Stereospecific Ring-Opening Metathesis Polymerization (ROMP) of Norbornene and Tetracyclododecene by Mo and W Initiators

Stereospecific Ring-Opening Metathesis Polymerization (ROMP) of Norbornene and Tetracyclododecene by Mo and W Initiators

by

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Abstract

In this paper we report the synthesis of >98% *cis,isotactic* and *cis,syndiotactic* polynorbornene (poly(NBE)) and poly(*endo,anti*-tetracyclododecene) (poly(TCD)). *Cis,isotactic* poly(NBE) and poly(TCD) were prepared employing Mo-based biphenolate imido alkylidene initiators, Mo(NR)(CHCMe$_2$Ph)(Biphen) (Biphen = e.g., 3,3′-(*t*-Bu)$_2$-5,5′-6,6′-(CH$_3$)$_4$-1,1′-biphenyl-2,2′-diolate), while *cis,syndiotactic* poly(NBE) and poly(TCD) were prepared employing W-based imido or oxo monoaryloxide pyrrolide (MAP) initiators, W(X)(CHR')(Pyrrolide)(OTer) (X = NR or O; OTer = a 2,6-terphenoxide). Addition of 1-hexene or coordinating solvents such as THF do not decrease the stereospecificity of the polymerization. *Cis,iso* and *cis,syndio* dyads can be distinguished through examination of ^{1}H and ^{13}C NMR spectra of the two polymers in a mixture. The polymers were hydrogenated to give *isotactic* and *syndiotactic* H-poly(NBE) and H-poly(TCD).

INTRODUCTION

For several decades the Ring-Opening Metathesis Polymerization (ROMP) of strained cyclic olefins (especially norbornenes and norbornadienes) has been an important application of the olefin metathesis reaction.[1] With the discovery and development of well-defined catalysts based on Mo, W, and Ru in the last 25 years,[2] it has become possible to control the synthesis of polymers prepared through ROMP with ever-increasing precision.[3,4] Ideally it would be desirable to prepare any stereoregular polymer from any monomer, i.e., with either a *cis* or a *trans* structure and a single tacticity. It has been known for some time that the properties of a purely *isotactic* or *syndiotactic* polymer such as polypropylene can differ dramatically (e.g., in melting point, crystallinity, etc.) and those differences usually prove vitally important in terms of applications.[5]

The four possible regular structures of polynorbornenes and polynorbornadienes are *cis,isotactic*, *cis,syndiotactic*, *trans,isotactic*, and *trans,syndiotactic*. The *cis,isotactic* (meso dyads) and *cis,syndiotactic* (racemo dyads) structures for polynorbornene are shown in Figure 1. The tacticity remains upon hydrogenation of all C=C double bonds (Figure 1). When Mo and W initiators are employed in ROMP, it has been possible to prepare examples of all four possible structures made from a relatively small collection of monomers, although so far not all four structures from a *single* monomer have been prepared by varying the initiator.[4] The most common polymer structures that can be generated today are *cis,isotactic* and *cis,syndiotactic*, largely from Mo and W initiators.[4] *Cis,isotactic* structures can be prepared through enantiomorphic site control employing biphenolate imido alkylidene initiators,[6] e.g., **6** - **10** in Figure 2. Enantiomorphic site control in this context means that the monomer is forced by the chiral (*rac*) biphenolate to approach the metal-carbon double bond repeatedly from the same side after each insertion to give the next alkylidene. *If* biphenolate initiators yield a highly regular structure, then the structure would seem most likely to be *isotactic* for this reason. *Cis,syndiotactic* structures are generated through stereogenic metal control[4,7] employing Mo or W monoaryloxide pyrrolide (MAP) imido alkylidene initiators or W oxo alkylidene MAP initiators, e.g. **2** - **5** in Figure 2. The configuration at the metal center switches with each insertion, which causes the monomer to approach the stereogenic metal first from one side of the M=C double bond and then the other. Theoretical studies have suggested that the

monomer approaches the metal *trans* to the pyrrolide.[8] MAP catalysts produce *cis,syndiotactic* polymers *relatively* reliably, although there are now examples of MAP catalysts that produce *trans,isotactic*[7b] polymers as a consequence of a (proposed) rearrangement of the five-coordinate metallacyclobutane intermediate that takes place faster than the metallacycle opens to give product, but the configuration at the metal center does not change as a result of that particular rearrangement.[4b]

The prototypical monomer used in ROMP is norbornene (NBE). *Endo,anti*-Tetracyclododecene (TCD) is a bulky relative of NBE. Polymers formed from both are shown in Figure 3 along with the numbering scheme that we employ here. (Other numbering schemes have been used in other studies.[12]) Polymerization and hydrogenation of each could lead to potentially interesting crystalline and relatively oxygen-stable polymers analogous to hydrogenated polydicyclopentadiene.[9] A recent study of the synthesis of highly tactic poly(NBE) and poly(TCD) with molybenum- and tungsten-based initiator precursors has been published by Hayano.[10] NMR spectra can be found in the literature that purport to be of a *cis* and highly tactic poly(NBE),[11] but tacticities cannot be confirmed without authentic samples of both. In the past, tacticities of poly(NBE) samples have been determined through ^{13}C NMR examination of their hydrogenated polymers.[1,12]

We report here the stereospecific polymerization of both NBE and TCD to give >98% *cis,isotactic* and >98% *cis,syndiotactic* polymers with well-defined Mo and W initiators.

RESULTS

The initiators employed in this study are shown in Figure 2. These initiators were chosen because the MAP (MonoAryloxidePyrrolide) species (**2** - **5**) are the leading candidates to yield *cis,syndiotactic* polymers, while the biphenolates **6** - **10** are the leading candidates to yield *cis,isotactic* polymers, according to studies in the last several years.[4] Complex **1** typically forms polymers from achiral norbornenes and norbornadienes that contain both *cis* and *trans* C=C bonds. In some cases *trans*,*syndiotactic* polymers are formed from **1** through a form of chain end control.[4] Polymers prepared from **1** will serve as a reference with which the *cis*,*tactic* polymers can be compared.

ROMP of Norbornene (NBE)

In order to obtain polymers with relatively low molecular weights, 100 equivalents of NBE were initially employed with each initiator. The number average molecular weight for these polymers in theory under ideal circumstances therefore should be ~10,000. All reactions were performed at room temperature in dichloromethane; all were complete in a few seconds. All polymerizations were quenched after two minutes through addition of benzaldehyde to the reaction. Polymer yields were essentially 100%.

The stereoregularities of all polymers were evaluated through ^{1}H and ^{13}C NMR methods. In ^{1}H NMR spectra of poly(NBE), resonances for *cis* olefinic protons appear at 5.21 ppm, whereas resonances for *trans* olefin protons are found at ~5.35 ppm (see SI). All polymers that were prepared from initiators shown in Figure 2 (except **1**) were largely or exclusively *cis*. The results are summarized in Table 1. Representative ^{13}C NMR spectra (recorded at 22 °C in $CDCl_3$) are shown in Figure 4 for polymers prepared from **1**, **2a**, and **7**.

As expected, initiator **1** produces a poly(NBE) that contains both *cis* and *trans* double bonds. In the ^{13}C NMR spectrum, resonances for olefinic carbons in *cis* double bonds are found around 133.8 ppm and for *trans* double bonds around 133.0 ppm (Figure 4A and SI). The ratio of *cis* and *trans* double bonds for poly(NBE) prepared with **1** is roughly 1:1.

Initiators **2a**, **2b**, **2c**, **3**, and **5** yield identical *cis* and highly tactic poly(NBE)s. The ^{13}C NMR spectrum of poly(NBE)$^{\mathbf{2a}}$ (prepared with **2a**) is shown in Figure 4B. If a poly(NBE) is a single *cis* structure, MAP intiators (**2a**, **2b**, **2c**, **3**, and **5**) are more likely to yield *cis*,*syndio*-poly(NBE) as a consequence of stereogenic metal control. The proton NMR spectra of the *cis*,*syndio*-poly(NBE) samples are especially well-resolved because of the long range structure of these polymers. (See SI for full spectra).

Initiators **7**, **9**, and **10** yield a highly tactic, all *cis* poly(NBE) whose ^{13}C NMR spectrum again consists of four sharp resonances (Figure 4C). (The ^{1}H NMR spectrum as well as the full ^{13}C NMR spectrum are shown in the SI.) These samples should have a *cis*,*isotactic* structure since they are formed from biphenolate initiators. Although the chemical shifts in the ^{13}C NMR spectra for *cis*,*syndio* and *cis*,*iso* are almost identical (at 100.61MHz), the resonances for *cis*,*syndio*-poly(NBE) at 42.68 and 33.19 ppm should be distinguishable from the corresponding resonances for *cis*,*iso*-poly(NBE) at 42.61 and

33.24 ppm, respectively. In order to determine whether this is true or not, ^{13}C NMR spectra were obtained for a 9:1 mixture of *iso*-poly(NBE) and *syndio*-poly(NBE) (Figure 5A). It clearly is possible to differentiate the two tacticities even if one is present only as 10% of the mixture, at least if the mixture consists of two separate polymers, each with relatively sharp resonances. To our knowledge, this is the first time that high purity *cis,syndiotactic*-poly(NBE) and *cis,isotactic*-poly(NBE) have been prepared and compared in this manner, although hydrogenated poly(NBE)s have been compared in ^{13}C NMR studies for some time.[12]

Small chemical shift differences alone are likely to be unreliable for identifying the tacticity of a *cis*-poly(NBE) that appears to have a single tacticity as a consequence of small referencing errors, variable temperature, instrument variations, etc. For example, $Mo(NC_6F_5)(\eta^2\text{-}CH_2{=}CH_2)(ODFT)_2$ was reported to polymerize NBE to give a *cis* polymer with sharp resonances in the ^{13}C NMR spectrum (in $CDCl_3$ at 22 °C) at 134.00, 42.83, 38.72, and 33.34 ppm.[11b] (The method of forming the alkylidene in this case is not known.) If we assume that these chemical shifts are systematically off by 0.13 ppm (due to some experimental error), i.e., if we assume that the shift for the olefinic carbons are 133.87(1) ppm in both tactic polymers (Figures 4 and 5), then the chemical shifts (133.87, 42.70, 38.59, 33.21) match best with those of *cis,syndiotactic*-poly(NBE). However, a ^{13}C NMR spectrum (at 100 MHz ^{13}C or higher) of an unknown *cis,* tactic-poly(NBE) mixed with an authentic sample of *cis,syndiotactic*-poly(NBE) clearly is the most reliable method of assigning tacticity. Eliminating errors through NMR examination of mixtures of various hydrogenated poly(NBE)s is the normal method of identifying tacticities.[12a]

The ^{13}C NMR spectrum of a *cis* polymer (as determined through proton NMR studies) prepared with W biphenolate complex initiator **8**, a W analog of initiator **7**, is shown in Figure 5B. In this case, both tacticities at the dyad level can be observed in roughly a 60:40 (*iso*:*syndio*) ratio, even though all resonances are broadened significantly compared to those shown in Figure 4A as a consequence of nearby structural variation beyond the dyad level. The resonances at 42.62 (*iso*) and 42.68 ppm (*syndio*) are easily observed in the atactic polymer, as are those at 33.19 (*syndio*) and 33.24 ppm (*iso*). Even the two olefinic carbon resonances are resolvable (barely at 100.61MHz) at 133.86 (*syndio*)

and 133.88 ppm (*iso*). We propose that enantiomorphic site control is simply not successful employing **8**, i.e., NBE approaches either side of the W=C bond. Perhaps binding of NBE to yield an olefin/alkylidene intermediate is more reversible in the case of **7** (the Mo analog), *relative to* the rate of forming a metallacyclobutane intermediate (essentially irreversibly), than in the case of **8**. Clearly additional studies will be required to determine whether this difference is a general phenomenon to be expected of a W initiator that is an exact analog of a Mo biphenolate initiator.

At this point we can conclude that when the poly(NBE) that is formed is all *cis* and tactic, *cis,syndio*-poly(NBE) is obtained with MAP catalysts (**2a**, **2b**, **2c**, **3** and **5**) and *cis,iso*-poly(NBE) is obtained with Mo biphenolates (**7**, **9**, and **10**). The polymer derived using **4** has ~20% *trans* double bonds and we have no knowledge as to whether *trans* dyads are *syndio* or *iso* or both. Complex **6** gives a highly structured polymer with less than 5% of a visible *trans* fraction and a ≥95% *cis,isotactic* dyad microstructure.

We have the most confidence in assigning the structure of the poly(NBE) formed with the Mo biphenolate catalysts (**7**, **9**, and **10**) as *cis,isotactic*, because the chirality at the metal center is fixed by the biphenolate ligand and the monomer therefore should add at each stage to the same side of the Mo=C bond if the reaction is under enantiomorphic site control. *Cis,syndiotactic* dyads can form in some cases by mistake, as in the case of poly(NBE) formed from **8**, but formation of a >99% *cis,syndiotactic* structure from a *biphenolate* initiator would require a creative explanation.

We have not explored proton and carbon NMR spectra of *cis,tactic*-poly(NBE)s at different temperatures or in a range of solvents. Samples with higher molecular weights are likely to be less mobile (and less soluble) than those with relatively low molecular weights (~10,000 for poly(NBE) here, in theory) and resolution of resonances for "large" polymers should depend much more on the solvent employed and the temperature. Exploring a range of solvents is sometimes limited by solubility issues for many stereoregular, crystalline polymers.

Selected ^{1}H NMR decoupling experiments are completely consistent with the synthesis of polymers that contain a single microstructure. In Figure 6, NMR experiments in which the H1 and H2 protons are selectively decoupled are summarized for *cis,syndiotactic* poly(NBE). (The full spectra as well as the analogous experiments with

cis,isotactic-poly(NBE) are given in the Supporting Information.) Upon selective decoupling the methine protons (H2), the resonance for H1 collapses from a second-order "doublet" into a sharp singlet. The aliphatic protons H5 and H6 yield doublets of doublets due to coupling with each other and to the methine protons H2. One would expect the appearance of a doublet upon selectively decoupling the methine protons H2, which is what is observed (Figure 6B). Protons H3 and H4, which both give multiplets in ^{1}H NMR spectra, give well-resolved doublets of doublets after decoupling protons H2. In the same manner the methine resonance for the H2 protons sharpens upon decoupling the olefinic protons H1 (Figure 6C). All observations for both *cis,syndiotactic* and *cis,isotactic* poly(NBE) are consistent with the polymers having a single structure.

ROMP of Tetracyclododecene (TCD)

Polymerizations of TCD employing all initiators we tried were complete within seconds. The polymerizations were conducted at room temperature in dichloromethane and were quenched after one minute through addition of a large excess of benzaldehyde. All highly tactic poly(TCD)s precipitated out of the reaction mixture, but dissolved in $CDCl_3$ at 55°C. In contrast, the polymers derived from **1**, **2b**, and **2c** are soluble in $CDCl_3$ at room temperature. For the poly(TCD)s the ratios of *cis* and *trans* double bonds were determined from ^{1}H NMR spectra through integration of the resonances for the methine protons on C2 and C5 (Figure 3). A chemical shift of 2.97 ppm is characteristic of a *cis* structure, whereas a resonance at 2.71 ppm is characteristic of a *trans* structure. In poly(TCD) *cis* and *trans* olefinic protons are not resolvable at the field strengths used in this study.

Poly(TCD) generated from **1** contains 80% *trans* double bonds. Its ^{13}C NMR spectrum is shown in Figure 7 and its ^{1}H NMR spectrum in the Supporting Information (SI). Initiator **2a**, which yielded *cis*,*syndio*-poly(NBE), yielded poly(TCD) that is only 80% *cis* (see spectra in the SI). Initiators **3** and **4** produce identical poly(TCD) samples that we propose have a *cis,syndiotactic* structure. The ^{13}C NMR spectrum of *cis,syndio*-poly(TCD) shows seven distinct carbon resonances (Figure 7). Proton NMR spectra are also well-resolved (see SI).

Initiators **6-10** all produce what we propose to be *cis,isotactic*-poly(TCD), the ^{13}C NMR spectrum of which is shown in Figure 7C. Again, the spectrum is simple, with seven

relatively sharp resonances. In this case, the chemical shift differences (at 100.61 MHz) are more significant than the chemical shift differences between *cis,iso* and *cis,syndio*-poly(NBE), with five of the seven resonances (for C1/C6, C2/C5, C7, C3/C4, and C8/C11 in poly(TCD)) being potentially resolvable in a mixture. These resonances were shown to be resolvable for a 70:30 mixture (*iso* from **7** to *syndio* from **3**), as shown in Figure 8. Only resonances for C12 and the sp^3 hybridized carbons (C9 and C10) cannot be resolved (at 100.61 MHz). In the ^1H NMR spectrum of this mixture most of the resonances overlap, but those for the methine protons at the C3/C4 position are clearly separated (Figure 8). A chemical shift of 2.36 ppm is indicative of a *cis,isotactic* microstructure and a chemical shift of 2.31 ppm denotes a *cis,syndiotactic* microstructure. It should be noted that in a polymer in which the two type of dyads are both found, the ^{13}C NMR or proton NMR resonances may be broadened or additional splitting may be observed due to *rac* and *meso* variations beyond the dyad level.

The tungsten biphenolate complex **8** initiates formation of *cis,isotactic*-poly(TCD), in contrast to its behavior in the polymerization of NBE (Table 1). Initiator **4**, which yields poly(NBE) that possesses 20% *trans* configured double bonds, gives *cis,syndiotactic*-poly(TCD). This finding is understandable if one considers the increased steric bulk of TCD compared to NBE and consequently the lower tendency for the monomer to add (in an *anti* fashion) to the *syn* alkylidene to give a *trans* metallacyclobutane and subsequently a *trans* C=C bond upon opening the metallacycle. The respective ^{13}C NMR spectra, which show seven distinct resonances, are given in the Supporting Information. Complex **5**, a W MAP catalyst featuring the bulky 2,6-diisopropylphenylimido ligand that is *cis,syndio* selective in the ROMP of NBE does not yield a regular poly(TCD) structure; most likely the imido group is too large to accommodate a monomer as large as TCD in a selective manner. The Mo biphenolates **6** and **10**, which produced *cis,iso*-poly(NBE), also yield *cis,iso*-poly(TCD). Both **6** and **10** feature the fluorinated biphenolate 3,3′-(*t*-Bu)$_2$-5,5′-$(CF_3)_2$-6,6′-$(CH_3)_2$-1,1′-biphenyl-2,2′-diolate and comparatively small imido substituents. Complex **9** also gives *cis,isotactic*-poly(TCD). In fact, all well-defined Mo and W biphenolate alkylidenes yield poly(TCD) with a single structure as a consequence of enantiomorphic site control. Proton decoupling NMR experiments for *cis,isotactic*-poly(TCD) and *cis,syndiotactic*-poly(TCD)

analogous to those described in the first section above for poly(NBE)s are completely consistent with the two poly(TCD)s each having a single structure (see SI).

Preparation of Hydrogenated Polymers

The ROMP derived polymers were hydrogenated by diimine generated *in situ via* thermal decomposition of *p*-Tos-$NHNH_2$.[13] Four equivalents of *p*-Tos-$NHNH_2$ per monomer unit were employed in $CHCl_3$ at 130°C.

Tactic and irregular poly(NBE) was hydrogenated smoothly within six hours. The hydrogenated polymer was soluble in chloroform at a reaction temperature of 130°C but precipitated from solution upon cooling the solution to room temperature. NMR spectra for all *isotactic* H-poly(NBE)s had to be recorded at 120°C in $C_2D_2Cl_4$, whereas *syndiotactic* or atactic polymers were soluble enough at 55°C in $CDCl_3$ to obtain high quality NMR spectra.

Figure 9 shows that the carbon NMR spectrum of *syndiotactic* H-poly(NBE) consists of the expected[1,12] four sharp resonances. The carbon NMR spectrum of *isotactic* H-poly(NBE) prepared employing catalyst **7** is equally simple (see SI). The chemical shifts for the carbon atoms in *syndiotactic* and *isotactic* H-poly(NBE) differ by only 0.1-0.2 ppm. For a mixture composed of 50% *isotactic* H-poly(NBE) (made with catalyst **7**) and 50% *syndiotactic* H-poly(NBE) (made with catalyst **2a**) only the resonance for C7 shows splitting that indicates the presence of two polymers having different tacticities (see SI). Therefore the microstructures can barely be differentiated with certainty, even when each polymer is a single structure, under the conditions that we have employed here. For the sample of H-poly(NBE) prepared from the poly(NBE) made from **8**, the resonances for C7 in the two types of dyads are not resolvable (see SI). It should be noted that separate resonances for meso (*iso*) and racemo (*syndio*) dyads in hydrogenated polynorbornene have been observed (resolved) under other conditions (other solvents) and in soluble samples that do not have a single tacticity.[10,12]

Cis,syndiotactic and irregular poly(TCD) could be hydrogenated smoothly. The ^{13}C NMR spectra of irregular and *syndiotactic* H poly(TCD) are shown in Figure 10. For the *syndiotactic* polymer seven distinct singlets are visible. The resonances for irregular H-poly(TCD) suggests the presence of the two different microstructures at the dyad level.

For the methine carbons (C3 and C4) two clearly separated resonances are observed for the irregular polymer whereas for *syndiotactic* H poly(TCD) a sharp singlet is observed. The chemical shift of 51.747 ppm for the sharp singlet exactly matches one of the resonances observed for the irregular polymer, which strongly suggests that the chemical shift of 51.646 ppm found for the other resonance can be ascribed to the *isotactic* polymer. For pure *syndiotactic* H-poly(TCD), carbon C7 gives a sharp singlet in the ^{13}C NMR spectrum whereas the resonance is broadened in atactic H poly(TCD) and shows splitting which could partly be resolved. The methine carbons C8 and C11 produce a sharp singlet for the single structured H-poly(TCD), whereas the resonance is broadened and splitting is noticeable for the atactic polymer. *Syndiotactic* poly(TCD) is soluble in $CDCl_3$ at 55°C whereas *isotactic* poly(TCD) appears to be a highly crystalline polymer that could not be dissolved in any common solvent at temperatures up to 150°C.

Variations in the method of polymerization

In several experiments 5 mol% of 1-hexene was added as a chain transfer agent. In no case did addition of 1-hexene lead to any significant change or degradation of the structure of the polymer. Therefore, 1000 equivalents of monomer could be polymerized smoothly in the presence of 5% 1-hexene (Table 2). All reactions were performed at room temperature and were terminated through the addition of benzaldehyde after 45 minutes. In the ROMP of TCD initiated by W-MAP complex **3** as well as in the ROMP of NBE and TCD by Mo-biphenolate catalyst **7**, all monomer was consumed after 10 minutes. When the reaction mixtures were stirred for 45 minutes before termination, the structures and stereoregularities were unchanged. The ROMP reactions of NBE by W MAP catalysts **2a** and **3** noticeably slowed down upon addition of a chain transfer agent, providing all *cis* configured *syndio* tactic polymers in ~100% yield only after ~45 minutes under the conditions employed. We propose that the stability of the unsubstituted metallacyclobutane complex that is likely to be formed in the presence of 1-hexene, is the reason why reactions are sometimes slower in the presence of 1-hexene, expecially for W initiators, whose metallacyclobutane complexes are generally more stable to loss of olefin than corresponding molybdacyclobutane complexes. The clear advantage of a terminal

olefin chain transfer reagent is that catalyst loadings can be reduced and high molecular weights can be avoided.

Several reactions were performed in THF or toluene (Table 3). The monomer concentration was 2 wt% for all experiments. In no case did we observe any degradation of the structure, although THF slowed the reaction when W-MAP initiators were used. The ROMP of TCD was complete after one minute in all cases and the polymer precipitated within seconds. MAP catalysts **2a** and **3** polymerized 100 equivalents of NBE within 10 minutes in THF. When Mo initiators **7**, **2b**, and **2c** were used, polymerizations of NBE were complete after 2 minutes. When toluene was used as the solvent, full monomer conversion was observed after 2-3 minutes for all catalysts, but gels were formed under these conditions.

DISCUSSION

Initiators that contain biphenolate ligands such as Biphen (along with a few related binaphtholate ligands) have been found to polymerize several monomers to give *cis,isotactic* polymers with essentially only one long range structure.[4] The monomers that have been polymerized stereospecifically in this manner include 2,3-R_2norbornadienes where the R groups are esters (CO_2Me, CO_2Menthyl, or CO_2Pantolactonyl) or CF_3,[6a,b,c] or enantiomerically pure *exo,endo*-2,3-R_2norbornenes where R is CO_2R' (R' = Me, Et, *t*-Bu), CH_2OMe, or Me.[6a,b,7d] The structure can be confirmed directly for the polymers made from an enantiomerically pure *exo,endo*-2,3-R_2norbornene or the 2,3-dicarboalkoxynorbornadienes where the ester contains a menthyl or pantolactonyl group. 1-Methyl-1-phenylcyclopropene (MPCP)[7c,14] has been polymerized by a biphenolate to give (it is proposed) a *cis,isotactic* polymer. While a "mistake" can be made employing a catalyst that is expected to exert enantiomorphic site control, as was found in the case of polymerization of norbornene by **8**, it is difficult to imagine the "mistakes" repeating perfectly to give a *cis,syndiotactic* polymer instead of a *cis,isotactic* polymer. Therefore, formation of *cis,isotactic* polymers from Mo or W catalysts that contain a biphenolate or binaphtholate ligand seems to be on relatively secure ground.

Cis,syndiotactic polymers have been made with MonoAryloxidePyrrolide (MAP) catalysts and 2,3-R_2norbornadienes where the R groups are esters (CO_2Me, CO_2Menthyl, or

CO_2Pantolactonyl) or CF_3,[7a,7c,15] enantiomerically pure *exo,endo*-2,3-(CO_2R')$_2$norbornenes where R' = Me, Et, *t*-Bu,[7b] or 1-methyl-1-phenylcyclopropene (MPCP).[7c] The *cis,isotactic* and *cis,syndiotactic* forms of poly(MPCP) can be distinguished clearly by NMR spectra, but neither can be proven. The *cis,syndiotactic* structure can be confirmed for the polymers made from 2,3-(CO_2Menthyl)$_2$norbornadiene. Formation of the *cis,syndiotactic* structure depends upon inversion at the metal through an interchange of pyrrolide and aryloxide ligands in a five-coordinate intermediate metallacyclobutane before the metallacyclobutane ring opens.

The stereoselective polymerization of several 7-isopropylidene-2,3-disubstituted norbornadienes, 7-oxa-2,3-dicarboalkoxynorbornadienes, and 11-oxa-benzonorbornadienes with a single tungsten oxo alkylidene catalyst, W(O)(CH-*t*-Bu)(OHMT)(Me_2Pyr) (OHMT = 2,6-dimesitylphenoxide; Me_2Pyr = 2,5-dimethylpyrrolide) has been reported to give *cis,tactic* polymers.[16] The structure of poly(7-oxa-2,3-dicarbomenthoxynorbornadiene) was shown to be *cis,syndiotactic*, but the structure of poly(7-isopropylidene-2,3-dicarbomenthoxynorbornadiene) was shown to be *cis,isotactic*. It was proposed that the configuration of the metal is retained in the case of 7-isopropylidene-2,3-dicarbomenthoxynorbornadiene as a consequence of a rapid opening of the metallayclobutane ring relative to any five-coordinate rearrangement at the metal. The other polymers are proposed to have a *cis,syndiotactic* structure, but that has been proven only for poly(7-oxa-2,3-dicarbomenthoxynorbornadiene).

