SYNTHESIS OF ALTERNATING TRANS-AB COPOLYMERS THROUGH RING-OPENING METATHESIS POLYMERIZATION INITIATED BY MO-LYBDENUM ALKYLIDENES

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ABSTRACT: Four alternating AB copolymers have been prepared through ring-opening metathesis polymerization (ROMP) with Mo(NR)(CHCMe6)(OCMe(CF3)2)2 initiators (R = 2,6-Mes2C6H3 (1) or 2,6-i-Pr2C6H3 (2)). The AB monomer pairs copolymerized by 1 are cyclooctene (A) and 2,3-dicarbomethoxy-7-isopropylidenenorbornadiene (B), cycloheptene (A') and dimethylspiro[2.2.1]hepta-2,5-diene-2,3-dicarboxylate-7,1'-cyclopropane] (B'), A and B', and A' and B; A' and B' and A and B' are also copolymerized by 2. The >90% poly(A-alt-B) copolymers are formed with hetero dyads (AB) that have the trans configuration. Evidence suggests that one trans hetero C=C bond is formed when A (A or A') reacts with the syn form of the alkylidene made from B (syn-MB = syn-MB or syn-MB') to give anti-MA, while the other trans C=C bond is formed when B reacts with anti-MA to give syn-MB. Cis and trans AA dyads are proposed to arise when A reacts with anti-MA in competition with B reacting with anti-MA.

AB copolymers in which monomers A and B are incorporated in a perfectly alternating manner (poly(A-alt-B)) are rare relative to homopolymers. Perhaps the best known are AB copolymers prepared from CO and olefins or CO2 and epoxides. Synthesis of AB copolymers when one of the monomers is CO or CO2 has been relatively successful because neither CO nor CO2 can be homopolymerized.

In the last ten to fifteen years, ring-opening metathesis polymerization (ROMP) has been employed to make alternating AB copolymers, in some cases with an AB structure greater than 95%. In some cases, an acyclic diene is employed as one of the monomers, as in the copolymerization of 1-substituted cyclobutenes and cyclohexene. (Because the free energy for polymerization of cyclohexene is positive, it is proposed that only a cyclohexene is incorporated between two units arising from the cyclobutene.) Other simple cyclic olefins such as cyclooctene are often partnered with a relatively strained olefin such as a norbornene. Formation of an AB copolymer with a single structure via ROMP preferably should also include control of stereochemistry, the most fundamental of which is restricting the configuration of the cis or trans C=C bond that is formed. When well-defined catalysts are employed, attempts to control polymer structure include varying the catalyst in order to slow polymerization of one of the monomers. To the best of our knowledge all attempts to prepare AB copolymers via ROMP with well-defined catalysts, except in the special case where A and B are enantiomers vide infra, have thus far employed Ru-based catalysts.

We showed recently that some norbornenes and norbornadienes are polymerized very slowly, if at all, by several Mo or W imido alkylidene or Ru carbene complexes. A monomer that resists homopolymerization by imido alkylidene initiators is 2,3-dicarbomethoxy-7-isopropylidenenorbornadiene (B). Monomer B is polymerized readily by W(OC)(CH-t-Bu)(MePyr)(OCHT)(PME, Ph) (OCHT = O-2,6-Mes2C6H3, MePyr = 2,5-dimethylpyrroli dine), especially in the presence of B(C6F5)3, which accelerates ROMP through binding of B(C6F5)3 to the oxo ligand. In 1990 we found that B reacts slowly with Mo(NAr)(CH-t-Bu)(O-t-Bu) (Ar = 2,6-i-Pr2C6H3) to give a first insertion product, but no further reaction between the first insertion product and B was observed, even at 55 °C. An X-ray structure showed that the first insertion product contains a syn alkylidene (vide infra) and a trans C≡C bond; the isopropylidene and one carbomethoxy group block each side of the Mo≡C bond toward incoming B.

During the process of exploring several molybdenum imido alkylidene catalysts for the homopolymerization of B we found that Mo(NAr')(CHCMe6Ph)(OCMe(CF3)2)2 (1, Ar' = 2,6-

\[\text{MePyr} = 2,5\text{-dimethylpyrroli dine}\]

\[\text{vide infra}\]

\[\text{B(C6F5)3}\]

\[\text{BAr'} = 2,6\text{-i-Pr2C6H3}\]

\[\text{BCH-t-Bu}(\text{O-t-Bu})\]

\[\text{vide infra}\]

\[\text{OCHT} = \text{O-2,6-Mes2C6H3}, \text{MePyr} = 2,5\text{-dimethylpyrroli dine}\]

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\[\text{vide infra}\]

\[\text{OCHT} = \text{O-2,6-Mes2C6H3}, \text{MePyr} = 2,5\text{-dimethylpyrroli dine}\]
MeC,H3) initiates the polymerization of B relatively slowly in CDCl3 or toluene-d8. Nevertheless, B and cyclooctene (A, Figure 1, 50 equiv of each) are copolymerized by initiator I in CDCl3 or C6D6 in 1-2 h to give largely (>90%) trans-poly(A-alt-B) (Figure 2). Proton NMR spectra in CDCl3 of trans-poly(A-alt-B) show primarily two types of trans olefinic protons bound to C=C bonds (Figure 3a), a doublet for H4 and a double triplet (overlapping) for H2, characteristic of a trans C=C bond. An IR spectrum also shows a strong peak at 967 cm−1, characteristic of a trans olefin. Proton/proton COSY NMR studies are all completely consistent with the proposed structure. A plot of ln[A] vs. t is approximately linear with kobs = 29×103 s−1 in CDCl3; a plot of ln[B] vs. t is approximately linear with kobs = 20×103 s−1 (Table 1). Because different data are acquired at different stages during the reactions and not all plots are perfectly linear fits (see Supporting Information), the kobs values are useful only for rough comparisons.

