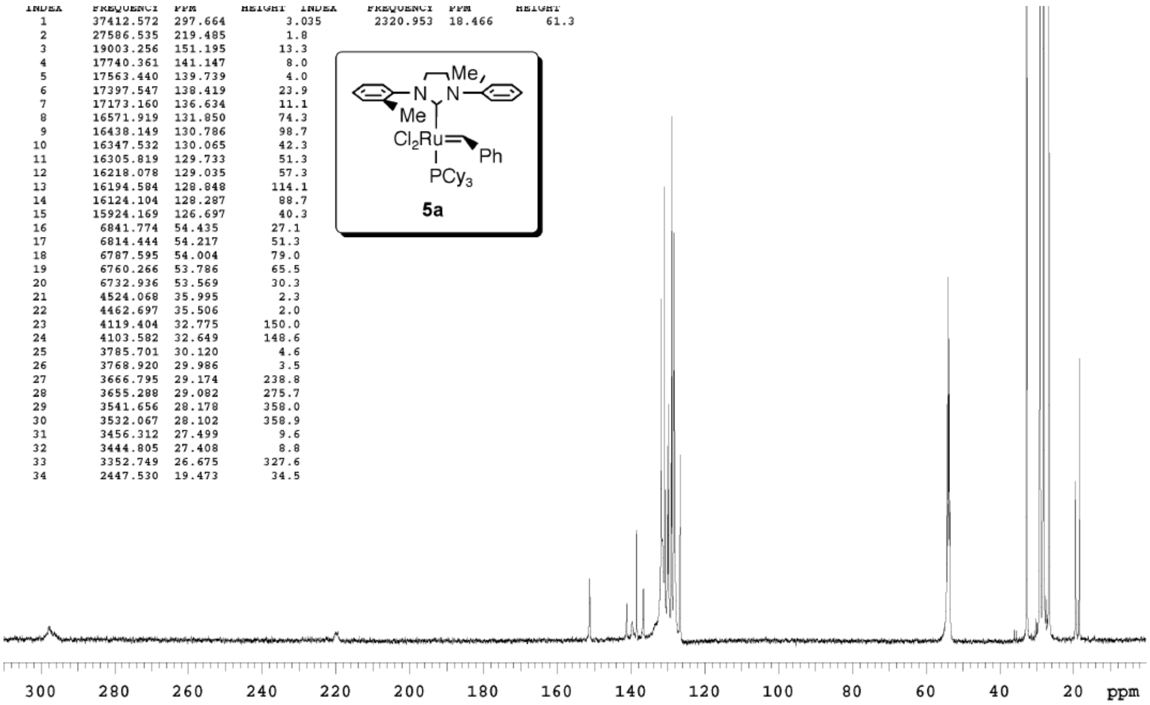
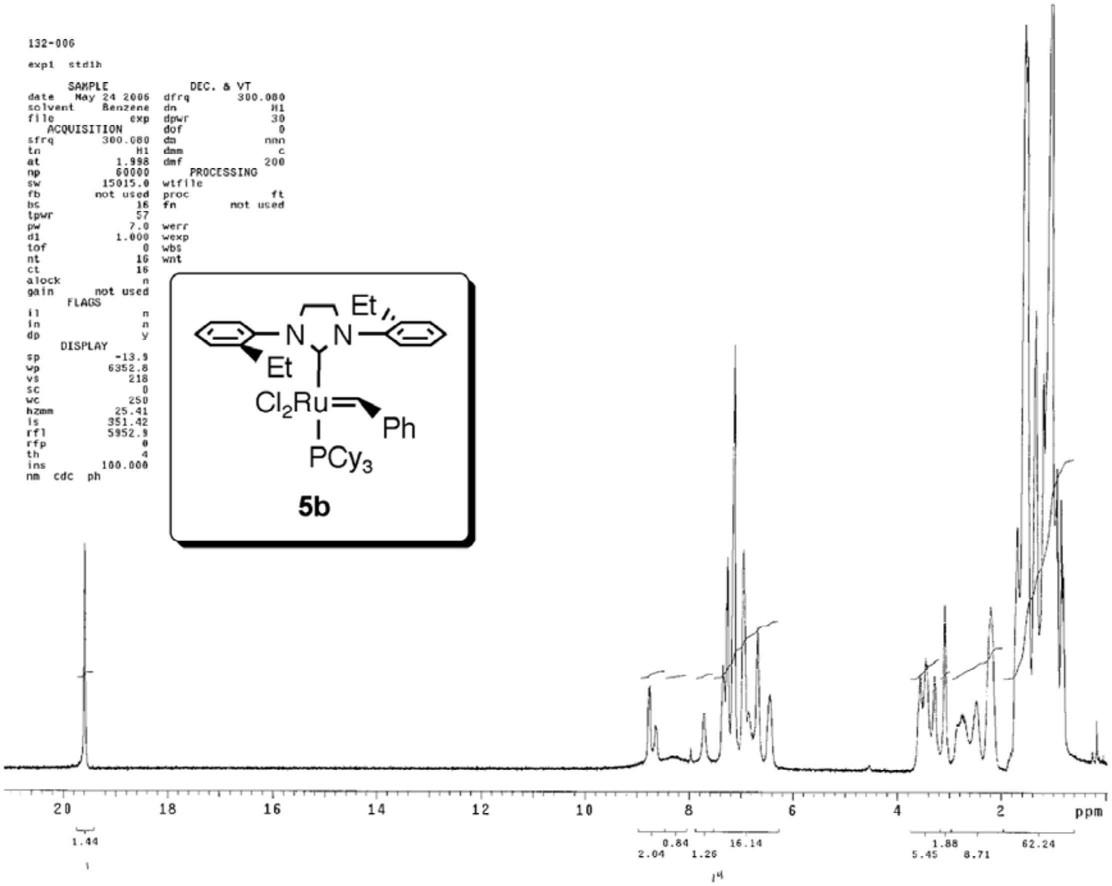