The synthesis of poly(NBE), poly(TCD), and poly(DCPD), and their hydrogenated versions, employing Mo or W catalyst precursors plus an alkylating agent such as Et_2Al(OEt), has been studied for the last dozen years by Hayano.[9] A few catalyst precursors such as W(NR)Cl_4(Et_2O) can lead to as high as 80% *syndiotactic*-H-poly(DCPD),[9a,f] while Mo or W M(X)(biphenoxide)$_2$ precursors (X = oxo or imido and the biphenoxide is (e.g.) 3,3′-(*t*-Bu)$_2$-5,5′-6,6′-(CH_3)$_4$-1,1′-biphenyl-2,2′-diolate) can lead to as high as 95% *isotactic*-H-poly(DCPD).[9b,d,e] The actual catalysts that are prepared under these circumstances are likely to be of the M(X)(CHR)(biphenoxide) type, but the amount that is actually formed is likely to be a small percentage of the total. For that reason they must be remarkably efficient and reactive in order to produce 95% *isotactic* hydrogenated polymer. *Isotactic* and *syndiotactic*-H-poly(DCPD) are both relatively crystalline and high melting, although

their recrystallization behaviors differ remarkedly, with only *syndiotactic*-H-poly(DCPD) recrystallizing relatively rapidly. It is perhaps not surprising in light of the results reported here that synthesis of *syndiospecific* initiators *via* an *in situ* synthesis method appears to be more difficult than synthesis of *isospecific* initiators. It also would seem to be more difficult to form only one *syndiospecific* or *isospecific* species through *in situ* syntheses that dominates all others in terms of reactivity, in comparison to using a well-defined initiator.

CONCLUSION

We have shown how to prepare poly(NBE)s and poly(TCD)s that have essentially 100% *cis,isotactic* or *cis,syndiotactic* structures employing well-defined Mo and W alkylidene initiators. Of the initiators that we explored, the most efficient for forming *cis,isotactic* polymers are Mo imido biphenolates, while the most efficient for forming *cis,syndiotactic* structures are tungsten oxo or tungsten or molybdenum imido MAP complexes that contain a terphenoxide ligand. The polymerizations proceed rapidly and in essentially 100% yields at room temperature in dichloromethane, toluene, and (at a reduced rate) THF. Addition of a chain transfer agent allows the catalyst loading to be reduced without negatively affecting the stereoselectivities. This contribution demonstrates the general importance of employing single, tunable, identifiable catalysts in order to make polymers from various other cyclic olefins with essentially 100% stereospecificity. Although a few exceptions are known at this time, the method of forming *cis,isotactic* and *cis,syndiotactic* polymers from biphenolates and MAP initiators, respectively, seems to have a significant degree of generality.

Experimental

General Remarks

Reactions were all carried out in a N_2-filled glovebox. Norbornene (Sigma-Aldrich) and tetracyclododecene (TCI America) were stored as dichloromethane solutions over molecular sieves (3 Å). *p*-Toluenesulfonyl hydrazide (*p*-Tos-$NHNH_2$) was purchased from Sigma-Aldrich and was used without further purification. The initiators Mo(N-2,6-*i*-Pr_2Ph)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$ (**1**),[17] W(N-*t*-Bu)(CHCMe$_3$)(pyr)(OHMT) [**2a**, OHMT=O-2,6-(2,4,6-$Me_3C_6H_2$)$_2$$C_6H_3$], [18] Mo(N-*t*-Bu)(CHCMe$_3$)(pyr)(OHMT)(**2b**),[18]

Mo(NAdamantyl)(CHCMe$_3$)(pyr)(OHMT) (**2c**),[18] W(O)(CHCMe$_2$Ph)(Me$_2$Pyr)(OHMT)(PMePh$_2$) (**3**),[19] W(O)(CHCMe$_2$Ph)(Me$_2$Pyr)(ODFT)(PMePh$_2$) [**4**, DFTO= O-2,6-(C$_6$F$_5$)$_2$C$_6$H$_3$],[19,20] W(N-2,6-*i*-Pr$_2$Ph)(CHCMe$_2$Ph)(pyr)(OHMT) (**5**),[21,22] Mo(N-2,6-Me$_2$Ph)(CHCMe$_2$Ph)(THF)(*rac*-biphenCF$_3$) [**6**, biphenCF$_3$ = 3,3′-(*t*-Bu)$_2$-5,5′-(CF$_3$)$_2$-6,6′-(CH$_3$)$_2$-1,1′-biphenyl-2,2′-diolate,[23] Mo(N-2,6-Me$_2$Ph)(CHCMe$_2$Ph)(*rac*-biphen) [**7**, biphen = 3,3′-(*t*-Bu)$_2$-5,5′,6,6′-(CH$_3$)$_4$-1,1′-biphenyl-2,2′-diolate],[23] W(N-2,6-Me$_2$Ph)(CHCMe$_2$Ph)(*rac*-biphen) (**8**),[24] Mo(N-2,6-*i*-Pr$_2$Ph)(CHCMe$_2$Ph)(*rac*-biphen-*t*-Bu) [**9**, biphen-*t*-Bu = 3,3′-(*t*-Bu)$_2$-5,5′-(*t*-Bu)$_2$-6,6′-(CH$_3$)$_2$-1,1′-biphenyl-2,2′-diolate],[23] and Mo(N-Ad)(CHCMe$_2$Ph)(THF)(*rac*-biphenCF$_3$) (**10**)[23] were prepared according to published procedures.

NMR spectra were recorded on 400 or 500 MHz NMR spectrometers in CDCl$_3$ at 25 °C and 55 °C or in C$_2$D$_2$Cl$_4$ (1,1,2,2-tetrachloroethane-d$_2$) at 120 °C and data are listed in parts per million (ppm) downfield from tetramethylsilane (TMS) as an internal standard. For ^{1}H NMR CDCl$_3$: 7.26 ppm, C$_2$D$_2$Cl$_4$: 5.97 ppm. For ^{13}C NMR CDCl$_3$: 77.00 ppm, C$_2$D$_2$Cl$_4$: 73.88 ppm.

ROMP Reactions

All polymerizations were performed at room temperature. To a stirred dichloromethane solution containing 2 wt% monomer (20 mg NBE or TCD / 1 g CH$_2$Cl$_2$), a solution of a given initiator was added in one portion (1 mol% catalyst in 0.2 mL CH$_2$Cl$_2$). Benzaldehyde was added to the reaction after a specific period of time (for NBE: 2 min; for TCD: 1 min, Table 1). The polymers were precipitated from methanol and all solvents removed *in vacuo*.

***Cis,syndiotactic*-poly(NBE)**

^{1}H NMR (400.13 MHz, CDCl$_3$, 25°C): δ 5.28-5.16 (m, 2H), 2.87-2.73 (m, 2H), 1.94-1.86 (m, 1H), 1.85-1.75 (m, 2H), 1.43-1.30 (m, 2H), 1.02 (dd, J = 10.3 Hz, 1H) ppm; ^{13}C NMR (100.61 MHz, CDCl$_3$, 25°C): δ 133.86 (C1/C6), 42.68 (C7), 38.59 (C2/C5), 33.19 (C3/C4) ppm.

***Cis,isotactic*-poly(NBE)**

^{1}H NMR (400.13 MHz, $CDCl_3$, 25°C): δ 5.25-5.19 (m, 2H), 2.86-2.72 (m, 2H), 1.96-1.88 (m, 1H), 1.84-1.78 (m, 2H), 1.42-1.32 (m, 2H), 1.02 (dd, J = 10.4 Hz, 1H) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$, 25°C): δ 133.87 (C1/C6), 42.61(C7), 38.60 (C2/C5), 33.24 (C3/C4) ppm.

***Cis,syndiotactic*-poly(TCD)**

^{1}H NMR (400.13 MHz, $CDCl_3$, 55°C): δ 5.51 (d, J = 5.9 Hz, 2H), 3.04-2.88 (m, 2H), 2.31 (s, 2H), 2.04 (d, J = 7.4 Hz, 2H), 1.84-1.76 (m, 1H), 1.42-1.31 (m, 4H), 1.05 (d, J = 6.9 Hz, 2H), 0.98 (d, J = 9.8 Hz, 1H) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$, 55°C): δ 131.37 (C1/C6), 53.53 (C2/C5), 43.46 (C7), 42.01 (C3/C4), 38.03 (C8/C11), 36.13 (C12), 29.89 (C9/C10)ppm.

***Cis,isotactic*-poly(TCD)**

^{1}H NMR (400.13 MHz, $CDCl_3$, 55°C): δ 5.50 (d, J = 5.4 Hz, 2H), 3.04-2.88 (m, 2H), 2.36 (s, 2H), 2.07 (d, J = 6.9 Hz, 2H), 1.82-1.70 (m, 1H), 1.44-1.28 (m, 4H), 1.06 (d, J = 6.0 Hz, 2H), 0.98 (d, J = 9.4 Hz, 1H) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$, 55°C): δ 131.85 (C1/C6), 54.04 (C2/C5), 43.17(C7), 41.99 (C3/C4), 38.18 (C8/C11), 36.08 (C12), 29.77 (C9/C10)ppm.

Hydrogenation of poly(NBE) and poly(TCD). Hydrogenation reactions were performed at 130°C in a pressure tube. Four equivalents of *p*-Tos-$NHNH_2$ per monomer unit were added to a chloroform solution containing 2 wt.% polymer. The reaction was stirred vigorously for 6 h. The reaction mixture was allowed to cool to room temperature and was then poured into excess methanol. The samples were washed repeatedly with methanol and all solvents were removed *in vacuo*.

***Syndiotactic* H-poly(NBE)**

^{1}H NMR (400.13 MHz, $C_2D_2Cl_4$, 120°C): δ 2.01-1.95 (m, 1H), 1.90-1.74 (m, 4H), 1.40-1.36 (m, 4H), 1.28-1.20 (m, 2H), 0.75 (dd, J = 9.4 Hz, 1H) ppm; ^{13}C NMR (100.61 MHz, $C_2D_2Cl_4$, 120°C): δ 40.58 (C7), 40.40 (C2/C5), 35.39 (C1/C6), 31.74 (C3/C4) ppm.

***Isotactic* H-poly(NBE)**

^{1}H NMR (400.13 MHz, $C_2D_2Cl_4$, 120°C): δ 2.03-1.93 (m, 1H), 1.91-1.71 (m, 4H), 1.37 (s, 4H), 1.24 (bs, 2H), 0.75 (dd, J = 9.4 Hz, 1H) ppm; ^{13}C NMR (100.61 MHz, $C_2D_2Cl_4$, 120°C): δ 40.60 (C7), 40.41 (C2/C5), 35.40 (C1/C6), 31.74 (C3/C4) ppm.

Atactic H-poly(TCD)

^{1}H NMR (400.13 MHz, $C_2D_2Cl_4$, 120°C): δ 2.28 (s, 2H), 2.02 (bs, 4H), 1.86 (bs, 1H), 1.58-1.37 (m, 6H), 1.31 (d, J = 9.5 Hz, 1H), 1.14 (d, J = 6.7 Hz, 2H), 1.00 (d, J = 9.3 Hz, 1H), 0.91-0.88 (m, 1H) ppm; ^{13}C NMR (100.61 MHz, $C_2D_2Cl_4$, 120°C): δ 51.75 (*syndio*), 51.65 (*iso*), 43.50, 41.37 (m), 37.13, 36.39, 30.32, 29.88 ppm.

***Syndiotactic* H-poly(TCD)**

^{1}H NMR (400.13 MHz, $C_2D_2Cl_4$, 120°C): δ 2.28 (s, 2H), 2.02-1.94 (m, 4H), 1.88-1.86 (m, 1H), 1.60-1.38 (m, 6H), 1.31 (d, J = 9.1 Hz, 1H), 1.15 (d, J = 6.6 Hz, 2H), 1.00 (d, J = 9.8 Hz, 1H), 0.97-0.88 (m, 1H) ppm; ^{13}C NMR (100.61 MHz, $C_2D_2Cl_4$, 120°C): δ 51.75 (C3/C4), 43.50 (C2/C5), 41.28 (C7), 37.19 (C8/C11), 36.39 (C12), 30.30 (C1/C6), 29.89 (C9/C10) ppm.

Acknowledgments

R.R.S. thanks the Department of Energy (DE-FG02-86ER13564) for research support. We thank Dr. William P. Forrest and Dr. Jeffrey H. Simpson for help with decoupling experiments. The authors thank Hyangsoo Jeong for samples of initiators **2a** and **7**.

Supporting Information Available Complete proton NMR spectra and carbon NMR spectra for all polymers prepared here (Figure S1-S45).

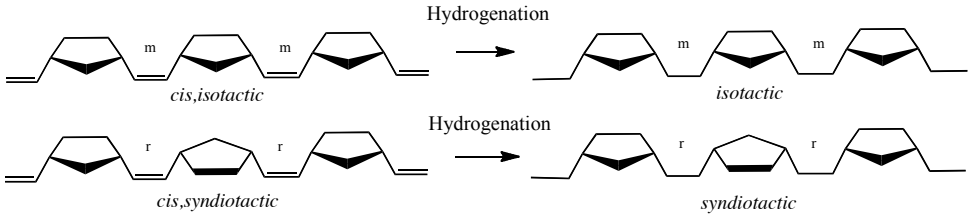

Figure 1. The structures of *cis,isotactic* and *cis,syndiotactic* polynorbornene and hydrogenated versions.

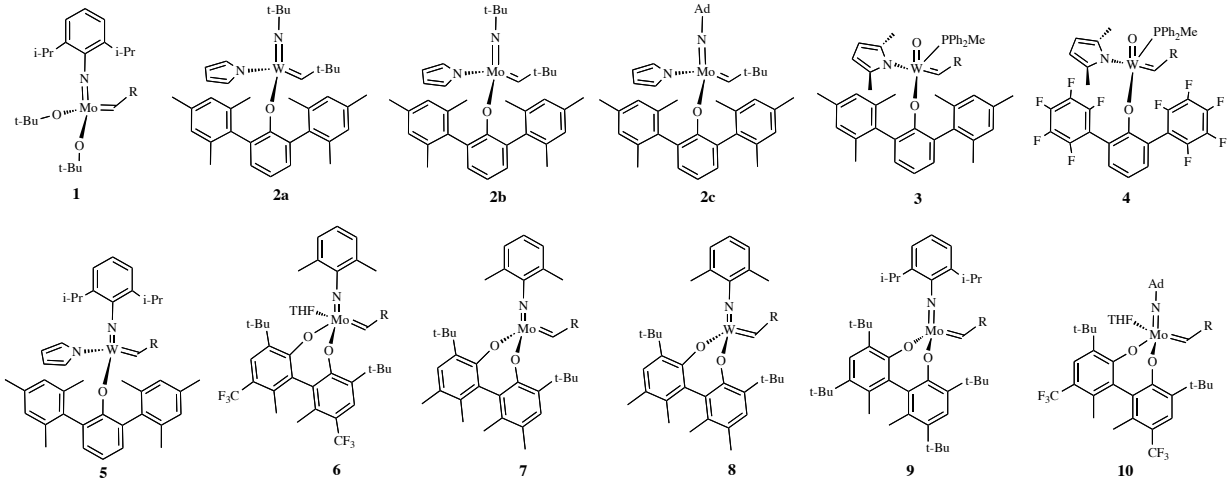

Figure 2. Initiators explored in this study (R = CMe_2Ph, Ad = 1-adamantyl).

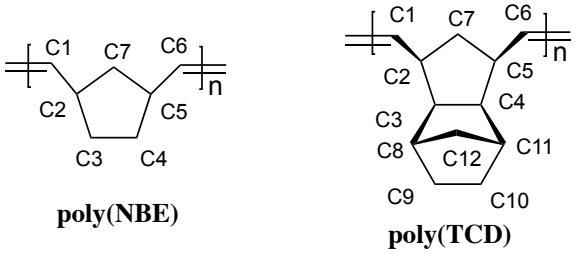

Figure 3. Numbering scheme in poly(NBE) and poly(TCD).

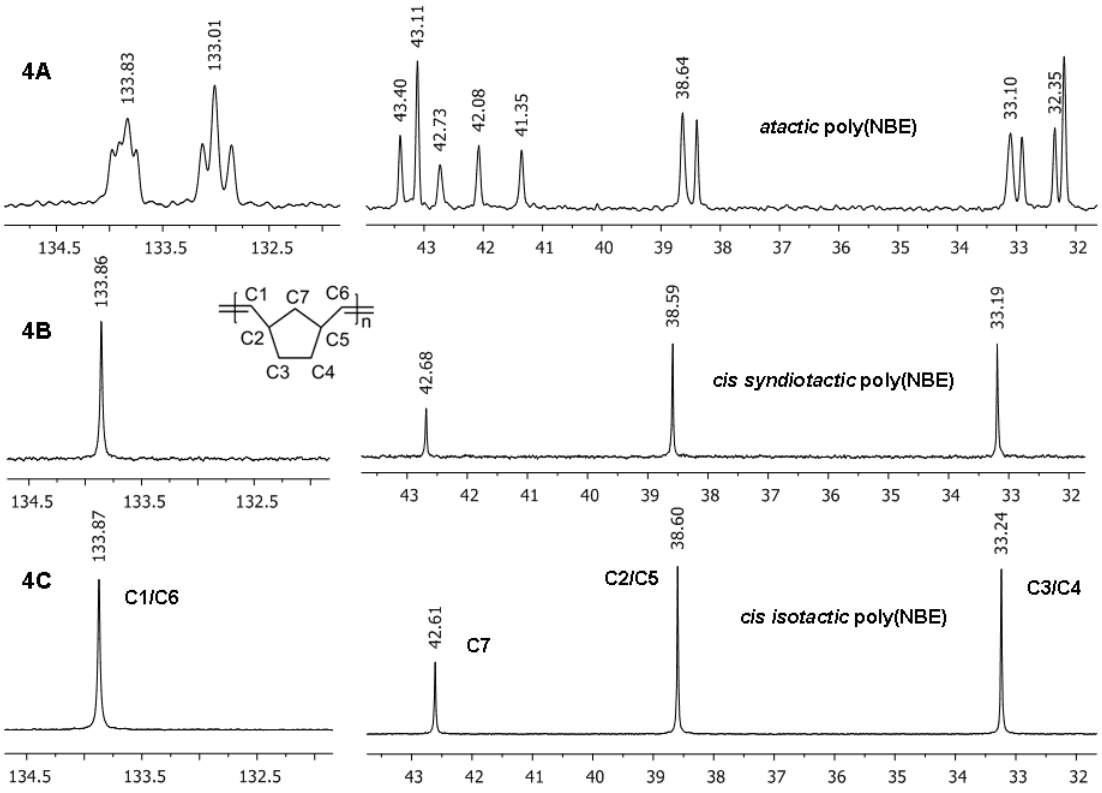

Figure 4. ^{13}C NMR spectra ($CDCl_3$, 22 °C, 100.61 MHz) of atactic poly(NBE) derived from **1** (4A), *cis,syndio*tactic-poly(NBE) made from **2a** (4B), and *cis,isotactic*-poly(NBE) made from **7** (4C). (Full spectra are shown in the Supporting Information.)

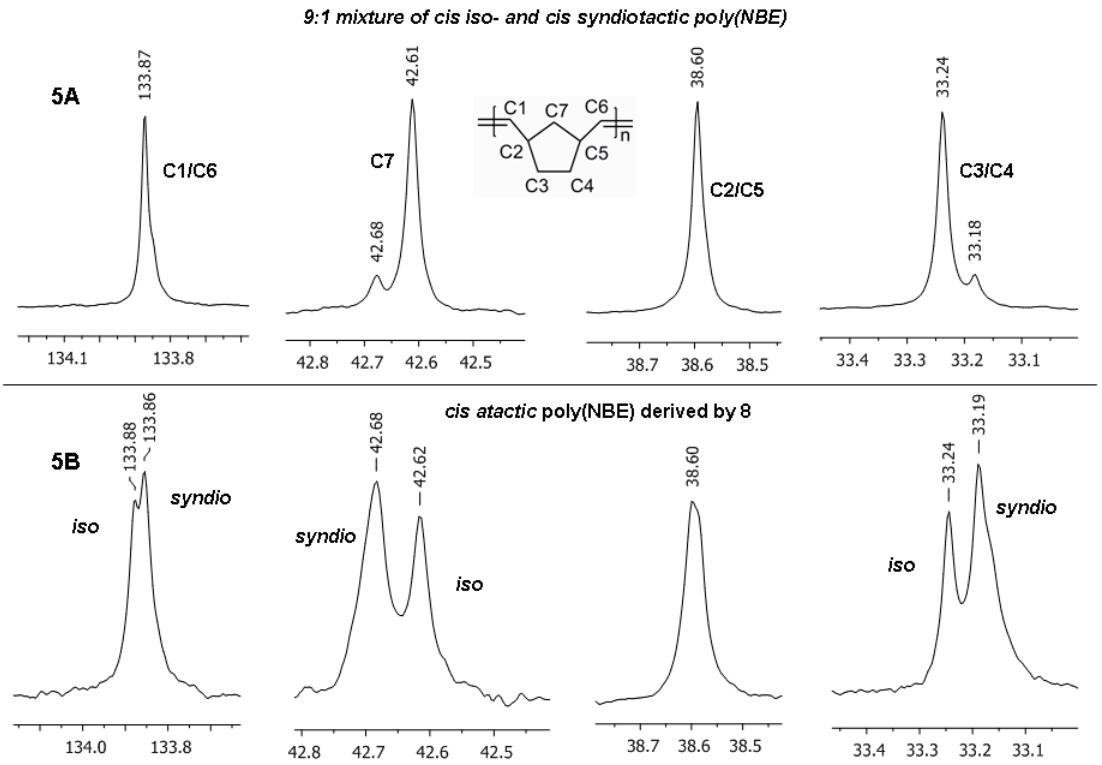

Figure 5. 5A: ^{13}C NMR spectrum ($CDCl_3$, 22 °C, 100.61 MHz) of amixture of *cis,isotactic*-poly(NBE) made from **7** (90 wt%) and *cis,syndiotactic*-poly(NBE) made from **2** (10 wt%); 5B: ^{13}C NMR spectrum of all *cis*, atactic poly(NBE) made from **8**.

(See SI for full spectra.)

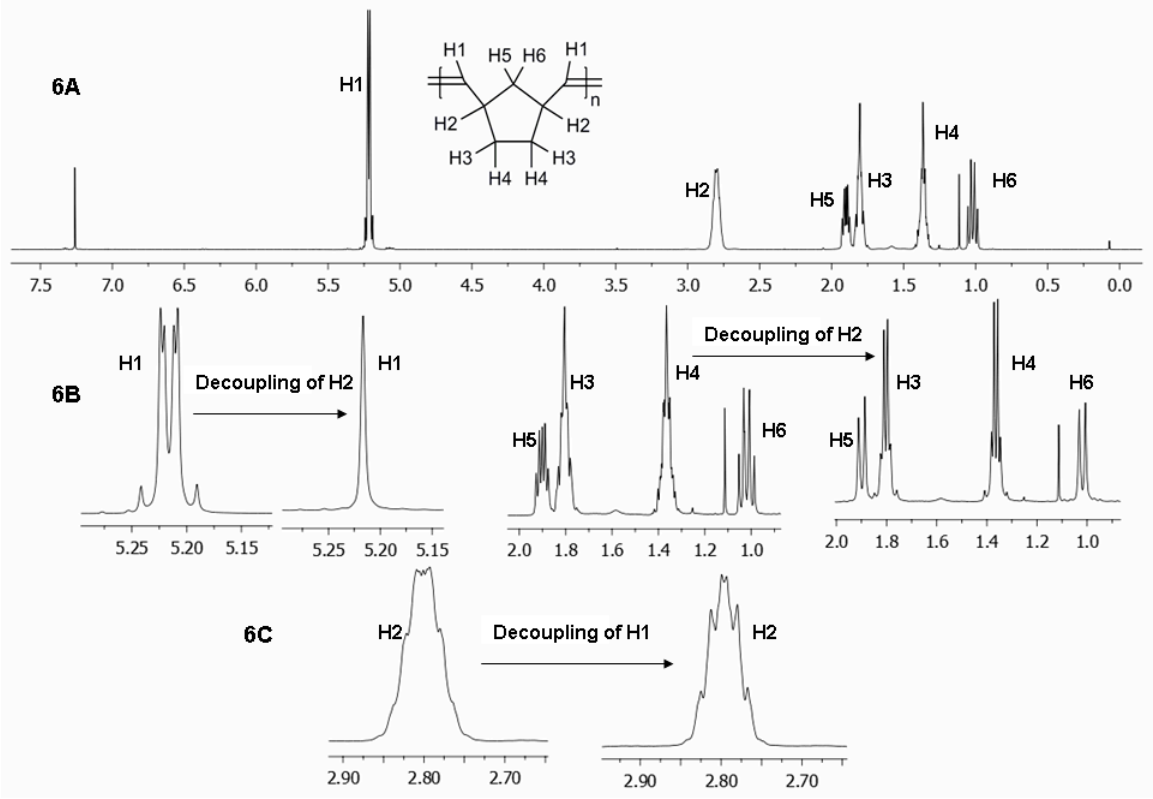

Figure 6. *Cis,syndiotactic* poly(NBE) made from **3** (^{1}H NMR, 400.13 MHz, $CDCl_3$, 6A). Selective ^{1}H decoupling of methine protons H2 (6B). Selective ^{1}H decoupling of olefinic protons H1 (6C). (See SI for full spectra.)

