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Z-Selective Ring-Opening Metathesis Polymerization of 3-Substituted Cyclooctenes by Monoaryloxide Pyrrolide Imido Alkylidene (MAP) Catalysts of Molybdenum and Tungsten

by

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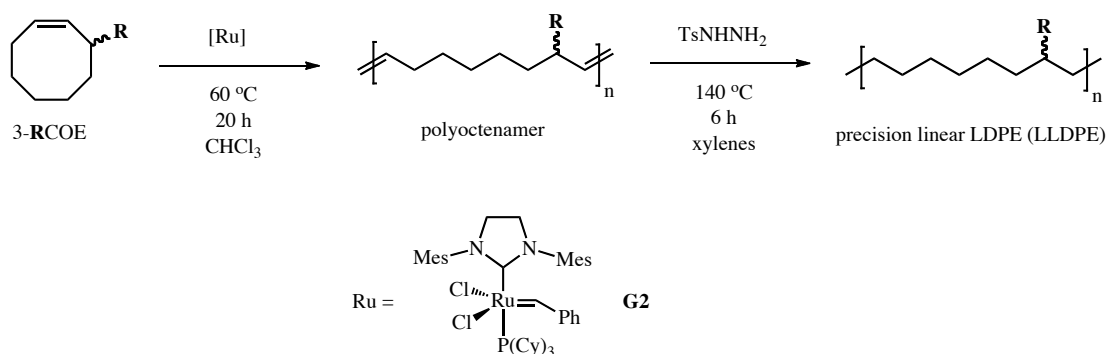
Abstract

Ring-opening metathesis polymerization of a series of 3-substituted cyclooctenes (3-MeCOE, 3-HexCOE, and 3-PhCOE) initiated by various Mo and W MAP complexes leads to *cis*,HT-poly(3-RCOE) polymers. The apparent rate of polymerization of 3-HexCOE by W(N-t-Bu)(CH-t-Bu)(Pyr)(OHMT) (**1c**) (Pyr = pyrrolide; OHMT = O-2,6-Mesityl₂C₆H₃) is greater than the rate of polymerization by Mo(N-t-Bu)(CH-t-Bu)(Pyr)(OHMT) (**1b**), but both gave the same *cis*,HT polymer structures. Formation of HT-poly(3-RCOE) employing **1c** takes place *via* propagating species in which the R group (methyl, hexyl, or phenyl) is on C2 of the propagating alkylidene chain, a type of intermediate that has been modeled through the preparation of W(N-t-Bu)(CHCHMeEt)(Pyr)(OHMT). The rate of ROMP is exceedingly sensitive to steric factors, e.g., W(N-t-Bu)(CH-t-Bu)(Me₂Pyr)(OHMT), the dimethylpyrrolide analog of **1c**, essentially did not polymerize 3-HexCOE at 22 °C. Upon cooling a sample of W(N-t-Bu)(CHCHMeEt)(Pyr)(OHMT) and 3-methyl-1-pentene in CDCl₃ to -20 °C the alkylidene resonances for W(N-t-Bu)(CHCHMeEt)(Pyr)(OHMT) disappear and resonances that can be ascribed to protons in a *syn*_α/*syn*_{α'} disubstituted TBP metallacyclobutane complex appear. 3-Methyl-1-pentene is readily lost from this metallacycle on the NMR time scale at RT.

Introduction

A report in 2011¹ described the *trans*- and head-to-tail-selective (*trans*,HT) ring-opening metathesis polymerization (ROMP) of a series of 3-substituted cyclooctenes (3-RCOE; R = Me, Et, Hex, Ph) employing ruthenium catalyst **G2** as the initiator (Scheme 1). This is a relatively rare example² of a ROMP by a ruthenium-based catalyst that results in formation of a polymer with a high degree of stereoselectivity and regioselectivity. Hydrogenation of the resulting poly(3-RCOE) samples led to precision linear low-density polyethylenes (LLDPEs). Racemic monomers were employed and no stereoselectivity between neighboring monomer units in the polymer was reported.

Scheme 1. ROMP of 3-substituted cyclooctenes followed by hydrogenation.



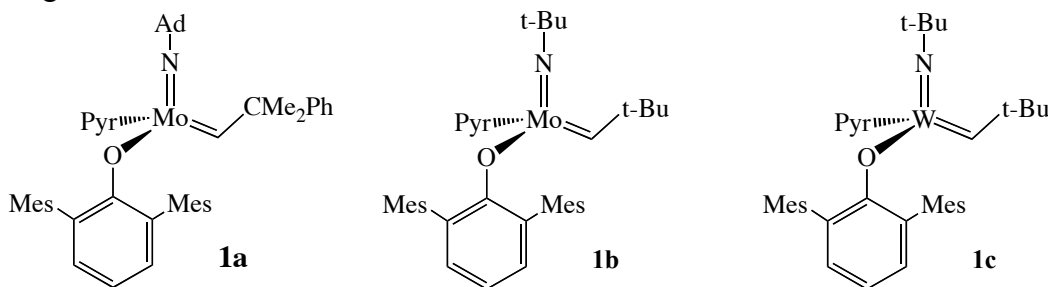
Certain Mo-based and W-based MonoAryloxy Pyrrolide (MAP) catalysts of the type $\text{M}(\text{NR})(\text{CHR}')(\text{Pyrrolide})(\text{OR}'')$ are highly selective for forming polymers with *Z*-olefin linkages from substituted norbornenes and norbornadienes.^{3,4} Even cyclooctene and 1,5-cyclooctadiene could be polymerized *Z*-selectively to give *cis*-polycyclooctene and *cis*-poly-1,5-cyclooctadiene;^{3a} we believe these to be the first reports of the *Z*-selective ROMP of each of these monomers.⁵ MAP catalysts also can produce polymers from racemic 2,3-disubstituted norbornenes to give *cis*,*syndiotactic*,*alt* polymer structures in which the chirality of the monomer alternates (*alt*) along the *cis*,*syndiotactic* chain.^{3c} (An alternating structure results from inversion of the configuration of a metal center with each insertion.) We became interested in whether *Z*-selective ROMP using

MAP catalysts could be extended to the 3-RCOE monomers and report the results of our first investigations here.

RESULTS

Synthesis of a Molybdenum *t*-Butylimido MAP Catalyst

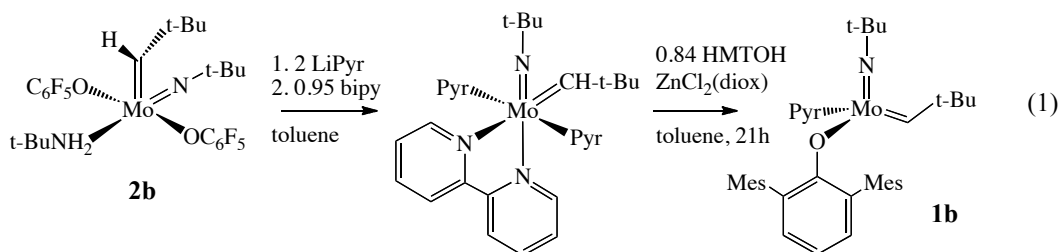
We began our investigations with the adamantylimido complex $\text{Mo}(\text{NAd})(\text{CHCMe}_2\text{Ph})(\text{Pyr})(\text{OHMT})$ ($\text{OHMT} = 2,6\text{-dimesitylphenoxide}$, **1a**; see below), because it has been shown to be highly *Z*-selective for ROMP of substituted norbornadienes.^{3a} The recently prepared alkylimido MAP catalyst of tungsten, $\text{W}(\text{N-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{Pyr})(\text{OHMT})$ (**1c**),⁶ was also chosen to study for comparative purposes. The polymerization behavior by unknown $\text{Mo}(\text{N-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{Pyr})(\text{OHMT})$ (**1b**) could provide a direct comparison between Mo (**1b**) and W (**1c**) in the context of ROMP of 3-RCOEs. Therefore, we first explored the possibility of synthesizing **1b**.



Osborn, *et al.*⁷ reported that the reaction between $\text{Mo}(\text{N-}t\text{-Bu})_2(\text{CH}_2\text{-}t\text{-Bu})_2$ and hexafluoro-2-propanol generated $\text{Mo}(\text{N-}t\text{-Bu})(\text{CH-}t\text{-Bu})[\text{OCH}(\text{CF}_3)_2]_2(\text{t-BuNH}_2)$, which he reported to be an oil, in a yield of 80%. We obtained $\text{Mo}(\text{N-}t\text{-Bu})_2(\text{CH}_2\text{-}t\text{-Bu})_2$ in 92% yield from $\text{Mo}(\text{N-}t\text{-Bu})_2\text{Cl}_2(1,2\text{-dimethoxyethane})$ as described in the literature,⁸ and from it $\text{Mo}(\text{N-}t\text{-Bu})(\text{CH-}t\text{-Bu})[\text{OCH}(\text{CF}_3)_2]_2(\text{t-BuNH}_2)$ (**2a**) in 26% yield. In contrast to Osborn's report we obtained **2a** as an off-white solid. The low yield is possibly a consequence of the high solubility of **2a** in pentane. A search for compounds analogous to **2a** that could be obtained in higher yields led to the finding that $\text{Mo}(\text{N-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OC}_6\text{F}_5)_2(\text{t-BuNH}_2)$ (**2b**) can be obtained in 84% yield upon treating $\text{Mo}(\text{N-}t\text{-Bu})_2(\text{CH}_2\text{-}t\text{-Bu})_2$ with two equivalents of pentafluorophenol. This synthesis is related to the synthesis of **2b** through selective protonation

of the more basic *t*-butylimido group by pentafluorophenol in the mixed imido species, $\text{Mo}(\text{N}-2,6\text{-i-Pr}_2\text{C}_6\text{H}_3)(\text{N}-t\text{-Bu})(\text{CH}_2\text{CMe}_2\text{R})_2$ ($\text{R} = \text{Me}$ or Ph).⁹

Treatment of **2b** with two equivalents of lithium pyrrolide in toluene did not appear to form an isolable bispyrrolide complex in high yield. We have found that syntheses of parent bispyrrolide complexes of this general type are often problematic, for reasons that are not yet clear; syntheses that employ 2,2'-bipy adducts as intermediates have been more successful.¹⁰ Therefore, two equivalents of lithium pyrrolide were added at -35 °C to **2b** in diethyl ether (eq 1). Subsequent addition of 2,2'-bipy led to formation of $\text{Mo}(\text{N}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{Pyr})_2(\text{bipy})$ (eq 1). The MAP complex, $\text{Mo}(\text{N}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{Pyr})(\text{OHMT})$ (**1b**), was then formed upon treatment of a solution of isolated $\text{Mo}(\text{N}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{Pyr})_2(\text{bipy})$ with a mixture of $\text{ZnCl}_2(\text{dioxane})$ and 0.84 equivalents of HMTOH in toluene followed by sonication of the mixture for 21 h.⁶



An X-ray structural study of **1b** revealed the expected structure with the neopentylidene in the *syn* orientation with the *t*-butyl group pointing toward to the imido group (Figure S11, Supporting Information). Bond distances and angles are similar to those expected for molybdenum and tungsten imido alkylidene complexes of this general type.⁶ Crystallographic details can be found in the Supporting Information.

ROMP of 3-RCOE ($\text{R} = \text{Me}$, Hex , Ph)

Three 3-RCOE monomers (where $\text{R} = \text{methyl}$, *n*-hexyl, or phenyl) were polymerized in bulk by $\text{Mo}(\text{NAd})(\text{CHCMe}_2\text{Ph})(\text{Pyr})(\text{OHMT})$ (**1a**), $\text{Mo}(\text{N}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{Pyr})(\text{OHMT})$ (**1b**), and $\text{W}(\text{N}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{Pyr})(\text{OHMT})$ (**1c**) at monomer to catalyst ratios of $\sim 5000:1$ ($\text{R} = \text{Me}$, Hex) or $\sim 1000:1$ ($\text{R} = \text{Ph}$). The results are summarized in Table 1. ROMP of 5000 equivalents of bulk

3-MeCOE or 3-HexCOE with initiators **1a-1c** at room temperature led to conversion of monomer to >98% *cis*,HT-poly(3-RCOE) (HT = head-to-tail), which was isolated by pouring the reaction mixture into methanol. 3-HexCOE is polymerized more slowly than 3-MeCOE as a consequence of the steric demand of the hexyl group relative to the methyl group. Three days at room temperature gave a 78% conversion of 3-HexCOE to *cis*,HT-poly(3-HexCOE) with **1a** (0.02 mol%) as the initiator. Polymerization of 3-HexCOE could be carried out with 0.01 mol% **1c** (78% conversion in 2 days at room temperature). The rate of polymerization of 3-PhCOE at 0.02 mol% catalyst loading was impractically slow at 22 °C for all catalysts, so 0.1 mol% catalyst loadings were employed. Initiator **1c** appears to be the most active initially for polymerization of 3-PhCOE, but the conversion after 24 h was similar to the conversion employing **1b**. Polymerization of 3-HexCOE (5000 equiv) employing **1c** at 60 °C yielded poly(3-HexCOE) (46% conversion after 4 h, 71% conversion after 1 day), compared with a 25% conversion after 4 h at room temperature. Proton NMR spectra of samples prepared at 60 °C were identical to those of poly(3-HexCOE) prepared with **1c** at room temperature.

Proton and ¹³C NMR spectra of isolated polymers display the number of resonances expected for a *cis*,HT structure, i.e., eight backbone resonances (two olefinic and six aliphatic) and one, six, and four side-chain resonances for R = Me and Hex, and Ph, respectively (Figure 1). Head-to-tail regioregularity was confirmed employing gCOSY NMR methods; the olefinic protons (Figures 1a, 1b, 1c) were found to be coupled with a $J_{HH} \sim 10$ Hz, consistent with formation of *cis*,HT linkages. A 500 MHz ¹H NMR spectrum of a mixture of *cis*,HT-poly(3-HexCOE) (prepared employing **1a** as the initiator) and *trans*,HT-poly(3-HexCOE) (prepared as reported in the literature¹) clearly shows resonances for all four of the expected olefinic protons in the mixture of two polymers (Figure 2).

