A Highly Reusable Rhodium Catalyst-Organic Framework for the Intramolecular Cycloisomerization of 1,6-Enynes

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Supporting Information

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I. General Procedures

^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra were recorded using Varian Inova (300, 400, 500 MHz) or Varian Unity (500 MHz) spectrometers. ^{1}H-NMR and ^{13}C-NMR chemical shifts are reported in parts per million (δ) relative to TMS with the solvent as the internal reference. ^{31}P-NMR chemical shifts are reported in parts per million (δ) relative to an external reference of 85% $H_3PO_{4(aq)}$. Selected NMR spectra have been vertically and horizontally enhanced to better show characteristic chemical shifts. Gas chromatography analyses were carried out using a Hewlett-Packard 5890 chromatograph equipped with a flame ionization detector, a 3392A integrator, and a Supelco Beta Dex^{TM} 120 fused silica capillary column (30m x 0.25mm x 0.25μm). Polarimetry data was recorded using a Perkin Elmer 241 Polarimeter and using the sodium D line (589nm) with a cell length of 10.002 cm.

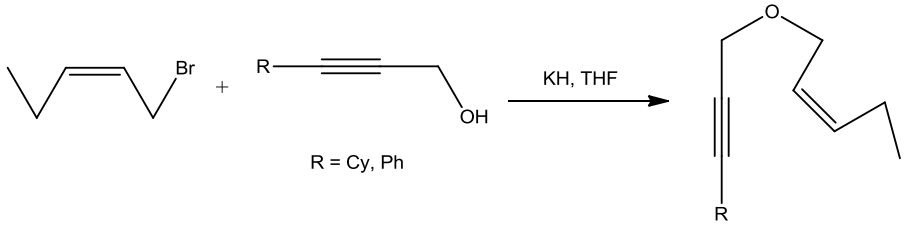
Unless otherwise stated, all experiments were performed under an inert atmosphere using standard Schlenk and glove-box techniques. Argon and nitrogen gas (Praxair, 99.998%) were passed through a drying train containing 3Å molecular sieves and indicating Drierite^{TM} before use. All solvents were dried and distilled under a nitrogen atmosphere using standard drying agents, unless otherwise noted. All common reagents and solvents were obtained from Sigma-Aldrich Co. and used without further purification, unless otherwise stated. The ROMP catalyst bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride and (*R*)-BINAP were obtained from Strem Chemicals, Inc. and used without further purification. $[RhCl(C_2H_4)_2]_2$ was synthesized according to literature procedures[1]. $BaSO_4$ (white reflectance) was obtained from Eastman Chemical Co., Inc. and washed thoroughly with CH_2Cl_2 and MeOH and dried under vacuum prior to use.

[1] Cramer, R., *Inorg. Synth.* **1990**, *28* (Reagents Transition Met. Complex Organomet. Synth.), 86-88.

II. Synthesis of Substrates

General Procedure for Synthesis of Enyne Substrates

Substrates **6** and **7** were synthesized according to a modified literature procedure[2] in which both preparations utilize *cis*-2-penten-1-bromide and the corresponding propynyl alcohol.



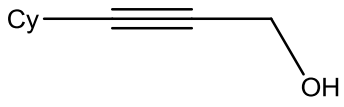
Synthesis of cis-2-penten-1-bromide

In 60 mL of diethyl ether, 5.2 mL of *cis*-2-penten-1-ol (4.643g, 53.4mmol) and 0.5 mL of pyridine are cooled to -40^{o}C. To this mixture, 2.03 mL of phosphorous (III) bromide (5.784g, 21.3mmol) was added via syringe. This mixture was allowed to stir and warm to room temperature slowly over 2 hours, and then maintained at room temperature for an additional hour. The reaction was then quenched by addition of 100 mL of saturated $NaHCO_3$ in distilled water. The aqueous layer was extracted with 3 x 50 mL diethyl ether; the organic layer was then dried over $MgSO_4$ and filtered. The product was isolated as a colorless liquid and then purified by silica gel flash chromatography using 50:1 petroleum ether : diethyl ether as eluent, R_f = 0.4. Yield = 5.973 g (39.8mmol, 75%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm 1.00-1.05 (t, J=7.6Hz, 3H), 2.12-2.22 (quintet, J=7.3Hz, 2H), 4.01 (d, J=8.1Hz, 2H), 5.56-5.72 (m, 2H).

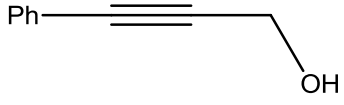
[2] Hashmi, A.S.K.; Haufe, P.; Nass, A.R. *Adv. Synth. Catal.* **2003**, *345*(11), 1237-1241.

Synthesis of propynyl alcohols

Under an inert atmosphere, 38.8 mmol of the desired acetylene (R=Ph,Cy) in 30 mL of THF was cooled to -78^{o}C. To this, 38.8 mmol of 1.6M n-butyllithium in hexanes was added dropwise over 30 minutes. The solution was then warmed to 0^{o}C, 62 mmol of paraformaldehyde was then added as a solid while flushing with N_2, and the solution warmed to room temperature over 1 hour, after which it is heated to 45^{o}C for 90 minutes. This solution is then cooled to room temperature and quenched with 125 mL of 10% NH_4Cl in distilled water. After separation of phases, the aqueous layer was extracted with 3 x 50 mL diethyl ether; the organic layer was then dried over $MgSO_4$ and filtered. The product was isolated as a yellow oil and was purified by silica gel flash chromatography using 60:40 CH_2Cl_2 : hexanes as eluent. The spectroscopic data was in accordance with the literature[2].



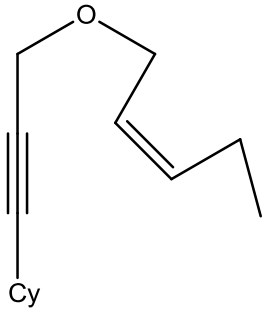
Yield = 4.962 g (35.9mmol, 93%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm 1.26-1.66 (m, 7H), 1.69-1.81 (m, 2H), 1.81-1.93 (m, 2H), 2.38-2.52 (m, 1H), 4.33 (d, J=1.8Hz, 2H).



Yield = 4.611 g (34.9mmol, 90%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm 4.53 (s, 2H), 7.27-7.36 (m, 3H), 7.40-7.43 (m, 2H).

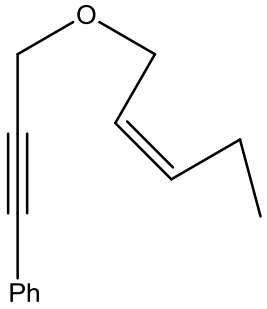
Synthesis of 1,6-enyne substrates (6, 7)

In a typical experiment, a 200 mL round-bottom flask equipped with stir bar was charged with 1.301 g of a 30 wt% dispersion of KH in mineral oil (0.390g, 9.7mmol). The flask was then evacuated and backfilled 3 times with nitrogen gas. The KH was then rinsed with 4 x 5 mL THF to quantitatively remove the mineral oil. To the KH, another 20 mL of THF was added, and the mixture cooled to 0^{o}C. Next, 1.002 g (6.7mmol) of *cis*-2-penten-1-bromide was added by cannulation under an inert atmosphere, followed by 2 x 5 mL THF rinses. This was followed by addition of 6.1mmol of the propynyl alcohol via cannulation under an inert atmosphere, followed by 2 x 5 mL THF rinses. Upon addition of the alcohol, H_2 gas evolves, and the reaction mixture goes to a bright orange color. The reaction was allowed to warm up to room temperature, and then stirred for 3 hours, after which the reaction was quenched with 50 mL distilled water. The aqueous phase was then extracted with 3 x 50 mL of diethyl ether; the organic layer was then dried over $MgSO_4$ and filtered. The product was isolated as a yellow oil and was purified by silica gel flash chromatography using 50:1 petroleum ether : diethyl ether as eluent.



Yield = 0.852 g (4.1mmol, 68%), R_f = 0.3. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 0.91 (t, J=7.6Hz, 3H), 1.15-1.29 (m, 3H), 1.29-1.48 (m, 3H), 1.57-1.66 (m, 2H), 1.67-1.76 (m, 2H), 2.03 (pd, J=1.2, 7.4Hz, 2H), 2.28-2.37 (m, 1H), 4.00-4.03 (m, 2H), 4.03 (d, J=2.2Hz, 2H), 5.35-

5.57 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm 14.05, 20.76, 24.70, 25.80, 28.99, 32.52, 57.19, 64.28, 75.82, 90.60, 124.80, 135.74; anal. calcd. for $C_{14}H_{22}O$ (206.32): C 81.50, H 10.75; found C 81.51, H 10.68.



Yield = 0.610 g (3.0mmol, 49%), R_f = 0.2. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 1.07 (t, J=7.5Hz, 3H), 2.14-2.28 (m, 2H), 4.25 (d, J=6.6Hz, 2H), 4.43 (s, 2H), 5.56-5.64 (m, 1H), 5.68-5.76 (m, 1H), 7.30-7.42 (m, 3H), 7.47-7.56 (m, 2H); anal. calcd. for $C_{14}H_{16}O$ (200.28): C 83.96, H 7.99; found: C 83.60, H 8.36. The spectroscopic data was in accordance with the literature[2].

