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Catalytic Nucleophilic Allylation Driven by the Water–Gas Shift Reaction

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Abstract

The ruthenium-catalyzed allylation of aldehydes with allylic pro-nucleophiles has been demonstrated to be an efficient means to form carbon–carbon bonds under mild conditions. The evolution of this reaction from the initial serendipitous discovery to its general synthetic scope is detailed, highlighting the roles of water, CO, and amine in the generation of a more complete catalytic cycle. The use of unsymmetrical allylic pro-nucleophiles was shown to give preferential product formation through the modulation of reaction conditions. Both (*E*)-cinnamyl acetate and vinyl oxirane were efficiently used to form the *anti*-branched products (up to >20:1 *anti/syn*) and *E*-linear products (up to >20:1 *E/Z*) in high selectivity with aromatic, α,β -unsaturated, and aliphatic aldehydes, respectively. Attempts to render the reaction enantioselective are highlighted and include enantioenrichment of up to 75:25 for benzaldehyde.

Graphical abstract

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Notes

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Supporting Information

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Optimization studies, GC response factors/retention times, and ^1H and ^{13}C NMR spectra (PDF)

INTRODUCTION

The quintessential transformation in organic synthesis is the formation of a carbon–carbon bond. One of the more commonly applied methods to generate this bond, which has been extensively studied, is the allylation of carbonyl compounds due to the impressive versatility and capacity to generate two or more new stereogenic centers with high levels of stereocontrol.^{1–4} The major drawback with many of the current allylation methods is the requirement of a preformed allylmatal species, and thus, the production of significant amounts of metal waste and a lack of atom-economy. In response to this shortcoming, a major focus of research in recent years has been to develop reactions that are catalytic in metal.⁵ One such method is the ruthenium-catalyzed nucleophilic allylation, recently developed by these laboratories, which uses carbon monoxide as the stoichiometric reductant and only produces AcOH and CO₂ as the stoichiometric byproducts.⁶ The process by which this reaction uses CO as the terminal reductant is known as the water–gas shift reaction (WGSR), a transformation of long-standing industrial relevance that converts a mixture of carbon monoxide and water into hydrogen and carbon dioxide (eq 1).^{7–12}

Industrially, this reaction is used to refine synthesis gas (CO + H₂), as the ratio of CO to H₂ can vary depending upon on the method of production.¹³ As industrial processes require specific percentages of each gas for high efficiency, the WGSR can adjust this ratio to the optimal value or remove CO altogether by converting it to CO₂. One specific application for the WGSR is that of the Haber–Bosch process for ammonia synthesis,¹⁴ in which CO is removed from synthesis gas, producing high purity H₂ to avoid poisoning the Fe-based ammonia synthesis catalyst. Furthermore, the Fischer–Tropsch process for producing hydrocarbons and the production of methanol from synthesis gas are industrial applications of the WGSR.^{15,16}

More interestingly from the perspective of organic synthesis is the application of the WGSR to drive reductive processes. For these reactions, the reduction potential of the WGSR is employed to either reduce organic compounds or aid in the turnover of a catalytic cycle. These reactions include hydro-formylations, nitro reductions, reductive aminations, and hydrogenation of carbonyls and alkenes.¹⁷ One of the chief advantages of using the WGSR in organic synthesis is the avoidance of other stoichiometric reducing agents as are typically employed in these reductive processes. This objective is in line with the first of the “Grand Challenges” identified by the NRC report “*Sustainability in the Chemical Industry*” which calls for the reduction of waste and the identification of environmentally benign strategies (“*it is better to prevent waste than to clean it up after it is formed*”).¹⁸ The ruthenium-catalyzed allylation satisfies this criterion through the use of CO as the terminal reductant in place of other stoichiometric reducing agents and because of the negligible impact of the waste that it produces.

BACKGROUND

General Catalytic Allylation Reactions Avoiding the Use of Superstoichiometric Amounts of Metals

An ideal carbonyl allylation reaction uses allyl sources that do not require the stoichiometric use of metal reagents. Substoichiometric amounts of metal catalysts or Lewis acids can perform many of the same reactions as the allylmetals and generate less metal waste. As some of these reactions do not employ metals as the reductant for the catalytic cycle, other means of allowing for catalyst turnover must be employed.

For example, Krische and co-workers have developed a highly efficient and selective catalytic allylation of aldehydes that employs an iridium-based, transfer hydrogenation catalyst to produce homoallylic alcohols in high yield and enantioselectivity starting from allylic acetates, dienes, or allenes.¹⁹ Through the use of these iridium catalysts, the formation of enantioenriched products containing quaternary stereocenters,²⁰ the hydroxymethylation of allylic acetates by enantio-topic π -facial discrimination,²¹ and asymmetric allylation of glycidols while avoiding the common match-mismatch concerns²² can be efficiently conducted. Also highlighted is the precise chemoselectivity that this method entails as demonstrated through the enantioselective allylation at the site of a single alcohol in a polyol without the need for protecting groups.²³ Progress has also been made by employing other metal catalysts in this method, specifically ruthenium, while maintaining the reactivity profile of the iridium catalysts in the allylation reactions of allenes and dienes with aldehydes.^{24–27} In an impressive illustration of the utility of the transfer hydrogenation methodology, Krische synthesized the natural product swinholide A in only 15 steps (longest linear sequence), as compared to previous syntheses which required 27–35 steps.²⁸ This accomplishment is possible because of the greatly increased “redox-economy” that is allowed through the use of transfer hydrogenation as many traditional redox and C–C bond formations steps can be combined into a single step.

Another method in which the formal allylation of carbonyl compounds can be achieved, with high atom economy and without a stoichiometric metal additive, is the carbonyl ene reaction. This reaction has found success in the synthesis of highly enantioenriched products via a six-electron pericyclic process between an olefin bearing an allylic hydrogen and an enophile, which is typically an electron-deficient multiple bond.^{26,29} Alper and co-workers have shown that a rhodium-catalyzed allylation reaction is also possible through the use of an ionic diamine carbonyl rhodium complex and a stoichiometric amount of Cs_2CO_3 .³⁰

Catalytic Nucleophilic Allylation of Aldehydes Employing CO as the Reductant

An early report from Watanabe and co-workers described the formation of homoallylic alcohols under catalysis by ruthenium using a trialkylamine as the reducing agent. This reaction employs 140 psi of CO in combination with a superstoichiometric amount of aldehyde with respect to allyl acetate to produce homoallylic alcohols in good to moderate yields (Scheme 1).³¹

In the case of RuCl_3 , a ruthenium carbonyl species is proposed to be the active catalyst. When RuCl_3 is employed in the reaction under a CO atmosphere, FT-IR absorptions

indicative of a carbonyl species are observed. Alternatively, when RuCl_3 is employed under an Ar atmosphere, the same FT-IR absorptions are not observed and the homoallylic alcohol is not formed. The formation of a ruthenium carbonyl species is further confirmed by the fact that the reaction of an independently synthesized ruthenium π -allyl complex with benzaldehyde in a stoichiometric reaction gives the intended homoallylic alcohol product in 66% yield by GC (Scheme 2).³² As the use of a CO atmosphere is not required in this stoichiometric reaction, this suggests that CO is required only to form the initial ruthenium metal complex or to serve to stabilize the ruthenium carbonyl species in the catalytic reaction.

According to Kondo, the superstoichiometric amount of Et_3N is required as it is the stoichiometric reductant. To provide evidence for this hypothesis, the authors employed deuterium-labeled Et_3N , benzaldehyde, and solvent in a stoichiometric reaction with a π -allyl ruthenium complex to determine the source of hydrogen in the reaction (Scheme 3).³² Deuterium is incorporated into the homoallylic alcohol product only when deuterated Et_3N is employed. This result therefore identifies Et_3N as the reductant for the catalytic reaction and the source of the necessary hydrogen.

On the basis of these experimental observations, Kondo proposed a catalytic cycle (Scheme 4). After oxidative addition of allyl acetate to the ruthenium(0) metal center **i** and the formation of π -allyl complex **ii**, an insertion of an aldehyde into this complex forms species **iii**. Coordination of Et_3N to **iii** and subsequent β -hydride elimination generates the hydridoruthenium(II) complex **iv** which can then undergo reductive elimination to release the homoallylic alcohol product, regenerating the ruthenium(0) catalyst **i**. This catalytic cycle thereby forms the homoallylic alcohol product with only AcOH and an enamine as the stoichiometric byproducts.

The requirement for high temperatures may limit the types of functional groups that can be used in this reaction. Furthermore, the superstoichiometric use of aldehyde (which is often the precious synthetic material) is undesirable. Despite these deficiencies, this reaction was believed to be a good starting point because, at the onset of this project, very few reports mentioned the nucleophilic activity of π -allyl ruthenium complexes.³³ Considering the uniqueness of this reactivity and the potential for applications in carbonyl allylation, this process was chosen for investigation. Furthermore, at the time it was one of only a few carbonyl allylation reactions that were truly catalytic in metal.

RESULTS

Development of the Ruthenium-Catalyzed Nucleophilic Allylation Reaction

Initial Reaction Discovery—To orient the efforts in seeking a more efficient ruthenium-catalyzed allylation, reactions at lower temperature, lower catalyst loading, and in various solvents were executed (Table 1). Because of the high pressure of CO required, a six-well autoclave was employed to perform the optimization. In each of these experiments, a low product yield was observed.

To answer the question whether the conversion was low because of slow catalyst turnover or because the catalyst was rendered inactive after a certain period, reaction progress was monitored over time. Interestingly, it was discovered that in some cases the reaction proceeded faster after the reaction vessel was cooled and opened in air for sampling (Figure 1). As demonstrated for dioxane, after first opening the autoclave around 24 h, the conversion of **1a** was roughly 20% but after the vessel was resealed and reheated, the conversion at 36 h was nearly 100%. It appeared as though some variable was introduced to the reaction upon opening the vessel to air, leading to a significant increase in conversion.

To identify the origin of this effect, a battery of experiments was performed in which controlled amounts of oxygen and/or water were blended into the reaction mixtures (Table 2). Dioxane was chosen as the reaction solvent and for practical purposes; from here on, benzaldehyde was used as the limiting reagent and allyl acetate was used in slight excess (1.1–1.2 equiv). Without water or oxygen, product yield was low, and very little of **2** was consumed (entry 1). As soon as water was introduced into the reaction, the yield of **3a** sharply increased (entries 2 and 3), but as soon as the CO pressure was lowered to 120 psi, a small negative impact was observed with respect to yield (entry 4). The inclusion of oxygen into the reaction gave a corresponding increased **3a** yield but also resulted in a significant propene formation (a product of unproductive consumption of **2**) (entries 5 and 6). The best conditions seemed to be 120/20 psi of $P_{\text{CO}}/P_{\text{oxygen}}$ and 0.3 equiv of water and were used in the next experiments.

Next, the stoichiometry of Et_3N was systematically varied (Table 3). Interestingly, the conversions were the same when the stoichiometry of Et_3N was varied between 10 and 150 mol % (entries 2–5). However, in the absence of an amine, no reaction occurred (entry 1).

It was striking to see that only 10 mol % of Et_3N was needed under the new conditions to provide the 42–44% conversions. Obviously, at such a low stoichiometry Et_3N could not account for the amount of hydrogen that is incorporated into the product and acetic acid byproduct. The ^1H NMR spectra of these reaction mixtures (without workup) did not show any new signals besides those of the product, acetic acid, Et_3N (as the $\text{Et}_3\text{NH}^+\text{OAc}^-$ salt), and propene (in trace amounts), indicating that solvent is not the hydrogen source. Thus, water seemed to be the only possible hydrogen source in these new conditions.

To prove support for that hypothesis, more water was added into the reaction mixture while keeping Et_3N at low concentrations (Table 4). With a reduced amount of Et_3N , the reaction became more water tolerant (Table 2, entry 6 vs Table 4, entry 1 and Table 2, entry 3 vs Table 4, entry 4). The reaction reached 95% conversion at 70 °C in 24 h when 1.5 equiv of water was used along with 10 mol % of Et_3N and without addition of oxygen (entry 4). Increasing the amount of water to 15 equiv gave a lower yield under similar conditions, likely due to faster unproductive consumption of **2** as significant amounts of propene were observed (entry 5). These results marked a critical departure from the original conditions in which Et_3N was believed to be the stoichiometric reducing reagent. In this new system, CO must be the stoichiometric reducing reagent which in combination with water provides the necessary hydrogen atoms and allows for turnover of the catalyst (WGSR).

To fully elucidate the role of the amine in the reaction, a more precise evaluation of Et₃N loadings was undertaken (Table 5). Again at low Et₃N loading, little to no product was generated (entries 1–6). However, at around 4.0 mol % of Et₃N, a dramatic change was observed in which the yield of **3a** jumped from 2% to 85% (entries 6 and 7). Further increases of amine loading resulted in the nearly complete consumption of **1a** and a slight decrease in the yield of **3a** at the highest amine loading (entries 8–12). These results indicate that Et₃N has a very specific role in the proper functioning of this reaction at a value of about 1.5 times the ruthenium catalyst loading. This survey was also conducted with another ruthenium source, [RuCl₂(*p*-cymene)]₂ (see Table S6), and again, a clear turnover point was observed; this time between 2.0 and 2.5 mol % of Et₃N, illustrating that there is possibly a connection between the oxidation state of the ruthenium and the required loading of amine.

To gain additional information into the role of amine, a stoichiometric reaction between RuCl₃·xH₂O and dicyclohexylamine was run (Scheme 5). Dicyclohexylamine was chosen to allow for identification of any oxidation products. Indeed, 52% of cyclohexanone was observed in the reaction analysis by GC–MS (single point calibration), a product that would arise from hydrolysis of the oxidized amine.

To further explore the effect of the ruthenium source on the reaction efficiency, a ruthenium catalyst and additive survey was conducted (Table 6). As was the case with RuCl₃·xH₂O, addition of Et₃N to reactions employing allylRu(CO)₃Br and allylRu(CO)₃OAc significantly improved the conversions (entries 1–6). The observation that reactions with RuCl₃ and allylRu(CO)₃Br showed higher conversions than reactions with allylRu(CO)₃OAc (entries 2, 4, and 6) indicated a possible halide affect. Indeed, when tetrabutylammonium chloride (TBACl) was added to a reaction catalyzed by allylRu-(CO)₃OAc, the conversion improved from 44 to 81% even in the absence of Et₃N (entries 7 and 8). The addition of Et₃N had no further impact on the yield for allylRu(CO)₃OAc with TBACl (entry 9). A significant improvement in conversion was observed when TBACl was added to reaction containing Ru₃(CO)₁₂, from 15 to 78% (entries 10 and 11). Further increases to the TBACl loading actually had a negative effect on overall conversion (entries 12–14). When other counteranions were used with the tetraalkylammonium salt, lower conversions were observed again demonstrating the unique effect of chloride (entries 12, 15, and 16). The effect of inorganic salts was significantly less than their corresponding ammonium salts, likely owing to the lower solubility of lithium salts (entries 11, 16, and 17).

Further Reaction Optimization—As the standard reaction conditions (1.1 equiv of **2**, 1.5 equiv of H₂O, 10 mol % of Et₃N, 70 °C, 30 psi CO) were now established, it was prudent to further explore the components of the reaction. The effect of catalyst loading was briefly evaluated (Table 7). At loadings as low as 1 mol %, the reaction still showed relatively good conversion (entry 1), while at 2 or 3 mol % all of the starting material was converted after 24 h (entries 2 and 3).

As different CO pressures have been used in the prior experiments, a systematic study of CO pressures was warranted to determine an optimum value. Furthermore, this is a significant variable as lowering this parameter would allow for reactions to be run using more common reaction assemblies. Pressures of CO ranging from 15 to 200 psi were therefore next

examined (Table 8). The reaction could still proceed at pressures as low as 15 psi of CO, but would require longer reaction time for full aldehyde conversion (entry 1). At CO pressures of 30 psi and above, conversions did not change significantly, indicating that saturation of the solvent by CO might have occurred (entries 2–6). This was a significant advance because it demonstrates that the reaction can now be easily adapted to glass reactors.

Next, the effect of temperature on the conversion of **1a** was examined (Table 9). As a note, for convenience in monitoring reactions, when conducting the temperature survey, reactions were run in normal round-bottom flasks under a balloon of CO. At temperatures as low as 40 °C, the reaction was still shown to be active, but sluggish (entries 1 and 2). Increasing the temperature to 50 °C resulted in only slightly higher conversion than 40 °C (entries 3 and 4). Even at 60 °C for 18 h, the reaction had only progressed to about 25% conversion and required another 6 h to approach 45%. At the 18 h time point, the reaction at 70 °C was already at 48% conversion (entries 5–7). As such, 70 °C was proven to be an optimal temperature for the reaction of **1a** and **2**.

The leaving group on the allyl component was next investigated (Table 10). The use of a benzoyl or carbonate leaving group had slightly higher efficiency than the parent acetate leaving group (entries 1–3). The use of diallyl carbonate is of particular interest as the byproducts would be CO₂ and allyl alcohol. This change would create less acidic reaction conditions than that occurs with the stoichiometric formation of AcOH with the use of allyl acetate. Interestingly, whereas allyl chloride gave good conversion to the desired product, under the same reaction conditions, allyl bromide yielded only trace amounts of product (entries 4 and 5). Allyl alcohol reacted sluggishly when it was employed, likely due to the poor leaving group ability of the hydroxyl group (entry 6).

In addition to dioxane, several other solvents were evaluated for their usefulness in the reaction (Table 11). The reaction proceeded with allyl acetate as the solvent, but no impact on the rate of the reaction was observed (entry 1). Ketones and esters could be used as the solvent, showing that the reaction is highly chemoselective for aldehydes as no byproduct resulting from the allylation of the solvent was observed (entries 2–4). Whereas a coordinating ethereal solvent such as THF gave full conversion to product (entry 5), the use of solvents such as DMF or DMSO afforded lower yields (entries 6 and 7). The use of primary alcohols such as methanol and ethanol afforded lower conversion, owing to the formation of acetals as detected by ¹H NMR spectroscopy (entries 8 and 9). However, if a more hindered alcohol such as *i*-PrOH was employed, no acetal formation was detected and there was full conversion to product (entry 10). In light of several solvent options, the use of dioxane was maintained due to its more favorable chemical properties for the reaction, such as boiling point and solubility of the reagents.

The requirement for an allyl pro-nucleophile was demonstrated as the use of propargyl derivatives were completely unreactive under several different reaction conditions. In each case, only starting material was recovered.

