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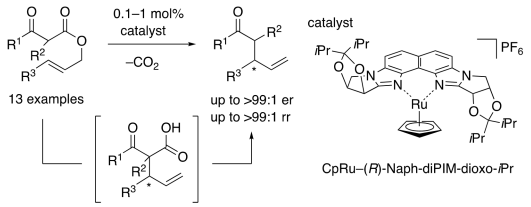

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CpRu^{II}-Chiral Bisamidine Complex Catalyzed Asymmetric Carroll-type Decarboxylative Allylation of β-Keto Allyl Esters

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ABSTRACT

Carroll-rearrangement-type intramolecular decarboxylative allylation of β-keto allyl esters with a cationic CpRu complex bearing a chiral bisamidine-type bidentate ligand is reported. The catalytic system allows the efficient transformation of the mono substituted, 3-arylallyl esters of β-keto acids to the corresponding γ,δ-enones. Notably, the catalytic turnover is more than an order higher than that of the previously reported examples. The developed reaction system displays improved regioselectivity and enantioselectivity and a broad substrate scope. Mechanistic studies using NMR experiments, substrate-structure/reactivity relationship studies, and cross-over experiment reveal a possible reaction pathway involving the enolate of the β-keto acid.

1. Introduction

Catalytic allylation of nucleophiles (NuH) with electrophilic allyl donors originated from Tsuji's seminal report, and expansions to the asymmetric variants were reported first by Trost [1]. Due to their utility in providing chiral olefinic motifs, these types of reactions have been widely employed and are called Tsuji–Trost reactions (T–T reactions). The asymmetric T–T reaction is a fundamental synthetic method, building on which, several related studies have been reported until now [2]. Originally, allyl halides or allyl esters were employed as the allyl donors in reaction with anion equivalents generated from NuH and a base (BM) and proceeded with the stoichiometric generation of the corresponding metal salt (MX) as the waste. Recently, a new trend has emerged with a shift from the desalt-type reactions to dehydrative ones, wherein an allylic alcohol and NuH are reacted in the absence of stoichiometric activation agents [3]. Our pioneering contribution in this area involved the establishment of asymmetric dehydrative allylations of protic nucleophiles under cationic CpRu complex catalysis in the presence of a catalytic amount of Brønsted acids [4]. Similar to our report, various related metal-catalyzed reactions employing Pd, Rh, Ir, Au, and Hg-based catalysts have also been investigated [5–9]. Direct dehydrogenative allylation using simple alkenes by the oxidative allylic C-H substitution has also been under development [10,11]. An alternative method for such substitution-type reactions involves intramolecular rearrangement through bond cleavage and formation, as shown in Figure 1, and furnishes the desired C-allylated product. In this reaction, an allylic β-keto ester reacts with the catalyst to generate the carboxylate anion and π-allyl species upon the oxidative addition. The resulting carboxylate transforms into a carbanion and attacks the π-allyl ligand. Decarboxylation occurs in due course, and the γ,δ-enone is obtained. This reaction is formally similar to the Carroll rearrangement, and its mechanism is similar to that of the T–T reaction [12]. Since decarboxylation is the driving force for the transformation, the substrate scope of this approach is limited in comparison to T–T reactions. However, this approach has several merits, such as the possibility to generate unstable carbanion equivalents of simple ketones with low acidities under mild conditions, and the regioselective α/α' allylation of the generated unsymmetrical ketones at the carbon previously bearing the carboxylate moiety. On the basis of these advantages, various Pd catalyzed transformations have been developed [13]. As shown in Figure 1a, symmetrical allylic moieties have been utilized for the construction of chiral centers at the β-position of the ketone. In other cases, the unsubstituted allyl group was introduced at the α-position of α-substituted β-keto esters with stereochemical control at the α-carbon (Fig. 1b). While significant progress has been achieved in this area, in the early stage, there were no reports on the use of mono substituted allyl esters of the kind shown in Figure 1c, since nucleophiles tend to attack the less substituted carbon of the π-allyl species in Pd-catalyzed allylation. This limitation has been overcome with the reports by Lacour using ruthenium catalysis [14] and by You using iridium catalysis [15] which delivered the products with high branch (**B**)/linear (**L**) ratios. However, there is still room for improvement of the catalyst loading (2–4 mol%) and enantioselectivity (up to 98:2) of this transformation. Further, reported examples where high **B**/**L** ratios were achieved are limited. In this paper, we present a novel high-performance

catalytic method for decarboxylative intramolecular allylation of β-keto allyl esters by employing our original CpRu–chiral bisamidine catalytic system, which was developed for dehydrative allylation. We also carried out experiments to gain insight into the mechanism of the developed transformation.

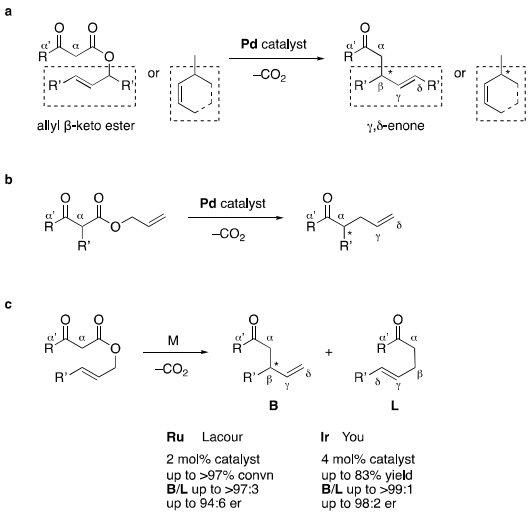


Figure 1. Catalytic asymmetric decarboxylative allylation of allyl β-keto esters.

2. Reactivity of the catalysts

2-1. Catalyst design. The CpRu complex (**1**, Fig. 2) with the chiral bisamidine ligand Naph-diPIM-dioxo-*i*Pr, is known to display high catalytic activity and enantioselectivity in asymmetric dehydrative allylations of carbon nucleophiles with cinnamyl alcohols in the presence of Brønsted acid catalysts [4b]. Under highly acidic conditions, simple ketones have been used as nucleophiles in these types of reactions [4c]. Importantly, this catalytic system tolerates the use of allyl esters as allyl donors [4d]. This superior performance of complex **1** results from the many beneficial characteristics of the Naph-diPIM- dioxo-*i*Pr ligand, which include high stability and high oxidative

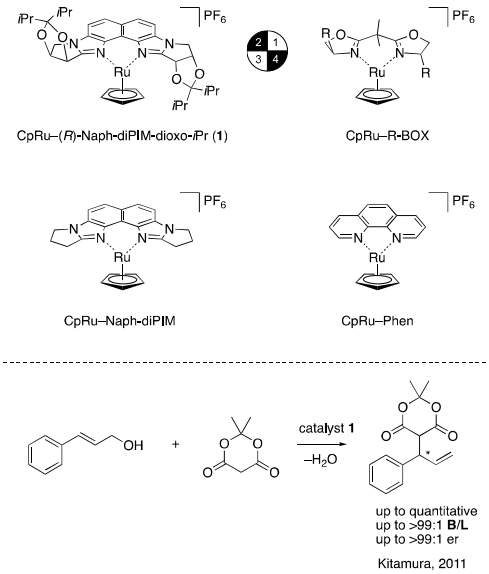
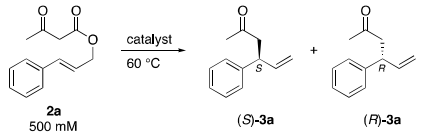


Figure 2. CpRu–(*R*,*R*)-Naph-diPIM-dioxo-*i*Pr (**1**), CpRu–R-BOX, and related complexes (top), and dehydrative allylation (bottom).

addition ability of its metal complex resulting from 1) high planarity, 2) high σ donation ability, and 3) the 90° bite angle, and high enantioselectivity resulting from 4) the efficient chiral environment imparted by the dioxolane framework. Indeed, **1** showed better performance than the corresponding CpRu complex bearing the privileged sp^2N bidentate ligand *t*-Bu-BOX, which does not possess the aforementioned properties [4b]. Encouraged by these distinct advantages in allylations using complex **1**, we investigated its use for decarboxylative allylations.

2-2. Reactivity of CpRu–Naph-diPIM-dioxo-*i*Pr complex. We began by evaluating the reaction with (*E*)-3-phenylprop-2-en-1-yl 3-oxobutanoate (**2a**, 500 mM) as the substrate, with 1 mol% of the CpRu complex **1** (5 mM) as the catalyst in dichloromethane (CH_2Cl_2) at 60 °C. The product yield and **B**/**L** ratio (**3**/**4**) were determined by ^{1}H-NMR analysis. Under these conditions, the substrate was completely converted to the product 4-phenylhex-5-en-2-one (**3a**) after 6 h (Table 1, entry 1), and importantly, the regioisomeric linear product **4a** was not generated at all. Notably, the *S*/*R* ratio of **3a** was 99:1. Furthermore, the catalyst loading could be reduced to 0.2 mol%

Table 1. Asymmetric decarboxylative allylation of (*E*)-3-phenylprop-2-en-1-yl 3-oxobutanoate (**2a**) catalyzed by CpRu–(*R*,*R*)-Naph-diPIM-dioxo-*i*Pr (**1**)[a]



