Chapter 2

Design and Synthesis of Supported Molecular REMP Catalysts

2.0 – Abstract

The history and applications of ring-expansion metathesis polymerization (REMP) for the synthesis of cyclic polymers is discussed. Although ruthenium-based REMP catalysts have been explored and developed, significant limitations prompted the design and synthesis of a new family of REMP catalysts. The new supported molecular REMP catalyst was devised and its synthesis discussed. Despite challenging synthetic steps with low yields, multi gram quantities of the supported REMP catalysts were prepared. The synthesis reported may be adapted for future catalyst design.

Chapter 2 Acknowledgments

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2.1 – Introduction

The first ring-expansion metathesis polymerization (REMP)(Fig 2.1) catalyst (**2.1**), developed in our group in 2002, provided the first strategy for the preparation of all-hydrocarbon cyclic polyolefins via ring-expansion (Fig 2.1).[1] The distinguishing design feature of REMP catalyst **2.1** was the alkyl tether between the two carbene ligands which was designed to selectively produce cyclic polyolefins from cyclic olefin monomers.[1] Catalyst **2.1** also provided a novel strategy for the preparation of cyclic polyethylene (PE) using a living polymerization strategy: hydrogenation of any cyclic polyalkenamer (e.g., cyclic PCOE) prepared with **2.1** could be hydrogenated to PE (Fig 2.1, right). This early report also supposed a REMP catalytic cycle to rationalize the selective formation of cyclic polymers (Fig 2.2).

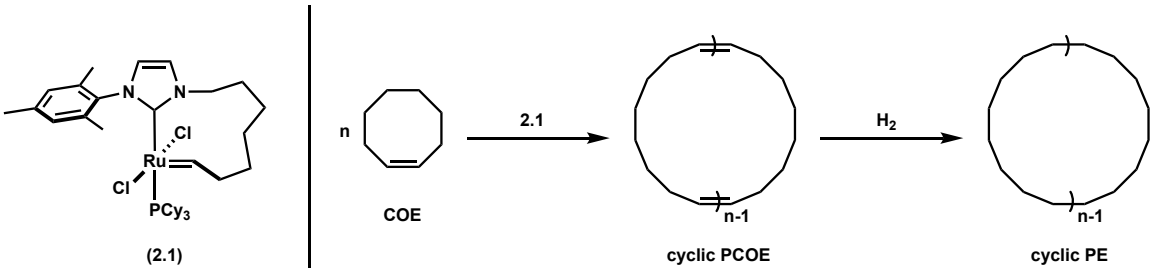


Figure 2.1 | REMP catalyst (2.1) (left) and the REMP of COE by 2.1 to produce cyclic PCOE and subsequent hydrogenation to cyclic PE (right).

The importance of monomer purity in the REMP of cyclododecatriene (CDT) using **2.1** was established.[2] Our group reported the synthetic strategy for a family of REMP catalysts similar to **2.1,** but with varying tether lengths between

NHC ligand and alkylidene, and the degree of saturation of the NHC ligand backbone (Fig 2.3).[4] Subsequently, the catalyst-dependent polymerization profiles[5] for **2.1**-**2.6** were studied and structure-property relationships were established. As with common ROMP catalysts, saturation of the NHC ligand increased the activity of **2.5** and **2.6** relative to **2.3** and **2.4**. Additionally, the tether length dictated relative rates of intra- and intermolecular chain transfer: longer tethers produced higher M_w chains due to reduced intramolecular chain transfer. Our group also expanded the monomer scope so that ultra-high MW brush and dendritic cyclic polymers could be prepared from norbornene-based monomers (Fig 2.4)

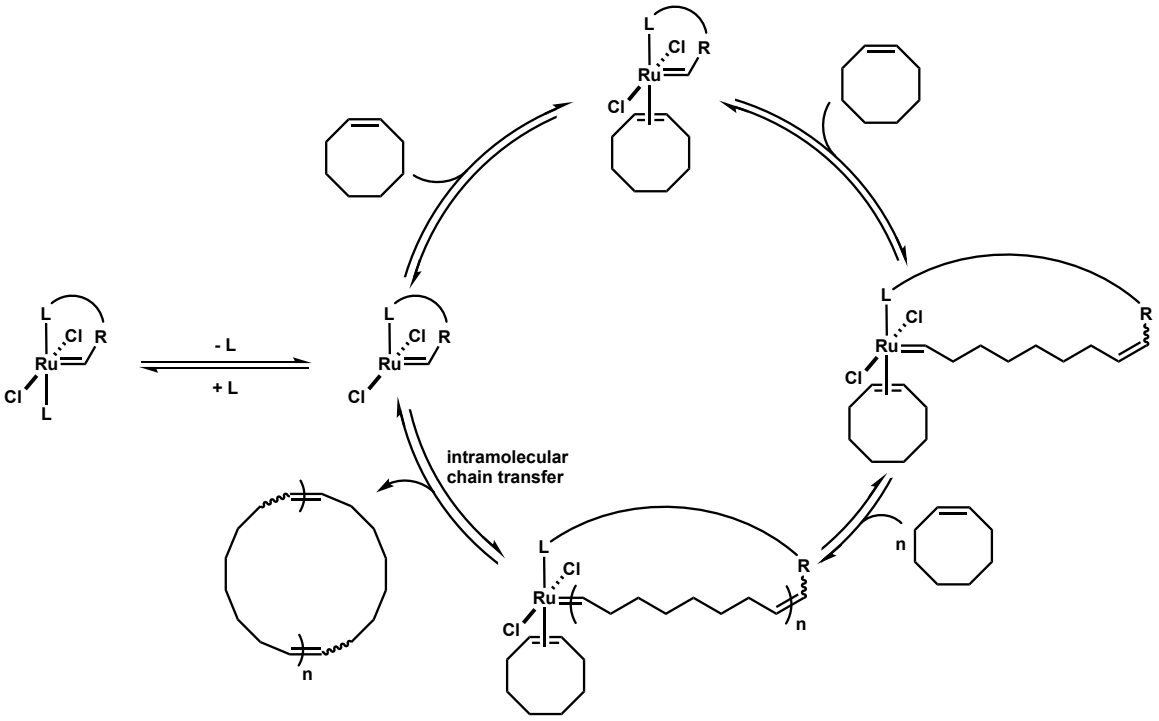


Figure 2.2 | The REMP catalytic cycle.

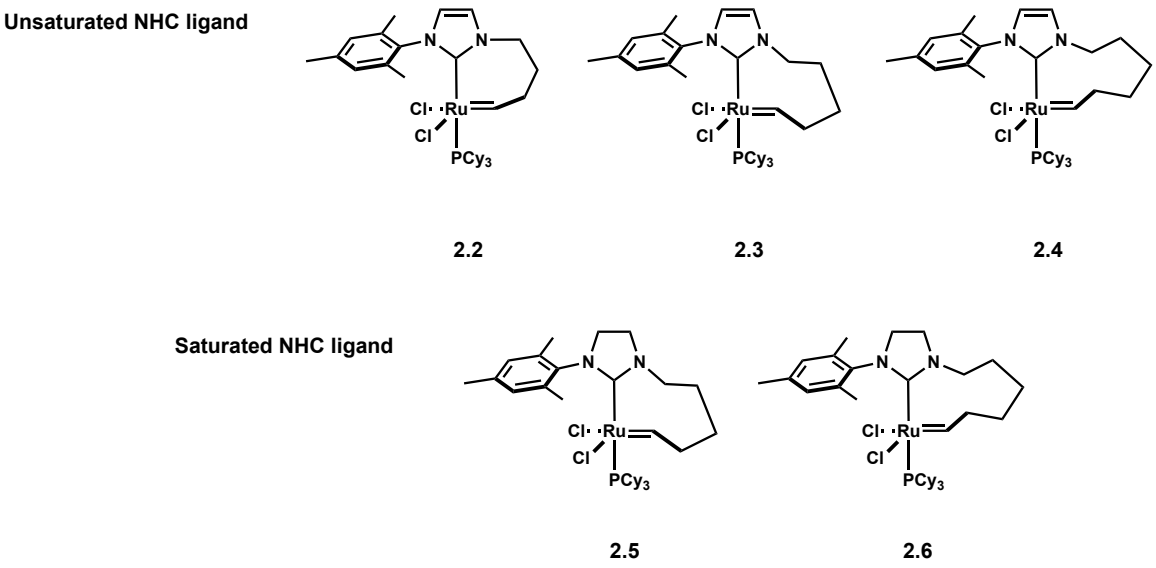


Figure 2.3 | Homogeneous REMP catalysts with unsaturated NHC ligand (top) and saturated NHC ligand (bottom).

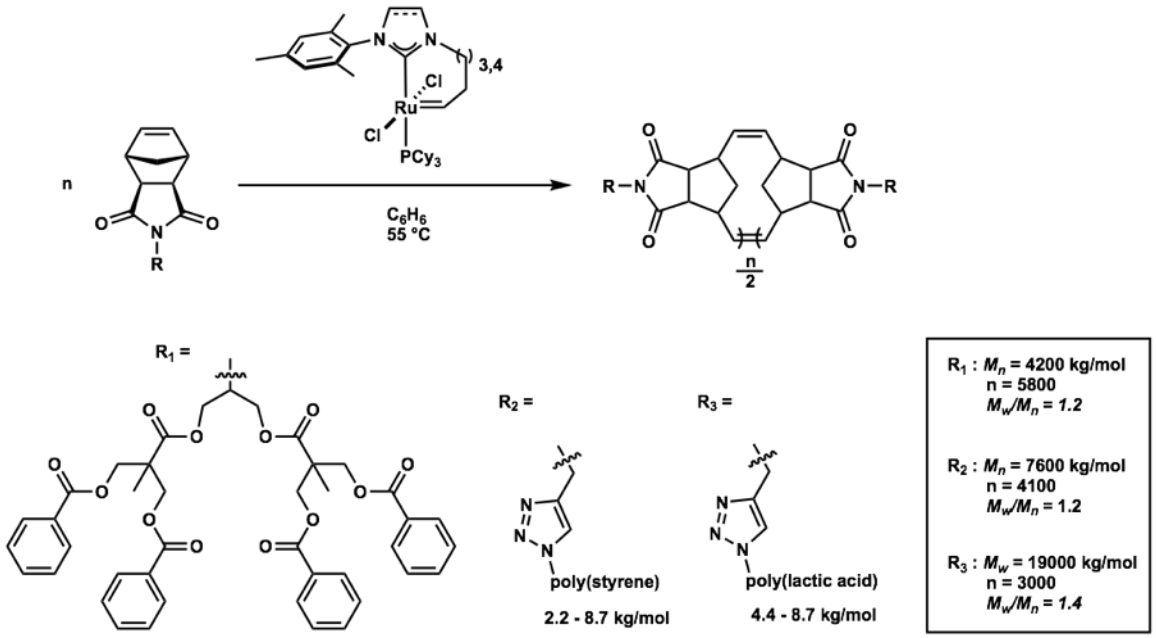


Figure 2.4 | Cyclic brush and dendritic polymers.

Efficient ROMP methodology, often utilizing common commercially available ruthenium-based catalysts (Fig 2.5), is characterized by the linear relationship between M_n and monomer conversion—this equates to a controlled, living polymerization which provides low dispersity ($Đ$) material in high yield. The goal of similarly improving REMP methodology ca. 2003 – 2011 in our group focused on catalyst development,[4,5] mechanistic studies,[4,6] and expansion of monomer scope.[7-9] The unifying obstacle in these efforts was the poor performance of all REMP catalysts we pursued.

