DOI: 10.1002/adsc.201200967

Chiral NCN Pincer Rhodium(III) Complexes with Bis(imidazolinyl)phenyl Ligands: Synthesis and Enantioselective Catalytic Alkynylation of Trifluoropyruvates with Terminal Alkynes

Tao Wang,[a] Jun-Long Niu,[a] Shuang-Liang Liu,[a] Juan-Juan Huang,[a] Jun-Fang Gong,[a,*] and Mao-Ping Song[a,*]

[a] The College of Chemistry and Molecular Engineering, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Zhengzhou University, Zhengzhou 450052, People's Republic of China
Fax: (+86)-371-6778-3012; phone: (+86)-371-6778-3012; e-mail: gongjf@zzu.edu.cn or mpsong@zzu.edu.cn

Received: November 12, 2012; Published online: February 28, 2013

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201200967.

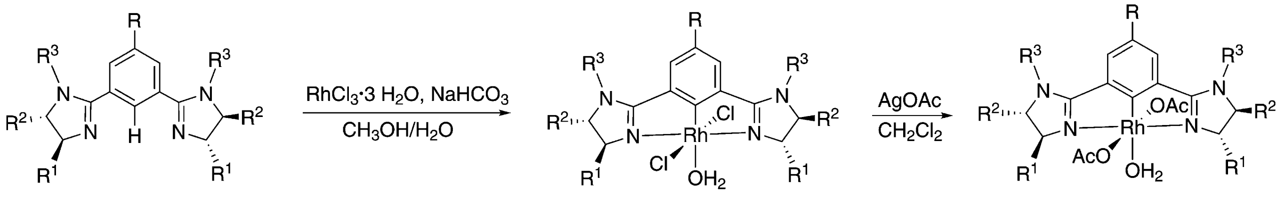
Abstract: A series of new chiral C_2-symmetrical NCN pincer rhodium(III) complexes with bis(imidazolinyl)phenyl ligands have been conveniently synthesized from easily available materials. The complexes were subsequently applied in the enantioselective addition of terminal alkynes to trifluoropyruvates. With catalyst loading of 1.5–3.0 mol%, the alkynylation of ethyl or methyl trifluoropyruvate with a variety of electronically and structurally diverse terminal alkynes gave the optically active trifluoromethyl-substituted tertiary propargylic alcohols with enantioselectivities of up to >99% *ee* and high yields. Although good to excellent enantioselectivities (85–98% *ee*) could be achieved only for some of the aliphatic terminal alkynes under the optimized conditions, the enantioselectivities were consistently excellent (94% to >99% *ee*) in the case of aromatic as well as heteroaromatic alkynes and enynes.

Keywords: asymmetric alkynylation; Phebim ligands; pincer rhodium(III) complexes; terminal alkynes; trifluoropyruvates

Introduction

The synthesis of optically active propargylic alcohols by enantioselective alkynylation of carbonyl compounds[1] has received much attention in recent years, because propargylic alcohols can serve as useful building blocks for a wide range of natural products and pharmaceutical molecules. Although the catalytic asymmetric alkynylation of aldehydes has been well studied and great progresses have been made,[2] the alkynylation of ketones is still regarded as a challenging task mostly due to their lower reactivities. In reported alkynylation of ketones, stoichiometric amounts of metal acetylides, which were generated *in situ* from terminal alkynes and excess metal reagents such as organolithium, organomagnesium or diorganozinc compounds, were usually employed as nucleophiles (alkynylating reagents) with stoichiometric[3] or catalytic amounts[4] of chiral ligands (in some cases with chiral metal complexes) for controlling the absolute configurations. For example, when zinc phenylacetylide (prepared *in situ* from phenylacetylene and excess dimethylzinc) was added to aryl methyl ketones in the presence of a catalytic amount of $Cu(OTf)_2$/chiral camphorsulfonamide complex (10 mol%) as the catalyst, high yields and enantioselectivities (up to 97% *ee*) could be achieved.[4b,i] Alkynylsilanes such as (trimethoxy)(phenylethynyl)silane were also successfully used as alternative alkynylating reagents.[5] In addition, Jiang and co-workers demonstrated that terminal alkynes were viable nucleophiles for the alkynylation of α-keto esters in the presence of catalytic $Zn(OTf)_2$/chiral amino alcohol (20 mol%) and the corresponding tertiary propargylic alcohols were produced in high yields with up to 94% *ee*.[6] Although the catalyst loading of 20 mol% is relatively high, this may represent the most atom-economical strategy for the asymmetric alkynylation of ketones since both the metal and ligand are substoichiometric. On the other hand, the alkynylation of α-CF_3-substituted carbonyl compounds, which are the highly activated ketones, is particularly appealing since the obtained α-CF_3-substituted chiral tertiary alcohols are important intermediates for drugs or candidates with unusual biological activities such as efavirenz.[7] Efavirenz is a potent non-nucleoside HIV reverse transcriptase inhibitor for AIDS treatment. Its synthesis was realized by the addition of stoichiometric metal acetylide (*in situ* formed) to trifluoromethyl ketone in the presence of a stoichiometric chiral auxiliary, which is also in fact the first report on enantioselective alkynylation of a ketone.[3,8] Later, Shibasaki and co-workers disclosed preliminary results on the asymmetric alkynylation of trifluoroacetophenone with phenylacetylene catalyzed by copper-diphosphine or Cu-Pybox complex (10–20 mol%).[9] Similar to what was reported by Jiang,[6] this direct catalytic alkynylation procedure was quite simple, unfortunately, only moderate enantioselectivity was observed (up to 52% *ee*). Recently, Ma and co-workers developed an efficient titanium(IV)-catalyzed enantioselective addition of zinc alkynylides to various trifluoromethyl ketones by using catalytic chiral *Cinchona* alkaloids as ligands.[10] Both enantiomers of trifluoromethylated tertiary propargylic alcohols could be accessed in good to high yields (up to 98%) and enantioselectivities (up to 94% *ee*) with the aid of BaF_2 as an additive. Besides trifluoromethyl ketones, the commercially available trifluoropyruvates can also be used as versatile fluorine-containing reagents for the construction of chiral fluorinated products. Unlike catalytic asymmetric carbonyl-ene, aldol as well as Friedel–Crafts reactions with trifluoropyruvate,[7] much less work on the catalytic enantioselective alkynylation of trifluoropyruvates has been reported. To the best of our knowledge, there are only two examples of this reaction.[11,12,13] One was by Mikami and co-workers, who used alkynylsilanes as nucleophiles and a dicationic Pd/(*S*)-BINAP complex (5.0 mol%) as the catalyst.[11] In this case, high enantioselectivities (up to >99% *ee*) were obtained and the system could also be applied to polyynylsilanes. The other was reported by Ohshima, Mashima and co-workers, who directly used terminal alkynes including aryl- as well as alkyl-substituted alkynes as nucleophiles to react with ethyl trifluoropyruvate.[12] In the presence of 3.0 mol% of C_1-symmetrical Rh complexes with 1,3-bis(2′-oxazolinyl)-phenyl ligands (Phebox) as the catalysts, the alkynylation proceeded well in Et_2O at room temperature without addition of an external base, giving the corresponding tertiary propargylic alcohols in high yields and enantioselectivities (up to >99% *ee*).

Although excellent results have been obtained with C_1-symmetrical Rh/Phebox complexes[14] for the direct catalytic asymmetric alkynylation of ethyl trifluoropyruvate, the design and development of easily accessible, economical and highly enantioselective chiral catalysts as well as an extension of the substrate scope are still worthwhile projects. In the previous studies, we have synthesized a series of C_2-symmetrical NCN pincer Pt(II), Pd(II) and Ni(II) complexes with anionic tridentate 1,3-bis(2′-imidazolinyl)phenyl ligands (abbreviated as Phebim) *via* the direct metal-induced C−H bond activation of the Phebim-H ligands.[15,16] And the cationic Pt-aquo complex was found to be an effective catalyst for the asymmetric Friedel–Crafts alkylation of indoles with nitroalkenes (up to 83% *ee*).[15d] Similar to the Phebox ligands, the electronic and conformational properties of Phebim ligands can be easily tuned by using different chiral amino alcohols. Moreover, a further tune of these properties for Phebim ligands can be achieved by appropriate choice of substituent on the additional nitrogen atom. Following our interest in the pincer metal complexes[17] and particularly, as a continuation of our studies on the pincer metal complexes with Phebim ligands, herein we report the first synthesis of C_2-symmetrical Rh(III)/Phebim complexes (Scheme 1) and their application in the catalytic asymmetric alkynylation of trifluoropyruvates with various terminal alkynes. The complexes were found to be effective and highly enantioselective not only for the reactions of ethyl trifluoropyruvate but also for those of methyl trifluoropyruvate with a catalyst loading of 1.5–3.0 mol%. The terminal alkynes used in the alkynylation can be aromatic including phenyl-



1a–e

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

2a (57%); **2b** (52%); **2c** (26%); **2d** (34%); **2e** (31%)

3a (95%); **3b** (82%); **3c** (92%); **3d** (85%); **3e** (90%)

Scheme 1. Synthesis of chiral C_2-symmetrical NCN pincer rhodium(III) complexes with bis(imidazolinyl)phenyl ligands.

acetylene, substituted phenylacetylenes and naphthylacetylene as well as heteroaromatic ones such as thiophene acetylenes. They can also be enynes and other aliphatic alkynes. Furthermore, in the alkynylation of ethyl trifluoropyruvate the C_2-symmetrical Rh/Phebim complexes gave better enantioselectivities than the reported C_1-symmetrical Rh/Phebox complexes under similar reaction conditions and the enantioselectivities were $>97\%$ *ee* in most cases.

