Synthesis of Alternating trans-AB Copolymers through Ring-Opening Metathesis Polymerization Initiated by Molybdenum Alkylidenes

Citation: Jeong, Hyangsoo; John, Jeremy M.; Schrock, Richard R. and Hoveyda, Amir H. "Synthesis of Alternating trans-AB Copolymers through Ring-Opening Metathesis Polymerization Initiated by Molybdenum Alkylidenes." Journal of the American Chemical Society 137, no. 6 (February 2015): 2239–2242. © 2015 American Chemical Society (ACS)

As Published: http://pubs.acs.org/doi/abs/10.1021/jacs.5b00221

Publisher: American Chemical Society (ACS)

Persistent URL: http://hdl.handle.net/1721.1/108278

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

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

Hyangsoo Jeong,[‡] Jeremy M. John,[‡] Richard R. Schrock,[‡]* Amir H. Hoveyda[†]

[‡]Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

[†]Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467

ABSTRACT: Four alternating AB copolymers have been prepared through ring-opening metathesis polymerization (ROMP) with Mo(NR)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ initiators (R = 2,6-Me$_2$C$_6$H$_3$ (**1**) or 2,6-*i*-Pr$_2$C$_6$H$_3$ (**2**)). The AB monomer pairs copolymerized by **1** are cyclooctene (**A**) and 2,3-dicarbomethoxy-7-isopropylidenenorbornadiene (**B**), cycloheptene (**A'**) and dimethylspiro[bicyclo[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 heterodyads (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.[1] Perhaps the best known are AB copolymers prepared from CO and olefins[1b] or CO_2 and epoxides.[1c-f] Synthesis of AB copolymers when one of the monomers is CO or CO_2 have been relatively successful because neither CO nor CO_2 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%.[2] In some cases, an acyclic diene is employed as one of the monomers.[2o] The ideal circumstance for preparing an AB copolymer is one in which two monomers that cannot be homopolymerized undergo the cross polymerization steps selectively,[1a] as in the copolymerization of 1-substituted cyclobutenes and cyclohexene.[2a] (Because the free energy for polymerization of cyclohexene is positive,[3] it is proposed that only one 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*),[4,5] have thus far employed Ru-based catalysts.[6]

We showed recently[7] 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**, Figure 1). Monomer **B** *is* polymerized readily by W(O)(CH-*t*-Bu)(Me$_2$Pyr)(OHMT)(PMe$_2$Ph) (OHMT = O-2,6-Mes$_2$C$_6$H$_3$, Me$_2$Pyr = 2,5-dimethylpyrrolide),[8] especially in the presence of B(C$_6$F$_5$)$_3$, which accelerates ROMP through binding of B(C$_6$F$_5$)$_3$ to the oxo ligand.[8,9] In 1990 we found that **B** reacts slowly with Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) to give a first insertion product, but no further reaction between the first insertion product and **B** was observed, even at 55 °C.[10] 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**.

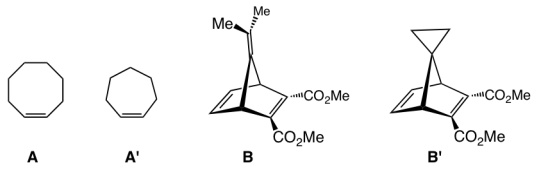


Figure 1. Monomers explored in this study

During the process of exploring several molybdenum imido alkylidene catalysts for the homopolymerization of **B** we found that Mo(NAr')(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (**1**, Ar' = 2,6-

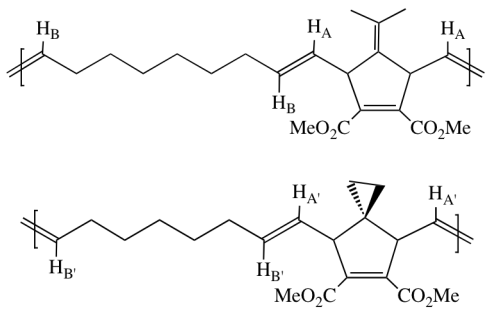


Figure 2. The repeat unit of *trans*-poly(**A**-*alt*-**B**) (top) and *trans*-poly(**A'**-*alt*-**B'**).

$Me_2C_6H_3$) initiates the polymerization of **B** relatively slowly in $CDCl_3$ or toluene-d_8. Nevertheless, **B** and cyclooctene (**A**, Figure 1, 50 equiv of each) are copolymerized by initiator **1** in $CDCl_3$ or C_6D_6 in 1-2 h to give largely (>90%) *trans*-poly(**A**-*alt*-**B**) (Figure 2). Proton NMR spectra in $CDCl_3$ of *trans*-poly(**A**-*alt*-**B**) show primarily two types of *trans* olefinic protons bound to C=C bonds (Figure 3a), a double doublet for H_A and a double triplet (overlapping) for H_B; the coupling between H_A and H_B is approximately 15.5 Hz, 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 $k_{obs} = 29x10^{-5}$ s^{-1} in $CDCl_3$; a plot of ln[**B**] *vs*. t is approximately linear with $k_{obs} = 20x10^{-5}$ 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 k_{obs} values are useful only for rough comparisons.

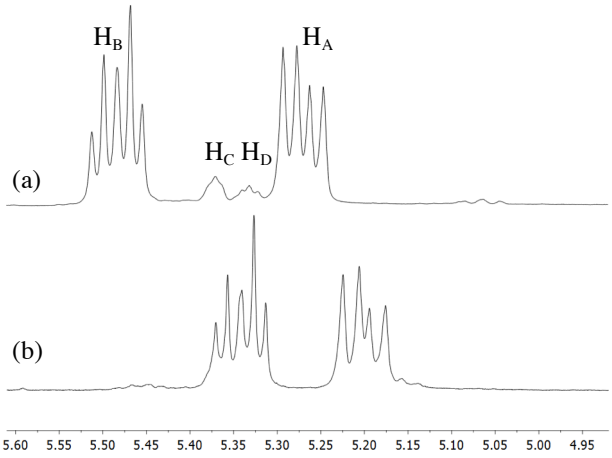


Figure 3. The olefinic region of the ^1H NMR spectra of (a) *trans*-poly(**A**-*alt*-**B**) and (b) *trans*-poly(**A'**-*alt*-**B'**) in $CDCl_3$ prepared from **1**.

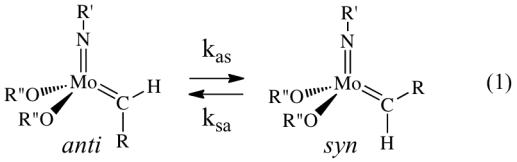
Table 1. Polymerization of 50:50:1 (A:B:catalyst) at 22 °C.[a]

Comb	Solv	Monomer (M)	$k_{obs}x10^{-5}$ s^{-1}(A)	$kx10^{-5}$ s^{-1}(B)
A/B/1	$CDCl_3$	0.12	29	20
A/B/1	THF-d_8	0.16	3.4	3.3
A'/B'/1	Tol-d_8	0.20	23	16
A'/B'/1[b]	Tol-d_8	0.20	26	16
A'/B'/2	Tol-d_8	0.20	3.1	2.7

[a] See Supporting Information for details. [b]**A':B':1** = 100:100:1.

Olefinic proton resonances H_C and H_D between the resonances for H_B and H_A (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 **1** in $CDCl_3$ or toluene-d_8. The % heterodyads and homodyads can be assessed relatively accurately through integration of the resonances for H_A and H_B protons versus those for H_C and H_D.

Compound **1** will also initiate copolymerization of cycloheptene (**A'**) and **B'** in toluene-d_8 to give *trans*-poly(**A'**-*alt*-**B'**) (Figure 2, bottom) with $k_{obs} = 23x10^{-5}$ s^{-1} for **A'** and $16x10^{-5}$ 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. $Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ (**2**) also will initiate the copolymerization of **A'** and **B'** in toluene-d_8 with $k_{obs} = 3.1x10^{-5}$ s^{-1} for **A'** and $2.7x10^{-5}$ 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.



Important features of complexes of type **1** and **2** are *syn* and *anti* isomers and interconversion of them in the absence of olefin through rotation about the M=C bond (eq 1).[11,12] A relatively extensive study of *syn* and *anti* isomers of Mo imido neopentylidene complexes[12] revealed that the *syn* isomer is usually the one observed, with K_{eq} ([*syn*]/[*anti*]) being as large as 1500 and the relative rate constants for *anti* to *syn* (k_{as}) and *syn* to *anti* (k_{sa}) conversions varying by several orders of magnitude for different OR" and R' combinations. *Syn* and *anti* isomers also were shown to exhibit different reactivities toward 5,6-bistrifluoromethylnorbornadiene (NBDF6), with the *anti* isomer reacting much more rapidly with NBDF6 than the *syn* isomer reacts with NBDF6. For A (**A** or **A'**) and B (**B** or **B'**), either a *syn* or *anti* isomer of MB (M is the metal and B is the last inserted monomer) can react with A and A can approach MB in two ways to give *cis* or *trans* metallacyclobutane intermediates; therefore, there are four possible reactions of MB with A to give one AB heterodyad and four possible reactions of MA (A last inserted) with B to give the other AB heterodyad. Likewise, there are four possible reactions of MA with A to give AA homodyads, and four possible reactions of MB with B to give BB homodyads. All evidence suggests that only two of the four steps that could yield *trans* AB dyads in *trans*-poly(**A**-*alt*-**B**) and *trans* **A'B'** linkages in *trans*-poly(**A'**-*alt*-**B'**) comprise the core of the proposed mechanism (Figure 4).

A model for the reaction of *syn*-**MA** with **B** is the reaction of *syn*-**1** with 0.7 equivalents of **B**, which generates a *syn* first insertion product that contains a *cis* C=C bond (*syn*-$\mathbf{MB}_{cis}$), not a *trans* C=C bond. If *syn*-**1** is an appropriate model for *syn*-**MA**,

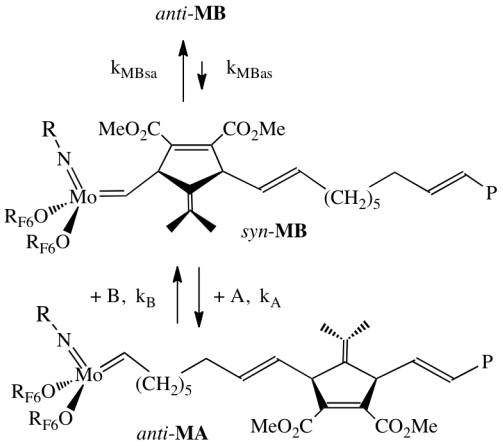


Figure 4. The proposed mechanism of forming *trans*-poly(**A**-*alt*-**B**) (P = polymer).

then **B** does not react with *syn*-**MA** to give *syn*-$\mathbf{MB}_{trans}$ during formation of *trans*-poly(**A**-*alt*-**B**). At room temperature *syn*-**MB** is converted into a mixture of *syn*-**MB** and *anti*-**MB** through rotation about the Mo=C bond. During copolymerization *syn*-**MB** and *anti*-**MB** are observed; their ratio at equilibrium in the absence of olefin is K_{eq} = [*syn*]/[*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-*t*-butoxide analog of *anti*-$\mathbf{MB}_{trans}$, a first insertion product (*vide supra*), is the *syn* isomer in solution ($J_{CH^{\alpha}}$ = 128 Hz) and in the solid state.[10]

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*-**1** can by prepared through photolysis of *syn*-**1** in toluene-d_8 at -78 °C (see SI).[12] Addition of 0.5 equivalents of **B** to a mixture of *anti*-**1** (~45%) and *syn*-**1** followed by warming the reaction slowly to 22 °C revealed that **B** reacts with *anti*-**1** to give a *syn* first insertion product that contains a *trans* C=C bond (*syn*-$\mathbf{MB}_{trans}$) much faster than the rate at which *syn*-**1** reacts with **B** to give *syn*-$\mathbf{MB}_{cis}$. *Syn*-$\mathbf{MB}_{trans}$ also readily interconverts with *anti*-$\mathbf{MB}_{trans}$ at 22 °C. If *anti*-**1** 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** initially, which then begins to isomerize to give a mixture of *syn*-**MB** and *anti*-**MB** (Figure 4).

The mechanism of copolymerization of **A'** and **B'** 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'** at initial concentrations of **B'** that are 5x[*syn*-**2**], 20x[*syn*-**2**], and 30x[*syn*-**2**] (pseudo first-order conditions), does *not* depend upon the concentration of **B'**. The rate constant for consumption of *syn*-**2** ($10x10^{-5}$ s^{-1}) is close to that published for conversion of *syn*-**2** to *anti*-**2** in toluene-d_8 at 22 °C ($k_{2as} = 7x10^{-5}$ s^{-1}),[12] and the first insertion product in the reaction between *syn*-**2** and **B'** 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*-$\mathbf{MB'}_{trans}$, which then forms a mixture of *syn*-$\mathbf{MB'}_{trans}$ and *anti*-$\mathbf{MB'}_{trans}$.

The question concerning how the other *trans* AB dyad is formed can be answered through an experiment that employs the first insertion product ($\mathbf{MB'}_{trans}$) obtained in a reaction of *syn*-**2** with one equivalent of **B'** (see SI); $\mathbf{MB'}_{trans}$ is approximately a 95:5 *anti*:*syn* mixture at equilibrium (K_{eq} = [*syn*-$\mathbf{MB'}_{trans}$]/[*anti*-$\mathbf{MB'}_{trans}$] = 0.05), the same as found for [*syn*-$\mathbf{MB}_{cis}$]/[*anti*-$\mathbf{MB}_{cis}$] in the **AB** system above. Addition of 50 or 75 equivalents of **A'** to isolated *anti*-$\mathbf{MB'}_{trans}$ leads to a consumption of *anti*-$\mathbf{MB'}_{trans}$ at a rate that is first order in [*anti*-$\mathbf{MB'}_{trans}$], but *independent* of [**A'**] with $k_{obs} = 6.2x10^{-5}$ s^{-1}. Therefore the rate limiting step for this reaction is conversion of *anti*-$\mathbf{MB'}_{trans}$ to *syn*-$\mathbf{MB'}_{trans}$, *i.e.*, $k_{obs} = 6.2x10^{-5}$ s^{-1} = k_{MBas} (Figure 4). We conclude that the other AB linkage is formed in a reaction between **A'** and *syn*-$\mathbf{MB'}_{trans}$.

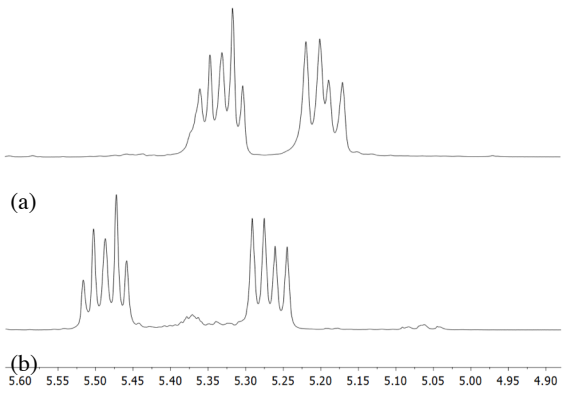


Figure 5. The olefinic region of the ^{1}H NMR spectra of (a) *trans*-poly(**A**-*alt*-**B'**) and (b) *trans*-poly(**A'**-*alt*-**B**) prepared with **1**.

Two other combinations of A and B and initiator yield high quality copolymers; those combinations are **A/B'/1** and **A'/B/1**, 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 and a *trans* C=C bond, followed by the reaction of *syn*-MB with A to give *anti*-MA and a *trans* C=C bond (A stands for either **A** or **A'**; and B stands for either **B** or **B'**; 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 *trans* 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.

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/1** 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 poly**A**, and monomer **B** then added, virtually no **B** is consumed. Therefore, rapid "unzipping" or "editing" of preformed linear and cyclic poly$A^{2k,o,s}$ 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'**) 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'**) force *trans* double bonds to form in reactions between a "large" alkylidene (*syn*-MB) and "small" monomer (A), or a "small" alkylidene (*anti*-MA) and "large" monomer (B). **B** does react readily with *syn*-**1** 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.[12] Interestingly, *trans*-poly(**A**-*alt*-**B**) is formed in THF with equal specificity and the observed "first order" rate constant is approximately $3.4x10^{-5}$ s^{-1} for **A** and $3.3x10^{-5}$ s^{-1} 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,[13] 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_p versus k_i" takes on a new complexity when two isomers of both the initiating and any propagating alkylidenes 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-methylnorbornene), was prepared by Hamilton and Rooney employing a "classical" catalyst of unknown structure and type derived from $ReCl_5$.[5] Related *cis,syndiotactic,alt* polymers have been prepared recently with Mo MAP (MonoAryloxide Pyrrolide) initiators.[5] 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,syndiotactic* 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 (COPASI).[14,15] 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.

AUTHOR INFORMATION

Corresponding Author

rrs@mit.edu

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

(1) (a) Odian, G. Principles of Polymerization, Fourth Edition; John Wiley & Sons, Inc.: Hoboken, New Jersey, 2004. (b) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (c) Platel, R. H.; Hodgson, L. M.; Williams, C. K. *Polymer Reviews* **2008**, *48* 11. (d) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 11018. (e) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28*, 7577. (f) Super, M.; Berluche, E.; Costello, C.; Beckman, E. *Macromolecules* **1997**, *30*, 368.

(2) (a) Tan, L.; Parker, K. A.; Sampson, N. S. *Macromolecules* **2014**, *47*, 6572. (b) Song, A.; Parker, K. A.; Sampson, N. S. *J. Am. Chem. Soc.* **2009**, *131*, 3444. (c) Song, A.; Parker, K. A.; Sampson, N. S. *Org. Lett.* **2010**, *12*, 3729. (d) Sutthasupa, S.; Shiotsuki, M.; Masuda, T.; Sanda, F. *J. Am. Chem. Soc.* **2009**, *131*, 10546. (e) Nakade, H.; Ilker, M. F.; Jordan, B. J.; Uzun, O.; LaPointe, N. L.; Coughlin, E. B.; Rotello, V. M. *Chem. Commun.* **2005**, 3271. (f) Lichtenheldt, M.; Wang, D.; Vehlow, K.; Reinhardt, I.; Kühnel, C.; Decker, U.; Blechert, S.; Buchmeiser, M. R. *Chem. Eur. J.* **2009**, *15*, 9451. (g) Vehlow, K.; Lichtenheldt, M.; Wang, D,; Blechert, S.; Buchmeiser, M. R. *Macromol. Symp.* **2010**, *296*, 44. (h) Ilker, M. F.; Coughlin, E. B. *Macromolecules* **2002**, *35,* 54. (i) Bornand, M.; Torker, S.; Chen, P. *Organometallics* **2007**, *26*, 3585. (j) Romulus, J.; Tan, L.; Weck, M.; Sampson, N. S. *ACS Macro Lett.* **2013**, *2*, 749. (k) Daeffler, C. S.; Grubbs, R. H. *Macromolecules* **2013**, *46*, 3288. (l) Abbas, M.; Wappel, J.; Slugovc, C. *Macromol. Symp.* **2012**, *311*, 122. (m) Buchmeiser, M. R.; Ahmad, I.; Gurram, V.; Kumar, P. S. *Macromolecules* **2011**, *44*, 4098. (n) Demel, S.; Slugovc, C.; Stelzer, F.; Fodor-Csorba, K.; Galli, G. *Macromol. Rapid Commun.* **2003**, *24*, 636. (o) Choi, T.-L.; Rutenberg, I. M.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2002**, *41*, 3839. (p) Al Samak, B.; Amir-Ebrahimi, V.; Corry, D. G.; Hamilton, J. G.; Rigby, S.; Rooney, J. J.; Thompson, J. M. *J. Mol. Catal. A: Chem.* **2000**, *160*, 13. (q) Konzelman, J.; Wagener, K. B. *Macromolecules* **1996**, *29*, 7657. (r) Wu, Z.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 3502. (s) Ding, L.; Zheng, X.-Q.; Lu, R.; An, J.; Qiu, J. *Polym. Int.* **2014**, *63*, 997. (t) Vehlow, K.; Wang, D.; Buchmeiser, M. R.; Blechert, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 2615.

(3) (a) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, 1997. (b) Ivin. K. J.; *Olefin Metathesis*; Academic Press, 1983.

