

Supporting Information

Thermally Stable, Latent Olefin Metathesis Catalysts

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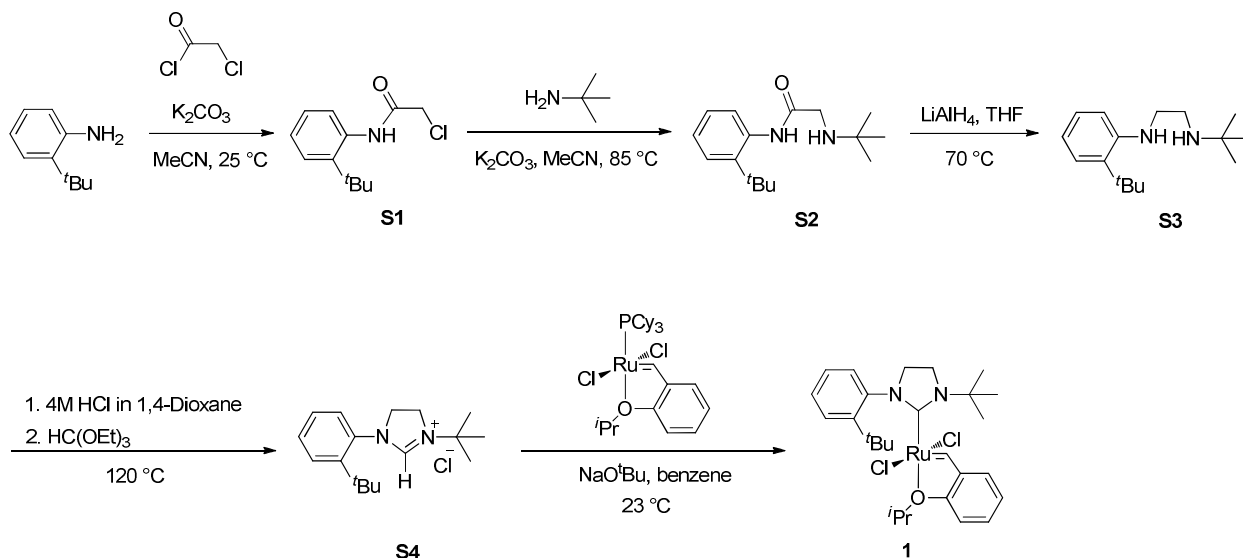
General Information.

^1H and ^{13}C NMR spectra were recorded on a Varian Mercury (^1H , 300 MHz), a Varian Inova 400 (^1H , 400 MHz), a Varian Inova 500 (^1H , 500 MHz; ^{13}C , 125 MHz), or an automated Varian Inova 500 (^1H , 500 MHz; ^{13}C , 125 MHz) spectrometer and chemical shifts are reported in ppm downfield from Me_4Si by using the residual solvent peak as an internal standard. Gel permeation chromatography (GPC) analyses were carried out in HPLC grade tetrahydrofuran on two MZ-Gel 10 μm columns (Analysetechnik) connected in series with a miniDAWN TREOS multiangle laser light scattering (MALLS) detector and an Optilab rex differential refractometer (both from Wyatt Technology). No calibration standards were used, and dn/dc values were obtained for each injection by assuming 100% mass elution from the columns. High resolution mass spectrometry (FAB) was done at the California Institute of Technology Mass Spectrometry Facility. X-ray crystallographic structures were obtained at the Beckman Institute X-ray Crystallography Laboratory at the California Institute of Technology. All air-sensitive reactions were conducted either in a nitrogen atmosphere glovebox or under an argon atmosphere using standard Schlenk-line techniques.

Materials.

Toluene, benzene, benzene- d_6 , and tetrahydrofuran were dried by passage through solvent purification systems.¹ Ruthenium catalyst precursors $\text{RuCl}_2(\text{PCy}_3)(=\text{CH}-o\text{-O}^i\text{Pr}-\text{C}_6\text{H}_4)$ and $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})$ were received from Materia, Inc. 1-Hexene was dried over calcium hydride and distilled prior to use. 1-Octene, 5-hexenyl acetate, 4-penten-1-ol, 3-methyl-1-hexene, 3,5,5-trimethyl-1-hexene, allyl alcohol, allyl acetate, allyl ethyl ether, allyl benzene, and allyloxytrimethylsilane were degassed before use. All other reagents and solvents were used as purchased without further purification.

Synthesis of Catalyst 1.



Synthesis of **S1**. Anhydrous potassium carbonate (136.7 mmol, 18.9 grams) and acetonitrile (175 mL) were added to a 500 mL RB flask containing a stir bar. 2-*tert*-butyl aniline (134 mmol, 20.9 mL) was added via syringe with stirring, and chloroacetyl chloride (134 mmol, 10.7 mL) was then added dropwise. The reaction was stirred at room temperature for 48 hours, after which the resulting mixture was filtered through a thin pad of silica gel. The filtrate was concentrated under partial vacuum on a rotary evaporator, and hexanes were added to the obtained cream colored residue. The hexanes dissolved away the off-white color and the remaining white solids were filtered and washed with more hexanes to yield **S2** (20.40 g, 67% yield). ¹H NMR (CDCl₃, 500 MHz): δ 8.44 (s, 1H), 7.66 (dd, *J* = 10 Hz, 3 Hz, 1H), 7.42 (dd, *J* = 10.5 Hz, 3 Hz, 1H), 7.28 – 7.16 (m, 2 H), 4.26 (s, 2H), 1.43 (s, 9H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 163.96, 142.52, 134.32, 127.11, 126.98, 126.89, 126.76, 43.38, 34.79, 30.83 ppm.

