DOI: 10.1002/ejoc.200600383

Rhodium-Catalyzed Regio-, Diastereo-, and Enantioselective Intermolecular [4+2] Carbocyclization of 4-Alkynals with Electron-Deficient Alkenes

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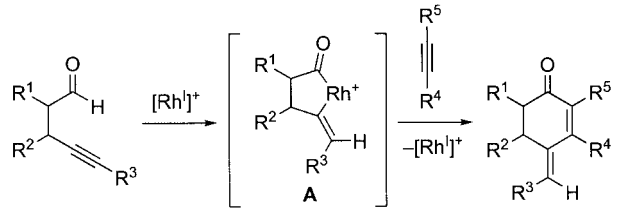
Keywords: Alkenes / Alkynes / Aldehydes / Asymmetric catalysis / Carbocyclization / Rhodium

We established that a cationic rhodium(I)/dppf or dppb complex catalyzes a regio- and diastereoselective intermolecular [4+2] carbocyclization of 5-trimethylsilyl-4-pentynals with electron-deficient alkenes leading to cyclohexanones. We also established that a cationic rhodium(I)/(*R*,*R*)-Walphos complex catalyzes a regio- and enantioselective intermolecular [4+2] carbocyclization of 5-substituted 4-pentynals and 2-alkynylbenzaldehydes with *N*,*N*-dialkylacrylamides leading to enantio-enriched cyclohexanones and tetralones, respectively. A single olefin isomer was produced in every carbocyclization. Regioselectivities of the alkene insertion depend on the alkenes used. Mechanistic study suggested that a key intermediate in this intermolecular [4+2] carbocyclization is a five-membered acylrhodium intermediate, formed by *cis* addition of the rhodium hydride to the metal-bound alkyne. This method serves as an attractive new route to highly functionalized cyclohexanones in view of the one-step access to 5-substituted 4-pentynals and 2-alkynylbenzaldehydes starting from readily available terminal alkynes.

Introduction

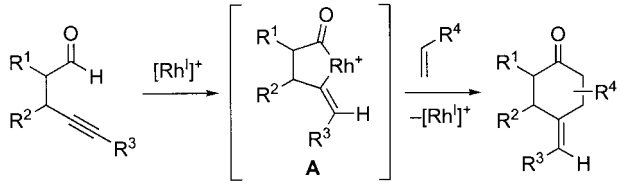
Transition-metal-catalyzed carbocyclization is one of the most valuable tools for the rapid construction of carbocycles.[1] Among them, [4+2] carbocyclization of dienes or enynes with alkynes or alkenes is widely used for the construction of six-membered ring carbon skeletons.[2–5] For the synthesis of six-membered carbonyl compounds, the [4+2] carbocyclization of cyclic acylmetal intermediates with alkynes or alkenes is a highly attractive method, however, only a few examples have been reported to date.[6–8] Furthermore, although some transition-metal-catalyzed enantioselective *intramolecular* [4+2] carbocyclizations have been reported,[4] an enantioselective *intermolecular* [4+2] carbocyclization has been achieved in a limited success.[5]

Liebeskind et al. reported that maleoylcobalt and phthaloylcobalt complexes react with alkynes leading to quinones and naphthoquinones, respectively, although stoichiometric metal reagents are required.[6] A catalytic carbocyclization involving cyclic acylmetal intermediates was reported by Murakami et al. Five-membered acylrhodium intermediates, formed catalytically by the oxidative addition of rhodium between the carbonyl carbon and the α-carbon of cyclobutanones, react intramolecularly with alkenes leading to bicyclic cyclohexanones, although those fail to react intermolecularly with alkenes.[7] A successful generation of such five-membered acylrhodium intermediates **A** was realized by the intramolecular *cis* addition of the rhodium hydride to the metal-bound triple bond of 4-alkynals. This intermediates **A** reacts with alkynes leading to substituted cyclohexenones in high yield (Scheme 1).[8]



Scheme 1. Rhodium-catalyzed intermolecular [4+2] carbocyclization of 4-alkynals with alkynes leading to cyclohexenones.

This result prompted our investigation of intercepting metalacycle **A** with alkenes, instead of alkynes. In this article, we describe that cationic rhodium(I) complexes catalyze a regio-, diastereo-, and enantioselective intermolecular [4+2] carbocyclization of 4-alkynals with electron-deficient



Scheme 2. Rhodium-catalyzed intermolecular [4+2] carbocyclization of 4-alkynals with alkenes leading to cyclohexanones.

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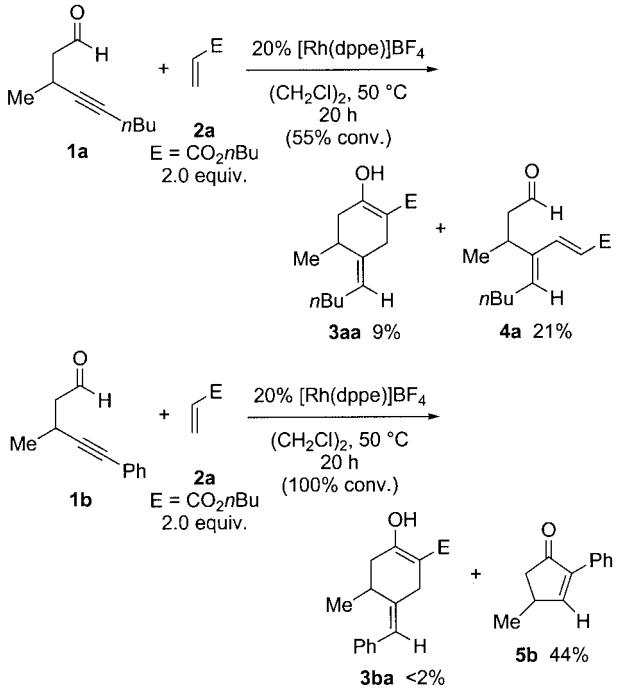
alkenes leading to cyclohexanones, presumably via the common intermediates **A** (Scheme 2).[9]

Results and Discussion

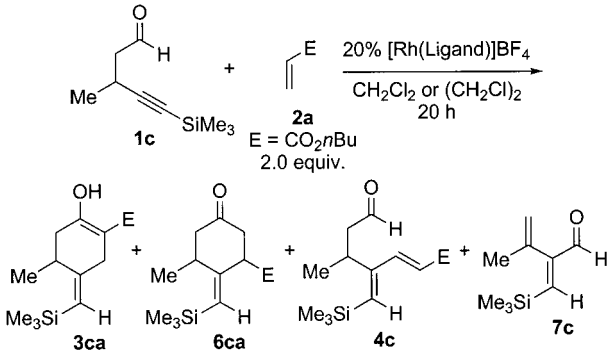
Regio- and Diastereoselective [4+2] Carbocyclization of 5-Substituted 4-Pentynals with Electron-Deficient Alkenes: We first examined the [4+2] carbocyclization of 5-butyl-3-methyl-4-pentynal (**1a**) with various alkenes in the presence of catalytic amount of [Rh(dppe)]BF_4, which was used for the [4+2] carbocyclization of 4-alkynals with alkynes.[8] We found that the use of electron-deficient alkenes such as butyl acrylate (**2a**) furnished the cyclohexanone **3aa** in low yield along with the diene **4a**. However, the reaction of 3-methyl-5-phenyl-4-pentynal (**1b**) furnished the cyclohexanone **3ba** in a trace amount (<2% yield); it furnished the cyclopentenone **5b** as a major product (Scheme 3).[10]



Scheme 3. Rhodium-catalyzed [4+2] carbocyclization of 5-alkyl- and 5-phenyl-4-pentynals with butyl acrylate.

Fortunately, the reaction of 3-methyl-5-trimethylsilyl-4-pentynal (**1c**) furnished the desired cyclohexanones **3ca** and **6ca**, and the former being obtained as a major isomer (Table 1, Entry 1). Screening of phosphane ligands revealed that although the use of dppp (Entry 2), dppb (Entry 3), BINAP (Entry 4), and dppf (Entry 5) increased the yield of cyclohexanones, but accompanied with various byproducts (dppp, dppb: complex mixture; BINAP, dppf: dienal[11] **7c**). Increasing the amount of **2a** is effective for dppf to decrease the generation of the dienal **7c** and increases the yield of cyclohexanones to 74% (5 equiv., Entry 6) and 81% (10 equiv., Entry 7). On the contrary, the amount of **2a** did not affect the yield of the cyclohexanones in the case of dppb as a ligand (Entry 8).

Table 1. Screening of reaction conditions for rhodium-catalyzed [4+2] carbocyclization of 5-trimethylsilyl-4-pentynal with butyl acrylate.

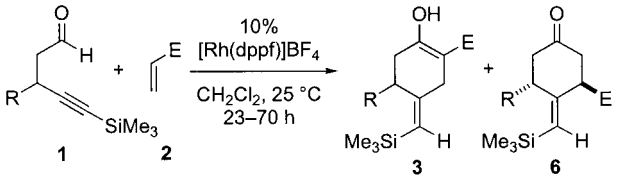


Entry	Ligand	Temp. [°C]	Conv. [%]	Yield [%][a] 3ca+6ca (3ca:6ca)	4c	7c
1	dppe	50	38	23 (80:20)	7[b]	0
2	dppp	50	62	32 (83:17)	0	0
3	dppb	50	100	63 (65:35)	0	0
4	BINAP	25	84	43 (58:42)	0	30
5	dppf	25	96	49 (77:23)	0	14
6[c]	dppf	25	100	74 (78:22)	0	9
7[d]	dppf	25	100	81 (78:22)	0	6
8[d]	dppb	50	100	62 (66:34)	0	0

[a] GC yields. [b] Isolated yield. [c] **2a**: 5 equiv. [d] **2a**: 10 equiv.

A series of electron-deficient alkenes were subjected to the above optimal reaction conditions (Table 2, Entries 1–6). Primary (**2a**,**b**: Entries 1 and 2), secondary (**2c**: Entry 3), and tertiary (**2d**: Entry 4) alkyl acrylates cleanly afforded the corresponding cyclohexanones. Not only acrylates, but also *n*-hexyl vinyl ketone (**2e**: Entry 5) and *N*,*N*-dimethylacrylamide (**2f**: Entry 6) afforded the corresponding cyclohexanones. With respect to regiochemistry, the electron-withdrawing group of the alkene is preferentially incorporated α to the ring carbonyl (product **3**) when primary and secondary alkyl acrylates were used (Entries 1–3). Interestingly, the opposite regioselectivity (product **6**) was observed when *tert*-butyl acrylate (**2d**), *n*-hexyl vinyl ketone (**2e**), and *N*,*N*-dimethylacrylamide (**2f**) were used (Entries 4–6). We have also explored the scope of this process with respect to 5-trimethylsilyl-4-pentynals (Entries 7–10). The reaction tolerates a range of substituents at the 3 position such as butyl (**1d**: Entries 7 and 8) and phenyl (**1e**: Entries 9 and 10) substituents.[12] In these reactions, the use of *tert*-butyl acrylate (**2d**) increased the yield of product **6**. A single olefin isomer was produced in each cycloaddition shown in Table 2. The product **3** consists of a mixture of keto and enol isomers, but product **6** could have two possible diastereomers. Importantly, these reactions are highly diastereoselective and afforded product **6** as a single diastereomer.[13] Unfortunately, substituted acrylates (methyl methacrylate and methyl crotonate) and other electron-deficient alkenes (acrylonitrile and phenyl vinyl sulfone) could not participate in this carbocyclization.

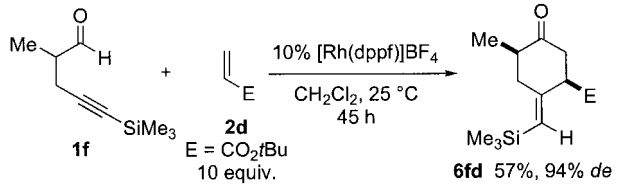
Table 2. Rhodium-catalyzed regio- and diastereoselective [4+2] carbocyclization of 5-trimethylsilyl-4-pentynals with electron-deficient alkenes.



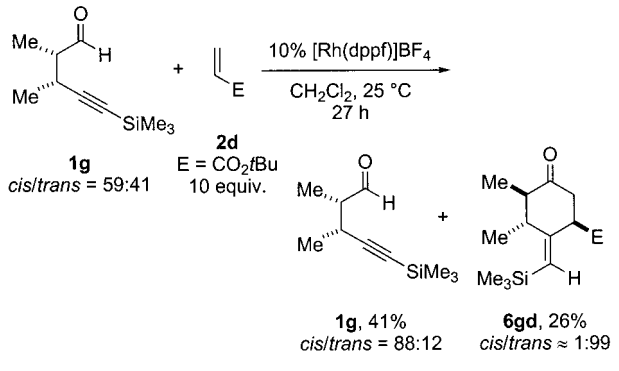
Entry	1 (R)	2 (E, equiv.)	Yield [%][a] (3:6)	*de* [%] 6
1	**1c** (Me)	**2a** (CO_2nBu, 10)	76 (81:19)	>99
2	**1c** (Me)	**2b** (CO_2iBu, 10)	76 (84:16)	>99
3	**1c** (Me)	**2c** (CO_2Cy, 10)	79 (73:27)	>99
4	**1c** (Me)	**2d** (CO_2tBu, 10)	86 (28:72)	>99
5[b]	**1c** (Me)	**2e** (COn-C_6H_{13}, 2.0)	69 (–)[e]	>99
6[c]	**1c** (Me)	**2f** ($CONMe_2$, 1.0)	63 (11:89)	>99
7	**1d** (*n*Bu)	**2a** (CO_2nBu, 10)	77 (84:16)	>99
8	**1d** (*n*Bu)	**2d** (CO_2tBu, 10)	77 (32:68)	>99
9[d]	**1e** (Ph)	**2a** (CO_2nBu, 10)	72 (91:9)	>99
10[d]	**1e** (Ph)	**2d** (CO_2tBu, 10)	73 (52:48)	>99

[a] Yields of isolated products. [b] Catalyst: 20% [Rh(dppf)]BF_4. [c] Catalyst: 20% [Rh(dppb)]BF_4. Solvent: $(CH_2Cl)_2$. Temperature: 80 °C. [d] Temperature: 8 °C. [e] Yield of **6ce**. Product **3ce** could not be isolated due to its low yield.

The reaction of the 2-substituted alkynal **1f** with *tert*-butyl acrylate (**2d**) also proceeded to give the corresponding cyclohexanone **6fd** with high diastereoselectivity (Scheme 4).



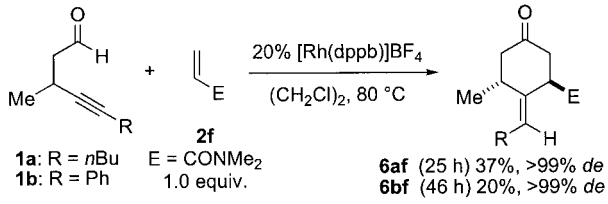
Scheme 4. Rhodium-catalyzed regio- and diastereoselective [4+2] carbocyclization of 2-methyl-5-trimethylsilyl-4-pentynal with *tert*-butyl acrylate.



Scheme 5. Rhodium-catalyzed diastereoselective kinetic resolution of 2,3-dimethyl-5-trimethylsilyl-4-pentynal.

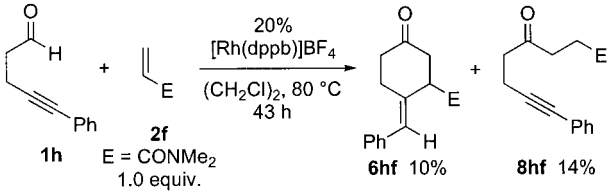
In the case of the alkynal **1g** bearing substituents at both 2 and 3 positions, one diastereomer preferentially reacted with **2d** to afford the cyclohexanone **6gd** in 26% yield as a single diastereomer; the unreacted alkynal **1g** was recovered in 41% yield with *cis*/*trans* = 88:12 (Scheme 5).

