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Selective Isomerization of Terminal Alkenes to (*Z*)-2-Alkenes Catalyzed by an Air-Stable Molybdenum(0) Complex

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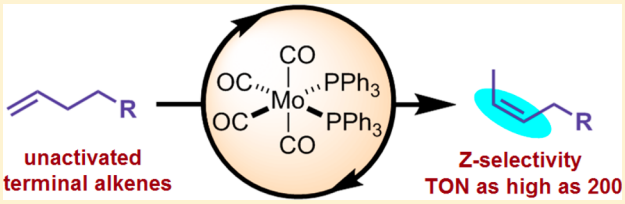
Supporting Information

ABSTRACT: Positional and stereochemical selectivity in the isomerization of terminal alkenes to internal alkenes is observed using the *cis*-$Mo(CO)_4(PPh_3)_2$ precatalyst. A *p*-toluenesulfonic acid (TsOH) cocatalyst is essential for catalyst activity. Various functionalized terminal alkenes have been converted to the corresponding 2-alkenes, generally favoring the *Z* isomer with selectivity as high as 8:1 *Z*:*E* at high conversion. Interrogation of the catalyst initiation mechanism by ^{31}P NMR reveals that *cis*-$Mo(CO)_4(PPh_3)_2$ reacts with TsOH at elevated temperatures to yield a phosphine-ligated Mo hydride (MoH) species. Catalysis may proceed via 2,1-insertion of a terminal alkene into a MoH group and stereoselective *β*-hydride elimination to yield the (*Z*)-2-alkene.



INTRODUCTION

Alkene-containing compounds are an important class of organic building blocks largely due to the diversity of alkene functionalization methods available.[1,2] Alkene isomers of different substitution and stereochemistry can have different physical and chemical properties, and therefore, synthetic methods that access specific alkene isomers are desirable.[3] Advances in transition-metal-catalyzed alkene isomerization have recently emerged,[4−11] finding applications in complex molecule synthesis[12,13] and tandem catalysis.[14] However, due to the often negligible differences in heats of formation of alkene isomers,[15,16] isomerization under thermodynamic control tends to give mixtures of products, generally favoring (*E*)-alkenes. Isomerization that proceeds via transition-metal hydride catalysts can enable kinetic preference for (*Z*)-2-alkenes on the basis of the reduced steric hindrance of an η^2-bound (*Z*)-alkene.[9]

Notable catalysts for selective alkene isomerization are represented in Figure 1. Skrydstrup and co-workers[5] have reported that $Pd(P^tBu_3)_2(H)(Cl)$, generated in situ from $Pd(P^tBu_3)_2$ and isobutyryl chloride, is highly active for *E*:*Z* alkene interconversion and will selectively isomerize terminal allylbenzenes and other allylic substrates to the respective (*E*)-2-alkenes. Isomerizing terminal alkenes with longer alkyl chains to the 2-alkene without forming higher internal isomers is more challenging. Grotjahn's catalyst,[6,7] $[(Cp)Ru(PR_3)(NCCH_3)][PF_6]$ (where PR_3 is an imidazol-2-yl-substituted phosphine), promotes the selective one-carbon migration of terminal alkenes, favoring selectivity for the (*E*)-2-alkene. Recently, Huang and co-workers[8] reported a NCP pincer-ligated Ir catalyst that generates 2-alkenes from a broad scope of terminal alkenes with high selectivity for the *E* isomer (∼1:30 *Z*:*E*).

Catalysts that favor the less thermodynamically stable (*Z*)-alkene isomers are less common. A breakthrough in this area was realized by Weix, Holland, and co-workers,[9] who showed that a (nacnac)Co complex forms (*Z*)-2-alkenes from a variety of terminal olefins. However, this catalyst suffers from overisomerization to higher alkene isomers, and stereoselectivity degrades with longer reaction duration. Hilt and co-workers[10] reported a procedure for *Z*-selective isomerization of terminal alkenes with bisphosphine-ligated Co catalysts, $HPPh_2$, ZnI_2, and Zn powder cocatalysts. The Hilt group followed up with a similar procedure using bisphosphine-ligated Ni catalysts for alkene isomerizations.[11] The state of the art in *Z*-selective isomerization of *unactivated* terminal alkenes is represented by the work of Weix, Holland, and Hilt: typical stereoselectivity reported by either Co catalyst is ∼(5−7):1 *Z*:*E* of the 2-alkene. Hilt's Ni catalyst is reported to invoke higher

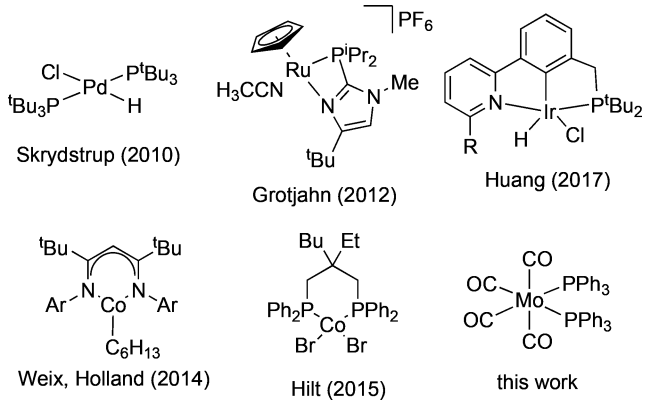


Figure 1. Selected recent examples of organometallic catalysts for selective alkene isomerization.[4−10]

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selectivity for the (*Z*)-2-alkene (~9:1 *Z*:*E*); however, these reactions were performed at −60 to −10 °C, where the equilibrium lies closer to (*Z*)-alkene.

Beyond positional and stereochemical selectivity, a practical isomerization precatalyst would be simple to prepare, air stable, active enough for low catalyst loadings (<1 mol %), and general for a wide variety of substrates.[7] In considering these attributes, low-valent Mo complexes have great promise as alkene isomerization precatalysts.[17−21] A patent[17] suggests that $Mo(CO)_6$ (**1**) is active for isomerization under thermal conditions (>150 °C), and qualitative positional selectivity is reported. We reasoned that, if alkene isomerization occurred under milder conditions with preformed Mo complexes, selectivity and activity could be improved. Indeed, phosphine-ligated Mo^0 complexes selectively promote the one-carbon migration of functionalized terminal alkenes to (*Z*)-2-alkenes when an acid cocatalyst is employed. Preliminary mechanistic experiments demonstrate the competency of the acid cocatalyst to generate a Mo hydride species (MoH), with isomerization plausibly occurring via 2,1-insertion of a terminal alkene into the MoH, followed by selective *β*-hydride elimination to furnish (*Z*)-2-alkene.

RESULTS AND DISCUSSION

Simple, air-stable, phosphine-ligated Mo^0 complexes were targeted and prepared by literature procedures (Figure 2).[22−25] **1** is refluxed in PhMe with piperidine to generate *cis*-$Mo(CO)_4(pip)_2$ (**2**). **2** can be converted to *cis*-$Mo(CO)_4(PPh_3)_2$ (**3-cis**) by the addition of 2 equiv of PPh_3 in refluxing CH_2Cl_2, while the thermodynamic product, *trans*-$Mo(CO)_4(PPh_3)_2$ (**3-trans**), is generated on refluxing in PhMe. By analogy, bidentate ligands (dppf,[26,27] dppbz,[28,29] DPE-phos, xantphos) were used to prepare complexes **4a−d**.

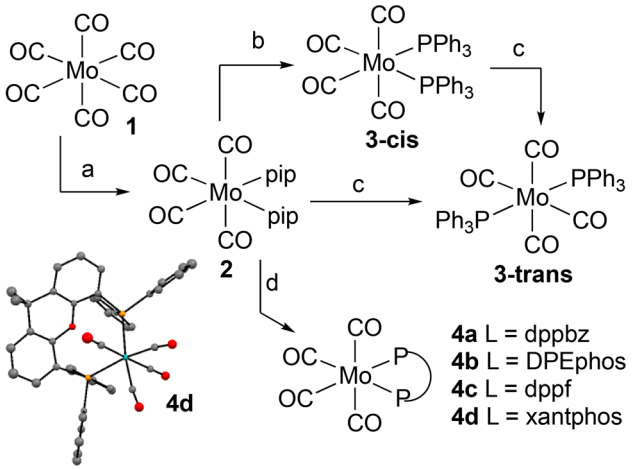
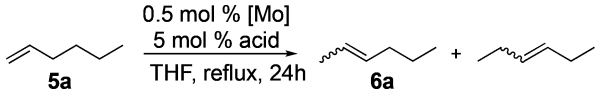


Figure 2. Synthesis of relevant Mo complexes. Reaction conditions: (a) **1**, 5−7 equiv of piperidine, refluxing PhMe; (b) **2**, 2 equiv of PPh_3, refluxing CH_2Cl_2; (c) **2** with 2 equiv of PPh_3 or **3-cis**, refluxing PhMe; (d) **2** and 1 equiv of L, refluxing CH_2Cl_2. Bottom left: X-ray structure of **4d**.

