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Chiral Bis(imidazolinyl)phenyl NCN Pincer Rhodium(III) Catalysts for Enantioselective Allylation of Aldehydes and Carbonyl−Ene Reaction of Trifluoropyruvates

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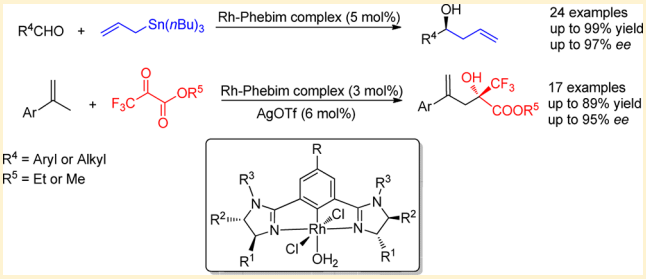
Supporting Information

ABSTRACT: Chiral NCN pincer rhodium(III) complexes with bis(imidazolinyl)phenyl ligands were found to be effective catalysts for the allylation of a variety of electronically and structurally diverse aldehydes with allyltributyltin, giving the corresponding optically active homoallylic alcohols in high yields with enantioselectivities of up to 97% *ee*. These complexes were also applied in the carbonyl−ene reaction of ethyl or methyl trifluoropyruvate with various 2-arylpropenes. With the aid of silver trifluoromethanesulfonate, the pincer rhodium(III) catalysts could catalyze the reaction to provide the corresponding chiral α-hydroxy-α-trifluoromethyl esters in good yields with high stereoselectivities (up to 95% *ee*).



INTRODUCTION

The uniquely intramolecular, terdentate coordination of pincer ligands to metal centers in a meridional fashion through σ and/or dative bonds results in transition-metal pincer complexes that exhibit generally high stabilities toward heat, air, and moisture. Since the independent pioneering work of Shaw[1] and van Koten and Noltes[2] in the 1970s, a wide variety of chemical motifs and various transition metals have been introduced into pincer skeletons. By systematic ligand modifications and/or variation of the metal center, it has been possible to readily control the reactivities, stabilities, and other important properties of the pincer metal complexes. Consequently, such complexes have been widely utilized in organic synthesis, organometallic catalysis, materials science, and the related areas.[3] Although these species have been found to be particularly useful as catalysts in a number of metal-mediated organic transformations, the development of known or new chiral pincer metal complexes with excellent catalytic activities and stereoselectivities still constitutes one of the most challenging and formidable endeavors in the field of pincer chemistry. Baratta and co-workers[4] demonstrated that a series of chiral CNN pincer Ru(II) and Os(II) complexes show high enantioselectivities in ketone hydrogenation (up to 99% *ee*) and transfer hydrogenation (up to 99% *ee*). Recently, Duan and co-workers[5] extended the enantioselective hydrophosphination of several kinds of electron-deficient alkenes with secondary phosphines using the known bisphosphine PCP pincer Pd(II) catalysts, giving chiral phosphine derivatives with excellent enantioselectivities. In addition, it is worth mentioning that chiral NCN pincer metal complexes (e.g., M = Pd,[6] Pt,[7] Ni,[8] Ru,[9] Rh,[10] Ir[10d,11] and Fe[12]) with tridentate bis(oxazolinyl)-phenyl (Phebox) ligands have been extensively investigated and used in asymmetric catalysis, with most of the work being reported by Nishiyama.[13] Among them, the Rh−Phebox complexes have attracted much attention and displayed high stereoselectivities in various catalytic asymmetric reactions such as conjugate reductions (up to 99% *ee*),[10g,h] reductive aldol reactions (up to 98% *ee*),[10d,e] β-boration of α,β-unsaturated carbonyl compounds (up to 97% *ee*),[10i] and alkynylation of α-keto esters (up to >99% *ee*).[10f] On the other hand, we have reported C_2-symmetric NCN pincer Pd(II),[14] Pt(II),[15] and Ni(II)[16] complexes with chiral 1,3-bis(2′-imidazolinyl)phenyl (Phebim) ligands, which are structural analogues of Phebox ligands. Compared with Phebox ligands, Phebim ligands have the advantage of further tunability of the electron density and steric bulkiness of the ligands by appropriate choice of the substituent on the additional nitrogen atom.[17] The preliminary attempt using a Pd−Phebim complex with a (4*S*)-phenyl substituent as the catalyst for the asymmetric addition of diphenylphosphine to chalcone gave the expected adduct in 84% yield with 85% *ee*.[14b] Also, a cationic Pt−Phebim complex activated the asymmetric Friedel−Crafts alkylation of indoles with nitroalkenes with up to 83% *ee*.[15b] During our study, Nakamura and co-workers[18] also explored the applications of Pd−Phebim complexes in asymmetric catalysis. They corroborated that the Pd complexes are highly enantioselective catalysts for the reaction of benzyl nitriles with imines (up to 92% *ee*), the aza-Morita−Baylis−Hillman reaction of acrylonitrile with imines (up to 98% *ee*), the decarboxylative Mannich-type reaction of cyanoacetic acids with imines (up to 90% *ee*), and allylation of ketimines (up to 95% *ee*). Furthermore, it was

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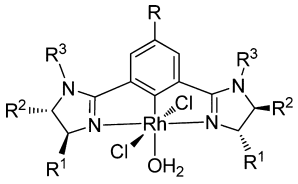
found that the related bis(imidazolidine) NCN pincer Pd(II) complexes exhibited high performance in the asymmetric reaction of nitroalkenes with malononitriles (up to 93% *ee*).[19] Very recently, we reported the first synthesis of NCN pincer Rh(III) complexes with bis(imidazolinyl)phenyl ligands, including (Phebim)$RhCl_2(H_2O)$ complexes **1a–e** (Scheme 1)

Scheme 1. Chiral C_2-Symmetric NCN Pincer Rhodium(III) Complexes with Bis(imidazolinyl)phenyl Ligands



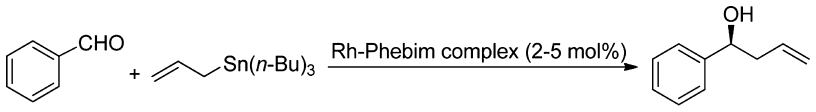
1a R = R^2 = H, R^1 = Ph, R^3 = *p*-Tol
1b R = R^2 = H, R^1 = Bn, R^3 = *p*-Tol
1c R = H, R^1 = R^2 = Ph, R^3 = Cy
1d R = H, R^1 = R^2 = Ph, R^3 = *p*-Tol
1e R = NO_2, R^1 = R^2 = Ph, R^3 = *p*-Tol
1f R = R^2 = H, R^1 = *t*-Bu, R^3 = *p*-Tol

as well as the corresponding (Phebim)$Rh(OAc)_2(H_2O)$ complexes. The potential of these complexes in the catalytic asymmetric alkynylation of trifluoropyruvates with terminal alkynes was evaluated.[20] The results of the studies indicated that in the presence of 3.0 mol % (Phebim)$Rh(OAc)_2(H_2O)$ complex, excellent enantioselectivities (21 examples, 94–99% *ee*) could be obtained in the alkynylation of ethyl or methyl trifluoropyruvate with a range of terminal alkynes, including aromatic and heteroaromatic alkynes and conjugated enynes. Moreover, the C_2-symmetric Rh–Phebim complexes consistently provided better enantioselectivities than the related C_2- or C_1-symmetric Rh–Phebox complexes[10f] in the addition of aromatic terminal alkynes to ethyl trifluoropyruvate under similar reaction conditions. Encouraged by the above results and also in continuation of our investigations of the pincer metal complexes,[21] we decided to further determine the activity and stereocontrolling potential of the chiral pincer Rh–Phebim complexes. The highly enantioselective allylation of aldehydes and carbonyl–ene reaction of trifluoropyruvates using these complexes as the catalysts are described in this report.