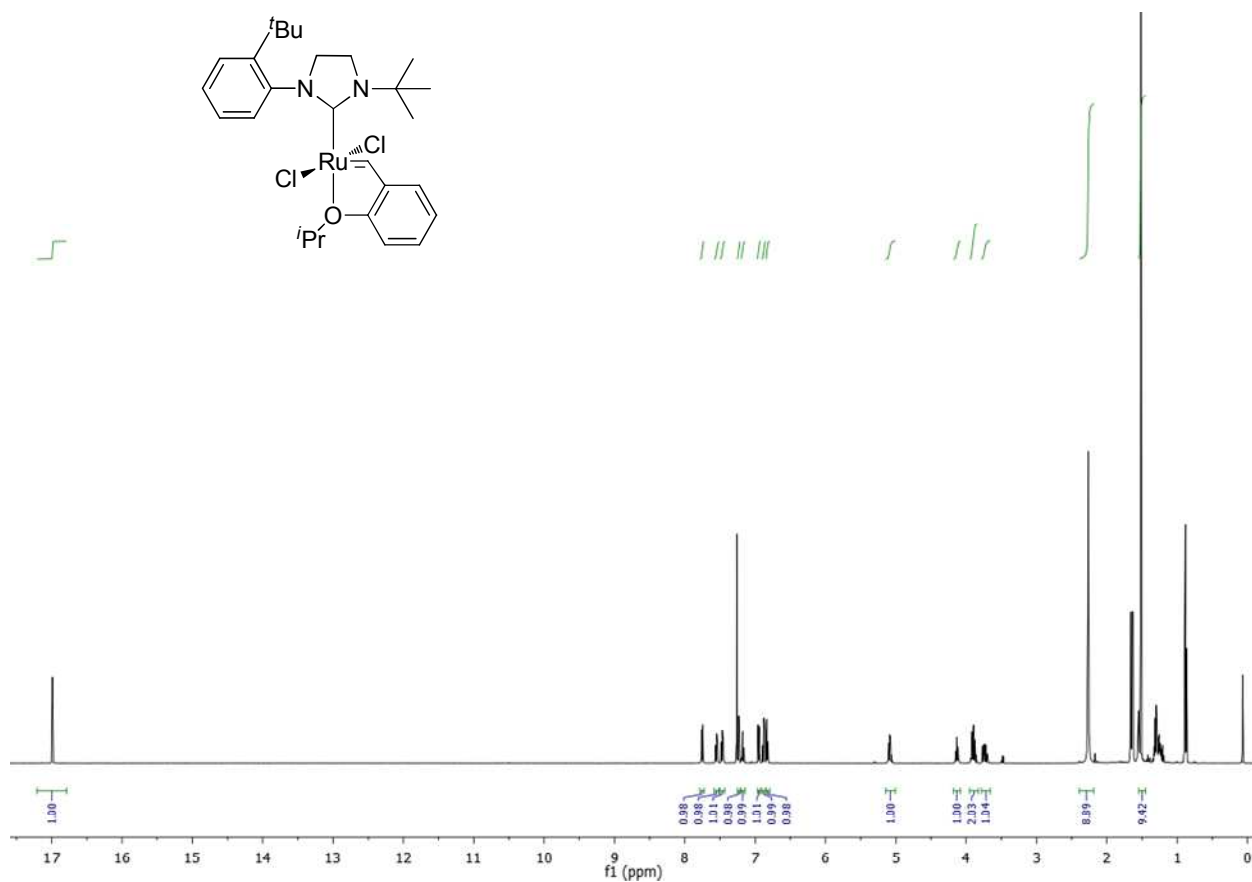
Synthesis of **S2**. Anhydrous potassium carbonate (88.3 mmol, 12.2 grams) and **S1** (41.0 mmol, 9.2 g) were added to a 100 mL round bottom flask containing a stir bar. Acetonitrile (50 mL) was added, followed by *tert*-butyl amine (41.0 mmol, 4.3 mL). A reflux condenser was attached to the flask, and the reaction was heated at 85 °C for 40 hours with stirring. The crude reaction mixture was then filtered through a thin pad of silica gel, and the filtrate was concentrated *in vacuo*. The crude solids obtained were then dissolved in diethyl ether and loaded onto a silica gel column for purification (100% diethyl ether as the eluting solvent). The product was isolated as white solids (4.225 g) in 40% yield. ¹H NMR (CDCl₃, 500 MHz): δ 9.74 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 3.40 (s, 2H), 1.45 (s, 9H), 1.16 (s, 9H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 170.71, 140.42, 135.74, 127.02, 126.55, 125.11, 124.99, 51.49, 46.97, 34.68, 30.63, 29.24 ppm.

Synthesis of **S3**. In a nitrogen atmosphere glovebox, **S2** (4.2 grams, 16.0 mmol) was added to a 100 mL round bottom flask containing a stir bar, followed by the addition of dry tetrahydrofuran (THF) (50 mL). In a vial, lithium aluminum hydride (2.3 grams, 60.6 mmol) was weighed out and dry THF (15 mL) was slowly added. This lithium aluminum hydride suspension was then very slowly added to the solution of **S2**, and the round bottom flask was sealed and brought out of the glovebox. The reaction was heated at 70 °C for 6 days, and then removed from the oil bath and allowed to cool. Water was slowly added to quench, and the THF/water mixture was stirred for 3 hours. The mixture was then extracted with methylene chloride (6 x 20 mL). The combined organic layers were dried over MgSO₄ and filtered. Concentration of the filtrate afforded a clear oil. The oil (4.10 g) was a mixture of product **S3** and unreacted starting material **S2** (95% and 5%, respectively). This crude mixture was carried directly on to the next step in the synthesis. ¹H NMR (CDCl₃, 500 MHz): δ 7.27 – 7.23 (m, 1H), 7.13 (td, *J* = 8.0, 1.3 Hz, 1H), 6.78 – 6.56 (m, 2H), 3.25 – 3.10 (m, 2H), 2.97 – 2.90 (m, 2H), 1.45 (s, 9H), 1.14 (s, 9H) ppm.