Traces of olefinic products (~1% P2 in Figure 3a for 3-MeCOE) were observed after 1 h in addition to the major *cis*,HT-poly(3-MeCOE) product when initiators **1b** and **1c** were employed. These impurities are proposed to be either cyclic oligomers arising from backbiting during

Table 1. Summary of ROMP reactions in bulk 3-RCOE to give >98% *cis*,HT polymer.^a

R	n ^b	Mo(NAd) (1a)		Mo(N-t-Bu) (1b)		W(N-t-Bu) (1c)	
		time	%conv	time	%conv	time	%conv
Me	5000	30m	48	5m	47	5m	80
		4h	97	1h	98	1h	>99
Hex	5000	4h	10	4h	19	4h	25
		1d	42	1d	35	1d	70
Ph	1000	4h	1	4h	24	4h	36
		1d	22	1d	86	1d	87

^a All polymerizations carried out at 22 °C. Conversions are reported as the average of two runs. ^b Ratio of monomer to initiator.

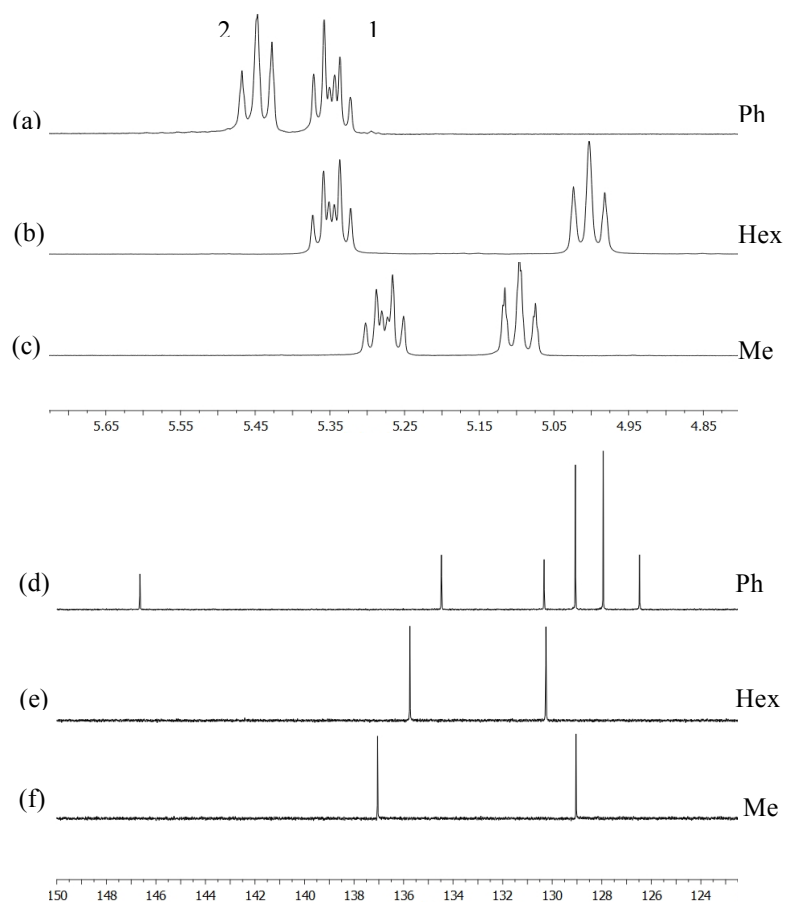


Figure 1. Olefinic (¹H) and olefinic and aryl(¹³C) regions of the ¹H(top) (500 MHz in CDCl₃) and ¹³C(bottom) NMR spectra of isolated *cis*,HT-poly(3-RCOE) (R = Ph(a,d), Hex(b,e), Me(c,f); >98% *cis*) prepared using **1c**.

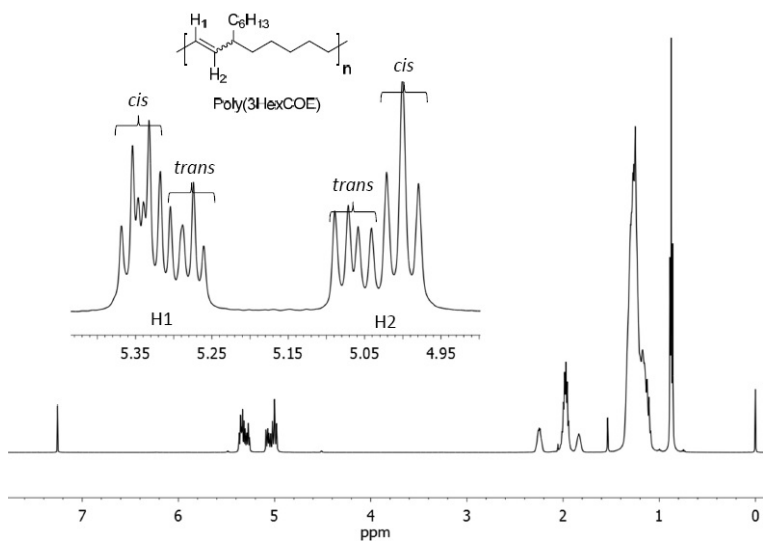


Figure 2. ^1H NMR spectrum (500 MHz in CDCl_3) of a mixture of *cis*-poly(3-HexCOE) prepared using **1a** and *trans*-poly(3-HexCOE) prepared using **G2**.

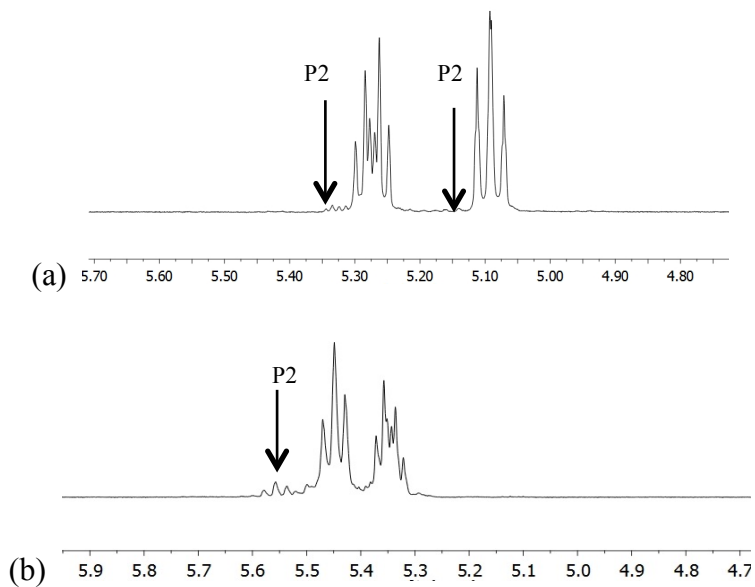


Figure 3. (a) ^1H NMR spectrum (500 MHz in CDCl_3) of the olefinic region of *cis*,HT-poly(3-MeCOE) prepared from **1c** after 1 h. (b) ^1H NMR spectrum (500 MHz in CDCl_3) of *cis*,HT-poly(3-PhCOE) prepared from **1c** (1% loading) after 4 h.

polymerization or regioisomers having HH/TT linkages; *trans*,HT-poly(3-MeCOE)¹ was not observed. gCOSY NMR studies of samples similar to those employed for the spectra in Figures 3 were inconclusive in terms of distinguishing whether the impurities arise from *cis*-HT or from *cis*-HH/TT linkages. We have observed that polymerization in C₆D₆ at concentrations of 0.6-1.1 M monomer and 1-7 mol% **1a** not only is relatively slow, but produces a complex mixture of products that we propose are formed when backbiting competes with chain propagation under these conditions.

Minor olefinic resonances also appear for an additional product (P2 in Figure 3b) during polymerization of 3-PhCOE. The percentage of P2 increased relative to *cis*,HT-poly(3-PhCOE) between 4 and 24 h as determined by analysis of aliquots by ¹H NMR spectroscopy. When 1% catalyst **1c** was employed, >99% of the monomer was converted to *cis*,HT-poly(3-PhCOE) after 4 hours and the ratio of *cis*,HT-poly(3-PhCOE) to P2 was found to be 8:1. After 24 h, P2 was largely consumed and the relative ratio of *cis*,HT-poly(3-PhCOE) to P2 increased to 27:1; therefore, it appears that P2 is consumed to yield *cis*,HT-poly(3-PhCOE). P2 impurities were not found in the polymers that had been isolated from methanol, consistent with them being cyclic oligomers formed through backbiting.

The rate of opening an unsubstituted metallacyclobutane ring in a molybdacyclobutane complex to yield a proposed methyldene/ethylene intermediate has been proposed to be at least 1000x greater than the rate of opening a tungstacyclobutane complex to yield a methyldene/ethylene intermediate.¹¹ These findings led to the proposal that Mo catalysts are inherently faster than W analogs if breakdown of the metallacyclic ring is rate limiting. However, for ROMP of 3-HexCOE, tungsten (**1c**) is more efficient than molybdenum (**1b**) (See Table 1). One possible reason is that the metallacyclobutanes in these ROMP reactions are substituted and therefore cannot be compared to unsubstituted metallacyclobutane complexes; the rate limiting steps in the two circumstances might be different. It also should be noted that the intermediate in the published studies¹¹ may *not* be a methyldene/ethylene complex, but another type of square pyramidal metallacyclobutane in which a metallacycle α carbon atom is in the apical position.¹²

Size Exclusion Chromatography (SEC) data for several polymers prepared with **1c** are shown in Table 2. The number-average molar mass (M_n) for poly(3-MeCOE) and poly(3-HexCOE) samples did not precisely agree with the calculated values, perhaps because of a combination of backbiting and k_p/k_i issues (*vide infra*). In all cases, high molecular masses were achieved and the dispersity values for the polymers prepared during these studies varied between ~ 1.2 and 2.0 . Hydrogenation of isolated *cis*,HT-poly(3-HexCOE) and *cis*,HT-poly(3-MeCOE) samples generated with **1a** gave linear polyethylenes that are identical to those obtained through hydrogenation of *trans*,HT-poly(3-RCOE).¹

Table 2. Characterization Data for *cis*-HT-poly(3-RCOE) prepared using ~ 0.02 mol% initiator **1c** at 22 °C.^a

R	Equiv 3-RCOE	% conv	M_n (calcd) ^a	M_n (SEC LS) ^b	M_n (SEC PS) ^c	PDI
Me	4975	99	612		706	1.9
Hex	4884	67	636	430	416	1.7
Hex ^d	4884	63	598	480	375	1.8

^a M_n calcd = (MW of 3-RCOE) \times [3-RCOE]₀/[initiator]₀ \times conversion in units of kg mol⁻¹; ^bDetermined by SEC using THF as an eluent at 25 °C and a multiangle light scattering detector. ^cDetermined by SEC using THF as an eluent at 25 °C and refractive index detector relative to PS standards. ^dThis sample had been stored for several weeks in air.

The nature of the propagating species and k_p/k_i

In polymerizations of 3-RCOE monomers, four propagating alkylidenes are possible (Figure 4). The first type has the R group on the C2 carbon atom of the alkylidene chain. Two diastereomers of this type, **A** and **B**, are possible. If both diastereomers are present the alkylidene proton resonances in **A** and **B** could have different chemical shifts, but each would be a doublet if the alkylidene proton is coupled only to the proton on C2. The second type of possible propagating species, **C** and **D**, has the R group on C7 in the chain. The configuration at C7 in **C** and **D** is unlikely to make any difference in the chemical shift of the alkylidene proton, and a triplet (or perhaps a doublet of doublets) pattern should be observed. Both *syn* and *anti* isomers of any alkylidene could be present in theory, but so far the vast majority of 14e MAP species have

been found to contain only *syn* alkylidene isomers. (One exception are complexes that contain a 2,6-dimesitylphenylimido ligand.¹³)

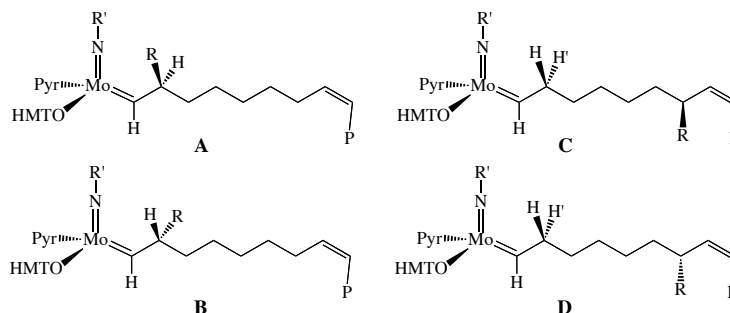


Figure 4. Four possible propagating species for a given configuration at the metal center (P = polymer). Only the *syn* alkylidene isomers are depicted.

When 100 equivalents of 3-RCOE (R = Hex or Ph) or 200 equivalents of 3-MeCOE are added to **1c** and each polymerization is allowed to proceed essentially to completion (>95%) then samples are obtained whose proton NMR spectra in the alkylidene proton region are shown in Figures 5a, 5b, and 5c. In addition to a resonance for any remaining **1c**, two doublets are observed for the alkylidene proton in the propagating species in each case. (A weak resonance for the minor diastereomer is found at ~8.25 ppm in Figure 5b.) All resonances have ¹⁸³W satellites (S = 1/2, ~14% of the total) with *J*_{HW} values of ~20 Hz. No other alkylidene resonances with significant intensities that can be ascribed to propagating species are present. All data are consistent with two propagating species **A** and **B** (or their enantiomers) being present in poly(3-MeCOE) (resonances at ~8.29 and ~8.19 ppm), in poly(3-HexCOE) (resonances at ~8.26 (weak) and ~8.09 ppm), and in poly(3-PhCOE) (resonances at ~8.45 and ~8.40 ppm). The origin of the additional fine structure in the resonances at 8.19, 8.09, and 8.40 ppm in Figures 5a, 5b, and 5c, respectively, has not yet been determined.