(4) (a) Hamilton, J. G.; Ivin, K. J.; Rooney, J. J. *Brit. Polym. J.* **1984**, *16*, 21. (b) Hamilton, J. G.; Ivin, K. J.; Rooey, J. J.; Waring, L. C. *J. Chem. Soc., Chem. Comm.* **1983**, 159.

(5) Flook, M. M.; Ng, V. W. L.; Schrock, R. R. *J. Am. Chem. Soc.* **2011**, *133*, 1784.

(6) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746.

(7) Forrest, W. P.; Weis, J. G.; John, J. M.; Axtell, J. C.; Simpson, J. H.; Swager, T. M.; Schrock, R. R. *J. Am. Chem. Soc.* **2014**, *136*, 10910.

(8) (a) Peryshkov, D. V.; Schrock, R. R.; Takase, M. K.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 20754. (b) Peryshkov, D. V.; Schrock, R. R. *Organometallics* **2012**, *31*, 7278. (c) Peryshkov, D. V.; Forrest, W. P., Jr.; Schrock, R. R.; Smith, S. J.; Müller, P. *Organometallics* **2013**, *32*, 5256.

(9) Forrest, W. P.; Axtell, J. C.; Schrock, R. R. *Organometallics* **2014**, *33*, 2313.

(10) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112* , 8378.

(11) Schrock, R. R. *Acc. Chem. Res.* **2014**, *47*, 2457.

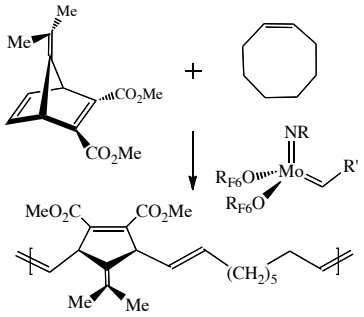
(12) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831.

(13) (a) Schrock, R. R.; Lee, J.-K.; O'Dell, R.; Oskam, J. H. *Macromolecules* **1995**, *28*, 5933. (b) Feast, W. J.; Gibson, V. C.; Ivin, K. J.; Kenwright, A. M.; Khosravi, E. *J. Mol. Catal.* **1994**, *90*, 87. (c) Feast, W. J.; Gibson, V. C.; Ivin, K. J.; Kenwright, A. M.; Khosravi, E. *J. Chem. Soc., Chem. Commun.* **1994**, 1399.

(14) Hoops, S.; Sahle, S.; Gauges, R.; Lee, C.; Pahle, J.; Simus, N.; Singhal, M.; Xu, L.; Mendes, P.; Kummer, U. *Bioinformatics* **2006**, *22*, 3067.

(15) (a) Christianson, M. D.; Tan, E. H. P.; Landis, C. R. *J. Am. Chem. Soc.* **2010**, *132*, 11461. (b) Moscato, B. M.; Zhu, B.; Landis, C. R. *Organometallics* **2012**, *31*, 2097. (c) Keitz, B. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 16277. (d) Watkins, A. L.; Landis, C. R. *J. Am. Chem. Soc.* **2010**, *132*, 10306.

TOC



Supporting Information for

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

Hyangsoo Jeong,[‡] Jeremy M. John,[‡] Richard R. Schrock,[‡*] Amir H. Hoveyda[†]

[‡]Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

[†]Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467

RECEIVED DATE (automatically inserted by publisher); rrs@mit.edu

Table of Contents

Experimental section

General considerations S4

Polymer syntheses and characterization S5 – S26

Figure S1. ^{1}H NMR spectrum of *trans*-poly[**A**-*alt*-**B**] by catalyst **1**

Figure S2. ^{13}C NMR spectrum of *trans*-poly[**A**-*alt*-**B**] by catalyst **1**

Figure S3. ^{1}H–^{1}H gCOSY spectrum of *trans*-poly[**A**-*alt*-**B**] by catalyst **1**

Figure S4. IR spectrum of *trans*-poly[**A**-*alt*-**B**] by catalyst **1**

Figure S5. ^{1}H NMR spectrum of *trans*-poly[**A**-*alt*-**B'**] by catalyst **1**

Figure S6. ^{13}C NMR spectrum of *trans*-poly[**A**-*alt*-**B'**] by catalyst **1**

Figure S7. ^{1}H–^{1}H gCOSY spectrum of *trans*-poly[**A**-*alt*-**B'**] by catalyst **1**

Figure S8. IR spectrum of *trans*-poly[**A**-*alt*-**B'**] by catalyst **1**

Figure S9. ^{1}H NMR spectrum of *trans*-poly[**A'**-*alt*-**B'**] by catalyst **1**

Figure S10. ^{13}C NMR spectrum of *trans*-poly[**A'**-*alt*-**B'**] by catalyst **1**

Figure S11. ^{1}H–^{1}H gCOSY spectrum of *trans*-poly[**A'**-*alt*-**B'**] by catalyst **1**

Figure S12. IR spectrum of *trans*-poly[**A'**-*alt*-**B'**] by catalyst **1**

Figure S13. ^{1}H NMR spectrum of *trans*-poly[**A'**-*alt*-**B**] by catalyst **1**

Figure S14. ^{13}C NMR spectrum of *trans*-poly[**A'**-*alt*-**B**] by catalyst **1**

Figure S15. ^{1}H–^{1}H gCOSY spectrum of *trans*-poly[**A'**-*alt*-**B**] by catalyst **1**

Figure S16. IR spectrum of *trans*-poly[**A'**-*alt*-**B**] by catalyst **1**

ROMP of *cis*-cycloheptene by catalyst **2** and *cis*-cyclooctene by catalyst **1**

Comparison between four *trans* copolymers formed from **1** and **2** S26 – S27

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 $CDCl_3$.

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 $CDCl_3$.

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 $CDCl_3$.

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 product of catalyst **2** with **B'** S27 – S29

Figure S21. ^{1}H NMR spectrum of the first insertion product between **2** and **B'**

Figure S22. ^{19}F NMR spectrum of the first insertion product between **2** and **B'**

Figure S23. ^{13}C NMR spectrum of the first insertion product between **2** and **B'**

Details of Kinetic Experiments I S30 – S37

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 $CDCl_3$

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

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

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

Details of Kinetic Experiments II S38 – S44

Rate of consumption of **A'** by the first insertion complex **2** with **B'** in toluene-d_8

Rate of consumption of **B'** by **2** in toluene-d_8

Observation of *anti*-**MB**$_{cis}$ and *syn*-**MB**$_{cis}$ by catalyst **1** S45 – S46

Photolysis of **1** and addition of **B** by varying the temperature S46 – S49

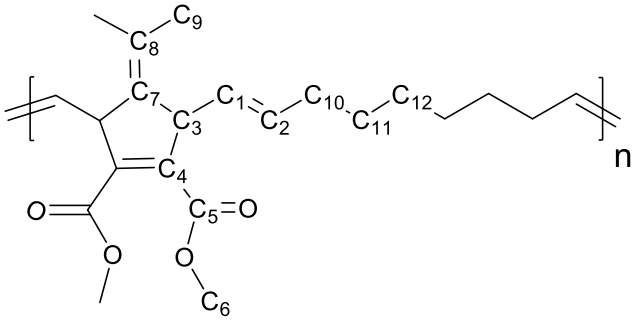
Figure S24. ^{1}H–^{1}H gCOSY spectrum of the olefinic region of *syn*-**MB**$_{cis}$ and *syn*-**MB**$_{trans}$ at -10 °C

References S50

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}.

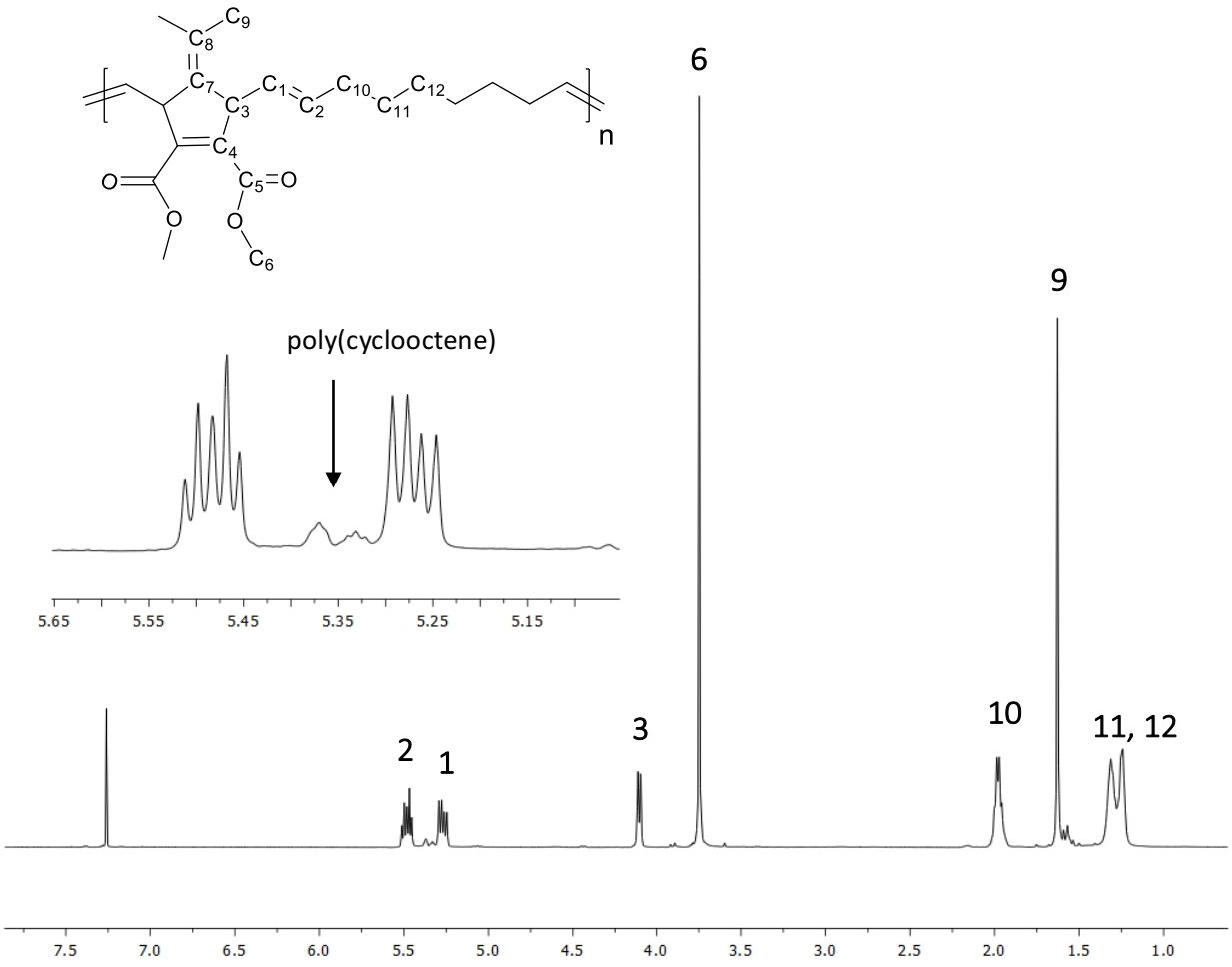


Figure S1. ^{1}H NMR spectrum of *trans*-poly[**A**-*alt*-**B**] (in $CDCl_3$, 500 MHz).

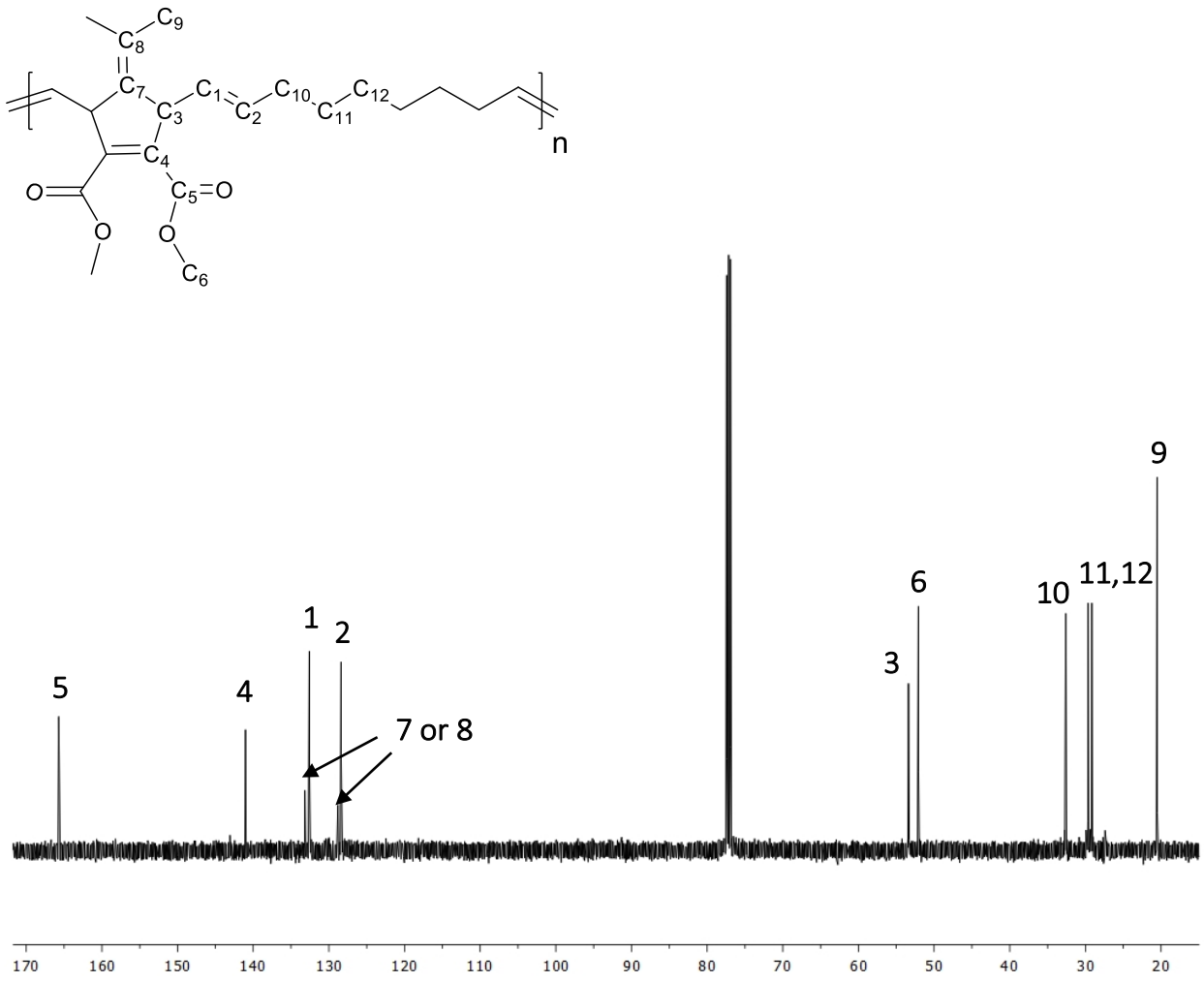


Figure S2. ^{13}C NMR spectrum of *trans*-poly[**A**-*alt*-**B**] (in $CDCl_3$, 125 MHz).

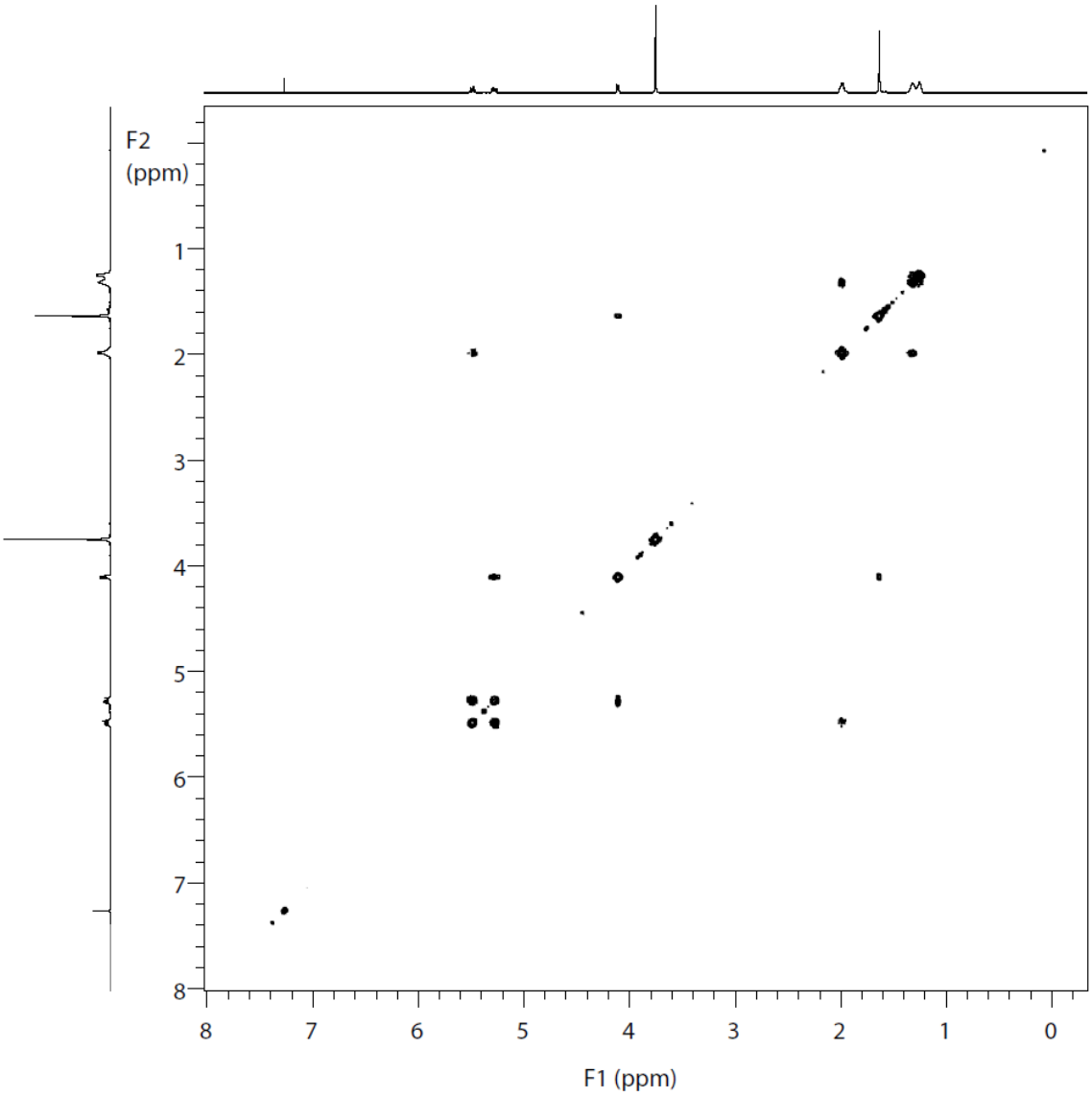


Figure S3. ^{1}H–^{1}H gCOSY spectrum of *trans*-poly[**A**-*alt*-**B**] (in $CDCl_3$, 500 MHz).