5a

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	37412.572	297.664	3.0	35	2320.953	18.466	61.3
2	27586.535	219.485	1.8				
3	19003.256	151.195	13.3				
4	17740.361	141.147	8.0				
5	17563.440	139.739	4.0				
6	17397.547	138.419	23.9				
7	17173.160	136.634	11.1				
8	16571.919	131.850	74.3				
9	16438.149	130.786	98.7				
10	16347.532	130.065	42.3				
11	16305.819	129.733	51.3				
12	16218.078	129.035	57.3				
13	16194.584	128.848	114.1				
14	16124.104	128.287	88.7				
15	15924.169	126.697	40.3				
16	6841.774	54.435	27.1				
17	6814.444	54.217	51.3				
18	6787.595	54.004	79.0				
19	6760.266	53.786	65.5				
20	6732.936	53.569	30.3				
21	4524.068	35.995	2.3				
22	4462.697	35.506	2.0				
23	4119.404	32.775	150.0				
24	4103.582	32.649	148.6				
25	3785.701	30.120	4.6				
26	3768.920	29.986	3.5				
27	3666.795	29.174	238.8				
28	3655.288	29.082	275.7				
29	3541.656	28.178	358.0				
30	3532.067	28.102	358.9				
31	3456.312	27.499	9.6				
32	3444.805	27.408	8.8				
33	3352.749	26.675	327.6				
34	2447.530	19.473	34.5				



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132-006

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sfrq       300.080  dm              nnn
tn              H1  dmm               c
at           1.998  dmf             200
np           60000        PROCESSING
sw         15015.0  wtfile
fb        not used  proc             ft
bs              16  fn         not used
tpwr            57
pw             7.0  werr
d1           1.000  wexp
tof              0  wbs
nt              16  wnt
ct              16
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp           -13.9
wp          6352.8
vs             218
sc               0
wc             250
hzmm         25.41
is          351.42
rfl         5952.9
rfp              0
th               4
ins        100.000
nm  cdc  ph
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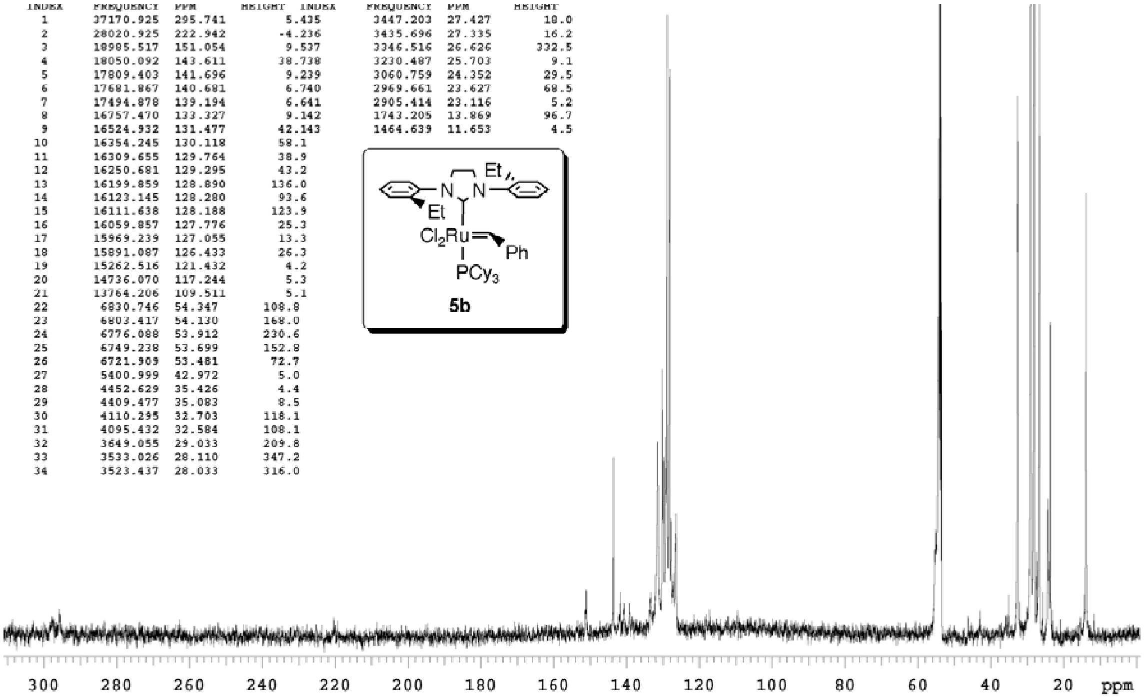