Entry	Catalyst (mol%)	Solvent	Time (h)	Yield (%)[b]	*S*:*R*[c]
1	**1** (1)	CH_2Cl_2	6	99 (92)	99:1
2[d]	**1** (1)	CH_2Cl_2	6	60 (56)	>99:1
3	**1** (0.2)	CH_2Cl_2	24	99 (92)	99:1
4	**1** (0.1)	CH_2Cl_2	48	90[e] (85)	99:1
5	**1** (1)	$CHCl_3$	6	90 (80)	>99:1
6	**1** (1)	CH_2ClCH_2Cl	6	97 (90)	>99:1
7	**1** (1)	THF	6	70 (65)	>99:1
8	**1** (1)	Ether	6	82[e] (76)	99:1
9	**1** (1)	*t*-BuOH	6	98 (91)	98:2
10	**1** (1)	DMA	6	10 (4)	>99:1
11	**1** (1)	CH_3CN	6	<1 (—)	—
12	**1** (1)	Toluene	6	49[e] (28)	>99:1
13	CpRu–(*R*,*R*)-*t*-Bu-BOX (1)	CH_2Cl_2	6	<1 (—)	—
14	CpRu–(*R*,*R*)-Ph-BOX (1)	CH_2Cl_2	6	<1 (—)	—
15	CpRu–Naph-diPIM (1)	CH_2Cl_2	6	98 (95)	—
16	CpRu–Phen (1)	CH_2Cl_2	6	66 (60)	—

[a]Reagents and conditions: [**2**] = 500 mM; 60 °C.
[b]Determined by ^{1}H-NMR analysis. Values in parentheses are isolated yields.
[c]Determined by HPLC analysis.
[d]rt.
[e]Intermolecular reaction product (*E*)-3-phenylprop-2-en-y-yl 2-(1-phenylprop-2-en-1-yl)-3-oxobutanoate (**5a**) was obtained in 10% (Entry 4), 9% (Entry 8), and 35% (Entry 12) yield, respectively.

(Entry 3). While the high reactivity and selectivity were retained even with 0.1 mol% of **1**, *ca.* 10% of the side product **5a** was generated *via* intermolecular allylation (Entry 4) under these conditions. Chloroform ($CHCl_3$), dichloroethane (CH_2ClCH_2Cl), *tert*-butyl alcohol (*t*-BuOH), THF, and diethyl ether (ether) could be used as solvents, but the product arising from the side reaction increased with their use (Entries 5–9). The reactivities decreased in DMA, acetonitrile (CH_3CN), and toluene (Entries 10–12), and were completely suppressed with the replacement of Naph-diPIM-dioxo-*i*Pr ligand with R-BOX ligand (R = *t*-Bu or Ph) (Entries 13 and 14) [14a]. Although achiral 1,10-phenanthroline (Phen) furnished considerable reactivity with high **3**/**4** ratio, the reaction using achiral Naph-diPIM [11b] complex was faster and highlighted the importance of the ligand's structural properties for this transformation (Entries 15 and 16).

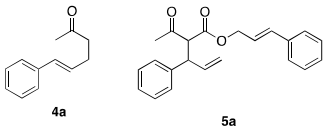


Figure 3. Linear adduct **4a** and intermolecular adduct **5a**.

2-3. Substrate scope. Having optimized the catalytic reaction, we turned attention to explore its scope. The presence of electron-donating substituents on the phenyl group attached to the propenyl moiety accelerated the reactivity, whereas electron-withdrawing groups decelerated it (Table 2, entries 1–5), which suggests that the oxidative addition is the rate-determining step (see below). The phenyl group could be replaced with heteroaromatic rings such as *N*-Boc-pyrrole, *N*-Boc-indole, furan, and thiophene (Entries 6–9). Particularly, the electron-rich pyrrole and indole displayed high reactivity. While the presence of aliphatic substituents on the propenyl group suppressed the reactivity completely (Entries 10 and 11), the introduction of methyl groups on the double bond of the cinnamyl-type substrates lowered the reactivity (Entries 12 and 13). Next, we evaluated substitutions at the 2- and/or 4-carbon of the β-keto acid moiety. The ethyl substituted ketone **3n** was generated with the use of 3-oxopentanoic ester **2n**, which contained the ethyl group instead of the methyl group of **2a** (Entry 14). The introduction of more sterically-demanding *iso*-propyl or *tert*-butyl groups led to lower yields of **3** along with the increased formation of the by-product **5** with an increase in the bulkiness of the substrate (Entries 15 and 16). The introduction of the phenyl group at the ketone did not have any negative impact (Entry 17). With the introduction of a single methyl group at the 2-position of substrate **2r**, the corresponding product **3r** was formed in a 1:1 diastereomeric ratio (Entry 18). The product **3r** is a regioisomer of **3n**, generated from **2n**, both products could be synthesized selectively on demand by changing the substrates structure (Entries 14 and 18) [14b]. However, the dimethylated substrate **2s** was not suitable (Entry 19). While the cyclic keto ester **2t** was a suitable substrate (Entry 20), it delivered the product in a low diastereomeric ratio.

3. Mechanism

3-1. Catalytic cycle. Taking into account the results obtained from the optimization and the substrate scope, we propose a catalytic cycle of the reaction, using **2a** as the representative substrate (Fig. 4). First, the double bond of the substrate **2a** coordinates with **1** to form the substrate/catalyst complex. Through the ensuing oxidative addition, the π-allyl ruthenium(IV) complex **A** is formed, which has the β-keto carboxylate as the counter anion. The carboxylate anion is then reversibly isomerized to an enolate and this anion attacks the π-allyl ligand to regenerate **1** together with the formation of the β-keto acid adduct **6** (**path A**). Finally, the decarboxylation of **6** delivers **3**. Upon formation of the intermediate **A** in the catalytic cycle, the carboxylate oxygen could attack the π-allyl ligand to form **1** and **2** reversibly. As the electron-donating substituents on the cinnamyl moiety were found to accelerate the reactivity (see Table 2, entries 1–5), the rate-determining step would be the oxidative addition from consideration of the Hammett rule (σ_{OCH3}, –0.27; σ_H, 0; σ_{Cl}, 0.23; σ_{CF3}, 0.54. $\rho < 0$), wherein an allylic cationic carbon is generated. In the case of bulky substrates such as **2o** and **2p**, the intermolecular allylation product **5** is generated through a competitive proton transfer between the enolate and the other substrate **2**, owing to their low nucleophilic addition abilities (**path C**). The observation of **5**, which results from proton transfer, suggests that the anion is formed during the catalytic cycle, due to which the mechanistic pathway involving the chiral Lewis-acid catalyzed Carroll-type pericyclic rearrangement is excluded [16,17]. Intramolecular hydrogen bond between carboxylic acid and enolate may suppress the proton transfer from other β-keto ester **2**. The regio- and enantio-selection originate from the nucleophilic addition step, in a manner similar to that reported in asymmetric dehydrative allylation [4b]. The nucleophile attacks from the outside to the ruthenium of π-allyl complex preferentially at the more electronically positive C(3) carbon rather than at the C(1) carbon. The π-allyl species exits in a $C(3)_{Re}$-Ru configuration due to the chiral environment of the Naph-diPIM-dioxo-*i*Pr, which results in the generation of product **3** with an *S*-configuration.

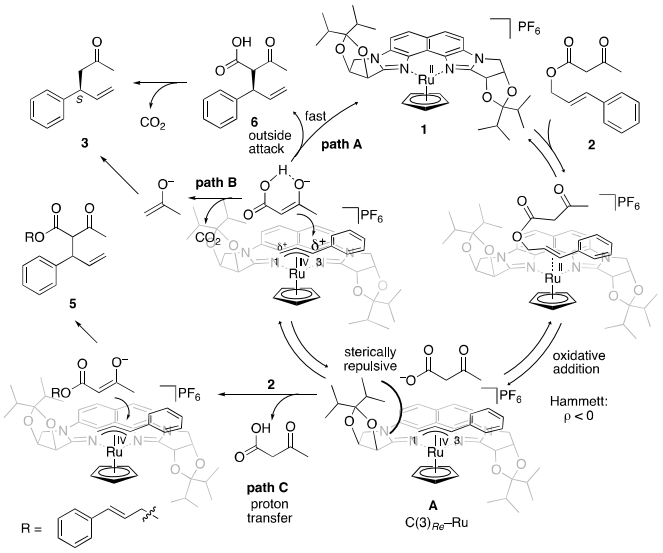
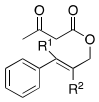
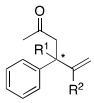
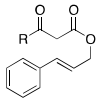
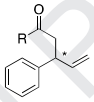
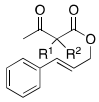
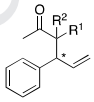
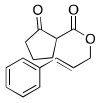
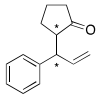


Figure 4. Proposed catalytic cycle.