Studies into the Catalytic Cycle—To gain a deeper understanding as to what species may be forming during the course of the reaction, 1-methylallyl acetate and crotyl acetate

were each employed under the reaction conditions (Scheme 6). In both cases, the same α -isomer was isolated as the sole product with similarly low *syn/anti* ratios. This result suggests that crotyl and 1-methylallyl acetates form the same intermediate, which in turn leads to the same product mixture.

Scope of the Ruthenium-Catalyzed Nucleophilic Allylation Reaction

Prior Published Work—Using the optimized conditions, a wide range of aldehydes were shown to be viable substrates for the allylation reaction employing allyl acetate.⁶ This work emphasized the general nature of the reaction and demonstrated that steric and electronic factors of the aldehydes had a minimal effect on the course of the allylation reaction. Furthermore, some chemoselectivity for the reaction was demonstrated as aldehydes containing functional groups prone to reduction (nitro, esters, and alkenes) were stable under the reducing CO environment (Figure 2).

The general scope of the allyl pro-nucleophile was expanded, and the chemoselective nature of the reaction further demonstrated in a subsequent report that employed allyl pro-nucleophiles with a substitution at the 2-position.³⁴ The substituents included ketone, ester, styrenyl, and protected aldehyde functional groups that were all shown to be stable under the reactions conditions when reacted with a range of aldehydes (Figure 3).

Catalytic Nucleophilic Allylation with (*E*)-Cinnamyl Acetate. Reaction

Optimization—The use of *E*-cinnamyl acetate (*E*)-**6** is of interest as it would form an unsymmetrical π -allyl complex, leading to a number of isomeric products. Initial evaluation of conditions involved a 40 h reaction at 85 °C with two solvents and several ruthenium catalyst systems (Table 12). Overall, the use of dioxane gave poor yield of product as only the use of RuCl₃·xH₂O gave close to 50% conversion of **1a** (entry 1). With either Ru₃(CO)₁₂/TBACl or Ru(bpy)₃-(CO)₂Cl₂, only about 25% of **1a** was converted, demonstrating a significant difference in reactivity (entries 2 and 3). However, the use of all three ruthenium sources in EtOH led to efficient conversions of **1a** (entries 4–7). Furthermore, qualitative ¹H NMR analysis showed nearly complete formation of the branched product in EtOH as compared to dioxane, whereas the linear product was formed in higher yield.

To reduce the reaction time and temperature, experiments were run for 20 h at 75 °C with two different loadings of ruthenium catalyst, and it was determined that 5 mol % of RuCl₃ led to higher conversions of the product (see Table S14). However, the formation of acetals was noted in EtOH, particularly with aliphatic aldehydes such as hydrocinnamaldehyde, detracting from productive reaction. To mitigate acetal formation, a survey of solvents was conducted (see Table S15), and it was found that the use of *t*-BuOH was appropriate to avoid acetal formation and maintain high selectivity for the desired product in the use of aliphatic aldehydes.

The selective formation of *anti*-**7a** from (*E*)-cinnamyl acetate was unexpected, as reactions employing crotyl acetate gave very low *syn/anti* selectivity (vide infra). To probe if this result arose from a 6-membered transition state, (*Z*)-cinnamyl acetate (*Z*)-**6** was employed under the same conditions (Table 13). The use of (*Z*)-**6** led to the same composition of

product **7a** as from (*E*)-**6** and in similar yield and selectivity. Furthermore, only (*Z*)-**6** was recovered from the reactions, and no (*E*)-**6** was observed in the crude reaction mixture by ¹H NMR analysis.

Preparative Scale Allylation Reactions—Using the conditions identified by the optimization, the allylation of a set of aldehydes on a preparative scale (1.0 mmol) was performed (Table 14). Good to excellent yields were observed with the use of most aldehydes (most yields >70%). The use of electron-rich aldehydes (**1e**) afforded lower yields than the electron-neutral (**1a**) or electron-poor (**1d**, **1f**, **1g**, and **1h**) aldehydes. Decreased electron density in the aldehyde lowers the LUMO and thereby decreased the energy of activation barrier for the addition. Aldehydes with extended π -systems (**1b** and **1i**) were viable substrates under the reaction conditions and gave comparable yields to **1a**. Aryl aldehydes with increased steric bulk, such as **1j** and **1k**, generated the allylation product in high yield, which is in sharp contrast to the more sterically encumbered alkyl aldehydes **1n** and **1p** which gave greatly diminished yield. In the case of **1n**, appreciable conversions in 24 h were only obtainable after the concentration was doubled (from 0.4 to 0.8 M) to increase the reaction rate. The successful use of the aldehydes with easily reduced functional groups (nitro, alkenyl, halide) under the reducing conditions further highlights the chemoselectivity of the ruthenium-catalyzed reaction.

In all cases, the *anti/syn* ratio of the products was >20:1, revealing the preference for a single thermodynamically stable intermediate leading to product. In general, the solvent choice did not have an impact on the *anti/syn* ratio, except in the case of **1m** in EtOH, in which the *anti/syn* ratio was closer to 8:1. Changing the solvent to *t*-BuOH maintained the high level of selectivity displayed with the other aldehydes. Similarly with **1l**, the use of *t*-BuOH gave a cleaner reaction profile. The primary effect of solvent in the other reactions was to avoid formation of acetals, especially in the case of the aliphatic aldehydes (**1n**, **1o**, and **1p**) in which the use of *t*-BuOH inhibited acetal formation.

Catalytic Nucleophilic Allylation with Vinyl Oxirane. Reaction Optimization—

To further the investigations into unsymmetrical allyl pro-nucleophiles, vinyl oxirane **9** was next evaluated under the standard reaction conditions (Table 15). The use of Ru₃(CO)₁₂ and TBACl gave nearly full conversion of **1a** to **10a** with complete selectivity (entry 1). In the case of [RuCl₂(*p*-cymene)]₂ without TBACl, good conversion was observed, but with much lower selectivity, as was the case with RuCl₃ (entries 2 and 4). However, upon the addition of 3 mol % TBACl, **10a** was formed selectively (entries 3 and 5).

To explore the reactivity of other aldehydes, the same conditions with Ru₃(CO)₁₂/TBACl for **1a** were applied to **1b**, **1c**, and **1e** (Table 16). Under these conditions, there was a significant amount of aldehyde remaining in each case using 3 mol % of Ru/TBACl, but the selectivity remained high for **10** (entries 1, 4, and 7). An increase to 5 mol % of Ru/TBACl increased the yields of **10**; however, in each case nearly all of the allyl source was consumed (entries 2, 5, and 8). To further improve the yields, the loadings of **9** and H₂O were increased, which led to higher yields of **10** (entries 3, 6, and 9). These conditions were then used in the substrate survey.

As the vinyl oxirane used in these reactions was racemic, the effect of using enantioenriched (*S*)-**9** was tested which afforded product **9a** in racemic form suggesting that some stereoablative or racemization process was occurring (Scheme 7).

Preparative-Scale Allylation Reactions—Using the optimized conditions, the allylation was performed on the same set of aldehydes on a preparative scale (1.0 mmol) (Table 17). Good to excellent yields were observed with the use of nearly all aldehydes (most yields >80%). The use of electron-rich aldehydes (**1e**) afforded the respective products in lower yields than the electron-neutral (**1a**) or electron-poor (**1d**, **1f**, **1g**, and **1h**) aldehydes. The use of **1e** also required an increase in reaction concentration (from 0.4 to 0.8 M) to achieve good conversion in 24 h as the electron-rich aldehyde was slow to react under these conditions. The aldehydes with extended π -systems (**1b** and **1i**) were also viable substrates and gave comparable yields to **1a**. With bulky aryl aldehydes, such as **1j** and **1k**, the linear product was generated in high yields. However, when the alkyl aldehydes with more steric encumbrance (**1n** and **1p**) were used, the product yield was greatly diminished. As with the use of **1e**, **1n** required a reaction concentration of 0.8 M to achieve appreciable conversion values in 24 h. Heteroaromatic aldehydes (**1j** and **1m**) reacted well under the reaction conditions to give good to excellent yields.

In nearly all cases, the *E*-linear isomer was the major product; however, the selectivities varied from excellent (>100:1) to modest (4:1), and even in one case, with **1n**, the *Z*-isomer was the major product in an *E/Z* ratio of 1:1.5. These observations demonstrate the effect that very sterically encumbered aldehydes have on the transition state leading to the allylation. An obvious trend is the relative low selectivity exhibited by the alkyl aldehydes (**1c**, **1n**, **1o**, and **1p**) and the electron-rich aldehydes (**1e** and **1l**). For **1n** and **1p**, this result could be attributed to high steric encumbrance, but for **1c** and **1o**, it might instead have to do with the greater flexibility of the R group on the aldehyde that could destabilize the transition state that leads to the *E*-linear product. The electron-deficient aldehydes for the most part exhibited excellent *E/Z* selectivities, with the possible exception of **1f**, which was only 6:1.

Catalytic Nucleophilic Allylation with Other Allyl Pro-nucleophiles—Two additional unsymmetrical allylic acetates that were worthy of study to further explore electronic and steric factors involved in reaction are crotyl acetate and ethyl (*E*)-4-acetoxybut-2-enoate. For crotyl acetate, high yields and the exclusive formation of the branched product were promising; however, the product was formed with low diastereomeric (*anti/syn*) selectivity (Table 18). Once again, better yields were observed at higher reaction temperatures (entries 1, 2, and 4), and little difference was found when Ru₃(CO)₁₂ was used as the catalyst instead of RuCl₃·*x*H₂O (entries 1 and 2). Crotyl carbonate showed similar reactivity and selectivity (entry 4); but interestingly, crotyl benzoate was completely unreactive when RuCl₃ was used as the catalyst (entry 6). Employing Ru₃(CO)₁₂, on the other hand, yielded **13a** in 78% with *anti/syn* selectivity of 1.8:1. Further attempts to improve the *anti/syn* selectivity using a variety of additives and conditions were ultimately unsuccessful (see Tables S20–S23).

To fully explore all reaction parameters, the effects of the electronic properties of the reacting partners were investigated. For this purpose, an allylic acetate containing an electron-withdrawing group was used (Table 19). Initial attempts using dioxane as the solvent gave the linear product **16a** exclusively, but in poor yield (entries 1–3). The use of EtOH did result in the formation of branched product and in higher selectivities than crotyl acetate (up to 14:1 favoring the *syn* isomer), but the selectivity of branched/linear products dropped, and at best, a 2:1 ratio was obtained (entries 4–6). It was also observed that higher yields were obtained if the reaction was conducted at lower reaction temperature but over a longer period of time (entry 6); however, this resulted in significantly lower *anti/syn* ratio.

Potential for Large-Scale Reactions—Among the substrates investigated, the allylation employing vinyl oxirane was a particularly interesting case as the product of this reaction was a linear 1,5-diol, which presented an synthetically useful target, and a practical synthesis was sought. The reaction was performed on a 10 mmol scale to afford a 97% yield after column chromatography and a somewhat decreased *E/Z* ratio of 10:1 (Scheme 8). Similarly, the reaction between 2-methoxybenzaldehyde and allyl acetate was conducted on 10 mmol scale to yield 97% of the desired product.

Chiral Ligands in the Ruthenium-Catalyzed Nucleophilic Allylation Reaction

At the outset of studies to render the reaction enantioselective, it was important to recognize that allylruthenium agents typically react with carbonyl compounds through a 6-membered transition state.³⁵ This feature presents the opportunity to apply methods that have been successfully employed in other related reactions to induce stereo-selection.^{1–5} Two viable strategies presented themselves: (1) the inclusion of a chiral ion that will associate with the ruthenium metal and direct the approach of the incoming aldehyde³⁶ or (2) the formation of a discrete ligated ruthenium complex that will prefer a particular 6-membered transition state leading to enantioenriched products.^{37–41}

Inspiration for the first approach came from the requirement of a soluble chloride source to engender sufficient activity when a zerovalent ruthenium complex was employed (Table 6). This requirement implies that an anionic ruthenium carbonyl species is needed to effect oxidative addition to allyl acetate. Therefore, it was reasonable to assume that a chiral anion instead of chloride or a chiral counteranion could influence the bond forming event in the metal coordination sphere. Unfortunately, neither of these approaches resulted in any enantioenrichment of the product.

To assess the second approach, a series of chiral ruthenium complexes were employed in the reaction between **1a** and **2** (Table 20). The first catalyst structure investigated was designed with maximum binding to the ruthenium center in mind by the tridentate Phe-box ligand⁴² (**Cat 1**, entry 1) which has two Ru–N dative bonds to the ruthenium and a single C–Ru bond as well. Also tested was a Pybox⁴³ type ligand complex (**Cat 2**, entry 2) which maintains the tridentate nature of Phe-box but alters the electronic properties of the catalyst through the exchanging of a C–Ru covalent bond for a N–Ru dative bond. Lastly, a benzyl ruthenacycle⁴¹ (**Cat 3**, entry 3) was employed as bidentate ligand with a C–Ru bond. Each of these catalysts yielded **3a** but in racemic form.

Next examined were bidentate ligand complexes containing dative N–Ru bonds and included those with no carbon bridge (**Cat 4**), a one-carbon bridge (**Cat 5a**), a two-carbon bridge (**Cat 6**), or a mixed, pyridine–oxazoline backbone (**Cat 7**). The adjustment of this bridge would allow for a different bite angle for each complex on the ruthenium metal center, which would in turn adjust the location of the stereogenic atoms in the reaction sphere. Each of these complexes were tested under the standard reaction conditions (Table 21). Although all complexes were competent, only **Cat 5a** showed any enantioenrichment (entry 2).

To determine if low selectivity resulted from ligand dissociation from the ruthenium center, an experiment was run with the addition of more ligand (Table 22). Interestingly, an increase in the *er* value was observed, first to up to 70:30 with 6 mol % added ligand (entry 1) and then to a maximum of 75:25 with 30 mol % added ligand (entry 2). As this ligand system seemed viable for the generation of an enantioselective allylation reaction, further studies were directed toward exploring the identity of the substituents at the stereogenic carbon of **Cat 5a**.

To expand the chemical space for **Cat 5a**, additional bisoxazoline ligands were synthesized, complexed to ruthenium, and tested under both the standard reaction conditions and with an additional equivalent (with respect to Ru mol %) of the corresponding ligand (Chart 1 and Table 23). In general, the addition of ligand caused a higher *er* value, but with diminished yield. The replacement of the *p*-cymene ring with a benzene ring as the bound arene in **Cat 5b** resulted in an increase in enantioenrichment as compared to **Cat 5a** both with and without added ligand (Table 23, entries 1 and 2, vs Table 22, entries 1 and 2). The use of a benzyl substituent in **Cat 5c** gave a nearly racemic yield, but added ligand was able to approach the selectivity of **Cat 5a** (entries 3 and 4), a trend that was repeated with **Cat 5d** (entries 5 and 6). Interestingly, when a catalyst related to **Cat 5a** but with a dimethyl bridge was used, **Cat 5e**, the product was observed, but in racemic form (entry 7). The *tert*-butyl substituted **Cat 5f** inverted the sense of enantioinduction, but added ligand in this case gave racemic product (entries 9 and 10). The alkyl-substituted complexes **Cat 5g** and **Cat 5h** each gave racemic product, even with added ligand (entries 11–14), similar to the benzyl-substituted complexes, highlighting the general lack of selectivity for alkyl-substituted bisoxazolines for this reaction. When the phenyl ring of **Cat 5a** was bonded in such a way to exclude free rotation as with the case of **Cat 5i**, all enantioenrichment was lost (entry 15). However, when an additional ring was added, as in the case of **Cat 5j**, the *er* was nearly unchanged (entries 17 and 18). The inclusion of additional phenyl rings at the 5 and/or 5' position of the bisoxazoline ring maintained enantioenrichment and in the case of **Cat 5l** with added ligand, gave the best *er* value yet observed of 22:78, albeit in a yield of 22% (entry 22). Finally, the addition of methyl groups at the 2,3,5 position of the parent backbone, **Cat 5m**, resulted in little to no enantioenrichment (entry 23).

In the course of the executing these reactions, a color change was observed when Et₃N was added to the solution containing the catalyst and solvent, except in the case of **Cat 5e**. A series of experiments using variable amounts of Et₃N were run to further explore this effect (Table 24). Without Et₃N, no immediate color change was observed, the yield was very low,

and the product was racemic (entry 1). Increasing the amount of Et₃N increased the yield and selectivity to a maximum of 65:35 (entries 2–5).

DISCUSSION

Roles of Reaction Components and Formulation of a Catalytic Cycle

On the basis of the observations gathered during the discovery and optimization of the present reaction, several conclusions could be drawn that allowed the formulation of a catalytic cycle and the identification of roles of each reagent.

Rationale for Role of Soluble Chloride—In the first step of the catalytic cycle, the formation of a π -allylruthenium complex must form directly from allyl acetate and Ru₃(CO)₁₂. However, this reaction is not feasible because it has been shown that Ru₃(CO)₁₂ does not react with allyl acetate even in refluxing toluene.³² Therefore, a different form of low-valent ruthenium must participate in that step. The salutary effect of added halide is likely the means by which this step is possible as it provides a more nucleophilic form of ruthenium needed for the oxidative addition. As indicated in Table 6, entry 10, only 15% conversion of aldehyde was observed in the absence of halide. The effect of halides on the structure and reactivity of ruthenium carbonyl complexes has been the subject of countless investigations since the early 1980s but *none mentioned the effect in the allylation reaction*.⁴⁴ Geoffroy⁴⁵ has shown that halide anions (X[−]) can displace one or more CO ligands in the Ru₃(CO)₁₂ complex to produce anionic species such as [Ru₃(CO)₁₁X][−],⁴⁶ [Ru₃(CO)₁₀X][−], [Ru₄(CO)₁₃X][−].