![Figure 3. The olefinic region of the 1H NMR spectra of (a) trans-poly(A-alt-B) and (b) trans-poly(A-alt-B) in CDCl3, prepared from I.](image)

<table>
<thead>
<tr>
<th>Comb</th>
<th>Solv</th>
<th>Monomer (M)</th>
<th>kobs×103 s−1(A)</th>
<th>kobs×103 s−1(B)</th>
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<tbody>
<tr>
<td>A/B/1</td>
<td>CDCl3</td>
<td>0.12</td>
<td>29</td>
<td>20</td>
</tr>
<tr>
<td>A/B/1</td>
<td>THF-d8</td>
<td>0.16</td>
<td>3.4</td>
<td>3.3</td>
</tr>
<tr>
<td>A'/B'/2</td>
<td>Tol-d8</td>
<td>0.20</td>
<td>23</td>
<td>16</td>
</tr>
<tr>
<td>A'/B'/2b</td>
<td>Tol-d8</td>
<td>0.20</td>
<td>26</td>
<td>16</td>
</tr>
<tr>
<td>A'/B'/2</td>
<td>Tol-d8</td>
<td>0.20</td>
<td>3.1</td>
<td>2.7</td>
</tr>
</tbody>
</table>

*See Supporting Information for details. **A':B':1 = 100:100:1.

Olefine proton resonances H4 and H5 between the resonances for H2 and H3 (Figure 3a) can be assigned to trans and cis (respectively) homopolymer (AA) dyads that are formed from cyclooctene, as shown through polymerization of cyclooctene alone by 1 to give poly(cyclooctene) (a 4:1 mixture of trans and cis). Typically 3%-9% homopolymer dyads are formed when 50 equivalents each of A and B are copolymerized by I in CDCl3 or toluene-d8. The % heterodyads and homodyads can be assessed relatively accurately through integration of the resonances for H4 and H3 protons versus those for H2 and H5.

Compound 1 will also initiate copolymerization of cycloheptene (A') and B' in toluene-d8 to give trans-poly(A'-alt-B') (Figure 2, bottom) with kobs = 23×103 s−1 for A' and 16×103 s−1 for B' (Table 1). The proton NMR spectrum of trans-poly(A'-alt-B') is similar to that for trans-poly(A-alt-B) (Figure 3b). Low intensity resonances in the baseline are proposed to be either homopolymer linkages (A'A') or end group olefinic protons. The similarities of the olefinic regions of the NMR spectra leave no doubt that the two copolymers are both trans AB copolymers. Mo(NAr)(CHCMe2Ph)OOCMe(CF3)2 (2) also will initiate the copolymerization of A' and B' in toluene-d8 with kobs = 3.1×103 s−1 for A' and 2.7×103 s−1 for B' (Table 1) and A and B' (no rate determined). Note that this reaction is approximately an order of magnitude slower than A'/B'/1. All indications are that the mechanisms of forming trans-poly(A'-alt-B') and trans-poly(A-alt-B) are analogous.

![](image)

Figure 4. The proposed mechanism of forming trans-poly(A-alt-B) (P = polymer).
then B does not react with syn-MA to give syn-MB<sub>trans</sub> during formation of trans-poly(A-alt-B). At room temperature syn-MB<sub>trans</sub> is converted into a mixture of syn-MB<sub>trans</sub> and anti-MB<sub>trans</sub> by rotation about the Mo=C bond. During copolymerization syn-MB<sub>trans</sub> and anti-MB<sub>trans</sub> are observed; their ratio at equilibrium in the absence of olefin is $K_{eq} = [\text{syn}]/[\text{anti}] = 0.05$. It is highly unusual to find a four-coordinate alkylidene of the type employed here that is essentially entirely anti; for example, the bis-i-butoxide analog of anti-MB<sub>trans</sub>, a first insertion product (vide supra), is the syn isomer in solution ($\nu_C = 128$ Hz) and in the solid state.  

If B does not react with syn-MA to yield a trans-AB linkage, then a trans C=C bond must be formed when B reacts with anti-MA. Anti-I can be prepared through photolysis of syn-I in toluene-<em>d</em><sub>8</sub> at -78 °C (see SI).  

Addition of 0.5 equivalents of B to a mixture of anti-I (~45%) and syn-I followed by warming the reaction slowly to 22 °C revealed that B reacts with anti-I to give a syn first insertion product that contains a trans C=C bond (syn-MB<sup>trans</sup>) much faster than the rate at which syn-I reacts with B to give syn-MB<sub>trans</sub>. Syn-MB<sup>trans</sup> also readily interconverts with anti-MB<sup>trans</sup> at 22 °C. If anti-I is an appropriate model for anti-MA (Figure 4), these data suggest that one of the trans linkages is formed through reaction of anti-MA with B to give syn-MB<sub>trans</sub> initially, which then begins to isomerize to give a mixture of syn-MB<sub>trans</sub> and anti-MB<sub>trans</sub> (Figure 4).

The mechanism of copolymerization of A<sup>‘</sup> and B<sup>‘</sup> by syn-2 appears to be analogous to that for forming poly(A-alt-B) by syn-1 just described. Evidence consists of the fact that the rate of reaction of syn-2 with B<sup>‘</sup> at initial concentrations of B<sup>‘</sup> that are 5X[syn-2], 20X[syn-2], and 30X[syn-2] (pseudo first-order conditions), does not depend upon the concentration of B<sup>‘</sup>. The rate constant for consumption of syn-2 (10X[syn-2] s<sup>-1</sup>) is close to that published for conversion of syn-2 to anti-2 in toluene-<em>d</em><sub>8</sub> at 22 °C ($k_{eq} = 7X10^5$ s<sup>-1</sup>), and the first insertion product in the reaction between syn-2 and B<sup>‘</sup> contains a trans C=C bond. Therefore, conversion of syn-2 to anti-2 is rate limiting and anti-2 reacts with B to form the trans first insertion product, syn-MB<sup>trans</sup>, which then forms a mixture of syn-MB<sup>trans</sup> and anti-MB<sup>trans</sup>.

The question concerning how the other AB dyad is formed can be answered through an experiment that employs the first insertion product (MB<sub>trans</sub>) obtained in a reaction of syn-2 with one equivalent of B<sup>‘</sup> (see SI); MB<sub>trans</sub> is approximately a 95:5 raining/syn mixture at equilibrium ($k_{eq} = [\text{syn-MB}_{trans}]/[\text{anti-MB}_{trans}] = 0.05$), the same as found for [syn-MB<sub>trans</sub>]/[anti-MB<sub>trans</sub>] in the AB system above. Addition of 50 or 75 equivalents of A<sup>‘</sup> to isolated anti-MB<sup>trans</sup> leads to a consumption of anti-MB<sup>trans</sup> at a rate that is first order in anti-MB<sup>trans</sup>, but independent of [A<sup>‘</sup>] with $k_{obs} = 6.2X10^5$ s<sup>-1</sup>. Therefore the rate limiting step for this reaction is conversion of anti-MB<sup>trans</sup> to syn-MB<sup>trans</sup>, i.e., $k_{obs} = 6.2X10^5$ s<sup>-1</sup> = $k_{syn}$ (Figure 4). We conclude that the other AB linkage is formed in a reaction between A<sup>‘</sup> and syn-MB<sup>trans</sup>, two other combinations of A and B and initiator yield high quality copolymers; those combinations are A/B'/1 and A/B'/4, the third and fourth examples reported here (Figure 5). The copolymer formed with the combination A/B'/2 contains approximately ~10% homopolymer dyads (see SI).  