The reactions of 5-butyl-3-methyl-4-pentynal (**1a**) and 3-methyl-5-phenyl-4-pentynal (**1b**) with *N*,*N*-dimethylacrylamide (**2f**) also proceeded to give the corresponding cyclohexanones **6af** and **6bf** in 37% and 20% yield, respectively, as a single diastereomer by using [Rh(dppb)]BF_4 as a catalyst (Scheme 6).[14]



Scheme 6. Rhodium-catalyzed regio- and diastereoselective [4+2] carbocyclization of 5-butyl- and 5-phenyl-3-methyl-4-pentynals with *N*,*N*-dimethylacrylamide.

Regio- and Enantioselective [4+2] Carbocyclization of 4-Alkynals with Electron-Deficient Alkenes: Next, we investigated the reaction of 5-substituted 4-pentynals having no substituent at both 2 and 3 positions with electron-deficient alkenes to develop an enantioselective variant of this [4+2] carbocyclization. After screening various 5-substituted 4-pentynals, alkenes, and rhodium(I) complexes, we found that the reaction of 5-phenyl-4-pentynal (**1h**) with *N*,*N*-dimethylacrylamide (**2f**) in the presence of catalytic amount of [Rh(dppb)]BF_4 furnished the cyclohexanone **6hf** in low yield along with the alkynyl ketone **8hf** (Scheme 7).



Scheme 7. Rhodium-catalyzed regioselective [4+2] carbocyclization of 5-phenyl-4-pentynal with *N*,*N*-dimethylacrylamide.

The enantioselective [4+2] carbocyclization of **1h** with **2f** was examined using various chiral bidentate phosphane ligands (Figure 1), which have the large P–M–P natural bite angles to facilitate the reductive elimination step (Table 3). The study revealed that the use of (*S*,*S*)-DIOP, (*R*)-Tol-BINAP, and (*R*)-(*S*)-**9** furnished the cyclohexanone **6hf**, but both yield and *ee* were low (Entries 1–3). The use of (*R*)-(*S*)-**10**, which has the coordinating dimethylamino group, completely shut down the reaction (Entry 4). We were pleased to find that the use of (*R*)-(*R*)-Walphos [(*R*)-(*R*)-**11**][15] dramatically increased both yield and *ee* of **6hf** (Entry 5). The reaction could be carried out using 5–10% catalyst, although lower yield and *ee* were observed (Entries 6 and 7).

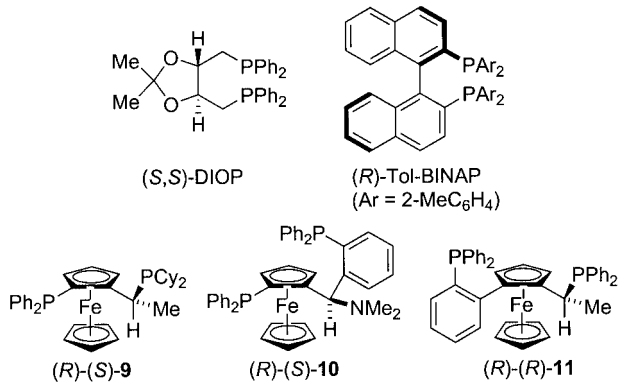
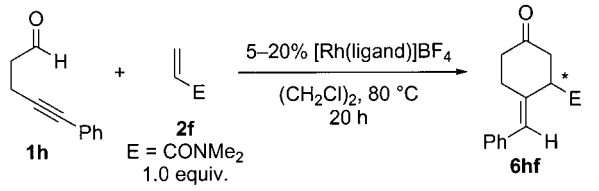


Figure 1. Structures of chiral bidentate phosphane ligands.

Table 3. Screening of ligands for rhodium-catalyzed regio- and enantioselective [4+2] carbocyclization of 5-phenyl-4-pentynal with *N*,*N*-dimethylacrylamide.

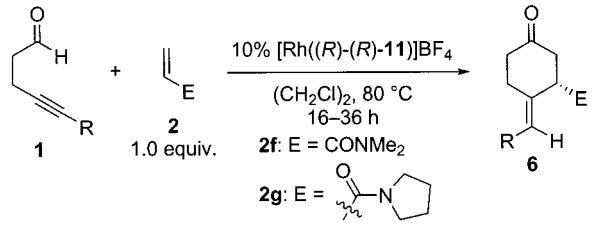


Entry	Ligand	Catalyst [%]	Yield [%][a]	*ee* [%]
1	(*S*,*S*)-DIOP	20	10	37
2	(*R*)-Tol-BINAP	20	9	2
3	(*R*)-(*S*)-**9**	20	15	20
4	(*R*)-(*S*)-**10**	20	0	–
5	(*R*)-(*R*)-**11**	20	72[b]	>99
6	(*R*)-(*R*)-**11**	10	57[b]	>99
7	(*R*)-(*R*)-**11**	5	52[b]	98

[a] NMR yield. [b] Yields of isolated products.

A series of the 5-substituted 4-pentynals **1h**–**n** were subjected to the above optimal reaction conditions (Table 4). The reactions of aryl (**1h**–**k**, Entries 1–4), alkenyl (**1l**, Entry 6), and alkyl (**1m**, Entry 7) substituted 4-pentynals with **2f** afforded the corresponding cyclohexanones in good yield with high enantioselectivity. Not only *N*,*N*-dimethylacrylamide (**2f**), but also *N*-acryloylpyrrolidine (**2g**) can be employed (Entry 5). However, the use of substituted acrylamides (*N*,*N*-dimethylmethacrylamide, 1-pyrrolidin-1-yl-but-2-en-1-one, and *N*-methylmaleimide) did not afford the desired carbocyclization products. Although the enantioselectivity was very high, the reaction of 5-trimethylsilyl-4-pentynal (**1n**) proceeded in low yield (Entry 8). Importantly, these [4+2] carbocyclizations of **1h**–**n** with **2f**,**g** are highly regioselective and no regioisomer was detected in the crude reaction mixtures.[16] The absolute configuration of (+)-**6kf** was determined to be *S* by an anomalous dispersion method (Figure 2).

Table 4. Rhodium-catalyzed regio- and enantioselective [4+2] carbocyclization of 5-substituted 4-pentynals with *N*,*N*-dialkylacrylamides.



Entry	**1** (R)	**2**	**6**	Yield [%][a]	*ee* [%]
1	**1h** (Ph)	**2f**	(+)-**6hf**	57	>99
2	**1i** (4-MeOC$_6$H$_4$)	**2f**	(+)-**6if**	58	>99
3	**1j** (4-F$_3$CC$_6$H$_4$)	**2f**	(+)-**6jf**	51	94
4	**1k** (4-ClC$_6$H$_4$)	**2f**	(*S*)-(+)-**6kf**	68	>99
5	**1k** (4-ClC$_6$H$_4$)	**2g**	(+)-**6kg**	77	>99
6[b]	**1l** (1-cyclohexenyl)	**2f**	(+)-**6lf**	50	97
7[b,c]	**1m** (*n*Bu)	**2f**	(+)-**6mf**	77	>99
8[b]	**1n** (Me$_3$Si)	**2f**	(+)-**6nf**	25	>99

[a] Yields of isolated products. [b] Catalyst: 20%. [c] Temperature: 40 °C.

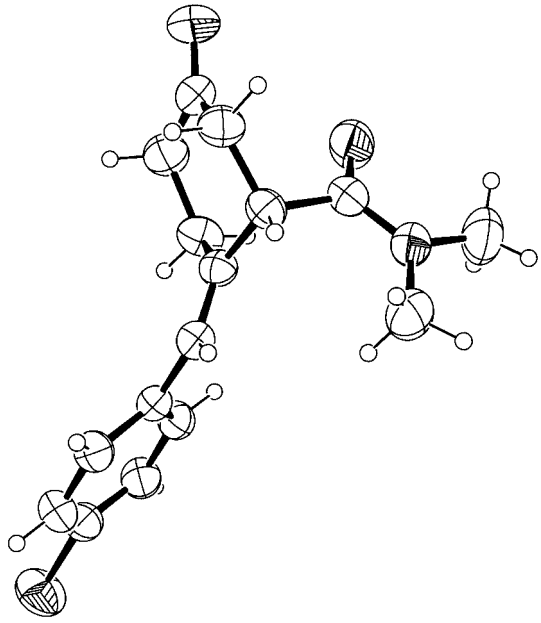
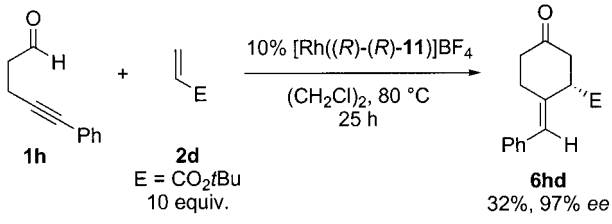


Figure 2. ORTEP diagram of (*S*)-(+)-**6kf**. Ellipsoids drawn at the 50% probability level.

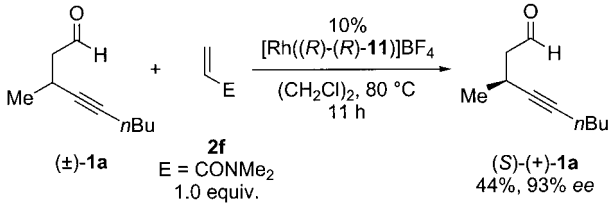
Not only *N*,*N*-dialkylacrylamides but also *tert*-butyl acrylate (**2d**) could be used for this regio- and enantioselective [4+2] carbocyclization, and the corresponding enantio-enriched cyclohexanone was obtained in 32% yield with 97% *ee* (Scheme 8).

We anticipated that enantioselective kinetic resolution of a 3-substituted 4-alkynal would proceed through the reaction with *N*,*N*-dimethylacrylamide (**2f**) by using [Rh((*R*,*R*)-**11**)]BF$_4$ as a catalyst. Indeed, the kinetic resolution of (±)-**1a** proceeded to give enantio-enriched alkynal (*S*)-(+)-**1a** in



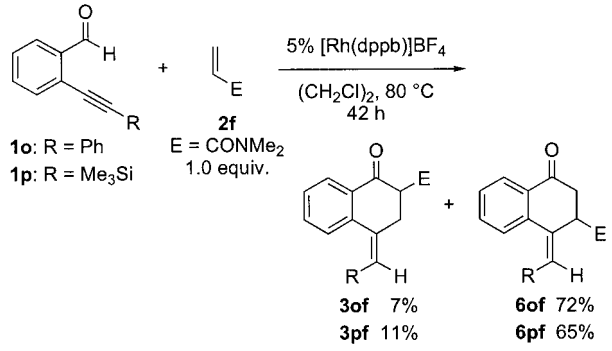
Scheme 8. Rhodium-catalyzed regio- and enantioselective [4+2] carbocyclization of 5-phenyl-4-pentynal with *tert*-butyl acrylate.

44% isolated yield with 93% *ee*, although another enantiomer (*R*)-(–)-**1a** was decomposed to give a complex mixture of products (Scheme 9).



Scheme 9. Rhodium-catalyzed enantioselective kinetic resolution of 3-methyl-4-nonynal.

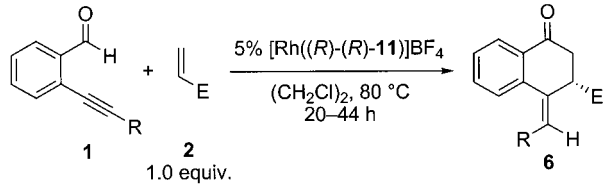
Regio- and Enantioselective [4+2] Carbocyclization of 2-Alkynylbenzaldehydes with *N*,*N*-Dialkylacrylamides: Benzene-linked 4-alkynals, 2-alkynylbenzaldehydes, are versatile substrates due to their facile preparation starting from 2-bromobenzaldehyde and terminal alkynes through Sonogashira coupling.[17–18] Therefore, the intermolecular [4+2] carbocyclization of 2-alkynylbenzaldehydes with **2f** leading to functionalized tetralone derivatives was investigated. Fortunately, the reaction of 2-alkynylbenzaldehydes **1o** and **1p** with **2f** in the presence of [Rh(dppb)]BF_4 as a catalyst proceeded to give the corresponding tetralone derivatives in high yield with good regioselectivity (Scheme 10).



Scheme 10. Rhodium-catalyzed regioselective [4+2] carbocyclization of 2-alkynylbenzaldehydes with *N*,*N*-dimethylacrylamide.

Next, the enantioselective [4+2] carbocyclization of 2-alkynylbenzaldehydes **1o**–**t** with the *N*,*N*-dialkylacrylamides **2f**,**g** was investigated (Table 5). Aryl- (Entries 1–3), alkenyl- (Entry 4), and alkyl-substituted (Entries 5 and 6) 2-ethynylbenzaldehydes afforded the corresponding cyclohexanones in good yield with high enantioselectivity. The reaction of the trimethylsilyl-substituted 2-ethynylbenzaldehyde **1p** proceeded in low yield, but high enantioselectivity was observed (Entry 7). As demonstrated in Table 4, no regioisomer was detected in these reactions.[16] In general, the reactions of the 2-alkynylbenzaldehydes **1o**–**t** are more facile than those of the 5-substituted 4-pentynals **1h**–**n**, which allow lower catalyst loading. Because the [4+2] carbocyclization of 2-alkynylbenzaldehydes with alkynes did not proceed at all, this successful [4+2] carbocyclization of 2-alkynylbenzaldehydes with *N*,*N*-dialkylacrylamides is noteworthy.

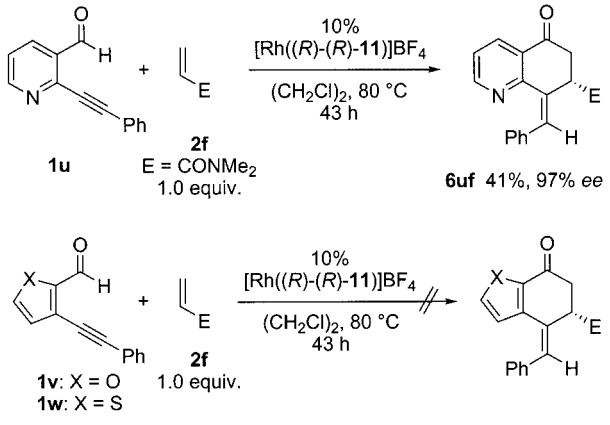
Table 5. Rhodium-catalyzed regio- and enantioselective [4+2] carbocyclization of 2-alkynylbenzaldehydes with *N*,*N*-dialkylacrylamides.



Entry	1 (R)	2	6	Yield [%][a]	*ee* [%]
1	**1o** (Ph)	**2f**	(+)-**6of**	80	97
2	**1o** (Ph)	**2g**	(+)-**6og**	80	97
3	**1q** (2-ClC_6H_4)	**2f**	(+)-**6qf**	94	90
4	**1r** (1-cyclohexenyl)	**2f**	(+)-**6rf**	56	99
5	**1s** (*n*Bu)	**2f**	(+)-**6sf**	56	>99
6	**1t** (Cl(CH_2)$_3$)	**2f**	(+)-**6tf**	81	97
7	**1p** (Me_3Si)	**2f**	(+)-**6pf**	26	>99

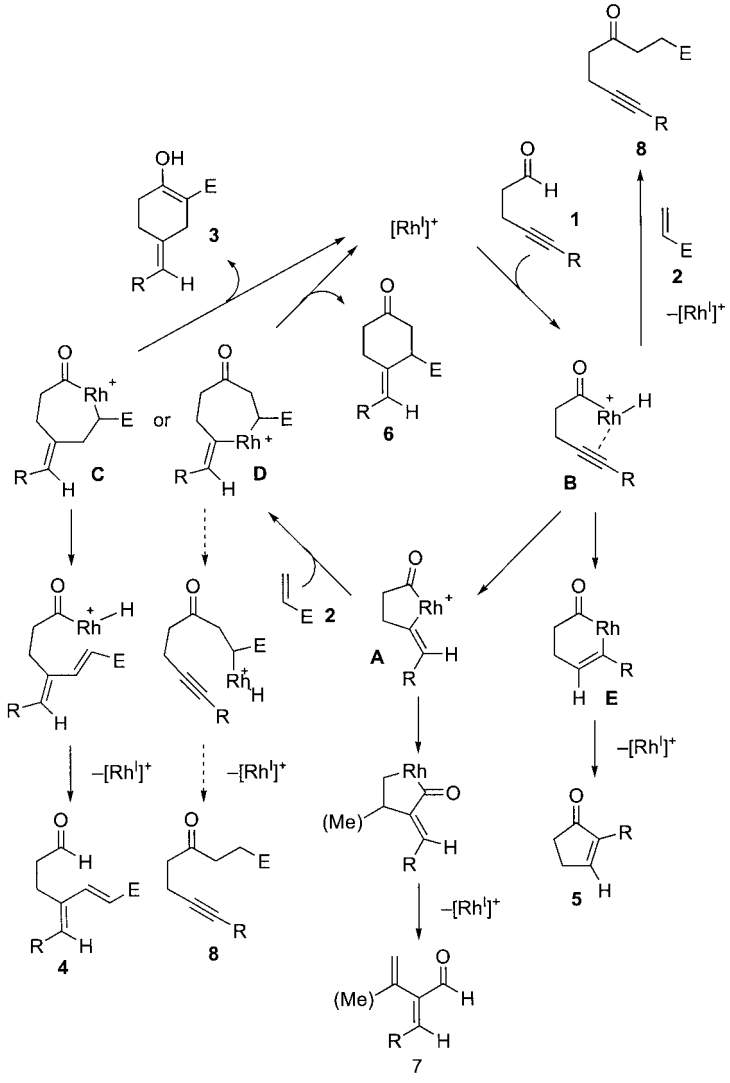
[a] Yields of isolated products.