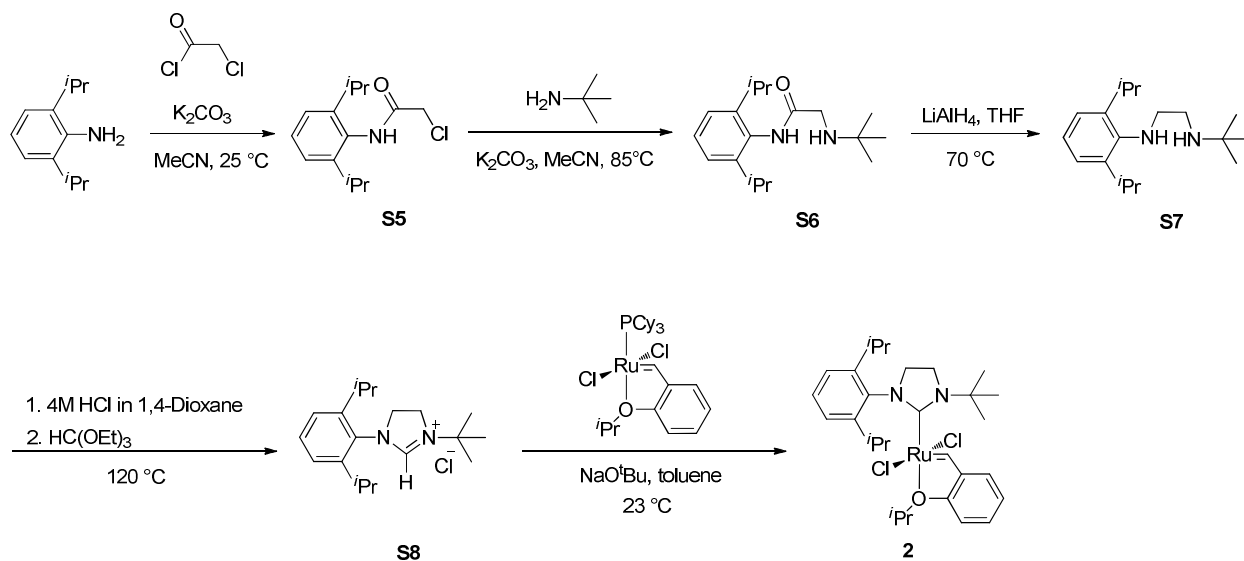
Synthesis of **S4**. **S3** (7.1 mmol, 1.76 g crude) was transferred to a 50 mL Schlenk tube containing a stir bar. Under an atmosphere of argon on the Schlenk line, 4M HCl in 1,4-dioxane (7.0 mL) was added via syringe through the septum cap. The mixture was stirred at room temperature for 2 hours. Vacuum was then applied to the Schlenk tube to remove excess HCl and 1,4-dioxane.

The Schlenk tube was placed back under an argon atmosphere and anhydrous triethyl orthoformate (35.5 mmol, 5.9 mL) was added via syringe. The Schlenk tube was sealed under the argon atmosphere and heated to 120 °C for 19 hours. After allowing the solution to cool, the crude mixture was added to a silica gel column for purification of the product (solvent system 5% MeOH in CH₂Cl₂). The product was isolated as a white powder (0.6549 g, 31% yield). ¹H NMR (CDCl₃, 500 MHz): δ 8.21 (s, 1H), 8.09 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.47 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.35 (pd, *J* = 7.3, 1.8 Hz, 2H), 4.50 (t, *J* = 10.5 Hz, 2H), 4.32 (t, *J* = 10.4 Hz, 2H), 1.58 (s, 9H), 1.39 (s, 9H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 156.27, 131.51, 131.29, 129.79, 129.51, 128.12, 127.66, 57.51, 55.10, 35.72, 32.24, 28.23, 25.79 ppm.

Synthesis of **1**. In a nitrogen atmosphere glovebox, **S4** (2.1 mmol, 0.620 g), sodium *tert*-butoxide (4.4 mmol, 0.420 g), and RuCl₂(PCy₃)₂(=CH-*o*-O^{*i*}PrC₆H₄) (1.9 mmol, 1.16 g) were added to a 100 mL round bottom flask. Dry benzene (40 mL) was added to this mixture and the flask was sealed and brought out of the glovebox. The reaction was stirred at 30 °C for 12 hours. The crude mixture was then loaded directly onto a silica gel column. The eluting solvent was 10% diethyl ether in pentane, and the gradient was increased to 50% ether in pentane. The product was isolated from a green band that came off of the column. Concentration of fractions from this green band afforded **1** as a glittery, green powder (0.251 g) in 24% yield. ¹H NMR (CDCl₃, 500 MHz): δ 16.99 (s, 1H), 7.75 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.46 (ddd, *J* = 8.4, 7.1, 1.6 Hz, 1H), 7.24 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.20 – 7.14 (m, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.83 (dd, *J* = 7.5, 1.8 Hz, 1H), 5.15 – 5.00 (m, 1H), 4.17 – 4.08 (m, 1H), 3.97 – 3.81 (m, 2H), 3.75 – 3.71 (m, 1H), 2.26 (s, 6H), 1.66 (d, *J* = 6.2 Hz, 3H), 1.63 (d, *J* = 6.2 Hz, 3H), 1.52 (s, 6H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 212.15, 153.33, 147.68, 144.93, 144.32, 132.48, 131.05, 129.33, 128.74, 128.39, 123.70, 122.78, 113.40, 77.48, 77.23, 76.98, 74.71, 57.93, 56.78, 46.01, 36.95, 32.58, 29.97, 22.71, 22.65 ppm. HRMS: [C₂₇H₃₈Cl₂N₂ORu] [(M+2)-H₂] Calculated = 578.1405. Found = 578.1392.



Synthesis of Catalyst 2.



Synthesis of **S5**. Anhydrous potassium carbonate (112.8 mmol, 15.6 grams) and acetonitrile (150 mL) were added to a 250 mL RB flask containing a stir bar. 2,6-Diisopropyl aniline (56.4 mmol, 10.0 mL) was added via syringe with stirring, and chloroacetyl chloride (56.4 mmol, 4.5 mL)

was then added dropwise. The reaction was stirred at room temperature for 43 hours, after which the resulting mixture was filtered through a thin pad of silica gel. The filtrate was concentrated under partial vacuum on a rotary evaporator, and hexanes were added to the obtained pale colored residue. The hexanes dissolved away the pale color and the remaining white solids were filtered and washed with more hexanes to yield **S5** (11.33 g, 79% yield). ^1H NMR (CDCl_3 , 500 MHz): δ 7.79 (s, 1H), 7.32 (t, $J = 8$ Hz, 1H), 7.20 (d, $J = 7$ Hz, 2H), 4.27 (s, 2H), 3.02 (sept, $J = 6.5$ Hz, 2H), 1.21 (d, $J = 7$ Hz, 12H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz): δ 165.45, 146.16, 130.12, 129.00, 123.83, 43.02, 29.08, 23.82 ppm.

