# Ruthenium Catalyzed Ring-Closing Methesis to Form Tetrasubstituted Olefins

**Jacob M. Berlin, Katie Campbell, Tobias Ritter, Timothy W. Funk, Anatoly Chlenov, Robert H. Grubbs***

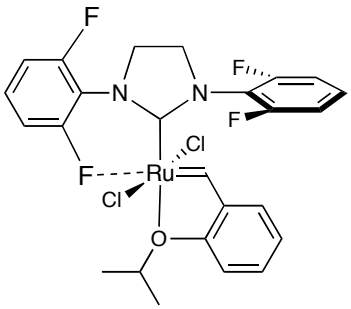
*The Arnold and Mabel Beckman Laboratories of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125*

*rhg@its.caltech.edu*



**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. Catalyst precursors $(PCy_3)_2(Cl)_2Ru{=}CHPh$ and **S10** were gifts from Materia, Inc.

# Catalyst Synthesis and Activity Plots

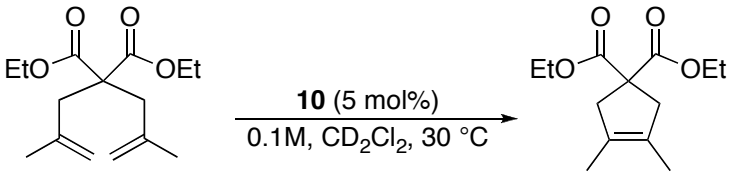


**10**

**Preparation of Catalyst 10**

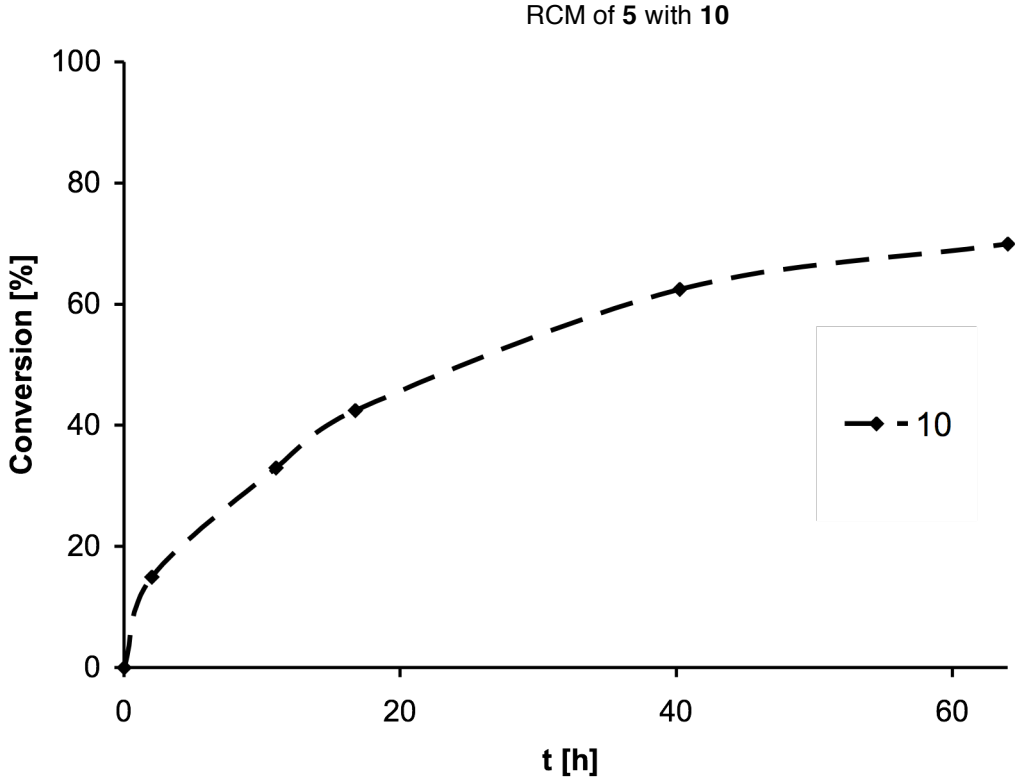
For a synthesis of **10**, see Ritter, T.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 11768.

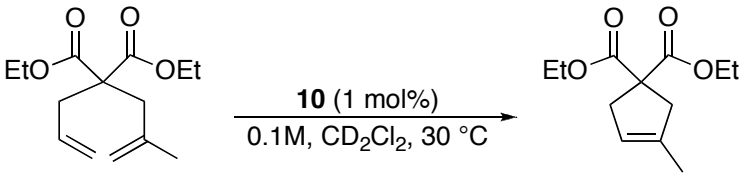
**Standard activity plots for 10.**




**5** **6**

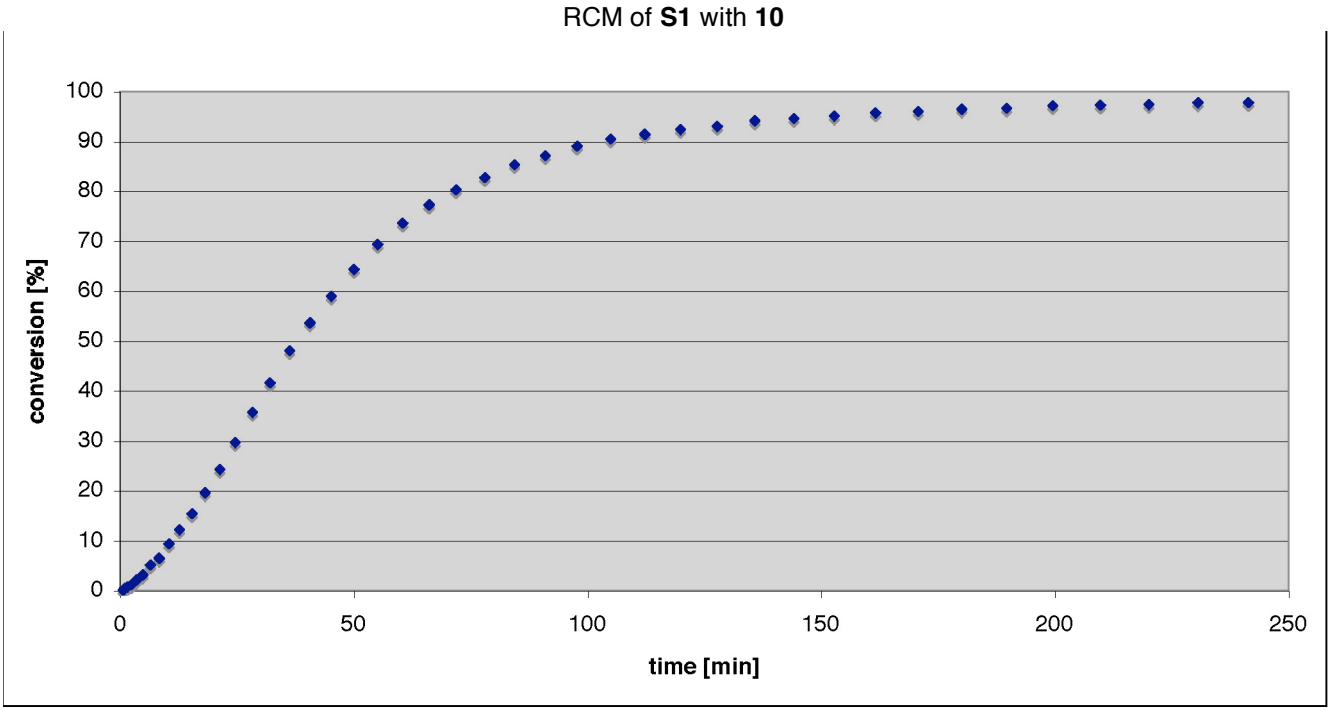
Conditions (full experimental is given for use of catalyst **12**): 0.8 ml of $CD_2Cl_2$ total, 0.08 mmol of **5**, 0.004 mmol of **10**. The plot is below.

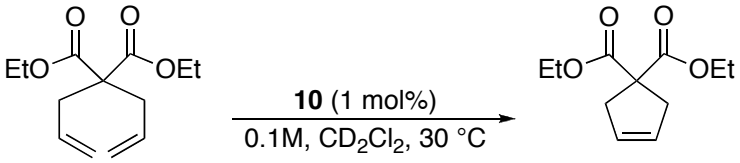





**S1** **S2**

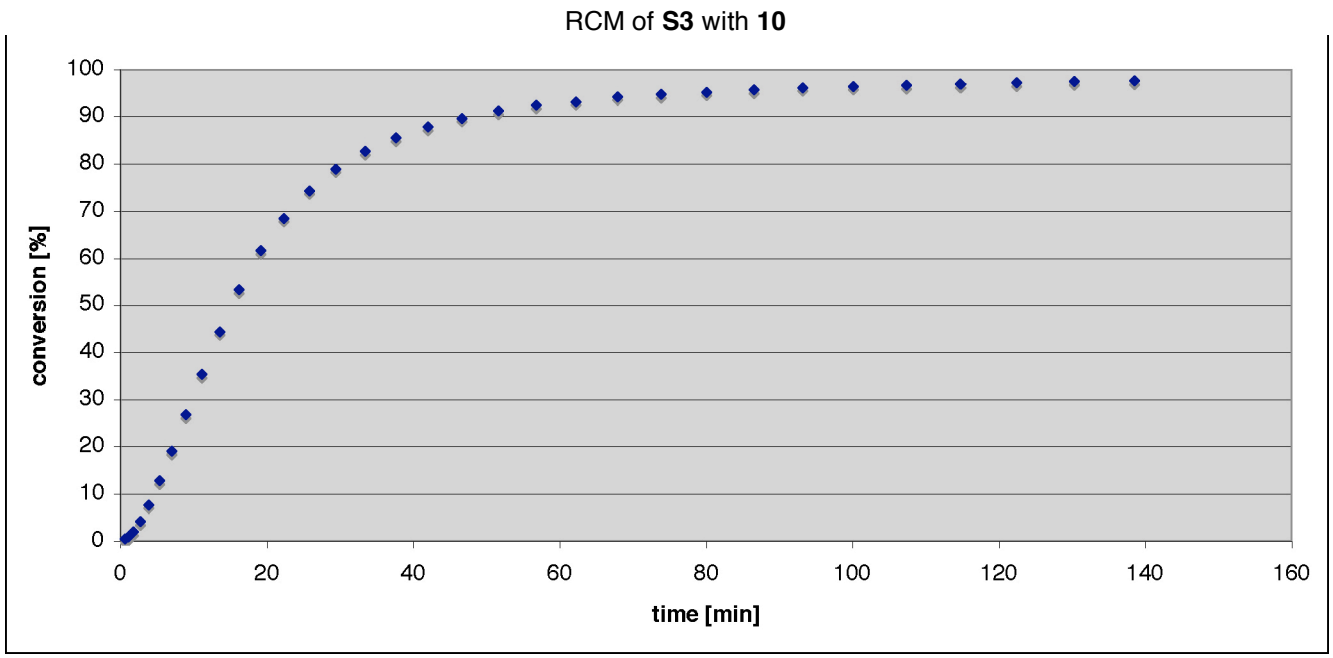
The same conditions were used as before: 0.8 ml of $CD_2Cl_2$ total, 0.08 mmol of **S4**, 0.008 mmol of **10**. The plot is below.



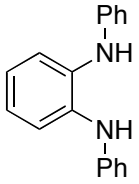

**S3** **S4**

The same conditions were used as before: 0.8 ml of $CD_2Cl_2$ total, 0.08 mmol of **5**, 0.004 mmol of **10**. The plot is below.




A portion of this graph is also presented in Ritter, T.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 11768.

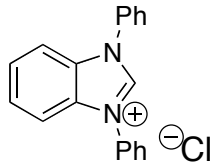
**Preparation of Catalyst 11**




**S5**

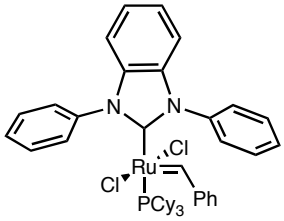
**Synthesis of *N, N'*-Diphenyl-1,2-diaminobenzene.** $Pd(OAc)_2$ (86 mg, 0.379 mmol), [*t*–$Bu_3PH$]$BF_4$ (110 mg, 0.379 mmol), and NaO*t*–Bu (1.22 g, 12.7 mmol) were placed in a dry Schlenk flask equipped with a stir bar. The flask was evacuated and backfilled twice with argon. Dry toluene (10 mL) was added and the resulting solution was degassed by vigorously bubbling argon through the mixture for 30 min. 1,2-Dibromobenzene (0.51 mL, 4.24 mmol) was added followed by aniline (0.81 mL, 8.91 mmol). The flask was sealed under argon and heated to 110 $^oC$ for 14 h. The reaction mixture was allowed to cool to rt, then saturated $NH_4Cl$ (20 mL) was added under Ar.

The mixture was transferred to a separatory funnel using 40 mL of $Et_2O$, and then washed with two further portions of saturated $NH_4Cl$. The organic layer was dried using $MgSO_4$ and filtered. The solvent was removed and the resulting oil was applied to a silica gel column using pentane/$CH_2Cl_2$ (2:1) as eluent. Compound **S5** (0.92 g, 84% yield) was isolated as an off-white solid. The spectral data for **S5** were consistent with that reported in the literature.[1]




**S6**

**Synthesis of *N, N'*-Diphenylbenzimidazolium chloride.** Imidazolium salt **S6** was synthesized as previously reported.[2] Spectral data for **S6** were consistent with that reported in the literature.

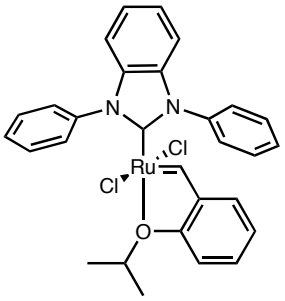



**S7**

**Synthesis of catalyst S7.** In the glovebox, benzimidazolium salt **S6** (80 mg, 0.26 mmol) was added to a Schlenk tube containing dry benzene (6 mL). $KOC(CF_3)_2CH_3$ (69 mg, 0.31 mmol) was added and the mixture was stirred at rt for 60 min. $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (107 mg, 0.13 mmol) was added to the mixture and then the flask was sealed and removed from the glovebox. The reaction mixture was heated at 60 ºC for 5 h. After cooling to rt, the mixture was directly applied to a TSI silica gel column and eluted using a pentane/$Et_2O$ (5:1) mixture. This yielded complex **S7** (54 mg, 51% yield) as an unstable, colorless solid that rapidly decomposes in air, yielding a brownish oil. $^1$H NMR (300 MHz, $CD_2Cl_2$) $\delta$ 19.40 (1H, d, $J_{H-P}$ = 6 Hz), 8.08 (2H, d, $J$ = 8 Hz), 7.74 (2H, t, $J$ = 8 Hz), 7.64–7.59 (1H, m), 7.46–7.41 (1H, m), 7.36 (2H, s), 7.24–6.94 (11H, m), 2.13–2.01 (3H, m), 1.60–1.56 (15H, m), 1.23–1.04 (15H, m). $^{13}$C NMR (75 MHz, $CD_2Cl_2$) $\delta$ 151.0, 137.8, 137.1, 133.5 (d, $J_{C-P}$ = 435 Hz), 130.6, 129.9, 129.8,

[1] Wenderski, T.; Light, K. M.; Ogrin, D.; Bott, S. G.; Harlan, C. J. *Tetrahedron Lett.* **2004**, *45*, 6851.
[2] Huang, W.; Guo, J.; Xiao, Y.; Zhu, M.; Zou, G.; Tang, J. *Tetrahedron*, **2005**, *61*, 9783.

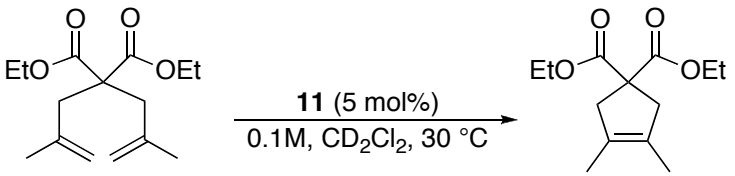
129.5, 129.0, 128.7, 128.6, 128.5, 128.3, 123.6, 123.4, 111.2, 110.1, 32.8 (d, $J_{C-P}$ = 15 Hz), 29.2, 28.0 (d, $J_{C-P}$ = 10 Hz), 26.6. $^{31}$P NMR (121 MHz, $CD_2Cl_2$) δ 22.74. HRMS (FAB, $C_{44}H_{53}N_2PCl_2Ru$) calc. 812.2367, found 812.2339.



**11**

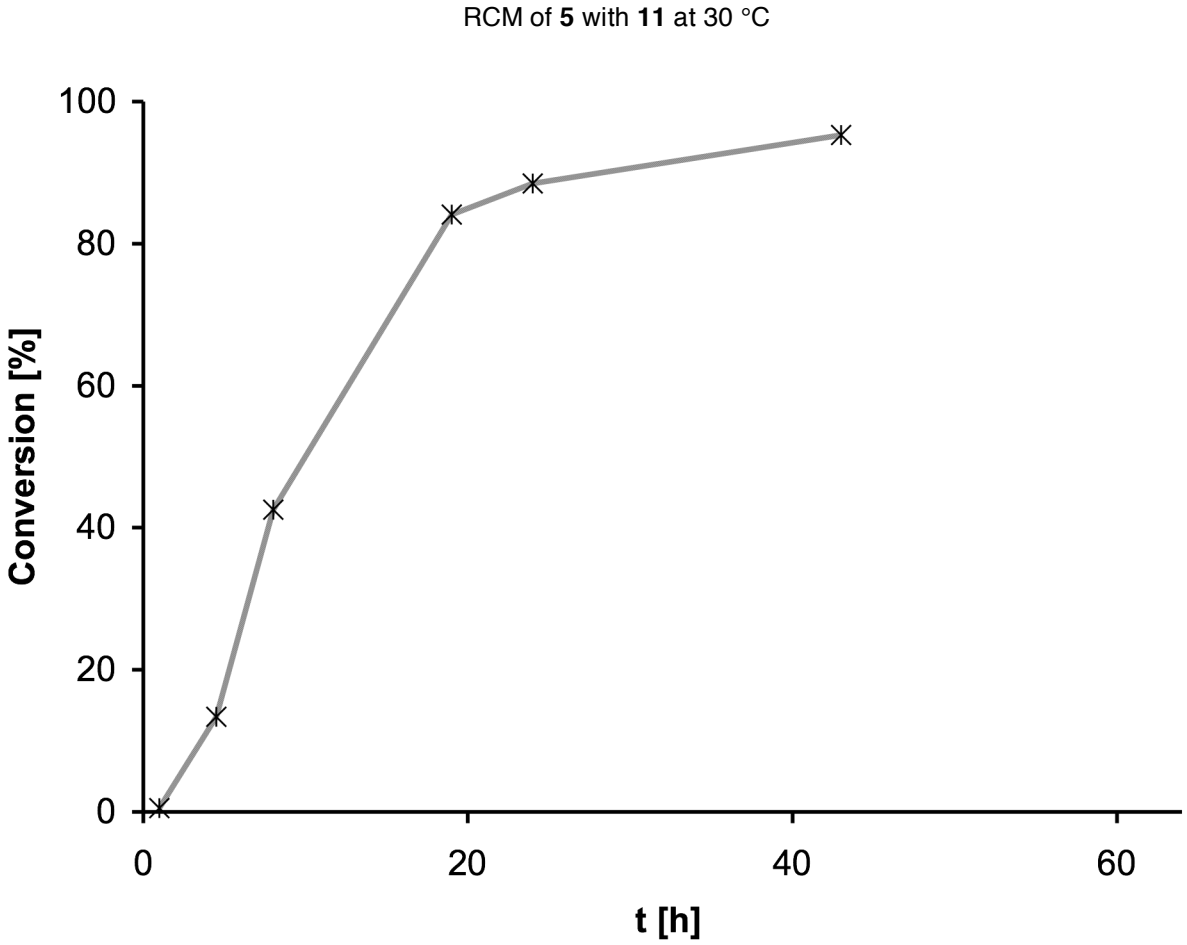
**Synthesis of catalyst 11.** Ruthenium complex **S7** (80 mg, 0.098 mmol) was dissolved in $CH_2Cl_2$ (2 mL). 2-Isopropoxystyrene (16 mg, 0.099 mmol) was added and the mixture was stirred at rt in the presence of air for 4 days. The solvent was removed and the resulting mixture was applied to a bed of TSI silica gel. Excess styrene was eluted using pentane/$CH_2Cl_2$ (1:5). Flushing with neat $CH_2Cl_2$, followed by solvent removal yielded catalyst **11** (48 mg, 83% yield) as a greenish-brown solid. $^1$H NMR (300 MHz, $CD_2Cl_2$) δ 16.64 (1H, s), 8.29 (2H, br m), 7.91 (2H, br m), 7.68 (5H, br m), 7.62–7.56 (2H, m), 7.25 (4H, br m), 7.02–6.91 (3H, br m), 5.11 (1H, septet, $J_{H-H}$ = 6 Hz), 1.60 (6H, d, $J_{H-H}$ = 6 Hz). $^{13}$C NMR (75 MHz, $CD_2Cl_2$) 130.4, 122.9, 122.1, 113.5, 109.7, 75.7, 22.2 (carbon resonances for the N-heterocyclic carbene ligand were not observed due to poor signal to noise and line broadening resulting from slow exchange). HRMS (FAB, $C_{29}H_{26}N_2OCl_2Ru$) calc. 590.0466, found 590.0452. Single crystals of catalyst **11**, suitable for crystallographic analysis, were grown by slow evaporation from a $CH_2Cl_2$/benzene solution of **11**. CCDC 605939.

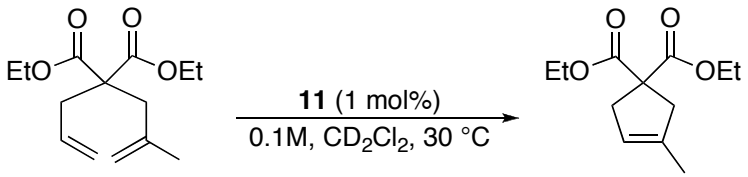
**Standard Plots for 11**.




**5** **6**

The same conditions were used as before: 0.8 ml of $CD_2Cl_2$ total, 0.08 mmol of **5**, 0.004 mmol of **11**. The plot is below.