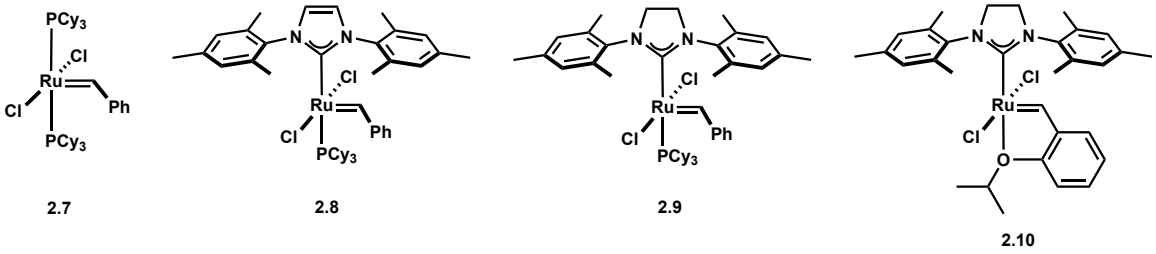


Figure 2.5 | Ruthenium-based olefin metathesis catalysts commonly used in ROMP.

The problems with catalysts **2.1** - **2.6** were three-fold: 1) poor activity; 2) poor scalability; 3) ineffective separation from the bulk material. Although the activity of unsaturated catalysts **2.1** - **2.4** was improved through saturation of the NHC backbone in **2.5** and **2.6**, these catalysts still performed poorly in comparison to **2.7** - **2.10**. The dual-chelating ligand—the alkyl tether from the NHC ligand to the alkylidene (**2.1** - **2.6**)—is the critical design feature which

produces cyclic polymers, but the concomitant electronic effects from these modifications are well-known to lower the stability and activity in olefin metathesis catalysts. This is why almost all commercially available ruthenium-based olefin metathesis catalysts with NHC ligands have aryl groups at both N1 and N3, and bear a benzylidene as opposed to an alkylidene. Attempts to incorporate the structural features unique to **2.1** – **2.6** into catalysts with similar electronics to **2.7 – 2.10** were unsuccessful.

Additionally, the poor activity of **2.1** – **2.6** necessitated high catalyst loading for REMP reactions. Synthesis of these catalysts was non-trivial, so the scale-up necessary to produce large quantities of material was highly impractical. Ironically, the final step in the syntheses of REMP catalysts **2.1** – **2.6** was a ring-closing metathesis (RCM) reaction that required prohibitively high dilution for scale up—REMP was originally conceived to circumvent this exact problem in cyclic polymer synthesis (see intro).

The aforementioned concerns with activity and scalability were compounded by another fundamental problem. Highly pure cyclic polymers could only be isolated if the REMP catalyst was completely removed from the bulk material. No such isolation procedure could be developed because **2.1** – **2.6** were invariably still incorporated into a cyclic polymer backbone, even when all monomer was consumed. The best isolation procedure developed was to rapidly precipitate the polymer under air, leaving the ruthenium catalyst in solution. This involved transferring the REMP reaction from an inert environment to atmospheric

O_2 and adventitious compounds potentially detrimental to polymerization and topological fidelity. Based on NMR experiments, the REMP catalyst was invariably still active and bound to the growing polymer chain at all times due to its living nature. We believe that the linear contaminants in the cyclic polymers isolated with this strategy arose from oxidative decomposition and subsequent chain cleavage localized at the catalyst active site. That is, decomposition at the metal center was thought to induce chain cleavage, resulting in linear chains. We were unable to envision a superior strategy for polymer isolation.

Despite earnest efforts to develop REMP methodology sufficiently to reliably produce large quantities of highly pure cyclic polymer, these problems proved insurmountable. We recognized that to overcome these challenges, a new approach was necessary. Our acceptance of this fact led us to design a radically different REMP catalyst and synthetic methodology. *The path toward, and realization of, a superior REMP strategy began in 2013 and is the subject of this dissertation.*

2.2 – Results and Discussion

The inadequacy of homogeneous REMP catalysts prompted us to investigate a catalyst with minimal structural differences from an existing ROMP catalyst already proven to perform well with common cycloolefin monomers and in a variety of chemical environments. The 2nd Generation Hoveyda-Grubbs catalyst (Fig. 2.3, **2.10**) fulfilled this requirement and was chosen as the template for a new REMP catalyst.

We proposed that as a key design feature, tethering both the NHC ligand and the benzylidene ligand to a solid support would produce catalysts with similar electronic and steric parameters to catalyst **2.10**, but that would lead exclusively to cyclic products. Condensation of these tethers in a ring-closing reaction would then impart the catalyst with the requisite cyclic topology of a REMP catalyst. Additionally, a molecular REMP catalyst covalently bound to a solid surface could be easily separated by filtration, a key advantage over previous catalysts.

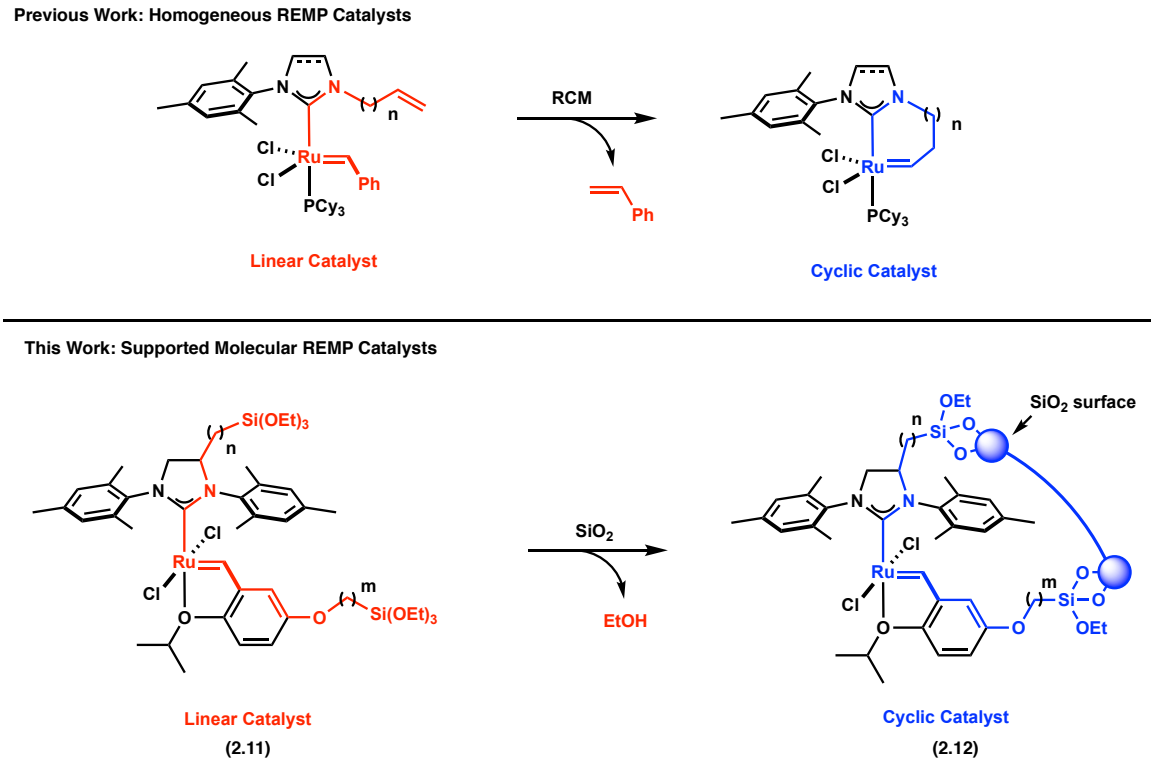


Figure 2.6 | The final ring-closure step to create a new family of REMP catalysts (top), and the analogous final ring-closure step for the previous family of homogeneous REMP catalysts (bottom).

We proposed that catalyst **2.11**, bearing triethoxysilyl-terminated alkyl chains from both NHC ligand and benzylidene ligand, would minimize structural

and electronic distinctions from **2.10** and could easily be attached to silica gel by the displacement of ethanol via Si-OH surface functionality. Ring-closing of **2.11** via condensation of both tethers to the SiO_2 surface would furnish **2.12** (Fig 2.6). Coincidentally and fortuitously, catalyst **2.12** had been reported already in the patent literature,[10] although it had been developed for use in flow reactors for traditional small molecule cross metathesis and ring-closing metathesis reactions. There were also a few examples in the literature describing other types of mono-tethered supported metathesis catalysts. [11-1411-14]

The polymerization profiles of the first generation of homogeneous REMP catalysts **2.1** – **2.6** showed a strong dependence on the tether length between NHC and alkylidene ligands,[5] so a modular approach to catalysts of the type **2.12** with varying tether lengths was targeted. The following describes the synthesis of these catalysts, beginning with the synthesis of triethoxysilyl-functionalized NHC and benzylidene ligands.

The NHC ligands were synthesized over 4 steps beginning with the commercially available starting materials 2,4,6-trimethylaniline and glyoxal to create the diimine **2.13** (Fig 2.7). The synthesis of NHCs with different tether lengths then diverges to form **2.14** and **2.15** using a 3-carbon or 11-carbon Grignard reagent, respectively. Formation of the imidazolidinium chloride salts **2.16** and **2.17** proved facile using $HC(OEt)_3$. A hydrosilylation reaction using Karstedt's Pt^0 catalyst was used to prepare the final NHC-precursors **2.18** and

2.19; indeed, it was this step that introduced the greatest synthetic challenges of any discussed in this chapter. The hydrosilylated NHC-precursors were extremely hygroscopic and surfactant-like during the arduous purification procedure which involved multiple precipitations, aqueous work ups, and rounds of chromatographic purification. In addition, the products were simultaneously acid- and base-sensitive and could not be heated above room temperature without decomposition.

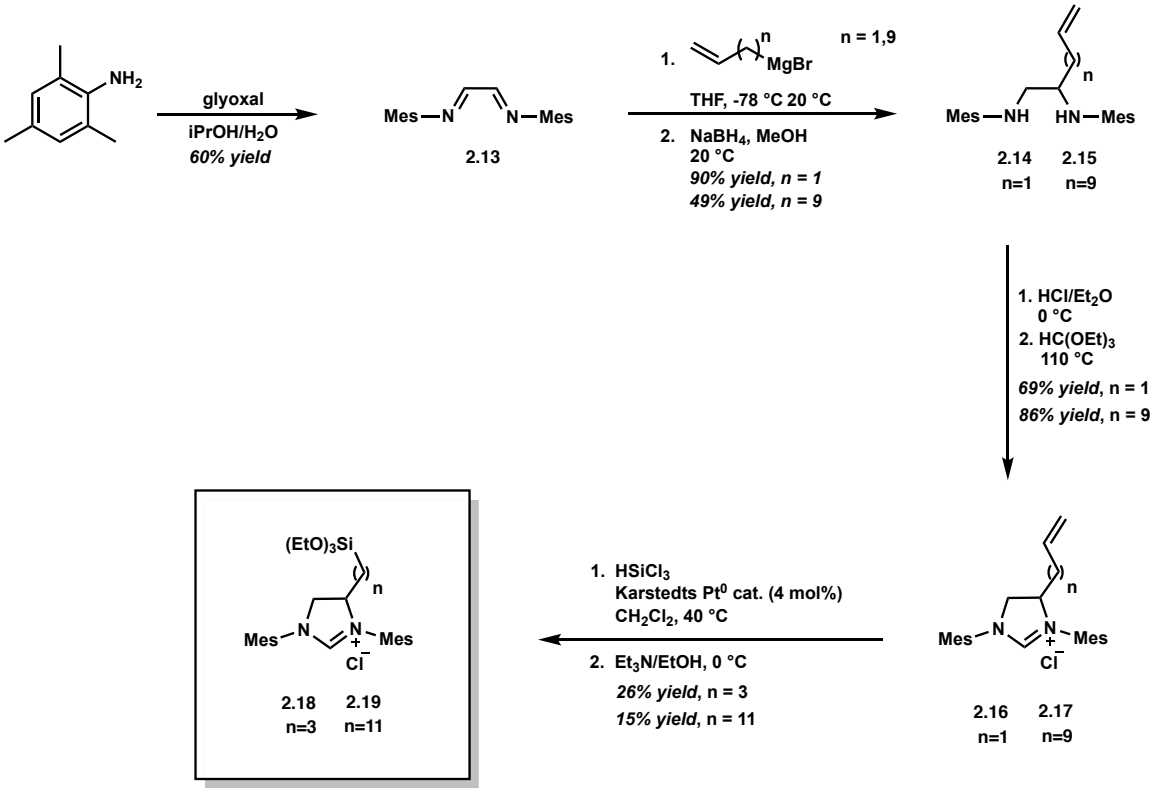


Figure 2.7 | Synthetic scheme for triethoxysilyl-functionalized NHCs **2.18 - 2.19**.