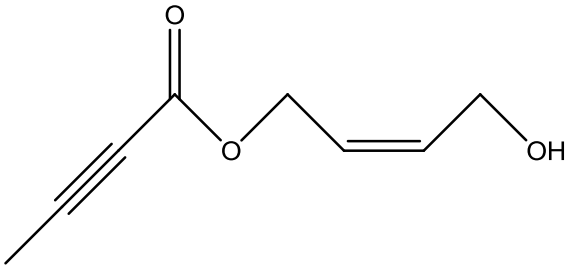
Synthesis of Ester Substrate

Substrate **8** was synthesized according to the following modified literature procedure outlined by Zhang *et al.*[3].

A 200mL round-bottom flask equipped with a stir bar was charged with 16 mmol (1.35 g) of 2-butynoic acid and 0.16 mmol (19.6 mg) of 4-dimethylaminopyridine (DMAP). The flask was then evacuated and backfilled 3 times with nitrogen gas. These were then dissolved in 32mL of dry CH_2Cl_2 resulting in the formation of a yellow solution. Next, 16 mmol (1.41 g, 1.31 mL) of (*Z*)-2-buten-1,4-diol was added to the flask and the solution was then cooled to

[3] Lei, A.; He, M.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 8198.
[4] Ralph, C.K.; Bergens, S.H. *Organometallics* **2007**, *26*, 1571-1574.

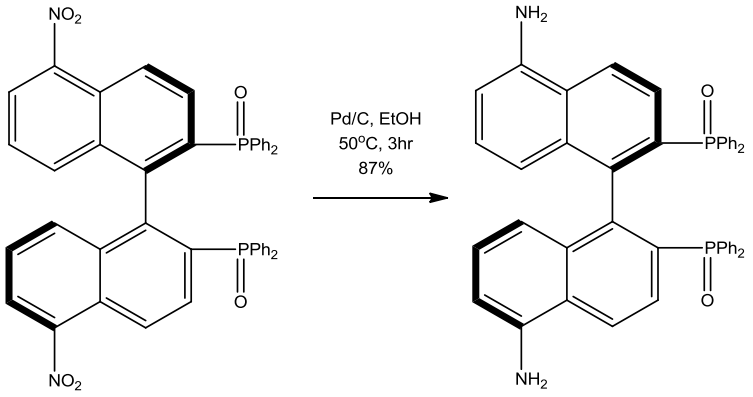
0^oC. Finally, 17.6 mmol (3.64 g) of 1,3-dicyclohexylcarbodiimide (DCC) dissolved in 16mL of CH_2Cl_2 was added dropwise to the flask at 0^oC over a period of 2 hours. Upon addition of DCC, solid 1,3-dicyclohexylurea (DCU) is produced. After 2 hours, the product solution was filtered and the product concentrated via rotary evaporation to give a yellow oil. The crude product was a 50:50 mixture of the desired mono-ester compound and the undesired di-ester compound. The product was further purified by silica gel flash chromatography using 100% CH_2Cl_2 as eluent, $R_f = 0.1$.



Yield = 1.157g (7.5mmol, 47%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm 1.98 (s, 3H), 4.26 (t, J=4.5Hz, 2H), 4.75 (d, J=5.1Hz, 2H), 5.68-5.61 (m, 1H), 5.91-5.85 (m, 1H). The spectroscopic data was identical to that in the literature[3].

III. Synthesis of (*R*)- 5,5'-dinorimido-BINAP (2)

This was prepared as reported previously[4], except for the reduction of *(R)*-5,5'-dinitro-BINAP dioxide to (*R*)-5,5'-diamino-BINAP dioxide, which is reported here. In addition, to obtain rotamerically pure (*R*)-5,5'-dinorimido BINAP (**2**), the ligand was stirred at 90^oC in toluene for 3 days during which one rotamer precipitated out of solution.



Synthesis of (R)-5,5'-diamino-BINAP dioxide

A glass autoclave equipped with a ½" stir bar was charged with 0.912 g of (*R*)-5,5'-dinitro-BINAP dioxide (1.22mmol) along with 0.1368 g of 5 wt% palladium on carbon (6.43×10^{-5}mol of Pd). The autoclave was purged with H_2(g) for 20 minutes, then charged with 15 mL of anhydrous ethanol (degassed with H_2(g) for 20 minutes). The vessel was sealed, pressurized to 45 psi, and lowered into a 50°C oil bath with moderate stirring for 3 hours. Aliquots taken at 3 hours indicated that the reaction was complete by ^{1}H-NMR and ^{31}P-NMR. The reaction mixture was filtered to remove the Pd/C. The filtrate was concentrated under reduced pressure and was purified by flash chromatography (neutral alumina) using 93:7 CH_2Cl_2 : ethanol as eluent, R_f = 0.75. Yield = 0.726 g (1.06mmol, 87%). The spectroscopic data was in accordance with the literature[4]. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 4.12 (br s, 4H), 6.28-6.30 (m, 2H), 6.59-6.64 (m, 4H), 7.21-7.27 (m, 9H), 7.34-7.46 (m, 9H), 7.67-7.72 (m, 4H), 7.81 (d, J=8.2Hz, 2H); ^{31}P-NMR (162 MHz, $CDCl_3$) δ ppm 29.95 (s, 1P).

IV. Synthesis of $BaSO_4$ Supported Rhodium Catalyst

Synthesis of [RhCl((R)-5,5'-dinorimido-BINAP)]$_2$ (4)

Under a nitrogen atmosphere, a solution of 32.2 mg (3.40 x 10^{-5}mol) of rotamerically pure (*R*)-5,5'-dinorimido-BINAP (**2**) in 0.5 mL of CD_2Cl_2 was added to a slurry of 7.0 mg (1.82 x 10^{-5}mol) $[RhCl(C_2H_4)_2]_2$ in 0.1 mL of CD_2Cl_2 in an NMR tube. The NMR tube was shaken, and occasionally purged with nitrogen gas for 30 minutes, before ^{1}H-NMR and ^{31}P-NMR spectra were obtained. Upon addition of the ligand solution to the $[RhCl(C_2H_4)_2]_2$ slurry, there was a rapid color change from yellow-orange to brick red, with accompanying evolution of ethylene gas. After identification of **4** by NMR, the compound was used immediately and without isolation as attempts at isolation resulted in decomposition of the product. The spectroscopic data was in accordance with the literature spectrum of $[RhCl(BINAP)]_2$[5]. ^{1}H-NMR (400 MHz, CD_2Cl_2) δ ppm 1.67 (d, J=8.4Hz, 2H), 1.81 (d, J=8.4Hz, 2H), 3.48-3.53 (m, 4H), 3.56-3.60 (m, 4H), 6.28 (dd, J=2.0Hz, 2H), 6.38 (dd, J=2.0Hz, 2H), 6.47 (d, J=4.8Hz, 2H), 6.57 (d, J=4.8Hz, 2H), 6.60-6.76 (m, 4H), 6.81-6.90 (m, 2H), 6.92 (d, J=7.2Hz, 2H), 7.05 (m, 2H), 7.22 (t, J=8.6Hz, 2H), 7.41 (m, 6H), 7.73 (br s, 4H), 7.98 (br s, 4H); ^{31}P-NMR (161 MHz, CD_2Cl_2) δ ppm 50.77 (d, J=194.1Hz, 2P).

Preparation of Catalyst-Organic Framework (5)

In a typical experiment, 36.9 mg (1.70 x 10^{-5} mol) of $[RhCl((R)$-5,5'-dinorimido-BINAP$)]_2$ (**4**) was prepared in 0.6 mL of CD_2Cl_2 in an NMR tube as described above. Under a nitrogen atmosphere 26.6 µL of COE (2.04 x 10^{-4} mol) is added to the solution and the tube was shaken. The color of the solution remains brick red. This solution is then cannulated, under a nitrogen

[5] Tokunaga, N.; Yoshida, K.; Hayashi, T. *Proceedings of the National Academy of Sciences of the United States of America* **2004**, *101*(15), 5445-5449.

atmosphere, into a Schlenk tube equipped with a stir bar and rinsed in with 1.0 mL of CH_2Cl_2. Next, 1.5 mg (1.82 x 10^{-6} mol) of *trans*-$RuCl_2(PCy_3)_2$(=CHPh) (**3**, Grubbs' 1st Generation) is dissolved in 1.1 mL of CH_2Cl_2, yielding a purple solution. This solution is then cannulated, under a nitrogen atmosphere, into the Schlenk tube. The vessel is then sealed and placed, with moderate stirring, into an oil bath at 40°C for 24 hours. This mixture is then diluted with 10 mL more of CH_2Cl_2.

Deposition of Catalyst-Organic Framework 5 onto $BaSO_4$

10 g of $BaSO_4$ was washed consecutively with 4 x 50 mL of CH_2Cl_2 followed by 3 x 50 mL MeOH, and then dried under vacuum at room temperature overnight.