Table 2. Scope and limitation of the CpRu complex **1**-catalyzed decarboxylative allylation[a]

Entry	Substrate		Product	Time (h)	Yield (%)[b]	Er[c]
1		Ar = C_6H_5 (**2a**)		6	99 (92)	99:1
2		*o*-$CH_3OC_6H_4$ (**2b**)		6	99 (92)	>99:1
				(48)[d]	(99 (95))[d]	(99:1)[d]
3		*p*-$CH_3OC_6H_4$ (**2c**)		6	99 (91)	99:1
				(48)[d]	(99 (92))[d]	(99:1)[d]
4		*p*-ClC_6H_4 (**2d**)		18	90 (81)[e]	>99:1
5		*p*-$CF_3C_6H_4$ (**2e**)		24 (5 mol%)	68 (52)[e]	99:1
6		Het = *N*-Boc-2-pyrrolyl (**2f**)		6	99 (95)	>99:1
7		*N*-Boc-3-indolyl (**2g**)		6	99 (80)	99:1
8		2-furanyl (**2h**)		24	99 (90)	>99:1
9		2-thiophenyl (**2i**)		24	99 (95)	>99:1
10		R = cyclohexyl (**2j**)		18	<1	—
11		R = *tert*-C_4H_9 (**2k**)		18	<1	—
12		R^1 = H; R^2 = CH_3 (**2l**)		18	<1	—
13		R^1 = CH_3; R^2 = H (**2m**)		18	<1	—
14		R = C_2H_5 (**2n**)		18	95 (89)[e]	>99:1
15		2-C_3H_7 (**2o**)		18	88 (70)[e]	99:1
16		*tert*-C_4H_9 (**2p**)		18	59 (41)[e]	99:1
17		C_6H_5 (**2q**)		18	98 (90)	>99:1
18		R^1 = CH_3; R^2 = H (**2r**)		18	93 (79) dr = 1:1.08	99:1, >99:1
19		R^1 = R^2 = CH_3 (**2s**)		18	<1 (—)	—
20	 (**2t**)			18	95 (85) dr = 1:1.10	>99:1, 99:1

[a]Reagents and conditions: [**2**] = 500 mM; [**1**] = 5 mM; CH_2Cl_2; 60 °C.
[b]Determined by ^{1}H-NMR analysis. Values in parentheses are isolated yields.
[c]Determined by HPLC analysis.
[d]0.1 mol% of 1 was used.
[e]Side products **5** were formed in 5% (Entry 4), 8% (Entry 5), 5% (Entry 14), 12% (Entry 15), and 41% (Entry 16) yield, respectively.

3-2. Equilibrium of the oxidative addition step. To gain further insight into the oxidative addition step, we attempted to observe π-allyl species using NMR. However, as shown in Fig. 5, the NMR spectra indicated the absence of the π-allyl complex upon the reaction of **1** with cinnamyl benzoate (**7**), which was used to mimic the substrate **2**. This result is consistent with the perspective that the oxidative addition product is in equilibrium and is highly biased toward the ruthenium(II) species in the equilibrium.

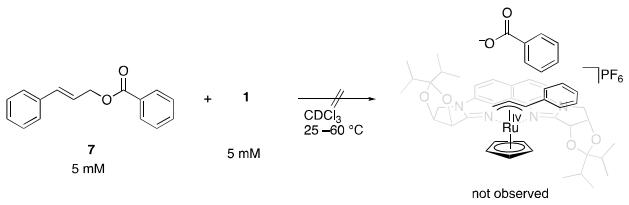


Figure 5. Investigation of oxidative addition of cinnamyl carboxylic ester and CpRu complex **1**.

3-3. Pathway of nucleophilic addition. Considering the possible pathways for the nucleophilic addition step, we cannot exclude the possibility of the pathway wherein the β-keto carboxylate undergoes decarboxylation to form a simple ketone enolate, which then undergoes nucleophilic addition, as reported previously (Fig. 4. **path B**) [18]. Since the non-protic 2,2-dimethylated substrate **2s** shows virtually no reactivity under the current reaction conditions (Table 2, entry 19), unlike the previous ones, the pathway involving the deprotonation of β-keto carboxylate (**path A**) is more plausible [19] rather than a conventional decarboxylation pathway. As shown in Figure 6, when a mixture of **2a** and **2u** (500 mM for each) was reacted under the standard reaction conditions, the adducts **3a** and **3u**

were obtained as the sole products, and the crossover products **3a'** and **3u'** were not obtained at all. A conversion of *ca*. 80% was achieved for both substrates after 2 h, which indicates the competitive reactivity of **2a** and **2u**, and their conversion in parallel. To the best of our knowledge, this is the first example wherein such crossover products were not generated [13a,13j,14b,15]. Therefore, this reaction may proceed *via* a different mechanism from the other reported ones, and the nucleophilic addition is much faster than the oxidative addition.

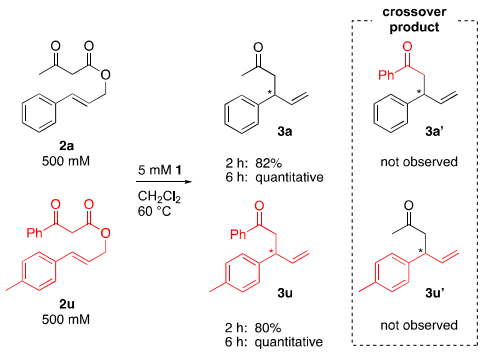


Figure 6. Crossover experiments.

4. Conclusion

We successfully employed a CpRu–chiral bisamidine complex, which was previously used for catalyzing dehydrative allylation, for intramolecular decarboxylative allylation. The regioselectivity of the electrophilic carbon for the allylation and its enantiofacial selectivity have been fairly improved in comparison to the previously reported method. Importantly, the catalyst loading has been reduced by one-tenth. This strategy allows bond formation between the less acidic ketone nucleophiles and aromatic/vinyl substituted carbons. Similar to the conventional reactions, unsymmetrical ketones can be allylated regiospecifically at the carbon previously attached to the carboxylic group in the substrate. Additionally, we proposed a new reaction pathway based on the results of the substrate structure-reactivity relationships, NMR, and crossover experiments. Notably, no crossover was observed, which indicates that the reaction proceeds selectively *via* intramolecular rearrangement. These results suggest that the reaction mechanism involves an enolate of the β-keto acid as the carbon nucleophile, and not the decarboxylated ketone enolate. Further investigation of the mechanism and the extension of this method to the synthesis of structurally complex compounds will be reported in due course.

5. Experimental

5.1. General

Instrument. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA-600 spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane or in ppm relative to $CDCl_3$ (δ 7.26 in ^{1}H NMR, and δ 77.0 in ^{13}C NMR). The signal patterns of ^{1}H NMR are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad signal. High-resolution mass spectra (HRMS) were measured by ESI ionization method on a Bruker compact system. High performance liquid chromatography (HPLC) analyses were performed on a Shimadzu LC-10A system. Specific rotations were measured on a JASCO P-2200 polarimeter. **Silica gels.** Analytical thin-layer chromatography (TLC) was performed using Merck 5715 plates precoated with silica gel 60 F_{254} (layer thickness, 0.25 mm). The product spots were visualized with a solution of phosphomolybdic acid (PMA), *p*-anisaldehyde, iodine (I_2), or cerium ammonium molybdate (CAM). Flash silica-gel column chromatography (SiO_2-chromatography) was performed using Daiko AP 300. **Solvent.** Solvents for the catalytic allylation and the synthesis of Ru complexes were dried, degassed at reflux temperature in the presence of the following appropriate drying agents (250 mg/100 mL) under an Ar stream for 6 h, and distilled into Schlenk flasks: calcium hydride for CH_2Cl_2, $CHCl_3$, CH_2ClCH_2Cl, DMA, *t*-BuOH, and CH_3CN; sodium for diethyl ether (Et_2O), THF, and toluene; and MS4A for acetone. These solvents were degassed by three freeze–thaw cycles before used. $CDCl_3$ was purchased from Cambridge Isotope Laboratories and purified by alumina column chromatography. It was degassed by three freeze–thaw cycles before used in the ^{1}H-NMR study. All other solvents were obtained commercially and used without further purification unless stated otherwise. **Manipulation.** A Teflon-coated magnetic bar was used for stirring of a reaction mixture. Room temperature (rt) was in the range of 28 °C from 25 °C. Reactions at higher temperature than rt were carried out by use of oil bath. Reactions at 0 °C was carried out by use of an ice bath. Solvents after general workup process were removed by means of a rotary evaporator. Concentration of a reaction mixture in a Schlenk tube was performed by connecting to a vacuum-Ar line via a cold trap cooled by liquid N_2. Organic extract obtained by a general partition-based workup was dried over anhydrous Na_2SO_4 for ca. 30 min. Brine means saturated aqueous NaCl. All of metal-catalyzed reactions were carried out under Ar atmosphere by use of a general Schlenk technique unless otherwise specified. A Schlenk with Teflon J. Young valve was specified by "Young Schlenk." Schlenks were dried, before use, at ca. 250 °C by use of a heat gun under a reduced pressure. Silicon grease was used for connecting to a reflux condenser and a glass stopper. Liquid reagents were introduced by use of a syringe via a septum rubber. After introduction, the septum was replaced with a glass stopper or with a Young valve. Degassed solvents and degassed solutions of reagents, catalysts, and substrates were transferred to another Schenk by use of a gas-tight syringe or cannulation method. Cannulation was performed by use of a stainless tube through a septum rubber under a slightly positive pressure of Ar. One freeze-thaw cycle consists of i) freezing a liquid mixture, ii) evacuation of the system at the freezing stage, iii) closing the system, iv) thawing the frozen liquid, and v) releasing the negative pressure to atmospheric pressure by filling Ar gas. For the general synthesis of substrates under Ar atmosphere, non-degassed solvents were used.