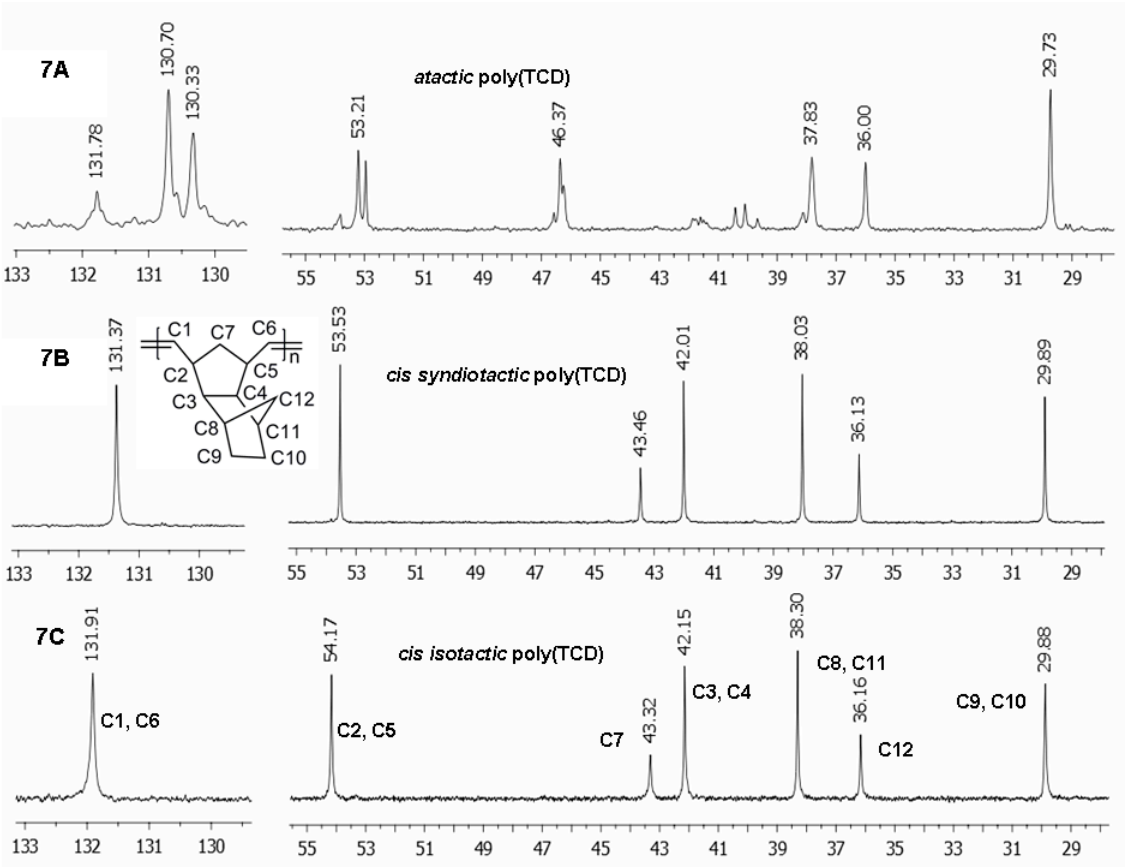

Figure 7. ^{13}C NMR spectra ($C_2D_2Cl_4$, 55°C, 100.61 MHz) of atactic poly(TCD) derived from **1** (7A), *cis,syndiotactic*-poly(TCD) derived from **3** (7B), and *cis,isotactic*-poly(TCD) derived from **7** (7C). (See SI for full spectra.)

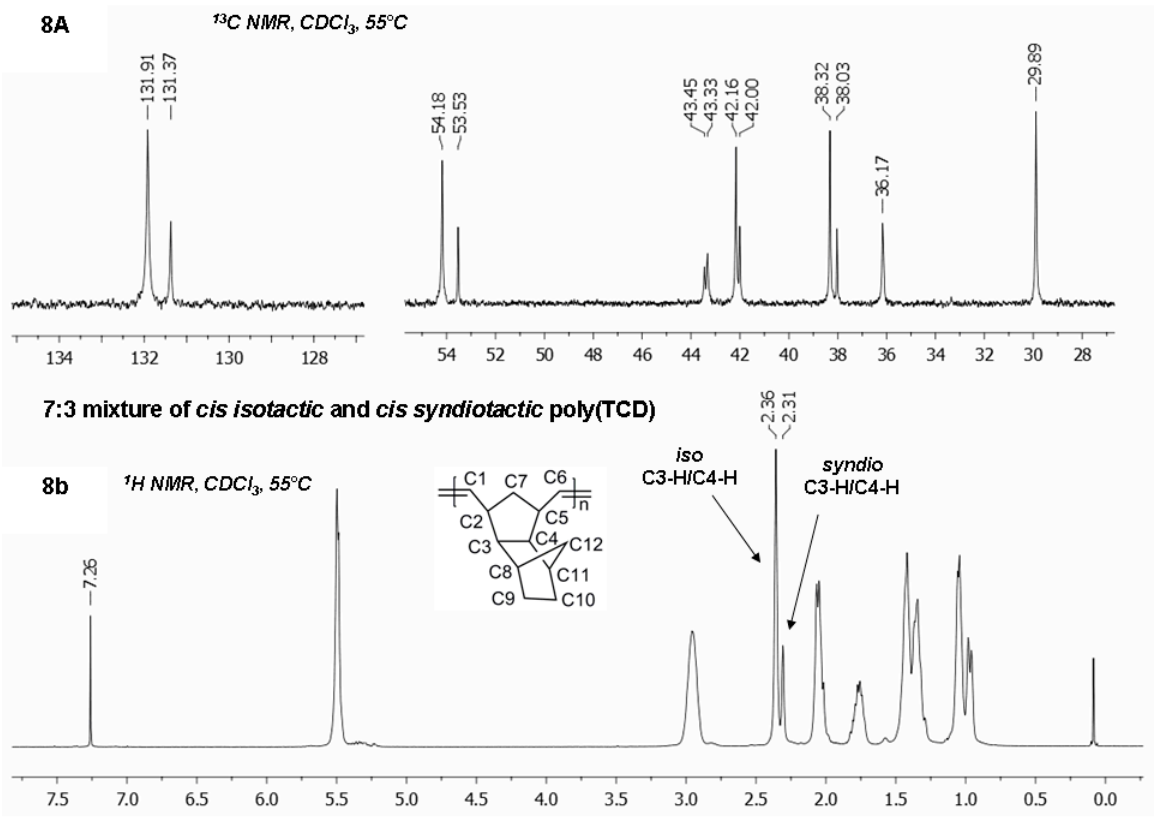

Figure 8. Mixture of *cis,isotactic*-poly(TCD) (70 wt%) derived from **7** and *cis,syndiotactic*-poly(TCD) (30 wt%) derived from **3**; ^{13}C NMR (8A, 100.61 MHz), ^{1}H NMR (8B, 400.13 MHz). (See SI for full spectra.)

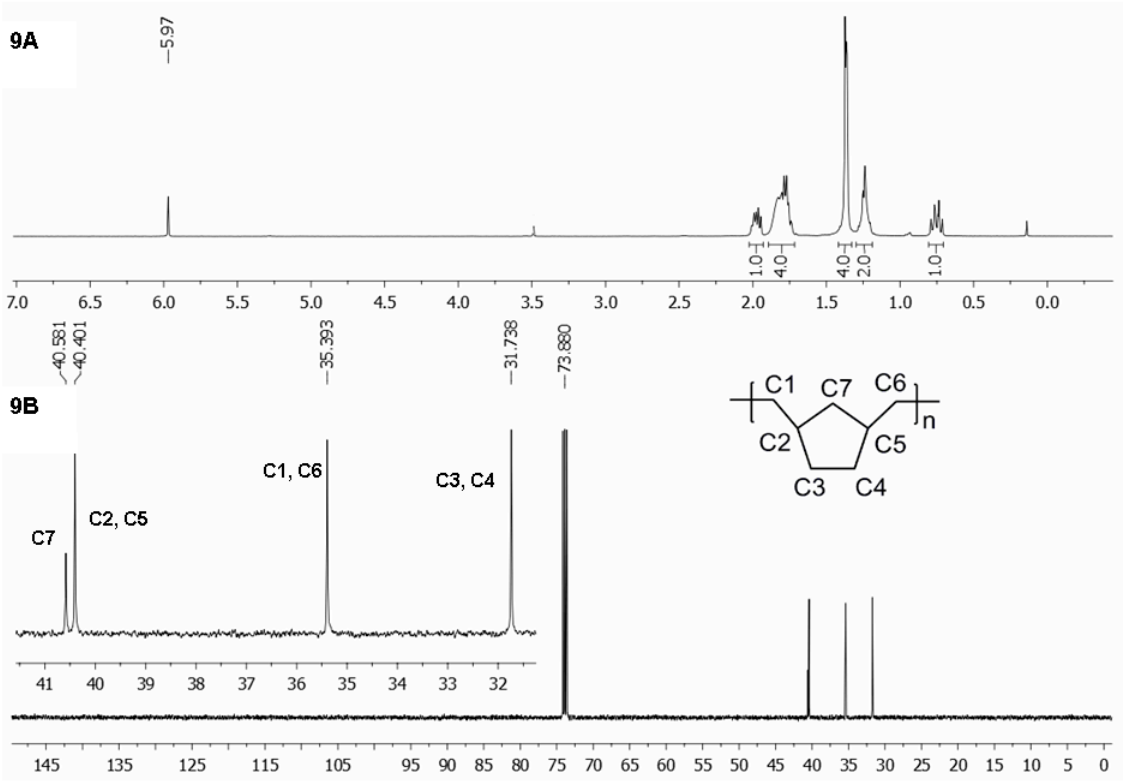

Figure 9. *Syndiotactic*-H-poly(NBE) derived from **2**: ^{1}H NMR (9A, 400.13 MHz) and ^{13}C NMR (9B, 100.61 MHz) recorded in $C_2D_2Cl_4$ at 120°C.

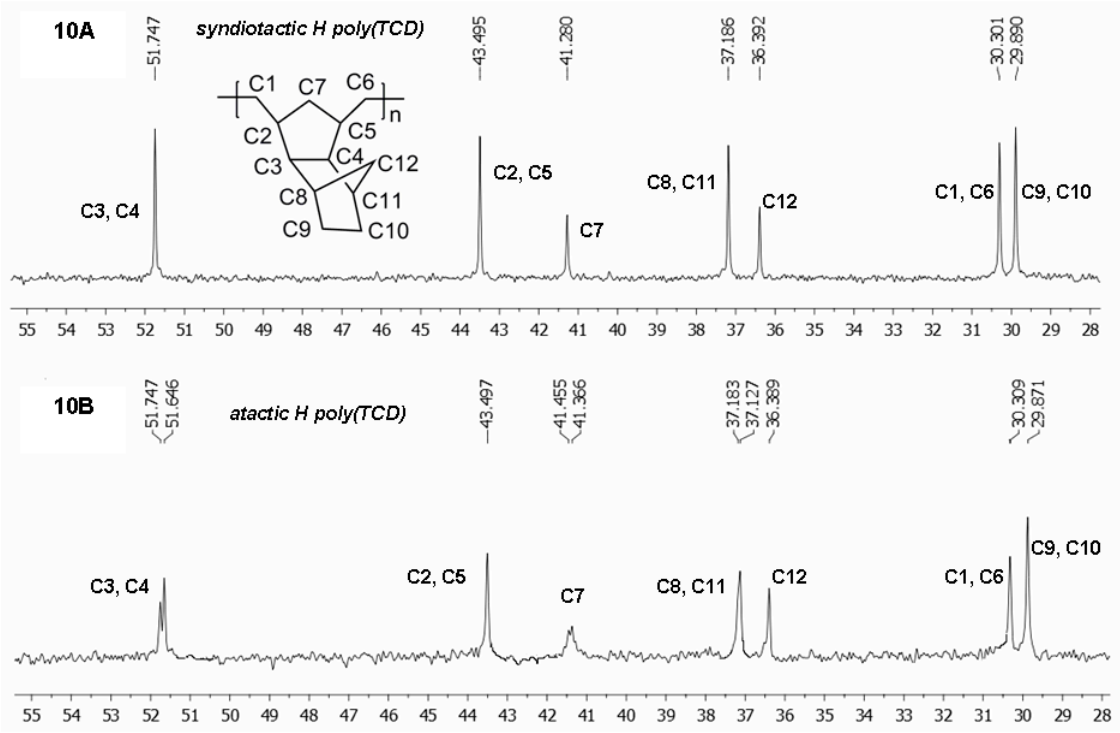

Figure 10. ^{13}C NMR spectra of *syndiotactic*-H-poly(TCD) derived from **3** (10A) and atactic-H-poly(TCD) derived from **1** (10B). Spectra recorded at 120°C at 100.61 MHz in $C_2D_2Cl_4$. (See SI for full spectra.)

Table 1. ROMP of Norbornene (NBE) and Tetracyclododecene (TCD).

Catalyst [a]	**Monomer**	***cis* [%]** [b]	**Tacticity** [b]
1	NBE	50	*atactic*
	TCD	20	*atactic*
2a	NBE	>98	*syndio*
	TCD	~80	~80% *cis, syndio*
2b	NBE	>98	*syndio*
	TCD	~73	*atactic*
2c	NBE	>98	*syndio*
	TCD	~66	*atactic*
3	NBE	>98	*syndio*
	TCD	>98	*syndio*
4	NBE	~80	~80% *cis, syndio*
	TCD	>98	*syndio*
5	NBE	>98	*syndio*
	TCD	50	*atactic*
6	NBE	>95	≥95% *iso*
	TCD	>98	*iso*
7	NBE	>98	*iso*
	TCD	>98	*iso*
8	NBE	>98	*atactic*
	TCD	>98	*iso*
9	NBE	>98	*iso*
	TCD	>98	*iso*
10	NBE	>98	*iso*
	TCD	>98	*iso*

[a] Polymerized in CH_2Cl_2 at 22 °C, 2 min for NBE, 1 min for TCD, 1 mol% catalyst, 2 wt% monomer; all polymer yields were ~100%. [b] Determined by ^{1}H and ^{13}C NMR.

Table 2. Polymers obtained in the presence of 5 mol% 1-hexene.

Catalyst [a]	**Monomer**	***cis* [%]** [b]	**Tacticity** [b]
2a	NBE	>98	*syndio*
3	NBE	>98	*syndio*
3	TCD	>98	*syndio*
7	NBE	>98	*iso*
7	TCD	>98	*iso*

[a] Reaction conditions: CH_2Cl_2, 22 °C, 45 min, 0.1 mol% catalyst,2 wt% monomer, 5 mol% 1-hexene; all polymer yields were ~100%. [b] Determined by ^{13}C NMR.

Table 3. Polymers obtained in THF or toluene.

Catalyst[a]	**Solvent**	**Monomer**	***cis* [%]** [b]	**(%) Tacticity** [b]
2a	THF	NBE	>98	*syndio*
2a	Toluene	NBE	>98	*syndio*
3	THF	NBE	>98	*syndio*
3	Toluene	NBE	>98	*syndio*
3	THF	TCD	>98	*syndio*
3	Toluene	TCD	>98	*syndio*
7	THF	NBE	>98	*iso*
7	Toluene	NBE	>98	*iso*
7	THF	TCD	>98	*iso*
7	Toluene	TCD	>98	*iso*

[a] Reaction conditions: 22 °C, 1-10 min, 1 mol% catalyst, 2 wt% monomer; all polymer yields were ~100%. [b] Determined by ^{13}C NMR.

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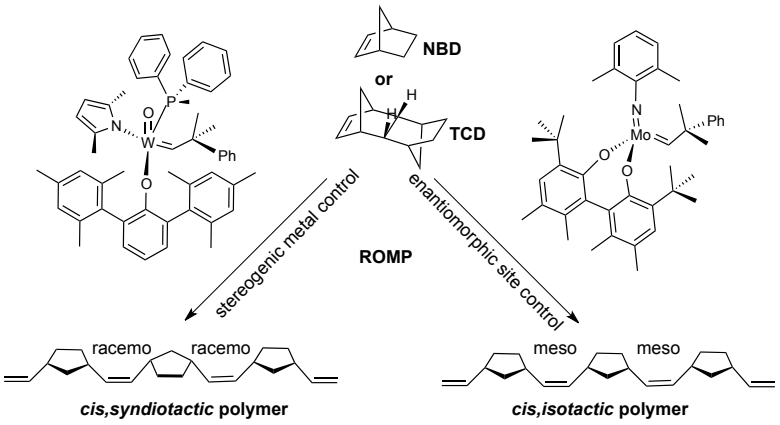
for

Stereospecific Ring-Opening Metathesis Polymerization (ROMP) of Norbornene and Tetracyclododecene by Mo and W Initiators

by

Benjamin Autenrieth and Richard R. Schrock



Supporting Information for

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

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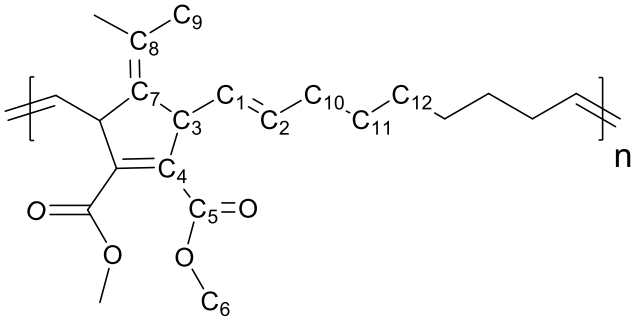
Experimental

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 δ (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_2SO_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-isopropylidenenorbornadiene (**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$_3$)$_2$)$_2$[3] (catalyst **1**) and Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$,[4] (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}).

Polymerization of *trans*-poly[A-*alt*-B] by catalyst 1.



Formation of *trans*-poly[A-*alt*-B]. A stock solution of Mo(NAr')(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (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 ^{1}H 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. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ 5.48 (dt, $^3J_{HH}$ = 15 and 7 Hz, 2H, H_2), 5.27 (dd, $^3J_{HH}$ = 15.5 and 8 Hz, 2H, H_1), 4.11 (d, $^3J_{HH}$ = 8 Hz, 2H, H_3), 3.75 (s, 6H, H_6), 1.98 (m, 4H, H_{10}), 1.63 (s, 6H, H_9), 1.30 (m, 8H, H_{11} and H_{12}); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ 165.71 (C_5), 141.02 (C_4), 133.17 (C_7 or C_8), 132.58 (C_1), 128.80 (C_7 or C_8), 128.38 (C_2), 53.39 (C_3), 52.06 (C_6), 32.59 (C_{10}), 29.65 (C_{11} or C_{12}), 29.15 (C_{11} or C_{12}), 20.52 (C_9). IR (neat): 2924, 2854, 1721, 1641, 1435, 1323, 1270, 1208, 1133, 1098, 1023, 967 (*trans*), 919, 777 cm^{-1}.

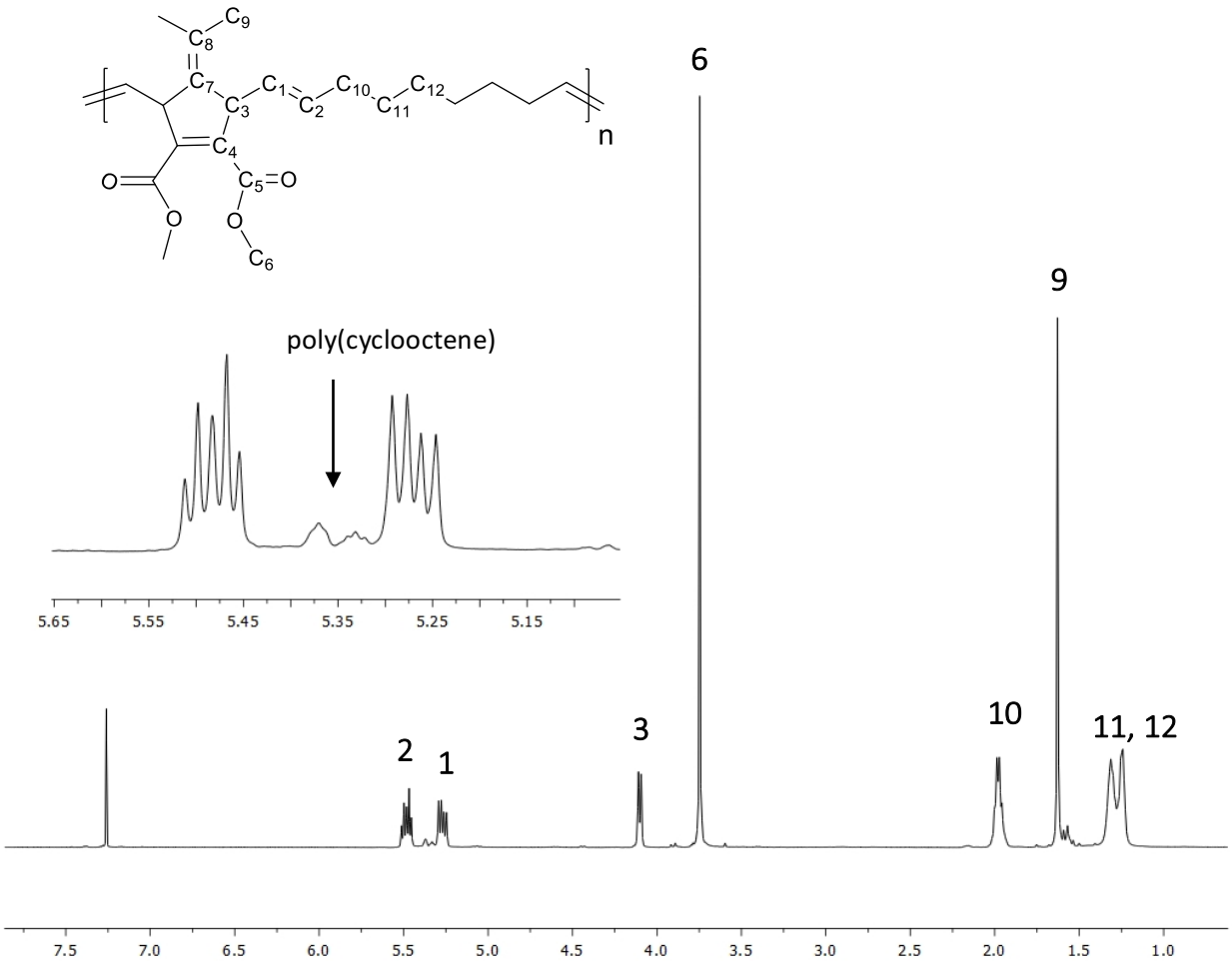


Figure S1. ^{1}H NMR spectrum of *trans*-poly[**A**-*alt*-**B**] (in $CDCl_3$, 500 MHz).

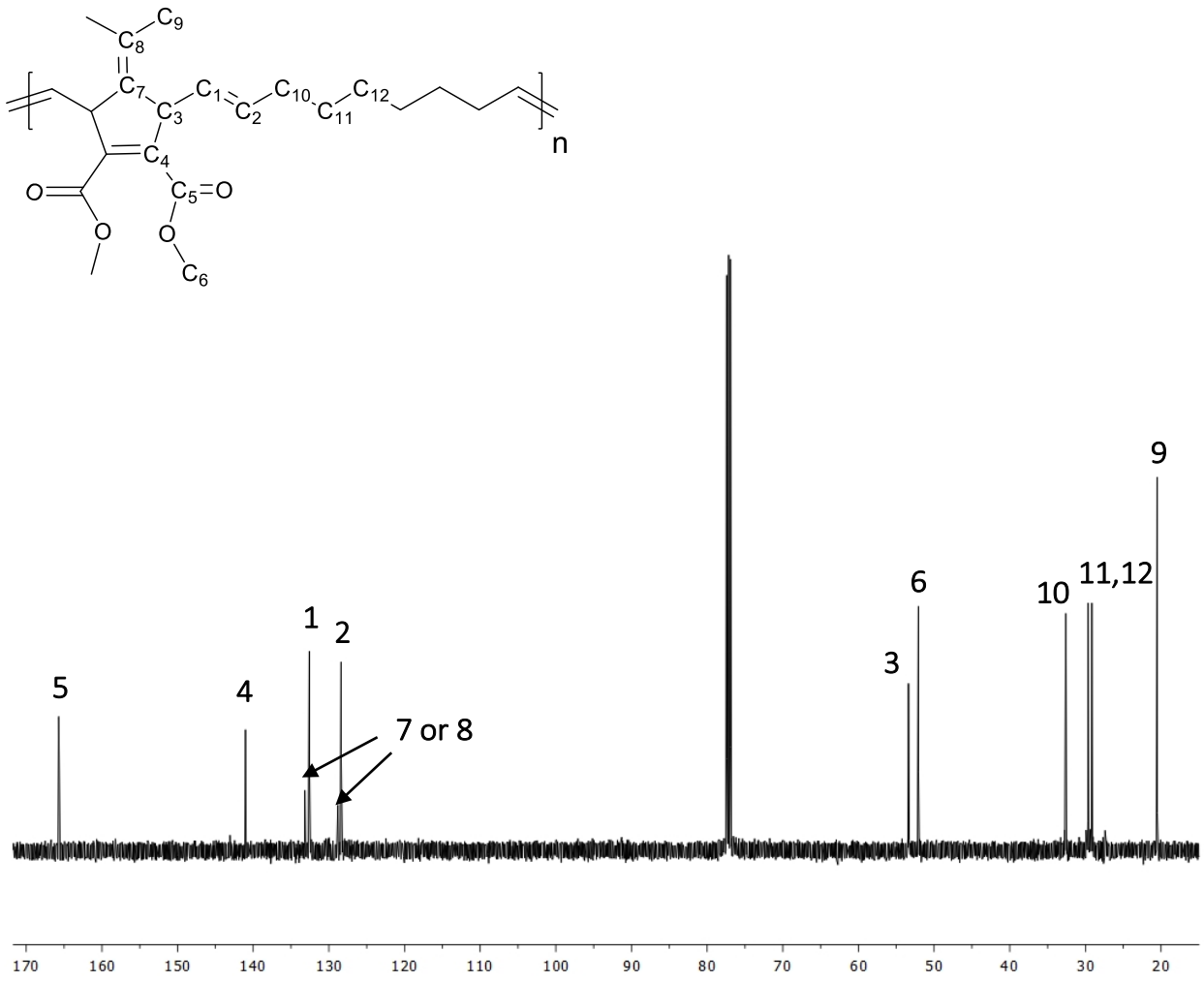


Figure S2. ^{13}C NMR spectrum of *trans*-poly[**A**-*alt*-**B**] (in $CDCl_3$, 125 MHz).

