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Cooperative Catalytic Reactions Using Distinct Transition-Metal Catalysts: Ruthenium- and Copper-Catalyzed Enantioselective Propargylic Alkylation

Masahiro Ikeda, Yoshihiro Miyake, and Yoshiaki Nishibayashi*[a]

Abstract: The enantioselective propargylic alkylation of propargylic alcohols with β-ketoesters in the presence of a thiolate-bridged diruthenium complex and a copper complex as co-catalyst affords the corresponding propargylic alkylated products in excellent yields as a mixture of two diastereoisomers with high enantioselectivity (up to 95% enantiomeric excess (*ee*)). The findings reported herein not only open up a new type of enantioselective propargylic substitution reaction, but also a new aspect of cooperative catalytic reactions using distinct transition metals to realize a useful transformation that cannot be achieved by a single catalyst.

Keywords: allenylidene · cooperative reaction · copper · propargylic substitution reaction · ruthenium

Introduction

In the field of organic chemistry, more efficient and valuable synthetic methodologies for the highly enantioselective construction of carbon-carbon bonds are still required because of strong demands for operationally simple and environmentally friendly reaction conditions to synthesize useful compounds. Recently, the combination of distinct catalysts for dual activation of distinct reacting partners[1,2] has emerged as a new strategy for developing novel and valuable reactions that are difficult or impossible by the use of single catalysts. Moreover, the generation of byproducts is minimized in these reaction systems because they do not require a stoichiometric amount of activating reagent to activate the substrates. However, as yet there have only been a few successful examples because there is the potential for a multitude of side reactions and different catalysts can mutually interfere in each reaction step.

In sharp contrast to allylic substitution reactions catalyzed by transition-metal complexes,[3] much less attention has been paid to the corresponding propargylic substitution reactions, presumably because of their difficulty. To the best of our knowledge, only two reaction systems have hitherto been reported that enable the successful accomplishment of enantioselective propargylic substitution reactions. One is the ruthenium-catalyzed enantioselective propargylic substitution reaction reported by our group.[4] The other is the copper-catalyzed enantioselective propargylic amination reported by our group[5] and van Maarseveen's group.[6] Unfortunately, however, suitable nucleophiles are quite limited.

Quite recently, we found the ruthenium-catalyzed propargylic alkylation of propargylic alcohols with enamines generated in situ from aldehydes and secondary amines as carbon-centered nucleophiles to give the corresponding propargylic alkylated products with high enantioselectivity (up to 99% enantiomeric excess (*ee*)).[7] In this reaction system, the transition-metal catalyst (ruthenium complex) and the organocatalyst (secondary amine) activate the propargylic alcohol and the aldehyde, respectively, and cooperatively promote the propargylic alkylation enantioselectively.

To realize a novel type of enantioselective propargylic alkylation, we decided to introduce another type of cooperative catalytic reaction using distinct transition-metal catalysts.[1,8] Surprisingly, cooperative catalytic reactions of nucleophilic and electrophilic intermediates activated only by distinct transition metals[8] are extremely rare, being even less well explored than cooperative catalytic reactions using a transition-metal catalyst and an organocatalyst.[2] In cooperative catalytic reactions, unexpected interactions, such as redox processes between the respective transition-metal catalysts as well as undesirable side reactions, need to be avoided so as to favor the target reactions. To avoid such difficulties, compatibility between the respective catalysts first needs to be established.

We have now found that ruthenium- and copper-catalyzed propargylic alkylation of propargylic alcohols with β-ketoesters affords the corresponding propargylic alkylated products in high yields with excellent enantioselectivities. In the present reaction system, the transition-metal catalysts (ruthenium and copper complexes) activate propargylic alcohols and β-ketoesters, respectively, thereby cooperatively promoting the propargylic alkylation enantioselectively (Scheme 1). In fact, we have delineated the precise roles of the ruthenium–allenylidene complex and the β-ketoester activated by the copper complex as key reactive intermediates.

[a] M. Ikeda, Dr. Y. Miyake, Prof. Dr. Y. Nishibayashi
Institute of Engineering Innovation
School of Engineering, The University of Tokyo
Yayoi, Bunkyo-ku, Tokyo, 113-8656 (Japan)
Fax: (+81) 3-5841-1175
E-mail: ynishiba@sogo.t.u-tokyo.ac.jp

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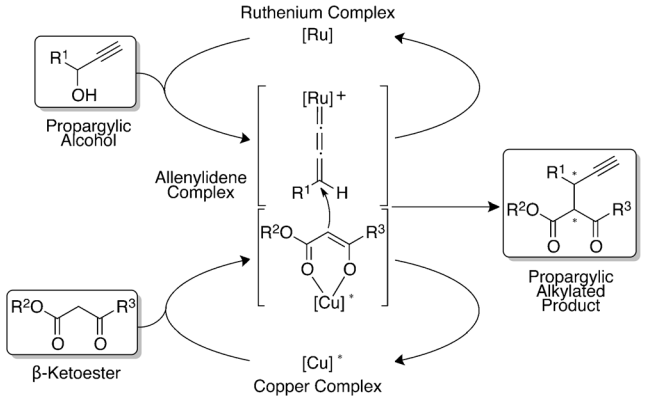


Scheme 1. Cooperative catalytic reactions using distinct transition-metal catalysts.

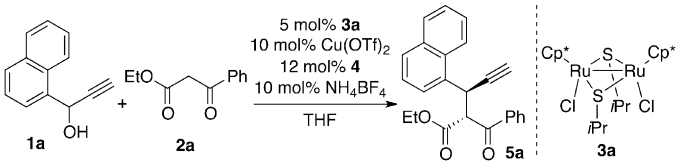
Enolates generated in situ from copper complexes[9,10] and β-ketoesters have been used as carbon-centered nucleophiles, but successful examples have been limited to enantioselective addition reactions to carbonyls and related compounds. Our findings reported herein constitute the first application of these enolates to asymmetric substitution reactions such as benzylic, allylic, and propargylic substitution reactions. We believe that the method described in this article represents a new type of enantioselective dual catalytic reaction using a pair of distinct transition-metal catalysts.[1,8] Our preliminary results are described herein.

Results and Discussion

Treatment of 1-(1-naphthyl)-2-propyn-1-ol (**1a**) with three equivalents of ethyl 3-oxo-3-phenylpropanoate (**2a**) in the presence of catalytic amounts of thiolate-bridged diruthenium complex $[Cp^*RuCl(\mu_2\text{-}S\textit{i}Pr)]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$; **3a**), a complex of $Cu(OTf)_2$ with (4*R*,4′*R*,5*S*,5′*S*)-2,2′-(cyclopropane-1,1-diyl)-bis(4,5-diphenyl-4,5-dihydrooxazole) (**4a**), and NH_4BF_4 in THF at room temperature for 120 h gave ethyl 2-benzoyl-3-(naphthalen-1-yl)-4-pentynoate (**5a**) in 96% isolated yield as a mixture of two diastereoisomers (*anti*-**5a**/*syn*-**5a** = 4:1) with 86% *ee* of *anti*-**5a** (Table 1, entry 1). Other bis(oxazoline) ligands such as **4b** worked effectively, but substantially lower diastereo- and enantioselectivities were observed when **4c** or **4d** were used as bis(oxazoline) ligands (Table 1, entries 2–4).[11] The use of only 1.5 equivalents of **2a** with respect to **1a** was sufficient to promote the propargylic alkylation (Table 1, entry 5). The reaction proceeded smoothly even at −10 °C, higher diastereo- and enantioselectivities being observed (Table 1, entry 6). Separately, we confirmed that the use of either **3a** or the copper complex alone did not promote the propargylic alkylation. These results indicated that **3a** and the copper complex acted cooperatively as catalysts to promote the catalytic reaction enantioselectively.

Next, propargylic alkylations of a variety of propargylic alcohols were carried out by using **3a** and the copper complex with **4a** as the co-catalysts. Typical results are shown in Table 2. Similarly high enantioselectivity was observed when 1-(2-naphthyl)-2-propyn-1-ol (**1b**) was used as the substrate (Table 2, entry 2). However, the enantioselectivity decreased slightly when 1-phenyl-2-propyn-1-ol (**1c**) was used as the substrate (Table 2, entry 3). Introduction of a methoxy or methyl group at the *para*-position of a benzene ring on the propargylic alcohol had little effect on the reactivity or the

Table 1. Enantioselective propargylic alkylation of 1-(1-naphthyl)-2-propyn-1-ol (**1a**) with β-ketoester **2a**.[a]



Entry	**2a** [equiv]	**4**	*T* [°C]	*t* [h]	Yield of **5a** [%][b]	*anti*/*syn* ratio of **5a**[c]	*ee* of *anti*-**5a** [%][d]
1	3.0	**4a**	RT	120	96	4:1	86
2	3.0	**4b**	RT	120	93	4:1	84[e]
3	3.0	**4c**	RT	120	50	3:1	10
4	3.0	**4d**	RT	120	79	1:1	54
5	1.5	**4a**	RT	120	94	4:1	86
6	1.5	**4a**	−10	45	94	7:1	93

[a] All reactions of **1a** (0.20 mmol) with **2a** (0.30 mmol) were carried out in the presence of **3a** (0.010 mmol), $Cu(OTf)_2$ (0.020 mmol), **4** (0.024 mmol), and NH_4BF_4 (0.020 mmol) in THF (4 mL). [b] Isolated yield. [c] Determined by ^1H NMR spectroscopy. [d] Determined by HPLC. [e] The opposite absolute configuration (2*S*,3*S*) was found.