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INDEX   FREQUENCY   PPM       HEIGHT  INDEX   FREQUENCY   PPM      HEIGHT
  1     37170.925   295.741    5.435          3447.203   27.427     18.0
  2     28020.925   222.942   -4.236          3435.696   27.335     16.2
  3     18985.517   151.054    9.537          3346.516   26.626    332.5
  4     18050.092   143.611   38.738          3230.487   25.703      9.1
  5     17809.403   141.696    9.239          3060.759   24.352     29.5
  6     17681.867   140.681    6.740          2969.661   23.627     68.5
  7     17494.878   139.194    6.641          2905.414   23.116      5.2
  8     16757.470   133.327    9.142          1743.205   13.869     96.7
  9     16524.932   131.477   42.143          1464.639   11.653      4.5
 10     16354.245   130.118   58.1
 11     16309.655   129.764   38.9
 12     16250.681   129.295   43.2
 13     16199.859   128.890  136.0
 14     16123.145   128.280   93.6
 15     16111.638   128.188  123.9
 16     16059.857   127.776   25.3
 17     15969.239   127.055   13.3
 18     15891.087   126.433   26.3
 19     15262.516   121.432    4.2
 20     14736.070   117.244    5.3
 21     13764.206   109.511    5.1
 22      6830.746   54.347   108.8
 23      6803.417   54.130   168.0
 24      6776.088   53.912   230.6
 25      6749.238   53.699   152.8
 26      6721.909   53.481    72.7
 27      5400.999   42.972     5.0
 28      4452.629   35.426     4.4
 29      4409.477   35.083     8.5
 30      4110.295   32.703   118.1
 31      4095.432   32.584   108.1
 32      3649.055   29.033   209.8
 33      3533.026   28.110   347.2
 34      3523.437   28.033   316.0
```
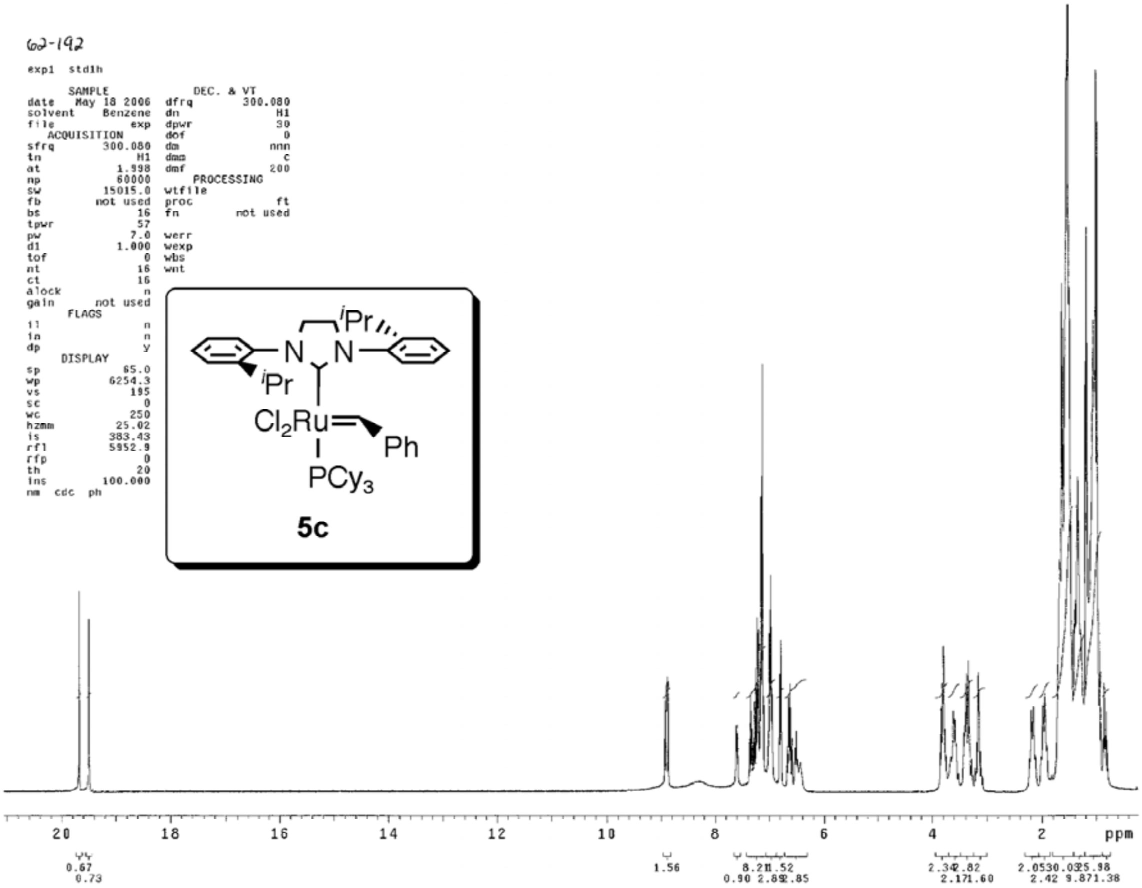
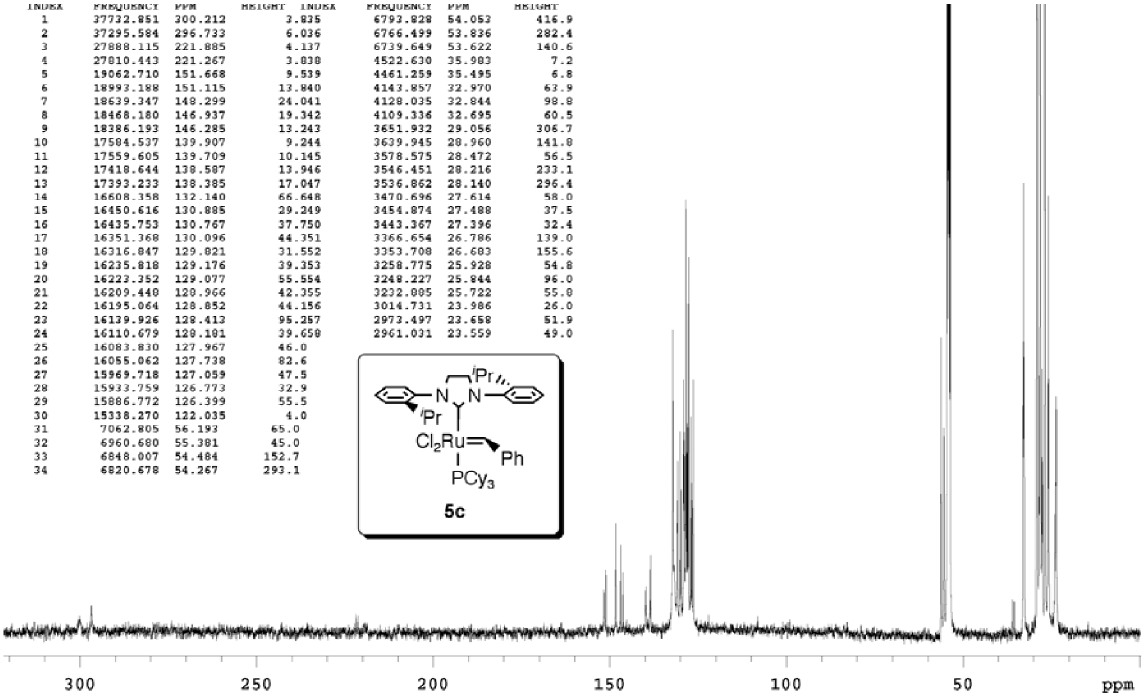

5b

62-192