The enantioselective [4+2] carbocyclization of heterocyclic 4-alkynals with **2f** was also investigated. The reaction of the pyridine-linked 4-alkynal **1u** with **2f** proceeded to give the corresponding bycyclic pyridine derivative **6uf** in 41% yield with 97% *ee*. However, no reaction was observed in the case of the furan- or thiophene-linked 4-alkynal **1v** or **1w** (Scheme 11).



Scheme 11. Rhodium-catalyzed regio- and enantioselective [4+2] carbocyclization of heterocyclic 4-alkynals with *N*,*N*-dimethylacrylamide.

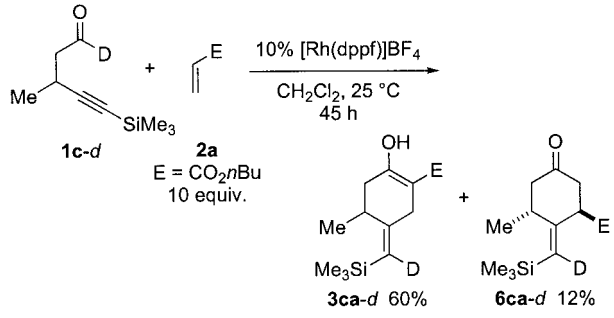
Mechanistic Consideration for Rhodium-Catalyzed Intermolecular [4+2] Carbocyclization of 4-Alkynals with Electron-Deficient Alkenes: Scheme 12 shows a possible mecha-



Scheme 12. Possible mechanism for rhodium-catalyzed intermolecular [4+2] carbocyclization of 4-alkynals with electron-deficient alkenes.

nism for this carbocyclization.[19] We infer that an oxidative addition of the aldehyde C–H bond to rhodium(I) affords the acylrhodium hydride **B**. The *cis* addition of the rhodium hydride to the metal-bound alkyne then provides the five-membered acylrhodium intermediate **A**.[20] Complexation of the alkene **2**, followed by insertion affords the metallacycles **C** and **D**. Reductive elimination furnishes cyclohexanones **3** and **6**, respectively, and regenerates the Rh catalyst. The diene **4** is generated through β-hydride elimination from the metallacycle **C** followed by reductive elimination. The dienal **7** is generated through carbonyl migration of the acylrhodium intermediate **A** followed by β-hydride elimination.[11] On the other hand, *trans* addition of the rhodium hydride to the metal-bound alkyne then provides the six-membered acylrhodium intermediate **E**. Reductive elimination furnishes cyclopentenone **5** and regenerates the Rh catalyst.[10]

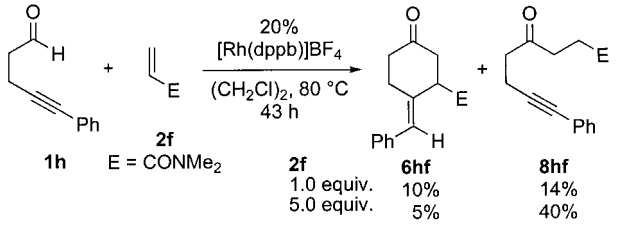
Consistent with these pathways, the reaction of the deuterium-labeled 4-alkynal **1c**-*d* with **2a** led to stereospecific incorporation of deuterium in the α position of the trimethylsilyl group of cyclohexanones (Scheme 13).



Scheme 13. Deuterium labeling study.

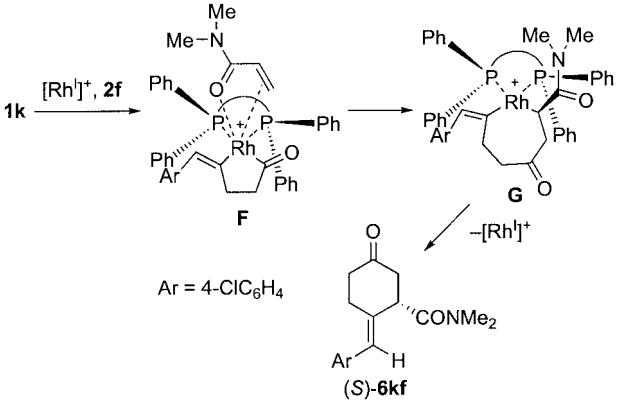
The formation of the alkynyl ketone **8hf** is possible through both β hydride elimination from the metallacycle **D** and carbometallation of the intermediate **B** with alkene **2f** prior to hydrometallation (Scheme 12).[21] If the latter reaction is the major pathway, the reaction of 5-phenyl-4-pentynal (**1h**) with excess **2f** by using [Rh(dppb)]BF_4 as a catalyst should increased the yield of **8hf**. Indeed, the yield of

8hf was significantly increased, which supports the carbometallation of intermediate **B** with **2f** leading to **8hf** (Scheme 14).



Scheme 14. Rhodium-catalyzed reaction of 5-phenyl-4-pentynal with excess *N*,*N*-dimethylacrylamide.

A possible mechanism of the selective formation of (*S*)-**6kf** is depicted in Scheme 15. Regio- and enantioselectivity are determined by preferential formation of the intermediate **F** followed by the insertion of **2f** to form the intermediate **G**, in order to avoid the steric repulsion between NMe_2 group of **2f** and PPh_2 group of (*R*,*R*)-**11**. Reductive elimination of rhodium gives (*S*)-**6kf** and regenerates the rhodium catalyst.



Scheme 15. Possible mechanism of the selective formation of (*S*)-**6kf**.

Conclusions

In conclusion, we established that a cationic rhodium(I)/dppf or dppb complex catalyzes a regio- and diastereoselective intermolecular [4+2] carbocyclization of 5-trimethylsilyl-4-pentynals with electron-deficient alkenes leading to cyclohexanones. We also established that a cationic rhodium(I)/(*R*,*R*)-Walphos complex catalyzes a regio- and enantioselective intermolecular [4+2] carbocyclization of 5-substituted 4-pentynals and 2-alkynylbenzaldehydes with *N*,*N*-dialkylacrylamides leading to enantio-enriched cyclohexanones and tetralones, respectively. A single olefin isomer was produced in every carbocyclization. Regioselectivities of the alkene insertion depend on the alkenes used. Mechanistic study suggested that a key intermediate in this intermolecular [4+2] carbocyclization is a five-membered acylrhodium intermediate, formed by the *cis* addition of the rhodium hydride to the metal-bound alkyne. This method serves as an attractive new route to highly functionalized cyclohexanones in view of the one-step access to 5-substituted 4-pentynals (1,4-addition of terminal alkynes to α,β-unsaturated aldehydes) and 2-alkynylbenzaldehydes (Sonogashira coupling of terminal alkynes with 2-bromobenzaldehyde).

Experimental Section

General Methods: ^{1}H NMR spectra were recorded with JEOL AL 300 (300 MHz) or JEOL AL 400 (400 MHz). ^{13}C NMR spectra were obtained with complete proton decoupling with JEOL AL 300 (75 MHz) or JOEL AL 400 (100 MHz). HRMS data were obtained with JEOL JMS-700. Infrared spectra were obtained with a JASCO A-302. The chiral ligands **9**, **10**, and **11** were obtained from Solvias AG under their University Ligand Kit program. Anhydrous CH_2Cl_2 (Aldrich, No. 27,099–7) and anhydrous $(CH_2Cl)_2$ (Aldrich, No. 28,450–5) were used as received. Solvents for the synthesis of substrates were dried with molecular sieves (4 Å, Wako) prior to use. All reagents were obtained from commercial sources and used as received, unless otherwise indicated. All reactions were carried out under argon or nitrogen in oven-dried glassware, unless otherwise indicated.

Starting Materials: The 4-alkynals **1a**–**n** were synthesized through 1,4-addition of the corresponding terminal alkynes and α,β-unsaturated aldehydes according to the literature procedure.[22] 4-Alkynals **1o**–**w** were synthesized through Sonogashira coupling of the corresponding terminal alkynes and bromides according to the literature procedure.[23] The 4-alkynal **1c**-*d* was synthesized through the following sequences: 1) Jones oxidation of **1c**, 2) reduction with $LiAlD_4$, 3) Swern oxidation, according to the literature procedure.[10a] 4-Alkynals **1a**,[24] **1b**,[10a] **1e**,[11] **1f**,[25] **1h**,[26] **1j**,[27] **1m**,[28] **1n**,[29] **1o**,[17] **1p**,[30] **1r**,[24] **1s**,[31] **1u**,[32] **1v**,[33] and **1w**[34] were reported in the literatures. The ketone **2e**[35] and the amide **2g**[36] were reported in the literatures.

Aldehyde 1c: Colorless oil. IR (neat): $\tilde{\nu}$ = 2910, 2180, 1725, 1250, 845, 760 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.79 (t, J = 2.1 Hz, 1 H), 3.00 (sext, J = 6.9 Hz, 1 H), 2.54 (ddd, J = 16.8, 6.9, 2.1 Hz, 1 H), 2.49 (ddd, J = 16.8, 6.9, 2.1 Hz, 1 H), 1.22 (d, J = 6.9 Hz, 3 H), 0.14 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 201.0, 109.1, 85.7, 49.8, 21.6, 20.9, 0.0 ppm. HRMS (EI): calcd. for $C_9H_{16}OSi$ $[M-H]^+$ 167.0892; found: 167.0839.

Aldehyde 1d: Colorless oil. IR (neat): $\tilde{\nu}$ = 2930, 2180, 1725, 1250, 845, 760 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.80 (t, J = 2.1 Hz, 1 H), 2.87 (quint, J = 6.9 Hz, 1 H), 2.57 (ddd, J = 16.5, 6.9, 2.1 Hz, 1 H), 2.49 (ddd, J = 16.5, 6.9, 2.1 Hz, 1 H), 1.26–1.54 (m, 6 H), 0.91 (t, J = 6.9 Hz, 3 H), 0.14 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 201.4, 108.1, 86.7, 48.3, 34.4, 29.2, 27.0, 22.3, 13.9, 0.1 ppm. HRMS (EI): calcd. for $C_{12}H_{22}OSi$ $[M]^+$ 210.1440; found: 210.1380.

Aldehyde 1g: Pale yellow oil. IR (neat): $\tilde{\nu}$ = 2960, 2180, 1725, 1250, 845, 760 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, mixture of diastereomers, *cis*:*trans* = 59:41): δ = 9.76 (d, J = 2.1 Hz, 1 H, *trans*), 9.70 (d, J = 1.8 Hz, 1 H, *cis*), 2.87–3.01 (m, 1 H, *cis*), 2.74–2.85 (m, 1 H, *trans*), 2.30–2.46 (m, 2 H, *cis* and *trans*), 1.14–1.24 (m, 12 H, *cis* and *trans*), 0.15 (s, 9 H, *trans*), 0.14 (s, 9 H, *cis*) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 204.2, 203.9, 108.0, 107.5, 86.9, 86.8, 50.5, 50.2, 28.1, 27.5, 18.6, 18.1, 11.2, 10.4, 0.0 ppm. HRMS (EI): calcd. for $C_{10}H_{18}OSi$ $[M]^+$ 182.1127; found: 182.1064.

Aldehyde 1i: Pale orange oil. IR (neat): $\tilde{\nu}$ = 3350, 2875, 2800, 2680, 1708, 1590, 1492, 1275, 1230, 1163, 1020, 820 cm^{-1}. ^{1}H NMR

($CDCl_3$, 300 MHz): δ = 9.85 (s, 1 H), 7.27–7.35 (m, 2 H), 6.75–6.87 (m, 2 H), 3.80 (s, 3 H), 2.67–2.79 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 200.7, 159.2, 132.9, 115.4, 113.8, 86.1, 81.2, 55.2, 42.7, 12.6 ppm. HRMS (EI): calcd. for $C_{12}H_{12}O_2$ $[M]^+$ 188.0837; found: 188.0814.

Aldehyde 1k: Pale brown solid; m.p. 40–41 °C. IR (neat): $\tilde{\nu}$ = 2870, 2780, 2680, 1700, 1472, 1370, 1340, 1083, 820 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 9.84–9.86 (m, 1 H), 7.21–7.33 (m, 4 H), 2.68–2.81 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 200.2, 133.8, 132.8, 128.5, 121.8, 88.8, 80.3, 42.5, 12.6 ppm. HRMS (EI): calcd. for $C_{11}H_9ClO$ $[M - Cl]^+$ 157.0653; found:157.0634.

Aldehyde 1l: Pale yellow oil. IR (neat): $\tilde{\nu}$ = 2910, 1720, 1342, 920, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 9.81 (t, J = 1.2 Hz, 1 H), 5.96–6.08 (m, 1 H), 2.57–2.72 (m, 4 H), 1.98–2.16 (m, 4 H), 1.48–1.68 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 200.7, 134.0, 120.5, 84.7, 83.3, 42.8, 29.3, 25.5, 22.3, 21.5, 12.6 ppm. HRMS (EI): calcd. for $C_{11}H_{14}O$ $[M]^+$ 162.1045; found: 162.0967.

Aldehyde 1q: Pale yellow solid; m.p. 65–67 °C. IR (neat): $\tilde{\nu}$ = 2795, 1680, 1565, 1470, 1455, 1415, 1250, 1185, 740 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 10.72 (s, 1 H), 7.93–8.00 (m, 1 H), 7.65–7.71 (m, 1 H), 7.54–7.63 (m, 2 H), 7.40–7.50 (m, 2 H), 7.22–7.35 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.7, 136.1, 135.9, 133.7, 133.2, 129.9, 129.4, 128.9, 127.1, 126.5, 126.3, 122.3, 92.9, 89.9 ppm. HRMS (EI): calcd. for $C_{15}H_9ClO$ $[M]^+$ 240.0342; found: 240.0386.

Aldehyde 1t: Pale yellow oil. IR (neat): $\tilde{\nu}$ = 2800, 1675, 1580, 1420, 1260, 1230, 1183, 750 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 10.51 (d, J = 0.9 Hz, 1 H), 7.87–7.92 (m, 1 H), 7.49–7.58 (m, 2 H), 7.37–7.44 (m, 1 H), 3.73 (t, J = 6.6 Hz, 2 H), 2.71 (t, J = 6.6 Hz, 2 H), 2.11 (quint, J = 6.6 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.6, 135.9, 133.6, 133.3, 128.1, 127.09, 127.05, 95.6, 77.3, 43.6, 31.2, 17.1 ppm. HRMS (EI): calcd. for $C_{12}H_{11}ClO$ $[M]^+$ 206.0498; found: 206.0486.

Aldehyde 1c-*d*: Colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.00 (sext, J = 6.9 Hz, 1 H), 2.59 (dd, J = 16.8, 6.9 Hz, 1 H), 2.49 (dd, J = 16.8, 6.9 Hz, 1 H), 1.24 (d, J = 6.9 Hz, 3 H), 0.14 (s, 9 H) ppm. ^2H NMR ($CDCl_3$, 61 MHz): δ = 9.83 (s) ppm.