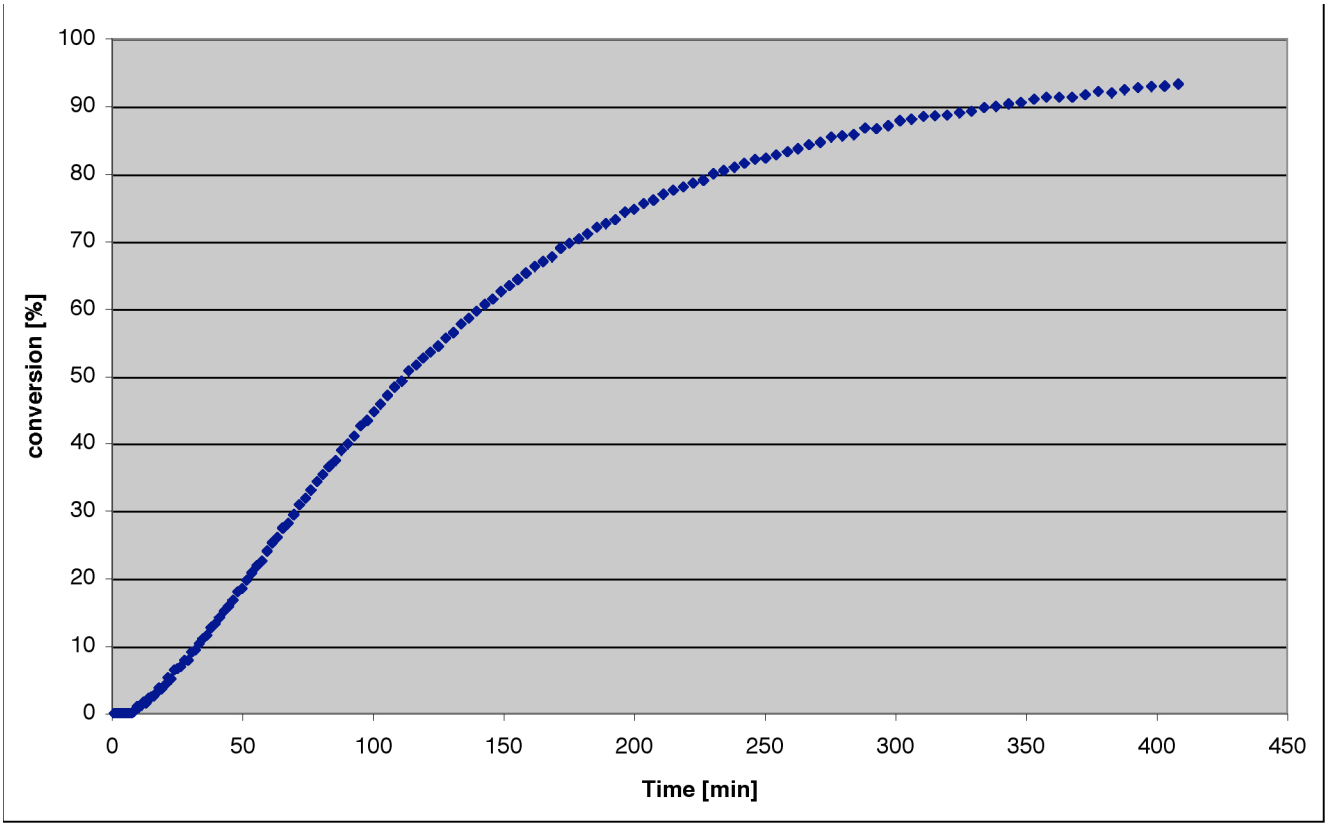


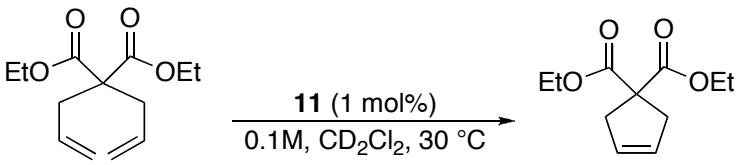




**S1** **S2**

The same conditions were used as before: 0.8 ml of $CD_2Cl_2$ total, 0.08 mmol of **S4**, 0.008 mmol of **11**. The plot is below.

RCM of **S1** with **11** at 30 °C

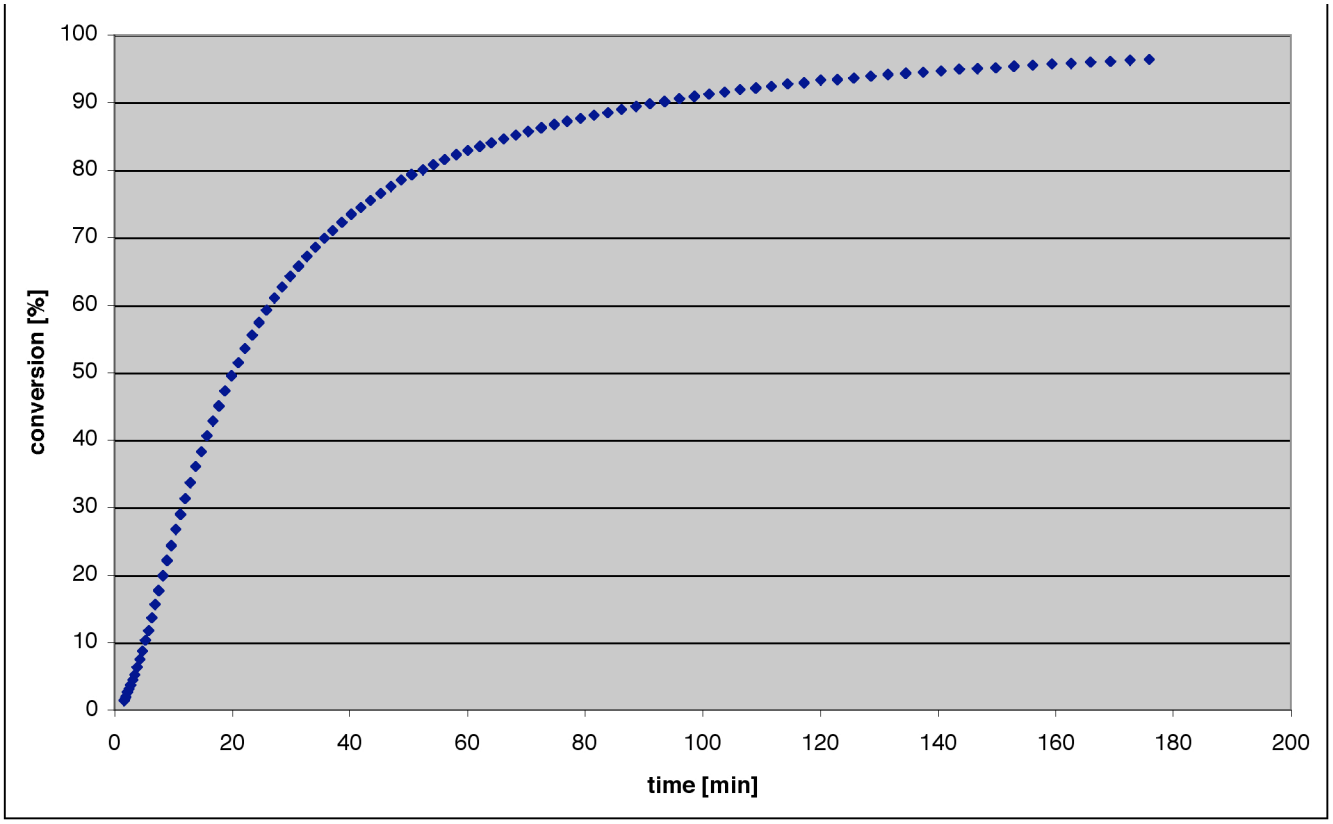


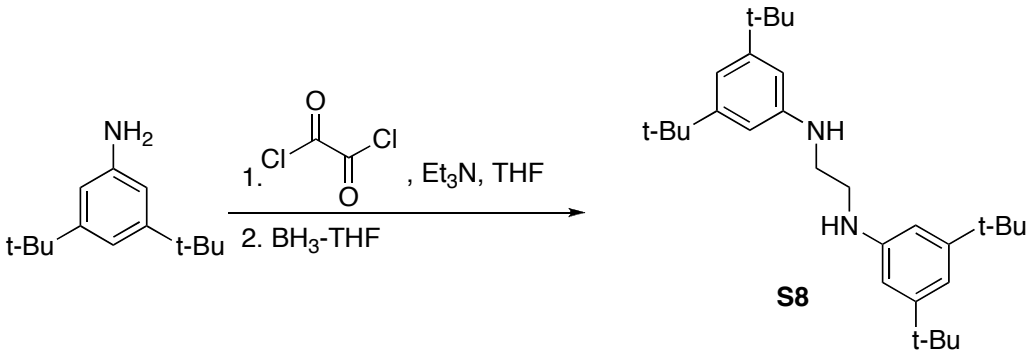

**S3** **S4**

The same conditions were used as before: 0.8 ml of $CD_2Cl_2$ total, 0.08 mmol of **5**, 0.004 mmol of **11**. The plot is below.

RCM of **S3** with **11** at 30 °C




**Preparation of catalyst 12.**



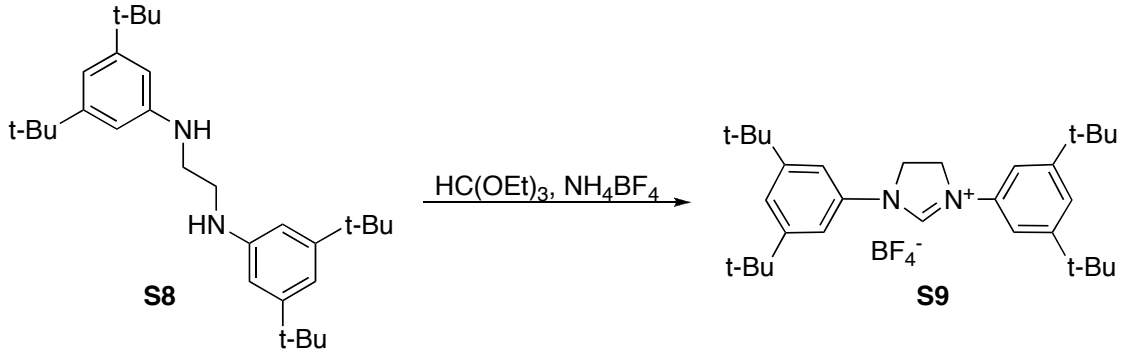

**S8**

**Preparation of diamine S8.** This is a two step procedure.

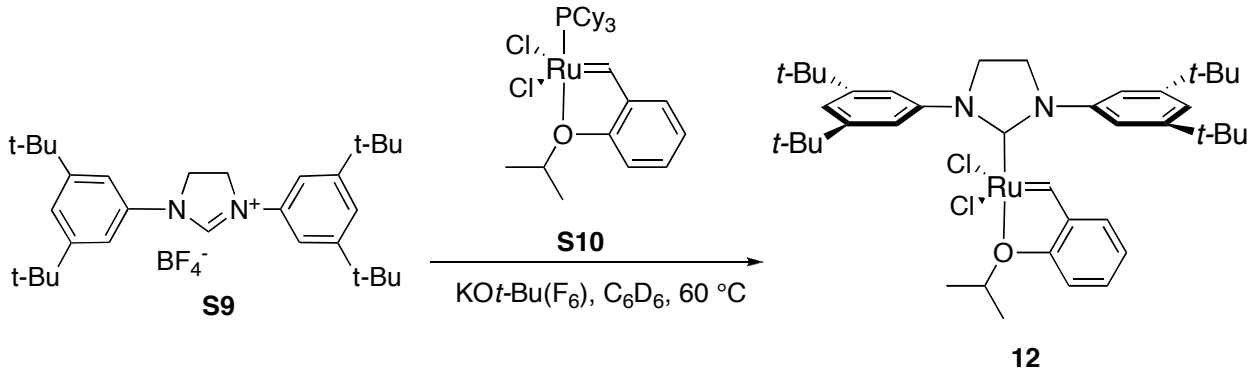
***N,N'*-Bis(3,5-di-t-butylphenyl) oxamide.** Oxalyl chloride (2.16 mL, 25 mmol) was added dropwise to a stirred solution of 3,5-di-t-butylaniline (10.28 g, 50 mmol) and triethylamine (7.0 mL, 50 mmol) in THF (200 mL) at 0 °C. Upon addition, the reaction was allowed to warm up to r.t. and stirred for 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 (2x100 mL), and dried *in vacuo*. Obtained 9.07 g (78%) of *N,N'*-Bis(3,5-di-t-butylphenyl) oxamide as a white solid.

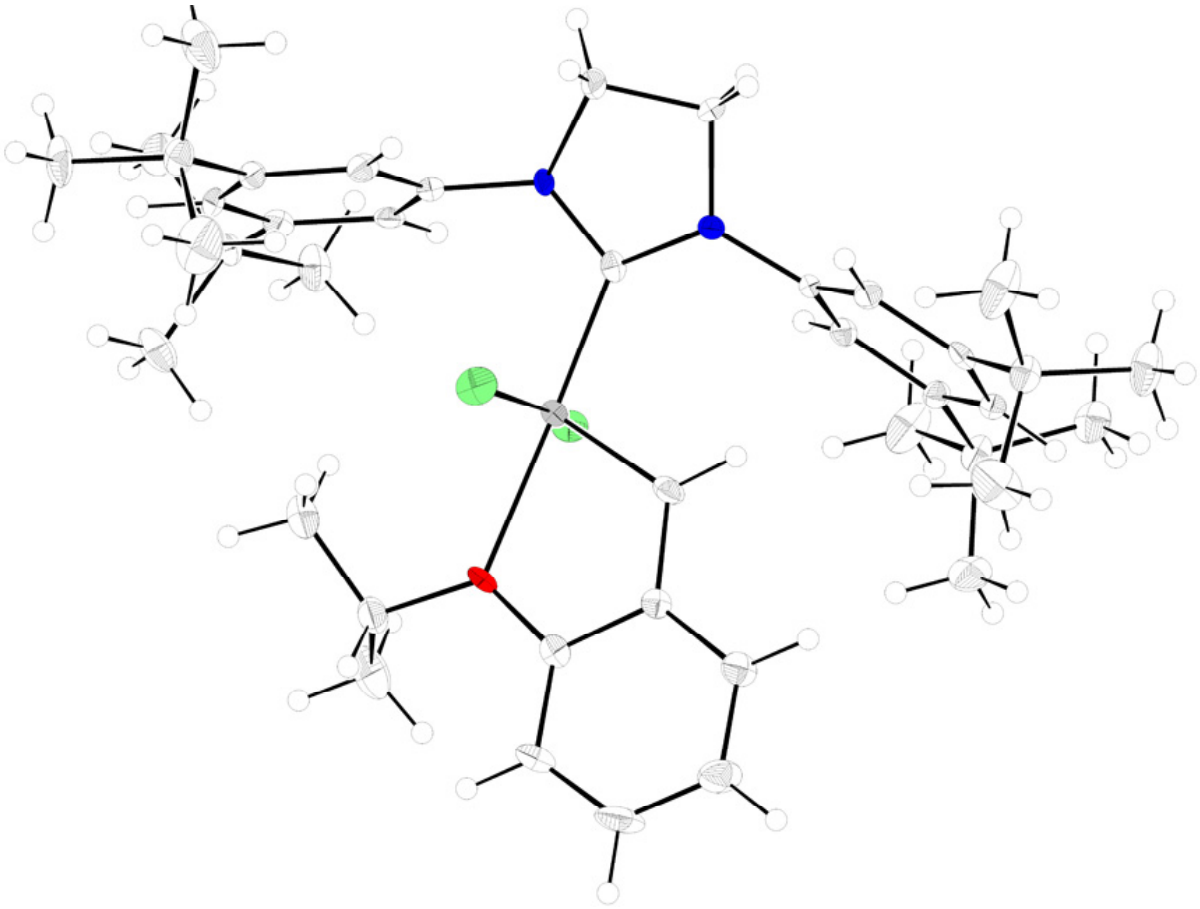
***N,N'*-Bis(3,5-di-t-butylphenyl)ethylenediamine (S8).** A 1M solution of $BH_3$-THF in THF (125 mL, 125 mmol) was added dropwise with stirring to the solid oxamide (9.06 g, 19.52 mmol) at r.t. The resulting homogeneous mixture was then refluxed for 15 h, allowed to cool down to r.t. and carefully quenched by adding water. The mixture was then concentrated and extracted with ether. Column chromatography (2:1 hexanes – dichloromethane, silica gel) afforded 6.51 g (76%) of pure **S8** as a colorless oil and 1.27 g of impure **S8** (contaminated with 3,5-di-t-butylaniline) which was subjected to a second chromatographic purification. The combined yield of **S8** was 86%. $^1$H NMR (300 MHz, $CDCl_3$) δ 6.85 (2H, t, J = 1.5 Hz), 6.55 (4H, d, J = 1.8 Hz), 5.31 (2H, s), 3.45 (4H, s), 1.31 (36H, s); $^{13}$C (75 MHz, $CDCl_3$) δ 152.1, 147.8, 112.8, 107.9, 44.1, 35.1, 31.7; HRMS (EI+) calc for $C_{30}H_{49}N_2$, 437.3896. Found 437.3902.




**Preparation of diamine salt S9.** Triethyl orthoformate (150 mL) was added to a mixture of **S1** (6.51 g, 14.93 mmol) and ammonium tetrafluoroborate (1.57 g, 14.93 mmol) 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. Upon cooling, **S9** precipitated as white needles. The precipitate was collected by filtration, washed with hexanes and dried in vacuo to afford 7.9 g of **S9** (>90%) containing a small amount of triethyl orthoformate in the crystal lattice. Dissolving this crude product in a minimal amount of dichloromethane and adding diethyl ether afforded pure **S9**. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.57 (1H, s), 7.42 (2H, t, J = 1.5 Hz), 7.23 (4H, d, J = 1.8 Hz), 4.69 (4H, s), 1.32 (36H, s); $^{13}$C (75 MHz, $CDCl_3$) δ 153.6, 151.4, 135.4, 123.1, 114.9, 50.5, 35.4, 31.5. HRMS (EI+) calc for $C_{31}H_{47}N_2$, 447.3739, found 447.3729.




**Catalyst 12**. Diamine salt **S9** (156 mg, .3 mmol), KO*t*-Bu($F_6$) (66 mg, .3 mmol), and ruthenium complex **S10** (132 mg, .22 mmol) were all combined in toluene in a glove box. The flask was removed and stirred at 60 °C for 18 hours in a fume hood. The reaction mixture was then directly purified by flash column chromatography (5% $Et_2O$/Hexanes, run 2 times) to yield catalyst **12** (34 mg, 20%) as a green oil. The catalyst was then lyophilized from benzene to give a pale green solid. It should be noted that by $^1H$ NMR the conversion to **12** is 50%. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 16.91 (1H, s), 8.14-8.13 (2H, m), 7.73 (2H, m), 7.64 (1H, m), 7.52 (1H, m), 7.06-6.92 (2H, m), 6.62 (1H, t, J = 7.5 Hz), 6.31 (1H, d, J = 8.4 Hz), 4.47 (1H, quint, J = 6 Hz), 3.51 (4H, s), 1.51 (18H, s), 1.35 (6H, d, J = 6 Hz), 1.24 (18H, s); HRMS (EI+) calc for $C_{41}H_{58}N_2OCl_2Ru$ 766.2970. Found 766.3007. An X-ray crystal structure has also been obtained for this structure.

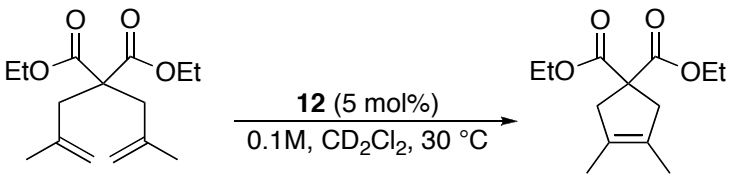


CCDC 622049

**Standard activity plots for 12**.

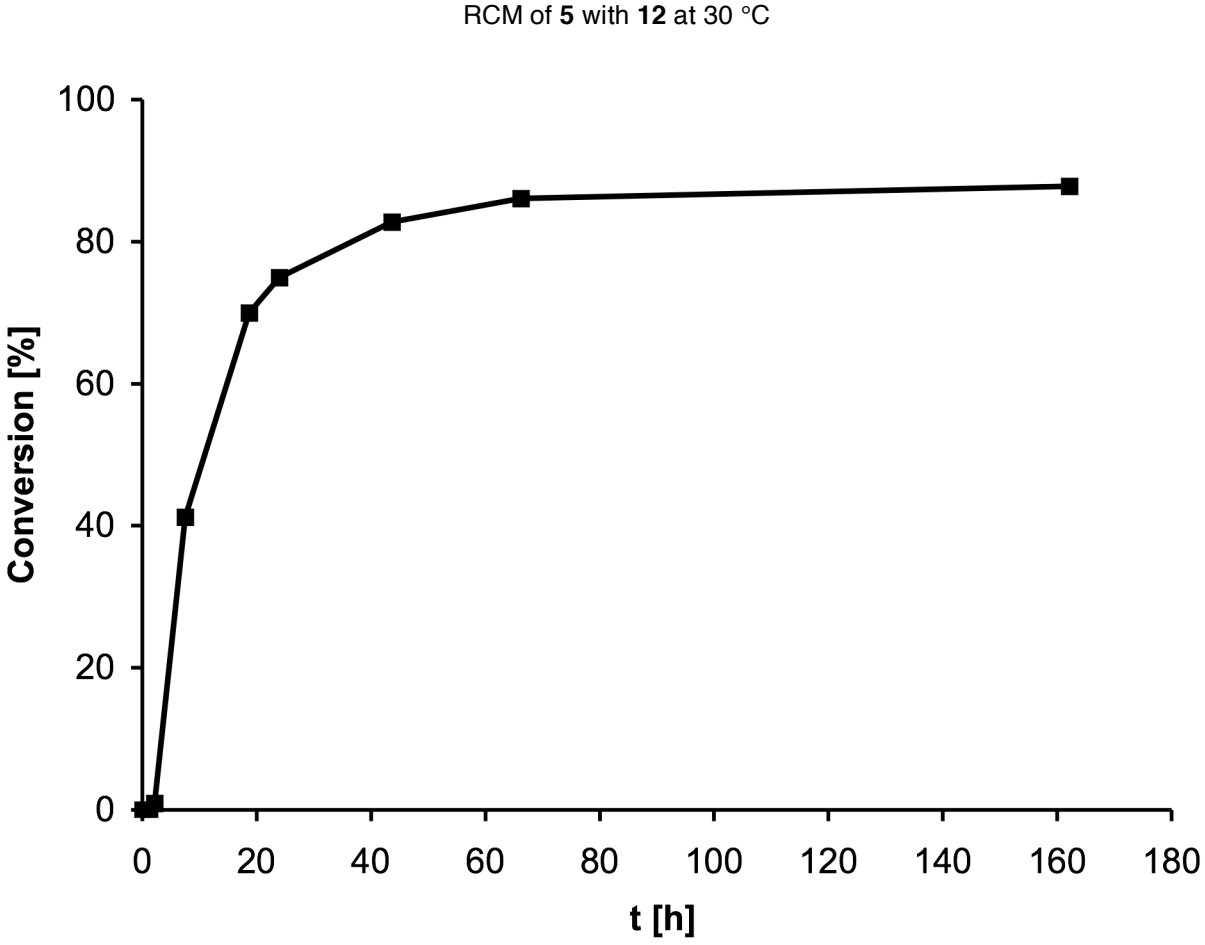
Preparation of stock solutions. Catalyst **12** (14 mg) was placed in a 2ml volumetric flask and taken into a glove box. In the glove box, 2ml of $CD_2Cl_2$ was added to make stock solution **A**. 0.44 ml of **A** was then transferred to another 2ml volumetric flask and diluted to 2ml with $CD_2Cl_2$ to make stock solution **B**.