```
exp1  stdlh

      SAMPLE              DEC. & VT
date   May 18 2006   dfrq        300.080
solvent    Benzene   dn               H1
file           exp   dpwr             30
   ACQUISITION       dof               0
sfrq       300.080   dm              nnn
tn              H1   dmm               c
at           1.998   dmf             200
np           60000        PROCESSING
sw         15015.0   wtfile
fb        not used   proc             ft
bs              16   fn         not used
tpwr            57
pw             7.0   werr
d1           1.000   wexp
tof              0   wbs
nt              16   wnt
ct              16
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp            65.0
wp          6254.3
vs             195
sc               0
wc             250
hzmm         25.02
is          383.43
rfl         5952.9
rfp              0
th              20
ins        100.000
nm  cdc  ph
```

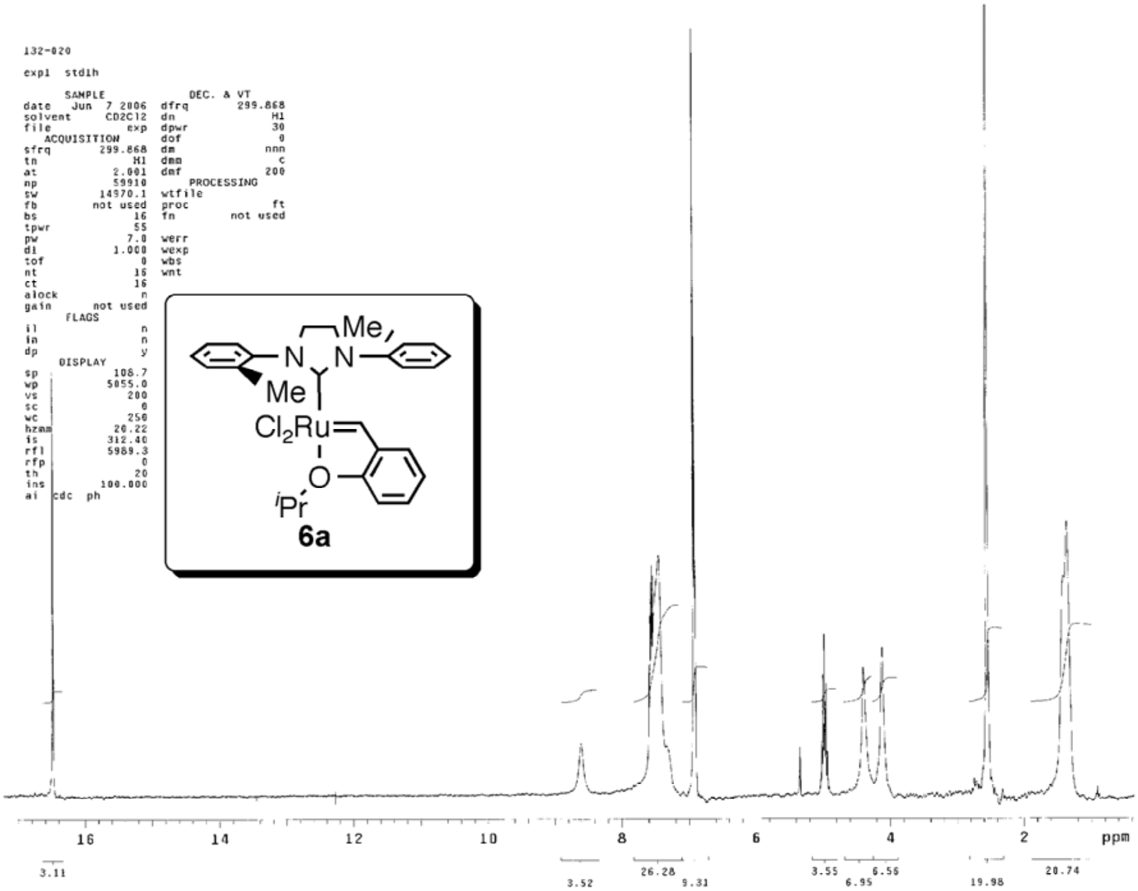


5c

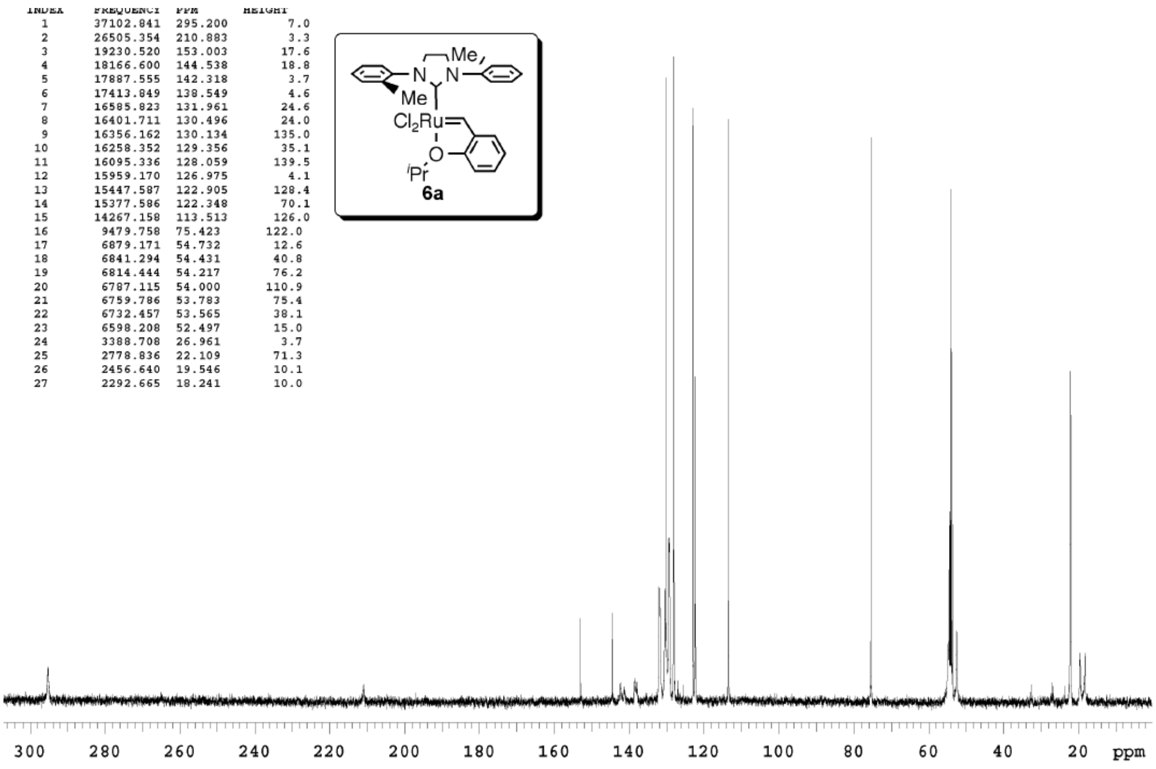