We propose that the four copolymers described here are formed through reaction of anti-MA with B to give syn-MB<sub>trans</sub> and a trans C=C bond, followed by the reaction of syn-MB<sub>trans</sub> with A to give anti-MA and a trans C=C bond (A stands for either A or A<sup>‘</sup>; and B stands for either B or B<sup>‘</sup>; the AB system is shown in Figure 4). This mechanism seems remarkable given the number of possible reactions to give cis or trans AB linkages (eight) and the number of possible reactions to give cis or syn AA or BB linkages (eight). An interconversion of anti-MA formed in this copolymerization and syn-MA is not shown in Figure 4 because preliminary modeling of the mechanism (vide infra) suggests that the rate of conversion of anti-MA to syn-MA does not compete with the rate of reaction of anti-MA with B to give syn-MB<sub>trans</sub>. It would now appear that syn and anti isomers are an advantage for forming a trans AB copolymer of the quality observed here, i.e., syn and anti alkylidene isomers form sequentially with each insertion of A or B to give copolymer only when trans linkages are formed.

We propose that AA linkages arise through a reaction between anti-MA and A to give a cis or trans AA dyad. The percentages of trans-poly(A-alt-B) in the mixtures vary somewhat with conditions, but are usually in the range 90 - 95% for all four copolymers. Therefore, B must react with anti-MA approximately 20 times faster than A reacts with anti-MA. AA dyads can be minimized if A is added slowly to B in the presence of initiator; for example, addition of A in an A/B/I copolymerization employing a syringe pump over a period of 0.5 h gave the lowest percentage of AA linkages (~3%) we have observed so far. If monomer A is added first to the initiator to generate polyA, and monomer B then added, virtually no B is consumed. Therefore, rapid "unzipping" or "editing" of preformed linear and cyclic polyA<sup>2,9,10</sup> is not a competitive pathway to trans-poly(A-alt-B) on the time scale observed in a copolymerization of A and B.

It is likely that formation of trans linkages selectively in the systems described here can be attributed to the high steric demands of one of the two monomers (B or B<sup>‘</sup>) coupled with the high ring strain of norbornadienes. Cyclooctene and cycloheptene are much less strained than a norbornene or norbornadiene and sterically less demanding. The "large" monomers (B and B<sup>‘</sup>) force trans double bonds to form in reactions between a "large" alkylidene (syn-MB<sub>trans</sub>) and "small" monomer (A), or a "small" alkylidene (anti-MA) and "large" monomer (B). B does react readily with syn-I to give a cis syn first insertion product, as described earlier, but these conditions are much different from conditions in the copolymerization where only anti-MA is available to react with B on the time scale of the reaction.

THF is known to slow conversion anti to syn isomers by binding to the metal in the anti isomer.  

Interestingly, trans-poly(A-alt-B) is formed in THF with equal specificity and the observed "first order" rate constant is approximately 3.4X10<sup>5</sup> s<sup>-1</sup> for A and 3.3X10<sup>5</sup> s<sup>-1</sup> for B (Table 1).

The findings reported here reveal that syn and anti isomers are still very much a feature of reactions that involve Mo and W alkylidene complexes, a subject that has been attracting attention for the past two decades, but also a subject that relies on circumstances that produce reliable evidence, as reported here. Our findings raise the question as to whether reactions with well-defined Mo and W initiators that have been explored for ROMP in the past have fully considered the consequences of syn
and anti isomers and their widely variable rates of interconversion. Even \( k_r \) versus \( k_a \) takes on a new complexity when two isomers of both the initiating and any propagating alkylidienes are accessible.

We have described here the first syntheses of stereoregular alternating AB copolymers (in which A and B are not enantiomers) formed through ROMP with Mo catalysts. A special type of AB copolymer, poly[(R)-alt-(S)-1-methylborocene], was prepared by Hamilton and Rooney employing a "classical" catalyst of unknown structure and type derived from ReCl\(_5\). Related cis,syn-diads,alt polymers have been prepared recently with Mo MAP (MonoAryloxide Pyrrolide) initiators. In polymerizations of this type the configuration of the stereogenic metal center switches with each insertion, thus promoting incorporation of enantiomers alternately while also promoting formation of a basic cis,syn-diads structure.

The time dependent concentrations of various intermediates and monomers consumed, along with syn and anti interconversion rates, ultimately should provide a basis for modeling the copolymerizations using a Complex Pathway Simulator (COPASIL). Preliminary simulations are in agreement with the mechanism shown in Figure 4. Intimate knowledge of the factors that produce the results reported here we hope can then be employed to answer the following: what other trans-poly(A-alt-B) copolymers can be formed, to what extent is a "large" monomer that is not homopolymerized readily and a "small" monomer that is homopolymerized readily required, and what catalysts are most efficient under what conditions?

ASSOCIATED CONTENT

Experimental details for the synthesis of all inorganic compounds and polymers (50 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

R.R.S. thanks the Department of Energy (DE-FG02-86ER13564) and the National Institutes of Health (Grant GM-59426 to R.R.S. and A.H.H.) for financial support. We thank Professor Timothy M. Swager for use of his Thermo Scientific Nicolet 6700 FT-IR and Dr. Peter E. Sues for useful discussions.