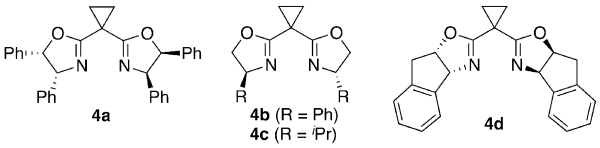
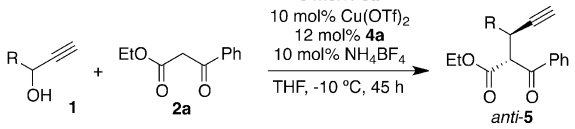


Table 2. Enantioselective propargylic alkylations of propargylic alcohols (**1**) with β-ketoester **2a**.[a]



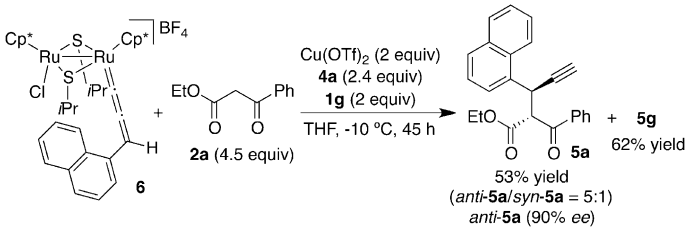
Entry	**1**	Yield of **5**[b] [%]	*anti*-**5**/*syn*-**5**[c]	*ee* of *anti*-**5** [%][d]
1	R = 1-naphthyl (**1a**)	94 (**5a**)	7:1	93
2	R = 2-naphthyl (**1b**)	90 (**5b**)	6:1	95
3	R = Ph (**1c**)	93 (**5c**)	4:1	83
4	R = *p*-$MeOC_6H_4$ (**1d**)	91 (**5d**)	3:1	81
5	R = *p*-MeC_6H_4 (**1e**)	87 (**5e**)	3:1	86
6	R = *p*-PhC_6H_4 (**1f**)	89 (**5f**)	2:1	93
7	R = *o*-$MeOC_6H_4$ (**1g**)	98 (**5g**)	15:1	93
8	R = *o*-MeC_6H_4 (**1h**)	97 (**5h**)	7:1	90
9	R = *o*,*p*-$(MeO)_2C_6H_3$ (**1i**)	92 (**5i**)	4:1	85

[a] All reactions of **1** (0.20 mmol) with **2a** (0.30 mmol) were carried out in the presence of **3a** (0.010 mmol), $Cu(OTf)_2$ (0.020 mmol), **4a** (0.024 mmol), and NH_4BF_4 (0.020 mmol) at −10 °C in THF (4 mL) for 45 h. [b] Isolated yield. [c] Determined by ^1H NMR spectroscopy. [d] Determined by HPLC.

enantioselectivity for the propargylic alkylated products (Table 2, entries 4 and 5), but higher enantioselectivity was observed when a phenyl group was introduced at the *para*-position of a benzene ring on the propargylic alcohol (Table 2, entry 6). Interestingly, the introduction of a methoxy or methyl group at the *ortho*-position of a benzene ring on the propargylic alcohol substantially increased the enantioselectivity (Table 2, entries 7–9). No reaction occurred at all under the same conditions when 1-cyclohexyl-2-propyn-1-ol was used as the substrate, indicating that the presence of an aryl moiety at the propargylic position of **1** is necessary to achieve the reaction.

Propargylic alkylations with other β-ketoesters also proceeded smoothly to give the corresponding propargylic alkylated products with high enantioselectivities. Typical results are shown in Table 3. Reactions of **1a** with benzyl 3-oxo-3-phenylpropanoate (**2b**), methyl 3-oxo-3-phenylpropanoate (**2c**), and ethyl 3-(4-methoxyphenyl)-3-oxopropanoate (**2d**) under the same reaction conditions gave the corresponding alkylated products with similar high enantioselectivities (Table 3, entries 1–3). When other β-ketoesters such as ethyl 3-(naphthalen-1-yl)-3-oxopropanoate (**2e**), ethyl 3-(naphthalen-2-yl)-3-oxopropanoate (**2f**), and ethyl 3-oxo-3-(*p*-tolyl)-propanoate (**2g**) were used in place of **2a**, the corresponding propargylic alkylated products were obtained in similarly high yields with high enantio- and diastereoselectivities (Table 3, entries 4–6). The introduction of a chloro substituent at the *para*-position of the benzene ring appended to the β-ketoester had little effect on the reactivity or the enantioselectivity for the propargylic alkylated product (Table 3, entry 7). Reactions of other propargylic alcohols **1b** and **1g**, as well as **1a**, with various β-ketoesters also gave similarly good results (Table 3, entries 8–10).

We investigated the following stoichiometric and catalytic reactions to gain insight into the reaction pathway. Treatment of a ruthenium–allenylidene complex **6**[12] with 4.5 equivalents of **2a** in the presence of 2 equivalents of $Cu(OTf)_2$ with 2.4 equivalents of **4a** together with 2 equivalents of **1g** in THF at −10 °C for 45 h gave **5a** in 53% isolated yield, based on **6**, as a mixture of two diastereoisomers (*anti*-**5a**/*syn*-**5a** = 5:1; *anti*-**5a** (90% *ee*)), together with **5g** in 62% isolated yield based on **1g**, as shown in Scheme 2.[13]



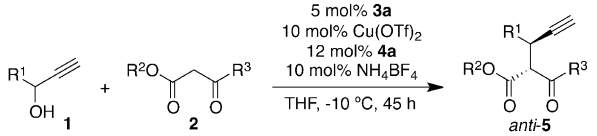
Scheme 2. Stoichiometric reaction of a ruthenium allenylidene complex with a β-ketoester in the presence of a copper complex.

Furthermore, the reaction of **1a** with **2a** in the presence of catalytic amounts of **6** and $Cu(OTf)_2$ with **4a** at −10 °C for 45 h afforded **5a** in 86% yield as a mixture of two diastereoisomers (*anti*-**5a**/*syn*-**5a** = 7:1; *anti*-**5a** (93% *ee*)). Separately, we confirmed that no reaction at all occurred when a propargylic alcohol bearing an internal alkyne moiety was subjected to the same reaction conditions. Thus, these results clearly indicated that the propargylic alkylation proceeded via ruthenium–allenylidene complexes as key reactive intermediates.[14]

A proposed reaction pathway is shown in Scheme 3. The initial step is the formation of an allenylidene complex (**B**) by the reaction of propargylic alcohol **1** with **3** via a vinylidene complex (**A**). Subsequent attack of an enolate (**E**), generated in situ from β-ketoester **2** and $Cu(OTf)_2$ bearing **4**, upon the γ-carbon of **B** results in the formation of another vinylidene complex (**D**) via an alkynyl complex (**C**). After transformation of the vinylidene complex **D** into the corresponding π-alkyne complex, the alkylated product **5** is formed by ligand exchange with another molecule of propargylic alcohol **1**. As described in our previous reports,[12] we believe that the synergistic effect between the two ruthenium atoms in the diruthenium complex is also quite important for promoting this catalytic reaction.

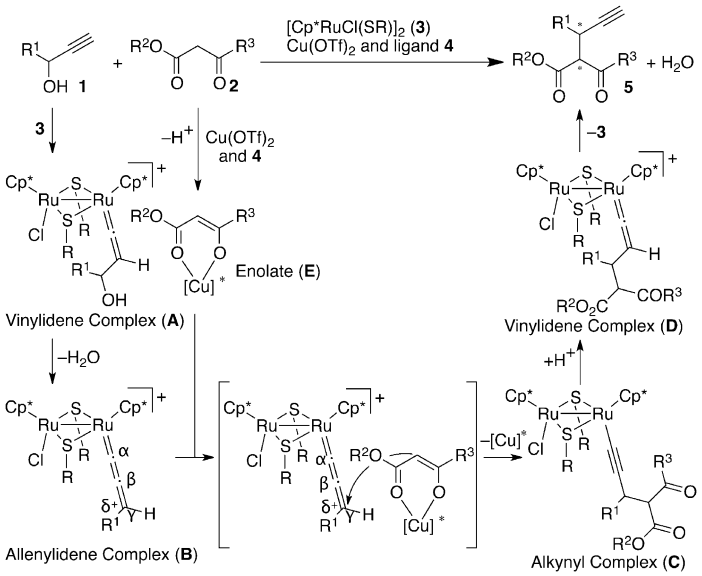
To obtain some information on the enantioselective propargylic alkylation, the stereochemistry of the product **5b** was determined. After one recrystallization of *anti*-**5b**, enantiomerically pure *anti*-**5b** was isolated, and its absolute configuration was determined as (2*R*,3*R*) by X-ray analysis.[15]

Table 3. Enantioselective propargylic alkylations of propargylic alcohols (**1**) with β-ketoesters (**2**).[a]