Results and Discussion

As shown in Scheme 1, the rhodium(III) chloride complexes (Phebim)$RhCl_2(H_2O)$ **2a–e** with different electronic and conformational properties could be conveniently prepared in a way similar to that reported for (Phebox)$RhCl_2(H_2O)$ complexes[18] by heating the Phebim-H ligands **1** and triply hydrated rhodium trichloride in wet methanol in the presence of sodium bicarbonate. Then the chloride complexes were readily converted to the corresponding acetate complexes (Phebim)$Rh(OAc)_2(H_2O)$ **3a–e** by reaction with an excess of silver acetate in CH_2Cl_2. All of the new compounds were fully characterized by elemental analysis (HR-MS for the new ligands **1d** and **1e**), ^{1}H NMR, ^{13}C NMR, and IR spectra. The elemental analysis and some of the ^{1}H NMR spectra of the Rh/Phebim complexes indicated the coordination of one molecule of H_2O to the rhodium atom. In addition, the formation of the expected NCN pincer Rh(III) complexes is unambiguously confirmed by the single crystal X-ray diffraction analysis of complexes **2c′** and **2d′** (Figure 1 and Figure 2, respectively), in which a dichloromethane or acetone molecule, the solvent used in recrystallization takes the place of the H_2O molecule in complexes **2c** and **2d**. A similar phenomenon was observed with (Phebox)$RhCl_2(H_2O)$ complexes.[19]

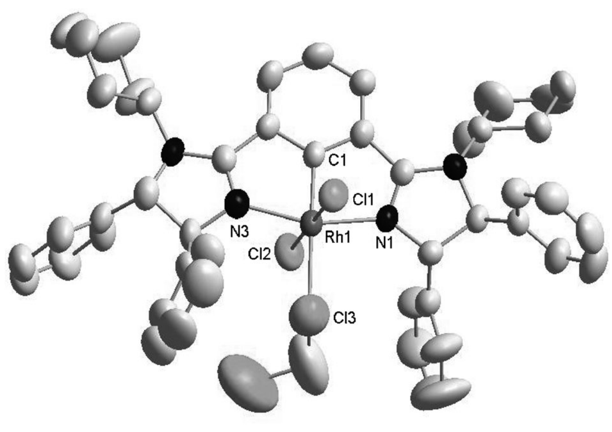


Figure 1. Molecular structure of **2c′**. Hydrogen atoms are omitted for clarity.

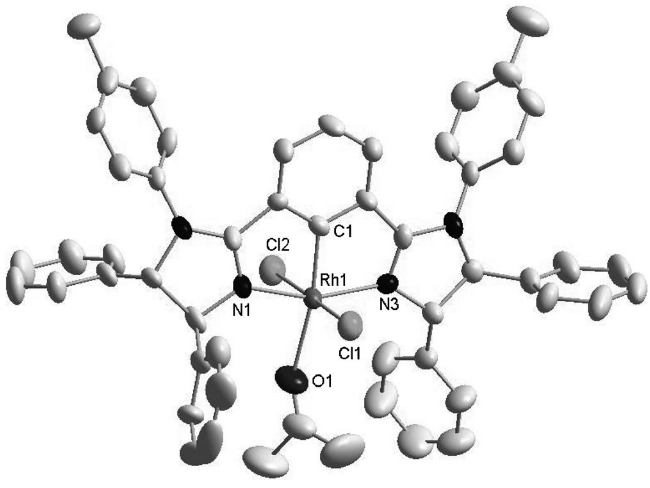
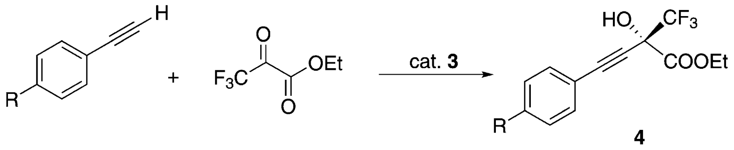


Figure 2. Molecular structure of **2d′**. Hydrogen atoms are omitted for clarity.

With the C_2-symmetrical NCN pincer Rh(III)/Phebim complexes in hand, their potential in the catalytic enantioselective alkynylation of trifluoropyruvates with terminal alkynes was then evaluated. In the beginning, the addition of phenylacetylene to ethyl trifluoropyruvate was chosen as a model with the acetate complex **3a** as the catalyst. A rough survey of reaction conditions indicated that the yields of the catalysis products were largely dependent on the reaction temperature and the solvent used, although good to excellent enantioselectivities (88–98% *ee*) could be obtained in all cases (Table 1, entries 1–6). Higher temperature was beneficial for the reaction and Et_2O was found to be the most appropriate solvent among the tested solvents including CH_2Cl_2, Et_2O, toluene and THF. The alkynylation proceeded very well at 25 °C in Et_2O with 3.0 mol% of **3a** giving the tertiary propargylic alcohol in 98% yield and 97% *ee* after 24 h (Table 1, entry 4). In contrast, no reaction occurred when the related chloride complex **2a** was employed as the catalyst under the same reaction conditions. This was in accordance with the literature results for Rh(III)/Phebox complexes suggesting that the acetate moiety on the Rh may act as an internal base to deprotonate the terminal alkyne.[12] Further studies revealed that in the reaction with 4-methoxyphenylacetylene as an alkynylating reagent complex **3a** only afforded a 86% yield with 83% *ee* (entry 7) although it gave excellent results in the reaction with phenylacetylene. Then the performance of the other four Rh complexes **3b–e** in this reaction was examined. It was found that the ligand structure of the Rh(III)/Phebim complexes had an obvious effect on both yield and enantioselectivity. In comparison with **3a** which has an (*S*)-phenyl substituent, complex **3b** with an (*S*)-benzyl substituent resulted in a lower yield and enantioselectivity (entry 8). Complex **3c**

Table 1. Optimization of conditions for the catalytic asymmetric alkynylation of ethyl trifluoropyruvate using the NCN pincer Rh(III)/Phebim complexes **3** as the catalysts.[a]



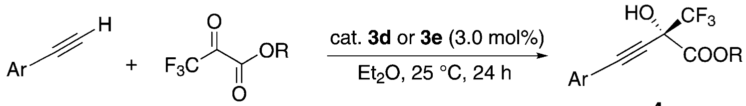
Entry	Catalyst (mol%)	R	Solvent	Temperature [°C]	Product	Yield[b] [%]	*ee*[c,d] [%]
1	**3a** (3.0 mol%)	H	CH_2Cl_2	r.t.[e]	**4a**	24	95
2	**3a** (3.0 mol%)	H	Et_2O	r.t.[e]	**4a**	62	98
3	**3a** (5.0 mol%)	H	Et_2O	25	**4a**	99	97
4	**3a** (3.0 mol%)	H	Et_2O	25	**4a**	98	97
5	**3a** (3.0 mol%)	H	toluene	25	**4a**	15	96
6	**3a** (3.0 mol%)	H	THF	25	**4a**	21	88
7	**3a** (3.0 mol%)	MeO	Et_2O	25	**4b**	86	83
8	**3b** (3.0 mol%)	MeO	Et_2O	25	**4b**	84	75
9	**3c** (3.0 mol%)	MeO	Et_2O	25	**4b**	36	97
10	**3d** (3.0 mol%)	MeO	Et_2O	25	**4b**	89	97
11	**3e** (3.0 mol%)	MeO	Et_2O	25	**4b**	99	98

[a] The reaction was run with terminal alkyne (0.24 mmol), ethyl trifluoropyruvate (0.20 mmol), solvent (2 mL) for 24 h.
[b] Isolated yields.
[c] Enantiomeric excess was determined by chiral HPLC analysis.
[d] The absolute configurations of the products were assigned to be *S* by comparison of optical rotations with those in ref.[12]
[e] About 14 °C.

