

Synthesis and Optical Spectroscopy of Oligo(1,6-heptadiynes) with a Single Basic Structure Prepared through Adamantylimido-Based Molybdenum Wittig and Metathesis Chemistry

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Abstract: Linear oligoynes of 1,6-heptadiynes (derived from dialkyl dipropargylmalonates) with a single basic structure and up to 23 conjugated double bonds were synthesized through Wittig-like reactions between bimetallic Mo-alkylidene compounds and aldehyde-capped oligoynes. The relatively rigid and isomerically pure oligoynes have structures with alternating *cis*, *trans* conjugated double bonds in which the *cis* double bond is part of a cyclopentene ring. Molecular weights have been confirmed through MALDI-MS measurements of samples purified by HPLC. Optical spectra of the purified samples show significant vibronic resolution, even in room temperature samples, and are remarkably similar to those of simple polyenes and carotenoids. Therefore, a systematic investigation of the dependence of the allowed electronic transition energies (electronic origins) on conjugation lengths has become possible. Studies of seven allowed transitions for molecules with 5–23 double bonds ($= N$) indicate asymptotic convergence (with approximately a $1/N$ dependence) to a common long polyene limit at $\sim 16\,000\text{ cm}^{-1}$. The convergence of these electronic transitions agrees with theoretical treatments of polyene excited-state energies and is consistent with the absorption spectra of analogous diethyl dipropargylmalonate polymers ($1/N \approx 0$).

Introduction

Organic molecules that contain linear networks of conjugated π bonds exhibit unique and useful electronic properties. Naturally occurring polyenes such as retinal serve as chromophores in vision and in phototrophic archaea, e.g. *halobacteria*, and longer carotenoids function as antenna pigments in photosynthetic bacteria and plants.¹ Carotenoids also quench chlorophyll triplet states, preventing damage due to the photosensitization of singlet oxygen.^{1c,2} Linearly conjugated polymers are semiconductors and can be used as active materials in a range of optoelectronic devices.³ More experimentally accessible and more easily characterized simple polyenes have served as models for developing theoretical descriptions of the relevant excited electronic states.^{2,4} Extension of our understanding of short, model polyenes to longer systems, including conjugated polymers, has been hampered by complications imposed by

conformational disorder⁵ and *trans/cis* (*E/Z*) isomerization in long polyene chains. Even for simple *all-trans* polyenes characterized by single ground-state geometries, electronic excitation leads to a distribution of isomers and distorted *all-trans* structures in both the ground and excited states.⁶ The challenges in relating the optical and photochemical properties of polyenes to their molecular structures thus are still significant.

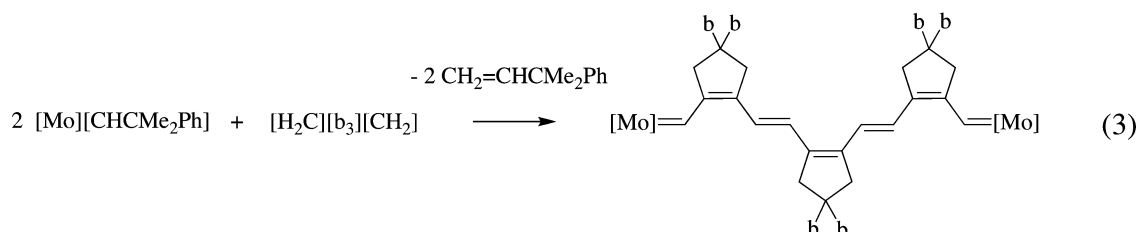
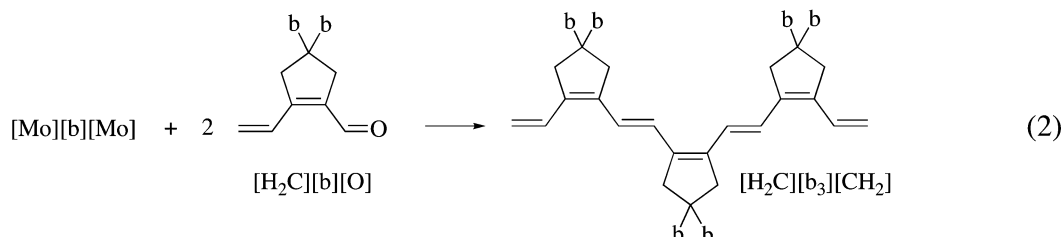
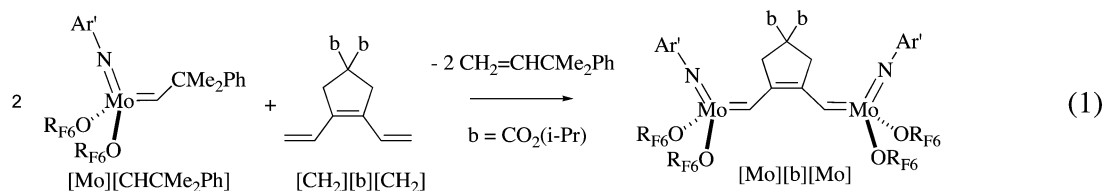
Poly[1,6-heptadiynes] such as poly[dialkyl dipropargylmalonates], which are formed in an alkylidene-catalyzed cyclopolymerization reaction, are highly conjugated, relatively soluble, and relatively stable in air.⁷ Usually a mixture of five-membered rings and six-membered rings are formed through tail-to-tail and head-to-tail cyclopolymerization processes, respectively.

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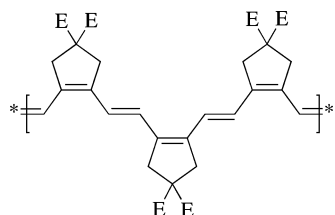
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Five-membered rings are believed to form through addition of the first triple bond to an alkylidene (*syn* or *anti*) to give a metallacyclobutene with the (previous alkyne) substituent in the α position, while six-membered rings result from addition of the first triple bond to an alkylidene (*syn* or *anti*) to give a metallacyclobutene with the previous alkyne substituent in the β position. Imido alkylidene bisalkoxide catalysts can be chosen so that polymers that contain all six-membered rings⁸ or >95% five-membered rings⁹ are formed. Polymers that contain all six-membered rings are not stereoregular as a consequence of *E/Z* isomerism. In contrast, polymers that contain all five-membered rings have a single structure in which the cyclopentene rings are connected by *trans* double bonds, as shown below (where E = ester).



Stoichiometric syntheses have been developed recently that yield a series of stable, rigid oligoenes containing five-membered rings.¹⁰ These molecules have planar π -electron frameworks that

are resistant to conformational disorder and thermal or photochemical isomerization. The peripheral ester substituents contribute to the solubility of these oligoenes in a variety of organic solvents and allow optical spectra to be obtained in low-temperature glasses. These synthetic advances permit a more systematic study of transition energies and band gaps as a function of conjugation length and provide new insights into the properties of one-dimensional conjugated systems in the long polyene limit.

The stoichiometric approach to oligoenes relies upon the synthesis of bimetallic alkylidene complexes in reactions between oligoenes and neopentylidene or neophylidene species followed by Wittig-like reactions between the bimetallic species and an unsaturated aldehyde. The first bimetallic alkylidene is formed as shown in eq 1. Upon treatment of $[\text{Mo}][\text{b}][\text{Mo}]$ with the unsaturated aldehyde, $[\text{H}_2\text{C}][\text{b}][\text{O}]$, the “trimer”, $[\text{H}_2\text{C}][\text{b}_3][\text{CH}_2]$, is formed (eq 2; $\text{Ar}' = 2,6$ -dimethylphenyl). (In the formulas, $[\text{b}_n]$ denotes the number of repeat units that contain isopropyl esters; this nomenclature matches that used in a previous paper.¹⁰) Reaction between $[\text{H}_2\text{C}][\text{b}_3][\text{CH}_2]$ and $[\text{Mo}][\text{CHCMe}_2\text{Ph}]$ then produces the larger bimetallic species, $[\text{Mo}][\text{b}_3][\text{Mo}]$ (eq 3). Treatment of $[\text{Mo}][\text{b}_3][\text{Mo}]$ with $[\text{H}_2\text{C}][\text{b}][\text{O}]$ then produces the pentamer, etc. The key features of this approach to fixed-length oligoenes are that an oligoene produced in a given Wittig-like reaction can be employed to prepare the next bimetallic Wittig reagent, and the chain can be grown in two directions. X-ray structural studies of the dimer and the trimer established the alternating *cis,trans* structure of these oligoenes, while three bimetallic reagents were also characterized through X-ray studies.¹⁰

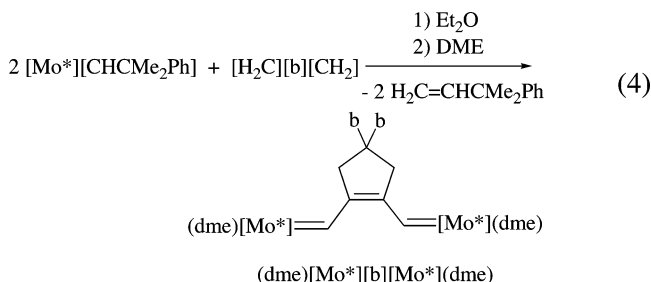
Complications arose in the dimethylphenylimido (NAr') system that prevented extension of this approach beyond the pentamer. For this reason, we turned to Mo complexes that contain other imido groups in the hope that similar complications could be

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avoided. Among the possible alternative imido ligands, we chose the adamantylimido group. The reason is that the adamantylimido ligand is more electron donating than an arylimido ligand, and adamantylimido complexes have produced unusual results in asymmetric metathesis reactions that could not be duplicated with catalysts that contain arylimido ligands.¹¹ In this paper we describe the synthesis, purification, and optical characterization of oligoenes with a single basic structure and up to 23 conjugated double bonds. This work essentially doubles the conjugation lengths available from previous synthetic work or from the isolation of natural carotenoids.

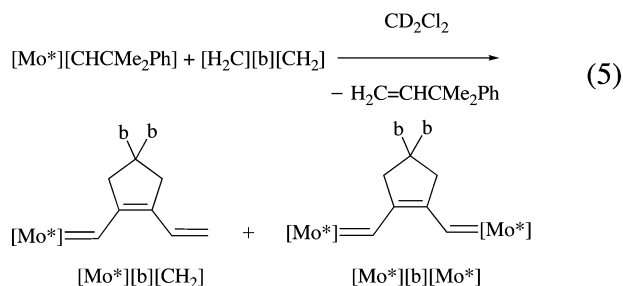
Results

Reactions That Involve NAdamantyl Species That Contain One Five-Membered Ring. The reaction between $[H_2C][b][CH_2]$ (eq 1) and 2 equiv of $Mo(NAd)(CHCMe_2Ph)(OR_F)_2$ ($[Mo^*]-[CHCMe_2Ph]$, Ad = 1-adamantyl) yielded what appeared to be the desired bimetallic species, $[Mo^*][b][Mo^*]$, according to 1H NMR spectra in CD_2Cl_2 , although all efforts to isolate that species in crystalline form failed. Fortunately, addition of dimethoxyethane (dme) to the viscous residue followed by concentration of the solution *in vacuo* and addition of pentane led to the dark orange dme adduct of the desired species in 59% yield (eq 4).



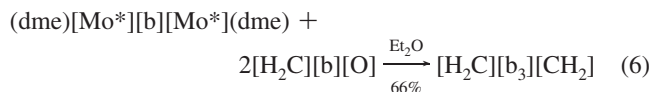
This bimetallic compound was found to be a mixture of *syn/syn* (84%) and *syn/anti* (16%) isomers in CD_2Cl_2 , according to proton NMR spectra. (In a *syn* species the alkylidene points toward the imido ligand, whereas in an *anti* species the alkylidene points away from the imido ligand.) In a *syn/syn* species the alkylidene has a *syn* configuration at each end. Similar findings have been reported for other bimetallic species in this general category.¹²

In a reaction between $[H_2C][b][CH_2]$ and 1 equivalent of $[Mo^*][CHCMe_2Ph]$ in CD_2Cl_2 , the monometallic species, $[Mo^*][b][CH_2]$, was observed after 30 min as the major product in a mixture that contained $[Mo^*][b][Mo^*]$ and unreacted $[Mo^*][CHCMe_2Ph]$, according to NMR spectra (eq 5). After 1 day, the major product was found to be $[Mo^*][b][Mo^*]$. These results suggest that $[Mo^*][b][CH_2]$ is the intermediate in the reaction in which $[Mo^*][b][Mo^*]$ is formed, as one might expect.