It is relatively straightforward, although not highly accurate, to calculate *k_p/k_i* from the data shown in Figure 5.¹⁴ The relevant equation¹⁵ is $M - M_0 = -r(I - I_0) + rI_0 \ln(I/I_0)$, where $r = k_p/k_i$, M_0 and M are the initial and final monomer concentrations, and I_0 and I are the initial and

final initiator concentrations, respectively. When M goes to 0 at some time t , and if $r \gg 1$, then $r = (M_0/I_0)/[I/I_0 - \ln(I/I_0) - 1]$. For $R = \text{Me}$, $M_0/I_0 = 200$ and $I/I_0 = 0.40$, from which $r (= k_p/k_i)$ is calculated to be 630. (This value was obtained from an analogous 600 MHz spectrum in which the two overlapping resonances in Figure 5a are better resolved.) For $R = \text{Hex}$, $M_0/I_0 = 100$, $I/I_0 = 0.37$, and r is calculated to be 280. For $R = \text{Ph}$, $M_0/I_0 = 100$, $I/I_0 = 0.23$, and $r = 140$. The decrease in k_p/k_i ($630 \rightarrow 280 \rightarrow 140$) as the size of R increases ($\text{Me} \rightarrow \text{Hex} \rightarrow \text{Ph}$) is expected on the basis of increased steric hindrance in the propagating species. The overall rate also decreases in this order as a consequence of increased steric hindrance overall, as noted earlier.

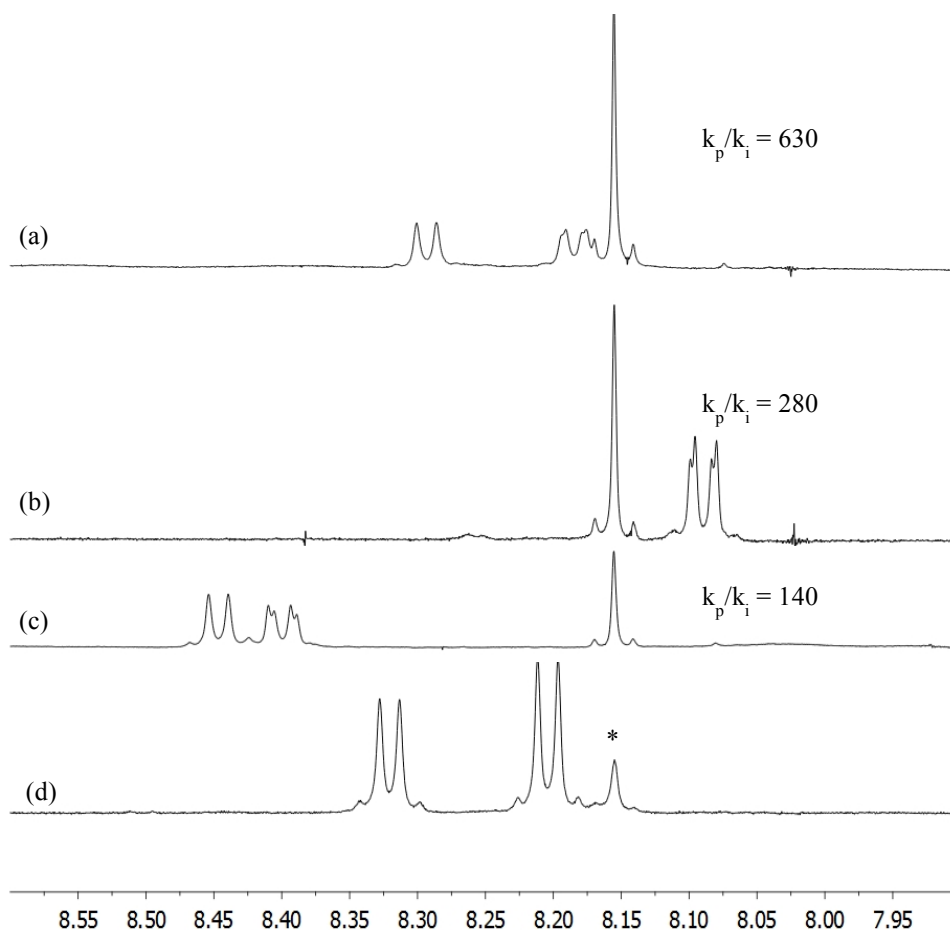


Figure 5. Proton NMR 500 MHz spectra in the alkylidene proton region of poly(3-RCOE) samples in CDCl_3 prepared through polymerization of x equivalents of bulk 3-RCOE with **1c** (*): (a) $R = \text{Me}$, $x = 200$; (b) $R = \text{Hex}$, $x = 100$; (c) $R = \text{Ph}$, $x = 100$. (d) NMR spectrum in CDCl_3 of $\text{W}(\text{N}-t\text{-Bu})(\text{CHCHMeEt})(\text{Pyr})(\text{OHMT})$ prepared through addition of 3 equiv of 3-methyl-1-pentene to **1c** (*) followed by removal of all free alkenes *in vacuo*.

The value for k_p corresponds to the sum of the rate constants for reaction of both diastereomers **A** and **B** with either enantiomer of the monomer, i.e., $k_p = k_{pA} + k_{pB}$. Both **A** and **B** must react with one enantiomer or the other of the monomer to give an HT insertion product, but at present no details are known. For example, it is not known whether the incoming monomer must add only *trans* to the pyrrolide, as has been proposed in other ROMP polymerizations with MAP species,^{3a-d} or whether this "rule" is not necessarily followed in some circumstances.^{3f}

Consistent with the spectra in Figures 5a-5c, two doublets are also observed upon treating **1c** with 3-methyl-1-pentene, followed by removing all alkenes *in vacuo* (Figure 5d). The alkylidene resonances for the two diastereomers of W(N-t-Bu)(CHCHMeEt)(Pyr)(OHMT) are observed at ~8.20 and ~8.32 ppm in a ratio of ~4:3 with approximately the same J_{HW} (20 Hz) and $^2J_{HH}$ (10 Hz) as found in Figures 5a-5c. Decoupling the CH_β alkylidene proton in each diastereomer (at 3.66 and 3.74 ppm) led to collapse of the doublet structures at ~8.20 and ~8.32 ppm, respectively, to singlets, as expected. Note that no fine structure is observable on either resonance in Figure 5d.

We noticed that in the presence of 3-methyl-1-pentene the alkylidene resonances for the two diastereomers of W(N-t-Bu)(CHCHMeEt)(Pyr)(OHMT) (Figure 5d) are broadened to a degree that depends upon the amount of 3-methyl-1-pentene present, which suggests that 3-methyl-1-pentene is reacting with W(N-t-Bu)(CHCHMeEt)(Pyr)(OHMT) in a degenerate metathesis that results in exchange of alkylidenes. Upon cooling a sample of W(N-t-Bu)(CHCHMeEt)(Pyr)(OHMT) and 3-methyl-1-pentene in CDCl₃ to -20 °C the alkylidene resonances disappear and resonances that can be ascribed to protons in a TBP metallacyclobutane complex appear at ~4.30, ~0, and ~-1.0 ppm (Figure 6). We assign these resonances to H_α and H'_α (at ~4.30 ppm) and to the two inequivalent H_β protons (not shown) in the TBP metallacycle drawn in Figure 6. In order for the two α metallacycle protons to be inequivalent a mirror plane must not be present, i.e., either the CHMeEt groups are *R,R/S,S* with the nitrogen of the pyrrolide ligand (N_p , not shown in the drawing) in the equatorial plane in a symmetrical position with respect to the two α carbon atoms of the metallacycle, or *R,S/S,R* with N_p located off

to one side or the other (with $N_P-W-C_\alpha \neq N_P-W-C_{\alpha'}$). The latter structure could be described as either a "distorted TBP" or a square pyramidal (SP') form of the metallacyclobutane, an example of which has been crystallographically characterized recently.¹⁶ However, the SP' structure is not

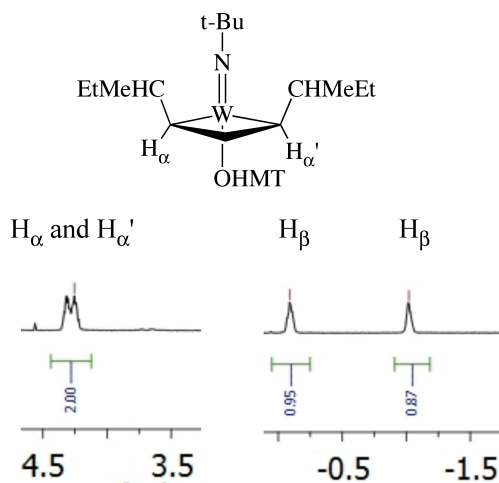


Figure 6. Partial proton NMR spectrum in the metallacyclobutane region after addition of 3 equiv of 3-methyl-1-pentene to **1c** in $CDCl_3$ and cooling the sample to $-20\text{ }^\circ\text{C}$. (The pyrrolide ligand is omitted in the drawing.)

observed *in solution* as a consequence of its ready interconversion with the "symmetric" TBP structure. Therefore, we conclude that the CHMeEt groups have the same configuration (*R,R/S,S*) in the structure shown in Figure 6. "Degenerate" metathesis reactions that consist of methyldiene transfer via α,α' disubstituted metallacyclobutane complexes have long been proposed to be facile.¹⁷ To our knowledge these observations are the first that directly reveal the ease of alkylidene exchange in an environment that restricts formation of metallacycles to those in which the α and α' substituents are *syn* with respect to the imido ligand ($syn_\alpha/syn_{\alpha'}$).

An abbreviated drawing of a proposed $syn_\alpha/syn_\beta/syn_{\alpha'}$ metallacycle intermediate in the ROMP of 3-RCOE monomers is shown in Figure 7 (**E**) along with the unobserved mechanistic alternative (**F**). Of the three substituents on the carbon atoms in the metallacyclobutane ring, only one is a methylene group in **E** (on C_β) but two are methylene groups in **F** (on C_α and $C_{\alpha'}$). Therefore, on the surface **E** would appear to be the sterically more demanding situation, yet the reaction proceeds via **E** (*vide supra*). Clearly the steric interactions within these intermediates are

subtle, extensive, and likely to depend upon configurations at chiral carbon in the substituents, the configurations of which are not known. Finally, it is not certain that the configuration of the metal inverts with each insertion, as found in the ROMP of certain norbornenes by MAP initiators related to those employed here.^{3c}

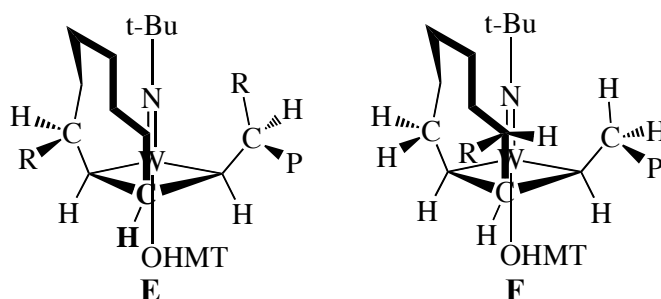


Figure 7. A stylized drawing of the $syn_\alpha/syn_\beta/syn_\alpha$ metallacycle intermediate **E** in the polymerization of 3-RCOE (P = polymer) with **1c**, and **F** in the unobserved mechanistic alternative propagating species. (The pyrrolide ligand is omitted and the configuration of each trisubstituted syn substituent in each is an arbitrary choice.)

Other Initiators

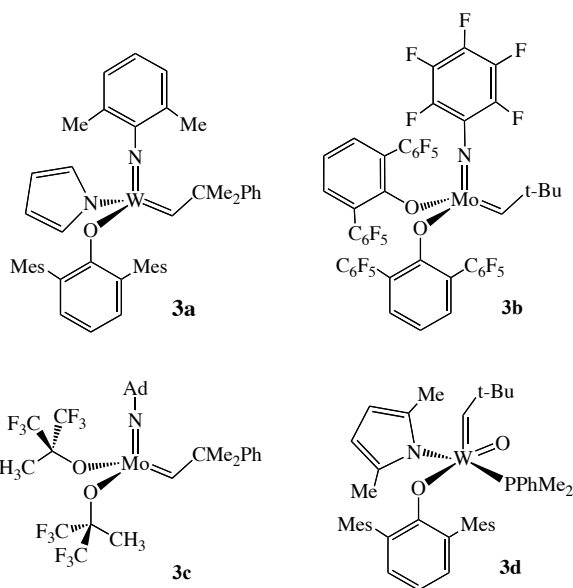
The results of the syntheses of poly(3-HexCOE) employing initiators W(N-2,6-Me₂C₆H₃)(CHCMe₂Ph)(Pyr)(OHMT) (**3a**),¹⁸ Mo(NC₆F₅)(CHCMe₂Ph)(ODFT)₂ (**3b**, ODFT = 2,6-bis(pentafluorophenyl)phenoxide),¹⁹ Mo(NAd)(CHCMe₂Ph)[OC(CF₃)₂Me]₂ (**3c**),²⁰ and W(O)(CH-t-Bu)(Me₂Pyr)(OHMT)(PPhMe₂) (**3d**)²¹ are shown in Table 3. Initiator **3a** performs well in terms of *Z*-selectivity (>98%), but the apparent polymerization rate is approximately half the rate of polymerization of 3-HexCOE by **1b** or **1c**. The bisaryloxy (**3b**) and bisalkoxy (**3b**) initiators allow significant amounts of *trans* polymer HT linkages to form. W(O)(CH-t-Bu)(Me₂Pyr)(OHMT)(PPhMe₂) was found to be a poor catalyst. Coordination of the phosphine to tungsten in the propagating species formed from **3d** could slow the rate of polymerization to some degree, although the phosphine is known to be 60% dissociated in a 20 mM solution of **3d** itself in C₆D₆.²¹

It is interesting to note that the rate of formation of >98% *cis* polymer from **3a** (1175 TO/day) is essentially the same as the rate of formation of 57% *cis* polymer (1200 TO/day) prepared from **3c** (Table 3). It also should be noted that an analog of **1c** bearing a 2,5-dimethylpyrrolide ligand, i.e., W(N-*t*-Bu)(CH-*t*-Bu)(Me₂Pyr)(OHMT), showed essentially no ROMP activity with 3-HexCOE. The dramatic decrease in activity upon replacing a parent pyrrolide ligand in **1c** with a 2,5-dimethylpyrrolide ligand emphasizes the sensitive nature of the polymerization to steric changes and possibly also indicates that a 2,5-dimethylpyrrolide in the

Table 3. Summary of other polymerizations of 5000 equivalents of neat 3-HexCOE at 22 °C.