The relatively poor yields for **2.18** and **2.19** (Fig 2.5), 26% and 11%, respectively, were hard fought and ultimately sufficient for the purpose of

preparing REMP catalysts. Nonetheless, the method for their preparation described herein admittedly precludes synthesis at gram-scale at the present time, so the pursuit of an alternative strategy for **2.18** and **2.19** might eventually be required.

The synthetic strategy for the benzylidene ligands was straightforward (Fig 2.8) and began with 2,5-dihydroxybenzaldehyde (**2.20**). Following selective pivalate protection of the hydroxyl group at the 5-position of **2.20**, an alkylation with isopropyl iodide produced the benzaldehyde **2.22** in good yield. Wittig olefination of **2.22** led to an 80% yield with an inconsequential 70:30 *cis:trans* mixture of **2.23**, as the vinyl group would ultimately undergo a cross-metathesis reaction in the final step of the REMP catalyst synthesis, thus ablating the olefin geometry upon attachment of the catalyst.

Deprotection of **2.23** provided the key phenol intermediate **2.24** in excellent yield. Alkylation of phenol **2.24** with a triethoxysilyl-terminated alkyl iodide or bromide (chlorides were unreactive) was a straightforward and modular strategy to provide access to benzylidene ligands with any tether length desired. Triethoxysilyl-functionalized alkyl bromides can be easily accessed from hydrosilylation of the appropriate commercially-available olefin (Fig 2.9, left) and triethoxysilyl-functionalized alkyl iodides can be easily accessed via a Finkelstein reaction of the appropriate commercially-available triethoxysilyl-terminated alkyl chloride (Fig 2.9, right). This strategy was used for benzylidene ligands **2.25** and

2.26 with 3-carbon and 11-carbon tethers, respectively. We envision that future catalyst development will exploit this modularity to explore structure-property relationships of other REMP catalysts with different tether lengths.

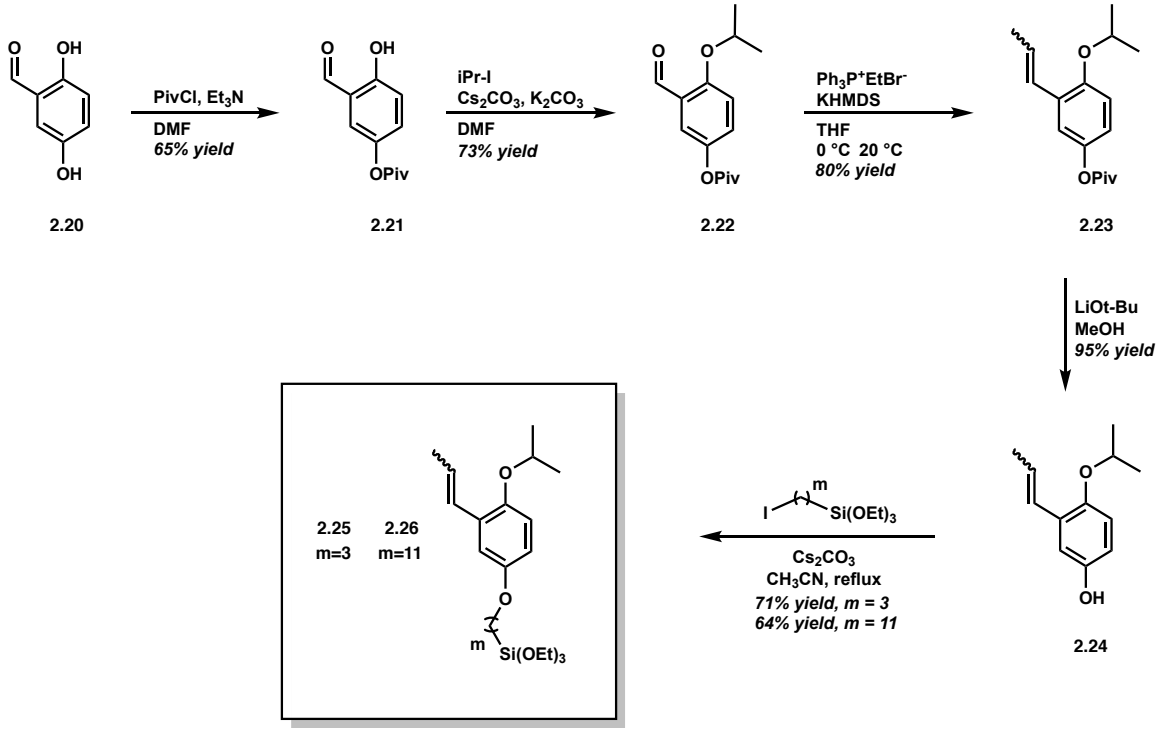


Figure 2.8 | Synthetic scheme for triethoxysilyl-functionalized benzylidene ligands **2.25** - **2.26**.

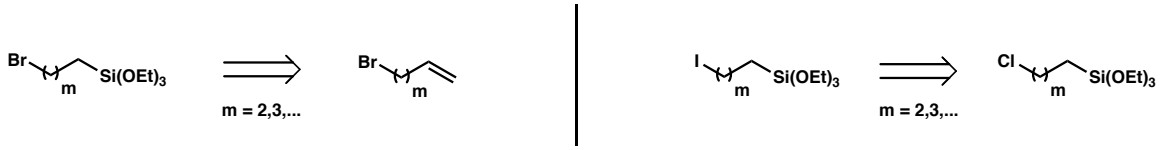


Figure 2.9 | Simple access to triethoxysilyl-terminated alkyl bromides (left) and triethoxysilyl-terminated alkyl iodides (right).

The NHC ligand precursors **2.18** and **2.19**, and benzylidene ligand precursors **2.25** and **2.26**, were successfully isolated in sufficient quantity to begin

the final phase of the molecular REMP catalyst synthesis (Fig 2.10). Metalation of **2.7** (the 1st generation Grubbs catalyst) with **2.18** or **2.19** provided the mono-tethered catalysts **2.27** and **2.28**, with 3- and 11-carbon tethers, respectively, in acceptable yields. Molecular REMP catalysts **2.29** – **2.32** (Fig 2.8, bottom right) were then accessed by the four combinations of cross-metathesis reactions of benzylidene precursors **2.25** and **2.26** with catalysts **2.27** and **2.28.**

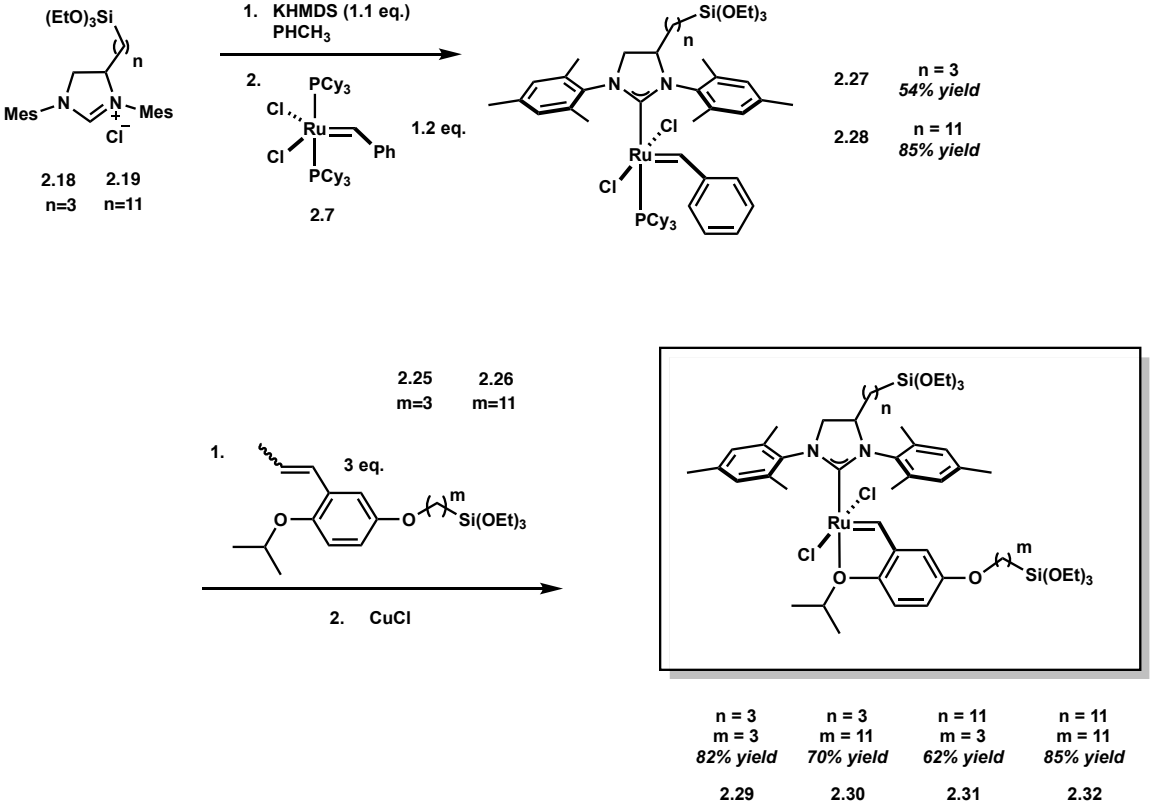


Figure 2.10 | The synthesis of catalysts **2.29** – **2.32**.

The final step in preparing the supported molecular REMP catalysts **2.33** - **2.36** was the ring-closure reaction with the surface of particulate SiO_2 (Fig 2.11),

which is a well-known strategy for surface functionalization. Trialkoxysilyl moeities are commonly chosen to attach organic molecules to hydroxyl-terminated surfaces, such as ZrO_2, Fe_2O_3, and SiO_2. [15-17] Simply stirring **2.33** – **2.36** in a $SiO_2/PhCH_3$ slurry successfully tethered them to the surface, although a Soxhlet extraction of the SiO_2 using CH_2Cl_2 for at least 9 days was necessary to remove residual homogeneous catalyst (**2.29** – **2.32**). To verify that all homogeneous catalyst had been washed away, aliquots of the extraction solvent were periodically added to neat COD until its polymerization could not be observed by GPC.