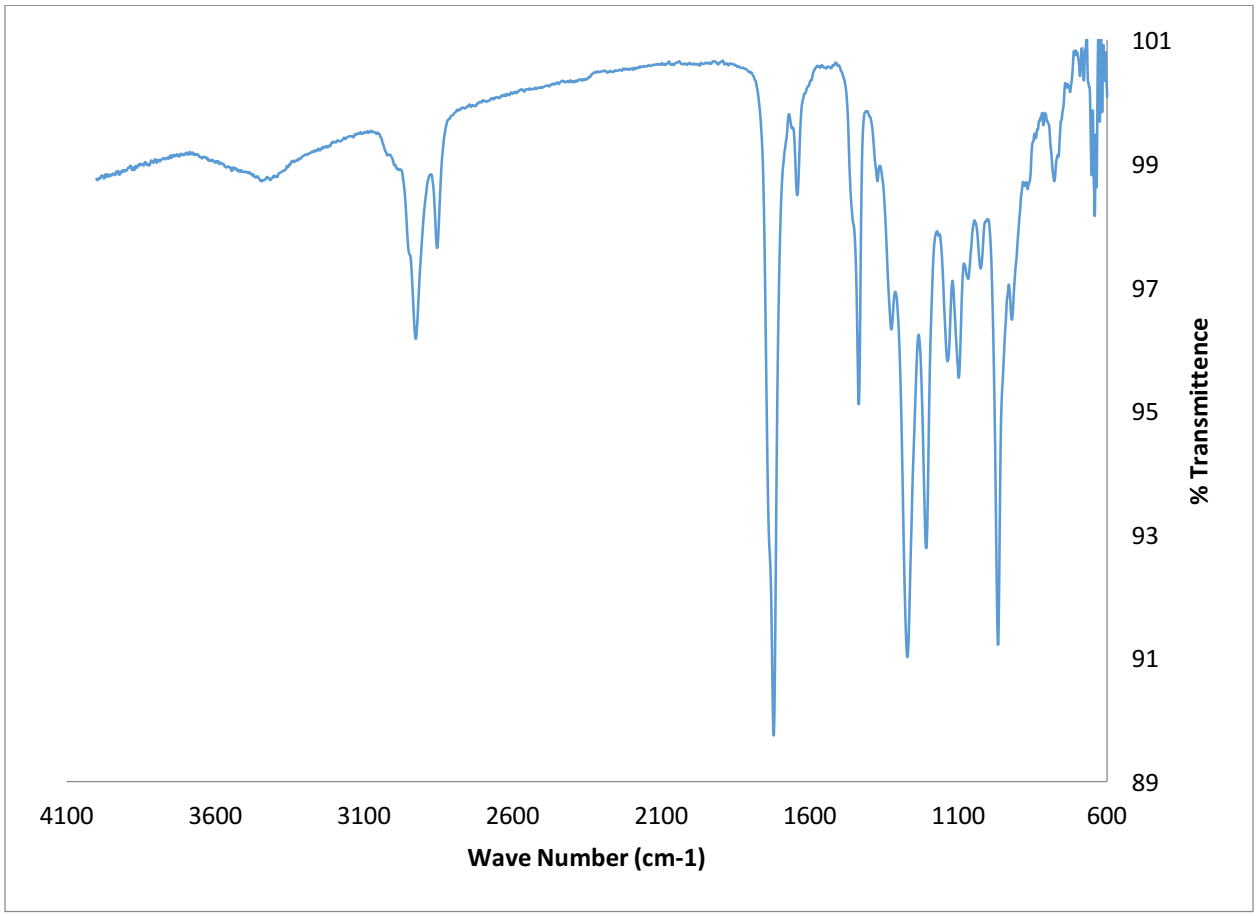
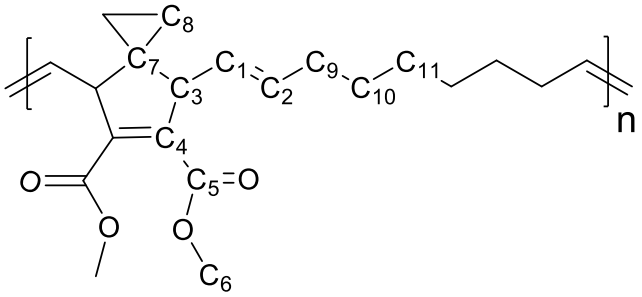


Figure S4. IR spectrum of *trans*-poly[**A**-*alt*-**B**] (neat).

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}.

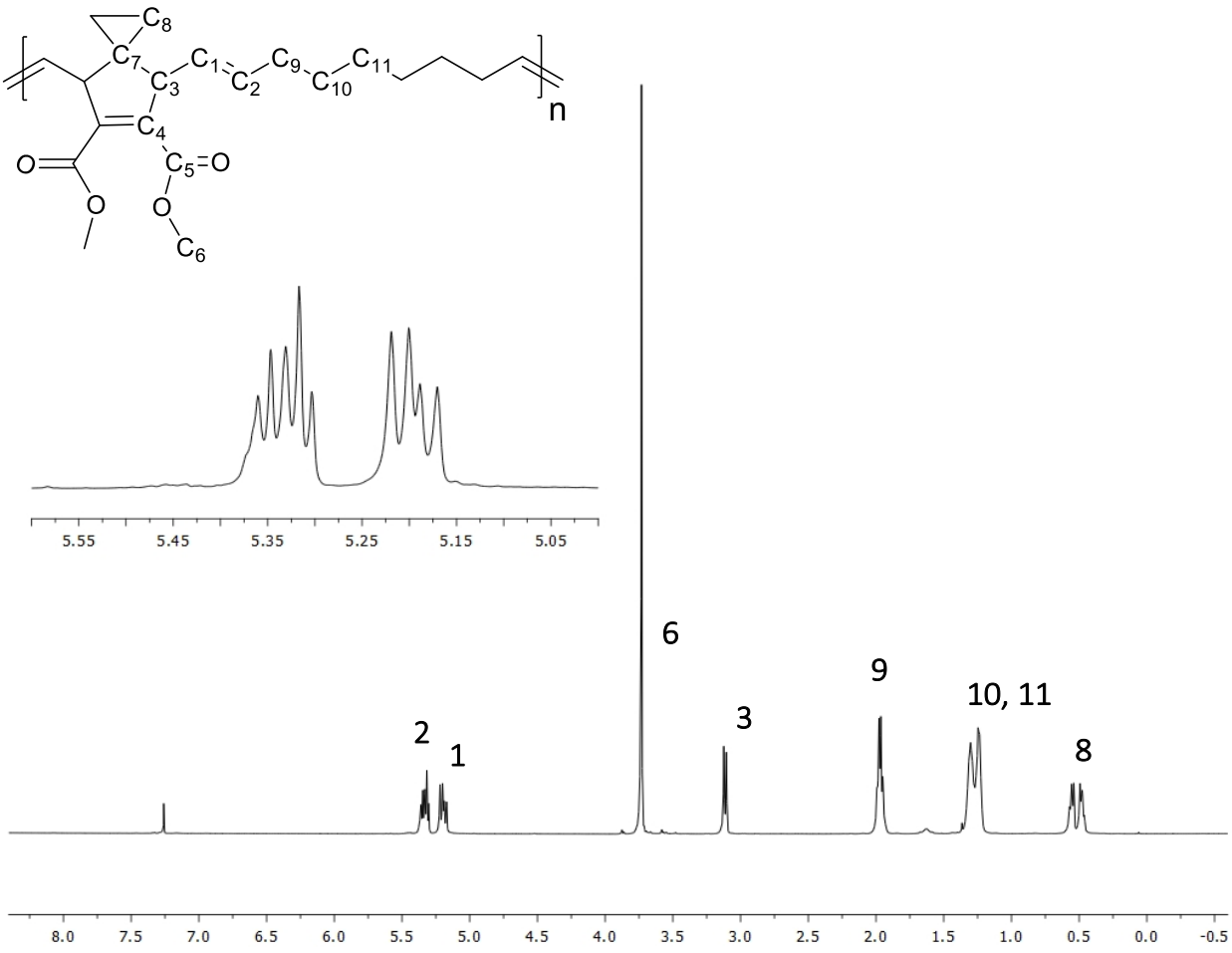


Figure S5. ^{1}H NMR spectrum of *trans*-poly[**A**-*alt*-**B'**] (in $CDCl_3$, 500 MHz).

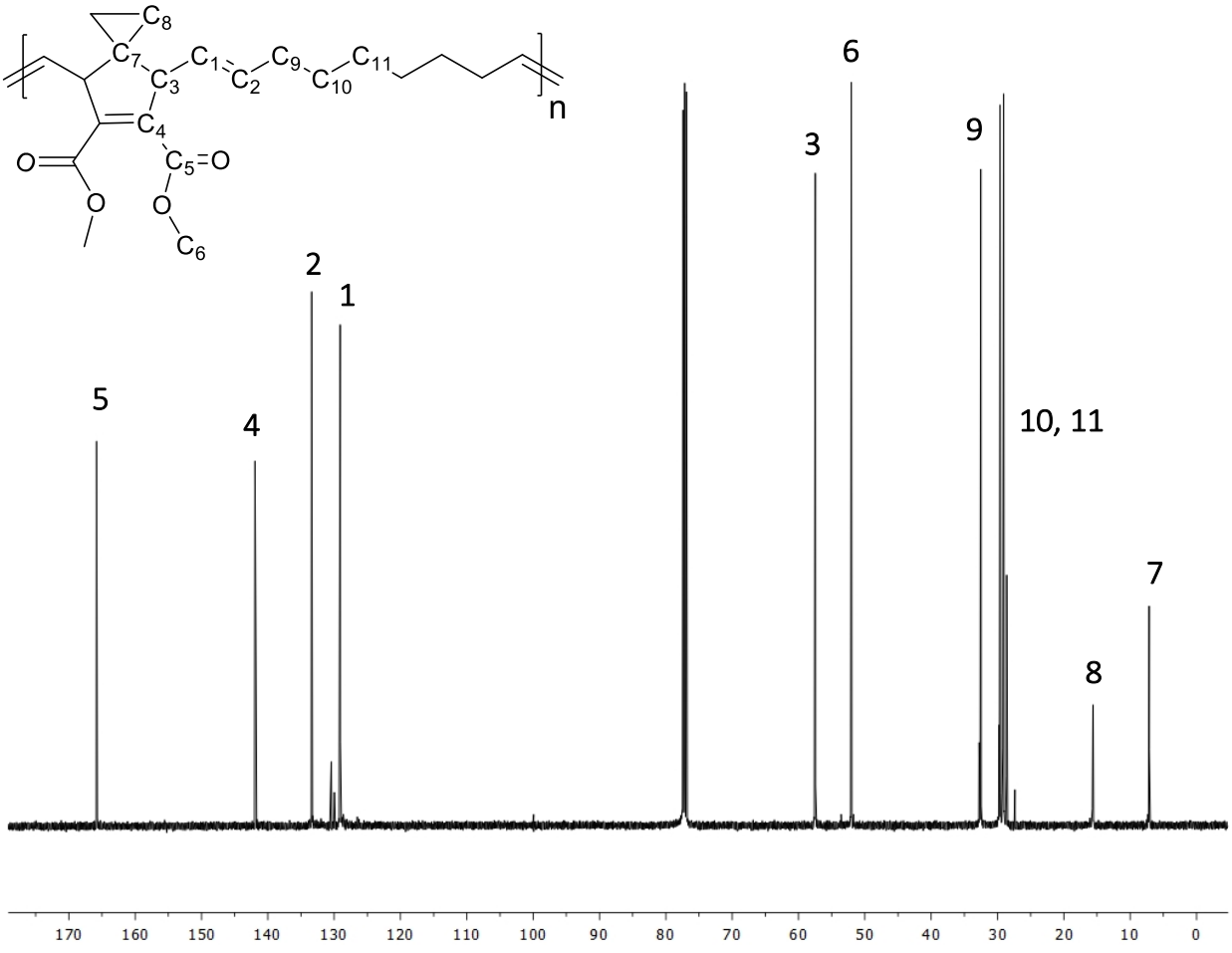


Figure S6. ^{13}C NMR spectrum of *trans*-poly[**A**-*alt*-**B'**] (in $CDCl_3$, 125 MHz).

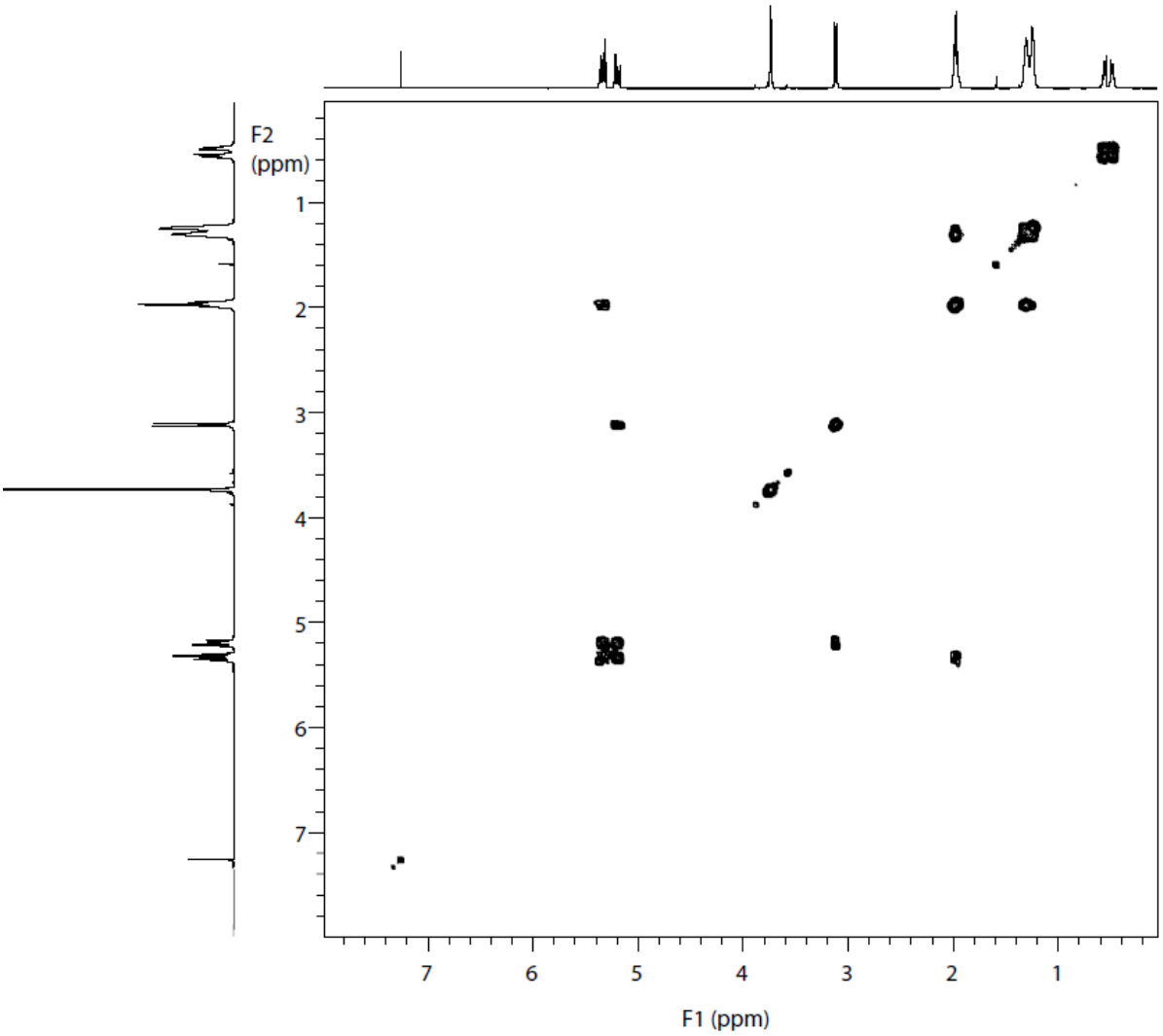


Figure S7. ^{1}H–^{1}H gCOSY spectrum of *trans*-poly[**A**-*alt*-**B'**] (in $CDCl_3$, 500 MHz).

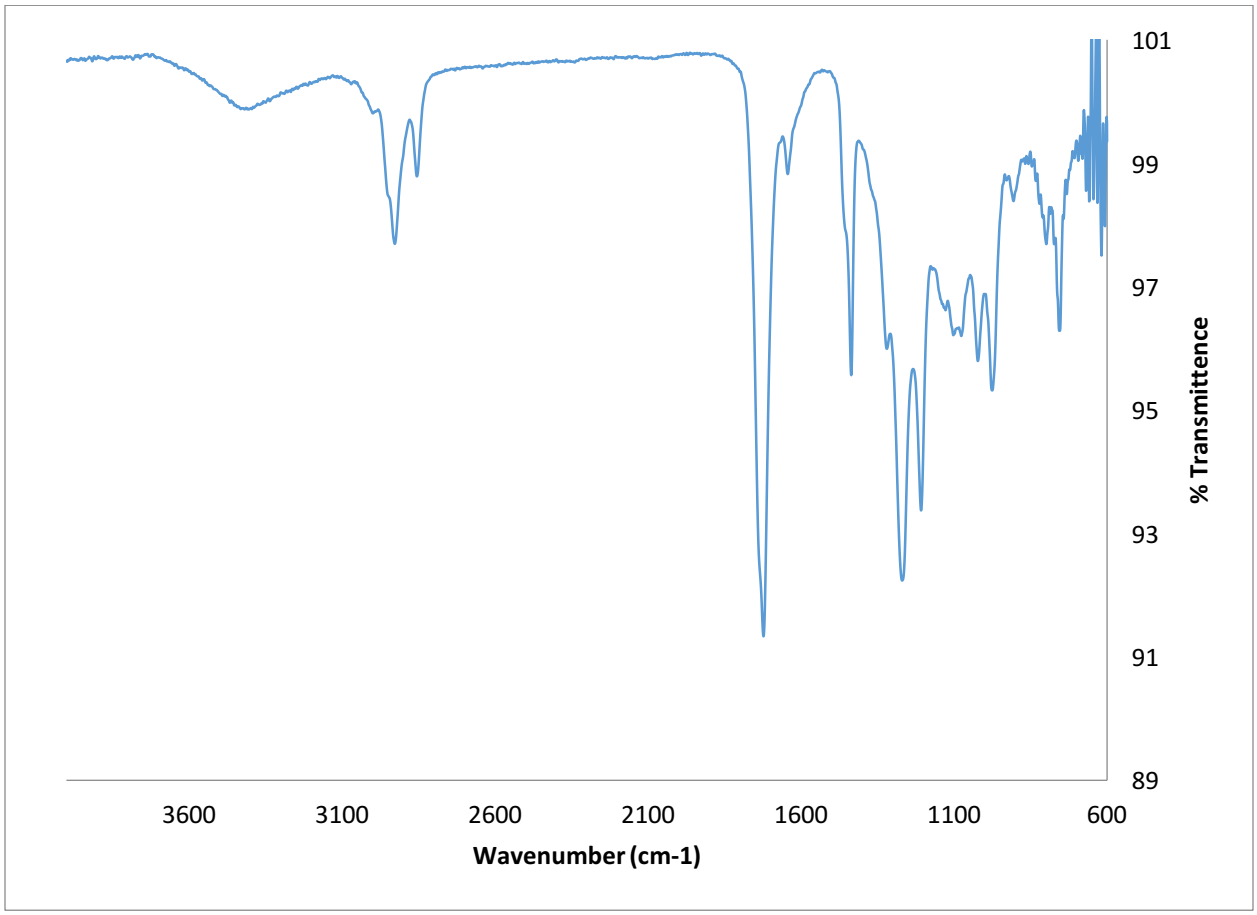
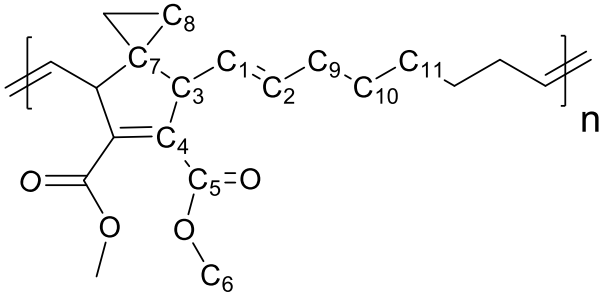


Figure S8. IR spectrum of *trans*-poly[**A**-*alt*-**B'**] (neat).

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}.