Amatore and Jutand have established the role of chloride ion in palladium-catalyzed, cross-coupling reactions in which anionic chloropalladium(0) ate species participate in the oxidative addition step.^{47,48} By analogy, it can be postulated that the rate enhancement caused by chloride observed in this process arises from chloride-ligated anionic complexes formed by displacement of carbon monoxide ligand(s) from the neutral Ru(0) carbonyl species by chloride. These anionic complexes should be more nucleophilic than the neutral Ru(0) complexes and thus can readily react with allyl acetate to form the requisite π -allylruthenium complex, which ultimately delivers the allyl group to the aldehyde. It is possible that this process occurs by the coordination of the aldehyde carbonyl to the ruthenium center causing a shift of the π -allylruthenium from the η^3 - to the η^1 -binding mode and the (η^1 -allyl)ruthenium undergoes the nucleophilic attack at the carbonyl.⁴⁹

Rationale for Required CO Pressure—During the course of optimization, it was observed that the minimum pressure of CO required for efficient reactivity was 30 psi. A calculation of CO solubility was conducted to explain this observation. Table 25 shows the available data for CO solubility in dioxane at different temperatures.^{50,51} On the basis of eq 2, in which k_1 and k_2 are Henry's constants at temperatures T_1 and T_2 , the coefficient c was calculated to be 376.51 ($R^2 = 0.9882$). Linear regression provided $k_{343} = 2158.1$ (L·psi mol^{−1}); thus, the solubility of CO at 343 K (70 °C) is 4.63×10^{-4} mol·L^{−1}·psi^{−1}.

$$\ln k_1 - \ln k_2 = c \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (2)$$

Assuming that other solutes do not significantly affect the CO solubility, the amount of CO in the 2.5 mL dioxane solution at 70 °C at 30 psi should be approximately 0.035 mmol, which is very close to the total amount of ruthenium (0.030 mmol). Thus, 30 psi of CO translates to 1:1 molar ratio of solvated CO/Ru. If the reaction is run under a balloon of CO, the ratio of solvated CO/Ru is approximately 1:2. As such, the reaction was slower at that pressure because not enough CO is present in the solution and the rate of CO uptake by ruthenium is faster than the rate of CO diffusion into the solution at that pressure. The fact that the reaction does not proceed faster at higher CO pressures indicated that the concentration of CO is not present in the rate equation and the necessary pre-equilibria prior to the turnover-limiting step are saturated.

Role of Amine—On the basis of the evidence obtained in the course of this study, it is highly likely that the role of amine in the reaction is to aid in the reduction of higher valent ruthenium species [Ru(III) or Ru(II)] to Ru(0) so the catalytic cycle can begin. The evidence for this is as follows:

- (1) If amine is acting only as a reductant for the catalyst, then it should only be required for high oxidation states of ruthenium precatalysts. $\text{Ru}_3(\text{CO})_{12}$ is able to function without added amine (as long as a soluble halide is present). However, neither Ru(III) or Ru(II) sources reacted in the absence of added amine.
- (2) The amount of amine corresponds closely to the stoichiometry needed to reduce each high-oxidation ruthenium source to Ru(0) considering that Et_3N acts as a two-electron reductant. For reduction of RuCl_3 to Ru(0), 1.5 mol equiv of Et_3N are required. The following equations illustrate this point.

For the full reduction of RuCl_3 to Ru(0), a total of three electrons would be needed:

Because Et_3N is a two-electron reductant, 1.5 equiv would be needed to provide the necessary electrons for full reduction of RuCl_3 (eq 3):

(3)

Therefore, as shown, a requirement of around 4.5 mol % of Et₃N is needed to fully reduce 3 mol % of RuCl₃, as observed in Table 5, entries 6–8.

This same principle can be applied to the use of [RuCl₂(*p*-cymene)]₂ for which 1 molar equiv of Et₃N was required to reduce Ru(II) to Ru(0) (see Table S6). The more gradual turning point observed with the use of this catalyst may arise because some Ru(0) is formed in the initial reduction from Ru(II) to Ru(0) even with low loadings of Et₃N. RuCl₃ needs almost a full molar equivalent of Et₃N before any appreciable Ru(0) can be formed, thus explaining why some product was formed when only 4.0 mol % of Et₃N was used (Table 5).

(3) The oxidation of the amine should lead to the formation of an iminium ion, which under the aqueous conditions of the reaction should convert to a carbonyl compound. The use of dicyclohexylamine and subsequent observation of cyclohexanone demonstrates this very fact. A 52% conversion of dicyclohexylamine to cyclohexanone was observed, which corresponds to the consumption of 0.21 mmol of amine (from an initial loading of 0.40 mmol). The amount of amine consumed is 1.72 times the RuCl₃ loading of 0.12 mmol and corresponds well with 1.5 reducing equivalents required for the full reduction of Ru(III)Cl₃ to a Ru(0) species.

Taken together, these three points provide good evidence for the role of amine as the means by which the higher oxidation states of ruthenium are reduced to enter the catalytic cycle. The action of the WGSR can also contribute to this reduction as the use of RuCl₃ without added amine in other WGSR-driven reactions finds ample precedent.¹⁷

Formulation of the Catalytic Cycle—From these considerations, a more complete mechanism for the full catalytic cycle can be presented (Scheme 9). Following initial reduction of higher valent ruthenium by the amine or the WGSR to the Ru(0) species **v** or addition of chloride (in the case of Ru₃(CO)₁₂), oxidative addition to allyl acetate occurs to give a Ru(II) π -allyl species **vi**. The aldehyde next inserts into the nucleophilic allylmethyl species **vi** next inserts by coordination of the carbonyl group to the Ru(II) center (via the η^1 form of **vi**) to generate **vii**. Hydrolysis of the alkoxide **vii** then releases the homoallylic alcohol product and generates a Ru(II) hydroxide species **viii**. By means of the water–gas shift reaction,⁵² CO may undergo migratory insertion into the Ru(II)–OH bond yielding **ix** which can be followed by a β -hydride elimination to release CO₂ and form **x**. Subsequent reductive elimination of Ru(II) hydride **x** intermediate regenerates Ru(0) complex **v**, and forms acetic acid as the second byproduct.

Configurational Stability of the π -Allylruthenium Intermediate

Several studies have investigated the configurational stability of the π -allyl moiety that forms after ruthenium oxidatively adds into the allyl pro-nucleophile.^{32,53} The relative rate of any isomerization event in comparison to the product formation (by aldehyde insertion) is an important feature of the reaction as this can influence the stereoselectivity of the process. This situation does not obtain with the 2-substituted allyl pro-nucleophiles, but in the case of unsymmetrical pronucleophiles **6** and **9**, the structure and configurational stability of intermediates is crucial for determining the product structure. The use of (*E*)-**6** leads to the selective formation of *anti*-**7**, as is expected if the allylation event proceeds through a closed,

six-membered transition state (Scheme 10),⁵⁴ which has been computationally documented for the ruthenium-catalyzed allylation of aldehydes.³⁵ The use of (*E*)-cinnamyl acetate in other allylation reactions has also been demonstrated to be selective for the *anti*-branched product.⁵⁵

The use of (*Z*)-**6** also led to *anti*-**7** selectively, not the expected product *syn*-**7** that would result from a closed transition state. Two rationales could explain this observation: (1) the reaction actually occurs through an open transition state that is not sensitive of the double bond geometry (type 2)⁵⁴ or (2) the aldehyde insertion occurs after a rearrangement of the π -allyl complex to form the more thermodynamically stable π -allyl complex with the *E*-configuration (type 3). It is more likely that the rearrangement pathway is operative as typical allylation reactions that involve an open transition state form the *syn*-product selectively.⁵⁴ Therefore, a η^3 – η^1 – η^3 rearrangement can be invoked to explain the formation of the *anti*-**7** product (Scheme 11). Furthermore, the use of enantioenriched (*S*)-**9** did not result in enriched **10** (Scheme 14), even though the insertion of ruthenium in the allyl pro-nucleophile via a S_N2' mechanism would result in a chiral π -allyl complex (Scheme 12). Again, a η^3 – η^1 – η^3 rearrangement prior to aldehyde insertion could result in the isomerization of the species, yielding racemic **10**. However, a nonselective aldehyde insertion cannot be ruled out, in lieu of a nonconfigurationally stable π -allyl, which would also result in the formation of racemic **10**.

Selective Formation of the Linear Product with Vinyl Oxirane

Interestingly, the use of **9** under the optimized conditions led to the selective formation of the linear homoallylic alcohol with an *E*-double bond configuration, **10**. The branched product (**11**) was observed only as the minor product when an alcohol solvent was used, and even then in low yield. While the use of **9** as an allyl pro-nucleophile in aldehyde allylations is known, it often selectively forms the branched product⁵⁶ or forms the linear product with *E/Z* ratios that range from poor to selective for the *Z*-double bond configuration.⁵⁷ The use of **9** in this ruthenium-catalyzed allylation of aldehydes is, therefore, a unique case for the highly selective formation of the (*E*)-**10** product. Alternative methods to generate the linear product involve the use of allyl-boron reagents but which are selective for the formation of *Z* geometries.^{58–60} Araki and co-workers observe selective formation of the linear product in the indium-mediated allylation reaction using vinyl oxirane. To account for this selectivity, two cyclic intermediates are rationalized to form upon generation of the η^1 -allylindium, each containing an O–In bond. The first consists of a 4-membered ring with an exocyclic allyl that leads to the linear product (Scheme 13, a, top). The intermediate that leads to the branched product involves all of the atoms in a 6-membered ring (Scheme 13, a, bottom). While this rationale can be applied in the formation of linear product for the ruthenium catalyzed allylation, the selective *E*-bond geometry cannot. Instead, it is possible that the transition state resulting from the four-membered intermediate as prescribed by Araki et al. has instead an equatorial methyl-alkoxide bound to the ruthenium, which would give the desired (*E*)-**10** product (Scheme 13, b).

Other Allyl Pro-nucleophile Reactivities

The use of crotyl acetate led to a nonselective formation of branched diastereomers. The high branched selectivity corresponds to reaction via the more stable η^1 -allyl ruthenium complex with the increased steric contributions due to the methyl distal to the ruthenium center prior to aldehyde insertion. The lack of *syn/anti* selectivity points to a weak preference for an *E* or *Z* vinyl methyl group during the course of η^3 - η^1 - η^3 rearrangements prior to aldehyde insertion. This rearrangement pathway is known for both palladium⁶¹ and ruthenium⁵³ catalysts, and a mixture of *syn* and *anti* products can result from geometrically pure starting crotyl.⁶²

Rationale for Methylene-Bridged Bisoxazoline Selectivity

Through the course of testing seven initial ligand backbones (**Cat 1–Cat 7**), only a single structure was shown to be capable of inducing enantioenrichment in the homoallylic alcohol, namely **Cat 5a**. This observation is intriguing as the difference between some of the catalysts is minimal. In the case of **Cat 1** and **Cat 2**, the distance between the ruthenium metal center and stereogenic carbon is farther than the other catalysts tested owing to the planar, three-carbon bridge present in the ligand backbone, which might keep the stereodefining features of the catalyst too far from the reaction center. In the case of **Cat 3**, it is possible that the methyl group is not a large enough group to influence the orientation of the aldehyde and allyl, especially when one-half of the complex has no stereodefining features, similar to **Cat 7**. However, in the cases of **Cat 4–Cat 6**, the difference of a single carbon in the backbone of the ligand was enough to provide any stereoinduction only when a single-carbon bridge was present as both a zero-carbon and two-carbon bridge gave no stereoinduction (**Cat 4** and **Cat 6**). This trend seems peculiar considering how similar these catalyst structures are.

The most likely rationales for these results include: (1) the fact that **Cat 5e** also gave no enantioenrichment despite it being very similar to **Cat 5a/Cat 5b** and (2) the dependence on the inclusion of Et₃N for reactivity and enantioenrichment. It is highly likely that a hydrogen on the methylene bridge of **Cat 5** is being removed, generating a new species (**Cat 5b'**) that might be what leads to the enantioenrichment of **3a** (Scheme 14). The complex **Cat 5b'** would bind more tightly to the ruthenium metal, as the one nitrogen is now anionic, likely reducing the chance for ligand decomplexation and an increase in a background, racemic reaction. The other initial ligand backbones are unable to undergo a deprotonation event or, if they can, as in the case of **Cat 3**, the resulting species is achiral.

CONCLUSION

The ruthenium-catalyzed allylation reaction employing CO as the terminal reductant is a highly efficient and atom-economical process for the formation of homoallylic alcohols from aldehydes. The use of inexpensive and noncorrosive allyl acetates and other allyl pro-nucleophiles, water, and a low pressure of carbon monoxide can affect this transformation. For the simple allyl acetates, reagents were used in near stoichiometric amounts, even the CO gas, and only moderate reagent excesses were required for the more reactive allyl

pronucleophiles. The use of nonsymmetrical allyl pro-nucleophiles further illustrates the potential for a wide range of allyl pronucleophiles to be employed in the reaction.

The role of each reaction component has been defined and optimized, including the more definitive role of amine in the reaction. The reaction is catalytic in ruthenium, and because the stoichiometric byproducts are carbon dioxide and acetic acid, it is environmentally benign and readily adaptable to large-scale operation. The method shows good substrate generality, functional group compatibility, and high tolerance to electronic and steric factors. Most importantly, the reaction has been shown to be highly chemoselective for reactions only at an aldehyde carbonyl. The only substrates that do not react are the ones that include unprotected N-heterocycles (such as pyridine, pyrrole, or indole) or alkynes as these functional groups inhibit the reaction owing to their strong binding to low valent ruthenium.

The type of allyl pro-nucleophiles that can be employed in the reaction has been expanded to include unsymmetrical allyl sources as demonstrated through the use of (*E*)-cinnamyl acetate and vinyl oxirane. Both of these allyl pro-nucleophiles gave selective formation of a single constitutional isomer, often in high selectivity. For (*E*)-cinnamyl acetate, only the *anti*-branched product was formed across a wide range of aldehydes examined. In the case of vinyl oxirane, the selective formation of the linear product over the branched product is impressive as well is the selective formation of the *E*-double bond isomer, which is often the minor isomer formed when the linear product is made. In both cases, the deliberate choice of solvent and/or additives to the reaction was able to achieve this high selectivity.

Finally the use of chiral ruthenium bisoxazoline complexes has allowed for the enantioselective generation of homoallylic alcohols, albeit in moderate enrichment. Of particular note was the importance of the bisoxazoline backbone to the effectiveness of the reaction as only a methylene-bridged bisoxazoline was able to induce enantioenrichment. A survey of bisoxazoline ring substituents did reveal that the proximity of the stereocenter substituent to the ruthenium metal had a significant impact on the ability of the complex to yield enantioenriched product. Furthermore, the addition of free ligand and a corresponding increase in *er* revealed that an equilibrium between ligated and unligated ruthenium was likely responsible for the rate of the background, racemic reaction which is known to be highly efficient for the substrates employed. Additional ligands that take into account the observations and findings from this survey could allow for a future, highly enantioselective reaction to be designed.

EXPERIMENTAL SECTION

General Experimental Procedures

General Reactions—All reactions were performed in oven-dried (120 °C) and/or flame-dried glassware under an atmosphere of dry nitrogen or argon, unless noted. Reaction solvents tetrahydrofuran (Fisher, HPLC grade) and DMSO (Fisher, ACS grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvent toluene (Fisher, ACS grade) was dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon. Reaction solvent

dioxane (Fisher, ACS grade) was distilled over sodium prior to use and had 26.5 $\mu\text{g/mL}$ of water. Reaction solvents methanol (Fisher, ACS grade), ethanol (Fisher, ACS grade), and acetonitrile (Aldrich, ACS grade) were distilled from CaH_2 . Solvents for filtration and chromatography were certified ACS grade. Solvents for chromatography were: hexanes (Optima grade), diethyl ether (ACS grade), and dichloromethane (ACS grade).

Reaction Setup—All carbonylation reactions were performed in either: (1) a six-well autoclave (Figure S1), which allows for independent control of gas pressure in each well via the individual valves, equipped with a temperature probe connected to a magnetic stirrer (IKA Labortechnik) bearing a heat control element OR (2) a Fischer-Porter Tube submerged in an oil bath with the use of a magnetic stirrer (IKA Labortechnik) for heating and a connected temperature probe to maintain temperature.

NMR Spectroscopy— ^1H and ^{13}C spectra were recorded on a 500 MHz, ^1H (126 MHz, ^{13}C) spectrometer. Spectra were referenced to residual chloroform (7.26 ppm, ^1H ; 77.16 ppm, ^{13}C) or when the chloroform peak is obscured in the ^1H NMR spectrum, to isolated singlets in the product spectrum corroborated with a more diluted sample. Chemical shifts are reported in parts per million (ppm), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), and br (broad). Coupling constants, J , are reported in Hertz with integration provided and assignments indicated. Assignments are corroborated by 2D experiments (COSY, HMQC, HMBC).

Infrared Spectroscopy—Infrared spectra (IR) were recorded on a PerkinElmer Spectrum Two ATR spectrometer using neat sample. Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 67–100%); m (medium, 34–66%); w (weak, 0–33%).

Mass Spectrometry—Chemical Ionization (CI) spectra were performed with methane reagent gas with either a doublefocusing sector field or time-of-flight (TOF) mass analyzer. Electrospray ionization (ESI) mass spectra were performed on a Micromass Quattro spectrometer. Data are reported in the form of (m/z) (intensity relative to the base peak = 100 where applicable).

Melting Points—Melting points (mp) were determined in vacuum-sealed capillary tubes using a Thomas-Hoover melting point apparatus and are corrected.

Elemental Analysis—Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory or by Robertson Microlit Laboratories and is the average of two runs.

Distillation—Bulb-to-bulb distillation was performed on a Büchi GKR-50 Kugelrohr with boiling points (bp) corresponding to uncorrected air-bath temperatures (ABT). A vacuum of 10^{-5} to 10^{-8} mmHg was achieved using a diffusion pump.

Liquid Chromatography—Analytical thin-layer chromatography was performed on silica gel 60 F254 plates. Visualization was accomplished with UV light and/or potassium permanganate (KMnO_4) solution. Retention factor (R_f) values reported were measured using

a 10 × 2 cm TLC plate in a developing chamber containing the solvent system described. Flash column chromatography was performed using 40–63 μm particle size (230–400 mesh, 60 Å pore size) SiO_2 .

Gas Chromatography—Analytical gas chromatography (GC) was performed using a Hewlett-Packard 5890 Series II gas chromatograph fitted with a flame ionization detector (H_2 carrier gas, 1 mL/min). Injections were made on a Hewlett-Packard HP-1 (30 m) capillary column. The injector temperature was 250 °C, the detector temperature was 300 °C, with a split ratio of 100:1. Retention times (t_R) and integrated ratios were obtained using Agilent Chemstation Software.

Chiral Stationary Phase HPLC—Analytical chiral stationary normal-phase high-pressure liquid chromatography was performed on an Agilent 1100 HPLC equipped with a Chiralpak IB-3 column or Astec Cellulose DMP column.

Chemicals—Hydrocinnamaldehyde (Alfa), *trans*-cinnamaldehyde (Aldrich), pyridine (Fisher), triethylamine (Fisher), allyl methyl carbonate (Aldrich), benzaldehyde (Aldrich), furfural (Alfa), 4-methoxybenzaldehyde (Aldrich), 4-(trifluoromethyl)benzaldehyde (Oakwood), were distilled prior to use. 4-Nitrobenzaldehyde was sublimed prior to use. Ruthenium(III) chloride hydrate and triruthenium dodecacarbonyl were purchased from Strem Chemical and stored and handled in a drybox and used as received. All other reagents were purchased from Aldrich, Fisher, Oakwood, or Strem and used as received.