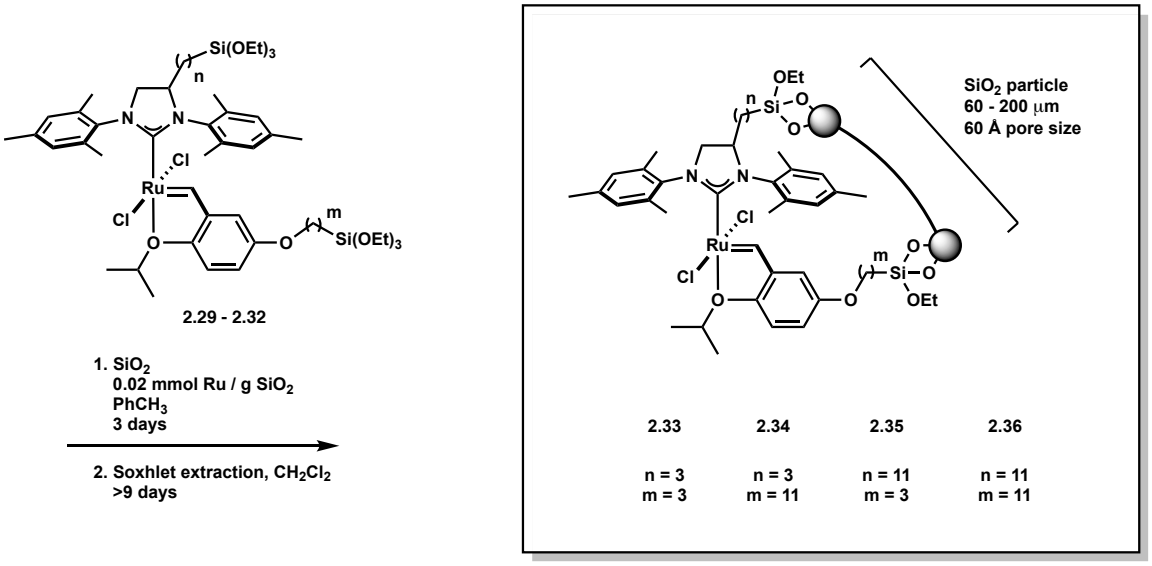


Figure 2.3 | Surface attachment of homogeneous REMP catalysts **2.29 - 2.32** to give supported molecular REMP catalysts **2.33 – 2.26**.

2.3 – Conclusions and Future Outlook

The inherent problems of REMP methodology were discussed, and the poor performance of REMP catalysts was identified as the likely origin of the large

majority of previous negative and inconclusive results from our group. A new REMP catalyst strategy was envisioned, whereby structural elements of the current state-of-the-art ROMP catalysts could be incorporated into a new family of molecular REMP catalysts supported on the surface of silica gel. The synthesis of the new generation of REMP catalysts was reported and shown to be modular for varying tether lengths. This work provided the means to expand REMP methodology for the preparation of large quantities of highly pure cyclic polyolefins.

2.4 – Experimental

General Information: All reactions were carried out in glassware flame-dried in vacuo (100 mTorr) unless otherwise specified. Reactions were performed using air-free Schlenk technique (100 mTorr vacuum and UHP grade 5.0 argon gas) on the benchtop or in a Vacuum Atmospheres glovebox (N_2-filled, O_2 concentration < 0.25 ppm) unless otherwise specified. All solvents were purchased from Sigma-Aldrich (anhydrous, 99.9%) and further purified by passage through solvent purification columns, sparged with argon, and then stored over 4 Å molecular sieves in Strauss flasks, unless otherwise specified.[15] All 1st generation Grubbs catalyst was received from Materia, Inc. (Pasadena, CA) and used without further purification. All other reagents were purchased from Sigma-Aldrich and used as received unless otherwise stated. All reactions performed in Schlenk tubes at elevated temperature were done so with a blast shield in place. Room temperature was 18-20 °C for all syntheses described herein.

All ^{1}H NMR spectra were acquired using a Varian Inova 500 MHz or Bruker 400 MHz spectrometer and are reported relative to residual $CHCl_3$ (δ 7.26 ppm), C_6H_6 (δ 7.16 ppm), or CH_2Cl_2 (δ 5.32 ppm). All ^{13}C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (125 MHz) or Bruker 400 MHz spectrometer (100 MHz) and are reported relative to $CHCl_3$ (δ 77.16 ppm), C_6H_6 (δ 128.06), or CH_2Cl_2 (δ 53.84 ppm). Data for ^{1}H NMR are reported as: chemical shift (δ ppm), multiplicity, coupling constant (Hz), integration value). Multiplicities are reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). Processing of all NMR data was performed with MestReNova version 10.0 from Mestrelabs Research S.L.

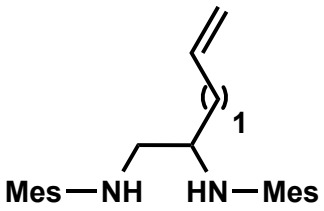
Size-exclusion chromatography (SEC) data was obtained with an HPLC system consisting of two two Agilent PLgel MIXED-B 300×7.5 mm columns with 10 μm beads, and an Agilent 1260 Series pump and autosampler; the columns were connected in series with a Wyatt 18-angle DAWN HELEOS multi-angle laser light scattering detector and Optilab rEX differential refractive index detector. The mobile phase was either pure THF or stabilized THF (50-150 ppm butylated hydroxytoluene (BHT).

Synthesis of NHC precursors 2.13 – 2.19

The following was developed from previously reported procedures.[10]

2.13

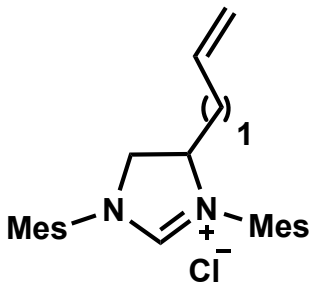
25 mL of 2,4,6-trimethylaniline (24.1 g, 0.178 mmol, 2.25 equiv.) was stirred in 100 mL of isopropyl alcohol and 200 mL deionized water at 0 °C in a 500 mL round bottom flask, in air. A 40% aqueous glyoxal solution (9 mL, 79 mmol, 1.0 equiv.) was added dropwise to the stirring solution and gradually warmed to room temperature. After 12 hours the solution was concentrated via rotovapory distillation. The yellowish-brown precipitate was collected on a coarse frit and washed with water (x1) and hexanes (x3), recrystallized from 1:1 acetone : CH_2Cl_2, and concentrated in vacuo overnight to yield **2.13** as a bright yellow crystalline solid (XX g, XX %). ^{1}H NMR analysis showed a 90:10 mixture of trans/cis isomers and was used without further purification. *Trans* isomer*:* ^{1}H NMR (300 MHz, chloroform-*d*) δ 8.09 (d, *J* = 0.5 Hz, 1H), 6.91 (s, 2H), 2.29 (s, 3H), 2.16 (d, *J* = 0.6 Hz, 7H), 2.01 (d, *J* = 14.5 Hz, 1H). *Cis* isomer: ^{1}H NMR (300 MHz, chloroform-*d*) δ 8.50 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 6.81 (s, 4H), 2.23 (s, 6H), 2.01 (d, *J* = 14.6 Hz, 12H). HRMS (FAB+): found 293.2014, calculated 293.2018.



2.14

A 1 L 2-neck flask was charged with a stir bar and flame dried under vacuum. **2.13** (4.58 g, 15.7 mmol, 1.00 equiv.) was added as a solid and the flask was again pumped on and backfilled with argon. The flask was cooled to -78 °C in a dry ice/acetone bath and 0.4 L THF was cannula transferred into the flask to give a yellow slurry. A 1.0 M solution of allylmagnesium bromide in Et_2O (16.2 mL, 16.2 mmol, 1.03 equiv.) was added dropwise over 1-2 minutes. The mixture then changed to amber/reddish-brown upon warming to room temperature. After 90 minutes, 100 mL MeOH was poured into the stirring reaction mixture, followed by solid $NaBH_4$ (3.56 g, 94.2 mmol, 6.00 equiv.). This mixture was stirred for 3 hours and then slowly quenched with saturated aqueous NH_4Cl until bubbling ceased. The reaction mixture was then extracted with hexanes (x3) and the combined organic layers were washed with water, dried over $MgSO_4$, filtered, and concentrated via rotovapory distillation to provide a crude yellow-brown viscous oil which was then purified by flash column chromatography (25:1 hexanes : EtOAc) to give **2.14** as a faintly yellow oil (2.28 g, 43% yield)(the fractions which were not pure were discarded so that the next step could proceed more cleanly). ^{1}H NMR (400 MHz, methylene chloride-d_2) δ 6.79 (dd, J = 6.6, 0.8 Hz, 4H), 5.80

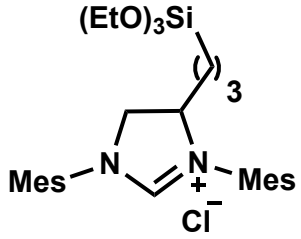
(dddd, *J* = 17.1, 10.2, 8.1, 6.1 Hz, 1H), 5.13 – 5.00 (m, 2H), 3.51 (ddt, *J* = 8.2, 6.9, 4.7 Hz, 1H), 3.17 (dd, *J* = 12.0, 4.6 Hz, 1H), 2.79 (dd, *J* = 12.1, 6.9 Hz, 1H), 2.25 (s, 12H), 2.20 (s, 3H), 2.19 (s, 3H).



2.16

The diamine **2.14** (2.28 g, 6.63 mmol) was transferred to a heavy-walled Schlenk tube equipped with a magnetic stir bar and dissolved in Et_2O. The mixture stirred and was cooled in a 0 °C ice bath. A 2.0 M HCl/Et_2O solution was added dropwise (3.98 mL, 7.95 mmol, 1.20 equiv.) which caused a precipitate to form immediately. All volatile material was removed carefully in vacuo (<100 mTorr) and the solid residue was dissolved in triethyl orthoformate (15 mL, 13.4 g, 90.2 mmol, 13.6 equiv.) which was added via needle and syringe from a sure-seal bottle (neat reaction conditions). The mixture was then stirred at 95 °C overnight. All volatiles were removed in vacuo (100 mTorr) and the sticky brown solid was transferred to a fine fritted filter and then triturated with Et_2O (x3), pentane (x1), and Et_2O (x1). The triturand was then concentrated in vacuo (100 mTorr) to provide **2.16** as a very fine white powder (1.75 g, 69% yield) which could easily be inadvertently sucked into the Schlenk manifold during evacuation. ^{1}H NMR (400 MHz,

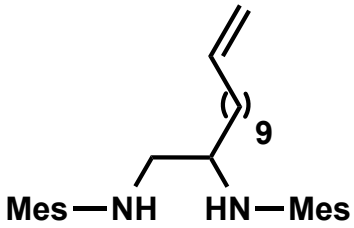
methylene chloride-d_2) δ 10.35 (s, 1H), 7.09 (d, J = 6.9 Hz, 4H), 5.72 – 5.60 (m, 1H), 5.30 – 5.17 (m, 2H), 4.92 – 4.79 (m, 1H), 4.50 (t, J = 11.7 Hz, 1H), 4.02 (dd, J = 12.1, 8.4 Hz, 1H), 2.75 – 2.51 (m, 4H), 2.46 (d, J = 18.3 Hz, 12H), 2.37 (d, J = 2.6 Hz, 6H). ^{13}C NMR (400 MHz, methylene chloride-d_2) δ 142.55, 142.43, 137.95, 136.86, 132.54, 132.17, 132.11, 131.86, 122.15, 64.75, 38.85, 27.06, 22.75, 22.71, 20.86, 20.17.