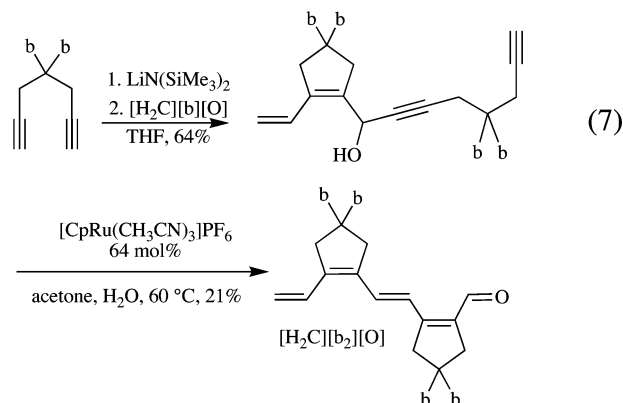


Reaction of $(dme)[Mo^*][b][Mo^*](dme)$ with two equivalents of $[H_2C][b][O]$ produced the expected trimer $[H_2C][b_3][CH_2]$ in 66% yield after separation of the product mixture by silica

gel column chromatography (eq 6). There was no evidence for formation of $[H_2C][b_2][CH_2]$. The relatively high isolated yield of $[H_2C][b_3][CH_2]$ and the absence of $[H_2C][b_2][CH_2]$ contrasts sharply with the results in the analogous $Mo(NAr')$ system where a mixture is obtained in relatively low yield.¹⁰

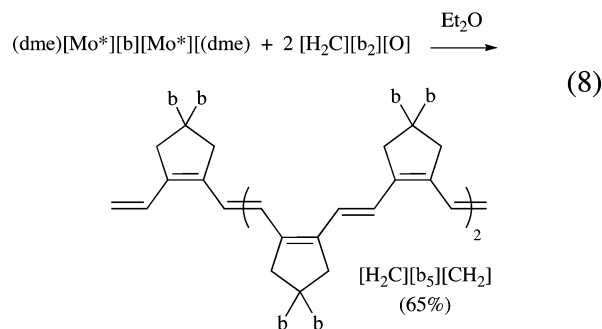


In theory, much longer oligoenes could be prepared more readily if aldehydes longer than $[H_2C][b][O]$, e.g., $[H_2C][b_2][O]$ (eq 7), could be prepared through reactions that do not involve Mo alkylidenes as stoichiometric reagents.



The alcohol in eq 7 could be obtained in 64% yield as white crystals, after silica gel column chromatography. The unsubstituted dimeric aldehyde $[H_2C][b_2][O]$ was then obtained by the method reported by Trost,¹³ but only in a disappointing 21% yield, and only then with a 64% loading of Ru catalyst. By comparison, $[Me_2C][b_2][O]$ was obtained in 57% yield with a 16% loading of Ru catalyst, while $[H_2C][b][O]$ was obtained in 55% yield with a 12% loading of Ru .¹⁴ An attempt to synthesize $[H_2C][b_2][O]$ using $[Cp^*Ru(CH_3CN)_3]PF_6$ ($Cp^* = \eta^5-C_5Me_5$)¹⁵ as a catalyst instead of $[CpRu(CH_3CN)_3]PF_6$ was not successful.

When $(dme)[Mo^*][b][Mo^*](dme)$ was treated with $[H_2C][b_2][O]$ in diethyl ether, orange $[H_2C][b_5][CH_2]$ was obtained in 65% yield (eq 8).



HPLC studies on a sample isolated as described above showed that the sample of $[H_2C][b_3][CH_2]$ was contaminated with small amounts of impurities with shorter retention times (Figure 1).

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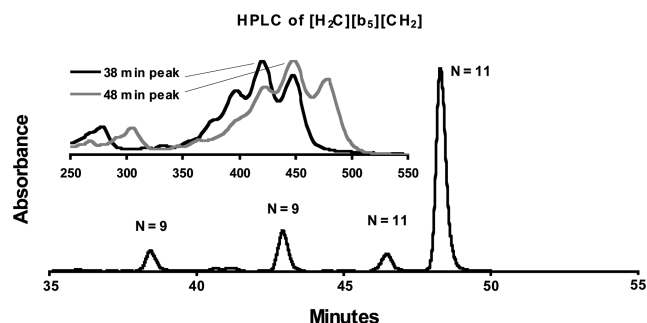
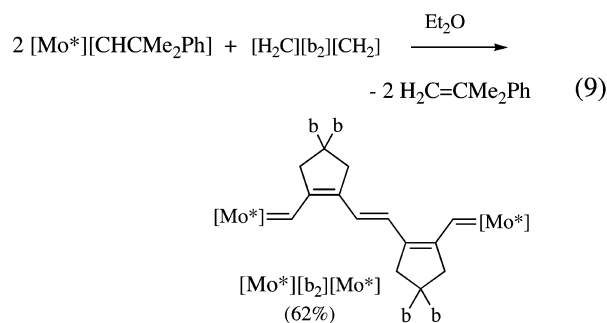


Figure 1. HPLC of $[H_2C][b_5][CH_2]$, detected at 400 nm. Inset: Normalized absorption spectra of peaks at 38 and 48 min, corresponding to $[H_2C][b_4][CH_2]$ and $[H_2C][b_5][CH_2]$, respectively.

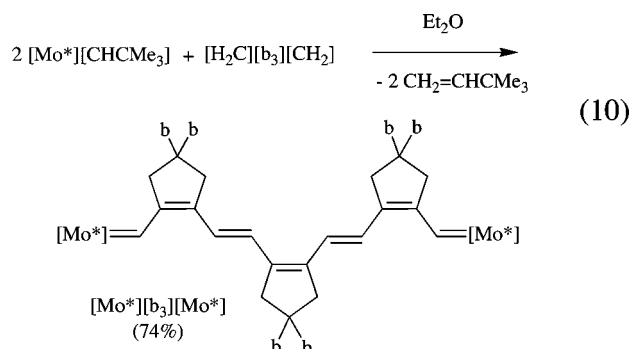
The two components with the longest retention times have well-resolved, superimposable absorption spectra ($\lambda_{\max} \approx 450$ nm), which suggests that $N = 11$ for these species. The identity of the $N = 11$ peak with the shorter retention time is not known, although hydrolysis of an ester to give an acid would be high on the list of possibilities. As shown in case of the dimer and trimer, the π -conjugation in the polyene chain was not altered upon changing from ethyl ester to isopropyl esters; the UV-vis spectra of $[H_2C][b_2][CH_2]$, $[H_2C][a_2][CH_2]$, and $[H_2C][b_3][CH_2]$, $[H_2C][aba][CH_2]$ ($b = i$ -Pr ester and $a = Et$ ester substituted 5-membered rings) were superimposable.¹⁰ The HPLC in Figure 1 also reveals two species (10–20% of the total) with shorter conjugation lengths. The well-resolved absorption spectrum ($\lambda_{\max} \approx 420$ nm) of the impurity eluting around 43 min can be identified as $[H_2C][b_4][CH_2]$ ($N = 9$),¹⁰ while the peak at 38 min appears to be another version of $[H_2C][b_4][CH_2]$, although its spectrum is significantly broader. Formation of $[H_2C][b_4][CH_2]$ cannot be explained through a mechanism similar to that proposed elsewhere¹⁰ for formation of $[H_2C][b_2][CH_2]$, i.e., a competition between a reaction of the $HC=O$ and the $CH_2=CH-$ group in $[H_2C][b_2][O]$. At this time, our only explanation is that internal *trans* double bonds in $[H_2C][b_n][CH_2]$ and (dme)[Mo^*][b_n][CH_2] also undergo metathesis to some degree, as was proposed in the system involving 2,6-dimethylphenylimido species.¹⁰ Repeated HPLC analyses of this and other samples described here showed that the major species present was the one that was sought. There is no evidence that other geometric isomers are present. Replacing *trans* double bonds with *cis* bonds typically has significant effects on the electronic spectra; e.g., the main absorption band shifts to shorter wavelengths, and there is an increase in the intensity of the higher energy “*cis*-band” region in the absorption spectrum.^{1a} We only see impurities with the same basic structure but different conjugation lengths. The new synthetic products thus are much more homogeneous than previous samples of carotenoids and simple polyenes, which are prone to thermal and photochemical isomerization during and after their syntheses.

Bimetallic NAdamantyl Species That Contain More Than One Five-Membered Ring. The reaction of $[H_2C][b_2][CH_2]$ with 2 equiv of $[Mo^*][CHCMe_2Ph]$ gave $[Mo^*][b_2][Mo^*]$ in 62% yield (eq 9).



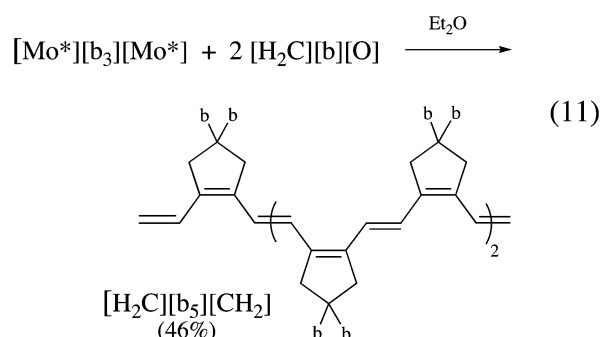
$[Mo^*][b_2][Mo^*]$ is only slightly soluble in CD_2Cl_2 , but NMR data could be acquired in $THF-d_8$. $[Mo^*][b_2][Mo^*]$ was found to be contaminated with $[Mo^*][b_2][CH_2]$, as indicated by the presence of $=CH_2$ signals that did not belong to unreacted $[H_2C][b_2][CH_2]$ and by elemental analysis. Multiple attempts to synthesize $[Mo^*][b_2][Mo^*]$ led to crude products in which the ratios between the monometallic intermediate $[Mo^*][b_2][CH_2]$ and $[Mo^*][b_2][Mo^*]$ varied significantly.

The reaction between $[H_2C][b_3][CH_2]$ and 2 equiv of $[Mo^*][CHCMe_2R]$ ($R = Ph, Me$) produced $[Mo^*][b_3][Mo^*]$ (eq 10).



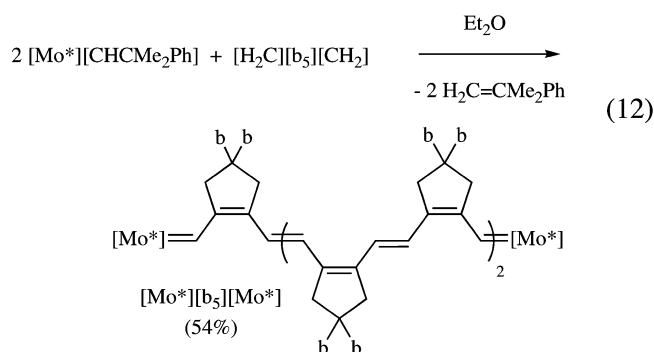
The purity of $[Mo^*][b_3][Mo^*]$ was higher when $[Mo^*][CHCMe_3]$ was employed instead of $[Mo^*][CHCMe_2Ph]$. $[Mo^*][b_3][Mo^*]$ was only partially soluble in CD_2Cl_2 , but proton NMR spectra could be obtained in both CD_2Cl_2 and $THF-d_8$. $[Mo^*][b_3][Mo^*]$ was found to be a mixture of *syn/syn* (major), *anti/anti*, and *syn/anti* isomers in CD_2Cl_2 on the basis of integration of the alkylidene H_α resonances in the 1H NMR (CD_2Cl_2) spectrum, although overlap prevented accurate determination of ratios. In $THF-d_8$, only the *syn/syn* isomer was observed. It is not known to what degree the *syn* or *anti* nature of alkylidenes impacts the purity of $[H_2C][b_n][CH_2]$ products in subsequent steps.

Reaction of $[Mo^*][b_3][Mo^*]$ with 2 equiv of $[H_2C][b][O]$ yielded $[H_2C][b_5][CH_2]$ in 46% yield (eq 11). Proton and ^{13}C NMR spectra (in CD_2Cl_2) were identical to those found for $[H_2C][b_5][CH_2]$ synthesized as shown in eq 8.



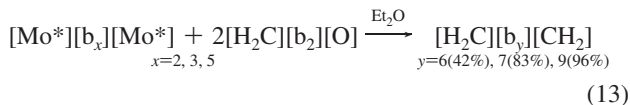
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The reaction shown in eq 12 employed the pentamer synthesized as in eq 8 without further purification. $[\text{Mo}^*][\text{b}_5][\text{Mo}^*]$ was only partially soluble in CD_2Cl_2 , but NMR spectra could be obtained in both CD_2Cl_2 and $\text{THF-}d_8$.