3.014 g (1.29 x 10^{-2} mol) of the washed and dried $BaSO_4$ in a 250 mL round-bottom flask equipped with a stir bar was back-filled with nitrogen gas. To this flask was added 20 mL of CH_2Cl_2 and with slow stirring to create a slurry. The reaction mixture that contains the catalyst-organic framework **5** prepared above was cannulated onto the $BaSO_4/CH_2Cl_2$ slurry, creating a tan-colored mixture. The polymer reaction vessel is rinsed with 3 x 5 mL CH_2Cl_2 that were added to the slurry and the slurry was stirred for 20 minutes to achieve an even distribution of the catalyst-organic framework on the $BaSO_4$. The solvent was then removed slowly under reduced pressure (1 hour) with rapid stirring at room temperature. After the removal of the solvent to dryness, the flask was dried further under vacuum for 1 hour. After the initial drying, the supported catalyst is rinsed with 3 x 50 mL of MeOH to remove any polymerized COE and low molecular weight polymer. The MeOH portions were decanted off the support with a cannula under N_2. Filtration was avoided to prevent plugging of the filter. After the final rinse, the catalyst was dried for 1 hour under vacuum, then immediately transferred to the glove box,

where it was stored in the freezer. NMR spectra recorded in CD_2Cl_2 of the pumped down MeOH residue showed only poly(COE) present. There was also no observable signal in the ^{31}P-NMR spectrum.

Analysis of the Alternating ROMP Assembly of the Catalyst-Organic Framework 5

^{1}H-NMR spectra were recorded over time during a polymerization at room temperature (Figure 1). From *in situ* peak-height comparison of alkene signals, a general rate of reaction was determined. After ~3 hours of reaction time, the ratio of COE to norimido consumed is ~1.7. After ~7 hours of reaction time, the ratio was still ~1.7. After ~24 hours, all of the norimido units and 80% of the COE had been consumed, corresponding to a ratio of COE to norimido consumed of ~2.4 at the end of polymerization.

After the majority of the norimido units had been consumed, a peak at δ=5.4ppm began to grow in more and more quickly. This peak has the same shape and chemical shift as poly(COE) made by ROMP[6]. We propose that once all the norimido groups are consumed, then the remaining COE undergoes ROMP. We therefore postulate that the ratio of COE to norimido groups within the framework is ~1.7:1, and that some portion of the remaining COE is grafted to the outside of the framework as poly(COE).

[6] Simon, C.Y.; Coughlin, E.B. *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, *48*, 2557-2563.

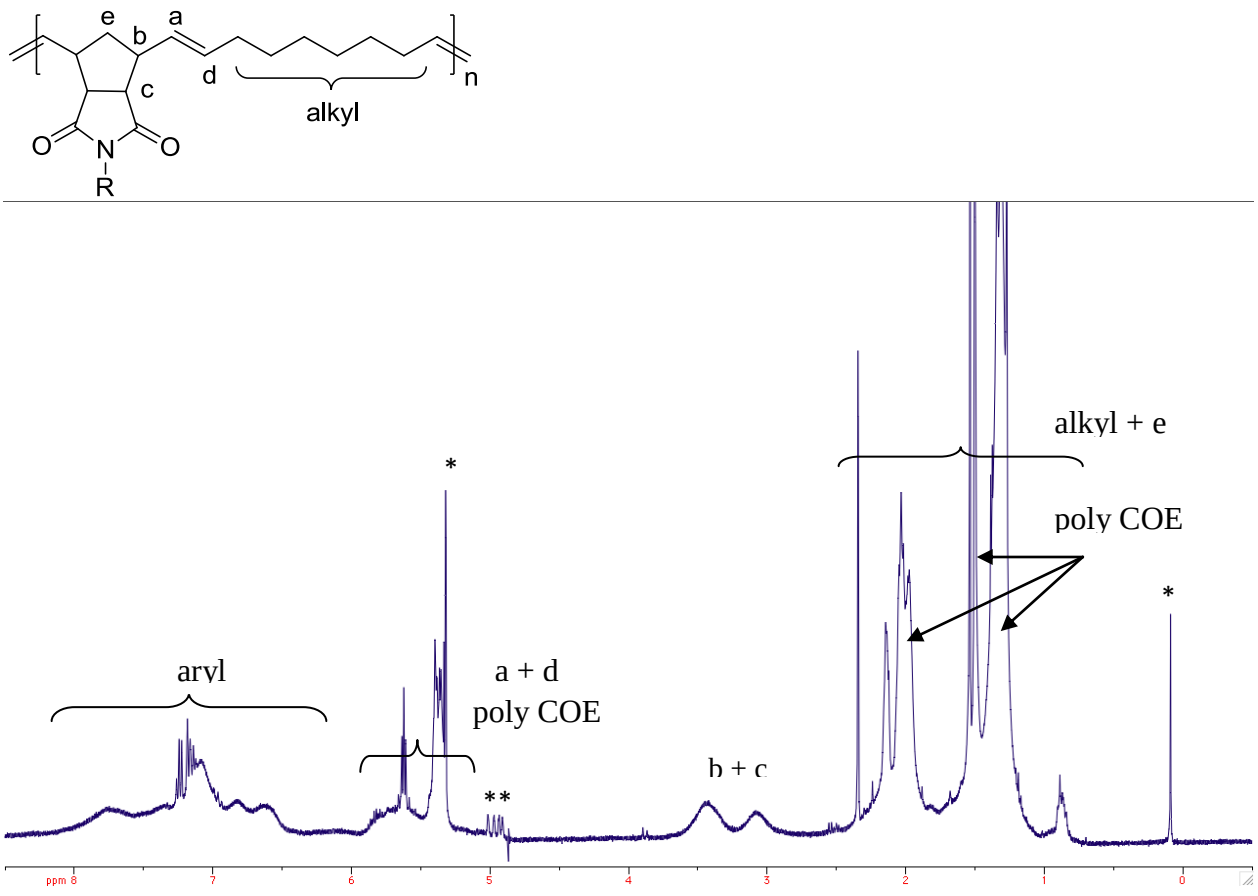


Figure 1. ^{1}H-NMR spectra during alternating-ROMP of [RhCl((*R*)-5,5'-dinorimido-BINAP)]$_2$ (**4**) and COE with Grubbs' 1st generation catalyst (**3**) at 24hr. (400MHz, CD_2Cl_2, 27.0^{o}C) R = BINAP-RhCl dimer. * = Residual CH_2Cl_2 solvent and TMS signal. ** = Product of ROMP between COE and residual ethylene from the synthesis of [RhCl((*R*)-5,5'-dinorimido-BINAP)]$_2$ (**4**). Control experiments with COE, ethylene and Grubbs' 1st generation catalyst (**3**) confirmed this product. NMR analysis of the washings showed that this undesired side-product is removed from the product catalyst-organic framework **5** via the MeOH washings.

V. Representative Procedures for Enantioselective Rhodium-Catalyzed Intramolecular Cycloisomerization of 1,6-Enynes

All substrates and solvents were bubbled for 30 minutes under argon or nitrogen gas prior to use.

Low-Loading Cycloisomerizations of 1,6-Enynes with Reuse

In a typical experiment, a Schlenk flask equipped with a Teflon™ valve was charged with 0.4736 g of supported catalyst (**5**/$BaSO_4$) (5.66 mg of "[RhCl((*R*)-5,5'-dinorimido-BINAP)]$_2$", 2.61 x 10^{-3} mmol) under an inert atmosphere. A NMR tube was charged with 1.05 x 10^{-2} mmol of $AgSbF_6$ under N_2 in the dark and sealed using a rubber septum. 0.105 mmol of substrate was then added into the flask containing the catalyst, rinsed in with 0.5 mL of 1,4-dioxanes and stirred for 1 minute. Next, 0.1 mL of 1,4-dioxanes was added to the $AgSbF_6$, which was then cannulated onto the substrate/catalyst mixture, along with 5 x 0.1 mL rinses of 1,4-dioxanes. The Schlenk flask was then sealed with the Teflon™ valve and then placed into an oil bath set at 60°C. After 3 hours, an aliquot was taken via inverse filtration under an inert atmosphere, and analyzed by ^{1}H-NMR. Upon confirmation that the initial batch reaction was complete, the Schlenk flask was charged with 5 mL of 1,4-dioxanes and stirred for 5 minutes. The solvent and cyclized product was then removed by inverse filtration, and the catalyst was again treated with another 5 mL of 1,4-dioxanes. As soon as the 2 x 5 mL rinses of 1,4-dioxanes were collected, the Schlenk flask containing the catalyst was charged with 0.525 mmol of substrate and 2.61 mL of 1,4-dioxanes. The flask was then sealed and again immersed in an oil bath. The temperature of the oil bath was modified depending on the amount of conversion obtained. All further reuses were carried out in this manner.

High-Loading Cycloisomerizations of 1,6-Enynes

For these experiments, the supported catalyst-organic framework (**5**/$BaSO_4$) and the $AgSbF_6$ were weighed into the same flask.