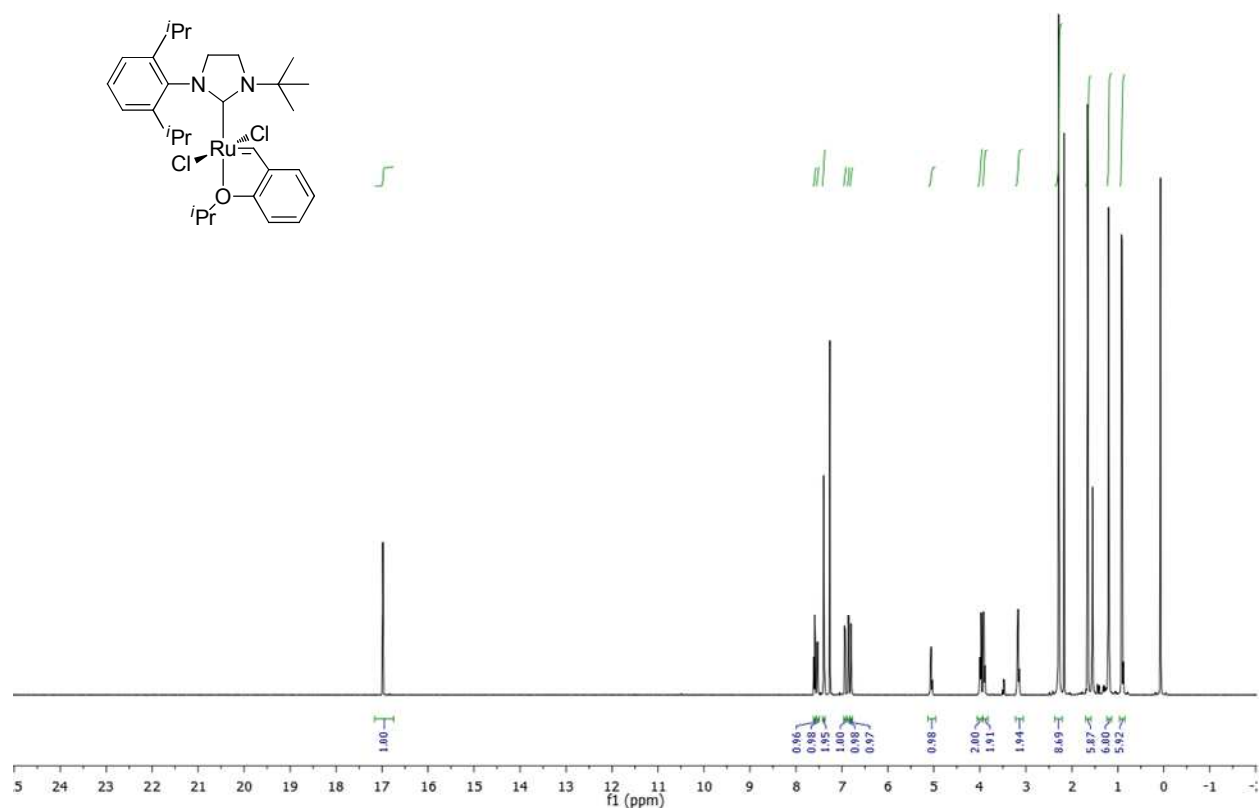
Synthesis of **S6**. Anhydrous potassium carbonate (42.3 mmol, 5.85 grams) and **S5** (20.6 mmol, 5.23 g) were added to a 100 mL round bottom flask containing a stir bar. Acetonitrile (40 mL) was added, followed by *tert*-butyl amine (20.6 mmol, 2.2 mL). A reflux condenser was attached to the flask, and the reaction was heated at 85 °C for 2 days with stirring. The crude reaction mixture was then filtered through a thin pad of silica gel, and the filtrate was concentrated *in vacuo*. The crude solids obtained were then dissolved in diethyl ether and loaded onto a silica gel column for purification (100% diethyl ether as the eluting solvent). The product was further purified by crystallization from layering methylene chloride (2 mL) with hexanes (10 mL). **S6** was obtained as white crystals (1.271 g, 33% yield). ^1H NMR (CDCl_3 , 500 MHz): δ 9.00 (s, 1H), 7.30 – 7.27 (m, 1H), 7.18 (d, $J = 7.7$ Hz, 2H), 3.42 (s, 2H), 3.02 (sept, $J = 6.9$ Hz, 2H), 1.21 (s, 6H), 1.20 (s, 6H), 1.18 (s, 9H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz): δ 172.34, 145.91, 131.72, 128.17, 123.61, 51.40, 46.38, 29.32, 29.08, 23.80 ppm.

Synthesis of **S7**. In a nitrogen atmosphere glovebox, **S6** (0.702 grams, 2.42 mmol) was added to a 100 mL round bottom flask containing a stir bar, followed by the addition of dry THF (5 mL). In a separate flask, lithium aluminum hydride (0.383 grams, 10.1 mmol) was weighed out and dry THF (5 mL) was slowly added. This lithium aluminum hydride suspension was then very slowly added to the solution of **S6**, and the round bottom flask was sealed and brought out of the glovebox. The reaction was heated while sealed at 70 °C for 5 days, after which it was removed from the oil bath and allowed to cool. Water was slowly added, and the mixture was then extracted with methylene chloride (4 x 20 mL). The combined organic layers were dried over MgSO_4 and filtered. Concentration of the filtrate afforded a clear oil. The oil (0.632 g) was a mixture of product **S7** and unreacted starting material **S6** (90% and 10%, respectively). This crude mixture was carried directly on to the next step in the synthesis. ^1H NMR (CDCl_3 , 500 MHz): δ 7.09 (d, $J = 8.0$ Hz, 2H), 7.05 – 7.00 (m, 1H), 3.32 – 3.35 (m, 2H), 2.95 (t, $J = 5.6$ Hz, 2H), 2.82 (t, $J = 5.6$ Hz, 2H), 1.24 (d, $J = 6.8$ Hz, 12H), 1.14 (s, 9H) ppm.