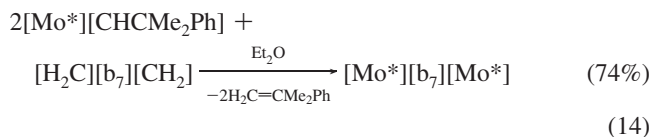
According to ^1H NMR (CD_2Cl_2) spectroscopy and elemental analysis, the deep red product isolated in the first crop was contaminated with small amounts of impurities that contain $\text{CH}=\text{CH}_2$ end groups. The bimetallic compound that was isolated from the filtrate (second crop) did not appear to contain any monometallic impurity but analyzed as $[\text{Mo}][\text{b}_4][\text{Mo}]$. $[\text{Mo}^*][\text{b}_5][\text{Mo}^*]$ was a mixture of *syn/syn* (major), *anti/anti*, and *syn/anti* isomers in CD_2Cl_2 on the basis of integration of the alkylidene H_α resonances in the ^1H NMR spectrum, although overlap prevented the determination of accurate ratios.

All reactions between $[\text{Mo}^*][\text{b}_n][\text{Mo}^*]$ species ($x = 2, 3, 5$), isolated as described above, and $[\text{H}_2\text{C}][\text{b}_y][\text{O}]$ produced the expected products, $[\text{H}_2\text{C}][\text{b}_y][\text{CH}_2]$ ($y = 6, 7, 9$; eq 13).

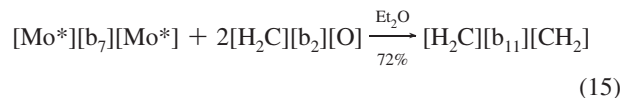


They were isolated simply by filtration when reactions were carried out in pentane. Each product was contaminated with shorter oligomers, as suggested by ^1H NMR and HPLC studies. The origin of the shorter oligomers is not known, although as mentioned earlier, we now believe that metathesis reactions can take place at internal *trans* $\text{C}=\text{C}$ bonds. The solubility of the $[\text{H}_2\text{C}][\text{b}_y][\text{CH}_2]$ species decreases steadily with increasing chain length.

Reaction of $[\text{H}_2\text{C}][\text{b}_7][\text{CH}_2]$ with 2 equiv of $[\text{Mo}^*][\text{CHCMe}_2\text{Ph}]$ led to $[\text{Mo}^*][\text{b}_7][\text{Mo}^*]$ (eq 14) in 74% yield.



$[\text{Mo}^*][\text{b}_7][\text{Mo}^*]$ was sparingly soluble in both CD_2Cl_2 and $\text{THF-}d_8$, and like its shorter analogues, it was contaminated with $[\text{Mo}^*][\text{b}_n][\text{CH}_2]$ impurities, according to ^1H NMR spectroscopy in CD_2Cl_2 . $[\text{Mo}^*][\text{b}_7][\text{Mo}^*]$ was found to be a mixture of *syn/syn* (major), *anti/anti*, and *syn/anti* isomers, but integrations of the alkylidene proton resonances in ^1H NMR spectra were not reliable as a consequence of overlap of resonances. Subsequent treatment of $[\text{Mo}^*][\text{b}_7][\text{Mo}^*]$ with 2 equiv of $[\text{H}_2\text{C}][\text{b}_2][\text{O}]$ led to $[\text{H}_2\text{C}][\text{b}_{11}][\text{CH}_2]$ in 72% yield (eq 15). $[\text{H}_2\text{C}][\text{b}_{11}][\text{CH}_2]$ was sparingly soluble in both CD_2Cl_2 and $\text{THF-}d_8$.



The $[\text{Mo}^*][\text{b}_n][\text{Mo}^*]$ ($n = 2, 3, 5, 7$) compounds often appear to be contaminated with monometallic species (either $[\text{Mo}^*][\text{b}_n][\text{CHCMe}_2\text{Ph}]$ or $[\text{Mo}^*][\text{b}_n][\text{CH}_2]$) or $[\text{Me}_2\text{PhCH}][\text{b}_n][\text{CHCMe}_2\text{Ph}]$ or $[\text{Me}_2\text{PhCH}][\text{b}_n][\text{CH}_2]$ species, along with unreacted $[\text{H}_2\text{C}][\text{b}_n][\text{CH}_2]$, and the problem becomes more pronounced as n increases. These products are believed to arise through back reaction of the initial metathesis product ($\text{CH}_2=\text{CHCMe}_2\text{Ph}$) with various monometallic or bimetallic species, including the desired $[\text{Mo}^*][\text{b}_n][\text{Mo}^*]$ species. Metathesis reactions at internal $\text{C}=\text{C}$ bonds also seem increasingly likely. Attempts to synthesize $[\text{Mo}^*][\text{b}_n][\text{Mo}]$ ($n = 9, 11$) species in a reaction between $[\text{H}_2\text{C}][\text{b}_9][\text{CH}_2]$ or $[\text{H}_2\text{C}][\text{b}_{11}][\text{CH}_2]$ with 2 equiv of $[\text{Mo}^*][\text{CHCMe}_2\text{Ph}]$ led to increasingly complex mixtures of products. Therefore, attempted syntheses of polyenes much longer than those reported here are likely to yield even more complex mixtures.

Absorption Spectroscopy of Oligoenes. Repeated HPLC and MALDI-FTMS analyses of the $[\text{H}_2\text{C}][\text{b}_n][\text{CH}_2]$ samples described here allowed all species of the type shown in eq 11 with $N = 5-23$ to be identified ($N = 2n + 1$); room-temperature absorption spectra of these polyenes are shown in Figure 2. All $E(0-0)$ absorption maxima for the $[\text{H}_2\text{C}][\text{b}_n][\text{CH}_2]$ oligoenes are listed in Table 1. Spectra were obtained directly from the diode array detector of the HPLC at the maxima of peaks in the chromatograms. The eluting HPLC bands also were collected. After the solvents were removed *in vacuo*, absorption spectra of the products obtained in 2-methyl-THF produced results comparable to those obtained directly from the HPLC. Impurities in the longer polyene samples ($N > 15$) led to overlapping HPLC peaks, and collection of pure samples of every product observed using the diode array detector therefore was not possible.

The spectra presented in Figures 1 and 2 are similar to those of well-studied model polyenes and carotenoids with $N \leq 13$.^{1a,2,4,16} The lowest energy, longest wavelength absorption bands are by far the strongest (molar absorptivities $>10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$)^{1a,10,14} and can be associated with $\text{HOMO} \rightarrow \text{LUMO}$ transitions in these π -conjugated systems.^{2,4} For polyenes with C_{2h} symmetry, this is the symmetry-allowed, $1^1\text{A}_g^- \rightarrow 1^1\text{B}_u^+$ transition, which is responsible for the intense colors of all polyenes and carotenoids. Room-temperature absorption spectra shown in Figure 2 are well resolved, but exhibit a systematic broadening of vibronic structure with increasing N . Nevertheless, the electronic origins ($0-0$ bands) are sufficiently resolved to allow the dominant $0-0$ $1^1\text{A}_g^- \rightarrow 1^1\text{B}_u^+$ transition energies to be measured accurately as a function of conjugation length.

Broadening of the absorption spectra with increasing N is similar to that observed for carotenoid systems and, in large part, can be ascribed to the effects of conformational disorder.⁵ In room-temperature solutions, this leads to a distribution of $\text{C}-\text{C}-\text{C}$ torsional angles and deviations from the planar geometries of the fully conjugated π electron framework. The impact of conformational disorder is confirmed through comparisons of spectra at room temperature and 77 K. In Figure 3, we compare the room-temperature and 77 K absorption spectra of $[\text{H}_2\text{C}][\text{b}_7][\text{CH}_2]$ ($N = 15$) in 2-methyltetrahydrofuran, which forms a rigid glass at low temperatures. The shift to longer wavelengths, the significant sharpening of the vibronic structure,

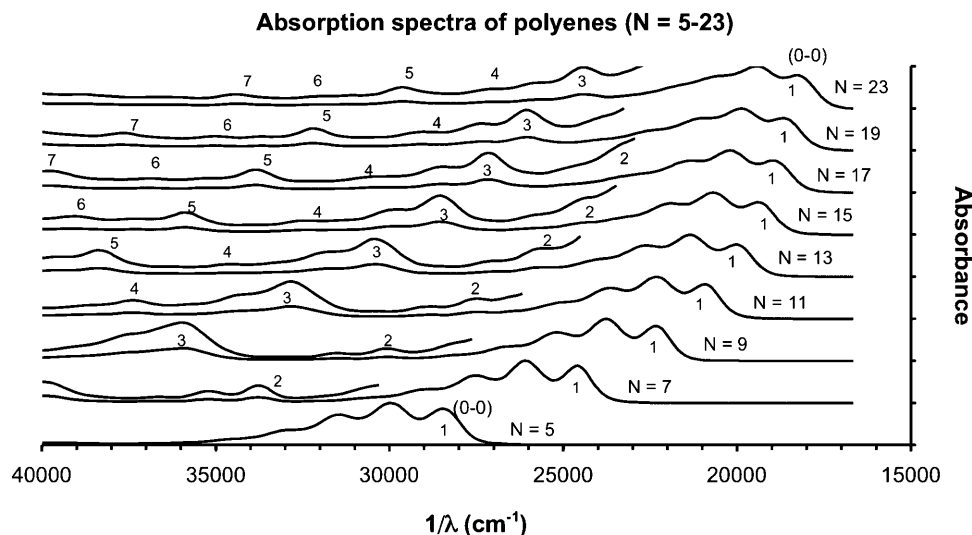


Figure 2. Room-temperature absorption spectra of polyenes $[H_2C][b_n][CH_2]$ ($n = 2, 3, 4, 5, 6, 7, 8, 9, 11$) recorded with the diode array detector in HPLC studies. N indicates the number of conjugated double bonds ($N = 2n + 1$). Expanded spectra are multiplied by 3. Integers designate electronic origins ((0–0) bands of allowed transitions).

Table 1. Wavelengths (nm) of the $E(0-0)$ Allowed Electronic Transitions for $[H_2C][b_n][CH_2]$ Species with N Double Bonds^a

N	1	2	3	4	5	6	7
5	352						
7	406	296	252				
9	448	332	278				
11	478	364	304	268	240		
13	498	391	328	290	260		
15	516	410	350	308	278	256	238
17	526	430	368	328	296	272	252
19	536		384	344	310	286	266
23	548		410		338	312	290

^a $N = 2n + 1$ = number of conjugated double bonds in the oligomer. Integers heading columns refer to the allowed electronic transitions indicated in Figures 2 and 4. Absorption spectra and positions of the (0–0) bands were obtained from the diode array detector of the HPLC in the eluting solvent (~30% $CH_3CN/70\%$ CH_3OH). Uncertainties are ± 2 nm.

and the increase in absorbance are typical of other members of this series and of what is observed in low-temperature spectra of model polyenes and carotenoids. These changes can be explained by the reduction in conformational distortion and the population of a more homogeneous distribution of mostly planar polyene structures at low temperatures.⁵ The low-temperature absorption spectrum (Figure 3) highlights the distinctive vibronic structure of polyene electronic spectra. These absorption patterns are ascribed to superpositions of absorption bands, including overtones and combination bands, of totally symmetric normal modes (a_g) involving C–C and C=C stretching.^{2,17} This vibronic structure facilitates the accurate measurement of the electronic origins both in room-temperature solutions and in low-temperature glasses.