The competency of the synthesized Mo complexes to isomerize terminal alkenes to internal alkenes was evaluated using 1-hexene (**5a**) (Table 1). On the basis of the ability of Brønsted acids to protonate Mo^0 to generate MoH species,[21,30,31] we reasoned that incorporation of acid cocatalysts to the reaction mixture could generate the MoH species necessary to observe alkene isomerization. *p*-Toluenesulfonic acid (TsOH) was chosen, as it is an easily dispensed solid acid and is readily prepared in anhydrous form. In the absence of acid, complexes **1**−**3** are not active for 1-hexene isomerization in refluxing THF. With added TsOH, **1** and **2** were active but poorly selective for alkene isomerization, while **3-cis** showed superior activity and selectivity. **5a** with 0.5 mol % of **3-cis** and 5 mol % of TsOH in refluxing THF generated (*Z*)-2-hexene (**6a**, 85% yield, 4.0:1 *Z*:*E*) after 24 h of reaction, with only trace 3-hexene generated. The use of $TsOH{\cdot}H_2O$ resulted in a more active, but less selective, catalyst. Surprisingly, **3-trans** was a significantly less active catalyst than **3-cis**, proceeding to only 46% conversion of **5a** under identical conditions. Although a cis phosphine orientation gave higher catalytic activity, cis-bidentate phosphine complexes **4a−d** were generally less active than **3-cis** under identical conditions. Performance comparable to that of catalyst **3-cis** could be achieved under modified conditions: complex **4d** (1 mol %) and $TsOH{\cdot}H_2O$ (10 mol %) in refluxing THF catalyzed the isomerization of **5a** to **6a** (91% yield, 4.2:1 *Z*:*E*). When isomerization was attempted with 5 mol % TsOH and no Mo catalyst, no conversion of **5a** is observed. We determined **3-cis** to be the optimal catalyst of those screened due to the ease and low cost of preparation, air stability, and a combination of catalytic activity and selectivity at low catalyst loadings.

Table 1. Initial Screening of Mo Catalysts in the Isomerization of 1-Hexene to Internal Alkenes[a]



entry	[Mo]	acid	conversn (%)[b]	yield of **6a** (%)[b]	*Z*:*E* (**6a**)[b]
1	**1**	N/A	2	nd	nd
2	**2**	N/A	3	nd	nd
3	**3-cis**	N/A	1	nd	nd
4	**1**	TsOH	61	37	1.6:1
5	**2**	TsOH	96	73	0.4:1
6	**3-cis**	TsOH	94	85	2.2:1
7[c]	**3-cis**	TsOH	94	91	4.0:1
8	**3-cis**	$TsOH{\cdot}H_2O$	96	79	1.1:1
9	**3-trans**	TsOH	46	44	8.1:1
10	**4a**	TsOH	4	nd	nd
11	**4b**	TsOH	4	nd	nd
12	**4c**	$TsOH{\cdot}H_2O$	67	65	5.6:1
13	**4d**	$TsOH{\cdot}H_2O$	23	nd	nd
14[d]	**4d**	$TsOH{\cdot}H_2O$	92	91	4.2:1

[a]Reaction conditions unless specified otherwise: 1 mmol of **5a**, 0.5 mol % of Mo catalyst, 5 mol % of TsOH or $TsOH{\cdot}H_2O$, 1 mL of THF, 66 °C, 24 h. [b]Determined by ^1H NMR. The remaining mass balance corresponds to other internal isomers. [c]Reaction time 30 min. [d]1 mol % of Mo catalyst and 10 mol % of acid were used.

The optimized conditions using **3-cis** were used to establish the substrate scope for the catalytic reaction (Chart 1). In general, high levels of both positional selectivity and stereoselectivity are observed in alkene isomerization (20 examples, 33−93% of the 2-alkene, up to 8.2:1 *Z*:*E* selectivity). **5a** and 1-octene (**5b**) are converted to the 2-alkenes under the standard conditions (0.5 mol % **3-cis**, 5 mol % TsOH, 1.0 M refluxing THF) to high conversion in 30 min. 2-Octene (**6b**) is formed in 87% yield (5.1:1 *Z*:*E*). Longer-chain alkenes (1-decene (**5c**) and 1-dodecene (**5d**)) require longer reaction times or higher

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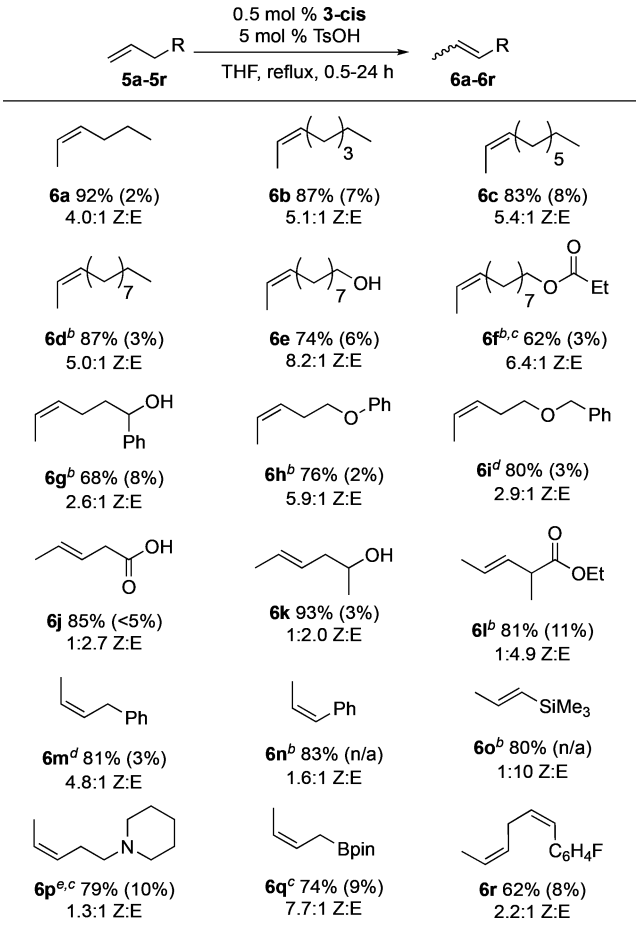
Chart 1. Substrate Scope[a]



[a]Reaction conditions unless specified otherwise: 1 mmol of **5**, 0.5 mol % of Mo catalyst, 5 mol % of TsOH, 1 mL of THF, 66 °C. The yields of 2-alkene are indicated; yields of higher internal alkene isomers are indicated in parentheses. Yield and selectivity are determined by ^{1}H NMR. [b]1 mol % of **3-cis**, 10 mol % of TsOH. [c]Selectivity determined by inverse-gated decoupled ^{13}C NMR. [d]2 mol % of **3-cis**, 20 mol % of TsOH. [e]Starting material and product were the HCl salt.

catalyst loadings. The reaction of **5c** under standard conditions forms 2-decene (**6c**, 83% yield, 5.4:1 *Z*:*E*) after 20 h of reaction. The reaction of **5d** using 1 mol % of **3-cis** gave **6d** in 87% yield (5.0:1 *Z*:*E*). Despite prolonged reaction times, only a small quantity of higher internal olefins was observed (8% for **5c**, 3% for **5d**).

Next, functionalized alkenes were evaluated in catalysis. The long-chain alcohol undec-10-en-1-ol (**5e**) is converted to the 2-alkene with high selectivity for the *Z* isomer under standard conditions to give undec-9-en-1-ol (**6e**, 74% yield, 8.2:1 *Z*:*E*). The ester undec-10-en-1-yl propionate (**5f**) is converted to 62% (6.5:1 *Z*:*E*) of the 2-alkene after 20 h of reaction using increased catalyst loadings. In addition, substrates with aryl substituents are slower, as indicated by substrates **5g**–**i**, and required higher catalyst and acid loadings. Using 1 mol % of **3-cis** and 10 mol % of TsOH, 1-phenylhex-4-en-1-ol (**6g**) was prepared in 68% yield (2.6:1 *Z*:*E*), and (pent-3-en-1-yloxy)-benzene was prepared in 76% yield (5.9:1 *Z*:*E*).