General Procedure 1 for Regio- and Diastereoselective [4+2] Carbocyclization of 4-Alkynals with Alkenes: (Table 2, Entry 1) Under Ar, CH_2Cl_2 (1.0 mL) solution of dppf (22.2 mg, 0.040 mmol) was added to CH_2Cl_2 (1.0 mL) solution of $[Rh(cod)_2]BF_4$ (16.2 mg, 0.040 mmol) and the mixture was stirred at room temperature for 5 min. H_2 was introduced to the resulting solution in Schlenk tube. After stirring for 0.5 h at room temperature, the resulting solution was concentrated to dryness. A CH_2Cl_2 solution (2 mL) of the aldehyde **1c** (67.3 mg, 0.400 mmol) and butyl acrylate (**2a**, 513 mg, 4.00 mmol) was added to the residue. The mixture was stirred at 25 °C for 45 h. The resulting solution was concentrated and purified by preparative TLC (hexane/EtOAc, 25:1), which furnished the ester **3ca** (73.3 mg, 0.247 mmol, 62%) and the ester **6ca** (17.1 mg, 0.058 mmol, 14%, >99% *de*).

Ester 3ca: Colorless oil. IR (neat): $\tilde{\nu}$ = 2945, 1653, 1618, 1402, 1350, 1265, 1223, 1202, 1080, 1045, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 12.17 (s, 1 H), 5.30 (d, J = 2.0 Hz, 1 H), 4.07–4.25 (m, 2 H), 3.19 (dt, J = 18.1, 2.6 Hz, 1 H), 2.86 (d, J = 18.1 Hz, 1 H), 2.77–2.96 (m, 1 H), 2.50–2.62 (m, 1 H), 2.19 (dd, J = 17.8, 1.3 Hz, 1 H), 1.58–1.72 (m, 2 H), 1.35–1.48 (m, 2 H), 1.12 (d, J = 7.0 Hz, 3 H), 0.96 (t, J = 7.5 Hz, 3 H), 0.11 (s, 9 H) ppm; vinyl proton of keto isomer: δ = 5.43 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 172.0, 169.6, 156.2, 123.1, 96.0, 64.1, 37.2, 34.1, 31.4, 30.6, 19.2, 13.7, 0.2 ppm. HRMS (EI): calcd. for $C_{16}H_{28}O_3Si$ $[M - CO_2C_4H_9]^+$ 195.1205; found 195.1144.

Ester 6ca: Colorless oil. IR (neat): $\tilde{\nu}$ = 2940, 1717, 1242, 1170, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 5.28 (d, J = 1.6 Hz, 1 H), 4.02–4.28 (m, 2 H), 3.69 (ddd, J = 12.0, 5.2, 1.6 Hz, 1 H), 3.08–3.23 (m, 1 H), 2.80 (dd, J = 15.2, 12.0 Hz, 1 H), 2.64 (dd, J = 14.4, 6.4 Hz, 1 H), 2.53 (ddd, J = 15.2, 5.2, 2.4 Hz, 1 H), 2.32 (dt, J = 14.4, 2.4 Hz, 1 H), 1.58–1.71 (m, 2 H), 1.39 (sext, J = 7.2 Hz, 2 H), 1.15 (d, J = 7.2 Hz, 3 H), 0.94 (t, J = 7.6 Hz, 3 H), 0.14 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 208.9, 172.4, 154.2, 125.1, 64.9, 47.7, 47.4, 43.5, 37.5, 30.6, 20.5, 19.1, 13.6, 0.0 ppm. HRMS (EI): calcd. for $C_{16}H_{28}O_3Si$ $[M]^+$ 296.1808; found: 296.1793.

Ester 3cb: (Table 2, Entry 2) Procedure 1 was followed using **1c** and **2b**. Reaction time: 45 h. Yield 64% (76 mg). Colorless oil. IR (neat): $\tilde{\nu}$ = 2945, 1660, 1620, 1405, 1350, 1270, 1225, 1202, 1082, 1050, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 12.16 (s, 1 H), 5.31 (d, J = 1.8 Hz, 1 H), 3.82–4.04 (m, 2 H), 3.21 (dt, J = 18.1, 2.4 Hz, 1 H), 2.87 (d, J = 18.1 Hz, 1 H), 2.79–2.97 (m, 1 H), 2.45–2.63 (m, 1 H), 2.19 (dd, J = 18.0, 1.3 Hz, 1 H), 2.01 (sept, J = 6.6 Hz, 1 H), 1.22 (d, J = 7.0 Hz, 3 H), 0.97 (d, J = 6.8 Hz, 6 H), 0.11 (s, 9 H) ppm; vinyl proton of keto isomer: δ = 5.44 (d, J = 1.8 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 172.0, 169.7, 156.2, 123.2, 96.1, 70.3, 37.3, 34.1, 31.4, 27.7, 19.2, 189.1, 0.2 ppm. HRMS (EI): calcd. for $C_{16}H_{28}O_3Si$ $[M - CO_2C_4H_9]^+$ 195.1205; found: 195.1165.

Ester 6cb: (Table 2, Entry 2) Yield 12% (14 mg). Pale yellow solid; m.p. 38–40 °C. IR (neat): $\tilde{\nu}$ = 2940, 1720, 1608, 1245, 1170, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.30 (d, J = 1.7 Hz, 1 H), 3.82–4.04 (m, 2 H), 3.70 (ddd, J = 11.5, 5.3, 1.7 Hz, 1 H), 3.14–3.24 (m, 1 H), 2.80 (dd, J = 15.0, 11.5 Hz, 1 H), 2.65 (dd, J = 14.5, 6.1 Hz, 1 H), 2.54 (ddd, J = 15.0, 5.3, 2.2 Hz, 1 H), 2.32 (dt, J = 14.5, 2.2 Hz, 1 H), 1.97 (sept, J = 6.8 Hz, 1 H), 1.15 (d, J = 7.1 Hz, 3 H), 0.94 (d, J = 6.6 Hz, 6 H), 0.14 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 208.7, 172.3, 154.1, 125.1, 71.2, 47.7, 47.6, 43.5, 37.5, 27.7, 20.7, 19.2, 0.1 ppm. HRMS (EI): calcd. for $C_{16}H_{28}O_3Si$ $[M]^+$ 296.1808; found: 296.1782.

Ester 3cc: (Table 2, Entry 3) Procedure 1 was followed using **1c** and **2c**. Reaction time: 45 h. Yield 61% (68 mg). Pale yellow oil. IR (neat): $\tilde{\nu}$ = 2940, 1650, 1618, 1350, 1265, 1223, 1204, 1048, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 12.24 (s, 1 H), 5.31 (d, J = 2.2 Hz, 1 H), 4.83–4.93 (m, 1 H), 3.19 (dt, J = 18.1 and 2.4 Hz, 1 H), 2.86 (d, J = 18.1 Hz, 1 H), 2.76–2.95 (m, 1 H), 2.46–2.62 (m, 1 H), 2.18 (d, J = 17.8 Hz, 1 H), 1.63–1.91 (m, 4 H), 1.20–1.58 (m, 6 H), 1.12 (d, J = 7.0 Hz, 3 H), 0.11 (s, 9 H) ppm; vinyl proton of keto isomer: δ = 5.42 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.5, 169.4, 156.3, 123.0, 96.3, 72.2, 37.3, 34.1, 31.51, 31.47, 25.4, 23.4, 19.2, 0.2 ppm. HRMS (EI): calcd. for $C_{18}H_{30}O_3Si$ $[M - CO_2C_6H_{11}]^+$ 195.1205; found: 195.1156.

Ester 6cc: (Table 2, Entry 3) Yield 18% (25 mg). Colorless solid; m.p. 40–42 °C. IR (neat): $\tilde{\nu}$ = 1930, 1720, 1608, 1243, 1180, 1025, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.34 (d, J = 1.8 Hz, 1 H), 4.79–4.92 (m, 1 H), 3.65 (ddd, J = 11.4, 5.4, 1.8 Hz, 1 H), 3.10–3.22 (m, 1 H), 2.79 (dd, J = 15.0, 11.4 Hz, 1 H), 2.65 (dd, J = 14.4, 6.0 Hz, 1 H), 2.52 (ddd, J = 15.0, 5.4, 2.1 Hz, 1 H), 2.31 (dt, J = 14.4, 2.1 Hz, 1 H), 1.64–1.93 (m, 4 H), 1.19–1.60 (m, 6 H), 1.15 (d, J = 7.2 Hz, 3 H), 0.14 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 209.0, 171.8, 154.3, 125.1, 73.3, 47.6, 47.4, 43.4, 37.5, 31.5, 31.4, 25.3, 23.6, 20.7, 0.0 ppm. HRMS (EI): calcd. for $C_{18}H_{30}O_3Si$ $[M]^+$ 322.1964; found: 322.1927.

Ester 3cd: (Table 2, Entry 4) Procedure 1 was followed using **1c** and **2d**. Reaction time: 45 h. Yield 24% (29 mg). Colorless oil. IR

(neat): $\tilde{\nu}$ = 2925, 1650, 1618, 1358, 1288, 1230, 1152, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 12.34 (s, 1 H), 5.30 (d, J = 2.0 Hz, 1 H), 3.14 (dt, J = 18.2, 2.4 Hz, 1 H), 2.80 (d, J = 18.2 Hz, 1 H), 2.68–2.96 (m, 1 H), 2.42–2.66 (m, 1 H), 2.16 (d, J = 17.8 Hz, 1 H), 1.51 (s, 9 H), 1.11 (d, J = 7.0 Hz, 3 H), 0.11 (s, 9 H) ppm; vinyl proton of keto isomer: δ = 5.42–5.44 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.7, 168.8, 156.5, 122.6, 96.9, 80.8, 37.1, 35.8, 34.0, 28.1, 19.1, 0.0 ppm. HRMS (EI): calcd. for $C_{16}H_{28}O_3Si$ $[M-CO_2C_4H_9]^+$ 195.1205; found: 195.1149.

Ester 6cd: (Table 2, Entry 4) Yield 62% (74 mg). Relative configuration was determined by NOESY experiment (see supporting information; for supp. inf. see also the footnote on the first page of this article). Pale brown solid; m.p. 46–47 °C. IR (neat): $\tilde{\nu}$ = 2950, 1720, 1610, 1365, 1250, 1155, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.41 (d, J = 1.8 Hz, 1 H, Ha), 3.56 (ddd, J = 11.4, 5.5, 1.8 Hz, 1 H, Hb), 3.05–3.23 (m, 1 H, Hc), 2.74 (dd, J = 15.2, 11.4 Hz, 1 H), 2.64 (dd, J = 14.7, 6.1 Hz, 1 H), 2.50 (ddd, J = 15.2, 5.5, 2.0 Hz, 1 H), 2.30 (dt, J = 14.7, 2.2 Hz, 1 H), 1.48 (s, 9 H), 1.14 (d, J = 7.3 Hz, 3 H), 0.15 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 209.0, 171.5, 154.5, 124.8, 81.4, 48.0, 47.5, 43.4, 37.5, 28.1 20.8, 0.1 ppm. HRMS (EI): calcd. for $C_{16}H_{28}O_3Si$ $[M]^+$ 296.1808; found: 296.1732.

Ketone 6ce: (Table 2, Entry 5) Procedure 1 was followed using **1c**, **2e** (2.0 equiv.), and 20% $[Rh(cod)_2]BF_4$/dppf. Reaction time: 43 h. Yield 69% (82 mg). Pale brown solid; m.p. 39–41 °C. IR (neat): $\tilde{\nu}$ = 2925, 1702, 1610, 1405, 1375, 1245, 1045, 845 cm^{-1}. ^{1}NMR (C_6D_6, 300 MHz): δ = 5.31 (d, J = 1.2 Hz, 1 H), 3.45 (ddd, J = 11.4, 4.8, 1.2 Hz, 1 H), 2.83–3.00 (m, 2 H), 2.29–2.52 (m, 3 H), 2.18 (dt, J = 14.4, 2.1 Hz, 1 H), 1.94–2.08 (m, 1 H), 1.55–1.73 (m, 2 H), 1.16–1.38 (m, 6 H), 0.98 (t, J = 6.9 Hz, 3 H), 0.96 (t, J = 6.9 Hz, 3 H), 0.13 (s, 9 H) ppm. ^{13}C NMR (C_6D_6, 75 MHz): δ = 208.5, 207.2, 157.9, 125.2, 52.7, 47.7, 43.2, 42.7, 38.3, 32.0, 29.2, 23.7, 22.8, 20.6, 14.2, –0.1 ppm. HRMS (EI): calcd. for $C_{18}H_{32}O_2Si$ $[M]^+$ 308.2172; found: 308.2169.

Amide 3cf and 6cf: (Table 2, Entry 6) Procedure 1 was followed using **1c**, **2f** (1.0 equiv.), and 20% $[Rh(cod)_2]BF_4$/dppb at 80 °C in $(CH_2Cl)_2$. Reaction time: 45 h. Yield 7% (7.4 mg). Pale yellow solid; m.p. 107–109 °C (mixture of isomers). IR (neat): $\tilde{\nu}$ = 3340, 2910, 1620, 1238, 835 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, **3cf/6cf** = 11:89): δ = 5.21 (d, J = 1.2 Hz, 1 H), 3.80 (ddd, J = 13.2, 5.2, 1.2 Hz, 1 H), 3.18–3.28 (m, 1 H), 3.03 (s, 3 H), 2.92 (s, 3 H), 2.88–3.08 (m, 1 H), 2.63 (dd, J = 14.0, 6.4 Hz, 1 H), 2.42 (ddd, J = 14.8, 5.2, 2.4 Hz, 1 H), 2.32 (dt, J = 14.0, 2.8 Hz, 1 H), 1.17 (d, J = 7.2 Hz, 3 H), 0.15 (s, 9 H) ppm; vinyl proton of minor isomer: δ = 5.42 (d, J = 1.6 Hz, 1 H, keto isomer), 5.27–5.29 (m, 1 H, enol isomer) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 210.1, 171.0, 154.4, 124.4, 48.3, 44.9, 44.1, 38.0, 36.8, 35.6, 19.6, –0.1 ppm. HRMS (EI): calcd. for $C_{14}H_{25}NO_2Si$ $[M]^+$ 267.1655; found: 267.1633.

Ester 3da: (Table 2, Entry 7) Procedure 1 was followed using **1d** and **2a**. Reaction time: 45 h. Yield 56% (60 mg). Colorless oil. IR (neat): $\tilde{\nu}$ = 2940, 1655, 1620, 1400, 1350, 1275, 1230, 1205, 1075, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 12.17 (s, 1 H), 5.35 (s, 1 H), 4.00–4.28 (m, 2 H), 3.10 (d, J = 17.5 Hz, 1 H), 2.83 (d, J = 17.5 Hz, 1 H), 2.37–2.73 (m, 2 H), 2.28 (d, J = 18.0 Hz, 1 H), 1.66 (quint, J = 6.9 Hz, 2 H), 1.09–1.53 (m, 8 H), 0.95 (t, J = 7.5 Hz, 3 H), 0.89 (t, J = 6.0 Hz, 3 H), 0.14 (s, 9 H) ppm; vinyl proton of keto isomer: δ = 5.47 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 172.0, 170.1, 155.3, 124.2, 96.4, 64.1, 39.6, 35.9, 32.4, 32.1, 30,7, 29.9, 23.0, 19.2, 14.0, 13.7, 0.4 ppm. HRMS (EI): calcd. for $C_{19}H_{34}O_3Si$ $[M-CO_2C_4H_9]^+$ 237.1674; found: 237.1618.