In addition to the strong and distinctive $1^1A_g^- \rightarrow 1^1B_u^+$ transitions, the room-temperature solution spectra have sufficient vibronic resolution to allow the identification and accurate location of at least six weaker absorption bands. These features can be assigned to allowed, singlet \rightarrow singlet transitions ($1^1A_g^- \rightarrow n^1B_u^+$ or $1^1A_g^- \rightarrow m^1A_g^+$),¹⁸ and the (0–0) bands are

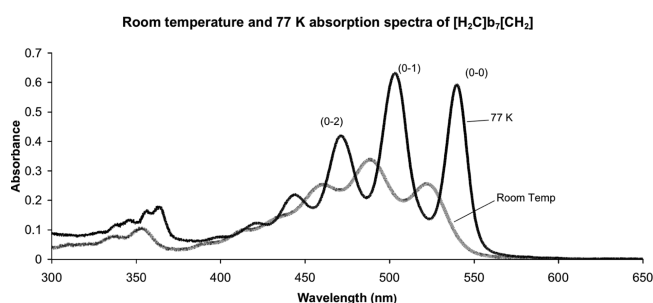


Figure 3. Room-temperature and 77 K absorption spectra of $[H_2C][b_7][CH_2]$ ($N = 15$) in 2-methyltetrahydrofuran.

indicated in Figure 2 and summarized in Table 1. The intensities of these absorptions show systematic decreases with increasing transition energy, but with an alternating pattern; i.e., transitions 1, 3, 5, and 7 are systematically stronger than transitions labeled 2, 4, and 6. The $[H_2C][b_n][CH_2]$ polyenes with even n belong to the C_{2h} point group, and polyenes with odd n belong to C_{2v} . However, the room-temperature spectra display no systematic differences in the patterns of relative intensities of the high-energy absorption bands for the C_{2h} and C_{2v} systems. The range of conjugation lengths studied and the level of resolution in the room-temperature spectra are unprecedented in polyene or carotenoid spectroscopy. The detection and analysis of these high-energy spectroscopic features significantly extends previous systematic studies of polyene and carotenoid absorption spectra, which have been limited to molecules with shorter conjugation lengths ($N \leq 13$).^{1a,2,4,6,19,20}

Polyene transition energies (ΔE) exhibit an asymptotic approach to a long polyene limit following the approximation

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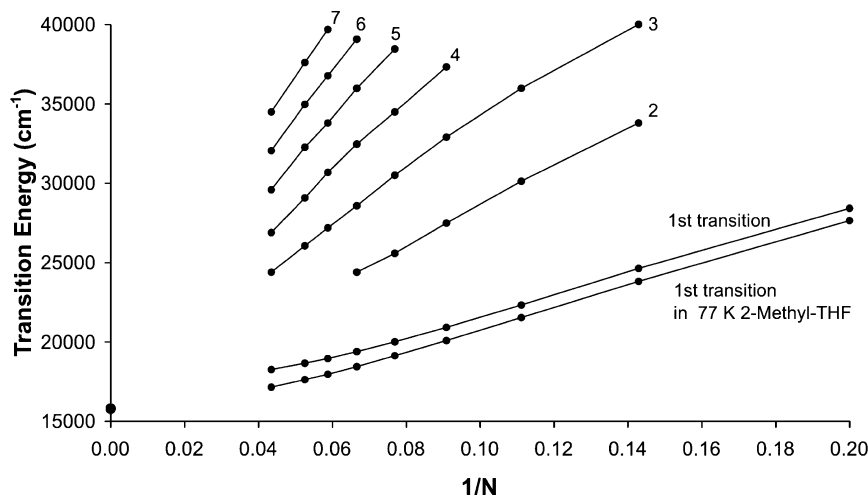


Figure 4. $E(0-0)$ vs $1/N$ for symmetry-allowed transitions of $[\text{H}_2\text{C}][\text{b}_n][\text{CH}_2]$. $n = 2, 3, 4, 5, 6, 7, 8, 9, 11$. N = number of conjugated double bonds = $2n + 1 = 5, 7, 9, 11, 13, 15, 17, 19, 23$. Spectra and $(0-0)$ transition energies were obtained from the diode array detector at maxima of HPLC peaks. The point at $1/N = 0$ is $E(0-0)$ for the first allowed transition ($1^1\text{A}_g^- \rightarrow 1^1\text{B}_u^+$) from the 77 K absorption spectrum of a related conjugated polymer that contains ethyl esters (poly(DEDPM)).²²

given in eq 16, where N is the number of conjugated double bonds and A represents the transition energy of the infinite polyene.²¹

$$\Delta E(N) = A + B/N \quad (16)$$

For example, for the $1^1\text{A}_g^- \rightarrow 1^1\text{B}_u^+$ ($0-0$) transition in di-*tert*-butyl polyenes, $A \approx 14\,000\text{ cm}^{-1}$,¹⁹ corresponding to a ($0-0$) wavelength of $\sim 700\text{ nm}$ in the long polyene limit. The unusually well resolved room-temperature spectra of these relatively planar oligoenes allow us to test the validity of eq 16 for all seven of the allowed electronic transitions noted in Figure 2. Figure 4 shows the correlation of the $E(0-0)$ transition energies with $1/N$ for the oligoenes. These plots follow the $1/N$ dependence on conjugation length indicated by eq 16. Furthermore, the slopes (B) of the higher energy transitions are systematically higher than those of lower energy transitions, and the seven transition energies appear to converge to the same long polyene limit. This convergence limit ($\sim 16\,000\text{ cm}^{-1}$) is consistent with the $1^1\text{A}_g^- \rightarrow 1^1\text{B}_u^+$ ($0-0$) band ($15\,800\text{ cm}^{-1}$) in a 77 K glass of a diethyl dipropargylmalonate (DEDPM) polymer ($1/N \approx 0$) containing a mixture of five- and six-membered rings.²² As expected, differences in absorption spectra between a DEDPM polymer containing a mixture of five- and six-membered rings and one that contains all five-membered rings disappear in the long polyene limit.

There is theoretical precedent for the asymptotic convergence of all allowed singlet \rightarrow singlet transitions in linearly conjugated systems. In the absence of alternation of carbon–carbon bond lengths along the polyene chain, simple particle-in-a-box or Hückel models predict a $1/N$ dependence of energies and $A = 0$ for all allowed electronic transitions of π -conjugated systems. The inclusion of bond alternation leads to a finite long polyene energy gap ($A \neq 0$) as described by eq 16. More sophisticated theoretical approaches to polyene excited electronic states^{18,23} lead to predictions similar to those given by eq 16, but with

higher A values for the allowed (e.g., $1^1\text{A}_g^- \rightarrow 1^1\text{B}_u^+$) transitions than for the forbidden (e.g., $1^1\text{A}_g^- \rightarrow 2^1\text{A}_g^-$) electronic transitions. These treatments also show that 2^1A_g^- , and not 1^1B_u^+ , is the lowest lying excited singlet state for longer polyene systems ($N \geq 4$).^{2,4b,c,6,17,19} The current study focuses on the symmetry-allowed transitions observed in simple absorption measurements, but future work will explore the energies of the forbidden states, particularly the low-energy 2^1A_g^- states, which play important roles in the photophysics and photochemistries of these systems.^{2,4,20}

The data presented in Figure 4 indicate a curvature for large N in the plot of the $1^1\text{A}_g^- \rightarrow 1^1\text{B}_u^+$ transition energy vs $1/N$. We can compare the room-temperature $E(0-0)$ data (obtained directly from the HPLC diode array detector) with the 77 K spectra of polyenes collected from the HPLC and reconstituted in 2-Me-THF (Figure 4). The two sets of data show parallel trends, with the low-temperature spectra shifted to lower energy, as previously noted (Figure 3). In the 77 K samples, the conformational disorder presumably has been eliminated or significantly reduced, although it may be difficult to induce all the double bonds in molecules such as the $N = 23$ species to become perfectly coplanar. Nevertheless, the lowering of $E(0-0)$ upon cooling is comparable for $N = 5$ and $N = 23$ (580 vs 920 cm^{-1}), with only a slightly larger shift in the more highly conjugated system. The apparent agreement between the extrapolation to the infinite polyene and the $E(0-0)$ measured for the $1^1\text{A}_g^- \rightarrow 1^1\text{B}_u^+$ transition of the DEDPM polymer ($1/N \approx 0$) leaves open the questions of both the suitability of the $1/N$ extrapolations and the extent to which cooling these systems to 77 K completely eliminates conformational disorder, either in the oligoenes or in the DEDPM polymers. It also should be pointed out that the simple linear extrapolation (eq 16) applies to polyenes in the gas phase and that stabilization due to the interaction between the large $1^1\text{A}_g^- \rightarrow 1^1\text{B}_u^+$ transition dipole with the solvent will lead to a red shift proportional to the solvent polarizability and the electric dipole transition moment.¹⁷ Previous work has shown that transition dipoles in these polyenes increase with conjugation length.^{10,14} Solvent stabilization of the $1^1\text{A}_g^- \rightarrow 1^1\text{B}_u^+$ transition thus would counteract the deviations due to conformational disorder and also must be accounted for in evaluating the applicability of eq 16 in the

(21) There is theoretical justification for using $\Delta E(N) = A + B/(2N + 1)$,¹⁸ but we choose to use the simpler expression for our data, which focus on systems with large N .

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long polyene limit (Figure 4). The other transitions are considerably weaker, and their $E(0-0)$ values would have a significantly smaller dependence on the solvent polarizability.

Discussion and Conclusions

We have described a method of preparing oligoenes that represent portions of polymers obtained through ring-closing metathesis polymerization of dialkyl dipropargylmalonates to give polymers that contain all five-membered rings. Regioregular oligomers containing up to 23 conjugated double bonds were synthesized through alternating Wittig-like reactions of bimetallic Mo-alkylidene compounds with aldehydes, followed by metathesis reactions between unsubstituted oligoenes with Mo(NAd)(CHCMe₂Ph)(OR_{F6})₂. Analogous reactions with NAr' species prevented formation and isolation of pure species as the polyene backbone became longer and all species became increasingly less soluble.¹⁰ We had hoped to be able to carry out syntheses without isolation and purification of polyenes at each stage, but side reactions clearly prevent this synthetic simplification, even in the adamantylimido ligand (Ad) system. The dramatic differences between the NAr' systems and the NAd systems suggest that other imido systems might yield purer products in higher yields and that even longer oligoenes might be synthesized using the methodology described here. It remains to be seen whether this new methodology can be employed for variations other than diisopropyl malonates. Although this approach employs Mo-alkylidenes as stoichiometric reagents, we can envision no more practical method of preparing oligoenes of this type with a comparable chain lengths. We hope to employ HPLC techniques in order to clarify issues concerning the nature of various impurities and to better understand the long-term stability of these molecules.

The spectroscopic properties of the newly synthesized oligoenes are in good agreement with those of less highly conjugated polyenes and carotenoids.^{2,4} The [H₂C][b_n][CH₂] systems have significant advantages for optical studies compared to previously studied systems: they have a single structure and are not prone to rapid thermal or photochemical degradation or to C=C bond isomerization. Oligoenes with methylene end groups are relatively stable and give rise to well-resolved spectra, even in room-temperature solutions. These molecules are relatively soluble in standard organic solvents, including those available for low-temperature optical studies. The primary result of the current synthetic work is a more complete picture of the optical properties of linear systems with extensive conjugation. The synthesis of oligoenes with N as large as 23 essentially doubles the range of conjugation lengths addressed in previous studies of polyenes and carotenoids.^{2,4} Further studies of the excited-state energies and lifetimes of these systems promise to provide insights on the optimization of the electronic properties of carotenoids in photosynthetic systems and a better understanding of energy transfer between carotenoids and chlorophylls.

Preliminary optical studies on the longer systems have uncovered several new, high-energy electronic transitions. The excited-state energies show $\sim 1/N$ dependences, with convergence of all the allowed electronic transitions to a common long polyene limit. This behavior is consistent with previous theoretical predictions of the electronic states of infinite polyenes^{18,23} and connects to our previous work on the low-temperature absorption spectrum of a highly conjugated diethyl dipropargylmalonate polymer.⁵ We observe small but systematic deviations of the transition energies from the simple $1/N$, long polyene

behavior. These deviations may result from persistent conformational disorder, even in low-temperature glasses of these highly purified samples. Future optical studies will explore similar systematic behavior of the energies and dynamics of "forbidden" electronic states on conjugation length, e.g., the low-lying $2^1A_g^-$ state, which plays important roles in the photochemistry and photophysics of both short and long polyenes.

Experimental Section

General Comments. All air- and moisture-sensitive materials were manipulated in oven-dried (200 °C) glassware under an atmosphere of nitrogen on a dual-manifold Schlenk line or in a Vacuum Atmospheres glovebox. HPLC-grade organic solvents were sparged with nitrogen and dried by passage through activated alumina prior to use (for diethyl ether, pentane, THF, and methylene chloride) and then stored over 4 Å Linde-type molecular sieves. NMR solvents (C₆D₆, CD₂Cl₂, and THF-*d*₈) were stored over 4 Å Linde-type molecular sieves. NMR spectra were recorded on Varian 500 or Varian 300 spectrometers. Chemical shifts for ¹H and ¹³C spectra were referenced to the residual ¹H/¹³C resonances of the deuterated solvent (¹H: C₆D₆, δ 7.16; CD₂Cl₂, δ 5.32; THF-*d*₈, δ 3.58. ¹³C: C₆D₆, δ 128.39; CD₂Cl₂, δ 54.00; THF-*d*₈, δ 67.57) and are reported as parts per million relative to tetramethylsilane. ¹⁹F NMR spectra were referenced externally to fluorobenzene (δ -113.15 ppm upfield of CFC1₃). UV-vis spectra were recorded using a Hewlett-Packard 8452A diode array spectrophotometer at approximately 22 °C. High-resolution mass spectrometry (EI and ESI) measurements were performed at the MIT Department of Chemistry Instrument Facility. Elemental analyses were performed by Columbia Analytical Services, Tucson, AZ, and Midwest Microlab LLC, Indianapolis, IN.