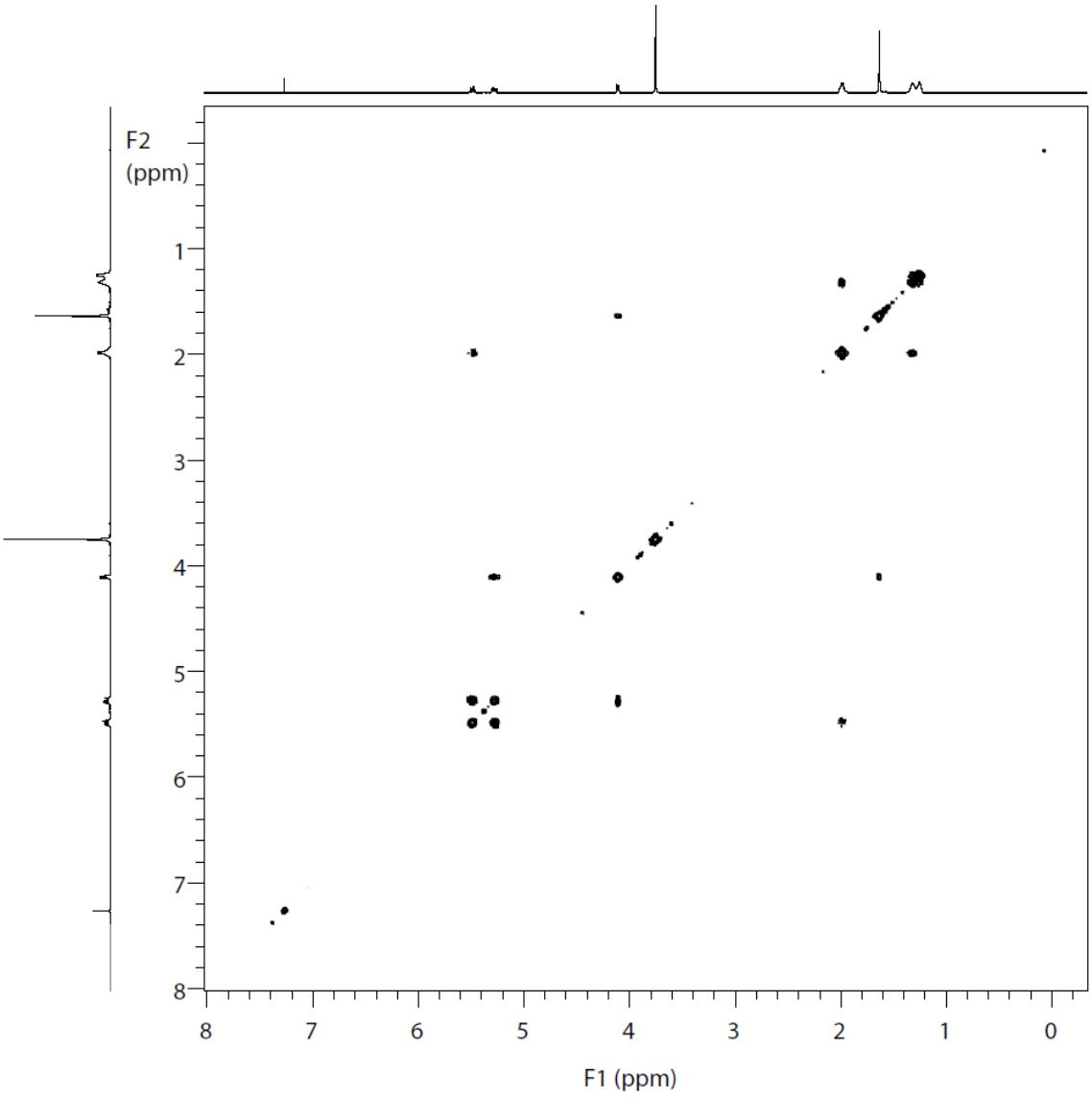


Figure S3. ^{1}H–^{1}H gCOSY spectrum of *trans*-poly[**A**-*alt*-**B**] (in $CDCl_3$, 500 MHz).

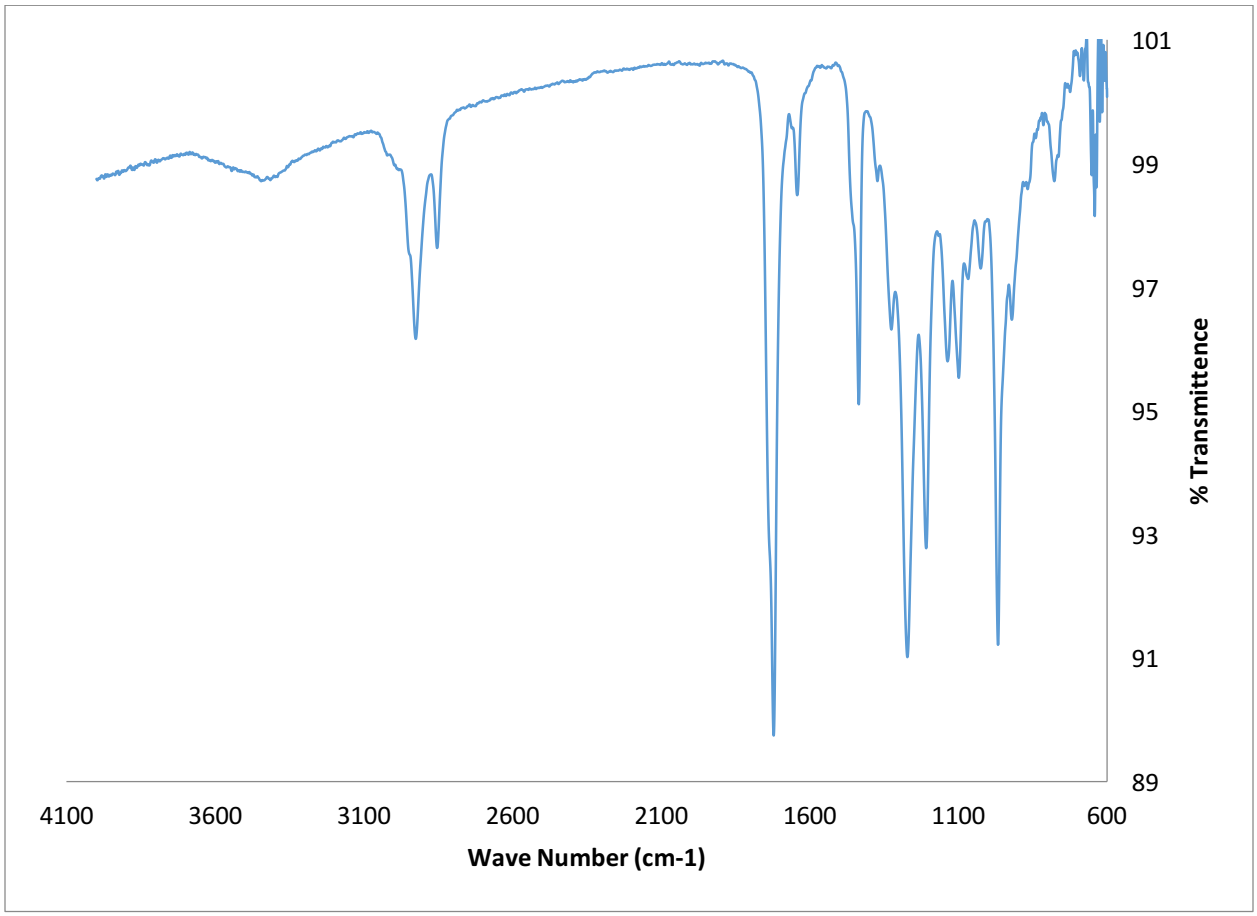
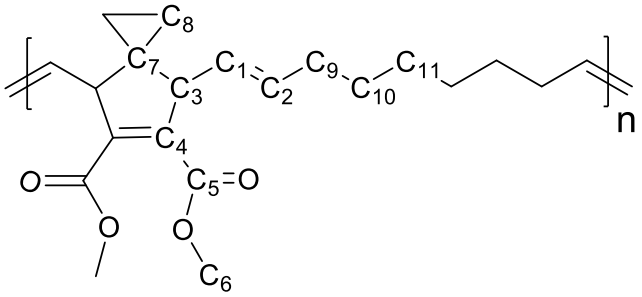


Figure S4. IR spectrum of *trans*-poly[**A**-*alt*-**B**] (neat).

Polymerization of *trans*-poly[A-*alt*-B'] by catalyst 1.



Formation of *trans*-poly[A-*alt*-B']. A solution of Mo(NAr')(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (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 ^{1}H 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). ^{1}H NMR (CDCl$_3$, 20 °C) δ 5.32 (dt, $^3J_{HH}$ = 15 and 7 Hz, 2H, H$_2$), 5.20 (dd, $^3J_{HH}$ = 15 and 9.5 Hz, 2H, H$_1$), 3.73 (s, 3H, H$_6$), 3.13 (d, $^3J_{HH}$ = 9 Hz, 2H, H$_3$), 1.98 (m, 4H, H$_9$), 1.30-1.24 (m, 8H, H$_{10}$ and H$_{11}$), 0.57-0.46 (m, 4H, H$_8$); ^{13}C NMR (CDCl$_3$, 20 °C) δ 165.8 (C$_5$), 141.9 (C$_4$), 133.4 (C$_2$), 129.1 (C$_1$), 57.5 (C$_3$), 52.0 (C$_6$), 32.5 (C$_9$), 29.6 (C$_{10}$ or C$_{11}$), 29.1 (C$_{10}$ or C$_{11}$), 15.6 (C$_8$), 7.15 (C$_7$). IR (neat): 2926, 2854, 1721, 1642, 1435, 1323**,** 1206, 1126, 1101, 1098, 1021, 973 (*trans*), 905, 797, 754 cm^{-1}.

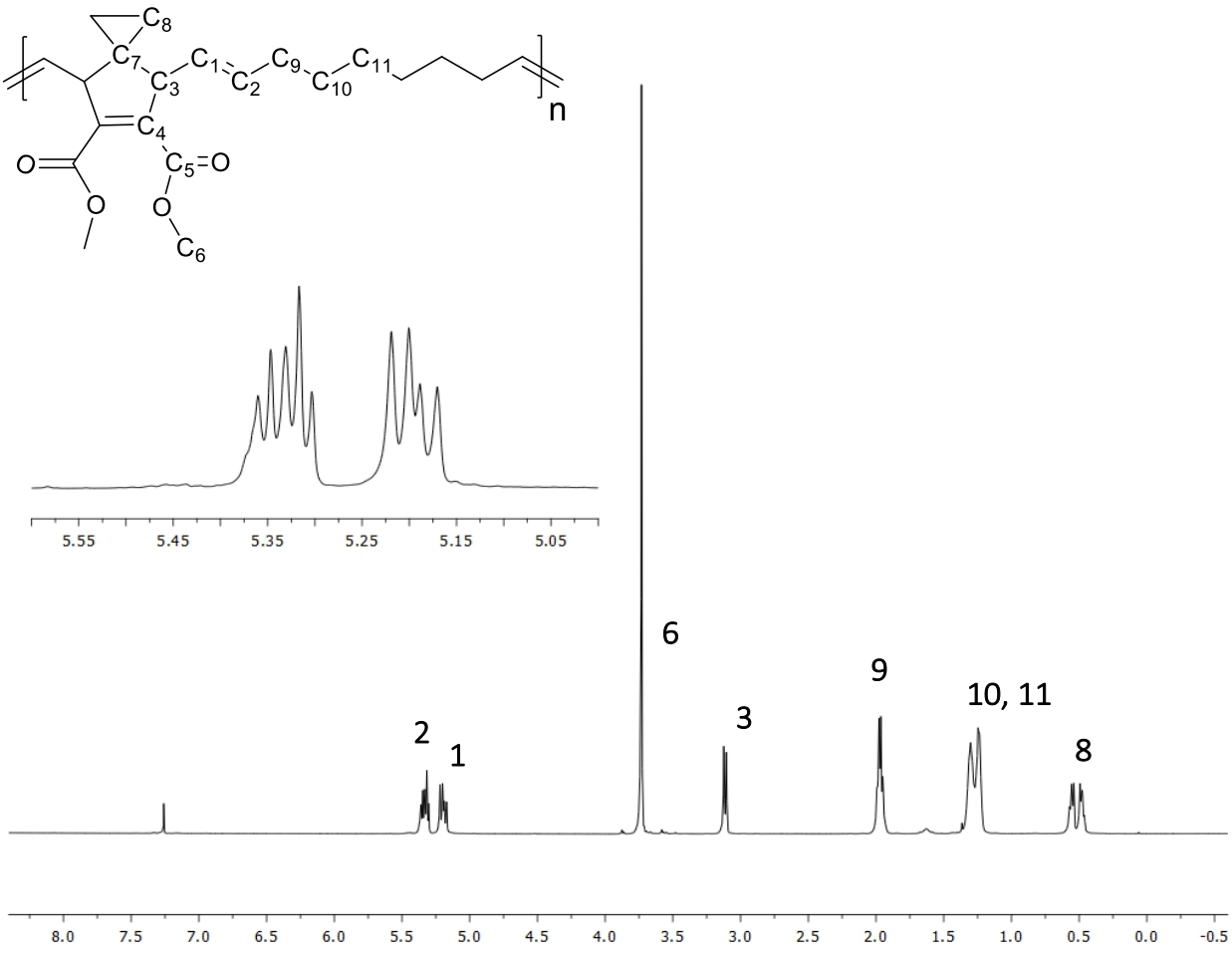


Figure S5. ^{1}H NMR spectrum of *trans*-poly[**A**-*alt*-**B'**] (in $CDCl_3$, 500 MHz).

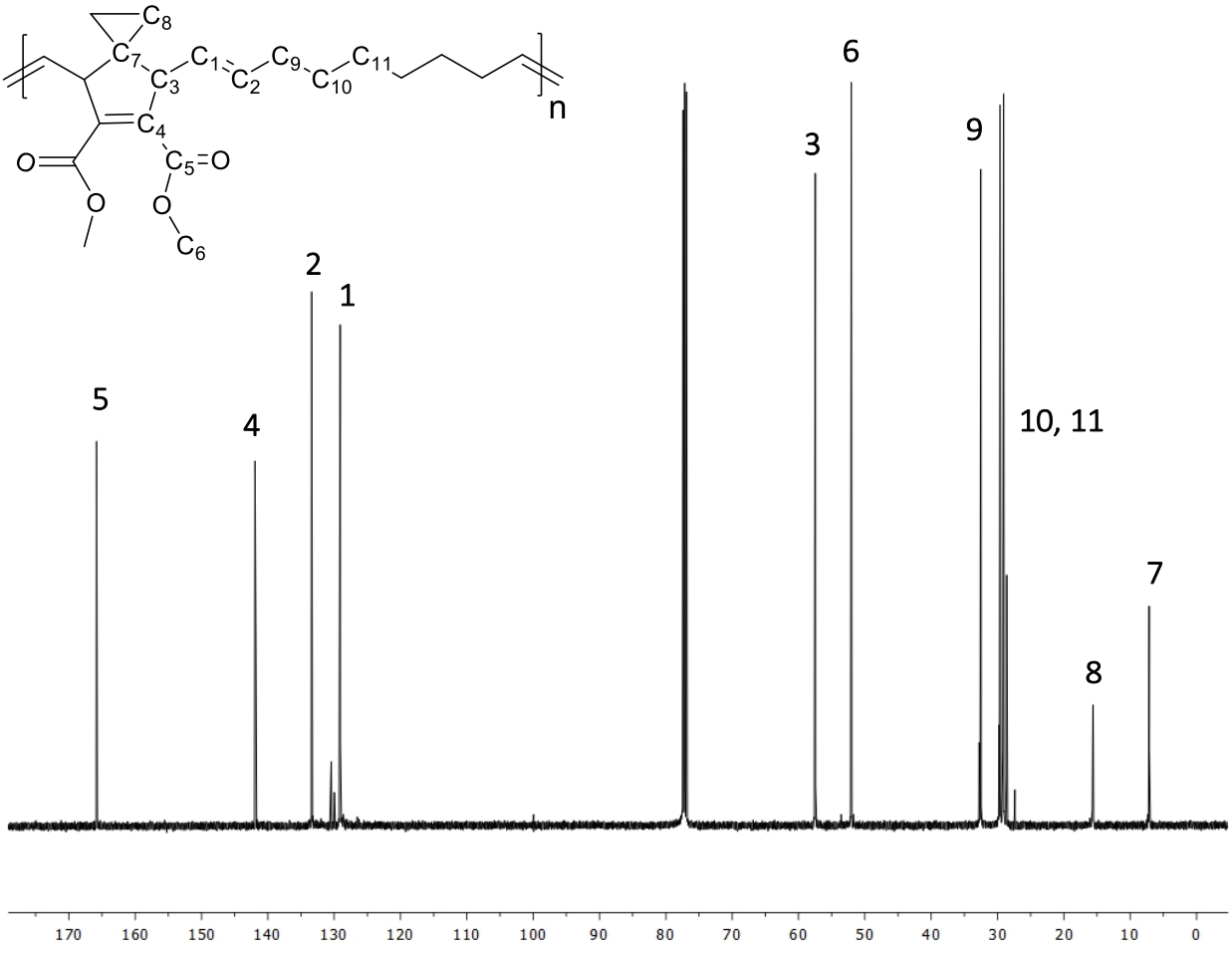


Figure S6. ^{13}C NMR spectrum of *trans*-poly[**A**-*alt*-**B'**] (in $CDCl_3$, 125 MHz).

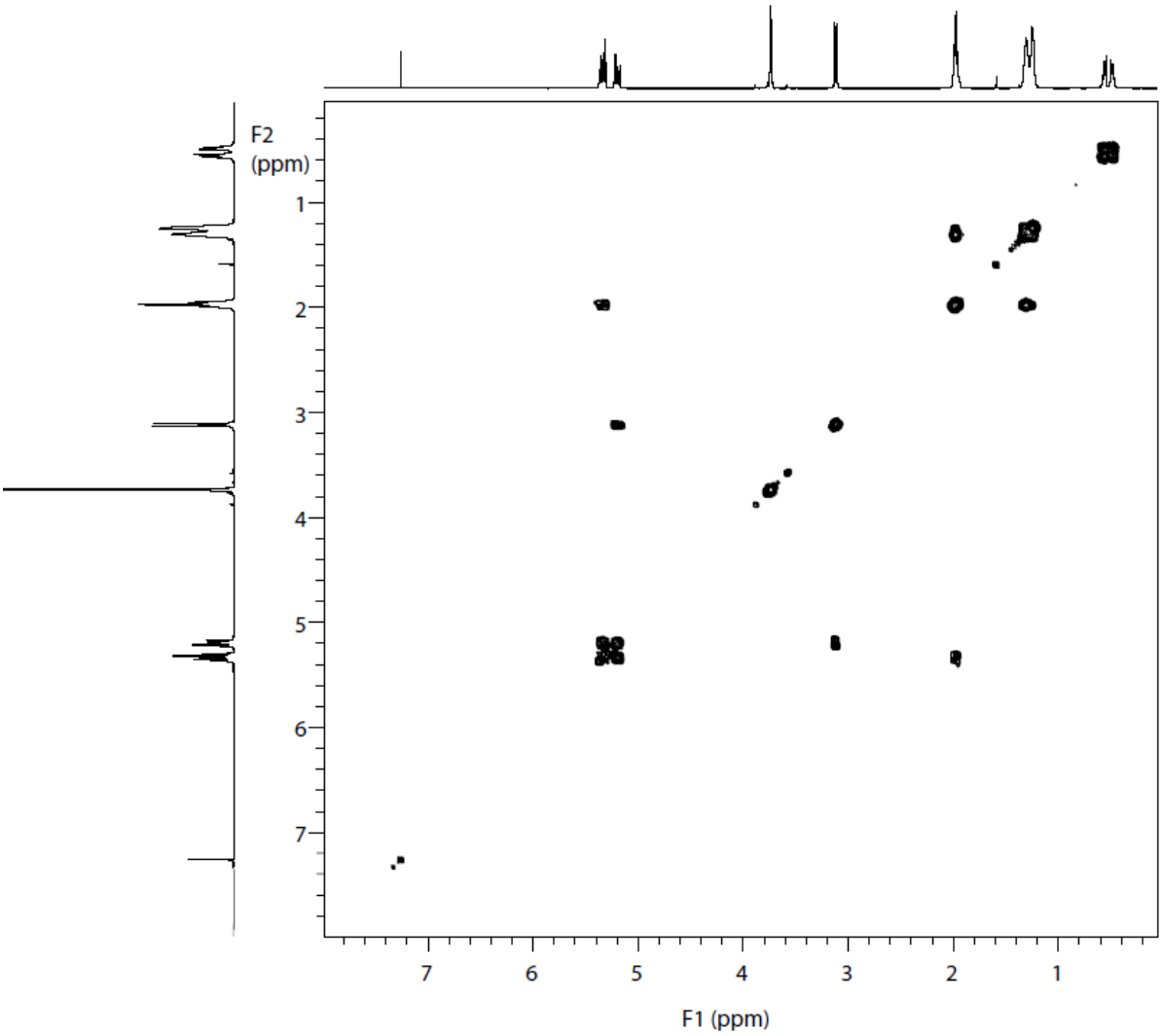


Figure S7. ^{1}H–^{1}H gCOSY spectrum of *trans*-poly[**A**-*alt*-**B'**] (in $CDCl_3$, 500 MHz).

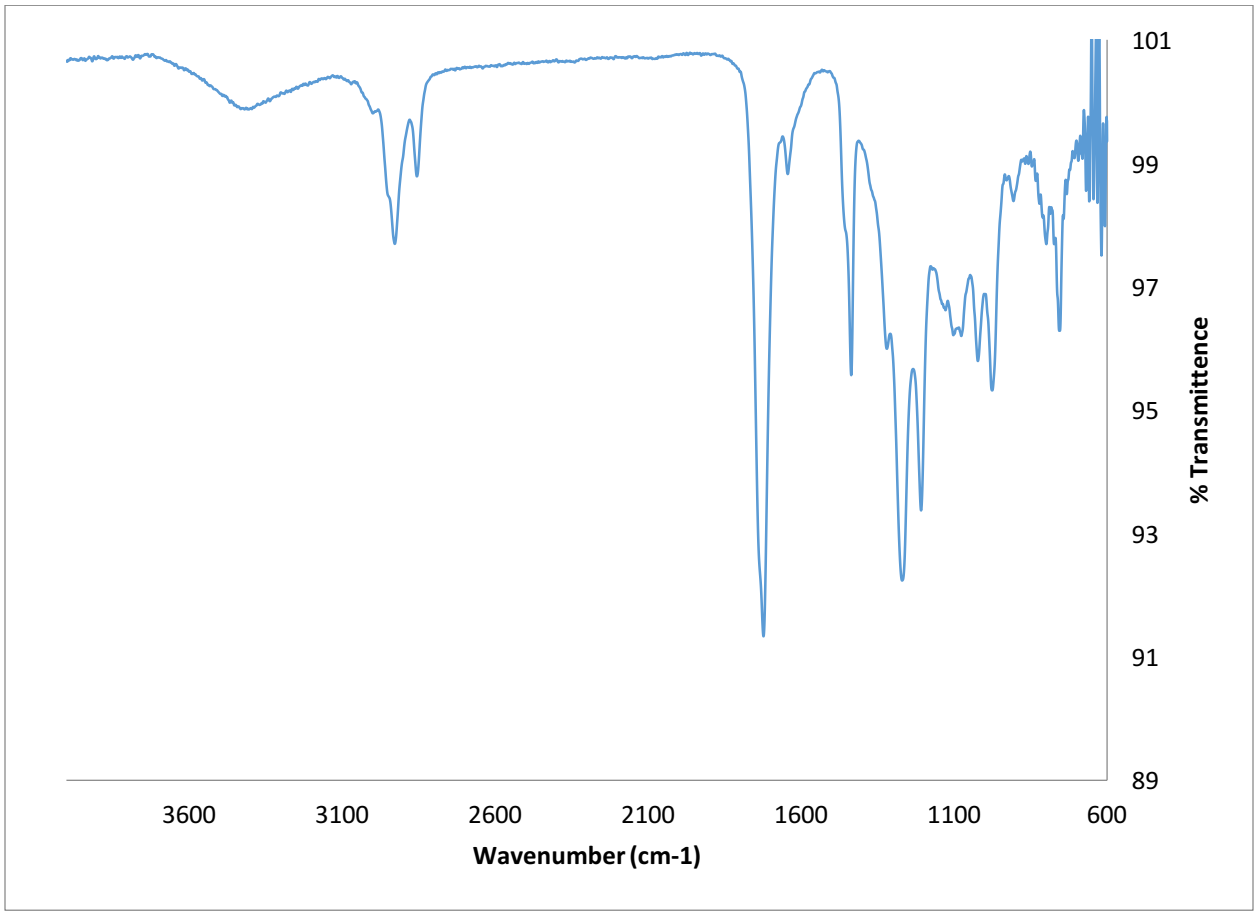
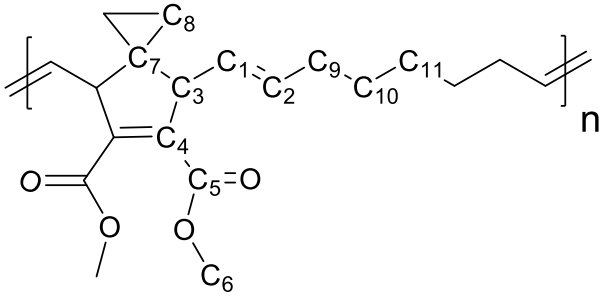


Figure S8. IR spectrum of *trans*-poly[**A**-*alt*-**B'**] (neat).

Polymerization of *trans*-poly[A'-*alt*-B'] by catalyst 1.



Formation of of *trans*-poly[A'-*alt*-B']. A stock solution of $Mo(NAr')(CHCMe_2Ph)(OCMe(CF_3)_2)_2$ (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 ^{1}H 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. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ 5.34 (dt, $^3J_{HH}$ = 15 and 7 Hz, 2H, H_2), 5.20 (dd, $^3J_{HH}$ = 15.5 and 9 Hz, 2H, H_1), 3.74 (s, 6H, H_6), 3.12 (d, $^3J_{HH}$ = 9.5 Hz, 2H, H_3), 1.97 (m, 4H, H_{10}), 1.36-1.25 (m, 6H, H_{10} and H_{11}), 0.56-0.48 (m, 4H, H_8); ^{13}C NMR ($CDCl_3$, 20 °C) δ 165.8 (C_5), 141.9 (C_4), 133.4 (C_2), 129.1 (C_1), 57.4 (C_3), 52.1 (C_6), 32.5 (C_9), 29.5 (C_{10} or C_{11}), 28.7 (C_{10} or C_{11}), 15.6 (C_8), 7.17 (C_7). IR (neat): 2926, 2853, 1722, 1642, 1435, 1319**,** 1271, 1206, 1129, 1101, 1074, 1021, 969 (*trans*), 770 cm^{-1}.