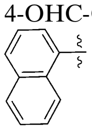
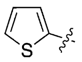
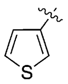
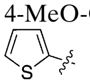
with (*S*,*S*)-phenyl substituents and an *N*-Cy substituent produced a rather modest yield (36%), however, we were happy to see that an excellent enantioselectivity (97% *ee*) could be obtained (entry 9). Replacement of the *N*-Cy substituent in complex **3c** by *N*-p-tolyl substituent furnished complex **3d** and the use of **3d** led to a significant increase in yield (89% *vs.* 36%) without loss of enantioselectivity (entry 10). Finally, complex **3e**, which has the same imidazoline ring as **3d** and an additional NO_2 group at the *para* position to the metal, was found to be the best catalyst with excellent yield and enantioselectivity (99% yield and 98% *ee*, entry 11).

Since both complexes **3d** and **3e** performed rather well in the selected alkynylation, they were both applied as the catalysts in the following experiments to explore the scope of the alkynylation. It was found that the two complexes were really effective and highly enantioselective catalysts for the alkynylation of ethyl and methyl trifluoropyruvates with various aromatic terminal alkynes (Table 2). In all cases, the corresponding α-CF_3 substituted tertiary propargylic alcohols were isolated in good to excellent chemical yields. When phenylacetylene and substituted phenylacetylenes acted as alkynylating reagents to react with ethyl trifluoropyruvate, complex **3e** afforded *ee* values higher than 96% regardless of the electronic property and the position of the substituent in the alkynes (entries 1–11). The substituent can be an electron-donating group such as Me or the aforementioned OMe and also be an electron-withdrawing group such as Br, F, CF_3, NO_2 or CHO. And it can be located at the 2-, 3- or 4-position of the alkynyl group. For example, excellent yields and enantioselectivities were achieved with the 2-, 3- and 4-methylphenylacetylenes (90–96% yields, 99% *ee*, entries 2–4). In fact, complex **3d** could also give excellent enantioselectivities in these reactions except for 3-methylphenylacetylene (see also entries 1–11). In comparison with **3e**, complex **3d** resulted in slightly lower yields and/or enantioselectivities. Among the substituted phenylacetylenes, the 4-ethynylbenzaldehyde was somewhat special since it bore a reactive aldehyde group. In this case, the two Rh complexes could still produce the desired propargylic alcohol in good yields and excellent enantioselectivities (75–80% yields, 96% *ee*, entry 11). It should be mentioned that in the above alkynylation the C_2-symmetrical Rh/Phebim complexes **3d** and **3e** consistently provided better enantioselectivities than the reported C_2- or C_1-symmetrical Rh/Phebox complexes.[12] Furthermore, with the current two Rh catalysts the aromatic terminal alkynes can be extended to 1-naphthylacetylene (entry 12) as well as heteroaromatic terminal alkynes[20] such as thiophene acetylenes (entries 13 and 14), and excellent stereocontrol (97 to >99% *ee*) was also observed. Although complex **3d** gave comparable enantioselectivities to complex **3e** in the alkynylation of ethyl trifluoropyruvate, in the reaction of methyl trifluoropyruvate it was obviously inferior to complex **3e** (entries 15–18). With the latter as the catalyst, alkynylations of methyl trifluoropyruvate with some representative aromatic and heteroaromatic al-

Table 2. Catalytic asymmetric alkynylation of ethyl and methyl trifluoropyruvate with aromatic and heteroaromatic terminal alkynes using complex **3d** and **3e** as the catalyst.[a]



4

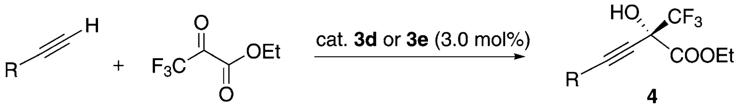
Entry	Ar	R	Product	Catalyst **3d** Yield[b] [%]	Catalyst **3d** *ee*[c,d] [%]	Catalyst **3e** Yield[b] [%]	Catalyst **3e** *ee*[c,d] [%]
1	Ph	Et	**4a**	99	97	99	98
2	4-Me-C_6H_4	Et	**4c**	88	97	91	99
3	3-Me-C_6H_4	Et	**4d**	92	88	96	99
4	2-Me-C_6H_4	Et	**4e**	87	99	90	99
5	4-F-C_6H_4	Et	**4f**	90	98	91	98
6	2-F-C_6H_4	Et	**4g**	80	99	86	>99
7	4-Br-C_6H_4	Et	**4h**	86	99	89	99
8	3-Br-C_6H_4	Et	**4i**	83	97	87	99
9	4-CF_3-C_6H_4	Et	**4j**	82	98	84	98
10	4-O_2N-C_6H_4	Et	**4k**	80	97	85	97
11	4-OHC-C_6H_4	Et	**4l**	75	96	80	96
12		Et	**4m**	89	98	93	98
13		Et	**4n**	83	99	85	>99
14		Et	**4o**	84	97	88	98
15	Ph	Me	**4p**	89	86	95	99
16	3-Me-C_6H_4	Me	**4q**	85	46	91	95
17	4-MeO-C_6H_4	Me	**4r**	85	88	90	94
18		Me	**4s**	86	99	90	>99

[a] The reaction was run with aryl-substituted terminal alkyne (0.24 mmol), trifluoropyruvate (0.20 mmol), 3.0 mol% of Rh complex at 25 °C for 24 h in Et_2O (2 mL).
[b] Isolated yields.
[c] Enantiomeric excess was determined by chiral HPLC analysis.
[d] The absolute configurations of the known products were assigned to be *S* by comparison of optical rotations with those in ref.[12] and the configurations of the new products were assigned by analogy.

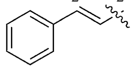
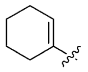
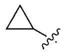
kynes all afforded the expected products in excellent yields and *ee* values (90–95% yields, 94 to >99% *ee*).

Encouraged by the remarkable results with aromatic or heteroaromatic alkynes, our attention was next turned to alkynylation with aliphatic terminal alkynes. However, it was found that the reactions did not proceed as smoothly as expected. For example, when 4-phenyl-1-butyne reacted with ethyl trifluoropyruvate under the above standard conditions low yields (29–34%) were obtained after 48 h although the enantioselectivities were excellent (96–97% *ee*, Table 3, entry 1). Then numerous attempts including varying the solvent, temperature, the ratio of alkyne and trifluoropyruvate as well as the addition of additive were made to improve the yield of this alkynylation reaction.[21] After much effort, a 77% yield with 98% *ee* could be finally achieved when the reaction was conducted in a mixed solvent of toluene and Et_2O at 70 °C in the presence of complex **3e** with the ratio of alkyne and trifluoropyruvate being 3:1 (entry 2). In contrast with 4-phenyl-1-butyne, the related 4-phenyl-1-butyn-3-ene which is an enyne readily reacted with ethyl trifluoropyruvate under the aforementioned standard conditions to produce the addition product in good yields with excellent enantioselectivities (82–86% yields, 99% *ee*, entry 3). Similarly, cyclohexenylacetylene, a cyclic enyne could also afford the corresponding product in good yields after 48 h with excellent enantioselectivities (80–81% yields, 97–98% *ee*, entry 4). The results suggested that the alkynylation with aliphatic terminal alkynes might be correlated with the acidity of the alkynes. With the more acidic alkynes like enynes, the reaction became easier. Finally, addition of several other aliphatic terminal alkynes to ethyl trifluoropyruvate under the modified conditions was investigated with the complex **3e** as the cat-

Table 3. Catalytic asymmetric alkynylation of ethyl trifluoropyruvate with aliphatic terminal alkynes using complex **3d** or **3e** as the catalyst.[a]



