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Direct Conjugate Addition of Alkynes with α,β-Unsaturated Carbonyl Compounds Catalyzed by NCN-Pincer Ru Complexes

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Abstract: NCN-pincer Ru-complexes containing bis(oxazolinyl)phenyl ligands serve as suitable catalysts in the direct conjugate additions of α,β-unsaturated carbonyl compounds, including ketones, esters, and amides, as well as vinylphosphonates, giving various β-alkynyl carbonyl and phosphonate compounds. A bis(oxazolinyl)phenyl (phebox)–Ru complex also catalyzes the asymmetric conjugate addition of an alkyne with a β-substituted, α,β-unsaturated ketone to produce a chiral β-alkynyl ketone.

Keywords: alkynes · conjugate addition · pincer complex · ruthenium · α,β-unsaturated compounds

Introduction

Direct conjugate addition of terminal alkynes to α,β-unsaturated carbonyl compounds is an attractive reaction due to its powerful and atom-economic process to construct β-alkynyl carbonyl compounds.[1] Transition-metal complexes containing Rh,[2] Ru,[3] Cu,[4] and Pd[5] have been developed as active catalysts for this reaction. Recently, asymmetric catalysis has also been developed for the transformation of α,β-unsaturated thioamides,[6] Meldrum's acid derivatives,[7] as well as α,β-unsaturated ketones and aldehydes.[8,9] In contrast, the conjugate addition of a terminal alkyne to a simple α,β-unsaturated amide has not been well explored.

Since the reactivity and selectivity of transition-metal catalysis are most likely controlled by auxiliary ligands, pincer metal complexes containing carbon-based meridional ligands have been studied as active catalysts.[10–12] Recently, a NCN pincer Rh complex containing bis(oxazolinyl)phenyl (phebox) ligands was used as a catalyst in activation of a terminal alkyne to generate the Rh-acetylide complex and in direct addition of a terminal alkyne to unsaturated organic molecules.[13,14] In particular, Ohshima and Mashima demonstrated highly effective enantioselective direct alkynylation of activated ketones by a chiral phebox–Rh complex.[14] The chiral phebox–Ru complex has also been utilized in direct asymmetric alkynylation of aldehydes.[15] Thus, chiral NCN-pincer Rh- and Ru-complexes are potential catalysts for alkynylation reactions through direct activation of terminal alkynes. Herein, we report on the utilization of the phebox–Ru complexes in the direct conjugate-addition of various α,β-unsaturated ketones, esters and amides, as well as vinylphosphonate. The phebox–Ru complex also serves as a chiral catalyst for asymmetric conjugate addition of an α,β-unsaturated ketone.

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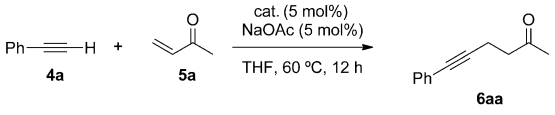
Results and Discussion

Recently, we reported several acetate complexes containing group 8 and 9 metals with phebox ligands.[16] Initially, we evaluated the catalytic activity of these phebox complexes for conjugate addition of an alkyne with α,β-unsaturated ketones (Table 1). Reaction of phenylacetylene **4a** with meth-

Table 1. Conjugate addition of phenylacetylene (**4a**) with methylvinylketone (**5a**).[a]

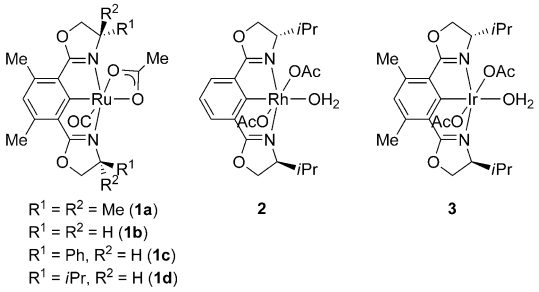


4a 5a 6aa

Entry	Cat.	Solvent	Yield [%][b]
1	**1a**	THF	83
2	**1b**	THF	12
3	**1c**	THF	92
4	**1d**	THF	91
5[c]	**1c**	THF	65
6[d]	**1c**	THF	11
7	**1c**	IPA	72
8	**1c**	toluene	68
9[e]	**1c**	THF	84
10	**2**	THF	46
11	**3**	THF	9
12[f]	pybox–Ru	THF	7