```
INDEX   FREQUENCY   PPM      HEIGHT  INDEX   FREQUENCY   PPM      HEIGHT
  1     37732.851  300.212     3.835          6793.828  54.053     416.9
  2     37295.584  296.733     6.036          6766.499  53.836     282.4
  3     27888.115  221.885     4.137          6739.649  53.622     140.6
  4     27810.443  221.267     3.838          4522.630  35.983       7.2
  5     19062.710  151.668     9.539          4461.259  35.495       6.8
  6     18993.188  151.115    13.840          4143.857  32.970      63.9
  7     18639.347  148.299    24.041          4128.035  32.844      98.8
  8     18468.180  146.937    19.342          4109.336  32.695      60.5
  9     18386.193  146.285    13.243          3651.932  29.056     306.7
 10     17584.537  139.907     9.244          3639.945  28.960     141.8
 11     17559.605  139.709    10.145          3578.575  28.472      56.5
 12     17418.644  138.587    13.946          3546.451  28.216     233.1
 13     17393.233  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          3454.874  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     16316.847  129.821    31.552          3353.708  26.683     155.6
 19     16235.818  129.176    39.353          3258.775  25.928      54.8
 20     16223.352  129.077    55.554          3248.227  25.844      96.0
 21     16209.440  128.966    42.355          3232.085  25.722      55.8
 22     16195.064  128.852    44.156          3014.731  23.986      26.0
 23     16139.926  128.413    95.257          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     15933.759  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
 32      6960.680  55.381    45.0
 33      6848.007  54.484   152.7
 34      6820.678  54.267   293.1
```

5c

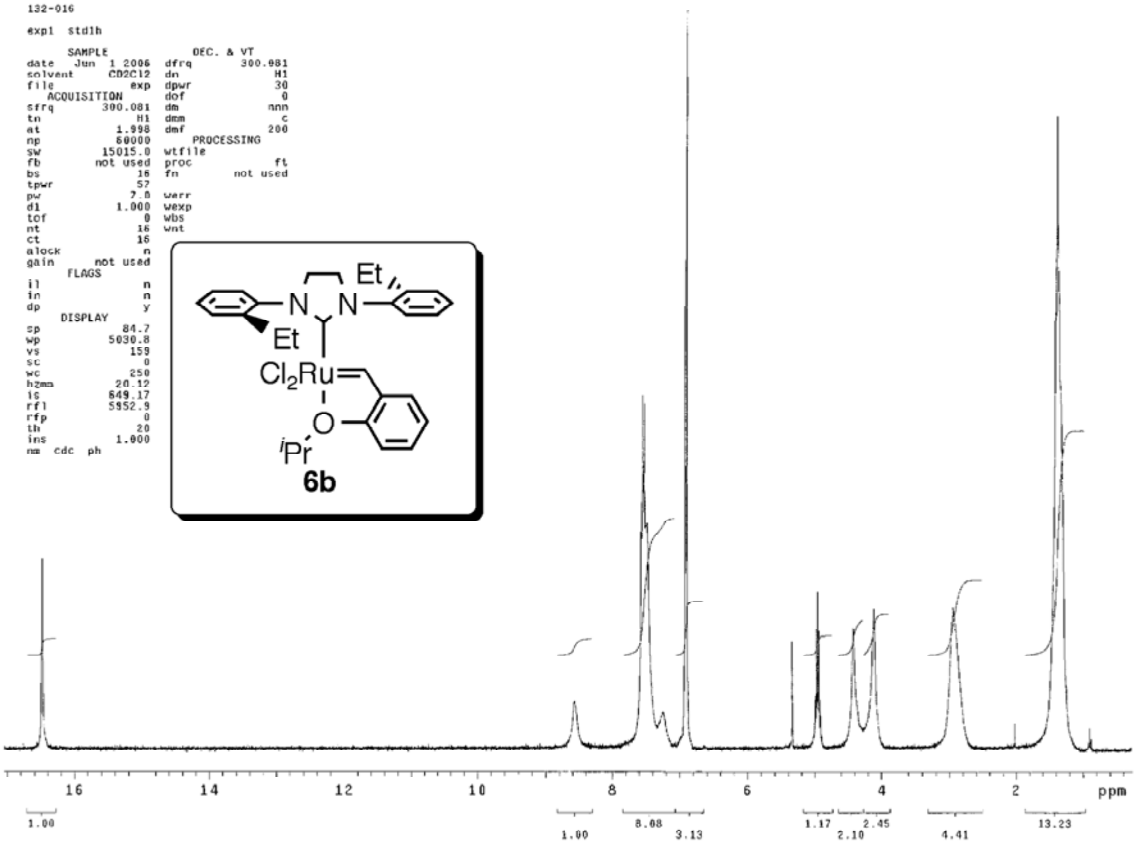


```
132-020

exp1  std1h

      SAMPLE              DEC. & VT
date   Jun  7 2006  dfrq        299.868
solvent     CD2Cl2  dn               H1
file           exp  dpwr             30
   ACQUISITION      dof               0
sfrq       299.868  dm              nnn
tn              H1  dmm               c
at           2.001  dmf             200
np           59910       PROCESSING
sw         14970.1  wtfile
fb        not used  proc             ft
bs              16  fn         not used
tpwr            55
pw             7.0  werr
d1           1.000  wexp
tof              0  wbs
nt              16  wnt
ct              16
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp           108.7
wp          5055.0
vs             200
sc               0
wc             250
hzmm         20.22
is          312.40
rfl         5989.3
rfp              0
th              20
ins        100.000
ai   cdc  ph
```



INDEX	FREQUENCY	PPM	HEIGHT
1	37102.841	295.200	7.0
2	26505.354	210.883	3.3
3	19230.520	153.003	17.6
4	18166.600	144.538	18.8
5	17887.555	142.318	3.7
6	17413.849	138.549	4.6
7	16585.823	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

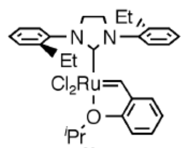
6a



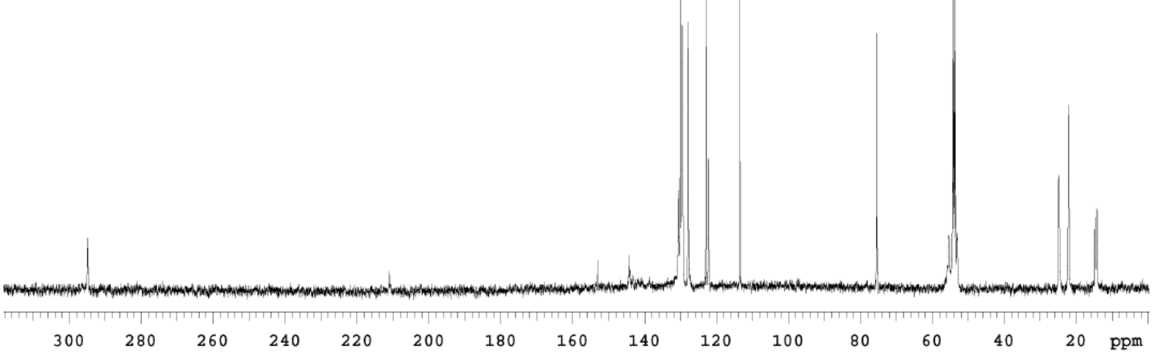
```
132-016