5.2. Substrates

Following substrates were prepared according to the reported methods. (*E*)-3-phenylprop-2-en-1-yl 3-oxobutanoate (**2a**) [20], (*E*)-3-(2-methoxyphenyl)prop-2-en-1-yl 3-oxobutanoate (**2b**) [20], (*E*)-3-(4-methoxyphenyl)prop-2-en-1-yl 3-oxobutanoate (**2c**) [20], (*E*)-3-(4-chlorophenyl)prop-2-en-1-yl 3-oxobutanoate (**2d**) [20], (*E*)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-yl 3-oxobutanoate (**2e**) [20], (*E*)-2-methyl-3-phenylprop-2-en-1-yl 3-oxobutanoate (**2l**) [14d], (*E*)-3-phenylprop-2-en-1-yl 3-oxopentanoate (**2n**) [20], (*E*)-3-phenylprop-2-en-1-yl 4-methyl-3-oxopentanoate (**2o**) [14b], (*E*)-3-phenylprop-2-en-1-yl 3-oxo-3-phenylpropanoate (**2q**) [15], (*E*)-3-phenylprop-2-en-1-yl 2-methyl-3-oxobutanoate (**2r**) [21], (*E*)-3-phenylprop-2-en-1-yl 2,2-dimethyl-3-oxobutanoate (**2s**) [14b], (*E*)-3-phenylprop-2-en-1-yl 1-oxocyclopent-2-ylcarboxylate (**2t**) [14d], and (*E*)-3-(4-methylphenyl)prop-2-en-1-yl 3-phenyl-3-oxobutanoate (**2u**) [15].

Substrates **2f**, **2g**, **2h**, **2i**, **2j**, **2k**, and **2m** were prepared from corresponding allyl alcohol and diketene. A representative synthetic procedure for **2f** is shown below. For the other compounds, synthetic parameters, yield, and physical properties were described. The compound **2p** was prepared from cinnamyl alcohol and β-keto ester by transesterification as shown below.

*5.2.1. (E)-3-(N-Boc-pyrrol-2-yl)prop-2-en-1-yl 3-oxobutanoate (**2f**)*

A dry and Ar-filled 100-mL three-necked round-bottom flask was charged with (*E*)-3-(*N*-Boc-pyrrol-2-yl)prop-2-en-1-ol [22] (1.00 g, 4.48 mmol), THF (20 mL), and *N*,*N*-dimethyl-4-aminopyridine (DMAP) (54.7 mg, 0.448 mmol) at rt. The resulting solution was cooled to 0 °C, and to this was added diketene (0.377 g, 4.48 mmol). After the solution was stirred at reflux temperature for 2 h, the solution was partitioned with Et_2O (50 mL) and H_2O (50 mL). The organic layer was washed with brine (20 mL), dried over Na_2SO_4 (10 g), and then concentrated. The resulting crude mixture was subjected to SiO_2-chromatography (SiO_2, 100 g, hexane–ethyl acetate 20:1 eluent) to give the product **2f** as a colorless oil (0.826 g, 60% yield). ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 9H, $C(CH_3)_3$), 2.29 (s, 3H, CH_3), 3.48 (s, 2H, $COCH_2CO$), 4.76 (d, *J* = 6.89 Hz, 2H, CH_2O), 6.07 (dt, *J* = 15.2 and 6.89 Hz, 1H, C*H*=CH), 6.14 (t, *J* = 3.44 Hz, 1H, aromatic), 6.44 (s, 1H, aromatic), 7.23 (s, 1H, aromatic), 7.27 (d, *J* = 15.8 Hz, 1H, CH=C*H*). ^{13}C NMR ($CDCl_3$) δ 28.0, 30.2, 50.1, 66.2, 84.1, 110.9, 111.8, 121.7, 122.4, 126.2, 132.5, 149.3, 166.9, 200.5. The spectra were observed as a 90:10 mixture of ketone and enol forms. HRMS (ESI) *m*/*z*: calcd for $C_{16}H_{21}NNaO_5$ $[M+Na]^+$, 330.1312; found, 330.1316.

*5.2.2. (E)-3-(N-Boc-indol-3-yl)prop-2-en-1-yl 3-oxobutanoate (**2g**)*

(*E*)-3-(*N*-Boc-indol-3-yl)prop-2-en-1-ol [23] (0.900 g, 5.20 mmol); THF (20 mL); DMAP (63.6 mg, 0.520 mmol); diketene (0.656 g, 7.80 mmol); 2 h. Et_2O (50 mL) and H_2O (50 mL), brine (20 mL), Na_2SO_4 (10 g). SiO_2-chromatography (SiO_2, 100 g, hexane–ethyl acetate 15:1 eluent). **2g** (1.19 g, 88% yield). ^{1}H NMR ($CDCl_3$) δ 16.7 (s, 9H, $C(CH_3)_3$), 2.29 (s, 3H, CH_3), 3.51 (s, 2H, $COCH_2CO$), 4.83 (d, *J* = 5.50 Hz, 2H, CH_2O), 6.37 (dt, *J* = 15.8 and 6.87 Hz, 1H, C*H*=CH), 6.79 (d, *J* = 16.5 Hz, 1H, CH=C*H*), 7.29 (t, *J* = 7.56 Hz, 1H, aromatic), 7.35 (t, *J* = 7.56 Hz, 1H, aromatic), 7.65 (s, 1H, aromatic), 7.77 (d, *J* = 7.56 Hz, 1H, aromatic), 8.17 (d, *J* = 6.87 Hz, 1H, aromatic). ^{13}C NMR ($CDCl_3$) δ 28.2, 30.2, 50.1, 66.5, 84.0, 101.4, 115.4, 117.6, 119.9, 122.5, 123.0, 124.8, 126.6, 128.4, 135.9, 149.4, 166.9, 200.4. The spectra were observed as an 85:15 mixture of ketone and enol forms. HRMS (ESI) *m*/*z*: calcd for $C_{20}H_{23}NNaO_5$ $[M+Na]^+$, 380.1468; found, 380.1471.

*5.2.3. (E)-3-Furan-2-ylprop-2-en-1-yl 3-oxobutanoate (**2h**)*

(*E*)-3-Furan-2-ylprop-2-en-1-ol [23] (1.00 g, 8.06 mmol); THF (20 mL); DMAP (98.5 mg, 0.806 mmol); diketene (0.678 g, 8.06 mmol); 2 h. Et_2O (50 mL) and H_2O (50 mL), brine (20 mL), Na_2SO_4 (10 g). SiO_2-chromatography (SiO_2, 100 g, hexane–ethyl acetate 20:1 eluent). **2h** (1.28 g, 76% yield). ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3H, CH_3), 3.49 (s, 2H, $COCH_2CO$), 4.77 (d, *J* = 6.20 Hz, 2H, CH_2O), 6.20 (dt, *J* = 15.8 and 6.89 Hz, 1H, C*H*=CH), 6.30 (d, *J* = 2.75 Hz, 1H, aromatic), 6.38 (br, 1H, aromatic), 6.48 (d, *J* = 15.8 Hz, 1H, CH=C*H*), 7.36 (s, 1H, aromatic). ^{13}C NMR ($CDCl_3$) δ 30.2, 50.0, 65.5, 109.1, 111.3, 120.8, 122.8, 142.5, 151.6, 166.8, 200.4. The spectra were observed as an 89:11 mixture of ketone and enol forms. HRMS (ESI) *m*/*z*: calcd for $C_{11}H_{12}NaO_4$ $[M+Na]^+$, 231.0628; found, 231.0647.

*5.2.4. (E)-3-Thiophen-2-ylprop-2-en-1-yl 3-oxobutanoate (**2i**)*

(*E*)-3-Thiophen-2-ylprop-2-en-1-ol [24] (0.838 g, 7.13 mmol); THF (20 mL); DMAP (87.1 mg, 0.713 mmol); diketene (0.600 g, 7.13 mmol); 2 h. Et_2O (50 mL) and H_2O (50 mL), brine (20 mL), Na_2SO_4 (10 g). SiO_2-chromatography (SiO_2, 100 g, hexane–ethyl acetate 15:1 eluent). **2i** (1.28 g, 80% yield). ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3H, CH_3), 3.49 (s, 2H, $COCH_2CO$), 4.76 (d, *J* = 6.89 Hz, 2H, CH_2O), 6.10 (dt, *J* = 15.2 and 6.89 Hz, 1H, C*H*=CH), 6.80 (d, *J* = 15.8 Hz, 1H, CH=C*H*), 6.97 (dd, *J* = 5.16 and 4.13 Hz, 1H, aromatic), 7.00 (d, *J* = 3.44 Hz, 1H, aromatic), 7.20 (d, *J* = 4.82 Hz, 1H, aromatic). ^{13}C NMR ($CDCl_3$) δ 30.2, 50.0, 65.6, 121.7, 125.1, 126.7, 127.4, 128.1, 140.9, 166.8, 200.3. The spectra were observed as a 90:10 mixture of ketone and enol forms. HRMS (ESI) *m*/*z*: calcd for $C_{11}H_{12}NaO_{3S}$ $[M+Na]^+$, 247.0399; found, 247.0438.

*5.2.5. (E)-3-Cyclohexylprop-2-en-1-yl 3-oxobutanoate (**2j**)*

(*E*)-3-Cyclohexylprop-2-en-1-ol [24] (2.10 g, 1.50 mmol); THF (15 mL); DMAP (110 mg, 0.900 mmol); diketene (1.39 g, 16.5 mmol); THF (15 mL); 1 h. Et_2O (50 mL) and H_2O (20 mL), brine (20 mL), Na_2SO_4 (10 g). SiO_2-chromatography (SiO_2, 250 g, hexane–ethyl acetate 10:1 eluent). **2j** (3.22 g, 96% yield). ^{1}H NMR ($CDCl_3$) δ 1.01–1.31 (m, 5H, cyclohexyl), 1.71 (brd, *J* = 10.3 Hz, 5H, cyclohexyl), 1.97 (br, 1H, cyclohexyl), 2.27 (s, 3H, CH_3), 3.46 (s, 2H, $COCH_2CO$), 4.58 (d, *J* = 6.20 Hz, 2H, CH_2O), 5.51 (dt, *J* = 15.2 and 6.89 Hz, 1H, C*H*=CH), 5.74 (dd, *J* = 15.5 and 6.89 Hz, 1H, CH=C*H*). ^{13}C NMR ($CDCl_3$) δ 25.9, 26.1, 30.1, 32.5, 40.3, 50.1, 66.4, 120.6, 143.0, 166.9, 200.6. The spectra were observed as a 91:9 mixture of ketone and enol forms. HRMS (ESI) *m*/*z*: calcd for $C_{13}H_{20}NaO_3$ $[M+Na]^+$, 247.1310; found, 247.1332.