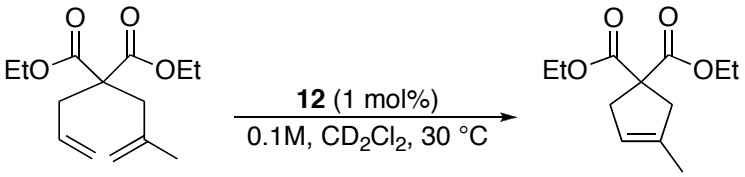
Activity studies.




**5** **6**

In a glove box, 0.44 ml of stock solution **A** (3.1 mg of **12**, 0.004 mmol) was transferred to a screw cap NMR tube. $CD_2Cl_2$ (.36 ml) was added and then **5** (21.5 μl, 0.08 mmol). The NMR tube was sealed, removed from the glove box and heated to 30 °C. A graph of conversion over time follows.

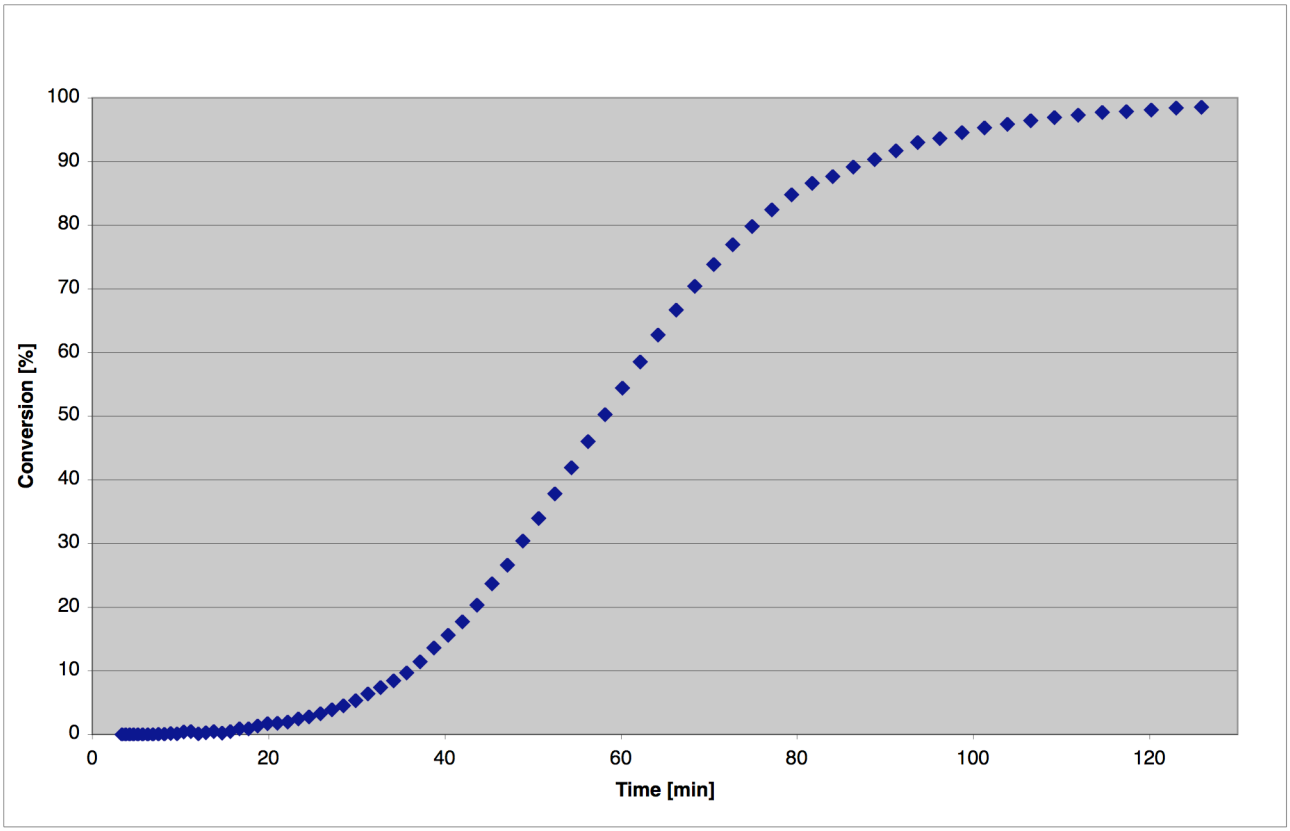


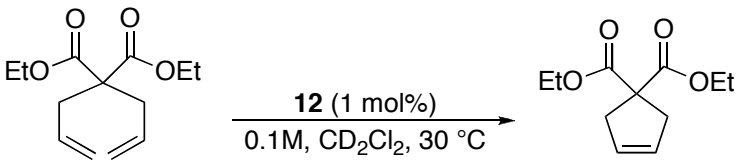




**S1** **S2**

In a glove box, 0.4 ml of stock solution **B** (0.6 mg of **12**, 0.0008 mmol) was transferred to a screw cap NMR tube. $CD_2Cl_2$ (.4 ml) was added and the NMR tube was sealed and transferred to a 500 MHz NMR which was warmed to 30 °C. The NMR tube was then ejected, **S1** (20.5 μl, 0.08 mmol) was added and the tube was injected for data collection. A graph of conversion over time follows.

RCM of **S1** with **12** at 30 °C

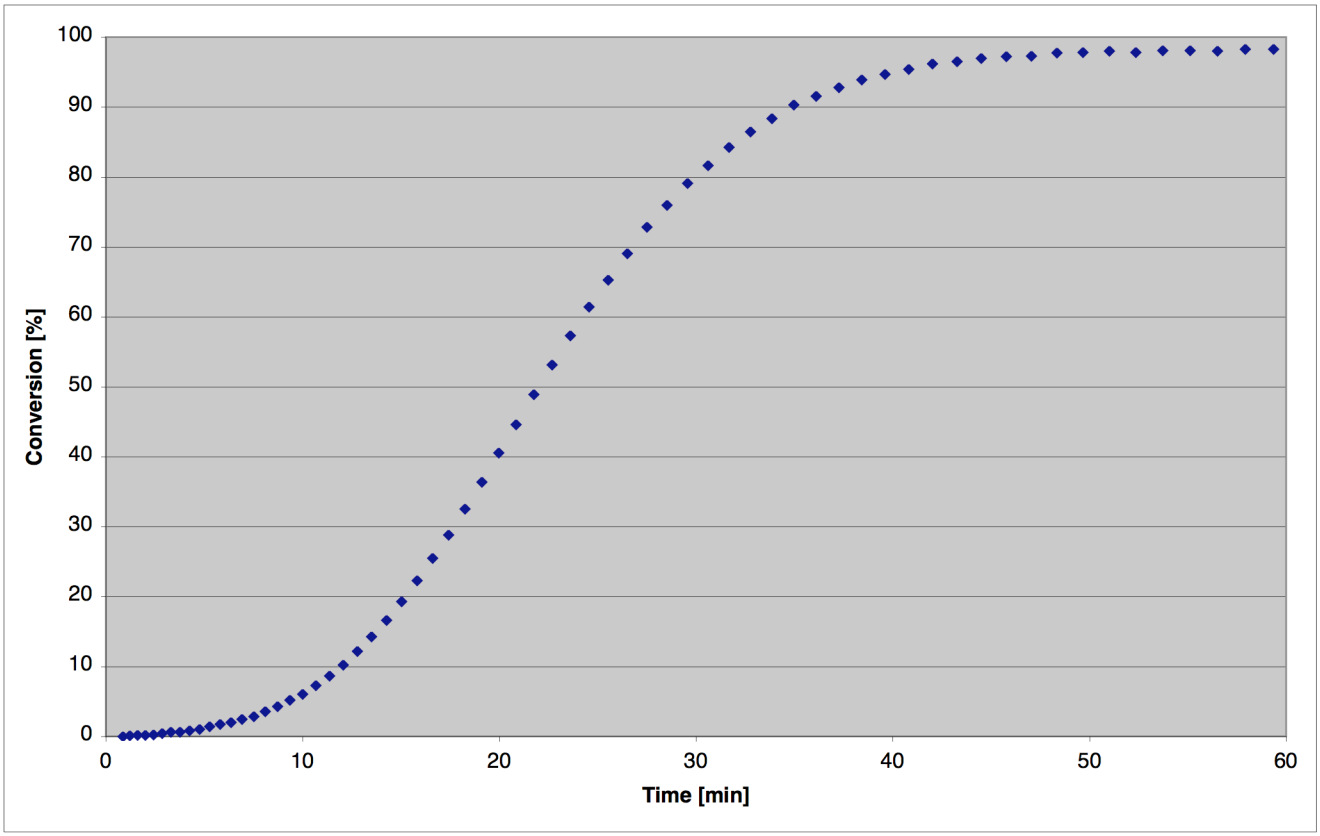


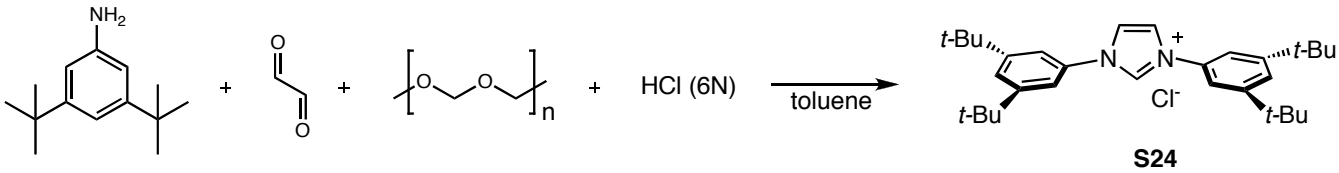




**S3** **S4**

In a glove box, 0.4 ml of stock solution **B** (0.6 mg of **12**, 0.0008 mmol) was transferred to a screw cap NMR tube. $CD_2Cl_2$ (.4 ml) was added and the NMR tube was sealed and transferred to a 500 MHz NMR which was warmed to 30 °C. The NMR tube was then ejected, **S3** (19.5 μl, 0.08 mmol) was added and the tube was injected for data collection. A graph of conversion over time follows.

RCM of **S3** with **12** at 30 °C

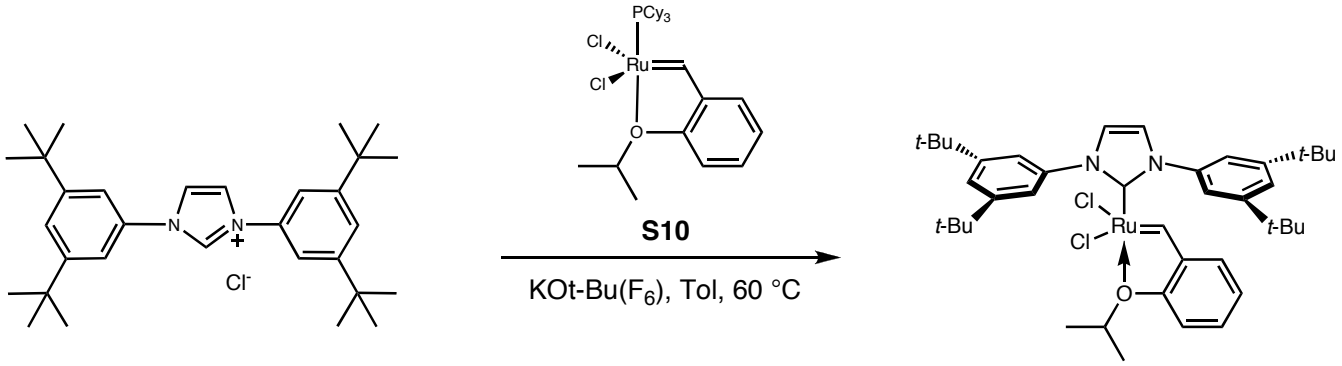



**S24**

**Diamine Salt S24**. A solution of 3,5-ditertbutylaniline (3 g, 14.6 mmol) in toluene (5 ml) was added to a solution of paraformaldehyde (220 mg, 7.3 mmol) in toluene (5 ml). The reaction was then stirred at 100 °C for 1.5 hours. The reaction was cooled to 40 °C and 6N HCl (1.2 ml, 7.3 mmol) was added. The reaction was stirred for 5 minutes, glyoxal (837 $\mu$l, 7.3 mmol) was added and the reaction was stirred another 5 minutes. The reaction was stirred at 100 °C for 14 hours, cooled to RT and purified by column chromatography (5% MeOH/$CH_2Cl_2$) to yield a brown foam. This foam was washed with $Et_2O$ to yield 806 mg (23%) of a white solid. $^1$H NMR (300 MHz, $CDCl_3$)

δ 11.89 (br, 1H), 7.78-7.76 (m, 6H), 7.59 (s, 2H), 1.42 (s, 36H); HRMS (EI+) calc for $C_{31}H_{45}N_2$, 445.3583. Found 445.3561.

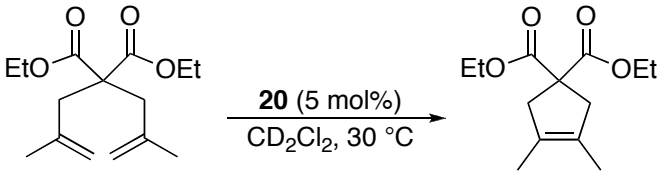



**S24** **20**

**Ruthenium Catalyst 20**. In a glove box, diamine salt **S24** (63 mg, .13 mmol), ruthenium precursor **S10** (78 mg, .13 mmol) and KO*t*-Bu($F_6$) (29 mg, .13 mmol) were combined in toluene. The flask was sealed, removed from the glove box and stirred at 60 °C for 18 hours. The reaction was concentrated and purified by flash column chromatography (5% --> 20% $Et_2O$/Pent). There were 3 bands that could be isolated from this column, first 2 brown bands and then one green band. The second brown band was the desired product; however, it was not completely pure after one column. Recolumning in 10% $Et_2O$/Pentane gave a brown oil product completely pure by $^1H$ NMR (9 mg, 9%) and another fraction still slightly impure (18 mg, 18%). The products were lyophilized from benzene to give solids. $^1H$ NMR (300 MHz, $CDCl_3$) δ 16.78 (s, 1H), 8.13 (br, 2H), 7.74-7.62 (m, 4H), 7.07-7.04 (m, 1H), 6.97 (dd, J = 3, 1.5 Hz, 1H), 6.66 (t, J = 7.5 Hz, 3H), 6.34 (d, J = 8.4 Hz, 1H), 4.49 (sept, J = 6 Hz, 1H), 1..44 (d, J = 6 Hz, 6H), 1.44 (br, 18H), 1.18 (br, 18H); HRMS (EI+) calc for $C_{41}H_{56}Cl_2N_2ORu$, 764.2814. Found 764.2842.

Activity plots for **20**.

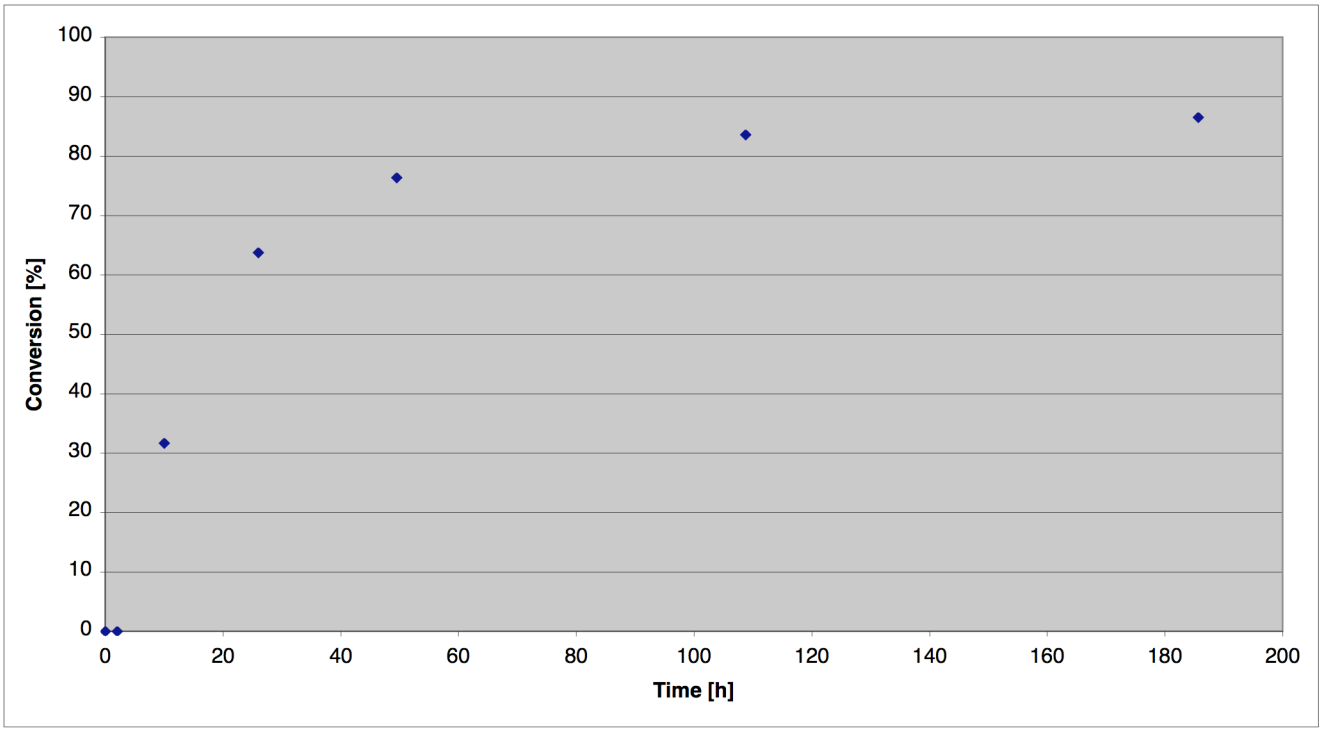
Preparation of stock solutions. Catalyst **20** (9 mg) was placed in a 2ml volumetric flask and taken into a glove box. In the glove box, 2ml of $CD_2Cl_2$ was added to make stock solution **A**. 0.33 ml of **A** was then transferred to another 2ml volumetric flask and diluted to 2ml with $CD_2Cl_2$ to make stock solution **B**.



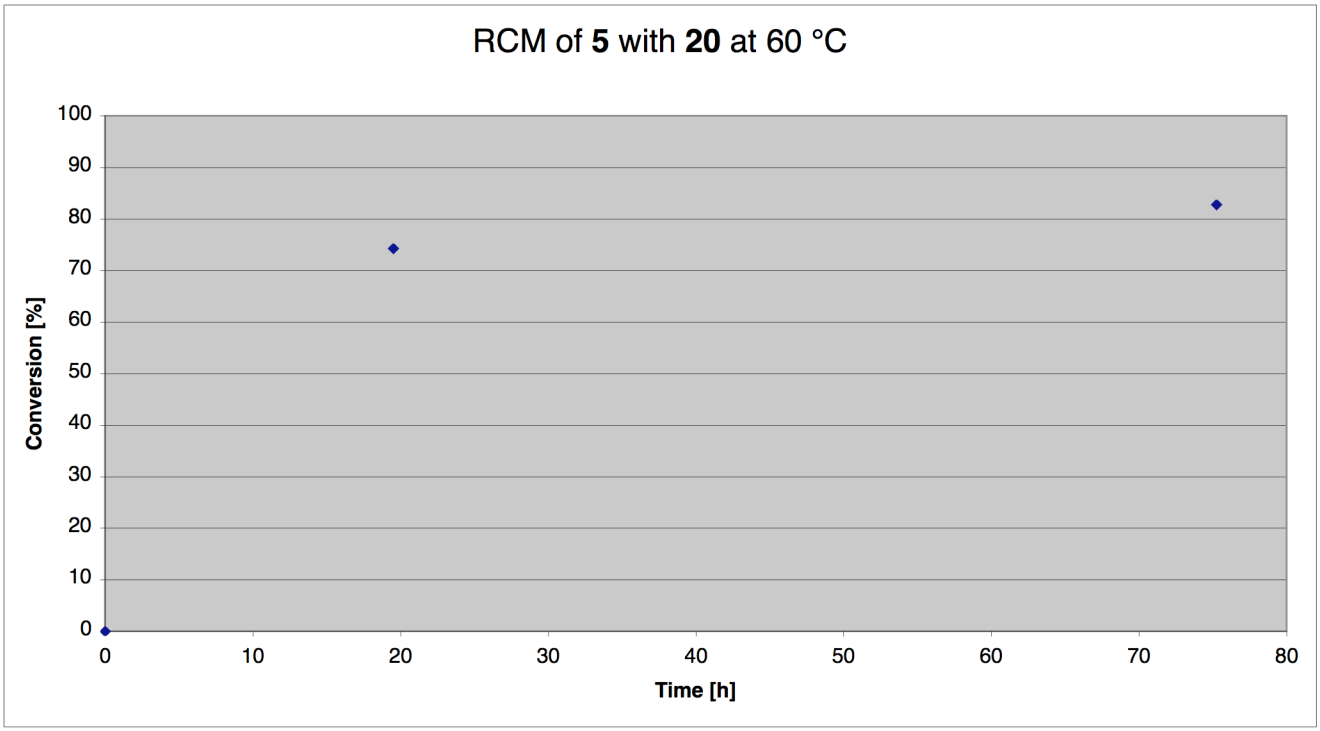

**5** **6**

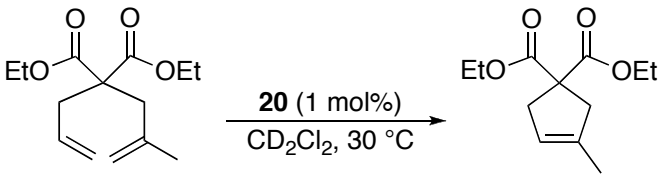
In a glove box, 0.67 ml of stock solution **A** (3 mg of **20**, 0.004 mmol) was transferred to a screw cap NMR tube. $CD_2Cl_2$ (.13 ml) was added and then **5** (21.5 μl, 0.08 mmol). The NMR tube was sealed, removed from the glove box and heated to 30 °C. A graph of conversion over time follows.