REFERENCES


Supporting Information for

Synthesis of Alternating trans-AB Copolymers Through Ring-Opening Metathesis Polymerization Initiated by Molybenum Alkylidenes

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References
Experimental

General considerations. All air-sensitive manipulations were performed under nitrogen in a drybox or using Schlenk techniques. All glassware was oven-dried and allowed to cool under vacuum or nitrogen before use. $^1$H (500 MHz) and $^{13}$C NMR (125 MHz) spectra were obtained on Varian 500 MHz spectrometers, and $^{19}$F (282 MHz) NMR spectra were obtained on Bruker 400 MHz spectrometer. All reported in $\delta$ (parts per million), and referenced to residual $^1$H/$^{13}$C signals of the deuterated solvent ($^1$H($\delta$) benzene 7.16, chloroform 7.26, tetrahydrofuran 3.58, toluene 2.08; $^{13}$C($\delta$) benzene 128.06, chloroform 77.16, toluene 20.43; $^{19}$F($\delta$) external PhF standard -113.15). Low temperature $^1$H NMR experiments were conducted on a variable temperature Varian Inova 500 MHz spectrometer capable of a temperature range of -100 °C to +150 °C. $^1$H-$^1$H gCOSY, HSQC, DEPT NMR experiments were conducted on a Varian Inova 500 MHz spectrometer. Pentane was washed with H$_2$SO$_4$, followed by water, and saturated aqueous NaHCO$_3$, and dried over CaCl$_2$ pellets over at least two weeks prior to use in the solvent purification system. HPLC grade diethyl ether, toluene, tetrahydrofuran, pentane, and methylene chloride were sparged with nitrogen and passed through activated alumina. In addition, benzene was passed through a copper catalyst. Organic solvents were then stored over activated 4 Å Linde-type molecular sieves. Deuterated solvents were degassed and stored over activated 4 Å Linde-type molecular sieves. Benzaldehyde was distilled and stored under nitrogen. 2,3-dicarbomethoxy-7-isopropylideneborbornadiene (B)$^1$ and dimethylspiro[bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate-7,1'-cyclopropane (B')$^2$, were prepared according to published literature procedures. cis-Cyclooctene (95%) (A) was purchased from Alfa Aesar and distilled before use. cis-Cycloheptene (>$96\%$) (B) was purchased from TCI America and distilled before use. Mo(NAr')(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (catalyst 1) and Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$, (catalyst 2) (NAr$' = 2,6$-Me$_2$C$_6$H$_3$N; NAr = 2,6-i-Pr$_2$C$_6$H$_3$N) were prepared according to literature procedures. Unless otherwise noted, all other reagents were obtained from commercial sources and used as received. ATR-FT-IR spectra were acquired using a Thermo Scientific Nicolet 6700 FT-IR with a Ge crystal for ATR and are reported in terms of frequency of absorption (cm$^{-1}$).

Formation of trans-poly[A-alt-B]. A stock solution of Mo(NAr')(CHCMe₂Ph)(OCMe(CF₃)₂)₂ (4.7 mg, 6.6 µmol, 180 µL) was added to a vigorously stirring solution of 2,3-dicarbomethoxy-7-isopropylidenenorbornadiene (B) (81.5 mg, 0.33 mmol) in benzene (0.9 mL) and cis-cyclooctene (A) (43 µL, 0.33 mmol) was added via syringe. The solution was stirred for 1 h and 30 minutes. At this point, the conversion was observed >97% by ¹H NMR spectroscopy. Benzaldehyde was added to quench the polymerization and the mixture was stirred for 1 h. The mixture was poured into excess MeOH and the precipitated polymer (107 mg, 0.30 mmol, 91% yield) was isolated by centrifugation and vacuum dried overnight. ¹H NMR (500 MHz, CDCl₃, 20 °C) δ 5.48 (dt, ³J_HH = 15 and 7 Hz, 2H, H₂), 5.27 (dd, ³J_HH = 15.5 and 8 Hz, 2H, H₁), 4.11 (d, ³J_HH = 8 Hz, 2H, H₃), 3.75 (s, 6H, H₆), 1.98 (m, 4H, H₁₀), 1.63 (s, 6H, H₉), 1.30 (m, 8H, H₁₁ and H₁₂); ¹³C NMR (125 MHz, CDCl₃, 20 °C) δ 165.71 (C₅), 141.02 (C₄), 133.17 (C₇ or C₈), 132.58 (C₁), 128.80 (C₇ or C₈), 128.38 (C₂), 53.39 (C₃), 52.06 (C₆), 32.59 (C₁₀), 29.65 (C₁₁ or C₁₂), 29.15 (C₁₁ or C₁₂), 20.52 (C₉). IR (neat): 2924, 2854, 1721, 1641, 1435, 1323, 1270, 1208, 1133, 1098, 1023, 967 (trans), 919, 777 cm⁻¹.
Figure S1. $^1$H NMR spectrum of trans-poly[A-alt-B] (in CDCl$_3$, 500 MHz).
**Figure S2.** $^{13}$C NMR spectrum of trans-poly[A-alt-B] (in CDCl$_3$, 125 MHz).
Figure S3. $^1\text{H}-^1\text{H}$ gCOSY spectrum of trans-poly[A-alt-B] (in CDCl$_3$, 500 MHz).
Figure S4. IR spectrum of trans-poly[A-alt-B] (neat).

Formation of trans-poly[A-alt-B']. A solution of Mo(NAr')(CHMe₂Ph)(OCMe(CF₃)₂)₂ (4.7 mg, 6.6 μmol) was added to a vigorously stirring solution of dimethylspiro[bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate-7,1'-cyclopropane (B') (82.1 mg, 0.351 mmol) in benzene (0.9 mL). cis-cyclooctene (A) (46 μL, 0.351 mmol) was added via syringe and the solution was stirred for 1 h 20 min at room temperature. After 1 h, conversion was 98% and it was monitored via ¹H NMR. The polymerization was quenched by addition of benzaldehyde. The entire mixture was added to excess MeOH. The precipitated polymer was isolated by centrifugation and vacuum dried overnight (84 mg, 0.24 mmol, 70% yield). ¹H NMR (CDCl₃, 20 °C) δ 5.32 (dt, 3J_HH = 15 and 7 Hz, 2H, H₂), 5.20 (dd, 3J_HH = 15 and 9.5 Hz, 2H, H₁), 3.73 (s, 3H, H₆), 3.13 (d, 3J_HH = 9 Hz, 2H, H₃), 1.98 (m, 4H, H₀), 1.30-1.24 (m, 8H, H₁₀ and H₁₁), 0.57-0.46 (m, 4H, H₈); ¹³C NMR (CDCl₃, 20 °C) δ 165.8 (C₅), 141.9 (C₄), 133.4 (C₂), 129.1 (C₁), 57.5 (C₃), 52.0 (C₆), 32.5 (C₉), 29.6 (C₁₀ or C₁₁), 29.1 (C₁₀ or C₁₁), 15.6 (C₈), 7.15 (C₇). IR (neat): 2926, 2854, 1721, 1642, 1435, 1323, 1206, 1126, 1101, 1098, 1021, 973 (trans), 905, 797, 754 cm⁻¹.
**Figure S5.** $^1$H NMR spectrum of *trans*-poly[A-*alt*-B'] (in CDCl$_3$, 500 MHz).
Figure S6. $^{13}$C NMR spectrum of trans-poly[A-alt-B'] (in CDCl$_3$, 125 MHz).
Figure S7. $^1$H–$^1$H gCOSY spectrum of trans-poly[A-alt-B'] (in CDCl$_3$, 500 MHz).
Figure S8. IR spectrum of trans-poly[A-alt-B'] (neat).
Polymerization of trans-poly[A'-alt-B'] by catalyst 1.