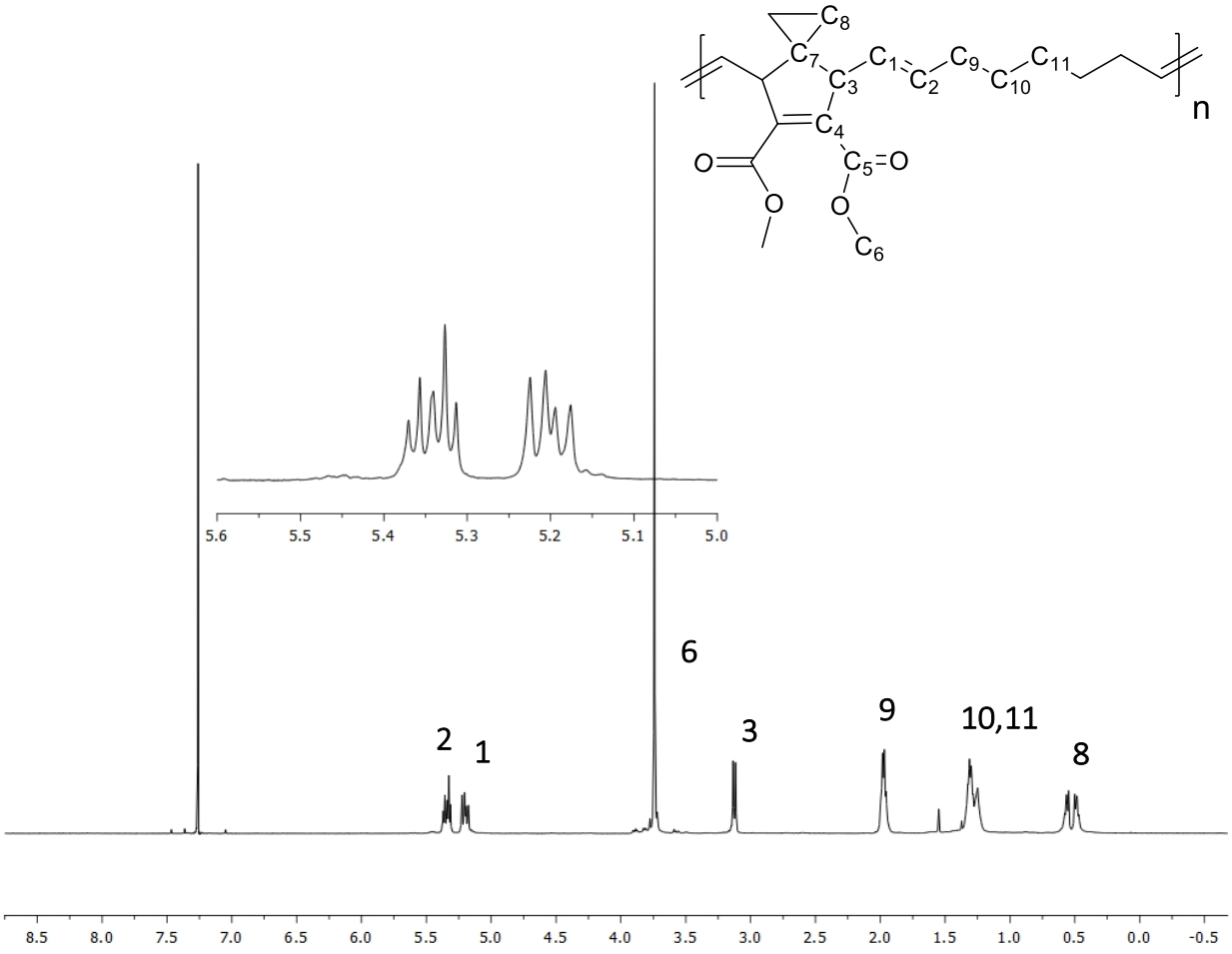


Figure S9. ^{1}H NMR spectrum of *trans*-poly[**A'**-*alt*-**B'**] (in $CDCl_3$, 500 MHz).

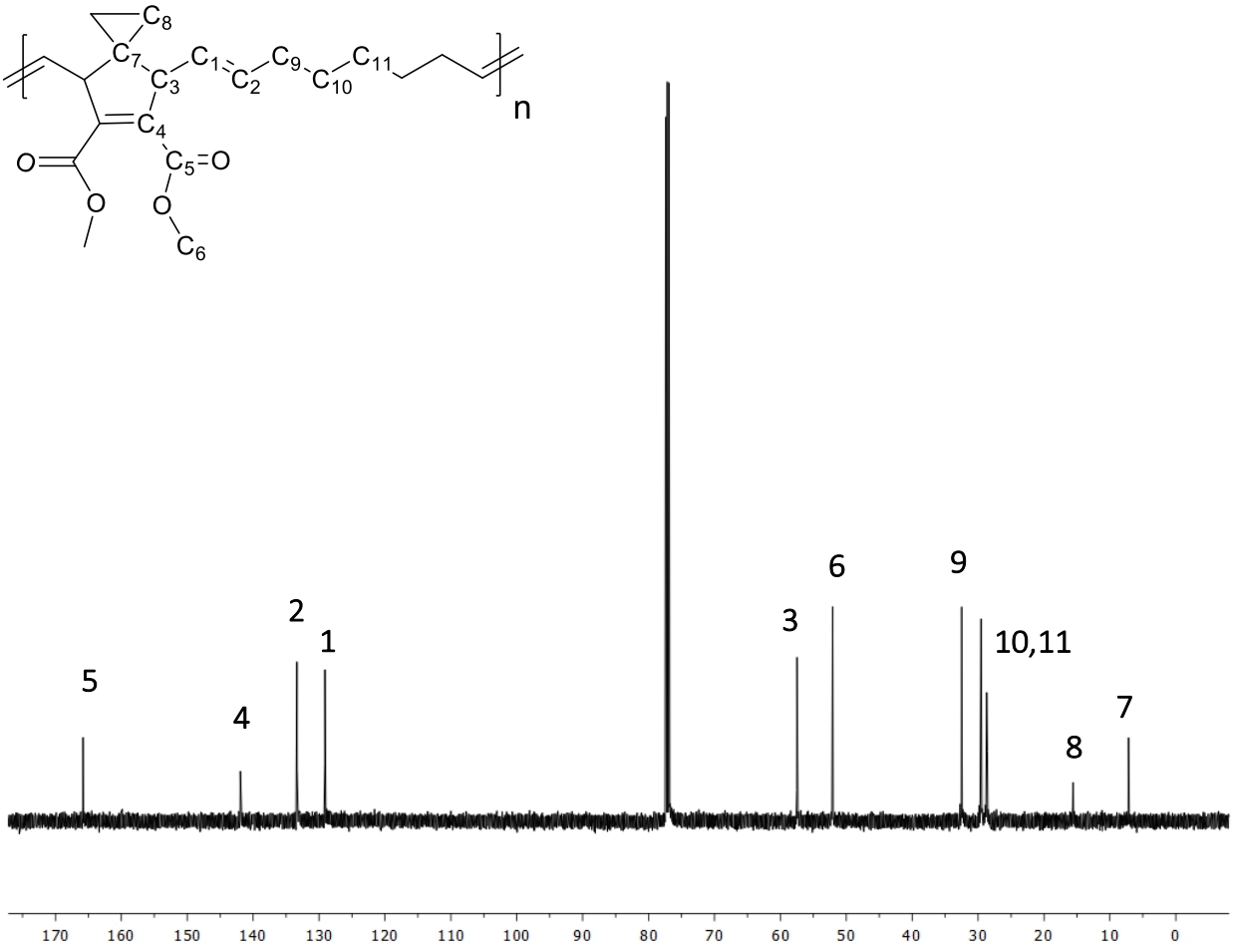


Figure S10. ^{13}C NMR spectrum of *trans*-poly[**A'**-*alt*-**B'**] (in $CDCl_3$, 125 MHz).

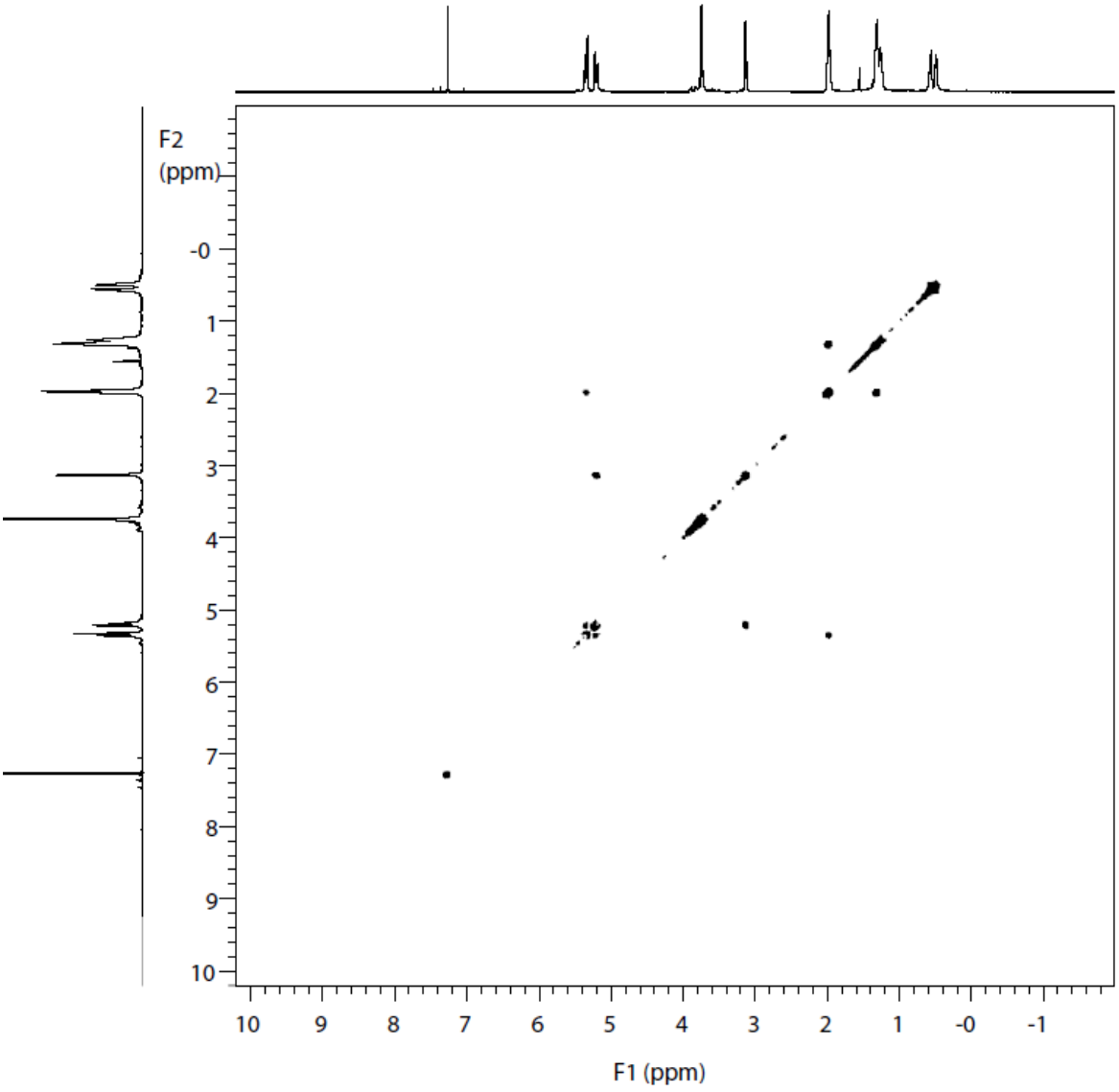


Figure S11. ^{1}H–^{1}H gCOSY spectrum of *trans*-poly[**A'**-*alt*-**B'**] (in $CDCl_3$, 500 MHz).

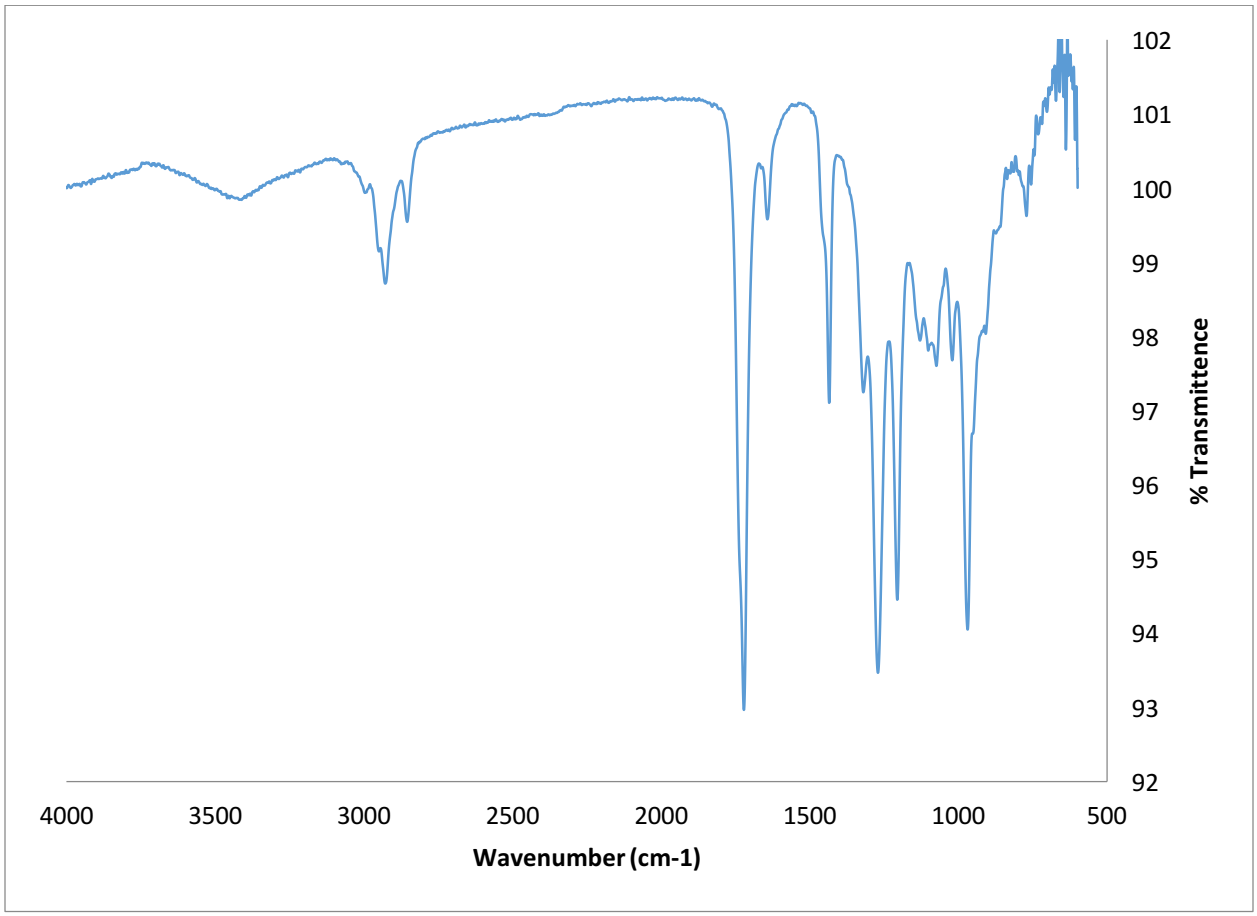
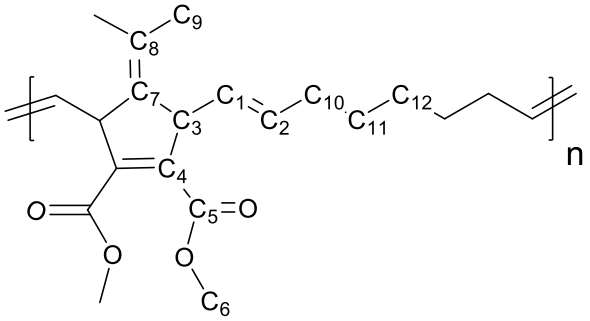


Figure S12. IR spectrum of *trans*-poly[**A'**-*alt*-**B'**] (neat).

Polymerization of *trans*-poly[A'-*alt*-B] by catalyst 1.



Formation of *trans*-poly[A'-*alt*-B]. A stock solution of Mo(NAr')(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (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 ^{1}H 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. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ 5.48 (dt, $^3J_{HH}$ = 15.5 and 6.5 Hz, 2H, H_2), 5.26 (dd, $^3J_{HH}$ = 15 and 8 Hz, 2H, H_1), 4.11 (d, $^3J_{HH}$ = 7.5 Hz, 2H, H_3), 3.75 (s, 6H, H_6), 1.97 (m, 4H, H_{10}), 1.63 (s, 6H, H_9), 1.30 (m, 6H, H11, H_{12}); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ 165.71 (C_5), 141.03 (C_4), 133.16 (C_7 or C_8), 132.57 (C_1), 128.87 (C_7 or C_8), 128.40 (C_2), 53.41 (C_3), 52.07 (C_6), 32.58 (C_{10}), 29.59 (C_{11} or C_{12}), 28.83 (C_{11} or C_{12}), 20.54 (C_9). IR (neat): 2924, 2853, 1722, 1642, 1434, 1324, 1270, 1207, 1134, 1097, 1024, 966 (*trans*), 919, 775 cm^{-1}.

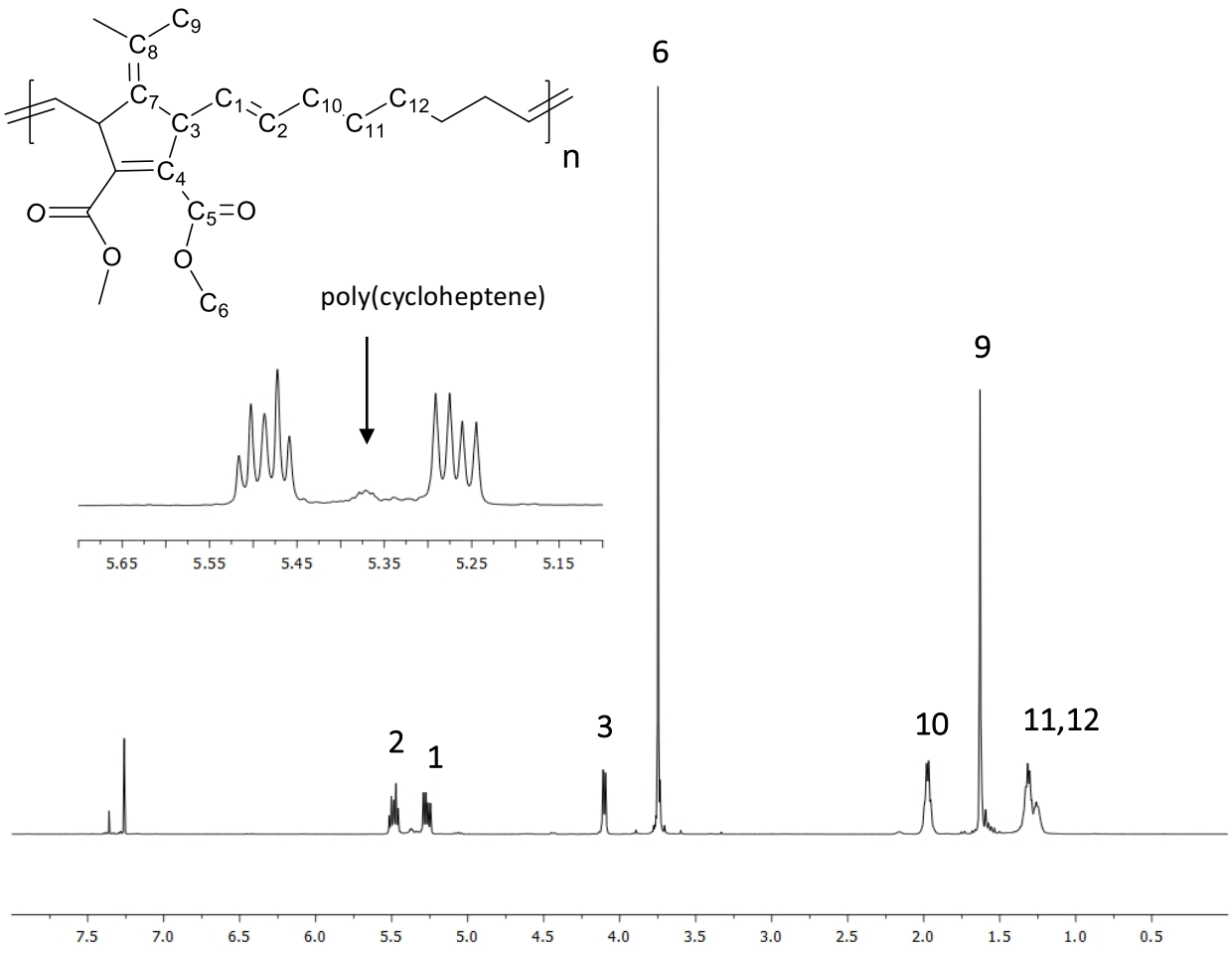


Figure S13. ^{1}H NMR spectrum of *trans*-poly[**A'**-*alt*-**B**] (in $CDCl_3$, 500 MHz).

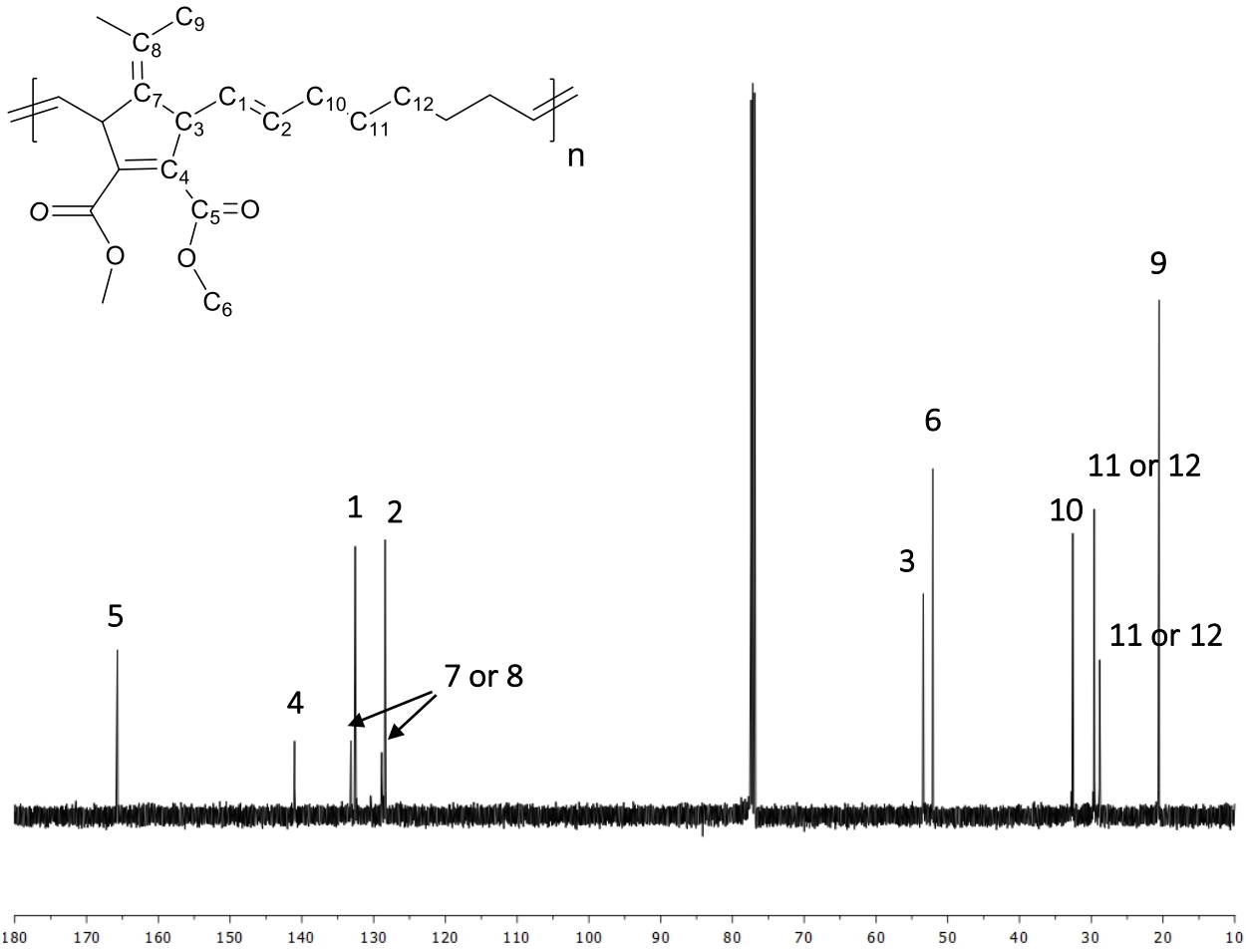


Figure S14. ^{13}C NMR spectrum of *trans*-poly[**A'**-*alt*-**B**] (in $CDCl_3$, 500 MHz).

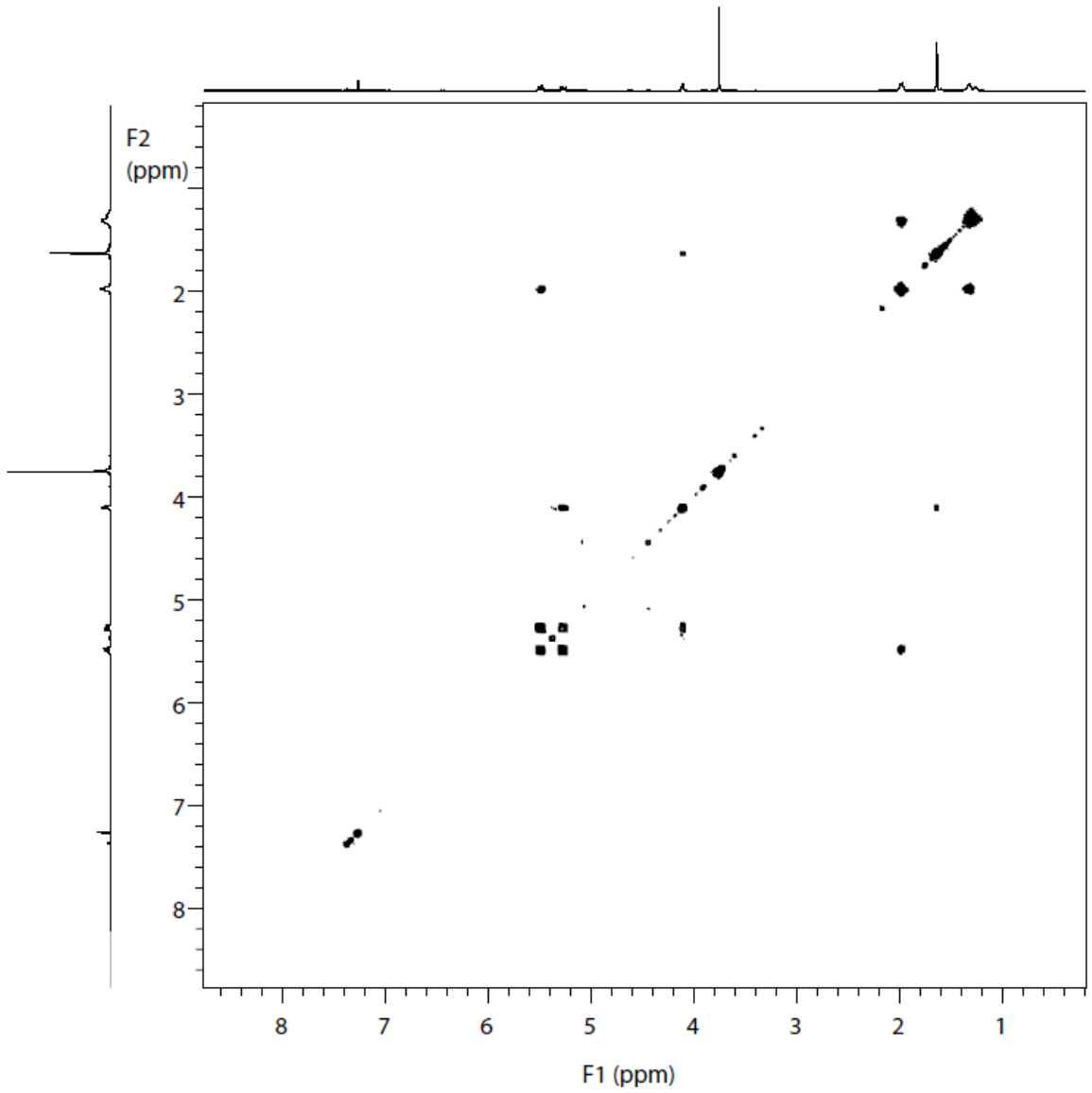


Figure S15. ^{1}H–^{1}H gCOSY spectrum of *trans*-poly[**A'**-*alt*-**B**] (in $CDCl_3$, 500 MHz).