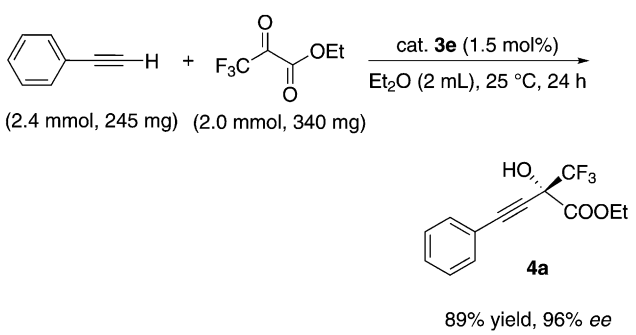
4

Entry	R	Temperature [°C]	Solvent	Product	Catalyst **3d** Yield[b] [%]	Catalyst **3d** *ee*[c,d] [%]	Catalyst **3e** Yield[b] [%]	Catalyst **3e** *ee*[c,d] [%]
1[e]	$PhCH_2CH_2$	25	Et_2O	**4t**	29	96	34	97
2	$PhCH_2CH_2$	70	toluene-Et_2O	**4t**	–	–	77	98
3[e,f]		25	Et_2O	**4u**	82	99	86	99
4[e]		25	Et_2O	**4v**	80	97	81	98
5	*t*-Bu	70	toluene-Et_2O	**4w**	–	–	68	95[g]
6		70	toluene-Et_2O	**4x**	–	–	85	85[g]
7	*n*-Pr	70	toluene-Et_2O	**4y**	–	–	71	85[g]
8	*n*-C_6H_{13}	70	toluene-Et_2O	**4z**	–	–	73	52
9	$(EtO)_2CH$	70	toluene-Et_2O	**4#**	–	–	80	63

[a] The reaction was run with aliphatic terminal alkyne (0.60 mmol), ethyl trifluoropyruvate (0.20 mmol), 3.0 mol% of Rh complex for 48 h in Et_2O or toluene-Et_2O (2 mL).
[b] Isolated yields.
[c] Enantiomeric excess was determined by chiral HPLC analysis.
[d] The absolute configurations of the known products were assigned to be *S* by comparison of optical rotations with those in ref. [12] and the configurations of the new products were assigned by analogy.
[e] Terminal alkyne (0.24 mmol), ethyl trifluoropyruvate (0.20 mmol).
[f] Reaction time was 24 h.
[g] The absolute configurations of the products were assigned to be *R*.

alyst (entries 5–9). Overall, the results were not as good as those in the alkynylation with aromatic alkynes and enynes although in some cases good to excellent enantioselectivities were achieved (entries 5–7).

To further extend the potential application of the present system, the alkynylation of ethyl trifluoropyruvate with phenylacetylene was carried out on a larger scale (2.0 mmol) with the loading of complex **3e** being reduced from 3.0 mol% to 1.5 mol%. An 89% yield with 96% *ee* could still be obtained (Scheme 2).



Scheme 2. Scaled-up version of the asymmetric alkynylation of ethyl trifluoropyruvate with phenylacetylene.

Conclusions

In conclusion, a new class of NCN pincer Rh(III) complexes with Phebim ligands as chiral catalysts has been developed. These complexes are easy to prepare and their structures can be readily modified as well. Furthermore, they have revealed high activity and enantioselectivity in the catalytic asymmetric alkynylation of trifluoropyruvates with terminal alkynes. With a typical catalyst loading of 3.0 mol%, a variety of electronically and structurally diverse terminal alkynes including phenylacetylenes, naphthylacetylene, thiophene acetylenes, enynes as well as some other aliphatic alkynes reacted smoothly with ethyl or methyl trifluoropyruvate to afford the optically active CF_3-substituted tertiary propargylic alcohols in high yields with enantioselectivities of up to >99% *ee*. Further modification of the pincer Rh/Phebim complexes and their applications in asymmetric catalysis are in progress.

Experimental Section

General Procedures

Solvents were dried with standard methods and freshly distilled prior to use if needed. The 1,3-bis(2′-imidazolinyl)benzene ligands **1a–e** were synthesized according to the literature method reported by us.[15b] Melting points were measured on a WC-1 instrument and are uncorrected. Infrared spectra were obtained with a Bruker VECTOR 22 spectrophotometer in KBr pellets. NMR spectra were recorded on a Bruker DPX 400 instrument using TMS as an internal standard. HR-MS were determined on a Waters Q-Tof Micro MS/MS system ESI spectrometer. Elemental analyses were measured on a Thermo Flash EA 1112 elemental analyzer. Optical rotations were recorded on a Perkin–Elmer 341 polarimeter.

General Procedure for the Synthesis of (Phebim)$RhCl_2(H_2O)$ Complexes 2a–e

Bis(imidazoline)benzene **1** (0.55 mmol), $RhCl_3 \cdot 3H_2O$ (131 mg, 0.50 mmol), and sodium bicarbonate (46 mg, 0.55 mmol) were added in a 50-mL flask. After addition of methanol (20 mL) and H_2O (2 mL), the resulting solution mixture was stirred at 65 °C for 14 h. After cooling, filtration, and evaporation, the residue was purified by preparative TLC on silica gel plates using CH_2Cl_2 (for **2a**, **2c–e**) or CH_2Cl_2/ethyl acetate 20/1 (for **2b**) as the eluent.

New ligand (1d): Yield: 53%; mp 117–119 °C; $[\alpha]_D^{20}$: +444 (*c* 0.540, $CHCl_3$). IR (KBr): ν = 3421, 3027, 2920, 2363, 1618, 1569, 1511, 1383, 1266, 1110, 813, 754, 697, 516 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (s, 1H, ArH), 7.73 (dd, 2H, *J* = 1.7, 7.8 Hz, ArH), 7.43–7.40 (m, 4H, ArH), 7.37–7.32 (m, 10H, ArH), 7.28–7.25 (m, 7H, ArH), 6.90 (d, *J* = 8.2 Hz, 4H, ArH), 6.59 (d, *J* = 8.2 Hz, 4H, ArH), 5.07 (d, *J* = 6.5 Hz, 2H, NCH), 4.59 (d, *J* = 6.5 Hz, 2H, NCH), 2.24 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5, 145.2, 144.8, 142.6, 136.2, 132.6, 132.3, 131.7, 130.9, 130.5, 130.2, 129.5, 129.2, 128.8, 128.0, 127.9, 126.0, 80.4, 80.1, 22.3; MS (ESI^+): *m/z* = 699.5 (M+H); HR-MS (positive ESI): *m/z* = 699.3486 $[M+H]^+$, calcd. for $C_{50}H_{43}N_4$: 699.3488.

Ligand (1e): Yield: 30%; mp 123–125 °C; $[\alpha]_D^{20}$: +385 (*c* 0.300, $CHCl_3$). IR (KBr): ν = 3463, 3113, 2961, 2231, 1757, 1441, 1293, 1233, 1191, 1121, 1023, 985, 852, 810, 710 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (d, *J* = 1.5 Hz, 2H, ArH), 8.38 (t, *J* = 1.5 Hz, 1H, ArH), 7.45–7.35 (m, 10H, ArH), 7.32–7.28 (m, 6H, ArH), 7.26–7.24 (m, 4H, ArH), 6.96 (d, *J* = 8.2 Hz, 4H, ArH), 6.60 (d, *J* = 8.2 Hz, 4H, ArH), 5.11 (d, *J* = 7.4 Hz, 2H, NCH), 4.58 (d, *J* = 7.4 Hz, 2H, NCH), 2.27 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4, 147.8, 142.9, 142.8, 140.5, 136.1, 135.5, 132.9, 130.0, 129.1, 128.9, 128.1, 127.7, 126.8, 126.6, 125.4, 125.3, 79.7, 78.9, 21.0; MS (ESI^+): *m/z* = 744.5 (M+H); HR-MS (positive ESI): *m/z* = 744.3333 $[M+H]^+$, calcd. for $C_{50}H_{42}N_5O_2$: 744.3339.

Pincer Rh(III) chloride complex (2a): Yield: 57%; mp 199–202 °C; $[\alpha]_D^{20}$: +912 (*c* 0.176, $CHCl_3$). IR (KBr): ν = 3422, 3177, 3029, 2921, 2857, 1577, 1490, 1404, 1254, 1159, 1106, 1038, 1022, 823, 762, 699, 522 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 7.1 Hz, 4H, ArH), 7.36 (t, *J* = 7.3 Hz, 4H, ArH), 7.32–7.22 (m, 10H, ArH), 6.73–6.65 (m, 3H, ArH), 5.35 (app t, *J* = 11.5 Hz, 2H, NCH), 4.49 (app t, *J* = 10.2 Hz, 2H, NC*H*H), 3.83 (dd, *J* = 9.6, 12.3 Hz, 2H, NCH*H*), 2.41 (s, 6H, CH_3), 1.97 (br s, 2H, OH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 140.2, 138.2, 137.8, 134.7, 130.3, 128.6, 128.3, 128.2, 126.4, 121.2, 66.5, 64.0, 21.2; aal. found: C 60.48, H 4.91, N 6.98; calcd. for $C_{38}H_{35}Cl_2N_4ORh \cdot 0.25\,CH_2Cl_2$: C 60.55, H 4.72, N 7.38.