In a typical experiment, under nitrogen or argon atmosphere, a Schlenk flask equipped with a Teflon™ valve was charged with 0.1011 g of supported catalyst (**5**/$BaSO_4$) (1.24 mg of "$[RhCl((R)\text{-}5,5'\text{-dinorimido-BINAP})]_2$", 5.74×10^{-4} mmol) and 5.74×10^{-3} mmol of $AgSbF_6$. Next, 0.575 mmol of substrate in 0.6 mL of 2-MeTHF was cannulated onto the catalyst/silver mixture and the Schlenk flask was sealed with the Teflon™ valve. The Schlenk flask was then placed in an oil bath set at 70°C. After 2 hours, an aliquot was taken via inverse filtration and the extent of reaction determined by ^{1}H-NMR.

Homogeneous Cycloisomerizations of 6 in Dioxane and DCE

6.3 mg of $[RhCl(BINAP)]_2$ (3.99×10^{-3} mmol) and 5.5 mg of $AgSbF_6$ (1.59×10^{-2} mmol) were weighed out in a glove box into separate NMR tubes and sealed with rubber septa. The catalyst was then dissolved in 0.6mL of 1,4-dioxane and transferred to a Schlenk flask equipped with a Teflon™ valve, followed by 2 x 0.2mL rinses of 1,4-dioxane. Next, the $AgSbF_6$ was rinsed into the Schlenk flask with 0.2mL of 1,4-dioxane, followed by a further 2 x 0.2mL of 1,4-dioxane. Lastly, 32.9 mg of cyclohexyl substrate **6** (0.159 mmol) was added to the Schlenk flask. The flask was then sealed and stirred in an oil bath set at 40°C. After 2 hours, an aliquot was taken and ^{1}H-NMR showed that 100% conversion had been achieved and a mixture of cycloisomerization products had been obtained, probably due to olefin isomerization.

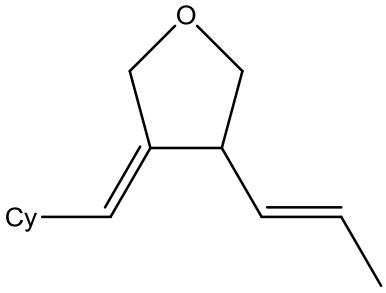
3.7 mg of $[RhCl(COD)]_2$ (7.5×10^{-3}mmol), 10.3 mg of $AgSbF_6$ (3.0×10^{-2} mmol) and 9.4 mg of (*R*)-BINAP (1.5×10^{-2} mmol) were weighed in a glove box into separate NMR tubes and

sealed with rubber septa. The (*R*)-BINAP was dissolved in 0.5mL of DCE and cannulated onto the $[RhCl(COD)]_2$ followed by a 0.1mL rinse of DCE. This was followed by addition of 31 mg of cyclohexyl substrate **6** (0.150 mmol) to the catalyst/ligand solution. Next, the $AgSbF_6$ was dissolved in 0.4mL of DCE and this was cannulated into the NMR tube containing the substrate, ligand and catalyst. The solution turned from a dark red color to an orange/brown color immediately and a solid (AgCl) was visible in the NMR tube. The NMR tube was then shaken for 5 minutes at room temperature and then run immediately through a Fluorosil™ plug to remove any metal residues. ^{1}H-NMR showed 100% conversion and that a complex mixture of products was obtained.

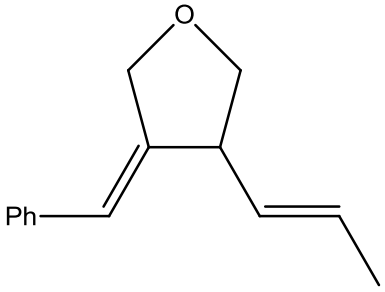
Optimized Cycloisomerizations of Ester Substrate

In these optimized experiments it was found that swelling the catalyst-organic framework in the presence of $AgSbF_6$ for 30 minutes at 40^{o}C maximized the initial rate and yields obtained from the catalyst.

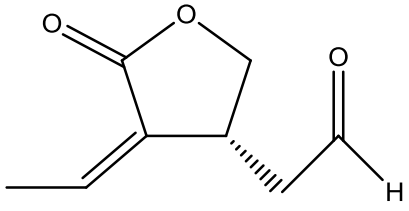
A Schlenk flask equipped with a Teflon™ valve was charged with 0.1090 g of supported catalyst (**5**/$BaSO_4$) (1.33 mg of "$[RhCl((R)$-5,5'-dinorimido-BINAP$]_2$", 6.16 x 10^{-4} mmol) and 6.16 x 10^{-3} mmol of $AgSbF_6$. The Schlenk flask was then removed from the glove box and covered in tinfoil. Next, 0.4 mL of 1,4-dioxanes is added to the Schlenk flask and stirred at 40^{o}C for 30 minutes. 0.123 mmol of ester substrate **8** in 0.2 mL of 1,4-dioxanes was cannulated onto the catalyst/silver mixture followed by a 0.3 mL rinse of 1,4-dioxanes. The Schlenk flask was then sealed with the Teflon™ valve and placed in an oil bath set at 70^{o}C. Conversion was monitored by ^{1}H-NMR of aliquots.



^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm 1.00-1.30 (m, 6H), 1.54-1.59 (br m, 3H), 1.67-1.74 (br m, 1H), 1.71 (dd, J=1.6, 6.6Hz, 3H), 1.88 (m, 1H), 3.19 (q, J=6Hz, 1H), 3.40 (t, J=6.4Hz, 1H), 4.00 (t, J=6Hz, 1H), 4.30 (dt, J=1.7, 10Hz, 1H), 4.40 (d, J=9.6Hz, 1H), 5.01-5.06 (m, 1H), 5.17-5.25 (m, 1H), 5.45-5.58 (m, 1H); ^{13}C APT NMR see spectral data section; MS (EI) m/z: [M^+] 206; >95% *ee*.



^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm 1.76 (dd, J=1.5, 6.9Hz, 3H), 3.38-3.50 (m, 2H), 4.06-4.12 (m, 1H), 4.60 (dt, J=2.2, 14.1Hz, 1H), 4.74 (dd, J=2.1, 14.1Hz, 1H), 5.29-5.40 (m, 1H), 5.60-5.71 (m, 1H), 6.25 (q, J=2.3Hz, 1H), 7.12-7.17 (m, 2H), 7.18-7.24 (m, 1H), 7.29-7.37 (m, 2H); The spectroscopic data was identical to the literature[2]; MS (EI) m/z: [M^+] 200; >99% *ee*.

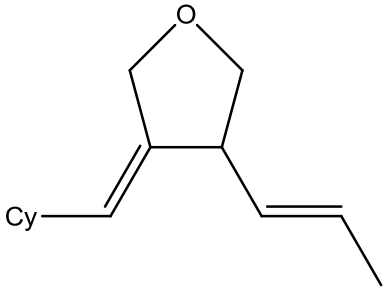


^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm 2.21 (dd, J=1.8, 7.2Hz, 3H), 2.72 (dd, J=8.5, 18.8Hz, 1H), 2.88 (dd, J=5.1, 18.9Hz, 1H), 3.43-3.57 (br m, 1H), 3.84 (dd, J=5.4, 9.3Hz, 1H), 4.55 (t, 8.7Hz, 1H), 6.29 (dq, J=1.9, 7.5Hz, 1H), 9.82 (s, 1H); The spectroscopic data was identical to the literature[3]; MS (EI) m/z: [M^+] 154; >99% *ee*.

VI. Determination of Enantiomeric Excess

Synthesis of Racemic Products

6.8 mg of $[Rh(NBD)_2](SbF_6)$[7] (1.3×10^{-2}mmol) dissolved in 1 mL of DCE and 1.3×10^{-1}mmol of substrate in 0.3 mL of DCE were both cannulated into a Schlenk flask, followed by 2 x 0.4 mL rinses of DCE. The Schlenk tube was then placed in an oil bath at 65°C. Within 5 minutes the reaction solution went from red to brown in color. After 1.5 hours, 100% conversion to the racemic product was achieved.



12.6 mg of racemic cyclohexyl product (6.11×10^{-2} mmol) was dissolved in 0.6 mL of benzene-d^6 in an NMR tube. A solution of 22.1 mg of europium-tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] (1.85×10^{-2} mmol) in benzene-d^6 was also prepared. The europium solution was added in 10µL increments until the signal originally at 3.41 ppm had shifted to ~6.5 ppm, where the peak was cleanly resolved into two signals in a

[7] Synthesized via a modified literature procedure: Green, M.; Kuc, T.A.; Taylor, S. *Chem. Commun.* **1970**, 1553.

1:1 ratio (Figure 2). Only one signal, that at δ=6.4ppm, was observed when the experiment was repeated with cyclohexyl product from the catalyst-organic framework catalyzed cycloisomerization (Figure 3). From the spectra obtained, it was determined that the *ee* was >95%.