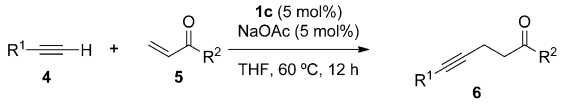
[a] Reaction condition: **4a** (2 mmol), **5a** (1 mmol), cat. (5 mol% to **5a**), NaOAc (5 mol% to **5a**), 60 °C, 12 h. [b] Yield of the isolated product. [c] Absence of NaOAc. [d] Addition of AcOH (5 mol%) in place of NaOAc. [e] **4a** (1 mmol). [f] $[RuCl(p\text{-cymene})_2]_2$ (10 mol%) and (*S*,*S*)-2,6-bis(4-phenyl-2-oxazolinyl)pyridine (pybox) (10 mol%).

ylvinylketone **5a** proceeded smoothly in the presence of the achiral phebox–Ru complex **1a** (5 mol%) and NaOAc (5 mol%) to give the corresponding β-alkynyl ketone **6aa** in 83% yield (Table 1, entry 1). However, utilization of the Ru complex **1b** containing the sterically less-hindered phebox ligand showed a lower catalytic activity (Table 1, entry 2). In contrast, the phebox–Ru complexes **1c** and **1d** with chiral ligands enhanced the product yields (Table 1, entries 3 and 4). Thus, the size of the phebox ligands affected the outcome of the catalytic reaction. Although the absence of NaOAc gave the product in moderate yield, addition of acetic acid in place of NaOAc hampered the catalytic reaction (Table 1, entries 5 and 6). The catalytic reaction was also affected by solvents; use of IPA and toluene decreased the product yields (Table 1, entries 7 and 8). This result is in contrast to 1,2-addition of a terminal alkyne to an aromatic aldehyde catalyzed by the phebox–Ru complex, in which IPA was a suitable solvent to prevent the undesirable homodimerization reaction of alkynes.[15] When the catalytic reaction with one equivalent of **4a** was performed, the product **6aa** was obtained in 84% yield (Table 1, entry 9). We also verified the catalytic ability of the phebox–Rh acetate complex **2**, which serves as an efficient catalyst in alkynylation of activated ketones.[14] Unfortunately, the use of the Rh complex **2** and related Ir complex **3** resulted in lower yields (Table 1, entries 10 and 11). Pybox–Ru is ineffective in the conjugate reaction, giving lower yields of **6aa** (Table 1, entry 12).[17]



Next, the conjugate addition of several alkynes **4a–h** with α,β-unsaturated ketones **5a** and **5b** was examined in the presence of **1c** (5 mol%) and NaOAc (5 mol%) in THF at 60°C (Table 2). Other aromatic alkynes gave the corresponding β-alkynyl ketones **6ba–6fa** in 71–95% yields (Table 2, entries 1–5). On the other hand, the use of trimethylsilylacetylene **4g** and cyclohexylacetylene **4h** resulted in a lower yield (Table 2, entries 6 and 7). In previous literature, $[Ru(O_2CH)(CO)_2(PPh_3)]_2$,[3a] $[Ru_3(CO)_{12}]$[3b] and $[Pd(OAc)_2]$/PMe_3[5b–c] were also found to behave similarly. Phenylvinylketone **5b** was used as an acceptor to produce the alkynyl ketone **6ab** in 88% yield. In these reactions, the side products of enynes arising from the homodimerization were below about 7%, except **4d**. However, in the reaction with **4d**, enyne byproducts were obtained in approximately 25% yield (based on **4d**) presumably due to the enhanced reactivity of the C≡C bond by the electron-withdrawing CF_3 group.