Formation of trans-poly[A'-alt-B']. A stock solution of Mo(NAr')(CHCMe2Ph)(OCMe(CF3)2)2 (6.0 mg, 8.4 µmol, 229 µL) was added to a vigorously stirring solution of dimethylspiro[bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate-7,1'-cyclopropane (B') (98.5 mg, 0.42 mmol) and cis-cycloheptene (A') (49 µL, 0.42 mmol) in benzene (0.9 mL). The solution was stirred for 1 h and 50 minutes. At this point, the conversion was observed >96% by 1H NMR spectroscopy. The benzaldehyde was added to quench the polymerization and the mixture was stirred for 1 h. The mixture was poured into excess MeOH and the precipitated polymer (81 mg, 0.245 mmol, 58% yield) was isolated by centrifugation and vacuum dried overnight. 1H NMR (500 MHz, CDCl3, 20 °C) δ 5.34 (dt, 3JHH = 15 and 7 Hz, 2H, H2), 5.20 (dd, 3JHH = 15.5 and 9 Hz, 2H, H1), 3.74 (s, 6H, H6), 3.12 (d, 3JHH = 9.5 Hz, 2H, H3), 1.97 (m, 4H, H10), 1.36-1.25 (m, 6H, H10 and H11), 0.56-0.48 (m, 4H, H8); 13C NMR (CDCl3, 20 °C) δ 165.8 (C5), 141.9 (C4), 133.4 (C2), 129.1 (C1), 57.4 (C3), 52.1 (C6), 32.5 (C9), 29.5 (C10 or C11), 28.7 (C10 or C11), 15.6 (C8), 7.17 (C7). IR (neat): 2926, 2853, 1722, 1642, 1435, 1319, 1271, 1206, 1129, 1101, 1074, 1021, 969 (trans), 770 cm⁻¹.
Figure S9. $^1$H NMR spectrum of trans-poly[A'-alt-B'] (in CDCl$_3$, 500 MHz).
Figure S10. $^{13}$C NMR spectrum of trans-poly[\(A'-alt-B'\)] (in CDCl$_3$, 125 MHz).
Figure S11. $^1$H–$^1$H gCOSY spectrum of $trans$-poly[$A'$-$alt$-$B'$] (in CDCl$_3$, 500 MHz).
Figure S12. IR spectrum of trans-poly[A'-alt-B'] (neat).

Formation of trans-poly[A'-alt-B]. A stock solution of Mo(NAr')(CHCMe₂Ph)(OCMe(CF₃)₂)₂ (4.5 mg, 6.4 µmol, 200 µL) was added to a vigorously stirring solution of 2,3-dicarbomethoxy-7-isopropylidenenorbornadiene (B) (79.2 mg, 0.32 mmol) and cis-cycloheptene (A') (37 µL, 0.32 mmol) in benzene (0.9 mL). The solution was stirred for 1 h and 45 minutes. At this point, the conversion was observed >98% by ¹H NMR spectroscopy. The benzaldehyde was added to quench the polymerization and the mixture was stirred for 1 h. The mixture was poured into excess MeOH and the precipitated polymer (95 mg, 0.28 mmol, 86% yield) was isolated by centrifugation and vacuum dried overnight. ¹H NMR (500 MHz, CDCl₃, 20 °C) δ 5.48 (dt, ³J₃₅₂ = 15.5 and 6.5 Hz, 2H, H₂), 5.26 (dd, ³J₃₅₂ = 15 and 8 Hz, 2H, H₁), 4.11 (d, ³J₃₅₂ = 7.5 Hz, 2H, H₃), 3.75 (s, 6H, H₆), 1.97 (m, 4H, H₁₀), 1.63 (s, 6H, H₀), 1.30 (m, 6H, H₁₁, H₁₂); ¹³C NMR (125 MHz, CDCl₃, 20 °C) δ 165.71 (C₅), 141.03 (C₄), 133.16 (C₇ or C₈), 132.57 (C₁), 128.87 (C₇ or C₈), 128.40 (C₂), 53.41 (C₃), 52.07 (C₆), 32.58 (C₁₀), 29.59 (C₁₁ or C₁₂), 28.83 (C₁₁ or C₁₂), 20.54 (C₀). IR (neat): 2924, 2853, 1722, 1642, 1434, 1324, 1270, 1207, 1134, 1097, 1024, 966 (trans), 919, 775 cm⁻¹.
Figure S13. $^1$H NMR spectrum of trans-poly[A'-alt-B] (in CDCl$_3$, 500 MHz).
Figure S14. $^{13}$C NMR spectrum of trans-poly[A'-alt-B] (in CDCl$_3$, 500 MHz).
Figure S15. $^1$H–$^1$H gCOSY spectrum of trans-poly[A'-alt-B] (in CDCl$_3$, 500 MHz).
Figure S16. IR spectrum of trans-poly[A'-alt-B] (neat).
ROMP of cis-cycloheptene:
A 1 mL C₆D₆ solution of Mo(NAr)(CHMe₂Ph)(OCCH₃(CF₃)₂)₂ (15.9 mg, 20.0 µmol) was added to a rapidly stirred solution of cis-cycloheptene (100 mg, 1.00 mmol) in 4 mL of C₆D₆. The resulting yellow solution that was formed was stirred for 12 h. The polymerization was then quenched by addition of the solution to stirring MeOH (40 mL). The precipitated polymer was isolated by centrifugation and vacuum dried. Isolated yield was 50.4 mg or 50.4%. ¹H NMR of the waxy solid showed a 18:82 mixture of cis- and trans-poly(cycloheptene).

