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

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Supporting Information

ABSTRACT: Four alternating AB copolymers have been prepared through ring-opening metathesis polymerization (ROMP) with $Mo(NR)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ initiators (R = 2,6-$Me_2C_6H_3$ (**1**) or 2,6-*i*-$Pr_2C_6H_3$ (**2**)). The A:B monomer pairs copolymerized by **1** are cyclooctene (**A**):2,3-dicarbomethoxy-7-isopropylidenenorbornadiene (**B**), cycloheptene (**A′**):dimethylspiro[bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate-7,1′-cyclopropane] (**B′**), **A**:**B′**, and **A′**:**B**; **A′**:**B′** and **A**:**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.

Copolymers of the type AB, 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 has been relatively successful because neither CO nor CO_2 can be homopolymerized.

In the past 10−15 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

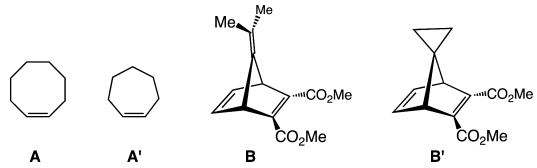

Figure 1. Monomers explored in this study.

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 $W(O)(CH\text{-}t\text{-}Bu)(Me_2Pyr)(OHMT)(PMe_2Ph)$ (OHMT = *O*-2,6-$Mes_2C_6H_3$, Me_2Pyr = 2,5-dimethylpyrrolide),[8] especially in the presence of $B(C_6F_5)_3$, which accelerates ROMP through binding of $B(C_6F_5)_3$ to the oxo ligand.[8,9] In 1990, we found that **B** reacts slowly with $Mo(NAr)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$ (Ar = 2,6-*i*-$Pr_2C_6H_3$) 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**.

During the process of exploring several molybdenum imido alkylidene catalysts for the homopolymerization of **B**, we found that $Mo(NAr')(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ (**1**, Ar′ = 2,6-$Me_2C_6H_3$) 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 $CDCl_3$, toluene-d_8, or C_6D_6 in 1−2 h to give largely (>90%) *trans*-poly(**A**-*alt*-**B**) (Figure 2). ^1H 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 ∼15.5 Hz, characteristic of a *trans* C=C bond. An IR spectrum also shows a strong peak at 967 cm^{-1}

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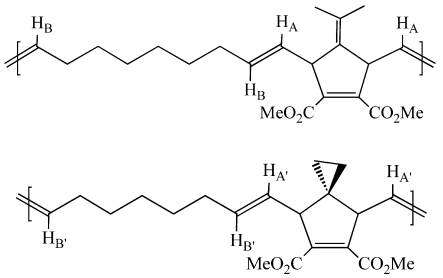


Figure 2. Repeat unit of *trans*-poly(**A**-*alt*-**B**) (top) and *trans*-poly(**A′**-*alt*-**B′**) (bottom).

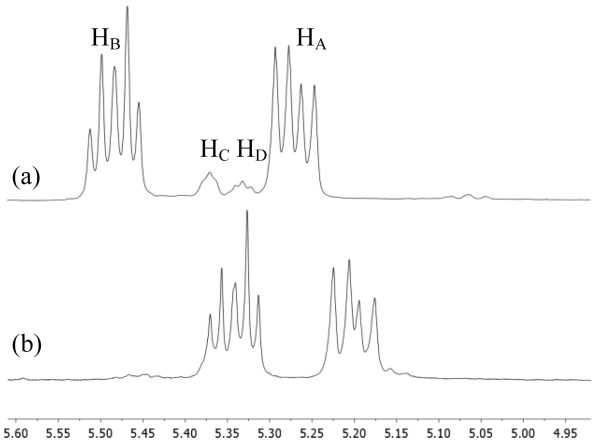


Figure 3. Olefinic region of the ^{1}H NMR spectra of (a) *trans*-poly(**A**-*alt*-**B**) and (b) *trans*-poly(**A′**-*alt*-**B′**) in $CDCl_3$ prepared from **1**.

characteristic of a *trans* olefin. ^{1}H/^{1}H COSY NMR studies are all completely consistent with the proposed structure. A plot of ln[**A**] vs *t* is approximately linear, with $k_{obs} = 29 \times 10^{-5}$ s^{-1} in $CDCl_3$; a plot of ln[**B**] vs *t* is approximately linear, with $k_{obs} = 20 \times 10^{-5}$ s^{-1} (Table 1). Because different data are acquired at

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

			k_{obs} ($\times 10^{-5}$ s^{-1})	
	solvent	monomer concn (M)	**A**	**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

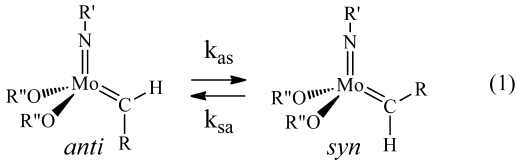
[a]See Supporting Information for details. [b]**A′**:**B′**:**1** = 100:100:1.

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.

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 equiv 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 $k_{obs} = 23 \times 10^{-5}$ s^{-1} for **A′** and 16×10^{-5} s^{-1} for **B′** (Table 1). The ^{1}H 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$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (**2**) also will initiate the copolymerizations of **A′** and **B′** in toluene-d_8, with $k_{obs} = 3.1 \times 10^{-5}$ s^{-1} for **A′** and 2.7×10^{-5} s^{-1} for **B′** (Table 1), and **A** and **B′** (no rate determined). Note that the **A′B′** reaction is ∼1 order of magnitude slower than that of **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 their interconversion 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; thus, 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).

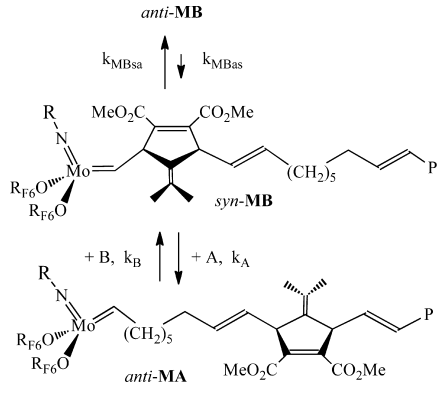


Figure 4. Proposed mechanism of forming *trans*-poly(**A**-*alt*-**B**) (P = polymer).

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A model for the reaction of *syn*-**MA** with **B** is the reaction of *syn*-**1** with 0.7 equiv 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**, 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 $K_{eq} = 0.05$. It is highly unusual to find a four-coordinate alkylidene of the type employed here that is essentially entirely *anti*; for example, the bis-*tert*-butoxide analogue 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 equiv 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), then 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 includes the fact that the rate of reaction of *syn*-**2** with **B′** at initial concentrations of **B′** that are 5×[*syn*-**2**], 20×[*syn*-**2**], and 30×[*syn*-**2**] (pseudo-first-order conditions) does *not* depend upon the concentration of **B′**. The rate constant for consumption of *syn*-**2** (10×10^{-5} s^{-1}) is close to that published for conversion of *syn*-**2** to *anti*-**2** in toluene-d_8 at 22 °C ($k_{2as} = 7 \times 10^{-5}$ s^{-1}),[12] and the first insertion product in the reaction between *syn*-**2** and **B′** contains a *trans* C═C bond. Thus, 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 of 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 1 equiv of **B′** (see SI); $\mathbf{MB'}_{trans}$ is an ∼95:5 *anti*:*syn* mixture at equilibrium ($K_{eq} = [\textit{syn}\text{-}\mathbf{MB'}_{trans}]/[\textit{anti}\text{-}\mathbf{MB'}_{trans}] = 0.05$), the same as found for $[\textit{syn}\text{-}\mathbf{MB}_{cis}]/[\textit{anti}\text{-}\mathbf{MB}_{cis}]$ in the **AB** system above. Addition of 50 or 75 equiv of **A′** to isolated *anti*-$\mathbf{MB'}_{trans}$ leads to consumption of *anti*-$\mathbf{MB'}_{trans}$ at a rate that is first-order in $[\textit{anti}\text{-}\mathbf{MB'}_{trans}]$ but *independent* of [**A′**], with $k_{obs} = 6.2 \times 10^{-5}$ s^{-1}. Thus, the rate-limiting step for this reaction is conversion of *anti*-$\mathbf{MB'}_{trans}$ to *syn*-$\mathbf{MB'}_{trans}$, i.e., $k_{obs} = 6.2 \times 10^{-5}$ s^{-1} = $k_{\mathbf{MB}as}$ (Figure 4). We conclude that the other AB linkage is formed in a reaction between **A′** and *syn*-$\mathbf{MB'}_{trans}$.

Two other combinations of A, 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 by the combination **A**:**B′**:**2** contains ∼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.

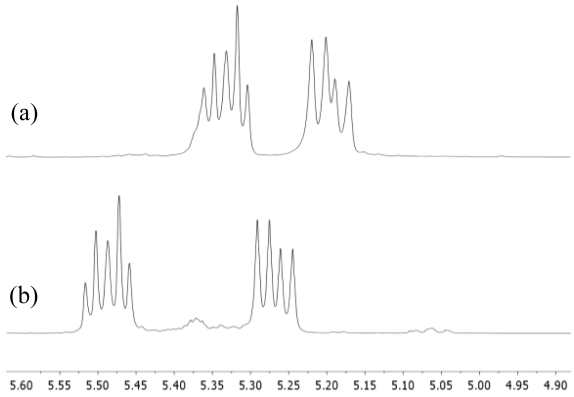

Figure 5. Olefinic region of the ^{1}H NMR spectra of (a) *trans*-poly(**A**-*alt*-**B′**) and (b) *trans*-poly(**A′**-*alt*-**B**) prepared with **1**.

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. Thus, B must react with *anti*-MA ∼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** is then added, virtually no **B** is consumed. Thus, 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 of *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

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observed "first-order" rate constant is ~3.4×10^{-5} s^{-1} for **A** and 3.3×10^{-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 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. We hope that intimate knowledge of the factors that produce the results reported here can then be employed to answer the following: What other *trans*-poly(A-*alt*-B) copolymers can be formed, to what extent are 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

Supporting Information

Experimental details for all syntheses. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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