General Procedures

General Allylation Procedure for Preparative-Scale Allylation Reactions of Allylic Acetates—In a glovebox, to a glass Fischer–Porter tube (150 mL) containing a Teflon-coated, magnetic stir bar were added RuCl_3 (5 mol %) and (if indicated) TBACl (5 mol %). The tube was covered with a rubber septa before being removed from the glovebox. Outside the glovebox, the tube was charged sequentially with solvent (EtOH, *t*-BuOH, or 1,4-dioxane, 1.25–2.5 mL), H_2O (1.5 or 2.5 equiv), Et_3N (0.1 equiv), allyl pronucleophile (*E*)-**6** or **9**, and aldehyde **1** (1.00 mmol, 1.0 equiv) via syringe. The Fischer–Porter tube then was charged with CO gas (100 psi) and pressure was released to a vented hood four times before the CO gas was maintained at 40 psi and the valves were closed. The Fischer–Porter tube was inserted into a preheated oil bath (either 75 or 85 °C) that was placed onto a magnetic stirrer with a temperature probe inserted into the oil bath. The stirring and heating was maintained for 24 h. Upon elapse of the reaction time, the Fischer–Porter tube was removed from the oil bath and allowed cool to ambient temperature (within 10 min) upon which time, the outlet was connected to a vented hood and the pressure in the Fischer–Porter tube was gently released. The inlet was then connected to a nitrogen line, and the system was purged by N_2 (which was passed through a drying tube filled with Drierite) for 15 min before the autoclave was opened. The reaction mixture was transferred to a 20 mL glass scintillation vial with the aid of 3 mL of methylene chloride. The solvent was removed under reduced pressure by rotary evaporation (25 °C, 20 mmHg) before being purified by the indicated method.

Preparation of Products Resulting from the use of (E)-Cinnamyl Acetate

Preparation of trans-1,2-Diphenylbut-3-en-1-ol (**7a**)—

Following the general allylation procedure, **1a** (102 μL , 1.0 mmol), RuCl_3 (13.0 mg, 0.05 mmol, 0.05 equiv), (*E*)-**6** (202 μL , 1.2 mmol, 1.2 equiv), H_2O (27 μL , 1.5 mmol, 1.5 equiv), Et_3N (14 μL , 0.1 mmol, 0.1 equiv), and EtOH (2.5 mL) were combined under 40 psi of CO at 85 °C for 24 h. Workup and purification by silica gel column chromatography (70 g SiO_2 , 3.5×20.5 cm column, Et_2O /hexane (1:9 (500 mL) $\rightarrow$ 1:4 (500 mL))) provided **7a** (191 mg, 85%) as a colorless oil. The spectroscopic data matched those from the literature.⁶³ Data for **7a**: ^1H NMR (500 MHz, CDCl_3) 7.25–7.17 (m, 5H, C(aryl)H), 7.17–7.12 (m, 3H, C(aryl)H), 7.08–7.03 (m, 2H, C(aryl)H), 6.26 (ddd, $J = 17.1, 10.3, 8.9$ Hz, 1H, C(3)H), 5.28 (ddd, $J = 10.2, 1.6, 0.7$ Hz, 1H, C(4)H_{cis}), 5.23 (ddd, $J = 17.0, 1.6, 0.9$ Hz, 1H, C(4)H_{trans}), 4.86 (d, $J = 7.7$ Hz, 1H, C(1)H), 3.56 (t, $J = 8.3$ Hz, 1H, C(2)H), 2.51–2.23 (m, 1H, br OH); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) 142.0, 140.7, 138.0, 128.5, 128.5, 128.0, 127.6, 126.8, 126.7, 118.6, 77.4, 59.4; MS (ESI) 247.0 (MNa^+ , 62), 118.9 (100); TLC R_f 0.258 (Et_2O /hexane, 1:4) [UV, KMnO_4].

Preparation of trans-(E)-1,4-Diphenylhexa-1,5-dien-3-ol (7b**)**—Following the general allylation procedure, **1b** (126 μL , 1.0 mmol), RuCl_3 (13.0 mg, 0.05 mmol, 0.05 equiv), (*E*)-**6** (252 μL , 1.5 mmol, 1.5 equiv), H_2O (27 μL , 1.5 mmol, 1.5 equiv), Et_3N (14 μL , 0.1 mmol, 0.1 equiv), and EtOH (2.5 mL) were combined under 40 psi of CO at 85 °C for 24 h. Workup and purification by silica gel column chromatography (80 g SiO_2 , 4.5×13.5 cm column, Et_2O /hexane (1:9 (750 mL) $\rightarrow$ 1:4 (600 mL) $\rightarrow$ 1:3 (300 mL))) provided **7b** (228 mg, 85%) as a white solid. The spectroscopic data matched those from the literature.⁶⁴ Data for **7b**: ^1H NMR (500 MHz, CDCl_3) 7.40–7.30 (m, 2H, C(aryl)H), 7.30–7.23 (m, 6H, C(aryl)H), 7.25–7.18 (m, 2H, C(aryl)H), 6.54 (dd, $J = 15.9, 1.3$ Hz, 1H, C(2')H), 6.22 (ddd, $J = 17.1, 10.3, 8.8$ Hz, 1H, C(3)H), 6.10 (dd, $J = 15.9, 6.2$ Hz, 1H, C(1')H), 5.32–5.21 (m, 2H, C(4)H), 4.52 (ddd, $J = 7.5, 4.5, 1.7$ Hz, 1H, C(1)H), 3.47 (dd, J

= 8.9, 7.0 Hz, 1H, C(2)H), 2.00 (d, J = 3.4 Hz, 1H, br OH); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) 140.7, 137.9, 136.9, 131.2, 129.8, 128.7, 128.7, 128.6, 128.5, 127.6, 127.0, 126.6, 118.4, 77.4, 77.4, 77.2, 76.9, 75.2, 57.7; MS (ESI) 273.1 (MNa^+ , 100); TLC R_f 0.365 (Et_2O /hexane, 1:4) [UV, KMnO_4].

Preparation of trans-1,4-Diphenylhex-5-en-3-ol (7c)—Following the general allylation procedure, **1c** (132 μL , 1.0 mmol), RuCl_3 (13.0 mg, 0.05 mmol, 0.05 equiv), (*E*)-**6** (202 μL , 1.2 mmol, 1.2 equiv), H_2O (27 μL , 1.5 mmol, 1.5 equiv), Et_3N (14 μL , 0.1 mmol, 0.1 equiv), and *t*-BuOH (2.5 mL) were combined under 40 psi of CO at 85 °C for 24 h. Workup and purification by silica gel column chromatography (80 g SiO_2 , 4.5 $\times$ 13.5 cm column, Et_2O /hexane (1:9 (750 mL) $\rightarrow$ 1:4 (500 mL))) provided **7c** (197 mg, 78%) as a colorless oil. The spectroscopic data matched those from the literature.⁶⁵ Data for **7c**: ^1H NMR (500 MHz, CDCl_3) 7.37–7.28 (m, 2H, C(aryl)H), 7.25–7.19 (m, 3H, C(aryl)H), 7.19–7.13 (m, 3H, C(aryl)H), 7.13–7.08 (m, 2H, C(aryl)H), 6.11 (ddd, J = 16.9, 10.3, 9.2 Hz, 1H, C(3)H), 5.26–5.18 (m, 2H, C(4)H), 3.81 (td, J = 7.7, 3.5 Hz, 1H, C(1)H), 3.28 (dd, J = 9.2, 7.4 Hz, 1H, C(2)H), 2.84 (ddd, J = 13.9, 9.7, 5.4 Hz, 1H, C(2a')H), 2.63 (ddd, J = 13.7, 9.7, 6.9 Hz, 1H, C(2b')H), 1.86 (s, 1H, br OH), 1.77–1.59 (m, 2H, C(1')H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) 142.2, 141.4, 138.4, 128.8, 128.5, 128.5, 128.4, 128.4, 128.4, 128.0, 126.8, 125.8, 118.1, 77.4, 77.3, 77.1, 76.9, 73.3, 57.6, 36.1, 32.1.; MS: (ESI) 275.1 (MNa^+ , 100); TLC R_f 0.262 (Et_2O /hexane, 1:4) [UV, KMnO_4].

Preparation of trans-1-(4-Nitrophenyl)-2-phenylbut-3-en-1-ol (7d)—Following the general allylation procedure, **1d** (151 mg, 1.0 mmol), RuCl_3 (13.0 mg, 0.05 mmol, 0.05 equiv), (*E*)-**6** (202 μL , 1.2 mmol, 1.2 equiv), H_2O (27 μL , 1.5 mmol, 1.5 equiv), Et_3N (14 μL , 0.1 mmol, 0.1 equiv), and EtOH (2.5 mL) were combined under 40 psi of CO at 85 °C for 24 h. Workup and purification by silica gel column chromatography (70 g SiO_2 , 3.5 $\times$ 20.5 cm column, Et_2O /hexane (1:4 (750 mL) $\rightarrow$ 1:7 (250 mL) $\rightarrow$ 1:3 (500 mL))) provided

7d (196 mg, 73%) as a yellow solid. The spectroscopic data matched those from the literature.⁶³ Data for **7b**: ¹H NMR (500 MHz, CDCl₃) 8.08–8.01 (m, 2H, C(aryl')H), 7.32–7.15 (m, 5H, C(aryl)H), 7.07–7.01 (m, 2H, C(aryl')H), 6.23 (ddd, *J* = 17.1, 10.2, 9.1 Hz, 1H, C(3)H), 5.32 (dd, *J* = 10.1, 1.4 Hz, 1H, C(4)H_{cis}), 5.26 (dt, *J* = 17.1, 1.1 Hz, 1H, C(4)H_{trans}), 4.93 (dd, *J* = 7.9, 2.2 Hz, 1H, C(1)H), 3.48 (t, *J* = 8.5 Hz, 1H, C(2)H), 2.51 (d, *J* = 2.3 Hz, 1H, br OH); ¹³C{¹H} NMR (125 MHz, CDCl₃) 149.2, 147.2, 139.6, 136.9, 128.8, 128.2, 127.5, 127.2, 123.1, 119.6, 76.8, 76.5, 59.6; MS: (ESI) 292.1 (MNa⁺, 69); TLC *R*_f 0.169 (Et₂O/hexane, 1:4) [UV, KMnO₄].

Preparation of trans-1-(4-Methoxyphenyl)-2-phenylbut-3-en-1-ol (7e)—Following the general allylation procedure, **7e** (122 μ L, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), (*E*)-**6** (252 μ L, 1.5 mmol, 1.5 equiv), H₂O (27 μ L, 1.5 mmol, 1.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and EtOH (2.5 mL) were combined under 40 psi of CO at 85 °C for 24 h. Workup and purification by silica gel column chromatography (70 g SiO₂, 3.5 $\times$ 20.5 cm column, Et₂O/hexane (1:9 (800 mL) $\rightarrow$ 1:4 (500 mL)) then 100% Et₂O (100 mL)) provided **7e** (168 mg, 66%) as a yellow solid. The spectroscopic data matched those from the literature.⁶⁶ Data for **7e**: ¹H NMR (500 MHz, CDCl₃) 7.23–7.18 (m, 2H, C(aryl)H), 7.17–7.12 (m, 1H, C(aryl)H), 7.10–7.02 (m, 4H, C(aryl)H, C(aryl')H), 6.78–6.71 (m, 2H, C(aryl')H), 6.25 (ddd, *J* = 17.0, 10.3, 8.9 Hz, 1H, C(3)H), 5.27 (ddd, *J* = 10.2, 1.7, 0.7 Hz, 1H, C(4)H_{cis}), 5.24 (ddd, *J* = 17.1, 1.7, 0.9 Hz, 1H, C(4)H_{trans}), 4.81 (dd, *J* = 7.9, 2.2 Hz, 1H, C(1)H), 3.75 (s, 3H, C(5')H₃), 3.54 (t, *J* = 8.4 Hz, 1H, C(2)H), 2.28 (d, *J* = 2.4 Hz, 1H, br OH); ¹³C{¹H} NMR (125 MHz, CDCl₃) 158.9, 140.8, 138.3, 134.1, 128.4, 127.9, 126.6, 118.3, 113.4, 76.3, 76.9, 59.4, 55.2; MS (ESI) 277.1 (MNa⁺, 98); TLC *R*_f 0.142 (Et₂O/hexane, 1:4) [UV, KMnO₄].

Preparation of trans-2-Phenyl-1-(4-(trifluoromethyl)phenyl)but-3-en-1-ol (7f)—Following the general allylation procedure, **1f** (137 μ L, 1.0 mmol), RuCl₃ (13.0 mg, 0.05

mmol, 0.05 equiv), (*E*)-**6** (252 μ L, 1.5 mmol, 1.5 equiv), H₂O (27 μ L, 1.5 mmol, 1.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and EtOH (2.5 mL) were combined under 40 psi of CO at 85 °C for 24 h. Workup and purification by silica gel column chromatography (70 g SiO₂, 3.5 $\times$ 20.5 cm column, Et₂O/hexane (1:9 (750 mL) $\rightarrow$ 1:4 (500 mL) $\rightarrow$ 1:3 (400 mL))) provided **7f** (228 mg, 78%) as a colorless oil. The spectroscopic data matched those from the literature.⁶³ Data for **7f**: ¹H NMR (500 MHz, CDCl₃) 7.46 (d, *J* = 8.2 Hz, 2H, C(aryl')H), 7.28–7.21 (m, 4H, C(aryl)H), 7.21–7.15 (m, 1H, C(aryl)H), 7.10–7.01 (m, 2H, C(aryl')H), 6.24 (ddd, *J* = 17.1, 10.2, 9.0 Hz, 1H, C(3)H), 5.30 (dd, *J* = 10.3, 1.5 Hz, 1H, C(4)H_{cis}), 5.25 (dt, *J* = 17.0, 1.2 Hz, 1H, C(4)H_{trans}), 4.89 (dd, *J* = 7.6, 1.6 Hz, 1H, C(1)H), 3.51 (t, *J* = 8.4 Hz, 1H, C(2)H), 2.44 (d, *J* = 2.4 Hz, 1H, br OH); ¹³C{¹H} NMR (125 MHz, CDCl₃) 145.9, 140.1, 137.3, 129.7 (q, *J* = 32.3 Hz), 128.7, 128.4, 127.1, 124.9 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 27.2 Hz), 119.2, 76.8, 59.5; ¹⁹F{¹H} NMR (470 MHz, CDCl₃) δ –62.5; MS (ESI) 315.1 (MNa⁺, 23), 118.9 (100); TLC *R*_f 0.254 (Et₂O/hexane, 1:4) [UV, KMnO₄].

Preparation of trans-1-(4-chlorophenyl)-2-phenylbut-3-en-1-ol (7g)—Following the general allylation procedure, **1g** (141 mg, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), (*E*)-**6** (252 μ L, 1.5 mmol, 1.5 equiv), H₂O (27 μ L, 1.5 mmol, 1.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and EtOH (2.5 mL) were combined under 40 psi of CO at 85 °C for 24 h. Workup and purification by silica gel column chromatography (70 g SiO₂, 3.5 $\times$ 20.5 cm column, Et₂O/hexane (1:9 (750 mL) $\rightarrow$ 1:4 (500 mL) $\rightarrow$ 1:3 (300 mL))) provided **7g** (234 mg, 90%) as a colorless oil. The spectroscopic data matched those from the literature.⁶³ Data for **7g**: ¹H NMR (500 MHz, CDCl₃) 7.25–7.19 (m, 2H, C(aryl)H), 7.19–7.14 (m, 3H, C(aryl)H), 7.09–7.00 (m, 4H, C(aryl)H), 6.23 (ddd, *J* = 17.1, 10.3, 9.0 Hz, 1H, C(3)H), 5.29 (ddd, *J* = 10.2, 1.5, 0.6 Hz, 1H, C(4)H_{cis}), 5.25 (ddd, *J* = 17.1, 1.6, 1.0 Hz, 1H, C(4)H_{trans}), 4.81 (dd, *J* = 8.0, 1.7 Hz, 1H, C(1)H), 3.48 (t, *J* = 8.4 Hz, 1H, C(2)H), 2.35 (d, *J* = 2.3 Hz, 1H, br OH); ¹³C{¹H} NMR (125 MHz, CDCl₃) 140.4, 140.3, 137.7, 133.2, 128.6, 128.4, 128.2, 128.2, 126.9, 119.0, 76.7, 59.6; MS: (ESI) 283.0 (MNa⁺ + 2, 17), 281.0 (MNa⁺, 58); TLC *R*_f 0.236 (Et₂O/hexane, 1:4) [UV, KMnO₄].

Preparation of trans-1-(4-Bromophenyl)-2-phenylbut-3-en-1-ol (7h)—Following the general allylation procedure, **1h** (185 mg, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), (*E*)-**6** (252 μ L, 1.5 mmol, 1.5 equiv), H₂O (27 μ L, 1.5 mmol, 1.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and EtOH (2.5 mL) were combined under 40 psi of CO at 85 °C for 24 h. Workup and purification by silica gel column chromatography (70 g SiO₂, 3.5 $\times$ 20.5 cm column, Et₂O/hexane (1:9 (750 mL) $\rightarrow$ 1:4 (500 mL) $\rightarrow$ 1:3 (300 mL))) provided **7h** (278 mg, 90%) as a white solid. The spectroscopic data matched those from the literature.⁶³ Data for **7h**: ¹H NMR (500 MHz, CDCl₃) 7.38–7.30 (m, 2H, C(aryl')H), 7.25–7.19 (m, 2H, C(aryl)H), 7.19–7.11 (m, 1H, C(aryl)H), 7.07–7.02 (m, 2H, C(aryl')H), 7.02–6.95 (m, 2H, C(aryl')H), 6.22 (ddd, *J* = 17.1, 10.2, 9.0 Hz, 1H, C(3)H), 5.29 (ddd, *J* = 10.2, 1.6, 0.6 Hz, 1H, C(4)H_{cis}), 5.24 (ddd, *J* = 17.1, 1.6, 0.9 Hz, 1H, C(4)H_{trans}), 4.80 (d, *J* = 7.9 Hz, 1H, C(1)H), 3.47 (t, *J* = 8.4 Hz, 1H, C(2)H), 2.48–2.23 (m, 1H br OH); ¹³C{¹H} NMR (125 MHz, CDCl₃) 140.9, 140.3, 137.6, 131.1, 128.7, 128.5, 128.4, 127.0, 121.4, 119.0, 76.9, 76.7, 59.5; MS (ESI) 328.1 (MNa⁺ + 2, 8), 326.1 (MNa⁺, 10), 327.0 (47); TLC *R*_f 0.255 (Et₂O/hexane, 1:4) [UV, KMnO₄].