cis-poly(cycloheptene):
¹H NMR (CDCl₃, 500.43 MHz, 20 °C): δ 5.36 (t, 3JHH = 4.5 Hz, 2H), 2.03 (bm, 4H), 1.31 (bm, 6H). ¹³C NMR (CDCl₃, 125.79 MHz, 20 °C): δ 130.00 (=CH), 28.87 (=CHCH₂), 27.34 (CH₂CH₂CH₂).

trans-poly(cycloheptene):
¹H NMR (CDCl₃, 500.43 MHz, 20 °C): δ 5.39 (t, 3JHH = 4.5 Hz, 2H), 1.97 (bm, 4H), 1.35 (bm, 6H). ¹³C NMR (CDCl₃, 125.79 MHz, 20 °C): δ 130.46 (=CH), 32.74 (=CHCH₂), 29.68 (CH₂CH₂CH₂).

ROMP of cis-cyclooctene:
In a J-Young NMR tube, a 0.2 mL solution of Mo(NAr’)(CHMe₂Ph)(OCCH₃(CF₃)₂)₂ (2.4 mg, 3.4 µmol) was added to cis-cyclooctene (22 µL, 0.169 mmol) in a 0.4 mL of C₆D₆. After 1h, the complete consumption of monomer was observed, and the polymerization was quenched by addition of benzaldehyde. The mixture was poured into stirring MeOH (5 mL) and the precipitated polymer was isolated by centrifugation and vacuum dried (5 mg). ¹H NMR of the polymer showed a 20:80 mixture of cis- and trans-poly(cyclooctene).

cis-poly(cyclooctene):
¹H NMR (CDCl₃, 500 MHz, 20 °C): δ 5.34 (t, 3JHH = 4.8 Hz, 2H), 2.00 (m, 4H), 1.33 -1.27 (m, 8H). ¹³C NMR (CDCl₃, 125.79 MHz, 20 °C): δ 130.02 (=CH), 29.90 (=CHCH₂), 29.34 (CH₂CH₂CH₂), 27.37 (CH₂CH₂CH₂).
trans-poly(cyclooctene):

$^1$H NMR (CDCl$_3$, 500 MHz, 20 °C): δ 5.38 (t, $^3J_{HH} = 3.4$ Hz, 2H), 1.96 (m, 4H), 1.33 -1.27 (m, 8H). $^{13}$C NMR (CDCl$_3$, 125.79 MHz, 20 °C): δ 130.48 (=CH), 32.76 (=CHCH$_2$), 29.79 (CH$_2$CH$_2$CH$_2$), 29.20 (CH$_2$CH$_2$CH$_2$).

**Comparison between four trans copolymers formed from 1 and 2**

Polymerization reactions employing catalyst 2 were analogous as those of catalyst 1 (vide supra), but the mixtures were stirred overnight to complete the polymerization.

Comparison between trans-poly(A-alt-B') formed from 1 and 2

**Figure S17.** Comparison of the olefinic region $^1$H NMR spectrum of trans-poly(A-alt-B') formed from 1 (left) and 2 (right) in CDCl$_3$.

Comparison between trans-poly(A'-alt-B') formed from 1 and 2

**Figure S18.** Comparison of the olefinic region $^1$H NMR spectrum of trans-poly(A'-alt-B') formed from 1 (left) and 2 (right) in CDCl$_3$. 

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Comparison between \textit{trans}-poly(A'-alt-B) formed from 1 and 2

![Figure S19](image1.png)

\textbf{Figure S19.} Comparison of the olefinic region $^1$H NMR spectrum of \textit{trans}-poly(A'-alt-B) formed from 1 (left) and 2 (right) in CDCl$_3$.

Comparison between \textit{trans}-poly(A-alt-B) formed from 1 and 2

![Figure S20](image2.png)

\textbf{Figure S20.} Comparison of the olefinic region $^1$H NMR spectrum of \textit{trans}-poly(A-alt-B) formed from 1 (left) and 2 (right) in CDCl$_3$.

\textbf{Synthesis of the first insertion complex of 2 and B'}

A 1.0 mL toluene solution of B' (1.05 equiv., 32.1 mg, 27.2 µL, 137 µmol) was added to a rapidly stirred solution of 2 (1.0 equiv, 100 mg, 130.6 µmol in 1.0 mL of toluene) followed by a 1.0 mL toluene wash. The progress of the reaction was monitored via $^1$H NMR spectroscopy after 24 h. Once all the initiator was consumed the solvent was removed \textit{in vacuo}. 2 mL of pentane was then added to dissolve the red-orange residue and then removed \textit{in vacuo}. This process was repeated two times. The residue was then dissolved in 1 mL of Et$_2$O and recrystallized at –30 °C. The mother liquor was decanted and the orange crystals washed with 1 mL of Et$_2$O pre-chilled to –30 °C. The solid was then dried under vacuum for 5 h. Isolated yield = 39.1 mg or 30%. $^1$H NMR (500.43 MHz, CDCl$_3$, 20 °C): $\delta$ 12.31 (d, $^3$J$_{HH}$ = 8.4 Hz, 1H, \textit{syn} alkylidene, a, 3%), 11.80 (d, $^3$J$_{HH}$ = 3.8 Hz, 1H, \textit{anti} alkylidene, a, 97%), 7.32-7.10 (8 aromatic H), 5.73 (d, $^3$J$_{HH}$ = 15.5 Hz, 1H, h), 5.24 (m, b), 5.06 (dd, $^3$J$_{HH}$ = 15.5 Hz and 9.6 Hz, 1H, g), 4.07 (hept, $^3$J$_{HH}$ = 6.9 Hz, 2H, l), 3.98 (s, OCH$_3$, c), 3.81 (dd, $^3$J$_{HH}$ = 9.6 Hz and $^4$J$_{HH}$ = 3.6 Hz, 