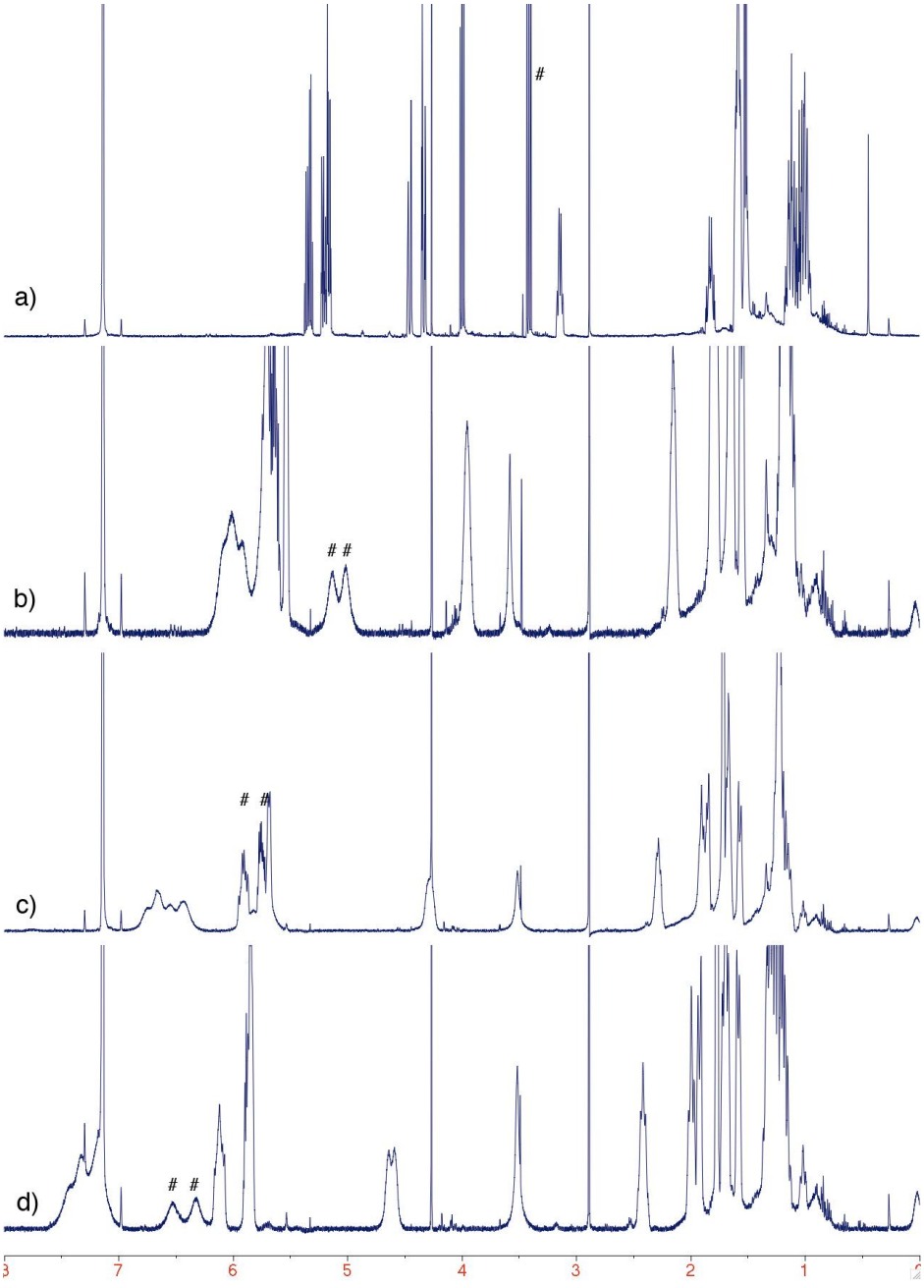


Figure 2. Effects of addition of Europium tris[3-heptafluoropropylhydroxymethylene)-(+)-camphorate] in the ^{1}H-NMR spectra of the racemic (*Z*)-3-(cyclohexylmethylene)-4-((*E*)-prop-1-enyl)tetrahydrofuran (500 MHz, C_6D_6, 27^{o}C). (a) 0 mol %; (b) 4 mol %; (c) 6 mol %; (d) 8 mol %.

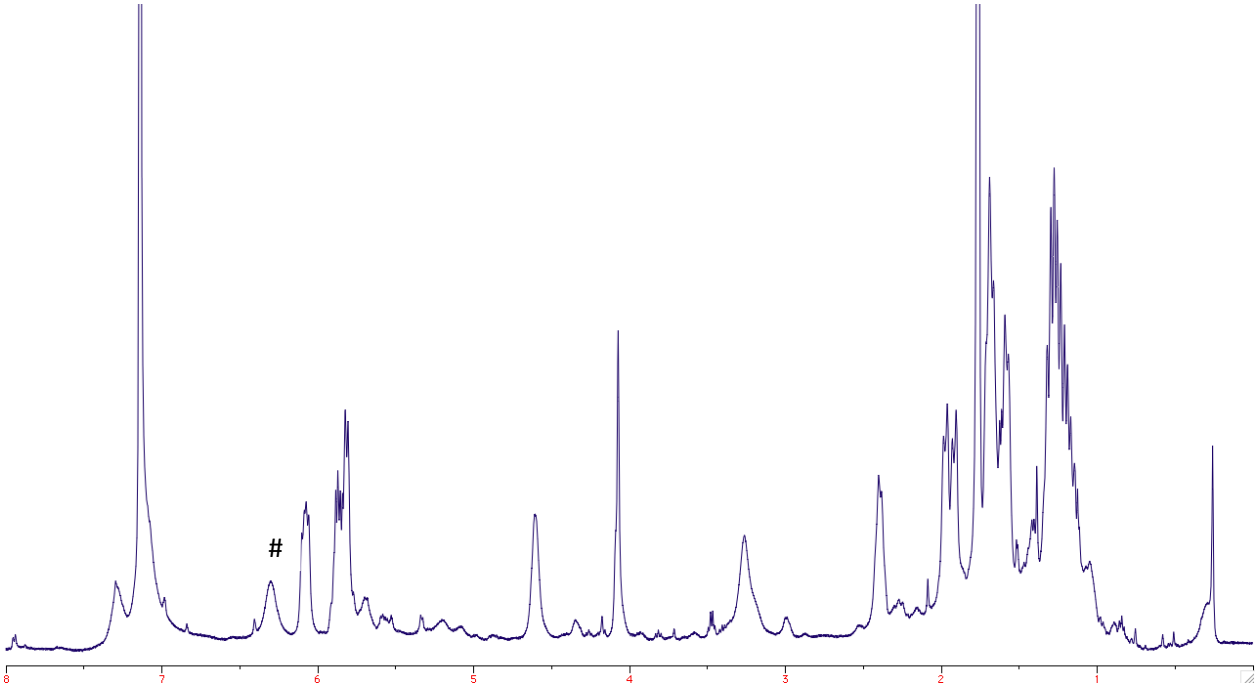
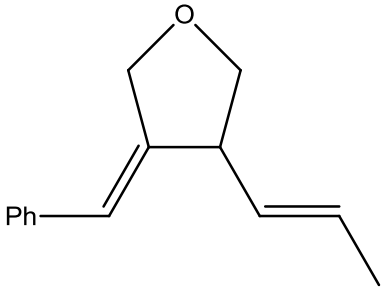
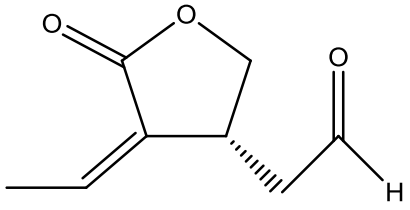


Figure 3. ^{1}H-NMR spectrum (500 MHz, C_6D_6, 27^{o}C) of the product, (*Z*)-3-(cyclohexylmethylene)-4-((*E*)-prop-1-enyl)tetrahydrofuran, from the reuse of the catalyst-organic framework **5** in the cycloisomerization of **6**, reacted with 8 mol % of the chiral NMR shift reagent Europium tris[3-heptafluoropropylhydroxymethylene)-(+)-camphorate].

The shifted peak (indicated by the #) is the only detectable enantiomer, thereby indicating an *ee* >95%. Absolute configuration was not determined.



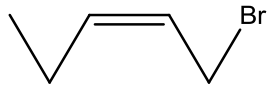
The *ee* of phenyl cyclized product was determined with chiral gas chromatography and confirmed with the racemic product. The cyclization poduct was passed through a Fluorosil™ plug using CH_2Cl_2 as eluent. The eluted compound was concentrated under reduced pressure, and a solution was prepared in CH_2Cl_2 at a concentration of 2 mg per 1 mL. Next, 1 µL was injected into the GC under the following conditions: helium carrier gas (20 psig); initial temperature of 100°C, rate of 0.4°C/min up to 220°C; injector temperature of 220°C; detector temperature of 220°C. Retention time for the racemic product: 122.6 minutes for enantiomer 1 and 123.4 minutes for enantiomer 2. From the chromatograms, it was determined that *ee* >99%. Absolute configuration was not determined.