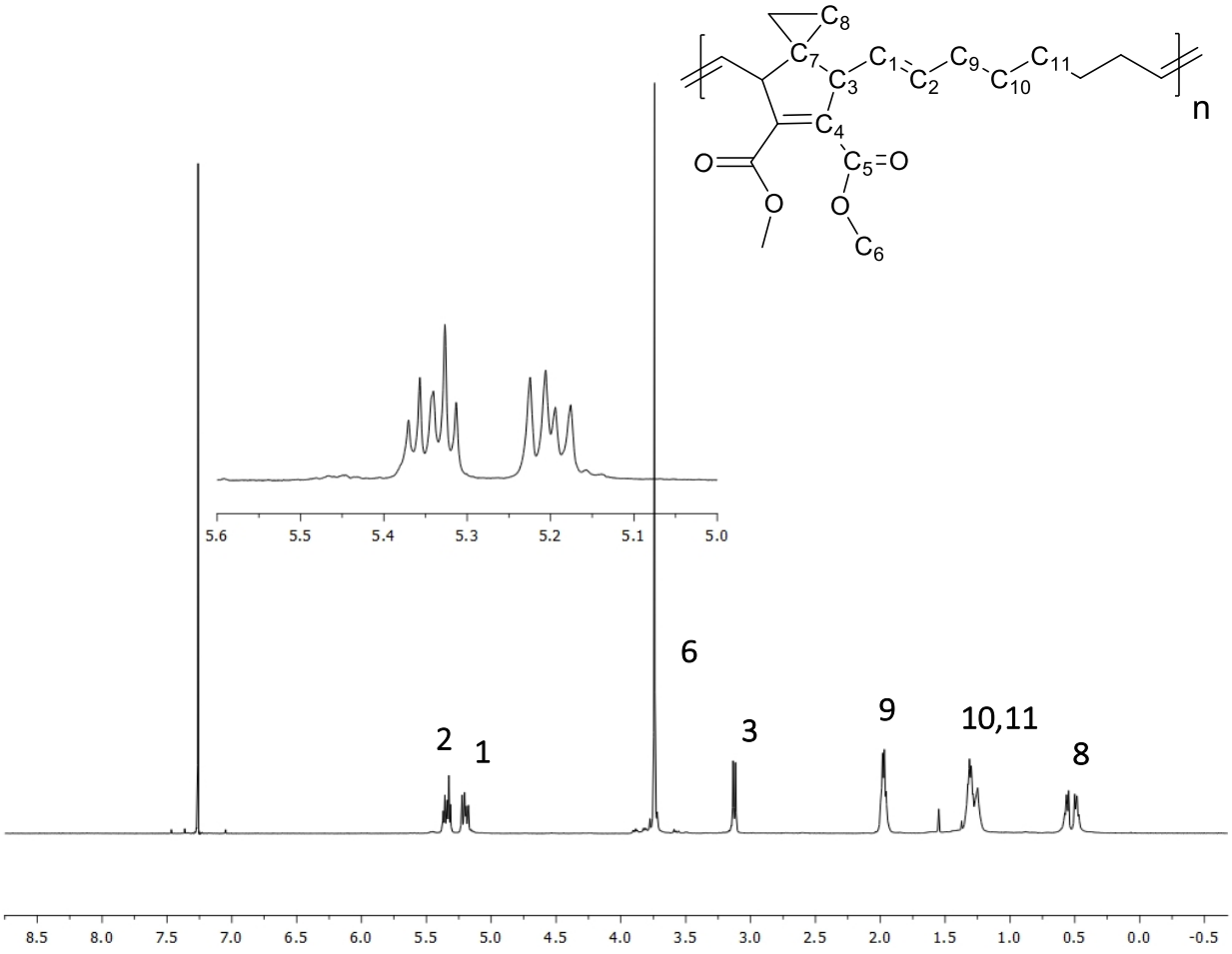


Figure S9. ^{1}H NMR spectrum of *trans*-poly[**A'**-*alt*-**B'**] (in $CDCl_3$, 500 MHz).

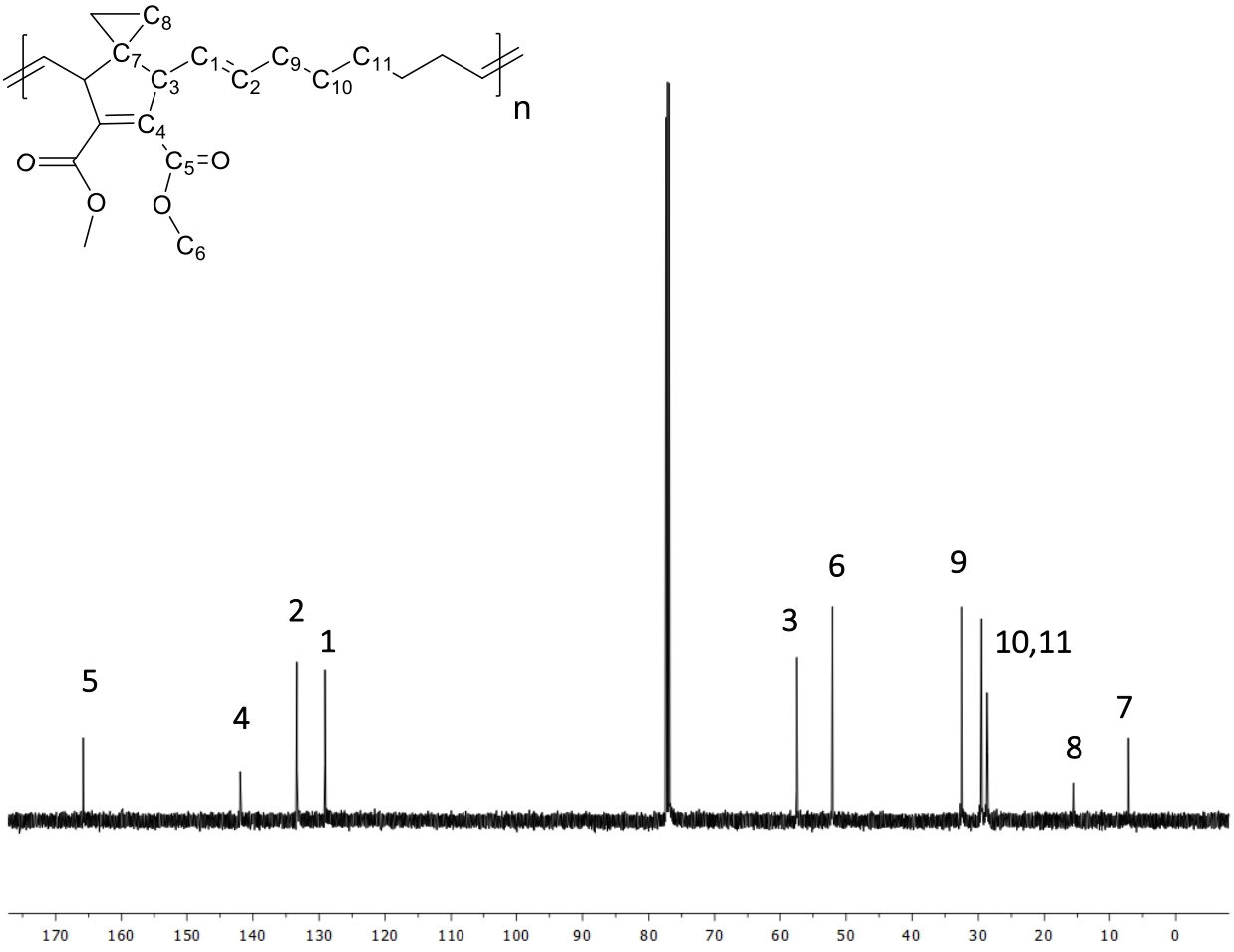


Figure S10. ^{13}C NMR spectrum of *trans*-poly[**A'**-*alt*-**B'**] (in $CDCl_3$, 125 MHz).

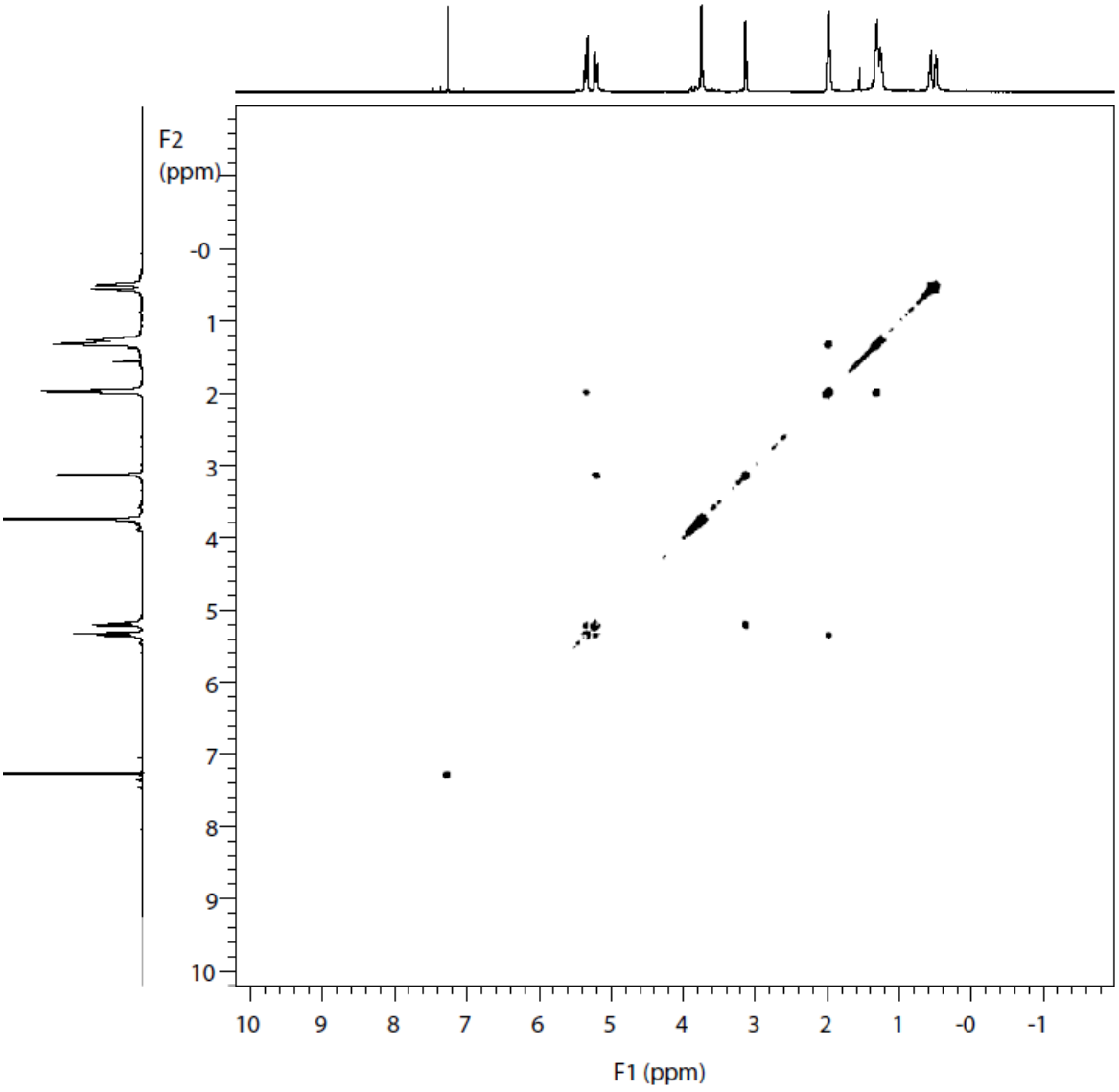


Figure S11. ^{1}H–^{1}H gCOSY spectrum of *trans*-poly[**A'**-*alt*-**B'**] (in $CDCl_3$, 500 MHz).

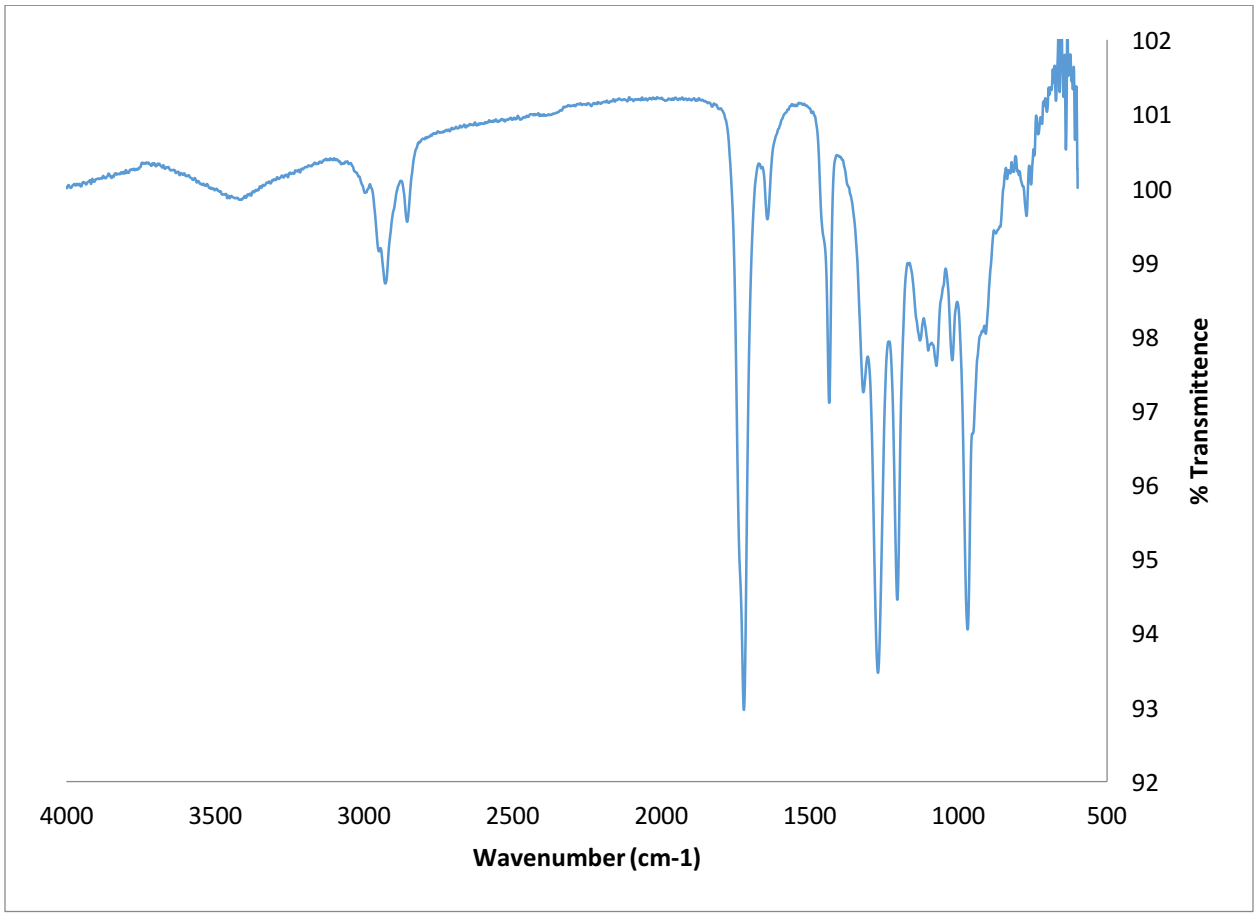
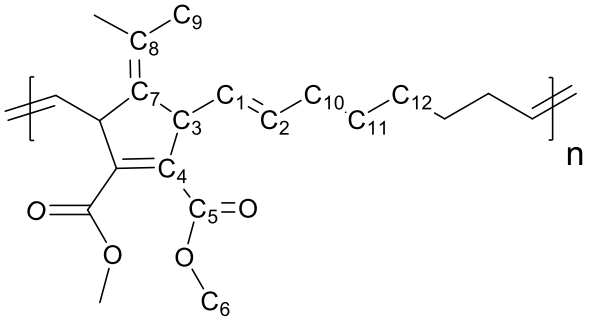


Figure S12. IR spectrum of *trans*-poly[**A'**-*alt*-**B'**] (neat).

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}.

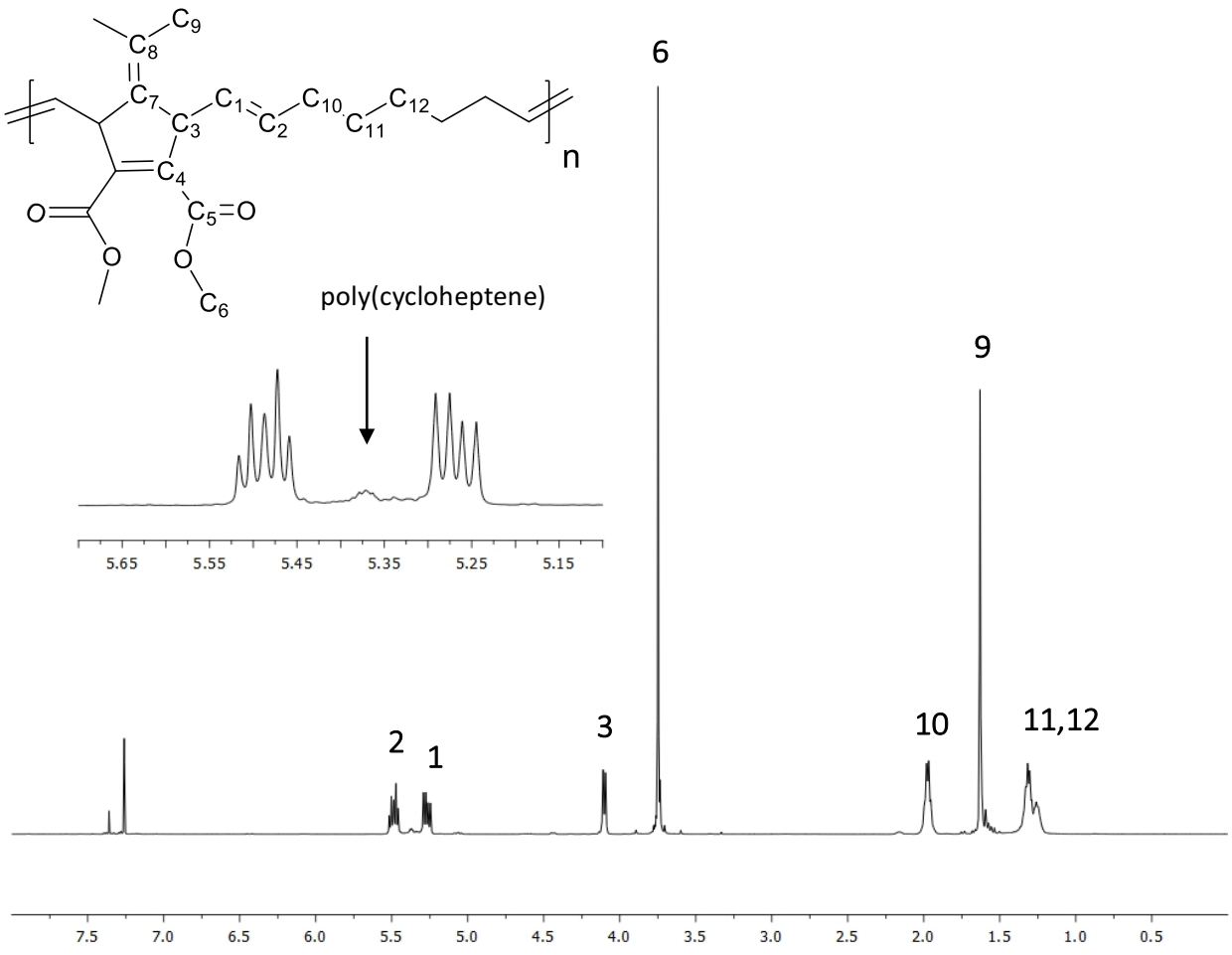


Figure S13. ^{1}H NMR spectrum of *trans*-poly[**A'**-*alt*-**B**] (in $CDCl_3$, 500 MHz).