<u>Initiator</u>	<u>Time</u>	<u>% conv</u>	<u>% <i>cis</i>,HT</u>	<u>~TO/day^a</u>
W(N-2,6-Me ₂ C ₆ H ₃)(CHCMe ₂ Ph)(Pyr)(OHMT) (3a)	4 h	3	nd	
	2 d	47	>98	1175
Mo(NC ₆ F ₅)(CHCMe ₂ Ph)(ODFT) ₂ (3b)	4 h	15	83 ^b	
	1 d	51	82 ^b	2550
Mo(NAd)(CHCMe ₂ Ph)[OC(CF ₃) ₂ Me] ₂ (3c)	4 h	7	66 ^b	
	2 d	48	57 ^b	1200
W(O)(CH- <i>t</i> -Bu)(Me ₂ Pyr)(OHMT)(PPhMe ₂) (3d)	4 h	< 2	n/d	
	1 d	< 2	n/d	n/d

^aApproximate turnovers per day. ^bRemaining amount is *trans*,HT polymer.



initiator is undesirable *per se* in these particular polymerizations. Finally, ROMP of 3-*i*-PrCOE at room temperature by **1a**, **1b**, or **1c**, failed, probably for steric reasons associated with the 3-*i*-PrCOE itself in an intermediate related to **E** shown in Figure 7.

CONCLUSIONS

Highly *cis*,HT-selective ROMP of a series of 3-substituted cyclooctenes (3-MeCOE, 3-HexCOE, and 3-PhCOE) can be carried out in bulk monomer with Mo and W MAP complexes at room temperature. The apparent rate of polymerization of 3-HexCOE by W(N-*t*-Bu)(CH-*t*-Bu)(Pyr)(OHMT) (**1c**) is greater than the rate of polymerization by Mo(N-*t*-Bu)(CH-*t*-Bu)(Pyr)(OHMT) (**1b**), but both gave the same *cis*,HT polymer structures. The rate of ROMP with **1b** and **1c** is exceedingly sensitive to steric factors, e.g., W(N-*t*-Bu)(CH-*t*-Bu)(Me₂Pyr)(OHMT), the dimethylpyrrolide analog of **1c**, essentially did not polymerize 3-HexCOE at 22 °C. Formation of HT-poly(3-RCOE) employing **1c** takes place *via* propagating species in which the R group is on C2 of the propagating alkylidene chain.

EXPERIMENTAL SECTION

Mo(N-*t*-Bu)(CH-*t*-Bu)[OCH(CF₃)₂]₂(NH₂-*t*-Bu). Mo(N-*t*-Bu)₂(CH₂-*t*-Bu)₂ (0.52 g, 1.38 mmol) was dissolved in diethyl ether (15 mL) and the solution was stood at -30 °C for 2 h. Hexafluoro-2-propanol (0.32 mL, 3.04 mmol) was added and the mixture was stirred at room temperature for 23 h. The solvents were removed *in vacuo*. A small quantity of pentane was added to the off-white solid and the first crop of product was collected via filtration. The filtrate was concentrated and cooled to -30 °C to give a second crop of product; total yield 0.23 g (26%): ¹H NMR (500 MHz, C₆D₆) δ 12.81 (s, 1H, Mo=CH), 6.00 (m, 1H, (CF₃)₂CH), 4.48 (m, 1H, (CF₃)₂CH), 2.67 (d, 1H, H₂N-*t*Bu), 2.45 (d, 1H, H₂N-*t*Bu), 1.12 (s, 9H, Me), 1.07 (s, 9H, Me), 0.7 (s, 9H, Me); ¹⁹F NMR (300 MHz, C₆D₆) δ -74.61, -75.20, -76.08; ¹³C (125 MHz, C₆D₆) δ 302.03, 83.91 (quintet), 74.11 (quintet), 71.49, 71.33, 50.71, 45.65, 45.43, 31.83, 30.75, 30.22. Anal. Calcd for C₁₉H₃₂F₁₂N₂O₂Mo: C, 35.41; H, 5.01; N, 4.35. Found: C, 35.40; H, 5.01; N, 4.34.

Mo(N-t-Bu)(CH-t-Bu)(OC₆F₅)₂(NH₂-t-Bu). Mo(N-t-Bu)₂(CH₂-t-Bu)₂ (1.96 g, 5.16 mmol) was dissolved in diethyl ether (30 mL) and the solution was chilled to -30 °C. Pentafluorophenol (1.99 g, 10.83 mmol) was added and the mixture was allowed to stir at room temperature for 4 h. The solvents were removed *in vacuo*. Pentane was added and the off-white precipitate was collected; yield 2.93 g (84%): ¹H NMR (500 MHz, C₆D₆) δ 13.21 (s, 1H, Mo=CH), 2.64 (d, 1H, H₂N-t-Bu), 2.50 (d, 1H, H₂N-t-Bu), 1.23 (s, 9H, Me), 0.93 (s, 9H, Me), 0.67 (s, 9H, Me); ¹⁹F NMR (300 MHz, C₆D₆) δ -162.71, -164.18, -168.06, -168.67, -174.76; ¹³C (125 MHz, C₆D₆) δ 340.94, [145.73, 142.29, 141.97, 140.40, 139.99, 139.55, 137.61; overlapping aryl resonances split due to fluorine coupling], 72.43, 50.96, 45.82, 30.84, 30.44, 30.07. Anal. Calcd for C₂₅H₃₀F₁₀N₂O₂Mo: C, 44.39; H, 4.47; N, 4.14. Found: C, 44.29; H, 4.48; N, 4.06.

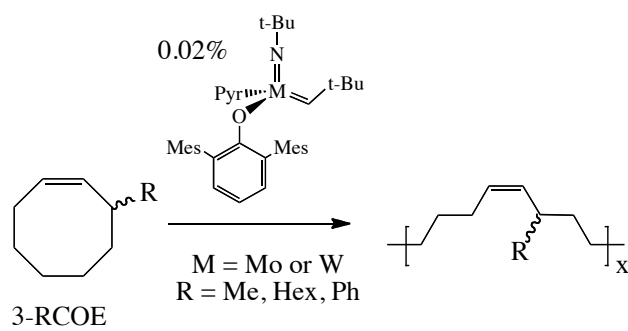
Mo(N-t-Bu)(CH-t-Bu)(Pyr)₂(bipy). Mo(N-t-Bu)(CH-t-Bu)(OC₆F₅)₂(NH₂-t-Bu) (0.53 g, 0.79 mmol) was suspended in toluene (20 ml) and the mixture was chilled to -30 °C. LiPyr (0.115 g, 1.58 mmol) was added in one portion and the mixture was allowed to stir at room temperature for 3 h, during which time LiOC₆F₅ salts precipitated out. The mixture was filtered through a pad of Celite on a glass frit, and the salts were washed with toluene. 2,2'-Bipy (0.111 g, 0.71 mmol) was added to the solution and the mixture was allowed to stir at room temperature overnight. The resulting red precipitate was collected by filtration and dried *in vacuo*; yield 0.526 g (61%). At room temperature, three isomers were observed in NMR spectra: ¹H NMR (500 MHz, CD₂Cl₂) δ 14.03 (s, 1H, Mo=CH), 13.46 (s, 1H, Mo=CH), 13.01 (s, 1H, Mo=CH), 9.55 (d, 1H, bipy), 9.49 (d, 1H, bipy), 9.21 (d, 1H, bipy), 9.00 (d, 1H, bipy), 8.71 (d, 1H, bipy), 8.55 (d, 1H, bipy), 8.10-7.94 (m, 12H, bipy), 7.65-7.49 (m, 6H, bipy), 6.83 (m, 2H, NC₄H₂), 6.66 (m, 2H, NC₄H₂), 6.28 (m, 2H, NC₄H₂), 6.15 (m, 4H, NC₄H₂), 6.11 (m, 2H, NC₄H₂), 6.06 (m, 2H, NC₄H₂), 6.04 (m, 2H, NC₄H₂), 5.65 (m, 4H, NC₄H₂), 5.59 (m, 2H, NC₄H₂), 1.56 (s, 9H, Me), 1.52 (s, 9H, Me), 1.44 (s, 9H, Me), 1.34 (s, 9H, Me), 1.21 (s, 9H, Me), 1.00 (s, 9H, Me). The product was too insoluble to purify readily through recrystallization, and several elemental analyses produced variable results. Therefore Mo(N-t-Bu)(CH-t-Bu)(Pyr)₂(bipy) was employed in the synthesis of Mo(N-t-Bu)(CH-t-Bu)(Pyr)(OHMT) (see immediately below) without purification.

Mo(N-t-Bu)(CH-t-Bu)(Pyr)(OHMT). Mo(N-t-Bu)(CH-t-Bu)(Pyr)₂(bipy) (200 mg, 0.381 mmol), ZnCl₂(dioxane) (85.4 mg, 0.381 mmol), and HMTOH (105.6 mg, 0.320 mmol) were dissolved in toluene (40 mL) in a 100 mL Schlenk bomb. The bomb was placed in a sonicator for 21 h. The mixture was filtered through a pad of Celite on a glass frit and solvents were removed from the filtrate *in vacuo*. The residue was extracted with a small amount of pentane. The extract was filtered through a pad of Celite and the solvents were removed *in vacuo* to give a yellow solid; yield 189.8 mg (94%): ¹H NMR (500 MHz, C₆D₆) δ 11.07 (s, 1H, Mo=CH), 6.98-6.86 (m, 7H, aryl), 6.64 (m, 2H, NC₄H₂), 6.46 (m, 2H, NC₄H₂), 2.24 (s, 6H, OHMT methyls), 2.15 (s, 6H, OHMT methyls), 1.99 (s, 6H, OHMT methyls), 1.11 (s, 9H, Me), 0.99 (s, 9H, Me); ¹³C NMR (125 MHz, C₆D₆) δ 287.72, 158.31, 136.90, 136.87, 136.67, 136.15, 132.55, 131.83, 129.95, 129.44, 128.62, 122.44, 109.78, 73.92, 44.84, 31.36, 30.89, 21.22, 21.00, 20.18. Anal. Calcd for C₃₇H₄₈N₂OMo: C, 70.23; H, 7.65; N, 4.43. Found: C, 69.93; H, 7.93; N, 4.35.

Acknowledgment. RRS is grateful to the Department of Energy (DE-FG02-86ER13564) for research support. MAH is grateful for support from the Abu Dhabi-Minnesota Institute for Research Excellence (ADMIRE). The MIT Department of Chemistry thanks the NSF (CHE-9808061) for funds to purchase a 500 MHz NMR instrument.

Supporting Information Available. General experimental details, proton NMR spectra of new compounds, synthetic procedures, analytical data for *cis*,HT-poly(3-RCOE) polymers, and details of the X-ray study. Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

TOC



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Supporting Information for

Z-selective Ring-Opening Metathesis Polymerization of 3-Substituted Cyclooctenes by Monoaryloxide Pyrrolide Imido Alkylidene (MAP) Catalysts of Molybdenum and Tungsten

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Mo(N-t-Bu)(CHCMe₃)[OCH(CF₃)₂]₂(NH₂-t-Bu)

Mo(N-t-Bu)(CHCMe₃)(OC₆F₅)₂(NH₂-t-Bu)

Mo(N-t-Bu)(CHCMe₃)(pyr)₂(bipy)

Mo(N-t-Bu)(CHCMe₃)(pyr)(OHMT)

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cis,HT-poly(3-MeCOE)

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General considerations

All manipulations of air and moisture sensitive materials were conducted under a nitrogen atmosphere in a Vacuum Atmospheres glovebox or on a dual-manifold Schlenk line. The glassware, including NMR tubes were oven-dried prior to use. Diethyl ether, pentane, toluene, THF, dichloromethane, and benzene were degassed and passed through activated alumina columns and stored over 4 Å Linde-type molecular sieves prior to use. Dimethoxyethane was dried from dark purple solution of sodium benzophenone ketyl, and degassed by the freeze-pump-thaw technique. The deuterated solvents were dried over 4 Å Linde-type molecular sieves prior to use. Hydrogenation of the polymers was performed as described by Hillmyer *et al.*¹

Materials.