HPLC separations were achieved using an Agilent 1100 Series HPLC equipped with a diode array detector and a Phenomenex UltraCarb 5 ODS C18 column (4.5 × 250 mm with 5 μ m particles). The mobile phase was changed with a linear gradient from 37% acetonitrile, 48% methanol, and 15% water to 30% acetonitrile and 70% methanol 50 min after injection. The diode array detector collected spectra from 200 to 800 nm with 2-nm resolution. Individual peaks were collected and reconstituted in 2-methyl-THF and other solvents for further analytical and spectroscopic investigation.

HPLC-purified fractions were analyzed using a HiResMALDI Fourier transform mass spectrometer (IonSpec, Lake Forest, CA) equipped with a Cryomagnetics (Oak Ridge, TN) 4.7-T actively shielded superconducting magnet. The matrix solution was 1.3 M 2,5-dihydroxybenzoic acid (Sigma Aldrich; 98%, sublimed prior to use) in acetone, doped with 0.5% of 0.1 M aqueous NaCl. Samples were prepared by first applying 0.5 μ L of the matrix solution to form a thin film. Samples, dissolved in methylene chloride, then were applied to the matrix.

Ions were generated using a pulsed nitrogen laser (337 nm) and were transported from the external ion source to the closed cylindrical ICR cell using a quadrupole ion guide. The ion guide radio frequency potential and trapping delay time were optimized to transmit and trap ions of a selected mass range (optimized for m/z 1500 or 2500). A pulse of argon was introduced to the vacuum system during trapping to elevate the system pressure transiently for collisional cooling. All spectra were measured using ion accumulation techniques, where ions from three to seven successive laser shots were accumulated in the cell. A delay of 5–10 s preceded ion detection, which occurred with analyzer pressures of 1×10^{-10} – 5×10^{-10} Torr. Transients were apodized using a Blackman function and zero-filled prior to fast Fourier transformation.

Room-temperature and 77 K absorption spectra were obtained at 0.2 nm resolution using a Cary 400 UV-visible spectrophotometer. Solutions in anhydrous 2-methyl-THF in cryogenic cuvettes were placed in a quartz cryostat with flat windows. The temperature of the cryostat then was slowly lowered to form a 77 K glass. Given

the imperfect optical quality of the 2-methyl-THF glass and the attenuation/reflection of light by the multiple-windowed cryostat, the absorption spectrum of pure 2-methyl-THF at 77 K was subtracted from the raw sample spectra to obtain corrected, low-temperature absorption spectra.

$\text{Mo}(\text{NAd})(\text{CHCMe}_2\text{Ph})(\text{OR}_{\text{F}_6})_2$, $^{24} [\text{CH}_2][\text{b}][\text{O}]$, $^{14} [\text{CH}_2][\text{b}][\text{CH}_2]$, $^{14} [\text{CH}_2][\text{b}_2][\text{CH}_2]$, $^{10} [\text{CH}_2][\text{b}_4][\text{CH}_2]$, 10 and $[\text{CpRu}(\text{CH}_3\text{CN})_3]\text{PF}_6^{25}$ were prepared as described in the literature. $[\text{CH}_2][\text{b}_8][\text{CH}_2]$ ($N = 17$) is a byproduct in the synthesis of $[\text{CH}_2][\text{b}_9][\text{CH}_2]$ ($N = 19$); no attempts were made to synthesize it independently.

Observation of $[\text{Mo}^*][\text{b}][\text{Mo}^*]$. A solution of $[\text{CH}_2][\text{b}][\text{CH}_2]$ (117 mg, 0.4 mmol) in diethyl ether (3 mL) was added to a solution of $\text{Mo}(\text{NAd})(\text{CHCMe}_2\text{Ph})(\text{OR}_{\text{F}_6})_2$ (593 mg, 0.8 mmol) in diethyl ether (3 mL), and the mixture was stirred overnight. The solvent was removed *in vacuo* to yield a viscous residue whose ^1H NMR spectra (in C_6D_6) showed it to consist of largely a single product, $[\text{Mo}^*][\text{b}][\text{Mo}^*]$ (δ 12.67 ppm). Although no solid product could be isolated, addition of dme was found to yield $(\text{dme})[\text{Mo}^*][\text{b}][\text{Mo}^*]$ - (dme), as described below. $[\text{Mo}^*][\text{b}][\text{Mo}^*]$: ^1H NMR (C_6D_6) δ 12.67 (2H, $\text{Mo}=\text{CHR}$), 5.15–5.00 (m, 2H, CH, $\text{CO}_2(i\text{-Pr})$), 4.47 (4H, CH_2), 2.28 (broad, 12H, CH_2 , Ad), 1.89 (broad, 6H, CH, Ad), 1.39 (broad, 12H, CH_2 , Ad), 1.27 (12H, $\text{OCMe}(\text{CF}_3)_2$), 1.07 (d, $J = 6$ Hz, 12H, Me, $\text{CO}_2(i\text{-Pr})$); ^1H NMR (CD_2Cl_2) δ 12.93 (1H, $\text{Mo}=\text{CHR}$ *syn/anti*, 10%), 12.23 (2H, $\text{Mo}=\text{CHR}$ *syn/syn*, 80%), 12.04 (1H, $\text{Mo}=\text{CHR}$ *syn/anti*, 10%), 5.12–5.06 (m, 2H, CH, $\text{CO}_2(i\text{-Pr})$), 4.16 (4H, CH_2), 2.22 (12H, CH_2 , Ad), 2.18 (6H, CH, Ad), 1.71 (12H, CH_2 , Ad), 1.29 (12H, Me, $\text{CMe}(\text{CF}_3)_2$), 1.25 (d, $J = 6.5$ Hz, 12H, Me, $\text{CO}_2(i\text{-Pr})$).

$(\text{dme})[\text{Mo}^*][\text{b}][\text{Mo}^*](\text{dme})$: ^1H NMR (C_6D_6) δ 12.34 (2H, $\text{Mo}=\text{CHR}$), 5.20–4.95 (m, 2H, CH, $\text{CO}_2(i\text{-Pr})$), 4.51 (4H, CH_2), 3.28 (20H, overlapping CH_2 and CH_3 , dme), 2.33 (12H, CH_2 , Ad), 1.96 (6H, CH, Ad), 1.65–1.35 (m, 24H, overlapping CH_2 (Ad) and $\text{OCMe}(\text{CF}_3)_2$), 1.06 (d, $J = 6$ Hz, 12H, Me, $\text{CO}_2(i\text{-Pr})$).

Observation of $[\text{Mo}^*][\text{b}][\text{CH}_2]$. The reaction between $\text{Mo}(\text{NAd})(\text{CHCMe}_2\text{Ph})(\text{OR}_{\text{F}_6})_2$ (25 mg, 0.034 mmol) and $[\text{CH}_2][\text{b}][\text{CH}_2]$ (10 mg, 0.034 mmol) in CD_2Cl_2 in a J. Young NMR tube was monitored by ^1H NMR spectroscopy. After 30 min, alkylidene resonances ascribed to the monometallic intermediate were observed at δ 13.23 (*anti*, 20%) and 12.46 (*syn*, 80%, $J_{\text{CH}} = 123$ Hz), in addition to those for $[\text{Mo}^*][\text{CHCMe}_2\text{Ph}]$ and $[\text{Mo}^*][\text{b}][\text{Mo}^*]$. Other resonances that can be ascribed to the *syn* species are found at 6.63 (dd, $J = 17$, 11 Hz, 1H, $-\text{CH}=\text{CH}_2$), 3.56 (2H, CH_2), and 3.38 (2H, CH_2) ppm. Resonances that can be ascribed to the *anti* species are found at 6.55 (dd, $J = 17$, 11 Hz, 1H, $-\text{CH}=\text{CH}_2$), 5.43 (d, $J = 11$ Hz, 1H, $-\text{CH}=\text{CHH}$), 5.38 (d, $J = 17$ Hz, 1H, $-\text{CH}=\text{CHH}$), 3.75 (2H, CH_2), 3.62 (2H, CH_2).

Synthesis of $(\text{dme})[\text{Mo}^*][\text{b}][\text{Mo}^*](\text{dme})$. Solid $\text{Mo}(\text{NAd})(\text{CHCMe}_2\text{Ph})(\text{OR}_{\text{F}_6})_2$ (519 mg, 0.7 mmol) was added to a stirred solution of $[\text{CH}_2][\text{b}][\text{CH}_2]$ (102 mg, 0.35 mmol) in diethyl ether (5 mL). After 24 h, dme (~ 1 mL) was added to the solution, the solvent was removed by rotary evaporation, and pentane (5 mL) was added to the brown residue to yield a dark orange precipitate. The precipitate was filtered off, washed with cold pentane (3×1 mL), and dried *in vacuo*; yield 360 mg of orange-brown $(\text{dme})[\text{Mo}^*][\text{b}][\text{Mo}^*](\text{dme})$. The filtrate was concentrated *in vacuo* and stored at -30 °C overnight. The precipitate that formed yielded a second crop of 40 mg; total yield 69%. A small amount of the monometallic derivative was observed as an impurity in the ^1H NMR spectrum in CD_2Cl_2 (δ 12.39 ppm). Recrystallization of the crude product from dme yielded 343 mg (59%) of pure $(\text{dme})[\text{Mo}^*][\text{b}][\text{Mo}^*](\text{dme})$: ^1H NMR (CD_2Cl_2) δ 13.26 (2H, $\text{Mo}=\text{CHR}$, *anti/anti* isomer, <1%), 12.91 (1H, $\text{Mo}=\text{CHR}$, *syn/anti* isomer, 8%), 12.09 ($J_{\text{C-H}} = 124$ Hz, 2H, $\text{Mo}=\text{CHR}$, *syn/syn* isomer, 84%), 11.94 (1H, $\text{Mo}=\text{CHR}$, *syn/anti* isomer, 8%). The following

signals are reported for the major isomer only: δ 5.04 (septet, $J = 6.5$ Hz, 2H, CH, $\text{CO}_2(i\text{-Pr})$), 4.14 (4H, CH_2), 3.72 (8H, CH_2 , dme), 3.53 (12H, Me, OMe), 2.22 (12H, CH_2 , Ad), 2.14 (6H, CH, Ad), 1.68 (12H, CH_2 , Ad), 1.23 (d, $J = 6.5$ Hz, 12H, Me, $\text{CO}_2(i\text{-Pr})$), 1.14 (12H, Me, $\text{CMe}(\text{CF}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 247.6 ($\text{Mo}=\text{CHR}$), 171.7 ($\text{C}=\text{O}$, $\text{CO}_2(i\text{-Pr})$), 130.2 ($\text{C}=\text{C}$), 125.3 (q, $J_{\text{C-F}} = 291$ Hz, CF_3), 81.1 (septet, $J_{\text{C-H}} = 29$ Hz, $\text{OCMe}(\text{CF}_3)_2$), 77.8 (quat, $\text{N-C}(\text{Ad})$), 71.2 (OCH_2 , dme), 69.4 (OCHMe_2), 60.5 (OMe, dme), 56.5 (quat), 47.6 (CH_2), 43.7 (CH_2 , Ad), 36.3 (CH_2 , Ad), 30.2 (CH, Ad), 21.9 (Me, $\text{CO}_2(i\text{-Pr})$), 18.8 (Me, $\text{OCMe}(\text{CF}_3)_2$). ^{19}F NMR (C_6D_6) δ -77.7 (broad) overlapping -77.9 (broad); ^1H NMR (C_6D_6) δ 12.34 (2H, $\text{Mo}=\text{CHR}$): δ 5.20–4.95 (m, 2H, CH, $\text{CO}_2(i\text{-Pr})$), 4.51 (4H, CH_2), 3.28 (20H, overlapping CH_2 and CH_3 , dme), 2.33 (12H, CH_2 , Ad), 1.96 (6H, CH, Ad), 1.65–1.35 (m, 24H, overlapping CH_2 (Ad) and $\text{OCMe}(\text{CF}_3)_2$), 1.06 (d, $J = 6$ Hz, 12H, Me, $\text{CO}_2(i\text{-Pr})$). Anal. Calcd for $\text{C}_{59}\text{H}_{82}\text{F}_{24}\text{Mo}_2\text{N}_2\text{O}_{12}$: C, 42.71; H, 4.98; N, 1.69. Found: C, 42.93; H, 5.02; N, 1.68.