exp1  std1h

      SAMPLE             DEC. & VT
date   Jun  1 2006   dfrq      300.081
solvent     CD2Cl2   dn             H1
file           exp   dpwr           30
   ACQUISITION       dof             0
sfrq       300.081   dm            nnn
tn              H1   dmm             c
at           1.998   dmf           200
np           60000        PROCESSING
sw         15015.0   wtfile
fb        not used   proc           ft
bs              16   fn       not used
tpwr            57
pw             7.0   werr
d1           1.000   wexp
tof              0   wbs
nt              16   wnt
ct              16
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp            84.7
wp          5030.8
vs             159
sc               0
wc             250
hzmm         20.12
is          649.17
rfl         5952.9
rfp              0
th              20
ins          1.000
nm  cdc  ph
```

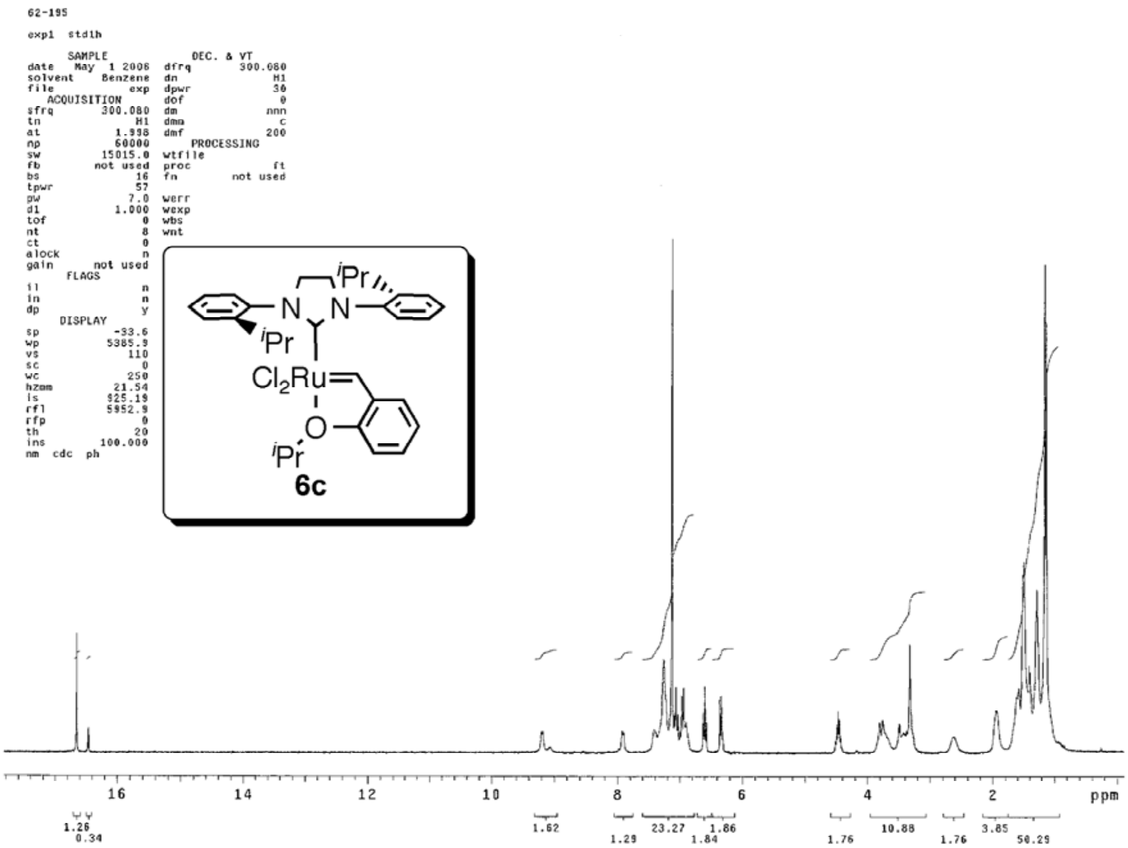
6b