Synthesis of **S8**. **S7** (2.28 mmol, 0.631 g crude) was transferred to a 50 mL Schlenk tube containing a stir bar. Under an atmosphere of argon on the Schlenk line, 4M HCl in 1,4-dioxane (2.3 mL) was added via syringe through the septum cap. The mixture was stirred at room temperature for 2 hours. Vacuum was then applied to the Schlenk tube to remove excess HCl and 1,4-dioxane. The Schlenk tube was placed back under an argon atmosphere and anhydrous triethyl orthoformate (22.8 mmol, 3.8 mL) was added via syringe. The Schlenk tube was sealed

under the argon atmosphere and heated to 120 °C for 18 hours. After allowing the solution to cool, the crude mixture was added to a silica gel column to purify (solvent system 5% MeOH in CH₂Cl₂). The product was isolated as a white powder (0.269 g) in 41% yield. ¹H NMR (CDCl₃, 500 MHz): δ 8.69 (s, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 8 Hz, 2H), 4.53 (t, *J* = 10.5 Hz, 2H), 4.33 (t, *J* = 11.5 Hz, 2H), 2.94 (sept, *J* = 6.5 Hz, 2H), 1.61 (s, 9H), 1.29 (d, *J* = 7 Hz, 12H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 156.64, 146.76, 131.28, 130.59, 125.12, 58.07, 54.00, 46.96, 29.07, 28.68, 25.16, 24.45 ppm.

Synthesis of **2**. In a nitrogen atmosphere glovebox, **S8** (0.464 mmol, 0.150 g), sodium *tert*-butoxide (1.0 mmol, 0.098 g), and RuCl₂(PCy₃)(=CH-*o*-O^{*i*}PrC₆H₄) (0.499 mmol, 0.300 g) were added to a 100 mL round bottom flask. Dry toluene (10 mL) was added to this mixture and the flask was sealed and brought out of the glovebox. The reaction was stirred at room temperature for 7 hours. The crude mixture was then loaded directly onto a silica gel column. The eluting solvent was 10% diethyl ether in pentane, and the gradient was increased to 50% ether in pentane. The product was isolated from a green band that came off of the column. Concentration of fractions from this green band afforded **2** as a dark green powder (0.097 grams, 35% yield). ¹H NMR (CDCl₃, 500 MHz): δ 16.96 (s, 1H), 7.57 (t, *J* = 8 Hz, 1H), 7.52 – 7.49 (m, 1H), 7.37 (d, *J* = 8 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.78 – 6.75 (m, 1H), 5.04 (sept, *J* = 6.5 Hz, 1H), 3.98 – 3.95 (m, 2H), 3.90 – 3.86 (m, 2H), 3.14 (sept, *J* = 6.5 Hz, 2H), 2.26 (s, 9H), 1.62 (d, *J* = 6 Hz, 6H), 1.17 (d, *J* = 7 Hz, 6H), 0.89 (d, *J* = 7 Hz, 6H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 208.29, 153.04, 148.51, 145.01, 139.37, 130.77, 129.50, 125.17, 123.79, 122.73, 113.40, 74.75, 56.53, 54.96, 45.96, 30.17, 28.07, 26.07, 24.23, 22.76 ppm. HRMS: [C₃₅H₄₀Cl₂N₂ORu] [(M+2)-H₂] Calculated = 676.1562. Found = 676.1570.



Latent cross-metathesis reactions.

The latent cross-metathesis screens were carried out by two methods; both methods produced the same result. The first method of screening the catalysts for latency for cross-metathesis of a substrate involved setting up two duplicate, identical experiments, with one reaction at 25 °C and the other reaction at 85 °C. The conversion of substrate to product for both reactions was measured by ^1H NMR. The second method entailed taking one reaction and observing it over a given time period at 25 °C, and then taking an ^1H NMR spectrum to determine the percent conversion, if any. This same exact reaction was subsequently heated at 85 °C. Both sets of experiments gave the same degree of latency at ambient temperature, and the same conversion to product upon heating for a given amount of time. Catalyst **1** gave a mixture of *cis* and *trans* product isomers, which had overlapping peaks in the NMR spectra.

Representative latent cross-metathesis of 1-hexene.

In a glovebox under a nitrogen atmosphere, catalyst **1** (0.0047 mmol, 2.7 mg) was added to an NMR tube. Benzene- d_6 (0.50 mL) was added via syringe, followed by 1-hexene (0.24 mmol, 30 μL), which was added via a 50 μL syringe. This gave a concentration of 1-hexene in benzene of 0.5M. The NMR tube was then sealed shut and the contents mixed, after which the NMR tube was brought out of the glovebox and heated while sealed at 85 °C in an oil bath for 24 hours. An

^1H NMR spectrum was taken to determine the percent conversion of 1-hexene to 5-decene, which was calculated to be 90%. The proton NMR spectrum matched reported NMR spectra for this product.^{2,3} ^1H NMR of 5-decene (500 MHz, C_6D_6): δ 5.41-5.47 (m, 2H), 1.93-2.07 (m, 4H), 1.22-1.37 (m, 8H), 0.88 (t, $J=7.1$ Hz, 6H) ppm.

Representative latent cross-metathesis of 1-octene.