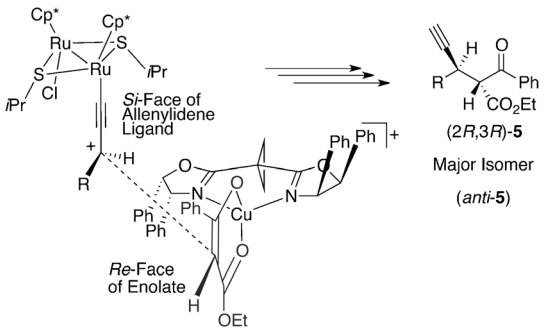
Entry	**1**	**2**	Yield of **5**[b] [%]	*anti*-**5**/*syn*-**5**[c]	*ee* of *anti*-**5** [%][d]
1	R^1 = 1-naphthyl (**1a**)	R^2 = Bn, R^3 = Ph (**2b**)	95 (**5j**)	5:1	91
2	R^1 = 1-naphthyl (**1a**)	R^2 = Me, R^3 = Ph (**2c**)	99 (**5k**)	4:1	86
3	R^1 = 1-naphthyl (**1a**)	R^2 = Et, R^3 = *p*-$MeOC_6H_4$ (**2d**)	97 (**5l**)	6:1	89
4	R^1 = 1-naphthyl (**1a**)	R^2 = Et, R^3 = 1-naphthyl (**2e**)	92 (**5m**)	12:1	90
5	R^1 = 1-naphthyl (**1a**)	R^2 = Et, R^3 = 2-naphthyl (**2f**)	96 (**5n**)	10:1	92
6	R^1 = 1-naphthyl (**1a**)	R^2 = Et, R^3 = *p*-MeC_6H_4 (**2g**)	95 (**5o**)	10:1	94
7	R^1 = 1-naphthyl (**1a**)	R^2 = Et, R^3 = *p*-ClC_6H_4 (**2h**)	94 (**5p**)	3:1	86
8	R^1 = 2-naphthyl (**1b**)	R^2 = Et, R^3 = 2-naphthyl (**2f**)	93 (**5q**)	6:1	92
9	R^1 = *o*-$MeOC_6H_4$ (**1g**)	R^2 = Bn, R^3 = Ph (**2b**)	98 (**5r**)	7:1	91
10	R^1 = *o*-$MeOC_6H_4$ (**1g**)	R^2 = Et, R^3 = *p*-ClC_6H_4 (**2h**)	94 (**5s**)	6:1	92

[a] All reactions of **1** (0.20 mmol) with **2** (0.30 mmol) were carried out in the presence of **3a** (0.010 mmol), $Cu(OTf)_2$ (0.020 mmol), **4a** (0.024 mmol), and NH_4BF_4 (0.020 mmol) at −10 °C in THF (4 mL) for 45 h. [b] Isolated yield. [c] Determined by ^1H NMR spectroscopy. [d] Determined by HPLC.



Scheme 3. Proposed reaction pathway for the propargylic alkylation of propargylic alcohols with β-ketoesters.

To account for the enantioselective and diastereoselective formation of (2*R*,3*R*)-**5**, we propose transition states between the ruthenium–allenylidene complex and the copper-enolate complex as indicated in Scheme 4.[16] In this reaction



Scheme 4. Asymmetric induction of propargylic alkylation between allenylidene and copper complexes.

system, the distorted tetrahedral copper-enolate proposed by Jørgensen and co-workers[10b] attacks the *Si*-face of the allenylidene complex from the *Re*-face of the enolate, leading to carbon–carbon bond formation. We believe this to be the first successful example of enantioselective propargylation of β-ketoesters with propargylic alcohols to give the corresponding α-propargyl β-ketoesters with high enantioselectivity.

Conclusion

We have found the ruthenium- and copper-catalyzed enantioselective propargylic alkylation of propargylic alcohols with β-ketoesters to give the corresponding propargylic alkylated products in excellent yields as a mixture of two diastereoisomers with high enantioselectivity (up to 95% *ee*). This catalytic reaction is considered to represent a new type of enantioselective propargylic substitution reaction,[17] in which an enolate generated in situ from a copper complex and a β-ketoester enantioselectively attacks the ruthenium–allenylidene complex. In the present reaction system, the transition-metal catalysts (ruthenium complex and copper complex) activate propargylic alcohols and β-ketoesters, respectively, and both catalysts act cooperatively and simultaneously to promote the propargylic alkylation enantioselectively. We believe that the findings described herein will not only open up a new type of enantioselective propargylic substitution reaction, but also a new aspect of cooperative catalytic reactions using distinct transition metals to achieve more valuable transformations that cannot be realized by a single catalyst. Further work is currently in progress to apply this strategy to other reaction systems.

Experimental Section

General methods: ^{1}H NMR (270 MHz) and ^{13}C NMR (67.8 MHz) spectra were measured on a JEOL Excalibur 270 spectrometer using $CDCl_3$ as solvent. HPLC analyses were performed on a Hitachi L-7100 apparatus equipped with a UV detector using 25 cm × 4.6 mm DAICEL Chiralcel OZ-H and OJ-H and Chiralpak AS-H, AD, IC, and ID columns. Elemental analyses were performed at the Microanalytical Center of the University of Tokyo. Mass spectra were measured on a JEOL JMS-700 mass spectrometer. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods, then distilled under N_2 and degassed before use. Propargylic alcohols **1** were prepared by reaction of the corresponding aldehydes with ethynylmagnesium bromide (0.5 M in THF). Thiolate-bridged diruthenium complexes **3** were prepared according to our previously reported procedure.[12,18,19] Ethyl 3-oxo-3-phenylpropanoate (**2a**) is a commercially available reagent. β-Ketoesters (**2b–2h**)[20] and optically pure bis(oxazoline) ligands **4**[21] were synthesized according to literature procedures.

General procedure for the preparation of a propargylic alkylated product (5) by the reaction of a propargylic alcohol (1) with a β-ketoester (2): A typical experimental procedure for the reaction of 1-(1-naphthyl)-2-propyn-1-ol (**1a**) with ethyl 3-oxo-3-phenylpropanoate (**2a**) was as follows. A 20 mL Schlenk flask was charged with (4*R*,4′*R*,5*S*,5′*S*)-2,2′-(cyclopropane-1,1-diyl)-bis(4,5-diphenyl-4,5-dihydrooxazole) (**4a**; 11.6 mg, 0.024 mmol) and $Cu(OTf)_2$ (7.2 mg, 0.020 mmol) under N_2. The mixture was stirred under vacuum for 2 h and then an atmosphere of N_2 was admitted to the flask. Anhydrous THF (1.0 mL) was added and the solution was stirred for 2 h. After cooling the reaction flask to −10 °C, a solution of ethyl 3-oxo-3-phenylpropanoate (**2a**; 57.6 mg, 0.30 mmol) in anhydrous THF (3.0 mL) was added to the reaction mixture, and then $[Cp^*RuCl(\mu_2\text{-}SiPr)]_2$ (**3a**; 6.9 mg, 0.010 mmol), NH_4BF_4 (2.1 mg, 0.020 mmol), and 1-(1-naphthyl)-2-propyn-1-ol (**1a**; 36.4 mg, 0.20 mmol) were added successively under N_2. The reaction flask was kept at −10 °C for 45 h. After concentration of the reaction mixture under reduced pressure, the residue was purified by column chromatography (SiO_2; eluent: hexane/ethyl acetate, 95:5 to 85:15) to give ethyl 2-benzoyl-3-(naphthalen-1-yl)-4-pentynoate (**5a**) as a colorless oil (67.1 mg, 0.188 mmol, 94% isolated yield, *anti*-**5a**/*syn*-**5a** = 7:1).

Data for 5a: *anti*-isomer: ^{1}H NMR: δ = 8.38 (d, J = 8.6 Hz, 1H), 8.08–8.11 (m, 2H), 7.42–7.88 (m, 9H), 5.48 (dd, J = 10.5 and 2.7 Hz, 1H), 5.23 (d, J = 10.5 Hz, 1H), 3.68 (q, J = 7.0 Hz, 2H), 2.18 (d, J = 2.7 Hz, 1H), 0.68 ppm (t, J = 7.0 Hz, 3H); *syn*-isomer: ^{1}H NMR: δ = 8.41 (d, J = 8.6 Hz, 1H), 8.09–8.12 (m, 2H), 7.28–7.35 (m, 3H), 5.24 (d, J = 10.0 Hz, 1H), 4.27 (q, J = 7.0 Hz, 2H), 2.34 (d, J = 2.7 Hz, 1H), 1.26 ppm (t, J =

7.0 Hz, 3H); *anti*-isomer: ^{13}C NMR: δ = 192.2, 166.6, 136.4, 134.0, 133.8, 133.6, 131.0, 128.93, 128.91, 128.7, 128.55, 126.6, 126.3, 125.8, 125.3, 123.59, 83.6, 71.9, 61.6, 59.7, 33.4, 13.6 ppm; *syn*-isomer: ^{13}C NMR: δ = 191.7, 167.4, 135.9, 134.1, 133.7, 130.7, 128.51, 128.49, 128.46, 126.4, 125.7, 125.2, 123.65, 83.3, 72.5, 62.0, 59.4, 33.6, 14.0 ppm; HRMS (EI): *m*/*z*: calcd for $C_{24}H_{20}O_3$ [*M*]: 356.1412; found: 356.1409. The optical purity of **5a** was determined by HPLC analysis; DAICEL Chiralpak IC, hexane/*i*PrOH = 97:3, flow rate = 1.0 mL min^{-1}, λ = 254 nm; retention times: 17.0 min (*anti*-major) and 30.2 min (*anti*-minor), 93% *ee* (*anti*); 19.4 min (*syn*-minor) and 23.9 min (*syn*-major), 1% *ee* (*syn*).