Table 2. Conjugate addition of alkynes with α,β-unsaturated ketones catalyzed by **1c**.[a]

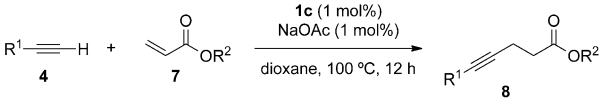


Entry	Alkyne, R^1	Ketone, R^2	Product	Yield [%][b]
1	4-MeC_6H_4 (**4b**)	Me (**5a**)	**6ba**	86
2	4-$MeOC_6H_4$ (**4c**)	Me (**5a**)	**6ca**	78
3	4-$CF_3C_6H_4$ (**4d**)	Me (**5a**)	**6da**	95
4	2-naphthyl (**4e**)	Me (**5a**)	**6ea**	94
5	2-furyl (**4f**)	Me (**5a**)	**6fa**	71
6	$SiMe_3$ (**4g**)	Me (**5a**)	**6ga**	55
7	Cyclohexyl (**4h**)	Me (**5a**)	**6ha**	6
8	Ph (**4a**)	Ph (**5b**)	**6ab**	88

[a] Reaction condition: alkyne **4** (2 mmol), ketone **5** (1 mmol), phebox–Ru cat. **1c** (5 mol% to **5**), NaOAc (5 mol% to **5**), THF (4 mL), 60°C, 12 h. [b] Yield of the isolated product.

The phebox–Ru complex **1c** was found to be a good catalyst in the conjugate addition of alkynes with α,β-unsaturated esters (Table 3). The reaction of phenylacetylene **4a** with ethyl acrylate **7a** in the presence of **1c** (5 mol%) and NaOAc (5 mol%) proceeded at 60°C to give the desirable β-alkynyl ester **8aa** in 99% yield (Table 3, entry 1). The catalytic reaction also proceeded in the presence of **1c** (1 mol%) and NaOAc at 100°C (Table 3, entry 2). Similarly, the use of other esters **7b–f** produced the corresponding β-alkynyl esters **8ab–8af** in high yields (Table 3, entries 3–7). In this case, the size of the ester substituents did not affect the yield. Furthermore, other aromatic alkynes **4b–e** reacted

Table 3. Conjugate addition of alkynes with α,β-unsaturated esters catalyzed by **1c**.[a]



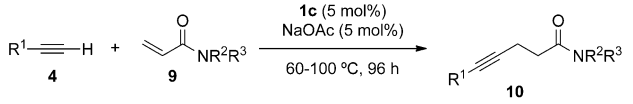
Entry	Alkyne, R^1	Ester, R^2	Product	Yield [%][b]
1[c]	Ph (**4a**)	Et (**7a**)	**8aa**	99
2	Ph (**4a**)	Et (**7a**)	**8aa**	96
3	Ph (**4a**)	Me (**7b**)	**8ab**	94
4	Ph (**4a**)	*t*Bu (**7c**)	**8ac**	90
5	Ph (**4a**)	*i*Bu (**7d**)	**8ad**	99
6	Ph (**4a**)	cyclohexyl (**7e**)	**8ae**	99
7	Ph (**4a**)	Ph (**7f**)	**8af**	90
8	4-MeC_6H_4 (**4b**)	Et (**7a**)	**8ba**	99
9	4-$MeOC_6H_4$ (**4c**)	Et (**7a**)	**8ca**	93
10	4-$CF_3C_6H_4$ (**4d**)	Et (**7a**)	**8da**	99
11	2-naphthyl (**4e**)	Et (**7a**)	**8ea**	96
12	$SiMe_3$ (**4g**)	Et (**7a**)	**8ga**	90
13	Cyclohexyl (**4h**)	Et (**7a**)	**8ha**	32