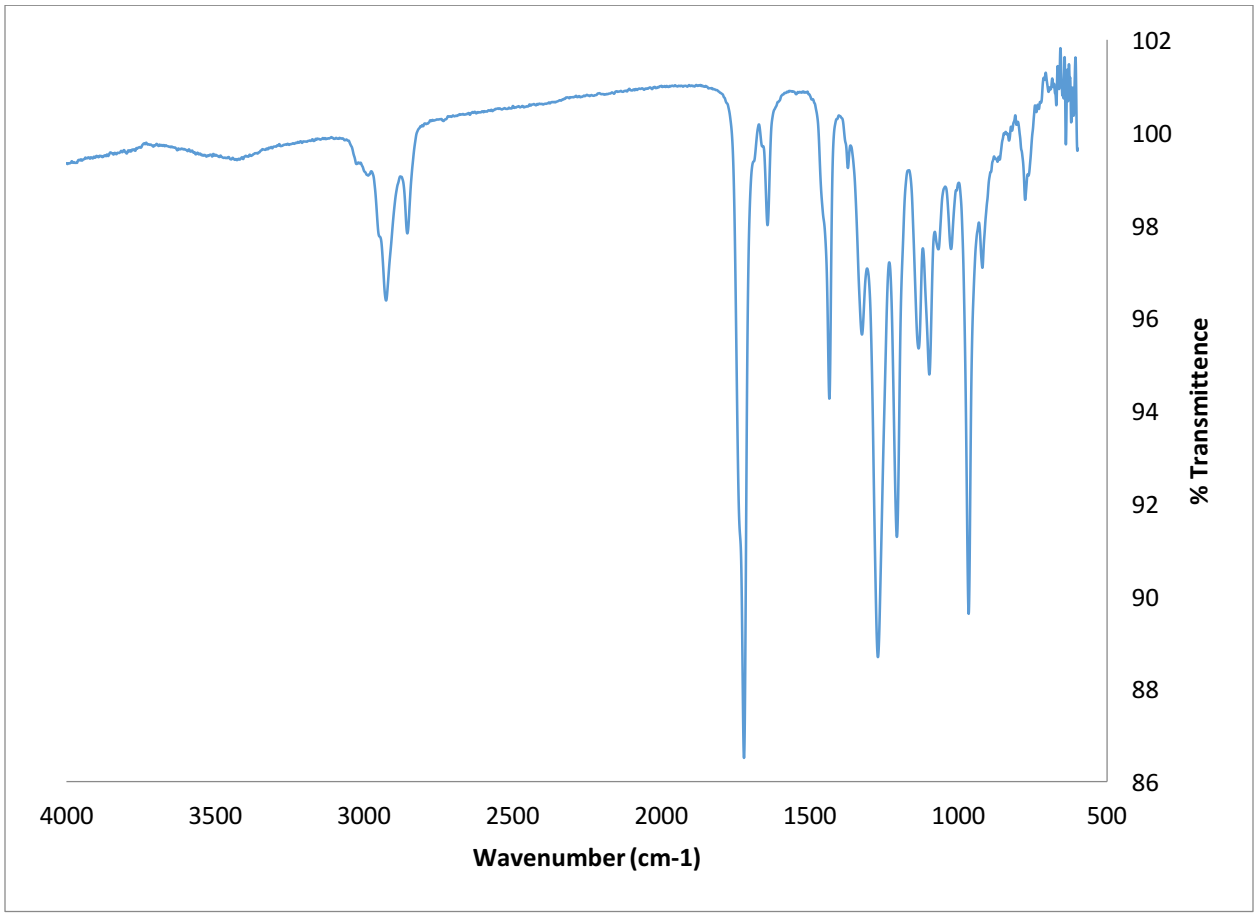


Figure S16. IR spectrum of *trans*-poly[**A'**-*alt*-**B**] (neat).

ROMP of *cis*-cycloheptene:

A 1 mL C_6D_6 solution of Mo(NAr)(CHCMe$_2$Ph)(OCCH$_3$(CF$_3$)$_2$)$_2$ (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 C_6D_6. 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%. ^{1}H NMR of the waxy solid showed a 18:82 mixture of *cis*- and *trans*-poly(cycloheptene).

cis-poly(cycloheptene):

^{1}H NMR ($CDCl_3$, 500.43 MHz, 20 °C): δ 5.36 (t, $^3J_{HH}$ = 4.5 Hz, 2H), 2.03 (bm, 4H), 1.31 (bm, 6H). ^{13}C NMR ($CDCl_3$, 125.79 MHz, 20 °C): δ 130.00 (=*C*H), 28.87 (=CH*C*H$_2$), 27.34 (CH$_2$*C*H$_2$CH$_2$).

trans-poly(cycloheptene):

^{1}H NMR ($CDCl_3$, 500.43 MHz, 20 °C): δ 5.39 (t, $^3J_{HH}$ = 4.5 Hz, 2H), 1.97 (bm, 4H), 1.35 (bm, 6H). ^{13}C NMR ($CDCl_3$, 125.79 MHz, 20 °C): δ 130.46 (=*C*H), 32.74 (=CH*C*H$_2$), 29.68 (CH$_2$*C*H$_2$CH$_2$).

ROMP of *cis*-cyclooctene:

In a J-Young NMR tube, a 0.2 mL solution of Mo(NAr')(CHCMe$_2$Ph)(OCCH$_3$(CF$_3$)$_2$)$_2$ (2.4 mg, 3.4 μmol) was added to cis-cyclooctene (22 μL, 0.169 mmol) in a 0.4 mL of C_6D_6. 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). ^{1}H NMR of the polymer showed a 20:80 mixture of *cis*- and *trans*-poly(cyclooctene).

cis-poly(cyclooctene):

^{1}H NMR ($CDCl_3$, 500 MHz, 20 °C): δ 5.34 (t, $^3J_{HH}$ = 4.8 Hz, 2H), 2.00 (m, 4H), 1.33 -1.27 (m, 8H). ^{13}C NMR ($CDCl_3$, 125.79 MHz, 20 °C): δ 130.02 (=*CH*), 29.90 (=CH*C*H$_2$), 29.34 (CH$_2$*C*H$_2$CH$_2$), 27.37 (CH$_2$*C*H$_2$CH$_2$).

trans-poly(cyclooctene):

^{1}H NMR ($CDCl_3$, 500 MHz, 20 °C): δ 5.38 (t, $^{3}J_{HH}$ = 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 (=CH*C*H_2), 29.79 (CH_2*C*H_2CH_2), 29.20 (CH_2*C*H_2CH_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**

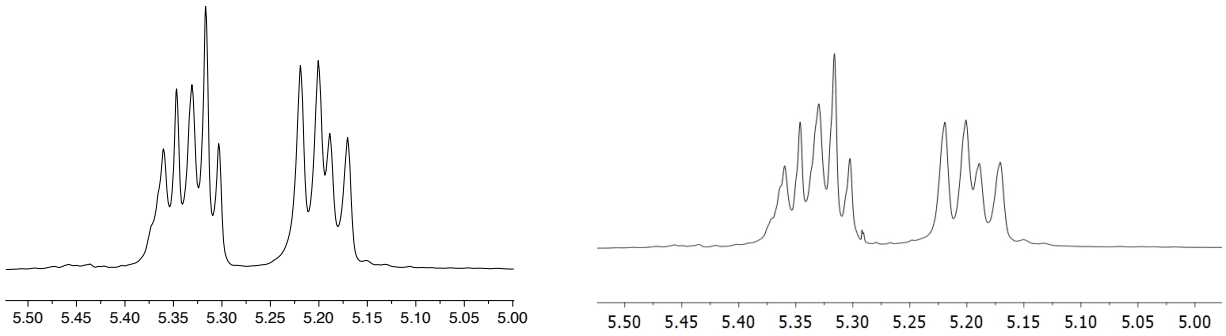


Figure S17. Comparison of the olefinic region ^{1}H NMR spectrum of *trans*-poly(**A**-*alt*-**B'**) formed from **1** (left) and **2** (right) in $CDCl_3$.

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

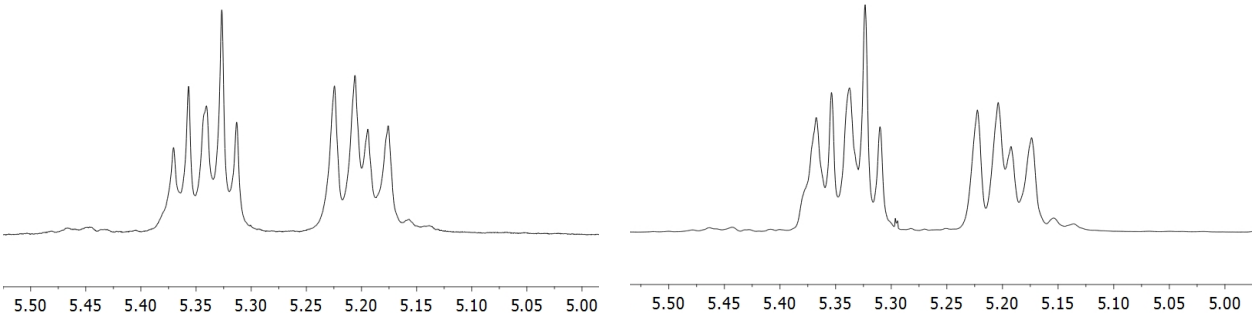


Figure S18. Comparison of the olefinic region ^{1}H NMR spectrum of *trans*-poly(**A'**-*alt*-**B'**) formed from **1** (left) and **2** (right) in $CDCl_3$.

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

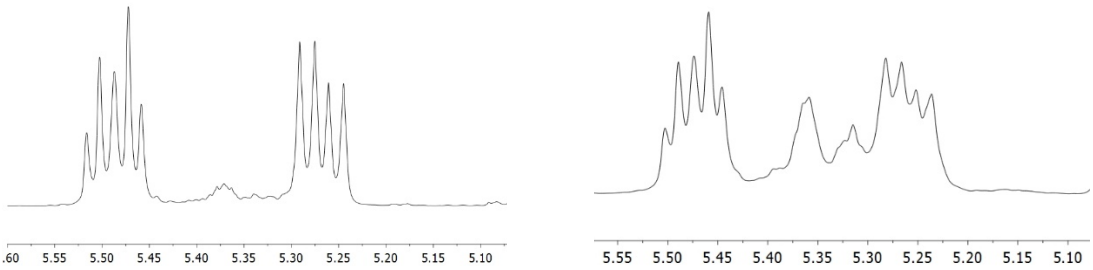


Figure S19. Comparison of the olefinic region ^{1}H NMR spectrum of *trans*-poly(**A'**-*alt*-**B**) formed from **1** (left) and **2** (right) in $CDCl_3$.

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

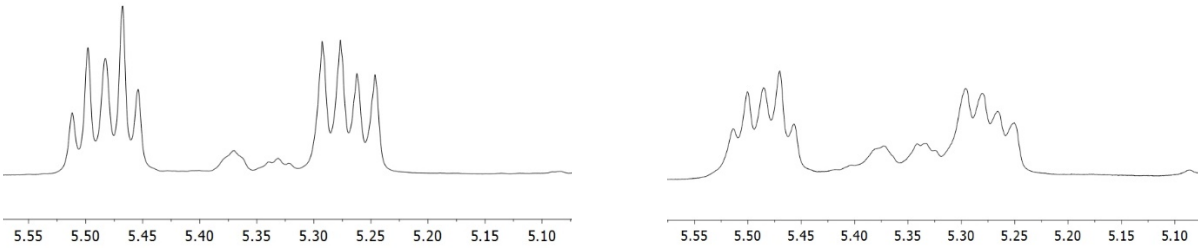


Figure S20. Comparison of the olefinic region ^{1}H NMR spectrum of *trans*-poly(**A**-*alt*-**B**) formed from **1** (left) and **2** (right) in $CDCl_3$.

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 *in vacuo*. 2 mL of pentane was then added to dissolve the red-orange residue and then removed *in vacuo*. This process was repeated two times. The residue was then dissolved in 1 mL of Et_2O and recrystallized at –30 °C. The mother liquor was decanted and the orange crystals washed with 1 mL of Et_2O 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): δ 12.31 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H, *syn* alkylidene, a', 3%), 11.80 (d, $^{3}J_{HH}$ = 3.8 Hz, 1H, *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,

1H, f), 3.78 (s, OCH_3, j), 1.36 (s, 2 CH_3, i), 1.33 (bd, $^3J_{HH}$ = 6.8 Hz, $2CH_3$, k *or* m), 1.32 (bd, $^3J_{HH}$ = 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}).

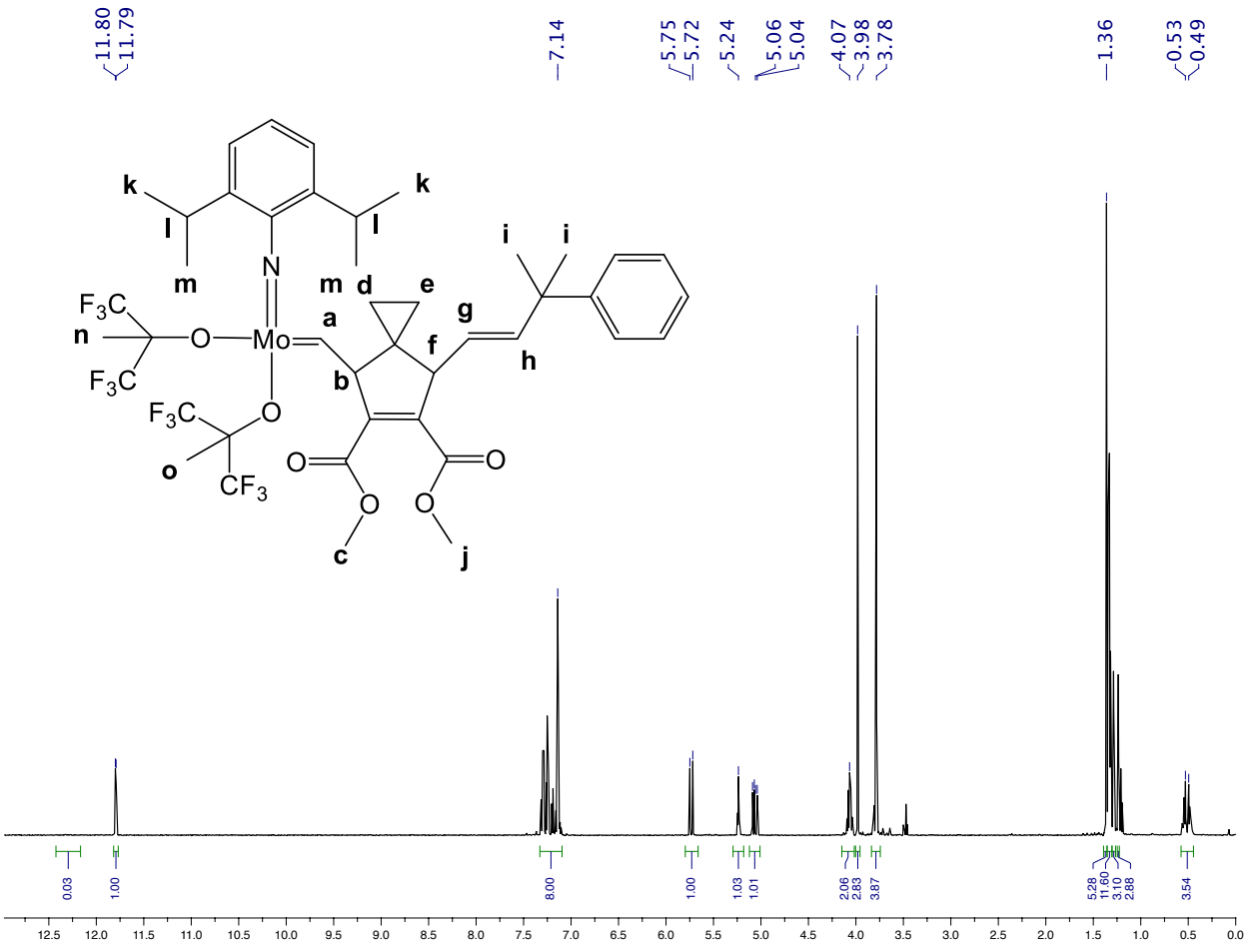


Figure S21. ^{1}H NMR (500.43 MHz) of the first insertion product between **2** and **B'** in $CDCl_3$

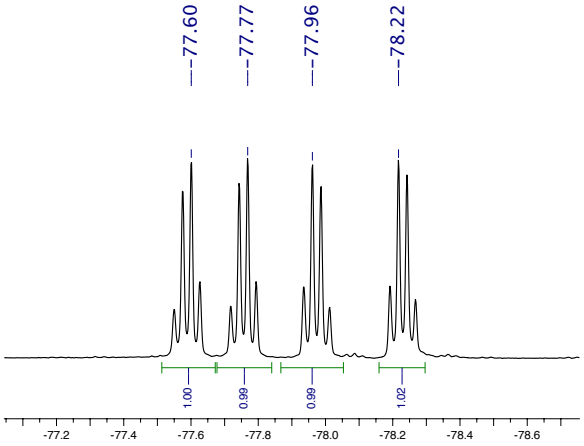


Figure S22. The ^{19}F NMR of the first insertion complex between **2** and **B'** in $CDCl_3$

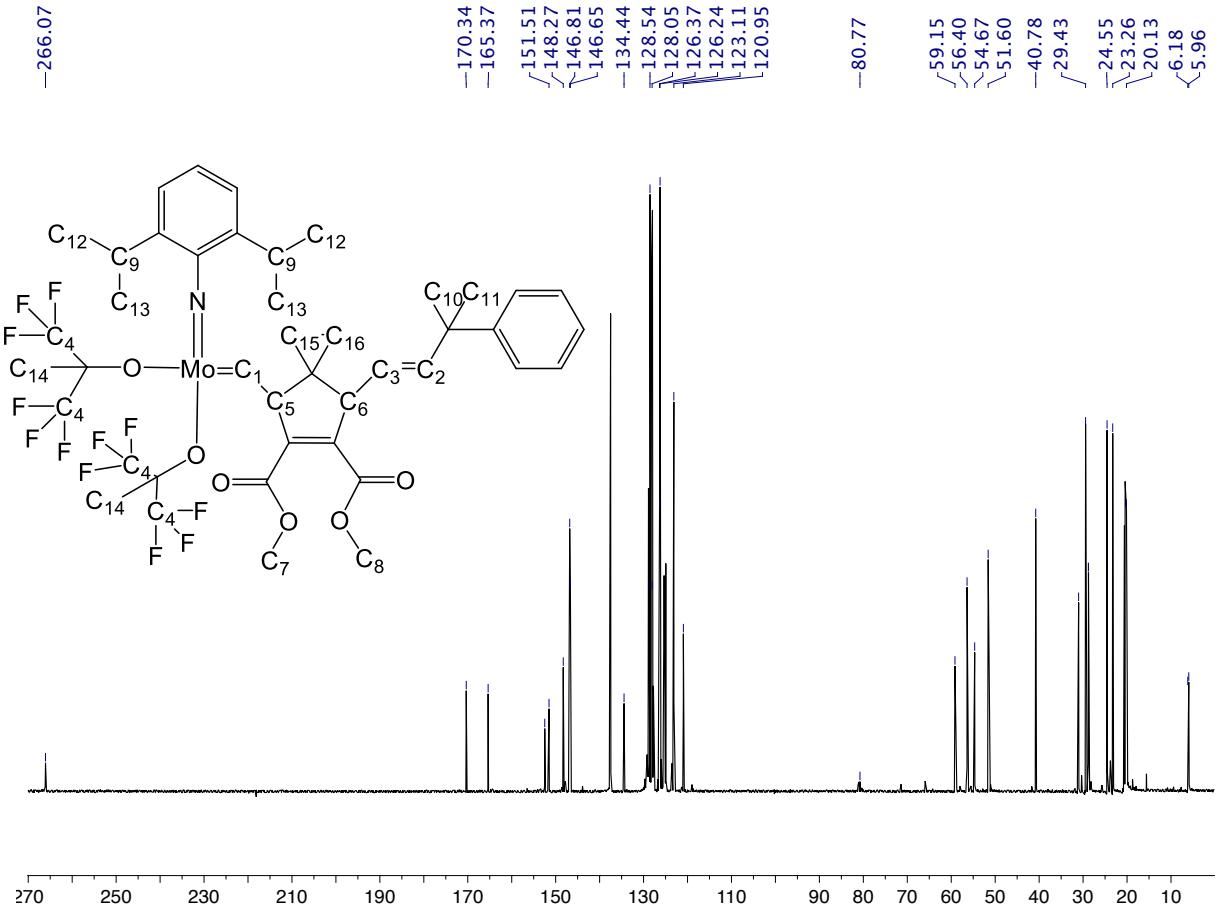
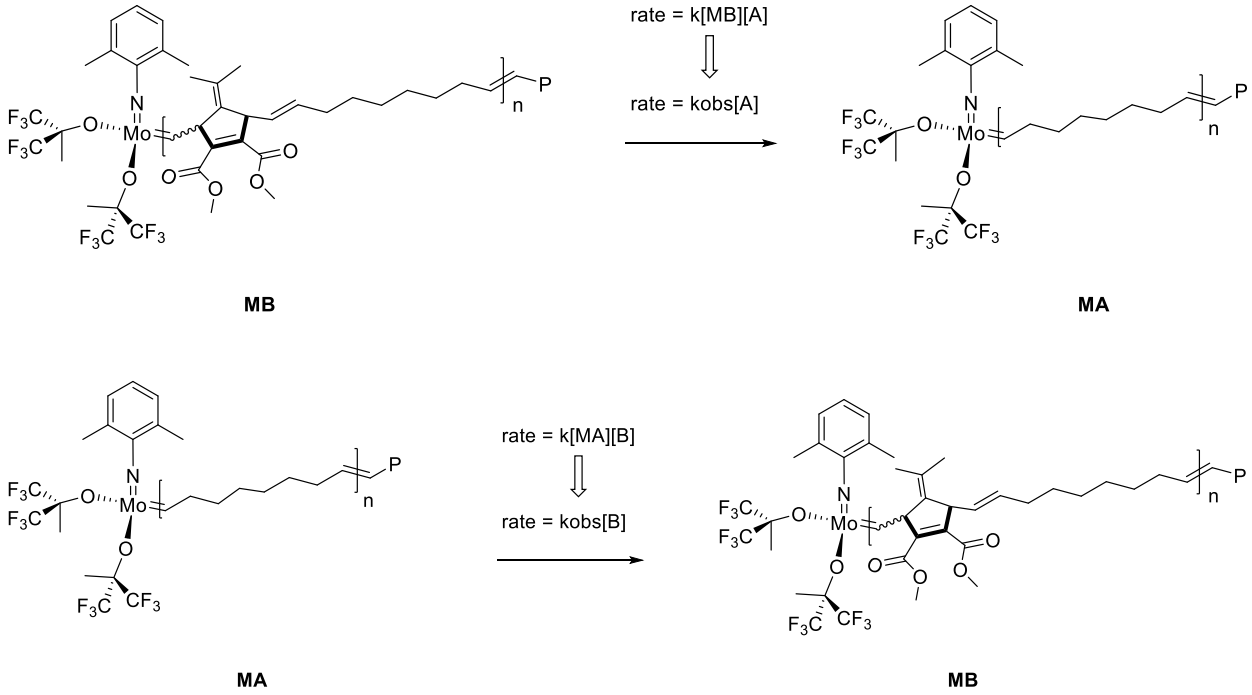


Figure S23. ^{13}C NMR spectrum (125.79 MHz) of first insertion complex between **2** and **B'** in toluene-d_8.

Details of Kinetic Experiments I



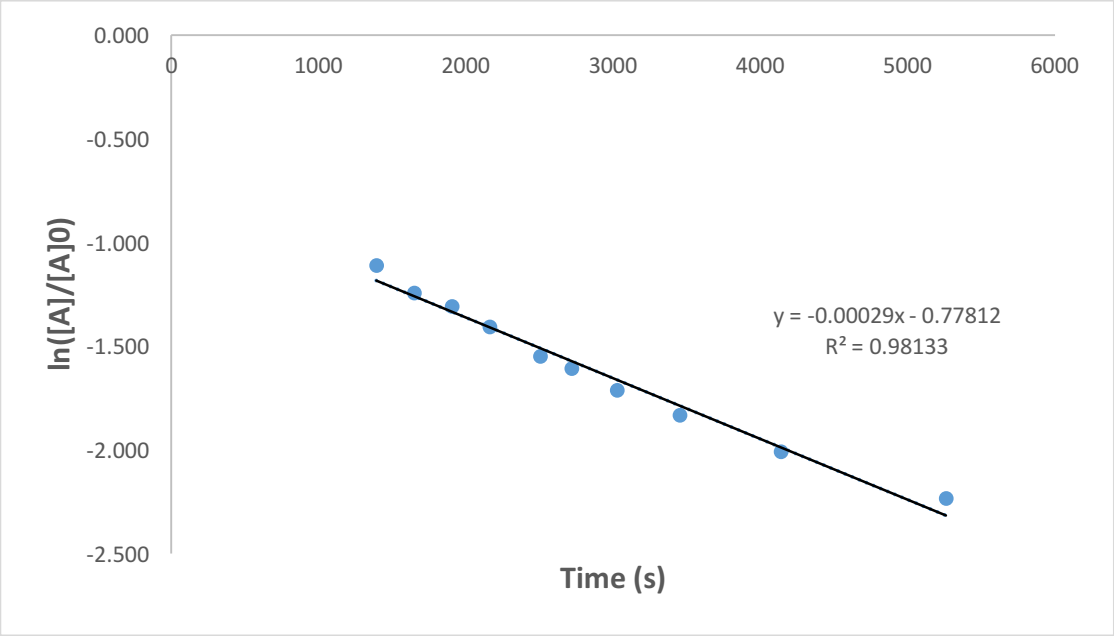
Combination of A/B/Cat	Equivalents A/B/Cat	Solvent	Concentration of Monomer (M)	k_{obs} (A) (x 10^{-5} s^{-1})	k_{obs} (B) (x 10^{-5} s^{-1})
A/B/1	50/50/1	$CDCl_3$	0.12	29	20
A'/B'/1	50/50/1	Toluene-d_8	0.20	23	16
A'/B'/1	100/100/1	Toluene-d_8	0.20	26	16
A'/B'/2	50/50/1	Toluene-d_8	0.20	3.1	2.7
A/B/1	50/50/1	THF-d_8	0.16	3.4	3.3

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

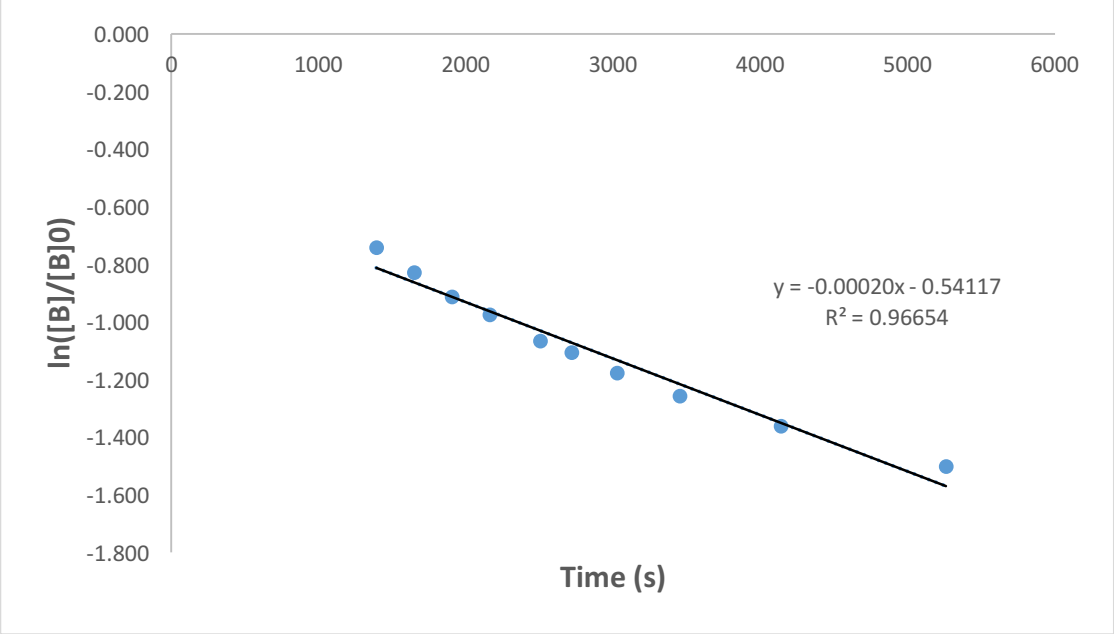
Rate of consumption of A and B by catalyst 1 in $CDCl_3$.