Ethyl 2-benzoyl-3-(naphthalen-2-yl)pent-4-ynoate (5b): Isolated yield 90% (*anti*-**5b**/*syn*-**5b** = 6:1). A white solid. *anti*-isomer: ^{1}H NMR: δ = 8.11–8.14 (m, 2H), 7.81–7.88 (m, 4H), 7.46–7.65 (m, 6H), 4.96 (d, *J* = 10.5 Hz, 1H), 4.84 (dd, *J* = 10.5 and 2.7 Hz, 1H), 3.83 (m, 2H), 2.19 (d, *J* = 2.7 Hz, 1H), 0.85 ppm (t, *J* = 7.0 Hz, 3H); *syn*-isomer: ^{1}H NMR: δ = 7.33–7.74 (m, 6H), 4.25 (q, *J* = 7.0 Hz, 2H), 2.37 (d, *J* = 2.7 Hz, 1H), 1.26 ppm (t, *J* = 7.0 Hz, 3H); *anti*-isomer: ^{13}C NMR: δ = 192.1, 166.5, 136.4, 135.1, 133.8, 133.3, 132.8, 129.0, 128.8, 128.5, 127.87, 127.63, 127.55, 126.3, 126.1, 126.02, 83.6, 72.2, 61.7, 61.2, 37.4, 13.6 ppm; *syn*-isomer: ^{13}C NMR: δ = 191.5, 167.2, 135.9, 135.4, 133.7, 133.2, 132.6, 128.64, 128.56, 128.41, 127.90, 127.7, 127.5, 125.99, 125.96, 83.4, 72.5, 62.0, 61.3, 37.1, 14.0 ppm; elemental analysis calcd (%) for $C_{24}H_{20}O_3$: C 80.88, H 5.66; found: C 80.87, H 5.86. The optical purities of *anti*-**5b** and *syn*-**5b** were determined by HPLC analysis; DAICEL Chiralpak AD, hexane/*i*PrOH = 97:3, flow rate = 0.25 mL min^{-1}, λ = 254 nm; retention times for *anti*-**5b**: 75.3 min (minor) and 82.8 min (major), 95% *ee*; retention times for *syn*-**5b**: 69.2 min (major) and 90.9 min (minor), 65% *ee*. Colorless needle-shaped crystals of (2*R*,3*R*)-**5b** suitable for X-ray analysis were obtained by recrystallization of **5b** from methanol.

Ethyl 2-benzoyl-3-phenylpent-4-ynoate (5c): Isolated yield 93% (*anti*-**5c**/*syn*-**5c** = 4:1). A colorless oil. *anti*-isomer: ^{1}H NMR: δ = 8.08–8.11 (m, 2H), 7.32–7.64 (m, 8H), 4.84 (d, *J* = 10.5 Hz, 1H), 4.66 (dd, *J* = 10.5 and 2.4 Hz, 1H), 3.88 (q, *J* = 7.0 Hz, 2H), 2.15 (d, *J* = 2.4 Hz, 1H), 0.93 ppm (t, *J* = 7.0 Hz, 3H); *syn*-isomer: ^{1}H NMR: δ = 7.84–7.88 (m, 2H), 7.14–7.41 (m, 8H), 4.85 (d, *J* = 10.5 Hz, 1H), 4.73 (dd, *J* = 10.5 and 2.4 Hz, 1H), 4.22 (qd, *J* = 7.0 and 2.4 Hz, 2H), 2.32 (d, *J* = 2.4 Hz, 1H), 1.25 ppm (t, *J* = 7.0 Hz, 3H); *anti*-isomer: ^{13}C NMR: δ = 192.1, 166.5, 137.7, 136.3, 133.8, 128.9, 128.7, 128.6, 128.4, 127.7, 83.6, 71.9, 61.6, 61.3, 37.2, 13.6 ppm; *syn*-isomer: ^{13}C NMR: δ = 191.7, 167.1, 138.0, 136.0, 133.6, 128.55, 128.52, 128.3, 127.5, 83.4, 72.2, 61.9, 61.2, 37.1, 14.0 ppm; HRMS (EI): *m*/*z*: calcd for $C_{20}H_{18}O_3$ [*M*]: 306.1256; found: 306.1252. The optical purities of *anti*-**5c** and *syn*-**5c** were determined by HPLC analysis; DAICEL Chiralpak IC, hexane/*i*PrOH = 97:3, flow rate = 0.5 mL min^{-1}, λ = 254 nm; retention times for *anti*-**5c**: 31.6 min (major) and 60.0 min (minor), 83% *ee*; retention times for *syn*-**5c**: 27.5 min (minor) and 44.7 min (major), 55% *ee*.

Ethyl 2-benzoyl-3-(4-methoxyphenyl)pent-4-ynoate (5d): Isolated yield 91% (*anti*-**5d**/*syn*-**5d** = 3:1). A colorless oil. *anti*-isomer: ^{1}H NMR: δ = 8.08–8.12 (m, 2H), 7.59–7.64 (m, 1H), 7.50–7.54 (m, 2H), 7.34–7.39 (m, 2H), 6.86–6.90 (m, 2H), 4.805 (d, *J* = 10.8 Hz, 1H), 4.62 (dd, *J* = 10.8 and 2.4 Hz, 1H), 3.90 (qd, *J* = 7.0 and 1.4 Hz, 2H), 3.80 (s, 3H), 2.14 (d, *J* = 2.4 Hz, 1H), 0.97 ppm (t, *J* = 7.0 Hz, 3H); *syn*-isomer: ^{1}H NMR: δ = 7.86–7.89 (m, 2H), 7.47–7.54 (m, 1H), 7.30–7.41 (m, 4H), 6.73–6.76 (m, 2H), 4.812 (d, *J* = 10.5 Hz, 1H), 4.69 (dd, *J* = 10.5 and 2.4 Hz, 1H), 4.22 (qd, *J* = 7.0 and 2.4 Hz, 2H), 3.71 (s, 3H), 2.32 (d, *J* = 2.4 Hz, 1H), 1.24 ppm (t, *J* = 7.0 Hz, 3H); *anti*-isomer: ^{13}C NMR: δ = 192.2, 166.6, 159.1, 136.4, 133.8, 129.7, 129.49, 128.9, 128.72, 114.0, 83.9, 71.7, 61.6, 61.5, 55.3, 36.5, 13.7 ppm; *syn*-isomer: ^{13}C NMR: δ = 191.8, 167.2, 158.8, 136.1, 133.6, 130.1, 129.45, 128.65, 128.6, 113.9, 83.7, 72.0, 61.9, 55.2, 36.3, 14.0 ppm; HRMS (EI): *m*/*z*: calcd for $C_{21}H_{20}O_4$ [*M*]: 336.1362; found: 336.1353. The optical purities of *anti*-**5d** and *syn*-**5d** were determined by HPLC analysis; DAICEL Chiralpak IC, hexane/*i*PrOH = 97:3, flow rate = 1.0 mL min^{-1}, λ = 254 nm; retention times for *anti*-**5d**: 29.6 min (major) and 49.6 min (minor), 81% *ee*; retention times for *syn*-**5d**: 24.2 min (minor) and 32.8 min (major), 59% *ee*.

Ethyl 2-benzoyl-3-(*p*-tolyl)pent-4-ynoate (5e): Isolated yield 87% (*anti*-**5e**/*syn*-**5e** = 3:1). A colorless oil. *anti*-isomer: ^{1}H NMR: δ = 8.08–8.11 (m, 2H), 7.58–7.64 (m, 1H), 7.50–7.53 (m, 2H), 7.32–7.35 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.62 (dd, *J* = 10.8 and 2.4 Hz, 1H), 3.89 (qd, *J* = 7.0 and 1.1 Hz, 2H), 2.33 (s, 3H), 2.13 (d, *J* = 2.4 Hz, 1H), 0.96 ppm (t, *J* = 7.0 Hz, 3H); *syn*-isomer: ^{1}H NMR: δ = 7.86–7.90 (m, 2H), 7.47–7.54 (m, 1H), 7.27–7.41 (m, 4H), 7.03 (d, *J* = 8.1 Hz, 2H), 4.83 (d, *J* = 10.5 Hz, 1H), 4.70 (dd, *J* = 10.5 and 2.4 Hz, 1H), 4.22 (qd, *J* = 7.2 and 3.2 Hz, 2H), 2.31 (d, *J* = 2.4 Hz, 1H), 2.23 (s, 3H), 1.24 ppm (t, *J* = 7.2 Hz, 3H); *anti*-isomer: ^{13}C NMR: δ = 192.2, 166.6, 137.5, 136.4, 134.7, 133.7, 129.30, 128.9, 128.72, 128.24, 83.8, 71.7, 61.6, 61.33, 36.9, 21.1, 13.7 ppm; *syn*-isomer: ^{13}C NMR: δ = 191.7, 167.2, 137.1, 136.1, 135.1, 133.6, 129.25, 128.68, 128.6, 128.19, 83.7, 72.0, 62.0, 61.35, 36.7, 21.0, 14.0 ppm; HRMS (EI): *m*/*z*: calcd for $C_{21}H_{20}O_3$ [*M*]: 320.1412; found: 320.1425. The optical purities of *anti*-**5e** and *syn*-**5e** were determined by HPLC analysis; DAICEL Chiralpak IC, hexane/*i*PrOH = 95:5, flow rate = 1.0 mL min^{-1}, λ = 254 nm; retention times for *anti*-**5e**: 14.7 min (major) and 27.1 min (minor), 86% *ee*; retention times for *syn*-**5e**: 12.8 min (minor) and 18.0 min (major), 43% *ee*.