```
INDEX    FREQUENCY    PPM      HEIGHT
  1      37061.128  294.868     11.1
  2      26521.177  211.009      3.8
  3      19239.150  153.072      6.2
  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     57.5
  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
```



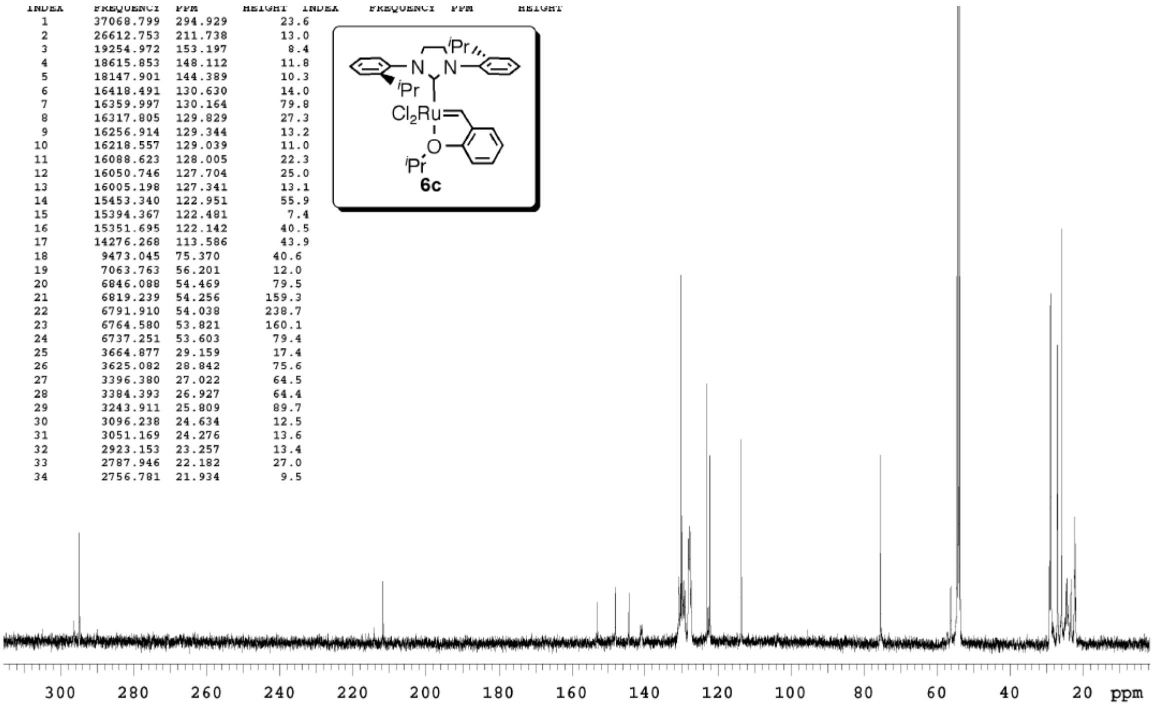
6b





```
62-195

exp1  stdlh

      SAMPLE              DEC. & VT
date   May  1 2006   dfrq       300.080
solvent     Benzene  dn              H1
file            exp  dpwr            30
   ACQUISITION       dof              0
sfrq        300.080  dm             nnn
tn               H1  dmm              c
at            1.998  dmf            200
np            60000       PROCESSING
sw          15015.0  wtfile
fb         not used  proc            ft
bs               16  fn        not used
tpwr             57
pw              7.0  werr
d1            1.000  wexp
tof               0  wbs
nt                8  wnt
ct                0
alock             n
gain       not used
       FLAGS
il                n
in                n
dp                y
      DISPLAY
sp            -33.6
wp           5385.9
vs              110
sc                0
wc              250
hzmm          21.54
is           525.19
rfl          5952.9
rfp               0
th               20
ins         100.000
nm  cdc  ph
```

6c



```
INDEX    FREQUENCY   PPM       HEIGHT  INDEX     FREQUENCY  PPM       HEIGHT
  1      37068.799  294.929      23.6
  2      26612.753  211.738      13.0
  3      19254.972  153.197       8.4
  4      18615.853  148.112      11.8
  5      18147.901  144.389      10.3
  6      16418.491  130.630      14.0
  7      16359.997  130.164      79.8
  8      16317.805  129.829      27.3
  9      16256.914  129.344      13.2
 10      16218.557  129.039      11.0
 11      16088.623  128.005      22.3
 12      16050.746  127.704      25.0
 13      16005.198  127.341      13.1
 14      15453.340  122.951      55.9
 15      15394.367  122.481       7.4
 16      15351.695  122.142      40.5
 17      14276.268  113.586      43.9
 18       9473.045  75.370      40.6
 19       7063.763  56.201      12.0
 20       6846.088  54.469      79.5
 21       6819.239  54.256     159.3
 22       6791.910  54.038     238.7
 23       6764.580  53.821     160.1
 24       6737.251  53.603      79.4
 25       3664.877  29.159      17.4
 26       3625.082  28.842      75.6
 27       3396.380  27.022      64.5
 28       3384.393  26.927      64.4
 29       3243.911  25.809      89.7
 30       3096.238  24.634      12.5
 31       3051.169  24.276      13.6
 32       2923.153  23.257      13.4
 33       2787.946  22.182      27.0
 34       2756.781  21.934       9.5
```

6c

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.