RCM of **5** with **20** at 30 °C



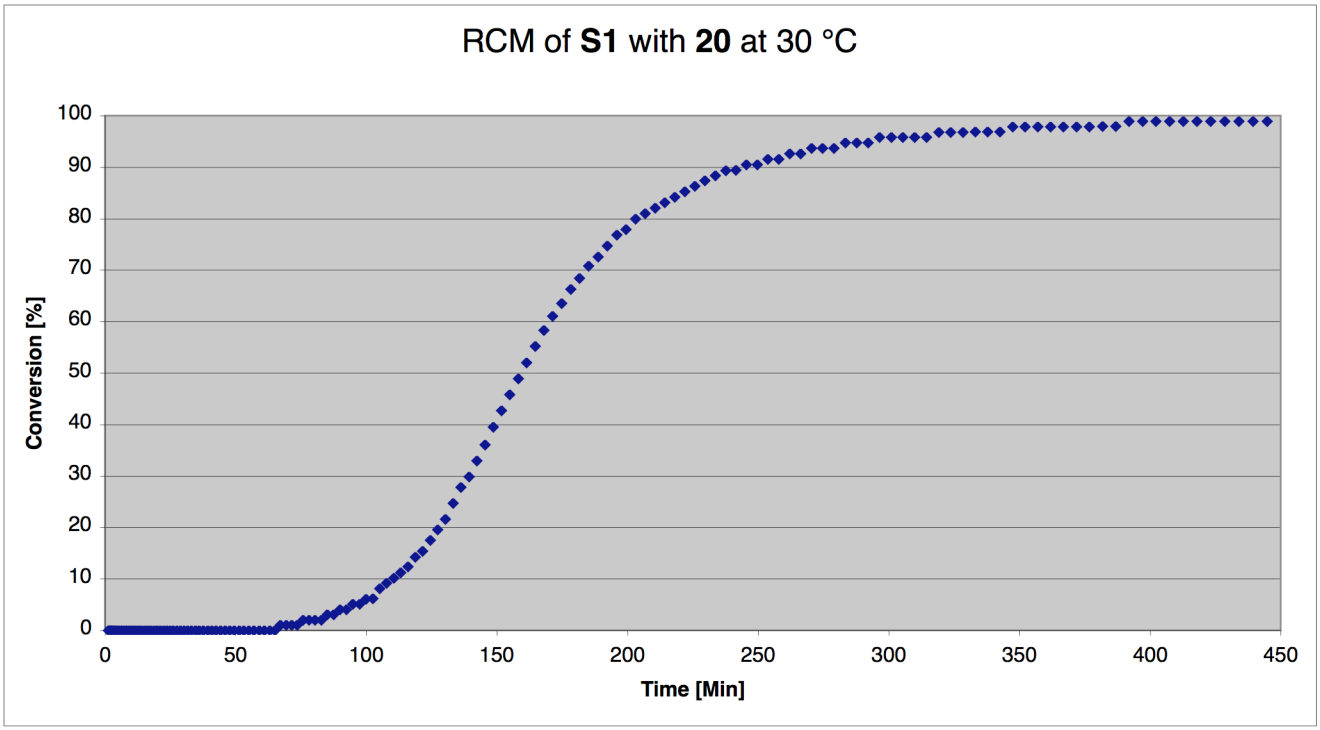

This experiment was repeated in $C_6D_6$ at 60 °C to examine the impact of temperature. Catalyst **20** (3 mg, 0.004 mmol) and $C_6D_6$ (.8 ml) were combined in a screw cap NMR tube and **5** (21.5 μl, 0.08 mmol) was added. The NMR tube was sealed, removed from the glove box and heated to 60 °C. A graph of conversion over time follows.

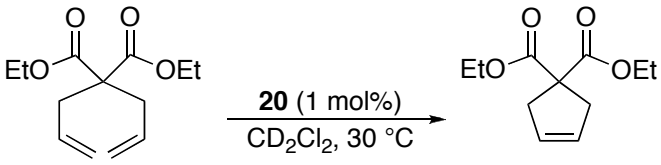



**S1** **S2**

In a glove box, 0.8 ml of stock solution **B** (0.6 mg of **20**, 0.0008 mmol) was transferred to a screw cap NMR tube. The NMR tube was sealed and transferred to a 500 MHz NMR which was warmed to 30 °C. The NMR tube was then ejected, **S1** (20.5 μl, 0.08 mmol) was added and the tube was injected for data collection. A graph of conversion over time follows.

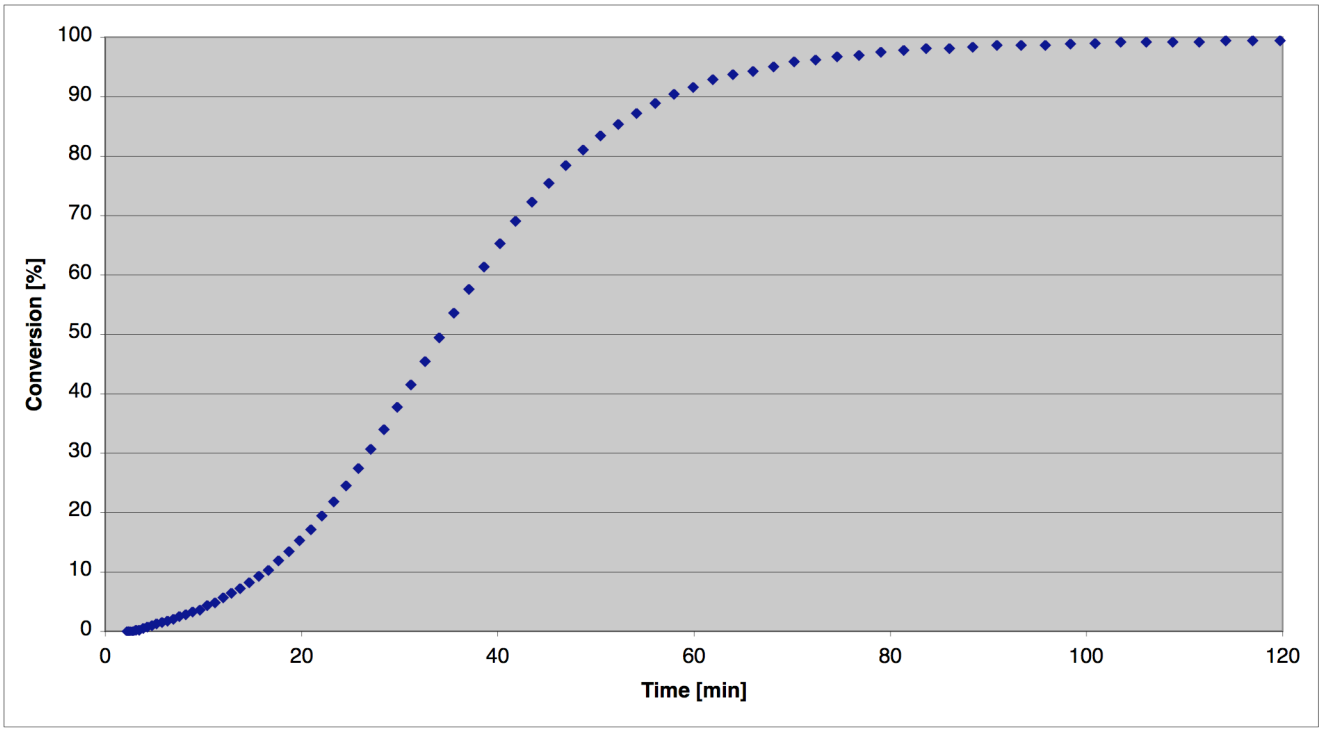


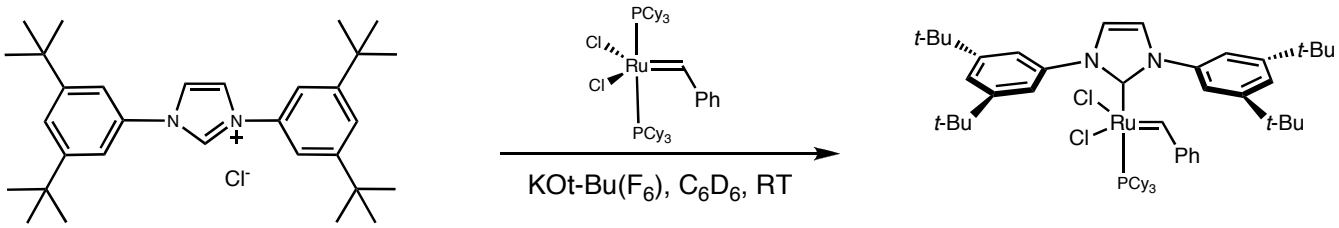




**S3** **S4**

In a glove box, 0.8 ml of stock solution **B** (0.6 mg of **20**, 0.0008 mmol) was transferred to a screw cap NMR tube. The NMR tube was sealed and transferred to a 500 MHz NMR which was warmed to 30 °C. The NMR tube was then ejected, **S3** (19.5 μl, 0.08 mmol) was added and the tube was injected for data collection. A graph of conversion over time follows.

RCM of **S3** with **20** at 30 °C



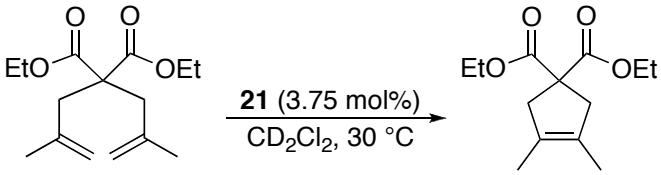




**S24** **21**

**Ruthenium Catalyst 21**. In a glove box, diamine salt **S24** (162 mg, .34 mmol), ruthenium precursor $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (150 mg, .27 mmol) and KO*t*-Bu($F_6$) (74 mg, .34 mmol) were combined in $C_6D_6$ and stirred at RT for 2.5 hours. The flask was sealed, removed from the glove box and the reaction was concentrated and purified by flash column chromatography (2.5% --> 5% $Et_2O$/Pent) to yield a brown oil. The brown oil was lyophilized from benzene to give a brown solid (66 mg, 25%). $^1$H NMR (300 MHz, $CDCl_3$) δ 20.07 (d, J = 10.5 Hz, 1H), 8.03 (br, 2H), 7.60 (t, 1.8 Hz, 1H), 6.86-6.81 (m, 2H), 6.51 - 6.47 (m, 1H), 1.81 - 1.07 (m).

Standard activity plots for **21**.

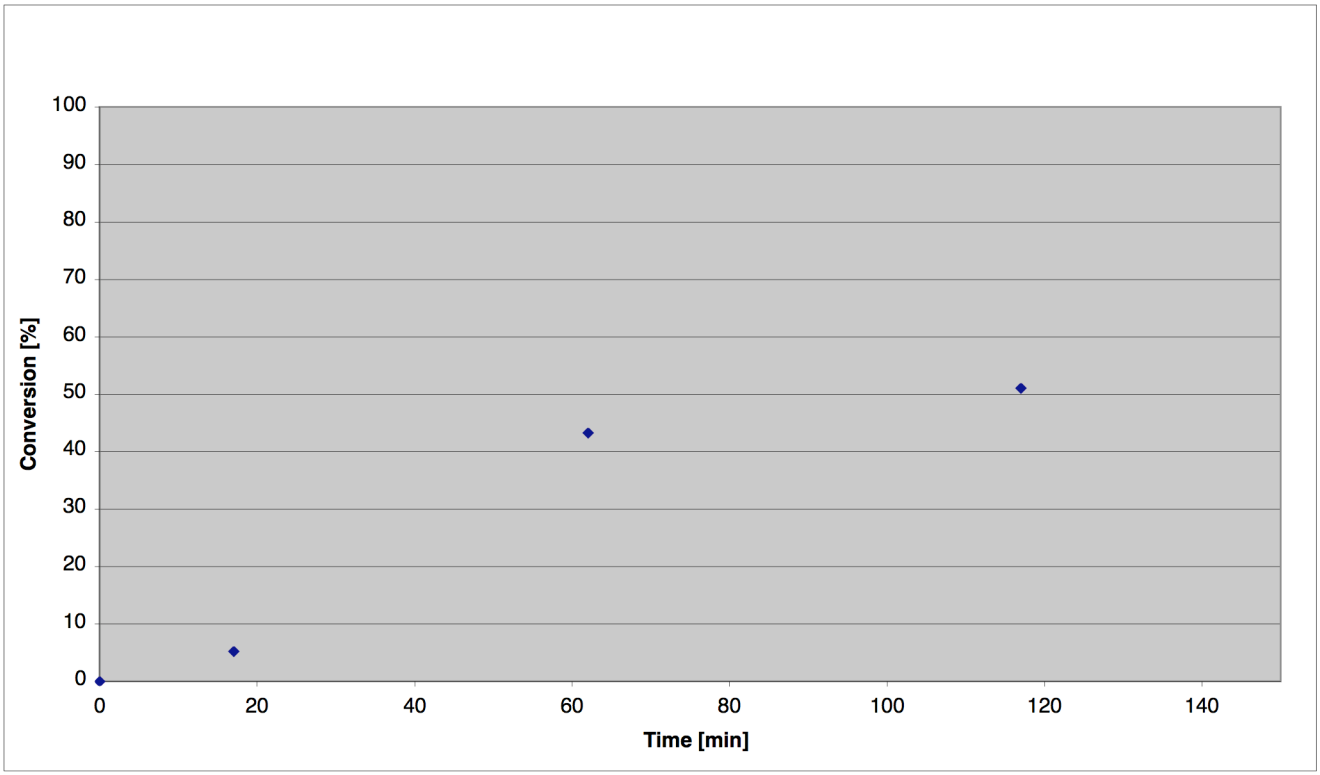
Preparation of stock solutions. Catalyst **21** (11 mg) was placed in a 2ml volumetric flask and taken into a glove box. In the glove box, 2ml of $CD_2Cl_2$ was added to make stock solution **A**. 0.4 ml of **A** was then transferred to another 2ml volumetric flask and diluted to 2ml with $CD_2Cl_2$ to make stock solution **B**.




**5** **6**

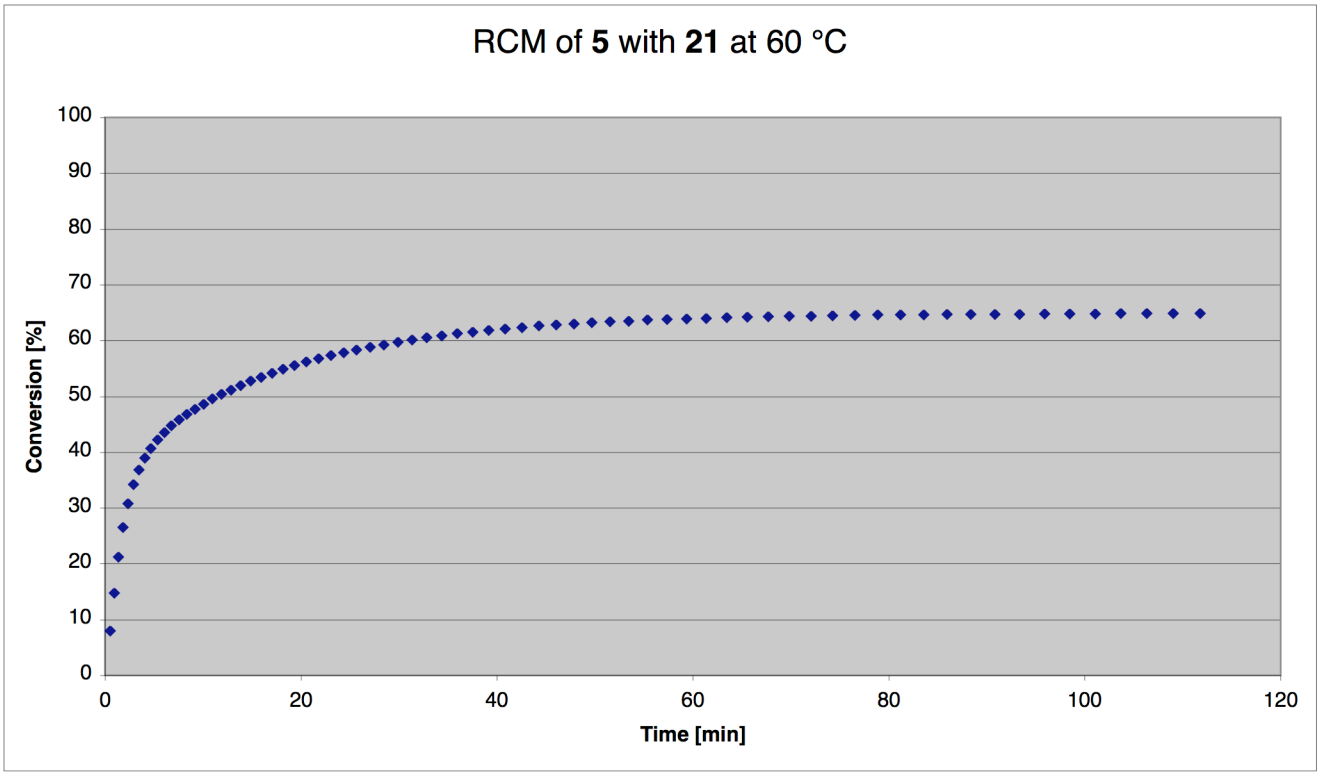
In a glove box, 0.55 ml of stock solution **A** (3 mg of **3**, 0.003 mmol) was transferred to a screw cap NMR tube. $CD_2Cl_2$ (.25 ml) was added and then **10** (21.5 μl, 0.08 mmol). The NMR tube was sealed, removed from the glove box and heated to 30 °C. A graph of conversion over time follows. No further conversion is observed after 2 hours.

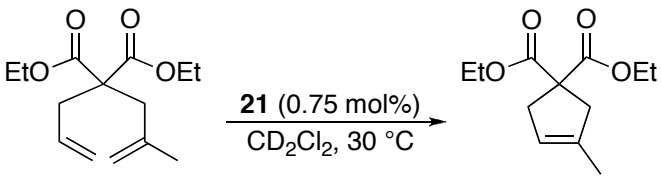
RCM of **5** with **21** at 30 °C




This experiment was repeated in $C_6D_6$ at 60 °C to examine the impact of temperature. Catalyst **21** (3 mg, 0.003 mmol) and $C_6D_6$ (.8 ml) were combined in a screw cap NMR tube. The NMR tube was sealed and transferred to a

500 MHz NMR which was warmed to 60 °C. The NMR tube was then ejected, **5** (21.5 μl, 0.08 mmol) was added and the tube was injected for data collection. A graph of conversion over time follows.

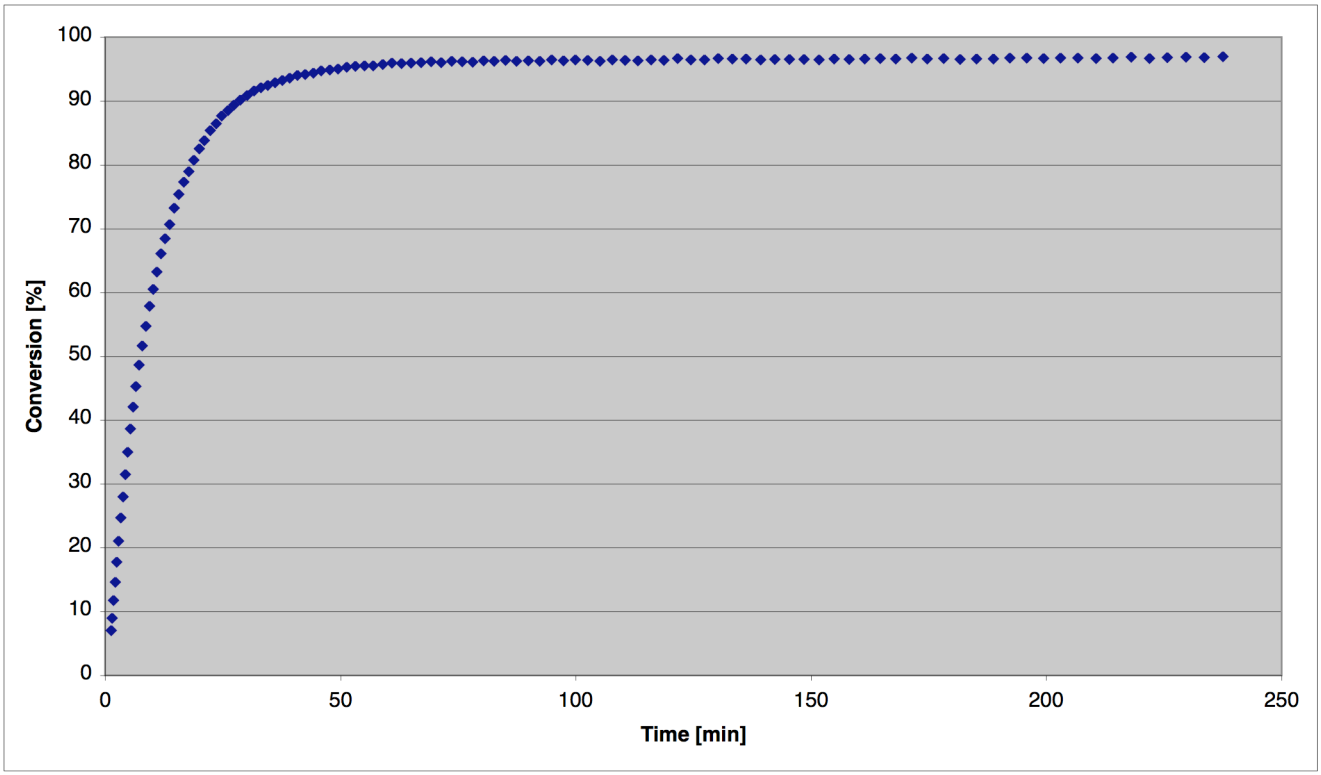


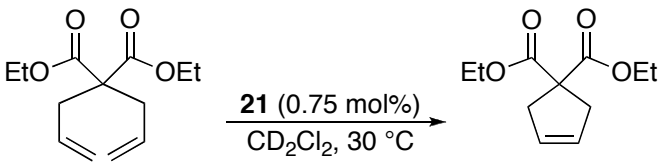




**S1** **S2**

In a glove box, 0.55 ml of stock solution **B** (0.6 mg of **21**, 0.0008 mmol) was transferred to a screw cap NMR tube and 0.25 ml of $CD_2Cl_2$ was added. The NMR tube was sealed and transferred to a 500 MHz NMR which was warmed to 30 °C. The NMR tube was then ejected, **S1** (20.5 μl, 0.08 mmol) was added and the tube was injected for data collection. A graph of conversion over time follows.

RCM of **S1** with **21** at 30 °C

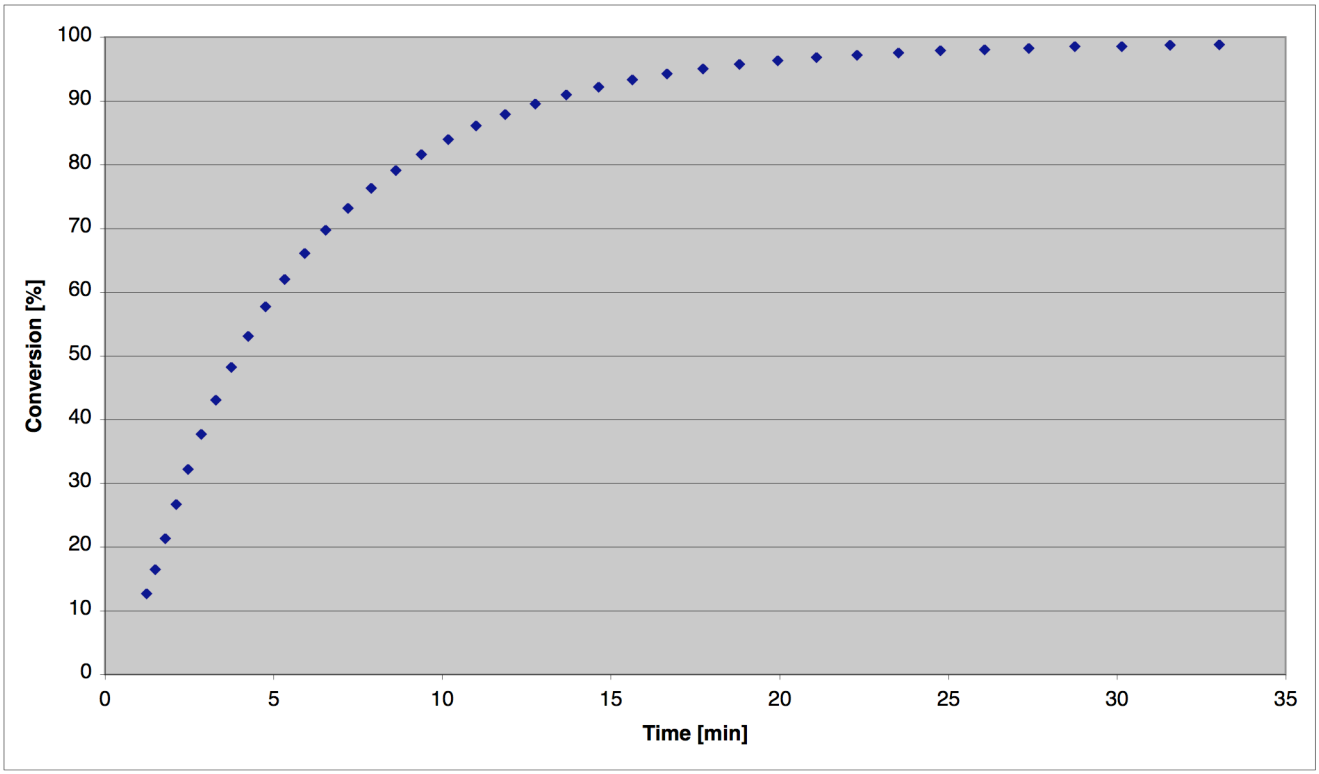


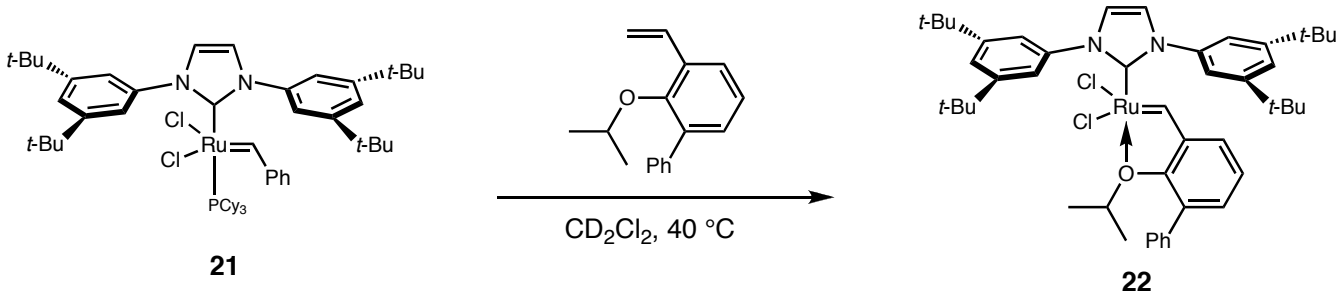




**S3** **S4**

In a glove box, 0.55 ml of stock solution **B** (0.6 mg of **21**, 0.0008 mmol) was transferred to a screw cap NMR tube and 0.25 ml of $CD_2Cl_2$ was added. The NMR tube was sealed and transferred to a 500 MHz NMR which was warmed to 30 °C. The NMR tube was then ejected, **S3** (19.5 μl, 0.08 mmol) was added and the tube was injected for data collection. A graph of conversion over time follows.

RCM of **S3** with **21** at 30 °C

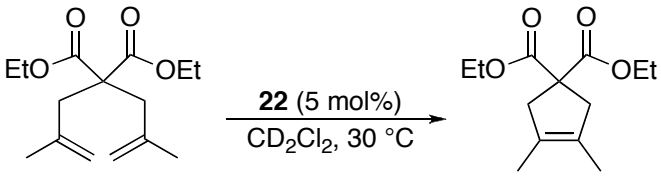



**21** **22**

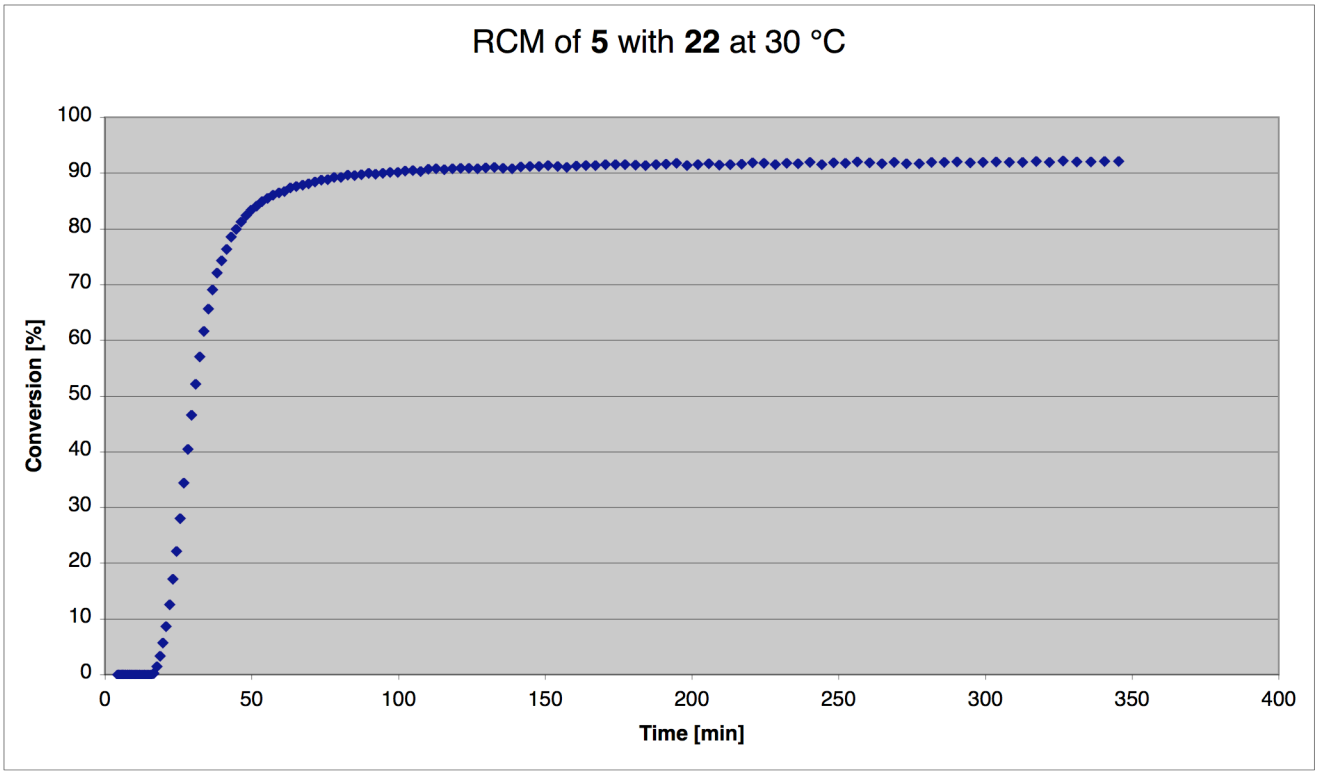
**Ruthenium Catalyst 22**. In a screw cap NMR tube, ruthenium compound **21** (10 mg, .01 mmol), 2-isopropoxy-3-vinylbiphenyl (5 mg, .02 mmol) and CuCl (1 mg, .01 mmol) were combined in $CD_2Cl_2$ (1 ml) in the glove box. The reaction was heated at 40 °C for 29 hours, concentrated and purified by column chromatography (10% --> 25% $Et_2O$/Pentange) to yield a grayish green oil. This oil was lyophilized from benzene to yield a solid (2 mg, 25%). $^1H$ NMR (300 MHz, $CDCl_3$) δ 16.77 (s, 1H), 7.89 (s, 1H), 7.66 - 7.59 (m, 6H), 7.50 - 7.38 (m, 7H), 7.02 (t, J = 4.5 Hz, 1H), 6.72 (dd, J = 3.6, 1.2 Hz, 1H), 4.45 (sept, J = 3.6 Hz, 1H), 1.47 (s, 18H), 1.30 (s, 18H), 0.95 (d, J = 3.6 Hz, 6H).

Activity plot for **22**.

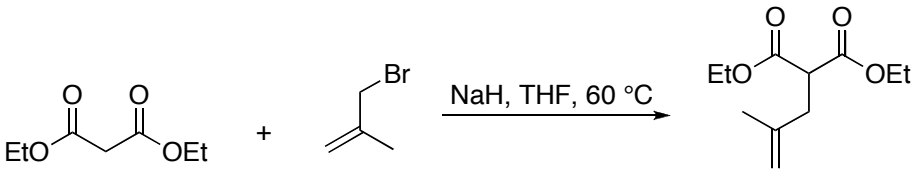



**5** **6**

In a glove box, catalyst **22** (2 mg, .002 mmol) was combined with $CD_2Cl_2$ (.4 ml) in a screw cap NMR tube. The NMR tube was sealed and transferred to a 500 MHz NMR which was warmed to 30 °C. The NMR tube was then ejected, **5** (11 μl, 0.04 mmol) was added and the tube was injected for data collection. A graph of conversion over time follows.



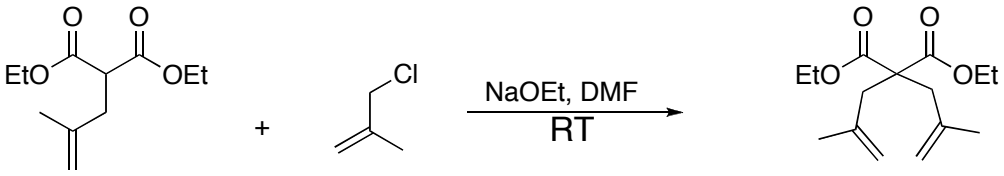
## Synthesis of RCM substrates.




**S10** **S11** **S12**

**Preparation of Diethyl methallylmalonate S12.**

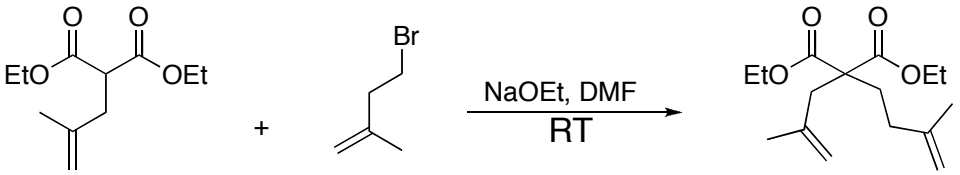
Diethyl methallylmalonate is a known compound: Begley, M. J.; Housden, N.; Johns, A.; Murphy, J. A. *Tetrahedron* **1991**, *47*, 8417, but we report our synthesis for convenience. NaH (238 mg, 9.9 mmol) was suspended in THF (10 ml) and diethyl malonate (1.5 ml, 9.9 mmol) was added dropwise with vigorous bubbling observed. 3-bromo-2-methyl-propene (1 ml, 9.9 mmol) was added dropwise and the reaction was stirred at 60 °C for 24 hours. The reaction was cooled to RT and quenched with water. A copious amount of $Et_2O$ was added and the water layer was removed. The organic fraction was dried with $MgSO_4$, concentrated and purified by column chromatography (10% EtOAc/Hex) to yield 1.481g (70 %) of diethyl methallylmalonate (**S12**). $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 4.75 (d, J = 18 Hz, 2H), 4.19 (q, J = 6.9 Hz, 4H), 3.57 (t, J = 7.8 Hz), 2.61 (d, J = 7.8 Hz, 2H), 1.74 (s, 3H), 1.26 (t, J = 7.2 Hz, 6H).




**S12** **S13** **5**

**Preparation of Substrate 5.**

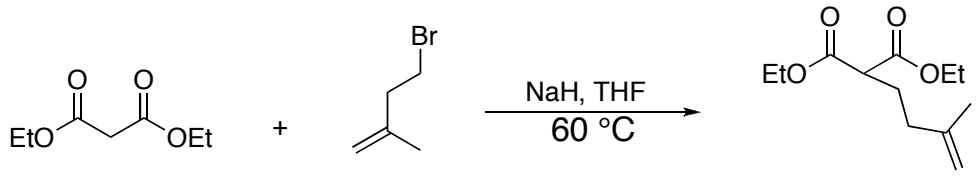
Substrate **5** was prepared from diethyl methallylmalonate (**S12**) as it has been prepared previously in our group: Kirkland, T. A.; Grubbs, R. H. *J. Org. Chem.* **1997**, *62,* 7310.




**S12** **S14** **13**

**Preparation of Substrate 13.**

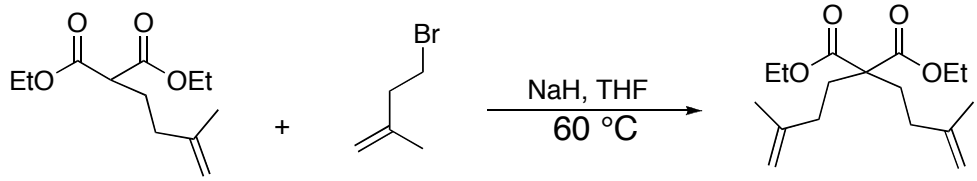
Substrate **13** was prepared from diethyl methallylmalonate (**S12**) as it has been prepared previously in our group: Kirkland, T. A.; Grubbs, R. H. *J. Org. Chem.* **1997**, *62,* 7310.




**S10** **S14** **S15**

**Preparation of Diethyl 2-(3-methylbut-3-enyl)malonate S15.**

NaH (523 mg, 21.8 mmol) was suspended in THF (10ml) and diethyl malonate (1.5 ml, 9.9 mmol) was added dropwise with vigorous bubbling observed. The reaction was heated to 60 °C and 4-bromo-2-methyl-1-butene[3] (2.33 ml, 21.8 mmol) was added dropwise. The reaction was stirred for 20 hours, cooled to RT, quenched with water and copious $Et_2O$ was added. The organic layer was separated, dried with $MgSO_4$, concentrated and purified by column chromatography (5% EtOAc/Hex) to yield 715 mg (32%) of **S15.** $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.72 (d, J = 18 Hz, 2H), 4.19 (q, J = 7.2 Hz, 4H), 3.36-3.30 (m, 1H), 2.05-2.04 (m, 4H), 1.72 (s, 3H), 1.26 (t, J = 7.2 Hz, 6H); $^{13}$C (75 MHz, $CDCl_3$) $\delta$ 169.7, 144.3, 11.4, 61.6, 51.6, 35.5, 26.9, 22.4, 14.3.



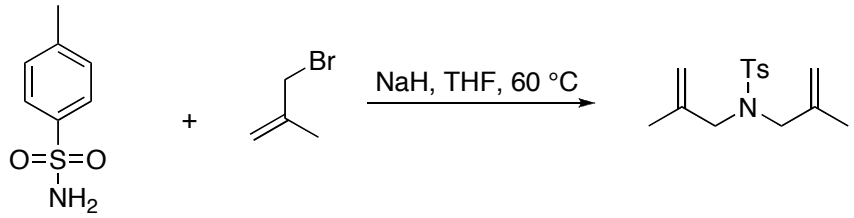

**S15** **S14** **14**

**Preparation of substrate 14**.

NaH (82 mg, 3.4 mmol) was suspended in THF (5 ml) and **S13** (715 mg, 3.1 mmol) was added dropwise. The reaction was heated to 60 °C and vigorous bubbling was observed. 4-bromo-2-methyl-1-butene[1] (336 μl, 3.1 mmol) was added dropwise. The reaction was stirred for 20 hours, cooled to RT, quenched with water and copious $Et_2O$ was added. The organic layer was separated, dried with $MgSO_4$, concentrated and purified by column chromatography (5% EtOAc/Hex) to yield 412 mg (45%) of **14.** $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 4.76 (d, J =

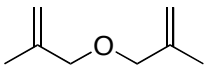
[3] Scholte, A. A.; Eubanks, L. M.; Poulter, C. D.; Vederas, J. C. *Bioorg. MEd. Chem.* **2004**, *12*, 763.

19.8, 4H), 3.93 (q, J = 7.2 Hz, 4H), 2.33-2.29 (m, 4H), 2.07-2.02 (m, 4H), 1.59 (s, 6H), 0.87 (t, J = 6.9 Hz, 6H); $^{13}$C (75 MHz, $CDCl_3$) δ 171.3, 144.9, 110.7, 60.9, 57.4, 32.6, 31.2, 22.4, 14.0. HRMS (EI+) calc for $C_{17}H_{29}O_4$, 297.2066, found 297.2069.



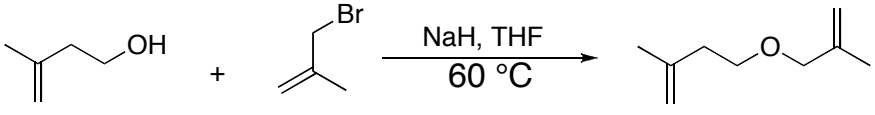

**S15** **S11** **15**

**Preparation of substrate 15.** NaH (1.39 g, 58 mmol) was suspended in THF (130 ml) at 0 °C and p-toluenesulfonamide (**S15**) (5 g, 29 mmol) was added in THF (10 ml). The reaction was warmed to RT and heated to 60 °C, whereupon the reaction started to foam vigorously. The reaction was cooled to RT and stirred for 15 minutes. 3-bromo-2-methylpropene (8.8 ml, 87 mmol) was added in THF (10 ml) and the reaction was heated to 60 °C again. The reaction stirred for 24 hours and was then quenched with water. The organic layer was removed, dried over $MgSO_4$, concentrated, and purified by column chromatography (20% EtOAc/Hex) to yield 2 g (25 %) of diene **15**. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.1, 2H), 4.81 (d, J = 24.6 Hz, 4H), 3.70 (s, 4H), 2.42 (s, 3H), 1.60 (s, 6H); $^{13}$C (75 MHz, $CDCl_3$) δ 143.3, 140.3, 137.7, 129.7, 127.5, 114.8, 53.3, 21.8, 20.2. HRMS (EI+) calc for $C_{15}H_{22}NO_2S$, 280.1371, found 280.1373.




**16**

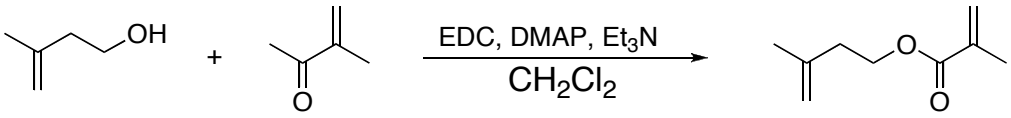
Diene **16** was purchased from "Monomer and Polymer, and Dajac Labs" and used as received.




**S16** **S11** **17**

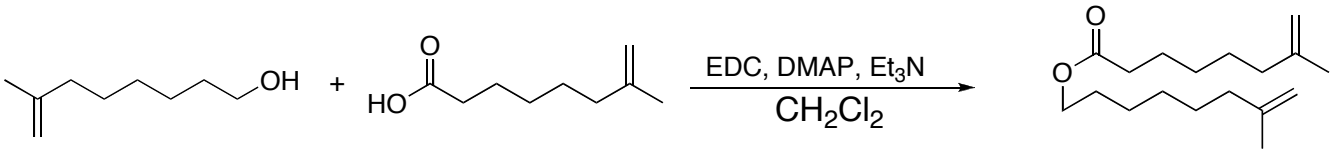
**Preparation of substrate 17.** NaH (264 mg, 11 mmol) was suspended in THF (10 ml) at 0 °C and 3-methylbut-3-en-1-ol (**S16**) (1.11 ml, 11 mmol) was added dropwise. The solution bubbled and turned yellow. The solution

was heated to 60 °C and 3-bromo-2-methylpropene (1ml, 9.9 mmol) was added. The reaction was stirred for 48 hours, cooled to RT and quenched with water. The reaction was extracted 4 times with $Et_2O$ and the combined organic fractions were dried with $MgSO_4$, concentrated and purified by column chromatography (5% $Et_2O$/Pent). The column fractions were concentrated to **17** using a rotovap with an ice bath. This gave 1.22 g (88%) of diene **17**. $^1$H NMR (300 MHz, $CDCl_3$) δ 4.92 (d, J = 21.9, 2H), 4.75 (d, J = 12.9, 2H), 3.88 (s, 2H), 3.51 (t, J = 6.9 Hz, 2H), 2.31 (t, J = 6.9 Hz, 2H), 1.74 (d, J = 6 Hz, 6H); $^{13}$C (75 MHz, $CDCl_3$) δ 143.2, 142.6, 112.2, 11.7, 75.1, 68.7, 38.1, 22.9, 19.7; HRMS (EI+) calc for $C_9H_{16}O$, 140.1201, found 140.1199.




**18**

**Preparation of substrate 18.** 3-methyl-3-buten-1-ol (853 mg, 9.9 mmol), methacrylic acid (853 mg, 9.9 mmol) and DMAP (120 mg, .99 mmol) were dissolved in $CH_2Cl_2$, the solution was cooled to 0 °C, flushed with argon, and EDC (1.898 mg, 9.9 mmol) was added. Then $Et_3N$ (2.67 ml, 19.8 mmol) was added and the reaction was stirred for 24 hours. Precipitates were observed and 50 ml of $Et_2O$ was added. The solution was washed with water, 1N HCl, water and brine, dried over $MgSO_4$, concentrated and purified by column chromatography (10% EtOAc/Hex) to yield 703 mg (46%) of substrate **18**. $^1$H NMR (300 MHz, $CDCl_3$) δ 6.09-6.08 (m, 1H), 5.54-5.53 (m, 1H), 4.80 (s, 1H), 4.74 (s, 1H), 4.25 (t, J = 6.6 Hz, 2H), 2.37 (t, J = 6.6 Hz, 2H), 1.92 (s, 3H), 1.76 (s, 3H); $^{13}$C (75 MHz, $CDCl_3$) δ 146.9, 142.0, 136.6, 125.6, 112.5, 63.1, 36.9, 22.7, 18.5; HRMS (EI+) calc for $C_9H_{14}O_2$, 154.0994, found 154.0994.




**S17** **S18** **19**

**Preparation of substrate 19**. Primary alcohol **S17**[4] (747 mg, 4.78 mmol), carboxylic acid **S18** (747 mg, 4.78 mmol) and DMAP (58 mg, .478 mmol) were dissolved in $CH_2Cl_2$, the solution was cooled to 0 °C, flushed with argon, and EDC (916 mg, 4.78 mmol) was added. Then $Et_3N$ (1.3 ml, 9.6 mmol) was added and the reaction was stirred for 24 hours. Precipitates were observed and 50 ml of $Et_2O$ was added. The solution was washed with water, 1N HCl, water and brine, dried over $MgSO_4$, concentrated and purified by column chromatography (5%

EtOAc/Hex) to yield 1.115 g (83%) of substrate **19**. $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.66 (d, J = 8.7 Hz, 4H), 4.05 (t, J = 6.9 Hz, 2H), 2.29 (t, J = 7.5 Hz, 2H), 2.00 (t, J = 7.8 Hz, 2H), 1.70 (s, 6H), 1.68-1.28 (m, 14H); $^{13}$C (75 MHz, $CDCl_3$) $\delta$ 148.0, 146.3, 146.2, 131.9, 110.0, 109.9, 64.6, 37.9, 37.8, 34.6, 29.1, 29.0, 28.8, 27.7, 27.4, 26.1, 25.1, 22.6; HRMS (EI+) calc for $C_{18}H_{32}O_2$, 280.2402, found 280.2390.

## RCM to form tetrasubstituted olefins using 3, 10, 11, 12.

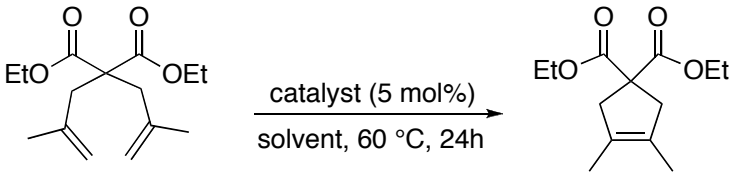
**Standard RCM procedure for table 3.**

**For Conversions**: Catalyst **3**, **12**, or **11** (.02 mmol) was weighed into a 2 ml volumetric flask that was taken into the glove box. $C_6D_6$ (2 ml) was added and then 0.4 ml of the solution (.004 mmol of catalyst) was transferred to a screw cap NMR tube. The solution in the NMR tube was diluted with 0.4 ml of $C_6D_6$ and the tube was sealed with a screw cap that had a built in septa. The NMR tube was removed from the glove box, the substrated (.08 mmol) was injected and the tube was heated to 60 °C in an oil bath. After 24 hours, the tube was removed and an NMR was taken to determine conversion.

Conversions for catalyst **10** were obtained using a slightly different procedure because **10** is insoluble in benzene. Instead, catalyst **10** (18.5 mg, .03 mmol) was dissolved in $CDCl_3$ (5.92 ml) and then 0.8 ml of the solution (.004 mmol of catalyst) was transferred to a screw cap NMR tube, which was sealed with a screw cap that had a built in septa. The NMR tube was removed from the glove box, the substrated (.08 mmol) was injected and the tube was heated to 60 °C in an oil bath. After 24 hours, the tube was removed and an NMR was taken to determine conversion.

**For Isolated Yields:** Catalyst **12** (7 mg, .009 mmol) was weighed into a 1 dram vial . A stirbar was added and the vial was taken into the glove box where $C_6D_6$ (1.8 ml) was added. The vial was sealed with a screw cap that had a built in septa and removed from the box. The substrate (0.185 mmol) was injected and the vial was heated to 60 °C in an oil bath. After 24 hours, the solution was concentrated and the product was purified by column chromatography.

[4] Taber, D. F.; Christos, T. E.; Neubert, T. D.; Batra, D. *J. Org. Chem.* **1999**, *64*, 9673.

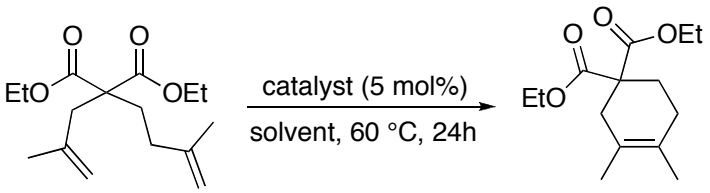



**5** **6**

**For Conversion:** The SM methylene signal at 2.99 ppm was compared to the product signal at 3.14 ppm.

**For Isolated Yield:** 50 μl of **5** was used. The rxn was columned in 5% EtOAc/Hex to yield 38.5 mg (86 %).

Product **6** is a known compound and our spectral data matches the published data: Kirkland, T. A.; Grubbs, R. H. *J. Org. Chem.* **1997**, *62,* 7310.

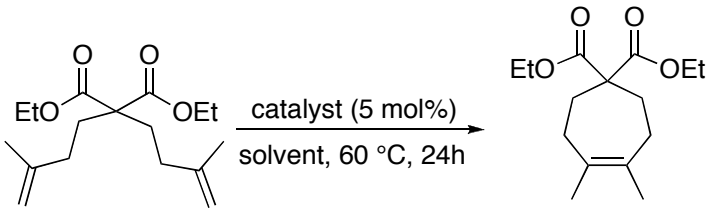



**13** **S19**

**For Conversion:** The SM methylene signal at 2.72 ppm was compared to the product signal at 2.63 ppm.

**For Isolated Yield:** 52 μl of **13** was used. The rxn was columned in 5% EtOAc/Hex to yield **S19** quantitatively.

Product **S19** is a known compound and our spectral data matches the published data: Kirkland, T. A.; Grubbs, R. H. *J. Org. Chem.* **1997**, *62,* 7310.

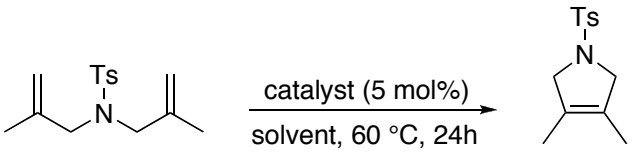



**14** **S20**

**For Conversion:** The SM methyl group signal at 1.59 ppm was compared to the product signal at 1.50 ppm.

**For Isolated Yield:** 55 μl of **14** was used. The rxn was columned in 5% EtOAc/Hex to yield 23 mg (47 %).

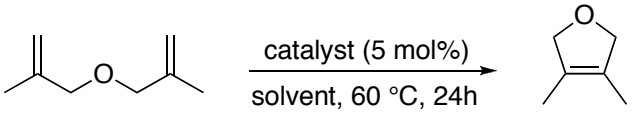
Product **S20** is a known compound and our spectral data matches the published data: Fürstner, A.; Thiel, O. R.; Ackermann, L.; Schanz, H.-J.; Nolan, S. P. *J. Org. Chem.* **2000**, *65*, 2204.




**15** **S21**

**For Conversion:** The SM methyl group signal at 3.62 ppm was compared to the product signal at 3.84 ppm.

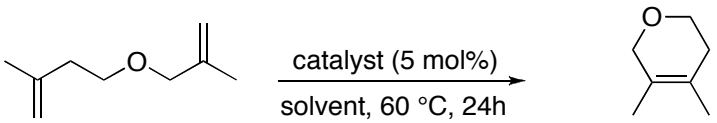
**For Isolated Yield:** 52 μl of **15** was used. The rxn was columned in 25% EtOAc/Hex to yield **S21** quantitatively. Product **S21** is a known compound and our spectral data matches the published data: Arisawa, M.; Terada, Y.; Takahashi, K.; Nakagawa, M.; Nishida, A. *J. Org. Chem.* **2006**, *71*, 4255.




**16** **S22**

**For Conversion:** The SM methylene signal at 3.68 ppm was compared to the product signal at 4.45 ppm.

**For Isolated Yield:** Product **S22** was not isolated due to its high volatility. Product **S22** is a known compound and our spectral data matches the published data: Ripoll, J.-L. *Tetrahedron Lett.* **1974**, *15,* 1665. A $^1$H NMR is reported here for convenience: $^1$H NMR (300 MHz, $CDCl_3$) δ 4.45 (s, 4H), 1.23 (s, 6H).




**17** **S23**

**For Conversion:** The SM methylene signal at 3.51 ppm was compared to the product signal at 3.76 ppm. The impurity has a signal at 4.26 ppm.

**For Isolated Yield:** An isolated yield was not obtained for **S23** due to its high volatility. A sample was isolated by column chromatography (5% $Et_2O$/Hex) but the solvent could not be fully removed for the $^1$H NMR so the methyl groups could not be rigorously identified. $^1$H NMR (300 MHz, $CDCl_3$) δ 3.92 (s, 2H), 3.76 (t, J = 6 Hz, 2H), 2.01 (s, 2H).

# Spectra of novel compounds

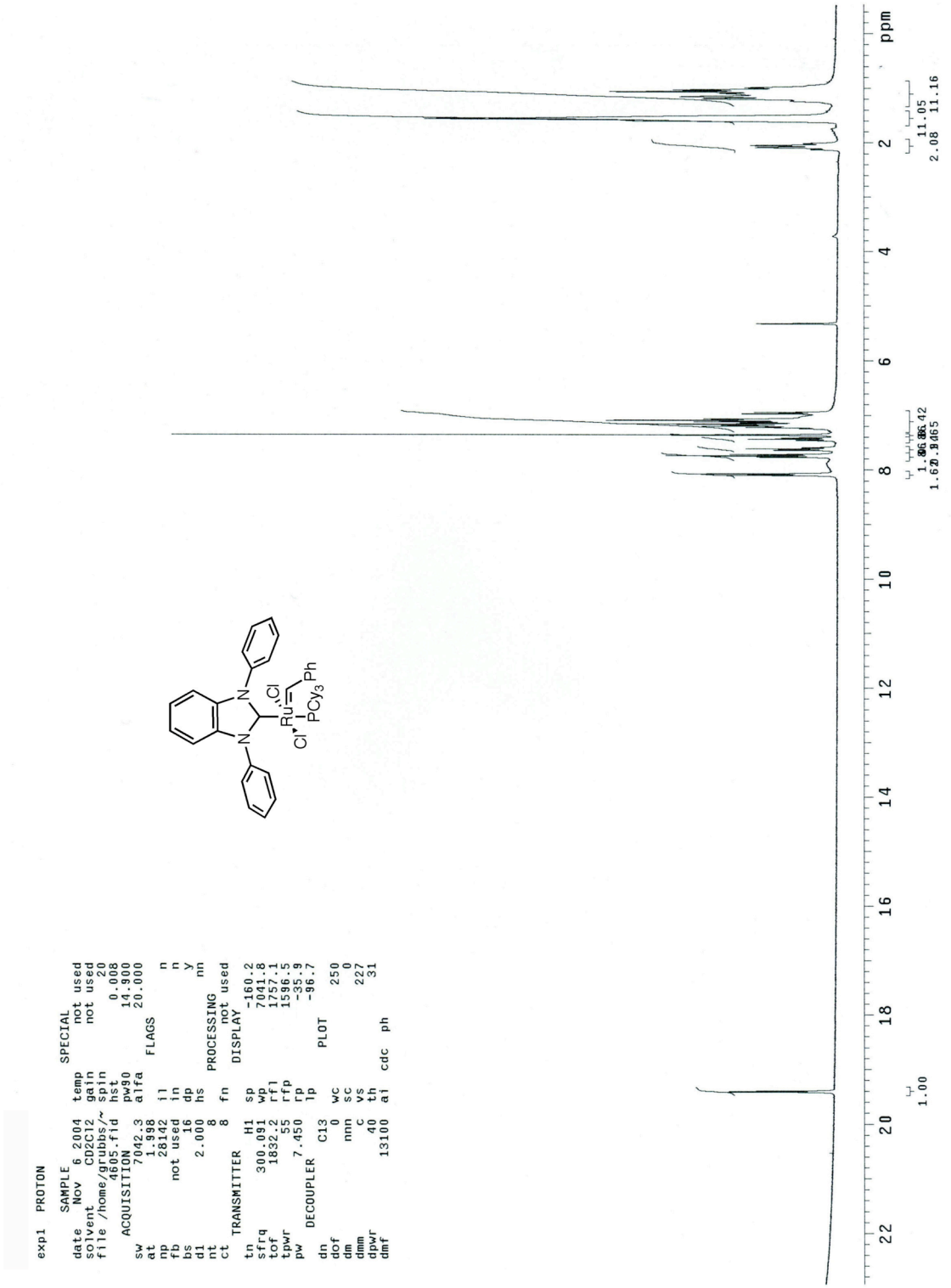



**Figure SI.1:** $^1$H NMR spectrum (300 Mz, $CD_2Cl_2$) of complex **S7**.

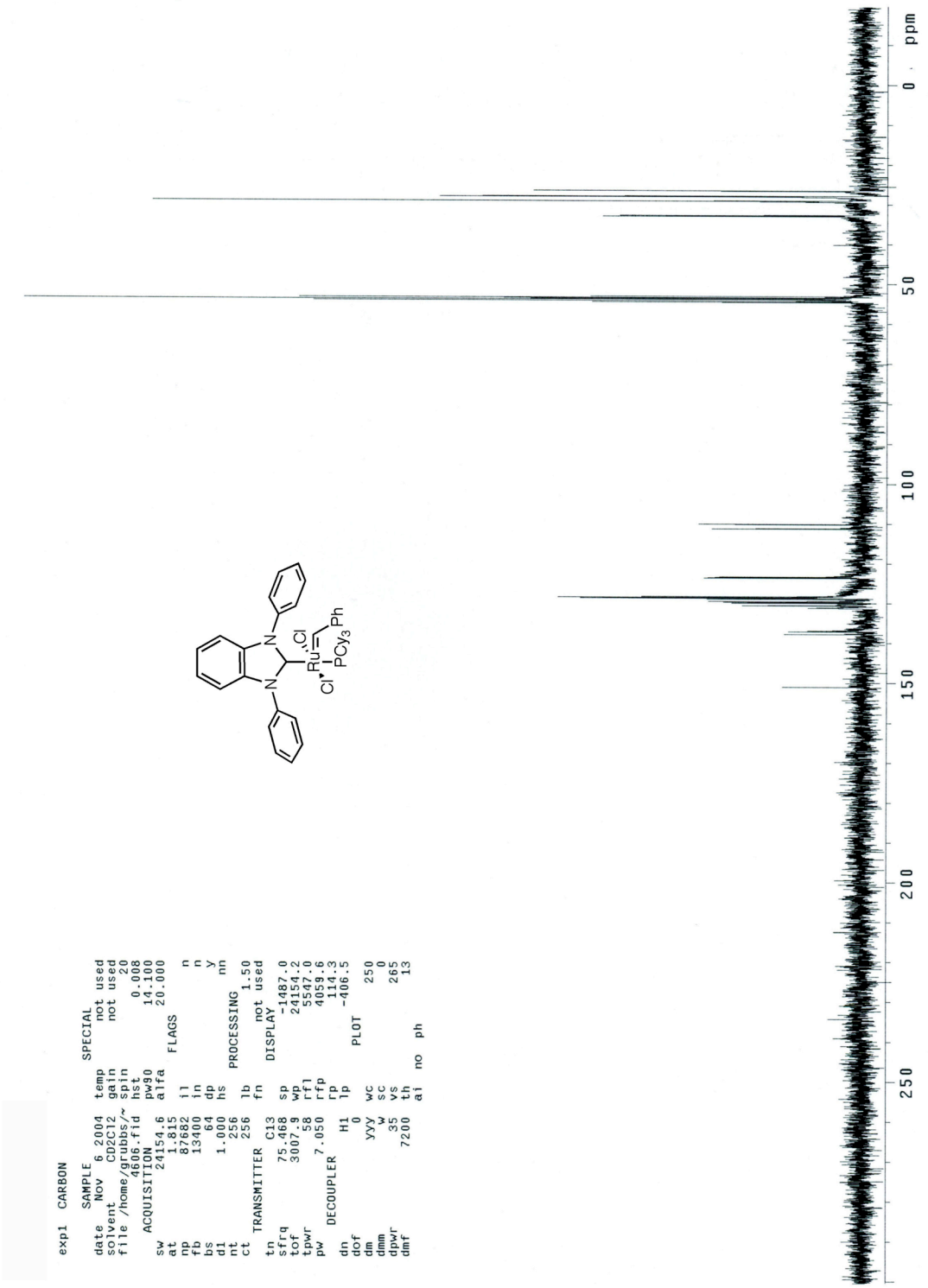



**Figure SI.2:** $^{13}C$ NMR spectrum (75 Mz, $CD_2Cl_2$) of complex **S7**.


**Figure SI.3:** $^1$H NMR spectrum (300 Mz, $CD_2Cl_2$) of complex **11**.

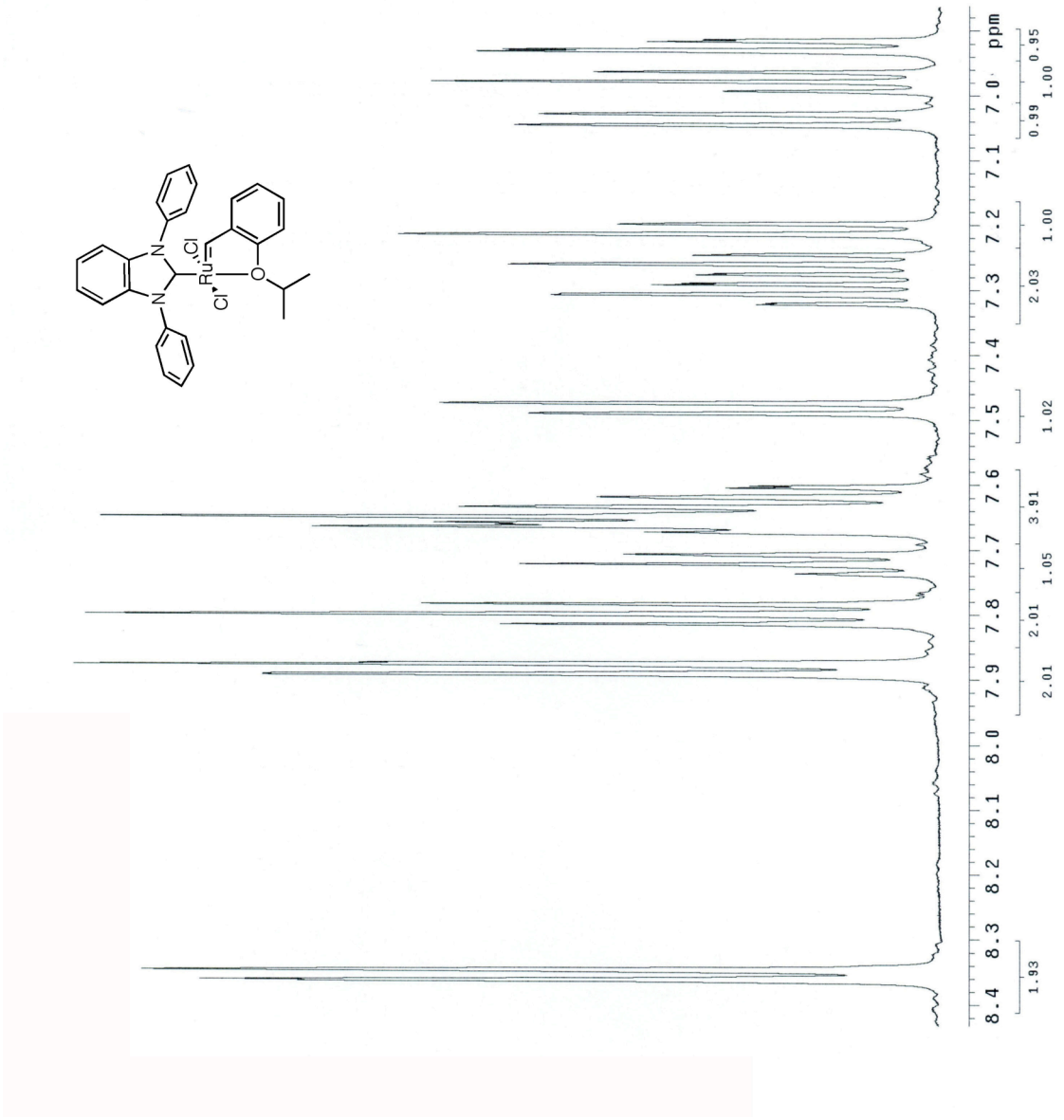



**Figure SI.4:** Partial $^{1}H$ NMR spectrum (500 Mz, $CD_2Cl_2$) of complex **11** acquired at –30 ºC. An expansion of the aromatic region is shown.

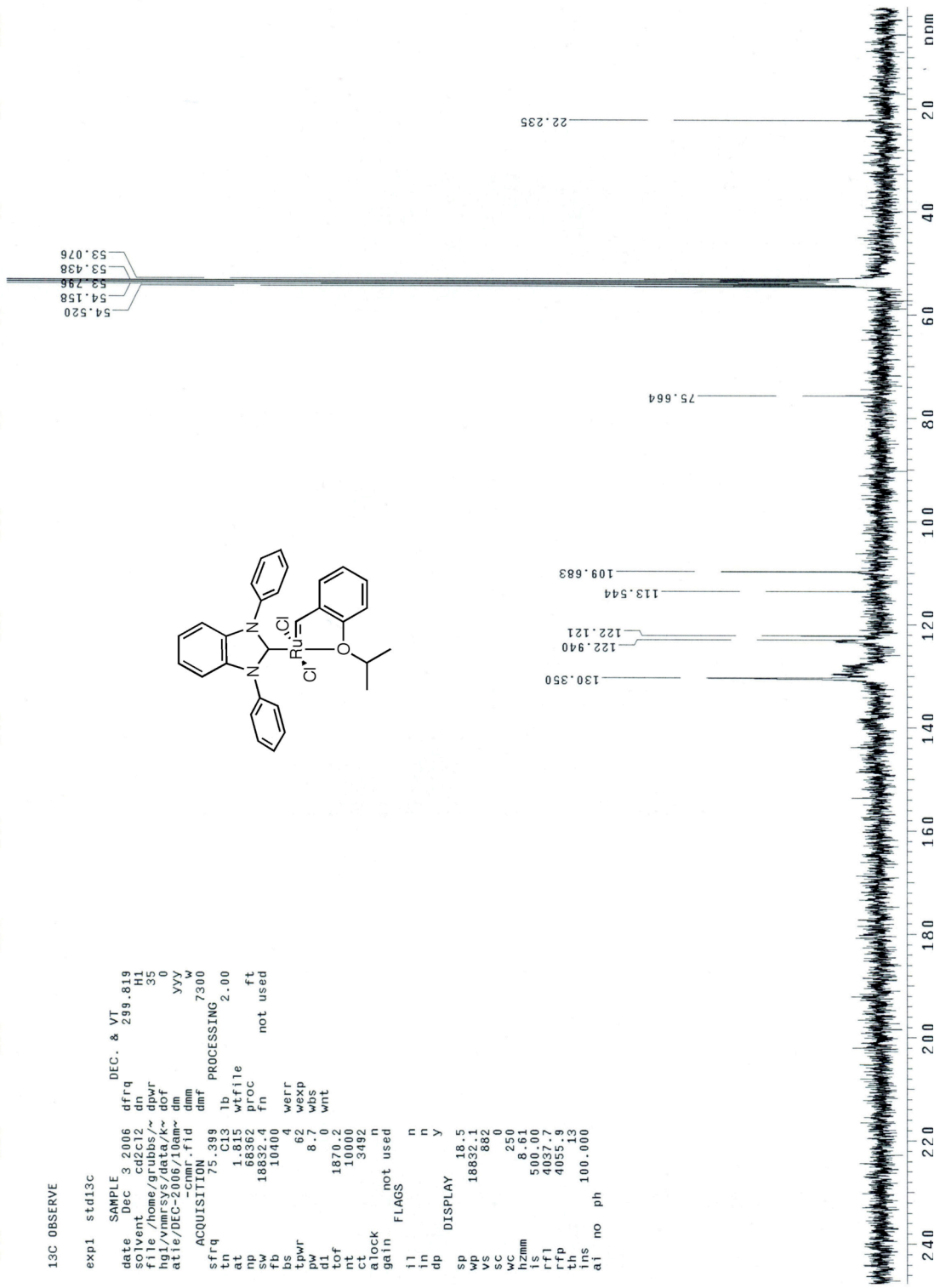
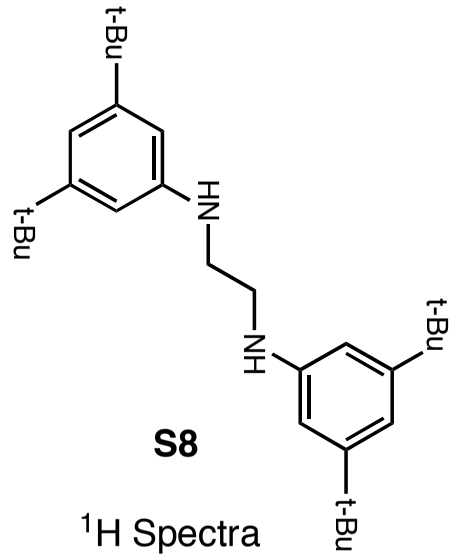


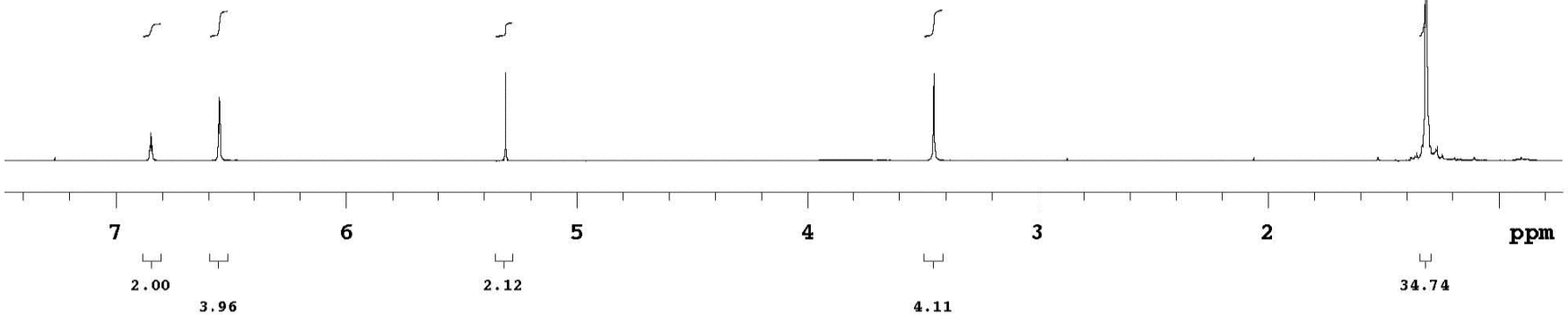

**Figure SI.5:** $^{13}C$ NMR spectrum (75 Mz, $CD_2Cl_2$) of complex **11**.

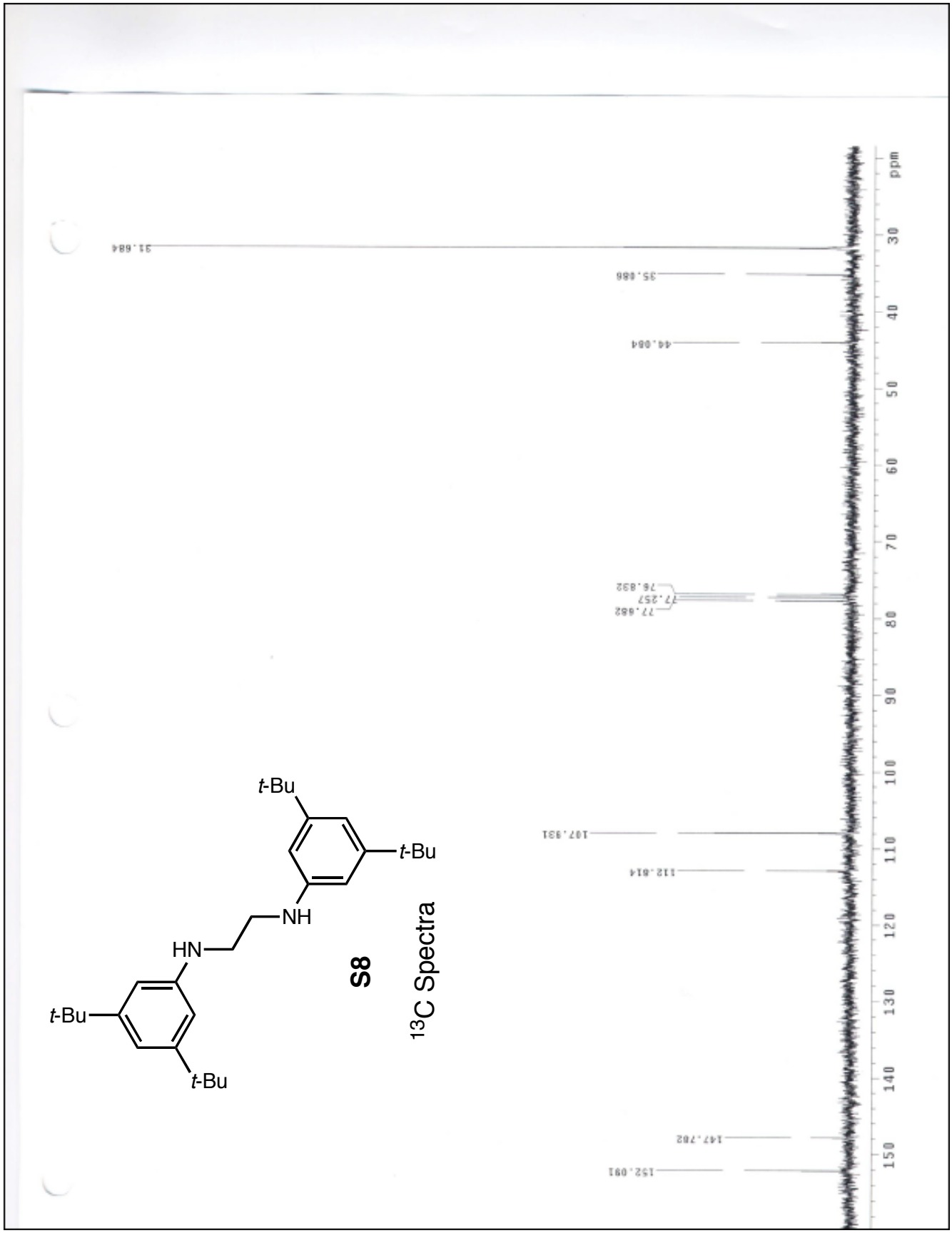
| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 2053.400 | 6.849 | 4.6 |
| 2 | 1964.281 | 6.552 | 10.2 |
| 3 | 1962.631 | 6.546 | 9.6 |
| 4 | 1591.029 | 5.307 | 14.2 |
| 5 | 1034.589 | 3.451 | 14.1 |
| 6 | 394.806 | 1.317 | 164.7 |




**S8**

$^1$H Spectra

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t-Bu
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HN
t-Bu
t-Bu
S8
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44.084
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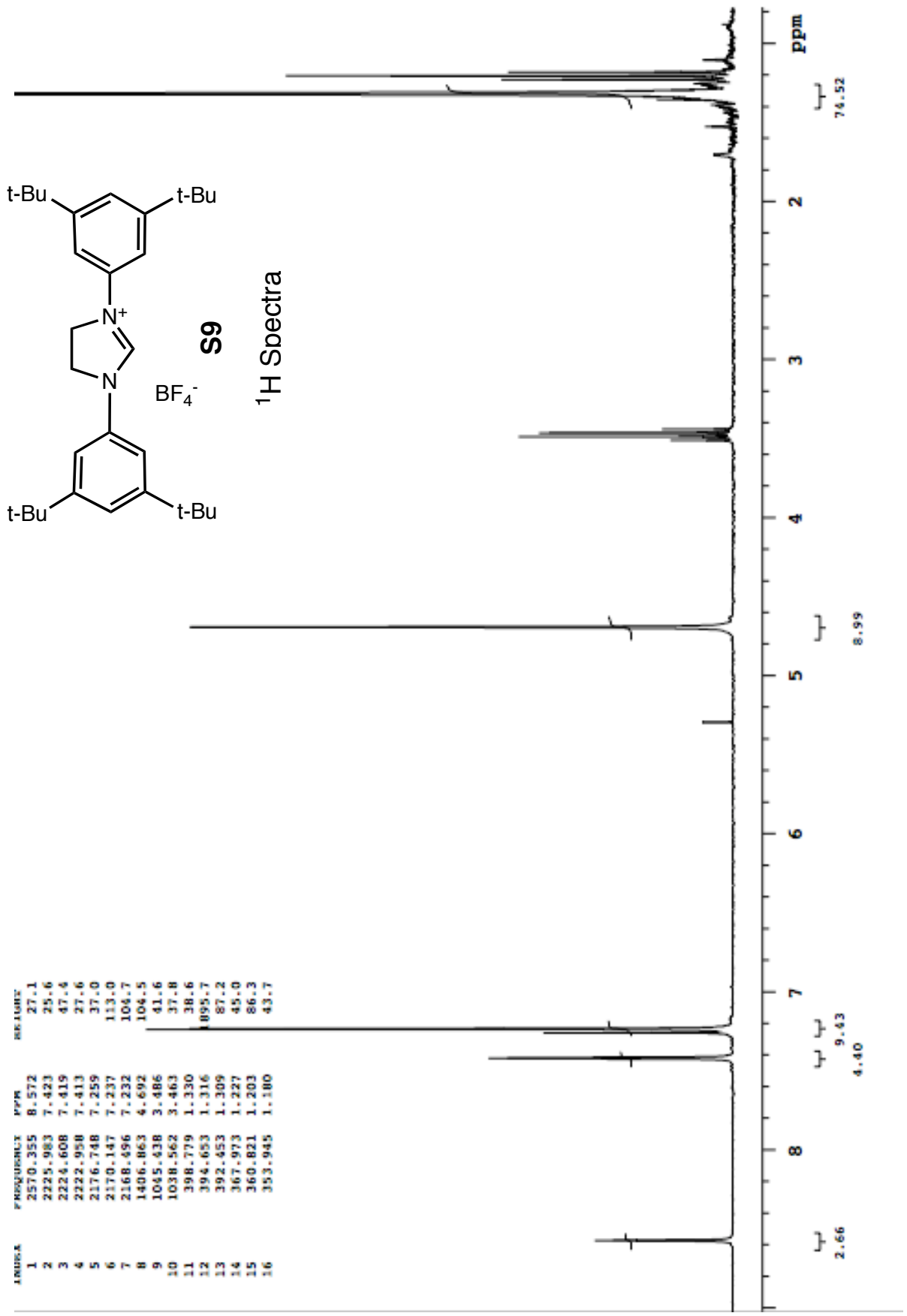
77.682
107.931
112.814
147.782
152.091
ppm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t-Bu
t-Bu
N+
N
BF4-
S9
1H Spectra
ppm
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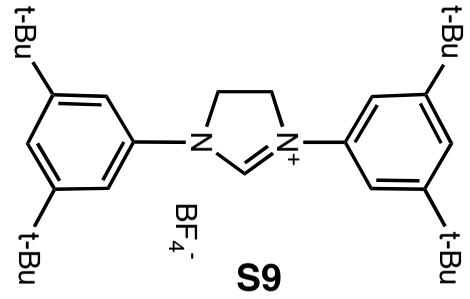
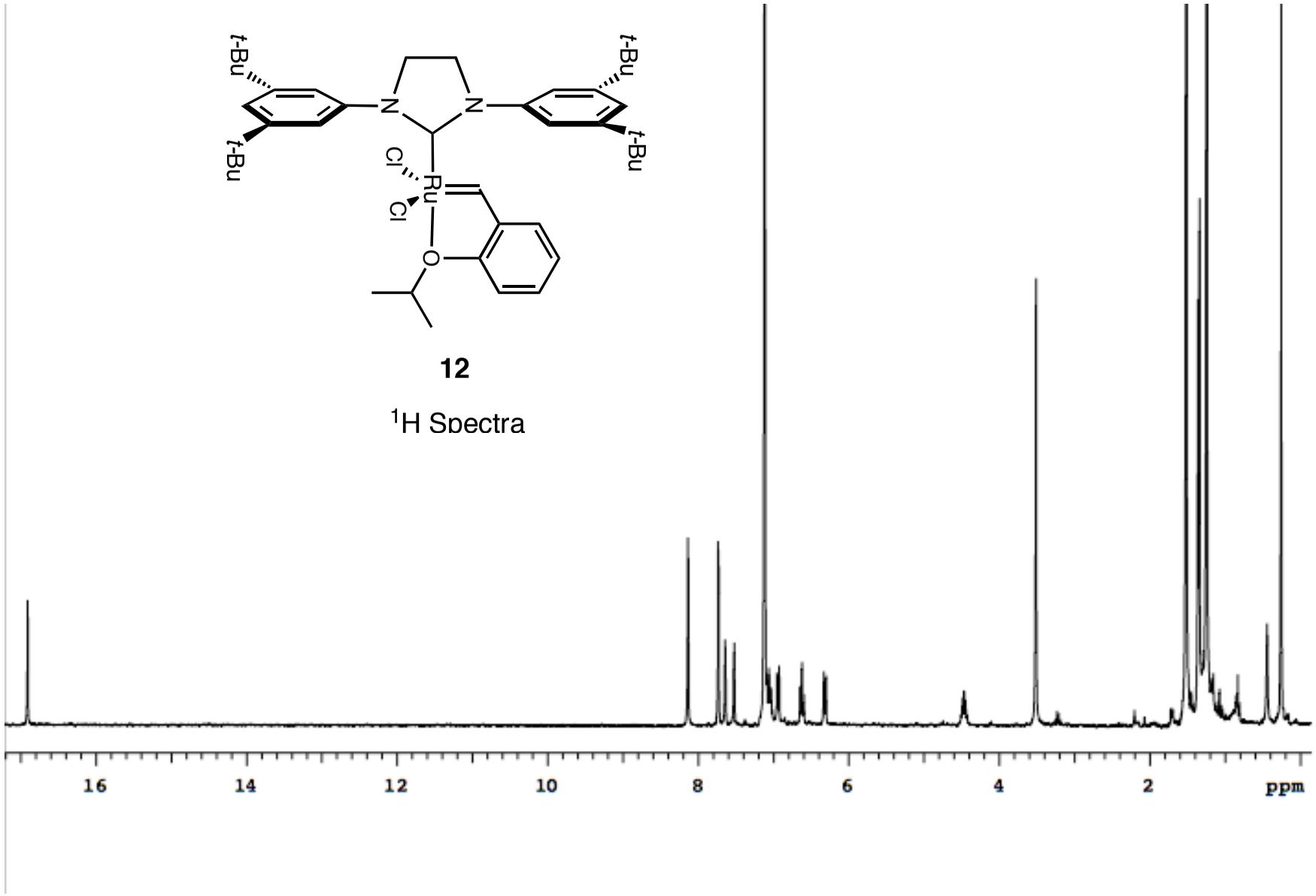
9.43
4.40
74.52
8.99

| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 11583.529 | 153.625 | 39.2 |
| 2 | 11416.914 | 151.415 | 9.1 |
| 3 | 10209.093 | 135.397 | 15.0 |
| 4 | 9284.119 | 123.129 | 17.2 |
| 5 | 8666.324 | 114.936 | 42.8 |
| 6 | 5857.905 | 77.690 | 32.3 |
| 7 | 5825.841 | 77.264 | 33.4 |
| 8 | 5793.778 | 76.839 | 34.0 |
| 9 | 3810.994 | 50.543 | 20.0 |
| 10 | 2671.881 | 35.435 | 30.2 |
| 11 | 2381.592 | 31.586 | 12.0 |
| 12 | 2371.859 | 31.456 | 152.3 |