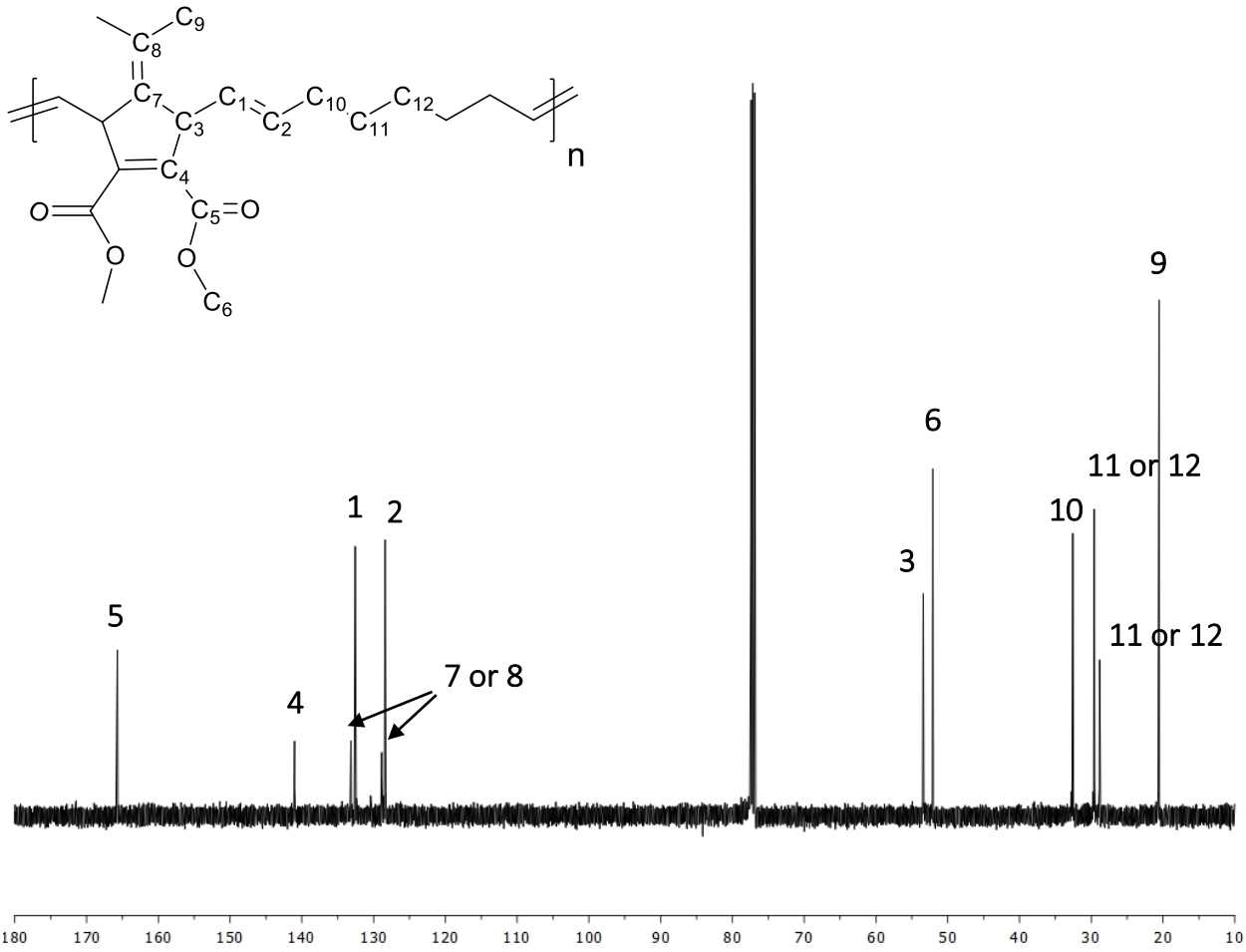


Figure S14. ^{13}C NMR spectrum of *trans*-poly[**A'**-*alt*-**B**] (in $CDCl_3$, 500 MHz).

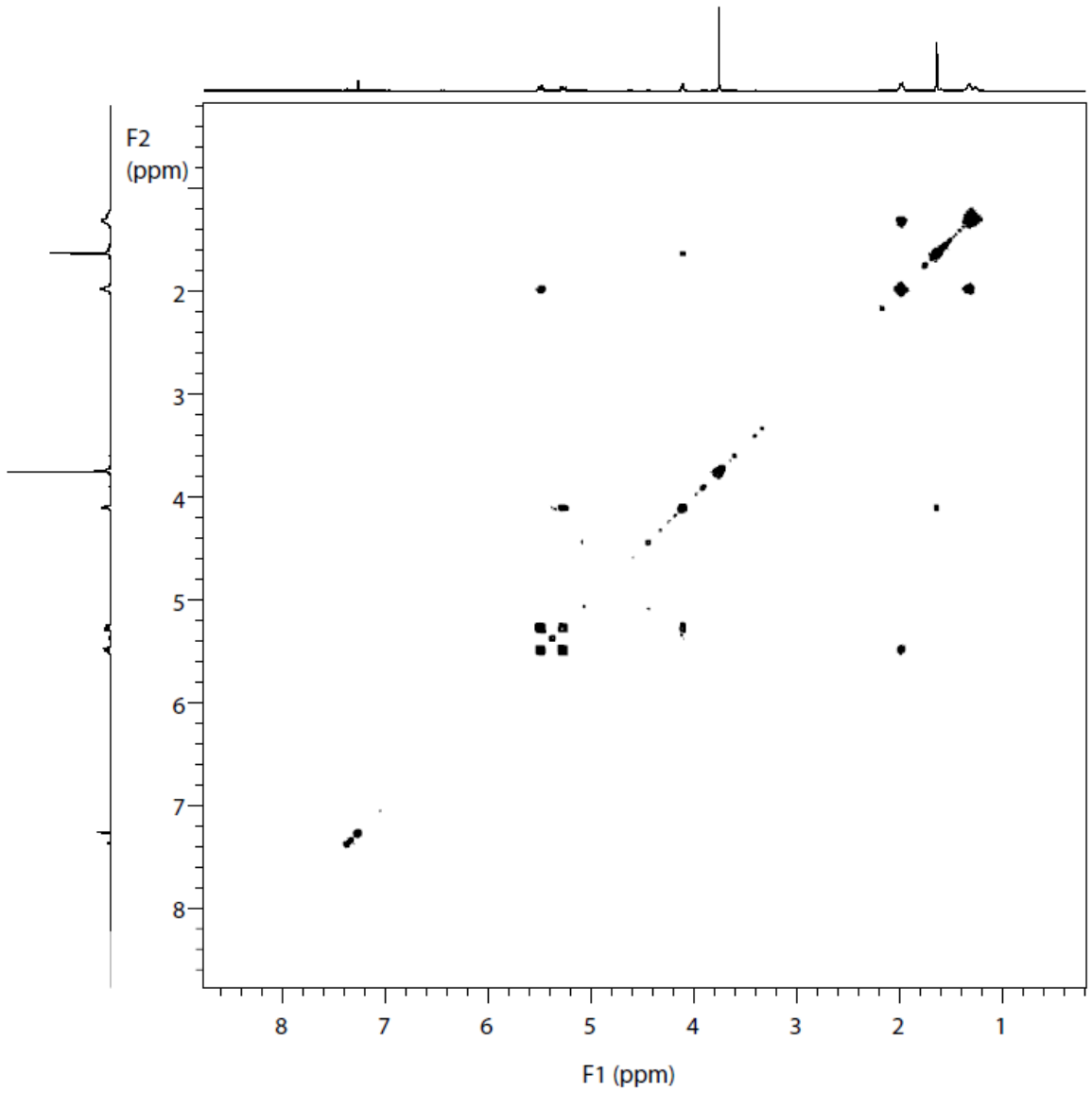


Figure S15. ^{1}H–^{1}H gCOSY spectrum of *trans*-poly[**A'**-*alt*-**B**] (in $CDCl_3$, 500 MHz).

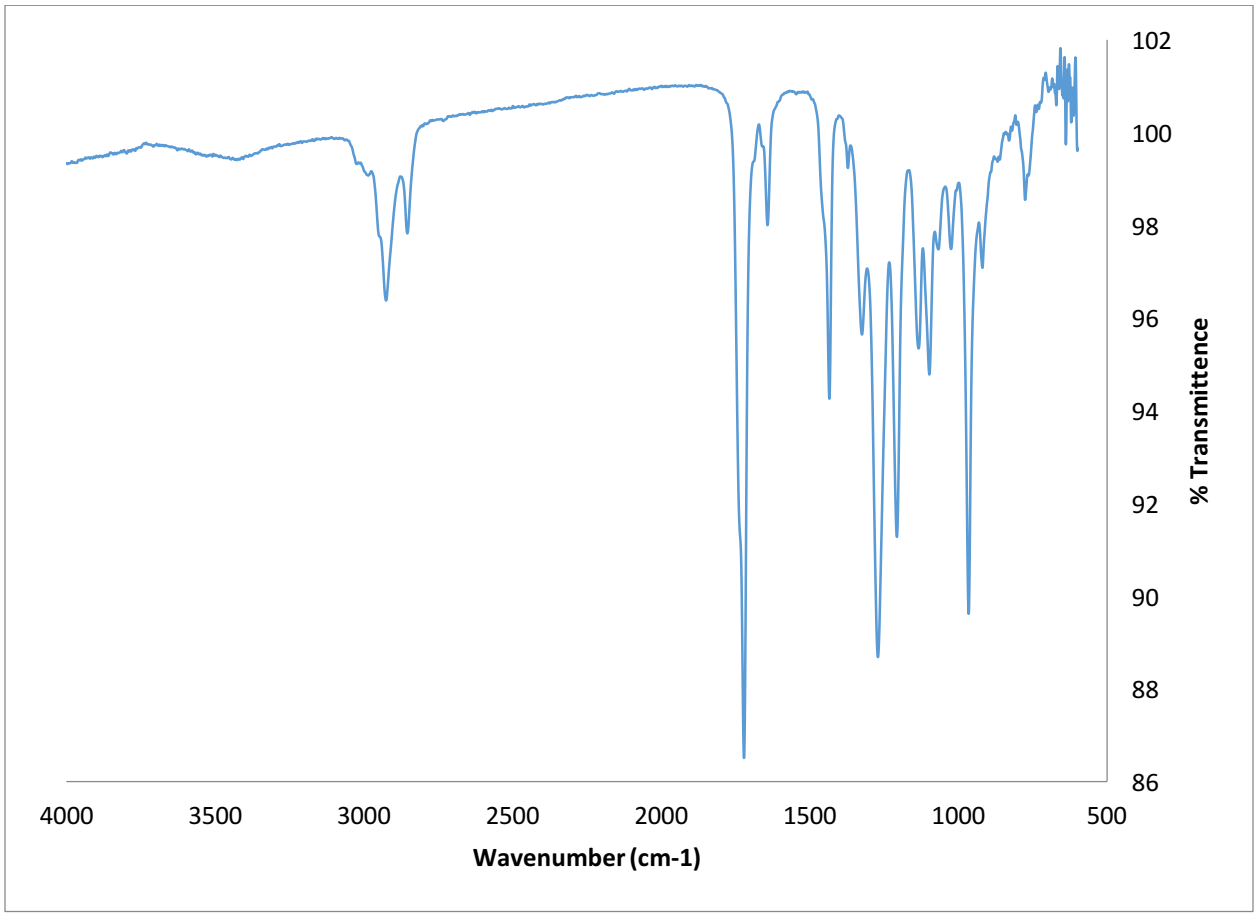


Figure S16. IR spectrum of *trans*-poly[**A'**-*alt*-**B**] (neat).

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**

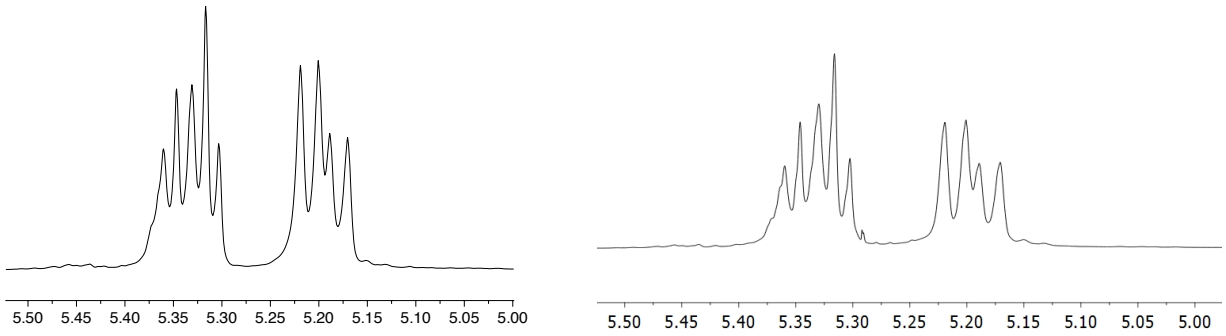


Figure S17. Comparison of the olefinic region ^{1}H NMR spectrum of *trans*-poly(**A**-*alt*-**B'**) formed from **1** (left) and **2** (right) in $CDCl_3$.

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

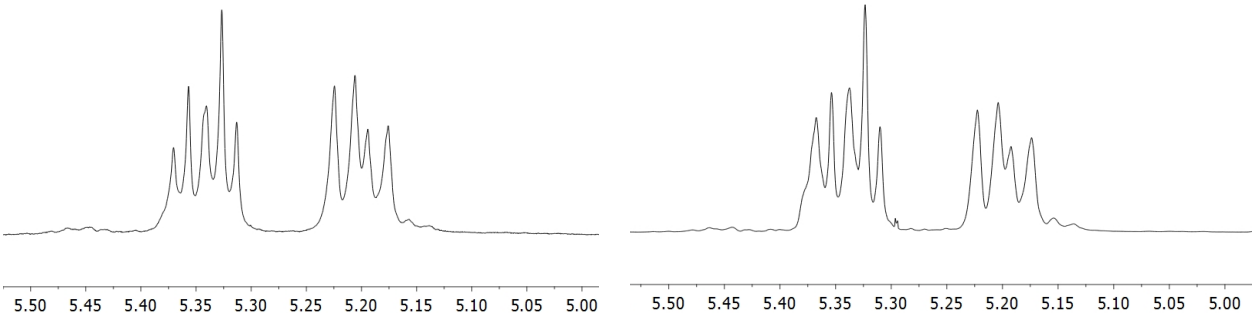


Figure S18. Comparison of the olefinic region ^{1}H NMR spectrum of *trans*-poly(**A'**-*alt*-**B'**) formed from **1** (left) and **2** (right) in $CDCl_3$.

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

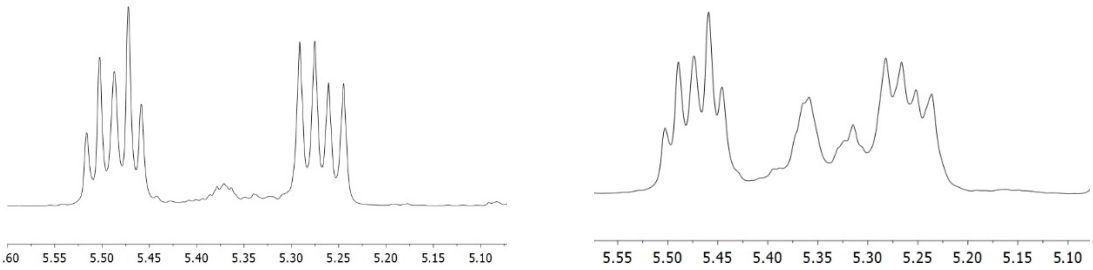


Figure S19. Comparison of the olefinic region ^{1}H NMR spectrum of *trans*-poly(**A'**-*alt*-**B**) formed from **1** (left) and **2** (right) in $CDCl_3$.

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

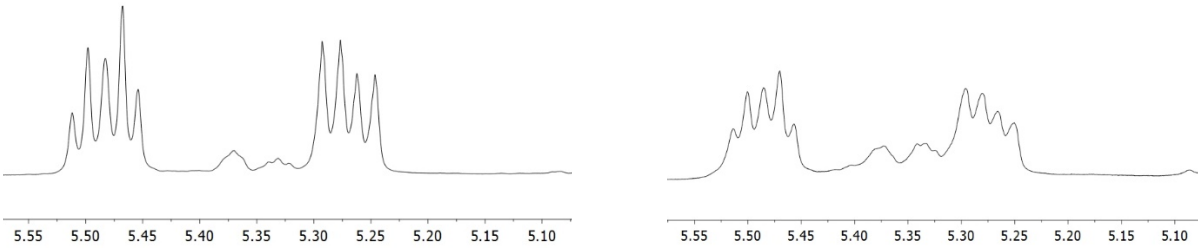


Figure S20. Comparison of the olefinic region ^{1}H NMR spectrum of *trans*-poly(**A**-*alt*-**B**) formed from **1** (left) and **2** (right) in $CDCl_3$.

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}).

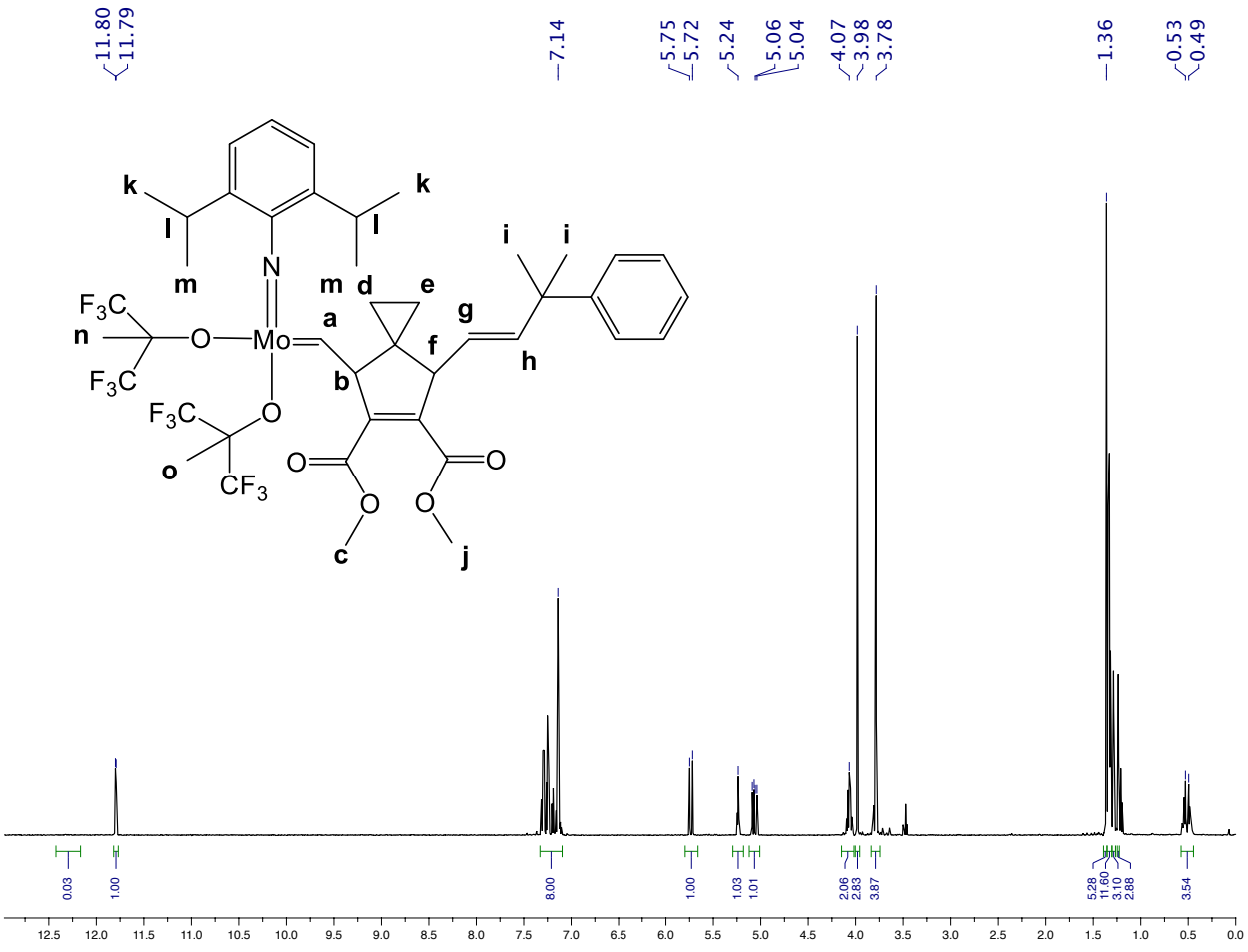


Figure S21. ^{1}H NMR (500.43 MHz) of the first insertion product between **2** and **B'** in $CDCl_3$

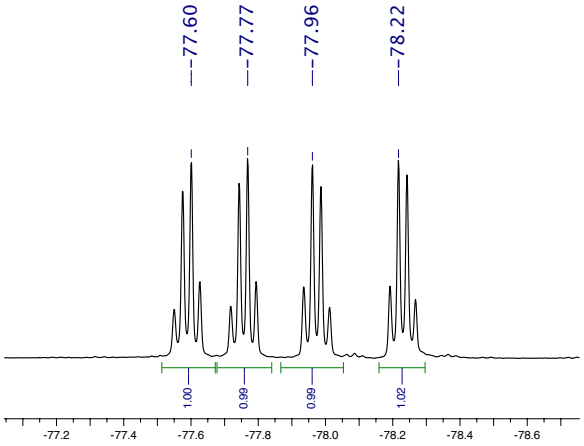


Figure S22. The ^{19}F NMR of the first insertion complex between **2** and **B'** in $CDCl_3$