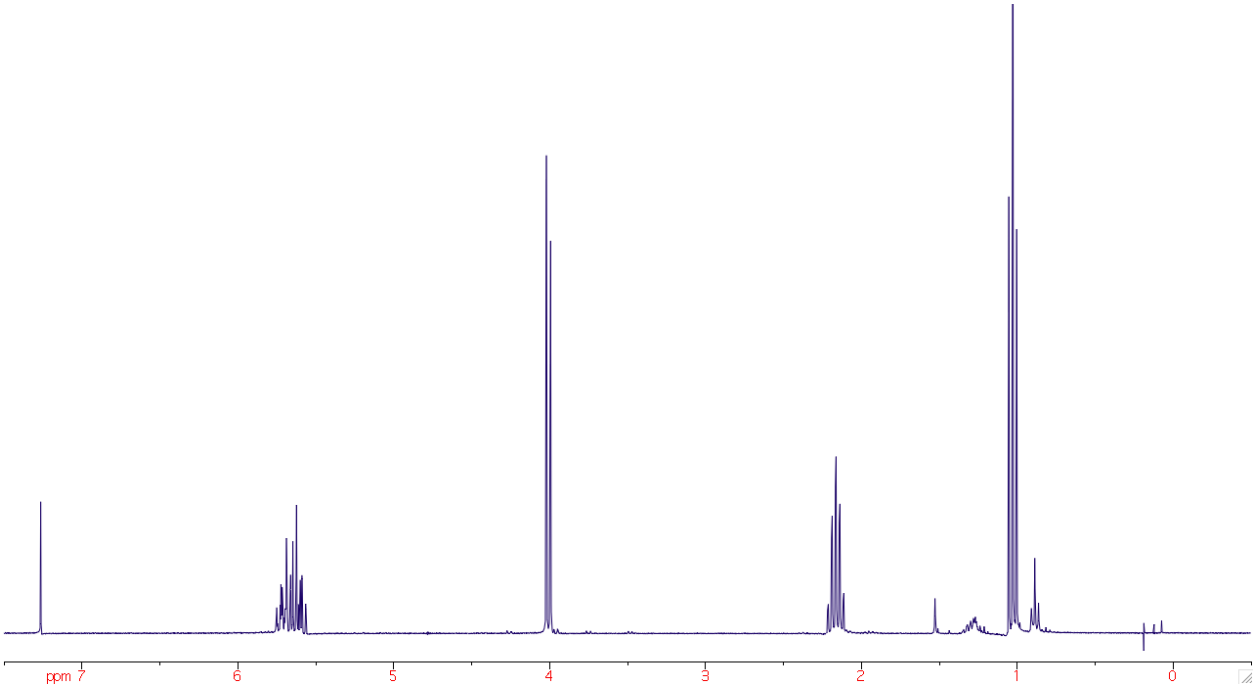
[α] = +51.79, c=0.2, CH_2Cl_2; From Zhang *et al.*[3] for the (*R*) enantiomer, [α] = +92.400, c=1, CH_3Cl.

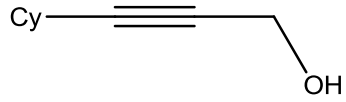
The *ee* of **9** was determined with chiral gas chromatography including comparison to the racemic product. Sample preparation was the same as mentioned above. 1µL of the solution was injected into the GC under the following conditions: helium carrier gas (20 psig; temperature of 140°C; injector temperature of 220°C; detector temperature of 220°C. Retention time for the racemic product: 37.057 minutes for enantiomer 1 and 38.840 minutes for enantiomer 2. From the chromatograms it was determined that *ee* >99%.

VII. Spectral Data

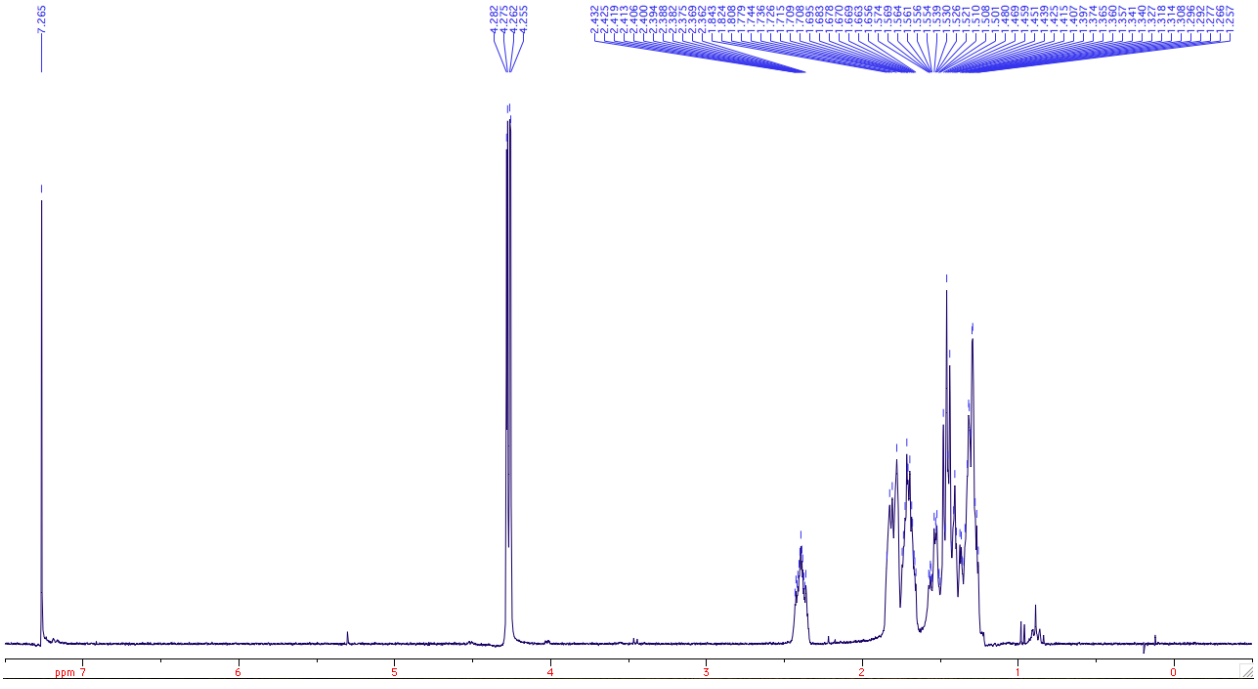


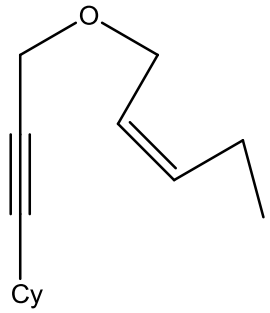
^{1}H NMR spectrum (300MHz, $CDCl_3$)



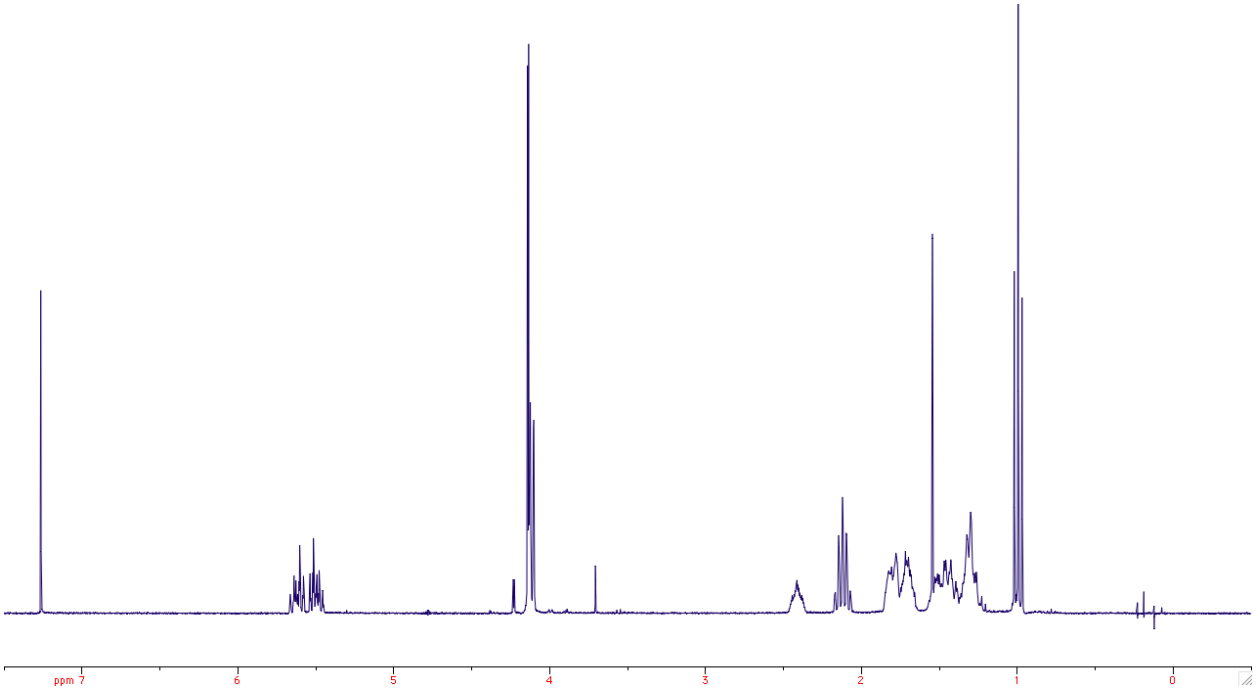


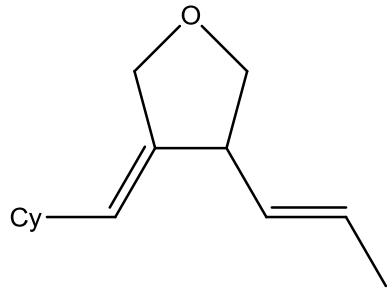
^{1}H-NMR Spectrum (300MHz, $CDCl_3$)