2.18

The olefin-terminated NHC salt **2.16** was added to a flame dried Schlenk tube under argon (2.11 g, 5.50 mmol, 1.00 equiv.) with stir bar and 10 mL CH_2Cl_2 was cannula transferred. The mixture was cooled to 0 °C and $HSiCl_3$ (22.2 mL, 29.8 g, 220 mmol, 40 equiv.) was added via needle and syringe from a sure-seal bottle. A 0.05 M solution of Karstedt's Pt^0 catalyst in xylenes (4.18 mL, 0.209 mmol, 3.8 mol%) was added in three portions over 15 minutes. The reaction was heated to 40 °C and stirred in the dark for 16 hours. The temperature was lowered to 0 °C and external cold trap (-196 °C) was used to concentrate the reaction mixture in vacuo as it was stirring rapidly (100 mTorr) (necessary to remove excess $HSiCl_3$, which is highly corrosive and volatile). 10 mL of CH_2Cl_2 was then added to redissolve the crude reaction mixture. A 1:1 EtOH:Et_3N (*v/v*) solution was added

dropwise via needle and syringe (10 mL) at 0 °C which produced a white smoke-like substance that gradually dissolved (presumably $Et_3N{\cdot}HCl$). The mixture turned brown gradually and was concentrated via rotovapory distillation after 2 hours. Care was taken to not heat above room temperature. Anhydrous $PhCH_3$ was added to precipitate $Et_3N{\cdot}HCl$; the solution was then filtered through a F porosity frit and concentrated in vacuo (100 mTorr). Silica gel for flash column chromatography was loaded using 2% EtOH/CH_2Cl_2 with 1% additional Et_3N. Two column volumes of 2% EtOH/CH_2Cl_2 were then flushed through the silica gel before the crude residue was eluted using 2% → 5% → 8% EtOH/CH_2Cl_2. Purity of fractions was determined primarily using ^1H NMR due to poor resolution by TLC. The clean fractions were concentrated via rotovapory distillation, redissolved in CH_2Cl_2, and washed with water (x3) to remove residual $Et_3N{\cdot}HCl$. The organic layer was concentrated via rotovapory distillation and the residue lyophilized from C_6H_6 to furnish the silylated NHC salt **2.18** as a hygroscopic white powder (0.78 g, 26% yield). ^1H NMR (400 MHz, methylene chloride-d_2) δ 10.51 (s, 1H), 7.16 – 6.93 (m, 4H), 4.70 (dq, J = 11.4, 8.5 Hz, 1H), 4.54 – 4.42 (m, 1H), 3.95 (dd, J = 11.8, 9.1 Hz, 1H), 3.76 (q, J = 7.0 Hz, 6H), 2.52 – 2.40 (m, 12H), 2.37 (s, 6H), 1.86 (q, J = 7.9, 7.4 Hz, 2H), 1.52 – 1.29 (m, 2H), 1.18 (t, J = 7.0 Hz, 9H), 0.69 – 0.58 (m, 2H).

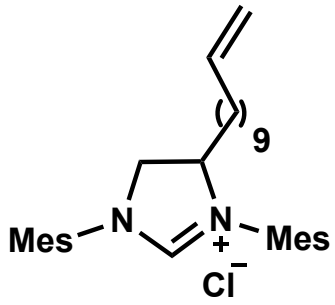


2.15

To a 100 mL Schlenk flask was added Mg^0 (0.510 g, 21.0 mmol, 1.01 equiv., freshly cleaned with aqueous 1 M HCl, dried in vacuo), THF (26.7 mL), and 11-bromo-1-undecene (4.61 mL, 4.90 g, 21.0 mmol, 1.01 equiv.). The solution turned metallic gray after stirring overnight and no Mg^0 was evident. This 0.67 M (assumed) 11-undecenyl-1-magnesium bromide solution was used without titration.

A 1.0 L 2-neck flask was charged with a stir bar and flame dried under vacuum. **2.13** (6.10 g, 20.8 mmol, 1.00 equiv.) was added as a solid and the flask was again pumped on and backfilled with argon. The flask was cooled to -78 °C in a dry ice/acetone bath and 0.3 L THF was cannula transferred into the flask. The yellow solid did not appear fully dissolved. All of the 0.67 M 11-undecenyl-1-magnesium bromide solution (31.3 mL. 1.01 equiv.) was added via syringe over 5 minutes. The mixture then changed to amber/reddish brown upon warming to room temperature. After 2 hours, the reaction mixture was diluted with MeOH (100 mL) and solid $NaBH_4$ (4.7 g, 124 mmol, 6.0 equiv.) was added. After 3 hours the solution was quenched by the dropwise addition of saturated aqueous NH_4Cl until bubbling ceased. The reaction mixture was extracted with hexanes (3x200 mL)

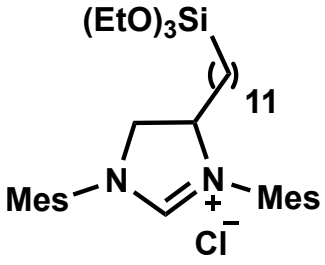
and the combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated to provide 8.2 g crude yield. Flash column chromatography (SiO_2, 25:1 hexanes : EtOAc) provided the diamine **2.15** (3.49 g, 37% yield) which was used without further purification. ^{1}H NMR (400 MHz, chloroform-*d*) δ 6.92 – 6.74 (m, 4H), 5.83 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.13 – 4.81 (m, 2H), 3.45 (q, *J* = 6.7, 6.0 Hz, 1H), 3.21 (dd, *J* = 11.8, 4.4 Hz, 1H), 2.76 (dd, *J* = 11.8, 7.1 Hz, 1H), 2.36 – 2.17 (m, 18H), 2.11 – 1.98 (m, 2H), 1.50 – 1.20 (m, 16H).



2.17

The diamine **2.15** (1.69 g, 3.77 mmol, 1.00 equiv.) was transferred to a heavy-walled Schlenk tube and dissolved in Et_2O. The mixture stirred and was cooled in a 0 °C ice bath. A 2.0 M HCl/Et_2O solution was added dropwise (2.26 mL, 4.52 mmol, 1.20 equiv.) which caused a precipitate to form immediately. All volatile material was removed carefully in vacuo (<100 mTorr) before the solid residue was dissolved in triethyl orthoformate (6.26 mL, 5.58 g, 37.7 mmol, 10.0 equiv.) which was added via needle and syringe from a sure-seal bottle (neat reaction conditions). The mixture stirred at 110 °C overnight. All volatiles were

removed in vacuo (100 mTorr) and the sticky brown solid was transferred to a fine fritted filter and then triturated with Et_2O (x3), pentane (x2), and Et_2O (x3). The triturand was then concentrated in vacuo (100 mTorr) to provide **2.17** as a very fine white powder (0.951 g, 51% isolated yield) which could easily be inadvertently sucked into the Schlenk manifold during evacuation. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.47 (s, 1H), 7.04 – 6.90 (m, 4H), 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.03 – 4.85 (m, 2H), 4.71 (tt, *J* = 9.2, 4.6 Hz, 1H), 3.89 (dd, *J* = 11.7, 8.9 Hz, 1H), 2.50 – 2.24 (m, 18H), 2.04 – 1.98 (m, 2H), 1.76 (dd, *J* = 10.2, 6.2 Hz, 2H), 1.42 – 1.13 (m, 19H), 0.92 – 0.80 (m, 2H). HRMS (FAB+): found 459.3727, calculated 459.3739.



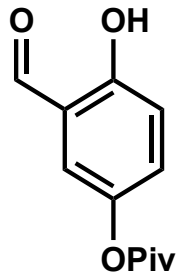
2.19

The olefin-terminated NHC salt **2.17** was added to a flame dried Schlenk tube under argon (1.50 g, 3.03 mmol, 1.00 equiv.) with stir bar and 20 mL CH_2Cl_2 was cannula transferred. The mixture was cooled to 0 °C and $HSiCl_3$ (30 mL, 22 g, 163 mmol, 54 equiv.) was added via needle and syringe from a sure-seal bottle. A 0.05 M solution of Karstedt's Pt^0 catalyst in xylenes (2.30 mL, 0.115 mmol, 3.8 mol%) was added in three portions over 15 minutes. The reaction was heated to 40 °C and stirred in the dark for 16 hours. The temperature was lowered to 0 °C

and an external cold trap (-196 °C) was used to concentrate the reaction mixture in vacuo as it was stirring rapidly (100 mTorr) (necessary to remove excess $HSiCl_3$, which is highly corrosive and volatile). 20 mL of CH_2Cl_2 was then added to redissolve the crude reaction mixture. A 1:1 EtOH:Et_3N (*v/v*) solution was added dropwise via needle and syringe (20 mL) at 0 °C which produced a white smoke-like substance that gradually dissolved (presumably $Et_3N{\cdot}HCl$). The mixture turned brown gradually and was concentrated via rotovapory distillation after 3 hours. Care was taken to not heat above room temperature. Anhydrous $PhCH_3$ was added to precipitate $Et_3N{\cdot}HCl$; the solution was then filtered through a F porosity frit and concentrated in vacuo (100 mTorr). Silica gel for flash column chromatography was loaded using 2% EtOH/CH_2Cl_2 with 1% additional Et_3N. Two column volumes of 2% EtOH/CH_2Cl_2 were then flushed through the silica gel before the crude residue was eluted using 2% → 5% EtOH/CH_2Cl_2. Purity of fractions was determined primarily using ^{1}H NMR due to poor resolution by TLC. The clean fractions were concentrated via rotovapory distillation, redissolved in CH_2Cl_2, and washed with water (x5) to remove residual $Et_3N{\cdot}HCl$. The organic layer was concentrated via rotovapory distillation and the residue lyophilized from C_6H_6 to furnish the silylated NHC salt **2.19** as a hygroscopic white powder (0.30 g, 15% isolated yield). ^{1}H NMR (500 MHz, benzene-d_6) δ 10.60 (s, 1H), 7.08 – 6.96 (m, 4H), 4.77 (ddt, *J* = 13.7, 9.3, 4.4 Hz, 1H), 4.60 (t, *J* = 11.4 Hz, 1H), 3.87 (q, *J* = 7.0 Hz, 7H), 2.57 – 2.43 (m, 12H), 2.35 (d, *J* = 4.5 Hz, 6H), 1.54 – 1.22 (m, 27H), 0.85 – 0.52 (m, 2H).

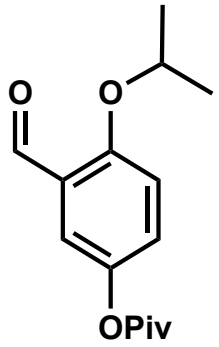
Synthesis of Benzylidene Ligands

The following was developed from previously reported procedures.[10]



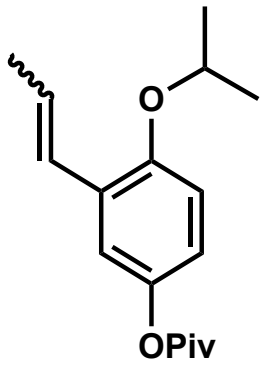
2.21

A 250 mL 3-neck round bottom flask with stir bar was flame-dried and fitted with a dropping funnel. Solid 2,5-dihydroxybenzaldehyde (9.68 g. 70.1 mmol, 1.00 equiv.) was added and dissolved in DMF (0.2 L) and cooled to 0 ºC. Triethylamine (10.5 mL, 80.5 mmol, 1.15 equiv.) was added via needle and syringe. Pivaloyl chloride (9.05 mL, 73.6 mmol, 1.05 equiv.) was added to the dropping funnel via needle and syringe and was then added dropwise to the stirring reaction mixture over 1 hour which produced bubbling and a white gas. After 15 hours the reaction mixture was poured into water (200 mL), extracted with EtOAc (200 mL x5), washed with brine, dried over MgSO4, filtered, concentrated via rotovapory distillation. Flash column chromatography (25:75 hexanes:EtOAc) provided the desired product **2.21** as a colorless oil (11.4 g, 73% yield) (the primary impurity was 2,5-di-pivalated benzaldehyde, a pink oil which eluted first). ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.28 – 9.79 (m, 1H), 7.24 (dd, *J* = 4.5, 2.9 Hz, 1H), 7.08 – 6.94 (m, 2H), 1.43 (s, 9H).