Ester 6da: (Table 2, Entry 7) Yield 65% (15 mg). Pale yellow oil. IR (neat): $\tilde{\nu}$ = 2925, 1720, 1608, 1245, 1175, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.28 (d, J = 1.5 Hz, 1 H), 4.02–4.28 (m, 2 H), 3.60 (ddd, J = 12.3, 5.4, 1.5 Hz, 1 H), 2.85–3.00 (m, 1 H), 2.79 (dd, J = 15.0, 12.3 Hz, 1 H), 2.35–2.66 (m, 3 H), 1.53–1.76 (m, 2 H), 1.05–1.51 (m, 8 H), 0.94 (t, J = 7.5 Hz, 3 H), 0.89 (t, J = 7.2 Hz, 3 H), 0.15 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 208.7, 172.2, 153.8, 125.1, 64.6, 47.2, 46.1, 43.8, 42.8, 33.3, 30.4, 29.2, 22.5, 18.9, 13.7, 13.4, 0.0 ppm. HRMS (EI): calcd. for $C_{19}H_{34}O_3Si$ $[M]^+$ 338.2277; found: 338.2233.

Ester 3dd: (Table 2, Entry 8) Procedure 1 was followed using **1d** and **2d**. Reaction time: 23 h. Yield 25% (33 mg). Colorless oil. IR (neat): $\tilde{\nu}$ = 2940, 1650, 1620, 1355, 1285, 1240, 1150, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 12.32 (s, 1 H), 5.34 (d, J = 1.7 Hz, 1 H), 3.03 (dt, J = 17.8, 2.4 Hz, 1 H), 2.77 (d, J = 1.78 Hz, 1 H), 2.64 (q, J = 6.8 Hz, 1 H), 2.38–2.55 (m, 1 H), 2.25 (d, J = 18.0 Hz, 1 H), 1.50 (s, 9 H), 1.15–1.49 (m, 6 H), 0.89 (t, J = 6.8 Hz, 3 H), 0.11 (s, 9 H) ppm; vinyl proton of keto isomer: δ = 5.45–5.48 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.9, 169.4, 155.8, 123.9, 97.4, 81.0, 39.7, 36.0, 32.54, 32.51, 29.9, 28.3, 23.0, 14.1, 0.5 ppm. HRMS (EI): calcd. for $C_{19}H_{34}O_3Si$ $[M-CO_2C_4H_9]^+$ 237.1674; found: 237.1639.

Ester 6dd: (Table 2, Entry 8) Yield 52% (71 mg). Pale yellow oil. IR (neat): $\tilde{\nu}$ = 2940, 1720, 1368, 1250, 1155, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.40 (d, J = 1.7 Hz, 1 H), 3.48 (ddd, J = 12.1, 5.1, 1.7 Hz, 1 H), 2.81–2.95 (m, 1 H), 2.72 (dd, J = 14.5, 12.1 Hz, 1 H), 2.36–2.59 (m, 3 H), 1.48 (s, 9 H), 1.10–1.43 (m, 6 H), 0.89 (t, J = 6.6 Hz, 3 H), 0.15 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 209.1, 171.5, 154.5, 125.0, 81.2, 47.8, 46.1, 43.9, 43.0, 33.5, 29.3, 27.9, 22.7, 13.9, 0.1 ppm. HRMS (EI): calcd. for $C_{19}H_{34}O_3Si$ $[M]^+$ 338.2277; found: 338.2242.

Ester 3ea: (Table 2, Entry 9) Procedure 1 was followed using **1e** and **2a** at 8 °C. Reaction time: 44 h. Yield 66% (94 mg). Colorless oil. IR (neat): $\tilde{\nu}$ = 2920, 1650, 1615, 1400, 1350, 1272, 1240, 1213, 1065, 840, 735, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 12.24 (s, 1 H), 7.14–7.36 (m, 5 H), 5.51 (s, 1 H), 3.92–4.20 (m, 3 H), 2.97 (d, J = 18.3 Hz, 1 H), 2.71–2.85 (m, 3 H), 1.50–1.66 (m, 2 H), 1.34 (sext, J = 7.8 Hz, 2 H), 0.90 (t, J = 7.5 Hz, 3 H), 0.20 (s, 9 H) ppm; vinyl proton of keto isomer: δ = 5.66–5.69 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.8, 169.6, 154.3, 140.7, 128.4, 126.6, 126.4, 125.5, 97.0, 64.1, 43.1, 33.9, 32.3, 30.5, 19.1, 13.7, 0.4 ppm. HRMS (EI): calcd. for $C_{21}H_{30}O_3Si$ $[M-CO_2C_4H_9]^+$ 257.1361; found: 257.1376.

Ester 6ea: (Table 2, Entry 9) Yield 6% (9.3 mg). Pale brown oil. IR (neat): $\tilde{\nu}$ = 2920, 1720, 1598, 1245, 1175, 840, 750, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.18–7.42 (m, 5 H), 5.64 (d, J = 1.5 Hz, 1 H), 4.26–4.38 (m, 1 H), 4.01–4.24 (m, 2 H), 3.44 (ddd, J = 10.5, 5.4, 1.5 Hz, 1 H), 3.16 (dt, J = 15.9, 1.8 Hz, 1 H), 2.83 (dd, J = 15.9, 6.0 Hz, 1 H), 2.73 (dd, J = 15.9, 10.5 Hz, 1 H), 2.43 (ddd, J = 15.9, 5.4, 1.8 Hz, 1 H), 1.52–1.70 (m, 2 H), 1.37 (sext, J = 7.5 Hz, 2 H), 0.94 (t, J = 7.2 Hz, 3 H), 0.17 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 208.3, 172.3, 152.5, 140.4, 128.9, 127.9, 127.0, 126.9, 64.8, 47.2, 45.5, 44.8, 43.3, 30.5, 19.1, 13.6, 0.0 ppm. HRMS (EI): calcd. for $C_{21}H_{30}O_3Si$ $[M]^+$ 358.1964; found: 358.1981.

Ester 3ed: (Table 2, Entry 10) Procedure 1 was followed using **1e** and **2d** at 8 °C. Reaction time: 70 h. Yield 38% (54 mg). Colorless solid; m.p. 83–84 °C. IR (neat): $\tilde{\nu}$ = 2925, 1648, 1617, 1390, 1355, 1285, 1243, 1218, 1158, 1060, 840, 750, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 12.41 (s, 1 H), 7.13–7.39 (m, 5 H), 5.50 (s, 1 H), 4.02 (d, J = 5.7 Hz, 1 H), 2.94 (d, J = 18.0 Hz, 1 H), 2.69–2.85 (m, 3 H), 1.43 (s, 9 H), 0.20 (s, 9 H) ppm; vinyl proton of keto isomer: δ = 5.66 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.6, 169.0, 154.7, 140.9, 128.4, 126.7, 126.4, 125.3, 98.0, 81.1,

43.2, 33.9, 32.7, 28.2, 0.4 ppm. HRMS (EI): calcd. for $C_{21}H_{30}O_3Si$ $[M-CO_2C_4H_9]^+$ 257.1361; found: 257.1376.

Ester 6ed: (Table 2, Entry 10) Yield 35% (50 mg). Pale yellow solid; m.p. 80–82 °C. IR (neat): $\tilde{\nu}$ = 2900, 1705, 1600, 1365, 1250, 1203, 1145, 838, 768, 702 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.13–7.42 (m, 5 H), 5.79 (d, J = 1.5 Hz, 1 H), 4.29 (d, J = 3.9 Hz, 1 H), 3.37 (ddd, J = 9.3, 5.7, 1.5 Hz, 1 H), 3.14 (d, J = 15.9 Hz, 1 H), 2.83 (dd, J = 15.9, 5.7 Hz, 1 H), 2.64 (dd, J = 15.9, 9.3 Hz, 1 H), 2.37 (ddd, J = 15.9, 5.7, 1.2 Hz, 1 H), 1.45 (s, 9 H), 0.16 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 208.6, 171.5, 152.5, 140.6, 128.8, 128.0, 126.9, 126.7, 81.3, 47.9, 45.2, 44.5, 42.8, 27.9, –0.1 ppm. HRMS (EI): calcd. for $C_{21}H_{30}O_3Si$ $[M-C_4H_9]^+$ 301.1259; found: 301.1288.

Ester 3aa: (Scheme 3) Procedure 1 was followed using **1a**, **2a** (2.0 equiv.), and 20% $[Rh(nbd)_2]BF_4$/dppe at 50 °C in $(CH_2Cl)_2$. Reaction time: 20 h. Yield 9% (10 mg). Colorless oil. IR (neat): $\tilde{\nu}$ = 2920, 1650, 1615, 1270, 1220, 1080, 820 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 12.17 (s, 1 H), 5.24 (dt, J = 7.5, 2.1 Hz, 1 H), 4.07–4.25 (m, 2 H), 2.93–3.11 (m, 2 H), 2.77 (d, J = 18.0 Hz, 1 H), 2.43–2.55 (m, 1 H), 1.92–2.18 (m, 3 H), 1.58–1.72 (m, 2 H), 1.23–1.49 (m, 6 H), 1.67 (d, J = 7.2 Hz, 3 H), 0.96 (t, J = 7.5 Hz, 3 H), 0.89 (t, J = 7.2 Hz, 3 H) ppm; vinyl proton of keto isomer: δ = 5.33 (t, J = 7.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 172.2, 170.1, 136.4, 123.7, 96.5, 64.1, 37.1, 32.2, 30.7, 28.6, 28.0, 26.6, 22.3, 19.2, 18.9, 14.0, 13.7 ppm. HRMS (EI): calcd. for $C_{17}H_{28}O_3$ $[M-CO_2C_4H_9]^+$ 179.1435; found: 179.1411.

Ester 4a: (Scheme 3) Yield 21% (24 mg). Colorless oil. IR (neat): $\tilde{\nu}$ = 2925, 1710, 1615, 1270, 1165 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 9.69 (t, J = 1.8 Hz, 1 H), 7.20 (d, J = 15.9 Hz, 1 H), 5.97 (d, J = 15.9 Hz, 1 H), 5.89 (t, J = 7.2 Hz, 1 H), 4.15 (t, J = 6.6 Hz, 2 H), 3.43 (sext, J = 7.2 Hz, 1 H), 2.55–2.72 (m, 2 H), 2.16–2.28 (m, 2 H), 1.55–1.72 (m, 2 H), 1.27–1.49 (m, 6 H), 1.19 (d, J = 7.2 Hz, 3 H), 0.95 (t, J = 7.2 Hz, 3 H), 0.92 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 201.2, 167.3, 146.0, 139.5, 139.0, 117.1, 64.3, 48.8, 31.4, 30.7, 28.3, 27.2, 22.4, 19.3, 19.2, 13.9, 13.7 ppm. HRMS (EI): calcd. for $C_{17}H_{28}O_3$ $[M]^+$ 280.2038; found: 280.2047.

Ketone 5b: (Scheme 3)[10a] Procedure 1 was followed using **1b**, **2a** (2.0 equiv.), and 20% $[Rh(nbd)_2]BF_4$/dppe at 50 °C in $(CH_2Cl)_2$. Reaction time: 20 h. Yield 44% (30 mg). Colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.66–7.72 (m, 3 H), 7.28–7.43 (m, 3 H), 3.01 (d-quint, J = 7.2, 2.4 Hz, 1 H), 2.82 (dd, J = 18.9, 6.6 Hz, 1 H), 2.17 (dd, J = 18.9, 2.4 Hz, 1 H), 1.26 (d, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 207.3, 163.9, 142.3, 131.4, 128.36, 128.34, 127.1, 44.4, 32.9, 20.2 ppm.

Ester 6fd: (Scheme 4) Procedure 1 was followed using **1f** and **2d**. Reaction time: 45 h. Yield 57% (68 mg). Relative configuration was determined by NOESY experiment (see Supporting Information). Pale yellow oil. IR (neat): $\tilde{\nu}$ = 2925, 1720, 1610, 1360, 1245, 1150, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.61 (s, 1 H, Ha), 3.43–3.56 (m, 1 H, Hb), 2.63–2.75 (m, 2 H, Hc and Hf), 2.49 (ddd, J = 15.0, 6.6, 0.9 Hz, 1 H, Hd), 2.28–2.43 (m, 2 H, He and Hg), 1.42 (s, 9 H), 1.11 (d, J = 6.3 Hz, 3 H), 0.16 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 209.5, 171.6, 149.8, 129.5, 81.4, 55.6, 44.7, 42.9, 37.9, 27.8, 15.1, –0.1 ppm. HRMS (EI): calcd. for $C_{16}H_{28}O_3Si$ $[M]^+$ 296.1808; found: 296.1769.

Ester 6gd: (Scheme 5). Under Ar, CH_2Cl_2 (1.0 mL) solution of dppf (22.2 mg, 0.040 mmol) was added to CH_2Cl_2 (1.0 mL) solution of $[Rh(cod)_2]BF_4$ (16.2 mg, 0.040 mmol) and the mixture was stirred at room temperature for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring for 0.5 h at room temperature, the resulting solution was concentrated to dryness. A CH_2Cl_2 solution (2 mL) of the aldehyde **1g** (72.9 mg, 0.400 mmol, *cis*/*trans* = 59:41) and *tert*-butyl acrylate (**2d**, 513 mg, 4.00 mmol) was added to the residue. The mixture was stirred at 25 °C for 27 h. The resulting solution was purified by silica gel column chromatography (hexane/Et_2O, 40:1), which furnished the aldehyde **1g** (29.6 mg, 0.162 mmol, 41%, *cis*/*trans* = 88:12) and the ester **6gd** (32.1 mg, 0.103 mmol, 26%, *cis*/*trans* ≈ 1:99). Relative configuration was determined by NOESY experiment (see supporting information). Colorless oil. IR (neat): $\tilde{\nu}$ = 2950, 1715, 1605, 1360, 1243, 1145, 838 cm^{-1}. ^1H NMR (C_6D_6, 300 MHz): δ = 5.66 (s, 1 H, H_a), 3.50 (ddd, J = 12.9, 5.4, 1.8 Hz, 1 H, H_b), 2.96–3.11 (m, 1 H, H_d), 2.29–2.50 (m, 2 H, H_c and H_f), 2.11–2.23 (m, 1 H, H_e), 1.39 (s, 9 H), 0.95 (d, J = 7.2 Hz, 3 H), 0.90 (d, J = 6.9 Hz, 3 H), 0.07 (s, 9 H) ppm. ^{13}C NMR (C_6D_6, 75 MHz): δ = 210.2, 171.3, 154.6, 125.4, 80.7, 51.7, 48.1, 44.8, 40.7, 28.0, 20.6, 17.4, 0.3 ppm. HRMS (EI): calcd. for $C_{18}H_{30}O_3Si$ $[M]^+$ 310.1965; found: 310.1986.

Amide 6af: (Scheme 6) Procedure 1 was followed using **1a**, **2f** (1.0 equiv.), and 20% $[Rh(cod)_2]BF_4$/dppb at 80 °C in $(CH_2Cl)_2$. Reaction time: 25 h. Yield 37% (37 mg). Pale yellow oil. IR (neat): $\tilde{\nu}$ = 2850, 1702, 1620, 1390, 1250, 1218, 1130, 1050, 702, 470 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.11 (t, J = 7.2 Hz, 1 H), 3.72 (dd, J = 12.6, 3.9 Hz, 1 H), 3.35 (d-quint, J = 6.6, 2.7 Hz, 1 H), 3.02 (s, 3 H), 2.95 (s, 3 H), 2.85–2.97 (m, 1 H), 2.59 (dd, J = 14.1, 6.6 Hz, 1 H), 2.40 (ddd, J = 14.7, 4.8, 2.1 Hz, 1 H), 2.29 (dt, J = 14.1, 2.1 Hz, 1 H), 2.11 (q, J = 7.2 Hz, 2 H), 1.24–1.42 (m, 4 H), 1.13 (d, J = 6.9 Hz, 3 H), 0.90 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 210.9, 171.2, 136.2, 125.1, 48.1, 44.9, 42.3, 36.8, 35.5, 31.7, 31.5, 27.1, 22.3, 19.5, 13.8 ppm. HRMS (EI): calcd. for $C_{15}H_{25}NO_2$ $[M]^+$ 251.1885; found: 251.1858.