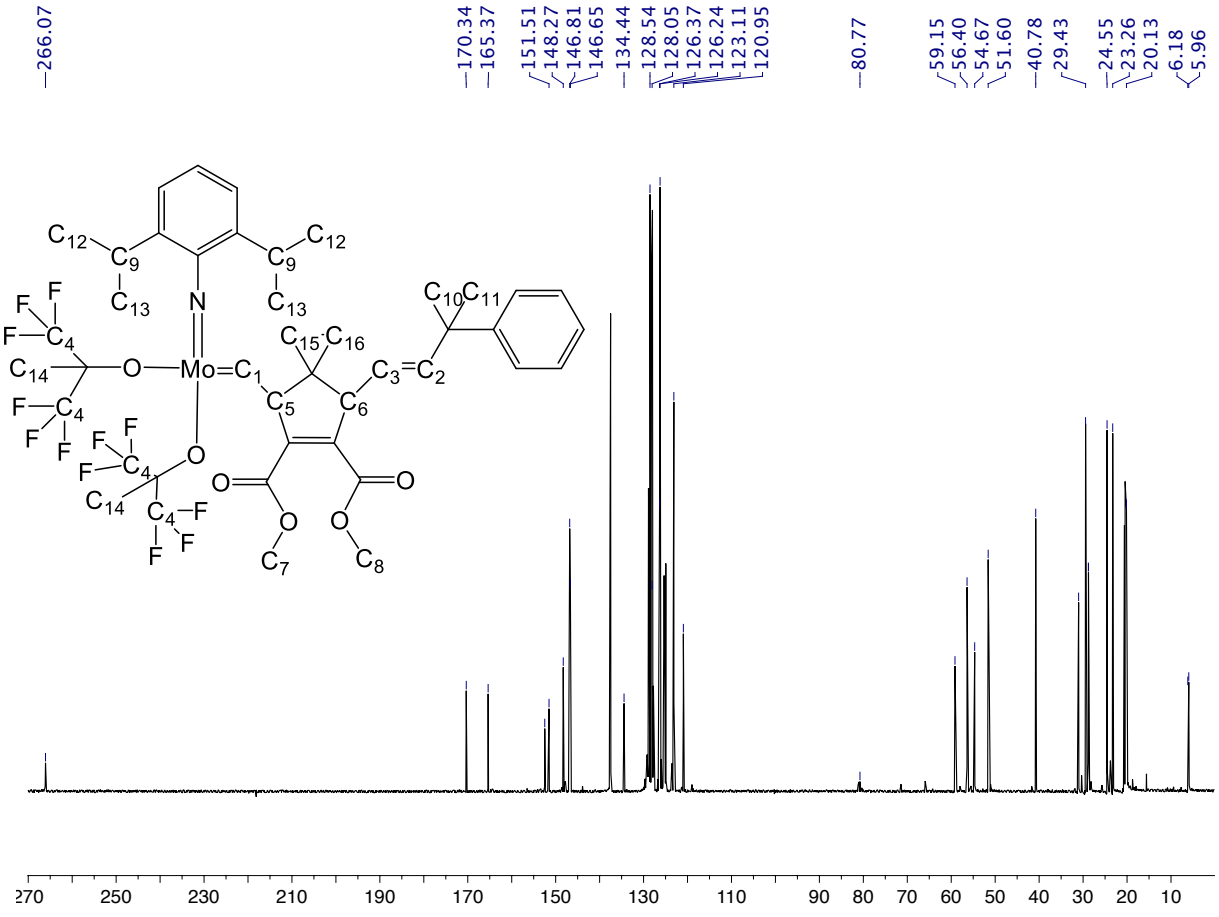
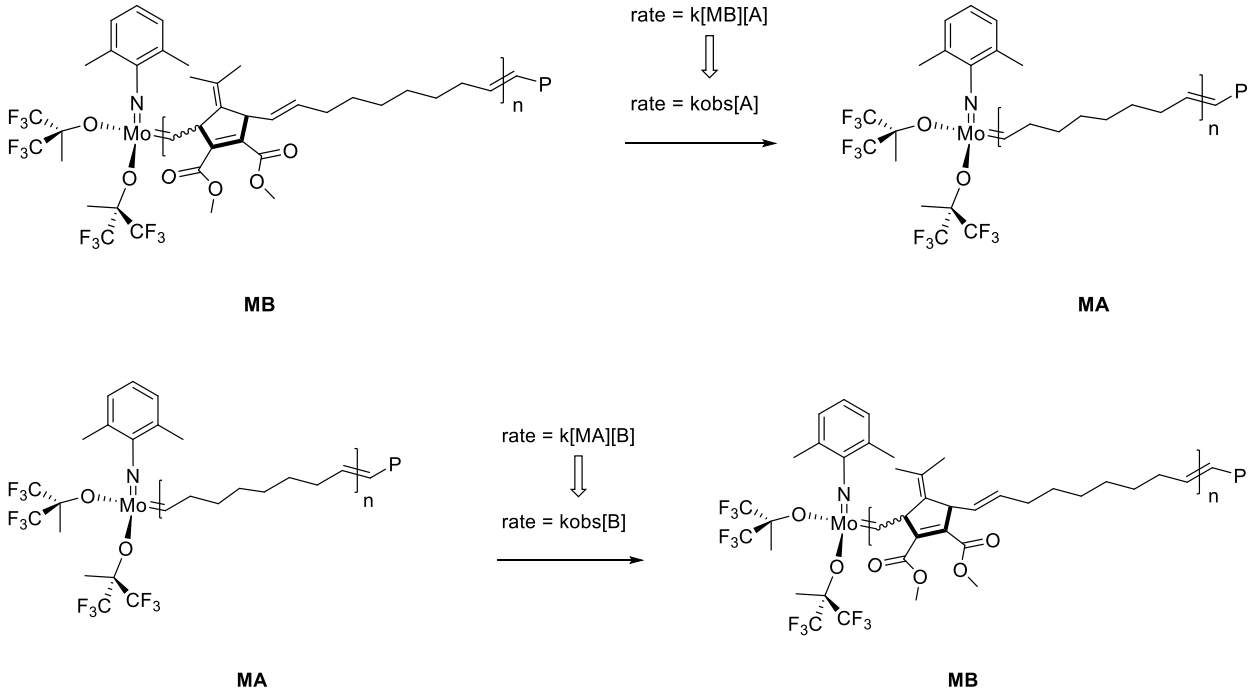


Figure S23. ^{13}C NMR spectrum (125.79 MHz) of first insertion complex between **2** and **B'** in toluene-d_8.

Details of Kinetic Experiments I



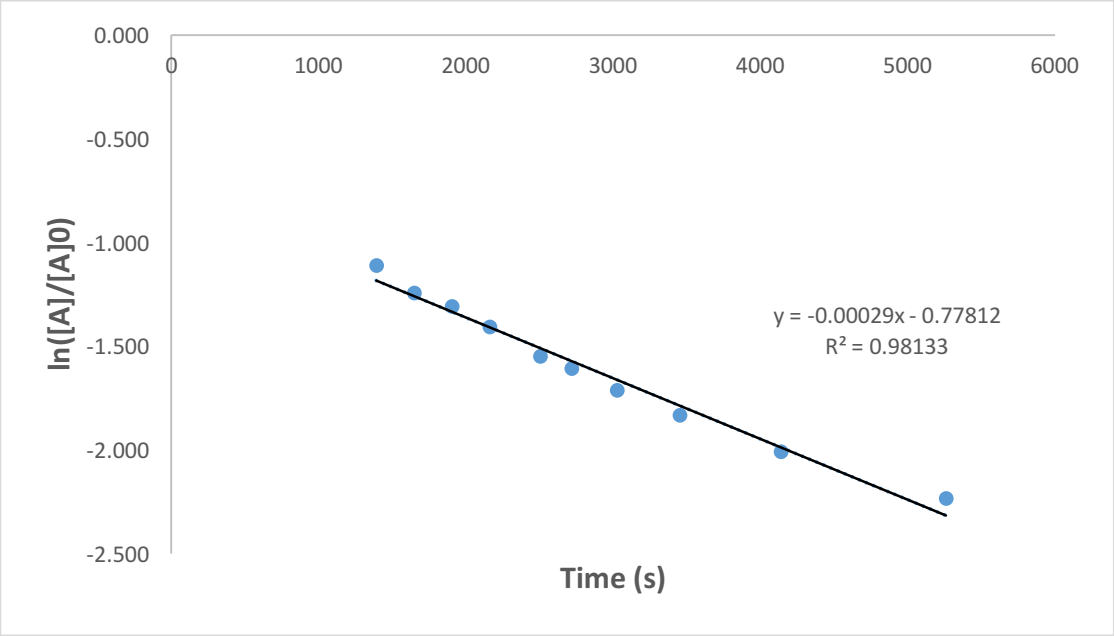
Combination of A/B/Cat	Equivalents A/B/Cat	Solvent	Concentration of Monomer (M)	k_{obs} (A) (x 10^{-5} s^{-1})	k_{obs} (B) (x 10^{-5} s^{-1})
A/B/1	50/50/1	$CDCl_3$	0.12	29	20
A'/B'/1	50/50/1	Toluene-d_8	0.20	23	16
A'/B'/1	100/100/1	Toluene-d_8	0.20	26	16
A'/B'/2	50/50/1	Toluene-d_8	0.20	3.1	2.7
A/B/1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

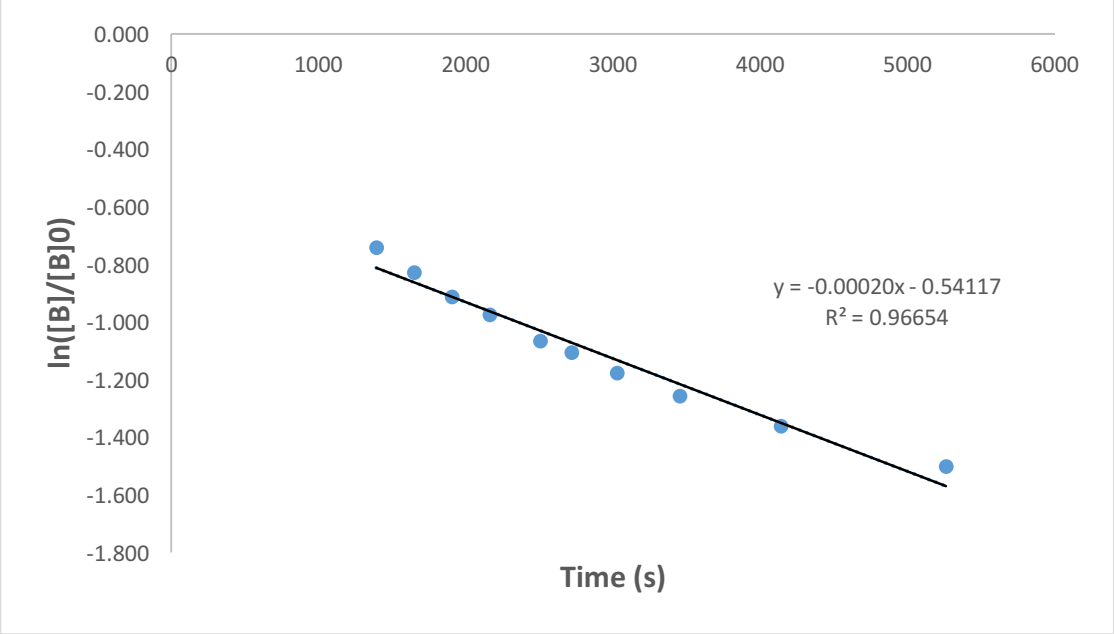
Rate of consumption of A and B by catalyst 1 in $CDCl_3$.

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}

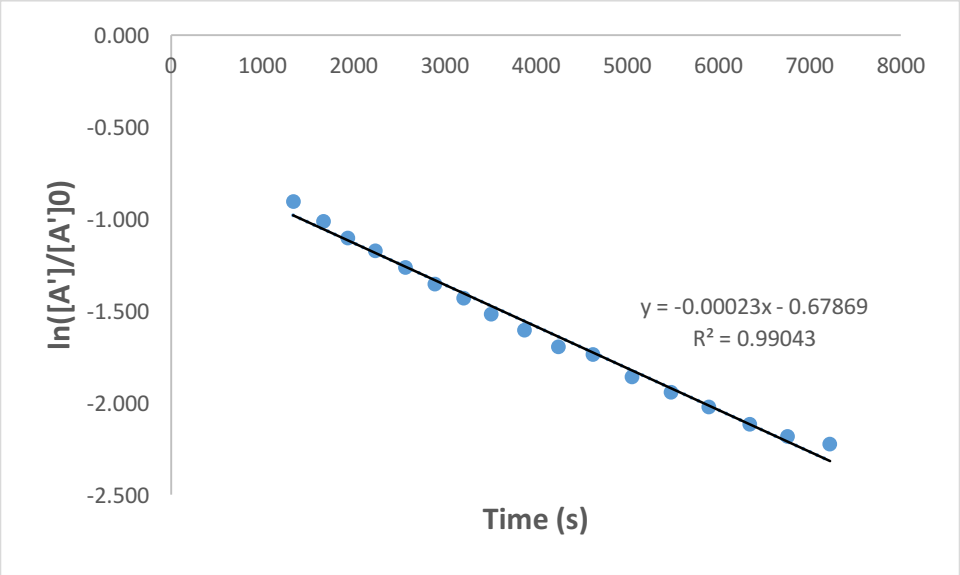


Slope (k_{obs}) = 2.0 x 10^{-4} s^{-1}

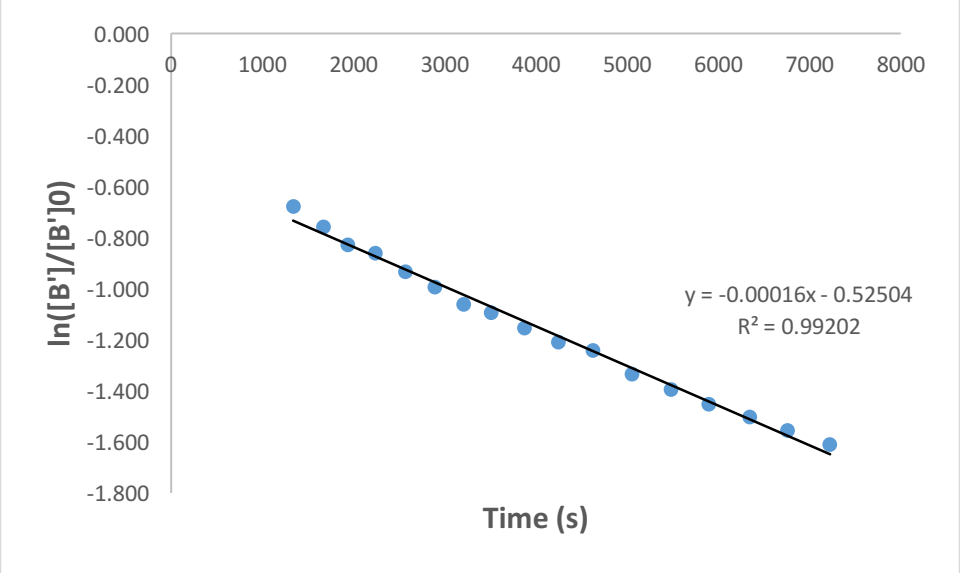
Rate of consumption of A' and B' by catalyst 1 in toluene-d_8.

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}



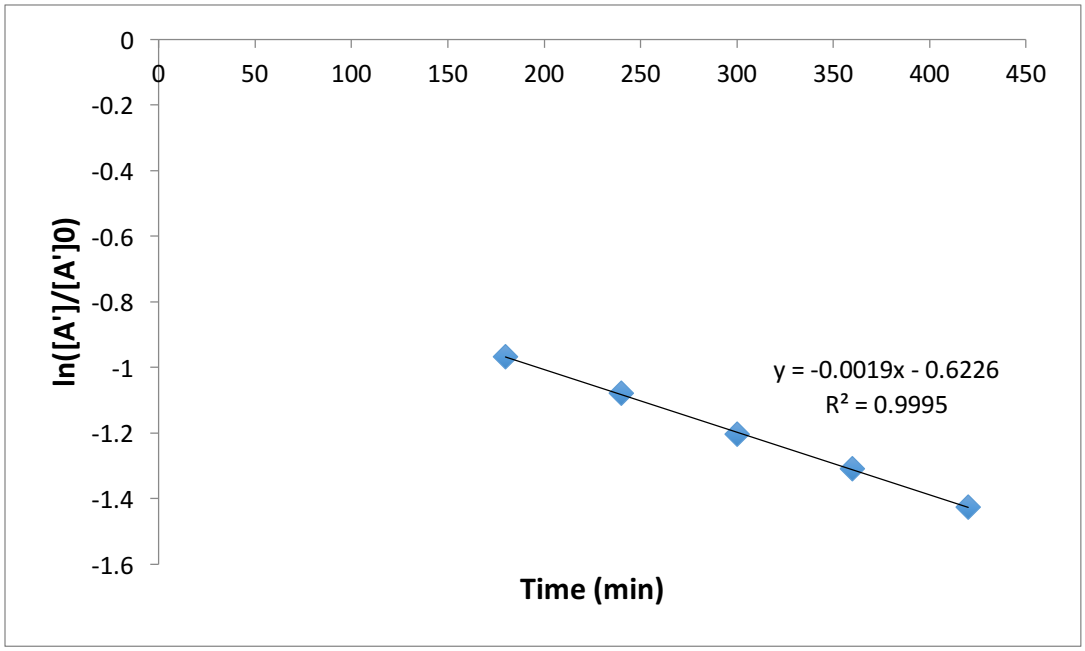
Slope (kobs) = 1.6 x 10^{-4} s^{-1}

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

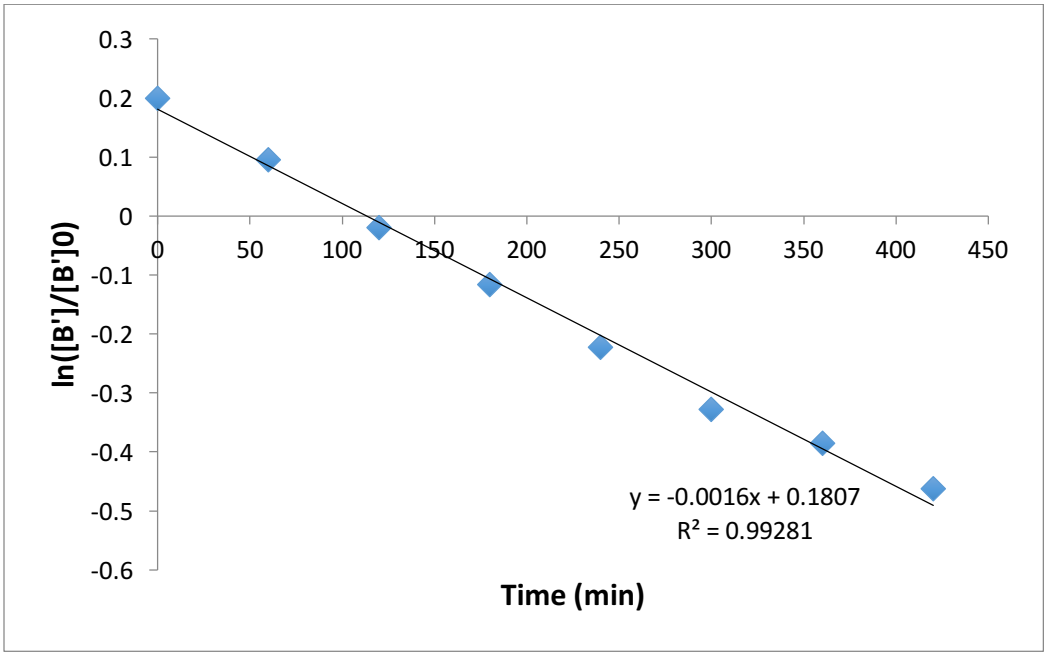
In a J-Young NMR tube, 50 equivalents of **B'** (0.119 mmol, 27.8 mg) and 50 equivalents of **A'** (0.119 mmol, 14 μL) in 0.6 mL of toluene-d_8 were added and consumption of each monomer were monitored over 1 half live.