RESULTS AND DISCUSSION

Allylation of Aldehydes. Catalytic asymmetric allylation of aldehydes with allyltributyltin can provide direct, efficient access to potentially useful chiral homoallylic alcohols as important building blocks for the construction of various biologically active compounds. Therefore, there has been intense research activity in this area in recent years, leading to the development of a large and diverse array of chiral ligands attached to metals such as Ti,[22] In,[23] and Bi.[24] Although a lot of achiral pincer complexes, particularly pincer Pd(II) complexes with structural diversity,[3n,25] have been successfully applied in the allylation of aldehydes and exhibited high catalytic activity, the chiral ones in the asymmetric allylation have not afforded impressive enantioselectivitities.[10a,b,26] The highest enantioselectivity was only 62% *ee*[26a] when chiral pincer Pd(II) complexes were utilized as the catalysts for this transformation. Better enantioselectivities were obtained with 5 mol % pincer Rh–Phebox catalysts, albeit with a limited substrate scope (eight examples, 35–80% *ee*).[10a,b] Moreover, excellent enantioselectivities (up to 99% *ee*) have been achieved by using methallyltributyltin instead of allyltributyltin as the allyl source.[10c] It was believed that these Rh(III) complexes acted as traditional Lewis acid catalysts in the above allylation reactions. Overall, there is still much room for improvement in the chiral pincer complex-catalyzed enantioselective allylation of aldehydes with allyltributyltin. Also, literature results revealed that the chiral Rh–Phebox complexes were rather promising in this reaction. Therefore, it seemed to be necessary to investigate the potential of our previously reported structurally very related pincer Rh–Phebim complexes in the asymmetric allylation. The current experiment began with the allylation of benzaldehyde with allyltributyltin in the presence of 5 mol % pincer Rh–Phebim complex at room temperature in CH_2Cl_2 as the model

Table 1. Optimization of Reaction Conditions for the Asymmetric Allylation of Benzaldehyde with Allyltributyltin Using the Pincer Rh–Phebim Complexes 1 as Catalysts[a]



2a **3** (1.5 equiv) **4a**

entry	cat.	solvent	yield (%)[b]	*ee* (%)[c,d]
1	**1a**	CH_2Cl_2	52	30
2	**1b**	CH_2Cl_2	71	77
3	**1c**	CH_2Cl_2	41	40
4	**1d**	CH_2Cl_2	46	42
5	**1e**	CH_2Cl_2	35	45
6	**1f**	CH_2Cl_2	40	50
7[e]	**1b**	CH_2Cl_2	92	90
8[e,f]	**1b**	CH_2Cl_2	83	86
9[e,g]	**1b**	CH_2Cl_2	57	83
10[e]	**1b**	$CHCl_3$	46	77
11[e]	**1b**	$ClCH_2CH_2Cl$	91	90
12[e]	**1b**	toluene	67	69
13[e]	**1b**	THF	41	47

[a]Reaction conditions: benzaldehyde (0.20 mmol), allyltributyltin (0.30 mmol), cat. **1** (5 mol %), solvent (2 mL), rt, 6 h. [b]Isolated yields. [c]Determined by chiral HPLC. [d]The absolute configuration of the product was assigned to be *S* by comparison of optical rotation with that in ref 10a,b. [e]In the presence of 4 Å molecular sieves (250 mg). [f]Cat. **1b** (4 mol %). [g]Cat. **1b** (2 mol %), 12 h.

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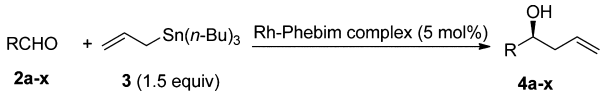
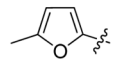
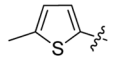
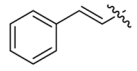
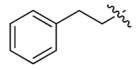
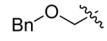
Table 2. Asymmetric Allylation of Aldehydes with Allyltributyltin Using the Pincer Rh−Phebim Complex 1b as the Catalyst[a]



Entry	R	Product	Yield[b] (%)	*ee*[c,d] (%)
1	Ph	**4a**	92	90(61)[e]
2	4-$O_2NC_6H_4$	**4b**	99	80
3	3-$O_2NC_6H_4$	**4c**	86	85
4	4-$CF_3C_6H_4$	**4d**	99	86
5	4-ClC_6H_4	**4e**	92	86
6	2,4-$Cl_2C_6H_3$	**4f**	97	84
7	4-BrC_6H_4	**4g**	95	88(43)[e]
8	3-BrC_6H_4	**4h**	92	90
9	2-$MeOC_6H_4$	**4i**	82	93
10	3-$MeOC_6H_4$	**4j**	80	92
11	4-$MeOC_6H_4$	**4k**	85	88(80)[e]
12	4-MeC_6H_4	**4l**	92	97
13	3-MeC_6H_4	**4m**	80	87
14	4-NCC_6H_4	**4n**	80	80
15	4-$Me_2NC_6H_4$	**4o**	84	92
16	1-naphthyl	**4p**	88	94
17	2-naphthyl	**4q**	90	92
18		**4r**	82	90(58)[e]
19		**4s**	78	93
20		**4t**	84	95
21		**4u**	80	92
22		**4v**	95	86(77)[e]
23		**4w**	80	37(63)[e,f]
24		**4x**	80	85(35)[e]

[a]Reaction conditions: aldehyde (0.20 mmol), allyltributyltin (0.30 mmol), cat. **1b** (5 mol %), CH_2Cl_2 (2 mL), 4 Å molecular sieves (250 mg), rt, 6 h. [b]Isolated yields. [c]Determined by chiral HPLC. [d]The absolute configurations of the products were assigned to be *S* by comparison of optical rotations with those in ref 10a,b or by analogy. [e]Literature results from ref 10a,b with Rh−Phebox catalysts are given in parentheses. [f]The absolute configuration of the product was assigned to be *R* by comparison of the optical rotation with that in ref 10a,b.

reaction. It was found that complex **1b** with the (4*S*)-benzyl substituent gave the best results among the six Rh−Phebim complexes, producing the expected homoallylic alcohol **4a** in 71% yield with 77% *ee* (Table 1, entries 1−6). Gratifyingly,

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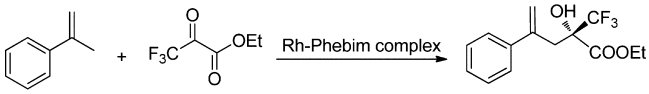
both the yield and enantioselectivity were significantly improved by the addition of 4 Å molecular sieves (92% yield with 90% *ee*; entry 7). When the catalyst loading was reduced from 5 mol % to 4 or 2 mol %, a decrease in both the yield and enantioselectivity was observed, although good enantioselectivities could still be obtained (entries 8 and 9). In addition, CH_2Cl_2 was found to be the most appropriate solvent for the reaction among the tested solvents, including CH_2Cl_2, $CHCl_3$, $ClCH_2CH_2Cl$, toluene, and THF (entry 7 vs entries 10−13).