[a] Reaction conditions: alkyne **4** (2 mmol), ester **7** (1 mmol), phebox–Ru cat. **1c** (1 mol% to **7**), NaOAc (1 mol% to **7**), dioxane (4 mL), 100°C, 12 h. [b] Yield of the isolated product. [c] Reaction conditions: alkyne **4** (2 mmol), ester **7** (1 mmol), phebox–Ru cat. **1c** (5 mol% to **7**), NaOAc (5 mol% to **7**), THF (4 mL), 60°C, 12 h.

with ethyl acrylate **7a** to give the coupling products in 93–99% yields (Table 3, entries 8–11). In contrast to the reaction with ketone **5a**, the ester **7a** was employed as an acceptor for silylacetylene **4g** and alkylacetylene **4h** to give the desired β-alkynyl esters in 90 and 32% yields, respectively (Table 3, entries 12 and 13).

In comparison with α,β-unsaturated ketones and esters, α,β-unsaturated amides are considered to be poor acceptors for the reaction with nucleophiles. In addition, the presence of the N−H functionality of an amide could induce the addition of the N−H group of an amide to the C≡C triple bond as the side reaction. For example, Gooßen and co-workers described that the addition of an amide to alkynes in the presence of a Ru catalyst proceeded smoothly to produce the corresponding enamides.[18] In contrast, the phebox–Ru complex **1** was successfully used in conjugate addition of terminal alkynes with α,β-unsaturated amides. The catalytic reaction of phenylacetylene **4a** with acrylamide **9f** was found to be slow. The desirable β-alkynyl amide **10af** was obtained in 35 and 51% yield after heating at 60°C for 12 and 24 h, respectively. The product yield was reached to 92% by conducting the reaction for 96 h (Table 4, entry 6). This catalytic

Table 4. Conjugate addition of alkynes with α,β-unsaturated amides and catalyzed by **1c**.[a]

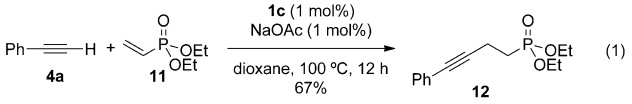


Entry	Alkyne, R^1	Amide, NR^2R^3	Condition[b]	Product	Yield [%][b]
1	Ph (**4a**)	NMe_2 (**9a**)	A	**10aa**	94
2	Ph (**4a**)	NEt_2 (**9b**)	B	**10ab**	67
3	Ph (**4a**)	morpholinyl (**9c**)	B	**10ac**	98
4	Ph (**4a**)	NH*i*Pr (**9d**)	B	**10ad**	99
5	Ph (**4a**)	NH*t*Bu (**9e**)	B	**10ae**	90
6	Ph (**4a**)	NH_2 (**9f**)	A	**10af**	92
7	4-MeC_6H_4 (**4b**)	NH_2 (**9f**)	A	**10bf**	94
8	4-$MeOC_6H_4$ (**4c**)	NH_2 (**9f**)	B	**10cf**	97
9	4-$CF_3C_6H_4$ (**4d**)	NH_2 (**9f**)	A	**10df**	93
10	$SiMe_3$(**4g**)	NH_2 (**9f**)	B	**10gf**	95

[a] Reaction conditions: alkyne **4** (2 mmol), amide **9** (1 mmol), phebox–Ru cat. **1c** (5 mol% to **9**), NaOAc (5 mol% to **9**). [b] Condition A: THF, 60°C, 96 h; Condition B: dioxane, 100°C, 96 h. [c] Yield of the isolated product.