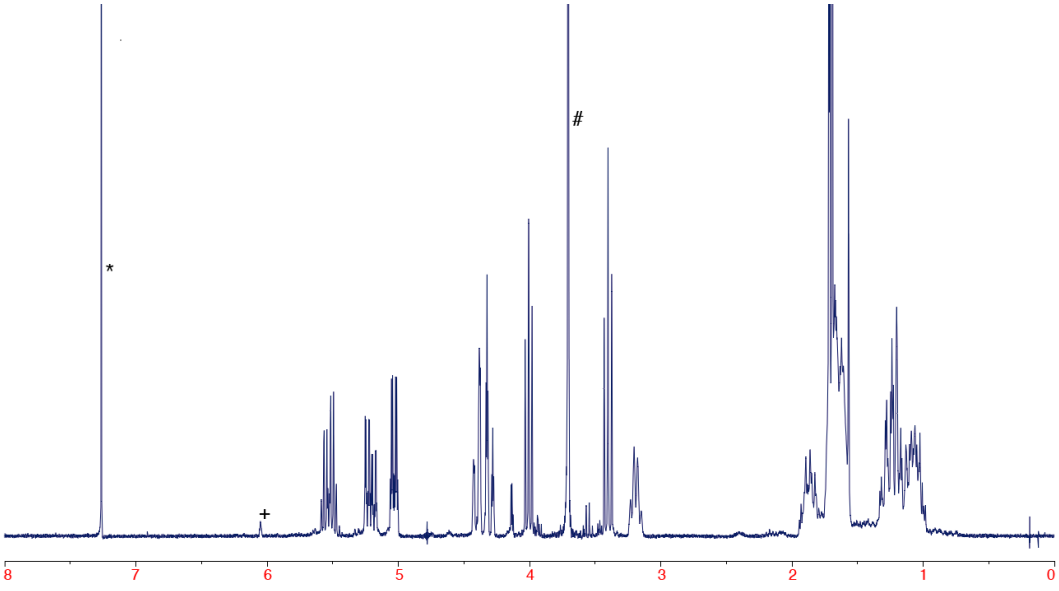


^{1}H-NMR Spectrum of **6** (400MHz, $CDCl_3$)

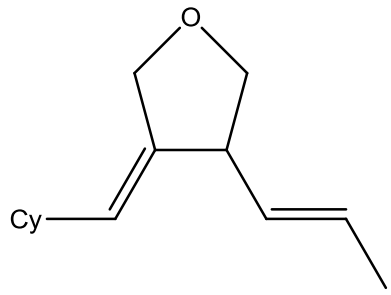




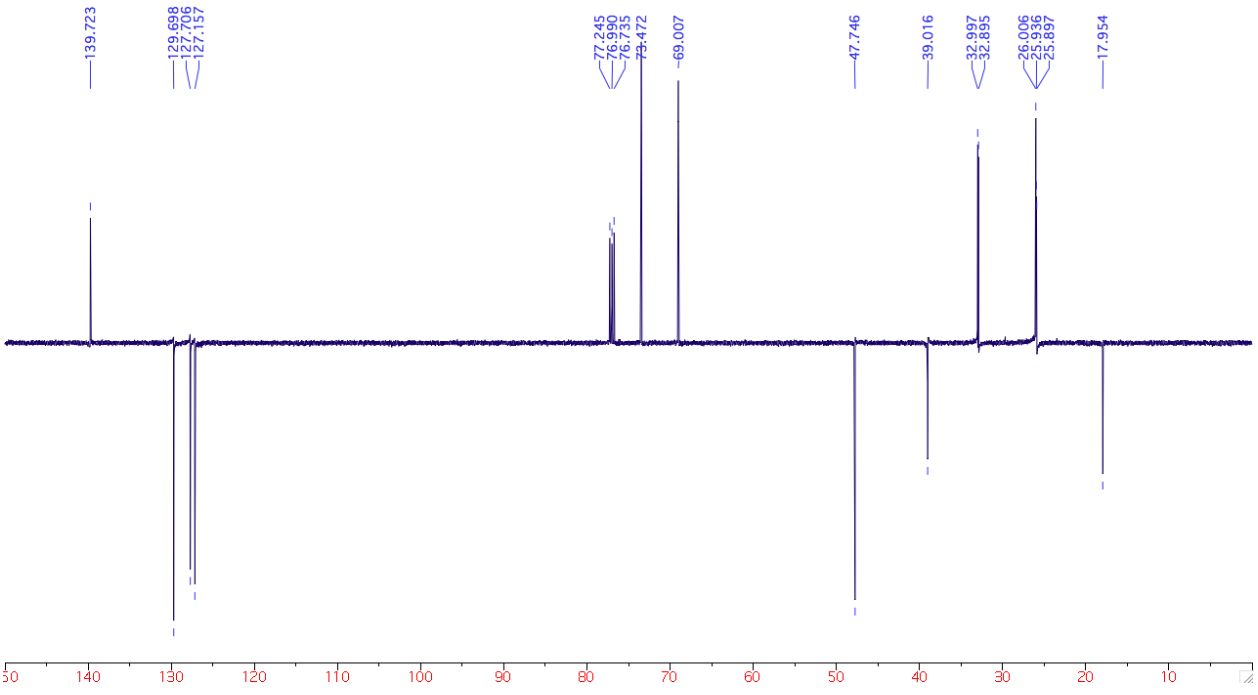
^{1}H-NMR Spectrum (300 MHz, $CDCl_3$)



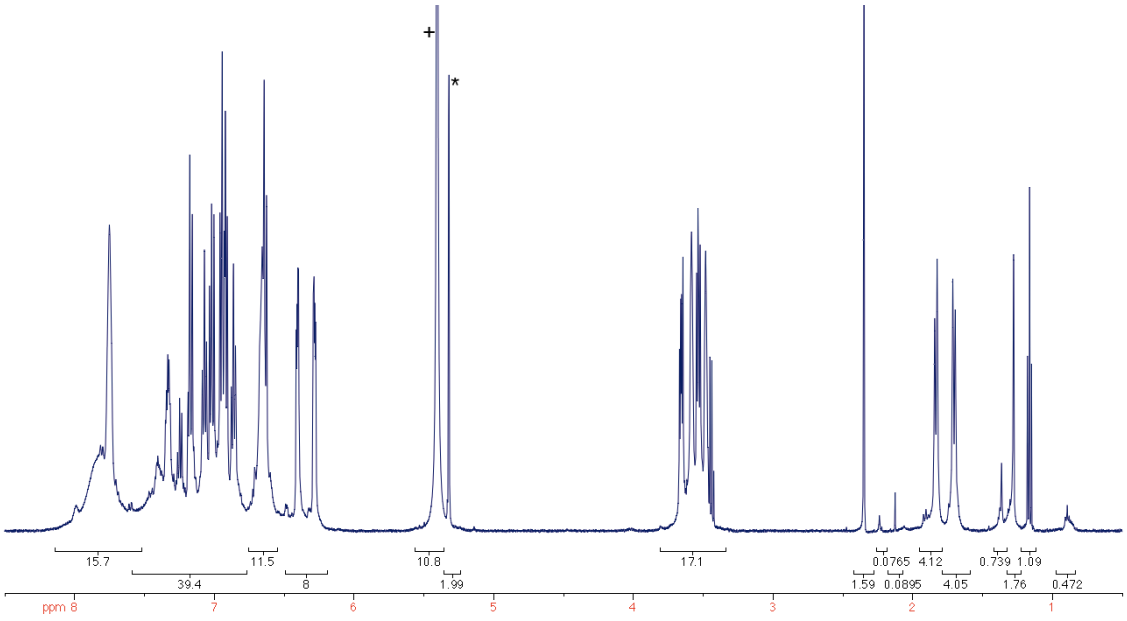
The peak indicated by * is the residual $CDCl_3$ signal. The peak indicated by + is attributed to a side-product, likely a result of olefin isomerization. The peak indicated by # is the residual 1,4-dioxane solvent peak.