*5.2.6. (E)-4,4-Dimethylpent-2-en-1-yl 3-oxobutanoate (**2k**)*

(*E*)-4,4-Dimethylpent-2-en-1-ol [25] (2.28 g, 20.0 mmol); THF (20 mL); DMAP (147 mg, 1.20 mmol); diketene (1.85 g, 22.0 mmol); 1 h. Et_2O (50 mL) and H_2O (50 mL), brine (20 mL), Na_2SO_4 (10 g). SiO_2-chromatography (SiO_2, 250 g, hexane–ethyl acetate 15:1 then 10:1 eluent). **2k** (3.44 g, 87% yield). ^{1}H NMR ($CDCl_3$) δ 1.0□□□□, 9H, $C(CH_3)_3$), 2.28 (s, 3H, CH_3), 3.47 (s, 2H, $COCH_2CO$), 4.59 (d, *J* = 6.20 Hz, 2H, CH_2O), 5.47 (dt, *J* = 15.8 and 6.89 Hz, 1H, C*H*=CH), 5.80 (d, *J* = 15.8 Hz, 1H, CH=C*H*). ^{13}C NMR ($CDCl_3$) δ 29.2, 33.1, 50.2, 66.5, 118.1, 147.9, 166.9, 200.5. The spectra were observed as an 86:14 mixture of ketone and enol forms. HRMS (ESI) *m*/*z*: calcd for $C_{11}H_{18}NaO_3$ $[M+Na]^+$, 221.1148; found, 221.1160.

*5.2.7. (E)-3-Phenylbut-2-en-1-yl 3-oxobutanoate (**2m**)*

(*E*)-3-Phenylbut-2-en-1-ol [26] (0.740 g, 5.00 mmol); THF (25 mL); DMAP (61.1 mg, 0.500 mmol); diketene (1.69 g, 20.0 mmol); 2 h. Et_2O (50 mL) and H_2O (50 mL), brine (20 mL), Na_2SO_4 (10 g). SiO_2-chromatography (SiO_2, 100 g, hexane–ethyl acetate 15:1 eluent). **2m** (1.09 g, 92% yield). ^{1}H NMR ($CDCl_3$) δ 2.12 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.49 (s, 2H, $COCH_2CO$), 4.86 (d, *J* = 6.89 Hz, 2H, CH_2O), 5.90 (t, *J* = 6.89 Hz, 1H, CH=), 7.28 (t, *J* = 7.57 Hz, 1H, aromatic), 7.33 (t, *J* = 7.57 Hz, 2H, aromatic), 7.40 (d, *J* = 7.57 Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$) δ 16.2, 30.2, 50.1, 62.5, 120.6, 125.8, 127.6, 128.3, 141.0, 142.4, 167.1, 200.5. The spectra were observed as a 90:10 mixture of ketone and enol forms. HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{16}NaO_3$ $[M+Na]^+$, 255.0992; found, 255.0977.

*5.2.8. (E)-3-Phenylprop-2-en-1-yl 4,4-dimethyl-3-oxopentanoate (**2p**)*

A dry and Ar-filled 300-mL three-necked flask was charged with methyl 4,4-dimethyl-3-oxopentanoate (3.16 g, 20.0 mmol), cinnamyl alcohol (10.8 g, 80.0 mmol), toluene (80 mL), and then $NaBO_3$ (807 mg, 8.09 mmol). After 24 h stirring, the suspension was filtered. The filtrate was concentrated to give a crude product (ca. 10 g). This was subjected to SiO_2-chromatography (SiO_2, 100 g, hexane–ethyl acetate 15:1 eluent) to give the product **2p** (4.55 g, 87% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 9H, $C(CH_3)_3$), 3.60 (s, 2H, $COCH_2CO$), 4.79 (d, *J* = 6.19 Hz, 2H, CH_2O), 6.28 (dt, *J* = 16.5 and 6.87 Hz, 1H, C*H*=CH), 6.66 (d, *J* = 15.8 Hz, 1H, CH=C*H*), 7.25 (t, *J* = 7.56 Hz, 1H, aromatic), 7.32 (t, *J* = 7.56 Hz, 2H, aromatic), 7.39 (d, *J* = 7.65 Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$) δ 26.1, 43.9, 65.8, 122.7, 126.6, 128.1, 128.6, 134.5, 136.1, 167.5, 207.8. The spectra were observed as an 86:14 mixture of ketone and enol forms. HRMS (ESI) *m/z*: calcd for $C_{16}H_{20}NaO_3$ $[M+Na]^+$, 283.1305; found, 283.1352.

5.3. Standard reaction

5.3.1. General procedure

A 5-mL Young Schlenk was charged with (*R,R*)-Naph-diPIM-dioxo-*i*Pr (2.73 mg, 5.00 μmol) and $[RuCp(CH_3CN)_3]PF_6$ (2.71 mg, 5.00 μmol). To this was added acetone (5.00 mL) and the resulting suspension was stirred at 60 °C for 30 min to be a clear yellow solution. This was used as a 10-mM solution of $[RuCp((R,R)$-Naph-diPIM-dioxo-*i*Pr$)]PF_6$ ((*R*)-**1**).

A solution of (*R*)-**1** (10.0 mM in acetone, 0.500 mL, 5.00 μmol) was charged into a 5-mM Young Schlenk and concentrated. To the residue was added a 500 mM solution of (*E*)-3-phenylprop-2-en-1-yl 3-oxobutanoate (**2a**) in CH_2Cl_2 (1.00 mL, 0.500 mmol). The solution was stirred at 60 °C for 6 h. The resulting yellow solution was concentrated, and the residue was purified by SiO_2-chromatography (SiO_2, 10 g, hexane–ethyl acetate 10:1 eluent) to give a 4-phenylhex-5-en-2-one (**3a**) (80.2 mg, 92% yield). The enantiomeric ratio of the product **3a** was determined to 99:1 by HPLC analysis (CHIRALPAK AD-H (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 220 nm light; t_R, 20.0 min (minor), 22.1 min (major)). **3a**: ^{1}H NMR ($CDCl_3$) δ 2.09 (s, 3H, CH_3), 2.83 (dd, *J* = 15.8 and 6.89 Hz, 1H, C*H*H), 2.88 (dd, *J* = 15.8 and 7.57 Hz, 1H, CH*H*), 3.91 (q, *J* = 6.89 Hz, 1H, CH), 5.02 (d, *J* = 17.2 Hz, 1H, =C*H*H), 5.06 (d, *J* = 10.3 Hz, 1H, =CH*H*), 5.93–6.00 (m, 1H, C*H*=CH_2), 7.20 (d, *J* = 8.26 Hz, 2H, aromatic), 7.21 (t, *J* = 6.20 Hz, 1H, aromatic), 7.30 (t, *J* = 8.26 Hz, 2H, aromatic). $[\alpha]_D^{27}$ –15.8 (*c* 1.05, $CHCl_3$). The ^{1}H-NMR data were consisted with reported values [20]. Absolute configuration of the product was determined to be *S* by comparison of specific rotation with the reference ($[\alpha]_D^{26}$ –13.3 (*c* 0.31, $CHCl_3$) for *S* (85:15 er) [6]).

In another batch, to the reaction crude mixture obtained by the same procedure as above was added a mesitylene solution (1.00 M in $CDCl_3$, 0.500 mL, 0.500 mmol). A part of the solution (ca. 0.6 mL) was subjected to ^{1}H-NMR analysis with the 10 sec repetition time so that the integrations of the ^{1}H-signal areas become accurate as much as possible. The conversion was determined to >99% as no signal of **2a** was observed within the range of S/N ratio 200. The NMR yield was determined to >99% by comparison of the signal intensities of **3a** (δ 2.07 (s)) and mesitylene (δ 2.27 (s)) to be 1.00:3.00.

5.3.2. 10-g scale reaction

A 10-mM solution of $[RuCp((R,R)$-Naph-diPIM-dioxo-*i*Pr$)]PF_6$ ((*R*)-**1**) in acetone (9.16 mL, 91.6 μmol) was prepared in a 5-mL Young Schlenk. After concentration of the solution in vacuo, (*E*)-3-phenylprop-2-en-1-yl 3-oxobutanoate (**2a**) (500 mM in CH_2Cl_2, 91.6 mL, 10.0 g, 45.8 mmol) were introduced. The resulting yellow solution was stirred for 24 h at 60 °C. The whole system was cooled to rt and concentrated to afford a colorless oil. This was purified by SiO_2-chromatography (500 g, hexane–ethyl acetate 10:1 eluent) to give a 4-phenylhex-5-en-2-one (**3a**) (7.42 g, 93% yield, 99:1 er).

5.4. Generality

The reaction procedure is the same as that described in the standard reaction using **2a** to give **3a**. Listed below are the reaction conditions, workup processes, yields, and physical properties.