Under the above optimized reaction conditions, various aldehydes reacted smoothly with allyltributyltin to give the corresponding chiral homoallylic alcohols in high chemical yields and enantioselectivities (Table 2). Both electron-donating and electron-withdrawing groups in the substituted benzaldehydes were tolerated, and good to excellent enantioselectivities were obtained (80−97% *ee*; entries 1−15). Roughly, the electron-withdrawing group showed some beneficial effect on the yield of the catalysis product while the electron-donating group was beneficial for the enantioselectivity compared with benzaldehyde. The position of the group on the aryl ring also had some influence on the yield and/or enantioselectivity. For example, the reactions of 2-, 3-, and 4-methoxybenzaldehyde with allyltributyltin afforded the expected adducts in 82, 80, 85% yield, respectively, with 93, 92, and 88% *ee*, respectively (entries 9−11). For 1- and 2-naphthaldehyde, excellent enantioselectivities were achieved (94 and 92% *ee*, respectively; entries 16 and 17). Particularly, when heteroaromatic aldehydes such as thiophene- and furan-2-carboxaldehyde were used as substrates, excellent stereocontrol of the alcohol products was always observed (90−95% *ee*; entries 18−21). These aldehydes are somewhat special since they bear ligating atoms that may deactivate the catalyst. In fact, in the case of pyridine-2-carboxaldehyde, no allylation occurred under the present reaction conditions (data not shown in Table 2). Besides aromatic and heteroaromatic aldehydes, allylations of several aliphatic aldehydes were also examined. It was found that *trans*-*β*-phenylacrolein, which is an enal, afforded high enantioselectivity (86% *ee*; entry 22), while for 3-phenylpropanal, a rather low enantiomeric excess was obtained (37% *ee*; entry 23). Nonetheless, the use of *α*-benzyloxyacetaldehyde as the substrate gave the corresponding chiral homoallylic alcohol with good stereocontrol (85% *ee*; entry 24). The above results confirm that the Rh−Phebim complexes are highly enantioselective catalysts for the asymmetric allylation of aldehydes with allyltributyltin. It is worth pointing out that in the allylation of six specific aldehydes, the Rh−Phebim complexes invariably provided much better enantioselectivities than the related Rh−Phebox complexes[10a,b] under similar reaction conditions (entries 1, 7, 11, 18, 22, and 24). Furthermore, to the best of our knowledge, Rh−Phebim catalysts are the most effective among the pincer catalysts for the studied allylation in regard to the scope of aldehyde substrate and the product enantioselectivity.

Carbonyl−Ene Reaction. The chiral Lewis acid- or Brønsted acid-catalyzed enantioselective carbonyl−ene reaction of trifluoropyruvates,[27] which can construct a tetrasubstituted stereogenic center, continues to receive considerable attention in asymmetric synthesis because the obtained *α*-CF_3-substituted optically active homoallylic alcohols are important intermediates for drug molecules. On the basis of the successful application of the Rh−Phebim complexes in the aforementioned asymmetric allylation, where they may act as Lewis acid catalysts similar to the Rh−Phebox complexes,[10a−c] it was of interest to further explore their performance in the Lewis acid-catalyzed carbonyl−ene reaction. To the best of our knowledge, there is no report on the use of pincer catalysts in this reaction. The addition of 2-phenylpropene to ethyl trifluoropyruvate was selected as the model reaction, and a brief optimization of reaction conditions is summarized in Table 3. No reaction

Table 3. Optimization of the Reaction Conditions for the Asymmetric Carbonyl−Ene Reaction of Ethyl Trifluoropyruvate Using the Pincer Rh−Phebim Complexes 1 as Catalysts[a]



5a 6a 7a

entry	cat.	solvent	additive	yield (%)[b]	*ee* (%)[c,d]
1	**1a**	$ClCH_2CH_2Cl$	–	0	–
2	**1a**	$ClCH_2CH_2Cl$	$AgSbF_6$	21	33
3	**1b**	$ClCH_2CH_2Cl$	$AgSbF_6$	31	8
4	**1c**	$ClCH_2CH_2Cl$	$AgSbF_6$	51	0
5	**1d**	$ClCH_2CH_2Cl$	$AgSbF_6$	10	0
6	**1e**	$ClCH_2CH_2Cl$	$AgSbF_6$	15	9
7	**1f**	$ClCH_2CH_2Cl$	$AgSbF_6$	82	54
8	**1f**	$ClCH_2CH_2Cl$	$AgBF_4$	74	39
9	**1f**	$ClCH_2CH_2Cl$	AgOTf	89	93
10[e]	**1f**	$ClCH_2CH_2Cl$	AgOTf	<5	n.d.[f]
11	**1f**	$ClCH_2CH_2Cl$	Me_3SiOTf	<5	n.d.[f]
12	**1f**	CH_2Cl_2	AgOTf	88	89
13	**1f**	$CHCl_3$	AgOTf	49	53
14	**1f**	toluene	AgOTf	41	40

[a]Reaction conditions: ethyl trifluoropyruvate (0.20 mmol), 2-phenylpropene (0.24 mmol), Rh complex **1** (3 mol %), additive (6 mol %), solvent (2 mL), rt, 16 h. [b]Isolated yields. [c]Determined by chiral HPLC. [d]The absolute configuration of the product was assigned to be *S* by comparison of optical rotation with that in ref 27c. [e]3 mol % AgOTf. [f]Not determined.

occurred in the presence of Rh−Phebim complex **1a** containing the (4*S*)-phenyl substituent as the catalyst (entry 1). When 2 equiv of $AgSbF_6$ relative to complex **1a** was added to the reaction mixture to enhance the Lewis acidity of the Rh(III) catalyst, the expected product could be isolated, albeit in rather modest yield and enantioselectivity (21% yield with 33% *ee*; entry 2). When the other five Rh−Phebim complexes **1b−f** were examined in the presence of $AgSbF_6$ (entries 3−7), it was found that both the reactivity and selectivity of the reaction were greatly influenced by the ligand structure of the Rh−Phebim complex. Although complex **1b** with the (4*S*)-benzyl substituent gave the best results in the allylation, it afforded only 8% *ee* in the carbonyl−ene reaction (entry 3). Pleasingly, complex **1f** with the (4*S*)-*tert*-butyl substituent provided hopeful results (82% yield with 54% *ee*; entry 7). Further studies revealed that the anion of the Ag(I) salt played a key role for effective stereocontrol of the reaction (entries 7−9). When AgOTf instead of $AgSbF_6$ was used to abstract the chloride in complex **1f**, the enantioselectivity of the reaction was significantly improved to 93% *ee* (entry 9). It was found that the amount of AgOTf was also crucial for the reaction. With 1 equiv of AgOTf relative to complex **1f**, only a trace amount of the expected alcohol product was isolated (<5% yield; entry 10). When the reaction of ethyl trifluoropyruvate with 2-phenylpropene was carried out in the presence of 6 mol

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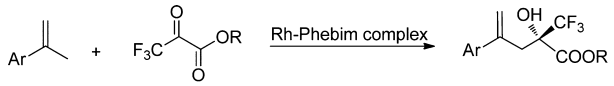
% AgOTf without the pincer Rh−Phebim complex, the expected product was not detected after stirring at room temperature in 1,2-dichloroethane (DCE) for 16 h (data not shown in Table 3). In addition, the use of Me_3SiOTf as an additive to activate the neutral pincer Rh−Phebim complex **1f** proved to be ineffective (entry 11). Finally, a quick survey of different solvents, including DCE, CH_2Cl_2, $CHCl_3$, and toluene indicated that DCE was the most appropriate solvent (entry 9 vs entries 12−14). Thus, the optimized conditions include using complex **1f** in the presence of 2 equiv of AgOTf as the catalyst and DCE as the solvent.

With the optimal conditions established, the scope of the reaction with respect to various alkenes was investigated (Table 4). A broad range of 2-arylpropenes (**5a−l**) underwent the desired reaction with trifluoropyruvates to provide the corresponding α-hydroxy-α- trifluoromethyl esters (**7a−q**) in high yields with good to excellent enantioselectivities. In the reaction of ethyl trifluoropyruvate, an evident electronic effect on the enantioselectivy was observed. In comparison with 2-phenylproene (93% *ee*; entry 1), 2-arylpropenes containing an electron-donating group such as alkyl on the phenyl group provided obviously lower stereoselectivities (74−89% *ee*; entries 2−5), while those with an electron-withdrawing group such as 4-F, 4-Cl, 4-Br, 3-Cl, or 3-Br on the phenyl ring gave comparable or slightly higher enantioselectivities (91−95% *ee*; entries 6−10). Similarly, 2-naphthylpropenes, which are more electron-rich than 2-phenylpropene, also afforded lower stereoselectivities (75 and 81% *ee*; entries 11 and 12). In addition, the asymmetric carbonyl−ene reaction of methyl trifluoropyruvate with several representative alkenes was also studied. Although good results (60−82% yield with 65−77% *ee*) could still be obtained, the yields and *ee* values were obviously inferior to those in the corresponding reactions of ethyl trifluoropyruvate (entries 13−17). In these reactions, an electron-withdrawing group on the phenyl ring of the 2-arylpropene had a detrimental effect on the stereoselectivity instead.

Table 4. Substrate Scope for the Catalytic Asymmetric Carbonyl−Ene Reaction of Trifluoropyruvates Using the Pincer Rh−Phebim Complex 1f as the Catalyst[a]



5a-l **6a** R = Et, **6b** R = Me **7a-q**

entry	Ar	R	product	yield (%)[b]	*ee* (%)[c,d]
1	Ph	Et	**7a**	89	93
2	4-MeC_6H_4	Et	**7b**	85	77
3	3-MeC_6H_4	Et	**7c**	85	89
4	4-EtC_6H_4	Et	**7d**	87	74
5	4-*t*BuC_6H_4	Et	**7e**	87	74
6	4-FC_6H_4	Et	**7f**	80	91
7	4-ClC_6H_4	Et	**7g**	88	95
8	3-ClC_6H_4	Et	**7h**	80	94
9	4-BrC_6H_4	Et	**7i**	85	94
10	3-BrC_6H_4	Et	**7j**	80	93
11	1-naphthyl	Et	**7k**	81	75
12	2-naphthyl	Et	**7l**	87	81
13	Ph	Me	**7m**	82	77
14	4-ClC_6H_4	Me	**7n**	81	70
15	3-ClC_6H_4	Me	**7o**	62	65
16	4-BrC_6H_4	Me	**7p**	80	71
17	3-BrC_6H_4	Me	**7q**	60	74

[a]Reaction conditions: trifluoropyruvate (0.20 mmol), alkene (0.24 mmol), Rh complex **1f** (3 mol %), AgOTf (6 mol %), $ClCH_2CH_2Cl$ (2 mL), rt, 16 h. [b]Isolated yields. [c]Determined by chiral HPLC. [d]The absolute configurations of the products were assigned to be *S* by comparison of optical rotations with those in ref 27c or by analogy.

In the enantioselective allylation of aldehydes with allyltin reagents catalyzed by pincer Rh−Phebox complexes, a detailed mechanistic study by Nishiyama and coauthors[10b] revealed that the (Phebox)$RhCl_2$ fragment generated by release of H_2O from the neutral pincer (Phebox)$RhCl_2(H_2O)$ complex was the catalytically active species. This fragment activates the carbonyl group of the aldehyde through coordination of the carbonyl oxygen to the rhodium center. The allyltin then attacks the activated aldehyde to give the homoallylic alcohol product. Thus, the allylation proceeds via a Lewis acid-catalyzed mechanism. In view of the high structural similarity between Rh−Phebim and Rh−Phebox complexes, it seems to be reasonable to deduce that the neutral (Phebim)$RhCl_2(H_2O)$ complexes **1** also act as traditional Lewis acid catalysts in the allylation. In fact, there is some evidence that the coordinated H_2O molecule in the (Phebim)$RhCl_2(H_2O)$ complex dissociates easily and that the carbonyl compound can coordinate to the Rh(III) center of the (Phebim)$RhCl_2$ fragment. In our previous studies, crystals of the corresponding acetone- or dichloromethane-coordinated complexes were always obtained when we performed recrystallization in acetone or dichloromethane to get crystals of (Phebim)$RhCl_2(H_2O)$ complexes.[20] This phenomenon means that in the allylation the (Phebim)-$RhCl_2(H_2O)$ complex can also release H_2O to give the (Phebim)$RhCl_2$ fragment, which can activate the aldehyde just as the (Phebox)$RhCl_2$ fragment does. In contrast to allylation, the Lewis acid-catalyzed carbonyl−ene reaction of trifluoropyruvate did not occur in the presence of (Phebim)-$RhCl_2(H_2O)$ complexes **1**. It seemed that the electrophilicity of the metal center in these neutral complexes was not high enough to activate trifluoropyruvate. Fortunately, the Lewis acidity of the complexes could be enhanced by abstraction of chloride from the Rh(III) center to form the corresponding cationic species. Not unexpectedly, the carbonyl−ene reaction proceeded in the presence of Ag(I) salts, particularly AgOTf. Since 2 equiv of AgOTf relative to Rh−Phebim complex **1** was essential for smooth reaction, an in situ-generated dicationic Rh(III) species, [(Phebim)$Rh(H_2O)$][$OTf]_2$, is considered to be the active catalyst, which can activate trifluoropyruvate through chelate coordination of both carbonyl oxygen atoms to the rhodium center. A catalytic cycle for the carbonyl−ene reaction is proposed in Scheme S1 in the Supporting Information.

CONCLUSIONS

In conclusion, we have shown that chiral NCN pincer Rh−Phebim complexes are highly enantioselective catalysts for the allylation of aldehydes with allyltributyltin, giving the corresponding catalysis products in high yields with enantioselectivities of up to 97% *ee*. The current process tolerates a range of aldehyde substrates under mild conditions, and the Rh−Phebim catalysts were found to be much superior to the closely related Rh−Phebox catalysts with respect to substrate scope and enantioselectivity. In addition, in the presence of AgOTf, the aforementioned Rh−Phebim complexes gave

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effective catalysts with high stereoselectivities (up to 95% *ee*) for the asymmetric carbonyl−ene reaction of trifluoropyruvates with 2-arylpropenes, a reaction which was catalyzed for the first time by pincer metal complexes. The scope of the alkene substrates are relatively broad. Further experiments to study the applications of the Rh−Phebim catalysts to other reactions are in progress.

EXPERIMENTAL SECTION

General. Solvents were dried with standard methods and freshly distilled prior to use if needed. The 2-arylpropenes were synthesized according to the literature methods.[28] All other chemicals were used as purchased. NMR spectra were recorded with $CDCl_3$ as the solvent and TMS as an internal standard. HRMS data were acquired on a Q-Tof Micro MS/MS ESI mass spectrometer.

Synthesis of the NCN Pincer (Phebim)$RhCl_2(H_2O)$ Complexes 1a−f. The ligands and the corresponding NCN pincer (Phebim)-$RhCl_2(H_2O)$ complexes **1a−f** were prepared according to the procedure reported previously by us.[20] The analytical data of the new complex **1f** is given in the next paragraph.

*(2,6-Bis((S)-4-tert-butyl-1-p-tolyl-4,5-dihydro-1H-imidazol-2-yl)-phenyl)$RhCl_2(H_2O)$ (**1f**).* Yellow solid (149.9 mg, 43%); mp 180−182 °C. $[\alpha]_D^{20}$ = +885 (*c* 0.156, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.6 Hz, 4H, ArH), 7.20 (d, *J* = 8.4 Hz, 4H, ArH), 6.63 (dd, *J* = 6.7, 8.7 Hz, 1H, ArH), 6.56−6.54 (m, 2H, ArH), 4.29 (app t, *J* = 11.8 Hz, 2H, NCH), 4.18 (dd, *J* = 9.2, 10.8 Hz, 2H, NCH*H*), 3.82 (dd, *J* = 9.2, 12.6 Hz, 2H, NCH*H*), 2.40 (s, 6H, CH_3), 1.62 (br s, 2H, OH_2), 1.32 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 138.4, 137.9, 134.8, 130.3, 128.2, 126.3, 121.8, 72.1, 56.9, 33.7, 26.9, 21.2. Anal. Found: C, 58.09; H, 6.01; N, 7.91. Calcd for $C_{34}H_{43}Cl_2N_4ORh$: C, 58.54; H, 6.21; N, 8.03.

General Procedure for the Asymmetric Allylation of Aldehydes with Allyltributyltin by the NCN Pincer (Phebim)-$RhCl_2(H_2O)$ Complexes 1. Under an argon atmosphere, to a suspension of 4 Å molecular sieves (250 mg) in CH_2Cl_2 (2 mL) was added the NCN pincer (Phebim)$RhCl_2(H_2O)$ complex **1** (0.01 mmol, 5.0 mol %), aldehyde (0.20 mmol), and allyltributyltin (0.30 mmol, 93.0 μL) at room temperature. After the resulting solution mixture was stirred at that temperature for 6 h, the residue was purified by preparative TLC on silica gel plates eluting with CH_2Cl_2 to afford the homoallylic alcohol.

*(S)-1-Phenylbut-3-en-1-ol (**4a**).*[10a,b,22−24,29,30] Pale-yellow oil (27.2 mg, 92%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 100/5, flow rate = 0.5 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 15.3 min, 17.5 min (major), 90% *ee*. $[\alpha]_D^{20}$ = −52.0 (*c* 0.840, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.25 (m, 5H), 5.85−5.75 (m, 1H), 5.18−5.12 (m, 2H), 4.72 (dd, *J* = 5.5, 7.4 Hz, 1H), 2.55−2.46 (m, 2H), 2.17 (br s, 1H, OH).

*(S)-1-(4-Nitrophenyl)but-3-en-1-ol (**4b**).*[22b,29,31a] Pale-yellow oil (38.3 mg, 99%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 48.9 min, 52.5 min (major), 80% *ee*. $[\alpha]_D^{20}$ = −45.5 (*c* 1.000, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 5.84−5.74 (m, 1H), 5.20−5.15 (m, 2H), 4.86 (dd, *J* = 4.7, 7.9 Hz, 1H), 2.59−2.53 (m, 1H), 2.50−2.42 (m, 2H).

*(S)-1-(3-Nitrophenyl)but-3-en-1-ol (**4c**).*[29,31a] Pale-yellow oil (33.2 mg, 86%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 41.8 min, 46.0 min (major), 85% *ee*. $[\alpha]_D^{20}$ = −48.2 (*c* 0.388, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (t, *J* = 1.8 Hz, 1H), 8.14−8.12 (m, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 5.85−5.75 (m, 1H), 5.22−5.17 (m, 2H), 4.87 (dd, *J* = 4.8, 7.8 Hz, 1H), 2.61−2.44 (m, 2H), 2.37 (br s, 1H, OH).

*(S)-1-(4-(Trifluoromethyl)phenyl)but-3-en-1-ol (**4d**).*[30,31b] Pale-yellow oil (42.8 mg, 99%). The enantiomeric excess was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 15.6 min (major), 16.9 min, 86% *ee*. $[\alpha]_D^{20}$ = −45.3 (*c* 0.524, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 5.83−5.73 (m, 1H), 5.19−5.15 (m, 2H), 4.78 (dd, *J* = 4.9, 7.8 Hz, 1H), 2.56−2.41 (m, 2H), 2.29 (br s, 1H, OH).

*(S)-1-(4-Chlorophenyl)but-3-en-1-ol (**4e**).*[23,24,30,31a,b] Pale-yellow oil (33.6 mg, 92%). The enantiomeric excess was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 100/2, flow rate = 0.5 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 29.1 min (major), 31.5 min, 86% *ee*. $[\alpha]_D^{20}$ = −43.6 (*c* 0.520, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.26 (m, 4H), 5.82−5.72 (m, 1H), 5.17−5.13 (m, 2H), 4.70 (dd, *J* = 5.2, 7.6 Hz, 1H), 2.53−2.40 (m, 2H), 2.19 (br s, 1H, OH).

*(S)-1-(2,4-Dichlorophenyl)but-3-en-1-ol (**4f**).*[32] Pale-yellow oil (42.1 mg, 97%). The enantiomeric excess was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 11.8 min, 13.7 min (major), 84% *ee*. $[\alpha]_D^{20}$ = −81.9 (*c* 0.764, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 2.1 Hz, 1H), 7.26 (dd, *J* = 2.0, 8.4 Hz, 1H), 5.88−5.78 (m, 1H), 5.19−5.15 (m, 2H), 5.08 (dd, *J* = 3.5, 8.0 Hz, 1H), 2.62−2.56 (m, 1H), 2.36−2.29 (m, 2H).

*(S)-1-(4-Bromophenyl)but-3-en-1-ol (**4g**).*[10a,b,29] Pale-yellow oil (43.1 mg, 95%). The enantiomeric excess was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 100/1, flow rate = 1.0 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 31.3 min (major), 34.9 min, 88% *ee*. $[\alpha]_D^{20}$ = −42.5 (*c* 0.720, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 5.81−5.71 (m, 1H), 5.17−5.12 (m, 2H), 4.67 (dd, *J* = 5.3, 7.5 Hz, 1H), 2.52−2.39 (m, 2H), 2.26 (br s, 1H, OH).

*(S)-1-(3-Bromophenyl)but-3-en-1-ol (**4h**).*[33] Pale-yellow oil (41.8 mg, 92%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 24.9 min, 26.9 min (major), 90% *ee*. $[\alpha]_D^{20}$ = −39.5 (*c* 0.626, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.41−7.39 (m, 1H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 5.84−5.73 (m, 1H), 5.19−5.15 (m, 2H), 4.71−4.68 (m, 1H), 2.55−2.41 (m, 2H), 2.16 (br s, 1H, OH).

*(S)-1-(2-Methoxyphenyl)but-3-en-1-ol (**4i**).*[24,30] Pale-yellow oil (29.2 mg, 82%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 99.5/0.5, flow rate = 1.0 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 24.9 min (major), 29.4 min, 93% *ee*. $[\alpha]_D^{20}$ = −51.2 (*c* 0.364, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.27−7.22 (m, 1H), 6.98−6.94 (m, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 5.90−5.80 (m, 1H), 5.16−5.09 (m, 2H), 4.96 (t, *J* = 3.7 Hz, 1H), 3.85 (s, 3H, OCH_3), 2.62−2.47 (m, 3H).

*(S)-1-(3-Methoxyphenyl)but-3-en-1-ol (**4j**).*[30,31a,b] Pale-yellow oil (28.5 mg, 80%). The enantiomeric excess was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 99.5/0.5, flow rate = 1.0 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 42.6 min (major), 46.9 min, 92% *ee*. $[\alpha]_D^{20}$ = −48.0 (*c* 0.340, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.24 (m, 1H), 6.94−6.93 (m, 2H), 6.83−6.80 (m, 1H), 5.87−5.76 (m, 1H), 5.19−5.13 (m, 2H), 4.72 (t, *J* = 6.2 Hz, 1H), 3.82 (s, 3H, OCH_3), 2.57−2.45 (m, 2H), 2.07 (br s, 1H, OH).

*(S)-1-(4-Methoxyphenyl)but-3-en-1-ol (**4k**).*[10a,b,24,30,31a,b] Pale-yellow oil (30.3 mg, 85%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/3, flow rate = 0.5 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 28.1 min, 30.6 min (major), 88% *ee*. $[\alpha]_D^{20}$ = −49.8 (*c* 0.550, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.85−5.74 (m, 1H), 5.17−5.11 (m, 2H), 4.69 (t, *J* = 6.5 Hz, 1H), 3.80 (s, 3H, OCH_3), 2.49 (t, *J* = 6.8 Hz, 2H), 2.04 (br s, 1H, OH).

*(S)-1-(4-Methylphenyl)but-3-en-1-ol (**4l**).*[23b,24,29,30,31a] Pale-yellow oil (29.9 mg, 92%). The enantiomeric excess was determined on a Daicel Chiralcel OB-H column with hexane/2-propanol = 99/1, flow

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rate = 1.0 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 27.1 min (major), 35.5 min, 97% *ee*. $[\alpha]_D^{20} = -59.6$ (*c* 0.826, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.84−5.74 (m, 1H), 5.17−5.10 (m, 2H), 4.68 (t, *J* = 6.5 Hz, 1H), 2.51−2.47 (m, 2H), 2.34 (s, 3H, CH_3), 2.10 (br s, 1H, OH).

(S)-1-(3-Methylphenyl)but-3-en-1-ol (**4m**).[29,31b] Pale-yellow oil (25.9 mg, 80%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 18.7 min, 19.7 min (major), 87% *ee*. $[\alpha]_D^{20} = -48.0$ (*c* 0.100, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.23 (t, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 7.4 Hz, 1H), 5.86−5.76 (m, 1H), 5.19−5.13 (m, 2H), 4.70 (dd, *J* = 5.3, 7.6 Hz, 1H), 2.56−2.44 (m, 2H), 2.36 (s, 3H, CH_3), 2.03 (br s, 1H, OH).

(S)-1-(4-Cyanophenyl)but-3-en-1-ol (**4n**).[30,31c] Pale-yellow oil (27.7 mg, 80%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 46.7 min, 48.9 min (major), 80% *ee*. $[\alpha]_D^{20} = -59.7$ (*c* 0.378, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 5.82−5.72 (m, 1H), 5.19−5.14 (m, 2H), 4.80 (dd, *J* = 4.7, 7.9 Hz, 1H), 2.57−2.40 (m, 2H), 2.37 (br s, 1H, OH).

(S)-1-(4-(Dimethylamino)phenyl)but-3-en-1-ol (**4o**).[34] Pale-yellow oil (32.2 mg, 84%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 100/0.5, flow rate = 1.0 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 104.8 min (major), 115.6 min, 92% *ee*. $[\alpha]_D^{20} = -61.0$ (*c* 0.112, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 5.87−5.76 (m, 1H), 5.18−5.10 (m, 2H), 4.64 (t, *J* = 6.3 Hz, 1H), 2.94 (s, 6H, CH_3), 2.53−2.49 (m, 2H).

(S)-1-(Naphthalen-1-yl)but-3-en-1-ol (**4p**).[23b,24,31a] Pale-yellow oil (34.9 mg, 88%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow rate = 0.8 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 15.1 min (major), 18.7 min, 94% *ee*. $[\alpha]_D^{20} = -90.9$ (*c* 0.492, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 7.4 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 7.1 Hz, 1H), 7.52−7.45 (m, 3H), 5.97−5.86 (m, 1H), 5.51 (dd, *J* = 4.0, 8.3 Hz, 1H), 5.23−5.16 (m, 2H), 2.78−2.72 (m, 1H), 2.63−2.55 (m, 1H), 2.24 (br s, 1H, OH).

(S)-1-(Naphthalen-2-yl)but-3-en-1-ol (**4q**).[23,24,31a,b] Pale-yellow oil (35.7 mg, 90%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow rate = 0.8 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 17.9 min (major), 21.0 min, 92% *ee*. $[\alpha]_D^{20} = -57.9$ (*c* 0.550, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.82−7.78 (m, 4H), 7.49−7.43 (m, 3H), 5.86−5.76 (m, 1H), 5.19−5.12 (m, 2H), 4.87 (dd, *J* = 5.6, 7.2 Hz, 1H), 2.62−2.52 (m, 2H), 2.25 (br s, 1H, OH).

(S)-1-(Furan-2-yl)but-3-en-1-ol (**4r**).[10a,b,31b] Pale-yellow oil (22.6 mg, 82%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 99.5/0.5, flow rate = 0.5 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 70.6 min (major), 77.7 min, 90% *ee*. $[\alpha]_D^{20} = -14.0$ (*c* 0.100, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 0.9 Hz, 1H), 6.33 (dd, *J* = 1.9, 3.0 Hz, 1H), 6.25 (d, *J* = 3.2 Hz, 1H), 5.86−5.76 (m, 1H), 5.17 (t, *J* = 11.2 Hz, 2H), 4.75 (t, *J* = 6.4 Hz, 1H), 2.68−2.57 (m, 2H), 2.11 (br s, 1H, OH).

(S)-1-(5-Methylfuran-2-yl)but-3-en-1-ol (**4s**).[23a] Pale-yellow oil (23.7 mg, 78%). The enantiomeric excess was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 300/1, flow rate = 1.0 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 55.1 min (major), 64.4 min, 93% *ee*. $[\alpha]_D^{20} = -25.0$ (*c* 0.226, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 6.12 (d, *J* = 3.0 Hz, 1H), 5.90 (dd, *J* = 0.9, 3.0 Hz, 1H), 5.87−5.77 (m, 1H), 5.21−5.13 (m, 2H), 4.68 (t, *J* = 6.6 Hz, 1H), 2.63−2.59 (m, 2H), 2.28 (s, 3H, CH_3), 2.04 (br s, 1H, OH).

(S)-1-(Thiophen-2-yl)but-3-en-1-ol (**4t**).[24,31a,b] Pale-yellow oil (25.9 mg, 84%). The enantiomeric excess was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 100/5, flow rate = 0.5 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 20.2 min (major), 23.0 min, 95% *ee*. $[\alpha]_D^{20} = -31.0$ (*c* 0.280, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (dd, *J* = 1.6, 4.8 Hz, 1H), 6.99−6.96 (m, 2H), 5.88−5.78 (m, 1H), 5.22−5.15 (m, 2H), 4.98 (t, *J* = 6.4 Hz, 1H), 2.64−2.60 (m, 2H), 2.24 (br s, 1H, OH).

(S)-1-(5-Methylthiophen-2-yl)but-3-en-1-ol (**4u**). Pale-yellow oil (26.9 mg, 80%). The enantiomeric excess was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 100/2, flow rate = 0.8 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 19.3 min (major), 21.0 min, 92% *ee*. $[\alpha]_D^{20} = -21.1$ (*c* 0.408, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 6.75 (d, *J* = 3.4 Hz, 1H), 6.59 (dd, *J* = 0.9, 3.3 Hz, 1H), 5.88−5.77 (m, 1H), 5.20−5.13 (m, 2H), 4.87 (t, *J* = 6.4 Hz, 1H), 2.60−2.57 (m, 2H), 2.46 (s, 3H, CH_3), 2.18 (br s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 139.3, 134.0, 124.6, 123.8, 118.6, 69.5, 43.6, 15.4. HRMS (positive ESI): $[M + H]^+$ calcd for $C_9H_{13}OS$: 169.0687. Found: 169.0684.

(S)-(E)-1-Phenyl-1,5-hexadien-3-ol (**4v**).[10a,b,31a] Pale-yellow oil (33.1 mg, 95%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow rate = 0.5 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 14.6 min, 20.3 min (major), 86% *ee*. $[\alpha]_D^{20} = -20.7$ (*c* 0.760, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.39−7.37 (m, 2H), 7.33−7.29 (m, 2H), 7.25−7.21 (m, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.23 (dd, *J* = 6.3, 15.9 Hz, 1H), 5.91−5.80 (m, 1H), 5.20−5.15 (m, 2H), 4.38−4.33 (m, 1H), 2.47−2.34 (m, 2H), 1.90 (br s, 1H, OH).

(R)-1-Phenyl-5-hexen-3-ol (**4w**).[10a,b,31a] Pale-yellow oil (28.2 mg, 80%). The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow rate = 0.5 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 15.0 min (major), 20.0 min, 37% *ee*. $[\alpha]_D^{20} = +14.6$ (*c* 0.506, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.30−7.24 (m, 2H), 7.21−7.16 (m, 3H), 5.87−5.76 (m, 1H), 5.16−5.12 (m, 2H), 3.70−3.64 (m, 1H), 2.84−2.77 (m, 1H), 2.72−2.64 (m, 1H), 2.35−2.29 (m, 1H), 2.22−2.14 (m, 1H), 1.81−1.75 (m, 2H), 1.74 (br s, 1H, OH).

(S)-1-Benzyloxy-4-penten-2-ol (**4x**).[10b,31d] Pale-yellow oil (30.7 mg, 80%). The enantiomeric excess was determined on a Daicel Chiralcel OB-H column with hexane/2-propanol = 90/10, flow rate = 0.5 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 21.3 min (major), 24.9 min, 85% *ee*. $[\alpha]_D^{20} = +3.7$ (*c* 0.920, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37−7.24 (m, 5H), 5.87−5.76 (m, 1H), 5.13−5.07 (m, 2H), 4.54 (s, 2H), 3.86 (s, 1H), 3.50 (dd, *J* = 3.4, 9.5 Hz, 1H), 3.37 (dd, *J* = 7.4, 9.5 Hz, 1H), 2.49 (br s, 1H, OH), 2.25 (t, *J* = 6.7 Hz, 2H).

General Procedure for the Asymmetric Catalytic Carbonyl−Ene Reaction by the NCN Pincer (Phebim)$RhCl_2(H_2O)$ Complexes 1. Under an argon atmosphere, the NCN Pincer (Phebim)-$RhCl_2(H_2O)$ complex **1** (0.006 mmol, 3.0 mol %) was dissolved in 2 mL of $ClCH_2CH_2Cl$, and AgOTf (0.012 mmol, 6.0 mol %) was added. The resulting mixture was stirred at room temperature for 10 min. Ethyl trifluoropyruvate or methyl trifluoropyruvate (0.20 mmol) was added, followed by alkene (0.24 mmol), and then the resulting solution mixture was stirred at room temperature for 16 h. The residue was purified by preparative TLC on silica gel plates eluted with CH_2Cl_2/petroleum ether to afford the desired product.

(S)-Ethyl 2-Hydroxy-4-phenyl-2-(trifluoromethyl)pent-4-enoate (**7a**).[27c] Colorless oil (51.3 mg, 89%). The enantiomeric excess was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 100/1, flow rate = 1.0 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 12.9 min (major), 17.6 min, 93% *ee*. $[\alpha]_D^{20} = -60.3$ (*c* 0.992, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.34−7.26 (m, 5H), 5.39 (s, 1H), 5.28 (s, 1H), 4.07−3.99 (m, 1H), 3.78 (s, 1H), 3.67−3.58 (m, 1H), 3.28 (d, *J* = 14.0 Hz, 1H), 3.03 (d, *J* = 14.0 Hz, 1H), 1.11 (t, *J* = 7.2 Hz, 3H).

(S)-Ethyl 2-Hydroxy-4-(p-tolyl)-2-(trifluoromethyl)pent-4-enoate (**7b**).[27c] Colorless oil (51.4 mg, 85%). The enantiomeric excess was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 100/1, flow rate = 1.0 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 11.3 min (major), 15.2 min, 77% *ee*. $[\alpha]_D^{20} = -20.1$ (*c* 0.996, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.35 (s,

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1H), 5.22 (s, 1H), 4.09−4.01 (m, 1H), 3.76 (s, 1H), 3.72−3.64 (m, 1H), 3.25 (d, J = 14.0 Hz, 1H), 3.02 (d, J = 14.0 Hz, 1H), 2.33 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H).

*(S)-Ethyl 2-Hydroxy-4-(m-tolyl)-2-(trifluoromethyl)pent-4-enoate (**7c**).*[27a,d] Colorless oil (51.3 mg, 85%). The enantiomeric excess was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 100/1, flow rate = 0.5 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 9.6 min, 11.1 min (major), 89% *ee*. $[\alpha]_D^{20}$ = −69.7 (*c* 0.690, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (t, J = 7.5 Hz, 1H), 7.13−7.07 (m, 3H), 5.36 (s, 1H), 5.25 (s, 1H), 4.07−3.99 (m, 1H), 3.78 (s, 1H), 3.68−3.60 (m, 1H), 3.27 (d, J = 14.0 Hz, 1H), 3.01 (d, J = 14.0 Hz, 1H), 2.35 (s, 3H), 1.11 (t, J = 7.2 Hz, 3H).

*(S)-Ethyl 4-(4-Ethylphenyl)-2-hydroxy-2-(trifluoromethyl)pent-4-enoate (**7d**).*[27a,d] Colorless oil (55.0 mg, 87%). The enantiomeric excess was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 300/1, flow rate = 1.0 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 6.9 min, 7.4 min (major), 74% *ee*. $[\alpha]_D^{20}$ = −95.3 (*c* 0.770, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 5.36 (s, 1H), 5.23 (s, 1H), 4.06−3.98 (m, 1H), 3.78 (s, 1H), 3.66−3.58 (m, 1H), 3.26 (d, J = 14.0 Hz, 1H), 3.01 (d, J = 14.0 Hz, 1H), 2.63 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H), 1.10 (t, J = 7.2 Hz, 3H).

*(S)-Ethyl 4-(4-(tert-Butyl)phenyl)-2-hydroxy-2-(trifluoromethyl)-pent-4-enoate (**7e**).*[27a,d] Colorless oil (59.9 mg, 87%). The enantiomeric excess was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 300/1, flow rate = 1.0 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 10.1 min, 12.8 min (major), 74% *ee*. $[\alpha]_D^{20}$ = −59.0 (*c* 0.927, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 5.37 (s, 1H), 5.24 (s, 1H), 4.02−3.94 (m, 1H), 3.80 (s, 1H), 3.57−3.49 (m, 1H), 3.27 (d, J = 13.9 Hz, 1H), 3.00 (d, J = 13.8 Hz, 1H), 1.30 (s, 9H), 1.07 (t, J = 7.2 Hz, 3H).

*(S)-Ethyl 4-(4-Fluorophenyl)-2-hydroxy-2-(trifluoromethyl)pent-4-enoate (**7f**).*[27c] Colorless oil (49.0 mg, 80%). The enantiomeric excess was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 100/1, flow rate = 0.5 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 18.2 min (major), 19.7 min, 91% *ee*. $[\alpha]_D^{20}$ = −71.1 (*c* 0.604, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.28 (m, 2H), 7.02−6.98 (m, 2H), 5.34 (s, 1H), 5.25 (s, 1H), 4.13−4.05 (m, 1H), 3.79−3.71 (m, 1H), 3.77 (s, 1H), 3.23 (d, J = 14.1 Hz, 1H), 3.02 (d, J = 14.0 Hz, 1H), 1.16 (t, J = 7.2 Hz, 3H).

*(S)-Ethyl 4-(4-Chlorophenyl)-2-hydroxy-2-(trifluoromethyl)pent-4-enoate (**7g**).*[27c] Colorless oil (56.8 mg, 88%). The enantiomeric excess was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 100/1, flow rate = 0.5 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 12.5 min, 14.2 min (major), 95% *ee*. $[\alpha]_D^{20}$ = −65.0 (*c* 0.824, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.25 (m, 4H), 5.38 (s, 1H), 5.28 (s, 1H), 4.15−4.07 (m, 1H), 3.82−3.74 (m, 1H), 3.77 (s, 1H), 3.21 (d, J = 14.1 Hz, 1H), 3.03 (d, J = 14.1 Hz, 1H), 1.16 (t, J = 7.2 Hz, 3H).

*(S)-Ethyl 4-(3-Chlorophenyl)-2-hydroxy-2-(trifluoromethyl)pent-4-enoate (**7h**).*[27c] Colorless oil (51.6 mg, 80%). The enantiomeric excess was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 100/1, flow rate = 0.5 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 11.3 min, 13.8 min (major), 94% *ee*. $[\alpha]_D^{20}$ = −19.2 (*c* 0.476, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.31 (m, 1H), 7.26−7.20 (m, 3H), 5.40 (s, 1H), 5.32 (s, 1H), 4.15−4.07 (m, 1H), 3.80−3.72 (m, 1H), 3.78 (s, 1H), 3.23 (d, J = 14.1 Hz, 1H), 3.02 (d, J = 14.1 Hz, 1H), 1.17 (t, J = 7.2 Hz, 3H).

*(S)-Ethyl 4-(4-Bromophenyl)-2-hydroxy-2-(trifluoromethyl)pent-4-enoate (**7i**).*[27c] Colorless oil (62.4 mg, 85%). The enantiomeric excess was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 100/1, flow rate = 0.5 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 13.4 min, 15.0 min (major), 94% *ee*. $[\alpha]_D^{20}$ = −47.8 (*c* 1.000, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.6 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 5.38 (s, 1H), 5.28 (s, 1H), 4.15−4.07 (m, 1H), 3.83−3.73 (m, 1H), 3.76 (s, 1H), 3.21 (d, J = 14.1 Hz, 1H), 3.03 (d, J = 14.0 Hz, 1H), 1.17 (t, J = 7.2 Hz, 3H).