Synthesis of $[\text{H}_2\text{C}][\text{b}_3][\text{CH}_2]$. Aldehyde $[\text{H}_2\text{C}][\text{b}][\text{O}]$ (128 mg, 0.43 mmol) was added to a stirred solution of $(\text{dme})[\text{Mo}^*][\text{b}][\text{Mo}^*]$ - (dme) (360 mg, 0.06 mmol) in Et_2O (30 mL), and the solution was stirred overnight. No color change was observed. The solvent was removed *in vacuo*. An aliquot of the viscous residue was dissolved in 0.7 mL of CD_2Cl_2 , and the solution was transferred to a J. Young NMR tube. According to ^1H NMR (CD_2Cl_2) spectroscopy, no Mo -alkylidene and aldehyde species are present. Chromatography on a silica gel column, using a mixture of Et_2O :hexane = 1:3 as eluent, yielded 117 mg (66% yield) of trimer $[\text{H}_2\text{C}][\text{b}_3][\text{CH}_2]$ as a yellow powder.

Synthesis of Diisopropyl 3-(1-Hydroxy-5,5-bis(isopropoxycarbonyl)octa-2,7-diynyl)-4-vinylcyclopent-3-ene-1,1-dicarboxylate. Diisopropyl 2,2-di(prop-2-ynyl)malonate (1.71 g, 5.70 mmol) was added to a stirred volume of THF (200 mL) in a 500 mL Schlenk flask. The solution was cooled to -78 °C, and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF, 6.45 mL, 6.45 mmol) was added with a syringe. After 1 h, $[\text{H}_2\text{C}][\text{b}][\text{O}]$ (1.9 g, 6.45 mmol) was added, and the mixture was warmed to room temperature overnight. Water (10 mL) was added to the mixture, and the solvent was removed *in vacuo*. Water (100 mL) was added to the residue, and the organics were extracted with diethyl ether (3×50 mL). The combined organic layers were dried over MgSO_4 , and the solvent was removed on a rotary evaporator. The crude product was purified by column chromatography using a mixture of Et_2O :hexanes = 2:3 as eluent; yield 2.3 g (64%) of the pale yellow alcohol ($R_f = 0.27$): ^1H NMR (C_6D_6) δ 6.45 (dd, $J = 18$, 11, 1H, $\text{CH}_2=\text{CHR}$), 5.15–5.12 (broad m, 1H, $\text{R}_2\text{CH}(\text{OH})$), 5.10–4.91 (m, 6H, $=\text{CH}_2$ overlapping with CH, $\text{CO}_2(i\text{-Pr})$), 3.72 (d, $J = 18$, 1H, CH_2), 3.62 (d, $J = 18$, 1H, CH_2), 3.46 (d, $J = 17$, 1H, CH_2), 3.41 (d, $J = 17$, 1H, CH_2), 3.33 (d, $J = 2$, 2H, CH_2), 3.30 (d, $J = 3$, 2H, CH_2), 1.68 (t, $J = 3$, 1H, $\equiv\text{CH}$), 1.51 (d, $J = 5$, OH), 1.10–0.97 (overlapping m, 24H, Me, $\text{CO}_2(i\text{-Pr})$); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 171.9 ($\text{C}=\text{O}$), 171.5 ($\text{C}=\text{O}$), 168.70 ($\text{C}=\text{O}$), 168.67 ($\text{C}=\text{O}$), 137.5, 134.4, 129.9, 116.5 ($=\text{CH}_2$), 83.5, 80.6, 79.4, 72.4, 69.9, 69.8, 69.22, 69.19, 58.4, 57.5, 57.2, 41.5 (CH_2), 41.1 (CH_2), 23.6 (CH_2), 23.4 (CH_2), 21.9 (Me), 21.82 (Me), 21.76 (Me); HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{42}\text{NaO}_9$ ($\text{M} - \text{Na}^+$) 581.2721, found 581.2743; calcd for $\text{C}_{62}\text{H}_{84}\text{NaO}_{18}$ ($2\text{M} - \text{Na}^+$) 1139.5555, found 1139.5558.

Synthesis of (E)-Diisopropyl 3-(2-(4,4-Bis(isopropoxycarbonyl)-2-vinylcyclopent-1-enyl)vinyl)-4-formylcyclopent-3-ene-1,1-dicarboxylate ($[\text{H}_2\text{C}][\text{b}_2][\text{O}]$). Diisopropyl 3-(1-hydroxy-5,5-bis(isopropoxycarbonyl)octa-2,7-diynyl)-4-vinylcyclopent-3-ene-1,1-dicarboxylate (2.1 g, 3.72 mmol), 200 mL of acetone, and 5 mL of water were added to a 500 mL Schlenk flask, and the solution was warmed to 60 °C. $[\text{RuCp}(\text{NCMe})_3]\text{PF}_6$ (912 g, 2.03 mmol) was added, and the mixture was stirred for 2 h. Besides the spot corresponding to the starting alcohol ($R_f = 0.26$), an additional spot ($R_f = 0.42$) could be observed on TLC (using a mixture of Et_2O :hexane = 2:3 as eluent). $[\text{RuCp}(\text{NCMe})_3]\text{PF}_6$ (120 mg, 0.26 mmol) was added, and the heating was continued. After 1 h, the TLC spot corresponding to unreacted starting alcohol was still observed. The

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mixture was stirred overnight at room temperature and warmed to 60 °C after 9 h. $[\text{RuCp}(\text{NCMe})_3]\text{PF}_6$ (163 mg, 0.36 mmol) was added and the heating continued. After 1 h, the reaction appeared to be complete. The solvent was removed by rotary evaporation, and the crude reaction mixture was purified by silica gel column chromatography (pretreated with NEt_3) using a Et_2O :hexane = 2:3 mixture as eluent, yielding 430 mg (21% yield) of off-white crystals: ^1H NMR (C_6D_6) δ 9.72 (1H, CHO), 6.66 (2H, $\text{RCH}=\text{CHR}$), 6.43 (dd, $J = 17, 11$ Hz, 1H, $\text{CH}_2=\text{CHR}$), 5.14–4.90 (m, 6H, $=\text{CH}_2$ overlapping with CH, $\text{CO}_2(i\text{-Pr})$), 3.67 (2H, CH_2), 3.54 (2H, CH_2), 3.52 (2H, CH_2), 3.47 (2H, CH_2), 1.06–0.92 (overlapping m, 24H, Me, $\text{CO}_2(i\text{-Pr})$); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 186.1 ($\text{CH}=\text{O}$), 171.5 ($\text{C}=\text{O}$), 171.2 ($\text{C}=\text{O}$), 152.4, 140.7, 136.9, 135.6, 129.8, 128.9, 121.6, 117.8 ($=\text{CH}_2$), 69.64 (OCHMe_2), 69.57 (OCHMe_2), 57.6 (quat), 57.3 (quat), 42.5 (CH_2), 42.0 (CH_2), 41.7 (CH_2), 40.1 (CH_2), 21.8 (Me), 21.80 (Me), 21.76 (Me), 21.68 (Me); HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{43}\text{O}_9$ ($\text{M} - \text{H}^+$) 559.2902, found 559.2909; calcd for $\text{C}_{62}\text{H}_{85}\text{O}_{18}$ ($2\text{M} - \text{H}^+$) 1117.5736, found 1117.5767; calcd for $\text{C}_{31}\text{H}_{42}\text{NaO}_9$ ($\text{M} - \text{Na}^+$) 581.2721, found 581.2746; calcd for $\text{C}_{62}\text{H}_{84}\text{NaO}_{18}$ ($2\text{M} - \text{Na}^+$) 1139.5555, found 1139.5646.

Synthesis of $[\text{H}_2\text{C}][\text{b}_3][\text{CH}_2]$. Solid $[\text{H}_2\text{C}][\text{b}_2][\text{O}]$ (112 mg, 0.2 mmol) in Et_2O (5 mL) was added to a stirred solution of (dme) $[\text{Mo}^*][\text{b}][\text{Mo}^*](\text{dme})$ (166 mg, 0.1 mmol) in Et_2O (10 mL). The solution turned brown immediately, and an orange precipitate was observed after 1 h. The mixture was stirred overnight. The solvent was removed *in vacuo*, and an aliquot of the orange residue was dissolved in CD_2Cl_2 (0.7 mL) and transferred to a J. Young NMR tube. The ^1H NMR (CD_2Cl_2) spectrum showed no unreacted starting materials, the major component of the mixture being unsubstituted oligoene species. Pentane (3 mL) was added to the residue, and the orange precipitate was triturated for 1 h and filtered through a frit, yielding 88 mg (65% yield) of $[\text{H}_2\text{C}][\text{b}_3][\text{CH}_2]$ as an orange powder: HRMS (MALDI-TOF) m/z calcd for $\text{C}_{77}\text{H}_{104}\text{NaO}_{20}$ ($\text{M} - \text{Na}^+$) 1371.7013, found 1371.7368; UV/vis $\lambda_{\text{max}} = 455$ nm, $\epsilon = 10.7 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ in CH_2Cl_2 .

Synthesis of $[\text{Mo}^*][\text{b}_2][\text{Mo}^*]$. Solid $\text{Mo}(\text{NAd})(\text{CHCMe}_2\text{Ph})(\text{OR}_{\text{F}_6})_2$ (346 mg, 0.47 mmol) was added to a stirred solution of $[\text{CH}_2][\text{b}_2][\text{CH}_2]$ (130 mg, 0.235 mmol) in Et_2O (10 mL). The solution turned brown immediately, and after 2 h, a brick-red precipitate was observed. After 48 h, the solvent was removed by rotary evaporation, and pentane (5 mL) was added to the residue. The precipitate was filtered off, washed with pentane (3×0.5 mL), and dried *in vacuo*; yield 220 mg of brick-red product. The filtrate was concentrated *in vacuo*. Pentane (5 mL) was added to the filtrate, and more brick-red precipitate (30 mg) was recovered, for a 62% total yield. The following NMR spectra are reported for the major (*syn/syn*) isomer of $[\text{Mo}^*][\text{b}_2][\text{Mo}^*]$ only: ^1H NMR ($\text{THF}-d_8$) δ 12.65 (2H, $\text{Mo}=\text{CHR}$), 6.37 (2H, $\text{CHR}=\text{CHR}$), 5.03 (septet, $J = 6$ Hz, 4H, CH, $\text{CO}_2(i\text{-Pr})$), 3.85 (4H, CH_2), 3.68 (4H, CH_2), 2.24 (12H, CH_2 , Ad), 2.14 (6H, CH, Ad), 1.70 (12H, CH_2 , Ad), 1.28–1.21 (overlapping m, 36H, $\text{CMe}(\text{CF}_3)_2 + \text{Me}$, $\text{CO}_2(i\text{-Pr})$); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$) δ 256.2 ($\text{Mo}=\text{CHR}$), 171.6 ($\text{C}=\text{O}$, $\text{CO}_2(i\text{-Pr})$), 145.1, 126.2 (q, $J_{\text{C-F}} = 291$ Hz, CF_3), 125.4, 123.2, 82.0–81.0 (m, $\text{OCMe}(\text{CF}_3)_2$), 77.2 (quat, $\text{NC}(\text{Ad})$), 69.5 (OCHMe_2), 57.7 (quat), 48.2 (CH_2), 44.6 (CH_2 , Ad), 40.7 (CH_2), 36.8 (CH_2 , Ad), 30.9 (CH, Ad), 22.0 (Me, $\text{CO}_2(i\text{-Pr})$), 21.9 (Me, $\text{CO}_2(i\text{-Pr})$), 19.2 (Me, $\text{OCMe}(\text{CF}_3)_2$); ^{19}F NMR (CD_2Cl_2) δ –78.8 (broad), –79.2 (broad). Anal. Calcd for $\text{C}_{66}\text{H}_{82}\text{F}_{24}\text{Mo}_2\text{N}_2\text{O}_{12}$ ($[\text{Mo}^*][\text{b}_2][\text{Mo}^*]$): C, 45.47; H, 4.74; N, 1.61. Anal. Calcd for $\text{C}_{49}\text{H}_{63}\text{F}_{12}\text{MoNO}_{10}$ ($[\text{Mo}^*][\text{b}_2][\text{CH}_2]$): C, 51.18; H, 5.52; N, 1.22. Found: C, 49.98; H, 5.92, N, 1.80.