Complex (2b): Yield: 52%; mp 228–230 °C; $[\alpha]_D^{20}$: +369 (*c* 0.170, $CHCl_3$). IR (KBr): ν = 3415, 2923, 1757, 1580, 1512, 1405, 1300, 1158, 1095, 817, 702, 466 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.26 (m, 7H, ArH), 7.23–7.17 (m, 7H, ArH), 7.11 (d, *J* = 8.3 Hz, 4H, ArH), 6.69–6.63 (m, 3H, ArH), 4.71–4.63 (m, 2H, NCH), 4.07 (app t, *J* = 10.0 Hz, 2H, NC*H*H), 3.81 (dd, *J* = 7.2, 9.7 Hz, 2H, NCH*H*), 3.72 (dd, *J* = 3.8, 14.0 Hz, 2H, CH_2Ph), 2.91 (dd, *J* = 10.5, 14.0 Hz, 2H, CH_2Ph), 2.81 (br s, 2H, OH_2), 2.38 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 138.1, 138.0, 137.5, 134.6, 130.1, 129.3, 128.6, 128.0, 126.4, 126.2, 121.4, 63.4, 59.8, 41.0, 21.1; anal. found: C 60.75, H 4.68, N 6.92; calcd. for $C_{40}H_{39}Cl_2N_4ORh \cdot 0.5\,CH_2Cl_2$: C 60.20, H 4.99; N 6.93.

Complex (2c): Yield: 26%; mp 221–223 °C; $[\alpha]_D^{20}$: +432 (*c* 0.116, $CHCl_3$). IR (KBr): ν = 3421, 3193, 2929, 2854, 1704, 1569, 1531, 1486, 1403, 1270, 1094, 756, 700, 475 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.0 Hz, 2H, ArH), 7.36–7.24 (m, 21H, ArH), 4.84 (d, *J* = 8.4 Hz, 2H, NCH), 4.75 (d, *J* = 8.4 Hz, 2H, NCH), 4.48–4.41 (m, 2H, NCy-H), 2.00–1.74 (m, 4H, CyH), 1.68–1.53 (m, 4H, CyH), 1.44–1.23 (m, 6H, CyH), 0.98–0.87 (m, 6H, CyH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.2, 143.6, 141.0, 136.2, 128.8, 128.4, 128.0, 127.9, 127.8, 127.4, 127.1, 122.7, 75.9, 71.7, 57.6, 33.8, 30.9, 26.0, 25.8, 25.2; anal. found: C 63.90, H 5.89, N 6.17; calcd. for $C_{48}H_{51}Cl_2N_4ORh \cdot 0.5\,CH_2Cl_2$: C 63.58, H 5.72, N 6.11.

Complex (2d): Yield: 34%; mp 216–218 °C; $[\alpha]_D^{20}$: +646 (*c* 0.118, $CHCl_3$). IR (KBr): ν = 3420, 3167, 1701, 1576, 1483, 1403, 1158, 1103, 751, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 6.9 Hz, 4H, ArH), 7.36–7.24 (m, 18H, ArH), 7.13–7.06 (m, 5H, ArH), 6.75 (br s, 1H, ArH), 6.70–6.66 (m, 1H, ArH), 6.59 (d, *J* = 8.0 Hz, 2H, ArH), 5.25 (d, *J* = 10.0 Hz, 2H, NCH), 4.76 (d, *J* = 10.0 Hz, 2H, NCH), 2.32 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 140.1, 139.6, 138.3, 137.6, 134.9, 130.2, 128.9, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 121.7, 80.4, 76.0, 21.2; anal. found: C 65.79, H 5.01, N 5.70; calcd. for $C_{50}H_{43}Cl_2N_4ORh \cdot 0.25\,CH_2Cl_2$: C 66.25, H 4.81, N 6.15.

Complex (2e): Yield: 31%; mp 255–257 °C; $[\alpha]_D^{20}$: +678 (*c* 0.134, $CHCl_3$). IR (KBr): ν = 3423, 3168, 1698, 1590, 1513, 1486, 1452, 1398, 1329, 1271, 1106, 746, 699, 471 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.38 (m, 6H, ArH), 7.34–7.25 (m, 17H, ArH), 7.21–7.13 (m, 5H, ArH), 6.82 (br s, 2H, ArH), 5.26 (d, *J* = 11.2 Hz, 2H, NCH), 4.86 (d, *J* = 11.2 Hz, 2H, NCH), 2.35 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 143.7, 139.4, 139.2, 138.7, 136.5, 135.3, 130.6, 129.0, 128.9, 128.6, 128.4, 128.3, 128.1, 122.3, 80.4, 76.2, 21.2; anal. found: C 63.23, H 4.64, N 6.97; calcd. for $C_{50}H_{42}Cl_2N_5O_3Rh \cdot 0.25\,CH_2Cl_2$: C 63.14, H 4.48, N, 7.33.

General Procedure for the Synthesis of (Phebim)Rh(OAc)$_2$(H$_2$O) Complexes 3a–e

To a stirred solution of **2** (0.20 mmol) in CH_2Cl_2 (5 mL) was added AgOAc (67 mg, 0.40 mmol), the resulting solution mixture was stirred at room temperature for 12 h. After filtration and concentration under vacuum, the residue was purified by preparative TLC on silica gel plates eluting with CH_2Cl_2/ethyl acetate (10/1) to afford the corresponding complexes **3a–e**.

Pincer Rh(III) acetate complex (3a): Yield: 95%; mp 154–156 °C; $[\alpha]_D^{20}$: +325 (*c* 0.156, $CHCl_3$). IR (KBr): ν = 3416, 3168, 1757, 1626, 1578, 1514, 1400, 1321, 1158, 1104, 696, 476 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.41 (m, 4H, ArH), 7.31–7.22 (m, 14H, ArH), 6.72 (s, 3H, ArH), 5.39 (dd, *J* = 8.6, 11.1 Hz, 2H, NCH), 4.49 (dd, *J* = 9.7, 11.1 Hz, 2H, NC*H*H), 4.03 (dd, *J* = 8.6, 9.7 Hz, 2H, NCH*H*), 3.60 (br s, 2H, OH_2), 2.41 (s, 6H, CH_3), 1.54 (s, 6H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.0, 168.1, 141.6, 138.2, 137.6, 135.0, 130.3, 128.4, 127.9, 127.82, 127.76, 126.2, 121.2, 66.3, 63.6, 23.7, 21.2; anal. found: C 60.80, H 5.14, N 6.50; calcd. for $C_{42}H_{41}N_4O_5Rh \cdot 0.75\,CH_2Cl_2$: C 60.52, H 5.05, N 6.60.

Complex (3b): Yield: 82%; mp 195–197 °C; $[\alpha]_D^{20}$: +336 (*c* 0.128, $CHCl_3$). IR (KBr): ν = 3416, 3167, 1758, 1622, 1582, 1536, 1513, 1494, 1400, 1326, 1097, 819, 705, 472 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (br s, 2H, OH_2), 7.32 (d, *J* = 7.1 Hz, 4H, ArH), 7.29–7.25 (m, 4H, ArH), 7.21–7.13 (m, 6H, ArH), 7.04 (d, *J* = 7.9 Hz, 4H, ArH), 6.68–6.61 (m, 3H, ArH), 4.75–4.67 (m, 2H, NCH), 4.14–4.05 (m, 2H, NC*H*H), 3.83 (dd, *J* = 7.4, 9.6 Hz, 2H, NCH*H*), 3.65 (dd, *J* = 3.9, 13.7 Hz, 2H, $PhCH_2$), 2.86 (dd, *J* = 9.1, 13.7 Hz, 2H, $PhCH_2$), 2.37 (s, 6H, CH_3), 1.83 (s, 6H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.9 (d, *J* = 26.8 Hz), 182.3, 167.5, 137.98, 137.95, 137.4, 135.0, 130.1, 129.7, 128.4, 127.5, 126.4, 126.0, 121.2, 63.6, 59.3, 40.3, 23.9, 21.1; anal. found: C 63.92, H 5.49, N 6.67; calcd. for $C_{44}H_{45}N_4O_5Rh \cdot 0.25\,CH_2Cl_2$: C 63.73, H 5.50, N 6.72.