N-t-butyltrimethylsilylamine was either prepared from TMSCl and *t*-BuNHLi in ether or purchased from Sigma-Aldrich. Pyridinium chloride was purchased from Sigma-Aldrich and dried before use. HCl solution was prepared by bubbling HCl gas into diethyl ether solution and was titrated before use. Lipyr was prepared by addition of one equivalent of *n*-BuLi to a cold ether solution of pyrrole, and the solids were collected on a frit, washed with cold ether and dried *in vacuo*. Cyclooctene (95%) was purchased from Alfa Aesar and distilled before use. 3-MeCOE, 3-HexCOE, 3-PhCOE, and 3-*i*PrCOE were synthesized as reported¹ and were degassed by a minimum of three freeze-pump-thaw cycles and dried over 4 Å Linde-type molecular sieves prior to use. Hydrogenation of the polymers was performed as described in the literature¹. Grignard reagents were titrated against *n*-butanol with 1,10-phenanthroline as an indicator immediately prior to use. HIPTOH² (HIPT = 2,6-(2,4,6-*i*Pr₃C₆H₂)₂C₆H₃), HMTOH³ (HMT = 2,6-(2,4,6-Me₃C₆H₂)₂C₆H₃), ZnCl₂(dioxane)⁴, Mo(N-*t*-Bu)₂Cl₂(dme), Mo(N-*t*-Bu)₂(CH₂CMe₃)₂,⁵ Mo(N-*t*-Bu)(CHCMe₃)(OCH(CF₃)₂)₂(NH₂-*t*-Bu)⁶, Mo(NAd)(CHCMe₂Ph)(pyr)(OHMT)⁷, W(N-*t*-Bu)(CHCMe₃)(2,5-Me₂pyr)(OHMT), W(N-*t*-Bu)(CHCMe₃)(pyr)(OHMT)⁸, Mo(NAd)(CHCMe₂Ph)(OC(CF₃)₂Me)₂⁹, and Mo(NAr)(CH₂)(pyr)(OHIPT)¹⁰ were prepared according to literature procedures. W(NAr')(CHCMe₂Ph)(pyr)(OHMT)¹¹ (Ar' = 2,6-Me₂C₆H₃), Mo(NC₆F₅)(CHCMe₂Ph)(ODFT)₂ (ODFT = 2,6-bis(pentafluorophenyl)phenoxide)¹², and W(O)(CHCMe₃)(Me₂pyr)(PMe₂Ph)(OHMT)¹³ were from Erik Townsend, Jian Yuan, and Dmitry Peryshkov respectively. Unless otherwise noted, all other reagents were obtained from commercial sources and used as received.

Instrumentation.

^1H , ^{13}C spectra were acquired at room temperature using 300MHz and 500MHz spectrometers. Chemical shifts for ^1H and ^{13}C spectra are reported as parts per million relative to tetramethylsilane, and referenced to the residual $^1\text{H}/^{13}\text{C}$ resonances of the deuterated solvent (^1H (δ) : benzene 7.16, chloroform 7.26, methylene chloride 5.32; ^{13}C (δ) : benzene : 128.06, chloroform 77.16, methylene chloride 53.84). Chemical shifts for ^{19}F are reported as parts per million relative to trichlorofluoromethane, and referenced using an external standard of fluorobenzene (δ -113.15). Number-average molar masses (M_n) were determined by size exclusion chromatography (SEC) using tetrahydrofuran (THF) as the mobile phase (25 °C, 1 ml/min flow rate). This instrument is equipped with 3 Waters Styragel columns, together with a Wyatt DAWN Heleos II light scattering detector and Wyatt OPTILAB T-rEX refractive index detector (658nm wavelength).

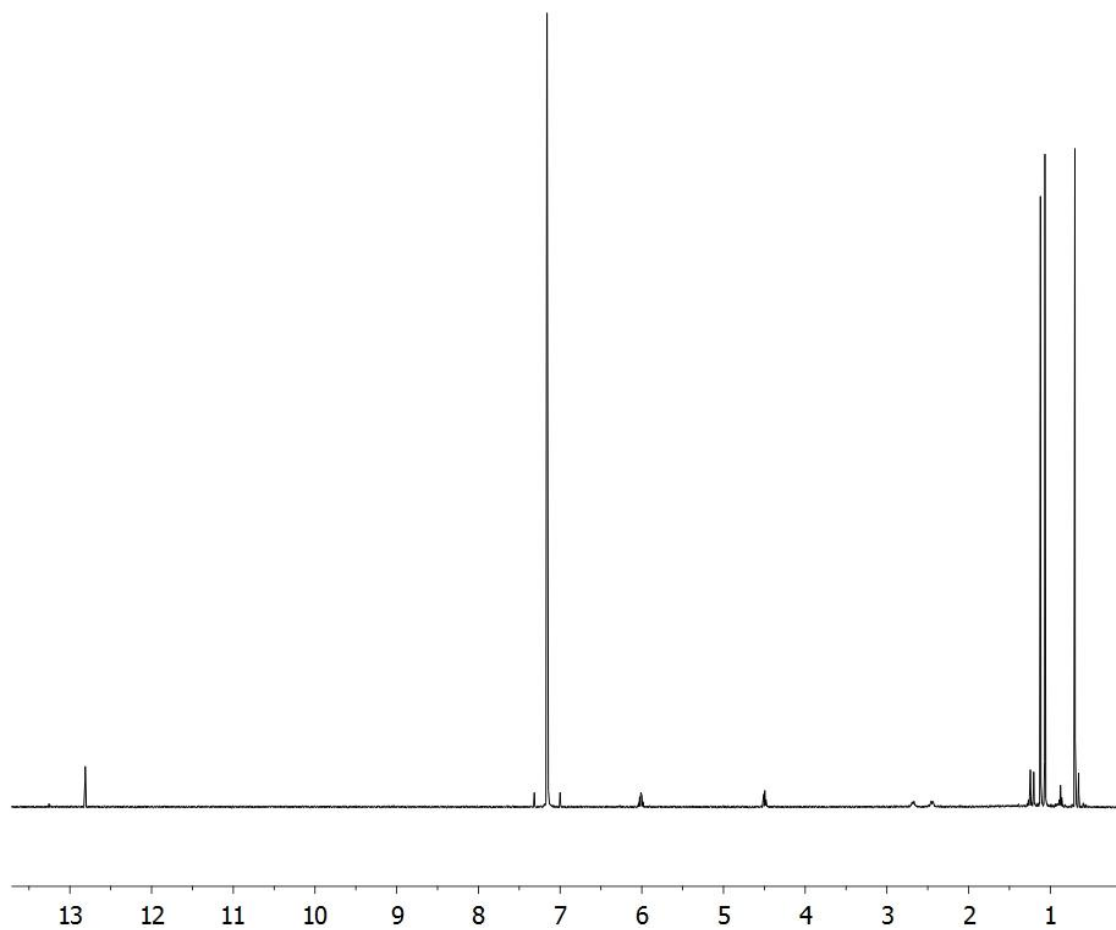


Figure S1. ¹H NMR spectrum of Mo(N-t-Bu)(CH-t-Bu)[OCH(CF₃)₂]₂(NH₂-t-Bu) (in C₆D₆, 500 MHz).

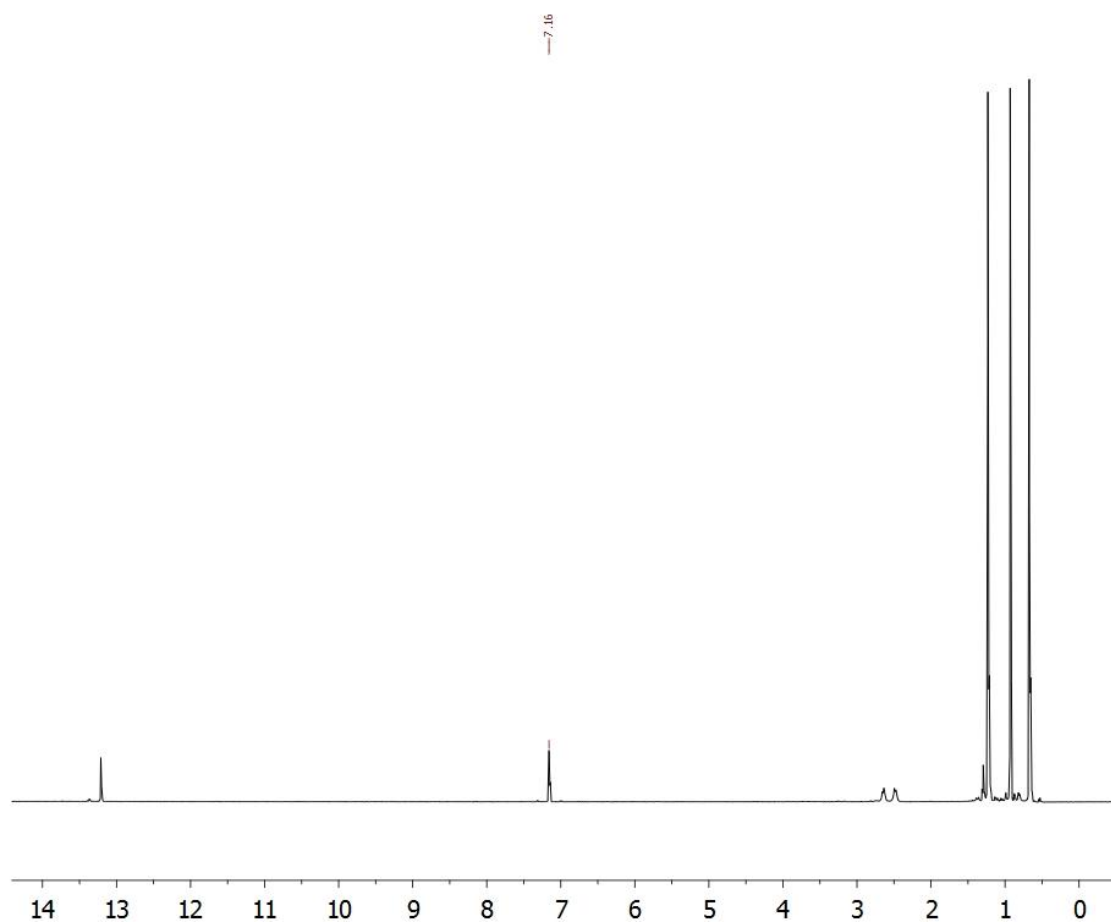


Figure S2. ¹H NMR spectrum of Mo(N-t-Bu)(CH-t-Bu)(OC₆F₅)₂(NH₂-t-Bu) (in C₆D₆, 500 MHz).

Mo(N-t-Bu)(CH-t-Bu)(pyr)₂(bipy)

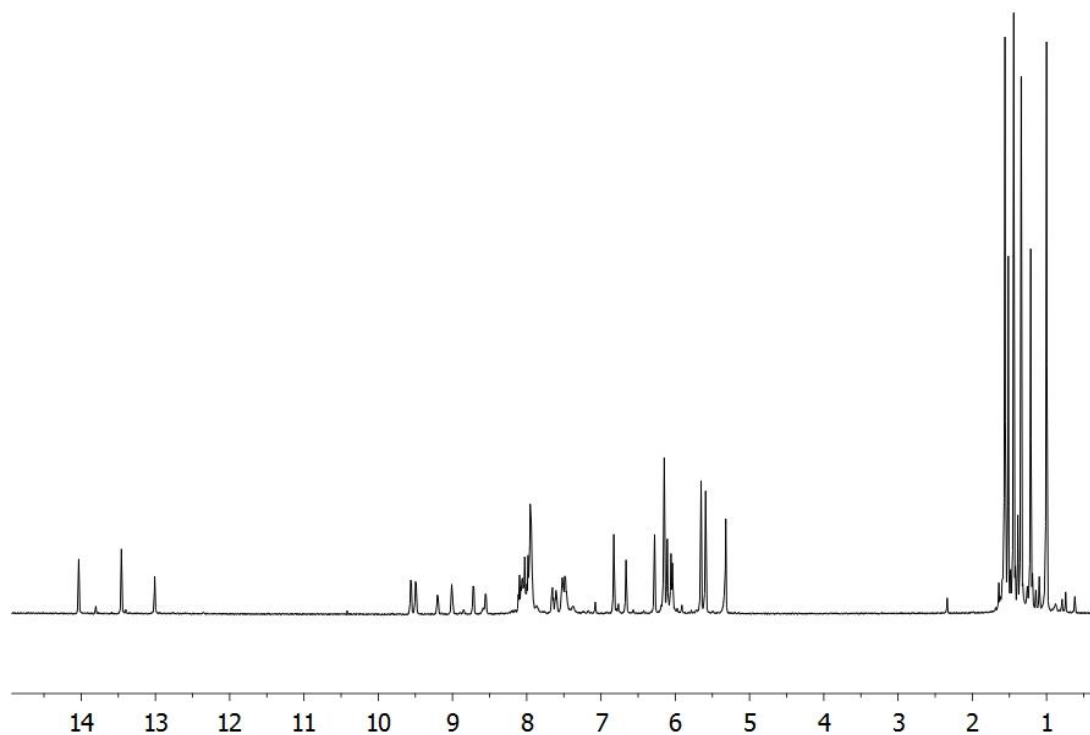


Figure S3. ¹H NMR spectrum of Mo(N-t-Bu)(CH-t-Bu)(pyr)₂(bipy) (in CD₂Cl₂, 500 MHz).