Synthesis of $[\text{Mo}^*][\text{b}_3][\text{Mo}^*]$. Solid $\text{Mo}(\text{NAd})(\text{CHCMe}_3)(\text{OR}_{\text{F}_6})_2$ (83 mg, 0.12 mmol) was added to a stirred solution of $[\text{CH}_2][\text{b}_3][\text{CH}_2]$ (50 mg, 0.06 mmol) in pentane (10 mL). A red precipitate was observed after 2–3 min. The volatiles were removed *in vacuo*, pentane (10 mL) was added to the residue, and the mixture was stirred overnight. The next day, the precipitate was filtered on a frit, washed with pentane (3×3 mL), and dried *in vacuo*, yielding

90 mg (74% yield) of brick-red powder of spectroscopically pure $[\text{Mo}^*][\text{b}_3][\text{Mo}^*]$.

In an alternative synthesis, solid $[\text{Mo}^*]\text{CHCMe}_2\text{Ph}$ (234 mg, 0.32 mmol) was added to a stirred solution of $[\text{CH}_2][\text{b}_3][\text{CH}_2]$ (130 mg, 0.16 mmol) in Et_2O (10 mL). The solution turned brown immediately, and after 1 h, a brick-red precipitate was observed. After 48 h, the solvent was removed by rotary evaporation, and the residue was triturated in pentane (5 mL) for 2 h. The precipitate was filtered on a frit, washed with pentane (3×3 mL), and dried *in vacuo*, yielding 280 mg (88% yield) of brick-red powder. According to ^1H and ^{13}C NMR ($\text{THF}-d_8$) spectroscopy, the major component was bimetallic $[\text{Mo}^*][\text{b}_3][\text{Mo}^*]$, but monometallic $[\text{Mo}^*][\text{b}_3][\text{CH}_2]$ could be observed as an impurity.

The following NMR spectra are reported for the major isomer of $[\text{Mo}^*][\text{b}_3][\text{Mo}^*]$ (*syn/syn*) only: ^1H NMR (CD_2Cl_2) δ 13.19 ($\text{Mo}=\text{CHR}$, 13%), 13.16 ($\text{Mo}=\text{CHR}$, 8%), 12.63 ($J_{\text{C-H}} = 129$ Hz, $\text{Mo}=\text{CHR}$, 79%), 6.53 (d, $J = 15$ Hz, 2H, $\text{CHR}_1=\text{CHR}_2$), 6.42 (d, $J = 15$ Hz, 2H, $\text{CHR}_1=\text{CHR}_2$), 5.10–4.97 (m, 6H, CH, $\text{CO}_2(i\text{-Pr})$), 3.79 (4H, CH_2), 3.70 (4H, CH_2), 3.33 (4H, CH_2), 2.20 (12H, CH_2 , Ad), 2.17 (6H, CH, Ad), 1.70 (12H, CH_2 , Ad), 1.38 (broad, 12H, CH_3 , $\text{CMe}(\text{CF}_3)_2$), 1.28–1.17 (m, 36H, CH_3 , $\text{CO}_2(i\text{-Pr})$); ^1H NMR ($\text{THF}-d_8$) δ 12.63 ($J_{\text{C-H}} = 123$ Hz, 2H, $\text{Mo}=\text{CHR}$, *syn/syn* isomer), 6.69 (d, $J = 15.3$ Hz, 2H, $\text{CHR}_1=\text{CHR}_2$), 6.59 (d, $J = 15.3$ Hz, 2H, $\text{CHR}_1=\text{CHR}_2$), 5.07–4.97 (m, 6H, CH, $\text{CO}_2(i\text{-Pr})$), 3.83 (4H, CH_2), 3.75 (4H, CH_2), 3.35 (4H, CH_2), 2.24 (12H, CH_2 , Ad), 2.14 (6H, CH, Ad), 1.70 (12H, CH_2 , Ad), 1.38–1.20 (overlapping m, 48H, $\text{CMe}(\text{CF}_3)_2 + \text{CH}_3$, $\text{CO}_2(i\text{-Pr})$); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$) δ 257.0 ($\text{Mo}=\text{CHR}$), 171.77 ($\text{C}=\text{O}$, $\text{CO}_2(i\text{-Pr})$), 171.4 ($\text{C}=\text{O}$, $\text{CO}_2(i\text{-Pr})$), 144.4, 138.4, 126.2 (q, $J_{\text{C-F}} = 292$ Hz, CF_3), 126.1, 124.1, 123.6, 82.0–81.0 (m, $\text{OCMe}(\text{CF}_3)_2$), 77.2 (quat, $\text{NC}(\text{Ad})$), 69.6 (OCHMe_2), 57.9 (quat), 57.5 (quat), 48.37 (CH_2), 44.6 (CH_2 , Ad), 41.8 (CH_2), 40.6 (CH_2), 36.8 (CH_2 , Ad), 30.8 (CH, Ad), 22.1 (CH_3 , $\text{CO}_2(i\text{-Pr})$), 21.9 (CH_3 , $\text{CO}_2(i\text{-Pr})$), 21.8 (CH_3 , $\text{CO}_2(i\text{-Pr})$), 19.2 (CH_3 , $\text{OCMe}(\text{CF}_3)_2$); ^{19}F NMR (CD_2Cl_2) δ –80.7 (broad), –81.0 (broad). Anal. Calcd for $\text{C}_{59}\text{H}_{82}\text{F}_{24}\text{Mo}_2\text{N}_2\text{O}_{12}$: C, 48.46; H, 5.12; N, 1.40. Found: C, 48.60; H, 5.37; N, 1.44.

Reaction of $[\text{Mo}^*][\text{b}_3][\text{Mo}^*]$ with $[\text{H}_2\text{C}][\text{b}][\text{O}]$. Synthesis of

Pentamer $[\text{H}_2\text{C}][\text{b}_5][\text{CH}_2]$. Solid $[\text{Mo}^*][\text{b}_3][\text{Mo}^*]$ (163 mg, 0.081 mmol) was added to a stirred solution of aldehyde $[\text{H}_2\text{C}][\text{b}][\text{O}]$ (48 mg, 0.162 mmol) in 10 mL of Et_2O . The solution turned brown, and the mixture was stirred overnight. An orange precipitate was observed. An aliquot of the mixture was concentrated *in vacuo*, the residue was dissolved in C_6D_6 (0.5 mL), and the solution was transferred to a J. Young NMR tube. The ^1H NMR spectrum indicated that all the aldehyde and Mo -alkylidene starting materials had been consumed, and resonances that could be assigned to unsubstituted oligomers were observed. The product mixture was filtered off, and the precipitate was washed with pentane (3×1 mL) and dried *in vacuo*, yielding 20 mg of $[\text{H}_2\text{C}][\text{b}_5][\text{CH}_2]$. The filtrate was concentrated *in vacuo* and passed through an alumina column using a mixture of Et_2O :hexane = 3:1 as eluent, in air. An orange fraction eluted with this solvent mixture. After removal of the solvent, the residue was washed with Et_2O (2×1 mL) and dried *in vacuo*, yielding 30 mg (46% total yield) of orange $[\text{H}_2\text{C}][\text{b}_5][\text{CH}_2]$: HRMS (ESI) m/z calcd for $\text{C}_{77}\text{H}_{105}\text{O}_{20}$ ($\text{M} - \text{H}^+$) 1349.7194, found 1349.7156; calcd for $\text{C}_{77}\text{H}_{104}\text{NaO}_{20}$ ($\text{M} - \text{Na}^+$) 1371.7013, found 1371.6987.

Synthesis of $[\text{Mo}^*][\text{b}_5][\text{Mo}^*]$. Solid $\text{Mo}(\text{NAd})(\text{CHCMe}_2\text{Ph})(\text{OR}_{\text{F}_6})_2$ (95 mg, 0.128 mmol) was added to a stirred slurry of $[\text{CH}_2][\text{b}_5][\text{CH}_2]$ (86 mg, 0.064 mmol) in Et_2O (10 mL). No color change was observed. After 24 h, a dark red precipitate was observed. The next day, the solvent was removed *in vacuo*, and the residue was triturated with pentane (10 mL). The precipitate was filtered off, washed with pentane (3×3 mL), and dried *in vacuo*, yielding 87 (54% yield) mg of dark red powder. According to ^1H and ^{13}C NMR ($\text{THF}-d_8$) spectroscopy, the major component was $[\text{Mo}^*][\text{b}_5][\text{Mo}^*]$, but impurities containing $\text{CH}=\text{CH}_2$ could be observed. Anal. Calcd for $\text{C}_{111}\text{H}_{142}\text{F}_{24}\text{Mo}_2\text{N}_2\text{O}_{24}$ ($[\text{Mo}^*][\text{b}_5][\text{Mo}^*]$):

C, 52.57; H, 5.64; N, 1.10. Calcd for $C_{94}H_{123}F_{12}MoNO_{22}$ ($[Mo^*][b_5]-[CH_2]$): C, 58.11; H, 6.38; N, 0.72. Found: C, 55.21; H, 6.23; N, 0.71.

The filtrate was concentrated *in vacuo*, pentane (5 mL) was added to the dark red residue, and the precipitate formed was triturated overnight. The next day, the precipitate was filtered on a frit and dried *in vacuo*, yielding 15 mg of a dark red powder. 1H NMR (CD_2Cl_2) δ 13.20 (Mo=CHR, 12%), 13.16 (Mo=CHR, 13%), 12.52 (Mo=CHR, 75%), 6.75 (CHR=CHR, 2H), 6.72 (CHR=CHR, 2H), 6.53 (d, J = 15, 2H, $CHR_1=CHR_2$), 6.47 (d, J = 15 Hz, 2H, $CHR_1=CHR_2$), 5.10–4.98 (m, 10H, CH, $CO_2(i-Pr)$), 3.75 (CH_2 , 4H), 3.72 (CH_2 , 4H), 3.46 (CH_2 , 4H), 3.37 (CH_2 , 4H), 3.25 (CH_2 , 4H), 2.20 (CH_2 , 12H, Ad), 2.18 (CH, 6H, Ad), 1.70 (CH_2 , 12H, Ad), 1.37 (broad, 12H, CH_3 , $CMe(CF_3)_2$), 1.29–1.19 (m, 60H, CH_3 , $CO_2(i-Pr)$); 1H NMR (THF- d_8) δ 13.30 (Mo=CHR, 26%), 12.62 (Mo=CHR, 74%), 6.92–6.80 (m, 4H), 6.74–6.58 (m, 4H), 5.08–4.95 (m, 10H, CH, $CO_2(i-Pr)$), 3.87 (CH_2 , 4H), 3.70 (CH_2 , 4H), 3.52 (CH_2 , 4H), 3.37 (CH_2 , 4H), 3.22 (CH_2 , 4H), 2.24 (CH_2 , 12H, Ad), 2.14 (CH, 6H, Ad), 1.71 (CH_2 , 12H, Ad), 1.27 (broad, 12H, CH_3 , $CMe(CF_3)_2$), 1.26–1.20 (m, 60H, CH_3 , $CO_2(i-Pr)$); $^{13}C\{^1H\}$ NMR (THF- d_8), major species δ 257.3 (Mo=CHR), 171.9 (C=O), 171.8 (C=O), 171.7 (C=O), 144.1, 144.0, 139.4, 139.2, 138.4, 137.7, 137.3, 126.2 (q, J_{C-F} = 291 Hz, CF_3), 126.4, 124.6, 82.0–81.0 (m, $OCMe(CF_3)_2$), 77.2 (quat, NC(Ad)), 69.8–69.4 (broad, $OCHMe_2$), 57.9 (quat), 57.81 (quat), 57.79 (quat), 48.5 (CH_2), 44.7 (CH_2 , Ad), 42.4 (CH_2), 42.3 (CH_2), 41.7 (CH_2), 40.5 (CH_2), 36.8 (CH_2 , Ad), 30.9 (CH, Ad), 22.2–21.8 (broad, CH_3 , $CO_2(i-Pr)$), 19.2 (broad, $OCMe(CF_3)_2$); ^{19}F NMR (THF- d_8); major species δ –78.1. Anal. Calcd for $C_{111}H_{142}F_{24}Mo_2N_2O_{24}$ ($[Mo^*][b_5]-[Mo^*]$): C, 52.57; H, 5.64; N, 1.10. Anal. Calcd for $C_{96}H_{122}F_{24}Mo_2N_2O_{20}$ ($[Mo^*][b_4][Mo^*]$): C, 50.75; H, 5.41; N, 1.23. Found: C, 50.75; H, 5.39; N, 1.25.