2.22

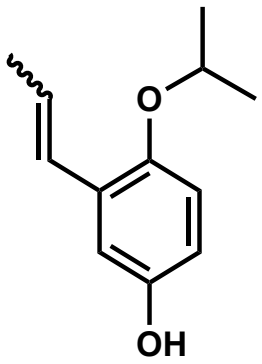
2.21 (5.62 g, 25.28 mmol, 1.00 equiv.) was dissolved in DMF (0.1 L) in a 2-neck round bottom flask. Solid K_2CO_3 (5.24 g, 37.9 mmol, 1.5 equiv.) and solid Cs_2CO_3 (0.70 g, 5.06 mmol, 0.20 equiv.) were added to the stirring solution. 2-iodopropane (6.44 g, 37.9 mmol, 1.5 equiv.) was added via needle and syringe and the mixture stirred at room temperature. Upon complete consumption of starting material by TLC, the reaction mixture was poured into water (0.7 L) and extracted with EtOAc (100 mL x5). The combined organic extracts were washed with 5% aqueous LiCl (x2) and water (x1), dried over $MgSO_4$, filtered, concentrated via rotovapory distillation, and further purified using flash column chromatography (10:90 hexanes : EtOAc) to give **2.22** as a colorless oil (5.44 g, 83% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ 10.44 (s, 1H), 7.48 (d, *J* = 3.0 Hz, 1H), 7.22 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 4.66 (hept, *J* = 6.1 Hz, 1H), 1.41 (d, *J* = 6.1 Hz, 6H), 1.35 (s, 9H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 189.35, 177.23, 158.14, 144.31, 128.96, 126.13, 120.64, 115.02, 71.76, 39.05, 27.13, 22.00.



2.23

2.22 (1.54 g, 5.83 mmol, 1.00 equiv.) was dissolved in THF (50 mL) and stirred at 0 °C in a 500 mL 2-neck round bottom flask which had been flame dried. A KHMDS/THF solution was prepared in the glovebox (1.28 g, 6.41 mmol, 1.10 equiv.) and transferred to $EtPPh_3Br$ (2.38 g, 6.41 mmol, 1.10 equiv.) which was dissolved in THF (50 mL) and stirred in a 100 mL 2-neck round bottom flask at 0 °C. (Note: LHMDS/THF solution was not suitable for this reaction as it lead to undesired side-products). The ylide solution (vibrant orange) was cannula transferred to the reaction flask which was then allowed to gradually warm to room temperature overnight. The reaction was monitored after 16 hours by TLC (40:60 CH_2Cl_2: hexanes) at which point all starting material was consumed. The reaction mixture was then poured into Et_2O (1 L) to precipitate phosphine oxides and KBr, filtered to remove phosphine oxides and KBr, dried over $MgSO_4$, filtered, and concentrated via rotovapory distillation. The crude reaction mixture was further purified by flash column chromatography (40:60 CH_2Cl_2 : hexanes) to provide a mixture of *cis/trans* (69:31) olefinated product **2.23** as a clear oil (1.30

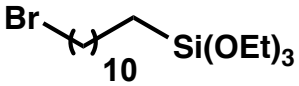
g, 80% yield) which was concentrated in vacuo (100 mTorr) and used for further syntheses as the mixture of *cis* and *trans* isomers. ^{1}H NMR (500 MHz, methylene chloride-d_2) δ 7.17 – 6.50 (m, 4H), 6.28 (dq, J = 15.9, 6.7 Hz, 0.29 H (*trans*)), 5.88 (dq, J = 11.6, 7.1 Hz, 0.71 H (*cis*)), 4.55 (hept, J = 6.1 Hz, 1H), 1.93 (ddd, J = 33.9, 6.9, 1.8 Hz, 3H), 1.43 – 1.37 (m, 16H). ^{13}C NMR (500 MHz, methylene chloride-d_2) δ 153.05, 128.39, 126.97, 126.80, 124.93, 122.99, 120.20, 120.15, 118.84, 114.90, 114.48, 71.30, 53.88, 53.66, 53.44, 53.29, 53.23, 53.07, 53.01, 38.85, 26.90, 26.89, 22.34, 21.89, 14.39, 13.82.



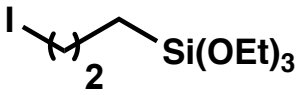
2.24

2.23 (1.30 g, 4.71 mmol, 1.00 equiv) was stirred in MeOH (50 mL) at 0 ºC in a 250 mL round bottom flask. Solid LiO^tBu (1.885 g, 23.4 mmol, 5 equiv.) was added in one portion and the reaction mixture was allowed to gradually warm to room temperature. After reaction completion by TLC (10:90 hexanes: EtOAc), the reaction mixture was quenched with addition of saturated aqueous NH_4Cl until bubbling ceased. The mixture was added to 500 mL EtOAc and washed with

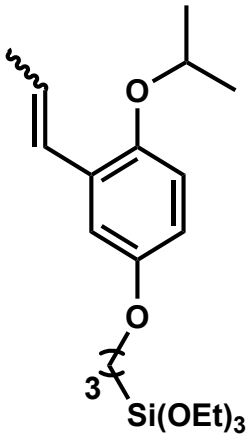
water (3x). The organic layer was dried over $MgSO_4$, filtered, concentrated via rotovapory distillation, and further purified by flash column chromatography to provide the desired product as a colorless oil (0.904 g, 95% yield). ^{1}H NMR (400 MHz, methylene chloride-d_2) δ 6.92 (d, J = 3.1 Hz, 1H), 6.86 – 6.76 (m, 2H), 6.73 – 6.62 (m, 2H), 6.56 – 6.46 (m, 1H), 6.22 (dq, J = 15.9, 6.6 Hz, 1H), 5.82 (dq, J = 11.7, 7.1 Hz, 1H), 4.65 – 4.60 (m, 1H), 4.37 (dtd, J = 12.1, 6.1, 0.5 Hz, 1H), 1.91 (dd, J = 6.7, 1.8 Hz, 1H), 1.87 (dd, J = 7.1, 1.9 Hz, 3H), 1.32 (d, J = 6.1 Hz, 3H), 1.30 (d, J = 6.1 Hz, 6H). ^{13}C NMR (500 MHz, CD_2Cl_2) δ 149.69, 149.08, 129.26, 126.59, 126.27, 125.45, 125.35, 117.09, 116.71, 114.08, 113.94, 112.27, 72.14, 71.99, 21.94, 18.57, 14.48. HRMS (FAB+): found 192.1168, calculated 192.1150.



A flame dried Schlenk tube was charged with $HSi(OEt)_3$ (5.5 mL, 0.030 mmol, 1.3 equiv.) and 11-bromo-1-undecene (5.0 mL, 22.8 mmol, 1.0 equiv.). A 0.05 M solution of Karstedt's Pt^0 catalyst (1.125 mL, 0.04 equiv.) was added via needle and syringe and the mixture stirred at 50 °C for 4 hours. 11-bromoundecyl)triethoxysilane was obtained from flash column chromatography (1% to 3% Et_2O: pentane) (visualized TLC with phosphomolybdic acid stain) as a clear oil. ^{1}H NMR (400 MHz, chloroform-d) δ 3.84 (q, J = 7.0 Hz, 6H), 3.43 (t, J = 6.9 Hz, 2H), 1.94 – 1.80 (m, 2H), 1.51 – 1.19 (m, 26H), 0.73 – 0.48 (m, 2H). ^{13}C NMR (400 MHz, chloroform-d) δ 58.31, 34.12, 33.21, 32.86, 29.56, 29.50, 29.45, 29.25, 28.79, 28.20, 22.77, 18.33, 10.39.



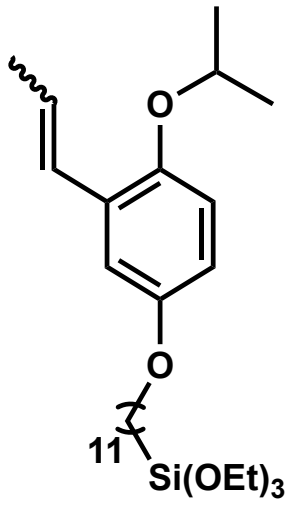
A 100 mL 2-neck round bottom flask was charged with (3-chloro-propyl) triethoxysilane (4.8 g, 0.20 mmol, 1.0 equiv.) and dissolved in dry acetone (30 mL). Recently dried solid NaI (12.0 g, 0.80 mmol, 4.0 equiv.) was added and the suspension stirred for 16 hours. The mixture was poured into pentane (100 mL) to precipitate inorganic salts and concentrated in vacuo (100 mTorr). The yellow oil was then flushed through a silica plug with 10:90 Et_2O: pentane and concentrated in vacuo (100 mTorr) to yield a 75:25 mixture of (3-iodo-propyl) triethoxysilane: (3-chloro-propyl)triethoxysilane which was used without further purification. ^{1}H NMR (400 MHz, benzene-*d*6) δ 3.72 (qd, *J* = 7.0, 2.9 Hz, 6H), 3.20 (t, *J* = 6.8 Hz, 0H), 2.83 (t, *J* = 7.0 Hz, 0H), 1.91 – 1.76 (m, 0H), 1.12 (td, *J* = 7.0, 1.6 Hz, 1H), 0.73 – 0.49 (m, 0H).



2.25

Phenol **2.24** (0.120 g, 0.624 mmol, 1.0 equiv.) was stirred in CH_3CN (5 mL) in an oven dried 20 mL vial with septum cap. Solid Cs_2CO_3 (0.305 g, 0.936 mmol,

1.50 equiv.) was flame dried inside a 50 mL 2-neck round bottom flask. The phenol/CH_3CN solution was transferred via needle and syringe to the 2-neck flask and rinsed with an additional 5 mL CH_3CN which was transferred to the 2-neck flask. (3-iodo-propyl) triethoxysilane (0.50 mL, 75% purity) was added via needle and syringe. The reaction mixture stirred at reflux for 16 hours at which point TLC confirmed complete consumption of starting material. The reaction mixture was diluted with 1:1 pentane: Et_2O, the solid precipitate filtered off, and the organic layer concentrated via rotovapory distillation. The crude product was purified via flash column chromatography (3:97 EtOAc: hexanes) to provide **2.25** as a clear colorless oil (0.174 g, 70% yield). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.09 – 6.46 (m, 4H), 6.21 (dq, *J* = 15.9, 6.6 Hz, 1H), 6.30 – 5.71 (m, 1H), 5.81 (dq, *J* = 11.6, 7.1 Hz, 1H), 4.36 (dp, *J* = 7.7, 6.0 Hz, 1H), 3.92 (td, *J* = 6.7, 1.5 Hz, 2H), 3.86 (qd, *J* = 7.0, 0.7 Hz, 6H), 1.98 – 1.78 (m, 5H), 1.32 (dd, *J* = 9.0, 6.1 Hz, 6H), 1.25 (td, *J* = 7.0, 0.9 Hz, 9H), 0.86 – 0.70 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 153.46, 152.80, 149.67, 148.75, 129.68, 129.26, 126.65, 126.09, 125.84, 125.68, 117.13, 116.86, 116.53, 113.63, 113.33, 111.99, 77.23, 72.32, 72.27, 70.47, 70.40, 58.43, 58.32, 22.89, 22.27, 18.90, 18.46, 18.32, 14.78, 6.51. HRMS (FAB+),: found 397.1765, calculated 397.1773.