Mo(N-t-Bu)(CH-t-Bu)(pyr)(OHMT)

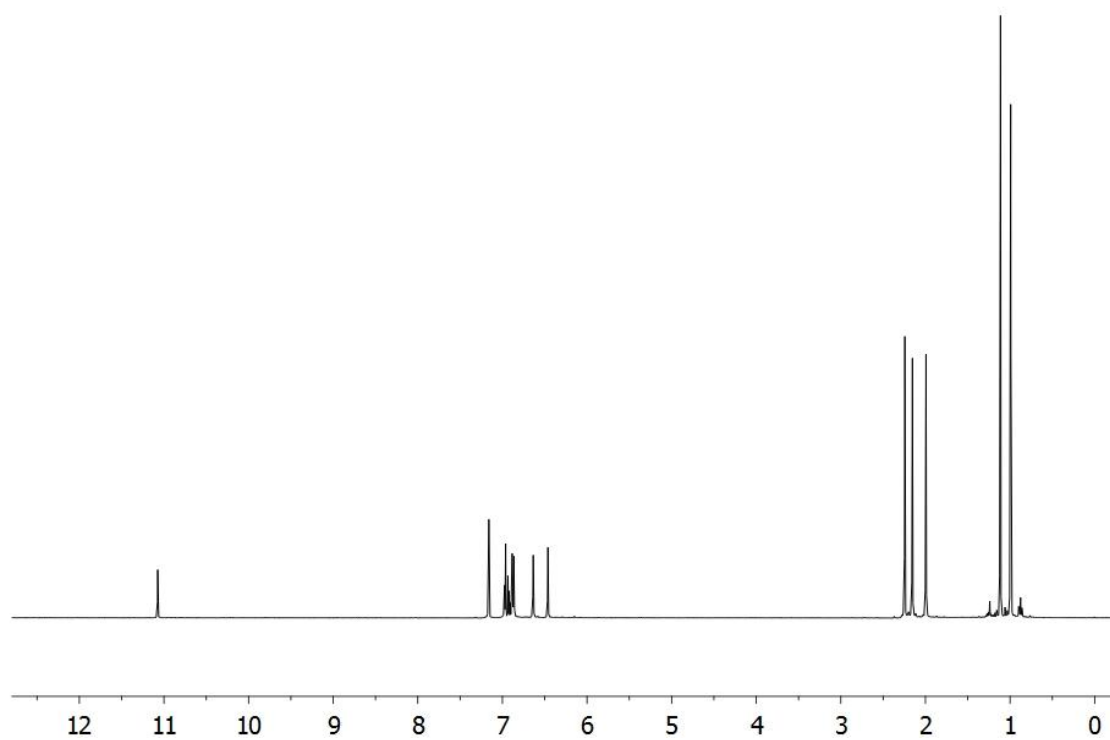


Figure S4. ¹H NMR spectrum of Mo(N-t-Bu)(CH-t-Bu)(pyr)(OHMT) (in C₆D₆, 500 MHz).

General procedure: ambient temperature polymerizations, neat monomer

In the glovebox, the Mo or W initiator was added as a stock solution in benzene to an 8 mL vial containing a stir bar. The benzene was frozen and removed by sublimation, and the monomer (250 μ L, 5000 equiv.) was added *via* syringe. The vial was capped and the mixture stirred at ambient temperature. Aliquots were removed from the box and quenched with wet CDCl_3 (stored under air without desiccant). The polymerization reactions were quenched by addition of 5 mL wet CHCl_3 (stored under air without desiccant) followed by sonication for 30 min. The polymers were precipitated by addition of this solution to 50 mL methanol. The precipitated polymers were freeze-dried overnight from frozen benzene solutions.

General procedure: elevated temperature polymerizations, neat monomer

Polymerizations at elevated temperatures were performed identically to those at ambient-temperature with the following exceptions: a small Schlenk tube with PTFE plug was used instead of a vial and, once the monomer was added, the tube was sealed, removed from the box, and heated with stirring in an oil bath. Aliquots were taken for monitoring in the glovebox.

Size Exclusion Chromatography

The R = Hex samples reported in Table 2 were prepared at 2~3 mg/ml concentrations in THF. Molar masses were calculated using the dn/dc values of 0.0887 and 0.0973 cm^3/g for the two samples as obtained from the refractive index detector and the known mass of the injected polymer sample. Polystyrene standards were used to determine the relative molar masses and dispersities.

***cis*,HT-poly(3-MeCOE)**

^1H NMR (500 MHz, CDCl_3) δ 5.27 (dt, $J = 10.8, 7.3$ Hz, 1H), 5.09 (apparent t, $J = 10.3$ Hz, 1H), 2.40 (m, 1H), 2.00 (m, 2H, $J = 7.2$ Hz), 1.38-1.10 (overlapping peaks, 8H), 0.91 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 136.5, 128.5, 37.7, 31.8, 30.1, 29.7, 27.7, 27.6, 21.6.

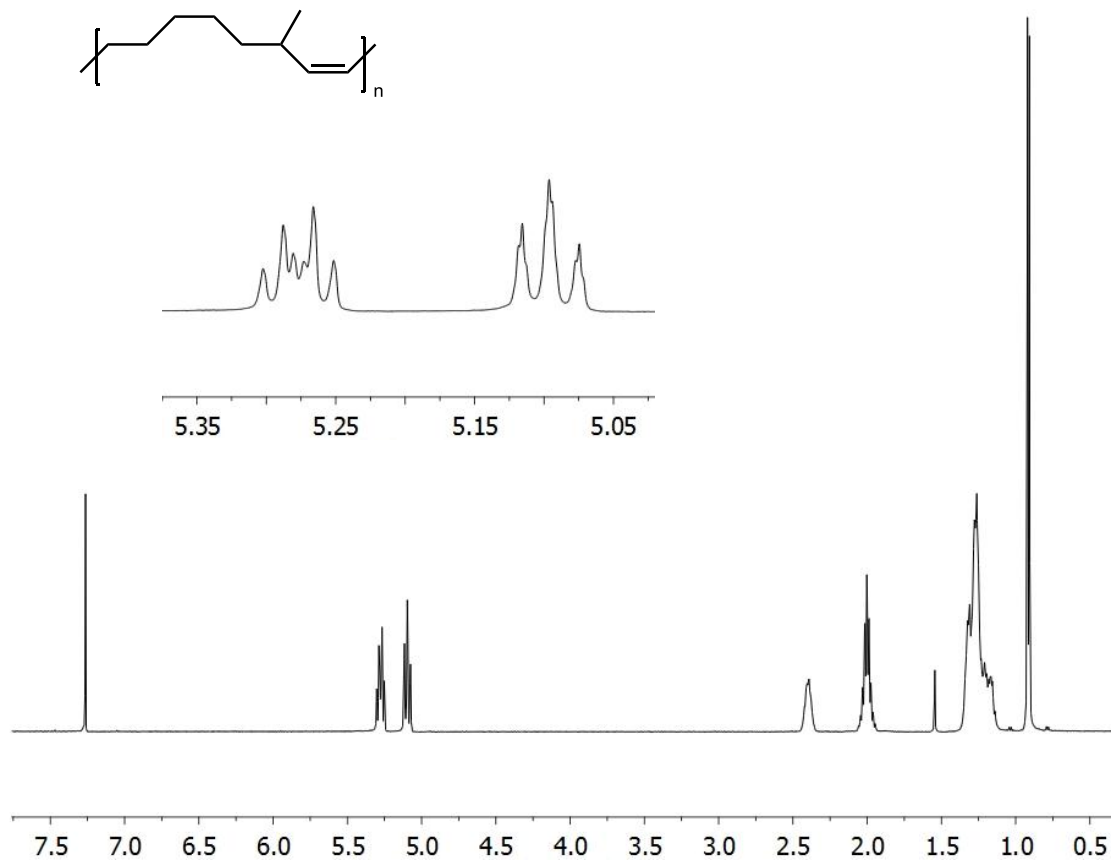


Figure S5. ^1H NMR spectrum of *cis*,HT-poly(3-MeCOE) (in CDCl_3 , 500 MHz).

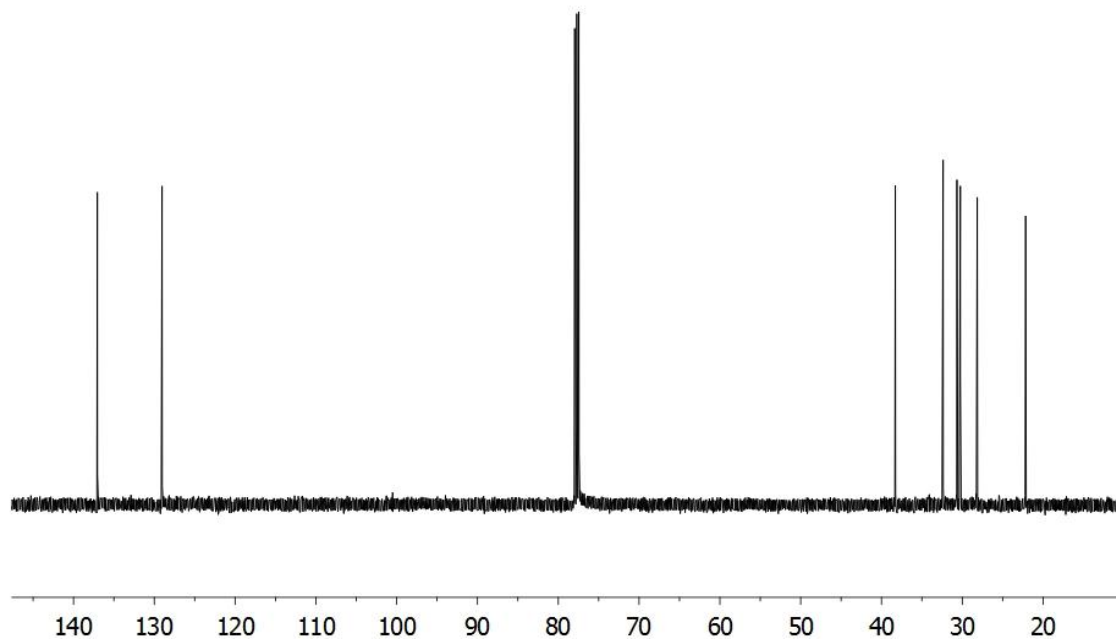
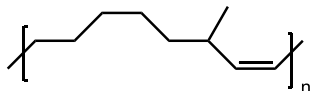


Figure S6. ^{13}C NMR spectrum of *cis*,HT-poly(3-MeCOE) (in CDCl_3 , 125 MHz).

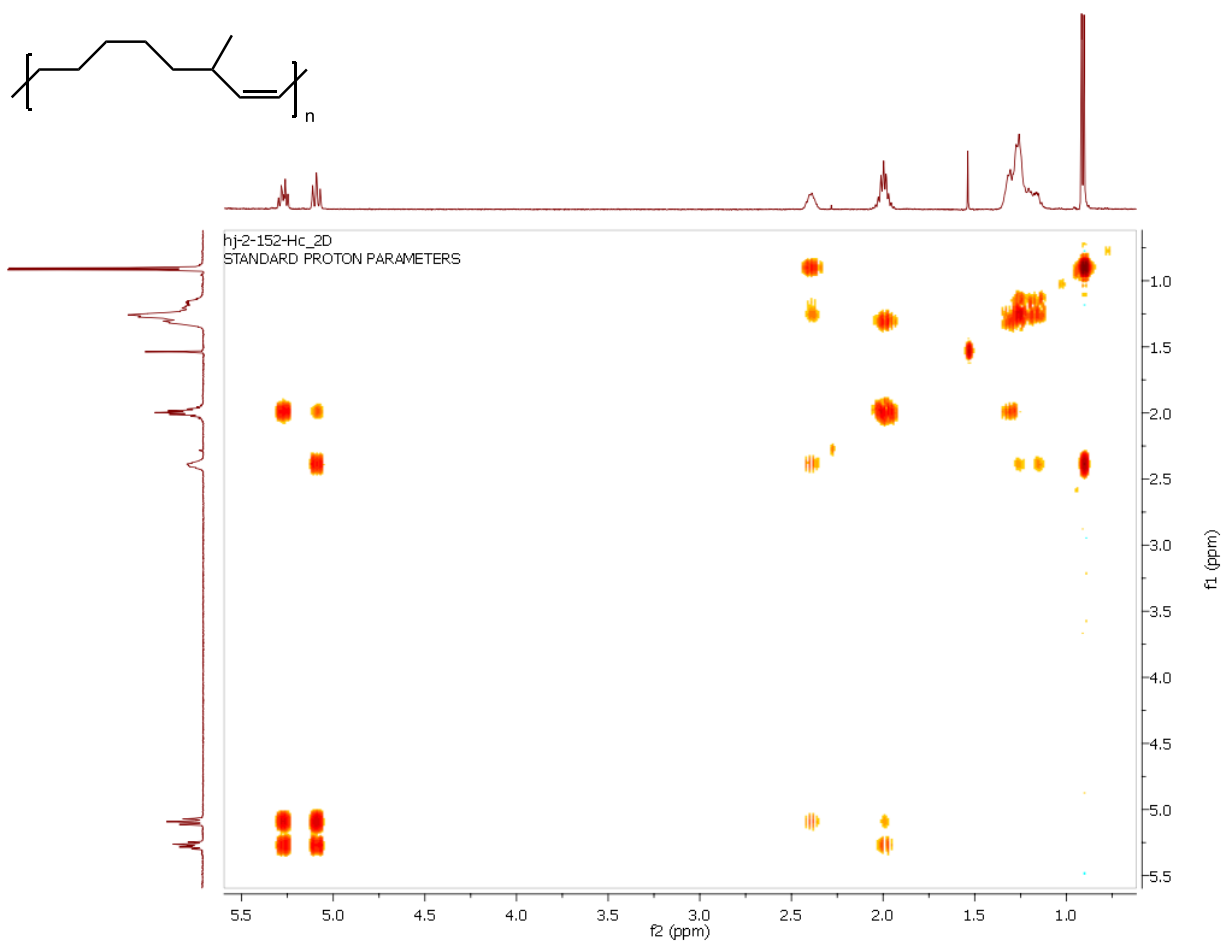


Figure S7. ¹H-¹H COSY spectrum of *cis*,HT-poly(3-MeCOE) (in CDCl₃, 500 MHz).

***cis*,HT-poly(3-HexCOE)**

^1H NMR (500 MHz, CDCl_3) δ 5.34 (dt, $J = 10.9, 7.2$ Hz, 1H), 5.00 (apparent t, $J = 10.5$ Hz, 1H), 2.25 (m, 1H), 1.98 (m, 2H), 1.40-1.05 (overlapping peaks, 18H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.2, 129.7, 37.4, 36.2, 36.2, 32.1, 30.2, 29.9, 29.8, 28.0, 27.5, 27.5, 22.9, 14.3.