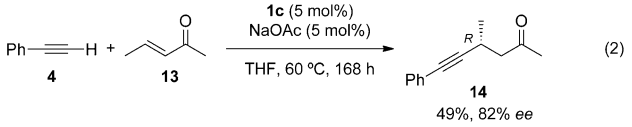
reaction with the amide derivatives was affected by the substituent on the nitrogen atom. Although the reaction with *N,N*-diethyl acrylamide **9b** gave a lower product yield of 67% even at 100°C, acryloylmorpholine **9c** gave the corresponding amide **10ac** in 98% yield at the same temperature (Table 4, entries 2 and 3). We also verified the catalytic activity of the phebox–Ru catalyst toward secondary and primary amides containing the N−H functionality. The reaction of isopropyl acrylamide **9d** and *tert*-butyl acrylamide **9e** at 100°C produced the corresponding β-alkynyl amides in high yields (Table 4, entries 4 and 5). Furthermore, the conjugate addition of **4a** with the N,N'-dimethyl acrylamide **9a** proceeded successfully, affording **10aa** in 94% yield (Table 4, entry 1). The catalytic reaction of **9f** with other aromatic alkynes **4b–d** and trimethylsilylacetylene **4g** also furnished the desired product in high yields (Table 4, entries 7–10). Since enamide byproducts produced by addition of amides to alkynes were not detected, the C−H bond activation of the terminal alkyne was considered to be the dominant reaction even in the presence of the N−H group.

Alkynyl phosphonate derivatives are known to be useful synthetic precursors as well as substructures for bioactive compounds.[19] The phebox–Ru acetate complex **1c** was used in conjugate addition of **4a** with diethyl vinylphosphonate (**11**) at 100°C to afford the corresponding β-alkynyl phosphonate **12** in 67% yield [Eq. (1)].



(1)

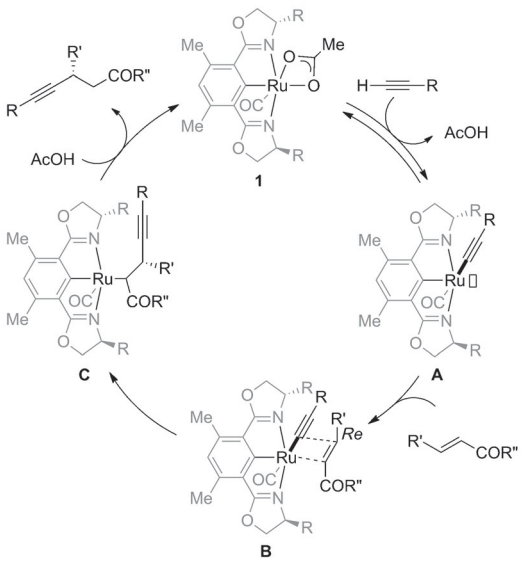
Finally, the asymmetric conjugate addition of an alkyne with an α,β-unsaturated compound was verified using the chiral phebox–Ru complex. When the phebox–Ru complex **1c** was used in the catalytic reaction of phenylacetylene (**4a**) with 3-penten-2-one (**13**), the catalytic reaction proceeded at 60°C to give the corresponding β-alkynyl substituted compound **14** in 49% yield with and enantiomeric excess (*ee*) of 82% [Eq. (2)].



(2)

Previously, we observed that **1a** catalyzed the H/D exchange reaction between the C(sp)-H of **4a** and [D_8]IPA to give [$\mathbf{D_1}$]**4a** (96% D).[15] This result suggested the formation of an Ru–acetylide intermediate by the reaction of **1** with an alkyne. In addition, we observed no kinetic isotope effect, which was determined by the independent reaction of **7b** with **4a** or [$\mathbf{D_1}$]**4a** (90% D) in [D_8]THF at 60°C. This result clearly indicated that the rate-determining step was not C−H bond activation.

A proposed mechanism for the catalytic conjugate addition of alkynes with α,β-unsaturated carbonyl compounds is shown in Scheme 1. First, an acetylide intermediate **A** is generated by C−H activation of a terminal alkyne with the Ru-acetate complex, in which the acetate ligand functions as a base to abstract the alkyne proton. This step is considered to be equilibrium, in which the presence of NaOAc is shifting the equilibrium towards the formation of **A**, whereas the presence of acetic acid is shifting the equilibrium inversely. Subsequent attack of the acetylide ligand at the β position of the α,β-carbonyl compound gives intermediate **C**, which



Scheme 1. Proposed mechanism.

then undergoes protonation to give the β-alkynyl compound. Based on the *R* configuration of **14** obtained in the asymmetric reaction with **13**, the *Re* face at the β-carbon in **13** is attacked by the Ru-ligated acetylide.

Conclusion

We have shown that NCN-pincer Ru-complexes containing phebox ligands are potential catalysts for direct conjugate addition of terminal alkynes to several types of α,β-unsaturated carbonyl compounds. In particular, the phebox–Ru complexes serve as good catalysts in the transformation of α,β-unsaturated amides and phosphonates to γ,δ-alkynyl derivatives. Asymmetric conjugate addition of an alkyne to an α,β-unsaturated ketone was catalyzed by the chiral phebox–Ru complex with enantiomeric induction. Further studies on the asymmetric reaction are currently in progress in our laboratory.

Experimental Section

Conjugate addition of 4a with 5a: Methylvinylketone **5a** (71.0 mg, 1.0 mmol) and phenylacetylene **4a** (204 mg, 2.0 mmol) were added to a mixture of phebox–Ru complex **1c** (29.3 mg, 0.050 mmol) and NaOAc (4.1 mg, 0.050 mmol) in THF (4 mL) at room temperature under Ar atmosphere. After stirring at 60 °C for 12 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with hexane/ethyl acetate (20:1) as the eluent to give **6aa** (159 mg, 0.92 mmol, 92% yield) as a solid. ^{1}H NMR (300 MHz, $CDCl_3$, RT): $\delta = 7.39$–7.36 (m, 2H), 7.29–7.26 (m, 3H), 2.81–2.76 (m, 2H), 2.70–2.65 (m, 2H), 2.22 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, RT): $\delta = 206.2$, 131.3, 128.0, 127.5, 123.3, 88.4, 80.9, 42.6, 30.1, 14.1 ppm; IR (KBr): $\tilde{\nu} = 2232$ (C≡C), 1718 cm^{-1} (C=O); HRMS (FAB) calcd for $C_{12}H_{12}O$: 172.0888; found: 172.0891 [M^+].

Conjugate addition of 4a with 7a: Ethyl acrylate **7a** (103 mg, 1.0 mmol), phenylacetylene **4a** (205 mg, 2.0 mmol) were added to a mixture of phebox–Ru complex **1c** (6.1 mg, 0.010 mmol) and NaOAc (1.0 mg, 0.012 mmol) in dioxane (4 mL), at room temperature under an Ar atmosphere. After stirring at 100 °C for 12 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with hexane/ethyl acetate (20:1) as the eluent to give **8aa** (200 mg, 0.99 mmol, 99% yield). ^{1}H NMR (300 MHz, $CDCl_3$, RT): $\delta = 7.40$–7.37 (m, 2H), 7.29–7.26 (m, 3H), 4.19 (q, J = 7.0 Hz, 2H), 2.77–2.72 (m, 2H), 2.66–2.61 (m, 2H) 1.29 ppm (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, RT): $\delta = 171.6$, 131.3, 128.0, 127.5, 123.3, 88.0, 81.1, 60.7, 33.8, 15.6, 14.4 ppm; IR (KBr): $\tilde{\nu} = 2239$ (C≡C), 1736 cm^{-1} (C=O); HRMS (FAB): *m/z* calcd for $C_{13}H_{14}O_2^+$: 203.1072; found: 203.1066 [M+H$^+$].

Conjugate addition of 4a with 9f: Phenylacetylene **4a** (205 mg, 2.0 mmol) was added to a mixture of acrylamide **9f** (71 mg, 1.0 mmol), phebox–Ru complex **1c** (29.5 mg, 0.051 mmol) and NaOAc (4.2 mg, 0.051 mmol) in THF (4 mL), at room temperature under an Ar atmosphere. After stirring at 60 °C for 96 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with chloroform/methanol (20:1) as the eluent to give **10af** (159 mg, 0.92 mmol, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$, RT): $\delta = 7.41$–7.36 (m, 2H), 7.29–7.25 (m, 3H), 3.04 (s, 3H), 2.98 (s, 3H), 2.80–2.74 (m, 2H), 2.67–2.63 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, RT): $\delta = 170.3$, 131.0, 127.7, 127.1, 123.2, 88.8, 80.4, 36.8, 35.1, 32.3, 15.3 ppm; IR (KBr): $\tilde{\nu} = 2245$ (C≡C), 1649 cm^{-1} (C=O); HRMS (FAB): *m/z* calcd for $C_{13}H_{16}NO^+$: 202.1232; found: 202.1228 [M+H$^+$].