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$^1$H, f), 3.78 (s, OCH$_3$, j), 1.36 (s, 2 CH$_3$, i), 1.33 (bd, $^3$J$_{HH} = 6.8$ Hz, 2CH$_3$, k or m), 1.32 (bd, $^3$J$_{HH} = 6.8$ Hz, 2CH$_3$, k or m), 1.29 (bs, CH$_3$, n or o), 1.24 (bs, CH$_3$, n or o), 0.53 (m, CH$_2$, d or e), 0.49 (CH$_2$, d or e); $^{19}$F NMR (376.46 MHz, CDCl$_3$, 20.0 °C): δ -77.60 (q, $J = 9.5$ Hz), -77.77 (q, $J = 9.4$ Hz), -77.99 (q, $J = 9.6$ Hz), -78.24 (q, $J = 9.5$ Hz); Assignment of the $^{13}$C NMR resonances was made with the assistance of a HSQC and DEPT experiment. $^{13}$C NMR (125.79 MHz, Toluene-$d_8$, 20.0 °C): δ 266.05 (C$_1$), 170.32 (C=O), 165.35 (C=O), 152.46 (quaternary), 151.49 (quaternary), 148.25 (quaternary), 146.79 (quaternary), 146.63 (C$_2$), 134.42 (quaternary), 128.52 (aromatic C), 128.03 (aromatic C, overlapping with toluene), 126.34 (aromatic C), 126.22 (aromatic C), 123.09 (aromatic C), 120.93 (C$_3$), 80.74 (C$_4$), 59.13 (C$_5$), 56.38 (C$_6$), 54.64 (C$_7$), 51.58 (C$_8$), 40.76 (quaternary), 31.00 (quaternary), 29.41 (C$_9$), 28.78 (C$_{10}$), 28.76 (C$_{11}$), 24.53 (C$_{12}$), 23.24 (C$_{13}$), 19.61 (C$_{14}$, overlapping with toluene), 6.16 (C$_{15}$), 5.93 (C$_{16}$).

Figure S21. $^1$H NMR (500.43 MHz) of the first insertion product between 2 and B' in CDCl$_3$
Figure S22. The $^{19}$F NMR of the first insertion complex between 2 and B' in CDCl$_3$.

Figure S23. $^{13}$C NMR spectrum (125.79 MHz) of first insertion complex between 2 and B' in toluene-$d_8$. 
**Details of Kinetic Experiments I**

<table>
<thead>
<tr>
<th>Combination of A/B/Cat</th>
<th>Equivalents A/B/Cat</th>
<th>Solvent</th>
<th>Concentration of Monomer (M) (x 10^{-5} s^{-1})</th>
<th>k_{obs} (A) (x 10^{-5} s^{-1})</th>
<th>k_{obs} (B) (x 10^{-5} s^{-1})</th>
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<td>20</td>
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<td>Toluene-d₈</td>
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<td>16</td>
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<td>50/50/1</td>
<td>THF-d₈</td>
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</tbody>
</table>

**Table S1.** List of k_{obs} values of monomer A/B or A'/B' using catalyst 1 and 2.
Rate of consumption of A and B by catalyst 1 in CDCl₃.

In a J-Young NMR tube, 50 equivalents of B (0.102 mmol, 25.4 mg) and 50 equivalents of A (0.102 mmol, 13 µL) in 0.85 mL of chloroform-d were added and consumption of each monomer were monitored over 2 half lives.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>ln([A]/[A]₀)</th>
<th>ln([B]/[B]₀)</th>
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<td>2162</td>
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<tr>
<td>2718</td>
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<tr>
<td>3027</td>
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<td>-1.178</td>
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<tr>
<td>3452</td>
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Slope ($k_{obs}$) = $2.9 \times 10^{-4}$ s$^{-1}$

Slope ($k_{obs}$) = $2.0 \times 10^{-4}$ s$^{-1}$
Rate of consumption of A' and B' by catalyst 1 in toluene-$d_8$.

In a J-Young NMR tube, 50 equivalents of B' (0.119 mmol, 27.8 mg) and 50 equivalents of A' (0.119 mmol, 14 µL) in 0.6 mL of toluene-$d_8$ were added and consumption of each monomer were monitored over 2 half lives.

<table>
<thead>
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<th>Time (s)</th>
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<th>ln([B']/[B']₀)</th>
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</table>
Slope ($k_{obs}$) = $2.3 \times 10^{-4}$ s$^{-1}$

**Rate of consumption of A' and B' by catalyst 2 in toluene-$d_8$.**

In a J-Young NMR tube, 50 equivalents of B' (0.119 mmol, 27.8 mg) and 50 equivalents of A' (0.119 mmol, 14 µL) in 0.6 mL of toluene-$d_8$ were added and consumption of each monomer were monitored over 1 half live.
<table>
<thead>
<tr>
<th>Time (min)</th>
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Slope (kobs) = 3.1 x 10⁻⁵ s⁻¹
Slope (kobs) = $2.7 \times 10^{-5}$ s$^{-1}$

**Rate of consumption of A and B by catalyst 1 in THF-$d_8$.**

In a J-Young NMR tube, 50 equivalents of B (0.0987 mmol, 24.5 mg) and 50 equivalents of A (0.0987 mmol, 13 µL) in 0.6 mL of THF-$d_8$ were added and consumption of each monomer were monitored over 3 half lives.

<table>
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<th>Time (s)</th>
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<th>$\ln([B]/[B]_0)$</th>
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Slope \((k_{\text{obs}}) = 3.4 \times 10^{-5} \text{ s}^{-1}\)

Slope \((k_{\text{obs}}) = 3.3 \times 10^{-5} \text{ s}^{-1}\)
Details of Kinetic Experiments II

Rate of consumption of A' by the first insertion complex of 2 with B' in Toluene-$d_8$.

In a J-Young NMR tube, 50 equivalents of A' (0.2 mmol, 19.2 mg, 23.3 µL) were added to the first insertion complex (4.0 mg, 4.0 µmol) in 0.7 mL of Toluene-$d_8$. Consumption of the monomer was monitored using tetramethylsilane as an internal standard.