Ethyl 3-[(1,1′-biphenyl)-4-yl]-2-benzoylpent-4-ynoate (5f): Isolated yield 89% (*anti*-**5f**/*syn*-**5f** = 2:1). A white solid. *anti*-isomer: ^{1}H NMR: δ = 8.10–8.13 (m, 2H), 7.30–7.65 (m, 12H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.72 (dd, *J* = 10.8 and 2.7 Hz, 1H), 3.91 (q, *J* = 7.0 Hz, 2H), 2.18 (d, *J* = 2.7 Hz, 1H), 0.95 ppm (t, *J* = 7.0 Hz, 3H); *syn*-isomer: ^{1}H NMR: δ = 7.88 (m, 2H), 4.89 (d, *J* = 10.5 Hz, 1H), 4.79 (dd, *J* = 10.5 and 2.4 Hz, 1H), 4.24 (qd, *J* = 7.0 and 2.7 Hz, 2H), 2.35 (d, *J* = 2.4 Hz, 1H), 1.26 ppm (t, *J* = 7.0 Hz, 3H); *anti*-isomer: ^{13}C NMR: δ = 192.1, 166.6, 140.7, 140.4, 136.8, 136.4, 133.8, 128.9, 128.78, 128.7, 127.34, 127.31, 127.04, 83.5, 72.0, 61.7, 61.2, 37.0, 13.7 ppm; *syn*-isomer: ^{13}C NMR: δ = 191.7, 167.2, 140.6, 140.5, 137.1, 136.0, 133.7, 129.0, 128.75, 128.6, 127.4, 127.27, 126.99, 83.4, 72.3, 62.0, 61.3, 36.7, 14.0 ppm; elemental analysis calcd (%) for $C_{26}H_{22}O_3$: C 81.65, H 5.80; found: C 81.56, H 5.95. The optical purities of *anti*-**5f** and *syn*-**5f** were determined by HPLC analysis; DAICEL Chiralcel OJ-H, hexane/*i*PrOH = 97:3, flow rate = 1.0 mL min^{-1}, λ = 254 nm; retention times for *anti*-**5f**: 68.1 min (minor) and 92.1 min (major), 93% *ee*; retention times for *syn*-**5f**: 46.6 min (minor) and 53.2 min (major), 71% *ee*.

Ethyl 2-benzoyl-3-(2-methoxyphenyl)pent-4-ynoate (5g): Isolated yield 98% (*anti*-**5g**/*syn*-**5g** = 15:1). A colorless oil. *anti*-isomer: ^{1}H NMR: δ = 8.01–8.06 (m, 2H), 7.53–7.61 (m, 1H), 7.39–7.51 (m, 3H), 7.21–7.28 (m, 1H), 6.88–6.94 (m, 2H), 5.16 (d, *J* = 9.7 Hz, 1H), 4.95 (dd, *J* = 9.7 and 2.7 Hz, 1H), 3.86–3.97 (m, 2H), 3.91 (s, 3H), 2.09 (d, *J* = 2.7 Hz, 1H), 0.95 ppm (t, *J* = 7.0 Hz, 3H); *syn*-isomer: ^{1}H NMR: δ = 7.90–7.93 (m, 2H), 7.14–7.18 (m, 1H), 5.08 (d, *J* = 8.6 Hz, 1H), 4.91 (dd, *J* = 8.6 and 2.4 Hz, 1H), 4.14–4.21 (m, 2H), 3.82 (s, 3H), 2.27 (d, *J* = 2.4 Hz, 1H), 1.19 ppm (t, *J* = 7.0 Hz, 3H); *anti*-isomer: ^{13}C NMR: δ = 192.8, 167.2, 157.1, 136.7, 133.5, 130.2, 129.0, 128.8, 128.6, 125.7, 120.8, 111.2, 83.3, 70.7, 61.4, 57.7, 55.7, 32.4, 13.7 ppm; *syn*-isomer: ^{13}C NMR: δ = 192.9, 167.7, 156.5, 136.2, 133.4, 130.0, 128.54, 128.51, 120.7, 110.8, 71.5, 61.5, 57.8, 55.4, 14.0 ppm; HRMS (EI): *m*/*z*: calcd for $C_{21}H_{20}O_4$ [*M*]: 336.1362; found: 336.1359. The optical purities of *anti*-**5g** and *syn*-**5g** were determined by HPLC analysis; DAICEL Chiralpak IC, hexane/*i*PrOH = 97:3, flow rate = 1.0 mL min^{-1}, λ = 254 nm; retention times for *anti*-**5g**: 46.9 min (major) and 82.7 min (minor), 93% *ee*; retention times for *syn*-**5g**: 57.8 min (major) and 73.1 min (minor), 44% *ee*.

Ethyl 2-benzoyl-3-(*o*-tolyl)pent-4-ynoate (5h): Isolated yield 97% (*anti*-**5h**/*syn*-**5h** = 7:1). A colorless oil. *anti*-isomer: ^{1}H NMR: δ = 8.12–8.16 (m, 2H), 7.44–7.65 (m, 4H), 7.15–7.24 (m, 3H), 5.05 (d, *J* = 10.8 Hz, 1H), 4.91 (dd, *J* = 10.8 and 2.4 Hz, 1H), 3.84 (q, *J* = 7.0 Hz, 2H), 2.51 (s, 3H), 2.07 (d, *J* = 2.4 Hz, 1H), 0.86 ppm (t, *J* = 7.0 Hz, 3H); *syn*-isomer: ^{1}H NMR: δ = 7.86–7.91 (m, 2H), 7.37–7.55 (m, 3H), 7.26–7.29 (m, 1H), 7.02–7.06 (m, 3H), 5.06 (d, *J* = 10.8 Hz, 1H), 4.89 (dd, *J* = 10.8 and 2.4 Hz, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 2.52 (s, 3H), 2.25 (d, *J* = 2.4 Hz, 1H), 1.25 ppm (t, *J* = 7.0 Hz, 3H); *anti*-isomer: ^{13}C NMR: δ = 192.2, 166.5, 136.4, 136.30, 136.0, 133.8, 130.9, 129.0, 128.7, 128.0, 127.6, 126.34, 83.7, 71.1, 61.6, 59.68, 33.1, 19.7, 13.5 ppm; *syn*-isomer: ^{13}C NMR: δ = 191.7, 167.4, 136.34, 136.2, 136.1, 133.6, 128.60, 128.58, 127.3, 127.1, 126.29, 83.5, 71.5, 62.0, 59.72, 33.0, 14.0 ppm; HRMS (EI): *m*/*z*: calcd for $C_{21}H_{20}O_3$ [*M*]: 320.1412; found: 320.1424. The optical purities of *anti*-**5h** and *syn*-**5h** were determined by HPLC analysis; DAICEL Chiralpak IC, hexane/*i*PrOH = 98:2, flow rate = 0.5 mL min^{-1}, λ = 254 nm; retention

times for *anti*-**5h**: 21.8 min (major) and 27.1 min (minor), 90% *ee*; retention times for *syn*-**5h**: 20.3 min (major) and 32.3 min (minor), 3% *ee*.

Ethyl 2-benzoyl-3-(2,4-dimethoxyphenyl)pent-4-ynoate (5i): Isolated yield 92% (*anti*-**5i**/*syn*-**5i** = 4:1). A colorless oil. *anti*-isomer: ^{1}H NMR: δ = 8.02–8.05 (m, 2H), 7.55–7.61 (m, 1H), 7.29–7.49 (m, 3H), 6.42–6.46 (m, 2H), 5.12 (d, J = 10.0 Hz, 1H), 4.87 (dd, J = 10.0 and 2.7 Hz, 1H), 3.93 (qd, J = 7.0 and 1.1 Hz, 2H), 3.88 (s, 3H), 3.79 (s, 3H), 2.08 (d, J = 2.7 Hz, 1H), 0.98 ppm (t, J = 7.0 Hz, 3H); *syn*-isomer: ^{1}H NMR: δ = 7.90–7.93 (m, 2H), 7.51–7.61 (m, 1H), 6.33 (d, J = 2.4 Hz, 1H), 5.06 (d, J = 8.4 Hz, 1H), 4.82 (dd, J = 8.4 and 2.7 Hz, 1H), 4.14–4.20 (m, 2H), 3.74 (s, 3H), 2.26 (d, J = 2.7 Hz, 1H), 1.20 ppm (t, J = 7.0 Hz, 3H); *anti*-isomer: ^{13}C NMR: δ = 192.9, 167.2, 160.5, 158.0, 136.7, 133.5, 130.7, 128.8, 128.55, 118.1, 104.44, 99.0, 83.6, 70.4, 61.4, 57.87, 55.6, 55.34, 32.0, 13.7 ppm; *syn*-isomer: ^{13}C NMR: δ = 193.0, 167.8, 160.3, 157.4, 136.2, 133.4, 130.5, 128.56, 128.50, 118.2, 104.39, 98.8, 83.0, 71.2, 61.5, 57.90, 55.4, 55.30, 32.1, 14.0 ppm; HRMS (EI): m/z: calcd for $C_{22}H_{22}O_5$ [M]: 366.1467; found: 366.1455. The optical purities of *anti*-**5i** and *syn*-**5i** were determined by HPLC analysis; DAICEL Chiralpak IC, hexane/*i*PrOH = 95:5, flow rate = 1.0 mL min^{-1}, λ = 254 nm; retention times for *anti*-**5i**: 49.6 min (major) and 82.0 min (minor), 85% *ee*; retention times for *syn*-**5i**: 55.3 min (major) and 77.5 min (minor), 58% *ee*.