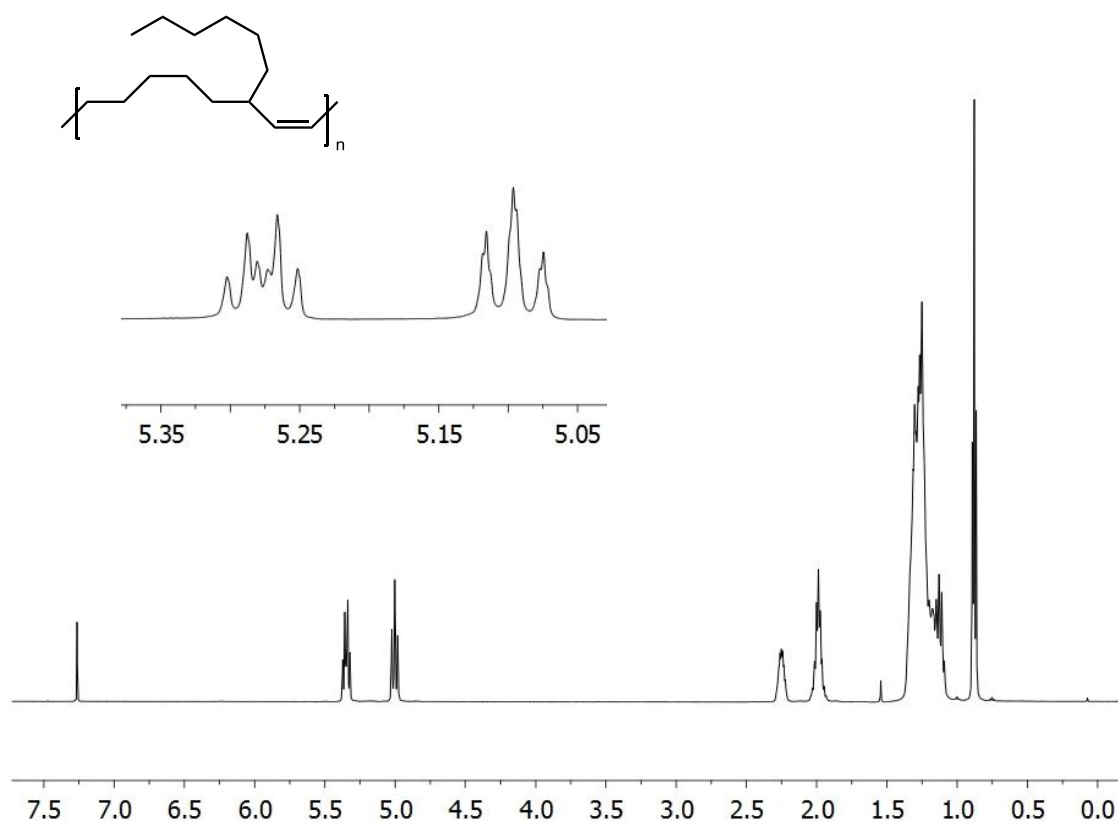


Figure S8. ^1H NMR spectrum of *cis*,HT-poly(3-HexCOE) (in CDCl_3 , 500 MHz).

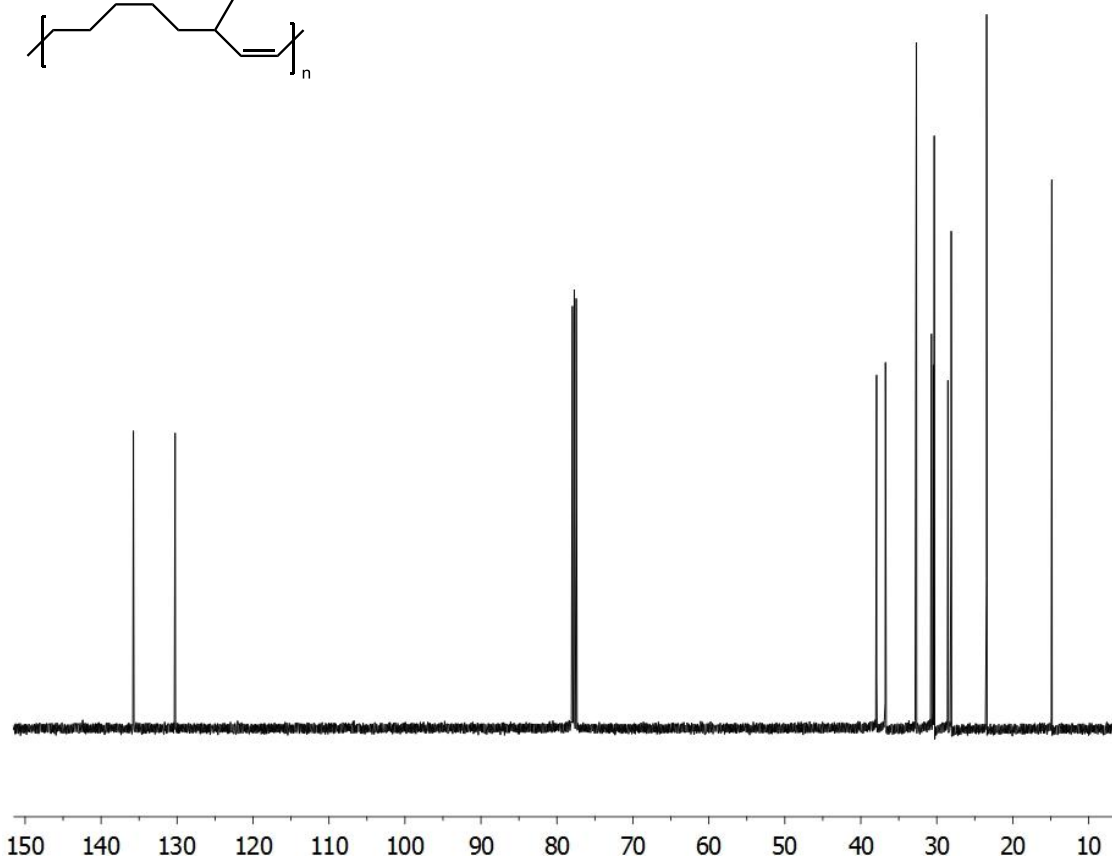
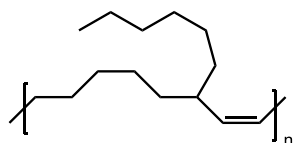


Figure S9. ^{13}C NMR spectrum of *cis*,HT-poly(3-HexCOE) (in CDCl_3 , 125 MHz).

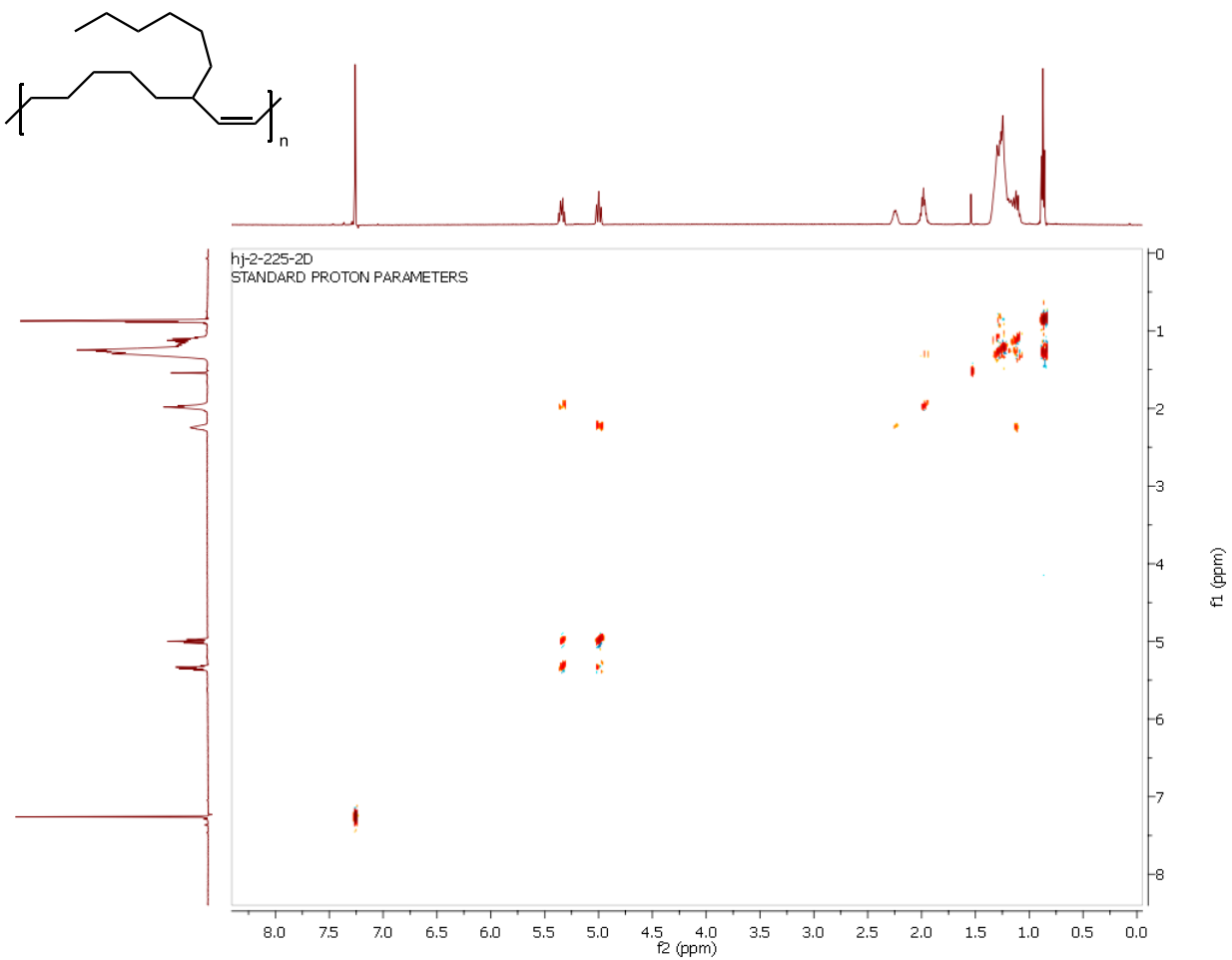


Figure S10. ¹H-¹H COSY spectrum of *cis*,HT-poly(3-HexCOE) (in CDCl₃, 500 MHz).

cis,HT-poly(3-PhCOE)

^1H NMR (500 MHz, CDCl_3) δ 7.27-7.24 (overlapping peaks, 2H), 7.16-7.13 (overlapping peaks, 3H), 5.46 (apparent t, $J = 10.3$ Hz, 1H), 5.36 (dt, $J = 10.7, 7.1$ Hz, 1H), 3.48 (apparent q, $J = 7.8$ Hz, 1H), 2.03 (m, 2H), 1.66-1.60 (m, 1H), 1.57-1.51 (m, 1H), 1.32-1.21 (overlapping peaks, 5H), 1.18-1.12 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 146.1, 129.8, 128.5, 127.4, 127.4, 125.9, 43.6, 37.1, 29.7, 29.5, 27.7, 27.6.

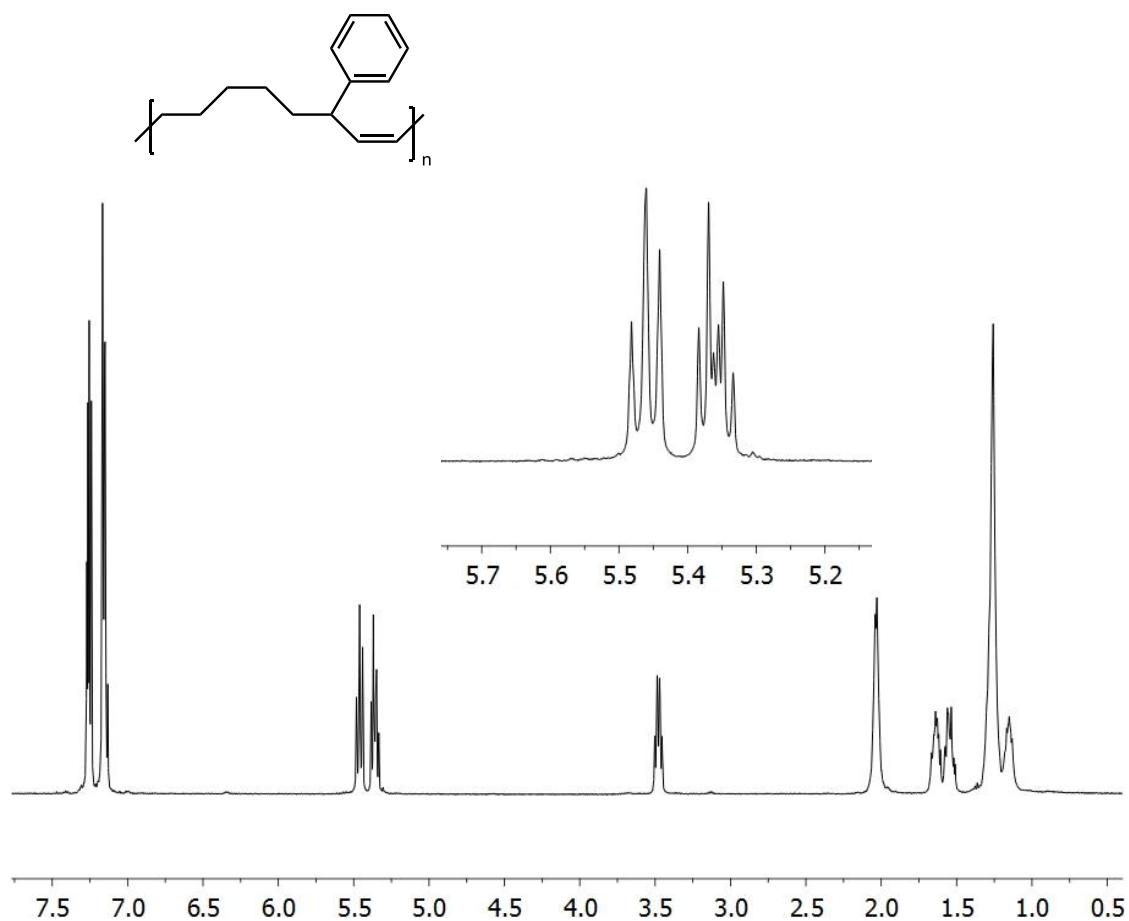


Figure S11. ^1H NMR spectrum of *cis,HT-poly(3-PhCOE)* (in CDCl_3 , 500 MHz).