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.

Time (s)	$\ln([A]/[A]_0)$	$\ln([B]/[B]_0)$
1392	-1.111	-0.743
1650	-1.245	-0.830
1906	-1.310	-0.913
2162	-1.409	-0.975
2508	-1.551	-1.068
2718	-1.608	-1.107
3027	-1.715	-1.178
3452	-1.833	-1.257
4142	-2.010	-1.363
5260	-2.234	-1.502



Slope (k_{obs}) = 2.9 x 10^{-4} s^{-1}

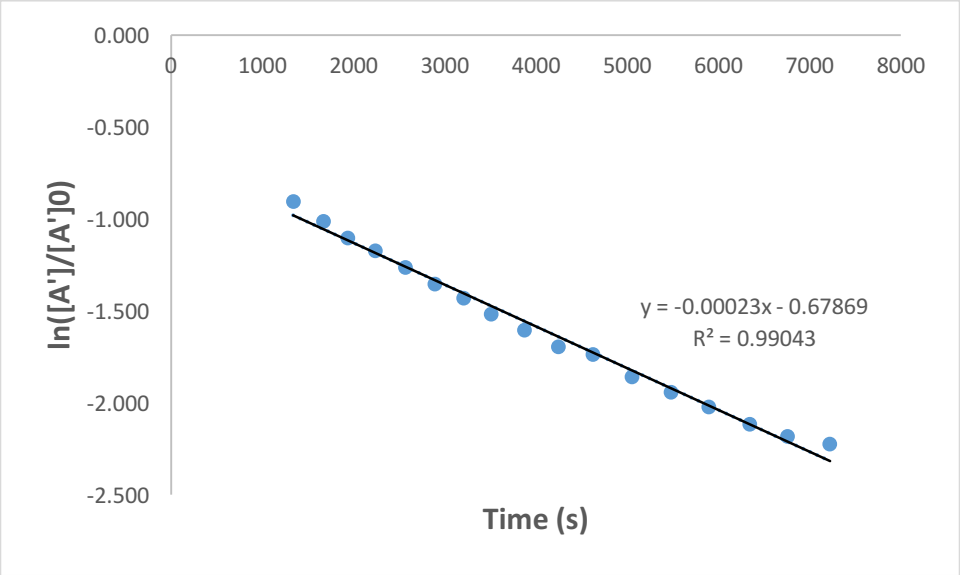


Slope (k_{obs}) = 2.0 x 10^{-4} s^{-1}

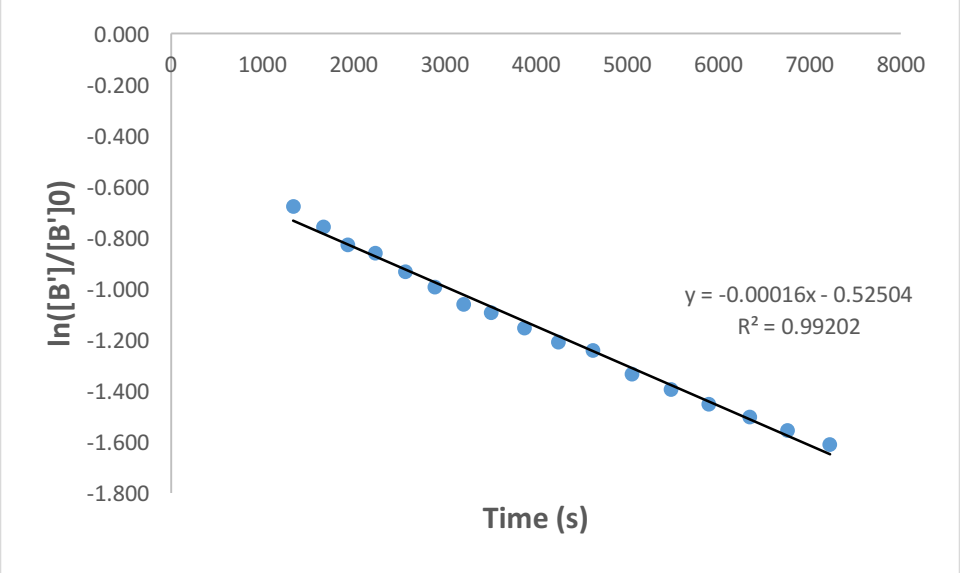
Rate of consumption of A' and B' by catalyst 1 in toluene-d_8.

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.

Time (s)	$\ln([A']/[A']_0)$	$\ln([B']/[B']_0)$
1336	-0.905	-0.676
1667	-1.015	-0.758
1937	-1.105	-0.827
2237	-1.174	-0.861
2569	-1.264	-0.933
2887	-1.355	-0.994
3203	-1.433	-1.061
3507	-1.517	-1.092
3873	-1.604	-1.153
4245	-1.697	-1.208
4624	-1.740	-1.240
5048	-1.861	-1.333
5480	-1.943	-1.394
5894	-2.022	-1.450
6342	-2.117	-1.502
6758	-2.184	-1.553
7220	-2.226	-1.608



Slope (k_{obs}) = 2.3 x 10^{-4} s^{-1}



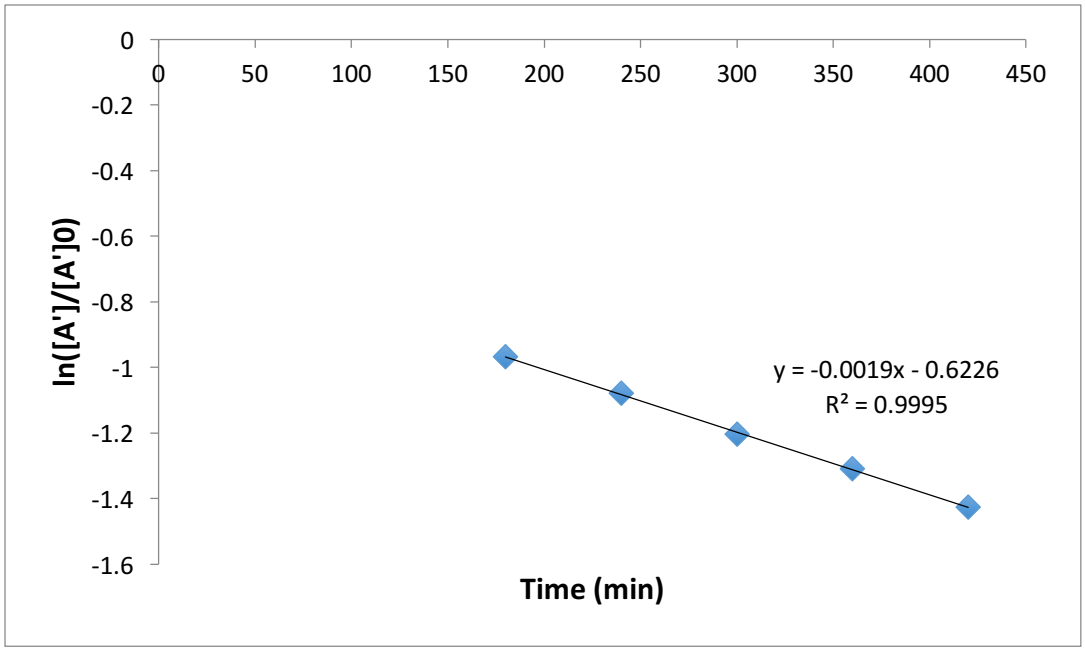
Slope (kobs) = 1.6 x 10^{-4} s^{-1}

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

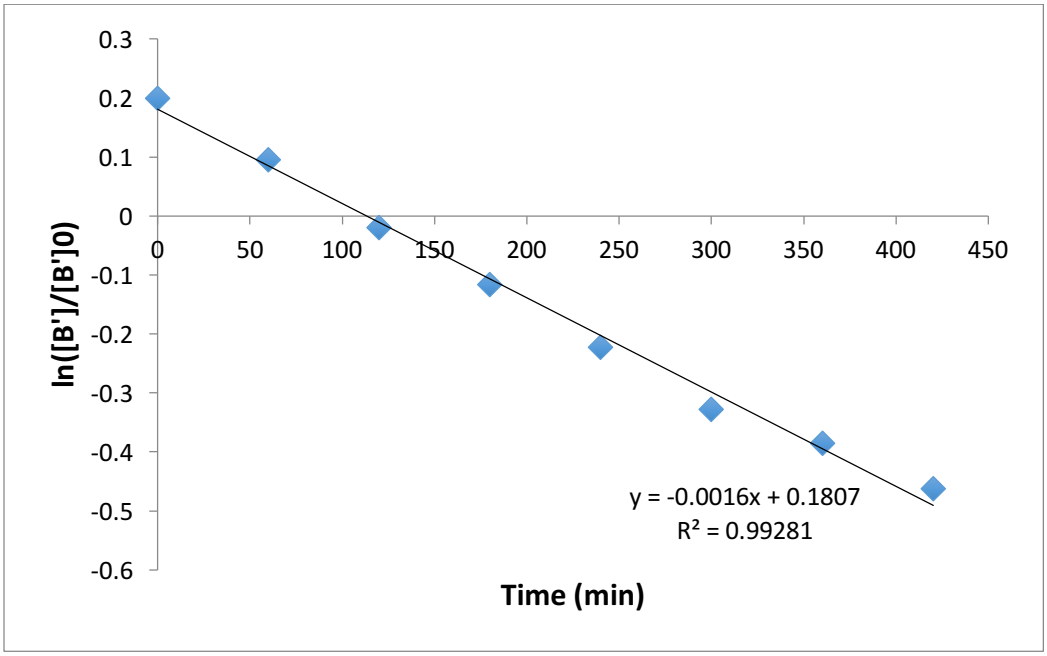
In a J-Young NMR tube, 50 equivalents of **B'** (0.119 mmol, 27.8 mg) and 50 equivalents of **A'** (0.119 mmol, 14 μL) in 0.6 mL of toluene-d_8 were added and consumption of each monomer were monitored over 1 half live.

Time (min)	$\ln([A']/[A']_0)$
180	-0.967
240	-1.078
300	-1.203
360	-1.309
420	-1.427

Time (min)	$\ln([B']/[B']_0)$
0	0.198
60	0.095
120	-0.020
180	-0.116
240	-0.223
300	-0.328
360	-0.385
420	-0.462



Slope (kobs) = $3.1 \times 10^{-5}\ s^{-1}$

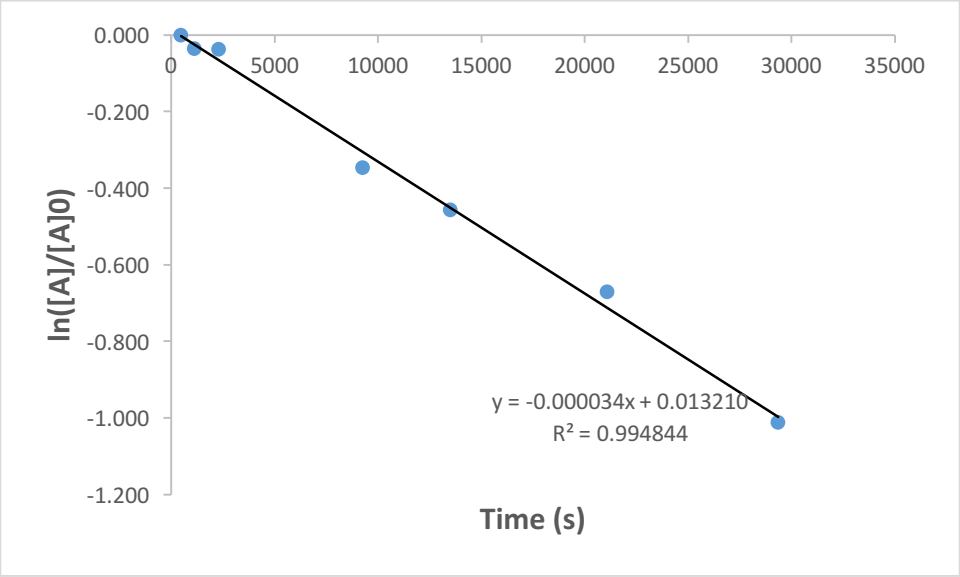


Slope (kobs) = 2.7×10^{-5} s^{-1}

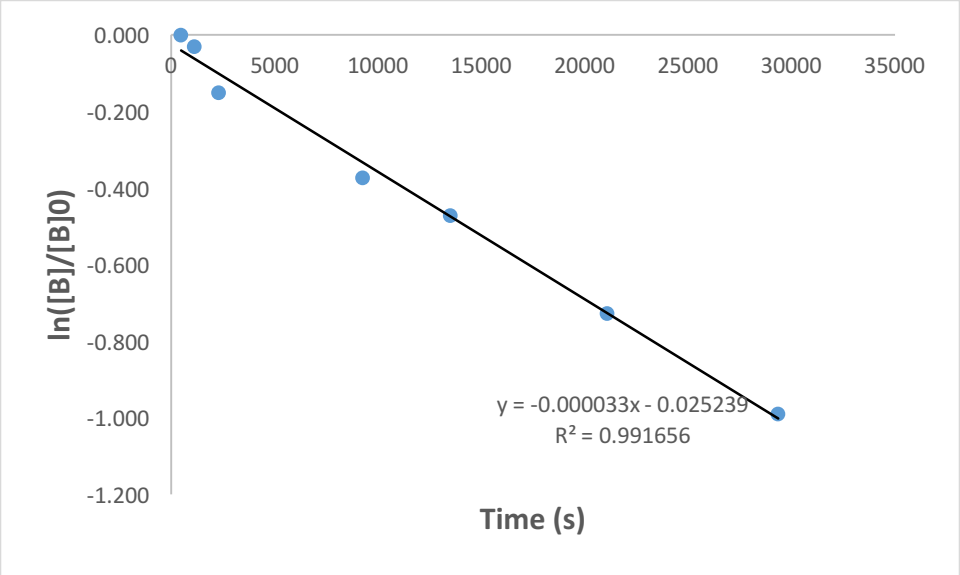
Rate of consumption of A and B by catalyst 1 in THF-d_8.

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.

Time (s)	$\ln([A]/[A]_0)$	$\ln([B]/[B]_0)$
1038	-1.177	-0.248
1308	-1.244	-0.302
1562	-1.276	-0.331
1864	-1.317	-0.362
2152	-1.362	-0.398
2415	-1.402	-0.431
2748	-1.452	-0.470



Slope (k_{obs}) = 3.4 x 10^{-5} s^{-1}



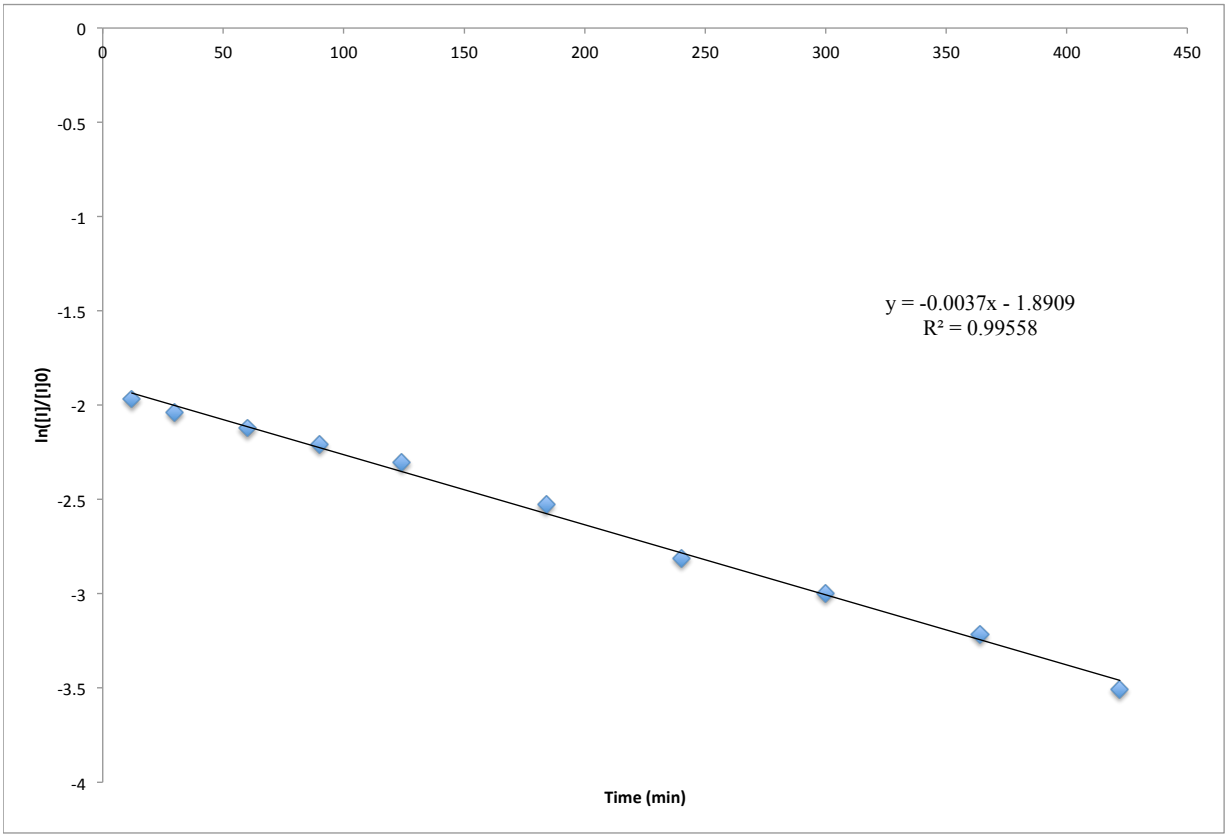
Slope (k_{obs}) = 3.3 x 10^{-5} s^{-1}

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.

Time (min)	$\ln([I]/[I]_0)$
12	-1.966
30	-2.040
60	-2.120
90	-2.207
124	-2.302
184	-2.525
240	-2.813
300	-2.995
364	-3.218
422	-3.506

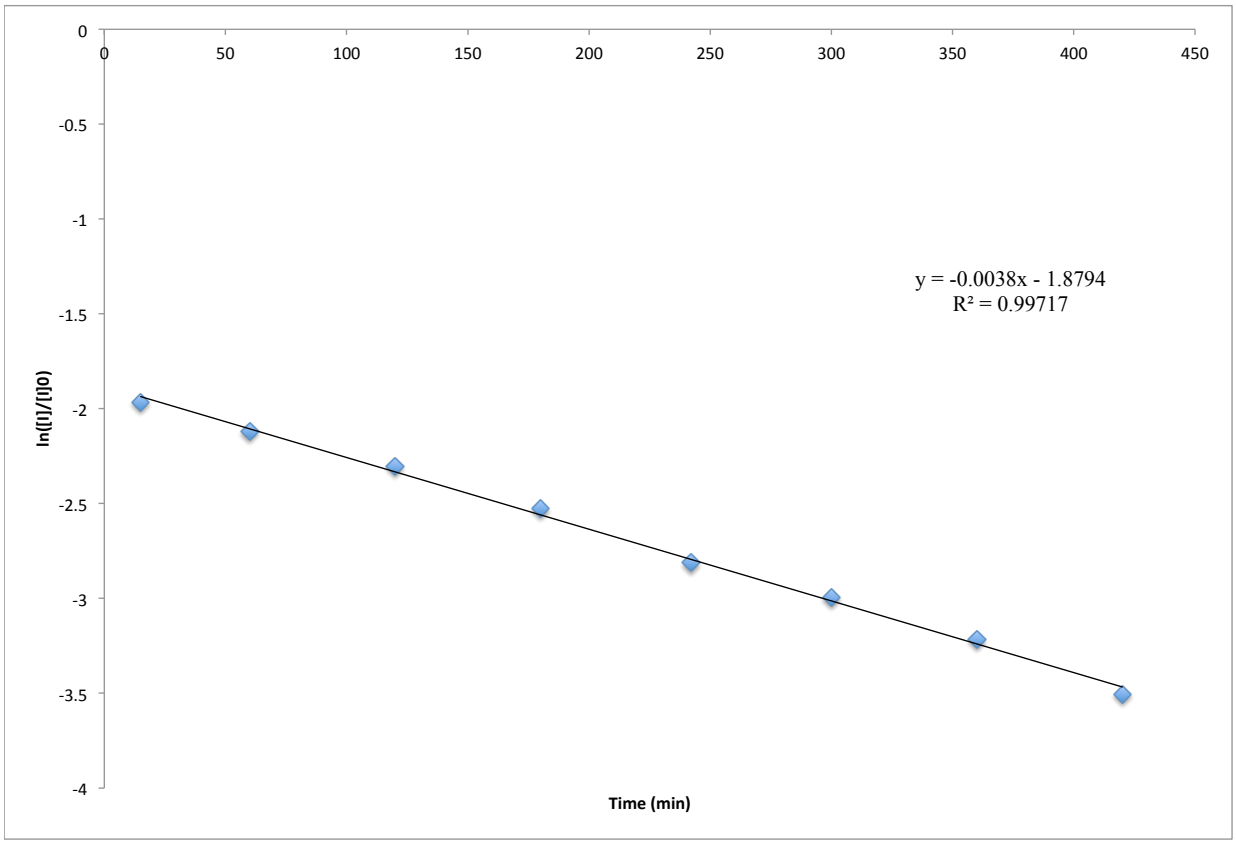


Slope (k_{obs}) = 6.2 x 10^{-5} s^{-1}

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.

Time (min)	[I]	ln([I]/[I]$_0$)
15	0.14	-1.966
60	0.12	-2.120
120	0.10	-2.302
180	0.08	-2.525
242	0.06	-2.813
300	0.05	-2.995
360	0.04	-3.218

420	0.03	-3.506

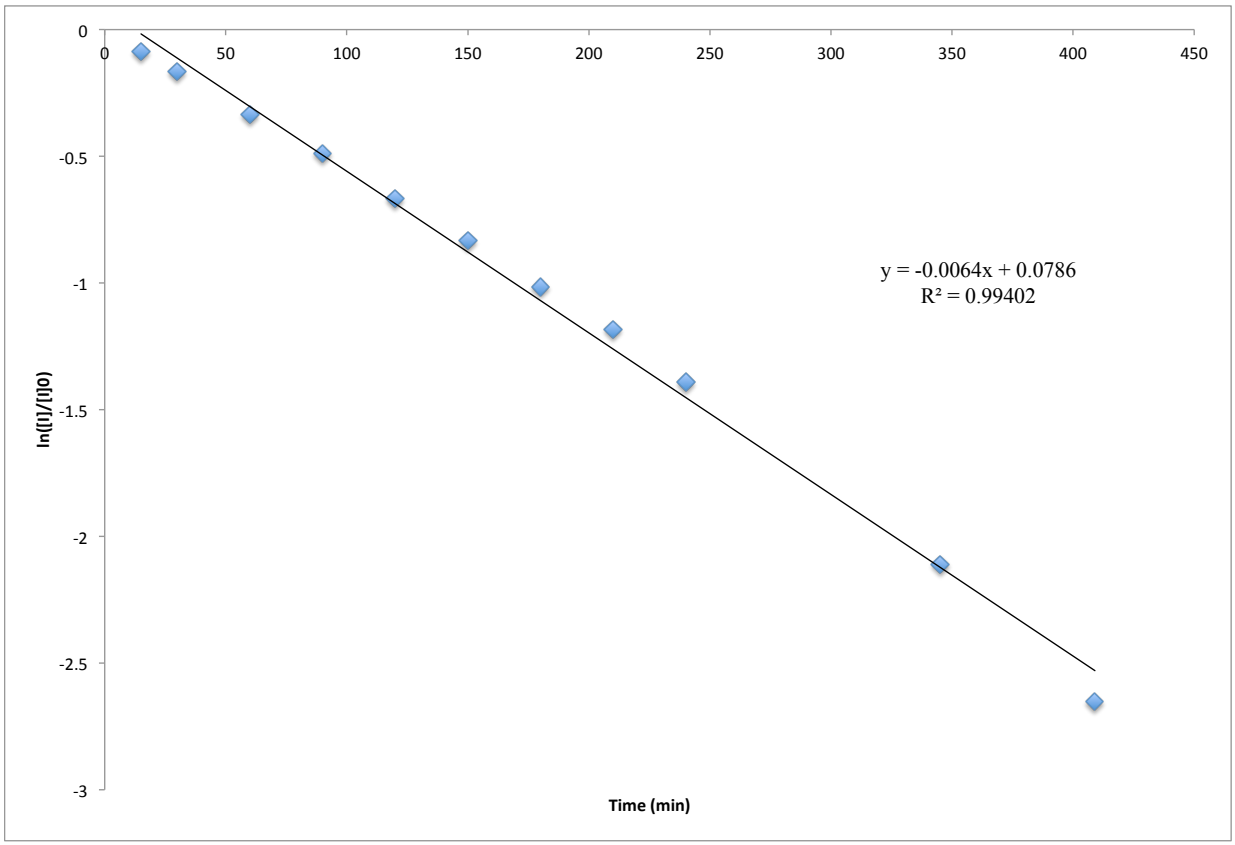


Slope (k_{obs}) = 6.3 x 10^{-5} s^{-1}

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.