Preparation of trans-1-(Naphthalen-2-yl)-2-phenylbut-3-en-1-ol (7i)—Following the general allylation procedure, **1i** (156 μ L, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), (*E*)-**6** (252 μ L, 1.5 mmol, 1.5 equiv), H₂O (27 μ L, 1.5 mmol, 1.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and EtOH (2.5 mL) were combined under 40 psi of CO at 85 °C for 24 h. Workup and purification by silica gel column chromatography (70 g SiO₂, 3.5 $\times$ 20.5 cm column, Et₂O/hexane (1:20 (400 mL) $\rightarrow$ 1:9 (500 mL) $\rightarrow$ 1:4 (750 mL))) provided **7i** (225 mg, 82%) as a white solid. The spectroscopic data matched those from the literature.⁶⁶ Data for **7i**: ¹H NMR (500 MHz, CDCl₃) 7.80–7.75 (m, 1H, C(aryl')H), 7.76–7.72 (m, 1H, C(aryl')H), 7.71 (d, *J* = 8.6 Hz, 1H, C(aryl')H), 7.65–7.59 (m, 1H, C(aryl')H), 7.48–7.41 (m, 2H, C(aryl')H), 7.29 (dd, *J* = 8.5, 1.7 Hz, 1H, C(aryl')H), 7.22–7.17 (m, 2H, C(aryl)H), 7.16–7.12 (m, 1H, C(aryl)H), 7.11–7.08 (s, 1H, C(aryl)H), 6.30 (ddd, *J* = 17.1,

10.2, 8.9 Hz, 1H, C(3)H), 5.29 (ddd, $J = 10.2, 1.6, 0.7$ Hz, 1H, C(4)H_{cis}), 5.25 (ddd, $J = 17.1, 1.6, 0.9$ Hz, 1H, C(4)H_{trans}), 5.03 (dd, $J = 7.6, 2.4$ Hz, 1H, C(1)H), 3.68 (t, $J = 8.2$ Hz, 1H, C(2)H), 2.42 (d, $J = 2.6$ Hz, 1H, br OH); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) 140.7, 139.5, 137.9, 133.2, 133.0, 128.5, 128.5, 128.1, 127.7, 126.8, 126.0, 125.8, 124.8, 118.7, 77.4, 59.1; MS (ESI) 297.1 (MNa^+ , 80); TLC R_f 0.254 (Et_2O /hexane, 1:4) [UV, KMnO_4].

Preparation of trans-1-(Naphthalen-1-yl)-2-phenylbut-3-en-1-ol (7j)—Following the general allylation procedure, **1j** (136 μL , 1.0 mmol), RuCl_3 (13.0 mg, 0.05 mmol, 0.05 equiv), (*E*)-**6** (252 μL , 1.5 mmol, 1.5 equiv), H_2O (27 μL , 1.5 mmol, 1.5 equiv), Et_3N (14 μL , 0.1 mmol, 0.1 equiv), and EtOH (2.5 mL) were combined under 40 psi of CO at 85 $^\circ\text{C}$ for 24 h. Workup and purification by silica gel column chromatography (70 g SiO_2 , 3.5 $\times$ 20.5 cm column, Et_2O /hexane (1:20 (900 mL) $\rightarrow$ 1:9 (500 mL) $\rightarrow$ 1:4 (500 mL))) provided **7j** (220 mg, 81%) as a white solid. The spectroscopic data matched those from the literature.⁶⁶ Data for **7j**: ^1H NMR (500 MHz, CDCl_3) 8.14–8.08 (m, 1H, C(aryl')H), 7.89–7.81 (m, 1H, C(aryl')H), 7.74 (dt, $J = 8.2, 1.0$ Hz, 1H, C(aryl')H), 7.54 (dt, $J = 7.2, 0.9$ Hz, 1H, C(aryl')H), 7.53–7.43 (m, 2H, C(aryl')H), 7.41 (dd, $J = 8.1, 7.2$ Hz, 1H, C(aryl')H), 7.29–7.20 (m, 4H, C(aryl)H), 7.20–7.13 (m, 1H, C(aryl)H), 6.32 (ddd, $J = 17.1, 10.3, 8.4$ Hz, 1H, C(3)H), 5.71 (dd, $J = 5.5, 3.1$ Hz, 1H, C(4)H_{cis}), 5.21 (ddd, $J = 10.3, 1.6, 0.8$ Hz, 1H, C(4)H_{trans}), 4.99 (ddd, $J = 17.2, 1.6, 1.0$ Hz, 1H, C(1)H), 3.94 (dd, $J = 8.5, 5.5$ Hz, 1H, C(2)H), 2.30 (d, $J = 3.2$ Hz, 1H, br OH); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) 141.8, 137.8, 136.8, 133.8, 130.6, 129.0, 128.6, 128.3, 128.2, 126.8, 126.0, 125.4, 125.2, 124.7, 123.3, 118.7, 74.3, 56.7; MS (ESI) 297.1 (MNa^+ , 93); TLC R_f 0.303 (Et_2O /hexane, 1:4) [UV, KMnO_4].

Preparation of trans-1-(2-Methoxyphenyl)-2-phenylbut-3-en-1-ol (7k)—Following the general allylation procedure, **1k** (136 mg, 1.0 mmol), RuCl_3 (13.0 mg, 0.05 mmol, 0.05

equiv), (*E*)-**6** (252 μ L, 1.5 mmol, 1.5 equiv), H₂O (27 μ L, 1.5 mmol, 1.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and EtOH (2.5 mL) were combined under 40 psi of CO at 85 °C for 24 h. Workup and purification by silica gel column chromatography (70 g SiO₂, 3.5 $\times$ 20.5 cm column, Et₂O/hexane (1:9 (750 mL) $\rightarrow$ 1:4 (500 mL) $\rightarrow$ 1:3 (250 mL))) provided **7k** (235 mg, 92%) as a colorless oil. The spectroscopic data matched those from the literature.⁶⁶ Data for **7k**: ¹H NMR (500 MHz, CDCl₃) 7.25–7.10 (m, 8H, C(aryl)H), 6.85 (td, *J* = 7.5, 1.1 Hz, 1H, C(aryl')H), 6.78 (dt, *J* = 7.6, 1.1 Hz, 1H, C(aryl')H), 6.30 (ddd, *J* = 17.1, 10.3, 8.5 Hz, 1H, C(3)H), 5.20 (ddd, *J* = 10.3, 1.8, 0.8 Hz, 1H, C(4)H_{cis}), 5.14 (dd, *J* = 6.9, 5.8 Hz, 1H, C(1)H), 5.09 (ddd, *J* = 17.2, 1.8, 1.1 Hz, 1H, C(4)H_{trans}), 3.74 (s, 3H, C(5')H₃), 2.65 (d, *J* = 5.9 Hz, 1H, br OH); ¹³C{¹H} NMR (125 MHz, CDCl₃) 156.5, 141.8, 138.1, 130.3, 128.4, 128.2, 128.1, 126.4, 120.5, 117.7, 110.4, 74.0, 56.81, 55.3; MS (ESI) 277.1 (MNa⁺, 68), 237.0 (100); TLC *R*_f 0.242 (Et₂O/hexane, 1:4) [UV, KMnO₄].

Preparation of trans-1-(Furan-2-yl)-2-phenylbut-3-en-1-ol (7l)—Following the general allylation procedure, **1l** (83 μ L, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), (*E*)-**6** (252 μ L, 1.5 mmol, 1.5 equiv), H₂O (27 μ L, 1.5 mmol, 1.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and *t*-BuOH (2.5 mL) were combined under 40 psi of CO at 85 °C for 24 h. Workup and purification by silica gel column chromatography (70 g SiO₂, 3.5 $\times$ 20.5 cm column, Et₂O/hexane (1:20 (900 mL) $\rightarrow$ 1:13 (500 mL) $\rightarrow$ 1:9 (1000 mL) $\rightarrow$ 1:7 (500 mL))) provided **7l** (195 mg, 91%) as a colorless oil. The spectroscopic data matched those from the literature.⁶⁶ Data for **7l**: ¹H NMR (500 MHz, CDCl₃) 7.32 (dd, *J* = 1.9, 0.9 Hz, 1H, C(4')H), 7.27–7.21 (m, 2H, C(aryl)H), 7.21–7.12 (m, 3H, C(aryl)H), 6.28–6.17 (ddd, *J* = 8.5, 8.5, 1.8 Hz, 1H, C(3)H), 6.21 (dt, *J* = 3.2, 0.7 Hz, 1H, C(3')H), 6.06 (dt, *J* = 3.2, 0.7 Hz, 1H, C(2')H), 5.28 (ddd, *J* = 10.2, 1.6, 0.9 Hz, 1H, C(4)H_{cis}), 5.24 (d, *J* = 2.6 Hz, 1H, C(4)H_{trans}), 4.90 (dd, *J* = 7.9, 4.0 Hz, 1H, C(1)H), 3.84 (t, *J* = 8.3 Hz, 1H, C(2)H), 2.27 (d, *J* = 4.2 Hz, 1H, br OH); ¹³C{¹H} NMR (125 MHz, CDCl₃) 154.3, 141.9, 140.5, 137.7, 128.6, 128.2, 126.9, 118.6, 110.2, 110.1, 107.7, 71.1, 56.0; MS (ESI) 237.0 (MNa⁺, 68), 197.0 (100); TLC *R*_f 0.200 (Et₂O/hexane, 1:4) [UV, KMnO₄].

Preparation of trans-2-Phenyl-1-(1-tosyl-1H-pyrrol-2-yl)but-3-en-1-ol (7m)—

Following the general allylation procedure, **1m** (249 mg, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), (*E*)-**6** (252 μ L, 1.5 mmol, 1.5 equiv), H₂O (27 μ L, 1.5 mmol, 1.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and *t*-BuOH (2.5 mL) were combined under 40 psi of CO at 85 °C for 24 h. Workup and purification by silica gel column chromatography (90 g SiO₂, 4.5 $\times$ 13.5 cm column, Et₂O/hexane (1:10 w/1% Et₃N (200 mL to treat column) and then (1:10 (850 mL) $\rightarrow$ 1:4 (500 mL) $\rightarrow$ 1:3 (600 mL) $\rightarrow$ 1:1 (300 mL))) provided **7m** (250 mg, 68%) as a colorless glassy oil. [Note: Compound is unstable to SiO₂]. Data for **7m**: bp 125 °C (ABT, 10⁻⁵ mm Hg) ¹H NMR (500 MHz, CDCl₃) 7.62 (d, *J* = 8.4 Hz, 1H, C(6')H), 7.28 (d, *J* = 8.4, 2H, C(7')H), 7.22 (dd, *J* = 3.3, 1.7 Hz, 1H, C(4')H), 7.18–7.11 (m, 3H, C(aryl)H), 7.01 (dd, *J* = 7.7, 1.8 Hz, 2H, C(aryl)H), 6.25–6.16 (ddd, *J* = 8.5, 8.5, 1.7, 1H, C(3)), 6.20 (dd, *J* = 3.3, 1.8, 1H, C(2')H), 6.15 (t, *J* = 3.4 Hz, 1H, C(3')), 5.25 (dd, *J* = 7.8, 4.2 Hz, 1H, C(1)H), 5.16 (ddd, *J* = 10.2, 1.6, 0.8 Hz, 1H, C(4)H_{cis}), 5.04 (dt, *J* = 17.1, 1.4 Hz, 1H, C(4)H_{trans}), 3.86 (t, *J* = 8.1 Hz, 1H, C(2)H), 2.58 (d, *J* = 4.2 Hz, 1H, br OH), 2.42 (s, 3H, C(9')H₃); ¹³C{¹H} NMR (125 MHz, CDCl₃) 145.1 C(8'), 141.6 C(5), 138.2 C(3), 136.5 C(5'), 136.0 C(1'), 130.2 C(7'), 128.6 C(aryl), 128.1 C(aryl), 126.8 C(6'), 126.6 C(aryl), 123.5 C(4'), 117.7 C(4), 114.4 C(2'), 111.8 C(3'), 68.7 C(1), 55.0 C(2), 21.8 C(9'); IR (neat) 3554 (w), 3439 (w), 3149 (w), 3063 (w), 3029 (w), 2980 (w), 2923 (w), 1597 (w), 1494 (w), 1453 (w), 1403 (w), 1363 (w), 1307 (w), 1293 (w), 1190 (m), 1173 (s), 1152 (m), 1090 (m), 1058 (m), 1018 (w), 1000 (w), 920 (w), 813 (w), 781 (w), 756 (w), 723 (m), 701 (m), 674 (s), 590 (s), 544 (m); MS (ESI) 390.1 (MNa⁺, 6), 352.1 (13), 351.1 (40), 350.1 (100); TLC *R*_F 0.103 (Et₂O/hexane, 1:4) [UV, KMnO₄]. CHN Anal. Calcd for C₂₁H₂₁NO₃S (367.46): C, 68.64; H, 5.76; N, 3.81. Found: C, 68.99; H, 5.59; N, 3.68.

Preparation of trans-2,2-Dimethyl-4-phenylhex-5-en-3-ol (7h)—Following the general allylation procedure, **1n** (109 μL , 1.0 mmol), RuCl_3 (13.0 mg, 0.05 mmol, 0.05 equiv), (*E*)-**6** (252 μL , 1.5 mmol, 1.5 equiv), H_2O (27 μL , 1.5 mmol, 1.5 equiv), Et_3N (14 μL , 0.1 mmol, 0.1 equiv), and *t*-BuOH (1.25 mL) were combined under 40 psi of CO at 85 °C for 24 h. Workup and purification by silica gel column chromatography (70 g SiO_2 , 3.5 $\times$ 20.5 cm column, Et_2O /hexane (1:50 (800 mL) $\rightarrow$ 1:20 (500 mL) $\rightarrow$ 1:13 (500 mL) $\rightarrow$ 1:9 (500 mL))) provided **7h** (27 mg, 13%) as a colorless oil. The spectroscopic data matched those from the literature.⁶⁷ Data for **7h**: ^1H NMR (500 MHz, CDCl_3) 7.39–7.35 (m, 2H, C(aryl)H), 7.31 (t, J = 7.3 Hz, 2H, C(aryl)H), 7.24–7.19 (m, 1H, C(aryl)H), 6.50 (d, J = 15.9 Hz, 1H, C(4) H_{cis}), 6.28 (ddd, J = 15.8, 8.2, 6.3 Hz, 1H, C(4) H_{trans}), 3.35 (dd, J = 10.6, 2.3 Hz, 1H, C(H)1), 2.51 (ddt, J = 14.1, 6.0, 1.7 Hz, 1H, C(2)H), 2.17 (dddd, J = 14.3, 10.5, 8.3, 1.1 Hz, 1H, C(3)H), 1.70–1.62 (m, 1H, C(1)OH), 0.96 (d, J = 1.2 Hz, 9H, C(2') $\text{H}_3 \times 3$); ^{13}C {1H} NMR (125 MHz, CDCl_3) 137.4, 132.9, 128.7, 128.2, 127.3, 126.2, 78.8, 77.4, 66.0, 35.9, 34.9, 25.9, 25.9, 15.4; MS (ESI) 204.1 (MH^+ , 6), 118.1 (100); TLC R_f 0.358 (Et_2O /hexane, 1:4) [KMnO_4].

Preparation of trans-3-Phenylnon-1-en-4-ol (7o)—Following the general allylation procedure, **1o** (120 μL , 1.0 mmol), RuCl_3 (13.0 mg, 0.05 mmol, 0.05 equiv), (*E*)-**6** (252 μL , 1.5 mmol, 1.5 equiv), H_2O (27 μL , 1.5 mmol, 1.5 equiv), Et_3N (14 μL , 0.1 mmol, 0.1 equiv), and *t*-BuOH (2.5 mL) were combined under 40 psi of CO at 85 °C for 24 h. Workup and purification by silica gel column chromatography (80 g SiO_2 , 4.5 $\times$ 13.5 cm column, benzene/ CH_2Cl_2 (1:1, 1500 mL)) and then (24 g SiO_2 , 2.5 $\times$ 13.5 cm column, Et_2O /hexane (1:99 (500 mL) $\rightarrow$ 1:50 (500 mL) $\rightarrow$ 1:20 (200 mL)) provided **7o** (125 mg, 57%) as a colorless oil. The spectroscopic data matched those from the literature.⁶⁸ Data for **7o**: ^1H NMR (500 MHz, CDCl_3) 7.35–7.29 (m, 2H, C(aryl)H), 7.25–7.17 (m, 3H, C(aryl)H), 6.13 (ddd, J = 17.0, 10.3, 9.1 Hz, 1H, C(3)H), 5.26–5.17 (m, 2H, C(4) H_{cis} , C(4) H_{trans}), 3.79 (q, J = 4.0, 3.3 Hz, 1H, C(1)H), 3.25 (dd, J = 9.3, 7.0 Hz, 1H, C(2)H), 1.83–1.71 (m, 1H,

C(1)OH), 1.42–1.14 (m, 8H, C(4')CH₂, C(3')CH₂, C(2')CH₂, C(1')CH₂), 0.85 (t, J = 7.0 Hz, 3H, C(5')H₃); ¹³C{¹H} NMR (125 MHz, CDCl₃) 138.5, 128.8, 128.1, 126.8, 118.0, 77.4, 74.1, 57.6, 34.5, 31.9, 25.5, 22.7, 14.2; MS (ESI) 241.1 (MNa⁺, 100); TLC R_f 0.351 (Et₂O/hexane, 1:4) [KMnO₄].