Complex (3c): Yield: 92%; mp 151–153 °C; $[\alpha]_D^{20}$: −14.0 (*c* 0.142, $CHCl_3$). IR (KBr): ν = 3417, 3172, 2928, 2854, 1758, 1626, 1531, 1488, 1400, 1320, 1095, 758, 698, 472 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.0 Hz, 2H, ArH), 7.37 (t, *J* = 7.9 Hz, 1H, ArH), 7.28–7.22 (m, 16H, ArH), 7.18–7.15 (m, 4H, ArH), 4.87 (d, *J* = 4.7 Hz, 2H, NCH), 4.82 (d, *J* = 4.7 Hz, 2H, NCH), 4.63 (br s, 2H, OH_2), 4.51–4.45 (m, 2H, NCy-H), 2.04–1.75 (m, 6H, CyH), 1.69–1.53 (m, 6H, CyH), 1.40 (s, 6H, OAc), 1.35–1.24 (m, 2H, CyH), 1.00–0.84 (m, 6H, CyH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.8 (d, *J* = 27.2 Hz), 180.8, 168.7, 144.2, 142.3, 136.3, 129.1, 128.6, 128.1, 127.7, 127.1, 126.7, 126.3, 122.5, 74.9, 70.7, 56.7, 34.0, 31.9, 29.8, 25.9, 25.2, 23.2; anal. found: C 67.30, H 6.57, N 5.35; calcd. for $C_{52}H_{57}N_4O_5Rh \cdot C_3H_6O$: C 67.47, H 6.49, N 5.72.

Complex (3d): Yield: 85%; mp 255–258 °C; $[\alpha]_D^{20}$: +198 (*c* 0.104, $CHCl_3$). IR (KBr): ν = 3416, 3197, 3030, 2922, 1628, 1575, 1534, 1485, 1403, 1318, 1158, 1108, 1018, 751,696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.25 (m, 18H, ArH), 7.24–7.20 (m, 5H, ArH), 7.10 (br s, 5H, ArH), 6.76–6.72 (m, 1H, ArH), 6.69–6.66 (m, 2H, ArH), 5.21 (d, *J* = 6.5 Hz, 2H, NCH), 5.10 (br s, 2H, OH_2), 4.90 (d, *J* = 6.5 Hz, 2H, NCH), 2.34 (s, 6H, CH_3), 1.58 (s, 6H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4 (d, *J* = 26.7 Hz), 181.0, 167.99, 167.96, 141.4, 141.0, 137.9, 137.3, 135.1, 130.1, 129.0, 128.6, 128.5, 127.84, 127.80, 127.4, 127.2, 127.0, 121.4, 79.2, 75.5, 23.3, 21.2; anal. found: C 65.80, H 5.12, N 5.34; calcd. for $C_{54}H_{49}N_4O_5Rh \cdot 0.75\,CH_2Cl_2$: C 65.72, H 5.09, N 5.60.

Complex (3e): Yield: 90%; mp 269–271 °C; $[\alpha]_D^{20}$: +160 (*c* 0.124, $CHCl_3$); IR (KBr): ν = 3416, 3165, 3031, 2924, 2361, 1757, 1630, 1590, 1488, 1396, 1326, 1104, 821, 758, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (s, 2H, ArH), 7.32–7.28 (m, 18H, ArH), 7.22–7.01 (m, 8H, ArH), 6.81 (br s, 2H, ArH), 5.17 (d, *J* = 7.0 Hz, 2H, NCH), 5.16 (br s, 2H, OH_2), 4.97 (d, *J* = 7.0 Hz, 2H, NCH), 2.37 (s, 6H, CH_3), 1.59 (s, 6H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.3 (d, *J* = 26.4 Hz), 181.0, 167.5, 143.3, 140.7, 140.3, 138.9, 136.2, 135.3, 130.5, 129.1, 128.74, 128.69, 128.2, 127.4, 127.2, 121.8, 79.3, 75.5, 23.3, 21.2; anal. found: C 63.06, H 4.75, N 6.58; calcd. for $C_{54}H_{48}N_5O_7Rh \cdot 0.75\,CH_2Cl_2$: C 62.89, H 4.77, N 6.70.

General Procedure for the Asymmetric Alkynylation of Trifluoropyruvate with Aromatic Terminal Alkynes by (Phebim)Rh(OAc)$_2$(H$_2$O) Complexes 3

Under an argon atmosphere, the (Phebim)Rh(OAc)$_2$(H$_2$O) complex **3** (0.006 mmol, 3.0 mol%) was dissolved in 2 mL of Et_2O. Ethyl trifluoropyruvate or methyl trifluoropyruvate (0.20 mmol) was added, followed by aromatic terminal alkyne (0.24 mmol), then the resulting solution mixture was stirred at 25 °C for 24 h. The residue was purified by preparative TLC on silica gel plates eluting with CH_2Cl_2/petroleum ether to afford the desired product.

General Procedure for the Asymmetric Alkynylation of Trifluoropyruvate with Aliphatic Terminal Alkynes by (Phebim)Rh(OAc)$_2$(H$_2$O) Complexes 3

Under an argon atmosphere, the (Phebim)Rh(OAc)$_2$(H$_2$O) complex **3** (0.006 mmol, 3.0 mol%) was dissolved in a mixed solvent of toluene and Et_2O (2 mL, v/v = 1:1). Ethyl trifluoropyruvate (0.20 mmol) was added, followed by aliphatic terminal alkyne (0.60 mmol), then the resulting solution mixture was stirred at 70 °C for 48 h. The residue was purified by preparative TLC on silica gel plates eluting with CH_2Cl_2/petroleum ether to afford the desired product.

The analytical data of the new catalysis products are given here and those of the known products are given in Supporting Information.

Compound (4g): The *ee* was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 300/1, flow = 0.25 mL min^{-1}, and detected at a UV wave length of 228 nm; retention times: 97.7 min, 104.4 min (major), >99% *ee*; $[\alpha]_D^{20}$: +52.3 (*c* 0.911, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.47 (m, 1H, Ar-H), 7.41–7.35 (m, 1H, Ar-H), 7.15–7.07 (m, 2H, Ar-H), 4.47 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 4.33 (br s, 1H, OH), 1.40 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 163.3 (d, $J_{C,F}$ = 253 Hz), 133.9, 131.6 (d, $J_{C,F}$ = 8.0 Hz), 124.0 (d, $J_{C,F}$ = 3.7 Hz), 121.7 (q, $J_{C,F}$ = 285 Hz), 115.7 (d, $J_{C,F}$ = 20 Hz), 109.4 (d, $J_{C,F}$ = 15 Hz), 84.7, 80.8, 71.7 (q, $J_{C,F}$ = 34 Hz), 65.2, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −78.1, −108.8; IR (KBr): ν = 3467, 2991, 2245, 1752, 1494, 1452, 1234, 1195, 1129, 1052, 760 cm^{-1}; HR-MS (positive ESI): *m/z* = 313.0467 [M + Na]$^+$, calcd. for $C_{13}H_{10}O_3F_4Na$: 313.0464.

Compound (4i): The *ee* was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 99/1, flow = 0.5 mL min^{-1}, and detected at a UV wave length of 228 nm; retention times: 24.3 min (major), 27.9 min, 99% *ee*; $[\alpha]_D^{20}$: +49.7 (*c* 0.535, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.65 (s, 1H, Ar-H), 7.52 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.43 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.21 (t, *J* = 7.9 Hz, 1H, Ar-H), 4.54–4.40 (m, 2H, OCH_2CH_3), 4.31 (br s, 1H, OH), 1.40 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 134.9, 132.9, 130.7, 129.9,122.6, 122.2, 121.7 (q, $J_{C,F}$ = 285 Hz), 85.5, 81.0, 71.7 (q, $J_{C,F}$ = 34 Hz), 65.2, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −78.1; IR (KBr): ν = 3466, 2988, 2242, 1751, 1473, 1227, 1195, 1127, 1053, 786 cm^{-1}; HR-MS (positive ESI): *m/z* = 372.9664 [M + Na]$^+$, calcd. for $C_{13}H_{10}O_3F_3BrNa$: 372.9663..

Compound (4k): The *ee* was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 99/1, flow = 1.0 mL min^{-1}, and detected at a UV wave length of 254 nm; retention times: 46.3 min (major), 59.2 min, 97% *ee*; $[\alpha]_D^{20}$: +39.8 (*c* 0.688, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.68 (d, *J* = 8.9 Hz, 2H, Ar-H), 4.57–4.42 (m, 2H, OCH_2CH_3), 1.41 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 148.0, 133.1, 127.3, 123.6, 120.1 (q, $J_{C,F}$ = 285 Hz), 84.8, 84.4, 71.5 (q, $J_{C,F}$ = 34 Hz), 65.4, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −78.0; IR (KBr): ν = 3447, 3178, 2925, 1757, 1638, 1526, 1456, 1398, 1351, 1195, 1129, 1095, 858, 751, 698 cm^{-1}; HR-MS (positive ESI): *m/z* = 340.0411 [M + Na]$^+$, calcd. for $C_{13}H_{10}O_5F_3NNa$: 340.0409.