In a glovebox under a nitrogen atmosphere, catalyst **1** (0.0053 mmol, 3.1 mg) was added to an NMR tube. Benzene- d_6 (0.53 mL) was added via syringe, followed by 1-octene (0.27 mmol, 42 μL), which was added via a 50 μL syringe. This gave a concentration of 1-octene in benzene of 0.5M. The NMR tube was then sealed shut and the contents mixed, after which the NMR tube was brought out of the glovebox and heated while sealed at 85 $^\circ\text{C}$ in an oil bath for 22 hours. An ^1H NMR spectrum was taken to determine the percent conversion of 1-octene to 7-tetradecene, which was calculated to be 76%. The proton NMR spectrum matched reported NMR spectra for this product.³ ^1H NMR of 7-tetradecene (500 MHz, C_6D_6): δ 5.42-5.49 (m, 2H), 1.97-2.09 (m, 4H), 1.20-1.40 (m, 12H), 0.89 (t, $J=7.1$ Hz, 6H) ppm.

Representative latent cross-metathesis of 5-hexenyl acetate.

In a glovebox under a nitrogen atmosphere, catalyst **1** (0.005 mmol, 2.9 mg) was added to an NMR tube. Benzene- d_6 (0.49 mL) was added via syringe, followed by 5-hexenyl acetate (0.25 mmol, 40 μL), which was added via a 50 μL syringe. This gave a concentration of 5-hexenyl acetate in benzene of 0.5M. The NMR tube was then sealed shut and the contents mixed, after which the NMR tube was brought out of the glovebox and heated while sealed at 85 $^\circ\text{C}$ in an oil bath for 22 hours. An ^1H NMR spectrum was taken to determine the percent conversion of 5-hexenyl acetate to 5-decenyl-1,10-diacetate, which was calculated to be 62%. The proton NMR spectrum matched reported NMR spectra for this product.⁴ ^1H NMR of 5-decenyl-1,10-diacetate (500 MHz, C_6D_6): δ 5.26-5.32 (m, 2H), 3.95-3.99 (m, 4H), 1.82-1.91 (m, 4H), 1.68 (s, 6H), 1.35-1.45 (m, 4H), 1.20-1.27 (m, 4H) ppm.

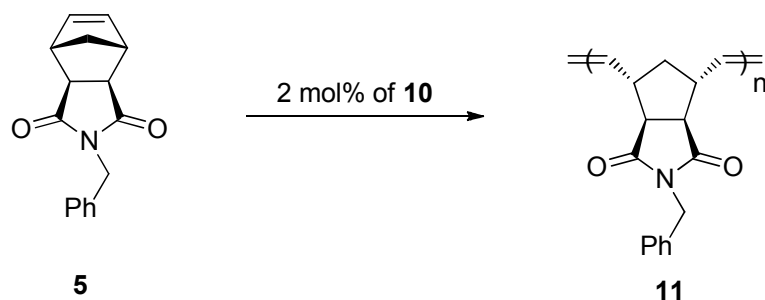
Representative latent cross-metathesis of 4-penten-1-ol.

In a glovebox under a nitrogen atmosphere, catalyst **1** (0.0052 mmol, 3.0 mg) was added to an NMR tube. Benzene- d_6 (0.51 mL) was added via syringe, followed by 4-penten-1-ol (0.26 mmol, 26 μL), which was added via a 50 μL syringe. This gave a concentration of 4-penten-1-ol in benzene of 0.5M. The NMR tube was then sealed shut and the contents mixed, after which the NMR tube was brought out of the glovebox and heated while sealed at 85 $^\circ\text{C}$ in an oil bath for 22 hours. An ^1H NMR spectrum was taken to determine the percent conversion of 4-penten-1-ol to 4-octene-1,8-diol, which was calculated to be 89%. The proton NMR spectrum matched reported NMR spectra for this product.⁵ ^1H NMR of 4-octene-1,8-diol (500 MHz, C_6D_6): δ 5.28-5.52 (m, 2H), 3.42 (t, $J=6.5$ Hz, 4H), 2.07-2.12 (m, 4H), 1.71 (s, 2H), 1.52-1.54 (m, 4H) ppm.

Representative latent cross-metathesis of 3-methyl-1-hexene.

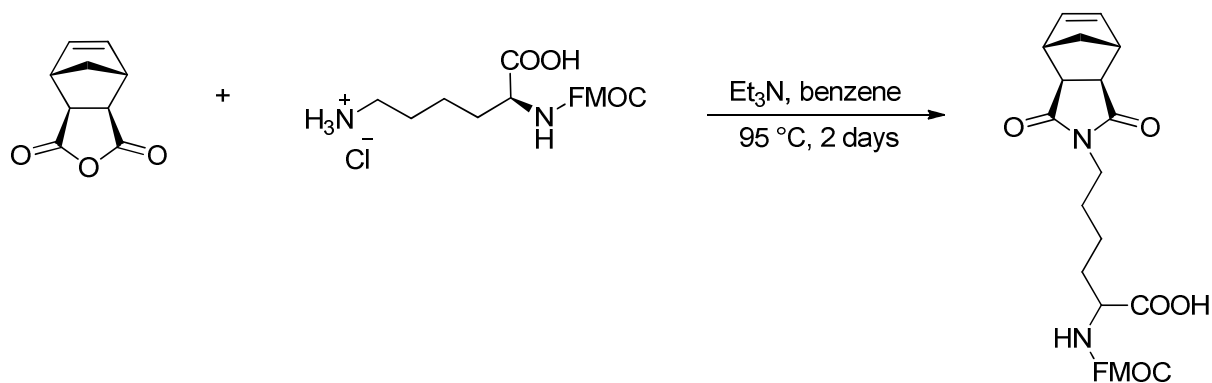
In a glovebox under a nitrogen atmosphere, catalyst **1** (0.005 mmol, 2.9 mg) was added to an NMR tube. Benzene-*d*₆ (0.51 mL) was added via syringe, followed by 3-methyl-1-hexene (0.25 mmol, 36 μ L), which was added via a 50 μ L syringe. This gave a concentration of 3-methyl-1-hexene in benzene of 0.5M. The NMR tube was then sealed shut and the contents mixed, after which the NMR tube was brought out of the glovebox and heated while sealed at 85 °C in an oil bath for 22 hours. An ¹H NMR spectrum was taken to determine the percent conversion of 3-methyl-1-hexene to 4,7-dimethyl-5-decene, which was calculated to be 17%. ¹H NMR of 4,7-dimethyl-5-decene (500 MHz, C₆D₆): δ 5.24-5.27 (m, 2H), 1.93-1.98 (m, 2H), 1.15-1.27 (m, 8H), 0.99-1.01 (m, 6H), 0.86 (t, *J*= 7.3 Hz, 6H) ppm.