Preparation of trans-1-Cyclohexyl-2-phenylbut-3-en-1-ol (7p)—Following the general allylation procedure, **1p** (112 mg, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), (*E*)-**6** (252 μ L, 1.5 mmol, 1.5 equiv), H₂O (27 μ L, 1.5 mmol, 1.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and *t*-BuOH (2.5 mL) were combined under 40 psi of CO at 85 °C for 24 h. Workup and purification by silica gel column chromatography (80 g SiO₂, 4.5 $\times$ 13.5 cm column, benzene/CH₂Cl₂ (1:1, 1500 mL)) and then (24 g SiO₂, 2.5 $\times$ 13.5 cm column, Et₂O/hexane (1:99 (500 mL) $\rightarrow$ 1:50 (500 mL) $\rightarrow$ 1:25 (200 mL)) provided **7p** (36 mg, 16%) as a colorless oil. The spectroscopic data matched those from the literature.⁶³ Data for **7p**: ¹H NMR (500 MHz, CDCl₃) 7.35–7.28 (m, 2H, C(aryl)H), 7.25–7.19 (m, 3H, C(aryl)H), 6.14 (ddd, J = 17.1, 10.2, 9.1 Hz, 1H, C(3)H), 5.26–5.14 (m, 2H, C(4)H_{cis}, C(4)H_{trans}), 3.57 (ddd, J = 7.1, 4.0, 2.7 Hz, 1H, C(1)H), 3.46–3.43 (m, 1H, C(2)H), 1.92–1.77 (m, 1H, C(1')H), 1.75–1.68 (m, 2H, C(cyclohex)H), 1.65 (d, J = 3.4 Hz, 1H, C(1)OH), 1.63–1.56 (m, 2H, C(cyclohex)H), 1.28–1.23 (m, 2H, C(cyclohex)H), 1.17–1.03 (m, 4H, C(cyclohex)H); ¹³C{¹H} NMR (125 MHz, CDCl₃) 142.2, 138.6, 128.9, 128.1, 126.7, 117.8, 78.2, 77.4, 53.8, 39.7, 30.4, 26.7, 26.6, 26.5, 26.1; MS (ESI) 253.1 (MNa⁺, 100); TLC R_f 0.352 (Et₂O/hexane, 1:4) [KMnO₄].

Preparation of Products Resulting from the Use of Vinyloxirane

Preparation of (*E*)-5-Phenylpent-2-ene-1,5-diol (10a)—Following the general allylation procedure, **1a** (102 μ L, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μ L, 2.5 mmol, 2.5 equiv), H₂O (45 μ L, 2.5 mmol, 2.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and dioxane (2.5 mL) were combined under 40 psi of CO at 75 °C for 24 h. Workup and purification by silica gel column chromatography (80 g SiO₂, 4.5 $\times$ 13.5 cm column, Et₂O/CH₂Cl₂ (1:1 (500 mL) $\rightarrow$ 4:1

(600 mL)) then Et₂O/MeOH (20:1, 400 mL) provided **10a** (150 mg, 88%) as a white solid as just the *E*-isomer. The spectroscopic data matched those from the literature.⁶⁹ Data for **10a**: ¹H NMR (500 MHz, CDCl₃) 7.31–7.26 (m, 3H, C(aryl')H), 7.24–7.14 (m, 2H, C(aryl')H), 5.78–5.48 (m, 2H, C(4)H, C(3)H), 4.64 (dd, *J* = 7.4, 5.5 Hz, 1H, C(1)H), 3.99 (d, *J* = 4.7 Hz, 1H, C(5)H), 2.61–2.48 (m, 1H, br C(1)OH), 2.48–2.37 (m, 1H, C(2)H), 2.14 (s, 1H, br C(5)OH); ¹³C{¹H} NMR (125 MHz, CDCl₃) 144.0, 132.8, 128.5, 128.5, 127.7, 125.9, 73.6, 63.4, 42.2; MS (ESI) 201.0 (MNa⁺, 100); TLC *R*_F 0.241 (Et₂O/CH₂Cl₂, 4:1) [UV, KMnO₄].

Preparation of (2E,6E)-7-Phenylhepta-2,6-diene-1,5-diol (10b)—Following the general allylation procedure, **1b** (126 μ L, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μ L, 2.5 mmol, 2.5 equiv), H₂O (45 μ L, 2.5 mmol, 2.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and dioxane (2.5 mL) were combined under 40 psi of CO at 75 °C for 24 h. Workup and purification by silica gel column chromatography (80 g SiO₂, 4.5 $\times$ 13.5 cm column, Et₂O/CH₂Cl₂ (1:1 (500 mL) $\rightarrow$ 4:1 (600 mL)) then Et₂O/MeOH (20:1, 400 mL) provided **10b** (175 mg, 87%) as a colorless oil with an *E/Z* ratio of 20:1. An analytically pure sample was prepared via distillation. Data for **10b**: bp 110 °C (ABT, 10⁻⁵ mm Hg); IR (neat) 3326 (m), 3082 (w), 3058 (w), 3026 (w), 2923 (w), 2867 (w), 1670 (w), 1578 (w), 1599 (w), 1494 (w), 1449 (w); MS (ESI) 227.1 (MNa⁺, 100); TLC *R*_F 0.228 (Et₂O/CH₂Cl₂, 4:1) [UV, KMnO₄]. CHN Anal. Calcd for C₁₃H₁₆O₂ (204.27): C, 76.44; H, 7.90. Found: C, 76.20; H, 7.81. A portion of the material was sacrificially purified to yield pure *E*-product and the spectra data is as follows: ¹H NMR (500 MHz, CDCl₃) 7.39–7.36 (m, 2H, C(aryl')H), 7.34–7.29 (m, 2H, C(aryl')H), 7.25–7.22 (m, 1H, C(aryl')H), 6.60 (dd, *J* = 15.7, 1.1 Hz, 1H, C(2')H), 6.24 (dd, *J* = 15.9, 6.4 Hz, 1H, C(1')H), 5.91–5.67 (m, 2H, C(4)H, C(3)H), 4.36 (d, *J* = 6.3 Hz, 1H, C(1)H), 4.19–4.10 (m, 2H, C(5)H₂), 2.53–2.25 (m, 2H, C(2)H₂), 2.03 (s, 1H, br C(1)OH), 1.68 (d, *J* = 7.2 Hz, 1H, C(5)OH); ¹³C{¹H} NMR (125 MHz, CDCl₃) 136.6 C(3'), 133.0 C(4), 131.6 C(1'), 130.6 C(2'), 128.7 C(aryl'), 128.0 C(3), 127.9 C(aryl'), 126.6 C(aryl'), 72.1 C(1), 63.6 C(5), 40.5 C(2).

Preparation of (E)-7-Phenylhept-2-ene-1,5-diol (10c)—Following the general allylation procedure, **1c** (132 μ L, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv),

TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μ L, 2.5 mmol, 2.5 equiv), H₂O (45 μ L, 2.5 mmol, 2.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and dioxane (2.5 mL) were combined under 40 psi of CO at 75 °C for 24 h. Workup and purification by silica gel column chromatography (80 g SiO₂, 4.5 $\times$ 13.5 cm column, Et₂O/CH₂Cl₂ (1:1 (500 mL) $\rightarrow$ 4:1 (600 mL)) then Et₂O/MeOH (20:1, 400 mL) provided **10c** (183 mg, 90%) as a colorless oil with an *E/Z* ratio of 6:1. The spectroscopic data matched those from the literature.⁷⁰ Data for **10c**: ¹H NMR (500 MHz, CDCl₃) 7.31–7.26 (m, 2H, C(aryl)H), 7.22–7.17 (m, 3H, C(aryl)H), 5.82–5.65 (m, 2H, C(3)H, C(4)H), 4.15–4.09 (m, 2H, C(5)H₂), 3.71–3.64 (m, 1H, C(1)H), 2.80 (dt, *J* = 13.6, 8.0 Hz, 1H, C(1')H_a), 2.68 (dt, *J* = 13.7, 8.1 Hz, 1H, C(1')H_b), 2.37–2.24 (m, 1H, C(2')H_a), 2.25–2.13 (m, 1H, C(2')H_b), 2.08–1.90 (m, 2H, br C(1)OH, br C(5)OH), 1.84–1.73 (m, 2H, C(2)H₂); ¹³C{¹H} NMR (125 MHz, CDCl₃) 142.1, 132.7, 128.6, 128.6, 128.5, 126.0, 70.4, 63.5, 40.5, 38.7, 32.1; MS (ESI) 229.0 (MNa⁺, 100); TLC *R*_f 0.253 (Et₂O/CH₂Cl₂, 4:1) [UV, KMnO₄].

Preparation of (E)-5-(4-Nitrophenyl)pent-2-ene-1,5-diol (10d)—Following the general allylation procedure, **1d** (151 mg, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μ L, 2.5 mmol, 2.5 equiv), H₂O (45 μ L, 2.5 mmol, 2.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and dioxane (2.5 mL) were combined under 40 psi of CO at 75 °C for 24 h. Workup and purification by silica gel column chromatography (80 g SiO₂, 4.5 $\times$ 13.5 cm column, Et₂O/CH₂Cl₂ (1:1 (500 mL) $\rightarrow$ 4:1 (600 mL)) then Et₂O/MeOH (20:1, 400 mL) provided **10d** (190 mg, 85%) as a yellow solid with an *E/Z* ratio of greater than 100:1. An analytically pure sample was prepared via recrystallization from hexanes. Data for **10d**: mp 100–102 °C; ¹H NMR (500 MHz, CDCl₃) 8.21 (dd, *J* = 8.6, 5.1 Hz, 2H, C(3')H), 7.53 (dd, *J* = 8.9, 0.7 Hz, 1H, C(2')H), 5.79 (dt, *J* = 15.4, 5.2, 1.1 Hz, 1H, C(4)H), 5.70 (dddt, *J* = 15.2, 7.6, 6.3, 1.3 Hz, 1H, C(3)H), 4.87 (dt, *J* = 7.9, 3.8 Hz, 1H, C(1)H), 4.14 (td, *J* = 5.2, 1.6 Hz, 2H, C(5)CH₂), 2.59–2.52 (m, 1H, C(2)H_a), 2.46 (dddd, *J* = 14.2, 8.4, 7.5, 0.9 Hz, 1H, C(2)H_b), 2.30 (d, *J* = 3.4 Hz, 1H, br C(1)OH), 1.46 (t, *J* = 5.5 Hz, 1H, br C(5)OH); ¹³C{¹H} NMR (125 MHz, CDCl₃) 151.2 C(4'), 147.5 C(1'), 134.1 C(4), 126.8 C(3), 126.7 C(3'), 123.8 C(2'), 72.6 C(1), 63.3 C(5), 42.5 C(2); IR (neat) 3331 (w), 2920 (w), 2854 (w), 1672 (w), 1599 (w), 1515 (s), 1428 (w); MS (ESI) 246.0; (MNa⁺, 100); TLC *R*_f 0.178 (Et₂O/CH₂Cl₂, 4:1) [UV, KMnO₄]. CHN Anal. Calcd for C₁₁H₁₃NO₄ (223.23): C, 59.19; H, 5.87; N, 6.27. Found: C, 58.96; H, 5.67; N, 6.21.

Preparation of (E)-5-(4-Methoxyphenyl)pent-2-ene-1,5-diol (10e)—Following the general allylation procedure, **1e** (122 μL , 1.0 mmol), RuCl_3 (13.0 mg, 0.05 mmol, 0.05 equiv), TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μL , 2.5 mmol, 2.5 equiv), H_2O (45 μL , 2.5 mmol, 2.5 equiv), Et_3N (14 μL , 0.1 mmol, 0.1 equiv), and dioxane (1.25 mL) were combined under 40 psi of CO at 75 $^\circ\text{C}$ for 24 h. Workup and purification by silica gel column chromatography (80 g SiO_2 , 4.5×13.5 cm column, $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (1:1 (500 mL) $\rightarrow$ 4:1 (600 mL)) then $\text{Et}_2\text{O}/\text{MeOH}$ (20:1, 400 mL) provided **10e** (110 mg, 53%) as a yellow oil with an *E/Z* ratio of 4:1. An analytically pure sample was prepared via distillation. Data for **10e**: bp 110 $^\circ\text{C}$ (ABT, 10^{-8} mm Hg); ^1H NMR (500 MHz, CDCl_3) 7.27 (d, $J = 8.4$ Hz, 2H, C(2')H), 6.88 (dd, $J = 8.1, 4.2$ Hz, 2H, C(3')H), 5.82–5.73 (m, 1H, C(4)H), 5.69 (dddt, $J = 15.4, 7.3, 6.6, 1.0$ Hz, 1H, C(3)H), 4.69 (dd, $J = 7.2, 6.2$ Hz, 1H, C(1)H), 4.10 (d, $J = 5.3$ Hz, 2H, C(5)H₂), 3.81 (s, 3H, C(5')H₃), 2.54–2.42 (m, 2H, C(2)H₂), 2.02 (s, 1H, C(1)OH), 1.47 (s, 1H, C(5)OH); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) 159.2 C(4'), 136.2 C(1'), 132.7 C(1), 128.6 C(3), 127.1 C(2'), 114.0 C(3'), 73.4 C(1), 63.6 C(5), 55.4 C(5'), 42.2 C(2); IR (neat): 3350 (w), 3003 (w), 2926 (w), 2838 (w), 1670 (w), 1612 (w), 1586 (w), 1512 (s), 1463.10 (w), 1442 (w), 1424 (w); MS (ESI) 231.0 (MNa^+ , 100); HRMS (ES⁺, TOF) calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3\text{Na}$ 231.0997, found 231.1003; TLC R_f 0.211 ($\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$, 4:1) [UV, KMnO_4].

Preparation of (E)-5-(4-(Trifluoromethyl)phenyl)pent-2-ene-1,5-diol (10f)—Following the general allylation procedure, **1f** (137 μL , 1.0 mmol), RuCl_3 (13.0 mg, 0.05 mmol, 0.05 equiv), TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μL , 2.5 mmol, 2.5 equiv), H_2O (45 μL , 2.5 mmol, 2.5 equiv), Et_3N (14 μL , 0.1 mmol, 0.1 equiv), and dioxane (2.5 mL) were combined under 40 psi of CO at 75 $^\circ\text{C}$ for 24 h. Workup and purification by silica gel column chromatography (80 g SiO_2 , 4.5×13.5 cm column, $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (1:1 (500 mL) $\rightarrow$ 4:1 (600 mL)) then $\text{Et}_2\text{O}/\text{MeOH}$ (20:1, 400 mL) and then subsequent recrystallization from hexanes provided **10f** (217 mg, 88%) as a white solid with an *E/Z* ratio of 6:1. Data for **10f**: mp 42–44 $^\circ\text{C}$; IR (neat) 3547 (w), 3368 (w), 2924 (w), 2868 (w), 1596 (w), 1477 (w), 1402 (w); MS (ESI) 26.91 (MNa^+ , 12), 229.0 (40), 211.1 (100); TLC R_f 0.258 ($\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$, 4:1) [UV, KMnO_4]. CHN Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{F}_3\text{O}_2$ (246.23): C, 58.54; H, 5.32. Found: C, 58.21; H, 5.13. A portion of the material was sacrificially purified to yield pure *E*-product and the spectra data is as follows: ^1H NMR (500 MHz, CDCl_3)

7.63–7.59 (m, 2H, C(3')H), 7.47 (dq, $J = 7.8, 0.9$ Hz, 2H, C(2')H), 5.79 (dt, $J = 15.4, 5.3, 1.1$ Hz, 1H, C(4)H), 5.69 (dddt, $J = 15.3, 7.8, 6.5, 1.3$ Hz, 1H, C(3)H), 4.81 (ddd, $J = 7.7, 4.7, 2.3$ Hz, 1H, C(1)H), 4.12 (dd, $J = 5.3, 2.5$ Hz, 2H, C(5)H₂), 2.57–2.49 (m, 1H, C(2)H_a), 2.49–2.43 (m, 1H, C(2)H_b), 2.28 (d, $J = 3.3$ Hz, 1H, br C(1)OH), 1.53 (s, 1H, br C(5)OH); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl₃) 147.9 C(1'), 133.6 C(4), 129.9 (q, $J = 32.3$ Hz, C(4')), 127.5 C(3), 126.2 C(2'), 125.5 (q, $J = 3.8$ Hz, C(3') $\times$ 2), 124.3 (q, $J = 272.3$ Hz, C(5')), 73.0 C(1), 63.4 C(5), 42.4 C(2); $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CDCl₃) δ –62.5.

Preparation of (E)-5-(4-chlorophenyl)pent-2-ene-1,5-diol (10g)—Following the general allylation procedure, **1g** (141 mg, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μL , 2.5 mmol, 2.5 equiv), H₂O (45 μL , 2.5 mmol, 2.5 equiv), Et₃N (14 μL , 0.1 mmol, 0.1 equiv), and dioxane (2.5 mL) were combined under 40 psi of CO at 75 °C for 24 h. Workup and purification by silica gel column chromatography (80 g SiO₂, 4.5 $\times$ 13.5 cm column, Et₂O/CH₂Cl₂ (1:1 (500 mL) $\rightarrow$ 4:1 (600 mL)) then Et₂O/MeOH (20:1, 400 mL) and then subsequent distillation provided **10g** (176 mg, 83%) as a colorless oil with an *E/Z* ratio of 14:1. Data for **10g**: bp 120 °C (ABT, 0.05 mmHg); ^1H NMR (500 MHz, CDCl₃) 7.31 (dd, $J = 6.5, 2.2$ Hz, 2H, C(3')H), 7.28 (dd, $J = 6.2, 2.2$ Hz, 2H, C(2')H), 5.80–5.71 (m, 1H, C(4)H), 5.71–5.59 (m, 1H, C(3)H), 4.70 (dd, $J = 7.7, 5.1$ Hz, 1H, C(1)H), 4.09 (dd, $J = 5.6, 1.3$ Hz, 2H, C(5)H₂), 2.55–2.31 (m, 2H, C(2)H₂), 1.99–1.66 (m, 2H, br C(1)OH, br C(5)OH); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl₃) 142.5 C(4'), 133.3 C(1'), 133.2 C(4), 128.7 C(3'), 127.9 C(3), 127.3 C(2'), 72.9 C(1), 63.4 C(5), 42.3 C(2); IR (neat) 3325 (m), 3029 (w), 2923 (w), 2868 (w), 1671 (w), 1597 (w), 1490 (m), 1408 (m); MS (ESI) 237.0 (MNa⁺ + 2, 25), 235.0 (MNa⁺, 65), 177.1 (100); TLC *R*_f 0.306 (Et₂O/CH₂Cl₂, 4:1) [UV, KMnO₄]. CHN Anal. Calcd for C₁₁H₁₃O₂Cl (212.67): C, 62.12; H, 6.16. Found: C, 61.91; H, 6.17.