*5.4.1. 4-(2-Methoxyphenyl)hex-5-en-2-one (**3b**)*

(*E*)-3-(2-Methoxyphenyl)prop-2-en-1-yl 3-oxobutanoate (**2b**) (500 mM in CH_2Cl_2, 1.00 mL, 124 mg, 0.500 mmol); 6 h. SiO_2-chromatography (10 g, 15:1 hexane–EtOAc eluent) to give 4-(2-methoxyphenyl)hex-5-en-2-one (**3b**) (94.0 mg, 92% yield, >99:1 er). ^{1}H NMR ($CDCl_3$) δ 2.12 (s, 3H, CH_3), 2.81 (dd, *J* = 16.5 and 6.20 Hz, 1H, C*H*H), 2.86 (dd, *J* = 15.8 and 8.26 Hz, 1H, CH*H*), 3.84 (s, 3H, OCH_3), 4.30 (q, *J* = 6.89 Hz, 1H, CH), 5.02 (d, *J* = 17.2 Hz, 1H, =C*H*H), 5.05 (d, *J* = 10.3 Hz, 1H, =CH*H*), 6.02 (m, 1H, C*H*=CH_2), 6.87 (d, *J* = 8.26 Hz, 1H, aromatic), 6.91 (t, *J* = 7.57 Hz, 1H, aromatic), 7.14 (d, *J* = 7.57 Hz, 1H, aromatic), 7.20 (t, *J* = 8.26 Hz, 1H, aromatic). HPLC condition: CHIRALPAK ID-3 (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 254 nm light; t_R, 26.7 min (major), 29.3 min (minor). $[\alpha]_D^{25}$ –22.6 (*c* 1.20, $CHCl_3$). ^{1}H-NMR data were consisted with reported values [20].

*5.4.2. 4-(4-Methoxyphenyl)hex-5-en-2-one (**3c**)*

(*E*)-3-(4-Methoxyphenyl)prop-2-en-1-yl 3-oxobutanoate (**2c**) (500 mM in CH_2Cl_2, 1.00 mL, 124 mg, 0.500 mmol); 6 h. SiO_2-chromatography (10 g, 15:1 hexane–EtOAc eluent) to give 4-(4-methoxyphenyl)hex-5-en-2-one (**3c**) (94.0 mg, 92% yield, 99:1 er). ^{1}H NMR ($CDCl_3$) δ 2.08 (s, 3H, CH_3), 2.79 (dd, *J* = 16.2 and 7.57 Hz, 1H, C*H*H), 2.85 (dd, *J* = 15.8 and 7.57 Hz, 1H, CH*H*), 3.78 (s, 3H, OCH_3), 3.86 (q, *J* = 6.89 Hz, 1H, CH), 4.99 (d, *J* = 17.2 Hz, 1H, =C*H*H), 5.04 (d, *J* = 10.3 Hz, 1H, =CH*H*), 5.91–5.98 (m, 1H, C*H*=CH_2), 6.84 (d, *J* = 8.26 Hz, 2H, aromatic), 7.12 (d, *J* = 8.95 Hz, 2H, aromatic). HPLC condition: CHIRALPAK ID-3 (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 210 nm light; t_R, 33.3 min (minor), 37.0 min (major). $[\alpha]_D^{27}$ –16.7 (*c* 1.00, $CHCl_3$). ^{1}H NMR spectra data were consistent with reported values [20].

*5.4.3. 4-(4-Chlorophenyl)hex-5-en-2-one (**3d**)*

(*E*)-3-(4-Chlorophenyl)prop-2-en-1-yl 3-oxobutanoate (**2d**) (500 mM in CH_2Cl_2, 1.00 mL, 126 mg, 0.500 mmol); 18 h. SiO_2-chromatography (10 g, 10:1 hexane–EtOAc eluent) to give 4-(4-chlorophenyl)hex-5-en-2-one (**3d**) (84.5 mg, 81% yield, >99:1 er). ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 3H, CH_3), 2.80 (dd, *J* = 16.5 and 7.57 Hz, 1H, C*H*H), 2.87 (dd, *J* = 16.5 and 7.57 Hz, 1H, CH*H*), 3.90 (q, *J* = 6.89 Hz, 1H, CH), 5.00 (d, *J* = 17.2 Hz, 1H, =C*H*H), 5.07 (d, *J* = 10.3 Hz, 1H, =CH*H*), 5.89–5.96 (m, 1H, C*H*=CH_2), 7.14 (d, *J* = 8.26 Hz, 2H, aromatic), 7.27 (d, *J* = 8.26 Hz, 2H, aromatic). HPLC condition: CHIRALPAK IE-3 (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 220 nm light; t_R, 24.2 min (major), 30.5 min (minor). $[\alpha]_D^{27}$ –7.41 (*c* 1.04, $CHCl_3$). ^{1}H-NMR data were consistent with reported values [20].

*5.4.4. 4-(4-(Trifluoromethyl)phenyl)hex-5-en-2-one (**3e**)*

(*E*)-3-(4-(Trifluoromethyl)phenyl)prop-2-en-1-yl 3-oxobutanoate (**2e**) (500 mM in CH_2Cl_2, 1.00 mL, 143 mg, 0.500

mmol); (*R*)-**1** (10.0 mM in acetone, 2.50 mL, 25.0 μmol); 24 h. SiO_2-chromatography (10 g, 10:1 hexane–EtOAc eluent) to give 4-(4-(trifluoromethyl)phenyl)hex-5-en-2-one (**3e**) (63.0 mg, 52% yield, 99:1 er). ^{1}H NMR ($CDCl_3$) δ 2.11 (s, 3H, CH_3), 2.84 (dd, *J* = 16.9 and 6.89 Hz, 1H, C*H*H), 2.92 (dd, *J* = 16.9 and 6.89 Hz, 1H, CH*H*), 4.00 (q, *J* = 6.89 Hz, 1H, CH), 5.03 (d, *J* = 17.2 Hz, 1H, =C*H*H), 5.10 (d, *J* = 10.3 Hz, 1H, =CH*H*), 5.91 (m, 1H, C*H*=CH_2), 7.33 (d, *J* = 7.57 Hz, 2H, aromatic), 7.56 (d, *J* = 8.26 Hz, 2H, aromatic). HPLC condition: CHIRALPAK AS-H (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 230 nm light; t_R, 10.5 min (minor), 13.1 min (major). $[\alpha]_D^{27}$ –5.15 (*c* 0.50, $CHCl_3$). ^{1}H-NMR data were consistent with reported values [20].

*5.4.5. 4-(N-Boc-pyrrol-2-yl)hex-5-en-2-one (**3f**)*

(*E*)-3-(*N*-Boc-pyrrol-2-yl)prop-2-en-1-yl 3-oxobutanoate (**2f**) (500 mM in CH_2Cl_2, 1.00 mL, 154 mg, 0.500 mmol); 6 h. SiO_2-chromatography (10 g, 10:1 hexane–EtOAc eluent) to give 4-(*N*-Boc-pyrrol-2-yl)hex-5-en-2-one (**3f**) (125 mg, 95% yield, >99:1 er). ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 9H, $C(CH_3)_3$), 2.16 (s, 3H, CH_3), 2.73 (dd, *J* = 16.2 and 8.26 Hz, 1H, C*H*H), 2.89 (dd, *J* = 16.2 and 6.20 Hz, 1H, CH*H*), 4.68 (q, *J* = 6.20 Hz, 1H, CH), 4.92 (dt, *J* = 17.2 and 1.38 Hz, 1H, =C*H*H), 5.03 (d, *J* = 10.3 Hz, 1H, =CH*H*), 5.95–6.02 (m, 2H, C*H*=CH_2 and aromatic), 6.08 (t, *J* = 3.44 Hz, 1H, aromatic), 7.20 (dd, *J* = 3.44 and 2.07 Hz, 1H, aromatic). ^{13}C NMR ($CDCl_3$) δ 28.0, 30.0, 36.9, 48.6, 83.7, 109.8, 111.0, 114.7, 121.6, 136.3, 139.5, 149.2, 207.0. HRMS (ESI) *m*/*z*: calcd for $C_{15}H_{21}NNaO_3$ $[M+Na]^+$, 286.1414; found, 286.1446. HPLC condition: CHIRALPAK IB (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 254 nm light; t_R, 12.3 min (major), 13.5 min (minor). $[\alpha]_D^{25}$ –0.291 (*c* 1.00, $CHCl_3$).

*5.4.6. N-Boc-4-indol-3-ylhex-5-en-2-one (**3g**)*

(*E*)-3-(*N*-Boc-indol-3-yl)prop-2-en-1-yl 3-oxobutanoate (**2g**) (500 mM in CH_2Cl_2, 1.00 mL, 179 mg, 0.500 mmol); 6 h. SiO_2-chromatography (10 g, 10:1 hexane–EtOAc eluent) to give *N*-Boc-4-indol-3-ylhex-5-en-2-one (**3g**) (125 mg, 80% yield, 99:1 er). ^{1}H NMR ($CDCl_3$) δ 1.67 (s, 9H, $C(CH_3)_3$), 2.16 (s, 3H, CH_3), 2.90–3.00 (m, 2H, CH_2), 4.17 (q, *J* = 6.89 Hz, 1H, CH), 5.10 (d, *J* = 9.64 Hz, 1H, =C*H*H), 5.12 (d, *J* = 17.2 Hz, 1H, =CH*H*), 5.96–6.03 (m, 1H, C*H*=CH_2), 7.23 (t, *J* = 7.57 Hz, 1H, aromatic), 7.31 (t, *J* = 7.57 Hz, 1H, aromatic), 7.37 (br, 1H, aromatic), 7.56 (d, *J* = 7.57 Hz, 1H, aromatic), 8.12 (br, 1H, aromatic). ^{13}C NMR ($CDCl_3$) δ 28.2, 30.6, 35.7, 47.9, 83.6, 115.3, 115.4, 119.6, 121.9, 122.3, 122.4, 124.4, 129.4, 135.7, 139.1, 149.7, 206.8. HRMS (ESI) *m*/*z*: calcd for $C_{19}H_{23}NNaO_3$ $[M+Na]^+$, 336.1570; found, 336.1563. HPLC condition: CHIRALPAK IG (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.4 mL/min; 254 nm light; t_R, 23.1 min (minor), 28.4 min (major). $[\alpha]_D^{25}$ +28.1 (*c* 1.00, $CHCl_3$).