Amide 6bf: (Scheme 6) Procedure 1 was followed using **1b**, **2f** (1.0 equiv.), and 20% $[Rh(cod)_2]BF_4$/dppb at 80 °C in $(CH_2Cl)_2$. Reaction time: 46 h. Yield 20% (22 mg). Pale yellow solid; m.p. 105–107 °C. IR (neat): $\tilde{\nu}$ = 2880, 1700, 1622, 1478, 1396, 1195, 1112, 1042, 698, 465 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.13–7.42 (m, 5 H), 6.28 (s, 1 H), 3.90 (ddd, J = 12.9, 4.5, 2.1 Hz, 1 H), 3.58 (d-quint, J = 6.6, 2.1 Hz, 1 H), 3.06 (s, 3 H), 3.03 (s, 3 H), 2.95–3.14 (m, 1 H), 2.58 (dd, J = 14.1, 6.6 Hz, 1 H), 2.50 (ddd, J = 14.7, 4.8, 2.4 Hz, 1 H), 2.23 (dt, J = 14.1, 2.4 Hz, 1 H), 1.25 (d, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 210.4, 170.9, 139.7, 136.7, 128.6, 128.4, 127.1, 125.0, 48.2, 45.1, 42.7, 37.0, 35.7, 32.3, 19.6 ppm. HRMS (EI): calcd. for $C_{17}H_{21}NO_2$ $[M]^+$ 271.1572; found: 271.1592.

Ester 4c: (Table 1, Entry 1) Yield 7% (8.3 mg). Colorless oil. IR (neat): $\tilde{\nu}$ = 2940, 1710, 1620, 1248, 1165, 843 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 9.72 (t, J = 1.8 Hz, 1 H), 7.24 (d, J = 15.6 Hz, 1 H), 6.11 (d, J = 15.6 Hz, 1 H), 6.00 (s, 1 H), 4.16 (t, J = 6.6 Hz, 2 H), 3.21–3.34 (m, 1 H), 2.62 (ddd, J = 16.8, 8.1, 1.8 Hz, 1 H), 2.54 (ddd, J = 16.8, 6.9, 1.8 Hz, 1 H), 1.60–1.71 (m, 2 H), 1.35–1.47 (m, 2 H), 1.18 (d, J = 6.9 Hz, 3 H), 0.95 (t, J = 6.9 Hz, 3 H), 0.14 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 200.8, 166.9, 155.0, 144.5, 135.2, 120.4, 64.4, 48.9, 33.7, 30.7, 19.7, 19.2, 13.7, –0.1 ppm. HRMS (EI): calcd. for $C_{16}H_{28}O_3Si$ $[M]^+$ 296.1808; found: 296.1805.

Aldehyde 7c: (Table 1, Entry 4) Yield 30% (20 mg). Colorless oil. IR (neat): $\tilde{\nu}$ = 2800, 1660, 1220, 815 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 9.41 (s, 1 H), 6.68 (s, 1 H), 5.08–5.12 (m, 1 H), 4.77–4.81 (m, 1 H), 1.85–1.89 (m, 3 H), 0.19 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.7, 159.0, 154.0, 141.9, 116.7, 22.7, –0.6 ppm. HRMS (EI): calcd. for $C_9H_{16}OSi$ $[M]^+$ 168.0970; found: 168.0898.

General Procedure 2 for Regio- and Enantioselective [4+2] Carbocyclization of 4-Alkynals with Alkenes: (Table 4, Entry 1) Under Ar, a CH_2Cl_2 (1.0 mL) solution of (*R*,*R*)-**11** (19.8 mg, 0.030 mmol) was added to a CH_2Cl_2 (1.0 mL) solution of $[Rh(cod)_2]BF_4$ (12.2 mg, 0.030 mmol) and the mixture was stirred at room temperature for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 0.5 h, the resulting solution was concentrated to dryness. A CH_2Cl_2 solution (1.5 mL) of the aldehyde **1h** (47.6 mg, 0.300 mmol) and *N*,*N*-dimethylacrylamide (**2f**, 29.7 mg, 0.300 mmol) was added to the residue. The mixture was stirred at 80 °C for 16 h. The resulting solution was concentrated and purified by preparative TLC (hexane/EtOAc, 1:4), which furnished the amide (+)-**6hf** (43.8 mg, 0.170 mmol, 57% yield, >99% *ee*) as a pale brown solid.

Amide (+)-6hf: Pale brown solid; m.p. 126–127 °C. $[\alpha]_D^{25}$ = +125.9 (*c* = 1.348, acetone, >99% *ee*). IR (neat): $\tilde{\nu}$ = 2900, 1693, 1630, 1395, 1130, 705 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.32–7.42 (m, 2 H), 7.20–7.32 (m, 3 H), 6.55 (s, 1 H), 3.91 (t, *J* = 5.4 Hz, 1 H), 3.12 (s, 3 H), 3.01 (s, 3 H), 2.67–2.90 (m, 3 H), 2.53–2.61 (m, 1 H), 2.49 (ddd, *J* = 15.0, 5.4 and 1.2 Hz, 1 H), 2.25–2.39 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 208.4, 171.4, 136.5, 135.7, 128.7, 128.3, 127.8, 127.1, 48.4, 44.7, 40.5, 37.4, 35.9, 25.2 ppm. HRMS (EI): calcd. for $C_{16}H_{19}NO_2$ $[M]^+$ 257.1416; found: 257.1436. CHIRALCEL OD-H, hexane/*i*PrOH, 70:30, 0.8 mL/min, retention times: 11.6 min (major isomer) and 16.9 min (minor isomer).

Amide (+)-6if: (Table 4, Entry 2) Procedure 2 was followed using **1i** and **2f**. Reaction time: 23 h. Yield 58% (50 mg, >99% *ee*). Pale orange oil. $[\alpha]_D^{25}$ = +110.8 (*c* = 0.352, acetone, >99% *ee*). IR (neat): $\tilde{\nu}$ = 3430, 2925, 1705, 1625, 1500, 1400, 1243, 1178, 1128, 1030, 835 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.13–7.21 (m, 2 H), 6.84–6.95 (m, 2 H), 6.48 (s, 1 H), 3.88 (t, *J* = 5.4 Hz, 1 H), 3.82 (s, 3 H), 3.10 (s, 3 H), 3.00 (s, 3 H), 2.66–2.90 (m, 3 H), 2.41–2.62 (m, 2 H), 2.23–2.39 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 208.4, 171.4, 158.5, 134.2, 129.9, 128.9, 127.3, 113.7, 55.3, 48.5, 44.8, 40.6, 37.5, 36.0, 25.2 ppm. HRMS (EI): calcd. for $C_{17}H_{21}NO_3$ $[M-CO_2NMe_2]^+$ 215.1072; found: 215.1028. CHIRALCEL OJ, hexane/*i*PrOH, 70:30, 1.2 mL/min, retention times: 18.5 min (major isomer) and 22.1 min (minor isomer).

Amide (+)-6jf: (Table 4, Entry 3) Procedure 2 was followed using **1j** and **2f**. Reaction time: 36 h. Yield 51% (50 mg, 94% *ee*). Pale yellow solid; m.p. 122–124 °C. $[\alpha]_D^{25}$ = +111.3 (*c* = 0.464, acetone, 94% *ee*). IR (neat): $\tilde{\nu}$ = 2920, 1705, 1628, 1400, 1320, 1115, 1070, 830 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.62 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 6.56 (s, 1 H), 3.94 (t, *J* = 5.4 Hz, 1 H), 3.13 (s, 3 H), 3.02 (s, 3 H), 2.68–2.92 (m, 3 H), 2.44–2.62 (m, 2 H), 2.26–2.41 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 207.6, 170.9, 139.99, 139.98, 137.9, 128.9, 126.3, 125.17 (q), 125.15, 48.2, 44.6, 40.3, 37.4, 36.0, 25.3 ppm. HRMS (EI): calcd. for $C_{17}H_{18}F_3NO_2$ $[M]^+$ 325.1290; found: 325.1284. CHIRALCEL OD-H, hexane/*i*PrOH, 70:30, 0.8 mL/min, retention times: 10.0 min (major isomer) and 12.6 min (minor isomer).

Amide (*S*)-(+)-6kf: (Table 4, Entry 4) Procedure 2 was followed using **1k** and **2f**. Reaction time: 16 h. Yield 68% (59 mg, >99% *ee*). Yellow solid; m.p. 159–161 °C. $[\alpha]_D^{25}$ = +121.4 (*c* = 0.702, acetone, >99% *ee*). IR (neat): $\tilde{\nu}$ = 3360, 2910, 1698, 1620, 1478, 1390, 1090, 820 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.30–7.40 (m, 2 H), 7.17 (d, *J* = 8.7 Hz, 2 H), 6.49 (s, 1 H), 3.91 (t, *J* = 5.4 Hz, 1 H), 3.12 (s, 3 H), 3.00 (s, 3 H), 2.66–2.90 (m, 3 H), 2.42–2.61 (m, 2 H), 2.24–2.39 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 208.1, 171.2, 136.6, 134.9, 133.0, 130.1, 128.5, 126.6, 48.3, 44.7, 40.4, 37.4, 36.0, 25.2 ppm. HRMS (EI): calcd. for $C_{16}H_{18}ClNO_2$ $[M]^+$ 291.1026; found: 291.0974. CHIRALCEL OD-H, hexane/*i*PrOH, 70:30, 0.8 mL/min, retention times: 12.6 min (major isomer) and 15.4 min (minor isomer). The absolute configuration was determined to be *S* configuration by the anomalous dispersion method.

Amide (+)-6kg: (Table 4, Entry 5) Procedure 2 was followed using **1k** and **2g**. Reaction time: 16 h. Yield 77% (73 mg, >99% *ee*). Pale brown solid; m.p. 126–128 °C. $[\alpha]_D^{25}$ = +74.9 (*c* = 1.102, acetone, >99% *ee*). IR (neat): $\tilde{\nu}$ = 3400, 2950, 2895, 1705, 1623, 1435, 1090, 830 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.29–7.37 (m, 2 H), 7.11–7.20 (m, 2 H), 6.49 (s, 1 H), 3.74 (t, *J* = 5.4 Hz, 1 H), 3.40–3.62 (m, 4 H), 2.70–2.90 (m, 3 H), 2.42–2.62 (m, 2 H), 2.24–2.40 (m, 1 H), 1.76–2.08 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 208.0, 169.6, 136.4, 134.9, 132.9, 130.1, 128.5, 126.4, 50.2, 46.6, 46.1, 44.2, 40.3, 26.2, 25.2, 24.2 ppm. HRMS (EI): calcd. for $C_{18}H_{20}ClNO_2$ $[M]^+$ 317.1183; found: 317.1192. Chiralpak AS, hexane/*i*PrOH, 70:30, 1.5 mL/min, retention times: 12.4 min (major isomer) and 17.2 min (minor isomer).

Amide (+)-6lf: (Table 4, Entry 6) Procedure 2 was followed using **1l**, **2f** and 20% catalyst. Reaction time: 20 h. Yield 50% (39 mg, 97% *ee*). Pale yellow solid; m.p. 99–100 °C. $[\alpha]_D^{25}$ = +134.7 (*c* = 1.680, acetone, 97% *ee*). IR (neat): $\tilde{\nu}$ = 3400, 2900, 1700, 1620, 1398, 1122 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.80 (s, 1 H), 5.54–5.67 (m, 1 H), 3.71 (t, *J* = 5.4 Hz, 1 H), 3.04 (s, 3 H), 2.97 (s, 3 H), 2.70–2.87 (m, 2 H), 2.46–2.70 (m, 2 H), 2.23–2.43 (m, 2 H), 2.00–2.18 (m, 4 H), 1.52–1.70 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 208.9, 171.7, 134.3, 132.3, 130.8, 127.7, 48.7, 45.0, 41.1, 37.3, 35.9, 29.1, 25.45, 25.42, 22.7, 21.9 ppm. HRMS (EI): calcd. for $C_{20}H_{23}NO_2$ $[M]^+$ 309.1729; found: 309.1739. CHIRALCEL OD-H, hexane/*i*PrOH, 85:15, 1.0 mL/min, retention times: 12.3 min (major isomer) and 17.0 min (minor isomer).

Amide (+)-6mf: (Table 4, Entry 7) Procedure 2 was followed using **1m**, **2f**, and 20% catalyst at 40 °C. Yield 77% (55 mg, >99% *ee*). Reaction time: 16 h. Pale yellow oil. $[\alpha]_D^{25}$ = +134.0 (*c* = 0.804, acetone, >99% *ee*). IR (neat): $\tilde{\nu}$ = 2910, 1708, 1628, 1398, 1130 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.40 (t, *J* = 7.2 Hz, 1 H), 3.69 (t, *J* = 5.4 Hz, 1 H), 3.02 (s, 3 H), 2.96 (s, 3 H), 2.74 (ddd, *J* = 15.3, 5.7 and 1.5 Hz, 1 H), 2.44–2.59 (m, 3 H), 2.25–2.40 (m, 2 H), 2.02–2.18 (m, 2 H), 1.24–1.43 (m, 4 H), 0.91 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 209.1, 171.7, 132.6, 128.2, 48.0, 45.0, 40.8, 37.3, 35.8, 31.9, 27.5, 24.4, 22.3, 13.9 ppm. HRMS (EI): calcd. for $C_{14}H_{23}NO_2$ $[M]^+$ 237.1729; found: 237.1686. Chiraldex B-DM column, 130 °C isothermal, retention times: 65.8 min (major isomer) and 66.1 min (minor isomer).

Amide (+)-6nf: (Table 4, Entry 8) Procedure 2 was followed using **1n**, **2f** and 20% catalyst. Reaction time: 25 h. Yield 25% (19 mg, >99% *ee*). Colorless oil. $[\alpha]_D^{25}$ = +112.7 (*c* = 0.262, acetone, >99% *ee*). IR (neat): $\tilde{\nu}$ = 2890, 1702, 1600, 1390, 1240, 1108, 830, 470 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.49 (s, 1 H), 3.75 (t, *J* = 5.4 Hz, 1 H), 3.02 (s, 3 H), 2.98 (s, 3 H), 2.27–2.84 (m, 6 H), 0.16 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 208.1, 171.2, 150.6, 127.9, 51.0, 45.0, 41.3, 37.5, 36.0, 30.1, 0.14 ppm. HRMS (EI): calcd. for $C_{13}H_{23}NO_2Si$ $[M]^+$ 253.1498; found: 253.1484. Chiraldex G-TA column, 130 °C isothermal, retention times: 77.5 min (major isomer) and 78.1 min (minor isomer).

Amide (+)-6of: (Table 5, Entry 1) Procedure 2 was followed using **1o**, **2f**, and 5% catalyst. Reaction time: 20 h. Yield 80% (73 mg, 97% *ee*). Orange solid; m.p. 56–58 °C. $[\alpha]_D^{25}$ = +201.0 (*c* = 1.534, acetone, 97% *ee*). IR (neat): $\tilde{\nu}$ = 2930, 1680, 1630, 1600, 1445, 1400, 1282, 1240, 1142, 772, 758, 730, 700 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.02–8.12 (m, 1 H), 7.28–7.37 (m, 1 H), 7.07–7.26 (m, 7 H), 6.67 (s, 1 H), 4.04 (dd, *J* = 6.9 and 4.5 Hz, 1 H), 3.25

(dd, J = 17.4 and 6.9 Hz, 1 H), 3.20 (s, 3 H), 2.94 (s, 3 H), 2.87 (dd, J = 17.4 and 4.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 196.2, 170.2, 137.5, 136.1, 134.1, 133.2, 132.2, 129.1, 128.9, 128.7, 128.5, 128.3, 127.5, 126.7, 48.7, 43.1, 37.6, 36.0 ppm. HRMS (EI): calcd. for $C_{20}H_{19}NO_2$ $[M-CONMe_2]^+$ 233.0967; found: 233.0984. Chiralpak AD, hexane/*i*PrOH, 90:10, 1.0 mL/min, retention times: 18.3 min (major isomer) and 22.7 min (minor isomer).

Amide (+)-6og: (Table 5, Entry 2) Procedure 2 was followed using **1o**, **2g**, and 5% catalyst. Reaction time: 20 h. Yield 80% (79 mg, 97% *ee*). Orange solid; m.p. 205–206 °C. $[\alpha]_D^{25}$ = +199.6 (c = 1.392, acetone, 97% *ee*). IR (neat): $\tilde{\nu}$ = 2960, 2880, 1678, 1615, 1598, 1430, 1330, 1278, 1222, 1178, 780, 760, 692 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.03–8.10 (m, 1 H), 7.27–7.36 (m, 1 H), 7.10–7.25 (m, 7 H), 6.68 (s, 1 H), 3.89 (t, J = 5.4 Hz, 1 H), 3.70 (dt, J = 9.9, 6.9 Hz, 1 H), 3.58 (dt, J = 9.9, 6.9 Hz, 1 H), 3.50 (dt, J = 12.0, 6.9 Hz, 1 H), 3.37 (dt, J = 12.0, 6.9 Hz, 1 H), 3.27 (dd, J = 17.4, 6.3 Hz, 1 H), 2.87 (dd, J = 17.4, 4.2 Hz, 1 H), 2.03 (quint, J = 6.9 Hz, 2 H), 1.86 (quint, J = 6.9 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 196.2, 168.7, 137.5, 136.2, 133.7, 133.2, 132.1, 129.0, 128.8, 128.6, 128.5, 128.3, 127.5, 126.7, 50.4, 46.8, 46.2, 42.7, 26.3, 24.1 ppm. HRMS (EI): calcd. for $C_{22}H_{21}NO_2$ $[M-CON(CH_2)_4]^+$ 233.0966; found: 233.0928. Chiralpak AD, hexane/*i*PrOH, 90:10, 1.0 mL/min, retention times: 21.5 min (major isomer) and 25.5 min (minor isomer).

Amide (+)-6qf: (Table 5, Entry 3) Procedure 2 was followed using **1q**, **2f**, and 5% catalyst. Reaction time: 20 h. Yield 94% (96 mg, 90% *ee*). Pale yellow oil. $[\alpha]_D^{25}$ = +185.5 (c = 1.040, acetone, 90% *ee*). IR (neat): $\tilde{\nu}$ = 2900, 1680, 1630, 1398, 1280, 1238, 1140, 1055, 758, 690 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.07 (dd, J = 7.5 and 1.2 Hz, 1 H), 7.38–7.45 (m, 1 H), 7.33 (dt, J = 7.5, 1.2 Hz, 1 H), 7.12–7.24 (m, 2 H), 6.91–7.06 (m, 3 H), 6.70 (s, 1 H), 4.10 (dd, J = 6.9, 4.5 Hz, 1 H), 3.28 (dd, J = 17.4, 6.9 Hz, 1 H), 3.25 (s, 3 H), 2.96 (s, 3 H), 2.89 (dd, J = 17.4, 4.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 195.9, 169.9, 136.8, 135.4, 135.0, 133.7, 133.0, 132.2, 131.0, 129.3, 128.9, 128.8, 128.6, 126.7, 126.5, 125.9, 48.5, 42.9, 37.6, 36.1 ppm. HRMS (EI): calcd. for $C_{20}H_{18}ClNO_2$ $[M]^+$ 339.1026; found: 339.0956. Chiralpak AD, hexane/*i*PrOH, 90:10, 1.0 mL/min, retention times: 21.1 min (major isomer) and 26.8 min (minor isomer).

Amide (+)-6rf: (Table 5, Entry 4) Procedure 2 was followed using **1r**, **2f**, and 5% catalyst. Reaction time: 44 h. Yield 56% (52 mg, 99% *ee*). Orange solid; m.p. 129–131 °C. $[\alpha]_D^{25}$ = +230.9 (c = 1.189, acetone, 99% *ee*). IR (neat): $\tilde{\nu}$ = 3300, 2910, 1680, 1630, 1445, 1395, 1283, 1240, 1142, 778 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.98–8.08 (m, 1 H), 7.46–7.54 (m, 1 H), 7.42 (dt, J = 7.2, 1.5 Hz, 1 H), 7.34 (dt, J = 7.2, 1.5 Hz, 1 H), 6.12 (s, 1 H), 5.64–5.75 (m, 1 H), 3.89 (dd, J = 6.9, 4.5 Hz, 1 H), 3.15 (dd, J = 17.4, 6.9 Hz, 1 H), 3.10 (s, 3 H), 2.90 (s, 3 H), 2.76 (dd, J = 17.4, 4.5 Hz, 1 H), 1.84–2.12 (m, 4 H), 1.50–1.65 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 196.5, 170.4, 138.7, 134.0, 132.6, 132.0, 131.9, 131.1, 130.1, 128.7, 128.1, 126.2, 48.6, 43.3, 37.5, 35.9, 28.4, 25.7, 22.7, 22.0 ppm. HRMS (EI): calcd. for $C_{20}H_{23}NO_2$ $[M]^+$ 309.1729; found: 309.1702. Chiralpak AD, hexane/*i*PrOH, 95:5, 1.0 mL/min, retention times: 23.3 min (major isomer) and 29.0 min (minor isomer).

Amide (+)-6sf: (Table 5, Entry 5) Procedure 2 was followed using **1s**, **2f**, and 5% catalyst. Reaction time: 28 h. Yield 56% (48 mg, >99% *ee*). Yellow solid; m.p. 82–83 °C. $[\alpha]_D^{25}$ = +151.0 (c = 1.038, acetone, >99% *ee*). IR (neat): $\tilde{\nu}$ = 2900, 1678, 1630, 1390, 1280, 1140, 770 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.02–8.14 (m, 1 H), 7.45–7.56 (m, 1 H), 7.32–7.42 (m, 2 H), 5.69 (t, J = 7.2 Hz, 1 H), 3.91 (dd, J = 6.3, 4.5 Hz, 1 H), 3.13 (dd, J = 17.4, 6.3 Hz, 1 H), 3.07 (s, 3 H), 2.89 (s, 3 H), 2.75 (dd, J = 17.4, 4.5 Hz, 1 H), 2.38 (q, J = 7.2 Hz, 2 H), 1.40–1.52 (m, 2 H), 1.34 (sext, J = 7.2 Hz, 2 H), 0.89 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 196.2, 170.5, 137.8, 132.7, 132.4, 132.1, 131.1, 127.9, 126.6, 48.6, 43.6, 37.4, 35.8, 32.2, 28.8, 22.3, 13.9 ppm. HRMS (EI): calcd. for $C_{18}H_{23}NO_2$ $[M]^+$ 285.1729; found: 285.1708. Chiralpak AD, hexane/*i*PrOH, 95:5, 1.0 mL/min, retention times: 18.1 min (major isomer) and 23.8 min (minor isomer).

Amide (+)-6tf: (Table 5, Entry 6) Procedure 2 was followed using **1t**, **2f**, and 5% catalyst. Reaction time: 20 h. Yield 81% (74 mg, 97% *ee*). Yellow solid; m.p. 82–84 °C. $[\alpha]_D^{25}$ = +107.9 (c = 1.922, acetone, 97% *ee*). IR (neat): $\tilde{\nu}$ = 3400, 2920, 1675, 1625, 1598, 1445, 1390, 1280, 1242, 1140, 770 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.03–8.13 (m, 1 H), 7.53 (dt, J = 5.7 and 1.2 Hz, 1 H), 7.31–7.45 (m, 2 H), 5.65 (t, J = 5.4 Hz, 1 H), 3.93 (m, 1 H), 3.55 (t, J = 4.8 Hz, 2 H), 3.12 (dd, J = 12.9, 4.8 Hz, 1 H), 3.07 (s, 3 H), 2.90 (s, 3 H), 2.75 (dd, J = 12.9, 3.9 Hz, 1 H), 2.56 (dq, J = 5.7 and 2.1 Hz, 2 H), 1.84–2.02 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 196.0, 170.3, 137.5, 133.7, 132.8, 132.5, 128.5, 128.3, 127.8, 126.7, 48.5, 44.3, 43.5, 37.4, 35.9, 32.7, 26.5 ppm. HRMS (EI): calcd. for $C_{17}H_{20}ClNO_2$ $[M-Cl]^+$ 270.1494; found: 270.1499. Chiralpak AD, hexane/*i*PrOH, 85:15, 1.0 mL/min, retention times: 11.4 min (major isomer) and 14.5 min (minor isomer).

Amide (+)-6pf: (Table 5, Entry 7) Procedure 2 was followed using **1p**, **2f**, and 5% catalyst. Reaction time: 42 h. Yield 26% (24 mg, >99% *ee*). Pale yellow solid; m.p. 151–152 °C. $[\alpha]_D^{25}$ = +150.2 (c = 1.115, acetone, >99% *ee*). IR (neat): $\tilde{\nu}$ = 2880, 1672, 1602, 1580, 1478, 1230, 1175, 830, 750, 468 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.00–8.07 (m, 1 H), 7.46–7.55 (m, 3 H), 5.78 (d, J = 0.9 Hz, 1 H), 3.97–4.04 (m, 1 H), 3.15 (dd, J = 17.1, 6.3 Hz, 1 H), 3.07 (s, 3 H), 2.89 (s, 3 H), 2.78 (dd, J = 17.1, 4.5 Hz, 1 H), 0.08 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 196.1, 170.2, 149.7, 139.8, 132.6, 132.4, 130.8, 129.1, 127.5, 126.3, 51.9, 43.4, 37.5, 35.8, 0.32 ppm. HRMS (EI): calcd. for $C_{17}H_{23}NO_2Si$ $[M-CH_3]^+$ 286.1263; found: 286.1221. CHIRALCEL OD-H, hexane/*i*PrOH, 85:15, 1.0 mL/min, retention times: 9.8 min (major isomer) and 14.5 min (minor isomer).

Ester (+)-6hd: (Scheme 8) Procedure 2 was followed using **1h** and **2d** (10 equiv.). Reaction time: 25 h. Yield 32% (28 mg, 97% *ee*). Pale yellow solid; m.p. 82–83 °C. $[\alpha]_D^{25}$ = +85.5 (c = 1.465, acetone, 97% *ee*). IR (neat): $\tilde{\nu}$ = 2920, 1704, 1138, 695, 470 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.31–7.42 (m, 2 H), 7.20–7.31 (m, 3 H), 6.66 (s, 1 H), 3.57–3.65 (m, 1 H), 2.96 (dt, J = 15.0, 6.0 Hz, 1 H), 2.66–2.84 (m, 2 H), 2.57 (dd, J = 15.0, 6.0 Hz, 1 H), 2.42–2.57 (m, 1 H), 2.27–2.41 (m, 1 H), 1.47 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 208.7, 171.7, 136.8, 134.5, 128.8, 128.7, 128.3, 127.0, 81.7, 51.1, 42.7, 39.7, 27.9, 24.9 ppm. HRMS (EI): calcd. for $C_{18}H_{22}O_3$ $[M-CO_2tBu]^+$ 185.0966; found: 185.0922. CHIRALCEL OD-H, hexane/*i*PrOH, 90:10, 1.0 mL/min, retention times: 7.4 min (major isomer) and 17.9 min (minor isomer).

Aldehyde (*S*)-(+)-1a: (Scheme 9) Under Ar, CH_2Cl_2 (1.0 mL) solution of (*R*,*R*)-**11** (39.5 mg, 0.060 mmol) was added to a CH_2Cl_2 (1.0 mL) solution of $[Rh(cod)_2]BF_4$ (24.4 mg, 0.060 mmol) and the mixture was stirred at room temperature for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 0.5 h, the resulting solution was concentrated to dryness. A CH_2Cl_2 solution (1.5 mL) of 3-methylnon-4-ynal (**1a**, 91.3 mg, 0.600 mmol) and *N*,*N*-dimethylacrylamide (**2f**, 59.5 mg, 0.600 mmol) was added to the residue. The mixture was stirred at 80 °C for 11 h. The resulting solution was concentrated [NMR yield of (*S*)-(+)-**1a** is 46% determined by dimethyl terephthalate as an internal standard] and purified by silica gel column chromatog-

raphy (pentane/Et_2O, 50:1), which furnished (*S*)-(+)-**1a**[37] (40.6 mg, 0.267 mmol, 44% isolated yield, 93% *ee*) as a colorless oil. $[\alpha]_D^{25}$ = +16.7 (*c* = 1.825, $CHCl_3$, 93% *ee*). Chiraldex B-DM column, 85 °C isothermal, retention times: 26.7 min (minor isomer) and 27.0 min (major isomer).

Amide 3of: (Scheme 10) Procedure 1 was followed using **1o**, **2f** (1.0 equiv.), and 5% $[Rh(cod)_2]BF_4$/dppb at 80 °C. Reaction time: 42 h. Yield 7% (6.4 mg). Pale yellow oil. IR (neat): $\tilde{\nu}$ = 2920, 1658, 1630, 1582, 1480, 1440, 1390, 1238, 1130, 1048, 730, 698, 472 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.00–8.06 (m, 1 H), 7.17–7.35 (m, 8 H), 6.77 (d, *J* = 1.8 Hz, 1 H), 4.06 (dd, *J* = 12.3, 4.5 Hz, 1 H), 3.39 (dt, *J* = 12.9, 1.8 Hz, 1 H), 3.18 (s, 3 H), 3.08 (s, 3 H), 2.78 (dd, *J* = 12.9 and 4.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.2, 169.3, 140.3, 136.9, 134.0, 132.7, 132.0, 129.0, 128.5, 128.4, 128.3, 128.1, 127.7, 127.4, 53.1, 39.1, 37.8, 35.9 ppm. HRMS (EI): calcd. for $C_{20}H_{19}NO_2$ $[M-CONMe_2]^+$ 233.0967; found: 233.0964.

Amide 3pf: (Scheme 10) Procedure 1 was followed using **1p**, **2f** (1.0 equiv.), and 5% $[Rh(cod)_2]BF_4$/dppb at 80 °C. Reaction time: 42 h. Yield 11% (9.9 mg). Pale yellow solid; m.p. 121–123 °C. IR (neat): $\tilde{\nu}$ = 2890, 1658, 1624, 1582, 1478, 1436, 1382, 1235, 1126, 1045, 830, 755, 470 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.97–8.05 (m, 1 H), 7.48–7.59 (m, 2 H), 7.37–7.46 (m, 1 H), 5.86 (d, *J* = 1.5 Hz, 1 H), 3.97 (dd, *J* = 12.6, 4.5 Hz, 1 H), 3.47 (dt, *J* = 12.6, 1.5 Hz, 1 H), 3.15 (s, 3 H), 3.06 (s, 3 H), 2.76 (dd, *J* = 12.6, 4.8 Hz, 1 H), 0.13 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.3, 169.3, 150.2, 142.1, 133.1, 131.5, 130.1, 128.8, 127.54, 127.48, 53.5, 42.4, 37.8, 35.8, 0.4 ppm. HRMS (EI): calcd. for $C_{17}H_{23}NO_2Si$ $[M-CONMe_2]^+$ 229.1049; found: 229.1026.

Amide (+)-6uf: (Scheme 11) Procedure 2 was followed using **1u** and **2f**. Reaction time: 43 h. Yield 41% (38 mg, 97% *ee*). Pale yellow oil. $[\alpha]_D^{25}$ = +214.3 (*c* = 1.115, acetone, 97% *ee*). IR (neat): $\tilde{\nu}$ = 2905, 1680, 1620, 1572, 1480, 1390, 1108, 722, 690, 470 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.46 (dd, *J* = 4.5 and 2.1 Hz, 1 H), 8.34 (dd, *J* = 8.1, 2.1 Hz, 1 H), 7.30 (dd, *J* = 8.1, 4.5 Hz, 1 H), 7.10–7.25 (m, 5 H), 6.86 (s, 1 H), 4.18 (t, *J* = 4.5 Hz, 1 H), 3.26 (dd, *J* = 17.4, 4.5 Hz, 1 H), 3.24 (s, 3 H), 2.89 (dd, *J* = 17.4, 4.5 Hz, 1 H), 2.88 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 195.3, 170.1, 155.1, 152.6, 135.6, 134.2, 133.0, 132.7, 129.3, 128.9, 127.83, 127.77, 124.0, 48.4, 43.2, 37.8, 36.1 ppm. HRMS (EI): calcd. for $C_{19}H_{18}N_2O_2$ $[M-CONMe_2]^+$ 234.0919; found: 234.0922. Chiralpak AD, hexane/*i*PrOH, 90:10, 1.0 mL/min, retention times: 21.4 min (major isomer) and 25.8 min (minor isomer).

Ester 3ca-*d*: (Scheme 13) Procedure 1 was followed using **1c**-*d* and **2a**. Reaction time: 45 h. Yield 60% (71 mg). Colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 12.18 (s, 1 H), 4.08–4.25 (m, 2 H), 3.19 (dd, *J* = 18.3, 2.7 Hz, 1 H), 2.86 (d, *J* = 18.0, Hz, 1 H), 2.76–2.96 (m, 1 H), 2.45–2.62 (m, 1 H), 2.19 (dd, *J* = 17.7, 1.2 Hz, 1 H), 1.58–1.72 (m, 2 H), 13.5–1.48 (m, 2 H), 1.12 (d, *J* = 6.9 Hz, 3 H), 0.96 (t, *J* = 7.5 Hz, 3 H), 0.11 (s, 9 H) ppm. ^2H NMR ($CDCl_3$, 61 MHz): δ = 5.33 (s) ppm.

Ester 6ca-*d*: (Scheme 13) Yield 12% (14 mg). Colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.03–4.27 (m, 2 H), 3.69 (dd, *J* = 12.0, 5.4 Hz, 1 H), 3.11–3.24 (m, 1 H), 2.80 (dd, *J* = 14.7, 12.0 Hz, 1 H), 2.64 (dd, *J* = 14.4, 6.3 Hz, 1 H), 2.53 (ddd, *J* = 14.7, 5.4, 2.1 Hz, 1 H), 2.27–2.37 (m, 1 H), 1.54–1.71 (m, 2 H), 1.39 (sext, *J* = 7.5 Hz, 2 H), 1.15 (d, *J* = 7.2 Hz, 3 H), 0.95 (t, *J* = 7.2 Hz, 3 H), 0.15 (s, 9 H) ppm. ^2H NMR ($CDCl_3$, 61 MHz): δ = 5. 34 (s) ppm.

Amide 8hf: (Scheme 14) Yield 40% (41 mg). Colorless oil. IR (neat): $\tilde{\nu}$ = 3400, 2900, 1705, 1630, 1395, 1095, 758, 695 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.33–7.39 (m, 2 H), 7.24–7.28 (m, 3 H), 3.03 (s, 3 H), 2.93 (s, 3 H), 2.83–2.88 (m, 2 H), 2.75–2.81 (m, 2 H), 2.67–2.71 (m, 2 H), 2.61–2.66 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 207.9, 171.3, 131.5, 128.1, 127.6, 123.6, 88.7, 80.8, 41.9, 37.3, 37.1, 35.5, 27.3, 14.0 ppm. HRMS (EI): calcd. for $C_{16}H_{19}NO_2$ $[M]^+$ 257.1416; found: 257.1377.

X-ray Crystallographic Studies of Amide 6kf: A crystal suitable for X-ray analysis was obtained by recrystallization from CH_2Cl_2/*n*-pentane. CCDC-277585 contains the supplementary crystallographic data for compound **4g**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): ^1H NMR spectra of **3**, **4**, **6**, **7**, and **8**, and NOESY spectra of **6cd**, **6fd**, and **6gd**.

Acknowledgments

We thank Solvias AG for the gift of chiral ligands **9**, **10**, and **11** under their University Ligand Kit program. We also thank Prof. K. Noguchi (Instrumentation Analysis Center, Tokyo University of Agriculture and Technology) for his X-ray crystallographic analysis and Prof. Gregory C. Fu (Massachusetts Institute of Technology) for his helpful encouragement.

[1] For reviews of transition-metal-catalyzed carbocyclizations, see: a) I. Ojima, M. Tzamarioudaki, Z. Li, R. J. Donovan, *Chem. Rev.* **1996**, *96*, 635–662; b) M. Lautens, W. Klute, W. Tam, *Chem. Rev.* **1996**, *96*, 49–92; c) P. A. Wender, J. A. Love, in: *Advances in Cycloaddition*, JAI Press: Greenwich, **1999**, vol. 5, p. 1–45; d) J. E. Robinson, in: *Modern Rhodium-Catalyzed Organic Reactions* (Ed.: P. A. Evans), Wiley-VCH, **2005**, p. 241.

[2] For transition-metal-catalyzed intramolecular [4+2] carbocyclizations. For Rh, see: a) D. Motoda, H. Kinoshita, H. Shinokubo, K. Oshima, *Angew. Chem.* **2004**, *116*, 1896–1898; *Angew. Chem. Int. Ed.* **2004**, *43*, 1860–1862; b) B. Wang, P. Cao, X. Zhang, *Tetrahedron Lett.* **2000**, *41*, 8041–8044; c) S. R. Gilbertson, G. S. Hoge, *Tetrahedron Lett.* **1998**, *39*, 2075–2078; d) P. A. Wender, T. E. Jenkins, S. Suzuki, *J. Am. Chem. Soc.* **1995**, *117*, 1843–1844; e) D. J. R. O'Mahony, D. B. Belanger, T. Livinghouse, *Org. Biomol. Chem.* **2003**, *1*, 2038–2040; f) R. S. Jolly, G. Luedtke, D. Sheehan, T. Livinghouse, *J. Am. Chem. Soc.* **1990**, *112*, 4965–4966; g) M. Murakami, M. Ubukata, K. Itami, Y. Ito, *Angew. Chem.* **1998**, *110*, 2362–2364; *Angew. Chem. Int. Ed.* **1998**, *37*, 2248–2250; h) B. Witulski, J. Lumtscher, U. Bergsträßer, *Synlett* **2003**, 708–710. For Ni, see; i) P. A. Wender, T. E. Smith, *Tetrahedron* **1998**, *54*, 1255–1275; j) P. A. Wender, T. E. Smith, *J. Org. Chem.* **1996**, *61*, 824–825; k) P. A. Wender, T. E. Smith, *J. Org. Chem.* **1995**, *60*, 2962–2963; l) P. A. Wender, T. E. Jenkins, *J. Am. Chem. Soc.* **1989**, *111*, 6432–6434. For Pd, see; m) J. R. Dunetz, R. L. Danheiser, *J. Am. Chem. Soc.* **2005**, *127*, 5776–5777; n) L. J. van Boxtel, S. Körbe, M. Noltemeyer, A. de Meijere, *Eur. J. Org. Chem.* **2001**, 2283–2292; o) M. Murakami, K. Itami, Y. Ito, *J. Am. Chem. Soc.* **1997**, *119*, 7163–7164; p) K. Kumar, R. Jolly, *Tetrahedron Lett.* **1998**, *39*, 3047–3048; q) T. Mandai, S. Suzuki, A. Ikawa, T. Murakami, M. Kawada, J. Tsuji, *Tetrahedron Lett.* **1991**, *32*, 7687–7688. For Co, see; r) G. Hilt, S. Lüers, K. I. Smolko, *Org. Lett.* **2005**, *7*, 251–253; s) G. Hilt, S. Lüers, K. Harms, *J. Org. Chem.* **2004**, *69*, 624–630; t) G. Hilt, K. I. Smolko, *Angew. Chem.* **2003**, *115*, 2901–2903; *Angew. Chem. Int. Ed.* **2003**, *42*, 2795–2797; u) G. Hilt, L. Steffen, *Synthesis* **2002**, 686–692; v) G. Hilt, S. Lüers, *Synthesis* **2003**, 1784–1786; w) G. Hilt, K. I. Smolko, B. V. Lotsch, *Synlett* **2002**, 1081–1084; x) G. Hilt, T. J. Korn, *Tetrahedron Lett.* **2001**, *42*, 2783–2785; y) G. Hilt, F. du Mesnil, *Tetrahedron Lett.* **2000**, *41*, 6757–6761. For Au, see; z) C. Nietro-Oberhuber, S. López, A. M. Echavarren, *J. Am. Chem. Soc.* **2005**, *127*, 6178–6179.

[3] For transition-metal-catalyzed intermolecular [4+2] carbocyclizations, see: a) S.-J. Paik, S. U. Son, Y. K. Chung, *Org. Lett.* **1999**, *1*, 2045–2047; b) I. Matsuda, M. Shibata, S. Sato, Y. Izumi, *Tetrahedron Lett.* **1987**, *28*, 3361–3362; c) K. Mach, H. Antropiusovä, L. Petrusovä, F. Turecek, V. Hanus, *J. Organomet. Chem.* **1985**, *289*, 331–339; d) H. tom Dieck, R. Diercks, *Angew. Chem.* **1983**, *95*, 801–802; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 778–779.

[4] For transition-metal-catalyzed enantioselective intramolecular [4+2] carbocyclizations, see: a) T. Shibata, K. Takasaku, Y. Takesue, N. Hirata, K. Takagi, *Synlett* **2002**, 1681–1682; b) H. Heath, B. Wolfe, T. Livinghouse, S. K. Bae, *Synthesis* **2001**, 2341–2347; c) S. R. Gilbertson, G. S. Hoge, D. G. Genov, *J. Org. Chem.* **1998**, *63*, 10077–10080; d) D. J. R. O'Mahony, D. B. Belanger, T. Livinghouse, *Synlett* **1998**, 443–445; e) L. Mckinstry, T. Livinghouse, *Tetrahedron* **1994**, *50*, 6145–6154.

[5] Murakami, Ito, and co-workers reported that the palladium-catalyzed enantioselective *intermolecular* [4+2] carbocyclization of vinylallenes with 1,3-dienes affords the optically active cyclohexenones with 63–89% *ee*, see: M. Murakami, R. Minamida, K. Itami, M. Sawamura, Y. Ito, *Chem. Commun.* **2000**, 2293–2294.

[6] For synthesis of quinones through reactions of maleoylcobalt complexes with alkynes, see: a) S. Iyer, L. S. Liebeskind, *J. Am. Chem. Soc.* **1987**, *109*, 2759–2770; b) L. S. Liebeskind, S. L. Baysdon, V. Goedken, R. Chidambaram, *Organometallics* **1986**, *5*, 1086–1092; c) L. S. Liebeskind, J. P. Leeds, S. L. Baysdon, S. Iyer, *J. Am. Chem. Soc.* **1984**, *106*, 6451–6453.

[7] a) M. Murakami, T. Itahashi, Y. Ito, *J. Am. Chem. Soc.* **2002**, *124*, 13976–13977; b) T. Matsuda, A. Fujimoto, M. Ishibashi, M. Murakami, *Chem. Lett.* **2004**, *33*, 876–877.

[8] K. Tanaka, G. C. Fu, *Org. Lett.* **2002**, *4*, 933–935.

[9] Preliminary results have been reported: K. Tanaka, Y. Hagiwara, K. Noguchi, *Angew. Chem.* **2005**, *117*, 7426–7429; *Angew. Chem. Int. Ed.* **2005**, *44*, 7260–7263.

[10] Rhodium-catalyzed intramolecular *trans* hydroacylation of 4-alkynals, see: a) K. Tanaka, G. C. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 11492–11493; b) K. Tanaka, G. C. Fu, *J. Am. Chem. Soc.* **2002**, *124*, 10296–10297; c) K. Tanaka, G. C. Fu, *J. Am. Chem. Soc.* **2003**, *125*, 8078–8079.

[11] K. Tanaka, G. C. Fu, *Chem. Commun.* **2002**, 684–685.

[12] The reaction of 3-phenyl-5-trimethylsilyl-4-pentynal was conducted at lower temperature (8 °C) to minimize the formation of dienal.

[13] For these cycloadditions in Table 2, the regioisomers have been easily separated by silica gel chromatography except Entry 6.

[14] Cyclopentenone **5b** was isolated in 29% yield as a major by-product.

[15] T. Sturm, W. Weissensteiner, F. Spindler, *Adv. Synth. Catal.* **2003**, *345*, 160–164.

[16] In the case of the reactions of **1h–u** using Rh^{I+}/(*R*,*R*)-**11**, no vinyl proton other than those of the desired cyclohexanones **6** was observed by ^1H NMR analyses of the crude reaction mixtures.

[17] Q. Huang, J. A. Hunter, R. C. Larock, *J. Org. Chem.* **2002**, *67*, 3437–3444.

[18] For rhodium-catalyzed [4+2] dimerization of 2-vinylbenzaldehyde, see: K. Kundu, J. V. McCullagh, A. T. Morehead Jr, *J. Am. Chem. Soc.* **2005**, *127*, 16042–16043.

[19] For mechanistic studies of the rhodium-catalyzed cyclization of 4-alkenals to cyclopentanones, see: a) D. P. Fairlie, B. Bosnich, *Organometallics* **1988**, *7*, 946–954; b) R. E. Campbell Jr, R. G. Miller, *J. Organomet. Chem.* **1980**, *186*, C27–C31; c) R. E. Campbell Jr, C. F. Lochow, K. P. Vora, R. G. Miller, *J. Am. Chem. Soc.* **1980**, *102*, 5824–5830.

[20] K. Tanaka, G. C. Fu, *Angew. Chem.* **2002**, *114*, 1677–1679; *Angew. Chem. Int. Ed.* **2002**, *41*, 1607–1609.

[21] Rhodium-catalyzed chelation-controlled intermolecular hydroacylation of aldehydes with alkenes, see: a) M. C. Willis, S. J. McNally, P. J. Beswick, *Angew. Chem.* **2004**, *116*, 344–347; *Angew. Chem. Int. Ed.* **2004**, *43*, 340–343; b) M. Tanaka, M. Imai, Y. Yamamoto, K. Tanaka, M. Shimowatari, S. Nagumo, N. Kawahara, H. Suemune, *Org. Lett.* **2003**, *5*, 1365–1367; c) C.-H. Jun, C. W. Moon, D.-Y. Lee, *Chem. Eur. J.* **2002**, *8*, 2423–2428.

[22] M. Eriksson, T. Iliefski, M. Nilsson, T. Olsson, *J. Org. Chem.* **1997**, *62*, 182–187.

[23] K. R. Roesch, R. C. Larock, *J. Org. Chem.* **2002**, *67*, 86–94.

[24] L. Brandsma, H. D. Verkruijsse, *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 319–320.

[25] C. R. Harris, S. D. Kuduk, A. Balog, K. Savin, P. W. Glunz, S. J. Danishefsky, *J. Am. Chem. Soc.* **1999**, *121*, 7050–7062.

[26] J. W. Herndon, J. J. Matasi, *J. Org. Chem.* **1990**, *55*, 786–788.

[27] N. Asao, T. Nogami, K. Takahashi, Y. Yamamoto, *J. Am. Chem. Soc.* **2002**, *124*, 764–765.

[28] A. V. R. Rao, S. Krishnappa, K. L. N. Reddy, K. A. Reddy, *Synth. Commun.* **1986**, *16*, 1141–1148.

[29] T. Honda, M. Hoshi, K. Kanai, M. Tsubuki, *J. Chem. Soc., Perkin Trans. 1* **1994**, *15*, 2091–2101.

[30] T. C. Bedard, J. S. Moore, *J. Am. Chem. Soc.* **1995**, *117*, 10662–10671.

[31] T. Morimoto, K. Fuji, K. Tsutsumi, K. Kakiuchi, *J. Am. Chem. Soc.* **2002**, *124*, 3806–3807.

[32] Q. Huang, J. A. Hunter, R. C. Larock, *J. Org. Chem.* **2002**, *67*, 3437–3444.

[33] P. Sagar, R. Fröhlich, E.-U. Würthwein, *Angew. Chem. Int. Ed.* **2004**, *43*, 5694–5697.

[34] J. Barluenga, H. Vazquez-Villa, A. Ballesteros, J. M. Gonzalez, *J. Am. Chem. Soc.* **2003**, *125*, 9028–9029.

[35] T. Shono, *J. Am. Chem. Soc.* **1979**, *101*, 984–987.

[36] A. Pouilhés, S. E. Thomas, *Tetrahedron Lett.* **1989**, *30*, 2285–2288.

[37] K. Tanaka, Y. Hagiwara, M. Hirano, *Angew. Chem.* **2006**, *118*, 2800–2803; *Angew. Chem. Int. Ed.* **2006**, *45*, 2734–2737.

Received: May 2, 2006
Published Online: June 7, 2006