Preparation of (E)-5-(4-bromophenyl)pent-2-ene-1,5-diol (10h)—Following the general allylation procedure, **1h** (185 mg, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μL , 2.5 mmol, 2.5 equiv), H₂O (45 μL , 2.5 mmol, 2.5 equiv), Et₃N (14 μL , 0.1 mmol, 0.1 equiv), and dioxane (2.5 mL) were combined under 40 psi of CO at 75 °C for 24 h. Workup and purification by silica gel

column chromatography (80 g SiO₂, 4.5 × 13.5 cm column, Et₂O/CH₂Cl₂ (1:1 (500 mL) → 4:1 (600 mL)) then Et₂O/MeOH (20:1, 400 mL) and then subsequent distillation provided **10h** (220 mg, 85%) as a colorless oil with an *E/Z* ratio of 18:1. Data for **10h**: bp 130 °C (ABT, 0.05 mmHg); IR (neat) 3340 (m), 2925 (w), 2869 (w), 1671 (w), 1592 (w), 1487 (m), 1404 (m); MS (ESI) 282.9 (MNa⁺ + 2, 41), 280.9 (MNa⁺, 41); TLC *R*_f 0.301 (Et₂O/CH₂Cl₂, 4:1) [UV, KMnO₄]. CHN Anal. Calcd for C₁₁H₁₃O₂Br (257.13): C, 51.38; H, 5.10. Found C, 51.07; H, 4.81. A portion of the material was sacrificially purified to yield pure *E*-product and the spectra data is as follows: ¹H NMR (500 MHz, CDCl₃) 7.46 (dd, *J* = 6.7, 1.8 Hz, 2H, C(3')H), 7.21 (dd, *J* = 6.7, 1.7 Hz, 2H, C(2')H), 5.79–5.71 (m, 1H, C(4)H), 5.66 (dddt, *J* = 15.3, 7.7, 6.6, 1.3 Hz, 1H, C(3)H), 4.69 (dd, *J* = 7.8, 5.1 Hz, 1H, C(1)H), 4.09 (dd, *J* = 5.7, 1.5 Hz, 2H, C(5)H₂), 2.51–2.34 (m, 2H, C(2)H₂), 1.95–1.79 (m, 1H, br C(1)OH), 1.80–1.75 (m, 1H, br C(5)OH). ¹³C{¹H} NMR (125 MHz, CDCl₃) 143.0 C(4'), 133.2 C(4), 131.6 C(3'), 127.9 C(3), 127.7 C(2'), 121.4 C(1'), 73.0 C(1), 63.4 C(5), 42.3 C(2).

Preparation of (E)-5-(Naphthalen-2-yl)pent-2-ene-1,5-diol (10i)—Following the general allylation procedure, **1i** (156 mg, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μL, 2.5 mmol, 2.5 equiv), H₂O (45 μL, 2.5 mmol, 2.5 equiv), Et₃N (14 μL, 0.1 mmol, 0.1 equiv), and dioxane (2.5 mL) were combined under 40 psi of CO at 75 °C for 24 h. Workup and purification by silica gel column chromatography (80 g SiO₂, 4.5 × 13.5 cm column, Et₂O/CH₂Cl₂ (1:1 (500 mL) → 4:1 (600 mL)) then Et₂O/MeOH (20:1, 400 mL) and then subsequent recrystallization from hexanes provided **10i** (220 mg, 95%) as a white solid with an *E/Z* ratio of greater than 100:1. Data for **10i**: mp 72–74 °C; ¹H NMR (500 MHz, CDCl₃) 7.86–7.80 (m, 3H, C(aryl')H), 7.79 (d, *J* = 1.5 Hz, 1H, C(2')H), 7.51–7.44 (m, 3H, C(aryl')H), 5.85–5.68 (m, 2H, C(4)H, C(3)H), 4.90 (td, *J* = 6.5, 5.6, 2.1 Hz, 1H, C(1)H), 4.10 (t, *J* = 4.5 Hz, 2H, C(5)H₂), 2.63–2.50 (m, 2H, C(2)H₂), 2.35–2.28 (m, 1H, br C(1)OH), 1.61 (d, *J* = 4.8 Hz, 1H, br C(5)OH); ¹³C{¹H} NMR (125 MHz, CDCl₃) 141.4 C(1'), 133.4 C(quat, aryl'), 133.1 C(quat, aryl'), 133.0 C(4), 128.4 C(aryl'), 128.3 C(3), 128.1 C(aryl'), 127.8 C(aryl'), 126.3 C(aryl'), 126.0 C(aryl'), 124.6 C(2'), 124.1 C(), 73.8 C(1), 63.5 C(5), 42.2 C(2); IR (neat) 3325 (m), 3054 (w), 2904 (w), 2867 (w), 1671 (w), 1634 (w), 1601 (w), 1508 (w), 1424 (w); MS (ESI) 251.1 (MNa⁺, 8), 193.1 (100); TLC *R*_f 0.283 (Et₂O/CH₂Cl₂, 4:1) [UV, KMnO₄]. CHN Anal. Calcd for C₁₅H₁₆O₂ (228.29): C, 78.92; H, 7.06. Found: C, 78.76; H, 7.05.

Preparation of (E)-5-(Naphthalen-1-yl)pent-2-ene-1,5-diol (10j)—Following the general allylation procedure, **1j** (136 μ L, 1.0 mmol), RuCl_3 (13.0 mg, 0.05 mmol, 0.05 equiv), TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μ L, 2.5 mmol, 2.5 equiv), H_2O (45 μ L, 2.5 mmol, 2.5 equiv), Et_3N (14 μ L, 0.1 mmol, 0.1 equiv), and dioxane (2.5 mL) were combined under 40 psi of CO at 75 $^\circ\text{C}$ for 24 h. Workup and purification by silica gel column chromatography (80 g SiO_2 , 4.5×13.5 cm column, $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (1:1 (500 mL) $\rightarrow$ 4:1 (600 mL)) then $\text{Et}_2\text{O}/\text{MeOH}$ (20:1, 400 mL) and then subsequent recrystallization from hexanes provided **10j** (210 mg, 92%) as a white solid with an *E/Z* ratio of greater than 100:1. Data for **10j**: mp 70–72 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) 8.06 (dd, $J = 7.4, 1.1$ Hz, 1H, C(10')H), 7.88 (dd, $J = 7.5, 2.1$ Hz, 1H, C(aryl')H), 7.78 (dt, $J = 8.2, 1.0$ Hz, 1H, C(aryl')H), 7.65 (dt, $J = 7.3, 0.9$ Hz, 1H, C(aryl')H), 7.56–7.44 (m, 3H, C(aryl')H), 5.84–5.80 (m, 2H, C(4)H, C(3)H), 5.53 (dt, $J = 7.8, 3.6$ Hz, 1H, C(1)H), 4.12 (t, $J = 4.7$ Hz, 2H, C(5) H_2), 2.81–2.68 (m, 1H, C(2) H_a), 2.65–2.56 (m, 1H, C(2) H_b), 2.33 (d, $J = 3.3$ Hz, 1H, br C(1)OH), 1.63 (d, $J = 5.8$ Hz, 1H, br C(5)OH); ^{13}C {1H} NMR (125 MHz, CDCl_3) 139.6 C(1'), 133.9 C(aryl'), 132.8 C(4), 130.4 C(aryl'), 129.1 C(aryl'), 128.8 C(3), 128.2 C(aryl'), 126.2 C(aryl'), 125.7 C(aryl'), 125.6 C(aryl'), 123.0 C(10'), 122.9 C(3), 70.4 C(1), 63.6 C(5), 41.3 C(2); IR (neat) 3341 (m), 3049 (w), 2915 (w), 2868 (w), 1670 (w), 1597 (w), 1511 (w), 1427 (w); MS (ESI) 251.1 (MNa^+ , 8), 194.1 (25), 193.1 (100); TLC R_f 0.305 ($\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$, 4:1) [UV, KMnO_4]. CHN Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$ (228.29): C, 78.92; H, 7.06. Found: C, 78.58; H, 7.05.

Preparation of (E)-5-(2-Methoxyphenyl)pent-2-ene-1,5-diol (10k)—Following the general allylation procedure, **1k** (136 mg, 1.0 mmol), RuCl_3 (13.0 mg, 0.05 mmol, 0.05 equiv), TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μ L, 2.5 mmol, 2.5 equiv), H_2O (45 μ L, 2.5 mmol, 2.5 equiv), Et_3N (14 μ L, 0.1 mmol, 0.1 equiv), and dioxane (2.5 mL) were combined under 40 psi of CO at 75 $^\circ\text{C}$ for 24 h. Workup and purification by silica gel column chromatography (80 g SiO_2 , 4.5×13.5 cm column, $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (1:1 (500 mL) $\rightarrow$ 4:1 (600 mL)) then $\text{Et}_2\text{O}/\text{MeOH}$ (20:1, 400 mL) provided **10k** (183 mg, 88%) as a slightly

yellow solid after a subsequent distillation with an *E/Z* ratio of 17:1. Data for **10k**: bp 125 °C (ABT, 0.05 mmHg); mp 70–72 °C; IR (neat) 3292 (m), 3200 (w), 2958 (w), 2928 (w), 2904 (w), 2837 (w), 1669 (w), 1600 (m), 1587 (w), 1488 (m), 1462 (m), 1438 (m), 1420 (m); MS (ESI) 231.1 (MNa⁺, 30), 173.1 (100); TLC *R_f* 0.301 (Et₂O/CH₂Cl₂, 4:1) [UV, KMnO₄]. CHN Anal. Calcd for C₁₂H₁₆O₃ (208.26): C, 69.21; H, 7.74. Found C, 68.85; H, 7.70. A portion of the material was sacrificially purified to yield pure *E*-product and the spectra data is as follows: ¹H NMR (500 MHz, CDCl₃) 7.32 (dd, *J* = 7.5, 1.7 Hz, 1H, C(aryl')H), 7.28–7.21 (m, 1H, C(aryl')H), 6.96 (td, *J* = 7.5, 1.1 Hz, 1H, C(aryl')H), 6.87 (dd, *J* = 8.2, 1.0 Hz, 1H, C(aryl')H), 5.74 (ddd, *J* = 4.7, 3.1, 1.8 Hz, 2H, C(4)H, C(3)H), 5.00–4.91 (m, 1H, C(1)H), 4.16–4.04 (m, 2H, C(5)H₂), 3.84 (s, 3H, C(7')), 2.76 (s, 1H, br C(1)OH), 2.67–2.42 (m, 2H, C(2)H₂), 1.92–1.80 (m, 1H, br C(5)OH); ¹³C{¹H} NMR (125 MHz, CDCl₃) 156.4 C(aryl'), 132.2 C(4), 131.9 C(1'), 129.4 C(3), 128.5 C(aryl'), 126.9 C(aryl'), 120.8 C(aryl'), 110.6 C(3'), 70.0 C(1), 63.7 C(5), 55.4 C(7'), 40.3 C(2).

Preparation of (E)-5-(Furan-2-yl)pent-2-ene-1,5-diol (10l)—Following the general allylation procedure, **1l** (83 μ L, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μ L, 2.5 mmol, 2.5 equiv), H₂O (45 μ L, 2.5 mmol, 2.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and dioxane (2.5 mL) were combined under 40 psi of CO at 75 °C for 24 h. Workup and purification by silica gel column chromatography (80 g SiO₂, 4.5 $\times$ 13.5 cm column, Et₂O/CH₂Cl₂ (1:1 (500 mL) $\rightarrow$ 4:1 (600 mL)) then Et₂O/MeOH (20:1, 400 mL) provided **10l** (150 mg, 89%) as a colorless oil with an *E/Z* ratio of 5.5:1. Data for **10l**: bp 100 °C (ABT, 0.05 mmHg); IR (neat): 3325 (m), 2913 (w), 2869 (w), 1672 (w), 1505 (w), 1424 (m); MS (ESI) 191.1 (MNa⁺, 60), 133.2 (100); HRMS (ES⁺, TOF) calcd for C₉H₁₂O₃Na 191.0684, found 191.0680; TLC *R_f* 0.301 (Et₂O/CH₂Cl₂, 4:1) [KMnO₄]. A portion of the material was sacrificially purified to yield pure *E*-product and the spectra data is as follows: ¹H NMR (500 MHz, CDCl₃) 7.38 (dd, *J* = 1.9, 0.8 Hz, 1H, C(4')H), 6.36–6.32 (m, 1H, C(3')H), 6.25 (tt, *J* = 3.3, 0.8 Hz, 1H, C(2')H), 5.80 (dt, *J* = 15.4, 5.4, 1.1 Hz, 1H, C(4)H), 5.70 (dt, *J* = 15.3, 7.0, 1.3 Hz, 1H, C(3)H), 4.75 (dd, *J* = 7.4, 5.7 Hz, 1H, C(1)H), 4.11 (dd, *J* = 5.6, 1.1 Hz, 2H, C(5)H₂), 2.63 (dddd, *J* = 7.2, 5.0, 3.0, 1.1 Hz, 2H, C(2)H₂), 2.15 (d, *J* = 17.0 Hz, 1H, br C(1)OH), 1.57 (s, 1H, br C(5)OH); ¹³C{¹H} NMR (125 MHz, CDCl₃) 156.1 C(1'), 142.2 C(4'), 133.1 C(4), 127.6 C(3), 110.3 C(3'), 106.3 C(2'), 67.3 C(1), 63.5 C(5), 38.6 C(2).

Preparation of (E)-5-(1-tosyl-1H-pyrrol-2-yl)pent-2-ene-1,5-diol (10m)—

Following the general allylation procedure, **1m** (250 mg, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μ L, 2.5 mmol, 2.5 equiv), H₂O (45 μ L, 2.5 mmol, 2.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and dioxane (2.5 mL) were combined under 40 psi of CO at 75 °C for 24 h. Workup and purification by silica gel column chromatography (80 g SiO₂, 4.5 $\times$ 13.5 cm column, Et₂O/CH₂Cl₂ (1:1 (500 mL) $\rightarrow$ 4:1 (600 mL)) then Et₂O/MeOH (20:1, 400 mL) provided **10m** (290 mg, 90%) as a white solid after recrystallization from hexanes with an *E/Z* ratio of 16:1. Data for **10m**: mp 80–82 °C; ¹H NMR (500 MHz, CDCl₃) 7.72–7.62 (m, 2H, C(6')H), 7.30–7.27 (m, 2H, C(7')H), 7.27 (d, *J* = 0.9 Hz, 1H, C(4')H), 6.29 (ddd, *J* = 3.5, 1.7, 0.7 Hz, 1H, C(3')H), 6.25 (t, *J* = 3.4 Hz, 1H, C(2')H), 5.73–5.62 (m, 2H, C(4)H, C(3)H), 4.93 (td, *J* = 6.7, 4.1 Hz, 1H, C(1)H), 4.05 (t, *J* = 4.7 Hz, 2H, C(5)H₂), 2.82 (d, *J* = 4.2 Hz, 1H, br C(1)OH), 2.57 (ddd, *J* = 6.6, 4.1, 1.2 Hz, 2H, C(2)H₂), 2.40 (s, 3H, C(9')H₃), 1.52–1.45 (m, 1H, br C(5)OH); ¹³C{¹H} NMR (125 MHz, CDCl₃) 145.3 C(8'), 137.5 C(1'), 136.4 C(5'), 132.3 C(4), 130.2 C(6'), 128.4 C(3), 126.8 C(7'), 123.7 C(4'), 112.8 C(3'), 111.8 C(2'), 65.3 C(1), 63.6 C(5), 38.4 C(2), 21.7 C(9'); IR (neat) 3547 (w), 3368 (w), 2924 (w), 2868 (w), 1596 (w), 1477 (w), 1402 (w); MS (EI) 344.1 (MNa⁺, 13), 304.1 (100); TLC *R*_f 0.269 (Et₂O/CH₂Cl₂, 4:1) [UV, KMnO₄]. CHN Anal. Calcd for C₁₆H₁₉NO₄S (321.39): C, 59.80; H, 5.96; N, 4.36. Found: C, 60.06; H, 5.93; N, 4.39.

Preparation of (E)-6,6-Dimethylhept-2-ene-1,5-diol and (Z)-6,6-Dimethylhept-2-ene-1,5-diol (10n)—

Following the general allylation procedure, **1n** (109 μ L, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μ L, 2.5 mmol, 2.5 equiv), H₂O (45 μ L, 2.5 mmol, 2.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and dioxane (1.25 mL) were combined under 40 psi of CO at 75 °C for 24 h. Workup and purification by silica gel column chromatography (80 g SiO₂, 4.5 $\times$ 13.5 cm column, Et₂O/CH₂Cl₂ (1:1 (500 mL) $\rightarrow$ 4:1 (600 mL)) then Et₂O/MeOH (20:1, 400 mL) provided

(*E*)-**10n** (19 mg, 22%) as a colorless oil and (*Z*)-**10n** (58 mg, 37%) as a colorless oil. The spectroscopic data for (*Z*)-**10n** matched those from the literature.⁷¹ Data for (*E*)-**10n**: ¹H NMR (500 MHz, CDCl₃) 5.75 (ddd, *J* = 4.3, 2.8, 1.1 Hz, 2H, C(3)H, C(4)H), 4.18–4.03 (m, 2H, C(5)H₂), 3.25 (dd, *J* = 10.6, 2.2 Hz, 1H, C(1)OH), 2.36–2.30 (m, 1H, C(2)H_a), 1.99 (dddd, *J* = 14.1, 10.7, 4.7, 2.4 Hz, 1H, C(2)H_b), 1.93–1.79 (m, 2H, br C(1)OH, br C(5)OH), 0.91 (s, 9H, C(2')H₃ × 3); ¹³C{¹H} NMR (125 MHz, CDCl₃) 132.1 C(4), 130.7 C(3), 78.8 C(1), 63.6 C(5), 34.9 C(2), 34.9 C(1'), 25.9 C(2') IR (neat): 3342 (s), 2955 (s), 2916 (m), 2870 (m), 1671 (w), 1479 (w), 1467 (m), 1430 (m); MS (ESI) 181.1 (MNa⁺, 100); HRMS (ES⁺, TOF) calcd for C₉H₁₈O₂Na, 181.1204, found 181.1198; TLC *R*_f 0.309 (Et₂O/CH₂Cl₂, 4:1) [KMnO₄]. Data for (*Z*)-**10n**: ¹H NMR (500 MHz, CDCl₃) 5.98–5.83 (m, 1H, C(4)H), 5.75–5.63 (m, 1H, C(5)H), 4.25 (dddd, *J* = 12.4, 7.5, 1.5, 0.7 Hz, 1H, C(5)H_a), 4.05 (dd, *J* = 12.3, 6.7 Hz, 1H, C(5)H_b), 3.23 (dd, *J* = 10.2, 2.5 Hz, 1H, C(1)H), 2.32–2.16 (m, 2H, C(2)H₂), 2.09 (s, 2H, br C(1)OH, br C(5)OH), 0.94 (s, 9H, C(2')H₃ × 3); ¹³C{¹H} NMR (125 MHz, CDCl₃) 131.6, 131.2, 78.5, 77.4, 66.0, 57.8, 35.1, 29.8, 25.8, 15.4; MS (ESI) 181.1 (MNa⁺, 100), 123.2 (6); TLC *R*_f 0.429 (EtOAc/hexane, 1:4) [KMnO₄].