With some substrates, selectivity for the (*E*)-2-isomer is observed. Pent-4-enoic acid (**5j**), hex-5-en-2-ol (**5k**), and ethyl 2-methylpent-4-enoate (**5l**) form (*E*)-2-isomers preferentially (**6j**, 85% yield, 1:2.7 *Z*:*E*; **6k**, 93% yield, 1:2 *Z*:*E*; **6l**, 81% yield, 1:4.9 *Z*:*E*). The oxygen functionalities of **5j**–**l** may chelate and favor formation of six-membered metallacycles where the substrate is prearranged to eliminate the (*E*)-alkene.[32] Absent a directing effect, other kinetic influences may allow product ratios to approach equilibrium mixtures of 2-isomers.[33]

In addition to aromatic groups, the reaction slowed when substrates with δ and ε substituents are used. The reaction of but-3-en-1-ylbenzene (**5m**) proceeded to only 11% conversion under standard conditions; however, at higher catalyst (2 mol % **3-cis**) and acid (20 mol % TsOH) loadings, prop-2-en-1-ylbenzene (**6m**) was formed in 81% yield and 4.8:1 *Z*:*E* selectivity. Similarly, the reaction of allylbenzene (**5n**) proceeded to only 9% conversion under standard conditions, but **6n** was formed in 83% yield (1.6:1 *Z*:*E*) using 1 mol % of **3-cis** and 20 mol % of TsOH. Higher catalyst loadings were also necessary to isomerize allyltrimethylsilane (**5o**), which is isomerized to the (*E*)-alkene (**6o**), likely due to the steric bulk of the $SiMe_3$ group.

Other substrates with potentially reactive functional groups were then evaluated: 1-(pent-4-en-1-yl)piperidine (**5p**) contains a Brønsted basic amine group which could potentially neutralize the acid necessary to generate an active catalyst. Although no conversion was observed using **5p**, the reaction of **5p·HCl** proceeded using 0.5 mol % of **3-cis** and 5 mol % of TsOH to generate **6p·HCl** (79% yield, 1.3:1 *Z*:*E*). 2-(But-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5q**) is a potential nucleophile yet still undergoes facile isomerization to yield the synthetically valuable allyl boronate ester[34] **6q** (74% yield, 7.7:1 *Z*:*E*). The 1,5-diene **5r**, featuring both internal and terminal alkene groups, is isomerized selectively to the (*Z*,*Z*)-2,5-diene **6r** (60%, 2:1 *Z*:*E*) with no evident isomerization of the internal alkene.

With the scope of alkene isomerization in hand, we sought a mechanistic rationale for the observed *Z* selectivity. Weix, Holland, and co-workers[9] propose that *Z*-selective Co isomerization proceeds through an inner-sphere alkyl[35] (Figure 3A)

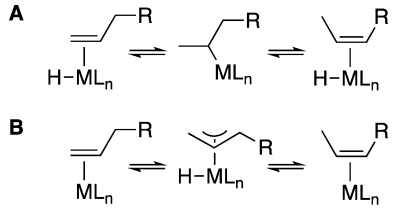


Figure 3. Commonly proposed mechanisms for metal mediated alkene isomerization: (A) alkyl mechanism; (B) allyl mechanism.

pathway. Here, a *Z*-selective alkyl mechanism requires alkene insertion into MoH to generate a Mo(alkyl) species followed by selective β-hydride elimination to furnish the respective (*Z*)-2-alkene. Other mechanisms proceeding through η^3-allyl[36] (Figure 3B), β-carbocation,[37] or radical intermediates are also possible.[9,13,38] Another mode of reactivity would involve the direct protonation of alkenes by acidic M–H species.[39]

In a thermodynamic mixture of linear alkenes generated by unselective isomerization catalysts, many internal isomers (*Z*-2, *E*-2, *Z*-3, *E*-3, etc.) are present. Our catalyst system apparently promotes a rapid conversion of 1-alkene to (*Z*)-2-alkenes, with comparatively slow *Z* to *E* isomerization of internal alkenes, as well as low rates of 2-alkene to 3-alkene isomerization. Indeed, catalyst **3-cis** is poorly reactive toward internal alkenes. (*Z*)-2-Hexene or (*E*)-2-hexene subjected to standard reaction

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conditions (0.5 mol % **3-cis**, 5 mol % TsOH, THF, reflux, 24 h) yields minimal conversion (<2%) to 3-hexenes. This observation is consistent with facile migratory insertion of a terminal alkene relative to internal alkenes. Trace 3-alkenes observed in catalysis could be generated directly from the terminal alkene through a "chain-walking" mechanism, rather than reinsertion of the 2-alkene products by a MoH species.[9] We also observed that catalysis was inhibited (<2% conversion) when the standard reaction conditions were modified with (a) 1 atm of CO, (b) additional PPh_3 (2−5 mol %), (c) TEMPO (2 mol %). Given the capacity of TEMPO to act as a M−H trap,[40] inhibition of catalysis by TEMPO may indicate M−H intermediates.

Catalyst initiation of **3-cis** was investigated by ^{31}P NMR in hopes of establishing the catalyst resting state. Substrate **5b** (1 mmol), **3-cis** (0.01 mmol), TsOH (0.1 mmol), and C_6D_6 (0.6 mL) were combined in an NMR tube and heated to 80 °C for 10 min. The reaction proceeded to 70% conversion of **5b** to **6b**, and the ^{31}P NMR spectrum (C_6D_6, 292 K) revealed conversion of **3-cis** to **3-trans**, *trans*-$Mo(CO)_4(PPh_3)_3$ (**7-trans**),[41] two unidentified $Mo(PPh_3)$ species, and the liberation of $HPPh_3^+$. The same ^{31}P NMR resonances are visible in the absence of alkene. Presumably, catalyst initiation begins by the dissociation of PPh_3 from **3-cis**,[22] consistent with inhibition by additional PPh_3 and with reduced catalytic activity when bidentate phosphines are employed. Solvent-dependent coordination behavior of **3-cis** is also observed. When **3-cis** is dissolved in CD_3CN, CO for CD_3CN ligand exchange is indicated by the formation of multiple CD_3CN-bound Mo species observed in the ^{31}P NMR spectrum. In contrast, no evidence for CO dissociation from **3-cis** is found in THF solvent, consistent with the reluctance of Mo^0 to liberate CO ligands.

In search of catalyst intermediates, we sought a MoH species capable of promoting alkene isomerization via an alkyl mechanism (Figure 3A). No MoH is observed when **3-cis** and TsOH are combined in THF (the solvent used under optimized catalytic conditions), but a MoH species can be generated from **3-cis** and TsOH in MeCN.[42] Although the complex could not be isolated and fully characterized, a resonance in the ^1H NMR spectrum (CD_3CN, 292 K) is observed at −4.3 ppm (**8-cis**, d, $^2J_{PH}$ = 66 Hz), consistent with an octahedral Mo complex with mutually cis H and PPh_3 ligands.[30,43] The resulting mixture of Mo species containing **8-cis** isomerizes **5b** to **6b** at room temperature. Without isolation of **8-cis**, catalytic activity cannot be unambiguously attributed to this hydride complex. Nonetheless, the observation of **8-cis** confirms TsOH can promote MoH formation under certain conditions.

Myriad six-coordinate catalyst intermediates can be envisaged for our system, as can seven-coordinate species, such as the isomerization-active seven-coordinate Mo hydride generated by Jones and co-workers[21] via addition of $HBF_4{\cdot}Et_2O$ to a Mo tricarbonyl pincer complex. Here, phosphine is unnecessary for isomerization activity but is necessary for (*Z*)-2-alkene selectivity (Table 1). However, on the basis of ^{31}P NMR studies of the **3-cis** reaction mixture, partial PPh_3 dissociation occurs readily during catalysis, and additional PPh_3 inhibits the reaction. PPh_3 could preserve selectivity for (*Z*)-2-alkenes as a sterically demanding ligand on the active catalyst species. Alternatively it can compete with 2-alkene for binding to the active catalyst (thereby slowing *Z* to *E* isomerization) or inhibit other isomerization catalysts that lack selectivity for the (*Z*)-2-alkene.

CONCLUSION

A method for selective alkene isomerization via Mo has been discovered. The methodology is complementary to the few available catalysts that form (*Z*)-2-alkenes from terminal alkenes, showing comparable or improved selectivity. The air-stable precatalyst **3-cis** is easily prepared with inexpensive ligands and with TON ranges as high as 200 and initial TOF ranges as high as 400 h^{-1}. A variety of functionalized alkenes are tolerated under the reaction conditions, though some substrates require higher catalyst and acid loadings. Efforts in our laboratory are underway to understand the origins of selectivity observed for this catalyst and develop additional synthetic protocols for selective transformations of alkenes.

EXPERIMENTAL SECTION

General Information. Air-free manipulations were performed under a dry N_2 atmosphere using a Vacuum Atmospheres inert-atmosphere glovebox or using standard Schlenk techniques. NMR spectra were collected on Bruker Avance III 500 MHz and DRX 500 MHz instruments. ^1H NMR chemical shifts (δ, ppm) are referenced to residual protio-solvent resonances, and ^{13}C NMR chemical shifts are referenced to the deuterated solvent peak. ^{31}P NMR and ^{19}F NMR chemical shifts are referenced to external standards. Microanalysis data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456. Toluene (PhMe), methylene chloride (CH_2Cl_2), tetrahydrofuran (THF), diethyl ether (Et_2O), and pentane were purified using a commercial solvent purification system. Unless otherwise noted, commercial chemicals were used as received without further purification. 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-crown-6), molybdenum hexacarbonyl ($Mo(CO)_6$), and sodium hexamethyldisilazide (NaHMDS) were supplied by Strem. Allylbenzene, allyltrimethylsilane, 1,2-bis(diphenylphosphino)benzene (dppbz), dec-1-ene, hex-1-ene, oct-1-ene, and piperidine were supplied by Sigma-Aldrich. 5-Bromobut-1-ene, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos), 1,1′-ferrocenediylbis(diphenylphosphine) (dppf), hex-5-en-2-one, 4-fluorobenzaldehyde, (oxidi-2,1-phenylene)bis(diphenylphosphine) (DPE-phos), 4-pentenoic acid, 4-phenylbut-1-ene, triphenylphosphine (PPh_3), and undec-10-en-1-ol were supplied by Oakwood. Ethyl 2-methylpent-4-enoate and propionyl chloride were supplied by Alfa Aesar. 2-(But-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and dodec-1-ene were supplied by Combi Blocks. *p*-Toluenesulfonic acid was supplied by Fisher. Deuterated solvents were supplied by Cambridge Isotopes.

***p*-Toluenesulfonic acid (Anhydrous).** $TsOH{\cdot}H_2O$ was placed in an oven-dried 250 mL round-bottom flask along with a stir bar, and the flask was sealed using a Schlenk adapter with a PTFE stopcock. The flask was placed under vacuum, submerged into an oil bath, and heated to 50 °C. As anhydrous TsOH was formed, the solids began to melt to form a viscous gray liquid. The liquid was stirred under vacuum at this temperature for 2 h. The mixture was then cooled to room temperature, at which point the liquid solidified. The flask was opened to air, and the solid was ground into a powder with a spatula. Then, the solids were placed under vacuum at room temperature overnight. ^1H NMR of the resulting solid indicated the absence of H_2O.

Synthesis and Characterization of Mo Complexes. *Mo(CO)$_4$(piperidine)$_2$ (**2**).* The complex was prepared by a modified literature procedure.[22] *Caution!* The following reaction evolves carbon monoxide and is performed in a sealed vessel. This procedure should be carried out behind a blast shield. An oven-dried thick-walled Schlenk tube was charged with $Mo(CO)_6$ (2 g, 7.58 mmol) under an N_2 atmosphere. The solids were suspended in 30 mL of PhMe, and piperidine (7 equiv, 5.3 mL, 53.0 mmol) was added. The tube was sealed with a PTFE stopper under inert conditions. The tube was submerged in an oil bath and heated to 120 °C. The reaction mixture was stirred at this temperature for 2 h. Periodically, the PTFE stopper was carefully opened to the reaction to vent CO pressure evolved

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during the reaction and quickly resealed. After completion of the reaction, a yellow crystalline solid precipitated. The solid was collected by filtration under N_2 (2.87 g, 78% yield). Anal. Calcd for $C_{14}H_{22}MoN_2O_4$: C, 44.45; H, 5.86; N, 7.41. Found: C, 44.395; H, 5.941; N, 7.145.

*cis-Mo(CO)$_4$(PPh$_3$)$_2$ (**3-cis**).* The complex was prepared by a modified literature procedure.[25] Under an N_2 atmosphere, an oven-dried Schlenk tube was charged with $Mo(CO)_4(piperidine)_2$ (1.0 g, 2.64 mmol) and the solid was dissolved in 15 mL of CH_2Cl_2. A solution of triphenylphosphine (2 equiv, 1.4 g, 5.3 mmol) in 10 mL of CH_2Cl_2 was added to the mixture. The tube was sealed with a PTFE stopper under inert conditions and then submerged in an oil bath preheated to 40 °C. The reaction mixture stirred at this temperature for 2 h. After it was cooled to room temperature, the mixture was opened to air and filtered through Celite. The solvent volume of the filtrate was reduced in vacuo, and the product was precipitated with MeOH to yield a pale yellow solid (1.94 g, 93%). Crystalline material was obtained by cooling a solution of **3-cis** in 4/1 Et_2O/CH_2Cl_2 to −30 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.3−7.1 (30H). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 215.3 (t, $^2J_{C-P}$ = 9.2 Hz), 210.5 (t, $^2J_{C-P}$ = 9.2 Hz), 136.5 (m), 133.7 (t, $^2J_{C-P}$ = 6.5 Hz), 129.7, 128.4 (t, $^2J_{C-P}$ = 4.6 Hz). ^{31}P NMR (202 MHz, $CDCl_3$, 292 K, ppm): δ 37.0. Anal. Calcd for $C_{40}H_{30}MoO_4P_2\cdot H_2O$: C, 64.01; H 4.30. Found: C, 64.333; H 4.109. ***trans*-Mo(CO)$_4$(PPh$_3$)$_2$ (3-trans)**[25] can be prepared by heating a toluene solution of **3-cis** to reflux.

*Mo(CO)$_4$(dppf) (**4a**), Mo(CO)$_4$(dppbz) (**4b**), Mo(CO)$_4$(DPE-phos) (**4c**), and Mo(CO)$_4$(xantphos) (**4d**).* These complexes can be prepared by literature methods.[25−29] **4d** can be prepared in higher purity via **3-cis**. Under an N_2 atmosphere, **3-cis** (0.9 g, 1.23 mmol) was placed in a vial and dissolved in 5 mL of PhMe. A separate solution of xantphos (0.71 g, 1.23 mmol) in 5 mL of PhMe was prepared, and the solutions were combined. The vial was sealed and heated to 110 °C for 2 h. Then, the reaction mixture was cooled to room temperature and the vial was opened to air. The solution was filtered through Celite and then evaporated. The resulting beige solids were rinsed with Et_2O to remove triphenylphosphine, and the product was then dried in vacuo (890 mg, 92% yield). X-ray-quality crystals were grown from a solution of **4d** in 4/1 Et_2O/CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.45 (2H, d), 7.22−7.07 (20H), 6.98 (2H, t), 1.55 (6H, t). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 215.9 (m), 210.0 (t), 134.7 (m), 133.2 (t), 132.3, 130.9, 120.5, 128.3 (t), 127.5, 124.1, 124.0, 123.3 (m), 35.39, 29.97. ^{31}P NMR (202 MHz, $CDCl_3$, 292 K, ppm): δ 20.8. Anal. Calcd for $C_{43}H_{32}MoO_5P_2\cdot C_7H_8$: C, 67.96; H, 4.56. Found: C, 67.402; H, 4.469.

Synthesis and Characterization of Alkene Substrates. *Undec-10-en-1-yl Propanoate (**5f**).*[44] A 500 mL round-bottom flask was charged with undec-10-en-1-ol (1.067 g, 6.27 mmol), 20 mL of CH_2Cl_2, and 2 mL of pyridine. The reaction mixture was cooled to 0 °C. A solution containing a slight excess of propionyl chloride (0.600 g, 6.5 mmol) in 10 mL of CH_2Cl_2 was added dropwise into the reaction mixture. The reaction mixture was then stirred vigorously at 0 °C for 30 min, after which the mixture was stirred at room temperature for 1 h. Dilute HCl in H_2O was then added to the solution. The organic layer was separated and rinsed with saturated Na_2CO_3(aq), H_2O, brine, and H_2O, dried over $MgSO_4$, filtered, and evaporated to yield a colorless liquid (0.874 g, 62%). ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 5.79 (1H, m), 5.00−4.89 (2H, m), 4.04 (2H, t, $^3J_{H-H}$ = 6.8 Hz), 2.30 (2H, q, $^3J_{H-H}$ = 7.5 Hz), 2.02 (2H, m), 1.60 (2H, m), 1.39−1.21 (12H, m), 1.12 (3H, t, J = 7.6 Hz).

*1-Phenylhex-5-en-1-ol (**5g**).*[45] In a N_2 atmosphere glovebox, an oven-dried 250 round-bottom flask was charged with Mg turnings (0.736 g, 30.2 mmol), a crystal of I_2, and anhydrous THF (15 mL). The mixture was stirred for 15 min at room temperature. A solution of 5-bromo-1-pentene (3.00 g, 20.1 mmol) in THF (20 mL) was added to the Mg dropwise via addition funnel, and the resultant solution was stirred for 1 h. The flask was then sealed with a rubber septum and removed from the glovebox. Under N_2, benzaldehyde (2.35 g, 22.1 mmol) was added dropwise via syringe, and the solution was stirred at room temperature for 1 h. The crude reaction mixture was quenched with water and extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and evaporated in vacuo to yield a yellow oil (2.00 g, 56%). ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.32−7.17 (5H, m), 5.72 (1H, m), 4.97−4.87 (2H, m), 4.57−4.52 (1H, m), 2.47 (1H, s), 2.00 (2H, m), 1.76−1.68 (1H, m), 1.67−1.59 (1H, m), 1.45 (1H, m), 1.30 (1H, m).

*(Pent-4-en-1-yloxy)benzene (**5h**).*[46] 5-Bromo-1-pentene (2.38 g, 15.9 mmol) was placed in a 250 mL round-bottom flask containing a suspension of phenol (1.50 g, 15.9 mmol) and K_2CO_3 (4.41 g, 31.88 mmol, 691.1 mg) in acetone (100 mL). The reaction mixture was heated to 66 °C for 20 h, cooled, and filtered. The solvent volume was reduced in vacuo, diluted with water, and extracted with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and evaporated in vacuo to yield a yellow oil (1.59 g, 57%). ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.22−7.15 (2H, m), 6.87−6.82 (2H, m), 5.78 (1H, m), 4.99 (1H, m), 4.92 (1H, m), 3.90 (2H, t, $^3J_{H-H}$ = 6.6 Hz), 2.16 (2H, m), 2.81 (2H, m).

*((Pent-4-en-1-yloxy)methyl)benzene (**5i**).*[9] In a N_2 atmosphere glovebox, NaH (0.400 g, 16.65) was slowly added to a solution of benzyl alcohol (1.50 g, 13.9 mmol) in DMF (20 mL) and stirred for 1 h. A solution of 5-bromo-1-pentene (2.07 g, 13.9 mmol) in 10 mL of DMF was slowly added to the reaction mixture, which was stirred at room temperature for 20 h. The reaction mixture was removed from the glovebox, diluted with water, and extracted with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and evaporated in vacuo to yield a yellow oil (0.894 g, 37%). ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.39−7.31 (Ar, 4H, m), 7.30−7.27 (Ar, 1H, m), 5.87−5.77 (alkene CH, 1H, m), 5.05−5.00 (alkene CH, 1H, dq), 4.98−4.94 (alkene CH, 1H, m), 4.51 (CH_2, 2H, s), 3.49 (CH_2, 2H, t), 2.15 (CH_2, 2H, m), 1.72 (CH_3, 3H, m).

*Hex-5-en-2-ol (**5k**).*[47] In an oven-dried 80 mL vial, $NaBH_4$ (1.55 g, 41.0 mmol) was added to a stirred solution of 5-hexen-2-one (2.01 g, 20.5 mmol) in EtOH (40 mL) at 0 °C. The resulting solution was warmed to room temperature and stirred for 18 h. The solution was poured into a saturated solution of NH_4Cl(aq). When effervescence had ceased, the mixture was extracted with ether. The combined extracts were washed with brine, dried over $MgSO_4$, and filtered, and the solvent was carefully removed in vacuo to yield a volatile, colorless oil (1.21 g, 59%). ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 5.84 (1H, m), 5.07−4.95 (2H, m), 3.83 (1H, m), 2.22−2.07 (2H, m), 1.61−1.50 (3H, m), 1.20 (3H, d, $^3J_{H-H}$ = 6.2 Hz).

*1-(Pent-4-en-1-yl)piperidine (**5p**).*[9] The compound was prepared in a fashion analogous to that for 1-(but-3-en-1-yl)piperidine. A 250 mL round-bottom flask was charged with a solution of 5-bromo-1-butene (5.00 g, 33.6 mmol), piperidine (2.39 mL, 28.1 mmol), 18-crown-6 (0.360 g, 1.36 mmol), K_2CO_3 (4.83 g, 35.0 mmol), and CH_3CN (40 mL). The reaction mixture was heated at reflux for 18 h. The crude reaction mixture was filtered through alumina, rinsed with water, and extracted with Et_2O. The organics were washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum. The desired product was isolated as an orange oil (1.91 g, 43%). ^{1}H NMR (500 MHz, $CDCl_3$, 292 K): δ 5.81 (1H, m), 5.03−4.92 (2H, m), 2.35 (4H, br s), 2.28 (2H, m), 2.39−2.36 (2H, m), 1.62−1.54 (6H, m), 1.42 (2H, m). 1-(pent-4-en-1-yl)piperidine·HCl (5p·HCl). A 1 M solution of HCl in Et_2O (4 mL) was placed in a 16 mL vial containing a solution of 1-(pent-4-en-1-yl)piperidine (0.500 g, 3.26 mmol) in THF (3 mL). The mixture was stirred at room temperature for 15 min, and then the solid was filtered, rinsed with ether, and dried in vacuo to yield a beige solid (0.548 g, 89%). ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 12.19 (1H, br s), 5.77 (1H, m), 5.07 (2H, m), 3.54 (2H, d), 2.91 (2H, m), 2.61 (2H, m), 2.34 (2H, m), 2.15 (2H, m), 2.05 (2H, m), 1.92 (1H, m), 1.85 (2H, m), 1.41 (1H, m). ^{13}C NMR (126 MHz, 292 K, $CDCl_3$, ppm): δ 136.0, 116.7, 57.0, 53.2, 30.8, 22.5, 22.4, 22.2.

*(Z)-1-Fluoro-4-(hexa-1,5-dien-1-yl)benzene (**5r**).*[48] The compound was prepared in a fashion analogous to that for (Z)-hexa-1,5-dien-1-ylbenzene. A solution of 5-bromo-1-pentene (1.50 g, 10.1 mmol) and triphenylphosphine (2.64 g, 10.1 mmol) in CH_3CN (40 mL) was refluxed for 3 days, after which the solvent was removed in vacuo to yield a white solid. The solid was rinsed with Et_2O to yield pent-4-en-1-yltriphenylphosphonium bromide (4.04 g, 97%). The solid was further oven-dried (120 °C) to remove residual H_2O. In an N_2

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atmosphere glovebox, pent-4-en-1-yltriphenylphosphonium bromide (3.62 g, 14.3 mmol) was placed in a 250 mL round-bottom flask and suspended in 25 mL of THF. A solution of NaHMDS (1.61 g, 8.80 mmol) in THF (10 mL) was added to the mixture, which was then stirred at room temperature for 30 min, yielding an orange solution. Then, a solution of 4-fluorobenzaldehyde (1.09 g, 8.80 mmol) in THF (5 mL) was added. The reaction mixture slowly turned beige, indicating consumption of the Wittig reagent. The mixture was stirred for 20 h at room temperature, after which the solvent was removed in vacuo. The resulting residual solid was stirred in hexane for 4 h, filtered, and concentrated under vacuum to yield a yellow oil. The oil was purified by column chromatography on silica (hexane) to give the product as a colorless liquid (1.00 g, 64%). ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.16−7.11 (Ar, 2H, m), 6.95−6.85 (Ar, 2H, m), 6.35−6.24 (alkene CH, 1H, m), 5.78−5.69 (alkene CH, 1H, m), 5.55 (alkene CH, 1H, dt, $^3J_{H-H}$ = 11.7, $^3J_{H-H}$ = 7.2 Hz), 4.97−4.88 (alkene CH, 1H, m), 2.33−2.27 (CH_2, 2H, m), 2.15−2.08 (CH_2, 2H, m).

General Procedure for Catalytic Reactions. In a nitrogen atmosphere glovebox, an 8 mL vial was charged with hex-1-ene (84 mg, 1 mmol), 500 μL of a 10 mM stock solution of **3-cis** in THF (5 μmol, 0.5 mol %), and 500 μL of a 100 mM stock solution of TsOH in THF (50 μmol, 5 mol %). The vial was capped and immersed in an aluminum heating block preheated to 80 °C. The reaction mixture was stirred at this temperature for 30 min, at which point the vial was cooled to room temperature and was opened to air. An aliquot of the reaction mixture was removed from the crude reaction mixture for ^{1}H NMR analysis. Unless otherwise noted, reactions were performed in triplicate. The conversion, yield, and selectivity represent an average of three trials. NMR yield and selectivity were determined using ^{1}H NMR by published methods.[6,8]

Attempted Catalysis with Internal Alkene Substrates. In a nitrogen atmosphere glovebox, an 8 mL vial was charged with (*Z*)-hex-2-ene or (*E*)-hex-2-ene (84 mg, 1 mmol), 500 μL of a 10 mM stock solution of **3-cis** in THF (5 μmol, 0.5 mol %), and 500 μL of a 100 mM stock solution of TsOH in THF (50 μmol, 5 mol %). The vial was immersed in an aluminum heating block preheated to 80 °C. The reaction mixture was stirred at this temperature for 24 h, at which point the vial was cooled to room temperature and was opened to air. An aliquot of the reaction mixture was removed from the crude reaction mixture for ^{1}H NMR analysis. Approximately 2% conversion was observed when (*Z*)-2-hexene was used as substrate. No conversion was observed for (*E*)-2-hexene.

Attempted Catalysis under Pressure of Carbon Monoxide. In a nitrogen atmosphere glovebox, an 8 mL vial was charged with hex-1-ene (84 mg, 1 mmol), 500 μL of a 10 mM stock solution of **3-cis** in THF (5 μmol, 0.5 mol %), and 500 μL of a 100 mM stock solution of TsOH in THF (50 μmol, 5 mol %). The vial was sealed with a rubber septum, and a carbon monoxide pressure was bubbled through the solution for 5 min. Then, the vial was immersed in an aluminum heating block preheated to 80 °C. The reaction mixture was stirred at this temperature for 30 min, at which point the vial was cooled to room temperature and was opened to air. An aliquot of the reaction mixture was removed from the crude reaction mixture for ^{1}H NMR analysis. Approximatley 2% conversion of the hex-1-ene substrate was observed.

Attempted Catalysis in the Presence of Added PPh_3. In a nitrogen atmosphere glovebox, an 8 mL vial was charged with hex-1-ene (84 mg, 1 mmol), PPh_3 (2−5 mol %), 500 μL of a 10 mM stock solution of **3-cis** in THF (5 μmol, 0.5 mol %), and 500 μL of a 100 mM stock solution of TsOH in THF (50 μmol, 5 mol %). The vial was immersed in an aluminum heating block preheated to 80 °C. The reaction mixture was stirred at this temperature for 30 min, at which point the vial was cooled to room temperature and was opened to air. An aliquot of the reaction mixture was removed from the crude reaction mixture for ^{1}H NMR analysis. Approximately 2% conversion of the hex-1-ene substrate was observed when 2 or 5 mol % added PPh_3 was present.

Attempted Catalysis with Added TEMPO. In a nitrogen atmosphere glovebox, an 8 mL vial was charged with hex-1-ene (84 mg, 1 mmol), TEMPO (2 mol %), 500 μL of a 10 mM stock solution of **3-cis** in THF (5 μmol, 0.5 mol %), and 500 μL of a 100 mM stock solution of TsOH in THF (50 μmol, 5 mol %). The vial was immersed in an aluminum heating block preheated to 80 °C. The reaction mixture was stirred at this temperature for 30 min, at which point the vial was cooled to room temperature and was opened to air. An aliquot of the reaction mixture was removed from the crude reaction mixture for ^{1}H NMR analysis. No conversion of the hex-1-ene substrate was observed.

Synthesis and Characterization of Alkene Products. Compounds were prepared using the General Procedure for Catalytic Reactions. Unless otherwise noted, 0.5 mol % of **3-cis** and 5 mol % of TsOH were used as catalysts.

*Hex-2-ene (**6a**).*[9] The compound was not isolated due to high volatility. The spectroscopic data agree with the literature.

*Oct-2-ene (**6b**).*[9] The compound was purified on a short pad of silica gel (pentane), and the product was carefully evaporated to obtain a mixture of isomers (25 mg, 22% yield). Oct-2-ene (**6b**) was present as approximately 84% of the mixture (5.3:1 *Z*:*E*) ,and oct-1-ene (**5b**) remained as 7% of the mixture. The total percentage of higher internal alkenes was 7%. Data for the *Z* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 5.49−5.32 (alkene CH, 2H, m), 2.09−1.90 (CH_2, 2H, m), 1.60 (CH_3, 3H, m), 1.39−1.23 (CH_2, 8H, m), 0.92−0.96 (CH_3, 3H, m). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 131.0 (alkene CH), 123.7 (alkene CH), 31.7 (CH_2), 29.4 (CH_2), 26.9 (CH_2), 22.7 (CH_2), 14.2 (CH_3), 12.9 (CH_3).

*Dec-2-ene (**6c**).*[49,50] The compound was purified on a short pad of silica gel (pentane), and the product was carefully evaporated to obtain as a mixture of isomers (37 mg, 26% yield). Dec-2-ene (**6c**) was present as approximately 77% of the mixture (5.5:1 *Z*:*E*), and dec-1-ene remained as 9% of the mixture. The total percentage of higher internal alkenes was <1%. Data for the *Z* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 5.47−5.31 (alkene CH, 2H, m), 2.07−2.00 (CH_2, 2H, m), 1.60−1.57 (CH_3, 3H, m), 1.42−1.22 (CH_2, 10H, m), 0.92−0.85 (CH_3, 3H, m). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 130.9 (alkene CH), 123.6 (alkene CH), 31.9 (CH_2), 29.6 (CH_2), 29.30 (CH_2), 29.27 (CH_2), 26.9 (CH_2), 22.7 (CH_2), 14.1 (CH_3), 12.7 (CH_3). Data for the *E* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 5.47−5.31 (alkene CH, 2H, m), 1.99−1.93 (CH_2, 2H, m), 1.65−1.57 (CH_3, 3H, m), 1.42−1.22 (CH_2, 10H, m), 0.92−0.85 (CH_3, 3H, m).

*Dodec-2-ene (**6d**).*[9,51] A 1 mol % amount of **3-cis** and 10 mol % of TsOH were used. The compound was purified on a short pad of silica gel (hexane), and the product was obtained as a mixture of isomers (161 mg, 96%). Dodec-2-ene (**6d**) was present as approximately 89% of the mixture (5.0:1 *Z*:*E*), and dodec-1-ene remained as 10% of the mixture. The total percentage of higher internal alkenes was <1%. Data for the *Z* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 5.47−5.31 (alkene CH, 2H, m), 2.06−2.02 (CH_2, 2H, m), 1.61 (CH_3, 2H, m), 1.39−1.21 (CH_2, 12H, m), 0.90 (CH_3, 3H, t, $^3J_{H-H}$ = 7.1 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): 130.9 (alkene CH), 123.6 (alkene CH), 29.7−29.4 (CH_2, multiple peaks overlap in this region), 26.9 (CH_2), 22.8 (CH_2), 14.1 (CH_3), 12.7 (CH_3).

*Undec-9-en-1-ol (**6e**).*[8,50] The compound was purified on a short pad of silica gel (hexane), and the product was obtained as a mixture of isomers (111 mg, 65%). Undec-9-en-1-ol (**6e**) was present as 83% (8.4:1 *Z*:*E*) of the mixture, and undec-10-en-1-ol (**5e**) remained as 11% of the mixture. The total percentage of higher internal alkenes was 5%. Data for the *Z* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 5.43−5.30 (alkene CH, 2H, m), 3.56 (CH_2, 2H, t, $^3J_{H-H}$ = 6.8 Hz), 2.57 (OH, 1H, s), 2.07−1.97 (2H, m), 1.91 (3H, m), 1.54−1.49 (2H, m), 1.38−1.19 (10H, m). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm, selected peaks): δ 130.8 (alkene CH), 123.8 (alkene CH), 62.7 (CH_2), 12.7 (CH_3). Data for the *E* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 5.43−5.30 (alkene CH, 2H, m), 3.56 (CH_2, 2H, t, $^3J_{H-H}$ = 6.8 Hz), 2.57 (OH, 1H, s), 2.07−1.97 (2H, m), 1.91 (3H, m), 1.68−1.55 (2H, m), 1.38−1.19 (10H, m). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm, selected peaks): δ 131.6 (alkene CH), 124.5 (alkene CH), 62.7 (CH_2), 17.9

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(CH_3). Data for undec-8-en-1-ol (*E* and *Z*) are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm, selected peaks): δ 0.94−0.90 (CH_3, 3H, m), 0.87−0.79 (CH_3, 3H, m). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm, selected peaks): δ 131.9 (alkene CH), 131.5 (alkene CH), 129.22 (alkene CH), 129.17 (alkene CH), 62.7 (CH_2), 20.7 (CH_2), 20.5 (CH_2), 14.4 (CH_3), 14.1 (CH_3). Data for other resonances from all present isomers are as follows. ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, selected peaks): δ 34.6, 34.5, 33.8, 32.7, 32.6, 31.6, 26.6, 29.6, 29.53, 29.52, 29.5, 29.4, 29.2, 29.1, 28.9, 26.8, 25.8, 25.2.

*Undec-9-en-1-yl Propionate (**6f**).*[52] A 1 mol % portion of **3-cis** and 10 mol % of TsOH were used. The compound was purified on a short pad of silica gel (hexane), and the product was obtained as a mixture of isomers (139 mg, 62%). Undec-9-en-1-yl propionate (**6f**) was present as 57% of the mixture, and undec-10-en-1-yl propionate (**5f**) remained as 34% of the mixture. The total percentage of higher internal alkenes was 9%. Data for the *Z* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 5.46−5.31 (m, 2H), 4.04 (t, $^3J_{H-H}$ = 6.8 Hz, 2H), 2.30 (q, $^3J_{H-H}$ = 7.5 Hz, 2H), 2.02 (m, 2H), 1.60 (m, 2H), 1.39−1.21 (m, 12H), 1.12 (t, J = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 174.3 (CO), 130.6 (alkene CH), 123.5 (alkene CH), 64.3 (CH_2), 33.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 28.6 (CH_2), 27.5 (CH_2), 26.7 (CH_2), 25.9 (CH_2),12.6 (CH_3), 9.0 (CH_3).

*1-Phenylhex-4-en-1-ol (**6g**).*[53−55] A 1 mol % portion of **3-cis** and 10 mol % of TsOH were used. The compound was purified on a short pad of silica gel (hexane), and the product was obtained as a mixture of isomers (148 mg, 84% yield). 1-Phenylhex-4-en-1-ol (**6g**) was present as approximately 63% of the mixture (2.3:1 *Z*:*E*). 1-phenylhex-5-en-1-ol (**5g**) remained as 21% of the mixture. 1-Phenylhex-5-en-1-ol (2.3:1 *Z*:*E*) constituted the majority of the remaining 16% of the mixture. Data for the *Z* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.29−7.04 (Ar, 5H, m), 5.44−5.24 (alkene CH, 2H, m), 4.59−4.49 (CH, 1H, m), 2.07−1.88 (CH_2, 2H, m), 1.7−1.5 (CH_2, 2H, m), 1.48 (CH_3, 3H, m). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 144.7 (Ar), 129.7 (Ar), 128.3 (alkene CH), 127.4 (Ar), 125.8 (Ar), 124.5 (alkene CH), 74.0 (CH), 38.6 (CH_2), 23.2 (CH_2), 12.7 (CH_3). Data for the *E* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.29−7.04 (Ar, 5H, m), 5.44−5.24 (alkene CH, 2H, m), 4.59−4.49 (CH, 1H, m), 2.00−1.89 (CH_2, 2H, m), 1.7−1.5 (CH_2, 2H, m), 1.48 (CH_3, 3H, m).^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 144.0 (Ar), 130.6 (alkene CH), 128.3 (Ar), 127.3 (Ar), 125.81 (Ar), 125.76 (alkene CH), 73.9 (CH), 38.4 (CH_2), 28.8 (CH_2), 17.9 (CH_3). Data for (*Z*)-1-phenylhex-3-en-1-ol are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm, selected peaks): δ 2.32−2.26(CH_2, 2H, m), 0.79 (CH_3, 3H, t, $^3J_{H-H}$ = 7.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm, selected peaks): δ 125.0 (alkene CH), 73.8 (CH), 42.5 (CH_2), 25.6 (CH_2), 14.0 (CH_3). Data for (*E*)-1-phenylhex-3-en-1-ol are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm, selected peaks): δ 2.39−2.32 (CH_2, 2H, m), 0.87 (CH_3, 3H, t, $^3J_{H-H}$ = 7.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm, selected peaks): δ 125.4 (alkene CH), 73.5 (CH), 42.7 (CH_2), 25.5 (CH_2), 13.7 (CH_3).

*Pent-3-en-1-yloxybenzene (**6h**).* A 1 mol % portion of **3-cis** and 10 mol % of TsOH were used. The compound was purified on a short pad of silica gel (hexane), and the product was obtained as a mixture of isomers (146 mg, 90% yield). Pent-3-en-1-yloxybenzene (**6h**) was present as 66% of the mixture (6.3:1 *Z*:*E*). Pent-4-en-1-yloxybenzene (*5h*) remained as 33% of the mixture. Higher internal isomers that were observed constituted <1% of the mixture. Data for the *Z* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.34−7.30 (Ar, 2H, m), 6.99−6.93 (Ar, 3H, m), 5.69−5.60 (alkene CH, 1H, m), 5.59−5.50 (alkene CH, 1H, m), 4.02−3.99 (CH_2, 2H, m), 2.59 (CH_2, 2H, m), 1.71 (CH_3, 3H, m). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 158.9 (Ar), 129.4 (Ar), 126.6 (CH), 125.7 (CH), 120.6 (Ar), 114.5 (Ar), 67.2 (CH_2), 27.2 (CH_2), 12.9 (CH_3). Data for the *E* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.34−7.30 (Ar, 2H, m), 6.99−6.93 (Ar, 3H, m), 5.69−5.60 (alkene CH, 1H, m), 5.59−5.50 (alkene CH, 1H, m), 4.02−3.99 (CH_2, 2H, m), 2.51 (CH_2, 2H, m), 1.73 (CH_3, 3H, m). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 159.0 (Ar), 126.8 (CH), 127.7 (CH), 67.0 (CH_2), 32.6 (CH_2), 18.1 (CH_3).

*Pent-3-en-1-yloxymethylbenzene (**6i**).*[9,56] A 2 mol % portion of **3-cis** and 20 mol % of TsOH were used. The compound was purified on a short pad of silica gel (hexane), and the product was obtained as a mixture of isomers (146 mg, 90% yield). Pent-3-en-1-yloxymethylbenzene (**6i**) was present as approximately 83% of the mixture (3.1:1 *Z*:*E*), and pent-4-en-1-yloxymethylbenzene (**5i**) remained as 14% of the mixture. The total percentage of higher internal alkenes was 2%. Data for the *Z* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.28−7.13 (Ar, 5H, m), 5.65−5.46 (alkene CH, 2H, m), 4.41 (CH_2, 2H, s), 3.38 (CH_2, 2H, m), 2.29 (CH_2, 2H, m), 1.53 (CH_3, 3H, m). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 138.5 (Ar), 128.4 (Ar), 127.9 (Ar), 127.7 (Ar), 126.5 (alkene CH), 125.9 (alkene CH), 72.9 (CH_2), 69.9 (CH_2), 27.8 (CH_2), 13.0 (CH_3).

*Pent-3-enoic Acid (**6j**).*[57−59] The compound was purified on a short pad of silica gel (pentane), and the product was carefully evaporated to obtain as a mixture of isomers (34 mg, 34% yield). **6j** was present as 76% of the mixture (2.8:1 *E*:*Z*). Pent-4-enoic acid (**5j**) remained as 20% of the mixture. Pent-2-enoic acid was present as 20% of the mixture. Data for the *E* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 10.4 (COOH, 1H, br s), 5.65−5.49 (alkene CH, 2H, m), 3.06 (CH_2, 2H, m), 1.70 (CH_3, 3H, dq, $^3J_{H-H}$ = 6.2, 1.3 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 178.9 (CO), 130.1 (alkene CH), 121.9 (alkene CH), 37.8 (CH_2), 17.9 (CH_3). Data for the *Z* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 10.4 (COOH, 1H, br s), 5.65−5.49 (alkene CH, 2H, m), 3.14 (CH_2, 2H, m), 1.64 (CH_3, 3H, m). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 178.7 (CO), 128.2 (alkene CH), 119.6 (alkene CH), 32.4 (CH_2), 25.4 (CH_2). Data for (*E*)-pent-2-enoic acid are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 10.4 (COOH, 1H, br s), 7.14 (alkene CH, 1H, dt, $^3J_{H-H}$ = 15.5, $^3J_{H-H}$ = 6.3 Hz), 5.87−5.78 (alkene CH, 1H, m), 2.29−2.20 (CH_2, 2H, m), 1.08 (CH_3, 3H, t, $^3J_{H-H}$ = 7.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 172.4 (CO), 153.9 (alkene CH), 120.9 (alkene CH), 25.4 (CH_2), 12.0 (CH_3).

*Hex-4-en-2-ol (**6k**).*[60−63] The compound was purified on a short pad of silica gel (pentane), and the product was carefully evaporated to obtain as a mixture of isomers (79 mg, 79% yield). Hex-4-en-2-ol (**6k**) was present as approximately 73% of the mixture (2.1:1 *E*:*Z*). Hex-5-en-1-ol (**5k**) remained as 3% of the mixture. Higher internal isomers (hex-3-en-2-ol) that were observed constituted 23% of the mixture. The greater percentage of hex-3-en-2-ol observed in the purified mixture is likely due to the greater volatility of **6k** in comparison to hex-3-en-2-ol. Data for the *E* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 5.58−5.51 (alkene CH, 1H, m), 5.45−5.37 (alkene CH, 1H, m), 3.75−3.70 (CH, 1H, m), 2.20−2.13 (CH_2, 1H, m), 2.10−1.99 (CH_2, 1H, m), 1.74 (OH, 1H, br s), 1.70−1.65 (CH_3, 3H, m), 1.16 (CH_3, 3H, d, $^3J_{H-H}$ = 6.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 128.9 (alkene CH), 127.1 (alkene CH), 67.2 (CH), 42.5 (CH_2), 22.6 (CH_3), 18.0 (CH_3). Data for the *Z* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 5.67−5.59 (alkene CH, m, 1H), 3.82 (CH, 1H, m), 2.28−2.20 (CH_2, 1H, m), 1.63 (CH_3, 3H, m), 1.19 (CH_3, 3H, d, $^3J_{H-H}$ = 6.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 127.1 (alkene CH), 126.1 (alkene CH), 67.7 (CH), 36.7 (CH_2), 22.7 (CH_3), 13.0 (CH_3).