Benzyl 2-benzoyl-3-(naphthalen-1-yl)pent-4-ynoate (5j): Isolated yield 95% (*anti*-**5j**/*syn*-**5j** = 5:1). A colorless oil. *anti*-isomer: ^{1}H NMR: δ = 8.35 (d, J = 7.8 Hz, 1H), 8.06–8.09 (m, 2H), 7.74–7.88 (m, 2H), 7.07–7.65 (m, 10H), 6.70–6.73 (m, 2H), 5.49 (dd, J = 10.4 and 2.7 Hz, 1H), 5.30 (d, J = 10.4, 1H), 4.64 (s, 2H), 2.17 ppm (d, J = 2.7 Hz, 1H); *syn*-isomer: ^{1}H NMR: δ = 8.37 (d, J = 7.8 Hz, 1H), 5.28 (d, J = 9.7 Hz, 1H), 5.22 (s, 2H), 2.26 ppm (d, J = 2.4 Hz, 1H); *anti*-isomer: ^{13}C NMR: δ = 192.0, 166.5, 136.4, 134.6, 134.09, 133.8, 133.4, 130.9, 128.9, 128.7, 128.6, 128.2, 128.0, 127.8, 126.4, 125.8, 125.3, 123.56, 83.5, 72.1, 67.2, 59.3, 33.6 ppm; *syn*-isomer: ^{13}C NMR: δ = 191.5, 167.3, 135.8, 135.1, 134.07, 133.6, 130.6, 128.51, 128.48, 128.43, 128.35, 128.3, 126.5, 125.7, 125.2, 123.58, 83.2, 72.6, 67.6, 59.4 ppm; HRMS (EI): m/z: calcd for $C_{29}H_{22}O_3$ [M]: 418.1569; found: 418.1556. The optical purities of *anti*-**5j** and *syn*-**5j** were determined by HPLC analysis; DAICEL Chiralcel OZ-H, hexane/*i*PrOH = 95:5, flow rate = 1.0 mL min^{-1}, λ = 254 nm; retention times for *anti*-**5j**: 9.6 min (minor) and 20.9 min (major), 91% *ee*; retention times for *syn*-**5j**: 11.2 min (major) and 64.5 min (minor), 13% *ee*.

Methyl 2-benzoyl-3-(naphthalen-1-yl)pent-4-ynoate (5k): Isolated yield 99% (*anti*-**5k**/*syn*-**5k** = 4:1). A colorless oil. *anti*-isomer: ^{1}H NMR: δ = 8.36 (d, J = 8.6 Hz, 1H), 8.06–8.09 (m, 2H), 7.42–7.89 (m, 9H), 5.48 (dd, J = 10.3 and 2.7 Hz, 1H), 5.23 (d, J = 10.3 Hz, 1H), 3.25 (s, 3H), 2.18 ppm (d, J = 2.7 Hz, 1H); *syn*-isomer: ^{1}H NMR: δ = 8.40 (d, J = 8.6 Hz, 1H), 7.25–7.33 (m, 3H), 5.46 (dd, J = 10.0 and 2.4 Hz, 1H), 5.28 (d, J = 10.0 Hz, 1H), 3.80 (s, 3H), 2.35 ppm (d, J = 2.4 Hz, 1H); *anti*-isomer: ^{13}C NMR: δ = 192.3, 167.1, 136.4, 134.08, 133.8, 133.47, 130.8, 129.0, 128.9, 128.8, 128.62, 126.6, 126.3, 125.8, 125.3, 123.4, 83.4, 72.2, 59.4, 52.5, 33.6 ppm; *syn*-isomer: ^{13}C NMR: δ = 191.6, 167.9, 135.9, 134.09, 133.6, 133.48, 130.7, 128.56, 128.5, 126.4, 125.7, 125.2, 123.6, 83.3, 72.4, 59.3, 53.0, 33.8 ppm; HRMS (EI): m/z: calcd for $C_{23}H_{18}O_3$ [M]: 342.1256; found: 342.1254. The optical purities of *anti*-**5k** and *syn*-**5k** were determined by HPLC analysis; DAICEL Chiralpak IC, hexane/*i*PrOH = 95:5, flow rate = 0.5 mL min^{-1}, λ = 254 nm; retention times for *anti*-**5k**: 29.2 min (major) and 45.0 min (minor), 86% *ee*; , retention times for *syn*-**5k**: 32.6 min (minor) and 40.0 min (major), 0% *ee*.

Ethyl 2-(4-methoxybenzoyl)-3-(naphthalen-1-yl)pent-4-ynoate (5l): Isolated yield 97% (*anti*-**5l**/*syn*-**5l** = 6:1). A colorless oil. *anti*-isomer: ^{1}H NMR: δ = 8.39 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 9.2 Hz, 2H), 7.42–7.88 (m, 6H), 6.96 (d, J = 9.2 Hz, 2H), 5.48 (dd, J = 10.5 and 2.4 Hz, 1H), 5.19 (d, J = 10.5 Hz, 1H), 3.87 (s, 3H), 3.67 (q, J = 7.0 Hz, 2H), 2.17 (d, J = 2.4 Hz, 1H), 0.67 ppm (t, J = 7.0 Hz, 3H); *syn*-isomer: ^{1}H NMR: δ = 8.43 (d, J = 8.4 Hz, 1H), 7.31 (dd, J = 8.1 and 7.3 Hz, 1H), 6.79 (d, J = 9.2 Hz, 1H), 5.22 (d, J = 10.5 Hz, 1H), 4.27 (qd, J = 7.0 and 2.4 Hz, 2H), 3.79 (s, 3H), 2.33 (d, J = 2.4 Hz, 1H), 1.28 ppm (t, J = 7.0 Hz, 3H); *anti*-isomer: ^{13}C NMR: δ = 190.5, 166.8, 164.1, 134.0, 133.8, 131.4, 131.01, 129.4, 128.9, 128.5, 126.5, 126.2, 125.74, 125.3, 123.7, 113.9, 83.8, 71.8, 61.5, 59.5, 55.5, 33.3, 13.4 ppm; *syn*-isomer: ^{13}C NMR: δ = 189.8, 167.7, 163.9, 134.1, 133.9, 130.98, 130.8, 128.4, 126.3, 125.68, 125.2, 123.8, 113.7, 83.5, 72.3, 61.9, 59.0, 55.4, 33.6, 14.1 ppm; HRMS (EI): m/z: calcd for $C_{25}H_{22}O_4$ [M]: 386.1518; found: 386.1523. The optical purities of *anti*-**5l** and *syn*-**5l** were determined by HPLC analysis; DAICEL Chiralpak IC, hexane/*i*PrOH = 90:10, flow rate = 0.5 mL min^{-1}, λ = 254 nm; retention times for *anti*-**5l**: 38.8 min (major) and 84.0 min (minor), 89% *ee*; retention times for *syn*-**5l**: 42.2 min (minor) and 62.0 min (major), 9% *ee*.

Ethyl 2-(1-naphthoyl)-3-(naphthalen-1-yl)pent-4-ynoate (5m): Isolated yield 92% (*anti*-**5m**/*syn*-**5m** = 12:1). A colorless oil. *anti*-isomer: ^{1}H NMR: δ = 8.71 (d, J = 8.4 Hz, 1H), 8.39 (d, J = 8.4 Hz, 1H), 7.38–8.04 (m, 12H), 5.55 (dd, J = 10.3 and 2.4 Hz, 1H), 5.26 (d, J = 10.3 Hz, 1H), 3.72 (q, J = 7.0 Hz, 2H), 2.20 (d, J = 2.4 Hz, 1H), 0.71 ppm (t, J = 7.0 Hz, 3H); *syn*-isomer: ^{1}H NMR: δ = 8.15 (d, J = 8.4 Hz, 1H), 5.51 (dd, J = 10.3 and 2.7 Hz, 1H), 5.38 (d, J = 10.3 Hz, 1H), 4.24 (q, J = 7.3 Hz, 2H), 2.37 (d, J = 2.7 Hz, 1H), 1.20 ppm (t, J = 7.3 Hz, 3H); *anti*-isomer: ^{13}C NMR: δ = 195.5, 166.7, 135.5, 134.0, 133.9, 133.6, 133.4, 130.9, 130.4, 128.9, 128.54, 128.52, 128.3, 128.2, 126.7, 126.5, 126.3, 125.9, 125.8, 125.3, 124.2, 123.5, 83.6, 72.4, 62.5, 61.58, 33.9, 13.4 ppm; *syn*-isomer: ^{13}C NMR: δ = 195.2, 167.4, 135.9, 134.1, 133.1, 131.1, 130.6, 129.9, 129.8, 128.7, 128.47, 128.1, 127.8, 127.7, 126.9, 126.43, 126.40, 125.7, 125.2, 124.0, 123.6, 83.4, 72.0, 61.9, 61.64, 14.0 ppm; HRMS (EI): m/z: calcd for $C_{28}H_{22}O_3$ [M]: 406.1569; found: 406.1588. The optical purities of *anti*-**5m** and *syn*-**5m** were determined by HPLC analysis; DAICEL Chiralcel OZ-H, hexane/*i*PrOH = 97:3, flow rate = 0.5 mL min^{-1}, λ = 254 nm; retention times for *anti*-**5m**: 20.0 min (minor) and 24.5 min (major), 90% *ee*; retention times for *syn*-**5m**: 22.0 min (minor) and 45.7 min (major), 78% *ee*.