Preparation of (E)-Dec-2-ene-1,5-diol (10o)—Following the general allylation procedure, **1o** (120 μ L, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μ L, 2.5 mmol, 2.5 equiv), H₂O (45 μ L, 2.5 mmol, 2.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and dioxane (2.5 mL) were combined under 40 psi of CO at 75 °C for 24 h. Workup and purification by silica gel column chromatography (80 g SiO₂, 4.5 × 13.5 cm column, Et₂O/CH₂Cl₂ (1:1 (500 mL) → 4:1 (600 mL)) then Et₂O/MeOH (20:1, 400 mL) provided **10o** (119 mg, 70%) as a colorless oil with an *E/Z* ratio of 4:1. The spectroscopic data matched those from the literature.⁷² Data for **10o**: ¹H NMR (500 MHz, CDCl₃) 5.80–5.66 (m, 2H, C(3)H, C(4)H), 4.12 (d, *J* = 4.0 Hz, 2H, C(5)H₂), 3.78–3.56 (m, 1H, C(1)H), 2.36–2.22 (m, 1H, C(2)H_a), 2.20–2.06 (m, 1H, C(2)H_b), 1.79–1.68 (m, 2H, br C(1)OH, C(5)OH), 1.52–1.37 (m, 4H, C(2')CH₂, C(1')CH₂), 1.38–1.19 (m, 4H, C(4')H₂, C(3')H₂), 0.99–0.81 (m, 3H, C(5')H₃); ¹³C{¹H} NMR (125 MHz, CDCl₃) 132.5, 128.9, 71.2, 63.6, 40.4, 37.0, 32.0, 25.5, 22.8, 14.2; MS (ESI) 170.6 (MH⁺, 4); TLC *R*_f 0.299 (Et₂O/CH₂Cl₂, 4:1) [KMnO₄].

Preparation of (E)-5-Cyclohexylpent-2-ene-1,5-diol (10p)—Following the general allylation procedure, **1p** (112 mg, 1.0 mmol), RuCl₃ (13.0 mg, 0.05 mmol, 0.05 equiv), TBACl (13.9 mg, 0.05 mmol, 0.05 equiv), **9** (201 μ L, 2.5 mmol, 2.5 equiv), H₂O (45 μ L, 2.5 mmol, 2.5 equiv), Et₃N (14 μ L, 0.1 mmol, 0.1 equiv), and dioxane (1.25 mL) were combined under 40 psi of CO at 75 °C for 24 h. Workup and purification by silica gel column chromatography (80 g SiO₂, 4.5 $\times$ 13.5 cm column, Et₂O/CH₂Cl₂ (1:1 (500 mL) $\rightarrow$ 4:1 (600 mL)) then Et₂O/MeOH (20:1, 400 mL) provided **10p** (45 mg, 24%) as a colorless oil. The spectroscopic data matched those from the literature.⁷³ Data for **10p**: ¹H NMR (500 MHz, CDCl₃) 5.79–5.70 (m, 2H, C(4)H, C(3)H), 4.16–4.10 (m, 2H, C(5)H₂), 3.42–3.37 (m, 1H, C(1)H), 2.34–2.29 (m, 1H, C(1)OH), 2.17–2.11 (m, 1H, C(cyclohexyl)H), 1.87–1.82 (m, 1H, C(cyclohexyl)H), 1.79–1.74 (m, 2H, C(2)H₂), 1.70–1.64 (m, 2H, C(cyclohexyl)H), 1.53 (s, 1H, br OH), 1.45–1.40 (m, 1H, C(cyclohexyl)H), 1.39–1.32 (m, 1H, C(cyclohexyl)H), 1.29–0.97 (m, 5H, C(cyclohexyl)H); ¹³C{¹H} NMR (125 MHz, CDCl₃) 132.3, 129.6, 75.4, 63.4, 43.4, 37.2, 29.2, 28.4, 26.7, 26.4, 26.3; MS (ESI) 207.1 (MNa⁺, 100); TLC *R*_f 0.280 (Et₂O/CH₂Cl₂, 4:1) [KMnO₄].

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
Reaction conversion over time.

Figure 2.
Catalytic nucleophilic allylation of aldehydes.

Figure 3.
Extension to 2-substituted allylic acetates.

Scheme 1.

Scheme 2.

Scheme 3.

Scheme 4.

Scheme 5.

Scheme 6.

Scheme 7.

Scheme 8.

Scheme 9.

Scheme 10.

Scheme 11.

Scheme 12.

Scheme 13.

Scheme 14.

Chart 1.
Chiral Ruthenium Bisoxazoline Complexes and Ligands

Table 1

Initial Survey of Solvents

entry	solvent	3a yield ^a (%)
1	cyclohexane	8
2	toluene	10
3	dioxane	21
4	THF	22
5	acetonitrile	12
6	DMSO	31

^aDetermined by ^1H NMR analysis using hexamethylbenzene as the internal standard.

Table 2

Effects of Water and Oxygen

entry	CO (psi)	O ₂ (psi)	H ₂ O (equiv)	1a recovery ^d (%)	2 recovery ^d (%)	3a yield ^d (%)
1	140	0	0.0	83	78	17
2	140	0	0.3	66	71	32
3	140	0	1.5	62	64	37
4	120	0	0.3	75	79	23
5 ^b	120	20	0.3	43	44	54
6 ^b	120	20	0.6	33	6	49

^aDetermined by ¹H NMR analysis using hexamethylbenzene as the internal standard.^bIn these reactions, propene was also observed.

Table 3Effects of Et₃N Stoichiometry

entry	Et ₃ N (mol %)	2 recovery ^a (%)	3a yield ^a (%)
1	0	110	0
2	10	64	42
3	50	66	43
4	100	67	44
5	150	67	44

^aDetermined by ¹H NMR analysis using hexamethylbenzene as the internal standard.

Table 4

Dual Effects of Water and Et₃N

entry	CO (psi)	O ₂ (psi)	H ₂ O (equiv)	2 recovery ^a (%)	3a yield ^a (%)
1	120	20	0.6	44	70
2	120	20	1.5	24	79
3	120	20	3.0	30	75
4	140	0	1.5	0	95
5 ^b	140	0	15.0	0	53

^a Determined by ¹H NMR analysis using hexamethylbenzene as the internal standard.^b A significant amount of propene was observed in this reaction.

Table 5Survey of Amine Loadings with RuCl₃

entry	Et ₃ N (mol %)	1a recovery ^a (%)	3a yield ^a (%)
1	0	94	0
2	1.0	91	<1
3	2.0	92	<1
4	2.5	93	2
5	3.0	97	3
6	3.5	98	2
7	4.0	18	85
8	4.5	6	94
9	5.0	5	79
10	10	1	80
11	20	1	79

^aDetermined by GC analysis using biphenyl as the internal standard.

Table 6Effect of Et₃N Stoichiometry, Ruthenium Catalyst, and Soluble Halide

entry	Ru catalyst	Et ₃ N (mol %)	additive (mol %)	3a yield ^a (%)	
1	RuCl ₃ ·xH ₂ O	0		0	
2	RuCl ₃ ·xH ₂ O	10		95	
3	allylRu(CO) ₃ Br	0		12	
4	allylRu(CO) ₃ Br	10		93	
5	allylRu(CO) ₃ OAc	0		43	
6	allylRu(CO) ₃ OAc	10		70	
7 ^b	allylRu(CO) ₃ OAc	0		44	
8 ^b	allylRu(CO) ₃ OAc	0	TBACl (3)	81	
9 ^b	allylRu(CO) ₃ OAc	10	TBACl (3)	82	
10 ^b	Ru ₃ (CO) ₁₂	10		15	
11 ^b	Ru ₃ (CO) ₁₂	10	TBACl (3)	78	
12 ^b	Ru ₃ (CO) ₁₂	0	TBACl (10)	80	
13 ^b	Ru ₃ (CO) ₁₂	0	TBACl (20)	75	
14 ^b	Ru ₃ (CO) ₁₂	0	TBACl (50)	65	
15 ^b	Ru ₃ (CO) ₁₂	0	TBAOAc (10)	49	
16 ^b	Ru ₃ (CO) ₁₂	0	TBAI (10)	68	
17 ^b	Ru ₃ (CO) ₁₂	0	LiCl (3)	43	
18 ^b	Ru ₃ (CO) ₁₂	0	LiOAc (3)	28	

^aDetermined by ¹H NMR analysis using hexamethylbenzene as the internal standard.^bThese reactions were performed under 30 psi of CO.

Table 7

Effect of Catalyst Loading on Product Conversion

entry	RuCl ₃ ·xH ₂ O (mol %)	2 recovery ^a (%)	3a yield ^a (%)
1	1	26	78
2	2	0	95
3	3	0	>99

^aDetermined by ¹H NMR analysis using hexamethylbenzene as the internal standard.

Table 8

Effect of CO Pressure on Product Conversion

entry	CO (psi)	2 recovery ^a (%)	3a yield ^a (%)
1	15	56	48
2	30	0	95
3	60	3	95
4	90	0	>99
5	120	0	98
6	200	0	95

^aDetermined by ¹H NMR analysis using hexamethylbenzene as the internal standard.

Table 9

Effect of Reaction Temperature on Product Conversion

entry	temp (°C)	time (h)	2 recovery ^a (%)	3a yield ^a (%)
1	40	18	95	10
2	40	24	90	20
3	50	18	89	13
4	50	24	77	26
5	60	18	83	25
6	60	24	64	43
7	70	18	56	48

^aDetermined by ¹H NMR analysis using hexamethylbenzene as the internal standard.

Table 10

Comparison of Leaving Groups on the Allyl Component

entry	X	3a yield ^a (%)
1	OAc	80
2	OBz	95
3	OC(O)OAllyl	98
4	Cl	78
5	Br	1
6	OH	7

^aDetermined by ¹H NMR analysis using hexamethylbenzene as the internal standard.

Table 11

Survey of Reaction Solvents

entry	solvent	2 recovery ^a (%)	3a yield ^a (%)
1	AllylOAc	N/A	91
2	EtOAc	18	94
3	acetone	25	68
4	cyclohexanone	0	90
5	THF	0	>99
6	DMF	44	49
7	DMSO	39	53
8 ^b	MeOH	50	10
9 ^b	EtOH	7	50
10	<i>i</i> -PrOH	5	100

^aDetermined by ^1H NMR analysis using as the internal standard.

^bSignificant amounts of acetal formation were observed (74% w/MeOH; 28% w/EtOH).

Table 12

Effect of Solvent and Ruthenium Catalyst on Conversion

entry	Ru catalyst ^a	solvent	1a recovery ^b (%)
1	RuCl ₃ ·xH ₂ O	dioxane	49
2	Ru ₃ (CO) ₁₂ /TBACl	dioxane	76
3	Ru(bpy)(CO) ₂ Cl ₂	dioxane	73
4	RuCl ₃ ·xH ₂ O	EtOH	28
5	Ru ₃ (CO) ₁₂ /TBACl	EtOH	23
6	Ru(bpy)(CO) ₂ Cl ₂	EtOH	22
7	[RuCl ₂ (<i>p</i> -cymene)] ₂	EtOH	12

^aWhen used, an equimolar amount of TBACl was added to Ru.^bDetermined by GC analysis using biphenyl as the internal standard.

Table 13

Effect of Double-Bond Geometry on Diastereomer Formation

entry	acetate	1a recovery ^a (%)	<i>anti</i> -7a yield ^a (%)	<i>syn</i> -7a yield ^a (%)	8a yield ^a (%)
1	(<i>E</i>)-6	3	73	3	8
2	(<i>Z</i>)-6	6	70	5	8

^a Determined by ¹H NMR analysis using hexamethylbenzene as the internal standard.

Table 14

Aldehyde Scope for (*E*)-Cinnamyl Acetate^{a-c}

$ \begin{array}{c} \text{R} \\ \parallel \\ \text{C} \\ \backslash \\ \text{H} \\ \text{1a} \end{array} + \begin{array}{c} \text{Ph} \\ \backslash \\ \text{CH=CH} \\ \backslash \\ \text{OAc} \\ \text{(E)-6} \\ \text{(1.5 equiv)} \end{array} \xrightarrow[\text{Et}_3\text{N (0.1 equiv)}]{\text{RuCl}_3 \cdot x\text{H}_2\text{O (3 mol \% Ru)}} \begin{array}{c} \text{OH} \\ \\ \text{R} \\ \\ \text{CH=CH} \\ \\ \text{Ph} \\ \text{7} \end{array} $ Reagents: CO (40 psi) , $\text{H}_2\text{O (1.5 equiv)}$, solvent (0.4 M) , 85°C, 24 h			
 7a: A 85% (>20:1)	 7b: A 85% (>20:1)	 7c: B 78% (>20:1)	 7d: A 73% (>20:1)
 7e: A 66% (>20:1)	 7f: A 78% (>20:1)	 7g: A 90% (>20:1)	 7h: A 90% (>20:1)
 7i: A 82% (>20:1)	 7j: A 81% (>20:1)	 7k: A 92% (>20:1)	 7l: B 91% (>20:1)
 7m: B 68% (>20:1)	 7n: C 13% (>20:1)	 7o: B 57% (>20:1)	 7p: B 16% (>20:1)

^aReaction conditions: (A) EtOH, 0.4 M; (B) *t*-BuOH, 0.4 M; (C) *t*-BuOH, 0.8 M.^bYield of isolated, purified products.^cValue in parentheses is the *anti/syn* ratio.

Table 15

Effect of Ruthenium Catalyst and TBACl Loading on Conversion

entry	Ru catalyst	TBACl (mol %)	1a recovery (%) ^a	10a yield (%) ^a	11a yield (%) ^a
1	Ru ₃ (CO) ₁₂	3	7	92	0
2	[RuCl ₂ (<i>p</i> -cymene)] ₂	0	15	62	19
3	[RuCl ₂ (<i>p</i> -cymene)] ₂	3	8	90	0
4 ^b	RuCl ₃ ·xH ₂ O	0	39	49	12
5	RuCl ₃ ·xH ₂ O	3	5	91	0

^aDetermined by ¹H NMR analysis using hexamethylbenzene as the internal standard.^bOnly 1.2 equiv of **9** was employed in this reaction.

Table 17

Aldehyde Scope for Vinyl Oxirane^{a-c} ^aReaction conditions: (A) 0.4 M; (B) 0.8 M.^bYield of isolated, purified products.^cValue in parentheses is the *E/Z* ratio.^d*E* and *Z* isomers were fully separable.

Table 19

Use of Ethyl (*E*)-4-Acetoxybut-2-enoate as Allyl Pro-nucleophile

entry	solvent	temp (°C)	time (h)	15a yield ^a (%)	anti/syn	16a yield ^a (%)
1	dioxane	75	20	0		47
2	dioxane	60	20	0		23
3	dioxane	60	40	0		40
4	EtOH	75	20	40	1:14	26
5	EtOH	60	20	25	1:13	19
6	EtOH	60	40	54	1:8	27

^aDetermined by ¹H NMR analysis using hexamethylbenzene as the internal standard.

Table 20

Survey of Chiral Ruthenium Complexes

The reaction scheme shows the asymmetric hydrogenation of benzaldehyde (**1a**) with allyl acetate (**2**) to form 1-allyl-1-phenylethanol (**3a**). The reaction conditions are: Ru Cat (6 mol % Ru), CO (40 psi), Et₃N (0.1 equiv), H₂O (1.5 equiv), dioxane (0.4 M), 75 °C, 20 h. Below the reaction scheme, the structures of three chiral ruthenium catalysts are shown: **Cat 1** (a binaphtholate-based complex with two tert-butyl groups), **Cat 2** (a binaphtholate-based complex with two isopropyl groups), and **Cat 3** (a ferrocenyl complex with a chiral ferrocenyl ligand and a PF₆⁻ counterion).

entry	Ru catalyst	1a yield ^a (%)	er ^b
1	Cat 1	38	49:51
2	Cat 2	98	49:51
3	Cat 3	75	49:51

^aDetermined by GC analysis using biphenyl as the internal standard.

^bDetermined by CSP-phase HPLC.

Table 21

Bidentate Oxazoline Ru-Complex Survey

entry	Ru catalyst	3a yield ^a (%)	er ^b
1	Cat 4	58	51:49
2	Cat 5a	90	60:40
3	Cat 6	46	51:49
4	Cat 7	94	51:49

^aDetermined by GC analysis using biphenyl as the internal standard.

^bDetermined by CSP-phase HPLC.

Table 22

Effect of Free Ligand Loading on Enantioenrichment and Yield of 3a

entry	L1 (mol %)	3a yield ^a (%)	er ^b
1	6	59	70:30
2	30	40	75:25

^aDetermined by GC analysis using biphenyl as the internal standard.^bDetermined by CSP-phase HPLC.

Table 23

Complexed Bisoxazoline Ligand Survey

entry	Ru catalyst	L1	3a yield (%) ^a	er ^b
1	Cat 5b	–	93	68:32
2		L1a	69	75:25
3	Cat 5c	–	60	55:45
4		L1b	5	58:42
5	Cat 5d	–	28	57:43
6		L1b	31	60:40
7	Cat 5e	–	32	51:49
8		L1a	1	NA
9	Cat 5f	–	61	35:65
10		L1c	54	48:52
11	Cat 5g	–	24	51:49
12		L1d	45	54:46
13	Cat 5h	–	53	52:48
14		L1e	18	54:46
15	Cat 5i	–	56	49:51
16		L1f	1	NA
17	Cat 5j	–	89	68:32
18		L1g	85	71:29
19	Cat 5k	–	73	36:64
20		L1h	64	31:69
21	Cat 5l	–	85	61:39
22		L1i	22	78:22
23	Cat 5m	–	72	44:56

^aDetermined by GC analysis using biphenyl as the internal standard.^bDetermined by CSP-phase HPLC.

Table 24Effect of Et₃N Loading on Enantioselectivity

entry	Et ₃ N (mol %)	3a yield ^a (%)	er ^b
1	0	3	51:49
2	5	95	57:43
3	10	79	64:36
4	20	88	65:36
5	40	80	64:36

^aDetermined by GC analysis using biphenyl as the internal standard..^bDetermined by CSP-phase HPLC.

Table 25

CO Solubility in Dioxane at 1 atm

temp (K)	solubility (10^{-4} mol·L ⁻¹ ·psi ⁻¹)
290.1	3.79
296.4	3.93
306.7	4.07
315.8	4.21