<table>
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Slope ($k_{\text{obs}}$) = $6.2 \times 10^{-5}$ s$^{-1}$

In a J-Young NMR tube, 75 equivalents of $A'$ (0.3 mmol, 29.2 mg, 35.3 µL) were added to the first insertion complex (4.0 mg, 4.0 µmol) in 0.7 mL of Toluene-$d_8$. Consumption of the monomer was monitored using tetramethylsilane as an internal standard.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>[I]</th>
<th>ln([I]/[I]₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.14</td>
<td>-1.966</td>
</tr>
<tr>
<td>60</td>
<td>0.12</td>
<td>-2.120</td>
</tr>
<tr>
<td>120</td>
<td>0.10</td>
<td>-2.302</td>
</tr>
<tr>
<td>180</td>
<td>0.08</td>
<td>-2.525</td>
</tr>
<tr>
<td>242</td>
<td>0.06</td>
<td>-2.813</td>
</tr>
<tr>
<td>300</td>
<td>0.05</td>
<td>-2.995</td>
</tr>
<tr>
<td>360</td>
<td>0.04</td>
<td>-3.218</td>
</tr>
</tbody>
</table>
Slope ($k_{obs}$) = $6.3 \times 10^{-5}$ s$^{-1}$
Rate of consumption of B' by 2 in Toluene-$d_8$.
In a J-Young NMR tube, 5 equivalents of B' (0.02 mmol, 4.7 mg, 4.0 µL) were added to 2 (3.1 mg, 4.0 µmol) in 0.7 mL of Toluene-$d_8$. Consumption of the monomer was monitored over 3 half lives.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>ln([I]/[I]₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>-0.086</td>
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<tr>
<td>30</td>
<td>-0.165</td>
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<tr>
<td>60</td>
<td>-0.336</td>
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<tr>
<td>90</td>
<td>-0.488</td>
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<tr>
<td>120</td>
<td>-0.667</td>
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<tr>
<td>150</td>
<td>-0.832</td>
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<tr>
<td>180</td>
<td>-1.015</td>
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<tr>
<td>210</td>
<td>-1.181</td>
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<tr>
<td>240</td>
<td>-1.391</td>
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<tr>
<td>345</td>
<td>-2.110</td>
</tr>
<tr>
<td>409</td>
<td>-2.652</td>
</tr>
</tbody>
</table>
Slope ($k_{obs}$) = 10.6 x $10^{-5}$ s$^{-1}$

In a J-Young NMR tube, 20 equivalents of $\mathbf{B'}$ (0.08 mmol, 18.7 mg, 15.9 µL) were added to 2 (3.1 mg, 4.0 µmol) in 0.7 mL of Toluene-$d_8$. Consumption of the monomer was monitored over 3 half lives.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>ln([I]/[I]$_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-0.095</td>
</tr>
<tr>
<td>30</td>
<td>-0.165</td>
</tr>
<tr>
<td>60</td>
<td>-0.231</td>
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<tr>
<td>120</td>
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<td>150</td>
<td>-0.970</td>
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<tr>
<td>180</td>
<td>-1.172</td>
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</tbody>
</table>
Slope ($k_{obs}$) = 10.8 x 10^{-5} s^{-1}

In a J-Young NMR tube, 30 equivalents of B' (0.12 mmol, 28.1 mg, 23.8 µL) were added to 2 (3.1 mg, 4.0 µmol) in 0.7 mL of Toluene-$d_8$. Consumption of the monomer was monitored over 3 half lives.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>ln([I]/[I]₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>-0.113</td>
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<tr>
<td>Time (s)</td>
<td>Value</td>
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<tr>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>30</td>
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<tr>
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<td>-0.482</td>
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<tr>
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<td>-0.693</td>
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<tr>
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<tr>
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<td>-1.488</td>
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<tr>
<td>240</td>
<td>-1.658</td>
</tr>
<tr>
<td>273</td>
<td>-1.894</td>
</tr>
<tr>
<td>300</td>
<td>-2.147</td>
</tr>
</tbody>
</table>

Slope ($k_{obs}$) = $1.13 \times 10^{-5}$ s$^{-1}$

$y = -0.0068x - 0.0544$

$R^2 = 0.99867$
Observation of \textit{anti-MB\textsubscript{cis}} and \textit{syn-MB\textsubscript{cis}} by catalyst 1

In a J-Young NMR tube, 0.7 equivalents of B (5.7 mg, 23 µmol) were added to a 0.7 mL toluene-$d_8$ solution of catalyst 1 (22.8 mg, 32 µmol) at room temperature. After 2 hours, a $^1$H NMR spectrum was taken and the major species was \textit{anti-MB\textsubscript{cis}} and the minor species was \textit{syn-MB\textsubscript{cis}}. The assignment of major olefinic peaks were confirmed by gCOSY and HSQC experiments. The sample was left in solution for 3 days to reach equilibrium and the $K_{eq}$ ($=\text{[syn-MB\textsubscript{cis}]/[anti-MB\textsubscript{cis}]}$) was found to be 0.05.

$^1$H NMR of alkylidene region:

$^1$H NMR of olefinic region:
Photolysis of 1 and addition of B by varying the temperature.

In a Wilmad screw-cap NMR tube, Mo(NAr')(CHCMe_2Ph)(OCMe(CF_3)_2)_2 (32.5 mg, 45.8 µmol) were dissolved in 0.6 mL of toluene-d_8. The sample was closed with a PTFE/silicon septum cap and irradiated at -78 °C in a Rayonet photolysis apparatus at 350 nm for 3 h. The sample was kept at -78 °C until it was placed in a 500 MHz NMR spectrometer preequalibrated to -50 °C. 45% of anti-1 was generated.

^1^H NMR of the alkylidene region at -50 °C:

\[ J_{HH} = 12 \text{ Hz} \]

\[ J_{CH} = 156 \text{ Hz} \]

\[ J_{CH} = 122 \text{ Hz} \]
After observation at -50 °C, the sample was returned to a -78 °C bath and 0.5 equivalents of B (5.1 mg, 20.5 µmol) in 0.1 mL of toluene-d₈ was added via a syringe. The consumption of B was monitored as the temperature was changed by +10 °C.

¹H NMR of the alkylidene region at -40 °C:

At -10 °C, both syn-MBₜrans and syn-MB₉iss species are resolved and olefinic peaks were assigned by gCOSY.

¹H NMR of the alkylidene region at -10 °C:

¹H NMR of the olefinic region at -10 °C:
$^1$H–$^1$H gCOSY spectrum of the olefinic region at -10 °C:
Figure S24. $^1$H-$^1$H gCOSY spectrum of the olefinic region of syn-MB$_{cis}$ and syn-MB$_{trans}$ at -10 °C
References