Compound (4n): The *ee* was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 300/1, flow = 0.8 mL min^{-1}, and detected at a UV wave length of 254 nm; retention times: 41.0 min, 46.2 min (major), > 99% *ee*; $[\alpha]_D^{20}$: +52.5 (*c* 0.828, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.33 (m, 2H, Ar-H), 6.99 (dd, *J* = 5.0, 3.8 Hz, 1H, Ar-H), 4.53–4.39 (m, 2H, OCH_2CH_3), 4.34 (br s, 1H, OH), 1.39 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 134.2, 129.0, 127.1, 120.3, 121.7 (q, $J_{C,F}$ = 285 Hz), 83.5, 80.8, 71.9 (q, $J_{C,F}$ = 34 Hz), 65.2, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −78.0; IR (KBr): ν = 3463, 2988, 2231, 1751, 1300, 1190, 1120, 1023, 855, 710 cm^{-1}; HR-MS (positive ESI): *m/z* = 301.0124, [M + Na]$^+$, calcd. for $C_{11}H_9O_3F_3SNa$: 301.0122.

Compound (4u): The *ee* was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 97/3, flow = 1.0 mL min^{-1}, and detected at a UV wave length of 254 nm; retention times: 17.0 min (major), 24.2 min, 99% *ee*; $[\alpha]_D^{20}$: +47.0 (*c* 0.858, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.31 (m, 5H, Ar-H), 7.09 (d, *J* = 16.4 Hz, 1H, -CH=C*H*), 6.15 (d, *J* = 16.4 Hz, 1H, -C*H*=CH), 4.53–4.38 (m, 2H, OCH_2CH_3), 1.39 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 144.7, 135.4, 129.4, 128.8, 126.6, 120.3 (q, $J_{C,F}$ = 285 Hz), 105.6, 86.5, 81.4, 71.6 (q, $J_{C,F}$ = 34 Hz), 65.1, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −78.2. IR (KBr): ν = 3448, 3175, 2925, 2857, 1751, 1626, 1456, 1399, 1179, 1107, 960, 750, 696 cm^{-1}; HR-MS (positive ESI): *m/z* = 299.0893 [M + H]$^+$, calcd. for $C_{15}H_{14}O_3F_3$: 299.0895.

Compound (4r): The *ee* was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 97/3, flow = 0.5 mL min^{-1}, and detected at a UV wave length of 254 nm; retention times: 31.4 min (major), 39.9 min, 94% *ee*; $[\alpha]_D^{20}$: +55.2 (*c* 0.308, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.85 (d, *J* = 8.8 Hz, 2H, Ar-H), 4.27 (br s, 1H, OH), 4.00 (s, 3H, $COOCH_3$), 3.81 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 160.6, 133.8, 121.8 (q, $J_{C,F}$ = 285 Hz), 114.0, 112.5, 87.6, 78.3, 71.8 (q, $J_{C,F}$ = 34 Hz), 55.3, 55.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −78.3; IR (KBr): ν = 3459, 2962, 2845, 2235, 1756, 1607, 1512, 1250, 1194, 1125, 1052, 986, 835, 802, 740, 540 cm^{-1}; HR-MS (positive ESI): *m/z* = 311.0506, [M + Na]$^+$, calcd. for $C_{13}H_{11}O_4F_3Na$: 311.0507.

Compound (4q): The *ee* was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 99/1, flow = 0.5 mL min^{-1}, and detected at a UV wave length of 228 nm; retention times: 31.7 min (major), 36.3 min, 95% *ee*; $[\alpha]_D^{20}$: +63.1 (*c* 0.408, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.30 (m, 2H, Ar-H), 7.24–7.18 (m, 2H, Ar-H), 4.28 (br s, 1H, OH), 4.01 (s, 3H, $COOCH_3$), 2.33 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 138.2, 132.7, 130.6, 129.3, 128.3, 121.7 (q, $J_{C,F}$ = 285 Hz), 120.3, 87.6, 79.1, 71.7 (q, $J_{C,F}$ = 34 Hz), 55.3, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −78.3. IR (KBr): ν = 3465, 2961, 2238, 1756, 1444, 1399, 1290, 1238, 1184, 1123, 1057, 988, 787, 739, 689 cm^{-1}; HR-MS (positive ESI): *m/z* = 295.0555, [M + Na]$^+$ calcd for $C_{13}H_{11}O_3F_3Na$: 295.0558.

Compound (4s): The *ee* was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 300/1, flow = 0.8 mL min^{-1}, and detected at a UV wave length of 254 nm; retention times: 62.8 min, 68.2 min (major), > 99% *ee*; $[\alpha]_D^{20}$: +70.6 (*c* 0.795, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.33 (m, 2H, Ar-H), 7.00–6.99 (m, 1H, Ar-H), 4.28 (br s, 1H, OH), 4.00 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 134.4, 129.0, 127.1, 121.6 (q, $J_{C,F}$ = 285 Hz), 120.2, 83.2, 81.0, 71.9 (q, $J_{C,F}$ = 34 Hz), 55.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −78.1; IR (KBr): ν = 3463, 3113, 2961, 2231, 1757, 1441, 1293, 1233, 1191, 1121, 1023, 985, 852, 810, 710 cm^{-1}; HR-MS (positive ESI): *m/z* = 286.9968, [M + Na]$^+$, calcd. for $C_{10}H_7O_3F_3SNa$: 286.9966.

Compound (4z): The *ee* was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 100/0.5, flow = 0.3 mL min^{-1}, and detected at a UV wave length of 215 nm; retention times: 22.9 min, 26.7 min (major), 52% *ee*; $[\alpha]_D^{20}$: +15.6 (*c* 0.680, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.48–4.35 (m, 2H, OCH_2CH_3), 4.21 (br s, 1H, OH), 2.26 (t, *J* = 7.1 Hz, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.59–1.50 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.43–1.34 (m, 5H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.32–1.26 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 0.89 (t, *J* = 6.9 Hz, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 120.4 (q, $J_{C,F}$ = 284 Hz), 89.2, 71.5, 71.2 (q, $J_{C,F}$ = 34 Hz), 64.8, 31.3, 28.4, 27.8, 22.5, 18.7, 14.0, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −78.7; IR (KBr): ν = 3480, 2935, 2864, 1750, 1463, 1299, 1244, 1170, 1103, 1016, 692 cm^{-1}; HR-MS (positive ESI): *m/z* = 303.1183, [M + Na]$^+$, calcd. for $C_{13}H_{19}O_3F_3Na$: 303.1184.

Supporting Information

CCDC 880619 (for **2c′**) and CCDC 880618 (for **2d′**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystal structure determination and crystallographic data of pincer Rh complexes **2c′** and **2d′**, additional results on the catalytic alkynylation of ethyl trifluoropyruvate with aliphatic terminal alkynes, characterization data of the known asymmetric catalysis products, figures of the ^{1}H and ^{13}C NMR spectra of the new compounds **1**–**3**, ^{1}H, ^{13}C and ^{19}F NMR spectra of the catalysis products **4** as well as their chiral HPLC spectra are available in the Supporting Information.

Acknowledgements

Financial support from the National Natural Science Foundation of China (Nos. 21072177 and 21272217) is gratefully acknowledged.

References

[1] For some recent reviews, see: a) L. Pu, *Tetrahedron* **2003**, *59*, 9873–9886; b) B. M. Trost, A. H. Weiss, *Adv. Synth. Catal.* **2009**, *351*, 963–983; c) L. Lin, R. Wang, *Curr. Org. Chem.* **2009**, *13*, 1565–1576.