Ethyl 2-(2-naphthoyl)-3-(naphthalen-1-yl)pent-4-ynoate (5n): Isolated yield 96% (*anti*-**5n**/*syn*-**5n** = 10:1). A colorless oil. *anti*-isomer: ^{1}H NMR: δ = 8.58 (s, 1H), 8.42 (d, J = 8.4 Hz, 1H), 8.16 (dd, J = 8.4 and 1.6 Hz, 1H), 7.43–7.96 (m, 11H), 5.55 (dd, J = 10.3 and 2.4 Hz, 1H), 5.39 (d, J = 10.3 Hz, 1H), 3.71 (q, J = 7.3 Hz, 2H), 2.19 (d, J = 2.4 Hz, 1H), 0.70 ppm (t, J = 7.3 Hz, 3H); *syn*-isomer: ^{1}H NMR: δ = 8.48 (d, J = 8.9 Hz, 1H), 8.38 (d, J = 8.9 Hz, 1H), 7.28 (dd, J = 8.1 and 7.3 Hz, 1H), 5.52 (dd, J = 10.3 and 2.4 Hz, 1H), 5.42 (d, J = 10.3 Hz, 1H), 4.28 (qd, J = 7.0 and 3.5 Hz, 2H), 2.37 (d, J = 2.4 Hz, 1H), 1.27 ppm (t, J = 7.0 Hz, 3H); *anti*-isomer: ^{13}C NMR: δ = 192.2, 166.8, 135.8, 134.1, 133.8, 133.6, 132.4, 131.1, 131.0, 129.8, 128.9, 128.7, 128.54, 127.7, 126.9, 126.6, 126.3, 125.8, 125.3, 124.2, 123.6, 83.6, 72.1, 61.6, 59.7, 33.5, 13.4 ppm; *syn*-isomer: ^{13}C NMR: δ = 191.6, 167.5, 135.6, 133.3, 132.2, 130.8, 130.7, 129.7, 128.8, 128.45, 128.4, 127.6, 126.8, 125.7, 125.2, 123.8, 123.7, 83.4, 72.5, 62.0, 59.4, 33.3, 14.1 ppm; HRMS (EI): m/z: calcd for $C_{28}H_{22}O_3$ [M]: 406.1569; found: 406.1552. The optical purities of *anti*-**5n** and *syn*-**5n** were determined by HPLC analysis; DAICEL Chiralpak AD, hexane/*i*PrOH = 97:3, flow rate = 0.5 mL min^{-1}, λ = 254 nm; retention times for *anti*-**5n**: 65.9 min (minor) and 73.5 min (major), 92% *ee*; retention times for *syn*-**5n**: 54.3 min (minor) and 115.2 min (major), 0% *ee*.

Ethyl 2-(4-methylbenzoyl)-3-(naphthalen-1-yl)pent-4-ynoate (5o): Isolated yield 95% (*anti*-**5o**/*syn*-**5o** = 10:1). A colorless oil. *anti*-isomer: ^{1}H NMR: δ = 8.39 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.42–7.88 (m, 6H), 7.29 (d, J = 8.1 Hz, 2H), 5.47 (dd, J = 10.5 and 2.7 Hz, 1H), 5.21 (d, J = 10.5 Hz, 1H), 3.66 (q, J = 7.0 Hz, 2H), 2.42 (s, 3H), 2.16 (d, J = 2.7 Hz, 1H), 0.67 ppm (t, J = 7.0 Hz, 3H); *syn*-isomer: ^{1}H NMR: δ = 8.42 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 5.23 (d, J = 10.0 Hz, 1H), 4.26 (qd, J = 7.0 and 1.6 Hz, 2H), 2.33 (d, J = 2.7 Hz, 1H), 2.32 (s, 3H), 1.27 ppm (t, J = 7.0 Hz, 3H); *anti*-isomer: ^{13}C NMR: δ = 191.7, 166.7, 144.8, 134.0, 133.93, 133.7, 131.0, 129.5, 129.1, 128.9, 128.5, 126.6, 126.25, 125.74, 125.3, 123.6, 83.7, 71.8, 61.5, 59.6, 33.3, 21.7, 13.4 ppm; *syn*-isomer: ^{13}C NMR: δ = 191.1, 167.5, 144.6, 134.1, 133.91, 133.8, 130.7, 129.2, 128.7, 128.4, 126.31, 125.69, 125.2, 123.7, 83.4, 72.4, 62.0, 59.2, 33.5, 21.6, 14.0 ppm; HRMS (EI): m/z: calcd for $C_{25}H_{22}O_3$ [M]: 370.1569; found: 370.1568. The optical purities of *anti*-**5o** and *syn*-**5o** were determined by HPLC analysis; DAICEL Chiralpak IC, hexane/*i*PrOH = 95:5, flow rate = 1.0 mL min^{-1}, λ = 254 nm; retention times for *anti*-**5o**: 18.1 min (major) and 43.1 min (minor), 94% *ee*; retention times for *syn*-**5o**: 20.1 min (minor) and 30.8 min (major), 3% *ee*.

Ethyl 2-(4-chlorobenzoyl)-3-(naphthalen-1-yl)pent-4-ynoate (5p): Isolated yield 94% (*anti*-**5p**/*syn*-**5p** = 3:1). A colorless oil. *anti*-isomer: ^{1}H NMR: δ = 8.35 (d, J = 8.9 Hz, 1H), 8.02 (d, J = 8.9 Hz, 2H), 7.44–7.89 (m, 7H), 7.27 (d, J = 8.9 Hz, 1H), 5.46 (dd, J = 10.3 and 2.4 Hz, 1H), 5.16

(d, $J=10.3$ Hz, 1H), 3.69 (q, $J=7.0$ Hz, 2H), 2.19 (d, $J=2.4$ Hz, 1H), 0.69 ppm (t, $J=7.3$ Hz, 3H); *syn*-isomer: ^{1}H NMR: $\delta=8.39$ (d, $J=8.9$ Hz, 1H), 7.42–7.81 (m, 9H), 7.31–7.34 (m, 1H), 5.43 (dd, $J=10.3$ and 2.4 Hz, 1H), 5.18 (d, $J=10.3$ Hz, 1H), 4.27 (qd, $J=7.0$ and 1.1 Hz, 2H), 2.35 (d, $J=2.4$ Hz, 1H), 1.28 ppm (t, $J=7.3$ Hz, 3H); *anti*-isomer: ^{13}C NMR: $\delta=191.2$, 166.4, 140.4, 134.7, 134.0, 133.4, 130.9, 130.3, 129.1, 128.8, 128.62, 126.6, 126.37, 125.82, 125.3, 123.5, 83.5, 72.1, 61.7, 59.7, 33.3, 13.4 ppm; *syn*-isomer: ^{13}C NMR: $\delta=190.8$, 167.2, 140.2, 134.2, 134.1, 133.5, 130.6, 129.8, 128.98, 128.96, 128.55, 126.41, 125.78, 125.2, 123.6, 83.1, 72.6, 62.2, 59.4, 33.7, 14.1 ppm; HRMS (EI): *m*/*z*: calcd for $C_{24}H_{19}ClO_3$ [*M*]: 390.1023; found: 390.1038. The optical purities of *anti*-**5p** and *syn*-**5p** were determined by HPLC analysis; DAICEL Chiralpak IC, hexane/*i*PrOH = 97:3, flow rate = 0.50 mL min^{-1}, $\lambda=254$ nm; retention times for *anti*-**5p**: 25.0 min (major) and 38.7 min (minor), 86% *ee*; retention times for *syn*-**5p**: 26.8 min (minor) and 33.0 min (major), 4% *ee*.

Ethyl 2-(2-naphthoyl)-3-(naphthalen-2-yl)pent-4-ynoate (5q): Isolated yield 93% (*anti*-**5q**/*syn*-**5q** = 6:1). A white solid. *anti*-isomer: ^{1}H NMR: $\delta=8.67$ (s, 1H), 8.17 (dd, $J=8.6$ and 1.9 Hz, 1H), 7.45–8.02 (m, 12H), 5.13 (d, $J=10.8$ Hz, 1H), 4.91 (dd, $J=10.8$ and 2.4 Hz, 1H), 3.75–3.91 (m, 2H), 2.19 (d, $J=2.4$ Hz, 1H), 0.86 ppm (t, $J=7.0$ Hz, 3H); *syn*-isomer: ^{1}H NMR: $\delta=8.46$ (s, 1H), 7.36–7.41 (m, 2H), 5.14 (d, $J=10.5$ Hz, 1H), 4.99 (dd, $J=10.5$ and 2.4 Hz, 1H), 4.24–4.28 (m, 2H), 2.40 (d, $J=2.4$ Hz, 1H), 1.27 ppm (t, $J=7.0$ Hz, 3H); *anti*-isomer: ^{13}C NMR: $\delta=192.0$, 166.6, 135.9, 135.1, 133.7, 133.3, 132.9, 132.4, 131.2, 129.9, 129.0, 128.7, 128.5, 127.9, 127.8, 127.7, 127.6, 126.9, 126.3, 126.13, 126.06, 124.3, 83.6, 72.2, 61.7, 61.3, 37.5, 13.7 ppm; *syn*-isomer: ^{13}C NMR: $\delta=191.3$, 167.3, 135.7, 135.5, 133.2, 132.6, 132.2, 130.9, 129.8, 128.9, 128.4, 127.5, 126.8, 126.0, 123.9, 83.5, 72.5, 62.1, 61.4, 37.2, 14.1 ppm; elemental analysis calcd (%) for $C_{28}H_{22}O_3$: C 82.74, H 5.46; found: C 82.56, H 5.72. The optical purities of *anti*-**5q** and *syn*-**5q** were determined by HPLC analysis; DAICEL Chiralpak AS-H, hexane/*i*PrOH = 97:3, flow rate = 0.35 mL min^{-1}, $\lambda=254$ nm; retention times for *anti*-**5q**: 42.2 min (minor) and 54.4 min (major), 92% *ee*; retention times for *syn*-**5q**: 33.9 min (major) and 39.4 min (minor), 53% *ee*.