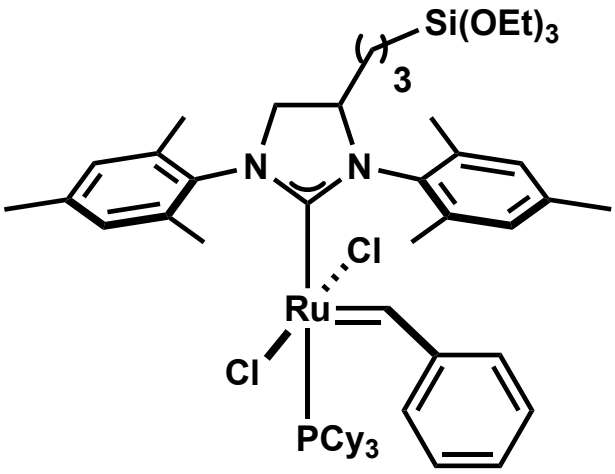
2.26

Phenol **2.24** (0.290 g, 1.51 mmol, 1.00 equiv.) was stirred in CH_3CN (15 mL) in an oven dried 20 mL vial with septum cap. Solid Cs_2CO_3 (0.736 g, 2.26 mmol, 1.50 equiv.) was flame dried inside a 100 mL 2-neck round bottom flask. The phenol/CH_3CN solution was transferred via needle and syringe to the 2-neck flask and rinsed with an additional 15 mL CH_3CN which was transferred to the 2-neck flask. (11-bromoundecyl)triethoxysilane (0.800 g, 2.06 mmol, 1.37 equiv.) was added via needle and syringe. The reaction mixture stirred at reflux overnight. The reaction mixture was diluted with 1:1 pentane: Et_2O and the solid precipitate filtered off, and the organic layer concentrated via rotovapory distillation. The crude product was purified via flash column chromatography (2:98 EtOAc: hexanes) to provide **2.26** as a clear, colorless oil (0.492 g, 64% isolated yield). ^1H NMR (400 MHz, chloroform-*d*) δ 7.01 – 6.48 (m, 4H), 5.82 (dq, *J* = 11.6, 7.1 Hz, 1H), 4.36 (dp, *J* = 7.5, 6.0 Hz, 1H), 3.93 (td, *J* = 6.6, 1.0 Hz, 2H), 3.84 (q, *J* = 7.0

Hz, 6H), 1.89 (ddd, *J* = 15.3, 6.9, 1.8 Hz, 3H), 1.78 (pd, *J* = 6.6, 2.1 Hz, 2H), 1.53 – 1.17 (m, 32H), 0.74 – 0.54 (m, 2H). ^{13}C NMR (400 MHz, chloroform-*d*) δ 129.67, 126.66, 126.10, 125.84, 125.67, 117.12, 116.83, 116.51, 113.58, 113.30, 111.94, 72.31, 68.56, 58.30, 33.23, 29.63, 29.61, 29.56, 29.46, 29.28, 26.10, 22.78, 22.28, 18.91, 18.33, 14.80, 10.39. HRMS (FAB+): found 508.3599, calculated 508.3584.

Homogeneous REMP Catalyst Synthesis

The following was developed from previously reported procedures.[10]

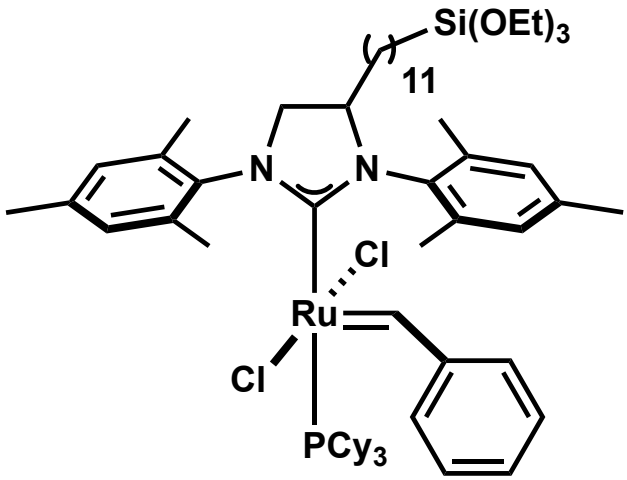


2.27

Outside the glovebox, a vacuum filtration tube half-filled with oven dried celite was fitted to a 25 mL 2-neck round bottom flask containing **2.7** (208 mg, 0.253 mmol, 1.25 equiv.), the first generation Grubbs catalyst. Solid **2.18** (114 mg, 0.202 mmol, 1.00 equiv.) was weighed into a 20 mL vial with stir bar and septum cap inside the glove box and then dissolved in $PhCH_3$ (2 mL). Solid

KHMDS (42.4 mg. 0.212 mmol, 1.05 equiv.) was dissolved in 2 mL $PhCH_3$ and transferred to the stirring solution of **2.18**. After 25 minutes, the vial was removed from the glovebox, and the amber solution was transferred via needle and syringe to the top of the celite plug within the vacuum filtration tube. Brief vacuum force was used to draw the solution into the stirring **2.7**. The original vial containing **2.18** was washed with $PhCH_3$ (5 mL)which was then transferred similarly to the stirring **2.7** via the vacuum filtration tube. After 3 hours, the reaction mixture was transferred directly onto silica gel for column chromatography (without concentration). The silica gel was untreated and the column was run without inert gas. The crude reaction mixture was eluted through the silica column with 10:90 Et_2O: pentane which easily separated the bright purple band (unreacted **2.7**, eluted first), from the pinkish-red band (desired product **2.27**, eluted second). This band was collected and concentrated via rotovapory distillation, redissolved in benzene, transferred to a storage vial, and lyophilized overnight (100 mTorr) to provide **2.27** as a red powder (115 mg, 54% yield). ^{1}H NMR (400 MHz, benzene-d_6) δ 19.69 (s, 1H), 7.03 – 6.88 (m, 5H), 3.69 (dq, J = 13.9, 7.0 Hz, 6H), 2.50 (d, J = 11.4 Hz, 6H), 2.21 (d, J = 15.7 Hz, 6H), 1.83 (d, J = 20.5 Hz, 6H), 1.58 (d, J = 15.9 Hz, 34H), 1.11 (dt, J = 10.6, 7.0 Hz, 32H), 0.43 (dt, J = 29.6, 7.9 Hz, 2H). ^{31}P NMR (400 MHz, benzene-d_6) δ 28.71 (s). ^{13}C NMR (400 MHz, C_6D_6) δ 151.66, 151.48, 137.85, 137.59, 137.54, 137.11, 136.88, 135.54, 134.40, 130.26, 129.97, 129.83, 129.41, 128.91, 128.21, 127.80, 127.56, 127.02, 64.63, 58.12, 58.09,

57.08, 36.44, 31.68, 31.51, 29.26, 27.91, 27.81, 26.25, 22.10, 20.89, 20.82, 20.72, 20.65, 20.30, 20.13, 19.99, 19.01, 18.78, 18.23, 18.20, 10.58, 10.48. HRMS (FAB+): found 1052.450, calculated 1052.449.

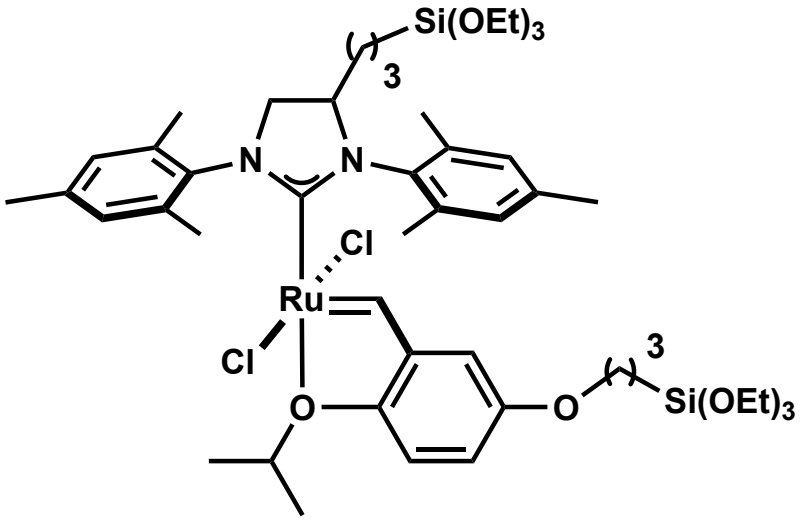


2.28

Outside the glovebox, a vacuum filtration tube with oven dried celite was fitted to a 50 mL 2-neck round bottom flask containing **2.7** (258 mg, 0.313 mmol, 1.25 equiv.), the first generation Grubbs catalyst. Solid **2.19** (172 mg, 0..261 mmol, 1.00 equiv.) was weighed into a 20 mL vial with stir bar and septum cap inside the glove box and then dissolved in 4 mL $PhCH_3$. Solid KHMDS (57 mg, 0.212 mmol, 1.10 equiv.) was dissolved in 4 mL $PhCH_3$ and transferred to the stirring solution of **2.19**. After 30 minutes, the vial was removed from the glovebox, and the amber solution was transferred via needle and syringe to the top of the

celite plug within the vacuum filtration tube. Brief vacuum force was used to draw the solution into the stirring **2.7**. The original vial containing **2.19** was washed with $PhCH_3$ (6 mL) which was then transferred via needle and syringe to **2.7** while stirring via the vacuum filtration tube. After 5 hours, the reaction mixture was transferred directly onto silica gel for column chromatography without concentration, via rotovapory distillation or otherwise. The silica gel was untreated and the column was run without inert gas. The crude reaction mixture was eluted through the silica column with 10:90 Et_2O: pentane which easily separated the bright purple band (unreacted **2.7**, eluted first), from the pinkish-red band (desired product **2.28**, eluted second). A green band developed at the top of the column but could not be eluted with any solvent and was never identified. The pinkish-red band was collected and concentrated via rotovapory distillation, redissolved in benzene, transferred to a storage vial, and lyophilized overnight (100 mTorr) to provide **2.28** as a sticky red solid (204 mg, 85% yield). ^{1}H NMR (400 MHz, benzene-d_6) δ 19.68 (s, 1H), 6.96 (q, J = 5.8 Hz, 7H), 3.82 (qd, J = 7.0, 1.6 Hz, 11H), 2.49 (d, J = 11.6 Hz, 6H), 2.21 (d, J = 13.8 Hz, 6H), 1.83 (d, J = 18.6 Hz, 7H), 1.71 – 1.47 (m, 34H), 1.18 (td, J = 7.0, 1.5 Hz, 17H), 0.82 – 0.74 (m, 4H). ^{31}P NMR (400 MHz, benzene-d_6) δ 28.76 (s). ^{13}C NMR (101 MHz, C_6D6) δ 151.64, 151.45, 139.11, 137.96, 137.73, 137.54, 137.21, 137.00, 136.68, 135.57, 134.41, 130.28, 130.08, 129.99, 129.86, 129.44, 129.14, 128.95, 64.75, 58.30, 58.27, 58.11, 57.25, 35.74, 35.13, 33.27, 31.95, 31.76, 31.67, 31.51, 31.39, 31.26, 29.78, 29.70,

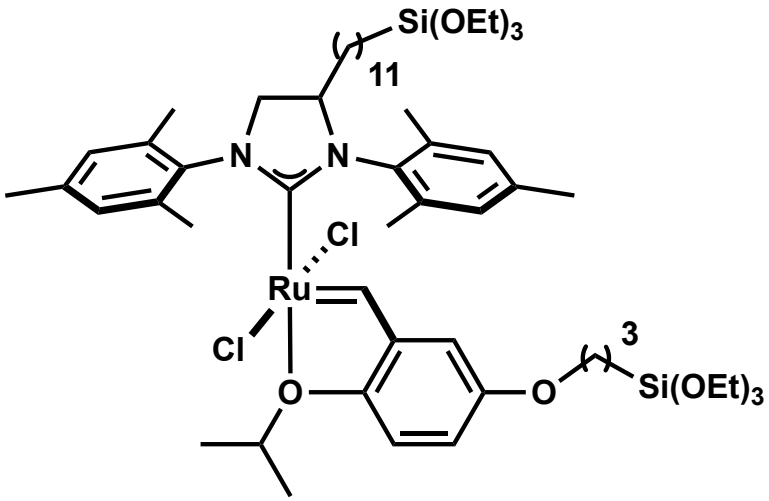
29.67, 29.60, 29.55, 29.53, 29.49, 29.47, 29.45, 29.39, 29.29, 29.28, 27.91, 27.81, 27.73, 27.64, 26.94, 26.82, 26.62, 26.48, 26.45, 26.40, 26.25, 23.16, 22.11, 20.89, 20.82, 20.76, 20.72, 20.65, 20.42, 20.33, 20.31, 19.05, 18.80, 18.31, 10.86. HRMS (FAB+): found 1164.575, calculated 1164.574.



2.29

Solid **2.27** (58.9 mg, .0551 mmol, 1.00 equiv.) was weighed into a 20 mL vial inside the glove box and then dissolved in $PhCH_3$ (5 mL). **2.25** (65.6 mg, 0.165 mmol, 3.00 equiv.) was dissolved in $PhCH_3$ (2 mL) and this solution was transferred to the dark red stirring solution of **2.27**. The reaction mixture turned brown over the course of 60 minutes, at which point CuCl (10 mg) was added directly to the solution as a powdery white solid. This suspension stirred in the glovebox for 4 hours and gradually became a forest green color during this period. This solution was transferred directly to a 10:90 Et_2O: pentane silica gel column and a few column volumes of 10:90 Et_2O: pentane were flushed through to elute an

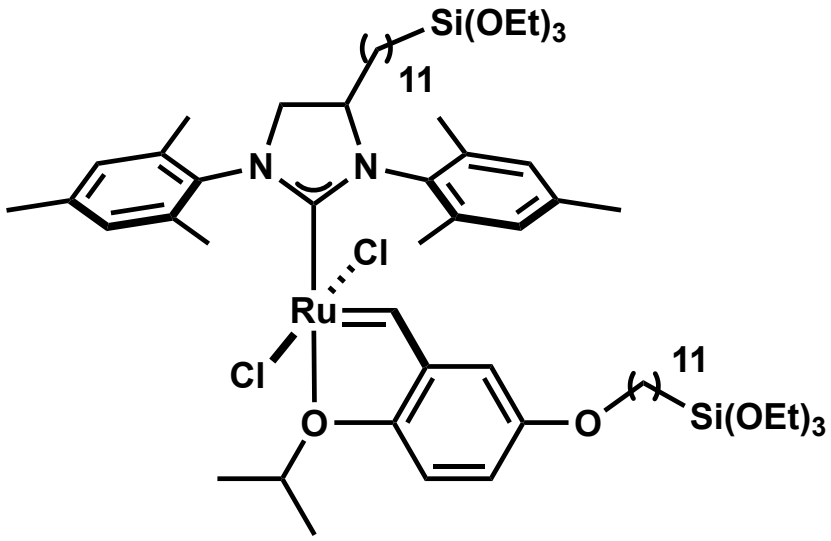
undesired broad yellow band. 30:70 Et_2O: pentane was then used to elute the green band which was collected, concentrated via rotovapory distillation, redissolved in Et2O, transferred to a storage vial, concentrated in vacuo (100 mTorr) to provide **2.29** as a dark green sticky solid (48 mg, 82%). ^{1}H NMR (400 MHz, benzene-d_6) δ 16.55 (s, 1H), 6.92 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.73 (d, *J* = 3.0 Hz, 1H), 6.34 – 6.14 (m, 1H), 4.44 (hept, *J* = 6.1 Hz, 1H), 4.32 – 4.18 (m, 1H), 3.77 (dq, *J* = 30.4, 7.0 Hz, 11H), 3.62 (t, *J* = 10.2 Hz, 1H), 3.48 (t, *J* = 10.2 Hz, 1H), 2.25 (d, *J* = 14.0 Hz, 5H), 2.09 – 1.97 (m, 2H), 1.86 – 1.57 (m, 2H), 1.37 – 1.25 (m, 6H), 1.25 – 1.11 (m, 16H), 0.98 – 0.81 (m, 2H), 0.51 (t, *J* = 7.9 Hz, 2H).



2.31

Solid **2.28 (**56 mg, 0.048 mmol, 1.0 equiv.) was dissolved in $PhCH_3$ (4 mL) in a 20 mL vial inside the glovebox. **2.25** (57 mg, 0.144 mmol, 3.0 equiv.) was dissolved in $PhCH_3$ (4 mL) and transferred to the stirring solution of **2.28.** The solution turned brown over the course of 1 hour, at which point CuCl (20 mg) was

added as a solid white powder. The reaction mixture turned green after 4 hours, and after an additional hour, it was added directly to a 10:90 Et_2O: pentane silica gel column and a yellow band eluted first. The green band of desired product **2.31** was eluted using 25:75 Et2O: pentane, collected, concentrated via rotovapory distillation, redissolved in Et2O, and transferred to a 20 mL storage vial, concentrated in vacuo to give **2.31** as a dark green sticky solid (34.9 mg, 62% yield). ^{1}H NMR (400 MHz, benzene-d_6) δ 16.32 (s, 1H), 6.70 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.51 (d, *J* = 3.0 Hz, 1H), 6.09 – 5.84 (m, 1H), 4.22 (hept, *J* = 6.1 Hz, 1H), 4.02 (tt, *J* = 11.5, 7.3 Hz, 1H), 3.61 (q, *J* = 7.1 Hz, 11H), 3.44 (dd, *J* = 11.6, 8.7 Hz, 1H), 3.22 (t, *J* = 10.2 Hz, 1H), 2.03 (d, *J* = 13.1 Hz, 6H), 1.88 – 1.71 (m, 2H), 1.50 – 1.38 (m, 3H), 1.19 – 1.06 (m, 8H), 0.97 (td, *J* = 7.0, 3.6 Hz, 17H), 0.84 – 0.72 (m, 2H), 0.70 – 0.61 (m, 2H), 0.61 – 0.54 (m, 2H). ^{13}C NMR (400 MHz, C_6D_6) δ 154.53, 146.39, 145.85, 140.26, 138.24, 138.20, 129.99, 129.54, 129.25, 128.32, 127.80, 127.57, 114.51, 112.94, 107.58, 74.41, 70.43, 58.24, 58.13, 34.03, 33.30, 30.56, 30.11, 29.74, 29.72, 29.65, 29.57, 29.49, 29.43, 26.98, 26.15, 25.82, 23.19, 21.08, 20.75, 20.68, 18.31, 18.29, 10.89, 6.91.



2.32

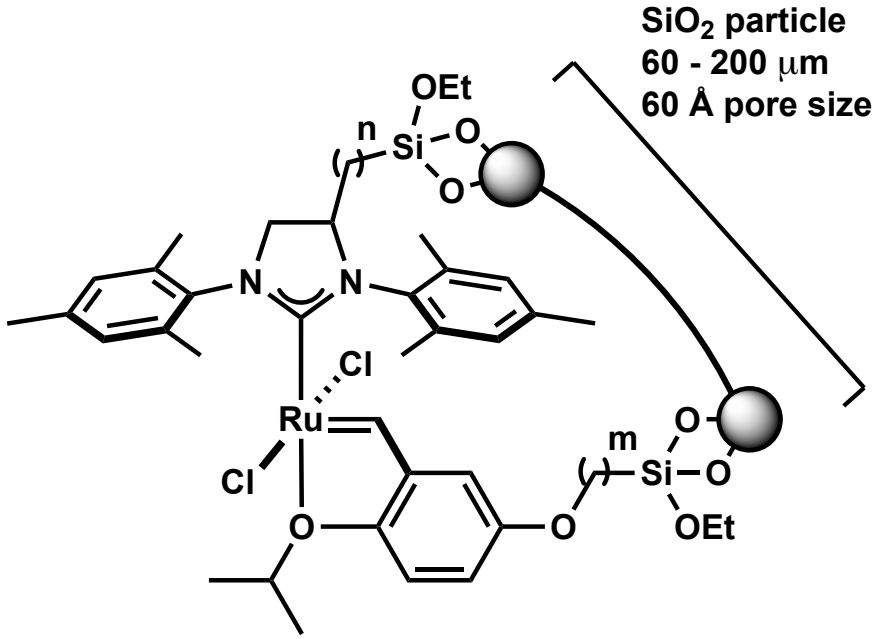
Solid **2.28 (**56 mg, 0.048 mmol, 1.0 equiv.) was dissolved in $PhCH_3$ (4 mL) in a 20 mL vial inside the glovebox. **2.26** (73.3 mg, 0.144 mmol, 3.0 equiv) was dissolved in $PhCH_3$ (4 mL) and transferred to the stirring solution of **2.28.** The solution turned brownish green over the course of 1 hour, at which point CuCl (20 mg) was added as a solid white powder. The reaction mixture turned green after 4 hours, and after an additional hour it was added directly to a 10:90 Et_2O: pentane silica gel column and a yellow band eluted first. The green band of desired product **2.32** was eluted using 30:70 Et_2O: pentane, collected, concentrated via rotovapory distillation, redissolved in Et_2O, and transferred to a 20 mL storage vial, and concentrated in vacuo to give **2.32** as a dark green sticky solid (34.9 mg, 62% yield).

^{1}H NMR (400 MHz, benzene-d_6) δ 16.35 (s, 1H), 6.72 (dd, J = 8.9, 3.0 Hz, 1H), 6.52 (d, J = 2.9 Hz, 1H), 6.22 – 5.64 (m, 1H), 4.24 (p, J = 6.2 Hz, 1H), 4.09 – 3.92 (m,

1H), 3.61 (qd, *J* = 7.0, 3.6 Hz, 11H), 3.54 – 3.40 (m, 2H), 3.22 (t, *J* = 10.1 Hz, 1H), 2.04 (d, *J* = 12.9 Hz, 6H), 1.53 – 1.37 (m, 4H), 1.26 – 1.17 (m, 4H), 1.16 – 1.05 (m, 19H), 0.97 (td, *J* = 7.0, 3.3 Hz, 17H), 0.84 – 0.72 (m, 2H), 0.63 – 0.53 (m, 4H).

Supported Molecular REMP Catalysts 2.33 – 2.36

The following was developed from previously reported procedures.[10]



2.33	2.34	2.35	2.36
n = 3	n = 3	n = 11	n = 11
m = 3	m = 11	m = 3	m = 11

General Procedure for 2.33 – 2.36: The corresponding molecular REMP catalyst (**2.29-2.32**) (0.100 mmol) was weighed into a 40 mL scintillation vial inside the glovebox and dissolved in $PhCH_3$ (10 mL). SiO_2 (5.00 g) was added as a powder along with stir bar and enough $PhCH_3$ to create a $SiO_2/PhCH_3$ slurry. The

suspension was then stirred in the glovebox for 3.5 days. The vial was then removed from the glove box, and the supernatant of the slurry was decanted. The slurry was concentrated in vacuo until it was a free-flowing green powder (100 mTorr, >1 day). At this point, the green powder was transferred to a cellulose extraction thimble and placed in a flame-dried Soxhlet extraction apparatus, under positive argon flow. The green powder was then continuously extracted with CH_2Cl_2 for 10 days. The extraction thimble was removed from the Soxhlet extraction apparatus, placed in a jar within a vacuum chamber and concentrated in vacuo (100 mTorr, 2 days). See Appendix for solid state ^{1}H NMR spectrum of **2.34**.

2.5 – References

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