*5.4.7. 4-Furan-2-ylhex-5-en-2-one (**3h**)*

(*E*)-3-Furan-2-ylprop-2-en-1-yl 3-oxobutanoate (**2h**) (500 mM in CH_2Cl_2, 1.00 mL, 104 mg, 0.500 mmol); 24 h. SiO_2-chromatography (10 g, 15:1 hexane–EtOAc eluent) to give 4-furan-2-ylhex-5-en-2-one (**3h**) (73.9 mg, 90% yield, >99:1 er). ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 3H, CH_3), 2.77 (dd, *J* = 16.5 and 7.57 Hz, 1H, C*H*H), 2.93 (dd, *J* = 16.5 and 6.89 Hz, 1H, CH*H*), 4.01 (q, *J* = 6.89 Hz, 1H, CH), 5.09 (d, *J* = 17.2 Hz, 1H, =C*H*H), 5.11 (d, *J* = 9.64 Hz, 1H, =CH*H*), 5.85–5.92 (m, 1H, C*H*=CH_2), 6.03 (d, *J* = 2.75 Hz, 1H, aromatic), 6.29 (s, 1H, aromatic), 7.32 (s, 1H, aromatic). ^{13}C NMR ($CDCl_3$) δ 30.4, 38.4, 46.8, 105.3, 110.2, 116.1, 137.6, 141.4, 155.6, 206.4. HRMS (ESI) *m*/*z*: calcd for $C_{10}H_{12}NaO_2$ $[M+Na]^+$, 187.0730; found, 187.0728. HPLC condition: CHIRALPAK IB (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 254 nm light; t_R, 13.7 min (major), 14.6 min (minor). $[\alpha]_D^{27}$ +46.3 (*c* 1.00, $CHCl_3$).

*5.4.8. 4-Thiophen-2-ylhex-5-en-2-one (**3i**)*

(*E*)-3-Thiophen-2-ylprop-2-en-1-yl 3-oxobutanoate (**2i**) (500 mM in CH_2Cl_2, 1.00 mL, 112 mg, 0.500 mmol); 24 h. SiO_2-chromatography (10 g, 10:1 hexane–EtOAc eluent) to give 4-thiophen-2-ylhex-5-en-2-one (**3i**) (85.6 mg, 95% yield, >99:1 er). ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 3H, CH_3), 2.85–2.94 (m, 2H, CH_2), 4.21 (q, *J* = 7.57 Hz, 1H, CH), 5.09 (d, *J* = 10.3 Hz, 1H, =C*H*H), 5.10 (d, *J* = 16.5 Hz, 1H, =CH*H*), 5.92–5.99 (m, 1H, C*H*=CH_2), 6.83 (d, *J* = 3.44 Hz, 1H, aromatic), 6.93 (dd, *J* = 4.82 and 3.44 Hz, 1H, aromatic), 7.16 (d, *J* = 4.82 Hz, 1H, aromatic). ^{13}C NMR ($CDCl_3$) δ 30.7, 39.8, 49.8, 115.3, 123.7, 124.0, 126.8, 139.9, 146.4, 206.4. HRMS (ESI) *m*/*z*: calcd for $C_{10}H_{12}NaO_2S$ $[M+Na]^+$, 203.0501; found, 203.0562. HPLC condition: CHIRALPAK IB (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 220 nm light; t_R, 16.8 min (major), 17.8 min (minor). $[\alpha]_D^{25}$ +15.8 (*c* 1.00, $CHCl_3$).

*5.4.9. 5-Phenylhept-6-en-3-one (**3n**)*

(*E*)-3-Phenylprop-2-en-1-yl 3-oxopentanoate (**2n**) (500 mM in CH_2Cl_2, 1.00 mL, 116 mg, 0.500 mmol); 18 h. SiO_2-chromatography (10 g, 10:1 hexane–EtOAc eluent) to give 5-phenylhept-6-en-3-one (**3n**) (83.8 mg, 89% yield, >99:1 er). ^{1}H NMR ($CDCl_3$) δ 0.98 (t, *J* = 7.57 Hz, 3H, CH_2CH_3), 2.26–2.35 (m, 1H, C*H*HCH$_3$), 2.35–2.44 (m, 1H, CH*H*CH$_3$), 2.79 (dd, *J* = 16.2 and 7.57 Hz, 1H, C*H*H), 2.86 (dd, *J* = 15.8 and 7.57 Hz, 1H, CH*H*), 3.93 (q, *J* = 6.89 Hz, 1H, CH), 5.02 (d, *J* = 17.2 Hz, 1H, =C*H*H), 5.05 (d, *J* = 10.3 Hz, 1H, =CH*H*), 5.93–6.00 (m, 1H, C*H*=CH_2), 7.18–7.23 (m, 3H, aromatic), 7.30 (t, *J* = 7.57 Hz, 2H, aromatic). HPLC condition: CHIRALPAK ID-3 (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 254 nm light; t_R, 13.3 min (minor), 14.3 min (major). $[\alpha]_D^{24}$ –22.6 (*c* 0.50, $CHCl_3$). ^{1}H-NMR data were consistent with reported values [20].

*5.4.10. 2-Methyl-5-phenyhept-6-en-3-one (**3o**)*

(*E*)-3-Phenylprop-2-en-1-yl 4-methyl-3-oxopentanoate (**2o**) (500 mM in CH_2Cl_2, 1.00 mL, 123 mg, 0.500 mmol); 18 h. SiO_2-chromatography (10 g, 15:1 hexane–EtOAc eluent) to give 2-methyl-5-phenylhept-6-en-3-one (**3o**) (70.8 mg, 70% yield, 99:1 er). ^{1}H NMR ($CDCl_3$) δ 0.97 (d, *J* = 6.87 Hz, 3H, CH_3), 1.04 (d, *J* = 6.87 Hz, 3H, CH_3), 2.46–2.54 (m, 1H, C*H*$(CH_3)_2$), 2.84 (dd, *J* = 16.2 and 7.57 Hz, 1H, C*H*H), 2.89 (dd, *J* = 16.5 and 6.87 Hz, 1H, CH*H*), 3.95 (q, *J* = 6.87 Hz, 1H, CH), 5.01 (d, *J* = 17.2 Hz, 1H, =C*H*H), 5.05 (d, *J* = 10.3 Hz, 1H, =CH*H*), 5.94–6.01 (m, 1H, C*H*=CH_2), 7.18–7.21 (m, 3H, aromatic), 7.29 (t, *J* = 7.56 Hz, 2H, aromatic). HPLC condition: CHIRALPAK IE-3 (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 220 nm light; t_R, 14.6 min (minor), 15.3 min (major). $[\alpha]_D^{25}$ –17.6 (*c* 1.01, $CHCl_3$). ^{1}H-NMR data were consistent with reported values [27].

*5.4.11. 2,2-Dimethyl-5-phenylhept-6-en-3-one (**3p**)*

(*E*)-3-Phenylprop-2-en-1-yl 4,4-dimethyl-3-oxopentanoate (**2p**) (500 mM in CH_2Cl_2, 1.00 mL, 130 mg, 0.500 mmol); 18 h. SiO_2-chromatography (10 g, 20:1 hexane–EtOAc eluent) to give 2,2-dimethyl-5-phenylhept-6-en-3-one (**3p**) (44.3 mg, 41% yield, 99:1 er). ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 9H, $C(CH_3)_3$), 2.85–2.95 (m, 2H, CH_2), 3.99 (q, *J* = 6.89 Hz, 1H, CH), 5.01 (d, *J* = 17.2 Hz, 1H, =C*H*H), 5.04 (d, *J* = 10.3 Hz, 1H, =CH*H*), 5.94–6.01 (m, 1H, C*H*=CH_2), 7.17–7.23 (m, 3H, aromatic), 7.29 (t, *J* = 7.57 Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$) δ 26.1, 42.3, 44.0, 44.1, 114.4, 126.4, 127.8, 128.5, 140.9, 143.4, 213.4. HRMS (ESI) *m*/*z*: calcd for $C_{15}H_{20}NaO$ $[M+Na]^+$, 239.1406; found, 239.1408. HPLC condition: CHIRALPAK IE-3 (0.46 cmϕ x 25

cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 220 nm light; t_R, 12.1 min (minor), 12.7 min (major). $[\alpha]_D^{25}$ –38.4 (*c* 1.00, $CHCl_3$).