*(S)-Ethyl 4-(3-Bromophenyl)-2-hydroxy-2-(trifluoromethyl)pent-4-enoate (**7j**).* Colorless oil (58.7 mg, 80%). The enantiomeric excess was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 100/1, flow rate = 0.5 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 12.0 min, 14.8 min (major), 93% *ee*. $[\alpha]_D^{20}$ = −78.9 (*c* 0.528, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (t, J = 1.7 Hz, 1H), 7.42−7.39 (m, 1H), 7.27−7.25 (m, 1H), 7.18 (t, J = 7.8 Hz, 1H), 5.39 (s, 1H), 5.31 (s, 1H), 4.15−4.07 (m, 1H), 3.80−3.72 (m, 1H), 3.78 (s, 1H), 3.22 (d, J = 14.1 Hz, 1H), 3.01 (d, J = 14.0 Hz, 1H), 1.17 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 143.2, 139.9, 130.7, 129.8, 129.7, 125.6, 123.3 (q, J_{C-F} = 285 Hz), 122.3, 120.6, 77.2 (q, J_{C-F} = 29 Hz), 63.7, 36.8, 13.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.5. HRMS (positive ESI): $[M + Na]^+$ calcd for $C_{14}H_{14}O_3F_3BrNa$: 388.9976. Found: 388.9964.

*(S)-Ethyl 2-Hydroxy-4-(naphthalen-1-yl)-2-(trifluoromethyl)pent-4-enoate (**7k**).* Colorless oil (54.8 mg, 81%). The enantiomeric excess was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 100/1, flow rate = 1.2 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 4.9 min, 5.6 min (major), 75% *ee*. $[\alpha]_D^{20}$ = −76.8 (*c* 0.718, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85−7.75 (m, 4H), 7.51−7.45 (m, 3H), 5.52 (s, 1H), 5.38 (s, 1H), 3.97−3.89 (m, 1H), 3.80 (s, 1H), 3.55−3.46 (m, 1H), 3.40 (d, J = 14.0 Hz, 1H), 3.14 (d, J = 14.0 Hz, 1H), 1.00 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 140.5, 139.4, 133.6, 131.0, 128.4, 127.9, 126.1, 126.0, 125.8, 125.5, 125.1, 123.4 (q, J_{C-F} = 285 Hz), 122.6, 76.7 (q, J_{C-F} = 28 Hz), 63.4, 39.3, 13.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.9. HRMS (positive ESI): $[M + Na]^+$ calcd for $C_{18}H_{17}O_3F_3Na$: 361.1027. Found: 361.1027.

*(S)-Ethyl 2-Hydroxy-4-(naphthalen-2-yl)-2-(trifluoromethyl)pent-4-enoate (**7l**).*[27a,d] Colorless oil (58.9 mg, 87%). The enantiomeric excess was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 100/1, flow rate = 0.5 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 13.7 min, 15.6 min (major), 81% *ee*. $[\alpha]_D^{20}$ = −59.1 (*c* 0.770, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83−7.76 (m, 4H), 7.48−7.42 (m, 3H), 5.52 (s, 1H), 5.37 (s, 1H), 3.96−3.88 (m, 1H), 3.81 (s, 1H), 3.54−3.46 (m, 1H), 3.40 (d, J = 14.0 Hz, 1H), 3.14 (d, J = 14.0 Hz, 1H), 0.99 (t, J = 7.2 Hz, 3H).

*(S)-Methyl 2-Hydroxy-4-phenyl-2-(trifluoromethyl)pent-4-enoate (**7m**).*[27b] Colorless oil (45.0 mg, 82%). The enantiomeric excess was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 100/1, flow rate = 1.0 mL/min, and detection at a UV wavelength of 220 nm. Retention times: 14.9 min (major), 16.8 min, 77% *ee*. $[\alpha]_D^{20}$ = −86.3 (*c* 0.488, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.25 (m, 5H), 5.39 (s, 1H), 5.27 (s, 1H), 3.76 (s, 1H), 3.37 (s, 3H), 3.29 (d, J = 13.9 Hz, 1H), 3.02 (d, J = 14.0 Hz, 1H).

*(S)-Methyl 4-(4-Chlorophenyl)-2-hydroxy-2-(trifluoromethyl)-pent-4-enoate (**7n**).*[27b] Colorless oil (50.0 mg, 81%). The enantiomeric excess was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 300/1, flow rate = 1.0 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 13.3 min, 14.9 min (major), 70% *ee*. $[\alpha]_D^{20}$ = −14.4 (*c* 0.458, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.25 (m, 4H), 5.38 (s, 1H), 5.27 (s, 1H), 3.73 (s, 1H), 3.49 (s, 3H), 3.23 (d, J = 14.0 Hz, 1H), 3.02 (d, J = 14.0 Hz, 1H).

*(S)-Methyl 4-(3-Chlorophenyl)-2-hydroxy-2-(trifluoromethyl)-pent-4-enoate (**7o**).* Colorless oil (38.3 mg, 62%). The enantiomeric excess was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 300/1, flow rate = 1.0 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 10.6 min, 13.8 min (major), 65% *ee*. $[\alpha]_D^{20}$ = −80.6 (*c* 0.428, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.30 (m, 1H), 7.26−7.25 (m, 2H), 7.23−7.19 (m, 1H), 5.41 (s, 1H), 5.30 (s, 1H), 3.74 (s, 1H), 3.51 (s, 3H), 3.24 (d, J = 14.0 Hz, 1H), 3.01 (d, J = 14.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 142.7, 139.9, 134.1, 129.5, 127.8, 126.8, 125.1, 123.2 (q, J_{C-F} = 285 Hz), 120.6, 77.2 (q, J_{C-F} = 29 Hz), 53.7, 37.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.4. HRMS (positive ESI): $[M + Na]^+$ calcd for $C_{13}H_{12}O_3F_3ClNa$: 331.0325. Found: 331.0321.

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*(S)-Methyl 4-(4-Bromophenyl)-2-hydroxy-2-(trifluoromethyl)-pent-4-enoate (**7p**).*[27b] Colorless oil (56.5 mg, 80%). The enantiomeric excess was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 300/1, flow rate = 1.0 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 15.0 min, 16.5 min (major), 71% *ee*. $[\alpha]_D^{20} = -115.6$ (*c* 0.463, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 5.39 (s, 1H), 5.27 (s, 1H), 3.73 (s, 1H), 3.50 (s, 3H), 3.22 (d, *J* = 14.0 Hz, 1H), 3.02 (d, *J* = 14.0 Hz, 1H).

*(S)-Methyl 4-(3-Bromophenyl)-2-hydroxy-2-(trifluoromethyl)-pent-4-enoate (**7q**).* Colorless oil (42.4 mg, 60%). The enantiomeric excess was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 300/1, flow rate = 1.0 mL/min, and detection at a UV wavelength of 254 nm. Retention times: 11.5 min, 14.9 min (major), 74% *ee*. $[\alpha]_D^{20} = -68.7$ (*c* 0.440, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (t, *J* = 1.8 Hz, 1H), 7.42−7.39 (m, 1H), 7.27−7.24 (m, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 5.40 (s, 1H), 5.30 (s, 1H), 3.75 (s, 1H), 3.51 (s, 3H), 3.23 (d, *J* = 14.1 Hz, 1H), 3.01 (d, *J* = 14.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 142.9, 139.8, 130.7, 129.8, 129.7, 125.5, 123.2 (q, J_{C-F} = 285 Hz), 122.3, 120.7, 77.1 (q, J_{C-F} = 29 Hz), 53.7, 37.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.4. HRMS (positive ESI): $[M + Na]^+$ calcd for $C_{13}H_{12}O_3F_3BrNa$: 374.9820. Found: 374.9822.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional catalytic results, a proposed reaction cycle for the asymmetric carbonyl−ene reaction, ^{1}H NMR and ^{13}C NMR spectra of complex **1f**, and NMR spectra and chiral HPLC traces for all of the catalysis products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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