[2] For examples on Zn-catalyzed asymmetric alkynylation of aldehydes, see: a) N. K. Anand, E. M. Carreira, *J. Am. Chem. Soc.* **2001**, *123*, 9687–9688; b) B. Jiang, Z. Chen, W. Xiong, *Chem. Commun.* **2002**, 1524–1525; c) M. Yamashita, K.-i. Yamada, K. Tomioka, *Adv. Synth. Catal.* **2005**, *347*, 1649–1652; d) D. P. G. Emmerson, W. P. Hems, B. G. Davis, *Org. Lett.* **2006**, *8*, 207–210; e) B. Zheng, S.-N. Li, J.-Y. Mao, B. Wang, Q.-H. Bian, S.-Z. Liu, J.-C. Zhong, H.-C. Guo, M. Wang, *Chem. Eur. J.* **2012**, *18*, 9208–9211. For Cu-catalyzed alkynylation, see: f) Y. Asano, K. Hara, H. Ito, M. Sawamura, *Org. Lett.* **2007**, *9*, 3901–3904; g) Y. Asano, H. Ito, K. Hara, M. Sawamura, *Organometallics* **2008**, *27*, 5984–5996. For In-catalyzed alkynylation, see: h) R. Takita, K. Yakura, T. Ohshima, M. Shibasaki, *J. Am. Chem. Soc.* **2005**, *127*, 13760–13761; i) S. Harada, R. Takita, T. Ohshima, S. Matsunaga, M. Shibasaki, *Chem. Commun.* **2007**, 948–950. For Ru-catalyzed alkynylation, see: j) J. Ito, R. Asai, H. Nishiyama, *Org. Lett.* **2010**, *12*, 3860–3862.

[3] a) A. Thompson, E. G. Corley, M. F. Huntington, E. J. J. Grabowski, J. F. Remenar, D. B. Collum, *J. Am. Chem. Soc.* **1998**, *120*, 2028–2038; b) L.-S. Tan, C.-Y. Chen, R. D. Tillyer, E. J. J. Grabowski, P. J. Reider, *Angew. Chem.* **1999**, *111*, 724–727; *Angew. Chem. Int. Ed.* **1999**, *38*, 711–713; c) F. Xu, R. A. Reamer, R. Tillyer, J. M. Cummins, E. J. J. Grabowski, P. J. Reider, D. B. Collum, J. C. Huffman, *J. Am. Chem. Soc.* **2000**, *122*, 11212–11218; d) B. Jiang, Y. Feng, *Tetrahedron Lett.* **2002**, *43*, 2975–2977.

[4] a) P. G. Cozzi, *Angew. Chem.* **2003**, *115*, 3001–3004; *Angew. Chem. Int. Ed.* **2003**, *42*, 2895–2898; b) G. Lu, X.-S. Li, X. Jia, W. L. Chan, A. S. C. Chan, *Angew. Chem.* **2003**, *115*, 5211–5212; *Angew. Chem. Int. Ed.* **2003**, *42*, 5057–5058; c) B. Saito, T. Katsuki, *Synlett* **2004**, 1557–1560; d) P. G. Cozzi, S. Alesi, *Chem. Commun.* **2004**, 2448–2449; e) Y.-F. Zhou, R. Wang, Z.-Q. Xu, W.-J. Yan, L. Liu, Y.-F. Kang, Z.-J. Han, *Org. Lett.* **2004**, *6*, 4147–4149; f) J.-C. Mao, B.-S. Wan, F. Wu, S.-W. Lu, *J. Mol. Catal. A: Chem.* **2005**, *237*, 126–131; g) Y.-F. Kang, L. Liu, R. Wang, Y.-F. Zhou, W.-J Yan, *Adv. Synth. Catal.* **2005**, *347*, 243–247; h) C. Chen, L. Hong, Z.-Q. Xu, L. Liu, R. Wang, *Org. Lett.* **2006**, *8*, 2277–2280; i) G. Lu, X.-S. Li, Y. M. Li, F. Y. Kwong, A. S. C. Chan, *Adv. Synth. Catal.* **2006**, *348*, 1926–1933; j) L. Liu, R. Wang, Y.-F. Kang, H.-Q. Cai, C. Chen, *Synlett* **2006**, 1245–1249; k) K. Tanaka, K. Kukita, T. Ichibakase, S. Kotani, M. Nakajima, *Chem. Commun.* **2011**, *47*, 5614–5616; l) T.-L. Liu, H. Ma, F.-G. Zhang, Y. Zheng, J. Nie, J.-A. Ma, *Chem. Commun.* **2011**, *47*, 12873–12875.

[5] a) T. Ueda, K. Tanaka, T. Ichibakase, Y. Orito, M. Nakajima, *Tetrahedron* **2010**, *66*, 7726–7731; b) K. Tanaka, T. Ueda, T. Ichibakase, M. Nakajima, *Tetrahedron Lett.* **2010**, *51*, 2168–2169.

[6] B. Jiang, Z. Chen, X. Tang, *Org. Lett.* **2002**, *4*, 3451–3453.

[7] For a general review on asymmetric construction of stereogenic carbon centers containing a CF_3 group, see: J. Nie, H.-C. Guo, D. Cahard, J.-A. Ma, *Chem. Rev.* **2011**, *111*, 455–529.

[8] A. S. Thompson, E. G. Corley, M. F. Huntington, E. J. J. Grabowski, *Tetrahedron Lett.* **1995**, *36*, 8937–8940.

[9] R. Motoki, M. Kanai, M. Shibasaki, *Org. Lett.* **2007**, *9*, 2997–3000.

[10] G.-W. Zhang, W. Meng, H. Ma, J. Nie, W.-Q. Zhang, J.-A. Ma, *Angew. Chem.* **2011**, *123*, 3600–3604; *Angew. Chem. Int. Ed.* **2011**, *50*, 3538–3542.

[11] K. Aikawa, Y. Hioki, K. Mikami, *Org. Lett.* **2010**, *12*, 5716–5719.

[12] a) H. Nishiyama, J. Ito, *Chem. Commun.* **2010**, *46*, 203–212; b) T. Ohshima, T. Kawabata, Y. Takeuchi, T. Kakinuma, T. Iwasaki, T. Yonezawa, H. Murakami, H. Nishiyama, K. Mashima, *Angew. Chem.* **2011**, *123*, 6420–6424; *Angew. Chem. Int. Ed.* **2011**, *50*, 6296–6300.

[13] For a non-enantioselective alkynylation of trifluoropyruvate catalyzed by AgF, see: G.-J. Deng, C.-J. Li, *Synlett* **2008**, 1571–1573.

[14] For reviews on the preparation and catalytic reactions of C_2-symmetrical metal/Phebox pincer complexes, see: ref.[12a] and a) H. Nishiyama, *Chem. Soc. Rev.* **2007**, *36*, 1133–1141; b) J. Ito, H. Nishiyama, *Synlett* **2012**, 509–523.

[15] a) X.-Q. Hao, J.-F. Gong, C.-X. Du, L.-Y. Wu, Y.-J. Wu, M.-P. Song, *Tetrahedron Lett.* **2006**, *47*, 5033–5036; b) L.-Y. Wu, X.-Q. Hao, Y.-X. Xu, M.-Q. Jia, Y.-N. Wang, J.-F. Gong, M.-P. Song, *Organometallics* **2009**, *28*, 3369–3380; c) D.-D. Shao, J.-L. Niu, X.-Q. Hao, J.-F. Gong, M.-P. Song, *Dalton Trans.* **2011**, *40*, 9012–9019; d) X.-Q. Hao, Y.-X. Xu, M.-J. Yang, L. Wang, J.-L. Niu, J.-F. Gong, M.-P. Song, *Organometallics* **2012**, *31*, 835–846.

[16] For the preparation of pincer Pd/Phebim complexes by oxidative method as well as their application in asymmetric catalysis, see: a) K. Hyodo, S. Nakamura, K. Tsuji, T. Ogawa, Y. Funahashi, N. Shibata, *Adv. Synth. Catal.* **2011**, *353*, 3385–3390; b) K. Hyodo, S. Nakamura, N. Shibata, *Angew. Chem.* **2012**, *124*, 10483–10487; *Angew. Chem. Int. Ed.* **2012**, *51*, 10337–10341.

[17] a) M.-J. Yang, Y.-J. Liu, J.-F. Gong, M.-P. Song, *Organometallics* **2011**, *30*, 3793–3803; b) T. Wang, X.-Q. Hao, X.-X. Zhang, J.-F. Gong, M.-P. Song, *Dalton Trans.* **2011**, *40*, 8964–8976; c) For a brief review, see: J.-L. Niu, X.-Q. Hao, J.-F. Gong, M.-P. Song, *Dalton Trans.* **2011**, *40*, 5135–5150.

[18] J. Ito, T. Shiomi, H. Nishiyama, *Adv. Synth. Catal.* **2006**, *348*, 1235–1240.

[19] Y. Motoyama, M. Okano, H. Narusawa, N. Makihara, K. Aoki, H. Nishiyama, *Organometallics* **2001**, *20*, 1580–1591.

[20] When 2-pyridine acetylene was used no reaction occurred possibly due to the coordination of pyridine N to the Rh catalyst.

[21] For additional results on the catalytic alkynylation of ethyl trifluoropyruvate with aliphatic terminal alkynes, please see the Supporting Information.