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 x 10^{-5} s^{-1}

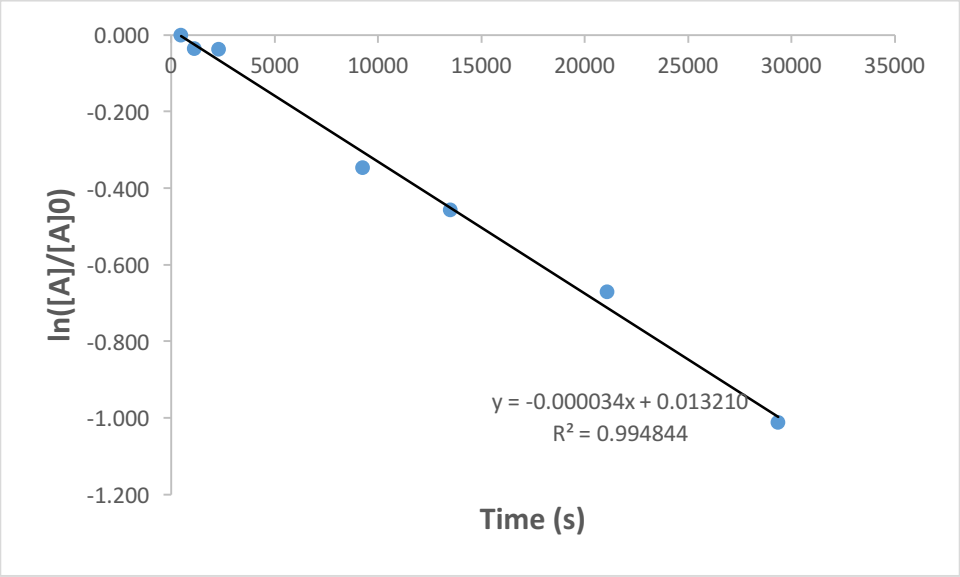


Slope (kobs) = 2.7×10^{-5} s^{-1}

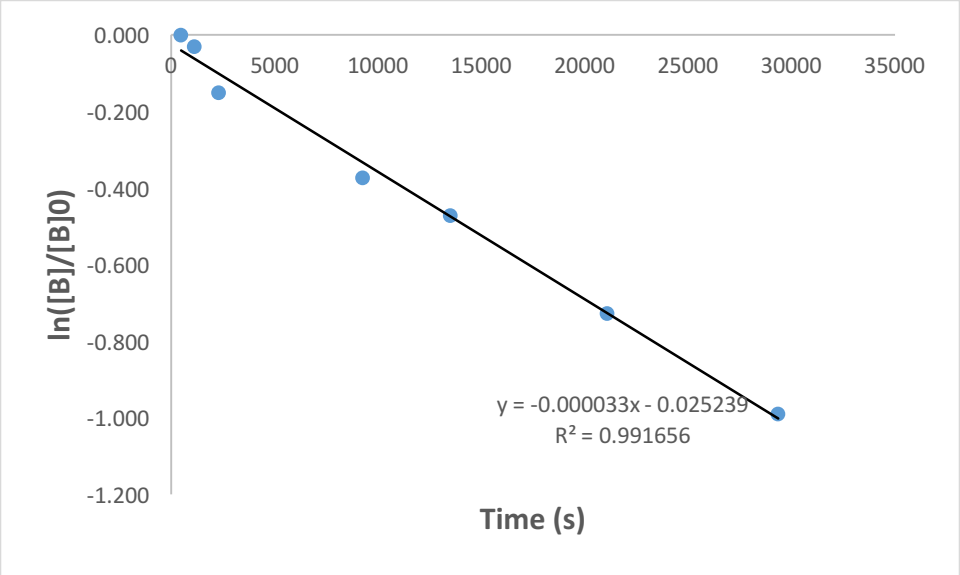
Rate of consumption of A and B by catalyst 1 in THF-d_8.