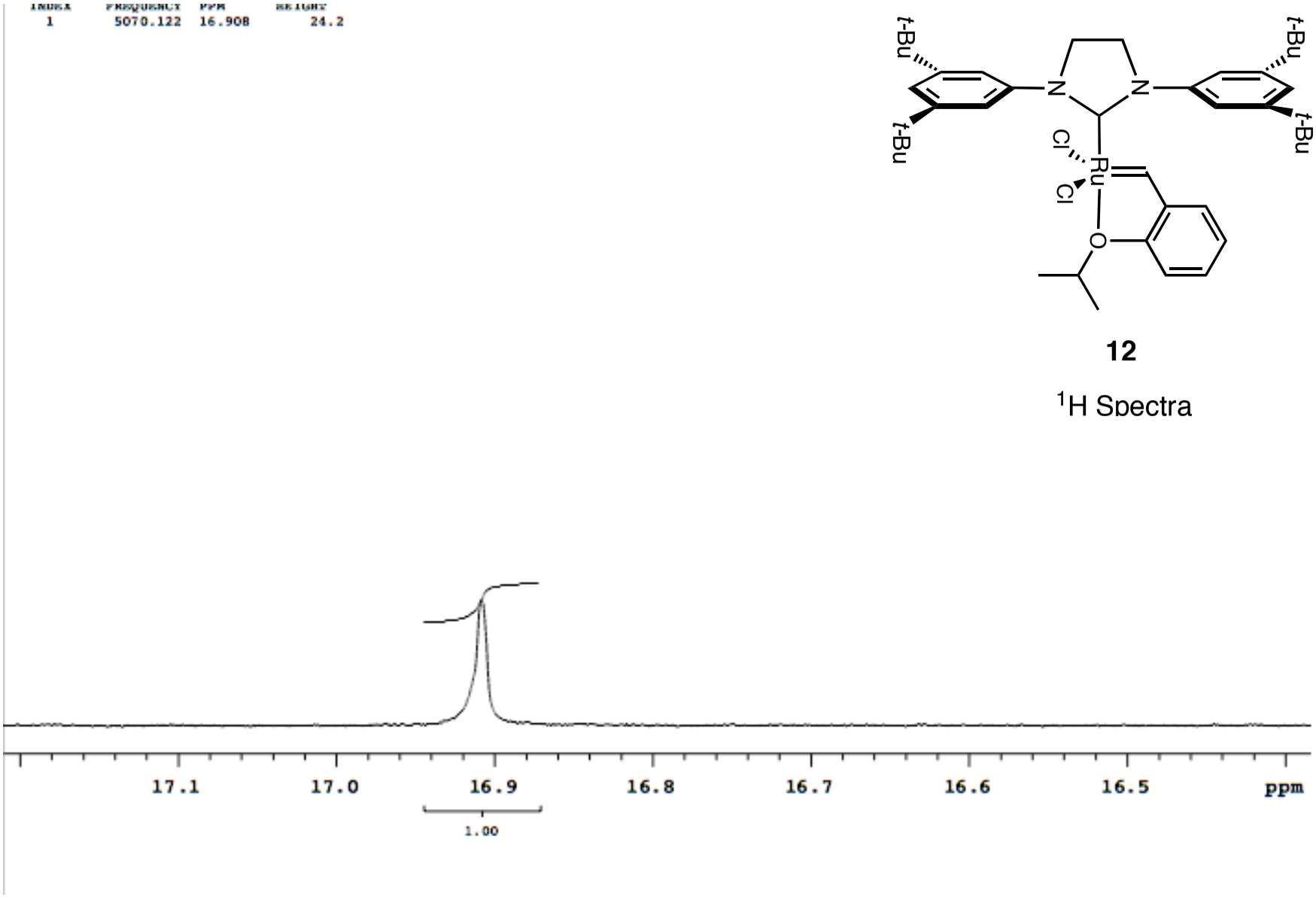

**S9**

$^{13}$C Spectra




**12**

$^{1}$H Spectra

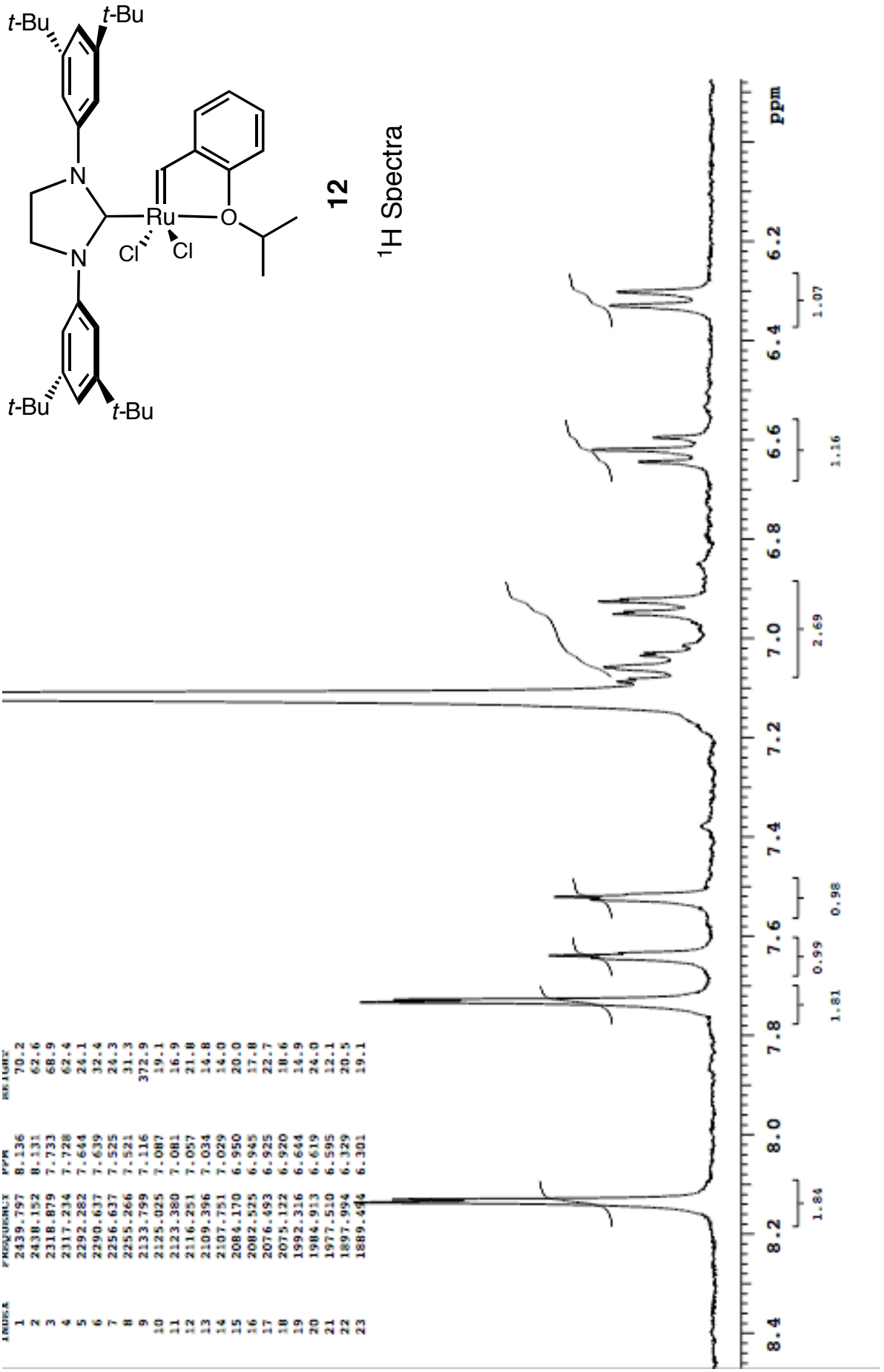






**12**

$^{1}$H Spectra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O
Cl
Cl
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1H Spectra
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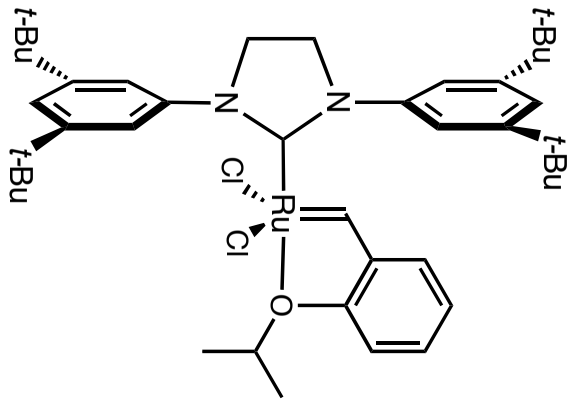
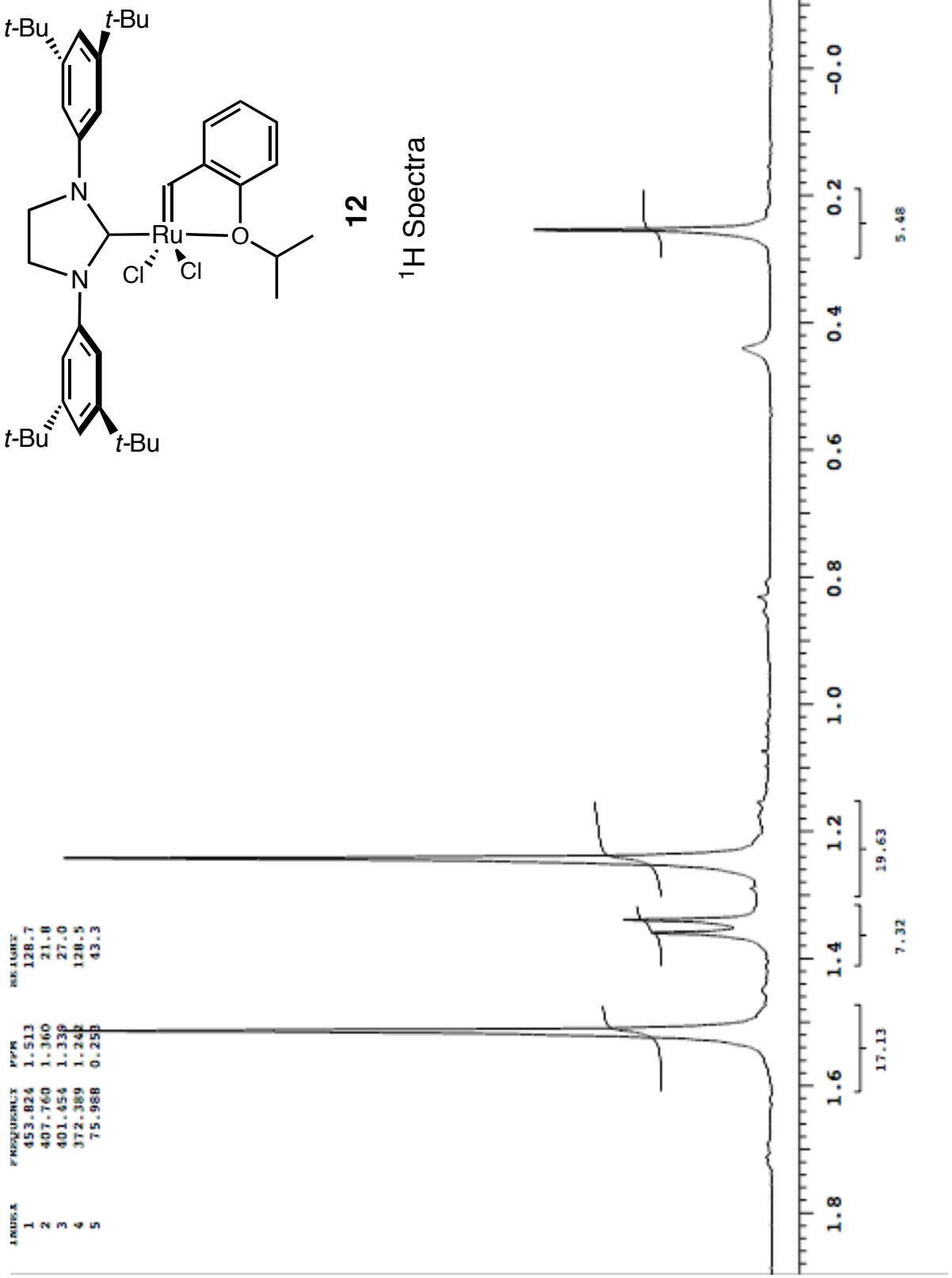
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
1.84
1.81
0.99
0.98
2.69
1.16
1.07

| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 1345.223 | 4.486 | 8.4 |
| 2 | 1339.465 | 4.467 | 10.5 |
| 3 | 1333.158 | 4.446 | 7.9 |
| 4 | 1052.934 | 3.511 | 128.7 |




**12**

$^1$H Spectra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O
Cl
Cl
N
t-Bu
t-Bu
12
1H Spectra
ppm
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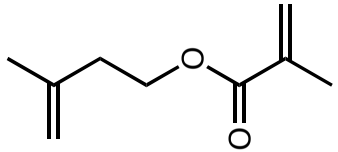
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
-0.0
17.13
7.32
19.63
5.48

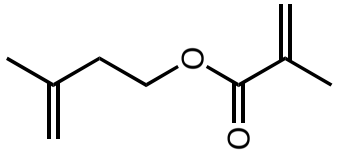
| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 1824.566 | 6.085 | 37.6 |
| 2 | 1823.740 | 6.082 | 44.6 |
| 3 | 1822.915 | 6.079 | 42.2 |
| 4 | 1822.090 | 6.076 | 28.7 |
| 5 | 1659.807 | 5.535 | 27.4 |
| 6 | 1658.431 | 5.531 | 39.6 |
| 7 | 1656.781 | 5.525 | 28.4 |
| 8 | 1584.991 | 5.286 | 99.2 |
| 9 | 1438.661 | 4.798 | 32.1 |
| 10 | 1422.982 | 4.745 | 31.0 |
| 11 | 1422.157 | 4.743 | 35.0 |
| 12 | 1421.057 | 4.739 | 32.0 |
| 13 | 1279.953 | 4.268 | 45.9 |
| 14 | 1273.076 | 4.245 | 94.6 |
| 15 | 1266.200 | 4.223 | 45.7 |
| 16 | 718.286 | 2.395 | 27.1 |
| 17 | 711.685 | 2.373 | 52.1 |
| 18 | 704.808 | 2.350 | 26.4 |
| 19 | 577.182 | 1.925 | 126.7 |
| 20 | 576.357 | 1.922 | 151.4 |
| 21 | 575.532 | 1.919 | 130.3 |
| 22 | 527.397 | 1.759 | 139.6 |



**18**

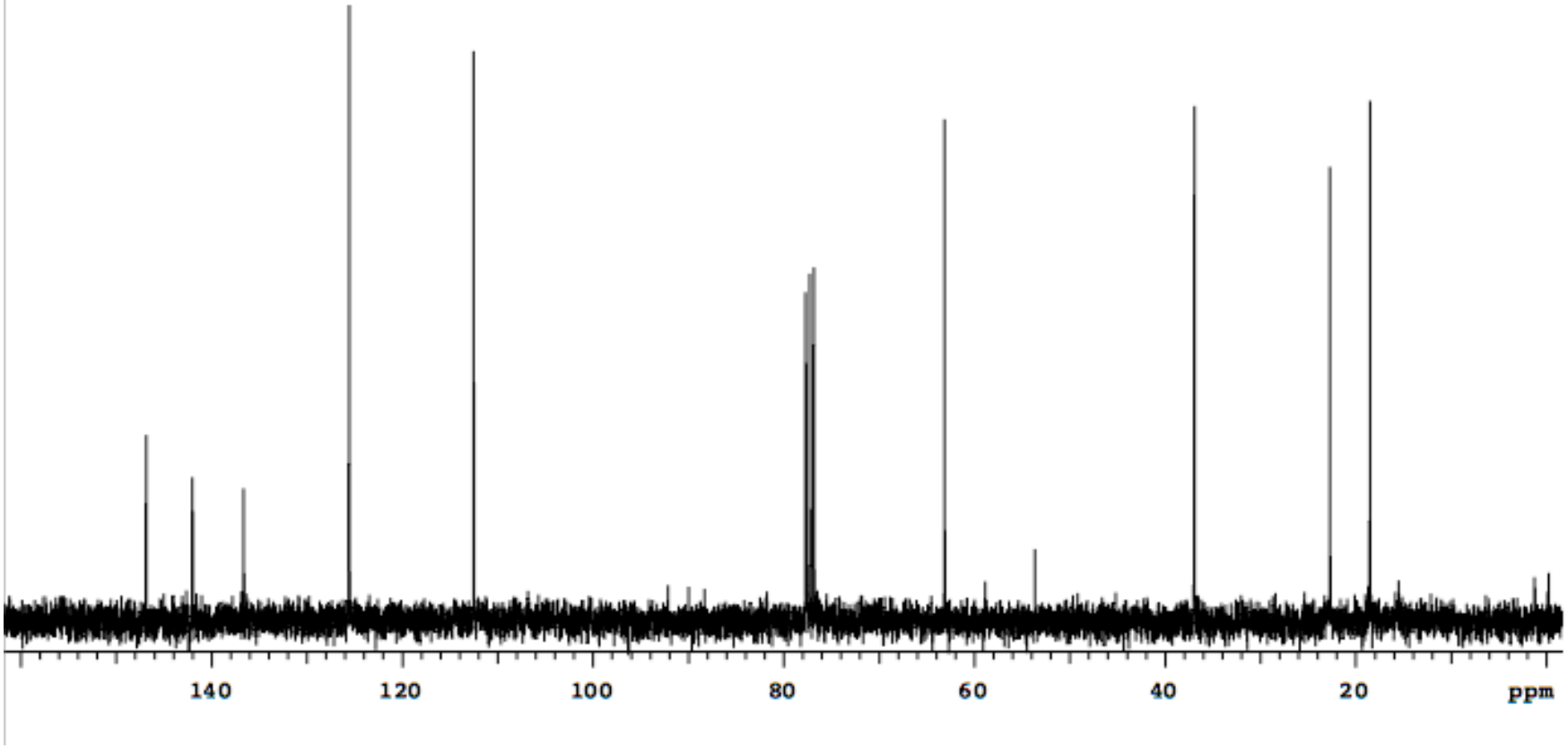
$^{1}$H Spectra

| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 11073.577 | 146.861 | 29.7 |
| 2 | 10706.278 | 141.990 | 22.9 |
| 3 | 10301.476 | 136.621 | 21.2 |
| 4 | 9467.539 | 125.561 | 98.6 |
| 5 | 8482.732 | 112.501 | 91.2 |
| 6 | 5857.533 | 77.684 | 52.6 |
| 7 | 5825.469 | 77.259 | 55.5 |
| 8 | 5793.692 | 76.838 | 56.5 |
| 9 | 4759.358 | 63.120 | 80.3 |
| 10 | 2784.590 | 36.930 | 82.4 |
| 11 | 1711.895 | 22.704 | 72.7 |
| 12 | 1395.554 | 18.508 | 83.3 |

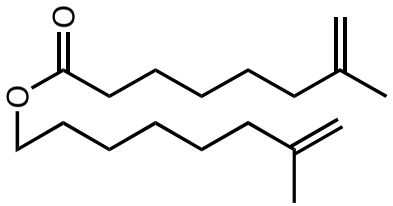


**18**

$^{13}C$ Spectra

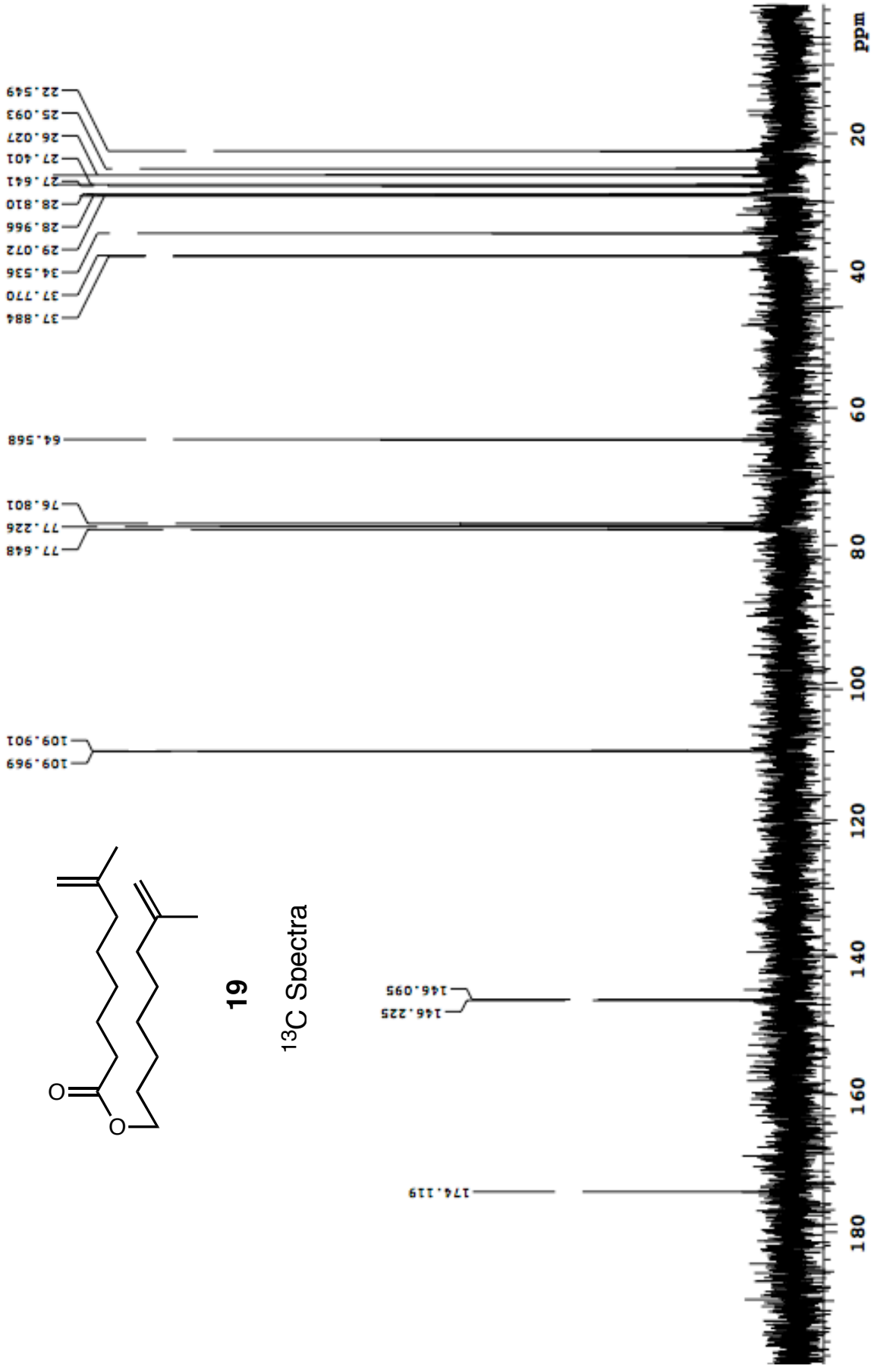


| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 1404.815 | 4.686 | 24.0 | 35 | 407.734 | 1.360 | 15.1 |
| 2 | 1403.990 | 4.683 | 28.2 | 36 | 406.358 | 1.355 | 17.1 |
| 3 | 1403.440 | 4.681 | 30.3 | 37 | 401.682 | 1.340 | 26.2 |
| 4 | 1402.615 | 4.678 | 30.4 | 38 | 400.582 | 1.336 | 27.3 |
| 5 | 1394.638 | 4.652 | 31.9 | 39 | 398.107 | 1.328 | 36.5 |
| 6 | 1393.813 | 4.649 | 32.5 | 40 | 395.081 | 1.318 | 25.8 |
| 7 | 1221.902 | 4.075 | 17.7 | 41 | 392.330 | 1.309 | 26.3 |
| 8 | 1220.802 | 4.072 | 14.2 | 42 | 385.179 | 1.285 | 11.5 |
| 9 | 1215.301 | 4.053 | 38.2 | 43 | 383.529 | 1.279 | 12.4 |
| 10 | 1214.201 | 4.050 | 29.1 | | | | |
| 11 | 1208.425 | 4.031 | 20.5 | | | | |
| 12 | 694.893 | 2.318 | 16.3 | | | | |
| 13 | 687.467 | 2.293 | 29.8 | | | | |
| 14 | 679.765 | 2.267 | 20.3 | | | | |
| 15 | 606.050 | 2.021 | 19.9 | | | | |
| 16 | 598.898 | 1.998 | 37.4 | | | | |
| 17 | 591.197 | 1.972 | 28.1 | | | | |
| 18 | 508.955 | 1.698 | 128.7 | | | | |
| 19 | 504.829 | 1.684 | 20.0 | | | | |
| 20 | 497.127 | 1.658 | 14.1 | | | | |
| 21 | 489.150 | 1.631 | 23.6 | | | | |
| 22 | 484.199 | 1.615 | 19.6 | | | | |
| 23 | 481.724 | 1.607 | 20.9 | | | | |
| 24 | 477.598 | 1.593 | 16.4 | | | | |
| 25 | 474.572 | 1.583 | 10.1 | | | | |
| 26 | 438.815 | 1.464 | 10.1 | | | | |
| 27 | 431.664 | 1.440 | 19.4 | | | | |
| 28 | 428.363 | 1.429 | 18.6 | | | | |
| 29 | 426.162 | 1.421 | 18.3 | | | | |
| 30 | 424.512 | 1.416 | 19.3 | | | | |
| 31 | 421.486 | 1.406 | 17.4 | | | | |
| 32 | 417.636 | 1.393 | 11.9 | | | | |
| 33 | 416.260 | 1.388 | 12.3 | | | | |
| 34 | 414.335 | 1.382 | 12.9 | | | | |



**19**

$^{1}$H Spectra




**19**

$^{13}$C Spectra