Time (min)	$\ln([I]/[I]_0)$
15	-0.086
30	-0.165
60	-0.336
90	-0.488
120	-0.667
150	-0.832
180	-1.015
210	-1.181
240	-1.391
345	-2.110
409	-2.652

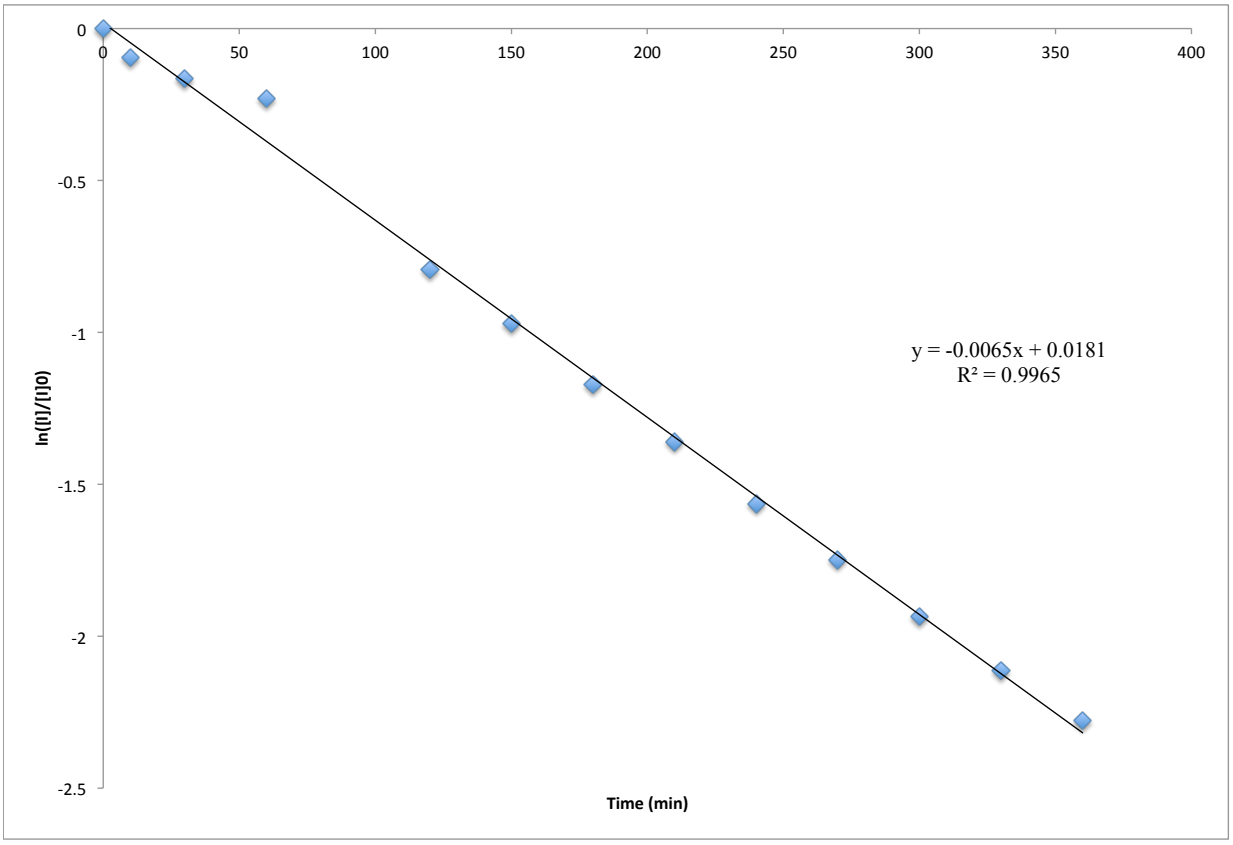


Slope (k_{obs}) = 10.6 x 10^{-5} s^{-1}

In a J-Young NMR tube, 20 equivalents of **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.

Time (min)	$\ln([I]/[I]_0)$
10	-0.095
30	-0.165
60	-0.231
120	-0.792
150	-0.970
180	-1.172

210	-1.361
240	-1.564
270	-1.749
300	-1.935
330	-2.113

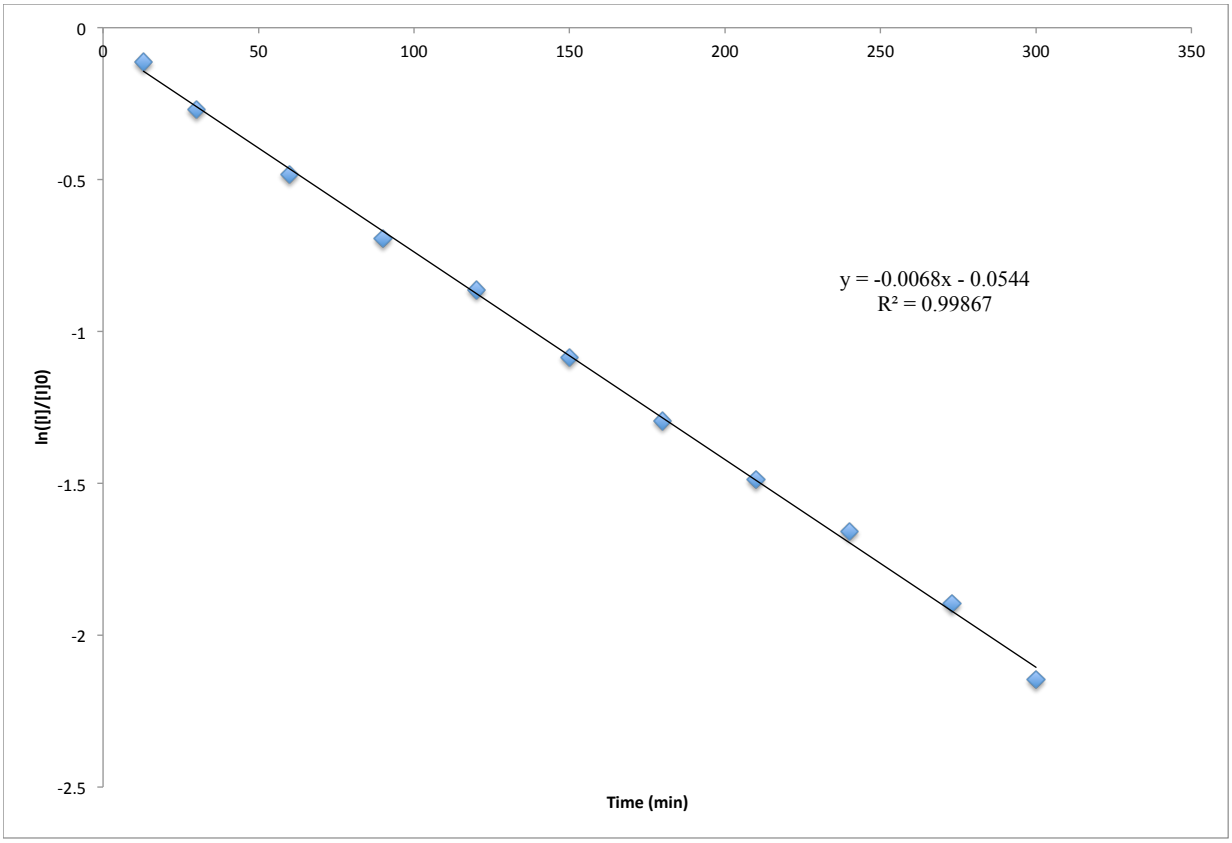


Slope (k_{obs}) = 10.8 x 10^{-5} s^{-1}

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.

Time (min)	ln([I]/[I]$_0$)
13	-0.113

30	-0.269
60	-0.482
90	-0.693
120	-0.862
150	-1.085
180	-1.294
210	-1.488
240	-1.658
273	-1.894
300	-2.147

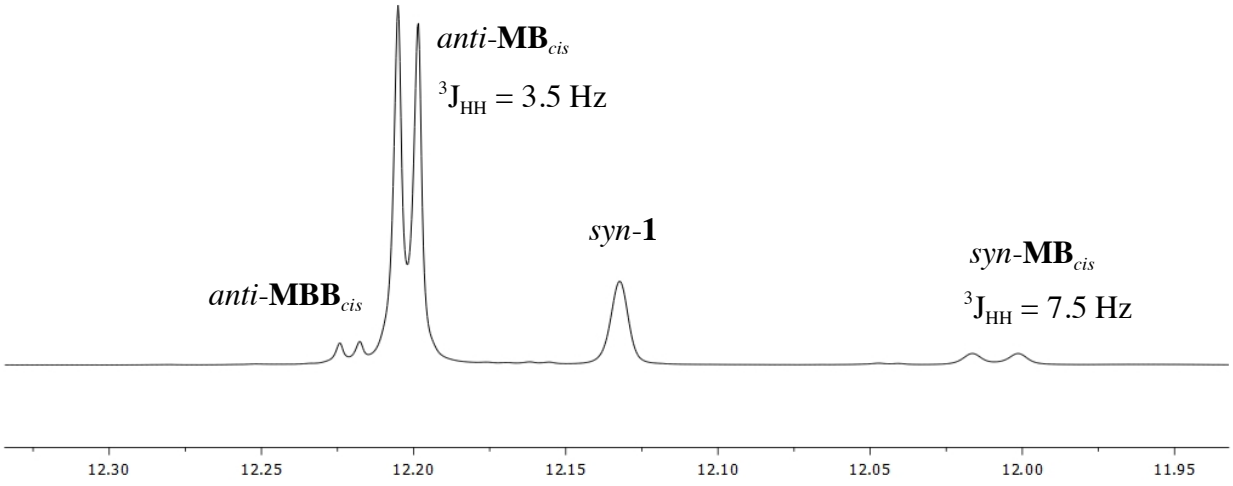


Slope (k_{obs}) = 11.3 x 10^{-5} s^{-1}

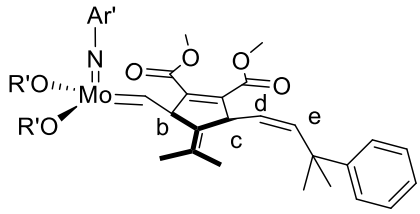
Observation of *anti*-MB$_{cis}$ and *syn*-MB$_{cis}$ by catalyst 1

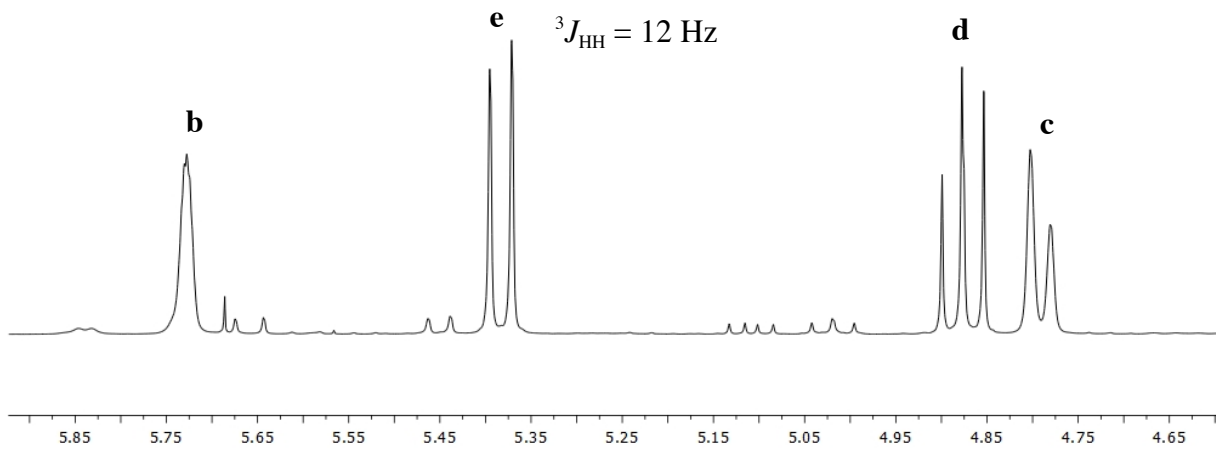
In a J-Young NMR tube, 0.7 equivalents of **B** (5.7 mg, 23 μmol) were added to a 0.7 mL toluene-d_8 solution of catalyst **1** (22.8 mg, 32 μmol) at room temperature. After 2 hours, a ^{1}H NMR spectrum was taken and the major species was *anti*-MB$_{cis}$ and the minor species was *syn*-MB$_{cis}$. 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} (=[*syn*-MB$_{cis}$]/[*anti*-MB$_{cis}$]) was found to be 0.05.

^{1}H NMR of alkylidene region:



^{1}H NMR of olefinic region:

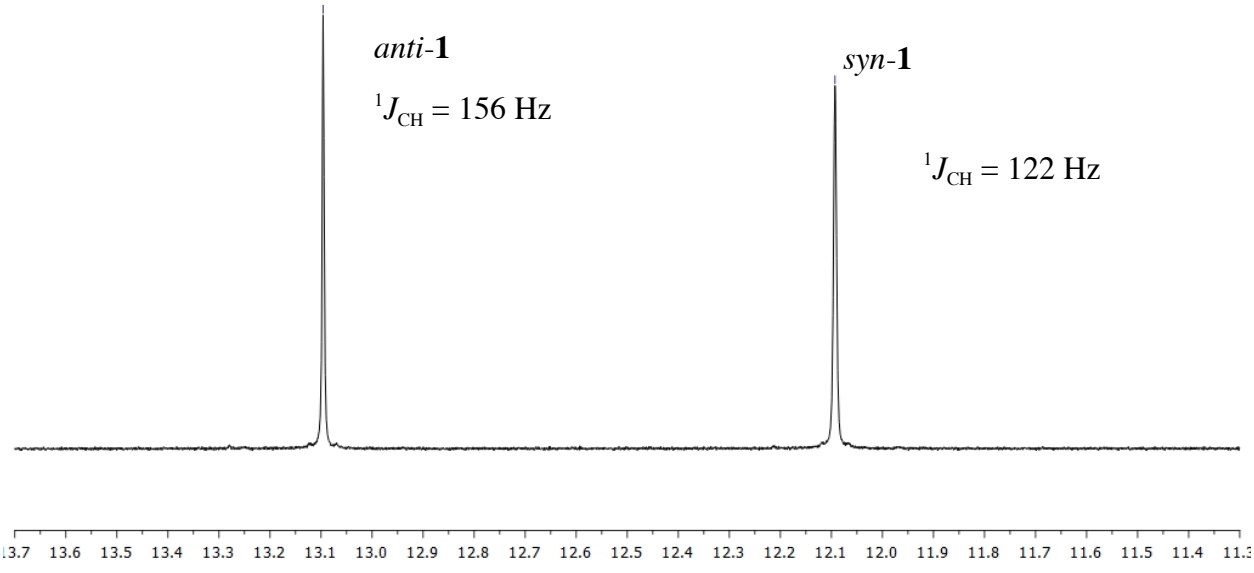




Photolysis of 1 and addition of B by varying the temperature.

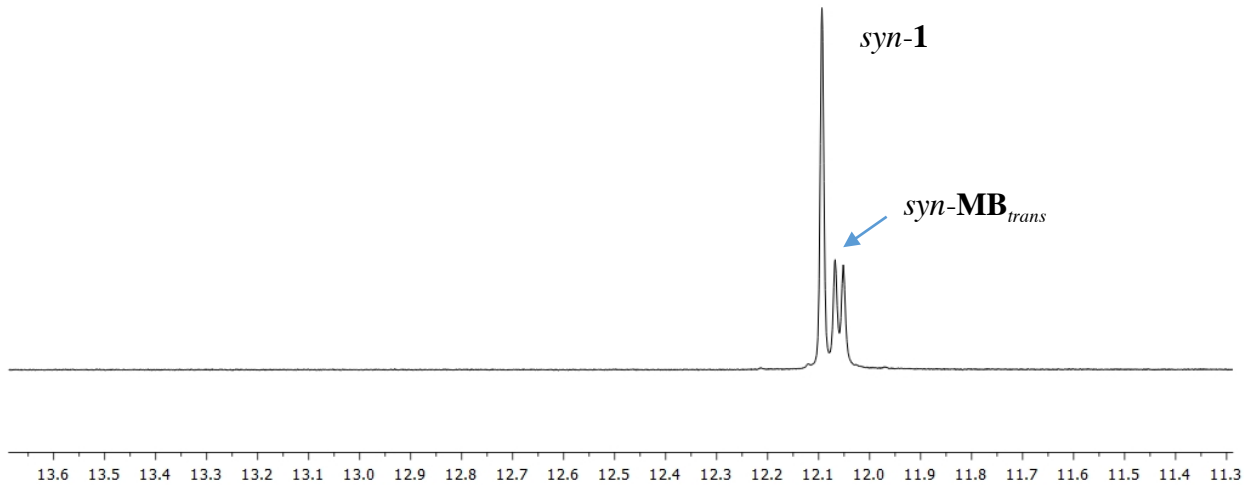
In a Wilmad screw-cap NMR tube, Mo(NAr')(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (32.5 mg, 45.8 µmol) were dissolved in 0.6 mL of toluene-d_8. The sample was closed with a PTFE/silicon septum cap and irradiated at -78 °C in a Rayonet photolysis apparatus at 350 nm for 3 h. The sample was kept at -78 °C until 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:



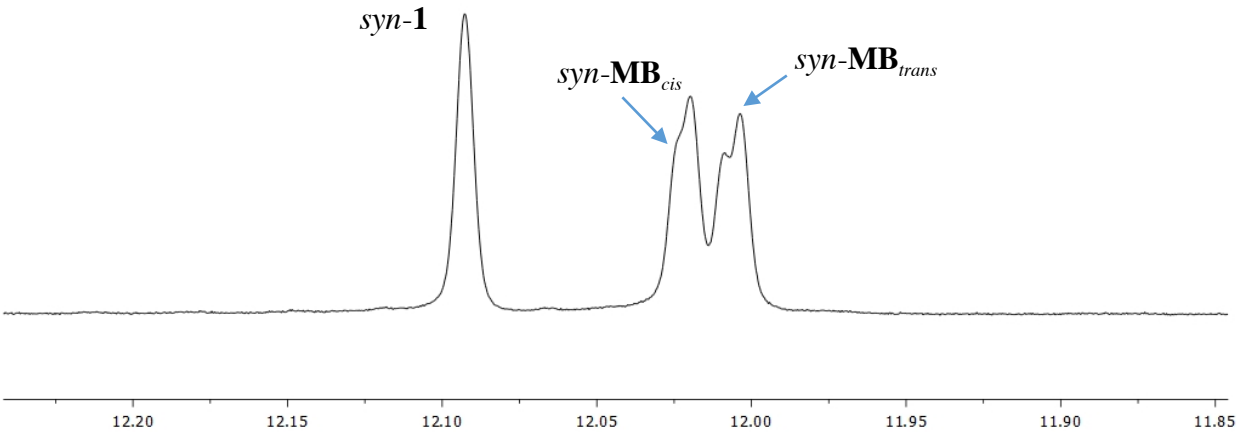
After observation at -50 °C, the sample was returned to a -78 °C bath and 0.5 equivalents of **B** (5.1 mg, 20.5 μmol) in 0.1 mL of toluene-d_8 was added via a syringe. The consumption of **B** was monitored as the temperature was changed by +10 °C.

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

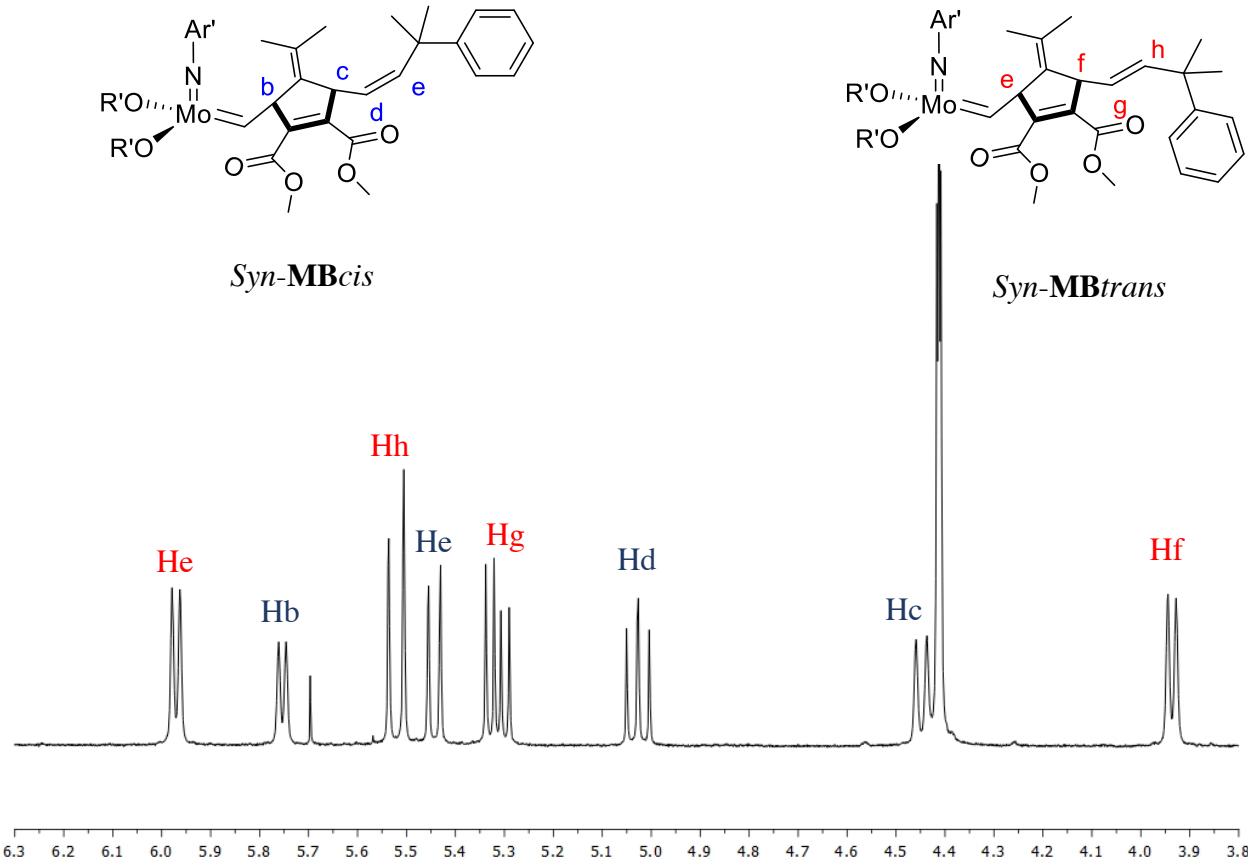


At -10 °C, both *syn*-**MB**$_{trans}$ and *syn*-**MB**$_{cis}$ species are resolved and olefinic peaks were assigned by gCOSY.

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



^{1}H NMR of the olefinic region at -10 °C:



$^{1}H–^{1}H$ gCOSY spectrum of the olefinic region at -10 °C:

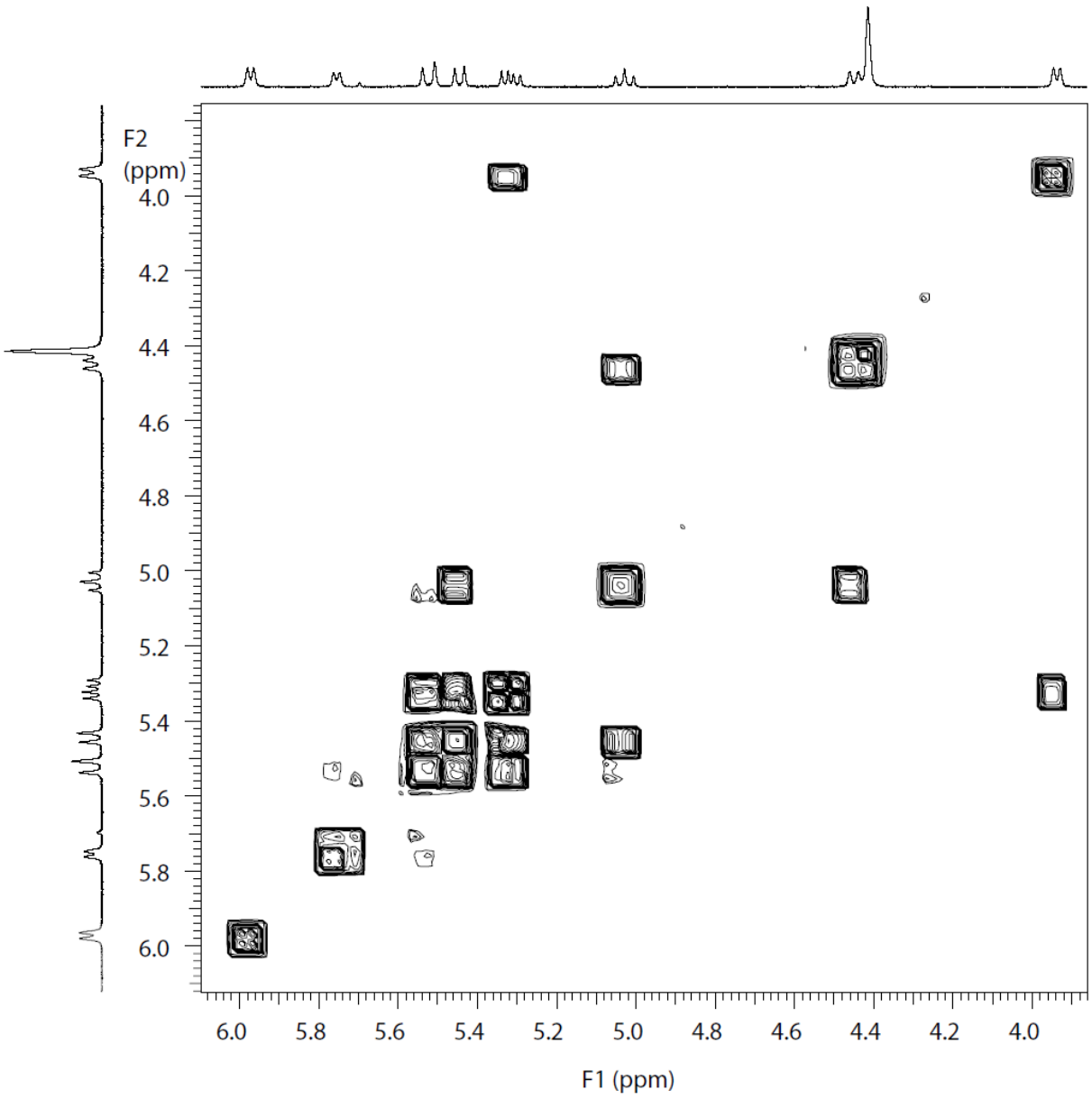


Figure S24. ^{1}H-^{1}H gCOSY spectrum of the olefinic region of *syn*-**MB**$_{cis}$ and *syn*-**MB**$_{trans}$ at -10 °C

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