^{13}C-NMR APT Spectrum (101MHz, $CDCl_3$)

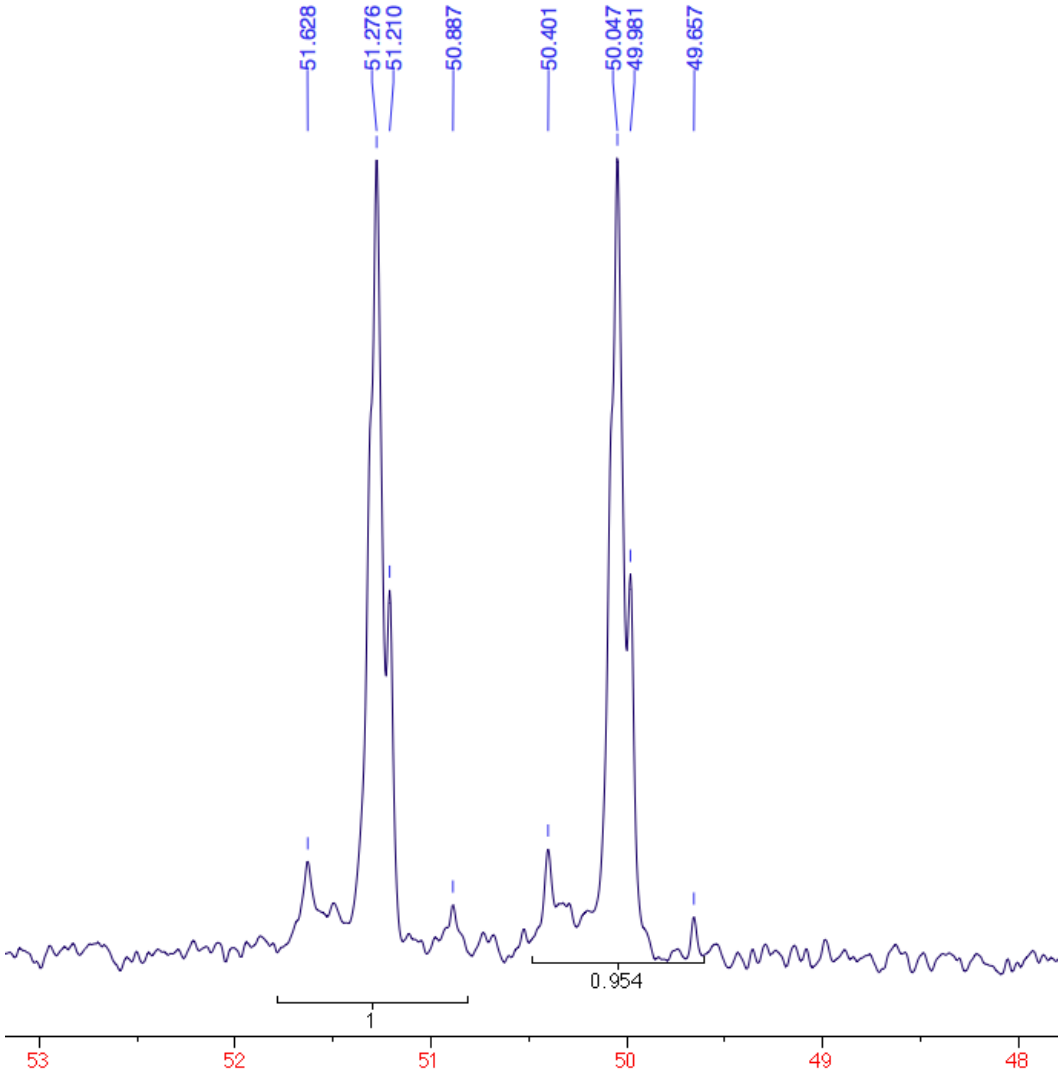


^{1}H-NMR Spectrum of [RhCl((R)-5,5'-dinorimido-BINAP)]$_2$ (**4**) (400MHz, CD_2Cl_2)



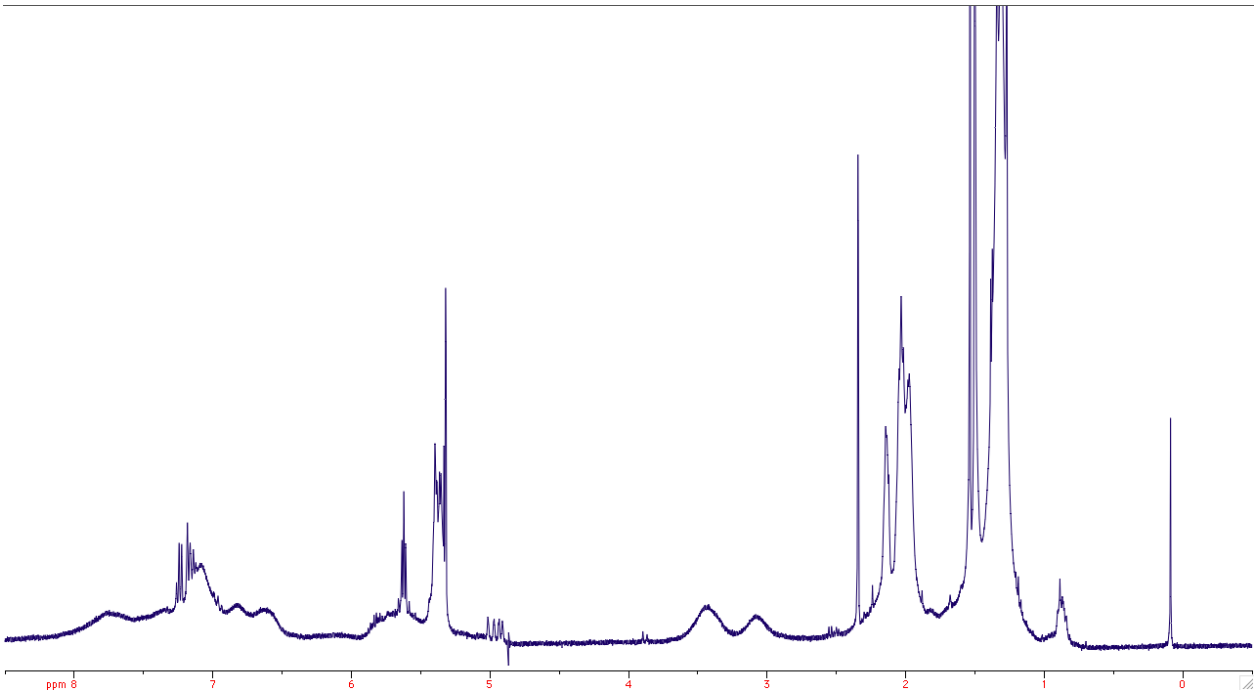
The peak indicated by the + is due to residual ethylene present. The peak indicated by the * is due to the CD_2Cl_2 NMR solvent.

^{31}P NMR Spectrum of [RhCl((R)-5,5'-dinorimido-BINAP)]$_2$ (**4**) (162MHz, CD_2Cl_2)

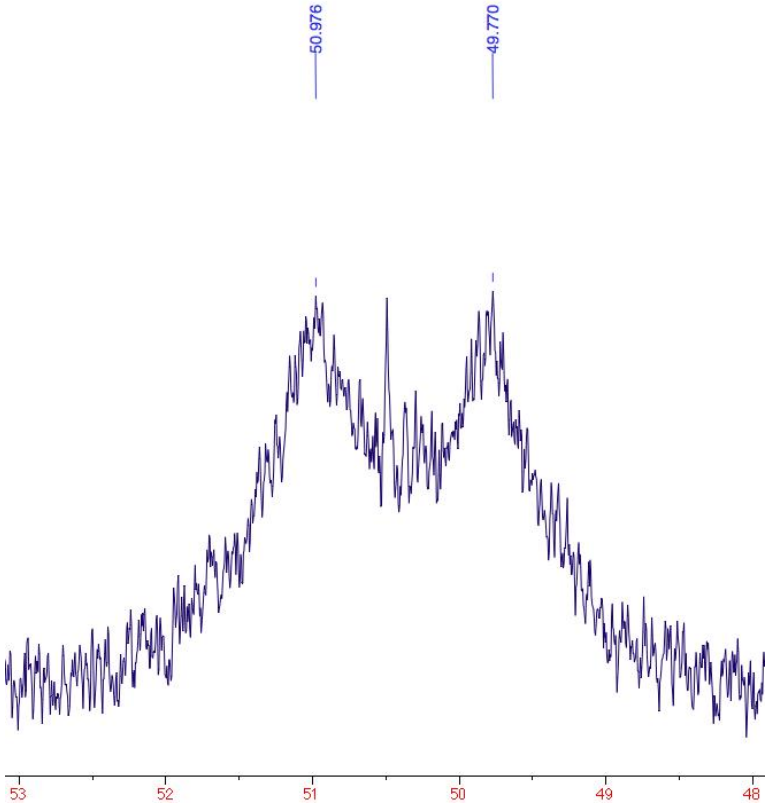


From this ^{31}P-NMR spectrum of [RhCl((*R*)-5,5'-dinorimido-BINAP)]$_2$ (**4**) taken after 30 minutes, it was observed that the other diastereomeric rotamer signals began to grow in. This compound was used immediately upon synthesis without isolation.

^{1}H-NMR spectrum of Catalyst-Organic Framework (**5**) (400MHz, CD_2Cl_2)



^{31}P NMR spectrum of Catalyst-Organic Framework (**5**) (162MHz, CD_2Cl_2)



The ^{31}P signal of the polymer **5** is found at δ = 50.4 ($^1J_{Rh\text{-}P}$ = 195Hz) whereas the monomer **4** ^{31}P signal is found at δ = 50.6 ($^1J_{Rh\text{-}P}$ = 199Hz). This shows that the electronic environment around the metal center essentially remains unaltered after the alternating ROMP is complete.