Latent ROMP of monomer **5**.



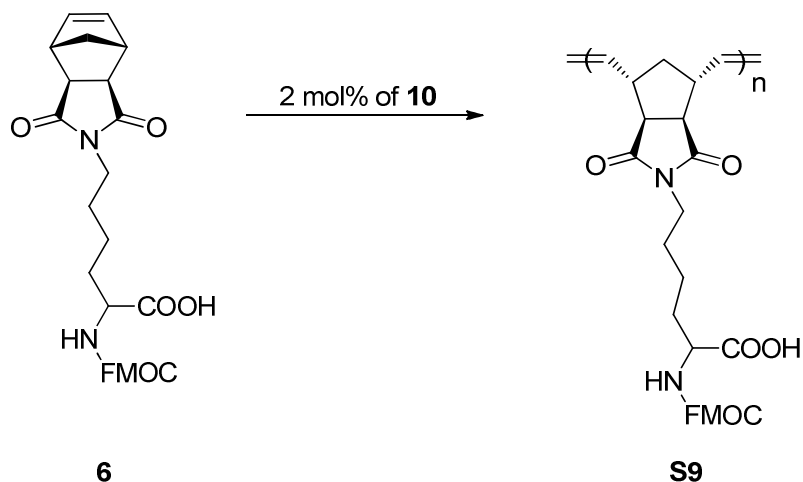
In a glovebox under a nitrogen atmosphere, complex **2** (0.0047 mmol, 2.9 mg) was added to an NMR tube. Subsequently, 25 equivalents of sodium iodide (0.12 mmol, 17.8 mg) were added (12.5 equivalents per chloride ligand), followed by the addition of THF-*d*₈ (0.89 mL) via syringe. The NMR tube was capped and the solution was mixed and left for 4 hours to allow the chloride ligands to exchange out for iodide ligands to give catalyst **10**. After 4 hours, monomer **5**^{6,7} (0.25 mmol, 64 mg) was added to the NMR tube, and the reaction was carried out at 25 °C. After 24 hours at 25 °C, a ¹H NMR spectrum was taken of the reaction mixture. Based on ¹H NMR spectroscopy, there was no conversion of monomer **5**. The NMR tube was then heated while sealed at 85 °C for 2 hours. After 2 hours at 85 °C, a ¹H NMR spectrum was taken of the reaction mixture. There was complete conversion of monomer to polymer (99%). The polymer was precipitated in methanol, which was decanted off. The white polymer was filtered and washed with methanol and then dried under vacuum to afford 52 mg of polymer **11** (81% isolated yield). ¹H NMR of polymer **11** (500 MHz, CDCl₃): δ 7.30-7.45 (m, 5H), 5.77-5.86 (m, 2H), 4.68 (s, br, 2H), 3.03-3.12 (m, 2H), 2.68-2.79 (m, 2H), 2.15-2.25 (m, 1H), 1.69-1.77 (m, 1H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 178.09, 136.15, 132.16, 131.95, 128.89, 128.83, 128.12, 51.20, 51.10, 46.05, 45.88, 42.39, 42.27 ppm. GPC data: *M*_n=24,300, PDI=1.16.

Synthesis of monomer 6.



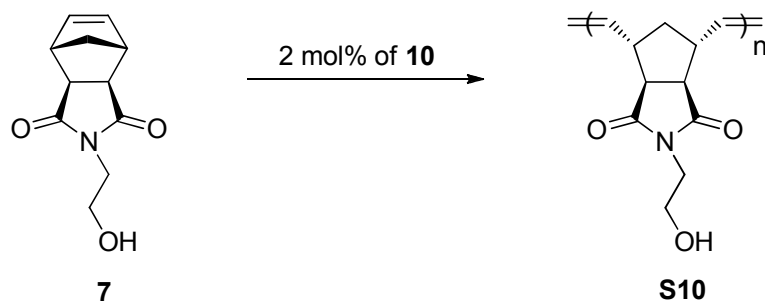
cis-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (7.3 mmol, 1.2 g) and Fmoc-Lys-OH hydrochloride (CAS # 139262-23-0) (7.6 mmol, 3.08 g) were dissolved in benzene (14 mL), and triethylamine (7.6 mmol, 1.06 mL) was added with stirring. The reaction was heated with a Dean-Stark trap at $95\text{ }^\circ\text{C}$ for two days, after which the solution was cooled to room temperature. 1M HCl was added to the solution, and the mixture was extracted two times with methylene chloride. The combined organic layers were washed with brine, and subsequently dried over Na_2SO_4 , filtered, and concentrated under vacuum. The product was purified by silica gel chromatography (3-10% methanol in ether). White solids (2.87g) were isolated in 76% yield. ^1H NMR (500 MHz, CDCl_3): δ 7.76 (d, $J = 7.5$ Hz, 2H), 7.64 – 7.59 (m, 2H), 7.39 (t, $J = 7.4$ Hz, 2H), 7.31 (t, $J = 7.4$ Hz, 2H), 6.25 (s, 2H), 4.32 – 4.45 (m, 3H), 4.22 (t, $J = 6.9$ Hz, 1H), 3.48 (t, $J = 7.0$ Hz, 1H), 3.45 – 3.35 (m, 1H), 3.26 (s, 2H), 2.67 (s, 2H), 1.89 – 1.98 (m, 1H), 1.72 – 1.83 (m, 1H), 1.66 – 1.53 (m, 2H), 1.50 (d, $J = 9.8$ Hz, 1H), 1.45 – 1.28 (m, 2H), 1.20 (d, $J = 9.6$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ 178.53, 143.91, 141.51, 138.03, 138.00, 127.95, 127.30, 125.35, 120.20, 110.20, 68.86, 67.36, 48.06, 47.36, 45.37, 42.96, 38.17, 31.56, 27.41, 22.60 ppm.

Latent ROMP of monomer 6.



In a glovebox under a nitrogen atmosphere, complex **2** (0.0028 mmol, 1.7 mg) was added to an NMR tube. Subsequently, 25 equivalents of sodium iodide (0.07 mmol, 11.1 mg) were added, followed by the addition of THF-*d*₈ (0.54 mL) via syringe. The NMR tube was capped and the solution was mixed and left for 4 hours to allow the chloride ligands to exchange out for iodide ligands to give catalyst **10**. After 4 hours, monomer **6** (0.15 mmol, 76 mg) was added to the NMR tube, and the reaction was carried out at 25 °C. After 37 hours at 25 °C, a ¹H NMR spectrum was taken of the reaction mixture. Based on ¹H NMR spectroscopy, there was no conversion of monomer **6**. The NMR tube was then heated while sealed at 85 °C for 2 hours. After 2 hours at 85 °C, a ¹H NMR spectrum was taken of the reaction mixture. There was 95% conversion of monomer to polymer. The polymer was precipitated in methanol, with the addition of pentane, which was decanted off. The white polymer was filtered and washed with methanol and then pentane, and dried under vacuum to afford 71.5 mg of polymer **S9** (94% isolated yield). ¹H NMR of polymer **S9** (500 MHz, THF-*d*₈): δ 7.73-7.78 (m, 2H), 7.62-7.69 (m, 2H), 7.30-7.36 (m, 2H), 7.23-7.29 (m, 2H), 5.62-5.74 (m, 2H), 4.27-4.35 (m, 2H), 4.17-4.25 (m, 2H), 3.35-3.43 (m, 2H), 2.80-2.95 (m, 2H), 2.25-2.70 (m, 6H), 1.46-1.62 (m, 2H+1H), 1.32-1.41 (m, 1H) ppm. GPC data: *M*_n=36,900, PDI=1.27.

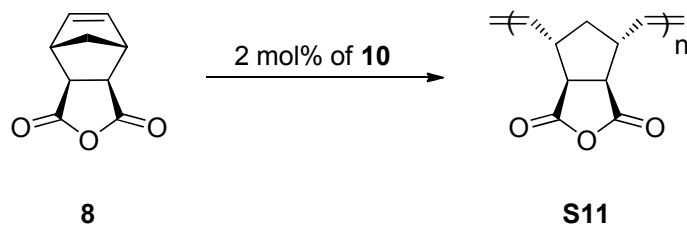
Latent ROMP of monomer **7**.



In a glovebox under a nitrogen atmosphere, complex **2** (0.0048 mmol, 2.9 mg) was added to an NMR tube. Subsequently, 25 equivalents of sodium iodide (0.12 mmol, 18 mg) were added, followed by the addition of THF-*d*₈ (0.91 mL) via syringe. The NMR tube was capped and the solution was mixed and left for 4 hours to allow the chloride ligands to exchange out for iodide ligands to give catalyst **10**. After 4 hours, monomer **7**⁸ (0.24 mmol, 50 mg) was added to the NMR tube, and the reaction was carried out at 25 °C. After 24 hours at 25 °C, a ¹H NMR spectrum was taken of the reaction mixture. Based on ¹H NMR spectroscopy, there was no conversion of monomer **7**. The NMR tube was then heated while sealed at 85 °C for 2 hours. After 2 hours at 85 °C, a ¹H NMR spectrum was taken of the reaction mixture. There was complete conversion of monomer to polymer. The polymer was precipitated in pentane, which was decanted off. The white polymer was filtered and washed with pentane and then dried under vacuum to afford 24.1 mg of polymer **S10** (48% isolated yield). ¹H NMR of polymer **S10** (500 MHz, THF-*d*₈): δ 6.24-6.31 (m, 2H), 3.57-3.63 (m, 2H), 3.51-3.56 (m, 2H), 3.10-3.17 (m, 2H),

2.64-2.68 (m, 2H), 1.37-1.42 (m, 2H) ppm. ^{13}C NMR (125 MHz, THF- d_8): δ 178.34, 138.77, 59.36, 48.72, 46.26, 43.55, 41.80 ppm. GPC data: $M_n=2,000$, PDI=3.25.

Latent ROMP of monomer **8**.



In a glovebox under a nitrogen atmosphere, complex **2** (0.0054 mmol, 3.3 mg) was added to an NMR tube. Subsequently, 25 equivalents of sodium iodide (0.14 mmol, 21 mg) were added, followed by the addition of THF- d_8 (1.0 mL) via syringe. The NMR tube was capped and the solution was mixed and left for 4 hours to allow the chloride ligands to exchange out for iodide ligands to give catalyst **10**. After 4 hours, monomer **8** (0.28 mmol, 46 mg) was added to the NMR tube, and the reaction was carried out at 25 °C. After 37 hours at 25 °C, a ^1H NMR spectrum was taken of the reaction mixture. Based on ^1H NMR spectroscopy, there was no conversion of monomer **8**. The NMR tube was then heated while sealed at 85 °C for 2 hours. After 2 hours at 85 °C, a ^1H NMR spectrum was taken of the reaction mixture. There was 78 percent conversion of monomer to polymer. The polymer was precipitated in pentane, which was decanted off. The white polymer was filtered and washed with pentane and then dried under vacuum to afford 31.1 mg of polymer **S11** (68% isolated yield). ^1H NMR of polymer **S11** (500 MHz, THF- d_8): δ 5.40-5.53 (m, 2H), 2.87-2.98 (m, 2H), 2.76-2.84 (m, 2H), 1.95-2.06 (m, 1H), 1.25-1.37 (m, 1H) ppm. ^{13}C NMR (125 MHz, THF- d_8): δ 174.35, 173.57, 133.12, 53.56, 51.59, 46.31, 46.19, 46.08, 39.96, 30.75 ppm. GPC data: $M_n=3,800$, PDI=1.79.

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