Synthesis of $[H_2C][b_6][CH_2]$. Solid $[Mo^*][b_2][Mo^*]$ (100 mg, 0.057 mmol) was added to a stirred solution of $[H_2C][b_2][O]$ (64 mg, 0.099 mmol) in Et_2O (10 mL). The solution turned brown immediately, and orange precipitate was observed after 1 h. The mixture was stirred overnight. The solvent was removed *in vacuo*, and 10 mL of a Et_2O :pentane = 2:3 mixture was added to the residue, yielding a dark orange precipitate, which was filtered off, washed with pentane (3 \times 1 mL), and dried *in vacuo*, yielding 39 mg (42% yield) of $[H_2C][b_6][CH_2]$ as a dark orange powder: 1H NMR (CD_2Cl_2) δ 6.90 (dd, J = 17, 11 Hz, 2H, $CH_2=CHR$), 6.74 (broad, 6H, =CHR), 6.69 (4H, =CHR), 5.244 (d, J = 17 Hz, 2H, $HCH=CHR$), 5.236 (d, J = 11 Hz, 2H, $HCH=CHR$), 5.10–4.97 (m, 12H, CH, $i-Pr$), 3.37 (12H, CH_2), 3.33 (4H, CH_2), 3.31 (4H, CH_2), 3.24 (4H, CH_2), 1.29–1.20 (m, 72H, Me, $i-Pr$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 171.9 (C=O), 171.84 (C=O), 171.80 (C=O), 137.7, 137.6, 137.5, 137.34, 137.31, 136.4, 130.0, 123.9, 123.72, 123.68, 123.4, 116.2 (=CH₂), 69.8 ($OCHMe_2$), 69.7 ($OCHMe_2$), 57.6 (quat), 57.47 (quat), 57.45 (quat), 41.90 (CH_2), 41.88 (CH_2), 41.77 (CH_2), 41.5 (CH_2), 41.4 (CH_2), 21.89 (Me), 21.87 (Me), 21.83 (Me); HRMS (MALDI-TOF) m/z calcd for $C_{92}H_{124}NaO_{24}$ ($M - Na^+$) 1635.8380, found 1635.9256; UV/vis λ_{max} = 476 nm, ϵ = 8.7×10^4 cm^{–1} M^{–1} in CH_2Cl_2 .

Synthesis of $[H_2C][b_7][CH_2]$. Solid $[H_2C][b_2][O]$ (45 mg, 0.08 mmol) was added to a stirred solution of $[Mo^*][b_3][Mo^*]$ (80 mg, 0.04 mmol) in Et_2O (20 mL). The solution turned brown immediately, and a dark orange precipitate was observed after 1 h. The mixture was stirred overnight. An aliquot of the mixture was concentrated *in vacuo* and dissolved in C_6D_6 (0.5 mL). The 1H NMR spectrum indicated that all the aldehyde and Mo–alkylidene starting materials had been consumed in the reaction, and resonances that could be assigned to unsubstituted oligomers were observed. The solvent from the bulk sample was removed *in vacuo*, and the residue was triturated in pentane (10 mL). The precipitate was filtered off, washed with pentane (3 \times 1 mL), and dried *in vacuo*, yielding 62 mg (83% yield) of red-orange $[H_2C][b_7][CH_2]$: 1H NMR (CD_2Cl_2) δ 6.90 (dd, J = 17, 11 Hz, 2H, $CH_2=CHR$), 6.74 (4H, =CHR), 6.73 (4H, =CHR), 6.70 (4H, =CHR), 5.25 (d, J = 17 Hz, 2H, $HCH=CHR$), 5.24 (d, J = 11 Hz, 2H, $HCH=CHR$), 5.06–5.01

(m, 14H, CH, $i-Pr$), 3.37 (16H, CH_2), 3.33 (4H, CH_2), 3.31 (4H, CH_2), 3.24 (4H, CH_2), 1.27–1.23 (m, 84H, Me, $i-Pr$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 171.9 (C=O), 171.83 (C=O), 171.79 (C=O), 137.65, 137.62, 137.60, 137.4, 137.34, 137.30, 136.4, 129.9, 123.9, 123.7, 123.4, 116.2 (=CH₂), 69.8 ($OCHMe_2$), 69.7 ($OCHMe_2$), 57.6 (quat), 57.5 (quat), 57.4 (quat), 41.9 (CH_2), 41.8 (CH_2), 41.5 (CH_2), 41.4 (CH_2), 21.88 (Me), 21.864 (Me), 21.855 (Me), 21.83 (Me); HRMS (ESI) m/z calcd for $C_{107}H_{144}NaO_{28}$ ($M - Na^+$) 1899.9742, found 1899.9845; calcd for $C_{107}H_{144}NaO_{28}$ ($M - 2Na^+$) 961.4814, found 961.4817; UV/vis λ_{max} = 489 nm, ϵ = 17.0×10^4 cm^{–1} M^{–1} in CH_2Cl_2 .

Synthesis of $[H_2C][b_9][CH_2]$. Solid $[Mo^*][b_5][Mo^*]$ (100 mg, 0.039 mmol) was added to a stirred solution of $[H_2C][b_2][O]$ (44 mg, 0.079 mmol) in Et_2O (10 mL). No color change was observed. The mixture was stirred for 72 h and filtered. The precipitate was washed with pentane (3 \times 1 mL), and dried *in vacuo*, yielding 50 mg of $[H_2C][b_9][CH_2]$ as a dark red powder. The filtrate was concentrated *in vacuo*, and 5 mL of a mixture of Et_2O :hexane = 2:3 was added to the residue in air. The dark red precipitate that was formed was filtered through a frit, washed with Et_2O (3 \times 1 mL), and dried *in vacuo*, yielding 40 mg (96% total yield) of dark red $[H_2C][b_9][CH_2]$: 1H NMR (CD_2Cl_2) δ 6.90 (dd, J = 17, 11 Hz, 2H, $CH_2=CHR$), 6.74 (8H, =CHR), 6.72 (4H, =CHR), 6.68 (4H, =CHR), 5.24 (d, J = 17 Hz, 2H, $HCH=CHR$), 5.23 (d, J = 11 Hz, 2H, $HCH=CHR$), 5.10–4.94 (m, 18H, CH, $i-Pr$), 3.37 (24H, CH_2), 3.32 (4H, CH_2), 3.30 (4H, CH_2), 3.23 (4H, CH_2), 1.28–1.18 (m, 108H, Me, $i-Pr$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 171.9 (C=O), 171.83 (C=O), 171.80 (C=O), 137.75–137.56 (broad), 137.5, 137.35, 137.30, 136.4, 129.9, 123.9, 123.8–123.6 (broad), 123.4, 116.2 (=CH₂), 69.8 ($OCHMe_2$), 69.7 ($OCHMe_2$), 57.6 (quat), 57.5 (quat), 57.4 (quat), 41.9 (CH_2), 41.8 (CH_2), 41.6 (CH_2), 41.4 (CH_2), 21.90 (Me), 21.87 (Me), 21.8 (Me); HRMS (ESI) m/z calcd for $C_{137}H_{184}NaO_{36}$ ($M - 2Na^+$) 1226.1193, found 1226.1189; UV/vis λ_{max} = 510 nm, ϵ = 11.1×10^4 cm^{–1} M^{–1} in CH_2Cl_2 .

Synthesis of $[Mo^*][b_7][Mo^*]$. Solid $Mo(NAd)(CHCMe_2Ph)-(OR_F)_2$ (36 mg, 0.048 mmol) was added to a stirred slurry of $[CH_2][b_7][CH_2]$ (45 mg, 0.024 mmol) in Et_2O (5 mL). No color change was observed. After 24 h, a dark red precipitate was observed. The precipitate was filtered, washed with Et_2O (three times, 3 mL), and dried *in vacuo*, yielding 35 mg of dark red powder. The filtrate was concentrated *in vacuo*, pentane (5 mL) was added to the dark red residue, and the precipitate formed was triturated overnight. The next day, the precipitate was filtered off and dried *in vacuo* to yield 20 mg (74% total yield) of a dark red $[Mo^*][b_7][Mo^*]$, which was sparingly soluble in both CD_2Cl_2 and THF- d_8 : 1H NMR (CD_2Cl_2) δ 13.19 (Mo=CHR, 16%), 13.16 (Mo=CHR, 14%), 12.50 (Mo=CHR, 70%), 6.74 (4H), 6.73 (2H), 6.69 (2H), 6.54 (d, J = 15, 2H, $CHR_1=CHR_2$), 6.46 (d, J = 15 Hz, 2H, $CHR_1=CHR_2$), 5.10–4.98 (m, 14H, CH, $CO_2(i-Pr)$), 3.75 (CH_2 , 4H), 3.74 (CH_2 , 4H), 3.47 (CH_2 , 4H), 3.37 (CH_2 , 8H), 3.24 (CH_2 , 8H), 2.20 (CH_2 , 12H, Ad), 2.18 (CH, 6H, Ad), 1.70 (CH_2 , 12H, Ad), 1.37 (broad, 12H, CH_3 , $CMe(CF_3)_2$), 1.29–1.19 (m, 84H, CH_3 , $CO_2(i-Pr)$); 1H NMR (THF- d_8) δ 13.19 (Mo=CHR, 14%), 13.16 (Mo=CHR, 18%), 12.54 (Mo=CHR, 68%), 6.88 (broad, 10H, $CHR=CHR$), 6.78–6.63 (m, 4H, $CHR=CHR$), 5.10–4.88 (m, 14H, CH, $CO_2(i-Pr)$), 3.88 (4H, CH_2), 3.70 (4H, CH_2), 3.53 (4H, CH_2), 3.37 (4H, CH_2), 3.34 (4H, CH_2), 3.23 (8H, CH_2), 2.24 (12H, CH_2 , Ad), 2.14 (6H, CH, Ad), 1.73 (12H, CH_2 , Ad), 1.32–1.15 (broad, 96H, overlapping CH_3 , $CMe(CF_3)_2$ + $CO_2(i-Pr)$); Selected $^{13}C\{^1H\}$ NMR (THF- d_8) (major species) δ 171.8 (C=O), 171.7 (C=O), 171.6 (C=O), 143.9, 139.4, 138.6, 138.4–137.5 (broad), 137.1, 126.3, 126.2 (q, J_{C-F} = 280 Hz, CF_3), 124.7–124.1 (broad), 77.2 (quat, NC(Ad)), 69.7–69.3 (broad, $OCHMe_2$), 57.9 (quat), 57.8 (quat), 57.7 (quat), 48.4 (CH_2), 44.6 (CH_2 , Ad), 42.5–41.6 (broad, CH_2), 40.4 (CH_2), 36.7 (CH_2 , Ad), 30.8 (CH, Ad), 22.1–21.7 (broad, Me, $CO_2(i-Pr)$), 19.1 (broad, $OCMe(CF_3)_2$).

Synthesis of $[H_2C][b_{11}][CH_2]$. Solid $[Mo^*][b_7][Mo^*]$ (50 mg, 0.016 mmol) was added to a stirred solution of aldehyde $[H_2C][b_2][O]$ (18 mg, 0.032 mmol) in Et_2O (20 mL). No color

change was observed. The mixture was stirred for 48 h and then filtered. The precipitate was washed with Et₂O (three times, 1 mL) and dried *in vacuo*, yielding 34 mg (72% yield) of [H₂C][b₁₁][CH₂] as a dark red powder that was sparingly soluble in both CD₂Cl₂ and THF-*d*₈: ¹H NMR (THF-*d*₈) δ 6.96 (dd, *J* = 17, 11 Hz, 2H, CH₂=CHR), 6.88 (20H, =CHR), 5.19 (d, *J* = 17 Hz, 2H, HCH=CHR), 5.15 (d, *J* = 11 Hz, 2H, HCH=CHR), 5.06–4.92 (m, 22H, CH, *i*-Pr), 3.42–3.18 (broad, 44H, CH₂), 1.30–1.15 (m, 132H, Me, *i*-Pr); ¹³C{¹H} NMR (THF-*d*₈) δ 172.0 (C=O), 171.9 (C=O), 171.8 (C=O), 138.5–138.1 (broad), 137.7, 137.4, 137.3, 136.8, 124.6–124.2 (broad), 102.8 (=CH₂), 69.7–69.5 (broad, OCHMe₂), 58.0 (quat), 57.9 (quat), 42.5–42.1 (broad, CH₂), 41.9 (CH₂), 22.2–21.8 (broad, Me); HRMS (ESI) *m/z* calcd for

C₁₆₇H₂₂₄NaO₄₄ (*M* – 2Na⁺) 1490.2554, found 1490.2579; UV/vis λ_{max} = 524 nm, ε = 14.4 × 10⁴ cm^{–1} M^{–1} in CH₂Cl₂.

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