Conjugate addition of 4a with 11: Diethyl vinylphosphonate **11** (166 mg, 1.0 mmol) and phenylacetylene **4a** (206 mg, 2.0 mmol) were added to a mixture of phebox–Ru complex **1c** (6.0 mg, 0.010 mmol) and NaOAc (0.8 mg, 0.01 mmol) in dioxane (4 mL) at room temperature under Ar atmosphere. After stirring at 100 °C for 12 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with chloroform/methanol (20:1) as the eluent to give **12** (179 mg, 0.67 mmol, 67% yield). ^{1}H NMR (300 MHz, $CDCl_3$, RT): $\delta = 7.40$–7.35 (m, 2H), 7.32–7.25 (m, 3H), 4.19–4.07 (m, 4H), 2.76–2.67 (m, 2H), 2.15–2.04 (m, 2H), 1.38–1.32 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, RT): $\delta = 131.2$, 127.7 (d, J = 110 Hz), 123.1, 88.1 (d, J = 82 Hz), 81.0 (d, J = 9.3 Hz), 61.7 ppm (d, J = 25.0 Hz), 26.4, 24.5, 16.6 (d, J = 22.8 Hz), 13.6 ppm (d, J = 15.9 Hz); ^{31}P NMR (121 MHz, $CDCl_3$, RT): $\delta = 29.6$ ppm; IR (KBr): $\tilde{\nu} = 2221$ cm^{-1} (C≡C). HRMS (FAB): *m/z* calcd for $C_{14}H_{19}NaO_3P^+$: 289.0970; found: 289.0980 [M+Na$^+$].

Conjugate addition of 4a with 13: phenylacetylene **4a** (111 mg, 1.1 mmol) and 3-penten-2-one **13** (21 mg, 0.25 mmol) were added to a mixture of phebox–Ru complex **1c** (7.6 mg, 0.013 mmol) and NaOAc (1.0 mg, 0.013 mmol) in THF (1 mL) at room temperature under an Ar atmosphere. After stirring at 60 °C for 168 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with hexane/ethyl acetate (20:1) as the eluent to give **14** (23 mg, 0.12 mmol, 49% yield). HPLC (Chiralcel OD-H, 1% *i*PrOH in hexane, 0.5 mL min^{-1}, 254 nm) $R_t = 23.5$ (*S*), 29.1 min (*R*). $[\alpha]_D^{28} = -23.0$ ($c = 0.52$, $CHCl_3$) [lit.[8a] $[\alpha]_D^{20} = +33.0$ ($c = 0.82$, $CHCl_3$, (*S*)]; ^{1}H NMR (300 MHz, $CDCl_3$, RT): $\delta = 7.39$–7.35 (m, 2H), 7.29–7.24 (m, 3H), 3.19 (ddq, J = 6.9, 7.2, 6.6 Hz, 1H), 2.79 (dd, J = 16.5, 6.9 Hz, 1H), 2.59 (dd, J = 16.5, 7.2 Hz, 1H), 2.22 (s, 3H), 1.29 ppm (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, RT): $\delta = 206.1$, 131.3, 128.0, 127.5, 123.3, 92.9, 80.8, 50.4, 30.6, 22.4, 21.1 ppm; IR (KBr): $\tilde{\nu} = 2233$ (C≡C), 1718 cm^{-1} (C=O); HRMS (FAB): *m/z* calcd for $C_{13}H_{15}O$: 187.1123; found: 187.1117 [M+H$^+$];

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