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}



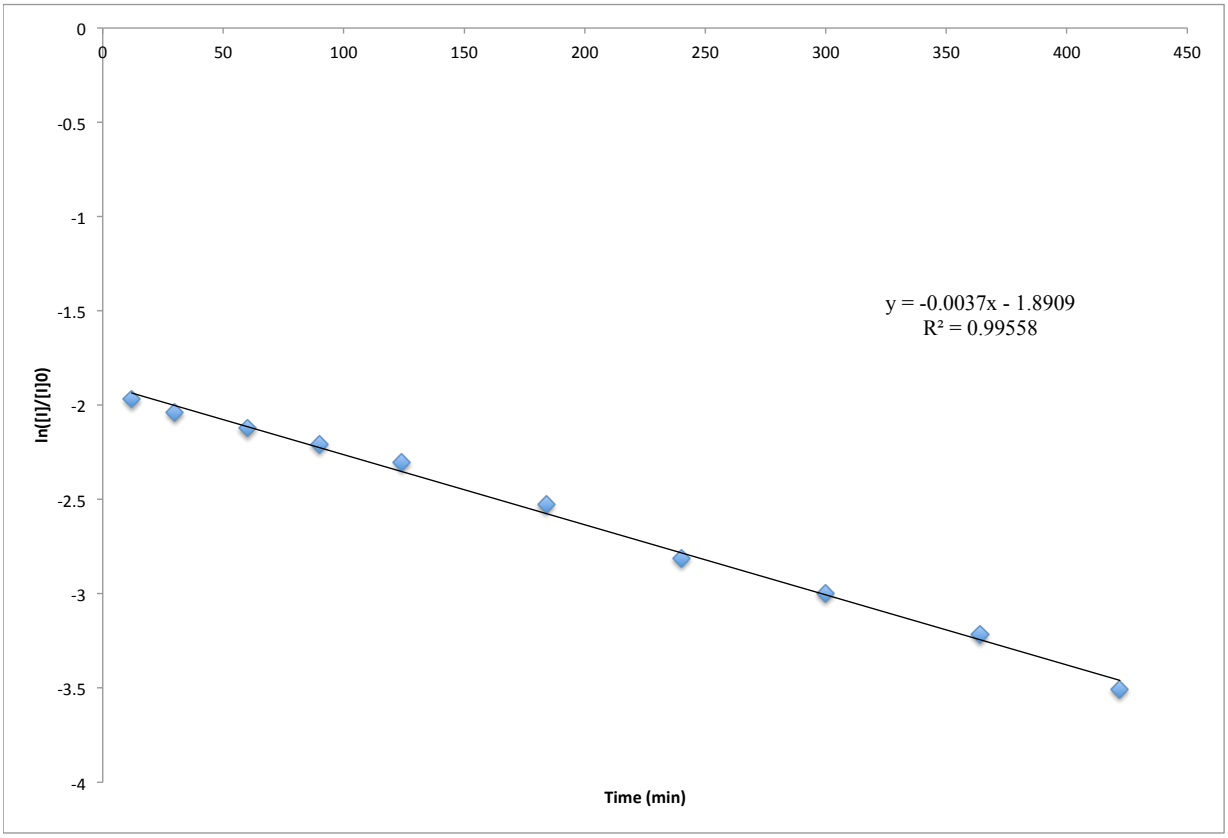
Slope (k_{obs}) = 3.3 x 10^{-5} s^{-1}

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

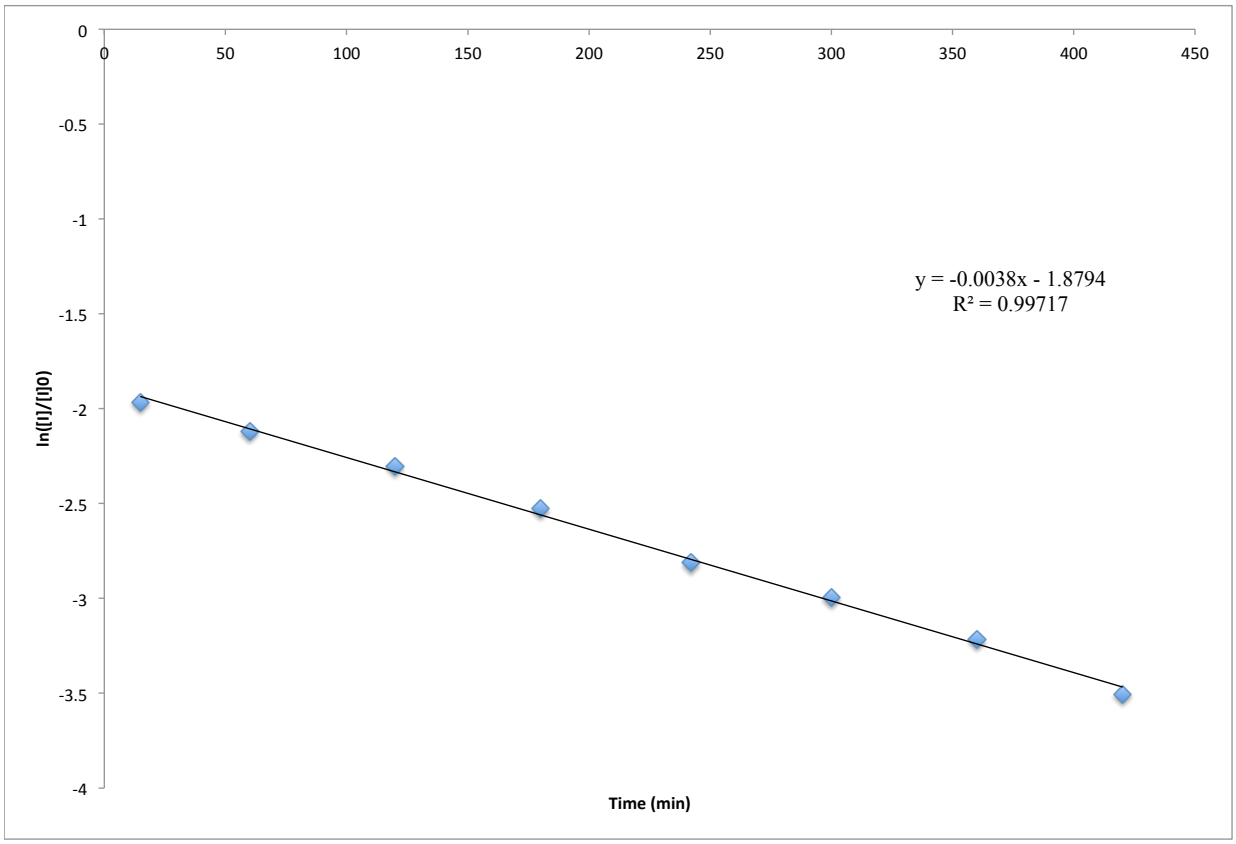


Slope (k_{obs}) = 6.2 x 10^{-5} s^{-1}

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

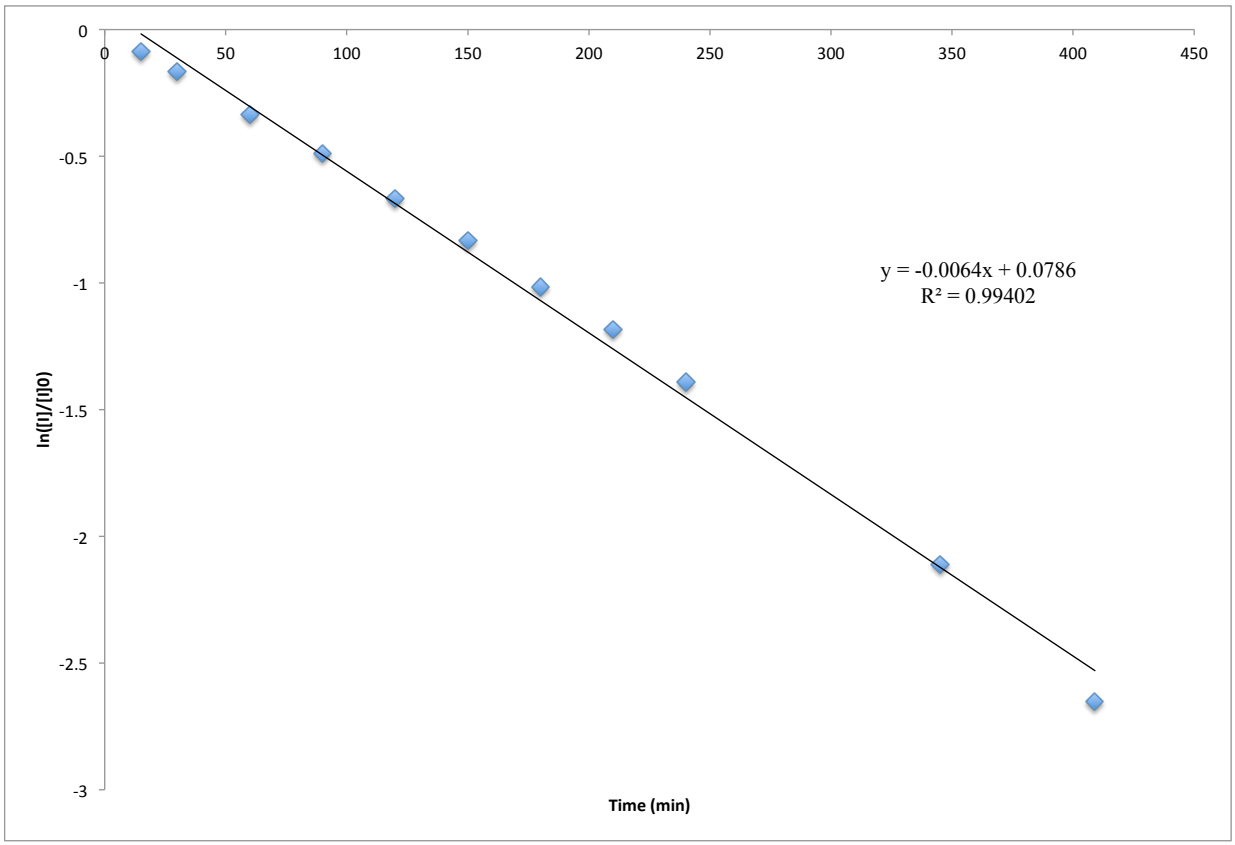


Slope (k_{obs}) = 6.3 x 10^{-5} s^{-1}

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

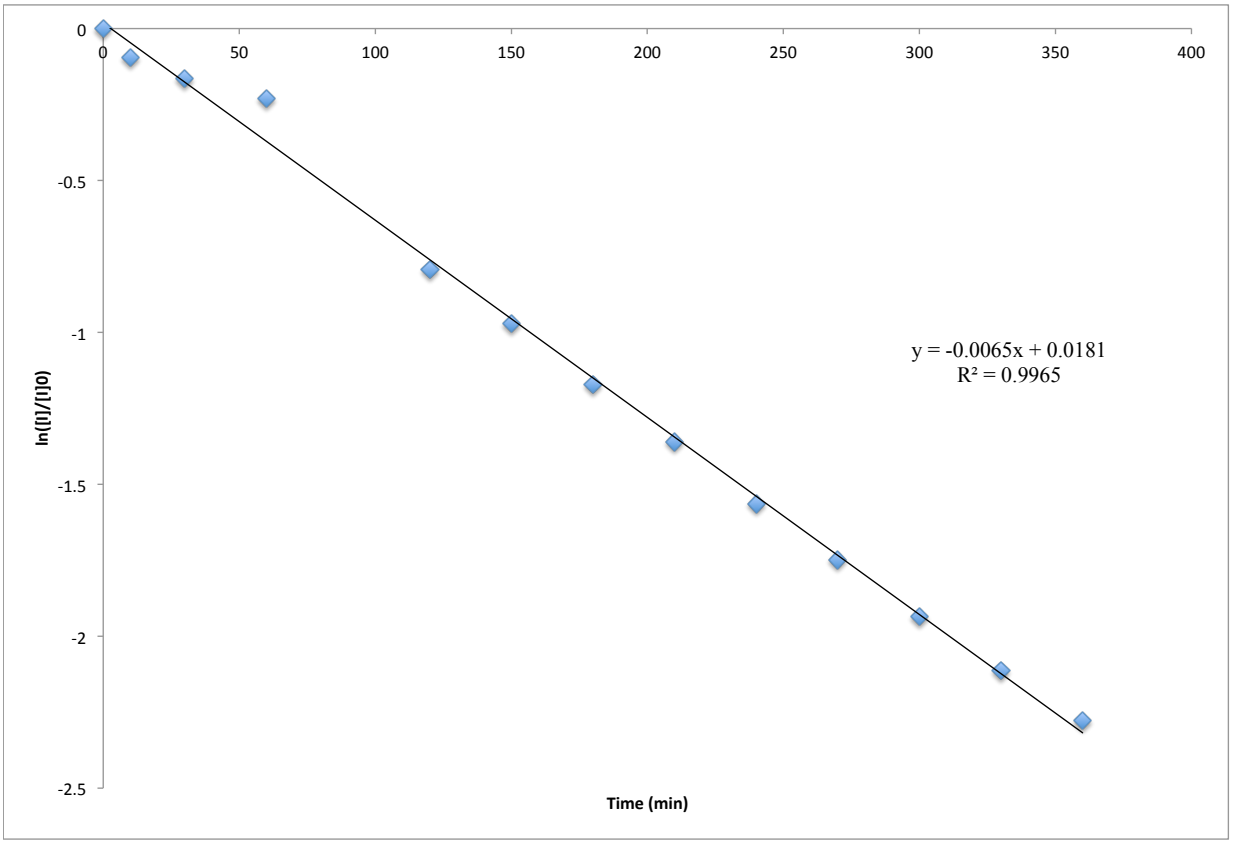


Slope (k_{obs}) = 10.6 x 10^{-5} s^{-1}

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

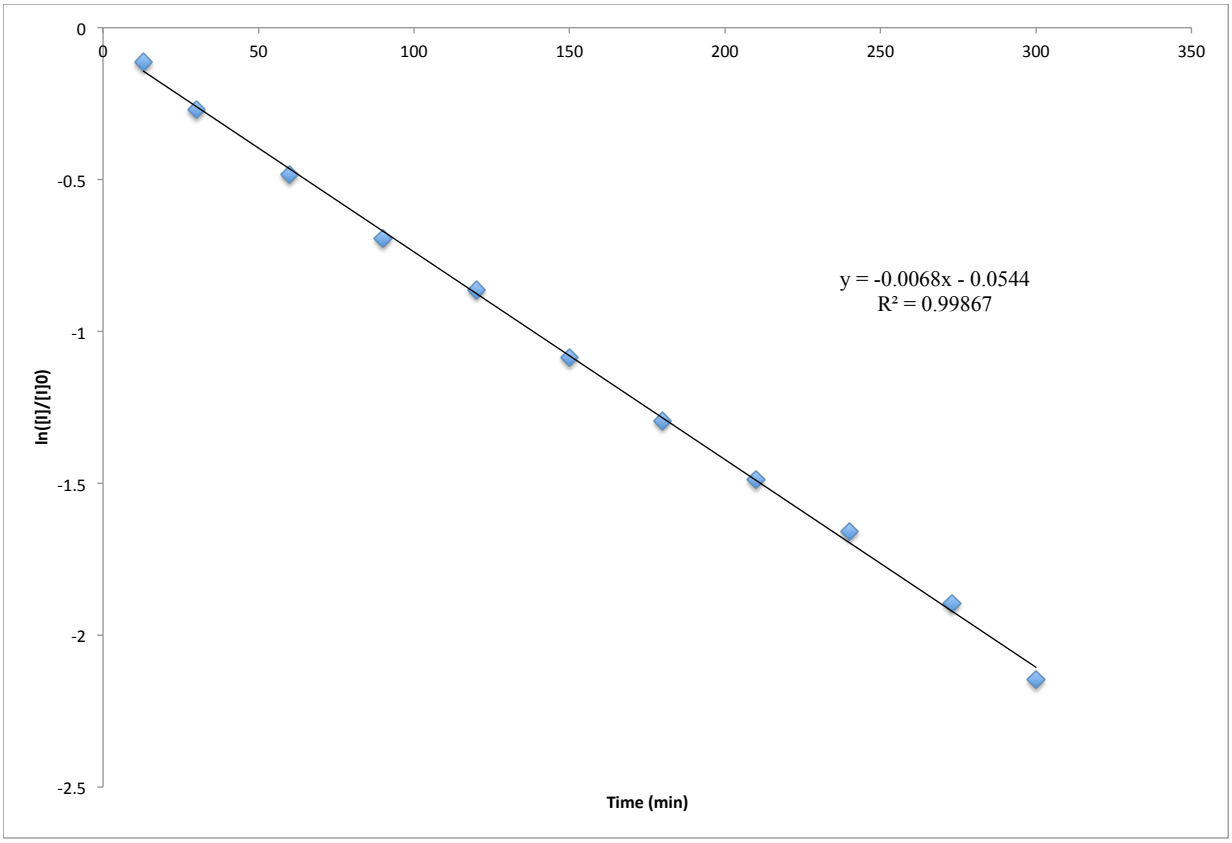


Slope (k_{obs}) = 10.8 x 10^{-5} s^{-1}

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

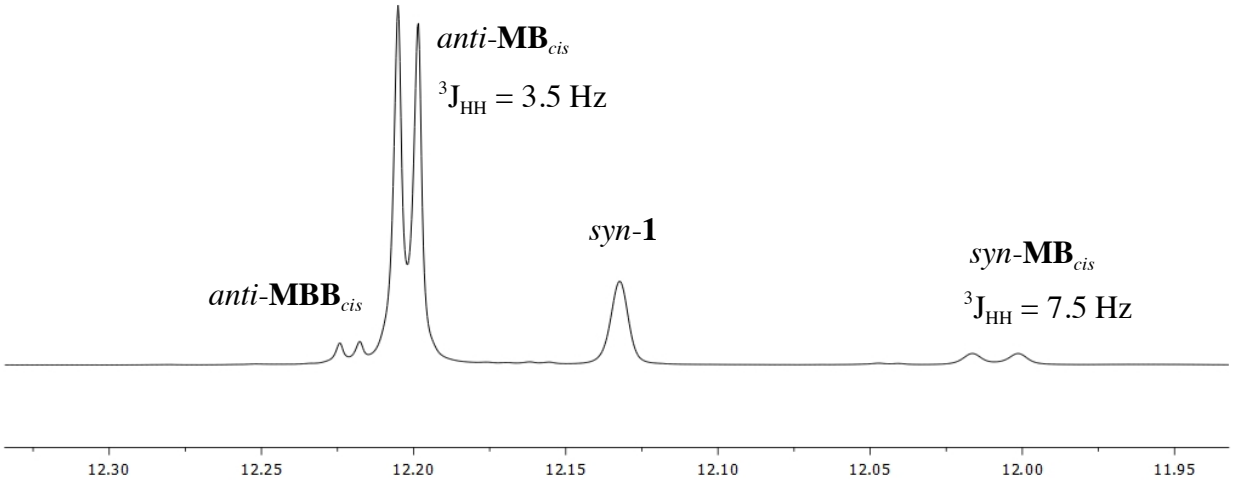


Slope (k_{obs}) = 11.3 x 10^{-5} s^{-1}

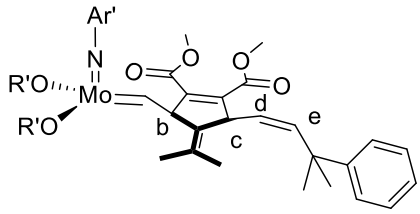
Observation of *anti*-MB$_{cis}$ and *syn*-MB$_{cis}$ by catalyst 1

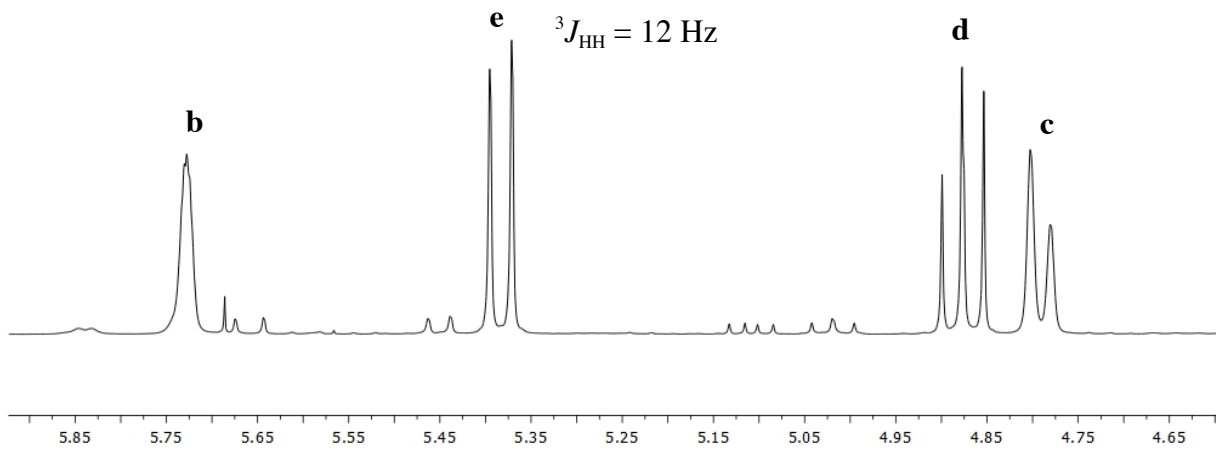
In a J-Young NMR tube, 0.7 equivalents of **B** (5.7 mg, 23 μmol) were added to a 0.7 mL toluene-d_8 solution of catalyst **1** (22.8 mg, 32 μmol) at room temperature. After 2 hours, a ^{1}H NMR spectrum was taken and the major species was *anti*-MB$_{cis}$ and the minor species was *syn*-MB$_{cis}$.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

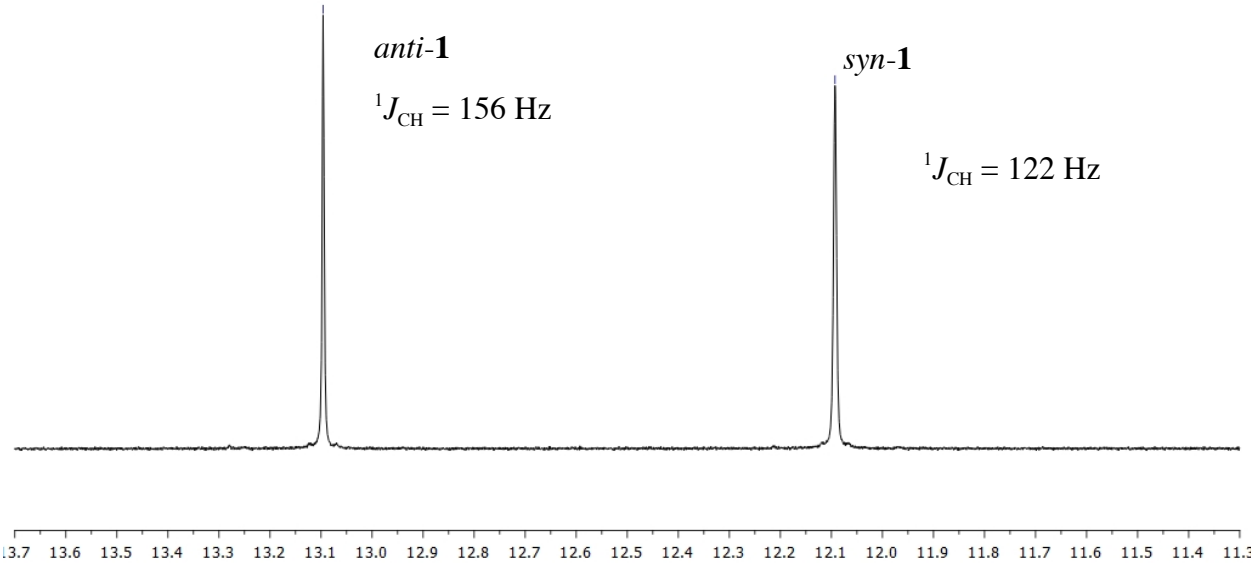




Photolysis of 1 and addition of B by varying the temperature.

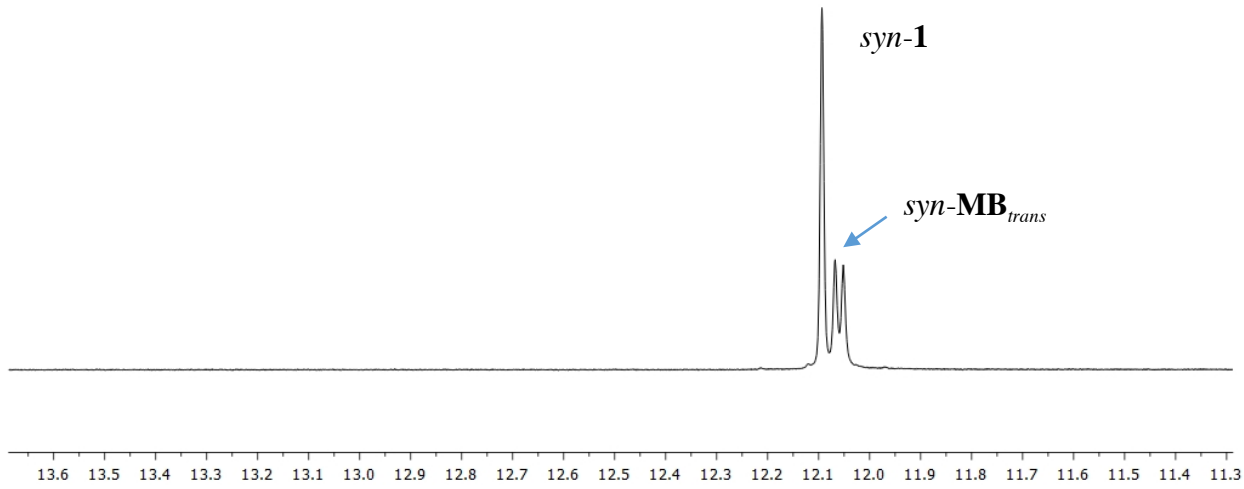
In a Wilmad screw-cap NMR tube, Mo(NAr')(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (32.5 mg, 45.8 µmol) were dissolved in 0.6 mL of toluene-d_8. The sample was closed with a PTFE/silicon septum cap and irradiated at -78 °C in a Rayonet photolysis apparatus at 350 nm for 3 h. The sample was kept at -78 °C until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



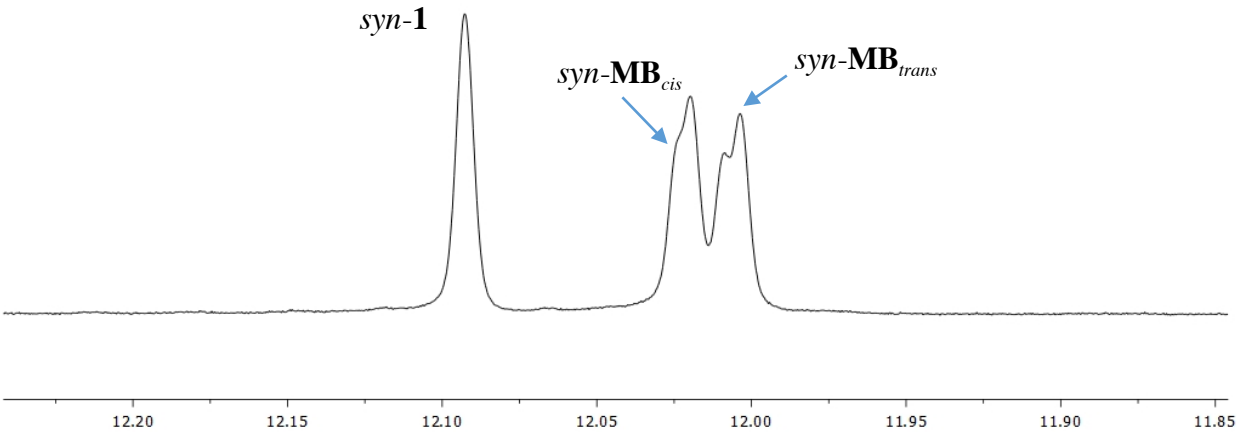
After observation at -50 °C, the sample was returned to a -78 °C bath and 0.5 equivalents of **B** (5.1 mg, 20.5 μmol) in 0.1 mL of toluene-d_8 was added via a syringe. The consumption of **B** was monitored as the temperature was changed by +10 °C.

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

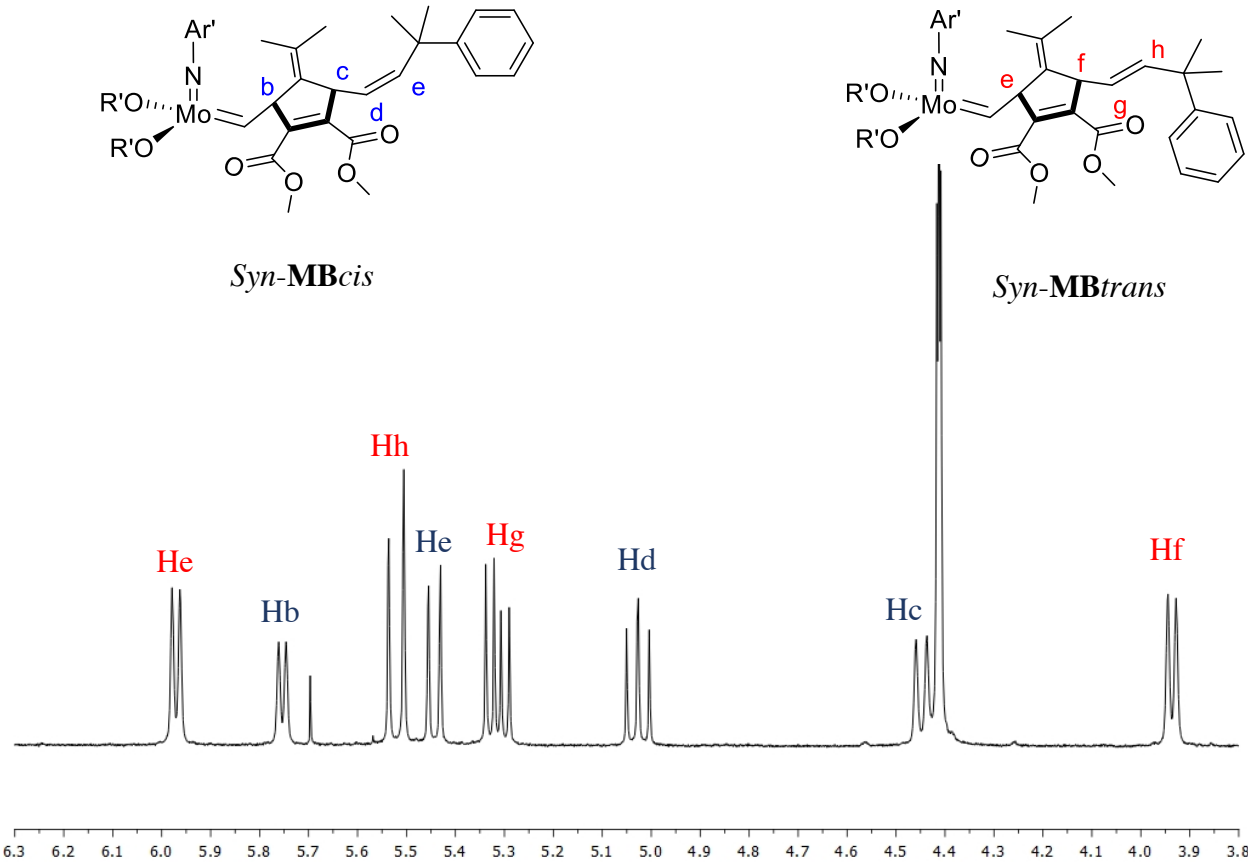


At -10 °C, both *syn*-**MB**$_{trans}$ and *syn*-**MB**$_{cis}$ species are resolved and olefinic peaks were assigned by gCOSY.

^{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:

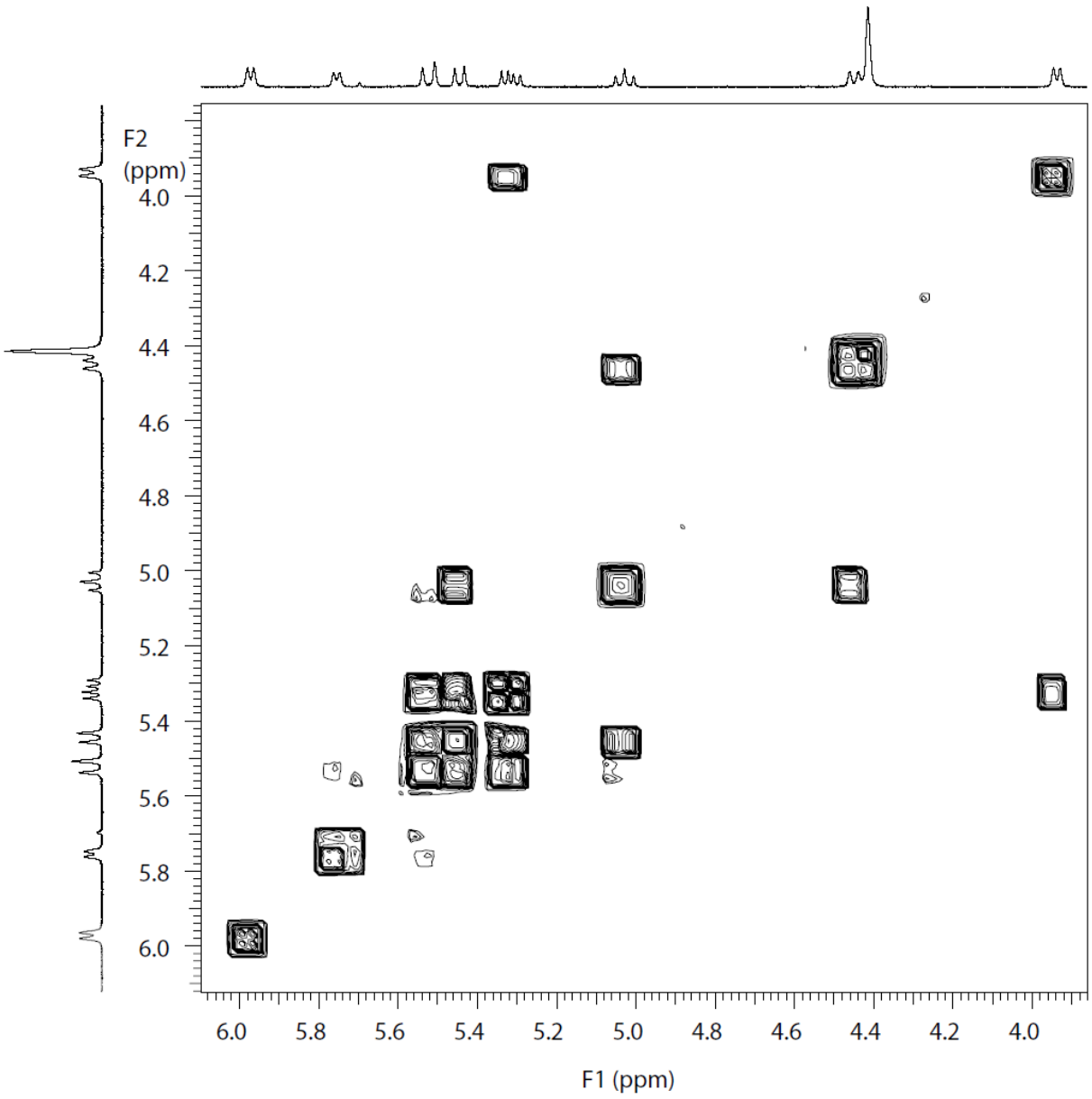


Figure S24. ^{1}H-^{1}H gCOSY spectrum of the olefinic region of *syn*-**MB**$_{cis}$ and *syn*-**MB**$_{trans}$ at -10 °C

References

[1] Alder, K.; Ruhmann, R. *Ann, Chem*. **1950**, *24*, 566.
[2] Valiulin, R. A.; Arisco, T. M.; Kutateladze, A. G. *J. Org. Chem*. **2013**, *78*, 2012.
[3] Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O' Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem*. **1993**, *459*, 185.
[4] Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.