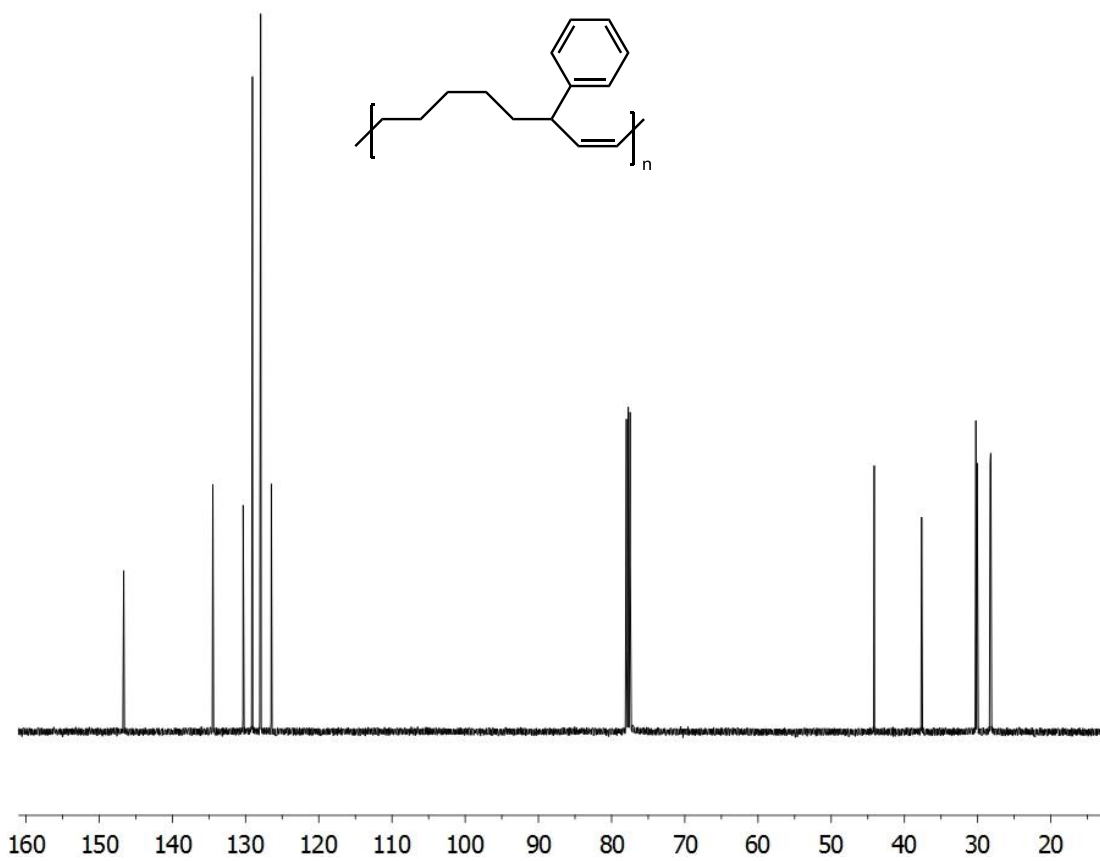


Figure S12. ^{13}C NMR spectrum of *cis*,HT-poly(3-PhCOE) (in CDCl_3 , 125 MHz).

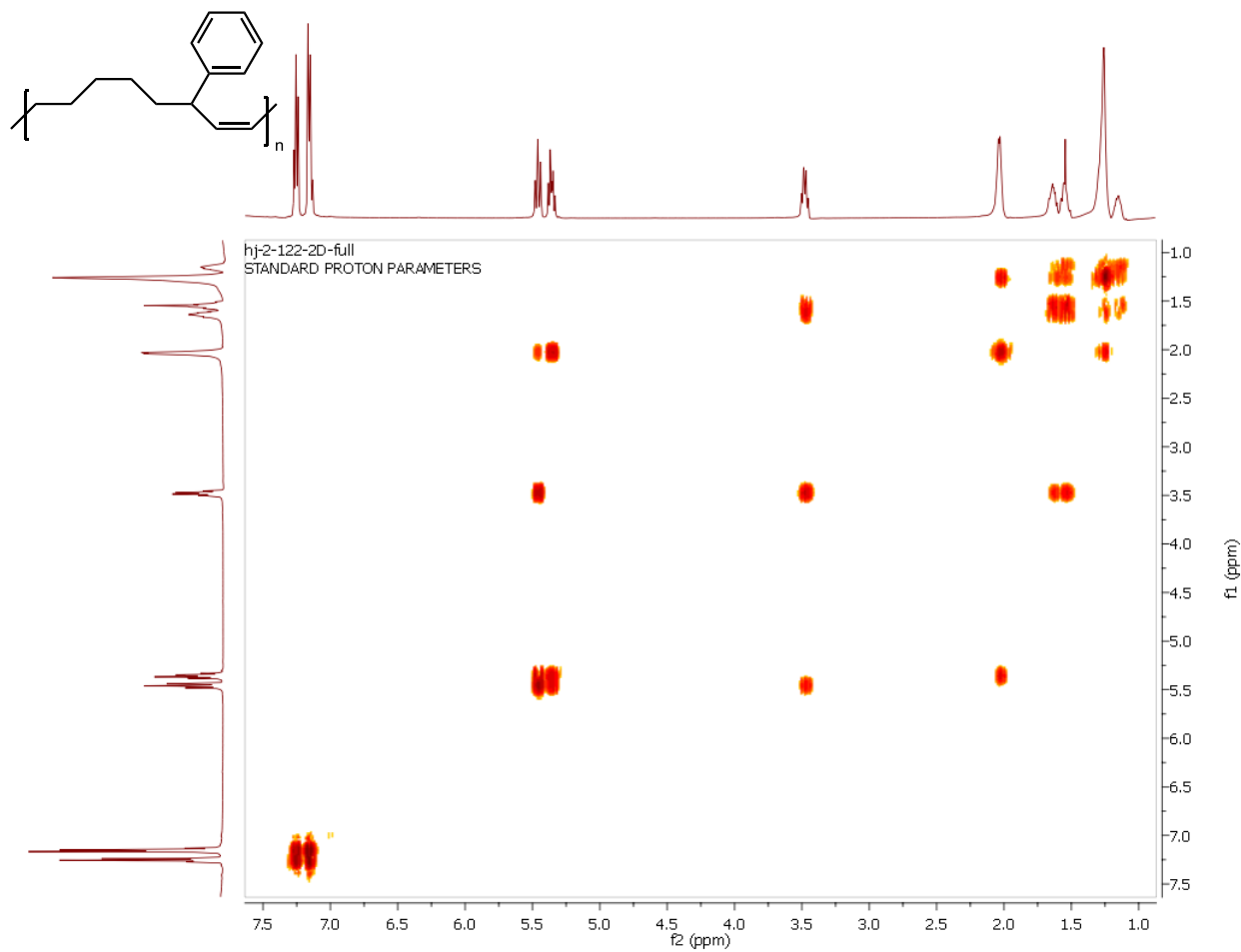


Figure S13. ¹H-¹H COSY spectrum of *cis*,HT-poly(3-PhCOE) (in CDCl₃, 500 MHz).

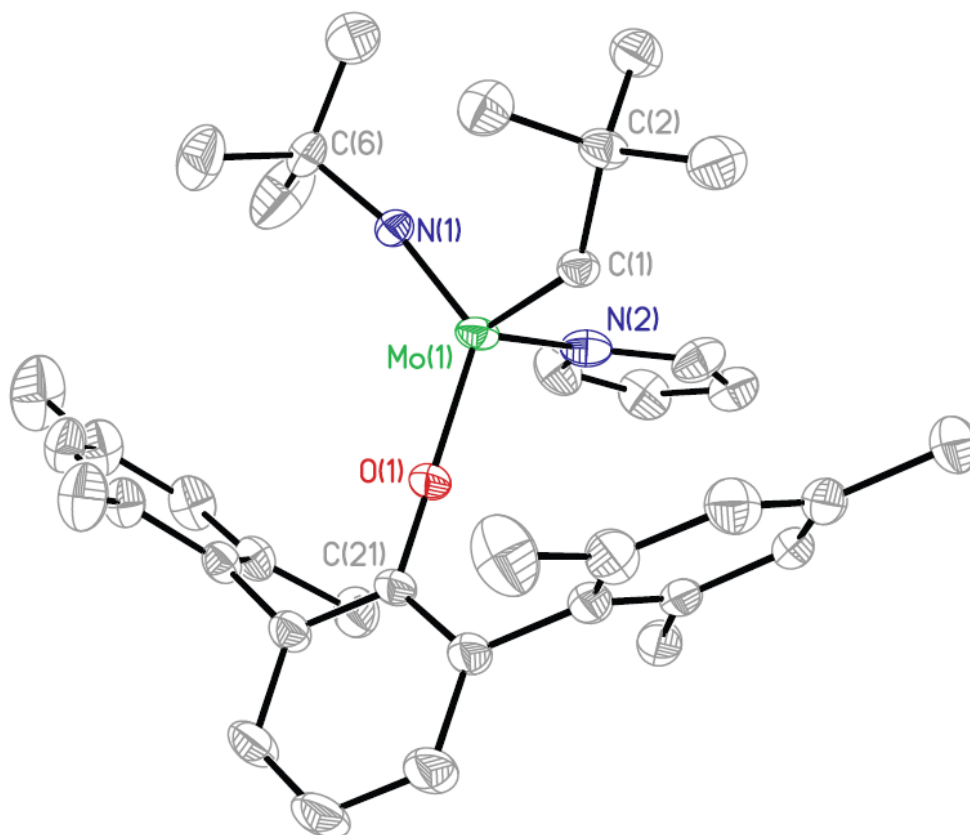


Figure S14. Thermal ellipsoid drawing of Mo(N-t-Bu)(CH-t-Bu)(pyr)(OHMT). Disorders were omitted for clarity. Selected distances (Å) and angles (°) : Mo(1)-N(1) = 1.6590(18), Mo(1)-C(1) = 1.904(2), Mo(1)-O(1) = 1.8833(9), Mo(1)-N(2) = 2.0342(12), N(1)-Mo(1)-O(1) = 126.52(8), N(1)-Mo(1)-C(1) = 104.91(10), N(1)-Mo(1)-N(2) = 104.53(7), Mo(1)-O(1)-C(21) = 174.14(10), Mo(1)-C(1)-C(2) = 140.9(3), Mo(1)-N(1)-C(6) = 168.7(3).

Crystal data and structure refinement

Low-temperature (100 K) diffraction data were collected by performing φ - and ω - scans on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart Apex II CCD detector with an $I\mu S$ source of Mo K_{α} radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using SHELXS¹⁴ and refined against F^2 on all data by full-matrix least squares with SHELXL-97¹⁵ using established refinement strategies.¹⁶ All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms (except that on the main component of the disordered alkylidene carbon, C1) were calculated geometrically and refined using a riding

model. The position of the hydrogen atom attached to C1 was taken from the Fourier synthesis and refined semi-freely with the help of a distance restraint. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atom to which they are bound (1.5 for methyl groups). Details of the crystal structure and its refinement are listed in Table S1.

$\text{MoC}_{37}\text{H}_{48}\text{N}_2\text{O}$ crystallized in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. The pyrrole and HMTO ligands of the central Mo atom were well behaved, but the two t-butyl-containing ligands were disordered over multiple positions. First, the positions of the alkylidene (C-t-Bu) and N-t-Bu ligands were swapped with respect to the Mo in a two-part disorder having a ratio that converged to 0.563(3). The minor component of the alkylidene ligand was then further disordered over two positions, with the major component converging to 0.310(4) of the remaining 0.437(3) occupancy. The N-t-Bu was thus disordered over two independent positions, and the alkylidene ligand was disordered over three independent positions. The occupancies of the three alkylidene components were restrained to sum to 1.0000(1). Rigid bond restraints and similarity restraints were employed on the displacement parameters, and similarity restraints were used for the 1-2 and 1-3 distances for all equivalent atoms involved in the disorders. In the two minor components of the alkylidene ligand, the equivalent carbon atoms bound to the Mo (C1A and C1B) as well as the equivalent neighboring carbon atoms (C2A and C2B) were constrained to have identical anisotropic displacement parameters.

Table S1. Crystal data and structure refinement for Mo(N-t-Bu)(CH-t-Bu)(pyr)(OHMT).

Identification code	x12178	
Empirical formula	C37 H48 Mo N2 O	
Formula weight	632.71	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.8579(5) Å	$\alpha = 90^\circ$
	b = 16.2400(7) Å	$\beta = 92.5340(10)^\circ$
	c = 18.1978(8) Å	$\gamma = 90^\circ$
Volume	3501.0(3) Å ³	
Z	4	
Density (calculated)	1.200 Mg/m ³	
Absorption coefficient	0.403 mm ⁻¹	
F(000)	1336	
Crystal size	0.22 x 0.22 x 0.20 mm ³	
Theta range for data collection	1.68 to 31.64°	
Index ranges	-17 ≤ h ≤ 17, -23 ≤ k ≤ 23, -25 ≤ l ≤ 26	
Reflections collected	97895	
Independent reflections	11674 [R(int) = 0.0328]	
Completeness to theta = 31.64°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9237 and 0.9166	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11674 / 624 / 520	
Goodness-of-fit on F ²	1.036	
Final R indices [I > 2σ(I)]	R1 = 0.0293, wR2 = 0.0736	
R indices (all data)	R1 = 0.0357, wR2 = 0.0773	
Largest diff. peak and hole	0.939 and -0.907 e.Å ⁻³	

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