*Ethyl 2-Methylpent-3-enoate (**6l**).*[33,64] A 1 mol % portion of **3-cis** and 10 mol % of TsOH were used. The compound was purified on a short pad of silica gel (hexane), and the product was obtained as a mixture of isomers (40 mg, 28% yield). Ethyl 2-methylpent-3-enoate (**6l**) was present as 65% of the mixture (13:1 *E*:*Z*). Ethyl 2-methylpent-4-enoate (**5l**) remained as 5% of the mixture. Higher internal isomers (ethyl 2-methylpent-2-enoate) constituted 16% of the mixture. The greater percentage of ethyl 2-methylpent-2-enoate observed in the purified mixture is likely due to the greater volatility of **6l** in comparison to ethyl 2-methylpent-2-enoate. Data for the *E* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 5.58−5.47 (alkene CH, 2H, m), 4.11 (CH_2, 2H, q, $^3J_{H-H}$ = 10.7 Hz, $^3J_{H-H}$ = 7.1 Hz), 1.69−1.64 (CH_3, m, 3H), 1.26−1.19 (CH_3, m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 175.1 (CO), 130.0 (alkene CH), 126.7 (alkene CH), 62.9 (CH), 60.4 (CH_2), 17.9 (CH_3), 17.4 (CH_3), 14.2 (CH_3). Data for ethyl 2-methylpent-2-enoate (*E* and

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Z) are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 6.75−6.71 (alkene CH, 1H, m), 4.20−4.15 (CH_2), 3.10−3.02 (Z, CH_2, 2H, m), 2.20−2.12 (E, CH_2, 2H, m), 1.81 (CH_3, 3H, s), 1.28 (CH_3, 3H, t, $^3J_{H-H}$ = 7.2 Hz), 1.04 (CH_3, 3H, t, $^3J_{H-H}$ = 7.6 Hz).^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 168.3 (CO), 143.7 (alkene CH), 127.2 (alkene C), 60.4 (CH_2), 42.7 (*Z*, CH_2), 32.0 (*E*, CH_2), 21.9 (CH_2), 13.04 (CH_3), 12.96 (CH_3), 12.2(CH_3).

*But-2-en-1-ylbenzene (**6m**).*[10] A 2 mol % portion of **3-cis** and 20 mol % of TsOH were used. The compound was purified on a short pad of silica gel (hexane), and the product was obtained as a mixture of isomers (130 mg, 98% yield). **6m** was present as 76% of the mixture (5.4:1 *Z*:*E*). **5m** remained as 16% of the mixture. But-1-en-1-ylbenzene was present as 8% of the mixture (5.8:1 *Z*:*E*). Data for the *Z* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.22−7.19 (Ar, 2H, m), 7.13−7.09 (Ar, 3H, m), 5.52 (alkene CH, 2H, m), 3.34 (CH_2, 2H, d, $^3J_{H-H}$ = 5.5 Hz), 1.65 (CH_3, 3H, m). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 141.2 (*i*-Ar), 129.0, 128.4, 128.33, 128.28, 125.8, 124.8, 33.1, 12.8. Data for the *E* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.22−7.19 (Ar, 2H, m), 7.13−7.09 (Ar, 3H, m), 5.52 (alkene CH, 2H, m), 3.24 (CH_2, 2H, d, $^3J_{H-H}$ = 6.5 Hz), 1.61 (CH_3, 3H, m).

*Prop-1-en-1-ylbenzene (**6n**).*[65] A 1 mol % portion of **3-cis** and 10 mol % of TsOH were used. The compound was purified on a short pad of silica gel (hexane), and the product was obtained as a mixture of isomers (64 mg, 54%). **6n** was present as 71% of the mixture (1.6:1 *Z*:*E*), and allylbenzene remained as 15% of the mixture. Data for the *Z* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.38−7.28 (Ar, 3H, m), 7.25−7.17 (Ar, 2H, m), 6.49−6.44 (alkene CH, 1H, m), 5.81 (alkene CH, 1H, dq, $^3J_{H-H}$ = 11.8, $^3J_{H-H}$ = 7.2 Hz), 1.93 (CH_3, 3H, dd, J = 7.3, 1.9 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 137.6, 129.8, 128.8, 128.1, 126.8, 126.4, 14.6. Data for the *E* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.38−7.28 (Ar, 3H, m), 7.25−7.17 (Ar, 2H, m), 6.44−6.40 (alkene CH, 1H, m), 6.25 (alkene CH, 1H, dq, $^3J_{H-H}$ = 15.8, $^3J_{H-H}$ = 6.5 Hz), 1.89 (CH_3, 3H, dd, $^3J_{H-H}$ = 6.6, $^3J_{H-H}$ = 1.6 Hz).

*Trimethyl(prop-1-en-1-yl)silane (**6o**).*[9] A 1 mol % portion of **3-cis** and 10 mol % TsOH were used. The compound was not isolated due to high volatility. The spectroscopic data agree with the literature.

*1-(pent-3-en-1-yl)piperidine (**6p**).* The crude reaction mixture was filtered, and a beige solid was collected and rinsed with ∼1 mL of THF and then Et_2O. Residual free amine was removed in vacuo to yield a mixture of isomers (177 mg, 93%). The mixture of alkenes contained 1-(pent-3-en-1-yl)piperidine (80%), 1-(pent-4-en-1-yl)piperidine (12%), and 1-(pent-2-en-1-yl)piperidine (8%). ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 11.9−11.6 (NH, 1H, br s), 5.59−5.47 (alkene CH, 1H, m), 5.29−5.19 (alkene CH, 1H, m), 3.51−3.35 (CH_2, 2H, m), 2.85−2.56 (CH_2, 2H, m), 2.71−2.47 (CH_2, 4H, m), 2.25−2.11 (CH_2, 2H, m), 1.86−1.71 (CH_2, 3H, m), 1.56 (CH_3, 3H, t, $^3J_{H-H}$ = 6.9 Hz), 1.44−1.29 (CH_2, 1H, m). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 129.3 (*E*, alkene CH), 128.2 (*Z*, alkene CH), 124.6 (E, alkene CH), 123.5 (*Z*, alkene CH), 56.4, 53.0, 52.9, 26.7, 22.43, 22.40, 22.3. 17.9 (*E*, CH_3), 12.9 (*Z*, CH_3).

*2-(But-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6q**).*[10,66−69] The compound was purified on a short pad of silica gel (Et_2O), and the product was obtained as a mixture of isomers (171 mg, 94%). The mixture of alkenes contained the title compound (**6r**, 78%), unreacted starting material (**5r**, 21%), and the respective 3-alkene (9%, 1.7:1 *Z*:*E*). Data for the *Z* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 5.52−5.42 (alkene CH, 2H, m), 1.66 (CH_2, 2H, d, $^3J_{H-H}$ = 7.3 Hz), 1.59 (CH_3, 3H, m), 1.24 (CH_3, 12H, s). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 124.9 (alkene CH), 123.6 (alkene CH), 83.0 ($C(CH_3)_2$), 24.6 (CH_3), 12.4 (CH_3). 11.3 (CH_2, br s). Data for the *E* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm, selected peaks): δ 5.52−5.33 (alkene CH, 2H, m), 1.64−1.61 (CH_2, CH_3, 5H). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 125.7 (alkene CH), 125.1 (alkene CH), 83.0 ($C(CH_3)_2$), 24.6 (CH_3), 12.4 (CH_3). Data for 3(*Z*)-2-(but-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm, selected peaks): δ 6.47−6.34 (alkene CH, 1H, m), 5.38 (alkene CH, 1H, dt, $^3J_{H-H}$ = 13.4, $^3J_{H-H}$ = 1.3 Hz), 2.44−2.35 (CH_2, 2H, m), 0.98 (CH_3, 3H, t, $^3J_{H-H}$ = 7.5 Hz). Data for (*E*)-2-(but-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm, selected peaks): δ 6.69 (alkene CH, 1H, dt, 17.8, 5.8 Hz).

*1-Fluoro-4-(penta-1,4-dien-1-yl)benzene (**6r**).* The compound is analogous to (penta-1,4-dien-1-yl)benzene.[69,70] The compound was purified on a short pad of silica gel (hexane), and the product was obtained as a mixture of isomers (102 mg, 58%). 1-Fluoro-4-(penta-1,4-dien-1-yl)benzene (**6r**) was present as approximately 64% of the mixture (5.3:1 *Z*:*E*), and 1-fluoro-4-(penta-1,5-dien-1-yl)benzene (**5r**) remained as 28% of the mixture. The total percentage of higher internal alkenes was approximately 8%. Data for the *Z* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.18−7.08 (Ar, 2H, m), 6.96−6.90 (Ar, 2H, m), 6.90−6.88 (alkene CH, 1H, m), 5.61−5.52 (alkene CH, 1H, m), 5.42−5.39 (alkene CH, 1H, m), 5.39−5.32 (alkene C H, 1H, m), 2.93 (CH_2, 2H, m), 1.53−1.50 (CH_3, 3H, m). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 131.0 (alkene CH), 128.1 (alkene CH), 125.0 (alkene CH), 26.8 (CH_2), 13.1 (CH_3). Data for the *E* isomer are as follows. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 2.89−2.83 (CH_2, 2H, m), 1.61−1.56 (CH_3, 3H, m).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00914.

Characterization of potential catalyst intermediates, NMR spectral data for products, and crystal structure report for **4d** (PDF)

Accession Codes

CCDC 1577757 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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