Benzyl 2-benzoyl-3-(2-methoxyphenyl)pent-4-ynoate (5r): Isolated yield 98% (*anti*-**5r**/*syn*-**5r** = 7:1). A colorless oil. *anti*-isomer: ^{1}H NMR: $\delta=$ 7.98–8.03 (m, 2H), 7.52–7.59 (m, 1H), 7.37–7.46 (m, 3H), 7.18–7.35 (m, 4H), 6.98–7.02 (m, 2H), 6.83–6.91 (m, 2H), 5.22 (d, $J=9.7$ Hz, 1H), 4.98 (dd, $J=9.7$ and 2.7 Hz, 1H), 4.89 (s, 2H), 3.82 (s, 3H), 2.09 ppm (d, $J=$ 2.7 Hz, 1H); *syn*-isomer: ^{1}H NMR: $\delta=7.87$–7.90 (m, 2H), 6.83 (m, 1H), 5.14 (s, 2H), 5.13 (d, $J=7.8$ Hz, 1H), 4.92 (dd, $J=7.8$ and 2.7 Hz, 1H), 3.80 (s, 3H), 2.23 ppm (d, $J=2.7$ Hz, 1H); *anti*-isomer: ^{13}C NMR: $\delta=$ 192.7, 167.1, 157.0, 136.7, 135.1, 133.5, 130.1, 128.8, 128.6, 128.3, 128.05, 127.9, 125.58, 120.78, 111.2, 83.2, 70.9, 67.0, 57.6, 55.6, 32.4 ppm; *syn*-isomer: ^{13}C NMR: $\delta=192.8$, 167.6, 156.4, 136.1, 135.2, 133.4, 130.0, 129.0, 128.53, 128.51, 128.2, 128.12, 125.62, 120.76, 110.8, 82.5, 71.8, 67.1, 57.8, 55.4, 32.5 ppm; HRMS (EI): *m*/*z*: calcd for $C_{26}H_{22}O_4$ [*M*]: 398.1518; found: 398.1516. The optical purities of *anti*-**5r** and *syn*-**5r** were determined by HPLC analysis; DAICEL Chiralcel OZ-H, hexane/*i*PrOH = 95:5, flow rate = 1.0 mL min^{-1}, $\lambda=254$ nm; retention times for *anti*-**5r**: 15.0 min (minor) and 37.7 min (major), 91% *ee*; retention times for *syn*-**5r**: 32.6 min (minor) and 96.5 min (major), 30% *ee*.

Ethyl 2-(4-chlorophenylcarbonyl)-3-(2-methoxyphenyl)pent-4-ynoate (5s): Isolated yield 94% (*anti*-**5s**/*syn*-**5s** = 6:1). A colorless oil. *anti*-isomer: ^{1}H NMR: $\delta=7.96$ (d, $J=8.6$ Hz, 2H), 7.36–7.45 (m, 3H), 7.22–7.28 (m, 1H), 6.88–6.94 (m, 2H), 5.10 (d, $J=9.5$ Hz, 1H), 4.93 (dd, $J=9.5$ and 2.4 Hz, 1H), 3.93 (q, $J=7.0$ Hz, 2H), 3.91 (s, 3H), 2.11 (d, $J=2.4$ Hz, 1H), 0.97 ppm (t, $J=7.0$ Hz, 3H); *syn*-isomer: ^{1}H NMR: $\delta=7.85$ (d, $J=$ 8.9 Hz, 2H), 7.36–7.47 (m, 3H), 7.18–7.22 (m, 1H), 6.86–6.89 (m, 1H), 6.75–6.78 (m, 1H), 5.02 (d, $J=8.4$ Hz, 1H), 4.88 (dd, $J=8.4$ and 2.4 Hz, 1H), 4.18 (qd, $J=7.0$ and 2.4 Hz, 2H), 3.81 (s, 3H), 2.28 (d, $J=2.4$ Hz, 1H), 1.20 ppm (t, $J=7.0$ Hz, 3H); *anti*-isomer: ^{13}C NMR: $\delta=191.8$, 167.0, 157.0, 140.0, 135.0, 130.2, 130.1, 129.1, 128.88, 125.46, 120.7, 111.2, 83.1, 70.9, 61.5, 57.5, 55.6, 32.4, 13.7 ppm; *syn*-isomer: ^{13}C NMR: $\delta=$ 167.5, 156.4, 139.9, 134.4, 129.92, 129.88, 128.90, 128.8, 125.50, 110.8, 82.5, 71.6, 61.6, 57.8, 55.4, 14.0 ppm; HRMS (EI): *m*/*z*: calcd for $C_{21}H_{19}ClO_4$ [*M*]: 370.0972; found: 370.0963. The optical purities of *anti*-**5s** and *syn*-**5s** were determined by HPLC analysis; DAICEL Chiralpak ID, hexane/*i*PrOH = 95:5, flow rate = 1.00 mL min^{-1}, $\lambda=254$ nm; retention times for *anti*-**5s**: 15.4 min (major) and 19.0 min (minor), 92% *ee*; retention times for *syn*-**5s**: 14.3 min (major) and 22.2 min (minor), 62% *ee*.

Preparation of allenylidene complex 6: Complex **3a** (220.3 mg, 0.318 mmol), NH_4BF_4 (66.7 mg, 0.636 mmol), and anhydrous $MgSO_4$ (440 mg) were placed in a 20 mL Schlenk flask under N_2. Anhydrous dichloromethane (20 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **1a** (115.9 mg, 0.636 mmol), the reaction flask was kept at room temperature for 4 h. The solvent was then removed under reduced pressure and the residue was recrystallized from dichloromethane/*n*-hexane to give dark-brown crystals of **6**·0.5 CH_2Cl_2 (144.3 mg, 0.152 mmol, 48%) suitable for X-ray crystallographic study. ^{1}H NMR: $\delta=9.89$ (s, 1H), 8.70 (d, $J=8.1$ Hz, 1H), 8.28 (d, $J=8.1$ Hz, 1H), 8.10 (dd, $J=7.6$ and 1.1 Hz, 1H), 7.96 (d, $J=8.4$ Hz, 1H), 7.80 (td, $J=7.6$ and 1.4 Hz, 1H), 7.59 (td, $J=8.1$ and 1.1 Hz, 1H), 7.51 (t, $J=7.6$ Hz, 1H), 4.42 (sept, $J=6.8$ Hz, 2H), 1.91 (s, 15H), 1.70 (s, 15H), 1.41 (d, $J=6.8$ Hz, 6H), 1.39 ppm (d, $J=6.8$ Hz, 6H); IR (KBr): $=1927$ cm^{-1} (s, C=C=C); elemental analysis calcd (%) for $C_{39}H_{52}BClF_4Ru_2S_2\cdot(CH_2Cl_2)_{0.5}$: C 49.84, H 5.61; found: C 49.75, H 5.72.

Stoichiometric reaction of complex 6 in the presence of 1g: A 20 mL Schlenk flask was charged with **4a** (41.5 mg, 0.0857 mmol) and $Cu(OTf)_2$ (25.8 mg, 0.0714 mmol) under N_2. The mixture was stirred under vacuum for 2 h and then an atmosphere of N_2 was admitted to the flask. Anhydrous THF (1.0 mL) was added and the solution was stirred for 2 h. After cooling the reaction flask to −10 °C, **2a** (30.9 mg, 0.161 mmol) was added to the reaction mixture, and then **6**·0.5 CH_2Cl_2 (34.0 mg, 0.0357 mmol) and a solution of **1g** (11.6 mg, 0.0714 mmol) in anhydrous THF (2 mL) were added successively under N_2. The reaction flask was kept at −10 °C for 45 h. After concentration of the reaction mixture under reduced pressure, the residue was purified by column chromatography (SiO_2; eluent: hexane/ethyl acetate, 95:5 to 85:15) to give **5a** as a colorless oil (6.7 mg, 0.0188 mmol, 53% isolated yield, *anti*-**5a**/*syn*-**5a** = 5:1, *anti*-**5a** (90% *ee*), *syn*-**5a** (4% *ee*)) and **5g** as a colorless oil (14.8 mg, 0.0440 mmol, 62% isolated yield, *anti*-**5g**/*syn*-**5g** = 6:1, *anti*-**5g** (87% *ee*), *syn*-**5g** (46% *ee*)).

Stoichiometric reaction of complex 6: A 20 mL Schlenk flask was charged with **4a** (37.5 mg, 0.0782 mmol) and $Cu(OTf)_2$ (23.6 mg, 0.0651 mmol) under N_2. The mixture was stirred under vacuum for 2 h and then an atmosphere of N_2 was admitted to the flask. Anhydrous THF (1.0 mL) was added and the solution was stirred for 2 h. After cooling the reaction flask to −10 °C, **2a** (12.5 mg, 0.0651 mmol) was added to the reaction mixture, and then **6**·0.5 CH_2Cl_2 (31.0 mg, 0.0326 mmol) was added under N_2. The reaction flask was kept at −10 °C for 45 h. The reaction was then quenched by the addition of water (10 mL), and the resulting mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After concentration under reduced pressure, the residue was purified by column chromatography (SiO_2; eluent: hexane/ethyl acetate, 95:5 to 85:15) to give **5a** as a colorless oil (1.2 mg, 0.0034 mmol, 10% isolated yield, *anti*-**5a**/*syn*-**5a** = 4:1, *anti*-**5a** (92% *ee*), *syn*-**5a** (6% *ee*)).

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