*5.4.12. 1,3-Diphenylpent-4-en-1-one (**3q**)*

(*E*)-3-Phenylprop-2-en-1-yl 3-oxo-3-phenylpropanoate (**2q**) (500 mM in CH_2Cl_2, 1.00 mL, 140 mg, 0.500 mmol), 18 h. SiO_2-chromatography (10 g, 20:1 hexane–EtOAc eluent) to give 1,3-diphenylpent-4-en-1-one (**3q**) (106 mg, 90% yield, >99:1 er). ^{1}H NMR ($CDCl_3$)□δ 3.37 (dd, *J* = 16.6 and 6.30 Hz, 1H, C*H*H), 3.44 (dd, *J* = 16.6 and 7.45 Hz, 1H, CH*H*), 4.14 (q, *J* = 6.87 Hz, 1H, CH), 5.03 (d, *J* = 17.2 Hz, 1H, =C*H*H), 5.07 (d, *J* = 10.3 Hz, 1H, =CH*H*), 6.01–6.09 (m, 1H, C*H*=CH_2), 7.20 (t, *J* = 7.45 Hz, 1H, aromatic), 7.26–7.32 (m, 4H, aromatic), 7.44 (t, *J* = 7.45 Hz, 2H, aromatic), 7.55 (t, *J* = 7.45 Hz, 1H, aromatic), 7.93 (d, *J* = 8.59 Hz, 1H, aromatic). HPLC condition: CHIRALCEL OD-H (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 254 nm light; t_R, 35.5 min (minor), 37.9 min (major). $[\alpha]_D^{26}$ –0.312 (*c* 1.10, $CHCl_3$). ^{1}H-NMR data were consistent with reported values [15].

*5.4.13. 3-Methyl-4-phenylhex-5-en-2-one (**3r**)*

(*E*)-3-Phenylprop-2-en-1-yl 2-methyl-3-oxobutanoate (**2r**) (500 mM in CH_2Cl_2, 1.00 mL, 116 mg, 0.500 mmol); 18 h. SiO_2-chromatography (10 g, 20:1 hexane–EtOAc eluent) to give 3-methyl-4-phenylhex-5-en-2-one (**3r**) (74.4 mg, 79% yield, 99:1 er and >99:1 er) as 1.00:1.08 diastereomeric mixture. Diastereomers could not be separated. Major diastereomer: ^{1}H NMR ($CDCl_3$)□δ 0.88 (d, *J* = 6.89 Hz, 3H, CHC*H*$_3$), 2.17 (s, 3H, $COCH_3$), 2.92–3.01 (m, 2H, CHCH), 4.99–5.04 (m, 2H, =CH_2), 5.87–6.00 (m, 1H, C*H*=CH_2), 7.13–7.34 (m, 5H, aromatic). Minor diastereomer: ^{1}H NMR ($CDCl_3$)□δ 1.14 (d, *J* = 6.89 Hz, 3H, CHC*H*$_3$), 1.88 (s, 3H, $COCH_3$), 3.43–3.49 (m, 2H, CHCH), 5.09 (d, *J* = 8.95 Hz, 1H, =C*H*H), 5.11 (d, *J* = 15.8 Hz, 1H, =CH*H*), 5.87–6.00 (m, 1H, C*H*=CH_2), 7.13–7.34 (m, 5H, aromatic). HPLC condition: CHIRALPAK IE-3 (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 220 nm light; t_R, 15.4 min (minor), 17.4 min (major) and 20.6 min (minor), 22.3 (major). $[\alpha]_D^{27}$ +46.3 (*c* 1.00, $CHCl_3$). ^{1}H-NMR data were consistent with reported values [27].

*5.4.14. 2-(1-Phenylprop-2-en-1-yl)cyclopentanone (**3t**)*

(*E*)-3-Phenylprop-2-en-1-yl 1-oxocyclopent-2-ylcarboxylate (**2t**) (500 mM in CH_2Cl_2, 1.00 mL, 122 mg, 0.500 mmol); 18 h. SiO_2-chromatography (10 g, 15:1 hexane–EtOAc eluent) to give 2-(1-phenylprop-2-en-1-yl)cyclopentanone (**3t**) (85.2 mg, 85% yield, and) as 1.00:1.10 diastereomeric mixture. $[\alpha]_D^{26}$ –53.0 (*c* 1.00, $CHCl_3$). HRMS (ESI) *m/z*: calcd for $C_{14}H_{16}NaO$ $[M+Na]^+$, 223.1093; found, 360.0190. The diastereomers were partially separated by preparative TLC (20 cm x 20 cm, 2 mm thickness plate, hexane–Et_2O 5:1 eluent). *Syn*-**3t**: ^{1}H NMR ($CDCl_3$) δ 1.50–1.60 (m, 1H, cyclopentyl), 1.65–1.80 (m, 2H, cyclopentyl), 1.85–1.94 (m, 1H, cyclopentyl), 2.00–2.18 (m, 1H, cyclopentyl), 2.21–2.28 (m, 1H, cyclopentyl), 2.54–2.60 (m, 1H, cyclopentyl), 3.88 (t, *J* = 5.51 Hz, 1H, CH), 5.09 (d, *J* = 1.72 Hz, 1H, =C*H*H), 5.15 (d, *J* = 10.3 Hz, 1H, =CH*H*), 6.16–6.25 (m, 1H, C*H*=CH_2), 7.16 (d, *J* = 7.57 Hz, 2H, aromatic), 7.20 (t, *J* = 7.57 Hz, 1H, aromatic), 7.27 (t, *J* = 7.57 Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$) δ 20.5, 26.4, 38.7, 48.3, 53.0, 115.1, 126.6, 128.3, 128.8, 139.7, 141.2, 219.7. >99:1 er (HPLC condition: CHIRALPAK IE-3 (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 220 nm light; t_R, 23.6 min (minor), 25.7 min (major)). *Anti*-**3t**: ^{1}H NMR ($CDCl_3$) δ 1.67–1.75 (m, 1H, cyclopentyl), 1.85–1.94 (m, 1H, cyclopentyl), 1.95–2.09 (m, 2H, cyclopentyl), 2.10–2.18 (m, 1H, cyclopentyl), 2.29–2.37 (m, 1H, cyclopentyl), 2.47–2.55 (m, 1H, cyclopentyl), 3.93 (dd, *J* = 8.26 and 4.13 Hz, 1H, CH), 5.06 (d, *J* = 1.72 Hz, 1H, =C*H*H), 5.11 (d, *J* = 9.64 Hz, 1H, =CH*H*), 5.98–6.05 (m, 1H, C*H*=CH_2), 7.19–7.27 (m, 3H, aromatic), 7.31 (t, *J* = 7.57 Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$) δ 20.6, 25.7, 38.9, 48.6, 54.6, 117.3, 126.4, 127.9, 128.5, 137.3, 141.7, 219.0. 99:1 er (HPLC condition: CHIRALPAK IE-3 (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 220 nm light; t_R, 23.8 min (major), 25.8 min (minor)). *Syn*/*anti* stereochemistry was assigned by comparison of ^{1}H-NMR spectra with reported values [28].

5.5. Cross-over experiments

A 10-mM solution of (*R*)-**1** (1.00 mL, 10.0 μmol) was transferred to a 5-mL Young Schlenk, and then concentrated. To the residue was added a solution of (*E*)-3-phenylprop-2-en-1-yl 3-oxobutanoate (**2a**) (1.00 M in CH_2Cl_2, 0.500 mL, 109 mg, 0.500 mmol) and a solution of (*E*)-3-(4-methylphenyl)prop-2-en-1-yl 3-phenyl-3-oxopropanoate (1.00 M in CH_2Cl_2, 0.500 mL, 147 mg, 0.500 mmol). The resulting yellow solution was stirred for 6 h at 60 °C. The whole system was cooled to rt and concentrated to afford a colorless oil. This was subjected to ^{1}H-NMR analysis to determine the conversion and the yield. The mixture was separated by SiO_2-chromatography (10 g, hexane–EtOAc 10:1 eluent) to give 4-phenylhex-5-en-2-one (**3a**) (80.2 mg, 92% yield, 99:1 er) and 1-phenyl-3-(*p*-tolyl)pent-4-en-1-one (**3u**) (113 mg, 90% yield, >99:1 er), respectively. **3u**: ^{1}H NMR ($CDCl_3$)□δ 2.31 (s, 3H, CH_3), 3.34 (dd, *J* = 16.5 and 6.89 Hz, 1H, C*H*H), 3.42 (dd, *J* = 16.5 and 7.57 Hz, 1H, CH*H*), 4.10 (q, *J* = 6.89 Hz, 1H, CH), 5.02 (d, *J* = 17.9 Hz, 1H, =C*H*H), 5.05 (d, *J* = 10.3 Hz, 1H, =CH*H*), 6.00–6.06 (m, 1H, C*H*=CH_2), 7.11 (d, *J* = 7.57 Hz, 2H, aromatic), 7.15 (d, *J* = 7.57 Hz, 2H, aromatic), 7.45 (t, *J* = 7.57 Hz, 2H, aromatic), 7.55 (t, *J* = 7.57 Hz, 1H, aromatic), 7.93 (d, *J* = 8.26 Hz, 1H, aromatic). HPLC condition: CHIRALPAK IB-3 (0.46 cmϕ x 25 cm); hexane–2-propanol 99:1 eluent, 0.5 mL/min; 220 nm light; t_R, 12.5 min (major), 13.5 min (minor). $[\alpha]_D^{27}$ +1.55 (*c* 1.02, $CHCl_3$). ^{1}H-NMR data of **3u** were consistent with reported values [15].

5.6. NMR experiments

A 10-mM solution of (*R*)-**1** (0.500 mL, 5.00 μmol) was transferred to a dry and Ar-filled 5-mm Young-type NMR tube. The solution was concentrated and to this was added $CDCl_3$ (0.50 mL). The resulting suspension was heated at 60 °C for 30 min to be a clear yellow solution. To the solution was added a solution of cinnamyl benzoate (**7**) (10.0 mM in $CDCl_3$, 0.500 mL, 2.38 mg, 5.00 μmol). The solution was subjected to ^{1}H-NMR analysis at 25 and 60 °C.

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Supplementary Material

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Declaration of interests

☑ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: